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Microwave Assisted Pincer-Ruthenium Catalyzed Guerbet Reaction for the Upgradation of Bio-Ethanol to Bio-Butanol

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1. Experimental Section

General Methods and Materials. All manipulations were carried out under purified Ar using a standard double manifold or a glove box. The solvents such as tetrahydrofuran (THF), hexane and toluene were dried via double distillation over Na/Benzophenone prior to the experiment.[1-2] Ethanol, methanol and isopropanol were dried and distilled under argon according to literature procedure.[1-2] All other compounds including pryidine-2,6-dicarboxylic acid, 4-Hydroxypyridine-2,6-dicarboxylic acid, *o*-penylenediamnine, $[RuCl_2(p\text{-cymene})]_2$, Al_2O_3 SiO_2, $MgSiO_3$, DMSO-d_6 and $CDCl_3$ were purchased either from MERCK or Sigma-Aldrich and used as such. The complexes **1a-d**, **2a-d**, **4a** and **5a** were prepared according to the literature procedure.[3-6]

Physical Measurements. ^1H, ^{13}C, ^{31}P NMR were recorded either on Bruker ASCEND 600 operating at 600 MHz for ^1H, 150 MHz for ^{13}C, 564 MHz for ^{31}P or on Bruker AVANCE 400 operating at 400 MHz for ^1H, 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. Fourier Transform Infrared (FT-IR) were recorded on Perkin Elmer Spectrum Two FT-IR spectrometer at room temperature with the region 400-4000 cm^{-1}. All microwave reactions were performed using a CEM Discover microwave system unit (operating at 110 V, microwave irradiation of 2.45 GHz, maximum microwave output of 300 W) in a 10 mL microwave tube. GC analyses (FID detection) were performed on a Agilent 8860-GC instrument fitted with Agilent Front SSL inlet N2 HP-5 the column (30 m length ´ 0.32 mm ID) using the following method: Agilent 8860-GC Detector, Oven temperature 60-300 °C, Time at starting temp: 0 min, Final time = 10 min, Flow rate (carrier): 1 mL/min (N2), Split ration: 250, Inlet temperature: 250 °C, Detector temperature: 300 °C. H_2 gas analysis (TCD detection) was performed on a Agilent 7820-GC instrument fitted with Agilent Front SSZ Inlet N2 HP-PLOT Q column (30 m length ´ 0.53 mm ID) using the following method: Agilent 7820-GC Detector, Oven temperature 40 °C, Time at starting temp: 0 min, Hold time = 10 min, Flow rate (carrier): 1 mL/min (N2), Split ration: 50, Inlet temperature: 40 °C, Detector temperature: 250 °C. The GC samples for the calibration curve calculations and all the analysis of GC samples were performed according to the protocol reported in literature.[5, 7-8] XPS analysis was carried out in ULVAC-PHI measurement in PHI 5000 VersaProb III scanning XPS microprobe.

Synthesis of 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridin-4-ol (C): To a two-necked round bottom flask (100 mL) containing 4-Hydroxypyridine-2,6-dicarboxylic acid (0.2 g, 1.09 mmol) and *o*-phenylenediamine (0.236g, 2.18 mmol), orthophosphoric acid (20 mL) was added. The reaction mixture was heated overnight at 150 °C. A bluish green precipitate was obtained to which sodium bicarbonate solution (10 mL) was added. The residue was filtered and washed with water (10 mL). The product was crystallized in methanol to obtain 0.195 g of an off-white solid in 55% yield. ^1H NMR (600 MHz, DMSO-d_6) δ = 13.10 (s, 2H), 7.70-7.64 (m, 4H), 7.43 (d, J = 19.7 Hz, 2H), 7.22 (d, J = 14.1 Hz, 4H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 169.74, 166.40, 166.05, 165.21, 150.64, 149.91, 149.23, 148.80, 122.94, 112.49, 111.16, 108.76. HRMS (ESI): *m/z* calculated for $[C_{19}H_{14}N_5O]^+$ Calculated = 328.1198, Found = 328.1187.

Synthesis of [(*p*-OH$^{Bim^2}$NNN)RuCl](PPh$_3$)$_2$]Cl (4b). To a two-necked round bottom flask (25 mL) containing 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridin-4-ol (0.093g, 0.28 mmol) and $RuCl_2(PPh_3)_3$ (0.270 g, 0.28 mmol), dry THF (5mL) was added under argon atmosphere. The reaction mixture was then refluxed for 12 h under argon. During the reaction, the color of the reaction mixture changed from brown to light pink. Subsequently, the solvent was evaporated under reduced pressure to obtain a dark green colored gel. The residue was washed with dry diethyl ether (3 x 5 mL) followed by hexane (3 x 5 mL). A green color solid (0.23 g) was

obtained in 79 % yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.68 (dd, J = 12.0, 7.4 Hz, 4H), 7.55 (t, J = 7.4 Hz, 2H), 7.47 (dt, J = 8.0, 4.0 Hz, 4H), 7.38 – 6.17 (m, 24H). ^{31}P NMR (243 MHz, $CDCl_3$) δ = 29.81. HRMS (ESI): *m/z* calculated for $[C_{57}H_{45}N_6P_2ORu]^+$ Calculated = 993.2205, Found = 993.2131

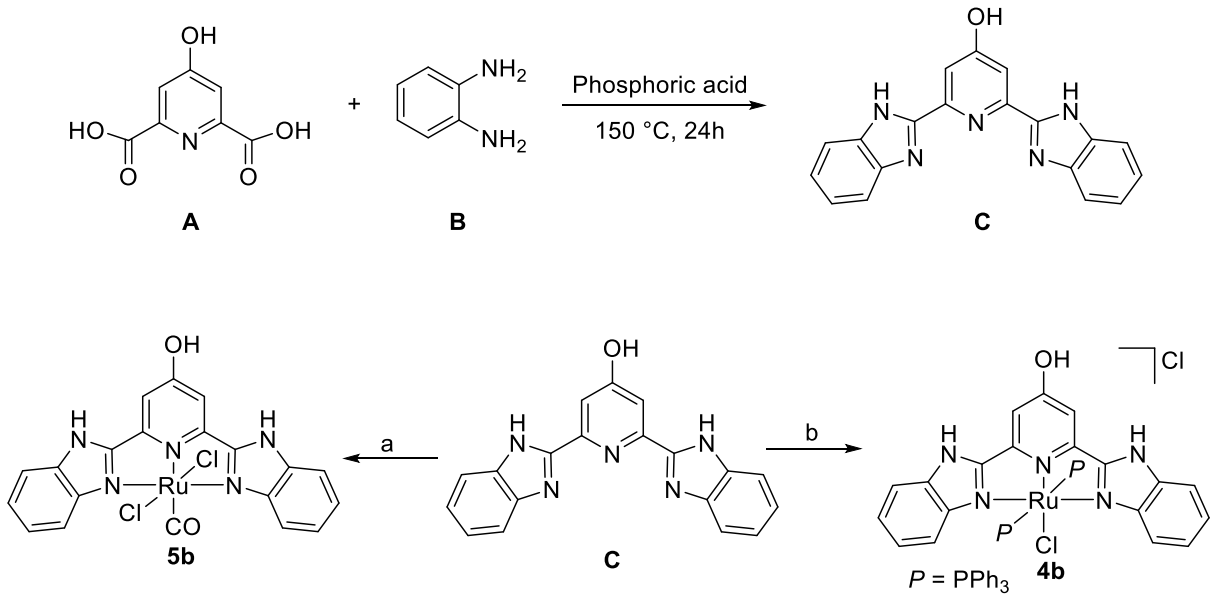
Synthesis of (*p*-OH^{Bim2}NNN)RuCl$_2$(CO) (5b). To a two-necked round bottom flask (25 mL) containing 2,6-bis(1H-benzo[d]imidazol-2-yl)pyridin-4-ol (0.05g, 0.15 mmol) and [RuCl$_2$(*p*-cymene)]$_2$ (0.047g, 0.08 mmol), dry THF (5mL) was added under argon atmosphere. The reaction mixture was then refluxed for 2 h under argon. Subsequently, an atmosphere of CO was introduced and the reaction mixture was further heated for another 10 h. During the reaction, the color of the reaction mixture changed from pink to brown color. Then the solvent was evaporated under reduced pressure to obtain a dark brown colored gel. The residue was washed with dry diethyl ether (3 x 5 mL) followed by hexane (3 x 5 mL). A yellowish brown color solid (0.07g) was obtained in 86 % yield. Low solubility posed challenges in NMR characterization. IR (cm^{-1}): ν = 3049. 2068, 1958, 1611, 1450, 1409, 1372, 1257, 1228, 1096, 1022, 866, 800, 734, 619, 543, 449, 422. HRMS (ESI): *m/z* calculated for $[C_{20}H_{13}N_5O_2ClRu]^+$ Calculated = 491.9833, Found = 491.9790.

General procedure for the Guerbet application reaction. A 10 mL microwave vial was charged with NaOEt (10 mol %) (0.116 g, 1.71 mmol) and **5b** (0.0013 g, 2.5 μmol) inside the glove box. This was followed by addition of dry ethanol (1 mL, 17.12 mmol) and dry toluene (50 μL) as an internal standard. The reaction mixture was heated at 110 °C under microwave conditions at an operating power of 75 W. At regular intervals about 20 μL of the sample was collected and analyzed by GC. The product was analyzed by GC analysis.

General syntehsis procedure for heterogenization.
A 10 mL schlenk flask was charged with solid support (Al2O3, SiO2 and MgSiO3) (300 mg) and the catalyst (15 mg, 5 % wt./wt.) inside the glovebox. Then KOH (4 mg) was introduced followed by addition of dry toluene (5 mL). The reaction mixture was then srtirred for two days under argon. The immobilization of the complex onto the solid was confirmed by its coloration and the concomitant decoloration of the solution. The excess solvent was decanted and the solid was washed by toluene (5mL). The solid was then dried under vaccum piror to its use in caytalysis.

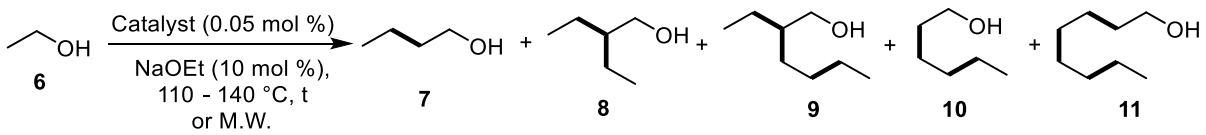
Computational details

The geometries of all the considered complexes were fully optimized using the DFT (PBEPBE)[9] method on the Gaussian-16 program package.[10] The LANL2DZ[11-13] and 6-311G(d,p) basis set with a polarization function were used respectively for the metal (Ru) and non-metal atoms. The empirical dispersion-GD3 was used in all molecular geometry optimization and energy computations. The transition states were located using the synchronous transit-guided quasi-Newton (QST2) Genecp (gen keyword with the effective core potential) was included to define the basis set. Method and basis set was selected on the basis of previous reports on pincer complexes. Frequency calculations characterize the obtained stationary points as minima structures or transition states based on the number of imaginary frequencies. Single point calculations were performed to calculate the relative free energy values at 110 °C.



a = $RuCl_2(PPh_3)_3$, THF at 70 °C, 12h
b = $[RuCl_2(p\text{-cymene})]_2$, at 70 °C for 2h, followed by another 10h under CO (1bar)

Scheme S1: Syntehsis of ligand and it's complexes.



Scheme S2: Upgradation of ethanol catalyzed by Pincer-Ru under conventional and microwave heating.

Table S1: Upgradation of ethanol catalyzed by **5a** under conventational and microwave heating.[a]

Entry	T (°C)	Time (min)	Yield(%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	140	30	8.1	0.2	0.0	0.1	0.0	8.4	98	336
		120	25.7	1.5	0.7	3.9	0.8	32.6	78	1320
		4320	36.3	3.5	2.0	8.0	2.7	52.5	69	2100
2	130	30	2.7	0.0	0.0	0.0	0.0	2.7	100	110
		120	6.5	0.0	0.0	0.0	0.0	6.5	100	260
		4320	29.6	5.7	0.5	4.1	0.4	40.3	73	1614
3	120	30	2	0.0	0.0	0.0	0.0	2	100	80
		120	6.0	0.0	0.0	0.0	0.0	6.0	100	240
		4320	29.6	2.8	0.0	3.1	0.0	35.4	84	1416
4	110	30	0.9	0.0	0.0	0.0	0.0	0.9	100	37
		120	3.8	0.0	0.0	0.0	0.0	3.8	100	152
		4320	21.7	2.8	0.0	0.9	0.0	25.4	85	1014
5[f]	110	30	10.9	1.4	0.0	2.1	0.0	14.4	79	580
		120	27.9	6.0	3.1	10.2	2.8	50.0	56	2000
6[f]	100	30	0.7	0	0	0	0	0.7	100	30
		120	2.0	0	0	0	0	2.0	100	80
7[g]	110	30	1.3	0.0	0.0	0.0	0.0	1.3	100	55
		120	7.1	0.4	0.2	0.5	0.1	8.2	88	330
8[h]	110	30	6.2	0.7	0.0	1.4	0.0	8.4	75	335
		120	19.9	3.2	1.5	4.6	1.2	30.4	67	1215
9[i]	110	30	11.8	0.9	0.2	1.6	0.0	14.5	86	580
		120	29.0	3.9	1.1	5.2	1.0	40.1	73	1600

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), NaOEt (10 mol %) and **5a** (0.025 mol%) at T °C. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/**5a** loading. [f]Under 75 W microwave. [g]Under 50 W microwave. [h]Under 65 W microwave. [i]Under 90 W microwave.

