

Supporting Information

Reforming of Ethanol to Hydrogen and Acetic Acid Catalyzed by Pincer–Ruthenium Complexes

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1. General Methods

All the experiments were performed either under air or an argon atmosphere. The amount of gas evolved was collected and measured by a manual gas burette (50 mL and 100 mL). The composition of the gas was analyzed by GC analysis and typically, only hydrogen was observed, though trace amounts of carbon dioxide was occasionally detected. For all the experiments, blank experiments were performed under same reaction conditions in the absence of catalyst and the gas volumes were corrected by blank values. The mmols of hydrogen gas liberated was obtained using the ideal gas equation and percent yield was calculated w.r.t limiting reagent i.e water (each mol of water gives 2 mols of hydrogen and one mole of acetic acid).

2. Optimization Tables

Table S1: The **4b catalyzed aqueous-phase reforming of ethanol using various bases.^a**

Entry	Base (X equivalents)	Volume of gas evolved (mL)	Volume of gas evolved in absence of catalyst (mL)	mmols of gas	Yield of H ₂ ^b (%)	Yield of (%)	of 3 ^c
1	KO ^t Bu (0.5)	37.4	13.2	0.99	21	19	
2	NaO ^t Bu (0.5)	25.4	12.2	0.54	12	11	
3	NaOH (0.5)	15.6	15.2	0.02	Trace	Trace	
4	KOH (0.5)	29.4	13.7	0.64	14	14	
5	NaOEt (0.5)	29.6	22.1	0.30	6.58	6.59	
6	Na ₂ CO ₃ (0.5)	20.8	20.7	0.01	Trace	Trace	
7	K ₂ CO ₃ (0.5)	23.7	20.5	0.13	1.12	2.7	
8	Cs ₂ CO ₃ (0.5)	16.5	16.2	0.01	Trace	Trace	
9	NaHCO ₃ (0.5)	16.6	15.6	0.04	1	1	
10	Na (0.5)	31.3	14	0.71	15.	15	
11	KO ^t Bu (1.0)	56	13.8	1.72	37	35	
12	KO ^t Bu (1.5)	93.5	14.2	3.24	70	73	
13	KOH (1.0)	33.9	14.4	1.72	17	17.4	
14	KOH (1.5)	44.5	15.3	3.24	25.7	25	

^aReaction conditions: Ethanol (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), base (0.5 equivalents), and **4b** (0.2 mol %) at 120 °C. Gas evolution was determined by burette measurements after deducting the blank contribution. ^bYield was calculated as moles of H₂ (as observed from GC and the amount of gas evolved)/moles of H₂O. ^cYield of acetic acid was calculated by ¹H NMR spectroscopy using DMSO as an internal standard.

Table S2: Aqueous-phase reforming of ethanol using various ruthenium catalysts.^a

Entry	Ru Catalysts (0.2 mol%)	Volume of gas evolved (mL)	Volume of gas evolved in absence of catalyst (mL)	mmols of gas in gas of	Yield of H ₂ ^b (%)	Yield of 3 ^c (%)
1	4a	81.9	14.2	2.77	60	59
2	4b	93.5	14.2	3.24	70	73
3	4c	79.6	14.2	2.67	58	58
4	4d	67.4	14.2	2.17	47	49
5	4e	68.1	14.2	2.20	48	47
6	4f	84.5	14.2	2.88	62	61
7	5a	33.7	14.2	0.80	17	18
8	5b	55.2	14.2	1.67	36	35
9	5c	63.1	14.2	2.00	43	43
10	5d	47.7	14.2	1.37	30	28
11	5e	92.9	14.2	3.22	69	70
12	5f	46.3	14.2	1.31	28	25
13	6a	39.0	14.2	1.01	22	23
14	6b	21.9	14.2	0.32	7	9
15	6c	48.4	14.2	1.40	30	32
16	RuCl ₂ (PPh ₃) ₃	25.4	14.2	0.46	10	10
17	RuCl ₃ ·3H ₂ O	71.8	14.2	2.35	51	46
18	[Ru(<i>p</i> -cymene)Cl ₂] ₂	55.2	14.2	1.68	36	48
19	[Ru(benzene)Cl ₂] ₂	37.3	14.2	0.94	21	14
20	5b ^d	90.4	14.2	3.11	67	66
21	6b ^d	96.4	14.2	3.35	72	71
22	5e ^e	60.3	14.2	1.88	41	44

^aReaction conditions: Ethanol (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), KO^tBu (0.5 equivalents), and **4b** (0.2 mol %) at 120 °C. Gas evolution was determined by burette measurements after deducting the blank contribution. ^bYield was calculated as moles of H₂ (as observed from GC and the amount of gas evolved)/moles of H₂O. ^cYield of acetic acid was calculated by ¹H NMR spectroscopy using DMSO as an internal standard. ^d1 equivalent of PPh₃ w.r.t **5b/6b** was added. ^e2 equivalent of PPh₃ w.r.t **5e** was added.

Table S3: The **4b catalyzed aqueous-phase reforming of ethanol under various conditions.^a**

Entry	4b (X mol%)	Volume of gas evolved (mL)	Volume of gas evolved in absence of catalyst (mL)	mmols of gas	Yield of H ₂ ^b (%)	Yield of 3 ^c (%)
1	0.2	93.5	14.2	3.24	70	73
2 ^d	0.2	91.1	14.2	3.14	68	73
3 ^{d,e}	0.2	28.5	10.6	0.73	16	16
4 ^{d,f}	0.2	100.1	16.4	3.42	74	77
5 ^{d,g}	0.2	90.7	16.2	3.04	66	61
6 ^{d,h}	0.2	98.1	18.9	3.24	70	69
7	0.1	81.9	14.2	2.77	60	59
8	0.4	90.3	14.2	3.11	67	71
9	0.6	93.1	14.2	3.22	70	66
10	0.8	90.1	14.2	3.10	67	67
11 ^{d,i}	Only EtOH	40.2	14.0	1.07	23	26
12 ^{d,j}	Only water	10.1	10.1	-	-	-

^aReaction conditions: Ethanol (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), KO^tBu (0.5 equivalents), and **4b** (Y mol %) at 120 °C. Gas evolution was determined by burette measurements after deducting the blank contribution. ^bYield was calculated as moles of H₂ (as observed from GC and the amount of gas evolved)/moles of H₂O. ^cYield of acetic acid was calculated by ¹H NMR spectroscopy using DMSO as an internal standard. ^dReaction was performed in air. ^eReaction was set up at 100 °C. ^fReaction was set up at 140 °C. ^g6.95 mmol of ethanol, 2.32 mmol of water, 3.48 mmol of KO^tBu and 0.005 mmol of **4b** were used. ^h9.27 mmol of ethanol, 2.32 mmol of water, 3.48 mmol of KO^tBu and 0.005 mmol of **4b** were used. ⁱ4.64 mmol of ethanol, 3.48 mmol of KO^tBu and 0.005 mmol of **4b** were used. ^j2.32 mmol of water, 3.48 mmol of KO^tBu and 0.005 mmol of **4b** were used.

3. Representative NMR spectra

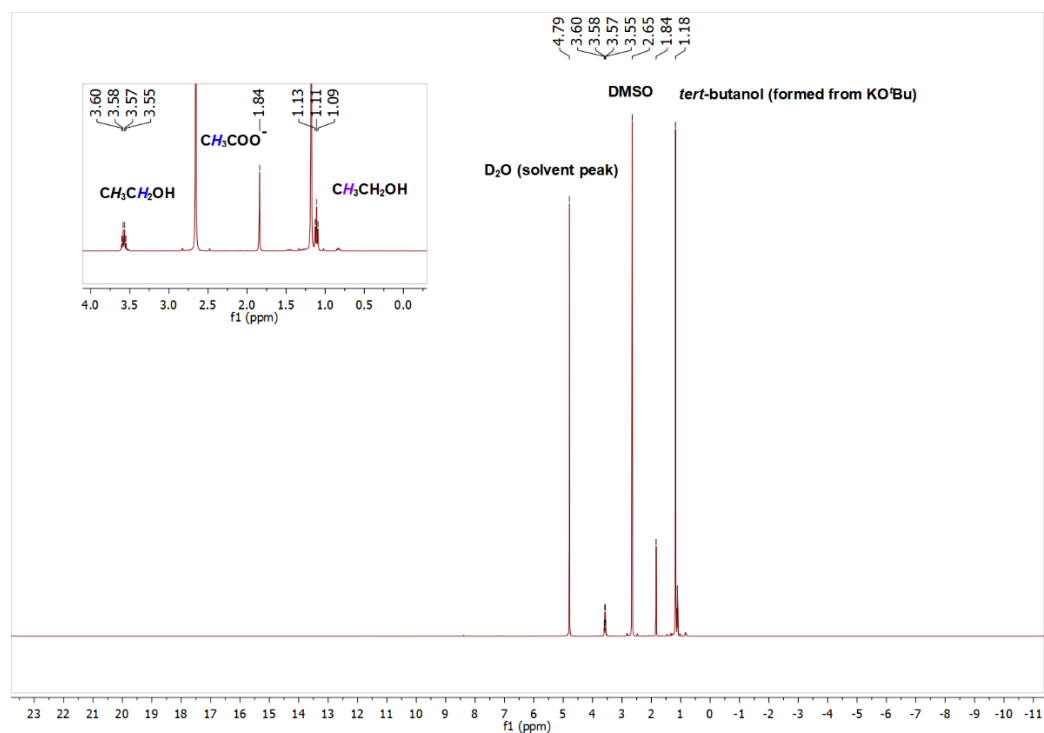


Figure S1. ^1H NMR of reaction mixture (in D_2O) obtained after the reaction. The yield of acetic acid is calculated using dimethyl sulfoxide (dms) as standard. Reaction condition: Ethanol (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Entry 1, Table 3).

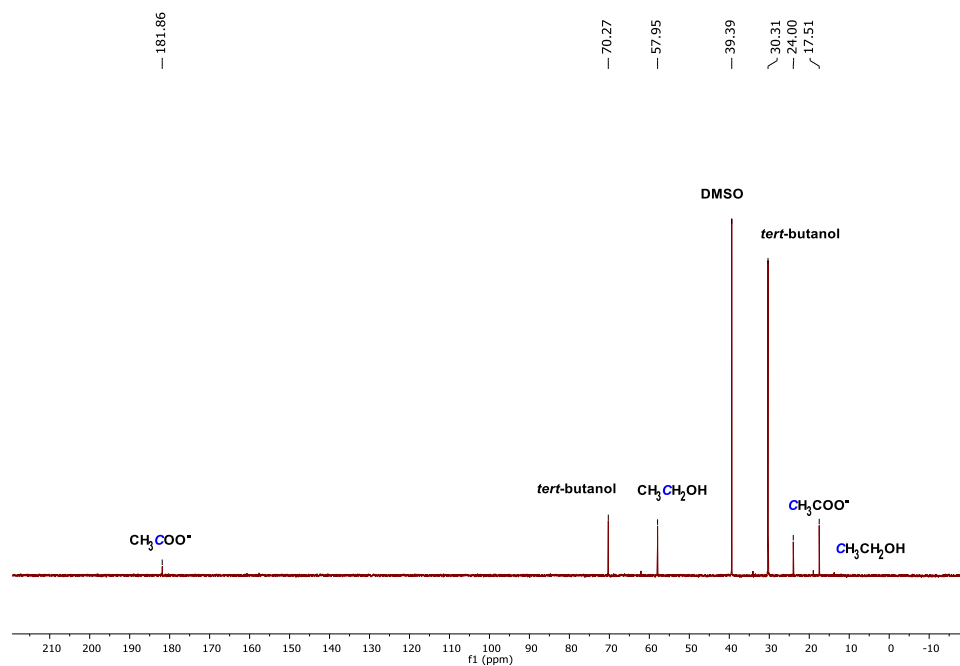


Figure S2. ^{13}C NMR of reaction mixture (in D_2O) obtained after the reaction. The yield of acetic acid is calculated using dimethyl sulfoxide (dms) as standard. Reaction condition: Ethanol (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Entry 1, Table 3).

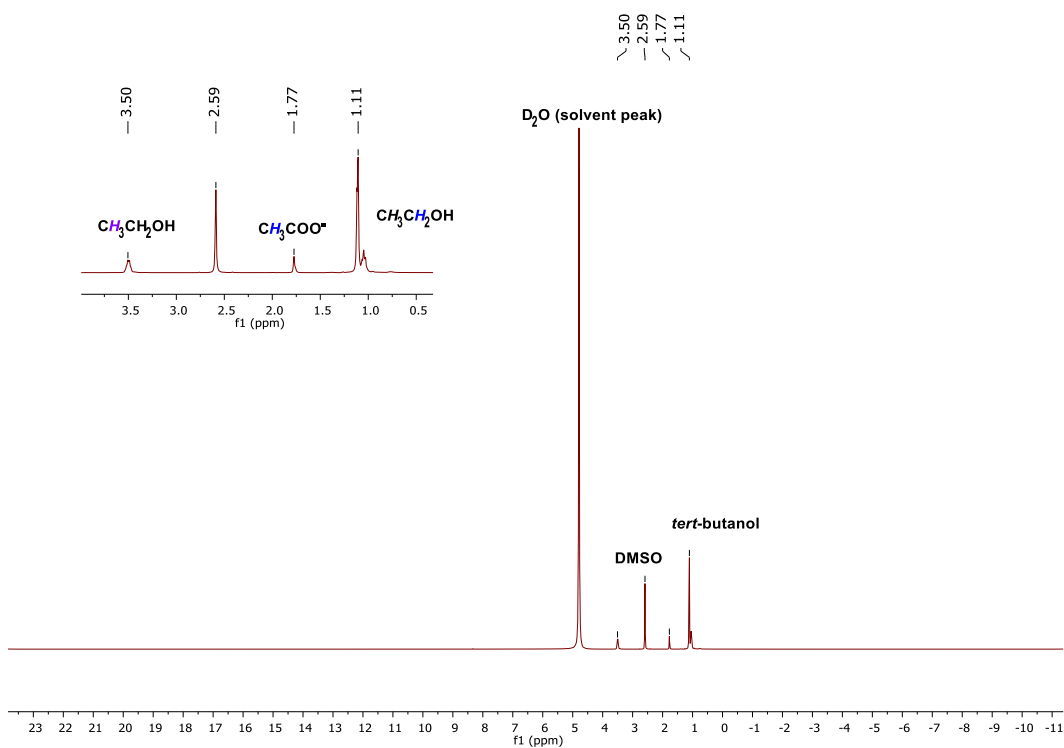


Figure S3. ^1H NMR of reaction mixture (in D_2O) obtained after the reaction. The yield of acetic acid is calculated using dimethyl sulfoxide (dmsO) as standard. Reaction condition: Ethanol (0.271 mL, 4.64 mmol), D_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 2, Scheme 1).

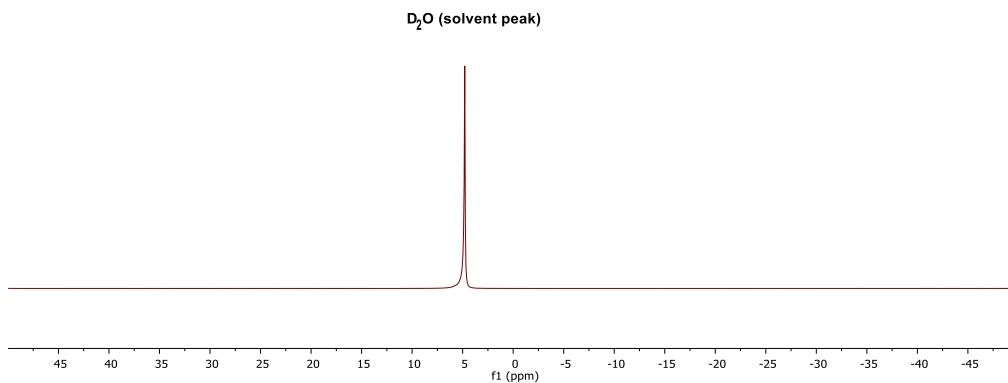


Figure S4. ^2H NMR of reaction mixture (in H_2O) obtained after the reaction. Reaction condition: Ethanol (0.271 mL, 4.64 mmol), D_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 2, Scheme 1). It shows no incorporation of deuterium.

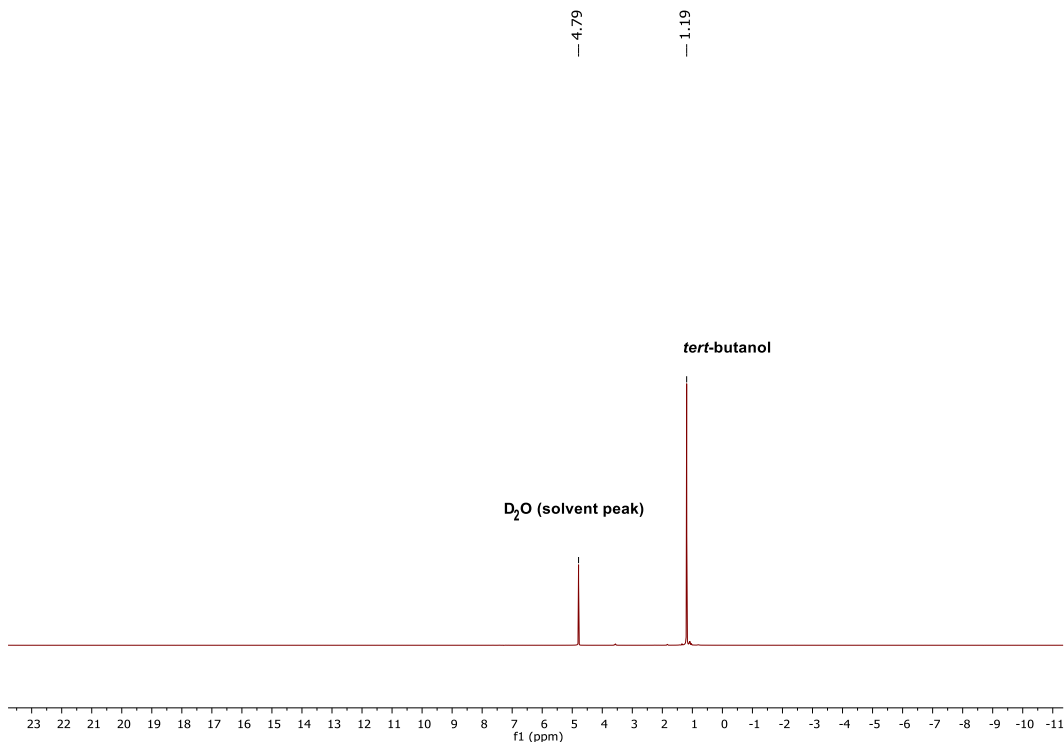


Figure S5. ^1H NMR of reaction mixture (in D_2O) obtained after the reaction. It implies that no deuterium loss has occurred during the reaction. Reaction condition: Ethanol- d_6 (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120°C (Equation 3, Scheme 1).

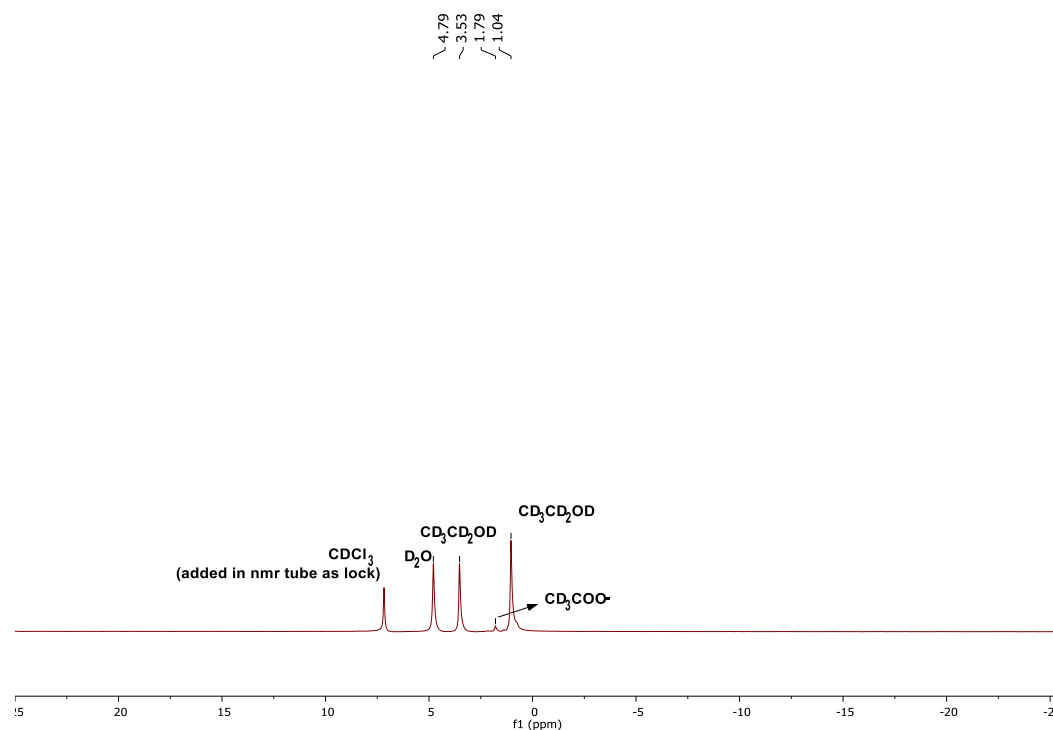


Figure S6. ^2H NMR of reaction mixture (in H_2O) obtained after the reaction. The yield of **3a** was calculated using CDCl_3 which was added as lock in nmr tube. Reaction condition: Ethanol- d_6 (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120°C (Equation 3, Scheme 1).

