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Electronic Supplementary Information

SABRE Hyperpolarization of Nicotinamide Derivatives and their Molecular Dynamics Properties

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1. Materials

2,4,6-Trimethylaniline (99 %), 40 % glyoxal in water, formic acid (HCOOH, 98 %), paraformaldehyde ($(HCHO)_n$, 95%), hydrochloric acid in dioxane (4M), dichloromethane anhydrous (DCM, 99.8 %), chloro(1,5-cycloctadiene)-iridium(I) dimer ($[Ir(COD)Cl]_2$, 97 %), pyridine anhydrous (99.8 %), nicotinamide (98 %), N-benzyl nicotinamide (95 %), nicotinic acid hydrazide (97 %), methanol-d_4 (MeOD-d_4, 99.8 %), and chloroform-d ($CDCl_3$, 99.8 %) were supplied by Sigma–Aldrich (MO, USA). Methanol (MeOH, 99.8 %), ethyl acetate (EtOAc, 99.8 %), hexane (HEX, 96 %), sodium bicarbonate ($NaHCO_3$, 99 %), magnesium sulfate anhydrous ($MgSO_4$, 99 %), potassium carbonate anhydrous (K_2CO_3, 99.5 %), and acetone (99.8 %) was obtained from Daejung Chemicals (Gyeonggi Do, South Korea). Silica gel 60 (0.040 – 0.063 mm) was bought from Merck (Burlington, MA, USA). DMSO-d_6 (99.9 %) was purchased from Cambridge Isotope Laboratories (MA, USA). Distilled water (DI H_2O, 18.2 MΩ-cm) was obtained using an Arioso Power water purification system (Human Corporation, South Korea).

2. Preparation of Iridium Catalyst

2.1. Synthesis of N,N'-Dimesitylethanediimine

The synthesis process followed previous reports.[1,2,3] Typically, a 100 mL round-bottom flask (RBF) was charged by 2,4,6-trimethylaniline (10.4 mL, 74.0 mmol) and 40 mL of methanol, and the mixture was stirred for 10 min. Then, 4.2 mL of 40% glyoxal in water (37 mmol) was added to the mixture. Subsequently, three drops of formic acid were added to the mixture and stirred at 25 ºC for 24 h. The yellow precipitate was filtered and washed three times with cold methanol until a brown precipitate was removed from the yellow powder. Finally, 8.6 g (29 mmol, 79 % yield) of N,N'-dimesitylethanediimine was dried under a vacuum oven at 50 ºC. The identity of this compound was confirmed by NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 2H), 6.93 (s, 4H), 2.32 (s, 6H), and 2.19 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 147.4, 134.1, 128.9, 126.5, 20.7, 18.2.

2.2. Synthesis of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride (IMes.HCl)

The preparation of IMes.HCl was modified from the previous process.[1,2] Typically, the 50 mL two necks round bottom flask (RBF) was charged by 1.08 g (3.68 mmol) of N,N'-dimesitylethanediimine in 20 mL ethyl acetate.

Other RBF was loaded 0.122 g (4 mmol) of paraformaldehyde and 1.4 mL (5.52 mmol) of HCl (4M in dioxane). The mixture was stirred until dissolving the paraformaldehyde. This solution was slowly dropped into the 2-necks RBF and gently heated at 40 ^{o}C for 1 hour. Then, this mixture was stirred for 24h at room temperature. The brown precipitate was filtered and dissolved into the $NaHCO_3$ saturated solution. Consequently, the aqueous was extracted three times with ethyl acetate (3 x 10 mL) to remove the organic impurities. Then, the aqueous was continuously extracted three times with dichloromethane (3 x 10 mL). The combined organic phase was dried by $MgSO_4$ anhydrous and filtered the $MgSO_4$, we reduced the solvent using a rotary evaporator. The crude oil was recrystallized by co-solvent CH_2Cl_2 (5 mL) and EtOAc (45 mL). The yield of IMes.HCl is 63.8 % (0.811 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.92 (s, 1H), 7.61 (s, 2H), 7.05 (s, 4H), 2.36 (s, 6H), and 2.21 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 139.9, 134.1, 130.6, 129.9, 124.3, 21.2, 17.7.

2.3. Synthesis of [(IMes)Ir(COD)Cl]

The preparation of [(IMes)Ir(COD)Cl] was modified from a previous procedure.[1, 4-6] A three-neck RBF and condenser were flame dried three times under the Schlenk line. The RBF was charged with IMes.HCl (71.2 mg, 0.208 mmol) and K_2CO_3 (140 mg, 1.02 mmol) in 30 mL of degassing acetone. The mixture was then stirred for 10 min. Subsequently, $[Ir(COD)Cl]_2$ (69.6 mg, 0.104 mmol) was added to this mixture, and the mixture was refluxed at 55 ^{o}C for 4 h. Acetone was removed in vacuo, and the crude powder was dissolved in DCM. The mixture was filtered through a silica gel column and washed with DCM until a colorless solution was obtained. The solvent was discarded using an evaporator. It was recrystallized from a mixture of hexane and DCM to obtain orange crystals (78 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (br, 2H), 7.02 (br, 2H), 6.98 (s, 2H), 4.18-4.17 (m, 2H), 3.00-2.99 (m, 2H), 2.38 (s, 6H), 2.37 (s, 6H), 2.18 (s, 6H), 1.79-1.62 (m, 4H), 1.40-1.23 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.8, 138.6, 137.3, 136.1, 134.4, 129.5, 128.1, 123.3, 82.5, 51.4, 33.5, 31.6, 28.9, 22.7, 21.1, 19.6, 18.2, 14.1.

3. Home-built Parahydrogen System

3.1. Parahydrogen generator

We fabricated the parahydrogen generator (pH_2) using a copper pipe with a 1/4" (6.35 mm) outer diameter (O.D.), which was bent into a helix coil with 15 turns (approximately 3 m) or 25 turns (approximately 5 m). Both copper helix coils have a 3 cm O.D. and a 2 cm inner diameter (I.D.). An iron oxide catalyst (FeOOH, 30–50 mesh, 371254-250G, Sigma-Aldrich) was used to convert oH_2 to pH_2 at cryogenic temperatures. We used 20 g and 30 g to fill the copper helix coil with 15 and 25 turns, respectively. In the head and tail of the copper tubing, the glass wool (Silanized, 20411, Supelco, Sigma-Aldrich) protected the iron oxide catalyst from the high flow rate of the hydrogen gas cylinder (99.999 % purity). The head and tail of the copper helix coil were also connected to a stainless-steel pipe with 1/4" O.D. through a brass Swagelok tube fitting union with 1/4" O.D. (part number (PN): B-400-6). The stainless-steel tubing passed through a hole in the rubber stopper (No.19, SL.Sto 6029, SciLab, South Korea). Three

holes were drilled in this rubber: two holes for stainless-steel tubing using gas in-out and one hole for vent tubing (preventing overpressure in the liquid nitrogen dewar) or connecting an oil-free dry scroll vacuum pump (nXDS-10i, Edwards, UK). This setup was placed in a 10 L liquid nitrogen dewar (MVE Lab10 Aluminum Cryogenic Dewar, Cryoport, Tennessee, USA).[7] There are two options to enrich parahydrogen: without and with the use of a scroll vacuum pump; we can obtain 50 % and 63 % pH_2 levels, respectively.

3.2. Parahydrogen bubbling system

After pH_2 enrichment, it was passed through a three-way valve (SS-43GXS4, 1/4", Swagelok, Ohio, USA), including one way for pH_2 enrichment and other way for nitrogen as a flush gas. The pH_2 enrichment goes to another three-way valve (SS-41GXS2, 1/8" (3.175 mm), Swagelok). Two 1/8" three-way valves were connected to an actuator (MS-151-SR, Swagelok). The actuator setup with an Arduino microcontroller is described in detail below. One of the two 1/8" three-way valves were connected in a bypass manner. The remaining valves were attached to a brass union tee (B-400-3, 1/4", Swagelok). The polytetrafluoroethylene (PTFE) tubing 1/4" (5033K31, McMaster-Carr, IL, USA) was connected to a plastic adapter (5016K423, 1/4" tube O.D. & 3/8" (9.525 mm) national pipe tapered (NPT) Female, McMaster-Carr), and this adapter was attached to the other adapter (5016K944, 3/8" tube O.D. & 3/8" NPT Female, McMaster-Carr). The PTFE disc 14.3 mm was placed in the 5016K944 adapter, and four holes, which include three holes for the inlet fused silica tubing of 363 μm O.D. & 100 μm I.D. (062469, Trajan Scientific and Medical, Australia) and one hole for the outlet polyether ether ketone (PEEK) tubing of 1/16" (1.5875 mm) O.D. & 0.03" I.D. (0.762 mm) (1302030005-50F, Trajan Scientific and Medical, Australia), were made by micro drilling. A home-built PEEK adapter was constructed to fit the NMR tube (504-PP-7; Wilmad-LabGlass, NJ, USA) to a 5016K944 adapter. This PEEK adapter has three parts: part 1 (2 mm length, 6.3 mm O.D., and 3.5 mm I.D.), part 2 (16 mm length, 9.5 mm O.D., and 3.5 mm I.D.), and part 3 (12 mm length, 8.7 mm O.D., and 5.0 mm I.D.). The back pressure of the system was controlled using a pressure gauge (0–1.0 MPa, Nisshin, Japan) and metering valve (SS-SS4-VH, 1/4", Swagelok, USA).

The actuator was controlled using a 3/2-way solenoid valve (KCC, KJAS39, South Korea). This solenoid valve was connected to the Arduino microcontroller, which includes a relay module, an IR sensor, four resistors, and four LED lights (see **Fig. S5**). A 6 atm air flow from the air compressor flip/flops the actuator to control the pH_2 bubbling time inside the NMR tube.

3.3. Solenoid coil as a polarizer

A small commercial air-core solenoid (Eisco Labs, US) was used to adjust the magnetic field using a direct current (DC) power supplier (OPE-305QI, ODA Technologies, South Korea). The magnetic field was measured using a Gaussian meter (5280, FW Bell, USA) equipped with an axial probe (SAD18-1904, FW Bell). The magnetic field of this air-core solenoid for the SABRE experiments ranged from 1 to 8 mT. A homemade plastic cylinder was placed inside the air-core solenoid to hold the spinner with the NMR tube to match the highest magnetic field

position when it was polarized in a low magnetic field.

4. Characterization

Solution-state ^{1}H NMR and ^{13}C NMR spectra of the samples were achieved at 25 °C using an Ascend 400 MHz NMR spectrometer (Bruker Biospin, Billerica, MA, USA). The 1H NMR and 13C NMR spectra in each step preparing the iridium catalyst were performed using π/2 pulse excitations, and the pulse strength was $\gamma B_1/2\pi$ = 25 kHz. A total of 16 and 1024 transients were obtained, and the time delay between each transient was 1 and 2 s in ^{1}H and ^{13}C NMR, respectively. For each transient, 65536 data points were obtained for acquisition times of 4.1 and 1.3 s for ^{1}H and ^{13}C NMR, respectively. During the ^{13}C NMR acquisition, WALTZ-16 1H decoupling was utilized with a pulse strength $\gamma B_1/2\pi$ = 2.8 kHz. The raw data were zero filled to 32768 complex data points. An exponential window function with 0.3 and 1.0 Hz line broadening was applied to the 1H and 13C NMR spectra using TopSpin 3.7 before Fourier transformation. All 1H and 13C NMR spectra were analyzed using Topspin 3.7 (Bruker, MA, USA) and OriginPro 2016 (OriginLab Corp., MA, USA).

5. SABRE Experiments

5.1. Parahydrogen level estimation

Parahydrogen is a nuclear spin isomer of molecular hydrogen (H_2) and orthohydrogen (oH_2). In diatomic molecules, exchange spin isomers can occur when the overall wave function is antisymmetric because protons are fermions (named after physicist Enrico Fermi).[8] The final wave functions that affect the exchange of hydrogen isomers are the rotational and spin Hamiltonian wave functions because the translational, vibrational, and electronic wave functions are identical during spin isomer exchange.[9-11] For the energies of the rotational states, the rotational quantum number (*J*) is even or odd if the rotational wave function is symmetric or anti-symmetric, respectively. When *J* is even, the spin Hamiltonian is anti-symmetric. Therefore, the nuclear spin state is the singlet state, known as pH_2, which is silent in NMR owing to the total nuclear spin (*I*) = 0. When *J* is odd, it is known as a triplet state, with *I* = 1. To confirm the pH_2 level, we performed NMR spectroscopy on pure H_2 at room temperature. Because parahydrogen is silent in NMR, only orthohydrogen can be observed. Therefore, we indirectly estimated the parahydrogen level based on the amount of orthohydrogen, expressed in Eq. (3.1) as follows:

$$f_{pH_2} = 1 - \frac{3\, I_{ortho\ at\ low\ temperature}}{4\, I_{ortho\ at\ room\ temperature}} \qquad \text{(Eq. S1)}$$

where $I_{ortho\ at\ room\ temperature}$ and $I_{othro\ at\ low\ temperature}$ are an integral of orthohydrogen at room temperature and low temperature, respectively. After 20 min, the pH_2 levels were approximately 50 % and 63 % at 77 K and 63 K, respectively (see **Fig. S1**).

The ^{1}H NMR spectra were obtained using π/2 pulse excitations, and the pulse strength was $\gamma B_1/2\pi$ = 25 kHz. A single scan was obtained with a delay of 1s. The 8192 data points were obtained for an acquisition time of 0.17 s. for

^{1}H and ^{13}C NMR, respectively. The raw data were zero filled to 8192 complex data points. An exponential window function with 0.3 Hz line broadening was applied to the NMR spectra using TopSpin 3.7 before Fourier transformation.

5.2. Activation iridium catalyst/substrate system

All the substrates containing the Ir catalyst were prepared in a glove box to reduce the effect of the oxygen in the air as a paramagnetic agent. The concentration ratio between the substrate and the catalyst was 10:1. Four substrates were investigated in this study: pyridine, nicotinamide, NAH, and BnNA. In particular, 52 mM of each substrate (2.5 μL pyridine, 3.8 mg nicotinamide, 4.3 mg NAH, and 6.6 mg BnNA) was charged into a vial and mixed with 5.2 mM (2 mg) [(IMes)Ir(COD)Cl] catalyst in 600 μL MeOD-d_4. The mixture was shaken until the powder dissolved.

The sample was locked and shimmed using the MeOD-d_4 solvent. The lock and sweep for manual insertion and ejection into a 400 MHz spectrometer were subsequently turned off when conducting the SABRE experiments. The Ir catalyst was activated in 15 min by the bubbling of pH_2 enrichment. Nonhydrogenated PHIP experiments were conducted to confirm this activation. PASADENA experiments were performed using high-field NMR (400 MHz). They were bubbled with pH_2 for 30 s with a five-second delay before a 1.38 s acquisition time. The $\pi/4$ (45^o) pulse excitation was applied to achieve the antiphase NMR signal. A zg pulse sequence was used to confirm the complete activation.

During the activation step, the COD moiety of the precatalyst is converted to cyclooctane (COA), which is then removed, leading to the formation of a ternary labile complex. This complex mediates a reversible exchange reaction, ultimately generating a hyperpolarized ligand.[12] The catalyst activation required approximately 15 min, and its completion was monitored by measuring the ^{1}H NMR spectrum of the post-activated sample to confirm COA formation (see **Fig. S6**) and verify the disappearance of hydride intermediate species at around -12 ppm and -17 ppm (see **Fig. S6**). The evidence of the accomplished activation appeared as peaks at 1.6 ppm (COA) and -22.5 ppm (Ir-HH).[12]

5.3. SABRE hyperpolarization experiments

After activation, the samples were placed in a polarizer and bubbled with pH_2 using an Arduino microcontroller. The precise bubbling duration was controlled using an IR remote controller. The samples were subsequently manually transferred to a high-field NMR within 5 s to obtain a hyperpolarized signal. The experiments were conducted three times to calculate the error bars. After 2 min of each SABRE experiment, the thermal conditions were measured to estimate the enhancement factor. All parameters under hyperpolarized and thermal conditions were similar. For instance, the acquisition time was 1 s, the time domain was 16384, the receiver gain was 10, and a single scan using $\pi/2$ pulse excitations was performed with a pulse strength of $\gamma B_1/2\pi = 25$ kHz.

The equation S2 of magnetic field dependence is expressed below:[11, 12]

$$B_{LAC} = \left|\frac{2\pi J_{AA'}}{\gamma_H(\delta_A - \delta_B)}\right| \quad \text{(Eq. S2)}$$

6. Exchange Spectroscopy and T_1 Relaxation Time

6.1. Exchange spectroscopy (EXSY)

Exchange spectroscopy was performed to estimate the dissociation rate (k_d) between the substrates and the Ir catalyst. These parameters were determined as previously reported.[13, 14] We used a selective Gaussian inversion pulse with a duration of 36 ms. The center of the spectrum (O1P) was 5 ppm. The selective signal was a free ortho proton of pyridine (8.55 ppm), nicotinamide (9.04 ppm), NAH (9.00 ppm), and BnNA (9.02 ppm) at 25 ºC. To calculate the k_d of each substrate based on the Eyring equation (S3), we adjusted the temperatures from 10 ºC to 55 ºC. At different temperatures, we used the zg pulse sequence to confirm the free ortho proton peak because it was slightly shifted than the peak at 25 ºC. The mixing time varied from 20 to 800 ms at all temperatures. The experimental data points and dissociation rates of the substrates were fitted and estimated using Spyder 5.4.3, Python 3.12 (Python Software Foundation, DE, USA).

$$ln\frac{k}{T} = \frac{-\Delta H^{\#}}{R}\frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^{\#}}{R} \quad \text{(Eq. S3)}$$

6.2. T_1 relaxation time

The T_1 relaxation time of thermal condition in all substrates were performed the inversion recovery using t1ir pulse sequence. In particular, the experiments were performed using $\pi/2$ pulse excitations, and the pulse strength was $\gamma B_1/2\pi$ = 25 kHz. A total of 8 transients were obtained, and the delay time between each transient was acquired at 5 s. The vdlist was selected from 10 ms to 128 s. For each transient, 32768 data points were obtained for an acquisition time of 3.4 s. The raw data were zero-filled to 32768 complex data points. An exponential window function with 0.3 Hz line broadening was applied to the 1H spectra using TopSpin 3.7 prior to Fourier transformation. All the thermal T_1 relaxation of ^{1}H NMR spectra were analyzed using the Topspin 3.7 (Bruker, MA, USA) and OriginPro 2016 program (OriginLab Corp., MA, USA).

