Electronic Supplementary Material (ESI) for Chemical Communications.

Selective and High Yield Transformation of Glycerol to Lactic Acid Using NNN Pincer Ruthenium Catalysts

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1. General Methods and Materials

All manipulations were carried out under purified Ar using a standard double manifold. Tetrahydrofuran (THF), 1,4-dioxane, *p*-xylene were dried via double distillation over Na/Benzophenone prior to experiment, ethanol was dried and distilled under argon according to literature procedure.[1-2] The compounds anhydrous glycerol, D_2O were purchased either from MERCK of Sigma-Aldrich and used as such. The ruthenium-pincer complexes **1a** and **1b** were synthesized following literature protocol.[3]

^{1}H, ^{13}C, ^{31}P NMR were recorded either on Bruker ASCEND 600 operating at 600 MHz for ^{1}H, 150 MHz for ^{13}C, 564 MHz for ^{31}P or on Bruker AVANCE 400 operating at 400 MHz for ^{1}H, 100 MHz for ^{13}C, 376 MHz for ^{31}P. The mass analysis was done using an Agilent Accurate-Mass Q-Toff ESI-MS 6520. X-ray crystallographic data were collected on Bruker Nonius Smart Apex III X-ray Single crystal diffractometer (CCD) or on Oxford SuperNova microfocus X-ray diffractometer with graphite-monochromatized Mo-Kα radiation. The data refinements and cell reduction were carried out by Bruker Apex III program or by CrysAlisPro. Structures were solved and further refined by full matrix leas-squares method using SHELXS-14.[4] The crystallographic data for the complex **1c** are provided in Table S1 and S2.

2. Experimental Section

Synthesis of 2,6-bis(1H-benzimidazol-2-yl)pyridine [2c],[5] To a one necked round bottomed flask (100 mL) pryidene-2,6-dicarboxylic acid (0.100 g, 1.2 mmol) and o-penylenediamnine (0.130g, 1.2 mmol) were taken in (10 mL) orthophosphoric acid. Then the reaction mixture was heated at 150 °C temperature overnight. A bluish green precipitate was obtained, 10 mL sodium bicarbonate solution was added into it. The residue was filtered and washed with water. The product was crystallized in methanol, an off white colored solid was obtained in 74 % yield (0.135 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.99 (s, 2H), 8.34 (d, J = 7.8 Hz, 2H), 8.17 (t, J = 9.0 Hz, 1H), 7.78 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.9 Hz, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.6 Hz, 2H). $^{13}C^{6}$ NMR (101 MHz, DMSO-d_6) δ = 150.45, 147.74, 144.15, 139.18, 134.35, 123.71, 122.19, 121.35, 119.70, 111.75.

Synthesis of [(^{im2}NNN)RuCl(PPh$_3$)$_2$]Cl [1c], To a two-neck round bottom flask containing 2,6–Bis(2–benzimidazolyl)pyridine (0.07 g, 0.224 mmol) and $RuCl_2(PPh_3)_3$ (0.250 g, 0.224

mmol), dry THF (5mL) was added under argon atmosphere. The reaction mixture was refluxed for 12 h during which the color of the reaction mixture changed from brown to orange. Solvent removal was followed by washing the residue with dry diethyl ether (3 x 5 mL) and then hexane (3 x 5 mL). An red orange colored solid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 14.30 (s, 2H), 8.49 (d, J = 8.1 Hz, 2H), 8.05 (br, 2H), 7.68 (dd, J = 12.0, 7.0 Hz, 1H), 7.55 (dd, J = 26.3, 5.3 Hz, 4H), 7.26 – 6.80 (m, 32H). ^{31}P NMR (162 MHz, $CDCl_3$) δ = 29.99 (minor, *cis*), 22.67 (major, *trans*). HRMS(ESI): Calculated for $[(^{im2}NNN)RuCl(PPh_3)_2]^+$ 972.1726, Found 972.1952.

Synthesis of $[(^{im2}NNN)RuCl(PPh_3)_2]PF_6$ [1d], In a Schlenk flask (10 mL) **1c** (0.052g, 0.15 mmol) and $NaPF_6$ (0.150g, 0.15 mmol) were taken in dry methanol (5 mL) under argon atmosphere. Then the reaction mixture was stirred for 12 h under argon. The color of the reaction mixture was change red orange to light orange. Solvent was then evaporated under vacuum. The residue was washed by dry ether (3 x 5 mL) followed by hexane (3 x 5 mL). A light orange colored solid was obtained. Poor solubility prevented characterization of this compound by NMR. HRMS(ESI): Calculated for $[(^{im2}NNN)RuCl(PPh_3)_2]^+$ 972.1726, Found 972.2608.

General procedure for 1 catalyzed glycerol (3) conversion to lactic acid (5), To a 25 ml two necked round bottomed flask containing degassed glycerol (**3**) (0.235g, 2.56 mmol), and **1c** (0.7 μmol), 0.58 equivalents of KOH (0.083 g, 1.48 mmol) was added under Ar atmosphere. This was followed by addition of ethanol (2 mL) and the resulting reaction mixture was heated at 140 ^{o}C for 48 hours. After the reaction, the mixture was then cooled to room temperature. An aliquot was withdrawn from the reaction mixture to a NMR tube containing the sodium acetate as the internal standard. NMR was recorded in D_2O and the yield was determined by comparing the integration of LA versus the internal standard. Ethylene glycol and formic acid were either present in trace amounts or completely absent. All the reaction products were identified by comparing with NMR spectra of previous reports.[7-9]

3. X-ray Analysis

Justification for the observed alerts in the Checkcif_report of (^{tBu2}NNN)RuCl$_2$(PPh$_3$) 1a

RINTA01_ALERT_3_A The value of Rint is greater than 0.25 Rint given 0.537

Author Response: The overall quality of the data was poor due to the highly sensitive and unstable nature of the compound that rendered the crystal quality low. Crystals diffracted extremely weakly and disintegrated during the data collection. Multiple attempts were made to grow better diffracting crystals, however, upon mounting, all yielded serious problems due to high instability of crystal owing to the easy dissociation of the phosphine. This resulted in weak diffraction and disorder in the solvent atom positions. These factors resulted in high Rint value.

PLAT020_ALERT_3_A The Value of Rint is Greater Than 0.12 ..... 0.537 Report

Author Response: The overall quality of the data was poor due to the highly sensitive and unstable nature of the compound that rendered the crystal quality low. Crystals diffracted extremely weakly and disintegrated during the data collection. Multiple attempts were made to grow better diffracting crystals, however, all yielded serious problems due to high instability of crystal owing to the easy dissociation of the phosphine. This resulted in weak diffraction and disorder in the solvent atom positions. These factors resulted in high Rint value.

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections (too) Low .. 38% Check

Author Response: The diffraction of the crystal was poor due to its highly unstable nature. Over the acquisition, the crystal got disintegrated which resulted in low numbers of observed reflections.

PLAT342_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.02047 Ang.

Author Response: Extremely poor-quality crystal owing to its unstable nature resulted in observation of streaky diffused Bragg peaks giving poor data, overall poor model and hence low bond precision. However, this does not indicate an incorrect atom type assignment

PLAT973_ALERT_2_B Check Calcd Positive Resid. Density on Ru1 1.89 eA-3

Author Response: Weak and relatively imprecise diffraction data resulted in slightly high residual density, which is common in these types of crystals (highly unstable organometallic complex)

Table S1. **Crystal structure and refinement parameters of (^{tBu2}NNN)RuCl$_2$(PPh$_3$) (1a) and [(^{Bim2}NNN)RuCl(PPh$_3$)$_2$]PF$_6$ (1d)**

Name	(^{tBu2}NNN)RuCl$_2$(PPh$_3$) (**1a**)	[(^{Bim2}NNN)RuCl(PPh$_3$)$_2$]PF$_6$(**1d**)
Empirical formula	$C_{35}H_{42}Cl_6N_3PRu$	$C_{55}H_{43}ClF_6N_5P_3Ru$
Formula weight	849.45	1117.37
Crystal size (mm^3)	0.31 x 0.26 x 0.22	0.32 x 0.28 x 0.24
Crystal system	orthorhombic	monoclinic
Space group	Pbca	$P2_1/n$
a (Å)	16.093(4)	9.9974(5)
b (Å)	20.363(5)	38.806(4)
c (Å)	23.088(6)	13.9459(7)
α (deg)	90.00	90.00
β (deg)	90.00	92.722(5)
γ (deg)	90.00	90.00
V (Å^3)	7566(3)	5404.4(7)
Z	8	4
ρ_{calc} (g cm^{-3})	1.491	1.373
μ (M_0 Kα) (mm^{-1})	0.910	0.494
F (000)	3472.0	2272.0
T(K)	296(2)	296
Range of indices (h; k; l)	-20, 20; -26, 26; -29, 29	-11, 11; -39, 46; -16, 16
Number of reflection collected	222123	20714
Unique reflection	8640	8995
Completeness to 2θ	99.9	99.9
R_{int}	0.5367	0.0848
Data / restraints / parameters	8640/108/449	9501/448/704
goodness-of-fit	1.013	1.148
$R_1[I \geq 2\sigma(I)]$	0.1091	0.1203
$wR_2[I \geq 2\sigma(I)]$	0.2416	0.2244
R_1 (all data)	0.2603	0.1516
wR_2 (all data)	0.3385	0.2418
Δ_r (max, min) e Å^{-3}	1.25/-0.97	0.93/-2.14

Table S2. **Selected Bond lengths (Å) and angles (°) around metal center in (^{tBu2}NNN)RuCl$_2$(PPh$_3$) (1a) and [(^{Bim2}NNN)RuCl(PPh$_3$)$_2$](PF$_6$) (1d)**

(^{tBu2}NNN)RuCl$_2$(PPh3) (**1a**)			
Ru1–N1	2.151 (9)	Ru1–Cl1	2.463 (3)
Ru1–N2	1.930 (8)	Ru1–Cl2	2.455 (3)
Ru1–N3	2.154 (10)	N1–C5	1.297 (14)
Ru1–P1	2.366 (3)	N3–C11	1.293 (13)
N1–Ru1–N2	78.9 (4)	N2–Ru1–P1	89.2 (3)
N1–Ru1–N3	155.6 (4)	N3–Ru1–P1	93.4 (3)
N1–Ru1–P1	94.4 (2)	N3–Ru1–Cl1	84.9 (3)
N1–Ru1–Cl1	85.2 (3)	N3–Ru1–Cl2	100.9 (3)
N1–Ru1–Cl2	100.8 (3)	P1–Ru1–Cl1	174.74 (11)
N2–Ru1–N3	78.1 (4)	P1–Ru1–Cl2	98.26 (12)
N2–Ru1–Cl1	85.5 (3)	Cl1–Ru1–Cl2	86.96 (11)
N2–Ru1–Cl2	172.5 (3)		
[(^{Bim2}NNN)RuCl(PPh$_3$)$_2$]PF$_6$ (**1d**)			
Ru1–N1	2.089 (7)	Ru1–P1	2.418 (3)
Ru1–N3	2.010 (8)	Ru1–P2	2.417 (3)
Ru1–N5	2.092 (8)	Ru1–Cl1	2.459 (2)
N1–Ru1–N3	79.2 (3)	N3–Ru1–Cl1	174.1 (2)
N1–Ru1–N5	157.7 (3)	N5–Ru1–P1	87.6 (2)
N1–Ru1–P1	89.1 (2)	N5–Ru1–P2	90.2 (2)
N1–Ru1–P2	93.1 (2)	N5–Ru1–Cl1	105.2 (2)
N1–Ru1–Cl1	97.1 (2)	Cl1–Ru1–P1	94.44 (9)
N3–Ru1–N5	78.8 (3)	Cl1–Ru1–P2	85.84 (9)
N3–Ru1–P1	90.0 (2)	P1–Ru1–P2	177.79 (9)
N3–Ru1–P2	89.8 (2)		

4. NMR and ESI-MS Spectra

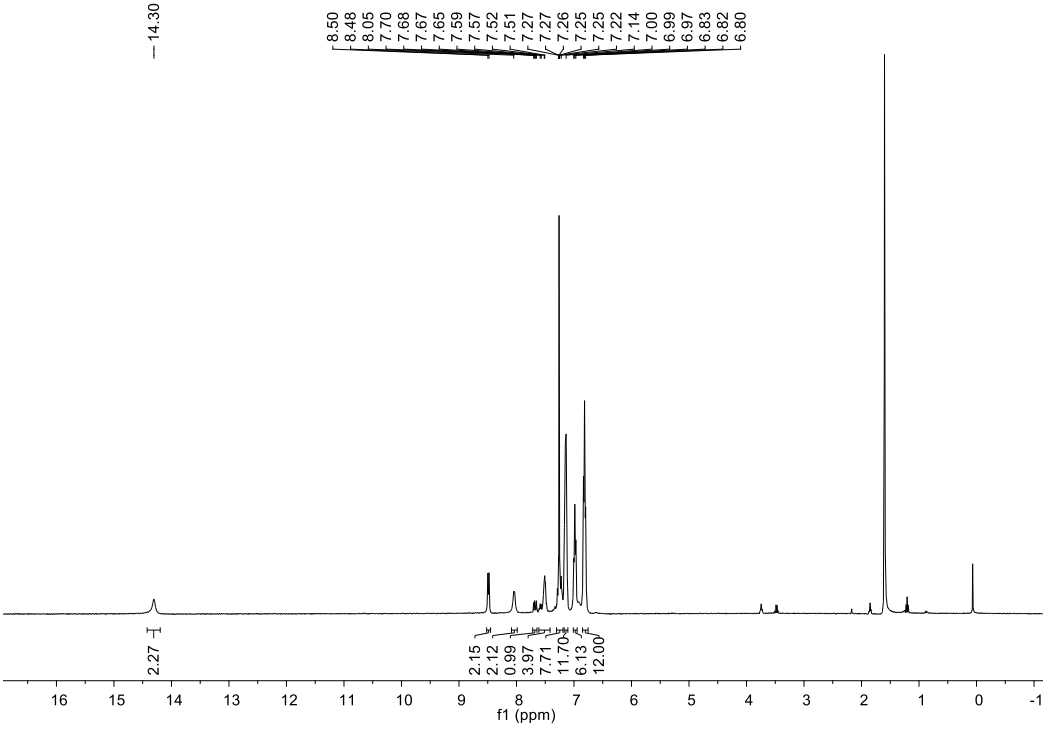


Figure S1: ^{1}H NMR Spectra of Complex **1c**

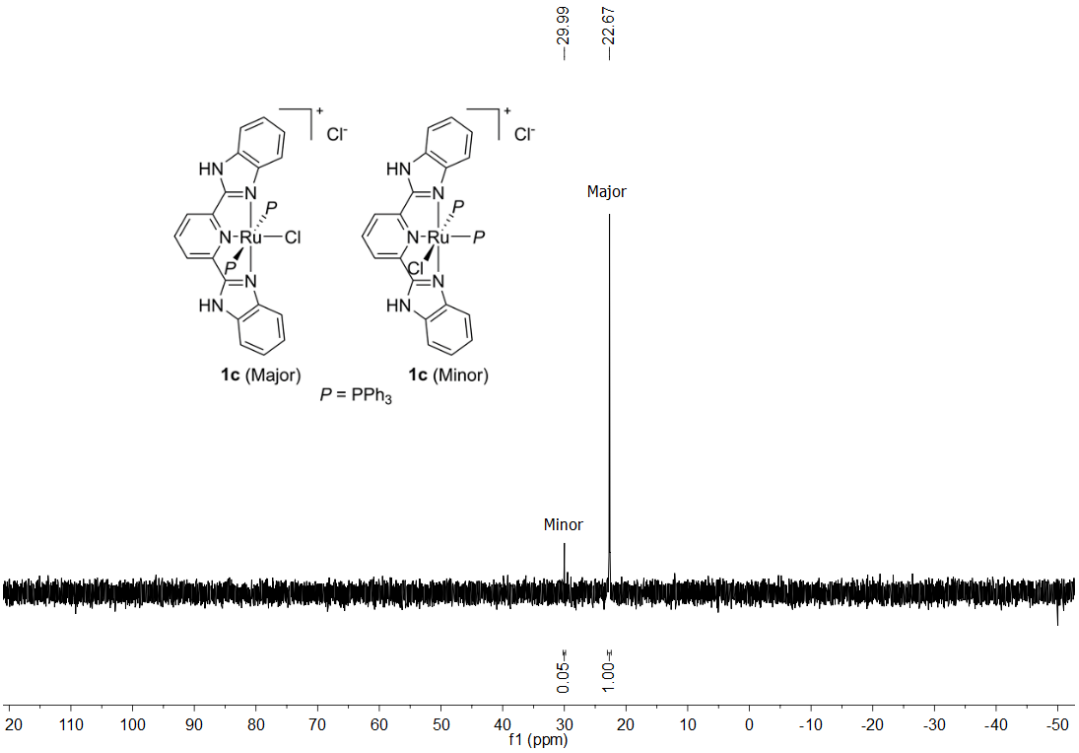


Figure S2: $^{31}P^{6}$ NMR Spectra of Complex **1c** with *trans* as the major isomer.

