Metal Control of Selectivity in Acetate-Assisted C-H Bond Activation: An Experimental and Computational Study of Heterocyclic, Vinylic and Phenylic C(sp^2)-H Bonds at Ir and Rh

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Supporting Information

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1. General.

Ligand **H-L_6** was obtained commercially and used without further purification. $[MCl_2Cp^*]_2$ (M = Ir, Rh) was synthesised according to the literature procedure.[1] CH_2Cl_2 was dried over CaH_2 and distilled prior to use. Dry MeOH was purchased for Acros Organics, extra dry over molecular sieves (MS), AcroSeal. ^1H and ^{13}C NMR spectra were recorded in ppm with reference to TMS as an internal standard at ambient temperature. FAB mass spectra were obtained on a Kratos concept mass spectrometer using NOBA as matrix. The electrospray (ES) mass spectra were recorded using a micromass Quattra LC mass spectrometer with MeCN as solvent.

2. General procedures

2a. General procedure for the synthesis of ligands L_1-L_5.

1 equiv. of aldehyde was added to a round-bottomed flask equipped with a stir bar and 5 g of activated 4 Å MS. A volume of dry MeOH (10-20 mL) was then added to the flask, followed by slow addition of 3 equiv. of isopropylamine. The reaction was left stirring for 2-3 hours. The solution was then filtered and dried on the rotary evaporator followed by high vacuum. No further purification was required.

2b. General procedure for the synthesis of ligand L_{3b}.

1.1 equiv. of thiophene-2-carbaldehyde was added to a round-bottomed flask equipped with a stir bar and 5 g of activated 4 Å MS. A volume of dry MeOH (10-20 mL) was then added to the flask, followed by slow addition of 1 equiv. of 3,5-dimethylaniline. The reaction was left stirring for 2-3 hours. The solution was then filtered and dried on the rotary evaporator. The crude product contain 5-7% of starting aldehyde and it was used for the cyclometallation reaction without further purification.

2c. General procedure for the cyclometallation reactions.

1 equiv. of $[MCl_2Cp^*]_2$ (M = Ir, Rh) and 4 equiv. of NaOAc (ratio Rh:NaOAc 1:2) was weighed and added to an oven-dried Schlenk tube equipped with a stirrer bar. The Schlenk tube was degassed three times and left under N_2 atmosphere. 7 mL of degassed solvent (CH_2Cl_2 or MeOH) was then added with a syringe followed by a solution (3 mL) of the relevant ligand (2.2 equiv, ratio Rh:ligand 1:1.1) . The Schlenk tube was sealed and left stirring at rt for 3 h to 4 d. Once full conversion or equilibrium was achieved, the reaction solution was filtered through celite, and concentrated to afford the crude product. The iridium complexes achieved full conversion and were purified by recrystallization from CH_2Cl_2/hexane. The rhodium complexes were purified by column chromatography on silica gel eluting with CH_2Cl_2 or CH_2Cl_2/MeOH (20/1), followed by recrystallization from CH_2Cl_2/hexane. For the synthesis of **Rh-L_1** and **Rh-L_2** a large excess of ligand was used (10 equiv., ratio Rh:ligand 1:5) to favour the forward reaction; however, isolation of pure samples of **Rh-L_1** and **Rh-L_2** was unsuccessful.

2d. General procedure for the competition experiments.

An oven-dried Schlenk tube equipped with a stirrer bar was degassed three times and left under N_2 atmosphere. The reagents were then added with the aid of solvent (CH_2Cl_2 or d^4-MeOD, total volume: 5 mL) in the following order: $[MCl_2Cp^*]_2$ (M = Ir, Rh) (0.0125 mmol, 9.9 mg (Ir), 7.7 mg (Rh)); NaOAc (0.1 mmol, 8.2 mg), 1,3,5-trimethoxybenzene (internal standard, 0.042 mmol, 7 mg), ligand 1 (0.125 mmol), ligand 2 (0.125 mmol). The Schlenk tube was then sealed and left stirring at rt.

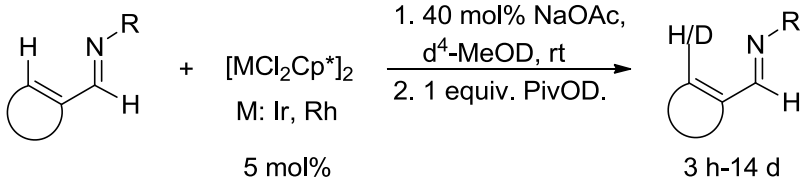
2e. General procedure for the deuteration experiments.

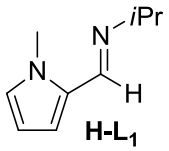
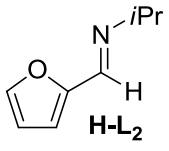
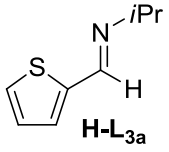
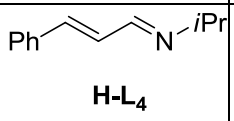
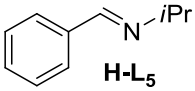
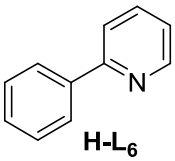
An NMR tube was charged with ligand **H-L$_{1\text{-}6}$** (0.25 mmol) followed by 0.25 mL of a d^4-MeOD solution of $[MCl_2Cp^*]_2$ (M = Ir, Rh) (0.0125 mmol, 9.9 mg (Ir), 7.7 mg (Rh)) followed by 0.25 mL of a d^4-MeOD solution of NaOAc (0.1 mmol, 8.2 mg). The percentage of deuteration was monitored and determined by ^{1}H NMR spectroscopy and the site of deuteration was confirmed by ^{2}H NMR spectroscopy.

2f. General procedure for the X-ray crystallography.

Data were collected on a Bruker Apex 2000 CCD diffractometer using graphite monochromated Mo-K_α radiation, λ = 0.7107 Å. The data were corrected for Lorentz and polarisation effects and empirical absorption corrections were applied. The structure was solved by direct methods and with structure refinement on F^2 employed SHELXTL version 6.10.[2] Hydrogen atoms were included in calculated positions (C—H = 0.95 – 0.98 Å) riding on the bonded atom with isotropic displacement parameters set to $1.5U_{eq}$ (C) for methyl hydrogen atoms and $1.2U_{eq}$ (C) for all other H atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters. Figures were drawn using the program ORTEP. [3]

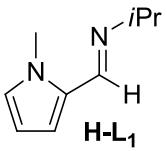
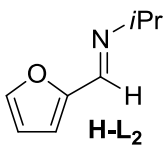
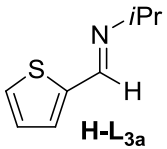
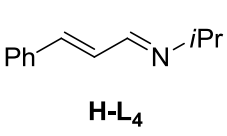
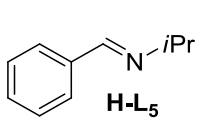
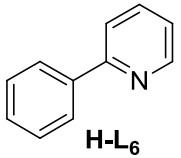
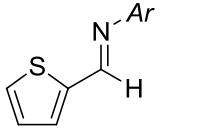
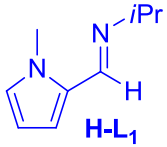
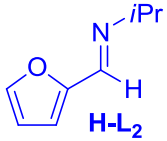
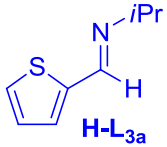
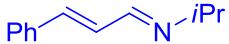
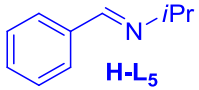
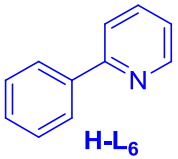
3. Table S1: Results of the deuteration experiments.[a]



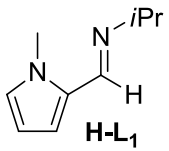
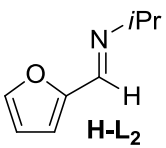
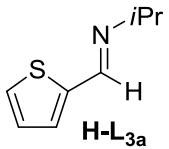
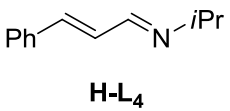
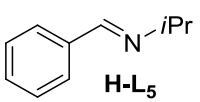
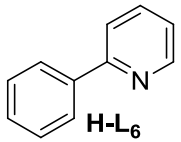
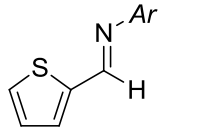
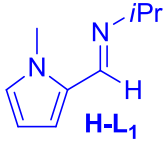
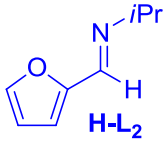
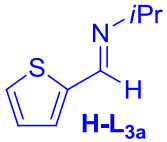
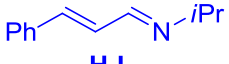
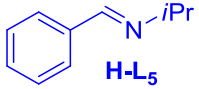
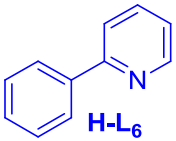
	M = Ir		M = Rh	
	Before PivOD	**After PivOD**	**Before PivOD**	**After PivOD**
 **H-L$_1$**	6 d: 10% D	10 d: 20% D	3 h: 87% D	N.D.
 **H-L$_2$**	7 d: <2% D	14 d: <2% D	6 d: 20% D	13 d: 44% D
 **H-L$_{3a}$**	7 d: <2% D	14 d: <2% D	8 D: 62% D	N.D.
 **H-L$_4$**	7 d: <2% D	14 d: <2% D	3 d: <2% D	14 d: 22% D
 **H-L$_5$**	7 d: <2% D	14 d: <2% D	2 d: 10%D	4 d: 92% D
 **H-L$_6$**	7 d: <2% D	14 d: <2% D	4 d: <2% D	8 d: 53% D

[a]D: Deuteration; N.D.: Not determined.

4. Table S2: Summary of the ratios for the iridium competition experiments. Ratios in brackets for the competition experiments in d^4-MeOD.

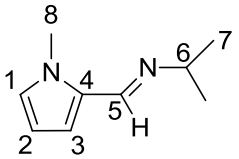
	 **H-L$_1$**	 **H-L$_2$**	 **H-L$_{3a}$**	 **H-L$_4$**	 **H-L$_5$**	 **H-L$_6$**	 Ar = 3,5-(Me)$_2$-C$_6$H$_3$ **H-L$_{3b}$**
 **H-L$_1$**		-	10 : 1	>20 : 1	8 : 1 (1.2 : 1)	1 : 2	-
 **H-L$_2$**	-		1 : 11 (1 : >20)	1.7 : 1	-	-	-
 **H-L$_{3a}$**	1 : 10	11 : 1 (>20 : 1)		>20 : 1	1 : 1.7	-	6 : 1 (3 : 1)
 **H-L$_4$**	1 : >20	1 : 1.7	1 : >20		-	-	-
 **H-L$_5$**	1 : 8 (1 : 1.2)	-	1.7 : 1	-		-	-
 **H-L$_6$**	2 : 1	-	-	-	-		-

5. Table S3: Summary of the ratios for the rhodium competition experiments. Top values in the cell indicate the ratio in the absence of PivOD. Bottom values indicate the ratio in the presence of PivOD.

	 **H-L$_1$**	 **H-L$_2$**	 **H-L$_{3a}$**	 **H-L$_4$**	 **H-L$_5$**	 **H-L$_6$**	 Ar = 3,5-(Me)$_2$-C$_6$H$_3$ **H-L$_{3b}$**
 **H-L$_1$**		1.5 : 1 to >20 : 1 0 : 0[a]	1 : >20 1 : >20	2 : 1	-	-	-
 **H-L$_2$**	1 : 1.5 to 1 : >20 0 : 0[a]		-	1 : 2.5	-	-	-
 **H-L$_{3a}$**	>20 : 1 >20 : 1	-		13 : 1 1 : 2	1 : 10 1 : >20	-	1 : 6 1 : >20
 **H-L$_4$**	1 : 2	2.5 : 1	1 : 13 2 : 1		1 : >20 1 : 10	-	-
 **H-L$_5$**	-	-	10 : 1 >20 : 1	>20 : 1 10 : 1		1 : >20 1 : >20	-
 **H-L$_6$**	-	-	-	-	>20 : 1 >20 : 1		-

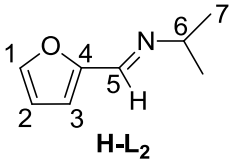
[a]After the addition of PivOD, neither **Rh-L$_1$** or **Rh-L$_2$** were present in the reaction solution of the competition reaction.

6. Analytical data of ligands and complexes.



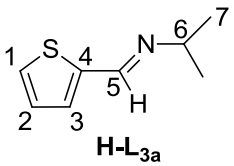
H-L$_1$

***N*-((1-methyl-1H-pyrrol-2-yl)methylene)propan-2-amine, H-L$_1$**. Brown oil, 2.55 g, 85% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (d, *J* = 6.3 Hz, 6H, H^7), 3.33 (septet, *J* = 6.3 Hz, 1H, H^6), 3.92 (s, 3H, H^8), 6.10-6.12 (m, 1H, H^2), 6.45 (dd, *J* = 3.7, 1.7 Hz, 1H, H^3), 6.66 (t, *J* = 1.9 Hz, 1H, H^1), 8.14 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.5 (C^7), 36.4 (C^8), 62.1 (C^6), 107.9 (C^2), 115.2 (C^3), 127.2 (C^1), 130.1 (C^4), 149.4 (C^5); HRMS for $C_9H_{15}N_2$ $[M+H]^+$: Calcd: 151.1235; Found: 151.1231.



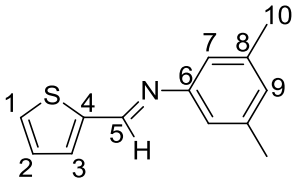
H-L$_2$

***N*-(furan-2-ylmethylene)propan-2-amine, H-L$_2$**. Black oil, 5.28 g, 77% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (d, *J* = 6.4 Hz, 6H, H^7), 3.48 (septet, *J* = 6.4 Hz, H^6), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H, H^2), 6.70 (d, *J* = 3.2 Hz, 1H, H^3), 7.50 (d, *J* = 1.8 Hz, 1H, H^1), 8.11 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2 (C^7), 61.7 (C^6), 111.5 (C^2), 113.5 (C^3), 144.5 (C^1), 147.1 (C^5), 151.6 (C^4); HRMS for $C_8H_{12}NO$ $[M+H]^+$: Calcd: 138.0919; Found: 138.0915.



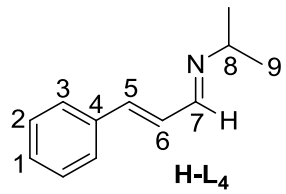
H-L$_{3a}$

***N*-(thiophen-2-ylmethylene)propan-2-amine**, **H-L$_{3a}$**.[4] Yellow oil, 6.50 g, 85% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (d, *J* = 6.3 Hz, 6H, H^7), 3.50 (septetd, *J* = 6.3, 1.0 Hz, 1H, H^6), 7.04 (dd, *J* = 5.0, 3.6 Hz, 1H, H^2), 7.27 (dd, *J* = 3.6, 1.0 Hz, 1H, H^3), 7.36 (dd, *J* = 5.0, 1.0 Hz, 1H, H^1). 8.38 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1 (C^7), 61.3 (C^6), 127.2 (C^3), 128.4 (C^4), 129.9 (C^2), 142.8 (C^1), 151.5 (C^5); HRMS for $C_8H_{12}NS$ $[M+H]^+$: Calcd: 154.0690; Found: 154.0695.



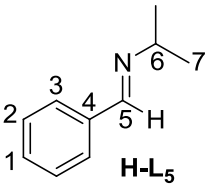
H-L$_{3b}$

3,5-Dimethyl-N-[thiophen-2-ylmethylidene]aniline, H-L$_{3b}$.[5] Orange solid, 9.7 g containing 7% of the corresponding aldehyde. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.31 (s, 6H, H^{10}), 6.83 (s, 2H, H^7), 6.84 (s, 1H, H^9), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H, H^2), 7.42 (dd, *J* = 3.6, 1.0 Hz, 1H, H^3), 7.44 (dd, *J* = 5.0, 1.0 Hz, 1H, H^1), 8.52 (d, *J* = 1.0 Hz, 1H, H^5);



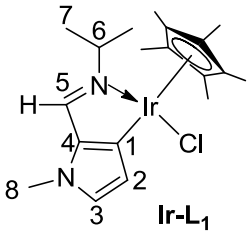
H-L$_4$

***N*-((*E*)-3-phenylallylidene)propan-2-amine, H-L$_4$**. Yellow oil, 8.1 g, 94% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.22 (d, *J* = 6.3 Hz, 6H, H^9), 3.40 (septet, *J* = 6.3 Hz, 1H, H^8), 6.90-6.91 (m, 2H, H^5 and H^6), 7.27-7.36 (m, 3H, H^1 and H^2), 7.45 (d, *J* = 7.7 Hz, 2H, H^3), 8.03 (t, *J* = 4.1 Hz, 1H, H^7); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.2 (C^9), 61.3 (C^8), 127.1 (C^3), 128.5 (C$^{5/6}$), 128.8 (C$^{1/2}$), 129.0 (C$^{1/2}$), 135.9 (C^4), 141.1 (C$^{5/6}$), 160.0 (C^7); HRMS for $C_{12}H_{16}N$ $[M+H]^+$: Calcd: 174.1283; Found: 174.1283.



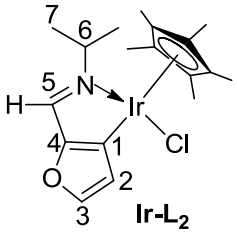
H-L$_5$

***N*-benzylidenepropan-2-amine, H-L$_5$.**[6] Colourless oil, 5.6 g, 76% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.27 (d, *J* = 6.4 Hz, 6H, H^7), 3.50 (septet, *J* = 6.4 Hz, 1H, H^6), 7.35-7.37 (m, 3H, H^1 and H$^{2/3}$), 7.70-7.72 (m, 2H, H$^{2/3}$), 8.26 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.1 (C^7), 61.7 (C^6), 128.1 (C$^{2/3}$), 128.5 (C$^{2/3}$), 130.4 (C^1), 136.5 (C^4), 158.4 (C^5); HRMS for $C_{10}H_{14}N$ $[M+H]^+$: Calcd: 148.1126; Found: 148.1124.



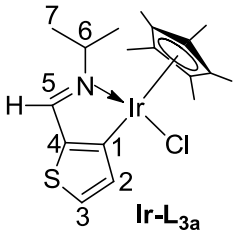
Ir-L$_1$

Dark red solid, 97 mg, 85% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.44 (d, *J* = 6.6 Hz, 3H, H^7), 1.46 (d, *J* = 6.6 Hz, 3H, $H^{7'}$), 1.74 (s, 15H, C_5Me_5), 3.74 (s, 3H, H^8), 4.16-4.24 (m, 1H, H^6), 6.32 (d, *J* = 2.2 Hz, 1H, H^2), 6.68 (d, *J* = 2.2 Hz, 1H, H^3), 7.90 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.4 (C_5Me_5), 23.7 (C^7), 24.4 ($C^{7'}$), 34.6 (C^8), 59.6 (C^6), 87.6 (C_5Me_5), 111.9 (C^2), 129.0 (C^3), 143.1 ($C^{1/4}$), 152.3 ($C^{1/4}$), 153.0 (C^5); MS (FAB): *m/z* 512 $[M]^+$, 477 $[M\text{-}Cl]^+$; HRMS for $C_{19}H_{28}{}^{191}IrN_2$ $[M\text{-}Cl]^+$: Calcd: 475.1859; Found: 475.1866.



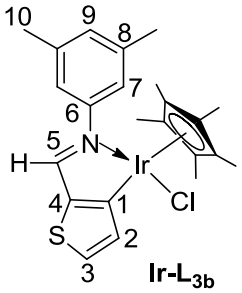
Ir-L$_2$

Black solid, 100 mg, 84% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.43 (d, *J* = 6.6 Hz, 3H, H^7), 1.47 (d, *J* = 6.6 Hz, 3H, $H^{7'}$), 1.75 (s, 15H, C_5Me_5), 4.22 (septet, *J* = 6.6 Hz, H^6), 6.73 (d, *J* = 1.6 Hz, 1H, H^2), 7.41 (d, *J* = 1.6 Hz, 1H, H^3), 8.12 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.4 (C_5Me_5), 23.6 (C^7), 24.2 ($C^{7'}$), 60.0 (C^6), 88.3 (C_5Me_5), 116.2 (C^2), 146.7 (C^3), 152.1 (C^4), 153.5 (C^5) (C^1 peak was not observed); MS (FAB): *m/z* 499 $[M]^+$, 464 $[M\text{-}Cl]^+$; HRMS for $C_{18}H_{25}{}^{191}IrNO$ $[M\text{-}Cl]^+$: Calcd: 462.1542; Found: 462.1534.



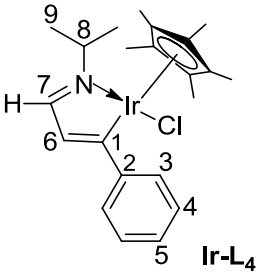
Ir-L$_{3a}$

Red solid. 350 mg, 85% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (d, *J* = 6.6 Hz, 3H, H^7), 1.51 (d, *J* = 6.6 Hz, 3H, $H^{7'}$), 1.74 (s, 15H, C_5Me_5), 4.26-4.32 (m, 1H, H^6), 7.25 (d, *J* = 4.7 Hz, 1H, H^2), 7.53 (d, *J* = 4.7 Hz, 1H, H^3), 8.24 (s, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.4 (C_5Me_5), 23.4 (C^7), 24.1 ($C^{7'}$), 60.4 (C^6), 88.6 (C_5Me_5), 132.4 (C^2), 133.5 (C^3), 140.2 (C^4), 161.5 (C^5) 173.7 (C^1); MS (FAB): *m/z* 515 $[M]^+$.



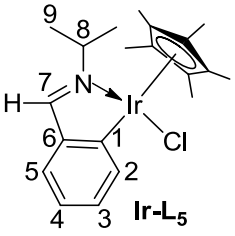
Ir-L$_{3b}$

Red solid, 90 mg, 88% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.53 (s, 15H, $C_5\mathit{Me}_5$), 2.35 (s, 6H, H^{10}), 6.89 (s, 1H, H^{9}), 7.17 (s, 2H, H^{7}), 7.34 (d, J = 5.0 Hz, 1H, H^{2}), 7.62 (d, J = 5.0 Hz, 1H, H^{3}), 8.14 (s, 1H, H^{5}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.0 ($C_5\mathit{Me}_5$), 21.3 (C^{10}), 89.1 (C_5Me_5), 120.3 (C^{7}), 128.2 (C^{9}), 132.8 (C^{2}), 135.6 (C^{3}), 138.5 (C^{8}), 141.3 (C^{4}), 151.6 (C^{6}), 165.1 (C^{5}), 177.9 (C^{1}); MS (FAB): *m/z* 577 $[M]^+$, 542 $[M\text{-}Cl]^+$. HRMS for $C_{23}H_{27}{}^{191}IrNS$ $[M\text{-}Cl]^+$: Calcd: 542.1493; Found: 542.1493.



Ir-L$_4$

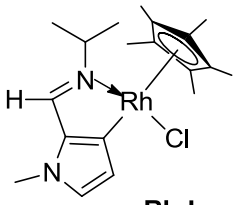
Red solid, 68 mg, 80% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (d, J = 7.0 Hz, 3H, H^{9}), 1.48 (s, 15H, $C_5\mathit{Me}_5$), 1.49 (d, J = 7.0 Hz, 3H, $H^{9'}$), 4.29 (septet, J = 7.0 Hz, 1H, H^{8}), 6.77 (d, J = 2.0 Hz, 1H, H^{6}), 7.17 (t, J = 7.5 Hz, 1H, H^{5}), 7.27 (t, J = 7.5 Hz, 2H, H^{4}), 7.42 (d, J = 7.5 Hz, 2H, H^{3}), 8.07 (s, 1H, H^{7}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.9 ($C_5\mathit{Me}_5$), 24.0 (C^{9}), 24.5 ($C^{9'}$), 59.7 (C^{8}), 90.2 (C_5Me_5), 126.4 (C^{3}), 126.7 (C^{5}), 127.3 (C^{4}), 129.6 (C^{6}), 149.4 (C^{2}), 169.6 (C^{7}), 201.4 (C^{1}); MS (FAB): 535 $[M]^+$, 500 $[M\text{-}Cl]^+$.



Ir-L$_5$

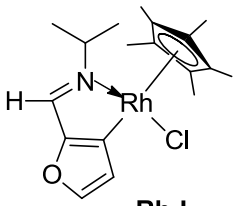
Red solid, 70 mg, 86% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.51 (d, J = 6.6 Hz, 3H, H^{9}), 1.52 (d, J = 6.6 Hz, 3H, $H^{9'}$), 1.71 (s, 15H, $C_5\mathit{Me}_5$), 4.31 (septetd, J = 6.6, 0.8 Hz, 1H, H^{8}), 6.97 (td, J = 7.4, 1.0 Hz, 1H, H^{4}), 7.14 (td, J = 7.4, 1.4 Hz, 1H, H^{3}), 7.51 (d, J = 7.5, 1.2 Hz, H^{5}), 7.74 (bd, J = 7.6 Hz, 1H, H^{2}), 8.40 (d, J = 0.5 Hz, 1H, H^{7}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.1 ($C_5\mathit{Me}_5$), 22.9 (C^{9}), 23.8 ($C^{9'}$), 60.8 (C^{8}), 88.7 (C_5Me_5), 121.7 (C^{4}), 128.1 (C^{5}),

131.3 (C^3), 134.5 (C^2), 147.1 (C^6), 167.6 (C^1), 171.0 (C^7); MS (FAB): *m/z* 509 $[M]^+$, 474 $[M\text{-}Cl]^+$; HRMS for $C_{20}H_{27}{}^{191}IrN$ $[M\text{-}Cl]^+$: Calcd: 472.1750; Found: 472.1738.



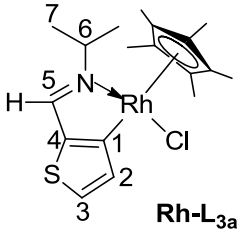
Rh-L$_1$

^{1}H NMR spectrum of crude reaction showed 41% conv. to **Rh-L$_1$**. Attempts to isolate this complex were unsuccessful. ^{1}H NMR (d^4-MeOD, 400 MHz) δ 1.26 (d, *J* = 6.4 Hz, 3H), 1.38 (d, *J* = 6.4 Hz, 3H), 1.60 (s, 15H), 3.67 (s, 3H), 4.08 (septet, *J* = 6.4 Hz, 1H), 6.36 (d, *J* = 2.2 Hz, 1H), 6.75 (d, *J* = 2.1 Hz, 1H), 8.06 (d, *J* = 4.1 Hz, 1H); MS (ES): *m/z* 387 $[M\text{-}Cl]^+$.



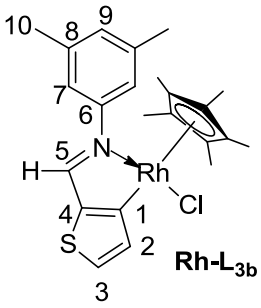
Rh-L$_2$

^{1}H NMR spectrum of crude reaction showed 16% conv. to **Rh-L$_2$**. Attempts to isolate this complex were unsuccessful. ^{1}H NMR (d^4-MeOD, 400 MHz) δ 1.32 (d, *J* = 6.6 Hz, 3H), 1.35 (d, *J* = 6.6 Hz, 3H), 1.59 (s, 15H), 4.16 (septet, *J* = 6.6 Hz, 1H), 6.77 (d, *J* = 1.6 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 8.09 (d, *J* = 4.1 Hz, 1H); MS (ES): *m/z* 374 $[M\text{-}Cl]^+$, 415 $[M\text{-}Cl+MeCN]^+$.



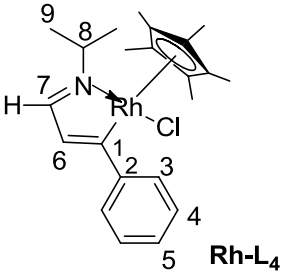
Rh-L$_{3a}$

Red solid, 68 mg, 59% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.49 (d, *J* = 6.6 Hz, 3H, H^7), 1.52 (d, *J* = 6.6 Hz, 3H, $H^{7'}$), 1.69 (s, 15H, C_5Me_5), 4.26-4.32 (m, 1H, H^6), 7.40 (d, *J* = 4.8 Hz, 1H, H^2), 7.56 (d, *J* = 4.8 Hz, 1H, H^3), 8.09 (d, *J* = 3.2 Hz, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.5 (C_5Me_5), 22.8 (C^7), 24.4 ($C^{7'}$), 58.6 (C^6), 95.6 (d, *J* = 6.0 Hz, C_5Me_5), 131.3 (C^3), 133.2 (C^2), 136.1 (C^4), 159.8 (C^5), 186.7 (d, *J* = 35.2 Hz, C^1); HRMS for $C_{20}H_{28}RhN_2S$ $[M\text{-}Cl+MeCN]^+$: Calcd: 431.1028; Found: 431.1042



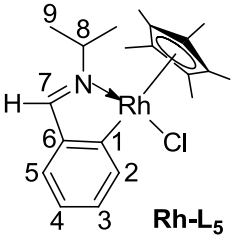
Rh-L$_{3b}$

Orange solid, 31 mg, 40% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 15H, $C_5\mathit{Me}_5$), 2.23 (s, 6H, H^{10}), 6.83 (s, 1H, H^9), 7.15 (s, 2H, H^7), 7.42 (d, J = 4.7 Hz, 1H, H^2), 7.59 (d, J = 4.7 Hz, 1H, H^3), 8.01 (d, J = 3.6 Hz, 1H, H^5); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 8.1 ($C_5\mathit{Me}_5$), 20.3 (C^{10}), 95.0 (d, J = 6.3 Hz, C_5Me_5), 118.9 (C^7), 127.2 (C^9), 132.2 (C^3), 132.5 (C^2), 136.7 (C^4), 137.6 (C^8), 149.7 (C^4), 161.4 (C^5), 189.5 (d, J = 37.0 Hz, C^1); MS (FAB): *m/z* 487 $[M]^+$, 452 $[M\text{-}Cl]^+$; HRMS for $C_{23}H_{27}RhNS$ $[M\text{-}Cl]^+$: Calcd: 452.0919; Found: 452.0900.



Rh-L$_4$

Red solid, 20 mg, 28% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 15H, $C_5\mathit{Me}_5$), 1.44 (d, J = 6.6 Hz, 3H, H^9), 1.49 (d, J = 6.6 Hz, 3H, $H^{9'}$), 4.26 (septet, J = 6.6 Hz, 1H, H^8), 6.41 (d, J = 1.7 Hz, 1H, H^6), 7.18-7.22 (m, 1H, H^5), 7.27-7.30 (m, 2H, H^4), 7.49-7.51 (m, 2H, H^3), 7.88 (dt, J= 3.9, 1.4 Hz, 1H, H^7); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 9.0 ($C_5\mathit{Me}_5$), 23.4 (C^9), 24.8 ($C^{9'}$), 58.3 (C^8), 96.7 (d, J = 5.5 Hz, C_5Me_5), 126.1 (C^3), 126.8 (C^5), 127.3 (C^4), 128.1 (C^2), 148.7 (C^2), 166.7 (C^7), 216.0 (d, J = 31.4 Hz, C^1); HRMS for $C_{22}H_{29}RhN$ $[M\text{-}Cl]^+$: Calcd: 410.1355; Found: 410.1373.

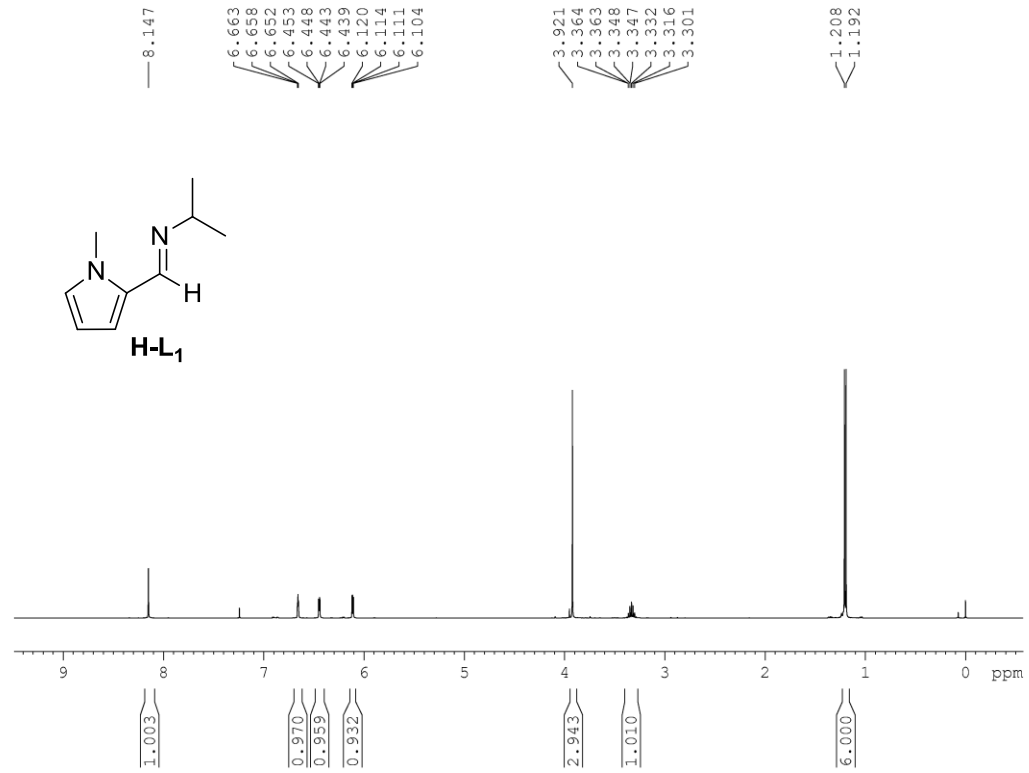


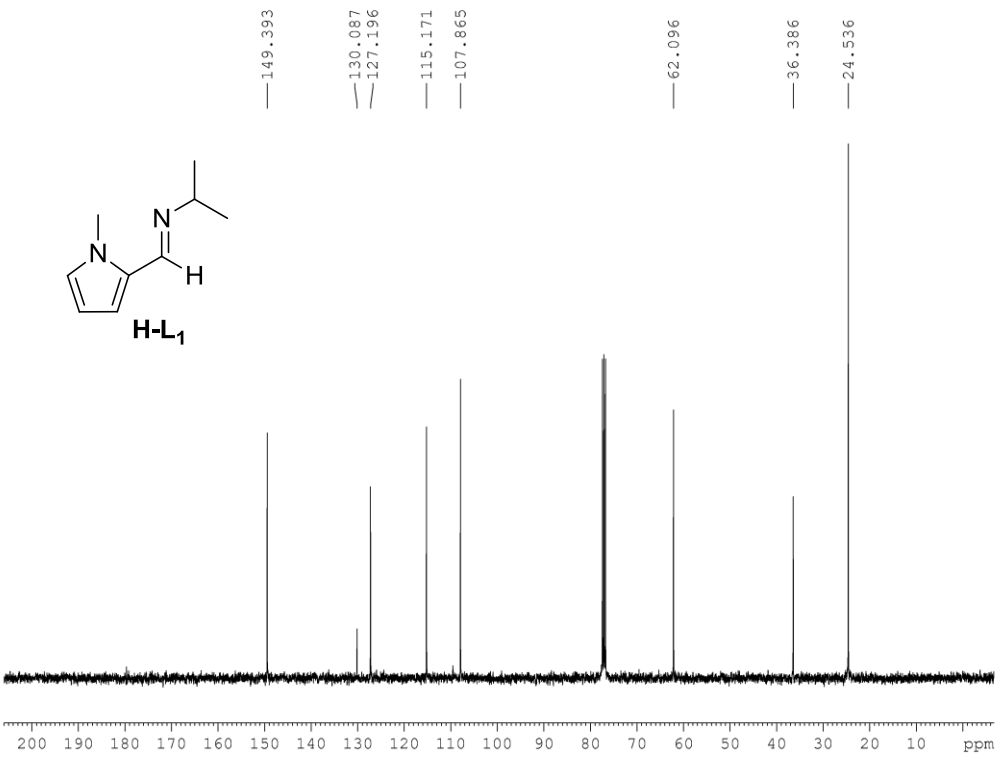
Rh-L$_5$

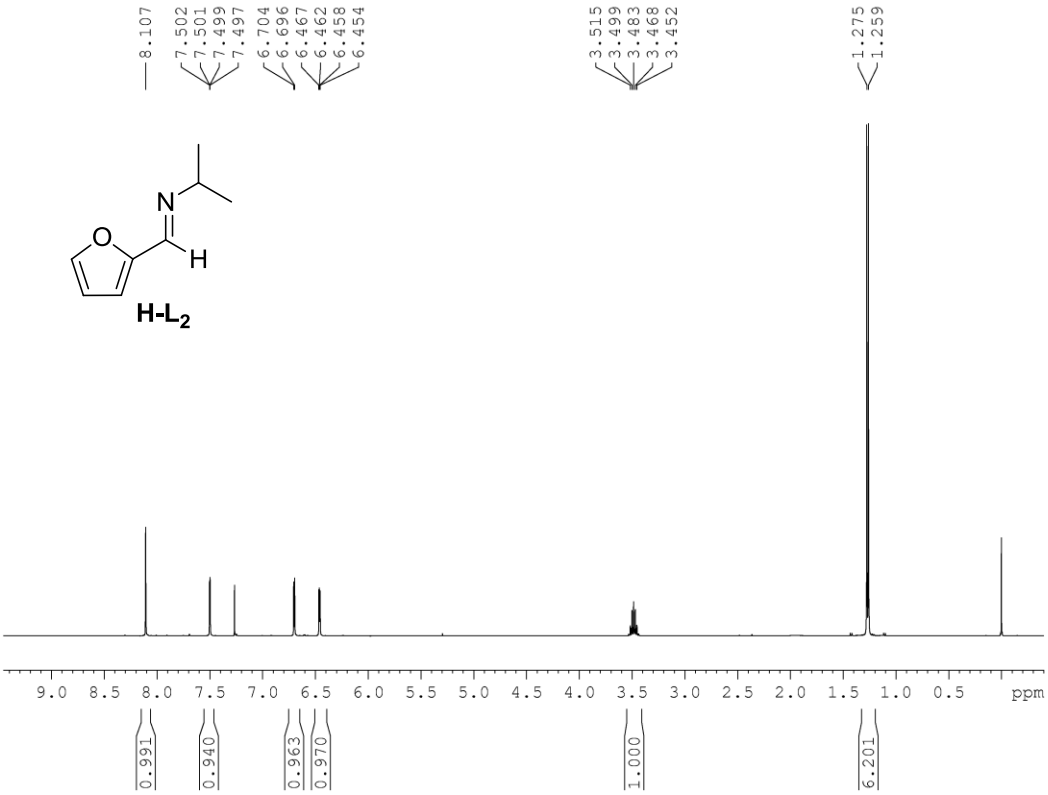
Orange solid, 51 mg, 76% isolated yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (d, J = 6.6 Hz, 3H, H^9), 1.54 (d, J = 6.6 Hz, 3H, $H^{9'}$), 1.66 (s, 15H, $C_5\mathit{Me}_5$), 4.29 (septetd, J = 6.6, 1.0 Hz, 1H, H^8), 7.00 (td, J = 7.4, 1.0 Hz, 1H, H^4), 7.20 (td, J = 7.4, 1.4 Hz, 1H, H^3), 7.40 (dd, J =

7.4, 1.4 Hz, H^5), 7.76 (d, *J* = 7.4 Hz, 1H, H^2), 8.16 (dd, *J* = 4.1, 1.0 Hz, 1H, H^7); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 9.3 (C_5Me_5), 22.3 (C^9), 24.1 ($C^{9'}$), 58.9 (C^8), 95.8 (d, *J* = 6.0 Hz, C_5Me_5), 122.3 (C^4), 128.0 (C^5), 130.5 (C^3), 135.9 (C^2), 146.0 (C^6), 168.5 (C^7), 183.3 (d, *J* = 32.0 Hz, C^1); HRMS for $C_{20}H_{28}ClRhN$ $[M+H]^+$: Calcd: 420.0965; Found: 420.0970.

7. ^{1}H and ^{13}C NMR spectra.



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3.468
3.452
1.275
1.259
N
O
H
H-L2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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0.940
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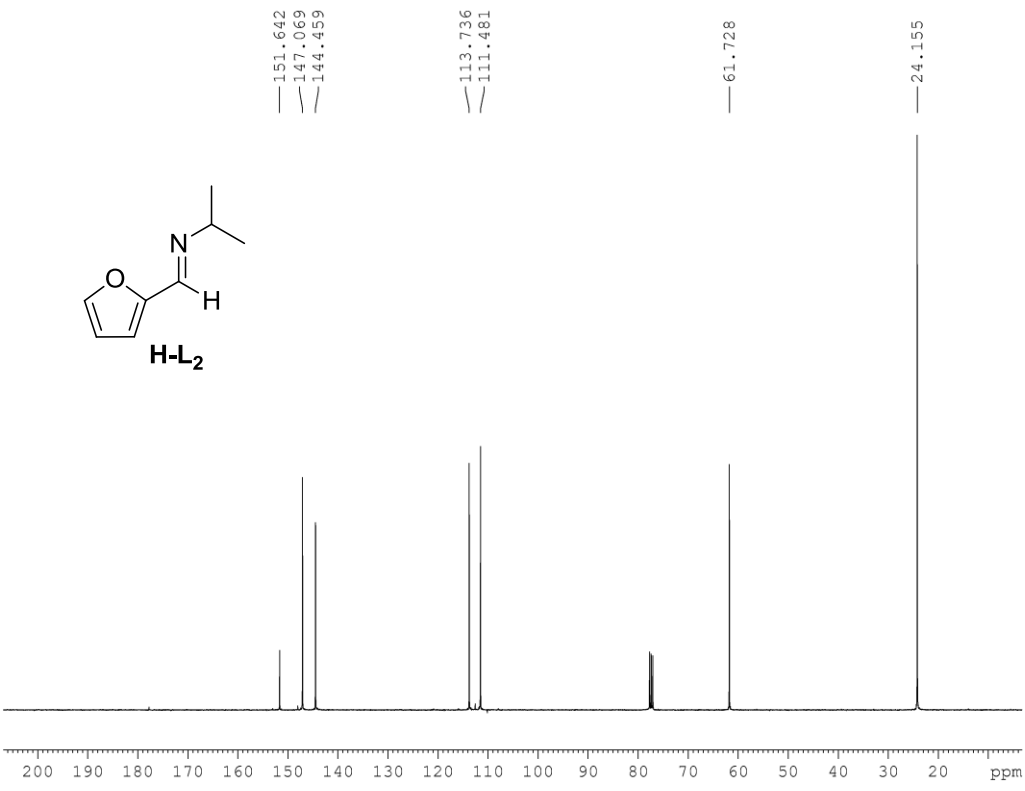
0.970
1.000
6.201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H-L2
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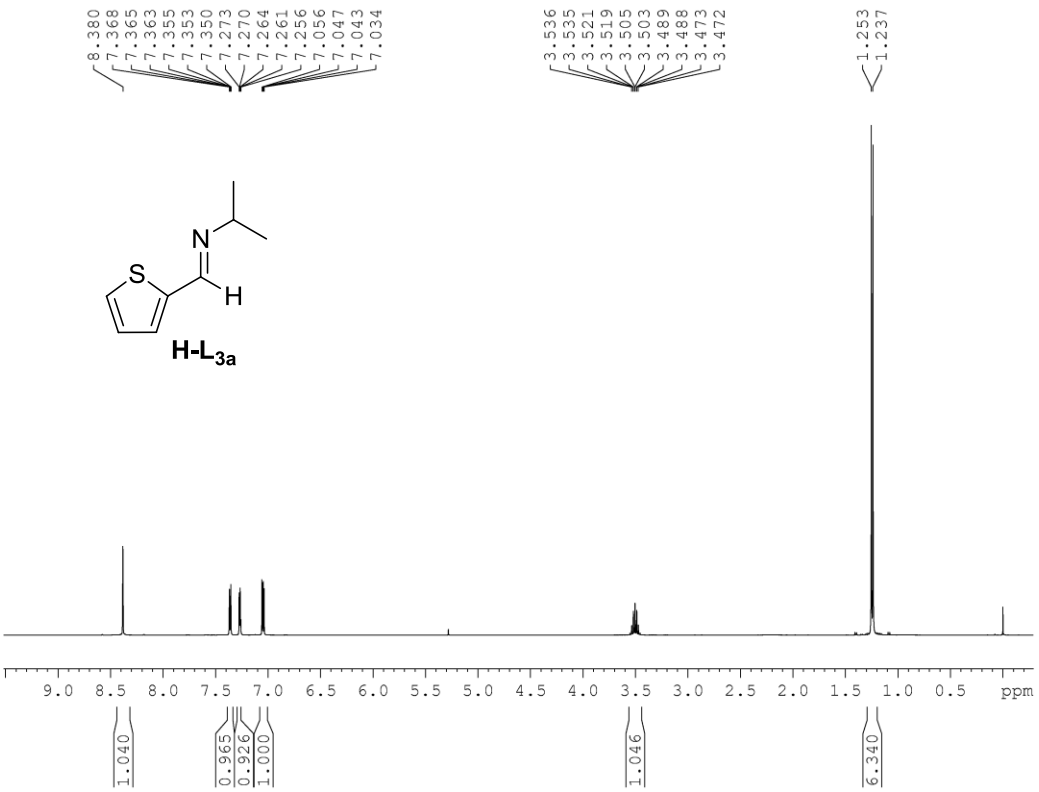
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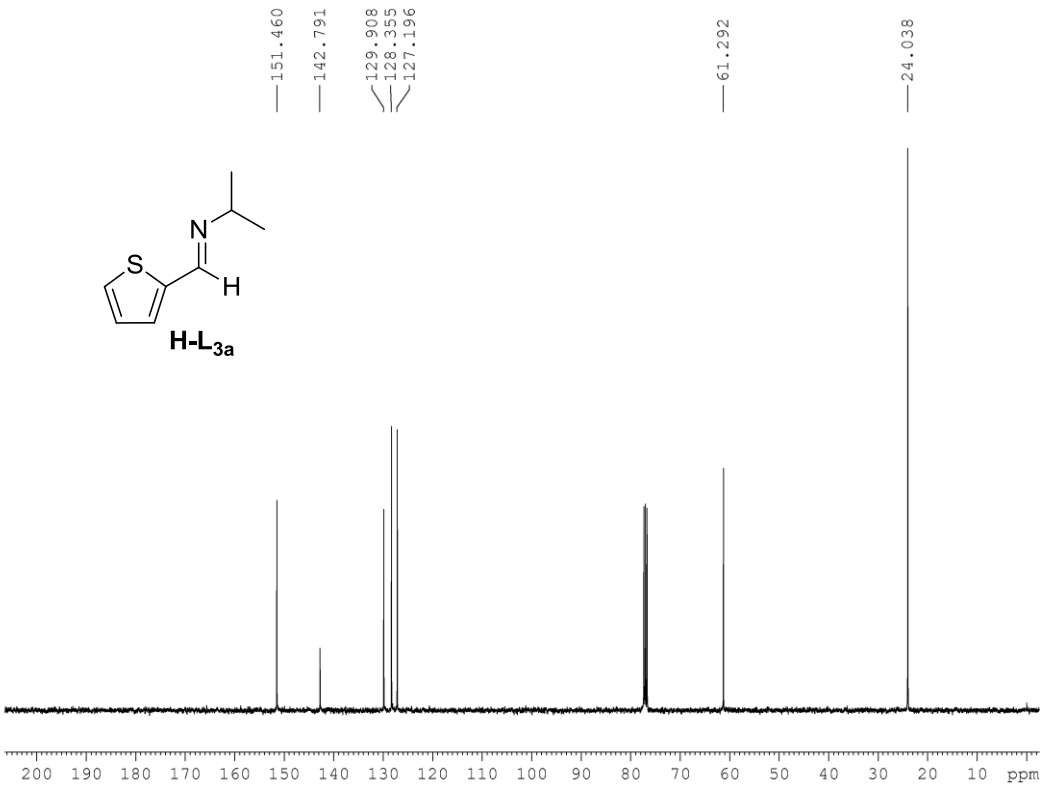
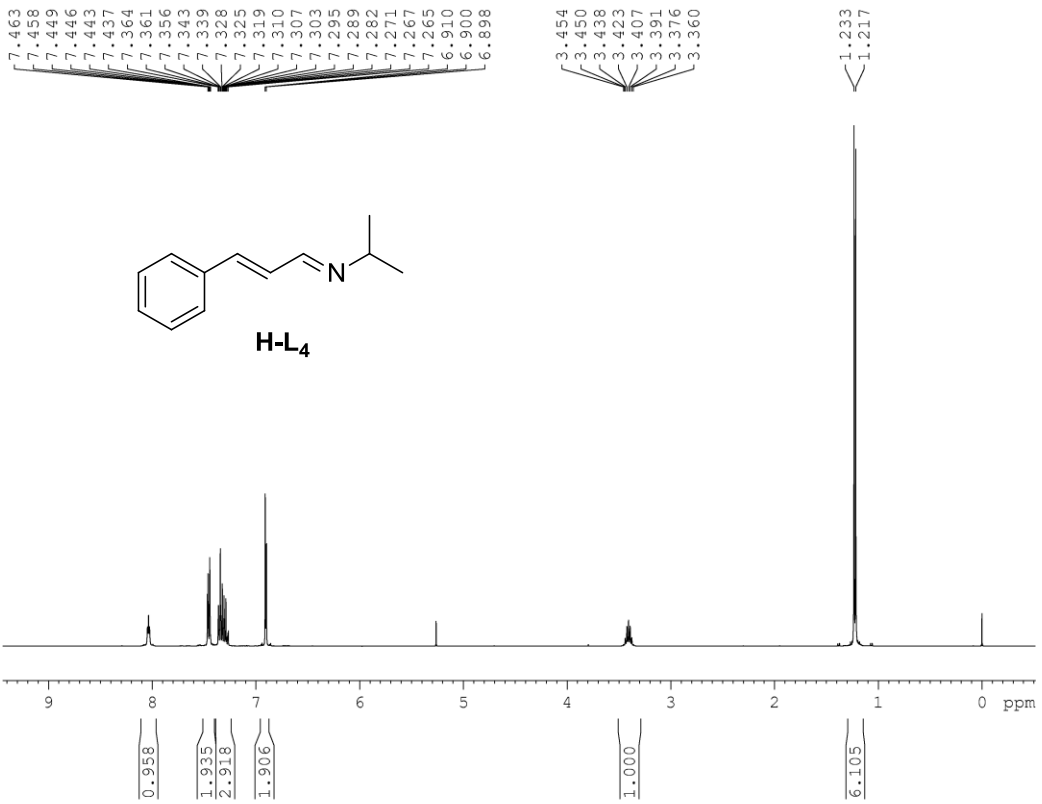
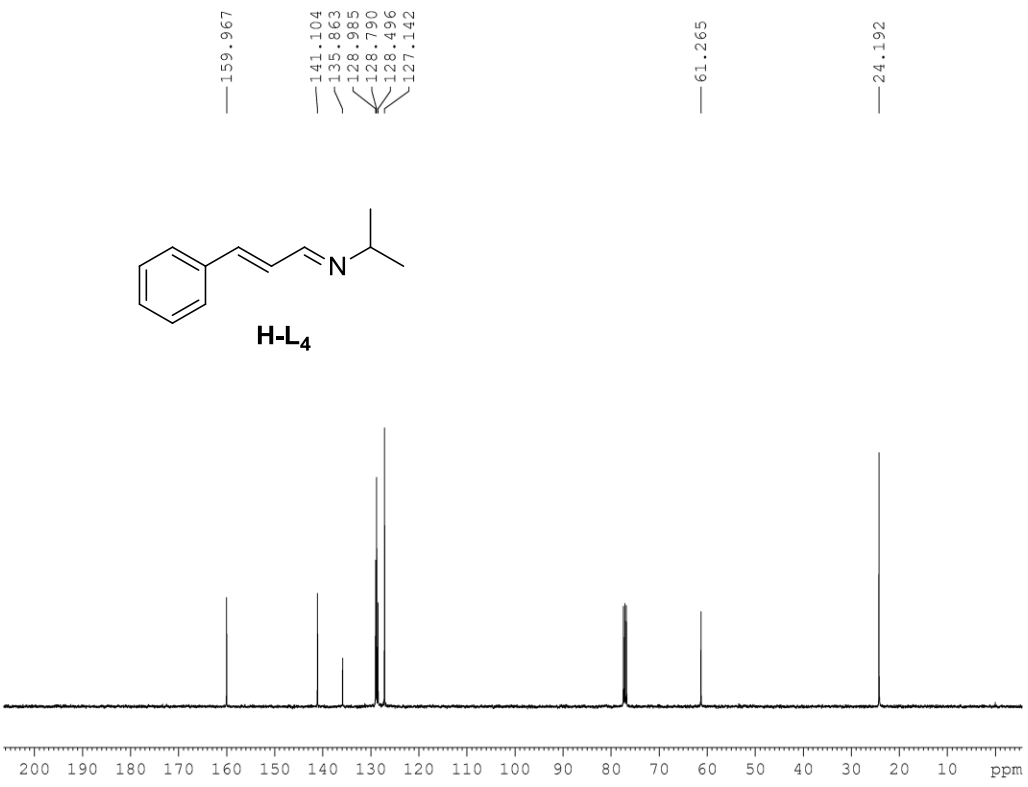
7.355
7.353
7.350
7.273
7.270
7.264
7.261
7.256
7.056
7.047
7.043
7.034
3.536
3.535
3.521
3.519
3.505
3.503
3.489
3.488
3.473
3.472
1.253
1.237
N
S
H
H-L3a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.040
0.965
0.926
1.000
1.046
6.340