The manually hyperpolarized experiments were acquired with different delay time. After hyperpolarized at polarizer, the sample was manually transferred to 400 MHz NMR spectrometer. We modified the delay time in the zg pulse sequence of Topspin program. We performed a different delay time, which was from 0 to 128 s. From each data point, we repeated the experiments three times to estimate the error bar. After each experiment, we waited 2 minutes for the complete relaxation of samples to the thermal condition. All the hyperpolarized T_1 relaxation of ^{1}H NMR spectra were analyzed using the Topspin 3.7 (Bruker, MA, USA) and OriginPro 2016 program (OriginLab Corp., MA, USA).

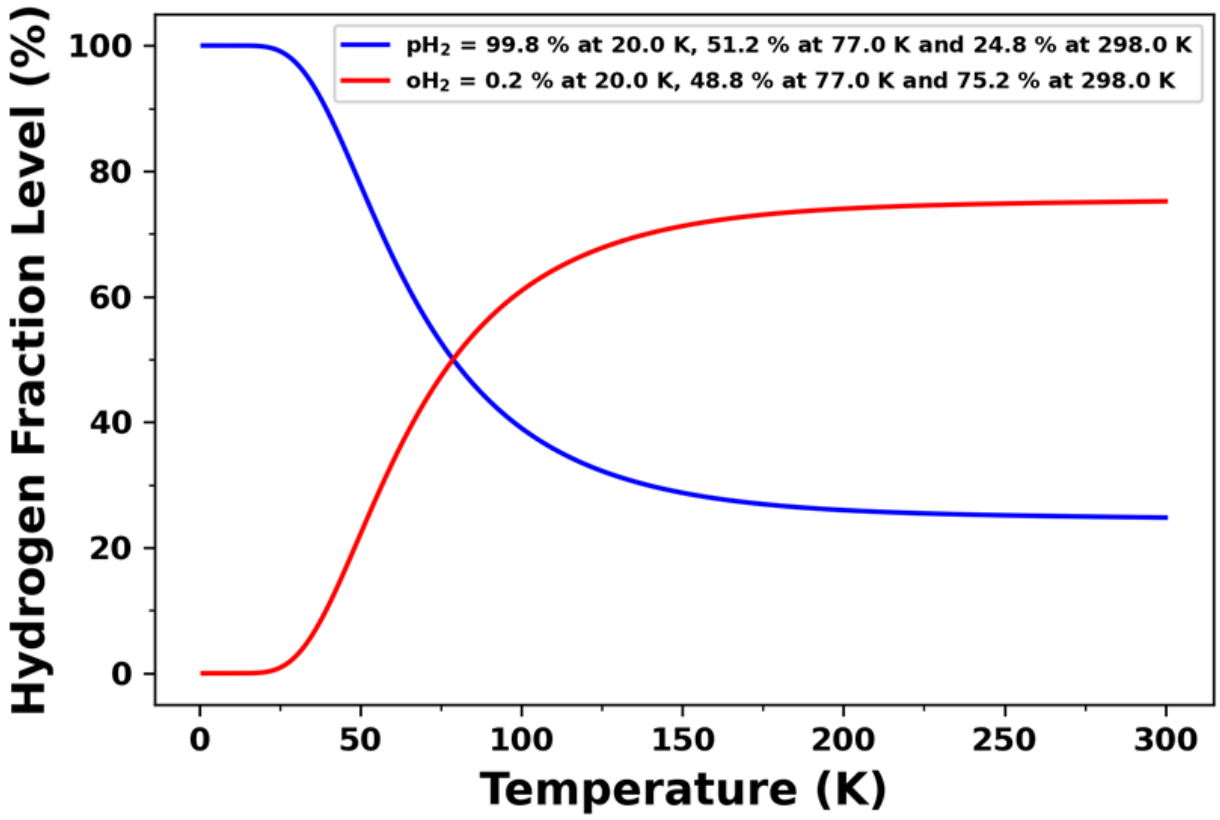


Fig. S1 The simulation hydrogen fraction level of orthohydrogen and parahydrogen depends on temperature. The equation was utilized to simulate as expressed below [11]:

$\frac{N_{para}}{N_{ortho}} = \frac{\sum_{J=0}^{2J}(2J+1)e^{\frac{-J(J+1)\theta_R}{T}}}{3\sum_{J=0}^{2J+1}(2J+1)e^{\frac{-J(J+1)\theta_R}{T}}} = \frac{1+5e^{\frac{-6\theta_R}{T}}+9e^{\frac{-6\theta_R}{T}}+\cdots}{3(3e^{\frac{-2\theta_R}{T}}+7e^{\frac{-12\theta_R}{T}}+\cdots)}$, with θ_R = 86.2 K, T is the temperature, J is the rotational quantum number.

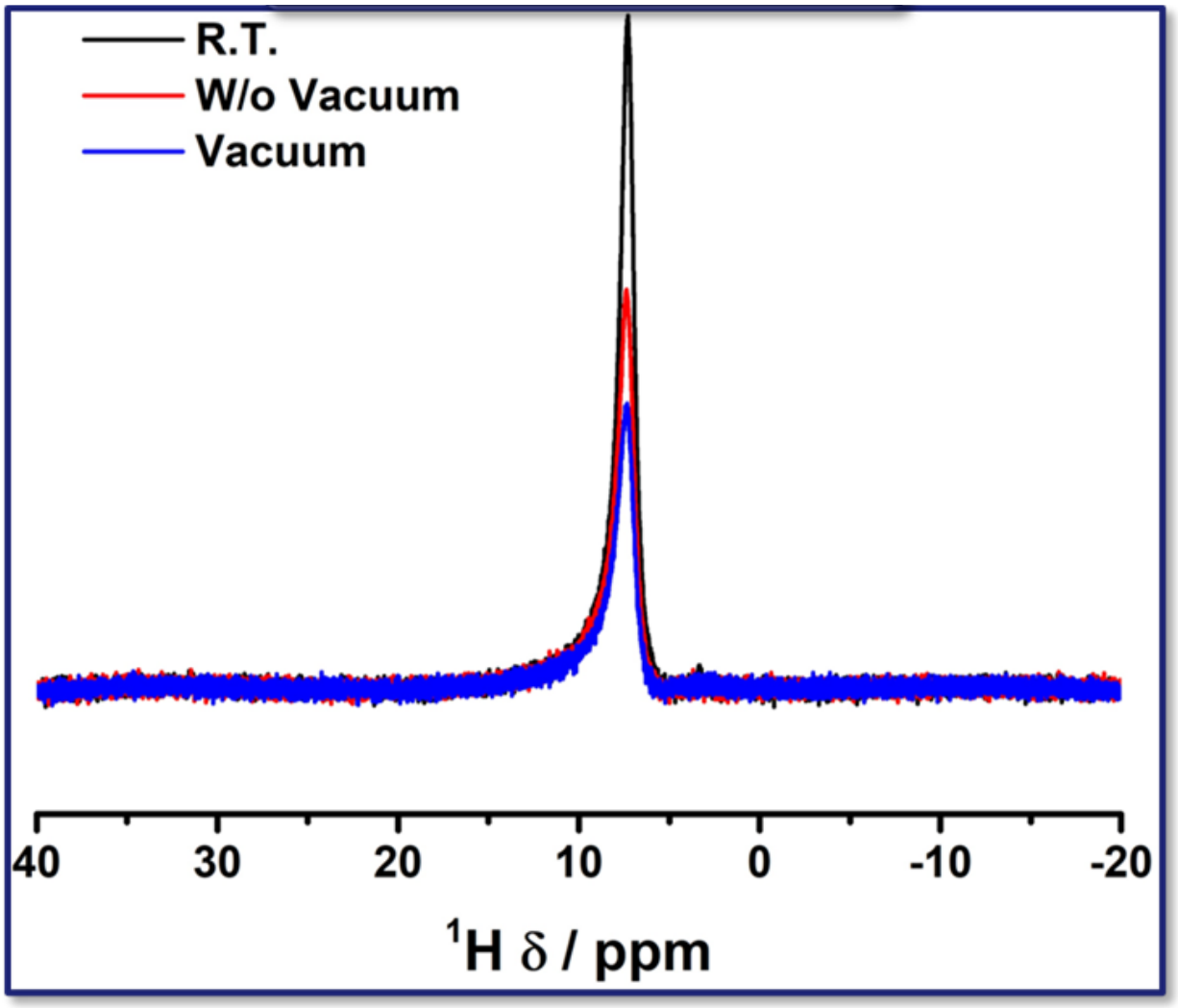


Fig. S2 The parahydrogen level at different condition. It is approximately 50 % and 63 % at 77 K (without vacuum) and 63 K (with vacuum), respectively.

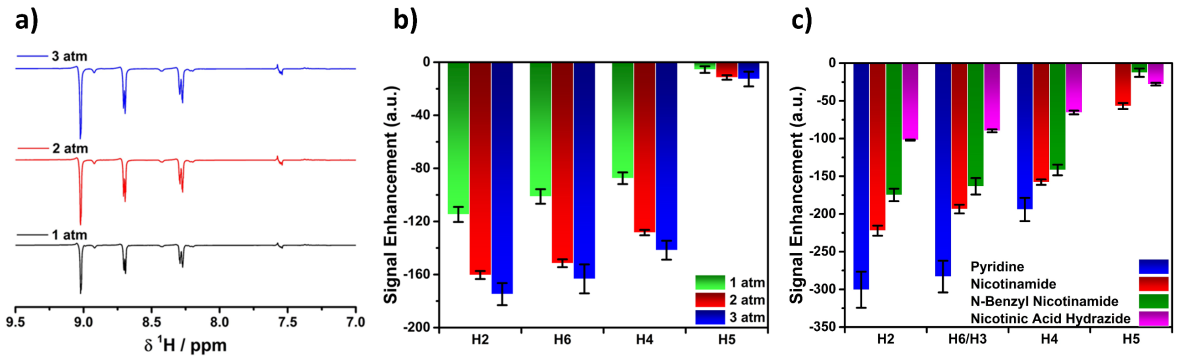


Fig. S3 a) NMR spectra of N-benzyl nicotinamide with different pressure at 298 K, 63 % pH_2, and 30 s bubbling. b) The signal enhancement of N-benzyl nicotinamide with error bar at three different pressure. c) The SABRE signal enhancement of four substrates at 3 atm, 63% of pH2, and 298 K. Each experiments were repeat three times to obtain the error bar.

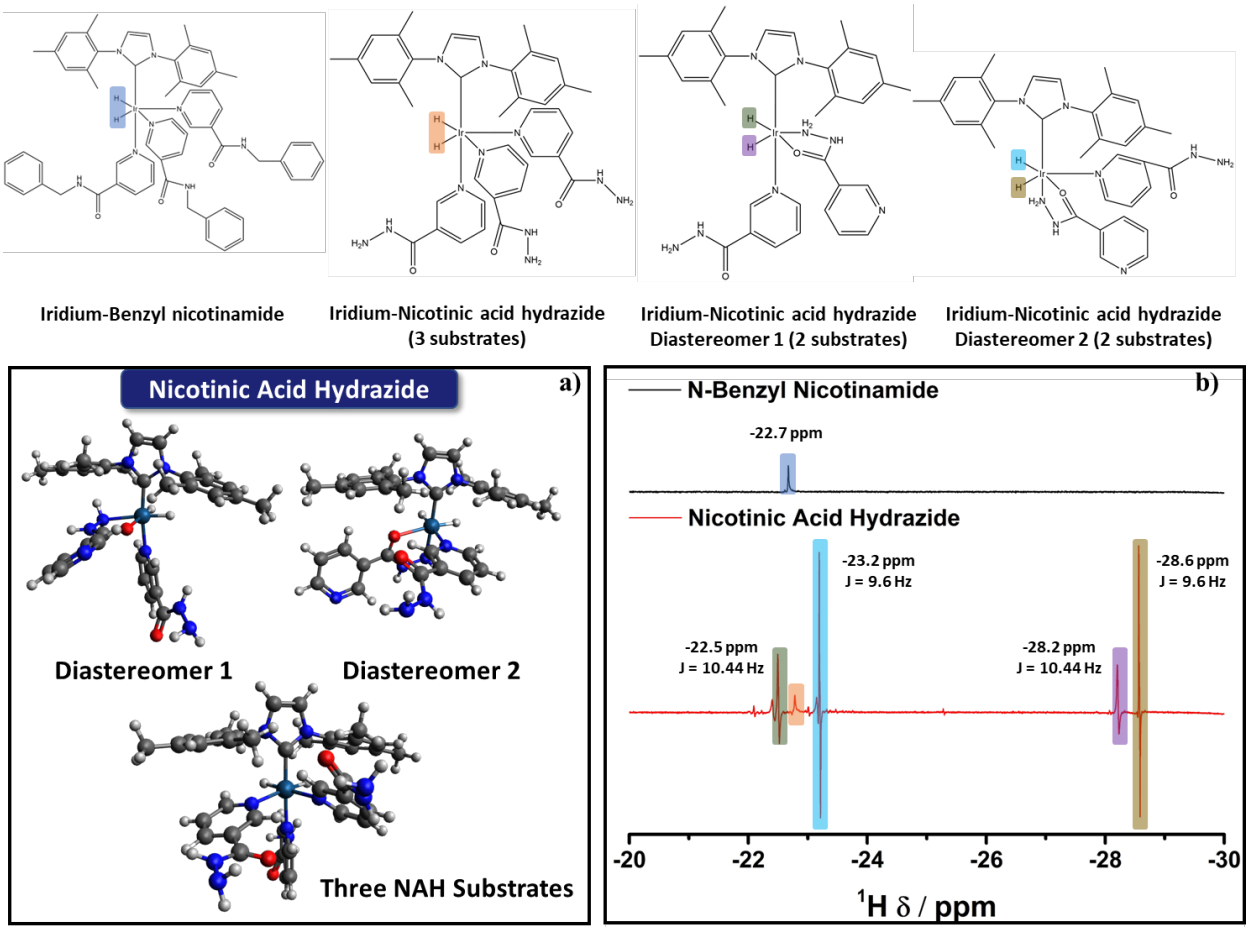


Fig. S4 a) The geometry structures of nicotinic acid hydrazide in DFT. b) Comparison of the different spectra between nicotinic acid hydrazide and N-benzyl nicotinamide in non-hydrogenation PASADENA experiments.

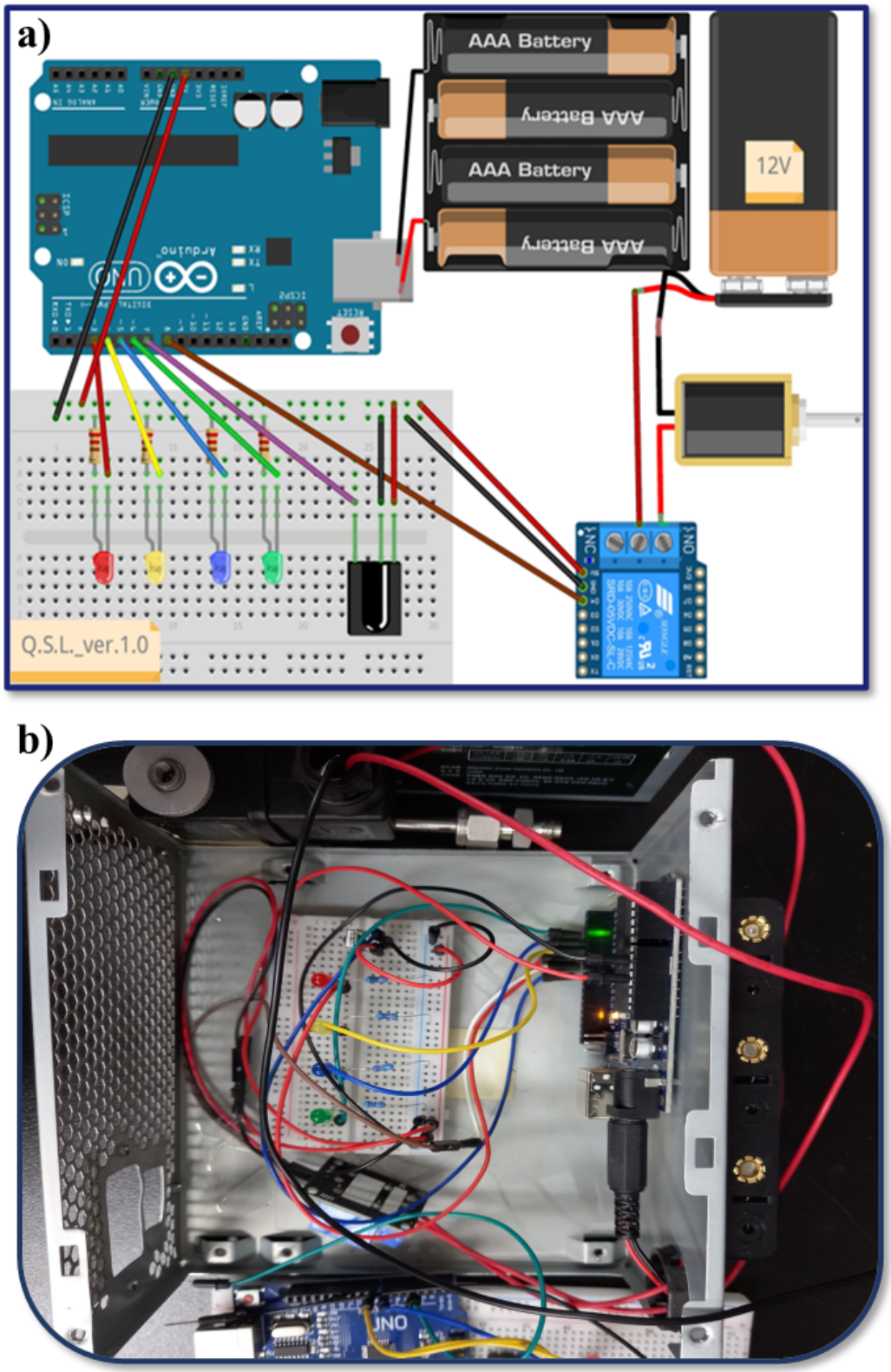


Fig. S5 a) Illustration schematic of Arduino circuit diagram and b) our Arduino microcontroller for bubbling pH_2.

