

Supporting Information

Dehydrogenation of Formic Acid Catalyzed by a Ruthenium Complex with an *N, N'*-Diimine Ligand

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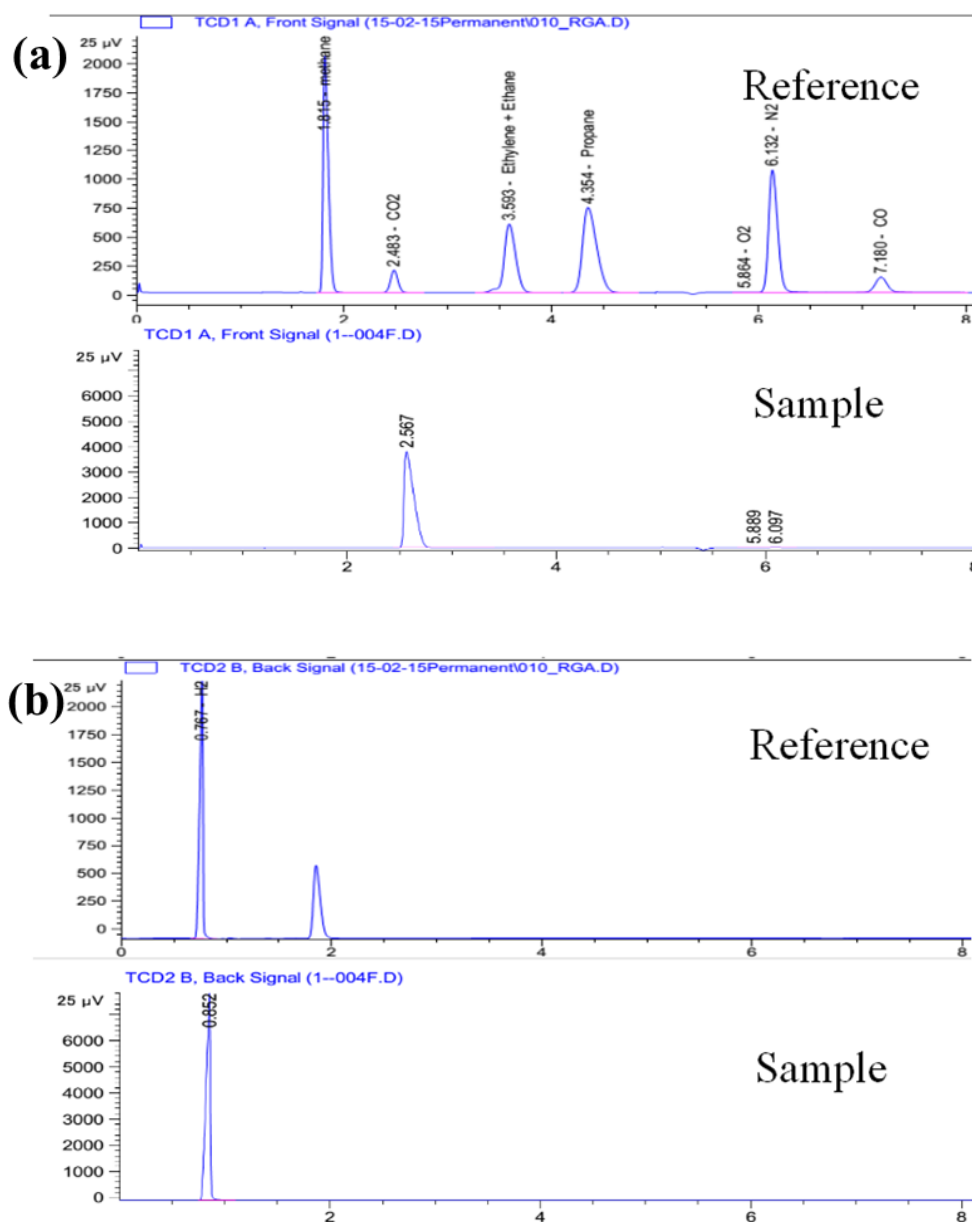


Figure S1. Composition analysis of the evolved gas mixture by GC: 2.0 μ mol of **1**, FA/SF (5.0 M, 5.0 mL), 90 $^{\circ}$ C. (a) TCD 1 for CO₂; (b) TCD 2 for H₂.

