Hydride-Mediated Ammonia Borane Dehydrogenation in Water by Arene-Ru(II) Catalysts Revealed through Real-Time Gas Evolution

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Supporting Information

1. Materials and methods

General Remarks:

All the experiments performed for the ammonia borane dehydrogenation reactions were conducted in deionized water at 25 °C. The chemicals, ammonium sulfate, sodium borohydride, potassium carbonate and potassium iodide were purchased from SRL chemicals limited and the solvents, like acetonitrile, tetrahydrofuran (THF), methanol and diethyl ether were procured from Finar Chemicals limited and dried before. Benzene Ruthenium (II) Dimer was purchased from TCI chemicals. Deuterated solvents ($CDCl_3$, DMSO-d_6 and D_2O) were purchased from TCI chemicals.

Instrumentation Details:

NMR spectroscopy. ^{1}H (400 MHz), ^{13}C (101 MHz) and ^{11}B (128 MHz) NMR spectra were recorded on a BRUKER ASCEND 400 NMR spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) relative to the residual solvent signals. For $CDCl_3$, solvent resonances at δ = 7.26 ppm (^{1}H) and δ = 77.16 ($^{13}C\{^{1}H\}$). For DMSO-d_6, solvent resonances δ = 2.50 ppm (^{1}H) and δ = 39.52 ppm ($^{13}C\{^{1}H\}$); the residual H_2O signal in DMSO-d_6 appeared at δ = 3.30 ppm in the ^{1}H NMR spectrum. For D_2O, solvent resonances at δ = 4.70 ppm in ^{1}H NMR. ^{1}H and ^{13}C NMR were referenced to TMS, whereas ^{11}B NMR spectra were referenced to $BF_3.OEt_2$ and to avoid signals caused by the NMR tube in the spectra, a quartz NMR tube has been used. Coupling constants (J) are reported in hertz (Hz). Signal multiplicities are denoted as follows: s = singlet, d = doublet, dd = doublet of doublets, td = triplet of doublets and m = multiplets.

Capillary method in ^{1}H and ^{11}B NMR spectroscopy. For reactions where the solvent signal (D_2O, δ = 4.70 ppm in the ^{1}H NMR spectrum and no signal in ^{11}B NMR) did not interfere with the compound resonances, the capillary method was employed. A sealed capillary tube containing deuterated solvent (D_2O) was inserted into the undeuterated sample (In water), enabling proper locking and shimming during NMR data acquisition.

FT-IR spectroscopy. Infrared (FT-IR) spectra were recorded using KBr pellets (for solid compounds) on the Bruker ALPHA II FT-IR spectrometer at 298 K and reported the υ_{max} in cm^{-1} (range 400 – 4000 cm^{-1}).

UV-vis spectroscopy. UV-visible spectra were recorded on a double-beam Shimadzu UV-Vis Spectrophotometer (Model No: UV-1900i) at 298 K.

Mass spectrometry. The high-resolution mass spectrometry was recorded on a Waters XEVO G2-XS QTOF High-Resolution Mass Spectrometer. The complex [Ru1-Ru3] in water and in the presence of ammonia borane has been recorded immediately after the sample preparation.

X-ray crystallographic analysis. Suitable diffraction-quality single crystals of the [**Ru1–Ru3**] complexes were obtained by slow evaporation as described in the synthesis section. Selected good-quality crystals were used for single-crystal X-ray diffraction measurements, which were carried out on a Rigaku Oxford Diffraction (2017) system equipped with a CCD Eos S2 detector at 298 K. Data were collected using a microfocus sealed X-ray tube with Mo-Kα radiation (λ = 0.71073 Å). CrysAlisPro software was used for data collection, reduction, and scaling. The crystal structure of the [**Ru1-Ru3**] complex was solved by the intrinsic phasing method using SHELXT within the Olex2 software package. Structure refinement was performed using SHELXL implemented in Olex2.

Gas evolution monitoring by a manometer. The amount of evolved hydrogen was determined using a manometer in a 5 mL double-jacketed reaction vessel. For each experiment, the reaction (working) cell contained 2 mL of reaction mixture and 3 mL of headspace; the reference cell was filled with 2 mL of water and the same 3 mL headspace volume to match the working cell. The differential pressure between the working and reference cells was measured with a TESTO 521 manometer (max limit: 210 hPa, $\pm$ 0.1 hPa accuracy). Measured pressure differences in hPa were converted to the amount of H_2 (µmol) using the ideal gas law, (PV=nRT). The conversion was performed using the relation,

$$n = \frac{PV}{RT}$$

Where,

n = number of moles of H_2 (µmol) evolved during the dehydrogenation of ammonia borane

P = pressure (1 hPa = 100 Pa)

V = overall volume of headspace in m^3 (1.96×10^{-5} m^3)

R = gas constant (8.314 J K^{-1} mol^{-1})

T = Absolute temperature of the headspace during the experiment (298 K).

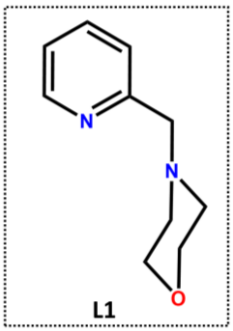
Gas detection and quantification by online gas chromatography.

The evolved hydrogen gas (H_2) was quantified using a CIC GC-2011 gas chromatograph equipped with a molecular sieve column and a thermal conductivity detector (TCD). Argon was employed as the carrier gas (flow rate: 5 kg/cm^2). The reaction was carried out in a glass vial sealed with a gas-tight screw cap fitted with an injection septum suitable for headspace sampling. Upon completion of the reaction, the headspace gas was sampled by inserting a needle connected directly to the gas chromatograph, enabling online H_2 detection. Quantification of H_2 was performed using a calibration curve generated by injecting known volumes of standard H_2 gas under identical conditions.

2. Synthesis and Characterization of ligands (L1-L3):

General procedure A: A 100 mL two-neck round-bottom flask was charged with 2-(chloromethyl)pyridine hydrochloride (1.0 equiv, 12.2 mmol), potassium carbonate (5.0 equiv, 61 mmol), and potassium iodide (0.2 equiv, 2.4 mmol) in 50 mL of dry acetonitrile. The resulting heterogeneous mixture was stirred at room temperature for 30 minutes. The amine (2.2 equiv, 26.8 mmol) was then added dropwise, stirred at RT for 12 h. Reaction mixture was monitored by TLC until the starting material, 2-(chloromethyl)pyridine hydrochloride, was fully consumed. After completion, the mixture was passed through a Celite pad and rinsed with acetonitrile. The combined filtrate was concentrated under reduced pressure to give a crude oily residue. Purification by silica gel column chromatography using 100% ethyl acetate as the eluent afforded the desired ligands (L1–L3). The NMR spectral data are consistent with those previously reported in the literature.[1,2]

4-(Pyridin-2-ylmethyl)morpholine (L1).



Yield: 83% (1.8 g)

Nature: Brown oil

Purification: Silica gel (EtOAc = 100%)

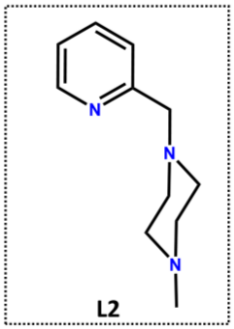
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.45 (d, J = 4.8 Hz, 1H), 7.53 (td, J = 7.7, 1.8 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.08 – 7.03 (m, 1H), 3.66 – 3.57 (m, 4H), 3.54 (s, 2H), 2.44 – 2.34 (m, 4H).

^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ (ppm): 157.96, 149.23, 136.35, 123.24, 122.07, 66.82, 64.86, 53.67.

IR (KBr, cm^{-1}): 2968, 1591, 1438, 1116 cm^{-1}.

HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{10}H_{15}N_2O$ $[M+H]^+$: 179.1184; found: 179.1193.

1-Methyl-4-(pyridin-2-ylmethyl)piperazine (L2).



Yield: 82% (1.9 g)

Nature: yellow oil

Purification: Silica gel (EtOAc = 100%)

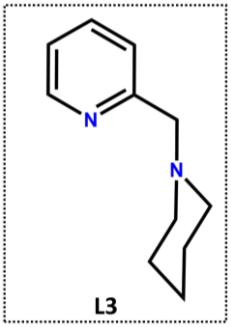
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.42 (d, J = 3.9 Hz, 1H), 7.52 – 7.50 (m, 1H), 7.26 (d, J = 16.2 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 3.54 – 3.52 (m, 2H), 2.38 (d, J = 23.5 Hz, 8H), 2.16– 2.13 (m, 3H).

^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ (ppm): 158.29, 149.15, 136.30, 123.22, 121.96, 64.44, 54.92, 53.14, 45.97.

IR (KBr, cm^{-1}): 2931, 1593, 1454, 1167 cm^{-1}.

HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{11}H_{18}N_3$ $[M+H]^+$: 192.1501; found: 192.1504.

2-(Piperidin-1-ylmethyl)pyridine (L3).



Yield: 90% (1.93 g)

Nature: Colorless oil

Purification: Silica gel (EtOAc = 100%)

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.50 (d, J = 3.9 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.7 Hz, 1H), 7.11 – 7.08 (m, 1H), 3.57 (s, 2H), 2.39 (s, 4H), 1.56 – 1.54 (m, 4H), 1.39 (s, 2H).

^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ (ppm): 159.06, 149.08, 136.27, 123.18, 121.83, 65.41, 54.74, 25.91, 24.23.

IR (KBr, cm^{-1}): 2937, 1589, 1436, 1112 cm^{-1}.

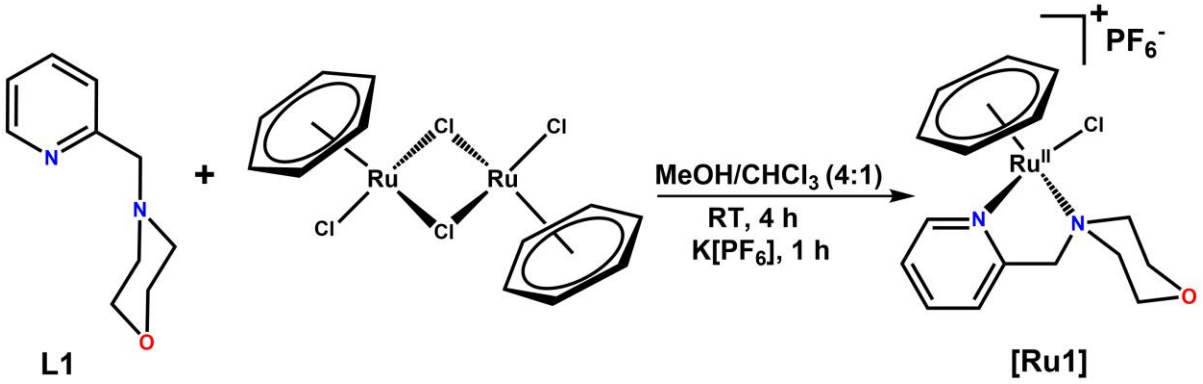
HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{11}H_{17}N_2$ $[M+H]^+$: 177.1392; found: 177.1398.

3. Synthesis and Characterization of complexes (Ru1-Ru3):

General procedure B:

The ligand (L1-L3, 2 equiv, 0.4 mmol) has been dissolved in methanol and added into a 100 mL single neck round bottom flask, to this solution ruthenium dimer (1 equiv, 0.2 mmol) pre-dissolved in MeOH/$CHCl_3$ mixture (4:1, v/v) was added dropwise and stirred at room temperature for 4 hours. Then the solution was concentrated under vacuum to reduce the volume to 3 mL, to this saturated K[PF_6] (1 equiv) was added and stirred at room temperature for one hour. The complex was concentrated in vacuo, triturated with methanol and diethyl ether, the formed precipitate was filtered and dried to get the pure complex [Ru1-Ru3].

Scheme S1. Synthetic route for the synthesis of [(η^6-benzene)-Ru^{II}(L1)Cl](PF_6):



Yield: 92% (99 mg)

Nature: Yellowish solid

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.39 (d, J = 5.5 Hz, 1H), 8.04 (t, J = 7.7 Hz, 1H), 7.59 – 7.55 (m, 2H), 6.09 (s, 6H), 4.73 (d, J = 15.6 Hz, 1H), 4.19 – 4.09 (m, 2H), 3.93 (d, J = 15.6 Hz, 1H), 3.74 – 3.69 (m, 1H), 3.61 (d, J = 7.5 Hz, 3H), 3.14 (d, J = 5.2 Hz, 1H), 3.02 – 2.99 (m, 1H).

^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ (ppm): 159.86, 155.62, 140.41, 125.58, 123.67, 86.32, 63.00, 62.09, 60.85.

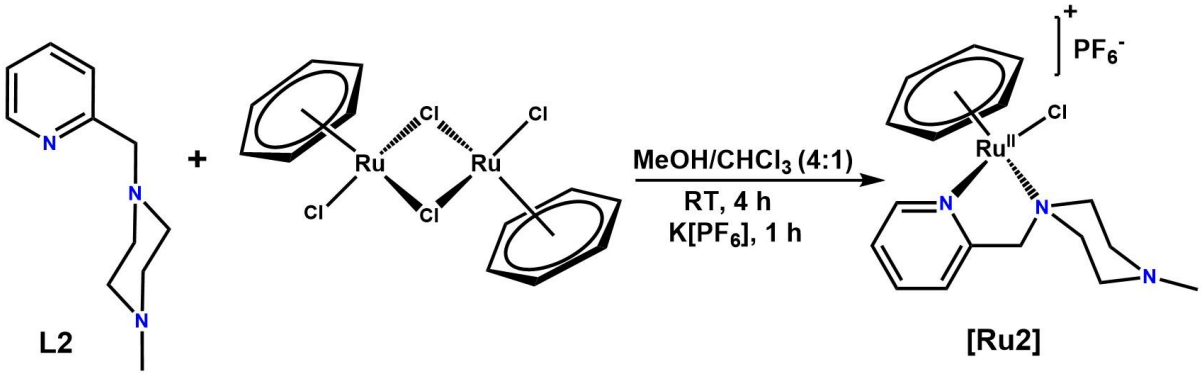
^{31}P NMR (162 MHz, DMSO-d_6) δ (ppm): -144.01 (m, PF_6).

^{19}F NMR (377 MHz, DMSO-d_6) δ (ppm): -69.80 (d, PF_6).

IR (KBr, cm^{-1}): 3091, 2958, 1612, 1440, 1110, 831 (P-F, PF_6), 557 (Ru-N_{py}) cm^{-1}.

HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{16}H_{20}ClN_2ORu$ $[M]^+$: 393.0340; found: 393.0341.

Scheme S2. Synthetic route for the synthesis of [(η^6-benzene)-Ru^{II}(L2)Cl](PF_6):



Yield: 93% (102 mg)

Nature: Greenish yellow solid

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.47 (s, 1H), 8.03 (td, J = 7.7, 0.9 Hz, 1H), 7.58 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 6.3 Hz, 1H), 6.08 (s, 6H), 4.46 (d, J = 15.4 Hz, 1H), 4.11 (t, J = 11.2 Hz, 1H), 3.93 (s, 1H), 3.77 (d, J = 15.5 Hz, 1H), 3.02 (d, J = 12.7 Hz, 1H), 2.68 (t, J = 10.6 Hz, 1H), 2.51 (s, 1H), 2.44 (d, J = 12.8 Hz, 1H), 2.35 (t, J = 11.8 Hz, 1H), 2.24 (s, 3H).

^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ (ppm): 160.33, 155.51, 140.44, 125.47, 123.79, 86.37, 61.59, 54.93, 50.28, 45.73.

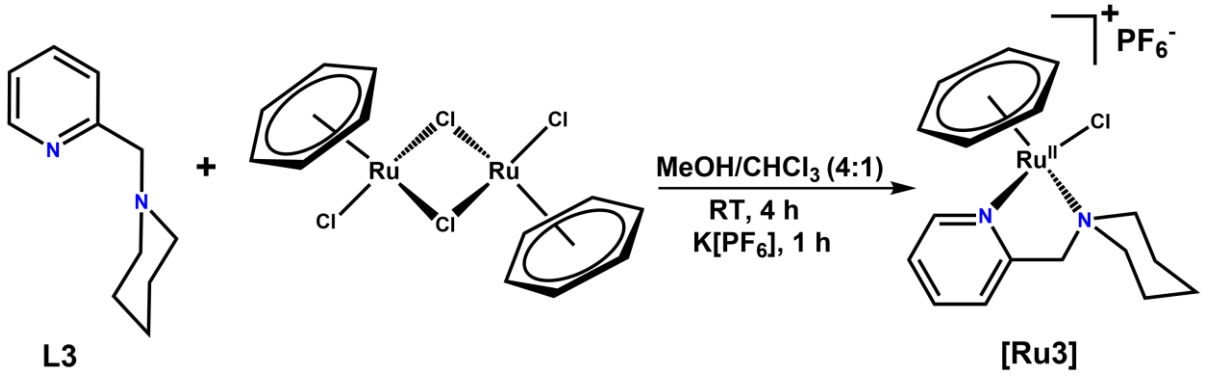
^{31}P NMR (162 MHz, DMSO-d_6) δ (ppm): -144.19 (m, PF_6).

^{19}F NMR (377 MHz, DMSO-d_6) δ (ppm): -69.99 (d, PF_6).

IR (KBr, cm^{-1}): 3062, 2940, 1610, 1440, 1005, 838 (P-F, PF_6), 557 (Ru-N_{py}) cm^{-1}.

HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{17}H_{23}ClN_3Ru$ $[M]^+$: 406.0656; found: 406.0656.

Scheme S3. Synthetic route for the synthesis of [(η^6-benzene)-Ru^{II}(L3)Cl](PF_6):



Yield: 89% (107 mg)

Nature: Yellowish brown solid

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.51 (d, J = 5.5 Hz, 1H), 8.02 (td, J = 7.7, 1.1 Hz, 1H), 7.59 – 7.53 (m, 2H), 6.08 (s, 6H), 4.41 (d, J = 15.6 Hz, 1H), 3.96 (t, J = 12.3 Hz, 1H), 3.79 (t, J = 14.5 Hz, 2H), 3.61 (d, J = 12.6 Hz, 1H), 3.00 (d, J = 13.1 Hz, 1H), 2.01 (d, J = 4.1 Hz, 1H), 1.67 (dd, J = 23.3, 14.0 Hz, 3H), 1.41 (d, J = 11.4 Hz, 1H), 1.32 (d, J = 14.3 Hz, 1H).

^{13}C{1H} NMR (101 MHz, DMSO-d_6) δ (ppm): 160.80, 155.52, 140.44, 125.32, 123.75, 86.36, 62.14, 22.59, 21.80, 21.27.

^{31}P NMR (162 MHz, DMSO-d_6) δ (ppm): -143.97 (m, PF_6).

^{19}F NMR (377 MHz, DMSO-d_6) δ (ppm): -69.77 (d, PF_6).

IR (KBr, cm^{-1}): 3079, 2931, 1610, 1440, 828 (P-F, PF_6), 557 (Ru-N_{py}) cm^{-1}.

HR-MS (ESI, positive mode, methanol): *m/z* calcd for $C_{17}H_{22}ClN_2Ru$ $[M]^+$: 391.0516; found: 391.0501.

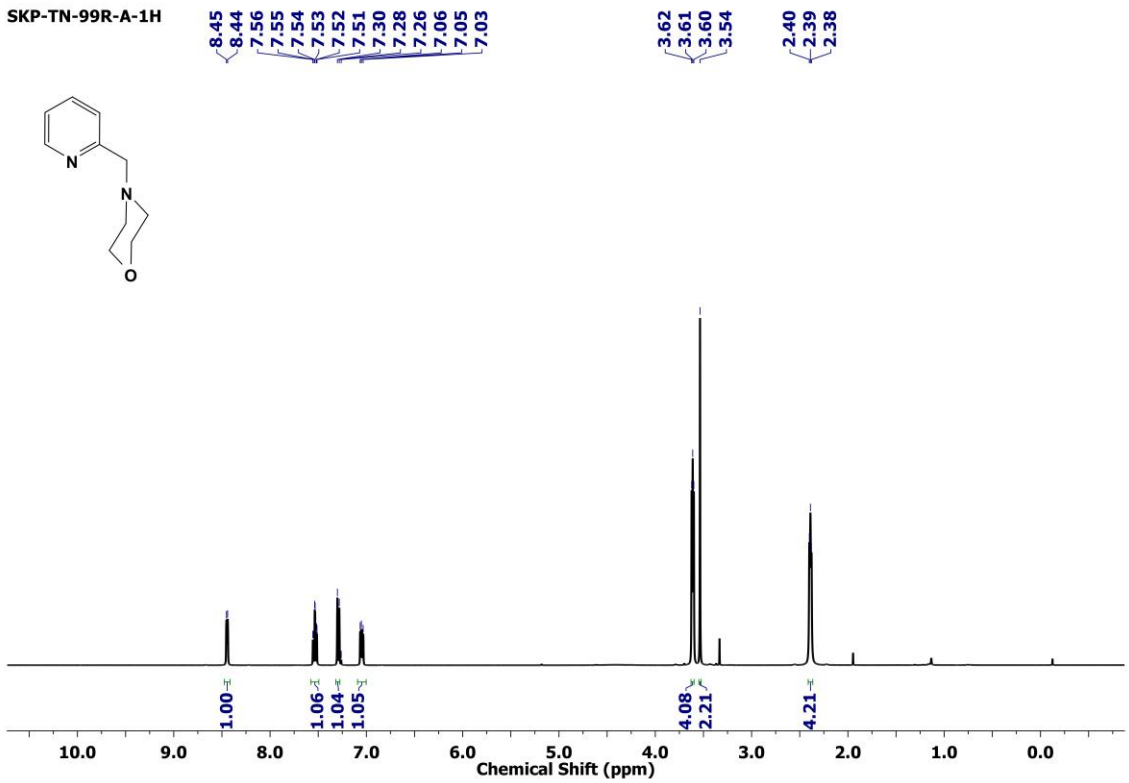


Figure S1. ^{1}H NMR (400 MHz) spectrum of 4-(Pyridin-2-ylmethyl)morpholine (L1) in $CDCl_3$.

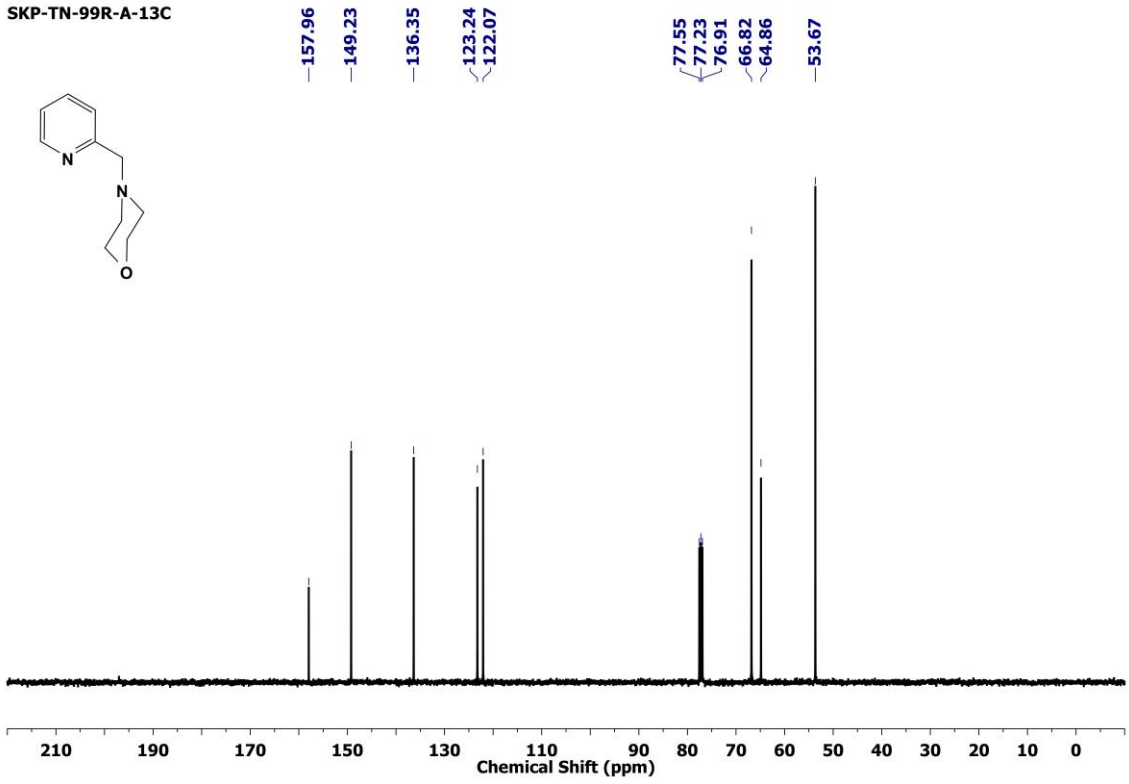


Figure S2. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 4-(Pyridin-2-ylmethyl)morpholine (L1) in $CDCl_3$.

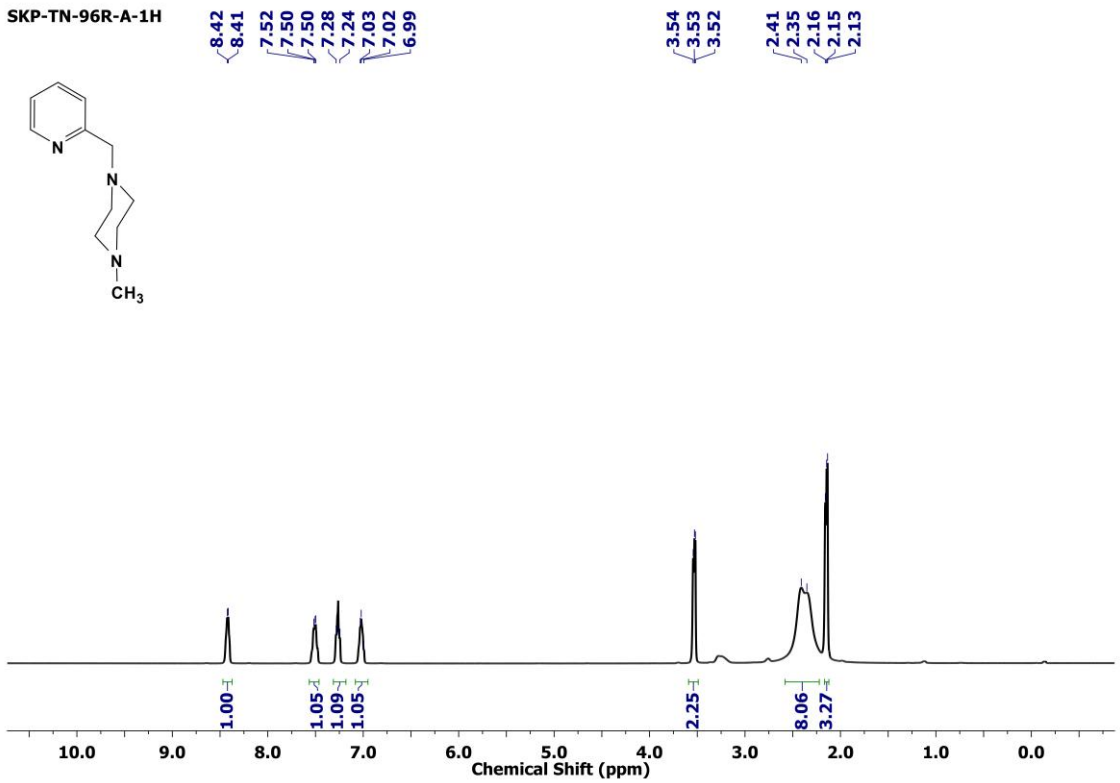


Figure S3. ^{1}H NMR (400 MHz) spectrum of 1-Methyl-4-(pyridin-2-ylmethyl)piperazine (L2) in $CDCl_3$.

