Selective, Remote Functional Group Directed C-H activation by an Ir(III) Phenanthroline Complex

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Supporting information

Experimental methods

All chemicals and solvents were used as purchased. ^{1}H NMR data was collected on a Bruker Ascend^{TM} 400MHz spectrometer with TMS as an internal standard. The MS for identification was performed on a Thermo Electron Orbitrap Velos.

Synthesis

All deuterated butanols were purchased from CDN isotopes. Triglyme and dimethylsulfate were purchased from Alfa Aeser and Sigma Aldrich respectively. The procedure used to synthesize the ether was adapted from the procedure used by Achet et.al. [1]

1. Achet, D., Rocrelle, D., Murengezi, I., Delmas, M., Gaset, A.; *Synthesis-Stuttgart,* 1986, 642-643.

1,1,2,2-d$_4$ methoxybutane

A mixture of n-butyl-1,1,2,2-d$_4$ alcohol (960µl , 9.95mmol), triglyme (10.5mL, 0.058mol) and DI water (1670µl, 0.092mol) were heated while stirring for 10 minutes in an oil bath with a temperature of 65^{0}C. Crushed KOH (2.1g, 0.037mol) was added to the stirred solution. Dimethyl sulfate (996µl, 0.01mol) was introduced to this mixture at a rate of 1.8mL/hr. Once all the dimethyl sulfate was added the reaction mixture was refluxed for 1.5 hours. The solution was left to cool to room temperature and the unreacted KOH was filtered out. The filtrate was distilled to obtain the

ether. The ether was collected at 71^0C. δ_H (400 MHz, $CDCl_3$) 3.34 (s, 3H), 1.39- 1.33 (q, 2H), 0.95- 0.91(t, 3H). $[M + Na]^+$seen at 115.0802

4,4,4-d_3 methoxybutane

A mixture of n-butyl-4,4,4-d_3 alcohol (960µl , 0.01mol), triglyme (10.5mL, 0.058mol) and DI water (1670µl, 0.092mol) were heated while stirring for 10 minutes in an oil bath with a temperature of 65^0C. Crushed KOH (2.1g, 0.037mol) was added to the stirred solution. Dimethyl sulfate (996µl, 0.01mol) was introduced to this mixture at a rate of 1.8mL/hr. Once all the dimethyl sulfate was added the reaction mixture was refluxed for 1.5 hours. The solution was left to cool to room temperature and the unreacted KOH was filtered out. The filtrate was distilled to obtain the ether. The ether was collected at 70^0C. δ_H (400 MHz, $CDCl_3$) 3.41- 3.37 (t, 2H), 3.34(s, 3H), 1.55-1.40(m, 2H), 1.38- 1.34(t, 2H).

3,3,4,4,4-d_5 methoxybutane

A mixture of n-butyl-4,4,4-d_3 alcohol (960µl , 9.81mmol), triglyme (10.5mL, 0.058mol) and DI water (1670µl, 0.092mol) were heated while stirring for 10 minutes in an oil bath with a temperature of 65^0C. Crushed KOH (2.1g, 0.037mol) was added to the stirred solution. Dimethyl sulfate (996µl, 0.01mol) was introduced to this mixture at a rate of 1.8mL/hr. Once all the dimethyl sulfate was added the reaction mixture was refluxed for 1.5 hours. The solution was left to cool to room temperature and the unreacted KOH was filtered out. The filtrate was distilled to obtain the ether. The ether was collected at 70^0C. δ_H (400 MHz, $CDCl_3$) 3.41 (s,3H), 3.32- 3.29 (t, 2H), 1.48-1.45 (t, 2H).

1,1,2,2,3,3-d_6 methoxybutane

A mixture of n-butyl-1,1,2,2,3,3-d_6 alcohol (960µl , 9.81mmol), triglyme (10.5mL, 0.058mol) and DI water (1670µl, 0.092mol) were heated while stirring for 10 minutes in an oil bath with a temperature of 65^0C. Crushed KOH (2.1g, 0.037mol) was added to the stirred solution. Dimethyl sulfate (996µl, 0.01mol) was introduced to this mixture at a rate of 1.8mL/hr. Once all the dimethyl sulfate was added the reaction mixture was refluxed for 1.5 hours. The solution was left to cool to room temperature and the unreacted KOH was filtered out. The filtrate was distilled to obtain the ether. The ether was collected at 71^0C. δ_H (400 MHz, $CDCl_3$) 3.34 (s,3H), 0.91 (s, 3H).

NMR of 1,1,2,2-d$_4$ methoxybutane

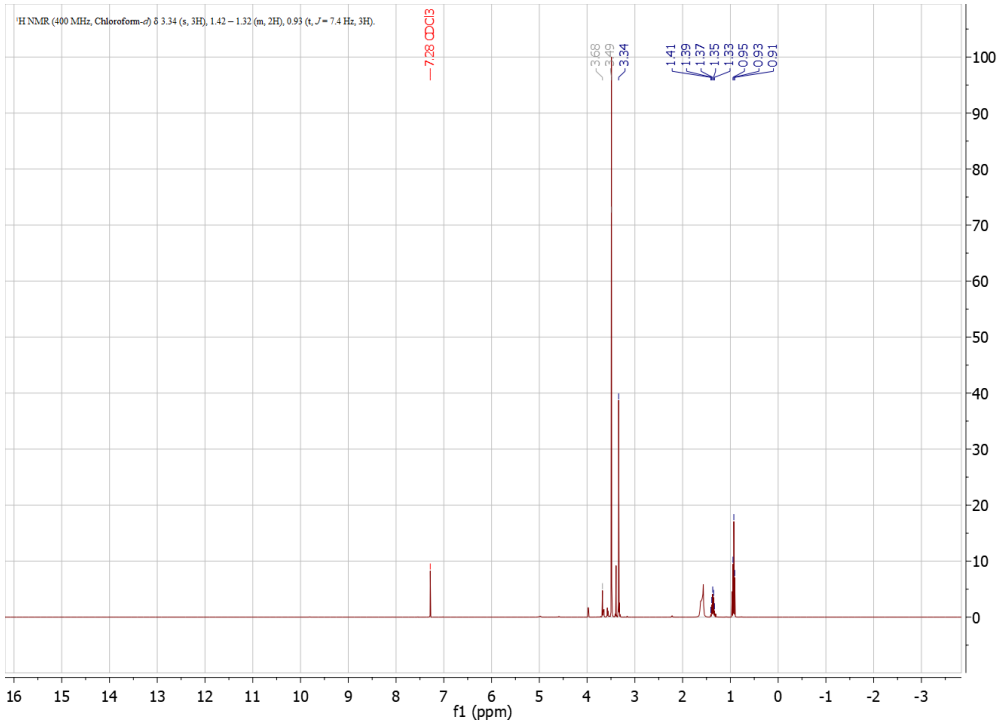


Figure S1 ^{1}H NMR (400 MHz, Chloroform-d) δ 3.34 (s, 3H), 1.42 – 1.32 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

NMR of 4,4,4-d_3 methoxybutane

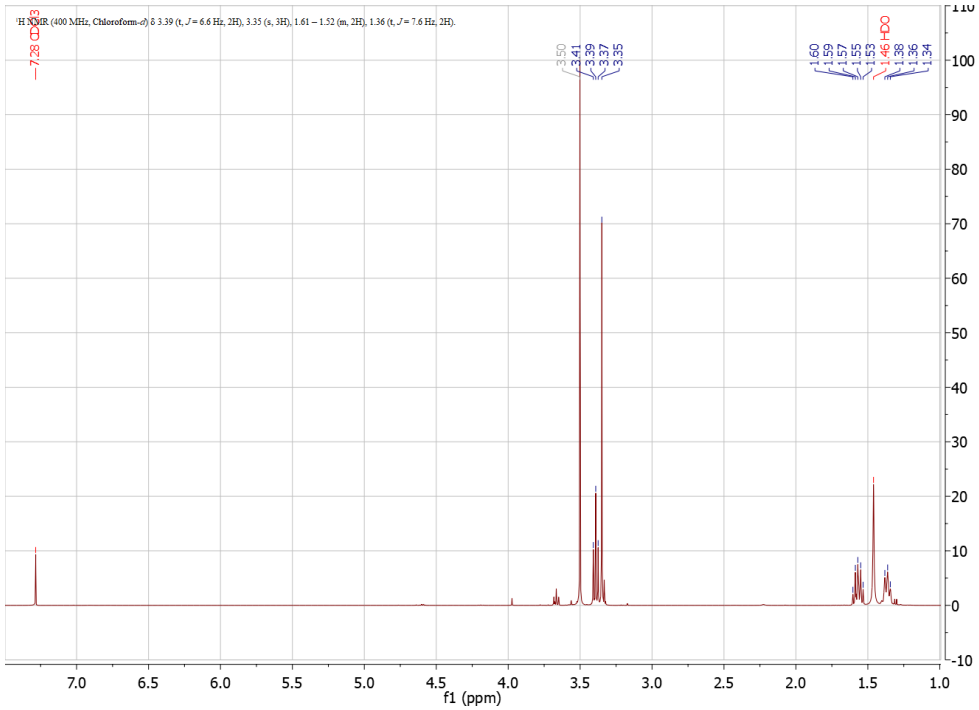


Figure S2 ^{1}H NMR (400 MHz, Chloroform-d) δ 3.39 (t, J = 6.6 Hz, 2H), 3.35 (s, 3H), 1.61 – 1.52 (m, 2H), 1.36 (t, J = 7.6 Hz, 2H).