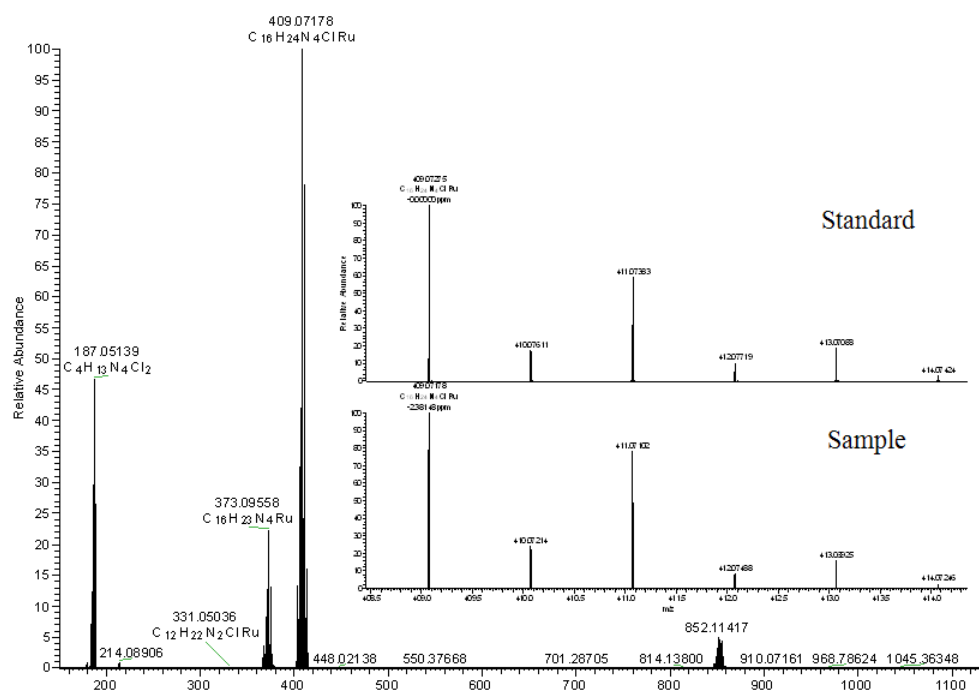


Figure S2. : LTQ-Orbitrap MS full scan: +Ve ESI about **1** in water

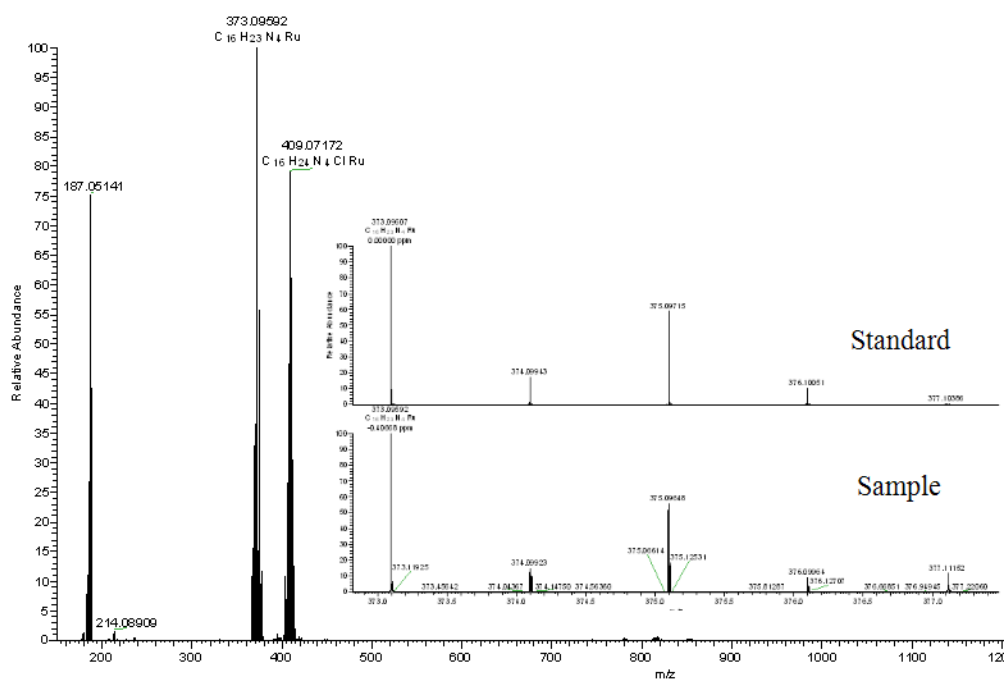


Figure S3. : LTQ-Orbitrap MS full scan: +Ve ESI about **1** and HCOONa in water

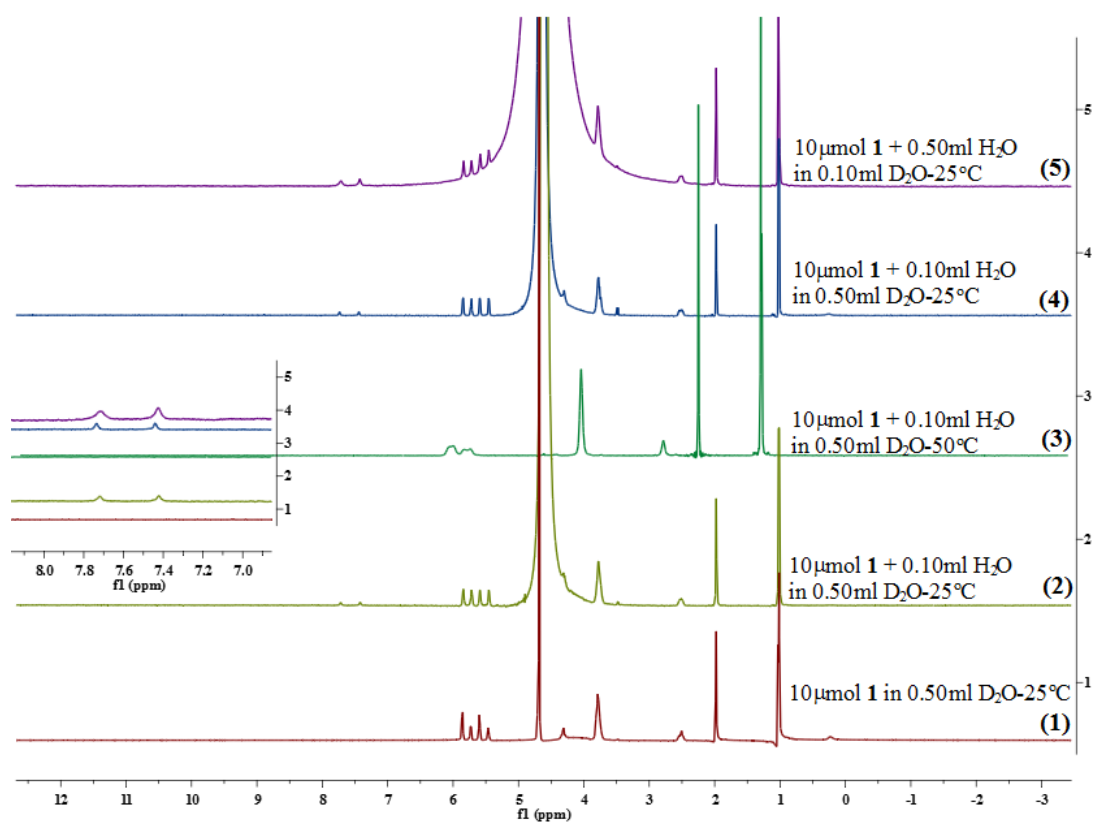


Figure S4. ^1H -NMR spectra of **1** in D_2O ((1)), **1** in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (1:5) at 25°C ((2), then warming up to 50°C ((3)) and cooling down to 25°C ((4)), **1** in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (5:1) ((5)); inset pictures: the area of 7-8ppm.

