

Supporting Information

Group 13 ion coordination to pyridyl breaks the reduction potential vs hydricity scaling relationship for dihydropyridinates.

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5. References

Experimental Section

Preparation of Compounds. All manipulations were carried out using standard Schlenk or glovebox techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and were degassed and stored over activated 3 Å molecular sieves prior to use. 2,6-bis(5-isobutyl-1-isopropyl-1H-pyrazol-3-yl)pyridine (pz₂P),¹ 4-AlCl₄,¹ and 1,3-dimethyl-1H-benzimidazolium iodide,² were synthesized according to literature methods. All other reagents were purchased from commercial vendors and used without further purification.

(pz₂^HP)-GaCl₂ (1H). 25 mg (0.059 mmol) compound **2H** was dissolved in 500 μL dry CD₃CN and transferred to a J-Young tube in a dry N₂ filled glovebox. 49.3 mg (0.065 mmol) of **1-GaCl₄** was dissolved in 500 μL CD₃CN and transferred to the J-young tube with compound **2H**. After letting the reaction sit undisturbed for 3 days, purple crystals of **1H** grew around the walls of the J-Young tube which were suitable for X-ray diffraction. The CD₃CN solution was decanted, and the crystals were washed with Et₂O brought up in benzene and lyophilized to give 14.9 mg (56% yield) of **1H** as a pink powder. ¹H NMR (600 MHz, C₆D₆): δ 5.92 (s, 2H), 5.50 (hept., *J* = 7.2 Hz, 2H), 4.94 (t, *J* = 3.5 Hz, 2H), 3.48 (t, *J* = 3.5 Hz, 2H), 2.07 (d, *J* = 7.2 Hz, 4H), 1.53 (m, 2H), 1.34 (d, *J* = 7.2 Hz, 12H), 0.65 (d, *J* = 6.6 Hz, 12H). ¹³C NMR (151 MHz, C₆D₆): δ 146.38, 146.02, 133.91, 100.15, 94.70, 54.96, 35.39, 28.17, 25.14, 22.45, 21.77. Anal Calcd for C₂₅H₃₈Cl₂N₅Ga: C, 54.67; H, 6.97; N, 12.75 Found: C, 54.39; H, 6.69; N, 12.36.

(pz₂^HP)CH₃ (2H). To a solution of 50 mg (0.088 mmol) **2-OTf** in anhydrous THF added 114 μL (0.114 mmol) of a 1 M solution of LiEt₃BH in THF. The solution turned from colorless to deep yellow quickly following the addition of the LiEt₃BH. The reaction solution was concentrated to dryness after 5 minutes. The concentrate was dissolved in benzene, filtered over celite and the solvent was removed *in vacuo*. The resulting oil was dissolved in hexanes, filtered and dried *in vacuo* to yield **2H** as a yellow oil (10 mg, 27 % yield). ¹H NMR (600 MHz, C₆D₆): δ 6.20 (s, 2H), 5.62 (m, 2H), 3.98 (hept, *J* = 6.7 Hz, 2H), 3.27 (m, 3H), 3.24 (m, 2H), 2.15 (d, *J* = 7.3 Hz, 4H), 1.65 (hept, *J* = 7.0 Hz, 2H), 1.34 (d, *J* = 6.5 Hz, 12H), 0.80 (d, *J* = 6.5 Hz, 12H). ¹³C NMR (151 MHz, C₆D₆): δ 148.47, 140.16, 140.06, 103.84, 48.96z, 38.52, 34.21, 31.56, 28.24, 24.31, 22.59, 22.14. (ESI-HRMS) *m/z*: [M+H]⁺. Calcd. for C₂₆H₄₁N₅ 424.3435, Found 424.3420.

(pz₂^{Pr}HP)-GaCl₂ (3H). A solution of 500 mg (1.23 mmol) pz₂P in THF was added 56.5 mg (2.43 mmol) of sodium and stirred until all the sodium was consumed, producing a deep red solution. 216 mg (1.23 mmol) of GaCl₃ in THF was then added dropwise and stirred an additional two hours during which time a brown/purple solution was produced. THF was removed *in vacuo* and the resulting powder dissolved in diethyl ether, filtered over celite, and concentrated (156 mg, 22 %). Crystals suitable for X-ray diffraction were grown as colorless plates from a saturated hexane solution. ¹H NMR (600 MHz, C₆D₆): δ 5.97 (s, 2H), 5.48 (hept, *J* = 7.3 Hz, 2H), 5.06 (d, *J* = 3.8 Hz, 2H), 3.52 (q, *J* = 4.0 Hz, 1H), 2.08 (d, *J* = 7.2 Hz, 4H), 1.76 (m, 1H), 1.53 (mr, 2H), 1.32 (m, 12H), 1.12 (d, *J* = 6.9 Hz, 6H), 0.64 (m, 12H). ¹³C NMR (151 MHz, C₆D₆): δ: 146.45, 146.14, 122.96, 100.27, 97.36, 54.97, 42.03, 36.74, 35.42, 28.20, 22.51, 21.79, 21.76, 19.30. Anal Calcd for C₂₈H₄₄Cl₂N₅Ga: C, 56.87; H, 7.5; N, 11.84 Found: C, 56.66; H, 7.48; N, 11.95.

Reactions to determine equilibria. Hydride transfer equilibria between 4-AlCl₄ or 1-GaCl₄ with **2H** were monitored by ¹H NMR spectroscopy in C₆D₆. Hydride transfer equilibria between **2H** and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole as well as **2⁺**-OTf and 1,3-dimethyl-2-phenyl-2,3-

dihydro-1*H*-benzo[d]imidazole were monitored by ¹H NMR spectroscopy in CD₃CN. Diagnostic signals for each species in solution were referenced to an internal standard of trimethoxy benzene. Sample preparation for each experiment is outlined below.

Reaction of 2H with 1-GaCl₄. Reaction solution was prepared by weighing 5 mg (0.012 mmol, 1 eq.) of 2H in a 20 mL vial and dissolving in 400 μL C₆D₆ and transferring to a NMR tube. To a separate vial was weighed first 8.9 mg (0.012 mmol, 1 eq.) 1-GaCl₄, then 7.3 mg (0.040 mmol, 3.3 eq.) trimethoxy benzene was added to vial. The solid 1-GaCl₄ and trimethoxy benzene were brought up in 400 μL C₆D₆ and transferred to NMR tube with 2H. The vial containing residual 1-GaCl₄ and trimethoxy benzene was then washed with an additional 100 μL C₆D₆ and transferred to the NMR tube.

Reaction of 2H with 4-AlCl₄. Reaction solution was prepared by weighing 5 mg (0.01 mmol, 1 eq.) of 2H in a 20 mL vial and dissolving in 400 μL C₆D₆ and transferring to a NMR tube. To a separate vial was weighed first 7.9 mg (0.01 mmol, 1 eq.) 4-AlCl₄, then 2.0 mg (0.01 mmol, 1 eq.) trimethoxy benzene was added to vial. The solid 4-AlCl₄ and trimethoxy benzene were brought up in 300 μL C₆D₆ and transferred to the NMR tube with 2H.

Reaction of 2-OTf and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole. Reaction solution was prepared by weighing 13 mg (0.02 mmol, 1 eq.) of 2-OTf in a 20 mL vial and dissolving in 500 μL CD₃CN and transferring to a NMR tube. To a separate vial was weighed first 5.4 mg (0.02 mmol, 1 eq.) 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole, then 4.0 mg (0.02 mmol, 1 eq.) trimethoxy benzene was added to vial. The solid 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole and trimethoxy benzene were brought up in 500 μL CD₃CN and transferred to the NMR tube with 2-OTf.

Reaction of 2H and 1,3-dimethyl-1*H*-benzimidazolium iodide. Reaction solution was prepared by weighing 10 mg (0.024 mmol, 1 eq.) of 2H in a 20 mL vial and dissolving in 500 μL CD₃CN and transferring to a NMR tube. To a separate vial was weighed first 6.6 mg (0.024 mmol, 1 eq.) 1,3-dimethyl-1*H*-benzimidazolium iodide, then 4.0 mg (0.024 mmol, 1 eq.) trimethoxy benzene was added to vial. The solid 1,3-dimethyl-1*H*-benzimidazolium iodide and trimethoxy benzene were brought up in 500 μL CD₃CN and transferred to the NMR tube with 2H.

