Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for:

Modulation of H^+/H^- Exchange in Iridium-hydride 2-Hydroxypyridine Complexes by Remote Lewis Acids

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Experimental Procedures

General Considerations.

All manipulations were performed under an inert glovebox atmosphere unless otherwise specified. Solvents were purified with a solvent purification system with columns containing a Cu catalyst, molecular sieves, and alumina. Deuterated solvents were purchased from Cambridge Isotope laboratory and degassed, passed through alumina, and stored over molecular sieves for a minimum of 3 days prior to any VT NMR H^+/H^- exchange measurements. 6,6'Dihydroxy-terpyridine (dhtp)[1] and $Ir(H)_5(PPh_3)_2$[2] were prepared as previously reported. Borane THF, sodium borohydride, $Zn(C_6F_5)_2$, and trimethyloxonium tetrafluoroborate were purchased from Sigma Aldrich respectively were stored in a glovebox and used without further purification.

NMR measurements were performed on Varian 700, 500 or 400 MHz spectrometers. ^1H and ^{13}C NMR are referenced to internal solvent residuals and are reported in parts per million (ppm) relative to tetramethylsilane. ^{19}F, ^{31}P, and ^{11}B NMR are referenced to $BF_3(OEt_2)$, 85% H_3PO_4, and $BF_3(OEt_2)$, respectively, using internal calibration to a unified scale from ^1H NMR solvent residuals. The following abbreviations are reported as follows: broad (br), singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), and triphenylphosphine (PPh_3). ^{13}C NMR, $^{31}P\{^1H\}$ resonances were observed as singlets unless noted otherwise. IR spectra were recorded on a Nicolet iS10 FT-IR spectrometer with an ATR accessory. Electronic absorption spectra were recorded at ambient temperature in sealed 1 cm quartz cuvettes with a Varian Cary-50 spectrophotometer. Mass spectra were recorded on a Bruker AutoFlex Speed MALDI-TOF and prepared in an anthracene matrix. Compounds were not suitably stable for elemental analysis.

Single crystals were mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K. Rigaku d*trek images were exported to CrysAlisPro[3] for processing and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package.[4]

Synthesis of 1. Benzene (90 mL) was added to dhtp (375.6 mg; 1.42 mmol) and $IrH_5(PPh_3)_2$ (1.022 g; 1.42 mmol) in Schlenk tube and sealed. The tube was heated to 80 °C and stirred. After 24 hours, the tube was allowed to cool, the reaction mixture was concentrated to 35 mL, and diluted with diethyl ether (35 mL). The solids were collected on a sintered glass frit and washed with 1:1 benzene:diethyl ether (30 mL). The solid was then extracted with dichloromethane, dried under reduced pressure. The solid crystallized from hot benzene and decanted to recover a pale yellow solid (1.112 g; 80%). Crystals of **1** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **1**. ^{1}H NMR, 700 MHz (CD_2Cl_2, 298 K): δ 10.55 (s, 1H, N*H*), 7.71 (d, *J* = 7.7 Hz, 1H), 7.45-7.17 (m, m, 33 H), 6.90 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 6.7 Hz, 1H), 6.43 (d, *J* = 9.1 Hz, 1H), 6.14 (d, *J* = 8.0 Hz, 1H), -17.59 (t, *J* = 16.5 Hz, 1H, Ir-H_b). ^{1}H NMR 500 MHz (CD_2Cl_2, 238 K): 10.63 (s, 1H), 9.94 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.49 – 7.09 (m, 33H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 6.8 Hz, 1H), 6.43 (d, *J* = 8.8 Hz, 1H), 6.10 (d, *J* = 7.5 Hz, 1H), -11.45 (s, 1H), -17.40 (t, *J* = 15.8 Hz, 1H). ^{13}C NMR 162 MHz (CD_2Cl_2, 298 K): 166.14, 162.95, 161.73, 152.23, 144.51, 141.27, 139.34, 134.03, 133.71 (t, *J* = 6.1 Hz) 133.60 129.78, 128.03(t, *J* = 4.9 Hz), 119.84, 118.26, 113.58, 104.64, 100.88. ^{31}P{^{1}H} NMR, 162 MHz (CD_2Cl_2, 298 K): 19.3. Selected IR data (ATR, neat) υ = 3313.8 (OH), 3053.4, 2167.2 (br, Ir-H), 1900.1 (br, Ir-H) 1652.3, 1598.8 cm^{-1}. UV-vis (λ_{max} = 354, 388 nm). MALDI-TOF of **1** – PPh_3: Calc. 983.23817; Found 979.754. For **1** – (2 PPh_3): Calc. 721.14704; Found 718.508.

Synthesis of 2.
Tetrahydrofuran (ca. 3 mL) was added to 5.2 (6.1 mg; 0.0062 mmol) and stirred to provide a white suspension. To the stirring suspension, $NaBH_4$ (81 μL of 0.08 M solution in dimethoxyethane; 0.0065 mmol) was added, resulting in a color change to bright yellow. After 14 hours, the reaction mixture was filtered and concentrated to dryness to provide the title compound as a yellow solid (5.3 mg; 85%). The compound was used without further purification. Crystals of **2** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **2**. ^{1}H NMR, 500 MHz (CD_2Cl_2, 238 K): 10.41 (d, *J* = 8.6, 1 H), 8.21 (d, *J* = 7.2, 1 H), 7.82 (d, *J* = 7.5, 1 H), 7.43 -7.26 (m, 43 H), 7.10 (d, *J* = 7.7, 1 H), 6.73 (d, *J* = 7, 1 H), 6.46 (d, *J* = 8.7, 1 H), 6.31 (d, *J* = 8.1, 1 H), 3.68 (br s, 2 H), -11.35 (m, br 1 H), -16.91 (t, *J* = 15.5, 1 H). ^{31}P{^{1}H} NMR, 162 MHz (CD_2Cl_2, 298 K): 19.45. ^{11}B NMR, 128 MHz (CD_2Cl_2, 298 K): -3.9 (br s). Selected IR data (ATR, neat) υ = 3059.6, 2925.1, 2858.6, 2410.7, 2182.2, 2050.0, 1926.6, 1945.1, 1572.2, 1433.4 cm^{-1}. UV-vis (λ_{max} = 373, 395 nm). MALDI-TOF of **2** – PPh_3: Calc. 995.25531; Found 992.479. For **2** – (2 PPh_3): Calc. 733.16417; Found 727.535.