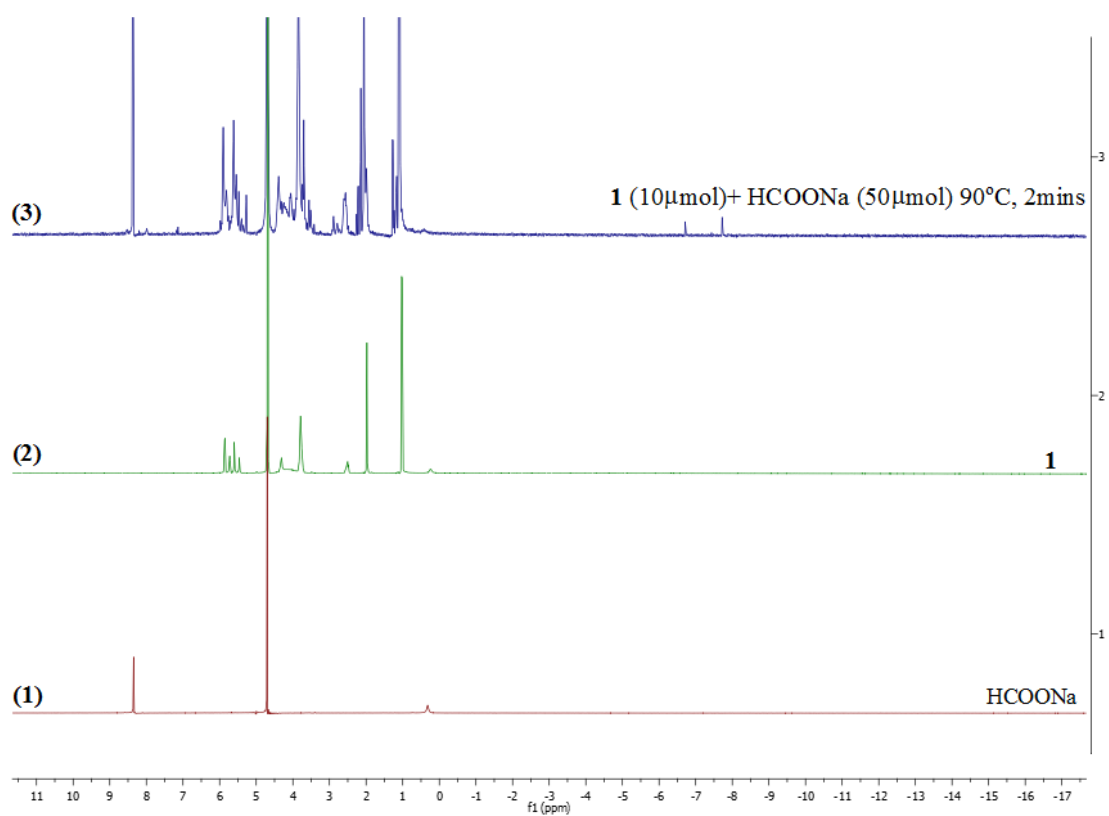


Figure S5. ^1H -NMR spectra of pure HCOONa in D_2O ((1)), **1** in D_2O ((2)), **1** and HCOONa in D_2O ((3));

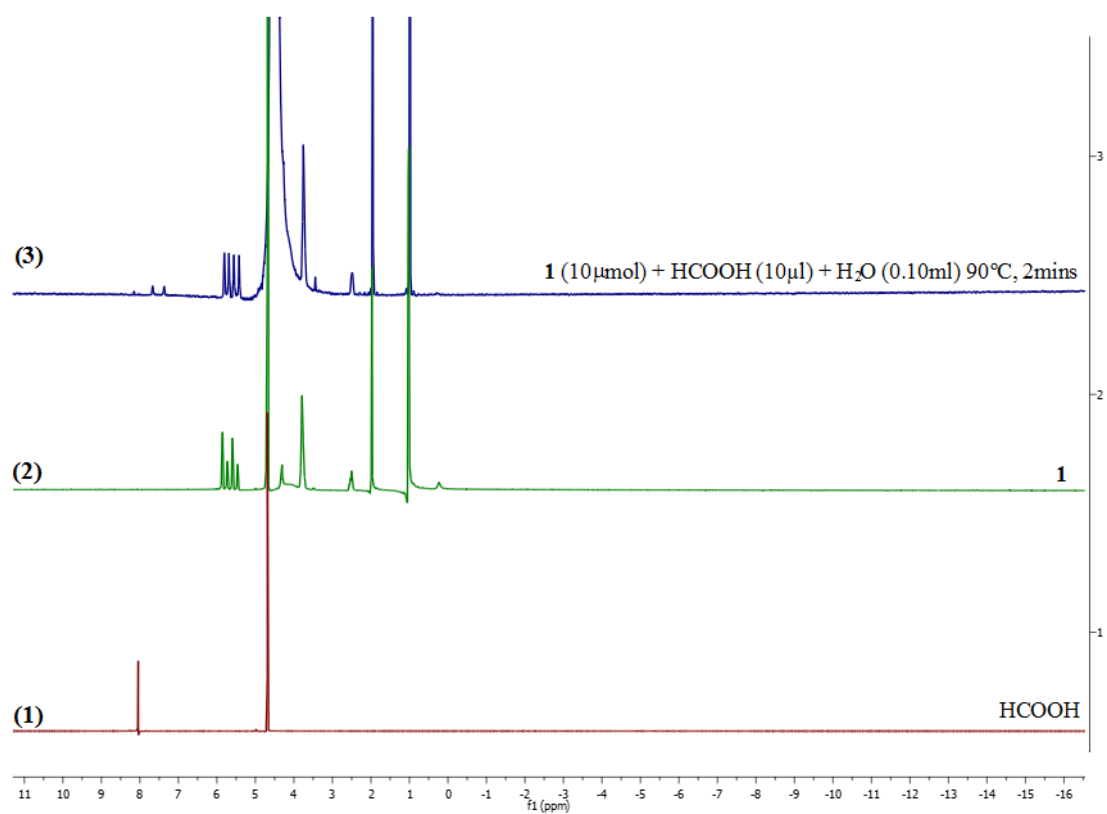


Figure S6. ^1H -NMR spectra of pure HCOOH in D_2O ((1)), **1** in D_2O ((2)), HCOOH in $\text{H}_2\text{O}/\text{D}_2\text{O}$ (1:5) ((3));

