Phosphine–free pincer–ruthenium catalyzed biofuel production: high rates, yields and turnovers of solventless alcohol alkylation

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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 experiment.[1] Ethanol was dried and distilled under argon according to literature procedure.[1] All other compounds including pryidine-2,6-dicarboxylic acid, *o*-penylenediamnine, $[RuCl_2(p\text{-cymene})]_2$, and $CDCl_3$ were purchased either from MERCK or Sigma-Aldrich and use as such. The complexes (**1a–e**) were prepared according to literature procedure.[2]

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}. X-ray crystallographic data were collected on Bruker Nonius Smart Apex III x-ray Single crystal diffractometer (CCD) with graphite - monochromatized Mo-Kα radiation. The data refinements and cell reduction were carried out using Bruker Apex III program. Structures were solved and further refined by full matrix least-squares method using SHELXS-14.[3] GC analyses were performed on a Agilent 7820-GC instrument fitted with Agilent Front SS7 enlet N2 HP5 column (30 m length, 0.32 mm ID) using the following method: Agilent 7820-GC Detector: FID starting temperature: 60 °C; Time at starting temp: 0 min; Ramp: 40 °C/min up to 300 °C with hold time = 4 min; Flow rate (carrier): 25 mL/min (N_2); Split ratio: 195; Inlet temperature: 250 °C; Detector temperature: 300 °C

Synthesis of 2,6-bis(1H-benzimidazol-2-yl)pyridine (3e), To a two-necked round bottom flask (100 mL) containing pyridine-2,6-dicarboxylic acid (0.084 g, 0.5 mmol) and *o*-phenylenediamine (0.108g, 1.0 mmol), orthophosphoric acid (10 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. The product was crystallized in methanol to obtain 0.135 g of an off-white solid in 74% yield. ^1H 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 NMR (101 MHz, DMSO-d_6) δ = 149.98, 147.23, 143.67, 138.70, 133.87, 123.24, 121.71, 120.88, 119.23, 111.27. HRMS (ESI): *m/z* calculated for $[\mathbf{3e}+H]^+$ Calculated = 312.1243, Found = 312.1413.

Synthesis of 2,6-bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridine (3f). To a round bottom flask (50 mL) containing **3e** (0.100g, 0.32 mmol) and KOH (0.090, 1.60 mmol), acetone (10 mL) was added and stirred for 15 minutes. Subsequently, methyl iodide (0.2 mL, 3.2 mmol) was added in dropwise fashion. The reaction was stirred at room temperature for additional 3 hours. The reaction mixture was poured into water (50 mL) and the resulting white precipitate was filtered. The residue was dried and recrystallized in methanol (off white solid, 0.098g, 90% yield). ^1H NMR (400 MHz, DMSO-d_6) δ = 8.40 (d, J = 7.7 Hz, 2H), 8.22 (t, J = 7.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.34 (dt, J = 24.4, 7.3 Hz, 4H), 4.27 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6) δ = 149.73, 149.30, 142.10, 138.54, 137.10, 125.05, 123.32, 122.51, 119.52, 110.92, 32.56. HRMS (ESI): *m/z* calculated for $[\mathbf{3f}+H]^+$ Calculated = 340.1556, Found = 340.1585.

Synthesis of $[(^{MeBim2}NNN)RuCl(PPh_3)_2]Cl$ (1f). To a two-necked round bottom flask (25 mL) containing 2,6-bis(1-methyl-1H-benzo[d]imidazol-2-yl)pyridine (0.07g, 0.206 mmol) and $RuCl_2(PPh_3)_3$ (0.200g, 0.207 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 pink colored gel. The residue was washed with dry diethyl ether (3 x 5 mL) followed by hexane (3 x 5 mL). A pink color solid (0.135g) was obtained in 83% yield. ^1H NMR (600 MHz, $CDCl_3$) δ = 8.76 (s, 2H), 8.40 (s, 1H), 8.27 (s, 1H), 8.00 (s, 1H), 7.84 (s, 1H), 7.67 (dd, J = 11.7, 7.8 Hz, 5H), 7.57 – 7.52 (m, 4H), 7.47 (t, J = 6.3 Hz, 5H), 7.39 (s, 3H), 7.08 (d, J = 44.4 Hz, 15H), 6.84 (s, 9H), 3.72 (d, J = 17.4 Hz, 6H).

$^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$) δ = 29.29,(1P) 23.27 (1P). HRMS (ESI): *m/z* calculated for [**1f**–Cl]$^+$ Calculated = 1000.2039, Found = 1000.2236.

General procedure for the synthesis of (^{R2}NNN)$RuCl_2$(CO) (2a; R = ^{t}Bu, 2b; R = Cy, 2c; R = ^{i}Pr and 2d; R = Ph). In a two-necked round bottom flask (25 mL), the ligand **3b** (0.030 g 0.100 mmol) and [$RuCl_2$(*p*-Cymene)]$_2$ (0.031 g, 0.050 mmol) were taken in dry THF (5 mL) under argon atmosphere. The reaction mixture was heated at 60 °C for 2h under argon atmosphere. Subsequently, the reaction mixture was further heated for another 10 h under an atmosphere of CO. The color of the reaction mixture changed from brown to dark greenish brown. This was followed by solvent evaporation to yield a dark green color solid which was washed by dry diethyl ether (3 x 5 mL) followed by hexane (2 x 5 mL) to yield 0.140 g of **2b** as a green color solid in 85% yield.

(^{tBu2}NNN)$RuCl_2$(CO) (**2a**). (0.044 g) 81% Yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (s, 1H), 8.02 (s, 1H), 7.97 – 7.87 (m, 1H), 7.74 (dd, *J* = 16.4, 7.9 Hz, 2H), 1.61 (s, 9H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 207.24, 161.20, 160.27, 159.13, 156.36, 138.99, 136.28, 126.25, 124.89, 68.27, 68.13, 29.91, 29.58. HRMS (ESI): *m/z* calculated for [**2a**–Cl]$^+$ Calculated = 410.0605, Found = 410.0610; *m/z* calculated for [**2a**–Cl+CH_3CN]$^+$ Calculated = 451.0871, Found = 451.0877. IR (cm^{-1}): ν = 2974, 2930, 2869, 2057, 1995, 1934 (s), 1602, 1584, 1462, 1424, 1395, 1372, 1237, 1191, 1157, 1072, 1039, 1026, 928, 808, 774, 753, 610, 585, 574, 507, 484, 407.

(^{Cy2}NNN)$RuCl_2$(CO) (**2b**). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 (s, 2H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 2H), 3.62 (t, *J* = 11.2 Hz, 2H), 2.07 – 1.23 (m, 20H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 205.21, 161.03, 155.99, 138.84, 123.97, 75.94, 33.44, 25.37, 25.02. HRMS (ESI): *m/z* calculated for [**2b**–Cl]$^+$ Calculated = 462.0918, Found = 462.0907; *m/z* calculated for [**2b**–Cl+CH_3CN]$^+$ Calculated = 503.1184, Found = 503.1164. IR (cm^{-1}): ν = 2924, 2853, 2056, 1944 (s), 1936 (s), 1739, 1606, 1542, 1461, 1449, 1425, 1345, 1261, 1161, 1149, 1085, 1075, 1056, 1025, 972, 891, 856, 803, 753, 699, 686, 559, 523, 517, 488, 471, 435.

(^{iPr2}NNN)$RuCl_2$(CO) (**2c**): (0.046 g) 80% Yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (s, 2H), 7.93 (t, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 4.03 (hept, *J* = 6.4 Hz, 2H), 1.51 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 205.10, 161.05, 156.03, 138.94, 124.10, 68.26, 23.17. HRMS (ESI): *m/z* calculated for [**2c**–Cl]$^+$ Calculated = 382.0292, Found = 382.0283; *m/z* calculated for [**2c**–Cl+CH_3CN]$^+$ Calculated = 423.0558, Found = 423.0556. IR (cm^{-1}): ν = 2987, 2987, 2973, 2931, 2895, 2059, 1995, 1952 (s), 1604, 1469, 1447, 1423, 1398, 1382, 1367, 1327, 1273, 1163, 1144, 1121, 934, 913, 810, 797, 751, 606, 570, 482, 446.

(^{Ph2}NNN)$RuCl_2$(CO) (**2d**): Yield 80%. Low solubility posed challenges in NMR characterization. HRMS (ESI): *m/z* calculated for [**2d**–Cl]$^+$ Calculated = 449.9947, Found = 449.9998. IR (cm^{-1}): ν = 3060, 2866, 2977, 2062, 1954 (s), 1604, 1584, 1523, 1485, 1453, 1417, 1348, 1315, 1271, 1191, 1163, 1075, 1064, 1053, 1027, 1001, 938, 917, 904, 800, 763, 748, 697, 597, 579, 564, 542, 506, 461, 432.

General procedure for the synthesis of 2e and 2f. To a two-necked round bottom flask (25 mL) containing ligand **3e** (0.025 g 0.08 mmol) and [$RuCl_2$(*p*-Cymene)]$_2$ (0.025 g, 0.04 mmol), dry THF (5 mL) was added under argon atmosphere. The reaction mixture was heated at 60 °C for 2 h under argon atmosphere. Subsequently an atmosphere of CO was introduced and the reaction mixture was further heated another 10 h. During the course of the reaction, the color of the reaction mixture changed from brown to straw color. Solvent evaporation yielded a dark green solid which upon washing with dry diethyl ether (3 x 5 mL) followed by hexane (2 x 5 mL) gave 0.037 g of **2e** as an orange yellowish solid in 74 % yield.

(^{Bim2}NNN)$RuCl_2$(CO) (**2e**). Low solubility posed challenges in NMR characterization. IR (cm^{-1}): ν = 3448 (br), 3053 (br), 2062, 1965 (s),1605, 1591, 1494, 1487, 1458, 1379, 1346, 1320, 1278, 1233, 1174, 1118, 1022, 996, 912, 849, 809, 761, 746, 674, 634, 596, 583, 572, 492, 434, 415. HRMS (ESI): *m/z* calculated for [**2e**–Cl]$^+$ Calculated = 475.8952, Found = 475.0000.

(^{MeBim2}NNN)$RuCl_2$(CO) (**2f**). (0.038 g) 71%, Low solubility posed challenges in NMR characterization. IR (cm^{-1}): ν = 1939, 1598, 1508, 1473, 1420, 1337, 1255, 1162, 1009, 866, 813, 801, 772, 758, 739, 602, 492, 435. HRMS (ESI): *m/z* calculated for [**2f**–Cl]$^+$ Calculated = 504.0165, Found = 504.0289; *m/z* calculated for [**2f**–Cl+CH_3CN]$^+$ Calculated = 545.0431, Found = 545.0539.

General procedure for alkylation reaction: In a 25 mL two necked round bottom flask, 1-phenyl ethanol or benzyl alcohol were taken under argon atmosphere. This was followed by addition of 5 mol % of NaOH and 0.00025 mol % of **2b** (from a stock solution either in 1-phenyl ethanol or benzyl alcohol). After the addition, the reaction mixture contained 0.5 mL (4.14 mmol) of 1-phenyl ethanol, 0.43 mL (4.14 mmol) of benzyl alcohol, 8 mg (0.21 mmol) of NaOH and 1 mg (20 μmol) of **2b**. The mixture was heated at 140 °C for 20 h under Ar. The reaction mixture was then cooled to room temperature followed by addition of toluene as an internal standard. The yield was determined by ^{1}H NMR spectroscopy.

General procedure for Guerbet reaction: A 5 mL Schlenk flask was charged with **2e** (1.8 mg, 4.28 μmol), ethanol (0.5 mL, 8.56 mmol) and of NaOEt (58 mg, 0.86 mmol). The volume was made up to 0.7 mL by using toluene which is used as an internal standard. The vessel was sealed and the reaction mixture was heated at 140 °C for 72 h. At regular intervals, an aliquot was taken out and the products were analyzed by GC.

Computational methodology: The geometries of all the considered complexes were fully optimized using the DFT (PBEPBE)[4] method on the Gaussian-16 program package.[5] The LANL2DZ[6] and 6-311G(d,p) basis set was used respectively for the metal (Ru) and non-metal atoms. 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 140 °C.

2. Crystallographic data and parameters

Table S1a: Crystallography data of complexes **2b** and **2c**

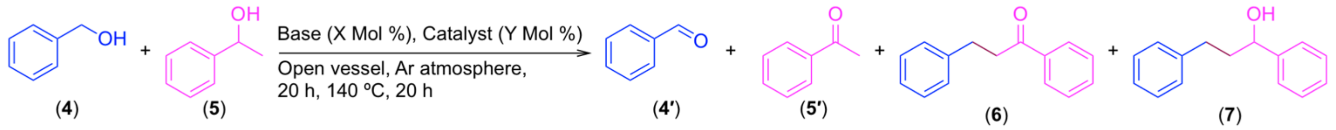
Name	**2b**	**2c**
Empirical formula	$C_{43}H_{60}Cl_4N_6O_5Ru_2$	$C_{14}H_{21}Cl_2N_3O_2Ru_2$
Formula weight	1084.91	435.31
Crystal size (mm^3)	0.27 x 0.25 x 0.24	0.28 x 0.26 x 0.21
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	12.5519(9)	9.2304(5)
b (Å)	23.6646(18)	10.8098(6)
c (Å)	16.9746(12)	18.2395(11)
α (deg)	90.00	90.00
β (deg)	94.020(2)	96.278(2)
γ (deg)	90.00	90.00
V ($Å^3$)	5029.7(6)	1809.00(18)
Z	4	4
ρ_{calc} (g cm^{-3})	1.438	1.598
μ (M_0 Kα) (mm^{-1})	0.859	1.170
F (000)	2178.0	726.0
T(K)	296(2)	296(2)
Range of indices (h; k; l)	-14, 14; -28, 28; -20, 20	-10, 10; -12, 12; -21, 21
Number of reflection collected	166251	72376
Unique reflection	8853	3184
Completeness to 2θ	99.9	99.6
R_{int}	0.1575	0.2104
Data / restraints / parameters	8853/0/549	3184/0/206
goodness-of-fit	0.925	1.042
$R_1[I \geq 2\sigma(I)]$	0.0672	0.0376
$wR_2[I \geq 2\sigma(I)]$	0.1315	0.0872
R_1 (all data)	0.0989	0.0455
wR_2 (all data)	0.1572	0.0939
Δ_r (max, min) e $Å^3$	0.85/-0.49	0.49/-1.31

Table S1b: Selective bond distance (Å) and bond angle (°) around the metal center of complexes **2b** and **2c**.

	2b	**2c**
Ru–N (Å) (Pyridine)	2.016 (6) Unit 1 2.014 (5) Unit 2	2.008 (3)
Ru–N (Å) (Imine)	2.088 (6) Unit 1 2.099 (7) Unit 1 2.103 (6) Unit 2 2.100 (6) Unit 2	2.106 (3) 2.096 (3)
Ru–Cl (Å)	2.397 (2) Unit 1 2.402 (2) Unit 1 2.391 (2) Unit 2 2.403 (2) Unit 2	2.3945 (9) 2.3948 (9)
Ru–C (Å) (Carbonyl carbon)	1.864 (8) Unit 1 1.870 (8) Unit 2	1.854 (4)
C≡O (Å) (Carbonyl carbon-oxygen)	1.143 (9) Unit 1 1.126 (9) Unit 2	1.141 (5)
(Imine)**N–Ru–N**(Imine) (°)	154.9 (3) Unit 1 154.2 (2) Unit 2	154.78 (12)
Ru–C≡O (°) (In carbonyl carbon)	179.3 (8) Unit 1 178.9 (7) Unit 2	178.4 (4)

3. Optimization Tables, Figures and Schemes

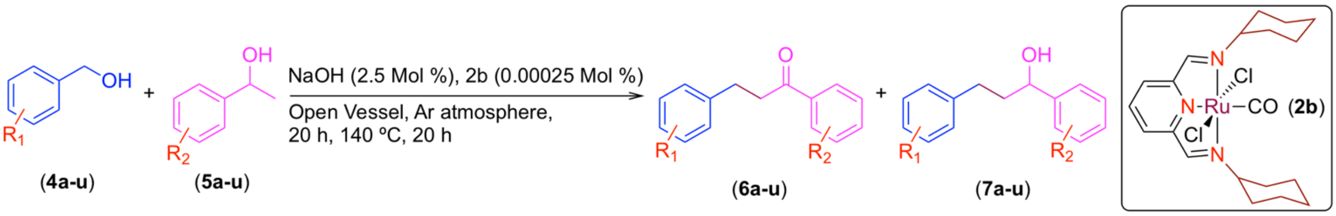
Table S2a. *β*–Alkylation of 1–Phenyl Ethanol with Benzyl Alcohol Catalyzed by **1** and **2** Under Varying Conditions[a]

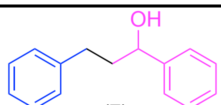
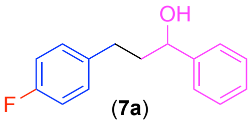
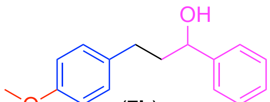
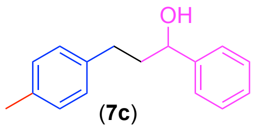
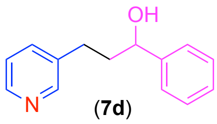
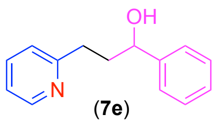
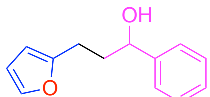
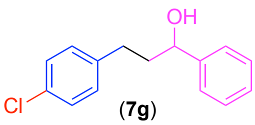
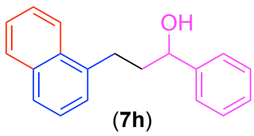
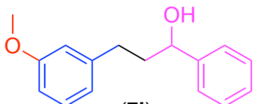
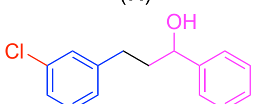
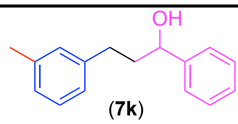
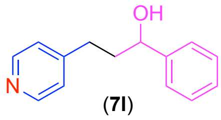
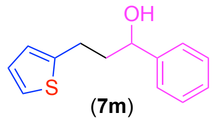
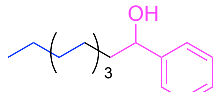
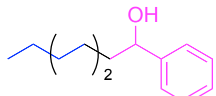
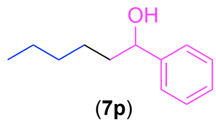
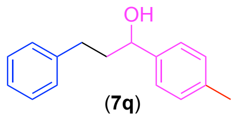
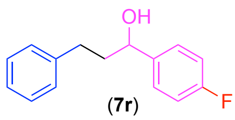
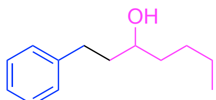
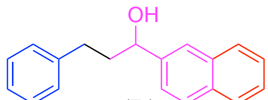
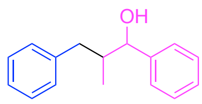


Entry	Catalyst (Y Mol %)[b]	Base (X Mol %)[b]	% Yield of Products[c]				Total Yield [TON]	Selectivity[d] towards **7**
			4′	**5′**	**6**	**7**		
1	**2b** (0.05)	NaO^{t}Bu, 5	0	13	12	57	82% [1640]	83%
2	**2b** (0.05)	KO^{t}Bu, 5	0	8	6	65	79% [1580]	91%
3	**2b** (0.05)	NaOH, 5	0	10	12	63	85% [1700]	84%
4	**2b** (0.05)	KOH, 5	0	6	8	63	77% [1540]	89%
5	**2b** (0.05)	Na, 5	0	13	11	65	89% [1780]	85%
6	**2b** (0.05)	K_2CO_3, 5	0	10	11	15	36% [720]	57%
7	**2b** (0.05)	Na_2CO_3, 5	0	10	trace	0	10% [200]	0
8	**2b** (0.05)	KO^{t}Bu, 2.5	0	10	8	65	83% [1660]	89%
9	**2b** (0.05)	KO^{t}Bu, 10	0	5	5	69	79% [1649]	93%
10	**2b** (0.05)	NaOH, 2.5	0	7	7	79	93% [1860]	91%
11	**2b** (0.05)	NaOH, 10	0	10	10	65	85% [1700]	88%
12	**2b** (0.025)	NaOH, 2.5	0	14	13	70	97% [3880]	84%
13	**2b** (0.025)	KO^{t}Bu, 2.5	0	14	15	68	97% [3880]	82%
14	–	KO^{t}Bu, 2.5	0	trace	1	6	7% [NA]	NA
15	**2b** (0.025)	–	0	5	2	4	11% [440]	NA
16	**2b** (0.0025)	NaOH, 2.5	0	16	16	63	99% [39600]	79%
17	**2b** (0.00025)	NaOH, 2.5	0	1	19	73	93% [372000]	79%
18	**1a** (0.00025)	NaOH, 2.5	0	2	7	78	87% [348000]	92%
19	**1b**(0.0025)	NaOH, 2.5	0	2	7	78	87% [348000]	92%
20	**1b** (0.00025)	NaOH, 2.5	0	1	7	81	89% [356000]	92%
21	**1c** (0.0025)	NaOH, 2.5	0	trace	10	79	89% [35600]	89%
22	**1c** (0.00025)	NaOH, 2.5	0	2	9	75	86% [344000]	89%
23	**1d** (0.00025)	NaOH, 2.5	0	2	15	65	80% [320000]	81%
24	**2a** (0.00025)	NaOH, 2.5	0	1	10	78	89% [356000]	88%
25	**2c** (0.00025)	NaOH, 2.5	0	1	10	78	89% [356000]	88%
26	**2d** (0.00025)	NaOH, 2.5	0	2	3	57	62% [248000]	95%

[a]Reaction conditions: 4.14 mmol of **4**, 4.14 mmol of **5**, X mol % of base and Y mol % of pincer-ruthenium. [b]Mol % of base and catalyst is with respect to total alcohol content (**4**+**5**). [c]Yield is determined from ^1H NMR using toluene as external standard. [d]Selectivity = Yield of **7**/Total Yield.

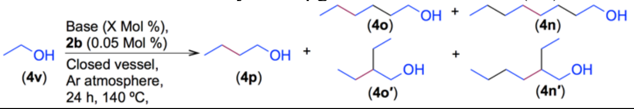
Table S2b. *β*–Alkylation of Substituted 1–Phenyl Ethanol with Various Benzyl Alcohols Catalyzed by 0.00025 Mol % of **2b**[a]



Entry	Product	7 Yield[b] [7 Selectivity][c]	Total TON (6 + 7)
1	 (7)	73 % [79:21]	372000
2	 (7a)	63 % [93:7]	368000
3	 (7b)	85 % [94:6]	360000
4	 (7c)	74 % [83:17]	356000
5	 (7d)	38 % [93:7] 46 %[d] [88:12]	164000 2080[d]
6	 (7e)	6 % [55:45] 30 %[d] [83:17]	44000 1440[d]
7	 (7f)	3 % [75:25] 63 %[d] [97:3]	16000 2600[d]
8	 (7g)	50 % [91:9]	220000
9	 (7h)	50 % [81:19]	248000
10	 (7i)	80 % [84:16]	380000
11	 (7j)	37 % [90:10] 48 %[d] [87:13]	160000 2200[d]
12	 (7k)	70 % [89:11]	316000
13	 (7l)	28 % [80:20]	140000
14	 (7m)	21 %[d] [100: 0]	840[d]
15	 (7n)	53 %[d] [99: 1]	2120[d]
16	 (7o)	30 %[d][99: 1]	1200[d]
17	 (7p)	32 %[d][91: 9]	1400[d]
18	 (7q)	73 % [88:12]	332000
19	 (7r)	10 % [83:17]	40000
20	 (7s)	19 % [99:1]	76000
21	 (7t)	77 % [95:5]	324000
22	 (7u)	36 % 2 Diastereomers [95:5]	144000

[a]Reaction conditions: 4.14 mmol of **4**, 4.14 mmol of **5**, 0.207 mmol of NaOH and 20 µmol of **2b**. [b]Yield is determined from ^{1}H NMR using toluene as external standard. [c]Selectivity = Yield of **7**/Total Yield. [d]Reaction performed with 0.025 mol % of **2**

Table S2c. The **2b** Catalyzed Upgradation of Ethanol (**4v**) to *n*–Butanol (**4p**)[a]



Entry	Base (mol %)	% Butanol Selectivity[b]	Total TON[c,b]
1	NaO^{t}Bu, 10	90	195
2	NaO^{t}Bu, 20	97	145
3	KOH, 10	85	155
4	KO^{t}Bu, 10	86	65
5	Et_3N, 10	ND	trace
6	K_2CO_3, 10	0	0
7	Mg, 10	0	0
8	NaH, 10	90	260
9	NaOH. 10	90	310
10	NaOH, 5	85	150
11	NaOH, 20	80	330
12[d]	NaOH, 10	90	290
13[d,e]	NaOH, 10	90	320
14[f]	NaOEt, 10	90	335
15[e,f]	NaOEt, 10	90	410

[a]Reaction conditions: 8.56 mmol of ethanol, X mol % of base and 4.28 µmol of **2b**. [b]Selectivity and TON were calculated by GC analysis using toluene as an internal standard. [c]Total ethanol converted to products. [d]The reaction was carried out at 150 °C. [e]Reaction was carried out for 48 h. [f]NaOEt was prepared *in-situ* using ethanol (110 mol %) and Na(10 mol %) prior to addition of **2b**

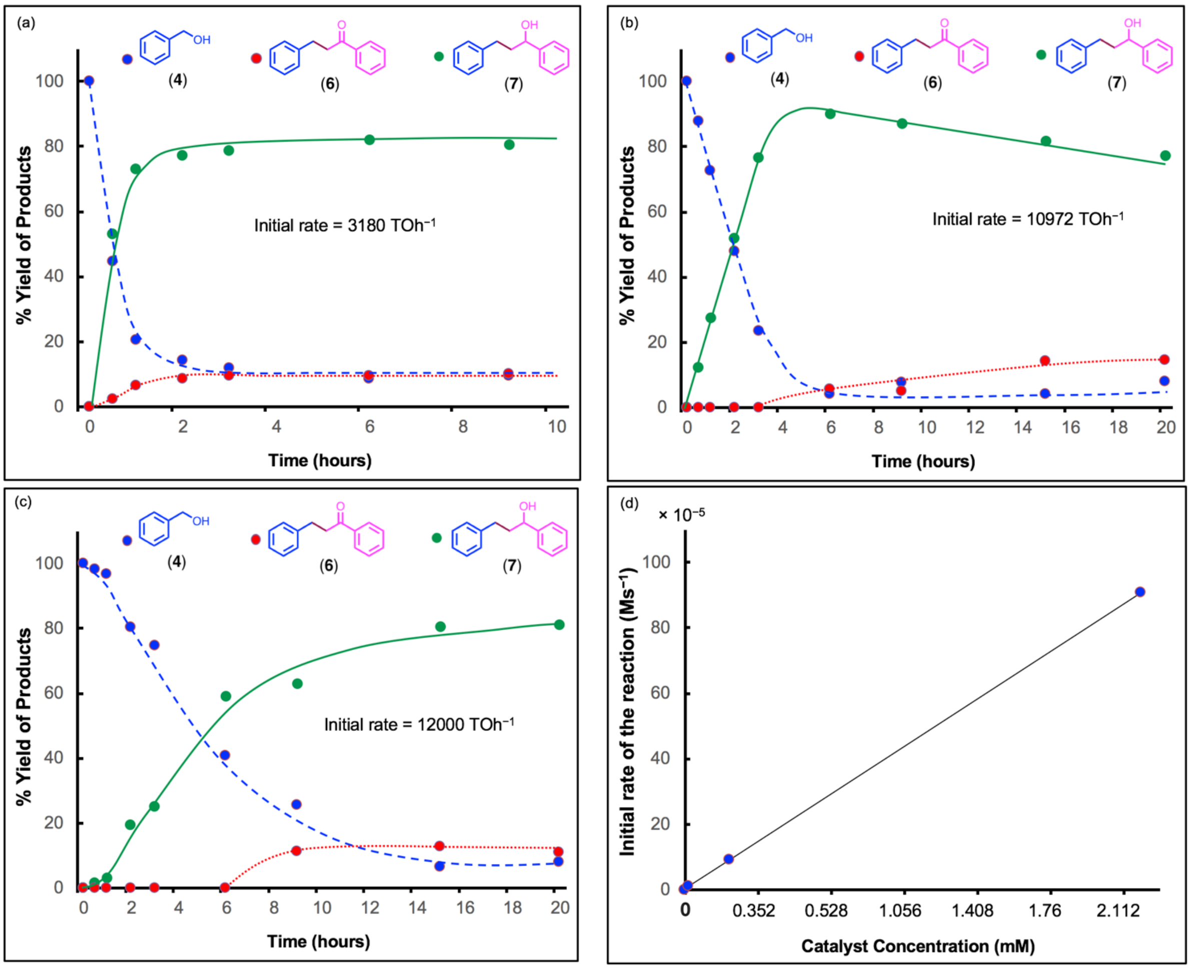


Figure S1. Time course of the reaction of benzyl alcohol (**4**) with 1–phenyl ethanol (**5**) at 140 °C catalyzed by (a) 0.025 mol % **2b**, (b) 0.0025 mol % **2b** and (c) 0.00025 mol % **2b**. (d) Plot of initial rate of the reaction vs catalyst concentration (0.022, 0.22 and 2.2 mM).

Dehydrogenation + Alcoholysis

$$(^{iPr2}NNN)RuCl(OEt) \overset{K_1}{\rightleftharpoons} (^{iPr2}NNN)RuClH + CH_3CHO$$

$$(^{iPr2}NNN)RuClH + EtOH \overset{K_2}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OEt) + H_2$$

$$2CH_3CHO \xrightarrow{k_3} CH_3CHCHCHO + H_2O$$

$$CH_3CHCHCHO + (^{iPr2}NNN)RuClH \overset{K_4}{\rightleftharpoons} (^{iPr2}NNN)RuCl(CH_3CH_2CHCHO)$$

$$(^{iPr2}NNN)RuCl(CH_3CH_2CHCHO) + EtOH \overset{K_5}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OEt) + CH_3CH_2CH_2CHO$$

$$(^{iPr2}NNN)RuClH + CH_3CH_2CH_2CHO \overset{K_6}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OCH_2CH_2CH_2CH_3)$$

$$(^{iPr2}NNN)RuCl(OCH_2CH_2CH_2CH_3) + EtOH \overset{K_7}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OEt) + CH_3CH_2CH_2CH_2OH$$

Dehydrogenation + Hydrogenation

$$(^{iPr2}NNN)RuCl(OEt) \overset{K_1}{\rightleftharpoons} (^{iPr2}NNN)RuClH + CH_3CHO$$

$$(^{iPr2}NNN)RuClH + EtOH \overset{K_2}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OEt) + H_2$$

$$2CH_3CHO \xrightarrow{k_3} CH_3CHCHCHO + H_2O$$

$$CH_3CHCHCHO + (^{iPr2}NNN)RuClH \overset{K_4}{\rightleftharpoons} (^{iPr2}NNN)RuCl(CH_3CH_2CHCHO)$$

$$(^{iPr2}NNN)RuCl(CH_3CH_2CHCHO) + H_2 \overset{K_5}{\rightleftharpoons} (^{iPr2}NNN)RuClH + CH_3CH_2CH_2CHO$$

$$(^{iPr2}NNN)RuClH + CH_3CH_2CH_2CHO \overset{K_6}{\rightleftharpoons} (^{iPr2}NNN)RuCl(OCH_2CH_2CH_2CH_3)$$

$$(^{iPr2}NNN)RuCl(OCH_2CH_2CH_2CH_3) + H_2 \overset{K_7}{\rightleftharpoons} (^{iPr2}NNN)RuClH + CH_3CH_2CH_2CH_2OH$$

Either for hydrogenation or for alcoholysis, $k_2 > k_{-2}$, and under low steady state concentration of $CH_3CHCHCHO$

