Mild Aromatic Palladium-Catalyzed Protodecarboxylation: Kinetic Assessment of the Decarboxylative Palladation and the Protodepalladation Steps

Joshua S. Dickstein, John M. Curto, Osvaldo Gutierrez, Carol A. Mulrooney, and Marisa C. Kozlowski*

Department of Chemistry, Roy and Diana Vagelos Laboratories, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Supporting Information

General Considerations

Unless otherwise stated all solvents and reagents were ACS reagent grade and were used without further purification. When necessary, solvents and reagents were dried prior to use. DMSO and DMF were distilled from BaO. Biphenyl was recrystallized from ethanol prior to use. Palladium(II) trifluoroacetate was purchased from either Acros or Strem. Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica-gel plates. Yields refer to isolated material judged to be ≥95% pure by ^{1}H NMR spectroscopy following silica gel chromatography with Silia-P flash silica gel (50-63 μm mesh particle size). Due to the volatility of some of the products, rotary evaporation was avoided as much as possible. With these sensitive products, the solvent was slowly evaporated on the bench-top. In addition, chromatography on these products was performed with the most volatile solvent system possible and the fractions were concentrated by slow evaporation on the bench-top.

^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer or 300 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) from tetramethylsilane (0 ppm) or from the solvent resonance ($CDCl_3$ 7.26 ppm, DMSO-d_6 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br = broad, m = multiplet), coupling constants, and number of protons. Proton decoupled ^{13}C NMR spectra were recorded on a 125 MHz spectrometer. Chemical shifts are reported in ppm from the solvent resonance ($CDCl_3$ 77.16 ppm).

Mass spectra were obtained utilizing high resonance with an ionization mode of either CI or ES or LC-TOF mass spectrometer using EI in positive or negative mode. Melting points are uncorrected.

GC analysis for reactions was conducted on an HP-1 column (Agilent): length = 30 m, ID = 0.32 mm, film = 0.25 mm, flow = 2 mL/min, Carrier gas = N_2, Detector (FID) = 250 ºC, Injector = 250 ºC, Pressure = 21.25 psi.

GC Calibration Procedure

Biphenyl (3.85 g, 0.025 mol) was diluted to 1.0 M with CH_2Cl_2 in a 25 mL volumetric flask. 2,6-Dimethoxybenzoic acid, **6a**, (4.55 g, 0.025 mol) was diluted to 1.0 M with MeOH in a 25 mL volumetric flask. 1,3-Dimethoxybenzene, **8a**, (4.55 g, 0.033 mol) was diluted to 1.3 M with CH_2Cl_2 in a 25 mL volumetric flask. The samples were examined by combining known volumes of each stock solution. Each sample was then diluted (100 μL in 1.5 mL CH_2Cl_2) and injected three times on the GC. The average ratio of the peak areas was used to calibrate each analyte with respect to the internal standard of biphenyl. The calibration curves for **6a** and **8a** are shown below.

Calibration of 2,6-Dimethoxybenzoic Acid (6a) to Biphenyl

Table S1 Primary data for the calibration of **6a**[a]

mmol **6a**/mmol **Biphenyl**	Area **6a**/Area **Biphenyl**[b]
0.2	0.1374
0.5	0.2511
1.0	0.4076
2.0	1.0583
5.0	2.7419

[a]GC Method: Flow = 2 mL/min; Hold oven temperature for time given = 80 ºC/5 min; Ramp rate of oven temperature in ºC/min = 10 ºC/min; Hold oven temperature for time given = 130 ºC/3 min. Retention times: t_R(**6a**) = 9.9 min, t_R(**Biphenyl**) = 5.5 min. Correction factor for **6a**; y = 1.80x. [b]Average of three injections on GC.

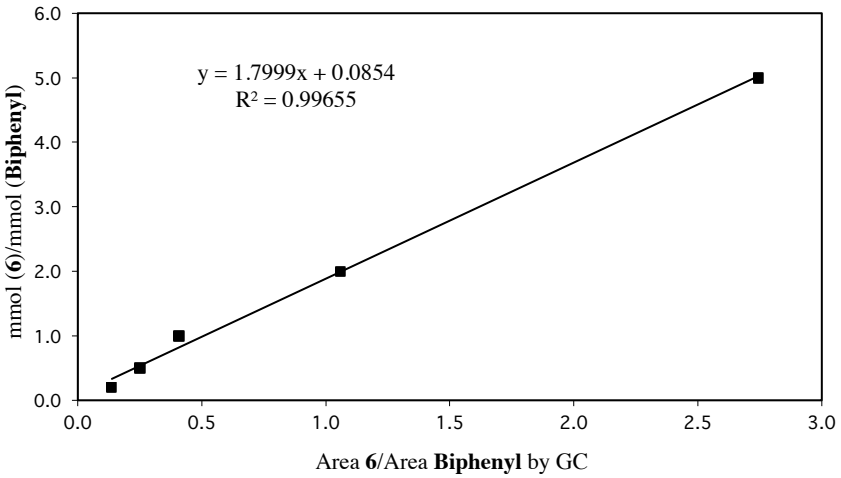


Figure S1 GC Calibration Curve for **6a**

Calibration of 1,3-Dimethoxybenzene (8a) to Biphenyl

Table S2 Primary data for the calibration of **8a**[a]

mmol **8a**/mmol **Biphenyl**	Area **8a**/Area **Biphenyl**[b]
0.2638	0.1346
0.6594	0.3368
1.3188	0.6971
2.6376	1.3494
6.5940	3.7586

[a]GC Method: Flow = 2 mL/min; Hold oven temperature for time given = 80 ºC/5 min; Ramp rate of oven temperature in ºC/min = 10 ºC/min; Hold oven temperature for time given = 130 ºC/3 min. Retention times: t_R(**8a**) = 1.6 min, t_R(**Biphenyl**) = 5.5 min. Correction factor for **8a**; y = 1.74x. [b]Average of three injections on GC.

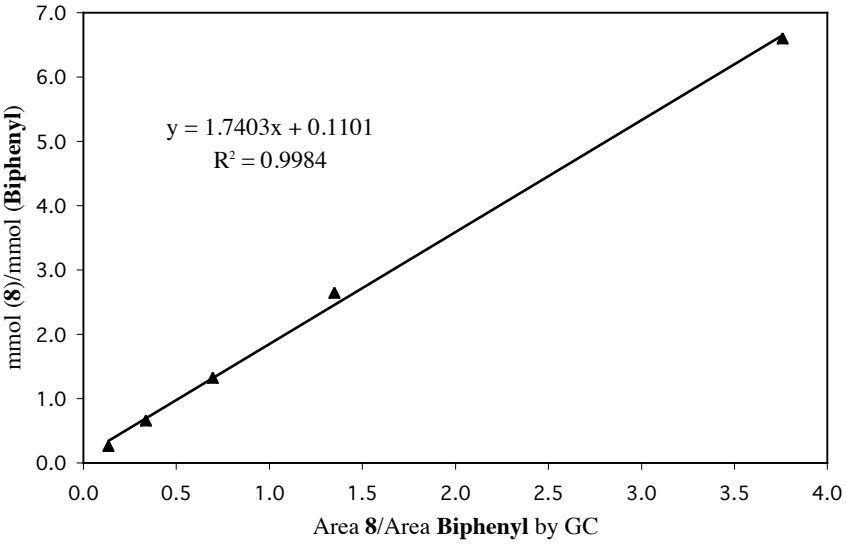
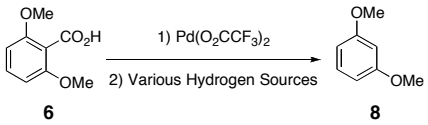


Figure S2 GC Calibration Curve for **8a**

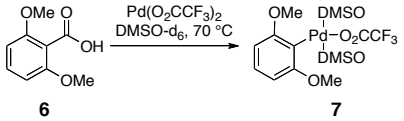
GC Reaction Monitoring for Table 1



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in the appropriate solvent (3.0 mL), was added palladium (II) trifluoroacetate (110 mg, 0.33 mmol) and biphenyl (51 mg, 0.33 mmol). The reaction mixture was then heated at 70 °C for 1 h. To this solution was added the appropriate hydrogen/hydride source at the temperature specified in Tables 1.1-1.3 above. At regular intervals, aliquots (~100 μL) were removed. To this aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% $MeOH/CH_2Cl_2$). The sample was then analyzed by gas chromatography (GC) using the conditions described above.

^{1}H NMR Monitoring of the Decarboxylative Palladation of 6 to 7 (Figure 1)



6 **7**

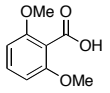
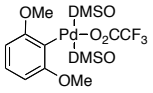
To a solution of 2,6-dimethoxybenzoic acid, **6a,** (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). A ^{1}H NMR

spectrum was then taken. The mixture was then warmed to 70 ºC and spectra were taken periodically throughout the course of the reaction. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S3**. The relevant ^{1}H NMR chemical shifts for **6a**,**7a**, and **8a** are listed in **Table S4**.

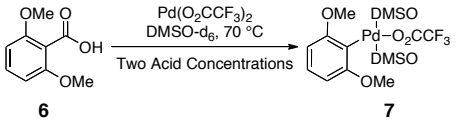
Table S3 Data Presented in **Figure 1** from ^{1}H NMR Measurements

Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)
0.0	0.088	9.0	0.046	23.0	0.024
3.0	0.075	10.0	0.043	33.0	0.016
5.0	0.063	11.0	0.041	43.0	0.012
6.0	0.060	12.0	0.040	55.0	0.009
7.0	0.056	13.0	0.038		
8.0	0.050	18.0	0.029		

Table S4 ^{1}H NMR Chemical Shifts of **6a**, **7a**, and **8a** in DMSO-d_6.

 **6**	 **7**	 **8**
7.27 (1H) 6.64 (2H) 3.74 (6H)	7.05 (1H) 6.35 (2H) 3.84 (6H)	7.14 (1H) 6.47 (2H) 6.43 (1H) 3.71 (6H)

^{1}H NMR Monitoring of the Acid Effect on Decarboxylative Palladation (Figure 2)



6 **7**

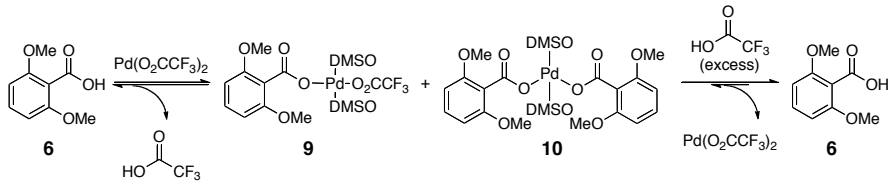
To a solution of 2,6-dimethoxybenzoic acid, **6a,** (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). A ^{1}H NMR spectrum was then taken. The mixture was then warmed to 70 ºC and spectra were taken periodically throughout the course of the reaction. A second experiment with 10 equiv of CH_3SO_3H (43 μL, 0.066 mmol) was conducted in the same manner and the two

experiments were compared. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S3** and **Table S5**.

Table S5 Data Presented in **Figure 2** from ^{1}H NMR Measurements

Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)
2.0	0.083	60.0	0.042
10.0	0.073	90.0	0.032
20.0	0.064	120.0	0.025
40.0	0.053		

Acid Equilibrium Experiment of 6a to 9a (Scheme 5 and Figure 3)



A ^{1}H NMR spectrum of a solution of 2,6-dimethoxybenzoic acid, **6a**, (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was taken. Then palladium(II) trifluoroacetate (22 mg, 0.066 mmol) was added and a second ^{1}H NMR spectrum was taken. Following that, trifluoroacetic acid (49 μL, 0.66 mmol) was added and a final ^{1}H NMR spectrum was obtained. The overlay of the three spectra depicting the shift in the equilibrium is shown in **Figure S3**.

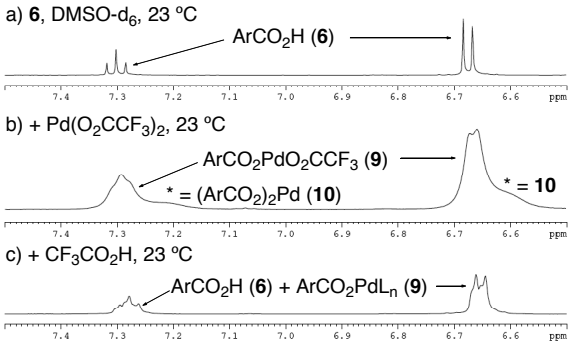
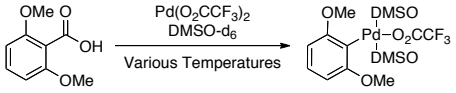


Figure S3 ^{1}H NMR Study of Acid Effect on Ligand Exchange. a) ^{1}H NMR spectrum of 2,6-dimethoxybenzoic acid (**6a**) in DMSO-d_6 at 23 ºC. b) ^{1}H NMR spectrum after addition of 1 equivalent $Pd(O_2CCF_3)_2$ at 23 ºC. c) ^{1}H NMR spectrum after addition of 10 equivalents of CF_3CO_2H at 23 ºC.

Decarboxylative Palladation Eyring Analysis (Figure 3).



6 **7**

To a solution of 2,6-dimethoxybenzoic acid, **6a**, (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). A ^{1}H NMR spectrum was then taken. The mixture was then warmed to 50 ºC and spectra were taken periodically throughout the course of the reaction. Three more experiments were conducted in the same manner at different temperatures (70, 90, and 110 ºC) and then all four experiments were compared. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S3** (70 ºC reaction), **Table S6**, **Table S7**, and **Table S8**. The rate data is shown in **Table S9.**

Table S6 Data Presented in **Table S9** from ^{1}H NMR Measurements at 50 ºC

Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)
0	0.088	40	0.067	150	0.042
2	0.085	60	0.060	180	0.038
10	0.081	90	0.052	240	0.032
20	0.076	120	0.047	265	0.028

Table S7 Data Presented in **Table S9** from ^{1}H NMR Measurements at 90 ºC

Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)
0	0.088	5	0.010	9	0.003
1.5	0.045	6	0.007	10	0.002
3	0.021	7	0.005		
4	0.013	8	0.004		

Table S8 Data Presented in **Table S9** from ^{1}H NMR Measurements at 110 ºC

Time (min)	[**6a**] (M)	Time (min)	[**6a**] (M)
0.5	0.085	2.5	0.007
1	0.049	3	0.005
1.5	0.023	3.5	0.002

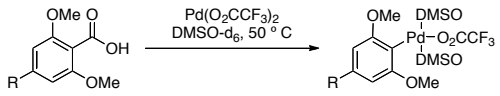
2	0.013	

Table S9 Decarboxylative Palladation Rates at Different Temperatures[a]

T	k (s^{-1})	$t_{1/2}$
50	7.0×10^{-5}	2.8 h
70	6.7×10^{-4}	17 min
90	5.9×10^{-3}	2.0 min
110	2.0×10^{-2}	35 sec

[a] Reaction conditions: initial concentration [**6a**] = 0.09 M and $[Pd(O_2CCF_3)_2]$ = 0.11 M, 0.75 mL DMSO-d_6. The Eyring equation is $\ln(kh/\kappa k_B T) = -(\Delta H^{\ddagger}/R)(1/T) + \Delta S^{\ddagger}/R$ where k is the experimentally determined rate, h is Planck's constant, κ is the transmission coefficient (and is assumed to be 1), k_B is Boltzmann's constant, T is the temperature of the reaction, and R is the gas constant. The Gibb's free energy is calculated using $\Delta G^{\ddagger}_{298} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

^{1}H NMR Hammett Study of Decarboxylative Palladation (Figure 4)



To a solution of 2,6-dimethoxy-4-methylbenzoic acid, (**6b**, R = Me), (13 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). A ^{1}H NMR spectrum was then taken. The mixture was then warmed to 50 ºC and spectra were taken periodically throughout the course of the reaction. Experiments with **6a** and **6c** (R = H and Cl) were conducted in the same manner and all three experiments were used to construct **Figure 4**. Ratios of the carboxylic acid starting materials, aryl palladium intermediates, and protodecarboxylated products were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S6** (**6a**, R = H), **Table S10**, (**6b**, R = Me), and **Table S12** (**6c**, R = Cl). The relevant ^{1}H NMR chemical shifts are listed in **Table S4** (**6a**, R = H), **Table S11** (**6b**, R = Me), and **Table S13** (**6c**, R = Cl).

Table S10 Data Presented in **Figure 4** from ^{1}H NMR Measurements of Decarboxylative Palladation of **6b** (R = Me) at 50 ºC

Time (h)	[**6b**, R = Me] (M)
0.5	0.047

1	0.034
1.5	0.027
2	0.022
2.5	0.019

Table S11 ^{1}H NMR Chemical Shifts of **6b**, **7b**, and **8b** (R = Me) in DMSO-d_6.

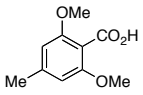
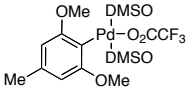
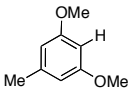
 **6**, R = Me	 **7**, R = Me	 **8**, R = Me
6.49 (2H) 3.72 (6H) 2.30 (3H)	6.24 (2H) 3.81 (6H) 2.27 (3H)	6.31 (2H) 6.25 (1H) 3.69 (6H) 2.22 (3H)

Table S12 Data Presented in **Figure 4** from ^{1}H NMR Measurements of Decarboxylative Palladation of **6c** (R = Cl) at 50 ºC

Time (min)	[**6c**, R = Cl] (M)	Time (min)	[**6c**, R = Cl] (M)
0	0.086	3	0.060
0.5	0.080	4	0.055
1	0.076	6	0.046
2	0.067	8.5	0.041

Table S13 ^{1}H NMR Chemical Shifts of **6c**, **7c**, and **8c** (R = Cl) in DMSO-d_6.

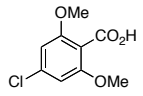
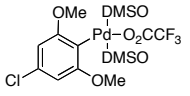
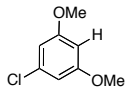
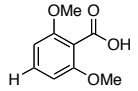
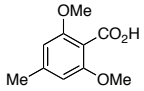
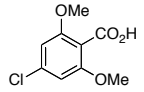
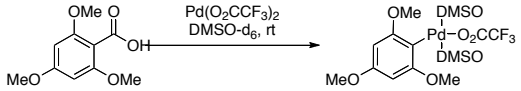
 **6**, R = Cl	 **7**, R = Cl	 **8**, R = Cl
6.76 (2H) 3.75 (6H)	6.43 (2H) 3.82 (6H)	6.55 (2H) 6.42 (1H) 3.70 (6H)

Table S14 Rate Data from Hammett Study of Decarboxylative Palladation

Substrate	σ_{para} values	k (s^{-1})
 **6**, R = H	0.00	6.95×10^{-5}
 **6**, R = Me	–0.14	1.28×10^{-4}
 **6**, R = Cl	0.24	2.50×10^{-5}

Decarboxylative Palladation of 2,4,6-Trimethoxybenzoic Acid (6d)



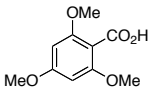
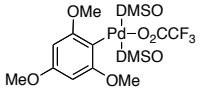
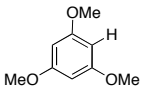
6, R = OMe **7**, R = OMe

To a solution of 2,4,6-trimethoxybenzoic acid, **(6d)**, (14 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). ^{1}H NMR spectra were taken periodically throughout the course of the reaction. The ratio of **6d**:**7d**:**8d** (R = OMe) was determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S15**. The relevant ^{1}H NMR chemical shifts are listed in **Table S16**.

Table S15 Data from the ^{1}H NMR Measurements of Decarboxylative Palladation of **6d** (R = OMe) at Room Temperature

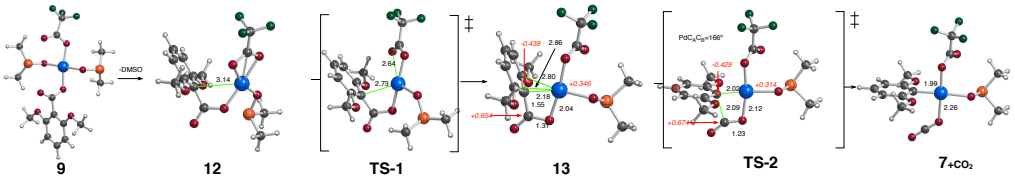
Time (h)	[**6d**, R = OMe] (M)
0	0.088
0.25	0.072
0.5	0.057
1	0.045
2	0.033
4	0.023

Table S16 ^{1}H NMR Chemical Shifts of **6d**, **7d**, and **8d** (R = OMe) in DMSO-d_6.

 **6**, R = OMe	 **7**, R = OMe	 **8**, R = OMe
6.23 (2H) 3.79 (3H) 3.74 (6H)	6.06 (2H) 3.81 (6H) 3.73 (3H)	6.08 (3H) 3.69 (9H)

Computational Work for Electrophilic Intramolecular Palladation followed by Decarboxylation (Figure 5)

All calculations were carried using B3LYP[1,2,3] or B3PW91[1,4,5,6] functionals using 6-31G(d) basis for main group elements and SDD or LANL2DZ for Pd in gas phase or in solvent (diethyl ether) using CPCM[7] solvation model. All stationary points were characterized as minima or transition state structures using frequency analysis. Intermediates **12** and **12a** differ in conformation of aryl ring in which aryl ring facing away from Pd is favored in all cases, presumably to avoid steric interactions with the CO_2CF_3 moiety.



	ΔH (ΔG)		ΔH‡ (ΔG‡)	wrt to **12**	ΔH (ΔG)	ΔH‡ (ΔG‡)	wrt to **12**	ΔH (ΔG)
B3LYP/LANL2DZ in DCM	0.0 (0.0)	26.6 (14.1)	27.9 (16.7)	1.3 (2.6)	18.1 (5.5)	31.7 (19.3)	5.1 (5.2)	24.4 (9.1)
B3LYP/SDD in DCM	0.0 (0.0)	21.0 (9.5)	23.5 (12.9)	2.5 (3.4)	12.9 (1.8)	27.7 (16.4)	6.7 (6.9)	21.4 (7.0)
B3LYP/SDD-gas	0.0 (0.0)	23.2 (10.1)	27.3 (15.5)	4.1 (5.4)	17.1 (3.2)	28.0 (14.8)	**4.8 (4.7)**	21.9 (7.1)
B3PW91/SDD-DCM	0.0 (0.0)	18.6 (7.6)	21.3 (10.5)	2.7 (2.9)	9.0 (-2.7)	24.5 (12.2)	**5.9 (4.6)**	19.7 (5.1)
B3PW91/SDD-gas	0.0 (0.0)	20.8 (7.7)	24.7 (13.4)	3.9 (5.7)	13.0 (1.0)	24.7 (12.1)	3.9 (4.4)	20.8 (5.0)
		another conformer **12a**		*wrt to* **12a**			*wrt to* **12a**	
		23.4 (10.6)		4.5 (6.1)			8.3 (8.7)	
		17.9 (6.3)		5.6 (6.6)			9.8 (10.1)	
		21.6 (8.3)		5.7 (7.2)			6.4 (6.5)	
		15.5 (3.2)		5.8 (7.3)			9.0 (9.0)	
		19.2 (6.4))		5.5 (7.0)			5.5 (5.7)	
BENZENE SYSTEM								
B3LYP/SDD in DCM	0.0 (0.0)	23.8 (11.7)	27.8 (16.2)	*wrt to* **12** 4.0 (4.5)	20.6 (8.9)	39.3 (26.5)	*wrt to* **12** 15.5 (14.8)	25.7 (9.7)
		another conformer **12a**		*wrt to* **12a** 10.1 (11.2)			*wrt to* **12a** 21.6 (21.5)	
		17.7 (5.0)						

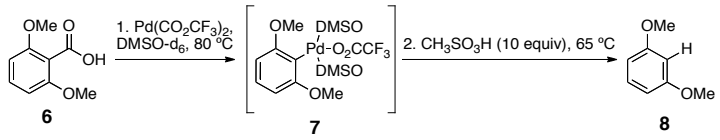
Figure S4 Relative enthalpies and free energies, in parenthesis, (kcal/mol; 298.15 K) calculated using either B3LYP or B3PW91 functional and 6-31G(d) basis for main group

elements and SDD (or LANL2DZ) for Pd in DCM (CPCM). Coordinates can be found on S40-S68.

Full Reference of Gaussian09:

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

^{1}H NMR Monitoring of the Protodepalladation of 7a to 8a (Figure 6)



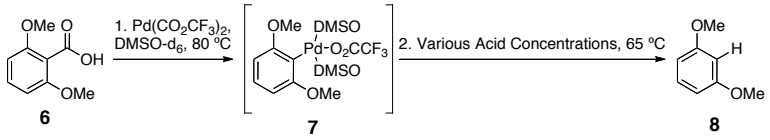
To a solution of 2,6-dimethoxybenzoic acid, **6a**, (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 mL) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). The mixture was heated at 80 ºC for 1 h, cooled to room temperature, and a ^{1}H NMR spectrum was taken. Methanesulfonic acid (43 μL, 0.66 mmol) was added and the mixture was heated to 65 ºC. ^{1}H NMR spectra were then taken periodically throughout the course of the reaction. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S17**.

Table S17 Data Presented in **Figure 6a** from ^{1}H NMR Measurements

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
1	0.081	29	0.022
2	0.079	47	0.009
8	0.063	75	0.000

25	0.028	

^{1}H NMR Monitoring of the Acid Effect on Protodepalladation



To a solution of 2,6-dimethoxybenzoic acid, **6a**, (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 mL) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). The mixture was heated at 80 ºC for 1 h, cooled to room temperature, and a ^{1}H NMR spectrum was taken. Methanesulfonic acid (43 μL, 0.66 mmol) was added and the mixture was heated to 65 ºC. ^{1}H NMR spectra were then taken periodically throughout the course of the reaction. The same experiment was also conducted with various amounts of CH_3SO_3H and then all experiments were compared. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S18**, **Table S19**, and **Table S20**. The equivalents of acid are based on the amount of methanesulfonic acid added to the reaction plus the one equivalent of trifluoroacetic acid liberated from palladium(II) trifluoroacetate during the reaction. The Lineweaver-Burke plot is depicted in **Figure S5**.