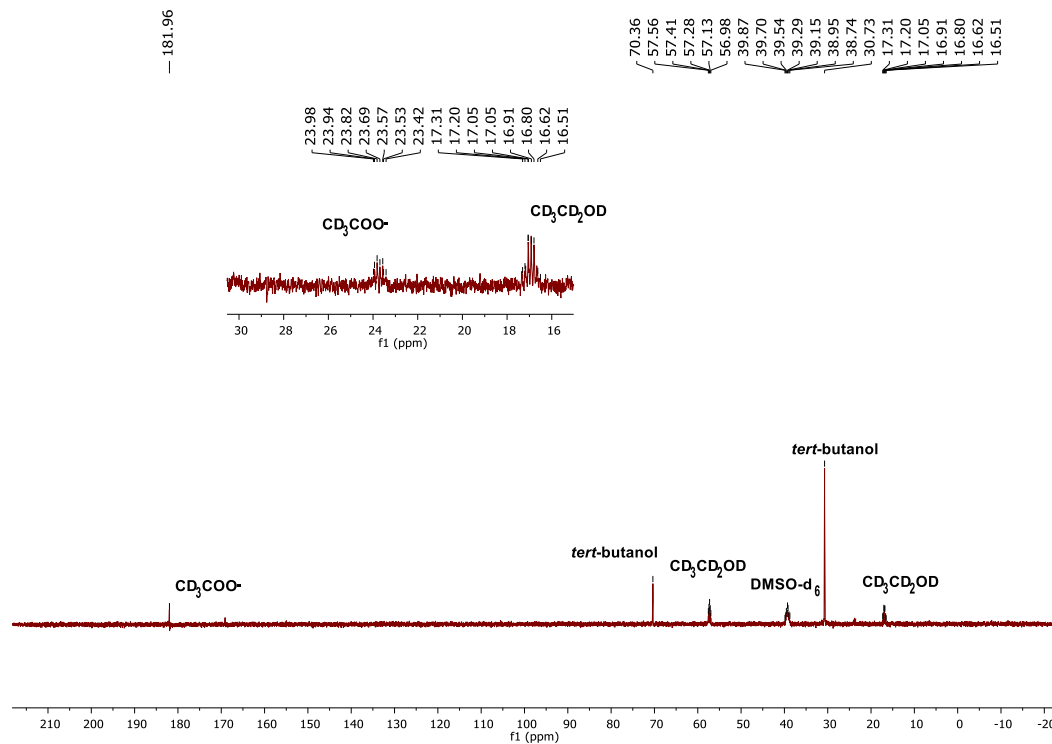


Figure S7. ¹³C NMR of reaction mixture (in D₂O) obtained after the reaction. Reaction condition: Ethanol-d₆ (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 3, Scheme 1).

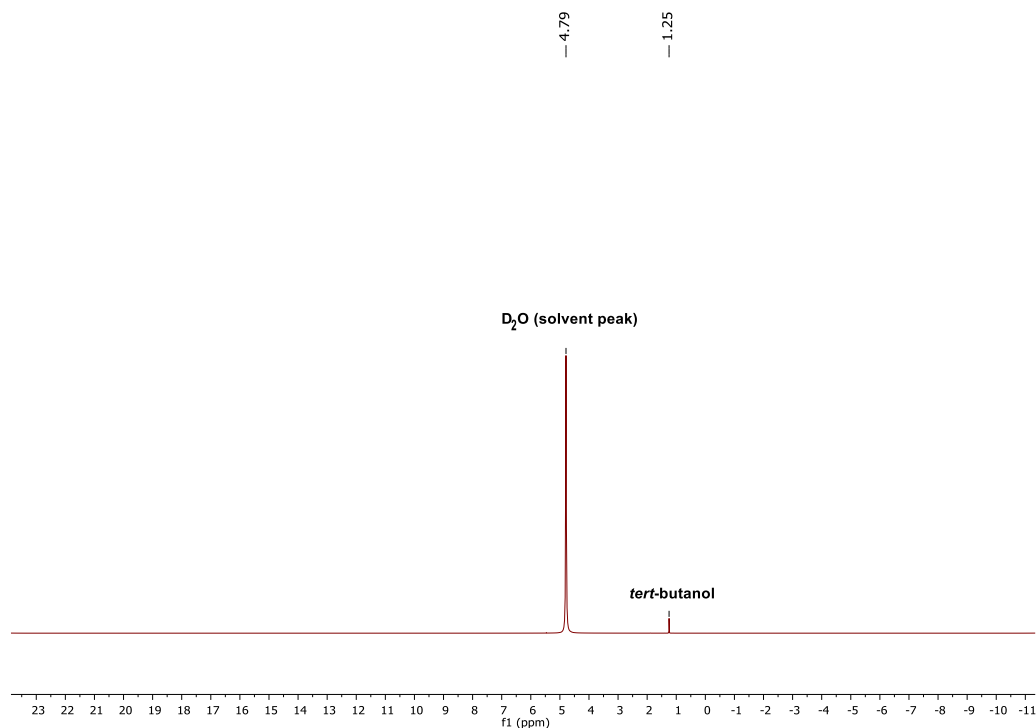


Figure S8. ¹H NMR of reaction mixture (in D₂O) obtained after the reaction. It implies that no deuterium loss has occurred during the reaction. Reaction condition: Ethanol-d₆ (0.271 mL, 4.64 mmol), D₂O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 4, Scheme 1).

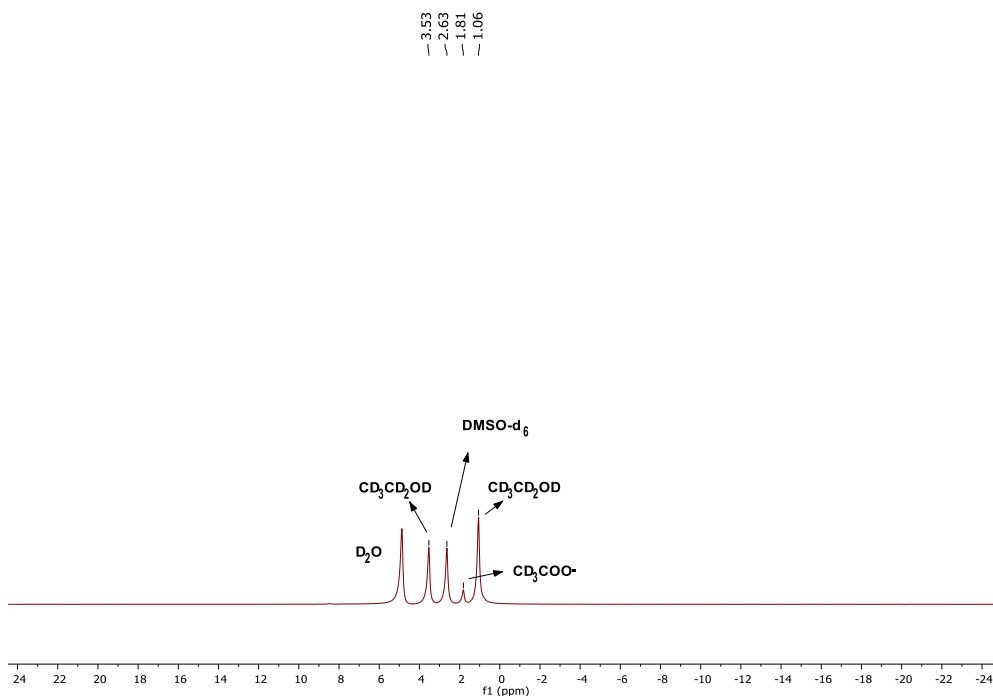


Figure S9. ²H NMR of reaction mixture (in H₂O) obtained after the reaction. The yield of **3b** was calculated using DMSO-d₆ as an internal standard. Reaction condition: Ethanol-d₆ (0.271 mL, 4.64 mmol), D₂O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 4, Scheme 1).

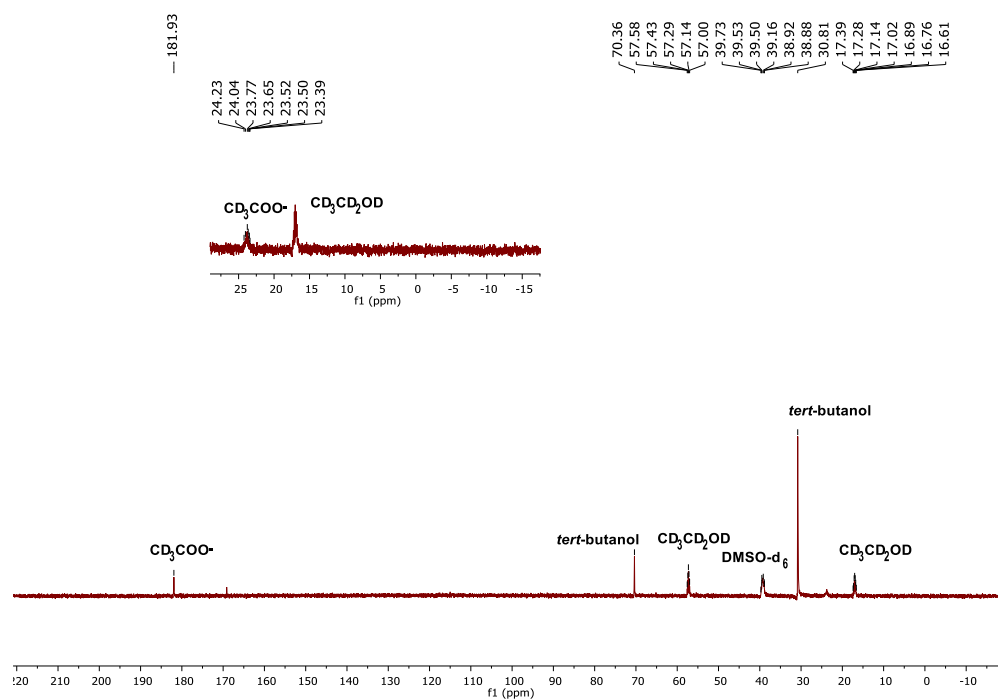
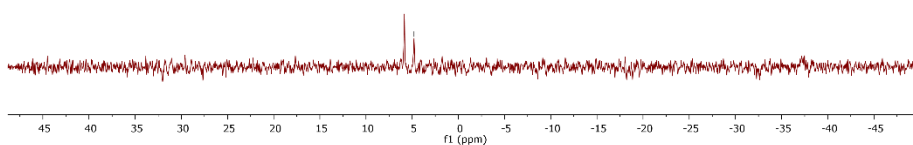


Figure S10. ¹³C NMR of reaction mixture (in D₂O) obtained after the reaction. Reaction condition: Ethanol-d₆ (0.271 mL, 4.64 mmol), D₂O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Equation 4, Scheme 1).

**^2H NMR of C_6H_6
purged with D_2
evolved from the
reaction (equation 4,
Scheme 1)**



**^2H NMR of
pure C_6H_6**

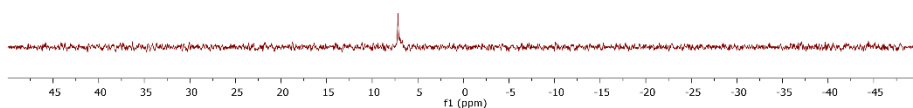


Figure S11. ^2H NMR of the gas collected from the reaction. Reaction conditions: **4b** (0.2 mol%), Ethanol- d_6 (4.64 mmol) with D_2O (2.32 mmol) in the presence of KO^tBu (3.48 mmol) at $120\text{ }^\circ\text{C}$ after 36 h (equation 4, Scheme 1). The NMR was recorded in C_6H_6 .

4. HRMS analysis of reaction mixture: Comparison of simulated and observed peaks

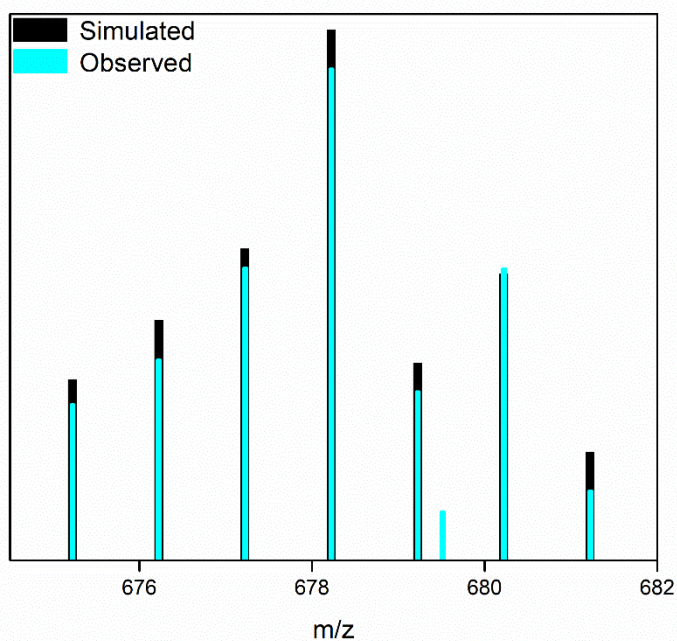


Figure S12. Simulated and observed HRMS(ESI) spectra of $[17b'-Cl]^+$ at m/z 678.2225 .

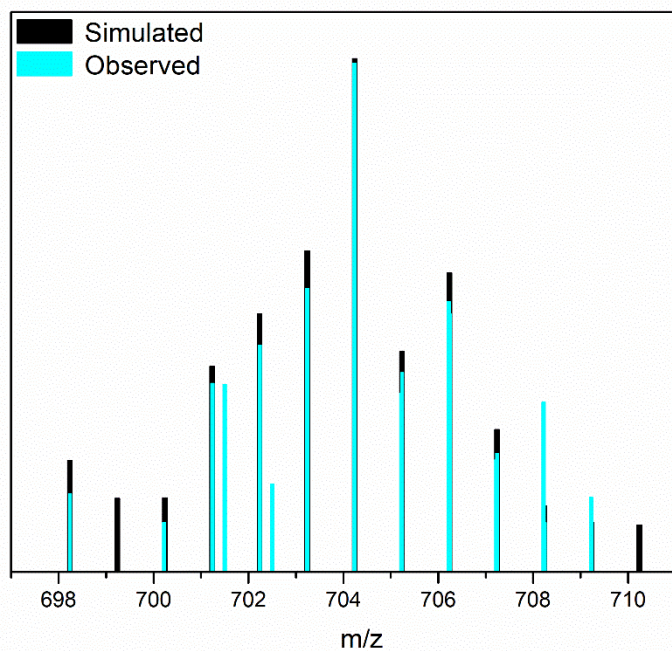


Figure S13. Simulated and observed HRMS(ESI) spectra of $[18b + H_2O + Na]^+$ at m/z 704.2373.

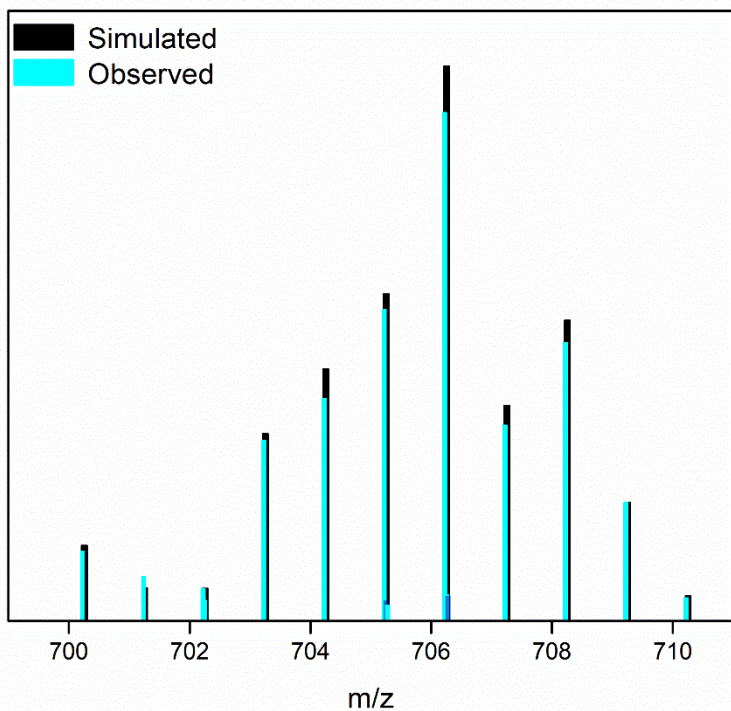


Figure S14. Simulated and observed HRMS(ESI) spectra of $[\mathbf{8b}' - \text{Cl}]^+$ at m/z 706.2208.

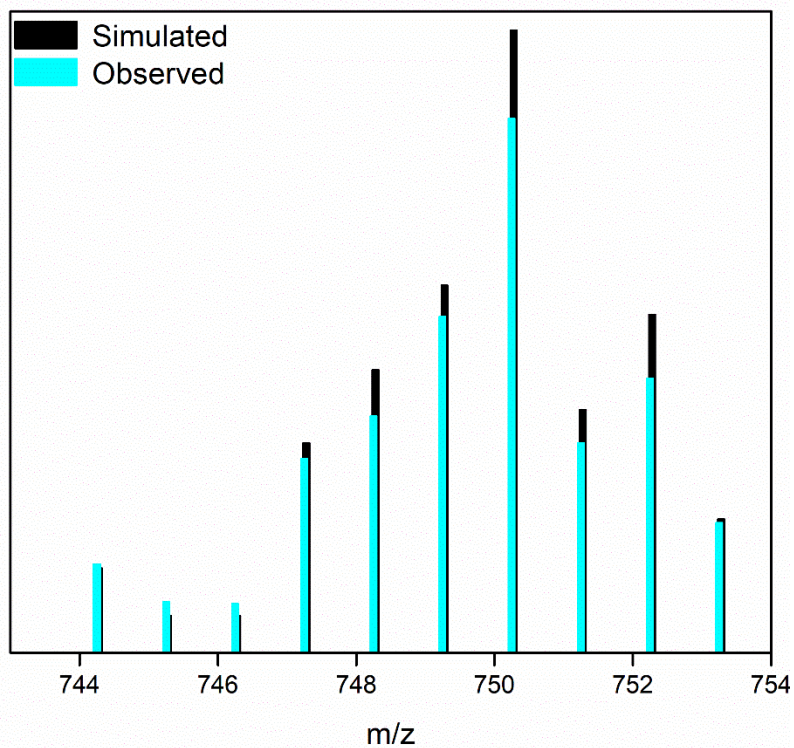


Figure S15. Simulated and observed HRMS(ESI) spectra of $[\mathbf{18b} + \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} + \text{Na}^+]$ at m/z 750.2649.

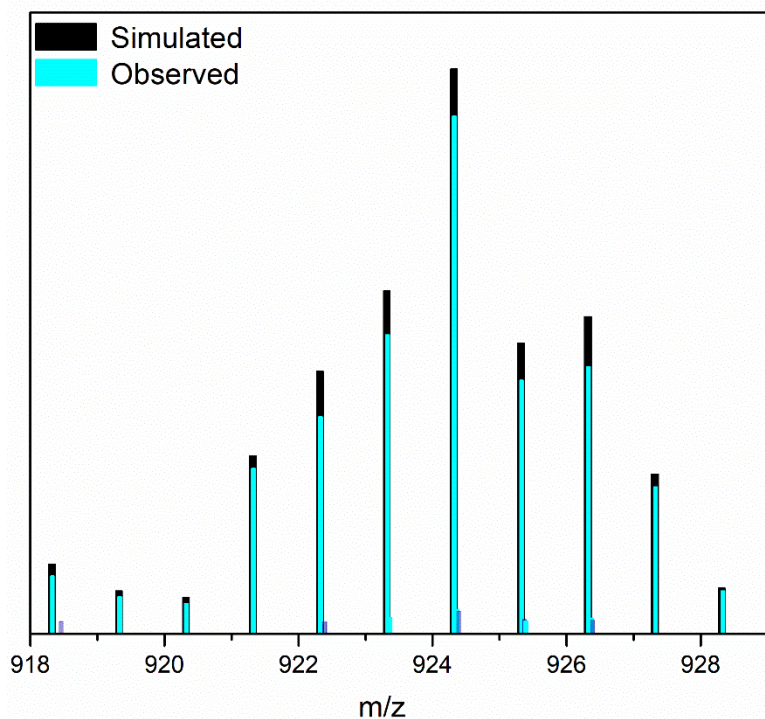


Figure S16. Simulated and observed HRMS(ESI) spectra of $[19b- Cl]^+$ at m/z 924.3252.

5. Representative GC spectra

GC analysis (TCD detection) was performed on a Agilent 7820-GC instrument fitted with Agilent Front SS7 inlet N2 HP-PLOT Q column (30 m length x 530 μ m x 40 μ m ID) using the following method:

Agilent 7820-GC Detector

TCD starting temperature 40 °C

Oven temperature 70 °C

Time at starting temp: 0 min

Hold time = 5 min

Ramp : 40 °C/min up to 250 °C

Flow rate (carrier): 25 mL/min (N₂)

Split ratio: 195

Inlet temperature: 40 °C

Detector temperature: TCD: 250

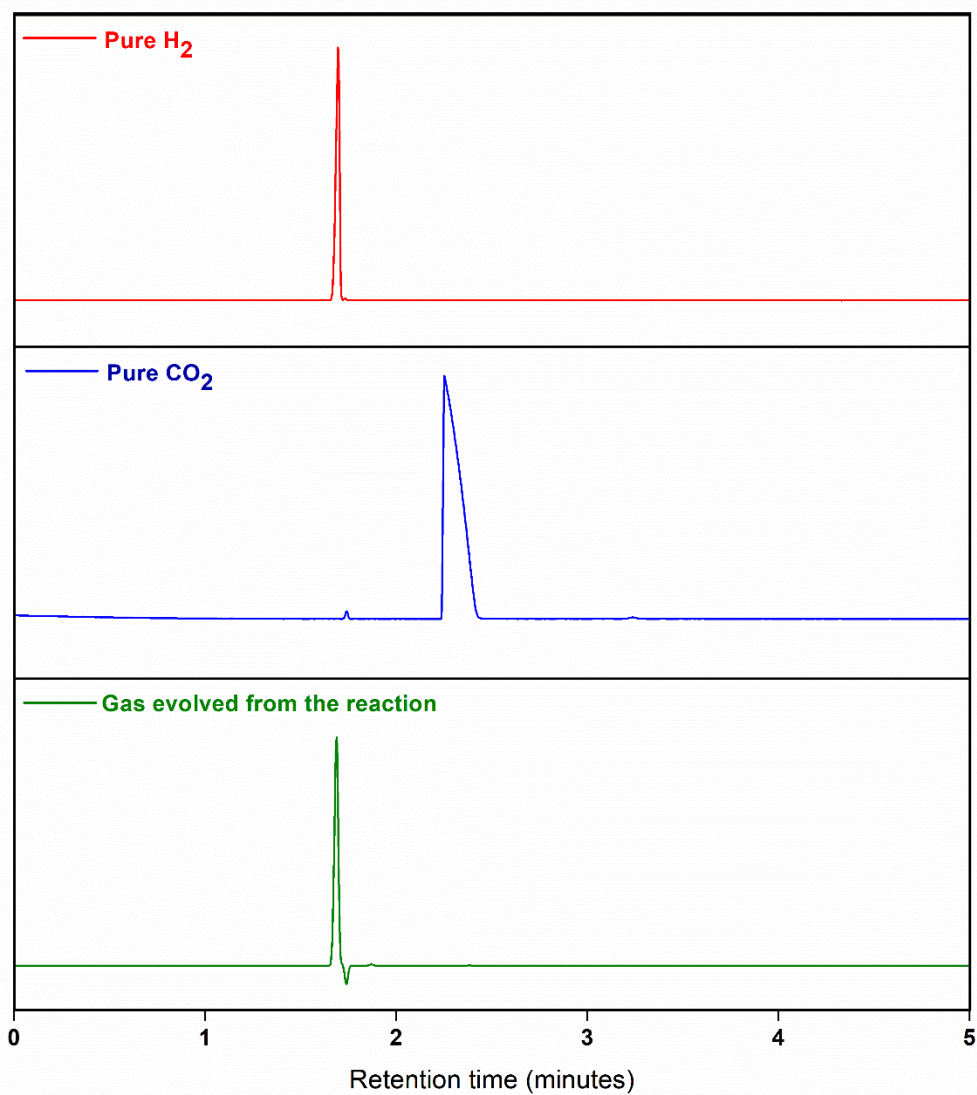


Figure S17. GC-TCD analysis of gas evolved from the ethanol reforming reaction along with H₂ and CO₂ gas (as reference sample). Reaction condition: Ethanol (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and **4b** (0.2 mol %) at 120 °C (Entry 1, Table 3).