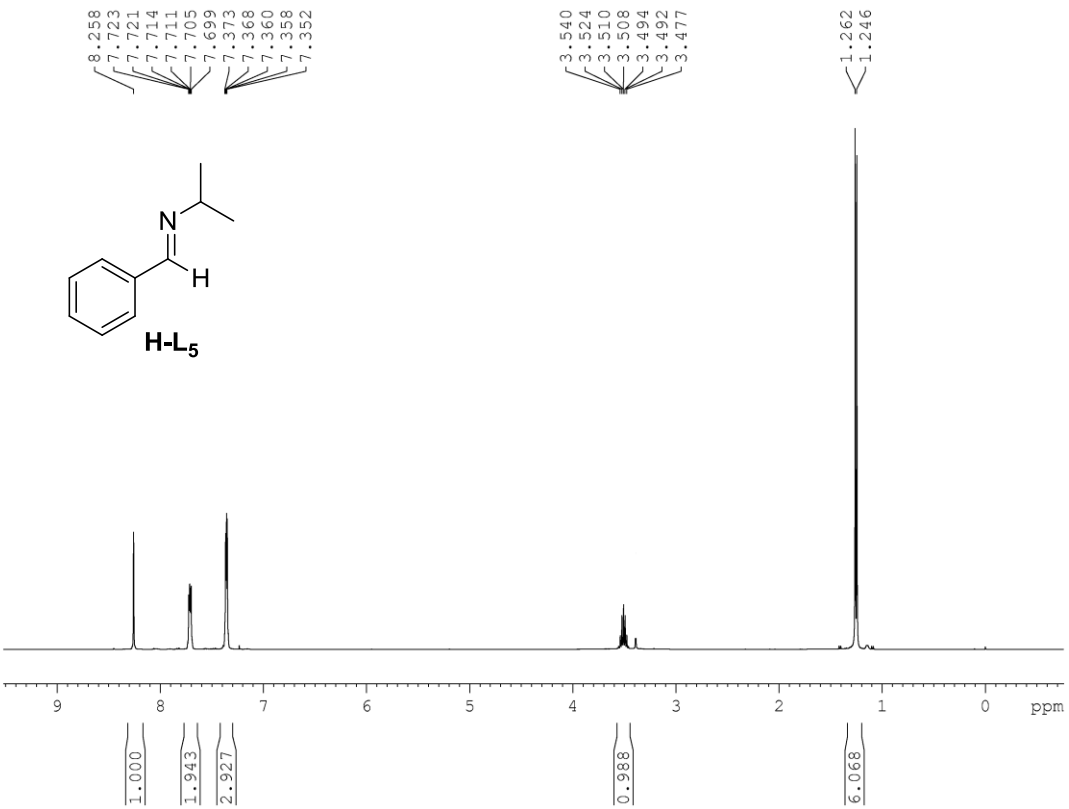

151.460
142.791
129.908
128.355
127.196
61.292
24.038
N
S
H
H-L3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

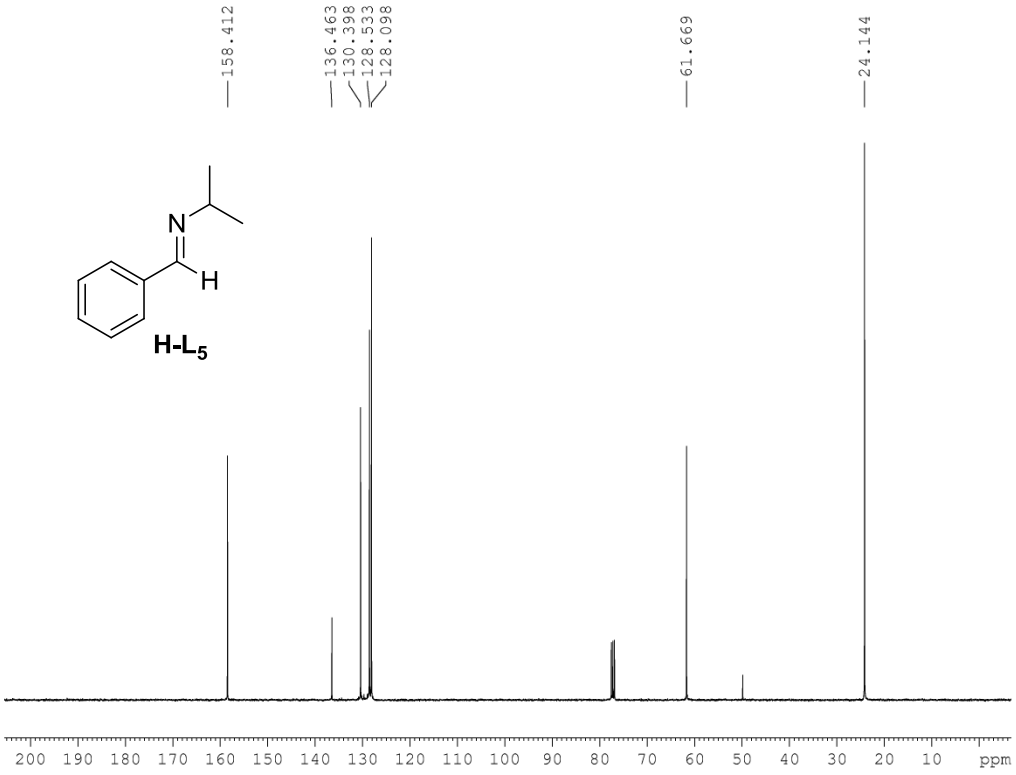

7.463
7.458
7.449
7.446
7.443
7.437
7.364
7.361
7.356
7.343
7.339
7.328
7.325
7.319
7.310
7.307
7.303
7.295
7.289
7.282
7.271
7.267
7.265
6.910
6.900
6.898
3.454
3.450
3.438
3.423
3.407
3.391
3.376
3.360
1.233
1.217
N
9
8
7
6
5
4
3
2
1
0 ppm
0.958
1.935
2.918
1.906
1.000
6.105

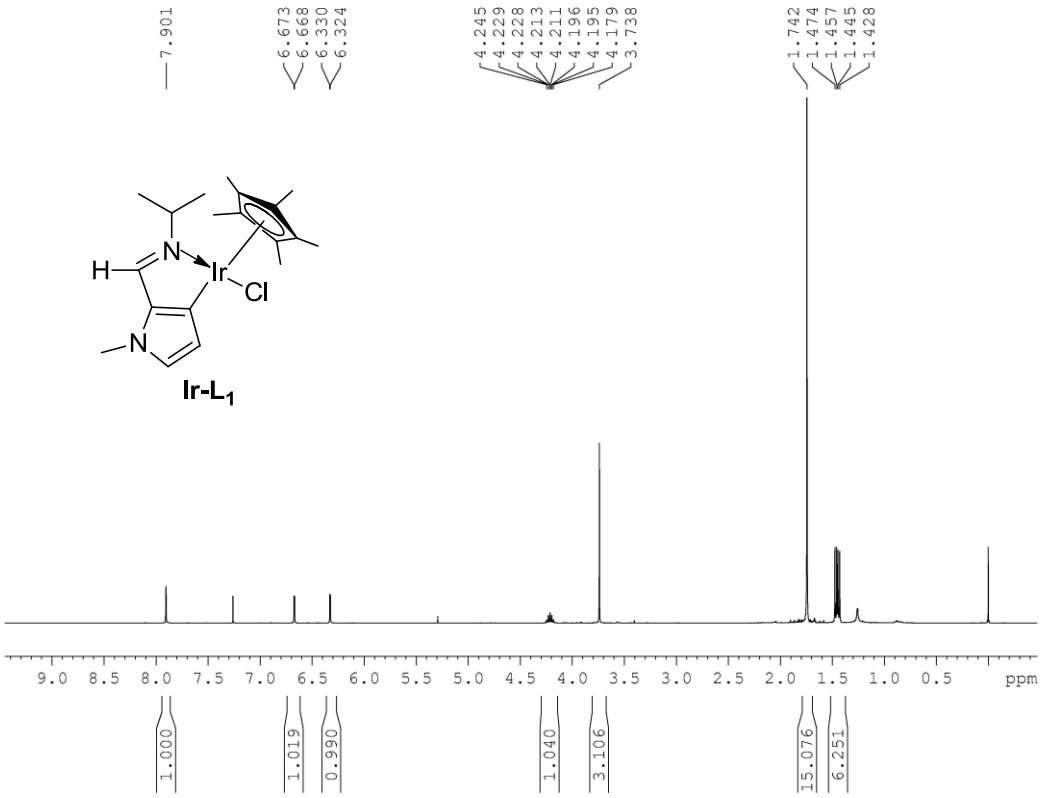
H-L$_4$

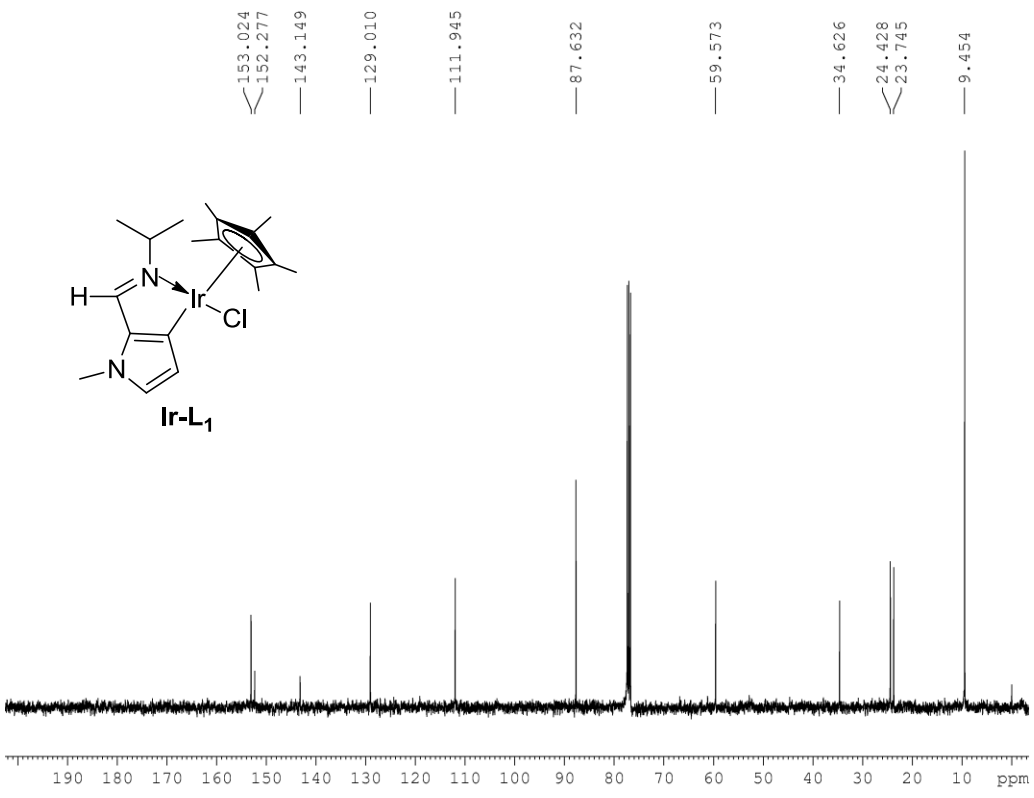

159.967
141.104
135.863
128.985
128.790
128.496
127.142
61.265
24.192
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

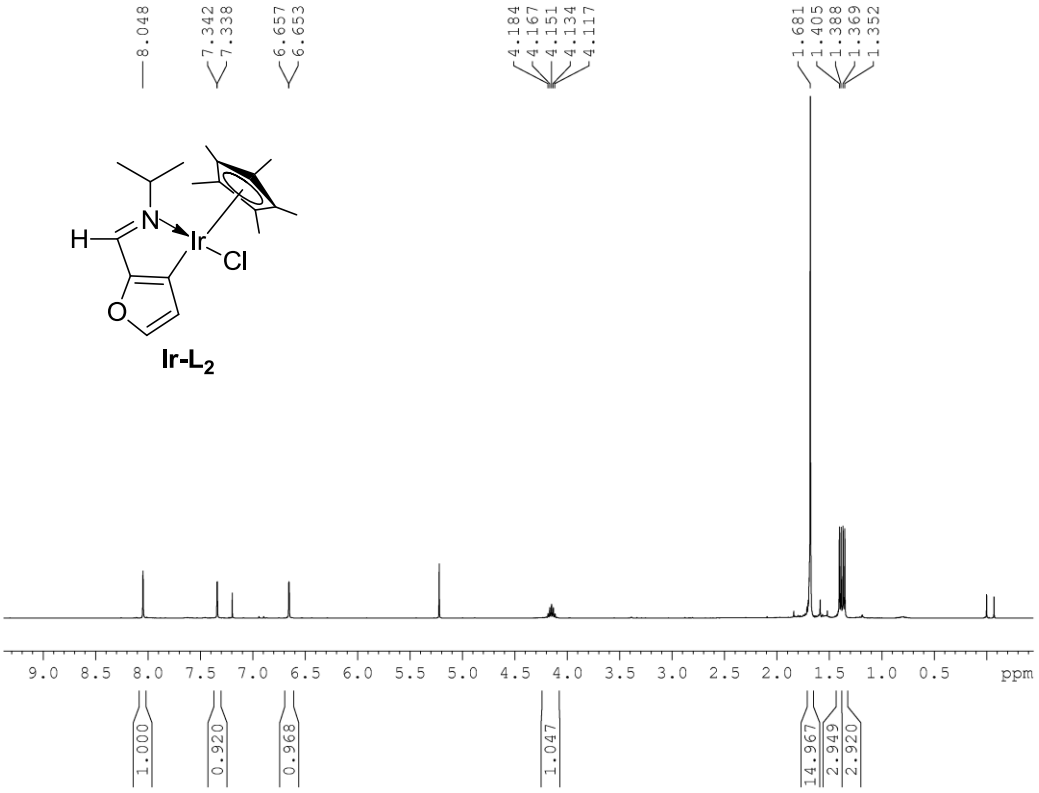
H-L$_4$

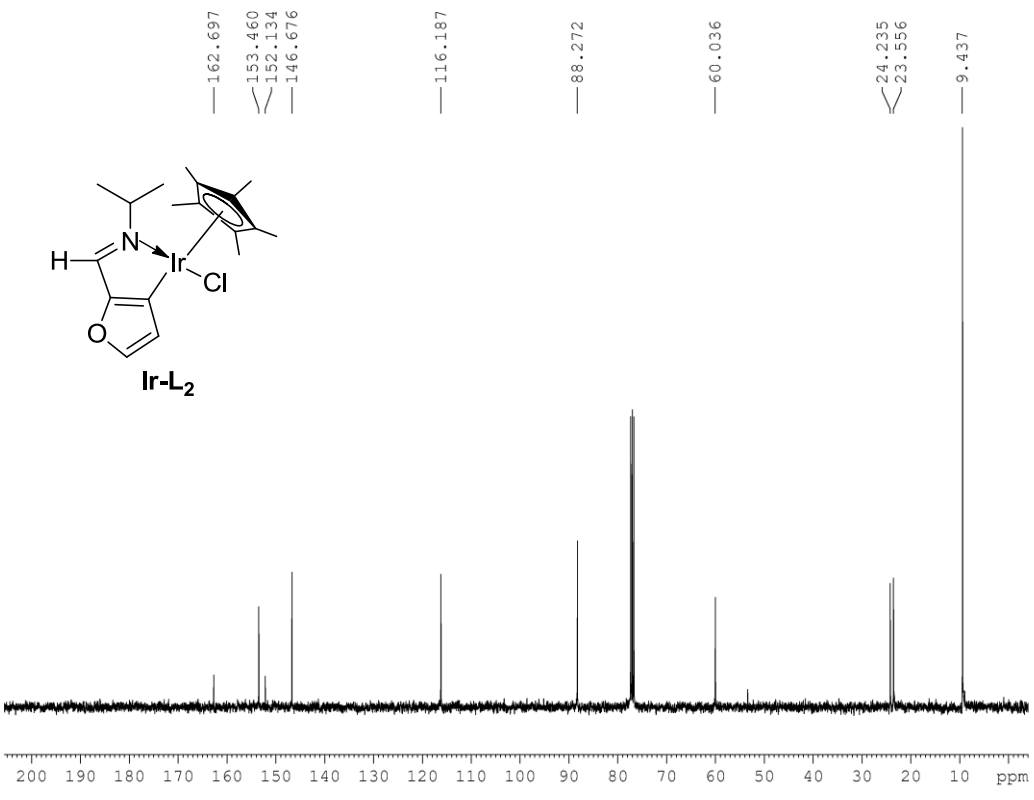

8.258
7.723
7.721
7.714
7.711
7.705
7.699
7.373
7.368
7.360
7.358
7.352
3.540
3.524
3.510
3.508
3.494
3.492
3.477
1.262
1.246
N
H
H-L5
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.943
2.927
0.988
6.068

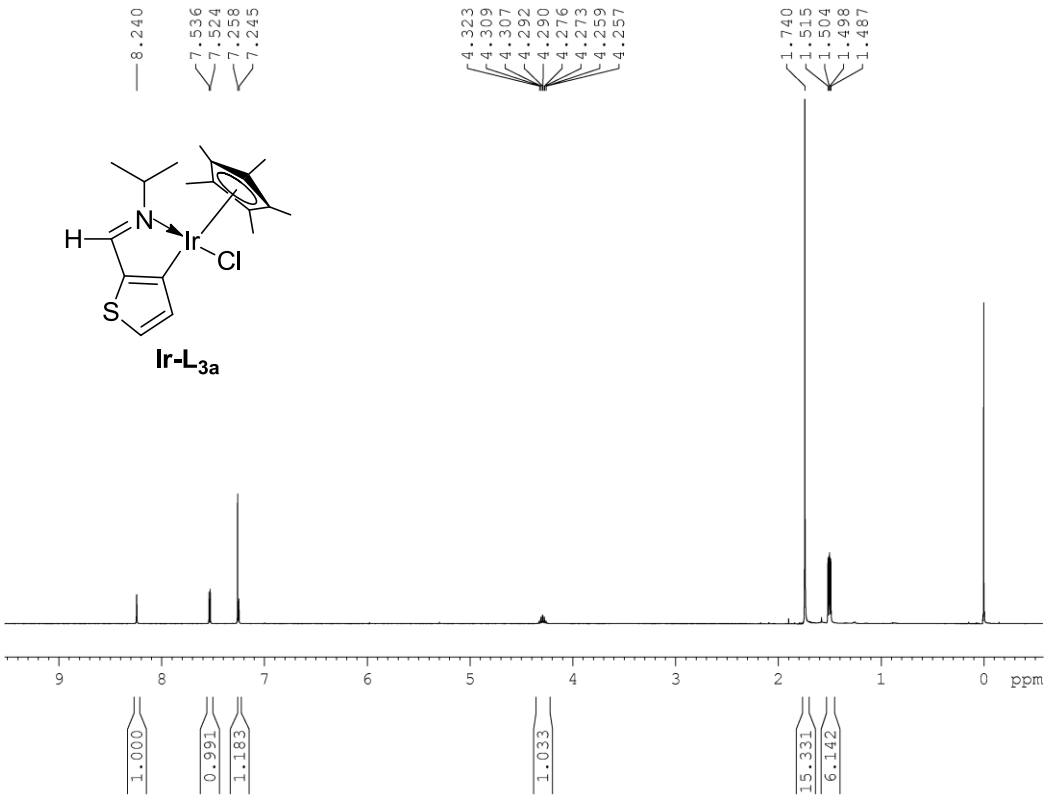

158.412
136.463
130.398
128.533
128.098
61.669
24.144
N
H
H-L5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

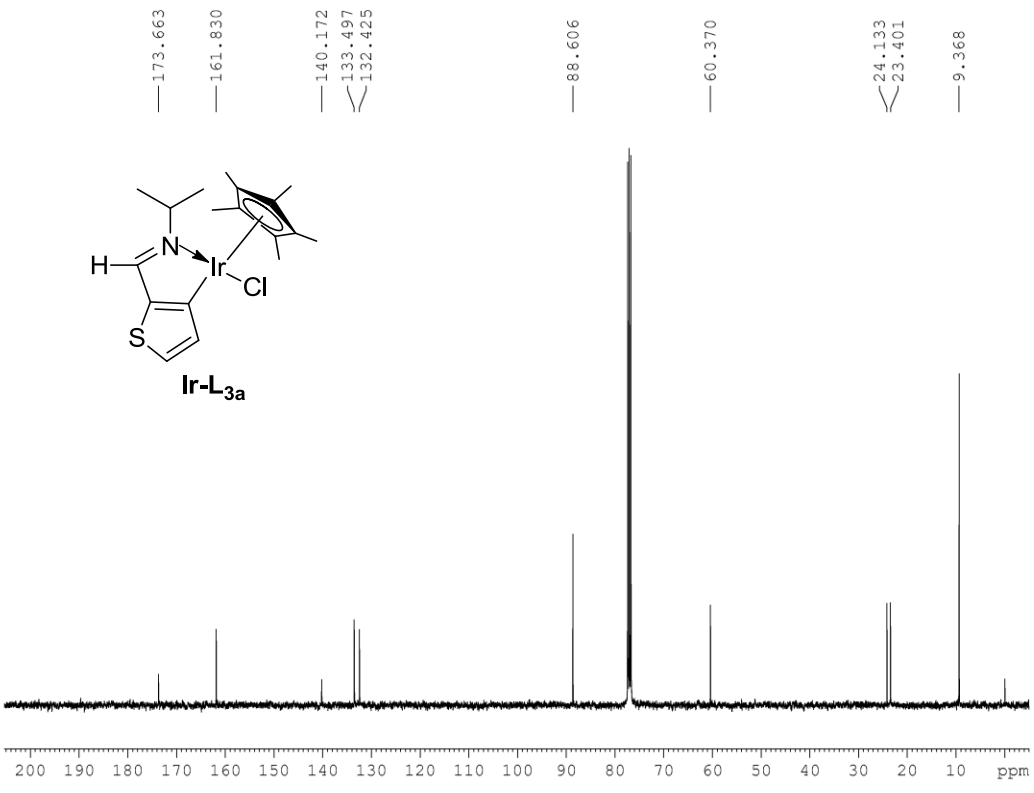

7.901
6.673
6.668
6.330
6.324
4.245
4.229
4.228
4.213
4.211
4.196
4.195
4.179
3.738
1.742
1.474
1.457
1.445
1.428
N
H
Ir
Cl
N
Ir-L1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.019
0.990
1.040
3.106
15.076
6.251


153.024
152.277
143.149
129.010
111.945
87.632
59.573
34.626
24.428
23.745
9.454
N
H
Ir
Cl
N
Ir-L1
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

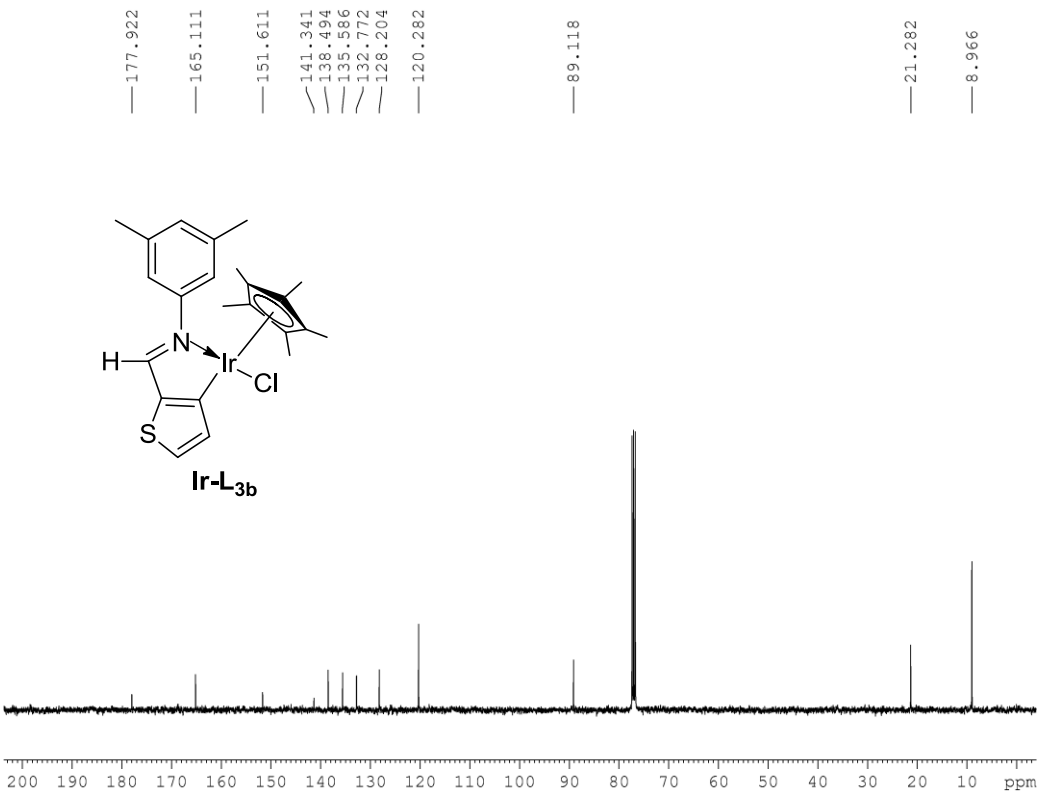

8.048
7.342
7.338
6.657
6.653
4.184
4.167
4.151
4.134
4.117
1.681
1.405
1.388
1.369
1.352
N
H
Ir
Cl
O
Ir-L2
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.920
0.968
1.047
14.967
2.949
2.920

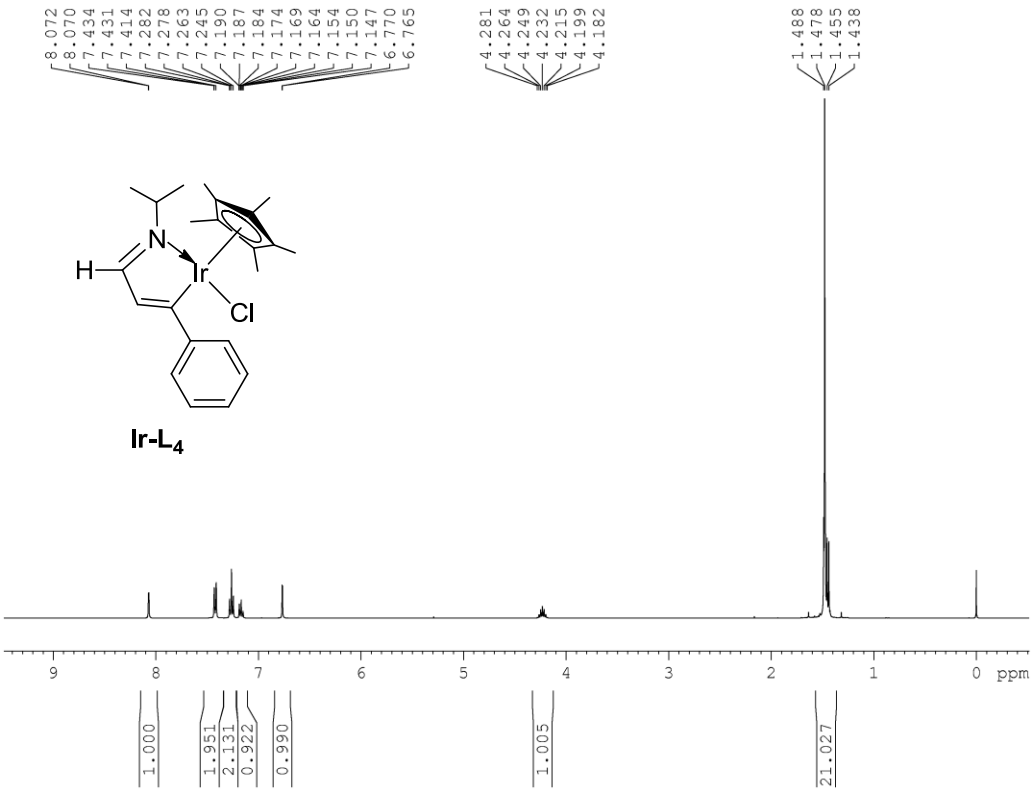

162.697
153.460
152.134
146.676
116.187
88.272
60.036
24.235
23.556
9.437
N
H
Ir
Cl
O
Ir-L2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.240
7.536
7.524
7.258
7.245
4.323
4.309
4.307
4.292
4.290
4.276
4.273
4.259
4.257
1.740
1.515
1.504
1.498
1.487
N
H
Ir
Cl
S
Ir-L3a
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.991
1.183
1.033
15.331
6.142

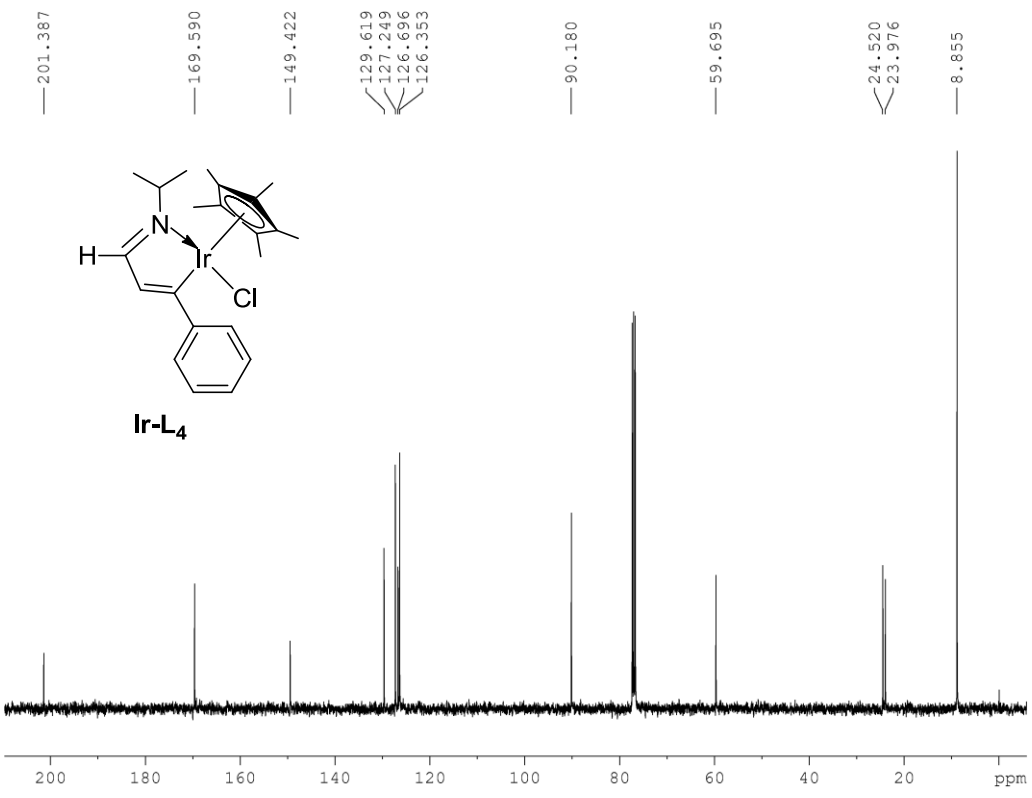

173.663
161.830
140.172
133.497
132.425
88.606
60.370
24.133
23.401
9.368
N
H
Ir
Cl
S
Ir-L3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.143
7.631
7.619
7.352
7.340
7.172
6.888
2.350
1.530
N
H
Ir
Cl
S
Ir-L3b
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.983
0.991
2.007
0.980
6.256
15.649

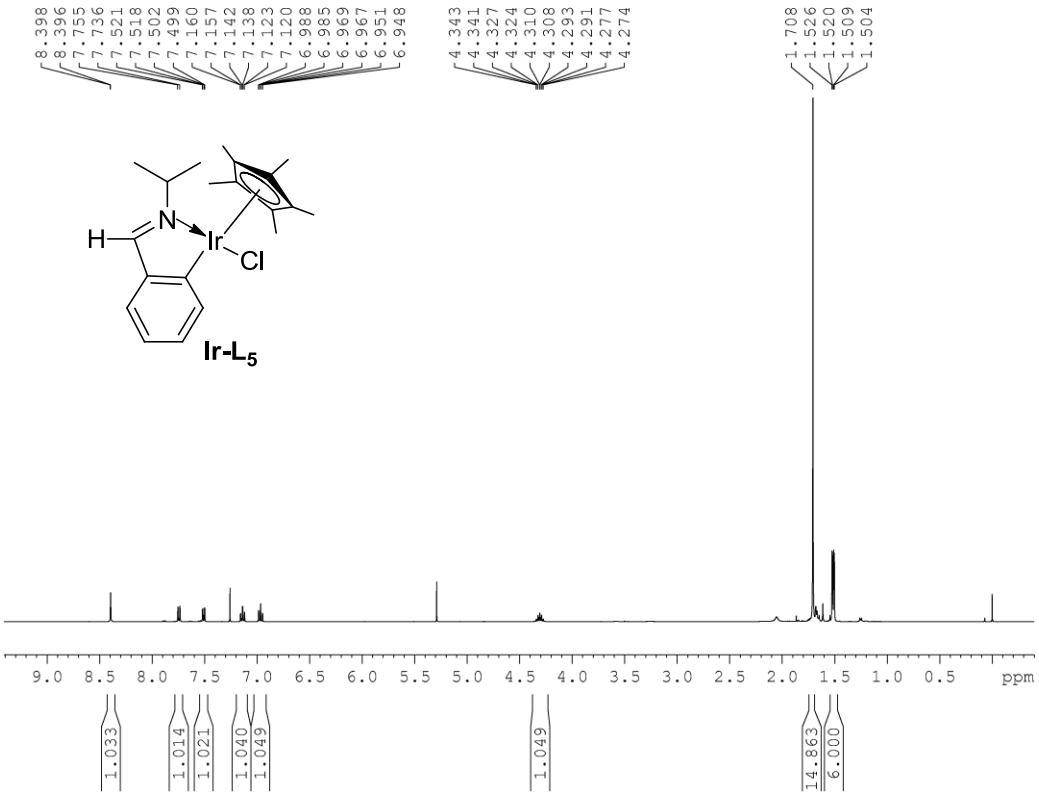

177.922
165.111
151.611
141.341
138.494
135.586
132.772
128.204
120.282
89.118
21.282
8.966
N
H
Ir
Cl
S
Ir-L3b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

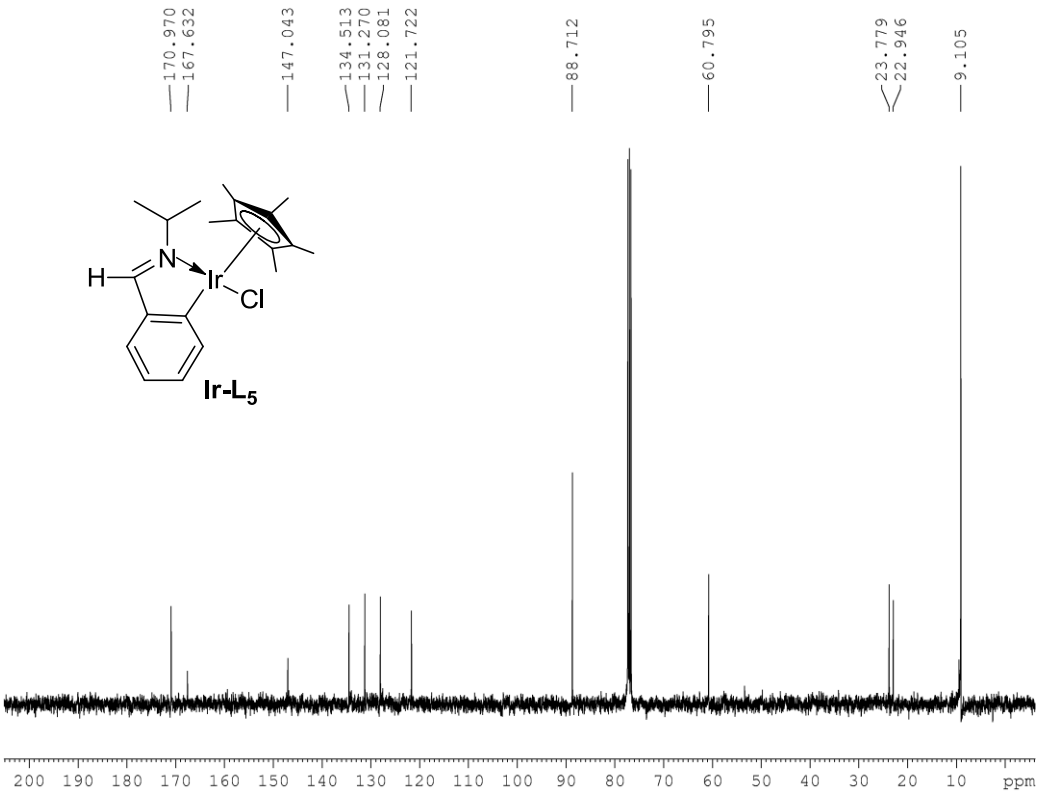

8.072
8.070
7.434
7.431
7.414
7.282
7.278
7.263
7.245
7.190
7.187
7.184
7.174
7.169
7.164
7.154
7.150
7.147
6.770
6.765
4.281
4.264
4.249
4.232
4.215
4.199
4.182
1.488
1.478
1.455
1.438
N
H
Ir
Cl
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.951
2.131
0.922
0.990
1.005
21.027

Ir-L$_4$

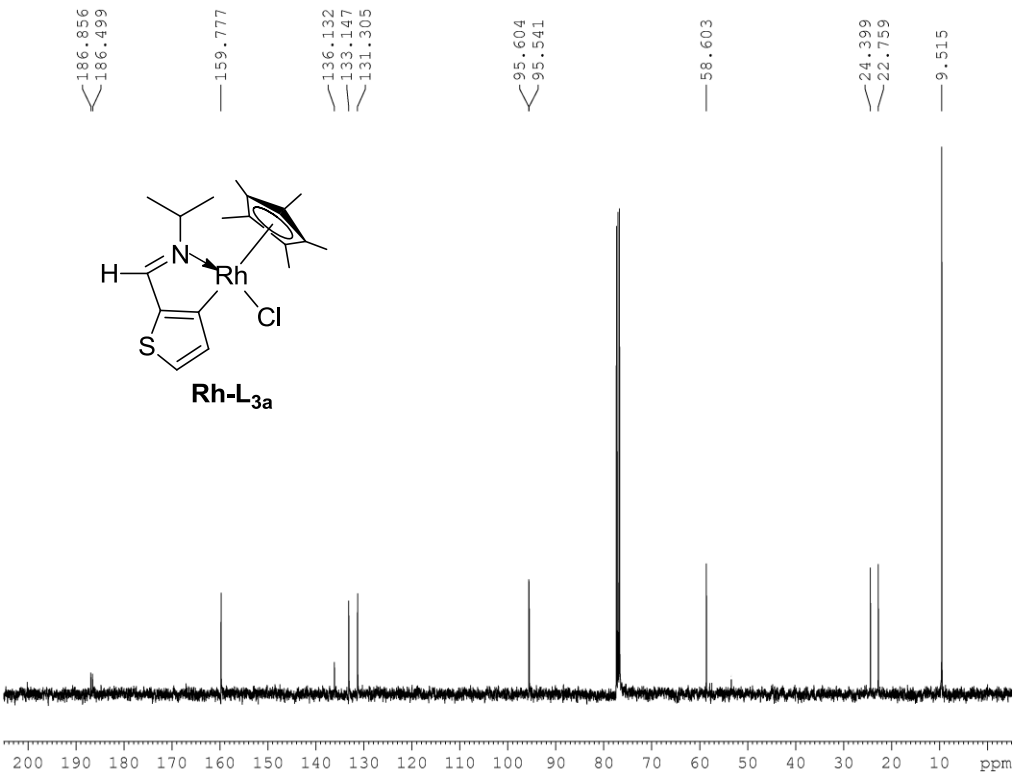

201.387
169.590
149.422
129.619
127.249
126.696
126.353
90.180
59.695
24.520
23.976
8.855
N
H
Ir
Cl
200
180
160
140
120
100
80
60
40
20
ppm

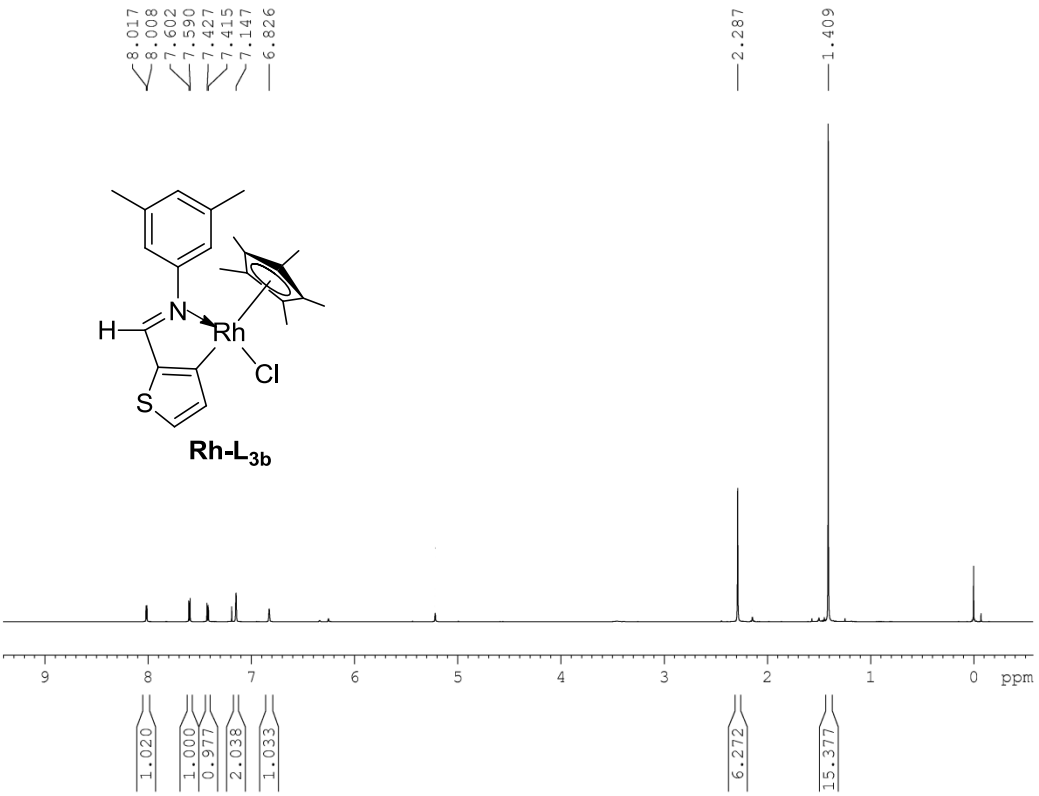
Ir-L$_4$

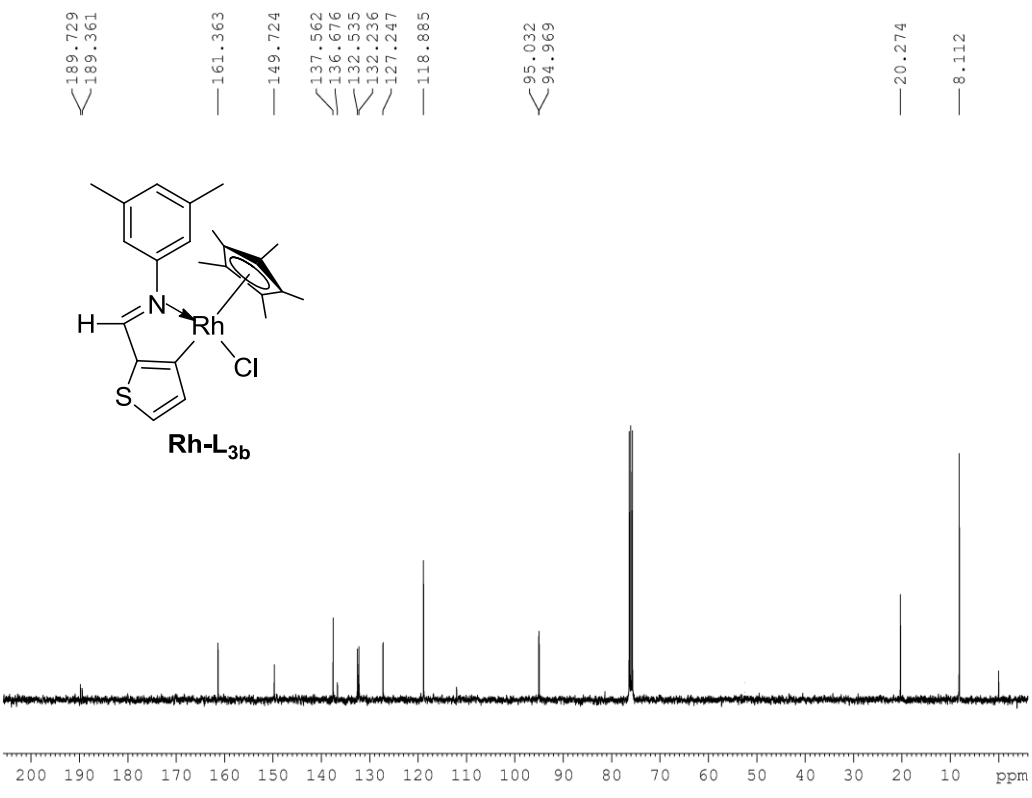

8.398
8.396
7.755
7.736
7.521
7.518
7.502
7.499
7.160
7.157
7.142
7.138
7.123
7.120
6.988
6.985
6.969
6.967
6.951
6.948
4.343
4.341
4.327
4.324
4.310
4.308
4.293
4.291
4.277
4.274
1.708
1.526
1.520
1.509
1.504
N
H
Ir
Cl
Ir-L5
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.033
1.014
1.021
1.040
1.049
1.049
14.863
6.000