$$\text{Rate} = (k_2)[(^{iPr2}NNN)RuClH][EtOH] \qquad (1)$$

Scheme S1. Rate Equation for the **2c** Catalyzed Alkylation of Alcohols

4. NMR spectra

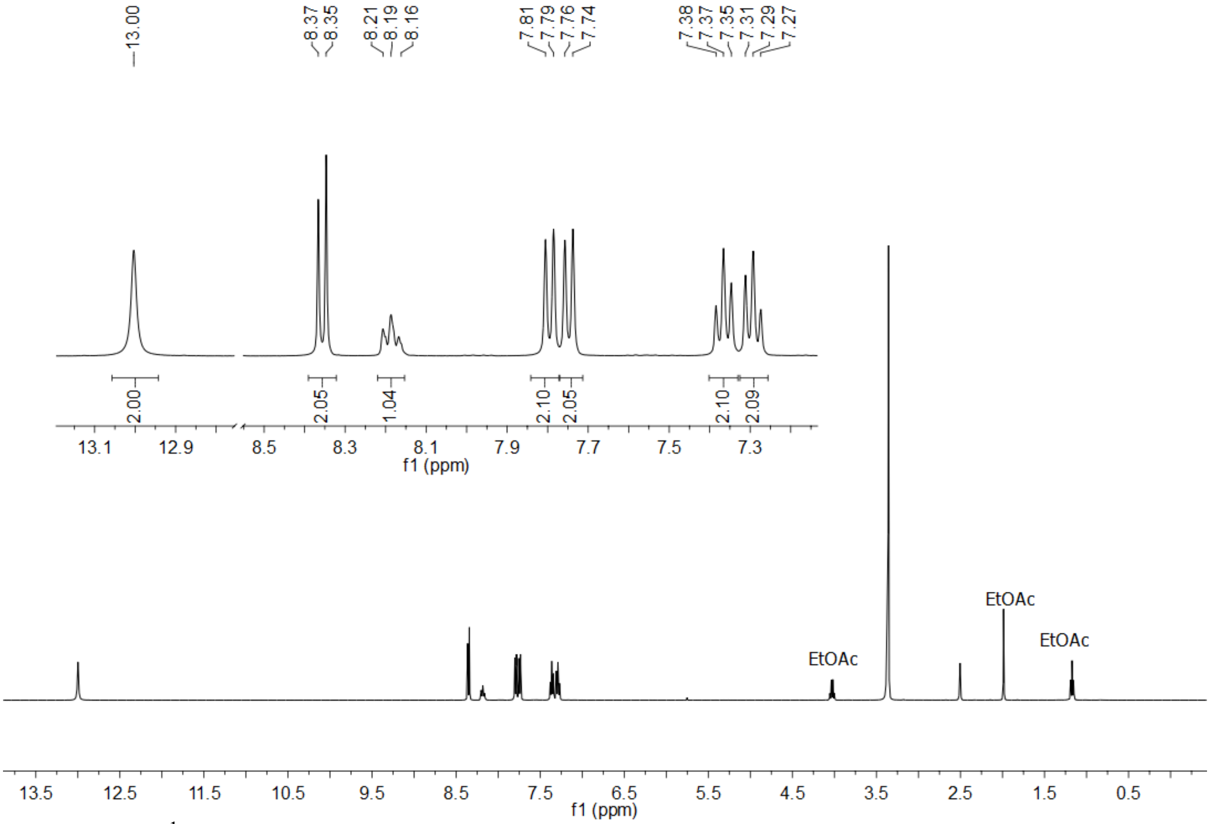


Figure S1e: ^{1}H NMR spectra of **3e**

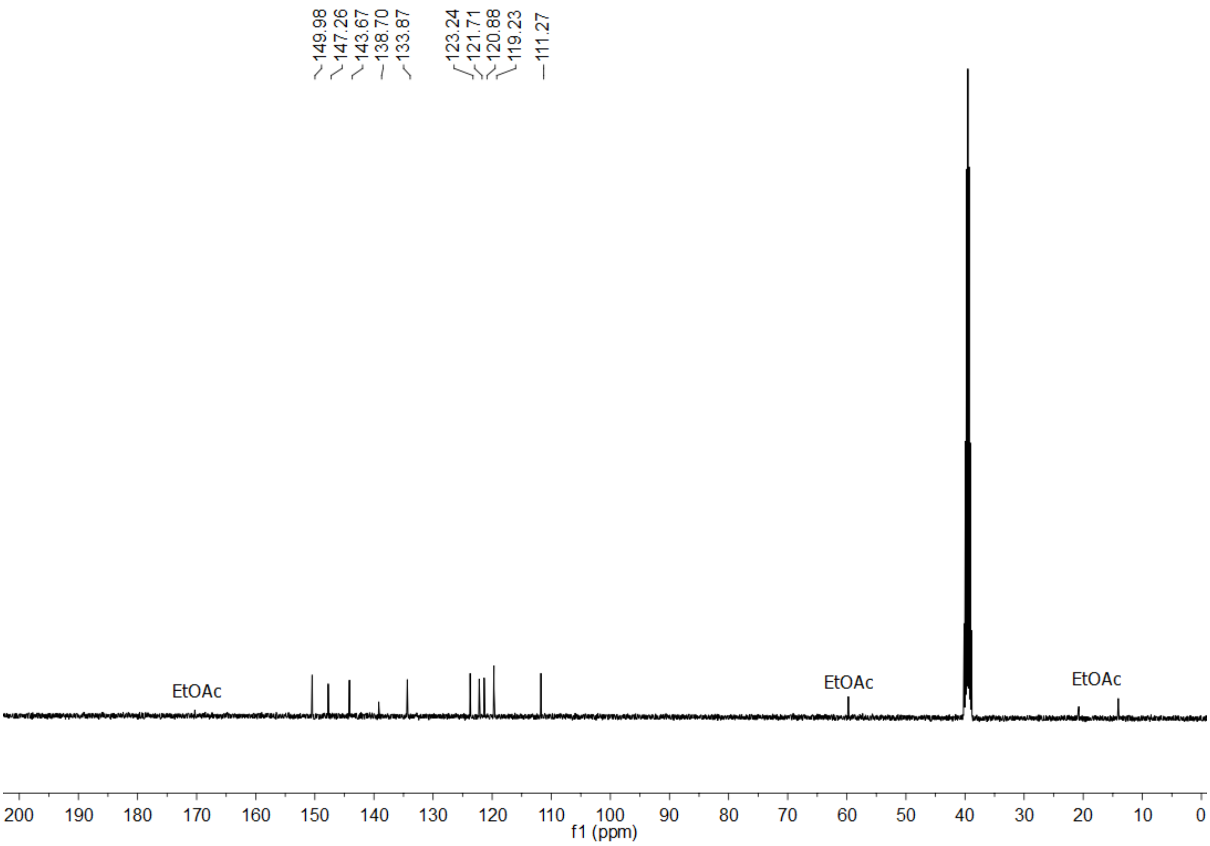


Figure S2: ^{13}C NMR spectra of **3e**

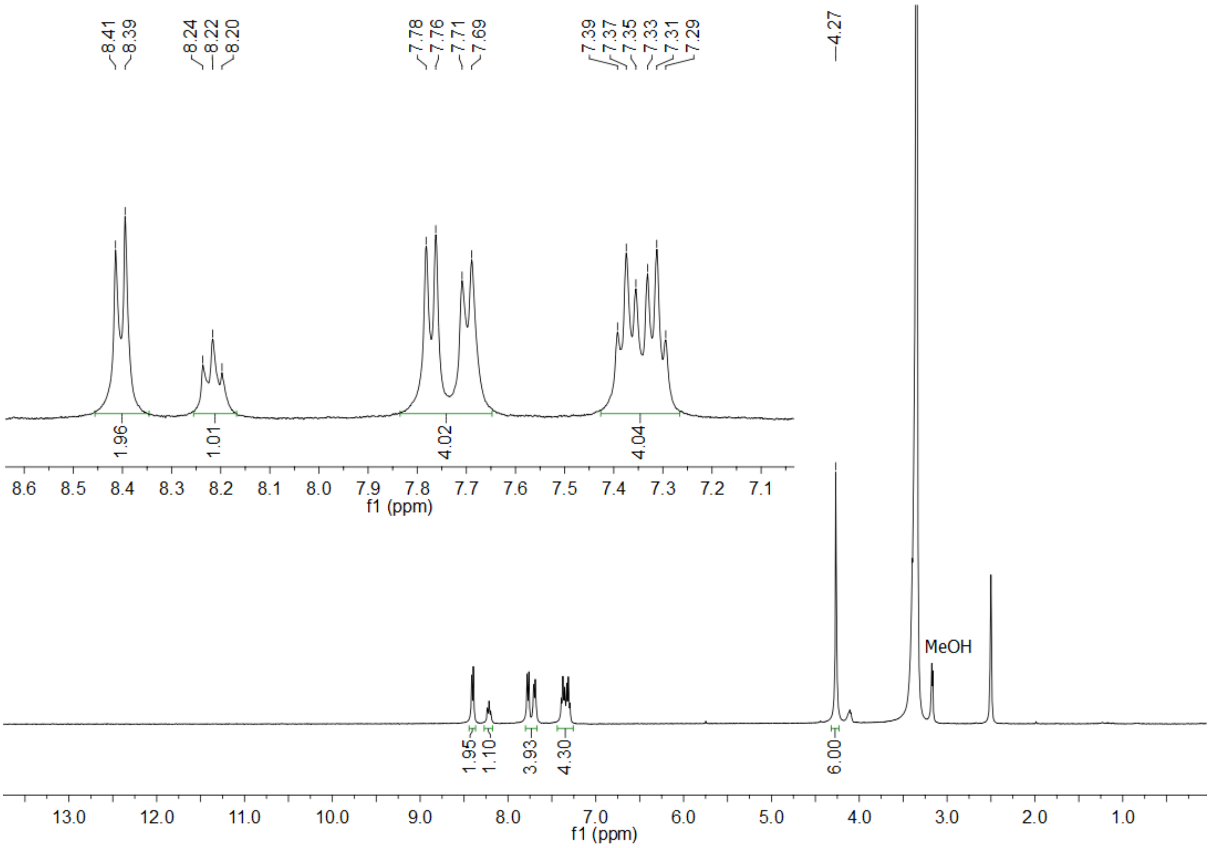


Figure S3: ^{1}H NMR spectra of **3f**

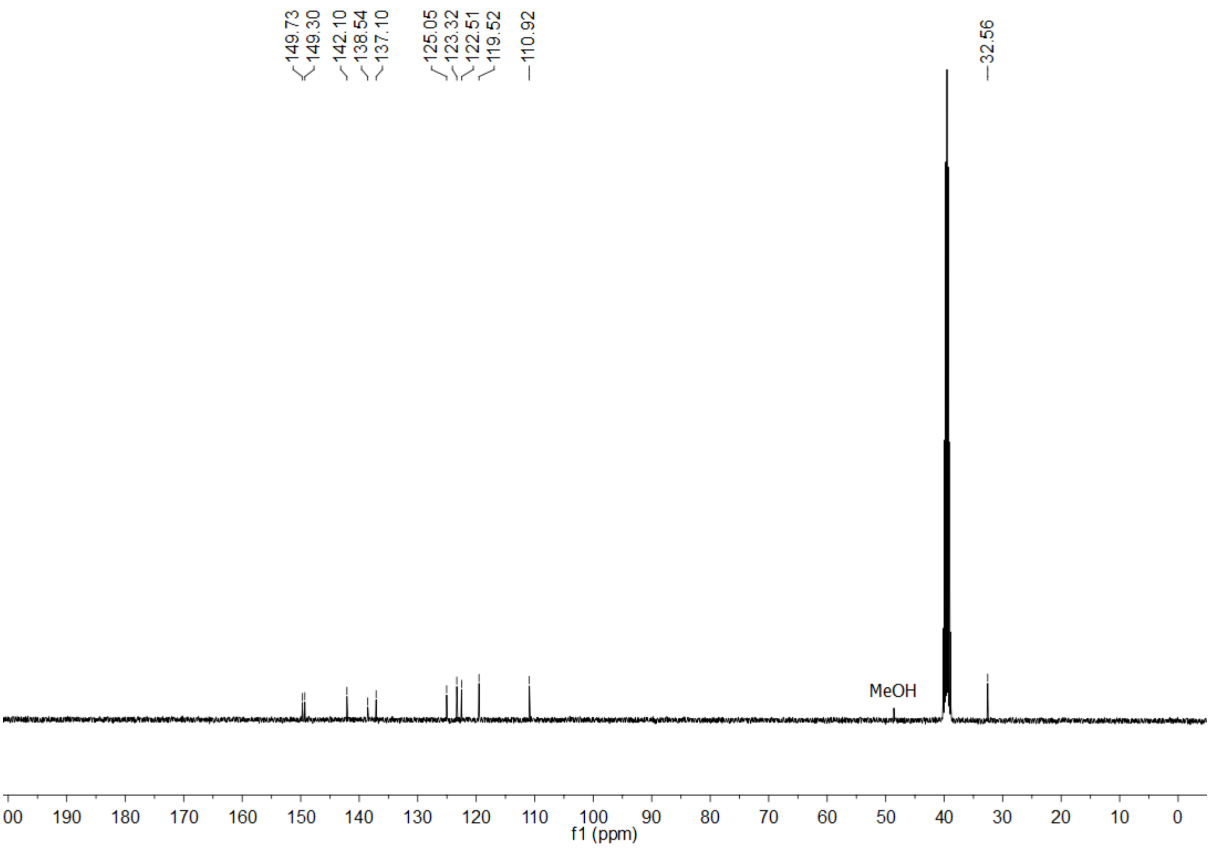


Figure S4: ^{13}C NMR spectra of **3f**

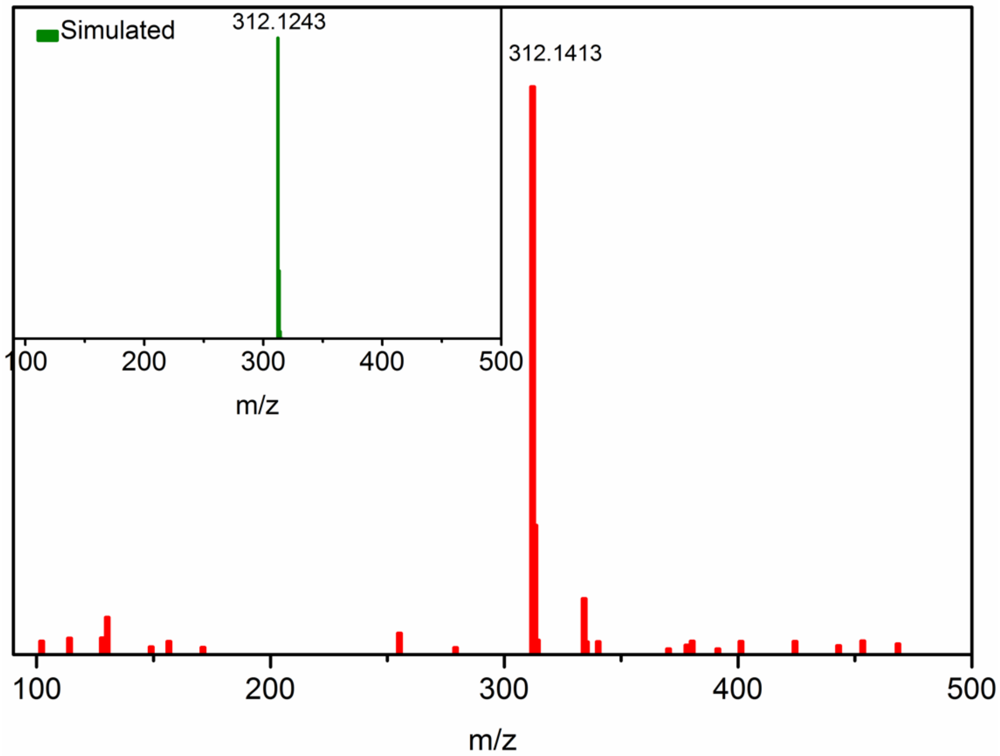


Figure S5: ESI-MS full spectra of **3e** with simulated data

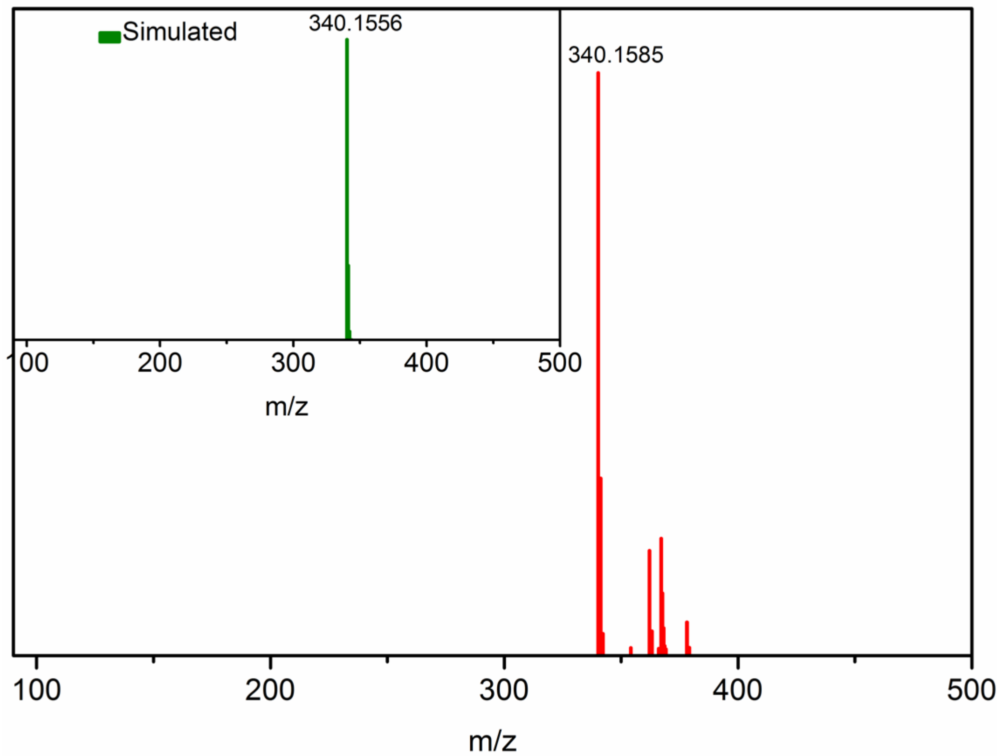


Figure S6: ESI-MS full spectra of **3f** with simulated data

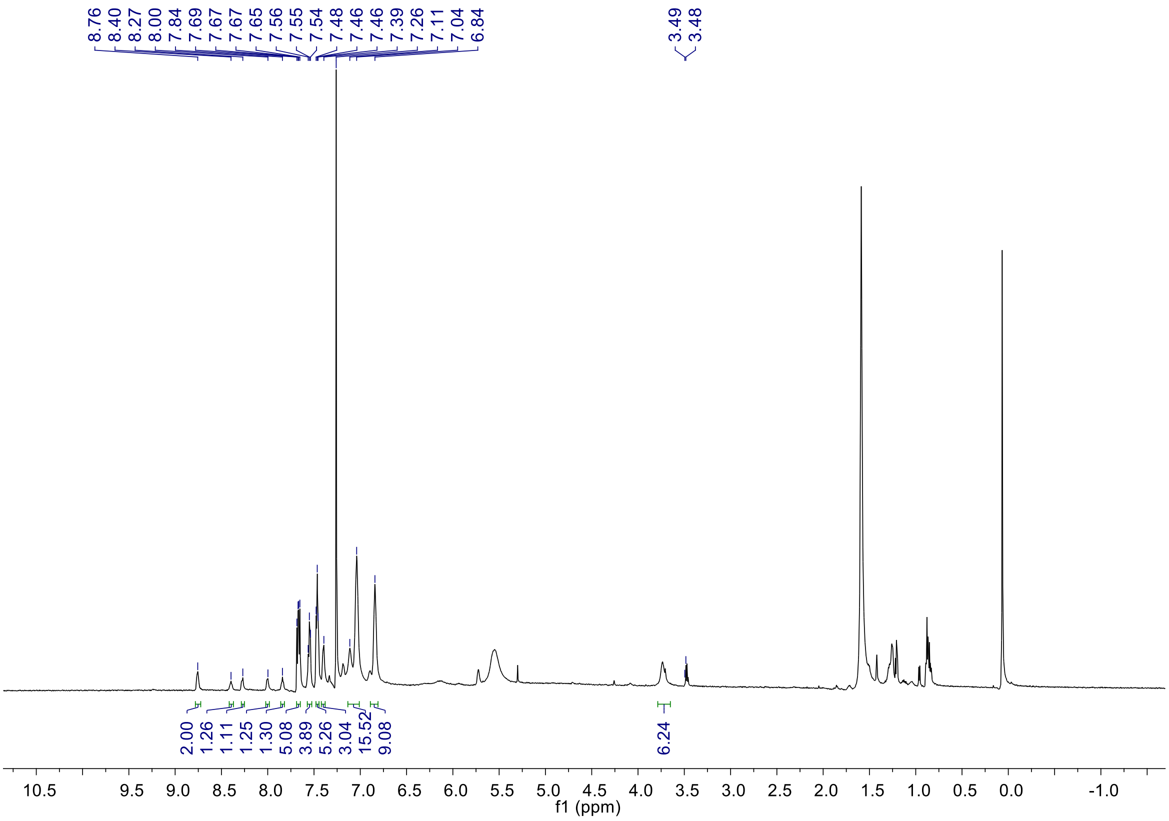


Figure S7: ^{1}H NMR spectra of [(^{MeBim2}NNN)RuCl(PPh_3)$_2$]Cl (**1f**)

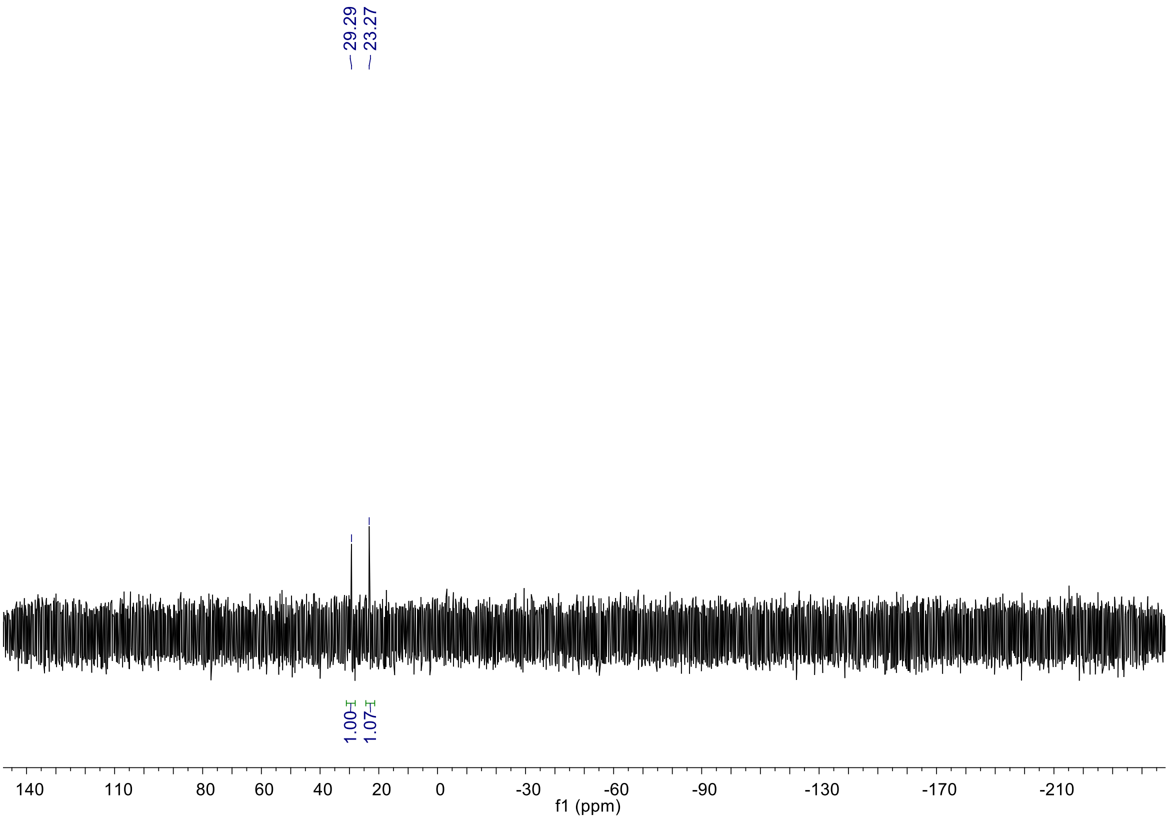


Figure S8: ^{31}P NMR spectra of [(^{MeBim2}NNN)RuCl(PPh_3)$_2$]Cl (**1f**)

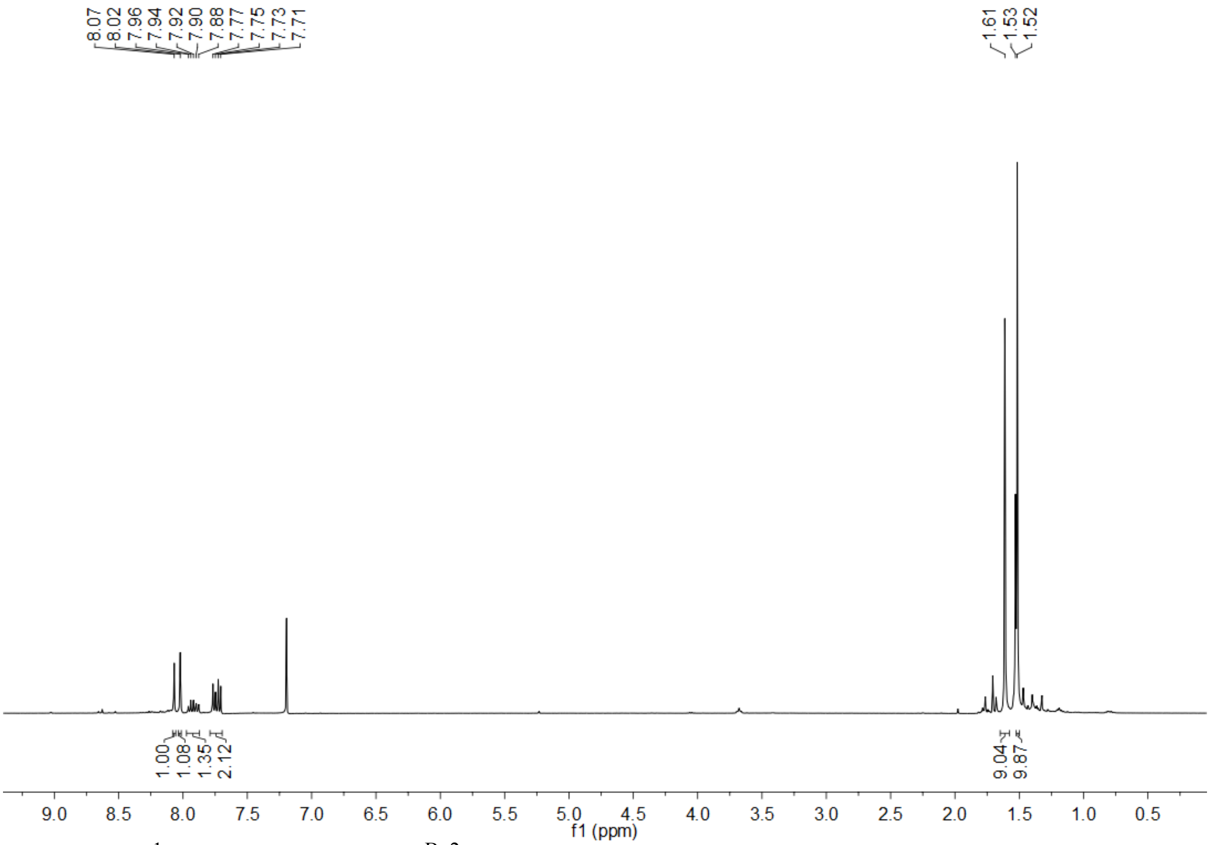


Figure S9: [1]H NMR spectra of ($^{t\mathrm{Bu2}}$NNN)RuCl$_2$(CO) (**2a**)

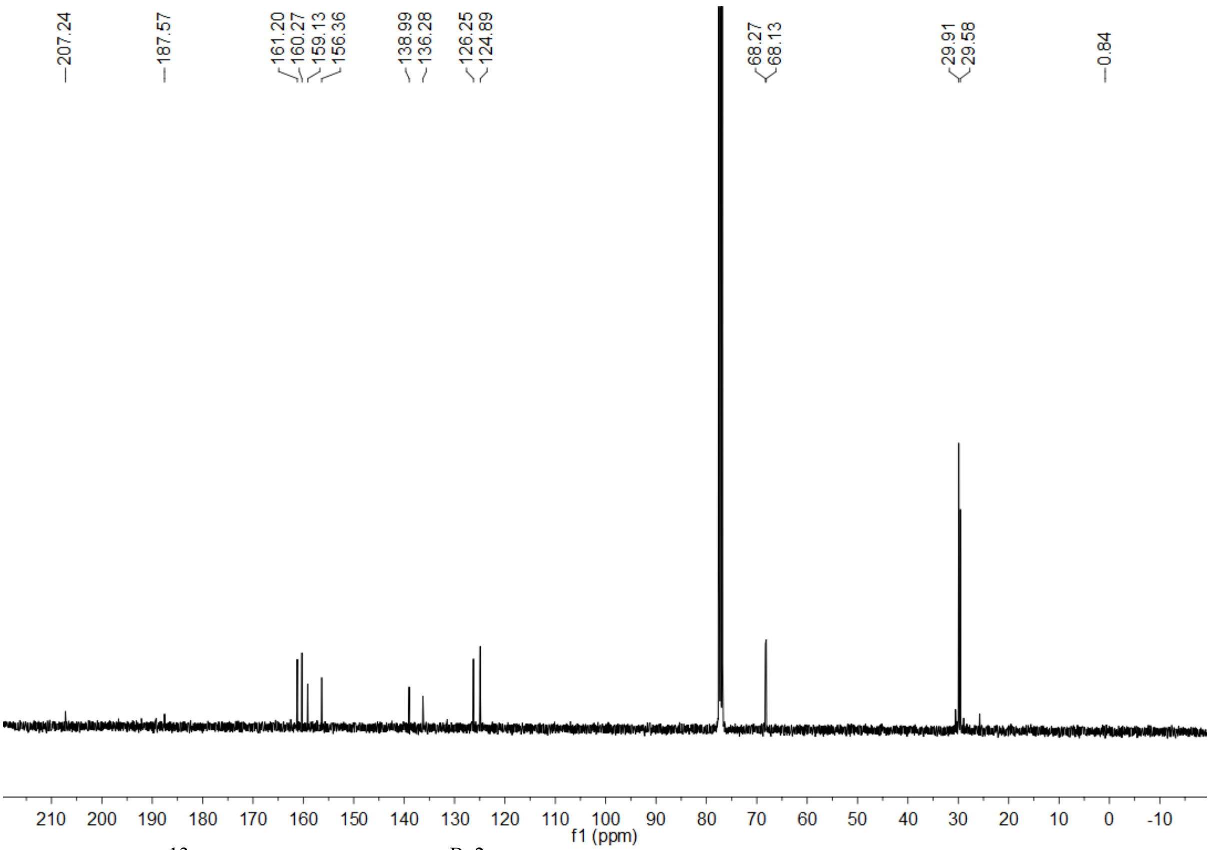


Figure S10: [13]C NMR spectra of ($^{t\mathrm{Bu2}}$NNN)RuCl$_2$(CO) (**2a**)

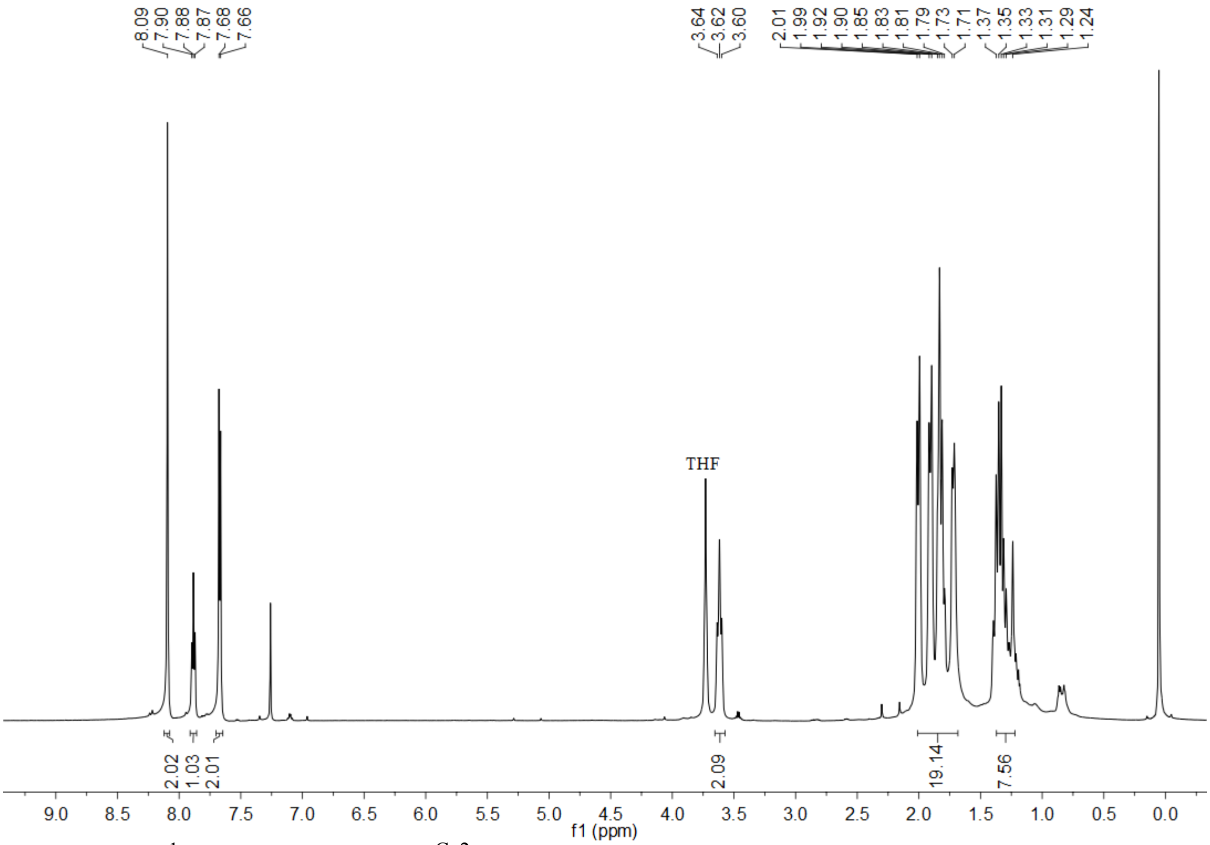


Figure S11: [1]H NMR spectra of (^{Cy2}NNN)RuCl$_2$(CO) (**2b**)

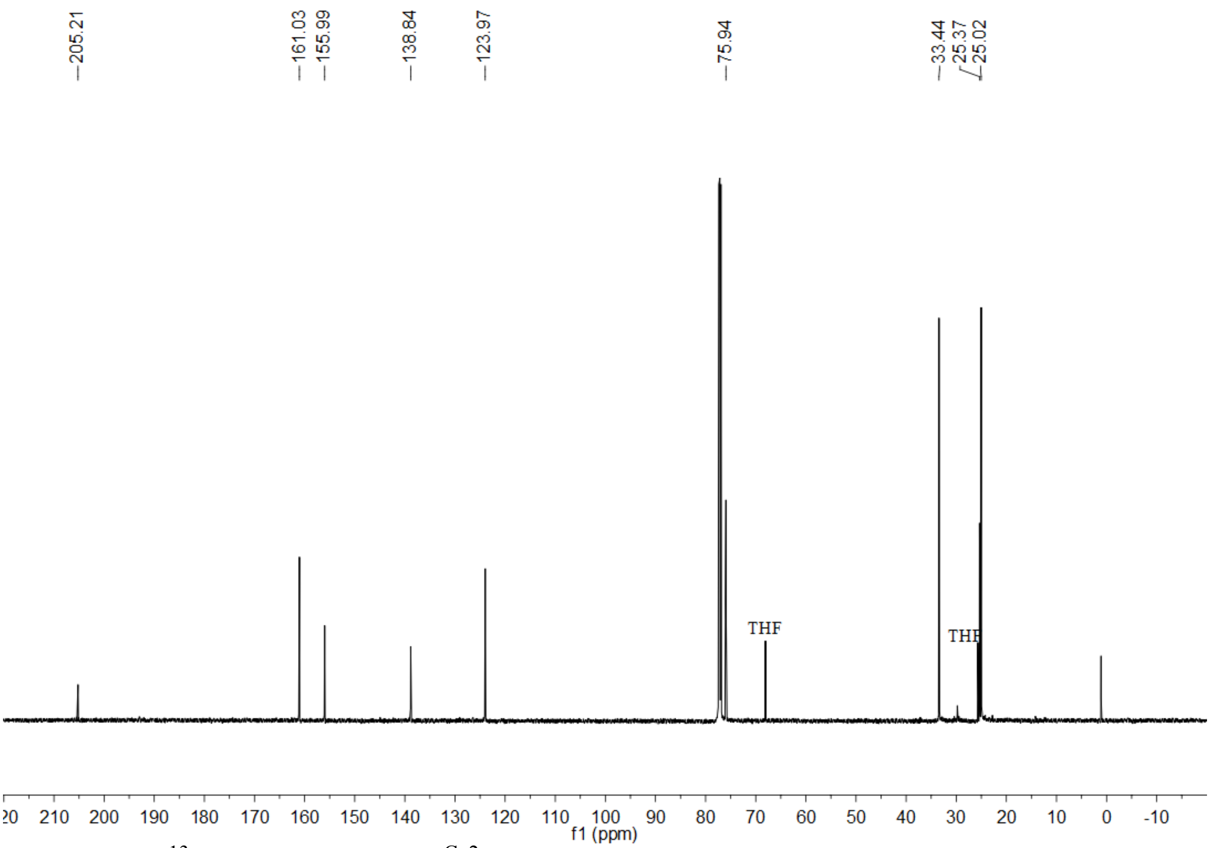


Figure S12: [13]C NMR spectra of (^{Cy2}NNN)RuCl$_2$(CO) (**2b**)

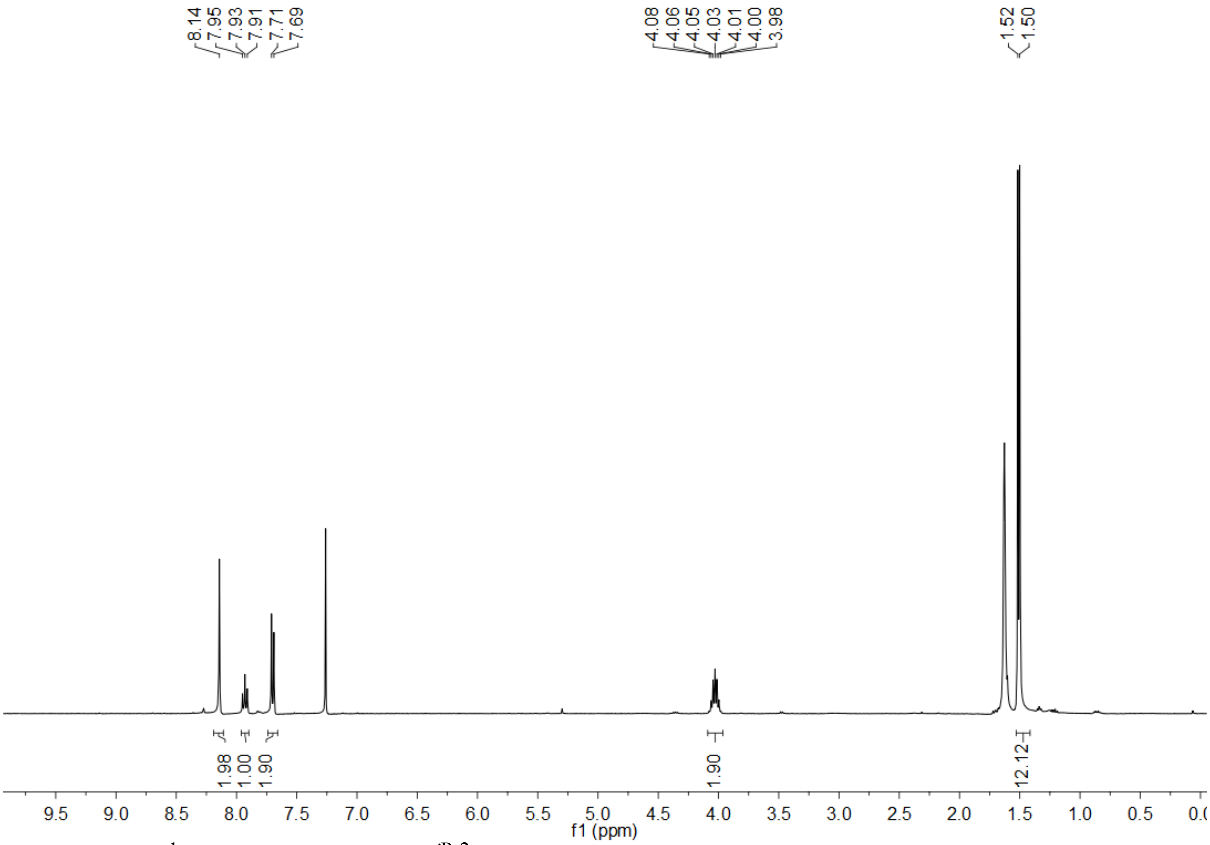


Figure S13: ^{1}H NMR spectra of (^{iPr2}NNN)RuCl$_2$(CO) (**2c**)

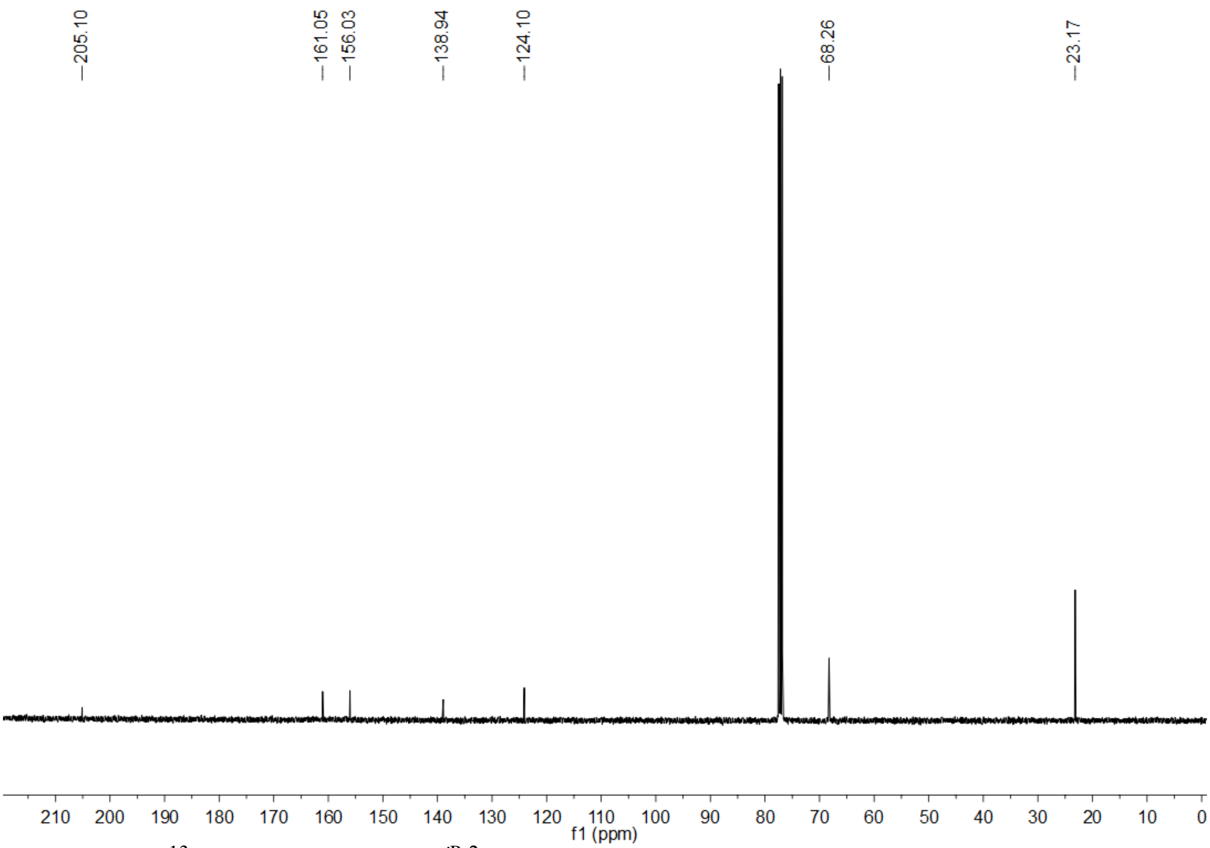


Figure S14: ^{13}C NMR spectra of (^{iPr2}NNN)RuCl$_2$(CO) (**2c**)

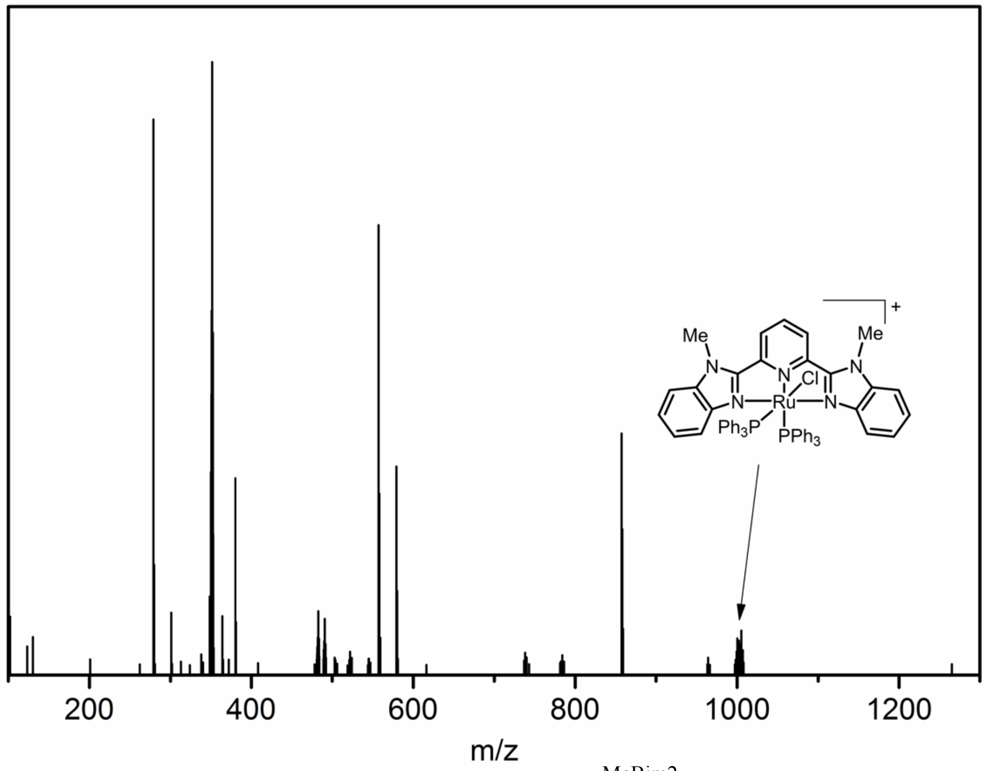


Figure S15: ESI-MS full spectra of complex [(^{MeBim2}NNN)RuCl(PPh_3)$_2$]Cl (**1f**)

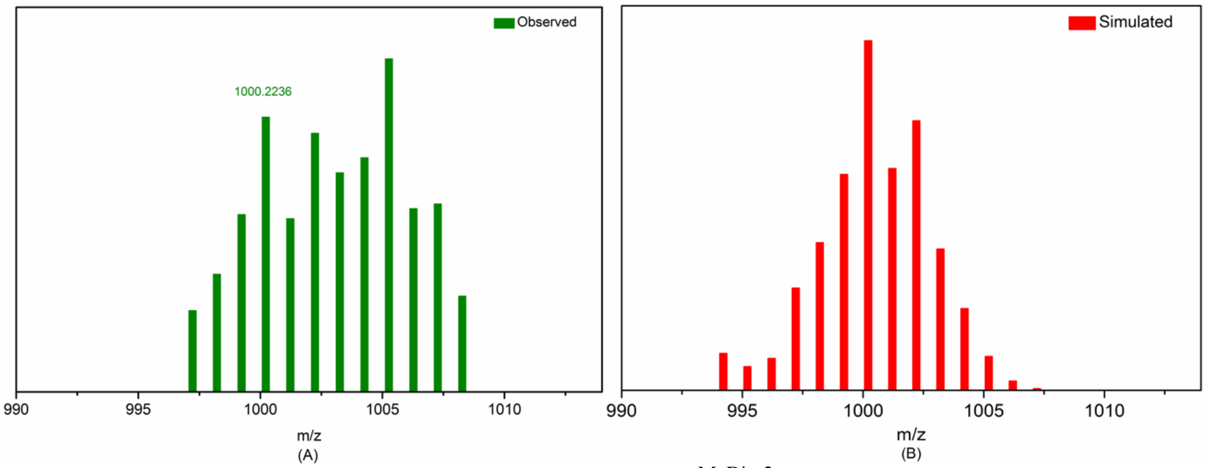


Figure S16: ESI-MS expanded spectra of complex [(^{MeBim2}NNN)RuCl(PPh_3)$_2$]Cl (**1f**) at m/z 1000.2236 (A) Observed (B) Simulated.