Alternative preparation of 2.
Dichloromethane (ca. 3 mL) was added to 1 (34 mg; 0.034 mmol) and stirred to provide a pale-yellow solution. To the stirring solution, BH_3·THF (34 μL of 1 M solution in tetrahydrofuran; 0.034 mmol) was added, resulting in a color change to bright yellow. The reaction was monitored by NMR spectroscopy after 2 hours indicating 66% yield. Additional BH_3·THF (14 μL of 1 M solution in tetrahydrofuran; 0.014 mmol) was added and monitored by NMR until > 95% yield was obtained. Crystallized **2** was obtained from the layered solution by filtration, dissolved in dichloromethane and dried under reduced pressure recover the title compound (27 mg; 82%).

Synthesis of 3.
Dichloromethane (ca. 5 mL) was added to 1 (29.4 mg; 0.029 mmol) and stirred until dissolved. To the stirring solution, a dichloromethane solution (ca. 5 mL) of $Zn(C_6F_5)_2$ (11.1 mg; 0.028 mmol) was added, resulting in a color change to bright yellow. After 2 hours, the reaction mixture was layered with pentane (ca. 10 mL) and left undisturbed for 24 h for slow diffusion forming yellow precipitate. The solution was decanted, and the precipitate dried under vacuum to isolate a yellow solid (26 mg; 72%). The compound was used without further purification. Crystals of **3** suitable for X-ray diffraction were grown from slow diffusion of layered pentane into a concentrated dichloromethane solution of **3**. ^{1}H NMR, 500 MHz (CD_2Cl_2, 238 K): 9.8 (d, *J* = 9, 2 H), 8.49 (d, *J* = 7.7, 2 H), 7.87 (d, *J* = 7.4, 2 H), 7.41– 6.8 (m, 80 H), 6.36 (d, *J* = 8, 2 H), 6.09 (d, *J* = 8.0, 2 H), -11.40 (s, 2 H), -17.60 (t, *J* = 16.4, 2 H). ^{13}C NMR 176 MHz (CD_2Cl_2, 298 K): 165.73, 162.61, 161.31, 159.62, 151.82, 144.10, 140.93, 139.48, 138.95, 133.55, 133.52, 133.49, 133.46, 133.35(t, *J* = 5.9 Hz), 133.25, 129.92, 129.38, 128.07, 127.62 (t, *J* = 4.2 Hz), 119.38, 117.85, 113.18, 104.24, 100.57. ^{19}F NMR 376 MHz (CH_2Cl_2 298 K): -117.8 (m, 4F), -159.76 (*J* = 18.7 Hz, 2F), -163.9 – -164.22 (m, 4F). ^{31}P{^{1}H} NMR, 162 MHz (CD_2Cl_2, 298 K): 20.2 – 17.9 (m), 14.2 – 11.19 (m). Selected IR data (ATR, neat) υ =3059.2, 2160.0 (br), 1908.8 (br) 1607.9, 1482.1 cm^{-1}. UV-vis (λ_{max} = 370, 393 nm). MALDI-TOF of **3** (2 PPh_3 + $Ir(H)_2$(dhtp-$ZnAr^F$)): Calc. 720.13921; Found 715.557.

In situ preparation and characterization of **3** and HC_6F_5. To a 5 mL dichloromethane solution of **1** (29.4 mg, 0.029 mmol), a freshly prepared solution of $Zn(C_6F_5)_2$ (9.8 mg, 0.029 mmol) in dichloromethane was added and stirred at room temperature turning bright yellow. An aliquot was removed transferred to an NMR tube and ^{19}F NMR spectrum was acquired (Figure S35).

Synthesis of 4.
A solution of 1 (36.5 mg; 0.03 mmol) in 4 mL CH_2Cl_2 was added dropwise to a stirring solution of $[Me_3O][BF_4]$ (5.4 mg; 0.035 mmol) in 4 mL CH_2Cl_2. The solution was stirred at ambient temperature for 18h, decanted then dried under reduced pressure to provide the title compound as a yellow solid (39 mg; 93%). The compound was used without further purification. Crystals of **4** suitable for X-ray diffraction were grown from vapor diffusion of diethyl ether into a dichloromethane solution of **4**. ^{1}H NMR 700 MHz ($CDCl_3$ 298 K) δ 8.19 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.91 (t, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 8.0 Hz, 1H), 7.65 (s, 1H), 7.37 – 7.27 (m, 6H), 7.25 – 7.12 (m, 25H), 7.10 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.80 – 6.64 (m, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 6.15 – 6.03 (m, 2H), 3.25 (s, 3H), -17.67 (td, *J* = 14.2, 7.0 Hz, 1H), -20.27 (td, *J* = 16.5, 7.5 Hz, 1H). ^{1}H NMR, 500 MHz (CD_2Cl_2, 298 K): 7.84 – 7.78 (m, 2H), 7.78 – 7.71 (m, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.36 – 6.75 (m, 31H), 6.57 (d, *J* = 8.2 Hz, 1H), 6.20 (d, *J* = 6.8 Hz, 1H), 3.26 (s, 3H), -17.62 (td, *J* = 14.1, 7.0 Hz, 1H), -20.15 (td, *J* = 16.3, 8.1 Hz, 1H). ^{1}H NMR (500 MHz, CD_2Cl_2 238 K) δ 7.98 (s, 1H), 7.77 (t, *J* = 7.9 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.40 – 7.08 (m, 31H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 6.16 (d, *J* = 7.2 Hz, 1H), 3.16 (s, 2H), -17.46 (td, *J* = 13.8, 6.9 Hz, 1H), -19.96 (td, *J* = 15.5, 7.4 Hz, 1H). ^{13}C NMR 126 MHz (CD_2Cl_2, 298 K): 162.61, 161.31, 160.26, 156.55, 156.11, 154.14, 141.38, 137.80, 137.38, 132.68 (t, *J* = 5.1 Hz), 131.35, 130.93, 130.61, 128.65 (t, *J* = 4.9 Hz), 123.87, 117.72, 116.84, 111.97, 109.55, 52.99. ^{31}P{^{1}H} NMR, 162 MHz (CD_2Cl_2, 298 K): 15.46 (s). ^{31}P NMR, 162 MHz (CD_2Cl_2, 298 K): 15.44 (apparent t, *J* = 13.5 Hz). ^{19}F NMR, 471 MHz (CD_2Cl_2, 298 K): -153.17 (d). ^{11}B 128 MHz (CD_2Cl_2) -1.58. Selected IR data (ATR, neat) υ = 3137.7, 3059.6, 2284.4, 2155.6, 1573.7, 1435.3, 1048.6 cm^{-1}. UV-vis (λ_{max} = 333 nm).