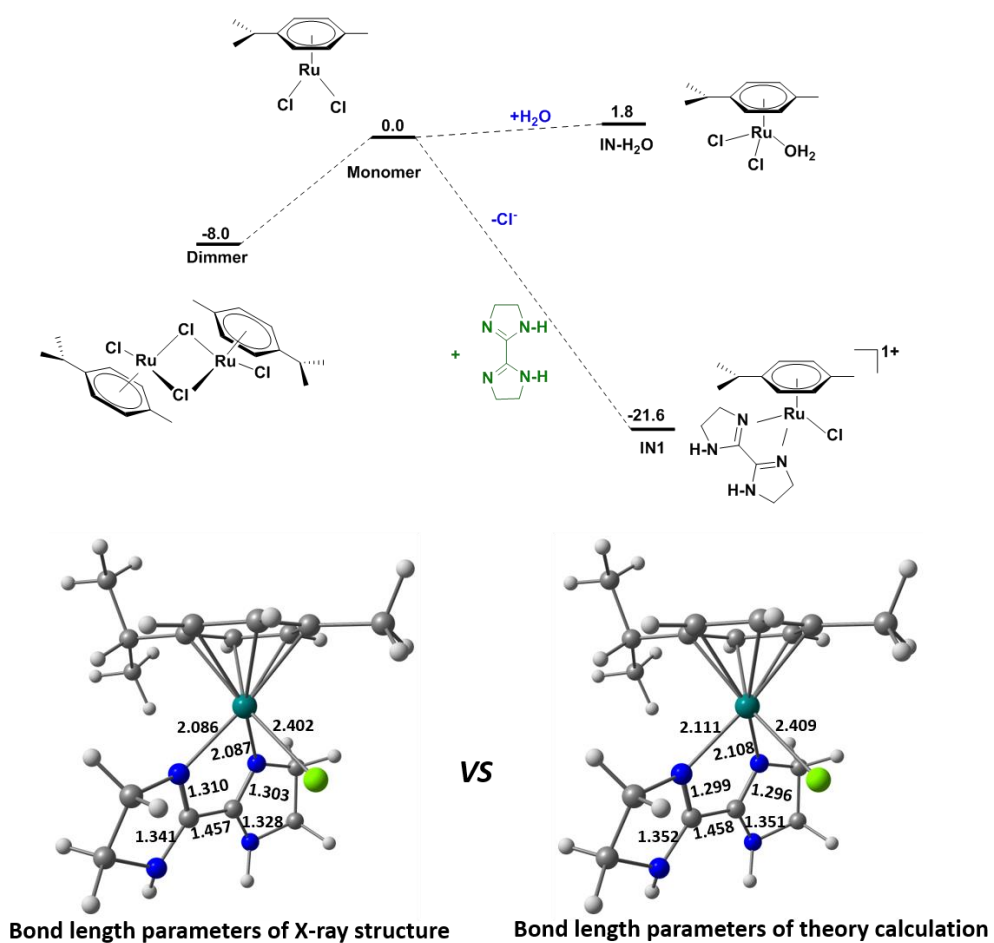


Figure S7. Relative free energy profiles for the activation of dimmer to chloride complex. Solvent corrected relative free energies in water are given in kcal mol⁻¹. Bond length parameters comparison between X-ray structure and theory calculation.

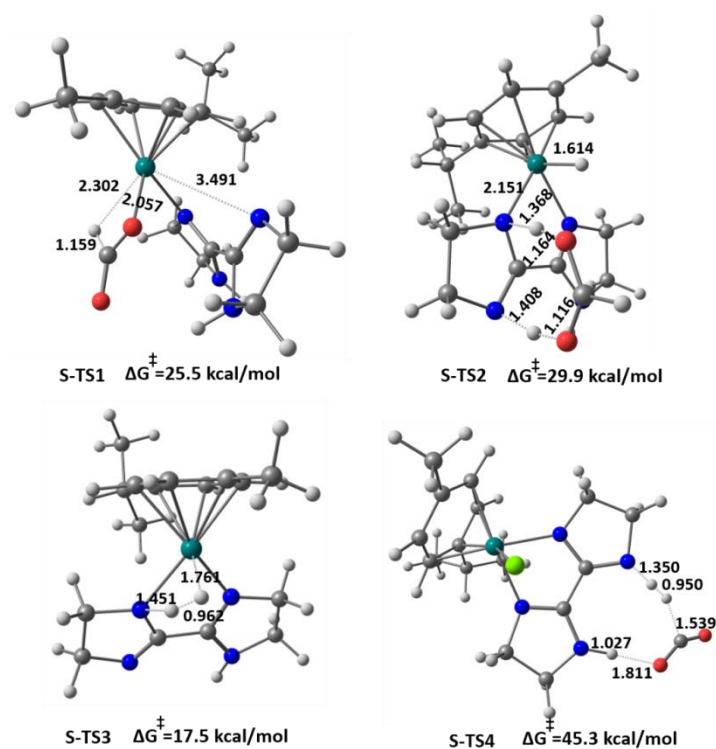


Figure S8. Optimized structures and active barriers of transitions state **S-TS1** with inner-sphere hydride transfer, transition states **S-TS2** and **S-TS3** which describe another possible H_2 formation pathway, and transition state **S-TS4** not involving metal center. Atoms Ru, C, N, and O are shown in green, gray, blue, and red, respectively. Calculated bond distances are shown in Å.

Attempts to locate transition states for the ligand deprotonation process involving one more water molecule did not yield any favorable interaction (+13.9 kcal/mol relative to **IN1**), suggestion that water may have little effect on this process.

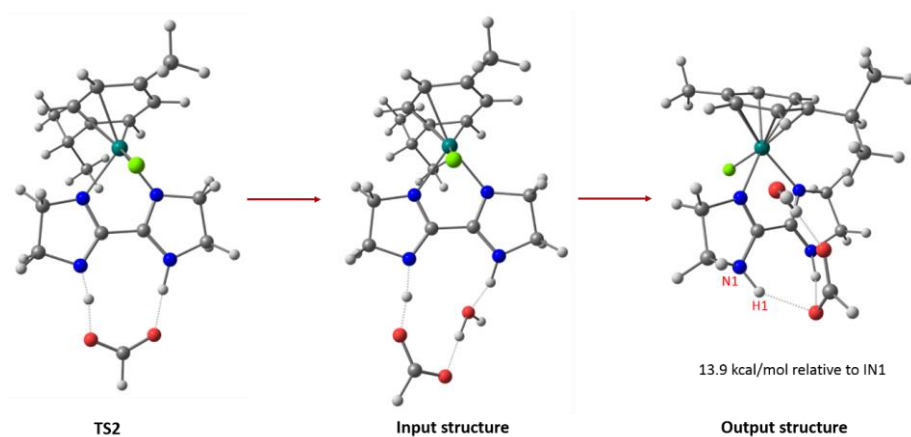


Figure S9. Atoms Ru, C, N, O, and Cl are shown in dark green, gray, blue, red, and light green, respectively.