X-ray Structure Determinations. X-ray diffraction studies were carried out on a Bruker SMART APEX Duo diffractometer equipped with a CCD detector.³ Measurements were carried out at -175 °C using Mo Kα (0.71073 Å) and Cu Kα (1.54178 Å) radiation. Crystals were mounted on a Kapton loop with paratone-N oil. The initial lattice parameters were obtained from least-squares analysis of more than 100 centered reflections; these parameters were later refined against all data. Data were integrated and corrected for Lorentz polarization effects using SAINT⁴ and were corrected for absorption effects using SADABS2.3.⁵ Space-group assignments were based on systematic absences, E statistics, and the successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps and were refined against all data using the SHELXTL 2014/7 software package.⁶ Thermal parameters for all non-H atoms were refined anisotropically. H atoms, where added, were assigned to ideal positions, and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached C atom (1.5 times for methyl H atoms).

Other Physical Measurements. ¹H and ¹³C NMR spectra were recorded at ambient temperature using a Varian 600 MHz spectrometer. Chemical shifts were referenced to a residual solvent. Elemental analyses were performed by the Microanalytical Laboratory at The University of California, Berkeley. For

HRMS analysis, samples were analyzed by flow-injection analysis into a Thermo Fisher Scientific LTQ Orbitrap XL (San Jose, CA) operated in the centroided mode. Samples were injected into a mixture of 50% MeOH and 0.1% Formic Acid/H₂O at a flow of 200 ul/min. Source parameters were 5kV spray voltage, capillary temperature of 275°C and sheath gas setting of 20. Spectral data were acquired at a resolution setting of 100,000 FWHM with the lockmass feature which typically results in a mass accuracy < 2 ppm.

2. Calculations and Equations

Calculation S1. Determination of species concentration during equilibrium reactions monitored by ¹H NMR.

Diagnostic signals for all peaks were integrated over a constant ppm range for each ¹H NMR spectrum recorded. Integration of the O-CH₃ signal from the trimethoxy benzene standard was set to 100.00 for each spectrum and concentrations of diagnostic signals were calculated from the peak integration relative to internal standard. Using equation S1

$$[X] = \frac{I_X * (9/H_X)}{100} * [Std.] \quad (\text{equation S1})$$

where [X] is the concentration of the species of interest, I_X is the raw integration of the species of interest, H_X is the number of protons corresponding to the signal of interest and [Std.] is the concentration of internal standard.

Calculation S2.

Equilibrium constants were calculated based off the concentration of each species at equilibrium determined by ¹H NMR (Figure 2).

$$K = \frac{[1 - GaCl_4][2H]}{[1H][2^+]} \quad (\text{equation S2})$$

Equilibrium concentrations were taken from empirical data at 94 hours for the reaction of **1**-GaCl₄ and **2H** (K₁) and at 94 hours for reaction of **4**-AlCl₄ and **2H** (K₂).

Equilibrium constant for the reaction of **1**-GaCl₄ with **2H** (K₁).

$$K_1 = \frac{[1 - GaCl_4][2H]}{[1H][2]} = \frac{4.00 * 3.13}{1.86 * 8.13} = 0.83$$

Equilibrium constant for the reaction of **4**-AlCl₄ with **2H** (K₂).

$$K_2 = \frac{[4 - AlCl_4][2H]}{[4H][2]} = \frac{9.328 * 0.912}{4.401 * 8.119} = 0.24$$

Calculation S3. Hydricity difference between two species in equilibrium.

$$\Delta G_{H-} = -RT \ln(K) \quad (\text{Equation S3})$$

Calculated difference in hydricity between **2H** and **1-GaCl₄**.

$$\Delta G_{H-1} = + 0.1 \pm 0.1 \text{ (kcal mol}^{-1}\text{)}$$

Calculated difference in hydricity between **2H** and **4-AlCl₄**.

$$\Delta G_{H-2} = + 0.8 \pm 0.1 \text{ (kcal mol}^{-1}\text{)}$$

3. Tables

Table S1. Crystallographic data for compounds **1H** and **3H**.

	1H ^a	3H ^b
Formula	C ₂₅ H ₃₈ Cl ₂ GaN ₅	C ₂₈ H ₄₄ Cl ₂ GaN ₅
Crystal size	0.612 × 0.251 × 0.134	0.385 × 0.174 × 0.066
Formula weight, g mol ⁻¹	549.22	591.30
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	13.1613(11)	12.1606(3)
<i>b</i> , Å	13.2286(11)	15.1860(4)
<i>c</i> , Å	15.7223(13)	16.3042(4)
<i>α</i> , deg	90	90
<i>β</i> , deg	93.540(2)	90.4970(13)
<i>γ</i> , deg	90	90
<i>V</i> , Å ³	2732.1(4)	3010.80(13)
<i>Z</i>	4	4
<i>T</i> , K	100(2)	100(2)
<i>ρ</i> , calcd, g cm ⁻³	1.335	1.304
Refl. Collected / 2 θ_{\max}	32223 / 61.46	16451 / 144.74
Unique refl. / <i>I</i> > 2 σ (<i>I</i>)	8344 / 7871	5910 / 5063
No. Parameters / restraints	450 / 0	375 / 57
λ , Å/ μ K α , cm ⁻¹	0.71073	1.54178
R ₁ /GOF	0.0203 / 1.057	0.0399 / 1.038
wR ₂ (<i>I</i> > 2 σ (<i>I</i>)) ^b	0.0530	0.1048
Residual density, e Å ⁻³	0.421 / -0.249	0.877 / -0.437

^a Obtained with graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. ^b Obtained with graphite-monochromated Cu K α (λ = 1.54178 Å) radiation ^c $R_1 = \sum || F_o | - F_c | / \sum | F_o |$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

Table S2. Selected bond length and angles for **1H** and **3H**.

	1H	3H
N _{pz} -C _{pz}	1.340(1)	1.344(3)
C _{pz} -C _o	1.463(1)	1.451(9)
N _{py} -C _o	1.386(1)	1.405(9)
C _o -C _m	1.344(1)	1.37(1)
C _m -C _{py}	1.508(1)	1.505(8)
C _{py} -C _{m'}	1.511(1)	1.509(7)
C _{m'} -C _{o'}	1.346(1)	1.29(2)
N _{py} -C _{o'}	1.391(1)	1.46(2)
C _{o'} -C _{pz'}	1.464(1)	1.46(2)
N _{pz'} -C _{pz'}	1.340(1)	1.339(3)
N _{py} -X	1.8991(9)	1.899(2)
τ ₅ ⁷	0.76	0.76

Table S3. Selected pyridine bond metrics for **4H**,¹ **1H**, and **3H**. See [Figure 1](#) for atom labelling Scheme.

	N _{py} -C _o	C _o -C _m	C _m -C _p	C _p -C _{m'}	C _{m'} -C _{o'}	C _{o'} -N _{py}	N _{py} -E
4H	1.3894(19)	1.333(2)	1.509(2)	1.511(2)	1.338(2)	1.3922(19)	1.869(1)
1H	1.389(1)	1.345(2)	1.511(2)	1.504(2)	1.342(2)	1.386(1)	1.898(1)
3H	1.37(1)	1.29(2)	1.507(7)	1.510(8)	1.38(1)	1.340(9)	1.900(2)

Table S4: Selected bond angles and torsions for, **4H**,¹ **1H**, and **3H**. See [Figure 1](#) for atom labelling Scheme.