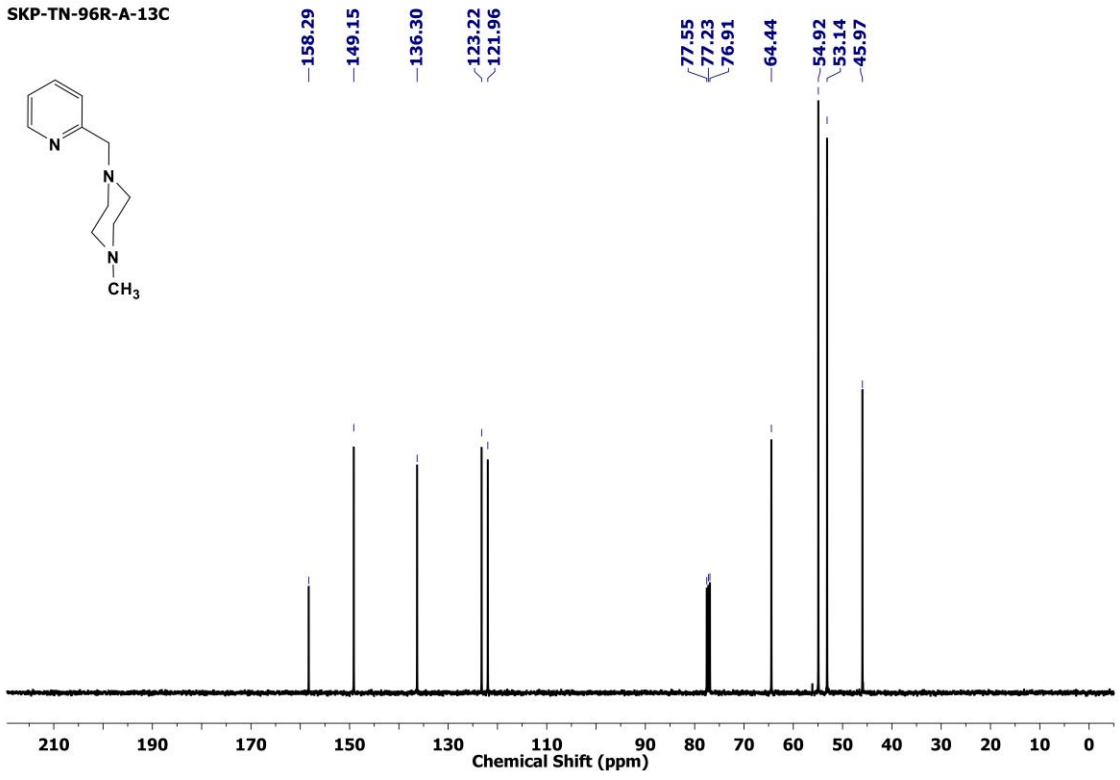


Figure S4. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 1-Methyl-4-(pyridin-2-ylmethyl)piperazine (L2) in $CDCl_3$.

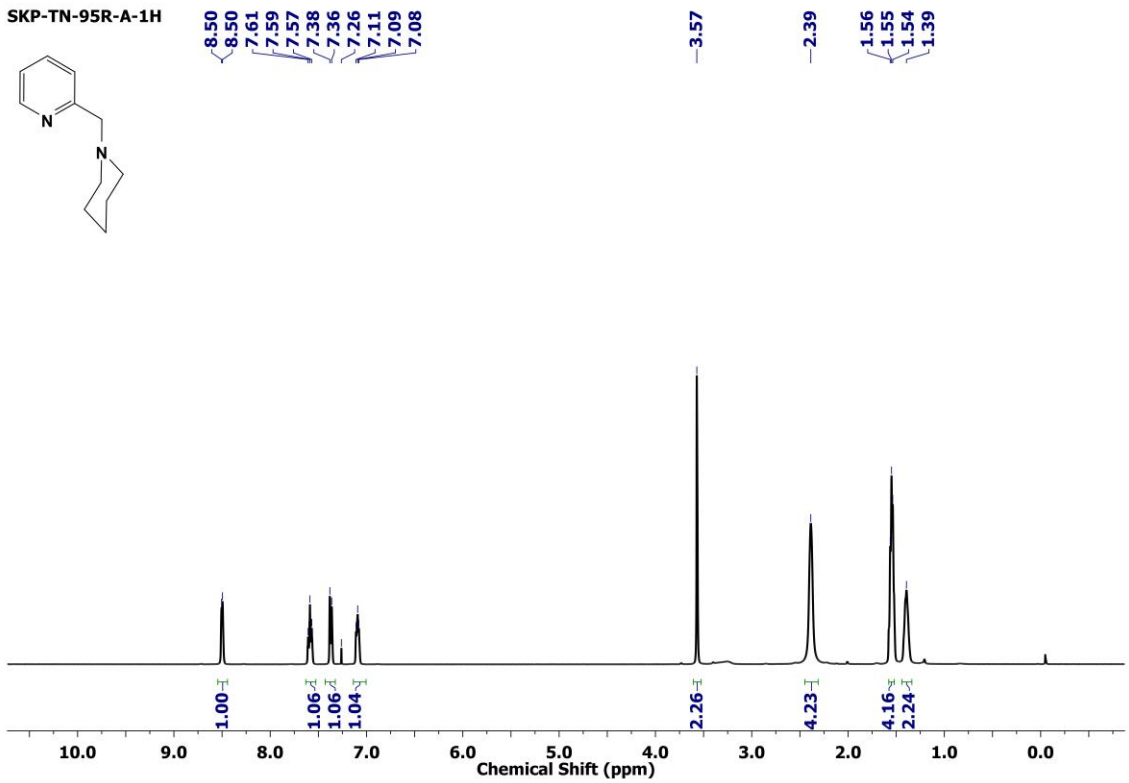


Figure S5. ^{1}H NMR (400 MHz) spectrum of 2-(Piperidin-1-ylmethyl)pyridine (L3) in $CDCl_3$.

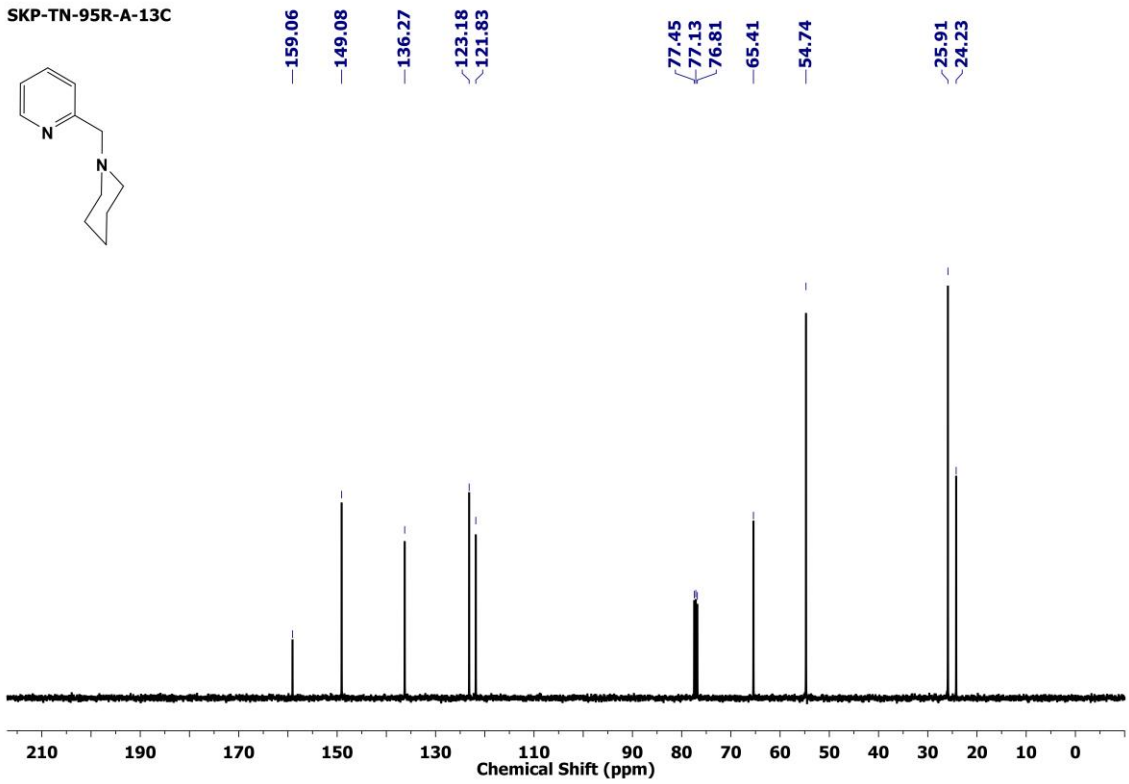


Figure S6. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of 2-(Piperidin-1-ylmethyl)pyridine (L3) in $CDCl_3$.

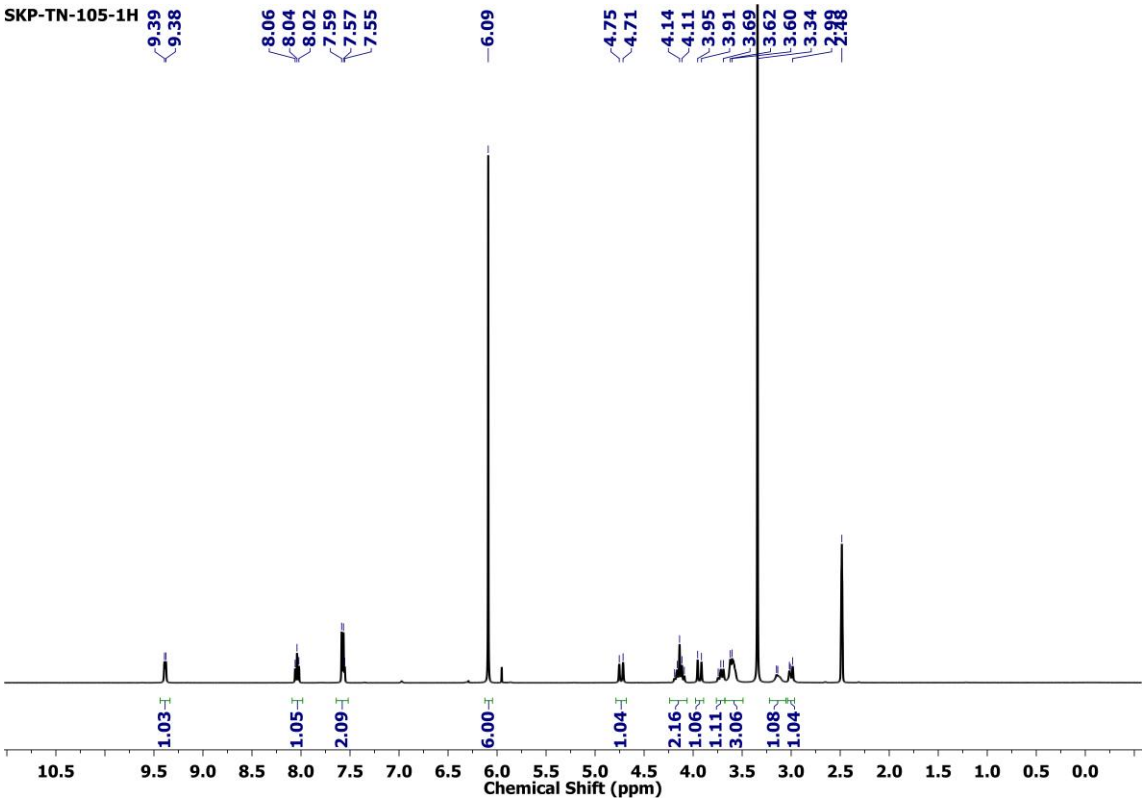


Figure S7. ^{1}H NMR (400 MHz) spectrum of [Ru1] in DMSO-d_6.

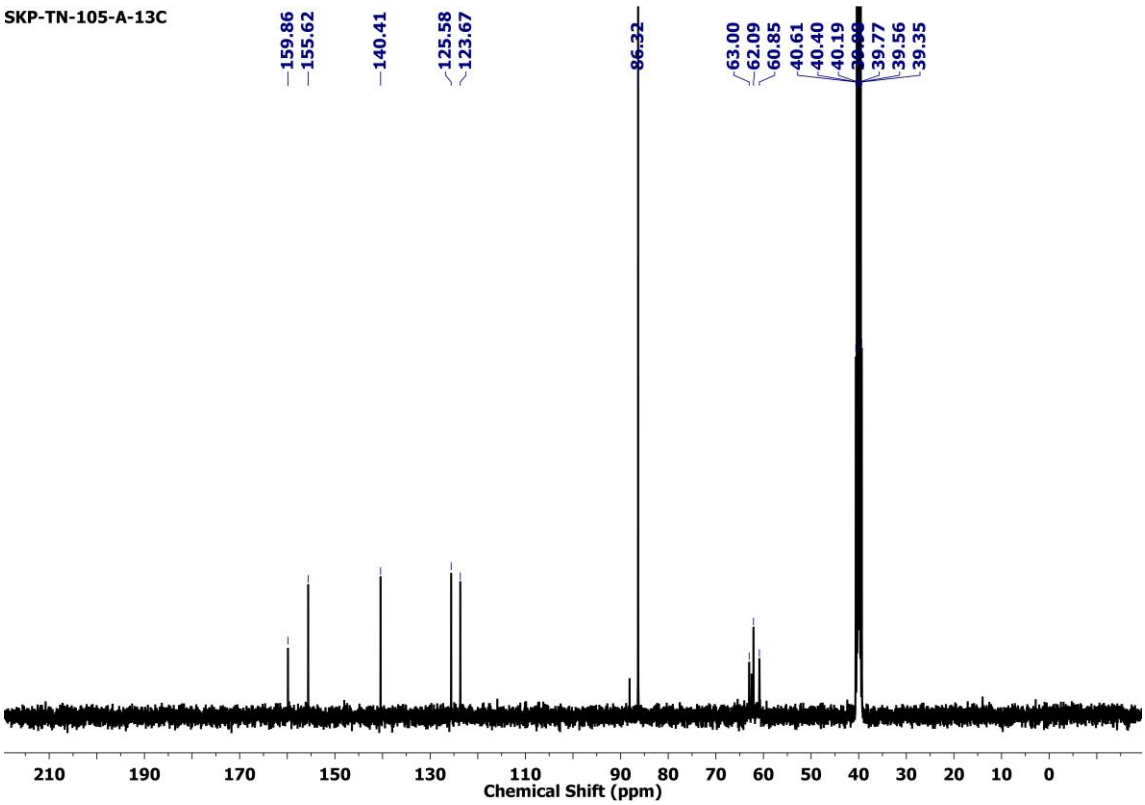


Figure S8. ^{13}C{^{1}H} NMR (101 MHz) spectrum of [Ru1] in DMSO-d_6.

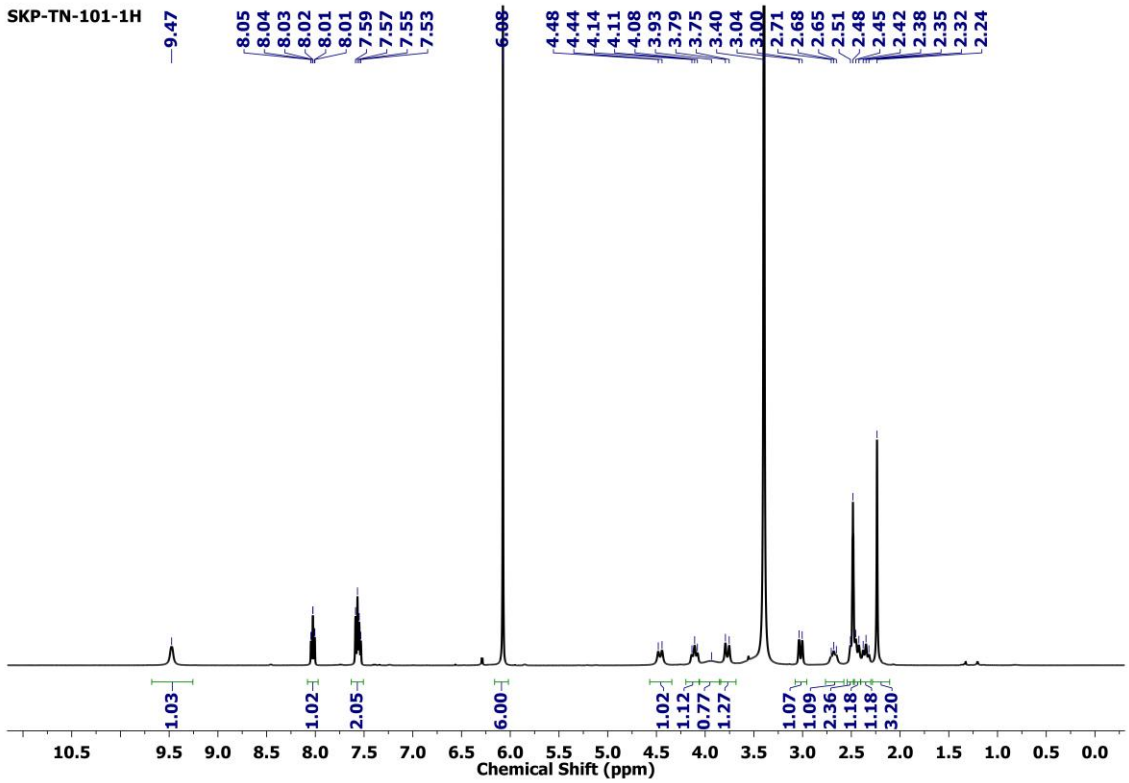


Figure S9. ^{1}H NMR (400 MHz) spectrum of [Ru2] in DMSO-d_6.

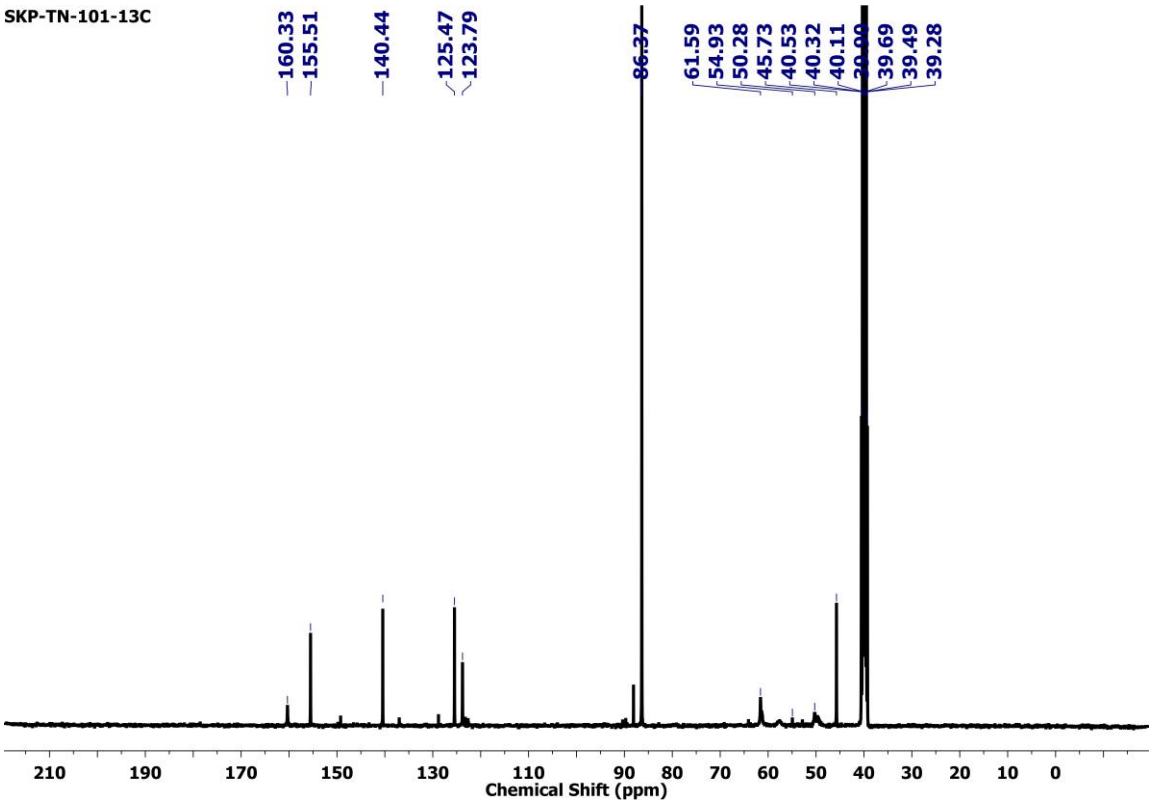


Figure S10. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of [Ru2] in DMSO-d_6.

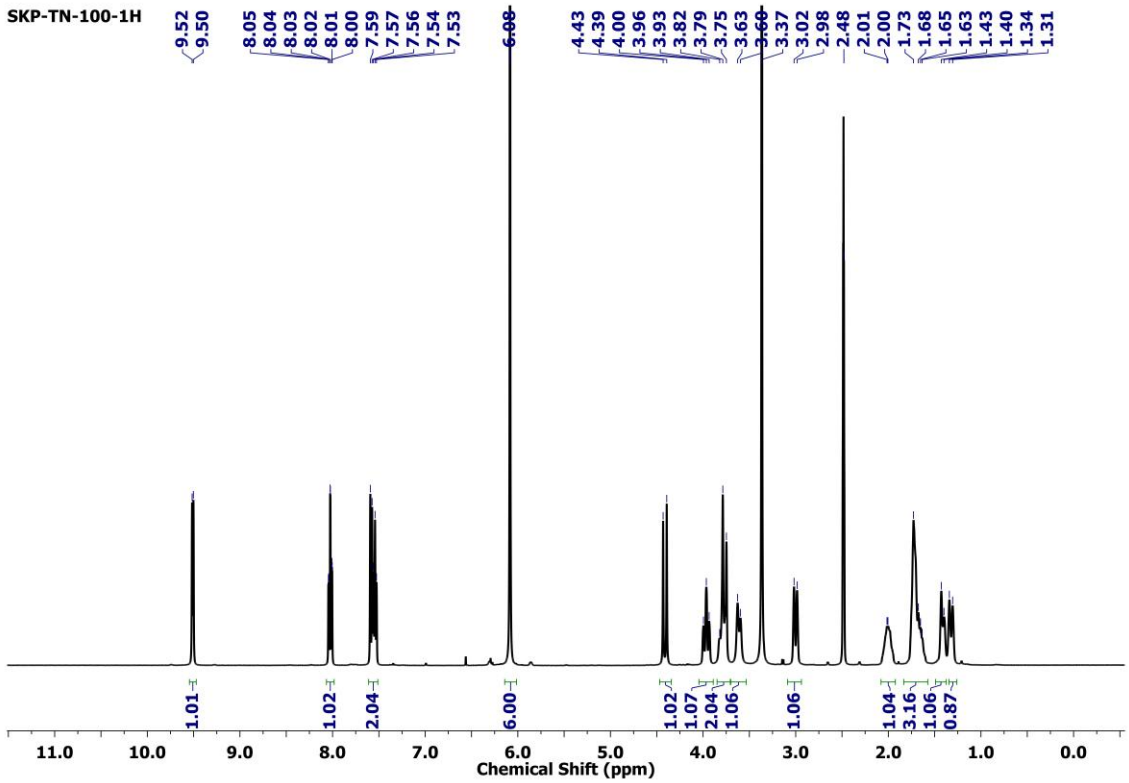


Figure S11. ^{1}H NMR (400 MHz) spectrum of [Ru3] in DMSO-d_6.

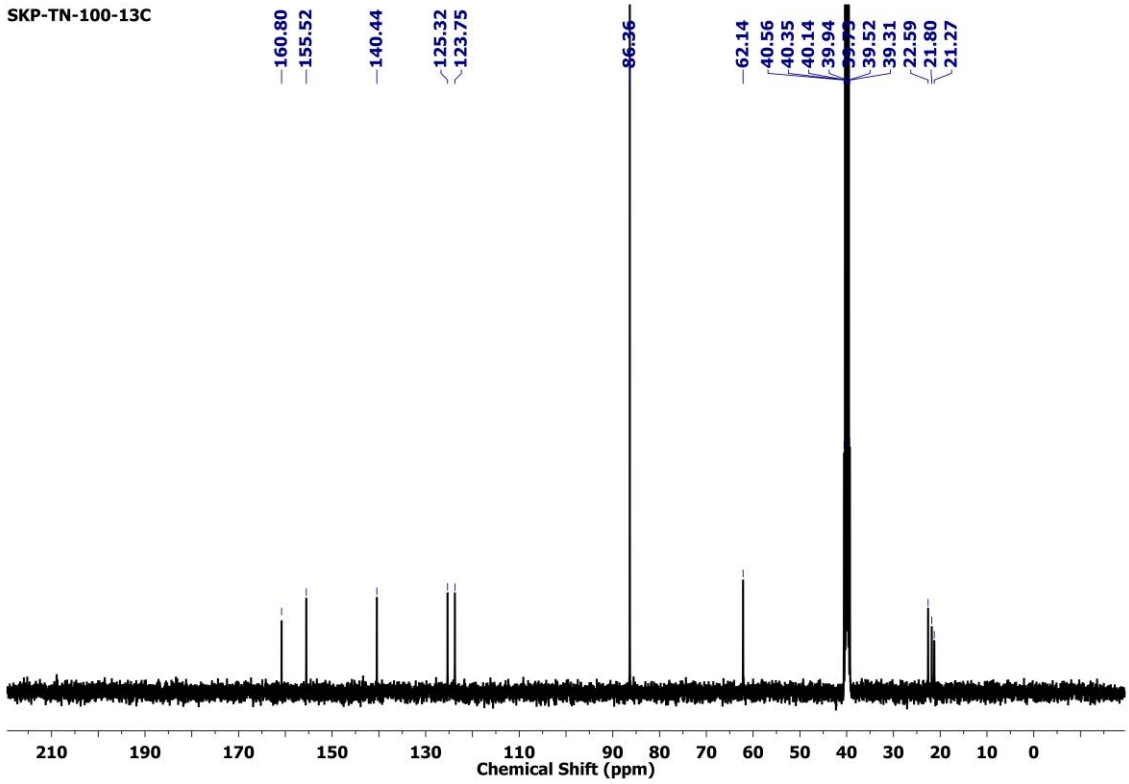


Figure S12. $^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of [Ru3] in DMSO-d_6.

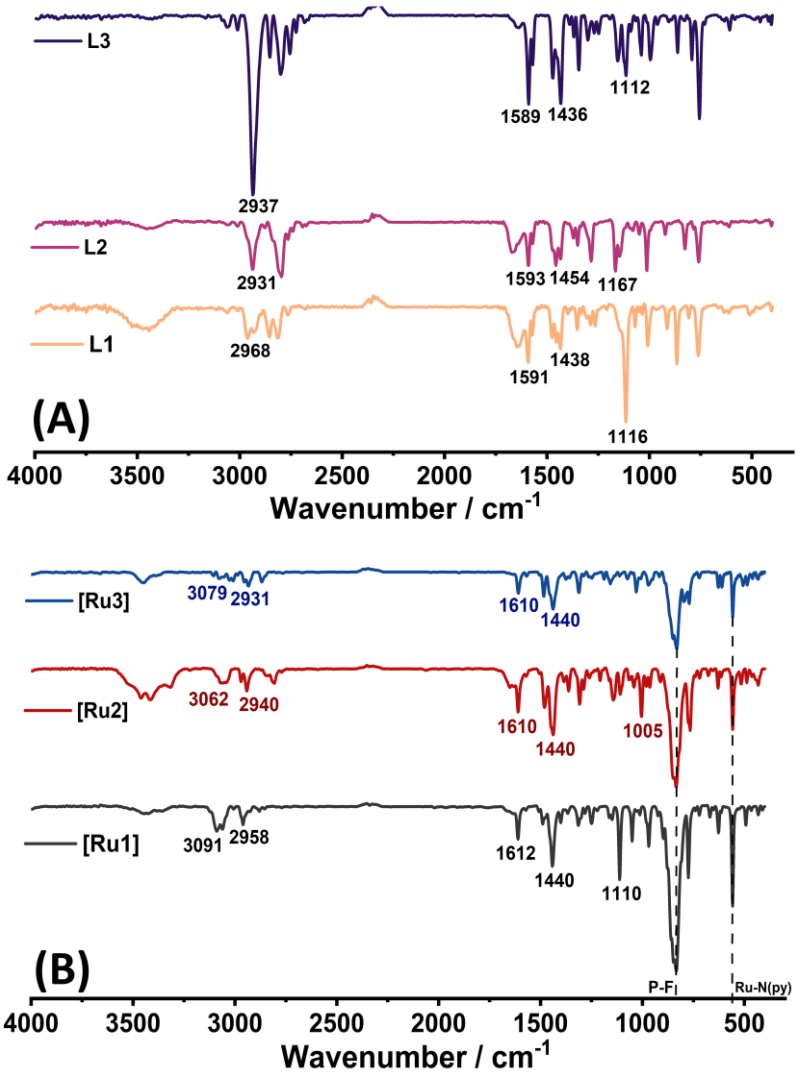


Figure S13. FT-IR for the solid samples **(A)** Ligand (L1-L3) and **(B)** complex (Ru1-Ru3) recorded at room temperature by preparing a KBr pellet, scanning from 400-4000 cm^{-1}.