NMR of 3,3,4,4,4-d_5 methoxybutane

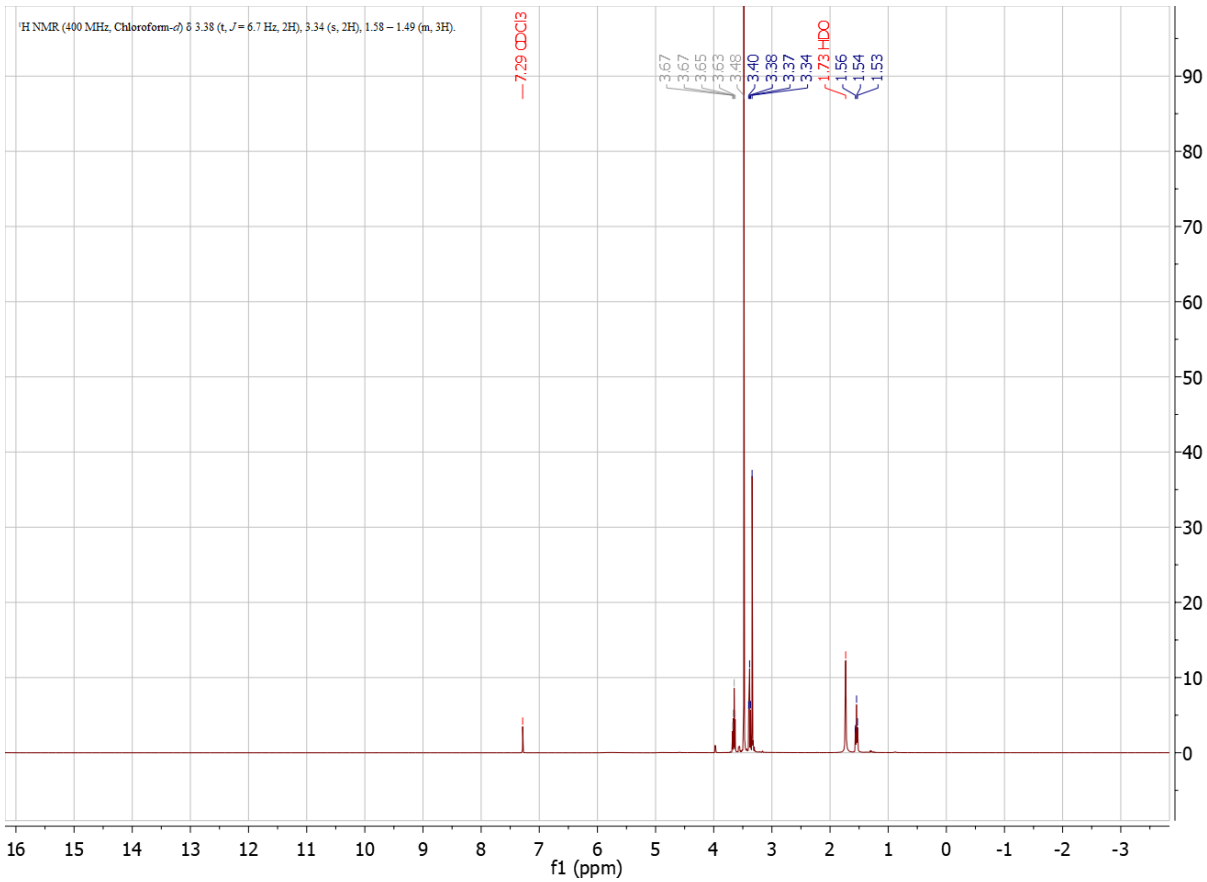


Figure S3 [1]H NMR (400 MHz, Chloroform-d) δ 3.38 (t, J = 6.7 Hz, 2H), 3.34 (s, 2H), 1.58 – 1.49 (m, 3H).

NMR of 1,1,2,2,3,3-d_6 methoxybutane

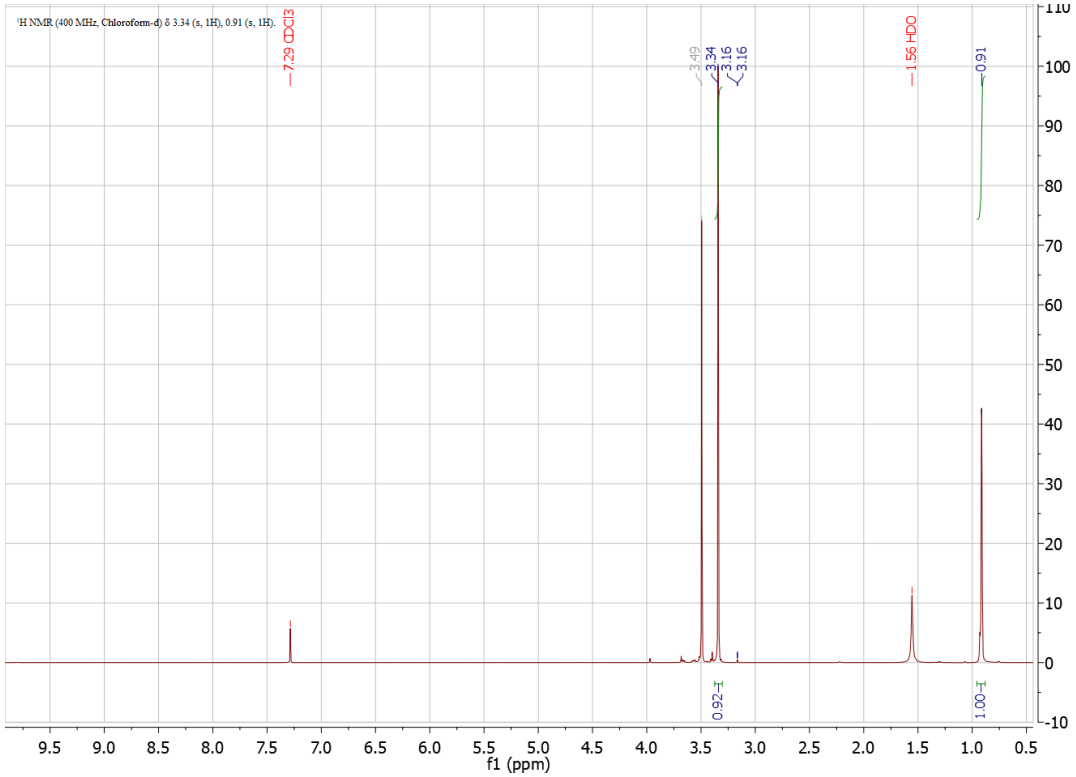


Figure S4 ^{1}H NMR (400 MHz, Chloroform-d) δ 3.34 (s, 1H), 0.91 (s, 1H).

Iridium(III) dichloride phenanthroline reaction with 1,1,2,2-d_4 methoxybutane

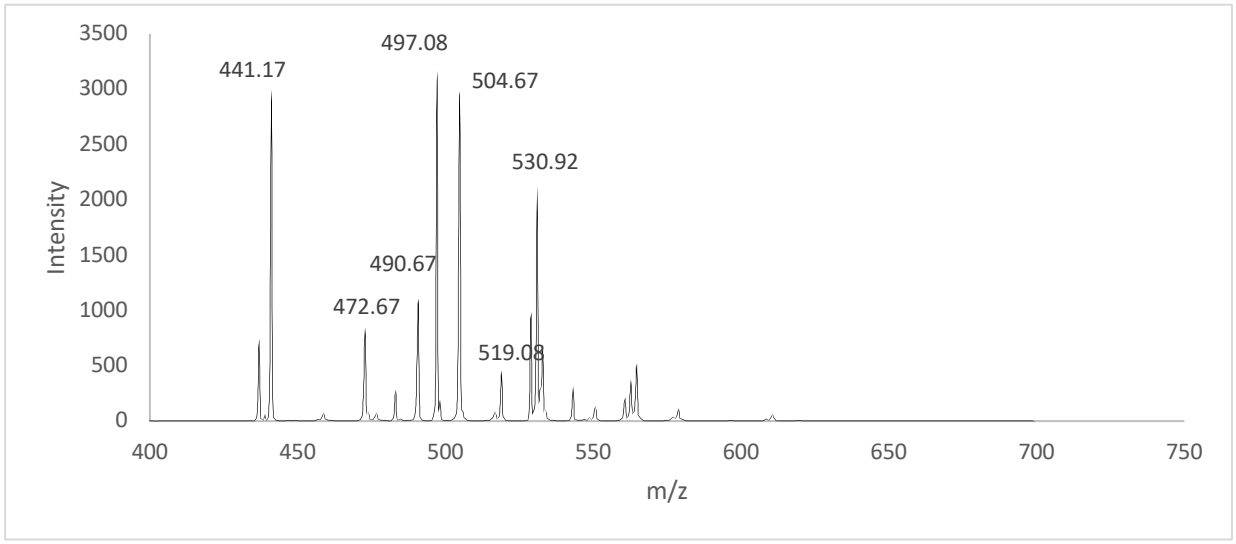


Figure S5 Peak at 441.17 is the iridium(III) phenanthroline complex, 472.67 is a methanol adduct, 490.67 is an adduct of one water and methanol molecules, 497.08 is the peak for C-H activation, 504.67 is an adduct of two methanol molecules, 510.08 and 530.92 are adducts of one and two methoxybutane molecules respectively