	Torsion angle N _{pz} -C _{pz} -C _o -N _{py}	Torsion angle N _{pz'} -C _{pz'} -C _{o'} - N _{py}	N _{pz} -M-N _{pz'} angle	Torsion angle M- N _{py} -C _o -C _{pz}	Torsion angle M- N _{py} -C _{o'} -C _{pz'}	Average of M- N _{py} -C _o -C _{pz} and M-N _{py} -C _{o'} -C _{pz'}	N _{pz} -C _{pz} - N _{pz'} -C _{pz'} torsion
4H	3.18	4.50	156.71(5)	4.60	1.82	3.21	14.25
1H	3.88	5.04	156.47(3)	5.18	1.77	3.48	15.75
3H	1.58	12.22	156.51(8)	7.44	8.95	9.2	14.77

4. Figures

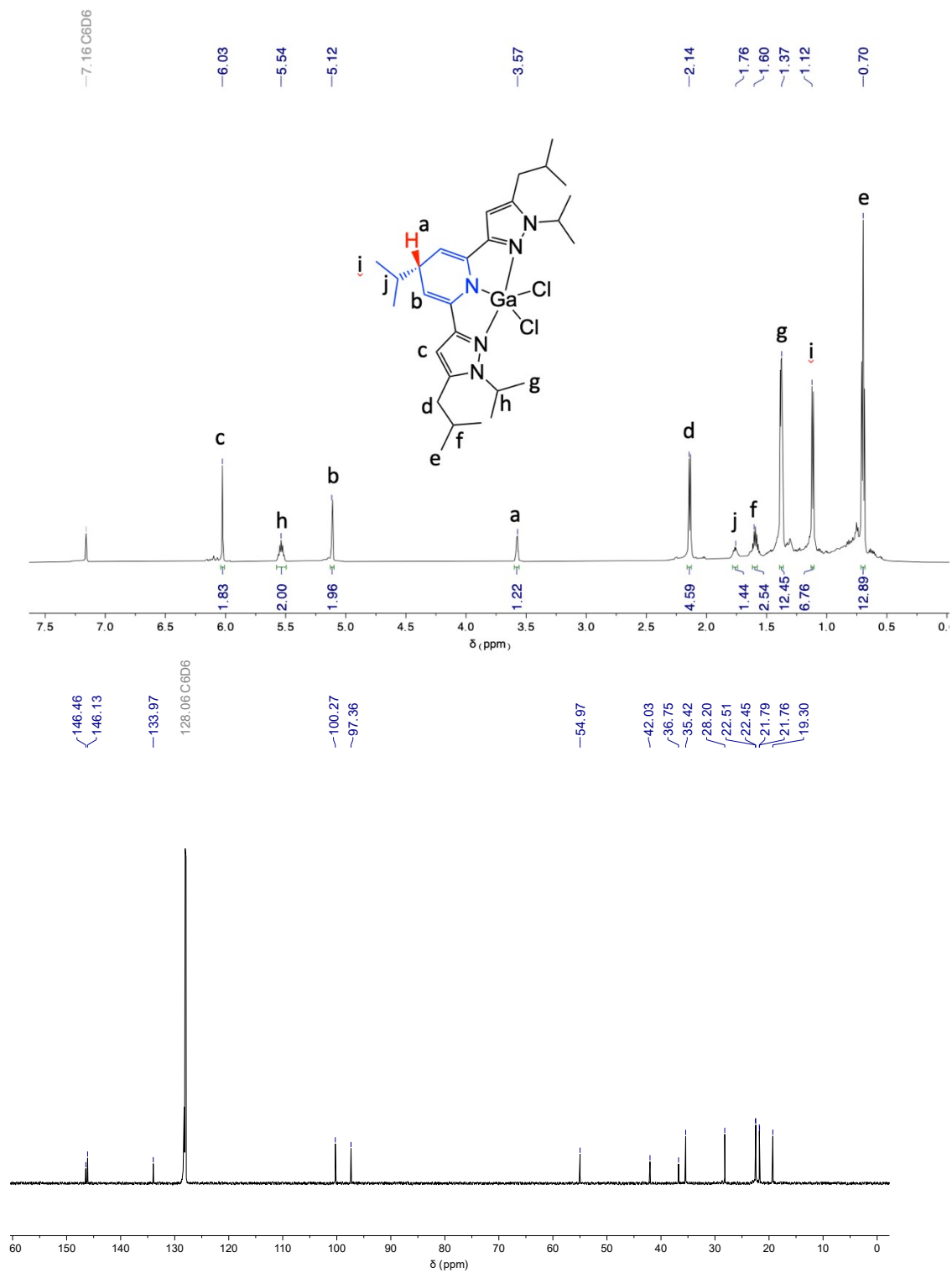


Figure S1. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of **3H** (C_6D_6).

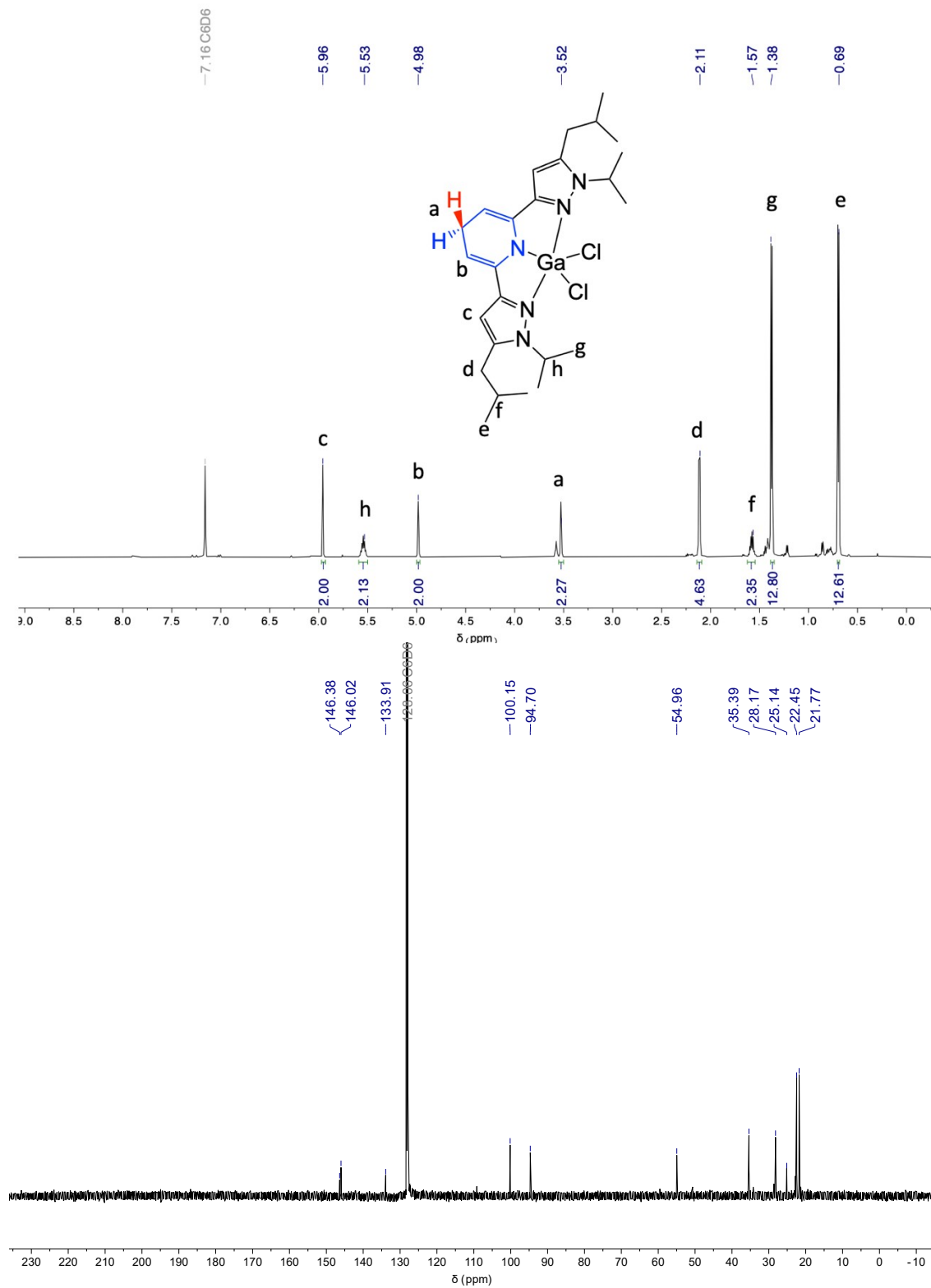


Figure S2. ¹H NMR (top) and ¹³C NMR (bottom) spectra of **1H** (C₆D₆).