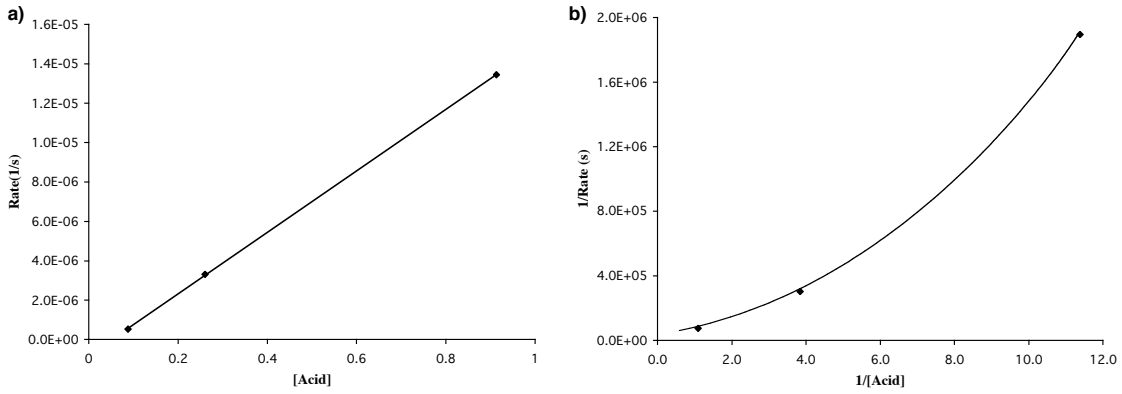


Figure S5 Acid Effect on the Protodepalladation of **7a** as Monitored by ^{1}H NMR Spectroscopy. Compound **6a** was mixed with $Pd(O_2CCF_3)_2$ in 0.75 mL DMSO-d_6 and heated to 80 ºC for 1 h. After cooling, a ^{1}H NMR spectrum was taken, CH_3SO_3H was added, and ^{1}H NMR monitoring was continued at 65 ºC. Three different acid concentrations were examined. Reaction conditions: a) [**6a**] = 0.09 M, [$Pd(O_2CCF_3)_2$] = 0.11 M, CH_3SO_3H (1 equiv). b) [**6a**] = 0.09 M, [$Pd(O_2CCF_3)_2$] = 0.10 M, CH_3SO_3H (3 equiv). c) [**6a**] = 0.08 M, [$Pd(O_2CCF_3)_2$] = 0.10 M, CH_3SO_3H (11 equiv).

Table S18 Data Presented in **Figure S5** from ^{1}H NMR Measurements Conducted with 1 Equivalent CH_3SO_3H

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0	0.078	24	0.073
1	0.077	48	0.074
8	0.077	117.5	0.062

Table S19 Data Presented in **Figure S5** from ^{1}H NMR Measurements Conducted with 3 Equivalents CH_3SO_3H

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0	0.076	28	0.058
1	0.077	46	0.045
7	0.073	74	0.032
24	0.062	95	0.026

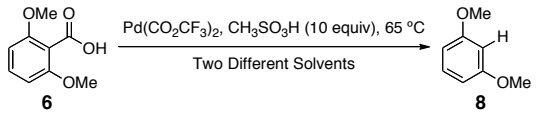
Table S20 Data Presented in **Figure S5** from ^{1}H NMR Measurements Conducted with 11 Equivalents CH_3SO_3H

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0	0.076	28	0.020
1	0.074	46	0.008
7	0.060	74	0.000
24	0.027		

Table S21 Rate Data from Monitoring Acid Effect on Protodepalladation

Acid (equiv)	[Acid]	k (s^{-1})
1.0	0.088	5.3×10^{-7}
3.0	0.26	3.3×10^{-6}
11	0.91	1.3×10^{-5}

GC Monitoring of the Effect of Solvent on Protodepalladation (Figure 7)



To a solution of **6a** (60 mg, 0.33 mmol) in the appropriate solvent (3.0 mL), was added palladium(II) trifluoroacetate (130 mg, 0.40 mmol) and biphenyl (51 mg, 0.33 mmol). To this solution was added CH_3SO_3H (210 μL, 3.3 mmol). The reaction mixture was heated at 65 ºC and at regular intervals aliquots (~100 μL) were removed. To each aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% MeOH/CH_2Cl_2). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations and the final data is shown in **Table S22** and **Table S23**.

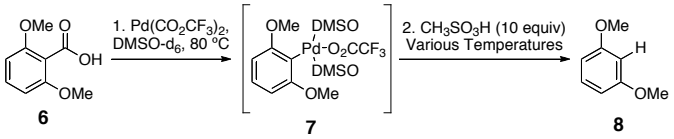
Table S22 Data Presented in **Figure 7** from GC Measurements

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0.00	0.102	0.83	0.091	1.67	0.080
0.17	0.101	1.00	0.089	1.83	0.070
0.33	0.099	1.17	0.086	2.00	0.074
0.50	0.097	1.33	0.083	24.00	0.028
0.67	0.094	1.50	0.082		

Table S23 Data Presented in **Figure 7** from GC Measurements

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0.00	0.102	0.83	0.028	1.67	0.010
0.17	0.075	1.00	0.024	1.83	0.011
0.33	0.064	1.17	0.014	2.00	0.011
0.50	0.055	1.33	0.014	24.00	0.019
0.67	0.039	1.50	0.011		

Protodepalladation Eyring Analysis (Figure 8).



To a solution of 2,6-dimethoxybenzoic acid, **6a,** (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 mL) was added palladium(II) trifluoroacetate (26 mg, 0.079 mmol). The mixture was heated at 80 ºC for 1 h, cooled to room temperature, and a ^{1}H NMR spectrum was taken. Methanesulfonic acid (43 μL, 0.66 mmol) was added and the mixture was heated to 50 ºC. ^{1}H NMR spectra were then taken periodically throughout the course of the reaction. Three more experiments were conducted in the same manner at different temperatures (70, 90, and 110 ºC) and then all four experiments were compared. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S24**, **Table S25**, **Table S26**, and **Table S27**. The rate data is shown in **Table S28**.

Table S24 Data Presented in **Figure 8** from ^{1}H NMR Measurements at 50 ºC

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0.00	0.076	25.50	0.054
1.00	0.076	33.50	0.051
3.00	0.075	52.00	0.040
7.50	0.071		

Table S25 Data Presented in **Figure 8** from ^{1}H NMR Measurements at 70 ºC

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0	0.079	9	0.039
1	0.070	16	0.024
3	0.061	23.5	0.009
6	0.048		

Table S26 Data Presented in **Figure 8** from ^{1}H NMR Measurements at 90 ºC

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0.02	0.079	0.13	0.071	0.59	0.037
0.03	0.079	0.15	0.070	0.77	0.030
0.05	0.077	0.17	0.069	1.00	0.022
0.07	0.077	0.22	0.064	1.28	0.016
0.08	0.076	0.27	0.060	1.53	0.012
0.10	0.075	0.31	0.054		
0.12	0.074	0.43	0.046		

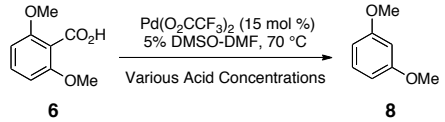
Table S27 Data Presented in **Figure 8** from ^{1}H NMR Measurements at 110 ºC

Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)	Time (h)	[**7a**] (M)
0.00	0.082	0.09	0.054	0.20	0.026
0.01	0.082	0.11	0.048	0.22	0.022
0.03	0.081	0.13	0.043	0.23	0.021
0.04	0.075	0.14	0.038	0.25	0.018
0.06	0.069	0.16	0.033	0.30	0.013
0.08	0.061	0.18	0.030	0.48	0.000

Table S28 Protonation Rates of **7a** to **8a** at Different Temperatures[a]

[a] Compound **6a** was mixed with $Pd(O_2CCF_3)_2$ in 0.75 mL DMSO-d_6 and heated to 80 ºC for 1 h. After cooling, a ^{1}H NMR spectrum was taken, CH_3SO_3H was added, and ^{1}H NMR monitoring was continued at the indicated temperature. Reaction conditions: initial concentration [**6a**] = 0.08 M and $[Pd(O_2CCF_3)_2]$ = 0.10 M, 10 equiv CH_3SO_3H, 0.75 mL DMSO-d_6

GC Monitoring of the Effect of Acid Concentration on Decarboxylation (Figure 9)



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in 5% DMSO-DMF (2.8 mL) was added palladium(II) trifluoroacetate (16 mg, 0.049 mmol) and biphenyl (51 mg, 0.33 mmol). To this solution was added CF_3CO_2H (250 μL, 3.3 mmol). The reaction mixture was

heated to 70 ºC and at regular intervals aliquots (~100 μL) were removed. To each aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% MeOH/CH_2Cl_2). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations. The same experiment was also conducted at various concentrations of CF_3CO_2H and then all five experiments were compared. The data presented in **Table S29**, **Table S30**, **Table S31**, **Table S32**, and **Table S33** represents an average of three trials conducted at each concentration.

Table S29 Data presented in **Figure 9** from GC measurements conducted with 0.5 equivalents of CF_3CO_2H with respect to **6a**

Time (h)	[**8a**] (M)
2	0.008
6	0.021
24	0.063
30	0.070

Table S30 Data presented in **Figure 9** from GC measurements conducted with 1.0 equivalents of CF_3CO_2H with respect to **6a**

Time (h)	[**8a**] (M)
2	0.011
6	0.031
24	0.076
30	0.077

Table S31 Data presented in **Figure 9** from GC measurements conducted with 2.0 equivalents of CF_3CO_2H with respect to **6a**

Time (h)	[**8a**] (M)
2	0.015
6	0.041
10	0.058
24	0.082

30	0.083

Table S32 Data presented in **Figure 9** from GC measurements conducted with 10 equivalents of CF_3CO_2H with respect to **6a**

Time (h)	[**8a**] (M)
2	0.022
6	0.055
24	0.087
30	0.088

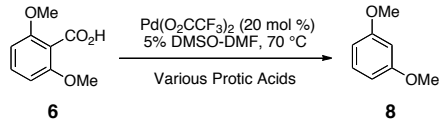
Table S33 Data presented in **Figure 9** from GC measurements conducted with 20 equivalents of CF_3CO_2H with respect to **6a**

Time (h)	[**8a**] (M)
2	0.013
6	0.030
24	0.073
30	0.077

Table S34 Rate Data from Monitoring Acid Concentration on Decarboxylation

Acid (equiv)	[Acid]	k (s^{-1})
0.5	0.071	9.6×10^{-6}
1.0	0.125	1.2×10^{-5}
2.0	0.232	1.4×10^{-5}
10	1.087	1.5×10^{-5}
20	2.114	1.6×10^{-5}

GC Reaction Monitoring of Acids in the Decarboxylation Reaction (Table 2)



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in 5% DMSO-DMF (3.0 mL), was added palladium(II) trifluoroacetate (22 mg, 0.066 mmol) and biphenyl (51 mg, 0.33 mmol). To

this solution was added the appropriate protic acid (10 equivalents) as specified in **Table 2**. The mixture was heated to 70 ºC and at regular intervals aliquots (~100 μL) were removed. To each aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% MeOH/CH_2Cl_2). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations. The results summarized in **Table 2** are depicted in **Figure S6**.

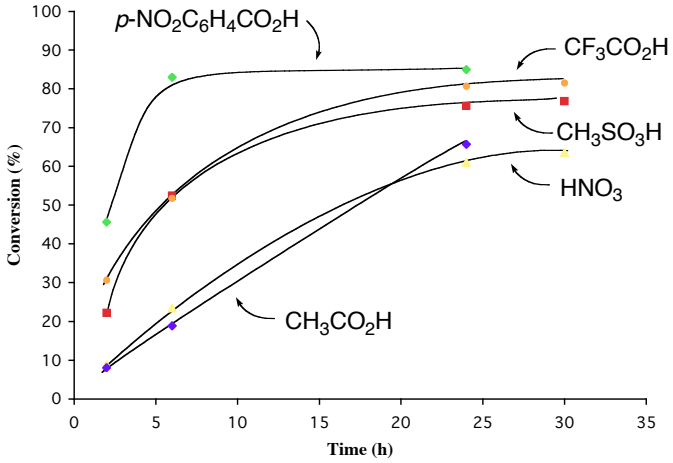
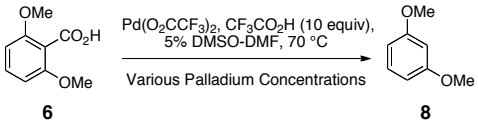


Figure S6. Conversion vs Time with Different Protic Acids.

GC Monitoring of Palladium Order in the Decarboxylation Reaction (Figure 10)



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in 5% DMSO-DMF (3.0 mL), was added palladium(II) trifluoroacetate (22 mg, 0.066 mmol) and biphenyl (51 mg, 0.33 mmol). To this solution was added CF_3CO_2H (250 μL, 3.3 mmol). The mixture was heated to 70 ºC and at regular intervals aliquots (~100 μL) were removed. To each aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% MeOH/CH_2Cl_2). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations. The same experiment was also conducted with various amounts of $Pd(O_2CCF_3)_2$ and then all

four experiments were compared. The final data is presented in **Table S35**, **Table S36**, and **Table S37**.

Table S35 Data presented in **Figure 10** from GC measurements conducted with 0.20 equivalents of $Pd(O_2CCF_3)_2$ with respect to **6a**

Time (h)	[**8a**] (M)
2	0.025
5	0.059
9	0.080
12	0.085
16	0.088
28	0.088

Table S36 Data presented in **Figure 10** from GC measurements conducted with 0.15 equivalents of $Pd(O_2CCF_3)_2$ with respect to **6a**

Time (h)	[**8a**] (M)
2	0.025
5	0.052
9	0.069
12	0.074
16	0.077
24	0.079

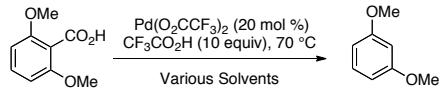
Table S37 Data presented in **Figure 10** from GC measurements conducted with 0.10 equivalents of $Pd(O_2CCF_3)_2$ with respect to **6a**

Time (h)	[**8a**] (M)
2	0.017
5	0.038
9	0.054
12	0.059
16	0.063
24	0.063

Table S38 Rate Data from Monitoring Palladium Order in the Decarboxylation

$Pd(O_2CCF_3)_2$ (equiv)	$[Pd(O_2CCF_3)_2]$	k (s^{-1})
0.20	0.020	5.1×10^{-5}
0.15	0.015	3.3×10^{-5}
0.10	0.010	2.2×10^{-5}

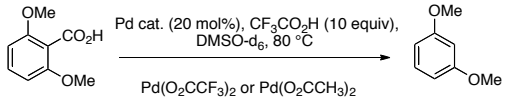
GC Reaction Monitoring of Solvents in the Decarboxylation Reaction (Table 3)



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in the appropriate solvent (3.0 mL) as specified in **Table 3**, was added palladium(II) trifluoroacetate (22 mg, 0.066 mmol) and biphenyl (51 mg, 0.33 mmol). To this solution was added CF_3CO_2H (250 μL, 3.3 mmol). The mixture was heated to 70 ºC and at regular intervals aliquots (~100 μL) were removed. To each aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% $MeOH/CH_2Cl_2$). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations.

^{1}H NMR Monitoring of $Pd(O_2CCH_3)_2$ vs $Pd(O_2CCF_3)_2$ in the Decarboxylation Reaction



6 **8**

To a solution of 2,6-dimethoxybenzoic acid, **6a**, (12 mg, 0.066 mmol) in DMSO-d_6 (0.75 mL) was added palladium(II) trifluoroacetate (4.4 mg, 0.013 mmol) and CH_3SO_3H (43 μL, 0.66 mmol). The mixture was heated to 80 ºC and ^{1}H NMR spectra were taken periodically throughout the course of the reaction. The same experiment was conducted with palladium(II) acetate. Ratios of **6a**:**7a**:**8a** were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S39** and **Table S40** and depicted in **Figure S7**.

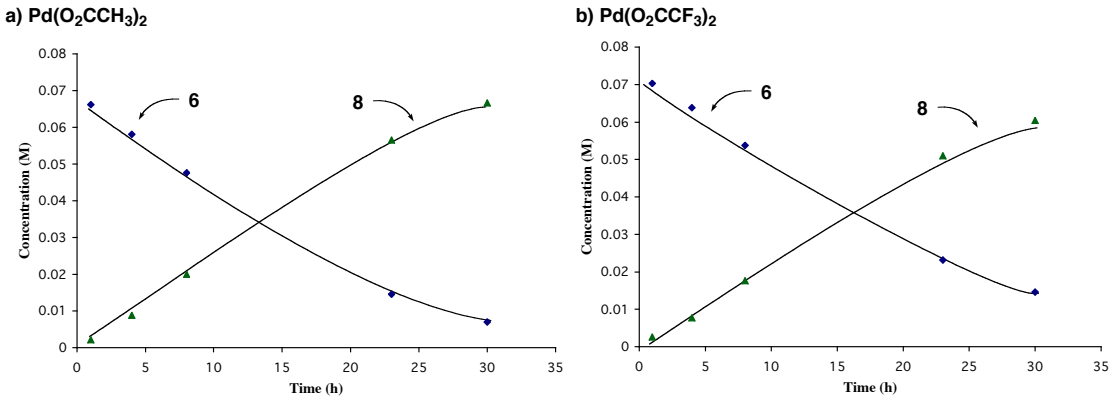


Figure S7. Comparison of $Pd(OAc)_2$ and $Pd(O_2CCF_3)_2$ in the decarboxylation of **6a** as monitored by ^1H NMR spectroscopy.

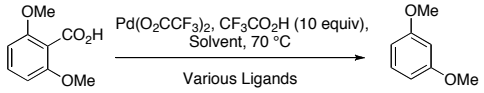
Table S39 Data presented in **Figure S7a** from ^1H NMR measurements conducted with $Pd(O_2CCH_3)_2$

Time (h)	[**6a**] (M)
0	0.083
1	0.066
4	0.058
8	0.048
23	0.015
30	0.007

Table S40 Data presented in **Figure S7b** from ^1H NMR measurements conducted with $Pd(O_2CCF_3)_2$

Time (h)	[**6a**] (M)
0	0.083
1	0.070
4	0.064
8	0.054
23	0.023
30	0.015

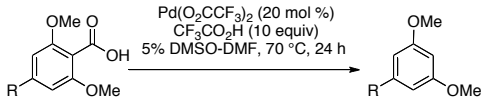
GC Reaction Monitoring of Ligands in the Decarboxylation Reaction (Table 4)



6 **8**

To a solution of **6a** (60 mg, 0.33 mmol) in the appropriate solvent (3.0 mL) specified in **Table 4**, was added palladium(II) trifluoroacetate (22 mg, 0.066 mmol), biphenyl (51 mg, 0.33 mmol), and CF_3CO_2H (250 μL, 3.3 mmol). To each solution was added the appropriate ligand as specified in **Table 4**. The mixture was heated to 70 ºC and at regular intervals aliquots (~100 μL) were removed. To this aliquot was added 1 M HCl and EtOAc. The solution was then shaken and the organic phase was filtered through SiO_2 (10% MeOH/CH_2Cl_2). The samples were then analyzed by gas chromatography (GC) using the conditions described in the general considerations.

^{1}H NMR Hammett Study of Aromatic Decarboxylation Reaction (Figure 11)



6 **8**

To a solution of 2,6-dimethoxy-4-methylbenzoic acid (**6b**, R = Me) (13 mg, 0.066 mmol) in DMSO-d_6 (0.75 ml) was added palladium(II) trifluoroacetate (4.4 mg, 0.013 mmol) and CH_3SO_3H (43 µL, 0.66 mmol). The mixture was then warmed to 70 ºC and spectra were taken periodically throughout the course of the reaction. Experiments with **6a,c-d** (R = H, Cl, and OMe) were conducted in the same manner and all four experiments were used to construct **Figure 11**. Ratios of the carboxylic acid starting materials, aryl palladium intermediates, and protodecarboxylated products were determined by comparison of ^{1}H NMR integrations and the final data is presented in **Table S41** (**6a**, R = H), **Table S42** (**6b**, R = Me), **Table S43** (**6c**, R = Cl), and **Table S44** (**6d**, R = OMe). The relevant ^{1}H NMR chemical shifts are listed in **Table S4**, **Table S11**, **Table S13**, and **Table S16**.

Table S41 Data presented in **Figure 11** from ^{1}H NMR measurements of the decarboxylation of **6a** (R = H) at 70 ºC

Time (h)	[**6a**, R = H] (M)	Time	[**6a**, R = H] (M)
0	0.083	33.5	0.041
1	0.078	48	0.029
6	0.070	60	0.021
24	0.050	81	0.010

Table S42 Data presented in **Figure 11** from ^{1}H NMR measurements of the decarboxylation of **6b** (R = Me) at 70 ºC

Time (h)	[**6b**, R = Me] (M)	Time (h)	[**6b**, R = Me] (M)
0	0.084	4	0.043
1	0.066	5	0.038
2	0.058	8	0.021
3	0.051		

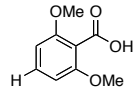
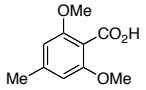
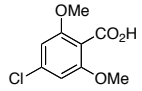
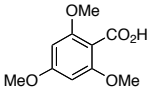
Table S43 Data presented in **Figure 11** from ^{1}H NMR measurements of the decarboxylation of **6c** (R = Cl) at 70 ºC

Time (h)	[**6c**, R = Cl] (M)	Time	[**6c**, R = Cl] (M)
0	0.083	60	0.045
1	0.081	72	0.040
7	0.072	97	0.032
24	0.060	120.5	0.025
33.5	0.056	168	0.014
48	0.049		

Table S44 Data presented in **Figure 11** from ^{1}H NMR measurements of the decarboxylation of **6d** (R = OMe) at 70 ºC

Time (min)	[**6d**, R = OMe] (M)	Time	[**6d**, R = OMe] (M)
4.00	0.066	8.25	0.005
5.25	0.041	9.00	0.003
6.50	0.025	9.75	0.002
7.25	0.013		

Table S45 Rate Data from Hammett Study of the Decarboxylation Reaction

Substrate	σ^+ values	k (s^{-1})
 **6**, R = H	0.00	6.8×10^{-6}
 **6**, R = Me	–0.31	4.6×10^{-5}
 **6**, R = Cl	0.11	2.8×10^{-6}
 **6**, R = OMe	–0.78	0.011

References

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

2) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

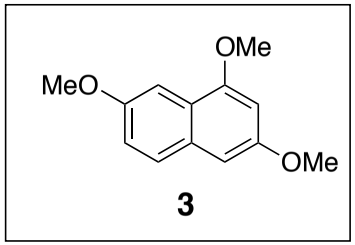
3) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

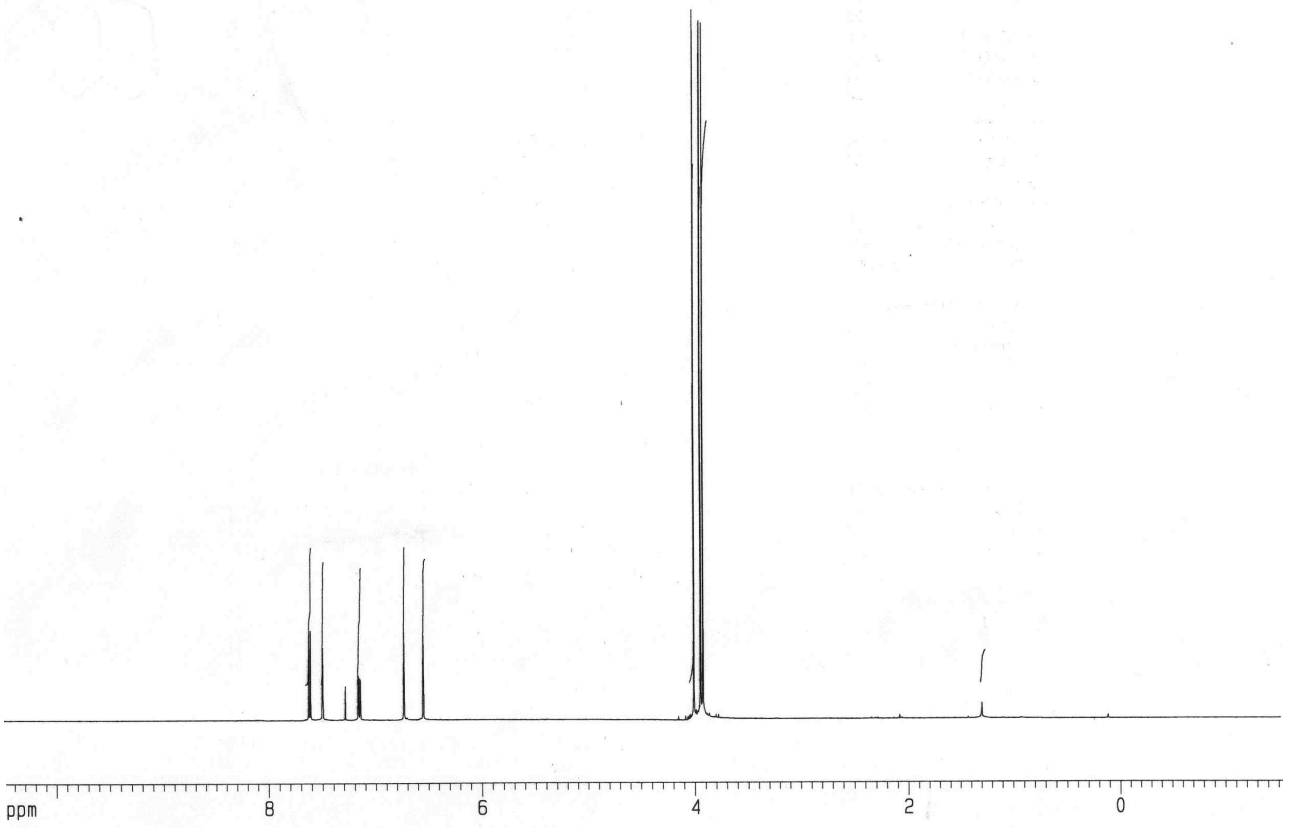
4) Perdew, J. P, In *Electronic Structure of Solids '91*P. Ziesche, H. Eschig, ed.; Akademie Verlag Berln, 1991 p11.