Table S2: Upgradation of ethanol catalyzed by **5a** in the presence of various bases.[a]

Entry	Base (X mol%)	Time (min)	Yield (%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	NaOEt	30	10.9	1.4	0.0	2.1	0.0	14.4	79	580
	10.0	120	27.9	6.0	3.1	10.2	2.8	50.0	56	2000
2	NaO^{t}Bu	30	2.0	0.0	0.0	0.0	0.0	2.0	100	80
	10.0	120	9.1	1.9	0.9	1.7	0.8	14.4	71	580
3	KO^{t}Bu	30	7.9	0.4	0.0	0.4	0.0	8.8	90	360
	10.0	120	34.5	3.9	1.1	6.5	0.2	46.1	74	1845
4	NEt_3	30	0.0	0.0	0.0	0.0	0.0	0.0	--	--
	10.0	120	0.0	0.0	0.0	0.0	0.0	0.0	--	--
5	Na_2CO_3	30	0.0	0.0	0.0	0.0	0.0	0.0	--	--
	10.0	120	0.0	0.0	0.0	0.0	0.0	0.0	--	--
6	K_2CO_3	30	0.4	0.0	0.0	0.0	0.0	0.4	100	20
	10.0	120	4.0	0.0	0.0	0.0	0.0	4.0	100	160
7	NaOH	30	9.8	0.8	0.1	2.2	0.0	12.9	77	520
	10.0	120	21.8	2.2	0.5	4.2	0.3	29.1	76	1160
8	KOH	30	11.6	0.0	0.0	0.0	0.0	11.6	100	480
	10.0	120	18.1	1.0	0.0	1.4	0.0	20.5	90	800
9	NaOEt	30	5.2	0.0	0.0	0.1	0.0	5.4	100	215
	2.5	120	19.5	1.1	0.1	2.3	0.4	23.3	83	930
10	NaOEt	30	2.1	0.0	0.0	0.0	0.0	2.1	100	80
	5.0	120	20.3	1.2	0.1	2.3	0.4	24.3	83	970
11	NaOEt	30	4.4	0.2	0.0	0.6	0.0	5.3	80	210
	7.5	120	29.0	2.1	0.8	3.8	0.7	36.4	81	1455
12	NaOEt	30	2.4	0.3	0.0	0.3	0.0	2.9	67	120
	20	120	8.1	0.5	0.2	0.7	0.0	9.5	89	380

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), base (X mol %) and **5a** (0.025 mol%) at 110 °C under 75 W microwave. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/**5a** loading.

Table S3: Upgradation of ethanol at various loading of **5a**.[a]

Entry	**5a** (Y mol %)	Time (min)	Yield (%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	0.025	30	10.9	1.4	0.0	2.1	0.0	14.4	79	580
		120	27.9	6.0	3.1	10.2	2.8	50.0	56	2000
2	0.050	30	13.8	0.7	0.1	1.5	0.0	16.1	88	320
		120	34.4	4.9	3.1	6.3	2.3	51.0	67	1020
3	0.075	30	14.9	1.0	0.2	0.7	0.1	16.9	88	230
		120	40.4	5.7	2.4	10.2	2.4	61.0	66	815
4	0.100	30	12.6	0.9	0.0	1.3	0.0	14.8	87	150
		120	41.1	10.2	2.5	12.8	2.1	68.7	59	690
5	0.500	30	15.2	1.2	0.2	1.1	0.0	17.7	86	35
		120	41.3	9.2	5.1	10.6	4.6	70.7	57	142
6	1.000	30	18.2	1.2	0.3	1.0	0.2	20.9	87	21
		120	42.0	10.1	3.7	10.8	5.2	71.8	57	72

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), NaOEt (10 mol %) and **5a** (Y mol %) at 110 °C under 75 W microwave. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/**5a** loading.

Table S4: Pincer-ruthenium catalyzed ethanol upgradation.[a]

Entry	Catalyst	Time (min)	Yield of **7** (%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	**2a**	30	3.8	0.0	0.0	0.0	0.0	3.8	100	160
		120	4.4	0.0	0.0	0.0	0.0	4.4	100	180
2	**2b**	30	3.1	0.0	0.0	0.0	0.0	3.1	100	120
		120	5.8	0.0	0.0	0.0	0.0	5.8	100	230
3	**2c**	30	2.7	0.0	0.0	0.0	0.0	2.7	100	105
		120	4.4	0.0	0.0	0.0	0.0	4.4	100	180
4	**2d**	30	1.8	0.1	0.0	0.1	0.0	2.0	100	80
		120	4.7	0.9	0.0	0.7	0.0	6.3	83	250
5	**5a**	30	10.9	1.4	0.0	2.1	0.0	14.4	79	580
		120	27.9	6.0	3.1	10.2	2.8	50.0	56	2000
6	**5b**	30	7.7	0.0	0.0	0.0	0.0	7.7	100	310
		120	45.0	5.0	0.2	9.7	1.7	61.5	74	2440
7	**1a**	30	3.1	0.0	0.0	0.0	0.0	3.1	100	125
		120	5.1	0.0	0.0	0.0	0.0	5.1	100	205
8	**1b**	30	5.0	0.0	0.0	0.0	0.0	5.0	100	205
		120	9.6	1.5	0.0	1.1	0.0	12.2	83	490
9	**1c**	30	4.7	0.0	0.0	0.0	0.0	4.7	100	190
		120	6.2	0.0	0.0	0.0	0.0	6.2	100	250
10	**1d**	30	2.3	0.0	0.0	0.0	0.0	2.3	100	90
		120	4.0	0.0	0.0	0.0	0.0	4.0	100	160
11	**4a**	30	7.7	0.7	0.0	0.9	0.0	9.4	89	375
		120	27.0	2.4	0.9	5.0	0.5	35.8	75	1430
12	**4b**	30	7	1	0.0	1	0.0	9	78	380
		120	27.1	1.3	0.3	2.5	0.1	31.4	87	1255

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), NaOEt (10 mol %) **1a-d, 2a-d, 4a-b** and **5a-b** (0.025 mol %) at 110 °C under 75 W microwave. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/catalyst loading.

Table S5. Upgradation of ethanol by **5a** and **5b** heterogenized on versions solid supports.[a]

Entry	Catalyst /Support	Time (min)	Yield (%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	**5a**	30	2.8	0.0	0.0	0.0	0.0	2.8	100	1245
		120	22.8	2.0	0.0	4.5	0.0	29.3	78	13022
2	**5a**/Neutral Alumina	30	4.2	0.0	0.0	0.0	0.0	4.2	100	1867
		120	6.9	0.7	0.1	1.2	0.3	9.2	75	4090
3	**5a**/Acidic Alumina	30	2.7	0.0	0.0	0.0	0.0	2.7	100	1080
		120	5.2	0.2	0.0	0.4	0.0	5.8	90	2580
4	**5a**/Basic Alumina	30	1.2	0.0	0.0	0.0	0.0	1.2	100	533
		120	4.6	0.2	0.0	0.3	0.0	5.1	92	2265
5	**5a**/Silica	30	2.2	0.0	0.0	0.0	0.0	2.2	100	975
		120	9.1	0.3	0.0	0.5	0.0	9.9	92	4400
6	**5a**/Florisil	30	2.1	0.0	0.0	0.0	0.0	2.2	95	980
		120	9.1	0.2	0.0	0.4	0.0	9.7	93	4310
7	**5b**	30	5.2	0.0	0.0	0.0	0.0	5.2	99	2310
		120	25.4	1.9	0.0	1.3	0.0	28.6	89	12710
8	**5b**/Neutral Alumina	30	6.2	0.2	0.0	2.9	0.0	9.3	67	4135
		120	13.0	0.7	0.0	5.8	0.0	19.6	66	8710
9	**5b**/Acidic Alumina	30	5.6	0.0	0.0	0.0	0.0	5.6	100	2489
		120	26.8	3.4	0.0	4.8	0.0	34.9	77	15510
10	**5b**/Basic Alumina	30	2.6	0.1	0.0	0.1	0.0	2.7	96	1200
		120	5.8	0.4	0.0	0.3	0.0	6.4	90	2845
11	**5b**/Silica	30	6.2	0.1	0.0	0.2	0.0	6.5	95	2890
		120	21.2	2.0	0.3	3.2	0.9	27.7	76	12310
12	**5b**/Florisil	30	2.9	0.0	0.0	0.0	0.0	2.9	100	1290
		120	9.6	0.8	0.0	0.5	0.0	10.9	88	4845
13[f]	Alumina Silica Florisil	120	0.0	0.0	0.0	0.0	0.0	0.0	--	--

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), NaOEt (10 mol %) **5a-b** (0.00225 mol %) at 110 °C under 75 W microwave. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/**5a-b** loading. [f]No Catalyst.

Table S6. Upgradation of ethanol by **4a** and **4b** heterogenized on versions solid supports.[a]

entry	Catalyst /Support	Time (min)	Yield of (%)[b]					Conversion of **6** (%)[c]	Selectivity of **7** (%)[d]	Total TON[e]
			7	**8**	**9**	**10**	**11**			
1	**4a**	30	9.0	0.5	0.0	0.7	0.0	10.1	90	4489
		120	19.1	2.8	1.2	2.5	1.3	26.9	71	11955
2	**4a**/Neutral Alumina	30	7.7	0.0	0.0	0.0	0.0	7.7	100	3380
		120	23.5	0.0	0.0	0.8	0.0	24.3	97	10800
3	**4a**/Acidic Alumina	30	trace	0.0	0.0	0.0	0.0	trace	--	--
		120	3.0	0.0	0.1	0.0	0.0	3.1	98	1375
4	**4a**/Basic Alumina	30	2.5	0.0	0.0	0.0	0.0	2.5	100	1110
		120	9.2	1.1	0.0	1.4	0.0	11.7	78	5200
5	**4a**/Silica	30	6.7	0.0	0.0	0.0	0.0	6.7	100	2978
		120	17.8	2.0	0.1	3.4	0.2	23.5	76	10445
6	**4a/**Florisil	30	5.2	0.3	0.0	0.5	0.0	6.0	86	2660
		120	15.2	2.1	0.4	2.5	0.5	20.7	73	9200
7	**4b**	30	5.8	0.3	0.0	0.4	0.0	6.5	89	2889
		120	19.7	1.6	0.5	1.7	0.6	24.1	82	10711
8	**4b**/Neutral Alumina	30	1.8	0.0	0.0	0.1	0.0	1.9	94	845
		120	6.2	0.5	0.0	0.5	0.0	7.1	87	3155
9	**4b**/Acidic Alumina	30	0.5	0.0	0.0	0.0	0.0	0.5	100	230
		120	1.0	0.0	0.0	0.0	0.0	1.0	100	444
10	**4b**/Basic Alumina	30	3.6	0.3	0.0	0.3	0.0	4.3	86	1865
		120	12.1	2.4	0.0	2.8	0.0	17.2	70	7645
11	**4b**/Silica	30	0.6	0.0	0.0	0.0	0.0	0.6	100	266
		120	2.2	0.0	0.0	0.0	0.0	2.2	100	978
12	**4b/**Florisil	30	0.6	0.0	0.0	0.0	0.0	0.6	100	270
		120	1.3	0.0	0.0	0.0	0.0	1.3	100	580

[a]Reaction condition: ethanol (1 mL, 17.12 mmol), NaOEt (10 mol %) **4a-b** (0.00225 mol %) at 110 °C under 75 W microwave. [b]Yield was determined by GC analysis using toluene as an internal standard. [c]Conversion was determined by GC analysis using toluene as an internal standard. [d]Selectivity = Yield of *n*-butanol/Conversion. [e]Total TON = Total yield of upgraded products/**4a-b** loading.