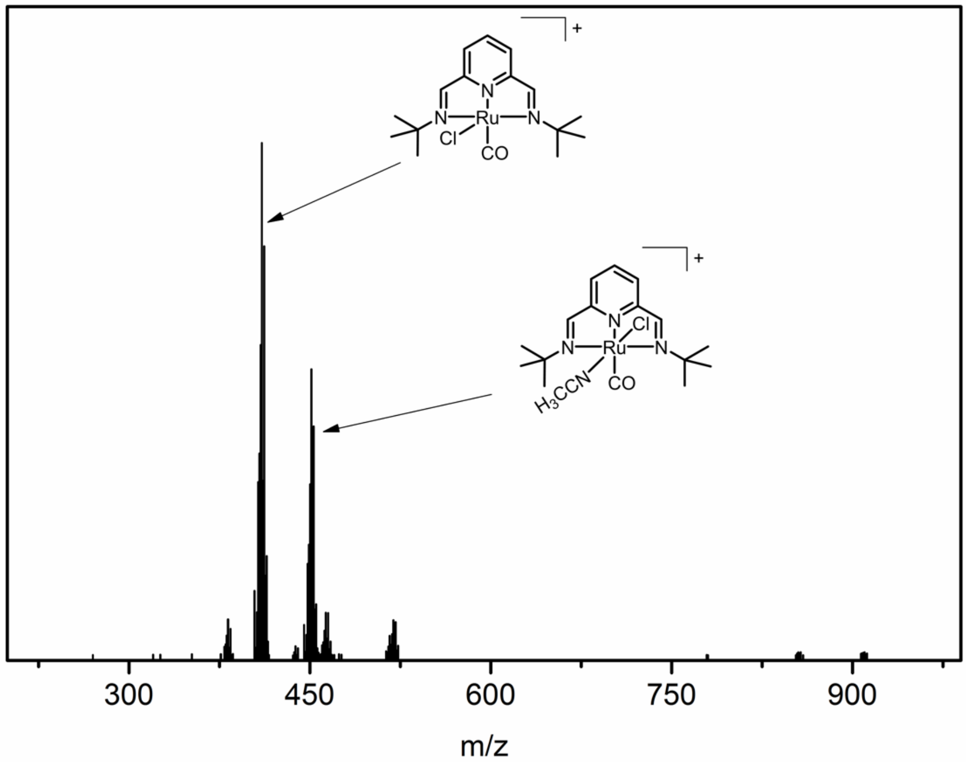


Figure S17: ESI-MS full spectra of complex (^{tBu2}NNN)RuCl$_2$(CO) (**2a**)

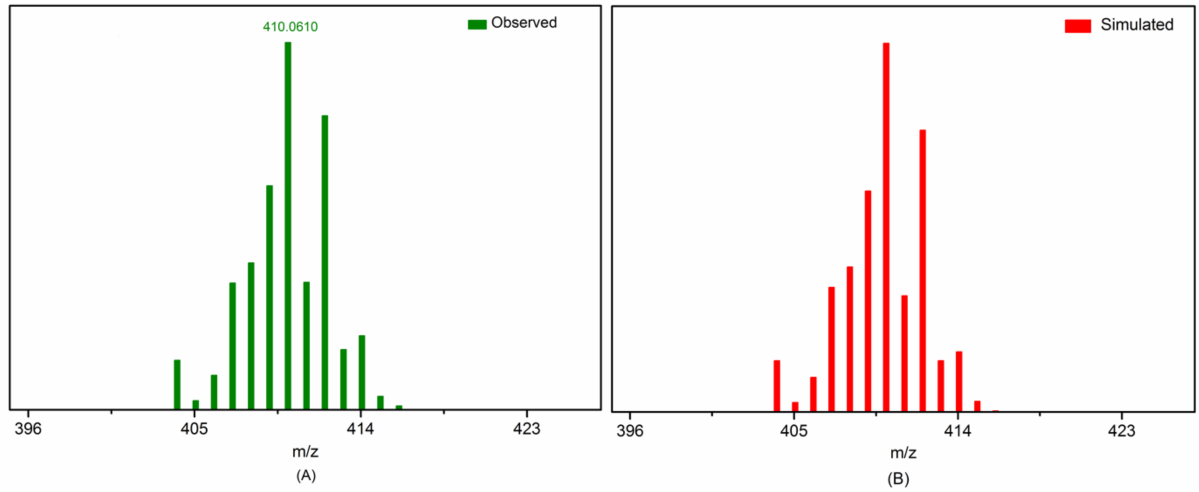


Figure S18: ESI-MS expanded spectra of complex (^{tBu2}NNN)RuCl$_2$(CO) (**2a**) at m/z 410.0610 (A) Observed (B) Simulated.

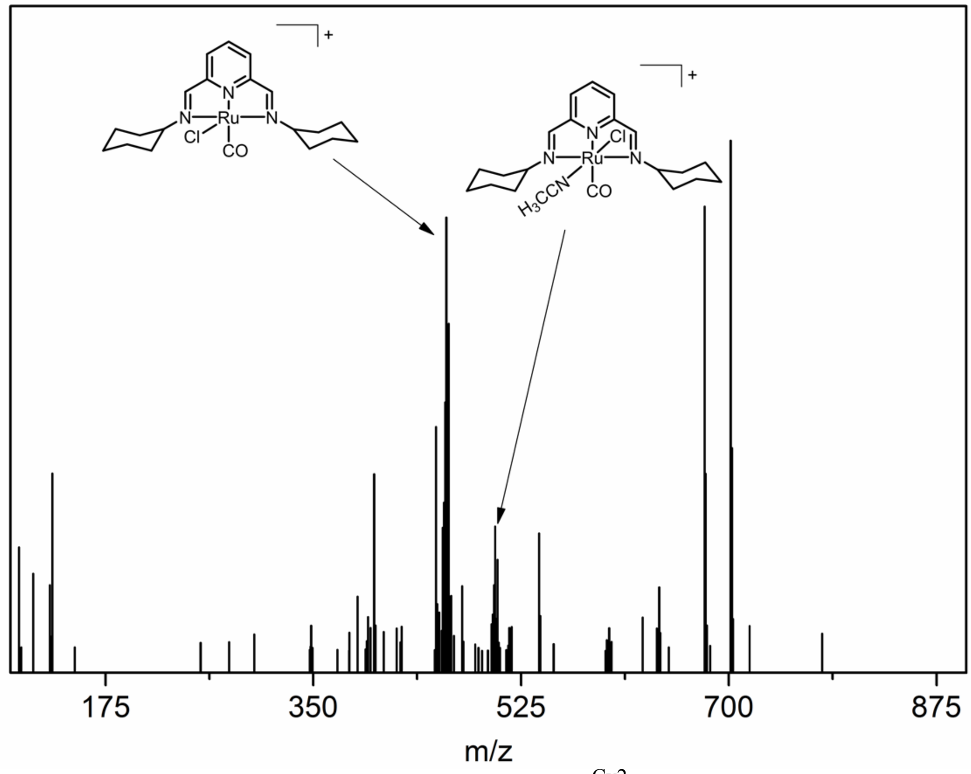


Figure S19: ESI-MS full spectra of complex (^{Cy2}NNN)RuCl$_2$(CO) (**2b**)

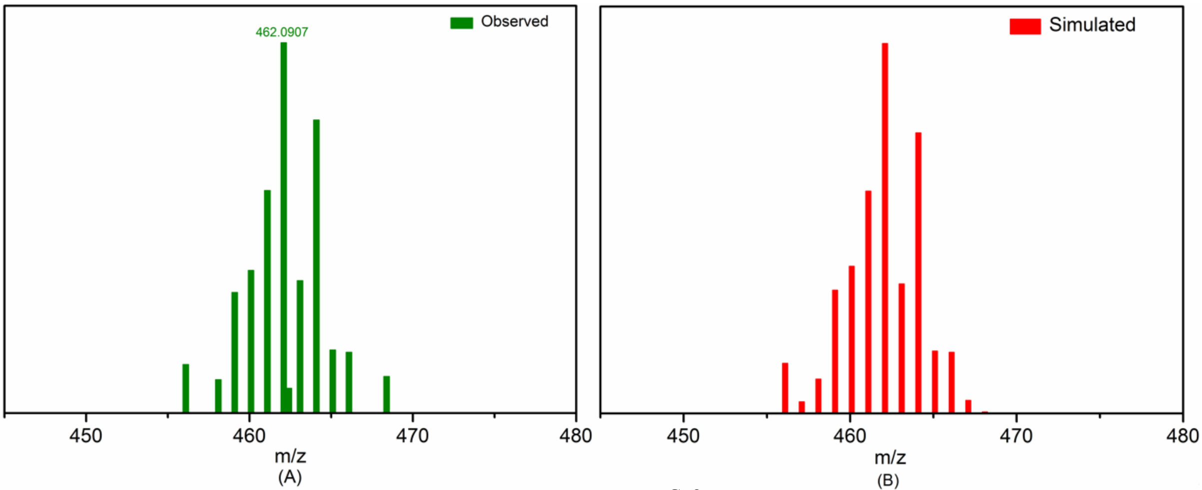


Figure S20: ESI-MS expanded spectra of complex (^{Cy2}NNN)RuCl$_2$(CO) (**2b**) at m/z 462.0907 (A) Observed (B) Simulated.

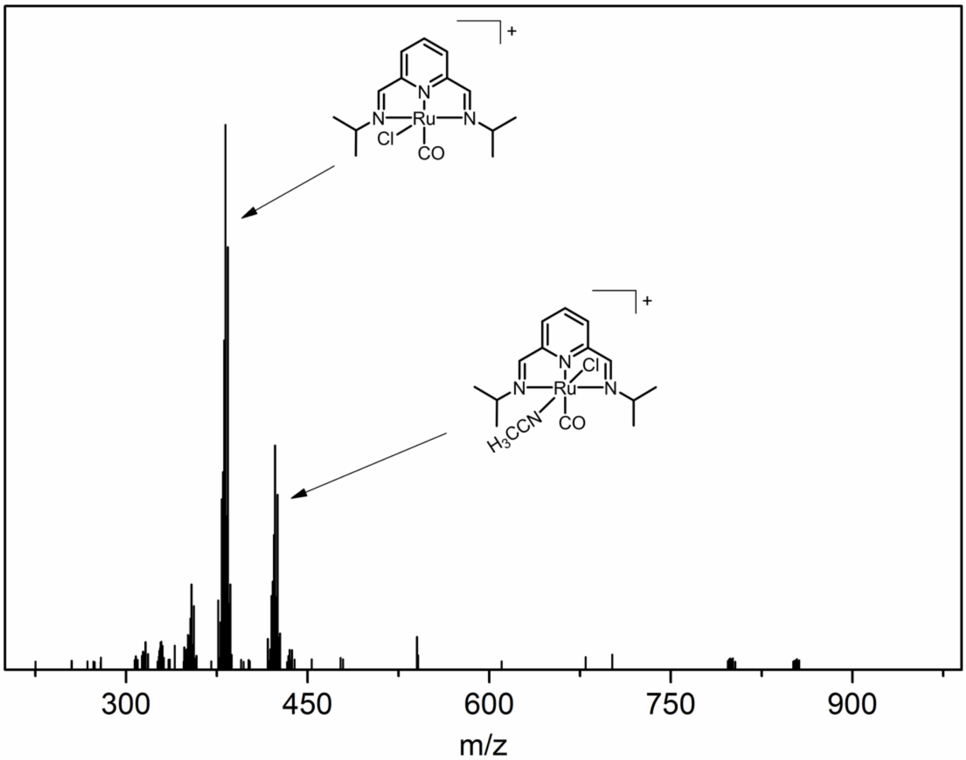


Figure S21: ESI-MS full spectra of complex (^{iPr2}NNN)RuCl$_2$(CO) (**2c**)

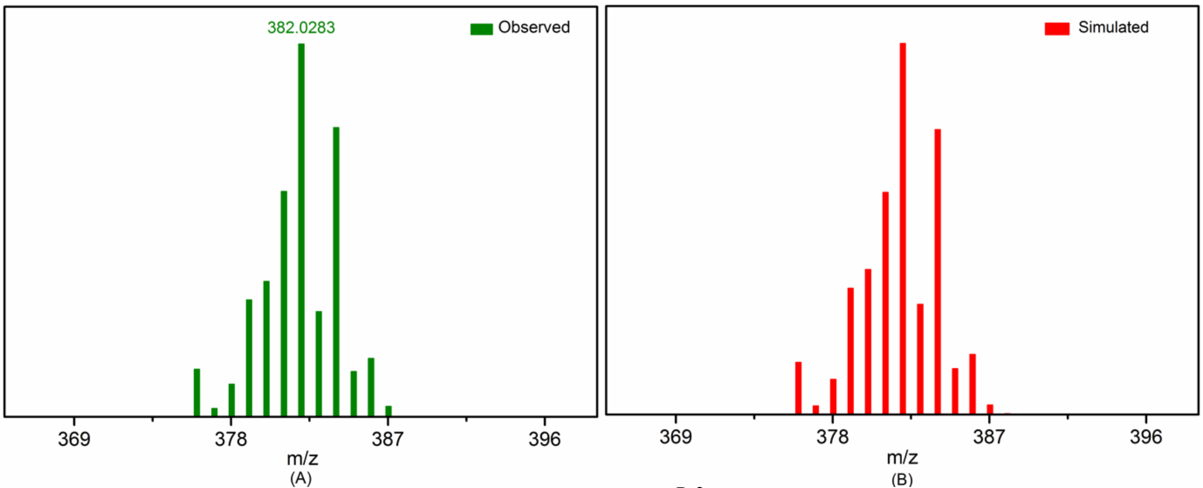


Figure S22: ESI-MS expanded spectra of complex (^{iPr2}NNN)RuCl$_2$(CO) (**2c**) at m/z 382.0283 (A) Observed (B) Simulated.

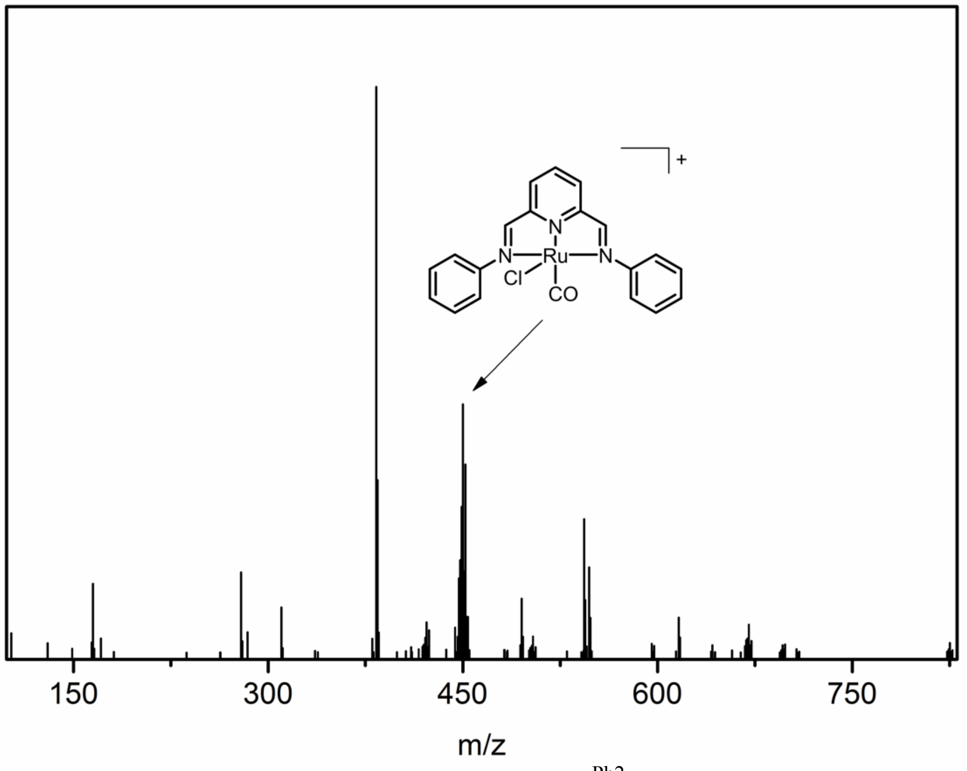


Figure S23: ESI-MS full spectra of complex (^{Ph2}NNN)RuCl$_2$(CO) (**2d**)

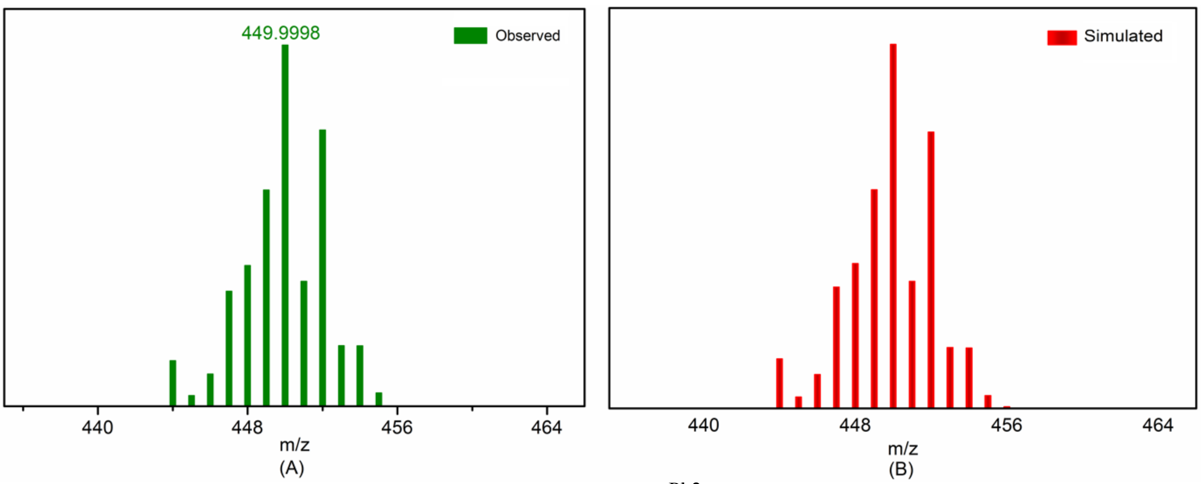


Figure S24: ESI-MS expanded spectra of complex (^{Ph2}NNN)RuCl$_2$(CO) (**2d**) at m/z 449.9998 (A) Observed (B) Simulated.

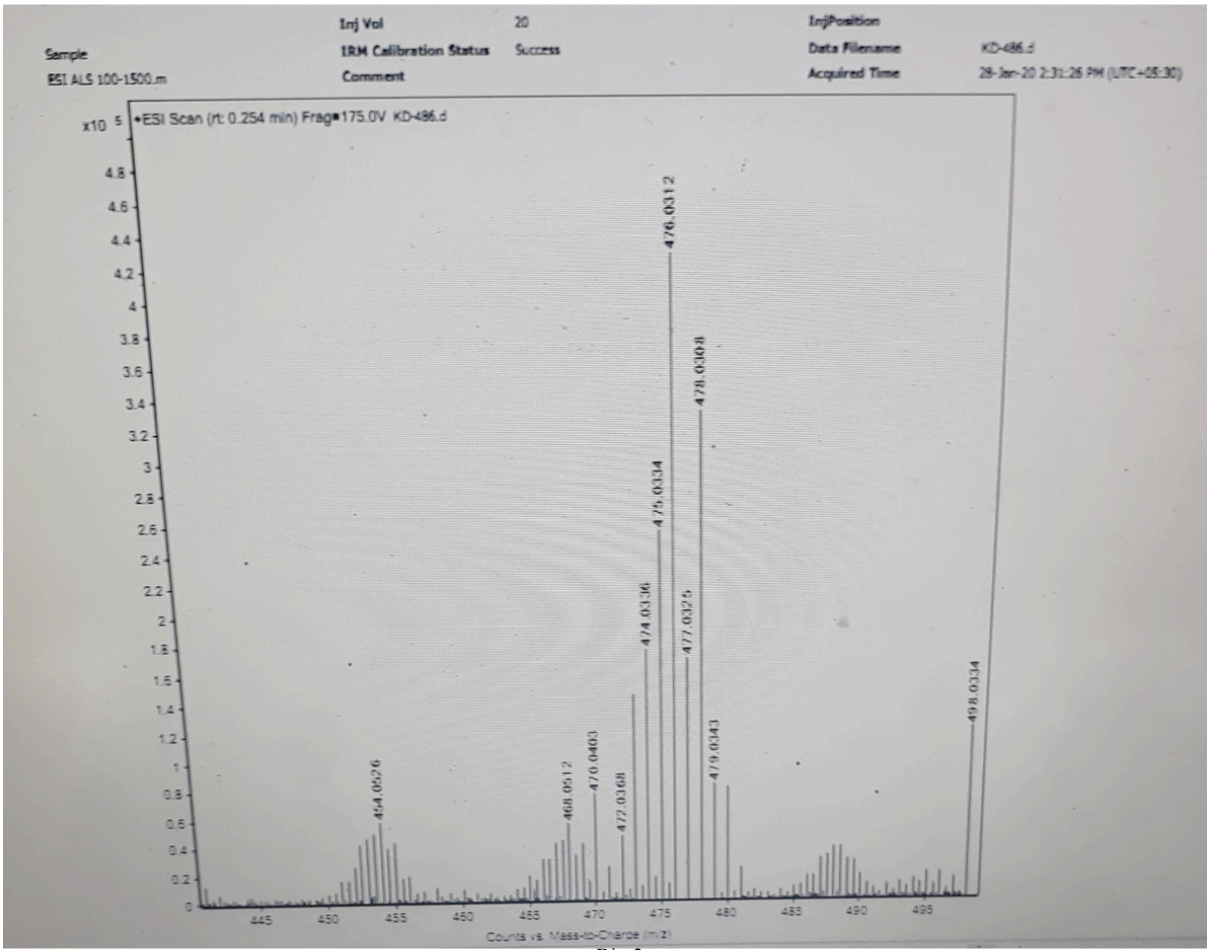


Figure S25: ESI-MS full spectra of complex (^{Bim2}NNN)RuCl$_2$(CO) (**2e**)

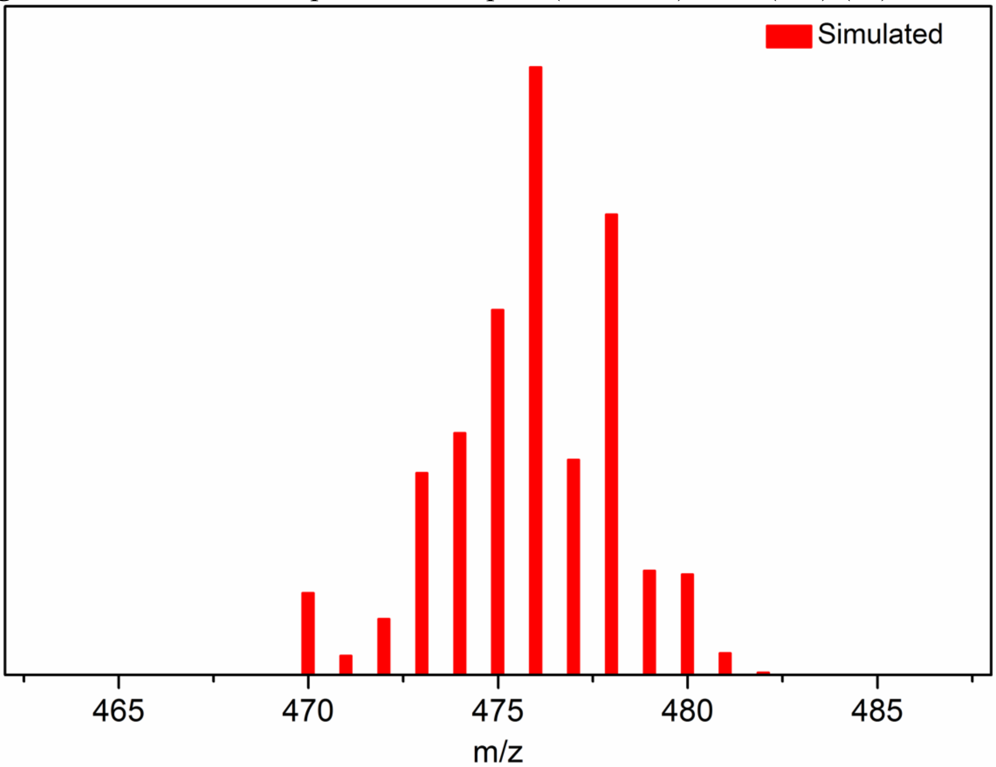


Figure S26: ESI-MS spectra of complex (^{Bim2}NNN)RuCl$_2$(CO) (**2e**) at m/z 475.9884 (Simulated).

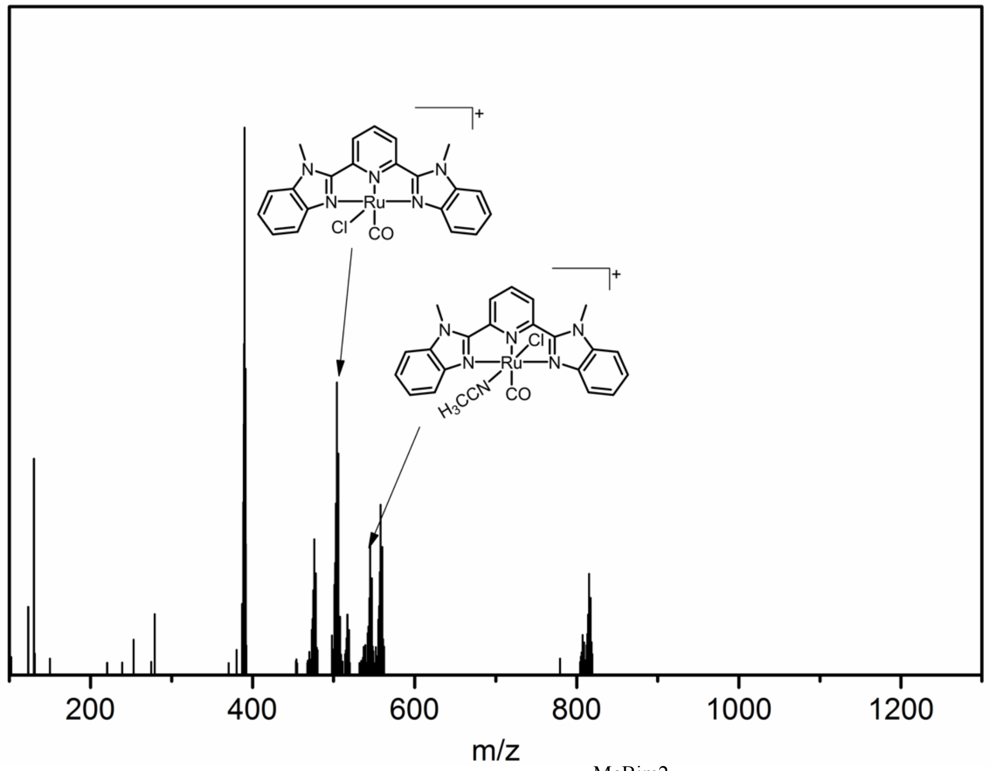


Figure S27: ESI-MS full spectra of complex (^{MeBim2}NNN)RuCl$_2$(CO) (**2f**)

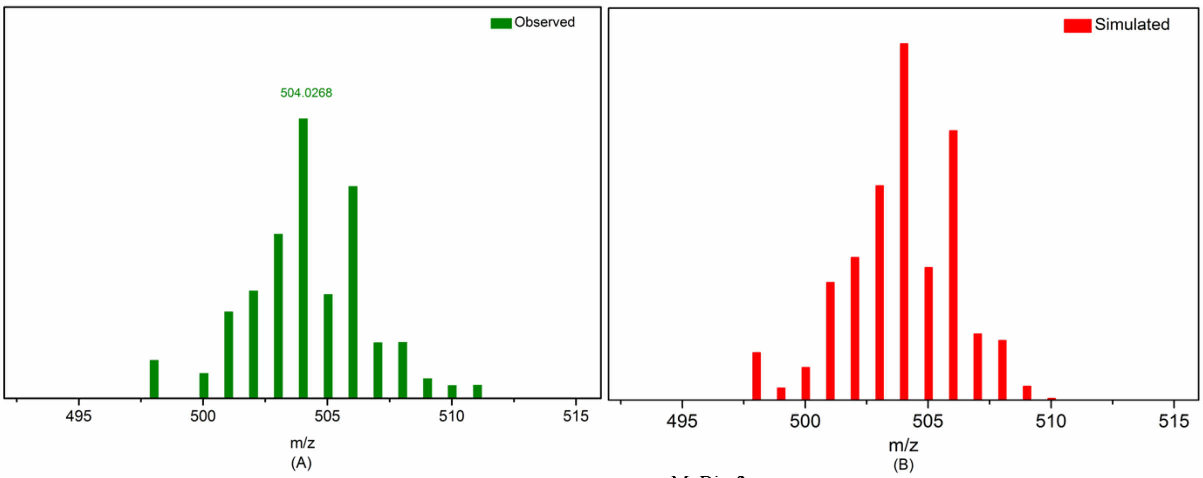


Figure S28: ESI-MS expanded spectra of complex (^{MeBim2}NNN)RuCl$_2$(CO) (**2f**) at m/z 504.0268 (A) Observed (B) Simulated.