5) Perdew, J. P.; Wang, Y. *Phys. Rev. B: Condens. Matter,* **1992**, *45*, 13244.

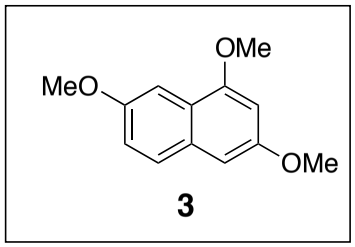
6) Perdew, J. P.; Berke, K.; Wang, Y. *Phys. Rev. B: Condens. Matter,* **1996**, *54*, 16533.

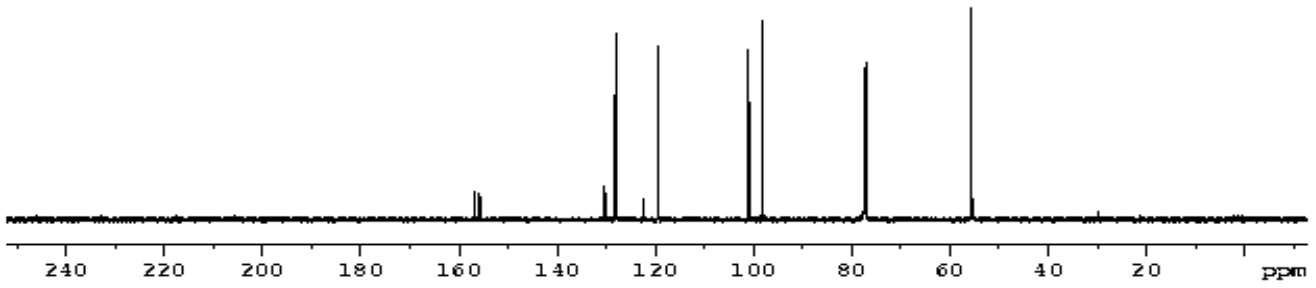
7) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.



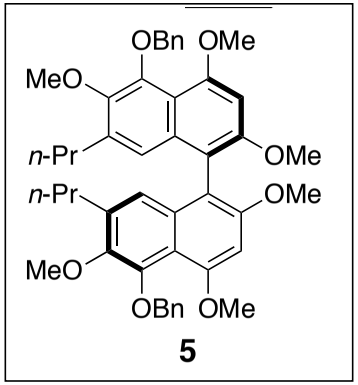


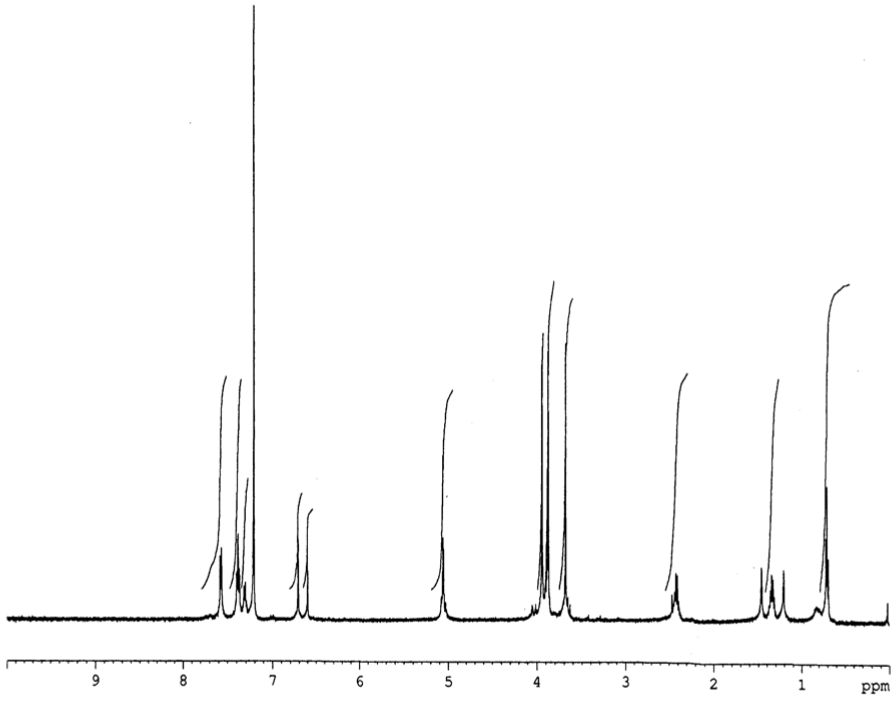
Scheme 1. 500 MHz ^{1}H NMR Spectrum of Compound **3** in $CDCl_3$



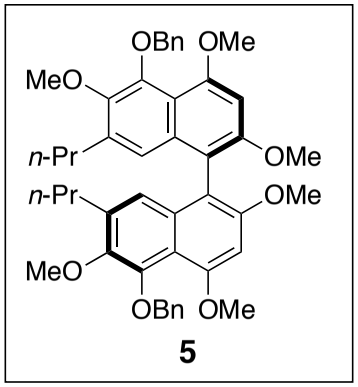


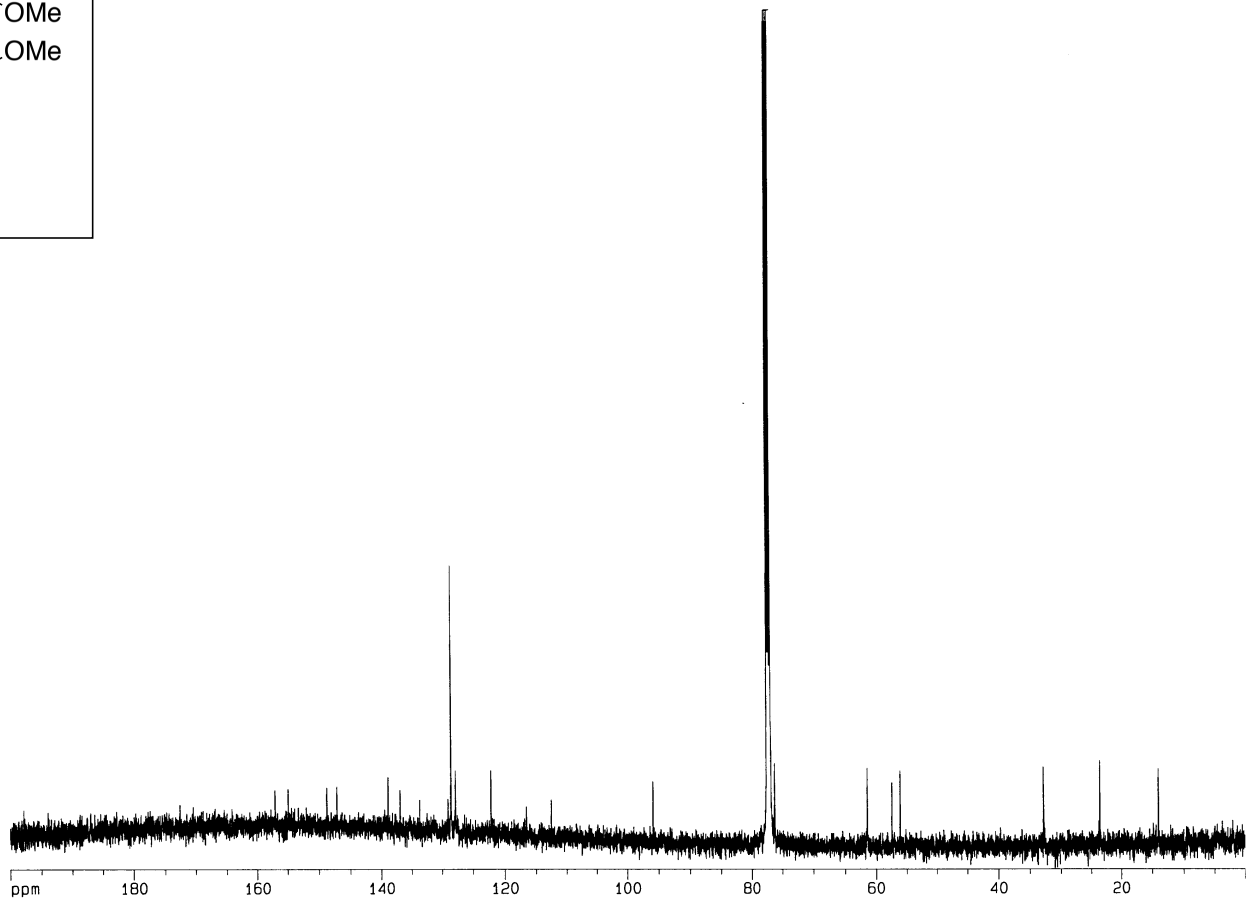
Scheme 1. 125 MHz ^{13}C NMR Spectrum of Compound **3** in $CDCl_3$



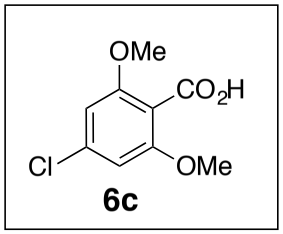


Scheme 2. 500 MHz ^{1}H NMR Spectrum of Compound **5** in $CDCl_3$





Scheme 2. 125 MHz ^{13}C NMR Spectrum of Compound **5** in $CDCl_3$



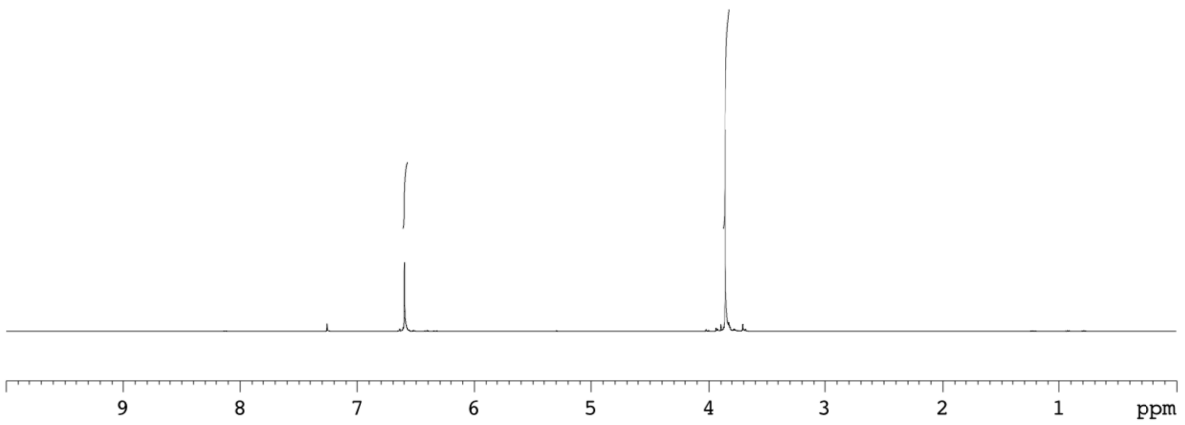
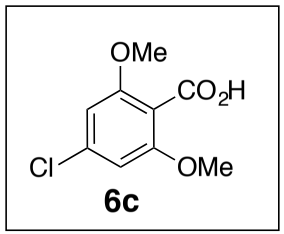


Figure 4. 500 MHz ^{1}H NMR Spectrum of Compound **6c** in $CDCl_3$



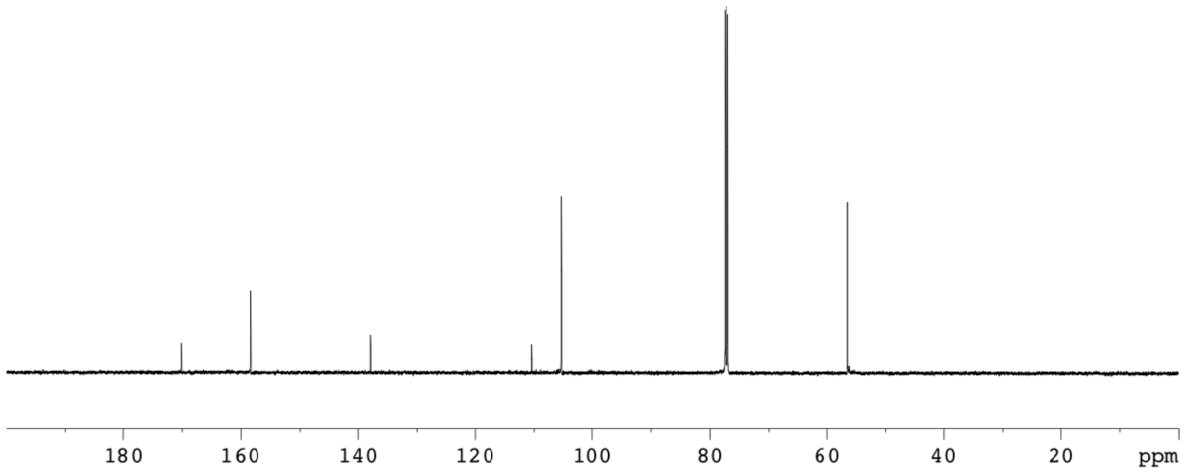
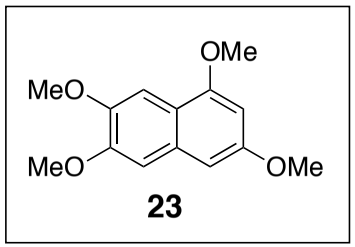


Figure 4. 125 MHz ^{13}C NMR Spectrum of Compound **6c** in $CDCl_3$



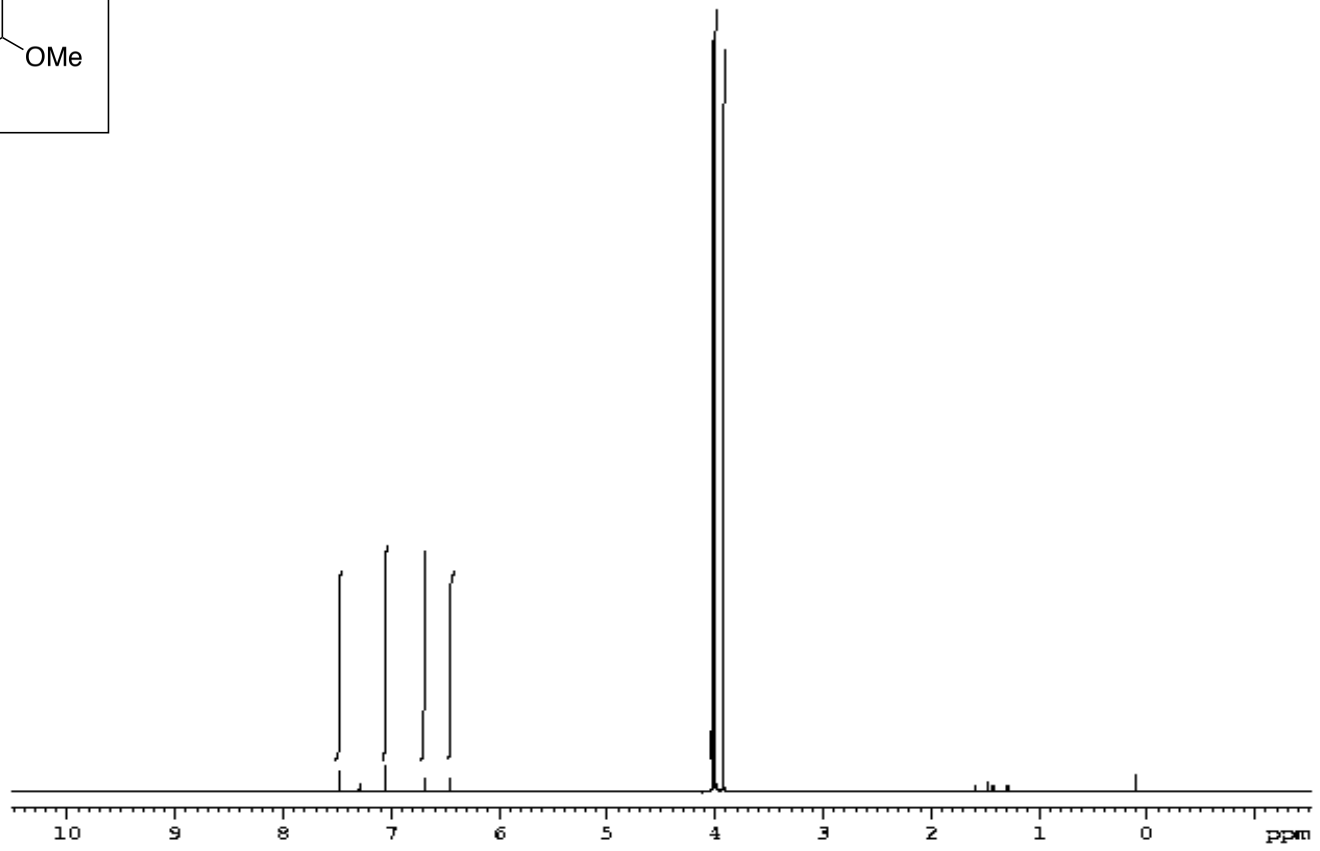
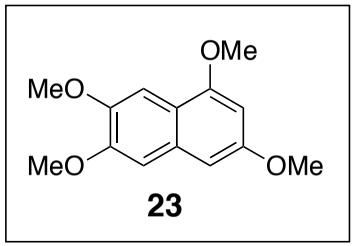


Table 6. 500 MHz ^{1}H NMR Spectrum of Compound **23** in $CDCl_3$



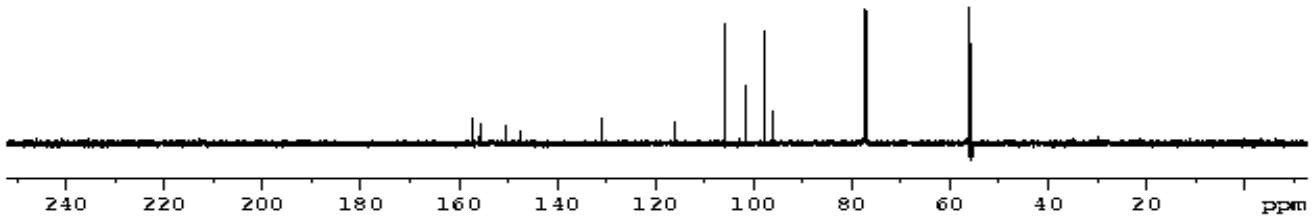
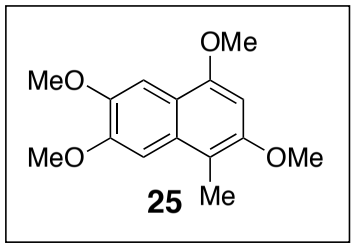


Table 6. 125 MHz ^{13}C NMR Spectrum of Compound **23** in $CDCl_3$



25

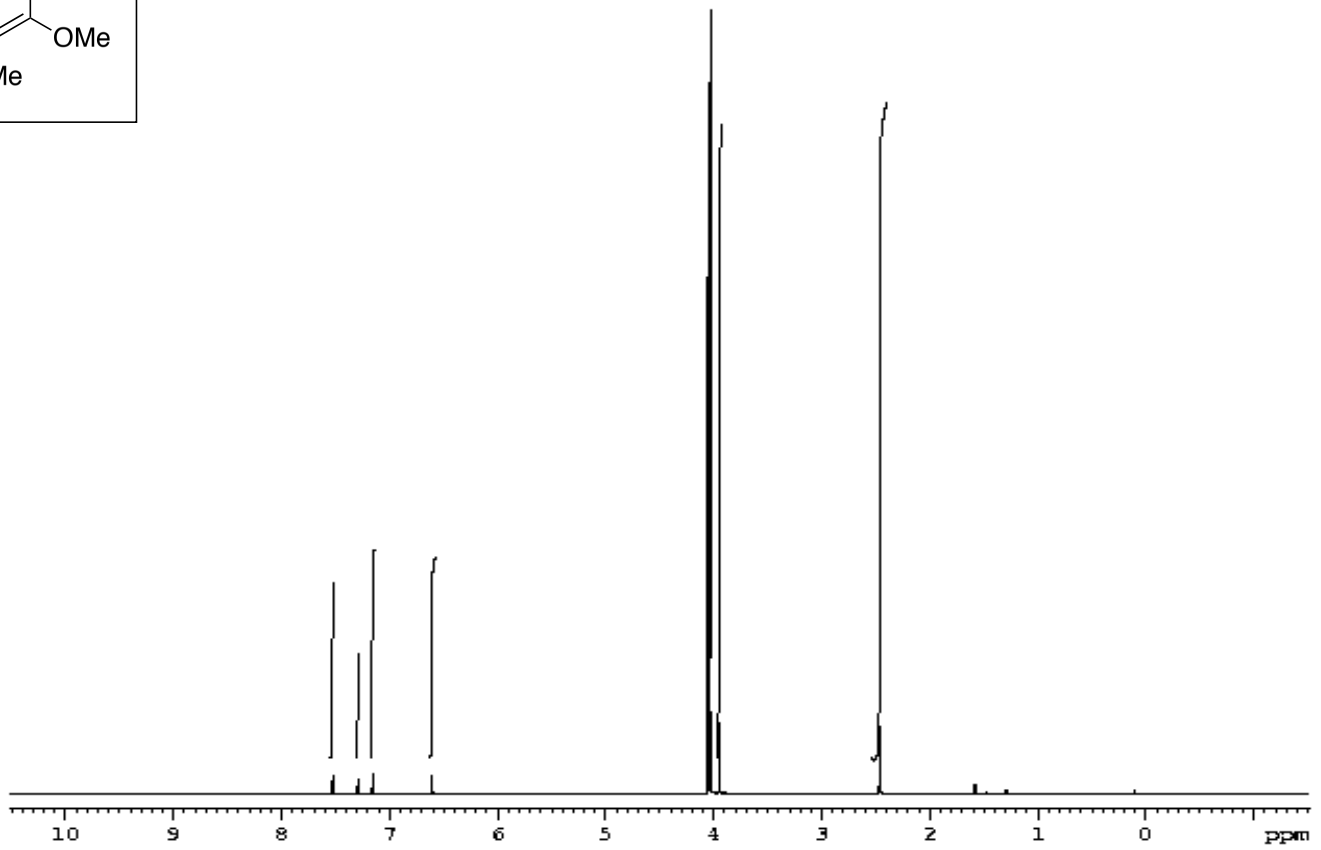
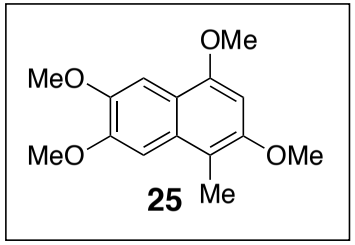


Table 6. 500 MHz ^{1}H NMR Spectrum of Compound **25** in $CDCl_3$



25

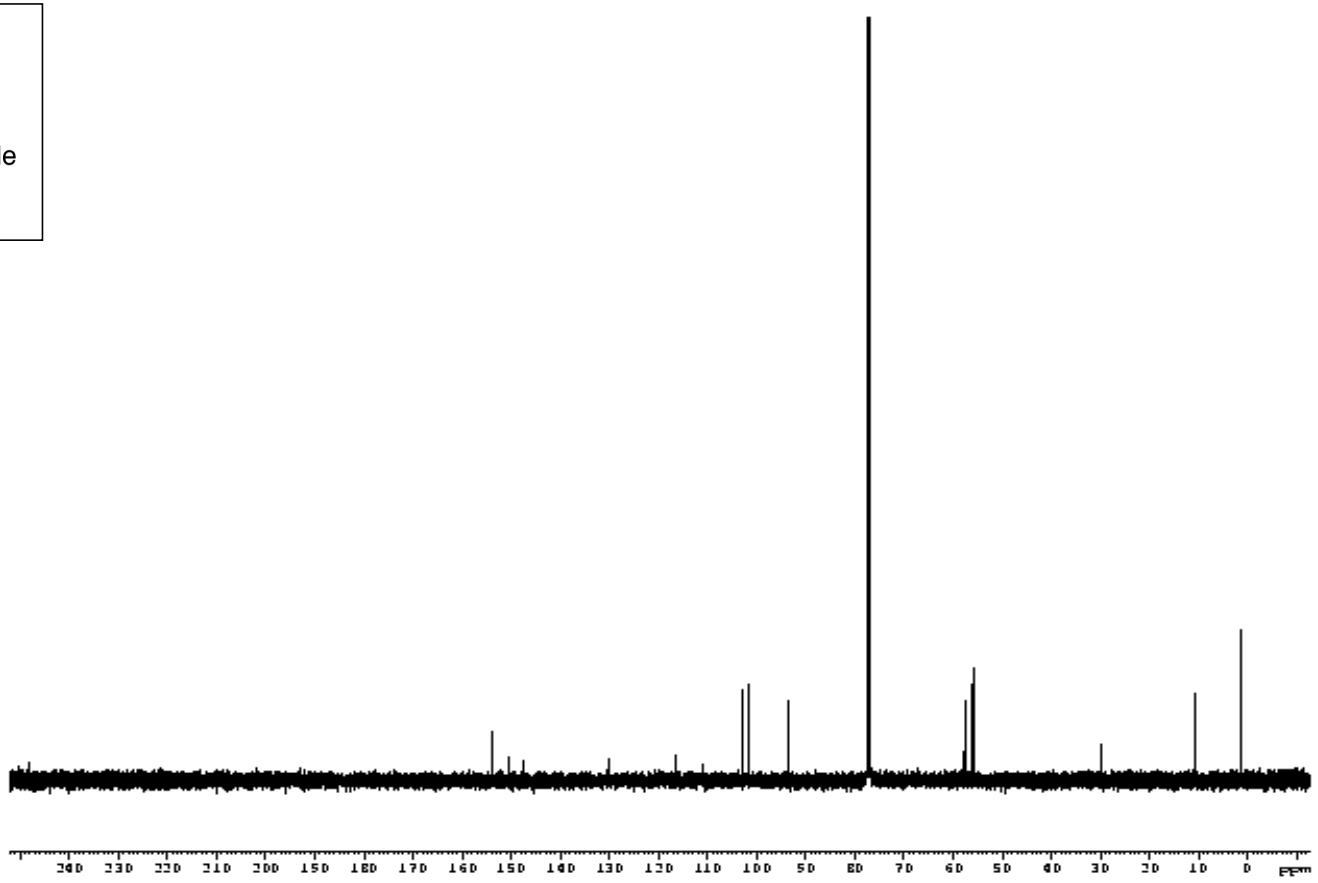
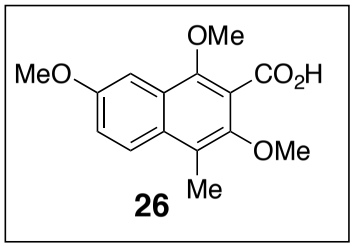