NMR and HRMS data

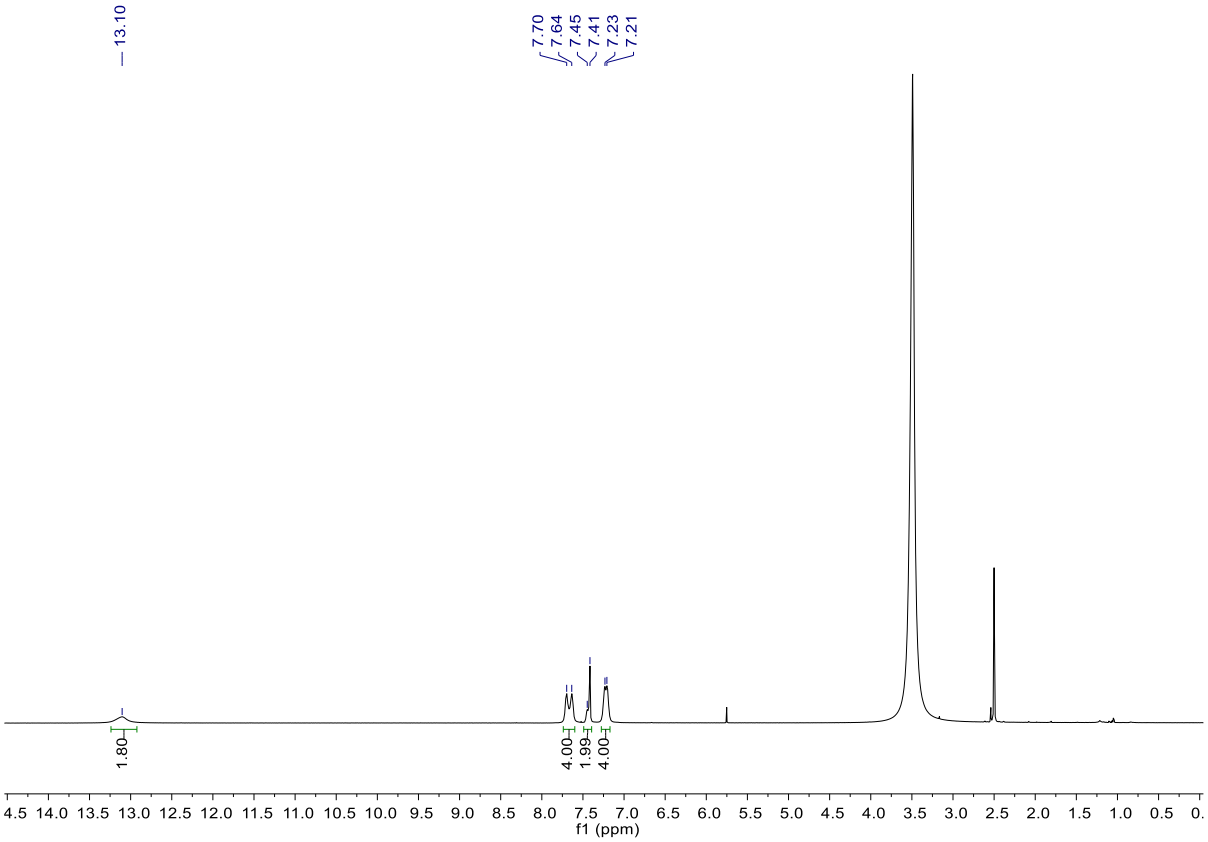


Figure S1: ^{1}H NMR spectra of (p-OH)Bim2NNN) ligand (**C**)

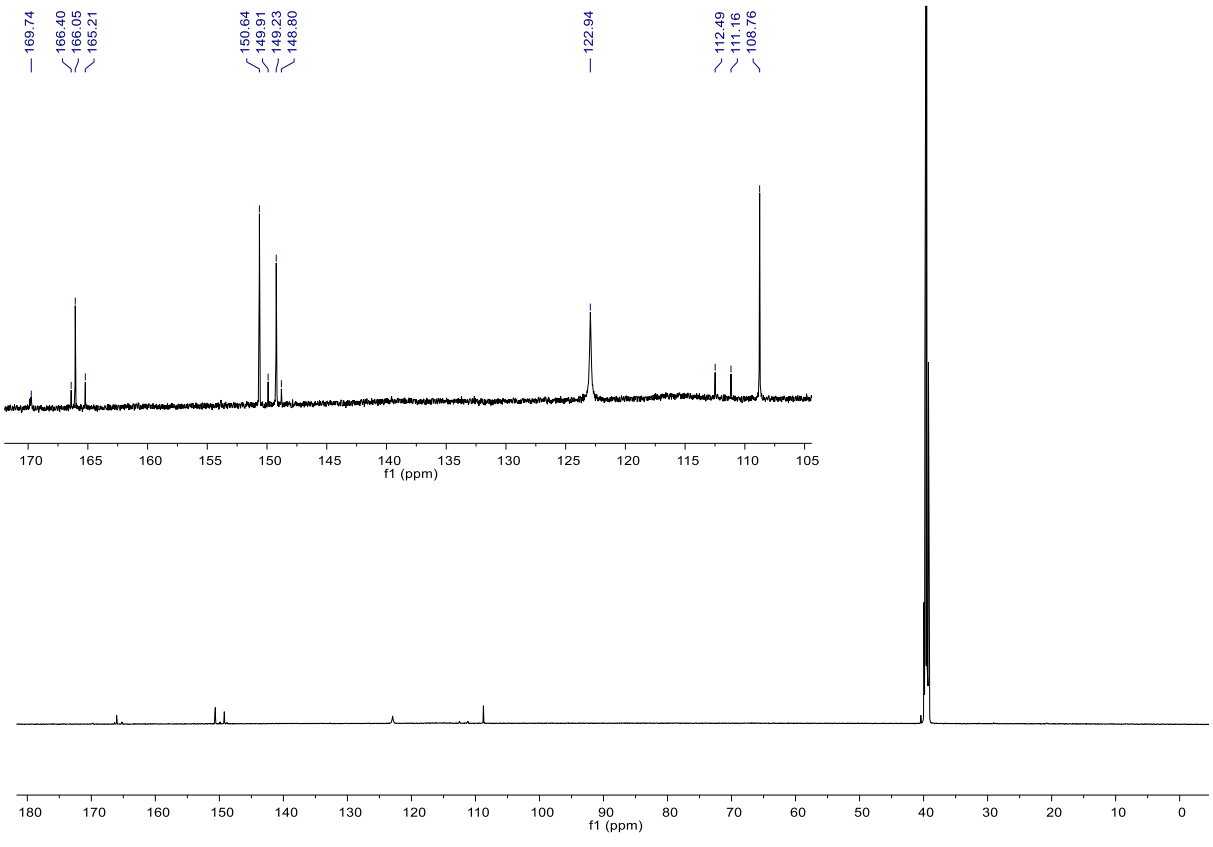


Figure S2: ^{13}C NMR spectra of (p-OH)Bim2NNN) ligand (**C**)

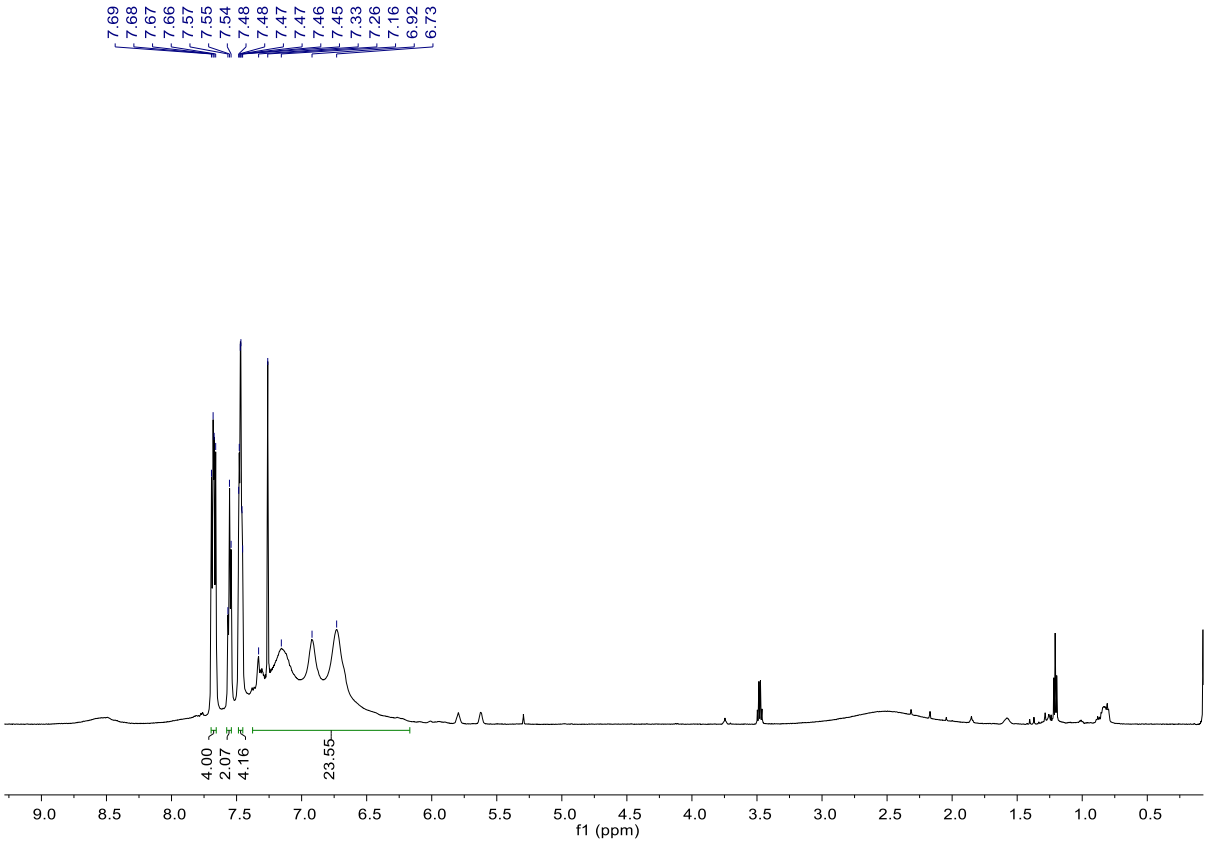


Figure S3: ^{1}H NMR spectra of [(p-OH)Bim2NNN)RuCl(PPh_3)$_2$]Cl (**4b**)

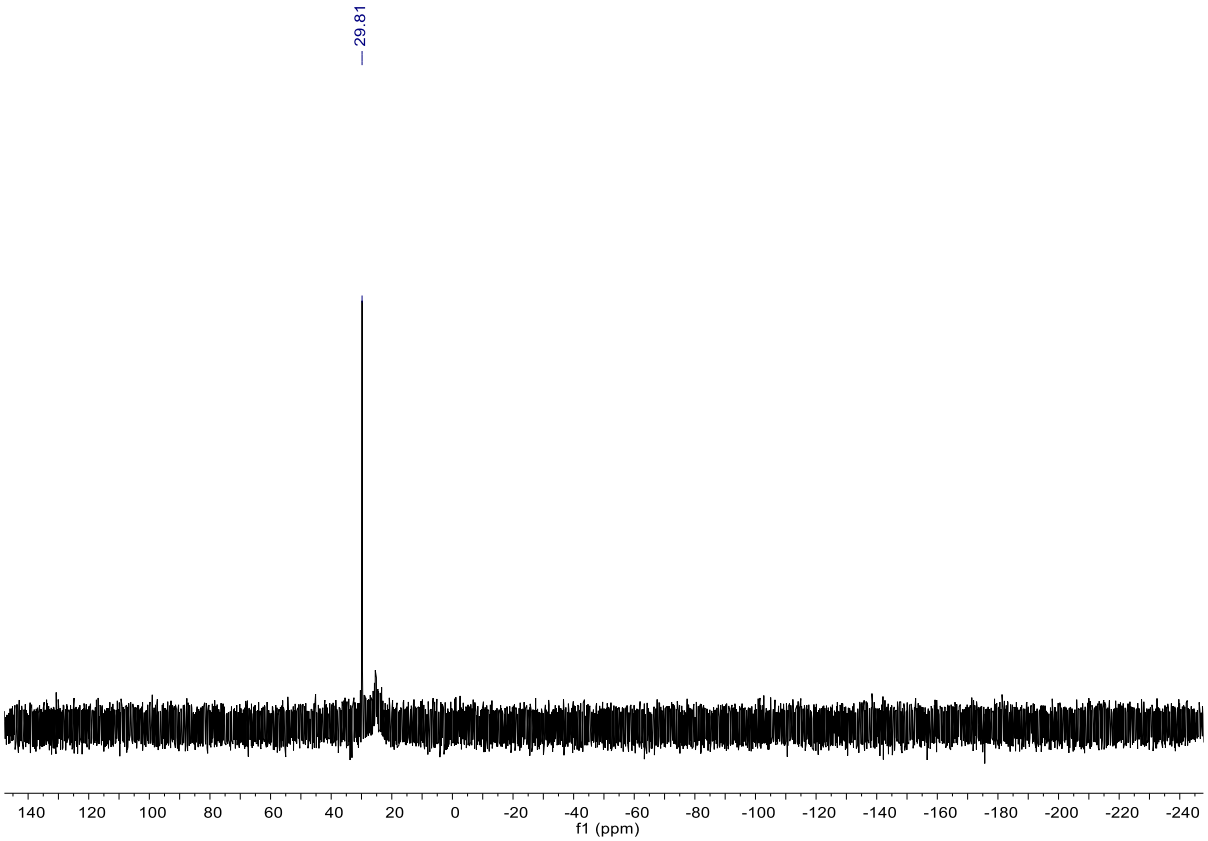


Figure S4: ^{31}P NMR spectra of [(p-OH)Bim2NNN)RuCl(PPh_3)$_2$]Cl (**4b**)