MALDI-TOF of **4** – PPh_3: Calc. 998.26165; Found 997.552. For **4**– (2 PPh_3): Calc. 735.16269 Found 731.904.

Deuterium incorporation into 1

An NMR tube containing **1** (2.5 mg, 0.0025 mmol) and 0.6 mL CD_2Cl_2 was frozen in liquid nitrogen, then CH_3OD (100 μL, 2.5 mmol) was added. The tube was then transferred to a 500 MHz NMR spectrometer that had been cooled to -35 °C and deuterium incorporation monitored for 1.5 hours. Immediate incorporation into the N-*H* was observed with limited incorporation over the duration was at -35 °C and the reaction was permitted to warm to -20 °C, then ambient room temperature. After 24h, the sample was cooled to -20 °C to assess final ^2H incorporation. See Figure S7.

Variable Temperature NMR Analysis

Variable Temperature NMR measurements

Samples were prepared at room temperature and allowed to cool in a 500 MHz NMR spectrometer and allowed to equilibrate for 15 min at each temperature prior to measurement.

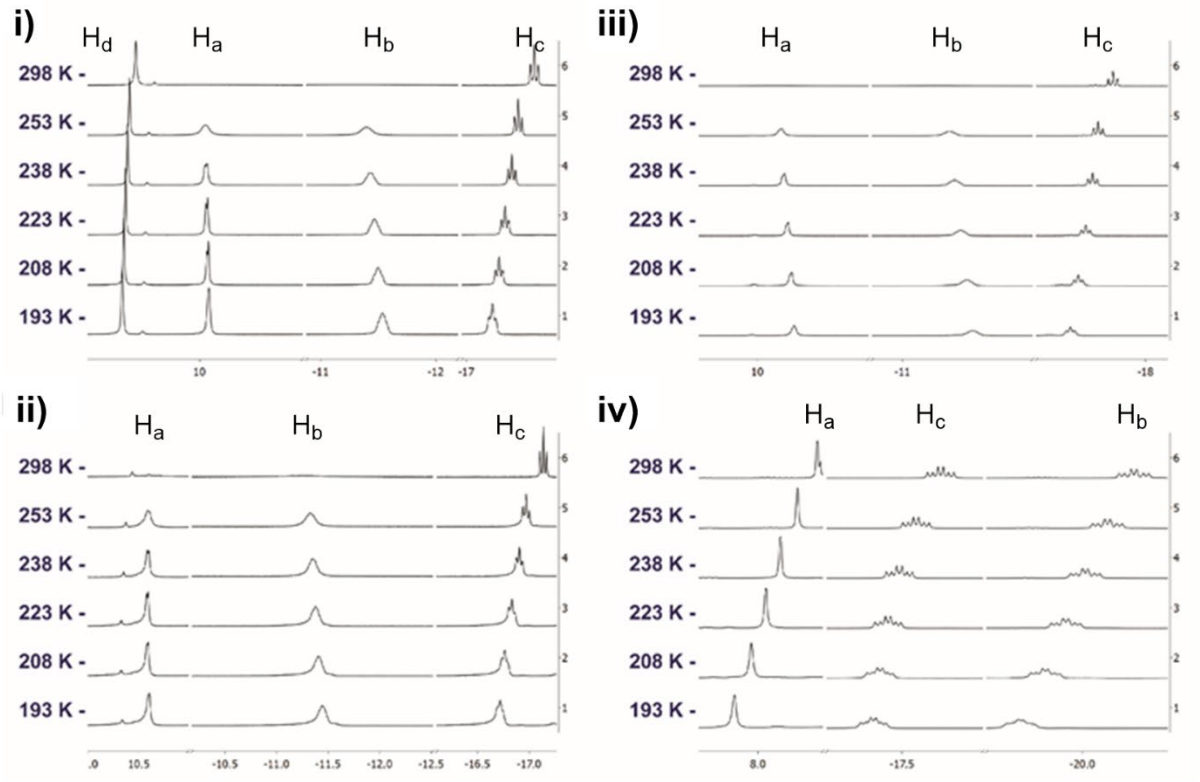


Figure S1. Truncated variable temperature ^1H NMR spectra of highlighting H_a and hydride signals of (i) **1**, (ii) **2**, (iii) **3**, (iv) **4** at specified temperatures in CD_2Cl_2.