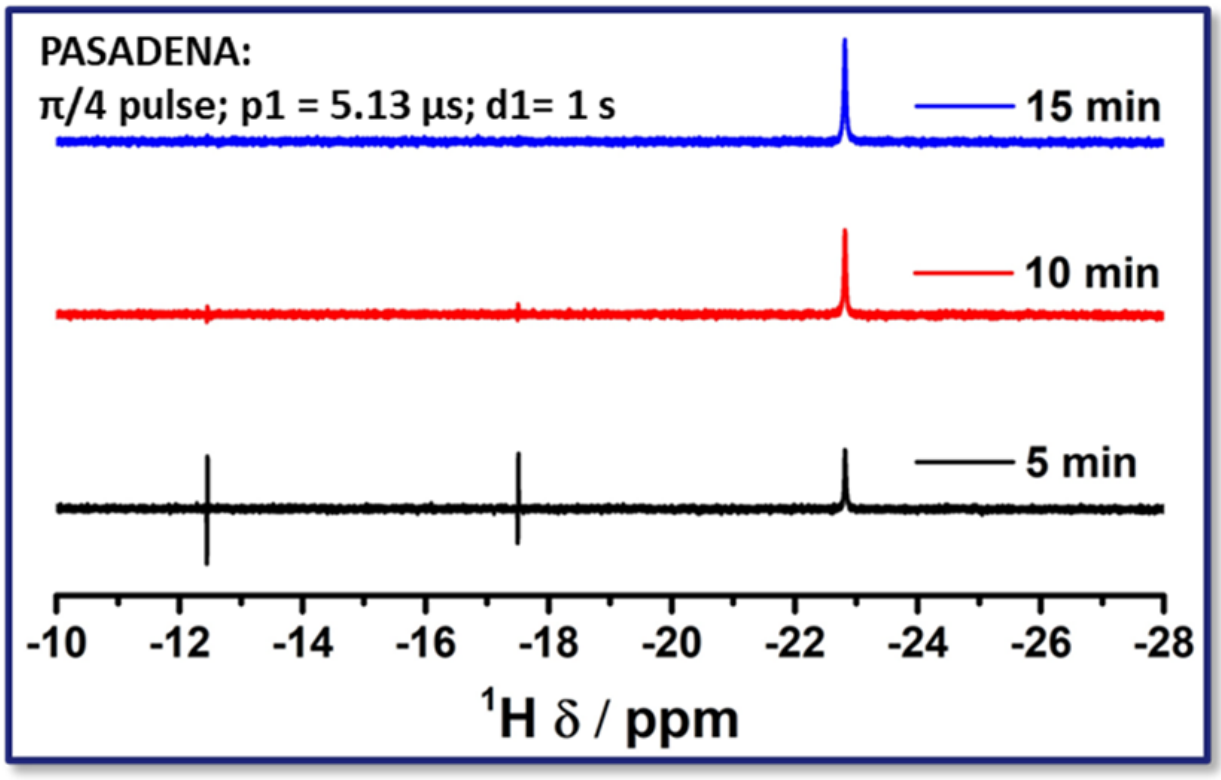


Fig. S6 ^{1}H NMR detection intermediate of iridium and pyridine complexes using non-hydrogenation (PASADENA) at high field NMR (400 MHz).

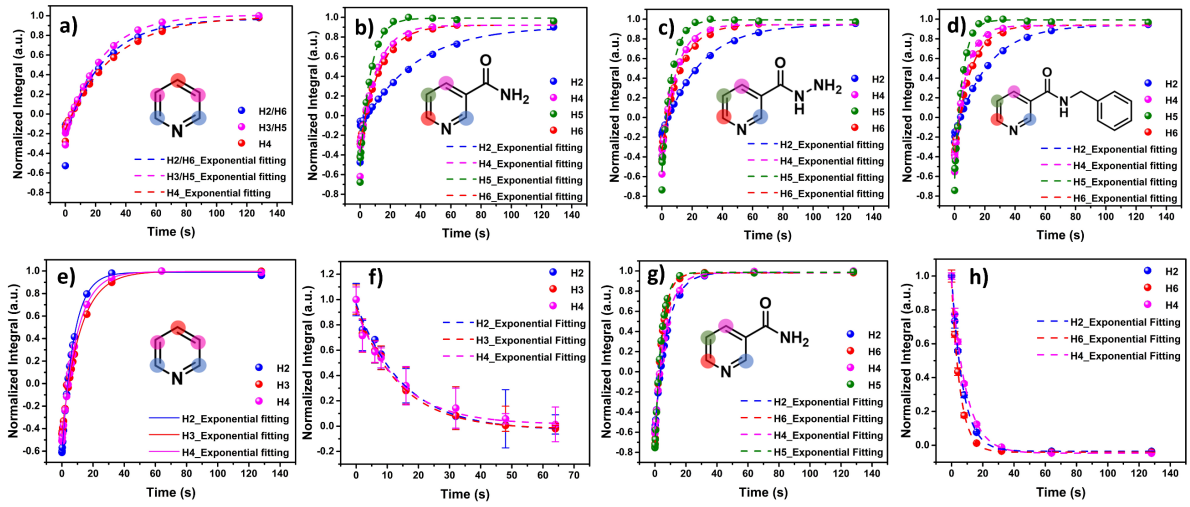


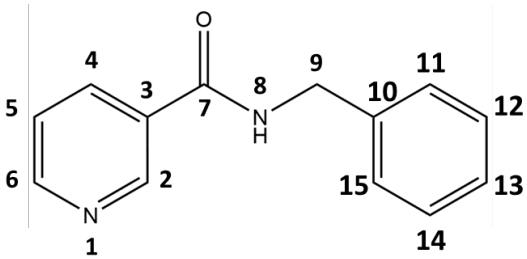
Fig. S7 T_1 relaxation time of a) pyridine, b) nicotinamide, c) nicotinic acid hydrazide, and d) N-benzyl Nicotinamide when absence of iridium catalyst. T_1 relaxation time of pyridine and nicotinamide at thermal (e and g) and hyperpolarized (f and h) conditions.

Table S1. Summary of normalized signal enhancement of N-benzyl nicotinamide and nicotinic acid hydrazide depending on the magnetic field.

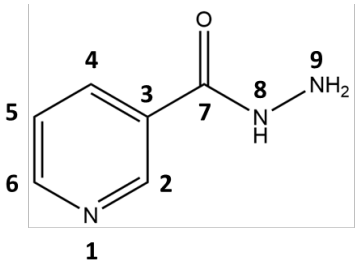
Substrates	$B_{polarizer}$ (mT)	ε_{H2} (a.u.)	ε_{H6} (a.u.)	ε_{H4} (a.u.)	ε_{H5} (a.u.)
N-Benzyl Nicotinamide (BnNA)	Earth Field	16.86 ± 2.66	19.44 ± 2.17	23.72 ± 0.50	30.64 ± 2.76
	1	17.86 ± 0.98	20.08 ± 0.97	26.55 ± 2.02	33.35 ± 1.65
	2	23.79 ± 1.92	26.14 ± 1.65	31.66 ± 0.96	30.88 ± 1.27
	3	28.03 ± 2.26	29.57 ± 2.95	33.75 ± 2.20	24.75 ± 1.18
	4	38.77 ± 0.45	37.12 ± 1.23	35.99 ± 1.84	14.70 ± 0.93
	5	39.88 ± 2.63	37.49 ± 2.64	36.98 ± 2.15	9.76 ± 0.17
	6	45.93 ± 4.73	41.83 ± 5.31	40.05 ± 3.13	3.68 ± 0.97
	6.5	46.93 ± 1.40	43.50 ± 1.43	41.27 ± 0.66	1.18 ± 0.98
	7	40.41 ± 1.46	37.58 ± 1.73	36.31 ± 1.27	1.74 ± 0.51
	8	32.72 ± 0.66	30.49 ± 1.18	30.83 ± 0.86	2.33 ± 0.66
Nicotinic acid hydrazide (NAH)	Earth Field	8.28 ± 0.49	9.45 ± 0.44	6.86 ± 0.61	13.39 ± 0.17
	1	13.85 ± 0.45	14.16 ± 0.33	10.42 ± 0.75	11.56 ± 0.26
	2	22.44 ± 0.92	22.91 ± 0.98	18.54 ± 1.09	8.13 ± 0.76
	3	27.81 ± 0.95	27.52 ± 1.02	19.55 ± 0.13	2.84 ± 0.53
	4	33.61 ± 0.96	30.32 ± 1.35	20.40 ± 1.25	1.02 ± 0.67

5	42.74 ± 1.27	36.80 ± 1.72	24.53 ± 1.35	5.74 ± 0.77
6	46.16 ± 1.90	41.28 ± 1.06	28.65 ± 0.24	9.76 ± 0.36
6.5	57.21 ± 2.52	50.51 ± 3.37	35.80 ± 2.23	13.62 ± 1.95
7	50.40 ± 2.37	40.50 ± 2.37	29.25 ± 1.32	13.56 ± 0.88
8	25.92 ± 0.57	22.29 ± 1.10	16.39 ± 0.45	6.91 ± 0.51

Table S2. Summary of NMR signal assignment of N-benzyl nicotinamide and nicotinic acid hydrazide.



N-Benzyl Nicotinamide



Nicotinic Acid Hydrazide

Substrates	**Position**	**^{1}H δ (ppm)**	**^{13}C δ (ppm)**
N-Benzyl Nicotinamide (BnNA)	2	9.10 (dd, 1H, ^{4}J = 2.24 Hz, ^{5}J = 0.8 Hz)	148.94
	3	-	130.29
	4	8.26 (ddd, 1H, ^{4}J = 1.71 Hz, ^{4}J = 2.24 Hz, ^{3}J = 7.96 Hz)	135.48
	5	7.52 (dddd, 1H, ^{5}J = 0.8 Hz, ^{3}J = 4.8 Hz, ^{3}J = 7.96 Hz)	123.93
	6	8.73 (dd, 1H, ^{4}J = 1.71 Hz, ^{3}J = 4.8 Hz)	152.34

	7	-	165.33
	8	9.27 (t, 1H, ^{3}J = 5.96 Hz)	-
	9	4.54 (d, 1H, ^{3}J = 5.96 Hz)	43.13
	10	-	139.77
	11	7.38-7.23 (m, 5H)	128.79, 127.75, 127.31
	12		
	13		
	14		
	15		
Nicotinic acid hydrazide (NAH)	2	8.98 (dd, 1H, ^{4}J = 2.27 Hz, ^{5}J = 0.88 Hz)	148.55
	3	-	129.35
	4	8.16 (ddd, 1H, ^{4}J = 1.71 Hz, ^{4}J = 2.27 Hz, ^{3}J = 7.93 Hz)	135.14
	5	7.48 (dddd, 1H, ^{5}J = 0.88 Hz, ^{3}J = 4.83 Hz, ^{3}J = 7.93 Hz)	123.95
	6	8.68 (dd, 1H, ^{4}J = 1.71 Hz, ^{3}J = 4.83 Hz)	152.22
	7	-	164.83
	8	9.98 (br, 1H)	-
	9	4.59 (br, 1H)	-

Table S3. The enthalpies, entropy, and free Gibbs energy at 298 K of transition state and dissociation rate at 298 K based on Eyring equation fitting.

Substrates	$\Delta H^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (J/mol.T)	$\Delta G^{\#}_{298}$_EXSY (kJ/mol)	$\Delta G^{\#}_{298}$_DFT (kJ/mol)	k_d^{298} (s^{-1})	R^2
Pyridine	80.37	44.70	67.05	45.40	10.82	0.993
Nicotinamide	76.80	28.80	68.22	54.96	7.86	0.970
N-Benzyl nicotinamide	70.84	8.66	68.26	60.78	7.05	0.988
Nicotinic acid hydrazide	196.50	377.40	84.04	46.88 & 59.95	0.011[a]	0.981

a: the dissociation rate (k_d) at 298 K is estimated based on the linear Eyring equation fitting. For instance, the linear fitting results are y = -9656.55 x + 29.10 (pyridine), y = -9402.24 x + 27.90 (nicotinamide), y = -9237.90 x + 27.22 (N-benzyl nicotinamide), and y = -23634.98 x + 69.15 (nicotinic acid hydrazide).

Table S4. Summary of bonding length between iridium and nitrogen of all substrates in DFT.

Substrates	Axial (Å)	Equatorial 1 (Å)	Equatorial 2 (Å)
Pyridine	2.122	2.175	2.227
Nicotinamide	2.124	2.168	2.218
N-Benzyl nicotinamide	2.122	2.172	2.221
Nicotinic acid hydrazide	2.123	2.174	2.220

7. Density Functional Theory (DFT) Calculations

To confirm the dissociation rate via EXSY, DFT calculations were conducted using the Gaussian 09 software package.[15, 16] The reactant iridium dihydride complex of all substrates includes pyridine (Py), nicotinamide (NA), N-benzyl nicotinamide (BnNA), and nicotinic acid hydrazide (NAH), were subjected to singlet multiplicity and +1 charge. The geometry optimization of ground states was computed at the BP86/Ianl2dz levels, and the energy minima were confirmed by the calculation with the absence of imaginary modes of vibrations.[17] For the purpose of finding transition state, a relaxed potential energy surface scan was performed with an increment step of 0.1Å and a total of 30 steps. The obtained saddle point will be located to transition state. The transition state was validated by the presence of only 1 imaginary mode of vibrations. The total electronic energy, thermal correction to energy, zero-point energy, thermal correction to enthalpy and thermal correction to Gibb free energy were carried out by vibrational frequency calculation. Consequently, the vibrational frequencies of the reactant and transition states were utilized to estimate zero-point energies (ZPE_E^0), enthalpies (ΔH), and free Gibbs energies (ΔG^{298}) at 298 K. The Cartesian coordinates, total electronic energies with zero points, enthalpies, and Gibbs free energies of the reactant and transition states are listed below. These valves are summarized in **Table S5**.

Table S5. Summary of sum of electronic and ZPE, sum of electronic and thermal enthalpies, sum of electronic and thermal free Gibbs energies for all substrates and transition state complex ($\Delta G^{\#}$) (1 Ha = 2625.5 kJ/mol).

Substrates	Complex	$E^0 + E_{ZPE}$ (Ha)	$E^0 + H_{corr}$ (Ha)	$E^0 + G_{corr}$ (Ha)	$\Delta G_r^{\#}$ (kJ/mol)
Pyridine (Py)	$[Ir(H_2)(IMes)(Py)_3]^+$	-1774.072040	-1774.028450	-1774.150350	45.502540
	$[Ir(H_2)(IMes)(Py)_2]$ …Py^+	-1774.049647	-1774.005353	-1774.133019	
Nicotinamide (NA)	$[Ir(H_2)(IMes)(NA)_3]^+$	-2280.079367	-2280.025791	-2280.172888	54.959592
	$[Ir(H_2)(IMes)(NA)_2]$ …NA^+	-2280.055497	-2280.001547	-2280.151955	
N-Benzyl Nicotinamide (BnNA)	$[Ir(H_2)(IMes)(BnNA)_3]^+$	-3090.713569	-3090.641684	-3090.836795	60.785576
	$[Ir(H_2)(IMes)(BnNA)_2]$ …$BnNA^+$	-3090.690247	-3090.618322	-3090.813643	
Nicotinic Acid Hydrazide (NAH)	$[Ir(H_2)(IMes)(NAH)_3]^+$	-2445.963167	-2445.904485	-2446.062521	46.883553
	$[Ir(H_2)(IMes)(NAH)_2]$ …NAH^+	-2445.944110	-2445.885781	-2446.044664	
	Dia1 $[Ir(H_2)(IMes)(NAH)_2]^+$	-1973.818888	-1973.771494	-1973.904806	-
	Dia2 $[Ir(H_2)(IMes)(NAH)_2]^+$	-1973.815659	-1973.768377	-1973.899914	59.955918
	Dia2 $[Ir(H_2)(IMes)(NAH)]$ …NAH^+	-1973.791028	-1973.743761	-1973.877078	

Substrates	Methods	T_{1_H2} (s)	T_{1_H6} (s)	T_{1_H4} (s)	T_{1_H5} (s)
Pyridine	Thermal (Absence Ir)	25.1 ± 0.09	23.3 ± 0.03 (H3 in Pyridine)	30.9 ± 0.02	-
	Thermal (Presence Ir)	7.64 ± 0.09	11.71 ± 0.48 (H3 in Pyridine)	9.75 ± 0.04	-
	Hyper-polarized	15.03 ± 0.14	13.90 ± 1.93 (H3 in Pyridine)	13.87 ± 2.11	-
Nicotinamide (NA)	Thermal (Absence Ir)	34.7 ± 0.09	13.0 ± 0.04	10.6 ± 0.07	6.92 ± 0.05
	Thermal (Presence Ir)	7.90 ± 0.10	4.53 ± 0.03	6.74 ± 0.10	4.22 ± 0.02
	Hyper-polarized	7.22 ± 0.05	5.47 ± 0.15	9.21 ± 0.11	-
N-Benzyl Nicotinamide (BnNA)	Thermal (Absence Ir)	21.6 ± 0.02	10.4 ± 0.02	7.41 ± 0.03	5.04 ± 0.04
	Thermal (Presence Ir)	5.08 ± 0.10	3.80 ± 0.03	5.37 ± 0.10	3.92 ± 0.02
	Hyper-polarized	4.62 ± 0.14	4.50 ± 0.17	6.94 ± 0.20	-
Nicotinic acid hydrazide (NAH)	Thermal (Absence Ir)	24.4 ± 0.04	11.7 ± 0.03	9.11 ± 0.05	6.32 ± 0.06
	Thermal (Presence	19.24 ± 0.22	10.27 ± 0.15	8.84 ± 0.11	6.17 ± 0.06

	Ir)				
	Hyper-polarized	20.40 ± 0.30	14.34 ± 0.24	13.75 ± 0.52	-

Table S6. Summary thermal and hyperpolarized T_1 relaxation time with and without iridium catalyst of pyridine, nicotinamide, N-benzyl nicotinamide, and nicotinic acid hydrazide.