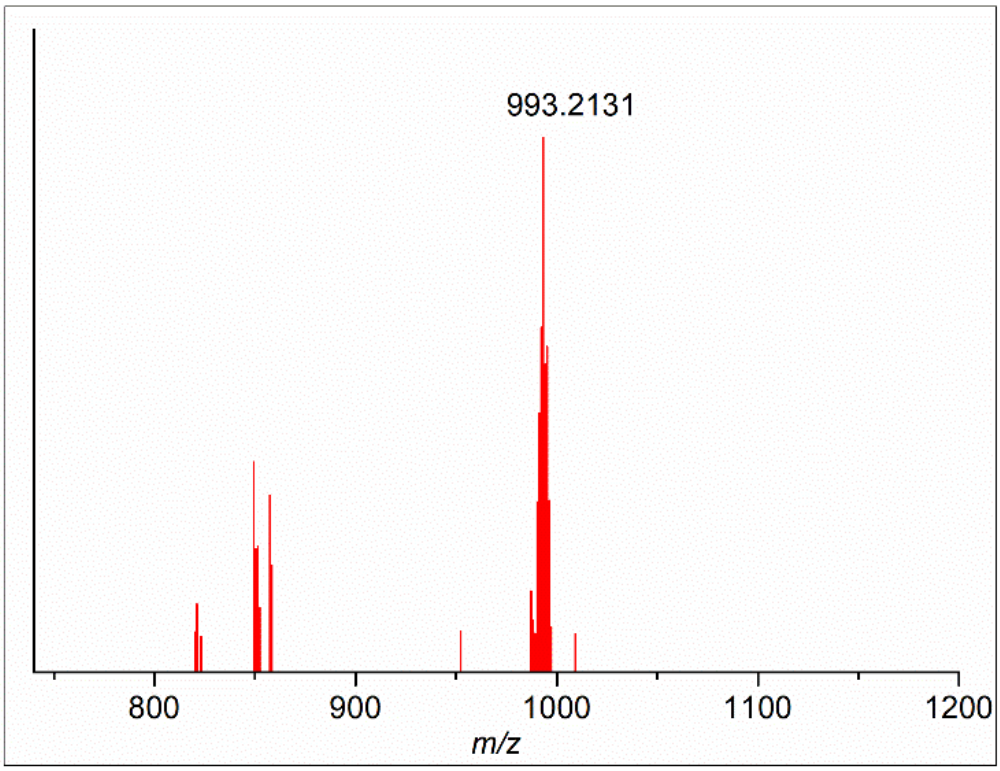


Figure S5: ESI-MS full spectra of **4b**

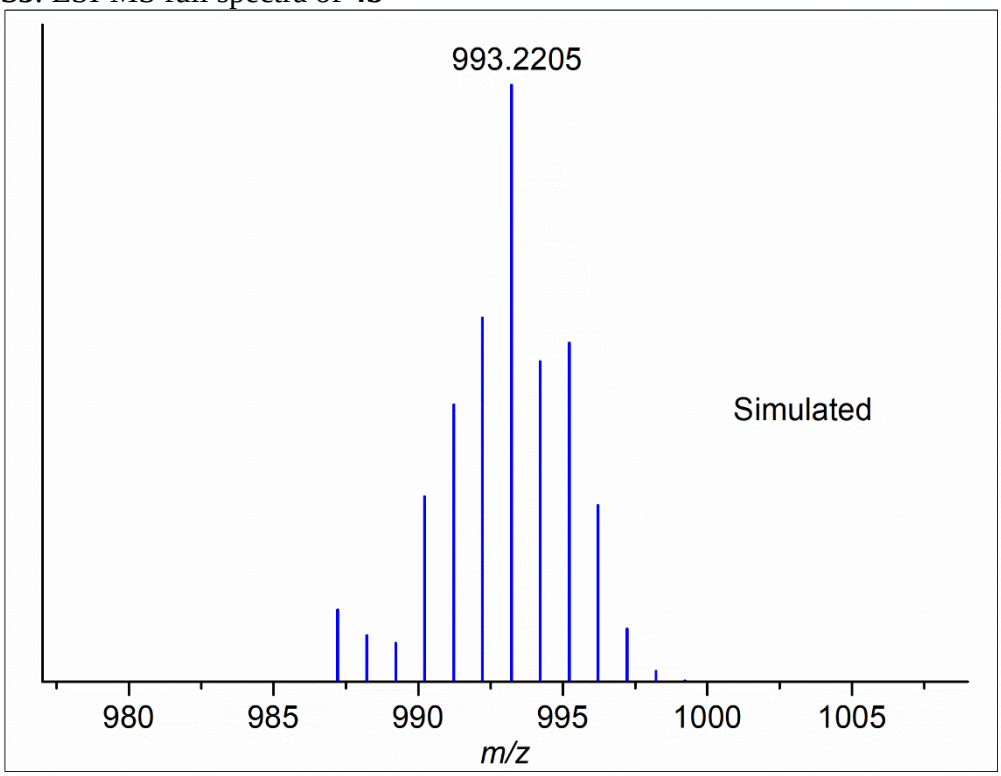


Figure S6: ESI-MS full spectra of **4b** with simulated data

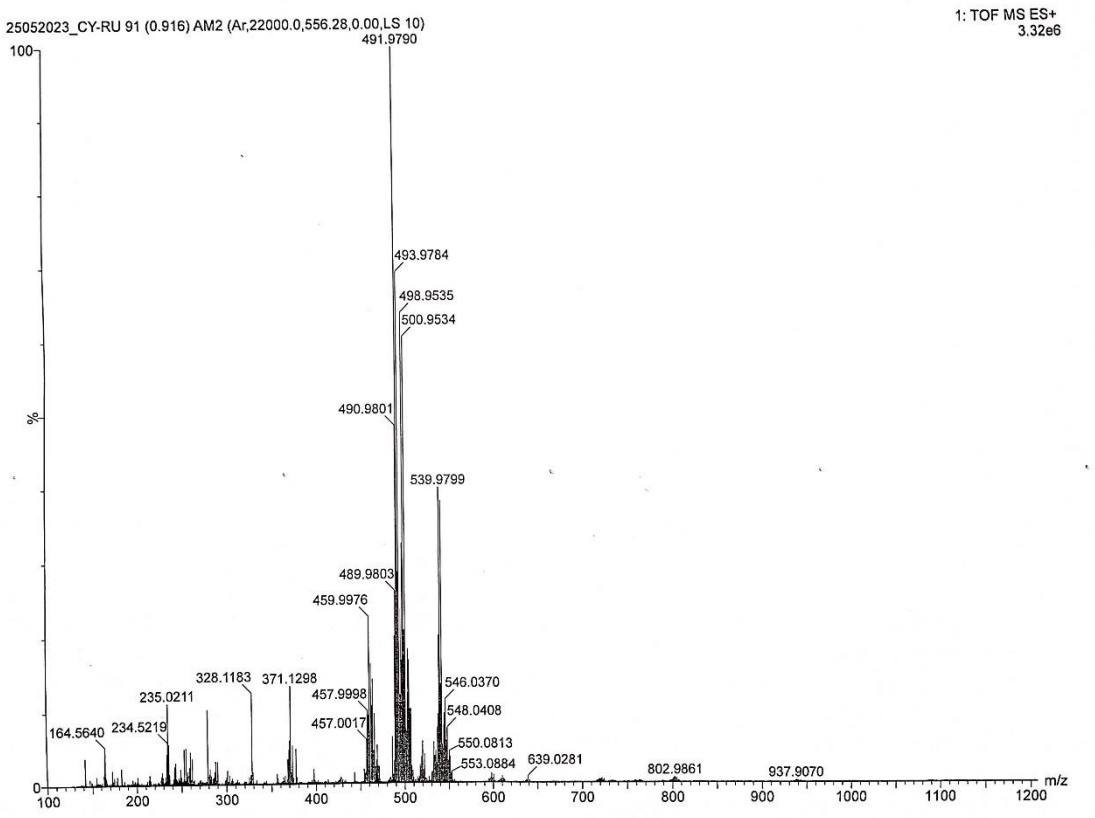


Figure S7: ESI-MS full spectra of **5b**

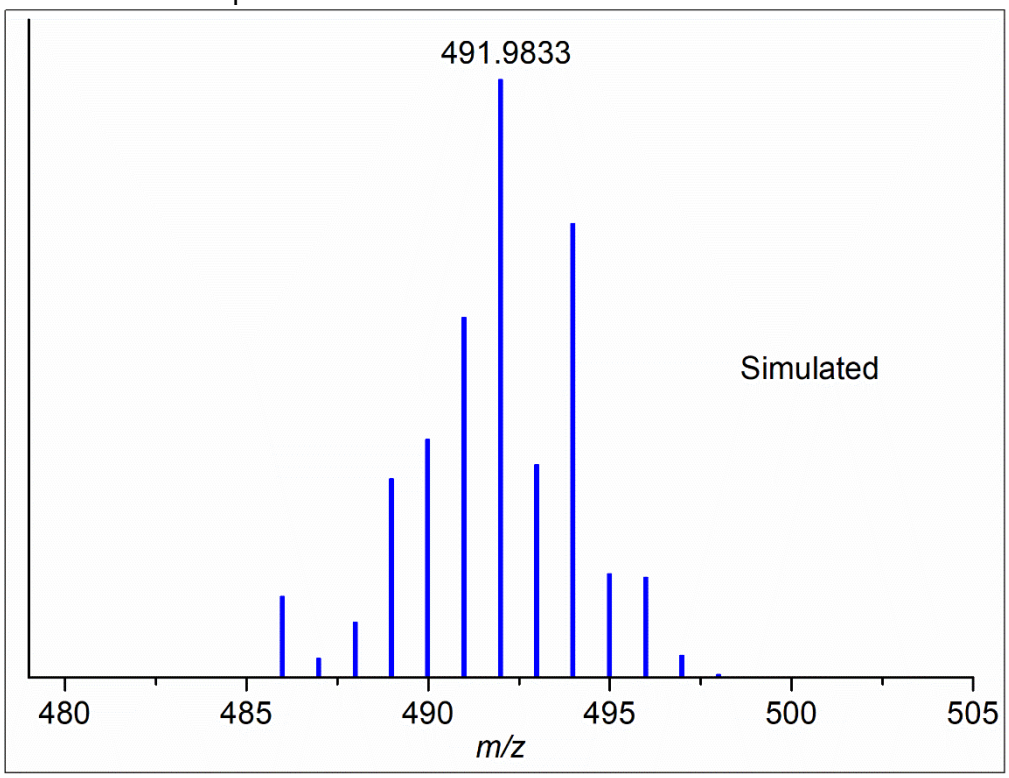


Figure S8: ESI-MS full spectra of **5b** with simulated data

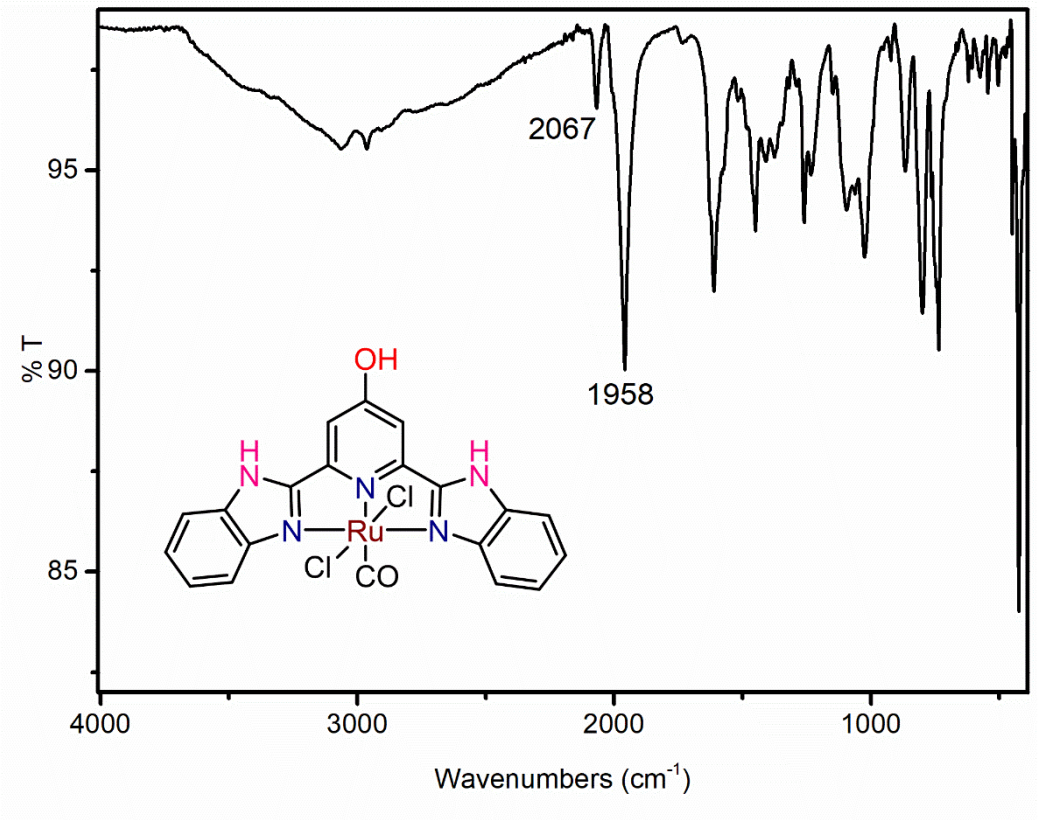


Figure S9: IR spectra of **5b**

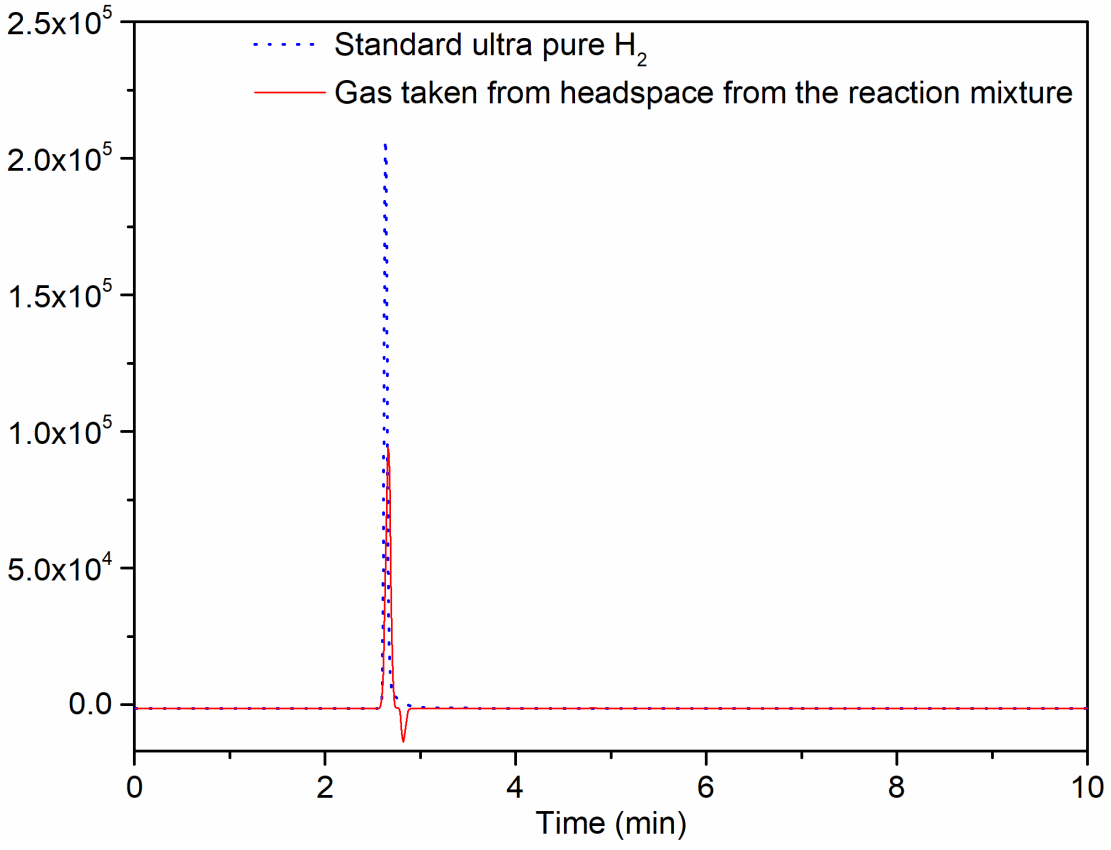


Figure S10: Hydrogen evolution detection by GC analysis.

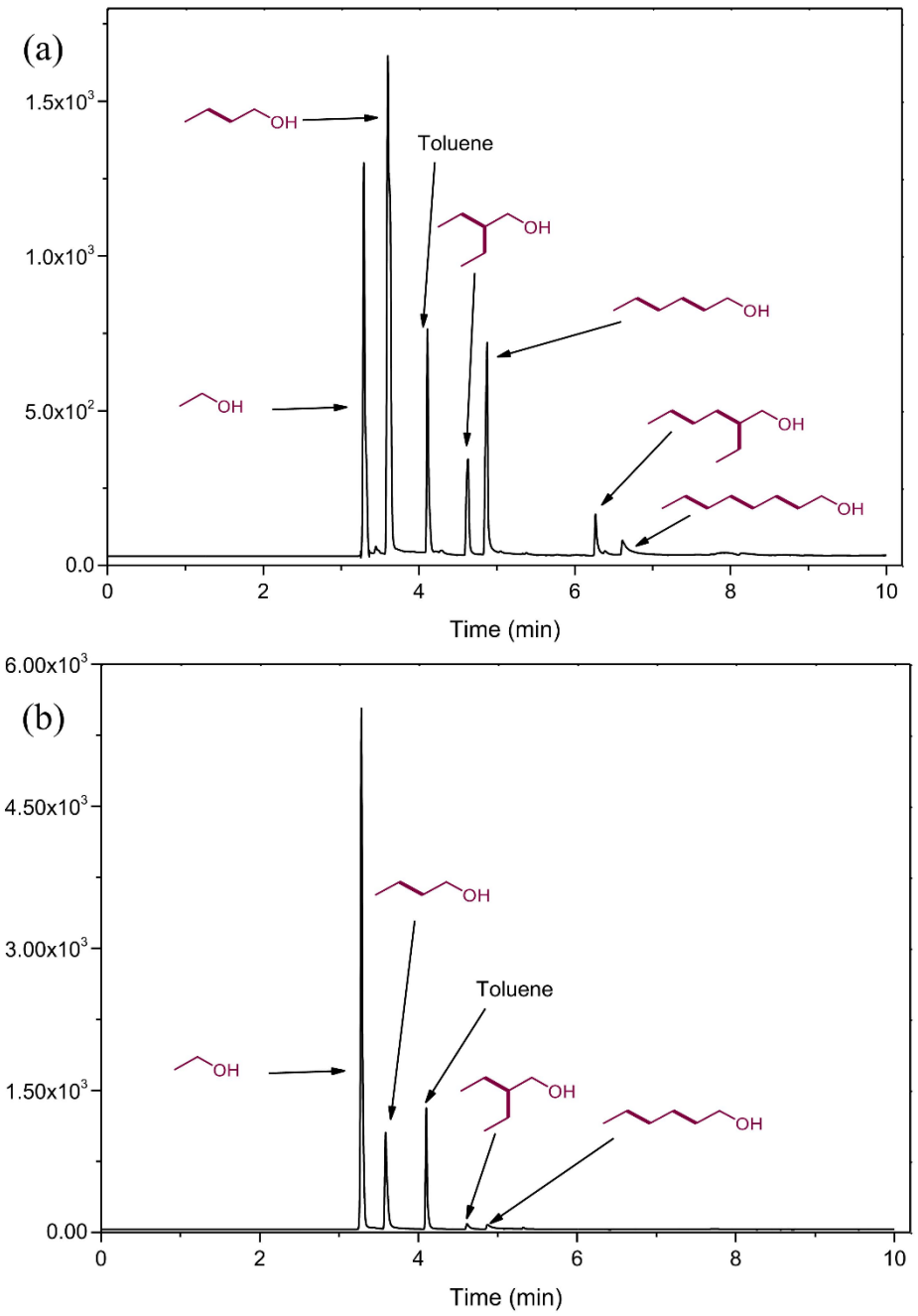


Figure S11: Two representative GC-FID spectra for Guerbet reaction.

Computational details

Table S6: Optimized XYZ coordinates for 12

C	-1.1245700	2.2155400	-0.3571400	C	5.7050400	-0.1082200	0.1574000
C	-1.1120500	3.5773300	-0.6655400	C	4.9286200	-2.3997200	0.5726200
C	0.1089600	4.2471000	-0.8296900	H	2.7722300	-2.7440400	0.5870400
C	1.3095400	3.5402600	-0.6779800	C	5.9678200	-1.4556000	0.4186300
C	1.2882500	2.1780700	-0.3705000	H	6.5132900	0.6164800	0.0402300
H	-2.0563700	4.1147500	-0.7755200	H	5.1842100	-3.4416500	0.7749600
H	0.1243100	5.3098400	-1.0719500	H	7.0049900	-1.7860000	0.5056000
H	2.2681700	4.0497200	-0.7973000	C	-2.2415700	1.3430000	-0.1477100
N	0.0701500	1.5025100	-0.2234500	C	-4.2515600	0.4117100	0.1500500
Ru	0.0497400	-0.3764600	0.1631200	H	-4.0224200	2.5134500	-0.2297800
H	-1.1907100	-1.0856000	-2.8600500	C	-3.2309600	-0.5690300	0.2900000
C	-0.9186600	-1.9483700	-2.2173800	C	-5.6053500	0.0950500	0.2972600
C	-0.4922900	-3.1302500	-3.0852300	C	-3.5543400	-1.8979800	0.5931400
O	0.1662000	-1.5919400	-1.3765700	C	-5.9114500	-1.2360500	0.5937200
Cl	0.0097200	-0.1453800	2.5570300	H	-6.3884100	0.8486200	0.1922700
H	-1.8263800	-2.2159300	-1.6381500	C	-4.9046000	-2.2149700	0.7412800
H	-0.2359300	-3.9934700	-2.4522700	H	-2.7636900	-2.6385000	0.7241600
H	-1.3026900	-3.4264900	-3.7710900	H	-6.9571100	-1.5240200	0.7199000