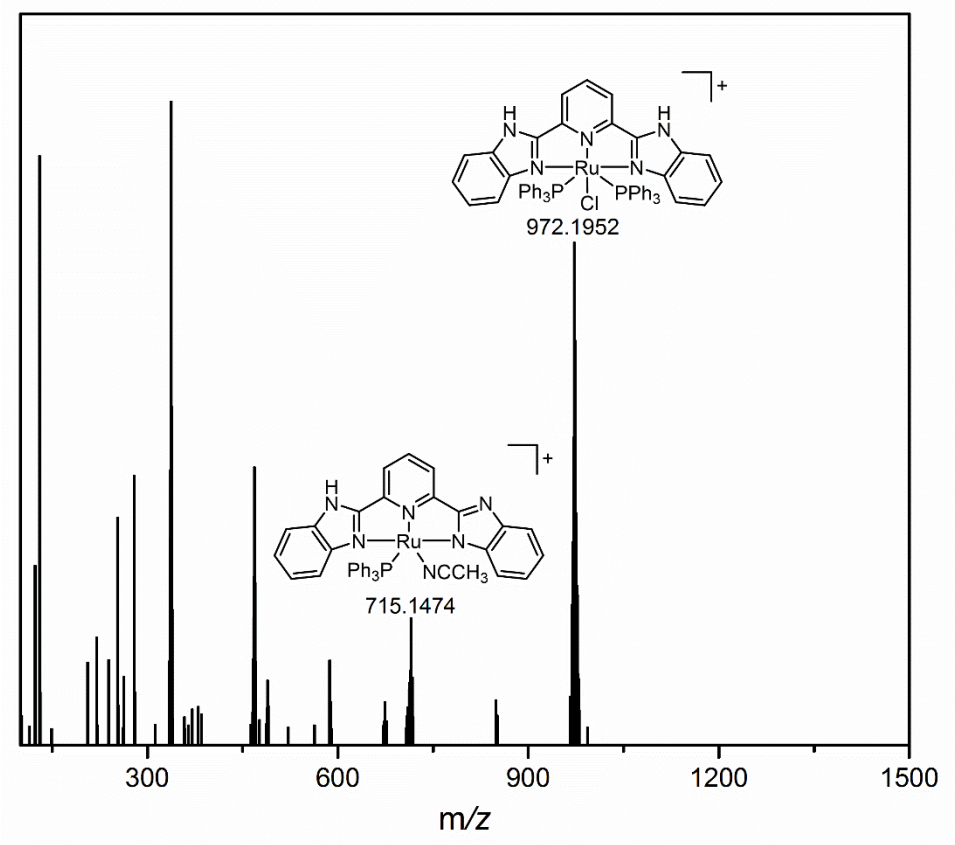


Figure S3: ESI-MS full Spectra of Complex **1c**

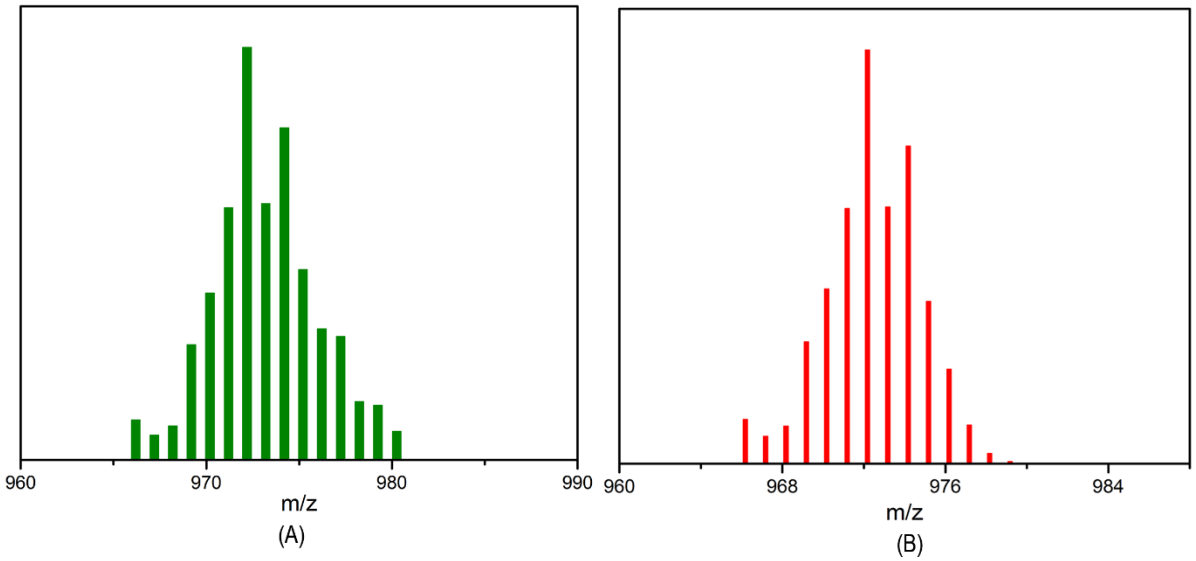


Figure S4: ESI-MS Expanded Spectra of Complex **1c** at m/z 972.1952 (A) observed (B) Simulated

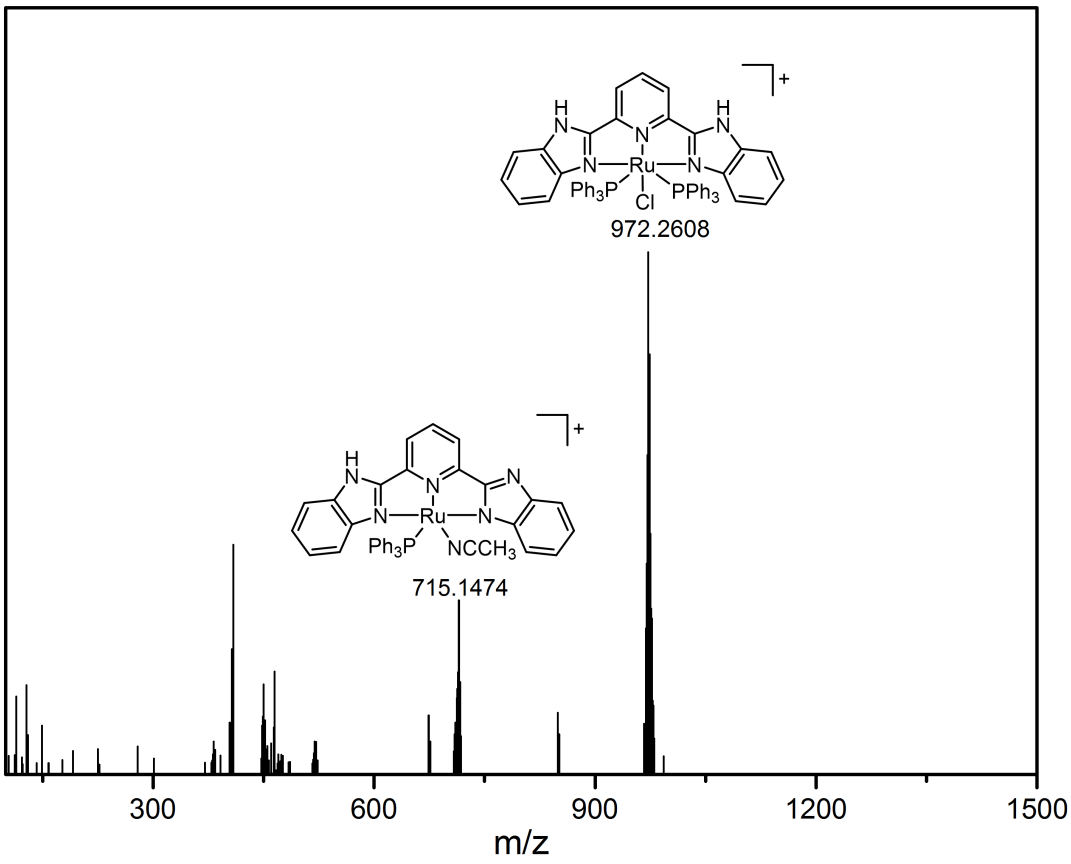


Figure S5: ESI-MS full Spectra of Complex **1d**

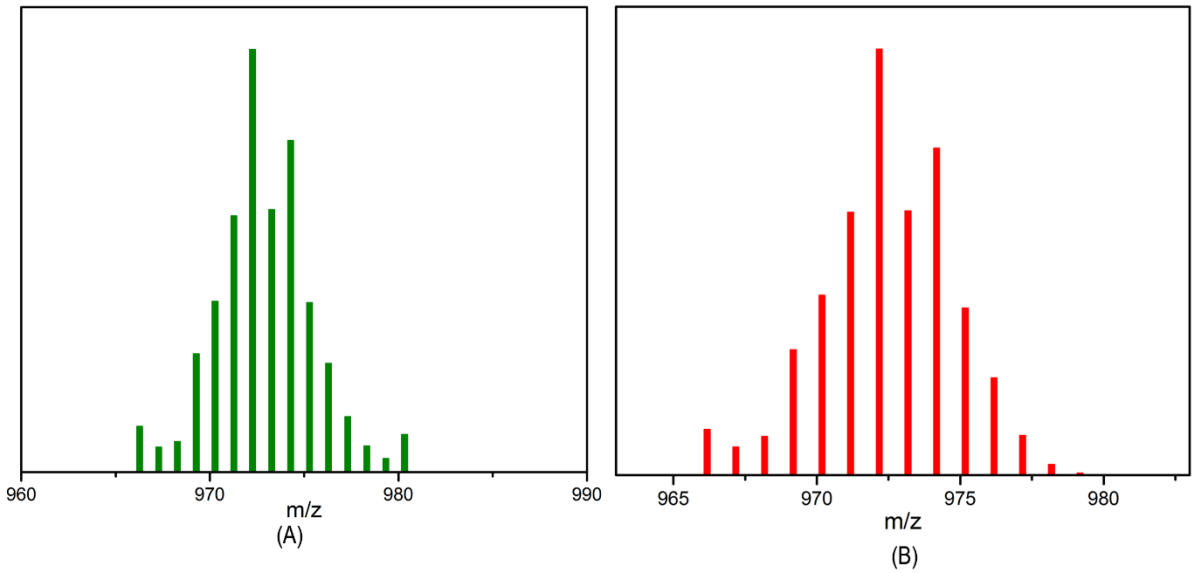


Figure S6: ESI-MS Expanded Spectra of Complex **1d** at 972.2608 (A) observed (B) Simulated

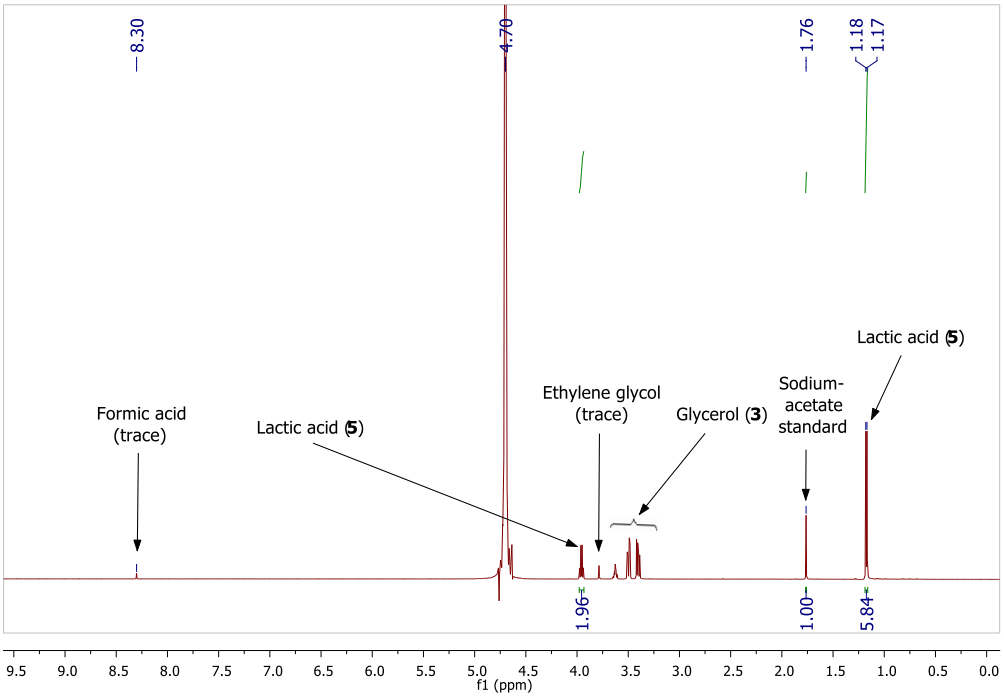


Figure S7: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation catalyzed by 0.03 mol% ($^{t\text{Bu2}}$NNN)RuCl$_2$(PPh$_3$) (**1a**) (Table 1, entry 1).

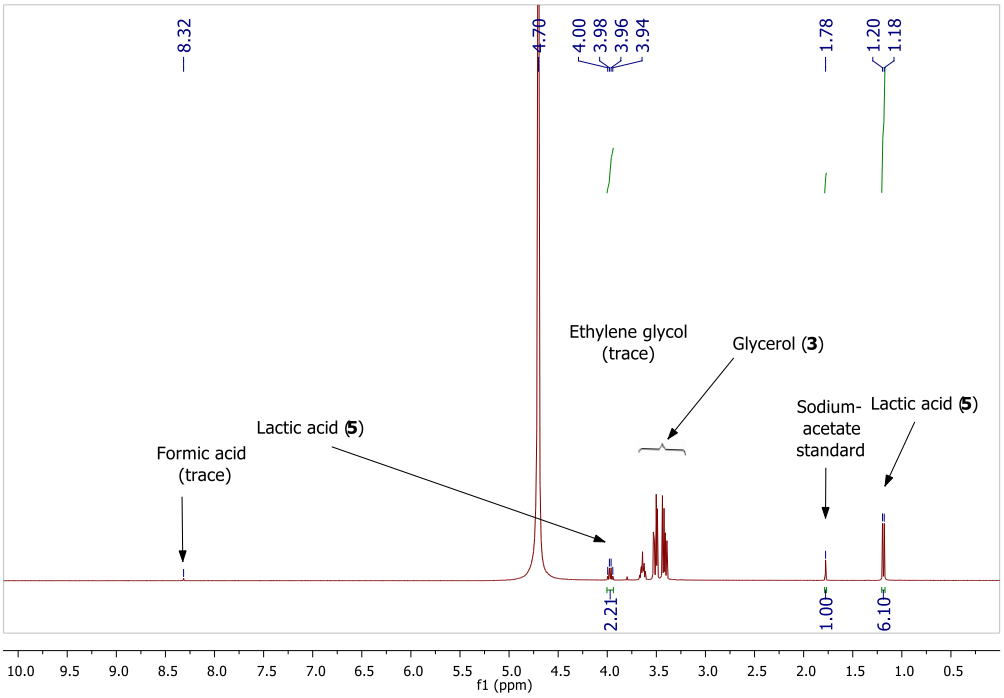


Figure S8: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation catalyzed by 0.03 mol% ($^{\text{Ph2}}$NNN)RuCl$_2$(PPh$_3$) (**1b**) (Table 1, entry 2).

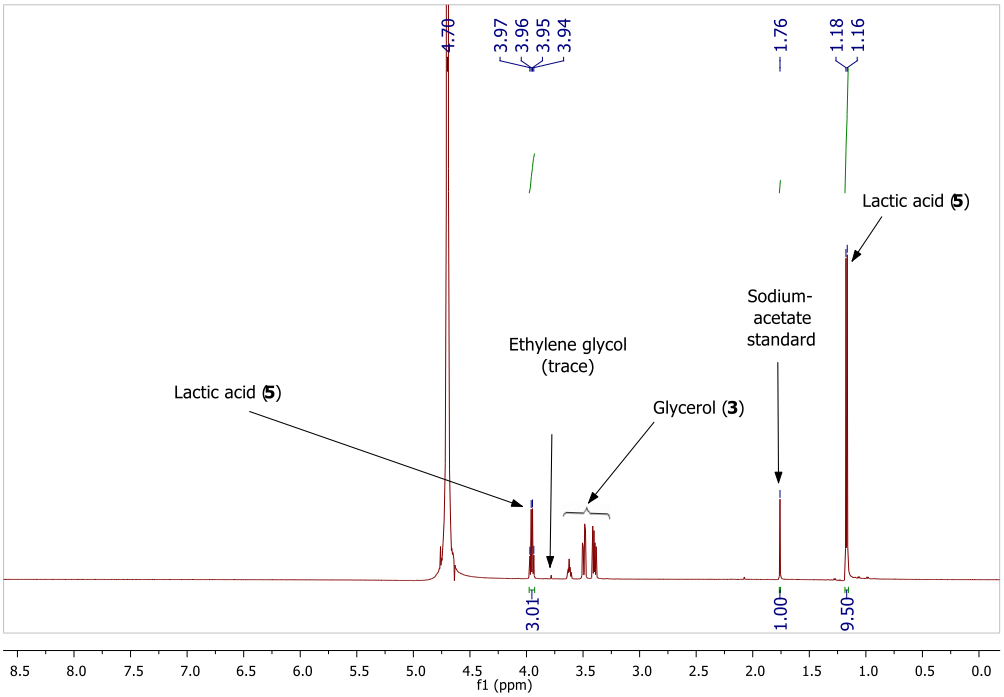


Figure S9: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation catalyzed by 0.03 mol% [(^{Bim2}NNN)RuCl(PPh$_3$)$_2$]Cl (**1c**) (Table 1, entry 3).