Note: All the samples were prepared inside the glove box to prevent the effect of oxygen (paramagnetic agent), which affects T_1 relaxation time.

7.1. Pyridine (Py)

7.1.1. Reactant: $[Ir(H_2)(IMes)(Py)_3]^+$

Ir	-0.14809	0.54669	-0.39523
N	-0.31854	2.56552	-1.02675
C	-0.7395	2.82947	-2.31452
C	-0.86127	4.1383	-2.81595
C	-0.54405	5.23853	-1.98301
C	-0.11658	4.97562	-0.66163
C	-0.0186	3.64095	-0.21961
H	0.30881	3.4064	0.79529
H	0.13968	5.78762	0.02555
H	-0.6287	6.26534	-2.35246
H	-1.1987	4.28537	-3.84618
H	-0.97023	1.95237	-2.92076
N	-1.15603	1.00009	1.47808
C	-2.23668	1.85527	1.4852
C	-2.94181	2.18202	2.66035
C	-2.53923	1.6163	3.89359
C	-1.44494	0.71947	3.89278
C	-0.78844	0.43377	2.67918
H	0.04091	-0.27653	2.63278

H	-1.10379	0.23873	4.81492
H	-3.06749	1.85718	4.82161
H	-3.79473	2.86469	2.60003
H	-2.53173	2.25453	0.51279
H	-1.59283	0.30069	-1.02418
H	0.48037	0.22893	-1.84434
C	-0.13907	-1.43856	-0.09589
N	-1.26852	-2.29153	-0.07165
C	-0.89437	-3.64685	0.06502
C	0.47719	-3.68418	0.12382
H	1.16785	-4.51702	0.21819
N	0.93256	-2.34781	0.0256
C	2.36367	-2.08534	-0.05674
C	2.98463	-2.13247	-1.33985
C	4.39299	-2.00005	-1.4031
C	5.18766	-1.85261	-0.23593
C	4.53398	-1.83416	1.0205
C	3.12547	-1.95842	1.13687
C	2.48089	-1.95322	2.51434
H	3.16586	-2.37636	3.2696
H	2.24938	-0.91682	2.8321
H	1.54208	-2.53306	2.5396
H	5.13237	-1.73975	1.93601
C	6.70358	-1.77205	-0.33117
H	7.02741	-1.24545	-1.24685
H	7.14076	-1.25194	0.53937
H	7.1492	-2.78556	-0.36534
H	4.8828	-2.03824	-2.38478

C	2.17313	-2.34502	-2.60749
H	1.40852	-1.55573	-2.73273
H	2.82581	-2.34328	-3.497
H	1.63581	-3.31246	-2.58604
H	-1.63208	-4.44294	0.09886
C	-2.67006	-1.93774	-0.27517
C	-3.55006	-1.89315	0.83856
C	-4.91931	-1.60237	0.59657
C	-5.42218	-1.39211	-0.70871
C	-4.5185	-1.49818	-1.80033
C	-3.14674	-1.78254	-1.61256
C	-2.21934	-1.93733	-2.80593
H	-2.77478	-1.82239	-3.75233
H	-1.41211	-1.18203	-2.77639
H	-1.73536	-2.93295	-2.8167
H	-4.89605	-1.37171	-2.82342
C	-6.89333	-1.08718	-0.94819
H	-7.46216	-1.05867	-0.00292
H	-7.02439	-0.11081	-1.4526
H	-7.35899	-1.85144	-1.5989
H	-5.60706	-1.5586	1.45121
C	-3.09258	-2.20669	2.2552
H	-2.0062	-2.07503	2.38293
H	-3.61007	-1.56333	2.98873
H	-3.33111	-3.25621	2.51845
N	1.88967	1.13194	0.28514
C	2.88481	1.2222	-0.6617
C	4.14288	1.79773	-0.39547

C	4.41746	2.30633	0.89522
C	3.40422	2.21626	1.87744
C	2.16698	1.63213	1.53689
H	1.36392	1.56689	2.27536
H	3.55987	2.59527	2.89253
H	5.38662	2.75969	1.12706
H	4.88898	1.84184	-1.19433
H	2.63319	0.82533	-1.6462

Sum of electronic and zero-point Energies = -1774.072040 Ha

Sum of electronic and thermal Enthalpies = -1774.028450 Ha

Sum of electronic and thermal Free Energies = -1774.150350 Ha

7.1.2.Transition state: $[Ir(H_2)(IMes)(Py)_2]\ldots Py^+$

Ir	-0.27019	0.35108	-0.58420
N	0.15054	2.25869	-1.38745
C	-0.30305	2.58363	-2.64902
C	-0.06828	3.84123	-3.23416
C	0.66364	4.81741	-2.51612
C	1.13905	4.48524	-1.22674
C	0.86731	3.20956	-0.69432
H	1.23853	2.90806	0.28770
H	1.71756	5.19944	-0.63332
H	0.86070	5.80254	-2.95066
H	-0.45260	4.04394	-4.23815
H	-0.85097	1.79813	-3.17283
N	-0.91467	1.31974	1.24050
C	-2.16774	1.87753	1.34371
C	-2.59481	2.55940	2.50095

C	-1.71531	2.67337	3.60344
C	-0.42262	2.10680	3.49717
C	-0.05119	1.44818	2.30769
H	0.95683	1.04276	2.15423
H	0.29474	2.17551	4.32078
H	-2.02578	3.19264	4.51596
H	-3.60094	2.98814	2.52951
H	-2.82031	1.75659	0.47614
H	-1.67286	0.40020	-1.24297
H	0.23703	-0.27608	-1.98191
C	-0.68207	-1.53033	-0.05209
N	-1.94102	-2.13253	0.11742
C	-1.82061	-3.51526	0.38517
C	-0.47603	-3.80732	0.39152
H	0.05218	-4.74190	0.55559
N	0.20915	-2.60042	0.12240
C	1.66196	-2.55057	0.02104
C	2.27317	-2.82114	-1.23646
C	3.68967	-2.87612	-1.28491
C	4.48862	-2.69477	-0.12773
C	3.83747	-2.44161	1.10759
C	2.42755	-2.37450	1.20945
C	1.75876	-2.16780	2.55925
H	1.30863	-3.10886	2.93130
H	2.49116	-1.82974	3.31177
H	0.94467	-1.42339	2.50600
H	4.43993	-2.30655	2.01502
C	6.00469	-2.79114	-0.19722

H	6.35895	-2.90697	-1.23603
H	6.48437	-1.89065	0.23060
H	6.37419	-3.65975	0.38079
H	4.17547	-3.08791	-2.24586
C	1.44687	-3.07543	-2.48625
H	0.81419	-2.20127	-2.72790
H	2.09763	-3.28286	-3.35240
H	0.76991	-3.94140	-2.35695
H	-2.68969	-4.14826	0.53783
C	-3.23578	-1.47406	0.02325
C	-3.89474	-1.08346	1.22153
C	-5.17655	-0.48587	1.11041
C	-5.80603	-0.28936	-0.14483
C	-5.12220	-0.71482	-1.31468
C	-3.84475	-1.32357	-1.25701
C	-3.16822	-1.83188	-2.52080
H	-3.75533	-1.56338	-3.41532
H	-2.14934	-1.41863	-2.63477
H	-3.06868	-2.93446	-2.50317
H	-5.60286	-0.58785	-2.29334
C	-7.19299	0.32820	-0.23978
H	-7.49271	0.80732	0.70834
H	-7.24431	1.08867	-1.04049
H	-7.95215	-0.44241	-0.47618
H	-5.69784	-0.18061	2.02684
C	-3.26707	-1.31831	2.58647
H	-2.20725	-1.00740	2.60946
H	-3.80997	-0.76266	3.36966

H	-3.29295	-2.39061	2.86114
N	3.07938	1.31306	0.99643
C	3.62045	0.88840	-0.19022
C	4.97046	1.11176	-0.54625
C	5.81259	1.79723	0.36169
C	5.27202	2.23195	1.59592
C	3.90853	1.97203	1.86754
H	3.45634	2.30059	2.81119
H	5.88673	2.76248	2.33019
H	6.86251	1.98836	0.11478
H	5.34557	0.75490	-1.51058
H	2.94284	0.35244	-0.86547

Sum of electronic and zero-point Energies = -1774.049647 Ha

Sum of electronic and thermal Enthalpies = -1774.005353 Ha

Sum of electronic and thermal Free Energies = -1774.133019 Ha

7.2. Nicotinamide (NA)

7.2.1. Reactant: $[Ir(H_2)(IMes)(NA)_3]^+$

Ir	-0.39316	0.52862	-0.28985
N	-0.62025	2.35421	0.77082
C	-1.24813	3.41423	0.15023
C	-1.42555	4.66720	0.77330
C	-0.91973	4.85618	2.08638
C	-0.28927	3.77415	2.73159
C	-0.16046	2.54344	2.05538
H	0.32214	1.68782	2.53176
H	0.10692	3.86937	3.74666
H	-1.02651	5.84002	2.55444

C	-2.07893	5.85641	0.09536
N	-2.90532	5.59528	-0.98369
H	-3.33595	6.39326	-1.45363
H	-3.17930	4.65566	-1.26678
O	-1.86616	7.03280	0.51766
H	-1.56506	3.21218	-0.87511
N	-0.85327	-0.60731	1.49824
C	-1.89834	-0.22941	2.31649
C	-2.23651	-0.93841	3.48415
C	-1.48572	-2.07913	3.85242
C	-0.42184	-2.48905	3.01175
C	-0.15494	-1.73651	1.84532
H	0.63164	-2.06857	1.16403
C	0.43882	-3.71616	3.22561
N	0.50233	-4.22396	4.50812
H	0.11873	-3.73888	5.31820
H	1.07416	-5.05574	4.66435
O	1.06648	-4.24213	2.25310
H	-1.75899	-2.64470	4.75021
H	-3.08367	-0.60068	4.08812
H	-2.46624	0.64460	1.99096
H	-1.96232	0.57369	-0.57677
H	-0.17556	1.40000	-1.63006
C	-0.38973	-1.09092	-1.47978
N	-1.50182	-1.90220	-1.80049
C	-1.15991	-2.90845	-2.73084
C	0.17334	-2.75296	-3.02146
H	0.83343	-3.31068	-3.67911

N	0.63648	-1.65218	-2.26348
C	2.01115	-1.19729	-2.42824
C	2.28883	-0.26565	-3.47306
C	3.63982	0.07668	-3.71888
C	4.70625	-0.49996	-2.97789
C	4.38825	-1.43484	-1.96370
C	3.04902	-1.81035	-1.67425
C	2.77796	-2.84638	-0.59513
H	3.51964	-3.66352	-0.63933
H	2.86056	-2.40380	0.41667
H	1.77707	-3.29961	-0.67520
H	5.19952	-1.90731	-1.39434
C	6.15204	-0.15912	-3.30644
H	6.27489	0.91287	-3.54622
H	6.83016	-0.40627	-2.47077
H	6.49868	-0.72915	-4.19047
H	3.86715	0.78756	-4.52402
C	1.17389	0.32945	-4.31825
H	0.44611	0.87954	-3.69226
H	1.57934	1.02244	-5.07496
H	0.60683	-0.45754	-4.85116
H	-1.89019	-3.62737	-3.08964
C	-2.88178	-1.75421	-1.35169
C	-3.38674	-2.63144	-0.35462
C	-4.74845	-2.49209	0.02568
C	-5.60394	-1.54203	-0.58057
C	-5.07285	-0.72339	-1.61384
C	-3.72374	-0.81912	-2.02547

C	-3.20126	0.03098	-3.17138
H	-4.00469	0.66035	-3.59119
H	-2.37637	0.68609	-2.83413
H	-2.80244	-0.59740	-3.99092
H	-5.73131	-0.00702	-2.12254
C	-7.06273	-1.41685	-0.16681
H	-7.31118	-2.10245	0.66149
H	-7.30208	-0.38735	0.16092
H	-7.73823	-1.65181	-1.01134
H	-5.14928	-3.15850	0.80054
C	-2.54692	-3.74440	0.25339
H	-1.46656	-3.53066	0.22365
H	-2.83730	-3.93141	1.30223
H	-2.70329	-4.69333	-0.29694
N	1.76603	0.78613	0.14796
C	2.51067	1.61878	-0.66024
C	3.79795	2.06539	-0.30635
C	4.36984	1.65733	0.92060
C	3.62034	0.79668	1.75921
C	2.33390	0.39293	1.33059
H	1.75219	-0.25257	1.99164
C	4.04704	0.30766	3.12672
N	5.39383	0.36719	3.42764
H	6.10683	0.63703	2.75168
H	5.69163	0.05759	4.35413
O	3.18811	-0.13768	3.95350
H	5.35441	2.03847	1.21465
H	4.33390	2.73582	-0.98403

H	2.03041	1.92824	-1.58909

Sum of electronic and zero-point Energies = -2280.079367 Ha

Sum of electronic and thermal Enthalpies = -2280.025791 Ha

Sum of electronic and thermal Free Energies = -2280.172888 Ha

7.2.2. Transition State: $[Ir(H_2)(IMes)(NA)_2]\ldots NA^+$

Ir	-0.73515	0.34087	-0.42993
N	0.06905	2.28855	-0.19731
C	-0.28702	3.27514	-1.09448
C	0.21305	4.59210	-1.02047
C	1.13726	4.91529	0.00729
C	1.49920	3.91581	0.93199
C	0.94865	2.62467	0.80702
H	1.21757	1.82905	1.50134
H	2.20585	4.11671	1.74212
H	1.55078	5.92833	0.04255
C	-0.13348	5.67960	-2.01942
N	-1.28633	5.51155	-2.76691
H	-1.51459	6.23351	-3.45227
H	-1.95870	4.76397	-2.60291
O	0.61441	6.69536	-2.14780
H	-0.95570	2.94168	-1.89101
N	-0.57974	0.00143	1.69216
C	-1.42143	0.62006	2.59067
C	-1.28583	0.44796	3.98202
C	-0.25206	-0.37417	4.48675
C	0.62441	-1.00994	3.56981

C	0.41805	-0.80354	2.18565
H	1.06979	-1.28357	1.45053
C	1.76531	-1.93096	3.95316
N	2.23533	-1.84431	5.24797
H	1.95022	-1.11391	5.89897
H	3.00719	-2.45748	5.51569
O	2.26071	-2.73877	3.10530
H	-0.16098	-0.52944	5.56752
H	-1.98605	0.95164	4.65468
H	-2.20794	1.24397	2.16064
H	-2.16855	0.93056	-0.33780
H	-0.81682	0.65156	-2.01128
C	-1.57786	-1.41591	-0.87040
N	-2.90849	-1.80872	-0.64313
C	-3.17017	-3.08546	-1.18971
C	-2.00031	-3.52000	-1.76951
H	-1.75930	-4.44188	-2.29036
N	-1.03777	-2.50322	-1.57291
C	0.32198	-2.63501	-2.08479
C	0.59447	-2.18387	-3.41166
C	1.88583	-2.42149	-3.94118
C	2.88620	-3.10659	-3.20052
C	2.57040	-3.54594	-1.89276
C	1.29090	-3.33659	-1.31398
C	0.99713	-3.89609	0.06893
H	1.07604	-5.00017	0.06185
H	1.71942	-3.52944	0.82125
H	-0.01529	-3.63937	0.42161

H	3.32747	-4.08281	-1.30650
C	4.24615	-3.39985	-3.81622
H	4.51447	-2.65625	-4.58769
H	5.04470	-3.41211	-3.05306
H	4.24819	-4.39322	-4.30640
H	2.10687	-2.08805	-4.96333
C	-0.47144	-1.50191	-4.25414
H	-0.83581	-0.57944	-3.76537
H	-0.07468	-1.23498	-5.24828
H	-1.34952	-2.15852	-4.40651
H	-4.14747	-3.55313	-1.11649
C	-3.92913	-1.03308	0.04622
C	-4.19074	-1.30495	1.41777
C	-5.21258	-0.55935	2.05939
C	-5.97603	0.41560	1.36808
C	-5.69758	0.63855	-0.00620
C	-4.68941	-0.08084	-0.69307
C	-4.44519	0.14253	-2.17711
H	-5.09940	0.94078	-2.56722
H	-3.39322	0.42006	-2.37499
H	-4.65093	-0.77561	-2.76022
H	-6.29031	1.37789	-0.56019
C	-7.09345	1.17496	2.06717
H	-6.95439	1.19000	3.16238
H	-7.15889	2.21972	1.71380
H	-8.07461	0.70171	1.86677
H	-5.42659	-0.75800	3.11759
C	-3.43066	-2.38347	2.17419

H	-2.34944	-2.36057	1.95070
H	-3.56603	-2.27070	3.26342
H	-3.79254	-3.39353	1.90016
N	2.75233	-0.05311	-0.18602
C	3.28934	0.08603	-1.44001
C	4.61926	0.51610	-1.65710
C	5.43627	0.81803	-0.54307
C	4.89954	0.67028	0.76184
C	3.55506	0.23258	0.87902
H	3.12778	0.11692	1.88084
C	5.62682	1.00059	2.04512
N	7.00928	0.99343	2.00360
H	7.53953	0.67529	1.19370
H	7.51631	1.23363	2.85679
O	4.98414	1.27012	3.10995
H	6.45423	1.19323	-0.70254
H	4.99636	0.62533	-2.67848
H	2.62639	-0.15441	-2.27653