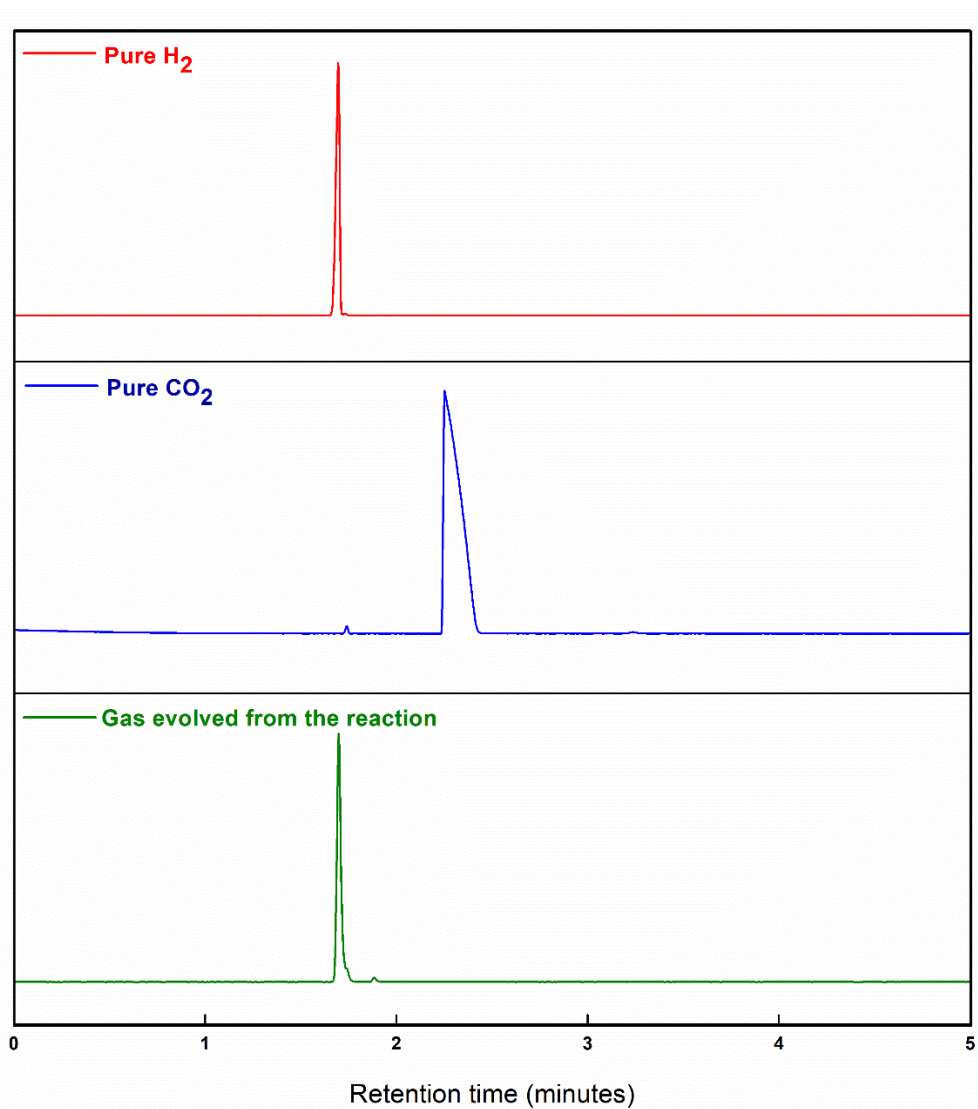


Figure S18. GC-TCD analysis of gas evolved from the ethanol reforming reaction along with H₂ and CO₂ gas (as reference sample). Reaction condition: Ethanol (0.271 mL, 4.64 mmol), H₂O (0.042 mL, 2.32 mmol), KO^tBu (1.0 equivalents), and **4b** (0.2 mol %) at 120 °C (Entry 11, Table 1).

6. Kinetic Studies: Reaction Profile diagram

The kinetic studies carried out at various catalyst and ethanol concentration for obtaining the rate order dependence are shown below. The reaction was done in a screw cap NMR tube. The concentration of acetic acid formed was analysed with time and plotted as a function of time.

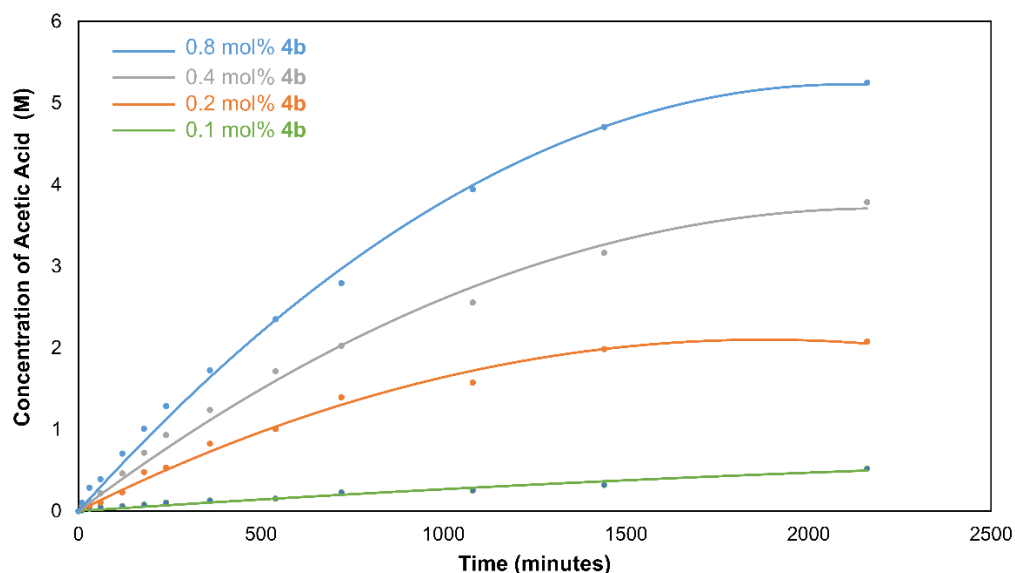


Figure S19. Reaction profile of acetic acid formation in the **4b** (0.8 mol%, 0.4 mol%, 0.2 mol% and 0.1 mol%) catalysed reaction of EtOH (7.14 mmol) with D₂O (3.57 mmol) in the presence of KO^tBu (1.78 mmol) at 120 °C. The reactions were performed using 0.5 equiv. of KO^tBu rather than 1.5 equiv. for the sake of ease of operation in NMR tube.

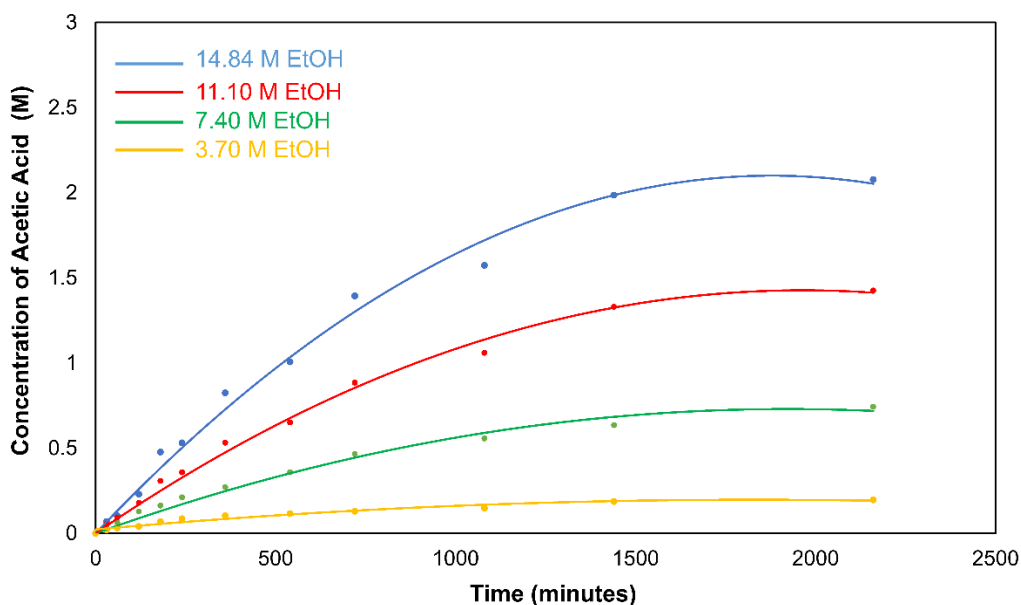


Figure S20. Reaction profile of acetic acid formation in the **4b** (0.2 mol%) catalysed reaction of EtOH (1.78 mmol, 3.56 mmol, 5.34 mmol, 7.14 mmol) with D₂O (3.57 mmol) in the presence of KO^tBu (1.78 mmol) at 120 °C. Dioxane was added as a make-up solvent. The reactions were performed using 0.5 equiv. of KO^tBu rather than 1.5 equiv. for the sake of ease of operation in NMR tube.

7. Kinetic Isotope Studies

The kinetic isotope effect experiment for the hydrogen production evolved in the two parallel reactions from $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ and $\text{CH}_3\text{CH}_2\text{OH}/\text{D}_2\text{O}$ (equations 1 and 2, Scheme 1).

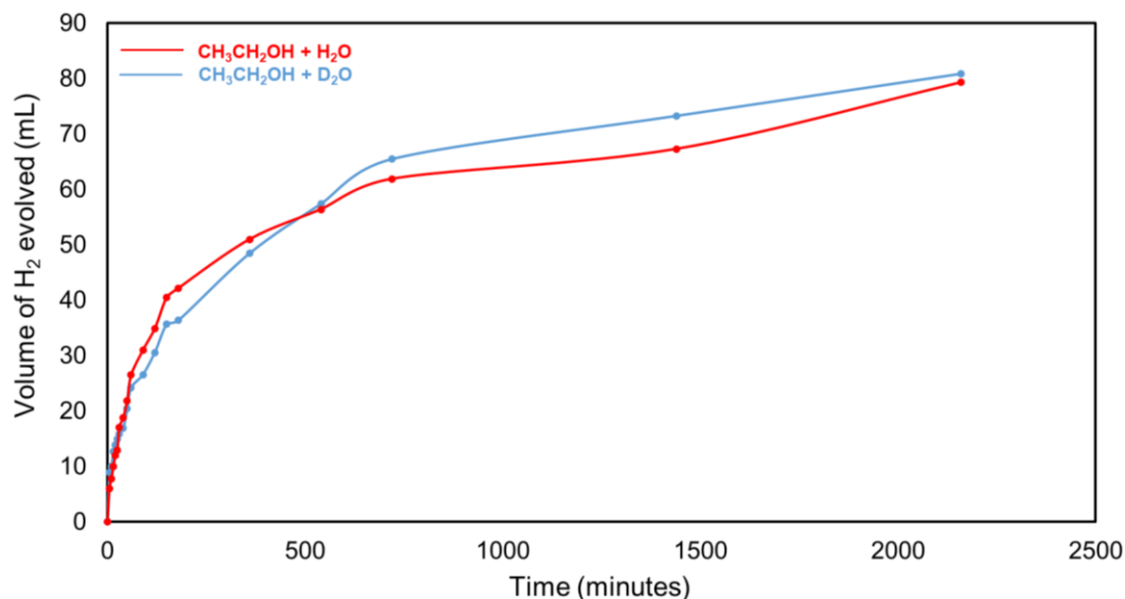


Figure S21. Reaction profile of gas evolution from the two parallel reactions in the **4b** (0.2 mol%) catalysed reaction of ethanol (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and ethanol (0.271 mL, 4.64 mmol), D_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents).

The kinetic isotope effect experiment for the hydrogen production evolved in the two parallel reactions from $\text{CH}_3\text{CH}_2\text{OH}/\text{H}_2\text{O}$ and $\text{CD}_3\text{CD}_2\text{OD}/\text{D}_2\text{O}$ (equations 1 and 4, Scheme 1).

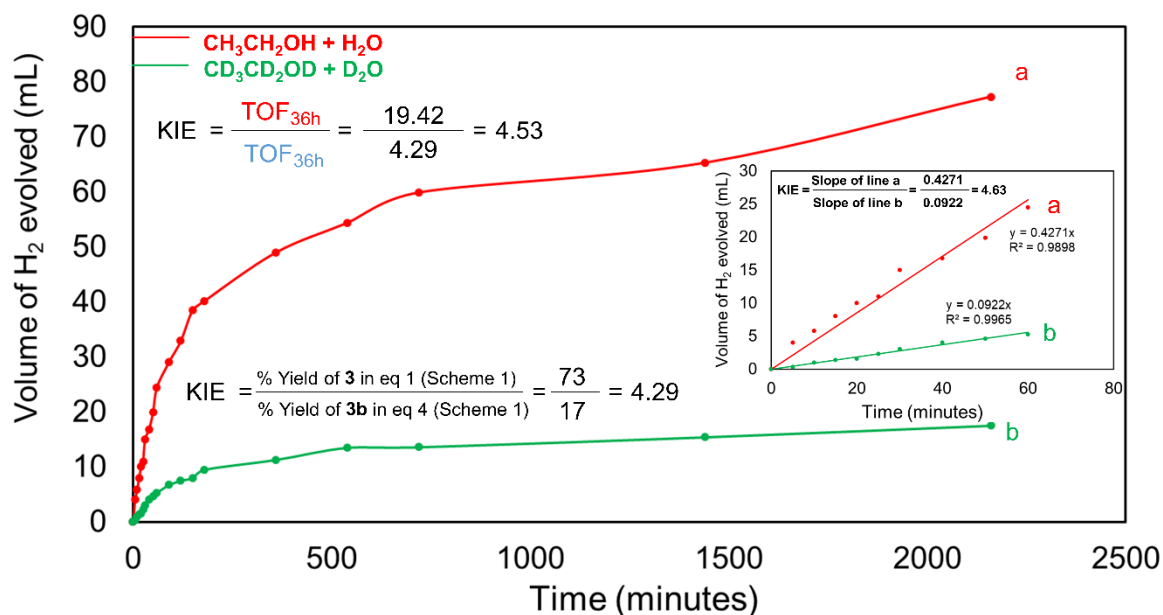


Figure S22. Reaction profile of gas evolution from the two parallel reactions in the **4b** (0.2 mol%) catalysed reaction of ethanol (0.271 mL, 4.64 mmol), H_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents), and ethanol- d_6 (0.271 mL, 4.64 mmol), D_2O (0.042 mL, 2.32 mmol), KO^tBu (1.5 equivalents).

8. ^{31}P NMR studies

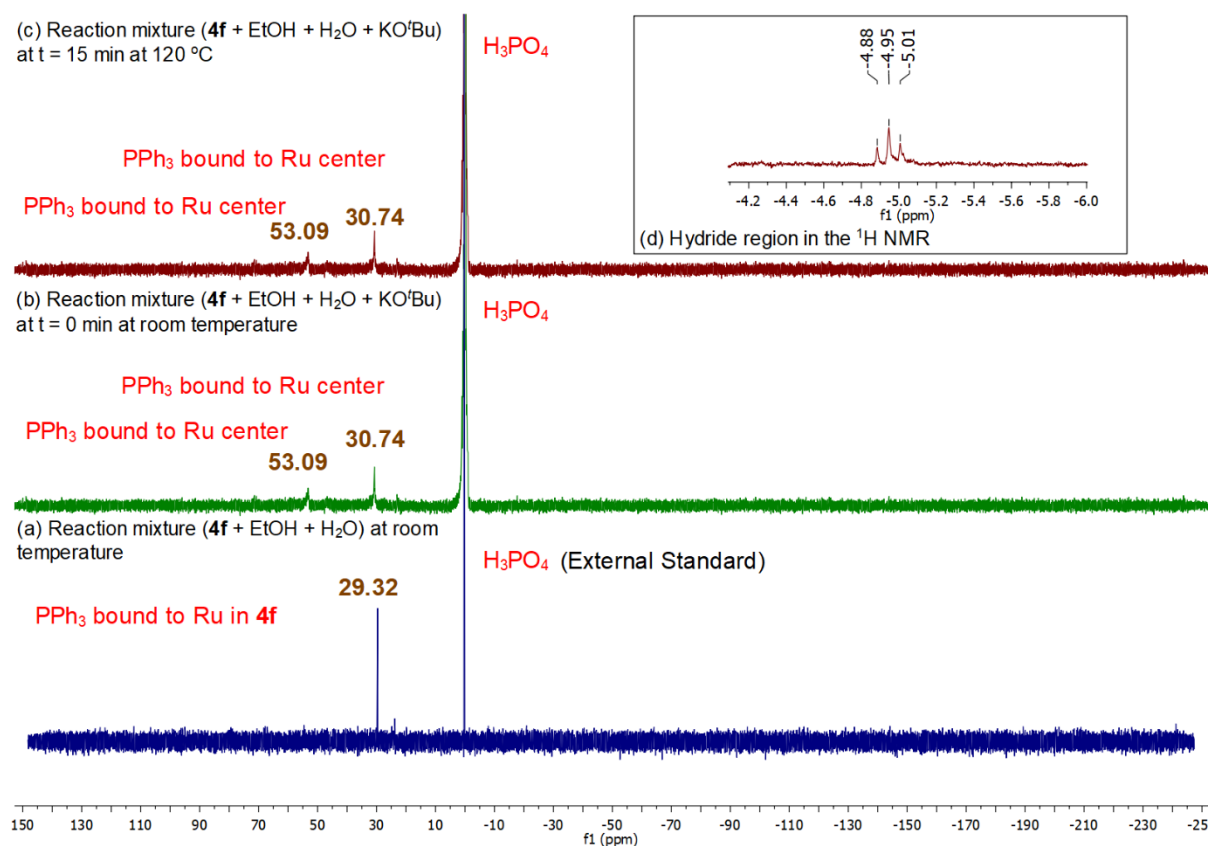


Figure S23. ^{31}P NMR spectra of (a) **4f** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) (b) **4f** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO^tBu (3.48 mmol) at room temperature. (c) **4f** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO^tBu (3.48 mmol) at 120 °C (phosphoric acid was used a ^{31}P standard). (d) The inset has the region of the corresponding ^1H NMR at 120 °C for 15 minutes in the presence of KO^tBu.

9. IR Studies

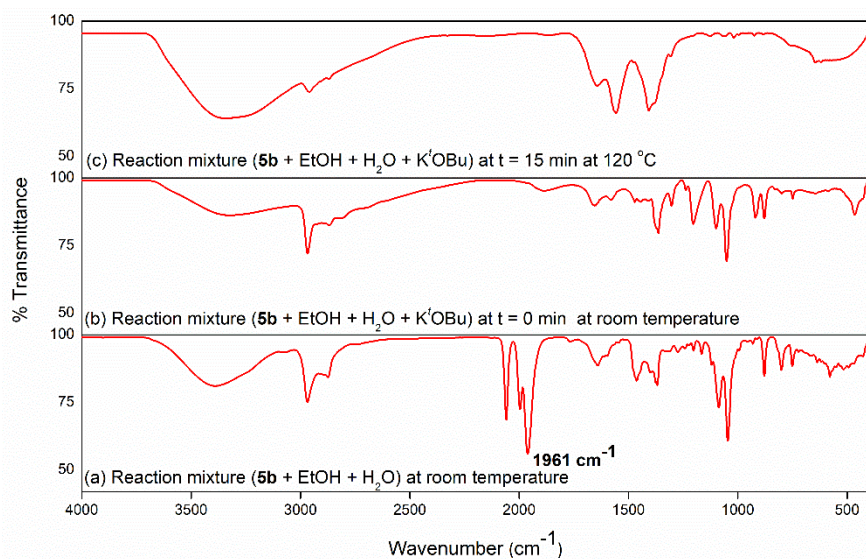


Figure S24. IR spectra of (a) **5b** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) (b) **5b** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO⁺Bu (3.48 mmol) at room temperature. (c) **5b** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO⁺Bu (3.48 mmol) after 15 min at of heating 120 °C.

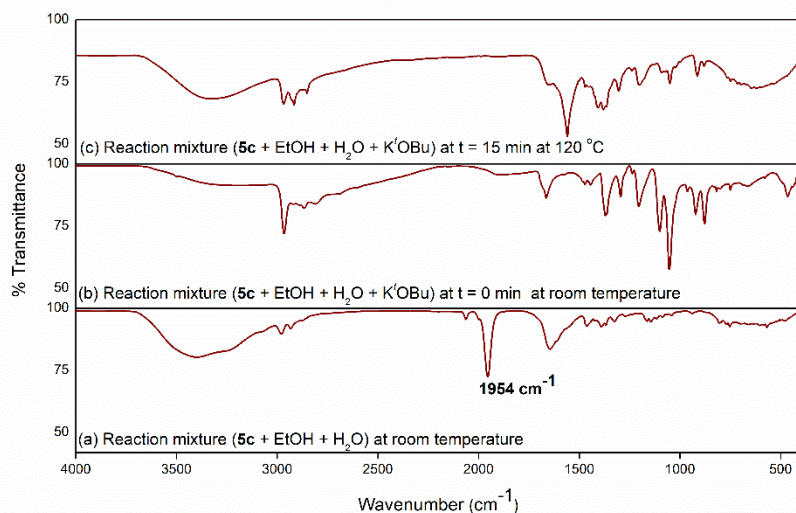


Figure S25. IR spectra of (a) **5c** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) (b) **5c** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO⁺Bu (3.48 mmol) at room temperature. (c) **5c** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO⁺Bu (3.48 mmol) after 15 min at of heating 120 °C.