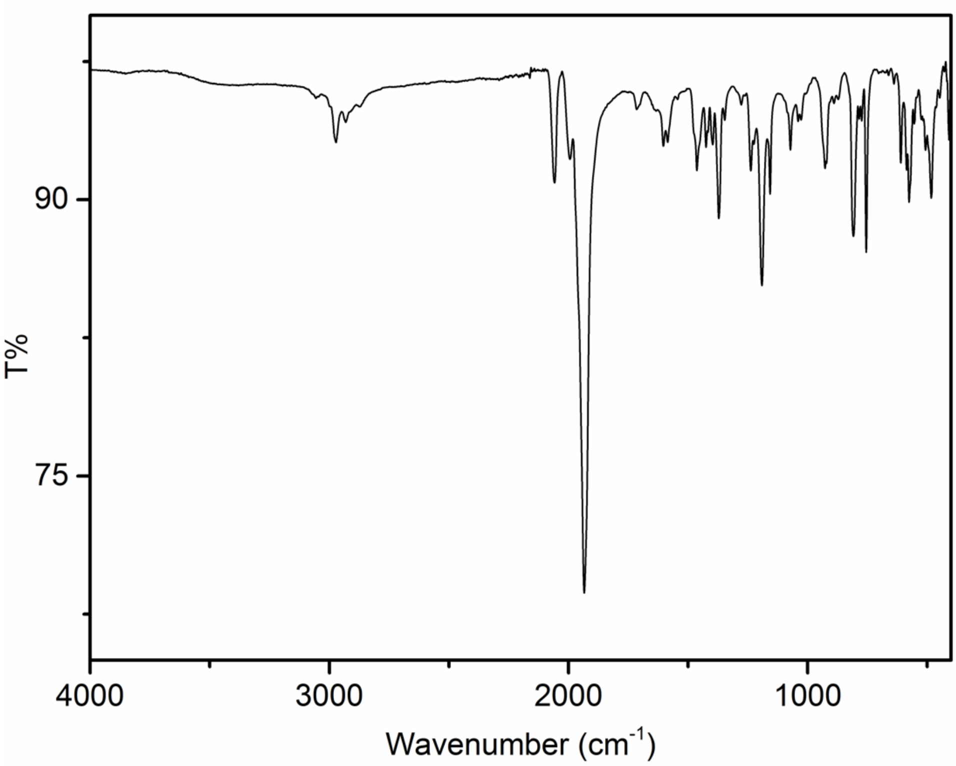


Figure S29: IR spectra of complex (^{tBu2}NNN)RuCl$_2$(CO) (**2a**)

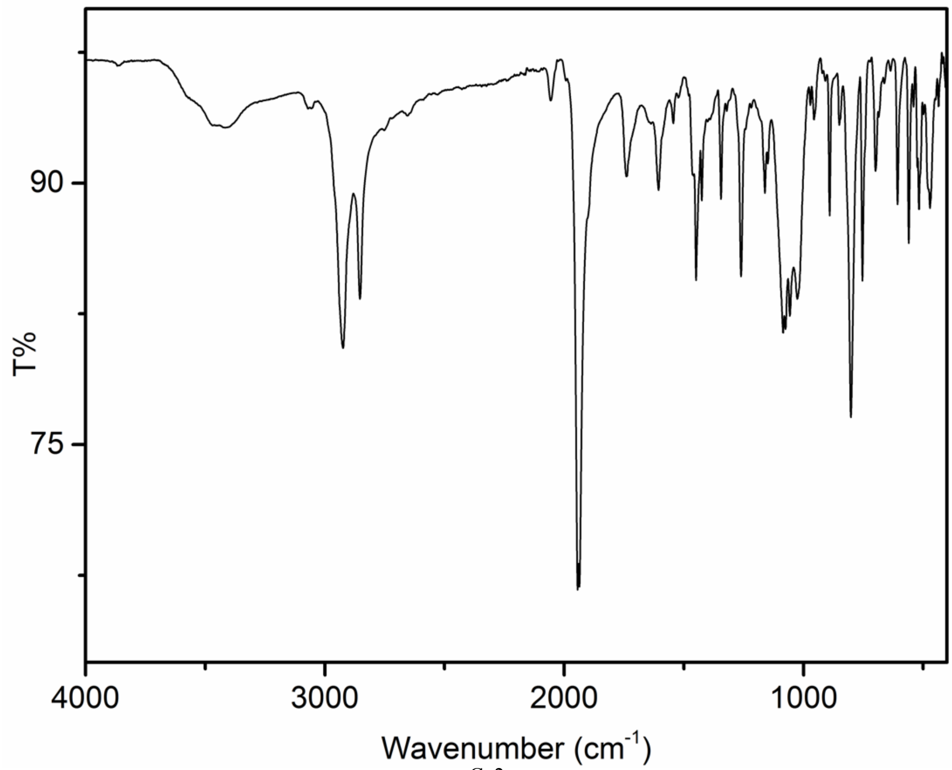


Figure S30: IR spectra of complex (^{Cy2}NNN)RuCl$_2$(CO) (**2b**)

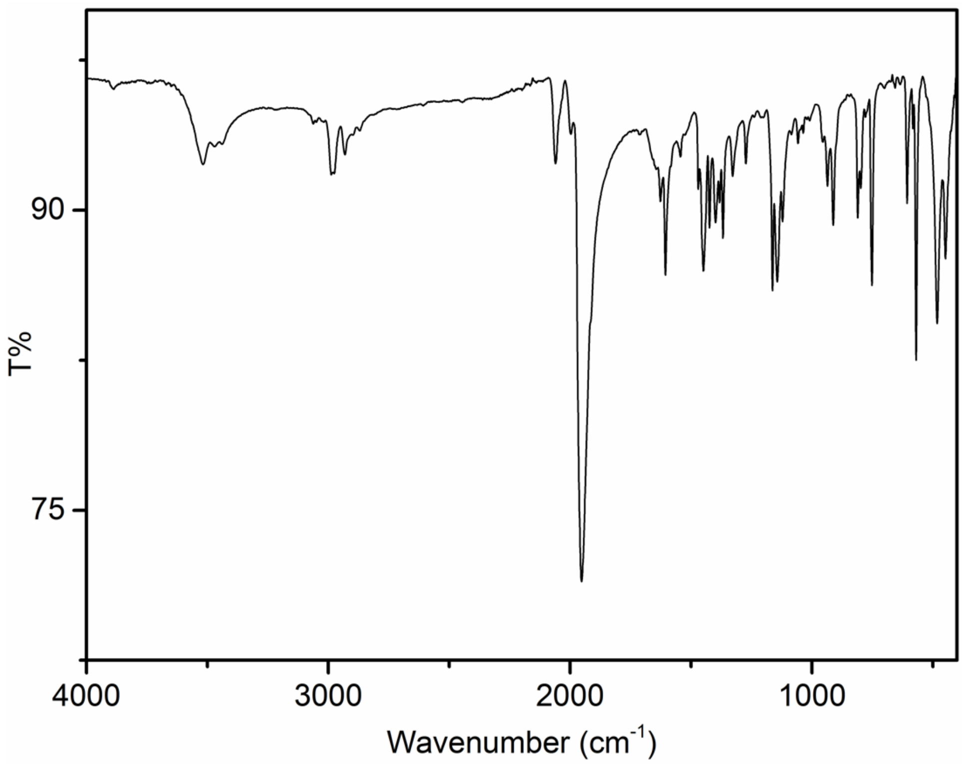


Figure S31: IR spectra of complex (^{iPr2}NNN)RuCl$_2$(CO) (**2c**)

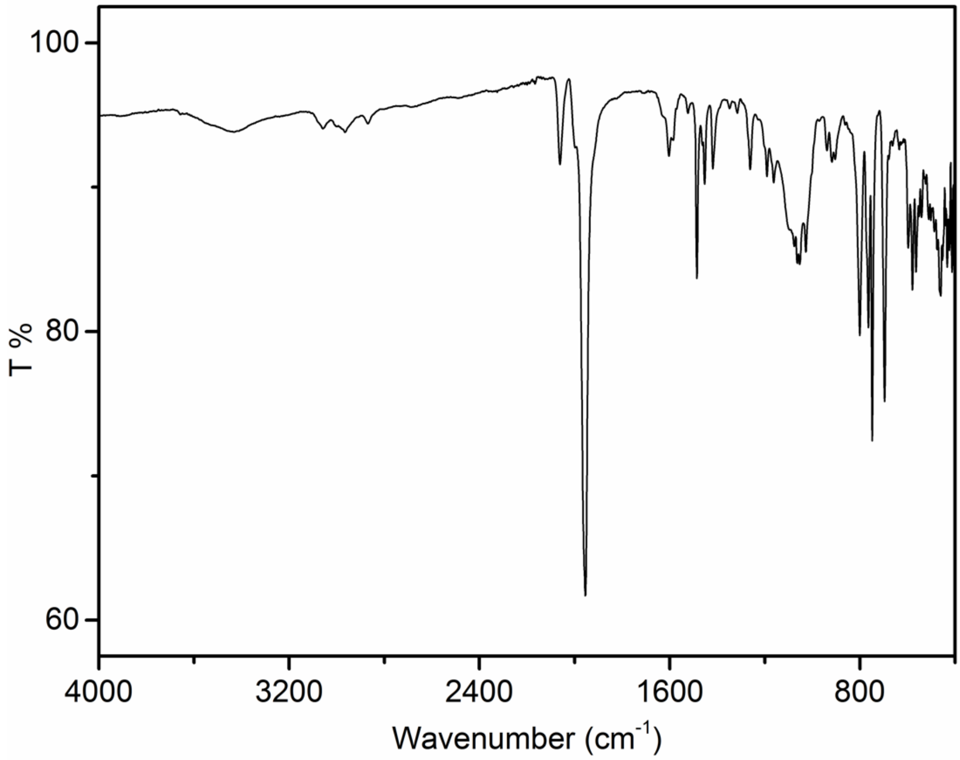


Figure S32: IR spectra of complex (^{Ph2}NNN)RuCl$_2$(CO) (**2d**)

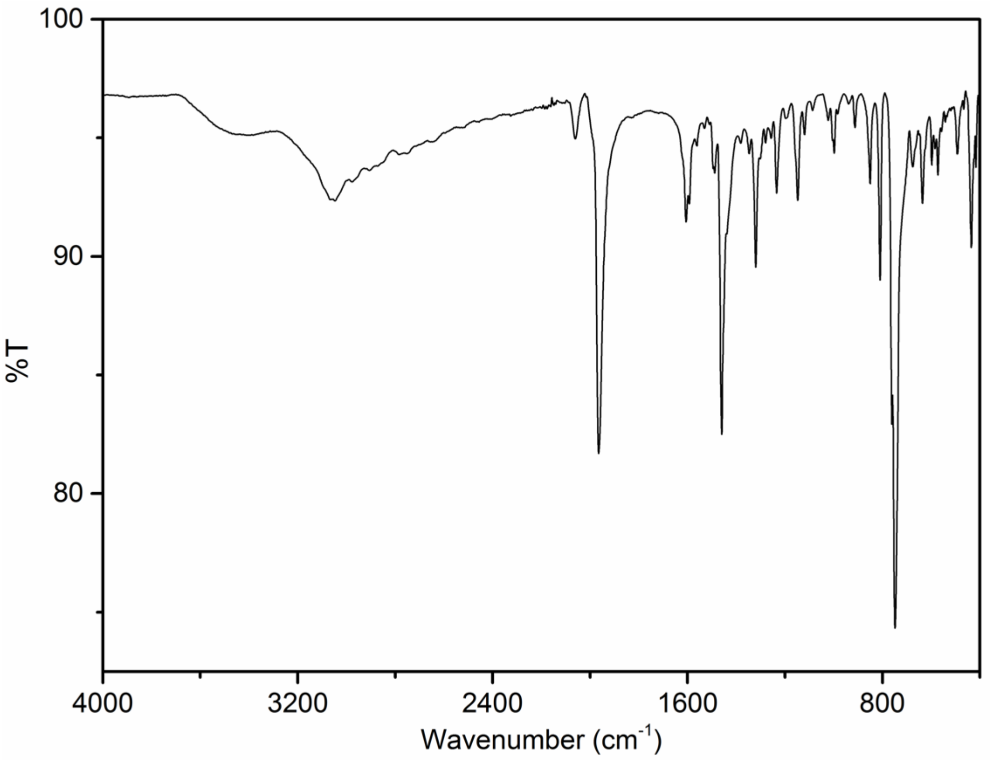


Figure S33: IR spectra of complex (^{Bim2}NNN)$RuCl_2$(CO) (**2e**)

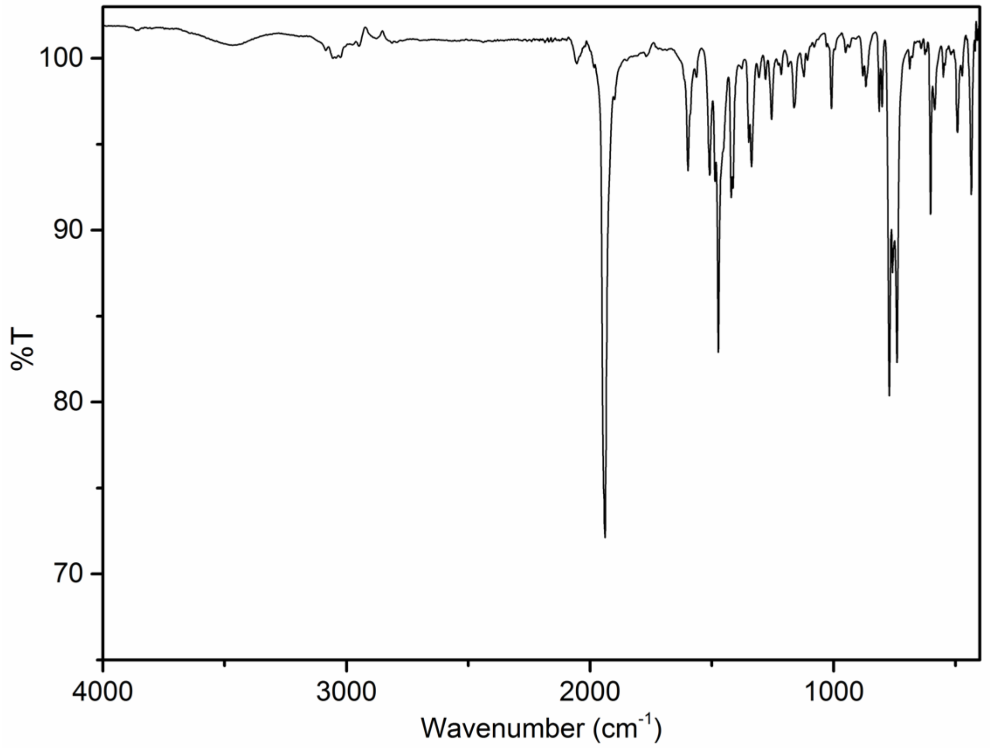


Figure S34: IR spectra of complex (^{MeBim2}NNN)$RuCl_2$(CO) (**2f**)

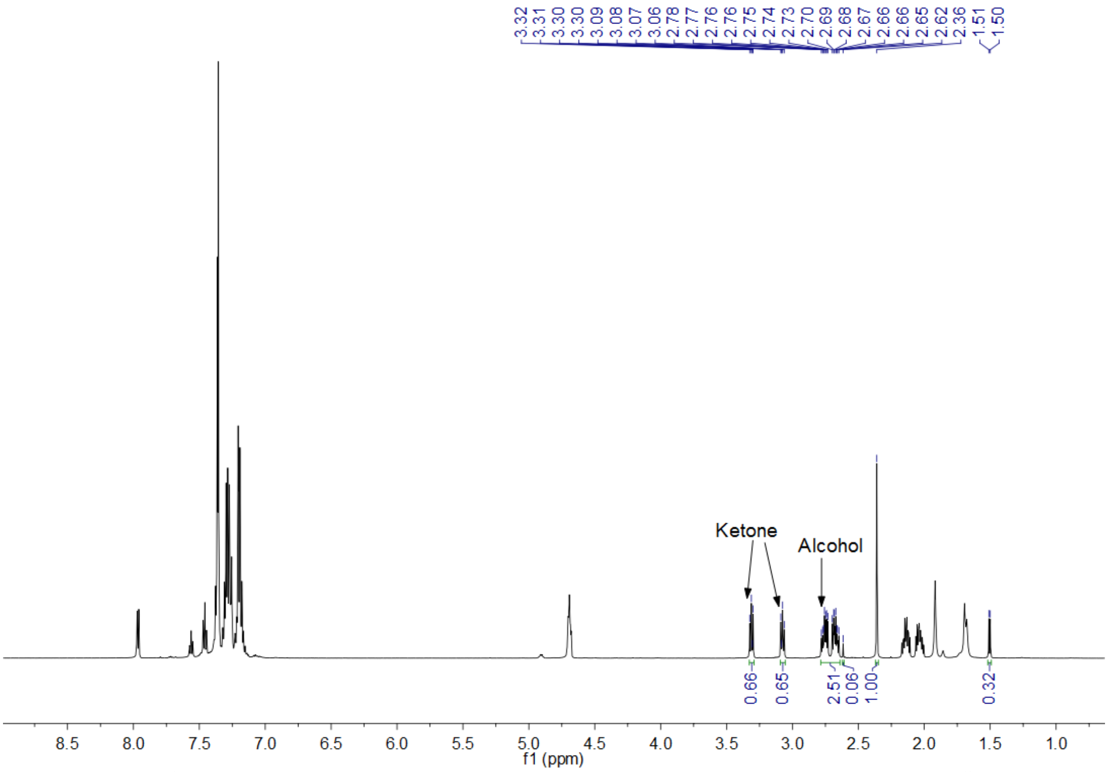


Figure S35: [1]H NMR spectra of *β*-alkylation of **5** with **4** catalyzed by **2b** ([Cy]NNN)$RuCl_2(CO)$ (0.00025 mol %) at 140 °C (Table 2, entry 1).

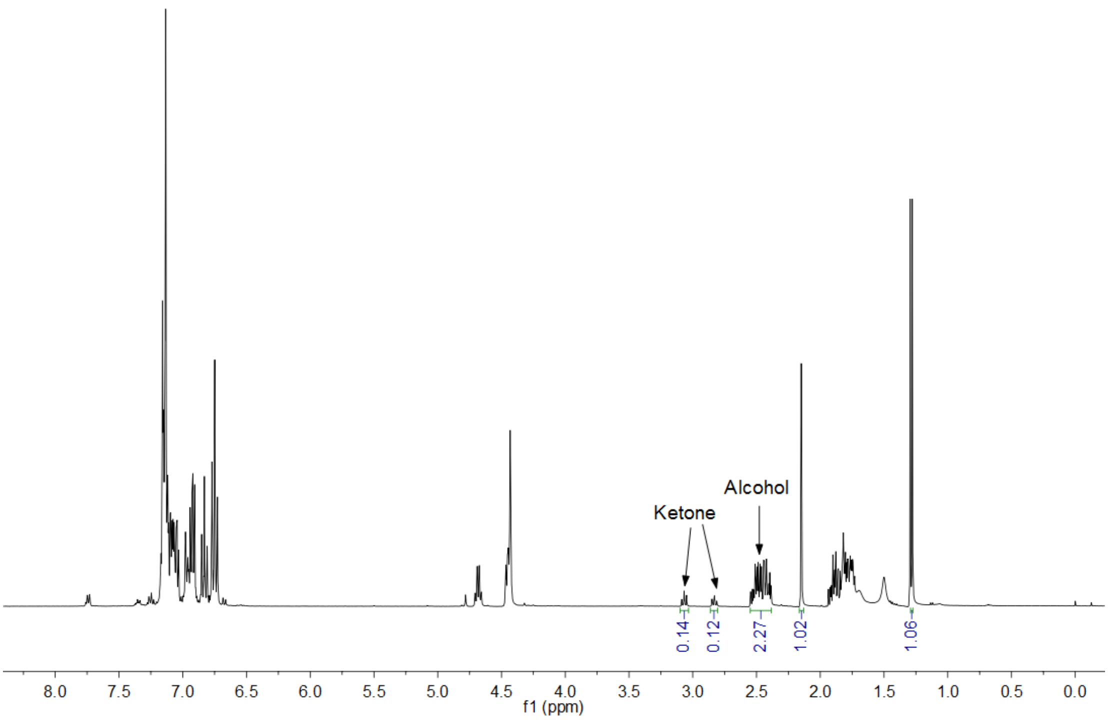


Figure S36: [1]H NMR spectra of *β*-alkylation of **5a** with **4a** catalyzed by **2b** ([Cy]NNN)$RuCl_2(CO)$ (0.00025 mol %) at 140 °C (Table 2, entry 2).

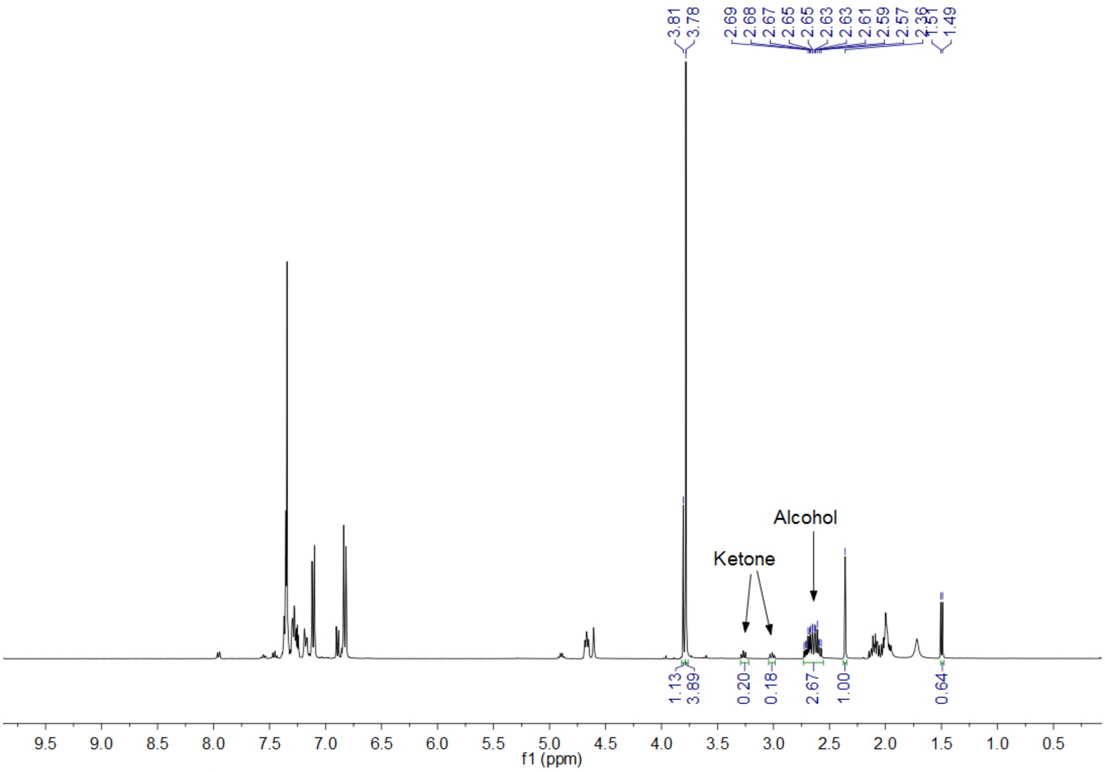


Figure S37: ^{1}H NMR spectra of *β*-alkylation of **5b** with **4b** catalyzed by **2b** (^{Cy}NNN)$RuCl_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 3).

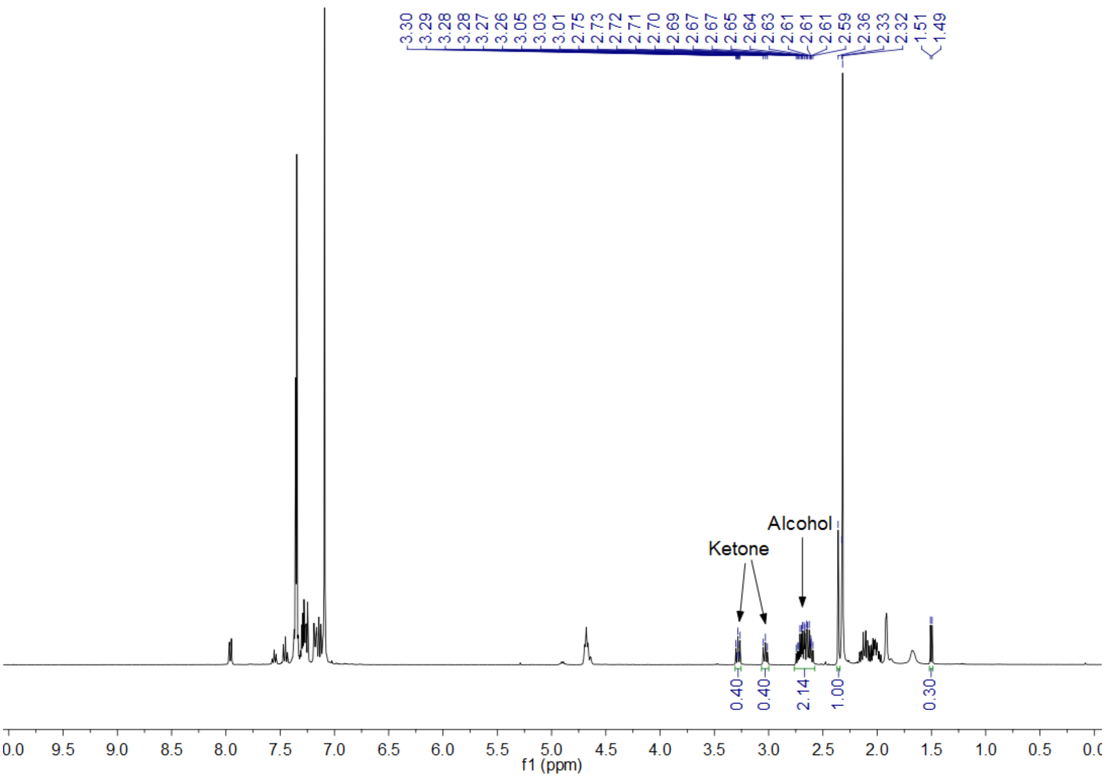


Figure S38: ^{1}H NMR spectra of *β*-alkylation of **5c** with **4c** catalyzed by **2b** (^{Cy}NNN)$RuCl_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 4).

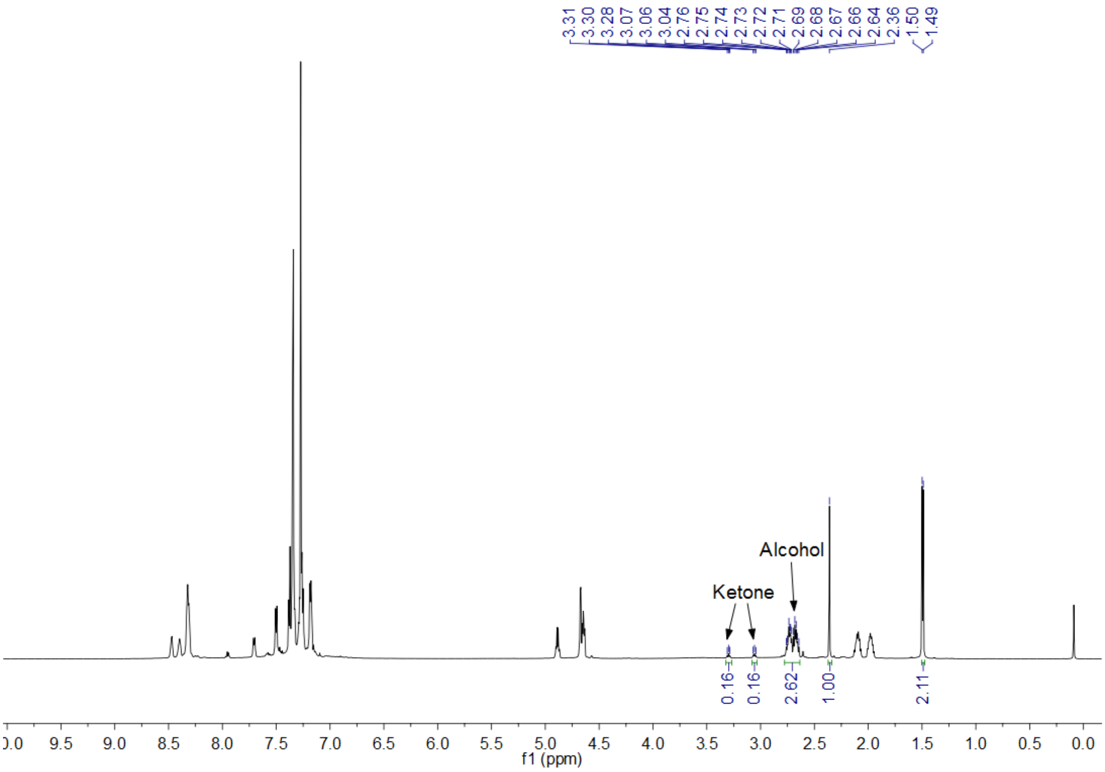


Figure S39: [1]H NMR spectra of *β*-alkylation of **5d** with **4d** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.025 mol %) at 140 °C (Table 2, entry 5).

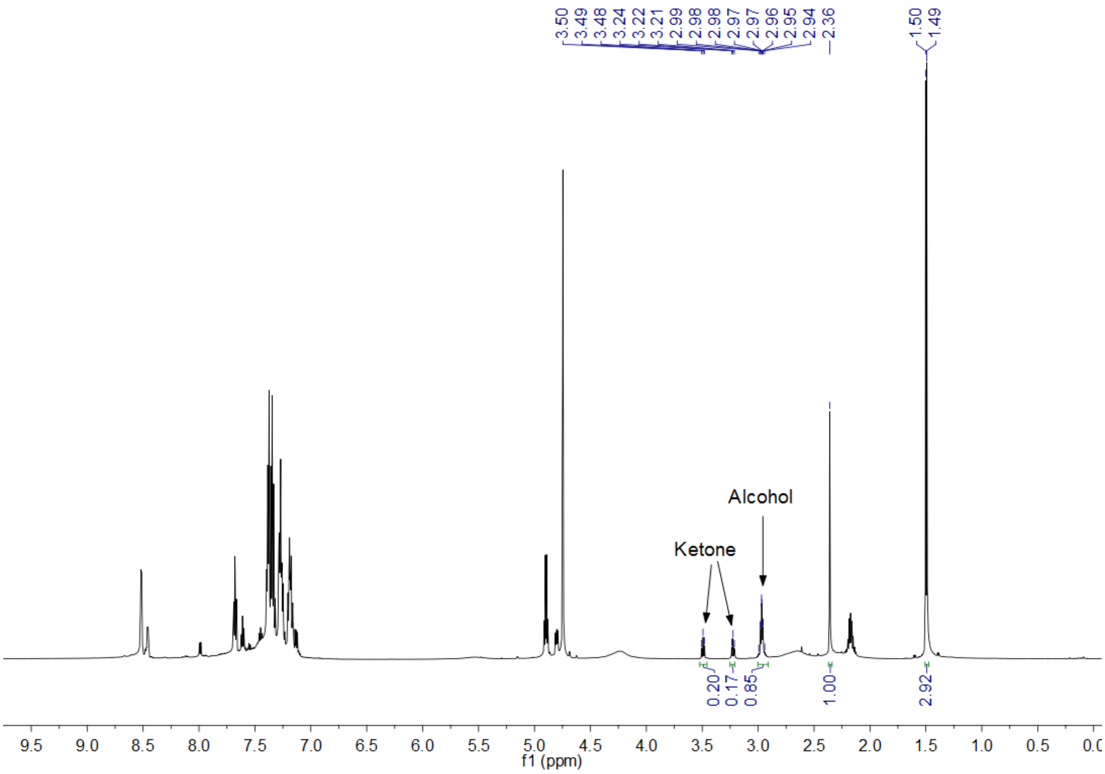


Figure S40: [1]H NMR spectra of *β*-alkylation of **5e** with **4e** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.025 mol %) at 140 °C (Table 2, entry 6).

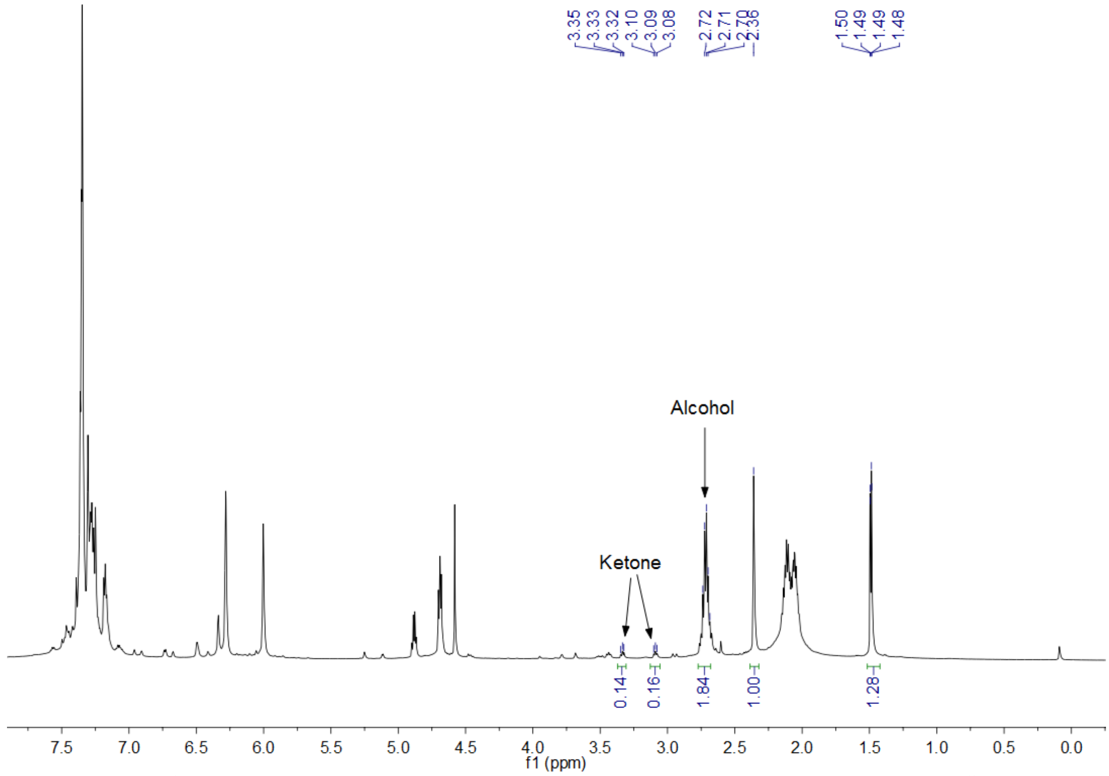


Figure S41: [1]H NMR spectra of *β*-alkylation of **5f** with **4f** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 7).

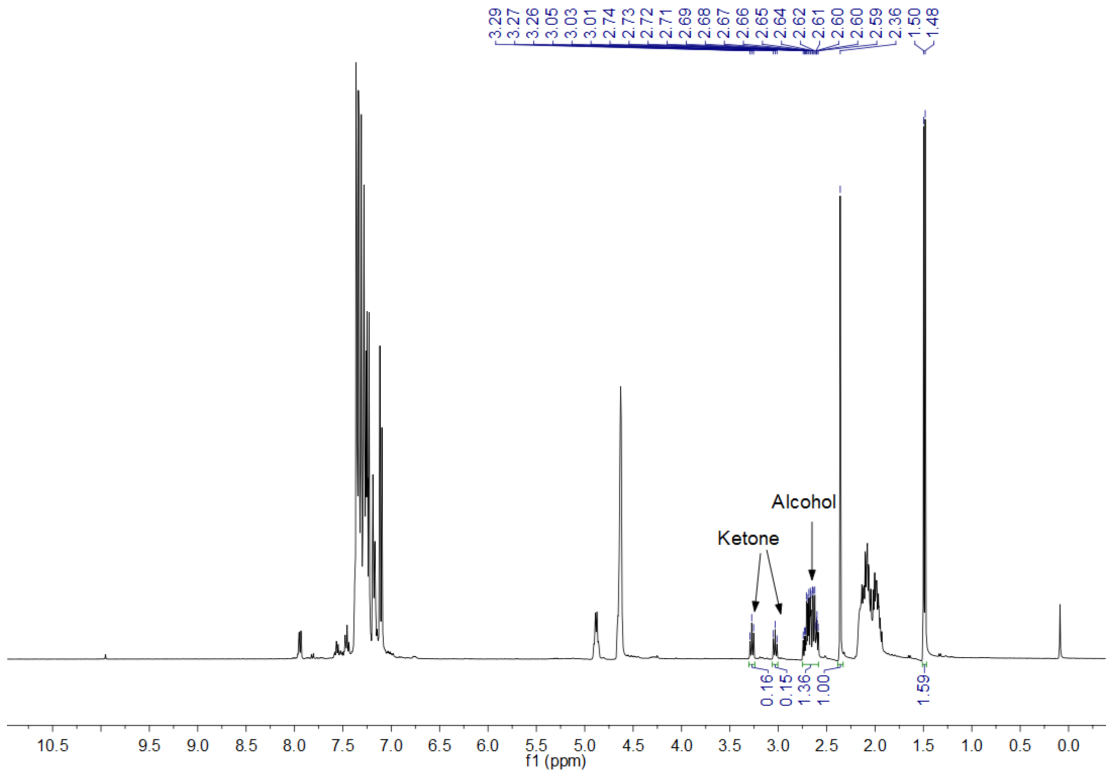


Figure S42: [1]H NMR spectra of *β*-alkylation of **5g** with **4g** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 8).

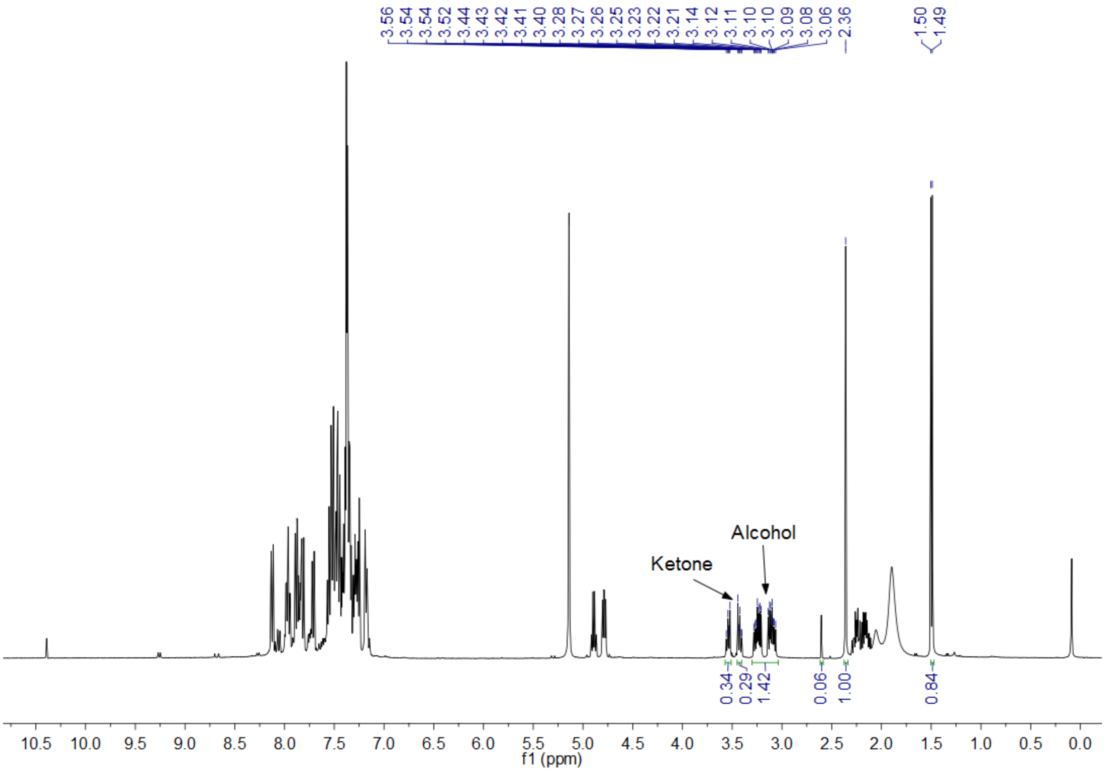


Figure S43: ^{1}H NMR spectra of *β*-alkylation of **5h** with **4h** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 9).

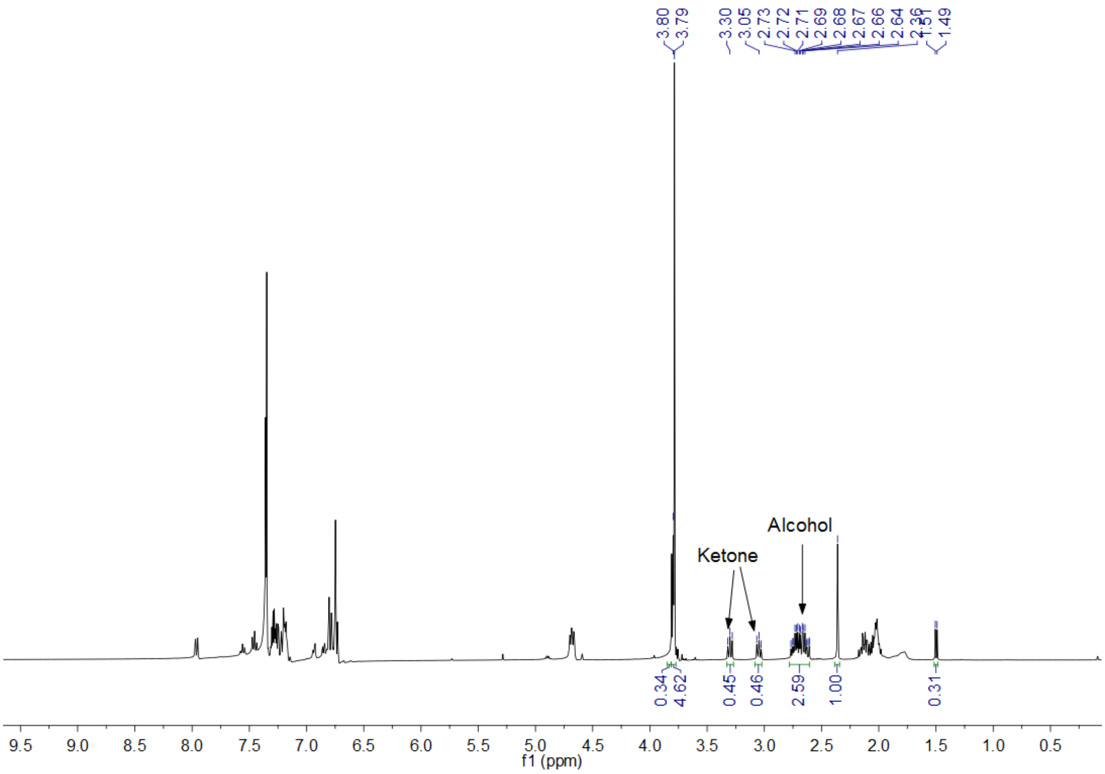


Figure S44: ^{1}H NMR spectra of *β*-alkylation of **5i** with **4i** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 10).