170.970
167.632
147.043
134.513
131.270
128.081
121.722
88.712
60.795
23.779
22.946
9.105
N
H
Ir
Cl
Ir-L5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

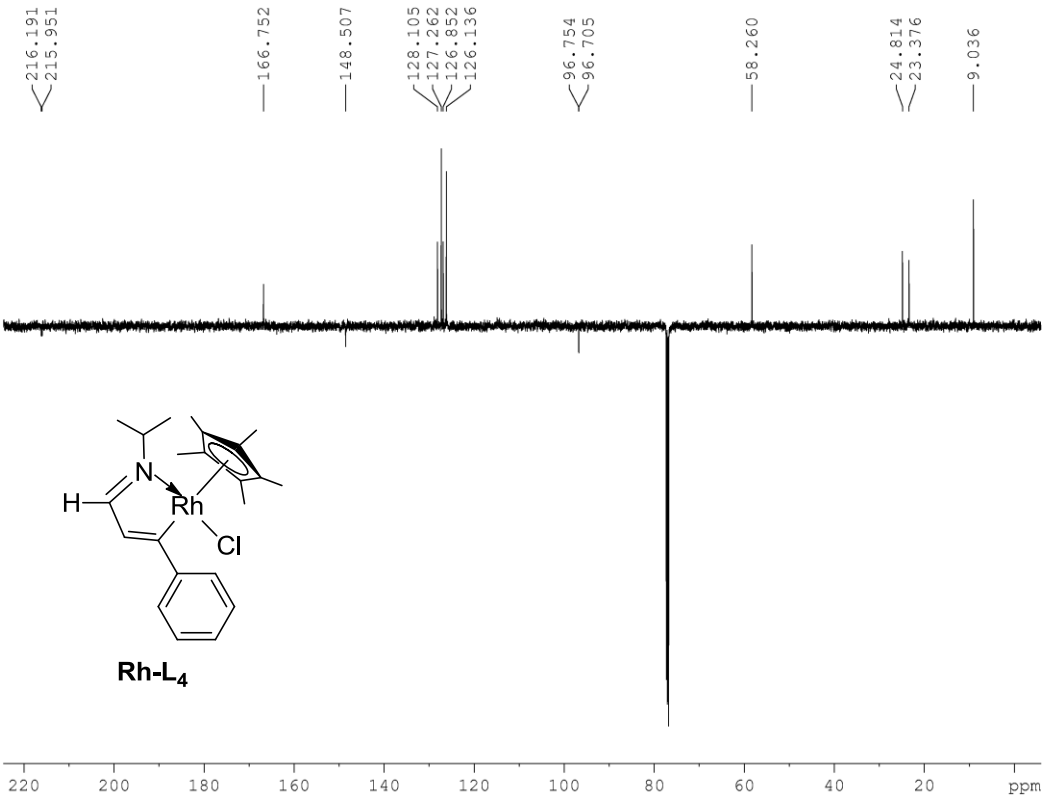

8.094
8.085
7.570
7.559
7.407
7.395
4.324
4.307
4.292
4.291
4.276
4.259
1.686
1.526
1.510
1.500
1.483
N
H
Rh
Cl
S
Rh-L3a
9
8
7
6
5
4
3
2
1
0
ppm
1.061
1.005
1.000
1.017
15.261
6.325

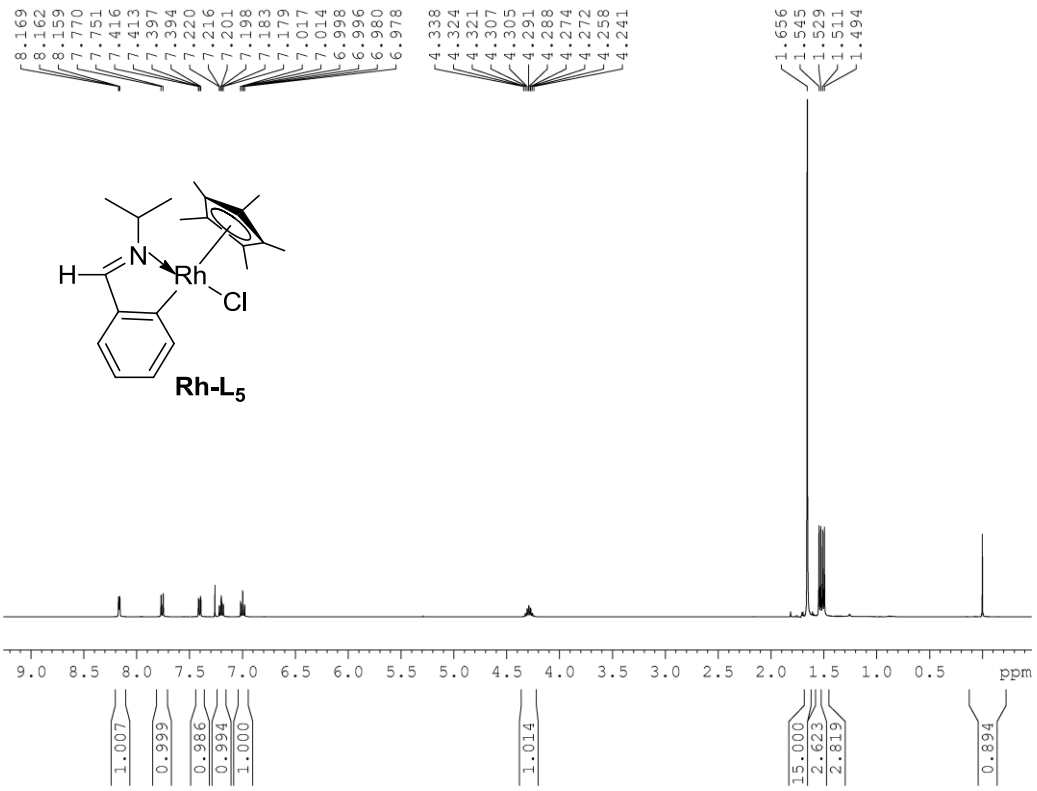

186.856
186.499
159.777
136.132
133.147
131.305
95.604
95.541
58.603
24.399
22.759
9.515
N
H
Rh
Cl
S
Rh-L3a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

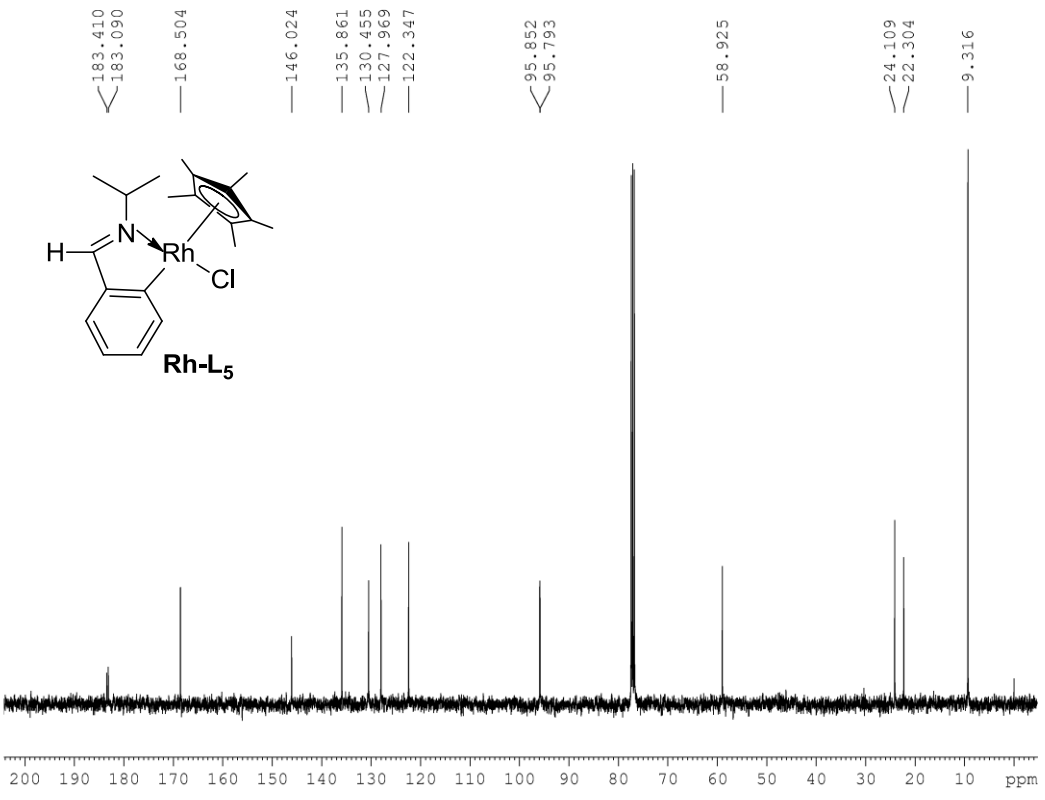

8.017
8.008
7.602
7.590
7.427
7.415
7.147
6.826
2.287
1.409
N
H
Rh
Cl
S
Rh-L3b
9
8
7
6
5
4
3
2
1
0
ppm
1.020
1.000
0.977
2.038
1.033
6.272
15.377


189.729
189.361
161.363
149.724
137.562
136.676
132.535
132.236
127.247
118.885
95.032
94.969
20.274
8.112
N
H
Rh
Cl
S
Rh-L3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

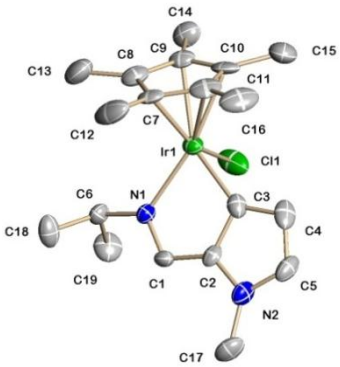

7.883
7.880
7.876
7.873
7.515
7.511
7.506
7.494
7.491
7.298
7.295
7.291
7.278
7.274
7.225
7.222
7.218
7.209
7.204
7.198
7.186
6.416
6.412
4.289
4.274
4.272
4.257
4.255
4.240
4.239
4.224
1.500
1.483
1.450
1.434
1.423
N
H
Rh
Cl
Rh-L4
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.902
2.079
0.954
0.913
0.977
2.923
2.985
15.219


216.191
215.951
166.752
148.507
128.105
127.262
126.852
126.136
96.754
96.705
58.260
24.814
23.376
9.036
N
H
Rh
Cl
Rh-L4
220
200
180
160
140
120
100
80
60
40
20
ppm


8.169
8.162
8.159
7.770
7.751
7.416
7.413
7.397
7.394
7.220
7.216
7.201
7.198
7.183
7.179
7.017
7.014
6.998
6.996
6.980
6.978
4.338
4.324
4.321
4.307
4.305
4.291
4.288
4.274
4.272
4.258
4.241
1.656
1.545
1.529
1.511
1.494
N
H
Rh
Cl
Rh-L5
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.007
0.999
0.986
0.994
1.000
1.014
15.000
2.623
2.819
0.894


183.410
183.090
168.504
146.024
135.861
130.455
127.969
122.347
95.852
95.793
58.925
24.109
22.304
9.316
N
H
Rh
Cl
Rh-L5
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

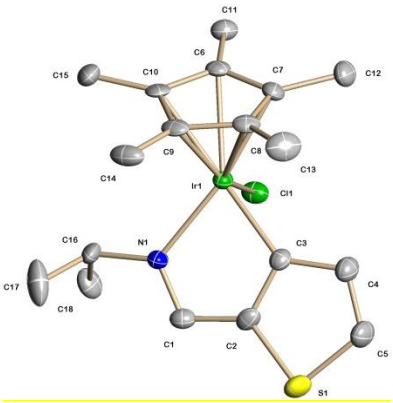
8. Crystal data for complexes Ir-L_1, Ir-L_{3a}, Ir-L_{3b}, Ir-L_4, Ir-L_5, Rh-L_{3a}, Rh-L_{3b}, Rh-L_4.



Crystal data and structure refinement for **Ir-L_1** (CCDC: 980293).

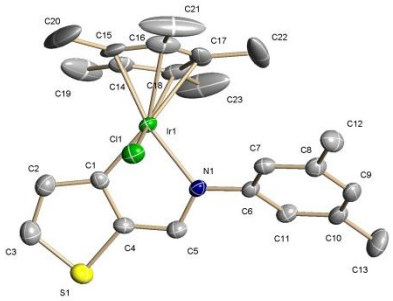
There are two molecule molecules in the unit cell, only one shown for clarity. H atoms omitted for clarity.

Identification code	12116	
Empirical formula	C19 H28 Cl Ir N2	
Formula weight	512.08	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 14.111(3) Å	α= 90°.
	b = 17.412(3) Å	β= 90.833(4)°.
	c = 15.429(3) Å	γ = 90°.
Volume	3790.3(12) $Å^3$	
Z	8	
Density (calculated)	1.795 Mg/m^3	
Absorption coefficient	7.187 mm^{-1}	
F(000)	2000	
Crystal size	0.15 x 0.12 x 0.07 mm^3	
Theta range for data collection	1.44 to 25.99°.	
Index ranges	-17<=h<=17, -21<=k<=16, -18<=l<=19	
Reflections collected	21084	
Independent reflections	7380 [R(int) = 0.0857]	
Completeness to theta = 25.99°	99.0 %	
Absorption correction	Empirical	
Max. and min. transmission	0.831 and 0.578	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7380 / 0 / 431	
Goodness-of-fit on F^2	0.848	
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.0682	
R indices (all data)	R1 = 0.0785, wR2 = 0.0758	
Largest diff. peak and hole	1.478 and -1.561 e.$Å^{-3}$	



Crystal data and structure refinement for **Ir-L$_{3a}$** (CCDC: 980294).

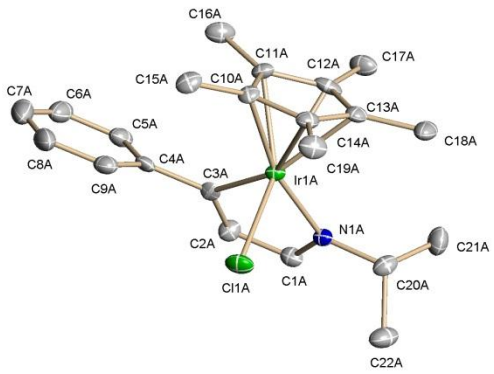
H atoms omitted for clarity.		
Identification code	12106	
Empirical formula	C18 H25 Cl Ir N S	
Formula weight	515.10	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.6461(17) Å	α= 90°.
	b = 8.621(2) Å	β= 92.184(4)°.
	c = 27.688(6) Å	γ = 90°.
Volume	1823.8(7) Å^3	
Z	4	
Density (calculated)	1.876 Mg/m^3	
Absorption coefficient	7.578 mm^{-1}	
F(000)	1000	
Crystal size	0.27 x 0.14 x 0.04 mm^3	
Theta range for data collection	1.47 to 27.00°.	
Index ranges	-9<=h<=9, -10<=k<=11, -35<=l<=35	
Reflections collected	14965	
Independent reflections	3936 [R(int) = 0.0711]	
Completeness to theta = 27.00°	98.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.862 and 0.544	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3936 / 0 / 206	
Goodness-of-fit on F^2	0.959	
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0571	
R indices (all data)	R1 = 0.0406, wR2 = 0.0598	
Largest diff. peak and hole	1.647 and -1.150 e.Å^{-3}	



Crystal data and structure refinement for **Ir-L$_{3b}$** (CCDC: 980295).

H atoms and lattice CH_2Cl_2 omitted for clarity. The methyl atoms of the Cp* ring are disordered.

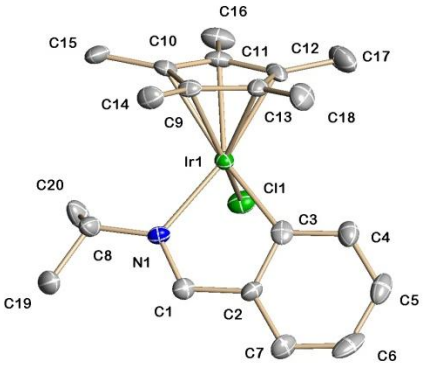
Identification code	04158	
Empirical formula	C24 H29 Cl3 Ir N S	
Formula weight	662.09	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.730(2) Å	α= 90°.
	b = 14.462(3) Å	β= 104.557(3)°.
	c = 16.791(4) Å	γ = 90°.
Volume	2521.8(9) Å^3	
Z	4	
Density (calculated)	1.744 Mg/m^3	
Absorption coefficient	5.707 mm^{-1}	
F(000)	1296	
Crystal size	0.40 x 0.34 x 0.09 mm^3	
Theta range for data collection	1.88 to 27.00°.	
Index ranges	-13<=h<=13, -18<=k<=18, -21<=l<=21	
Reflections collected	20722	
Independent reflections	5498 [R(int) = 0.1584]	
Completeness to theta = 27.00°	99.8 %	
Absorption correction	Integration	
Max. and min. transmission	0.5888 and 0.1532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5498 / 0 / 278	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0971	
R indices (all data)	R1 = 0.0456, wR2 = 0.0995	
Largest diff. peak and hole	2.805 and -1.924 e.Å^{-3}	



Crystal data and structure refinement for **Ir-L$_4$** (CCDC: 980296).

There are two molecule molecules in the unit cell, only one shown for clarity. H atoms omitted for clarity.

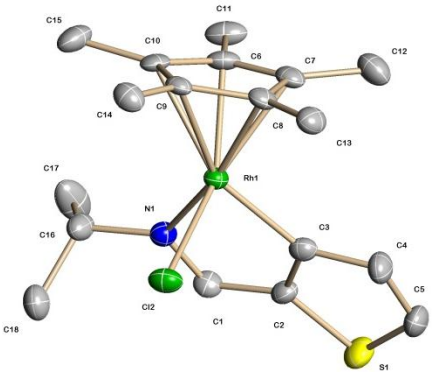
Identification code	09043	
Empirical formula	C22 H29 Cl Ir N	
Formula weight	535.11	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.207(5) Å	α= 90°.
	b = 25.172(11) Å	β= 108.180(8)°.
	c = 13.887(6) Å	γ = 90°.
Volume	4054(3) Å^3	
Z	8	
Density (calculated)	1.753 Mg/m^3	
Absorption coefficient	6.723 mm^{-1}	
F(000)	2096	
Crystal size	0.26 x 0.17 x 0.06 mm^3	
Theta range for data collection	1.62 to 27.00°.	
Index ranges	-15<=h<=15, -32<=k<=32, -17<=l<=17	
Reflections collected	33667	
Independent reflections	8846 [R(int) = 0.0863]	
Completeness to theta = 27.00°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.746 and 0.381	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8846 / 0 / 465	
Goodness-of-fit on F^2	0.918	
Final R indices [I>2sigma(I)]	R1 = 0.0390, wR2 = 0.0638	
R indices (all data)	R1 = 0.0588, wR2 = 0.0679	
Largest diff. peak and hole	2.351 and -1.662 e.Å^{-3}	



Crystal data and structure refinement for **Ir-L$_5$** (CCDC: 980297).

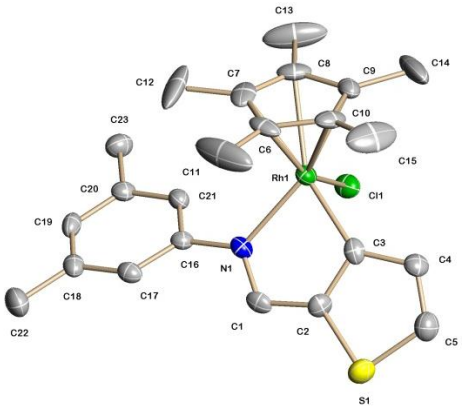
There are two molecule molecules in the unit cell, only one shown for clarity. H atoms omitted for clarity.

Identification code	13003	
Empirical formula	C20 H27 Cl Ir N	
Formula weight	509.08	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.1332(16) Å	α= 90°.
	b = 27.444(5) Å	β= 95.180(4)°.
	c = 17.333(3) Å	γ = 90°.
Volume	3853.1(13) Å^3	
Z	8	
Density (calculated)	1.755 Mg/m^3	
Absorption coefficient	7.068 mm^{-1}	
F(000)	1984	
Crystal size	0.23 x 0.16 x 0.08 mm^3	
Theta range for data collection	1.48 to 27.00°.	
Index ranges	-10<=h<=10, -35<=k<=35, -22<=l<=22	
Reflections collected	32190	
Independent reflections	8417 [R(int) = 0.0824]	
Completeness to theta = 27.00°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.831 and 0.469	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8417 / 0 / 429	
Goodness-of-fit on F^2	0.949	
Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0698	
R indices (all data)	R1 = 0.0569, wR2 = 0.0739	
Largest diff. peak and hole	2.264 and -1.129 e.Å^{-3}	



Crystal data and structure refinement for **Rh-L$_{3a}$** (CCDC: 980298).

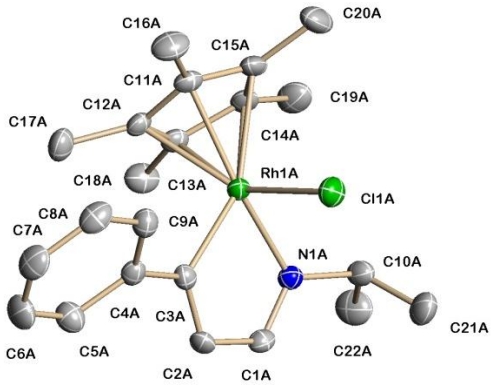
H atoms omitted for clarity.		
Identification code	13014	
Empirical formula	C18 H25 Cl N Rh S	
Formula weight	425.81	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.5951(16) Å	α= 90°.
	b = 8.5873(19) Å	β= 92.441(4)°.
	c = 28.051(6) Å	γ = 90°.
Volume	1827.8(7) Å^3	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	1.191 mm^{-1}	
F(000)	872	
Crystal size	0.13 x 0.12 x 0.07 mm^3	
Theta range for data collection	2.48 to 27.00°.	
Index ranges	-9<=h<=9, -10<=k<=10, -35<=l<=35	
Reflections collected	14888	
Independent reflections	3972 [R(int) = 0.0973]	
Completeness to theta = 27.00°	99.7 %	
Absorption correction	Empirical	
Max. and min. transmission	0.831 and 0.569	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3972 / 0 / 206	
Goodness-of-fit on F^2	0.890	
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.0736	
R indices (all data)	R1 = 0.0712, wR2 = 0.0800	
Largest diff. peak and hole	0.772 and -1.258 e.Å^{-3}	



Crystal data and structure refinement for **Rh-L$_{3b}$** (CCDC: 980299).

There are two molecule molecules in the unit cell, only one shown for clarity. H atoms and lattice CH_2Cl_2 omitted for clarity. The methyl atoms of the Cp* ring are disordered.

Identification code	13065	
Empirical formula	C24 H29 Cl3 N Rh S	
Formula weight	572.80	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.631(3) Å	α= 90°.
	b = 14.413(4) Å	β= 104.834(5)°.
	c = 16.681(4) Å	γ = 90°.
Volume	2470.9(11) Å^3	
Z	4	
Density (calculated)	1.540 Mg/m^3	
Absorption coefficient	1.112 mm^{-1}	
F(000)	1168	
Crystal size	0.27 x 0.20 x 0.03 mm^3	
Theta range for data collection	1.90 to 26.00°.	
Index ranges	-12<=h<=13, -17<=k<=17, -20<=l<=20	
Reflections collected	19112	
Independent reflections	4823 [R(int) = 0.1170]	
Completeness to theta = 26.00°	99.3 %	
Absorption correction	Empirical	
Max. and min. transmission	0.831 and 0.471	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4823 / 0 / 278	
Goodness-of-fit on F^2	0.903	
Final R indices [I>2sigma(I)]	R1 = 0.0517, wR2 = 0.0790	
R indices (all data)	R1 = 0.0928, wR2 = 0.0878	
Largest diff. peak and hole	0.701 and -0.535 e.Å^{-3}	



Crystal data and structure refinement for **Rh-L$_4$** (CCDC: 980300).

There are two molecule molecules in the unit cell, only one shown for clarity. H atoms omitted for clarity.

Identification code	13039	
Empirical formula	C22 H29 Cl N Rh	
Formula weight	445.82	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.211(3) Å	α= 90°.
	b = 25.326(5) Å	β= 108.751(4)°.
	c = 13.879(3) Å	γ = 90°.
Volume	4064.1(15) Å^3	
Z	8	
Density (calculated)	1.457 Mg/m^3	
Absorption coefficient	0.976 mm^{-1}	
F(000)	1840	
Crystal size	0.42 x 0.31 x 0.05 mm^3	
Theta range for data collection	1.61 to 27.00°.	
Index ranges	-15<=h<=15, -31<=k<=32, -17<=l<=17	
Reflections collected	33918	
Independent reflections	8860 [R(int) = 0.0665]	
Completeness to theta = 27.00°	99.9 %	
Absorption correction	Empirical	
Max. and min. transmission	0.831 and 0.633	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8860 / 0 / 465	
Goodness-of-fit on F^2	0.951	
Final R indices [I>2sigma(I)]	R1 = 0.0402, wR2 = 0.0736	
R indices (all data)	R1 = 0.0579, wR2 = 0.0783	
Largest diff. peak and hole	0.845 and -0.512 e.Å^{-3}	

9. Computational details

DFT calculations were run with Gaussian 03 (Revision D.01)[7] and Gaussian 09 (Revision A.02).[8] Geometry optimisations were performed with Gaussian 03 and the BP86 functional[9, 10] and employed a smaller basis set, BS1, in which Rh, Ir and S centers were described with the Stuttgart RECPs and associated basis sets[11] with additional d-orbital polarisation on S (ζ = 0.503)[12] and 6-31G** basis sets were used for all other atoms.[13, 14] The 'grid=ultrafine' option was used throughout as it was found to be necessary to achieve consistent results, in particular for the geometries of the Cp* rings. Different orientations of the N-^{i}Pr and N-xylyl substituents and the vinylimine substrate **H-L$_4$** were tested via rotation profiles around the appropriate bonds in both the free substrate and the N-bound metal complexes. Geometries computed with BS1/BP86 compared well with the experimental data that are available for several of the cyclometalated products (see Table S4). All stationary points were fully characterized *via* analytical frequency calculations as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). IRC calculations and subsequent geometry optimizations were used to confirm the minima linked by each transition state. Corrections for the effects of methanol (ε = 32.6) and dichloromethane solvent (ε = 8.93) were run with Gaussian 09 and used the polarisable continuum model.

In order to obtain improved energetics (in particular for Cl^-/OAc^- exchange processes) all energies were recomputed with a larger basis set, BS2, featuring cc-pVTZ-PP on Rh and Ir 6-311++g** on all other atoms. Further details on the basis set dependency are given in Table S5. The effects of functional choice were also tested (see Table S6). For this the BP86-optimised geometries were reoptimised with the selected functional in Gaussian 09 using BS1. Frequency calculations were again used to confirm the nature of all stationary points. Single point energy dispersion corrections were also assessed using Grimme's D3 parameter set[15] and showed the inclusion of dispersion to be important if the favourable thermodynamics implied from the experimental studies were to be reproduced for all the substrate/metal combinations. The final energies reported in the main text are free energies (298.15 K, 1 atm) based on the gas-phase BS1-optimised geometry, subsequently corrected for solvent (calculated with BS1), dispersion (D3 parameter set) and basis sets effects (BS2). Details of these different energy contributions for each reaction under consideration are given in Tables S7-S11 and Figures S1-S8.

10. Comparison of computed and experimetal geometric data.

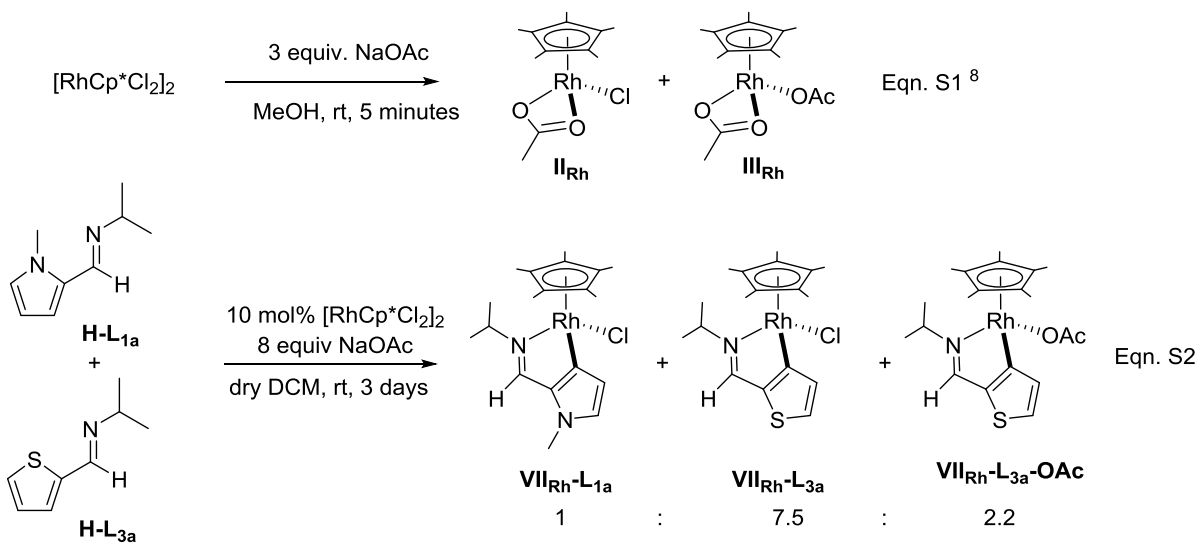
Table S4. (a) Comparison of key computed (plain text) and experimental (italics) geometric parameters (Å, °) for cyclometalated species. Atom numbering is that shown in Figure 2 of the main article.

	M-C(3)	**M-Cl(1)**	**M-N(I)**	**M-Cp*[a]**	**C-M-N**
VII_{Rh}-L_{3a}	2.015/*2.018(4)*	2.415/*2.393(11)*	2.114/*2.114(3)*	1.886/*1.825*	79.3/*79.0(15)*
VII_{Rh}-L_{3b}	2.011/*2.009(5)*	2.414/*2.374(13)*	2.124/*2.100(4)*	1.882/*1.810*	79.1/*78.3(18)*
VII_{Rh}-L_{4}	2.017/*2.020(3)*	2.415/*2.402(9)*	2.088/*2.077(3)*	1.907/*1.851*	79.1/*78.4(12)*
VII_{Ir}-L_{1}	2.020/*2.049(9)*	2.444/*2.400(2)*	2.134/*2.107(6)*	1.885/*1.817*	78.1/*77.3(3)*
VII_{Ir}-L_{3a}	2.023/*2.027(5)*	2.435/*2.392(13)*	2.121/*2.102(5)*	1.889/*1.821*	78.2/*77.8(17)*
VII_{Ir}-L_{3b}	2.019/*2.024(4)*	2.436/*2.393(12)*	2.129/*2.113(4)*	1.887/*1.818*	78.1/*77.6(16)*
VII_{Ir}-L_{4}	2.021/*2.031(5)*	2.436/*2.405(16)*	2.097/*2.074(5)*	1.911/*1.844*	78.1/*77.8(5)*
VII_{Ir}-L_{5}	2.032/*2.024(6)*	2.437/*2.393(16)*	2.102/*2.106(5)*	1.899/*1.828*	78.2/*78.0(2)*

[a] distance to the centroid of the central Cp* ring

11. Basis Set Effects

Calculations were run to assess the basis set dependency of the computed results and how these relate to the experimental observations. The energetics of Cl^-/OAc^- exchange were found to be particularly sensitive to basis set choice and two such processes are considered in detail here. Experimentally, two observations suggest that the free energy of Cl^-/OAc^- exchange should be close to zero: (i) opening of the $[RhCl_2Cp^*]_2$ dimer by NaOAc in the absence of substrate led to the observation of both the chloro-acetate species [RhCl(OAc)Cp*], **Rh_{II}**, and the *bis*-acetate species $[Rh(OAc)_2Cp^*]$, **Rh_{III}**, (see Eqn. S1[16]); (ii) in the competition experiment between substrates **H-L_{1a}** and **H-L_{3a}** the cyclometalated product derived from **H-L_{3a}** was observed as an equilibrium mixture of its chloro (**VII_{Rh}-L_{3a}**) and acetate adducts (**VII_{Rh}-L_{3a}-OAc**, Eqn. S2.).



The results of the basis set testing are given in Table S5 and show that the use of diffuse functions on the ligand heavy atoms is crucial to obtain a reasonable value for the Cl^-/OAc^- exchange energy. Without these the relative stabilities of the OAc adducts **III_{Rh}** and **VII_{Rh}-L_{3a}-OAc** are considerably over-estimated (Entries 1b, 1 and 2). Entry 4 shows that including diffuse functions on Cl, C, N and O improves the situation, while additional diffuse functions on H has little further effect (Entry 5). Use of larger basis sets on either the ligands (Entries 6-8) and rhodium (Entries 5, 9-12) did not significantly change the outcome. On the basis of these data the basis set associated with Entry 9 was employed for the final single-point calculations.

Table S5. Computed SCF energy change, (kcal/mol) for Cl^-/OAc^- exchange at $\mathbf{II_{Rh}}$ (Eqn. S1) and $\mathbf{VII_{Rh}\text{-}L_{3a}}$ (Eqn. S2) as a function of the basis set employed. Negative value indicates a greater stability of the OAc species involved in the exchange.

Entry	Rh	Cl	C, N, O, H	ΔE $\mathbf{II_{Rh} \rightarrow III_{Rh}}$	ΔE $\mathbf{VII_{Rh}\text{-}L_{3a} \rightarrow VII_{Rh}\text{-}L_{3a}\text{-}OAc}$
1b	SDDALL	SDDALL+D	6-31g**	-23.5	-21.9
1	SDDALL	6-31g**	6-31g**	-10.4	-8.5
2	SDDALL	6-311g**	6-311g**	-13.6	-11.3
3	SDDALL	6-311+g**	6-311+g**	-1.9	0.0
4	SDDALL	6-311++g**	6-311++g**	-1.7	0.1
4b	SDDALL	SDDALL+D	6-311++g**	-2.1	-0.5
5	SDDALL+F	6-311++g**	6-311++g**	-1.8	0.0
6	cc-pVTZ-PP	cc-pVTZ	cc-pVTZ	-1.5	0.1
7	cc-pVQZ-PP	cc-pVQZ	cc-pVQZ	-0.5	0.8
8	Aug-cc-pVQZ-PP	aug-cc-pVQZ	aug-cc-pVQZ	-1.1	a
9	cc-pVTZ-PP	6-311++g**	6-311++g**	-1.8	-0.2
10	cc-pVQZ-PP	6-311++g**	6-311++g**	-1.7	-0.2
11	aug-cc-pVTZ-PP	6-311++g**	6-311++g**	-1.6	-0.1
12	Aug-cc-pVQZ-PP	6-311++g**	6-311++g**	-1.6	-0.3
13	LANL2DZ	6-311++g**	6-311++g**	-1.9	0.1

[a] SCF convergence not achieved

12. Functional Testing.

The energetics of the reactions of $[RhCl_2Cp^*]_2$, $\mathbf{I_{Rh}}$, with OAc^- to give [RhCl(OAc)Cp*], $\mathbf{Rh_{II}}$, and $[Rh(OAc)_2Cp^*]$, $\mathbf{Rh_{III}}$, were assessed, as well as the energy of the final cyclometallated product $\mathbf{VII_{Rh}}$ formed with substrates $\mathbf{H\text{-}L_{1\text{-}6}}$. Relative free energies are given in Table S6 and include corrections for solvent (MeOH) and basis set effects. An additional correction for dispersion effects is included for all functionals, with the exception of M06, M06L, B97D and ωB97XD for which a treatment of dispersion is included in the original functional.

Table S6. Relative free energies (kcal/mol) of $\mathbf{II_{Rh}}$, $\mathbf{III_{Rh}}$ and $\mathbf{VII_{Rh}}$ computed with a range of density functionals. Values include corrections for solvent (MeOH) and basis set effects as well as dispersion correction for all functionals, with the exception of M06, M06L, B97D and ωB97XD.

	$\mathbf{H\text{-}L_1}$				$\mathbf{H\text{-}L_2}$			
	$\mathbf{II_{Rh}}$	$\mathbf{III_{Rh}}$	$\mathbf{VII_{Rh}}$	**ΔG**	$\mathbf{II_R}$	$\mathbf{III_{Rh}}$	$\mathbf{VII_{Rh}}$	**ΔG**
BP86	-8.6	-5.1	+0.5	+9.1	-8.6	-5.1	+0.3	+8.9
BP86-D3	-1.3	-0.4	-2.5	-1.2	-1.3	-0.4	-2.8	-1.5
B3P86	-7.7	-5.2	+1.1	+8.8	-7.7	-5.2	+0.6	+8.3
BLYP	-9.9	-6.5	+4.2	+14.1	-9.9	-6.5	+4.1	+14.0
BLYP-D3	-2.8	-1.9	+0.9	+3.7	-2.8	-1.9	+0.8	+3.6
B3LYP	-9.4	-7.1	+2.8	+12.2	-9.4	-7.1	+3.5	+12.9
B3LYP-D3	-3.2	-3.2	+0.1	+3.3	-3.2	-3.2	+1.0	+4.2
PBEPBE	-7.0	-3.3	+0.9	+7.9	-7.0	-3.3	+0.9	+7.9
PBEPBE-D3	-3.3	+1.3	-1.1	+2.2	-3.3	+1.3	-1.3	+2.1
PBE1PBE	-7.0	-4.2	+1.5	+8.4	-7.0	-4.2	+0.9	+7.9
PBE1PBE-D3	-2.9	-1.9	-0.4	+2.5	-2.9	-1.9	-1.1	+1.8
B3PW91	-8.8	-5.5	+1.6	+10.4	-8.8	-5.5	+1.4	+10.1
B3PW91-D3	-1.5	-0.7	-1.2	+0.3	-1.5	-0.7	-1.5	-0.1
M06	-2.1	-0.6	+1.5	+3.6	-2.1	-0.6	+2.0	+4.1
M06L	-7.2	-10.6	+3.7	+14.2	-7.2	-10.6	+3.7	+14.3
B97D	-4.8	-5.2	-5.5	-0.3	-4.8	-5.2	-4.6	+0.6
ωB97XD	-6.7	-7.3	-3.9	+3.4	-6.7	-7.3	-3.4	+3.9

	H-L_{3a}				H-L_4			
	II_{Rh}	III_{Rh}	VII_{Rh}	ΔG	II_R	III_{Rh}	VII_{Rh}	ΔG
BP86	-8.6	-5.1	-1.3	+7.3	-8.6	-5.1	-5.8	+2.8
BP86-D3	-1.3	-0.4	-5.3	-4.0	-1.3	-0.4	-14.0	-12.7
B3P86	-7.7	-5.2	-1.0	+6.6	-7.7	-5.2	-5.8	+1.9
BLYP	-9.9	-6.5	+2.3	+12.2	-9.9	-6.5	-1.6	+8.3
BLYP-D3	-2.8	-1.9	-2.0	+0.8	-2.8	-1.9	-7.7	-4.9
B3LYP	-9.4	-7.1	+1.8	+11.2	-9.4	-7.1	-2.3	+7.0
B3LYP-D3	-3.2	-3.2	-1.5	+1.7	-3.2	-3.2	-6.9	-3.7
PBEPBE	-7.0	-3.3	-0.8	+6.2	-7.0	-3.3	-5.9	+1.1
PBEPBE-D3	-3.3	+1.3	-3.5	-0.1	-3.3	+1.3	-8.7	-5.4
PBE1PBE	-7.0	-4.2	-0.9	+6.1	-7.0	-4.2	-5.7	+1.2
PBE1PBE-D3	-2.9	-1.9	-3.4	-0.5	-2.9	-1.9	-8.5	-5.7
B3PW91	-8.8	-5.5	-0.3	+8.4	-8.8	-5.5	-2.9	+5.9
B3PW91-D3	-1.5	-0.7	-4.2	-2.7	-1.5	-0.7	-8.6	-7.2
M06	-2.1	-0.6	+0.4	+2.5	-2.1	-0.6	-8.2	-6.1
M06L	-7.2	-10.6	+2.1	+12.7	-7.2	-10.6	-5.3	+5.3
B97D	-4.8	-5.2	-7.3	-2.1	-4.8	-5.2	-15.0	-9.8
ωB97XD	-6.7	-7.3	-5.2	+2.1	-6.7	-7.3	-14.9	-7.6

	H-L_5				H-L_6			
	II_{Rh}	III_{Rh}	VII_{Rh}	ΔG	II_R	III_{Rh}	VII_{Rh}	ΔG
BP86	-8.6	-5.1	-3.5	+5.1	-8.6	-5.1	-7.1	+1.5
BP86-D3	-1.3	-0.4	-7.7	-6.4	-1.3	-0.4	-9.0	-7.7
B3P86	-7.7	-5.2	-3.1	+4.6	-7.7	-5.2	-6.5	+1.2
BLYP	-9.9	-6.5	+0.9	+10.8	-9.2	-6.5	-3.7	+6.2
BLYP-D3	-2.8	-1.9	-3.7	-0.9	-2.8	-1.9	-6.0	-3.2
B3LYP	-9.4	-7.1	+0.4	+9.8	-8.7	-7.1	-4.1	+5.3
B3LYP-D3	-3.2	-3.2	-3.2	+0.0	-3.2	-3.2	-5.7	-2.5
PBEPBE	-7.0	-3.3	-3.1	+3.9	-6.3	-3.3	-6.5	+0.4
PBEPBE-D3	-3.3	+1.3	-5.9	-2.6	-3.3	+1.3	-8.1	-4.8
PBE1PBE	-7.0	-4.2	-2.6	+4.3	-6.3	-4.2	-6.2	+0.8
PBE1PBE-D3	-2.9	-1.9	-5.4	-2.5	-2.9	-1.9	-7.6	-4.7
B3PW91	-8.8	-5.5	-2.0	+6.7	-8.1	-5.5	-6.0	+2.7
B3PW91-D3	-1.5	-0.7	-6.2	-4.8	-1.5	-0.7	-7.9	-6.5
M06	-2.1	-0.6	-2.1	0.0	-2.1	-0.6	-3.6	-1.5
M06L	-7.2	-10.6	+0.7	+11.2	-7.2	-10.6	-1.4	+9.2
B97D	-4.8	-5.2	-9.8	-4.6	-4.8	-5.2	-11.5	-6.3
ωB97XD	-6.7	-7.3	-7.4	-0.1	-6.7	-7.3	-9.0	-1.7

13. Breakdown of Energy Contributions.

The following tables detail the evolution of the relative energies as the successive corrections to the initial SCF energy are included. Terms used are:

SCF	SCF energy computed with the BP86 functional with BS1
$\mathbf{H_{0K}}$	Enthalpy at 0 K
$\mathbf{G_{298}}$	Free energy at 298.15 K and 1 atm
$\mathbf{G_{DCM}}$	Free energy corrected for dichloromethane solvent
$\mathbf{G_{MeOH}}$	Free energy corrected for methanol solvent
$\mathbf{G_{D3}}$	Free energy corrected for dispersion effects
$\mathbf{G_{BS2}}$	Free energy corrected for basis effects with BS2
$\mathbf{G_{D3\text{-}DCM}}$	Free energy corrected for dispersion effects and dichloromethane solvent
$\mathbf{G_{D3\text{-}MeOH}}$	Free energy corrected for dispersion effects and dichloromethane solvent
$\mathbf{G_{BS2\text{-}D3\text{-}DCM}}$	Free energy corrected for basis set (BS2), dispersion effects and dichloromethane solvent
$\mathbf{G_{BS2\text{-}D3\text{-}MeOH}}$	Free energy corrected for basis set (BS2), dispersion effects and methanol solvent

In each case the final data used In the main article is highlighted in bold and a figure comparing the final data for the Rh and Ir congenors is supplied.

Table S7a. Computed energies (kcal/mol) for the reaction of **H-L$_1$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I$_{Rh}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II$_{Rh}$	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III$_{Rh}$	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV$_{Rh}$	61.5	64.1	69.2	-19.4	-26.6	63.3	100.6	-25.3	-32.5	6.2	**-1.0**
TS(IV-VI)$_{Rh}$	74.5	76.1	81.0	-9.3	-16.9	73.9	111.7	-16.4	-24.0	14.3	**6.8**
VI$_{Rh}$	68.8	70.9	75.8	-11.4	-18.4	68.7	107.8	-18.5	-25.5	13.4	**6.5**
VII$_{Rh}$	-14.1	-12.5	-11.7	-20.5	-21.4	-14.7	10.1	-23.5	-24.4	-1.6	**-2.5**

Table S7b. Computed energies (kcal/mol) for the reaction of **H-L$_1$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I$_{Ir}$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II$_{Ir}$	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III$_{Ir}$	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV$_{Ir}$	59.3	62.2	67.4	-21.4	-28.7	60.7	99.1	-28.2	-35.5	**3.4**	-3.8
TS(IV-VI)$_{Ir}$	73.1	74.7	79.9	-10.7	-18.3	71.8	111.0	-18.8	-26.4	**12.3**	4.7
VI$_{Ir}$	62.9	65.2	70.5	-17.2	-24.3	62.2	103.1	-25.6	-32.6	**7.0**	0.0
VII$_{Ir}$	-21.9	-20.2	-19.6	-28.4	-29.4	-23.3	2.1	-32.1	-33.1	**-10.4**	-11.4

Figure S1. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_1$** at [MCl$_2$Cp*]$_2$ (M = Rh, Ir). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

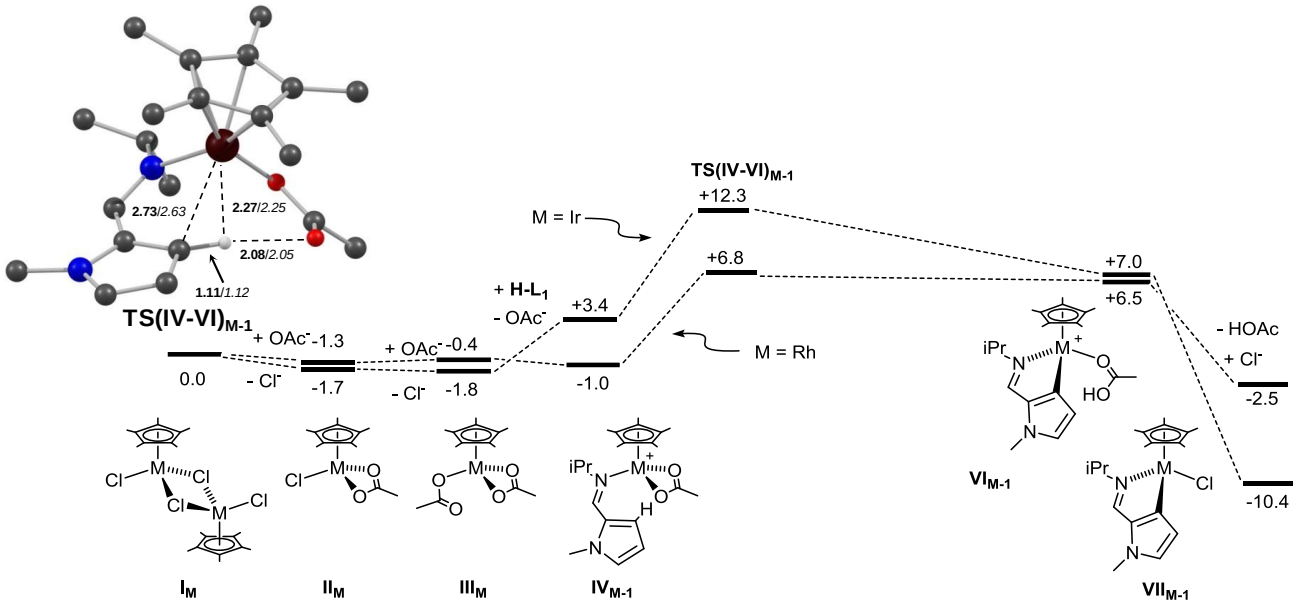


Table S8a. Computed energies (kcal/mol) for the reaction of **H-L$_2$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	60.5	63.2	68.0	-19.6	-26.6	62.6	100.0	-25.1	-32.0	6.9	**0.0**
TS(IV-VI)$_{Rh}$	77.9	78.2	83.8	-5.1	-12.2	76.9	116.0	-12.0	-19.1	20.2	**13.1**
VI_{Rh}	68.2	70.8	75.5	-11.7	-18.5	69.5	107.9	-17.7	-24.5	14.8	**7.9**
VII_{Rh}	-18.4	-16.4	-15.4	-21.5	-21.9	-18.5	6.8	-24.6	-25.0	-2.4	**-2.8**

Table S8b. Computed energies (kcal/mol) for the reaction of **H-L$_2$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	61.7	64.7	70.2	-18.2	-25.4	61.9	102.6	-26.6	-33.7	**5.8**	-1.3
TS(IV-VI)$_{Ir}$	78.9	80.5	86.7	-4.2	-11.7	77.2	118.9	-13.7	-21.2	**17.3**	9.8
VI_{Ir}	65.8	68.4	73.2	-15.4	-22.5	65.0	106.2	-23.6	-30.7	**9.5**	2.3
VII_{Ir}	-25.2	-23.1	-22.2	-29.3	-29.9	-26.0	-0.2	-33.1	-33.7	**-11.2**	-11.8

Figure S2. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_2$** at [MCl$_2$Cp*]$_2$ (M = Rh, Ir). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

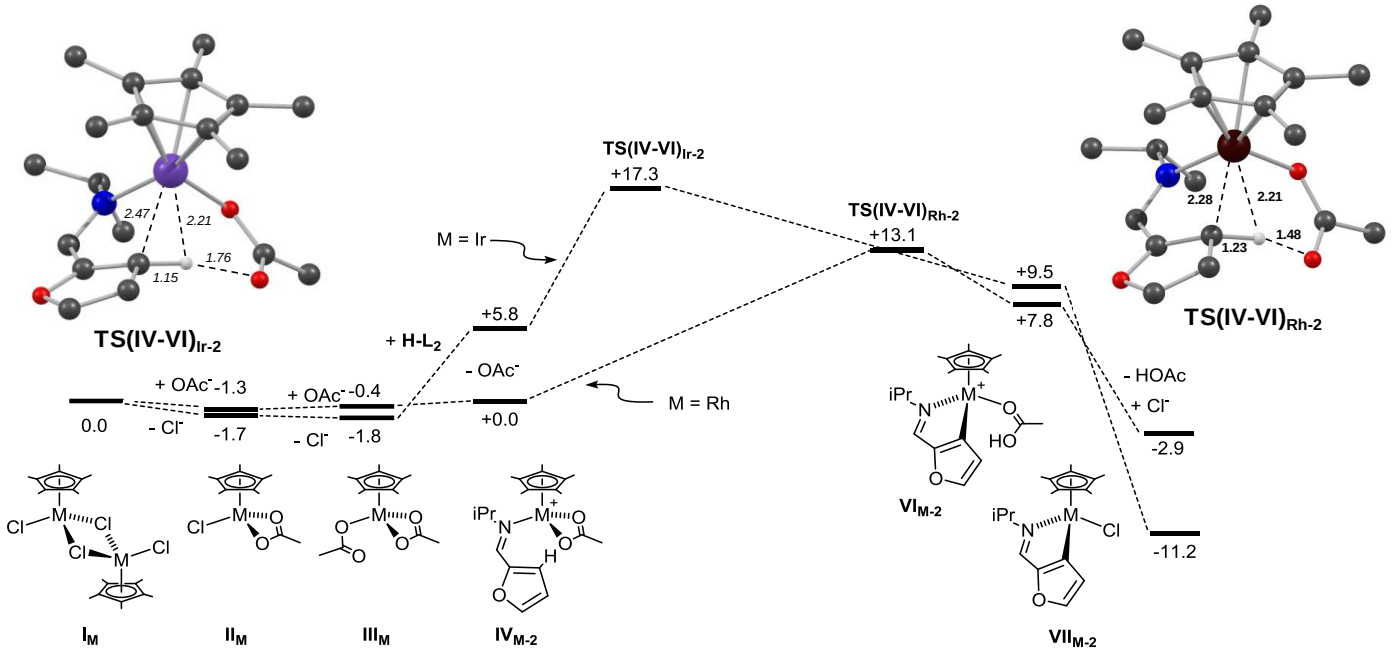


Table S9a. Computed energies (kcal/mol) for the reaction of **H-L$_{3a}$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	64.5	67.0	71.7	-16.5	-23.5	65.7	102.6	-22.5	-29.6	8.4	**1.3**
$TS(IV\text{-}V)_{Rh}$	78.7	79.8	85.3	-4.9	-12.3	77.2	115.9	-13.0	-20.4	17.6	**10.2**
V_{Rh}	78.7	79.9	83.6	-6.7	-14.1	75.5	114.3	-14.8	-22.2	15.9	**8.5**
$TS(V\text{-}VI)_{Rh}$	78.7	79.5	85.0	-4.8	-12.1	76.7	115.9	-13.1	-20.4	17.8	**10.5**
VI_{Rh}	67.8	70.6	75.7	-11.8	-18.7	68.6	107.3	-18.9	-25.8	12.7	**5.7**
VII_{Rh}	-18.9	-16.8	-15.8	-22.6	-23.1	-19.8	5.9	-26.6	-27.1	-4.8	**-5.3**

Table S9b. Computed energies (kcal/mol) for the reaction of **H-L$_{3a}$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	62.4	65.1	70.1	-18.4	-25.5	63.1	101.2	-25.4	-32.4	**5.8**	-1.3
$TS(IV\text{-}VI)_{Ir}$	77.2	78.7	83.9	-6.4	-13.8	75.2	114.6	-15.2	-22.6	**15.6**	8.1
VI_{Ir}	62.0	64.8	70.1	-18.0	-25.1	61.9	102.2	-26.2	-33.2	**5.9**	-1.1
VII_{Ir}	-26.7	-24.6	-23.6	-30.6	-31.1	-28.4	-1.9	-35.4	-35.9	**-13.7**	-14.2

Figure S3. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_{3a}$** at [MCl$_2$Cp*]$_2$ (M = Rh, Ir). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity. Data for both MeOH and dichloromethane solvent are supplied with those in bold indicating the solvent used experimentally.