Table 6. 125 MHz ^{13}C NMR Spectrum of Compound **25** in $CDCl_3$



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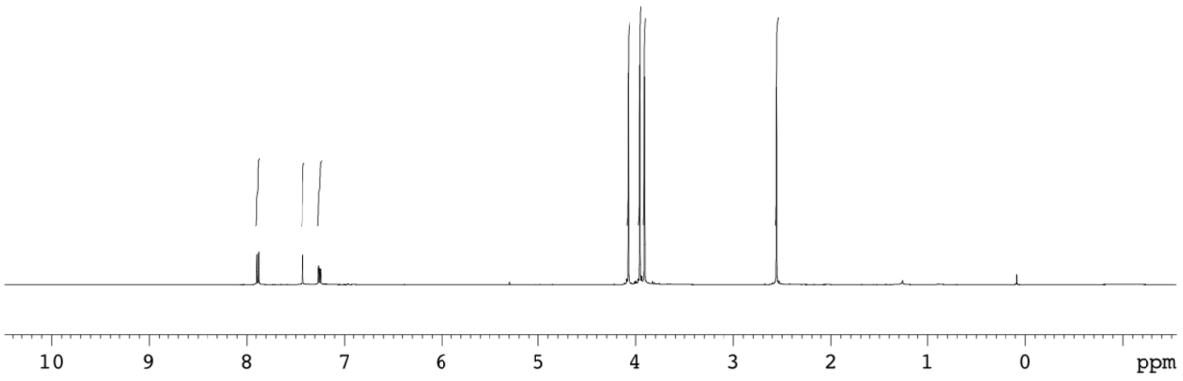
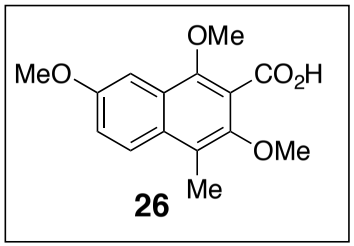


Table 6. 500 MHz ^{1}H NMR Spectrum of Compound **26** in $CDCl_3$



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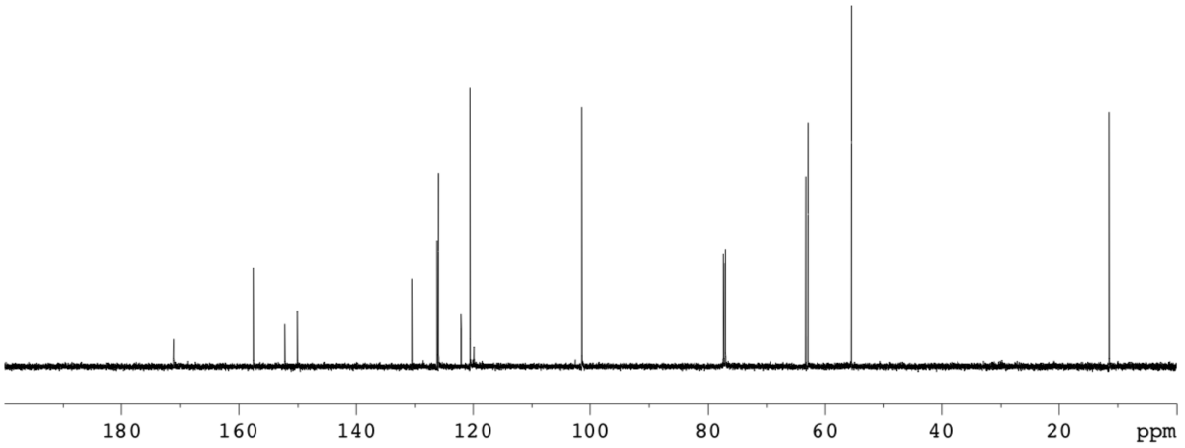

Table 6. 125 MHz ^{13}C NMR Spectrum of Compound **26** in $CDCl_3$

Coordinates and Energies for Figure 5 and Figure S4

B3LYP/6-31G(d) (SDD for PD)
in DCM (CPCM;UA0)

9

Zero-point correction= 0.362394 (Hartree/Particle)
Thermal correction to Energy= 0.397673
Thermal correction to Enthalpy= 0.398618
Thermal correction to Gibbs Free Energy= 0.288912
Sum of electronic and zero-point Energies= -2409.485318
Sum of electronic and thermal Energies= -2409.450038
Sum of electronic and thermal Enthalpies= -2409.449094
Sum of electronic and thermal Free Energies= -2409.558799

C	0.25383200	1.68488200	2.62751000
C	-0.09653500	1.47885700	3.97160300
C	0.18194300	2.97835500	2.08798300
C	-0.50933100	2.55256900	4.77298900
C	-0.23248500	4.05920200	2.87855200
C	-0.57091000	3.82812100	4.21191900
H	-0.29391600	5.06073300	2.47128400
H	-0.89147400	4.66300800	4.82886100
C	1.53786200	-4.08767100	-1.13659800
O	0.52724900	3.08363700	0.76840400
C	0.46423400	4.36709700	0.15154900
H	1.14557700	5.07650200	0.63596400
H	0.77405900	4.21486400	-0.88314400
H	-0.55575100	4.76860700	0.17125700
O	0.39345800	-3.62368800	-0.79105400
C	1.37395900	-5.41768400	-1.92102300
O	2.66500500	-3.63401800	-0.95215900
Pd	0.22958700	-1.88203000	0.27426200
O	1.94972300	0.34686200	1.59637600
C	3.15191300	-1.02538900	-2.87471500
H	2.49267100	-0.59127200	-3.63032900
H	4.18407500	-0.69440000	-3.01891000
H	3.10252500	-2.11481000	-2.88426800
C	2.67778700	1.29272900	-1.44091700
H	2.26498500	1.73082100	-0.53102200
H	3.72461900	1.58424400	-1.56397200
H	2.08866600	1.57481600	-2.31714300
S	2.61018900	-0.50651800	-1.22222900
O	1.05386400	-0.80252700	-1.27418900
H	-0.77809800	2.40495300	5.81162600
O	0.00675500	0.18959100	4.41211100
C	-0.27733800	-0.08510300	5.78117000
H	-1.31941900	0.15031400	6.02874000
H	-0.10693400	-1.15468600	5.91076200
H	0.39064100	0.47438700	6.44686000
F	2.55571000	-5.99875900	-2.17701400
F	0.75988100	-5.19414100	-3.10490700
F	0.61952900	-6.30220600	-1.23322000
C	0.74182500	0.52699400	1.78230800
O	-0.22389200	-0.20310300	1.31169800
S	-2.08157900	-3.41065100	1.93186800
O	-0.57654600	-2.98942400	1.82562100
C	-2.54289200	-4.21170600	0.36677900
H	-2.37334500	-3.52571300	-0.46571800
H	-1.91510400	-5.09742000	0.25731300
H	-3.59605900	-4.49714900	0.44162600
C	-3.07851800	-1.89877700	1.78315300
H	-2.82832900	-1.26320600	2.63390000
H	-2.84201600	-1.39020200	0.84597400
H	-4.13194000	-2.18939600	1.82402300

12

Zero-point correction= 0.280394 (Hartree/Particle)
Thermal correction to Energy= 0.308611
Thermal correction to Enthalpy= 0.309555
Thermal correction to Gibbs Free Energy= 0.216563
Sum of electronic and zero-point Energies= -1856.334929
Sum of electronic and thermal Energies= -1856.306712
Sum of electronic and thermal Enthalpies= -1856.305768
Sum of electronic and thermal Free Energies= -1856.398760

C	-1.48624600	-1.72789300	1.21130500
C	-2.71364900	-2.35988900	0.95031500
C	-0.75824700	-2.08133900	2.35942500
C	-3.19930200	-3.35267900	1.81251200
C	-1.23504200	-3.07191200	3.22839400
C	-2.45099300	-3.69264800	2.93940400
H	-0.68174800	-3.35342200	4.11568800
H	-2.82601400	-4.45917500	3.61187900
C	0.01132700	-5.00312400	-1.38864900
O	0.41185700	-1.39865400	2.54157200
C	1.19333000	-1.68857400	3.69851400
H	1.53270000	-2.73112900	3.69952100
H	2.05754500	-1.02523300	3.64627600
H	0.63208800	-1.48546000	4.61802000
O	1.23826400	-4.72222500	-1.24743100
C	-0.40459900	-6.46112000	-1.63384500
O	-0.87771500	-4.10977200	-1.27976100
Pd	0.67227700	-2.70634100	-0.85182900
O	-0.15086300	-0.90059700	-0.64261200
C	4.36066800	-0.23338300	0.27548500
H	4.95759700	-0.62330300	-0.55170900
H	4.61017300	0.81001000	0.48506800
H	4.50077400	-0.83884600	1.17280800
C	2.61229300	0.62203400	-1.70627700
H	1.60237900	0.55102500	-2.11279200
H	2.85332100	1.66374400	-1.47720700
H	3.34461400	0.18760000	-2.39112500
S	2.60171300	-0.31708800	-0.15284600
O	2.50561300	-1.83676300	-0.60709600
H	-4.14069000	-3.85132000	1.61826300
O	-3.35493500	-1.94200500	-0.17861100
C	-4.59425900	-2.55652800	-0.52296600
H	-5.34864800	-2.39551200	0.25619100
H	-4.91745200	-2.07414400	-1.44626200
H	-4.47013600	-3.63188200	-0.69645900
F	-0.52056600	-7.09333700	-0.45017200
F	0.51525400	-7.10232800	-2.36719500
F	-1.58355600	-6.52459300	-2.26504800
C	-1.01297900	-0.60714500	0.31407500
O	-1.42326400	0.53702900	0.45859700

12a

Zero-point correction= 0.280361 (Hartree/Particle)
Thermal correction to Energy= 0.308619
Thermal correction to Enthalpy= 0.309563
Thermal correction to Gibbs Free Energy= 0.216329
Sum of electronic and zero-point Energies= -1856.339805
Sum of electronic and thermal Energies= -1856.311547
Sum of electronic and thermal Enthalpies= -1856.310603
Sum of electronic and thermal Free Energies= -1856.403837

C	-1.93659400	0.46039500	-0.75805800
C	-2.02737700	1.31592700	0.35214800
C	-2.47403300	0.86568500	-1.99134600
C	-2.65432100	2.56440000	0.23706000
C	-3.10528600	2.11120500	-2.11535100
C	-3.18447700	2.94120800	-0.99703900
H	-3.52868200	2.43262600	-3.05880900
H	-3.67193400	3.90774400	-1.08974800
C	0.51844200	-4.95070300	-2.02485400
O	1.57849500	-4.69704300	-1.38122200
C	0.34795900	-6.32917900	-2.68092900
O	-0.37822400	-4.07087000	-2.17748300
Pd	0.84641400	-2.70811000	-1.09285200
O	-0.07157700	-0.92812800	-1.09577100
C	3.54609100	-0.72283400	1.95570900
H	4.45236100	-0.71730300	1.34590300
H	3.52206500	0.13332200	2.63477900
H	3.46668500	-1.65240200	2.52230600
C	2.47576500	0.88411100	-0.04179300
H	1.69128300	0.98913300	-0.79211900
H	2.44890300	1.72425400	0.65758800
H	3.45943300	0.78966200	-0.50776800
S	2.09317500	-0.63306600	0.87678900
O	2.41442600	-1.80934200	-0.13973200
H	-2.72976300	3.23364800	1.08520000
F	0.89460900	-7.28810600	-1.92081200
F	0.96806100	-6.33053900	-3.87666800
F	-0.94543100	-6.61441900	-2.87428200
C	-1.29641800	-0.90041500	-0.61751400
O	-1.88071700	-1.84988300	-0.10640200
O	-2.34143100	-0.03233400	-3.00954800
O	-1.46006100	0.84524000	1.50132100
C	-2.88136300	0.30100000	-4.28616300
H	-3.96602200	0.45180400	-4.23289600
H	-2.40696300	1.20002200	-4.69716200
H	-2.66406800	-0.55124800	-4.93111900
C	-1.55671500	1.64004200	2.68048400
H	-1.06509700	1.06546900	3.46659800
H	-1.04524900	2.60211100	2.55718500
H	-2.60294300	1.81599700	2.95677200

TS-1

Zero-point correction= 0.279784 (Hartree/Particle)
Thermal correction to Energy= 0.307576
Thermal correction to Enthalpy= 0.308520
Thermal correction to Gibbs Free Energy= 0.216876
Sum of electronic and zero-point Energies= -1856.330459
Sum of electronic and thermal Energies= -1856.302667
Sum of electronic and thermal Enthalpies= -1856.301723
Sum of electronic and thermal Free Energies= -1856.393367

C	-1.30146000	-0.72069700	-1.96872000
C	-0.79690700	-0.96739300	-3.26859600
C	-2.54582100	-1.27557600	-1.59174400
C	-1.49138800	-1.80112500	-4.15040100
C	-3.24294200	-2.11083100	-2.47464100
C	-2.70362000	-2.35934000	-3.73549100
H	-4.18772300	-2.55734100	-2.19198300
H	-3.24463700	-3.00596700	-4.42064800
C	-0.54801300	-4.65275500	-0.37825500
O	-2.98030400	-0.93102000	-0.35386000
C	-4.15745400	-1.56059000	0.15696000
H	-4.02973900	-2.64728400	0.19397600
H	-4.28455700	-1.16879300	1.16653100
H	-5.03580600	-1.30519000	-0.44637800
O	0.62120200	-4.24329600	-0.71549000
C	-0.72881800	-6.18271500	-0.45852500
O	-1.48229200	-3.92420600	-0.02496800
Pd	0.46589100	-2.21015400	-0.51876200
O	0.29917700	-0.23798200	-0.27547900
C	4.87887700	-1.21974300	0.44080100
H	5.29565000	-1.76754000	-0.40734800
H	5.46564100	-0.32355600	0.65871700
H	4.82508300	-1.85708300	1.32515200
C	3.49120900	0.23635700	-1.47273700
H	2.51280500	0.45901500	-1.90216900
H	4.00705200	1.16264300	-1.20470000
H	4.08976700	-0.36417100	-2.16175500
S	3.18547600	-0.70454200	0.04978200
O	2.55985300	-2.07338300	-0.43752900
H	-1.11279700	-2.00824200	-5.14328100
O	0.37155200	-0.33548200	-3.56336900
C	0.96019400	-0.55586100	-4.84653900
H	0.29244000	-0.22304400	-5.64874200
H	1.87201600	0.04151300	-4.85937400
H	1.21071400	-1.61327100	-4.98838400
F	-0.57187000	-6.60505600	-1.72974900
F	-1.94579800	-6.55664600	-0.04123900
F	0.18878300	-6.81132000	0.30196000
C	-0.61216100	0.28691500	-1.06873300
O	-0.88107400	1.47744600	-1.08264400

13

Zero-point correction= 0.280180 (Hartree/Particle)
Thermal correction to Energy= 0.308556
Thermal correction to Enthalpy= 0.309500
Thermal correction to Gibbs Free Energy= 0.217018
Sum of electronic and zero-point Energies= -1856.347989
Sum of electronic and thermal Energies= -1856.319613
Sum of electronic and thermal Enthalpies= -1856.318669
Sum of electronic and thermal Free Energies= -1856.411151

C	-1.49367900	-2.11308200	0.85057600
C	-2.40200500	-2.63885200	-0.13980500
C	-1.11611800	-2.96829700	1.94978800
C	-2.75515900	-3.98837600	-0.12521000
C	-1.47563500	-4.31724300	1.94764500
C	-2.27990200	-4.79609500	0.91124700
H	-1.16289300	-4.98379200	2.74065200
H	-2.56288200	-5.84488500	0.91956500
C	1.83762000	-4.46488900	-0.35845600
O	-0.43060600	-2.35852300	2.92890600
C	0.11078600	-3.14816200	3.99837300
H	0.80624600	-3.89754700	3.60744600
H	0.64254000	-2.44371500	4.63673200
H	-0.68915600	-3.63276000	4.56646200
O	0.80758000	-3.88902700	-0.86449400
C	2.05247600	-5.86988000	-0.98112900
O	2.62273400	-4.05814600	0.49575000
Pd	0.37998500	-1.98535700	-0.25005500
O	-0.28235600	-0.18253600	0.40146300
C	4.67936200	-1.83602600	-0.87141900
H	4.77952000	-1.79771400	-1.95891500
H	5.58545400	-1.47350700	-0.37847300
H	4.43755300	-2.84496800	-0.53276400
C	3.78791300	0.77824000	-1.12719200
H	2.98507400	1.49494900	-0.94380900
H	4.71166000	1.11947700	-0.65220700
H	3.93030200	0.62463500	-2.19971600
S	3.28945000	-0.78826000	-0.35792400
O	2.09397000	-1.26478800	-1.26540900
H	-3.40088000	-4.40942900	-0.88473200
O	-2.85550500	-1.73531700	-1.02259800
C	-3.68486000	-2.17506800	-2.10801600
H	-4.61473200	-2.61225500	-1.73162000
H	-3.90486900	-1.27797000	-2.68533900
H	-3.15095200	-2.89926000	-2.73131200
F	3.11300600	-6.49491500	-0.44756400
F	2.25717900	-5.77466000	-2.31292200
F	0.97083200	-6.65547400	-0.78994300
C	-1.36973200	-0.58232600	1.01130300
O	-2.17177300	0.10784600	1.61273800

TS-2

Zero-point correction= 0.277716 (Hartree/Particle)
Thermal correction to Energy= 0.306223
Thermal correction to Enthalpy= 0.307167
Thermal correction to Gibbs Free Energy= 0.214465
Sum of electronic and zero-point Energies= -1856.324524
Sum of electronic and thermal Energies= -1856.296017
Sum of electronic and thermal Enthalpies= -1856.295073
Sum of electronic and thermal Free Energies= -1856.387775

C	-1.35755100	-2.61069600	0.67570400
C	-2.49855300	-2.79515000	-0.16021500
C	-1.34786300	-3.25246800	1.94984800
C	-3.61431600	-3.50594000	0.29193400
C	-2.46297400	-3.96355800	2.40458000
C	-3.57494800	-4.07270500	1.56759500
H	-2.47552000	-4.43387200	3.37974200
H	-4.44135800	-4.62571500	1.91996500
C	1.92036900	-4.28248300	-0.63025900
O	0.83121800	-3.71617800	-0.99658800
C	2.30295900	-5.49985600	-1.51088800
O	2.71104200	-3.97148800	0.26065800
Pd	0.36314900	-1.92461700	-0.12133700
O	-0.44906700	-0.19780700	0.76952400
C	4.66748100	-1.74804600	-1.20728200
H	4.63939400	-1.32324800	-2.21401300
H	5.65266100	-1.61551500	-0.75169300
H	4.39878900	-2.80504300	-1.21966300
C	3.97901300	0.80504300	-0.41050700
H	3.26312200	1.44446200	0.11009800
H	4.97310000	0.92385000	0.02873500
H	3.99177700	1.03553100	-1.47871600
S	3.43220900	-0.91101500	-0.16956300
O	2.10646300	-0.98463300	-1.00008800
H	-4.49490500	-3.63151900	-0.32556000
F	1.28811600	-5.97119500	-2.25417100
F	2.76887100	-6.51391600	-0.75920100
F	3.29508700	-5.13033100	-2.35848500
C	-1.52212100	-0.57370600	1.23556600
O	-2.51661800	-0.30256200	1.81198300
O	-2.42240100	-2.21369100	-1.38160900
O	-0.21403400	-3.09099500	2.67398400
C	-0.15707900	-3.62333900	4.00124300
H	-0.25658600	-4.71399200	3.99139000
H	0.82645200	-3.34959800	4.38308000
H	-0.93530200	-3.18466500	4.63515800
C	-3.56024400	-2.27182300	-2.24769700
H	-3.27404900	-1.72033200	-3.14324000
H	-3.79810600	-3.30726500	-2.51379700
H	-4.43206200	-1.79764700	-1.78399800

7$_{+CO_2}$

Zero-point correction=	0.277776 (Hartree/Particle)
Thermal correction to Energy=	0.307565
Thermal correction to Enthalpy=	0.308510
Thermal correction to Gibbs Free Energy=	0.210723
Sum of electronic and zero-point Energies=	-1856.335810
Sum of electronic and thermal Energies=	-1856.306020
Sum of electronic and thermal Enthalpies=	-1856.305076
Sum of electronic and thermal Free Energies=	-1856.402863

C	-1.12936400	-2.90910400	0.55499800
C	-2.28840100	-3.12639900	-0.20762200
C	-1.11794000	-3.30897000	1.90101700
C	-3.42232400	-3.72793500	0.36256300
C	-2.24459200	-3.91208300	2.48387400
C	-3.38150000	-4.11482800	1.70207400
H	-2.24209100	-4.22002000	3.52278700
H	-4.25608600	-4.58169600	2.14705200
C	2.10254200	-4.38183200	-0.69243700
O	0.04552900	-3.06058900	2.58952700
C	0.13072300	-3.47516800	3.94974200
H	0.00205700	-4.56003800	4.04658900
H	1.13233200	-3.19855000	4.28237500
H	-0.61342800	-2.96431500	4.57306300
O	0.98504800	-3.87012100	-1.06299500
C	2.41292100	-5.67109200	-1.50017700
O	2.91256500	-3.99175200	0.14545500
Pd	0.47435600	-2.05662700	-0.25560100
O	-0.21610100	-0.05280100	0.53605000
C	4.78312700	-1.64475200	-1.20098500
H	4.76501700	-1.36910600	-2.25853400
H	5.73341800	-1.36564000	-0.73752300
H	4.59569000	-2.71108600	-1.06750500
C	3.89902900	0.93045600	-0.74119500
H	3.12377900	1.57783900	-0.32644900
H	4.86257600	1.15750100	-0.27733800
H	3.95004600	1.04284100	-1.82721300
S	3.44246800	-0.78020200	-0.33161900
O	2.16492600	-1.03539900	-1.19614000
H	-4.32095000	-3.89472600	-0.21947900
O	-2.23420600	-2.70881500	-1.51474300
C	-3.37243500	-2.92575100	-2.34304600
H	-4.25120600	-2.38770300	-1.96671900
H	-3.10349400	-2.53597100	-3.32596600
H	-3.60934200	-3.99331900	-2.42751400
F	3.51841600	-6.28506900	-1.05126200
F	2.61043800	-5.37012700	-2.80332200
F	1.39512300	-6.55340800	-1.43434000
C	-1.18684100	0.12964300	1.18124400
O	-2.13108000	0.35516400	1.81694000

B3LYP/6-31G(d) (SDD for PD)
gas phase

9

Zero-point correction=	0.362995 (Hartree/Particle)
Thermal correction to Energy=	0.397961
Thermal correction to Enthalpy=	0.398905
Thermal correction to Gibbs Free Energy=	0.291718
Sum of electronic and zero-point Energies=	-2409.451699
Sum of electronic and thermal Energies=	-2409.416733
Sum of electronic and thermal Enthalpies=	-2409.415789
Sum of electronic and thermal Free Energies=	-2409.522976

C	0.14897600	1.67259100	2.53971100
C	-0.31320200	1.42107500	3.84135900
C	0.16499600	2.99651100	2.07091900
C	-0.72930400	2.47118600	4.67164600
C	-0.26087000	4.05278600	2.88733600
C	-0.69746200	3.77465200	4.18135500
H	-0.25260000	5.07519500	2.53006000
H	-1.02234900	4.59178400	4.81985300
C	1.56433000	-4.12261200	-1.24345300
O	0.60226200	3.16453600	0.78518500
C	0.63297400	4.47655400	0.25024800
H	1.30877000	5.12950100	0.81820300
H	1.00519300	4.37444500	-0.77098500
H	-0.36809500	4.92673800	0.22558000
O	0.46638100	-3.71447700	-0.71809900
C	1.36703000	-5.50015400	-1.93244700
O	2.66402800	-3.58144300	-1.29742200
Pd	0.30631000	-1.94052100	0.27200400
O	1.89086000	0.48701000	1.41485300
C	3.13214500	-1.01583500	-2.92984900
H	2.44309900	-0.58341700	-3.66029300
H	4.15174800	-0.65087500	-3.08792700
H	3.11044000	-2.10551500	-2.95842000
C	2.64754400	1.25617200	-1.45675700
H	2.25869100	1.67704100	-0.52846200
H	3.68839000	1.55917200	-1.60887200
H	2.02858000	1.53711400	-2.31325700
S	2.60200500	-0.55011300	-1.25352100
O	1.05410200	-0.86095400	-1.30934700
H	-1.07622800	2.28156700	5.68028600
O	-0.31995400	0.10741900	4.22861500
C	-0.48361300	-0.18713000	5.60697500
H	-1.49462300	0.05782600	5.96078700
H	-0.31994500	-1.26214600	5.70272000
H	0.25096500	0.34886500	6.22114900
F	2.53623500	-6.10630300	-2.17912400
F	0.72980200	-5.33335900	-3.11505900
F	0.61692500	-6.33696800	-1.18346700
C	0.68858000	0.54908200	1.67647000
O	-0.23294200	-0.27385900	1.27603600
S	-1.89686800	-3.39885600	2.06041200
O	-0.39477600	-3.05496300	1.87262100
C	-2.50186700	-4.07046200	0.47835700
H	-2.34634600	-3.33584300	-0.31579200
H	-1.91197700	-4.96298700	0.26137100
H	-3.56092000	-4.32129800	0.59463900
C	-2.82161300	-1.82961900	2.07637700
H	-2.40777000	-1.23282600	2.89159800
H	-2.67107500	-1.29488900	1.13634400
H	-3.87724600	-2.06090500	2.25099700

12

Zero-point correction=	0.280662 (Hartree/Particle)
Thermal correction to Energy=	0.308887
Thermal correction to Enthalpy=	0.309831
Thermal correction to Gibbs Free Energy=	0.216518
Sum of electronic and zero-point Energies=	-1856.310071
Sum of electronic and thermal Energies=	-1856.281846
Sum of electronic and thermal Enthalpies=	-1856.280902
Sum of electronic and thermal Free Energies=	-1856.374215