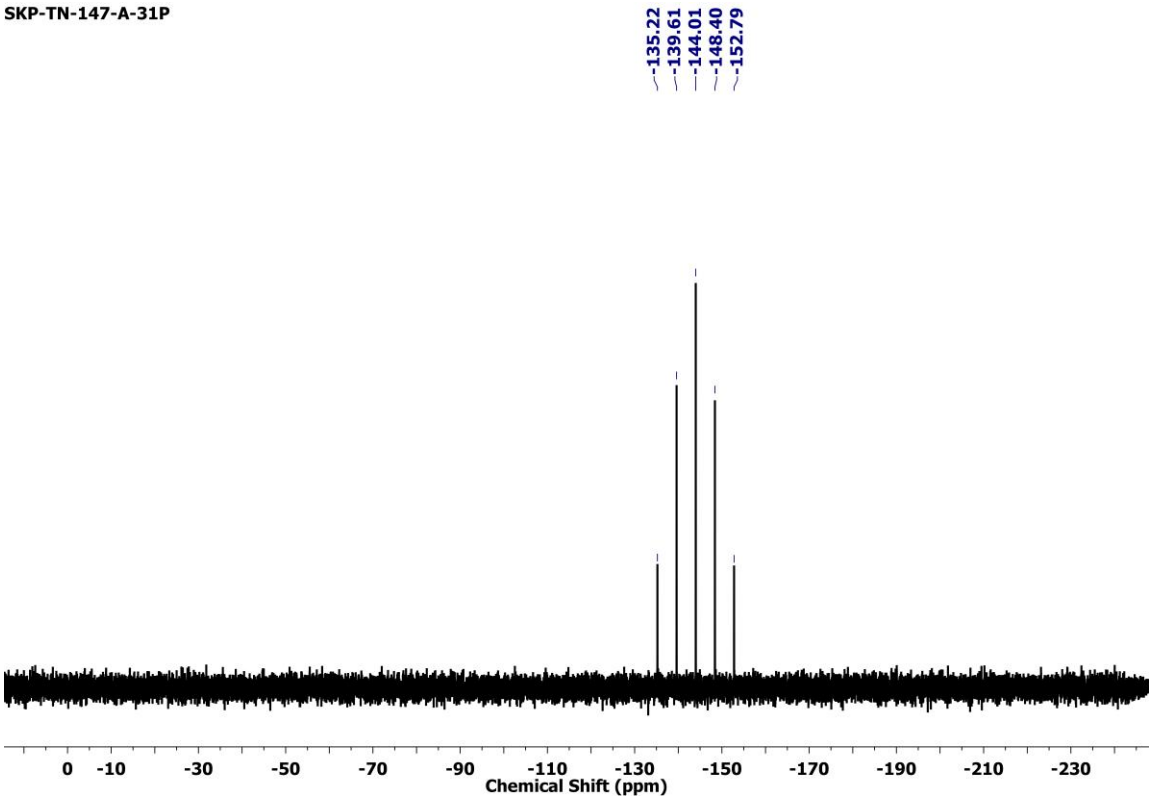


Figure S14. ^{31}P NMR (162 MHz) spectrum of [Ru1] in DMSO-d_6.

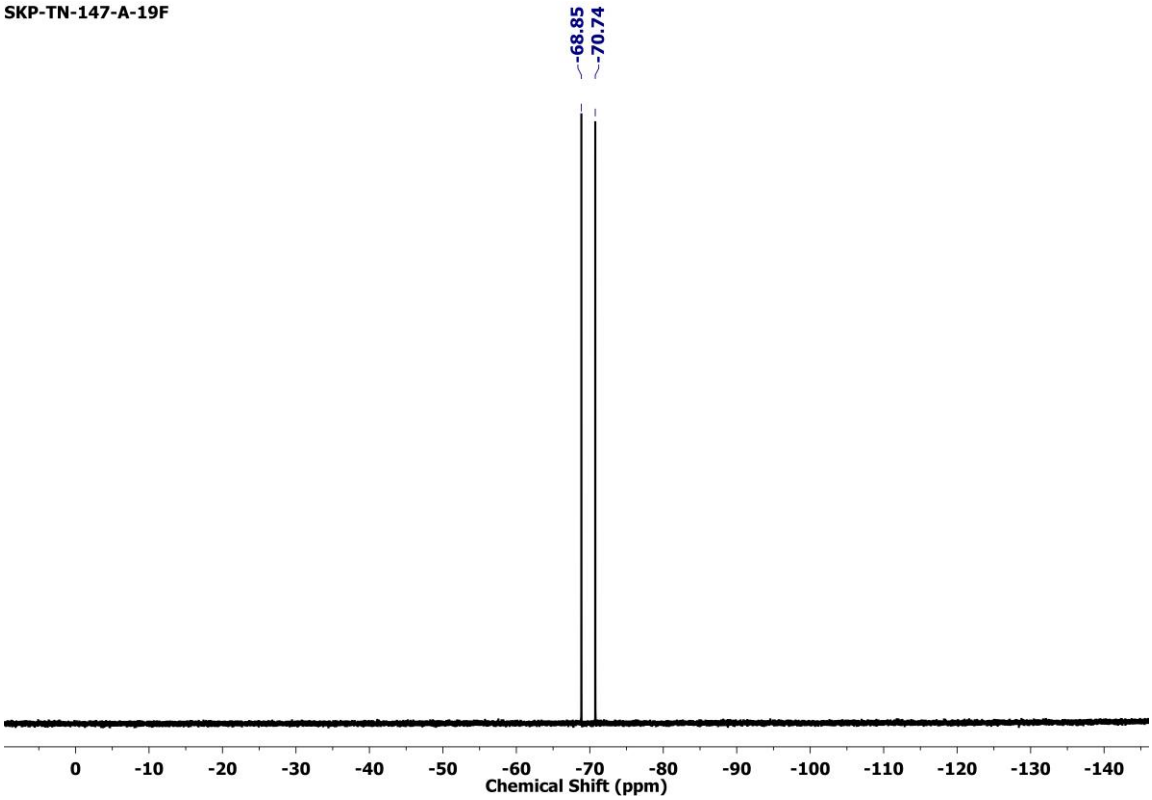


Figure S15. ^{19}F NMR (377 MHz) spectrum of [Ru1] in DMSO-d_6.

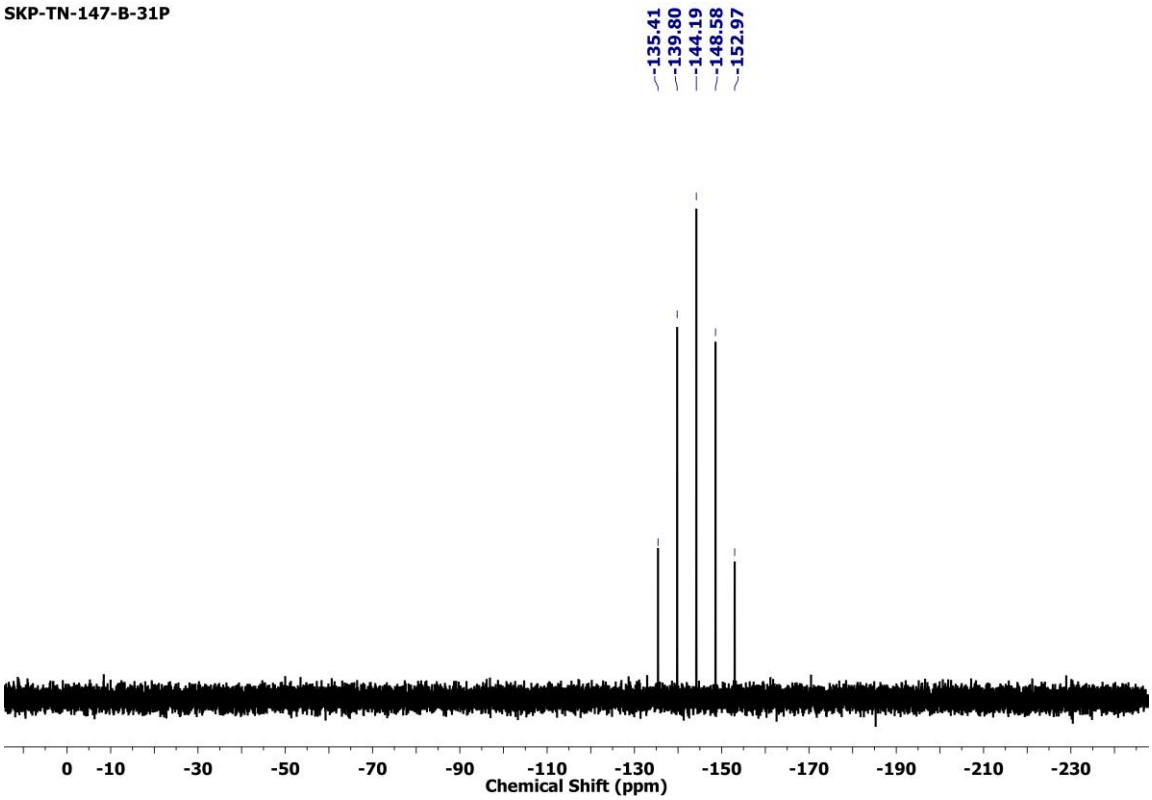


Figure S16. ^{31}P NMR (162 MHz) spectrum of [Ru2] in DMSO-d_6.

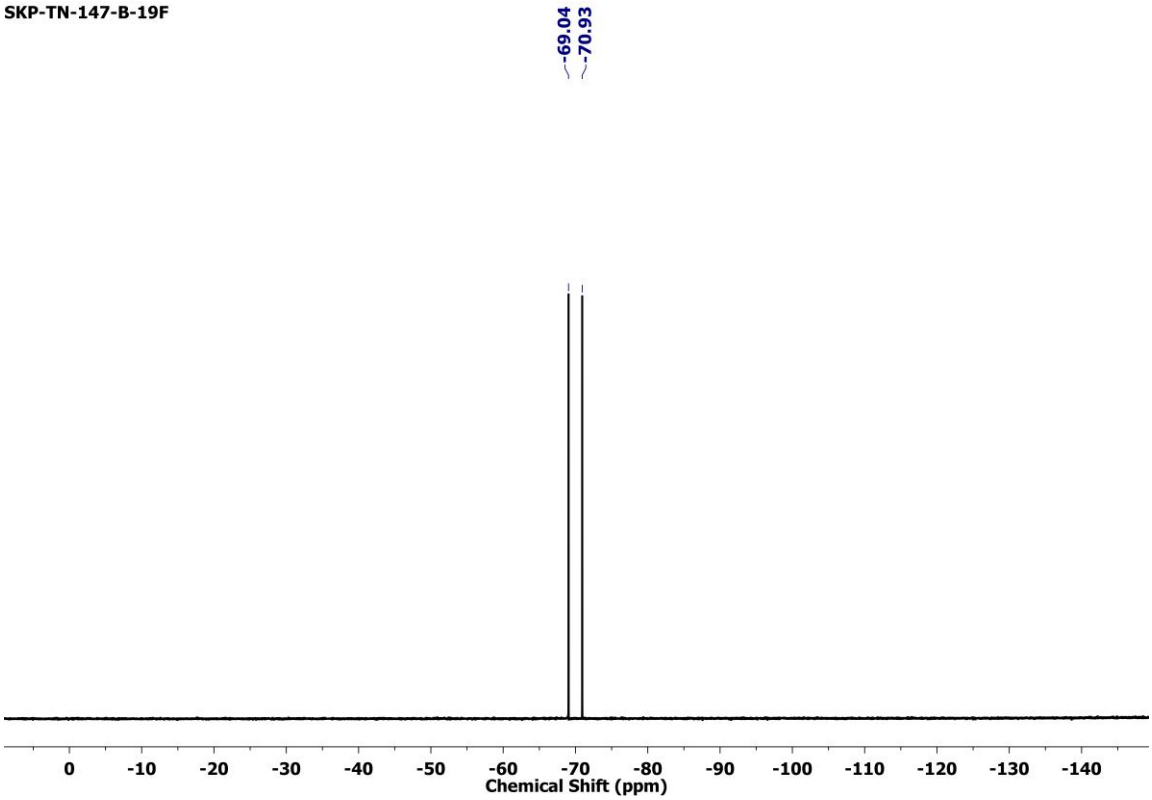


Figure S17. ^{19}F NMR (377 MHz) spectrum of [Ru2] in DMSO-d_6.

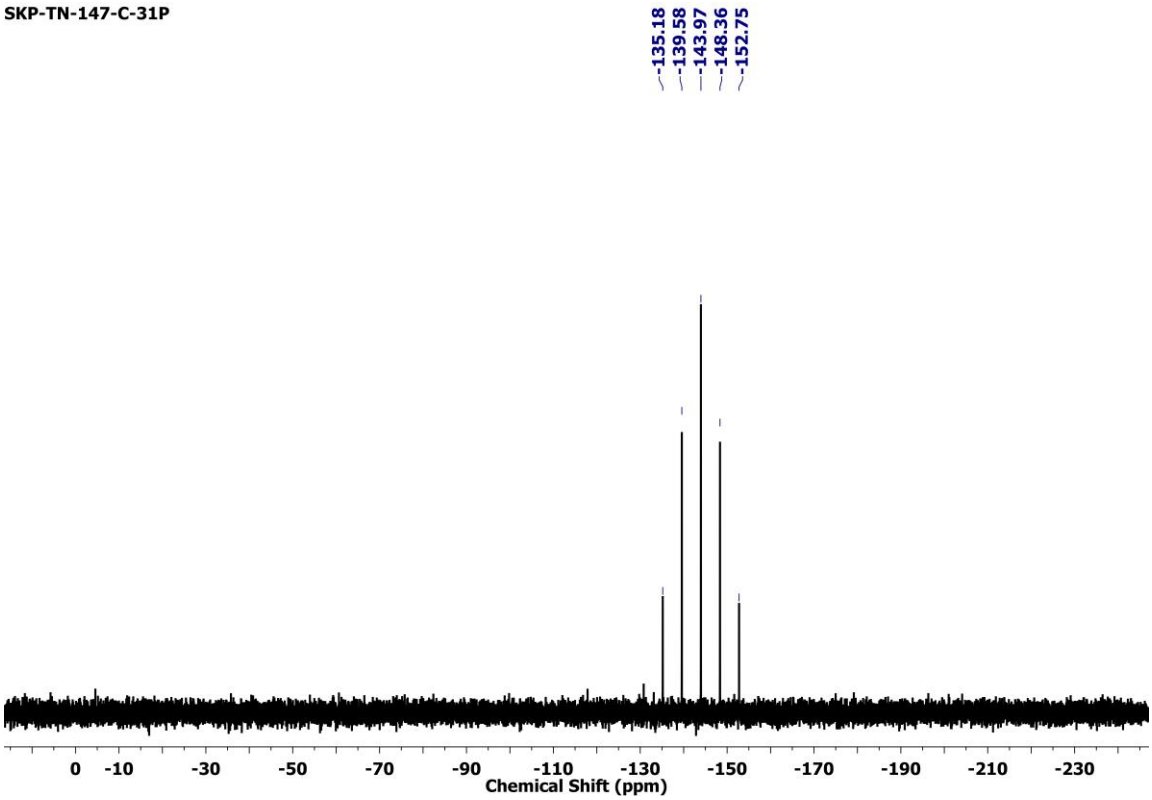


Figure S18. ^{31}P NMR (162 MHz) spectrum of [Ru3] in DMSO-d_6.

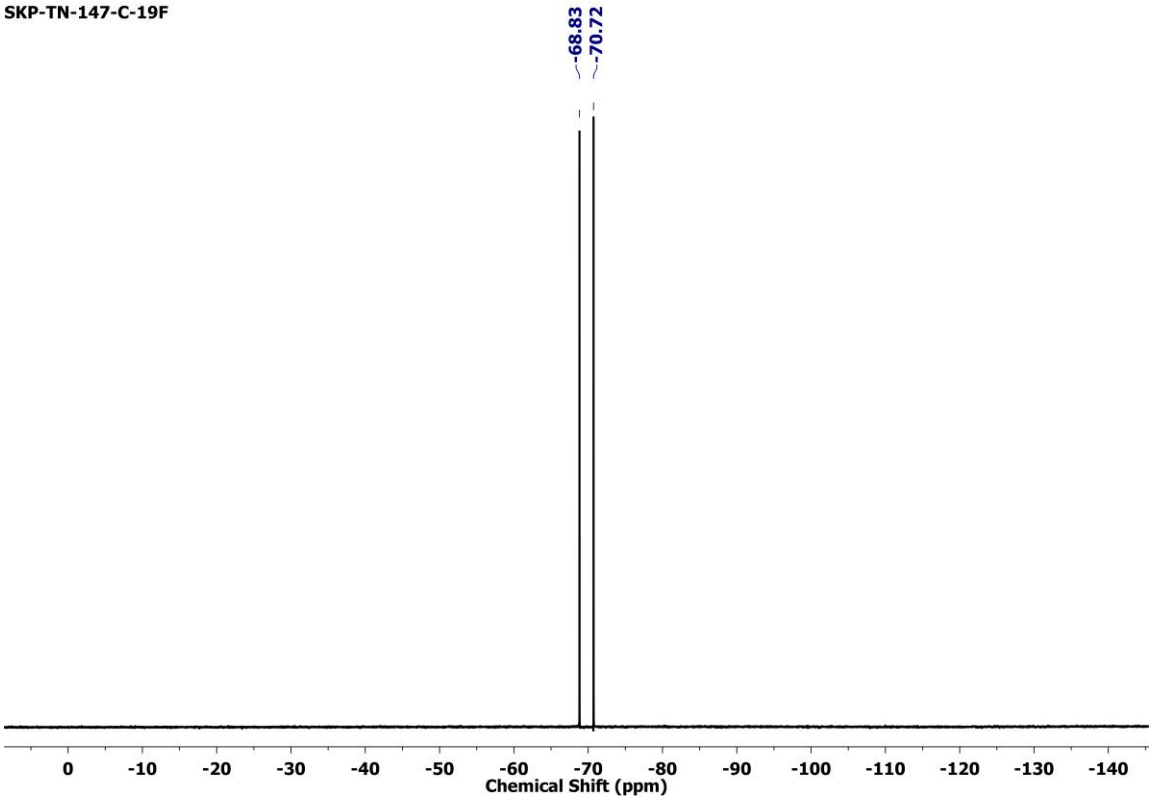


Figure S19. ^{19}F NMR (377 MHz) spectrum of [Ru3] in DMSO-d_6.

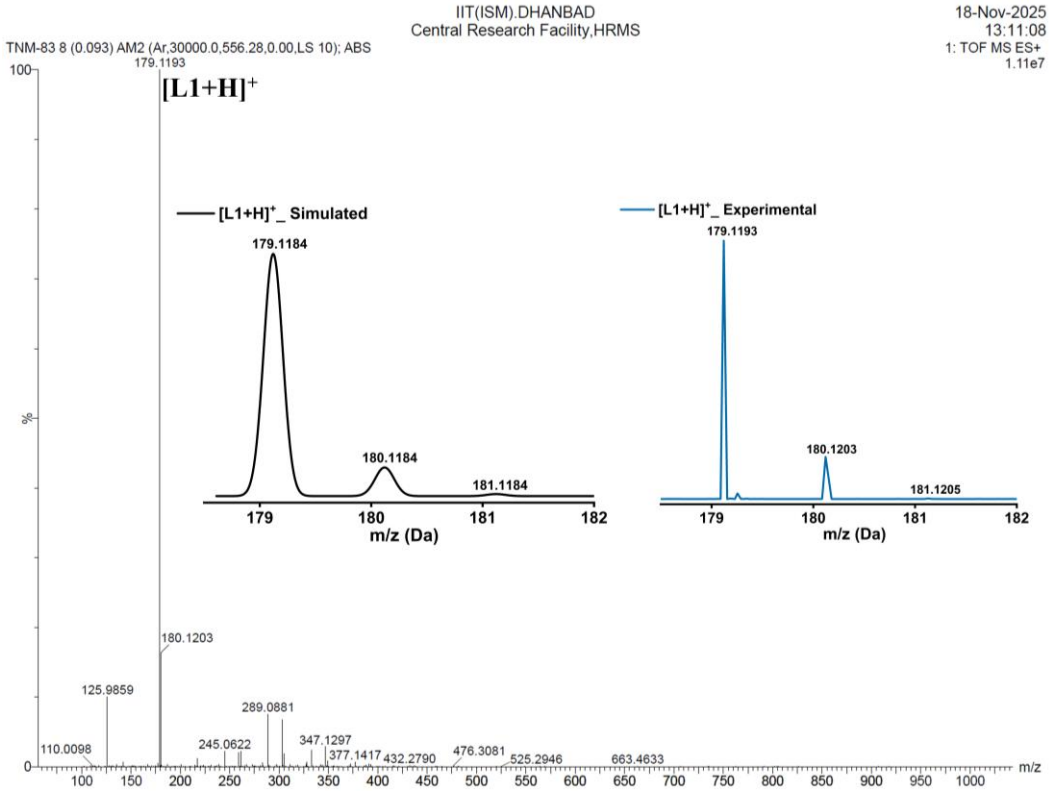


Figure S20. HR-MS (ESI, positive mode) spectrum of L1 in methanol.

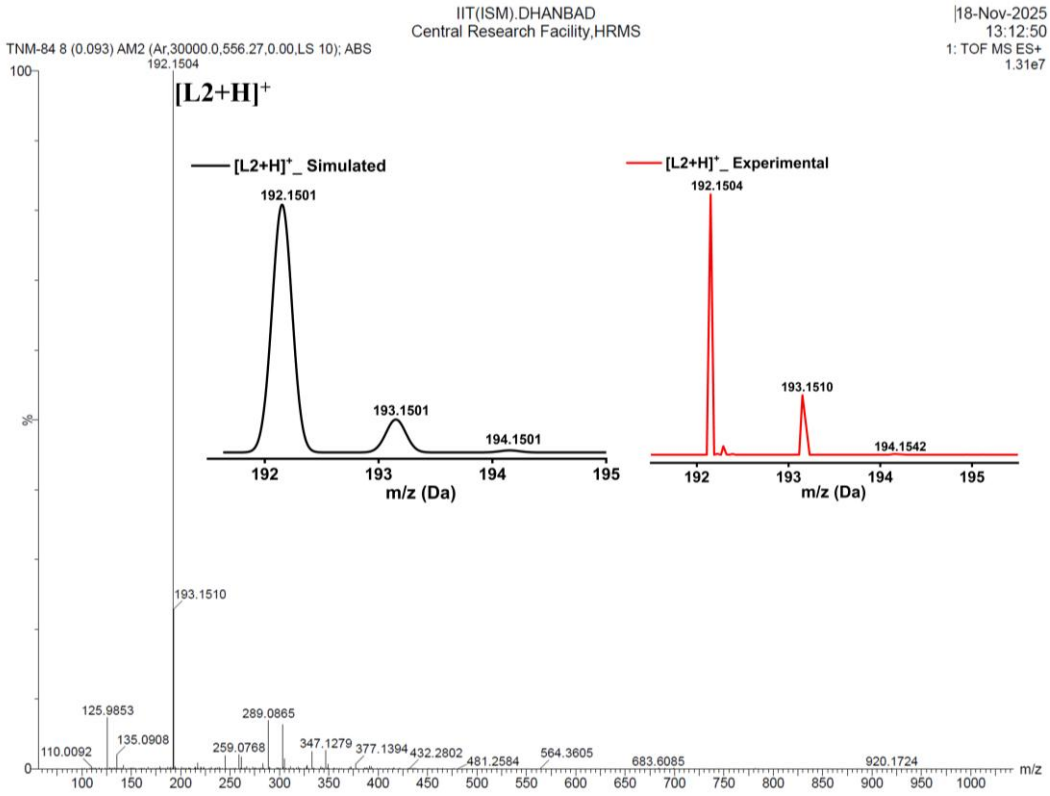


Figure S21. HR-MS (ESI, positive mode) spectrum of L2 in methanol.

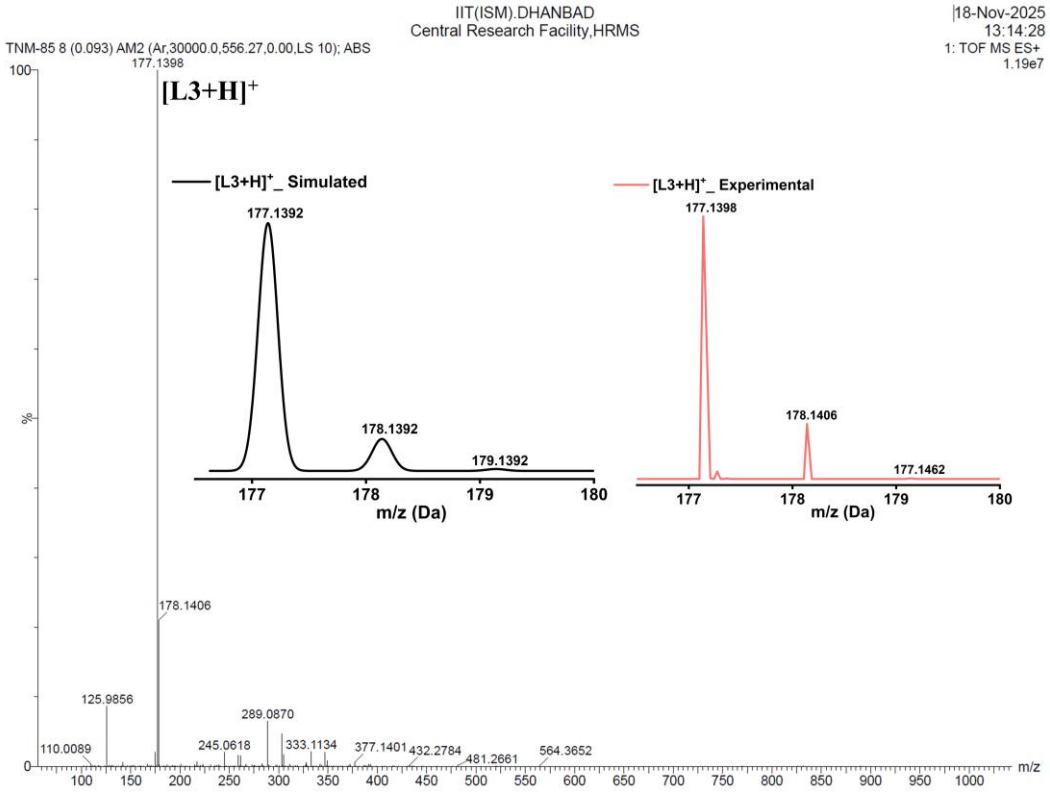


Figure S22. HR-MS (ESI, positive mode) spectrum of L3 in methanol.

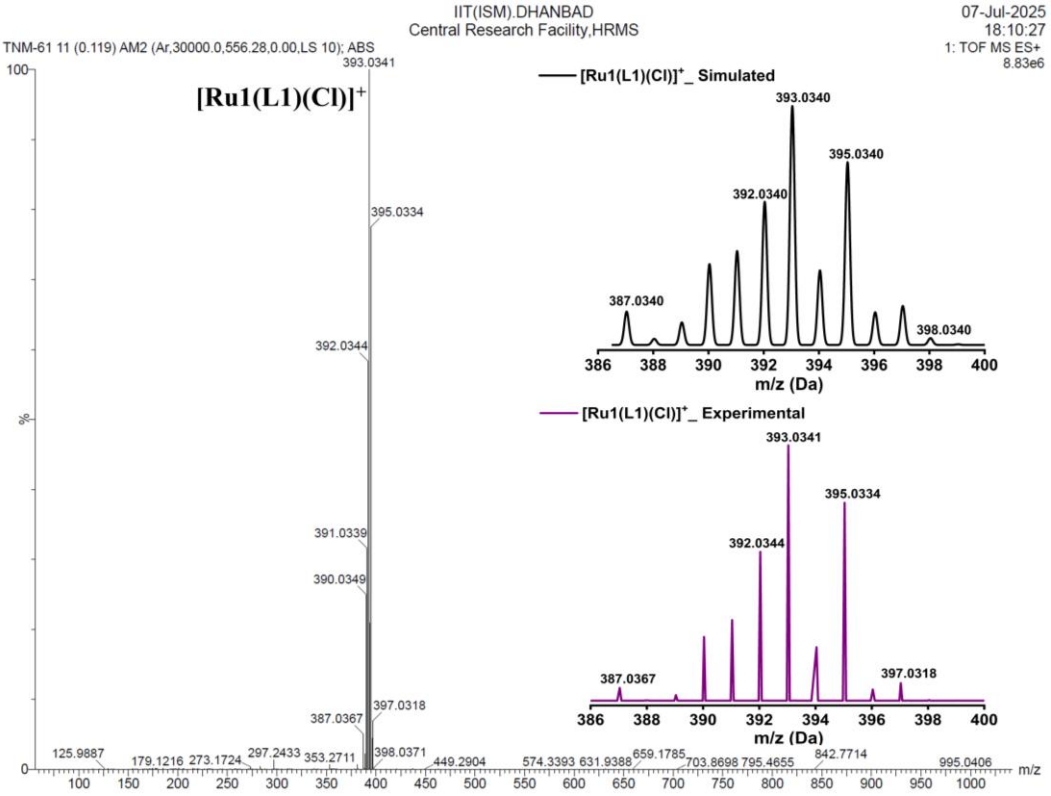


Figure S23. HR-MS (ESI, positive mode) spectrum of [Ru1] in methanol.