Sum of electronic and zero-point Energies = -2280.055497 Ha

Sum of electronic and thermal Enthalpies = -2280.001547 Ha

Sum of electronic and thermal Free Energies = -2280.151955 Ha

7.3. N-Benzyl nicotinamide (BnNA)

7.3.1. Reactant: $[Ir(H_2)(IMes)(BnNA)_3]^+$

Ir	1.26102	-0.20295	0.17524
N	1.69500	0.78997	-1.64897
C	3.01172	1.03548	-1.97917
C	3.39007	1.70281	-3.16332
C	2.37382	2.16264	-4.04220

C	1.02756	1.90400	-3.71725
C	0.72190	1.21558	-2.52523
H	-0.31143	1.00190	-2.24574
H	0.21198	2.23107	-4.36869
H	2.66720	2.71523	-4.94039
C	4.82852	2.01952	-3.52564
N	5.80541	1.22383	-2.95683
C	7.25053	1.44790	-3.20651
C	8.07163	1.38662	-1.92119
C	9.15009	0.47348	-1.80082
C	9.93343	0.43462	-0.62176
C	9.64120	1.30806	0.45224
C	8.56381	2.22241	0.34040
C	7.78523	2.26146	-0.83851
H	6.96127	2.98091	-0.92834
H	8.34208	2.90946	1.16543
H	10.24990	1.28286	1.36333
H	10.76934	-0.26998	-0.54412
H	9.38535	-0.20268	-2.63326
H	7.31952	2.43802	-3.69350
H	7.62301	0.69822	-3.93210
H	5.54724	0.41462	-2.38752
O	5.08939	2.97607	-4.32304
H	3.73338	0.70163	-1.23044
N	-0.27566	-1.39135	-0.79608
C	-0.03944	-1.96496	-2.02797
C	-0.99974	-2.75450	-2.68796
C	-2.26040	-2.97345	-2.08495
C	-2.51058	-2.40325	-0.81190
C	-1.48826	-1.63943	-0.20394
H	-1.64603	-1.23706	0.79899
C	-3.77942	-2.58859	-0.00686

N	-4.92111	-2.89233	-0.71730
H	-4.90833	-2.87730	-1.73988
C	-6.23168	-3.12208	-0.05933
H	-6.00613	-3.30376	1.00738
C	-6.98661	-4.28668	-0.69392
C	-8.26121	-4.08162	-1.28101
C	-8.97217	-5.16304	-1.85582
C	-8.41068	-6.46163	-1.85220
C	-7.13674	-6.67482	-1.26837
C	-6.43053	-5.59457	-0.69208
H	-5.45002	-5.76536	-0.22939
H	-6.70298	-7.68144	-1.25548
H	-8.96021	-7.30008	-2.29487
H	-9.95829	-4.99278	-2.30255
H	-8.70233	-3.07622	-1.28592
H	-6.84009	-2.19785	-0.11450
O	-3.76032	-2.45991	1.26244
H	-3.00264	-3.60534	-2.58596
H	-0.75295	-3.19781	-3.65712
H	0.95105	-1.79034	-2.45291
H	2.30996	-1.32355	-0.26132
H	2.49032	0.60499	0.83554
C	1.14177	-1.22374	1.90177
N	1.51787	-2.57062	2.10796
C	1.37876	-2.94861	3.46172
C	0.91672	-1.84865	4.14215
H	0.67245	-1.70501	5.19044
N	0.77491	-0.80636	3.19655
C	0.37944	0.52155	3.64766
C	1.40370	1.41429	4.08351
C	1.01371	2.65769	4.63566
C	-0.35237	3.01629	4.78581

C	-1.33726	2.09309	4.36029
C	-0.99977	0.83305	3.79772
C	-2.10789	-0.12400	3.38852
H	-2.91435	-0.13783	4.14326
H	-2.57732	0.19012	2.43600
H	-1.75799	-1.15998	3.25565
H	-2.39915	2.34266	4.48649
C	-0.74202	4.33468	5.43738
H	-0.02742	5.14004	5.18872
H	-1.75118	4.66056	5.12880
H	-0.75168	4.23979	6.54094
H	1.79241	3.35067	4.98020
C	2.87393	1.03935	3.98764
H	3.15965	0.79449	2.94771
H	3.51469	1.86479	4.34194
H	3.10369	0.14744	4.60169
H	1.61945	-3.95078	3.80336
C	2.07561	-3.50644	1.13796
C	1.24871	-4.52550	0.59527
C	1.83978	-5.45189	-0.30574
C	3.21341	-5.40282	-0.63995
C	4.01632	-4.39932	-0.03319
C	3.47607	-3.45085	0.86496
C	4.36910	-2.41870	1.53208
H	5.42288	-2.55973	1.23686
H	4.05927	-1.39340	1.25622
H	4.31422	-2.48912	2.63546
H	5.09146	-4.36620	-0.25326
C	3.82927	-6.41272	-1.59702
H	3.06848	-7.09560	-2.01291
H	4.33392	-5.90978	-2.44370
H	4.59278	-7.03078	-1.08706

H	1.20945	-6.24009	-0.73817
C	-0.20959	-4.69611	0.99362
H	-0.65645	-3.77182	1.39249
H	-0.81589	-5.03312	0.13403
H	-0.30857	-5.47024	1.78016
N	-0.03154	1.55563	0.58455
C	0.55736	2.70631	1.06269
C	-0.11142	3.94456	1.09011
C	-1.44058	4.03489	0.61737
C	-2.06461	2.85920	0.13196
C	-1.32165	1.65507	0.13465
H	-1.79552	0.75724	-0.26687
C	-3.45538	2.78569	-0.46241
N	-4.33605	3.78434	-0.10138
H	-4.06131	4.48731	0.58861
C	-5.71717	3.86560	-0.63916
C	-6.09130	5.29261	-1.03007
C	-7.18755	5.94323	-0.40840
C	-7.54918	7.26066	-0.78096
C	-6.81282	7.94187	-1.77863
C	-5.71524	7.29897	-2.40418
C	-5.35774	5.98300	-2.03259
H	-4.51450	5.48409	-2.52744
H	-5.14797	7.82080	-3.18355
H	-7.09222	8.96077	-2.06956
H	-8.40089	7.75122	-0.29631
H	-7.76476	5.41853	0.36435
H	-5.74380	3.17675	-1.50324
H	-6.43140	3.47836	0.11409
O	-3.77050	1.83399	-1.25322
H	-1.94740	5.00673	0.59839
H	0.41513	4.82628	1.46627

H	1.58784	2.60232	1.40314

Sum of electronic and zero-point Energies = -3090.713569 Ha

Sum of electronic and thermal Enthalpies = -3090.641684 Ha

Sum of electronic and thermal Free Energies = -3090.836795 Ha

7.3.2. Transition State: $[Ir(H_2)(IMes)(BnNA)_2]\ldots BnNA^+$

Ir	1.92393	-0.39694	0.34289
N	1.58634	1.10669	-1.10582
C	2.64364	1.88432	-1.53277
C	2.49839	2.91042	-2.49000
C	1.20684	3.16760	-3.02100
C	0.12441	2.37426	-2.59192
C	0.34295	1.35606	-1.64199
H	-0.47540	0.74285	-1.26093
H	-0.88692	2.53878	-2.97472
H	1.08876	3.98859	-3.73540
C	3.63297	3.81119	-2.94053
N	4.91851	3.33195	-2.77273
C	6.11319	4.13293	-3.13482
C	7.18389	4.08960	-2.04749
C	8.50608	3.68134	-2.35830
C	9.51065	3.67107	-1.36016
C	9.19930	4.06522	-0.03739
C	7.87960	4.47233	0.28171
C	6.87936	4.48533	-0.71694
H	5.86233	4.81610	-0.47040
H	7.63730	4.78984	1.30263
H	9.97672	4.06285	0.73512

H	10.53062	3.36121	-1.61487
H	8.75481	3.37968	-3.38431
H	5.74312	5.16028	-3.30812
H	6.53003	3.76833	-4.09426
H	5.07717	2.37873	-2.43887
O	3.37804	4.95001	-3.44746
H	3.59379	1.66889	-1.03818
N	0.59904	-1.70322	-0.75000
C	0.99695	-2.33477	-1.90779
C	0.10876	-3.10923	-2.67923
C	-1.23933	-3.23942	-2.27101
C	-1.65773	-2.58988	-1.08185
C	-0.70541	-1.84593	-0.34530
H	-0.99203	-1.33094	0.57691
C	-3.05851	-2.65517	-0.51115
N	-4.08844	-2.76033	-1.41387
H	-3.90383	-2.68800	-2.41798
C	-5.51724	-2.74637	-0.98713
H	-5.54963	-3.23319	0.00438
C	-6.39273	-3.46483	-2.00593
C	-7.34463	-2.74231	-2.77102
C	-8.16347	-3.40779	-3.71557
C	-8.03499	-4.80412	-3.90652
C	-7.08712	-5.53388	-3.14621
C	-6.27317	-4.86791	-2.20155
H	-5.55021	-5.43769	-1.60338
H	-6.99274	-6.61729	-3.28374
H	-8.67037	-5.32054	-4.63508

H	-8.89922	-2.84053	-4.29705
H	-7.44737	-1.65994	-2.62207
H	-5.83491	-1.69532	-0.84815
O	-3.24443	-2.58054	0.75177
H	-1.93345	-3.85643	-2.85302
H	0.47476	-3.60299	-3.58426
H	2.04521	-2.20824	-2.18770
H	3.19924	-0.85545	-0.41310
H	2.89420	0.65449	1.09180
C	2.42691	-1.68301	1.78281
N	3.44856	-2.64559	1.76352
C	3.57186	-3.28733	3.01736
C	2.62084	-2.73470	3.84622
H	2.36954	-2.93969	4.88257
N	1.92841	-1.76330	3.08892
C	0.82634	-0.97757	3.63091
C	1.11326	0.29087	4.22081
C	0.04210	1.00377	4.80663
C	-1.28057	0.48404	4.83410
C	-1.51769	-0.78325	4.25373
C	-0.47799	-1.54441	3.65603
C	-0.78775	-2.93167	3.11412
H	-0.97624	-3.63692	3.94720
H	-1.69675	-2.91408	2.48492
H	0.04075	-3.34537	2.51486
H	-2.53087	-1.20463	4.26706
C	-2.40269	1.26446	5.50234
H	-2.44075	2.30857	5.13882

H	-3.38634	0.79980	5.31628
H	-2.25604	1.30879	6.59893
H	0.24715	1.97710	5.27149
C	2.52783	0.84767	4.25841
H	2.92562	1.00252	3.23821
H	2.55452	1.81314	4.79200
H	3.22157	0.15700	4.77500
H	4.31229	-4.06118	3.19654
C	4.27598	-2.98823	0.61650
C	3.90301	-4.10105	-0.18919
C	4.73344	-4.43070	-1.28974
C	5.91483	-3.70172	-1.58333
C	6.26036	-2.61241	-0.74183
C	5.46394	-2.24186	0.37009
C	5.87337	-1.09077	1.27451
H	6.81592	-0.63372	0.92873
H	5.09269	-0.30770	1.30195
H	6.02452	-1.43081	2.31680
H	7.17836	-2.04596	-0.94496
C	6.81040	-4.10309	-2.74562
H	6.24092	-4.61521	-3.54123
H	7.31574	-3.22826	-3.19210
H	7.60207	-4.80051	-2.40822
H	4.45908	-5.28537	-1.92167
C	2.67192	-4.93592	0.12860
H	1.78830	-4.30703	0.33878
H	2.42706	-5.61122	-0.70904
H	2.83658	-5.56582	1.02412

N	-1.61564	1.13322	1.05055
C	-1.24828	2.40126	1.42280
C	-2.17242	3.46405	1.54791
C	-3.53769	3.22043	1.27052
C	-3.94278	1.91125	0.90067
C	-2.94238	0.90563	0.81204
H	-3.23583	-0.11629	0.55136
C	-5.35812	1.52587	0.53297
N	-6.36653	2.28711	1.09192
H	-6.13444	3.02614	1.75934
C	-7.79952	2.08364	0.77160
C	-8.46008	3.35572	0.24143
C	-9.60371	3.89719	0.88163
C	-10.22613	5.06464	0.37566
C	-9.70632	5.70331	-0.77482
C	-8.56276	5.16831	-1.41928
C	-7.94489	4.00210	-0.91438
H	-7.06565	3.58443	-1.42138
H	-8.16185	5.65675	-2.31506
H	-10.18770	6.60613	-1.16749
H	-11.11133	5.47243	0.87684
H	-10.01285	3.40472	1.77376
H	-7.82294	1.27051	0.02334
H	-8.33155	1.72536	1.67375
O	-5.58751	0.54614	-0.25300
H	-4.25497	4.04933	1.31139
H	-1.82455	4.46152	1.83407
H	-0.18122	2.55578	1.61530

Sum of electronic and zero-point Energies = -3090.690247 Ha

Sum of electronic and thermal Enthalpies = -3090.618322 Ha

Sum of electronic and thermal Free Energies = -3090.813643 Ha

7.4. Nicotinic acid hydrazide (NAH)

Iridium catalyst with three NAH compounds

7.4.1. Reactant: $[Ir(H_2)(IMes)(NAH)_3]^+$

Ir	-0.68688	-0.35177	0.20333
N	-1.29907	-1.65237	-1.35909
C	-2.41364	-2.44225	-1.16711
C	-2.89127	-3.33706	-2.14807
C	-2.18153	-3.45556	-3.37230
C	-1.04749	-2.64489	-3.57743
C	-0.63890	-1.75399	-2.56319
H	0.23356	-1.11121	-2.69518
H	-0.47335	-2.69475	-4.50710
H	-2.52668	-4.17959	-4.11720
C	-4.09271	-4.23291	-1.93563
N	-5.05435	-3.77279	-1.04174
H	-5.02256	-2.83059	-0.64673
N	-6.22989	-4.51293	-0.73146
H	-5.98708	-5.39366	-0.25548
H	-6.78098	-4.69688	-1.58328
O	-4.21135	-5.33485	-2.55280
H	-2.87501	-2.34474	-0.18238
N	-0.26021	1.22416	-1.23274
C	-1.16060	1.49422	-2.24224
C	-0.94112	2.50249	-3.19942

C	0.24342	3.27313	-3.14461
C	1.17138	3.01371	-2.10449
C	0.86998	1.99866	-1.16762
H	1.54763	1.82073	-0.32996
C	2.45262	3.78114	-1.87470
N	2.99548	4.42063	-2.98084
H	2.66756	4.21960	-3.92835
N	4.23153	5.12552	-2.91967
H	4.91395	4.60036	-2.35309
H	4.09305	6.07602	-2.54747
O	3.00988	3.81415	-0.73079
H	0.40819	4.07617	-3.87138
H	-1.69763	2.68407	-3.96830
H	-2.07149	0.89233	-2.23869
H	-2.18598	0.19239	0.24340
H	-1.13216	-1.49388	1.25026
C	-0.39964	0.83346	1.80023
N	-1.19914	1.93527	2.18071
C	-0.76842	2.49152	3.40508
C	0.30873	1.75162	3.82779
H	0.93576	1.83807	4.71020
N	0.52912	0.74892	2.85466
C	1.56940	-0.24722	3.07343
C	1.23622	-1.41005	3.83015
C	2.27477	-2.31745	4.14831
C	3.62125	-2.08254	3.76128
C	3.91195	-0.90660	3.02841
C	2.90621	0.03380	2.67930

C	3.28809	1.29165	1.91548
H	4.25552	1.68897	2.27028
H	3.41242	1.08202	0.83507
H	2.54059	2.09565	2.01045
H	4.94995	-0.69688	2.73831
C	4.72592	-3.04356	4.17429
H	4.38319	-4.09394	4.15230
H	5.61149	-2.95472	3.52064
H	5.06049	-2.83474	5.20929
H	2.03255	-3.21321	4.73492
C	-0.18457	-1.66261	4.30911
H	-0.89985	-1.66681	3.46560
H	-0.25695	-2.63047	4.83386
H	-0.52005	-0.87460	5.01051
H	-1.26614	3.34731	3.85101
C	-2.38334	2.46030	1.51020
C	-2.27723	3.64966	0.74032
C	-3.45812	4.16034	0.13868
C	-4.71888	3.54228	0.31573
C	-4.78916	2.38479	1.13695
C	-3.64248	1.83447	1.75501
C	-3.76028	0.62687	2.66980
H	-4.81028	0.29845	2.75410
H	-3.15484	-0.21767	2.29109
H	-3.39621	0.85640	3.68979
H	-5.76335	1.91048	1.31391
C	-5.97520	4.12102	-0.31792
H	-5.73419	4.89982	-1.06209

H	-6.57210	3.33842	-0.82192
H	-6.62819	4.58290	0.44772
H	-3.38782	5.07446	-0.46531
C	-0.97080	4.41653	0.60195
H	-0.08367	3.77406	0.72070
H	-0.90945	4.91909	-0.37945
H	-0.90157	5.20853	1.37373
N	1.26850	-1.38736	0.01886
C	1.42729	-2.60521	0.64537
C	2.50176	-3.46949	0.36216
C	3.47025	-3.09485	-0.59700
C	3.32910	-1.83942	-1.23909
C	2.21896	-1.03019	-0.90055
H	2.09673	-0.07674	-1.41847
C	4.23702	-1.30904	-2.32446
N	5.52689	-1.82196	-2.35441
H	5.88678	-2.41931	-1.60715
N	6.49746	-1.41589	-3.31188
H	6.58120	-0.38935	-3.33462
H	6.27507	-1.79319	-4.24397
O	3.83746	-0.42870	-3.15310
H	4.28087	-3.78589	-0.85399
H	2.56270	-4.43059	0.88043
H	0.65261	-2.87059	1.36536

Sum of electronic and zero-point Energies = -2445.963167 Ha

Sum of electronic and thermal Enthalpies = -2445.904485 Ha

Sum of electronic and thermal Free Energies = -2446.062521 Ha

7.4.2. Transition State: $[Ir(H_2)(IMes)(NAH)_2]\ldots NAH^+$

Calculating

Sum of electronic and zero-point Energies = Ha

Sum of electronic and thermal Enthalpies = Ha

Sum of electronic and thermal Free Energies = Ha

Iridium catalyst with two NAH compounds that include diastereomer 1 and 2.