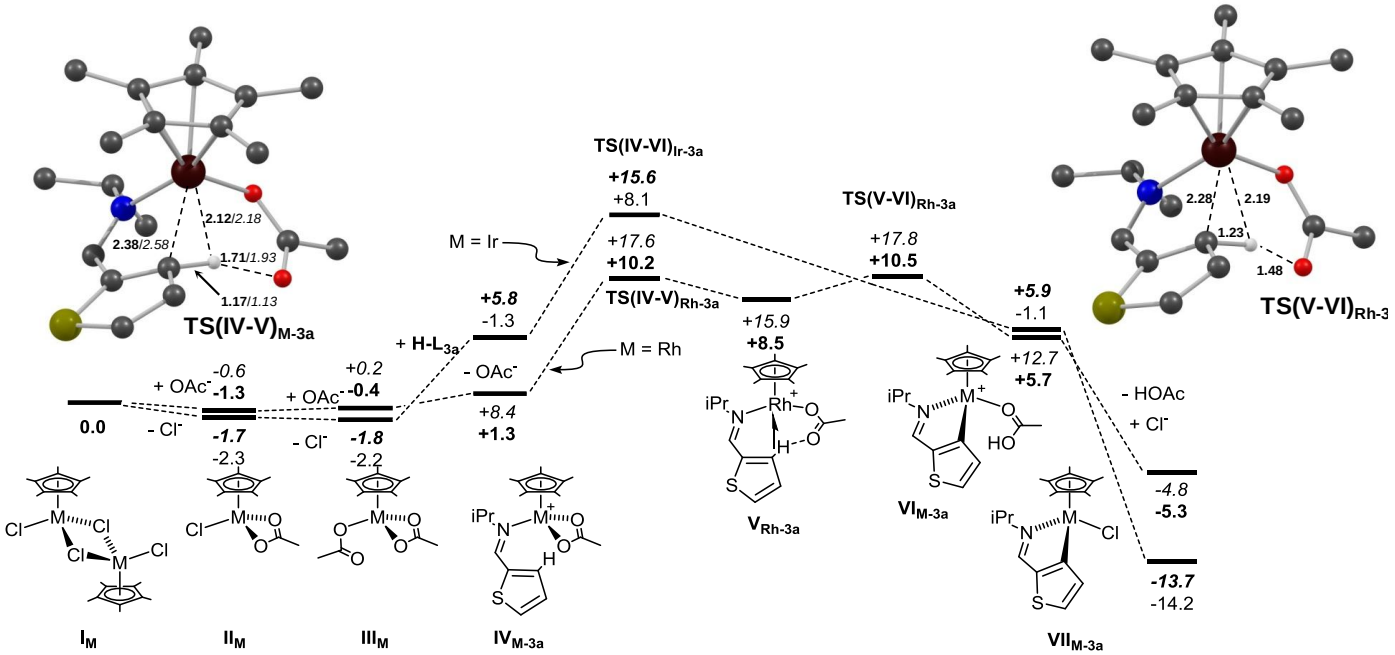


Table S10a. Computed energies (kcal/mol) for the reaction of **H-L$_{3b}$** at [$RhCl_2Cp^*]_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	64.2	66.6	71.8	-14.4	-21.3	64.3	103.2	-21.9	-28.9	9.4	**2.5**
$TS(IV\text{-}VI)_{Rh}$	79.2	80.6	86.3	-2.4	-9.7	77.6	116.9	-11.1	-18.4	19.5	**12.2**
VI_{Rh}	64.7	67.0	72.5	-12.9	-19.6	63.7	104.0	-21.6	-28.3	10.0	**3.3**
VII_{Rh}	-21.0	-19.2	-18.0	-23.9	-24.3	-23.5	3.6	-29.4	-29.7	-7.8	**-8.1**

Table S10b. Computed energies (kcal/mol) for the reaction of **H-L$_{3b}$** at [$IrCl_2Cp^*]_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	62.5	65.0	70.5	-16.0	-22.9	62.0	102.1	-24.5	-31.5	**7.1**	0.1
$TS(IV\text{-}VI)_{Ir}$	77.8	79.4	85.2	-3.8	-11.1	74.6	116.1	-14.3	-21.7	**16.6**	9.3
VI_{Ir}	59.3	61.8	67.4	-18.3	-25.2	57.7	99.6	-28.0	-34.9	**4.1**	-2.7
VII_{Ir}	-28.5	-26.6	-25.4	-31.4	-31.8	-31.7	-3.8	-37.8	-38.1	**-16.2**	-16.5

Figure S4. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_{3b}$** at [MCl$_2$Cp*]$_2$ (M = Ir, Rh). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

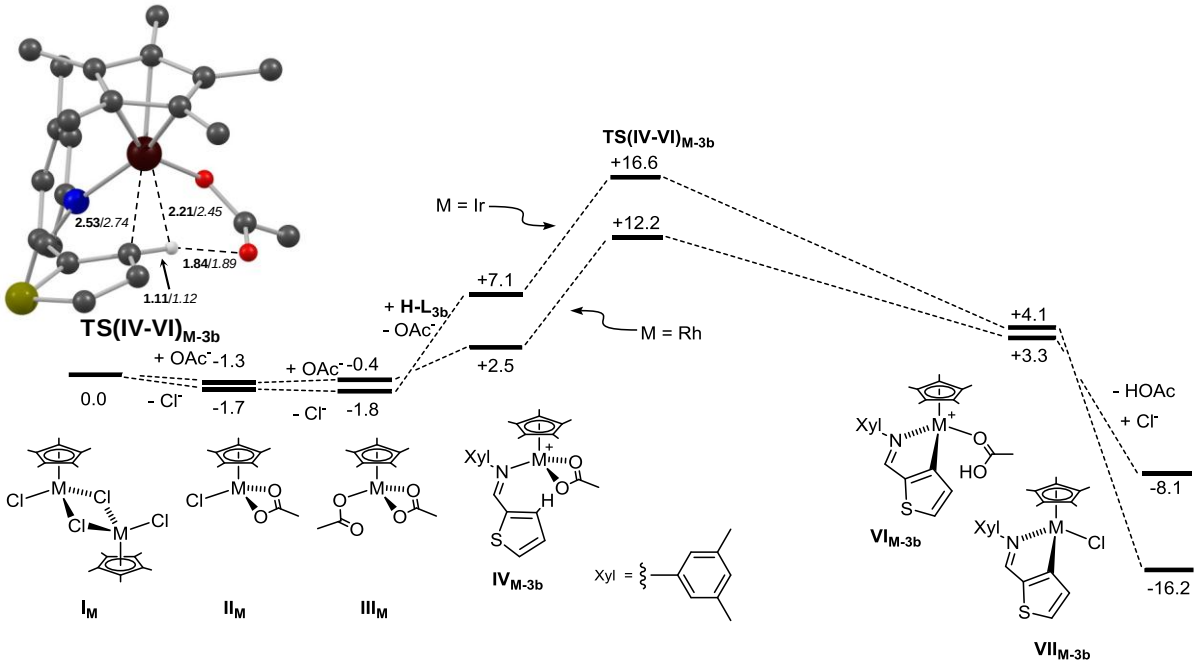


Table S11a. Computed energies (kcal/mol) for the reaction of **H-L$_4$** at [$RhCl_2Cp^*$]$_2$ (**I_{Rh}**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	57.0	59.6	64.0	-23.4	-30.4	59.8	95.7	-27.6	-34.6	4.1	**-2.9**
$TS(IV\text{-}VI)_{Rh}$	78.3	78.1	85.0	-2.4	-9.6	72.5	117.8	-14.9	-22.0	17.9	**10.8**
VI_{Rh}	66.2	69.3	75.8	-10.5	-17.3	63.5	108.8	-22.9	-29.7	10.1	**3.3**
VII_{Rh}	-22.0	-19.7	-17.6	-22.7	-22.9	-26.3	5.0	-31.5	-31.6	-8.9	**-9.1**

Table S11b. Computed energies (kcal/mol) for the reaction of **H-L$_4$** at [$IrCl_2Cp^*$]$_2$ (**I_{Ir}**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	54.7	57.4	62.1	-25.6	-32.7	57.0	93.9	-30.7	-37.8	**1.2**	-5.9
$TS(IV\text{-}V)_{Ir}$	74.1	75.9	82.4	-6.4	-13.7	70.3	114.2	-18.5	-25.8	**13.3**	6.0
V_{Ir}	73.9	75.3	81.2	-7.4	-14.7	68.2	113.1	-20.3	-27.6	**11.6**	4.3
$TS(V\text{- }VI)_{Ir}$	74.1	74.4	81.3	-6.8	-13.9	67.9	113.7	-20.1	-27.3	**12.3**	5.1
VI_{Ir}	60.1	63.3	70.0	-16.8	-23.8	56.4	103.6	-30.4	-37.4	**3.2**	-3.8
VII_{Ir}	-29.9	-27.6	-25.4	-30.7	-30.9	-35.0	-2.9	-40.3	-40.5	**-17.8**	-18.1

Figure S5. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_4$** at [MCl$_2$Cp*]$_2$ (M = Ir, Rh). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

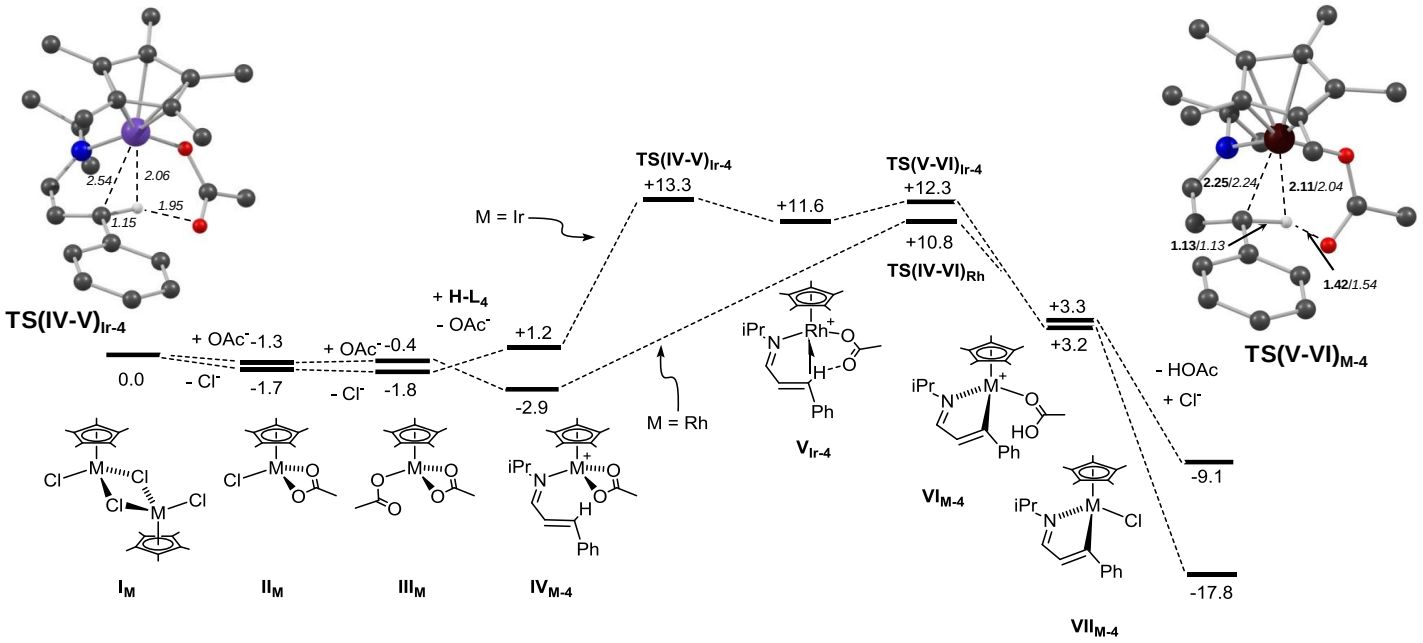


Table S12a. Computed energies (kcal/mol) for the reaction of **H-L$_{4'}$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	60.6	63.2	67.3	-22.5	-29.7	64.1	98.9	-25.6	-32.9	6.0	**-1.3**
TS(IV-VI)$_{Rh}$	79.7	81.3	85.4	-6.7	-14.3	80.3	116.4	-11.7	-19.4	19.3	**11.7**
VI_{Rh}	65.2	68.4	73.5	-15.1	-22.2	69.4	105.9	-19.2	-26.2	13.3	**6.2**
VII_{Rh}	-23.0	-20.7	-20.1	-26.6	-27.0	-21.4	2.4	-28.0	-28.4	-5.5	**-5.9**

Table S12b. Computed energies (kcal/mol) for the reaction of **H-L$_{4'}$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	58.5	61.3	65.9	-24.1	-31.4	61.9	97.6	-28.1	-35.4	**3.6**	-3.7
TS(IV-VI)$_{Ir}$	77.8	79.6	83.9	-8.3	-15.9	78.2	115.4	-13.9	-21.6	**17.7**	10.0
VI_{Ir}	58.6	62.0	67.3	-21.8	-29.0	62.1	100.2	-27.0	-34.1	**6.0**	-1.2
VII_{Ir}	-31.6	-29.2	-28.5	-35.2	-35.7	-30.5	-6.1	-37.3	-37.7	**-14.9**	-15.4

Figure S6. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_{4'}$** at $[MCl_2Cp^*]_2$ (M = Ir, Rh). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

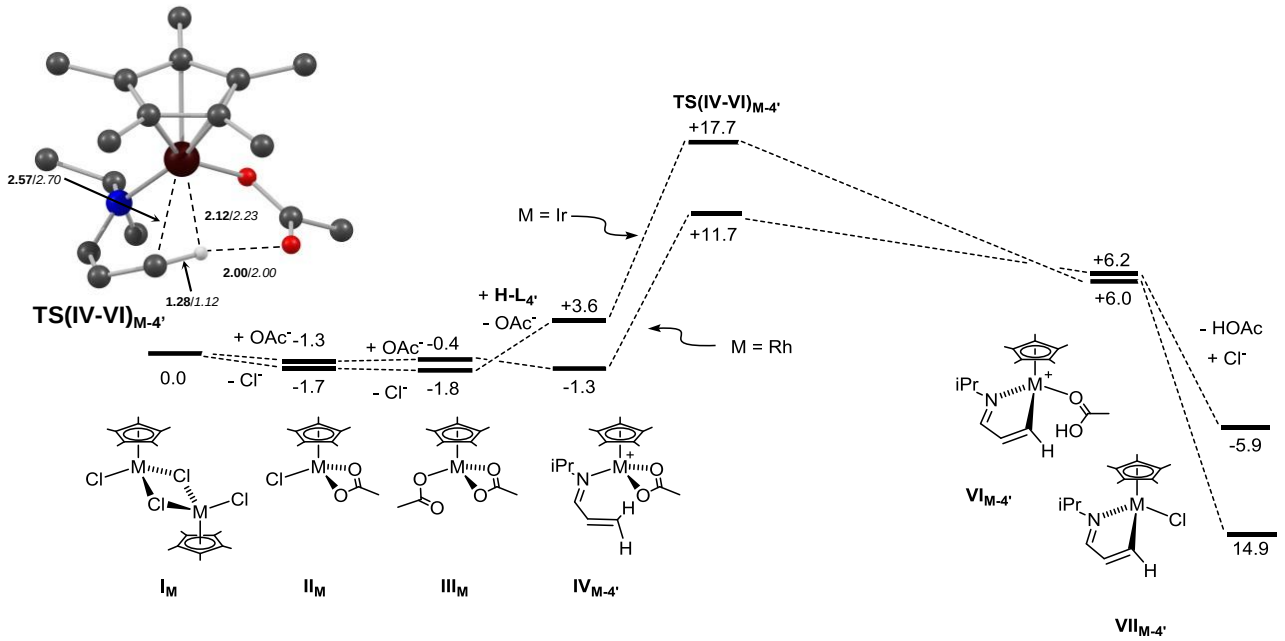


Table S13a. Computed energies (kcal/mol) for the reaction of **H-L$_5$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	64.2	66.8	71.4	-16.9	-24.0	64.8	102.9	-23.5	-30.7	7.9	**0.8**
TS(IV-VI)$_{Rh}$	77.3	77.4	83.2	-6.0	-13.2	74.6	115.1	-14.6	-21.8	17.3	**10.0**
VI_{Rh}	66.0	68.5	73.4	-14.0	-21.0	65.7	105.4	-21.7	-28.6	10.3	**3.3**
VII_{Rh}	-20.4	-18.5	-17.8	-25.0	-25.6	-22.1	4.3	-29.3	-29.9	-7.2	**-7.7**

Table S13b. Computed energies (kcal/mol) for the reaction of **H-L$_5$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	62.3	65.2	69.9	-18.7	-25.8	62.3	101.6	-26.3	-33.4	**5.4**	-1.8
TS(IV-VI)$_{Ir}$	75.0	76.6	82.1	-8.1	-15.6	72.8	113.2	-17.4	-24.8	**13.8**	6.3
VI_{Ir}	60.2	62.8	67.9	-20.2	-27.3	59.5	100.5	-28.5	-35.6	**4.1**	-3.0
VII_{Ir}	-28.0	-26.1	-25.2	-32.5	-33.1	-30.2	-3.1	-37.6	-38.2	**-15.5**	-16.1

Figure S7. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_5$** at [MCl$_2$Cp*]$_2$ (M = Ir, Rh). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.

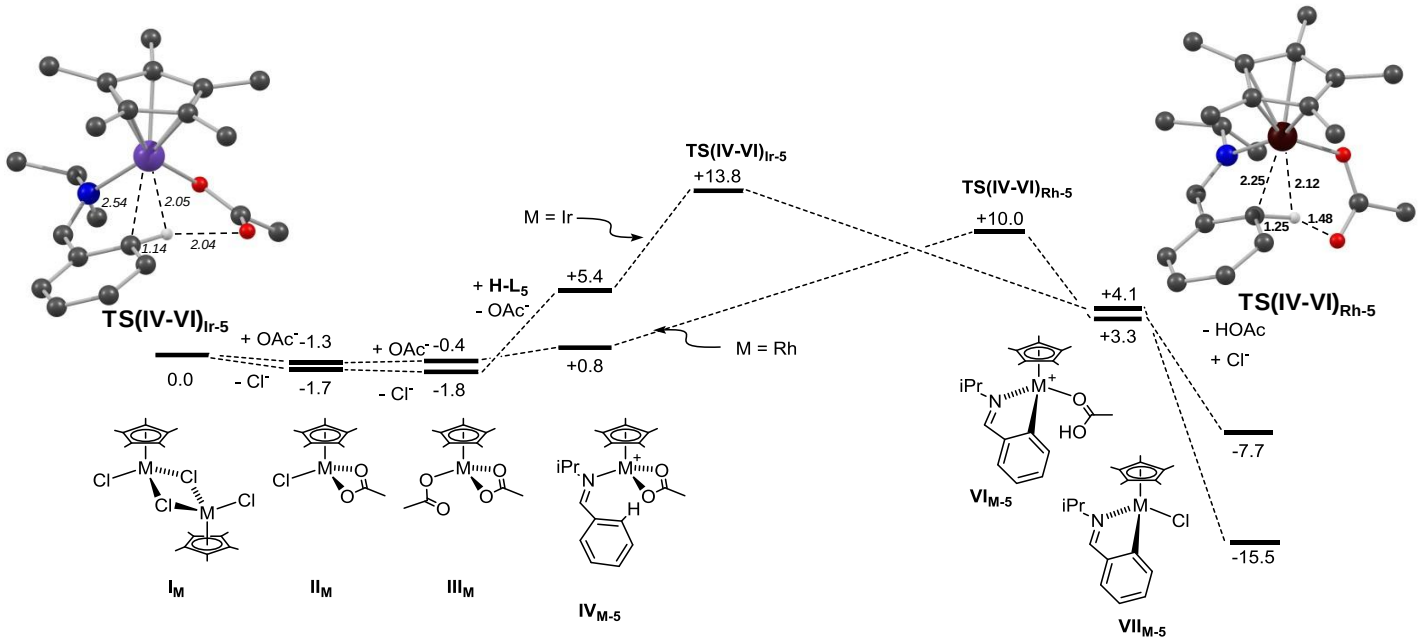


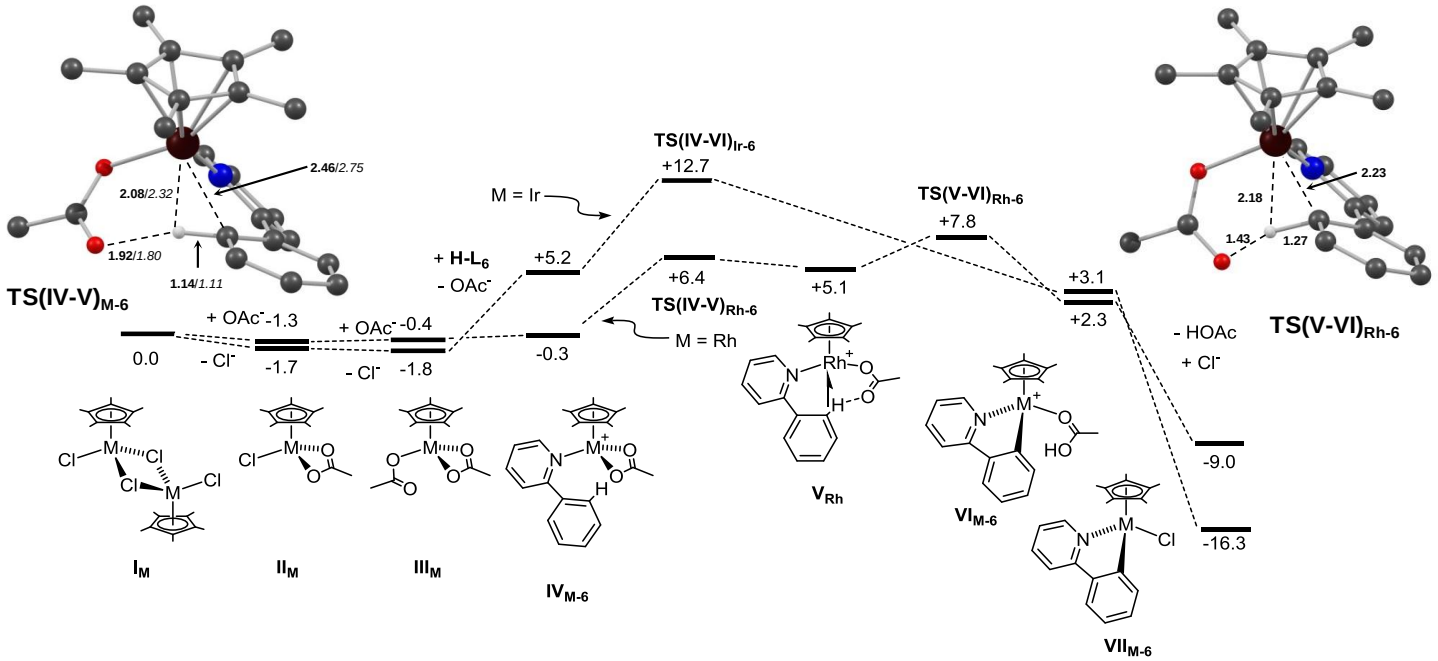
Table S14a. Computed energies (kcal/mol) for the reaction of **H-L$_6$** at [RhCl$_2$Cp*]$_2$ (**I$_{Rh}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Rh}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**
II_{Rh}	-23.4	-22.1	-23.6	-32.0	-32.7	-16.3	0.6	-24.8	-25.4	-0.6	**-1.3**
III_{Rh}	-47.1	-44.3	-40.1	-50.8	-51.3	-35.3	6.1	-46.0	-46.5	0.2	**-0.4**
IV_{Rh}	60.8	63.1	68.1	-19.1	-26.0	62.8	99.2	-24.4	-31.3	6.7	**-0.3**
$TS(IV\text{-}V)_{Rh}$	72.1	73.4	78.9	-10.9	-18.2	72.9	109.5	-16.8	-24.2	13.8	**6.4**
V_{Rh}	71.7	72.8	77.6	-12.0	-19.3	71.2	108.3	-18.4	-25.7	12.4	**5.1**
$TS(V\text{-}VI)_{Rh}$	72.4	71.9	77.7	-10.4	-17.5	71.5	109.2	-16.6	-23.7	14.9	**7.8**
VI_{Rh}	61.9	64.1	69.2	-17.5	-24.3	64.1	100.8	-22.5	-29.4	9.1	**2.3**
VII_{Rh}	-22.5	-21.2	-20.3	-28.2	-28.9	-22.3	1.5	-30.2	-30.9	-8.4	**-9.0**

Table S14b. Computed energies (kcal/mol) for the reaction of **H-L$_6$** at [IrCl$_2$Cp*]$_2$ (**I$_{Ir}$**). Data in bold are those used in the main text. See introduction to this section for definition of energy terms.

Structure	SCF	H_{0K}	G_{298}	G_{DCM}	G_{MeOH}	G_{D3}	G_{BS2}	$G_{D3\text{-}DCM}$	$G_{D3\text{-}MeOH}$	$G_{BS2\text{-}D3\text{-}DCM}$	$G_{BS2\text{-}D3\text{-}MeOH}$
I_{Ir}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	**0.0**	0.0
II_{Ir}	-24.8	-23.4	-24.5	-32.6	-33.3	-17.4	-0.7	-25.5	-26.2	**-1.7**	-2.3
III_{Ir}	-48.8	-45.9	-41.8	-52.3	-52.8	-37.3	4.2	-47.8	-48.3	**-1.8**	-2.2
IV_{Ir}	59.6	62.1	67.4	-20.0	-27.0	61.2	98.9	-26.3	-33.3	**5.2**	-1.9
$TS(IV\text{-}VI)_{Ir}$	71.1	72.6	77.8	-11.4	-18.8	70.7	109.0	-18.5	-25.8	**12.7**	5.4
VI_{Ir}	56.5	58.8	64.0	-23.2	-30.1	58.2	96.2	-29.0	-36.0	**3.1**	-3.8
VII_{Ir}	-29.8	-28.3	-27.4	-35.4	-36.1	-30.0	-5.7	-38.0	-38.8	**-16.3**	-17.1

Figure S8. Computed reaction profiles (kcal/mol) for C–H activation of **H-L$_6$** at [MCl$_2$Cp*]$_2$ (M = Ir, Rh). Computed transition state structures are shown for the C–H activation step, with data (Å) in plain text for M = Rh and italics for M = Ir. Non-participating H atoms are omitted for clarity.



14. Cartesian coordinates and calculated energies of all stationary points.

Cartesian coordinates are shown in Å and energies in atomic units.

AcO.log

```
SCF (BP86) Energy =     -228.501361393
Enthalpy 0K =           -228.454941
Enthalpy 298K =         -228.450378
Free Energy 298K =      -228.482794
PCM (DCM) Energy =      -228.5928155
PCM (MeOH) Energy =     -228.6016538
SCF (BP86+D3) Energy =  -228.5042578
SCF (BS2) Energy =      -228.6065408
Lowest Frequency =  30.7787 cm-1
O   1.12620  0.80575  0.00000
C   0.00000  0.22376  0.00000
O  -1.17210  0.70943  0.00000
C   0.04486 -1.36364  0.00000
H  -0.48996 -1.76127  0.88541
H   1.07794 -1.75961  0.00000
H  -0.48996 -1.76127 -0.88541
```

AcOH.log

```
SCF (BP86) Energy =     -229.088709030
Enthalpy 0K =           -229.028637
Enthalpy 298K =         -229.023982
Free Energy 298K =      -229.056007
PCM (DCM) Energy =      -229.0939666
PCM (MeOH) Energy =     -229.0946755
SCF (BP86+D3) Energy =  -229.0921525
SCF (BS2) Energy =      -229.1661934
Lowest Frequency =  62.0424 cm-1
O  -0.65950  1.20853  0.00002
C  -0.09257  0.12630 -0.00014
O  -0.77336 -1.06298 -0.00004
C   1.40378 -0.10143 -0.00006
H   1.69848 -0.68140  0.89001
H   1.92128  0.86620 -0.00512
H   1.69771 -0.69096 -0.88401
H  -1.72193 -0.80742  0.00045
```

Cl.log

```
SCF (BP86) Energy =     -15.1025038759
Enthalpy 0K =           -15.102504
Enthalpy 298K =         -15.101088
Free Energy 298K =      -15.117527
PCM (DCM) Energy =      -15.20132335
PCM (MeOH) Energy =     -15.21047981
SCF (BP86+D3) Energy =  -15.10250388
SCF (BS2) Energy =      -460.330815
Lowest Frequency =   N/A
Cl  0.00000  0.00000  0.00000
```

Ir_I.log

```
SCF (BP86) Energy =     -1049.57143254
Enthalpy 0K =           -1049.133175
Enthalpy 298K =         -1049.096228
Free Energy 298K =      -1049.203867
PCM (DCM) Energy =      -1049.593617
PCM (MeOH) Energy =     -1049.598021
SCF (BP86+D3) Energy =  -1049.680426
SCF (BS2) Energy =      -2831.049044
Lowest Frequency =  11.0006 cm-1
Ir  1.36881  0.36184  1.27876
Cl  0.95249  0.57252 -1.18249
Cl  2.20222 -1.87237  0.86461
C   1.64604  2.50901  1.58004
C   0.82292  1.97864  2.64264
C   1.59377  0.93449  3.34633
C   2.91231  0.86234  2.72347
C   2.94219  1.80230  1.60820
C   1.25256  3.60159  0.62999
C  -0.56813  2.42963  2.97808
C   1.14307  0.17824  4.56227
C   4.04192 -0.02201  3.15943
C   4.11784  2.09173  0.72074
Cl -0.95249 -0.57252  1.18249
Ir -1.36881 -0.36184 -1.27876
Cl -2.20222  1.87237 -0.86461
C  -1.64604 -2.50901 -1.58004
C  -0.82292 -1.97864 -2.64264
C  -1.59377 -0.93449 -3.34633
C  -2.91231 -0.86234 -2.72347
C  -2.94219 -1.80230 -1.60820
C  -1.25256 -3.60159 -0.62999
C   0.56813 -2.42963 -2.97808
C  -1.14307 -0.17824 -4.56227
C  -4.04192  0.02201 -3.15943
C  -4.11784 -2.09173 -0.72074
H   1.43034  4.59049  1.09318
H   1.83466  3.55018 -0.30235
H   0.18821  3.52470  0.35632
H  -0.52993  3.32412  3.62805
H  -1.13450  2.67861  2.06676
H  -1.12720  1.64431  3.50856
H   4.71651  2.92765  1.12954
H   4.77407  1.21283  0.62939
H   3.79057  2.37279 -0.29245
H   1.35801  0.75516  5.48168
H   0.05971 -0.01649  4.52960
H   1.65549 -0.79284  4.63930
H   4.65972  0.50323  3.91166
H   3.66841 -0.95657  3.60346
H   4.68432 -0.29796  2.31018
H  -4.65972 -0.50323 -3.91166
H  -4.68432  0.29796 -2.31018
H  -3.66841  0.95657 -3.60346
H  -1.35801 -0.75516 -5.48168
H  -1.65549  0.79284 -4.63930
H  -0.05971  0.01649 -4.52960
H   0.52993 -3.32412 -3.62805
H   1.12720 -1.64431 -3.50856
H   1.13450 -2.67861 -2.06676
H  -4.71651 -2.92765 -1.12954
H  -3.79057 -2.37279  0.29245
H  -4.77407 -1.21283 -0.62939
H  -1.43034 -4.59049 -1.09318
H  -0.18821 -3.52470 -0.35632
H  -1.83466 -3.55018  0.30235
```

Ir_II.log

```
SCF (BP86) Energy =     -738.224106442
Enthalpy 0K =           -737.956260
Enthalpy 298K =         -737.935353
Free Energy 298K =      -738.006280
PCM (DCM) Energy =      -738.2407828
PCM (MeOH) Energy =     -738.2436651
SCF (BP86+D3) Energy =  -738.2701634
SCF (BS2) Energy =      -1183.801799
Lowest Frequency =  14.3515 cm-1
C  -1.05135  1.70673  0.00018
C  -1.35236  0.89094 -1.17459
C  -1.85774 -0.40440 -0.73438
C  -1.85766 -0.40451  0.73450
C  -1.35224  0.89076  1.17486
Ir  0.15470 -0.12516 -0.00002
O   2.02681  0.25831 -1.09857
C   2.69477  0.32181 -0.00006
C   4.19612  0.41694 -0.00005
C  -1.18336  1.32830 -2.60033
C  -2.34833 -1.52468 -1.60439
C  -2.34816 -1.52492  1.60440
C  -1.18311  1.32791  2.60065
C  -0.60502  3.14080  0.00026
Cl  0.86076 -2.41622 -0.00034
O   2.02685  0.25804  1.09847
H  -2.09064  1.85702 -2.94719
H  -0.32679  2.01131 -2.71003
```

```
H  -1.01439  0.46817 -3.26584
H  -2.09038  1.85652  2.94768
H  -1.01402  0.46768  3.26600
H  -0.32657  2.01095  2.71036
H  -3.45197 -1.50753 -1.67466
H  -1.94075 -1.44883 -2.62418
H  -2.03857 -2.49948 -1.19657
H  -3.45179 -1.50775  1.67481
H  -2.03849 -2.49966  1.19638
H  -1.94045 -1.44925  2.62415
H  -1.47509  3.82449  0.00035
H   0.00235  3.37174  0.88951
H   0.00227  3.37186 -0.88902
H   4.55039  0.93408 -0.90388
H   4.55047  0.93268  0.90455
H   4.61101 -0.60572 -0.00089
```

Ir_III.log

```
SCF (BP86) Energy =     -951.661245340
Enthalpy 0K =           -951.344533
Enthalpy 298K =         -951.320087
Free Energy 298K =      -951.399113
PCM (DCM) Energy =      -951.6743649
PCM (MeOH) Energy =     -951.676699
SCF (BP86+D3) Energy =  -951.7143461
SCF (BS2) Energy =      -952.0803843
Lowest Frequency =  15.4883 cm-1
C  -1.88820  0.01137  1.06472
C  -2.19414  0.39948 -0.29306
C  -1.68015 -0.65622 -1.18452
C  -1.10553 -1.70426 -0.35806
C  -1.19654 -1.28906  1.03651
Ir -0.03820  0.18097 -0.05756
O   0.70537  2.03749 -1.01145
C   1.26576  2.40413  0.08583
C   2.15863  3.61614  0.14034
C  -2.92663  1.63167 -0.74081
C  -1.82510 -0.67369 -2.67883
C  -0.54204 -3.00820 -0.84206
C  -0.77808 -2.10379  2.22463
C  -2.22232  0.77822  2.31125
O   1.92262 -0.33187 -0.53357
O   1.06299  1.67982  1.13095
H  -3.99310  1.40424 -0.92651
H  -2.87927  2.42770  0.01840
H  -2.49913  2.03342 -1.67319
H  -1.52283 -2.89436  2.43645
H   0.20308 -2.56264  2.02988
H  -0.68788 -1.47565  3.12485
H  -2.81517 -1.07374 -2.96844
H  -1.73355  0.33999 -3.10011
H  -1.05393 -1.30309 -3.14866
H  -1.30471 -3.80322 -0.74217
H  -0.25167 -2.95251 -1.90289
H   0.34644 -3.28154 -0.25373
H  -3.14574  0.37990  2.77094
H  -1.41222  0.69872  3.05312
H  -2.38000  1.84687  2.09962
H   1.83238  4.36719 -0.59428
H   2.16646  4.04537  1.15294
H   3.18774  3.31045 -0.11483
C   2.54419 -1.37447 -0.00584
O   2.06593 -2.20720  0.78042
C   4.00781 -1.44789 -0.44918
H   4.37732 -2.47840 -0.34522
H   4.13318 -1.09474 -1.48413
H   4.61302 -0.79528  0.20385
```

Rh_I.log

```
SCF (BP86) Energy =     -1061.91976380
Enthalpy 0K =           -1061.481477
Enthalpy 298K =         -1061.444513
Free Energy 298K =      -1061.551530
PCM (DCM) Energy =      -1061.943255
PCM (MeOH) Energy =     -1061.947956
SCF (BP86+D3) Energy =  -1062.026567
SCF (BS2) Energy =      -2842.366139
Lowest Frequency =  13.3006 cm-1
Rh  1.34006  0.32441  1.23253
Cl  0.96901  0.58733 -1.20852
Cl  2.21781 -1.88436  0.85937
C   1.61525  2.47191  1.53591
C   0.79426  1.94440  2.59406
C   1.56202  0.90405  3.29520
C   2.87833  0.83460  2.68021
C   2.90611  1.76692  1.56519
C   1.21619  3.56216  0.58680
C  -0.59691  2.39791  2.92172
C   1.10152  0.13347  4.49732
C   4.01048 -0.04128  3.12398
C   4.07442  2.04252  0.66524
Cl -0.96901 -0.58733  1.20852
Rh -1.34006 -0.32441 -1.23253
Cl -2.21781  1.88436 -0.85937
C  -1.61525 -2.47191 -1.53591
C  -0.79426 -1.94440 -2.59406
C  -1.56202 -0.90405 -3.29520
C  -2.87833 -0.83460 -2.68021
C  -2.90611 -1.76692 -1.56519
C  -1.21619 -3.56216 -0.58680
C   0.59691 -2.39791 -2.92172
C  -1.10152 -0.13347 -4.49732
C  -4.01048  0.04128 -3.12398
C  -4.07442 -2.04252 -0.66524
H   1.33137  4.54845  1.07531
H   1.83815  3.55404 -0.32038
H   0.16671  3.44703  0.26982
H  -0.55833  3.32867  3.51911
H  -1.17603  2.59275  2.00448
H  -1.14175  1.63961  3.50309
H   4.67299  2.88856  1.05325
H   4.73348  1.16448  0.58761
H   3.73905  2.30258 -0.35094
H   1.29861  0.70397  5.42488
H   0.02035 -0.06964  4.44782
H   1.62190 -0.83342  4.57323
H   4.62272  0.49294  3.87494
H   3.64166 -0.97498  3.57342
H   4.65771 -0.31876  2.27905
H  -4.62272 -0.49294 -3.87494
H  -4.65771  0.31876 -2.27905
H  -3.64166  0.97498 -3.57342
H  -1.29861 -0.70397 -5.42488
H  -1.62190  0.83342 -4.57323
H  -0.02035  0.06964 -4.44782
H   0.55833 -3.32867 -3.51911
H   1.14175 -1.63961 -3.50309
H   1.17603 -2.59275 -2.00448
H  -4.67299 -2.88856 -1.05325
H  -3.73905 -2.30258  0.35094
H  -4.73348 -1.16448 -0.58761
H  -1.33137 -4.54845 -1.07531
H  -0.16671 -3.44703 -0.26982
H  -1.83815 -3.55404  0.32038
```

Rh_II.log

```
SCF (BP86) Energy =     -744.395956299
Enthalpy 0K =           -744.128317
Enthalpy 298K =         -744.107277
Free Energy 298K =      -744.178579
PCM (DCM) Energy =      -744.4138347
PCM (MeOH) Energy =     -744.4169504
SCF (BP86+D3) Energy =  -744.4406672
SCF (BS2) Energy =      -1189.457513
Lowest Frequency =  13.2428 cm-1
C   0.95219  1.70454 -0.00013
C   1.28478  0.90607  1.17245
C   1.83139 -0.36549  0.73198
C   1.83154 -0.36564 -0.73165
C   1.28497  0.90580 -1.17248
Rh -0.19195 -0.15521 -0.00002
O  -2.03834  0.18666  1.10201
C  -2.70093  0.22693 -0.00005
C  -4.20675  0.26746  0.00003
```

```
C   1.09143  1.33606  2.59666
C   2.35027 -1.47631  1.59638
C   2.35056 -1.47665 -1.59572
C   1.09186  1.33551 -2.59681
C   0.44032  3.11615 -0.00033
Cl -0.74943 -2.47327 -0.00006
O  -2.03837  0.18673 -1.10211
H   1.96300  1.92407  2.94018
H   0.19334  1.96377  2.70605
H   0.98021  0.47013  3.26660
H   1.96342  1.92355 -2.94028
H   0.98086  0.46944 -3.26661
H   0.19372  1.96311 -2.70649
H   3.45586 -1.45932  1.62612
H   1.98102 -1.38966  2.62960
H   2.02501 -2.45416  1.20738
H   3.45616 -1.45971 -1.62521
H   2.02516 -2.45441 -1.20662
H   1.98154 -1.39017 -2.62904
H   1.27806  3.83917 -0.00036
H  -0.17611  3.31965 -0.89006
H  -0.17623  3.31986  0.88927
H  -4.57986  0.76977  0.90483
H  -4.57993  0.77113 -0.90400
H  -4.58354 -0.76984 -0.00078
```

Rh_III.log

```
SCF (BP86) Energy =     -957.832721562
Enthalpy 0K =           -957.516178
Enthalpy 298K =         -957.491674
Free Energy 298K =      -957.570238
PCM (DCM) Energy =      -957.8467624
PCM (MeOH) Energy =     -957.8492812
SCF (BP86+D3) Energy =  -957.8843142
SCF (BS2) Energy =      -957.7360578
Lowest Frequency =  26.5366 cm-1
C  -1.91752  0.06349  1.01416
C  -2.19875  0.32614 -0.37258
C  -1.63071 -0.77401 -1.16577
C  -1.04378 -1.72801 -0.24423
C  -1.18044 -1.20467  1.10123
Rh -0.04856  0.21334 -0.08771
O   0.56849  2.09274 -1.01995
C   1.16496  2.43845  0.06479
C   2.03033  3.67333  0.11252
C  -2.94000  1.50106 -0.94093
C  -1.74067 -0.91736 -2.65593
C  -0.41542 -3.04186 -0.60386
C  -0.71777 -1.88555  2.35452
C  -2.30376  0.91351  2.18934
O   1.86509 -0.31873 -0.67940
O   1.03445  1.68620  1.10023
H  -3.97922  1.21775 -1.19233
H  -2.98121  2.33836 -0.22765
H  -2.45797  1.86803 -1.86113
H  -1.37047 -2.74583  2.59563
H   0.31665 -2.23884  2.21496
H  -0.73514 -1.19664  3.21322
H  -2.70419 -1.38502 -2.93474
H  -1.68594  0.06263 -3.15623
H  -0.93129 -1.54528 -3.05884
H  -1.14367 -3.85929 -0.44415
H  -0.10900 -3.06707 -1.66104
H   0.47291 -3.22365  0.01948
H  -3.19007  0.48989  2.69719
H  -1.48561  0.96592  2.92507
H  -2.54766  1.94249  1.88387
H   1.65255  4.43480 -0.58602
H   2.07341  4.07583  1.13533
H   3.05419  3.40159 -0.19657
C   2.55221 -1.23040 -0.01889
O   2.15225 -1.92536  0.93180
C   3.99279 -1.35098 -0.52968
H   4.36244 -2.37324 -0.36002
H   4.07177 -1.08271 -1.59393
H   4.63131 -0.65764  0.04499
```

1_Ir_IV.log

```
SCF (BP86) Energy =     -1183.86451158
Enthalpy 0K =           -1183.383667
Enthalpy 298K =         -1183.351516
Free Energy 298K =      -1183.447008
PCM (DCM) Energy =      -1183.914442
PCM (MeOH) Energy =     -1183.919386
SCF (BP86+D3) Energy =  -1183.953372
SCF (BS2) Energy =      -1184.316309
Lowest Frequency =  14.4129 cm-1
C  -2.28979 -1.58573  0.11765
C  -2.79435 -0.44717 -0.60955
C  -1.89779 -0.17761 -1.74403
C  -0.85081 -1.19687 -1.72242
C  -1.07349 -2.04985 -0.57148
Ir -0.77022  0.01777  0.10640
O  -1.25233  1.70178  1.44400
C  -0.64797  1.14604  2.43963
C  -0.54690  1.81663  3.77908
C  -4.02621  0.34370 -0.28649
C  -2.15874  0.82169 -2.83347
C   0.22911 -1.37848 -2.74822
C  -0.30669 -3.28912 -0.22154
C  -2.91354 -2.24340  1.31430
N   0.96240  1.16342 -0.31137
C   0.68787  2.57599 -0.78282
C   2.22995  0.80956 -0.27740
C   2.83501 -0.39874  0.18551
N   4.19916 -0.64112 -0.07553
C   4.55887 -1.82019  0.51318
C   3.45169 -2.35787  1.18182
C   2.37431 -1.47552  0.97897
O  -0.11671 -0.00650  2.21775
H   2.94045  1.55757 -0.66207
H   3.44952 -3.27729  1.76492
H   5.57657 -2.19739  0.41924
C   1.18812  2.81004 -2.21955
H  -0.40935  2.66257 -0.77694
C   1.25058  3.61619  0.20071
H  -4.86904 -0.01560 -0.90517
H  -4.31426  0.24035  0.76997
H  -3.88741  1.41505 -0.49894
H  -0.77408 -4.16058 -0.71729
H   0.74163 -3.23246 -0.54956
H  -0.31812 -3.48149  0.86256
H  -2.87366  0.40471 -3.56691
H  -2.59623  1.75198 -2.43811
H  -1.23996  1.08143 -3.38028
H  -0.11262 -2.08014 -3.53090
H   0.48512 -0.42871 -3.24171
H   1.14551 -1.79169 -2.29991
H  -3.52247 -3.11006  0.99820
H  -2.15050 -2.60918  2.01897
H  -3.57361 -1.55242  1.85997
H   1.37876 -1.53828  1.41003
H  -1.30818  2.60316  3.87693
H  -0.65735  1.07340  4.58317
H   0.45208  2.27393  3.88522
H   0.82861  3.78805 -2.57902
H   2.28983  2.82697 -2.28259
H   0.81663  2.03504 -2.90951
H   0.95311  4.62809 -0.12048
H   0.85762  3.45108  1.21493
H   2.35347  3.58901  0.23906
C   5.10313  0.19605 -0.86461
H   4.73953  0.31081 -1.89873
H   5.22367  1.19148 -0.40530
H   6.08892 -0.28826 -0.89415
```