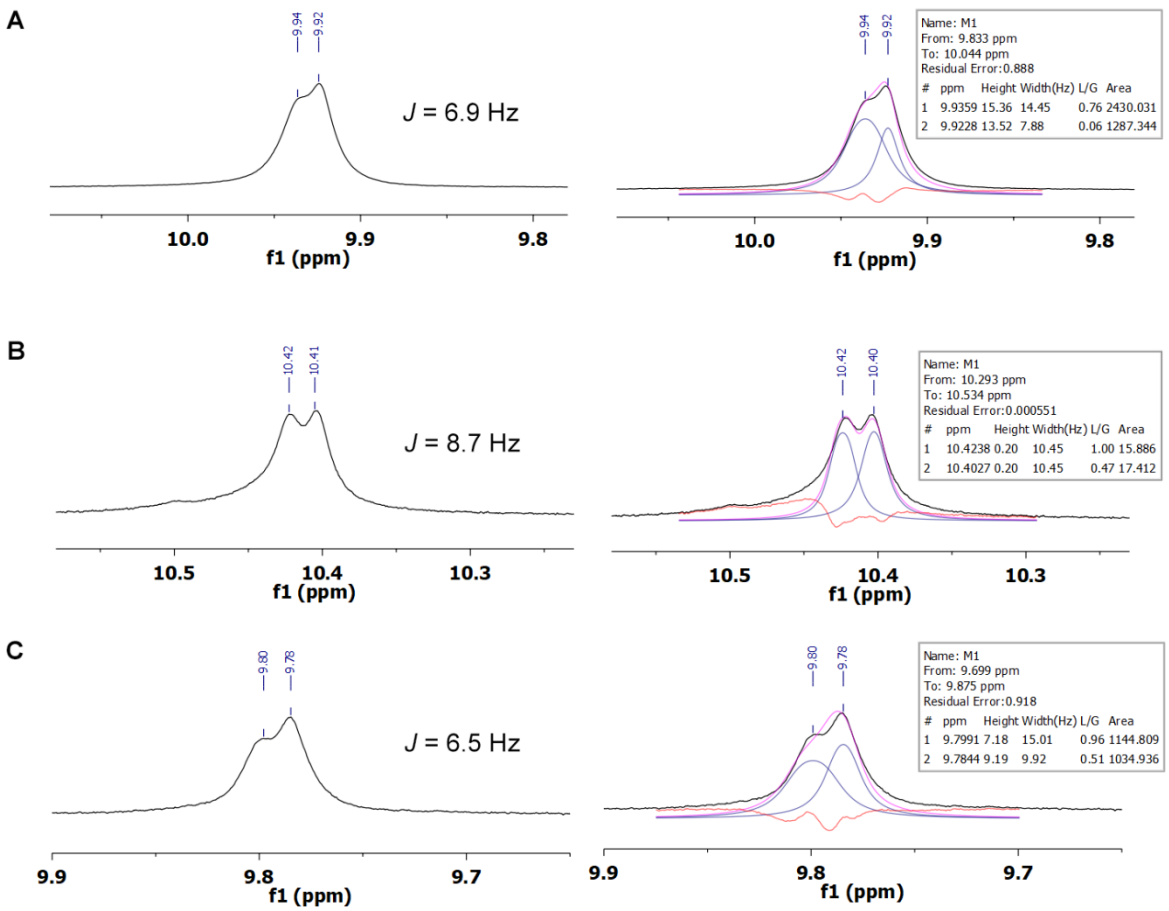


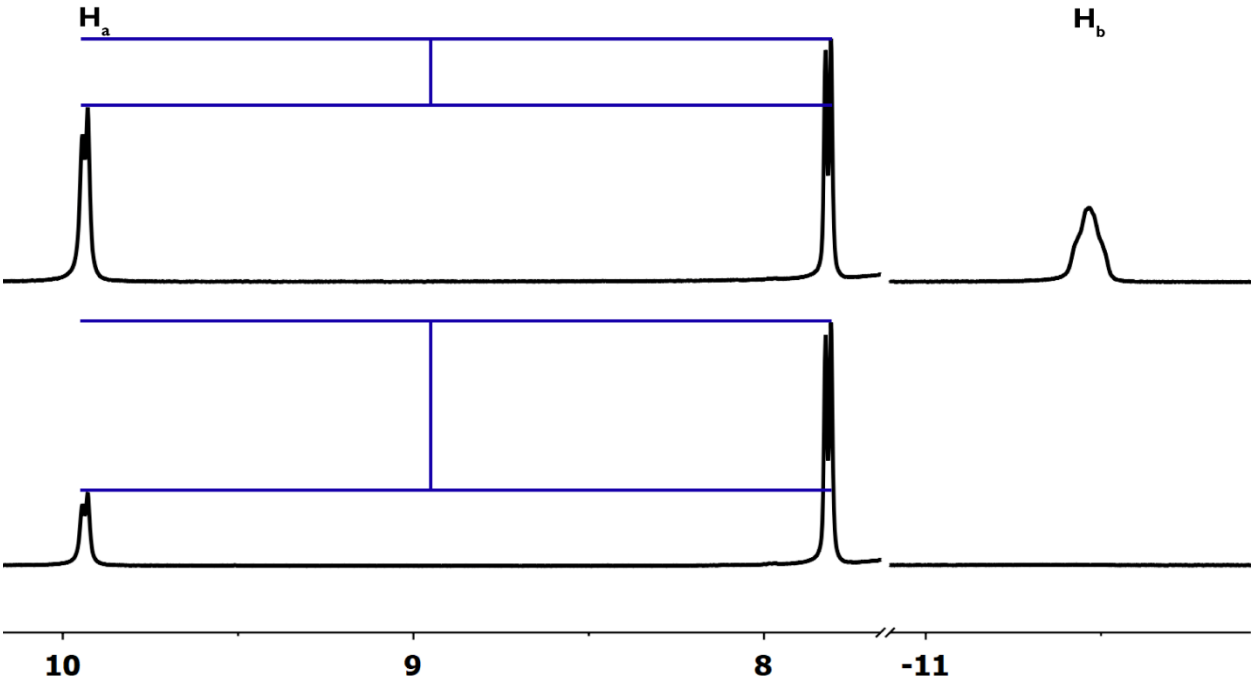
Figure S2. ^{1}H NMR $^{1}J_{HH}$ of O-*H* resonance of (A) **1**, (B) **2**, and (C) **3** at 238 K with corresponding fits (right).

Exchange measurements

To measure the exchange rate of the exchanging H^+/H^- nuclei, the following procedure was followed. Prior to performing saturation transfer experiments, the T_1 value of the exchanging resonances were determined at each temperature point. These values were used to determine the necessary saturation pulse width to completely suppress the hydride resonance (5 x T_1). To perform the saturation transfer, a standard PRESAT experiment in VNMRj was used. The preacquisition delay (d1) was modified for each experiment such that the sum of the preacquisition delay and saturation pulse width was a constant 2 seconds throughout the temperature range (d1 + saturation = 2 s). Each PRESAT experiment was performed in triplicate at each temperature point to provide error estimation. Integration against a C–H signal of the ligand provided an internal standard for measuring the extent of exchange (M/M_0). For a given exchange site (H_a) M is denoted as M_a, and rates were calculated according to equation 1.

$$k = \frac{1}{T_{1a}}\left(\frac{M_{0a}}{M_a} - 1\right) \qquad (1)$$

For compound **4** which was not observed to undergo H^+/H^- exchange via magnetization transfer, a maximum value approximated to 5% error in NMR integration was used (ie M_a= 0.95, M_{0a} = 1) affords a rate of 0.42 s^{-1} at 298 K.