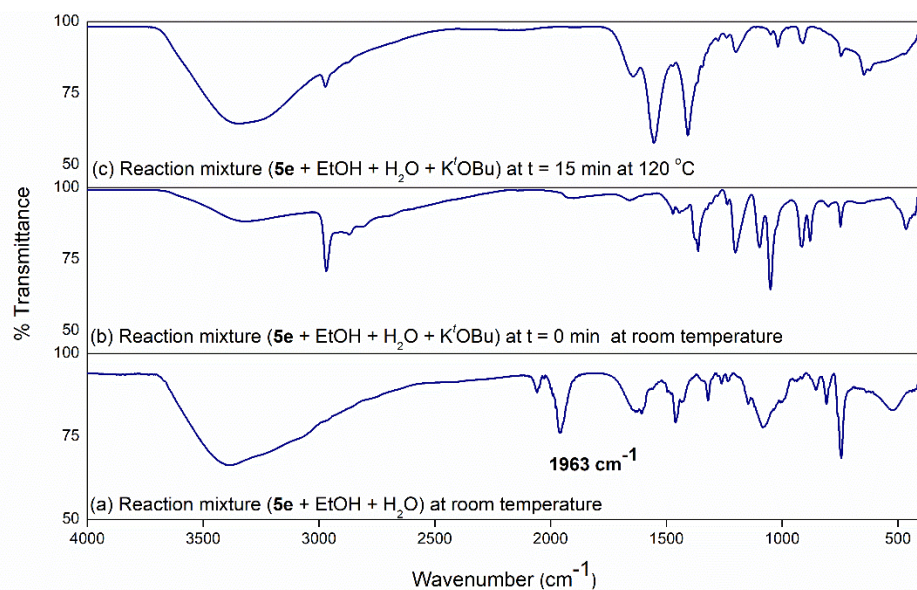


Figure S26. IR spectra of (a) **5e** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) (b) **5e** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO^tBu (3.48 mmol) at room temperature. (c) **5e** (0.8 mol%) in EtOH (4.64 mmol) with water (2.32 mmol) in the presence of KO^tBu (3.48 mmol) after 15 min at of heating 120 °C

10. Computational Studies

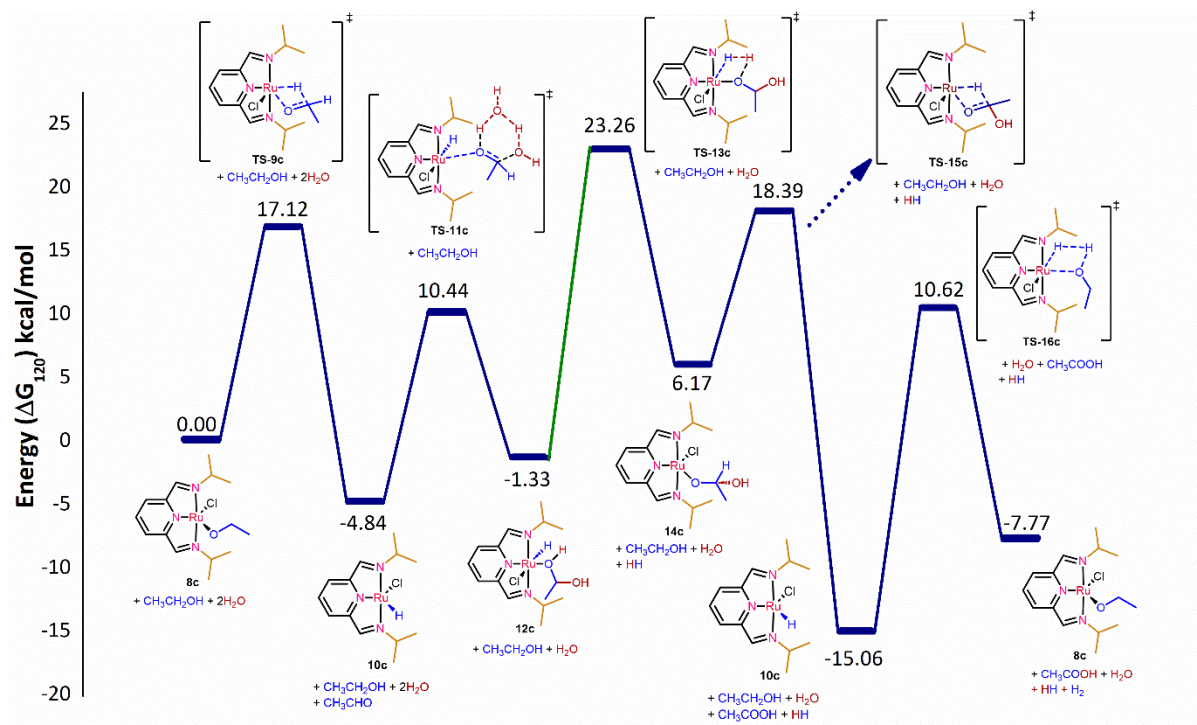


Figure S27. Free energy (ΔG_{120}) profile of the **4c** catalyzed reforming of ethanol at 120 °C.

Table S4. Energy barriers of the various species involved in ethanol reforming employing **4b**, **4c** and **5e**.

Entry	Path	Barrier (kcal/mol)
1	8b → TS-9b	14.08
2	8c → TS-9c	17.12
3	5e → TS-9e	10.06
4	10b → TS-11b	13.78
5	10c → TS-11c	15.28
6	10e → TS-11e	13.77
7	12b → TS-13b	23.19
8	12c → TS-13c	24.58
9	12e → TS-13e	24.18
10	14b → TS-15b	9.54
11	14c → TS-15c	12.22
12	14e → TS-15e	0.04
13	10b → TS-16b	23.25
14	10c → TS-16c	25.67
15	10e → TS-16e	23.41

Table S5: Optimized XYZ coordinates for complex **8b**

Ru	0.07298800	-0.01797000	-0.08929000
N	-1.97020500	0.29679000	0.02256100
N	0.03187200	1.84968300	0.14278700
N	2.08925100	0.39234300	-0.15985700
C	-2.28453400	1.57362300	0.17683500
H	-3.32122000	1.91904800	0.22322300
C	-1.19379300	2.49543600	0.27220200
C	2.35832100	1.67735500	-0.00706700
H	3.37434500	2.07435800	-0.07024800
C	1.23688200	2.54556100	0.19652300
C	-1.21707900	3.87989300	0.47466800
H	-2.17930500	4.38460800	0.57935700
C	1.21138900	3.93003300	0.39683600
H	2.15583100	4.47599300	0.43676400
C	-0.01382200	4.59712700	0.53734800
H	-0.03087700	5.67637300	0.69428900
Cl	0.03892600	-0.28544200	-2.46482700
O	0.26426900	-0.92920200	1.64035000
C	-0.80642500	-1.16689000	2.53877200
H	-1.34071400	-0.22043100	2.75519000
H	-1.55099600	-1.86672000	2.10320800
C	-0.24027200	-1.75738500	3.82741600
H	0.47622000	-1.05831400	4.28374700
H	-1.04539800	-1.96303100	4.55166200
H	0.28729700	-2.69973600	3.61573900
C	3.13612400	-0.59840700	-0.43271700
C	4.43133100	-0.05895600	-1.05755700
C	3.43809800	-1.40068600	0.85112600
H	2.67054200	-1.28675000	-1.16356400

C	5.38176900	-1.22419600	-1.37837900
H	4.93808700	0.62377100	-0.35028400
H	4.19711500	0.51785600	-1.96758500
C	4.40395000	-2.55463100	0.54754500
H	3.89098700	-0.71116400	1.58794500
H	2.49380400	-1.75665900	1.29003500
C	5.69254200	-2.05621600	-0.12461800
H	6.31203600	-0.83690700	-1.82524600
H	4.91277600	-1.87175200	-2.14168000
H	4.63926800	-3.09822300	1.47732500
H	3.90182600	-3.27909500	-0.12011300
H	6.34638000	-2.90566900	-0.38246000
H	6.25646200	-1.43059000	0.59257300
C	-3.02915600	-0.70769900	-0.17523700
C	-4.18303000	-0.62918000	0.84226600
C	-3.56338200	-0.65653300	-1.62118400
H	-2.52688800	-1.68242700	-0.03922900
C	-5.17800800	-1.77523300	0.60123000
H	-4.71442600	0.33342100	0.73418200
H	-3.77877800	-0.66420800	1.86705000
C	-4.57125500	-1.78858100	-1.86274200
H	-4.05188900	0.32341300	-1.77711500
H	-2.71455100	-0.71101700	-2.31919500
C	-5.71573900	-1.75848300	-0.83806500
H	-6.00667900	-1.71044600	1.32522500
H	-4.67073100	-2.73925200	0.79099400
H	-4.96863100	-1.72027700	-2.88847300
H	-4.04604200	-2.75926500	-1.79667800
H	-6.39997600	-2.60768500	-0.99920600
H	-6.31313000	-0.83985400	-0.98905700

Table S6: Optimized XYZ coordinates for complex **TS-9b**

C	-1.29261300	2.52781600	-0.30497300
C	-1.37872700	3.93371200	-0.23156200
C	-0.20320400	4.67608600	-0.10646200
C	1.04964300	4.03648400	-0.03357000
C	1.08684300	2.64111200	-0.11402800
H	-2.35341800	4.42451300	-0.24698800
H	-0.25648600	5.76457900	-0.04276700
H	1.96931300	4.61034200	0.09040000
C	2.25487700	1.76349000	-0.06585000
H	3.25808900	2.20209300	-0.03315000
C	-2.34960100	1.55052400	-0.31507300
H	-3.39921400	1.85580600	-0.28737600
N	2.06625900	0.47358500	-0.10345800
N	-0.06291200	1.93935400	-0.28081800
N	-2.00012300	0.26804500	-0.26584100
Ru	-0.00168200	-0.06911700	-0.19298700
H	-1.23839600	-1.78040500	-1.82994300
C	-0.14252400	-1.67928200	-1.67772400
C	0.60366100	-2.99890800	-1.72865200
O	0.42690400	-0.60904700	-2.18301200
Cl	-0.05851900	0.16767900	2.22514400
H	0.04226900	-1.66758300	0.18079700
H	1.63223300	-2.89289100	-1.35714100
H	0.08868900	-3.77092700	-1.13830900
H	0.64833500	-3.33566800	-2.77923600
C	3.18525500	-0.47365400	-0.15031900
C	4.58445400	0.11556600	-0.37304500
C	3.15398200	-1.35286900	1.11551500
H	2.93901000	-1.11477100	-1.01836500

C	5.62123900	-1.01694200	-0.48232500
H	4.85599900	0.76693200	0.47879500
H	4.60022900	0.73759100	-1.28461200
C	4.19671400	-2.47497900	1.02187300
H	3.35717800	-0.70935400	1.98980800
H	2.13726800	-1.74917200	1.25426400
C	5.60412100	-1.91946500	0.75981900
H	6.62523800	-0.58920100	-0.63709200
H	5.39704200	-1.62327500	-1.37929900
H	4.18242300	-3.07220700	1.94787900
H	3.91765600	-3.16259300	0.20126500
H	6.32945400	-2.74143100	0.64247200
H	5.93176600	-1.33298200	1.63821300
C	-3.05745100	-0.74524900	-0.06196500
C	-3.61663700	-0.66402500	1.37181900
C	-4.18386100	-0.69923300	-1.11041000
H	-2.54509700	-1.71584700	-0.15945500
C	-4.61955700	-1.79999700	1.61546000
H	-4.11803500	0.31234000	1.50500000
H	-2.77668400	-0.69596500	2.08272100
C	-5.17974200	-1.84296400	-0.86030300
H	-4.71835700	0.26581600	-1.04875800
H	-3.75131900	-0.76367100	-2.12267900
C	-5.74414000	-1.79605800	0.56829100
H	-5.03761000	-1.71647400	2.63184000
H	-4.08668100	-2.76811100	1.57711900
H	-5.99484700	-1.79937400	-1.60108700
H	-4.66534100	-2.80929400	-1.01709600
H	-6.42932000	-2.64355900	0.73474600
H	-6.34675800	-0.87614800	0.68781800

Table S7: Optimized XYZ coordinates for complex **10b**

Ru	0.00002900	-0.11848200	0.05710400
N	-2.02940700	0.28448100	0.03194000
N	-0.00003500	1.82055600	0.00324600
N	2.02943300	0.28464200	0.03361300
C	-2.31740200	1.57851900	-0.01654200
H	-3.34991100	1.94130000	-0.04271300
C	-1.20697400	2.49725300	-0.04087900
C	2.31736700	1.57868900	-0.01492800
H	3.34986400	1.94153900	-0.04046500
C	1.20688500	2.49733700	-0.04014100
C	-1.21667500	3.89705500	-0.11454000
H	-2.16933100	4.42884000	-0.14834600
C	1.21653800	3.89713700	-0.11381700
H	2.16917800	4.42898600	-0.14705300
C	-0.00008300	4.59328200	-0.14591700
H	-0.00010200	5.68307800	-0.20149000
Cl	0.00021500	-2.47833600	-0.29202700
H	-0.00064700	-0.04567100	1.62741700
C	3.13404900	-0.69940400	0.06230000
C	3.95218100	-0.67863700	-1.24213700
C	4.03887000	-0.53078800	1.29633300
H	2.63533500	-1.67981400	0.13161900
C	5.03686700	-1.76621000	-1.21220900
H	4.42569600	0.31312900	-1.36585600
H	3.27185100	-0.82405300	-2.09664500
C	5.12016700	-1.62224000	1.31857000
H	4.52346700	0.46301400	1.27182600
H	3.41937700	-0.56735000	2.20700000
C	5.94193600	-1.62309900	0.02072300

H	5.63412100	-1.72565300	-2.13787800
H	4.54955900	-2.75793500	-1.19531700
H	5.77684700	-1.48191500	2.19280800
H	4.63497400	-2.60722100	1.44426000
H	6.68893000	-2.43339200	0.04222700
H	6.50759400	-0.67495500	-0.05129100
C	-3.13401000	-0.69958300	0.06019000
C	-4.03522500	-0.53435200	1.29735300
C	-3.95587600	-0.67508200	-1.24177400
H	-2.63523200	-1.68024300	0.12548300
C	-5.11668500	-1.62563600	1.31962000
H	-4.51946100	0.45973700	1.27707200
H	-3.41302500	-0.57369400	2.20605100
C	-5.04044300	-1.76277600	-1.21175600
H	-4.42995700	0.31689000	-1.36148100
H	-3.27801100	-0.81803600	-2.09866700
C	-5.94206500	-1.62292000	0.02407900
H	-5.77089700	-1.48753900	2.19606100
H	-4.63131900	-2.61103200	1.44133600
H	-5.64028600	-1.71977600	-2.13563900
H	-4.55308200	-2.75454100	-1.19884700
H	-6.68905400	-2.43321900	0.04548300
H	-6.50786700	-0.67455400	-0.04383000

Table S8. Optimized XYZ coordinates for complex **TS-11b**

C	0.04538300	4.95042600	0.50407100
C	1.25023900	4.23709900	0.50104000
C	1.23457200	2.85677900	0.24775900
C	-1.15862400	2.90858800	0.02197200
C	-1.16701900	4.28911700	0.26436700
C	2.33741500	1.94512200	0.13292400
C	-2.26738200	2.02539100	-0.22131100
H	-3.29106200	2.40921900	-0.26626800
H	3.37113500	2.29964300	0.18545000
H	0.04970600	6.02390000	0.70056900
H	2.20119500	4.73701500	0.69316700
H	-2.11591800	4.82806600	0.27644300
N	-1.99175100	0.74599600	-0.38786900
N	2.03868200	0.67843000	-0.12262300
N	0.03304900	2.21789900	0.01087800
Ru	0.03024800	0.30678900	-0.19541500
Cl	-0.28215900	-0.08700300	2.38041400
C	0.77807900	-2.59218600	0.63728700
H	0.13132100	0.27467900	-1.78702200
O	0.17881000	-1.91864300	-0.40115500
H	1.50094900	-1.95661000	1.17223200
O	-1.85221600	-3.15977100	-0.10085800
H	-1.88841600	-4.03176500	-0.52531800
H	-0.94293300	-2.55546000	-0.50153000
O	-0.27863800	-2.88353600	1.70931000
H	-0.43280300	-1.93097000	2.10208000
H	-1.16558500	-3.13916100	1.03342500
C	1.36684900	-3.93500600	0.24256200
H	2.17507100	-3.77040300	-0.48453400

H	1.77076200	-4.45904800	1.12001200
H	0.60422500	-4.56884300	-0.23463000
C	3.13768300	-0.25894300	-0.42618300
C	3.95398200	0.16805500	-1.65917000
C	4.04975200	-0.50391700	0.79063600
H	2.63789100	-1.20663300	-0.68368300
C	5.01913500	-0.88889000	-1.98827100
H	4.44658600	1.13695800	-1.46018100
H	3.26791500	0.32173100	-2.50751400
C	5.11636800	-1.55891000	0.45892200
H	4.54368800	0.44354600	1.07327600
H	3.43783400	-0.80781200	1.65569200
C	5.93059500	-1.16266300	-0.78205900
H	5.61559200	-0.56562100	-2.85710500
H	4.51609600	-1.82752500	-2.28696200
H	5.78023700	-1.70768400	1.32613200
H	4.62071900	-2.53080500	0.27556700
H	6.66318600	-1.94943600	-1.02610400
H	6.51340000	-0.25045800	-0.55472000
C	-3.10697100	-0.19541200	-0.60172900
C	-3.81068900	-0.49336100	0.73741200
C	-4.12422200	0.22933100	-1.67636200
H	-2.63947200	-1.13079300	-0.93930000
C	-4.86702000	-1.58993600	0.55240200
H	-4.28250300	0.43775200	1.10399500
H	-3.05567300	-0.78065000	1.48476600
C	-5.16398300	-0.88649600	-1.86969300
H	-4.64625600	1.15485600	-1.37239600
H	-3.59566500	0.44708800	-2.61923000
C	-5.87462800	-1.22531300	-0.54948300

H	-5.38937000	-1.77213600	1.50619500
H	-4.34667000	-2.52646500	0.28580100
H	-5.89637200	-0.59023100	-2.63876200
H	-4.65362000	-1.79024800	-2.25115300
H	-6.59075200	-2.04970200	-0.70372400
H	-6.46921000	-0.34957500	-0.22708000

Table S9: Optimized XYZ coordinates for complex **12b**

C	0.06199600	4.94746000	0.24501000
C	1.27585000	4.24959600	0.18987900
C	1.26555600	2.85665700	0.03075900
C	-1.14623400	2.86519100	-0.00473100
C	-1.15450100	4.25833700	0.14968700
C	2.37407400	1.94671600	-0.08230100
C	-2.25437800	1.95306200	-0.09845600
H	-3.28685500	2.31031900	-0.03211800
H	3.40599400	2.30627100	-0.04570000
H	0.06402000	6.03188400	0.36650900
H	2.23003900	4.77355300	0.26853000
H	-2.10745200	4.78795900	0.19980800
N	-1.96131400	0.67383600	-0.25085500
N	2.07461500	0.67089600	-0.26169100
N	0.05778000	2.19183500	-0.07074400
Ru	0.06404700	0.29520500	-0.27183800
Cl	-0.04777700	-0.41360600	2.18696000
O	-1.15133500	-2.88593200	0.85855400
C	0.05119100	-2.99709100	0.17956400
H	0.91374400	-2.81247100	0.84196400
H	0.07084500	0.37084200	-1.87866700
H	-1.02467100	-2.10740500	1.47102200
O	0.20417300	-1.92015000	-0.82279700
H	-0.47727700	-2.06323000	-1.50461100
C	0.12877700	-4.34278500	-0.51388500
H	1.05117900	-4.42421100	-1.10498600
H	0.10691300	-5.14471500	0.23692800
H	-0.74177500	-4.47671900	-1.17662200
C	3.13566600	-0.34192700	-0.38354200

C	4.35950300	0.08503900	-1.20974100
C	3.55800200	-0.83070500	1.01694100
H	2.65134800	-1.18634500	-0.90448700
C	5.34215800	-1.09057300	-1.33769100
H	4.87940900	0.92544600	-0.71534600
H	4.03355900	0.43931500	-2.20175100
C	4.55266200	-1.99464400	0.89972600
H	4.02594700	0.01494400	1.55447300
H	2.66083200	-1.10840500	1.59247800
C	5.76988600	-1.61447500	0.04205100
H	6.22356500	-0.78267300	-1.92380400
H	4.85798000	-1.90693600	-1.90529500
H	4.87253900	-2.31560100	1.90449700
H	4.04105800	-2.86240800	0.44217200
H	6.44683400	-2.47745300	-0.06968800
H	6.34642900	-0.82767000	0.56349700
C	-3.05381200	-0.31699300	-0.29036600
C	-3.84614800	-0.35664700	1.02959700
C	-3.98413300	-0.12986600	-1.50210600
H	-2.55275300	-1.29338800	-0.38699100
C	-4.89146500	-1.48084700	0.98216500
H	-4.35011800	0.61488000	1.18587300
H	-3.14169100	-0.49416800	1.86473200
C	-5.03516100	-1.25061400	-1.54236300
H	-4.49264900	0.84911300	-1.43043900
H	-3.38366400	-0.11221900	-2.42684200
C	-5.82634900	-1.32662700	-0.22723800
H	-5.47153700	-1.49356700	1.91928900
H	-4.36693400	-2.45196800	0.92309400
H	-5.71568600	-1.09875000	-2.39631700

H	-4.52570500	-2.21696700	-1.71441400
H	-6.54672900	-2.16033900	-0.26457400
H	-6.42170800	-0.40153300	-0.11043800

Table S10: Optimized XYZ coordinates for complex **TS-13b**

C	-0.18779200	4.95193300	0.13090400
C	1.04595100	4.28712600	0.11915000
C	1.06659900	2.89300300	-0.02780900
C	-1.33301500	2.83680100	-0.12557800
C	-1.38410800	4.23114900	0.01445500
C	2.20030900	1.99792500	-0.08093400
C	-2.42661400	1.89675000	-0.23734100
H	-3.46252500	2.24537200	-0.26497600
H	3.22112000	2.39044100	-0.05021900
H	-0.21813300	6.03652100	0.24757600
H	1.98267600	4.83454600	0.23623500
H	-2.35066200	4.73662300	0.04861400
N	-2.11301800	0.62092300	-0.33038600
N	1.95230800	0.71280800	-0.21084500
N	-0.11222500	2.20948900	-0.16782400
Ru	-0.09132100	0.27129900	-0.22920200
Cl	-0.11228700	0.18048000	2.18102200
O	1.59815200	-3.04696400	-1.07480800
C	0.56353400	-2.79820200	-0.09699900
H	1.11588400	-2.39967800	0.77328500
H	0.00608500	-0.00410000	-1.95663400
H	1.14343300	-3.42243300	-1.85003900
O	-0.38955500	-1.88807000	-0.55410500
H	-0.03553300	-0.87700200	-1.57907500
C	-0.15492100	-4.09401300	0.27575300
H	0.56826500	-4.85985400	0.59250500
H	-0.86879800	-3.90860200	1.09114300
H	-0.71936300	-4.46442600	-0.59624800
C	-3.13382800	-0.43298000	-0.43111900