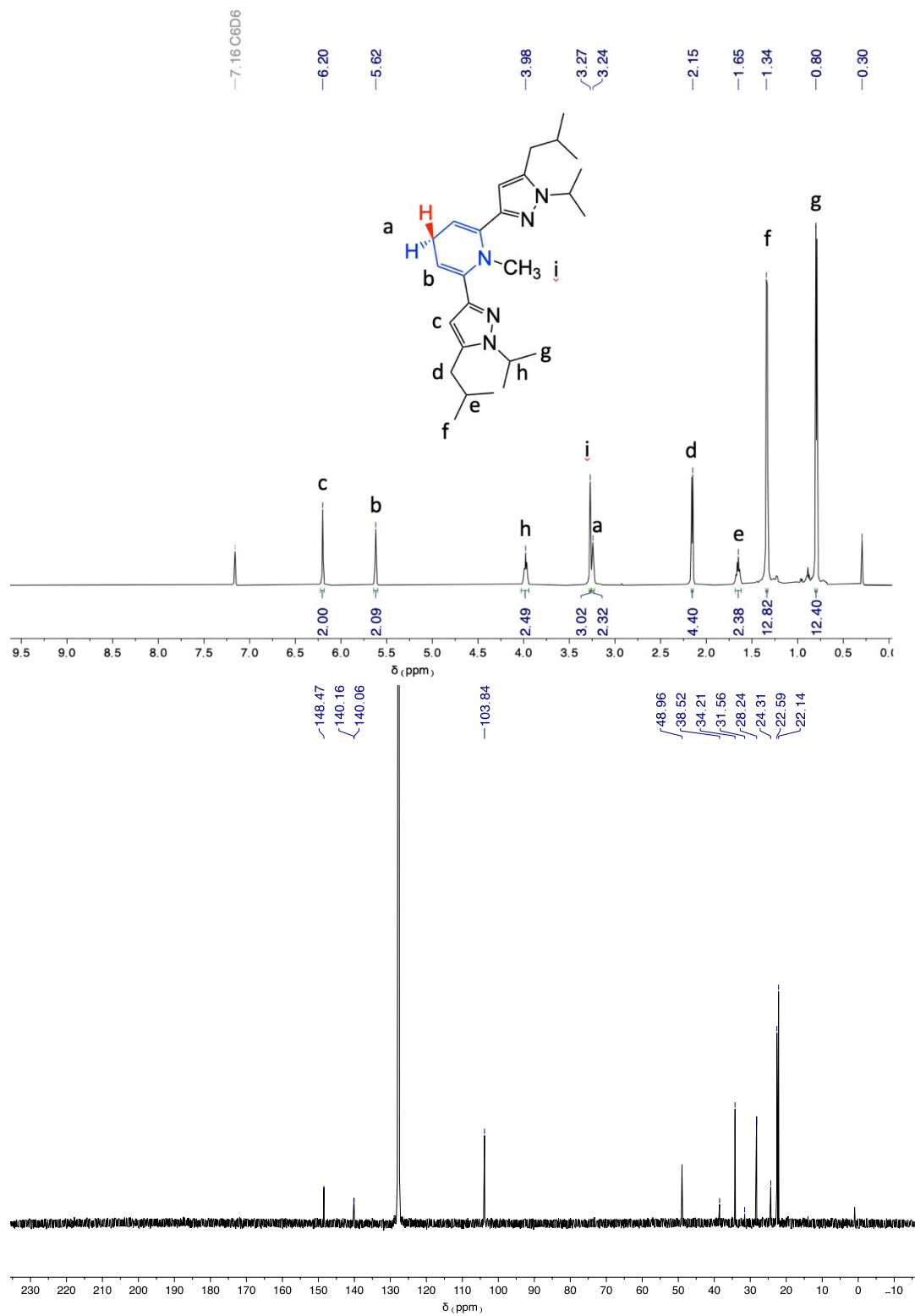


Figure S3. ¹H NMR (top) and ¹³C NMR (bottom) spectra of **2H** (C₆D₆).

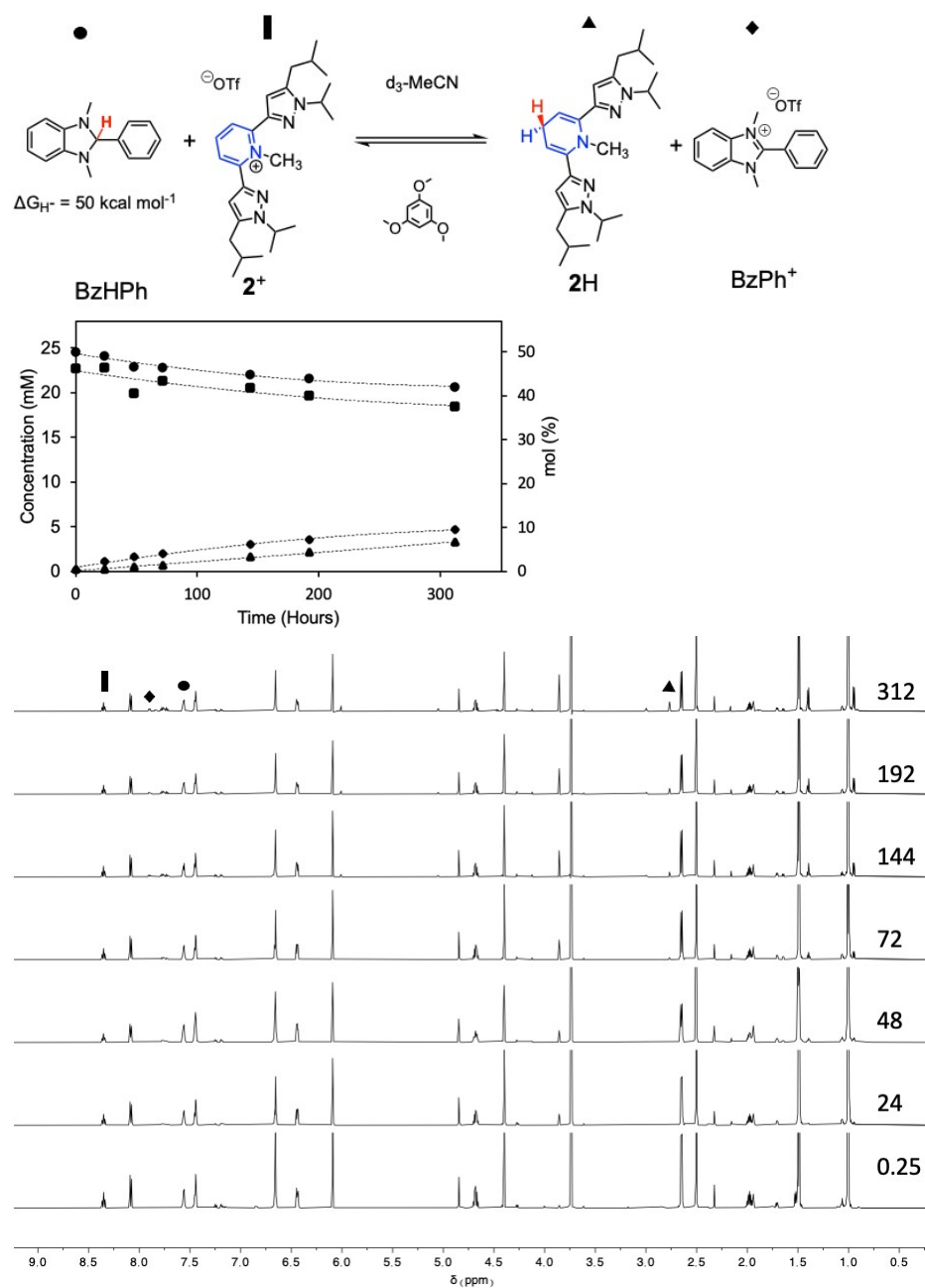


Figure S4: Reaction scheme (top), time dependent ¹H NMR, concentration vs time plots (middle) and spectra of reaction between **2-OTf** and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole at 0.25, 24, 48, 72, 144, 192 and 312 hours in CD₃CN with trimethoxy benzene as an internal standard (bottom). Circles, squares, triangles and diamonds correspond to compounds and their diagnostic ¹H NMR signal for 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (**BzHPh**), compound **2⁺**, **2H** and 1,3-dimethyl-2-phenyl-1H-benzo[d]imidazole-3-ium triflate (**BzPh⁺**) respectively.