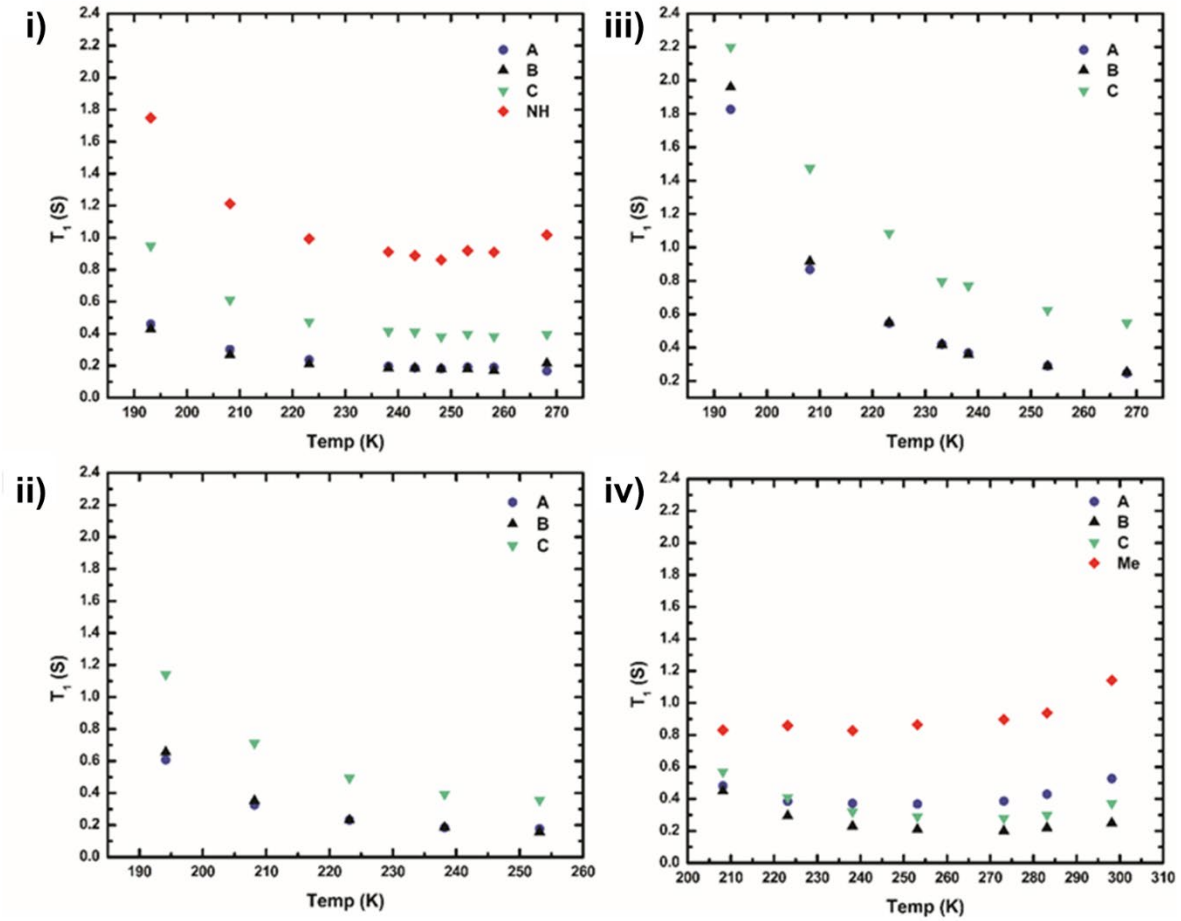

i)
A
B
C
NH
T1 (S)
Temp (K)
iii)
A
B
C
T1 (S)
Temp (K)
ii)
A
B
C
T1 (S)
Temp (K)
iv)
A
B
C
Me
T1 (S)
Temp (K)

Table S1. Integration values (M_{0a} and M_a) for magnetization transfer analysis of **1-3.**

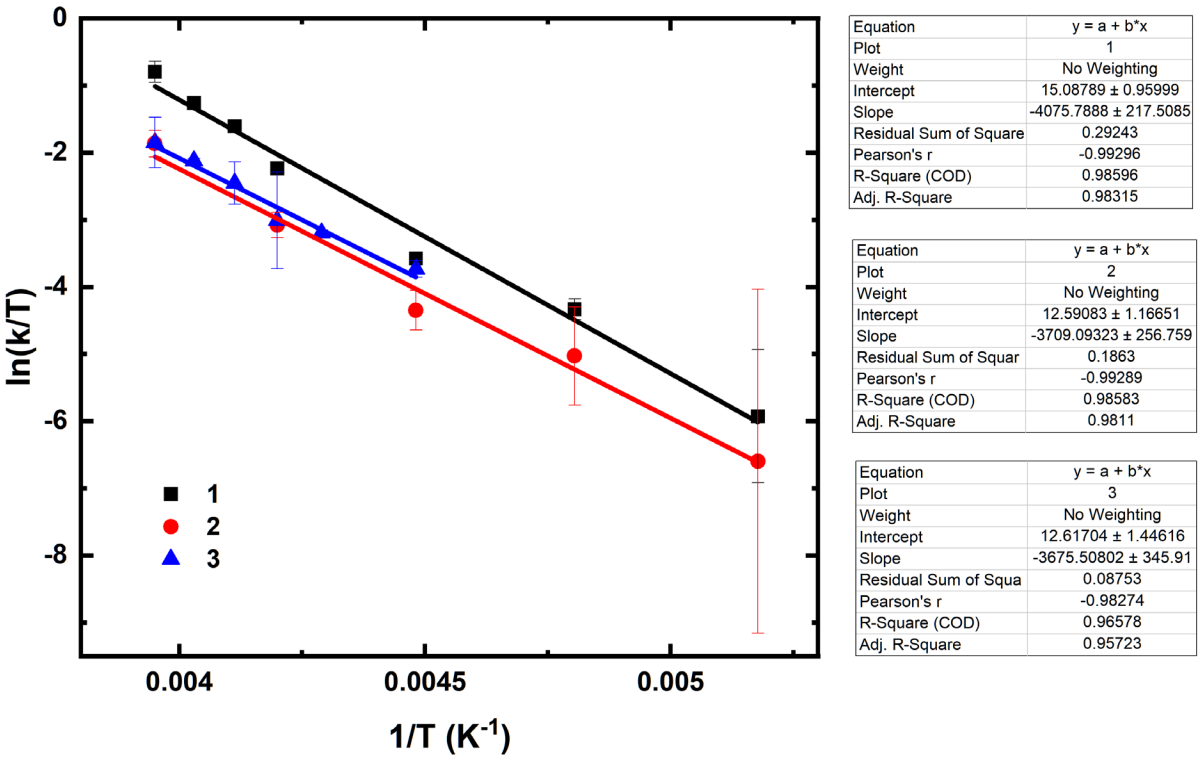
1							
Temperature (K)	**M_{0a}**	**M_a (1)**	**M_a (2)**	**M_a (3)**	**T_1 H_a (s)**	**k (s^{-1})**	**Standard deviation (s^{-1})**
253.15	1.00	0.05	0.04	0.04	0.191	114.1	8.2
248.15	1.00	0.07	0.07	0.07	0.182	70.2	0.6
243.15	1.00	0.10	0.10	0.10	0.186	48.7	2.0
238.15	0.98	0.16	0.16	0.17	0.196	25.5	0.4
223.15	1.00	0.41	0.41	0.40	0.237	6.3	0.1
208.15	1.02	0.55	0.54	0.58	0.302	2.7	0.2
193.15	1.00	0.84	0.84	0.76	0.460	0.5	0.2
2							
Temperature (K)	**M_{0a}**	**M_a (1)**	**M_a (2)**	**M_a (3)**	**T_1 H_a**	**k (s^{-1})**	**Standard deviation (s^{-1})**
253.15	0.95	0.14	0.13	0.13	0.177	39.1	1.9
238.15	0.97	0.31	0.33	0.32	0.184	11.0	0.5
223.15	1.00	0.61	0.61	0.58	0.231	2.9	0.2
208.15	0.96	0.66	0.68	0.61	0.326	1.4	0.2
193.15	0.88	0.85	0.67	0.75	0.609	0.26	0.2
3							
Temperature (K)	**M_{0a}**	**M_a (1)**	**M_a (2)**	**M_a (3)**	**T_1 H_a**	**k (s^{-1})**	**Standard deviation (s^{-1})**
253.15	1.01	0.09	0.07	0.08	0.291	39.8	3.7
248.15	1.13	0.10	0.10	-	0.333	29.8	0.2
243.15	1.24	0.16	0.17	0.15	0.330	20.8	1.6
238.15	1.10	0.21	0.16	0.32	0.368	11.1	3.8
233.15	1.12	0.24	0.21	0.24	0.420	9.5	0.6
223.15	1.24	0.29	0.29	0.27	0.545	5.3	0.1