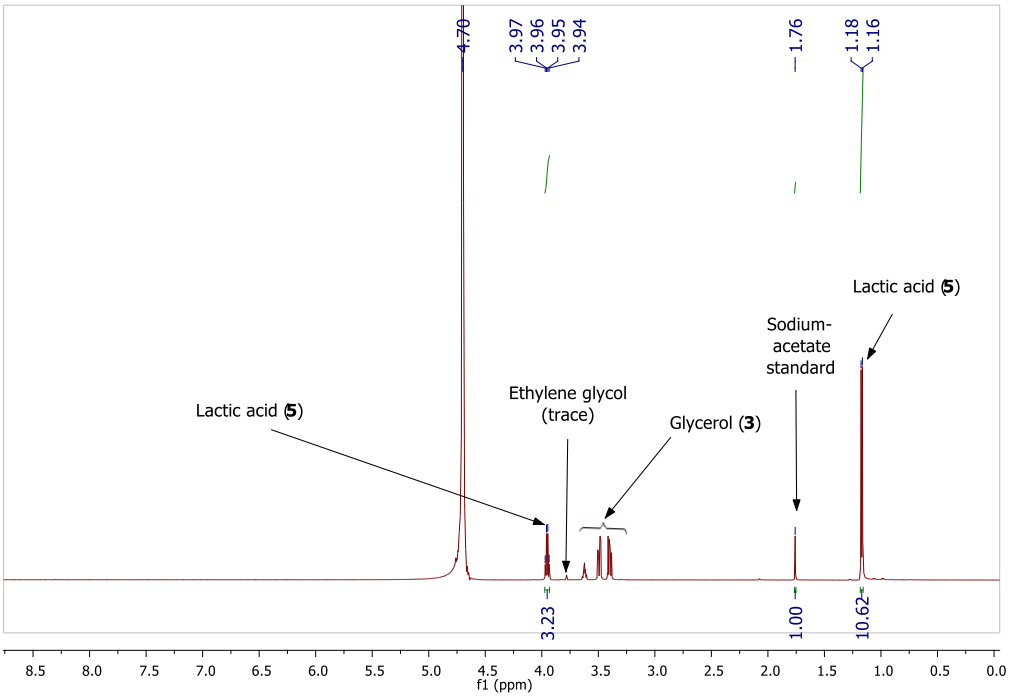


Figure S10: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation catalyzed by 0.03 mol% [(^{Bim2}NNN)RuCl(PPh$_3$)$_2$]PF$_6$ (**1d**) (Table 1, entry 4).

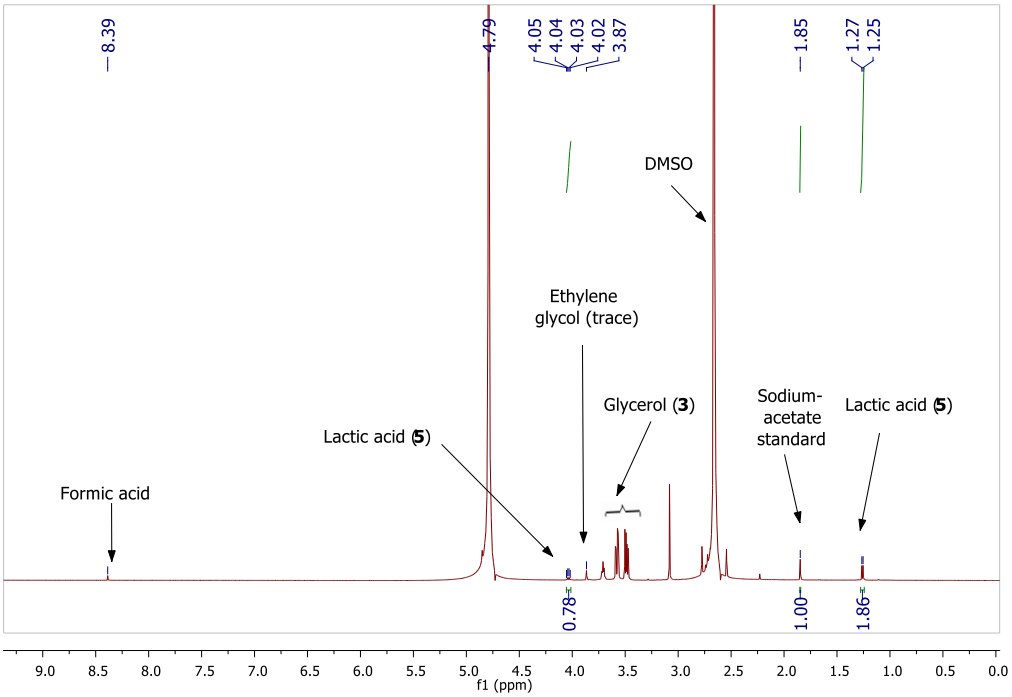


Figure S11: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in DMSO catalyzed by 0.03 mol% of **1c** (Table 2, entry 2).

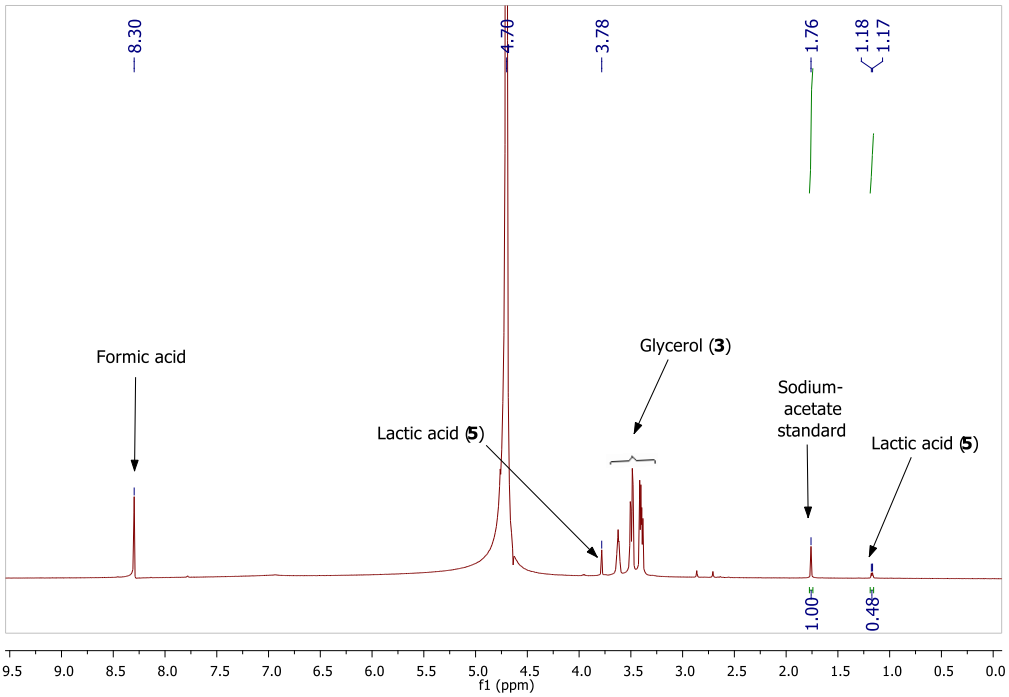


Figure S12: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in DMF catalyzed by 0.03 mol% of **1c** (Table 2, entry 3).

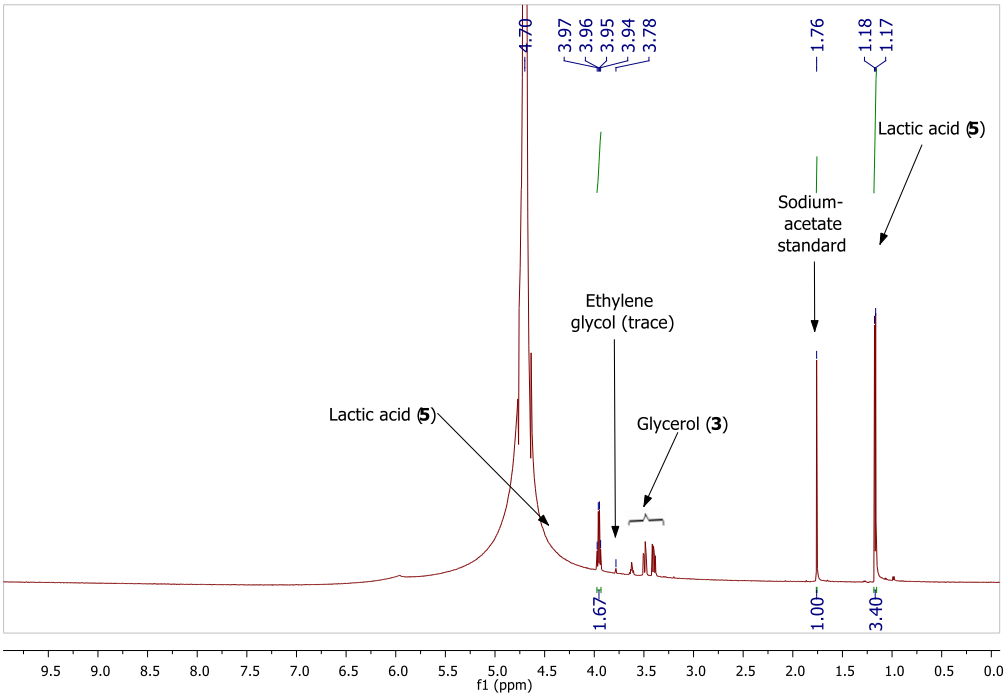


Figure S13: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in *p*-xylene catalyzed by 0.03 mol% of **1c** (Table 2, entry 4).

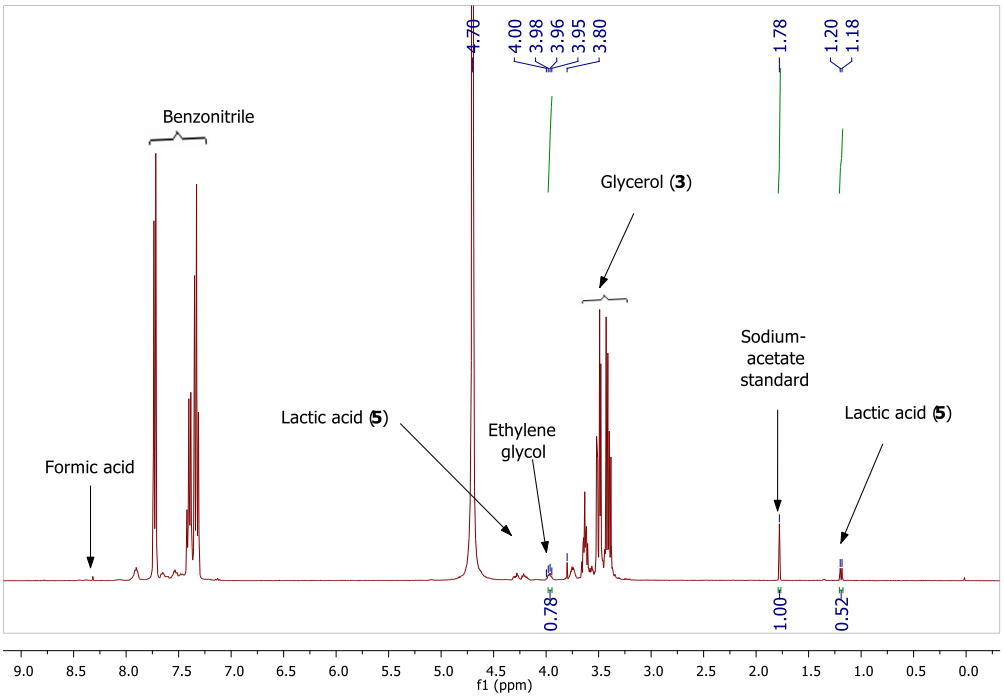


Figure S14: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in benzonitrile catalyzed by 0.03 mol% of **1c** (Table 2, entry 5).

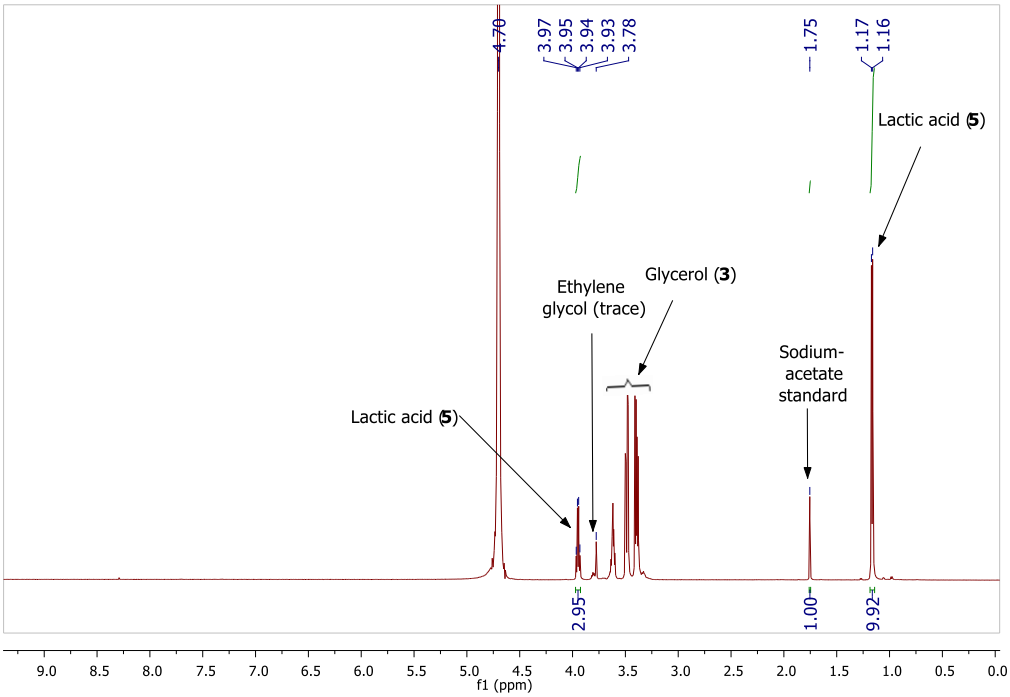


Figure S15: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in water catalyzed by 0.03 mol% of **1c** (Table 2, entry 6).

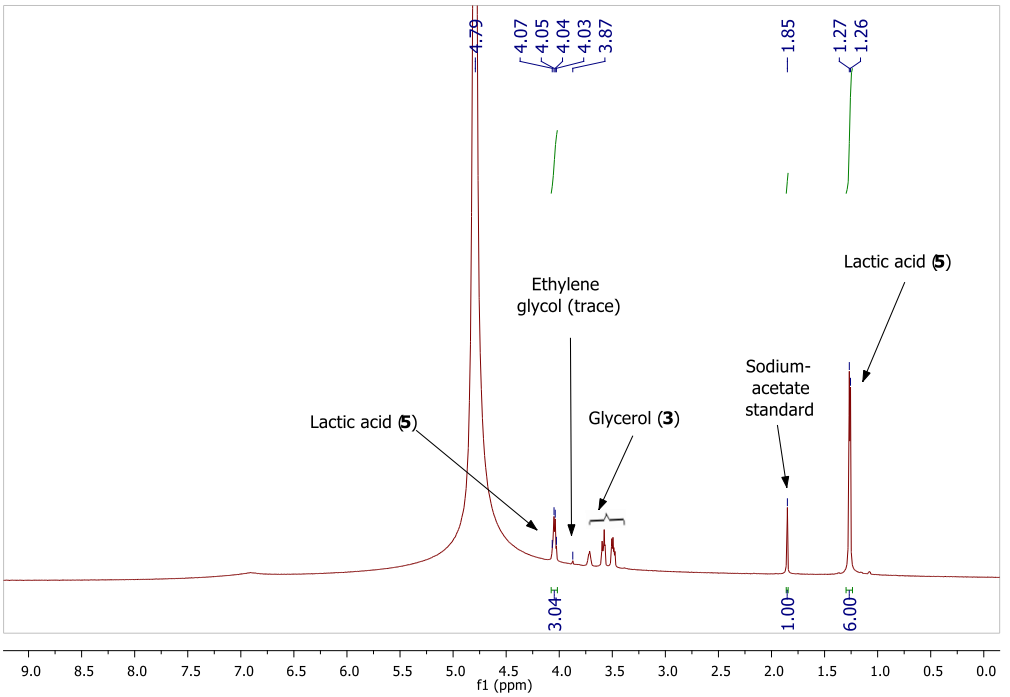


Figure S16: ^{1}H NMR spectra of glycerol (**3**) dehydrogenation in dioxane catalyzed by 0.03 mol% of **1c** (Table 2, entry 7).