C	-3.27591600	-1.12498100	0.94088000
C	-4.50056300	-0.00022700	-0.97709900
H	-2.69007800	-1.18152200	-1.11178800
C	-4.21309800	-2.33452200	0.82949700
H	-3.67157400	-0.39145400	1.66676100
H	-2.27835300	-1.42054000	1.29203300
C	-5.42528300	-1.22405600	-1.10127900
H	-4.97248200	0.72566300	-0.28919000
H	-4.38103600	0.50087700	-1.95311300
C	-5.57942600	-1.94750400	0.24553100
H	-4.33487600	-2.80018800	1.82111500
H	-3.73706400	-3.09395200	0.18195700
H	-6.40903100	-0.91203200	-1.48877800
H	-5.00097000	-1.92291200	-1.84560200
H	-6.21652700	-2.83945500	0.12623200
H	-6.10228200	-1.27989400	0.95575300
C	3.05965100	-0.25308500	-0.29759100
C	4.29064800	0.21162700	-1.09168600
C	3.46656200	-0.70828300	1.11973100
H	2.63428700	-1.12859600	-0.81508500
C	5.29289800	-0.95005000	-1.20290300
H	4.78838700	1.05831700	-0.58375200
H	3.98190600	0.56238000	-2.09113100
C	4.47388700	-1.86356700	1.02139500
H	3.91419100	0.15237500	1.65168000
H	2.56703100	-0.99246400	1.68696200
C	5.70137700	-1.46870700	0.18491400
H	6.18096900	-0.62734400	-1.77100600
H	4.82814200	-1.77153100	-1.77755900
H	4.78142400	-2.17812900	2.03214300

H	3.97260200	-2.72950100	0.55290100
H	6.38768600	-2.32547600	0.08301600
H	6.26286100	-0.67644100	0.71524800

Table S11: Optimized XYZ coordinates for complex **14b**

Ru	0.10418100	-0.06005900	-0.19443900
N	-1.93923200	0.25532600	-0.15684600
N	0.05862700	1.81791800	-0.13882500
N	2.12449300	0.34561000	-0.28209400
C	-2.25678900	1.53487500	-0.11194400
H	-3.29345800	1.88114900	-0.09208300
C	-1.16812500	2.46659800	-0.08703300
C	2.38681600	1.63876300	-0.23809300
H	3.40250700	2.03404700	-0.31829300
C	1.25903700	2.51909900	-0.13496400
C	-1.19909000	3.86289300	-0.02055600
H	-2.16452100	4.36997700	0.02374700
C	1.22898300	3.91753100	-0.06981800
H	2.17194900	4.46745600	-0.06973400
C	0.00106700	4.58936000	-0.01079900
H	-0.02201000	5.67863300	0.04070600
Cl	0.11519900	-0.63750200	-2.51471100
O	0.29312000	-0.65255800	1.69234900
C	-0.76124600	-0.62470700	2.61050000
H	-1.68069800	-1.09735300	2.21095100
O	-1.16712100	0.71691200	2.89768700
H	-0.34525200	1.18932500	3.12354000
C	-0.29972800	-1.35819200	3.87052800
H	-1.08441700	-1.31972800	4.63999700
H	-0.06491100	-2.40821600	3.64169300
H	0.61232900	-0.87818800	4.25958200
C	3.18113300	-0.66068300	-0.43737000
C	4.50114400	-0.16226100	-1.04301900
C	3.42845700	-1.36036300	0.91669000

H	2.74728300	-1.40245100	-1.13470300
C	5.47065600	-1.34072400	-1.23089300
H	4.97252300	0.57574800	-0.36740400
H	4.30680900	0.34227100	-2.00403400
C	4.41228800	-2.52712700	0.74708500
H	3.84389300	-0.61208400	1.61736000
H	2.46849400	-1.68793600	1.34296100
C	5.72713500	-2.07162500	0.09590500
H	6.41866100	-0.98097600	-1.66315200
H	5.04035400	-2.04830600	-1.96307100
H	4.60837700	-2.99489900	1.72587300
H	3.94347000	-3.30493000	0.11640100
H	6.39432100	-2.93411100	-0.06689200
H	6.25759300	-1.39024400	0.78734900
C	-2.99544400	-0.76722600	-0.24957000
C	-4.18318800	-0.55555400	0.70763600
C	-3.48062600	-0.91520000	-1.70583200
H	-2.50030200	-1.71457000	0.03220900
C	-5.15692200	-1.73936100	0.59941100
H	-4.72271200	0.37072500	0.43978500
H	-3.81592900	-0.42626200	1.73859100
C	-4.47404400	-2.07889800	-1.82362700
H	-3.96559100	0.03185300	-2.00801600
H	-2.61009900	-1.05775200	-2.36335500
C	-5.64886100	-1.92925500	-0.84422900
H	-6.00955600	-1.58628100	1.28099500
H	-4.64705500	-2.66042900	0.93826400
H	-4.84194800	-2.15048800	-2.86010000
H	-3.94303700	-3.02639900	-1.61641700
H	-6.31692800	-2.80395200	-0.90782700

H -6.25358800 -1.04997100 -1.13549100

Table S12: Optimized XYZ coordinates for complex **TS-15b**

C	-0.03698100	4.66413800	-0.48254100
C	1.18526800	3.98333200	-0.43893400
C	1.17498800	2.58020900	-0.32134200
C	-1.21861000	2.57098300	-0.28347300
C	-1.25513800	3.96772000	-0.40295400
C	2.28295000	1.65786800	-0.21303800
C	-2.32242900	1.63263700	-0.14506100
H	-3.35307300	2.00190700	-0.08865900
H	3.31233700	2.02534600	-0.16469200
H	-0.04435100	5.75215000	-0.57158500
H	2.13154300	4.52527800	-0.48379900
H	-2.20881000	4.49760600	-0.42531400
N	-2.04450300	0.35186000	-0.05615800
N	2.00470300	0.36334400	-0.12007200
N	-0.02033400	1.92715800	-0.26305000
Ru	-0.00024500	-0.06817000	-0.11498200
Cl	-0.03426400	0.00979500	2.29612000
O	1.45919600	-2.07287800	-2.10803600
C	0.16361800	-1.67313100	-1.88620900
H	0.02623200	-1.71881900	0.09583000
H	1.95839400	-1.24614200	-2.26039200
O	-0.18680900	-0.48847000	-2.22670700
C	-0.78613800	-2.84537600	-1.96284000
H	-0.88457700	-3.12636800	-3.02531000
H	-0.39873900	-3.70508600	-1.40376400
H	-1.76977900	-2.55896000	-1.57694700
C	-3.13546500	-0.60906800	0.19694600
C	-3.76887000	-0.38763200	1.58351300
C	-4.19761600	-0.62917100	-0.91752100

H	-2.63970900	-1.59253000	0.21932300
C	-4.81852200	-1.47175300	1.86400400
H	-4.24771400	0.60876200	1.60985500
H	-2.96767000	-0.38691200	2.33844400
C	-5.24536600	-1.71517200	-0.62806400
H	-4.69655000	0.35572800	-0.97301600
H	-3.70588600	-0.79459300	-1.89030000
C	-5.88345100	-1.52798400	0.75746500
H	-5.28909900	-1.29205800	2.84431400
H	-4.31275600	-2.45224100	1.93650100
H	-6.01768700	-1.71062500	-1.41455300
H	-4.75852300	-2.70723800	-0.67367200
H	-6.60320400	-2.33874700	0.95730900
H	-6.46282200	-0.58553200	0.76341700
C	3.10543900	-0.58744300	0.15236500
C	4.32163400	-0.44157900	-0.78092700
C	3.53366300	-0.51225300	1.63019700
H	2.66411400	-1.58238700	-0.01733800
C	5.34634500	-1.54710300	-0.48080000
H	4.79983400	0.54357400	-0.63391900
H	4.00540200	-0.48093900	-1.83895700
C	4.57059100	-1.60241100	1.93623900
H	3.96548800	0.48740800	1.82439600
H	2.63937000	-0.60775200	2.26442000
C	5.78070000	-1.51935700	0.99307600
H	6.22020500	-1.44002300	-1.14419100
H	4.89258300	-2.52818300	-0.71222000
H	4.89375200	-1.52449500	2.98707200
H	4.09107100	-2.59275500	1.82968200
H	6.48499000	-2.34286600	1.19618000

H 6.33108900 -0.57999400 1.18937400

Table S13: Optimized XYZ coordinates for complex **TS-16b**

C	0.04043000	4.86733200	0.12695800
C	1.24937900	4.16135400	0.07338200
C	1.21737100	2.76780700	-0.08081600
C	-1.18297100	2.79373900	-0.10407100
C	-1.18347600	4.18718100	0.04503100
C	2.31874000	1.83622200	-0.16127400
C	-2.31183600	1.89110100	-0.18348400
H	-3.33576400	2.27426800	-0.16870600
H	3.35078500	2.19774200	-0.13945900
H	0.05037200	5.95155500	0.25017400
H	2.20717200	4.67654400	0.16471500
H	-2.13081500	4.72461800	0.11364300
N	-2.04790600	0.60685100	-0.29871700
N	2.02941500	0.55861400	-0.29132400
N	0.01315200	2.12570300	-0.18972000
Ru	-0.03785500	0.18276400	-0.27642400
Cl	-0.00463900	0.10113600	2.13261800
C	0.48477800	-2.92887500	-0.38255100
H	0.86736100	-2.88542400	0.65806100
H	-0.00441400	-0.01257000	-2.03763400
O	-0.46501500	-1.91019500	-0.59930900
H	-0.16978600	-0.85525500	-1.70131000
C	-0.16652500	-4.28783100	-0.63666900
H	0.54753900	-5.11011400	-0.46409600
H	-1.02607000	-4.42438100	0.03741700
H	-0.53199700	-4.35045300	-1.67350000
C	-3.10604900	-0.41076400	-0.37558400
C	-3.21362100	-1.13657500	0.98250200
C	-4.47844100	0.08226100	-0.85180500

H	-2.71558600	-1.15779100	-1.09000000
C	-4.19561600	-2.31054200	0.87432400
H	-3.55337100	-0.41304400	1.74577300
H	-2.21213000	-1.47815300	1.27662500
C	-5.44660900	-1.10700200	-0.97396300
H	-4.89757800	0.80168100	-0.12382900
H	-4.38275600	0.60859300	-1.81731900
C	-5.57111200	-1.86442200	0.35699300
H	-4.29349900	-2.80067300	1.85674000
H	-3.77040100	-3.06564500	0.18759100
H	-6.43411800	-0.75264300	-1.31260700
H	-5.07434400	-1.79629500	-1.75405800
H	-6.24076800	-2.73242100	0.23878900
H	-6.04367300	-1.20143300	1.10584200
C	3.10641900	-0.44007000	-0.36616600
C	4.44741100	0.03283500	-0.94892900
C	3.31201500	-1.06688700	1.02882100
H	2.70995600	-1.23025500	-1.02870800
C	5.41356000	-1.15997700	-1.05553700
H	4.90453600	0.79417200	-0.29081900
H	4.28996100	0.50146900	-1.93537400
C	4.28860200	-2.24715800	0.94488300
H	3.71078000	-0.28420400	1.69990900
H	2.33887800	-1.36429900	1.44535400
C	5.62483100	-1.83331100	0.30978400
H	6.37675100	-0.82564100	-1.47445900
H	5.00028700	-1.89730200	-1.76836200
H	4.45269200	-2.66493400	1.95141700
H	3.82880500	-3.05311800	0.34318000
H	6.28910500	-2.70675400	0.20387500

H	6.14153500	-1.12485900	0.98387800
H	1.36884700	-2.81899500	-1.05280000

Table S14: Optimized XYZ coordinates for complex **4b**

Ru	0.02833100	-0.93025300	-0.36592500
P	-0.02123000	1.30758300	0.37235400
N	2.06183900	-1.13008600	0.01142400
N	-0.00138400	-1.75590900	1.39232900
N	-2.01590800	-1.13578600	-0.05748800
C	1.46151100	2.37823800	0.08642300
C	2.31626600	-1.74976900	1.14193400
H	3.33755900	-1.98870900	1.45499100
C	-1.35815900	2.46536000	-0.18008200
C	1.18594500	-2.13604100	1.95891500
C	-0.22966100	1.20946100	2.19992800
C	-2.31021600	-1.71943700	1.08274300
H	-3.34201700	-1.95064100	1.36589100
C	-1.20814900	-2.10025900	1.93997100
C	1.18392200	-2.82957600	3.17640500
H	2.12973300	-3.13002900	3.63033200
C	1.98528900	2.41134400	-1.21895700
H	1.53178500	1.78694000	-1.99529800
C	-1.24522900	-2.78210000	3.16333300
H	-2.20629800	-3.04430800	3.60852300
C	-1.87062000	2.35313100	-1.48258600
H	-1.48536500	1.56940100	-2.14150500
C	-0.04018200	-3.13445100	3.78462000
H	-0.05614200	-3.66983800	4.73533700
C	2.01402100	3.21277400	1.07375200
H	1.59183500	3.23162800	2.08027500
C	3.06907500	3.24241700	-1.51775000
H	3.46618300	3.26091300	-2.53549800
C	-1.51824300	1.16241600	2.76642900

H	-2.39457300	1.34262900	2.14064100
C	0.88123400	0.92952800	3.02027600
H	1.88514100	0.91482200	2.59040500
C	-1.79238800	3.51850100	0.64693800
H	-1.37358800	3.63960800	1.64831000
C	3.10666800	4.03261800	0.76935000
H	3.53448500	4.67080100	1.54644600
C	3.64174800	4.04422000	-0.52353400
H	4.49441300	4.68588400	-0.75788100
C	0.70795400	0.64861600	4.37812900
H	1.58086100	0.43555800	4.99960200
C	-2.83749300	3.25847100	-1.93464600
H	-3.22854200	3.16207500	-2.95040600
C	-1.68563700	0.88111600	4.12616500
H	-2.69234000	0.85434000	4.55014200
C	-2.76442600	4.41371500	0.19137900
H	-3.10244100	5.22214000	0.84425900
C	-0.57496200	0.62641200	4.93712500
H	-0.70799400	0.40408300	5.99820500
C	-3.29613400	4.28048200	-1.09739200
H	-4.05578600	4.98190200	-1.45071400
Cl	0.04850700	-3.23382400	-1.23084100
Cl	0.11487900	-0.17037500	-2.71721000
C	-3.07392300	-0.86074400	-1.04535600
C	-3.46462300	-2.16499200	-1.76899900
C	-4.30430400	-0.12988000	-0.48339600
H	-2.59796600	-0.21288200	-1.79657600
C	-4.45815500	-1.85898800	-2.89652400
H	-3.92002000	-2.85811300	-1.03684300
H	-2.54971800	-2.64497400	-2.14787500

C	-5.29335200	0.17000900	-1.62110600
H	-4.80863400	-0.75269000	0.27829000
H	-3.98503300	0.80437700	0.00841400
C	-5.69316500	-1.10654500	-2.37769800
H	-4.75674800	-2.79708900	-3.39215000
H	-3.94950800	-1.24836000	-3.66468600
H	-6.18432900	0.67862100	-1.21729700
H	-4.82018300	0.87978500	-2.32382500
H	-6.37099900	-0.85665100	-3.21066200
H	-6.26209900	-1.76788900	-1.69704400
C	3.15206900	-0.81347200	-0.92653400
C	4.39080300	-0.16581700	-0.28822100
C	3.51564000	-2.07802800	-1.73098900
H	2.71349500	-0.09969600	-1.63996900
C	5.41493700	0.17708000	-1.38274200
H	4.85959200	-0.85734300	0.43578400
H	4.09037900	0.74135300	0.26269200
C	4.54655000	-1.73102000	-2.81223400
H	3.92937700	-2.83350400	-1.03654600
H	2.59559000	-2.50041500	-2.16172000
C	5.79191000	-1.05945700	-2.21371100
H	6.31142300	0.62970400	-0.92760800
H	4.97883500	0.94564900	-2.04648100
H	4.82614000	-2.64362300	-3.36352700
H	4.07762000	-1.05268700	-3.54815800
H	6.50030900	-0.77877000	-3.01074500
H	6.31895300	-1.78476000	-1.56529400

Table S15: Optimized XYZ coordinates for transition state of dissociation of PPh₃ from **4b** to **7b**

Ru	1.35348000	-1.02881300	0.44066700
P	-1.64505600	1.10786100	-0.41182600
N	2.73415300	0.51122600	0.46688900
N	0.68105100	0.00502100	1.88778800
N	-0.39916600	-2.04418600	0.82847000
C	-2.94420700	0.41642700	-1.53873200
C	2.51987300	1.37193200	1.44284800
H	3.14289900	2.25725900	1.59097900
C	-2.62735700	1.96095900	0.89722100
C	1.36701500	1.13544300	2.27430700
C	-0.97796200	2.52019900	-1.40638800
C	-1.05213100	-1.55623900	1.86305300
H	-2.01755500	-1.95388900	2.18515900
C	-0.48266800	-0.39770500	2.50431400
C	0.86169900	1.91581500	3.32189600
H	1.39446200	2.82011000	3.62078400
C	-2.52197200	-0.60603300	-2.41097700
H	-1.47551800	-0.92563400	-2.39870600
C	-0.99451600	0.36697700	3.56006700
H	-1.92748100	0.06544400	4.03680500
C	-2.28206100	3.24314100	1.36260400
H	-1.51629500	3.81977300	0.83857300
C	-0.32068300	1.52593200	3.96379000
H	-0.73026100	2.13605200	4.76950600
C	-4.28865600	0.82918500	-1.56949800
H	-4.63249000	1.61894200	-0.89710400
C	-3.42809200	-1.20089400	-3.29466800
H	-3.08508200	-1.98980300	-3.96876000
C	-1.78868600	3.50112300	-2.00533900

H	-2.87518700	3.44658400	-1.89956900
C	0.41616200	2.58763400	-1.56610100
H	1.03894600	1.80333300	-1.12971400
C	-3.61443600	1.23669900	1.59934800
H	-3.88998500	0.23281800	1.26345500
C	-5.19368200	0.22406000	-2.44879400
H	-6.23640400	0.55175500	-2.46190800
C	-4.76720100	-0.79256900	-3.31161600
H	-5.47667700	-1.26414900	-3.99581500
C	0.99466700	3.62856100	-2.30291100
H	2.07987300	3.66560500	-2.43034000
C	-2.91051300	3.78758900	2.48846600
H	-2.62917000	4.78658100	2.83140400
C	-1.20932700	4.54059900	-2.73793700
H	-1.84499900	5.29923900	-3.20147500
C	-4.25015900	1.78802200	2.71469500
H	-5.02388500	1.21614200	3.23374000
C	0.18339300	4.60721500	-2.88566100
H	0.63216100	5.41866700	-3.46382300
C	-3.89796300	3.06638900	3.16796000
H	-4.39296100	3.49631400	4.04177100
Cl	2.57652800	-2.32164800	1.96697400
Cl	1.21053000	-1.13808600	-1.94054200
C	-0.93345300	-3.14595000	0.01806500
C	-0.07363700	-4.40749600	0.22550200
C	-2.42693400	-3.44692000	0.19281100
H	-0.76902900	-2.81415000	-1.02396600
C	-0.50968700	-5.51270500	-0.74681400
H	-0.18509000	-4.74434400	1.27212400
H	0.98747400	-4.14922000	0.08737400

C	-2.85418800	-4.54162300	-0.79850800
H	-2.62932600	-3.79860700	1.22188200
H	-3.01668700	-2.52893600	0.02674200
C	-2.01128800	-5.81453900	-0.62709300
H	0.08301300	-6.42374600	-0.56416300
H	-0.28211000	-5.19091300	-1.77962500
H	-3.92561300	-4.76549600	-0.66830500
H	-2.73900400	-4.15497500	-1.82782800
H	-2.31114300	-6.57277600	-1.36922400
H	-2.21525900	-6.25061800	0.36882900
C	3.83488900	0.67491600	-0.49436800
C	4.60035500	2.00240300	-0.42690600
C	4.78875900	-0.52888600	-0.37131200
H	3.34594000	0.59735100	-1.48525400
C	5.67329000	2.05183200	-1.52865200
H	5.09531900	2.10036000	0.55749600
H	3.90385800	2.85304800	-0.53071400
C	5.87563700	-0.47196900	-1.45323100
H	5.23992500	-0.51861400	0.63697000
H	4.20705000	-1.46007900	-0.44651700
C	6.63706000	0.86109200	-1.42399600
H	6.22475000	3.00441800	-1.46862400
H	5.17778100	2.03605500	-2.51700000
H	6.57106700	-1.31693500	-1.32372900
H	5.40291700	-0.60243100	-2.44393000
H	7.37894500	0.89980100	-2.23849700
H	7.20326700	0.93688700	-0.47696400

Table S16: Optimized XYZ coordinates for complex **7b**

C	1.21209800	2.41649500	-0.00038800
C	-1.21205000	2.41645800	-0.00040600
C	-1.21534800	3.81680600	-0.00066300
C	-0.00001900	4.51417300	-0.00078700
C	1.21533100	3.81684700	-0.00065200
H	-2.16924700	4.34675100	-0.00075600
H	-0.00003400	5.60497100	-0.00098200
H	2.16920900	4.34683200	-0.00073700
C	-2.32009700	1.49935300	-0.00034400
H	-3.35264700	1.86163800	-0.00055900
C	2.32014400	1.49941200	-0.00016200
Ru	0.00007200	-0.13264900	0.00018100
N	0.00002500	1.74919500	-0.00028000
N	2.02184500	0.21533500	0.00013600
N	-2.02184800	0.21529200	-0.00011600
Cl	-0.00009200	-0.67987900	2.30558000
Cl	-0.00001900	-0.68194600	-2.30477000
H	3.35270600	1.86164500	-0.00023400
C	3.08829000	-0.80026800	0.00035300
C	3.94687800	-0.73293000	-1.27655200
C	3.94811600	-0.73141100	1.27633100
H	2.56068600	-1.76941500	0.00120400
C	5.00369600	-1.84784600	-1.26862700
H	4.45041200	0.25019900	-1.32497200
H	3.28790300	-0.80674600	-2.15573800
C	5.00485000	-1.84641500	1.26869600
H	4.45183100	0.25170200	1.32312900
H	3.29000900	-0.80415300	2.15625800
C	5.86899500	-1.79590300	-0.00038900