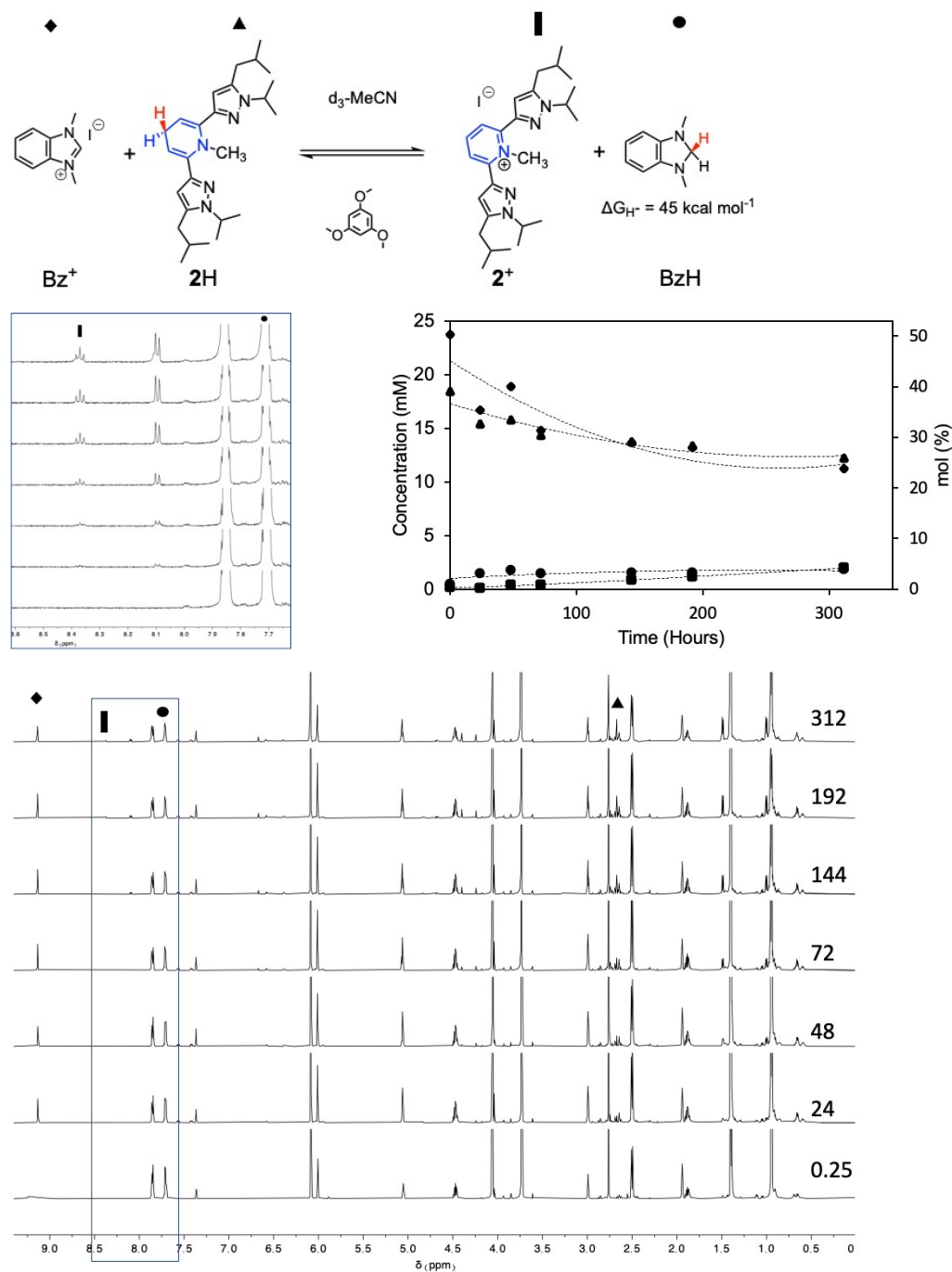


Figure S5: Reaction scheme (top), concentration vs time plots and amplified 1H NMR spectra (middle) and time dependent 1H NMR Spectra of reaction between **2H** and 1,3-dimethyl-1H-benzimidazolium iodide at 0.25, 24, 48, 72, 144, 192 and 312 hours in CD_3CN with trimethoxy benzene as an internal standard (bottom). Blue boxed area corresponds to region highlighted in the middle of the bottom spectra. Diamonds, triangles, squares, and circles correspond to compounds and their diagnostic 1H NMR signal for 1,3-dimethyl-1H-benzimidazolium iodide (Bz^+), compound **2H**, 2^+ and 1,3-dimethyl-2,3-dihydro-1H-benzo[d]imidazole (BzH) respectively.

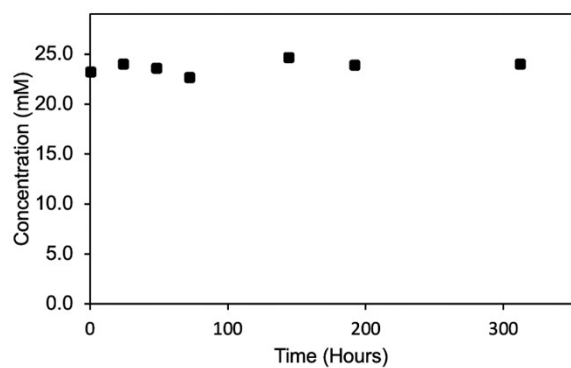
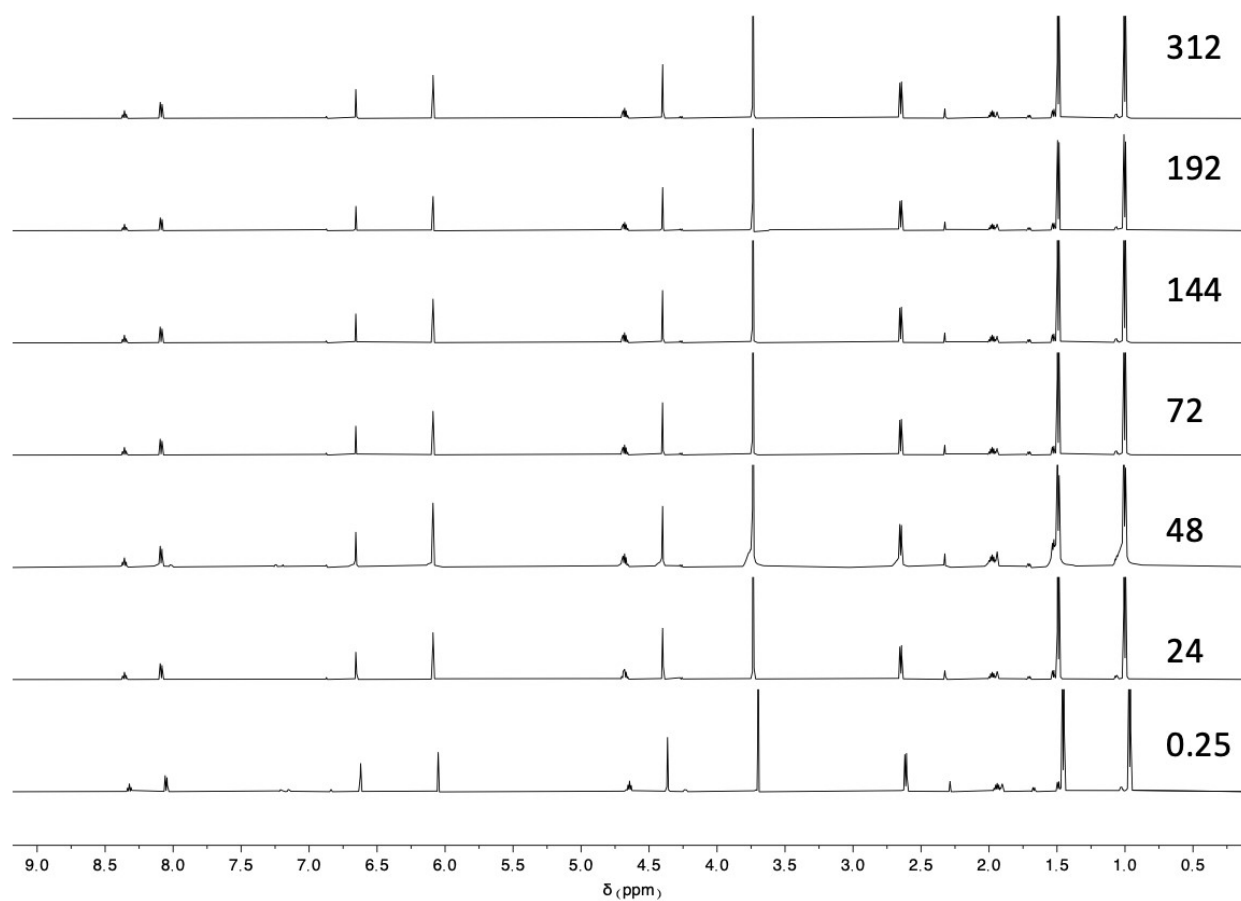