Iridium(III) dichloride phenanthroline reaction with 1,1,2,2,3,3-d_6 methoxybutane

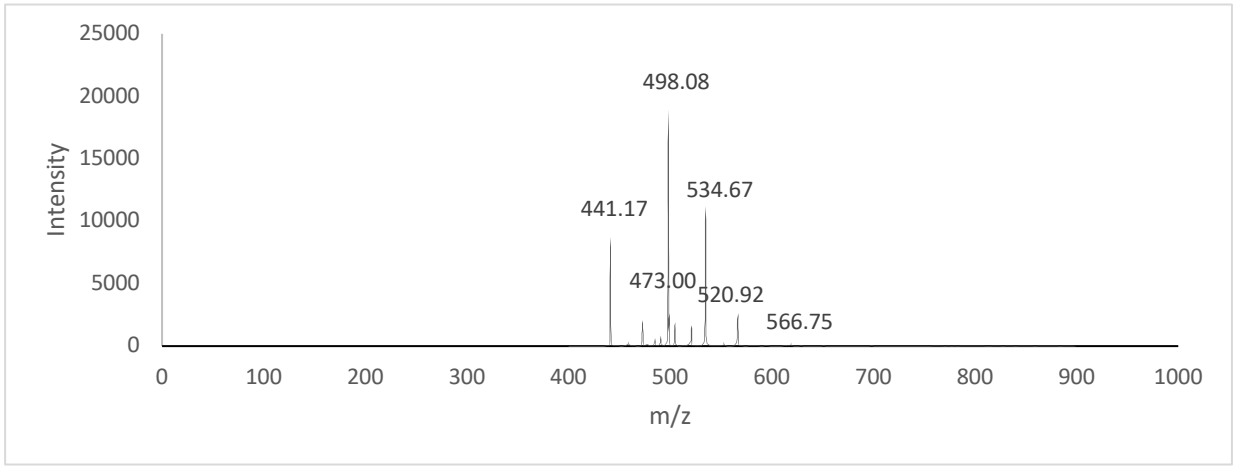


Figure S6 441.17 is the iridium(III) phenanthroline complex, 473.00 is a methanol adduct, 498.08 is the peak for C-D activation, 520.92 is adduct of two methanol molecules and a water molecule, peaks 534.67 and 566.75 are two and four methanol adducts respectively

Iridium(III)phenanthroline dichloride with 3,3,4,4,4-d_5 methoxybutane

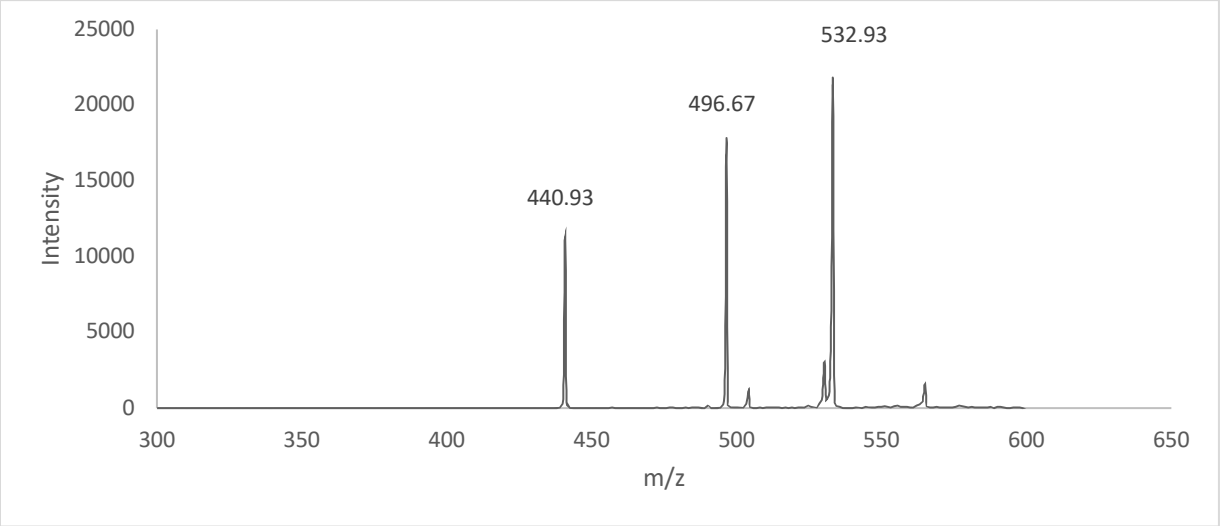


Figure S7 Peak at 440.93 is the iridium(III) phenanthroline complex, 496.67 is the peak for C-D activation and 532.93 is a methoxybutane adduct

Iridium(III) dichloride phenanthroline reaction with 4,4,4-d_3 methoxybutane

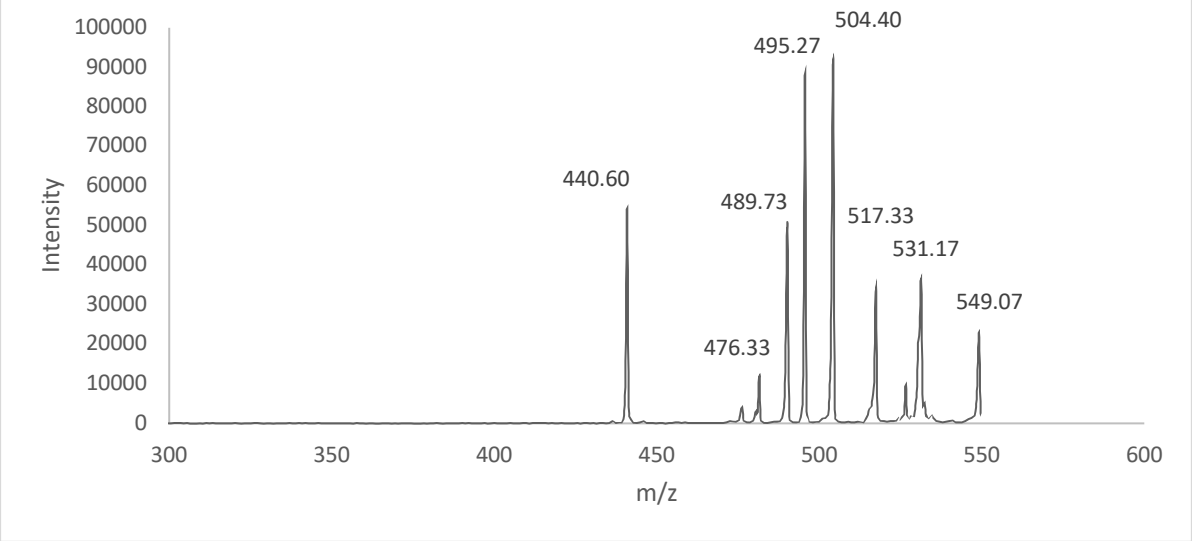


Figure S8 Peak at 440.60 is the iridium(III) phenanthroline complex, 476.33 and 489.73 are adducts of two water molecules and one methanol molecule respectively, 495.27 is the peak for C-H activation, 504.40 and 517.33 are adducts of two methanol molecules and one unreacted butanol molecule respectively, 531.17 is a methoxybutane adduct and 549.07 is an adduct of one methoxybutane molecule and one methanol molecule.

Iridium(III) dichloride phenanthroline reaction with a mixture of 1,1,2,2,3,3-d_6 and 4,4,4-d_3 methoxybutane

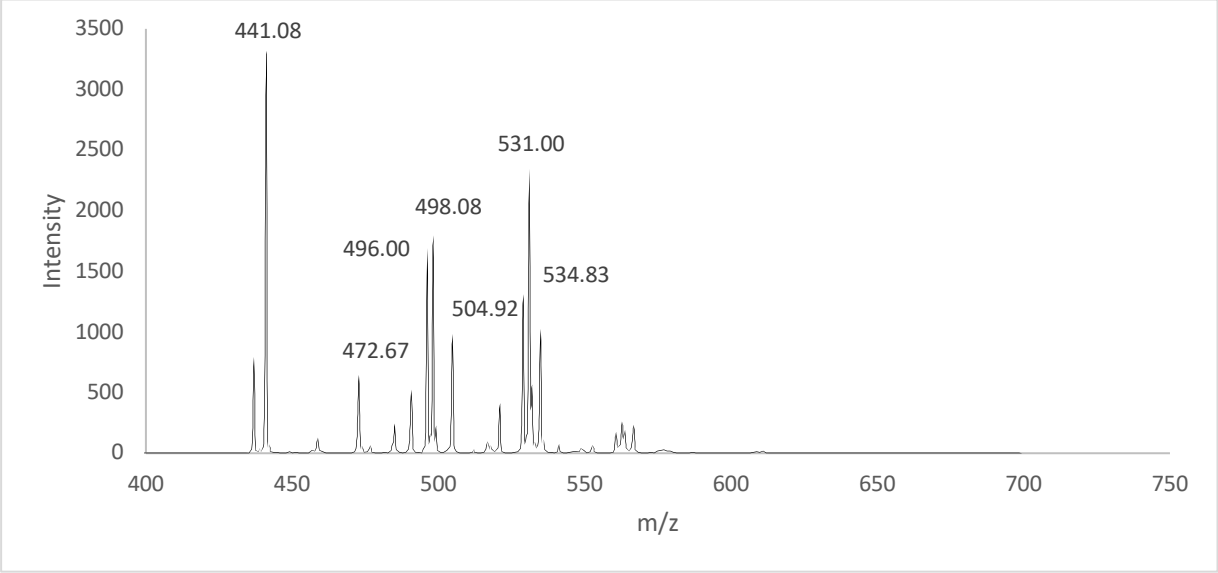


Figure S9 441.08 is the iridium(III) phenanthroline complex, 472.67 is a methanol adduct, 496.00 is the C-H activation of 4,4,4-d_3 methoxybutane, 498.08 is the C-D activation of 1,1,2,2,3,3-d_6 methoxybutane, 504.92 is an adduct of two methanol adducts and peaks 531.00 and 534.83 are adducts of 4,4,4-d_3 methoxybutane and 1,1,2,2,3,3-d_6 methoxybutane molecules respectively. Mixture was determined independently on a JEOL AccuTOF DART (28%/72% 1,1,2,2,3,3-d_6/4,4,4-d_3 methoxybutane). Product yields were corrected for ^{13}C and ^{17}O present in the methoxybutane based on natural abundances. Yields were also corrected for overlap from forward-edge peak broadening by using the ratio of the M-1 vs. M intensity for the reactant ion as a measure of the peak broadening effect. Although typically not necessary, the C-D activation for the delta-labeled ether is impacted by the much large peak for C-H activation.