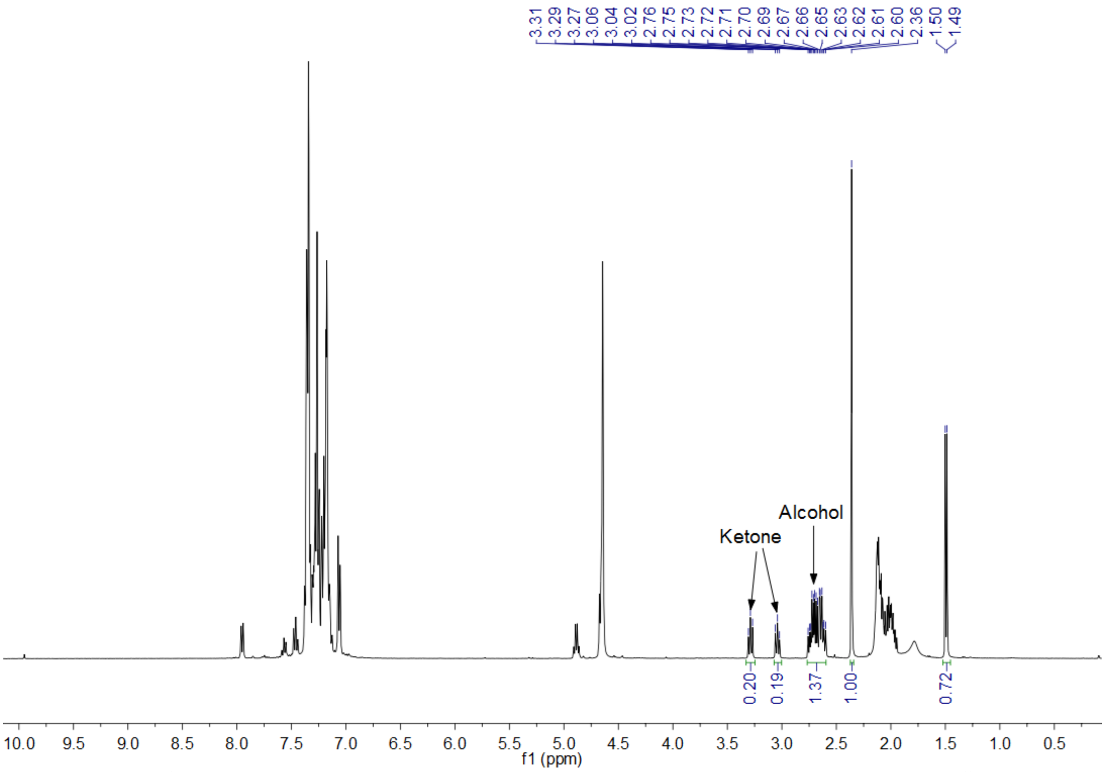


Figure S45: [1]H NMR spectra of *β*-alkylation of **5j** with **4j** catalyzed by **2b** ([Cy]NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 11).

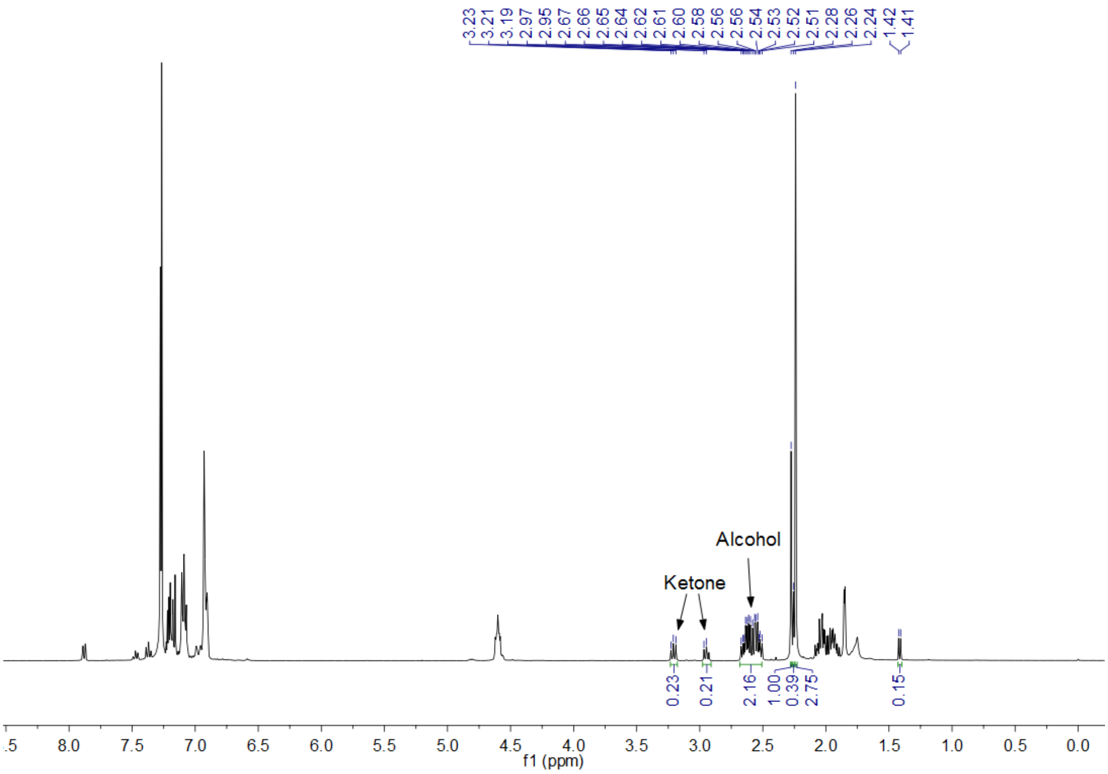


Figure S46: [1]H NMR spectra of *β*-alkylation of **5k** with **4k** catalyzed by **2b** ([Cy]NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 12).

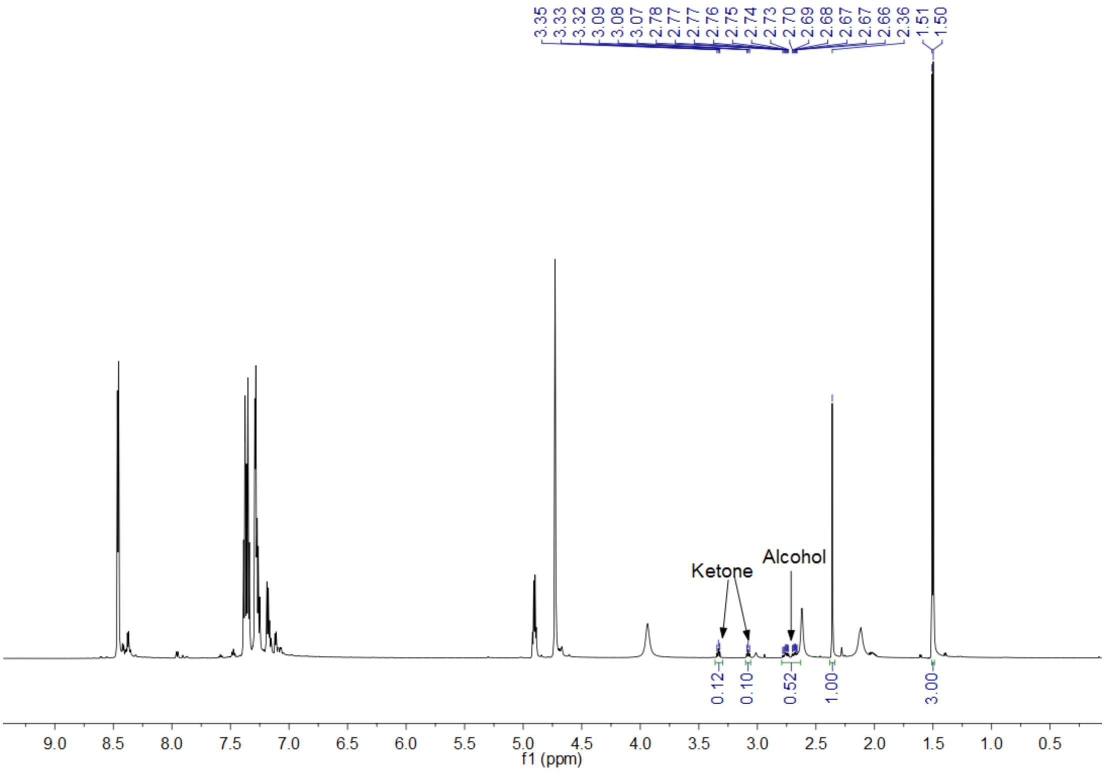


Figure S47: [1]H NMR spectra of *β*-alkylation of **5l** with **4l** catalyzed by **2b** ([Cy]NNN)$RuCl_2(CO)$ (0.00025 mol %) at 140 °C (Table 2, entry 13).

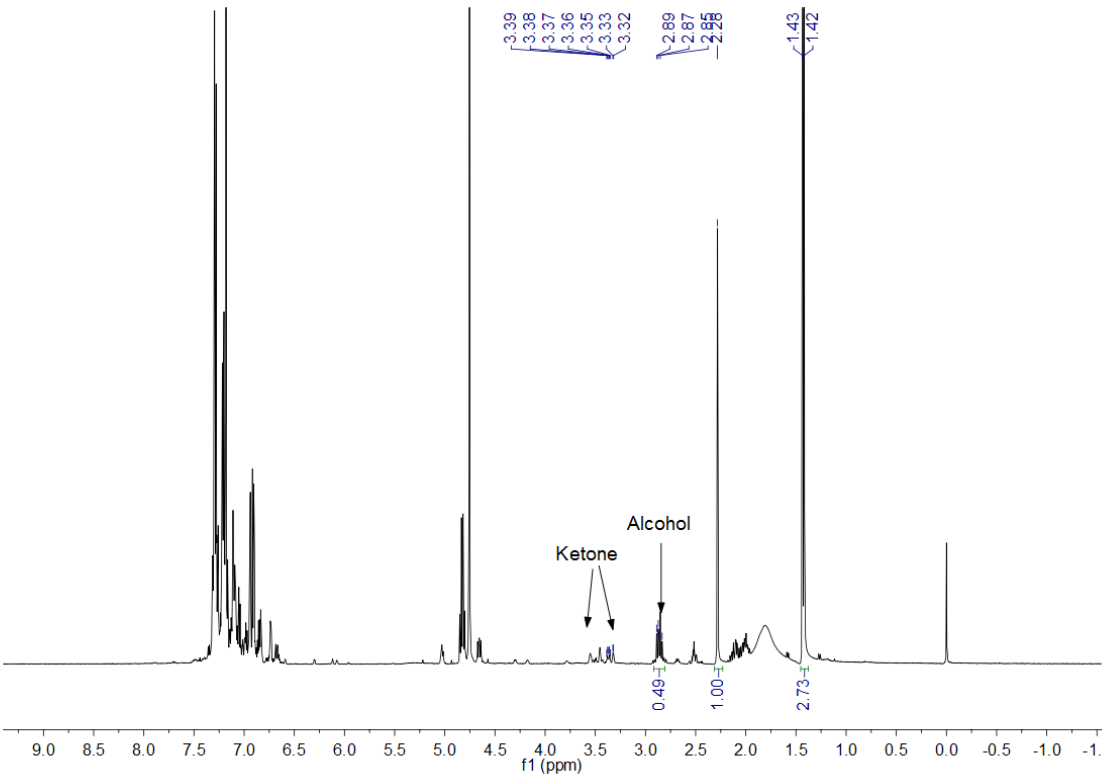


Figure S48: [1]H NMR spectra of *β*-alkylation of **5m** with **4m** catalyzed by **2b** ([Cy]NNN)$RuCl_2(CO)$ (0.025 mol %) at 140 °C (Table 2, entry 14).

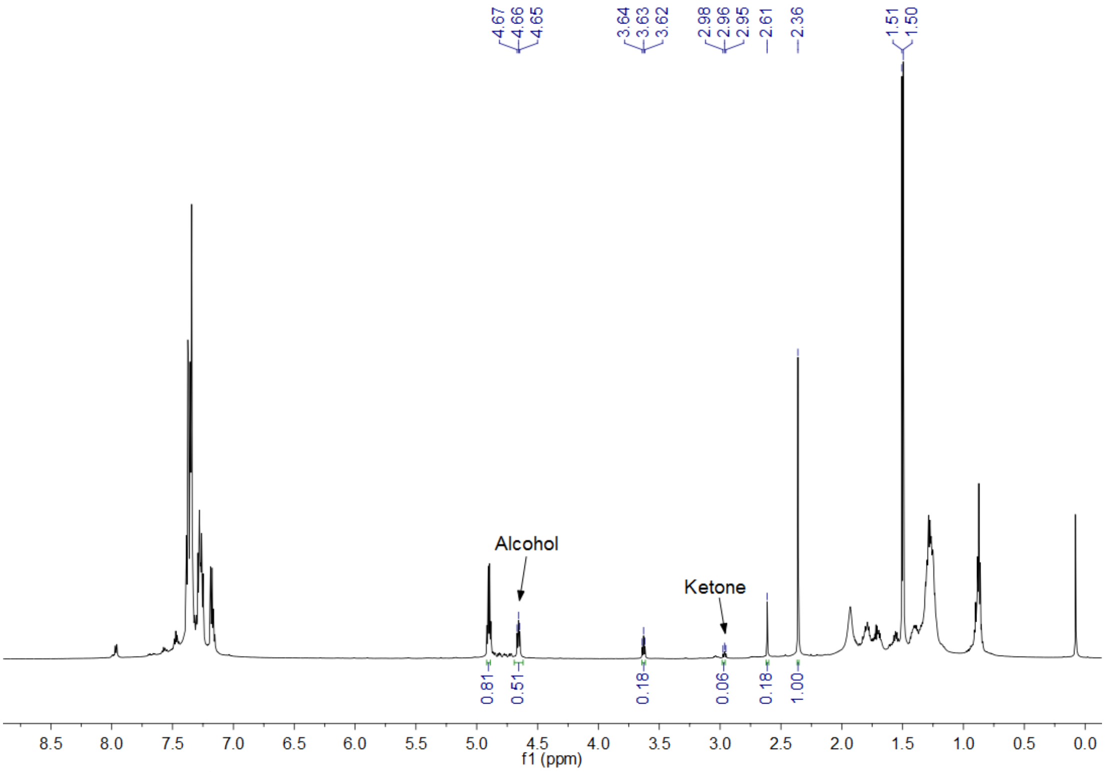


Figure S49: ^{1}H NMR spectra of *β*-alkylation of **5n** with **4n** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 15).

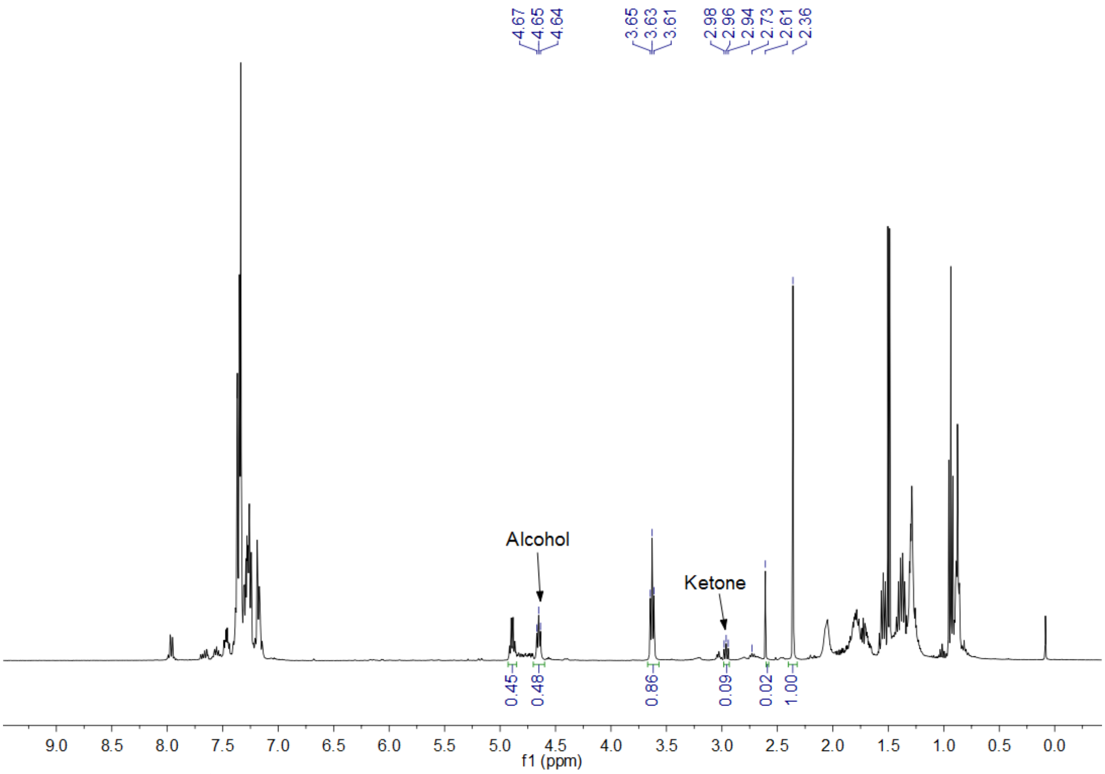


Figure S50: ^{1}H NMR spectra of *β*-alkylation of **5o** with **4o** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.025 mol %) at 140 °C (Table 2, entry 16).

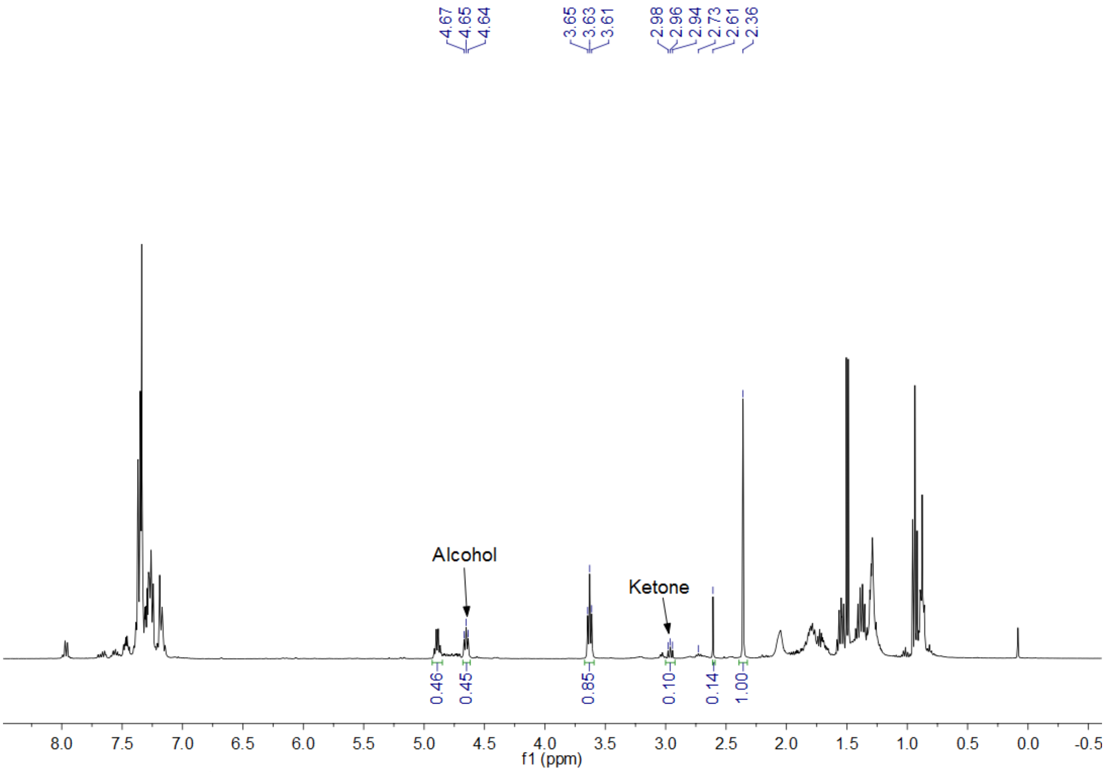


Figure S51: [1]H NMR spectra of *β*-alkylation of **5p** with **4p** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.025 mol %) at 140 °C (Table 2, entry 17).

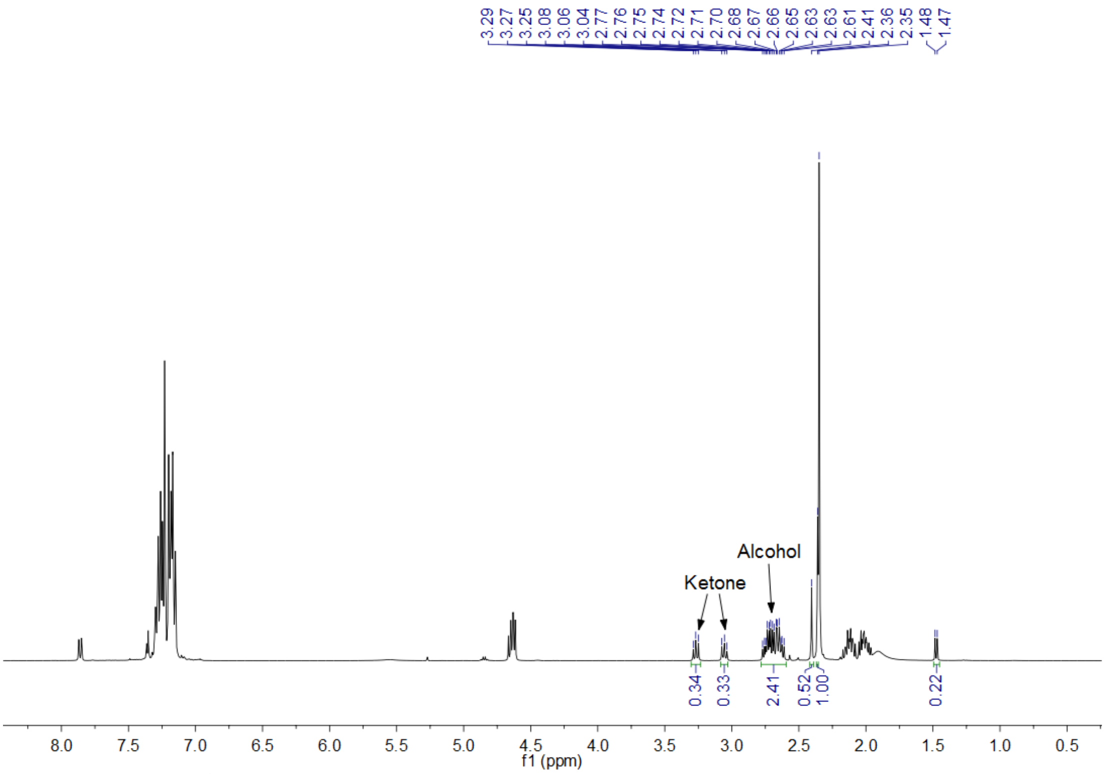


Figure S52: [1]H NMR spectra of *β*-alkylation of **5q** with **4q** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 18).

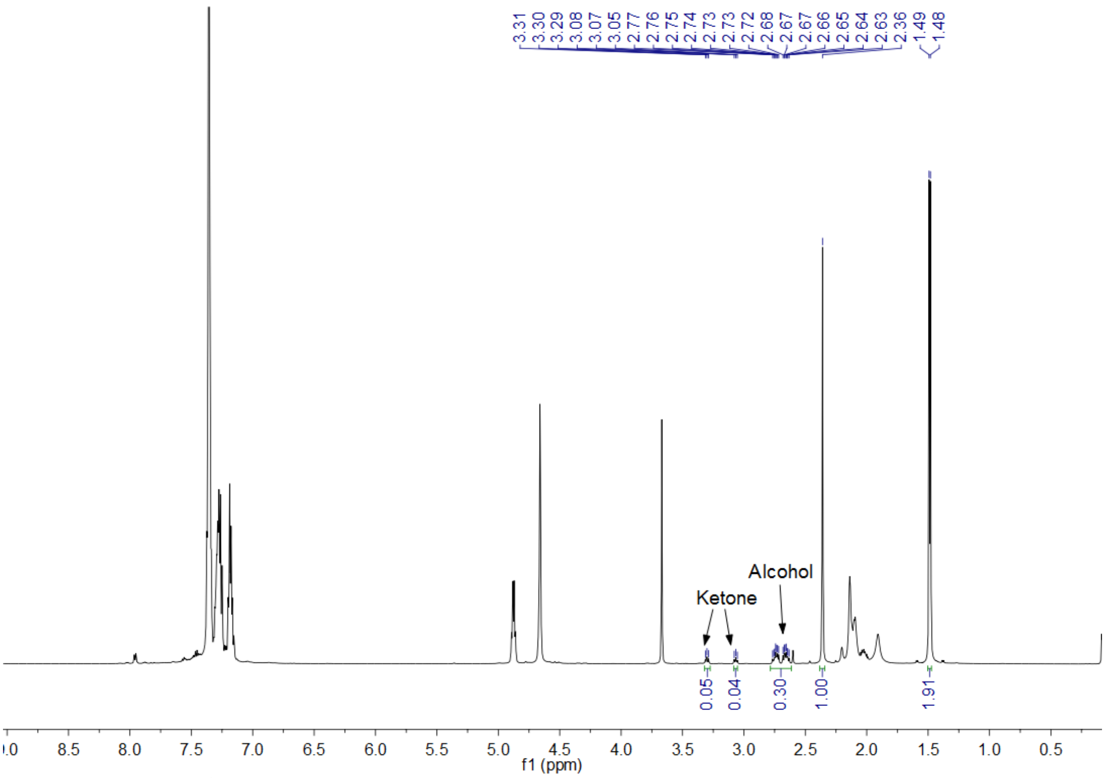


Figure S53: [1]H NMR spectra of *β*-alkylation of **5r** with **4r** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 19).

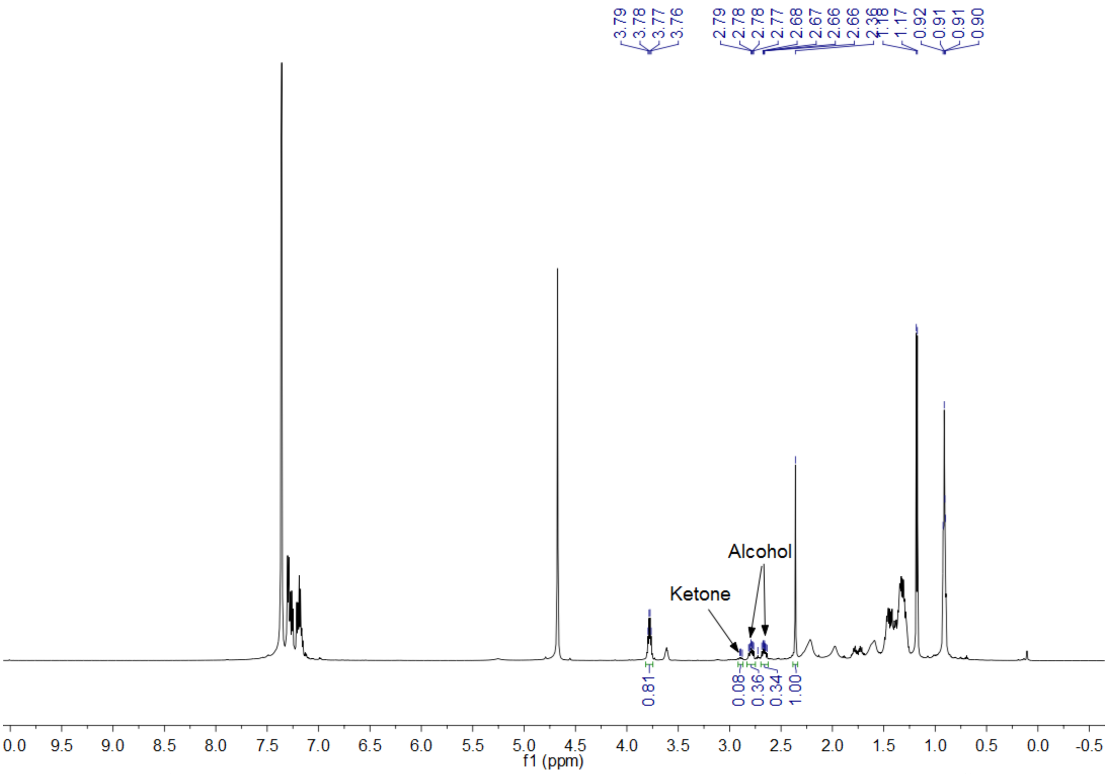


Figure S54: [1]H NMR spectra of *β*-alkylation of **5s** with **4s** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 20).

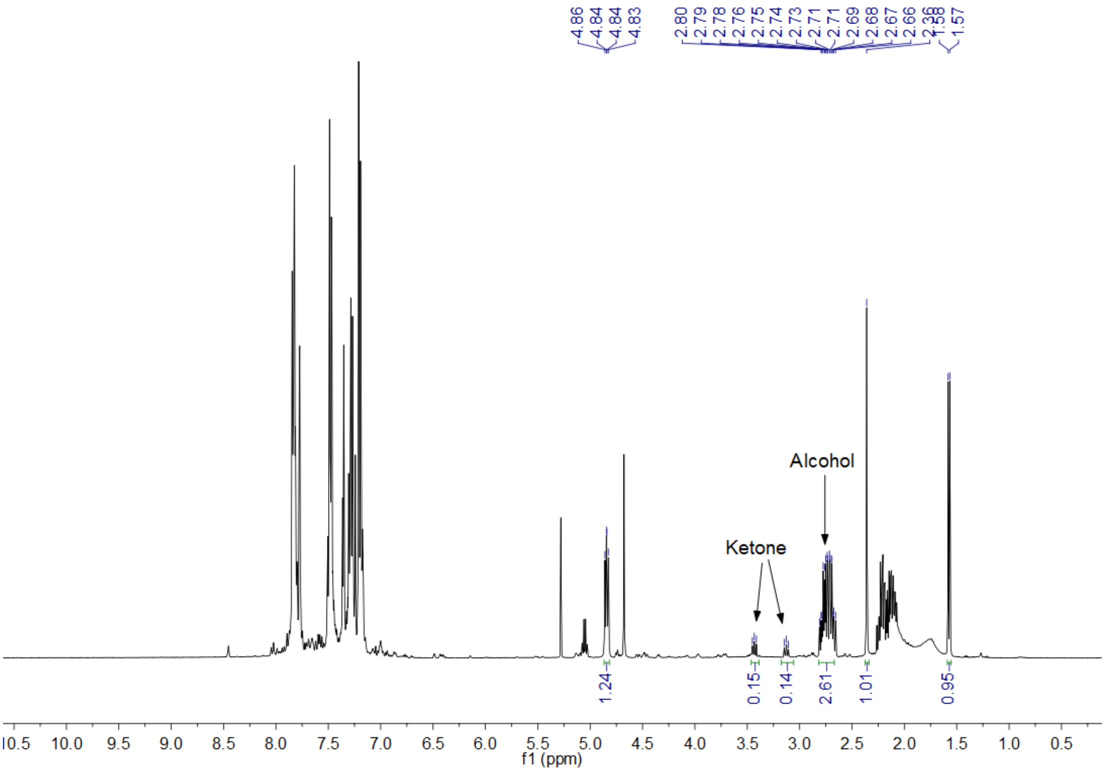


Figure S55: [1]H NMR spectra of *β*-alkylation of **5t** with **4t** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 21).

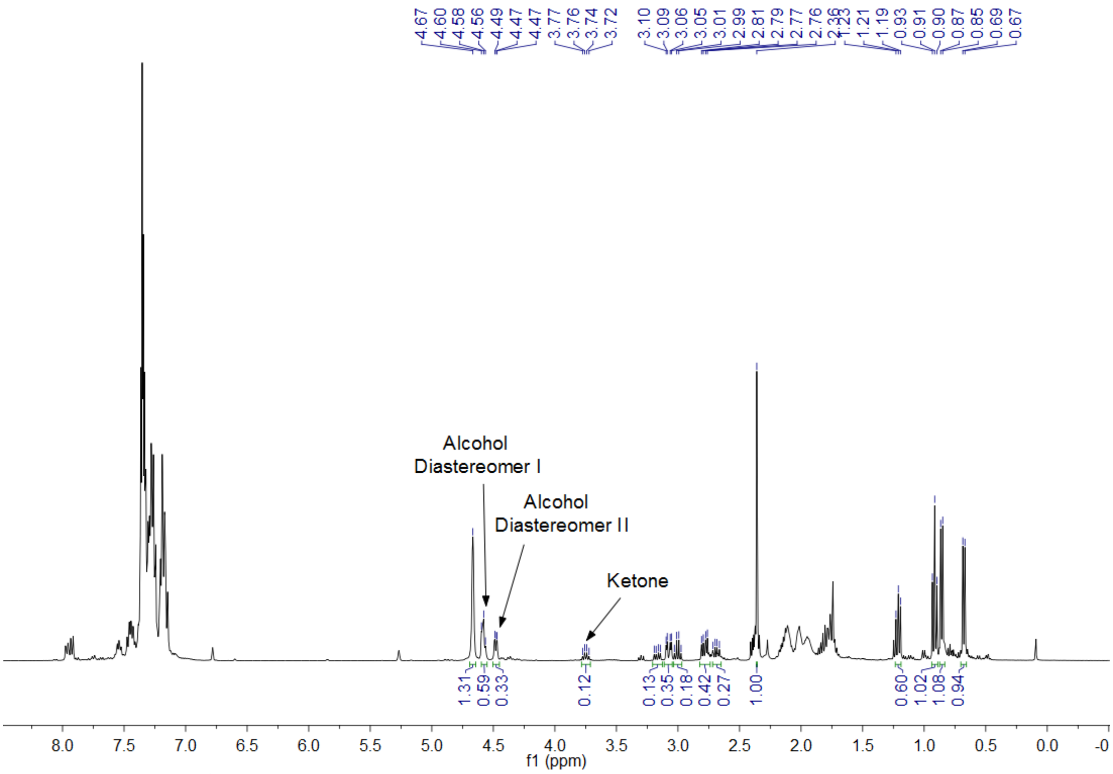


Figure S56: [1]H NMR spectra of *β*-alkylation of **5u** with **4u** catalyzed by **2b** (^{Cy}NNN)RuCl$_2$(CO) (0.00025 mol %) at 140 °C (Table 2, entry 22).

5. Kinetic Studies

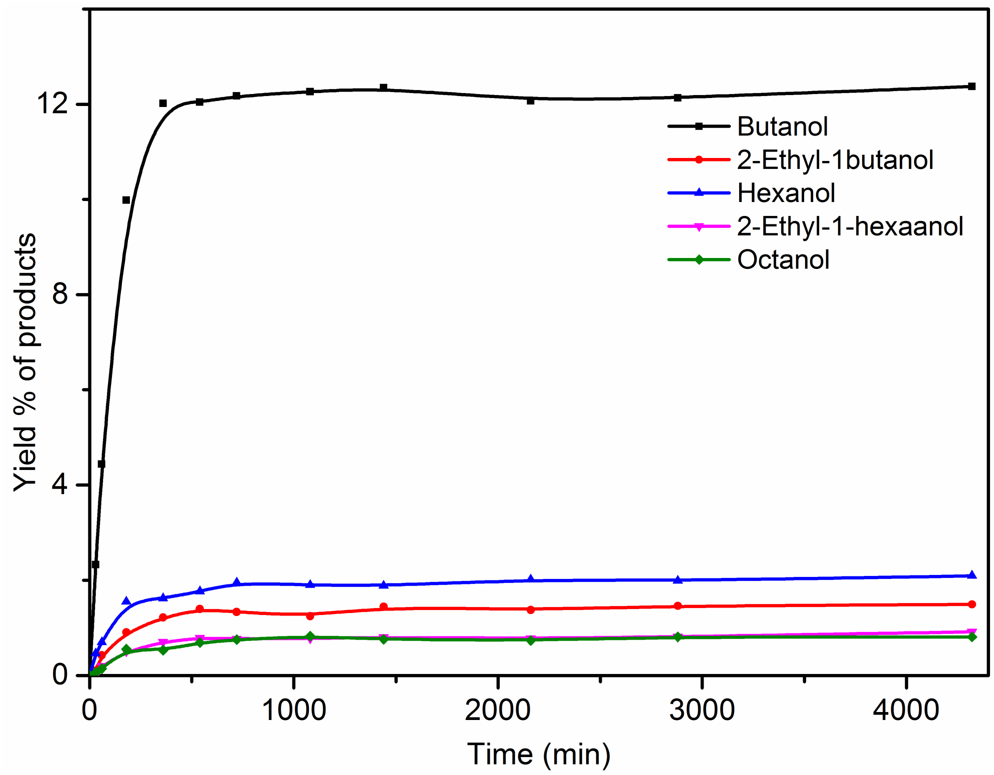


Figure S57: Ethanol upgradation to higher alcohol catalyzed by **1a**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **1a** = 7.8 mM (Table 3, entry 1).

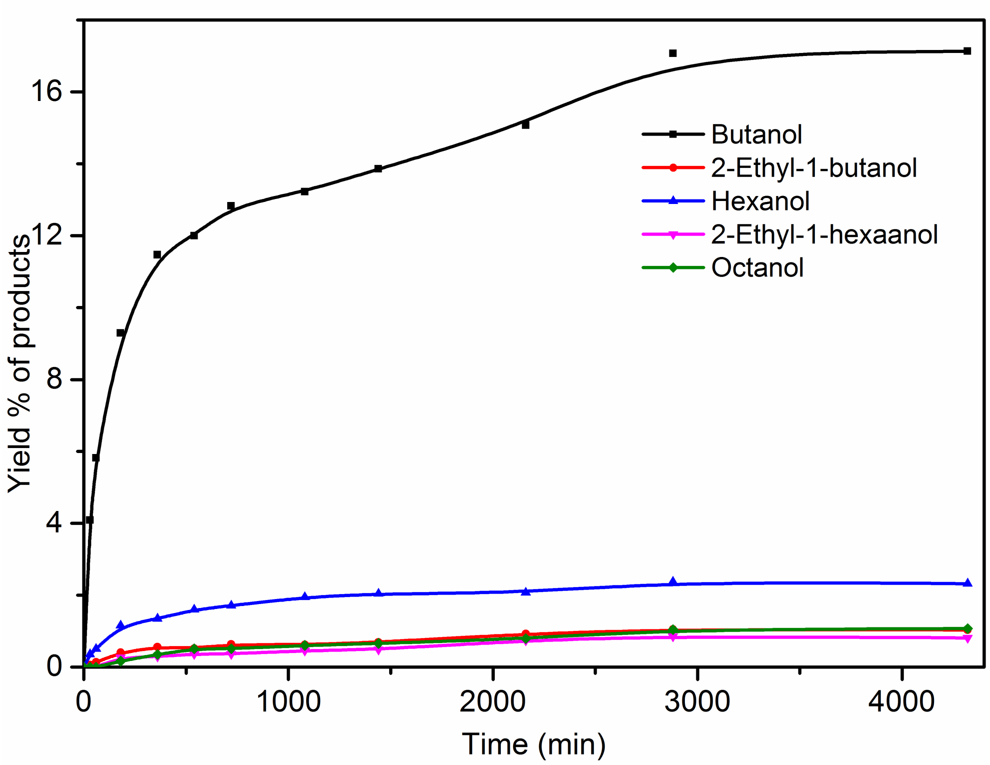


Figure S58: Ethanol upgradation to higher alcohol catalyzed by **1b**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **1b** = 7.8 mM (Table 3, entry 2).