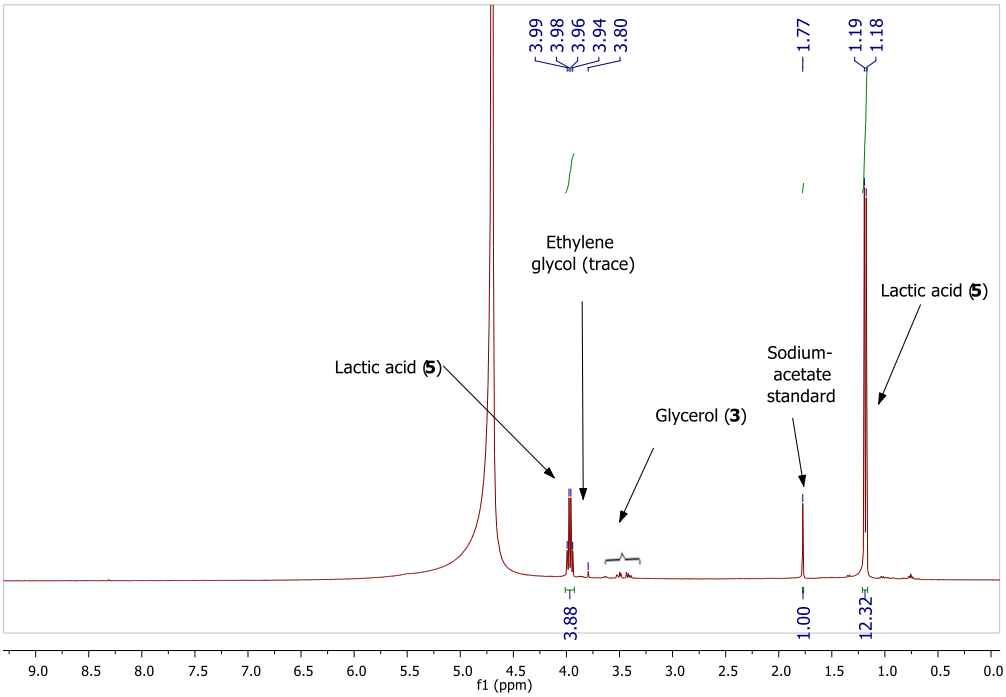


Figure S17: [1]H NMR spectra of glycerol (**3**) dehydrogenation in ethanol catalyzed by 0.03 mol% of **1c** (Table 2, entry 8).

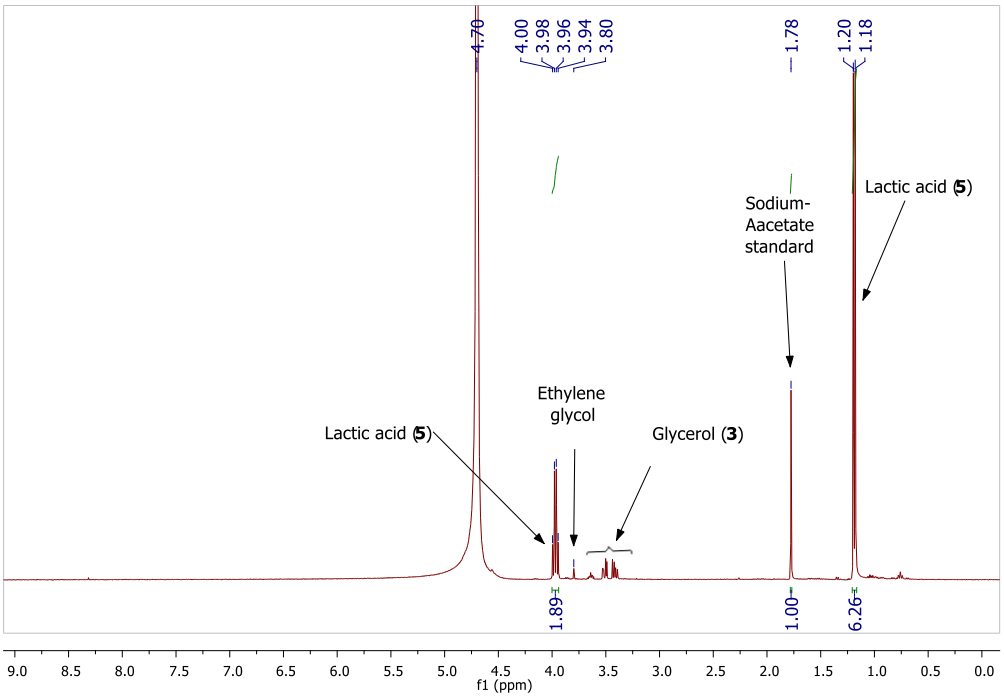


Figure S18: [1]H NMR spectra of glycerol (**3**) dehydrogenation in ethanol catalyzed by 0.03 mol% of **1c** (repeat reaction, Table 2, entry 8).

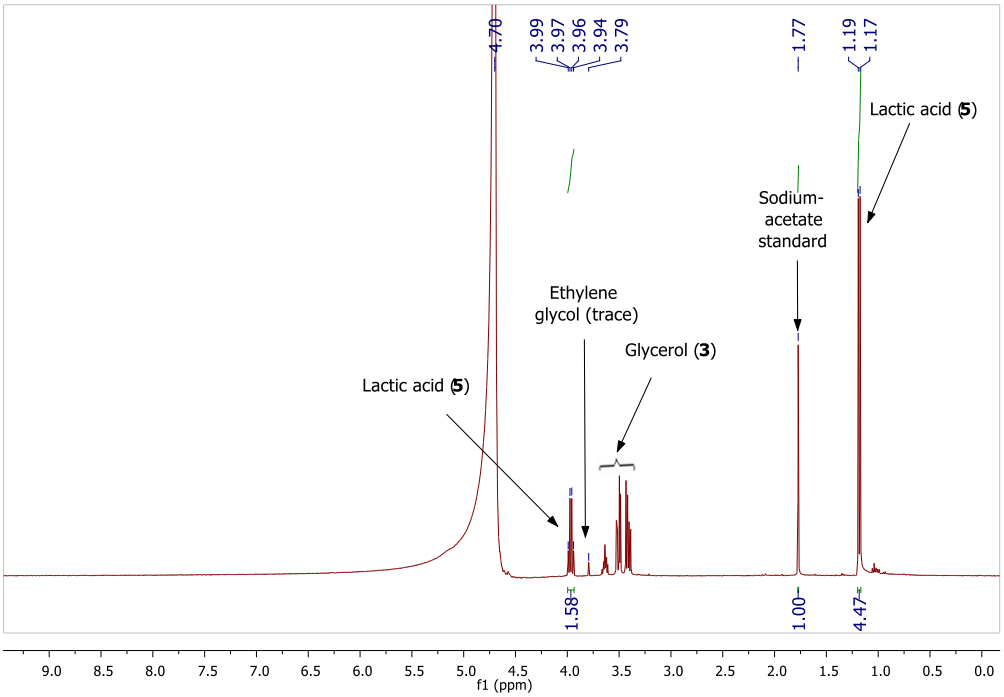


Figure S19: [1]H NMR spectra of glycerol (**3**) dehydrogenation without solvent catalyzed by 0.03 mol% of **1c** (Table 2, entry 9).

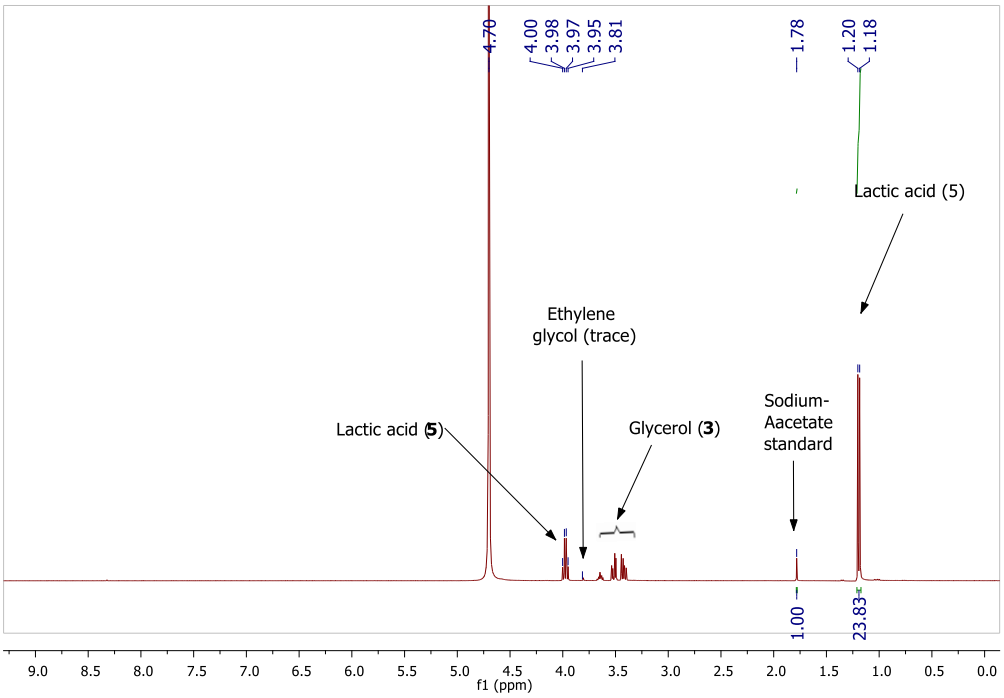


Figure S20: [1]H NMR spectra of glycerol (**3**) dehydrogenation in dioxane catalyzed by 0.03 mol% of **1c** (Table 2, entry 10).

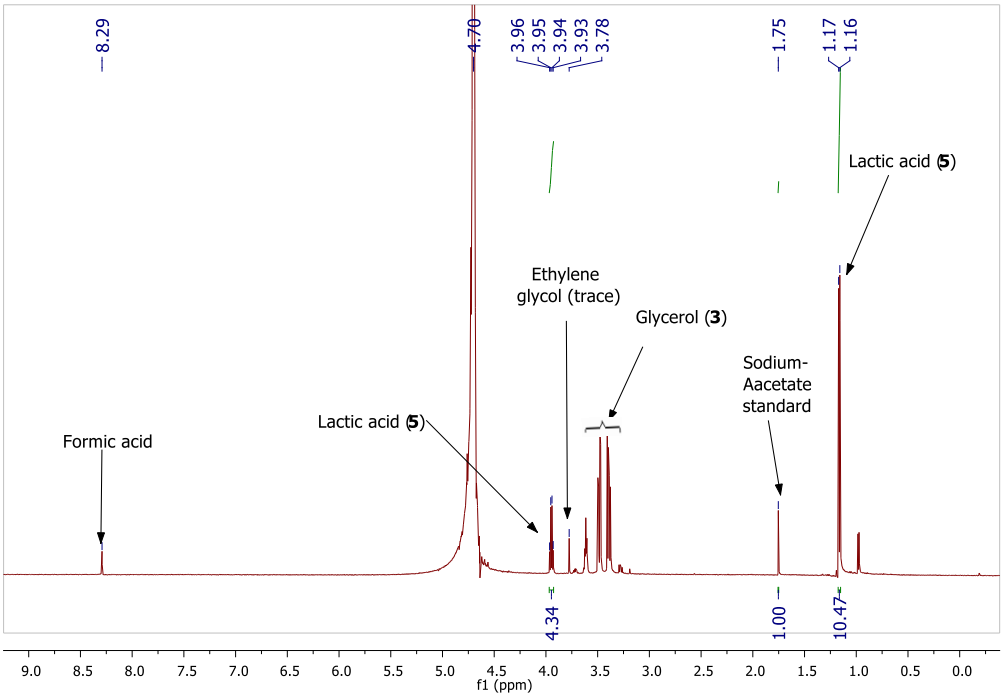


Figure S21: [1]H NMR spectra of glycerol (**3**) dehydrogenation in ethanol catalyzed by 0.03 mol% of **1c** (Table 2, entry 11).

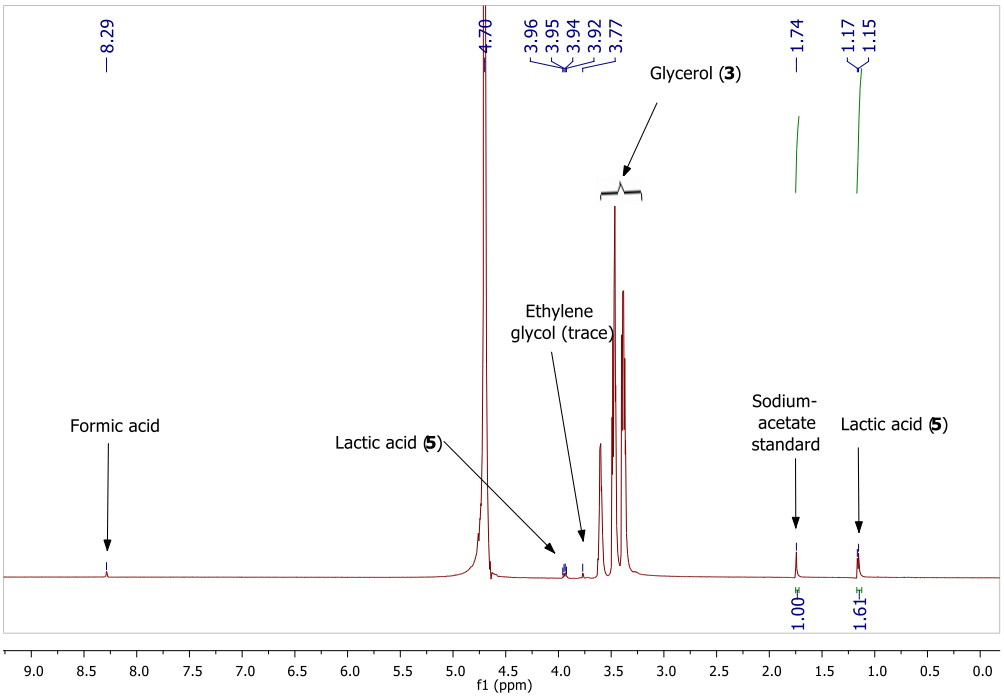


Figure S22: [1]H NMR spectra of glycerol (**3**) dehydrogenation in ethanol catalyzed by 0.003 mol% of **1c** (Table 2, entry 12).

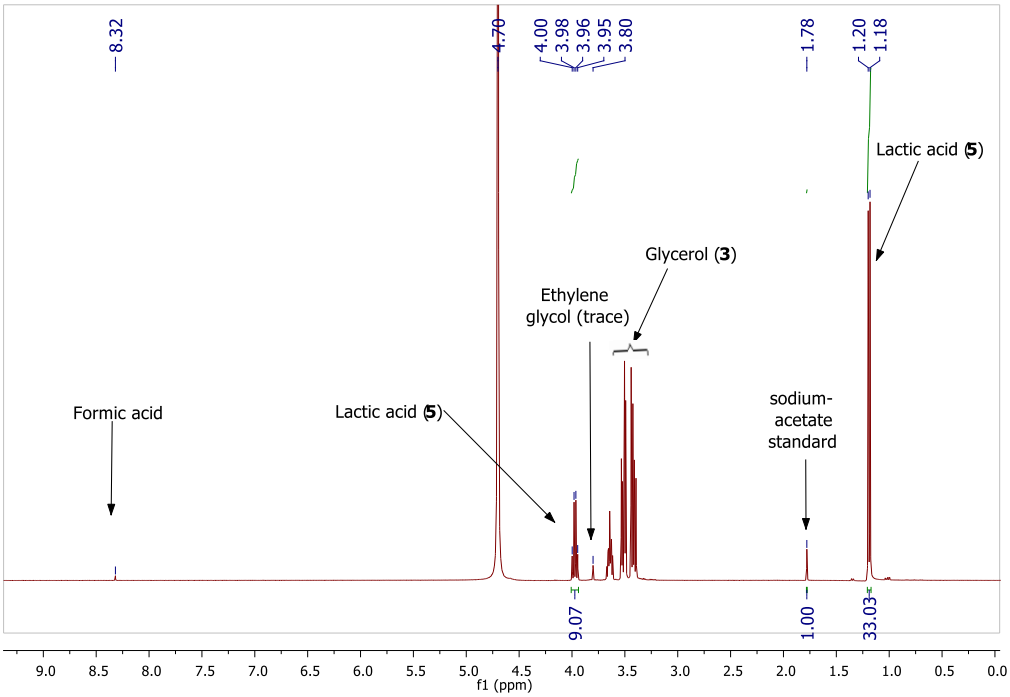


Figure S23: [1]H NMR spectra of glycerol (**3**) dehydrogenation in ethanol catalyzed by 0.003 mol% of **1c** (Table 2, entry 13).