H	5.63228300	-1.77187300	-2.17078800
H	4.49470700	-2.82767900	-1.32463100
H	5.63426000	-1.76950400	2.17020200
H	4.49584300	-2.82615100	1.32621900
H	6.59663600	-2.62388900	-0.00025500
H	6.45820000	-0.85956600	-0.00117600
C	-3.08831500	-0.80027500	-0.00016800
C	-3.94717100	-0.73244500	1.27653400
C	-3.94788100	-0.73185900	-1.27634700
H	-2.56074800	-1.76944200	-0.00057000
C	-5.00398800	-1.84736500	1.26879900
H	-4.45072400	0.25069800	1.32447800
H	-3.28838800	-0.80592500	2.15589200
C	-5.00465000	-1.84682700	-1.26852700
H	-4.45154900	0.25125600	-1.32360300
H	-3.28958600	-0.80495100	-2.15610400
C	-5.86903900	-1.79586000	0.00037300
H	-5.63275100	-1.77107800	2.17081000
H	-4.49501000	-2.82717900	1.32523900
H	-5.63388900	-1.77020200	-2.17017800
H	-4.49566000	-2.82659600	-1.32562600
H	-6.59669000	-2.62383700	0.00038800
H	-6.45823400	-0.85951600	0.00072200

Table S17: Optimized XYZ coordinates for complex **8c**

Ru	0.06804800	-0.36572300	-0.21789000
N	-1.95421100	-0.17551600	0.14855900
N	-0.03694000	1.49139700	0.08690800
N	2.04080200	0.15957500	-0.49517300
C	-2.30718900	1.06757400	0.41586000
H	-3.34804600	1.34239700	0.61864000
C	-1.26601700	2.05431200	0.40616900
C	2.25099600	1.45681300	-0.35209500
H	3.24676000	1.89344000	-0.48604400
C	1.11703800	2.26027100	-0.00967800
C	-1.34674100	3.42830200	0.65504700
H	-2.31374600	3.86747500	0.90618100
C	1.03750600	3.63780000	0.23459000
H	1.94410900	4.24117700	0.16109600
C	-0.19102500	4.22002300	0.56893600
H	-0.25080800	5.29214100	0.76070500
Cl	-0.37992100	-0.47988000	-2.57641700
C	3.19489400	-0.72436300	-0.74378600
C	3.68824400	-1.25323200	0.61319100
C	2.79599000	-1.85856900	-1.68859400
H	4.06424000	-0.43148100	1.24155600
H	2.03295100	-2.50061300	-1.21925300
C	-3.00974700	-1.21317000	0.03039700
C	-3.90400700	-0.91671800	-1.18487900
C	-2.36224400	-2.59323100	-0.09014800
H	-4.42987100	0.04397900	-1.08070400
H	-1.66274200	-2.78874900	0.73524300
H	-3.28509600	-0.87729800	-2.09349900
H	-3.13772900	-3.37390900	-0.08228700

H	-3.61708700	-1.17152600	0.95553600
H	3.99353500	-0.12188400	-1.21925800
H	2.37627000	-1.46976600	-2.62588100
H	2.85486000	-1.73395700	1.14731900
H	3.67538200	-2.48155200	-1.91224200
H	-4.65895600	-1.70969900	-1.29772000
H	-1.80860800	-2.66560000	-1.03976800
H	4.50043900	-1.98109400	0.46301600
O	0.51576700	-1.23556400	1.49728900
C	-0.29250400	-1.17522000	2.65647500
H	-0.43234000	-0.11908700	2.96546100
H	-1.30778700	-1.59253400	2.48262600
C	0.39913600	-1.95590300	3.77146100
H	1.39266200	-1.52957700	3.97561900
H	-0.19612500	-1.92727200	4.69846300
H	0.53260200	-3.00703500	3.47341900

Table S18: Optimized XYZ coordinates for complex **TS-9c**

C	-1.39021600	2.01541000	-0.43529100
C	-1.53720500	3.41440600	-0.53761500
C	-0.39437800	4.21573600	-0.51961700
C	0.88523200	3.64370100	-0.38148700
C	0.98180300	2.25224100	-0.28527100
H	-2.53231200	3.85738100	-0.60586800
H	-0.49417000	5.30026700	-0.59380500
H	1.78027700	4.26660600	-0.34387300
C	2.18744600	1.43802100	-0.14821300
H	3.16902900	1.92297200	-0.18766600
C	-2.40236700	0.99860300	-0.32282900
H	-3.46408200	1.25963500	-0.32857200
C	3.22675100	-0.74938600	0.01687000
H	2.99993000	-1.48490300	-0.77607600
C	3.23519100	-1.47648700	1.36954200
H	2.25195600	-1.92194500	1.57405600
H	4.00310300	-2.26478000	1.36447900
H	3.45529600	-0.76870700	2.18318400
C	4.57555900	-0.09823900	-0.29537400
H	4.57259100	0.41272300	-1.27088600
H	4.87548600	0.62110800	0.48420700
H	5.34816300	-0.88010800	-0.33041000
C	-3.02713000	-1.28018000	0.19317500
H	-2.47728100	-2.23239200	0.19075500
C	-3.55899800	-1.04696300	1.61372300
H	-4.15438700	-0.12133700	1.66526100
H	-4.20230000	-1.88825100	1.91449300
H	-2.72085600	-0.96041300	2.32003800
C	-4.13536000	-1.35783700	-0.86395700

H	-4.77091400	-0.45828500	-0.86625300
H	-3.71168700	-1.48457000	-1.87160000
H	-4.78617800	-2.21903200	-0.64925500
N	2.05820800	0.14685100	-0.02559900
N	-0.13680000	1.48691400	-0.34815800
N	-1.99834700	-0.25321000	-0.12839200
Ru	0.01295900	-0.49408900	-0.02852000
H	-1.14390600	-2.43539200	-1.45662200
C	-0.05425600	-2.26759400	-1.32084000
C	0.75176200	-3.54875100	-1.22496700
O	0.46580200	-1.23602800	-1.94578100
Cl	-0.04821500	0.01096100	2.34705300
H	0.14246400	-2.03275500	0.52529200
H	1.77424400	-3.35400800	-0.87360200
H	0.27300800	-4.27102700	-0.54765000
H	0.81113800	-4.00096400	-2.23045900

Table S19: Optimized XYZ coordinates for complex **10c**

Ru	-0.00004400	-0.39083900	0.01735800
N	-2.04583700	0.02899800	0.05241200
N	0.00024300	1.55161500	0.01484000
N	2.04583100	0.02841800	0.05236400
C	-2.31272400	1.32304000	0.02622500
H	-3.34574500	1.68830300	0.05440300
C	-1.20014500	2.23413800	-0.01773400
C	2.31312800	1.32237000	0.02610400
H	3.34626300	1.68731800	0.05421900
C	1.20082200	2.23379500	-0.01781600
C	-1.21343200	3.63376400	-0.08256500
H	-2.16828000	4.16181300	-0.11109400
C	1.21451700	3.63341500	-0.08266000
H	2.16951600	4.16118700	-0.11124800
C	0.00064200	4.33329000	-0.11175400
H	0.00079800	5.42320000	-0.16170500
Cl	-0.00039900	-2.74535800	-0.44984300
C	3.20323400	-0.89117800	0.15528900
C	3.02655400	-1.80402800	1.37277900
C	3.35622600	-1.67596700	-1.15327000
H	2.91028600	-1.21108900	2.29234400
H	2.46897800	-2.29980100	-1.33016900
C	-3.20353100	-0.89023500	0.15531300
C	-3.35682300	-1.67483600	-1.15332200
C	-3.02707700	-1.80327200	1.37269500
H	-3.48914600	-0.99101800	-2.00571600
H	-2.91053700	-1.21047100	2.29231400
H	-2.46975800	-2.29889500	-1.33034700
H	-3.91437000	-2.44599400	1.48122800

H	-4.10915100	-0.26935700	0.30558900
H	4.10906100	-0.27057300	0.30545400
H	3.48868700	-0.99228000	-2.00574700
H	2.13909100	-2.44002800	1.24853300
H	4.24147100	-2.32766200	-1.09072700
H	-4.24224700	-2.32628800	-1.09079300
H	-2.13984300	-2.43956500	1.24831500
H	3.91363400	-2.44704300	1.48131400
H	-0.00000400	-0.39274000	1.58438700

Table S20. Optimized XYZ coordinates for complex **TS-11c**

C	4.68355800	-0.00028100	0.51826400
C	3.99337800	-1.21330600	0.40678400
C	2.61991000	-1.20274300	0.11881600
C	2.63182900	1.19963900	0.07161300
C	4.00413600	1.21495100	0.35340000
C	1.72815000	-2.30763100	-0.08804600
C	1.73577500	2.31401700	-0.10220800
H	2.11068700	3.33929600	-0.04658700
H	2.09642600	-3.33781500	-0.09608900
H	5.75130700	-0.00059700	0.74366400
H	4.50597400	-2.16708100	0.54388000
H	4.52269500	2.16992600	0.45447100
N	0.46797100	2.03874200	-0.32378700
N	0.46122500	-2.00866100	-0.34277300
N	1.96557700	0.00186300	-0.05101600
Ru	0.05832500	-0.00815800	-0.29632200
C	-0.50780300	3.12723500	-0.53638700
H	-1.35048800	2.87875200	0.12797600
C	-1.01830700	3.04001200	-1.98224400
H	-1.87889700	3.71213700	-2.11697200
H	-0.22477800	3.33200600	-2.68906500
H	-1.32586600	2.01211100	-2.21939600
C	-0.02057700	4.53604600	-0.19005100
H	0.35230800	4.59480700	0.84414800
H	0.76913400	4.88721700	-0.87478800
H	-0.86554800	5.23456100	-0.28096700
C	-0.46007400	-3.11093100	-0.71673100
H	-1.40495700	-2.60437300	-0.96234000
C	0.01323600	-3.84423100	-1.97811000

H	0.94201700	-4.40798000	-1.79776700
H	-0.75531500	-4.55980600	-2.30888000
H	0.19451300	-3.12582100	-2.79091400
C	-0.69068900	-4.05386200	0.47203000
H	0.21659400	-4.63456500	0.70235900
H	-0.96418900	-3.48610800	1.37399200
H	-1.49881600	-4.76534900	0.24228400
Cl	-0.35874400	0.18856700	2.28561400
C	-2.84680400	-0.83126900	0.44650200
H	0.05859700	-0.01407100	-1.89181100
O	-2.16263000	-0.11752900	-0.51356600
H	-2.21490400	-1.61198900	0.89759200
O	-3.39301600	1.87200500	0.02739900
H	-4.24879300	1.99123700	-0.41416600
H	-2.78965900	1.01815100	-0.47971100
O	-3.15471400	0.08976900	1.62390600
H	-2.20394300	0.23293600	2.02823000
H	-3.41464400	1.05598900	1.04615500
C	-4.18153000	-1.37407200	-0.03342400
H	-4.00509000	-2.09194000	-0.84714700
H	-4.71836600	-1.87607000	0.78363200
H	-4.80928500	-0.56125300	-0.42916000

Table S21: Optimized XYZ coordinates for complex **12c**

C	-4.44866800	-1.18403600	0.29413400
C	-4.10593700	0.16935300	0.17518100
C	-2.76496500	0.52784300	-0.02093700
C	-2.12211800	-1.79367400	0.03074200
C	-3.45712300	-2.17210600	0.22735600
C	-2.18643400	1.83614400	-0.17531600
C	-0.94717900	-2.62330000	-0.04950200
H	-1.02346900	-3.70938800	0.05001400
H	-2.80944700	2.73467100	-0.16777900
H	-5.49064300	-1.46899900	0.44834500
H	-4.86608500	0.94991500	0.23892900
H	-3.70660700	-3.22917900	0.33425200
N	0.20374200	-2.01039200	-0.24300700
N	-0.87636900	1.88347500	-0.34721900
N	-1.80183700	-0.45944100	-0.10401700
Ru	0.02668600	0.05349700	-0.30039100
C	1.46050200	-2.77870500	-0.36579600
H	2.20308400	-2.17428800	0.18110500
C	1.86557600	-2.79951600	-1.84815800
H	2.88966900	-3.18567800	-1.96267500
H	1.18023000	-3.43968500	-2.42658100
H	1.80850200	-1.78833800	-2.27887000
C	1.43556400	-4.18361300	0.23986300
H	1.09290600	-4.15859300	1.28518400
H	0.79527100	-4.87661700	-0.33007000
H	2.45467100	-4.59784600	0.22718200
C	-0.18332100	3.18366900	-0.49338000
H	0.75891500	2.92625900	-1.00241500
C	-0.93896800	4.20458000	-1.35098700

H	-1.84347700	4.58367700	-0.84931000
H	-0.28866100	5.07136100	-1.54336400
H	-1.22940800	3.76998100	-2.31944300
C	0.15258800	3.72041900	0.90674800
H	-0.76426400	4.04582000	1.42415500
H	0.62149800	2.93563400	1.51845300
H	0.83374100	4.58199900	0.83027100
Cl	0.55117200	0.14704300	2.19899600
O	3.30302400	-0.26278700	1.06247800
C	3.15246900	0.92160000	0.36115800
H	2.70234000	1.71173400	0.98513900
H	0.01886600	0.02519200	-1.90992200
H	2.48301000	-0.33084400	1.63011800
O	2.14996700	0.78910800	-0.72189200
H	2.52447100	0.17799600	-1.38224600
C	4.48068000	1.33657900	-0.24046000
H	4.36554800	2.23893300	-0.85629200
H	5.20321100	1.53532100	0.56301800
H	4.88333600	0.51989900	-0.86177800

Table S22: Optimized XYZ coordinates for complex **TS-13c**

C	4.00079200	-2.26648300	-0.20140300
C	2.78541100	-2.96362300	-0.19190700
C	1.58416800	-2.24120400	-0.20181500
C	2.79567200	-0.16974300	-0.20913200
C	4.01256600	-0.86455100	-0.20107000
C	0.22676700	-2.73295600	-0.19479600
C	2.57026100	1.25781300	-0.14759100
H	3.41389900	1.94952100	-0.07456000
H	0.02694600	-3.80834900	-0.21124100
H	4.94282800	-2.81705700	-0.19143800
H	2.76160800	-4.05434700	-0.16377700
H	4.95219500	-0.31002400	-0.17700500
N	1.32289100	1.67215300	-0.15458100
N	-0.74304200	-1.84428100	-0.19961800
N	1.61577600	-0.87152100	-0.23968800
Ru	-0.04456000	0.12748900	-0.16433600
C	0.97717000	3.10365200	-0.02904500
H	0.13142200	3.09910300	0.67870500
C	0.45207900	3.60946700	-1.38155400
H	0.15157500	4.66408700	-1.28765600
H	1.23453900	3.53655000	-2.15396800
H	-0.42711400	3.02783000	-1.68513100
C	2.09663000	3.98675000	0.52523700
H	2.49153300	3.58910100	1.47244500
H	2.92855900	4.10753500	-0.18844000
H	1.69195800	4.99017400	0.72298700
C	-2.15429500	-2.29889500	-0.17854800
H	-2.71530300	-1.48906700	-0.66919700
C	-2.41769100	-3.59823100	-0.94711900

H	-2.00248400	-4.48552500	-0.44220700
H	-3.50480300	-3.74972400	-1.02184800
H	-2.01087600	-3.54925700	-1.96905000
C	-2.60470300	-2.39083800	1.28871300
H	-2.12635600	-3.25133400	1.78461700
H	-2.32034200	-1.48517400	1.84322400
H	-3.69675600	-2.51831400	1.33601500
Cl	-0.01669500	0.16771700	2.24594800
O	-3.71599100	0.42479700	-1.07737900
C	-3.03665600	1.11793600	-0.00818800
H	-3.02560400	0.38050400	0.81484200
H	-0.37089600	0.26060700	-1.87984300
H	-3.75190000	1.05701400	-1.81734900
O	-1.74691300	1.50409100	-0.36994900
H	-1.08289500	0.72999200	-1.46203400
C	-3.80984600	2.36730000	0.41110700
H	-4.85161800	2.11200300	0.65505300
H	-3.33323500	2.82906400	1.28750900
H	-3.79849800	3.10044100	-0.41251000

Table S23: Optimized XYZ coordinates for complex **14c**

Ru	0.08008800	-0.44114400	-0.28730400
N	-1.95326800	-0.16219700	-0.04817700
N	0.01007600	1.43969400	-0.23956700
N	2.07789900	-0.00299000	-0.53272900
C	-2.28057400	1.11004200	0.04369000
H	-3.31925200	1.43114200	0.17863900
C	-1.21266800	2.06398000	-0.05600000
C	2.31462300	1.29630900	-0.55167700
H	3.32703200	1.69183200	-0.68982400
C	1.18536700	2.16247800	-0.38198600
C	-1.26995800	3.45959500	-0.00649800
H	-2.23467900	3.94712300	0.14255300
C	1.13319900	3.56296700	-0.34073800
H	2.05788900	4.13095400	-0.45770200
C	-0.09285800	4.20972400	-0.15082400
H	-0.13412100	5.29917200	-0.11598500
Cl	-0.25419800	-0.90210700	-2.61922800
C	3.22055600	-0.93372300	-0.59744500
C	3.61787100	-1.30619900	0.84045900
C	2.85158000	-2.16507600	-1.42575300
H	3.97768500	-0.42275300	1.38966700
H	2.05486400	-2.74145200	-0.92828300
C	-3.03239400	-1.18006600	-0.05546600
C	-3.77894900	-1.13187700	-1.39855800
C	-2.43493700	-2.56472000	0.19736100
H	-4.25033500	-0.15108200	-1.56072900
H	-1.85703600	-2.59573200	1.13203700
H	-3.07239400	-1.31583600	-2.22128400
H	-3.23767700	-3.31493200	0.25724700

H	-3.73301300	-0.92681400	0.76368700
H	4.06294800	-0.40790200	-1.08797300
H	2.48580400	-1.88180200	-2.42161300
H	2.74392300	-1.70533400	1.37674700
H	3.73083600	-2.81892500	-1.52947400
H	-4.56561400	-1.90159000	-1.41732100
H	-1.76733300	-2.84326100	-0.63428300
H	4.41823400	-2.06177000	0.82617600
O	0.42677700	-0.96525100	1.60624600
C	-0.40564600	-0.59584600	2.66283000
H	-1.47462900	-0.81350500	2.46384100
O	-0.39336900	0.82363500	2.85885300
H	0.54956900	1.06448400	2.91440600
C	0.06251300	-1.34240800	3.91275000
H	-0.53359100	-1.03504500	4.78413000
H	-0.03131200	-2.42952300	3.77209600
H	1.12311900	-1.11097700	4.10113400

Table S24: Optimized XYZ coordinates for complex **TS-15c**

C	-0.12759300	4.20795700	-1.05225400
C	1.10297800	3.55277200	-0.94537100
C	1.11750700	2.18405800	-0.61082600
C	-1.26926000	2.16194200	-0.48460800
C	-1.33189700	3.52258400	-0.81094900
C	2.24118400	1.31931900	-0.34755900
C	-2.35947900	1.25279600	-0.15834700
H	-3.39222200	1.61998700	-0.15663900
H	3.26302800	1.70851200	-0.37894600
H	-0.15339600	5.26890200	-1.30796000
H	2.04038100	4.09079700	-1.09714400
H	-2.29316700	4.03597300	-0.86660400
N	-2.06885900	0.01048500	0.13499800
N	1.98928600	0.06401000	0.01025300
N	-0.06619600	1.53163100	-0.42804100
Ru	-0.00195100	-0.39325500	0.13629900
C	-3.15643200	-0.94843300	0.44389200
H	-2.64176900	-1.77374900	0.95876400
C	-3.74240900	-1.46622400	-0.87879200
H	-4.41389000	-2.31858500	-0.69335400
H	-4.32115700	-0.67231500	-1.37819000
H	-2.93686700	-1.77879600	-1.55855900
C	-4.22015000	-0.38611700	1.39303000
H	-3.74774700	0.03949600	2.29013200
H	-4.84257000	0.38675500	0.91447600
H	-4.89368000	-1.19850500	1.70508800
C	3.12842300	-0.77419100	0.48181500
H	2.72275300	-1.79465200	0.51206200
C	4.33005400	-0.75645700	-0.47301300

H	4.85159100	0.21345100	-0.47218200
H	5.05626100	-1.52000900	-0.15684600
H	4.03448300	-0.98137800	-1.51044200
C	3.50717200	-0.35894300	1.90921000
H	3.95147000	0.64975200	1.91732600
H	2.61481600	-0.34821800	2.55040800
H	4.24316700	-1.06688100	2.32056600
Cl	-0.05101500	0.29057900	2.44723100
O	1.53897000	-2.70325400	-1.35711800
C	0.21820100	-2.38757200	-1.13554300
H	0.06795000	-1.91767900	0.78098500
H	1.92455200	-1.90613700	-1.77105500
O	-0.28917200	-1.38670000	-1.76194800
C	-0.57872200	-3.63446900	-0.82555400
H	-0.70917500	-4.19426000	-1.76744900
H	-0.04579200	-4.26941100	-0.10806500
H	-1.56141000	-3.36706000	-0.42517600

Table S25: Optimized XYZ coordinates for complex **TS-16c**

C	-1.37337400	1.86756300	-0.77075800
C	-1.46609200	3.13971200	-1.35201700
C	-0.29010400	3.85468600	-1.62076900
C	0.96105600	3.31007800	-1.29956400
C	1.02178900	2.03455500	-0.72013200
H	-2.44606000	3.56445200	-1.57631100
H	-0.34999800	4.84748000	-2.06973500
H	1.88090600	3.86815200	-1.48290000
C	2.17984900	1.28155400	-0.30040600
H	3.18427100	1.69365000	-0.42926200
C	-2.43236300	0.97559300	-0.35616100
H	-3.48081300	1.26561500	-0.46864100
C	3.11499500	-0.72225500	0.71133000
H	2.86021000	-1.75354500	0.41614500
C	3.13530000	-0.67073500	2.24590900
H	2.14919400	-0.92566100	2.65631700
H	3.88706300	-1.37743600	2.62968300
H	3.39110700	0.34243800	2.59264500
C	4.47442400	-0.36964500	0.10122600
H	4.43712300	-0.35756100	-0.99945300
H	4.85073700	0.60400600	0.45421400
H	5.20963200	-1.12840700	0.40727400
C	-3.09540200	-1.13393100	0.66194500
H	-2.62193500	-1.58588600	1.54873600
C	-4.42458600	-0.50504400	1.08931700
H	-5.00296000	-0.12098100	0.23317900
H	-5.04273800	-1.27435700	1.57553800
H	-4.26449600	0.31127300	1.80937400
C	-3.28160800	-2.22184400	-0.40797800