Iridium(III) dichloride phenanthroline reaction with 1,1-d_2 butanol

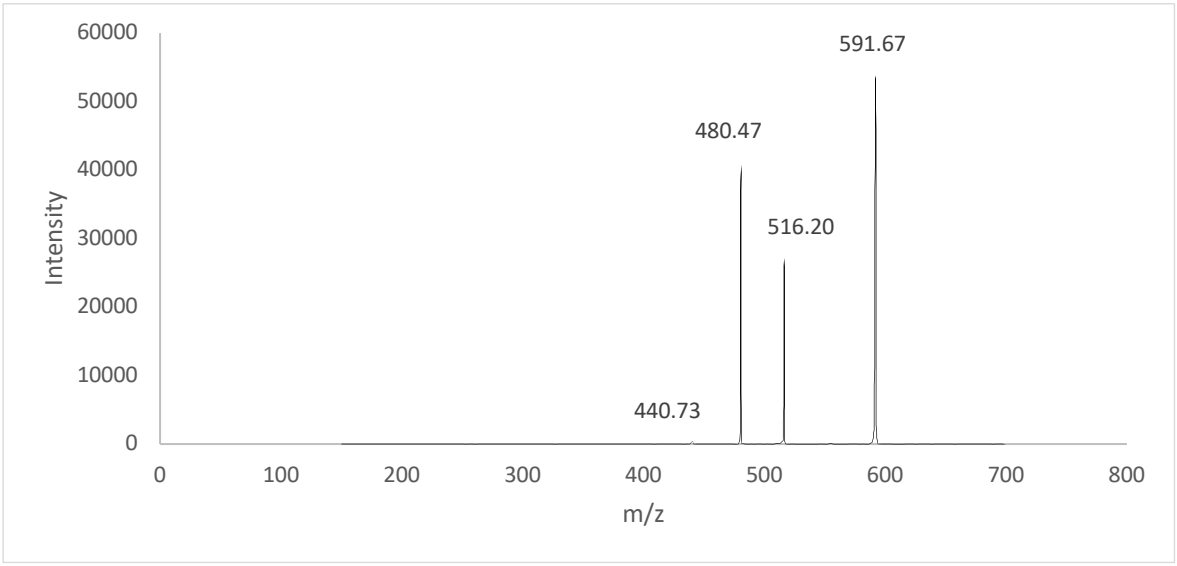


Figure S10 Peak at 440.73 is the iridium(III) phenanthroline complex ,480.47 is the peak for C-H activation , 516.20 and 591.67 are adducts of one and two butanol molecules respectively

Iridium(III) dichloride phenanthroline reaction with 1,1,2,2-d_4 butanol

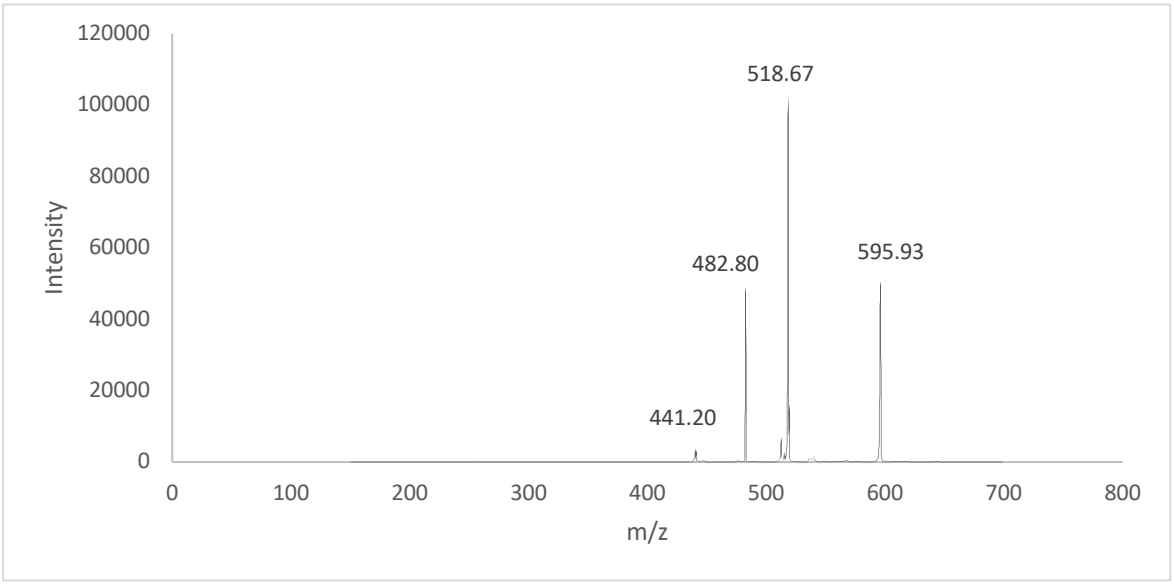


Figure S11 Peak at 441.20 is the iridium(III) phenanthroline complex, 482.80 is the peak for C-H activation, peaks 518.67 and 595.93 are adducts of one and two butanol molecules

Iridium(III) dichloride phenanthroline reaction with 1,1,2,2,3,3-d_6 butanol

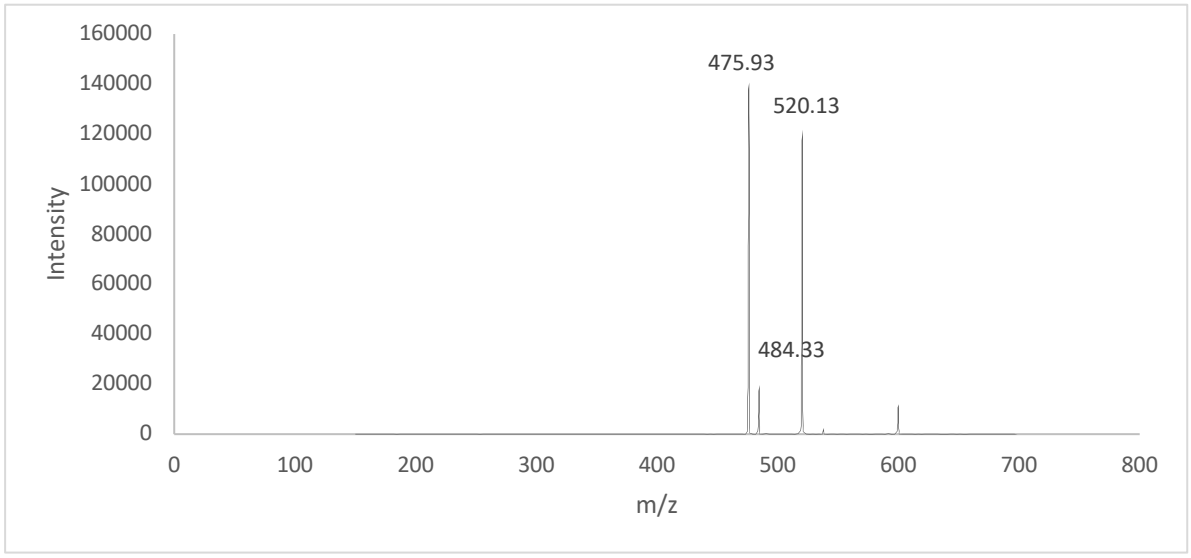


Figure S12 Peak 484.33 is C-H activation, peaks 520.13 and 476.93 are butanol and two water molecule adducts respectively