H	0.3961000	-2.8664200	-3.6781200	H	-5.1919600	-3.2399600	0.9832300
C	2.3796800	1.2727700	-0.1732800	N	-1.9997200	0.0302300	0.0845300
C	3.3079800	-0.6817100	0.2148900	N	2.0964400	-0.0300700	0.0666400
C	4.3604500	0.2625100	0.0572500	N	3.7415600	1.4790300	-0.1927000
H	4.2035700	2.3736500	-0.3064800	N	-3.5936900	1.6002300	-0.1330100
C	3.5881000	-2.0292700	0.4723800				

Table S7: Optimized XYZ coordinates for TS-13

C	-1.2379700	2.2375800	-0.2566800	C	5.6053500	0.0628200	0.2815500
C	-1.2745500	3.6406800	-0.3710100	C	4.9022900	-2.2786400	0.5024300
C	-0.0650900	4.3393900	-0.4259700	H	2.7616800	-2.7001500	0.3979500
C	1.1617300	3.6580200	-0.3604300	C	5.9095100	-1.2872000	0.4659400
C	1.1408100	2.2607900	-0.2376600	H	6.3859200	0.8261000	0.2702100
H	-2.2252300	4.1754900	-0.4115100	H	5.1886400	-3.3186000	0.6708000
H	-0.0734600	5.4268500	-0.5178400	H	6.9525400	-1.5828700	0.5963000
H	2.1037800	4.2072000	-0.4032800	C	-2.3177600	1.2892100	-0.1593200
N	-0.0397700	1.5860600	-0.2016700	C	-4.2980500	0.2806900	0.0829500
Ru	-0.0290100	-0.4408600	-0.0702900	H	-4.1313100	2.4123400	-0.0995000
H	-1.2928200	-2.3436600	-1.5781300	C	-3.2514800	-0.6814700	0.1106400
C	-0.2253000	-2.0378800	-1.5987600	C	-5.6406800	-0.0843000	0.2317000
C	0.7355200	-3.1845800	-1.8632800	C	-3.5334400	-2.0378200	0.3164600
O	0.0504000	-0.8751400	-2.1437400	C	-5.9055300	-1.4421500	0.4210000
Cl	-0.0104700	-0.2850500	2.3497300	H	-6.4444000	0.6543900	0.2101700
H	0.0164400	-2.0896700	0.1073500	C	-4.8699300	-2.4026400	0.4681400
H	1.7750000	-2.8534900	-1.7357800	H	-2.7169100	-2.7587500	0.3765800
H	0.5370000	-4.0487700	-1.2116400	H	-6.9403000	-1.7682700	0.5447100
H	0.6061400	-3.5024500	-2.9121500	H	-5.1254200	-3.4506800	0.6358500
C	2.2452000	1.3287000	-0.1242000	N	-2.0370800	-0.0356400	-0.0598600
C	3.2349700	-0.6076700	0.1355900	N	2.0056500	0.0014300	-0.0410400
C	4.2531900	0.3851900	0.1241000	N	3.5923600	1.5915900	-0.0469300
H	4.0152100	2.5129600	-0.0422600	N	-3.6773100	1.5063700	-0.0949200
C	3.5565500	-1.9556600	0.3418800				