C	-1.80566200	0.50606700	-0.77074400
C	-1.73300000	1.52094500	0.19065700
C	-2.55573800	0.72000700	-1.93941500
C	-2.41739100	2.73040100	0.00960800
C	-3.24245900	1.92613300	-2.13361000
C	-3.16542800	2.91353700	-1.15247300
H	-3.82891300	2.09607500	-3.02835700
H	-3.69810700	3.84939300	-1.29836100
C	0.63831600	-4.76381500	-2.36891700
O	1.60230300	-4.65791300	-1.55513700
C	0.47404300	-6.04707300	-3.19595300
O	-0.16944500	-3.80392400	-2.54376900
Pd	0.92484400	-2.68437800	-1.13674100
O	0.07095200	-0.87407400	-1.08748700
C	3.17199400	-0.89546000	2.39946900
H	4.14823700	-0.90678600	1.90833000
H	3.07874700	-0.03933800	3.07400200
H	3.01882200	-1.82529100	2.95118500
C	2.38429200	0.72399400	0.29851000
H	1.71860100	0.82193000	-0.55998500
H	2.24479800	1.56450200	0.98441700
H	3.42717600	0.63026800	-0.01559900
S	1.86464200	-0.80244200	1.14030600
O	2.32113800	-1.97770000	0.19592200
H	-2.36818800	3.51912600	0.75075200
F	0.97617300	-7.10306300	-2.54376900
F	1.13636100	-5.91163700	-4.36168000
F	-0.81631000	-6.27893400	-3.46697500
C	-1.13871700	-0.83550300	-0.55256900
O	-1.67941800	-1.74742900	0.04825600
O	-2.55702100	-0.31635200	-2.82026000
O	-0.94566800	1.24986100	1.28401700
C	-3.32395400	-0.20565900	-4.00798000
H	-4.39012200	-0.06663200	-3.78601900
H	-2.97303600	0.62257400	-4.63781000
H	-3.18372800	-1.14840600	-4.53856700
C	-1.07364400	2.09225800	2.41838100
H	-0.49331100	1.61886300	3.21360700
H	-0.67328300	3.09782800	2.22910500
H	-2.11947900	2.17712800	2.73805700

12a

Zero-point correction=	0.280743 (Hartree/Particle)
Thermal correction to Energy=	0.308899
Thermal correction to Enthalpy=	0.309843
Thermal correction to Gibbs Free Energy=	0.216867
Sum of electronic and zero-point Energies=	-1856.307484
Sum of electronic and thermal Energies=	-1856.279328
Sum of electronic and thermal Enthalpies=	-1856.278384
Sum of electronic and thermal Free Energies=	-1856.371360

C	-1.36601200	-1.70217200	1.30419400
C	-2.55036100	-2.36309700	0.94134500
C	-0.72609800	-2.04730200	2.50414100
C	-3.08367800	-3.36742200	1.76110500
C	-1.25206700	-3.04613400	3.33289700
C	-2.42744800	-3.69122700	2.94660100
H	-0.76307900	-3.32327600	4.25877400
H	-2.83982000	-4.46708100	3.58615400
C	-0.16011600	-4.99864500	-1.39461000
O	0.43182200	-1.36458000	2.76668400
C	1.08674300	-1.60547800	4.00076100
H	1.44402500	-2.64125100	4.07515500
H	1.94155700	-0.92667200	4.02365700
H	0.43049400	-1.38735500	4.85303300
O	1.08438100	-4.77744600	-1.33993400
C	-0.66979100	-6.42713700	-1.63255500
O	-0.99355000	-4.06341900	-1.20854300
Pd	0.63694200	-2.74713500	-0.88505000
O	-0.06144100	-0.91308500	-0.58463100
C	4.39225800	-0.29256200	-0.01978200
H	4.85860100	-0.55676400	-0.97197600
H	4.65424900	0.72634800	0.27986600
H	4.69619000	-1.00025800	0.75421400
C	2.34564600	0.71503000	-1.57989400
H	1.27872500	0.68314200	-1.80267900
H	2.63978100	1.72214900	-1.26841900
H	2.94370500	0.36950200	-2.42751800
S	2.58444700	-0.41419800	-0.17312600
O	2.49235900	-1.87495600	-0.76928800
H	-3.99358400	-3.88613100	1.48555300
O	-3.10711100	-1.95088300	-0.22962600
C	-4.17207400	-2.71241700	-0.77920900
H	-5.06366800	-2.67981800	-0.13916100
H	-4.40333800	-2.24663700	-1.73853200
H	-3.86745300	-3.75311100	-0.94135100
F	-0.72783500	-7.08043600	-0.45659500
F	0.15192300	-7.09714400	-2.45052100
F	-1.89745900	-6.41300400	-2.16977300
C	-0.83050100	-0.57696700	0.44932700
O	-1.07448400	0.59110800	0.68273100

TS-1

Zero-point correction=	0.280195 (Hartree/Particle)
Thermal correction to Energy=	0.307866
Thermal correction to Enthalpy=	0.308810
Thermal correction to Gibbs Free Energy=	0.217915
Sum of electronic and zero-point Energies=	-1856.300472
Sum of electronic and thermal Energies=	-1856.272802
Sum of electronic and thermal Enthalpies=	-1856.271857
Sum of electronic and thermal Free Energies=	-1856.362752

Pd	-0.33083100	0.12911100	-0.41511800
S	-3.29311700	-0.88762900	-0.54348000
F	4.32579500	-0.92599900	-1.61614300
F	3.06565700	-2.63788700	-2.09208300
F	3.65373900	-2.25378600	-0.02896900
O	1.12458400	-1.30322700	-0.24687400
O	-1.88507400	-1.22848500	0.05743600
O	-1.72900900	1.51939200	-0.63352800
O	1.91263900	0.26690500	-1.61675100
O	-2.05247400	3.64479100	-0.00949200
C	2.02724600	-0.80898700	-1.01073400
C	3.29524300	-1.66745100	-1.18329500
C	-4.12055900	-2.49857500	-0.38069300
C	-4.18785800	0.02480200	0.75267700
C	-1.33996100	2.66749000	-0.10185000
H	-5.17268900	-2.39054800	-0.65996100
H	-3.61844100	-3.18440700	-1.06612600
H	-4.01797200	-2.85508400	0.64729700
H	-5.24343700	0.08558500	0.46973900
H	-4.06220700	-0.49086400	1.70862600
H	-3.74574400	1.02165500	0.78246600
C	0.09377800	2.62172600	0.40519000
C	0.34644000	2.38736200	1.78000000
C	1.16482500	3.00847400	-0.43482300
C	1.64337100	2.48186100	2.29049300
C	2.46663000	3.10106500	0.07752100
C	2.68293800	2.83766600	1.42648000
H	1.85133100	2.29013400	3.33563500
H	3.29703600	3.36867100	-0.56327300
H	3.69268800	2.90869200	1.82182200
O	0.82568400	3.27712100	-1.71545400
O	-0.75052700	2.07370900	2.52204500
C	1.86505800	3.43639500	-2.67825400
H	2.50389800	2.54790300	-2.70277700
H	1.35785400	3.55598800	-3.63646300
H	2.46285900	4.33300900	-2.47141200
C	-0.57840800	1.80909900	3.90735300
H	-1.57598200	1.59694200	4.29489000
H	0.07002500	0.93903900	4.07027400
H	-0.16360700	2.67940500	4.43088600

13

Zero-point correction=	0.280556 (Hartree/Particle)
Thermal correction to Energy=	0.308848
Thermal correction to Enthalpy=	0.309792
Thermal correction to Gibbs Free Energy=	0.215397
Sum of electronic and zero-point Energies=	-1856.317233
Sum of electronic and thermal Energies=	-1856.288941
Sum of electronic and thermal Enthalpies=	-1856.287996
Sum of electronic and thermal Free Energies=	-1856.382392

C	-1.52192300	-2.05976500	0.80692200
C	-2.43584400	-2.60673000	-0.16006200
C	-1.10071500	-2.90358800	1.89370700
C	-2.77943600	-3.95961700	-0.12331100
C	-1.44928600	-4.25722400	1.91476200
C	-2.27178600	-4.75573400	0.90492500
H	-1.09770700	-4.91442200	2.69970300
H	-2.53544000	-5.80970100	0.92320100
C	1.82096300	-4.47951600	-0.38997900
O	-0.38480400	-2.28568800	2.84877800
C	0.30169400	-3.07696500	3.81954600
H	0.99333000	-3.77163300	3.32979900
H	0.85968700	-2.36676300	4.42983200
H	-0.40426500	-3.62633500	4.45282000
O	0.72506600	-3.97454300	-0.82660100
C	2.00398900	-5.93972000	-0.88136500
O	2.68235000	-3.97328100	0.32963800
Pd	0.33601900	-2.03578200	-0.31902800
O	-0.24808800	-0.19761200	0.26595900
C	4.69476800	-1.84683200	-0.90333000
H	4.78233100	-1.68004700	-1.98035800
H	5.57783300	-1.48025100	-0.37126100
H	4.52157400	-2.90114500	-0.67996800
C	3.64093800	0.71766700	-0.81499900
H	2.77501100	1.33825800	-0.57345400
H	4.51983200	1.06544100	-0.26365300
H	3.82119000	0.72624900	-1.89327500
S	3.22712300	-0.97304000	-0.28381300
O	2.10094700	-1.38117600	-1.28912100
H	-3.42829700	-4.39457100	-0.87260000
O	-2.90916700	-1.72117400	-1.05346900
C	-3.70946100	-2.18975400	-2.13721400
H	-4.64225700	-2.63552000	-1.77293200
H	-3.93523800	-1.30647900	-2.73458500
H	-3.15784500	-2.91767500	-2.74316200
F	3.16719600	-6.46084200	-0.46267600
F	1.98445100	-6.00091200	-2.22814400
F	1.00871000	-6.72764300	-0.41825800
C	-1.34482200	-0.52086500	0.91308300
O	-2.11107500	0.20697700	1.50156800

TS-2

Zero-point correction=	0.278234 (Hartree/Particle)
Thermal correction to Energy=	0.306640
Thermal correction to Enthalpy=	0.307584
Thermal correction to Gibbs Free Energy=	0.214393
Sum of electronic and zero-point Energies=	-1856.300091
Sum of electronic and thermal Energies=	-1856.271685
Sum of electronic and thermal Enthalpies=	-1856.270741
Sum of electronic and thermal Free Energies=	-1856.363932

C	-1.35673100	-2.52134600	0.66341800
C	-2.47605600	-2.73628700	-0.19130300
C	-1.32698000	-3.21184400	1.90909000
C	-3.54477900	-3.54523700	0.20640900
C	-2.39359000	-4.02032000	2.31320600
C	-3.48209100	-4.16967200	1.45272700
H	-2.38648500	-4.53485200	3.26615200
H	-4.31134400	-4.80000300	1.76378500
C	1.92285500	-4.25816300	-0.68467000
O	0.78615500	-3.71792900	-0.93176600
C	2.02506400	-5.66138500	-1.34088100
O	2.87479600	-3.83356500	-0.03117200
Pd	0.38553700	-1.88508900	-0.15199900
O	-0.38044600	-0.13881200	0.70843700
C	4.73825900	-1.66678700	-1.13044300
H	4.69254600	-1.25602000	-2.14285400
H	5.70553400	-1.46039600	-0.66205200
H	4.53195800	-2.73771400	-1.12530800
C	3.93375200	0.83405900	-0.30775000
H	3.17378900	1.44033400	0.19029700
H	4.90540700	0.98328600	0.17285300
H	3.97649600	1.09050800	-1.36978100
S	3.42504700	-0.90792600	-0.12519000
O	2.14825600	-0.97600500	-1.01154900
H	-4.40644900	-3.70134800	-0.43090300
F	1.12921500	-6.50941600	-0.79205200
F	3.24677500	-6.19419600	-1.17889700
F	1.77680400	-5.59969700	-2.66506300
C	-1.45239900	-0.51713900	1.18673300
O	-2.43208700	-0.21887500	1.77745200
O	-2.42876300	-2.08376400	-1.37642600
O	-0.21959800	-2.99927400	2.65991400
C	-0.11552500	-3.62627300	3.93371200
H	-0.13282300	-4.71850000	3.83928200
H	0.84810500	-3.31241600	4.33630400
H	-0.91923300	-3.30069100	4.60572300
C	-3.51492100	-2.22200800	-2.28604600
H	-3.25008200	-1.61557800	-3.15277700
H	-3.64007200	-3.26650400	-2.59512200
H	-4.45028500	-1.85088200	-1.84927100

7$_{+CO_2}$

Zero-point correction=	0.278499 (Hartree/Particle)
Thermal correction to Energy=	0.307995
Thermal correction to Enthalpy=	0.308939
Thermal correction to Gibbs Free Energy=	0.213150
Sum of electronic and zero-point Energies=	-1856.310837
Sum of electronic and thermal Energies=	-1856.281340
Sum of electronic and thermal Enthalpies=	-1856.280396
Sum of electronic and thermal Free Energies=	-1856.376185

C	-1.20904300	-2.83270100	0.61574900
C	-2.25179300	-3.24945800	-0.22640300
C	-1.29904900	-3.10333000	1.98658600
C	-3.35296800	-3.94865700	0.29344200
C	-2.39414300	-3.79709800	2.52228900
C	-3.40538600	-4.21863200	1.66024700
H	-2.46449300	-4.00704600	3.58322500
H	-4.25651900	-4.76086000	2.06356600
C	1.96195000	-4.19164900	-0.87852300
O	-0.25788800	-2.61748700	2.75666400
C	-0.21535700	-2.97492600	4.12976800
H	-0.21045500	-4.06434500	4.25780100
H	0.71782700	-2.56234200	4.51823900
H	-1.06073000	-2.54755100	4.68560000
O	0.80691400	-3.68722500	-1.10693600
C	2.27632000	-5.42435700	-1.76537900
O	2.85480400	-3.81336400	-0.11983600
Pd	0.40587900	-1.94749300	-0.11941900
O	-0.09059400	-0.06142200	1.02583800
C	4.56120300	-1.72894200	-1.66378500
H	4.36735600	-1.22991300	-2.61735700
H	5.61336300	-1.63837400	-1.37656700
H	4.27296800	-2.77936300	-1.70237300
C	4.16234600	0.74939100	-0.55982400
H	3.58339000	1.38046700	0.11824300
H	5.22111600	0.78227800	-0.28563000
H	4.01330700	1.07943300	-1.59154000
S	3.53638600	-0.95466300	-0.37097200
O	2.10891200	-0.84930400	-0.97326100
H	-4.15990100	-4.27700300	-0.35145100
O	-2.12421100	-2.91486700	-1.54602000
C	-3.03434200	-3.47475000	-2.47680200
H	-4.05798400	-3.10825600	-2.31719300
H	-2.68847600	-3.15397100	-3.46102200
H	-3.03189600	-4.57143700	-2.43049700
F	2.78113700	-6.42867000	-1.02826900
F	3.22086100	-5.06897800	-2.67542800
F	1.21947400	-5.89593500	-2.44097800
C	-0.76910100	0.06687700	1.98072200
O	-1.43044300	0.27437200	2.91311300

B3LYP/6-31G(d) (LANL2DZ for PD) in DCM

9

Zero-point correction=	0.362650 (Hartree/Particle)
Thermal correction to Energy=	0.397797
Thermal correction to Enthalpy=	0.398741
Thermal correction to Gibbs Free Energy=	0.290833
Sum of electronic and zero-point Energies=	-2408.288056
Sum of electronic and thermal Energies=	-2408.252909
Sum of electronic and thermal Enthalpies=	-2408.251965
Sum of electronic and thermal Free Energies=	-2408.359873

C	0.19626000	1.68360800	2.56165300
C	-0.30520200	1.43889400	3.85168600
C	0.24864900	3.00488800	2.08649400
C	-0.73187100	2.49861100	4.66449000
C	-0.18388900	4.07046800	2.88794300
C	-0.66509600	3.80010200	4.16856300
H	-0.14970900	5.09130300	2.52834500
H	-0.99788800	4.62360400	4.79425800
C	1.57021000	-4.09971400	-1.23166500
O	0.72476000	3.15656500	0.81382600
C	0.79257500	4.47105200	0.26749200
H	1.46079500	5.11321600	0.85340100
H	1.19400600	4.35382600	-0.74000600
H	-0.20078300	4.93165600	0.21241800
O	0.43881900	-3.65561500	-0.83008600
C	1.39977800	-5.46656700	-1.95049700
O	2.69309800	-3.60627700	-1.14942600
Pd	0.27469100	-1.88849700	0.21597300
O	1.92868700	0.39748900	1.52443800
C	3.08351600	-0.97786000	-3.01204300
H	2.40686400	-0.54214200	-3.75108500
H	4.10966000	-0.63534700	-3.17108200
H	3.04390400	-2.06758400	-3.03083400
C	2.61906600	1.31966200	-1.53913500
H	2.23803400	1.74247300	-0.60811300
H	3.66016500	1.61639500	-1.69436200
H	1.99919700	1.61334600	-2.38991500
S	2.56476300	-0.48252800	-1.34525000
O	1.01270100	-0.79017200	-1.37344000
H	-1.11133900	2.32036000	5.66294700
O	-0.32934500	0.12732300	4.23842700
C	-0.70354000	-0.17539500	5.58052700
H	-1.74185200	0.11355400	5.78237600
H	-0.60366500	-1.25724700	5.67870800
H	-0.04101500	0.31999200	6.30007100
F	2.57998100	-6.06289300	-2.18172800
F	0.78568200	-5.29488100	-3.14350700
F	0.64349800	-6.31867500	-1.22534400
C	0.71635900	0.54318100	1.71010400
O	-0.22896100	-0.20692300	1.23419700
S	-1.82945500	-3.45840900	2.10833400
O	-0.35174200	-3.02714900	1.83952500
C	-2.47633100	-4.17299400	0.56731700
H	-2.47420600	-3.41941100	-0.22363300
H	-1.81715000	-5.00024500	0.29881800
H	-3.48832500	-4.53570500	0.76669400
C	-2.82694200	-1.94213200	2.18277300
H	-2.40403900	-1.32964200	2.98114700
H	-2.76798600	-1.40752700	1.23278800
H	-3.85567300	-2.22953900	2.41693100

12

Zero-point correction=	0.280248 (Hartree/Particle)
Thermal correction to Energy=	0.308584
Thermal correction to Enthalpy=	0.309528
Thermal correction to Gibbs Free Energy=	0.216159
Sum of electronic and zero-point Energies=	-1855.143450
Sum of electronic and thermal Energies=	-1855.115114
Sum of electronic and thermal Enthalpies=	-1855.114170
Sum of electronic and thermal Free Energies=	-1855.207539

C	-1.93424600	0.46057300	-0.77236500
C	-2.02141200	1.31165500	0.34137800
C	-2.45323600	0.88038300	-2.00863600
C	-2.63029800	2.56915900	0.22773200
C	-3.06622200	2.13510100	-2.13128100
C	-3.14426500	2.95992800	-1.00898400
H	-3.47587900	2.46793300	-3.07688800
H	-3.61730900	3.93370200	-1.10069300
C	0.51950900	-4.98166300	-2.01024400
O	1.57700400	-4.72882600	-1.36410300
C	0.34542800	-6.36870300	-2.64902400
O	-0.37661500	-4.10475400	-2.17776900
Pd	0.84063100	-2.71933900	-1.07680300
O	-0.07995400	-0.93721600	-1.09099900
C	3.51211300	-0.69314400	1.97776300
H	4.42077500	-0.68678900	1.37167500
H	3.47905500	0.16868700	2.64917000
H	3.43776800	-1.61825400	2.55228200
C	2.43567200	0.88599800	-0.03963600
H	1.64966100	0.97773800	-0.79020400
H	2.40383100	1.73303100	0.65100200
H	3.41921200	0.79348100	-0.50614200
S	2.06357400	-0.62632700	0.89038300
O	2.40302600	-1.80567200	-0.11206300
H	-2.70376900	3.23501100	1.07873800
F	0.88582400	-7.32067100	-1.87473700
F	0.96761700	-6.39277900	-3.84379100
F	-0.94909300	-6.65222200	-2.84181400
C	-1.31356200	-0.91038100	-0.63489900
O	-1.91476700	-1.86077000	-0.14953900
O	-2.32156800	-0.01369500	-3.02981700
O	-1.46957900	0.82658900	1.49201100
C	-2.84065800	0.33470000	-4.31078300
H	-3.92378800	0.50015100	-4.27085400
H	-2.34896400	1.22952600	-4.71057900
H	-2.62682900	-0.51663200	-4.95827400
C	-1.56420600	1.61614400	2.67472900
H	-1.08654400	1.03043100	3.46129700
H	-1.03861300	2.57175800	2.56085900
H	-2.60990900	1.80523300	2.94430600

12a

Zero-point correction=	0.280356 (Hartree/Particle)
Thermal correction to Energy=	0.308609
Thermal correction to Enthalpy=	0.309554
Thermal correction to Gibbs Free Energy=	0.216647
Sum of electronic and zero-point Energies=	-1855.138303
Sum of electronic and thermal Energies=	-1855.110049
Sum of electronic and thermal Enthalpies=	-1855.109105
Sum of electronic and thermal Free Energies=	-1855.202012

C	-1.47545500	-1.72082800	1.20604700
C	-2.69525000	-2.36515200	0.93998200
C	-0.75150300	-2.06107600	2.36082400
C	-3.17986400	-3.35344800	1.80800600
C	-1.22864000	-3.04548700	3.23636300
C	-2.43786000	-3.67742400	2.94368600
H	-0.67887200	-3.31621700	4.12922900
H	-2.81213800	-4.44106700	3.61982300
C	-0.03157900	-5.01699000	-1.38005200
O	0.41286700	-1.36969100	2.54239900
C	1.19101400	-1.64446800	3.70454000
H	1.53398100	-2.68578500	3.71866200
H	2.05337400	-0.97890000	3.64784400
H	0.62655900	-1.43358100	4.62044900
O	1.20175200	-4.76275900	-1.25135900
C	-0.47569600	-6.46590600	-1.63449100
O	-0.90584800	-4.11155800	-1.25920500
Pd	0.68180800	-2.71468100	-0.84897100
O	-0.11310500	-0.89301800	-0.62720400
C	4.42696700	-0.28509700	0.20573200
H	4.96822800	-0.61725800	-0.68284600
H	4.68427000	0.74567100	0.46292800
H	4.63213700	-0.94428800	1.05112800
C	2.54812800	0.67326400	-1.59807100
H	1.50707600	0.64032600	-1.92174200
H	2.82728300	1.69503700	-1.32631600
H	3.21506800	0.27236400	-2.36497600
S	2.64331800	-0.36186100	-0.10991000
O	2.53216100	-1.85194600	-0.64203000
H	-4.11522200	-3.86209500	1.61045900
O	-3.33126700	-1.96055200	-0.19569500
C	-4.54964300	-2.60508900	-0.55751400
H	-5.32215200	-2.45676200	0.20638000
H	-4.86730900	-2.13633100	-1.48985100
H	-4.39772500	-3.67846700	-0.72119100
F	-0.59285800	-7.11120100	-0.45780000
F	0.42547600	-7.11689500	-2.38343800
F	-1.66179100	-6.50299600	-2.25564300
C	-1.00044600	-0.60365000	0.30661300
O	-1.42436000	0.53794100	0.43063300

TS-1

Zero-point correction=	0.279918 (Hartree/Particle)
Thermal correction to Energy=	0.307633
Thermal correction to Enthalpy=	0.308578
Thermal correction to Gibbs Free Energy=	0.217903
Sum of electronic and zero-point Energies=	-1855.135701
Sum of electronic and thermal Energies=	-1855.107986
Sum of electronic and thermal Enthalpies=	-1855.107041
Sum of electronic and thermal Free Energies=	-1855.197716

Pd	-0.35564700	0.12302800	-0.66597800
S	-3.35593100	-0.80169800	-0.33720000
F	4.22003500	-1.19723800	-2.15168600
F	2.93764300	-2.94708900	-1.96733100
F	3.79037400	-2.02823500	-0.18555900
O	1.06699300	-1.36948500	-0.59289400
O	-1.85652500	-1.24512800	-0.11291000
O	-1.71823600	1.57707600	-0.79978300
O	2.01060600	0.25988900	-1.79676300
O	-1.96858600	3.74853600	-0.35967800
C	2.02740400	-0.86103800	-1.27292600
C	3.26823200	-1.76931700	-1.40145300
C	-4.19815300	-2.40688200	-0.28726800
C	-3.87871300	-0.12333300	1.26281400
C	-1.29978100	2.72784400	-0.31568800
H	-5.27670200	-2.22899300	-0.29664200
H	-3.90062400	-2.95215500	-1.18490000
H	-3.89419400	-2.94698000	0.61204700
H	-4.94492400	0.11218800	1.20696900
H	-3.67590200	-0.84988100	2.05321000
H	-3.29760000	0.78799400	1.41521500
C	0.08015600	2.68032900	0.31075000
C	0.21246900	2.37611100	1.68624300
C	1.21821600	3.08271100	-0.42337700
C	1.46453500	2.43210600	2.30624400
C	2.47427500	3.13535500	0.19589900
C	2.57519100	2.80961400	1.54711800
H	1.58248900	2.19555700	3.35615000
H	3.35766600	3.42649200	-0.35804100
H	3.54877000	2.85207000	2.02722900
O	0.98578600	3.40305400	-1.72061500
O	-0.94766700	2.04954800	2.31909500
C	2.10632300	3.64346300	-2.57395600
H	2.76736400	2.77125000	-2.59620100
H	1.68754400	3.81557700	-3.56615400
H	2.66404000	4.53176400	-2.25618300
C	-0.89735500	1.72964600	3.71002300
H	-1.92537100	1.51116300	4.00025200
H	-0.26960900	0.84977200	3.89104400
H	-0.52317100	2.57637800	4.29616300

13

Zero-point correction=	0.280292 (Hartree/Particle)
Thermal correction to Energy=	0.308647
Thermal correction to Enthalpy=	0.309591
Thermal correction to Gibbs Free Energy=	0.216620
Sum of electronic and zero-point Energies=	-1855.151951
Sum of electronic and thermal Energies=	-1855.123596
Sum of electronic and thermal Enthalpies=	-1855.122652
Sum of electronic and thermal Free Energies=	-1855.215623