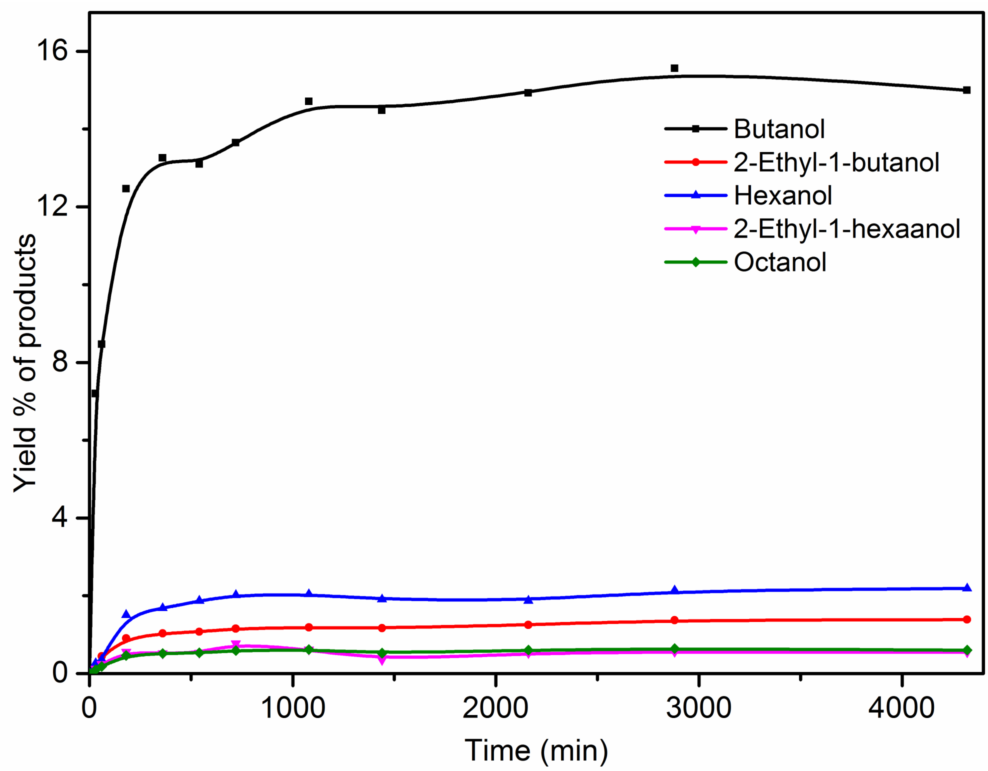


Figure S59: Ethanol upgradation to higher alcohol catalyzed by **1c**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **1c** = 7.8 mM (Table 3, entry 3).

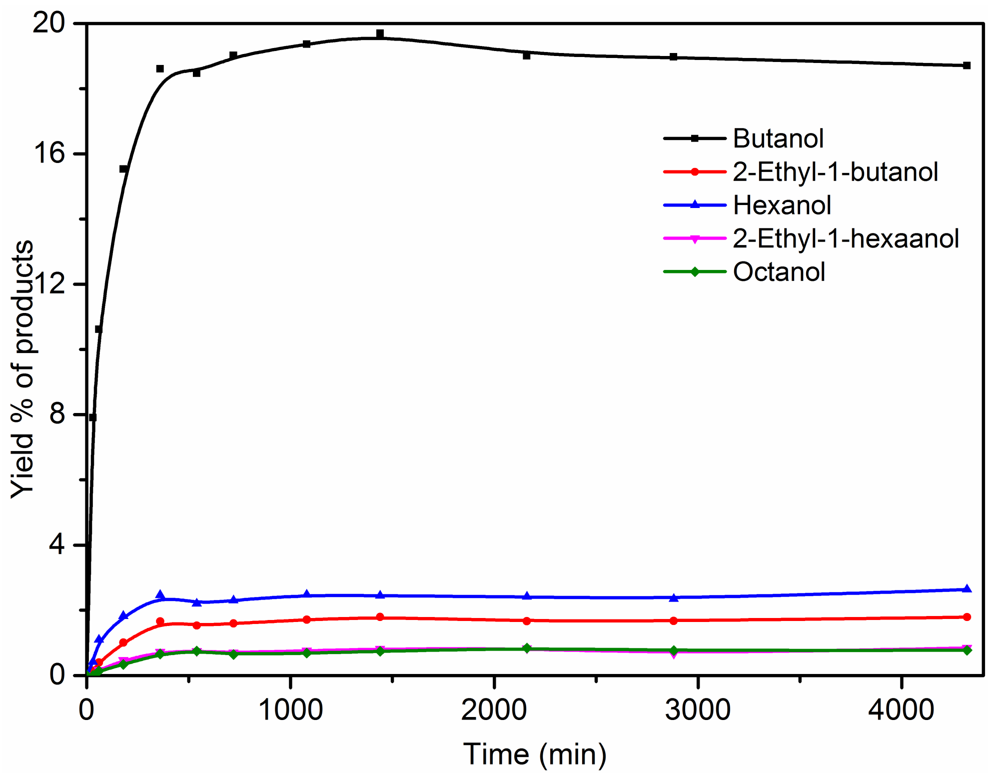


Figure S60: Ethanol upgradation to higher alcohol catalyzed by **1d**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **1d** = 7.8 mM (Table 3, entry 4).

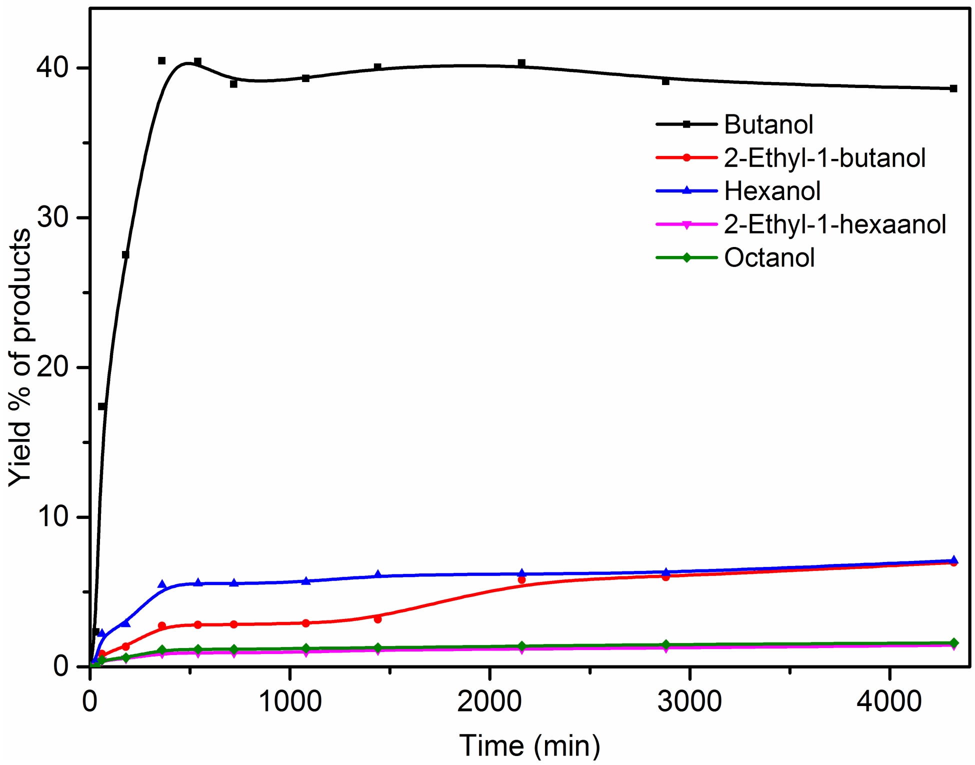


Figure S61: Ethanol upgradation to higher alcohol catalyzed by **1e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **1e** = 7.8 mM (Table 3, entry 5).

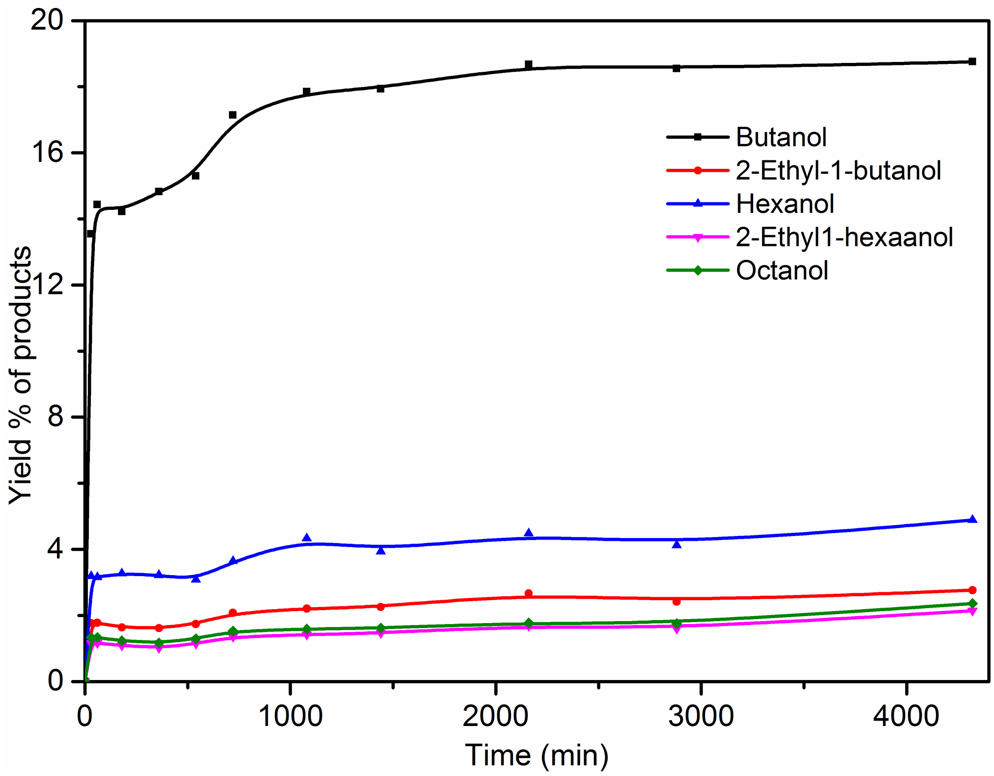


Figure S62: Ethanol upgradation to higher alcohol catalyzed by **1f**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M **1f** = 7.8 mM (Table 3, entry 6).

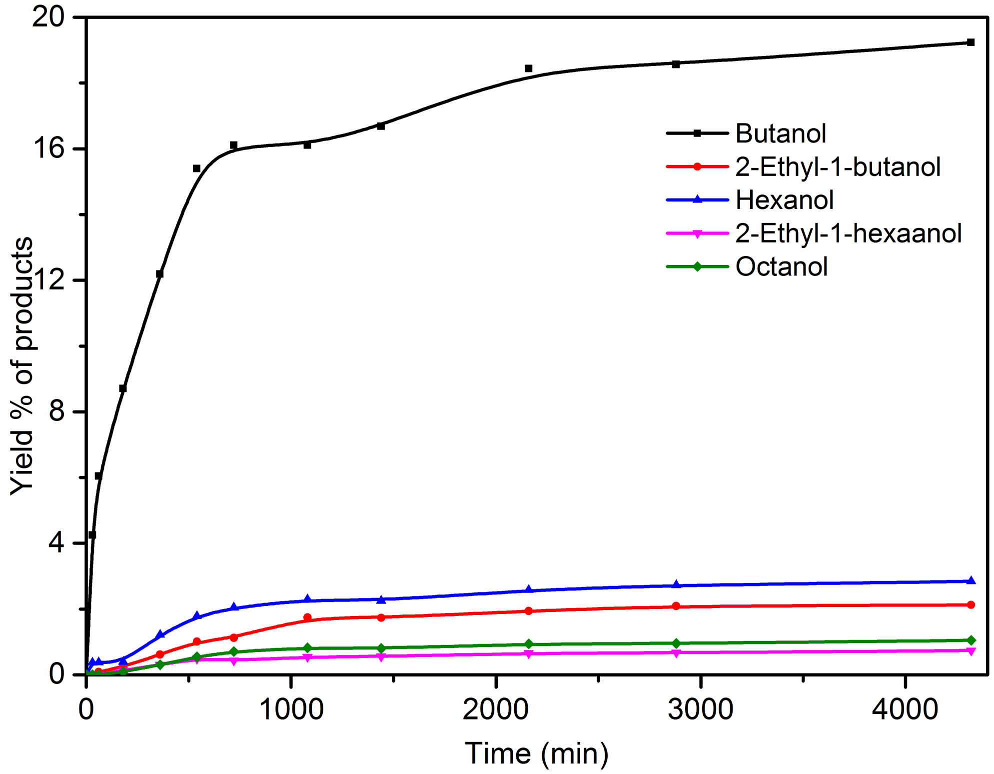


Figure S63: Ethanol upgradation to higher alcohol catalyzed by **2a**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2a** = 7.8 mM (Table 3, entry 7).

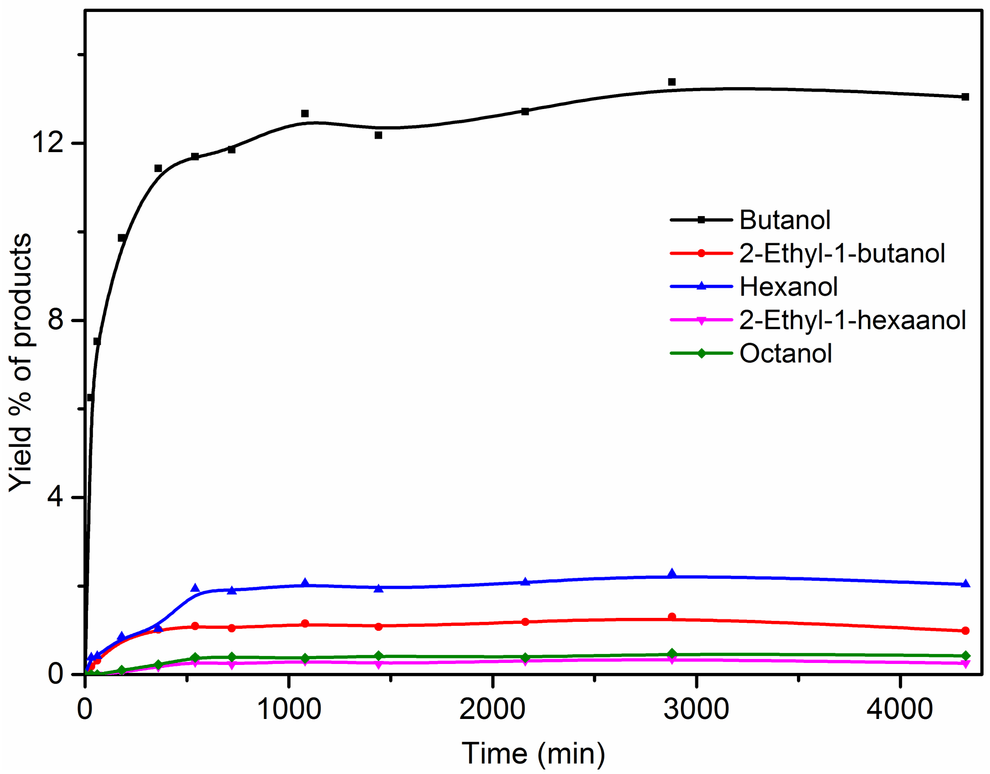


Figure S64: Ethanol upgradation to higher alcohol catalyzed by **2b**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2b** = 7.8 mM (Table 3, entry 8).

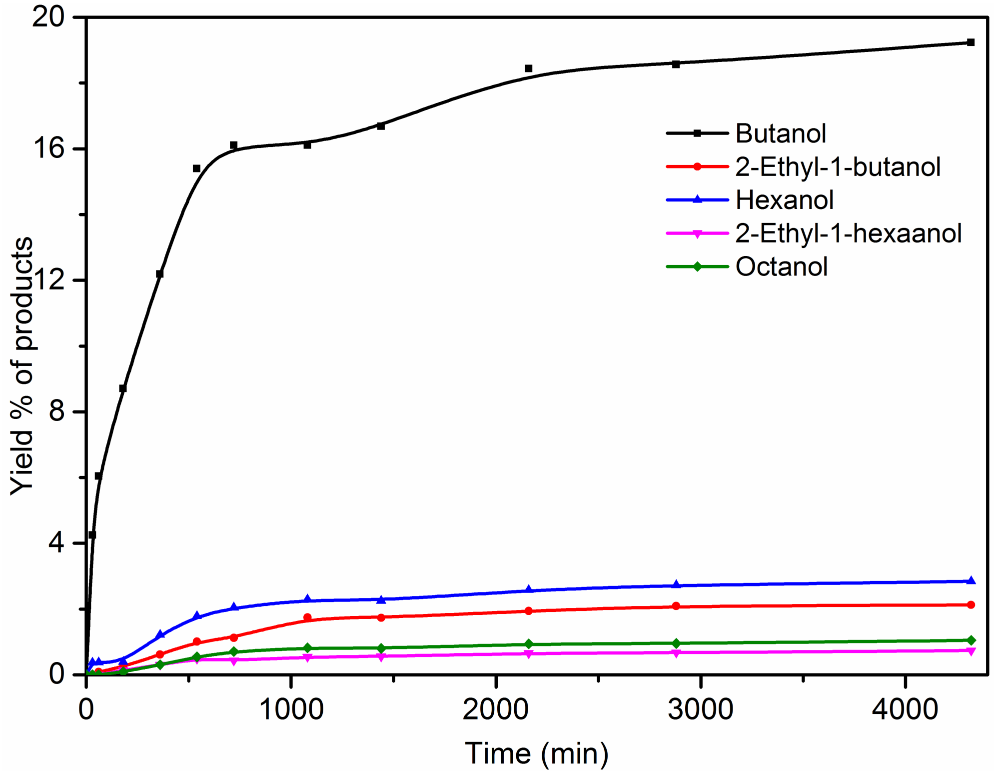


Figure S65: Ethanol upgradation to higher alcohol catalyzed by **2c**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2c** = 7.8 mM (Table 3, entry 9).

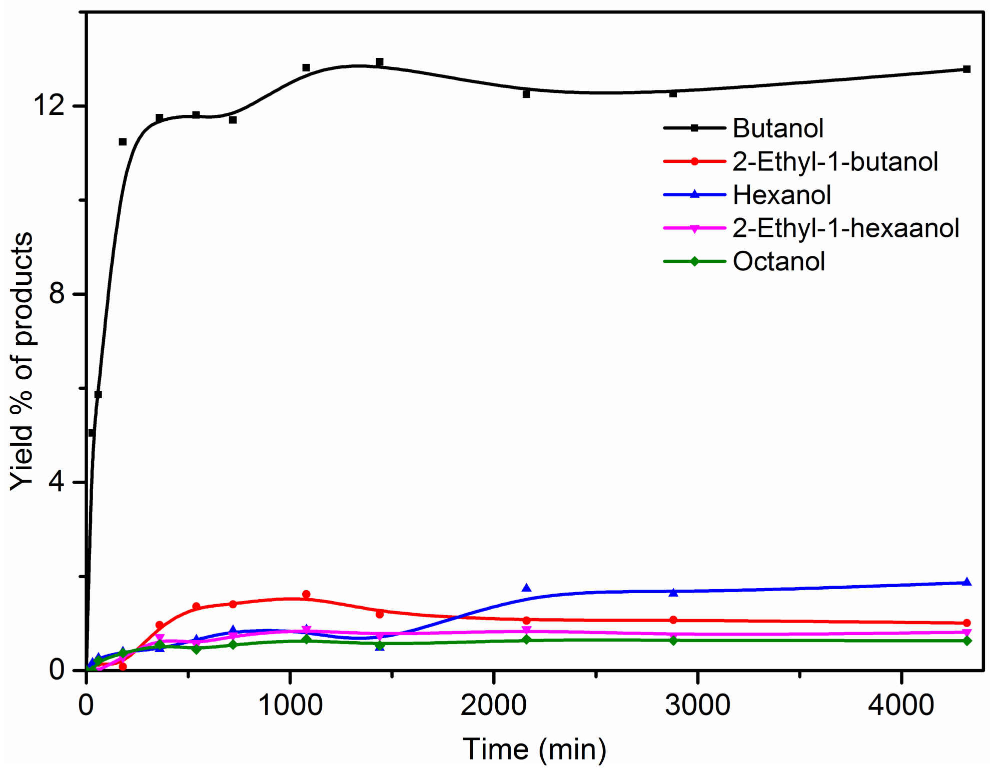


Figure S66: Ethanol upgradation to higher alcohol catalyzed by **2d**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2d** = 7.8 mM (Table 3, entry 10).

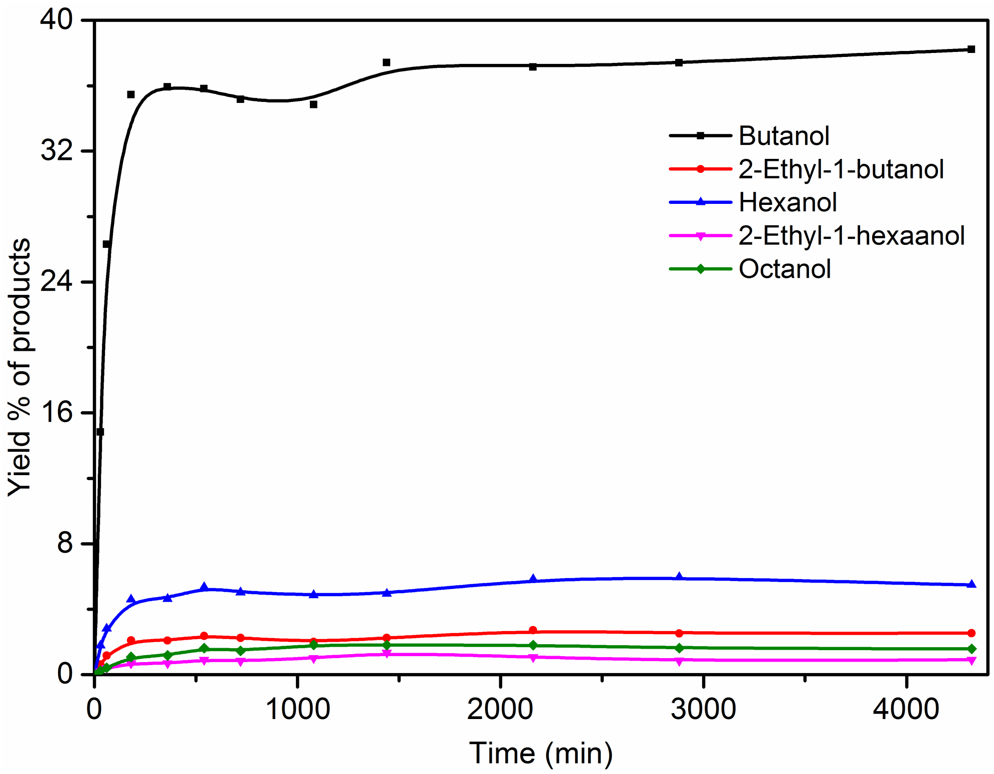


Figure S67: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 7.8 mM (Table 3, entry 11).

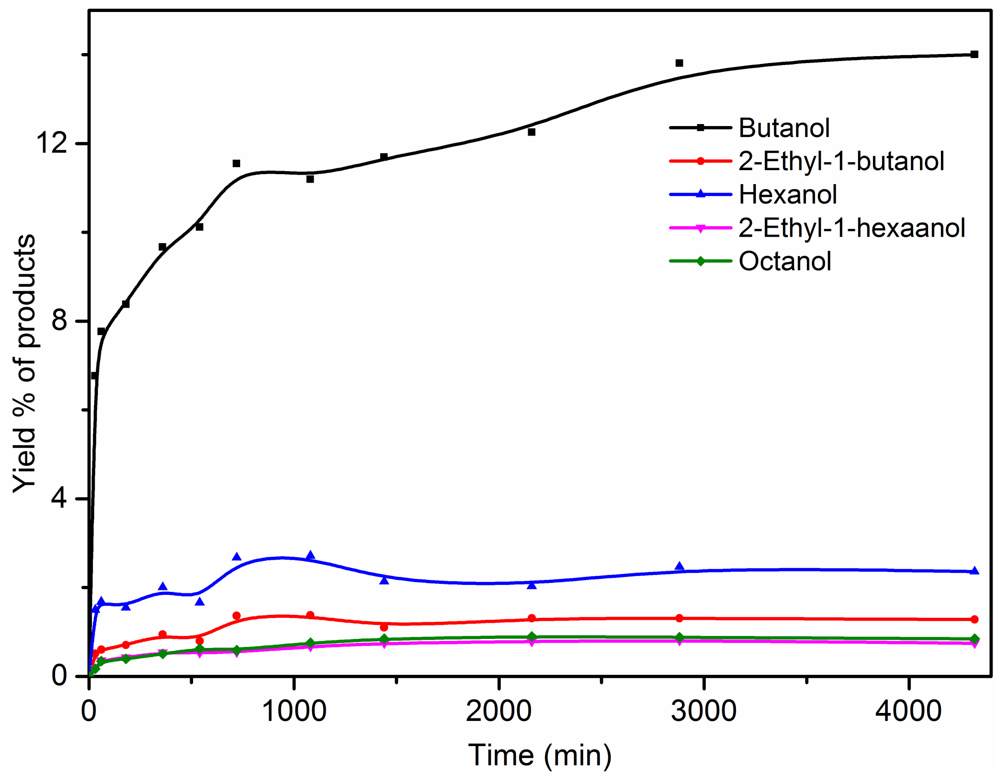


Figure S68: Ethanol upgradation to higher alcohol catalyzed by **2f**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2f** = 7.8 mM (Table 3, entry 12).

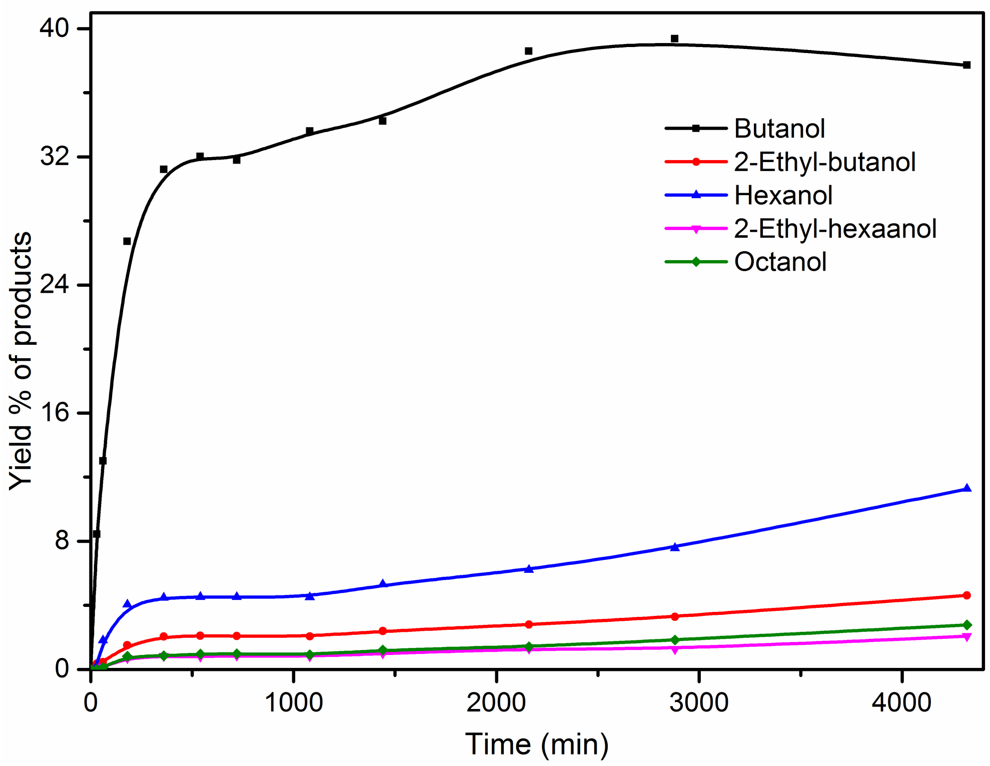


Figure S69: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 3.4 mM (Table 4, entry 1).

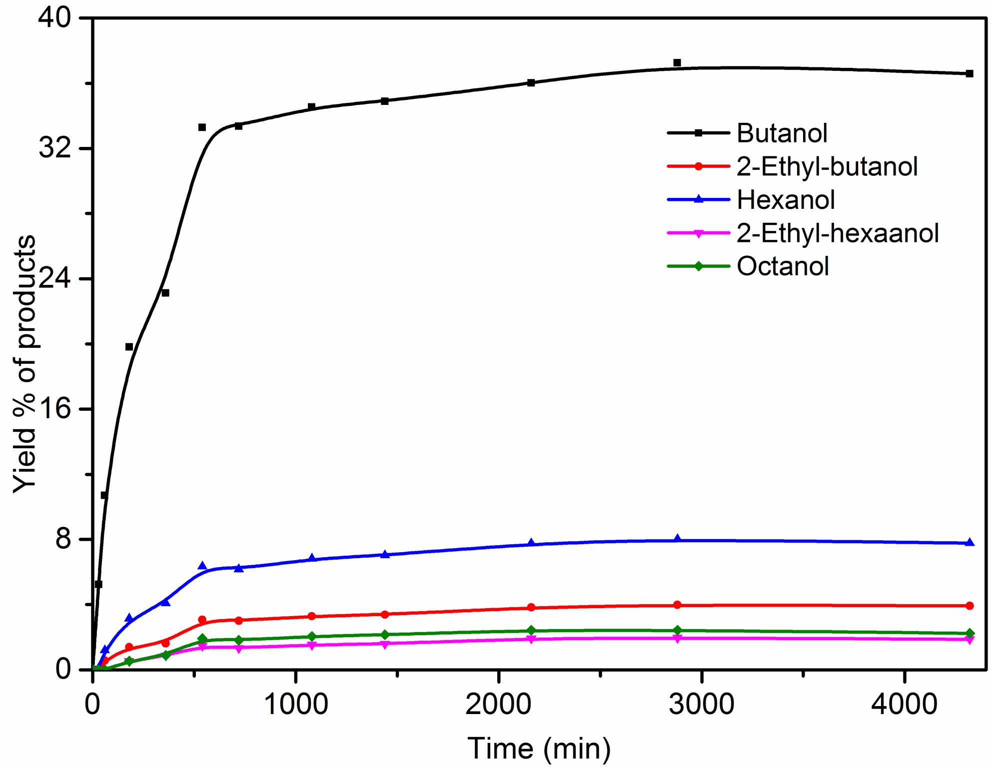


Figure S70: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 5.0 mM (Table 4, entry 2).

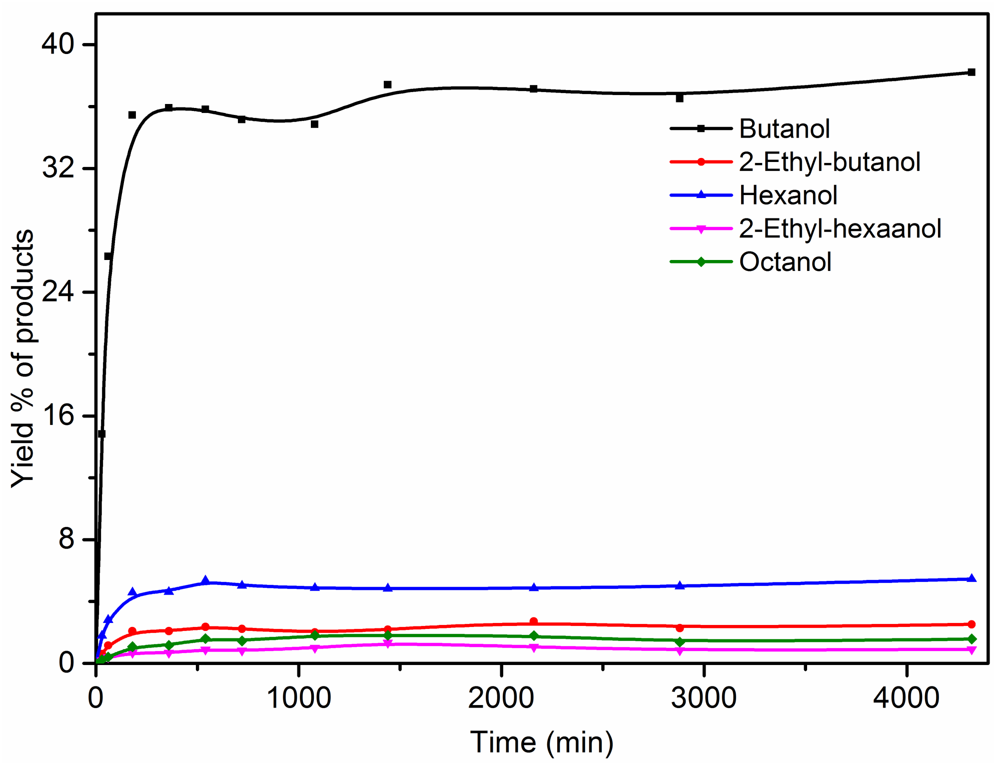


Figure S71: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 7.8 mM (Table 4, entry 3).

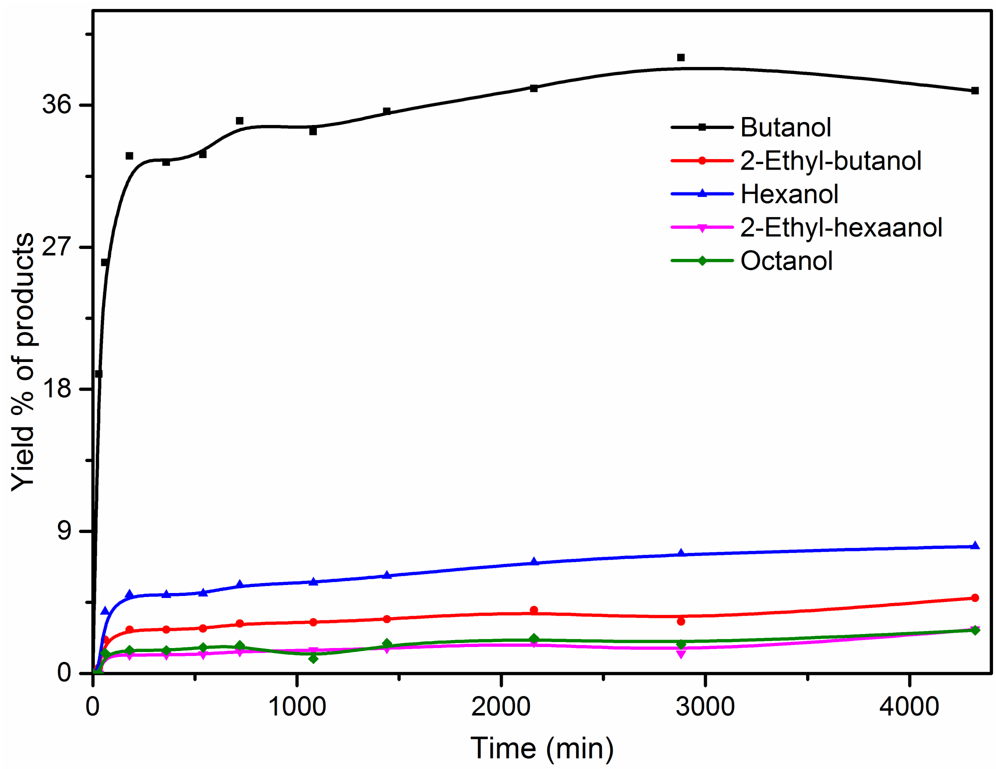


Figure S72: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 10.7 mM (Table 4, entry 4).

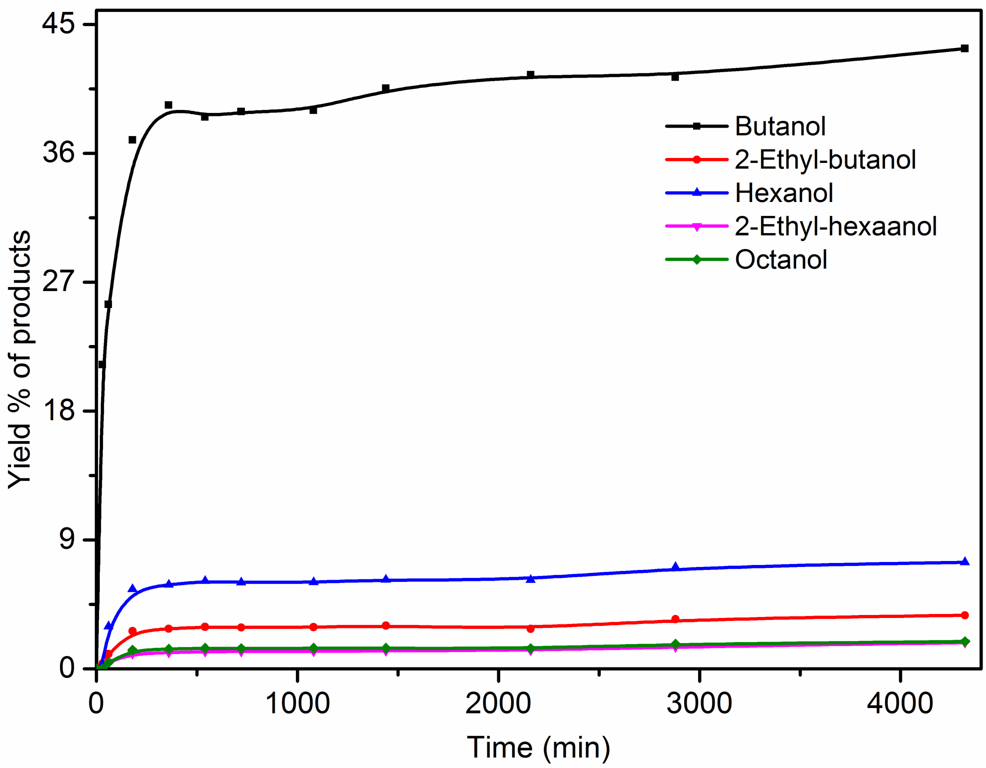


Figure S73: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 14.1 mM (Table 4, entry 5).