Table S8: Optimized XYZ coordinates for 14

C	-1.1977300	2.2060700	0.0207500	C	5.9302000	-1.4492100	-0.0550300
C	-1.2135400	3.6057400	0.0527800	H	6.4421900	0.6658600	-0.0311500
C	0.0000000	4.3079100	0.0666200	H	5.1799800	-3.4799200	-0.0771600
C	1.2135400	3.6057400	0.0527800	H	6.9731700	-1.7730100	-0.0672800
C	1.1977300	2.2060700	0.0207500	C	-2.2952300	1.2779000	0.0080100
H	-2.1633900	4.1444200	0.0674300	C	-4.2942300	0.2767900	-0.0197600
H	0.0000000	5.3982500	0.0910400	H	-4.0997800	2.4167500	0.0046800
H	2.1633900	4.1444200	0.0674300	C	-3.2591300	-0.6981100	-0.0243400
N	0.0000000	1.5073000	0.0042200	C	-5.6461900	-0.0816000	-0.0346000
Ru	0.0000000	-0.4490600	-0.0203900	C	-3.5580400	-2.0670000	-0.0457300
Cl	0.0000000	-2.8309300	0.2466600	C	-5.9302000	-1.4492100	-0.0550300
H	0.0000010	-0.3910700	-1.5828500	H	-6.4421900	0.6658600	-0.0311500
C	2.2952300	1.2779000	0.0080100	C	-4.9058600	-2.4231900	-0.0606900
C	3.2591300	-0.6981100	-0.0243400	H	-2.7430800	-2.7938300	-0.0453200
C	4.2942300	0.2767900	-0.0197600	H	-6.9731700	-1.7730100	-0.0672700
H	4.0997800	2.4167500	0.0046800	H	-5.1799800	-3.4799200	-0.0771600
C	3.5580400	-2.0670000	-0.0457300	N	-2.0284000	-0.0535200	-0.0039800
C	5.6461900	-0.0816000	-0.0346000	N	2.0284000	-0.0535200	-0.0039800
C	4.9058600	-2.4231900	-0.0606900	N	3.6531200	1.5070600	0.0016500
H	2.7430800	-2.7938300	-0.0453200	N	-3.6531200	1.5070600	0.0016500

Table S9: Optimized XYZ coordinates for TS-15

C	1.1061400	2.1436100	0.0344300	C	-4.9458700	-2.5293900	-0.2133300
C	1.1187800	3.5425400	0.1128500	H	-2.7899900	-2.8782200	-0.2957900
C	-0.0991500	4.2308900	0.1955600	C	-5.9787500	-1.5700100	-0.1121500
C	-1.3086800	3.5230500	0.1802500	H	-6.5094300	0.5321700	0.0664300
C	-1.2802200	2.1245300	0.1023100	H	-5.2098800	-3.5853900	-0.2972800
H	2.0635800	4.0892600	0.0971000	H	-7.0182800	-1.9044300	-0.1176600
H	-0.1063000	5.3200400	0.2545500	C	2.2063400	1.2227400	-0.0820400
H	-2.2611200	4.0554800	0.2151200	C	4.2048700	0.2357400	-0.2408800
N	-0.0816200	1.4481900	0.0627400	H	4.0034600	2.3709000	-0.1219800
Ru	-0.0761200	-0.5154900	-0.1524600	C	3.1715200	-0.7415000	-0.2544200
H	1.7993100	-1.8625300	2.0406300	C	5.5554900	-0.1170000	-0.3290400
C	0.9197100	-1.5174500	2.6205600	C	3.4757700	-2.1038500	-0.3712000
C	1.2262600	-0.1775000	3.2828800	C	5.8426800	-1.4799100	-0.4348300
O	-0.2448000	-1.4405400	1.8058000	H	6.3493100	0.6325100	-0.3191900
Cl	-0.0711000	-0.2453000	-2.5377100	C	4.8216400	-2.4565600	-0.4583100
H	-0.0633500	-2.3037900	-0.2977100	H	2.6700000	-2.8387300	-0.4063100
H	0.3589600	0.1657900	3.8671200	H	6.8848500	-1.7976600	-0.5074100
H	2.0930100	-0.2609300	3.9593800	H	5.0962900	-3.5087900	-0.5539000
H	1.4499700	0.5870800	2.5238100	N	1.9470400	-0.1053000	-0.1421000
C	-2.3707600	1.1872000	0.0373400	N	-2.0961000	-0.1331200	-0.0721700
C	-3.3131200	-0.7904600	-0.1028700	N	-3.7295900	1.4014900	0.0822900
C	-4.3587300	0.1690500	-0.0057000	N	3.5616100	1.4588300	-0.1289900
H	-4.1850400	2.3043600	0.1484000	H	0.7246100	-2.2821400	3.3988400
C	-3.6031800	-2.1562000	-0.2115100	H	-0.1473600	-2.1619300	0.6851400
C	-5.7066500	-0.2041200	-0.0080400				

Table S10: Optimized XYZ coordinates for TS-16

C	1.2801200	2.2097100	-0.0610500	H	-6.3205600	0.7578200	-0.6415000
C	1.3188900	3.6105200	-0.0313600	H	-5.1032000	-3.3946100	-0.8585100
C	0.1046000	4.3120600	-0.0130700	H	-6.8726900	-1.6627500	-0.8988300
C	-1.1144200	3.6266000	-0.0286400	C	2.3713100	1.2595200	-0.0931000
C	-1.0960300	2.2224900	-0.0591000	C	4.3605800	0.2537300	-0.2348800
H	2.2690900	4.1473300	-0.0193700	H	4.1697800	2.3924000	-0.2543700
H	0.1113800	5.4028400	0.0154700	C	3.3217400	-0.7157100	-0.1726400
H	-2.0578500	4.1748200	-0.0130800	C	5.7072200	-0.1110500	-0.3382000
N	0.0881100	1.5495400	-0.0656700	C	3.6154100	-2.0842300	-0.2400300
Ru	0.0806700	-0.4812300	-0.0179200	C	5.9835800	-1.4786100	-0.3867900
H	-1.9006700	-0.4917400	2.5048300	H	6.5047700	0.6329300	-0.3861000
C	-0.9231900	0.0468100	2.6024400	C	4.9559300	-2.4487900	-0.3441000
C	0.2451900	-0.6944400	2.1323100	H	2.8049200	-2.8142800	-0.2384700
O	-0.8982300	1.2017600	3.0339200	H	7.0216000	-1.8069000	-0.4703500
Cl	0.1244900	-0.5824000	-2.4771500	H	5.2223900	-3.5056800	-0.4050900
H	0.0856800	-2.1303600	-0.0912300	N	2.1044500	-0.0661500	-0.0690300
H	1.2106200	-0.2875300	2.4529500	N	-1.9521300	-0.0418100	-0.1402900
C	-2.1976300	1.2905800	-0.1291800	N	-3.5428100	1.5435900	-0.2641000
C	-3.1746600	-0.6608300	-0.3472000	N	3.7253900	1.4843800	-0.1785600
C	-4.1935600	0.3294300	-0.4084100	C	0.1877100	-2.0322400	1.5740400
H	-3.9703200	2.4618200	-0.3009100	H	1.1577100	-2.5454300	1.5915300
C	-3.4863800	-2.0157800	-0.5189300	C	-0.9577400	-2.9866900	1.8731600
C	-5.5390800	-0.0033500	-0.5986400	H	-1.9422800	-2.5148700	1.7635800
C	-4.8255400	-2.3487800	-0.7137400	H	-0.9261600	-3.8602000	1.2047300
H	-2.6895400	-2.7599300	-0.5264900	H	-0.8699100	-3.3477600	2.9121000
C	-5.8350300	-1.3599000	-0.7443300				

Table S11: Optimized XYZ coordinates for 17

C	1.2027000	2.2483700	0.0454800	H	-6.4090500	0.6760300	-0.4126000
C	1.2236100	3.6408500	0.1587500	H	-5.0420100	-3.3927300	-1.0109400
C	0.0128400	4.3400700	0.2852200	H	-6.8724800	-1.7336400	-0.8598500
C	-1.2001300	3.6436800	0.2672100	C	2.3027900	1.3288200	-0.1136000
C	-1.1906800	2.2473600	0.1491000	C	4.2879400	0.3233900	-0.3276600
H	2.1730900	4.1791800	0.1376500	H	4.1089600	2.4621300	-0.2072200
H	0.0176400	5.4269400	0.3749600	C	3.2453000	-0.6433900	-0.3192100
H	-2.1482700	4.1819500	0.3253700	C	5.6301600	-0.0490300	-0.4562000
N	0.0064300	1.5560100	0.0827100	C	3.5165100	-2.0132800	-0.4375100
Ru	0.0089200	-0.3778900	-0.1459000	C	5.8896800	-1.4168700	-0.5737300
H	-1.4608800	-2.2464800	1.4198400	H	6.4370300	0.6863800	-0.4676300
C	-0.3947000	-2.0655800	1.1587900	C	4.8545000	-2.3809100	-0.5641500
C	0.3435500	-1.1081400	1.9256700	H	2.6872900	-2.7239300	-0.4274700
O	0.1163600	-2.6459300	0.1209500	H	6.9243100	-1.7503100	-0.6786000
Cl	-0.0146900	-0.2098500	-2.5746500	H	5.1143600	-3.4366300	-0.6632100
H	-1.3904900	-0.3120600	2.9036600	N	2.0367400	0.0093700	-0.1860900
H	1.4290100	-1.2497000	1.9858200	N	-2.0038800	0.0146600	-0.1257100
C	-2.2871100	1.3298100	0.0241900	N	-3.6473700	1.5431200	-0.0398000
C	-3.2072800	-0.6335400	-0.3418400	N	3.6586800	1.5541500	-0.1901100
C	-4.2590700	0.3204900	-0.2814500	C	-0.3030400	-0.3848400	3.0828900
H	-4.1067700	2.4459800	-0.0120800	H	0.0663400	0.6552300	3.1218800
C	-3.4649300	-1.9839700	-0.6119000	C	-0.0374200	-1.0710300	4.4336600
C	-5.5960600	-0.0513000	-0.4581500	H	1.0436700	-1.1352500	4.6368500
C	-4.7974600	-2.3517600	-0.7914100	H	-0.5050100	-0.5202800	5.2655400
H	-2.6352100	-2.6890000	-0.6978700	H	-0.4348400	-2.0981400	4.4371600
C	-5.8424100	-1.4032900	-0.7103500				

Table S12: Optimized XYZ coordinates for TS-18

C	-1.2085200	2.2844900	-0.4570100	H	5.2602300	-3.0143300	1.2860800
C	-1.2572400	3.6370200	-0.8235300	H	7.0199200	-1.3410600	0.8011400
C	-0.0529200	4.3203900	-1.0465100	C	-2.2832100	1.3770300	-0.1363800
C	1.1759100	3.6663000	-0.8845800	C	-4.2559000	0.4016300	0.2391700
C	1.1740700	2.3121600	-0.5168500	H	-4.1109000	2.4334300	-0.4364100
H	-2.2128500	4.1557500	-0.9193100	C	-3.1988400	-0.5104800	0.5045500
H	-0.0726300	5.3737100	-1.3304400	C	-5.5985400	0.0424800	0.3983700
H	2.1134700	4.2063900	-1.0297000	C	-3.4687600	-1.8109100	0.9475400
N	-0.0053700	1.6403100	-0.3402700	C	-5.8510100	-1.2583400	0.8367300
Ru	0.0244300	-0.2784800	0.3008600	H	-6.4113200	0.7413100	0.1910100
H	-1.3865000	-3.0793200	-2.4859000	C	-4.8045500	-2.1695100	1.1094800
C	-1.3215800	-1.9900600	-2.2089100	H	-2.6442500	-2.4937600	1.1573300
C	0.0056100	-1.5614600	-1.7010500	H	-6.8854700	-1.5798700	0.9745000
O	-2.3032800	-1.2708600	-2.3521100	H	-5.0541100	-3.1744900	1.4553700
Cl	0.1165400	0.4769100	2.5856800	N	-1.9922700	0.1144600	0.2540600
H	2.1215100	-1.9439900	-1.7654300	N	2.0473600	0.1466300	0.1204200
H	0.1748000	-0.5283400	-2.0479300	N	3.6372600	1.6848800	-0.2894600
C	2.2845500	1.4295500	-0.2497400	N	-3.6433300	1.5781900	-0.1592000
C	3.2859800	-0.4285600	0.3535100	C	1.1954800	-2.4726300	-2.0408700
C	4.3027400	0.5308100	0.0929000	H	1.2385300	-2.6080600	-3.1378800
H	4.0632400	2.5799000	-0.5013200	C	1.1783700	-3.8488400	-1.3618400
C	3.6152700	-1.7178300	0.7908400	H	0.2906900	-4.4360400	-1.6445000
C	5.6604300	0.2280900	0.2418800	H	2.0668100	-4.4361000	-1.6401700
C	4.9674000	-2.0207100	0.9414500	H	1.1712400	-3.7506600	-0.2650000
H	2.8231500	-2.4329600	1.0165600	H	0.0383800	-1.8602500	0.8838100
C	5.9718900	-1.0648500	0.6682200	H	-0.0802100	-1.8697100	-0.2644700
H	6.4410600	0.9648800	0.0423200				