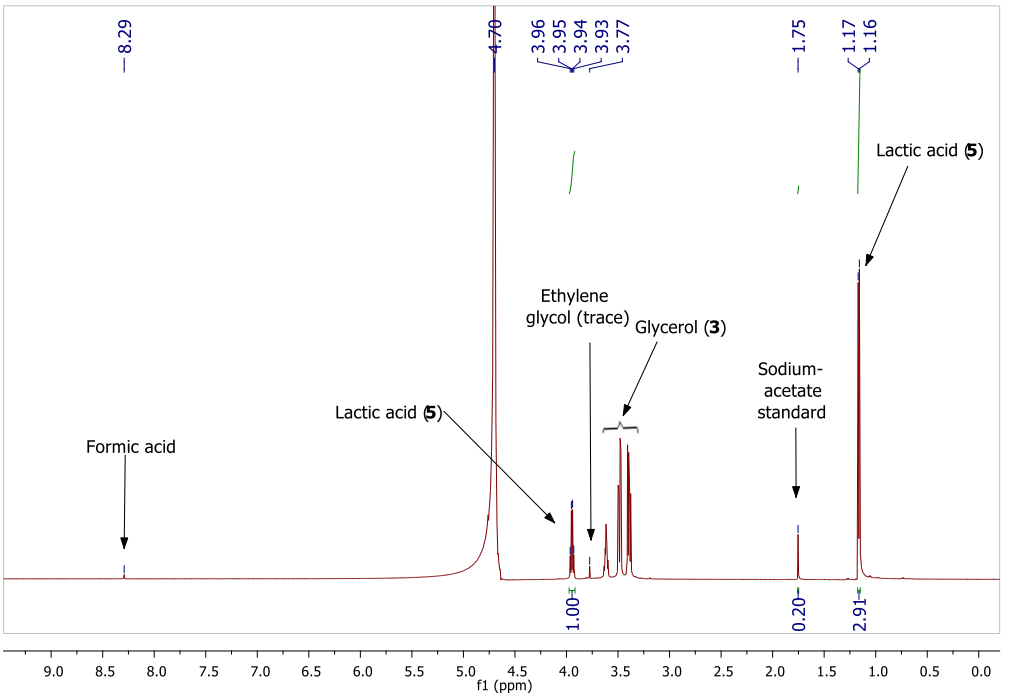
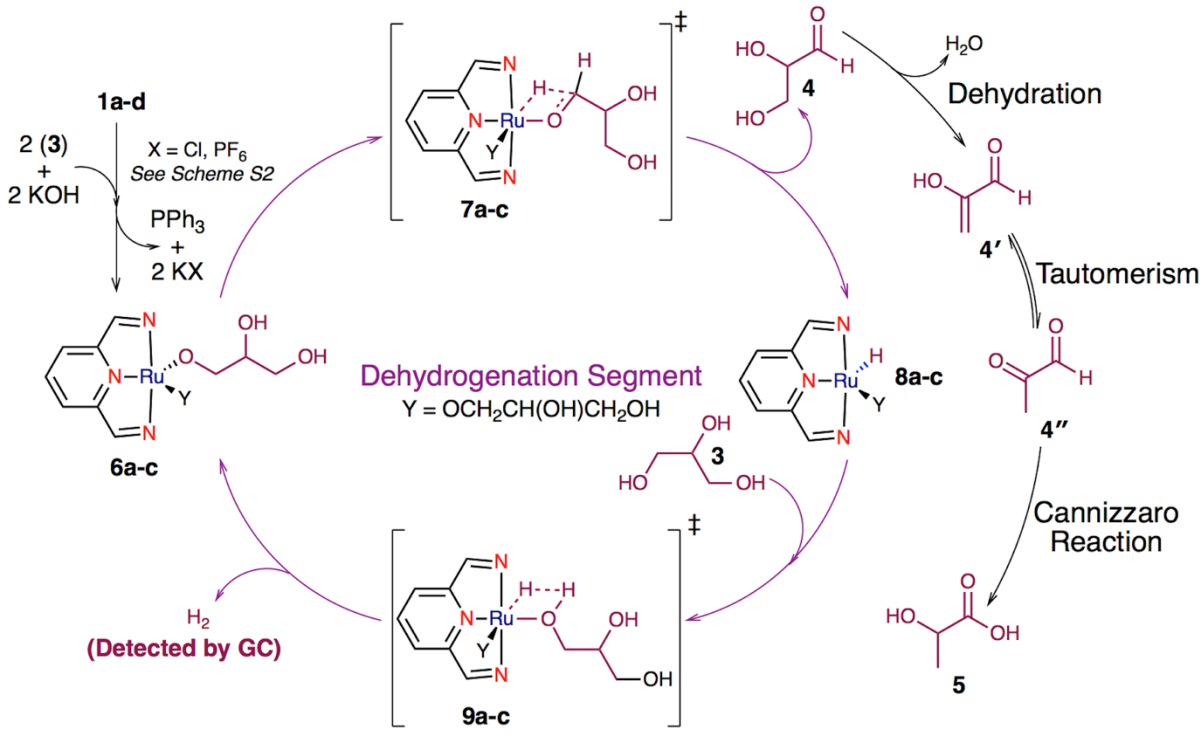


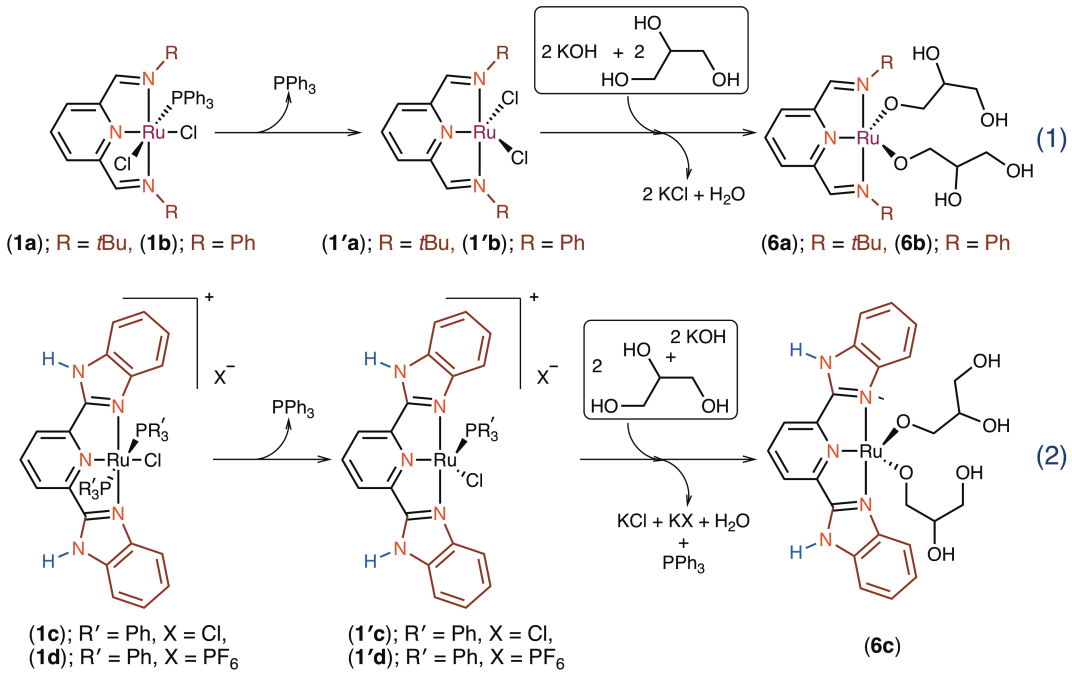
Figure S24: [1]H NMR spectra of glycerol (**3**) dehydrogenation without solvent catalyzed by 0.003 mol% of **1c** (Table 2, entry 14).

5. Computational Methodology:

All the calculations were performed using Gaussian-16 (revision C.01) program package.[10] PBEPBE level of DFT functional, along with LANL2DZ basis set for Ruthenium atom and 6-311G(d,p) basis set for all other atoms, was selected on the basis of previous reports for geometry optimization of all considered complexes.[11-14] Frequency calculations were performed at the same level of theory to confirm the minimum energy and transition state structures. TS: **7b** is a very close approximation. It is interesting to note that the inclusion of higher basis set or dispersion corrections has minimal affect on the overall energetics and no affect on the trend of the results (Table S3).



Scheme S1. Plausible mechanism involved in the (**1a–d**) catalyzed transformation of glycerol to lactic acid.



Scheme S2. Generation of catalytically active (**6a–c**) starting from (**1a–d**).

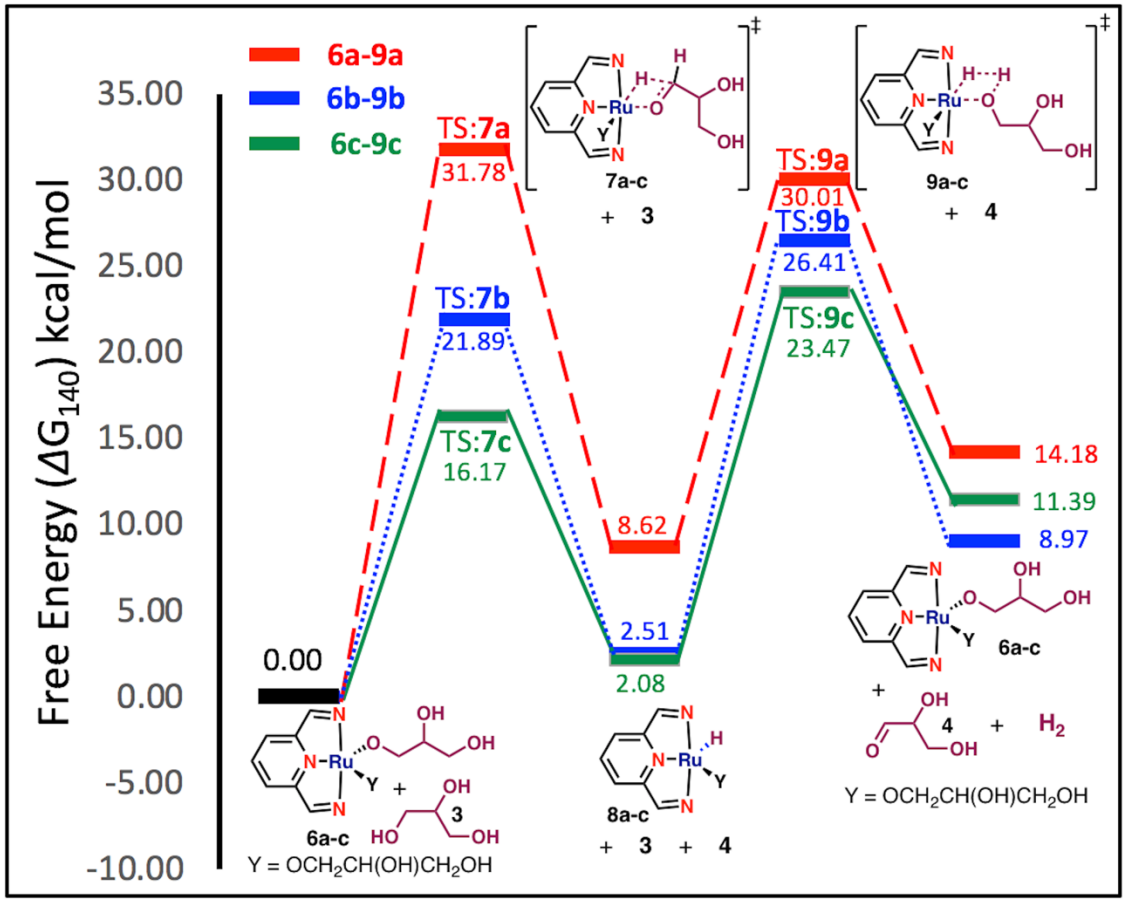


Figure S25. Free energy (140 °C) profile of the (**1a–d**) catalyzed glycerol dehydrogenation

Table S3: Effect of higher basis set and dispersion corrections on the energy profile (ΔE) of the reaction

Complex	PBEPBE/BS1	PBEPBE/BS2//PBEPBE/BS1	PBEPBE/BS1(D)//PBEPBE/BS1
6a	0.00	0.00	0.00
7a	32.45	32.62	32.19
8a	16.88	17.07	21.11
9a	38.19	36.84	38.88
6a + H_2	27.00	26.34	28.31
6b	0.00	0.00	0.00
7b	19.56	20.37	17.82
8b	8.01	10.07	8.63
9b	32.62	33.31	30.97
6b + H_2	21.02	21.79	21.03
6c	0.00	0.00	0.00
7c	20.59	20.99	20.42
8c	10.27	9.25	11.02
9c	37.10	32.67	41.53
6c + H_2	30.07	26.97	34.13

BS1 = LANL2DZ basis set for Ru and 6-311G(d,p) for all other atoms

BS2 = LANL2DZ basis set for Ru and 6-311++G(d,p) for all other atoms

(D) = Inclusion of dispersion corrections using EmpiricalDispersion=GD3

Table S4a: Optimized XYZ coordinates for complex **6a**

C	2.4220641	0.5035829	-0.2544121	H	-0.5312161	1.1830020	-2.2433528
C	3.6830846	0.2185735	-0.7867210	C	-1.5042097	1.1113155	-1.7214286
C	4.0319963	-1.1081309	-1.0820292	C	-2.6379619	0.9171378	-2.7646805
C	3.1219187	-2.1424282	-0.8365994	C	-3.8877093	0.3181040	-2.1152701
C	1.8556526	-1.8569608	-0.3075909	H	-3.7420424	-0.7600805	-1.9246899
H	4.3857702	1.0364674	-0.9556037	O	-1.5029117	0.0765618	-0.7618718
H	5.0165173	-1.3344276	-1.4929954	H	-1.6948240	2.1026523	-1.2612453
H	3.3826492	-3.1810637	-1.0491232	O	-2.9190593	2.1863043	-3.3707417
C	0.7844312	-2.7457914	0.0087492	H	-3.4176340	2.6777773	-2.6920899
H	0.8760037	-3.8201848	-0.1683610	O	-4.2292740	1.0155450	-0.9078552
C	1.8813386	1.7700604	0.1368056	H	-3.5188415	0.7582306	-0.2880152
H	2.4776536	2.6812473	0.0235152	H	-4.7379008	0.4396325	-2.8042578
C	-1.5262122	-3.0610298	0.7408039	H	-2.3061861	0.2597158	-3.5855040
C	-1.1623494	-4.3933539	1.4237578	C	-2.4866505	-2.2668601	1.6401519
H	-0.6158028	-4.2236155	2.3634332	H	-2.0089520	-2.0024331	2.5947205
H	-2.0881985	-4.9447335	1.6488290	H	-2.8081112	-1.3411931	1.1374645
H	-0.5533554	-5.0418178	0.7752740	H	-3.3849480	-2.8668269	1.8504909
C	-2.1776107	-3.3043037	-0.6360705	C	-1.3463471	2.8402514	1.5753005
H	-2.3403845	-2.3419016	-1.1424099	H	-1.9865293	2.4422564	0.7741704
H	-1.5296484	-3.9279462	-1.2718353	H	-1.3292760	2.1129422	2.4018719
H	-3.1431062	-3.8197671	-0.5137801	H	-1.8009601	3.7727986	1.9427361
C	0.0777671	3.1093423	1.0691225	H	0.5054088	0.6830040	4.4314549
C	0.9181875	3.7171200	2.2116655	C	1.0469251	0.2540854	3.5609859
H	1.9633370	3.8801573	1.9072888	C	2.1143131	-0.7330206	4.0786886
H	0.4957048	4.6932734	2.4954867	C	1.4765344	-2.0163649	4.6305038
H	0.9116819	3.0714897	3.1002364	H	0.6969995	-1.7709577	5.3792117
C	0.0540962	4.0957058	-0.1171076	O	0.1055942	-0.3867901	2.7117894
H	1.0712152	4.3622132	-0.4431213	O	3.0489993	-1.0746299	3.0504060
H	-0.4847972	3.6777021	-0.9782310	H	2.6438171	-1.8511555	2.6141956
H	-0.4500946	5.0254762	0.1878952	O	0.9419123	-2.7747179	3.5371182
N	-0.3191112	-2.2039180	0.5074273	H	0.3936569	-2.0969347	3.0599013
N	1.5198730	-0.5310148	-0.0365401	H	2.2395960	-2.6438665	5.1166972
N	0.6575805	1.7866011	0.6367265	H	2.6839698	-0.2199577	4.8761024
Ru	-0.1608691	-0.1573292	0.7248629	H	1.5751713	1.0746247	3.0458230