1_Ir_IV_TS_VI.log

```
SCF (BP86) Energy =     -1183.84248453
Enthalpy 0K =           -1183.363635
Enthalpy 298K =         -1183.331743
Free Energy 298K =      -1183.427157
PCM (DCM) Energy =      -1183.895256
PCM (MeOH) Energy =     -1183.900687
SCF (BP86+D3) Energy =  -1183.933413
```

SCF (BS2) Energy = -1184.295071
Lowest Frequency = -40.0508 cm-1
N 3.74237 -0.92461 0.36563
C 2.54495 -0.24371 0.54228
C 1.59516 -1.15579 1.06872
C 2.24986 -2.41247 1.18368
C 3.56359 -2.23504 0.74818
C 2.28985 1.11138 0.15555
N 1.05494 1.47852 -0.09327
C 0.73614 2.93534 -0.25161
H 3.10475 1.84653 0.09280
Ir -0.45736 -0.00010 -0.09589
C -2.45060 -0.83201 -0.53685
C -2.08096 0.26230 -1.45322
C -0.91377 -0.19233 -2.23832
C -0.52153 -1.48503 -1.74569
C -1.47848 -1.87715 -0.68428
H 1.84340 -3.32096 1.62502
H 4.39465 -2.93823 0.70663
C -1.46854 -3.16985 0.07587
C 0.57334 -2.35486 -2.28871
C -0.29703 0.55362 -3.38380
C -2.88768 1.50053 -1.70330
C -3.63160 -0.84121 0.38666
C 0.87726 3.66842 1.09421
C 1.57441 3.58613 -1.36698
H -0.32480 2.95464 -0.54888
H -4.50273 -1.28550 -0.12886
H -3.42679 -1.43319 1.29066
H -3.90975 0.17724 0.69734
H 0.15150 -3.09513 -2.99327
H 1.32492 -1.76486 -2.83502
H 1.08835 -2.90609 -1.48727
H -3.69738 1.28315 -2.42510
H -3.35372 1.87122 -0.77765
H -2.27410 2.30982 -2.12860
H -0.81859 0.28926 -4.32208
H -0.38405 1.64342 -3.25520
H 0.76694 0.30286 -3.51116
H -2.23421 -3.85344 -0.33442
H -0.49359 -3.67347 0.00151
H -1.68836 -2.99689 1.14084
O -1.04598 -0.99990 2.76189
C -1.24843 0.22862 2.73346
O -1.01412 0.99556 1.67414
C -1.74869 0.99442 3.94938
H -2.15291 1.98094 3.68256
H -2.51181 0.39532 4.46853
H -0.90882 1.13394 4.65140
H 0.65384 -0.93535 1.62644
H 0.53811 4.71183 0.98511
H 0.26696 3.17462 1.86444
H 1.93004 3.68757 1.42612
H 1.21123 4.61176 -1.54190
H 2.64036 3.66498 -1.09248
H 1.49951 3.02814 -2.31467
C 4.97205 -0.37198 -0.20683
H 4.83052 -0.10317 -1.26641
H 5.29252 0.51803 0.35798
H 5.76449 -1.12947 -0.13615

1_Ir_VI.log
SCF (BP86) Energy = -1183.85882588
Enthalpy 0K = -1183.378776
Enthalpy 298K = -1183.346453
Free Energy 298K = -1183.442086
PCM (DCM) Energy = -1183.906978
PCM (MeOH) Energy = -1183.911593
SCF (BP86+D3) Energy = -1183.950171
SCF (BS2) Energy = -1184.30911
Lowest Frequency = 17.7672 cm-1
N 3.75940 0.24238 -0.87470
C 2.49043 0.57830 -0.41677
C 1.58308 -0.48325 -0.67057
C 2.36692 -1.49951 -1.30030
C 3.68317 -1.01819 -1.41038
C 2.00086 1.72193 0.26006
N 0.70501 1.73108 0.52319
C 0.17574 2.90142 1.27475
H 2.63477 2.56126 0.58108
Ir -0.34085 -0.10049 -0.07794
C -2.56620 -0.79215 0.06190
C -2.57713 0.47877 -0.57445
C -1.66203 0.40746 -1.73294
C -1.21966 -0.97867 -1.86668
C -1.69493 -1.70716 -0.70369
H 2.04396 -2.48097 -1.64744
H 4.56714 -1.48821 -1.84131
C -1.57007 -3.18644 -0.46245
C -0.51469 -1.55601 -3.05843
C -1.48725 1.47794 -2.77273
C -3.48022 1.63252 -0.24447
C -3.31805 -1.18419 1.29892
C -0.39974 3.94468 0.30121
C -0.83047 2.47135 2.34783
H 1.04055 3.36579 1.79082
H -4.19672 -1.79882 1.03032
H -2.69119 -1.78717 1.97557
H -3.67810 -0.30783 1.85815
H -1.25863 -1.77190 -3.84707
H 0.23010 -0.86150 -3.47451
H -0.00494 -2.50036 -2.81751
H -4.42316 1.53204 -0.81412
H -3.74679 1.66730 0.82306
H -3.04086 2.60256 -0.51921
H -2.31868 1.44178 -3.50123
H -1.47845 2.48362 -2.32607
H -0.54659 1.34695 -3.32864
H -2.42124 -3.72767 -0.91568
H -0.64574 -3.59248 -0.90164
H -1.56528 -3.42361 0.61324
O 1.85064 -2.00566 1.78796
C 0.88357 -1.45485 2.49886
O 0.02968 -0.65631 2.03153
C 0.86355 -1.85352 3.94889
H 0.00383 -1.40234 4.45934
H 0.82326 -2.95204 4.03104
H 1.80014 -1.52904 4.43203
H 1.81219 -1.64098 0.84471
H -0.76222 4.82500 0.85759
H 0.36482 4.28147 -0.41795
H -1.24569 3.52815 -0.26724
H -1.19070 3.35735 2.89586
H -1.69792 1.96700 1.89308
H -0.37327 1.77540 3.06736
C 4.95698 1.07977 -0.81516
H 4.81699 2.00148 -1.40343
H 5.19205 1.34624 0.22848
H 5.80501 0.51964 -1.23293

1_Ir_VII.log
SCF (BP86) Energy = -970.007659634
Enthalpy 0K = -969.588815
Enthalpy 298K = -969.560374
Free Energy 298K = -969.647181
PCM (DCM) Energy = -970.0236579
PCM (MeOH) Energy = -970.0269701
SCF (BP86+D3) Energy = -970.0881969
SCF (BS2) Energy = -1415.626112
Lowest Frequency = 18.7076 cm-1
N -3.70826 -1.09106 0.16761
C -2.55121 -0.31333 0.15305
C -1.41109 -1.14264 -0.00860
C -1.92035 -2.46952 -0.10673
C -3.31533 -2.40183 0.00722
C -2.33849 1.08056 0.19958
N -1.06263 1.44586 0.16173
C -0.71411 2.88386 0.06792
H -3.13989 1.83081 0.23563
Ir 0.33823 -0.13692 -0.11642
Cl -0.04922 0.17691 -2.50929
C 2.66552 -0.03580 -0.39873
C 2.35777 0.67217 0.79326
C 1.59559 -0.22760 1.67825

```
C   1.54039 -1.53849  1.03594
C   2.12427 -1.40731 -0.28732
H  -1.35967 -3.39095 -0.26369
H  -4.06354 -3.19549 -0.00873
C   2.35084 -2.49594 -1.29866
C   1.06664 -2.80921  1.68258
C   1.20999  0.07335  3.10087
C   2.76455  2.07535  1.14543
C   3.38006  0.48007 -1.61313
H   0.38786  2.90751  0.05009
C  -1.22017  3.50831 -1.24699
C  -1.18926  3.66405  1.30946
H   4.30791 -0.09303 -1.79216
H   2.73453  0.37877 -2.50413
H   3.65120  1.54211 -1.50828
H   1.87636 -3.24840  2.29501
H   0.19852 -2.63259  2.33625
H   0.77130 -3.55805  0.93185
H   3.67271  2.07083  1.77762
H   2.98738  2.67546  0.24894
H   1.97813  2.59705  1.71582
H   2.06245 -0.08936  3.78861
H   0.88407  1.11965  3.21653
H   0.38113 -0.57138  3.43229
H   3.39358 -2.86588 -1.26370
H   1.68302 -3.35309 -1.11893
H   2.14819 -2.12726 -2.31725
C  -5.07458 -0.60930  0.28278
H  -5.76112 -1.46881  0.26816
H  -5.22394 -0.05915  1.22896
H  -5.33266  0.05766 -0.55936
H  -0.83552  4.53775 -1.35437
H  -0.88367  2.90277 -2.10314
H  -2.32358  3.55736 -1.26602
H  -0.82430  4.70476  1.26813
H  -2.29134  3.70226  1.36742
H  -0.81630  3.19969  2.23797
```

1_L-H_cis.log

```
SCF (BP86) Energy =     -460.876948954
Enthalpy 0K =           -460.666219
Enthalpy 298K =         -460.654209
Free Energy 298K =      -460.704815
PCM (DCM) Energy =      -460.880378
PCM (MeOH) Energy =     -460.8809979
SCF (BP86+D3) Energy =  -460.8975784
SCF (BS2) Energy =      -460.9917913
Lowest Frequency =  32.9000 cm-1
N  -1.74920  0.72351  0.00006
C  -1.12994 -0.52830  0.00001
C  -2.15075 -1.49592 -0.00004
C  -3.39514 -0.82198 -0.00002
C  -3.11242  0.54429  0.00005
C   0.29326 -0.80247 -0.00002
N   1.24418  0.07608 -0.00001
C   2.62136 -0.42081 -0.00001
H   0.51856 -1.89327 -0.00006
H  -1.98222 -2.57304 -0.00010
H  -4.38912 -1.26712 -0.00002
H  -3.77819  1.40696  0.00008
C   3.33329  0.07709 -1.27202
C   3.33327  0.07700  1.27204
H   2.63675 -1.53730 -0.00005
C  -1.08970  2.03159 -0.00003
H  -1.37951  2.60382 -0.89776
H  -1.37883  2.60363  0.89806
H  -0.00307  1.86191 -0.00042
H   4.38272 -0.26412  1.29090
H   3.32380  1.17984  1.30854
H   2.82914 -0.29870  2.17784
H   4.38273 -0.26404 -1.29089
H   2.82915 -0.29854 -2.17785
H   3.32382  1.17993 -1.30842
```

1_L-H_trans.log

```
SCF (BP86) Energy =     -460.871831105
Enthalpy 0K =           -460.661427
Enthalpy 298K =         -460.649338
Free Energy 298K =      -460.699996
PCM (DCM) Energy =      -460.877906982
PCM (MeOH) Energy =     -460.878996338
SCF (BP86+D3) Energy =  -460.892168144109
SCF (BS2) Energy =      -460.987475719
Lowest Frequency =  38.3849 cm-1
N  -2.14943  0.59769 -0.00057
C  -1.00053 -0.19954 -0.00039
C  -1.42411 -1.53747  0.00033
C  -2.83976 -1.54654  0.00013
C  -3.26042 -0.21591 -0.00012
C   0.33859  0.35921 -0.00043
N   1.39860 -0.38010 -0.00005
C   2.69258  0.30068 -0.00003
H   0.41138  1.47192 -0.00061
H  -0.74653 -2.38944  0.00054
H  -3.49329 -2.41802  0.00014
H  -4.26009  0.21691 -0.00024
C   3.46478 -0.09953  1.27187
C   3.46519 -0.10028 -1.27145
H   2.56252  1.41108 -0.00037
C  -2.19052  2.05525  0.00040
H  -3.24256  2.37602 -0.00515
H  -1.70452  2.46937  0.90023
H  -1.69503  2.47038 -0.89368
H   4.46211  0.37322 -1.28877
H   3.59531 -1.19519 -1.30770
H   2.91790  0.20729 -2.17804
H   4.46170  0.37396  1.28923
H   2.91719  0.20857  2.17810
H   3.59487 -1.19443  1.30881
```

1_Rh_IV.log

```
SCF (BP86) Energy =     -1190.03523335
Enthalpy 0K =           -1189.554765
Enthalpy 298K =         -1189.522485
Free Energy 298K =      -1189.618100
PCM (DCM) Energy =      -1190.085381
PCM (MeOH) Energy =     -1190.090390
SCF (BP86+D3) Energy =  -1190.121478
SCF (BS2) Energy =      -1189.971719
Lowest Frequency =  14.6189 cm-1
C  -2.35143 -1.61095  0.03419
C  -2.85788 -0.46134 -0.66973
C  -1.93870 -0.14515 -1.76621
C  -0.87868 -1.14437 -1.75003
C  -1.11759 -2.03695 -0.63861
Rh -0.87082  0.00855  0.12089
O  -1.45791  1.61066  1.47380
C  -0.88223  1.02291  2.46697
C  -0.84794  1.64641  3.83449
C  -4.10776  0.30144 -0.35300
C  -2.17495  0.89880 -2.81751
C   0.23300 -1.27395 -2.74850
C  -0.33714 -3.27073 -0.30334
C  -2.98584 -2.31048  1.19997
N   0.85298  1.19036 -0.25416
C   0.54953  2.60715 -0.67747
C   2.12314  0.85652 -0.22374
C   2.73510 -0.35725  0.22093
N   4.09678 -0.59758 -0.04985
C   4.45974 -1.78177  0.52779
C   3.35636 -2.32335  1.19898
C   2.27776 -1.43841  1.00914
O  -0.31550 -0.10897  2.23193
H   2.83096  1.61917 -0.58740
H   3.35752 -3.24621  1.77669
H   5.47678 -2.15841  0.42500
C   1.10028  2.93120 -2.07886
H  -0.54969  2.65920 -0.71526
C   1.03435  3.61718  0.37723
H  -4.92640 -0.03729 -1.01480
H  -4.42979  0.14846  0.68737
H  -3.97461  1.38260 -0.51337
H  -0.77235 -4.13627 -0.83811
H   0.71901 -3.18558 -0.59868
```

H -0.37709 -3.49694 0.77351
H -2.85821 0.50686 -3.59410
H -2.64178 1.80359 -2.39703
H -1.24213 1.19575 -3.31971
H -0.06136 -1.98110 -3.54575
H   0.46518 -0.31119 -3.22786
H   1.15238 -1.65814 -2.28054
H -3.53831 -3.20307 0.85313
H -2.23144 -2.64655 1.92858
H -3.70013 -1.66024 1.72679
H   1.28584 -1.50041 1.44979
H -1.66307 2.37515 3.94842
H -0.91668 0.86771 4.60882
H   0.11387 2.17042 3.97222
H   0.71039 3.90792 -2.40897
H   2.20150 3.00286 -2.09204
H   0.79729 2.17416 -2.82070
H   0.72361 4.63517 0.08944
H   0.60023 3.39313 1.36285
H   2.13486 3.61346 0.46481
C   4.99619 0.24715 -0.83606
H   4.62527 0.37425 -1.86609
H   5.12096 1.23737 -0.36665
H   5.98125 -0.23777 -0.87807

1_Rh_IV_TS_VI.log
SCF (BP86) Energy =   -1190.01442240
Enthalpy 0K =   -1189.535588
Enthalpy 298K =   -1189.503598
Free Energy 298K =   -1189.599278
PCM (DCM) Energy =   -1190.067305
PCM (MeOH) Energy =   -1190.072818
SCF (BP86+D3) Energy = -1190.102674
SCF (BS2) Energy =   -1189.952062
Lowest Frequency = -40.9386 cm-1
C -2.48370 -0.82535 -0.69436
C -2.07897 0.31912 -1.52052
C -0.86733 -0.07086 -2.26454
C -0.48622 -1.38225 -1.83164
C -1.49038 -1.84559 -0.84886
Rh -0.53932 0.00118 -0.09655
O -1.26184 0.91572 1.64122
C -1.48899 0.05468 2.61847
C -2.06281 0.67794 3.88320
C -2.87403 1.57204 -1.71859
C -0.20178 0.75319 -3.32520
C   0.65188 -2.20696 -2.35350
C -1.49336 -3.17631 -0.16114
C -3.71354 -0.90145 0.15761
N   0.96605 1.48388 0.00797
C   0.64995 2.94208 -0.09409
C   2.19751 1.10022 0.23404
C   2.48300 -0.26561 0.56481
N   3.71866 -0.88114 0.38208
C   3.60970 -2.20251 0.74469
C   2.30567 -2.45398 1.17912
C   1.58929 -1.23468 1.08047
O -1.23014 -1.16480 2.54165
H   3.01453 1.83690 0.19557
H   1.94424 -3.39261 1.59594
H   4.47522 -2.86188 0.69024
C   1.57939 3.68445 -1.07202
H -0.37813 2.97843 -0.49142
C   0.64765 3.58055 1.30757
H -3.66638 1.39849 -2.47147
H -3.36419 1.88872 -0.78518
H -2.24994 2.40244 -2.08329
H -2.23169 -3.84475 -0.64181
H -0.50942 -3.66420 -0.21876
H -1.76411 -3.06322 0.90024
H -0.68814 0.56443 -4.30022
H -0.28764 1.83138 -3.12019
H   0.86455 0.50328 -3.43160
H   0.27732 -2.94171 -3.09029
H   1.40650 -1.58489 -2.85805
H   1.15126 -2.76501 -1.54628
H -4.55551 -1.30039 -0.43783
H -3.55852 -1.56344 1.02193
H -4.00776 0.09105 0.53118
H   0.60019 -1.06798 1.55518
H -2.51804 1.66016 3.69301
H -2.80066 -0.00768 4.32628
H -1.24826 0.80342 4.61707
H   1.20095 4.70865 -1.22117
H   2.60731 3.77899 -0.68199
H   1.62319 3.18804 -2.05557
H   0.30949 4.62781 1.23901
H -0.02811 3.02952 1.97770
H   1.66423 3.57731 1.73841
C   4.92605 -0.25145 -0.15622
H   4.77171 0.07816 -1.19658
H   5.22052 0.61219 0.46185
H   5.74375 -0.98476 -0.13609

1_Rh_VI.log
SCF (BP86) Energy =   -1190.02354569
Enthalpy 0K =   -1189.543882
Enthalpy 298K =   -1189.511417
Free Energy 298K =   -1189.607480
PCM (DCM) Energy =   -1190.071581
PCM (MeOH) Energy =   -1190.076175
SCF (BP86+D3) Energy = -1190.111785
SCF (BS2) Energy =   -1189.959189
Lowest Frequency = 18.5218 cm-1
N   3.69510 0.21271 -0.85855
C   2.42112 0.54203 -0.40910
C   1.52845 -0.53198 -0.65599
C   2.32196 -1.54642 -1.27237
C   3.63412 -1.05459 -1.38144
C   1.93909 1.69077 0.27186
N   0.64943 1.71185 0.54242
C   0.13659 2.87464 1.31342
H   2.58909 2.51896 0.59440
Rh -0.39042 -0.12263 -0.07938
C -2.62028 -0.76007 -0.03174
C -2.57628 0.50087 -0.67806
C -1.62173 0.39677 -1.79784
C -1.20999 -0.99513 -1.90671
C -1.73991 -1.69617 -0.75913
H   2.01087 -2.53571 -1.60760
H   4.52511 -1.52164 -1.80108
C -1.63545 -3.16862 -0.47814
C -0.48549 -1.60064 -3.07216
C -1.36673 1.46146 -2.82531
C -3.45800 1.68297 -0.39454
C -3.41828 -1.13207 1.18142
C -0.39117 3.95947 0.35757
C -0.90651 2.43651 2.34771
H   0.99898 3.30394 1.86400
H -4.21250 -1.85205 0.91265
H -2.78093 -1.61367 1.94210
H -3.89790 -0.25694 1.64400
H -1.21108 -1.79500 -3.88366
H   0.29518 -0.93461 -3.46827
H -0.01699 -2.56136 -2.81304
H -4.38119 1.60363 -0.99898
H -3.76341 1.73866 0.66150
H -2.98047 2.63650 -0.66348
H -2.16452 1.45143 -3.59187
H -1.35020 2.46638 -2.37683
H -0.40670 1.30273 -3.33942
H -2.48658 -3.71096 -0.93090
H -0.71030 -3.59846 -0.89227
H -1.65336 -3.37581 0.60354
O   1.82069 -1.90162 1.88304
C   0.74481 -1.48070 2.52656
O -0.15452 -0.77640 2.00329
C   0.66855 -1.91257 3.96618
H -0.27147 -1.57390 4.41896
H   0.75074 -3.00980 4.03064
H   1.52413 -1.49269 4.52094
H   1.78919 -1.54560 0.93558
H -0.74750 4.83140 0.93093
H   0.39865 4.29968 -0.33218

H -1.23208 3.58040 -0.24410
H -1.25404 3.31133 2.92130
H -1.77802 1.97521 1.85612
H -0.48636 1.70087 3.05039
C   4.88913 1.05518 -0.78936
H   4.73875 1.98877 -1.35554
H   5.13305 1.29917 0.25781
H   5.73592 0.50951 -1.22825

1_Rh_VII.log
SCF (BP86) Energy =   -976.169524071
Enthalpy 0K =   -975.750665
Enthalpy 298K =   -975.722267
Free Energy 298K =   -975.808517
PCM (DCM) Energy =   -976.1859947
PCM (MeOH) Energy =   -976.1893794
SCF (BP86+D3) Energy = -976.2477903
SCF (BS2) Energy =   -1421.27216
Lowest Frequency = 20.3354 cm-1
N -3.63362 -1.10699 0.14253
C -2.47189 -0.33496 0.13626
C -1.34179 -1.16892 -0.04784
C -1.85524 -2.48952 -0.16939
C -3.25026 -2.41641 -0.04465
C -2.26562 1.06232 0.19882
N -0.99779 1.43902 0.16160
C -0.65794 2.87691 0.05696
H -3.07839 1.80208 0.23832
Rh 0.38636 -0.14444 -0.14689
Cl 0.05185 0.15975 -2.52536
C   2.70336 0.01303 -0.34708
C   2.34134 0.62270 0.88033
C   1.58877 -0.35795 1.67711
C   1.58994 -1.61508 0.94734
C   2.20057 -1.37497 -0.33855
H -1.30087 -3.41121 -0.34532
H -4.00279 -3.20579 -0.06903
C   2.45916 -2.37324 -1.43068
C   1.12770 -2.93845 1.48847
C   1.14458 -0.16738 3.10133
C   2.69153 2.00863 1.34382
C   3.44254 0.62481 -1.50050
H   0.44438 2.91082 0.05635
C -1.14792 3.47903 -1.27457
C -1.15827 3.67075 1.28019
H   4.39095 0.08877 -1.68799
H   2.82819 0.56617 -2.41737
H   3.68272 1.68386 -1.31741
H   1.90993 -3.37815 2.13551
H   0.20740 -2.83664 2.08428
H   0.92368 -3.65658 0.67937
H   3.55734 1.98193 2.03234
H   2.95804 2.66762 0.50226
H   1.85836 2.47842 1.89285
H   1.97078 -0.37660 3.80861
H   0.80662 0.86544 3.28390
H   0.31001 -0.84094 3.35185
H   3.52396 -2.67466 -1.44901
H   1.85333 -3.28298 -1.29630
H   2.20303 -1.94402 -2.41342
C -4.99710 -0.62160 0.28196
H -5.68828 -1.47660 0.24368
H -5.13783 -0.10114 1.24598
H -5.25607 0.07268 -0.53721
H -0.76738 4.50885 -1.39236
H -0.79604 2.86131 -2.11589
H -2.25135 3.52037 -1.30871
H -0.79866 4.71288 1.23031
H -2.26137 3.70351 1.31934
H -0.79804 3.22197 2.22138

2_Ir_IV.log
SCF (BP86) Energy =   -1164.40175167
Enthalpy 0K =   -1163.960419
Enthalpy 298K =   -1163.930298
Free Energy 298K =   -1164.020783
PCM (DCM) Energy =   -1164.451332
PCM (MeOH) Energy =   -1164.456080
SCF (BP86+D3) Energy = -1164.487784
SCF (BS2) Energy =   -1164.852936
Lowest Frequency = 16.5568 cm-1
O   4.23006 -0.12169 -0.79848
C   2.97140 0.06404 -0.23060
C   2.90904 -0.63941 0.97011
C   4.16583 -1.28654 1.13271
C   4.92398 -0.94324 0.02994
C   2.16805 1.00048 -0.96066
N   0.87902 1.24209 -0.88760
C   0.46180 2.49019 -1.63591
H   2.75561 1.60779 -1.67011
Ir -0.53698 -0.01984 0.09836
C -2.13204 -1.45090 0.57116
C -2.30984 -0.95046 -0.79793
C -1.14676 -1.32567 -1.57864
C -0.21891 -2.03654 -0.69852
C -0.84987 -2.12692 0.61828
H   4.48538 -1.90929 1.96671
H   5.93490 -1.19058 -0.28818
C -0.27668 -2.82464 1.81459
C   1.02209 -2.75265 -1.14513
C -0.96156 -1.16500 -3.05924
C -3.53288 -0.24059 -1.29382
C -3.14553 -1.36615 1.67607
C -0.97172 2.42612 -2.16295
C   0.68707 3.73134 -0.75157
H   1.14705 2.55940 -2.50408
H -3.86720 -2.19976 1.59756
H -2.67112 -1.42911 2.66735
H -3.71532 -0.42521 1.63112
H   0.75612 -3.75666 -1.52551
H   1.53104 -2.21368 -1.95898
H   1.74246 -2.88271 -0.32455
H -4.32627 -0.98043 -1.50798
H -3.92618 0.45947 -0.54003
H -3.33832 0.32174 -2.21850
H -1.13941 -2.13670 -3.55561
H -1.66889 -0.44226 -3.49114
H   0.06161 -0.84765 -3.31528
H -0.66840 -3.85766 1.85778
H   0.82054 -2.88618 1.76375
H -0.55417 -2.32150 2.75347
O   0.30930 0.70669 1.99368
C -0.49289 1.71823 2.03013
O -1.32513 1.82013 1.05268
C -0.43162 2.73192 3.13442
H -1.41049 3.21431 3.26831
H -0.10311 2.25913 4.07151
H   0.30492 3.51131 2.87137
H   2.07480 -0.61951 1.66751
H -1.17873 3.34477 -2.73670
H -1.11583 1.57106 -2.83969
H -1.69912 2.36989 -1.33820
H   0.49942 4.64107 -1.34566
H -0.00724 3.73289 0.10241
H   1.72295 3.77620 -0.37710

2_Ir_IV_TS_VI.log
SCF (BP86) Energy =   -1164.37748005
Enthalpy 0K =   -1163.938698
Enthalpy 298K =   -1163.908980
Free Energy 298K =   -1163.999329
PCM (DCM) Energy =   -1164.430730
PCM (MeOH) Energy =   -1164.436006
SCF (BP86+D3) Energy = -1164.462231
SCF (BS2) Energy =   -1164.829503
Lowest Frequency = -54.4600 cm-1
O -3.40217 1.97260 0.13011
C -2.48555 0.96894 0.30004
C -1.38474 1.40885 1.04488
C -1.66846 2.78802 1.34395
C -2.89283 3.06896 0.78101
C -2.63292 -0.30357 -0.33534
N -1.53270 -0.99630 -0.51010
C -1.61475 -2.43187 -0.92970

```
H  -3.61803 -0.68960 -0.62688
Ir  0.29964 -0.02366 -0.05243
C   2.49159  0.20572 -0.15820
C   1.96283 -0.56750 -1.29490
C   1.09778  0.33617 -2.07696
C   1.02654  1.59923 -1.38929
C   1.89450  1.51230 -0.19270
H  -1.08188  3.45814  1.97045
H  -3.52732  3.95281  0.76808
C   2.16882  2.63197  0.76730
C   0.32553  2.83645 -1.86750
C   0.46034  0.00164 -3.39213
C   2.41360 -1.93951 -1.69800
C   3.47310 -0.30825  0.85113
C  -2.13269 -3.29694  0.23386
C  -2.45247 -2.60835 -2.20915
H  -0.57206 -2.71856 -1.14187
H   4.49568 -0.25605  0.43502
H   3.45343  0.28563  1.77665
H   3.26700 -1.35810  1.11038
H   1.03561  3.48252 -2.41569
H  -0.50253  2.59574 -2.55138
H  -0.08404  3.42275 -1.03099
H   3.35378 -1.87361 -2.27703
H   2.60430 -2.57386 -0.81895
H   1.67021 -2.44518 -2.33357
H   1.16239  0.24289 -4.21148
H   0.22127 -1.06989 -3.46989
H  -0.46128  0.57829 -3.56236
H   3.08728  3.16726  0.46383
H   1.34742  3.36333  0.77981
H   2.31454  2.26029  1.79298
O   0.14119  0.07934  3.10863
C   0.36229 -1.09179  2.73669
O   0.40017 -1.48257  1.47205
C   0.58462 -2.20997  3.74299
H   0.94593 -3.13159  3.26688
H   1.29926 -1.87091  4.50878
H  -0.36792 -2.41684  4.25926
H  -0.69734  0.80276  1.73850
H  -2.09453 -4.36078 -0.05258
H  -1.51202 -3.14980  1.12966
H  -3.18031 -3.04687  0.47520
H  -2.36551 -3.65082 -2.55538
H  -3.52442 -2.41577 -2.03345
H  -2.10818 -1.94630 -3.02024
```

2_Ir_VI.log

```
SCF (BP86) Energy =     -1164.39511808
Enthalpy 0K =           -1163.954466
Enthalpy 298K =         -1163.924081
Free Energy 298K =      -1164.016094
PCM (DCM) Energy =      -1164.444901
PCM (MeOH) Energy =     -1164.449639
SCF (BP86+D3) Energy =  -1164.480896
SCF (BS2) Energy =      -1164.845246
Lowest Frequency =  11.8726 cm-1
O   3.52923  0.84367 -1.73423
C   2.30510  0.95235 -1.11605
C   1.69571 -0.28543 -0.89200
C   2.64891 -1.23341 -1.42052
C   3.71709 -0.49961 -1.90887
C   1.66483  2.14294 -0.69298
N   0.46102  1.97326 -0.17865
C  -0.23894  3.19038  0.31989
H   2.12499  3.13787 -0.76142
Ir -0.16251 -0.13887 -0.03787
C  -2.13301 -1.13936  0.71065
C  -2.50911 -0.18149 -0.27024
C  -1.74126 -0.47008 -1.50021
C  -1.00844 -1.71608 -1.28290
C  -1.16523 -2.08292  0.11310
H   2.58234 -2.32072 -1.44500
H   4.64922 -0.78026 -2.39596
C  -0.67198 -3.34278  0.76914
C  -0.32852 -2.52450 -2.34784
C  -1.93763  0.20572 -2.82748
C  -3.61181  0.83032 -0.15081
C  -2.62789 -1.22360  2.12361
C  -1.15157  3.76066 -0.78020
C  -0.98214  2.91316  1.63056
H   0.54634  3.94417  0.52924
H  -3.34482 -2.05877  2.22513
H  -1.80135 -1.41361  2.82751
H  -3.13845 -0.30133  2.43794
H  -1.08689 -3.13119 -2.87582
H   0.17423 -1.89020 -3.09296
H   0.41323 -3.21952 -1.92716
H  -4.56243  0.36774 -0.47645
H  -3.75642  1.17924  0.88295
H  -3.44669  1.70913 -0.79065
H  -2.81842 -0.21772 -3.34516
H  -2.10545  1.28724 -2.71239
H  -1.06381  0.06766 -3.48191
H  -1.42349 -4.14821  0.67314
H   0.26170 -3.70259  0.31016
H  -0.48594 -3.19407  1.84446
O   2.63003 -0.86515  1.81863
C   1.65255 -0.33298  2.53158
O   0.56919  0.07754  2.03818
C   1.92481 -0.24173  4.00626
H   1.03319  0.10887  4.54036
H   2.24202 -1.22513  4.38917
H   2.76138  0.45628  4.17892
H   2.37083 -0.82188  0.84710
H  -1.64803  4.67759 -0.42184
H  -0.57371  4.01241 -1.68440
H  -1.93267  3.03747 -1.06203
H  -1.48109  3.83366  1.97477
H  -1.74822  2.13355  1.49240
H  -0.29169  2.57443  2.41765
```

2_Ir_VII.log

```
SCF (BP86) Energy =     -950.553993676
Enthalpy 0K =           -950.174184
Enthalpy 298K =         -950.147852
Free Energy 298K =      -950.229563
PCM (DCM) Energy =      -950.5675961
PCM (MeOH) Energy =     -950.5703211
SCF (BP86+D3) Energy =  -950.6293236
SCF (BS2) Energy =      -1396.172676
Lowest Frequency =  20.1283 cm-1
O  -3.47486 -2.02168  0.32352
C  -2.51154 -1.03142  0.25098
C  -1.22305 -1.53721  0.05556
C  -1.41803 -2.96041 -0.00911
C  -2.77053 -3.18831  0.16005
C  -2.69991  0.36599  0.28287
N  -1.56892  1.05288  0.19809
C  -1.61420  2.53121  0.08096
H  -3.67870  0.85751  0.33984
Ir  0.19810 -0.11467 -0.11389
Cl -0.32492  0.06662 -2.48937
C   2.39805  0.60808 -0.46285
C   1.94388  1.20847  0.74235
C   1.48471  0.13794  1.64559
C   1.76556 -1.13989  0.99565
C   2.25297 -0.85849 -0.34336
H  -0.67074 -3.73588 -0.17614
H  -3.37155 -4.09587  0.18952
C   2.73542 -1.84723 -1.36727
C   1.66671 -2.49180  1.64388
C   1.07396  0.32544  3.08041
C   1.96304  2.67037  1.08965
C   2.91352  1.29595 -1.69252
H  -0.55976  2.83946 -0.00921
C  -2.34844  2.98056 -1.19695
C  -2.19905  3.17524  1.35295
H   3.96014  1.00241 -1.89178
H   2.30354  1.01458 -2.56959
H   2.88090  2.39190 -1.59271
H   2.58783 -2.70608  2.21728
H   0.81241 -2.54873  2.33615
H   1.54647 -3.29020  0.89553
```

H 2.85788 2.91391 1.69300
H 1.98607 3.30592 0.19034
H 1.08266 2.95917 1.68713
H 1.95889 0.38383 3.74315
H 0.49528 1.25325 3.21543
H 0.44692 -0.51061 3.42716
H 3.83982 -1.91941 -1.36404
H 2.33157 -2.85323 -1.17309
H 2.41090 -1.54937 -2.37737
H -2.25414 4.07307 -1.32465
H -1.91843 2.47480 -2.07558
H -3.42500 2.73974 -1.14593
H -2.12671 4.27459 1.29068
H -3.26518 2.91895 1.48167
H -1.65849 2.84007 2.25425

2_L-H_cis.log
SCF (BP86) Energy = -441.416531264
Enthalpy 0K = -441.245493
Enthalpy 298K = -441.235323
Free Energy 298K = -441.281586
PCM (DCM) Energy = -441.4216065
PCM (MeOH) Energy = -441.4225184
SCF (BP86+D3) Energy = -441.4317197
SCF (BS2) Energy = -441.5321516
Lowest Frequency = 48.2627 cm-1
O -1.63962 -0.99913 0.00034
C -1.25933 0.32706 -0.00019
C -2.38718 1.13272 -0.00024
C -3.51848 0.25803 0.00001
C -3.00586 -1.01917 0.00022
C 0.15062 0.66808 -0.00041
N 1.09811 -0.20614 0.00002
C 2.47218 0.29799 -0.00010
H 0.34303 1.76510 -0.00077
H -2.39278 2.22217 -0.00041
H -4.57167 0.53436 -0.00010
H -3.45893 -2.00822 0.00044
C 3.18018 -0.20531 1.27224
C 3.18031 -0.20628 -1.27197
H 2.49174 1.41491 -0.00052
H 4.23172 0.12857 -1.28896
H 3.16074 -1.30860 -1.30674
H 2.67986 0.17268 -2.17847
H 4.23158 0.12959 1.28907
H 2.67963 0.17434 2.17838
H 3.16064 -1.30760 1.30784

2_L-H_trans.log
SCF (BP86) Energy = -441.417956915
Enthalpy 0K = -441.246932
Enthalpy 298K = -441.236743
Free Energy 298K = -441.283056
PCM (DCM) Energy = -441.4216748
PCM (MeOH) Energy = -441.4223023
SCF (BP86+D3) Energy = -441.4332799
SCF (BS2) Energy = -441.5333821
Lowest Frequency = 47.3712 cm-1
O -2.19829 -1.09705 0.00005
C -1.22955 -0.10723 -0.00030
C -1.83739 1.13607 0.00056
C -3.24695 0.90227 -0.00030
C -3.41045 -0.46540 0.00031
C 0.14910 -0.56137 -0.00084
N 1.13819 0.26647 -0.00031
C 2.48762 -0.30076 -0.00001
H 0.27894 -1.66637 -0.00083
H -1.31281 2.08941 0.00088
H -4.04134 1.64730 -0.00064
H -4.28067 -1.11794 0.00041
C 3.21959 0.16859 -1.27180
C 3.21891 0.16808 1.27238
H 2.45276 -1.41670 -0.00025
H 4.25291 -0.21706 1.28926
H 3.25341 1.27012 1.30805
H 2.70080 -0.18706 2.17855
H 4.25359 -0.21659 -1.28827
H 2.70197 -0.18615 -2.17840
H 3.25416 1.27064 -1.30698

2_Rh_IV.log
SCF (BP86) Energy = -1170.57627749
Enthalpy 0K = -1170.135423
Enthalpy 298K = -1170.105013
Free Energy 298K = -1170.196672
PCM (DCM) Energy = -1170.626619
PCM (MeOH) Energy = -1170.631449
SCF (BP86+D3) Energy = -1170.656456
SCF (BS2) Energy = -1170.512654
Lowest Frequency = 16.7318 cm-1
C -2.11525 -1.66290 0.20226
C -2.73684 -0.51207 -0.40060
C -1.96777 -0.13819 -1.59048
C -0.88733 -1.10464 -1.73474
C -0.96135 -2.03163 -0.62814
Rh -0.67992 -0.00097 0.15714
O -1.13445 1.55259 1.61151
C -0.42332 0.96109 2.50984
C -0.23431 1.55447 3.87743
C -3.95935 0.20291 0.08726
C -2.35631 0.92757 -2.57216
C 0.09196 -1.17495 -2.86847
C -0.10902 -3.24715 -0.42659
C -2.58352 -2.41261 1.41437
N 0.95929 1.22376 -0.39013
C 0.59148 2.63112 -0.79815
C 2.22675 0.91089 -0.46998
C 2.88793 -0.29472 -0.06340
O 4.19984 -0.37400 -0.52370
C 4.72984 -1.51771 -0.01896
C 3.80999 -2.18211 0.76863
C 2.62289 -1.39771 0.74355
O 0.14038 -0.14836 2.17495
H 2.91790 1.65116 -0.90399
H 3.97725 -3.11030 1.31251
H 5.76068 -1.72448 -0.29975
C 1.02936 2.95649 -2.23776
H -0.50848 2.65607 -0.75063
C 1.13701 3.65205 0.21551
H -4.83812 -0.12575 -0.49807
H -4.16308 -0.00632 1.14743
H -3.86669 1.29343 -0.03428
H -0.58417 -4.11543 -0.92130
H 0.89588 -3.12453 -0.85733
H -0.00242 -3.49788 0.64031
H -3.10614 0.53257 -3.28297
H -2.80718 1.79905 -2.07164
H -1.49607 1.27690 -3.16255
H -0.29190 -1.85733 -3.64909
H 0.24897 -0.19178 -3.33655
H 1.06927 -1.56017 -2.53957
H -3.16539 -3.30179 1.10935
H -1.73712 -2.76138 2.02655
H -3.23111 -1.79327 2.05276
H 1.70230 -1.56391 1.29773
H -1.06414 2.23279 4.12220
H -0.15355 0.75688 4.63090
H 0.70633 2.13205 3.89745
H 0.60188 3.92740 -2.53655
H 2.12495 3.04145 -2.33514
H 0.67976 2.19487 -2.95407
H 0.78548 4.66238 -0.05093
H 0.78250 3.42378 1.23158
H 2.24063 3.66790 0.21646

2_Rh_IV_TS_VI.log
SCF (BP86) Energy = -1170.54859252
Enthalpy 0K = -1170.111497
Enthalpy 298K = -1170.082025
Free Energy 298K = -1170.171485
PCM (DCM) Energy = -1170.600920
PCM (MeOH) Energy = -1170.606045
SCF (BP86+D3) Energy = -1170.631086
SCF (BS2) Energy = -1170.484711

```
Lowest Frequency =  -123.1523 cm-1
C   2.53264 -0.25786 -0.05827
C   1.92843 -0.98982 -1.17260
C   1.25254 -0.01274 -2.02057
C   1.37865  1.28970 -1.40990
C   2.18815  1.13246 -0.19057
Rh  0.33426 -0.05860 -0.01159
O   0.21935 -1.49030  1.54289
C  -0.11172 -1.12117  2.74808
C  -0.03838 -2.19380  3.82083
C   2.12445 -2.44862 -1.45798
C   0.59252 -0.30717 -3.33375
C   0.92235  2.59475 -1.99297
C   2.66576  2.25098  0.68742
C   3.36880 -0.87963  1.01781
N  -1.62522 -0.68283 -0.62028
C  -1.96250 -2.04498 -1.11820
C  -2.54551  0.24419 -0.51260
C  -2.13702  1.43979  0.15791
O  -2.80801  2.62570  0.03193
C  -2.06347  3.55002  0.72582
C  -0.93613  2.97472  1.26759
C  -0.96329  1.57430  0.91335
O  -0.49035  0.04276  3.06318
H  -3.56836  0.10955 -0.88735
H  -0.21967  3.47682  1.91661
H  -2.48178  4.55423  0.75401
C  -3.02418 -2.04411 -2.23169
H  -1.01624 -2.43417 -1.53330
C  -2.37190 -2.94238  0.06745
H   3.09367 -2.61254 -1.96542
H   2.12908 -3.04102 -0.52987
H   1.33873 -2.84866 -2.11765
H   3.65222  2.60481  0.33415
H   1.97846  3.10919  0.66097
H   2.78215  1.93209  1.73455
H   1.33964 -0.22511 -4.14494
H   0.18331 -1.32834 -3.37073
H  -0.21755  0.40337 -3.55663
H   1.74644  3.06478 -2.56087
H   0.07831  2.45853 -2.68628
H   0.60860  3.30266 -1.21040
H   4.36432 -1.13946  0.61391
H   3.51772 -0.19738  1.86756
H   2.90523 -1.80578  1.39327
H  -0.62102  0.79006  1.79488
H   0.39664 -3.12483  3.43401
H   0.55634 -1.81902  4.66871
H  -1.05493 -2.38935  4.20009
H  -3.09078 -3.05693 -2.66039
H  -4.02907 -1.79356 -1.85147
H  -2.76918 -1.34486 -3.04525
H  -2.52911 -3.97373 -0.28883
H  -1.59114 -2.94775  0.84160
H  -3.31625 -2.58369  0.51191
```

2_Rh_VI.log

```
SCF (BP86) Energy =     -1170.56416230
Enthalpy 0K =           -1170.123269
Enthalpy 298K =         -1170.093062
Free Energy 298K =      -1170.184818
PCM (DCM) Energy =      -1170.613651
PCM (MeOH) Energy =     -1170.618314
SCF (BP86+D3) Energy =  -1170.645225
SCF (BS2) Energy =      -1170.499877
Lowest Frequency =  10.5354 cm-1
C  -2.29317 -0.87423  0.63912
C  -2.45595  0.59291  0.58111
C  -2.19299  1.01075 -0.75188
C  -1.81671 -0.17553 -1.54252
C  -1.98465 -1.34666 -0.68489
Rh -0.33033 -0.07921  0.01768
O   0.36025  0.22695  2.08357
C   1.24506 -0.41030  2.70921
C   1.54596 -0.13688  4.15660
C  -2.85412  1.44484  1.74960
C  -2.33173  2.39479 -1.31214
C  -1.59799 -0.19730 -3.02796
C  -1.94764 -2.77670 -1.13588
C  -2.57861 -1.71521  1.84899
N   1.19897  1.29924 -0.65042
C   1.16536  2.76897 -0.42638
C   2.26120  0.72480 -1.17450
C   2.20565 -0.69549 -1.19240
O   3.14624 -1.54009 -1.73658
C   2.66698 -2.80009 -1.50188
C   1.45471 -2.76900 -0.83305
C   1.12970 -1.38075 -0.61955
O   1.98281 -1.36154  2.16107
H   3.12048  1.29727 -1.54534
H   0.89025 -3.65049 -0.53021
H   3.29511 -3.61170 -1.86486
C   1.77483  3.57292 -1.58932
H   0.09427  3.02263 -0.35786
C   1.82739  3.11662  0.92202
H  -3.90921  1.25927  2.02130
H  -2.23982  1.21601  2.63646
H  -2.74878  2.51797  1.53064
H  -2.94733 -3.06594 -1.50950
H  -1.22786 -2.93274 -1.95291
H  -1.69400 -3.46220 -0.31264
H  -3.30824  2.48899 -1.82269
H  -2.29581  3.16853 -0.52996
H  -1.55520  2.61586 -2.06140
H  -2.56639 -0.26260 -3.55845
H  -1.08971  0.71497 -3.37638
H  -0.98967 -1.06188 -3.33382
H  -3.66786 -1.87749  1.95141
H  -2.09999 -2.70423  1.78298
H  -2.23237 -1.22422  2.77197
H   1.70991 -1.44807  1.19274
H   0.85893  0.61962  4.55525
H   1.46497 -1.07098  4.73596
H   2.58706  0.21338  4.25465
H   1.56174  4.64368 -1.43928
H   2.87204  3.46946 -1.64096
H   1.34912  3.27107 -2.56059
H   1.71812  4.19425  1.12791
H   1.36278  2.55513  1.74701
H   2.90562  2.88107  0.89570
```

2_Rh_VII.log

```
SCF (BP86) Energy =     -956.715807917
Enthalpy 0K =           -956.336088
Enthalpy 298K =         -956.309757
Free Energy 298K =      -956.391126
PCM (DCM) Energy =      -956.7297782
PCM (MeOH) Energy =     -956.732573
SCF (BP86+D3) Energy =  -956.7887966
SCF (BS2) Energy =      -1401.818656
Lowest Frequency =  19.8836 cm-1
O  -3.34284 -2.14908  0.30614
C  -2.40863 -1.12960  0.23789
C  -1.11278 -1.59802  0.02087
C  -1.26486 -3.02309 -0.06442
C  -2.60903 -3.29263  0.11706
C  -2.65648  0.26181  0.28324
N  -1.56394  0.99939  0.19670
C  -1.67429  2.47173  0.06640
H  -3.66095  0.70140  0.34346
Rh  0.22979 -0.11085 -0.14205
Cl -0.25011  0.03791 -2.50550
C   2.38469  0.71456 -0.42880
C   1.89303  1.22792  0.79885
C   1.48994  0.09373  1.64334
C   1.83897 -1.12869  0.93834
C   2.31574 -0.75856 -0.37437
H  -0.49739 -3.77416 -0.25024
H  -3.18360 -4.21734  0.14069
C   2.82894 -1.66929 -1.45276
C   1.79966 -2.51438  1.51818
C   1.04603  0.18899  3.07694
C   1.83217  2.66939  1.21907
C   2.88023  1.48250 -1.61832
```

```
H  -0.63361  2.83139  0.00573
C  -2.38887  2.87136 -1.23915
C  -2.32873  3.10028  1.31230
H   3.93859  1.24097 -1.82609
H   2.28640  1.22023 -2.51267
H   2.80458  2.57016 -1.46446
H   2.71582 -2.70464  2.10812
H   0.93265 -2.65499  2.18218
H   1.74749 -3.28143  0.73022
H   2.69461  2.92216  1.86441
H   1.85542  3.35024  0.35353
H   0.92065  2.88828  1.79967
H   1.91582  0.25392  3.75912
H   0.42384  1.08204  3.24792
H   0.45369 -0.69142  3.37151
H   3.93472 -1.65085 -1.49348
H   2.51557 -2.71125 -1.28330
H   2.44075 -1.35906 -2.43679
H  -2.34057  3.96525 -1.38007
H  -1.91052  2.37290 -2.09689
H  -3.45399  2.58047 -1.21440
H  -2.30365  4.20102  1.23970
H  -3.38614  2.79813  1.40965
H  -1.80330  2.79934  2.23441
```