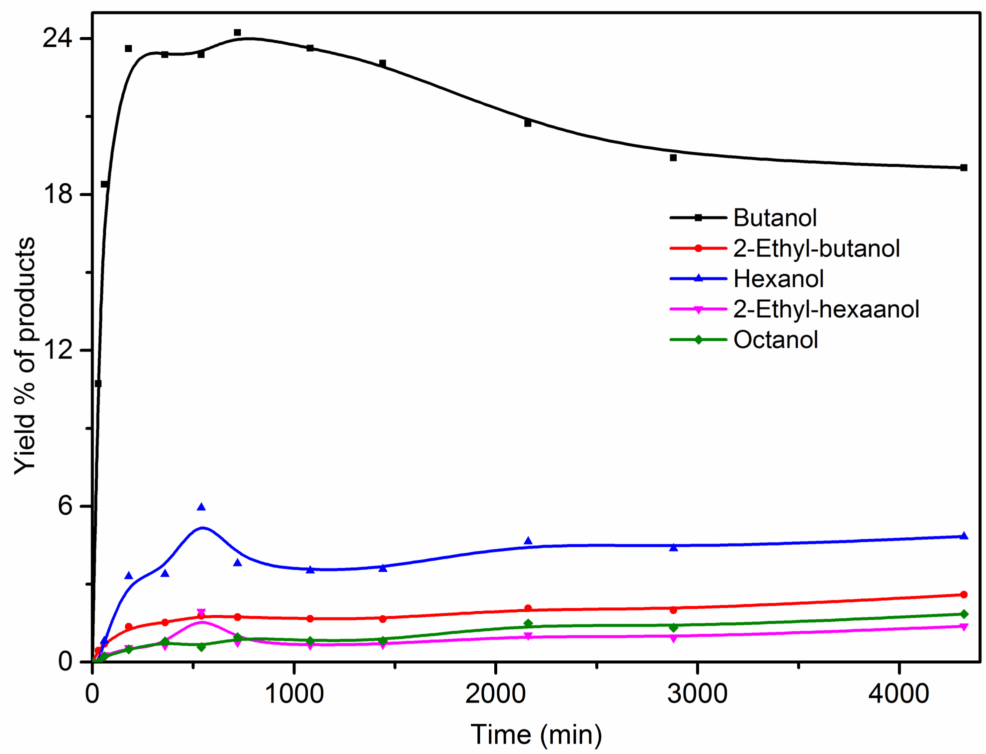


Figure S74: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 6.11 M; **2e** = 7.8 mM.

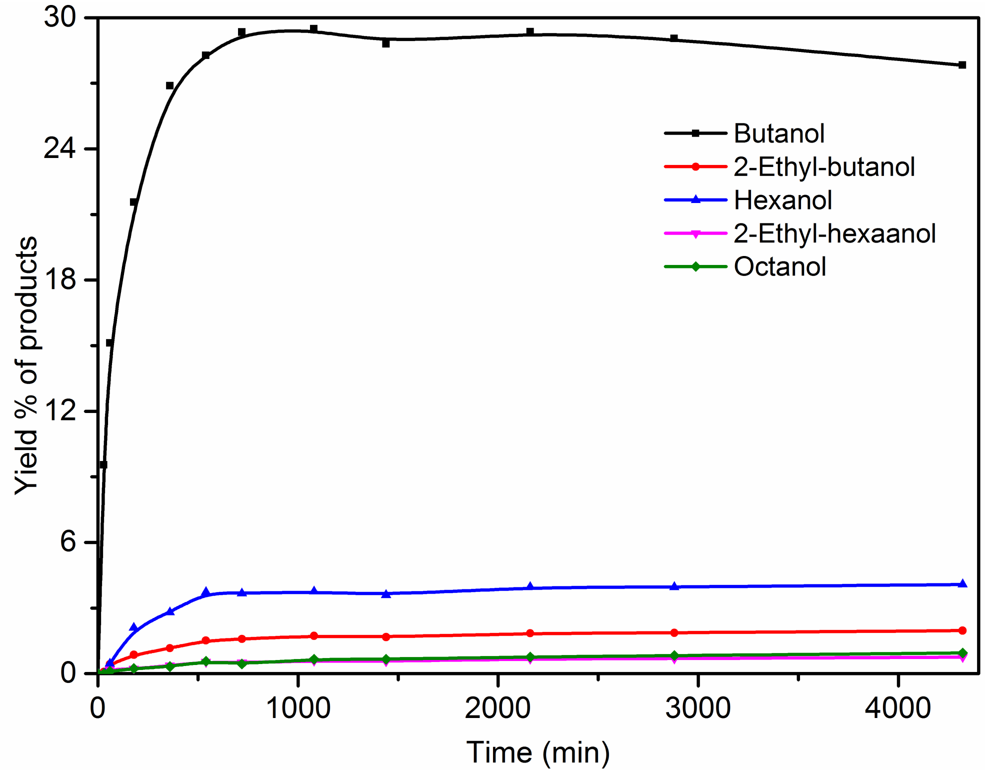


Figure S75: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 8.56 M; **2e** = 7.8 mM

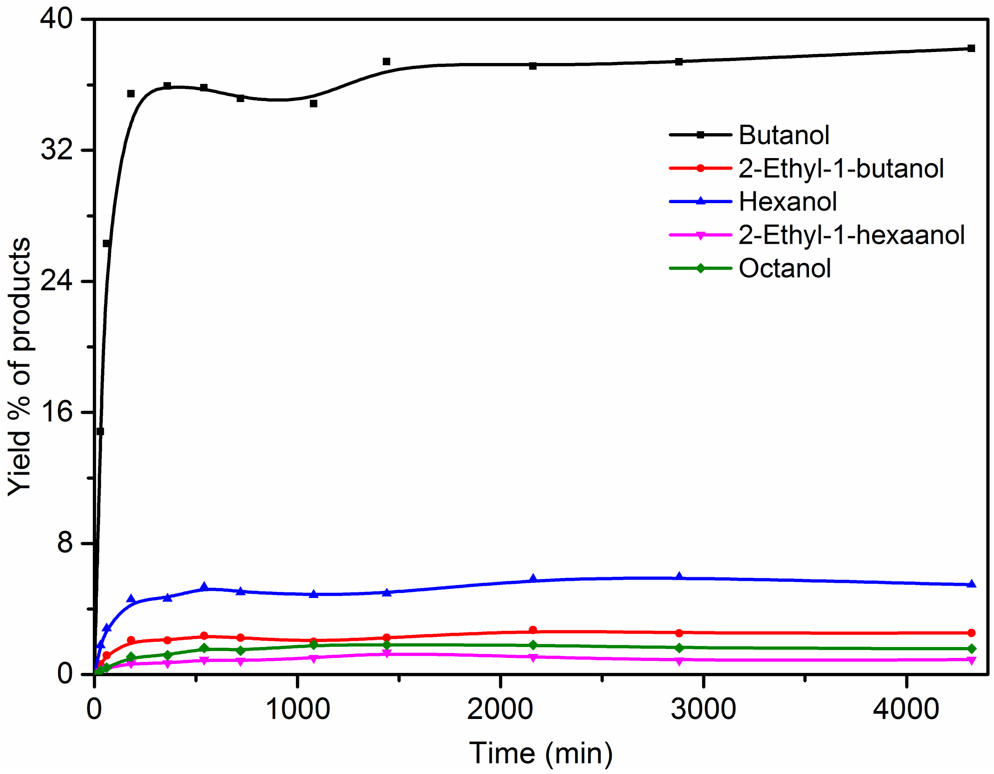


Figure S76: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 12.23 M; **2e** = 7.8 mM.

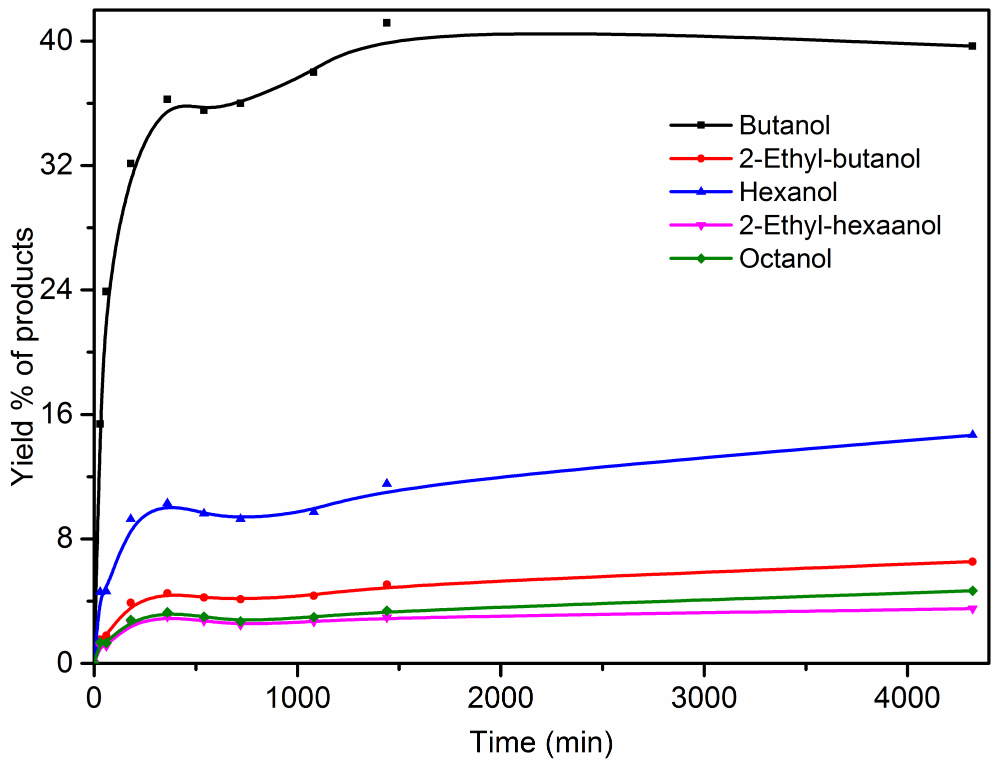


Figure S77: Ethanol upgradation to higher alcohol catalyzed by **2e**. Reaction condition: Temperature 140 °C; ethanol = 13.46 M; **2e** = 7.8 mM.

6. Computational study

Table S3a: Optimized XYZ coordinates for complex **8**

C	-0.24056267	1.00167213	-2.78071527	H	-0.62273141	5.03823395	0.85120840
C	0.01625185	0.78312355	-4.13922126	H	0.54966404	3.69926311	0.63397604
C	0.57345030	-0.43308712	-4.55744273	C	-2.65776044	3.95791229	-0.74900853
C	0.87499244	-1.42851886	-3.61733585	H	-2.37235387	4.47112828	-1.68070776
C	0.61516417	-1.21164230	-2.25977032	H	-3.46317839	3.24327337	-0.97546659
H	-0.22088786	1.56967002	-4.85805112	H	-3.05933953	4.72383583	-0.06852417
H	0.77469387	-0.60474581	-5.61560098	N	0.50682374	-1.61849826	0.04762996
H	1.31717313	-2.37725696	-3.92728824	N	0.05405280	-0.00158679	-1.86420901
C	0.87416333	-2.06702691	-1.13851319	N	-0.97278274	2.07841680	-0.82769406
H	1.38631299	-3.02373941	-1.26900375	Ru	-0.32887485	0.26935147	-0.03881637
C	-0.79892631	2.15251265	-2.13739237	H	-3.37235941	0.63098531	-0.83093114
H	-1.06316880	3.04489218	-2.71206562	C	-3.32785023	0.24520821	0.20907138
C	0.77776422	-2.37682276	1.28517593	C	-4.51557673	-0.67222313	0.44227363
H	1.10317878	-1.59942142	1.99911955	C	-5.73443331	-0.15323906	0.90519389
C	1.89168937	-3.42151873	1.17428043	C	-4.42380136	-2.04503631	0.16670224
H	2.82146571	-2.98286473	0.78164743	C	-6.84698073	-0.98442045	1.07437646
H	2.10390230	-3.82408231	2.17586250	H	-5.81188834	0.91317133	1.14055394
H	1.60083130	-4.27394440	0.53869226	C	-5.53296434	-2.87892788	0.34202489
C	-0.54019447	-2.98512462	1.79241290	H	-3.46678767	-2.44608009	-0.17305098
H	-1.33884922	-2.23074521	1.80730615	C	-6.74911187	-2.35191359	0.79281171
H	-0.85868026	-3.80802923	1.13180018	H	-7.78897361	-0.56568070	1.43752926
H	-0.40049323	-3.38993218	2.80635636	H	-5.44790382	-3.94736006	0.12706889
C	-1.46259134	3.26391182	-0.08190456	H	-7.61450319	-3.00447039	0.93134148
H	-1.79623153	2.86119883	0.88868680	O	-2.11092005	-0.44235073	0.41813625
C	-0.29708535	4.23047861	0.17765609	Cl	1.71444971	1.19680295	0.79016465
H	0.04459319	4.68393357	-0.76683355	H	-3.42431856	1.12614583	0.87822730

Table S3b: Optimized XYZ coordinates for complex **9**

C	-1.25977606	0.51411895	-2.48400249
C	-1.51711974	0.09500377	-3.79327094
C	-1.07273508	-1.16345421	-4.22338505
C	-0.36887114	-1.99672641	-3.34436791
C	-0.11535852	-1.57639086	-2.03311265
H	-2.06375131	0.75875422	-4.46546890
H	-1.27250308	-1.49242418	-5.24396992
H	-0.00670606	-2.97496269	-3.66644819
C	0.60596838	-2.24513734	-0.98996446
H	1.10434450	-3.20036202	-1.17436960
C	-1.61659495	1.74500042	-1.84249458
H	-2.14642827	2.52849736	-2.39104520
C	1.43462290	-2.18542360	1.30863477
H	1.92367243	-1.30035409	1.75257230
C	2.52412965	-3.19055091	0.92445616
H	3.20506423	-2.77766283	0.16501015
H	3.11889033	-3.43119833	1.81820215
H	2.10350095	-4.13890094	0.55181993
C	0.44368638	-2.76258992	2.33280127
H	-0.36113192	-2.04341090	2.53950889
H	-0.01303311	-3.68621203	1.94117749
H	0.96917731	-3.00582065	3.26892522
C	-1.53942258	3.15964886	0.12796216
H	-1.55664327	2.89000319	1.19746074
C	-0.36464031	4.12276113	-0.10153522
H	-0.33327972	4.44274517	-1.15551122
H	-0.48658388	5.01700706	0.52917681
H	0.59068494	3.63640736	0.13859628
C	-2.88798305	3.79998495	-0.22780563
H	-2.88883493	4.22685073	-1.24321916
H	-3.71171793	3.07420126	-0.15333182
H	-3.08994712	4.62749187	0.46884847
N	0.67050946	-1.62782252	0.17522512
N	-0.57637559	-0.33151005	-1.62053123
N	-1.27791388	1.87841774	-0.57282910
Ru	-0.26600304	0.21547148	0.15676474
H	-2.96107092	1.21345094	1.53450824
C	-2.97014612	0.10280203	1.55258838
C	-3.91575527	-0.36795930	0.45010952
C	-5.09279785	0.34725500	0.17297048
C	-3.64678904	-1.53307394	-0.28259217
C	-5.98181458	-0.08923733	-0.81486445
H	-5.31672650	1.25705018	0.74013649
C	-4.53267305	-1.97027235	-1.27426157
H	-2.72916933	-2.08451369	-0.06763573
C	-5.70228910	-1.25112472	-1.54463102
H	-6.89239031	0.48020459	-1.01852305
H	-4.30644385	-2.87741094	-1.84077277
H	-6.39226622	-1.59211192	-2.32028265
O	-1.66644885	-0.42209937	1.40246546
Cl	1.88249099	1.25661442	-0.04351836
C	-3.47728483	-0.34270454	2.93596680
H	-3.50928822	-1.44148373	2.98314414
H	-2.79731159	0.02521717	3.71884647
H	-4.48901704	0.04632830	3.12843757

Table S3c: Optimized XYZ coordinates for complex **10**

C	2.89535630	0.53699707	-0.89435594	H	1.72546685	5.09802960	1.75109234
C	4.09769406	0.08685429	-1.45370772	H	2.61172479	3.58111828	2.05300705
C	4.20989602	-1.27782435	-1.77780119	C	0.37678111	4.21725005	-0.57628339
C	3.15700940	-2.16210198	-1.53262049	H	1.15810606	4.52370769	-1.29085106
C	1.96493399	-1.66080820	-0.96872750	H	-0.34932101	3.59728563	-1.12019628
H	4.92598631	0.77668192	-1.62242433	H	-0.12184132	5.12269126	-0.19859582
H	5.13807509	-1.65264739	-2.21361887	N	-0.22341826	-1.66807849	-0.04037455
H	3.25259048	-3.22515758	-1.76010686	N	1.87224712	-0.33049561	-0.69973223
C	0.76847160	-2.36733933	-0.57885508	N	1.37963983	2.08762510	0.08836944
H	0.70025840	-3.45170265	-0.69657646	Ru	0.17695442	0.32472310	0.16194754
C	2.56209401	1.87907147	-0.42032423	H	-1.88308057	2.24925424	-0.08218835
H	3.31717632	2.67219888	-0.47338574	C	-1.72781197	1.24078855	-0.51930511
C	-1.39430896	-2.41304892	0.50091387	C	-2.98969853	0.43069041	-0.56464403
H	-2.21123490	-1.67962536	0.50262148	C	-3.94221470	0.52289634	0.46449497
C	-1.10034418	-2.81192297	1.95471864	C	-3.26530199	-0.36762120	-1.68618376
H	-0.75075836	-1.94541727	2.53298869	C	-5.14056031	-0.19041170	0.38561349
H	-2.01446079	-3.21480075	2.41769462	H	-3.73081136	1.14665935	1.33864743
H	-0.31751788	-3.58654003	1.99480763	C	-4.46705532	-1.07868613	-1.76654702
C	-1.83076394	-3.60873847	-0.35411399	H	-2.52274962	-0.40591775	-2.48636833
H	-1.95403571	-3.32323420	-1.40943188	C	-5.40547266	-0.99637949	-0.73059025
H	-1.12746672	-4.45472260	-0.29215236	H	-5.87210361	-0.11833632	1.19419021
H	-2.80287000	-3.96952928	0.01384283	H	-4.67702133	-1.69396553	-2.64526493
C	1.00323542	3.42991211	0.58774448	H	-6.34491968	-1.55059079	-0.79498290
H	0.22541511	3.22115617	1.33871785	O	-0.86727353	1.13958364	-1.51002350
C	2.13850034	4.19653766	1.27384468	Cl	1.23385957	-0.03277054	2.32419525
H	2.91005766	4.53387973	0.56313594	H	-1.11777408	0.72001633	1.10250569

Table S3d: Optimized XYZ coordinates for complex **11**

C	3.17046176	-0.31616040	-0.80003377
C	4.24825884	-1.06951036	-1.28480419
C	4.09890811	-2.45485493	-1.43870732
C	2.88836557	-3.07507760	-1.10474455
C	1.82578255	-2.29484967	-0.62462355
H	5.18922633	-0.57372148	-1.52953324
H	4.93138495	-3.05311626	-1.81257618
H	2.76289803	-4.15455004	-1.20583069
C	0.51133284	-2.71440395	-0.21166178
H	0.23174819	-3.77115210	-0.24253501
C	3.10166824	1.09903003	-0.53314226
H	3.97617392	1.73959759	-0.68934525
C	-1.65817408	-2.19831232	0.71968694
H	-2.31072551	-1.33821818	0.51730186
C	-1.57204994	-2.38676105	2.24192947
H	-1.12172481	-1.50665890	2.72029349
H	-2.58228504	-2.54550003	2.64970141
H	-0.95243563	-3.26399012	2.48936112
C	-2.25864870	-3.42361951	0.02050585
H	-2.24061335	-3.31126999	-1.07410295
H	-1.74750866	-4.36136242	0.29275796
H	-3.30896277	-3.52584617	0.33098560
C	1.88904865	3.01690511	0.27658319
H	0.86698145	3.15123187	0.65627216
C	2.86082877	3.35512571	1.41546575
H	3.91029974	3.28620581	1.08691348
H	2.68359708	4.38542534	1.76070208
H	2.70940257	2.66696084	2.25923728
C	2.07243881	3.90359391	-0.96194734
H	3.10216151	3.84574343	-1.34978725
H	1.38232914	3.59796261	-1.76136575
H	1.87004683	4.95453598	-0.70429801
N	-0.32739872	-1.78501415	0.20477519
N	1.98190789	-0.93589893	-0.49880423
N	1.96222006	1.57681272	-0.07959470
Ru	0.49864787	0.12755317	0.17580127
C	-1.54596055	1.48171014	-0.76984896
C	-2.88723552	0.76590503	-0.64046665
C	-3.75103803	0.97675170	0.44793570
C	-3.29292140	-0.08328890	-1.68034759
C	-4.99359076	0.33943150	0.50021220
H	-3.43580600	1.62414817	1.27161782
C	-4.54196813	-0.71359897	-1.63355491
H	-2.60479379	-0.23499176	-2.51478603
C	-5.39449784	-0.50690847	-0.54329436
H	-5.65198554	0.50047291	1.35752863
H	-4.85097311	-1.36834387	-2.45258382
H	-6.36844293	-1.00079272	-0.50459145
O	-0.72386327	1.02637195	-1.68365868
Cl	1.13394870	-0.00927663	2.46854035
H	-0.99365641	1.18336817	0.65578316
C	-1.66060529	3.02679071	-0.66052659
H	-2.71269951	3.34378476	-0.62272584
H	-1.15080831	3.43859647	0.21955335
H	-1.19565928	3.44852142	-1.56246151

Table S3e: Optimized XYZ coordinates for complex **12** and **4′**

C	0.75973480	-1.29977012	2.38358141	H	0.20954201	-3.93618989	-2.41216257
C	0.98458361	-1.50009694	3.75248746	H	1.34371358	-2.64685306	-1.93902717
C	1.66484966	-0.51900025	4.48791531	C	-1.66038863	-3.55602711	-0.37962122
C	2.11044018	0.65354135	3.86175527	H	-1.27842962	-4.35808313	0.27308935
C	1.87091946	0.83348674	2.49218715	H	-2.45220135	-2.99884956	0.14413828
H	0.62596470	-2.41293551	4.23156791	H	-2.11702489	-4.04546143	-1.25325620
H	1.84355432	-0.66657777	5.55420770	N	1.85620552	1.88147153	0.37611637
H	2.63351188	1.42758572	4.42642077	N	1.20804918	-0.14339515	1.77894114
C	2.21612077	1.95079808	1.64665306	N	0.02016953	-1.73598407	0.18437915
H	2.74896575	2.81483193	2.05332035	Ru	0.84048363	0.14136796	-0.09908167
C	0.10352073	-2.16387150	1.43231044	H	-0.49993787	0.81396243	0.35311184
H	-0.29502410	-3.13484380	1.73907729	C	-3.41378367	-0.11536267	-0.61352265
C	2.20587607	2.97261324	-0.56556769	C	-4.04884609	1.04418674	-1.27944756
H	1.32580791	3.04656390	-1.22522634	C	-3.25541631	1.90116635	-2.06359034
C	3.39075000	2.51218806	-1.42944276	C	-5.42834077	1.28619777	-1.14022096
H	3.15041035	1.56714664	-1.93537307	C	-3.84213210	2.99582885	-2.70532304
H	3.60723400	3.26837942	-2.19933191	H	-2.18528169	1.69392320	-2.17078196
H	4.29232379	2.37621955	-0.81012452	C	-6.00748519	2.38099511	-1.77830078
C	2.46317128	4.33545346	0.08331495	H	-6.01599969	0.59904032	-0.52665768
H	1.63826798	4.63160581	0.74966829	C	-5.21410365	3.23567411	-2.56102242
H	3.40534497	4.35862471	0.65500170	H	-3.23134825	3.66074368	-3.32021117
H	2.54752493	5.09644794	-0.70668321	H	-7.07744907	2.57575902	-1.67280561
C	-0.55422330	-2.61594065	-0.86629568	H	-5.67188844	4.09227697	-3.06231457
H	-0.97776392	-1.91444922	-1.60258243	O	-4.00996436	-0.95074173	0.05570586
C	0.59820076	-3.35985782	-1.55896926	Cl	0.47609921	0.42947800	-2.45395428
H	1.08889830	-4.05753149	-0.86075622	H	-2.30721907	-0.17874394	-0.76598056

Table S3f: Optimized XYZ coordinates for complex **12** and **5′**

C	3.18525192	0.31715218	2.62760162	C	-0.79941540	1.90219024	2.91283281
C	4.25629097	0.43767661	3.52345396	H	-0.67257096	1.58521434	3.96115029
C	5.53398507	0.01619822	3.12826404	H	-0.18992202	2.80217654	2.73669012
C	5.73802136	-0.51915269	1.84878430	H	-1.85697060	2.17233578	2.77543268
C	4.65183283	-0.63020430	0.96949837	N	3.45505071	-1.13533008	-1.00152963
H	4.08616058	0.85923852	4.51587057	N	3.39859111	-0.21588254	1.37273547
H	6.37362607	0.10700265	3.81925724	N	0.98104197	0.46017164	1.79592714
H	6.72875045	-0.84734782	1.52883765	Ru	1.91236066	-0.37474214	0.14654880
C	4.62281024	-1.13685707	-0.38074986	H	2.24703975	1.06445050	-0.37305335
H	5.53636184	-1.49730302	-0.86193449	C	-3.44206682	1.58186040	-0.06365739
C	1.80158618	0.68545865	2.80665455	C	-2.76234819	2.75009778	-0.71947922
H	1.45760497	1.13817233	3.74080096	C	-1.95978009	2.60876139	-1.86702716
C	3.34067039	-1.66617877	-2.38233660	C	-2.91807081	4.02410119	-0.14050639
H	2.56750408	-1.03331147	-2.84688198	C	-1.32459294	3.72466894	-2.42106939
C	2.78574231	-3.09775864	-2.31444377	H	-1.79715096	1.62295644	-2.30737879
H	1.83300675	-3.11252172	-1.76789944	C	-2.29919189	5.13826675	-0.70613537
H	2.60408446	-3.47590268	-3.33204145	H	-3.53855916	4.10901129	0.75439333
H	3.50367363	-3.76908005	-1.81553818	C	-1.49881969	4.98947663	-1.84793646
C	4.62377722	-1.58497415	-3.21469086	H	-0.68790467	3.60411506	-3.30043238
H	5.05434081	-0.57185587	-3.19834680	H	-2.43601399	6.12591445	-0.25902394
H	5.39162628	-2.30067300	-2.87837777	H	-1.00797345	5.86083089	-2.28856605
H	4.38784004	-1.83466121	-4.25989819	O	-3.86357217	1.67568302	1.08959383
C	-0.46069935	0.78931641	1.91843380	Cl	0.05100582	-0.80497966	-1.31558664
H	-0.73896512	1.12349235	0.90639046	C	-3.57808579	0.29369635	-0.84552717
C	-1.23792624	-0.50233308	2.21904440	H	-3.98820098	0.47320741	-1.85148214
H	-0.96391325	-0.89400781	3.21241837	H	-2.58550582	-0.17482975	-0.97782858
H	-2.31665061	-0.28646289	2.21049828	H	-4.22914105	-0.39251865	-0.29060954
H	-1.02472918	-1.26748463	1.45942859				

Table S3g: Optimized XYZ coordinates for complex **13**

C	1.95622672	-0.94205915	1.89701953	H	3.35294692	-3.69957484	-0.86031903
C	2.47396195	-0.86824204	3.19763961	C	-0.12622752	-3.53336193	-1.25507969
C	2.50180390	0.37149278	3.85205909	H	-0.37402936	-4.09013080	-0.33661602
C	2.03150234	1.52389656	3.20763995	H	-0.85485895	-2.71975580	-1.36761886
C	1.51758246	1.41686441	1.90705699	H	-0.21821359	-4.21863315	-2.11125284
H	2.85981212	-1.76728552	3.68144207	N	0.55546749	2.10441755	-0.14303746
H	2.90468754	0.44182490	4.86374570	N	1.46754650	0.19011590	1.29572355
H	2.07019421	2.49773227	3.69902450	N	1.35293889	-1.89397953	-0.17833944
C	0.99231843	2.45528101	1.05154475	Ru	0.78841309	0.06875453	-0.52971924
H	0.95464105	3.49071963	1.40064562	H	-2.08592295	1.02391250	0.75900182
C	1.88368584	-2.08206682	1.01079442	C	-2.32181622	0.48609508	-0.18060202
H	2.28897616	-3.05042732	1.31758756	C	-3.70176854	-0.13634937	-0.06857552
C	0.04243344	3.13396020	-1.07933059	C	-4.84515475	0.66020814	-0.24235619
H	-0.85830857	2.67425536	-1.52048514	C	-3.86133833	-1.49510015	0.23893756
C	1.06157571	3.33269048	-2.21080854	C	-6.12407892	0.11335871	-0.10101502
H	1.33796428	2.37023193	-2.66076852	H	-4.73304752	1.71961493	-0.49497378
H	0.63099513	3.98839281	-2.98320884	C	-5.14135168	-2.04480798	0.37427156
H	1.98111965	3.79754333	-1.82320886	H	-2.96976047	-2.11255761	0.36206479
C	-0.36381745	4.46318377	-0.43538752	C	-6.27626678	-1.24384342	0.20786006
H	-1.06845914	4.32084766	0.39908250	H	-7.00443122	0.74549764	-0.24180837
H	0.50663866	5.03232873	-0.07131252	H	-5.25251171	-3.10620626	0.61066530
H	-0.86125665	5.08655758	-1.19303306	H	-7.27490313	-1.67458222	0.31245331
C	1.30810129	-2.98740833	-1.17477148	O	-1.32756141	-0.50118343	-0.42373339
H	1.54329453	-2.47505035	-2.12281011	Cl	2.97010892	0.41851499	-1.45255810
C	2.33423539	-4.10341714	-0.95920758	H	0.03646008	-0.05925451	-2.16349197
H	2.10458318	-4.72080500	-0.07527786	H	-0.76201800	-0.31930038	-1.53562254
H	2.31836853	-4.77326512	-1.83182988	H	-2.33704874	1.24623870	-0.98802998

Table S3h: Optimized XYZ coordinates for complex **14**

C	2.36915624	1.13827196	-1.39986941	H	-0.58813895	4.01368579	0.44265767
C	3.20105948	1.18958093	-2.52702639	H	-1.22666265	2.53832448	1.20964288
C	3.45174866	0.01132719	-3.24461120	H	-0.86636363	3.98259042	2.20731087
C	2.89170000	-1.20450341	-2.82905406	N	0.65400454	-2.10598117	-0.01422754
C	2.06260214	-1.22332549	-1.69775261	N	1.79799006	-0.05318891	-1.03090527
H	3.65390113	2.13648344	-2.82628355	N	1.23276923	1.89049847	0.52949998
H	4.09914296	0.03829647	-4.12263942	Ru	0.68597160	-0.11274827	0.57077641
H	3.10089388	-2.13174726	-3.36548589	C	-2.22410502	-0.49077778	-0.66176838
C	1.39274395	-2.34488529	-1.08203038	C	-3.68010627	-0.15015671	-0.37090787
H	1.49457600	-3.34891754	-1.50275790	C	-4.09448144	1.18623392	-0.25116462
C	2.02855226	2.19437068	-0.47255707	C	-4.63838120	-1.16842942	-0.25223512
H	2.45526713	3.19450414	-0.59085234	C	-5.43903631	1.49478480	-0.02253107
C	-0.01919829	-3.22619673	0.68897278	H	-3.34743784	1.97930416	-0.32684958
H	-0.99367001	-2.80859215	0.99427477	C	-5.98531285	-0.86206740	-0.02823593
C	0.76249128	-3.55720118	1.96885246	H	-4.32497388	-2.21438494	-0.33212891
H	0.94042598	-2.65134524	2.56309279	C	-6.38950081	0.47243403	0.08730019
H	0.19459717	-4.28431233	2.56948191	H	-5.74754477	2.53899608	0.07331196
H	1.74217192	-3.99331444	1.71893882	H	-6.71860616	-1.66702812	0.06531575
C	-0.27568988	-4.47187174	-0.16564756	H	-7.43941617	0.71463246	0.26838433
H	-0.79062195	-4.22620897	-1.10777485	O	-1.36569845	0.42429441	0.02614577
H	0.65356725	-5.01474029	-0.40153108	Cl	2.59315378	-0.48632384	1.97424058
H	-0.91675182	-5.16453148	0.39960058	H	-0.42697651	-0.17531803	1.98796137
C	0.90013774	2.88975574	1.56887558	H	-1.07371629	0.08647125	1.23104663
H	0.92912863	2.30261601	2.50224298	H	-2.04616665	-1.52520025	-0.30845117
C	1.89107456	4.05022449	1.69528633	C	-1.92070628	-0.42673649	-2.16380284
H	1.84839872	4.73520588	0.83256199	H	-0.87005492	-0.69474316	-2.35079085
H	1.63380314	4.64061044	2.58730378	H	-2.57024587	-1.11495789	-2.72723822
H	2.92299303	3.68753228	1.81513876	H	-2.09396831	0.59450663	-2.53589875
C	-0.53807858	3.38267872	1.34504934				

Table S3i: Optimized XYZ coordinates for complex **12** and **6′**

C	-1.53290475	-0.46119051	-1.79865503	N	-1.00909012	-1.02512862	-0.65307081
C	-2.07441743	-1.28476648	-2.79487914	N	-0.84439617	1.51702228	-0.70851057
C	-2.07453937	-2.67498599	-2.61234327	Ru	-0.23797478	0.12134253	0.69943212
C	-1.53792623	-3.23573890	-1.44408202	H	-1.63989902	0.19804562	1.39969694
C	-1.00282446	-2.39225626	-0.46020069	C	-1.98321778	3.83984939	2.99101243
H	-2.49297776	-0.83717212	-3.69795376	C	-0.89284367	4.47873841	3.57918822
H	-2.49428429	-3.32353292	-3.38289958	C	-0.99897130	5.81245402	4.00152027
H	-1.53086126	-4.31674797	-1.29205389	C	-2.20386464	6.50414016	3.82972027
C	-0.40460383	-2.73641765	0.80694022	C	-3.29436117	5.86608701	3.23608820
H	-0.33818145	-3.77951193	1.12871584	C	-3.20718414	4.52349870	2.80270247
C	-1.42070579	0.97709642	-1.76852997	H	-1.87163403	2.79920519	2.67677010
H	-1.80499328	1.58453775	-2.59245472	H	0.04208323	3.92652953	3.69763850
C	0.68978293	-2.01843353	2.86051219	H	-0.14242742	6.30923353	4.46348126
H	0.41186846	-1.15203423	3.48171739	H	-2.29306818	7.54233521	4.15828363
C	2.21499711	-1.98395485	2.67446543	H	-4.23623137	6.40444897	3.09831971
H	2.52517039	-1.02569821	2.23619656	C	-4.37855609	3.91776120	2.18176913
H	2.71117000	-2.09249639	3.65084564	H	-5.27174927	4.55134122	2.10810629
H	2.54523316	-2.80856515	2.02180737	C	-4.51009844	2.66519249	1.67742396
C	0.22118743	-3.30271652	3.55096270	H	-3.67952815	1.95751063	1.71082875
H	-0.87679599	-3.35183913	3.61375829	C	-5.80534126	2.23985633	1.09377594
H	0.58794813	-4.21178909	3.04703906	C	-5.93121360	0.84938397	0.52628821
H	0.61873003	-3.32172667	4.57657657	C	-4.84752399	-0.03287498	0.35529146
C	-0.66237876	2.98834415	-0.62745483	C	-7.21686298	0.42870962	0.13316677
H	-0.77305104	3.21525785	0.44465237	C	-5.04848216	-1.30398615	-0.19406315
C	0.78431949	3.32411798	-1.02323257	H	-3.83378712	0.26038393	0.63587828
H	0.96220752	3.08435855	-2.08432609	C	-7.41813582	-0.84062096	-0.40648587
H	0.96951786	4.39843525	-0.87286461	H	-8.04113457	1.13240257	0.26659751
H	1.49323427	2.76243922	-0.39955169	C	-6.33217872	-1.71194451	-0.57201412
C	-1.68511919	3.81144811	-1.41535342	H	-4.19745344	-1.97580286	-0.32912018
H	-1.53914204	3.73762644	-2.50541320	H	-8.42232628	-1.15553224	-0.70074759
H	-2.71724230	3.51593705	-1.17226218	H	-6.48713048	-2.70721330	-0.99625579
H	-1.56946655	4.87148830	-1.14530051	O	-6.78205943	2.99774166	1.07273359
N	0.04473498	-1.74176714	1.55288680	Cl	0.99524240	1.48899648	2.23072975

Table S3j: Optimized XYZ coordinates for complex **15**

C	-2.98488522	1.15912867	-0.22230070	N	-2.36262368	0.05157314	0.27716438
C	-4.35824076	1.34995085	0.02192873	N	-0.82405009	1.57733155	-1.08828681
C	-5.05602825	0.38883936	0.75715214	Ru	-0.43890459	-0.22006333	-0.18997155
C	-4.40059208	-0.76118631	1.23018271	H	1.01926590	-0.37678054	-0.94826129
C	-3.03527191	-0.91180394	0.96130184	C	0.97565336	3.07658337	1.53880724
H	-4.86362528	2.23428906	-0.36981071	C	0.60766302	4.33456970	2.02652595
H	-6.12115236	0.52438521	0.95364691	C	-0.41303729	4.45840226	2.97602646
H	-4.94044234	-1.53012971	1.78532175	C	-1.05518247	3.30275632	3.43923526
C	-2.17365102	-2.02966936	1.30955377	C	-0.68672130	2.04833969	2.95088626
H	-2.59584474	-2.88254866	1.85048820	C	0.32955271	1.90285572	1.98053646
C	-2.07915600	1.98646302	-0.97484068	H	1.79979474	3.00875061	0.82439435
H	-2.42468499	2.91228595	-1.43951980	H	1.13683778	5.22410003	1.67422424
C	-0.02975848	-3.13680328	1.26236692	H	-0.69528479	5.44115817	3.36022412
H	0.84436409	-2.67383477	1.75159118	H	-1.84624980	3.37986427	4.18961667
C	0.45573792	-3.76698219	-0.05134638	H	-1.19468100	1.15161420	3.31727615
H	0.86311870	-3.00419811	-0.72783381	C	0.68497117	0.54233146	1.51705377
H	1.23686068	-4.51010956	0.16891122	H	0.63438728	-0.21721662	2.30432353
H	-0.37584971	-4.25920926	-0.57789141	C	1.63575563	0.26147374	0.46541366
C	-0.61127944	-4.18877578	2.21044452	H	2.05156501	1.12161447	-0.07230738
H	-0.95184594	-3.75155596	3.16259167	C	2.66259094	-0.82918773	0.66957352
H	-1.44615472	-4.74746626	1.75581985	C	3.75654092	-0.99027180	-0.34788090
H	0.17751193	-4.91793970	2.44633562	C	3.75307796	-0.34993283	-1.60197934
C	0.10638784	2.36255630	-1.93915273	C	4.83625491	-1.83121856	-0.01604800
H	1.08869983	2.25041950	-1.45254369	C	4.80637175	-0.54592503	-2.49946938
C	0.18030952	1.70892205	-3.32772199	H	2.91314889	0.28153754	-1.89862432
H	-0.76597567	1.85966843	-3.87040044	C	5.89130720	-2.01883652	-0.90810109
H	0.99462749	2.16491050	-3.91240854	H	4.81783487	-2.32483831	0.95769459
H	0.34255445	0.62496235	-3.24534161	C	5.87877808	-1.37595814	-2.15334017
C	-0.19837800	3.86255847	-2.02281313	H	4.78644819	-0.05515502	-3.47513997
H	-1.09430975	4.07404431	-2.62774798	H	6.72672194	-2.66831143	-0.63625531
H	-0.32678955	4.30494005	-1.02343577	H	6.70229099	-1.52570542	-2.85568154
H	0.64549610	4.36822067	-2.51632540	O	2.64063544	-1.54990855	1.66879424
N	-0.91755993	-1.99448304	0.94953734	Cl	-1.22684307	-1.47489627	-2.18294442