Table S4b: Optimized XYZ coordinates for complex **6b**

C	-1.3385253	2.3196083	-0.2518320	C	-5.5453356	-1.4234835	0.3721690
C	-1.2833135	3.6058770	-0.8045726	H	-4.6525699	0.2301467	-0.6829454
C	-0.0458578	4.1965163	-1.0938464	C	-4.1611410	-2.5097066	2.0315527
C	1.1454354	3.5080317	-0.8249043	H	-2.1824312	-1.6719384	2.3038908
C	1.1072838	2.2252100	-0.2655024	C	-5.3747946	-2.4223021	1.3385969
H	-2.2170491	4.1343344	-1.0055500	H	-6.4756615	-1.3666255	-0.1978429
H	-0.0097860	5.1956577	-1.5294330	H	-4.0104318	-3.2937011	2.7770163
H	2.1149208	3.9602186	-1.0431553	H	-6.1756625	-3.1376502	1.5371635
C	2.1816423	1.3725291	0.0898062	C	2.8750665	-0.7323775	0.9702221
H	3.2251828	1.6768534	-0.0252495	C	4.0386845	-0.8988865	0.1915787
C	-2.4758395	1.5442729	0.0889135	C	2.6916332	-1.5212331	2.1225476
H	-3.4904091	1.9191723	-0.0669066	C	5.0071321	-1.8318519	0.5721856
N	1.8564479	0.1823229	0.6133605	H	4.1645763	-0.3208619	-0.7270941
N	-0.1381328	1.6450041	0.0199827	C	3.6702238	-2.4445556	2.4953654
N	-2.2456454	0.3261760	0.6048509	H	1.7923559	-1.3576688	2.7211639
Ru	-0.2077558	-0.0669339	0.8113686	C	4.8294402	-2.6060406	1.7250411
H	0.0970436	-3.2280453	-1.4128506	H	5.9002039	-1.9626311	-0.0436609
C	0.5205165	-2.2445143	-1.1168473	H	3.5274700	-3.0418981	3.3989347
C	0.9297605	-1.4765307	-2.3904865	H	5.5875644	-3.3356475	2.0176544
C	1.9989264	-2.2403215	-3.1851227	H	-1.2078508	-0.3285733	4.4062773
H	2.8630477	-2.5088714	-2.5479488	C	-1.0345851	0.4856200	3.6773332
O	-0.4909304	-1.5947156	-0.3846517	C	-0.6244861	1.7462857	4.4683390
H	1.4289466	-2.4410070	-0.5094451	C	-0.4168648	2.9660734	3.5668804
O	-0.1787970	-1.1977613	-3.2388815	H	0.3156011	2.7433242	2.7723164
H	-0.3207174	-2.0290240	-3.7318449	O	-0.0163446	0.1025042	2.7696041
O	1.4272333	-3.4008897	-3.8187806	O	-1.6300045	2.0336768	5.4413386
H	1.2995615	-4.0708884	-3.1275750	H	-2.2979222	2.5425774	4.9405156
H	2.3542877	-1.6063790	-4.0105952	O	-1.6778072	3.4080660	3.0270831
H	1.3360438	-0.4986168	-2.0774997	H	-1.8753548	2.8514202	2.2535850
C	-3.3097721	-0.5756713	0.8248519	H	-0.0428302	3.8043187	4.1741212
C	-4.5246657	-0.5084003	0.1105445	H	0.3124807	1.5343646	5.0108685
C	-3.1336336	-1.6027598	1.7726319	H	-2.0022841	0.6804815	3.1759617

Table S4c: Optimized XYZ coordinates for complex **6c**

C	-1.3875888	2.5912384	-0.2426056	C	-3.5991773	-1.7662443	-0.0224730
C	-1.5021600	3.9794569	-0.3407512	C	-5.9860743	-1.2148924	-0.0835339
C	-0.3531284	4.7815829	-0.2680698	C	-4.9391312	-2.1531516	0.0245533
C	0.9024499	4.1726906	-0.1238746	H	-6.5328038	0.8828791	-0.2702297
C	0.9968102	2.7820125	-0.0406075	H	-7.0215199	-1.5589886	-0.0431993
H	-2.4838152	4.4395674	-0.4765631	H	-5.1835598	-3.2081642	0.1634966
H	-0.4335141	5.8663595	-0.3396196	H	-2.7962091	-2.4883041	0.1223936
H	1.8078860	4.7830281	-0.0885159	N	3.5015188	2.2937843	0.0954250
C	2.1672413	1.9595408	0.0188355	C	4.2421132	1.1210900	0.0551627
C	-2.4194111	1.5989473	-0.2938356	C	5.6178673	0.8735113	0.0948880
C	3.2930230	0.0680070	-0.0560478	C	3.7114569	-1.2655949	-0.1538079
C	-3.3112970	-0.4031654	-0.1933468	C	5.0840914	-1.5122775	-0.1183307
N	2.0167869	0.6132135	-0.0643379	C	6.0193051	-0.4624024	0.0090959
N	-0.1476812	1.9800682	-0.0867266	H	2.9666705	-2.0503646	-0.2882823
N	-2.0980903	0.2808586	-0.2672474	H	5.4468133	-2.5392761	-0.1942206
Ru	0.0284925	0.0331008	-0.1545079	H	7.0851982	-0.6979575	0.0366071
H	-0.1733532	-2.9571285	-2.5182053	H	6.3470342	1.6810975	0.1862894
C	-0.3083458	-2.7036441	-1.4489236	H	-4.2580466	2.6746694	-0.3029126
C	0.0103484	-3.9745747	-0.6097105	H	3.8712652	3.2327171	0.1901847
C	0.2998692	-3.6802309	0.8617618	H	1.4060208	0.4527120	2.6160176
H	1.1892315	-3.0366294	0.9578739	C	0.7243141	-0.4085173	2.7223323
O	0.5370737	-1.6376648	-1.0978420	C	0.1492536	-0.3901325	4.1601157
H	-1.3783390	-2.4578646	-1.3113005	C	-0.9581755	-1.4237353	4.3887328
O	-1.0583169	-4.9192335	-0.7406749	H	-1.7835999	-1.2664565	3.6727390
H	-1.7324244	-4.6257532	-0.1013752	O	-0.3311988	-0.3671522	1.7745559
O	-0.8353206	-3.0842903	1.5245607	O	1.2248202	-0.6351243	5.0685936
H	-0.7382267	-2.0919865	1.4731845	H	1.2918146	-1.6116526	5.0739900
H	0.4970948	-4.6380192	1.3700205	O	-0.4218381	-2.7493929	4.3074421
H	0.9054727	-4.4670222	-1.0287422	H	-0.5483736	-3.0400597	3.3745490
N	-3.7820841	1.7800716	-0.3282505	H	-1.3471027	-1.2923764	5.4122736
C	-4.3811544	0.5344371	-0.2558018	H	-0.2449933	0.6172122	4.3782521
C	-5.7247013	0.1504423	-0.2156781	H	1.3386207	-1.3271168	2.6149358

Table S4d: Optimized XYZ coordinates for complex **7a**

C	-0.59929162	3.10802988	-0.34099135	H	-1.87998499	-0.70396372	-1.92955414
C	-0.36164469	4.49455871	-0.40699054	C	-0.83658551	-1.04726902	-2.04985919
C	0.94116421	4.96075371	-0.58512256	C	-0.83850036	-2.51772917	-2.52601803
C	2.00473693	4.04372808	-0.67770405	C	0.23334178	-3.45247707	-1.95469167
C	1.72611214	2.67697562	-0.60339106	H	1.22719200	-2.97877515	-1.98972300
H	-1.19773079	5.18933974	-0.30492893	O	0.03819774	-0.19399350	-2.47708066
H	1.13717911	6.03286503	-0.63851108	H	-0.40246622	-1.38224199	-0.39959429
H	3.03491077	4.38434856	-0.79769952	O	-2.12599377	-3.08525208	-2.29300040
C	2.68549442	1.59636072	-0.65310243	H	-2.01182840	-3.60796544	-1.47236835
H	3.74773148	1.84737421	-0.74572111	O	-0.11870619	-3.86312758	-0.62646760
C	-1.84322448	2.44364439	-0.14077743	H	-0.11082579	-3.04420660	-0.08456169
H	-2.75619646	3.03236492	-0.03173188	H	0.26160106	-4.37709910	-2.54986235
C	3.28419121	-0.73177726	-0.72743046	H	-0.69981274	-2.44037075	-3.62142395
C	4.70978396	-0.30709553	-0.32171439	C	2.84888904	-1.87642336	0.19626467
H	4.72987625	0.11216333	0.69639058	H	2.90730538	-1.55891940	1.24681512
H	5.35612155	-1.19728825	-0.33302246	H	1.80936059	-2.16401229	-0.00119851
H	5.15836770	0.41872358	-1.01739071	H	3.49853631	-2.75269165	0.04992383
C	3.27701412	-1.15531469	-2.21210012	C	-3.21610081	-0.96860971	0.45277688
H	2.24698035	-1.26959162	-2.57459671	H	-2.73865755	-1.56276142	-0.33408872
H	3.75556748	-0.37861043	-2.82940014	H	-2.71406472	-1.15683921	1.41038613
H	3.83120484	-2.09743761	-2.34626110	H	-4.25142104	-1.33106699	0.55120209
C	-3.26703948	0.52810735	0.11538804	H	-1.43007443	0.28868097	2.36640478
C	-3.97691215	1.23723823	1.29420994	C	-0.40367442	-0.05681130	2.59366354
H	-4.22506242	2.28781029	1.08424052	C	-0.48352277	-1.57204674	2.88599149
H	-4.92366459	0.71658966	1.50174683	C	0.75926470	-2.09298804	3.61117750
H	-3.36198305	1.19637528	2.20530399	H	1.67367518	-1.75733210	3.09231728
C	-4.08809089	0.74440307	-1.17512363	O	0.51452634	0.28634937	1.60069561
H	-4.14978839	1.81116560	-1.43900437	O	-1.64508232	-1.88164065	3.66113773
H	-3.65164934	0.20606271	-2.02883372	H	-1.34417796	-1.77482773	4.58553714
H	-5.11237369	0.36859286	-1.02702163	O	0.74567550	-1.66355293	4.98892380
N	2.26844444	0.36177220	-0.60232759	H	0.95141732	-0.71348873	4.98497063
N	0.44607104	2.22818262	-0.46616851	H	0.74588483	-3.19203309	3.65013788
N	-1.86825925	1.11037167	-0.09536862	H	-0.58660599	-2.08763932	1.91385981
Ru	0.04032066	0.28602768	-0.36761041	H	-0.10680702	0.46546993	3.53514691

Table S4e: Optimized XYZ coordinates for complex **7b**

C	-1.39305169	3.10290350	-0.19589604	C	0.42188241	-1.86512133	3.80182112
C	-1.47026083	4.50391562	-0.27855164	H	-0.47058990	-2.45326133	4.08731045
C	-0.29622055	5.24474776	-0.45338825	O	0.34964934	0.51098548	1.87561921
C	0.94400440	4.59507087	-0.54572125	O	1.36521869	0.36506672	4.27466853
C	0.98940560	3.19666376	-0.45841771	H	1.56592982	0.71696951	3.38110433
H	-2.44092725	4.99766485	-0.20526950	O	0.73262349	-2.15596004	2.42307671
H	-0.34553548	6.33263152	-0.52247800	H	0.79968745	-1.27539210	1.97747294
H	1.86809757	5.16203839	-0.67055641	H	1.26370164	-2.18472584	4.44184689
C	2.14159394	2.33978073	-0.56148219	H	-0.44048643	-0.29558711	4.99356306
H	3.14283923	2.74789322	-0.73520798	H	-1.11847694	1.19151224	3.18331186
C	-2.45761499	2.14938175	-0.11616731	C	3.05212283	0.16224447	-0.70095192
H	-3.50935074	2.44793721	-0.13825868	C	3.81471421	0.27983013	-1.87638241
N	1.95453921	1.03475634	-0.45629495	C	3.36490898	-0.83096636	0.24274651
N	-0.17101529	2.47880888	-0.28855863	C	4.88010186	-0.59638566	-2.10476543
N	-2.12384158	0.85736078	-0.06131188	H	3.53388324	1.02443172	-2.62420628
Ru	-0.06811879	0.51288200	-0.10932336	C	4.43725378	-1.69378267	0.00870833
H	-1.41651049	-1.62980829	-1.22427820	H	2.78462371	-0.89589702	1.16494497
C	-0.37335302	-1.38131537	-1.50085435	C	5.19391310	-1.58524133	-1.16601164
C	0.45581396	-2.63943307	-1.80060051	H	5.45932462	-0.51074024	-3.02696929
C	0.70782364	-3.54236870	-0.59069858	H	4.67580462	-2.46243348	0.74710387
H	1.47832717	-3.10262429	0.06470543	H	6.01742028	-2.27753066	-1.35345222
O	-0.13210782	-0.26739570	-2.12609300	C	-3.17994384	-0.08068874	-0.28747373
H	0.18763912	-1.17718990	0.13244435	C	-3.41071856	-1.13848771	0.60681455
O	-0.28899208	-3.34063516	-2.81144961	C	-3.95598995	0.02262346	-1.45633814
H	-1.06202847	-3.71025116	-2.34505468	C	-4.41224024	-2.07310120	0.34018485
O	-0.50254162	-3.78028912	0.13879683	H	-2.81479916	-1.19627902	1.51632490
H	-0.41269565	-3.27576320	0.97076231	C	-4.95437430	-0.92051721	-1.71847283
H	1.08098723	-4.51025782	-0.97065436	H	-3.73426569	0.81680886	-2.17238697
H	1.40894045	-2.33466595	-2.25964490	C	-5.18517960	-1.97106212	-0.82412581
H	-1.38351521	-0.47562040	2.56214823	H	-4.58054039	-2.89411783	1.04040648
C	-0.61452645	0.25058457	2.88640996	H	-5.54377550	-0.83901151	-2.63461333
C	0.15935072	-0.36997423	4.06782265	H	-5.96155088	-2.71000311	-1.03323206

Table S4f: Optimized XYZ coordinates for complex **7c**

C	-1.3077416	2.8952876	0.0434524	C	-3.6251449	-1.3978475	-0.2435661
C	-1.3471447	4.2897370	0.1808290	C	-5.9903452	-0.8248154	0.0430445
C	-0.1451899	5.0051963	0.2396764	C	-4.9631959	-1.7759561	-0.1435418
C	1.0792029	4.3220064	0.1727313	H	-6.5125241	1.2725618	0.2882431
C	1.0730990	2.9285417	0.0488147	H	-7.0254736	-1.1648207	0.1156458
H	-2.3035430	4.8129365	0.2440727	H	-5.2233505	-2.8339544	-0.2094305
H	-0.1598171	6.0911693	0.3398280	H	-2.8304249	-2.1315503	-0.3875653
H	2.0202535	4.8740687	0.2180986	N	3.5299254	2.3247131	0.0697846
C	2.1934579	2.0234067	-0.0161247	C	4.2411515	1.1398871	-0.0055658
C	-2.3953297	1.9589212	-0.0283448	C	5.6126785	0.8723294	0.0477485
C	3.2623409	0.1159483	-0.1482782	C	3.6688244	-1.2255223	-0.2262789
C	-3.3323596	-0.0290226	-0.1501889	C	5.0358833	-1.4957073	-0.1685070
N	1.9951392	0.6928224	-0.1593345	C	5.9933969	-0.4674079	-0.0365976
N	-0.1036149	2.2287065	-0.0306391	H	2.9454718	-2.0356669	-0.3287505
N	-2.1181459	0.6451299	-0.2067529	H	5.3733609	-2.5323925	-0.2257299
Ru	-0.1025248	0.2444998	-0.3107900	H	7.0538416	-0.7244278	0.0033294
H	-1.6383538	-0.8718102	-2.2035723	H	6.3504982	1.6700876	0.1548591
C	-0.5309608	-0.9110794	-2.2482113	H	-4.2035123	3.0470389	0.2842057
C	-0.0667577	-2.2511795	-2.8457809	H	3.9203765	3.2514544	0.1992810
C	1.3392399	-2.6819196	-2.4128084	H	1.4210994	0.0044015	2.8404462
H	1.9929345	-1.7917755	-2.3771377	C	0.7929713	-0.7770502	2.3629640
O	0.1360638	0.1775178	-2.4750660	C	0.3263325	-1.8013493	3.4361696
H	-0.1623250	-1.4204856	-0.6870115	C	-0.9084431	-2.5689197	2.9449179
O	-1.0210673	-3.2703979	-2.5742521	H	-1.8126784	-1.9507588	3.0930018
H	-0.6394487	-3.7678023	-1.8217193	O	-0.3092290	-0.2357281	1.6733344
O	1.2979670	-3.3803242	-1.1570568	O	1.4173266	-2.6754937	3.7633353
H	0.9118068	-2.7659425	-0.4937663	H	1.5509369	-3.2197218	2.9665774
H	1.7538203	-3.4048672	-3.1296038	O	-0.7865420	-2.9534900	1.5657851
H	-0.0637278	-2.0732166	-3.9387244	H	-0.7944808	-2.0780767	1.1133179
N	-3.7506250	2.1579129	0.1065917	H	-1.0107914	-3.4926260	3.5358650
C	-4.3731994	0.9207704	0.0433313	H	0.0725584	-1.2923805	4.3812893
C	-5.7159108	0.5407173	0.1396690	H	1.4698855	-1.3449396	1.6899264