3a_Ir_IV.log

```
SCF (BP86) Energy =     -1487.40427866
Enthalpy 0K =           -1486.966471
Enthalpy 298K =         -1486.935583
Free Energy 298K =      -1487.028655
PCM (DCM) Energy =      -1487.454384
PCM (MeOH) Energy =     -1487.459196
SCF (BP86+D3) Energy =  -1487.488979
SCF (BS2) Energy =      -1487.863768
Lowest Frequency =  16.9555 cm-1
C  -2.02007 -1.81882  0.23614
C  -2.72716 -0.78163 -0.47183
C  -1.94396 -0.40919 -1.66186
C  -0.76432 -1.26900 -1.69357
C  -0.78920 -2.11740 -0.51800
Ir -0.75164 -0.01563  0.11523
O  -1.40140  1.65971  1.39463
C  -0.71743  1.22347  2.39746
C  -0.66898  1.95872  3.70499
C  -4.03978 -0.16829 -0.08723
C  -2.40418  0.52714 -2.74101
C   0.26437 -1.31941 -2.78441
C   0.16634 -3.22810 -0.20255
C  -2.46453 -2.53013  1.48077
N   0.82422  1.29762 -0.40488
C   0.37671  2.65842 -0.90857
C   2.11751  1.08210 -0.42850
C   2.87262 -0.04730  0.05211
S   4.54386 -0.18376 -0.51110
C   4.80985 -1.58239  0.46226
C   3.68859 -1.92477  1.20450
C   2.58844 -1.05875  0.97570
O  -0.05870  0.13092  2.20950
H   2.73063  1.87698 -0.88260
H   3.67258 -2.76401  1.90325
H   5.78012 -2.07953  0.43913
C   0.77752  2.88650 -2.37640
H  -0.72132  2.62860 -0.84360
C   0.87931  3.78293  0.01209
H  -4.85148 -0.62929 -0.67938
H  -4.26861 -0.32279  0.97736
H  -4.05349  0.91476 -0.28541
H  -0.19475 -4.16611 -0.66449
H   1.17555 -3.02646 -0.59086
H   0.24213 -3.40299  0.88177
H  -3.07781 -0.00242 -3.44005
H  -2.96251  1.38192 -2.32797
H  -1.56159  0.92086 -3.32902
H   0.34680 -0.35842 -3.31384
H   1.25895 -1.58447 -2.39460
H  -0.02182 -2.08551 -3.52800
H  -2.93670 -3.49433  1.21800
H  -1.61597 -2.74345  2.14943
H  -3.20087 -1.94020  2.04680
H   1.63826 -1.11263  1.50780
H  -0.67508  1.24377  4.54163
H   0.27137  2.53355  3.76708
H  -1.51501  2.65496  3.78933
H   0.30260  3.81091 -2.74334
H   1.86682  3.00919 -2.50144
H   0.44889  2.05557 -3.02154
H   0.45862  4.74572 -0.32157
H   0.56061  3.61469  1.05171
H   1.97903  3.87221 -0.01182
```

3a_Ir_IV_TS_VI.log

```
SCF (BP86) Energy =     -1487.38073905
Enthalpy 0K =           -1486.944844
Enthalpy 298K =         -1486.914420
Free Energy 298K =      -1487.006688
PCM (DCM) Energy =      -1487.433772
PCM (MeOH) Energy =     -1487.439087
SCF (BP86+D3) Energy =  -1487.468225
SCF (BS2) Energy =      -1487.840891
Lowest Frequency =  -50.7303 cm-1
C  -2.25246 -1.28798 -0.31004
C  -2.12984 -0.24709 -1.34739
C  -0.93594 -0.56794 -2.15792
C  -0.29209 -1.71111 -1.56990
C  -1.11376 -2.15398 -0.41875
Ir -0.43024 -0.06828 -0.07138
O  -1.16958  1.00433  1.58615
C  -1.04860  0.41712  2.77025
C  -1.70172  1.18046  3.91198
C  -3.16161  0.79354 -1.66219
C  -0.51827  0.14723 -3.40755
C   0.91448 -2.42649 -2.10139
C  -0.83864 -3.34981  0.44375
C  -3.37011 -1.39819  0.68256
N   0.75145  1.66520 -0.30862
C   0.14198  3.01645 -0.54940
C   2.04777  1.56375 -0.14801
C   2.59464  0.31206  0.30012
S   4.23447 -0.21249 -0.01334
C   3.92606 -1.74510  0.74121
C   2.62920 -1.85414  1.21101
C   1.85473 -0.67831  0.96833
O  -0.43329 -0.65043  2.95811
H   2.69880  2.43094 -0.32536
H   2.26789 -2.71576  1.77605
H   4.73552 -2.47184  0.82139
C   0.72730  3.68548 -1.80617
H  -0.92693  2.80984 -0.71804
C   0.27530  3.89909  0.70395
H  -3.94749  0.36005 -2.30889
H  -3.64764  1.16760 -0.74825
H  -2.72798  1.65134 -2.19917
H  -1.45408 -4.20358  0.10555
H   0.21601 -3.65601  0.38458
H  -1.08118 -3.14714  1.49829
H  -1.01194 -0.31843 -4.28043
H  -0.81437  1.20710 -3.38979
H   0.56871  0.09151 -3.56979
H   0.59803 -3.28663 -2.71977
H   1.53031 -1.76928 -2.73368
H   1.55103 -2.81209 -1.29052
H  -4.21705 -1.94533  0.22967
H  -3.05605 -1.94276  1.58505
H  -3.73507 -0.40592  0.98861
H   0.91869 -0.51812  1.58506
H  -2.37837  1.96855  3.55401
H  -2.24675  0.47339  4.55596
H  -0.91111  1.63835  4.53030
H   0.16118  4.60573 -2.02283
H   1.78142  3.97930 -1.66554
H   0.66568  3.02760 -2.68823
H  -0.26801  4.84538  0.54685
H  -0.15125  3.38939  1.58020
H   1.33161  4.14598  0.90791
```

3a_Ir_VI.log

SCF (BP86) Energy = -1487.40485230
Enthalpy 0K = -1486.966971
Enthalpy 298K = -1486.936259
Free Energy 298K = -1487.028710
PCM (DCM) Energy = -1487.454380
PCM (MeOH) Energy = -1487.459110
SCF (BP86+D3) Energy = -1487.491436
SCF (BS2) Energy = -1487.862734
Lowest Frequency = 17.7841 cm-1

C	-2.05630	-1.47608	0.55513
C	-2.67789	-0.15208	0.32422
C	-2.41363	0.23753	-1.01847
C	-1.58520	-0.81246	-1.64932
C	-1.46857	-1.91382	-0.68783
Ir	-0.37689	-0.12991	0.00976
O	-0.07248	0.69898	2.04508
C	0.84267	0.43558	2.86964
C	0.83103	1.00256	4.26117
C	-3.45517	0.60566	1.35981
C	-2.92537	1.45774	-1.72564
C	-1.22536	-0.87943	-3.10696
C	-0.94012	-3.28361	-0.99478
C	-2.21717	-2.28870	1.80893
N	0.73739	1.56861	-0.65414
C	0.20355	2.96168	-0.69205
C	2.00655	1.34282	-0.93361
C	2.44415	-0.00097	-0.75901
S	4.01770	-0.70084	-1.07590
C	3.45526	-2.23558	-0.49778
C	2.12647	-2.21125	-0.09148
C	1.50710	-0.92464	-0.23967
O	1.87236	-0.34491	2.59659
H	2.66804	2.15566	-1.25927
H	1.63140	-3.09929	0.30775
H	4.14096	-3.08426	-0.48916
C	0.47414	3.64729	-2.04409
H	-0.88599	2.84871	-0.57292
C	0.73625	3.78518	0.49573
H	-4.42452	0.11043	1.55038
H	-2.91079	0.64593	2.31776
H	-3.66301	1.63896	1.04394
H	-1.74157	-3.88068	-1.46749
H	-0.09030	-3.25254	-1.69280
H	-0.62589	-3.81844	-0.08552
H	-3.82088	1.19330	-2.31777
H	-3.21903	2.25447	-1.02496
H	-2.18322	1.86748	-2.42877
H	-2.06132	-1.30755	-3.69073
H	-1.00940	0.11917	-3.51701
H	-0.33974	-1.51101	-3.27384
H	-3.19456	-2.80583	1.80892
H	-1.43365	-3.05635	1.90126
H	-2.18114	-1.65419	2.70834
H	1.79225	-0.65123	1.63935
H	-0.06431	1.61640	4.41837
H	0.86306	0.18053	4.99512
H	1.73772	1.60984	4.41891
H	-0.06103	4.61008	-2.08218
H	1.54554	3.86509	-2.19196
H	0.12974	3.02684	-2.88778
H	0.26468	4.78171	0.50476
H	0.51121	3.28731	1.45168
H	1.82809	3.92878	0.42075

3a_Ir_VII.log

SCF (BP86) Energy = -1273.56002751
Enthalpy 0K = -1273.183265
Enthalpy 298K = -1273.156411
Free Energy 298K = -1273.239533
PCM (DCM) Energy = -1273.573768
PCM (MeOH) Energy = -1273.576584
SCF (BP86+D3) Energy = -1273.63781
SCF (BS2) Energy = -1719.185399
Lowest Frequency = 17.1113 cm-1

S	-4.21372	-0.66067	0.26284
C	-2.60240	0.04122	0.20605
C	-1.58325	-0.91089	0.00398
C	-2.14989	-2.22040	-0.12660
C	-3.52896	-2.24098	-0.00261
C	-2.20408	1.40150	0.24528
N	-0.89975	1.60568	0.16700
C	-0.37621	2.99217	0.06322
H	-2.90764	2.24203	0.30418
Ir	0.27901	-0.13368	-0.11840
Cl	-0.07546	0.20948	-2.50656
C	2.59482	-0.34994	-0.43073
C	2.40078	0.41815	0.74854
C	1.54385	-0.35643	1.66365
C	1.30888	-1.66189	1.05248
C	1.88295	-1.63642	-0.28108
H	-1.57368	-3.12693	-0.32681
H	-4.19420	-3.10426	-0.05424
C	1.95237	-2.76662	-1.26966
C	0.69267	-2.84637	1.74159
C	1.22485	0.01906	3.08492
C	2.99371	1.76284	1.06229
C	3.35390	0.04202	-1.66396
H	0.71839	2.87686	0.00670
C	-0.84752	3.67657	-1.23398
C	-0.71033	3.81631	1.32133
H	4.18834	-0.65940	-1.84489
H	2.68637	0.01863	-2.54416
H	3.77367	1.05642	-1.58150
H	1.45115	-3.35662	2.36419
H	-0.14164	-2.54832	2.39543
H	0.30654	-3.58195	1.01965
H	3.90959	1.65096	1.67282
H	3.26875	2.31364	0.14892
H	2.29635	2.39132	1.64059
H	2.05429	-0.25766	3.76403
H	1.05926	1.10342	3.18772
H	0.31528	-0.49148	3.43756
H	2.94181	-3.26186	-1.24385
H	1.18903	-3.53192	-1.05746
H	1.77676	-2.39810	-2.29332
H	-0.34167	4.65036	-1.35447
H	-0.61718	3.03846	-2.10153
H	-1.93599	3.86192	-1.21505
H	-0.21894	4.80288	1.26921
H	-1.79624	3.99145	1.41540
H	-0.36830	3.30390	2.23633

3a_L-H_cis.log

SCF (BP86) Energy = -764.421655843
Enthalpy 0K = -764.253743
Enthalpy 298K = -764.243102
Free Energy 298K = -764.290694
PCM (DCM) Energy = -764.4258552
PCM (MeOH) Energy = -764.4266404
SCF (BP86+D3) Energy = -764.4378262
SCF (BS2) Energy = -764.5433941
Lowest Frequency = 43.3258 cm-1

S	1.57040	-1.17592	0.00017
C	1.01453	0.48973	-0.00005
C	2.08928	1.37228	0.00001
C	3.35467	0.71541	-0.00022
C	3.23120	-0.66155	0.00005
C	-0.40331	0.80934	-0.00015
N	-1.31812	-0.09916	-0.00021
C	-2.71597	0.33425	-0.00011
H	-0.63935	1.89770	-0.00019
H	1.95840	2.45783	-0.00001
H	4.31608	1.23444	-0.00046
H	4.02676	-1.40712	0.00006
C	-3.39858	-0.20318	-1.27225
C	-3.39820	-0.20262	1.27249
H	-2.78768	1.44826	-0.00033
H	-4.46440	0.08130	1.28953
H	-3.32638	-1.30278	1.30795
H	-2.91623	0.20039	2.17855
H	-4.46477	0.08081	-1.28915
H	-2.91683	0.19934	-2.17864

```
H  -3.32685 -1.30336 -1.30718
```

3a_L-H_trans.log

```
SCF (BP86) Energy =     -764.418790059
Enthalpy 0K =           -764.250941
Enthalpy 298K =         -764.240253
Free Energy 298K =      -764.287997
PCM (DCM) Energy =      -764.422509968
PCM (MeOH) Energy =     -764.423170795
SCF (BP86+D3) Energy =  -764.434997200694
SCF (BS2) Energy =      -764.540883192
Lowest Frequency =  41.0568 cm-1
S  -2.29029 -1.15552 -0.00013
C  -0.94404 -0.02499 -0.00003
C  -1.40763  1.28565 -0.00030
C  -2.82789  1.37668 -0.00020
C  -3.44643  0.13845  0.00020
C   0.43090 -0.51665  0.00011
N   1.43814  0.28792  0.00004
C   2.77716 -0.30410  0.00015
H   0.55808 -1.62324  0.00023
H  -0.72027  2.13379 -0.00046
H  -3.38137  2.31894 -0.00027
H  -4.51252 -0.08757  0.00044
C   3.51700  0.15080 -1.27216
C   3.51693  0.15109  1.27239
H   2.72104 -1.41924  0.00027
H   4.54339 -0.25369  1.28937
H   3.57267  1.25226  1.30781
H   2.99213 -0.19377  2.17867
H   4.54346 -0.25399 -1.28899
H   2.99225 -0.19426 -2.17839
H   3.57274  1.25196 -1.30783
```

3a_Rh_IV.log

```
SCF (BP86) Energy =     -1493.57515477
Enthalpy 0K =           -1493.137649
Enthalpy 298K =         -1493.106658
Free Energy 298K =      -1493.199927
PCM (DCM) Energy =      -1493.625482
PCM (MeOH) Energy =     -1493.630348
SCF (BP86+D3) Energy =  -1493.657265
SCF (BS2) Energy =      -1493.519373
Lowest Frequency =  14.3651 cm-1
C  -2.08219 -1.84697  0.14305
C  -2.78667 -0.79595 -0.54321
C  -1.98107 -0.37193 -1.69284
C  -0.79095 -1.21007 -1.72670
C  -0.83518 -2.10302 -0.59051
Rh -0.84783 -0.03158  0.13162
O  -1.58989  1.53800  1.44943
C  -0.92745  1.05804  2.44552
C  -0.93910  1.72564  3.79195
C  -4.11504 -0.21391 -0.16823
C  -2.41778  0.61233 -2.73717
C   0.26819 -1.20052 -2.78829
C   0.13303 -3.20403 -0.28383
C  -2.54323 -2.60589  1.35184
N   0.71233  1.32648 -0.34230
C   0.22969  2.68915 -0.78989
C   2.00635  1.13600 -0.37445
C   2.77161  0.00138  0.08317
S   4.43679 -0.13194 -0.49528
C   4.70952 -1.53846  0.46618
C   3.59456 -1.88417  1.21584
C   2.49329 -1.01466  1.00246
O  -0.23394 -0.00675  2.23058
H   2.61307  1.94946 -0.80625
H   3.58400 -2.72726  1.91010
H   5.67907 -2.03629  0.43118
C   0.67812  3.02907 -2.22285
H  -0.86855  2.61381 -0.77437
C   0.64748  3.77338  0.21835
H  -4.90541 -0.65405 -0.80410
H  -4.37243 -0.41974  0.88089
H  -4.13567  0.87697 -0.31709
H  -0.20186 -4.13688 -0.77589
H   1.14622 -2.97677 -0.64676
H   0.18947 -3.40568  0.79705
H  -3.07289  0.11427 -3.47633
H  -2.99159  1.44433 -2.29925
H  -1.56373  1.03511 -3.28707
H   0.02358 -1.95141 -3.56209
H   0.33994 -0.22268 -3.28741
H   1.25833 -1.45297 -2.37894
H  -2.97532 -3.57681  1.04715
H  -1.70970 -2.81258  2.04130
H  -3.31646 -2.05657  1.90923
H   1.54743 -1.06756  1.54363
H  -1.82701  2.36465  3.89958
H  -0.90977  0.96974  4.59108
H  -0.03801  2.35502  3.89497
H   0.16777  3.94829 -2.55346
H   1.76266  3.21908 -2.29262
H   0.42413  2.22459 -2.93243
H   0.20923  4.74111 -0.07622
H   0.28838  3.53007  1.22938
H   1.74405  3.89509  0.24990
```

3a_Rh_IV_TS_V.log

```
SCF (BP86) Energy =     -1493.55243533
Enthalpy 0K =           -1493.117180
Enthalpy 298K =         -1493.087036
Free Energy 298K =      -1493.178229
PCM (DCM) Energy =      -1493.606037
PCM (MeOH) Energy =     -1493.611426
SCF (BP86+D3) Energy =  -1493.637806
SCF (BS2) Energy =      -1493.497131
Lowest Frequency =  -16.7753 cm-1
C  -2.12734 -1.58444 -0.15125
C  -2.10899 -0.66349 -1.29084
C  -0.88822 -0.93343 -2.05636
C  -0.13133 -1.93670 -1.35804
C  -0.90766 -2.34068 -0.17043
Rh -0.43075 -0.17818 -0.02874
O  -1.46078  0.95349  1.41332
C  -1.08738  0.87983  2.67424
C  -1.98563  1.63248  3.64708
C  -3.23748  0.23877 -1.68888
C  -0.53083 -0.30666 -3.37020
C   1.14277 -2.57706 -1.82296
C  -0.53397 -3.43910  0.78005
C  -3.23768 -1.68580  0.84838
N   0.50704  1.64682 -0.56481
C  -0.23034  2.85856 -1.03268
C   1.80677  1.67756 -0.41498
C   2.43121  0.54700  0.21701
S   4.11083  0.09993  0.04446
C   3.85841 -1.33181  0.99652
C   2.54934 -1.46076  1.42371
C   1.70749 -0.38859  0.98338
O  -0.07910  0.26520  3.08752
H   2.39524  2.54808 -0.73751
H   2.22253 -2.25586  2.09738
H   4.70701 -1.98156  1.21504
C   0.41925  3.50684 -2.26912
H  -1.23056  2.48637 -1.31086
C  -0.39155  3.85690  0.12958
H  -4.01126 -0.33705 -2.23080
H  -3.71560  0.69320 -0.80726
H  -2.90347  1.04696 -2.35792
H  -0.99318 -4.38904  0.44842
H   0.55431 -3.59366  0.81445
H  -0.88859 -3.23625  1.80229
H  -0.97052 -0.90124 -4.19247
H  -0.92780  0.71611 -3.45850
H   0.55750 -0.27466 -3.52938
H   0.91867 -3.52415 -2.34787
H   1.69097 -1.93022 -2.52446
H   1.81278 -2.81120 -0.98137
H  -4.10736 -2.19199  0.39124
H  -2.93797 -2.26294  1.73530
H  -3.56218 -0.68614  1.17866
H   0.81473 -0.10873  1.68072
```

H -2.87287 2.05130 3.15343
H -2.29000 0.95002 4.45636
H -1.40315 2.44480 4.11210
H -0.25283 4.28803 -2.65940
H   1.37602 4.00018 -2.02774
H   0.59691 2.77361 -3.07285
H -1.01329 4.70670 -0.19701
H -0.87680 3.37339 0.98945
H   0.59016 4.25127 0.44409

3a_Rh_V.log
SCF (BP86) Energy =   -1493.55244058
Enthalpy 0K =   -1493.117020
Enthalpy 298K =   -1493.085917
Free Energy 298K =   -1493.180962
PCM (DCM) Energy =   -1493.606122
PCM (MeOH) Energy =   -1493.611544
SCF (BP86+D3) Energy = -1493.637845
SCF (BS2) Energy =   -1493.497033
Lowest Frequency = 12.6854 cm-1
C -2.13800 -1.56236 -0.18694
C -2.09829 -0.63073 -1.31794
C -0.87265 -0.90756 -2.07548
C -0.13337 -1.92304 -1.37801
C -0.92476 -2.32817 -0.19995
Rh -0.43345 -0.17115 -0.03698
O -1.45846 0.95980 1.40689
C -1.12480 0.81895 2.67486
C -2.01486 1.57891 3.64998
C -3.21374 0.28531 -1.72050
C -0.49793 -0.27548 -3.38189
C   1.13971 -2.57131 -1.83431
C -0.56713 -3.43243 0.74977
C -3.25994 -1.66380 0.79969
N   0.51939 1.65534 -0.53285
C -0.20991 2.88239 -0.97442
C   1.81756 1.67940 -0.37198
C   2.43788 0.53624 0.24223
S   4.11746 0.09074 0.05981
C   3.86739 -1.35444 0.99130
C   2.55918 -1.48939 1.41969
C   1.71818 -0.41056 0.99696
O -0.16029 0.14009 3.08869
H   2.41001 2.55596 -0.67065
H   2.23238 -2.29405 2.08187
H   4.71626 -2.00763 1.19806
C   0.42209 3.52441 -2.22327
H -1.22259 2.52849 -1.22934
C -0.32566 3.87678 0.19631
H -3.98412 -0.27813 -2.28006
H -3.70080 0.73258 -0.84013
H -2.86393 1.09875 -2.37489
H -1.03595 -4.37661 0.41520
H   0.51924 -3.59915 0.78771
H -0.92258 -3.22611 1.77102
H -0.93271 -0.86272 -4.21203
H -0.88782 0.75012 -3.46829
H   0.59215 -0.24911 -3.52986
H   0.91237 -3.51411 -2.36555
H   1.69933 -1.92578 -2.52794
H   1.80028 -2.81505 -0.98801
H -4.12490 -2.16783 0.33123
H -2.97132 -2.24348 1.68863
H -3.58722 -0.66466 1.12851
H   0.80821 -0.16129 1.67173
H -2.86820 2.05605 3.14941
H -2.37238 0.88392 4.42619
H -1.40879 2.34649 4.15886
H -0.24063 4.32430 -2.59104
H   1.39687 3.99188 -2.00332
H   0.56168 2.79286 -3.03591
H -0.94404 4.73678 -0.10926
H -0.79512 3.39528 1.06612
H   0.66891 4.25676 0.48733

3a_Rh_V_TS_VI.log
SCF (BP86) Energy =   -1493.55244841
Enthalpy 0K =   -1493.117765
Enthalpy 298K =   -1493.087710
Free Energy 298K =   -1493.178696
PCM (DCM) Energy =   -1493.605349
PCM (MeOH) Energy =   -1493.610646
SCF (BP86+D3) Energy = -1493.638177
SCF (BS2) Energy =   -1493.496681
Lowest Frequency = -112.1344 cm-1
C -2.13150 -1.60051 -0.02967
C -2.16661 -0.71471 -1.19438
C -0.97220 -0.99070 -1.99130
C -0.17859 -1.97175 -1.29561
C -0.90905 -2.35395 -0.07462
Rh -0.42933 -0.18747 -0.00229
O -1.42445 0.96529 1.45586
C -0.92918 1.06201 2.66522
C -1.79957 1.80533 3.66736
C -3.31707 0.16896 -1.57293
C -0.66460 -0.39405 -3.33166
C   1.08068 -2.61553 -1.79571
C -0.50385 -3.43924 0.87861
C -3.20153 -1.67680 1.01528
N   0.49368 1.61231 -0.65657
C -0.25025 2.79659 -1.17691
C   1.79934 1.63522 -0.55333
C   2.42287 0.52838 0.11703
S   4.09537 0.05419 -0.03597
C   3.82160 -1.33291 0.97618
C   2.51096 -1.42563 1.40695
C   1.67893 -0.36150 0.92235
O   0.18195 0.59803 3.02423
H   2.38679 2.47772 -0.94338
H   2.17703 -2.18885 2.11342
H   4.66116 -1.98448 1.22276
C   0.42737 3.44542 -2.39754
H -1.22991 2.39562 -1.48813
C -0.48367 3.81041 -0.03986
H -4.10384 -0.42367 -2.07661
H -3.76949 0.63890 -0.68590
H -3.01342 0.96596 -2.26955
H -0.96808 -4.39490 0.57143
H   0.58553 -3.58936 0.88431
H -0.83090 -3.22706 1.90818
H -1.12577 -1.01334 -4.12333
H -1.07422 0.62261 -3.43313
H   0.41743 -0.35715 -3.52820
H   0.84200 -3.56674 -2.30643
H   1.60616 -1.97327 -2.51860
H   1.77694 -2.84185 -0.97353
H -4.10209 -2.16017 0.59507
H -2.87964 -2.26202 1.88901
H -3.48632 -0.66903 1.35864
H   0.85775 0.03454 1.69572
H -2.75142 2.12718 3.22425
H -1.98954 1.15048 4.53282
H -1.24605 2.68192 4.04127
H -0.25730 4.19225 -2.83071
H   1.35258 3.98193 -2.12690
H   0.66562 2.70498 -3.17886
H -1.10101 4.64498 -0.41108
H -1.00290 3.33497 0.80434
H   0.47648 4.22372 0.31409

3a_Rh_VI.log
SCF (BP86) Energy =   -1493.56978767
Enthalpy 0K =   -1493.131901
Enthalpy 298K =   -1493.101236
Free Energy 298K =   -1493.193589
PCM (DCM) Energy =   -1493.619003
PCM (MeOH) Energy =   -1493.623696
SCF (BP86+D3) Energy = -1493.653585
SCF (BS2) Energy =   -1493.512935
Lowest Frequency = 15.2382 cm-1
C -2.72441 -0.22128 0.21407
C -2.40190 -0.01928 -1.15333
C -1.50484 -1.11023 -1.57952
C -1.40930 -2.05832 -0.47326

```
C  -2.07769 -1.47362  0.65854
Rh -0.42600 -0.14557  0.02708
O  -0.29267  0.84586  1.98609
C   0.66483  0.89510  2.79814
C   0.54940  1.60198  4.12008
C  -2.93182  1.05192 -2.05977
C  -1.04004 -1.35653 -2.98616
C  -0.82922 -3.43886 -0.55660
C  -2.26569 -2.09254  2.01313
C  -3.58235  0.64033  1.09184
N   0.67124  1.46087 -0.88502
C   0.11404  2.81107 -1.16296
C   1.93478  1.18702 -1.12155
C   2.38122 -0.10430 -0.70221
S   3.97703 -0.81084 -0.87166
C   3.44455 -2.22735 -0.02471
C   2.11081 -2.16178  0.36022
C   1.46735 -0.94143 -0.02927
O   1.84433  0.33854  2.57244
H   2.60103  1.91991 -1.59384
H   1.63317 -2.97122  0.91682
H   4.15154 -3.04013  0.14922
C   0.83211  3.56497 -2.29544
H  -0.92693  2.62949 -1.47981
C   0.07799  3.64068  0.13625
H  -3.81872  0.67077 -2.59970
H  -3.24700  1.95111 -1.50810
H  -2.19669  1.34752 -2.82494
H  -3.24021 -2.61311  2.06402
H  -1.48176 -2.83166  2.23845
H  -2.25874 -1.33020  2.80794
H  -0.82594 -0.41475 -3.51474
H  -0.12763 -1.97159 -3.00682
H  -1.81942 -1.89088 -3.56123
H  -1.58440 -4.11986 -0.99111
H   0.06364 -3.47754 -1.19821
H  -0.56333 -3.83681  0.43449
H  -4.52796  0.12273  1.33536
H  -3.07460  0.86482  2.04491
H  -3.83794  1.59478  0.60783
H   1.80793 -0.11989  1.67615
H  -0.45257  2.03205  4.23927
H   0.75835  0.89263  4.93779
H   1.31102  2.39677  4.18126
H   0.24940  4.46520 -2.54867
H   1.83803  3.90915 -1.99958
H   0.92177  2.95138 -3.20742
H  -0.42646  4.60332 -0.04887
H  -0.46276  3.11025  0.93476
H   1.10372  3.85329  0.48466
```

3a_Rh_VII.log

```
SCF (BP86) Energy =     -1279.72176279
Enthalpy 0K =           -1279.345078
Enthalpy 298K =         -1279.318237
Free Energy 298K =      -1279.400952
PCM (DCM) Energy =      -1279.735898
PCM (MeOH) Energy =     -1279.738762
SCF (BP86+D3) Energy =  -1279.797148
SCF (BS2) Energy =      -1724.83139
Lowest Frequency =  17.6929 cm-1
S  -4.15175 -0.63797  0.25922
C  -2.52849  0.04108  0.20508
C  -1.53308 -0.92347 -0.02494
C  -2.11571 -2.22024 -0.17929
C  -3.49528 -2.22206 -0.04415
C  -2.12316  1.40300  0.25133
N  -0.82417  1.60709  0.16161
C  -0.29759  2.98903  0.03722
H  -2.83161  2.24081  0.31549
Rh  0.31932 -0.14430 -0.14754
Cl -0.00308  0.15454 -2.52260
C   2.62445 -0.35745 -0.40664
C   2.39909  0.36750  0.79122
C   1.53402 -0.44322  1.66053
C   1.32276 -1.72346  1.00640
C   1.91993 -1.65008 -0.30655
H  -1.55531 -3.13135 -0.40173
H  -4.17402 -3.07417 -0.10630
C   1.99417 -2.73523 -1.34260
C   0.69294 -2.93041  1.64237
C   1.16686 -0.11068  3.08046
C   2.97601  1.70418  1.16376
C   3.41341  0.07122 -1.60815
H   0.79800  2.87337 -0.00435
C  -0.75402  3.64341 -1.28088
C  -0.64427  3.84234  1.27263
H   4.25357 -0.62308 -1.79138
H   2.76690  0.07261 -2.50461
H   3.82977  1.08306 -1.48511
H   1.42933 -3.44219  2.29005
H  -0.17548 -2.66032  2.26330
H   0.35400 -3.65826  0.88952
H   3.87252  1.57724  1.79968
H   3.27895  2.28228  0.27637
H   2.25887  2.31381  1.73817
H   1.97097 -0.41255  3.77934
H   1.00305  0.97075  3.21284
H   0.24438 -0.62816  3.38702
H   2.99856 -3.19954 -1.36105
H   1.26009 -3.53231 -1.14538
H   1.78367 -2.32680 -2.34474
H  -0.24443  4.61266 -1.42053
H  -0.51771  2.98281 -2.12995
H  -1.84242  3.83051 -1.27535
H  -0.14948  4.82608  1.20321
H  -1.73058  4.02295  1.35011
H  -0.31385  3.35096  2.20338
```

3b_Ir_IV.log

```
SCF (BP86) Energy =     -1679.14840127
Enthalpy 0K =           -1678.661258
Enthalpy 298K =         -1678.626165
Free Energy 298K =      -1678.730266
PCM (DCM) Energy =      -1679.196866
PCM (MeOH) Energy =     -1679.201711
SCF (BP86+D3) Energy =  -1679.242958
SCF (BS2) Energy =      -1679.650572
Lowest Frequency =  16.3692 cm-1
C   1.83336 -2.50788  0.11729
C   0.79734 -2.62260 -0.90724
C   0.92802 -1.50478 -1.82899
C   2.05824 -0.68530 -1.38313
C   2.61083 -1.31349 -0.19210
Ir  0.52531 -0.75130  0.19593
O  -1.02348 -1.30778  1.64803
C  -0.48036 -0.60449  2.57954
C  -1.10213 -0.46856  3.93754
C  -0.20522 -3.73396 -0.98801
C   0.16576 -1.29542 -3.10549
C   2.65099  0.46368 -2.14478
C   3.80862 -0.84362  0.57636
C   2.11889 -3.50337  1.20529
N  -0.71777  0.95136 -0.19089
C  -2.14553  0.76597 -0.26547
C  -0.29668  2.18508 -0.41989
C   0.99791  2.75100 -0.15540
S   1.44152  4.21919 -1.03515
C   2.93481  4.33951 -0.17827
C   3.08453  3.32650  0.75912
C   1.98969  2.42393  0.77726
O   0.61724  0.00289  2.26747
H  -1.04000  2.86948 -0.85740
H   3.94639  3.25849  1.42682
H   3.62182  5.15599 -0.40326
H   0.27047 -4.62836 -1.43078
H  -0.58069 -4.01132  0.00935
H  -1.06675 -3.46749 -1.61814
H   4.70189 -1.39925  0.23574
H   3.99865  0.22816  0.41951
H   3.69517 -1.02494  1.65653
H   0.76470 -1.66309 -3.95897
H  -0.78949 -1.84081 -3.11380
H  -0.04851 -0.23024 -3.28384
```

```
H   3.35577  0.07958 -2.90568
H   1.87820  1.04339 -2.67206
H   3.20320  1.15254 -1.48892
H   2.81330 -4.28251  0.84088
H   2.58479 -3.02452  2.08032
H   1.20012 -4.00675  1.54347
H   1.87489  1.60025  1.48381
H  -1.83096  0.36019  3.91881
H  -1.64297 -1.38864  4.20315
H  -0.33590 -0.23918  4.69184
C  -2.68494 -0.39026 -0.85872
C  -4.07623 -0.55829 -0.95745
C  -4.91711  0.44388 -0.43025
C  -4.40264  1.59776  0.19101
C  -3.00535  1.74615  0.27523
H  -2.00753 -1.15809 -1.24091
C  -4.66712 -1.78045 -1.62668
H  -6.00396  0.31045 -0.48799
C  -5.32864  2.65492  0.75253
H  -2.58401  2.60711  0.80564
H  -5.52099 -2.17739 -1.05312
H  -5.04160 -1.53809 -2.63751
H  -3.92434 -2.58765 -1.73074
H  -4.81448  3.30302  1.48009
H  -5.71756  3.30465 -0.05228
H  -6.20078  2.20219  1.25195
```

3b_Ir_IV_TS_VI.log

```
SCF (BP86) Energy =     -1679.12396922
Enthalpy 0K =           -1678.638341
Enthalpy 298K =         -1678.603761
Free Energy 298K =      -1678.706916
PCM (DCM) Energy =      -1679.176296
PCM (MeOH) Energy =     -1679.181783
SCF (BP86+D3) Energy =  -1679.221722
SCF (BS2) Energy =      -1679.627179
Lowest Frequency =  -68.9571 cm-1
C   1.70992 -2.43286  0.38128
C   0.77707 -2.45728 -0.75134
C   1.24283 -1.46343 -1.74556
C   2.39562 -0.80103 -1.20266
C   2.66818 -1.39061  0.12639
Ir  0.63365 -0.52495  0.15638
O  -0.57434 -0.92352  1.78930
C  -0.93508  0.00753  2.67111
C  -1.93374 -0.50667  3.69625
C  -0.29019 -3.49086 -0.94727
C   0.65009 -1.25343 -3.10696
C   3.26563  0.19903 -1.90362
C   3.82682 -1.02979  1.00635
C   1.62590 -3.32811  1.58096
N  -0.81113  0.91858 -0.46440
C  -2.22031  0.68163 -0.50951
C  -0.37473  2.13319 -0.76123
C   0.93809  2.52205 -0.34460
S   1.91047  3.76306 -1.10938
C   3.18070  3.52462  0.05475
C   2.87336  2.55012  0.98845
C   1.58657  1.96880  0.77677
O  -0.52023  1.17748  2.67241
H  -1.04899  2.83625 -1.26794
H   3.52145  2.31797  1.83654
H   4.07485  4.14736 -0.00003
H   0.18134 -4.45265 -1.22443
H  -0.86653 -3.65473 -0.02355
H  -0.98607 -3.22262 -1.75611
H   4.69161 -1.67012  0.75054
H   4.13281  0.01683  0.86574
H   3.59712 -1.18730  2.07108
H   1.09651 -1.96974 -3.82112
H  -0.43885 -1.41430 -3.11050
H   0.84593 -0.23865 -3.48458
H   4.12348 -0.31728 -2.37295
H   2.71975  0.72678 -2.69990
H   3.66794  0.95120 -1.20802
H   1.91434 -4.35875  1.30748
H   2.29578 -2.99155  2.38574
H   0.59928 -3.35033  1.98095
H   0.98436  1.45217  1.56501
H  -2.91923 -0.62572  3.21505
H  -1.63236 -1.49418  4.07824
H  -2.02082  0.21107  4.52296
C  -2.70951 -0.56813 -0.93468
C  -4.09238 -0.80139 -1.01410
C  -4.97158  0.23526 -0.63603
C  -4.50603  1.48445 -0.17909
C  -3.11708  1.69699 -0.11153
H  -1.99837 -1.35198 -1.20531
C  -4.63448 -2.12565 -1.50693
H  -6.05247  0.05525 -0.67779
C  -5.47579  2.57062  0.23207
H  -2.72925  2.62969  0.31068
H  -5.47232 -2.47377 -0.88042
H  -5.01848 -2.03739 -2.53907
H  -3.86068 -2.90992 -1.50510
H  -5.00443  3.30214  0.90740
H  -5.84311  3.12353 -0.65147
H  -6.35828  2.15085  0.74144
```

3b_Ir_VII.log

```
SCF (BP86) Energy =     -1465.30721231
Enthalpy 0K =           -1464.881184
Enthalpy 298K =         -1464.850013
Free Energy 298K =      -1464.944593
PCM (DCM) Energy =      -1465.321064
PCM (MeOH) Energy =     -1465.323833
SCF (BP86+D3) Energy =  -1465.39476
SCF (BS2) Energy =      -1910.976141
Lowest Frequency =  14.5132 cm-1
S  -2.03241  4.02119 -0.36848
C  -1.05788  2.56497 -0.21624
C  -1.82244  1.37791 -0.19135
C  -3.21527  1.68693 -0.31595
C  -3.47456  3.04431 -0.40929
C   0.34887  2.41874 -0.20903
N   0.78031  1.16414 -0.12952
C   2.17967  0.89986 -0.12535
H   1.06644  3.24338 -0.30293
Ir -0.73938 -0.32304 -0.07948
Cl -0.63601 -0.36222 -2.51462
C  -0.55977 -2.66109  0.04269
C   0.25606 -2.12416  1.07412
C  -0.58193 -1.24177  1.90581
C  -1.95418 -1.33905  1.41722
C  -1.93586 -2.14626  0.20830
H  -4.01201  0.94051 -0.36059
H  -4.44388  3.53631 -0.50431
C  -3.11408 -2.58613 -0.61473
C  -3.16981 -0.80016  2.11660
C  -0.13921 -0.59130  3.18762
C   1.70854 -2.40263  1.33455
C  -0.14343 -3.57073 -1.07505
H  -0.70304 -4.52241 -1.02928
H  -0.35215 -3.09533 -2.05039
H   0.93136 -3.80451 -1.03176
H  -3.49771 -1.50798  2.90061
H  -2.96664  0.16998  2.59613
H  -4.01157 -0.66090  1.42139
H   1.82071 -3.06389  2.21430
H   2.18916 -2.89680  0.47707
H   2.27064 -1.47643  1.53837
H  -0.16999 -1.31169  4.02764
H   0.89356 -0.21606  3.10774
H  -0.78763  0.25930  3.44950
H  -3.42463 -3.61560 -0.35263
H  -3.98082 -1.92472 -0.45785
H  -2.86831 -2.56232 -1.68866
C   3.02731  1.55663  0.78903
C   4.41335  1.29688  0.79054
C   4.92522  0.36705 -0.13181
C   4.08992 -0.29922 -1.05557
C   2.71077 -0.03441 -1.03927
H   2.59621  2.25620  1.51442
C   5.32770  2.01982  1.75839
```

```
H   6.00118  0.15190 -0.13077
C   4.67944 -1.26242 -2.06570
H   2.02669 -0.51692 -1.74606
H   3.89872 -1.88081 -2.53664
H   5.20178 -0.71883 -2.87408
H   5.42013 -1.93498 -1.59937
H   6.27140  1.47048  1.90880
H   5.58977  3.02649  1.38342
H   4.85060  2.15645  2.74370
```

3b_Ir_VI.log

```
SCF (BP86) Energy =     -1685.31893396
Enthalpy 0K =           -1684.832205
Enthalpy 298K =         -1684.797032
Free Energy 298K =      -1684.900964
PCM (DCM) Energy =      -1679.200718
PCM (MeOH) Energy =     -1679.205356
SCF (BP86+D3) Energy =  -1679.249781
SCF (BS2) Energy =      -1679.654668
Lowest Frequency =  14.1721 cm-1
C   1.71599 -2.39266 -0.58098
C   0.26182 -2.65142 -0.63301
C  -0.30047 -1.82300 -1.64005
C   0.78212 -0.99656 -2.20788
C   2.03851 -1.44181 -1.61206
Rh  0.74931 -0.45820 -0.11842
O   0.49065 -0.87638  2.02557
C   0.94492 -0.25152  3.01664
C   0.64700 -0.67558  4.42786
C  -0.44700 -3.64145  0.24205
C  -1.72530 -1.78935 -2.10317
C   0.64517 -0.08679 -3.39450
C   3.41080 -1.06278 -2.08404
C   2.68385 -3.14881  0.28209
N  -0.73502  1.08265  0.03212
C  -2.14314  0.86774  0.05796
C  -0.24702  2.31148  0.04644
C   1.17362  2.41133  0.00841
S   2.16128  3.86114  0.01863
C   3.59628  2.88823  0.05269
C   3.32941  1.52362  0.05497
C   1.93043  1.21789  0.02276
O   1.71034  0.82300  2.91414
H  -0.91762  3.17722  0.12757
H   4.12995  0.78114  0.09215
H   4.57082  3.37889  0.07097
H  -0.16350 -4.67319 -0.03470
H  -0.17741 -3.49901  1.30209
H  -1.54005 -3.55721  0.15198
H   3.68563 -1.70207 -2.94347
H   3.46050 -0.01561 -2.41774
H   4.17372 -1.21644 -1.30566
H  -1.81894 -2.34956 -3.05194
H  -2.40927 -2.24313 -1.37157
H  -2.07157 -0.76028 -2.29047
H   0.72292 -0.66693 -4.33317
H  -0.33033  0.42353 -3.40145
H   1.43367  0.68095 -3.40916
H   2.89961 -4.13850 -0.16225
H   3.64140 -2.61653  0.38854
H   2.27369 -3.32385  1.28915
H   1.84406  1.01915  1.93499
H   0.04268  0.10422  4.92148
H   0.10033 -1.62654  4.43499
H   1.58554 -0.76658  4.99767
C  -2.66644 -0.15640  0.87386
C  -4.05456 -0.37212  0.93666
C  -4.90149  0.43413  0.14706
C  -4.39845  1.44991 -0.68913
C  -3.00604  1.65726 -0.73158
H  -1.97958 -0.76145  1.47446
C  -4.63667 -1.43320  1.84634
H  -5.98362  0.25968  0.17856
C  -5.33328  2.30756 -1.51448
H  -2.58838  2.41767 -1.40091
H  -5.13558 -0.97438  2.71862
H  -5.39739 -2.03815  1.32472
H  -3.85962 -2.11402  2.22927
H  -4.81250  2.78002 -2.36268
H  -6.17528  1.71831 -1.91277
H  -5.76654  3.11785 -0.90054
```

3b_Ir_V.log

```
SCF (BP86) Energy =     -1685.31893220
Enthalpy 0K =           -1684.832204
Enthalpy 298K =         -1684.797029
Free Energy 298K =      -1684.901006
PCM (DCM) Energy =      -1465.321064
PCM (MeOH) Energy =     -1465.323833
SCF (BP86+D3) Energy =  -1465.394760
SCF (BS2) Energy =      -1910.976141
Lowest Frequency =  13.8929 cm-1
C   1.71711 -2.39089 -0.58429
C   0.26322 -2.65178 -0.63310
C  -0.30268 -1.82400 -1.63863
C   0.77740 -0.99582 -2.20872
C   2.03580 -1.43935 -1.61599
Rh  0.74891 -0.45804 -0.11909
O   0.49171 -0.87631  2.02505
C   0.94850 -0.25376  3.01638
C   0.65194 -0.67943  4.42739
C  -0.44216 -3.64278  0.24364
C  -1.72857 -1.79241 -2.09861
C   0.63613 -0.08563 -3.39454
C   3.40644 -1.05834 -2.09114
C   2.68831 -3.14600  0.27596
N  -0.73516  1.08299  0.03302
C  -2.14327  0.86813  0.05932
C  -0.24691  2.31171  0.04759
C   1.17374  2.41130  0.00907
S   2.16166  3.86097  0.02009
C   3.59650  2.88784  0.05277
C   3.32939  1.52324  0.05394
C   1.93036  1.21779  0.02198
O   1.71577  0.81957  2.91444
H  -0.91730  3.17758  0.12920
H   4.12982  0.78060  0.09001
H   4.57114  3.37831  0.07110
H  -0.15652 -4.67406 -0.03256
H  -0.17166 -3.49875  1.30323
H  -1.53551 -3.56122  0.15478
H   3.67994 -1.69695 -2.95150
H   3.45408 -0.01097 -2.42447
H   4.17142 -1.21142 -1.31468
H  -1.82347 -2.35251 -3.04732
H  -2.41030 -2.24738 -1.36566
H  -2.07676 -0.76381 -2.28489
H   0.71048 -0.66546 -4.33367
H  -0.33943  0.42464 -3.39778
H   1.42454  0.68216 -3.41188
H   2.90684 -4.13394 -0.17091
H   3.64423 -2.61086  0.38267
H   2.27978 -3.32473  1.28304
H   1.84806  1.01738  1.93555
H   0.04640  0.09899  4.92174
H   0.10667 -1.63121  4.43400
H   1.59077 -0.76927  4.99684
C  -2.66619 -0.15563  0.87560
C  -4.05447 -0.37147  0.93881
C  -4.90149  0.43387  0.14874
C  -4.39867  1.44957 -0.68805
C  -3.00653  1.65739 -0.73044
H  -1.97910 -0.76049  1.47616
C  -4.63577 -1.43005  1.85190
H  -5.98353  0.25890  0.18018
C  -5.33421  2.30532 -1.51456
H  -2.58909  2.41768 -1.40001
H  -5.42902 -2.00660  1.34729
H  -3.86559 -2.13673  2.20052
H  -5.09311 -0.97062  2.74653
H  -4.80862  2.79717 -2.34858
H  -6.16176  1.70949 -1.93310
H  -5.78838  3.10009 -0.89554
```

3b_L-H_cis.log

SCF (BP86) Energy = -956.165883540
Enthalpy 0K = -955.948365
Enthalpy 298K = -955.933534
Free Energy 298K = -955.992946
PCM (DCM) Energy = -956.1716159
PCM (MeOH) Energy = -956.1726506
SCF (BP86+D3) Energy = -956.1894186
SCF (BS2) Energy = -956.3310415
Lowest Frequency = 24.8023 cm-1

S	-3.24823	-1.05255	-0.56088
C	-2.53767	0.34709	0.23023
C	-3.52705	1.20753	0.70122
C	-4.84636	0.74589	0.42966
C	-4.85187	-0.46167	-0.24566
C	-1.10390	0.50222	0.33366
N	-0.28168	-0.38879	-0.12999
C	1.10590	-0.16418	-0.07035
H	-0.76246	1.42355	0.85031
H	-3.29482	2.13897	1.22449
H	-5.75533	1.27838	0.71911
H	-5.71443	-1.04100	-0.57622
C	1.93792	-1.29327	0.10139
C	3.33433	-1.16037	0.16378
C	3.89811	0.12322	0.01197
C	3.09626	1.26414	-0.19196
C	1.69968	1.11044	-0.23134
H	1.46181	-2.27514	0.19407
C	4.21715	-2.36917	0.39735
H	4.98969	0.23372	0.02994
C	3.72841	2.63189	-0.35416
H	1.06449	1.97957	-0.43772
H	5.18057	-2.27463	-0.13133
H	4.44679	-2.49440	1.47182
H	3.72906	-3.29726	0.05742
H	3.07201	3.31716	-0.91555
H	3.92748	3.09948	0.62804
H	4.69317	2.57139	-0.88521

3b_L-H_trans.log

SCF (BP86) Energy = -956.163064273
Enthalpy 0K = -955.945584
Enthalpy 298K = -955.930724
Free Energy 298K = -955.989946
PCM (DCM) Energy = -956.168310380
PCM (MeOH) Energy = -956.169227135
SCF (BP86+D3) Energy = -956.186681313
SCF (BS2) Energy = -956.328482970
Lowest Frequency = 31.4355 cm-1

S	3.71448	0.99810	-0.66747
C	2.50699	-0.09279	0.00185
C	3.12079	-1.15652	0.65848
C	4.54033	-1.09173	0.62042
C	5.01098	0.01877	-0.06066
C	1.09212	0.18338	-0.17631
N	0.18658	-0.62823	0.27726
C	-1.17363	-0.28895	0.15600
H	0.83198	1.11040	-0.72902
H	2.53636	-1.94211	1.14112
H	5.20003	-1.83264	1.07860
H	6.04397	0.31704	-0.23859
C	-2.09020	-1.34481	-0.05213
C	-3.46471	-1.09356	-0.18565
C	-3.92379	0.23488	-0.06531
C	-3.03932	1.30324	0.18135
C	-1.66338	1.03241	0.28354
H	-1.69546	-2.36370	-0.12651
C	-4.43442	-2.22222	-0.47028
H	-4.99886	0.43920	-0.14621
C	-3.56460	2.71138	0.37600
H	-0.96550	1.84655	0.51082
H	-2.82164	3.46720	0.07156
H	-4.48481	2.88286	-0.20708
H	-3.81005	2.90345	1.43700
H	-5.40409	-2.05831	0.02941
H	-4.63814	-2.31037	-1.55359
H	-4.03460	-3.19240	-0.13263

3b_Rh_IV.log

SCF (BP86) Energy = -1685.31976139
Enthalpy 0K = -1684.832949
Enthalpy 298K = -1684.797746
Free Energy 298K = -1684.901967
PCM (DCM) Energy = -1685.368501
PCM (MeOH) Energy = -1685.373447
SCF (BP86+D3) Energy = -1685.411603
SCF (BS2) Energy = -1685.306672
Lowest Frequency = 17.5933 cm-1