Table S13: Optimized XYZ coordinates for TS-19

C	1.1960600	2.4814600	0.1230600	C	4.2728200	0.6054400	-0.3499200
C	1.2597900	3.8625100	0.3386800	H	4.0595200	2.6976100	0.0797300
C	0.0708100	4.5938400	0.4370700	C	3.2439700	-0.3694900	-0.4839900
C	-1.1619100	3.9406400	0.3095400	C	5.6278600	0.2940400	-0.4971200
C	-1.1838200	2.5585800	0.0952500	C	3.5787800	-1.6922500	-0.8045000
H	2.2254100	4.3628000	0.4310700	C	5.9386000	-1.0326000	-0.7997100
H	0.1033200	5.6703300	0.6090800	H	6.4060700	1.0520200	-0.3874700
H	-2.0960100	4.5017700	0.3759800	C	4.9286600	-2.0063600	-0.9565300
N	-0.0099700	1.8374400	0.0201300	H	2.7990500	-2.4368200	-0.9477200
Ru	-0.0934800	-0.1034700	-0.2410100	H	6.9843300	-1.3198700	-0.9267200
H	1.8831900	-0.7632500	2.3938500	H	5.2123500	-3.0294000	-1.2116700
C	1.0141300	-0.0556300	2.4357700	N	2.0109300	0.2383000	-0.2715300
C	-0.2940200	-0.6634800	2.0908700	N	-2.0870700	0.3578700	-0.2145200
O	1.1995200	1.1258600	2.7282200	N	-3.6628500	1.9481700	-0.0882000
Cl	-0.0835200	0.0457500	-2.6164400	N	3.6228400	1.7977000	-0.0834800
H	-1.5784600	-2.3786200	2.4410400	C	-0.7012500	-1.9181300	2.9251000
H	-1.0873800	0.0898000	2.1963100	H	-1.0397700	-1.5502800	3.9097100
C	-2.3136700	1.6808000	-0.0646100	C	0.3853000	-2.9794000	3.1262300
C	-3.3224900	-0.2520400	-0.3496000	H	1.2291100	-2.5983600	3.7209200
C	-4.3325700	0.7459800	-0.2709400	H	-0.0291800	-3.8485300	3.6596000
H	-4.0853500	2.8675600	-0.0292200	H	0.7866900	-3.3388600	2.1672900
C	-3.6490200	-1.6028100	-0.5308700	H	-0.3200000	-1.4851400	0.9929400
C	-5.6908400	0.4260700	-0.3687100	O	-0.5537400	-2.2205300	-0.1336600
C	-5.0030900	-1.9189100	-0.6252300	C	0.3566100	-3.2173300	-0.5578800
H	-2.8413500	-2.3349500	-0.5872100	H	1.2584000	-3.2360900	0.0921900
C	-6.0042700	-0.9235200	-0.5462400	H	0.6959800	-2.9918700	-1.5881500
H	-6.4696400	1.1891400	-0.3115900	C	-0.3239000	-4.5835200	-0.5172800
H	-5.3021700	-2.9591500	-0.7692100	H	0.3667100	-5.3782800	-0.8439200
H	-7.0532500	-1.2158200	-0.6291800	H	-0.6654100	-4.8157200	0.5038500
C	2.2754200	1.5457100	-0.0530400	H	-1.2001300	-4.5917600	-1.1833800

Table S14: Optimized XYZ coordinates for TS-20

C	-1.2863200	2.2671400	-0.2450100	H	6.3222600	0.8897200	0.5490100
C	-1.3297800	3.6622000	-0.4366300	H	5.1263000	-3.2500000	1.0137800
C	-0.1154100	4.3561200	-0.5058200	H	6.8837700	-1.5081400	0.9499500
C	1.1125200	3.6900700	-0.3724800	C	-2.3634400	1.3098600	-0.0809800
C	1.0894700	2.2962700	-0.1811300	C	-4.3466700	0.3086800	0.1805800
H	-2.2779800	4.1971700	-0.5142100	H	-4.1789600	2.4305400	-0.1006100
H	-0.1243200	5.4377000	-0.6533400	C	-3.2984300	-0.6472100	0.2680500
H	2.0506000	4.2470000	-0.4023900	C	-5.6902000	-0.0578000	0.3204900
N	-0.0902300	1.6353500	-0.1642300	C	-3.5705000	-1.9999400	0.5106700
Ru	-0.0701400	-0.4392500	0.1335100	C	-5.9470800	-1.4100300	0.5542500
H	1.7653600	-2.3548500	-1.7509300	H	-6.4990500	0.6726800	0.2565200
C	0.6995400	-2.7018200	-1.7889600	C	-4.9074300	-2.3646500	0.6498100
C	-0.3171500	-1.6296600	-1.6962600	H	-2.7449300	-2.7085700	0.5979000
O	0.4338500	-3.8905900	-1.8898000	H	-6.9817400	-1.7386800	0.6724700
Cl	-0.0635000	-0.0932700	2.5434700	H	-5.1624400	-3.4081000	0.8440300
H	-0.0546100	-2.0427600	0.3636500	N	-2.0843500	-0.0065200	0.0978100
H	-1.3443300	-2.0087200	-1.7254800	N	1.9511400	0.0385400	0.1654900
C	2.1868000	1.3658300	0.0332100	N	3.5320200	1.6358700	0.1326600
C	3.1797100	-0.5571700	0.3880200	N	-3.7234900	1.5265800	-0.0457400
C	4.1930100	0.4395200	0.3665600	C	-0.0692500	-0.2844500	-2.0899300
H	3.9512000	2.5589400	0.1214200	H	-0.9666600	0.2950100	-2.3449900
C	3.4963000	-1.9018500	0.6248800	C	1.1711100	0.1956700	-2.8060500
C	5.5424300	0.1258100	0.5637300	H	2.0792400	-0.3464100	-2.5113300
C	4.8390900	-2.2146000	0.8215000	H	1.0387700	0.0657900	-3.8947900
H	2.6996300	-2.6462600	0.6673000	H	1.3469200	1.2704400	-2.6362700
C	5.8433300	-1.2186500	0.7883800				

Table S15: Optimized XYZ coordinates for 21

C	1.0035300	2.3975700	-0.0618100	H	-6.6004600	0.6591300	-0.1520400
C	0.9778000	3.7829200	0.1414100	H	-5.2376200	-3.4155800	-0.7179600
C	-0.2542500	4.4404400	0.2589800	H	-7.0711800	-1.7730300	-0.4546300
C	-1.4466400	3.7092400	0.1687700	C	2.1337700	1.5308900	-0.2720700
C	-1.3927800	2.3246500	-0.0309000	C	4.1568800	0.6440200	-0.6207500
H	1.9120100	4.3445100	0.2061700	H	3.8986500	2.7230000	-0.1442400
H	-0.2851600	5.5188900	0.4182500	C	3.1559900	-0.3552600	-0.7609700
H	-2.4114700	4.2130500	0.2571900	C	5.5156000	0.3546600	-0.7822400
N	-0.1745100	1.6646100	-0.1440100	C	3.4960300	-1.6786500	-1.0738700
Ru	-0.1116100	-0.2807500	-0.4163100	C	5.8415000	-0.9683500	-1.0898500
H	0.7987500	-2.1200600	4.1351900	H	6.2861900	1.1203000	-0.6723000
C	1.5278800	-1.7591300	3.3578600	C	4.8509000	-1.9657800	-1.2342800
C	1.0166700	-1.7572900	1.9309500	H	2.7075700	-2.4258400	-1.1885700
O	2.6315700	-1.3689200	3.6892400	H	6.8914800	-1.2374900	-1.2224000
Cl	-0.0937500	-2.5632500	-1.2348400	H	5.1567200	-2.9851400	-1.4776700
H	0.3909500	-2.6452500	1.7454200	N	1.9100300	0.2171400	-0.5374200
H	1.8927600	-1.7884800	1.2694400	N	-2.1716000	0.0678700	-0.3379200
C	-2.4700700	1.3805300	-0.1527400	N	-3.8329500	1.5702500	-0.0963500
C	-3.3859300	-0.6038900	-0.4017800	N	3.4789600	1.8176700	-0.3215900
C	-4.4440600	0.3336300	-0.2503400	C	0.1846700	-0.4767000	1.6751700
H	-4.3027100	2.4610700	0.0178600	H	0.8101600	0.3946500	1.9516100
C	-3.6512000	-1.9694800	-0.5718000	C	-1.1159000	-0.4456500	2.4764900
C	-5.7863500	-0.0593900	-0.2670000	H	-0.9139600	-0.5237900	3.5616000
C	-4.9896000	-2.3605900	-0.5858900	H	-1.6671800	0.4934200	2.3218400
H	-2.8202100	-2.6667400	-0.6984000	H	-1.7789900	-1.2804200	2.2004100
C	-6.0367500	-1.4233200	-0.4366400				

Table S62: Optimized XYZ coordinates for TS-22

C	0.9374200	2.3697500	0.6512200	H	-5.0561000	-3.2953700	-1.5493100
C	0.8741500	3.6824200	1.1390700	H	-6.9528200	-1.8184300	-0.9581800
C	-0.3812200	4.2421700	1.4161700	C	2.0836300	1.5934200	0.2518600
C	-1.5508500	3.5036700	1.1886700	C	4.1273700	0.8601500	-0.2826300
C	-1.4407200	2.1934000	0.7015200	H	3.8030000	2.8306400	0.5060200
H	1.7842400	4.2664900	1.2893500	C	3.1559000	-0.1361500	-0.5751500
H	-0.4485500	5.2631200	1.7946900	C	5.4897800	0.6567500	-0.5267400
H	-2.5301800	3.9478600	1.3771500	C	3.5335400	-1.3568700	-1.1483200
N	-0.2078200	1.6341300	0.4688600	C	5.8512500	-0.5724700	-1.0827100
Ru	-0.0893400	-0.2179000	-0.3052000	H	6.2366400	1.4203000	-0.3004900
H	1.6376800	-3.3668100	0.3320200	C	4.8903500	-1.5609100	-1.3930400
C	1.7934800	-3.3307300	1.4456500	H	2.7723100	-2.0941500	-1.4065400
C	1.3889100	-2.0245900	2.0935400	H	6.9047200	-0.7709100	-1.2902000
O	2.2554600	-4.2881400	2.0348700	H	5.2200900	-2.5002700	-1.8406100
Cl	-0.2014100	0.6738400	-2.5613900	N	1.9020300	0.3334800	-0.2173300
H	2.1677700	-1.2857200	1.8295200	N	-2.1299500	0.0309400	-0.1203200
H	1.4262800	-2.1757500	3.1874100	N	-3.8458400	1.3900400	0.3982100
C	-2.4757200	1.2542400	0.3520000	N	3.4188400	1.9315800	0.2387800
C	-3.3136200	-0.6275000	-0.4112900	C	0.0162900	-1.4959600	1.6477300
C	-4.4085800	0.2187400	-0.0845600	H	-0.1581500	-0.5401600	2.1590800
H	-4.3475600	2.2269800	0.6721600	C	-1.1289400	-2.4572400	1.9756800
C	-3.5286300	-1.9044300	-0.9448200	H	-1.1274800	-2.7118100	3.0507400
C	-5.7347400	-0.1865300	-0.2684400	H	-2.1042800	-2.0146900	1.7304900
C	-4.8495700	-2.3086700	-1.1304000	H	-1.0494600	-3.4068700	1.4193400
H	-2.6756200	-2.5309800	-1.2095500	H	-0.0057500	-1.7891500	-0.9470200
C	-5.9326200	-1.4647200	-0.7955000	H	0.0488300	-1.8082000	0.1719500
H	-6.5763900	0.4626000	-0.0188100				

Table S17: Optimized XYZ coordinates for TS-23

C	0.9806700	2.5005700	-0.1519900	C	4.1200100	0.6925900	-0.3982800
C	0.9889500	3.8973600	-0.0742200	H	3.8317500	2.8024300	-0.1645400
C	-0.2215900	4.5809700	0.0977100	C	3.1235500	-0.3233400	-0.4654700
C	-1.4222100	3.8622100	0.1652600	C	5.4885600	0.4041400	-0.3992400
C	-1.3946000	2.4659900	0.0756000	C	3.5117800	-1.6696100	-0.5387200
H	1.9273400	4.4484400	-0.1614400	C	5.8495700	-0.9424900	-0.4672900
H	-0.2315400	5.6696600	0.1606200	H	6.2404400	1.1940100	-0.3457300
H	-2.3746800	4.3851400	0.2726800	C	4.8754000	-1.9616300	-0.5368000
N	-0.1934000	1.7898300	-0.0532700	H	2.7648200	-2.4587400	-0.6000600
Ru	-0.2087600	-0.1476500	-0.2866900	H	6.9076900	-1.2118200	-0.4686400
H	3.4948100	-0.6102800	2.8192400	H	5.1974200	-3.0033700	-0.5927300
C	2.4473500	-0.2547700	2.6227700	N	1.8650800	0.2667500	-0.4119100
C	1.4515700	-1.3683800	2.3958000	N	-2.2042400	0.2144700	-0.0429700
O	2.1938300	0.9365900	2.6276400	N	-3.8451900	1.7316400	0.1727600
Cl	-0.4331500	0.1059200	-2.6629600	N	3.4282600	1.8869100	-0.3275000
H	1.3900900	-1.8906000	3.3758300	C	0.0617600	-0.9412700	1.9140100
H	1.9459000	-2.1095800	1.7387500	H	-0.0088900	0.1474000	2.0813000
C	-2.4858600	1.5319400	0.0764700	C	-1.0910400	-1.6197900	2.6711700
C	-3.4153100	-0.4573200	-0.0459400	H	-1.0074100	-1.4502300	3.7600300
C	-4.4645000	0.4922800	0.0932600	H	-2.0626600	-1.2270000	2.3396800
H	-4.3084400	2.6304700	0.2387600	H	-1.1078600	-2.7085000	2.4998100
C	-3.6853400	-1.8275800	-0.1591600	H	-0.0713100	-1.7290400	0.7710200
C	-5.8070600	0.1016200	0.1297800	O	-0.5066400	-2.3166300	-0.2773900
C	-5.0241200	-2.2141500	-0.1224400	C	0.2513000	-3.1622400	-1.1343100
H	-2.8470800	-2.5184300	-0.2702000	H	1.0695600	-2.6045600	-1.6253000
C	-6.0642700	-1.2673700	0.0199300	H	-0.4198600	-3.4788500	-1.9539300
H	-6.6170500	0.8262000	0.2348800	C	0.7783800	-4.3860500	-0.3885200
H	-5.2803000	-3.2719800	-0.2099500	H	1.2979300	-5.0763100	-1.0736700
H	-7.0998300	-1.6136900	0.0414400	H	1.4854700	-4.0972000	0.4081200
C	2.0859900	1.5989200	-0.3194900	H	-0.0519400	-4.9301200	0.0875500