C	-1.51530000	-2.11194700	0.82345100
C	-2.41936100	-2.63964200	-0.17054500
C	-1.06450300	-2.99571200	1.87166500
C	-2.69971500	-4.00490600	-0.21167900
C	-1.35024500	-4.36106000	1.81099300
C	-2.15116600	-4.83441000	0.77042800
H	-0.97705200	-5.04634200	2.56074500
H	-2.37180800	-5.89718100	0.73079100
C	1.71891400	-4.42132200	-0.24798500
O	-0.38193300	-2.39806400	2.85942700
C	0.32450300	-3.21419100	3.80695000
H	1.04009800	-3.85915900	3.28759000
H	0.85175700	-2.51403700	4.45408200
H	-0.37151300	-3.81372500	4.40147900
O	0.80671000	-3.80318000	-0.90367200
C	1.88060400	-5.88086500	-0.75150500
O	2.42344400	-4.02638400	0.67994200
Pd	0.34371100	-1.89329400	-0.28639100
O	-0.38273700	-0.12600900	0.42062800
C	4.59013600	-1.82904400	-0.71346400
H	4.74411100	-1.87697200	-1.79445400
H	5.49481800	-1.49107300	-0.20079500
H	4.26758700	-2.79464000	-0.31855600
C	3.88440200	0.81217100	-1.19130600
H	3.12058800	1.58685800	-1.10017700
H	4.80352100	1.13131400	-0.69298400
H	4.06814600	0.57387400	-2.24170000
S	3.24855800	-0.66239000	-0.34587000
O	2.06663100	-1.11539600	-1.27504500
H	-3.33967100	-4.42488400	-0.97671900
O	-2.93389400	-1.72225000	-1.00316000
C	-3.76951200	-2.15492600	-2.08589200
H	-4.66952800	-2.64872100	-1.70661400
H	-4.04347300	-1.24645000	-2.62098000
H	-3.22062100	-2.82911600	-2.75101500
F	2.91098400	-6.50182600	-0.15569500
F	2.09015600	-5.92084300	-2.08382100
F	0.76329000	-6.59667600	-0.49276400
C	-1.44292800	-0.58300600	1.03318600
O	-2.26016200	0.05747300	1.66905300

TS-2

Zero-point correction=	0.277859 (Hartree/Particle)
Thermal correction to Energy=	0.306347
Thermal correction to Enthalpy=	0.307292
Thermal correction to Gibbs Free Energy=	0.214614
Sum of electronic and zero-point Energies=	-1855.130485
Sum of electronic and thermal Energies=	-1855.101997
Sum of electronic and thermal Enthalpies=	-1855.101052
Sum of electronic and thermal Free Energies=	-1855.193730

C	-1.36831200	-2.58468500	0.68373600
C	-2.50071200	-2.78476900	-0.16061600
C	-1.34203800	-3.24594300	1.94782400
C	-3.59868200	-3.53040700	0.27854000
C	-2.44033500	-3.99140700	2.38798600
C	-3.54611200	-4.11684500	1.54488700
H	-2.44329700	-4.47795700	3.35522000
H	-4.39857500	-4.69789000	1.88599900
C	1.90110600	-4.27042900	-0.63505200
O	0.81048500	-3.70953600	-0.99978300
C	2.27313500	-5.50778300	-1.49352000
O	2.70231500	-3.94840400	0.24265400
Pd	0.35578600	-1.90181300	-0.12094200
O	-0.47693600	-0.17544000	0.78411200
C	4.67317600	-1.75902500	-1.18537600
H	4.65799200	-1.35255700	-2.19995300
H	5.65478800	-1.62315400	-0.72311600
H	4.39880400	-2.81464800	-1.18102300
C	3.99725900	0.80965700	-0.43125800
H	3.28029000	1.46209800	0.07145000
H	4.98651800	0.92667300	0.01925100
H	4.02567500	1.02711200	-1.50192300
S	3.43112100	-0.89867600	-0.17468900
O	2.11552300	-0.97279000	-1.01272000
H	-4.47424800	-3.67002700	-0.34307400
F	1.26034700	-5.97303100	-2.24368600
F	2.70947200	-6.51897700	-0.71882400
F	3.28439400	-5.17291800	-2.33243400
C	-1.54437700	-0.57580100	1.24343900
O	-2.54283200	-0.31410200	1.82115000
O	-2.43650900	-2.17813900	-1.36790800
O	-0.21658800	-3.06242700	2.67591500
C	-0.14854200	-3.60852100	3.99687400
H	-0.21687900	-4.70140500	3.97412700
H	0.82542500	-3.31131700	4.38565100
H	-0.94116600	-3.19974800	4.63291900
C	-3.57005300	-2.24674300	-2.23826800
H	-3.29601700	-1.66908300	-3.12108200
H	-3.78102000	-3.28194500	-2.52718500
H	-4.45476700	-1.80492400	-1.76708400

7$_{+CO_2}$

Zero-point correction= 0.278012 (Hartree/Particle)
Thermal correction to Energy= 0.307725
Thermal correction to Enthalpy= 0.308670
Thermal correction to Gibbs Free Energy= 0.211526
Sum of electronic and zero-point Energies= -1855.143343
Sum of electronic and thermal Energies= -1855.113629
Sum of electronic and thermal Enthalpies= -1855.112685
Sum of electronic and thermal Free Energies= -1855.209829

C	-1.22195700	-2.90335800	0.49033400
C	-2.29440600	-3.30342600	-0.32033600
C	-1.27550900	-3.15140900	1.86773800
C	-3.40214900	-3.96117200	0.24107100
C	-2.37655200	-3.80553900	2.44213000
C	-3.42454000	-4.20743300	1.61391900
H	-2.42263900	-4.00094400	3.50698700
H	-4.27988500	-4.71758900	2.04851200
C	1.90891700	-4.33047000	-0.92162700
O	-0.19637500	-2.69776200	2.59742900
C	-0.16015200	-2.97585600	3.99543200
H	-0.18297700	-4.05514200	4.18540300
H	0.78239200	-2.56243700	4.35677900
H	-0.99355700	-2.49466800	4.52113300
O	0.81784700	-3.75540000	-1.27155000
C	2.19521200	-5.56683400	-1.81771400
O	2.71277100	-4.03839700	-0.03839100
Pd	0.37531600	-2.00348600	-0.27163400
O	-0.11683600	-0.10454200	0.91707300
C	4.69573100	-1.65190200	-1.16521000
H	4.70974400	-1.33013900	-2.20978000
H	5.64938000	-1.43686600	-0.67525500
H	4.45855600	-2.71381600	-1.08321000
C	3.90513600	0.93716500	-0.61868400
H	3.14633900	1.59751700	-0.19383600
H	4.86796400	1.11282000	-0.13153400
H	3.97861000	1.08671800	-1.69893100
S	3.37693200	-0.76930900	-0.28011700
O	2.10196300	-0.94339700	-1.15832500
H	-4.23614300	-4.27602300	-0.37499800
O	-2.19172400	-3.00058500	-1.65220100
C	-3.22035900	-3.44585500	-2.52874600
H	-4.18684400	-2.98789300	-2.28324500
H	-2.91671300	-3.13102400	-3.52849200
H	-3.32211300	-4.53801700	-2.50695300
F	3.29641600	-6.22406800	-1.42026800
F	2.38484500	-5.18855900	-3.10137700
F	1.16569400	-6.43875200	-1.79748800
C	-0.09955700	0.08537400	2.07903000
O	-0.08803500	0.34092600	3.21255900

B3PW91/6-31G(d) (SDD for PD) in DCM

9

Zero-point correction= 0.363766 (Hartree/Particle)
Thermal correction to Energy= 0.398888
Thermal correction to Enthalpy= 0.399833
Thermal correction to Gibbs Free Energy= 0.290845
Sum of electronic and zero-point Energies= -2408.857444
Sum of electronic and thermal Energies= -2408.822322
Sum of electronic and thermal Enthalpies= -2408.821378
Sum of electronic and thermal Free Energies= -2408.930365

C	0.24628100	1.63850600	2.62657700
C	-0.01899700	1.44290300	3.98922700
C	0.08795400	2.91445200	2.06987700
C	-0.43495900	2.51151300	4.79268700
C	-0.32949200	3.99013500	2.86278200
C	-0.58377400	3.77003900	4.21453200
H	-0.45670400	4.98130100	2.44323500
H	-0.90749000	4.60217900	4.83427300
C	1.54156800	-4.08133900	-1.11237500
O	0.36035100	3.00767000	0.73903300
C	0.20883400	4.27112700	0.11137100
H	0.88231000	5.01842800	0.54816800
H	0.47065400	4.11687700	-0.93624000
H	-0.82588400	4.62835000	0.17798800
O	0.38695300	-3.61274500	-0.82202800
C	1.41083200	-5.39848800	-1.91916300
O	2.65860200	-3.64222400	-0.85860500
Pd	0.21658700	-1.88639000	0.24560500
O	1.94008100	0.29394600	1.61185700
C	3.23672700	-1.06572700	-2.78241400
H	2.61131600	-0.62141800	-3.56087500
H	4.27765200	-0.74737300	-2.88974600
H	3.17802500	-2.15483900	-2.80347600
C	2.75602300	1.23470300	-1.36739900
H	2.31487400	1.67957400	-0.47400500
H	3.81167400	1.51078900	-1.44414900
H	2.20978700	1.53356900	-2.26580700
S	2.64862700	-0.55161400	-1.15755900
O	1.09698300	-0.81908100	-1.26323600
H	-0.64115700	2.37287500	5.84761600
O	0.16069700	0.17237000	4.44060200
C	-0.05569500	-0.08702200	5.81831900
H	-1.09538900	0.11285800	6.10529500
H	0.16032600	-1.14696100	5.95939200
H	0.61725400	0.50813500	6.44748400
F	2.60373000	-5.94805900	-2.17245800
F	0.80371500	-5.17176300	-3.10072500
F	0.67284800	-6.30502200	-1.25112200
C	0.73365600	0.48714500	1.77698800
O	-0.23183100	-0.22073600	1.28402500
S	-2.17058900	-3.32843500	1.83123200
O	-0.65074700	-2.98763400	1.74909600
C	-2.66650500	-4.02162800	0.24129100
H	-2.47371700	-3.30341400	-0.55924800
H	-2.08200200	-4.92945000	0.08363500
H	-3.73106700	-4.26608800	0.30399400
C	-3.08049900	-1.77263100	1.75309300
H	-2.80587600	-1.18920000	2.63340200
H	-2.81444900	-1.23115700	0.84239800
H	-4.14838700	-2.00850400	1.77706800

12

Zero-point correction= 0.281528 (Hartree/Particle)
Thermal correction to Energy= 0.309666
Thermal correction to Enthalpy= 0.310610
Thermal correction to Gibbs Free Energy= 0.216867
Sum of electronic and zero-point Energies= -1855.821578
Sum of electronic and thermal Energies= -1855.793440
Sum of electronic and thermal Enthalpies= -1855.792496
Sum of electronic and thermal Free Energies= -1855.886239

C	-1.93028400	0.45035100	-0.72097900
C	-2.07439000	1.28756900	0.39580700
C	-2.43173700	0.86353700	-1.96523000
C	-2.71264900	2.52773900	0.27414000
C	-3.07511200	2.10035700	-2.09450200
C	-3.20347900	2.91325600	-0.97100400
H	-3.47172900	2.42869400	-3.04809200
H	-3.70073100	3.87480000	-1.06837800
C	0.48571600	-4.92398700	-1.99907900
O	1.55407000	-4.67684600	-1.37137700
C	0.29632200	-6.30111200	-2.64762600
O	-0.40494000	-4.03951500	-2.13895200
Pd	0.83809300	-2.70103700	-1.07804600
O	-0.06481400	-0.92637000	-1.06821500
C	3.54973100	-0.67515500	1.89026100
H	4.46539400	-0.74336200	1.29809500
H	3.55514300	0.21855400	2.52008100
H	3.42468900	-1.56522900	2.51015100
C	2.57865100	0.85334100	-0.18986500
H	1.81793000	0.94720800	-0.96652700
H	2.56243700	1.73285100	0.46024500
H	3.56969600	0.70559300	-0.62619900
S	2.12611500	-0.58805900	0.79260200
O	2.41475800	-1.82167600	-0.15138300
H	-2.82740700	3.18557500	1.12778700
F	0.83224300	-7.25928600	-1.88606000
F	0.91068900	-6.31576800	-3.84139500
F	-0.99734400	-6.56935400	-2.83417800
C	-1.28011400	-0.90151700	-0.57583300
O	-1.85233900	-1.84800900	-0.05048300
O	-2.25827000	-0.01574000	-2.98539300
O	-1.54650300	0.81289600	1.55431300
C	-2.76602800	0.32925700	-4.26490600
H	-3.85364800	0.46741400	-4.23922500
H	-2.29072700	1.23872900	-4.65191000
H	-2.52321100	-0.51073100	-4.91702200
C	-1.69559900	1.59438300	2.72906300
H	-1.22865700	1.01961800	3.53010300
H	-1.18921200	2.56261700	2.63362700
H	-2.75333200	1.75749400	2.96798700

12a

Zero-point correction=	0.281744 (Hartree/Particle)
Thermal correction to Energy=	0.309716
Thermal correction to Enthalpy=	0.310661
Thermal correction to Gibbs Free Energy=	0.219014
Sum of electronic and zero-point Energies=	-1855.816477
Sum of electronic and thermal Energies=	-1855.788504
Sum of electronic and thermal Enthalpies=	-1855.787560
Sum of electronic and thermal Free Energies=	-1855.879207

C	-1.47452500	-1.73873300	1.20427800
C	-2.70929000	-2.35134100	0.94090800
C	-0.75385400	-2.10362300	2.35143400
C	-3.20705000	-3.34038500	1.79753600
C	-1.24313800	-3.09113300	3.21396700
C	-2.46436700	-3.69456100	2.92116400
H	-0.69415700	-3.38446700	4.10112000
H	-2.84911600	-4.46039700	3.58958500
C	0.03809200	-4.99083300	-1.35292800
O	0.41635500	-1.43587800	2.54054300
C	1.18270800	-1.74238600	3.69532000
H	1.51232400	-2.78829200	3.69035400
H	2.05459500	-1.08819400	3.65637500
H	0.61774900	-1.54068100	4.61321500
O	1.26005500	-4.70208800	-1.20450900
C	-0.36474700	-6.44979000	-1.60087500
O	-0.85412900	-4.10344800	-1.25370500
Pd	0.68200400	-2.70511600	-0.83204300
O	-0.13360400	-0.90784400	-0.63462200
C	4.32670900	-0.20926100	0.25818500
H	4.93408200	-0.60901800	-0.55703100
H	4.57045300	0.83878700	0.45211600
H	4.46805100	-0.79683600	1.16748700
C	2.59505800	0.59629600	-1.73218300
H	1.58870000	0.51261300	-2.14615400
H	2.82391800	1.64445600	-1.51905600
H	3.33518400	0.16082400	-2.40828700
S	2.58230500	-0.31152200	-0.17498200
O	2.50032200	-1.83337900	-0.59935400
H	-4.15531600	-3.82677200	1.60103800
O	-3.34418100	-1.91974300	-0.17913400
C	-4.59219800	-2.50746500	-0.51202700
H	-5.33711800	-2.33469500	0.27408000
H	-4.91600900	-2.01685600	-1.43091500
H	-4.49094100	-3.58453600	-0.69101400
F	-0.45328000	-7.09028500	-0.42433200
F	0.54866500	-7.07120200	-2.35198300
F	-1.54895400	-6.52123700	-2.21190900
C	-0.99238900	-0.61625200	0.31929100
O	-1.39608000	0.52735300	0.47246600

TS-1

Zero-point correction=	0.280933 (Hartree/Particle)
Thermal correction to Energy=	0.308585
Thermal correction to Enthalpy=	0.309529
Thermal correction to Gibbs Free Energy=	0.218188
Sum of electronic and zero-point Energies=	-1855.811782
Sum of electronic and thermal Energies=	-1855.784130
Sum of electronic and thermal Enthalpies=	-1855.783185
Sum of electronic and thermal Free Energies=	-1855.874527

Pd	-0.36499800	0.10194900	-0.52298800
S	-3.33738800	-0.84652100	-0.36497100
F	4.16818000	-1.23399500	-1.89568500
F	2.89594400	-2.98466100	-1.72039600
F	3.71524500	-2.05307200	0.06334400
O	1.02607200	-1.37985300	-0.32811300
O	-1.87333100	-1.18375600	0.10728900
O	-1.70706000	1.54080000	-0.75592200
O	1.91107500	0.17139600	-1.65351400
O	-1.94063200	3.71387600	-0.31980900
C	1.96621200	-0.91080400	-1.05757000
C	3.21368500	-1.80642500	-1.15792000
C	-4.10853400	-2.47276800	-0.30614800
C	-4.11896400	-0.08038900	1.06700600
C	-1.27720100	2.69153600	-0.29202100
H	-5.18012200	-2.35111500	-0.48710900
H	-3.66277700	-3.07052000	-1.10373000
H	-3.92435100	-2.93114000	0.66830200
H	-5.18151100	0.05798500	0.84752500
H	-3.97843400	-0.71142600	1.94818900
H	-3.63746300	0.88942700	1.20346000
C	0.12225900	2.63832400	0.28288000
C	0.30815500	2.36511100	1.65746900
C	1.22299800	3.05802400	-0.49443800
C	1.58125300	2.44362900	2.22709900
C	2.49792800	3.14015200	0.07595800
C	2.65428300	2.82887700	1.42356900
H	1.74232100	2.22439400	3.27586100
H	3.35597200	3.44240500	-0.51232100
H	3.64487800	2.89216400	1.86618100
O	0.93704700	3.36400500	-1.77889700
O	-0.81815400	2.04647300	2.33894300
C	2.00963300	3.71187500	-2.64510800
H	2.73542400	2.89474800	-2.71685300
H	1.55581800	3.88538500	-3.62137000
H	2.50986200	4.62733700	-2.30858800
C	-0.70550800	1.75074000	3.72503900
H	-1.71856900	1.53325800	4.06445200
H	-0.06757100	0.87530200	3.89276900
H	-0.31025500	2.60833500	4.28141400

13

Zero-point correction=	0.281207 (Hartree/Particle)
Thermal correction to Energy=	0.309531
Thermal correction to Enthalpy=	0.310475
Thermal correction to Gibbs Free Energy=	0.217712
Sum of electronic and zero-point Energies=	-1855.832084
Sum of electronic and thermal Energies=	-1855.803759
Sum of electronic and thermal Enthalpies=	-1855.802815
Sum of electronic and thermal Free Energies=	-1855.895578

C	-1.47040400	-2.10485300	0.85104200
C	-2.37289500	-2.62693000	-0.14338300
C	-1.09581500	-2.95962100	1.94853900
C	-2.72480600	-3.97500000	-0.13272900
C	-1.45432000	-4.30719200	1.94197700
C	-2.25263100	-4.78250700	0.90240400
H	-1.14313700	-4.97687500	2.73404000
H	-2.53407400	-5.83219200	0.90673600
C	1.82083300	-4.46923900	-0.35325700
O	-0.42017800	-2.35196800	2.92875000
C	0.09504700	-3.14105100	4.00206300
H	0.79114900	-3.89719800	3.62524800
H	0.62301900	-2.44148600	4.64912000
H	-0.71782500	-3.61782100	4.55898900
O	0.77939400	-3.90394900	-0.83991300
C	2.03767300	-5.86811600	-0.98265400
O	2.61557500	-4.05781700	0.48621300
Pd	0.37676500	-2.00624500	-0.23499700
O	-0.24911800	-0.19662500	0.39921300
C	4.66584300	-1.82920400	-0.88280200
H	4.76360000	-1.78747200	-1.97062100
H	5.56545500	-1.44698100	-0.39230600
H	4.45418200	-2.84621200	-0.54661400
C	3.72177800	0.74740700	-1.11472700
H	2.90542200	1.44715600	-0.92414200
H	4.63807600	1.10635000	-0.63768500
H	3.86746700	0.61097000	-2.18942600
S	3.26219400	-0.82584700	-0.36353200
O	2.08096400	-1.32439900	-1.26538200
H	-3.36633000	-4.39647900	-0.89670000
O	-2.82250600	-1.72398600	-1.02097200
C	-3.64422400	-2.16477900	-2.10250100
H	-4.57564800	-2.60180000	-1.72876300
H	-3.86459700	-1.26986700	-2.68336100
H	-3.10868100	-2.88932500	-2.72434900
F	3.09802300	-6.48980800	-0.45476100
F	2.24083700	-5.76337400	-2.30990200
F	0.96287000	-6.65650700	-0.79641200
C	-1.33844500	-0.57825200	1.00913600
O	-2.13298400	0.12113900	1.60604400

TS-2

Zero-point correction=	0.278632 (Hartree/Particle)
Thermal correction to Energy=	0.307187
Thermal correction to Enthalpy=	0.308131
Thermal correction to Gibbs Free Energy=	0.214384
Sum of electronic and zero-point Energies=	-1855.807650
Sum of electronic and thermal Energies=	-1855.779095
Sum of electronic and thermal Enthalpies=	-1855.778151
Sum of electronic and thermal Free Energies=	-1855.871898

C	-1.29947600	-2.64776400	0.63055700
C	-2.45083900	-2.78781400	-0.19255400
C	-1.30314300	-3.27726000	1.90586100
C	-3.58983300	-3.44919100	0.27297500
C	-2.44104600	-3.93892500	2.37482200
C	-3.56252800	-4.00796400	1.54991300
H	-2.46397600	-4.40219200	3.35417800
H	-4.44797500	-4.52286400	1.91390700
C	1.93098600	-4.33495100	-0.65740800
O	0.84615600	-3.75762300	-1.01697100
C	2.16473300	-5.62848000	-1.47796900
O	2.75742900	-4.00551000	0.18757700
Pd	0.40293400	-1.96969200	-0.16061200
O	-0.37954800	-0.23815100	0.72828900
C	4.73359100	-1.65577800	-0.99139400
H	4.75816100	-1.33535300	-2.03632500
H	5.67030000	-1.40930800	-0.48338000
H	4.53430100	-2.72601200	-0.91331700
C	3.84734900	0.88734700	-0.46477400
H	3.06472900	1.52250200	-0.04419200
H	4.79927500	1.09485900	0.03178900
H	3.92684200	1.04512400	-1.54368500
S	3.38038900	-0.82497400	-0.13630500
O	2.13543500	-1.04574500	-1.04762500
H	-4.48095800	-3.54285300	-0.33658400
F	1.11536900	-6.46500700	-1.38177600
F	3.25302400	-6.28771800	-1.06379400
F	2.33436200	-5.33548600	-2.78219700
C	-1.44635800	-0.58628400	1.21349800
O	-2.43094700	-0.32599100	1.80373400
O	-2.36109300	-2.21943500	-1.41456300
O	-0.16058300	-3.15766700	2.61638300
C	-0.11871000	-3.68888100	3.93666800
H	-0.26353600	-4.77492300	3.92954500
H	0.87749100	-3.45775200	4.31444300
H	-0.87318100	-3.21799200	4.57691500
C	-3.50456800	-2.24196600	-2.26258300
H	-3.20993700	-1.70956100	-3.16718000
H	-3.78525100	-3.26969600	-2.51845000
H	-4.35376100	-1.73079400	-1.79519200

7$_{+CO_2}$

Zero-point correction=	0.278956 (Hartree/Particle)
Thermal correction to Energy=	0.308605
Thermal correction to Enthalpy=	0.309549
Thermal correction to Gibbs Free Energy=	0.212090
Sum of electronic and zero-point Energies=	-1855.816340
Sum of electronic and thermal Energies=	-1855.786691
Sum of electronic and thermal Enthalpies=	-1855.785747
Sum of electronic and thermal Free Energies=	-1855.883206

C	-1.10901900	-2.90855800	0.54689000
C	-2.26717700	-3.12845200	-0.21361300
C	-1.09731000	-3.30036800	1.89369200
C	-3.39923100	-3.72637000	0.35950400
C	-2.22251200	-3.89970900	2.47872900
C	-3.35777500	-4.10605900	1.69900600
H	-2.22050600	-4.20305500	3.51990000
H	-4.23255000	-4.57095800	2.14665300
C	2.09141100	-4.37958900	-0.69757200
O	0.06069300	-3.04938100	2.57717300
C	0.13886600	-3.45293200	3.93430700
H	0.00874100	-4.53719600	4.03909000
H	1.13942700	-3.17626900	4.27043600
H	-0.60641000	-2.93633400	4.55207800
O	0.97651500	-3.86855400	-1.06719900
C	2.38674900	-5.67870700	-1.48999100
O	2.90530200	-3.98617700	0.13130500
Pd	0.48304200	-2.06650700	-0.26241200
O	-0.19819500	-0.08172500	0.52271400
C	4.77826400	-1.62189200	-1.19757100
H	4.76883900	-1.33117400	-2.25145000
H	5.72048700	-1.33717800	-0.72066700
H	4.61044800	-2.69434900	-1.08471800
C	3.85403500	0.91260200	-0.70503900
H	3.06922500	1.54265700	-0.28096900
H	4.81214900	1.14712600	-0.23306800
H	3.90819700	1.05007900	-1.78830900
S	3.42515500	-0.80090100	-0.33185300
O	2.16386100	-1.06405600	-1.20594100
H	-4.29914200	-3.89638000	-0.22125200
O	-2.21365400	-2.71867900	-1.51630600
C	-3.35145100	-2.93634600	-2.33372600
H	-4.22804000	-2.39505500	-1.95604800
H	-3.08823700	-2.55129900	-3.32020700
H	-3.59085300	-4.00401000	-2.41391300
F	3.49369600	-6.28629000	-1.04786600
F	2.56562300	-5.39951600	-2.79604200
F	1.37053100	-6.55398400	-1.39522400
C	-1.18509600	0.10419400	1.13890600
O	-2.14335800	0.33980100	1.74619600

B3PW91/6-31G(d) (SDD for PD) in gas phase

9

Zero-point correction= 0.364258 (Hartree/Particle)
Thermal correction to Energy= 0.399148
Thermal correction to Enthalpy= 0.400092
Thermal correction to Gibbs Free Energy= 0.292358
Sum of electronic and zero-point Energies= -2408.823741
Sum of electronic and thermal Energies= -2408.78885 1
Sum of electronic and thermal Enthalpies= -2408.787907
Sum of electronic and thermal Free Energies= -2408.895641