C	1.75145	-2.66336	0.12310
C	0.71207	-2.73053	-0.89737
C	0.89411	-1.62085	-1.81218
C	2.06439	-0.86375	-1.37247
C	2.59184	-1.51661	-0.19058
Rh	0.54008	-0.86190	0.22208
O	-0.99789	-1.40207	1.65316
C	-0.40926	-0.74333	2.58854
C	-1.01286	-0.60676	3.95673
C	-0.34627	-3.78838	-0.96811
C	0.13407	-1.36060	-3.07978
C	2.69863	0.26241	-2.13292
C	3.81336	-1.11005	0.57464
C	1.98089	-3.66407	1.21809
N	-0.61695	0.91240	-0.16679
C	-2.04708	0.79394	-0.23923
C	-0.13244	2.11974	-0.39412
C	1.19370	2.60795	-0.12266
S	1.73410	4.04697	-0.99485
C	3.22747	4.06998	-0.12879
C	3.30675	3.04684	0.80583
C	2.15599	2.21560	0.81479
O	0.71173	-0.17731	2.28546
H	-0.83275	2.85010	-0.83078
H	4.15811	2.92280	1.47900
H	3.96550	4.84278	-0.34623
H	0.09449	-4.72889	-1.34735
H	-0.77295	-3.99659	0.02611
H	-1.16710	-3.50820	-1.64465
H	4.67280	-1.72456	0.24735
H	4.07021	-0.05434	0.40416
H	3.68562	-1.26942	1.65693
H	0.71789	-1.72995	-3.94334
H	-0.83891	-1.87315	-3.09620
H	-0.04360	-0.28527	-3.23673
H	3.35947	-0.14925	-2.91897
H	1.94590	0.89145	-2.63195
H	3.30780	0.90925	-1.48490
H	2.62961	-4.48420	0.85854
H	2.47580	-3.20645	2.08847
H	1.03545	-4.11275	1.55967
H	1.98363	1.39851	1.51795
H	-1.61053	-1.49703	4.20148
H	-0.22826	-0.44852	4.71078
H	-1.68537	0.26842	3.96751
C	-2.63898	-0.34687	-0.81384
C	-4.03587	-0.45456	-0.91279
C	-4.83188	0.59225	-0.40264
C	-4.26687	1.73099	0.20273
C	-2.86471	1.81837	0.28681
H	-1.99737	-1.15208	-1.18078
H	-5.92357	0.50613	-0.45930
H	-2.40637	2.66677	0.80666
C	-4.68025	-1.66033	-1.56220
C	-5.14545	2.83609	0.74801
H	-5.54914	-2.01148	-0.98132
H	-5.04633	-1.41799	-2.57612
H	-3.97303	-2.50030	-1.65447
H	-5.49845	3.49551	-0.06546
H	-6.04085	2.42990	1.24626
H	-4.60553	3.46635	1.47259

3b_Rh_IV.log

SCF (BP86) Energy = -1685.31893396
Enthalpy 0K = -1684.832205
Enthalpy 298K = -1684.797032

```
Free Energy 298K =      -1684.900964
PCM (DCM) Energy =      -1685.366193
PCM (MeOH) Energy =     -1685.370782
SCF (BP86+D3) Energy =  -1685.412683
SCF (BS2) Energy =      -1685.305593
Lowest Frequency =  14.1720 cm-1
C   1.71599 -2.39266 -0.58098
C   0.26182 -2.65142 -0.63301
C  -0.30047 -1.82300 -1.64005
C   0.78212 -0.99656 -2.20788
C   2.03851 -1.44181 -1.61206
Rh  0.74931 -0.45820 -0.11842
O   0.49065 -0.87638  2.02557
C   0.94492 -0.25152  3.01664
C   0.64700 -0.67558  4.42786
C  -0.44700 -3.64145  0.24205
C  -1.72530 -1.78935 -2.10317
C   0.64517 -0.08679 -3.39450
C   3.41080 -1.06278 -2.08404
C   2.68385 -3.14881  0.28209
N  -0.73502  1.08265  0.03212
C  -2.14314  0.86774  0.05796
C  -0.24702  2.31148  0.04644
C   1.17362  2.41133  0.00841
S   2.16128  3.86114  0.01863
C   3.59628  2.88823  0.05269
C   3.32941  1.52362  0.05497
C   1.93043  1.21789  0.02276
O   1.71034  0.82300  2.91414
H  -0.91762  3.17722  0.12757
H   4.12995  0.78114  0.09215
H   4.57082  3.37889  0.07097
H  -0.16350 -4.67319 -0.03470
H  -0.17741 -3.49901  1.30209
H  -1.54005 -3.55721  0.15198
H   3.68563 -1.70207 -2.94347
H   3.46050 -0.01561 -2.41774
H   4.17372 -1.21644 -1.30566
H  -1.81894 -2.34956 -3.05194
H  -2.40927 -2.24313 -1.37157
H  -2.07157 -0.76028 -2.29047
H   0.72292 -0.66693 -4.33317
H  -0.33033  0.42353 -3.40145
H   1.43367  0.68095 -3.40916
H   2.89961 -4.13850 -0.16225
H   3.64140 -2.61653  0.38854
H   2.27369 -3.32385  1.28915
H   1.84406  1.01915  1.93499
H   0.04268  0.10422  4.92148
H   0.10033 -1.62654  4.43499
H   1.58554 -0.76658  4.99767
C  -2.66644 -0.15640  0.87386
C  -4.05456 -0.37212  0.93666
C  -4.90149  0.43413  0.14706
C  -4.39845  1.44991 -0.68913
C  -3.00604  1.65726 -0.73158
H  -1.97958 -0.76145  1.47446
C  -4.63667 -1.43320  1.84634
H  -5.98362  0.25968  0.17856
C  -5.33328  2.30756 -1.51448
H  -2.58838  2.41767 -1.40091
H  -5.13558 -0.97438  2.71862
H  -5.39739 -2.03815  1.32472
H  -3.85962 -2.11402  2.22927
H  -4.81250  2.78002 -2.36268
H  -6.17528  1.71831 -1.91277
H  -5.76654  3.11785 -0.90054
```

3b_Rh_VII.log

```
SCF (BP86) Energy =     -1471.46943725
Enthalpy 0K =           -1471.043497
Enthalpy 298K =         -1471.012309
Free Energy 298K =      -1471.106651
PCM (DCM) Energy =      -1471.483740
PCM (MeOH) Energy =     -1471.486621
SCF (BP86+D3) Energy =  -1471.554550
SCF (BS2) Energy =      -1916.622696
Lowest Frequency =  15.3464 cm-1
S  -2.17472  3.92702 -0.38828
C  -1.18710  2.47897 -0.21968
C  -1.94138  1.29039 -0.22643
C  -3.33156  1.57986 -0.38765
C  -3.60374  2.93648 -0.47691
C   0.22612  2.36084 -0.19824
N   0.68583  1.12093 -0.13025
C   2.08635  0.87868 -0.13063
H   0.92063  3.20772 -0.28270
Rh -0.81930 -0.37487 -0.10162
Cl -0.74627 -0.46470 -2.51396
C  -0.58299 -2.68466  0.08479
C   0.17335 -2.09659  1.13030
C  -0.72584 -1.23590  1.91403
C  -2.06907 -1.39364  1.38439
C  -1.97840 -2.21773  0.19980
H  -4.11830  0.82513 -0.45967
H  -4.57581  3.41859 -0.59305
C  -3.10423 -2.69451 -0.67280
C  -3.32613 -0.87902  2.02658
C  -0.35092 -0.52874  3.18679
C   1.62485 -2.31499  1.44706
C  -0.10180 -3.60835 -0.99427
H  -0.63148 -4.57702 -0.94319
H  -0.29505 -3.16402 -1.98765
H   0.97794 -3.80582 -0.91052
H  -3.65105 -1.57148  2.82569
H  -3.17807  0.11428  2.47820
H  -4.15153 -0.79887  1.30292
H   1.73056 -2.95471  2.34349
H   2.15417 -2.80583  0.61680
H   2.14492 -1.36488  1.65323
H  -0.39320 -1.21987  4.05079
H   0.67380 -0.12737  3.13378
H  -1.03243  0.31082  3.39566
H  -3.36055 -3.74803 -0.45094
H  -4.01328 -2.09061 -0.52445
H  -2.82453 -2.62392 -1.73675
C   2.93272  1.54653  0.77793
C   4.32092  1.30075  0.77164
C   4.83665  0.37296 -0.15120
C   4.00314 -0.30472 -1.06803
C   2.62141 -0.05418 -1.04407
H   2.49899  2.24349  1.50436
C   5.23466  2.03607  1.73072
H   5.91461  0.16816 -0.15529
C   4.59605 -1.26435 -2.07950
H   1.93660 -0.54608 -1.74407
H   3.82396 -1.91743 -2.51667
H   5.07357 -0.71659 -2.91248
H   5.37386 -1.90209 -1.62519
H   6.17219  1.48162  1.90017
H   5.50932  3.03166  1.33561
H   4.75154  2.19856  2.70903
```

3b_Rh_VI_TS_VI.log

```
SCF (BP86) Energy =     -1685.29591088
Enthalpy 0K =           -1684.810669
Enthalpy 298K =         -1684.776130
Free Energy 298K =      -1684.878955
PCM (DCM) Energy =      -1685.348526
PCM (MeOH) Energy =     -1685.354101
SCF (BP86+D3) Energy =  -1685.389658
SCF (BS2) Energy =      -1685.28395
Lowest Frequency =  -41.0563 cm-1
C   1.66000 -2.46156  0.14517
C   0.62313 -2.42913 -0.88508
C   1.03060 -1.44627 -1.90257
C   2.26076 -0.84671 -1.47593
C   2.64592 -1.47664 -0.19650
Rh  0.68332 -0.49944  0.06896
O  -0.48174 -0.90716  1.74722
C  -0.04575 -0.48795  2.92099
C  -0.93761 -0.88570  4.09028
C  -0.50424 -3.41230 -0.97519
C   0.31367 -1.18075 -3.19212
```

C 3.09042 0.13687 -2.24560
C 3.91067 -1.21335 0.56293
C 1.67040 -3.38119 1.32792
N -0.84897 0.94035 -0.36732
C -2.25468 0.71698 -0.35003
C -0.40190 2.16746 -0.56335
C 0.95592 2.47007 -0.22226
S 1.86134 3.81108 -0.89404
C 3.26455 3.36877 0.03112
C 3.05212 2.24788 0.81387
C 1.72967 1.72076 0.68531
O 0.98596 0.19288 3.09576
H -1.08110 2.94494 -0.94007
H 3.79402 1.86503 1.51772
H 4.16026 3.98842 -0.03055
H -0.09614 -4.41827 -1.18834
H -1.06072 -3.47522 -0.02634
H -1.20841 -3.16716 -1.78381
H 4.65160 -1.99836 0.32139
H 4.35337 -0.24355 0.29569
H 3.74392 -1.23551 1.65133
H 0.65809 -1.89880 -3.95960
H -0.77584 -1.29838 -3.09225
H 0.51490 -0.16763 -3.57133
H 3.87964 -0.39526 -2.80865
H 2.48484 0.69785 -2.97320
H 3.58568 0.86223 -1.58164
H 1.99634 -4.39060 1.01631
H 2.35850 -3.03008 2.11073
H 0.66469 -3.47010 1.76747
H 1.31919 1.05090 1.50513
H -1.67346 -1.65166 3.80974
H -0.30972 -1.24124 4.92160
H -1.47236 0.01182 4.44409
C -2.77272 -0.51070 -0.80292
C -4.15889 -0.73743 -0.82752
C -5.01447 0.28302 -0.36442
C -4.52059 1.50953 0.12560
C -3.13057 1.71511 0.13560
H -2.07940 -1.28473 -1.13708
H -6.09699 0.10805 -0.36233
H -2.72451 2.63213 0.57527
C -4.72922 -2.03818 -1.35038
C -5.46728 2.57354 0.63666
H -5.54620 -2.40465 -0.70715
H -5.14973 -1.90813 -2.36376
H -3.96241 -2.82733 -1.40684
H -6.23351 2.14253 1.30217
H -4.93425 3.36025 1.19334
H -6.00143 3.05919 -0.19960

4a_Ir_IV.log

SCF (BP86) Energy = -1244.03108403
Enthalpy 0K = -1243.528218
Enthalpy 298K = -1243.494575
Free Energy 298K = -1243.595106
PCM (DCM) Energy = -1244.080306
PCM (MeOH) Energy = -1244.085162
SCF (BP86+D3) Energy = -1244.118382
SCF (BS2) Energy = -1244.495847
Lowest Frequency = 15.8604 cm-1
Ir -1.17200 -0.16793 0.14139
N -0.23057 1.67358 -0.27160
C 1.06494 1.85657 -0.38960
C 2.08296 0.86713 -0.18873
C 3.40449 1.18289 -0.38586
C 4.56624 0.33002 -0.19112
H 1.76810 -0.12294 0.15449
C -2.91735 -1.43800 -0.29264
C -2.57407 -0.61467 -1.46282
C -1.23160 -1.00378 -1.88898
C -0.73499 -2.00316 -0.96262
C -1.79428 -2.28564 0.02172
O 0.01538 -0.17550 1.99325
C -0.84924 0.56233 2.60323
O -1.89350 0.90276 1.92596
C -1.12508 2.87364 -0.46085
C -0.98574 3.47178 -1.87200
C -4.22607 -1.38440 0.43655
C -3.51968 0.29308 -2.19491
C -0.51120 -0.50683 -3.10789
C 0.57166 -2.73351 -1.05566
C -1.71578 -3.32035 1.10658
C -0.63705 1.02376 4.01570
C -0.89002 3.92286 0.64010
H -2.14714 2.48007 -0.34447
H 1.41016 2.86766 -0.66014
H 3.63086 2.20072 -0.73691
H -4.97290 -2.00209 -0.09523
H -4.13845 -1.76875 1.46335
H -4.61740 -0.35659 0.48963
H -1.94623 -4.32046 0.69622
H -0.70930 -3.36389 1.55133
H -2.43386 -3.11739 1.91532
H 0.43125 -3.68027 -1.60984
H 1.33390 -2.14589 -1.58936
H 0.96300 -2.99075 -0.05882
H -4.12936 -0.28768 -2.91169
H -4.21306 0.79831 -1.50431
H -2.98422 1.06628 -2.76675
H -0.71030 -1.18338 -3.95894
H -0.84766 0.49958 -3.39836
H 0.57833 -0.47227 -2.95416
H -1.59917 1.25794 4.49313
H -0.09882 0.25549 4.59023
H -0.01773 1.93763 4.01242
H -1.61759 4.74342 0.52753
H -1.02594 3.47985 1.63805
H 0.12066 4.36158 0.57752
H -1.74324 4.25980 -2.01370
H 0.00314 3.93454 -2.03078
H -1.13620 2.70895 -2.65340
C 5.84098 0.82604 -0.57108
C 6.99206 0.04717 -0.41041
C 6.89323 -1.24109 0.14128
C 5.63787 -1.74574 0.53351
C 4.48635 -0.97243 0.37042
H 5.91649 1.83207 -0.99893
H 7.96646 0.44370 -0.71096
H 7.79227 -1.85119 0.27270
H 5.56537 -2.74484 0.97430
H 3.51941 -1.36790 0.69722

4a_Ir_IV_TS_V.log

SCF (BP86) Energy = -1244.00018371
Enthalpy 0K = -1243.498742
Enthalpy 298K = -1243.466118
Free Energy 298K = -1243.562688
PCM (DCM) Energy = -1244.051327
PCM (MeOH) Energy = -1244.056522
SCF (BP86+D3) Energy = -1244.098585
SCF (BS2) Energy = -1244.464976
Lowest Frequency = -33.4667 cm-1
Ir 0.53205 0.23200 0.08225
N 1.31797 -1.18041 -1.24427
C 0.49288 -1.81290 -2.05026
C -0.92151 -1.61975 -1.93553
C -1.45360 -1.10896 -0.76514
C -2.87798 -0.85425 -0.53937
H -1.56881 -1.95356 -2.75313
C 1.73968 1.98345 0.27854
C 0.94683 2.14153 -0.95776
C -0.44213 2.14581 -0.59111
C -0.53388 2.04675 0.88257
C 0.79775 1.99472 1.41114
O -0.54722 -2.05738 1.96641
C 0.66152 -1.86750 2.19098
O 1.42799 -1.01203 1.52535
C 2.76731 -1.56710 -1.21971
C 3.44645 -1.23361 -2.56084
C 3.23316 2.05430 0.39332
C 1.50077 2.35304 -2.33490
C -1.59917 2.38722 -1.51201
C -1.80833 2.12122 1.66745

```
C   1.20250  1.92007  2.85173
C   1.39512 -2.62213  3.29077
C   2.94719 -3.04402 -0.82851
H   3.20671 -0.94299 -0.42584
H   0.89463 -2.52361 -2.78569
H  -0.87641 -1.26444  0.22115
H   3.55229  3.10431  0.53161
H   3.59584  1.47737  1.25785
H   3.73192  1.67310 -0.51115
H   1.64829  2.88127  3.16455
H   0.34323  1.71480  3.50659
H   1.95131  1.12743  3.00936
H  -2.12938  3.17598  1.75240
H  -2.62132  1.56084  1.18071
H  -1.68399  1.72365  2.68554
H   1.58777  3.43719 -2.53405
H   2.50517  1.91758 -2.44339
H   0.84961  1.92234 -3.11070
H  -1.84558  3.46541 -1.51502
H  -1.36406  2.09684 -2.54719
H  -2.49976  1.84014 -1.19548
H   2.47084 -2.40057  3.30508
H   0.95184 -2.35215  4.26354
H   1.23411 -3.70316  3.15370
H   4.02116 -3.26364 -0.71173
H   2.44444 -3.26003  0.12589
H   2.54978 -3.72375 -1.60143
H   4.52897 -1.42387 -2.48102
H   3.05937 -1.86217 -3.38088
H   3.30264 -0.17769 -2.84111
C  -3.40939 -0.95843  0.77355
C  -4.78038 -0.77778  0.99745
C  -5.63979 -0.48009 -0.07450
C  -5.12415 -0.36584 -1.37925
C  -3.75745 -0.55190 -1.61284
H  -2.73662 -1.22206  1.59588
H  -5.18267 -0.87886  2.01019
H  -6.71012 -0.33744  0.10380
H  -5.79139 -0.12857 -2.21360
H  -3.36012 -0.44875 -2.62825
```

4a_Ir_V.log

```
SCF (BP86) Energy =     -1244.00056040
Enthalpy 0K =           -1243.499737
Enthalpy 298K =         -1243.466430
Free Energy 298K =      -1243.564612
PCM (DCM) Energy =      -1244.051305
PCM (MeOH) Energy =     -1244.056447
SCF (BP86+D3) Energy =  -1244.100388
SCF (BS2) Energy =      -1244.465136
Lowest Frequency =  19.8485 cm-1
Ir  0.45546  0.23570  0.10207
N   1.40907 -1.05299 -1.24968
C   0.64271 -1.66994 -2.12700
C  -0.77382 -1.52072 -2.03159
C  -1.29079 -1.01943 -0.84079
C  -2.72854 -0.84558 -0.59397
H  -1.41764 -1.87953 -2.84060
C   1.62868  2.03143  0.37557
C   0.81305  2.21973 -0.83629
C  -0.57153  2.17102 -0.44625
C  -0.64043  1.99098  1.01582
C   0.70745  1.94942  1.51492
O  -0.33610 -2.56474  1.41324
C   0.71813 -2.13198  1.92003
O   1.33071 -1.01729  1.55172
C   2.86888 -1.37458 -1.17353
C   3.60687 -0.85234 -2.42046
C   3.12185  2.14876  0.47417
C   1.32935  2.52345 -2.21118
C  -1.74349  2.44420 -1.33848
C  -1.89869  2.03003  1.83102
C   1.13795  1.80928  2.94281
C   1.39995 -2.86017  3.06826
C   3.11244 -2.87793 -0.95083
H   3.22613 -0.82923 -0.28551
H   1.09451 -2.33036 -2.87922
H  -0.72411 -1.37823  0.14291
H   3.40958  3.20254  0.64699
H   3.51633  1.55367  1.31222
H   3.62139  1.81734 -0.44926
H   1.61651  2.74584  3.28049
H   0.28652  1.60294  3.60723
H   1.86725  0.99061  3.05486
H  -2.20996  3.07979  1.98522
H  -2.72552  1.50338  1.33099
H  -1.75671  1.57409  2.82227
H   1.35084  3.61841 -2.36337
H   2.35414  2.15123 -2.35560
H   0.68987  2.09025 -2.99539
H  -1.98706  3.52209 -1.29431
H  -1.52597  2.19580 -2.38831
H  -2.63911  1.88600 -1.02924
H   2.44965 -2.55593  3.18076
H   0.86210 -2.62502  4.00268
H   1.32627 -3.94606  2.90984
H   4.18573 -3.05107 -0.76847
H   2.54971 -3.24860 -0.08074
H   2.82574 -3.47581 -1.83256
H   4.69052 -1.01569 -2.30394
H   3.28466 -1.38458 -3.33169
H   3.43688  0.22517 -2.57560
C  -3.25034 -1.03173  0.71227
C  -4.62770 -0.93538  0.94821
C  -5.50686 -0.63839 -0.10791
C  -5.00272 -0.44437 -1.40709
C  -3.62852 -0.54978 -1.65092
H  -2.56513 -1.29837  1.52332
H  -5.01909 -1.10216  1.95654
H  -6.58233 -0.56023  0.07874
H  -5.68436 -0.20924 -2.23036
H  -3.24156 -0.38700 -2.66249
```

4a_Ir_V_TS_VI.log

```
SCF (BP86) Energy =     -1244.00013414
Enthalpy 0K =           -1243.501174
Enthalpy 298K =         -1243.468695
Free Energy 298K =      -1243.564488
PCM (DCM) Energy =      -1244.049975
PCM (MeOH) Energy =     -1244.054972
SCF (BP86+D3) Energy =  -1244.100618
SCF (BS2) Energy =      -1244.463908
Lowest Frequency =  -186.0444 cm-1
Ir  0.42735  0.22792  0.10441
N   1.46430 -1.07229 -1.18198
C   0.72622 -1.76418 -2.02944
C  -0.69074 -1.64149 -1.94506
C  -1.19809 -1.01911 -0.80209
C  -2.64818 -0.85108 -0.59400
H  -1.33078 -2.10478 -2.70229
C   1.61183  2.07077  0.25559
C   0.71738  2.18307 -0.90653
C  -0.64281  2.13991 -0.42279
C  -0.61745  2.00264  1.03874
C   0.77020  1.99484  1.44398
O  -0.39301 -2.55030  1.32330
C   0.62630 -2.12150  1.92596
O   1.24095 -1.00446  1.62488
C   2.93605 -1.31783 -1.09223
C   3.10520  2.22866  0.24820
C   1.13695  2.44730 -2.32266
C  -1.86926  2.37975 -1.24856
C  -1.81176  2.08242  1.94431
C   1.28174  1.90855  2.84953
C   1.20571 -2.89538  3.09441
H   1.20439 -2.45099 -2.74039
H  -0.66909 -1.48641  0.25013
H   3.37448  3.29656  0.34779
H   3.57402  1.68981  1.08624
H   3.55251  1.86353 -0.68907
H   1.60580  2.91091  3.18399
H   0.50721  1.55387  3.54474
H   2.14503  1.22948  2.92363
H  -2.07417  3.14074  2.12819
```

```
H  -2.69080  1.58878  1.50321
H  -1.61438  1.61481  2.92097
H   1.14949  3.53711 -2.50896
H   2.14816  2.06620 -2.52790
H   0.44401  1.99312 -3.04718
H  -2.08411  3.46460 -1.25928
H  -1.73304  2.05771 -2.29195
H  -2.75146  1.86601 -0.84146
H   2.18953 -2.50634  3.38834
H   0.51306 -2.81451  3.94906
H   1.27490 -3.96191  2.83175
C  -3.19966 -0.90040  0.71164
C  -4.58278 -0.79623  0.90893
C  -5.44250 -0.62534 -0.19003
C  -4.91083 -0.56678 -1.49099
C  -3.53056 -0.68253 -1.69293
H  -2.53346 -1.06476  1.56413
H  -4.99348 -0.85809  1.92157
H  -6.52235 -0.53973 -0.03473
H  -5.57549 -0.42822 -2.34938
H  -3.12408 -0.62063 -2.70791
C   3.64541 -0.84596 -2.37592
H   3.27198 -0.69630 -0.24663
C   3.25632 -2.78884 -0.77070
H   4.34086 -2.90083 -0.60788
H   2.73574 -3.12029  0.14047
H   2.97380 -3.46071 -1.59875
H   4.73661 -0.94003 -2.25317
H   3.35271 -1.45848 -3.24568
H   3.41461  0.20647 -2.60702
```

4a_Ir_VI.log

```
SCF (BP86) Energy =     -1244.02248942
Enthalpy 0K =           -1243.518800
Enthalpy 298K =         -1243.485979
Free Energy 298K =      -1243.582392
PCM (DCM) Energy =      -1244.070441
PCM (MeOH) Energy =     -1244.075066
SCF (BP86+D3) Energy =  -1244.123369
SCF (BS2) Energy =      -1244.484474
Lowest Frequency =  20.9951 cm-1
Ir -0.37209 -0.21958  0.02119
N  -1.44764  1.18024 -1.16572
C  -0.68644  1.95910 -1.90783
C   0.73017  1.80146 -1.77971
C   1.14899  0.82606 -0.87432
C   2.59356  0.61995 -0.64128
H   1.41666  2.44256 -2.34373
C  -1.83269 -2.05640  0.02892
C  -0.76936 -2.09587 -0.99878
C   0.51356 -2.22065 -0.30266
C   0.26116 -2.07303  1.11336
C  -1.20237 -2.00431  1.29965
O   0.50461  3.01210  1.06873
C  -0.16172  2.28859  1.95260
O  -0.53189  1.09960  1.76308
C  -2.92865  1.30381 -1.16137
C  -3.50017  2.12391 -2.32814
C  -3.30721 -2.16586 -0.23582
C  -0.99248 -2.30887 -2.46984
C   1.82236 -2.57169 -0.94401
C   1.25154 -2.25942  2.22800
C  -1.87164 -1.90386  2.63796
C  -0.44851  2.99465  3.24750
C  -3.40788  1.85065  0.19700
H  -3.29996  0.26830 -1.25915
H  -1.13106  2.71093 -2.57002
H   0.67653  2.47417  0.23660
H  -3.62123 -3.22248 -0.14858
H  -3.90880 -1.58460  0.48048
H  -3.56966 -1.84136 -1.25472
H  -1.75357 -2.85086  3.19513
H  -1.41929 -1.10523  3.24941
H  -2.94876 -1.69932  2.54622
H   1.23913 -3.30939  2.57522
H   2.27692 -2.02852  1.90366
H   1.01207 -1.62385  3.09548
H  -1.15964 -3.38087 -2.68270
H  -1.87348 -1.75632 -2.83193
H  -0.12328 -1.98005 -3.05920
H   1.89978 -3.67224 -1.01734
H   1.90481 -2.16192 -1.96191
H   2.68067 -2.20811 -0.36097
H  -1.02631  2.34771  3.91877
H   0.50212  3.28328  3.72632
H  -1.00346  3.92582  3.04744
H  -4.50890  1.82659  0.24352
H  -3.00987  1.25432  1.03292
H  -3.08506  2.89842  0.32577
H  -4.59886  2.04336 -2.31026
H  -3.25375  3.19657 -2.24581
H  -3.15346  1.75320 -3.30717
C   3.09764  0.38906  0.66309
C   4.47441  0.25601  0.88977
C   5.37549  0.31644 -0.18748
C   4.89148  0.52668 -1.49025
C   3.51830  0.68814 -1.71564
H   2.39390  0.33626  1.49994
H   4.84706  0.10256  1.90770
H   6.44925  0.19771 -0.01298
H   5.58755  0.56545 -2.33408
H   3.14757  0.84317 -2.73424
```

4a_Ir_VII.log

```
SCF (BP86) Energy =     -1030.17976660
Enthalpy 0K =           -1029.737564
Enthalpy 298K =         -1029.708460
Free Energy 298K =      -1029.796008
PCM (DCM) Energy =      -1030.191353
PCM (MeOH) Energy =     -1030.193712
SCF (BP86+D3) Energy =  -1030.270814
SCF (BS2) Energy =      -1475.810261
Lowest Frequency =  25.0125 cm-1
Ir -0.34769  0.09298 -0.08459
N  -1.47180 -1.66259  0.13705
C  -0.75592 -2.75844  0.32071
C   0.65433 -2.59725  0.39256
C   1.09760 -1.29830  0.17188
C   2.54874 -1.03087  0.08161
H   1.32423 -3.45591  0.50929
C  -1.79716  1.78223  0.73857
C  -0.76062  1.32837  1.68346
C   0.53948  1.70149  1.12735
C   0.31262  2.22158 -0.20418
C  -1.14906  2.30430 -0.40876
Cl -0.36805 -0.33410 -2.48290
C  -2.93432 -1.75576 -0.10162
C  -3.66556 -2.35980  1.11270
C  -3.27577  1.72670  0.99967
C  -1.01416  0.86457  3.09225
C   1.84698  1.67866  1.86566
C   1.32902  2.82298 -1.13308
C  -1.78420  2.83057 -1.66177
C  -3.24467 -2.50906 -1.40929
H  -3.27074 -0.71323 -0.22370
H  -1.24657 -3.74054  0.36911
H  -3.59130  2.58660  1.62019
H  -3.86031  1.75938  0.06661
H  -3.55999  0.81324  1.54742
H  -1.50791  3.88826 -1.82354
H  -1.43992  2.24920 -2.53621
H  -2.88274  2.76863 -1.62223
H   1.32779  3.92723 -1.05674
H   2.34455  2.46848 -0.89961
H   1.11002  2.55419 -2.17960
H  -1.15249  1.72518  3.77474
H  -1.92039  0.24110  3.15492
H  -0.17185  0.26538  3.47133
H   1.97413  2.62305  2.42757
H   1.89209  0.84756  2.58658
H   2.70098  1.56948  1.18095
H  -4.32491 -2.45606 -1.63082
H  -2.68198 -2.06241 -2.24393
H  -2.96760 -3.57507 -1.33078
```

```
H  -4.75718 -2.31950  0.95677
H  -3.39069 -3.41787  1.26571
H  -3.42480 -1.80974  2.03817
C   3.08171 -0.28895 -1.00113
C   4.46300 -0.07220 -1.10682
C   5.33946 -0.56911 -0.12554
C   4.82376 -1.30422  0.95477
C   3.44475 -1.54176  1.05329
H   2.39168  0.07699 -1.76821
H   4.85931  0.48565 -1.96259
H   6.41650 -0.38705 -0.20423
H   5.49822 -1.69504  1.72472
H   3.04379 -2.11340  1.89764
```

4a_L-H.log

```
SCF (BP86) Energy =     -521.032681805
Enthalpy 0K =           -520.799530
Enthalpy 298K =         -520.786332
Free Energy 298K =      -520.840377
PCM (DCM) Energy =      -521.0408527
PCM (MeOH) Energy =     -521.0416791
SCF (BP86+D3) Energy =  -521.0579829
SCF (BS2) Energy =      -521.1643112
Lowest Frequency =  27.9911 cm-1
N  -2.76832 -0.64830 -0.33339
C  -1.79242  0.18540 -0.17695
C  -0.41226 -0.27860 -0.17242
C   0.64227  0.56849 -0.01282
C   2.06763  0.23256  0.01064
H  -0.27595 -1.35828 -0.30614
C  -4.15892 -0.17675 -0.32206
C  -4.40683  1.33633 -0.17969
C  -4.90557 -0.97432  0.76924
H  -4.57519 -0.50055 -1.29956
H  -1.93296  1.27887 -0.04236
H   0.41535  1.63759  0.11527
H  -5.99168 -0.78751  0.71804
H  -4.72286 -2.05365  0.64755
H  -4.55008 -0.67841  1.77178
H  -5.48786  1.54506 -0.24369
H  -4.05303  1.71670  0.79546
H  -3.90788  1.91512 -0.97623
C   3.01310  1.27283  0.18943
C   4.38833  1.00759  0.21926
C   4.85330 -0.30881  0.07055
C   3.92926 -1.35503 -0.10787
C   2.55627 -1.09071 -0.13767
H   2.65311  2.30184  0.30573
H   5.09840  1.82952  0.35873
H   5.92720 -0.52081  0.09318
H   4.28468 -2.38435 -0.22442
H   1.85200 -1.91702 -0.27730
```

4a_Rh_IV.log

```
SCF (BP86) Energy =     -1250.20159681
Enthalpy 0K =           -1249.698977
Enthalpy 298K =         -1249.665264
Free Energy 298K =      -1249.765821
PCM (DCM) Energy =      -1250.251064
PCM (MeOH) Energy =     -1250.255991
SCF (BP86+D3) Energy =  -1250.286420
SCF (BS2) Energy =      -1250.150951
Lowest Frequency =  16.1605 cm-1
Rh -1.31452 -0.20422  0.16289
N  -0.40381  1.66512 -0.19691
C   0.88653  1.86763 -0.30887
C   1.91368  0.87848 -0.14446
C   3.23185  1.20875 -0.33517
C   4.39982  0.35665 -0.17273
H   1.60636 -0.12386  0.16900
C  -3.05618 -1.43871 -0.35028
C  -2.69891 -0.57163 -1.47550
C  -1.35624 -0.94233 -1.90426
C  -0.87506 -1.98319 -1.02345
C  -1.93825 -2.29939 -0.06109
O  -0.12238 -0.34171  1.97758
C  -0.99716  0.34284  2.63179
O  -2.05097  0.71788  1.99009
C  -1.31868  2.85108 -0.33206
C  -1.15147  3.56274 -1.68730
C  -4.36987 -1.41204  0.36951
C  -3.62685  0.38450 -2.16566
C  -0.62232 -0.38993 -3.09021
C   0.43533 -2.70387 -1.12356
C  -1.87011 -3.37581  0.98206
C  -0.78232  0.71587  4.07183
C  -1.14560  3.81665  0.85450
H  -2.33536  2.42897 -0.28141
H   1.22671  2.89096 -0.54154
H   3.45076  2.23896 -0.65337
H  -5.11542 -2.00021 -0.19711
H  -4.29434 -1.84494  1.37767
H  -4.75849 -0.38638  0.46671
H  -2.08319 -4.36083  0.52755
H  -0.87119 -3.42925  1.44270
H  -2.60516 -3.21337  1.78459
H   0.30339 -3.64155 -1.69556
H   1.19796 -2.10384 -1.64257
H   0.82153 -2.97897 -0.12929
H  -4.23663 -0.15077 -2.91740
H  -4.32311  0.85928 -1.45641
H  -3.07864  1.18017 -2.69280
H  -0.81380 -1.02467 -3.97493
H  -0.95295  0.63004 -3.33656
H   0.46585 -0.36680 -2.92501
H  -1.74605  0.87861  4.57559
H  -0.20541 -0.06634  4.58685
H  -0.20187  1.65356  4.12244
H  -1.88282  4.63288  0.77875
H  -1.30851  3.29377  1.80872
H  -0.13979  4.27107  0.86107
H  -1.93248  4.33284 -1.79607
H  -0.17656  4.07203 -1.77255
H  -1.24482  2.85974 -2.53157
C   5.66911  0.86930 -0.54813
C   6.82510  0.09177 -0.41830
C   6.73674 -1.21185  0.09782
C   5.48689 -1.73314  0.48561
C   4.33047 -0.96113  0.35295
H   5.73667  1.88730 -0.94811
H   7.79524  0.50142 -0.71505
H   7.63965 -1.82089  0.20539
H   5.42250 -2.74423  0.89955
H   3.36813 -1.36964  0.67739
```

4a_Rh_IV_TS_VI.log

```
SCF (BP86) Energy =     -1250.16764670
Enthalpy 0K =           -1249.669362
Enthalpy 298K =         -1249.636829
Free Energy 298K =      -1249.732393
PCM (DCM) Energy =      -1250.217202
PCM (MeOH) Energy =     -1250.222272
SCF (BP86+D3) Energy =  -1250.265619
SCF (BS2) Energy =      -1250.115204
Lowest Frequency =  -550.9996 cm-1
Rh  0.49128  0.23269  0.15652
N   1.55750 -0.86206 -1.28714
C   0.81534 -1.43670 -2.20786
C  -0.61046 -1.35843 -2.09016
C  -1.13443 -0.93277 -0.87451
C  -2.58478 -0.77329 -0.67589
H  -1.24059 -1.69673 -2.92079
C   1.59708  1.96499  0.93483
C   1.20377  2.24634 -0.43420
C  -0.24265  2.21674 -0.50977
C  -0.75451  1.98857  0.84635
C   0.37022  1.82016  1.72223
O  -0.37423 -2.64102  1.02405
C   0.59469 -2.26396  1.75475
O   1.20419 -1.12900  1.61803
C   3.03865 -1.03891 -1.28191
C   2.98797  1.96532  1.49638
C   2.13018  2.58870 -1.56175
C  -1.07342  2.57911 -1.70476
```

```
C  -2.19321  2.07661  1.25316
C   0.33579  1.57329  3.19953
C   1.08374 -3.18352  2.85662
H   1.28651 -1.98634 -3.03468
H  -0.60529 -1.56414  0.12132
H   3.21678  2.94683  1.95229
H   3.10469  1.19930  2.27901
H   3.74643  1.78186  0.71939
H   0.65763  2.48177  3.74049
H  -0.67445  1.31303  3.54796
H   1.02083  0.75607  3.47805
H  -2.44068  3.13291  1.47034
H  -2.87037  1.72997  0.45949
H  -2.40479  1.49196  2.16063
H   2.28524  3.68347 -1.58548
H   3.11964  2.12200 -1.44166
H   1.71724  2.29241 -2.53777
H  -1.27680  3.66620 -1.70872
H  -0.56124  2.33392 -2.64788
H  -2.04378  2.05938 -1.69423
H   1.90147 -2.72453  3.42745
H   0.24297 -3.42430  3.52674
H   1.42377 -4.13255  2.41125
C  -3.18908 -1.09414  0.56724
C  -4.57356 -0.97687  0.74076
C  -5.38345 -0.51656 -0.31227
C  -4.80071 -0.18533 -1.54854
C  -3.41864 -0.31881 -1.73251
H  -2.56493 -1.47507  1.38120
H  -5.02567 -1.25003  1.69941
H  -6.46429 -0.41821 -0.17190
H  -5.42616  0.17508 -2.37131
H  -2.97036 -0.05931 -2.69774
C   3.66349 -0.84582 -2.67718
H   3.41689 -0.24515 -0.61533
C   3.41947 -2.40183 -0.67139
H   4.51732 -2.49566 -0.63255
H   3.02710 -2.49850  0.35102
H   3.02610 -3.22924 -1.28633
H   4.76064 -0.81457 -2.57855
H   3.42631 -1.68002 -3.35864
H   3.33325  0.09440 -3.14757
```

4a_Rh_VI.log

```
SCF (BP86) Energy =     -1250.18690299
Enthalpy 0K =           -1249.683463
Enthalpy 298K =         -1249.650551
Free Energy 298K =      -1249.746963
PCM (DCM) Energy =      -1250.234736
PCM (MeOH) Energy =     -1250.239302
SCF (BP86+D3) Energy =  -1250.284716
SCF (BS2) Energy =    -1250.134226
Lowest Frequency =  21.2177 cm-1
Rh  0.42291  0.24470  0.04070
N   1.54633 -1.07665 -1.19204
C   0.79839 -1.81231 -1.98250
C  -0.62617 -1.67791 -1.86041
C  -1.08143 -0.77132 -0.91200
C  -2.52481 -0.59854 -0.67142
H  -1.29318 -2.30613 -2.46371
C   1.83963  2.09319  0.08678
C   0.78037  2.14766 -0.94034
C  -0.50196  2.24374 -0.25217
C  -0.25390  2.06218  1.15417
C   1.20760  2.00214  1.35082
O  -0.39261 -3.01192  0.98352
C   0.20904 -2.28593  1.91529
O   0.53345 -1.08156  1.76689
C   3.02429 -1.20635 -1.16474
C   3.61944 -1.99470 -2.34191
C   3.31314  2.23036 -0.17050
C   1.00596  2.37853 -2.40714
C  -1.81191  2.59428 -0.89084
C  -1.25195  2.18244  2.26938
C   1.86733  1.87907  2.69127
C   0.47486 -3.02345  3.19796
C   3.46819 -1.79578  0.18843
H   3.40446 -0.17088 -1.22175
H   1.24920 -2.52794 -2.68189
H  -0.56109 -2.44614  0.17191
H   3.61430  3.28696 -0.04427
H   3.92097  1.63202  0.52645
H   3.58230  1.94670 -1.19973
H   1.68703  2.78818  3.29316
H   1.45644  1.02526  3.25666
H   2.95556  1.74309  2.60401
H  -1.24602  3.21253  2.67280
H  -2.27466  1.96558  1.92738
H  -1.01271  1.50384  3.10396
H   1.15806  3.45556 -2.60763
H   1.89753  1.84515 -2.77200
H   0.14395  2.04551 -3.00480
H  -1.90602  3.69530 -0.93543
H  -1.88518  2.21197 -1.92014
H  -2.66854  2.20431 -0.32216
H   0.97776 -2.36871  3.92008
H  -0.47693 -3.39004  3.61683
H   1.09832 -3.90937  2.99332
H   4.56774 -1.77771  0.26336
H   3.05046 -1.22337  1.03156
H   3.13782 -2.84530  0.27721
H   4.71799 -1.92576 -2.29334
H   3.35991 -3.06664 -2.29996
H   3.30209 -1.58996 -3.31750
C  -3.03558 -0.44777  0.64268
C  -4.41437 -0.34400  0.87115
C  -5.31172 -0.35549 -0.21093
C  -4.82164 -0.48550 -1.52195
C  -3.44600 -0.61488 -1.75196
H  -2.33607 -0.43351  1.48455
H  -4.79183 -0.25201  1.89468
H  -6.38737 -0.26058 -0.03364
H  -5.51503 -0.48612 -2.36890
H  -3.06989 -0.70703 -2.77618
```

4a_Rh_VII.log

```
SCF (BP86) Energy =     -1036.34125476
Enthalpy 0K =           -1035.899227
Enthalpy 298K =         -1035.870101
Free Energy 298K =      -1035.957365
PCM (DCM) Energy =      -1036.35319
PCM (MeOH) Energy =     -1036.355615
SCF (BP86+D3) Energy =  -1036.429862
SCF (BS2) Energy =      -1481.456031
Lowest Frequency =  23.8083 cm-1
Rh -0.40344  0.10444 -0.10424
N  -1.56862 -1.61004  0.14288
C  -0.86789 -2.70543  0.35321
C   0.54943 -2.56553  0.42645
C   1.02725 -1.29112  0.17450
C   2.47595 -1.03975  0.07452
H   1.19915 -3.43863  0.56104
C  -1.80301  1.78103  0.75957
C  -0.74235  1.34389  1.68025
C   0.53508  1.72184  1.09613
C   0.27480  2.22958 -0.22570
C  -1.18837  2.30025 -0.40492
Cl -0.36130 -0.30299 -2.48523
C  -3.02428 -1.69178 -0.13154
C  -3.79161 -2.31663  1.04984
C  -3.27380  1.72529  1.06195
C  -0.95952  0.86899  3.09094
C   1.86186  1.69729  1.79865
C   1.26750  2.80283 -1.19562
C  -1.85173  2.82726 -1.64272
C  -3.29946 -2.41797 -1.46248
H  -3.35531 -0.64616 -0.24238
H  -1.36496 -3.68533  0.41230
H  -3.56950  2.57954  1.70001
H  -3.88457  1.77043  0.14626
H  -3.54627  0.80737  1.60848
H  -1.58252  3.88598 -1.81118
H  -1.52459  2.24731 -2.52495
H  -2.94913  2.76278 -1.57901
```

```
H   1.24783  3.90920 -1.16789
H   2.29269  2.47636 -0.96358
H   1.03403  2.48438 -2.22524
H  -1.08737  1.72419  3.78253
H  -1.86070  0.24029  3.17167
H  -0.10476  0.27400  3.44873
H   2.00483  2.63993  2.36006
H   1.92940  0.86502  2.51658
H   2.69811  1.59154  1.09154
H  -4.37209 -2.35439 -1.71582
H  -2.70808 -1.95924 -2.27049
H  -3.02925 -3.48651 -1.39406
H  -4.87804 -2.26472  0.86451
H  -3.52937 -3.38000  1.18741
H  -3.57358 -1.78822  1.99343
C   3.01574 -0.32582 -1.02439
C   4.39865 -0.12264 -1.13203
C   5.27024 -0.60510 -0.13908
C   4.74775 -1.31097  0.95743
C   3.36688 -1.53385  1.06086
H   2.32869  0.02806 -1.79994
H   4.80037  0.41344 -1.99908
H   6.34884 -0.43401 -0.22089
H   5.41836 -1.69012  1.73651
H   2.96015 -2.08144  1.91824
```

5a_Ir_IV.log

```
SCF (BP86) Energy =     -1166.61666715
Enthalpy 0K =           -1166.145921
Enthalpy 298K =         -1166.114728
Free Energy 298K =      -1166.208660
PCM (DCM) Energy =      -1166.666228
PCM (MeOH) Energy =     -1166.671016
SCF (BP86+D3) Energy =  -1166.704576
SCF (BS2) Energy =      -1167.062288
Lowest Frequency =  9.7591 cm-1
Ir -0.70621 -0.05775  0.08228
N   0.69583  1.46504 -0.41271
C   2.00065  1.41916 -0.44323
C   2.92665  0.37527 -0.00371
C   4.20342  0.36812 -0.62325
C   5.16349 -0.58710 -0.27099
C   4.87855 -1.52361  0.73737
C   3.63205 -1.49755  1.38972
C   2.65484 -0.56314  1.02250
C  -2.44291 -0.94836 -0.90800
C  -1.34576 -0.82278 -1.86367
C  -0.23254 -1.63849 -1.36860
C  -0.65217 -2.24336 -0.11595
C  -2.02250 -1.81809  0.17767
O  -0.20167  0.27660  2.21105
C  -1.03866  1.25363  2.30350
C  -1.21510  2.02166  3.58101
O  -1.70246  1.54095  1.23601
C   0.07268  2.76649 -0.89598
C  -3.78569 -0.29479 -1.03182
C  -1.42507 -0.15616 -3.20616
C   1.04830 -1.90958 -2.10184
C   0.14501 -3.19808  0.71898
C  -2.86547 -2.28568  1.32937
C   0.41558  3.92305  0.05741
C   0.45330  3.08343 -2.35229
H  -1.01191  2.58988 -0.84549
H   2.50488  2.29451 -0.88481
H   6.13818 -0.59065 -0.76775
H   5.63512 -2.25764  1.03185
H   3.42978 -2.19851  2.20588
H   1.70736 -0.51484  1.56336
H  -4.48866 -0.99059 -1.52610
H  -4.20437 -0.03542 -0.04768
H  -3.73938  0.62205 -1.63847
H  -3.36354 -3.23971  1.07711
H  -2.25944 -2.45415  2.23295
H  -3.65113 -1.55616  1.57869
H  -0.13701 -4.23476  0.45667
H   1.22566 -3.08702  0.54855
H  -0.05559 -3.06078  1.79307
H  -1.89612 -0.83985 -3.93661
H  -2.02982  0.76352 -3.17684
H  -0.42681  0.09835 -3.59288
H   0.90359 -2.74886 -2.80689
H   1.37352 -1.03634 -2.68784
H   1.86385 -2.17947 -1.41518
H   4.43367  1.11270 -1.39392
H  -2.10283  2.66663  3.52712
H  -1.30209  1.32430  4.42888
H  -0.32343  2.64607  3.76191
H  -0.12828  4.82933 -0.25567
H   0.11915  3.68941  1.09105
H   1.49394  4.15729  0.04452
H  -0.13858  3.94617 -2.69909
H   1.51685  3.35608 -2.46001
H   0.24176  2.23506 -3.02165
```

5a_Ir_IV_TS_VI.log

```
SCF (BP86) Energy =     -1166.59650959
Enthalpy 0K =           -1166.127754
Enthalpy 298K =         -1166.097088
Free Energy 298K =      -1166.189324 PCM
PCM(DCM) Energy =      -1166.648558
PCM (MeOH) Energy =    -1166.653805
SCF (BP86+D3) Energy =  -1166.687120
SCF (BS2) Energy =      -1167.042971
Lowest Frequency =  -31.2506 cm-1
Ir -0.36799 -0.10587 -0.07000
N   0.47401  1.82442 -0.17656
C   1.76701  1.95893 -0.06414
C   2.60839  0.80439  0.20448
C   3.98391  0.79960 -0.11281
C   4.74933 -0.35459  0.10626
C   4.15562 -1.50260  0.66379
C   2.79257 -1.50147  1.00732
C   2.01219 -0.35535  0.77499
C  -2.05362 -0.41590 -1.34728
C  -0.84516 -0.51529 -2.19069
C  -0.04584 -1.60357 -1.69682
C  -0.77650 -2.23583 -0.57442
C  -2.01658 -1.53744 -0.39187
O  -0.20281 -0.98601  2.85642
C  -0.97285 -0.00880  2.80484
C  -1.68609  0.52464  4.03822
O  -1.22464  0.67864  1.69595
C  -0.38894  3.04995 -0.29410
C  -3.22322  0.49434 -1.57515
C  -0.54955  0.33233 -3.39156
C   1.23281 -2.10858 -2.29606
C  -0.33862 -3.44836  0.19385
C  -3.08949 -1.86811  0.60070
C  -0.36685  3.84776  1.02138
C   0.00486  3.90686 -1.51031
H  -1.40701  2.65790 -0.44512
H   2.22644  2.95317 -0.16259
H   5.81359 -0.35737 -0.14690
H   4.76508 -2.39038  0.85951
H   2.34443 -2.36226  1.51197
H   1.05662 -0.33174  1.39202
H  -3.95941  0.00454 -2.23960
H  -3.73356  0.73700 -0.63046
H  -2.92072  1.43723 -2.05663
H  -3.87349 -2.47404  0.11075
H  -2.69096 -2.44604  1.44727
H  -3.56485 -0.95783  0.99686
H  -0.90268 -4.33491 -0.14858
H   0.73079 -3.65645  0.04451
H  -0.51801 -3.31958  1.27284
H  -0.97911 -0.14345 -4.29246
H  -0.99699  1.33401 -3.30504
H   0.53220  0.44649 -3.55869
H   1.01457 -2.92902 -3.00429
H   1.76115 -1.31842 -2.85053
H   1.91751 -2.49997 -1.52889
H   4.44527  1.69341 -0.54617
H  -2.47930  1.24159  3.78534
H  -2.10308 -0.31899  4.60929
```

```
H  -0.94595  1.02155  4.68801
H  -1.08294  4.68332  0.95552
H  -0.65332  3.20413  1.86590
H   0.63271  4.27440  1.21397
H  -0.73341  4.71492 -1.63799
H   0.99011  4.38505 -1.37717
H   0.03077  3.31467 -2.43948
```