H	-3.80563800	-1.80500000	-1.28344700
H	-2.31154600	-2.60969700	-0.74715700
H	-3.88374300	-3.04895600	-0.00251800
N	1.97423000	0.08696900	0.22203200
N	-0.13823400	1.33712400	-0.49429800
N	-2.07966500	-0.17237500	0.18164500
Ru	-0.03499400	-0.40662500	0.36793200
H	1.52531200	-1.25319500	-2.35681400
C	1.13134100	-2.19579600	-1.93301800
C	0.81012100	-3.19100400	-3.04175400
O	-0.06282900	-1.92504900	-1.19674300
Cl	-0.20119100	0.57773200	2.54311200
H	0.08588300	-2.07486000	1.05124400
H	0.02733000	-2.25739700	0.02122100
H	1.91734800	-2.60910400	-1.26928800
H	0.03784300	-2.78237800	-3.71031000
H	1.70948700	-3.41175900	-3.63939400
H	0.43272000	-4.13339800	-2.61701200

Table S26: Optimized XYZ coordinates for complex **4c**

Ru	-0.87748100	-0.16959700	-0.93286100
P	1.06063300	0.12968900	0.39142900
N	-1.18165700	-2.06781200	-0.21549300
N	-2.13932300	0.18690200	0.48232500
N	-1.22223200	1.90594000	-1.19433400
C	1.97602600	-1.39314700	0.93910500
C	-2.07160900	-2.12489100	0.75558700
H	-2.38063600	-3.08091600	1.20912500
C	2.55413600	1.11229100	-0.12476300
C	-2.64938300	-0.87577900	1.19100000
C	0.47721300	0.98227000	1.92113000
C	-2.08144200	2.36809700	-0.31075100
H	-2.43728700	3.41380700	-0.35341900
C	-2.62143000	1.45685600	0.66928500
C	-3.62056400	-0.66082800	2.18538400
H	-4.01662100	-1.51821500	2.74830300
C	2.45248000	-2.23664000	-0.08951500
H	2.21956200	-1.99310800	-1.14021300
C	-3.58209600	1.71371100	1.66359900
H	-3.94592200	2.74009300	1.81335400
C	2.94601400	1.16347400	-1.47769900
H	2.32316300	0.66521300	-2.23961700
C	-4.07515200	0.64554000	2.43147100
H	-4.83021800	0.82880300	3.20946900
C	2.30595800	-1.68733200	2.27784800
H	1.99190200	-1.01868300	3.09185800
C	3.21367900	-3.37145800	0.22419100
H	3.57558800	-4.02069400	-0.58796300
C	0.46825500	2.39368900	1.97591500

H	0.94859000	2.97460900	1.17487200
C	-0.18720300	0.26253400	2.94065200
H	-0.24745200	-0.83439700	2.89124400
C	3.38145100	1.69914400	0.85809600
H	3.10839800	1.63869700	1.92247600
C	3.06177000	-2.83155800	2.58489400
H	3.30774200	-3.05240300	3.63520800
C	3.51185700	-3.67989200	1.56171800
H	4.10517700	-4.57444100	1.80605200
C	-0.80086400	0.93643700	4.00645500
H	-1.31344300	0.35749900	4.78973400
C	4.13410500	1.81978400	-1.83972000
H	4.42832100	1.85434800	-2.90006900
C	-0.14815800	3.06438700	3.04375200
H	-0.13763700	4.16495500	3.07108200
C	4.56153300	2.36020200	0.48745900
H	5.19328700	2.82023200	1.26303600
C	-0.77841600	2.33921300	4.06646200
H	-1.26188500	2.86546600	4.90353100
C	4.93924500	2.42644400	-0.86398900
H	5.86730800	2.94351300	-1.15309300
Cl	-2.76205900	-0.49990600	-2.39969400
Cl	0.60123400	-0.89482900	-2.75121700
C	-0.82943300	2.86722900	-2.25942600
C	0.47117100	3.58488800	-1.88268900
C	-0.75864700	2.18544000	-3.62397600
H	0.37415800	4.11540700	-0.91329400
H	0.04788800	1.42740900	-3.64875400
C	-0.64825200	-3.32613800	-0.78623500
C	-0.29047900	-4.37424100	0.27134500

C	-1.62849000	-3.84999000	-1.84552900
H	0.34257600	-3.94339900	1.07272200
H	-2.56938000	-4.20360600	-1.37375600
H	-1.18707300	-4.83870000	0.73285800
H	-1.88059100	-3.04601100	-2.56323600
H	0.26805800	-3.01412400	-1.32220200
H	-1.63537300	3.63666800	-2.29812600
H	-1.70505700	1.65626700	-3.84453200
H	1.31386300	2.87444200	-1.80864300
H	-1.16594100	-4.69792200	-2.38938400
H	0.28461600	-5.19116800	-0.20786300
H	-0.57066000	2.95019100	-4.40447400
H	0.72150300	4.33399000	-2.66019000

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Table S27: Optimized XYZ coordinates for transition state of dissociation of PPh₃ from **4c** to **7c**

Ru	2.02291500	-0.44598000	-0.25198500
P	-1.62442900	0.11006400	-0.19659300
N	2.41147800	1.55286200	-0.00329800
N	1.34021500	-0.20629200	1.48398800
N	1.30046200	-2.33023200	0.09514500
C	-2.79543100	-0.63377400	-1.43131100
C	2.06167600	1.99322000	1.19397700
H	2.18600600	3.04371000	1.49933500
C	-2.46139200	-0.19977400	1.41917400
C	1.44493700	1.03825500	2.07819600
C	-1.93368000	1.91084700	-0.52428000
C	0.78228700	-2.45689300	1.30644300
H	0.36674500	-3.41726600	1.65860900
C	0.76530100	-1.28185600	2.13565000
C	0.93494700	1.22844900	3.37378200
H	1.00932700	2.22155100	3.83965900
C	-2.27393900	-0.85280300	-2.72587200
H	-1.22035600	-0.60417200	-2.93583400
C	0.25480000	-1.11013800	3.43378600
H	-0.22039700	-1.96058300	3.94171200
C	-2.62419100	0.79968100	2.40261000
H	-2.35124300	1.84124400	2.17609700
C	0.33929100	0.14897900	4.04954700
H	-0.07214400	0.29204000	5.05844600
C	-4.14469700	-0.95344300	-1.16976700
H	-4.56676300	-0.78557100	-0.16697200
C	-3.09067700	-1.37989300	-3.73800800
H	-2.67236400	-1.54518500	-4.74301200

C	-3.18168800	2.53894400	-0.31848300
H	-4.02671800	1.96077500	0.08737900
C	-0.87202700	2.65748700	-1.07487800
H	0.08886300	2.15797200	-1.27013100
C	-2.79329700	-1.53426800	1.75855000
H	-2.65367200	-2.33563600	1.01500800
C	-4.95454800	-1.48927200	-2.18356400
H	-6.00587200	-1.73633300	-1.96744000
C	-4.43059900	-1.70393100	-3.46896200
H	-5.06830800	-2.12459100	-4.26182800
C	-1.05074100	4.01238700	-1.40236100
H	-0.21840600	4.58164700	-1.84504200
C	-3.12885800	0.48010600	3.67408800
H	-3.25168700	1.27748100	4.42369500
C	-3.35344700	3.89454900	-0.63326900
H	-4.32974500	4.37549800	-0.46527200
C	-3.30032800	-1.85030800	3.02615200
H	-3.56355800	-2.89314900	3.26302400
C	-2.28731200	4.63499300	-1.17440100
H	-2.42693200	5.69736300	-1.42776500
C	-3.47357200	-0.84218300	3.99145100
H	-3.87376700	-1.08938300	4.98664900
Cl	4.07770800	-1.03419600	0.62655800
Cl	1.45649900	-0.16450100	-2.53880600
C	1.30808300	-3.51601200	-0.78515400
C	0.12135200	-3.44478500	-1.75590400
C	2.64836500	-3.62661500	-1.51550000
H	0.09225100	-4.35848700	-2.38314300
H	3.49446900	-3.63769400	-0.80207100
C	3.02114100	2.44076200	-1.01183900

C	2.91798700	3.93569900	-0.70521500
C	4.47086300	2.00209400	-1.26444400
H	1.87325500	4.24952500	-0.50645400
H	5.09043600	2.15326300	-0.35725800
H	3.54553200	4.23032500	0.16201600
H	4.51890900	0.93064800	-1.53481500
H	2.44748500	2.21931800	-1.94042600
H	1.17949000	-4.41221300	-0.13363400
H	2.66951000	-4.55727500	-2.11704800
H	-0.84090000	-3.36343800	-1.21200000
H	0.22162800	-2.56169600	-2.41559100
H	4.90100700	2.59718900	-2.09439700
H	3.28175800	4.51046400	-1.57952600
H	2.78407800	-2.76473500	-2.19955400

Table S28: Optimized XYZ coordinates for complex **7c**

C	1.19751200	2.03775300	-0.04893400
C	-1.23404800	2.00555100	-0.06232400
C	-1.25496800	3.41067200	-0.08964100
C	-0.04587400	4.12777000	-0.09593600
C	1.18199000	3.44253900	-0.07445300
H	-2.22419500	3.92978600	-0.10048100
H	-0.06028000	5.22673600	-0.11610000
H	2.13736900	3.98683600	-0.07857600
C	-2.32519900	1.07033500	-0.02912600
H	-3.37329900	1.41139200	-0.02095100
C	2.31641500	1.13340000	-0.06633100
Ru	0.01272900	-0.50907400	0.01860200
N	-0.00838100	1.34777800	-0.04822600
N	2.02923600	-0.15769800	-0.04660200
N	-1.99118200	-0.21049600	0.00042000
C	3.06967800	-1.19497800	-0.16980400
C	4.43274500	-0.69239700	-0.65044300
C	3.17667500	-1.97540300	1.14876200
H	5.09641000	-1.56070400	-0.83045200
H	3.59425500	-1.33013200	1.94879500
C	-3.01943600	-1.27090700	0.03035800
C	-4.13736400	-0.99439100	1.04124900
C	-3.53181500	-1.53045200	-1.39342700
H	-3.71226800	-0.76905500	2.03923400
H	-4.21307200	-2.40480700	-1.40113500
Cl	-0.05990500	-0.87115400	2.31768000
H	2.18421100	-2.32527100	1.49120700
H	4.35243500	-0.12663800	-1.60037400

H	2.65623500	-1.87620500	-0.94759900
H	-4.09080300	-0.65059600	-1.77484800
H	-4.78815400	-0.15084900	0.73114400
H	3.84408700	-2.84996400	1.01654600
H	4.93370400	-0.05206000	0.10557400
H	-4.78482100	-1.88913300	1.13155000
H	-2.68087300	-1.72837500	-2.07435200
H	-2.47101800	-2.17419100	0.37135700
Cl	0.09087100	-1.36729300	-2.15006000
H	3.34800100	1.51208200	-0.13738700

Table S29: Optimized XYZ coordinates for complex **8e**

C	1.28836500	2.18559500	0.38769500
C	-5.60521300	0.11229500	-0.28868800
C	1.31156900	3.54645000	0.70139300
C	-4.90801800	-2.19646400	-0.74344600
C	0.11155900	4.25192200	0.86370000
H	-2.76911500	-2.62669500	-0.71680400
C	-1.11013100	3.58278600	0.70185700
C	-5.91323800	-1.21602000	-0.59515000
C	-1.12338000	2.22224500	0.38746300
H	-6.38677500	0.86729900	-0.18266000
H	2.27071900	4.05590800	0.81640600
H	-5.19659400	-3.21939000	-0.99265000
H	0.12780100	5.31346500	1.11116400
H	-6.95895300	-1.50060800	-0.72838000
H	-2.05404900	4.11972800	0.81726200
C	2.37869000	1.28143400	0.17903000
N	0.07030600	1.51022600	0.24693600
C	4.35879300	0.27199100	-0.05948100
Ru	0.04810100	-0.36762100	-0.15399000
C	3.30601900	-0.67265800	-0.21322600
C	5.70321900	-0.09809800	-0.16439400
C	3.58601300	-2.02071700	-0.46888200
O	0.18048000	-1.64418100	1.33199100
C	5.96571200	-1.44555300	-0.42522600
Cl	-0.00650500	-0.07948100	-2.54042500
H	6.51147100	0.62717700	-0.05073000
C	4.92644200	-2.39050800	-0.57339900
H	2.77067400	-2.73710200	-0.57677800

H	7.00273400	-1.77548000	-0.51575600
H	5.18183300	-3.43278300	-0.77422300
C	-2.24074100	1.35089900	0.17443000
N	2.09471100	-0.02105800	-0.06139200
C	-3.23212900	-0.55718800	-0.27510100
N	-2.00001500	0.03903500	-0.06349700
C	-4.25133600	0.42477600	-0.13348800
N	-3.59238300	1.61044200	0.15841100
N	3.74052100	1.48809200	0.19389600
C	-3.55769000	-1.88378600	-0.58673300
C	-0.88288100	-2.04340900	2.17991000
H	-1.06617400	-1.25363900	2.93755800
H	-1.83294200	-2.18556200	1.62543500
H	4.20238600	2.38314300	0.30470700
H	-4.01913800	2.52472500	0.25355300
C	-0.48932400	-3.34637400	2.87284300
H	0.44544100	-3.21009700	3.43671700
H	-1.27902400	-3.67551800	3.56769700
H	-0.32575100	-4.13949600	2.12722400

Table S30: Optimized XYZ coordinates for complex **TS-9e**

C	-1.23800000	2.23759100	-0.25657600
C	5.60540300	0.06284000	0.28112100
C	-1.27456800	3.64068700	-0.37103500
C	4.90241600	-2.27864500	0.50192000
C	-0.06510900	4.33939500	-0.42592500
H	2.76181500	-2.70019700	0.39781900
C	1.16171100	3.65802200	-0.36023600
C	5.90962300	-1.28718300	0.46533800
C	1.14077400	2.26080500	-0.23740600
H	6.38594800	0.82614900	0.26974000
H	-2.22523900	4.17548800	-0.41168200
H	5.18880600	-3.31861000	0.67019100
H	-0.07347000	5.42684100	-0.51787600
H	6.95267400	-1.58284800	0.59550400
H	2.10376200	4.20720500	-0.40305900
C	-2.31778100	1.28923100	-0.15926600
N	-0.03980300	1.58607500	-0.20141500
C	-4.29809000	0.28068500	0.08274200
Ru	-0.02904200	-0.44083400	-0.07014200
H	-1.29293000	-2.34364600	-1.57766500
C	-3.25151200	-0.68145800	0.11064600
C	-0.22543400	-2.03777700	-1.59840500
C	-5.64073900	-0.08433200	0.23126300
C	-3.53348300	-2.03780800	0.31647100
O	0.05023200	-0.87511800	-2.14359400
C	-5.90560700	-1.44217900	0.42053900
Cl	-0.01025300	-0.28535100	2.34992000
H	-6.44447100	0.65434700	0.20955800

H	0.01661400	-2.08956600	0.10740300
C	-4.86999900	-2.40264800	0.46791200
H	-2.71695500	-2.75872100	0.37679100
H	-6.94039300	-1.76831000	0.54405600
H	-5.12549200	-3.45068700	0.63561100
C	2.24518000	1.32870500	-0.12400900
N	-2.03709900	-0.03561100	-0.05969300
C	3.23501200	-0.60767700	0.13543600
N	2.00564800	0.00142000	-0.04094900
C	4.25321700	0.38519300	0.12390400
N	3.59234200	1.59161100	-0.04686300
N	-3.67735400	1.50636900	-0.09507600
C	3.55664600	-1.95567900	0.34161800
H	4.01520000	2.51297800	-0.04235400
H	-4.13136600	2.41232400	-0.09980500
C	0.73554900	-3.18433400	-1.86293800
H	0.53731900	-4.04853600	-1.21122600
H	0.60612400	-3.50229500	-2.91177200
H	1.77496500	-2.85295200	-1.73560800

Table S31: Optimized XYZ coordinates for complex **10e**

C	1.19776800	2.20608200	-0.02061400
C	-5.93010600	-1.44925600	0.05422800
C	1.21361200	3.60577600	-0.05247000
H	-6.44215300	0.66579100	0.02944400
C	0.00005800	4.30792500	-0.06629600
H	-5.17983700	-3.47993800	0.07745000
C	-1.21350200	3.60578500	-0.05260200
H	-6.97307800	-1.77306600	0.06606800
C	-1.19767700	2.20609000	-0.02068000
C	2.29524500	1.27789700	-0.00801700
H	2.16345000	4.14448600	-0.06699200
C	4.29419300	0.27670400	0.01933100
H	0.00006300	5.39827700	-0.09057800
H	-2.16333300	4.14450500	-0.06720100
C	3.25906600	-0.69815100	0.02424800
N	0.00004800	1.50740000	-0.00406400
C	5.64613500	-0.08175300	0.03386600
Ru	0.00006300	-0.44901500	0.02086200
C	3.55790400	-2.06706200	0.04571400
Cl	-0.00031900	-2.83092300	-0.24645100
C	5.93008500	-1.44938500	0.05429900
H	0.00033800	-0.39040900	1.58330700
H	6.44217600	0.66565800	0.03017900
C	-2.29519100	1.27793700	-0.00808700
C	4.90570100	-2.42331300	0.06033300
C	-3.25907600	-0.69808400	0.02454400
H	2.74288300	-2.79382600	0.04557000
C	-4.29417500	0.27679500	0.01915000

H	6.97304900	-1.77321800	0.06627200
H	5.17977000	-3.48005500	0.07681400
C	-3.55793700	-2.06698300	0.04631500
N	2.02834400	-0.05351300	0.00401200
C	-5.64612700	-0.08163300	0.03349300
N	-2.02833800	-0.05347900	0.00441200
C	-4.90574400	-2.42320500	0.06074000
N	-3.65308700	1.50708200	-0.00205500
H	-2.74292700	-2.79376300	0.04655500
N	3.65314200	1.50700900	-0.00170800
H	-4.09977900	2.41674600	-0.00746400
H	4.09985700	2.41666400	-0.00680600

Table S32. Optimized XYZ coordinates for complex **TS-11e**

C	-1.16038300	2.54641200	0.05433000
C	5.96432900	-0.89491400	-1.08474400
C	-1.17335700	3.90926100	0.37287800
H	6.44783400	1.14355300	-0.49879500
C	0.04044800	4.57901000	0.58005600
H	5.22530300	-2.84112200	-1.67772400
C	1.24730800	3.87494800	0.48704200
H	7.00534700	-1.16503200	-1.27339100
C	1.22469000	2.51392700	0.15637900
C	-2.26340300	1.65225000	-0.15830400
H	-2.12261600	4.43747500	0.48285200
C	-4.24906300	0.71906300	-0.58853000
H	0.04325200	5.63850200	0.83889300
H	2.19649700	4.37572200	0.68840800
C	-3.21981300	-0.25956900	-0.66619800
N	0.03248100	1.85677900	-0.08302900
C	-5.58899100	0.40012700	-0.83225100
Ru	0.00900300	-0.08477700	-0.25942800
C	-3.51402700	-1.58271500	-1.02168900
Cl	-0.01474900	-0.02575200	2.44536100
C	-5.86854900	-0.92657000	-1.16978100
H	0.02643200	-0.20541000	-1.84074100
H	-6.38041400	1.14982100	-0.77007100
C	2.31878900	1.60181000	-0.01301600
C	-4.84938900	-1.89960600	-1.26874500
C	3.28682700	-0.27379100	-0.60838500
H	-2.70798300	-2.31313500	-1.11188800
C	4.31591900	0.69259000	-0.42510900

H	-6.90245600	-1.21581800	-1.36945600
H	-5.11571900	-2.92062300	-1.54887200
C	3.60664300	-1.55553100	-1.07763600
N	-2.00217000	0.33981200	-0.37175600
C	5.66465100	0.39719700	-0.64705100
N	2.05750000	0.30332700	-0.30685000
C	4.95064600	-1.85141900	-1.30749500
N	3.67165600	1.85770100	-0.04601200
H	2.81765000	-2.27712600	-1.29003300
N	-3.61348800	1.90802500	-0.26522900
H	4.10579600	2.76002500	0.10983600
H	-4.05196800	2.81676300	-0.17129000
O	0.45038100	-2.97872300	2.05717100
C	0.66521800	-3.00032800	0.52342500
H	1.69435600	-2.61501300	0.42505100
H	0.67309000	-2.03840100	2.32734400
O	-0.25439100	-2.21873300	-0.11168700
H	-1.49789600	-2.26245100	0.84328300
C	0.55660800	-4.46704700	0.14432000
H	0.76257200	-4.57371100	-0.93042000
H	1.26723700	-5.07986600	0.71660000
H	-0.46602500	-4.82805300	0.33373500
O	-1.86919600	-2.36215200	1.81644900
H	-1.71438500	-1.43631200	2.15877400
H	-0.81813700	-2.81509800	2.11928900

Table S33: Optimized XYZ coordinates for complex **12e**

C	-1.17019300	2.55206100	-0.06962600
C	5.94597600	-1.09891800	-0.31780900
C	-1.18743700	3.94420200	0.08153400
H	6.45731500	0.98271500	0.05219500
C	0.02276300	4.63744900	0.21232600
H	5.19613900	-3.09276700	-0.70407200
C	1.23271800	3.93207300	0.19714000
H	6.98762800	-1.42671600	-0.32167700
C	1.21800900	2.54075800	0.03776500
C	-2.26901200	1.63624700	-0.17813300
H	-2.13801900	4.48074000	0.10729500
C	-4.27755900	0.66701700	-0.26005900
H	0.02251100	5.72131700	0.33351400
H	2.18239300	4.45911500	0.30846300
C	-3.25225900	-0.31960900	-0.30224400
N	0.02302100	1.85426900	-0.10940400
C	-5.63492700	0.33150300	-0.28412800
Ru	0.03175300	-0.06949400	-0.28897900
C	-3.58295600	-1.68164700	-0.33278300
Cl	-0.03575700	-0.57225600	2.23420000
C	-5.94504300	-1.02905500	-0.33817900
H	0.03016000	-0.01367300	-1.89322700
H	-6.41659500	1.09331500	-0.25301700
C	2.31628600	1.62084300	-0.02962700
C	-4.93639600	-2.01735000	-0.35236000
C	3.27479900	-0.33343700	-0.30708700
H	-2.80116600	-2.43951900	-0.26606200
C	4.31168300	0.61996500	-0.10747000