Table S4g: Optimized XYZ coordinates for complex **8a**

C	0.23602727	-3.17863032	-0.15635945	H	3.52475890	0.42178278	-1.83264317
C	1.28822195	-4.04483050	-0.49173242	C	4.20614481	1.27919026	-1.61072424
C	2.61433584	-3.61991743	-0.34688584	C	5.61613632	0.88718177	-1.15666197
C	2.89151146	-2.32201307	0.11237996	C	6.50147804	2.10972217	-0.91634345
C	1.83001115	-1.46811030	0.43526353	H	6.57659416	2.72125017	-1.83284601
H	1.05704612	-5.04551926	-0.86276143	O	3.80187810	2.43135103	-1.63226391
H	3.43358237	-4.29368543	-0.60330464	H	-1.04086198	-0.97423161	2.06729736
H	3.91453961	-1.95162453	0.20743506	O	5.42735385	0.16197065	0.07112432
C	1.89300397	-0.10095413	0.86390444	H	5.40776336	0.87286867	0.74803232
H	2.86235686	0.35685764	1.07073188	O	5.97925534	2.86203556	0.18696684
C	-1.16869475	-3.41796947	-0.17432120	H	5.17208536	3.28726835	-0.16226566
H	-1.55945576	-4.41755325	-0.37923210	H	7.51065030	1.78423700	-0.62496457
C	0.77250521	1.98563036	1.43778807	H	6.06868274	0.19295119	-1.88574677
C	0.52841501	2.84932551	0.18188801	C	-0.38363567	2.15439760	2.43877265
H	-0.39705067	2.50787436	-0.30422551	H	-1.33480803	1.86949430	1.96916710
H	0.42565588	3.90852508	0.46751945	H	-0.22635041	1.52147734	3.32579885
H	1.36873546	2.75675433	-0.52372292	H	-0.44309839	3.20476981	2.76468701
C	2.09068541	2.40430130	2.11363228	C	-4.04738438	-1.58833076	1.18927073
H	2.33277845	1.75506502	2.97018637	H	-3.60746238	-1.55089690	2.19711707
H	2.94366969	2.40664975	1.41669031	H	-3.87562864	-0.61456476	0.71425546
H	1.98337475	3.43239569	2.49018731	H	-5.13230087	-1.74881994	1.28740250
C	-3.42425186	-2.72931051	0.37363110	H	-3.48186144	-0.00218023	-1.34529708
C	-4.10558467	-2.85749122	-1.00279947	C	-3.00236703	0.97605766	-1.14671021
H	-3.67373008	-3.69163037	-1.57766039	C	-4.11402915	1.97425872	-0.74046057
H	-5.18291875	-3.04722499	-0.87727484	C	-3.55360114	3.34450529	-0.35886308
H	-3.98449983	-1.93731558	-1.59211006	H	-2.86177272	3.25563551	0.49571014
C	-3.59843144	-4.03987418	1.17041497	O	-1.97212821	0.92005333	-0.19334611
H	-3.31147466	-4.93317769	0.59588353	O	-5.04213456	2.10700558	-1.82094517
H	-3.00245955	-4.01229568	2.09539210	H	-4.60516808	2.73540214	-2.42775008
H	-4.65720814	-4.15901882	1.44691600	O	-2.91550040	3.96104704	-1.49328929
N	0.75433904	0.55776073	0.98515070	H	-2.05727421	3.51663315	-1.59826291
N	0.51917687	-1.90007583	0.31119340	H	-4.38530579	4.01160738	-0.08614240
N	-1.96859354	-2.40183548	0.15315108	H	-4.67827327	1.56802191	0.11738043
Ru	-0.92384028	-0.64577687	0.52379083	H	-2.59612073	1.31982649	-2.12390258

Table S4h: Optimized XYZ coordinates for complex **8b**

C	2.2155166	-2.6425781	-0.9590228	C	3.8985602	2.7126960	-1.9394621
C	2.9107423	-3.8594516	-0.9106071	H	4.2477635	0.8717759	-0.8573493
C	2.2455231	-5.0246776	-0.5083757	C	1.6943665	2.9736931	-2.9041246
C	0.8932586	-4.9712366	-0.1442906	H	0.3092928	1.3355715	-2.5765984
C	0.2041578	-3.7521348	-0.2053008	C	2.9813623	3.4757607	-2.6700261
H	3.9683602	-3.8813465	-1.1799874	H	4.8966853	3.1046821	-1.7308889
H	2.7844742	-5.9722065	-0.4651169	H	0.9685624	3.5640659	-3.4681456
H	0.3663475	-5.8670205	0.1901220	H	3.2634261	4.4626013	-3.0432462
C	-1.1591361	-3.4868200	0.1145443	C	-2.9624689	-1.9576750	0.1919207
H	-1.8444850	-4.2876246	0.4061716	C	-3.9366016	-2.8417440	-0.3163599
C	2.6973537	-1.3572770	-1.3367407	C	-3.3631067	-0.7708434	0.8294215
H	3.6874840	-1.2142918	-1.7770142	C	-5.2931601	-2.5541098	-0.1524454
N	-1.5708244	-2.2185006	0.0503551	H	-3.6288307	-3.7281467	-0.8755356
N	0.8660562	-2.6005930	-0.6178927	C	-4.7233910	-0.4982813	0.9958620
N	1.8424887	-0.3328079	-1.2121434	H	-2.5887450	-0.0777242	1.1682052
Ru	-0.0262541	-0.8997990	-0.4853481	C	-5.6924112	-1.3876480	0.5124717
H	-2.1300614	1.9283520	-0.7208524	H	-6.0423166	-3.2364115	-0.5610210
C	-2.6094650	2.1566493	-1.7026370	H	-5.0247257	0.4284873	1.4879699
C	-3.9419064	2.9084313	-1.6291526	H	-6.7545612	-1.1650358	0.6375270
C	-4.6492863	2.9468711	-2.9837894	H	-0.4694337	2.7061573	0.9037438
H	-4.0195764	3.4612043	-3.7324611	C	0.1259794	1.7747006	0.9790275
O	-2.1290388	1.7434190	-2.7497179	C	0.6144452	1.6608055	2.4416774
H	-0.4938430	-0.9920250	-1.9930970	C	1.4053138	0.3777852	2.7004083
O	-4.7438956	2.2569475	-0.6409682	H	0.7847619	-0.5135030	2.4932894
H	-5.0621747	1.4431527	-1.0816807	O	-0.6652536	0.6741328	0.5820353
O	-4.9833957	1.6160246	-3.3926547	O	1.4236801	2.8001450	2.7474064
H	-4.1341430	1.2105202	-3.6477605	H	2.2954514	2.5774443	2.3673851
H	-5.5986706	3.4924296	-2.8831081	O	2.6219478	0.3680989	1.9301209
H	-3.7467242	3.9313503	-1.2566228	H	2.3652734	0.1617193	1.0125278
C	2.2501713	0.9453942	-1.7026525	H	1.7157031	0.3516503	3.7556390
C	3.5412418	1.4497896	-1.4578598	H	-0.2548934	1.6887150	3.1207693
C	1.3192028	1.7214350	-2.4144581	H	1.0135763	1.9142090	0.3299814

Table S4i: Optimized XYZ coordinates for complex **8c**

C	-1.72000767	0.11129874	2.36467440	C	-3.67234254	0.73328809	-2.06909579
C	-1.88541322	-0.08448527	3.74086226	C	-6.08683597	0.74805187	-1.66141656
C	-0.76706343	-0.06150462	4.58291594	C	-4.98222749	0.87060555	-2.53044018
C	0.51155604	0.13368157	4.03624340	H	-6.77451475	0.42352657	0.37665676
C	0.65228230	0.31408489	2.65987328	H	-7.09676321	0.85897752	-2.06137922
H	-2.88145472	-0.26221163	4.15311296	H	-5.15722153	1.08265969	-3.58694353
H	-0.88582793	-0.21203014	5.65637447	H	-2.81628985	0.85000423	-2.73408787
H	1.39529756	0.14542123	4.67631768	N	3.16406515	0.60713321	2.28582468
C	1.85224152	0.47222621	1.88417069	C	3.93283086	0.74341335	1.13386151
C	-2.70871332	0.15130704	1.32942420	C	5.30363764	0.94404814	0.93785114
C	3.03553975	0.62668204	0.03816984	C	3.49198247	0.67819304	-1.28556067
C	-3.48346649	0.46375109	-0.70625877	C	4.86018080	0.87060798	-1.47732789
N	1.74746975	0.47654496	0.53285010	C	5.74727010	1.00796343	-0.38588980
N	-0.45796938	0.31796830	1.81834820	H	2.77904883	0.55137818	-2.10193819
N	-2.31226776	0.28754364	0.03252835	H	5.25922991	0.91519403	-2.49283068
Ru	-0.20951005	0.39388977	-0.12287951	H	6.81089074	1.16129364	-0.58090371
H	1.68278157	4.04111233	5.24804837	H	5.99603636	1.04138006	1.77628848
C	2.23559599	3.71638995	4.32893562	H	-4.60935147	0.11387569	2.29367721
C	2.05457915	4.68924619	3.15404159	H	3.41170500	1.01257717	3.19010660
C	1.75309601	3.95512220	1.84707308	H	-0.27777712	-0.62840167	-3.84142774
H	2.50453623	3.16369090	1.68293728	C	-0.48167441	-0.99695875	-2.81630536
O	2.91448535	2.70436477	4.31615679	C	-0.27493834	-2.53075166	-2.81163728
H	-0.40366250	1.97342125	-0.10834305	C	-0.43625865	-3.12245147	-1.41068685
O	1.03821342	5.63146094	3.46093103	H	0.32124586	-2.70302838	-0.72472232
H	0.21266678	5.19276600	3.17560963	O	0.34788437	-0.34350739	-1.88931539
O	0.43524373	3.43268404	2.02467744	O	-1.21694204	-3.13033922	-3.70857731
H	0.19224158	2.86842026	1.25648539	H	-2.04249278	-3.16820878	-3.18814611
H	1.79690951	4.67174378	1.00621371	O	-1.77435631	-2.90866241	-0.92209775
H	3.00834918	5.24195562	3.05434429	H	-1.83793104	-1.96179973	-0.69190007
N	-4.08185038	0.16715153	1.42974289	H	-0.30444982	-4.21378252	-1.46056614
C	-4.60470614	0.37087614	0.16363587	H	0.73279205	-2.77178603	-3.19054861
C	-5.91868342	0.50067004	-0.29706134	H	-1.56044065	-0.82220115	-2.62006587

Table S4j: Optimized XYZ coordinates for complex **9a**

C	-0.169760690	1.470337225	2.237758088	H	0.877651358	0.738185910	-2.005380552
C	-0.031561689	1.500733007	3.629989225	H	3.729188702	1.083337067	-1.935471490
C	0.410459342	0.349612195	4.301161049	C	3.059002204	0.554243984	-1.228957907
C	0.697706485	-0.814990540	3.579925298	C	3.632284839	0.678410565	0.183662726
C	0.551669682	-0.816517838	2.183621852	C	5.091145146	0.231657362	0.280028296
H	-0.277190648	2.411770112	4.178656490	O	1.794532839	1.213273319	-1.258686153
H	0.520079839	0.360056262	5.386571115	H	2.993933284	-0.502782177	-1.535411110
H	1.024866173	-1.723920735	4.088671881	O	3.559590344	2.040058083	0.604578662
C	0.794087667	-1.883163197	1.260414962	H	2.738422369	2.366353815	0.184786588
H	1.136480990	-2.854657587	1.628760144	O	5.242658305	-1.179183714	0.073807097
C	-0.638107638	2.520441090	1.368218827	H	4.821695808	-1.618892786	0.830662954
H	-0.948149618	3.476310069	1.798355481	H	5.686734819	0.722548419	-0.505221357
C	0.918028880	-2.829076990	-0.950321303	H	5.495824558	0.553885598	1.257668006
C	2.367171901	-3.314374434	-0.720656072	H	3.022713224	0.036553949	0.860541452
H	2.488626447	-3.796515850	0.261988442	C	-2.148498243	2.705939887	-1.843293259
H	2.623464060	-4.065586091	-1.483216650	H	-1.653821214	1.905496630	-2.409186327
H	3.096496483	-2.494043238	-0.794638585	H	-2.997121693	2.257286501	-1.308602806
C	0.753959782	-2.392839521	-2.410298745	H	-2.520593622	3.466628406	-2.547039615
H	-0.247811462	-1.979214538	-2.588473208	C	-0.057220563	-3.993040692	-0.664865065
H	1.489739171	-1.626534431	-2.690785577	H	-0.014194857	-4.310921980	0.388085839
H	0.897634065	-3.264112810	-3.067743716	H	-1.094492122	-3.723151468	-0.903610199
C	-1.166394080	3.362375122	-0.856670587	H	0.221143183	-4.858587404	-1.285812720
C	-1.884291875	4.516251464	-0.133123936	H	-2.168023899	-2.103673817	0.164115896
H	-1.211235455	5.092743406	0.520986036	C	-2.543441019	-1.375553875	-0.585124654
H	-2.270760420	5.214857452	-0.889464945	C	-4.072611020	-1.275753602	-0.450727941
H	-2.740779984	4.157353253	0.459009921	C	-4.734672638	-2.649381733	-0.351037213
C	0.061435466	3.916979707	-1.607066314	O	-2.033537938	-0.088438407	-0.333561856
H	0.732913940	4.448111375	-0.913770123	H	-2.283984328	-1.755765704	-1.592479380
H	0.636336924	3.110782327	-2.080019112	O	-4.396086291	-0.537750719	0.723637306
H	-0.270148073	4.627642615	-2.379971124	H	-3.643054351	0.088865431	0.788564487
N	0.606841967	-1.656439026	-0.035267913	O	-4.423252064	-3.489914865	-1.468981160
N	0.141116501	0.328856641	1.537504613	H	-4.777896029	-3.047742076	-2.257977494
N	-0.676359638	2.291994654	0.072757195	H	-4.350345876	-3.168114582	0.540707636
Ru	-0.071553007	0.319618740	-0.396756632	H	-5.826527974	-2.520755401	-0.219965727
H	-0.045535904	0.369216233	-2.213883841	H	-4.463714231	-0.750424684	-1.354155609