5a_Ir_VI.log

```
SCF (BP86) Energy =     -1166.62002176
Enthalpy 0K =           -1166.149671
Enthalpy 298K =         -1166.118570
Free Energy 298K =      -1166.211898
PCM (DCM) Energy =      -1166.668682
PCM (MeOH) Energy =     -1166.673376
SCF (BP86+D3) Energy =  -1166.709194
SCF (BS2) Energy =      -1167.064167
Lowest Frequency =  14.6526 cm-1
Ir -0.31497 -0.14575  0.00090
N   0.47759  1.73789 -0.56382
C   1.72410  1.73406 -0.96767
C   2.41765  0.46951 -0.96990
C   3.75304  0.31060 -1.39729
C   4.35936 -0.94930 -1.31350
C   3.63167 -2.03071 -0.78731
C   2.29594 -1.87180 -0.35957
C   1.63685 -0.62386 -0.45439
C  -2.53787 -0.62262  0.54215
C  -2.52397  0.01506 -0.72643
C  -1.62299 -0.75381 -1.61377
C  -1.21022 -1.95599 -0.88644
C  -1.68421 -1.83088  0.47213
O   2.13404 -0.38575  2.44739
C   1.06218  0.28744  2.82726
C   1.08222  0.74020  4.26041
O   0.08741  0.54265  2.07258
C  -0.26474  3.02872 -0.44027
C  -3.27800 -0.18652  1.77195
C  -3.32344  1.21322 -1.14820
C  -1.44948 -0.52201 -3.08871
C  -0.53697 -3.14794 -1.49951
C  -1.55967 -2.85640  1.56453
C   0.28566  3.85935  0.73397
C  -0.27183  3.81587 -1.76306
H  -1.29937  2.73639 -0.20131
H   2.22089  2.66734 -1.26801
H   5.39287 -1.08816 -1.64297
H   4.10543 -3.01487 -0.70599
H   1.77105 -2.74048  0.05174
H   2.04123 -0.62899  1.47562
H  -4.12391 -0.86906  1.97165
H  -2.62471 -0.20360  2.65991
H  -3.68452  0.83072  1.66921
H  -2.43031 -3.53813  1.55747
H  -0.65453 -3.47180  1.44465
H  -1.52000 -2.38481  2.55910
H  -1.29523 -3.74904 -2.03430
H   0.23769 -2.86107 -2.22639
H  -0.07712 -3.80084 -0.74265
H  -4.25271  0.88336 -1.64844
H  -3.61752  1.84149 -0.29299
H  -2.77692  1.84129 -1.86934
H  -2.28572 -0.97708 -3.65135
H  -1.43125  0.55191 -3.33095
H  -0.51331 -0.96735 -3.45818
H   4.30971  1.17040 -1.78713
H   0.15715  1.27549  4.50713
H   1.20377 -0.13361  4.92169
H   1.95410  1.39377  4.42851
H  -0.33131  4.76186  0.87561
H   0.26822  3.27782  1.66886
H   1.32201  4.18576  0.54044
H  -0.94146  4.68634 -1.67013
H   0.72966  4.19966 -2.02131
H  -0.62797  3.19415 -2.60102
```

5a_Ir_VII.log

```
SCF (BP86) Energy =     -952.774424904
Enthalpy 0K =           -952.365213
Enthalpy 298K =         -952.338064
Free Energy 298K =      -952.421702
PCM (DCM) Energy =      -952.7880508
PCM (MeOH) Energy =     -952.7908498
SCF (BP86+D3) Energy =  -952.8548652
SCF (BS2) Energy =      -1398.386238
Lowest Frequency =  17.8778 cm-1
C  -4.04691  0.26973  0.34662
C  -2.64949  0.45525  0.23222
C  -1.74656 -0.63747  0.01553
C  -2.32733 -1.91451 -0.13897
C  -3.71485 -2.10146 -0.01790
C  -4.58010 -1.01639  0.23594
C  -2.00044  1.73722  0.26234
N  -0.69215  1.74379  0.14928
C   0.03937  3.03574  0.04972
H  -2.56479  2.67682  0.34563
Ir  0.21639 -0.13277 -0.11685
Cl -0.12953  0.16033 -2.51171
C   2.45376 -0.79050 -0.45609
C   2.45248  0.10393  0.64662
C   1.50221 -0.41424  1.64702
C   1.01511 -1.70626  1.17487
C   1.53212 -1.90657 -0.16895
H  -1.69571 -2.77632 -0.37986
H  -4.13285 -3.10846 -0.13362
H  -5.65870 -1.17993  0.32491
H  -4.70164  1.13481  0.50823
C   1.37389 -3.12431 -1.03640
C   0.23422 -2.69501  1.99286
C   1.30524  0.14818  3.02849
C   3.30210  1.33217  0.81685
C   3.21831 -0.65392 -1.73967
H   3.88970 -1.51939 -1.88472
H   2.51941 -0.61224 -2.59455
H   3.83119  0.26036 -1.75612
H   2.25746 -3.78715 -0.96448
H   0.49190 -3.71475 -0.74089
H   1.24394 -2.83789 -2.09259
H   0.92585 -3.33200  2.57536
H  -0.44270 -2.19082  2.69998
H  -0.37954 -3.35584  1.36242
H   4.23342  1.09164  1.36399
H   3.59002  1.77040 -0.15198
H   2.78296  2.11136  1.39963
H   2.10197 -0.19776  3.71475
H   1.32888  1.24991  3.02239
H   0.33725 -0.16208  3.45166
H   1.10524  2.76083  0.09647
C  -0.22399  3.69860 -1.31535
C  -0.26891  3.97207  1.23277
H   0.38728  4.85764  1.18623
H  -1.31090  4.33502  1.21095
H  -0.10186  3.46628  2.19864
H   0.42618  4.58188 -1.43954
H  -0.02657  2.98268 -2.12881
H  -1.27368  4.03232 -1.39370
```

5a_L-H.log

```
SCF (BP86) Energy =     -443.633922159
Enthalpy 0K =           -443.433287
Enthalpy 298K =         -443.422310
Free Energy 298K =      -443.470422
PCM (DCM) Energy =      -443.6373629
PCM (MeOH) Energy =     -443.6380066
SCF (BP86+D3) Energy =  -443.6523377
SCF (BS2) Energy =     -443.7426737
Lowest Frequency =  41.1011 cm-1
C   1.93787 -1.28973 -0.00001
C   0.94837 -0.28345  0.00002
C   1.34579  1.07349  0.00000
C   2.70341  1.40921 -0.00003
C   3.68434  0.39885 -0.00006
C   3.29908 -0.95135 -0.00004
C  -0.47750 -0.66409  0.00007
```

```
N  -1.43039  0.20024  0.00006
C  -2.80673 -0.29780  0.00001
H  -0.67904 -1.76076  0.00002
H   3.00463  2.46227 -0.00004
H   4.74647  0.66590 -0.00009
H   4.05876 -1.74002 -0.00006
H   1.63183 -2.34292  0.00000
C  -3.51294  0.20767  1.27227
C  -3.51288  0.20772 -1.27226
H  -2.82720 -1.41402 -0.00001
H   0.56512  1.84030  0.00003
H  -4.56440 -0.12640 -1.29010
H  -3.49360  1.31015 -1.30694
H  -3.01224 -0.17145 -2.17852
H  -4.56446 -0.12645  1.29004
H  -3.01234 -0.17153  2.17853
H  -3.49367  1.31011  1.30698
```

5a_Rh_IV.log

```
SCF (BP86) Energy =     -1172.78788021
Enthalpy 0K =           -1172.317477
Enthalpy 298K =         -1172.286187
Free Energy 298K =      -1172.380113
PCM (DCM) Energy =      -1172.837586
PCM (MeOH) Energy =     -1172.842453
SCF (BP86+D3) Energy =  -1172.873229
SCF (BS2) Energy =      -1172.71828
Lowest Frequency =  8.9939 cm-1
Rh -0.79539 -0.07793  0.09299
N   0.58947  1.48711 -0.36043
C   1.89199  1.46700 -0.39182
C   2.82571  0.42018  0.02953
C   4.10469  0.42787 -0.58355
C   5.06534 -0.53153 -0.24307
C   4.77720 -1.48698  0.74645
C   3.52715 -1.47572  1.39255
C   2.54997 -0.53639  1.03716
C  -2.48948 -0.94340 -0.97744
C  -1.37270 -0.78458 -1.89521
C  -0.26959 -1.60599 -1.39989
C  -0.71277 -2.25149 -0.18161
C  -2.08602 -1.83661  0.09333
O  -0.35581  0.13556  2.22578
C  -1.21964  1.08600  2.33501
C  -1.44246  1.79342  3.64214
O  -1.86666  1.41425  1.26979
C  -0.06716  2.78214 -0.79736
C  -3.83325 -0.29568 -1.10924
C  -1.41221 -0.06116 -3.20870
C   1.03178 -1.84026 -2.10747
C   0.07197 -3.21907  0.64846
C  -2.94996 -2.33222  1.21601
C   0.19715  3.89295  0.23337
C   0.34685  3.20520 -2.21814
H  -1.14575  2.56284 -0.79542
H   2.39021  2.35954 -0.80787
H   6.04298 -0.52366 -0.73402
H   5.53416 -2.22426  1.03170
H   3.32248 -2.19151  2.19521
H   1.59883 -0.49884  1.57351
H  -4.53792 -1.00232 -1.58608
H  -4.24864 -0.01977 -0.12781
H  -3.79347  0.60917 -1.73380
H  -3.43630 -3.28395  0.93280
H  -2.36232 -2.51765  2.12839
H  -3.74627 -1.61347  1.46258
H  -0.20393 -4.25241  0.36589
H   1.15522 -3.10460  0.49751
H  -0.14658 -3.10029  1.72141
H  -1.85304 -0.71590 -3.98357
H  -2.02711  0.85104 -3.16147
H  -0.40412  0.21702 -3.55070
H   0.91134 -2.65450 -2.84624
H   1.36566 -0.94513 -2.65416
H   1.83161 -2.13092 -1.41095
H   4.33709  1.18740 -1.33890
H  -2.38313  2.36126  3.62092
H  -1.45239  1.06594  4.46834
H  -0.60779  2.49129  3.82810
H  -0.36618  4.79820 -0.04650
H  -0.12764  3.58758  1.23920
H   1.26752  4.15919  0.27356
H  -0.27802  4.05583 -2.53575
H   1.39684  3.53956 -2.27032
H   0.20531  2.38967 -2.94470
```

5a_Rh_IV_TS_VI.log

```
SCF (BP86) Energy =     -1172.76696883
Enthalpy 0K =           -1172.300637
Enthalpy 298K =         -1172.270291
Free Energy 298K =      -1172.361311
PCM (DCM) Energy =      -1172.818085
PCM (MeOH) Energy =     -1172.823179
SCF (BP86+D3) Energy =  -1172.855440
SCF (BS2) Energy =      -1172.696722
Lowest Frequency =  -179.8801 cm-1
Rh -0.34226 -0.24800  0.03720
N   0.08022  1.69456 -0.70176
C   1.34688  2.00282 -0.76377
C   2.32225  1.07208 -0.22667
C   3.69329  1.15032 -0.54067
C   4.57611  0.18471 -0.03381
C   4.09410 -0.83904  0.80334
C   2.73023 -0.90470  1.13744
C   1.80984  0.03778  0.62485
C  -2.07203 -1.12936 -0.98441
C  -0.93612 -1.15423 -1.89808
C   0.11032 -1.95406 -1.30549
C  -0.39582 -2.47587 -0.02811
C  -1.73273 -1.97779  0.15528
O   0.55212  0.95522  2.81523
C  -0.70675  1.00442  2.71755
C  -1.52786  1.51095  3.88977
O  -1.37287  0.63678  1.66074
C  -0.96833  2.65630 -1.15333
C  -3.41533 -0.50723 -1.22804
C  -0.89152 -0.51360 -3.25292
C   1.40633 -2.34068 -1.95513
C   0.29516 -3.48465  0.84258
C  -2.64943 -2.26468  1.30446
C  -1.41406  3.53650  0.03073
C  -0.54505  3.50262 -2.36693
H  -1.82094  2.02095 -1.44948
H   1.67275  2.95125 -1.21426
H   5.64132  0.23692 -0.27762
H   4.79185 -1.57227  1.22080
H   2.38768 -1.65809  1.85404
H   1.02048  0.39140  1.52682
H  -4.11331 -1.25486 -1.64941
H  -3.85744 -0.12851 -0.29332
H  -3.36087  0.32599 -1.94614
H  -3.49321 -2.89129  0.96314
H  -2.13531 -2.80126  2.11517
H  -3.06602 -1.33075  1.71608
H  -0.05115 -4.50108  0.57796
H   1.38588 -3.46296  0.70615
H   0.07568 -3.32942  1.91051
H  -1.28494 -1.22057 -4.00675
H  -1.51395  0.39313 -3.30121
H   0.13475 -0.25026 -3.55025
H   1.29381 -3.31221 -2.47094
H   1.72304 -1.60097 -2.70600
H   2.21720 -2.44318 -1.21809
H   4.06433  1.95261 -1.18795
H  -2.59123  1.59932  3.63060
H  -1.41063  0.81248  4.73481
H  -1.13297  2.48521  4.21765
H  -2.23698  4.19565 -0.29110
H  -1.76456  2.91837  0.86926
H  -0.57942  4.17082  0.37522
H  -1.42713  4.04210 -2.74769
H   0.20575  4.26699 -2.10416
H  -0.14538  2.88097 -3.18530
```

5a_Rh_VI.log

SCF (BP86) Energy = -1172.78500593
Enthalpy 0K = -1172.314765
Enthalpy 298K = -1172.283664
Free Energy 298K = -1172.376968
PCM (DCM) Energy = -1172.833311
PCM (MeOH) Energy = -1172.837901
SCF (BP86+D3) Energy = -1172.871964
SCF (BS2) Energy = -1172.714555
Lowest Frequency = 10.1936 cm-1

Rh	-0.34642	-0.17240	0.00261
N	0.35590	1.69986	-0.74307
C	-0.48108	2.92530	-0.82682
C	-0.79716	3.42975	0.59450
H	-1.42793	2.58634	-1.28423
C	0.10061	4.04308	-1.70581
C	1.60569	1.69649	-1.12472
C	2.35966	0.47353	-0.95109
C	1.63084	-0.59615	-0.33267
C	2.34449	-1.78305	-0.06247
C	3.70268	-1.91503	-0.42610
C	4.38624	-0.86365	-1.06038
C	3.71687	0.34075	-1.31569
C	-2.48962	-0.88204	0.52732
C	-2.55859	-0.21480	-0.72108
C	-1.59627	-0.86797	-1.62954
C	-1.05302	-2.03325	-0.94405
C	-1.52258	-1.99343	0.41934
C	-3.25235	-0.55166	1.77462
C	-3.50922	0.88470	-1.10143
C	-1.43545	-0.56058	-3.09057
C	-0.25979	-3.12866	-1.59264
C	-1.28264	-3.02340	1.48668
H	2.07434	2.59545	-1.54730
H	5.43726	-0.97994	-1.33971
H	4.22731	-2.85148	-0.20824
H	1.85185	-2.62165	0.44188
H	2.07766	-0.14970	1.53108
H	-3.96549	-1.36129	2.01364
H	-2.57403	-0.44519	2.63804
H	-3.82441	0.38228	1.67141
H	-2.08509	-3.78464	1.47921
H	-0.32774	-3.55179	1.33926
H	-1.26978	-2.56976	2.49032
H	-0.95459	-3.81899	-2.10588
H	0.44589	-2.74292	-2.34370
H	0.30929	-3.72079	-0.86115
H	-4.47597	0.45154	-1.41873
H	-3.71585	1.56987	-0.26429
H	-3.13627	1.47862	-1.95058
H	-2.22875	-1.06148	-3.67653
H	-1.51042	0.51958	-3.29179
H	-0.46514	-0.91165	-3.47338
H	4.24192	1.17855	-1.78853
O	2.11546	0.20285	2.47059
C	0.89850	0.58693	2.82645
O	-0.10142	0.53163	2.06925
C	0.79776	1.09963	4.23662
H	-0.22566	1.42960	4.45293
H	1.09534	0.30412	4.93994
H	1.50373	1.93422	4.37835
H	-1.51766	4.26217	0.54251
H	-1.22425	2.62978	1.21852
H	0.12023	3.80079	1.08321
H	-0.65157	4.84218	-1.80330
H	1.00059	4.49994	-1.25912
H	0.34704	3.69020	-2.72134

5a_Rh_VII.log

SCF (BP86) Energy = -958.936399484
Enthalpy 0K = -958.527365
Enthalpy 298K = -958.500174
Free Energy 298K = -958.583892
PCM (DCM) Energy = -958.9504097
PCM (MeOH) Energy = -958.9532688
SCF (BP86+D3) Energy = -959.0144643
SCF (BS2) Energy = -1404.032464
Lowest Frequency = 15.2404 cm-1

C	-3.97551	0.34838	0.37133
C	-2.57519	0.49838	0.24337
C	-1.71446	-0.61558	-0.01313
C	-2.32544	-1.86975	-0.19926
C	-3.71795	-2.02097	-0.06505
C	-4.54643	-0.91985	0.23200
C	-1.89439	1.76753	0.27801
N	-0.59246	1.75035	0.13788
C	0.16376	3.02283	0.00682
H	-2.44445	2.71618	0.37234
Rh	0.24491	-0.14731	-0.14903
Cl	-0.06877	0.10124	-2.52908
C	2.46481	-0.83527	-0.43512
C	2.44072	0.02329	0.69124
C	1.46530	-0.51705	1.65040
C	0.98239	-1.78396	1.13191
C	1.52463	-1.94634	-0.19762
H	-1.72152	-2.74120	-0.47360
H	-4.16614	-3.01183	-0.20467
H	-5.62815	-1.05468	0.33090
H	-4.60423	1.22659	0.56277
C	1.35449	-3.12091	-1.11927
C	0.16526	-2.78314	1.90038
C	1.22715	0.01299	3.03780
C	3.29648	1.23708	0.92374
C	3.26903	-0.67925	-1.69147
H	3.92995	-1.55204	-1.84250
H	2.59512	-0.60333	-2.56440
H	3.89803	0.22400	-1.66564
H	2.24307	-3.78041	-1.09414
H	0.48137	-3.73111	-0.83809
H	1.20742	-2.78261	-2.15814
H	0.82914	-3.41978	2.51505
H	-0.55264	-2.29086	2.57487
H	-0.40752	-3.44602	1.23466
H	4.19941	0.97387	1.50694
H	3.63421	1.68912	-0.02254
H	2.76224	2.01232	1.49820
H	1.99412	-0.36222	3.74268
H	1.26772	1.11397	3.06280
H	0.24143	-0.29401	3.42109
H	1.22516	2.72725	0.03187
C	-0.11703	3.67166	-1.36189
C	-0.09629	3.98207	1.18345
H	0.57496	4.85417	1.10748
H	-1.13172	4.36411	1.18231
H	0.08583	3.48732	2.15243
H	0.55095	4.53673	-1.51591
H	0.04384	2.93797	-2.16772
H	-1.16030	4.02910	-1.41949

6_Ir_IV.log

SCF (BP86) Energy = -1202.32500927
Enthalpy 0K = -1201.890601
Enthalpy 298K = -1201.861220
Free Energy 298K = -1201.950365
PCM (DCM) Energy = -1202.373878
PCM (MeOH) Energy = -1202.378594
SCF (BP86+D3) Energy = -1202.408536
SCF (BS2) Energy = -1202.779044
Lowest Frequency = 20.2208 cm-1

C	2.60327	-0.89630	-0.72888
C	1.82340	-1.89941	-0.04461
C	0.51683	-2.00179	-0.72094
C	0.52007	-1.06674	-1.83083
C	1.78658	-0.34735	-1.82641
Ir	0.78752	0.03154	0.06214
O	1.74332	1.63875	1.21837
C	1.19801	1.25070	2.32365
C	1.40453	1.99836	3.60831
N	-0.78657	1.48385	-0.19917
C	-2.13976	1.24524	-0.23357
C	-3.02365	2.26924	-0.64351
C	-2.54863	3.53046	-1.00885
C	-2.72191	-0.06168	0.17581
C	-2.42303	-0.64835	1.42612

```
C  -3.09706 -1.80852  1.83762
C  -4.06220 -2.40535  1.00973
C  -4.36068 -1.83243 -0.23829
C  -3.70588 -0.66110 -0.64718
O   0.44921  0.20583  2.25341
H   1.32357  1.31577  4.46655
H   0.62159  2.77015  3.70976
H   2.38220  2.50160  3.60649
H  -3.24201  4.31738 -1.32008
H  -4.09550  2.05666 -0.63506
H  -3.95394 -0.20815 -1.61355
H  -5.11307 -2.28892 -0.88886
H  -4.58764 -3.30728  1.33869
H  -2.87591 -2.23840  2.81982
H  -1.68566 -0.18235  2.08427
C   4.00683 -0.47548 -0.41161
C   2.25609  0.64351 -2.85139
C  -0.57221 -0.90438 -2.84535
C  -0.53519 -3.02372 -0.41725
C   2.25702 -2.74286  1.11749
H  -1.53512 -2.69240 -0.73365
H  -0.30080 -3.96414 -0.95080
H  -0.57963 -3.25098  0.65815
H   1.43198 -2.89861  1.82979
H   2.58581 -3.73568  0.75966
H   3.09653 -2.28724  1.66332
H  -0.61068  0.12022 -3.24620
H  -0.38584 -1.58653 -3.69503
H  -1.55707 -1.15367 -2.42341
H   4.14165  0.61020 -0.53636
H   4.29059 -0.73797  0.61818
H   4.70989 -0.98371 -1.09669
H   1.41585  1.19649 -3.29864
H   2.95639  1.37426 -2.41746
H   2.78527  0.12181 -3.67030
C  -1.16823  3.76694 -0.94180
C  -0.33169  2.72958 -0.53192
H  -0.73437  4.73684 -1.19763
H   0.74770  2.87081 -0.45386
```

6_Ir_IV_TS_VI.log

```
SCF (BP86) Energy =     -1202.30665923
Enthalpy 0K =           -1201.873908
Enthalpy 298K =         -1201.844786
Free Energy 298K =      -1201.933885
PCM (DCM) Energy =      -1202.358362
PCM (MeOH) Energy =     -1202.363586
SCF (BP86+D3) Energy =  -1202.391438
SCF (BS2) Energy =      -1202.76104
Lowest Frequency =  -67.4628 cm-1
C   2.53162 -0.65350 -0.60837
C   1.60884 -1.75477 -0.63543
C   0.56129 -1.47673 -1.64365
C   0.84108 -0.18832 -2.22190
C   2.03844  0.36398 -1.55312
Ir  0.53667  0.09612 -0.07075
O   1.17063  1.33414  1.51723
C   1.35490  0.64208  2.63068
C   1.85347  1.45504  3.81225
N  -1.08743  1.47039 -0.07443
C  -2.38183  1.04080  0.06647
C  -3.44584  1.96043 -0.01767
C  -3.18502  3.31885 -0.22208
C  -2.58352 -0.39204  0.36160
C  -1.62676 -1.06885  1.15957
C  -1.79756 -2.42814  1.47786
C  -2.92206 -3.12250  1.00438
C  -3.87195 -2.45756  0.20636
C  -3.70790 -1.10110 -0.11207
O   1.10575 -0.57923  2.71238
H   2.56064  0.85228  4.40129
H   0.99703  1.69166  4.46673
H   2.32194  2.39791  3.49691
H  -4.00796  4.03689 -0.28273
H  -4.46865  1.60008  0.11809
H  -4.44365 -0.59877 -0.74862
H  -4.74597 -2.99862 -0.16886
H  -3.06948 -4.17457  1.26732
H  -1.06845 -2.91787  2.13019
H  -0.82375 -0.52836  1.70164
C   3.77282 -0.54620  0.22570
C   2.74628  1.63425 -1.91372
C   0.09244  0.47499 -3.33873
C  -0.51043 -2.43485 -2.06977
C   1.72135 -3.00279  0.18684
H  -1.34512 -1.91661 -2.56496
H  -0.09566 -3.16722 -2.78674
H  -0.91980 -2.99412 -1.21515
H   0.76198 -3.53677  0.24330
H   2.46165 -3.68380 -0.27228
H   2.05004 -2.77281  1.21175
H   0.08041  1.57070 -3.22907
H   0.58141  0.24368 -4.30277
H  -0.94825  0.12276 -3.39798
H   3.97971  0.49742  0.50777
H   3.68739 -1.13955  1.14777
H   4.64173 -0.92082 -0.34554
H   2.05966  2.37664 -2.34888
H   3.23800  2.08402 -1.03755
H   3.52854  1.42423 -2.66719
C  -1.85123  3.74734 -0.31377
C  -0.83239  2.79689 -0.22713
H  -1.59514  4.80148 -0.44533
H   0.22307  3.07342 -0.27270
```

6_Ir_VI.log

```
SCF (BP86) Energy =     -1202.32990381
Enthalpy 0K =           -1201.895852
Enthalpy 298K =         -1201.866547
Free Energy 298K =      -1201.955782
PCM (DCM) Energy =      -1202.378399
PCM (MeOH) Energy =     -1202.383063
SCF (BP86+D3) Energy =  -1202.412768
SCF (BS2) Energy =      -1202.78275
Lowest Frequency =  17.1504 cm-1
C   2.74621  0.42985  0.25477
C   2.44677 -0.99281 -0.02823
C   1.85159 -1.06375 -1.34356
C   1.62582  0.30657 -1.80376
C   2.26908  1.21555 -0.82798
Ir  0.46823  0.00675 -0.00033
O   0.12914  0.14110  2.18928
C  -0.58686 -0.56884  2.94264
C  -0.60699 -0.35685  4.43039
N  -1.08448  1.44031 -0.08386
C  -2.32908  0.98768 -0.45980
C  -3.40305  1.89548 -0.55966
C  -3.21087  3.24643 -0.26079
C  -2.39265 -0.45904 -0.67465
C  -1.17329 -1.16709 -0.40335
C  -1.21619 -2.57890 -0.50414
C  -2.38975 -3.25479 -0.89052
C  -3.55917 -2.53638 -1.18877
C  -3.56155 -1.14052 -1.07337
O  -1.36861 -1.54401  2.51330
H  -0.33663 -1.29524  4.94183
H  -1.63002 -0.09863  4.75056
H   0.08746  0.44387  4.71273
H  -4.04288  3.95219 -0.34079
H  -4.38813  1.53185 -0.86184
H  -4.48032 -0.58651 -1.29339
H  -4.46731 -3.06193 -1.49752
H  -2.38587 -4.34763 -0.96019
H  -0.32052 -3.16670 -0.27689
H  -1.30438 -1.59640  1.51011
C   3.43714  0.91147  1.49621
C   2.42208  2.69734 -1.01541
C   1.13084  0.70488 -3.16586
C   1.61639 -2.29924 -2.16089
C   2.92363 -2.14998  0.80508
H   0.68165 -2.24451 -2.73875
H   2.45048 -2.41603 -2.87700
H   1.58680 -3.20793 -1.54163
H   2.33244 -3.05946  0.61630
```

```
H   3.97939 -2.38462  0.57458
H   2.86390 -1.92459  1.88148
H   0.63092  1.68594 -3.14513
H   1.97485  0.77543 -3.87689
H   0.41598 -0.03087 -3.56440
H   3.38763  2.00597  1.59772
H   2.99199  0.46546  2.40091
H   4.50375  0.62312  1.47645
H   1.54136  3.14363 -1.50444
H   2.59525  3.22240 -0.06278
H   3.29121  2.90495 -1.66630
C  -1.94131  3.68202  0.15674
C  -0.90784  2.74705  0.23516
H  -1.74914  4.72545  0.41805
H   0.09792  3.02541  0.55745
```

6_Ir_VII.log

```
SCF (BP86) Energy =     -988.481202592
Enthalpy 0K =           -988.108575
Enthalpy 298K =         -988.083106
Free Energy 298K =      -988.162976
PCM (DCM) Energy =      -988.4970696
PCM (MeOH) Energy =     -988.5001915
SCF (BP86+D3) Energy =  -988.555488
SCF (BS2) Energy =      -1434.101596
Lowest Frequency =  20.5666 cm-1
C  -2.70621  0.30906 -0.35003
C  -2.31550 -1.07580 -0.02124
C  -1.67963 -1.04802  1.28758
C  -1.55139  0.34790  1.68550
C  -2.25590  1.17102  0.68486
Ir -0.38928 -0.01481 -0.14913
Cl -0.07868  0.07433 -2.56068
N   1.22064  1.32572 -0.03105
C   2.47559  0.77737  0.12334
C   3.60381  1.62149  0.20501
C   3.45583  3.00591  0.11484
C   2.47786 -0.68008  0.14394
C   1.19354 -1.28028 -0.04744
C   1.15338 -2.68680 -0.17138
C   2.31413 -3.46496 -0.04242
C   3.56323 -2.85904  0.19879
C   3.64491 -1.46664  0.27823
H   4.33044  3.66070  0.17977
H   4.59472  1.17638  0.32703
H   4.61981 -0.99045  0.43470
H   4.46474 -3.47097  0.30339
H   2.24836 -4.55497 -0.13914
H   0.20286 -3.18295 -0.39508
C  -3.42210  0.69387 -1.61116
C  -2.48527  2.65292  0.79546
C  -1.03625  0.85010  3.00664
C  -1.32626 -2.23666  2.13493
C  -2.74357 -2.28830 -0.80066
H  -0.48710 -2.01572  2.81269
H  -2.19561 -2.53264  2.75126
H  -1.03562 -3.10410  1.52334
H  -2.16323 -3.17816 -0.50862
H  -3.81281 -2.51859 -0.63009
H  -2.59418 -2.13229 -1.88114
H  -0.55107  1.83436  2.90223
H  -1.86034  0.96108  3.73708
H  -0.29556  0.15815  3.43660
H  -3.61670  1.77639 -1.65722
H  -2.81249  0.41934 -2.49116
H  -4.39109  0.16815 -1.68297
H  -1.63612  3.16303  1.28029
H  -2.64312  3.11823 -0.19076
H  -3.37963  2.86749  1.41061
C   2.17063  3.54355 -0.08180
C   1.08673  2.66853 -0.16081
H   2.00647  4.61935 -0.18399
H   0.06960  3.02407 -0.33954
```

6_L-H.log

```
SCF (BP86) Energy =     -479.337880916
Enthalpy 0K =           -479.173096
Enthalpy 298K =         -479.164004
Free Energy 298K =      -479.208171
PCM (DCM) Energy =      -479.342503
PCM (MeOH) Energy =     -479.3433067
SCF (BP86+D3) Energy =  -479.3539761
SCF (BS2) Energy =      -479.454662
Lowest Frequency =  40.9281 cm-1
N   1.36757 -1.17190 -0.17535
C   0.76445  0.03297  0.00003
C   1.51751  1.21498  0.19276
C   2.91544  1.14939  0.17485
C  -0.72644  0.03162 -0.00424
C  -1.42056 -1.18857  0.16289
C  -2.82038 -1.22017  0.17331
C  -3.55774 -0.03499  0.01036
C  -2.88033  1.18196 -0.16920
C  -1.47883  1.21537 -0.17743
H   3.51159  2.05616  0.32286
H   1.01743  2.17027  0.37558
H  -0.97145  2.17066 -0.34648
H  -3.44496  2.10945 -0.31184
H  -4.65254 -0.05986  0.01763
H  -3.34005 -2.17457  0.31044
H  -0.83161 -2.10224  0.28129
C   3.53630 -0.09259 -0.02275
C   2.71058 -1.21702 -0.18246
H   4.62573 -0.19215 -0.04399
H   3.15292 -2.21216 -0.32673
```

6_Rh_IV.log

```
SCF (BP86) Energy =     -1208.49726593
Enthalpy 0K =           -1208.063197
Enthalpy 298K =         -1208.033692
Free Energy 298K =      -1208.123095
PCM (DCM) Energy =      -1208.546391
PCM (MeOH) Energy =     -1208.551160
SCF (BP86+D3) Energy =  -1208.578178
SCF (BS2) Energy =      -1208.436311
Lowest Frequency =  19.1867 cm-1
C   2.68728 -0.86898 -0.76281
C   1.89342 -1.90001 -0.14397
C   0.59517 -1.94979 -0.82929
C   0.61105 -0.94947 -1.87588
C   1.88305 -0.25053 -1.82491
Rh  0.89007  0.02883  0.07830
O   1.89348  1.54986  1.26211
C   1.37474  1.10036  2.35616
C   1.61783  1.78340  3.67250
N  -0.68820  1.49256 -0.12565
C  -2.04082  1.26880 -0.16952
C  -2.91730  2.31337 -0.54278
C  -2.42766  3.58167 -0.86291
C  -2.62543 -0.04856  0.20018
C  -2.29507 -0.68738  1.41664
C  -2.96026 -1.86346  1.79641
C  -3.94768 -2.42407  0.96933
C  -4.27708 -1.79921 -0.24564
C  -3.63026 -0.61271 -0.62236
O   0.62059  0.06258  2.26205
H   1.56194  1.05790  4.49708
H   0.83682  2.54659  3.83498
H   2.59444  2.28894  3.66891
H  -3.11271  4.38673 -1.14521
H  -3.99158  2.11260 -0.54067
H  -3.90114 -0.12048 -1.56310
H  -5.04673 -2.22770 -0.89509
H  -4.46642 -3.33845  1.27368
H  -2.71489 -2.33441  2.75374
H  -1.53952 -0.24977  2.07423
C   4.09295 -0.48300 -0.41656
C   2.36263  0.80744 -2.77376
C  -0.47918 -0.70998 -2.87615
C  -0.47107 -2.97218 -0.58649
C   2.30803 -2.80929  0.97302
H  -1.46690 -2.61005 -0.88168
H  -0.25048 -3.88228 -1.17632
H  -0.51776 -3.26509  0.47281
```

```
H   1.48030 -2.98101  1.67863
H   2.61033 -3.79129  0.56459
H   3.16012 -2.40399  1.53831
H  -0.49890  0.33547 -3.22025
H  -0.30844 -1.34765 -3.76325
H  -1.46809 -0.96430 -2.46635
H   4.23115  0.60914 -0.44531
H   4.38176 -0.83758  0.58366
H   4.79133 -0.92976 -1.14814
H   1.52794  1.38516 -3.19946
H   3.05442  1.50954 -2.28226
H   2.90787  0.34266 -3.61654
C  -1.04507  3.80233 -0.78754
C  -0.21961  2.74093 -0.41389
H  -0.60255  4.77722 -1.00737
H   0.86121  2.86909 -0.32563
```

6_Rh_IV_TS_V.log

```
SCF (BP86) Energy =     -1208.47915777
Enthalpy 0K =           -1208.046813
Enthalpy 298K =         -1208.017924
Free Energy 298K =      -1208.106000
PCM (DCM) Energy =      -1208.532326
PCM (MeOH) Energy =     -1208.537778
SCF (BP86+D3) Energy =  -1208.561095
SCF (BS2) Energy =      -1208.418861
Lowest Frequency =  -38.5656 cm-1
C   2.61832 -0.60907 -0.46181
C   1.78383 -1.77561 -0.41927
C   0.77610 -1.66824 -1.49259
C   0.99330 -0.42549 -2.17619
C   2.10387  0.27246 -1.51387
Rh  0.55546  0.03582 -0.05956
O   1.22640  1.46337  1.31566
C   1.13442  1.15785  2.60173
C   1.70156  2.22328  3.53201
N  -1.01936  1.41805 -0.32031
C  -2.30030  0.97745 -0.12370
C  -3.38666  1.85452 -0.31164
C  -3.15218  3.18173 -0.68628
C  -2.43526 -0.41871  0.33242
C  -1.36763 -0.99314  1.07806
C  -1.47427 -2.31639  1.55055
C  -2.61716 -3.07986  1.26763
C  -3.66174 -2.52015  0.50879
C  -3.57534 -1.19772  0.04752
O   0.61626  0.11547  3.04271
H   0.86133  2.74893  4.01637
H   2.32129  2.95772  2.99928
H   2.28445  1.73566  4.32816
H  -3.99008  3.87031 -0.82921
H  -4.40267  1.49581 -0.12851
H  -4.38925 -0.77978 -0.55376
H  -4.55154 -3.11468  0.28029
H  -2.70610 -4.10062  1.65223
H  -0.67956 -2.71733  2.18689
H  -0.58857 -0.37408  1.62951
C   3.80205 -0.31144  0.40606
C   2.73551  1.56000 -1.94796
C   0.25540  0.07590 -3.38066
C  -0.20207 -2.73878 -1.87336
C   1.97289 -2.95785  0.48377
H  -1.03398 -2.33750 -2.47124
H   0.30533 -3.51088 -2.48097
H  -0.62891 -3.23521 -0.98871
H   1.04873 -3.54486  0.58391
H   2.74851 -3.62500  0.06347
H   2.30134 -2.65412  1.48975
H   0.13998  1.17109 -3.36428
H   0.82107 -0.18127 -4.29524
H  -0.74388 -0.37591 -3.46861
H   3.77317  0.72827  0.76880
H   3.84637 -0.97991  1.27812
H   4.73379 -0.44482 -0.17338
H   2.03451  2.19137 -2.51567
H   3.10548  2.13367 -1.08371
H   3.59961  1.35448 -2.60744
C  -1.82889  3.62356 -0.84632
C  -0.78831  2.71229 -0.64497
H  -1.59873  4.65799 -1.11321
H   0.26193  3.00198 -0.72689
```

6_Rh_V.log

```
SCF (BP86) Energy =     -1208.47987334
Enthalpy 0K =           -1208.047750
Enthalpy 298K =         -1208.018181
Free Energy 298K =      -1208.108086
PCM (DCM) Energy =      -1208.532710
PCM (MeOH) Energy =     -1208.538118
SCF (BP86+D3) Energy =  -1208.562465
SCF (BS2) Energy =      -1208.419373
Lowest Frequency =  19.8319 cm-1
C  -2.71807  0.49747 -0.23632
C  -1.96753  1.71274 -0.07756
C  -1.00940  1.81191 -1.19303
C  -1.16902  0.64521 -2.01604
C  -2.19559 -0.20696 -1.40699
Rh -0.58678 -0.02405  0.01165
O  -1.15950 -1.57275  1.28802
C  -0.50251 -1.84256  2.40264
C  -1.12701 -2.95914  3.23014
N   1.04013 -1.26147 -0.52624
C   2.29464 -0.72451 -0.40335
C   3.42357 -1.46337 -0.80582
C   3.26105 -2.75575 -1.31670
C   2.34386  0.60982  0.21945
C   1.27596  0.94584  1.10591
C   1.29431  2.19362  1.76620
C   2.32976  3.10947  1.52664
C   3.36340  2.78197  0.62830
C   3.37664  1.53620 -0.01918
O   0.51835 -1.24313  2.79366
H  -0.34594 -3.46249  3.81719
H  -1.66291 -3.68178  2.59808
H  -1.85053 -2.51557  3.93562
H   4.13280 -3.33960 -1.62618
H   4.41984 -1.03122 -0.68207
H   4.18241  1.29785 -0.72128
H   4.16894  3.49793  0.43863
H   2.34845  4.06881  2.05324
H   0.52112  2.41961  2.50732
H   0.74810  0.08431  1.66711
C  -3.81792 -0.01303  0.64231
C  -2.75689 -1.47699 -1.97225
C  -0.45522  0.35457 -3.30195
C  -0.13720  2.99566 -1.48608
C  -2.21624  2.77566  0.95210
H   0.69411  2.73390 -2.15753
H  -0.73240  3.78438 -1.98249
H   0.29052  3.42587 -0.56795
H  -1.31960  3.38616  1.13261
H  -3.01468  3.45462  0.59867
H  -2.54445  2.34897  1.91233
H  -0.28413 -0.72442 -3.44108
H  -1.06868  0.70270 -4.15344
H   0.51585  0.86890 -3.35905
H  -3.56384 -1.01406  1.03150
H  -4.00019  0.65360  1.49762
H  -4.75621 -0.09553  0.06576
H  -2.02716 -2.00239 -2.60805
H  -3.08162 -2.16011 -1.17196
H  -3.63936 -1.25587 -2.60173
C   1.96997 -3.30206 -1.39998
C   0.88367 -2.52415 -0.98772
H   1.80039 -4.31603 -1.77066
H  -0.14277 -2.89890 -1.01057
```

6_Rh_V_TS_VI.log

```
SCF (BP86) Energy =     -1208.47875002
Enthalpy 0K =           -1208.049266
Enthalpy 298K =         -1208.020520
Free Energy 298K =      -1208.107852
PCM (DCM) Energy =      -1208.529356
PCM (MeOH) Energy =     -1208.534351
```

SCF (BP86+D3) Energy = -1208.561014
SCF (BS2) Energy = -1208.417071
Lowest Frequency = -303.5879 cm-1
C -2.76288 0.22620 -0.11396
C -2.11547 1.51137 -0.18721
C -1.24414 1.51076 -1.36927
C -1.37999 0.22414 -2.01378
C -2.29821 -0.59162 -1.22923
Rh -0.57042 -0.07284 0.02558
O -0.86291 -1.48625 1.56743
C -0.13786 -1.43798 2.64429
C -0.46543 -2.44443 3.73075
N 1.11766 -1.22150 -0.49935
C 2.33047 -0.58086 -0.46491
C 3.49993 -1.26508 -0.85076
C 3.42248 -2.60156 -1.25567
C 2.27792 0.79646 0.04661
C 1.12331 1.12977 0.83000
C 1.04850 2.43231 1.38096
C 2.05619 3.37938 1.14382
C 3.16708 3.04095 0.34858
C 3.28377 1.75123 -0.19257
O 0.79456 -0.60155 2.83528
H 0.46534 -2.89305 4.10978
H -1.14571 -3.22405 3.36280
H -0.94053 -1.91478 4.57360
H 4.32712 -3.14031 -1.55245
H 4.46379 -0.75219 -0.80201
H 4.14986 1.50296 -0.81512
H 3.94996 3.78132 0.15814
H 1.98824 4.37676 1.59007
H 0.21550 2.68509 2.04522
H 0.79786 0.26120 1.69068
C -3.75289 -0.22303 0.91706
C -2.80591 -1.96121 -1.57390
C -0.73153 -0.19143 -3.30042
C -0.48919 2.69341 -1.90051
C -2.41018 2.69661 0.68569
H 0.33720 2.38670 -2.55940
H -1.16561 3.33858 -2.49097
H -0.06482 3.30325 -1.08872
H -1.58888 3.42739 0.67169
H -3.31823 3.21081 0.31951
H -2.59559 2.40416 1.73112
H -0.50542 -1.26915 -3.31781
H -1.41672 0.01468 -4.14332
H 0.20142 0.36104 -3.48789
H -3.47135 -1.20522 1.33084
H -3.83081 0.49208 1.74894
H -4.75345 -0.32178 0.45859
H -2.09750 -2.51417 -2.21071
H -2.99912 -2.55821 -0.66868
H -3.75732 -1.88934 -2.13347
C 2.17545 -3.24843 -1.25279
C 1.04571 -2.52378 -0.86140
H 2.07358 -4.29746 -1.54159
H 0.05066 -2.97468 -0.82442

6_Rh_VI.log
SCF (BP86) Energy = -1208.49544912
Enthalpy 0K = -1208.061618
Enthalpy 298K = -1208.032246
Free Energy 298K = -1208.121440
PCM (DCM) Energy = -1208.543743
PCM (MeOH) Energy = -1208.548320
SCF (BP86+D3) Energy = -1208.575916
SCF (BS2) Energy = -1208.433516
Lowest Frequency = 16.6627 cm-1
C 2.52373 -0.95969 -0.06857
C 1.87880 -1.10208 -1.34735
C 1.59727 0.23681 -1.84824
C 2.25534 1.20254 -0.94383
C 2.79738 0.47859 0.14684
Rh 0.53566 0.00666 0.02169
O 0.36588 0.14234 2.20933
C -0.44590 -0.39626 3.00155
C -0.39317 -0.14646 4.48337
N -1.02674 1.41426 -0.10175
C -2.25388 0.93038 -0.48927
C -3.33979 1.81535 -0.64723
C -3.17438 3.17902 -0.38960
C -2.29353 -0.52727 -0.64243
C -1.07738 -1.21154 -0.31330
C -1.09906 -2.62381 -0.32552
C -2.25971 -3.33431 -0.68977
C -3.42862 -2.64532 -1.05318
C -3.44882 -1.24515 -1.01991
O -1.40775 -1.22263 2.61853
H -1.35200 0.28209 4.81893
H 0.42932 0.53709 4.72720
H -0.26403 -1.10310 5.01581
H -4.01487 3.86838 -0.51283
H -4.31211 1.42674 -0.95975
H -4.37065 -0.71585 -1.28372
H -4.32609 -3.19790 -1.34581
H -2.24618 -4.42933 -0.69051
H -0.20271 -3.18663 -0.04362
H -1.34953 -1.33944 1.62125
C 3.04156 -2.06507 0.80700
C 3.52375 1.02269 1.34061
C 2.35892 2.67755 -1.20288
C 1.01797 0.56571 -3.19433
C 1.64051 -2.37729 -2.09988
H 0.50031 1.53767 -3.18853
H 1.82007 0.62237 -3.95402
H 0.30020 -0.20114 -3.52321
H 0.68799 -2.36518 -2.65063
H 2.45379 -2.51514 -2.83633
H 1.64557 -3.25748 -1.43993
H 2.58596 3.24620 -0.28743
H 3.17424 2.87617 -1.92275
H 1.43552 3.08483 -1.64543
H 2.99531 -1.79091 1.87271
H 2.47221 -2.99742 0.66903
H 4.09929 -2.28354 0.56840
H 3.52067 2.12282 1.35867
H 3.06762 0.66492 2.27928
H 4.57700 0.68873 1.33633
C -1.92278 3.64858 0.04352
C -0.87697 2.73147 0.17611
H -1.75360 4.70291 0.27567
H 0.11667 3.03821 0.51197

6_Rh_VII.log
SCF (BP86) Energy = -994.643845119
Enthalpy 0K = -994.271349
Enthalpy 298K = -994.245854
Free Energy 298K = -994.325614
PCM (DCM) Energy = -994.6601754
PCM (MeOH) Energy = -994.663353
SCF (BP86+D3) Energy = -994.7159321
SCF (BS2) Energy = -1439.748412
Lowest Frequency = 19.1188 cm-1
C -2.38489 -1.02802 -0.03536
C -1.74014 -1.04835 1.25946
C -1.56397 0.32728 1.68177
C -2.25126 1.19263 0.70937
C -2.74170 0.37145 -0.33532
Rh -0.44102 -0.00350 -0.18889
Cl -0.19152 -0.00134 -2.58379
N 1.16512 1.32526 -0.07597
C 2.40717 0.76222 0.10418
C 3.54746 1.58946 0.19099
C 3.41940 2.97489 0.07649
C 2.38942 -0.69741 0.13426
C 1.10685 -1.28893 -0.07468
C 1.04546 -2.68989 -0.20820
C 2.19664 -3.48263 -0.06667
C 3.44737 -2.89076 0.19550
C 3.54484 -1.49901 0.28173
H 4.30231 3.61828 0.14428
H 4.53052 1.13336 0.33442
H 4.52360 -1.03525 0.45119
H 4.34062 -3.51296 0.31003

```
H   2.12024 -4.57135 -0.16996
H   0.09233 -3.17314 -0.44789
C  -2.82917 -2.20707 -0.85451
C  -3.47229  0.79793 -1.57389
C  -2.43297  2.67764  0.85958
C  -1.00629  0.78574  3.00119
C  -1.40505 -2.26337  2.07643
H  -0.50012  1.76067  2.90912
H  -1.81038  0.90050  3.75337
H  -0.27466  0.06607  3.40058
H  -0.53019 -2.09140  2.72270
H  -2.26057 -2.52964  2.72519
H  -1.18100 -3.13573  1.44420
H  -2.62292  3.16739 -0.10908
H  -3.29223  2.90391  1.51903
H  -1.54907  3.15497  1.31522
H  -2.63054 -2.03466 -1.92493
H  -2.30031 -3.12692 -0.55776
H  -3.91330 -2.39338 -0.73108
H  -3.64743  1.88476 -1.59221
H  -2.88294  0.53052 -2.47033
H  -4.45255  0.29257 -1.64227
C   2.14617  3.52778 -0.14873
C   1.05078  2.66472 -0.22827
H   1.99967  4.60399 -0.27181
H   0.04163  3.03307 -0.42766
```

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