7.4.3. Diastereomer 1: $[Ir(H_2)(IMes)(NAH)_2]^+$

Ir	-0.31578	-0.03799	-0.61858
H	0.63454	1.18890	-0.66515
H	-0.61773	0.30400	-2.16708
C	-1.77164	1.26028	-0.19471
N	-1.64265	2.64978	-0.03722
C	-2.90256	3.26485	0.13888
C	-3.84759	2.26403	0.09581
H	-4.92882	2.29644	0.19084
N	-3.15294	1.04967	-0.10407
C	-3.83209	-0.23738	-0.18043
C	-4.20172	-0.74742	-1.45951
C	-4.93380	-1.95798	-1.50052
C	-5.30679	-2.65046	-0.31862
C	-4.92155	-2.10794	0.93146
C	-4.20114	-0.88956	1.02966
C	-3.89067	-0.30978	2.40145
H	-4.78164	0.19858	2.81966
H	-3.60482	-1.11585	3.10026
H	-3.07588	0.43373	2.36885
H	-5.19545	-2.62825	1.85769
C	-6.13791	-3.92272	-0.39253

H	-5.94014	-4.48633	-1.32194
H	-5.94054	-4.58619	0.46826
H	-7.21987	-3.68535	-0.37948
H	-5.23257	-2.36049	-2.47716
C	-3.85665	-0.00635	-2.74162
H	-2.76269	0.10305	-2.86183
H	-4.25091	-0.54214	-3.62181
H	-4.28568	1.01407	-2.74809
H	-3.00442	4.33745	0.27457
C	-0.39360	3.39803	-0.03640
C	0.24460	3.66667	1.20766
C	1.44405	4.42132	1.18840
C	1.99664	4.92046	-0.01971
C	1.31861	4.64410	-1.23544
C	0.11677	3.89397	-1.27015
C	-0.60357	3.63468	-2.58279
H	-0.05925	4.08882	-3.42808
H	-0.70500	2.54958	-2.77267
H	-1.62624	4.05747	-2.57447
H	1.72533	5.03352	-2.17762
C	3.26062	5.76631	-0.00772
H	3.90740	5.52179	0.85338
H	3.85104	5.63183	-0.93152
H	3.01075	6.84297	0.06570
H	1.94797	4.63823	2.13915
C	-0.34938	3.18488	2.52214
H	-0.59941	2.10899	2.48920
H	0.35191	3.35412	3.35692

H	-1.28665	3.72348	2.76106
N	1.24547	-1.51671	-0.98673
C	2.55630	-1.30007	-1.36187
C	3.43147	-2.34999	-1.71159
C	2.93926	-3.68193	-1.70822
C	1.60172	-3.90805	-1.32643
C	0.78655	-2.81486	-0.96814
H	-0.26095	-2.94688	-0.69264
H	1.17987	-4.91712	-1.30943
H	3.60551	-4.49352	-2.01766
C	4.85897	-2.12357	-2.16116
N	5.48288	-0.97685	-1.68048
H	5.05839	-0.38870	-0.96027
N	6.81692	-0.62502	-2.03106
H	6.88198	-0.41431	-3.03739
H	7.47269	-1.37715	-1.77142
O	5.44730	-2.94698	-2.92605
H	2.85058	-0.24907	-1.40799
N	-1.18437	-1.86263	0.32174
N	-0.31404	-1.88139	1.44964
C	0.65763	-0.92176	1.66446
C	1.57319	-1.15602	2.84306
C	1.17283	-1.70843	4.08677
C	2.15021	-1.88772	5.09440
C	3.49042	-1.54001	4.83427
N	3.88545	-1.00223	3.62833
C	2.92925	-0.79276	2.66679
H	3.27284	-0.34185	1.73221

H	4.27797	-1.67625	5.57939
H	1.88224	-2.29468	6.07385
H	0.12524	-1.96339	4.28217
O	0.81865	0.07607	0.88675
H	-0.38813	-2.71198	2.04202
H	-0.64501	-2.07289	-0.53933
H	-1.66448	-0.95348	0.26594

Sum of electronic and zero-point Energies = -1973.818888 Ha

Sum of electronic and thermal Enthalpies = -1973.771494 Ha

Sum of electronic and thermal Free Energies = -1973.904806 Ha

7.4.4. Reactant (Diastereomer 2): $[Ir(H_2)(IMes)(NAH)_2]^+$

Ir	0.83466	-0.11327	-0.95450
N	-0.01856	-1.40298	0.54905
C	0.51100	-2.64060	0.84473
C	-0.14413	-3.54911	1.69922
C	-1.39751	-3.20403	2.25841
C	-1.94827	-1.93191	1.95735
C	-1.21502	-1.05492	1.12358
H	-1.59353	-0.05703	0.88747
C	-3.28049	-1.42451	2.45729
N	-4.29659	-2.35875	2.53404
H	-4.15591	-3.32959	2.24424
N	-5.63563	-2.01903	2.88269
H	-6.06642	-1.46635	2.11749
H	-5.64556	-1.51289	3.77929
O	-3.46034	-0.19260	2.73386
H	-1.91015	-3.89744	2.93443
H	0.32496	-4.51280	1.91831
H	1.47245	-2.87391	0.38086

H	2.22551	-0.80274	-0.98063
H	1.40817	0.79244	-2.16146
C	1.66232	1.23529	0.26248
N	2.98391	1.24360	0.73732
C	3.25411	2.41446	1.48081
C	2.09821	3.16309	1.48522
H	1.86909	4.12276	1.93874
N	1.13558	2.43917	0.74600
C	-0.22730	2.91832	0.55477
C	-0.53599	3.67064	-0.61635
C	-1.84490	4.19523	-0.73742
C	-2.82837	3.99939	0.26756
C	-2.47933	3.24803	1.41607
C	-1.17719	2.71364	1.59479
C	-0.83400	1.98997	2.88819
H	-0.63261	2.71719	3.69920
H	-1.68094	1.35695	3.20718
H	0.06295	1.35482	2.78911
H	-3.22463	3.08068	2.20358
C	-4.21147	4.61890	0.13298
H	-4.51598	4.71225	-0.92491
H	-4.97506	4.02505	0.66625
H	-4.22866	5.63753	0.56800
H	-2.09675	4.78308	-1.62967
C	0.50795	3.93632	-1.68952
H	0.88023	2.99342	-2.13171
H	0.08815	4.55753	-2.49890
H	1.38672	4.46852	-1.27734
H	4.22658	2.60021	1.92697
C	3.97526	0.19842	0.52559
C	4.12069	-0.81918	1.51072
C	5.11118	-1.81048	1.29903

C	5.95561	-1.79526	0.15854
C	5.78819	-0.75284	-0.78986
C	4.81245	0.26156	-0.62493
C	4.67158	1.38155	-1.64225
H	5.39754	1.26168	-2.46424
H	3.65295	1.40089	-2.07329
H	4.84535	2.37241	-1.18110
H	6.44150	-0.71875	-1.67122
C	7.04108	-2.84528	-0.02170
H	6.77694	-3.79517	0.47585
H	7.23201	-3.05657	-1.08893
H	7.99712	-2.49986	0.41841
H	5.23700	-2.60145	2.04966
C	3.26198	-0.83419	2.76578
H	2.18716	-0.73651	2.52840
H	3.40984	-1.76879	3.33321
H	3.51833	0.00703	3.43829
N	0.55895	-1.80654	-2.65515
N	-0.86010	-1.91293	-2.61855
C	-1.66293	-1.00242	-1.93905
C	-3.15367	-1.26185	-1.97792
C	-3.70967	-2.55029	-2.12401
N	-5.07124	-2.77850	-2.12308
C	-5.90616	-1.69542	-1.96187
C	-5.41617	-0.38464	-1.78953
C	-4.02551	-0.15662	-1.79167
H	-3.59455	0.83791	-1.63836
H	-6.12507	0.43647	-1.64916
H	-6.97462	-1.91559	-1.93952
H	-3.09564	-3.45024	-2.20386
O	-1.18434	-0.00023	-1.32604
H	-1.25248	-2.63822	-3.22255

H	0.95517	-1.93867	-1.71341
H	0.84654	-0.89813	-3.04913

Sum of electronic and zero-point Energies = -1973.815659 Ha

Sum of electronic and thermal Enthalpies = -1973.768377 Ha

Sum of electronic and thermal Free Energies = -1973.899914 Ha

7.4.5. Transition state (Diastereomer 2): [Ir(H_2)(IMes)(NAH)]…NAH^+

Ir	-1.00241	-0.37533	-0.93785
N	0.33259	2.37166	-0.63248
C	-0.29159	3.57725	-0.83183
C	0.28105	4.80523	-0.43198
C	1.54338	4.79578	0.20612
C	2.19952	3.55547	0.42053
C	1.55047	2.36880	-0.01317
H	2.01467	1.39365	0.16529
C	3.51354	3.40728	1.15151
N	4.40149	4.46950	1.03239
H	4.23008	5.24746	0.39136
N	5.66546	4.49726	1.68276
H	6.25132	3.70257	1.38866
H	5.55173	4.52134	2.70572
O	3.78727	2.36654	1.82964
H	1.98032	5.73566	0.56243
H	-0.25963	5.74117	-0.60079
H	-1.27888	3.53922	-1.30432
H	-2.46597	0.16338	-1.17818
H	-1.60007	-1.73978	-1.41047
C	-1.69840	-0.80631	0.86159
N	-3.01560	-0.65147	1.33580

C	-3.13704	-1.09817	2.66898
C	-1.89523	-1.54692	3.05922
H	-1.55023	-1.96765	3.99901
N	-1.02701	-1.37104	1.95990
C	0.37663	-1.75500	2.03595
C	0.74414	-3.07786	1.66660
C	2.09313	-3.46870	1.86020
C	3.06033	-2.58014	2.39799
C	2.65561	-1.26192	2.72950
C	1.31377	-0.83285	2.57693
C	0.90768	0.56315	3.02221
H	0.53062	0.55252	4.06419
H	1.77551	1.24402	2.98506
H	0.10353	0.98076	2.39132
H	3.39019	-0.55307	3.13123
C	4.49324	-3.03192	2.64122
H	4.70463	-4.00343	2.16007
H	5.22185	-2.28914	2.26619
H	4.68828	-3.15351	3.72424
H	2.38687	-4.49544	1.60506
C	-0.27199	-4.04816	1.08701
H	-0.70001	-3.65460	0.14577
H	0.19255	-5.02562	0.87311
H	-1.11754	-4.21971	1.77998
H	-4.08051	-1.05349	3.20486
C	-4.15061	-0.09580	0.61020
C	-4.41752	1.29684	0.71948
C	-5.55998	1.80889	0.05650

C	-6.43117	0.97206	-0.68740
C	-6.12917	-0.41208	-0.76792
C	-4.99868	-0.97142	-0.12331
C	-4.69662	-2.45649	-0.23168
H	-5.48069	-2.97757	-0.80647
H	-3.72780	-2.62515	-0.73981
H	-4.62754	-2.93721	0.76232
H	-6.79195	-1.07358	-1.34049
C	-7.67528	1.53723	-1.35556
H	-7.56845	2.61501	-1.57082
H	-7.89928	1.01748	-2.30431
H	-8.56142	1.41868	-0.70147
H	-5.77916	2.88188	0.13055
C	-3.49838	2.21370	1.51005
H	-2.46741	2.18269	1.10854
H	-3.85539	3.25707	1.47291
H	-3.43717	1.91620	2.57406
N	-0.28911	0.11361	-2.92263
N	1.06997	-0.34593	-3.13902
C	1.76174	-0.87164	-2.05922
C	3.18208	-1.25556	-2.26671
C	3.97717	-0.75064	-3.33609
N	5.27400	-1.11164	-3.54185
C	5.83078	-1.99766	-2.65813
C	5.13217	-2.52270	-1.54188
C	3.78802	-2.14861	-1.34066
H	3.20381	-2.52312	-0.49315
H	5.63415	-3.21169	-0.85640

H	6.86926	-2.28123	-2.86117
H	3.59315	-0.00082	-4.04232
O	1.17466	-1.01950	-0.92162
H	1.46734	-0.29430	-4.08063
H	-0.32443	1.14745	-2.98456
H	-0.92569	-0.32448	-3.60808

Sum of electronic and zero-point Energies = -1973.791028 Ha

Sum of electronic and thermal Enthalpies = -1973.743761 Ha

Sum of electronic and thermal Free Energies = -1973.877078 Ha

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9. Appendix

9.1. NMR spectra of N-benzyl nicotinamide (BnNA)

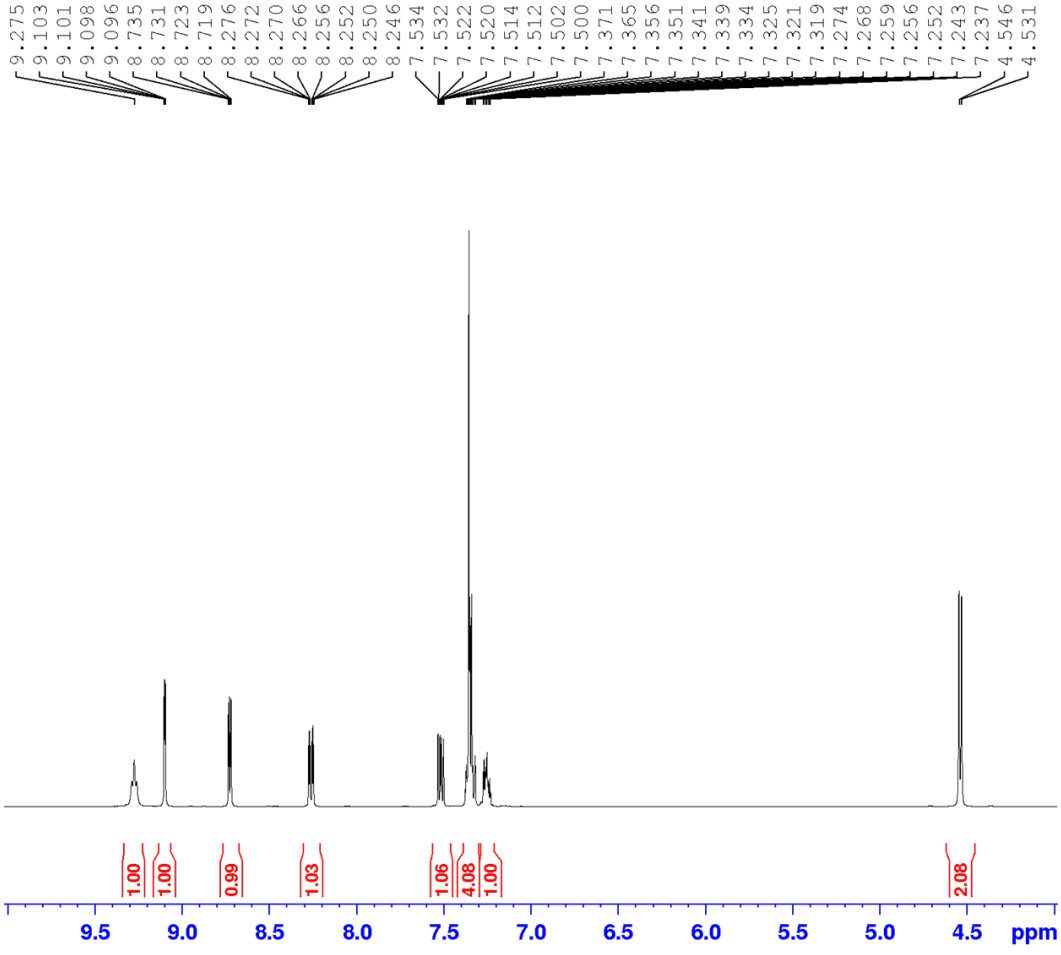

Figure A-1. ^{1}H NMR spectrum of N-benzyl nicotinamide in DMSO-d_6 at 400 MHz.

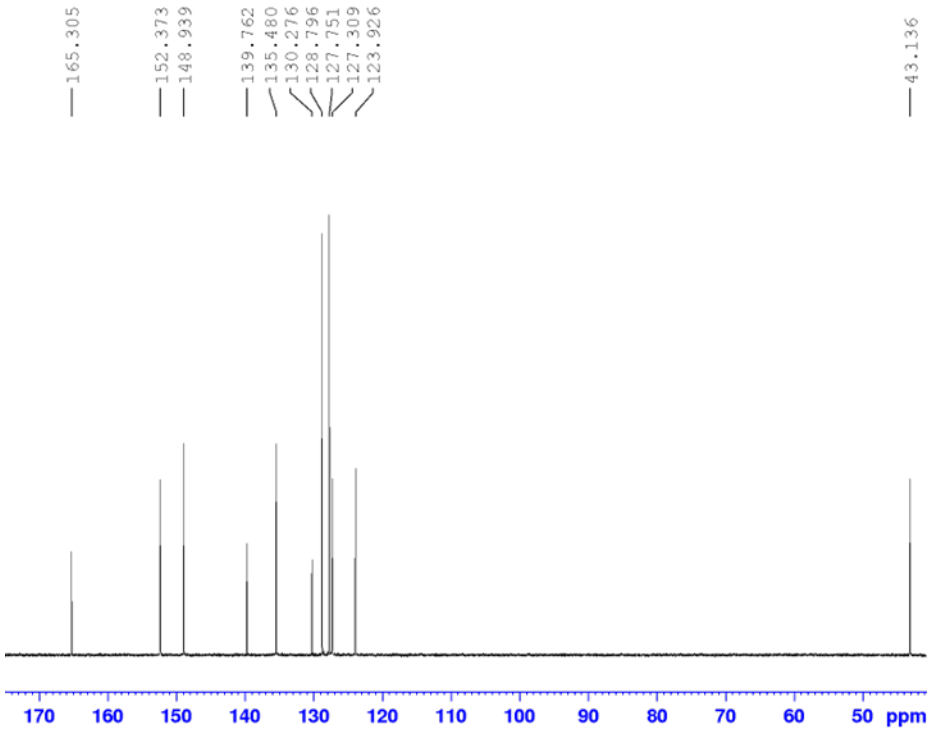

Figure A-2. ^{13}C NMR spectrum of N-benzyl nicotinamide in DMSO-d_6 at 100 MHz.