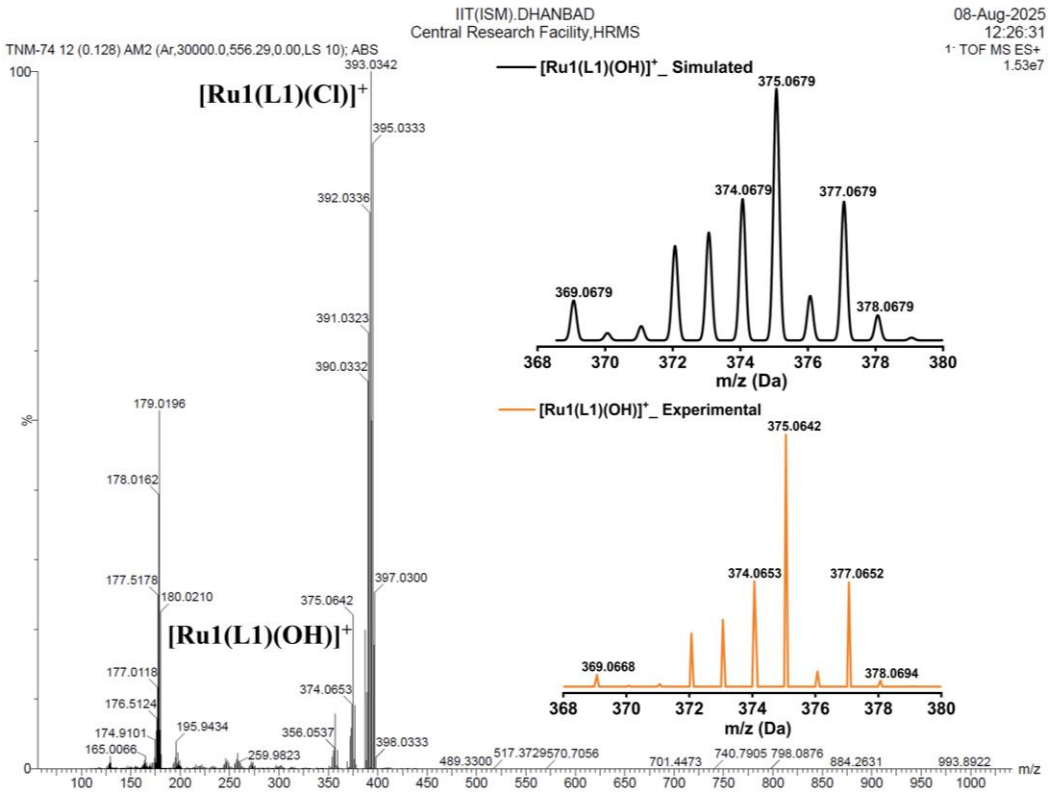


Figure S24. HR-MS (ESI, positive mode) spectrum of [Ru1] in water (recorded immediately after sample preparation).

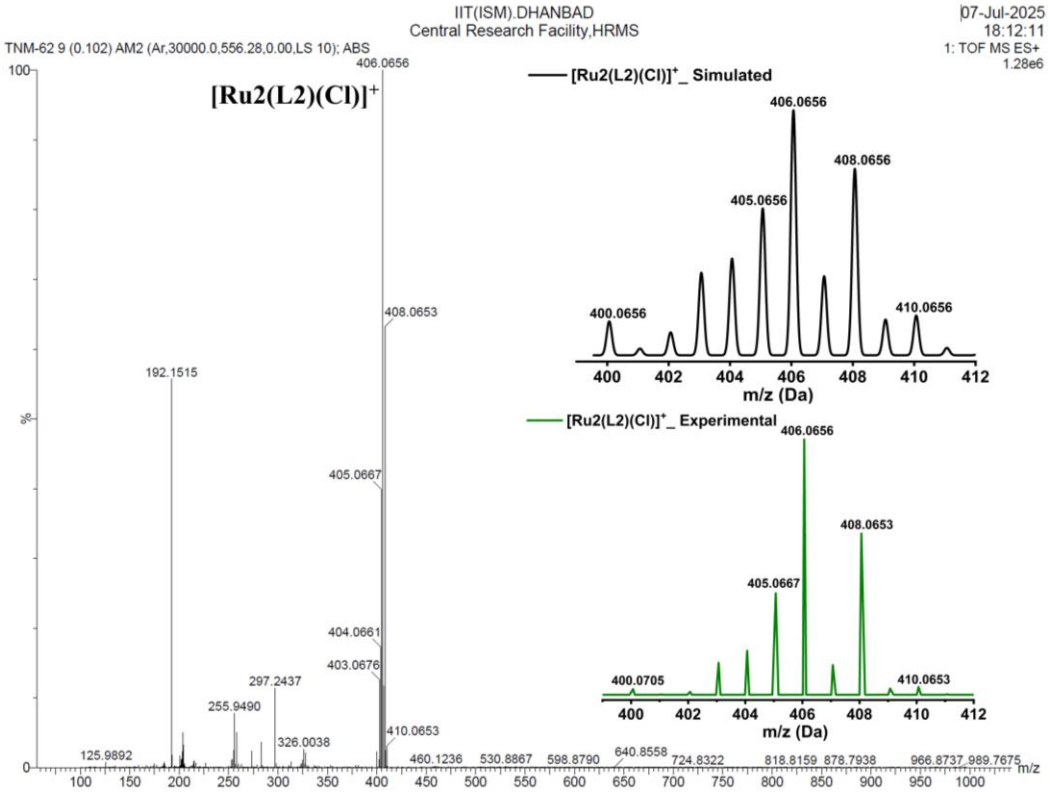


Figure S25. HR-MS (ESI, positive mode) spectrum of [Ru2] in methanol.

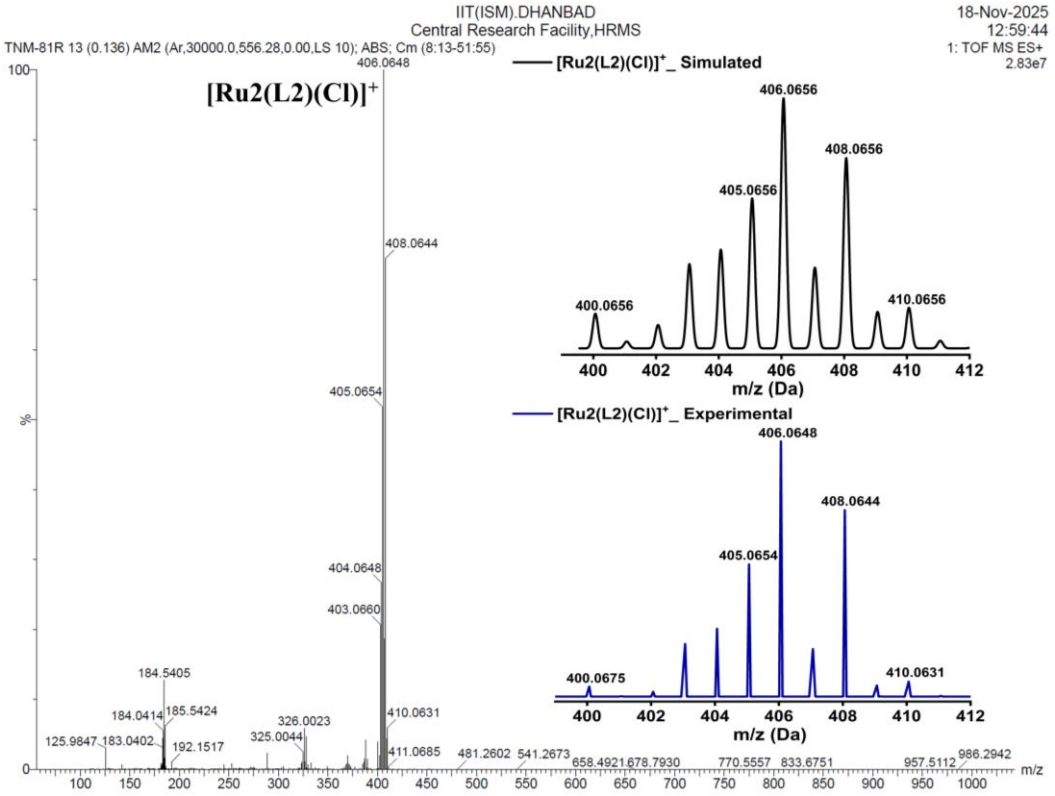


Figure S26. HR-MS (ESI, positive mode) spectrum of [Ru2] in water (recorded immediately after sample preparation.

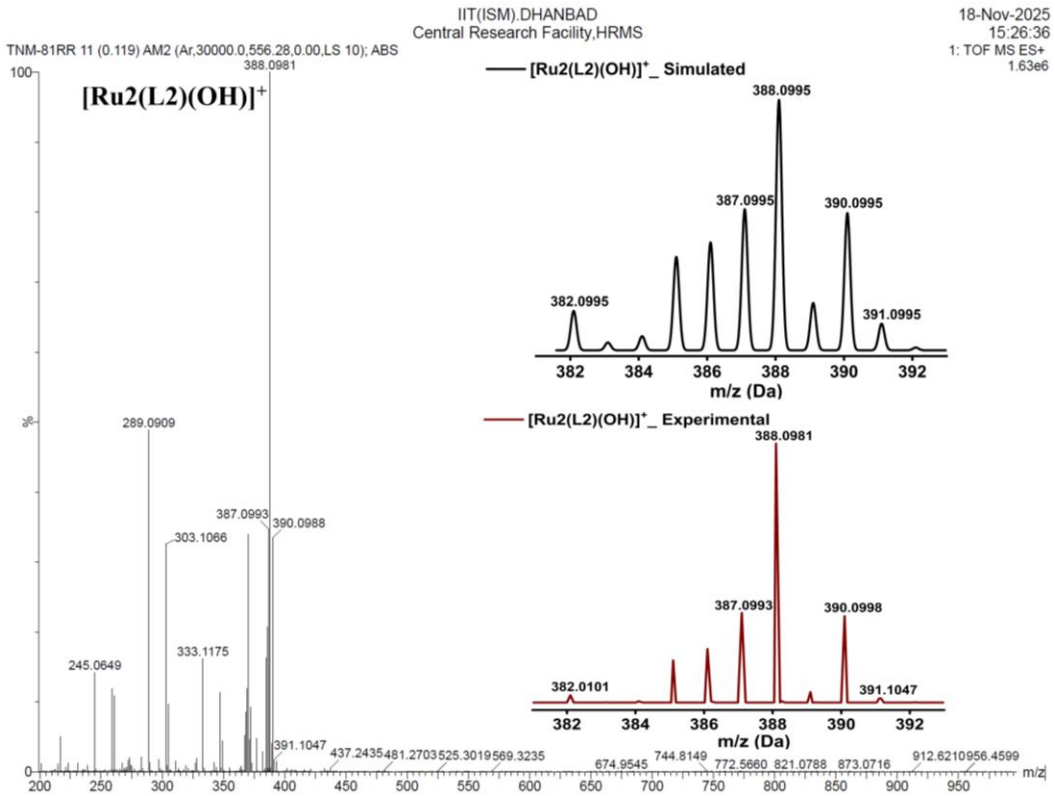


Figure S27. HR-MS (ESI, positive mode) spectrum of [Ru2] in water (recorded after 2 hours of sample preparation.

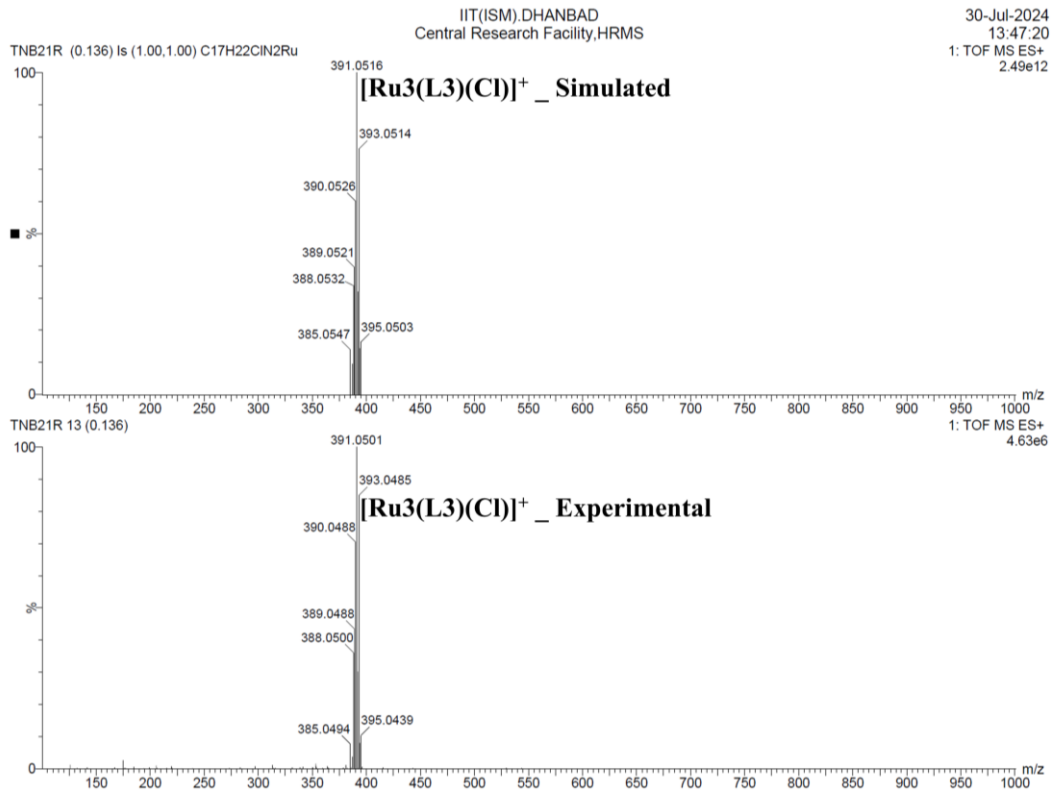


Figure S28. HR-MS (ESI, positive mode) spectrum of [Ru3] in methanol.

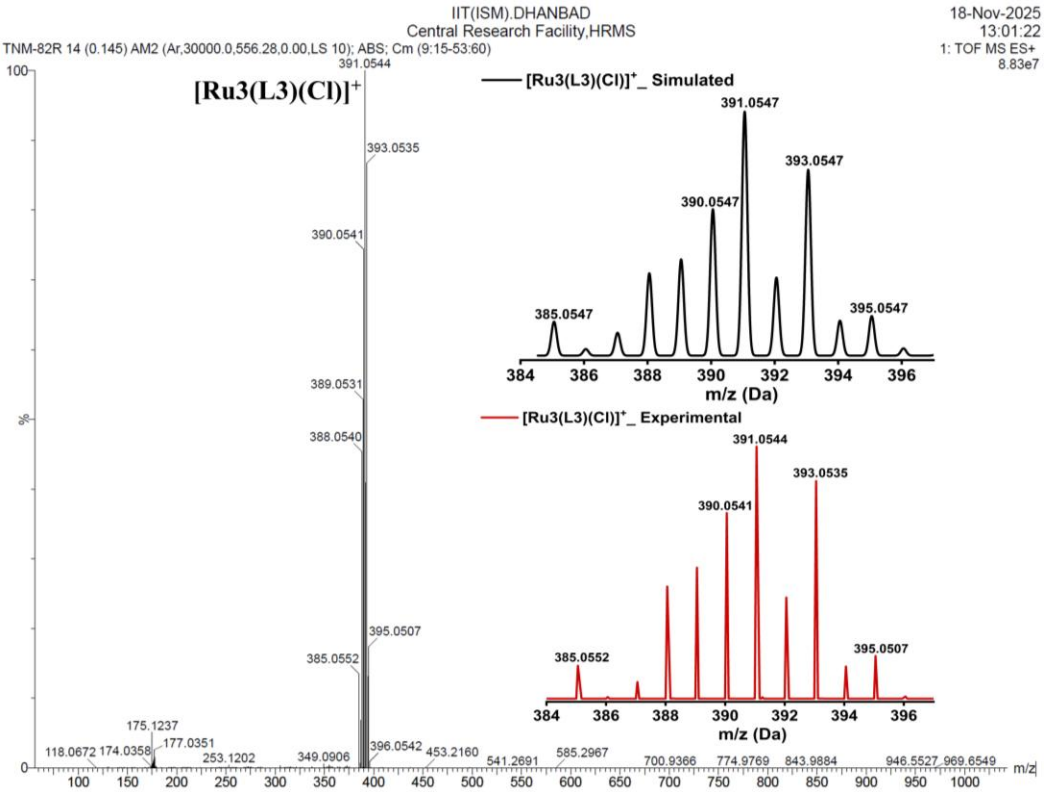


Figure S29. HR-MS (ESI, positive mode) spectrum of [Ru3] in water (recorded immediately after sample preparation.

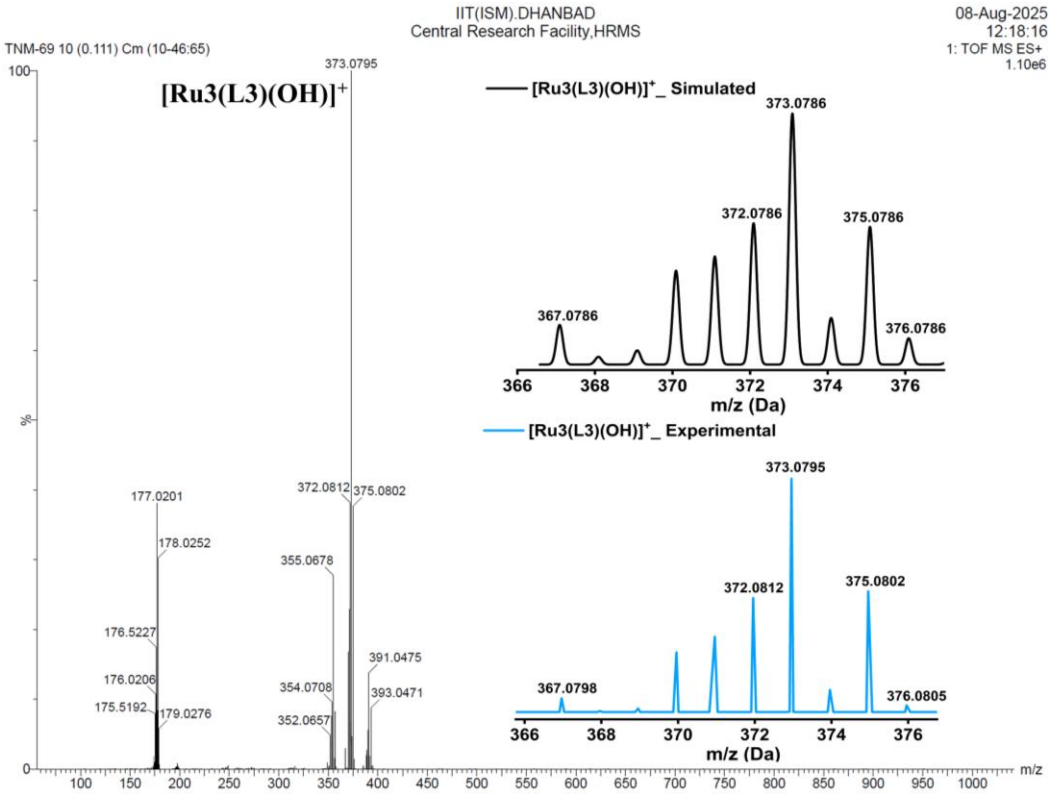


Figure S30. HR-MS (ESI, positive mode) spectrum of [Ru3] in water (recorded after 2 hours of sample preparation.

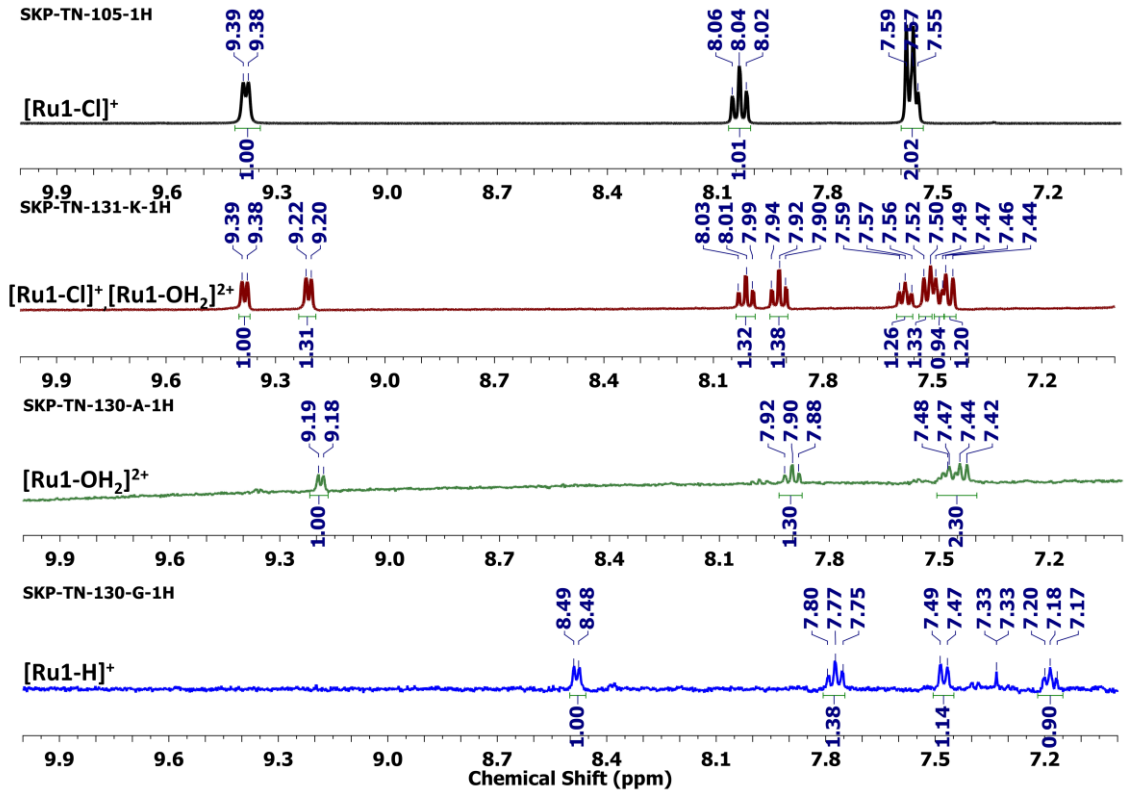


Figure S31. ^{1}H NMR spectrum during ammonia borane dehydrogenation using **[Ru1]** as the catalyst to identify ruthenium species in D_2O at 298 K.

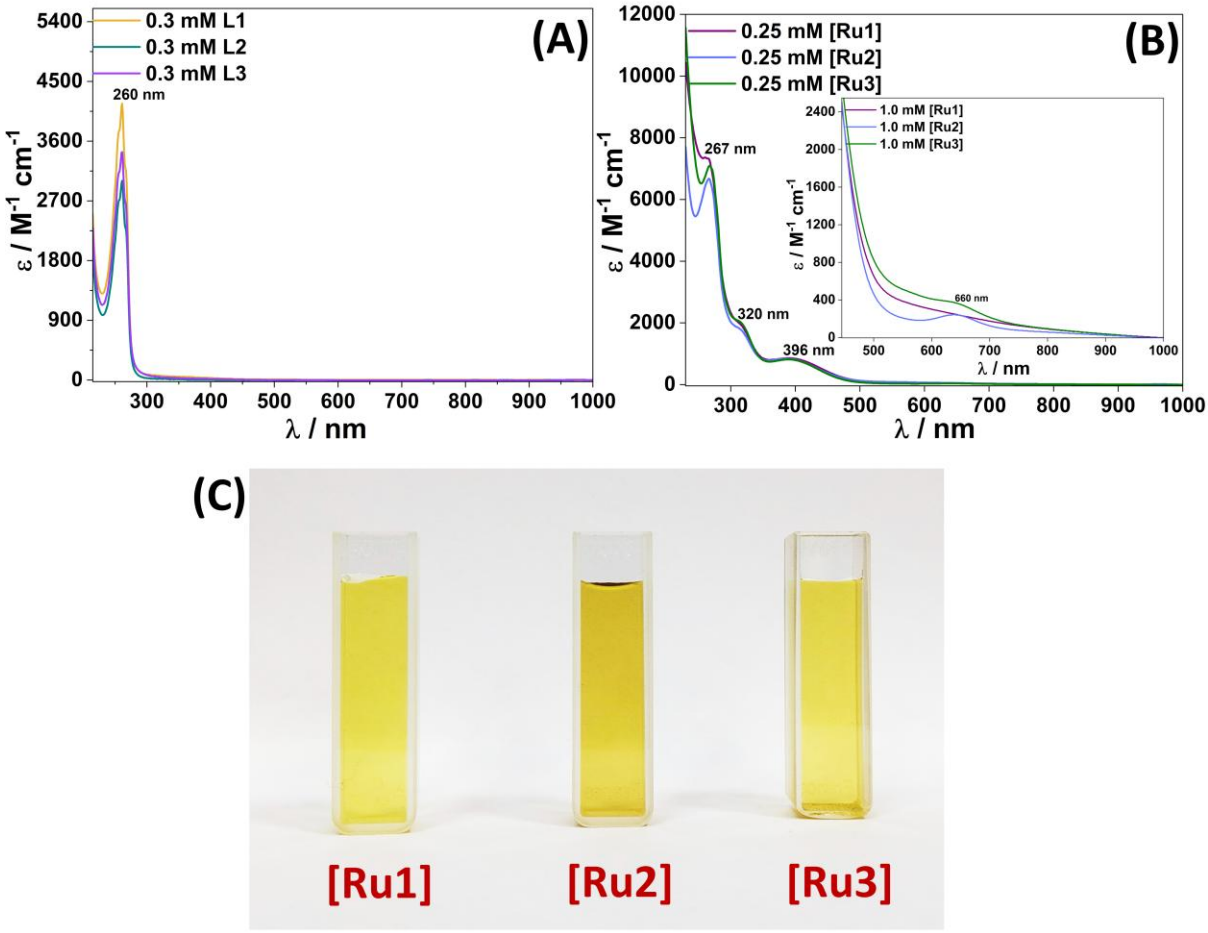


Figure S32. UV-visible spectra of (A) the ligand in methanol and (B) the complexes (Ru1: purple trace; Ru2: blue trace; Ru3: olive trace) in water, recorded using a double-beam Shimadzu UV-Vis spectrophotometer at 298 K. (C) Photographs showing the colors of the complexes (Ru1-Ru3, 1 mM) in water.