C	0.18098700	1.67159900	2.56198300
C	-0.17189200	1.41636700	3.89444800
C	0.10777600	2.98496900	2.07921600
C	-0.57957400	2.45648500	4.73847400
C	-0.30831200	4.03129900	2.91068300
C	-0.64252200	3.75086100	4.23222400
H	-0.37023800	5.04927800	2.54372100
H	-0.96075000	4.56143800	4.88297800
C	1.53944300	-4.10535400	-1.15828300
O	0.45054200	3.15112200	0.77095400
C	0.38121600	4.45062800	0.22586500
H	1.06266200	5.14258600	0.73889200
H	0.68586300	4.35492500	-0.81813400
H	-0.63991500	4.85301800	0.26610400
O	0.41968200	-3.67565400	-0.70869900
C	1.36062300	-5.48401900	-1.84392400
O	2.64780300	-3.58522700	-1.14147400
Pd	0.27151400	-1.91570900	0.28457800
O	1.88982800	0.49736800	1.38642900
C	3.17786000	-1.07879200	-2.82307600
H	2.51052700	-0.66511600	-3.58422900
H	4.20298300	-0.72269200	-2.96627900
H	3.15583000	-2.16948200	-2.82753000
C	2.68786400	1.21519200	-1.43158600
H	2.27880600	1.66568900	-0.52567300
H	3.73608000	1.50399200	-1.55915200
H	2.09829200	1.48403000	-2.31253300
S	2.61309100	-0.57221000	-1.18239100
O	1.06961500	-0.86313000	-1.27175100
H	-0.84526900	2.26694700	5.77225800
O	-0.08030500	0.11690100	4.28767600
C	-0.23093300	-0.17862200	5.65938100
H	-1.24979800	0.03235500	6.01361700
H	-0.03113100	-1.24724700	5.75728600
H	0.48591200	0.38219200	6.27348300
F	2.53311800	-6.08213400	-2.07016300
F	0.73937700	-5.33002800	-3.03163000
F	0.60835200	-6.31713200	-1.09972000
C	0.69659600	0.55765500	1.67786300
O	-0.23436800	-0.25876800	1.29942800
S	-2.02985700	-3.33305600	1.92668800
O	-0.52009100	-3.01063700	1.83935000
C	-2.53548300	-4.03084500	0.33660700
H	-2.31882700	-3.32148200	-0.46665300
H	-1.94913400	-4.93795300	0.17783300
H	-3.60365100	-4.26510300	0.38937200
C	-2.92561000	-1.76496900	1.83291800
H	-2.59913100	-1.16029200	2.68094300
H	-2.66791600	-1.24327600	0.90791200
H	-3.99782100	-1.97746800	1.89522900

12

Zero-point correction= 0.281868 (Hartree/Particle)
Thermal correction to Energy= 0.309936
Thermal correction to Enthalpy= 0.310880
Thermal correction to Gibbs Free Energy= 0.217695
Sum of electronic and zero-point Energies= -1855.791697
Sum of electronic and thermal Energies= -1855.763629
Sum of electronic and thermal Enthalpies= -1855.762685
Sum of electronic and thermal Free Energies= -1855.855870

C	-1.81485600	0.48215600	-0.70357600
C	-1.90296900	1.40465400	0.34558900
C	-2.40171100	0.79150800	-1.94017000
C	-2.57568100	2.62011800	0.17356100
C	-3.07870500	2.00341500	-2.12219000
C	-3.15644600	2.89946900	-1.06022000
H	-3.54250900	2.24693600	-3.07114200
H	-3.68212800	3.84098200	-1.19795900
C	0.51572100	-4.83742100	-2.18388600
O	1.52131300	-4.69727400	-1.43139900
C	0.30517300	-6.15712800	-2.93562000
O	-0.29635800	-3.88476200	-2.35842800
Pd	0.87054500	-2.71975300	-1.07722900
O	0.03866900	-0.91223100	-1.05301100
C	3.32511000	-0.66400400	2.12894500
H	4.27645200	-0.77662500	1.60249000
H	3.29880000	0.26834600	2.70080700
H	3.16570700	-1.51390600	2.79635400
C	2.50223500	0.71617400	-0.10003900
H	1.79310700	0.75003700	-0.92913300
H	2.44475700	1.63980300	0.48435100
H	3.51910400	0.53541100	-0.45922500
S	1.96874700	-0.66450900	0.93706400
O	2.33324500	-1.95758600	0.12787100
H	-2.64766600	3.34042200	0.98050000
F	0.79741800	-7.18342300	-2.23797600
F	0.94399400	-6.10080800	-4.11620600
F	-0.99106000	-6.37268900	-3.16660200
C	-1.15958800	-0.86248000	-0.49940600
O	-1.69619600	-1.76900300	0.10866500
O	-2.27158100	-0.15982400	-2.89619900
O	-1.27879700	1.04255700	1.50263200
C	-2.88796000	0.05194500	-4.14845300
H	-3.97525200	0.16806400	-4.04779500
H	-2.47412500	0.93241700	-4.65837700
H	-2.67319400	-0.84022500	-4.73862400
C	-1.52527100	1.81623200	2.65715600
H	-1.04118300	1.28888300	3.48178000
H	-1.09744500	2.82537900	2.57374200
H	-2.60000000	1.89781900	2.86376000

12a

Zero-point correction= 0.281894 (Hartree/Particle)
Thermal correction to Energy= 0.309953
Thermal correction to Enthalpy= 0.310897
Thermal correction to Gibbs Free Energy= 0.217190
Sum of electronic and zero-point Energies= -1855.789082
Sum of electronic and thermal Energies= -1855.761022
Sum of electronic and thermal Enthalpies= -1855.760078
Sum of electronic and thermal Free Energies= -1855.853786

C	-1.40432000	-1.73618700	1.21986000
C	-2.64861500	-2.29784600	0.90064100
C	-0.73722300	-2.15762700	2.37692800
C	-3.21570900	-3.27866500	1.72255200
C	-1.29473300	-3.13644700	3.20607100
C	-2.52987800	-3.68146400	2.86400400
H	-0.78519200	-3.47218800	4.10183700
H	-2.96796500	-4.44272800	3.50452600
C	0.06337200	-5.05725700	-1.23438200
O	0.46618700	-1.55768900	2.60746700
C	1.16142900	-1.90175000	3.78690400
H	1.44771200	-2.96195700	3.79413500
H	2.06313900	-1.28619800	3.79490900
H	0.56778800	-1.67968500	4.68332500
O	1.29373400	-4.78150800	-1.15102100
C	-0.37552000	-6.51272400	-1.43419100
O	-0.81010300	-4.15274900	-1.11166000
Pd	0.74911700	-2.77472700	-0.80224200
O	-0.00955900	-0.96322300	-0.60049000
C	4.34017200	-0.13395700	0.03697300
H	4.85715400	-0.43000800	-0.87941700
H	4.54902100	0.91045200	0.28746600
H	4.64604600	-0.78170500	0.86149100
C	2.32902300	0.68389000	-1.64058000
H	1.27461200	0.58944700	-1.90431100
H	2.55984400	1.72146500	-1.37934500
H	2.97629100	0.32304300	-2.44470300
S	2.55722700	-0.34335500	-0.17156400
O	2.55369100	-1.83246800	-0.68119900
H	-4.17352000	-3.72448700	1.48099100
O	-3.22064900	-1.82421300	-0.23309000
C	-4.44271400	-2.39204300	-0.65523300
H	-5.24027900	-2.22452600	0.08102600
H	-4.70093900	-1.88331600	-1.58551800
H	-4.33919200	-3.46787300	-0.84593800
F	-0.45779300	-7.11935800	-0.23948700
F	0.50827300	-7.17496100	-2.18500900
F	-1.57239300	-6.57295400	-2.02273600
C	-0.84248900	-0.62129700	0.37341600
O	-1.13216500	0.54292100	0.56101300

TS-1

Zero-point correction= 0.281333 (Hartree/Particle)
Thermal correction to Energy= 0.308889
Thermal correction to Enthalpy= 0.309833
Thermal correction to Gibbs Free Energy= 0.219028
Sum of electronic and zero-point Energies= -1855.782378
Sum of electronic and thermal Energies= -1855.754822
Sum of electronic and thermal Enthalpies= -1855.753877
Sum of electronic and thermal Free Energies= -1855.844682

Pd	-0.32446700	0.12968000	-0.42899600
S	-3.26796400	-0.85917700	-0.50740000
F	4.31609400	-0.84949500	-1.56416000
F	3.11333600	-2.59237400	-2.04681300
F	3.66246900	-2.18533900	0.01573200
O	1.12862300	-1.28232900	-0.21033200
O	-1.87080300	-1.18993700	0.10760800
O	-1.71833700	1.50002100	-0.69339200
O	1.86746000	0.26032200	-1.62728600
O	-2.06159800	3.60711100	-0.03087900
C	2.01469200	-0.79176400	-0.98998100
C	3.30460700	-1.61578200	-1.14200300
C	-4.09346800	-2.45572100	-0.32378800
C	-4.16768400	0.07053500	0.75473200
C	-1.34435300	2.63677700	-0.13712400
H	-5.14397600	-2.35364200	-0.61202500
H	-3.58939600	-3.15491900	-0.99467800
H	-3.99942100	-2.79874600	0.70990900
H	-5.22136700	0.12616200	0.46303100
H	-4.05136600	-0.42285200	1.72369100
H	-3.73092500	1.07069100	0.77021800
C	0.08370200	2.58299600	0.37635400
C	0.33005100	2.33781900	1.74822000
C	1.15520700	2.97886700	-0.45542100
C	1.62448800	2.42330900	2.26176400
C	2.45403100	3.06289500	0.06057200
C	2.66535600	2.78371300	1.40507100
H	1.83034600	2.21973600	3.30586300
H	3.28783200	3.33588500	-0.57473400
H	3.67475900	2.84681200	1.80360500
O	0.81923800	3.26445400	-1.72755700
O	-0.76547200	2.02477500	2.48222700
C	1.85930800	3.46140300	-2.67154100
H	2.51456100	2.58491300	-2.71161500
H	1.36063200	3.59357400	-3.63267200
H	2.44065700	4.36316100	-2.43998500
C	-0.59066900	1.74760100	3.85809000
H	-1.58747900	1.53594900	4.24818200
H	0.05393900	0.87269900	4.01133200
H	-0.17122300	2.61127900	4.38946100

13

Zero-point correction= 0.281791 (Hartree/Particle)
Thermal correction to Energy= 0.309901
Thermal correction to Enthalpy= 0.310845
Thermal correction to Gibbs Free Energy= 0.218874
Sum of electronic and zero-point Energies= -1855.801650
Sum of electronic and thermal Energies= -1855.773540
Sum of electronic and thermal Enthalpies= -1855.772596
Sum of electronic and thermal Free Energies= -1855.864567

C	-1.49715400	-2.05012500	0.80131200
C	-2.40082200	-2.59640600	-0.17233700
C	-1.07635500	-2.89352500	1.88565400
C	-2.73748300	-3.94936300	-0.14170400
C	-1.41827700	-4.24721800	1.90006600
C	-2.23146000	-4.74444900	0.88512000
H	-1.06582900	-4.90724400	2.68317400
H	-2.48852000	-5.80048500	0.89739900
C	1.80616300	-4.47332000	-0.40724600
O	-0.37423300	-2.27571300	2.84375600
C	0.28050600	-3.06594400	3.82693100
H	0.97466900	-3.77159400	3.35659300
H	0.83494600	-2.35999400	4.44555800
H	-0.44428500	-3.60355500	4.44948900
O	0.70193400	-3.97511800	-0.82072100
C	1.97413000	-5.94211900	-0.86993900
O	2.68046300	-3.96306900	0.28962400
Pd	0.33391200	-2.04626800	-0.30957200
O	-0.21900600	-0.20651400	0.26466000
C	4.67272600	-1.84057100	-0.92720300
H	4.75493300	-1.64970600	-2.00085500
H	5.55222800	-1.47147800	-0.39073000
H	4.52326800	-2.90384800	-0.72751600
C	3.58169500	0.68453900	-0.76871900
H	2.70482100	1.28326400	-0.51053100
H	4.45323300	1.03605300	-0.20776400
H	3.76188300	0.72956100	-1.84635000
S	3.20159100	-1.01609000	-0.28547100
O	2.08432600	-1.41799200	-1.29390400
H	-3.37851200	-4.38654800	-0.89742900
O	-2.87227700	-1.71240800	-1.06071100
C	-3.66236900	-2.18466200	-2.14153500
H	-4.59495300	-2.63432300	-1.78063700
H	-3.89148800	-1.30402300	-2.74180600
H	-3.10528800	-2.91007800	-2.74583700
F	3.21460700	-6.38866100	-0.64142400
F	1.72139500	-6.08000300	-2.18107700
F	1.11926300	-6.74099100	-0.19973900
C	-1.31754800	-0.51594600	0.90803100
O	-2.07928800	0.21798000	1.49101100

TS-2

Zero-point correction= 0.279373 (Hartree/Particle)
Thermal correction to Energy= 0.307685
Thermal correction to Enthalpy= 0.308629
Thermal correction to Gibbs Free Energy= 0.215700
Sum of electronic and zero-point Energies= -1855.783198
Sum of electronic and thermal Energies= -1855.754886
Sum of electronic and thermal Enthalpies= -1855.753942
Sum of electronic and thermal Free Energies= -1855.846871

C	-1.32767100	-2.55752400	0.63614500
C	-2.45963000	-2.74675100	-0.20118100
C	-1.30668200	-3.22042300	1.89232900
C	-3.55360600	-3.50257400	0.22621500
C	-2.39845500	-3.97558000	2.32662100
C	-3.50109500	-4.09947800	1.48397300
H	-2.39994700	-4.46954000	3.29136300
H	-4.35150200	-4.68854600	1.81908900
C	1.92472100	-4.25196800	-0.69861800
O	0.78630900	-3.72638000	-0.95205800
C	2.04484500	-5.65271700	-1.35065000
O	2.86647700	-3.81732400	-0.04102400
Pd	0.38690100	-1.90910600	-0.16831300
O	-0.36923400	-0.16566400	0.69517000
C	4.72319600	-1.65530000	-1.10993700
H	4.69026000	-1.24009800	-2.12125400
H	5.68146700	-1.44249200	-0.62592500
H	4.53263300	-2.72988300	-1.11628600
C	3.88433200	0.81129000	-0.28229300
H	3.11247300	1.40641100	0.21153700
H	4.84717800	0.96749600	0.21397900
H	3.93997600	1.08309100	-1.34020200
S	3.39399800	-0.92684700	-0.12599700
O	2.13673200	-1.00107700	-1.02834500
H	-4.42890000	-3.63911400	-0.39829700
F	1.16401100	-6.50842100	-0.80036500
F	3.27070400	-6.16573300	-1.18782900
F	1.79600400	-5.59780200	-2.67067600
C	-1.43853500	-0.52621500	1.17610800
O	-2.42095400	-0.24685800	1.76390300
O	-2.39879800	-2.12635200	-1.39794300
O	-0.18433700	-3.03785400	2.62052300
C	-0.09332300	-3.64473500	3.89729300
H	-0.15841000	-4.73707500	3.82281400
H	0.88778600	-3.36769500	4.28494100
H	-0.87338100	-3.27358100	4.57420500
C	-3.49720400	-2.24720900	-2.28418900
H	-3.22395100	-1.67443100	-3.17123200
H	-3.66596700	-3.29393500	-2.56503700
H	-4.41280900	-1.82972900	-1.84633600

7$_{+CO_2}$

Zero-point correction=	0.279339 (Hartree/Particle)
Thermal correction to Energy=	0.308938
Thermal correction to Enthalpy=	0.309882
Thermal correction to Gibbs Free Energy=	0.211967
Sum of electronic and zero-point Energies=	-1855.790716
Sum of electronic and thermal Energies=	-1855.761117
Sum of electronic and thermal Enthalpies=	-1855.760173
Sum of electronic and thermal Free Energies=	-1855.858088

C	-1.13682000	-2.82065200	0.58420800
C	-2.24716500	-3.11495800	-0.21855900
C	-1.15971700	-3.18586000	1.93582000
C	-3.36414000	-3.76959800	0.31863700
C	-2.27008100	-3.84034700	2.48622000
C	-3.35619500	-4.12718500	1.66410700
H	-2.29383600	-4.12597400	3.53233700
H	-4.21973700	-4.63746100	2.08343400
C	2.05096600	-4.26543200	-0.80313300
O	-0.04790000	-2.84515900	2.65994200
C	0.06027700	-3.33244200	3.98082000
H	-0.00752000	-4.42768100	4.01181600
H	1.04597500	-3.02340200	4.33414600
H	-0.70904700	-2.90467400	4.63891300
O	0.88028400	-3.79185100	-1.00881200
C	2.21200600	-5.64546100	-1.49135400
O	2.99753500	-3.79281600	-0.18039600
Pd	0.46938400	-1.98740800	-0.19584700
O	-0.17472000	-0.02436600	0.67699900
C	4.72337000	-1.63271900	-1.43412100
H	4.59312100	-1.20055600	-2.43039300
H	5.72730500	-1.43556800	-1.04537800
H	4.52524500	-2.70569600	-1.43767400
C	4.01882800	0.82256700	-0.47862400
H	3.31637700	1.42451600	0.10275400
H	5.03003200	0.94683700	-0.07896300
H	3.97500900	1.11783400	-1.53085200
S	3.50632500	-0.90912800	-0.30980000
O	2.16362300	-0.93571400	-1.07772100
H	-4.22717700	-4.00169100	-0.29595800
O	-2.16115300	-2.71270600	-1.51878300
C	-3.16472900	-3.13780700	-2.41583600
H	-4.14294700	-2.69971100	-2.17251200
H	-2.85188000	-2.78789500	-3.40136400
H	-3.25211200	-4.23202400	-2.43113200
F	3.44389600	-6.13862800	-1.31350500
F	1.99901000	-5.54567000	-2.81612600
F	1.33530900	-6.53475600	-0.99718100
C	-1.19183200	0.10212800	1.25986100
O	-2.17442700	0.30756500	1.83963600

BENZENE SYSTEM

B3LYP/6-31G(d) (SDD for PD)
in DCM

9

Zero-point correction=	0.297323 (Hartree/Particle)
Thermal correction to Energy=	0.327114
Thermal correction to Enthalpy=	0.328059
Thermal correction to Gibbs Free Energy=	0.231761
Sum of electronic and zero-point Energies=	-2180.512623
Sum of electronic and thermal Energies=	-2180.482832
Sum of electronic and thermal Enthalpies=	-2180.481887
Sum of electronic and thermal Free Energies=	-2180.578185

C	-3.96876200	-0.08156100	-0.29271300
C	-4.46379200	0.97236000	0.48894100
C	-4.86995300	-0.92658000	-0.95606900
C	-5.83951100	1.17567100	0.60479500
C	-6.24463300	-0.72311700	-0.84030300
C	-6.73225600	0.32894900	-0.05902100
H	-6.93541600	-1.38304400	-1.35811400
H	-7.80336200	0.48846700	0.03184900
C	3.03903400	-0.57000800	-0.44046400
O	2.32829600	0.29661900	0.18303800
C	4.54968600	-0.24225700	-0.29068200
O	2.69821800	-1.55868900	-1.08486100
Pd	0.28404700	0.27302900	0.10525300
O	-2.08559700	-1.27631300	-1.14762700
C	1.45064800	-3.87361500	0.87258800
H	1.33316000	-3.91338600	1.95819000
H	1.38109800	-4.87289500	0.43368100
H	2.39582400	-3.40721000	0.59242100
C	-1.31080200	-3.71719100	0.79972900
H	-2.17901200	-3.15321900	0.45805400
H	-1.32425600	-4.72485700	0.37514100
H	-1.26024700	-3.75267900	1.89056400
S	0.14159900	-2.84209900	0.15413600
O	0.19926700	-1.54629500	1.06642200
H	-6.21558400	1.99421700	1.21255900
F	5.31620300	-1.06370600	-1.02279700
F	4.93605000	-0.35627600	0.99918300
F	4.81277300	1.02518800	-0.68282100
C	-2.48989300	-0.33647800	-0.44449800
O	-1.72818600	0.48875500	0.21412100
S	0.64727300	3.47172500	-0.33218800
O	0.37590900	2.05466800	-0.94228200
C	2.15801900	3.37880300	0.67462900
H	2.02979200	2.65108000	1.47778400
H	2.97255200	3.07000700	0.01808200
H	2.34238600	4.38204100	1.06918000
C	-0.55993700	3.72306800	1.00168600
H	-1.55018100	3.74822900	0.54406500
H	-0.48965500	2.90277200	1.72014400
H	-0.33918000	4.68352600	1.47585400
H	-3.76689900	1.62581900	1.00240700
H	-4.47471100	-1.73728600	-1.55894700

12

Zero-point correction=	0.215284 (Hartree/Particle)
Thermal correction to Energy=	0.238129
Thermal correction to Enthalpy=	0.239073
Thermal correction to Gibbs Free Energy=	0.157434
Sum of electronic and zero-point Energies=	-1627.367599
Sum of electronic and thermal Energies=	-1627.344754
Sum of electronic and thermal Enthalpies=	-1627.343810
Sum of electronic and thermal Free Energies=	-1627.425449

C	-1.83786700	0.42476200	-0.35832100
C	-2.65931200	0.85159800	0.69514200
C	-1.79346400	1.17193600	-1.54471700
C	-3.42139300	2.01192700	0.56763700
C	-2.55952600	2.33118400	-1.67217000
C	-3.37273200	2.75392500	-0.61665200
H	-2.52323300	2.90381700	-2.59480500
H	-3.96807200	3.65739300	-0.71715200
C	0.25886000	-5.21280400	-1.30304500
O	1.46459300	-4.85446800	-1.16149900
C	-0.06625000	-6.69922700	-1.51313400
O	-0.67582700	-4.35824300	-1.31626300
Pd	0.78016400	-2.83337600	-1.07838300
O	-0.20404400	-1.08845800	-1.16731100
C	4.22853000	-0.27648100	0.34365900
H	4.91372500	-0.50281900	-0.47633500
H	4.39849000	0.73019900	0.73403700
H	4.32737300	-1.01074600	1.14519000
C	2.59665300	0.80910600	-1.62817000
H	1.62827700	0.75978100	-2.12792400
H	2.75611300	1.80763000	-1.21223400
H	3.40520400	0.53053700	-2.30802800
S	2.52086000	-0.37257700	-0.25453100
O	2.53425400	-1.79720200	-0.95439100
H	-4.05380900	2.33721600	1.38903700
F	0.76857500	-7.46956400	-0.80252200
F	0.07767100	-7.00640600	-2.81625200
F	-1.32493700	-6.97213800	-1.14911600
C	-1.03499000	-0.83398500	-0.17588000
O	-1.16095300	-1.53853400	0.82759100
H	-2.68869900	0.26217100	1.60540400
H	-1.16546700	0.83790000	-2.36346900

12a

Zero-point correction= 0.215090 (Hartree/Particle)
Thermal correction to Energy= 0.237944
Thermal correction to Enthalpy= 0.238888
Thermal correction to Gibbs Free Energy= 0.158227
Sum of electronic and zero-point Energies= -1627.357824
Sum of electronic and thermal Energies= -1627.334970
Sum of electronic and thermal Enthalpies= -1627.334026
Sum of electronic and thermal Free Energies= -1627.414688

C	-1.66423600	-1.76809900	1.03635900
C	-3.04796200	-1.94658500	1.18498400
C	-0.79122100	-2.40139500	1.93396600
C	-3.54993600	-2.77444200	2.18805700
C	-1.29626800	-3.21142400	2.95350400
C	-2.67413800	-3.40797300	3.07560200
H	-0.61356700	-3.68559200	3.65317500
H	-3.06485900	-4.04577600	3.86364600
C	0.29633300	-5.18888500	-1.30816300
O	1.51267300	-4.84195300	-1.25434400
C	-0.06806100	-6.63754900	-1.66486600
O	-0.62773300	-4.34447100	-1.11633400
Pd	0.86273600	-2.85064600	-0.86563500
O	-0.03265200	-1.07510400	-0.64771900
C	4.49418800	-0.33558800	0.23782200
H	5.03431900	-0.51221500	-0.69490000
H	4.71124500	0.65835900	0.63763800
H	4.73923900	-1.09916200	0.97825500
C	2.54045500	0.78822000	-1.38873000
H	1.50215000	0.73547600	-1.71818700
H	2.75707200	1.77355600	-0.96693800
H	3.22810000	0.54683100	-2.20273100
S	2.71146200	-0.44435900	-0.06825400
O	2.63965200	-1.84613700	-0.81200800
H	-4.62230600	-2.92018800	2.28309800
F	0.90142700	-7.48003000	-1.28703700
F	-0.22684300	-6.73980400	-2.99791100
F	-1.21349800	-6.99983200	-1.07283000
C	-1.18350800	-0.83432400	-0.03983900
O	-1.84136600	0.16014900	-0.33693500
H	-3.71933000	-1.43296500	0.50412300
H	0.28018200	-2.24432500	1.85430400

TS-1

Zero-point correction= 0.214616 (Hartree/Particle)
Thermal correction to Energy= 0.236890
Thermal correction to Enthalpy= 0.237834
Thermal correction to Gibbs Free Energy= 0.157926
Sum of electronic and zero-point Energies= -1627.350897
Sum of electronic and thermal Energies= -1627.328624
Sum of electronic and thermal Enthalpies= -1627.327680
Sum of electronic and thermal Free Energies= -1627.407588