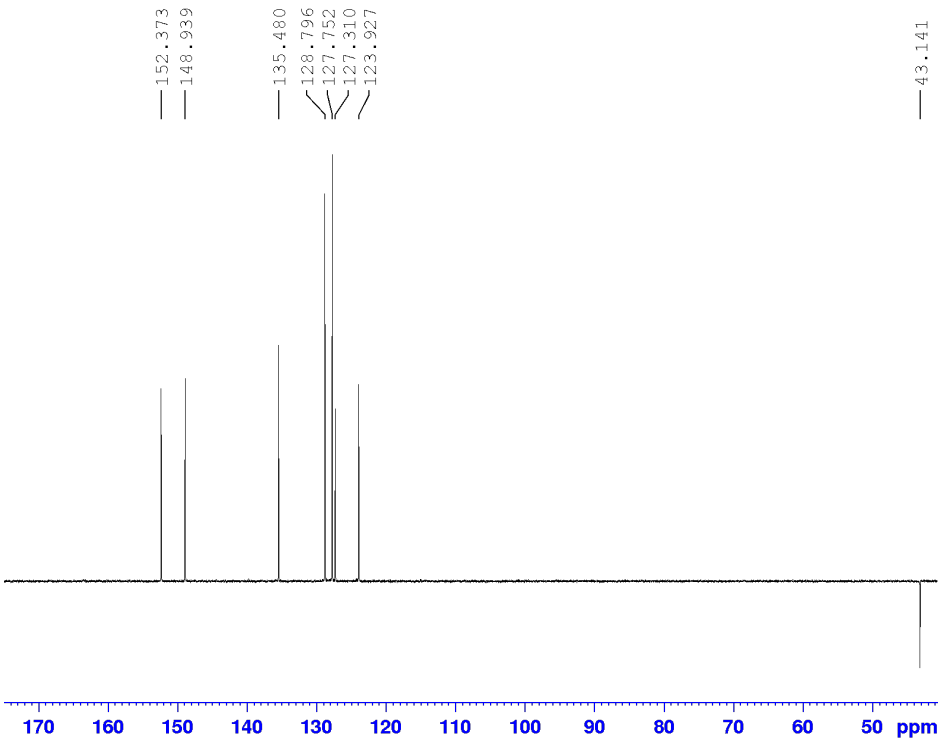

Figure A-3. DEPT-135 spectrum of N-benzyl nicotinamide in DMSO-d_6 at 100 MHz.

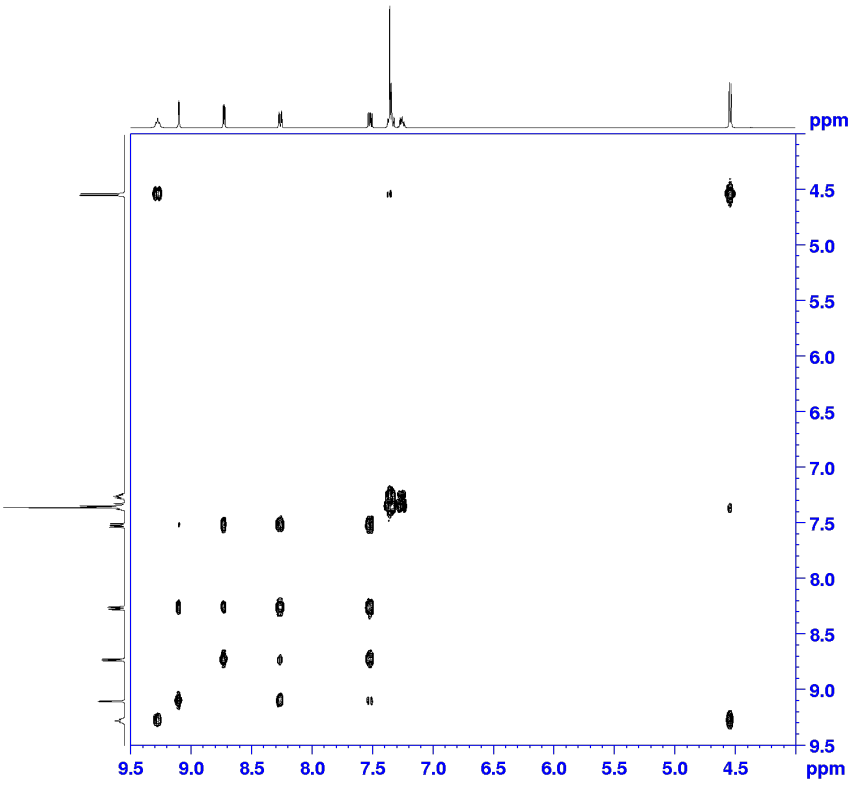

Figure A-4. 2D COSY ^{1}H-^{1}H NMR spectrum of N-benzyl nicotinamide in DMSO-d_6 at 400 MHz.

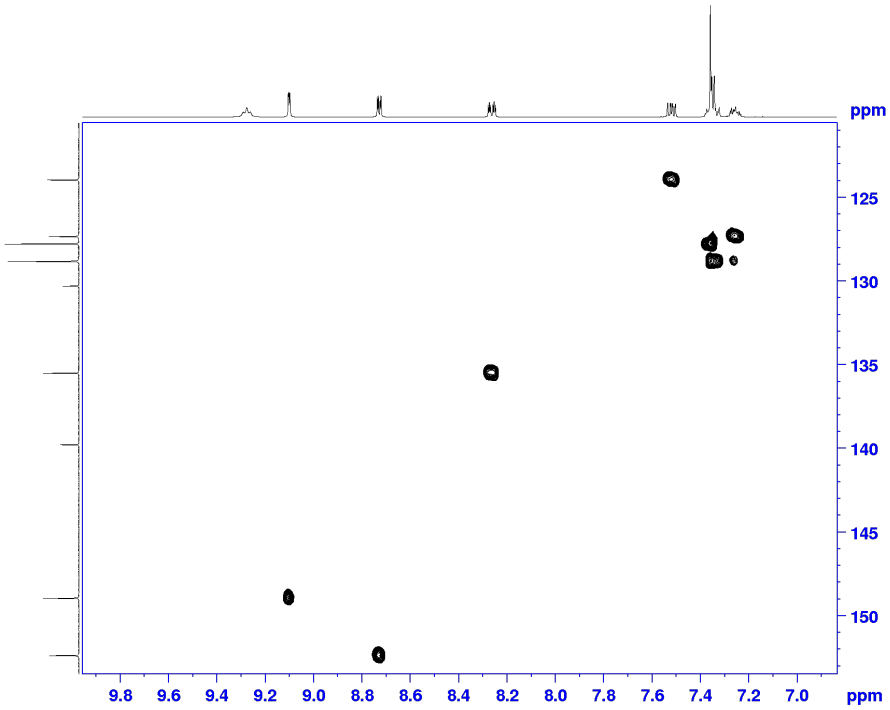

Figure A-5. 2D HSQC ^{1}H-^{13}C NMR spectrum of N-benzyl nicotinamide in DMSO-d_6.

9.2. NMR spectra of nicotinic acid hydrazide (NAH)

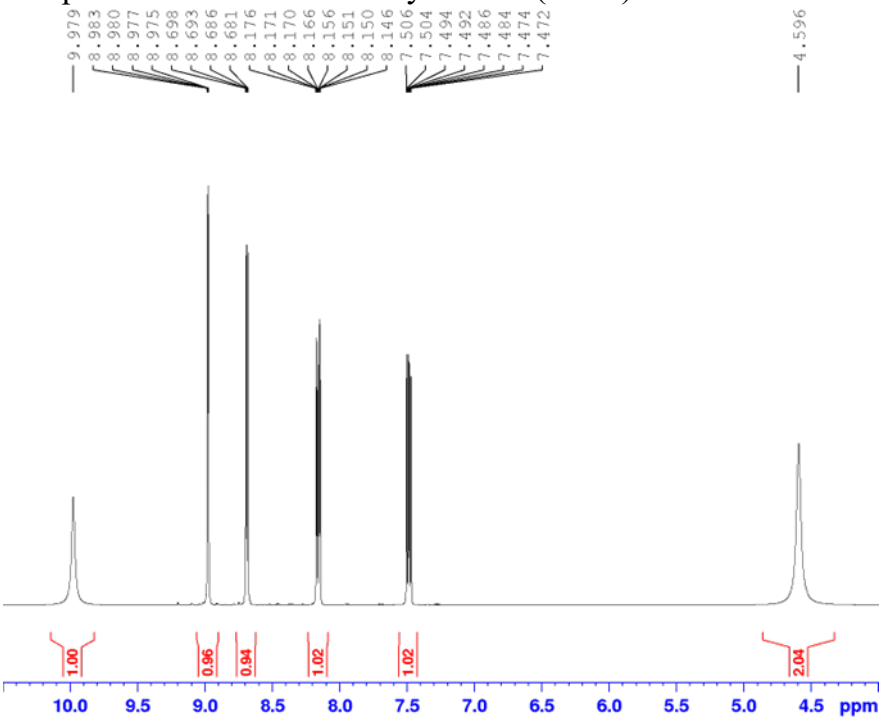

Figure A-6. ^{1}H NMR spectrum of nicotinic acid hydrazide in DMSO-d_6 at 400 MHz.

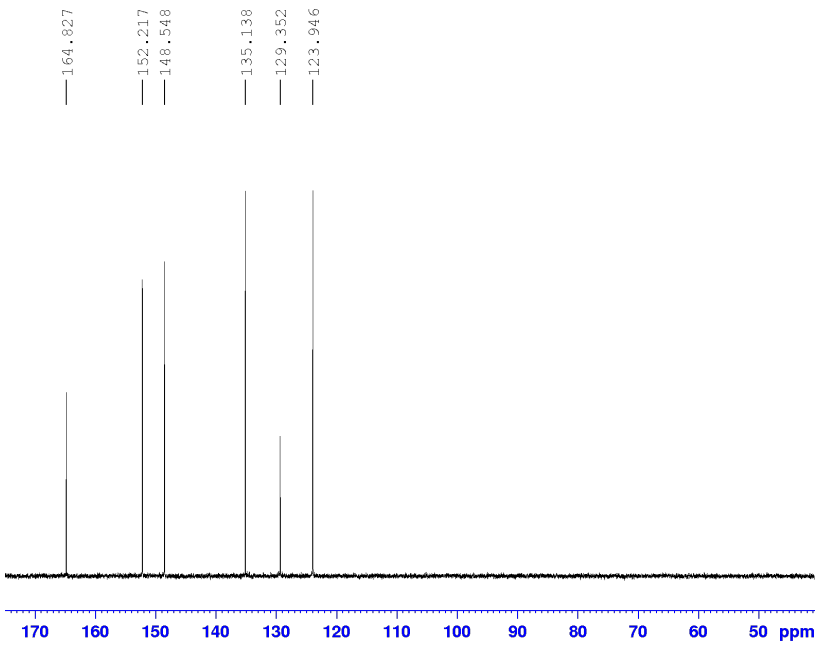

Figure A-7. ^{13}C NMR spectrum of nicotinic acid hydrazide in DMSO-d_6 at 100 MHz.

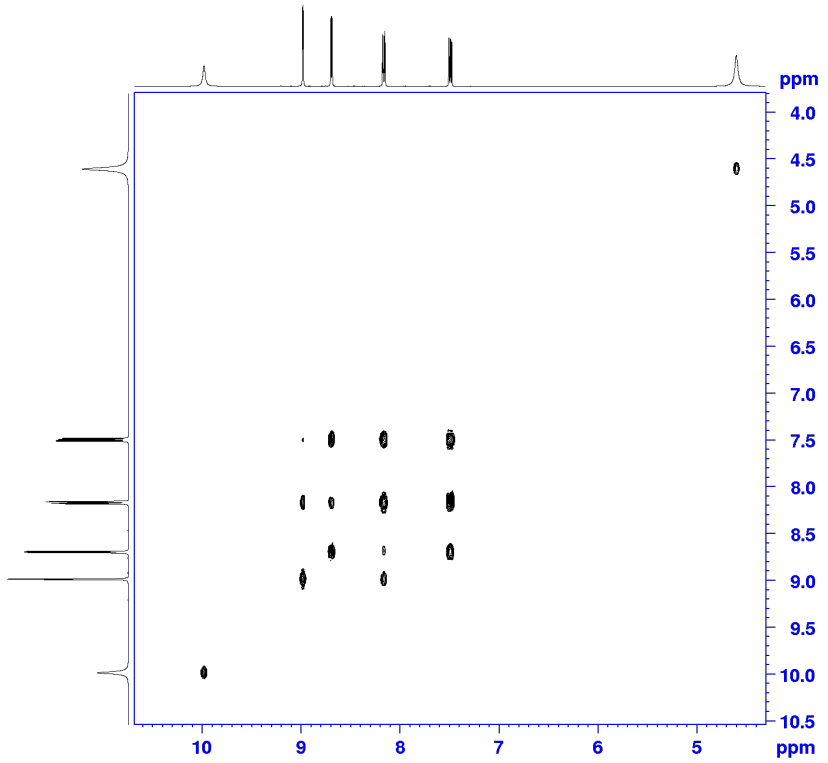

Figure A-8. 2D COSY ^{1}H-^{1}H NMR spectrum of nicotinic acid hydrazide in DMSO-d_6 at 400 MHz.

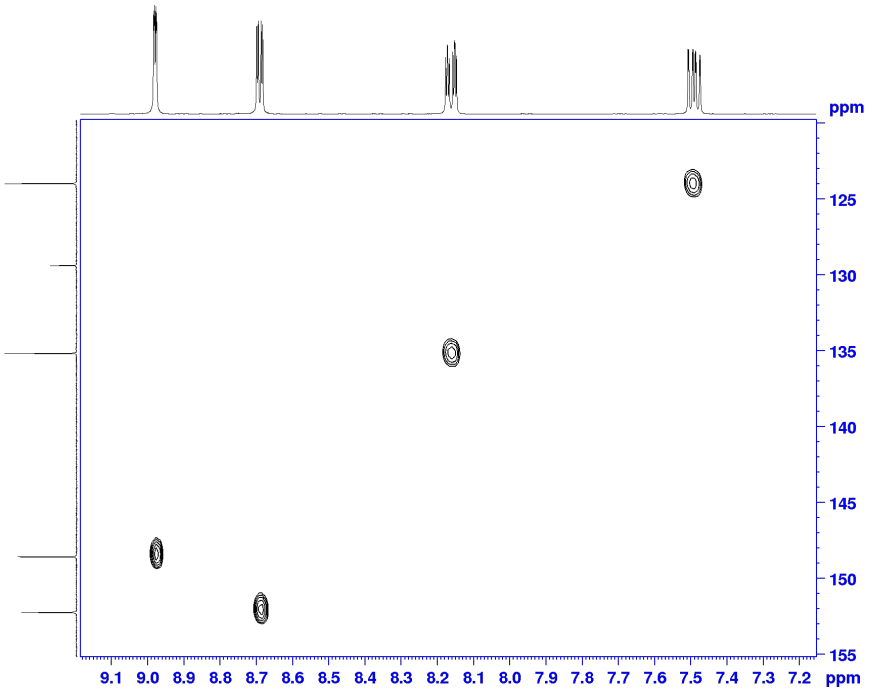

Figure A-9. 2D HSQC ^{1}H-^{13}C NMR of nicotinic acid hydrazide in DMSO-d_6.

9.3. SABRE hyperpolarized ^{1}H NMR spectra of pyridine.

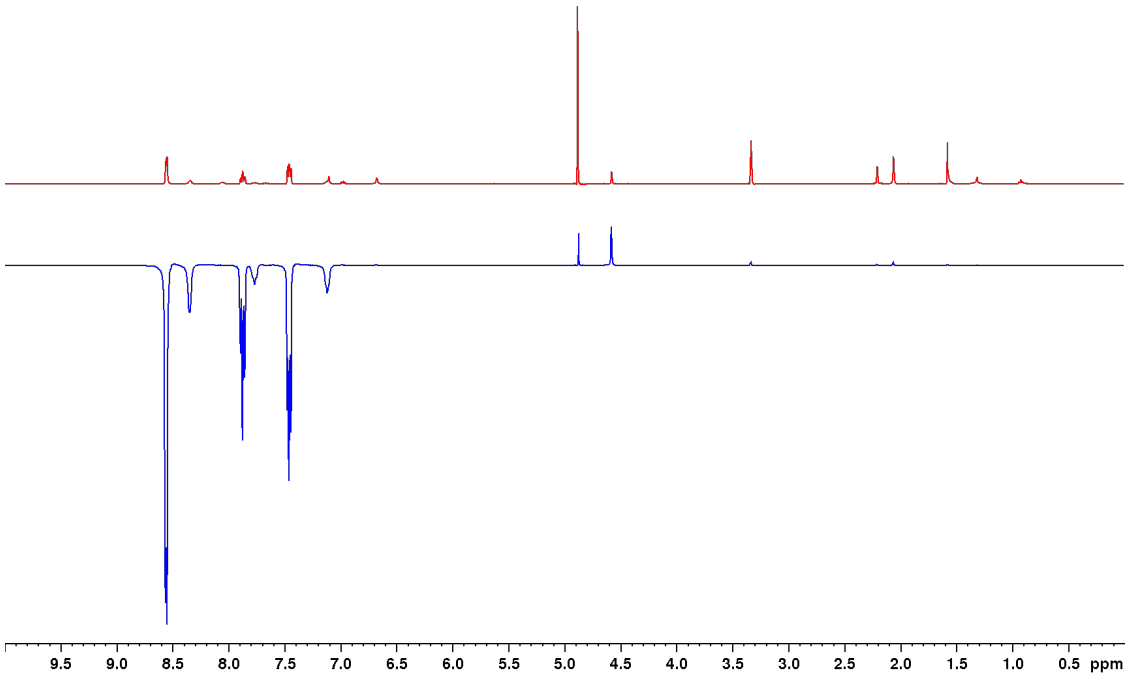

Figure A-10. ^{1}H NMR spectra of thermal (x16) and SABRE hyperpolarization of pyridine.