H	-6.99325800	-1.33497200	-0.35384700
H	-5.22534000	-3.07025600	-0.36231000
C	3.57809600	-1.68219200	-0.53298000
N	-2.01359400	0.31003900	-0.27387400
C	5.66120600	0.25229400	-0.10592100
N	2.04898900	0.31103800	-0.24420200
C	4.92316500	-2.04952500	-0.53280900
N	3.67455300	1.84006600	0.05390600
H	2.77034200	-2.39152600	-0.71559300
N	-3.62285900	1.88501600	-0.18453200
H	4.12012800	2.72768700	0.25467600
H	-4.05772900	2.79638800	-0.10027000
O	-1.02796500	-3.18030400	1.10423400
C	0.16048000	-3.27001500	0.40499200
H	1.02229700	-2.95228100	1.01640400
H	-0.94492500	-2.34155000	1.64536300
O	0.20464500	-2.28806400	-0.70604900
H	-0.51556200	-2.51626300	-1.32134900
C	0.32210600	-4.66751100	-0.16202600
H	1.23864800	-4.74504600	-0.76323200
H	0.36724700	-5.39363500	0.66137600
H	-0.54471300	-4.92391500	-0.79280900

Table S34: Optimized XYZ coordinates for complex **TS-13e**

C	1.07484200	2.20000600	0.40144600
C	-4.94747100	-2.33277700	-0.89608000
C	1.07886600	3.55665300	0.75278900
H	-2.78976700	-2.65679700	-1.00777700
C	-0.14259700	4.20269400	0.98194300
C	-5.98639900	-1.41948100	-0.60533300
C	-1.34723000	3.50111700	0.83391300
H	-6.52977000	0.58981600	0.02675100
C	-1.30859000	2.14675300	0.48019300
H	-5.20528700	-3.34282600	-1.22031600
H	2.01945200	4.10408500	0.83747900
H	-7.02407700	-1.74337600	-0.70870400
H	-0.15735200	5.25786900	1.25777200
C	2.18176400	1.33564700	0.08394000
H	-2.30315000	4.00806600	0.97845300
C	4.18124600	0.43387900	-0.35118700
N	-0.10617000	1.50162000	0.30417900
Ru	-0.09438800	-0.38393400	-0.30343800
C	3.16136100	-0.54473800	-0.50223800
H	1.60331100	-2.51282900	1.51619200
C	5.52967500	0.13416900	-0.57088000
C	0.85888000	-2.01155200	2.17713400
C	3.47348300	-1.85212400	-0.89452300
C	5.82597200	-1.17581300	-0.95387100
O	-0.30499400	-1.71136500	1.42432000
H	6.31410300	0.88435200	-0.45396000
Cl	-0.06635700	0.37044400	-2.57780100
C	4.81671500	-2.15149200	-1.11577200

H	-0.08419500	-2.09014700	-0.81820100
H	2.67557300	-2.58340800	-1.03158000
H	6.86638500	-1.45113000	-1.13820600
H	5.09843300	-3.15908100	-1.42729900
N	1.93418100	0.03342100	-0.21452400
C	-2.39449900	1.23754200	0.21749900
N	-2.11273800	-0.02761700	-0.16953200
C	-3.32530900	-0.66354600	-0.36538800
N	-3.75413200	1.43479700	0.28672200
C	-4.37642900	0.25083500	-0.07908500
N	3.53012600	1.60023000	0.02239600
C	-3.60686300	-1.97076100	-0.78134500
H	-0.20304600	-2.15645300	0.18107800
C	-5.72262200	-0.11193000	-0.19247000
H	3.96297800	2.50254000	0.18382900
H	-4.21516200	2.30020300	0.54305900
C	0.46436000	-2.92436000	3.32857700
H	1.34712500	-3.18244500	3.93146700
H	-0.26475900	-2.40018000	3.96297500
H	0.00379000	-3.84357700	2.94155300
O	1.43597900	-0.84490200	2.74260900
H	1.74486400	-0.32048700	1.98363400

Table S35: Optimized XYZ coordinates for complex **14e**

C	1.30563300	2.13061900	-0.15601200
C	-5.55762000	-0.11762800	-0.48524700
C	1.31038900	3.52777900	-0.14086200
C	-4.83156600	-2.46233900	-0.48029500
C	0.10408200	4.23562500	-0.19588800
H	-2.68399300	-2.85118300	-0.41891300
C	-1.10563100	3.52947600	-0.26059000
C	-5.84993100	-1.48396300	-0.50969100
C	-1.09903500	2.13469500	-0.27442000
H	-6.34926200	0.63383500	-0.51370900
H	2.26160600	4.06097200	-0.08202300
H	-5.10892500	-3.51779800	-0.51043500
H	0.10489600	5.32566100	-0.18338900
H	-6.89331400	-1.80226800	-0.55783000
H	-2.05688800	4.06455600	-0.29534600
C	2.41087000	1.22009100	-0.11587400
N	0.10112800	1.42492900	-0.23391700
C	4.40795000	0.21894600	-0.08736800
Ru	0.10290600	-0.48621400	-0.20849200
C	3.37218700	-0.75541400	-0.13567500
C	5.75906800	-0.13961400	-0.06343400
C	3.67813300	-2.12154100	-0.17124800
O	0.15294100	-0.85497700	1.76628700
C	6.04708200	-1.50653400	-0.09345600
Cl	0.17064100	-1.23053100	-2.49336400
H	6.55344800	0.60854000	-0.02643000
C	5.02526300	-2.48016000	-0.14864200
H	2.87716300	-2.85989200	-0.22764500

H	7.09019100	-1.82915900	-0.07801500
H	5.30010800	-3.53631000	-0.17856800
C	-2.20649600	1.22587100	-0.32641200
N	2.14949000	-0.10741200	-0.14803500
C	-3.17406800	-0.74325300	-0.39265600
N	-1.94970400	-0.10121400	-0.32410000
C	-4.20611900	0.23553500	-0.42632700
N	-3.55956000	1.46275800	-0.38338500
N	3.76733300	1.44970400	-0.07672800
C	-3.48376600	-2.10904600	-0.42288300
C	-0.95437500	-0.67927800	2.56900600
H	-1.86191900	-1.18028900	2.15240900
H	4.21468900	2.35875000	-0.06301600
H	-3.99949900	2.37461900	-0.42782700
C	-0.64093000	-1.24047400	3.95723300
H	0.23401300	-0.71208800	4.36172300
H	-1.49515400	-1.10545800	4.64100300
H	-0.41312300	-2.31452600	3.88992800
O	-1.22526500	0.74707000	2.64133000
H	-2.05170000	0.84001200	3.14556500

Table S36: Optimized XYZ coordinates for complex **TS-15e**

C	-1.16139600	2.33114800	-0.31383400
C	5.63556900	0.07098100	0.36268100
C	-1.17932600	3.71953800	-0.52691300
C	4.87755900	-2.22918500	0.76260100
C	0.04070500	4.39799600	-0.64531300
H	2.72712500	-2.60739600	0.66914400
C	1.25476400	3.70168300	-0.55031900
C	5.90696600	-1.26650800	0.65907000
C	1.22046100	2.31515800	-0.33701700
H	6.43362700	0.81371600	0.30277800
H	-2.12370500	4.26250400	-0.59891300
H	5.13729200	-3.25756200	1.02123700
H	0.04677500	5.47629900	-0.81205800
H	6.94144100	-1.57278200	0.82780200
H	2.20499700	4.23164200	-0.63907600
C	-2.25698900	1.41089800	-0.13743800
N	0.02650900	1.65531700	-0.23491400
C	-4.24887800	0.46071700	0.22489800
Ru	0.01643000	-0.34979700	-0.00889000
C	-3.22346400	-0.52475200	0.24913100
C	-0.14906600	-2.09967800	-1.64328400
C	-5.59125700	0.13495200	0.44573400
C	-3.52454400	-1.86713900	0.51800700
O	0.02738500	-0.90612400	-2.09123600
C	-5.87683100	-1.20823100	0.70168800
Cl	0.02602000	-0.20674800	2.38857300
H	-6.37854600	0.89127500	0.42974900
H	0.02400000	-2.02211100	0.11827500

C	-4.86262300	-2.19117400	0.73937700
H	-2.72393200	-2.60695900	0.55219200
H	-6.91198400	-1.50406500	0.88453900
H	-5.13450400	-3.22589800	0.95661200
C	2.30826400	1.37958300	-0.17548000
N	-2.00139400	0.08552300	0.00459300
C	3.25369500	-0.55683600	0.23754900
N	2.03876300	0.06318300	-0.00211400
C	4.29330000	0.41058900	0.16224200
N	3.66299100	1.61530600	-0.10726400
N	-3.60735200	1.66218800	-0.03131900
C	3.54117300	-1.89003900	0.55748100
H	4.10590000	2.52588000	-0.15233700
H	-4.03694000	2.58025900	-0.03587000
C	0.92892500	-3.15106300	-1.79694400
H	0.73472300	-4.02108900	-1.15745900
H	0.92245500	-3.47744700	-2.85006100
H	1.90644000	-2.71664700	-1.56434400
O	-1.39963400	-2.66934800	-1.74463500
H	-2.02109700	-1.92252600	-1.84621700

Table S37: Optimized XYZ coordinates for complex **TS-16e**

C	1.10370900	2.19179000	0.34573500
C	-4.90510200	-2.43502200	-0.65285100
C	1.10468000	3.56529300	0.62240800
H	-2.74503600	-2.75950900	-0.72328300
C	-0.11977400	4.22711800	0.78954500
C	-5.94784300	-1.50389400	-0.44528200
C	-1.32362500	3.52075100	0.66359700
H	-6.50017400	0.54893300	0.01643900
C	-1.28403100	2.14766500	0.38716100
H	-5.15813400	-3.46883000	-0.89594700
H	2.04529100	4.11441000	0.69670000
H	-6.98416600	-1.83767500	-0.52955500
H	-0.13587800	5.29658600	1.00351800
C	2.21155900	1.30348900	0.10784400
H	-2.28035000	4.03614500	0.76807300
C	4.21621000	0.37111100	-0.21780300
N	-0.07909900	1.49329900	0.25806500
Ru	-0.05718200	-0.42574100	-0.20809300
C	3.19103300	-0.60346100	-0.36438900
H	1.80510500	-2.20297500	1.76818600
C	5.56791700	0.05089200	-0.38176900
C	1.03075700	-1.70327100	2.38541600
C	3.50389800	-1.92823900	-0.69417500
C	5.86399000	-1.27579500	-0.70345900
O	-0.17690300	-1.52693500	1.64908900
H	6.35568900	0.79859700	-0.27019900
Cl	-0.05945200	0.11303700	-2.54689300
C	4.85064300	-2.24821900	-0.85956400

H	-0.03639400	-2.19527500	-0.52624000
H	2.70328800	-2.65724100	-0.82864400
H	6.90707600	-1.56676300	-0.84377300
H	5.13196900	-3.26972000	-1.12266900
N	1.96300200	-0.00342800	-0.14495600
C	-2.36638500	1.22074700	0.18450000
N	-2.07938900	-0.07180200	-0.09581000
C	-3.29029800	-0.72333600	-0.24784800
N	-3.72788100	1.41982500	0.22911100
C	-4.34525000	0.20884100	-0.04511000
N	3.56445700	1.55686900	0.08605300
C	-3.56605400	-2.06057000	-0.55837600
H	-0.12071600	-2.14355400	0.47171600
C	-5.68967400	-0.16603700	-0.13861200
H	3.99776200	2.46523100	0.20590200
H	-4.19199800	2.30496600	0.39679200
C	0.73490900	-2.53476200	3.62982500
H	1.64625100	-2.66982500	4.23526800
H	-0.02696100	-2.03781000	4.24894900
H	0.35133000	-3.52751500	3.34913400
H	1.44271400	-0.71563000	2.67221500

11. Arrhenius Plots

Calculation of Activation Energy (E_a)

To determine the activation energy using Arrhenius plot, the following rate law equation was employed as reported very recently by Qin and Zheng^{16c}. The evolution of gas recorded in 1 hour was used for the plot and rate constants at different reaction temperature (100-160 °C) were determined by good linear fitting using the below equation, where $[\text{EtOH}]_0$ and $[\text{H}_2\text{O}]_0$ refer to the initial concentration of ethanol and water, while $[\text{EtOH}]_t$ and $[\text{H}_2\text{O}]_t$ are the molar concentrations at time t .

$$\ln \frac{[\text{EtOH}]_t}{[\text{H}_2\text{O}]_t} = k([\text{EtOH}]_0 - [\text{H}_2\text{O}]_0) \cdot t + \ln \frac{[\text{EtOH}]_0}{[\text{H}_2\text{O}]_0} \dots\dots(1)$$

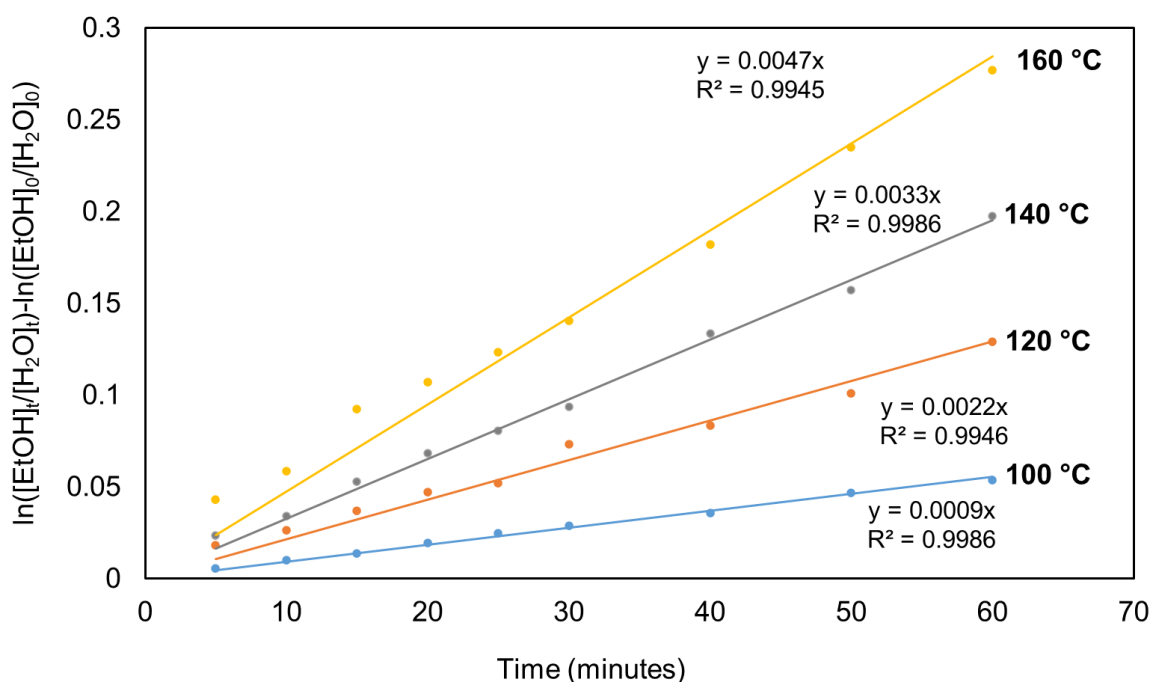


Figure S28. Plot for the calculation of rate constant by linear fitting based on eq 1. Reaction conditions : **4b** (0.2 mol%), EtOH (4.64 mmol) with H_2O (2.32 mmol) in the presence of KO^tBu (3.48 mmol) at 100 °C, 120 °C, 140 °C and, 160 °C. The H_2 evolved in first 1 hour of the reaction has been considered.

The value of rate constants at different temperature were obtained from the slopes of the graph shown in Figure S28 based on eq 1.

Further, Arrhenius equation (eq 2) was employed to obtain an activation energy (E_a) of 8.68 kcalmol⁻¹ by linear fitting of $\ln k$ versus $(1000/T)$,^{16c} where k = rate constant, R = gas constant (1.9872 calmol⁻¹K⁻¹) and T = temperature in K.

$$\ln k = \ln A - \frac{1000.E_a}{RT} \dots\dots\dots(2)$$

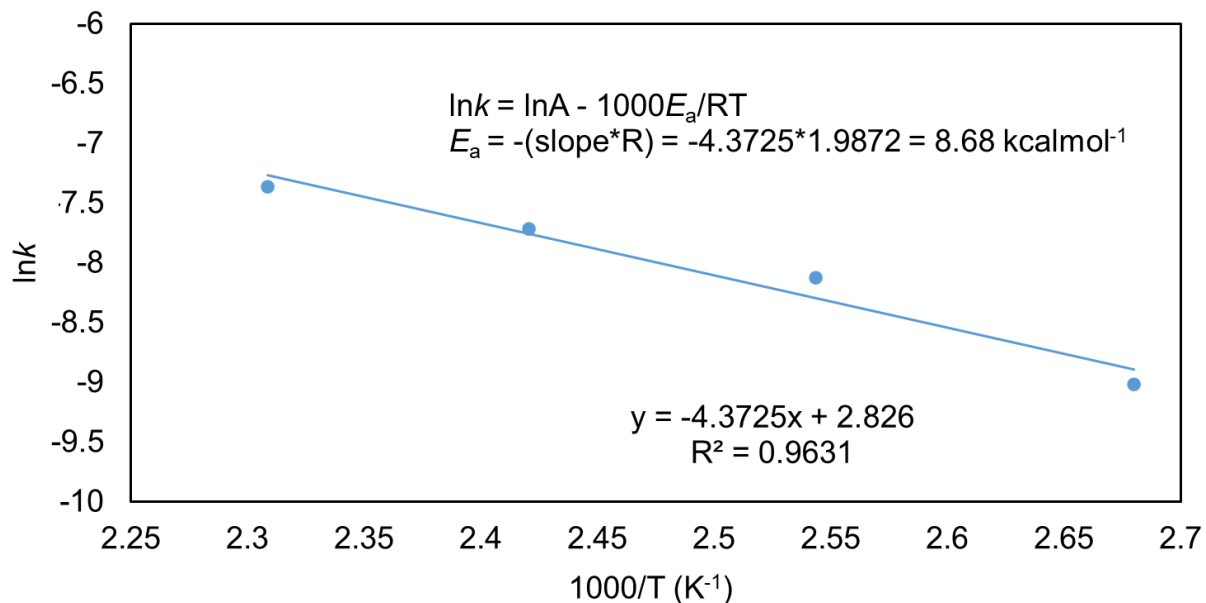


Figure S29. Arrhenius plot of $\ln k$ vs. $1000/T$ based on eq 2, at $T = 373.15$ K, 393.15 K, 413.15 K and 415.15 K.

The thermodynamic parameters, including activation Gibbs free energy (ΔG^\ddagger), activation enthalpy (ΔH^\ddagger) and activation entropy (ΔS^\ddagger) were calculated by using the Eyring equation (eq 3)¹⁰⁰, where where k = rate constant, k_B = Boltzmann constant, h = Planck's constant, R = gas constant ($1.9872 \text{ calmol}^{-1}\text{K}^{-1}$) and T = temperature in K.

The plot of $\ln(k/T)$ vs. $(1000/T)$, gave the value of $\Delta H^\ddagger = 7.89 \text{ kcalmol}^{-1}$ and $\Delta S^\ddagger = -0.55 \text{ kcalmol}^{-1}\text{K}^{-1}$. The Gibbs free energy, ΔG^\ddagger_{25} was calculated using $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$ which was found to be $24.28 \text{ kcalmol}^{-1}$.

$$\ln \frac{k}{T} = \ln \frac{k_B}{h} + \frac{\Delta S^\ddagger}{T} - \frac{\Delta H^\ddagger}{R} \left(\frac{1}{T}\right) \dots \dots \dots (3)$$

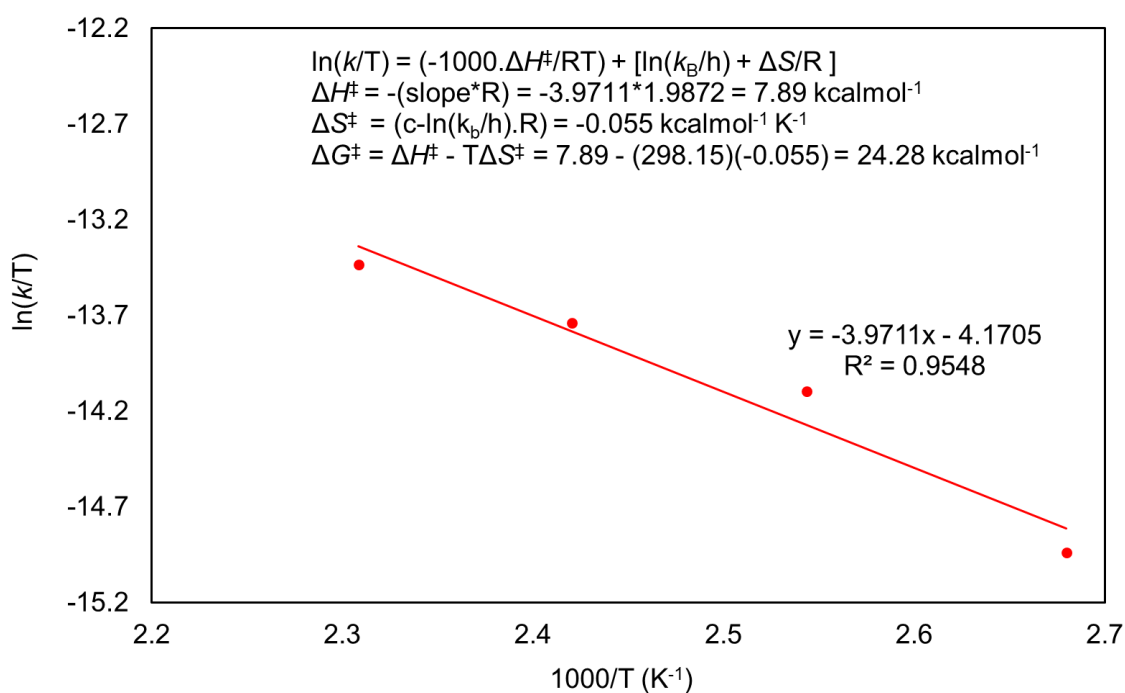


Figure S30. Eyring plot of $\ln(k/T)$ vs. $1000/T$ based on eq 3, at $T = 373.15 \text{ K}$, 393.15 K , 413.15 K and 415.15 K .