C	-1.10997500	-0.60409700	-2.54915500
C	-1.04018100	-0.50413000	-3.94528500
C	-2.00198300	-1.52180100	-1.96068500
C	-1.82448500	-1.33422200	-4.74419800
C	-2.79031300	-2.34992600	-2.76820100
C	-2.69557800	-2.26146700	-4.15735300
H	-3.48192600	-3.04832200	-2.30714100
H	-3.30707800	-2.90281200	-4.78542900
C	-0.63349700	-4.72933400	-0.03836300
O	0.52638500	-4.31674400	-0.40611400
C	-0.73426200	-6.26141800	0.11553400
O	-1.61105500	-4.00482900	0.17392500
Pd	0.31974200	-2.29120800	-0.52552600
O	0.18760100	-0.29271700	-0.56368200
C	4.56377100	-1.40070600	0.83185600
H	5.10319700	-1.81195900	-0.02403300
H	5.10890800	-0.56476000	1.27796800
H	4.38155600	-2.17279800	1.58154000
C	3.45218500	0.33600900	-1.03310400
H	2.54205000	0.77594300	-1.44650200
H	4.07752400	1.11538200	-0.58829100
H	4.00495000	-0.22488400	-1.79094700
S	2.94203900	-0.79461800	0.29247500
O	2.38543700	-2.08258600	-0.45072400
H	-1.76048800	-1.26020700	-5.82600800
F	0.17912900	-6.70857400	0.99942300
F	-0.49902700	-6.86732500	-1.06556500
F	-1.94831300	-6.63247500	0.54212200
C	-0.22053500	0.25351600	-1.69766900
O	0.11958700	1.38417000	-2.03426200
H	-0.36340100	0.21944500	-4.38866100
H	-2.14945800	-1.53308500	-0.88275900

13

Zero-point correction= 0.215067 (Hartree/Particle)
Thermal correction to Energy= 0.237850
Thermal correction to Enthalpy= 0.238794
Thermal correction to Gibbs Free Energy= 0.158850
Sum of electronic and zero-point Energies= -1627.362869
Sum of electronic and thermal Energies= -1627.340086
Sum of electronic and thermal Enthalpies= -1627.339141
Sum of electronic and thermal Free Energies= -1627.419085

C	-1.81495300	-1.83510400	0.86140300
C	-2.84837600	-2.17390600	-0.04513900
C	-1.18475300	-2.86030700	1.62804000
C	-3.23004600	-3.49553900	-0.18807000
C	-1.60996900	-4.20353900	1.47400600
C	-2.60868800	-4.51399300	0.57033100
H	-1.15719800	-4.97614500	2.08736300
H	-2.93649500	-5.54240400	0.45361000
C	1.83227500	-4.47728200	-0.33476800
O	0.78469000	-3.86056400	-0.74685300
C	2.16431000	-5.75722800	-1.14223100
O	2.60593200	-4.17329300	0.57277500
Pd	0.41639600	-2.06084500	0.13823400
O	-0.09486000	-0.27540900	0.93554500
C	4.68916000	-2.00200400	-0.81073500
H	4.69815300	-1.72653800	-1.86799700
H	5.64942600	-1.78133100	-0.33675900
H	4.43371800	-3.05447800	-0.67921400
C	3.89797500	0.62905200	-0.42273800
H	3.14538700	1.30890900	-0.01884600
H	4.87254300	0.83892500	0.02579800
H	3.94156100	0.70426000	-1.51191300
S	3.40196600	-1.05212200	0.04575400
O	2.11344800	-1.29399300	-0.83432100
H	-4.02389300	-3.75513400	-0.88212700
F	1.22512800	-6.08761300	-2.04273300
F	2.33141800	-6.80569600	-0.31388800
F	3.32665600	-5.57020500	-1.80771200
C	-1.39830800	-0.39416700	1.07832700
O	-2.17862900	0.51080700	1.32285200
H	-3.33593400	-1.38466300	-0.60847300
H	-0.54905700	-2.59927000	2.47093500

TS-2

Zero-point correction= 0.212171 (Hartree/Particle)
Thermal correction to Energy= 0.235316
Thermal correction to Enthalpy= 0.236260
Thermal correction to Gibbs Free Energy= 0.154531
Sum of electronic and zero-point Energies= -1627.333431
Sum of electronic and thermal Energies= -1627.310286
Sum of electronic and thermal Enthalpies= -1627.309342
Sum of electronic and thermal Free Energies= -1627.391070

C	-1.34380800	-2.48815600	0.59848100
C	-2.39619000	-2.65903700	-0.33633200
C	-1.34686100	-3.26986400	1.78179100
C	-3.41875700	-3.57048100	-0.08942800
C	-2.37104500	-4.18023000	2.02318600
C	-3.40481000	-4.32738900	1.08888800
H	-2.37089000	-4.77462500	2.93219500
H	-4.20609500	-5.03523600	1.28195000
C	1.94700300	-4.29718300	-0.48194800
O	0.91788500	-3.69741000	-0.95380100
C	2.34436300	-5.56701300	-1.27727600
O	2.67256400	-3.98724900	0.46358100
Pd	0.46931800	-1.87341300	-0.13505300
O	-0.29378200	-0.13661200	0.69477800
C	4.81257300	-1.91121900	-0.99581200
H	4.84063500	-1.56679500	-2.03264400
H	5.78148500	-1.77081400	-0.50885700
H	4.51042900	-2.95751100	-0.93758500
C	4.18686800	0.71708500	-0.42414700
H	3.47314500	1.41873000	0.01220600
H	5.16398200	0.83350800	0.05218700
H	4.25647900	0.86393900	-1.50489800
S	3.56580400	-0.95554500	-0.08243000
O	2.27543400	-1.04179900	-0.96911800
H	-4.22524100	-3.69442400	-0.80623700
F	1.42263800	-5.95830000	-2.17212800
F	2.57646900	-6.59929400	-0.44500300
F	3.49294300	-5.32062300	-1.95299200
C	-1.36801500	-0.54942900	1.15415000
O	-2.33919800	-0.23893500	1.75942400
H	-2.40955100	-2.06441600	-1.24601500
H	-0.54879300	-3.14747600	2.50913800

7$_{+CO_2}$

Zero-point correction=	0.212199 (Hartree/Particle)
Thermal correction to Energy=	0.236784
Thermal correction to Enthalpy=	0.237728
Thermal correction to Gibbs Free Energy=	0.150894
Sum of electronic and zero-point Energies=	-1627.356574
Sum of electronic and thermal Energies=	-1627.331989
Sum of electronic and thermal Enthalpies=	-1627.331045
Sum of electronic and thermal Free Energies=	-1627.417879

C	-1.19995000	-2.99760700	0.48615400
C	-2.12743300	-3.46970500	-0.45271200
C	-1.48479800	-3.10280300	1.85569000
C	-3.34118900	-4.01852500	-0.02326000
C	-2.69967300	-3.65928300	2.27890000
C	-3.62931200	-4.11416400	1.34145600
H	-2.91208600	-3.73708600	3.34246900
H	-4.57045600	-4.54564500	1.67144700
C	2.01934900	-4.42900500	-0.73548800
O	0.95858800	-3.83065400	-1.13468800
C	2.47828300	-5.55791700	-1.69454500
O	2.73348200	-4.19996600	0.24028300
Pd	0.46754200	-2.12046700	-0.09687000
O	-0.17800300	-0.19496300	0.93634800
C	4.79171100	-1.85178900	-1.10016300
H	4.77189200	-1.34960800	-2.07093600
H	5.77972000	-1.77476300	-0.63798900
H	4.50482300	-2.89955200	-1.19776600
C	4.18238800	0.63903000	-0.08667200
H	3.49024900	1.25545500	0.49074000
H	5.18040500	0.68330400	0.35771200
H	4.20282600	0.96301900	-1.13033100
S	3.57469100	-1.07183900	0.00323600
O	2.24771900	-1.03440200	-0.81910400
H	-4.05833200	-4.37613900	-0.75832400
F	1.51399700	-5.98725600	-2.52511600
F	2.93636300	-6.62024600	-1.00960900
F	3.49907000	-5.09210500	-2.45729400
C	-1.26670800	0.16038600	1.21570500
O	-2.32493000	0.54483700	1.49816000
H	-1.90711300	-3.41531100	-1.51582200
H	-0.76613000	-2.76244700	2.59864000

para-chloro-bismethoxy SYSTEM

B3LYP/6-31G(d) (SDD for PD)
in DCM

9

Zero-point correction= 0.352750 (Hartree/Particle)
Thermal correction to Energy= 0.389259
Thermal correction to Enthalpy= 0.390204
Thermal correction to Gibbs Free Energy= 0.278214
Sum of electronic and zero-point Energies= -2869.087389
Sum of electronic and thermal Energies= -2869.050880
Sum of electronic and thermal Enthalpies= -2869.049936
Sum of electronic and thermal Free Energies= -2869.161926

C	0.20641600	1.66718000	2.57240200
C	-0.27095000	1.43378000	3.87249900
C	0.23080300	2.98152200	2.07963800
C	-0.70647200	2.49360400	4.68201000
C	-0.20590700	4.05658100	2.86769400
C	-0.66103900	3.77908900	4.15257500
H	-0.19659500	5.07397300	2.50188900
C	1.59366500	-4.09150800	-1.21047200
O	0.68361100	3.12703100	0.80245600
C	0.72124200	4.43590500	0.23435200
H	1.38926000	5.09522600	0.80031200
H	1.10805400	4.30772200	-0.77704300
H	-0.28093900	4.87698700	0.18879100
O	0.44924500	-3.64910600	-0.83744200
C	1.43931800	-5.42008300	-1.99925800
O	2.71559700	-3.61614500	-1.05027100
Pd	0.27894100	-1.90718000	0.22598900
O	1.94387900	0.37597600	1.55496200
C	3.10305500	-1.00385100	-2.98472300
H	2.42741400	-0.57371900	-3.72797700
H	4.12928100	-0.66137100	-3.14340700
H	3.06557100	-2.09369100	-2.99749600
C	2.62988500	1.30358300	-1.52974400
H	2.24530300	1.73168300	-0.60278300
H	3.67054900	1.60228300	-1.68398300
H	2.01101500	1.58849900	-2.38421700
S	2.58189900	-0.49701600	-1.32227200
O	1.02717000	-0.80936500	-1.34821600
H	-1.06995500	2.33207300	5.68744100
O	-0.26831300	0.13357100	4.28079300
C	-0.64223500	-0.16189900	5.62670600
H	-1.68519900	0.11428900	5.82005000
H	-0.52658500	-1.24082900	5.73397200
H	0.01269500	0.34980200	6.34113000
F	2.62638100	-5.98588900	-2.26506400
F	0.81664900	-5.19577600	-3.17869500
F	0.69898800	-6.31683400	-1.31334600
C	0.73019200	0.52213300	1.72917000
O	-0.21278400	-0.22905100	1.25002900
S	-1.87488100	-3.44088000	2.09500000
O	-0.38421200	-3.04397300	1.82229600
C	-2.54236700	-4.14297100	0.55748600
H	-2.46003200	-3.41300700	-0.25122800
H	-1.95437400	-5.03265000	0.32673000
H	-3.58559500	-4.41408200	0.74223300
C	-2.84203200	-1.90473800	2.15881300
H	-2.43446600	-1.30768200	2.97630600
H	-2.74537400	-1.36412700	1.21534500
H	-3.88205700	-2.17582200	2.36050400
Cl	-1.21031500	5.12176700	5.15746500

12

Zero-point correction= 0.270531 (Hartree/Particle)
Thermal correction to Energy= 0.300125
Thermal correction to Enthalpy= 0.301070
Thermal correction to Gibbs Free Energy= 0.204561
Sum of electronic and zero-point Energies= -2315.941881
Sum of electronic and thermal Energies= -2315.912287
Sum of electronic and thermal Enthalpies= -2315.911343
Sum of electronic and thermal Free Energies= -2316.007851

C	-1.93454400	0.46452000	-0.76559900
C	-2.04136900	1.31829400	0.34365200
C	-2.45406100	0.87445300	-2.00425000
C	-2.66308400	2.57042800	0.22870000
C	-3.08336500	2.12068200	-2.14152800
C	-3.16825000	2.93426400	-1.01586500
H	-3.49528700	2.45115800	-3.08503300
C	0.50919300	-4.96050300	-2.00260800
O	1.56903100	-4.70435000	-1.35935500
C	0.33742500	-6.34197900	-2.65190600
O	-0.38588600	-4.07975100	-2.16020000
Pd	0.84042900	-2.71505800	-1.08243600
O	-0.07530800	-0.93205800	-1.09571900
C	3.54141700	-0.73468100	1.96585600
H	4.44975700	-0.73752500	1.35914200
H	3.52121700	0.12356300	2.64238700
H	3.45295300	-1.66206900	2.53467400
C	2.48907100	0.87515900	-0.03965900
H	1.70817200	0.98376200	-0.79328600
H	2.46522500	1.71731100	0.65740600
H	3.47373400	0.77313900	-0.50191000
S	2.09329800	-0.63708400	0.88142300
O	2.40968900	-1.81740200	-0.13204800
H	-2.75231400	3.24332900	1.07042000
F	0.88388600	-7.29736300	-1.88742800
F	0.95683100	-6.34913400	-3.84786900
F	-0.95630800	-6.62681800	-2.84298700
C	-1.29836300	-0.89834800	-0.61740300
O	-1.88921800	-1.83933000	-0.09925400
O	-2.31240300	-0.01443500	-3.02315200
O	-1.49508700	0.85169900	1.49921600
C	-2.83273900	0.32363300	-4.30877800
H	-3.91754100	0.47508000	-4.27011800
H	-2.34864000	1.22198800	-4.70878400
H	-2.60640100	-0.52812400	-4.95065900
C	-1.60676600	1.64576800	2.67983100
H	-1.12791000	1.06719300	3.47036000
H	-1.08973800	2.60538300	2.56415100
H	-2.65659500	1.82212500	2.94022600
Cl	-3.95398700	4.50582400	-1.17405700

12a

Zero-point correction=	0.270551 (Hartree/Particle)
Thermal correction to Energy=	0.300119
Thermal correction to Enthalpy=	0.301063
Thermal correction to Gibbs Free Energy=	0.204556
Sum of electronic and zero-point Energies=	-2315.936897
Sum of electronic and thermal Energies=	-2315.907329
Sum of electronic and thermal Enthalpies=	-2315.906385
Sum of electronic and thermal Free Energies=	-2316.002892

C	-1.48260800	-1.72967000	1.21526600
C	-2.71081000	-2.35874400	0.95500500
C	-0.75733100	-2.08678000	2.36296500
C	-3.20524100	-3.35223900	1.81281300
C	-1.23162800	-3.07646900	3.23581300
C	-2.44779200	-3.68194000	2.93231800
H	-0.68588200	-3.36615900	4.12317500
C	0.00450900	-4.99521300	-1.38498300
O	0.41194900	-1.41328500	2.55037700
C	1.19496700	-1.70836000	3.70728900
H	1.53013900	-2.75189100	3.70378800
H	2.06056900	-1.04758700	3.65327000
H	0.63478800	-1.50331000	4.62658500
O	1.23353100	-4.71678200	-1.25856500
C	-0.41888400	-6.45169200	-1.62618100
O	-0.88067300	-4.09892600	-1.26431300
Pd	0.67523700	-2.70121100	-0.85530400
O	-0.14673500	-0.89480600	-0.63378200
C	4.37597100	-0.23668000	0.24880400
H	4.96456300	-0.62309600	-0.58595900
H	4.62822800	0.80549300	0.46112400
H	4.52373300	-0.84670800	1.14177600
C	2.60939500	0.63044700	-1.71246500
H	1.59564000	0.56193600	-2.10975600
H	2.85304500	1.67088800	-1.48047200
H	3.33502400	0.19924000	-2.40638900
S	2.61320100	-0.31628100	-0.16370700
O	2.51064800	-1.83396700	-0.62389900
H	-4.14504600	-3.85266600	1.62486400
O	-3.35374000	-1.94370900	-0.16860900
C	-4.59492900	-2.55746300	-0.51545900
H	-5.34870700	-2.39515700	0.26351300
H	-4.91504800	-2.07257100	-1.43807800
H	-4.46927100	-3.63200100	-0.69071300
F	-0.53135700	-7.08153600	-0.44114700
F	0.49433600	-7.09729100	-2.36360600
F	-1.60141300	-6.51008200	-2.25106400
C	-1.00880800	-0.60485500	0.32154500
O	-1.42304800	0.53639700	0.47417400
Cl	-3.05966700	-4.92660600	4.02257500

TS-1

Zero-point correction=	0.270030 (Hartree/Particle)
Thermal correction to Energy=	0.299083
Thermal correction to Enthalpy=	0.300028
Thermal correction to Gibbs Free Energy=	0.205415
Sum of electronic and zero-point Energies=	-2315.931577
Sum of electronic and thermal Energies=	-2315.902524
Sum of electronic and thermal Enthalpies=	-2315.901580
Sum of electronic and thermal Free Energies=	-2315.996192

Pd	-0.38777200	0.15575000	-0.62957900
S	-3.37986500	-0.80820600	-0.36670200
F	4.11354000	-1.26407600	-2.19617900
F	2.95154700	-2.98500500	-1.54262000
F	3.87855100	-1.67321800	-0.07017100
O	1.03296700	-1.31582500	-0.50164500
O	-1.87698400	-1.21517600	-0.08452200
O	-1.74324700	1.61164100	-0.78747500
O	1.93980700	0.25578400	-1.80378800
O	-1.94221600	3.78342100	-0.29921000
C	1.98361000	-0.83185500	-1.21475400
C	3.25479600	-1.70334800	-1.26631600
C	-4.18847900	-2.43024400	-0.34240700
C	-3.97443600	-0.13278300	1.20999500
C	-1.29854400	2.74698100	-0.29144500
H	-5.26960000	-2.27338800	-0.38339600
H	-3.85385000	-2.96773500	-1.23157800
H	-3.90034400	-2.96513000	0.56528000
H	-5.04082500	0.08714500	1.11039100
H	-3.79231700	-0.85329400	2.01086500
H	-3.41381400	0.78796300	1.38079400
C	0.09653900	2.65697300	0.30310100
C	0.25580600	2.34839100	1.67566500
C	1.22282000	3.06571200	-0.44590700
C	1.51954300	2.38110200	2.27431300
C	2.49528200	3.10248700	0.14139500
C	2.60533700	2.75774600	1.48435300
H	1.66518300	2.13557400	3.31703700
H	3.37256000	3.39224700	-0.41983600
O	0.97334600	3.40820300	-1.72996300
O	-0.88668200	2.03427700	2.33554300
C	2.07845700	3.68459400	-2.59626000
H	2.74727100	2.82012600	-2.65273200
H	1.63970500	3.87861800	-3.57505600
H	2.62936500	4.57017800	-2.26107100
C	-0.80832100	1.68327500	3.72021100
H	-1.83311500	1.47611100	4.02792700
H	-0.19210200	0.78892900	3.86381300
H	-0.40691200	2.51207000	4.31311600
Cl	4.19852600	2.80137500	2.22980600

13

Zero-point correction= 0.270295 (Hartree/Particle)
Thermal correction to Energy= 0.299975
Thermal correction to Enthalpy= 0.300919
Thermal correction to Gibbs Free Energy= 0.205187
Sum of electronic and zero-point Energies= -2315.948162
Sum of electronic and thermal Energies= -2315.918482
Sum of electronic and thermal Enthalpies= -2315.917538
Sum of electronic and thermal Free Energies= -2316.013271

C	-1.48700400	-2.11246900	0.84890200
C	-2.39223000	-2.63955300	-0.14256600
C	-1.10781100	-2.97356100	1.94185300
C	-2.73261800	-3.99226100	-0.14798300
C	-1.44721900	-4.32760500	1.93185000
C	-2.24100600	-4.79495500	0.88342300
H	-1.13089600	-5.00236100	2.71478100
C	1.82482600	-4.45782600	-0.34496500
O	-0.43309600	-2.37157400	2.92881100
C	0.11153200	-3.16459000	3.99621100
H	0.81724700	-3.90216600	3.60191200
H	0.63173900	-2.45841400	4.64171900
H	-0.68715600	-3.66074400	4.55563500
O	0.80265800	-3.87268600	-0.85775800
C	2.01353100	-5.87554100	-0.94685800
O	2.61672100	-4.05122300	0.50254000
Pd	0.38280500	-1.96767500	-0.24785700
O	-0.29085600	-0.17006000	0.41263500
C	4.67414800	-1.83013100	-0.87642100
H	4.77190000	-1.79529600	-1.96424200
H	5.58404200	-1.47301400	-0.38650800
H	4.42589000	-2.83646200	-0.53456700
C	3.79844100	0.78953400	-1.13847500
H	3.00056400	1.51172000	-0.95491600
H	4.72585900	1.12670400	-0.66779800
H	3.93624000	0.63105000	-2.21086800
S	3.29322200	-0.77105700	-0.36208600
O	2.09148700	-1.24206900	-1.26496400
H	-3.37004200	-4.41922900	-0.90942100
O	-2.85757100	-1.73911000	-1.01729900
C	-3.68668700	-2.17717600	-2.10565600
H	-4.61012200	-2.62724600	-1.72924800
H	-3.91747300	-1.27595500	-2.67177000
H	-3.14555900	-2.88812200	-2.73749500
F	3.06767300	-6.50833000	-0.41020000
F	2.20992100	-5.80515000	-2.28122600
F	0.92045000	-6.63951600	-0.73475800
C	-1.37473800	-0.58015200	1.02026800
O	-2.18307900	0.09725400	1.62676700
Cl	-2.66507200	-6.49027300	0.87163100

TS-2

Zero-point correction= 0.267914 (Hartree/Particle)
Thermal correction to Energy= 0.297703
Thermal correction to Enthalpy= 0.298647
Thermal correction to Gibbs Free Energy= 0.202646
Sum of electronic and zero-point Energies= -2315.925936
Sum of electronic and thermal Energies= -2315.896147
Sum of electronic and thermal Enthalpies= -2315.895203
Sum of electronic and thermal Free Energies= -2315.991204

C	-1.36075700	-2.58524100	0.68347100
C	-2.49676600	-2.78345300	-0.15620100
C	-1.34714100	-3.24415700	1.94875200
C	-3.60405300	-3.51950000	0.27613900
C	-2.44635100	-3.98366200	2.39698300
C	-3.54444800	-4.09465200	1.54516700
H	-2.46057800	-4.46880600	3.36316100
C	1.90816500	-4.27574000	-0.62027700
O	0.82305100	-3.70349700	-0.99131800
C	2.28307100	-5.49984900	-1.49469700
O	2.69881100	-3.96466000	0.27023600
Pd	0.36615300	-1.91000900	-0.11983400
O	-0.43594300	-0.18116300	0.76898400
C	4.66636500	-1.75455300	-1.20034800
H	4.63992700	-1.33753200	-2.21032200
H	5.65123900	-1.61999100	-0.74473200
H	4.39582700	-2.81114000	-1.20457400
C	3.97910000	0.80626100	-0.42405100
H	3.26307100	1.44975400	0.09126900
H	4.97292800	0.92785100	0.01498800
H	3.99262100	1.02834700	-1.49400700
S	3.43201400	-0.90754600	-0.17012600
O	2.10659500	-0.98601400	-1.00283600
H	-4.48195800	-3.65863500	-0.33957000
F	1.26304800	-5.97238700	-2.22989600
F	2.74916800	-6.51006100	-0.73836900
F	3.27221600	-5.13843900	-2.34893000
C	-1.50898700	-0.56324200	1.23366800
O	-2.50230800	-0.28807700	1.81152200
O	-2.43339200	-2.18941400	-1.36767700
O	-0.22538900	-3.07361800	2.68188800
C	-0.16078000	-3.62517000	4.00278500
H	-0.23778200	-4.71702200	3.97438700
H	0.81632700	-3.33692200	4.38952800
H	-0.94880300	-3.21002700	4.63990900
C	-3.56595900	-2.26210300	-2.24235700
H	-3.28451800	-1.69503600	-3.12926200
H	-3.77843000	-3.29961700	-2.52034500
H	-4.44879600	-1.81013300	-1.77808700
Cl	-4.92926300	-5.01897700	2.09860300

7+CO_2

Zero-point correction= 0.268158 (Hartree/Particle)
Thermal correction to Energy= 0.299185
Thermal correction to Enthalpy= 0.300129
Thermal correction to Gibbs Free Energy= 0.199119
Sum of electronic and zero-point Energies= -2315.938613
Sum of electronic and thermal Energies= -2315.907586
Sum of electronic and thermal Enthalpies= -2315.906642
Sum of electronic and thermal Free Energies= -2316.007652

C	-1.18223500	-2.88696500	0.50230300
C	-2.26765600	-3.27339600	-0.29960100
C	-1.23389000	-3.15939200	1.87626200
C	-3.37830400	-3.93536200	0.25210900
C	-2.32961900	-3.81771600	2.45771900
C	-3.37390800	-4.19342000	1.61919900
H	-2.37645200	-4.03288000	3.51684200
C	1.92059000	-4.33417800	-0.90946900
O	-0.15403600	-2.72340800	2.60973400
C	-0.11906700	-3.00497900	4.00877600
H	-0.14770400	-4.08439600	4.19568100
H	0.82687400	-2.59842500	4.36836200
H	-0.94901700	-2.51775400	4.53382700
O	0.84874800	-3.72374300	-1.26693800
C	2.18342200	-5.56385900	-1.82028900
O	2.71557200	-4.07394900	-0.00928900
Pd	0.41834700	-1.99419900	-0.26271700
O	-0.04477400	-0.10991000	0.88575900
C	4.71640100	-1.68315000	-1.15156800
H	4.72505800	-1.38131200	-2.20201100
H	5.67365600	-1.46360400	-0.67072200
H	4.47411600	-2.74190600	-1.04741700
C	3.93624600	0.92168500	-0.65912500
H	3.18435400	1.59373800	-0.24066300
H	4.90508600	1.10411600	-0.18674400
H	3.99820100	1.04476800	-1.74339400
S	3.40963900	-0.77443900	-0.27606600
O	2.12619200	-0.96379500	-1.14961000
H	-4.22128800	-4.23998800	-0.35348200
O	-2.18190600	-2.95617200	-1.62678500
C	-3.22234500	-3.38503800	-2.50133800
H	-4.18249800	-2.92374900	-2.23982300
H	-2.92436900	-3.05772400	-3.49825200
H	-3.32716600	-4.47661600	-2.49233700
F	3.27395500	-6.24305000	-1.43341300
F	2.37383200	-5.17408500	-3.09990000
F	1.13792400	-6.41645500	-1.80359800
C	-0.37496400	0.07777600	2.00107800
O	-0.70219800	0.32643700	3.08688000
Cl	-4.76413100	-5.02720000	2.32496200