Iridium(III) dichloride phenanthroline reaction with 4,4,4-d_3 butanol

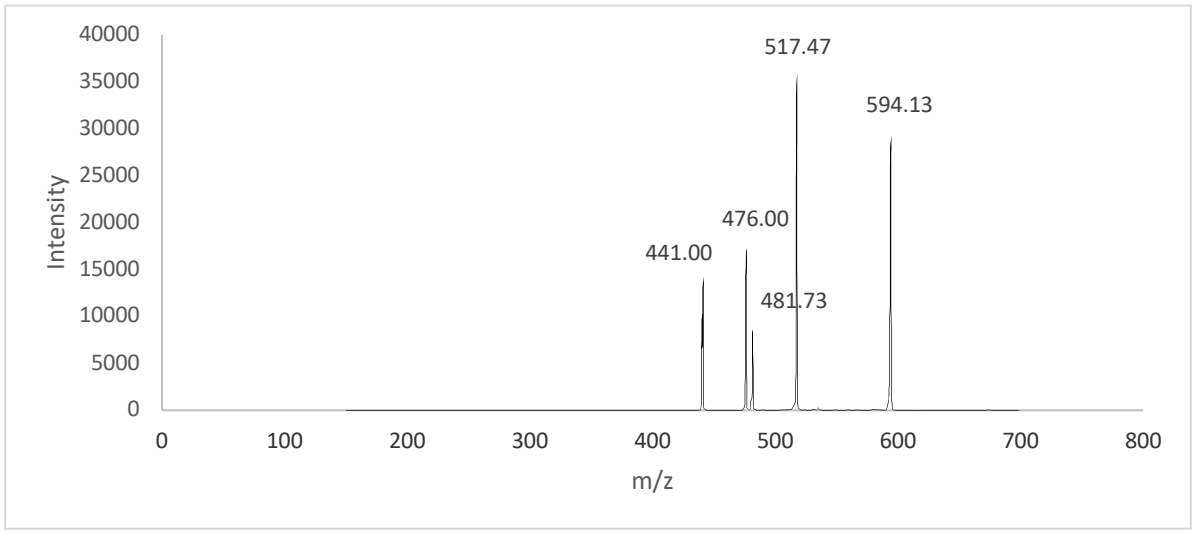


Figure S33 Peak at 441.00 is the iridium(III) phenanthroline complex , 481.73 is the peak for C-H activation, 476.00 is an adduct of two water molecules, peaks 517.47 and 594.13 are one and two butanol molecule adducts.

Iridium(III) dichloride phenanthroline reaction with a 50:50 mixture of 1,1,2,2,3,3-d_6 and 4,4,4-d_3 butanol

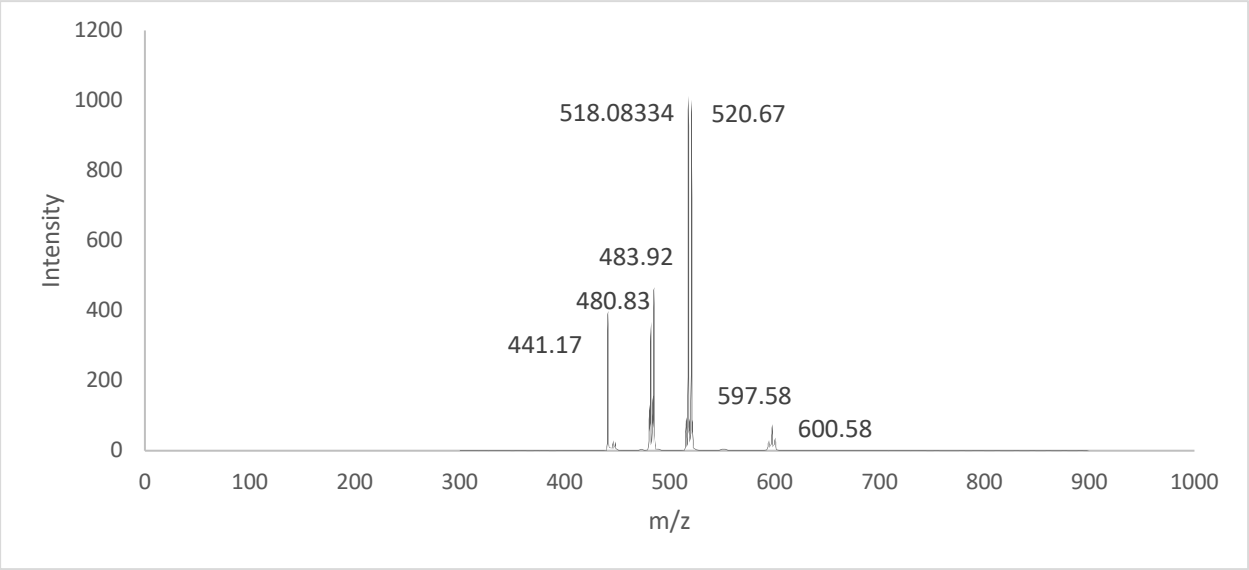


Figure S14 Iridium(III) phenanthroline with a 50:50 mixture of 1,1,2,2,3,3-d_6 butanol and 4,4,4-d_3 butanol. Peak at 441.17 is the iridium(III) phenanthroline complex, peaks 481, 518 and 597 are C-H activation, and adducts of one and two butanol molecules with 1,1,2,2,3,3-d_6 butanol. Peaks 484, 521 and 601 are C-H activation and adducts of one and two butanol molecules respectively with 4,4,4-d_3 butanol. Product yields were corrected for ^{13}C and ^{17}O present in the butanol based on natural abundances. Yields were also corrected for overlap from forward-edge peak broadening by using the ratio of the M-1 vs. M intensity for the reactant ion as a measure of the peak broadening effect. Although typically not necessary, the C-D activation for the delta-labeled ether is impacted by the much large peak for C-H activation. This is not an issue with the butanol, but was applied for consistency.

Relative rates of butanol vs methoxybutane

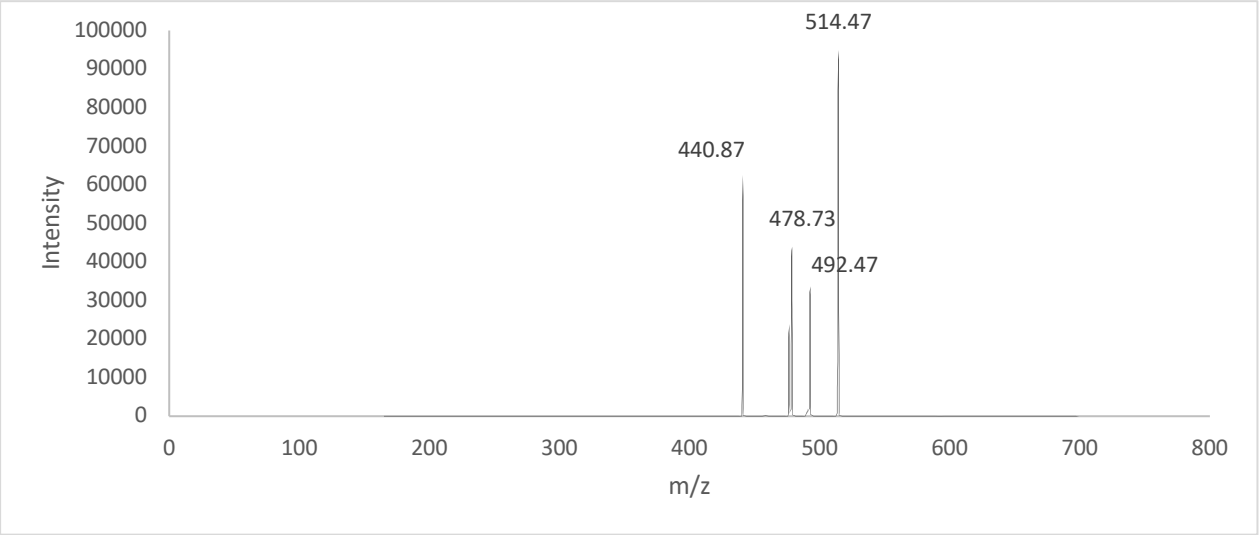


Figure S15 Peak 440.87 is the iridium(III) phenanthroline complex, 478.72 is the peak for C-H activation of butanol, 492.47 is the C-H activation of methoxybutane and 514.47 is an adduct of a butanol molecule.

DFT calculations

All calculations were performed using the LANL2DZ ECP basis set for Ir and M06/6-311+G** basis set for the other atoms in the complex. Electronic energy corrections were carried out at the QZVP level while Intrisic Reaction Coordinate (IRC) calculations were carried out to verify the transition state. Enthalpies given in hartree. The energy values given below are the from the enthalpy calculations carried out at the 6-311+G** level for all other atoms other than Ir as mentioned above.

Summary of computational data

Table S1 Summary of computational data (Hartree)

Complex	**Correction for Gibbs free energy**	**Correction for thermal enthalpy**	**Enthalpy**	**Imaginary frequency**
1,10-phenanthroline dichloride	0.132083	0.188621	-1596.061021	N/A
butanol	0.105766	0.143811	-233.6146441	N/A
Delta transition state structure for butanol	0.261996	0.331699	-1829.722645	365.53cm^{-1}
Gamma transition state structure for butanol	0.260473	0.331492	-1829.718079	246.10cm^{-1}
Delta activation butanol structure	0.262727	0.334416	-1829.732609	N/A
Gamma activated butanol structure	0.261239	0.333824	-1829.72976	N/A
methoxybutane	0.131004	0.172681	-272.9021051	N/A
Delta transition state structure for methoxybutane	0.285671	0.35888	-1869.001652	675.28cm^{-1}
Gamma transition state structure for methoxybutane	0.286767	0.35902	-1869.003443	389.58cm^{-1}
Delta activation methoxybutane structure	0.288122	0.363582	-1869.011614	N/A
Gamma activated methoxybutane structure	0.287676	0.362969	-1869.017302	N/A