Figure S6: Time dependent ^1H NMR spectra of 2^+ in CD_3CN with trimethoxy benzene as an internal standard recorded at 0.25, 24, 48, 72, 144, 192 and 312 hours (top) and corresponding concentration vs time plot (bottom).

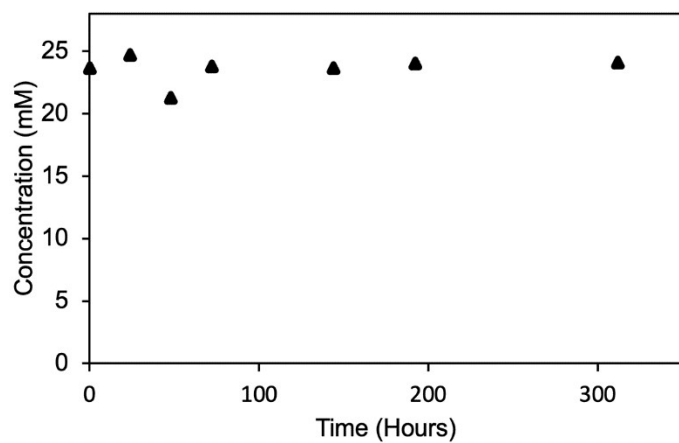
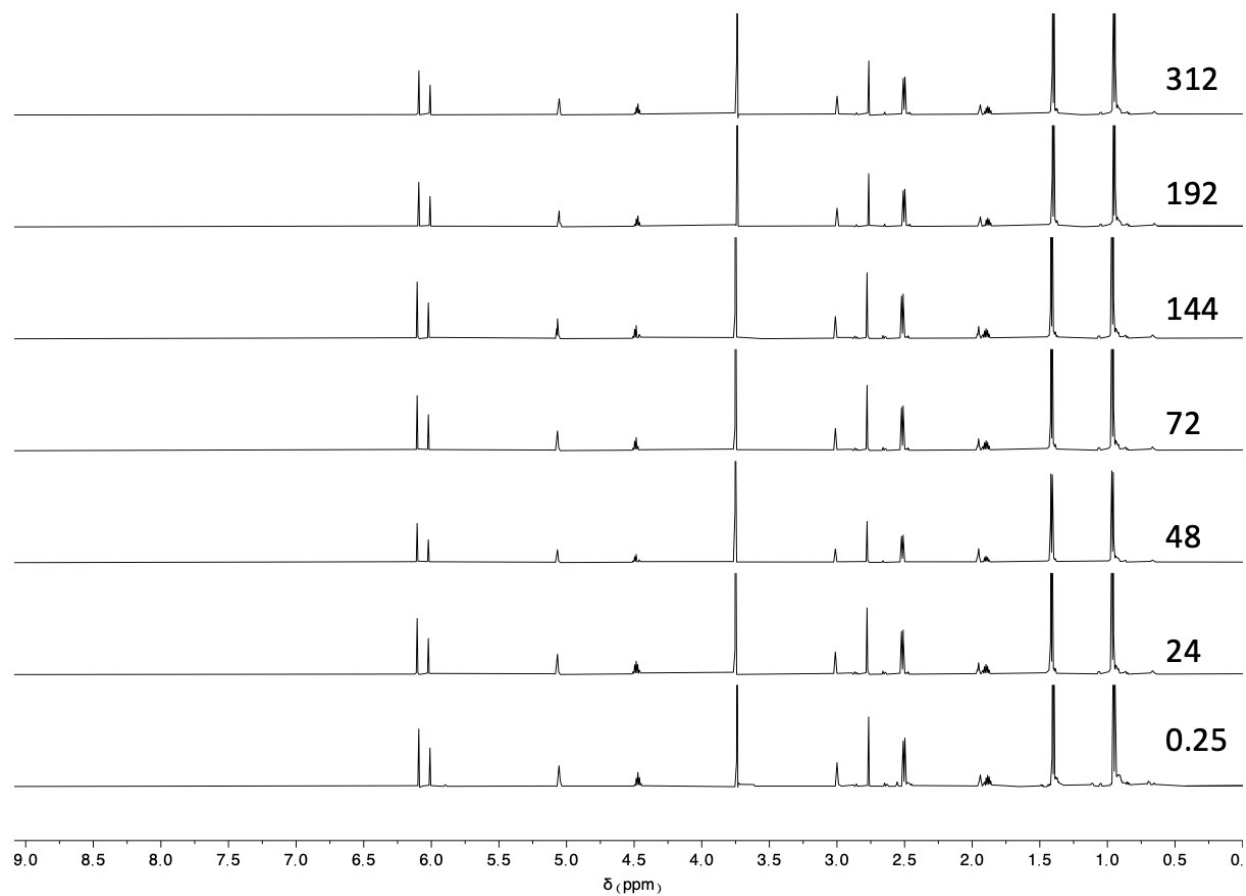


Figure S7: Time dependent ^1H NMR spectra of **2H** in CD_3CN with trimethoxy benzene as an internal standard recorded at 0.25, 24, 48, 72, 144, 192 and 312 hours (top) and corresponding concentration vs time plot (bottom).