Table S1. Crystallographic data and processing parameters for **[Ru1-Ru3]**

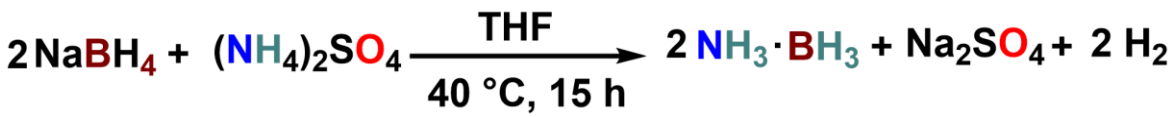
Complex	**[Ru1]**	**[Ru2]**	**[Ru3]**
Identification code	CCDC 2505754	CCDC 2505752	CCDC 2505753
Empirical formula	$C_{16}H_{20}ClF_6N_2OPRu$	$C_{17}H_{29}Cl_2N_3O_3Ru$	$C_{34}H_{40}Cl_2F_{12}N_4P_2Ru_2$
Formula weight	537.832	495.408	1067.687
Temperature (K)	293	293	293
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a (Å)	11.3484(5)	11.3950(7)	9.4601(16)
b (Å)	15.5897(6)	17.1279(9)	15.895(2)
c (Å)	11.7304(5)	11.6609(7)	26.358(6)
α (°)	90	90	90
β (°)	110.020(5)	110.596(7)	94.147(17)
γ (°)	90	90	90
Volume ($Å^3$)	1949.92(15)	2130.4(2)	3953.0(12)
Z	4	4	4
ρ_{calc} (g/cm^3)	1.832	1.545	1.794
μ (mm^{-1})	1.088	1.008	1.069
F (000)	1068.8	1012.7	2121.6
Crystal size (mm^3)	0.26 × 0.24 × 0.22	0.26 × 0.24 × 0.22	0.23 × 0.2 × 0.18
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection (°)	4.32 to 58.38	4.3 to 58.7	4.02 to 50
Index ranges	-15 ≤ h ≤ 15, -21 ≤ k ≤ 20, -15 ≤ l ≤ 11	-15 ≤ h ≤ 13, -23 ≤ k ≤ 14, -15 ≤ l ≤ 11	-12 ≤ h ≤ 11, -21 ≤ k ≤ 12, -33 ≤ l ≤ 35
Reflections collected	9821	10263	18943
Independent reflections	4519 [Rint = 0.0271, Rsigma = 0.0422]	4931 [Rint = 0.0273, Rsigma = 0.0402]	6741 [Rint = 0.0686, Rsigma = 0.1655]
Data/restraints/ parameters	4519/0/285	4931/7/255	6741/0/505
Goodness-of-fit on F^2	1.043	1.032	0.907
Final R indexes [I>=2σ (I)]	R1 = 0.0362, wR2 = 0.0833	R1 = 0.0337, wR2 = 0.0738	R1 = 0.0503, wR2 = 0.0526
Final R indexes [all data]	R1 = 0.0468, wR2 = 0.0897	R1 = 0.0508, wR2 = 0.0821	R1 = 0.1113, wR2 = 0.0663
Largest diff. peak/hole (e $Å^{-3}$)	0.85/-0.83	0.59/-0.46	1.06/-1.07

Table S2. Selected bond distances of the complexes [Ru1-Ru3]			
Atom	**[Ru1] / Å**	**[Ru2] / Å**	**[Ru3] / Å**
Ru–Cl	2.4054(10)	2.422(10)	2.4120(16)
Ru–N1 (pyridyl)	2.099(3)	2.111(3)	2.097(4)
Ru–N2 (amine)	2.191(3)	2.196(3)	2.178(4)
$Ru–C_{avg}$ (η^6-benzene)	2.187	2.189	2.192
$Ru–C_{centroid}$(η^6-benzene)	1.676	1.677	1.683
C6–N2 (amine)	1.496(4)	1.497(4)	1.506(6)
C8–O1	1.422(5)	–	–
C9–O1	1.432(5)	–	–
C8–N3	–	1.464(5)	–
C9–N3	–	1.464(5)	–
C11–N3	–	1.471(5)	–

Table S3. Selected bond angles of the complexes [Ru1-Ru3]			
Atom	**[Ru1] / °**	**[Ru2] / °**	**[Ru3] / °**
$N_{py}–Ru–N_{amine}$	77.90(11)	77.41(11)	77.08(14)
$N_{py}–Ru–Cl$	85.02(8)	86.73(8)	84.39(14)
$N_{amine}–Ru–Cl$	87.76(8)	86.73(7)	87.46(13)
$N_{py}–Ru–C_t$	132.41	131.41	132.97
$N_{amine}–Ru–C_t$	131.85	132.33	132.45
$Cl–Ru–C_t$	125.02	125.40	125.06

4. Synthesis of ammonia borane:

Scheme S4. Synthetic route for the ammonia borane ($NH_3.BH_3$)



Ammonia borane was prepared following a literature-reported procedure.[3] Sodium borohydride (2.00 g, 53 mmol) and ammonium sulfate (6.99 g, 53 mmol) were first thoroughly ground together in a mortar and transferred to a 500 mL double-neck round-bottom flask. Dry THF (250 mL) was then added, and the mixture was vigorously stirred at 40 °C for 12 h under a nitrogen atmosphere. The progress of the reaction was monitored by ^{11}B NMR spectroscopy. Upon completion, the reaction mixture was cooled to room temperature and filtered through a Celite pad. The filtrate was concentrated under reduced pressure to yield highly pure ammonia borane.

Yield: 83% (1.35 g)

Nature: White solid

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 4.42 (s, 3H, N-H), 1.43 – 1.10 (m, 3H, B-H).

^{11}B NMR (128 MHz, DMSO-d_6) δ (ppm): -22.99 (dd, J = 166.9, 78.3 Hz).

^{11}B NMR (128 MHz, D_2O) δ (ppm): -23.85 (q, J = 91.0 Hz).

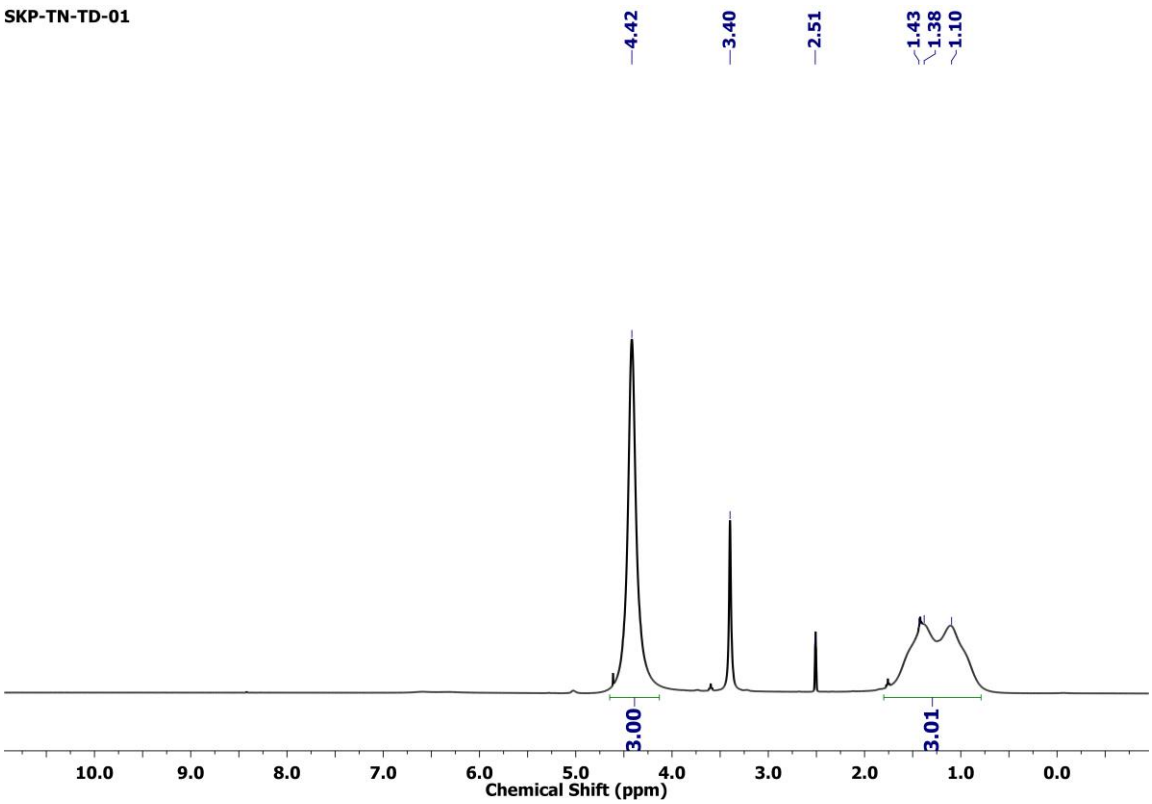


Figure S33. ^{1}H NMR (400 MHz) spectrum of ammonia borane in DMSO-d_6.

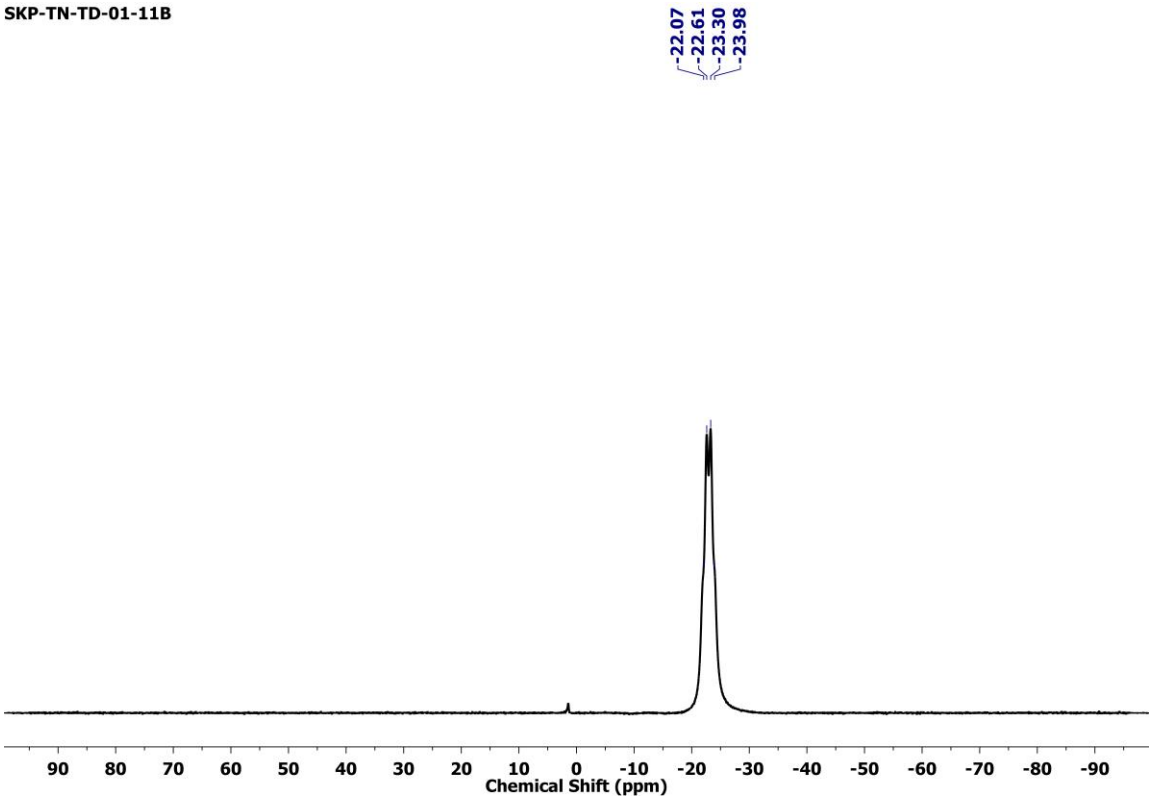


Figure S34. ^{11}B NMR (128 MHz) spectrum of ammonia borane in DMSO-d_6.

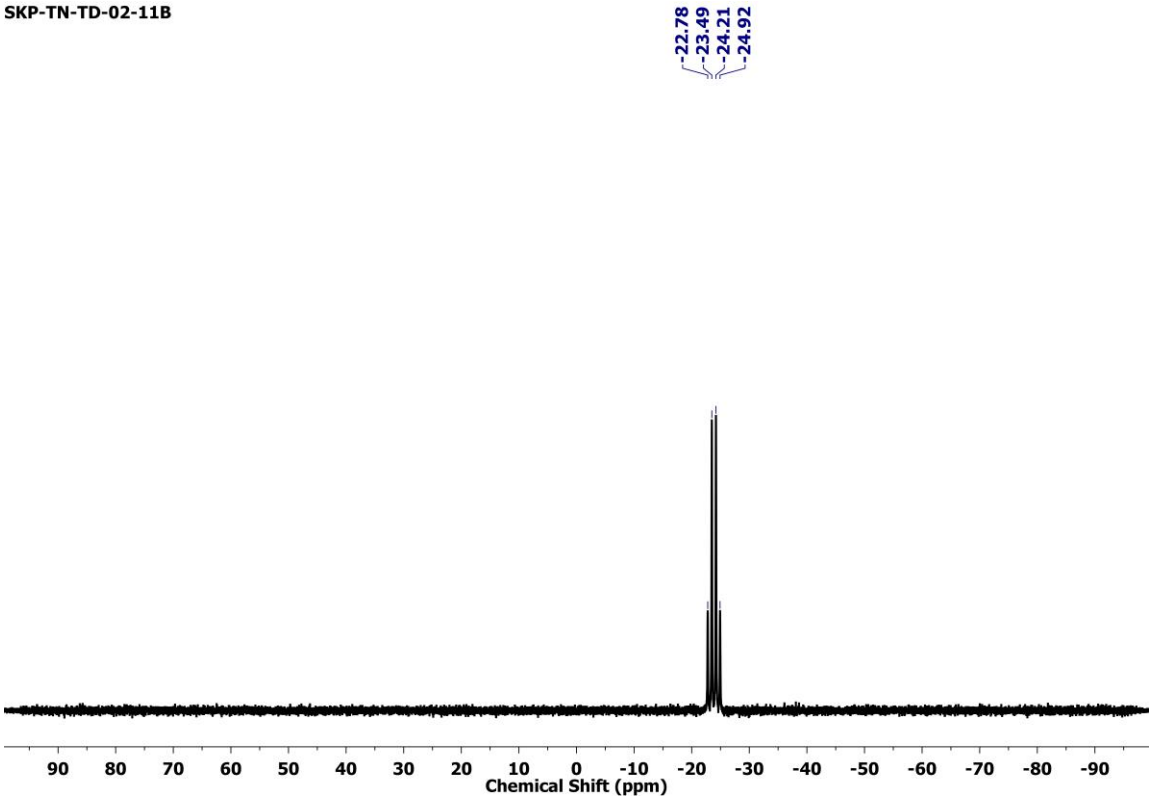


Figure S35. ^{11}B NMR (128 MHz) spectrum of ammonia borane in D_2O.

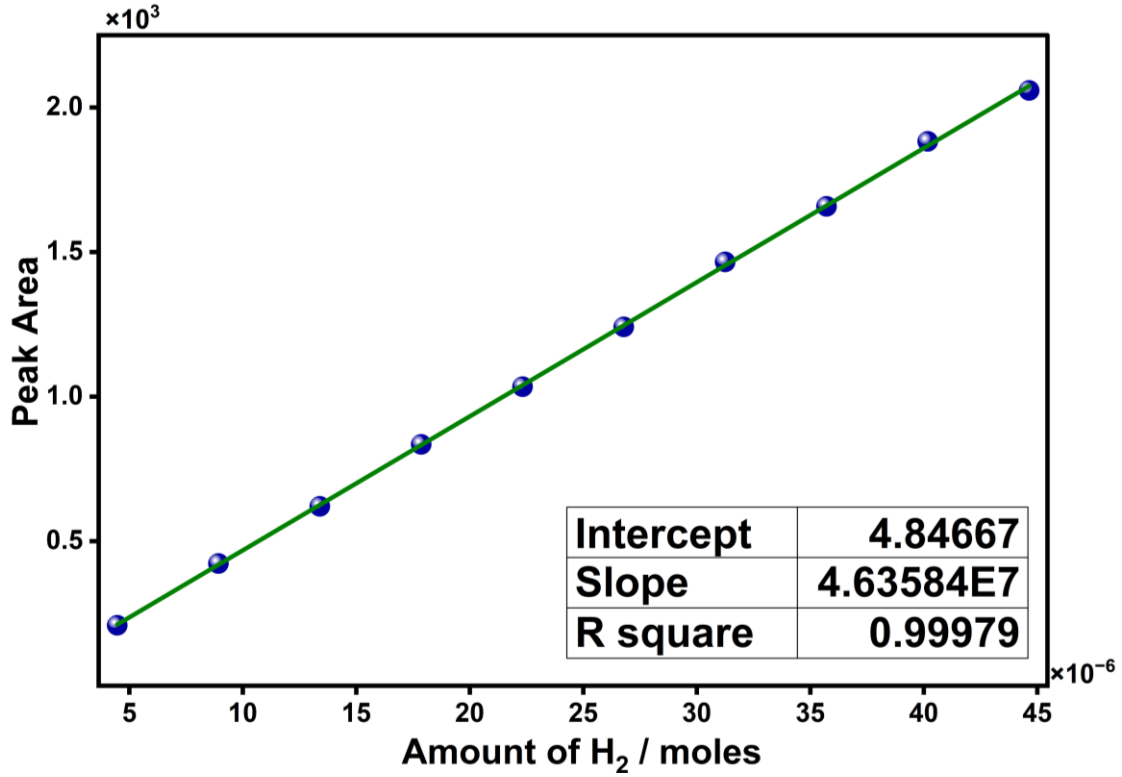


Figure S36. Gas chromatography calibration lines obtained for H_2.

Table S4. Homogeneous Ruthenium [Ru1] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	[Ru(mor)] (µmol)	Moles of H_2 (µmol)	TON	TOF (h^{-1})	Equivalents of H_2 per AB
32.29	1.86	64.26	34.55	69.1	1.98
64.79	1.86	120.98	65.04	130.08	1.87
97.18	1.86	183.08	98.43	196.86	1.88
129.58	1.86	253.14	136.1	272.2	1.95
161.97	1.86	272	146.24	292.48	1.68

Table S5. Homogeneous Ruthenium [Ru1] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	[Ru(mor)] (µmol)	Moles of H_2 (µmol)	TON	TOF (h^{-1})	Equivalents of H_2 per AB
161.97	0	29.41	-	-	0.18
161.97	0.74	145.53	196.7	393.4	0.9
161.97	1.12	181.9	162.41	324.82	1.12
161.97	1.49	212.92	142.9	285.8	1.31
161.97	1.86	272	146.24	292.48	1.68
161.97	2.23	317.13	142.21	284.42	1.96

Table S6. Homogeneous Ruthenium [Ru2] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	[Ru(mor)] (µmol)	Moles of H_2 (µmol)	TON	TOF (h^{-1})	Equivalents of H_2 per AB
32.29	1.86	95.28	51.22	102.44	2.95
64.79	1.86	172.54	92.76	185.52	2.66

97.18	1.86	236.69	127.25	254.5	2.44
129.58	1.86	279.82	150.44	300.88	2.16
161.97	1.86	309	166.13	332.26	1.91

Table S7. Homogeneous Ruthenium [Ru2] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	**[Ru(mor)] (µmol)**	**Moles of H_2 (µmol)**	**TON**	**TOF (h^{-1})**	**Equivalents of H_2 per AB**
161.97	0	29.41	-	-	0.18
161.97	0.74	182.99	247.28	494.56	1.13
161.97	1.12	220.22	196.62	393.24	1.36
161.97	1.49	298.49	200.33	400.66	1.84
161.97	1.86	309	166.13	332.26	1.91
161.97	2.23	328.44	147.28	294.56	2.03

Table S8. Homogeneous Ruthenium [Ru3] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	**[Ru(mor)] (µmol)**	**Moles of H_2 (µmol)**	**TON**	**TOF (h^{-1})**	**Equivalents of H_2 per AB**

32.29	1.86	72.83	39.16	78.32	2.25
64.79	1.86	144.14	77.49	154.98	2.22
97.18	1.86	198.14	106.53	213.06	2.04
129.58	1.86	265.78	142.89	285.78	2.05
161.97	1.86	299.37	160.95	321.9	1.85

Table S9. Homogeneous Ruthenium [Ru3] Catalysed AB Dehydrogenation Catalyst Performance (25 °C, water)

[AB] (µmol)	**[Ru(mor)] (µmol)**	**Moles of H_2 (µmol)**	**TON**	**TOF (h^{-1})**	**Equivalents of H_2 per AB**
161.97	0	29.41	-	-	0.18
161.97	0.74	166.79	225.39	450.78	1.03
161.97	1.12	200.95	179.42	358.84	1.24
161.97	1.49	265.78	178.38	356.76	1.64
161.97	1.86	299.37	160.95	321.9	1.85
161.97	2.23	327.14	146.7	293.4	2.02

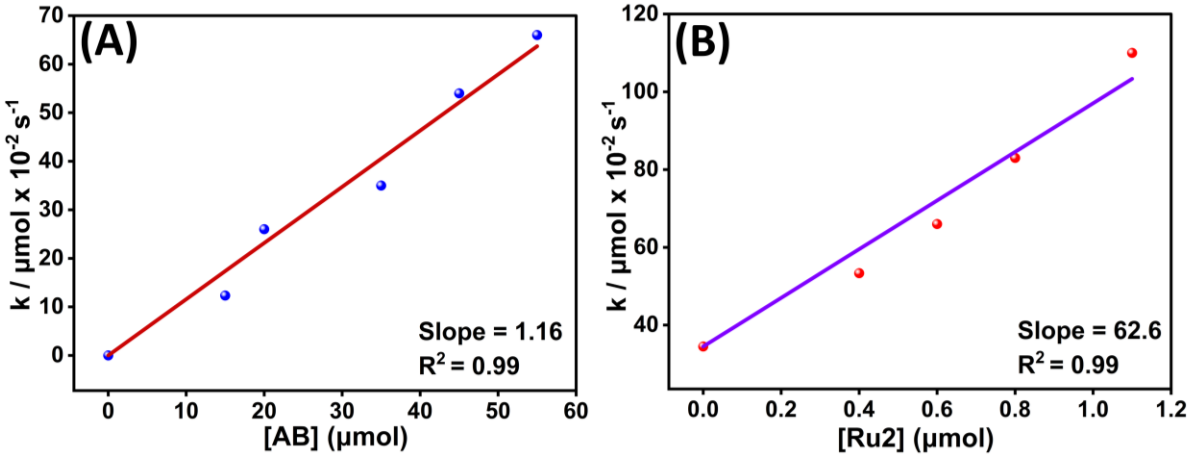


Figure S37. (A) Dependence of the H_2 evolution rate on the concentration of ammonia borane, (B) Dependence of the H_2 evolution rate on the concentration of Ru2.

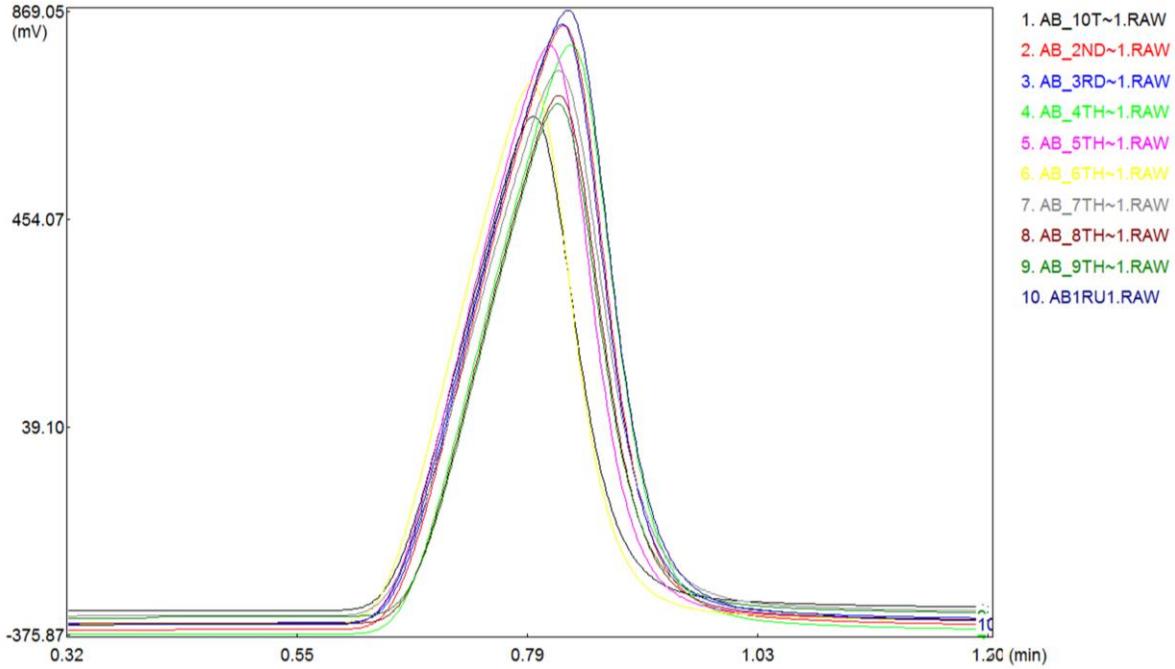


Figure S38. The overlaid gas chromatograms of H_2 evolution for the reaction of ammonia borane (161.97 µmol) with the first loading of Ru1 catalyst (1.86 µmol), followed by nine successive additions of ammonia borane (161.97 µmol), illustrate the recyclability performance of the catalyst.

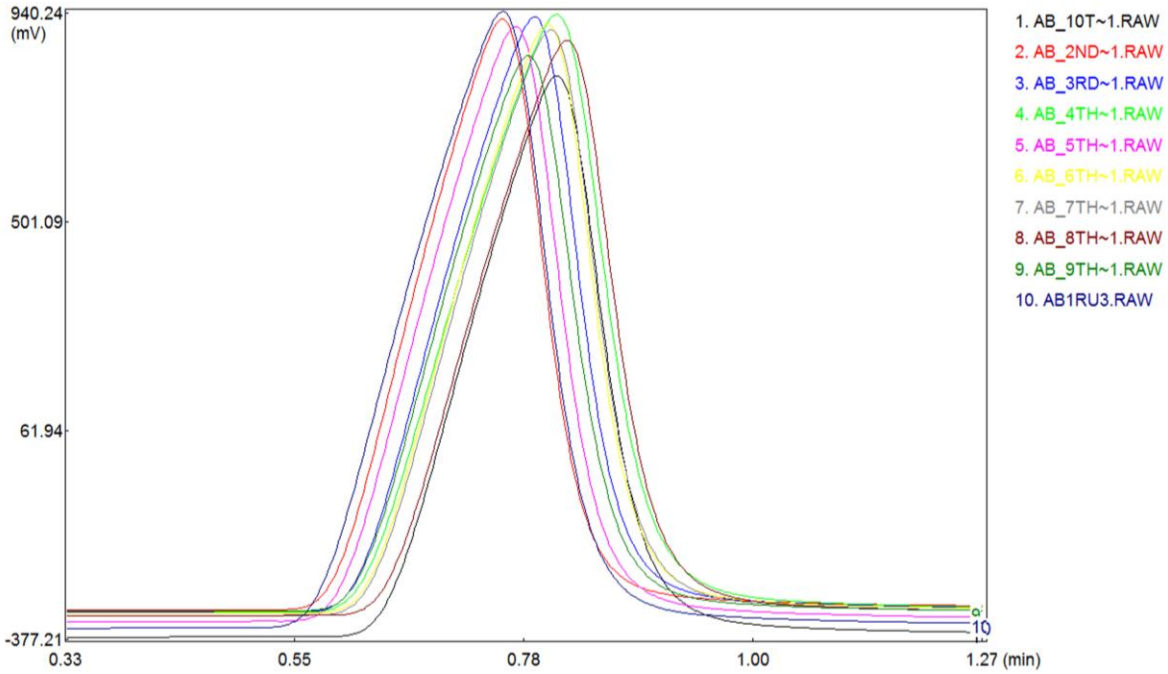


Figure S39. The overlaid gas chromatograms of H_2 evolution for the reaction of ammonia borane (161.97 µmol) with the first loading of Ru3 catalyst (1.86 µmol), followed by nine successive additions of ammonia borane (161.97 µmol), illustrate the recyclability performance of the catalyst.