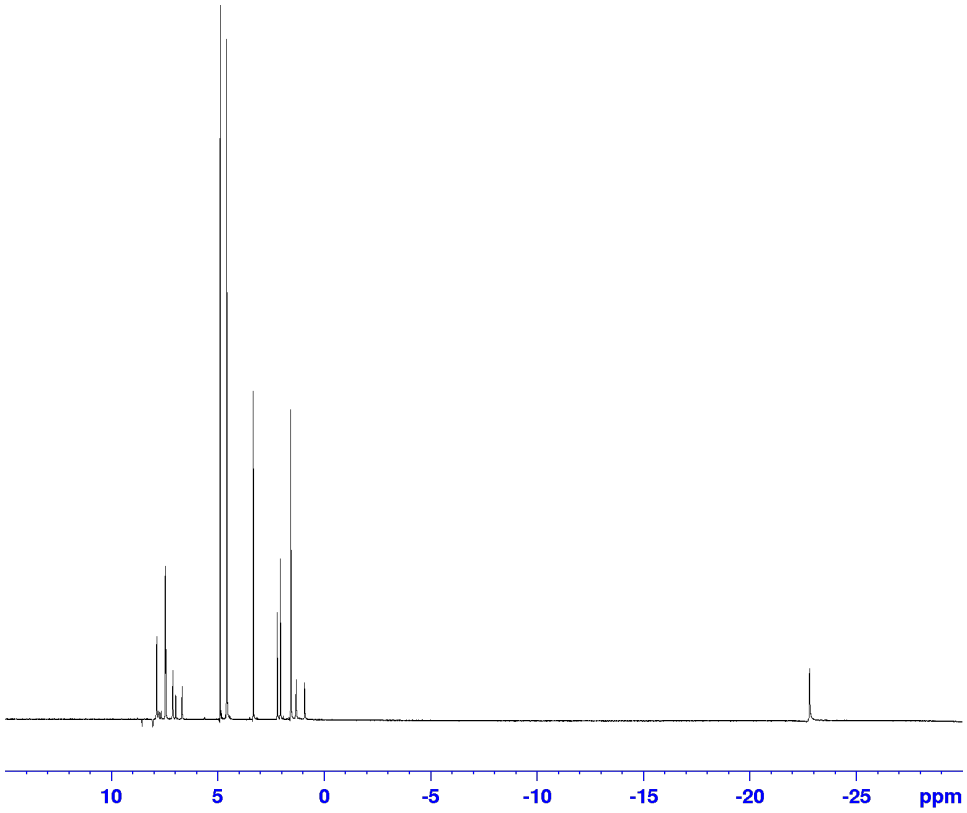

Figure A-11. ^{1}H NMR spectra of pyridine with PASADENA experiment.

9.4. SABRE hyperpolarized ^{1}H NMR spectra of nicotinamide.

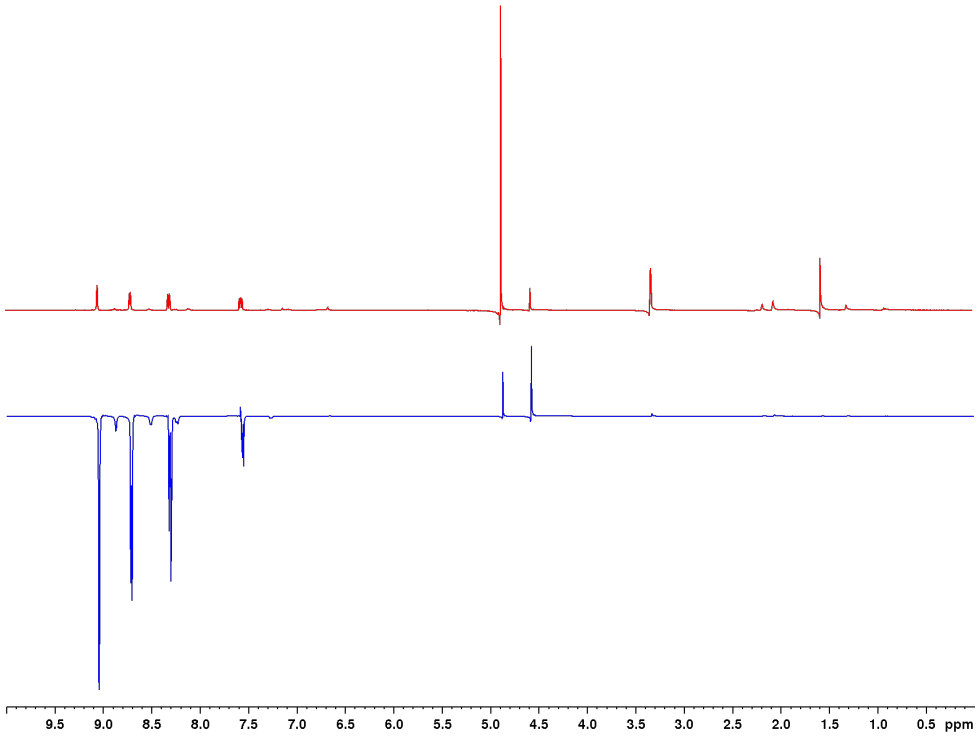

Figure A-12. ^{1}H NMR spectra of thermal (x16) and SABRE hyperpolarization of nicotinamide.

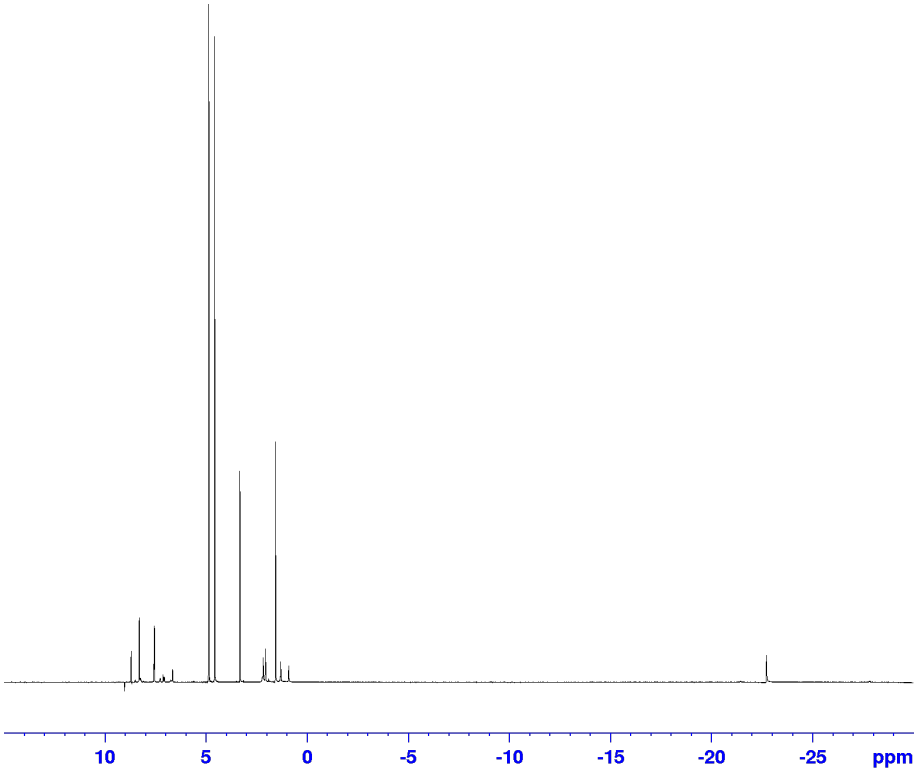

Figure A-13. ^{1}H NMR spectra of nicotinamide with PASADENA experiment.

9.5. SABRE hyperpolarized ^{1}H NMR spectra of N-benzyl nicotinamide.

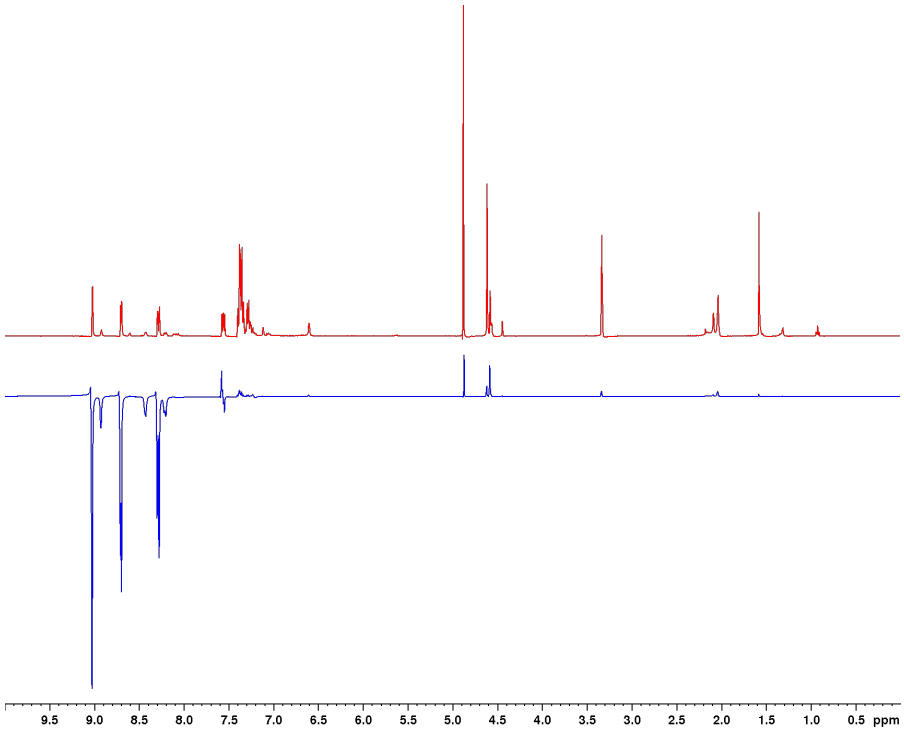

Figure A-14. ^{1}H NMR spectra of thermal (x16) and SABRE hyperpolarization of N-benzyl nicotinamide.

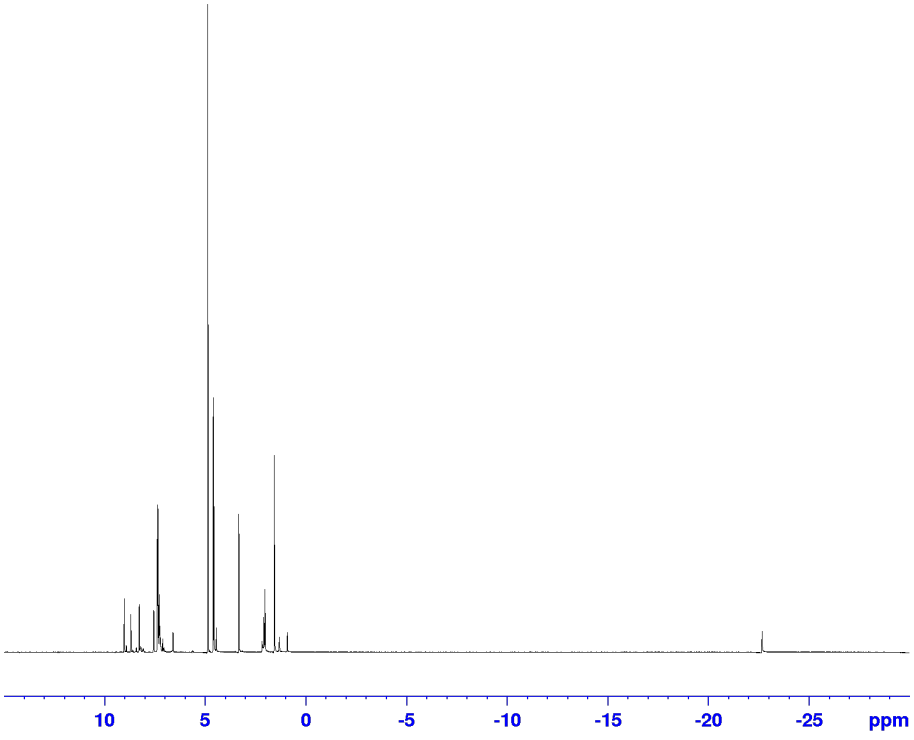

Figure A-15. ^{1}H NMR spectra of N-benzyl nicotinamide with PASADENA experiment.

9.6. SABRE hyperpolarized ^{1}H NMR spectra of nicotinic acid hydrazide.

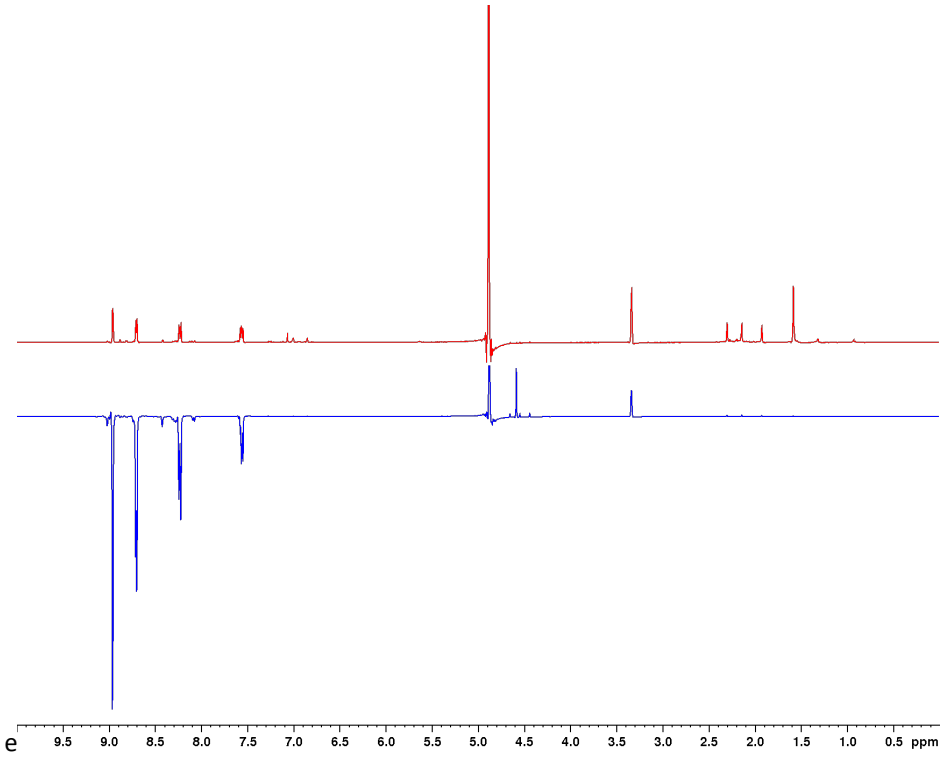

Figure A-16. ^{1}H NMR spectra of thermal (x16) and SABRE hyperpolarization of nicotinic acid hydrazide.

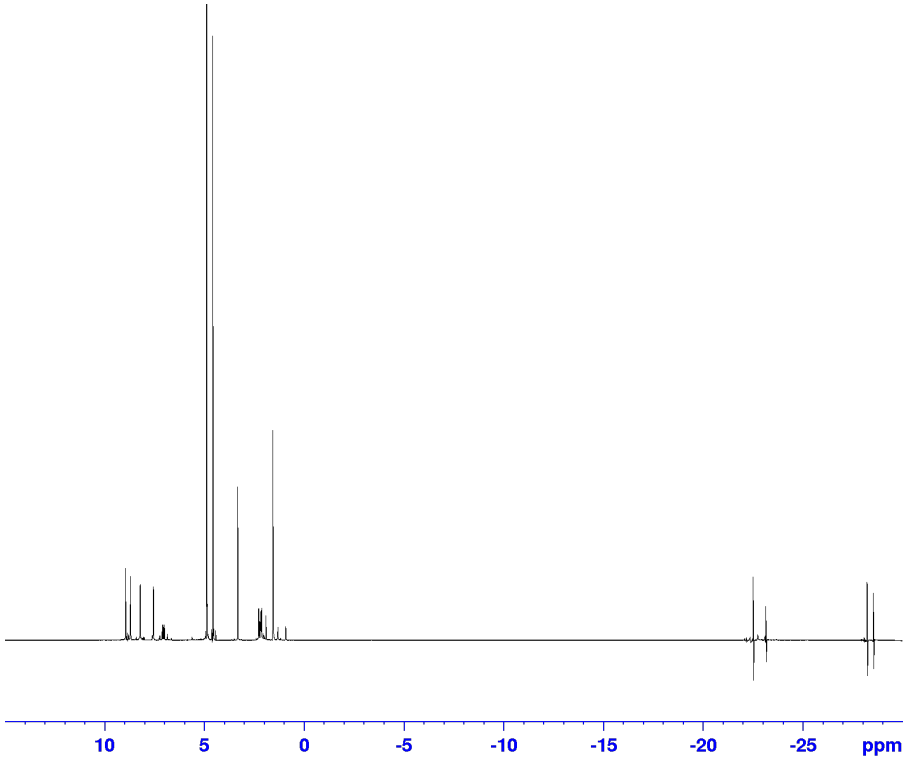

Figure A-17. ^{1}H NMR spectra of nicotinic acid hydrazide with PASADENA experiment.