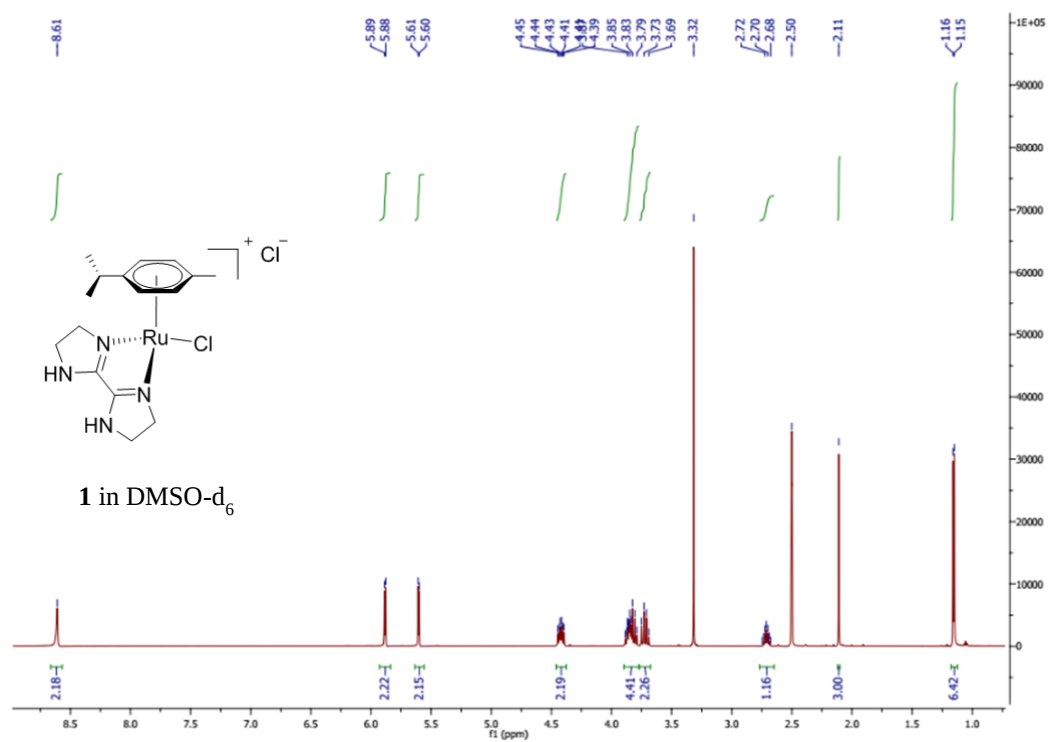


Figure S10. ¹H-NMR of **1** (600 MHz)

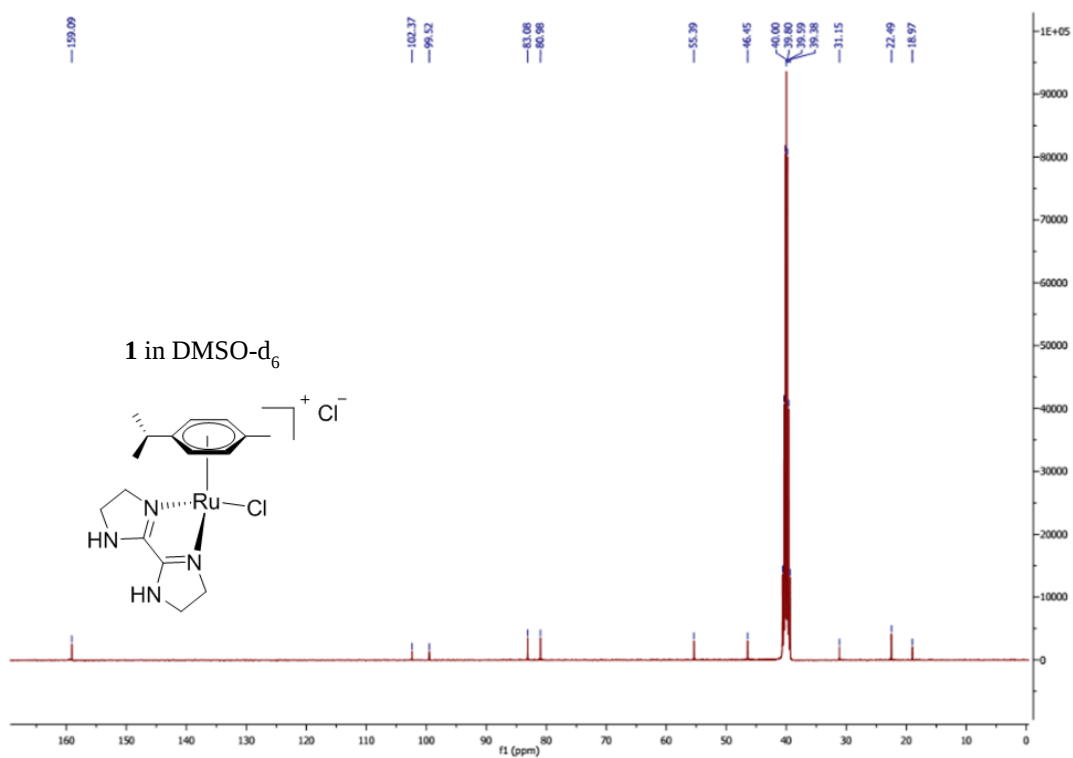


Figure S11. ¹³C-NMR of **1** (125 MHz)

Table S1. Dehydrogenation of FA/Sodium Salt in water using complex **1***

Entry	SF/FA	FA (10^{-2} mol)	Cat. (10^{-2} mol %)	TOF _{max} (h ⁻¹)	TON	Yield (%)
1	/	2.5	0.8	3750	11,670	93
2 [#]	Na ₂ SO ₄	2.5	0.8	3400	11,250	90

General: no reaction occurred in the absence of catalysts. Each reaction was repeated at least twice with an error less than 5%. The maximum of TOF was estimated based on the H₂ production in the first 10 mins. TONs and yields were determined when the reaction stopped and no more gas was generated. Temperature: 90 °C. All the initial volumes of reaction solutions are 5.0 ml. [#] The ratio of Na₂SO₄/FA is 2.