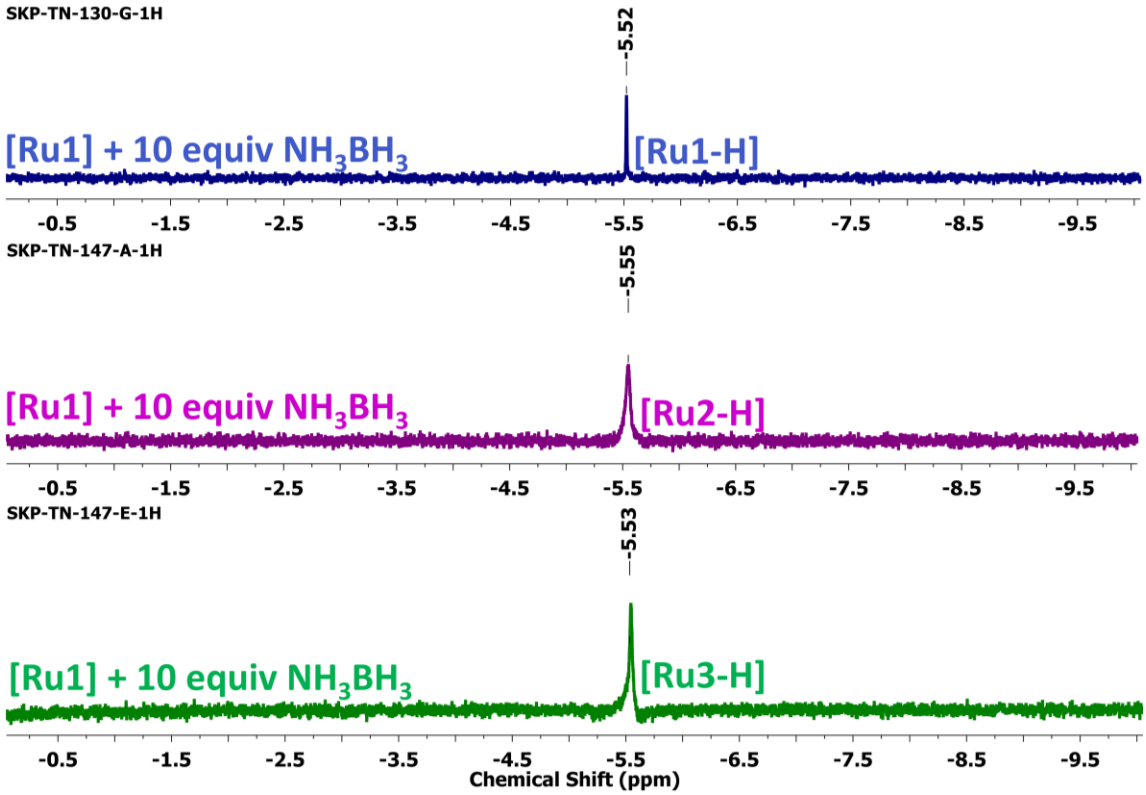


Figure S40. In situ ^{1}H NMR detection of Ruthenium-Hydride using **[Ru1-Ru3]** as the catalysts with the addition of 10 equivalents of ammonia borane in D_2O at 298 K.

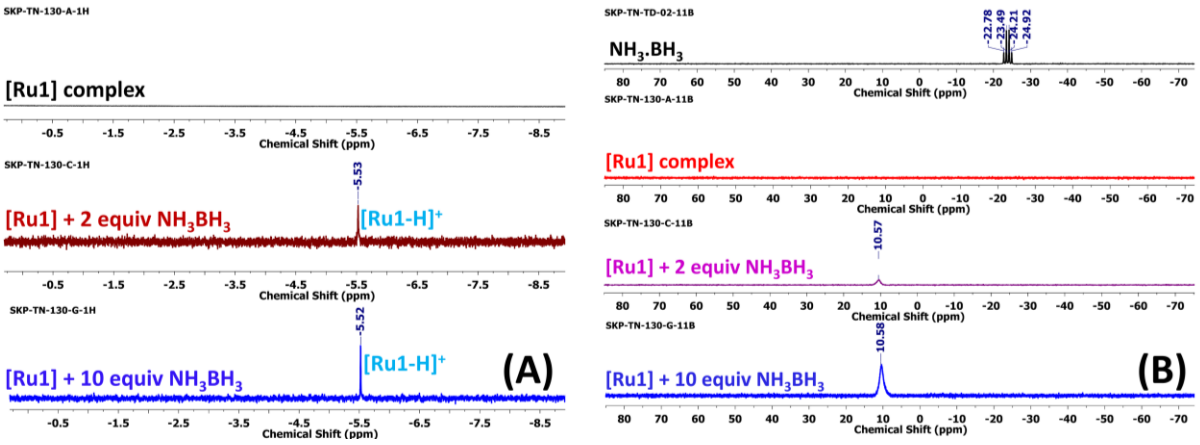


Figure S41. (A) ^{1}H and (B) ^{11}B NMR spectrum of [Ru1] with the addition of different equivalents of ammonia borane in D_2O at 298 K.

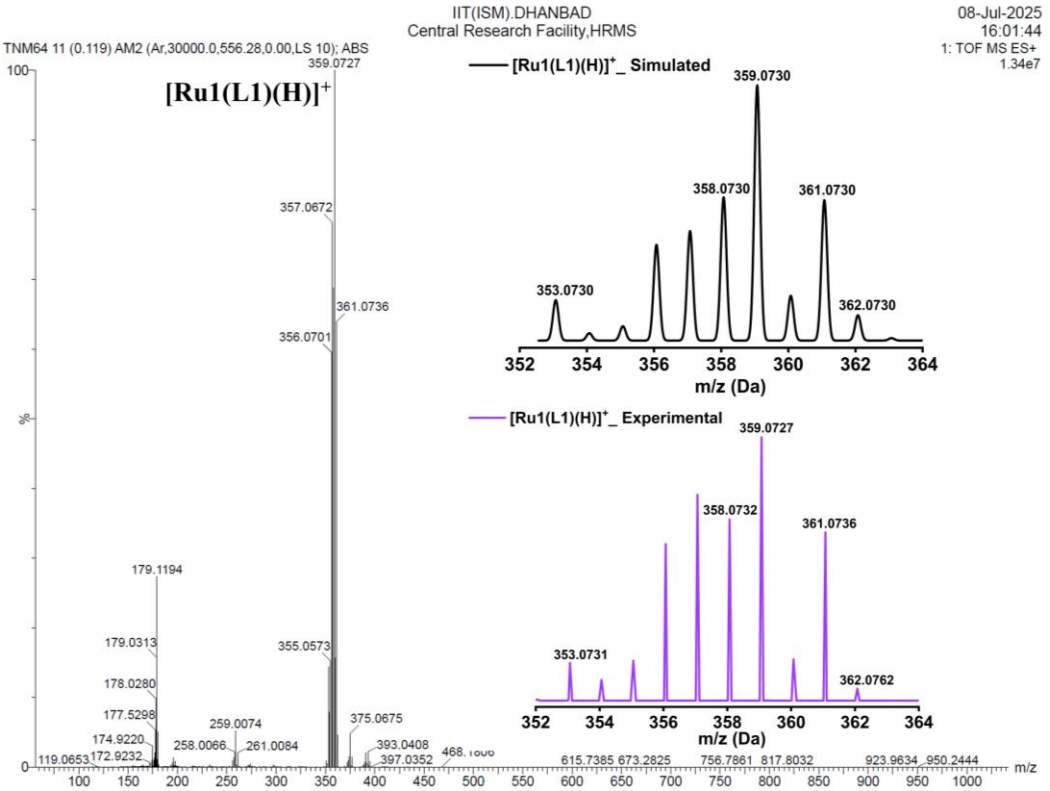


Figure S42. HR-MS (ESI, positive mode) spectrum of [Ru1] in water after the addition of 10 equiv of ammonia borane.

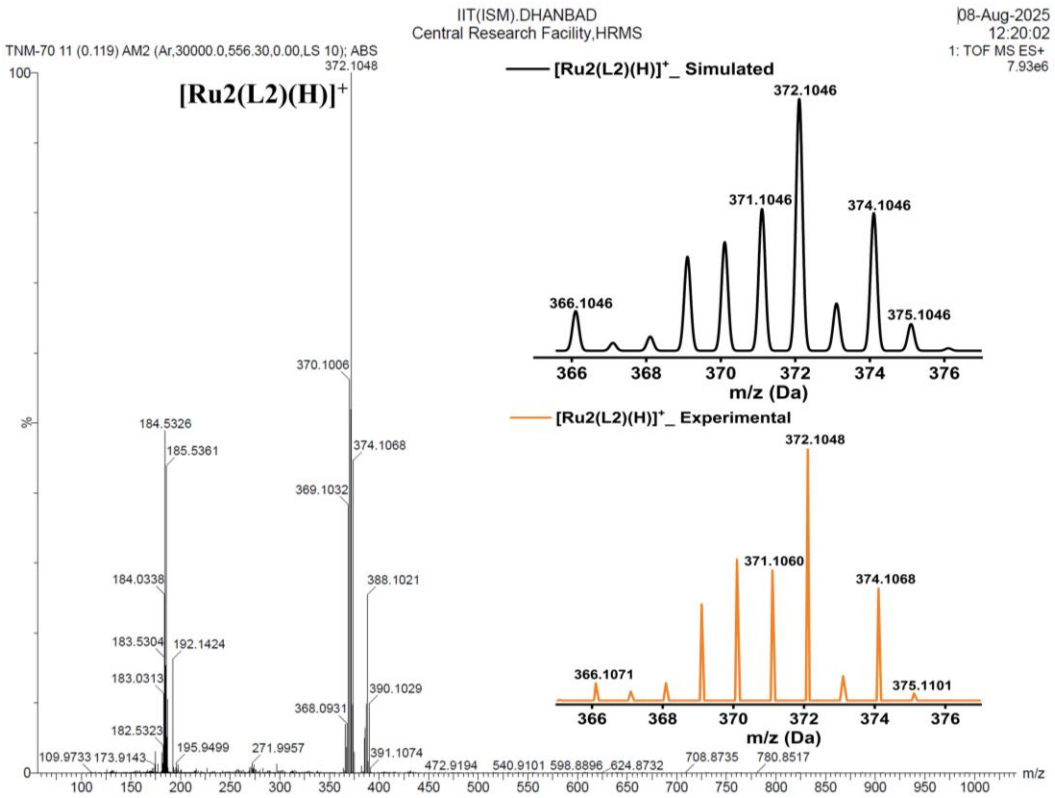


Figure S43. HR-MS (ESI, positive mode) spectrum of [Ru2] in water after the addition of 10 equiv of ammonia borane.

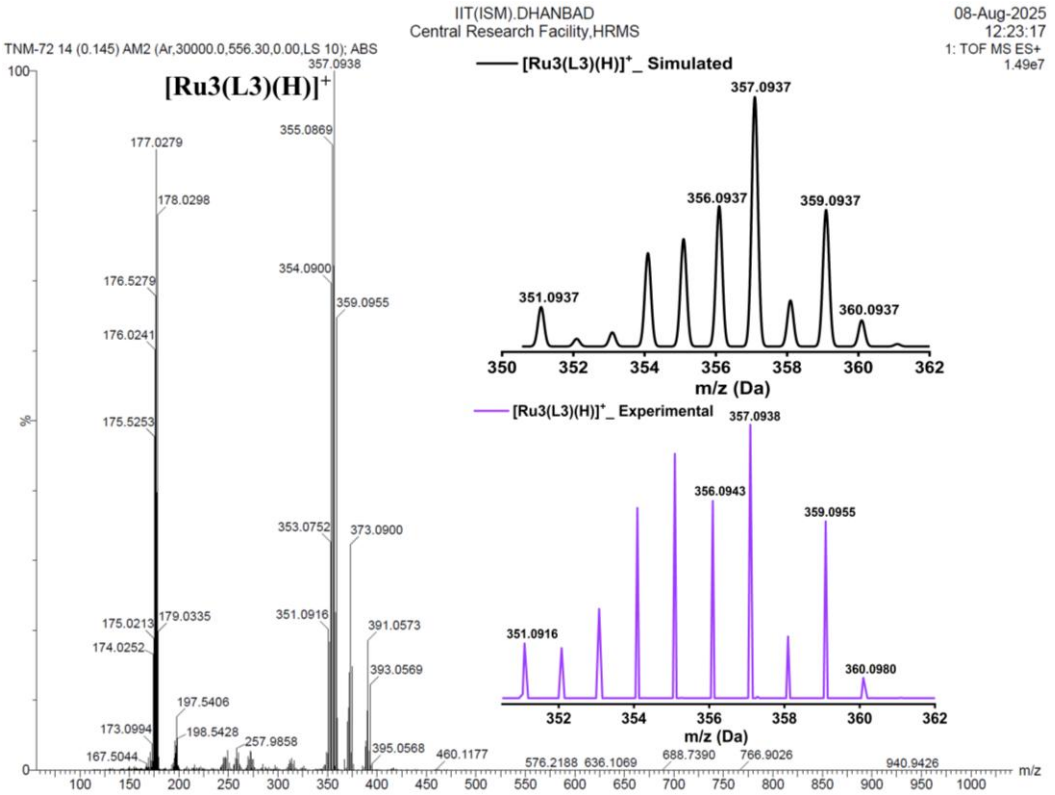


Figure S44. HR-MS (ESI, positive mode) spectrum of [Ru3] in water after the addition of 10 equiv of ammonia borane.

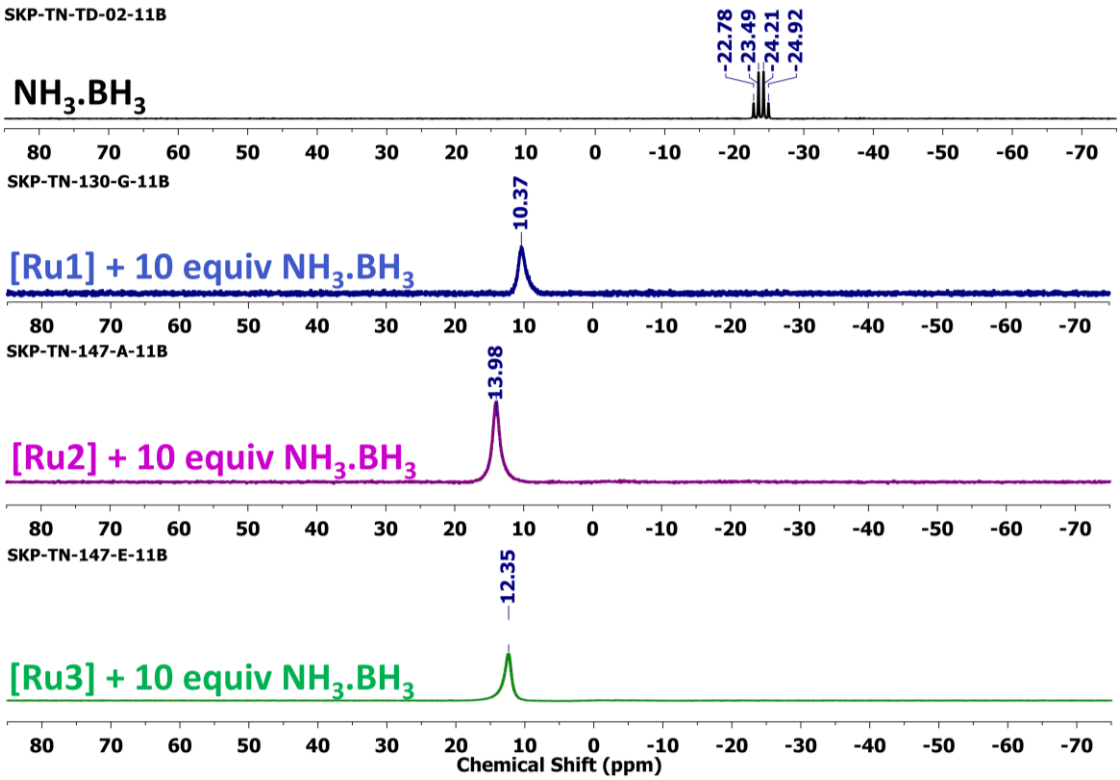
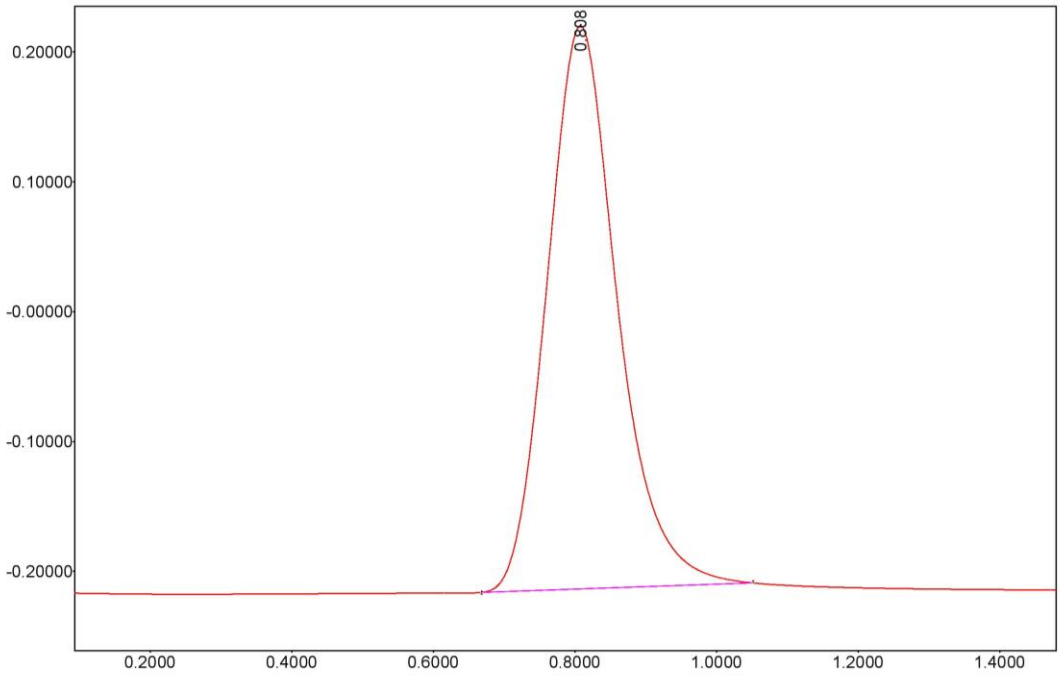
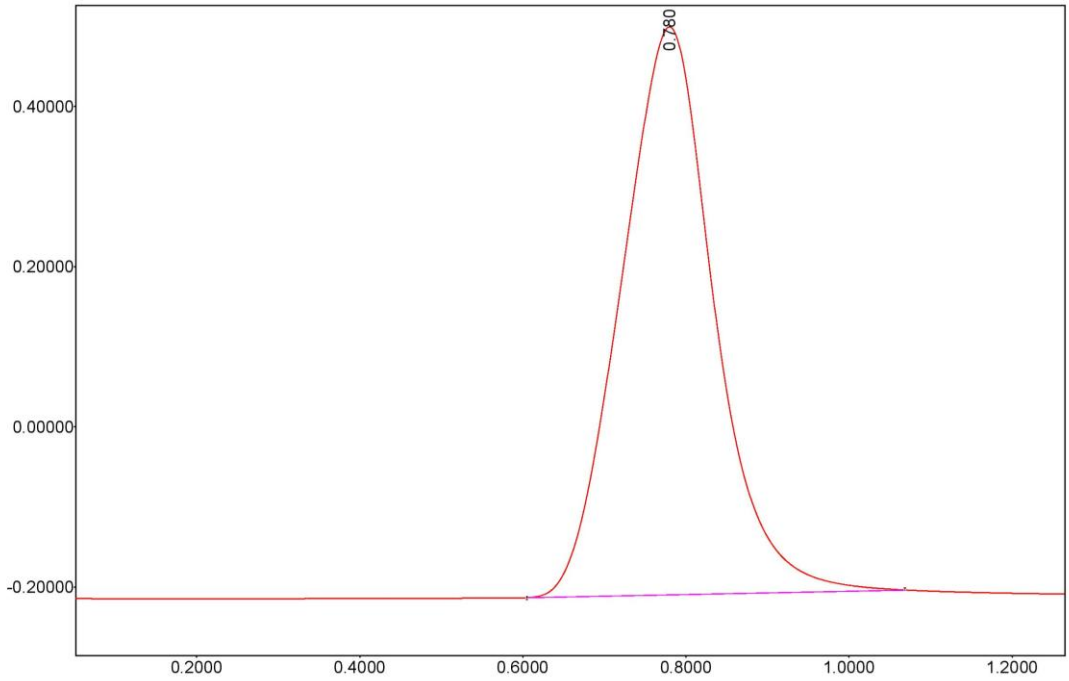


Figure S45. In situ ^{11}B NMR detection of borate species using **[Ru1-Ru3]** as the catalysts with the addition of 10 equivalents of ammonia borane in D_2O at 298 K.



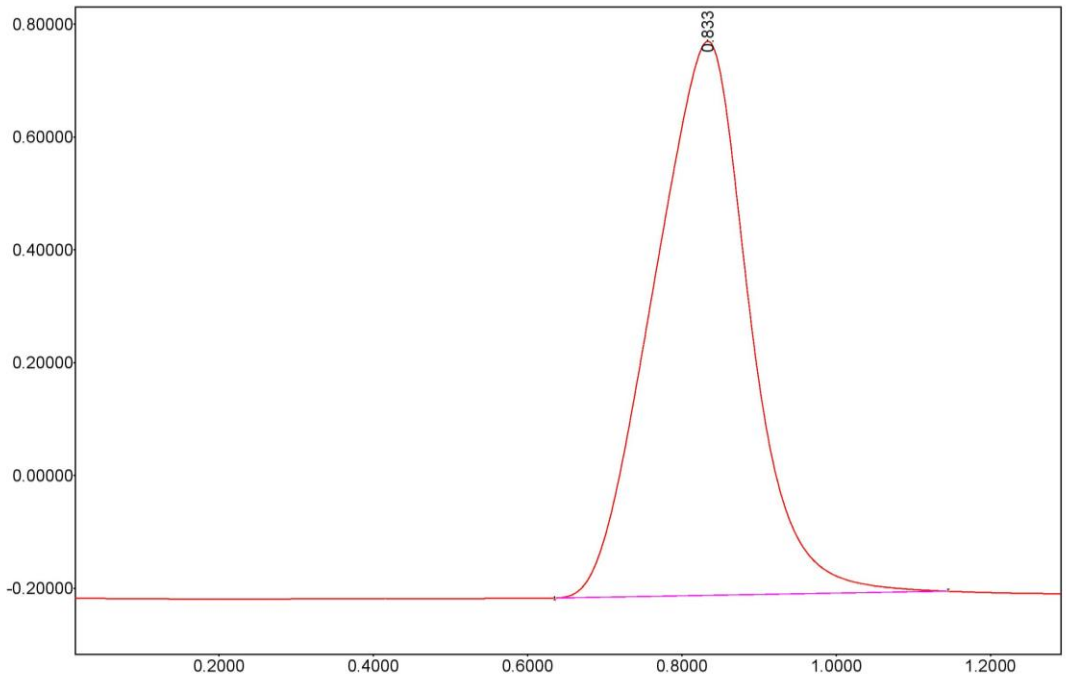
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.808	2979.978	BB	23.000	100.000

Figure S46. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 32.29 μmol) catalyzed by [Ru1] (1.86 μmol) at 25 °C for 30 min.



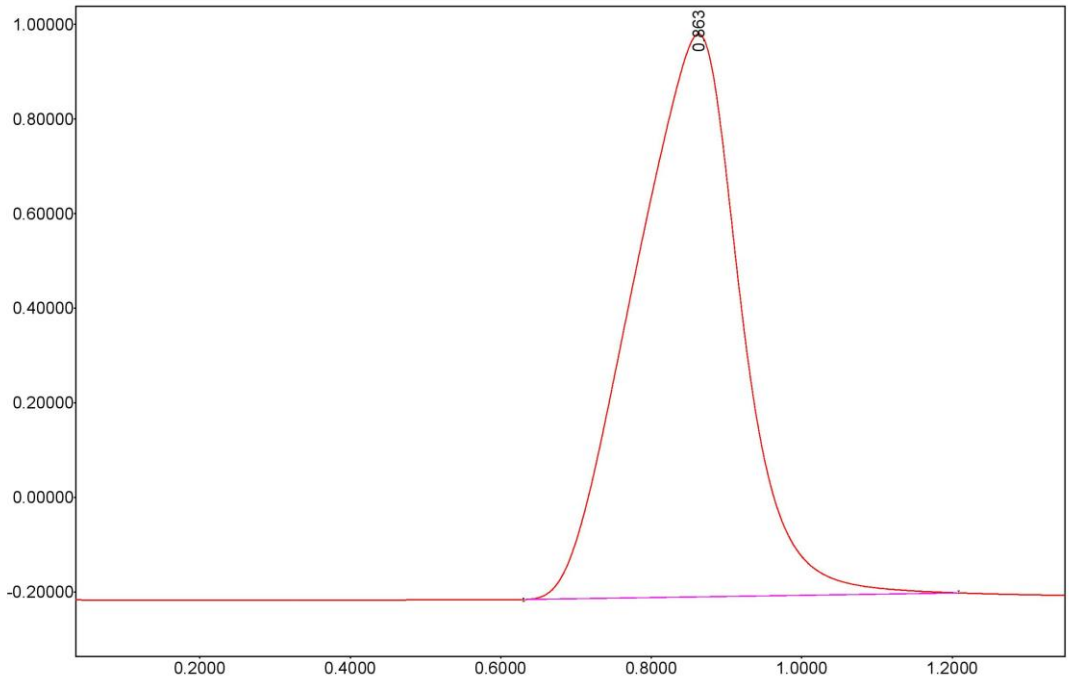
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.780	5606.244	BB	27.800	100.000

Figure S47. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 64.79 μmol) catalyzed by [Ru1] (1.86 μmol) at 25 °C for 30 min.



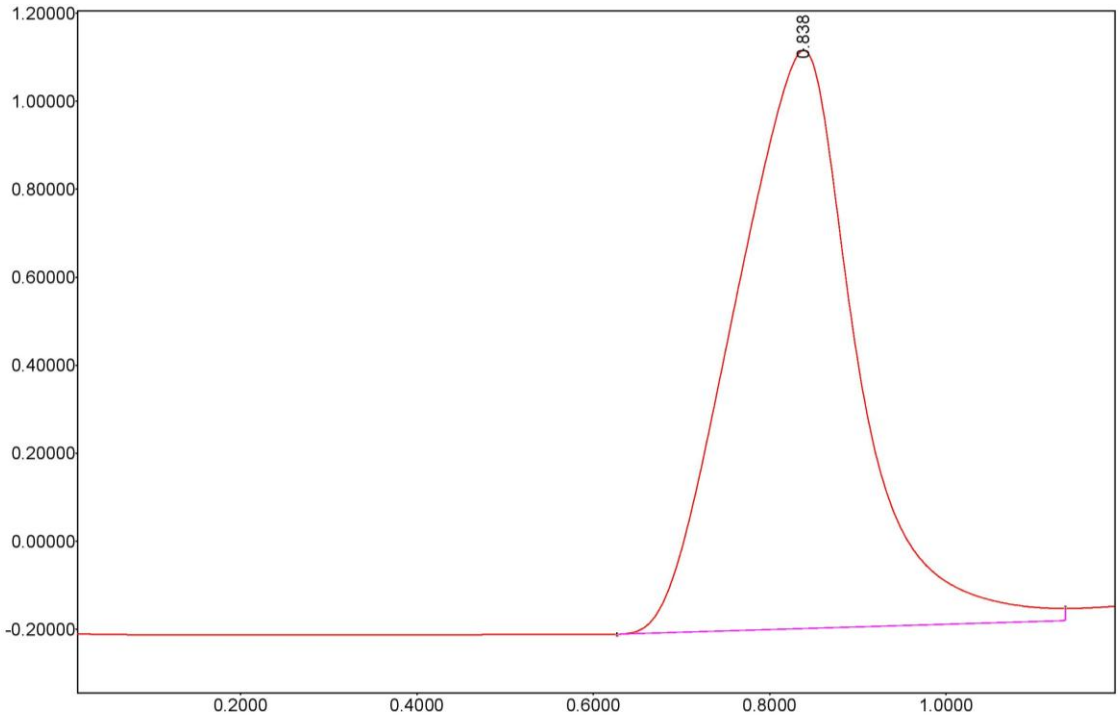
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.833	8481.468	BB	30.600	100.000

Figure S48. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 97.18 µmol) catalyzed by [Ru1] (1.86 µmol) at 25 °C for 30 min.



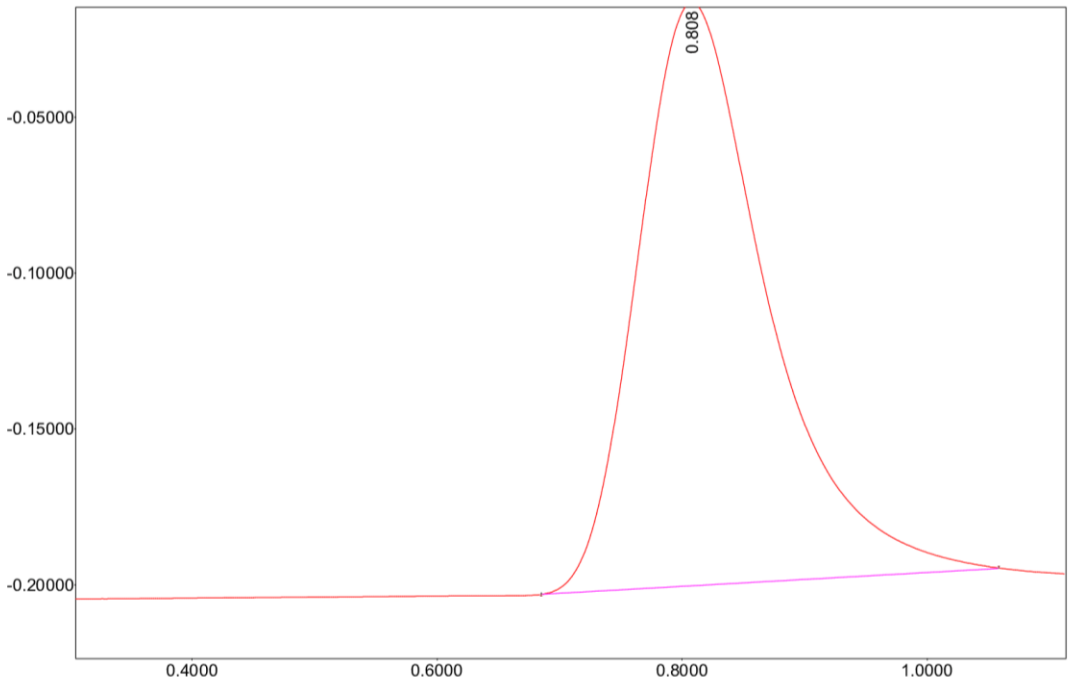
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.863	11725.290	BB	34.700	100.000

Figure S49. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 129.58 µmol) catalyzed by [Ru1] (1.86 µmol) at 25 °C for 30 min.