Eyring analysis:

The calculated temperature dependent exchange rates were interpreted for an Eyring analysis. Rate errors were low and global errors for thermochemical values calculated in accordance with recommended practices.[5] The thermochemical values are modeled for and upper bound of a 15% relative rate error and 1% relative temperature error.

Table S2. Variable temperature exchange rate Eyring analysis of **1-4:**

	1	**2**	**3**
Slope	-4075 ± 218	-3709 ± 257	-3675 ± 346
Intercept	15.1 ± 1.0	12.6 ±1.2	12.6 ± 1.4
$\Delta H^{\ddagger}$ (kcal/mol)	8.1 ± 0.6	7.4 ± 0.6	7.3 ± 1.2
$\Delta S^{\ddagger}$ (kcal mol^{-1} K^{-1})	-0.02 ± 2.5	-0.02 ± 2.6	-0.02 ± 4.8
$\Delta G^{\ddagger}_{298}$	13.2 ± 0.2	14.0 ± 0.2	13.9 ± 0.2
K_{298} (s^{-1})	1240 ± 430	350 ± 120	390 ± 134



Equation	y = a + b*x
Plot	1
Weight	No Weighting
Intercept	15.08789 ± 0.95999
Slope	-4075.7888 ± 217.5085
Residual Sum of Square	0.29243
Pearson's r	-0.99296
R-Square (COD)	0.98596
Adj. R-Square	0.98315

Equation	y = a + b*x
Plot	2
Weight	No Weighting
Intercept	12.59083 ± 1.16651
Slope	-3709.09323 ± 256.759
Residual Sum of Squar	0.1863
Pearson's r	-0.99289
R-Square (COD)	0.98583
Adj. R-Square	0.9811

Equation	y = a + b*x
Plot	3
Weight	No Weighting
Intercept	12.61704 ± 1.44616
Slope	-3675.50802 ± 345.91
Residual Sum of Squa	0.08753
Pearson's r	-0.98274
R-Square (COD)	0.96578
Adj. R-Square	0.95723

Figure S5. Eyring plot of magnetization transfer H_a/H_b exchange rate measurement of **1-3**.

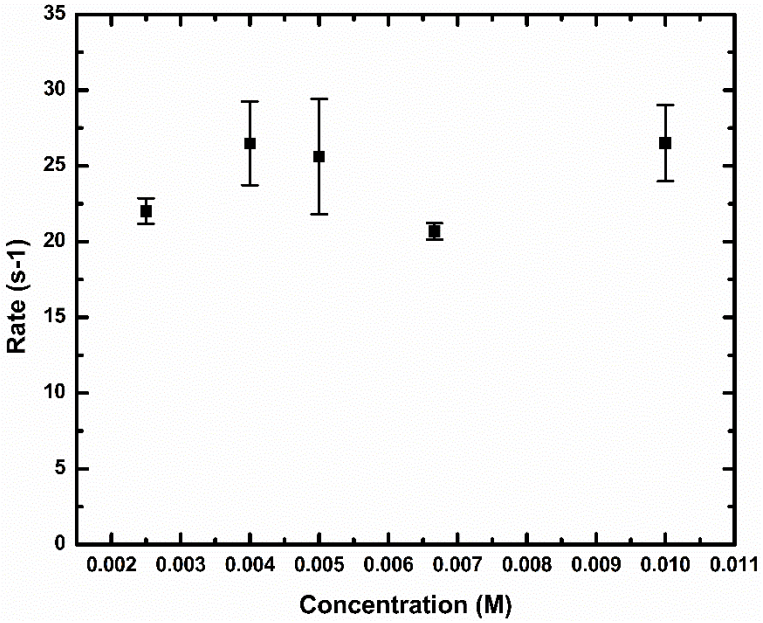


Figure S6. Concentration dependent ^{1}H NMR (CD_2Cl_2) magnetization H_a/H_b transfer rate of **1** at -35 °C spectra. Error bars reflect standard deviation from triplicate magnetization transfer measurements.