Table S2 APFD Double Hybrid Data

	Enthalpy (hartree)			Gamma vs. Delta (kcal/mol)	
	APFD	M06		APFD	M06
Delta transition state structure for butanol	-1829.350308	-1829.474211			
Gamma transition state structure for butanol	-1829.34656	-1829.46967		2.4	2.8
Delta transition state structure for methoxybutane	-1868.593344	-1868.717535			
Gamma transition state structure for methoxybutane	-1868.594646	-1868.718247		-0.8	-0.4
Note: Values will not match narrative because smaller basis set was used in these test calculations.					
Basis set: 6-311+G** on all atoms excpet Ir using LANL2DZ					
APFD: A. Austin, G. Petersson, M. J. Frisch, F. J. Dobek, G. Scalmani, and K. Throssell, "A density functional with spherical atom dispersion terms," J. Chem. Theory and Comput. 8 (2012) 4989					

XYZ coordinates of iridium(III)-1,10-phenanthroline dichloride

Correction for thermal enthalpies at 6-311+G** level: 0.188621

Energy at QZVP level: -1596.061021

H	1.09761	-4.48699	0.00040
C	1.21328	-3.40987	0.00011
H	3.35651	-3.44037	-0.00007
C	2.46075	-2.82684	-0.00014
N	0.15636	-1.29590	-0.00020
C	2.57223	-1.42525	-0.00037
C	0.06046	-2.61927	0.00003
C	1.37824	-0.70248	-0.00032
C	3.79422	-0.67951	-0.00051
H	-0.93768	-3.04589	0.00024
C	3.79422	0.67952	-0.00036
H	4.73116	-1.22754	-0.00069
H	4.73115	1.22755	-0.00042
C	2.57222	1.42525	-0.00004
C	2.46074	2.82685	0.00048

C	1.37824	0.70249	-0.00015
C	1.21328	3.40987	0.00086
H	3.35650	3.44038	0.00066
H	1.09760	4.48699	0.00136
C	0.06045	2.61927	0.00064
H	-0.93769	3.04589	0.00092
N	0.15636	1.29590	0.00014
Ir	-1.32841	-0.00000	-0.00006
Cl	-1.59234	-0.00066	2.31322
Cl	-1.59274	0.00066	-2.31314

XYZ coordinates of butanol

Correction for thermal enthalpies at 6-311+G** level: 0.143811

Energy at QZVP level: -233.6146441

C	2.49089	-0.29317	-0.00020
C	1.21551	0.52871	0.00041
C	-0.03087	-0.33918	-0.00014
C	-1.30218	0.47095	-0.00027
O	-2.39684	-0.42184	0.00058
H	-3.21475	0.07810	-0.00235
H	2.53937	-0.94195	0.88169
H	3.38499	0.33692	0.00082
H	2.53991	-0.93988	-0.88357
H	1.19985	1.19073	0.87813
H	1.19983	1.19198	-0.87637
H	-0.03319	-0.99817	0.87910
H	-0.03269	-0.99790	-0.87959
H	-1.32458	1.12503	-0.88833
H	-1.32407	1.12604	0.88708

XYZ coordinates of delta transition state structure of butanol

Correction for thermal enthalpies at 6-311+G** level: 0.331699

Energy at QZVP level: -1829.722645

Imaginary frequency: 365.53cm^{-1}

N	0.81118	1.31020	0.02398
C	2.02691	0.69034	-0.01249
C	2.05283	-0.73373	-0.03826
C	0.76872	2.63388	0.10562
H	-0.21372	3.08728	0.16752
C	3.23132	1.40976	-0.00725
C	1.92417	3.41657	0.11882
C	3.15370	2.81097	0.05356
H	4.06663	3.39914	0.05867
C	0.84144	-2.69664	-0.02982
H	-0.13907	-3.16479	-0.01144
C	2.01473	-3.45880	-0.07003
H	1.94708	-4.54008	-0.08064
C	3.27845	-1.41488	-0.07529
C	3.22994	-2.82018	-0.09216
H	4.15639	-3.38657	-0.12057
C	4.49159	-0.66104	-0.08729
H	5.43514	-1.19734	-0.11956
C	4.46765	0.69319	-0.05262
H	5.39112	1.26407	-0.05510
H	1.82642	4.49355	0.18228
N	0.86321	-1.37690	-0.01537
Ir	-0.78177	0.03578	0.03443
Cl	-0.90464	0.15426	-2.48999
O	-2.23668	-1.51921	0.23942

H	-2.27373	-1.63066	1.20644
Cl	-0.73961	-0.06437	2.36733
C	-3.59104	-1.39033	-0.26703
C	-4.27920	-0.15564	0.25595
C	-3.72109	1.14100	-0.31118
C	-2.33619	1.52345	0.19141
H	-4.11619	-2.30813	0.01405
H	-3.48704	-1.37468	-1.35606
H	-4.22957	-0.14697	1.35543
H	-5.34184	-0.24324	0.00042
H	-4.40906	1.95725	-0.05475
H	-3.74026	1.08007	-1.41003
H	-2.36571	1.72074	1.26969
H	-2.05078	2.47157	-0.28910
H	-1.45856	0.92861	-1.39049

XYZ coordinates of gamma transition state structure of butanol

Correction for thermal enthalpies at 6-311+G** level: 0.331492

Energy at QZVP level: -1829.718079

Imaginary frequency: 246.10cm^{-1}

N	0.65016	1.28579	0.06809
C	1.92242	0.79797	0.01857
C	2.09146	-0.61354	-0.04494
C	0.47498	2.59207	0.21511
H	-0.54814	2.93472	0.29812
C	3.04749	1.63489	0.05077
C	1.54340	3.48854	0.26568
C	2.82824	3.01714	0.16896
H	3.67633	3.69483	0.19630
C	1.07609	-2.67935	-0.10268

H	0.15094	-3.24941	-0.11102
C	2.31533	-3.32311	-0.18321
H	2.35055	-4.40442	-0.24065
C	3.37773	-1.16915	-0.11671
C	3.46439	-2.57070	-0.18528
H	4.44012	-3.04466	-0.24191
C	4.50866	-0.29606	-0.11042
H	5.50101	-0.73290	-0.16829
C	4.34881	1.04665	-0.02441
H	5.21106	1.70616	-0.00904
H	1.33510	4.54561	0.37889
N	0.96889	-1.36538	-0.02643
Ir	-0.82168	-0.12922	0.03118
Cl	-0.91308	-0.06329	-2.46090
C	-2.70242	0.98760	0.15126
C	-2.95179	2.28883	-0.59830
H	-2.88724	2.17827	-1.68889
H	-3.96793	2.64157	-0.38157
H	-2.28345	3.10264	-0.30719
C	-3.77477	-0.02665	-0.24100
H	-4.76952	0.36865	0.00636
H	-3.77085	-0.19436	-1.32761
C	-3.58078	-1.32623	0.47164
H	-3.67181	-1.20371	1.55677
H	-4.24945	-2.11852	0.12784
O	-2.21032	-1.75538	0.17742
H	-1.90966	-2.28452	0.93025
Cl	-0.77299	-0.19497	2.37360
H	-2.74798	1.17806	1.23028
H	-1.51322	0.72916	-1.28644

XYZ coordinates of the activated delta position of butanol

Correction for thermal enthalpies at 6-311+G** level: 0.334416

Energy at QZVP level: -1829.732609

N	0.81118	1.31020	0.02398
C	2.02691	0.69034	-0.01249
C	2.05283	-0.73373	-0.03826
C	0.76872	2.63388	0.10562
H	-0.21372	3.08728	0.16752
C	3.23132	1.40976	-0.00725
C	1.92417	3.41657	0.11882
C	3.15370	2.81097	0.05356
H	4.06663	3.39914	0.05867
C	0.84144	-2.69664	-0.02982
H	-0.13907	-3.16479	-0.01144
C	2.01473	-3.45880	-0.07003
H	1.94708	-4.54008	-0.08064
C	3.27845	-1.41488	-0.07529
C	3.22994	-2.82018	-0.09216
H	4.15639	-3.38657	-0.12057
C	4.49159	-0.66104	-0.08729
H	5.43514	-1.19734	-0.11956
C	4.46765	0.69319	-0.05262
H	5.39112	1.26407	-0.05510
H	1.82642	4.49355	0.18228
N	0.86321	-1.37690	-0.01537
Ir	-0.78177	0.03578	0.03443
Cl	-0.90464	0.15426	-2.48999
O	-2.23668	-1.51921	0.23942
H	-2.27373	-1.63066	1.20644

Cl	-0.73961	-0.06437	2.36733
C	-3.59104	-1.39033	-0.26703
C	-4.27920	-0.15564	0.25595
C	-3.72109	1.14100	-0.31118
C	-2.33619	1.52345	0.19141
H	-4.11619	-2.30813	0.01405
H	-3.48704	-1.37468	-1.35606
H	-4.22957	-0.14697	1.35543
H	-5.34184	-0.24324	0.00042
H	-4.40906	1.95725	-0.05475
H	-3.74026	1.08007	-1.41003
H	-2.36571	1.72074	1.26969
H	-2.05078	2.47157	-0.28910
H	-1.45856	0.92861	-1.39049

XYZ coordinates of the activated gamma position of butanol

Correction for thermal enthalpies at 6-311+G** level: 0.333824

Energy at QZVP level: -1829.72976

N	0.65016	1.28579	0.06809
C	1.92242	0.79797	0.01857
C	2.09146	-0.61354	-0.04494
C	0.47498	2.59207	0.21511
H	-0.54814	2.93472	0.29812
C	3.04749	1.63489	0.05077
C	1.54340	3.48854	0.26568
C	2.82824	3.01714	0.16896
H	3.67633	3.69483	0.19630
C	1.07609	-2.67935	-0.10268
H	0.15094	-3.24941	-0.11102