Table S17: Optimized XYZ coordinates for TS-24

C	1.2038200	-2.3804700	-0.7429900	H	-6.4062100	-1.0925300	0.1500100
C	1.2266600	-3.6930200	-1.2529400	H	-5.1694900	2.7462100	1.7331100
C	0.0097700	-4.3313300	-1.5102100	H	-6.9503400	1.1246000	1.1595400
C	-1.2101600	-3.6821800	-1.2582600	C	2.2929900	-1.5129700	-0.3720800
C	-1.1750200	-2.3778600	-0.7422600	C	4.2828000	-0.6401000	0.1529100
H	2.1716600	-4.2064000	-1.4393500	H	4.0943900	-2.6264500	-0.6364200
H	0.0070600	-5.3475500	-1.9082200	C	3.2467100	0.2859200	0.4543600
H	-2.1576100	-4.1848500	-1.4594400	C	5.6288100	-0.3495700	0.4015600
N	0.0125400	-1.7575800	-0.5104300	C	3.5431900	1.5233300	1.0400700
Ru	0.0223600	0.1473700	0.1982600	C	5.9080800	0.8938000	0.9721400
H	1.3293200	2.3807300	-0.6675400	H	6.4241500	-1.0608800	0.1700700
C	0.2611100	2.1052600	-0.7917200	C	4.8830500	1.8130000	1.2910300
C	-0.6979300	3.2879900	-0.7346600	H	2.7353200	2.2076600	1.3028400
O	-0.0070300	1.1572100	-1.6656200	H	6.9458800	1.1584600	1.1850500
Cl	-0.0233400	-0.7055700	2.4692000	H	5.1496300	2.7662700	1.7514500
H	-0.0160400	1.6709500	0.8498100	N	2.0263600	-0.2696700	0.1040600
H	-1.7221900	2.8956900	-0.6439200	N	-2.0168800	-0.2575200	0.0887000
H	-0.4853500	3.9033000	0.1579200	N	-3.6199000	-1.7622800	-0.3743400
C	-2.2697500	-1.5030200	-0.3715800	N	3.6495200	-1.7557100	-0.3701200
C	-3.2410100	0.2876600	0.4332800	C	-0.5952900	4.1484900	-2.0098200
C	-4.2689800	-0.6491700	0.1362700	H	-1.4074500	4.8954200	-1.9922200
H	-4.0522300	-2.6423100	-0.6321000	H	-0.7870000	3.4968800	-2.8789500
C	-3.5502800	1.5210300	1.0219900	C	0.7507800	4.8634100	-2.1777500
C	-5.6184100	-0.3727400	0.3808800	H	0.7526800	5.5019600	-3.0746500
C	-4.8931400	1.7969500	1.2700700	H	0.9711300	5.5063200	-1.3092300
H	-2.7490600	2.2096700	1.2917900	H	1.5821000	4.1489200	-2.2816100
C	-5.9099600	0.8689400	0.9483900				

Table S18: Optimized XYZ coordinates for 25

C	-1.0234900	2.1352500	0.2536500	H	6.6324800	0.6127700	-0.0678100
C	-1.0417600	3.5261100	0.1287200	H	5.3747800	-3.5296900	0.1150400
C	0.1616800	4.2311900	-0.0139500	H	7.1652100	-1.8250900	-0.0134200
C	1.3752900	3.5303900	-0.0265900	C	-2.1195500	1.2237900	0.3996400
C	1.3825200	2.1391700	0.0979100	C	-4.1066600	0.2287300	0.6353500
H	-1.9954900	4.0577200	0.1457400	H	-3.9147400	2.3661900	0.5414100
H	0.1536200	5.3166500	-0.1144400	C	-3.0725000	-0.7468600	0.5848800
H	2.3207200	4.0665200	-0.1336100	C	-5.4512000	-0.1274400	0.7771800
N	0.1819600	1.4310500	0.2207800	C	-3.3721100	-2.1117900	0.6845700
Ru	0.1960200	-0.4893900	0.3285100	C	-5.7336300	-1.4928800	0.8708300
H	-1.7842600	-1.8667300	-1.6637000	H	-6.2447000	0.6214000	0.8168400
C	-0.7934000	-1.9460800	-2.1560700	C	-4.7130000	-2.4679300	0.8274200
C	-0.7545000	-1.0957900	-3.4349600	H	-2.5701300	-2.8512800	0.6629800
O	0.2704700	-1.6074900	-1.2857300	H	-6.7714400	-1.8127700	0.9843200
Cl	0.2879200	-0.5207700	2.7290800	H	-4.9822800	-3.5224500	0.9122300
H	-0.6557800	-3.0106600	-2.4311600	N	-1.8559300	-0.1052600	0.4221200
H	0.2680300	-1.1694300	-3.8422800	N	2.2309000	-0.0967500	0.1551200
H	-1.4331100	-1.5484500	-4.1828200	N	3.8466400	1.4589800	0.0180100
C	2.4904200	1.2313700	0.0972400	N	-3.4707700	1.4556300	0.5152300
C	3.4526100	-0.7449700	0.1196000	C	-1.1275200	0.3806600	-3.2274100
C	4.4872900	0.2281200	0.0382400	H	-0.8062200	0.9615400	-4.1091300
H	4.2953400	2.3675300	0.0135000	H	-0.5472400	0.7755500	-2.3763000
C	3.7550700	-2.1120800	0.1443000	C	-2.6256500	0.6098700	-2.9952100
C	5.8372900	-0.1332400	-0.0100900	H	-3.0019000	0.0208300	-2.1445500
C	5.1010300	-2.4729900	0.0957400	H	-2.8418600	1.6697900	-2.7853300
H	2.9511100	-2.8471800	0.1973800	H	-3.2129300	0.3166100	-3.8811100
C	6.1230700	-1.5007300	0.0214100				

Table S19: Optimized XYZ coordinates for TS-26

C	1.4587300	2.2270400	0.8192400	H	-5.2153500	-2.3209100	-1.9304800
C	1.5678400	3.4852600	1.4263000	H	-6.9051700	-0.6568600	-1.2192500
C	0.4017400	4.2055000	1.7184800	C	2.4922400	1.3155200	0.4020900
C	-0.8537300	3.6757500	1.3896100	C	4.4144500	0.2581500	-0.0224600
C	-0.9225100	2.4147000	0.7829400	H	4.3699800	2.1896900	0.9156900
H	2.5489800	3.9044600	1.6574900	C	3.3141200	-0.5255600	-0.4676800
H	0.4720100	5.1872200	2.1887200	C	5.7364100	-0.1748800	-0.1689600
H	-1.7640100	4.2429500	1.5933100	C	3.5208200	-1.7686800	-1.0785300
N	0.2223300	1.6939900	0.5296200	C	5.9254700	-1.4180500	-0.7767900
Ru	0.1050900	-0.0413000	-0.4065100	H	6.5816800	0.4262300	0.1720500
H	-1.9088600	-2.0396200	1.0628400	C	4.8375500	-2.2012800	-1.2245900
C	-1.0760900	-1.8857900	1.7777400	H	2.6662700	-2.3527900	-1.4229100
C	-0.8893900	-3.1333100	2.6460300	H	6.9422100	-1.7931600	-0.9109200
O	0.1411900	-1.5981500	1.0956300	H	5.0372800	-3.1648100	-1.6974700
Cl	0.1744200	1.0845400	-2.5238400	N	2.1397600	0.1514000	-0.1913000
H	-1.3607500	-1.0232000	2.4114700	N	-1.8897100	0.4590000	-0.2350800
H	-0.1233600	-2.9141600	3.4093000	N	-3.4115200	1.9908300	0.3883800
H	-1.8369700	-3.3225300	3.1852000	N	3.8607600	1.4075300	0.5208400
C	-2.0728500	1.6738200	0.3344400	C	-0.4737400	-4.3837500	1.8554600
C	-3.1454700	-0.0083400	-0.5818300	H	-0.2822900	-5.2058600	2.5663400
C	-4.1213400	0.9478400	-0.1875900	H	0.4869400	-4.1731800	1.3566600
H	-3.8004300	2.8568800	0.7432900	C	-1.5053100	-4.8394700	0.8166200
C	-3.5229300	-1.1974400	-1.2185000	H	-1.6545200	-4.0823300	0.0302900
C	-5.4875700	0.7388700	-0.4033300	H	-1.1861000	-5.7680000	0.3185100
C	-4.8841700	-1.4069300	-1.4338300	H	-2.4869700	-5.0294000	1.2824100
H	-2.7588400	-1.9070700	-1.5395600	H	0.0589700	-1.8766500	-0.1994400
C	-5.8485500	-0.4560700	-1.0305300	H	-0.0069300	-1.6604900	-1.1782900
H	-6.2382200	1.4721000	-0.1017500				

Table S21: Optimized XYZ coordinates for H_2

H	0.0000000	0.0000000	0.3759500
H	0.0000000	0.0000000	-0.3759500

Table S22: Optimized XYZ coordinates for 6a

C	1.1716900	-0.1508100	0.0000040
H	1.1574300	-1.2481700	-0.0005850
H	1.7165600	0.2233200	0.8835900
H	1.7169500	0.2241600	-0.8829900
C	-0.2327700	0.3986600	-0.0000040
H	-0.2944200	1.5223800	-0.0000600
O	-1.2412500	-0.2761000	0.0000050

Table S23: Optimized XYZ coordinates for 6

C	1.2208100	-0.2243400	0.0000010
H	1.2814700	-0.8670600	-0.8911200
H	1.2814700	-0.8670400	0.8911300
H	2.0847100	0.4581900	-0.0000060
C	-0.0844200	0.5531600	0.0000000
H	-0.1308400	1.2082800	0.8947200
H	-0.1308400	1.2082700	-0.8947300
O	-1.1525500	-0.4015000	0.0000000
H	-1.9838800	0.0984500	0.0000040

Table S24: Optimized XYZ coordinates for 7a

C	0.0688200	0.6984000	0.0000700
C	1.5212100	0.4151800	0.0000230
O	2.0165300	-0.7026500	-0.0001000
C	-0.8427100	-0.2950000	0.0002410
C	-2.3232000	-0.1243000	-0.0000880
H	-2.7704300	-0.6178600	-0.8805700
H	-2.7708600	-0.6169400	0.8806900
H	-2.6236500	0.9333600	-0.0008020
H	2.1760300	1.3264400	0.0000000
H	-0.4491000	-1.3197700	0.0001800
H	-0.2389800	1.7502700	-0.0001750

Table S25: Optimized XYZ coordinates for 7b

C	-0.0970200	0.7463000	-0.0000020
H	0.0861400	1.4025800	0.8745500
H	0.0860600	1.4027000	-0.8745000
C	-1.5698900	0.4070400	-0.0000010
H	-2.2554000	1.2993500	-0.0000610
O	-2.0212300	-0.7208000	0.0000420
C	0.8375800	-0.4629600	-0.0000800
H	0.6072200	-1.0896900	0.8769200
H	0.6073500	-1.0894900	-0.8772700
C	2.3169000	-0.0681800	0.0000480
H	2.9675400	-0.9557800	-0.0000510
H	2.5728100	0.5319200	-0.8885500
H	2.5727200	0.5316600	0.8888500

Table S26: Optimized XYZ coordinates for 7

C	-0.0087500	0.7229100	-0.2045300
H	0.0225500	0.7443500	-1.3082500
C	-1.4599700	0.5169000	0.2389400
H	-1.5210800	0.5516200	1.3473000
O	-2.0406600	-0.6881600	-0.2715100
C	0.9523900	-0.3545500	0.3128500
H	0.8979700	-0.3907300	1.4168800
C	2.4026000	-0.1305300	-0.1255800
H	3.0682700	-0.9218000	0.2519600
H	2.4853800	-0.1186700	-1.2243500
H	2.7848900	0.8343700	0.2452500
H	-1.5862800	-1.4265300	0.1643100
H	-2.0905600	1.3323600	-0.1477900
H	0.6175500	-1.3439700	-0.0492000
H	0.3289300	1.7159700	0.1458300

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