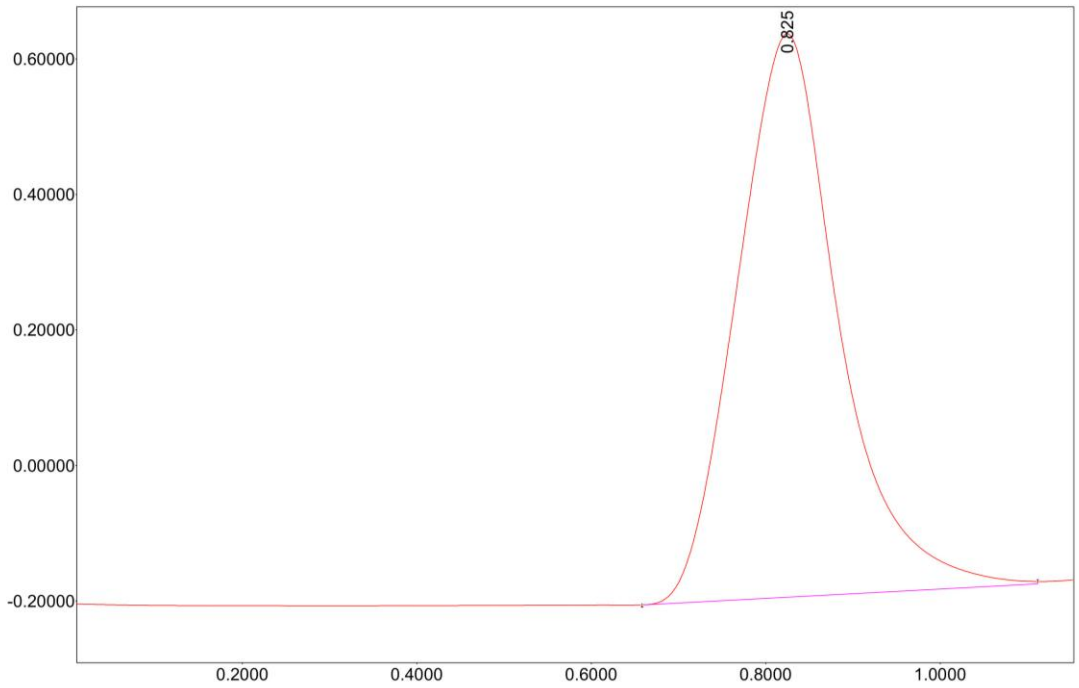
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.838	12597.905	BV	30.500	100.000

Figure S50. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru1] (1.86 µmol) at 25 °C for 30 min.



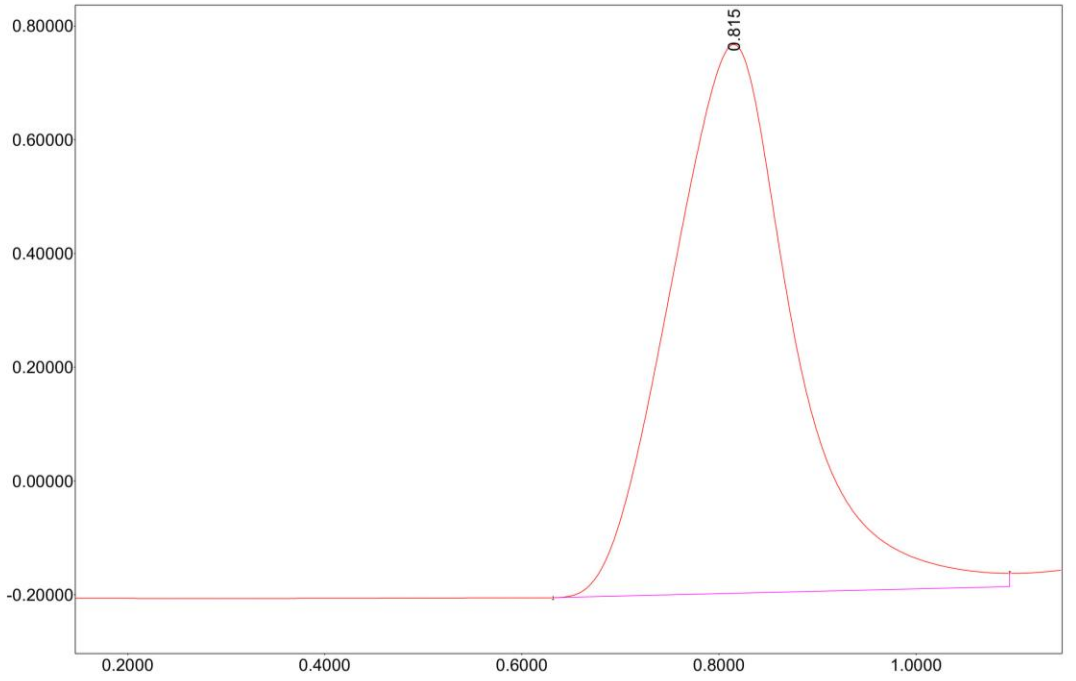
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.808	1366.599	BB	22.400	100.000

Figure S51. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) without the ruthenium catalyst at 25 °C for 30 min.



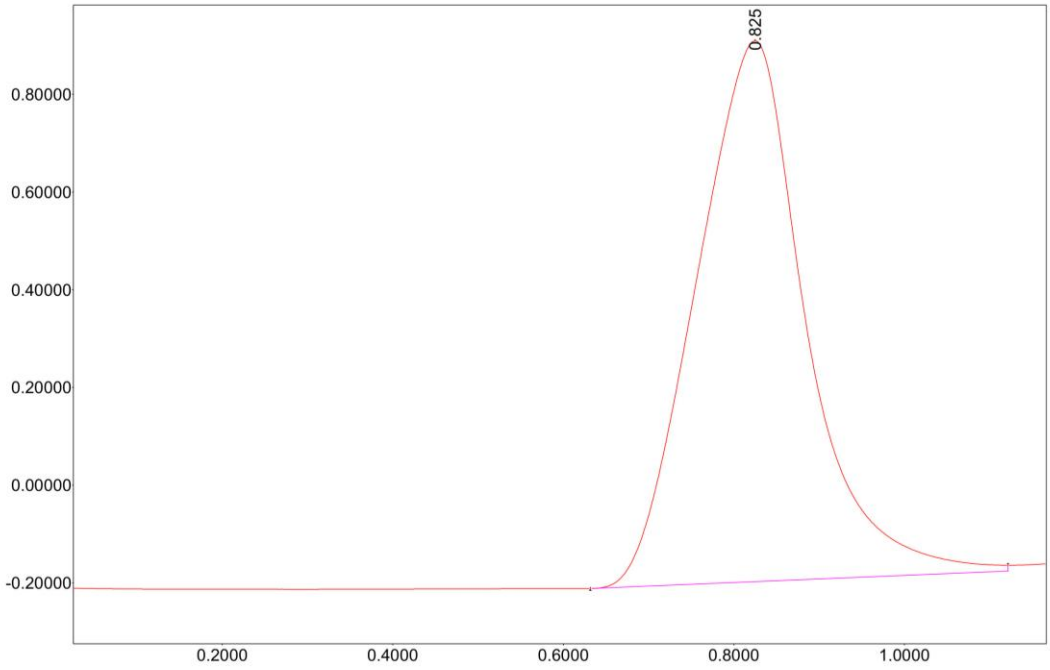
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.825	6742.828	BV	27.200	100.000

Figure S52. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru1] (0.74 µmol) at 25 °C for 30 min.



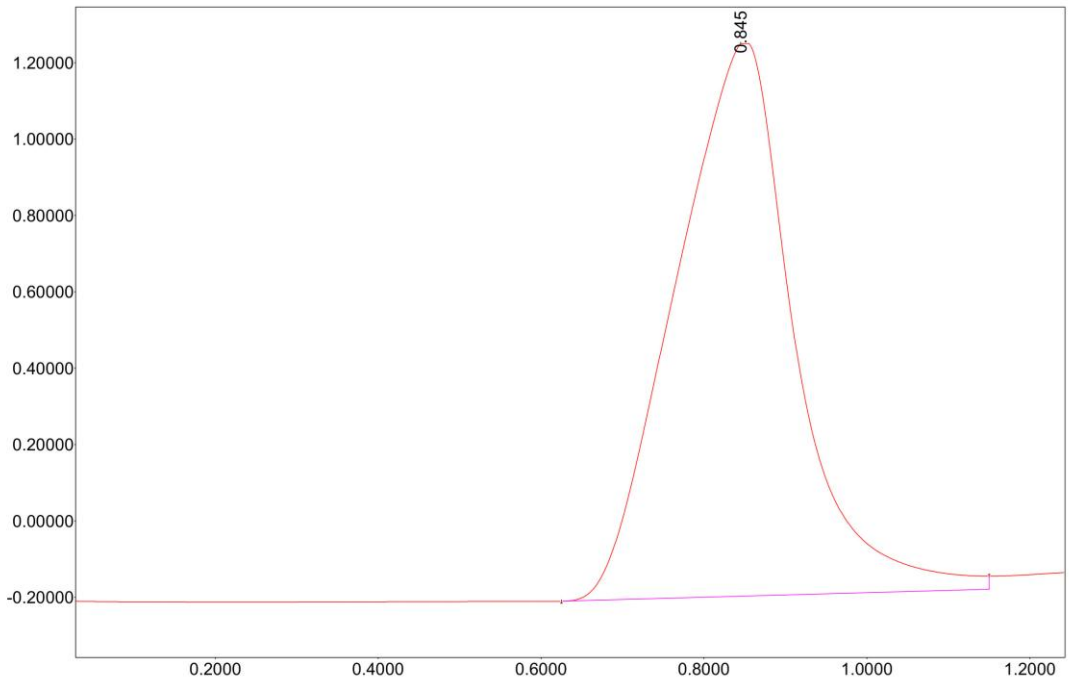
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.815	8426.938	BV	27.800	100.000

Figure S53. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru1] (1.12 µmol) at 25 °C for 30 min.



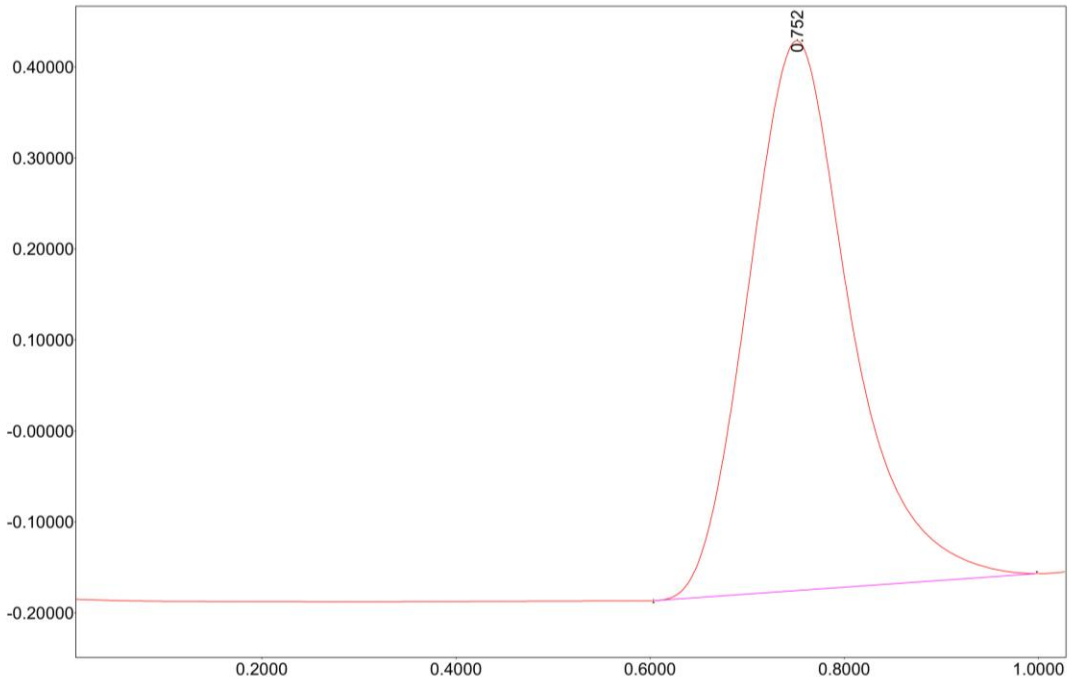
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.825	9863.265	BV	29.400	100.000

Figure S54. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru1] (1.49 µmol) at 25 °C for 30 min.



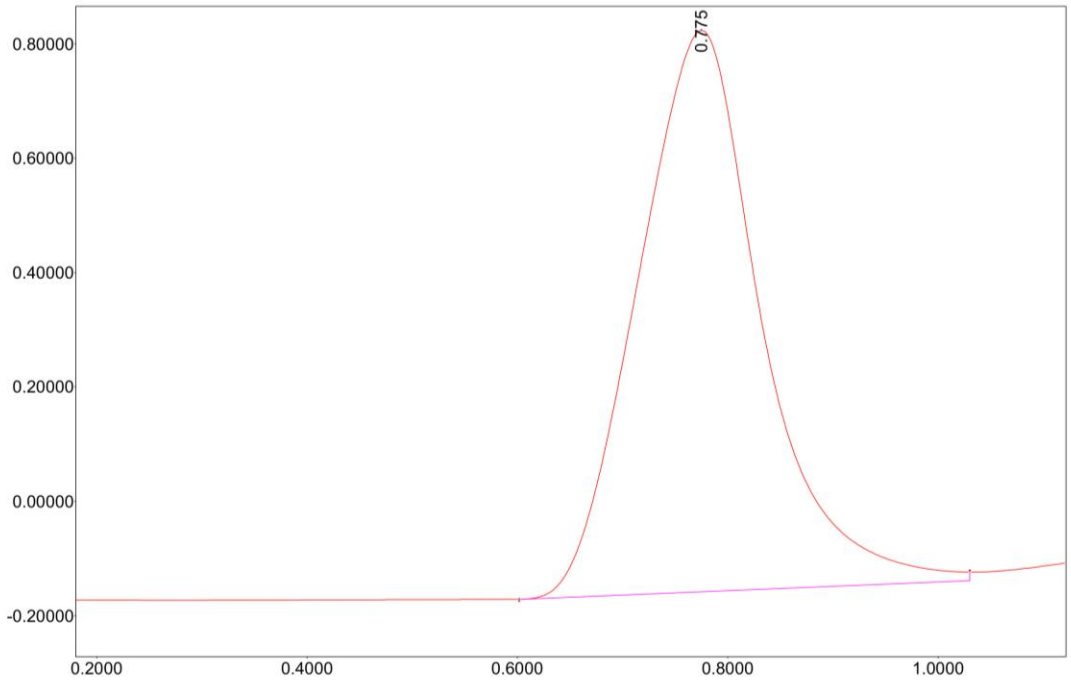
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.845	14687.825	BV	31.500	100.000

Figure S55. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru1] (2.23 µmol) at 25 °C for 30 min.



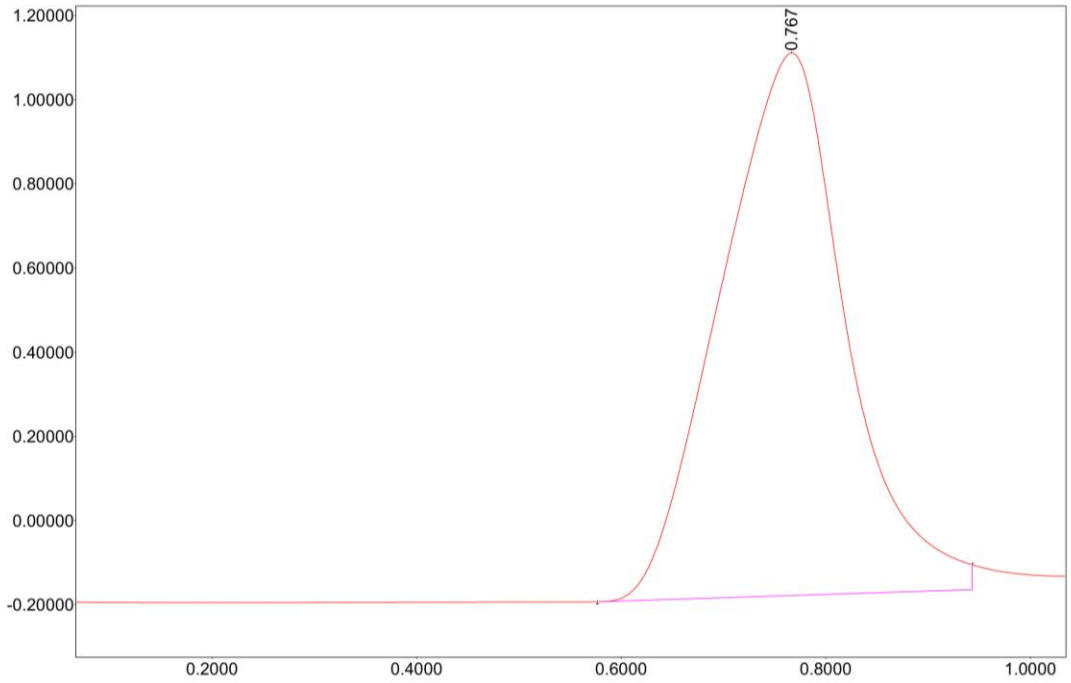
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.752	4416.219	BP	23.700	100.000

Figure S56. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 32.29 µmol) catalyzed by [Ru2] (1.86 µmol) at 25 °C for 30 min.



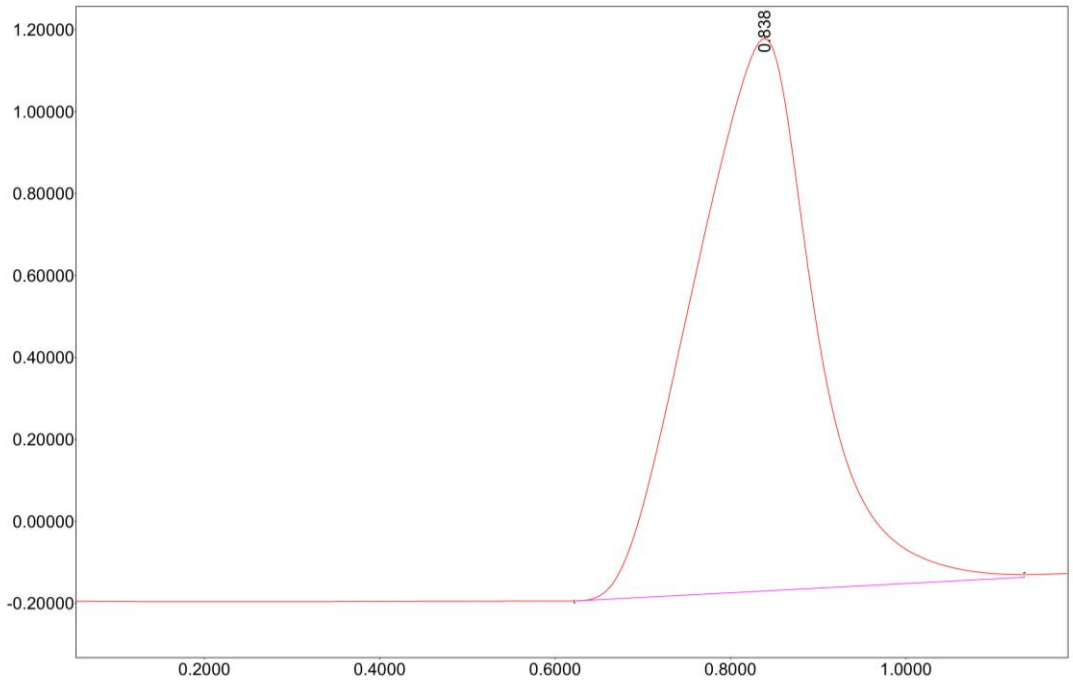
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.775	7993.621	BV	25.700	100.000

Figure S57. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 64.79 µmol) catalyzed by [Ru2] (1.86 µmol) at 25 °C for 30 min.



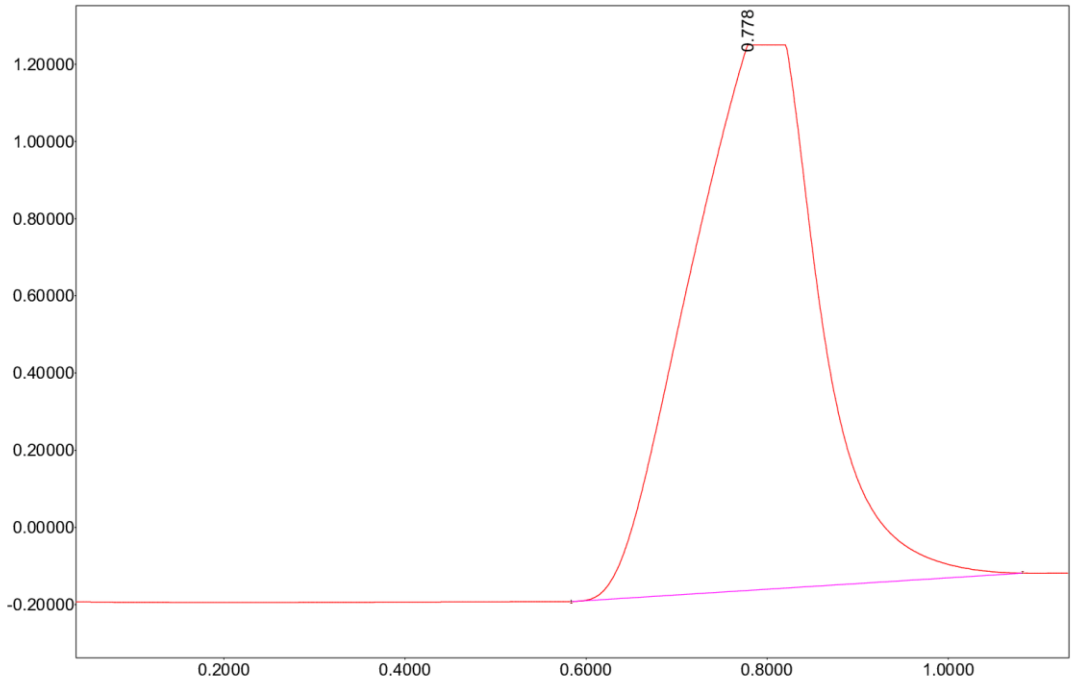
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.767	10963.391	BV	22.000	100.000

Figure S58. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 97.18 µmol) catalyzed by [Ru2] (1.86 µmol) at 25 °C for 30 min.



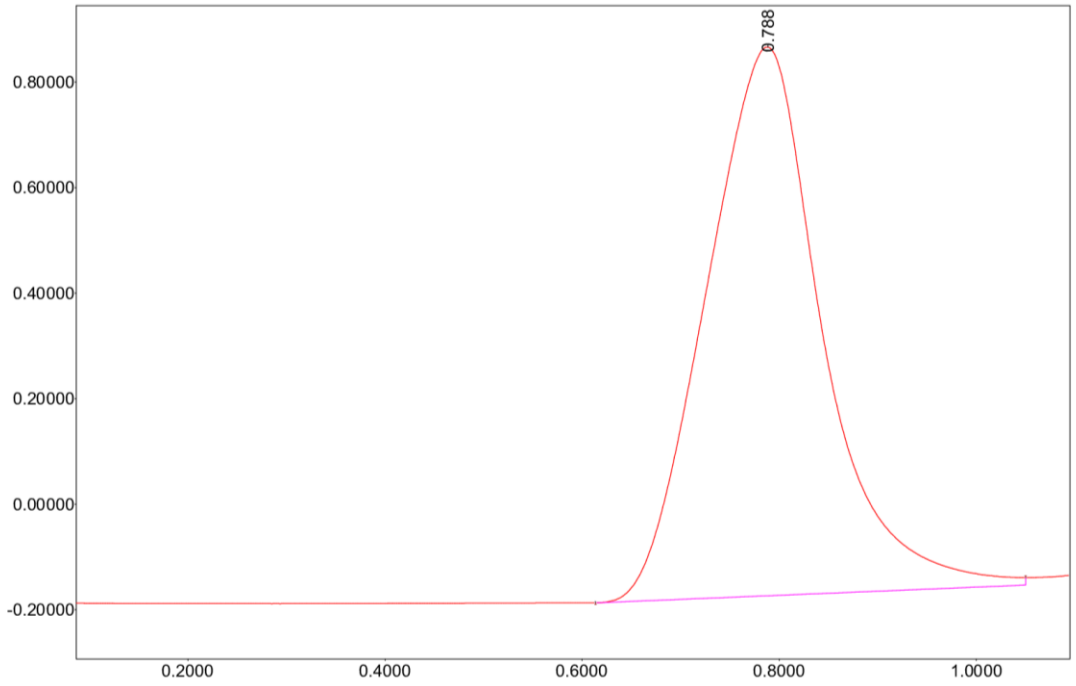
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.838	12960.336	BV	30.800	100.000

Figure S59. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 129.58 µmol) catalyzed by [Ru2] (1.86 µmol) at 25 °C for 30 min.



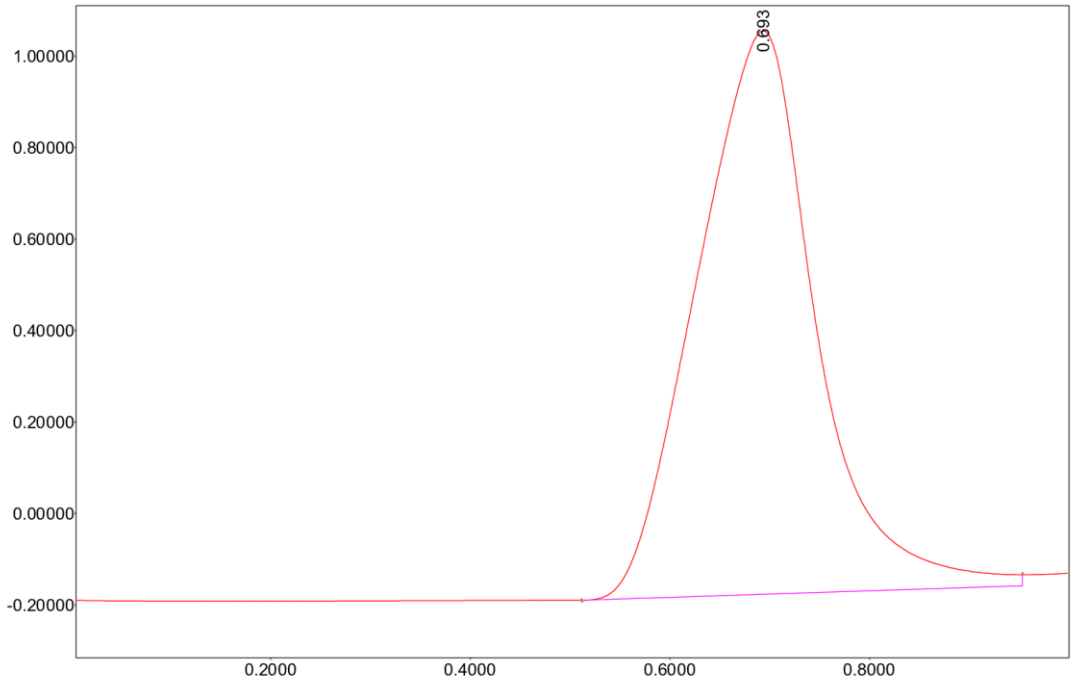
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.778	14311.646	BB	29.900	100.000

Figure S60. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru2] (1.86 µmol) at 25 °C for 30 min.