Table S2. Crystal data and structure refinement for Complex 1.

Identification code	Complex 1
Empirical formula	C ₁₆ H ₂₄ Cl ₂ N ₄ Ru
Formula weight	179.55
Temperature	160(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2(1)/c
Unit cell dimensions	a = 10.0036(5) Å α = 90°. b = 13.3611(7) Å β = 90°. c = 13.6771(7) Å γ = 90°.
Volume	1828.07(16) Å ³
Z, Calculated density	22, 3.588 Mg/m ³
Absorption coefficient	43.695 mm ⁻¹
F(000)	1826
Theta range for data collection	4.63 to 72.11 deg.
Limiting indices	-12<=h<=11, -15<=k<=16, -8<=l<=16
Reflections collected / unique	11625 / 3390 [R(int) = 0.0314]
Completeness to theta = 72.11	97.60%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3390 / 0 / 235
Goodness-of-fit on F ²	1.067
Final R indices [I>2 sigma (I)]	R1 = 0.0289, wR2 = 0.0770
R indices (all data)	R1 = 0.0296, wR2 = 0.0814
Absolute structure parameter	0
Largest diff. peak and hole	0.446 and -1.229 e.Å ⁻³

Cartesian coordinates, imaginary vibrational modes for transition states, and Gibbs free energies [in Hartree and at the M06/BSII//M06BSI level of theory] for the key structures involved in this study.

IN1

E= -1397.835652 (a.u.)

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100

H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN2

E=1013.881816(a.u.)

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C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600

C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN3

E=-1126.754031 (a.u.)

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C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400

H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN4

E=-938.1761309 (a.u.)

1 1

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C	-1.76039400	-1.97479100	-0.47966600
C	-2.48641700	-0.75093700	-0.40916200
C	-2.48809300	0.03090200	0.76667900
C	-1.79567400	-0.40805200	1.94225600
H	-0.59107000	-2.00815700	2.78702800
H	-0.44814900	-3.27309300	0.64886300

H	-2.97689500	-0.37432200	-1.30389600
H	-2.99631200	0.99285700	0.77723100
C	-1.72460800	-2.79470800	-1.73009000
H	-2.55927500	-3.50572300	-1.75383100
H	-1.79666200	-2.16059500	-2.61946400
H	-0.79639400	-3.37249800	-1.79693200
C	-1.84104400	0.46060300	3.17487300
H	-1.92533800	1.50193100	2.82132600
C	-0.60470300	0.35093300	4.05605300
H	0.32142400	0.49816100	3.48556500
H	-0.64346800	1.10216400	4.85214100
H	-0.54678000	-0.62754900	4.54925900
C	-3.10803900	0.12691600	3.96542100
H	-3.19819800	0.77860200	4.84100300
H	-4.01193900	0.24640200	3.35768100
H	-3.07430000	-0.91131500	4.31990700
Ru	-0.40110600	-0.34477600	0.13973800
C	2.23943200	-1.92013300	-1.00589000
C	3.74113800	-1.60674900	-0.89055500
H	1.89207800	-1.91475300	-2.04876900
H	4.20458100	-2.15150900	-0.05694500
H	4.52983500	0.25655200	-0.15920600
C	2.47593200	0.12498600	-0.15308200
N	1.58695600	-0.81185900	-0.30374200
N	3.72695900	-0.15827600	-0.61495700
C	1.61505800	3.56097400	0.86880500
C	0.36854600	2.70827100	1.17380100
H	3.44450800	2.76644800	0.05708900
H	1.90007300	4.20954300	1.70074500
H	0.18322900	2.62577200	2.25465200
C	1.96609200	1.37357300	0.37443400
N	2.64110800	2.52952500	0.62524600
N	0.69567100	1.37949200	0.64859900
H	1.47490400	4.18039700	-0.02660000
H	-0.54447500	3.08740500	0.70339400
H	1.96364700	-2.88207300	-0.56226700
H	4.29559800	-1.82848400	-1.80539000
H	-0.31544000	0.33137700	-1.31503700

IN5

E=-936.9811223 (a.u.)

0 1

C	2.80316000	2.34459000	-2.34864400
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C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700

H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN6

E=-1126.283692 (a.u.)

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000

H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN7

E=-937.6971401 (a.u.)

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200

C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

IN8

E=-1013.416815 (a.u.)

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400

C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

TS1

E=-1126.7198 (a.u.) -415.98 i cm-1

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400

N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

TS2

E=-1587.127435 (a.u.) -959.35 i cm-1

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100
H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700

H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

TS3

E=-1126.26652 (a.u.) -189.60 i cm-1

0 1

C	2.80316000	2.34459000	-2.34864400
C	1.30403500	1.99264400	-2.46681300
N	1.12542300	0.88491500	-1.52214100
C	2.30111000	0.55410400	-1.06929400
N	3.34688700	1.17980500	-1.62484600
C	2.32451700	-0.45312300	-0.00593900
N	1.06935700	-0.75949600	0.46476900
C	1.27605600	-1.84871100	1.41238100
C	2.82035400	-1.90890500	1.53297400
N	3.35693900	-1.03548700	0.48181100
H	3.29264800	2.46418900	-3.31983400
H	2.93860700	3.23948600	-1.73178800
H	0.66777800	2.83308100	-2.16191000
H	1.02412800	1.66765200	-3.47965800
H	0.85238800	-2.78732100	1.01927000
H	0.77716900	-1.63460000	2.36679500
H	3.16801200	-1.53465800	2.50586400
H	3.22179600	-2.92283900	1.42081400
C	1.02504200	2.80752200	0.63645600
O	2.26348900	2.72660800	0.57690000
O	0.21628000	3.61631000	0.13611100
H	0.52975400	1.94586300	1.22481500
Ru	-0.45787900	0.21592900	-0.32287100
C	-2.07903000	0.67839700	-1.73638500
C	-2.13472900	1.62748500	-0.69369300
C	-2.17093400	1.21190100	0.66685600
C	-2.19645300	-0.18769900	0.95299200
C	-2.12431600	-1.13573900	-0.09390600
C	-2.02835300	-0.72153900	-1.46246000
H	-1.91589600	1.02613800	-2.75426100
H	-1.97574600	2.68367500	-0.89978300
H	-2.15870300	-0.51692200	1.98926700
H	-2.03331400	-2.19613000	0.13967100
C	-2.13346700	2.23513000	1.75243300
H	-3.14387000	2.63034700	1.91936100