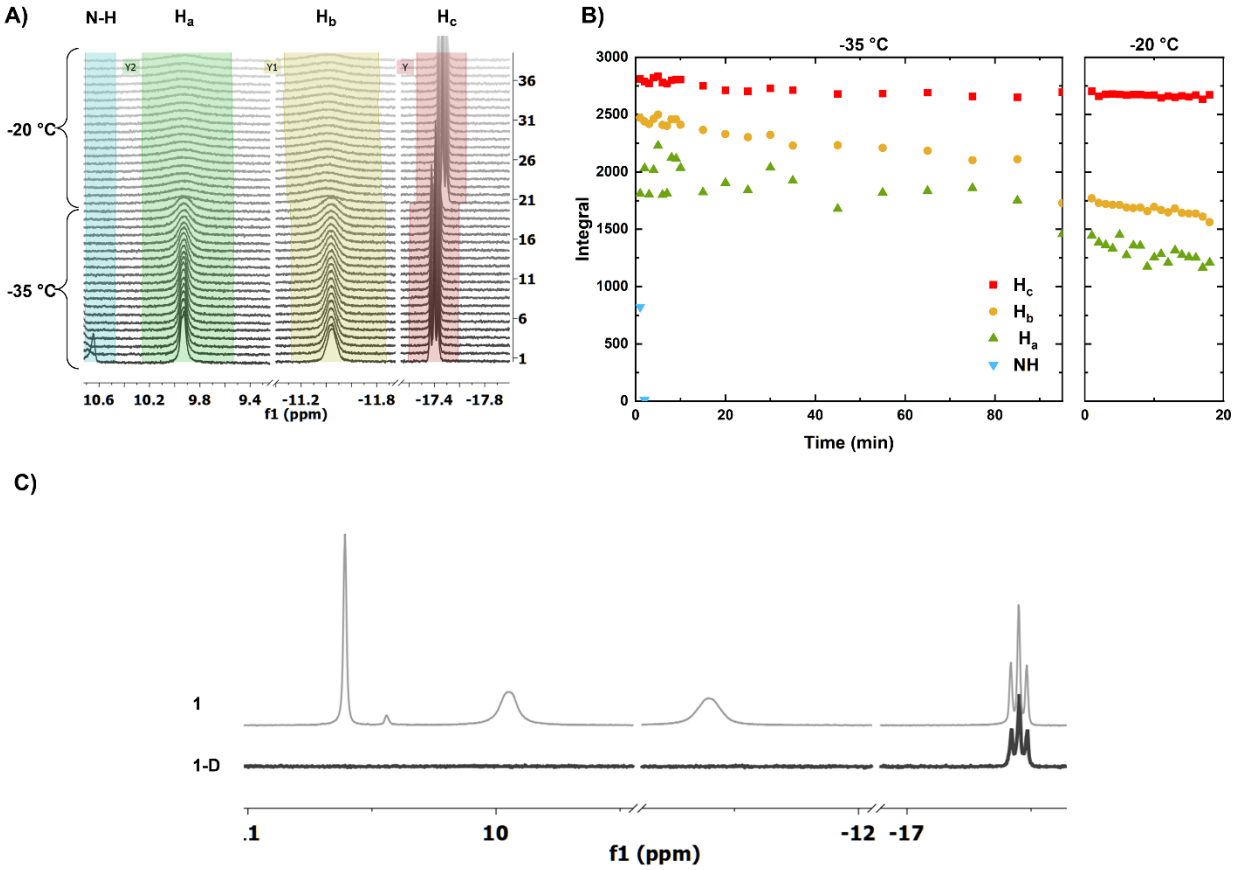


Figure S7. ^{1}H NMR spectra of (A) **1** with added CD_3OD. (B) Decay profiles of signal of Ha, Hb, Hc, and N-H at -35°C and -20 °C. (C) Comparison spectrum of **1** and deuterium incorporation to form **1-D** after 24h.

Spectra of Reported Compounds:

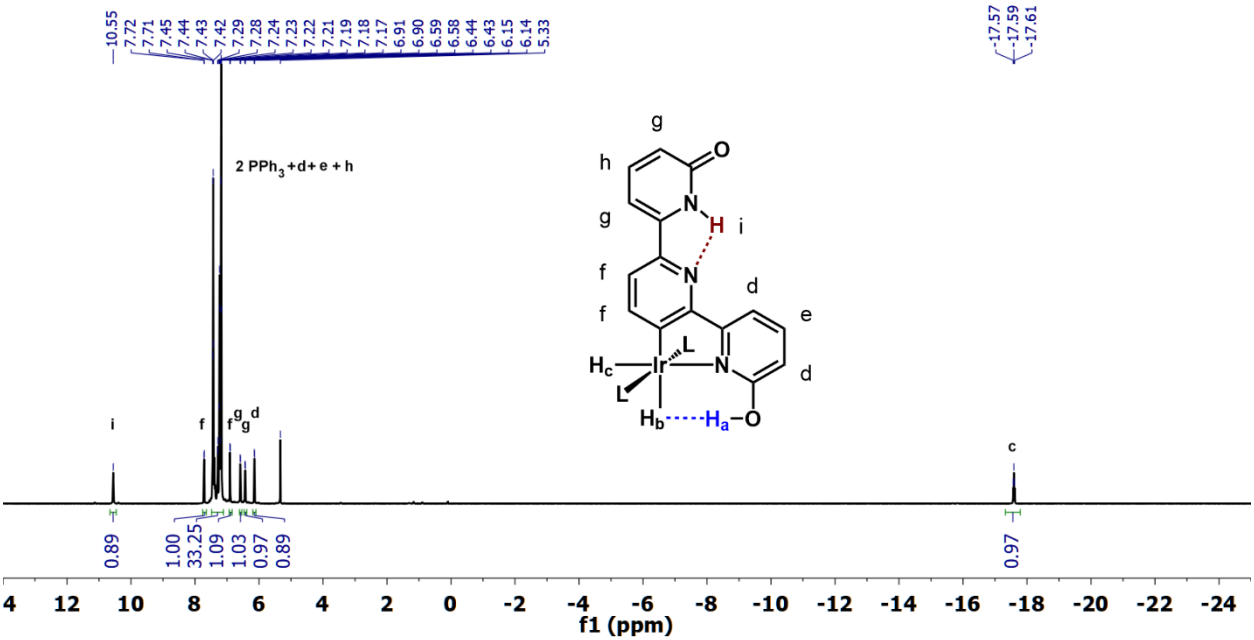


Figure S8. ^{1}H NMR spectrum (CD_2Cl_2, 700 MHz, 25 °C) of **1**.