Table S3k: Optimized XYZ coordinates for complex **16**

C	2.40856329	-1.11243207	-0.92736940	N	1.58640686	-0.19459807	-1.55509142
C	3.67967968	-1.37881658	-1.45029536	N	0.51935757	-1.32280577	0.46559470
C	4.09935023	-0.72662134	-2.61829895	Ru	-0.20021418	0.07417256	-0.89455298
C	3.23903491	0.16288910	-3.27522325	H	1.20198753	3.68242730	0.50096680
C	1.96796770	0.41444088	-2.73897469	C	-1.34292863	1.47210379	2.24312659
H	4.33026571	-2.09183008	-0.94061504	C	-1.59324581	1.27358675	3.60258194
H	5.09170748	-0.92507507	-3.02641100	C	-0.52808320	1.12681137	4.49998995
H	3.54060361	0.65851650	-4.19984784	C	0.78452809	1.17820229	4.01599200
C	0.90285577	1.21039873	-3.28555463	C	1.03696759	1.37640413	2.65448742
H	1.02974313	1.73810852	-4.23591401	C	-0.02404347	1.53412296	1.73666182
C	1.76297092	-1.69727885	0.21383020	H	-2.17964826	1.56560389	1.54563883
H	2.27943761	-2.44096136	0.82632280	H	-2.62477649	1.23509668	3.96179725
C	-1.41502227	1.93434717	-3.19300445	H	-0.71929886	0.97464202	5.56508764
H	-2.09437405	2.07881166	-2.33849662	H	1.62497231	1.06468219	4.70626647
C	-2.12575087	1.01088717	-4.19346779	H	2.06384968	1.39044644	2.28954943
H	-2.39256513	0.06260430	-3.70722844	C	0.15587158	1.81427574	0.27610231
H	-3.05054663	1.48736332	-4.55369276	C	1.27321110	2.77886822	-0.14246409
H	-1.47946398	0.80415636	-5.06233488	H	1.05080150	3.13843954	-1.15999451
C	-1.07886789	3.30186083	-3.80094139	C	2.74699465	2.38972949	-0.12022868
H	-0.51874026	3.93123693	-3.09192800	C	3.71688269	3.32655464	-0.80172291
H	-0.49301795	3.21880729	-4.73025242	C	3.34816196	4.56603092	-1.35891974
H	-2.01309771	3.82614016	-4.05291718	C	5.06749812	2.93249069	-0.85860874
C	-0.23250123	-1.97574255	1.56637158	C	4.30782377	5.38815543	-1.95786833
H	-0.90397167	-1.18862279	1.94330644	H	2.31113053	4.90433475	-1.31976212
C	-1.09806270	-3.10069643	0.97553186	C	6.02304487	3.74885851	-1.46254375
H	-0.46081391	-3.90065342	0.56359700	H	5.33508101	1.97105199	-0.41565768
H	-1.73189207	-3.53458425	1.76436093	C	5.64533084	4.98071593	-2.01418338
H	-1.75020253	-2.71043524	0.18261185	H	4.01068979	6.35068840	-2.38069251
C	0.63377028	-2.47694176	2.72741976	H	7.06707838	3.42905009	-1.50281773
H	1.22545491	-3.36740506	2.45804890	H	6.39320523	5.62353579	-2.48472264
H	1.31037162	-1.68995629	3.09133140	O	3.17526280	1.38360173	0.43722035
H	-0.02409680	-2.76744336	3.56006928	Cl	-2.59090486	-0.22634010	-0.70511725
N	-0.24171095	1.22725249	-2.61719173	H	-0.77958273	2.28901206	-0.07565158

Table S3l: Optimized XYZ coordinates for complex **17**

C	2.02439667	-1.54336761	-2.29443908
C	2.82571648	-1.96012136	-3.37014304
C	2.67806221	-1.33126874	-4.61249041
C	1.71859198	-0.32160827	-4.79083941
C	0.92778053	0.05665364	-3.69697403
H	3.54730332	-2.76733510	-3.23292177
H	3.30117780	-1.64056631	-5.45338266
H	1.57200872	0.14857239	-5.76505425
C	-0.20088886	0.96601938	-3.67154568
H	-0.55783210	1.40660358	-4.60716189
C	1.97855202	-2.04453971	-0.94330105
H	2.62411141	-2.86903513	-0.62259607
C	-2.15844315	1.81463813	-2.52433114
H	-2.81856855	0.99032623	-2.19204630
C	-2.65829880	2.32286818	-3.87956391
H	-2.72735218	1.51812889	-4.62693600
H	-3.66882372	2.73730316	-3.75064898
H	-2.02094423	3.12881968	-4.28100330
C	-2.21324959	2.91416390	-1.45986587
H	-1.93459592	2.50451470	-0.47999902
H	-1.53924003	3.74986961	-1.71086372
H	-3.23658844	3.31167485	-1.38803145
C	1.06574754	-2.06356356	1.26467549
H	1.88582133	-2.80395246	1.33984424
C	1.28254409	-0.99367281	2.33514189
H	0.44908444	-0.27602424	2.34222783
H	1.32843158	-1.47471891	3.32464565
H	2.21499397	-0.44297390	2.15809655
C	-0.27262999	-2.79099365	1.43982595
H	-1.10910602	-2.08603000	1.33418375
H	-0.40505458	-3.57629831	0.68237890
H	-0.30788778	-3.24775973	2.44145315
N	-0.82923305	1.15617972	-2.53026938
N	1.12613289	-0.52596386	-2.47659081
N	1.13839565	-1.47672941	-0.09600850
Ru	-0.01818494	0.00627390	-0.93733707
H	2.76790606	3.14262229	-0.73850800
C	0.03097405	3.01832063	2.06157768
C	0.08949648	3.49610557	3.37146507
C	1.30503161	3.49346191	4.06678584
C	2.45107855	3.00555279	3.43255970
C	2.38979377	2.51785739	2.12195428
C	1.17778376	2.51833412	1.40552452
H	-0.92427686	3.03453610	1.52898089
H	-0.81633354	3.87742059	3.84930639
H	1.35640143	3.86861617	5.09147753
H	3.40689920	2.99582268	3.96261656
H	3.29224444	2.11499945	1.66403850
C	1.04421931	2.06005493	-0.02951895
C	2.30164727	2.14541170	-0.90478560
H	1.98501237	2.15040036	-1.95977608
C	3.44195605	1.14608578	-0.76586542
C	4.52369076	1.17241574	-1.81713223
C	4.50565634	2.02287196	-2.93890691
C	5.61660529	0.30071672	-1.64521082
C	5.55317055	1.99765646	-3.86503519
H	3.67570480	2.71341991	-3.09795496
C	6.65997964	0.27421720	-2.56921919
H	5.61689047	-0.34677047	-0.76590126
C	6.63066231	1.12384162	-3.68387715
H	5.52818863	2.66330336	-4.73091487
H	7.50235687	-0.40593715	-2.42212241
H	7.44833826	1.10642144	-4.40845600
O	3.53031132	0.36377658	0.17642119
Cl	-1.73913973	-1.59564619	-1.53132462
H	0.31318466	2.72637738	-0.50366737
H	0.09058800	1.03915213	0.37773310
H	-0.95002017	0.44103156	0.40647509

Table S3m: Optimized XYZ coordinates for complex **18**

C	1.34989260	-2.70211736	-1.15718317	C	-0.00275068	-1.37717341	3.08784742
C	2.45506630	-3.48151251	-1.51980689	C	-0.69395484	-0.27018217	2.55285307
C	3.56203467	-2.86745509	-2.12257034	H	-2.54691024	0.85081132	2.66341962
C	3.55228123	-1.48993309	-2.37011653	H	-3.56101110	-0.55290776	4.42672521
C	2.43152729	-0.73654045	-1.99055701	H	-2.29603694	-2.49724604	5.37188220
H	2.43727351	-4.55820895	-1.34212719	H	-0.01040486	-3.00706124	4.49945282
H	4.42538028	-3.46788370	-2.41427238	H	0.98198786	-1.62966482	2.69558752
H	4.39434083	-0.99795100	-2.86019168	C	-0.14921086	0.63756621	1.48346289
C	2.20638771	0.67777008	-2.14069305	C	1.30343140	1.12942266	1.60567050
H	2.97939220	1.31577502	-2.57862581	H	1.43147181	2.00680285	0.95007475
C	0.10587729	-3.13143363	-0.56483941	C	2.50361254	0.22442920	1.37487498
H	-0.05053922	-4.17963568	-0.29703060	C	3.86570196	0.87491222	1.35252405
C	0.78669609	2.61173612	-1.89433616	C	4.08852078	2.23289583	1.65326862
H	0.11426889	2.87132986	-1.05952499	C	4.96855586	0.06302793	1.02394959
C	0.01657917	2.81120590	-3.20906647	C	5.38187161	2.76391565	1.62010952
H	-0.81755363	2.10129708	-3.28718300	H	3.25607329	2.88295705	1.92932519
H	-0.36962200	3.84049136	-3.26917619	C	6.25729705	0.59481793	0.98454935
H	0.68420377	2.63651569	-4.06771322	H	4.77865081	-0.98916673	0.80212530
C	2.01951891	3.52271134	-1.81506644	C	6.46764754	1.94805436	1.28241140
H	2.63151014	3.31397511	-0.92346096	H	5.54293949	3.81691440	1.86229563
H	2.66236622	3.43454677	-2.70507193	H	7.10369077	-0.04550001	0.72483149
H	1.68675558	4.57047365	-1.76434369	H	7.47711958	2.36521718	1.25579345
C	-2.13543557	-2.57821608	0.20361679	O	2.41267587	-0.99010125	1.22577233
H	-2.36340288	-1.75928452	0.90537676	Cl	-0.99090415	-0.74750621	-3.20326890
C	-3.17855654	-2.53776115	-0.92407675	H	-0.71006879	1.59045452	1.61078704
H	-2.98414395	-3.33311355	-1.66072943	O	-2.11860768	0.52249773	-0.34282186
H	-4.18222173	-2.69006941	-0.49733548	C	-2.57134913	1.78414010	-0.77057047
H	-3.14823657	-1.56998072	-1.43904195	H	-1.84965341	2.59149209	-0.50557986
C	-2.16726811	-3.90355367	0.96917584	H	-2.65942531	1.79748337	-1.87616519
H	-2.05963668	-4.77461732	0.30182679	C	-3.92065138	2.14984853	-0.17046040
H	-1.39063814	-3.94271950	1.74767829	C	-4.69606266	1.20116625	0.51046831
H	-3.14333839	-3.99701408	1.46764482	C	-4.42048711	3.45508609	-0.31508459
N	1.05723353	1.16462179	-1.71360944	C	-5.94610759	1.55113460	1.03714175
N	1.37079079	-1.34660062	-1.37323012	H	-4.30201101	0.18926944	0.61917700
N	-0.81535964	-2.21567631	-0.35899858	C	-5.66890021	3.80494626	0.20666228
Ru	-0.23019494	-0.33400728	-0.97607273	H	-3.82415535	4.20567483	-0.84465471
H	1.43822905	1.52525660	2.63550406	C	-6.43755582	2.85184132	0.88754272
C	-1.98559100	0.00009565	3.06049411	H	-6.54051330	0.80051899	1.56494467
C	-2.56117801	-0.79375222	4.05641073	H	-6.04295025	4.82487283	0.08552612
C	-1.85540226	-1.88047439	4.58496601	H	-7.41297365	3.12393266	1.29796259
C	-0.57483652	-2.16227461	4.09497415	H	-1.05191609	0.56778895	0.47538348

Table S3n: Optimized XYZ coordinates for complex **12** and **6**

C	1.92878339	0.69068991	2.19800275	N	0.12025996	-0.78373277	1.83294170
C	2.72505311	1.65360183	2.83441456	Ru	1.21660066	-1.15750437	0.11474905
C	3.91004833	2.08188933	2.21821045	H	0.47044267	-0.00151862	-0.63471803
C	4.29448881	1.55161457	0.97776570	C	-3.65989345	-1.77332178	-0.75356489
C	3.48397868	0.58867810	0.36116249	C	-3.98606955	-2.85955644	0.06595251
H	2.41560586	2.05953350	3.79938889	C	-5.00641448	-2.74197945	1.01838926
H	4.53650646	2.82994442	2.70683991	C	-5.69475508	-1.52956639	1.14586951
H	5.21383197	1.87846273	0.48834976	C	-5.36377027	-0.44531949	0.32454537
C	3.67442825	-0.08983768	-0.89753172	C	-4.34417814	-0.54991856	-0.63748860
H	4.54166752	0.13113998	-1.52592980	H	-2.85398777	-1.88197903	-1.48519244
C	0.67725162	0.11591050	2.62695518	H	-3.43483633	-3.79652303	-0.04412144
H	0.21178445	0.42641685	3.56649341	H	-5.26930458	-3.59315628	1.65151346
C	2.89767982	-1.73092668	-2.52071106	H	-6.49873451	-1.42975634	1.87982067
H	1.85989777	-1.86493849	-2.86562055	H	-5.91235682	0.49673433	0.42123988
C	3.46167918	-3.12463727	-2.20191295	C	-3.97731060	0.63035992	-1.50957004
H	2.82683725	-3.63425809	-1.46444371	H	-4.81468438	1.34336054	-1.55961754
H	3.48338438	-3.73526815	-3.11731226	C	-2.72640239	1.36769070	-1.00800737
H	4.48878121	-3.04756699	-1.80926050	H	-1.84905807	0.69515943	-1.01887386
C	3.70219255	-1.01834996	-3.61164105	C	-2.41232574	2.62236976	-1.81617787
H	3.33575238	0.00566289	-3.78196531	C	-1.19507384	3.42964520	-1.45328789
H	4.77959860	-0.97562744	-3.38282633	C	-0.28154357	3.03873329	-0.45681378
H	3.59594558	-1.57564451	-4.55420753	C	-0.96989633	4.62906172	-2.15510713
C	-1.16342793	-1.42276546	2.21446016	C	0.83449858	3.83199874	-0.17024578
H	-1.70352537	-1.53712152	1.26135356	H	-0.42555786	2.10518232	0.09076907
C	-0.87000626	-2.83307499	2.74976726	C	0.13966717	5.42227901	-1.86588766
H	-0.30471850	-2.78062212	3.69479254	H	-1.68997750	4.90985086	-2.92677161
H	-1.81832294	-3.35869870	2.93792769	C	1.04497433	5.02461131	-0.87179969
H	-0.29580943	-3.41135023	2.01306595	H	1.54239180	3.51494761	0.59962653
C	-2.03421590	-0.61283934	3.17871057	H	0.30393701	6.35264163	-2.41490605
H	-1.62530168	-0.58941193	4.20241791	H	1.91643229	5.64426538	-0.64584899
H	-2.17358554	0.42222273	2.82947765	O	-3.14226263	2.97962176	-2.73602526
H	-3.02792542	-1.08124730	3.23040554	Cl	0.00711168	-2.98274559	-0.85346606
N	2.75761755	-0.97397019	-1.25204233	H	-3.79992029	0.29795931	-2.54500992
N	2.32080072	0.17437691	0.97893251	H	-2.85202606	1.66104201	0.05122805

Table S3o: Optimized XYZ coordinates for complex **20**

C	1.92790098	-1.06097714	-1.13630101	N	0.71342136	-0.05674973	0.62963330
C	2.48313857	-2.08958556	-1.90955239	Ru	1.77704085	1.63648819	-0.08521284
C	3.31820448	-1.75560407	-2.98694656	C	3.57360199	2.01402875	1.63007199
C	3.60949230	-0.41446656	-3.26753453	C	4.58349127	2.98265700	1.08453138
C	3.04631907	0.59086221	-2.46424141	C	4.83630054	4.23114740	1.68566344
H	2.26750491	-3.13189683	-1.66762071	C	5.41341817	2.56463729	0.02569120
H	3.75034866	-2.54553903	-3.60373556	C	5.87604877	5.04505428	1.22875073
H	4.26098222	-0.14428685	-4.10085572	H	4.20582303	4.58671551	2.50249340
C	3.16187704	2.02026949	-2.58102169	C	6.44860791	3.38020643	-0.43268874
H	3.60575433	2.46721011	-3.47323832	H	5.23680510	1.58053451	-0.41139995
C	1.02034344	-1.15993514	-0.01793899	C	6.68496762	4.62513394	0.16611109
H	0.55351899	-2.12066767	0.22782626	H	6.05321666	6.01335739	1.70273019
C	2.31599266	4.19341577	-1.91565032	H	7.08588102	3.03797663	-1.25197490
H	1.21341749	4.18203104	-2.01936447	H	7.50064900	5.26019389	-0.18750236
C	2.92845914	4.74478232	-3.20652742	Cl	-0.32498750	2.68922724	-0.59027484
H	2.57690478	4.21748236	-4.10650813	C	3.33623592	2.09904730	3.13880885
H	2.63037915	5.79837682	-3.31018239	H	4.32691090	1.91531508	3.59900402
H	4.03069424	4.71423008	-3.18157907	H	3.05828367	3.12223950	3.43084787
C	2.64250789	5.08724302	-0.72113304	C	2.32025746	1.09451596	3.68495067
H	2.21649417	4.66057151	0.19708844	H	2.60062828	0.09076504	3.33046552
H	3.72819958	5.20788821	-0.59607879	H	1.33912957	1.32755059	3.24308964
H	2.19771085	6.08148077	-0.87996162	C	2.23595555	1.12375537	5.19393660
C	-0.42790379	-0.10696228	1.58723999	C	3.06675485	0.30577211	5.97926469
H	-0.42578435	0.87944384	2.07255601	C	1.34506246	1.99161953	5.84919281
C	-1.75223477	-0.25485879	0.82166057	C	3.01247607	0.35414675	7.37625164
H	-1.81516020	-1.24114258	0.33314260	H	3.76039774	-0.38200423	5.48578267
H	-2.59637359	-0.16638183	1.52329156	C	1.28699982	2.04350851	7.24599547
H	-1.84137022	0.53083967	0.05970895	H	0.68462191	2.62925263	5.25346762
C	-0.26856831	-1.19911650	2.65475798	C	2.12210286	1.22490300	8.01474964
H	-0.36916292	-2.20869915	2.22510807	H	3.66372346	-0.29374675	7.96834017
H	0.70122534	-1.13378544	3.16607048	H	0.58359461	2.72162866	7.73565003
H	-1.06145659	-1.08680056	3.40972613	H	2.07563842	1.26156447	9.10564896
N	2.60671049	2.76077862	-1.63139352	O	3.42833266	0.87185219	1.04631047
N	2.20414605	0.24831249	-1.43563573	H	1.80306538	2.66177724	1.28089628

Table S3p: Optimized XYZ coordinates for complex **21**

C	2.67038975	-0.30389774	-1.86420292	N	1.20938339	-0.42723856	-0.02663666
C	3.54998024	-0.73019976	-2.86371303	Ru	1.19207585	1.62316228	-0.40377039
C	4.03742997	0.19110879	-3.80286670	C	3.29220668	1.45237363	1.79546523
C	3.64078109	1.53180412	-3.74187451	C	4.54916171	1.05858186	1.02681093
C	2.76694767	1.95848442	-2.73320842	C	5.11779900	1.92680835	0.08253552
H	3.84276543	-1.78079473	-2.90138196	C	5.18110575	-0.16872434	1.28240837
H	4.72429339	-0.13907542	-4.58317065	C	6.29287221	1.57510529	-0.58990956
H	4.00453345	2.25920083	-4.47010576	H	4.61704955	2.87518364	-0.12493512
C	2.21582817	3.25971799	-2.49732919	C	6.35866144	-0.52208180	0.61428422
H	2.40475796	4.08623543	-3.18708211	H	4.74286523	-0.85582185	2.01378490
C	1.99203946	-1.08078772	-0.86502452	C	6.91837169	0.35050976	-0.32618075
H	2.07703508	-2.17009828	-0.85866851	H	6.72349100	2.26018449	-1.32490044
C	0.75328439	4.65679720	-1.12089275	H	6.83798444	-1.48176038	0.82472721
H	-0.24410973	4.34046656	-0.76849053	H	7.83582307	0.07628892	-0.85259180
C	0.56273534	5.60760816	-2.30595714	O	2.41835420	2.25285559	1.02353335
H	0.06332276	5.10641516	-3.14868946	Cl	-1.07514166	1.42570490	-1.16392226
H	-0.06971672	6.45062062	-1.99007709	C	3.67162840	2.26126720	3.05707251
H	1.51696942	6.03347228	-2.65680111	H	4.42561465	1.69380750	3.62948898
C	1.49822155	5.32524518	0.04692609	H	4.15779188	3.19617415	2.72955062
H	1.69587886	4.59830165	0.84732816	C	2.46316145	2.58626220	3.95523685
H	2.46680200	5.72347793	-0.29681752	H	2.00358735	1.64299275	4.29953010
H	0.90218294	6.15951227	0.44718989	H	1.70698818	3.10788012	3.34752909
C	0.24641722	-1.14672618	0.83901405	C	2.84101083	3.43180738	5.14993513
H	-0.72939576	-0.86514290	0.39826167	C	2.86047092	4.83467157	5.05992482
C	0.36840001	-2.67198488	0.83268217	C	3.21900557	2.83999998	6.36737057
H	1.34814548	-3.00502211	1.21389517	C	3.24575856	5.62175307	6.14993845
H	-0.40419825	-3.09406950	1.49189869	H	2.56324155	5.31280133	4.12146672
H	0.21365794	-3.10093102	-0.16888785	C	3.60474205	3.62234994	7.46112188
C	0.28396447	-0.58244247	2.26304883	H	3.20402505	1.74944610	6.45855886
H	1.19970034	-0.89275173	2.79105374	C	3.62017973	5.01762251	7.35571335
H	0.24246277	0.51680044	2.25155610	H	3.24878338	6.71101533	6.05981006
H	-0.58175486	-0.95128016	2.83286122	H	3.88978934	3.14124654	8.40022331
N	1.42921634	3.38468966	-1.44270181	H	3.91794360	5.63085733	8.20948615
N	2.30807965	1.03372394	-1.80260372	H	2.79393856	0.51727162	2.12361067

Table S3q: Optimized XYZ coordinates for complex **22**

C	1.81302555	-0.31344215	-2.51536784	Ru	1.57272975	1.68441316	-0.45977564
C	2.13577796	-0.80915297	-3.78584267	C	4.21715751	0.55367695	0.92480277
C	2.55937202	0.08414790	-4.77978060	C	4.79976875	-0.16926486	-0.27862777
C	2.65243474	1.45575917	-4.50712871	C	5.28138765	0.55108829	-1.38290951
C	2.33248196	1.91999987	-3.22339291	C	4.90966059	-1.56882578	-0.28414288
H	2.04642989	-1.87714689	-3.99122390	C	5.86058468	-0.11500701	-2.46787317
H	2.81027184	-0.28971936	-5.77379511	H	5.18214616	1.63884999	-1.38404156
H	2.96386048	2.16224531	-5.27874596	C	5.49209705	-2.23764862	-1.36651203
C	2.32566148	3.27404909	-2.71866927	H	4.53405262	-2.14096341	0.57037897
H	2.53404291	4.11856084	-3.38183158	C	5.96956463	-1.51088842	-2.46327600
C	1.26241584	-1.01749794	-1.37995733	H	6.22801214	0.45811061	-3.32291372
H	0.96778332	-2.06558042	-1.47669707	H	5.57020571	-3.32786349	-1.35532635
C	1.92587451	4.79706829	-0.85972138	H	6.42288279	-2.03015931	-3.31110464
H	1.08894547	4.70396870	-0.14790379	O	3.53820507	1.74915772	0.52914591
C	1.59548287	5.91284984	-1.85520171	Cl	-0.75528453	2.12798412	-0.81692738
H	0.70142873	5.66817603	-2.44788191	C	5.33222008	0.93640280	1.92045776
H	1.39012033	6.83862727	-1.29716703	H	5.92383915	0.03403064	2.15266678
H	2.43239597	6.12857999	-2.53943125	H	6.01651407	1.64167927	1.41838556
C	3.21272915	5.08775073	-0.07108680	C	4.79930412	1.55979076	3.22459120
H	3.46852612	4.24479614	0.58483113	H	4.12006518	0.84244456	3.71852369
H	4.05599018	5.24952095	-0.76236596	H	4.19920234	2.44987149	2.97516310
H	3.08424086	5.99536055	0.53792887	C	5.90905871	1.94426288	4.17686643
C	0.21905626	-0.90238186	0.81257042	C	6.37885511	1.03980660	5.14439505
H	-0.59672583	-0.15945498	0.89384444	C	6.52473518	3.20504486	4.09120978
C	-0.39959299	-2.27175745	0.51948551	C	7.43114223	1.38187875	6.00039247
H	0.36323953	-3.06397084	0.43622428	H	5.90699499	0.05609641	5.23057320
H	-1.06456492	-2.54510592	1.35184164	C	7.57745664	3.55197409	4.94414725
H	-1.00522726	-2.26234728	-0.39921330	H	6.16734039	3.92419215	3.34782944
C	0.98402061	-0.90935506	2.14067939	C	8.03516887	2.64030648	5.90240790
H	1.81771666	-1.63005103	2.11260414	H	7.77730285	0.66540714	6.74961923
H	1.37890544	0.09010079	2.36660555	H	8.03879329	4.53953503	4.86424319
H	0.30640263	-1.20353163	2.95622441	H	8.85482787	2.91088147	6.57212322
N	2.02303833	3.44299288	-1.44846383	H	3.51450569	-0.13350423	1.43265547
N	1.94204913	1.02735011	-2.25668485	H	2.48559644	2.03692692	1.16252135
N	1.05086181	-0.33094781	-0.27460027	H	1.46984077	2.25967263	1.24852018

Table S3r: Optimized XYZ coordinates for complex **23**

C	1.87496404	-0.60190163	-2.84045499	C	6.34166503	-1.33049086	-1.43474906
C	2.37679350	-1.20188641	-4.00285212	H	4.94781345	-1.72698848	0.17115372
C	2.94830593	-0.39611070	-4.99674691	C	6.88080236	-0.36487562	-2.29219412
C	3.00806001	0.99346169	-4.82834700	H	6.85842743	1.72026808	-2.86985716
C	2.50273432	1.56796178	-3.65443611	H	6.67187632	-2.37004357	-1.50337096
H	2.30989884	-2.28437499	-4.12529188	H	7.63536005	-0.64593091	-3.03071520
H	3.34219865	-0.85125609	-5.90675350	O	3.07756409	1.79654881	0.17337395
H	3.44113067	1.63416646	-5.59866233	Cl	-0.95072810	1.79567848	-1.84292724
C	2.48112038	2.95696954	-3.26458246	C	4.62736547	1.24251298	1.95543488
H	2.90209472	3.72736468	-3.91634480	H	5.43970796	0.53541400	2.19354446
C	1.17999484	-1.21435374	-1.73465228	H	5.10748565	2.21123449	1.73533296
H	0.91531435	-2.27508869	-1.77235282	C	3.68515879	1.37595246	3.16755765
C	1.92397409	4.62322887	-1.56829127	H	3.24865024	0.38357754	3.38652469
H	2.20349482	4.50791700	-0.50641838	H	2.84389062	2.04372060	2.92132598
C	0.47546359	5.13201508	-1.61007842	C	4.37383091	1.90594483	4.40761124
H	-0.19601987	4.41541530	-1.12082581	C	4.04838412	3.17135837	4.92320481
H	0.41038282	6.10205940	-1.09331159	C	5.35663117	1.14724898	5.06857788
H	0.14065013	5.26369611	-2.65109232	C	4.69111721	3.66796964	6.06324021
C	2.89732512	5.59413170	-2.24180227	H	3.27190569	3.76667806	4.43362133
H	3.92982065	5.21092744	-2.23882147	C	6.00107256	1.64073298	6.20680516
H	2.60697067	5.82180332	-3.28052511	H	5.61572011	0.15332810	4.69042482
H	2.89037335	6.54560662	-1.68957635	C	5.67136952	2.90621017	6.70748977
C	-0.06773484	-0.97963676	0.32681616	H	4.41863717	4.65280276	6.45095892
H	-0.73321673	-0.13167820	0.55758147	H	6.76011687	1.03447834	6.70775743
C	-0.94638289	-2.15980770	-0.10258323	H	6.17273014	3.29243438	7.59818296
H	-0.37068939	-3.08921456	-0.24313474	H	3.31817075	-0.14120237	0.91994018
H	-1.68782974	-2.35691209	0.68620670	O	1.02461174	2.69962248	0.78987314
H	-1.49030104	-1.92978279	-1.03047203	C	0.05425078	2.45257181	1.78218869
C	0.75674417	-1.31629773	1.57675910	H	-0.95062301	2.56851572	1.32770910
H	1.44770529	-2.15049034	1.37247624	H	0.10167753	1.41347049	2.17353001
H	1.34429062	-0.45092814	1.91326884	C	0.18423154	3.40686425	2.95921730
H	0.08962988	-1.61704572	2.39893851	C	-0.24405991	3.02355661	4.24060627
N	1.96410550	3.24135518	-2.08691183	C	0.71882576	4.69327551	2.78564853
N	1.96490804	0.75962165	-2.67766231	C	-0.15139290	3.90567144	5.32222069
N	0.81649017	-0.43794366	-0.73513815	H	-0.64935267	2.01813790	4.39365326
Ru	1.29873957	1.58317389	-1.06836876	C	0.81589114	5.57725928	3.86634692
C	3.92284947	0.75345017	0.67276971	H	1.06306373	4.98422762	1.79112691
C	4.93248672	0.36141243	-0.39147954	C	0.37996151	5.18775140	5.13865057
C	5.47639765	1.32312896	-1.25720475	H	-0.48406698	3.58774300	6.31349316
C	5.37241168	-0.96754180	-0.49323079	H	1.23323065	6.57636610	3.71463541
C	6.44325061	0.96190368	-2.20099320	H	0.45769417	5.87674108	5.98314786
H	5.11964705	2.35283625	-1.18861855	H	2.26357816	2.22505350	0.83891733

Table S3s: Optimized XYZ coordinates for complex **16′**

C	-1.10029000	-0.61966000	-2.00259000	N	1.15241000	0.06604000	-2.15129000
C	-2.43098000	-0.81751000	-2.39607000	Ru	1.19067000	-0.83397000	-0.27336000
C	-3.29507000	-1.53564000	-1.56171000	H	-0.51327000	1.94614000	2.30627000
C	-2.82264000	-2.07214000	-0.35723000	C	2.75814000	2.59149000	0.99944000
C	-1.48457000	-1.86274000	0.00603000	C	3.45014000	3.73150000	0.57963000
H	-2.77532000	-0.40884000	-3.34717000	C	2.91679000	4.54389000	-0.42732000
H	-4.33473000	-1.68910000	-1.85522000	C	1.68672000	4.19570000	-0.99889000
H	-3.47398000	-2.65600000	0.29502000	C	0.99908000	3.05136000	-0.58167000
C	-0.76848000	-2.40374000	1.13251000	C	1.52036000	2.21518000	0.43023000
H	-1.24853000	-3.12516000	1.79842000	H	3.18607000	1.96930000	1.79286000
C	-0.04025000	0.03051000	-2.71545000	H	4.40534000	3.98851000	1.04528000
H	-0.20213000	0.43646000	-3.71997000	H	3.45015000	5.43805000	-0.75864000
C	1.35571000	-2.75758000	2.25640000	H	1.25408000	4.82426000	-1.78239000
H	2.21471000	-3.08721000	1.64431000	H	0.04654000	2.78705000	-1.04068000
C	0.73418000	-3.99619000	2.90724000	C	0.84523000	0.96976000	0.93702000
H	0.38957000	-4.72081000	2.15466000	C	-0.56471000	1.15234000	1.52947000
H	1.50016000	-4.49240000	3.52112000	H	-0.82503000	0.23849000	2.09404000
H	-0.10559000	-3.74427000	3.57616000	C	-1.78558000	1.49941000	0.69261000
C	1.85258000	-1.76487000	3.31561000	C	-3.11371000	1.58229000	1.41242000
H	2.36391000	-0.90781000	2.85615000	C	-3.26713000	1.38300000	2.79788000
H	1.01447000	-1.38524000	3.92216000	C	-4.25346000	1.87938000	0.64133000
H	2.56509000	-2.26473000	3.98861000	C	-4.52900000	1.47710000	3.39317000
C	2.25159000	0.54231000	-3.04801000	H	-2.40105000	1.15874000	3.42307000
H	1.85639000	1.43358000	-3.57092000	C	-5.51236000	1.97156000	1.23423000
C	3.50854000	0.95133000	-2.28863000	H	-4.11413000	2.03502000	-0.43039000
H	4.00514000	0.06766000	-1.85786000	C	-5.65382000	1.77004000	2.61382000
H	4.21489000	1.41571000	-2.99414000	H	-4.63442000	1.32387000	4.46979000
H	3.29335000	1.67868000	-1.49572000	H	-6.38794000	2.20362000	0.62308000
C	2.56909000	-0.55701000	-4.07692000	H	-6.63875000	1.84400000	3.08116000
H	2.85644000	-1.48206000	-3.55469000	O	-1.74935000	1.72147000	-0.51499000
H	1.70068000	-0.77919000	-4.71500000	Cl	2.20040000	-2.92214000	-1.23983000
H	3.39920000	-0.23138000	-4.72278000	H	1.43159000	0.66318000	1.81955000
N	0.49811000	-2.06522000	1.26271000	H	2.88498000	-0.30676000	-0.14569000
N	-0.66021000	-1.11651000	-0.80059000	H	2.77480000	-0.79227000	0.54239000

Table S3t: Optimized XYZ coordinates for complex **12′**

C	-1.99173000	-2.09421000	-1.20158000	N	0.06547000	-2.59009000	-0.11472000
C	-3.11810000	-2.34007000	-1.99456000	Ru	-0.21460000	-0.59221000	0.60326000
C	-4.15103000	-1.38429000	-2.00904000	C	0.94812000	0.99092000	-0.70063000
C	-4.05934000	-0.22953000	-1.22408000	C	-0.02664000	1.95371000	-1.31203000
C	-2.90247000	-0.02606000	-0.45128000	C	-0.08765000	3.31012000	-0.93252000
H	-3.19818000	-3.26065000	-2.57617000	C	-0.84742000	1.52308000	-2.37267000
H	-5.04009000	-1.55771000	-2.61794000	C	-0.95852000	4.19649000	-1.57203000
H	-4.87276000	0.49843000	-1.20091000	H	0.55571000	3.68159000	-0.13296000
C	-2.64500000	0.99692000	0.53726000	C	-1.71282000	2.41047000	-3.01638000
H	-3.42485000	1.72131000	0.78383000	H	-0.77175000	0.48204000	-2.69163000
C	-0.86812000	-2.98453000	-0.93510000	C	-1.77806000	3.75090000	-2.61645000
H	-0.86108000	-3.99118000	-1.36913000	H	-0.98961000	5.24354000	-1.26023000
C	-1.40663000	1.68420000	2.50443000	H	-2.33306000	2.05573000	-3.84361000
H	-1.47493000	0.85946000	3.24017000	H	-2.45194000	4.44619000	-3.12264000
C	-2.52904000	2.68867000	2.78267000	Cl	-0.93080000	-1.68369000	2.61836000
H	-3.52029000	2.21460000	2.84460000	C	2.23989000	1.59637000	-0.14560000
H	-2.33773000	3.16662000	3.75444000	H	2.56541000	2.36759000	-0.87011000
H	-2.56122000	3.48511000	2.02059000	H	2.04179000	2.14095000	0.78985000
C	-0.02720000	2.31971000	2.67214000	C	3.38675000	0.59706000	0.06393000
H	0.74909000	1.57110000	2.46149000	H	3.61263000	0.10271000	-0.89434000
H	0.10003000	3.18425000	2.00270000	H	3.04284000	-0.18397000	0.76054000
H	0.09181000	2.66972000	3.70848000	C	4.62644000	1.27272000	0.60507000
C	1.16084000	-3.49346000	0.29954000	C	5.60965000	1.78602000	-0.25816000
H	1.34330000	-3.20184000	1.34626000	C	4.80955000	1.43169000	1.99022000
C	0.80852000	-4.98366000	0.26062000	C	6.74022000	2.43991000	0.24379000
H	0.71028000	-5.36888000	-0.76766000	H	5.48799000	1.66363000	-1.33894000
H	1.62011000	-5.55173000	0.73921000	C	5.93793000	2.08475000	2.49703000
H	-0.12100000	-5.18969000	0.81241000	H	4.05868000	1.02851000	2.67658000
C	2.41423000	-3.17276000	-0.52827000	C	6.90771000	2.59259000	1.62467000
H	2.27747000	-3.49567000	-1.57320000	H	7.49528000	2.82691000	-0.44530000
H	2.61075000	-2.09402000	-0.52512000	H	6.06392000	2.19191000	3.57745000
H	3.28302000	-3.70298000	-0.10977000	H	7.79162000	3.09944000	2.01912000
N	-1.51451000	0.94588000	1.21616000	O	0.94939000	-0.22936000	-1.14584000
N	-1.89431000	-0.93905000	-0.49164000	H	1.13273000	-0.37874000	1.49620000

7. References

1. (a) W. L. F. Armarego, C. Chai, Chapter 4 - Purification of Organic Chemicals. In *Purification of Laboratory Chemicals (Seventh Edition)*, W. L. F. Armarego, C. Chai, Butterworth-Heinemann: Boston, **2013**; pp 103-554; (b) W. L. F. Armarego, C. Chai, Chapter 5 - Purification of Inorganic and Metal-Organic Chemicals. In *Purification of Laboratory Chemicals (Seventh Edition)*, W. L. F. Armarego, C. Chai, Eds. Butterworth-Heinemann: Boston, **2013**; pp 555-661.
2. G. M. Sheldrick, *Acta Cryst.* 2015, **71**, 3-8.
3. J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Letters* 1996, **77,** 3865-3868.
4. R. C. Gaussian 16, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision C.01; Gaussian, Inc., Wallingford CT, **2016**.
5. P. J. Hay, W. R. Wadt, *J. Chem. Phys*. 1985, **82,** 270-283.
6. W. R. Wadt, P. J. Hay, *J. Chem. Phys*. 1985, **82,** 284-298.
7. P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82,** 299-310.