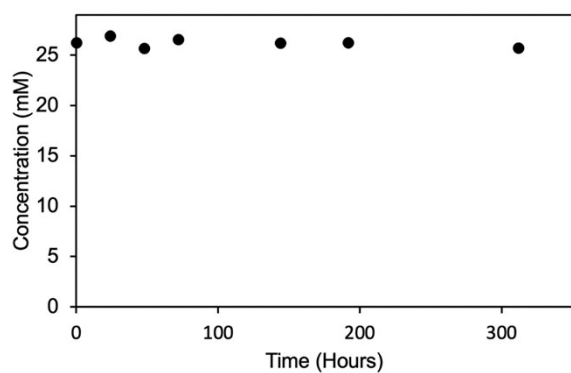
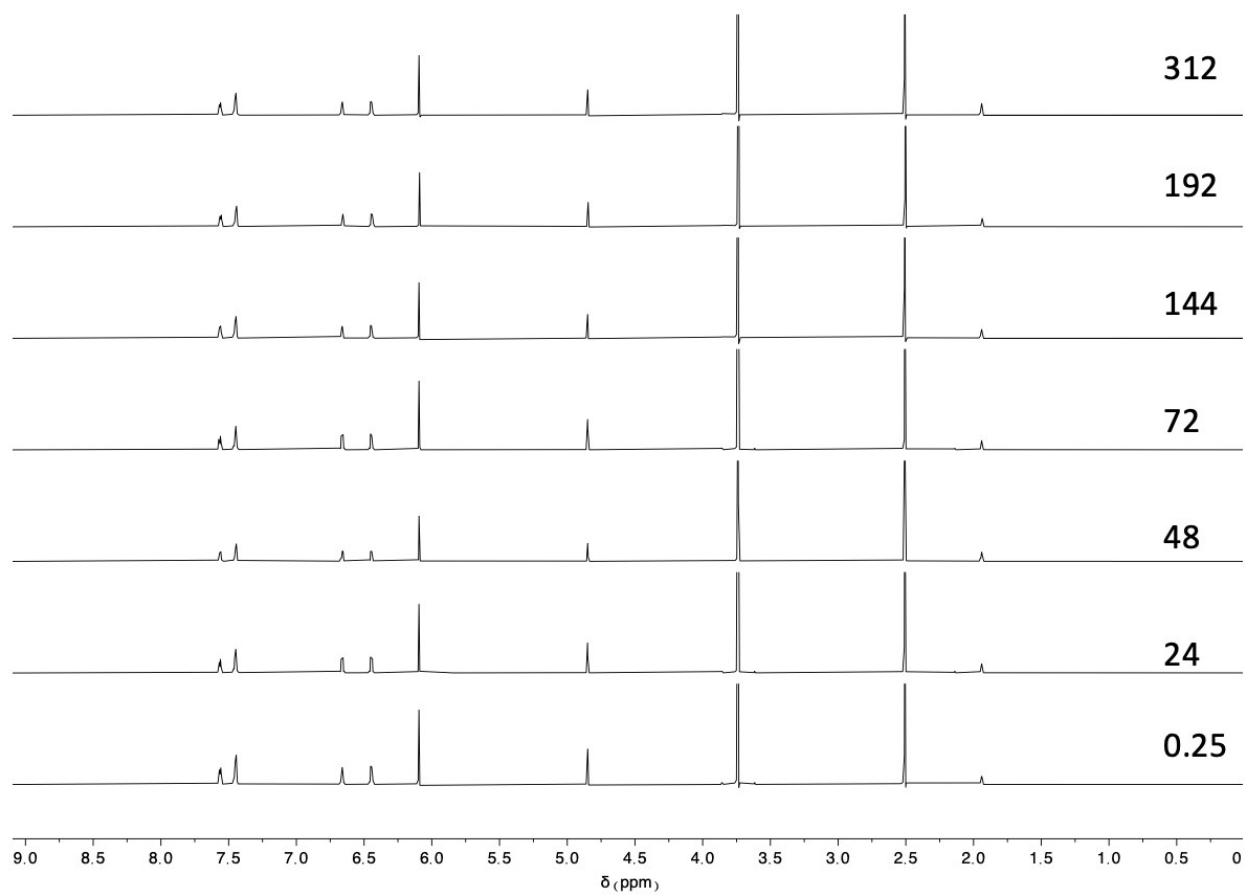


Figure S8: Time dependent ^1H NMR spectra of 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole in CD_3CN with trimethoxy benzene as an internal standard recorded at 0.25, 24, 48, 72, 144, 192 and 312 hours (top) and corresponding concentration vs time plot (bottom).

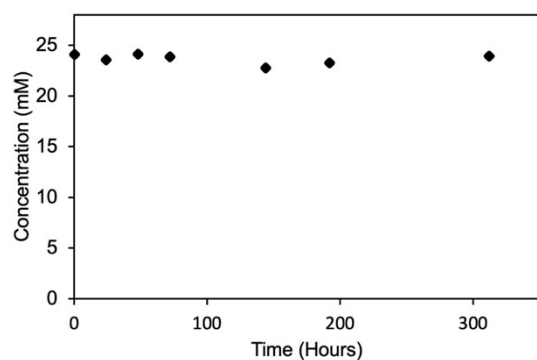
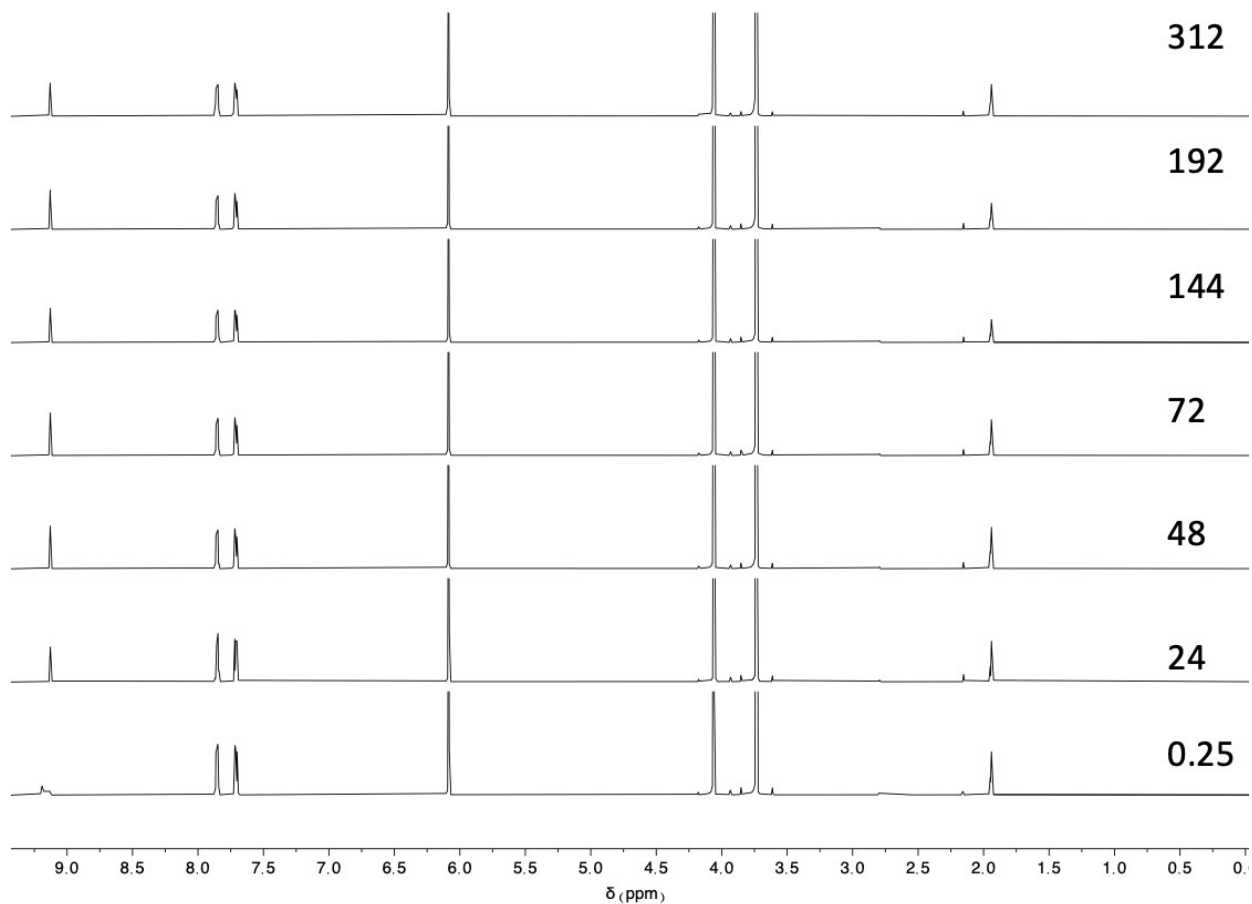


Figure S9: Time dependent ^1H NMR spectra of 1,3-dimethyl-1*H*-benzimidazolium iodide in CD_3CN with trimethoxy benzene as an internal standard recorded at 0.25, 24, 48, 72, 144, 192 and 312 hours and corresponding concentration vs time plot.