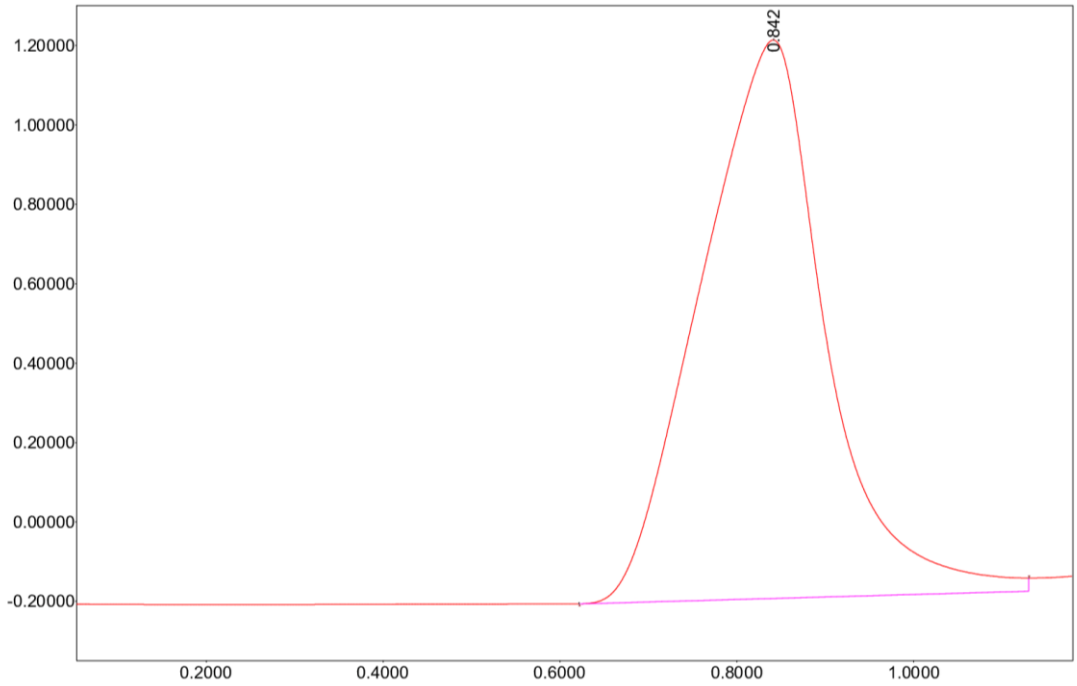
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.788	8477.201	BV	26.200	100.000

Figure S61. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru2] (0.74 µmol) at 25 °C for 30 min.



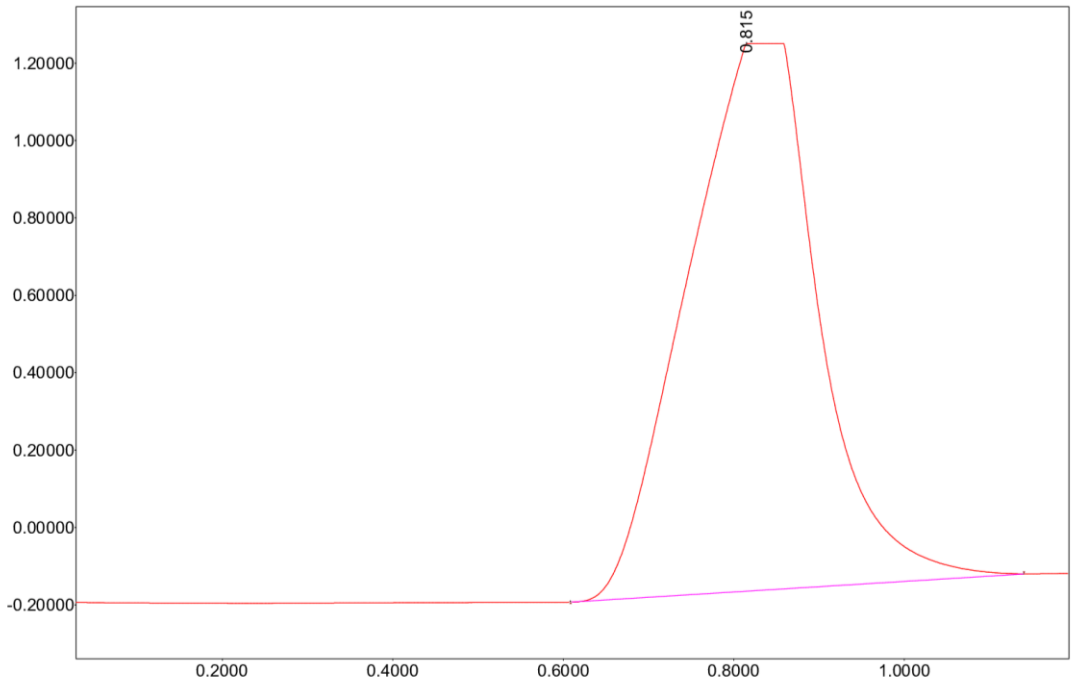
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.693	10201.193	BV	26.500	100.000

Figure S62. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru2] (1.12 µmol) at 25 °C for 30 min.



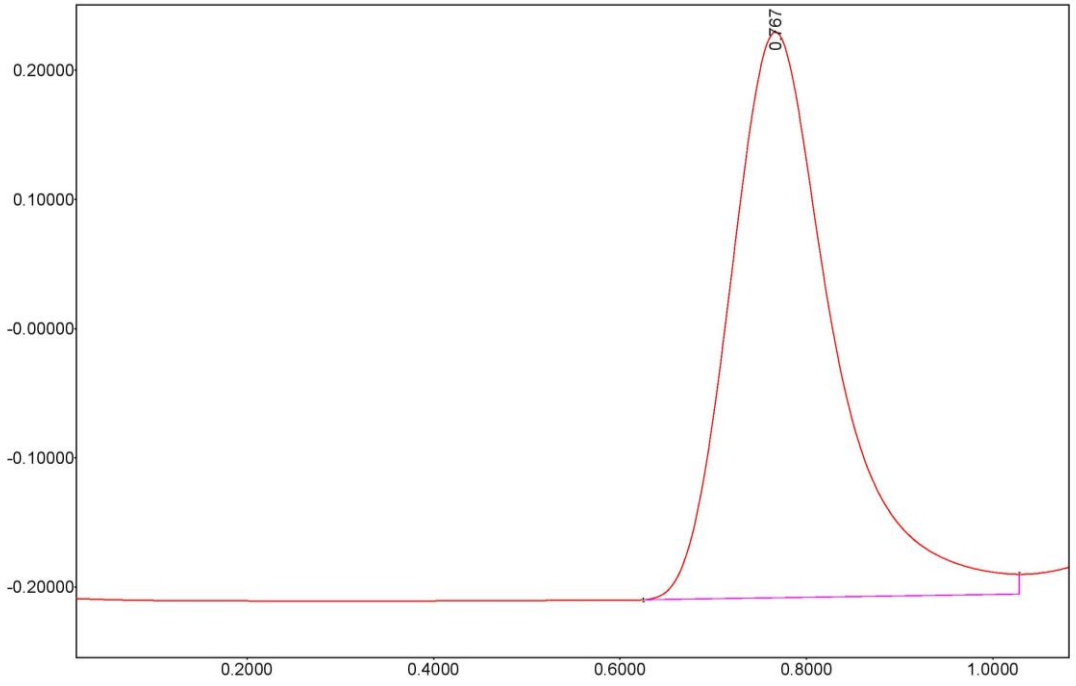
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.842	13825.146	BV	30.500	100.000

Figure S63. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru2] (1.49 µmol) at 25 °C for 30 min.



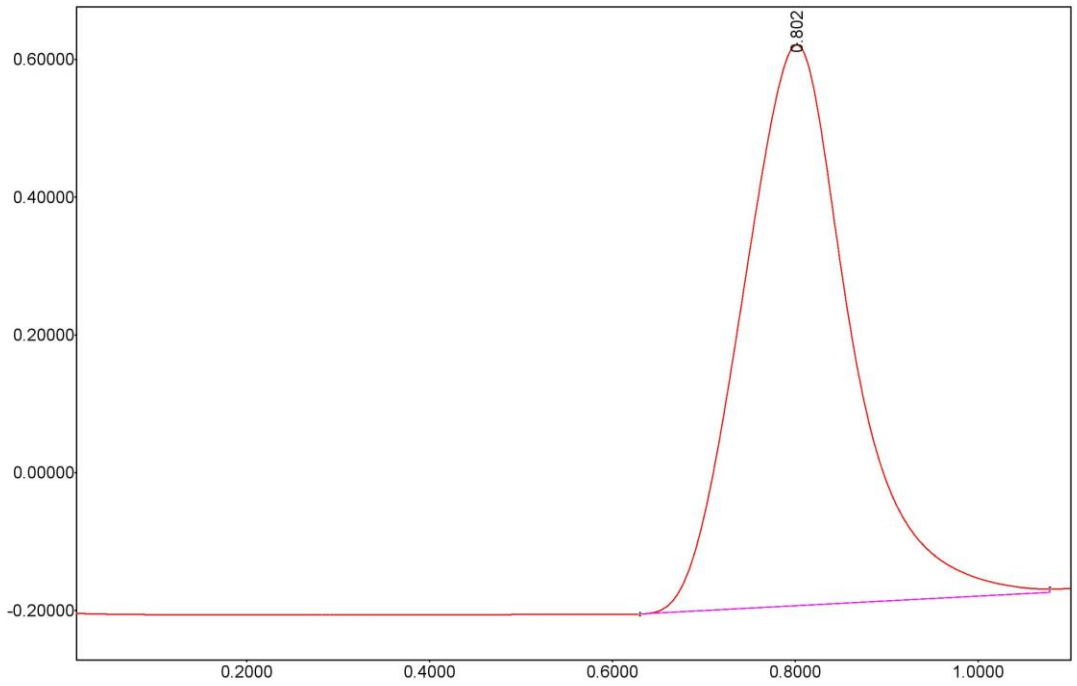
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.815	15211.434	BB	31.900	100.000

Figure S64. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru2] (2.23 µmol) at 25 °C for 30 min.



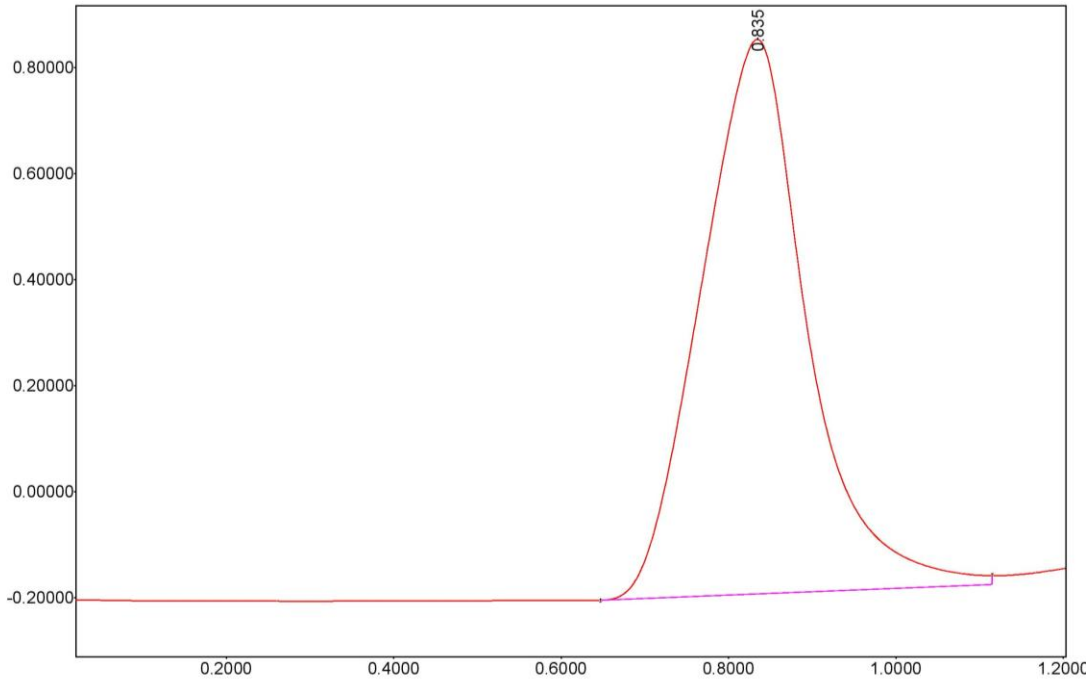
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.767	3376.899	BV	24.200	100.000

Figure S65. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 32.29 µmol) catalyzed by [Ru3] (1.86 µmol) at 25 °C for 30 min.



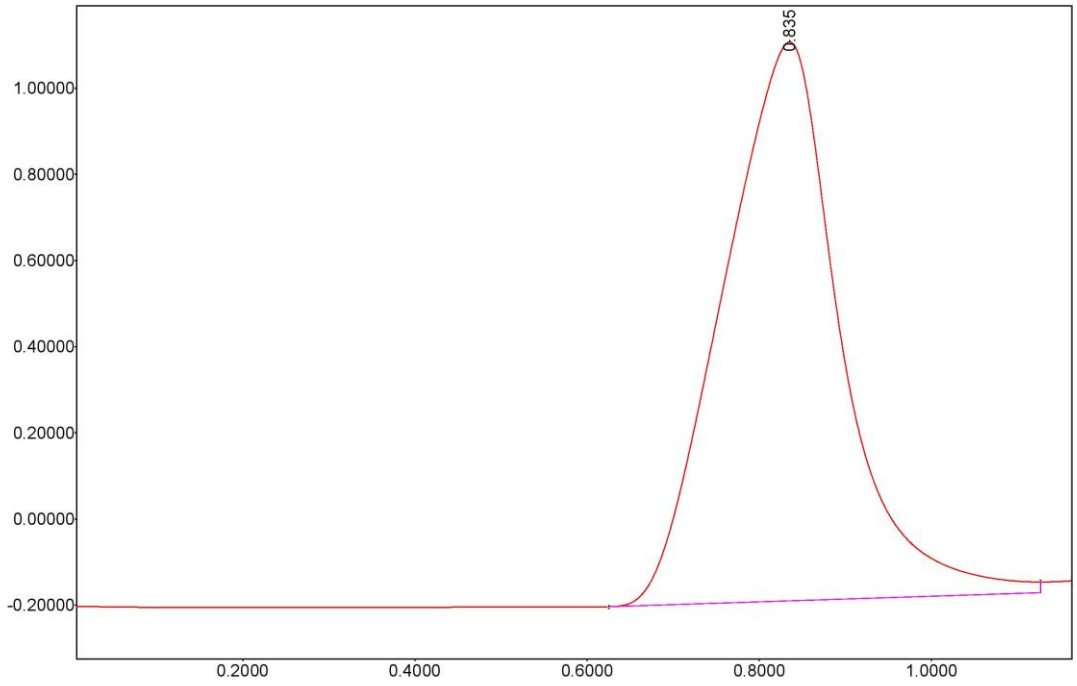
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.802	6678.604	BV	26.900	100.000

Figure S66. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 64.79 µmol) catalyzed by [Ru3] (1.86 µmol) at 25 °C for 30 min.



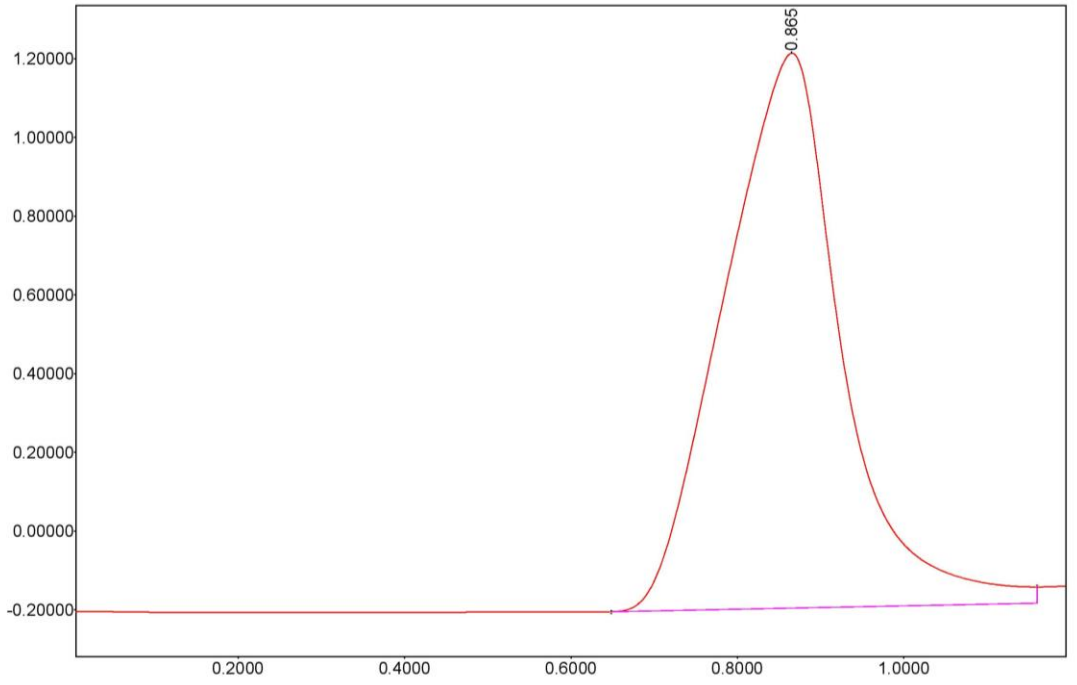
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.835	9178.708	BV	28.100	100.000

Figure S67. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 97.18 µmol) catalyzed by [Ru3] (1.86 µmol) at 25 °C for 30 min.



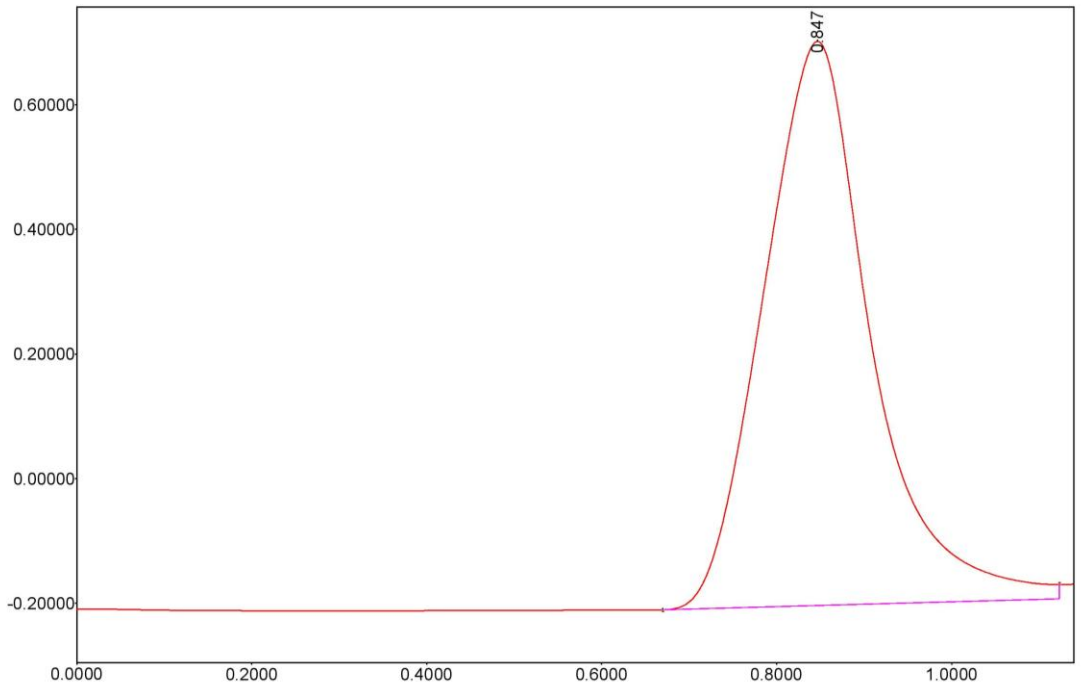
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.835	12310.236	BV	30.100	100.000

Figure S68. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 129.58 µmol) catalyzed by [Ru3] (1.86 µmol) at 25 °C for 30 min.



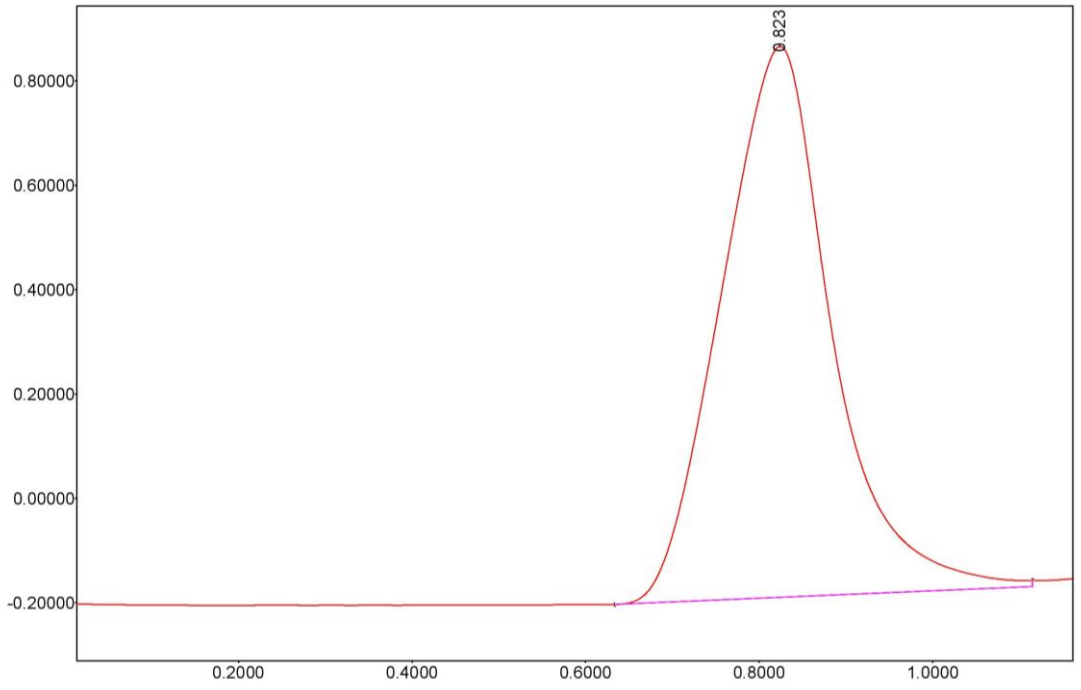
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.865	13865.649	BV	30.700	100.000

Figure S69. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru3] (1.86 µmol) at 25 °C for 30 min.



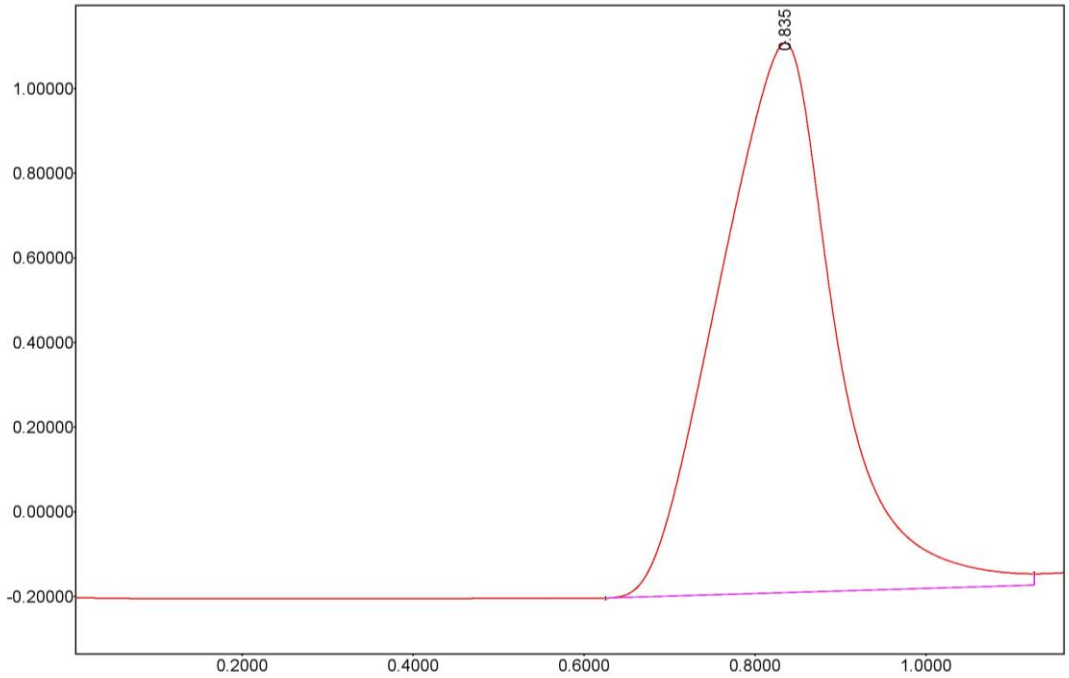
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.847	7727.040	BV	27.200	100.000

Figure S70. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru3] (0.74 µmol) at 25 °C for 30 min.



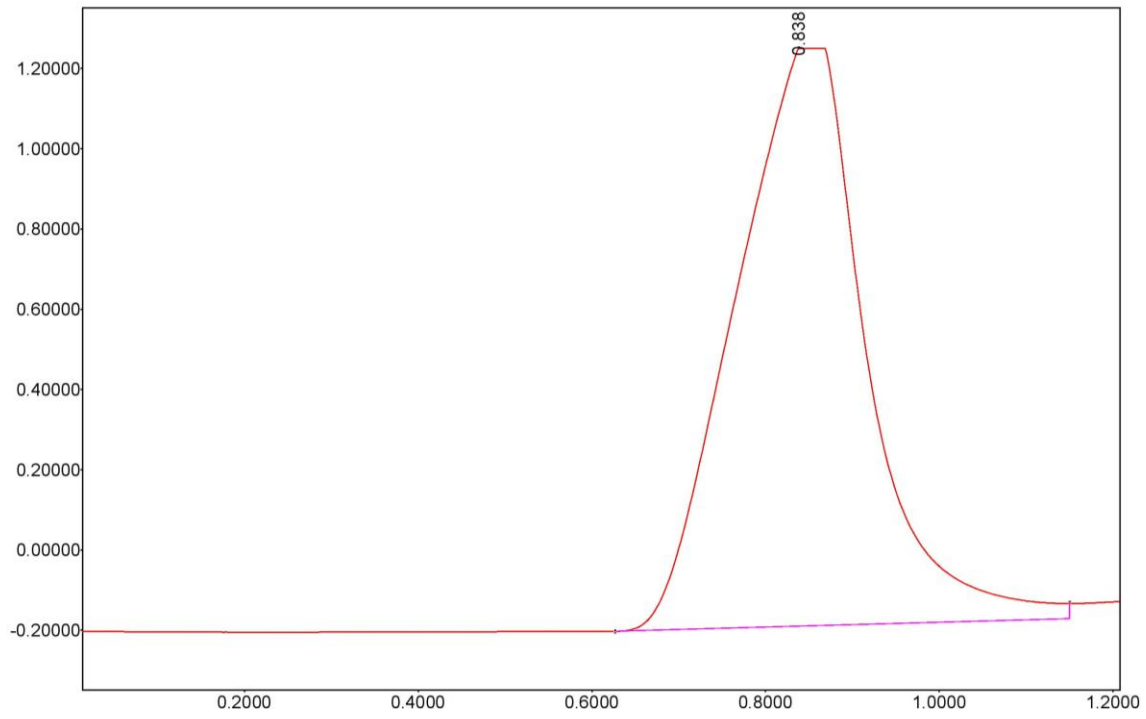
#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.823	9308.806	BV	28.900	100.000

Figure S71. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru3] (1.12 µmol) at 25 °C for 30 min.



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.835	12310.236	BV	30.100	100.000

Figure S72. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru3] (1.49 µmol) at 25 °C for 30 min.



#	RT(min)	Area(mV*sec)	Type	Width(sec)	Area%
1	0.838	15151.457	BV	31.400	100.000

Figure S73. Gas chromatogram (TCD) of H_2 produced from the dehydrogenation of ammonia borane (AB, 161.97 µmol) catalyzed by [Ru3] (2.23 µmol) at 25 °C for 30 min.

References:

1. B. S. Kim, J. Jiménez, F. Gao and P. J. Walsh, *Org. Lett.*, 2015, **17**, 5788–5791.
2. T. Thierry, E. Pfund and T. Lequeux, *Chem. Eur. J.*, 2021, **27**, 14826–14830.
3. L. Shi, Y. Liu, Q. Liu, B. Wei and G. Zhang, *Green Chem*., 2012, **14**, 1372–1375.