H	-1.77399200	1.80453300	2.69261000
H	-1.47237700	3.06024300	1.45053300
C	-1.89325900	-1.75486700	-2.55235900
H	-1.45685000	-2.64944400	-2.07935400
C	-0.96917100	-1.32795700	-3.68513700
H	-0.82177300	-2.16014400	-4.38214600
H	-1.39613500	-0.49864800	-4.26470600
H	0.01082000	-1.01499200	-3.30473900
C	-3.28363200	-2.11343600	-3.07723700
H	-3.22102300	-2.90332100	-3.83425700
H	-3.94368400	-2.46125700	-2.27387400
H	-3.75428800	-1.23739100	-3.54327200
H	4.16606300	1.28870600	-1.03872000

TS4

E=-1091.47491 (a.u.) -351.83 i cm-1

1 1

C	-2.32696200	0.31613700	1.28749800
C	-2.41219700	-1.02759400	0.81607900
C	-2.30094100	-1.31282200	-0.56439000
C	-2.12536500	-0.21853700	-1.47372900
C	-2.05801500	1.10299400	-0.99340300
C	-2.15738200	1.40960400	0.40227200
H	-2.30921600	0.49386500	2.36071200
H	-2.48961600	-1.84759800	1.52622800
H	-1.97418700	-0.42175500	-2.53094900
H	-1.83896000	1.91133700	-1.69036900
C	-2.30708400	-2.71840300	-1.06793700
H	-3.32642500	-3.00119700	-1.35707700
H	-1.66831300	-2.82880600	-1.94969300
H	-1.96695400	-3.42118300	-0.30168800
C	-2.04938700	2.84005300	0.86375100
H	-1.35750500	3.33924700	0.16616800
C	-1.49560100	2.99055500	2.27280200
H	-0.53183600	2.48027400	2.39419800
H	-1.34508800	4.05028200	2.50083400
H	-2.19468400	2.60294800	3.02536400
C	-3.42539100	3.49777600	0.73835600
H	-3.36928600	4.55701600	1.00925700
H	-3.82322900	3.43039600	-0.28067600
H	-4.14387000	3.01623900	1.41422700
Ru	-0.55086200	-0.07601900	0.08070400
C	0.73001300	-1.01974400	2.97339500

C	2.22629300	-1.09144900	3.33222500
H	0.14835500	-0.48440400	3.73852000
H	2.41678900	-0.97948400	4.40165600
H	3.75928300	-0.04251600	2.24875800
C	1.89350100	0.30497500	1.60157700
N	0.71957100	-0.24462100	1.72898700
N	2.78952800	0.03387000	2.56505600
C	2.96383200	2.08485700	-1.42409200
C	1.42733100	1.97152200	-1.55852900
H	4.04109200	1.12475600	0.17345100
H	3.33194700	3.09519900	-1.61795400
H	0.94042100	2.95425200	-1.61357100
C	2.07412200	1.12428600	0.40172500
N	3.20812400	1.69425600	-0.02357200
N	1.01025300	1.27563300	-0.33466000
H	1.12258100	1.39077000	-2.43816100
H	3.48153200	1.38268400	-2.08780800
H	0.27437500	-2.00415100	2.82520800
H	2.68323500	-2.02984000	2.98650200
H	0.34946600	-1.42459400	-0.67467200
C	3.75316700	-1.50677600	-0.14077700
H	4.04529200	-2.56707300	-0.30266600
O	2.65409600	-1.13589500	-0.67363700
H	1.19170100	-1.24918300	-0.59060100
O	4.52082300	-0.78308500	0.51533700

TS5

E=-1127.895485 (a.u.) -489.35 i cm-1

2 1

C	3.25125400	-2.18847800	1.55438300
C	1.86176100	-2.38922800	0.92813200
N	1.42138900	-1.02631900	0.59530900
C	2.44548100	-0.23804100	0.70476400
N	3.62393600	-0.84447700	1.04181500
C	2.19951800	1.15423700	0.33992100
N	0.96498100	1.42328600	0.02496200
C	0.92733000	2.80924100	-0.46337900
C	2.29504500	3.39317800	-0.05886900
N	3.07420700	2.16707800	0.20258100
H	3.20673500	-2.17304700	2.64974200
H	3.97877800	-2.94199400	1.24563200
H	1.89117600	-2.98223600	0.00349100
H	1.15210800	-2.87047700	1.60812300
H	0.08544500	3.35447600	-0.02612200

H	0.78690000	2.78668200	-1.55277700
H	2.75762100	3.98865300	-0.84894200
H	2.23329500	4.00236600	0.85125300
H	4.32075300	-0.32220000	1.56264100
H	0.29389900	-0.16652900	-1.73327500
H	3.97699300	2.20075700	0.65522900
H	2.35500900	-1.69808100	-2.31240200
O	3.69640200	-0.91812600	-1.95250500
H	4.14108500	-1.10122000	-1.11103000
H	4.38380900	-0.77444800	-2.61344900
H	1.15332300	-2.26092200	-3.25145600
O	1.39685600	-2.01842100	-2.34536300
H	0.74325200	-1.12819800	-1.91409400
Ru	-0.36537300	-0.20192700	-0.16716900
C	-1.67142200	-1.03626100	1.44804200
C	-1.81591300	-1.82630000	0.26735800
C	-2.18653800	-1.23705300	-0.96250400
C	-2.38678100	0.18154300	-0.99196700
C	-2.21813600	0.95109500	0.17419100
C	-1.86827200	0.35962700	1.43231000
H	-1.32534700	-1.51426500	2.36210800
H	-1.60390800	-2.89310700	0.30057200
H	-2.61263400	0.67135400	-1.93599500
H	-2.31259700	2.03465000	0.11229700
C	-2.33091800	-2.05375700	-2.20398400
H	-3.37388900	-2.37415300	-2.31480300
H	-2.07318800	-1.47570100	-3.09756600
H	-1.71316300	-2.95700000	-2.16514000
C	-1.70199400	1.23249300	2.64908700
H	-1.31398000	2.19950300	2.28791500
C	-0.72224800	0.67124000	3.66891600
H	0.24253600	0.41216600	3.21146600
H	-0.53892000	1.40915800	4.45561300
H	-1.12250200	-0.22152000	4.16582200
C	-3.07941400	1.46750100	3.27517400
H	-2.99795500	2.14639800	4.12970000
H	-3.78773900	1.90567700	2.56335500
H	-3.50275200	0.52189200	3.63671300