Table S4k: Optimized XYZ coordinates for complex **9b**

C	-1.49547175	1.48123928	1.68857733	C	-3.38804354	-2.21297083	-0.57196483
C	-1.48626267	2.56913958	2.57127118	C	-5.57857756	-0.78823385	-1.58937398
C	-0.26647721	2.99249903	3.12396284	H	-4.56572782	0.98861423	-0.88424478
C	0.92467124	2.33574195	2.79751128	C	-4.43335415	-2.88818259	-1.20221853
C	0.89309071	1.24024604	1.91636905	H	-2.51633637	-2.73901323	-0.17438887
H	-2.42107210	3.07591350	2.81616290	C	-5.53051339	-2.18139659	-1.71331559
H	-0.24785252	3.84144228	3.80914683	H	-6.41674178	-0.22845782	-2.01050228
H	1.87736565	2.65747040	3.22221656	H	-4.38702162	-3.97473573	-1.30317458
C	1.97057788	0.42569482	1.44814504	H	-6.33825828	-2.71361642	-2.22028315
H	2.99760881	0.56862462	1.79505267	C	2.68551762	-1.45972347	0.21061475
C	-2.61964372	0.87077638	1.03274019	C	3.51882088	-1.99916871	1.21243325
H	-3.64134877	1.21804917	1.21522989	C	2.82335468	-1.90238446	-1.11718487
N	1.67900389	-0.51642070	0.54509720	C	4.49591199	-2.93916422	0.87497427
N	-0.31610593	0.83393892	1.38127491	H	3.33911876	-1.73598925	2.25711545
N	-2.37840155	-0.16844631	0.24497574	C	3.81460259	-2.82749481	-1.44502333
Ru	-0.34171889	-0.62334343	0.09779297	H	2.15082540	-1.50966754	-1.87987284
H	-0.31432138	-1.73125867	-1.35703874	C	4.65775402	-3.34673113	-0.45361587
H	-0.35839354	-0.83224538	-1.81114697	H	5.12011518	-3.36909921	1.66158340
H	-1.54676882	-3.24465241	2.70540304	H	3.92400269	-3.15198643	-2.48216565
C	-1.15735506	-2.22008310	2.52989554	H	5.42241756	-4.08186042	-0.71341209
C	-0.16120992	-1.88625561	3.65740513	H	0.49140107	1.32823920	-3.44788306
C	-0.71254680	-2.17748266	5.05213650	C	0.66765413	1.16871376	-2.36589248
O	-0.46753646	-2.23867374	1.29760214	C	0.73195918	2.52536566	-1.66001802
H	-2.01559297	-1.52456495	2.55768529	C	1.68916193	3.50263885	-2.34199876
O	1.02817150	-2.65034235	3.46199070	O	-0.45433582	0.44725474	-1.85121379
H	1.03342956	-2.79089293	2.48850281	H	1.62230425	0.62962129	-2.24082094
O	-1.82606967	-1.33624536	5.37461328	O	-0.56667698	3.11513992	-1.63294584
H	-1.49349232	-0.42339147	5.36167011	H	-1.16597514	2.34209560	-1.59520259
H	-1.08456029	-3.21298526	5.09792444	O	3.04047746	3.03185436	-2.32863110
H	0.10853288	-2.08391688	5.78961798	H	3.31085928	2.98503334	-1.39684686
H	0.07748193	-0.79829429	3.60293087	H	1.41061513	3.61267279	-3.40156776
C	-3.45196925	-0.81573408	-0.42254772	H	1.58628944	4.49581601	-1.86391485
C	-4.54684626	-0.10195460	-0.94385546	H	1.09172711	2.35283411	-0.61920988

Table S4l: Optimized XYZ coordinates for complex **9c**

H	0.01931732	0.21333086	-1.97537900	C	-5.14810323	2.37852950	0.22669479
H	0.33199021	1.09222187	-1.63577433	C	-3.24155515	1.55514457	-1.75935509
H	2.58420780	1.64083658	-1.53289670	C	-5.38893970	2.55302720	-1.13852960
C	2.08478468	2.25155772	-0.75217812	C	-4.45297498	2.14860499	-2.11488452
C	2.28826089	3.73487751	-1.07572413	H	-5.87658419	2.69336103	0.97667288
C	3.75532219	4.10070895	-1.29910251	H	-6.32568007	3.01517513	-1.45690586
O	0.67903210	2.00996204	-0.73713996	H	-4.68481966	2.30539311	-3.17014894
H	2.55034347	2.00952945	0.21930854	H	-2.50767494	1.23540249	-2.50081821
O	1.57067705	4.07868309	-2.25885732	N	3.25380904	-1.61552958	1.77118256
H	0.71118926	3.62984698	-2.13944289	C	3.84561433	-1.86192390	0.54138744
O	4.55002308	3.89887170	-0.12585661	C	5.06114926	-2.45219074	0.18115099
H	4.19747473	4.49994456	0.55096151	C	3.22062208	-1.46875415	-1.79673402
H	4.18538497	3.45189195	-2.07787403	C	4.43141844	-2.05844974	-2.15724018
H	3.80705799	5.14437693	-1.66531506	C	5.33590873	-2.54042621	-1.18537180
H	1.90708516	4.32752709	-0.21055853	H	2.50787493	-1.09870774	-2.53543808
C	-1.14819672	0.41444135	2.49709749	H	4.68817533	-2.15346604	-3.21405352
C	-1.16601661	0.38049933	3.89799917	H	6.27402819	-2.99535419	-1.50963048
C	-0.06112364	-0.13035674	4.58945913	H	5.76383375	-2.82802171	0.92754713
C	1.04897247	-0.61429715	3.87697539	H	-3.79514040	1.61777274	2.71739731
C	1.03651483	-0.56818963	2.47988633	H	3.63185281	-1.86361447	2.67849941
H	-2.03909188	0.74145466	4.44591811	H	-2.13779328	-1.71112197	-1.81321339
H	-0.06608385	-0.16249777	5.67954800	C	-1.98388811	-2.15383487	-0.80305842
H	1.90715985	-1.02957724	4.40930955	C	-2.10794714	-3.68003796	-0.91609970
C	2.03848262	-1.01224863	1.54453849	C	-3.37043248	-4.12770854	-1.63804654
C	-2.14338849	0.88497003	1.57934551	O	-0.68033495	-1.90257054	-0.32327939
C	2.92948608	-1.37032371	-0.42915323	H	-2.77430326	-1.75955180	-0.13595793
C	-2.98328347	1.37439625	-0.39464197	O	-0.99445904	-4.18740270	-1.65103114
N	1.82561811	-0.84120748	0.21957527	H	-0.26765034	-3.59848240	-1.35895230
N	-0.04105658	-0.03904957	1.79774146	O	-4.49698680	-3.75423205	-0.83388196
N	-1.88841737	0.81424675	0.24681062	H	-5.29140461	-3.98750819	-1.33716826
Ru	-0.04126821	-0.00139112	-0.16806567	H	-3.39714505	-3.64895806	-2.63763135
N	-3.37492866	1.46099544	1.80865101	H	-3.31362165	-5.22428064	-1.78529589
C	-3.93302313	1.78378041	0.58183361	H	-2.12348312	-4.10244401	0.11143094

Table S4m: Optimized XYZ coordinates for complex **6a+H_2**

C	0.49340484	1.62744777	1.95723309	H	1.27728870	0.06583923	-4.16221787
C	0.82040410	1.76775822	3.31045179	H	3.32814999	-0.20660621	-2.47965847
C	1.06061657	0.63493760	4.09917003	C	2.72782062	-0.50310552	-1.59498836
C	0.96865057	-0.64468240	3.53297252	C	3.58969861	-0.31059038	-0.34087961
C	0.64603671	-0.78909736	2.17904145	C	4.93402338	-1.03307351	-0.42067789
H	0.88056137	2.77075203	3.73728505	O	1.61698629	0.36882409	-1.54131800
H	1.31350225	0.74830974	5.15392299	H	2.45249941	-1.56529497	-1.71360464
H	1.14304986	-1.53923114	4.13412814	O	3.83344158	1.08112775	-0.14880985
C	0.49701382	-1.98526475	1.41437186	H	3.02444957	1.49924718	-0.50971801
H	0.63683113	-2.96311410	1.88571952	O	4.78224498	-2.45954509	-0.40298229
C	0.18345711	2.63355902	0.99434404	H	4.43062628	-2.68986505	0.47272911
H	0.17656315	3.69142012	1.27274734	H	5.43740682	-0.79003404	-1.36932836
C	0.02730537	-3.12343581	-0.67623168	H	5.58046973	-0.67535833	0.40292585
C	1.32478412	-3.95982789	-0.61594003	H	3.02512648	-0.72254987	0.52849215
H	1.48297100	-4.38177378	0.38922984	C	-0.71887897	2.48547073	-2.59220885
H	1.24843064	-4.80563251	-1.31615973	H	0.20490992	1.97199190	-2.89513253
H	2.21569812	-3.37348484	-0.88373506	H	-1.52341455	1.74205046	-2.48871713
C	-0.27345266	-2.70912386	-2.12311380	H	-1.00161481	3.19918556	-3.38132671
H	-1.18880321	-2.09992433	-2.17104481	C	-1.13843042	-3.97093781	-0.12355951
H	0.55110923	-2.12219603	-2.55239523	H	-0.95631828	-4.27593190	0.91847843
H	-0.42251491	-3.60267208	-2.74816495	H	-2.09199314	-3.42840035	-0.16267986
C	-0.50699831	3.23226904	-1.26794904	H	-1.24068663	-4.88745019	-0.72497930
C	-1.82616003	3.90126159	-0.83043129	H	-2.64970549	-1.31588436	0.76810008
H	-1.70228062	4.47949329	0.09837301	C	-2.94625430	-0.82717694	-0.18200155
H	-2.17458378	4.59108209	-1.61459237	C	-4.30788300	-0.14235874	0.01613109
H	-2.60540770	3.14219475	-0.66633174	C	-5.33985207	-1.06815436	0.65829386
C	0.61462056	4.27542271	-1.43907957	O	-2.03119260	0.19104829	-0.53315379
H	0.78701826	4.85606697	-0.51993159	H	-3.03426471	-1.60893797	-0.96047600
H	1.55640965	3.78190453	-1.72214735	O	-4.14259355	1.00070799	0.85200528
H	0.34328626	4.98501694	-2.23575148	H	-3.23569951	1.29773726	0.62429968
N	0.18227705	-1.86050217	0.13285928	O	-5.57931529	-2.24044379	-0.12897289
N	0.42137798	0.34679196	1.40286598	H	-5.96818621	-1.93901804	-0.96656997
N	-0.10948760	2.22393698	-0.23275134	H	-4.95760011	-1.42143066	1.62861439
Ru	-0.03495753	0.16917970	-0.41487754	H	-6.26896539	-0.49826998	0.85182813
H	1.28905757	-0.08501262	-4.90072829	H	-4.68189123	0.17078535	-0.98681117

Table S4n: Optimized XYZ coordinates for complex **6b+H_2**

C	-1.59432984	0.25835668	2.31398523	C	1.92318150	-3.11662147	0.92990560
C	-1.71566835	0.66688357	3.64736206	C	3.33225682	-3.70976244	0.99510898
C	-0.64570642	1.30148082	4.29381226	O	0.32262182	-1.91222368	-0.42279239
C	0.55517674	1.53245908	3.60878670	H	1.70169124	-3.20642905	-1.21471363
C	0.68920353	1.13168772	2.27347215	O	1.81417570	-2.18395745	2.00946398
H	-2.65526441	0.48174964	4.17147195	H	0.94510485	-1.75874791	1.89447403
H	-0.74689164	1.61214327	5.33429290	O	3.53867740	-4.73084515	0.01716900
H	1.39884541	2.01855407	4.10235960	H	2.92036296	-5.44982244	0.22812385
C	1.80738412	1.26562876	1.40966812	H	4.07376015	-2.92435958	0.77930650
H	2.72600142	1.75454534	1.74296958	H	3.51499783	-4.07084452	2.02566020
C	-2.54090904	-0.40157628	1.48636379	H	1.18427139	-3.93877874	1.06248687
H	-3.54596953	-0.64928459	1.83750428	C	-3.00834269	-1.37897174	-0.64316681
N	1.67645721	0.79043115	0.16716621	C	-3.82232707	-2.43948801	-0.20078173
N	-0.38979537	0.50571761	1.63740067	C	-3.01608581	-1.01286370	-2.00251719
N	-2.15360075	-0.67490189	0.23590142	C	-4.64422313	-3.11153430	-1.10820929
Ru	-0.22626530	-0.03035398	-0.16438362	H	-3.77335727	-2.76152043	0.84173649
H	-0.84921089	-3.73381499	-1.69711979	C	-3.84977830	-1.68519378	-2.89683606
H	-1.03580824	-4.34160383	-2.10408018	H	-2.38364031	-0.18096805	-2.32169762
H	-0.72096470	3.10992376	-2.46168578	C	-4.66558687	-2.73569525	-2.45650082
C	-0.38000643	2.72674979	-1.47895573	H	-5.25989631	-3.94508375	-0.76205373
C	-0.96616255	3.61512355	-0.37381663	H	-3.86095158	-1.38803113	-3.94800138
C	-0.66370435	5.09900892	-0.58029752	H	-5.30721445	-3.26651033	-3.16312433
O	-0.91617922	1.41924344	-1.34267112	C	2.77083171	0.82564081	-0.72971319
H	0.72286166	2.76527251	-1.45379969	C	2.49843858	0.81397173	-2.11192755
O	-2.38002467	3.44976281	-0.32366490	C	4.11334683	0.81890590	-0.29598516
H	-2.50907052	2.51729444	-0.59221444	C	3.54339568	0.83929066	-3.03663100
O	0.73801283	5.38020470	-0.51588513	H	1.45745309	0.78969897	-2.44297869
H	1.02432344	5.15519621	0.38467634	C	5.15132567	0.83762133	-1.22920915
H	-0.99526274	5.40902439	-1.58354754	H	4.34441169	0.74942742	0.76867283
H	-1.24330904	5.68497877	0.15898684	C	4.87387692	0.85692681	-2.60166830
H	-0.50762793	3.29480023	0.59224700	H	3.31528403	0.83942015	-4.10466063
H	2.40887504	-1.67907197	-0.61741409	H	6.18641867	0.81763830	-0.88052244
C	1.63568043	-2.44349219	-0.41746948	H	5.69020612	0.86686291	-3.32675081

Table S4o: Optimized XYZ coordinates for complex **6c+H_2**

H	-1.44813314	-2.44629572	-4.80744797	C	5.32022068	-2.01916438	0.26406322
H	-1.39092973	-2.84645049	-4.16914931	C	3.32525966	-1.59637428	-1.75935887
H	-2.39723744	-1.85871709	-1.39979886	C	5.54829741	-2.35728932	-1.07291371
C	-1.82210887	-2.37569949	-0.60251033	C	4.56862019	-2.15023579	-2.06708922
C	-1.78395729	-3.87508575	-0.92240030	H	6.08294872	-2.18094346	1.02848071
C	-3.16177764	-4.47002667	-1.20609195	H	6.50922955	-2.79337787	-1.35350711
O	-0.47454600	-1.94002482	-0.55903621	H	4.79003894	-2.43144735	-3.09847436
H	-2.34513409	-2.20926682	0.35774965	H	2.55994001	-1.43476295	-2.52041161
O	-0.95905645	-4.09473683	-2.06857735	N	-3.33506902	1.60064748	1.48873195
H	-0.22065420	-3.46686106	-1.92608206	C	-3.95266805	1.63156053	0.24672708
O	-4.01940804	-4.41439169	-0.06148617	C	-5.21519632	2.06747266	-0.16579870
H	-3.59342500	-4.95123904	0.62703038	C	-3.31805490	0.98046644	-2.03070459
H	-3.66480336	-3.88894853	-1.99464122	C	-4.57826992	1.41565172	-2.44318137
H	-3.03081866	-5.50359203	-1.58162445	C	-5.50977398	1.94853546	-1.52710699
H	-1.34575746	-4.39965320	-0.04153029	H	-2.58626177	0.57760823	-2.73268375
C	1.24205042	-0.02149410	2.35112878	H	-4.85081190	1.34535250	-3.49797196
C	1.27693652	0.21478904	3.72504444	H	-6.48565239	2.27815010	-1.88940083
C	0.16256419	0.76215305	4.37920928	H	-5.93999883	2.48196589	0.53782121
C	-0.98782278	1.06963326	3.63798811	H	3.97097254	-1.01010195	2.66732226
C	-1.02390588	0.83643023	2.26307017	H	-3.72718753	1.93618731	2.36091177
H	2.17985220	-0.02974045	4.28929680	H	1.84433216	2.73219375	-2.34028923
H	0.19086178	0.94679399	5.45290673	C	1.81598814	2.12079625	-1.41486806
H	-1.86334801	1.49508401	4.13393315	C	2.08829559	3.03803481	-0.21333366
C	-2.07425346	1.06975654	1.32501865	C	3.35005918	3.87558218	-0.36013368
C	2.24579406	-0.56544948	1.49282248	O	0.49809597	1.61068398	-1.29548039
C	-3.00771913	1.08975332	-0.66860075	H	2.59188448	1.33830818	-1.48976742
C	3.07985256	-1.25233598	-0.42333089	O	0.98583676	3.92963673	-0.05272897
N	-1.86067472	0.74053491	0.02611007	H	0.23374689	3.40151692	-0.39586927
N	0.09216686	0.29027962	1.60389904	O	4.47308178	2.98655259	-0.29225011
N	1.96470613	-0.68598512	0.17191394	H	5.26140117	3.50738702	-0.50714276
Ru	0.04295181	-0.03522207	-0.26576112	H	3.31000551	4.42117280	-1.32424796
N	3.51515523	-1.02679196	1.76240394	H	3.36736626	4.62488665	0.45564687
C	4.07414258	-1.46548268	0.57161342	H	2.20506002	2.39683655	0.68788769

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