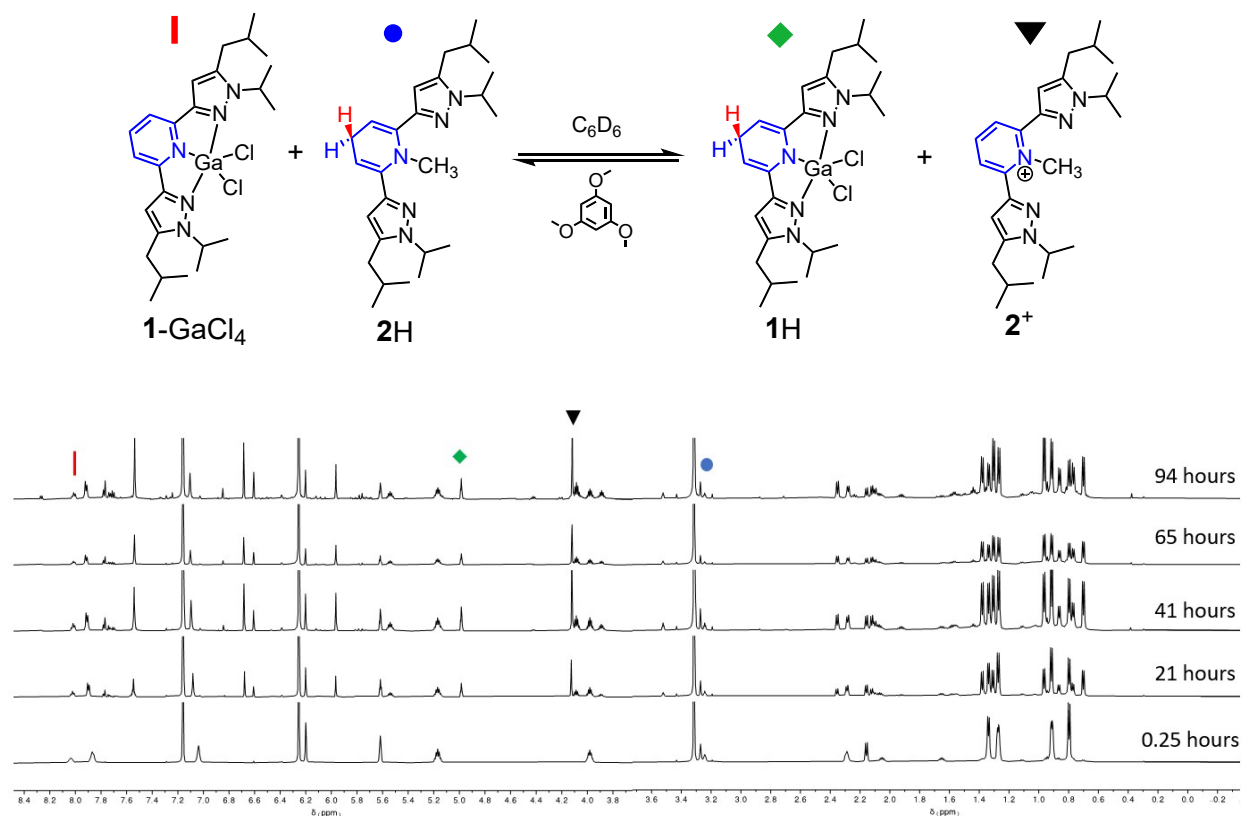


Figure S10. Reaction scheme of **1-GaCl₄** with **2H** in deuterated benzene with trimethoxy benzene as an internal standard (top). Stacked 1H NMR plot of reaction of **1-GaCl₄** and **2H**. Diagnostic peaks for the C_p-H signal for **1-GaCl₄** and **1H**, and the N-CH₃ for **2⁺** and **2H** species are marked with a red rectangle, green diamond, black triangle and blue circle respectively. There are two side by side spectra (from -0.2 to 3.6, right and 3.6 to 8.4 ppm, left) scaled such that relevant signals are easily seen. (bottom)

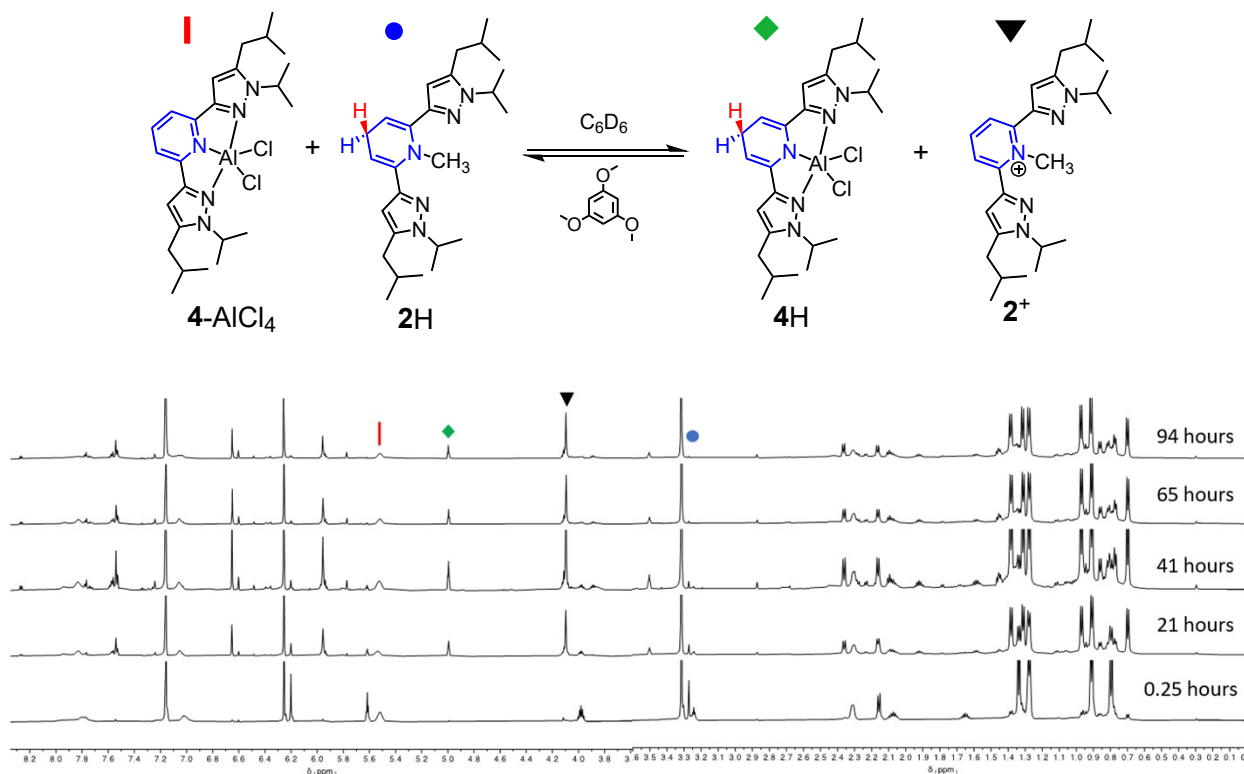


Figure S11. Reaction scheme of **4-AlCl₄** and **2H** in deuterated benzene with trimethoxy benzene as an internal standard (top). Stacked ¹H NMR plot of reaction **4-AlCl₄** and **2H**. Diagnostic peaks for the C_p-H signal for **4-AlCl₄** and **4H**, and the N-CH₃ signal for **2⁺** and **2H** species are marked with a red rectangle, green diamond, black triangle and blue circle respectively. There are two side by side spectra (from -0.2 to 3.6, right and 3.6 to 8.2 ppm, left) scaled such that relevant signals are easily seen (bottom).

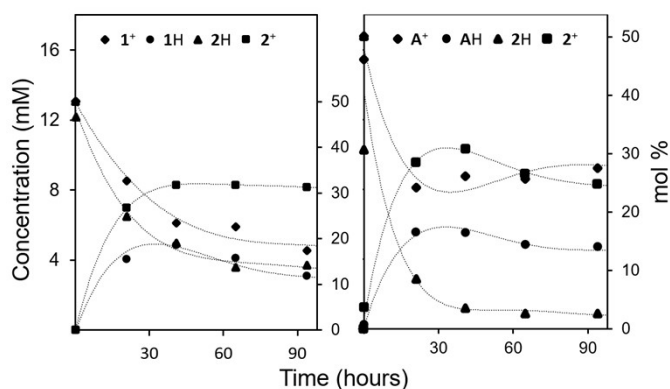


Figure S12: Concentration (mM) and mol % vs time (hours) plotted for: (left) reaction of **1-GaCl₄** with **2H**; (right) reaction of **4-AlCl₄** with **2H**. Lines added to serve as a visual aid but are not fits of the data. Each data point is average of three experiments. Data used to construct these plots shown in Figures S4 and S5.

5. References

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