C	2.31533	-3.32311	-0.18321
H	2.35055	-4.40442	-0.24065
C	3.37773	-1.16915	-0.11671
C	3.46439	-2.57070	-0.18528
H	4.44012	-3.04466	-0.24191
C	4.50866	-0.29606	-0.11042
H	5.50101	-0.73290	-0.16829
C	4.34881	1.04665	-0.02441
H	5.21106	1.70616	-0.00904
H	1.33510	4.54561	0.37889
N	0.96889	-1.36538	-0.02643
Ir	-0.82168	-0.12922	0.03118
Cl	-0.91308	-0.06329	-2.46090
C	-2.70242	0.98760	0.15126
C	-2.95179	2.28883	-0.59830
H	-2.88724	2.17827	-1.68889
H	-3.96793	2.64157	-0.38157
H	-2.28345	3.10264	-0.30719
C	-3.77477	-0.02665	-0.24100
H	-4.76952	0.36865	0.00636
H	-3.77085	-0.19436	-1.32761
C	-3.58078	-1.32623	0.47164
H	-3.67181	-1.20371	1.55677
H	-4.24945	-2.11852	0.12784
O	-2.21032	-1.75538	0.17742
H	-1.90966	-2.28452	0.93025
Cl	-0.77299	-0.19497	2.37360
H	-2.74798	1.17806	1.23028
H	-1.51322	0.72916	-1.28644

XYZ coordinates of methoxybutane

Correction for thermal enthalpies at 6-311+G** level: 0.172681

Energy at QZVP level: -272.9021051

C	3.04319	0.12713	0.00001
O	1.79287	-0.55302	-0.00000
C	0.70361	0.36748	-0.00000
C	-0.60845	-0.41017	0.00000
C	-1.80665	0.53965	-0.00000
C	-3.12787	-0.20855	0.00000
H	3.14223	0.74767	0.89656
H	3.84381	-0.61642	0.00001
H	3.14223	0.74767	-0.89656
H	0.76250	1.00062	-0.89279
H	0.76250	1.00062	0.89280
H	-0.64392	-1.06925	0.87688
H	-0.64392	-1.06925	-0.87687
H	-1.76202	1.18736	0.88355
H	-1.76202	1.18737	-0.88355
H	-3.96405	0.49771	-0.00000
H	-3.22167	-0.84158	0.88803
H	-3.22167	-0.84158	-0.88803

XYZ coordinates of delta transition state structure of methoxybutane

Correction for thermal enthalpies at 6-311+G** level: 0.35888

Energy at QZVP level: -1869.001652

Imaginary frequency: 675.28cm^{-1}

N	0.95449	-1.30364	-0.02574
C	2.13376	-0.61914	-0.00158
C	2.07782	0.80420	0.01232

C	0.98231	-2.62897	-0.10008
H	0.02565	-3.13642	-0.14336
C	3.37550	-1.27183	-0.02864
C	2.17829	-3.34728	-0.12533
C	3.37404	-2.67515	-0.08367
H	4.31798	-3.21164	-0.10439
C	0.76486	2.69204	-0.08818
H	-0.23553	3.11115	-0.14544
C	1.89322	3.51756	-0.13711
H	1.76476	4.59065	-0.21430
C	3.26513	1.55123	-0.02647
C	3.14230	2.94984	-0.08997
H	4.03704	3.56483	-0.12063
C	4.51840	0.86616	-0.02546
H	5.43014	1.45553	-0.03910
C	4.57039	-0.48755	-0.02341
H	5.52420	-1.00595	-0.03340
H	2.13848	-4.42834	-0.18229
N	0.85186	1.37792	0.01426
Ir	-0.70673	-0.14611	0.03652
Cl	-0.85892	-0.52895	2.56593
O	-2.36614	1.23291	0.14149
Cl	-0.63748	0.02724	-2.29016
C	-3.62116	1.13499	-0.58223
C	-3.86426	-0.24383	-1.13538
C	-3.56884	-1.34114	-0.12014
C	-2.11069	-1.76474	-0.12831
H	-3.61104	1.90434	-1.36283
H	-4.40674	1.38175	0.14453
H	-3.27950	-0.40595	-2.04602

H	-4.91876	-0.26686	-1.43315
H	-4.18708	-2.21902	-0.34585
H	-3.87543	-1.01336	0.88637
H	-1.42918	-1.20684	1.45957
C	-2.43915	2.17018	1.21325
H	-1.44646	2.27211	1.65155
H	-3.13572	1.81308	1.98088
H	-2.77913	3.13854	0.82961
H	-1.97534	-2.59185	0.59444
H	-1.84839	-2.18878	-1.10594

XYZ coordinates of gamma transition state structure of methoxybutane

Correction for thermal enthalpies at 6-311+G** level: 0.35902

Energy at QZVP level: -1869.003443

Imaginary frequency: 389.58cm^{-1}

N	-0.79822	1.28851	0.05500
C	-2.03712	0.73203	-0.02397
C	-2.12508	-0.68665	0.01063
C	-0.69190	2.61293	0.08331
H	0.30712	3.02392	0.16378
C	-3.20212	1.51017	-0.11066
C	-1.80308	3.45196	0.00995
C	-3.05772	2.90605	-0.09789
H	-3.93889	3.53711	-0.16470
C	-1.03320	-2.69851	0.17971
H	-0.09703	-3.23451	0.27118
C	-2.23980	-3.40265	0.11733
H	-2.22409	-4.48495	0.16465
C	-3.38334	-1.30554	-0.05833
C	-3.41632	-2.70857	-0.00471

H	-4.36996	-3.22552	-0.05860
C	-4.55511	-0.49676	-0.17126
H	-5.51957	-0.99172	-0.23110
C	-4.46836	0.85440	-0.19472
H	-5.36075	1.46765	-0.27222
H	-1.65189	4.52430	0.03535
N	-0.96671	-1.38000	0.12846
Ir	0.76072	-0.01321	0.10905
Cl	0.92233	0.30608	2.57811
C	3.68513	0.69456	0.26931
H	4.55113	1.25654	-0.10334
H	3.82802	0.56021	1.34861
C	3.65672	-0.65658	-0.37800
H	3.57008	-0.61090	-1.47167
H	4.52531	-1.26631	-0.10831
Cl	0.65014	-0.30741	-2.22202
H	2.32706	2.26337	0.74164
H	2.70539	1.48077	-2.17575
C	2.43606	2.16326	-1.36760
H	1.48354	2.61733	-1.65347
H	3.18950	2.96035	-1.33100
O	2.48173	-1.32648	0.14646
C	2.38379	-2.68224	-0.28719
H	3.38713	-3.11382	-0.32857
H	1.91120	-2.73857	-1.27400
H	1.81191	-3.22576	0.46544
C	2.39609	1.46049	-0.01973
H	1.48978	1.00230	1.33902

XYZ coordinates of the activated delta position of methoxybutane

Correction for thermal enthalpies at 6-311+G** level: 0.363582

Energy at QZVP level: -1869.011614

N	0.91502	-1.30300	0.00200
C	2.12200	-0.66718	-0.01108
C	2.13487	0.76030	0.00998
C	0.89343	-2.63030	-0.07713
H	-0.08098	-3.10185	-0.09645
C	3.33417	-1.37620	-0.07717
C	2.05478	-3.39883	-0.14018
C	3.27700	-2.77714	-0.13440
H	4.19871	-3.34893	-0.18654
C	0.94177	2.71933	-0.01237
H	-0.02544	3.20920	-0.01207
C	2.11042	3.48354	-0.09630
H	2.03826	4.56327	-0.15239
C	3.36293	1.44214	-0.06148
C	3.32379	2.84558	-0.10572
H	4.25293	3.40525	-0.16220
C	4.58064	0.69859	-0.10550
H	5.51820	1.24466	-0.14681
C	4.56624	-0.65447	-0.10903
H	5.49136	-1.22101	-0.15159
H	1.96654	-4.47694	-0.19993
N	0.94228	1.40036	0.06358
Ir	-0.73957	-0.12520	0.06832
Cl	-0.83249	-0.27908	2.58447
O	-2.50603	1.12631	0.19156
Cl	-0.68275	0.05480	-2.25311
C	-3.61998	1.02147	-0.73281
C	-3.90572	-0.41362	-1.10626

C	-3.55009	-1.38815	0.00785
C	-2.07045	-1.72737	-0.00515
H	-3.39577	1.64441	-1.60805
H	-4.47287	1.45867	-0.19690
H	-3.35597	-0.68697	-2.01271
H	-4.97126	-0.47275	-1.35198
H	-4.12477	-2.31351	-0.12776
H	-3.86445	-0.98024	0.98052
H	-1.73954	-1.20251	2.71282
C	-2.37846	2.45423	0.67540
H	-1.59165	2.46914	1.43056
H	-3.32215	2.76525	1.13555
H	-2.13938	3.14042	-0.14789
H	-1.84169	-2.41251	0.83087
H	-1.85128	-2.27325	-0.93390