DCOO-**E= -189.2900583(a.u.)**

C	0.00001100	0.30740000	-0.00007000
H(Iso=2)	-0.00018500	1.46381900	0.00012800
O	-1.13619900	-0.20677900	0.00001800
O	1.13621400	-0.20674900	0.00001800

D-IN3**E= -1126.402081(a.u.)**

H(Iso=2)	1.04512000	2.35097200	3.11164500
C	2.54071400	1.83333600	-2.39960300
C	1.06608400	1.88656800	-1.96380600
N	0.92496000	0.74804900	-1.05448300
C	2.12146400	0.38710600	-0.70208900
N	3.13845900	1.03906200	-1.31098000
C	2.18741100	-0.59313000	0.37702700
N	1.04077700	-0.98920600	0.83363300
C	1.29862000	-1.97297300	1.89234100
C	2.79698400	-1.80202500	2.19251000
N	3.28019000	-1.14144700	0.96028500
H	2.66420000	1.31548100	-3.36032600
H	3.00440200	2.81998800	-2.46784600
H	0.83499600	2.79869100	-1.39410400
H	0.36591200	1.81279100	-2.80246400
H	1.06834400	-2.97562000	1.50530500
H	0.66485400	-1.75567500	2.75603800
H	2.95634000	-1.14608900	3.05871400
H	3.31390400	-2.74982800	2.35780100

H	4.04405800	0.60546300	-1.43201100
C	0.53224600	1.48495100	2.64132200
O	0.20682000	0.50946200	3.30295800
O	0.35364600	1.67320900	1.37136400
H	4.15779500	-0.63854300	0.97402100
Ru	-0.61763600	0.17195100	0.26864600
C	-2.21502400	0.27411300	-1.21087700
C	-2.49590900	1.22216000	-0.19170300
C	-2.55391700	0.81706900	1.17333100
C	-2.31030400	-0.54511600	1.48470100
C	-2.02994100	-1.47521100	0.44621200
C	-2.00072400	-1.10393300	-0.92420300
H	-2.09237900	0.62877200	-2.23258200
H	-2.59808800	2.27512600	-0.44161300
H	-2.24034300	-0.84911400	2.52541200
H	-1.75506100	-2.49594600	0.71205300
C	-2.76198700	1.82113400	2.25592800
H	-3.83538800	1.92149600	2.45742100
H	-2.26515500	1.51006400	3.17941200
H	-2.37904400	2.80310500	1.96232400
C	-1.70527100	-2.13147100	-1.98759300
H	-1.11157400	-2.92171600	-1.49966500
C	-0.89477400	-1.58767800	-3.15642100
H	-0.62293100	-2.40356400	-3.83390700
H	-1.47278800	-0.86642500	-3.74937200
H	0.02828400	-1.10079100	-2.81608500
C	-3.02254100	-2.74124800	-2.46892500
H	-2.83707700	-3.52842800	-3.20733800
H	-3.59526600	-3.17763100	-1.64293900
H	-3.64837300	-1.97506300	-2.94529700

D-TS1**E=-1126.367259 (a.u.)**

H(Iso=2)	0.20964300	1.89300100	1.32960900
C	2.46728400	2.15163800	-2.14031000
C	0.98333200	2.13822400	-1.71688800
N	0.84844100	0.92109100	-0.91031400
C	2.05265400	0.51448100	-0.61606400
N	3.05030700	1.18580500	-1.19933500
C	2.12058700	-0.60173400	0.32698100
N	0.97696900	-1.13569900	0.63912800
C	1.23625600	-2.15972800	1.66204800
C	2.71191000	-1.93684800	2.04535100
N	3.21456500	-1.11651200	0.91887300
H	2.60837700	1.80865300	-3.17312100
H	2.92899500	3.13591400	-2.02998300
H	0.73139800	3.00343500	-1.08617100
H	0.29773000	2.12480800	-2.57116600
H	1.06081500	-3.15435200	1.23053100
H	0.56026900	-2.01141400	2.51000500
H	2.79922200	-1.36178500	2.97453300
H	3.27761200	-2.86713400	2.13186200
H	4.00311600	0.85754900	-1.25152000
C	0.84032800	1.29382200	2.11567300
O	0.13517400	0.62088800	2.89431900
O	2.06293400	1.38433400	1.95911700
H	3.96335500	-0.46401700	1.12638500
Ru	-0.68650700	0.12170800	0.27875200

C	-2.20599400	0.22235600	-1.23483400
C	-2.50778800	1.22960800	-0.27770900
C	-2.59288100	0.90899300	1.10186400
C	-2.43955000	-0.45788700	1.49448200
C	-2.17811900	-1.45407700	0.53578200
C	-2.02337700	-1.14198700	-0.85138700
H	-2.02521800	0.51169400	-2.26796000
H	-2.55916700	2.27144600	-0.58596600
H	-2.39559600	-0.69569000	2.55422300
H	-1.95441000	-2.46751600	0.86812200
C	-2.72645700	1.96270800	2.14781000
H	-3.72281900	1.90930600	2.60256000
H	-1.97898400	1.79600700	2.93330400
H	-2.59116800	2.96459100	1.73052700
C	-1.66625000	-2.22780000	-1.83267100
H	-1.10522400	-2.98657300	-1.26289100
C	-0.78536300	-1.75098900	-2.97911000
H	-0.46532200	-2.60682700	-3.58170700
H	-1.32741800	-1.07627700	-3.65460800
H	0.11101200	-1.23451500	-2.61308300
C	-2.95820000	-2.86287900	-2.35064200
H	-2.73096200	-3.69304200	-3.02736800
H	-3.58021400	-3.25023300	-1.53579500
H	-3.55165000	-2.12749400	-2.90947700