XYZ coordinates of the activated gamma position of methoxybutane

Correction for thermal enthalpies at 6-311+G** level: 0.362969

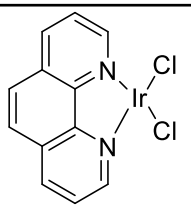
Energy at QZVP level: -1869.017302

N	0.77745	-1.28508	0.09942
C	2.02572	-0.74493	0.00340
C	2.14579	0.67621	0.02641
C	0.65860	-2.60989	0.12697
H	-0.34577	-3.00701	0.20676
C	3.17773	-1.54340	-0.09734
C	1.75620	-3.46519	0.04570
C	3.01643	-2.93703	-0.07791
H	3.88881	-3.57878	-0.15719
C	1.11013	2.71440	0.20614

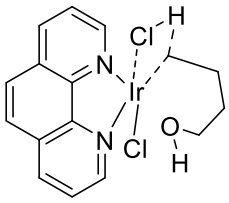
H	0.18761	3.27275	0.32278
C	2.32943	3.39290	0.10802
H	2.34148	4.47575	0.14571
C	3.41768	1.26620	-0.07415
C	3.48512	2.66848	-0.03527
H	4.45000	3.16061	-0.11624
C	4.57085	0.43417	-0.20350
H	5.54364	0.90878	-0.28932
C	4.45534	-0.91429	-0.21079
H	5.33254	-1.54755	-0.30087
H	1.58953	-4.53539	0.07021
N	1.00926	1.39820	0.16620
Ir	-0.78651	0.01525	0.09220
Cl	-0.91685	-0.06253	2.60237
C	-3.63758	-0.68892	0.34076
H	-4.50497	-1.29189	0.04009
H	-3.74358	-0.49785	1.41649
C	-3.67888	0.62691	-0.37543
H	-3.63954	0.51607	-1.46755
H	-4.54641	1.23839	-0.10418
Cl	-0.61574	0.21072	-2.22813
H	-2.12572	-2.12555	0.84022
H	-2.81643	-1.58932	-2.09656
C	-2.46332	-2.21043	-1.26873
H	-1.52178	-2.65309	-1.60746
H	-3.18789	-3.02445	-1.13178
O	-2.49248	1.34543	0.04948
C	-2.39549	2.63167	-0.56302
H	-3.38272	3.10201	-0.55106
H	-2.02679	2.54222	-1.59004

H	-1.71915	3.23493	0.04153
C	-2.32721	-1.41367	0.01721
H	-1.60359	-1.14844	2.80119

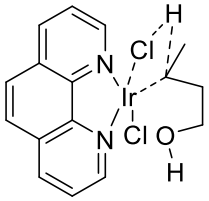
Optimized structures



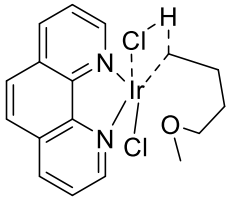
Iridium(III)-1,10-phenanthroline



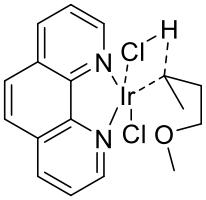
Delta transition state for butanol



Gamma transition state for butanol



Delta transition state for methoxybutane



Gamma transition state for methoxybutane

Figure S16 Optimized structures of iridium(III), 1-10-phenanthroline dichloride and transition state structures of butanol and methoxybutane

IRC of gamma transition state for 1-methoxybutane

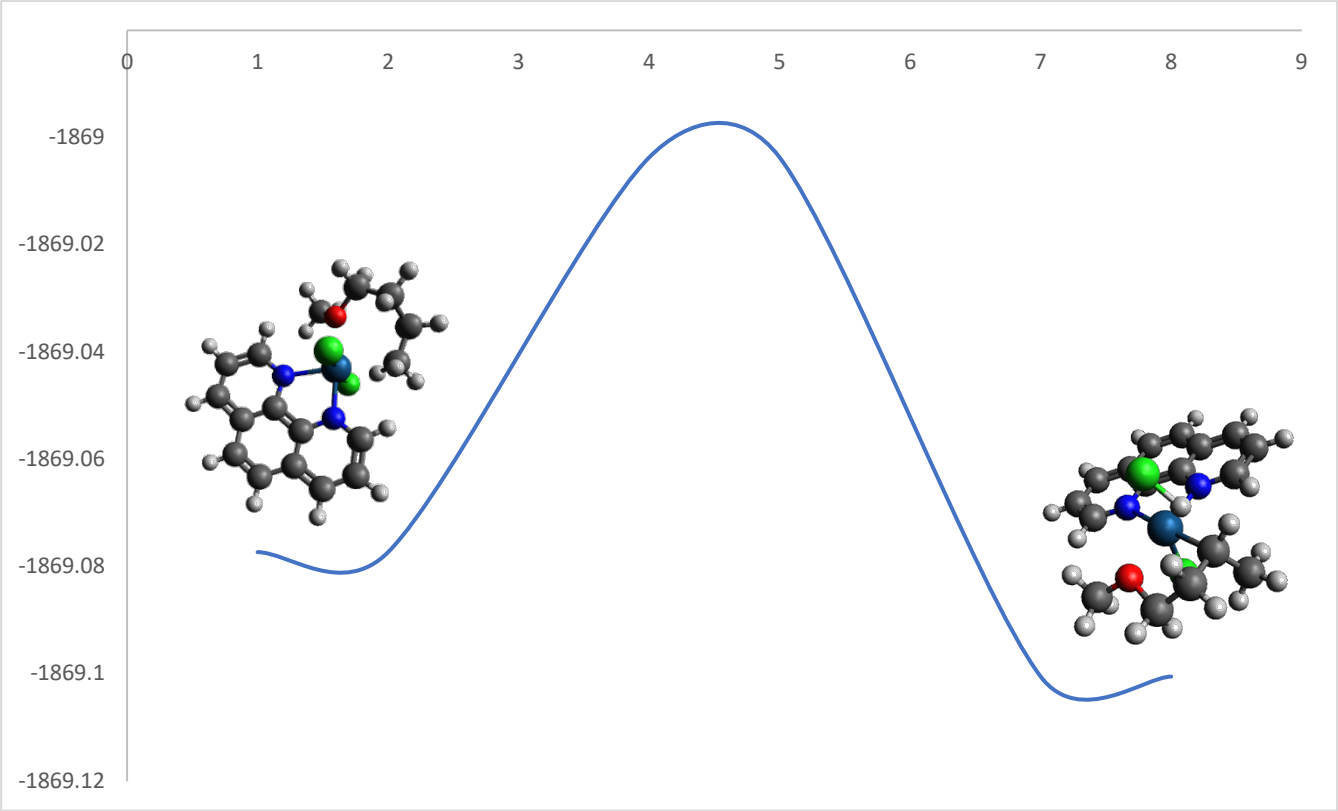


Figure S17 IRC of gamma transition state of methoxybutane

IRC of delta transition state for 1-methoxybutane

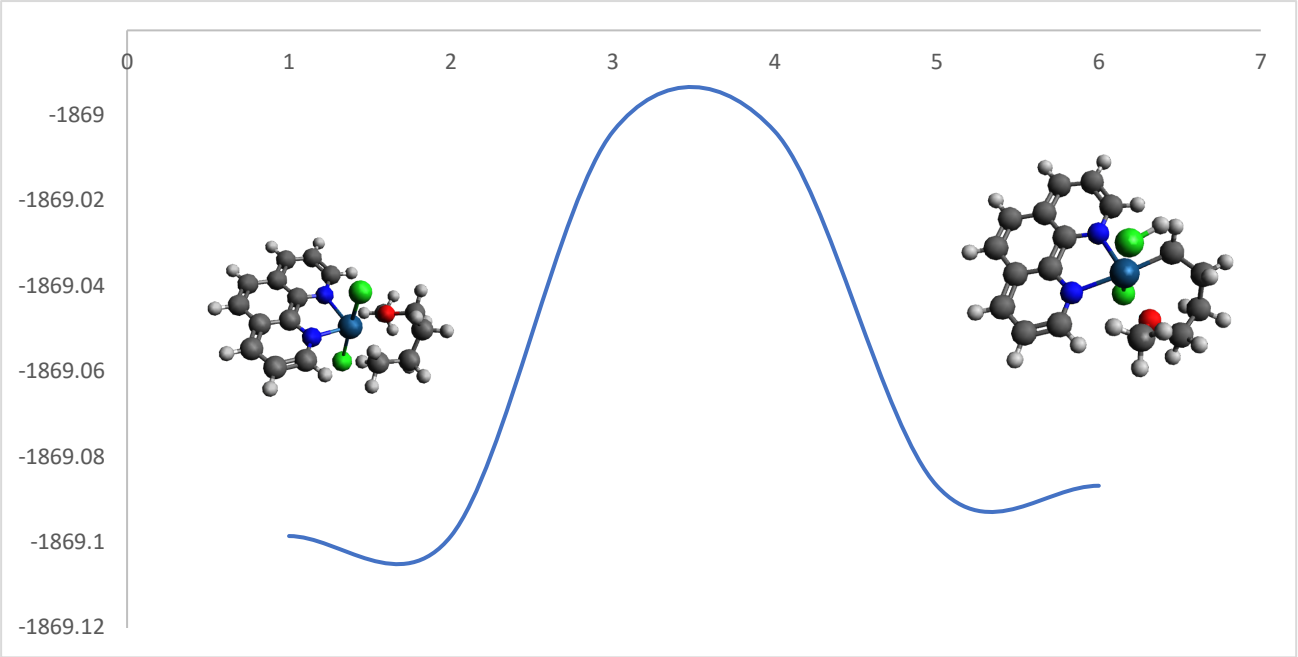


Figure S18 IRC of delta transition state of methoxybutane