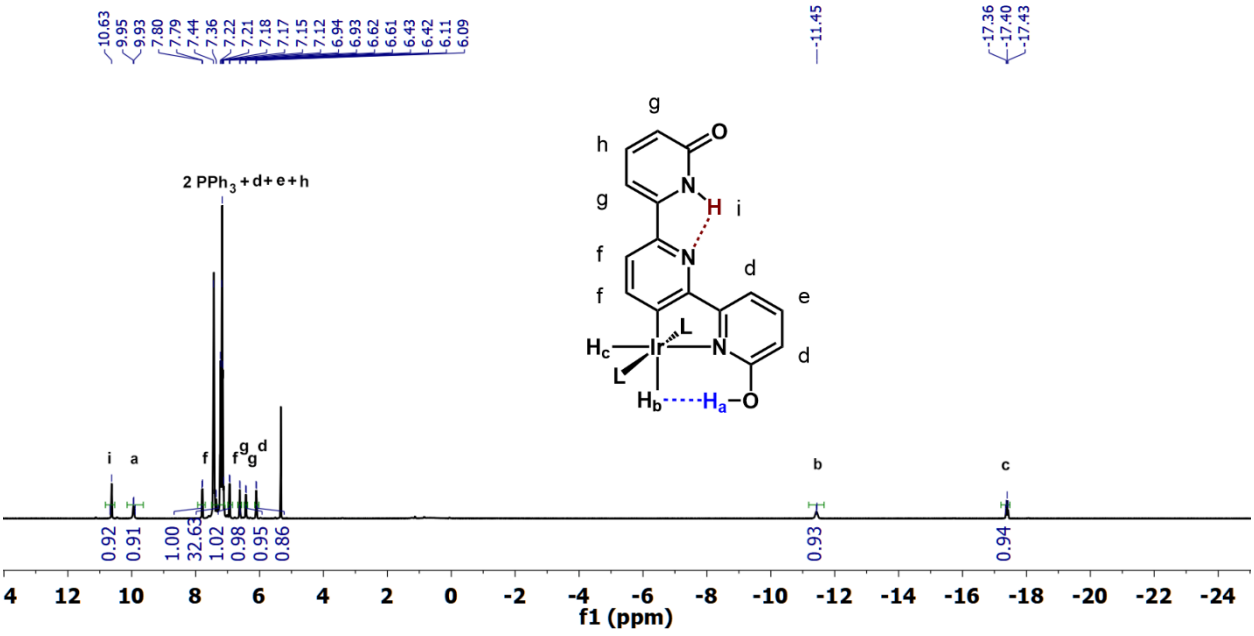


Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, -35 °C) of **1**.

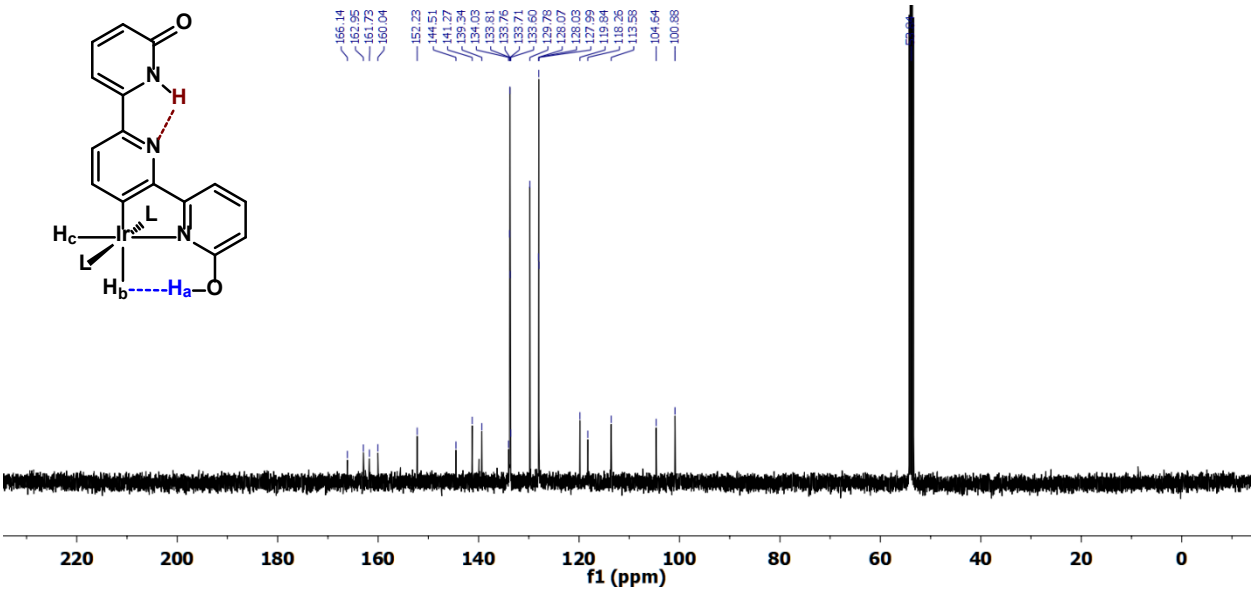


Figure S10. ^{13}C NMR spectrum (CD_2Cl_2, 126 MHz, 25 °C) of **1**.

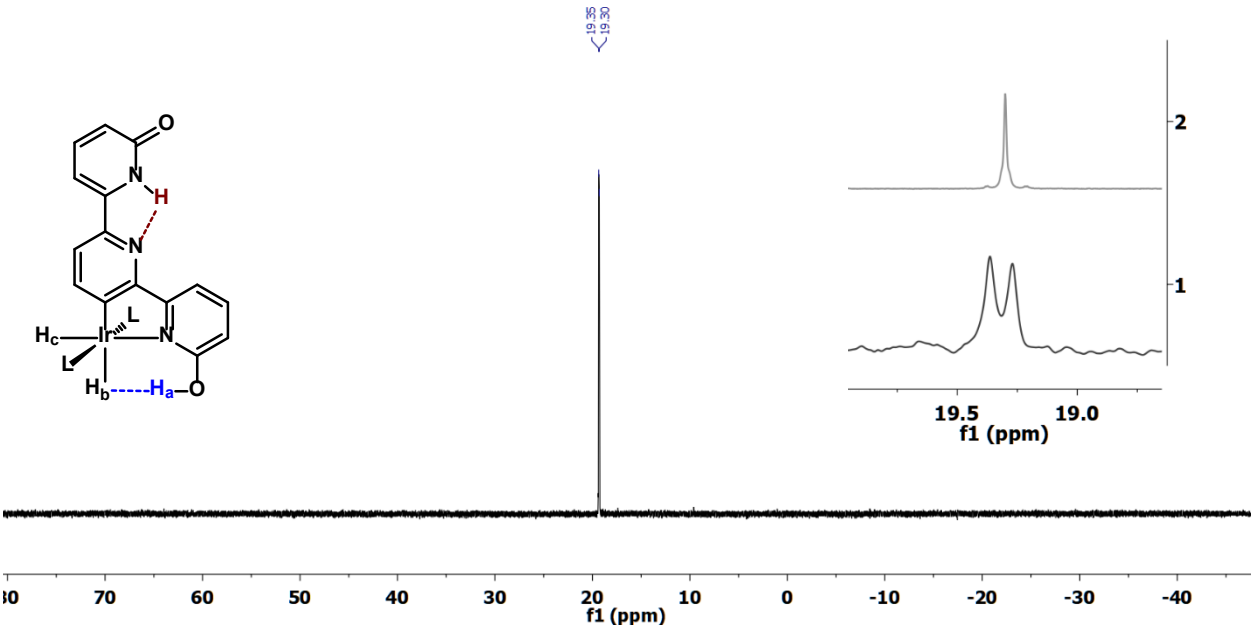


Figure S11. ^{31}P NMR spectrum (CD_2Cl_2, 162 MHz, 25 °C) of **1** with inset of $^{31}P\{^1H\}$ NMR (top) and ^{31}P spectra (bottom).

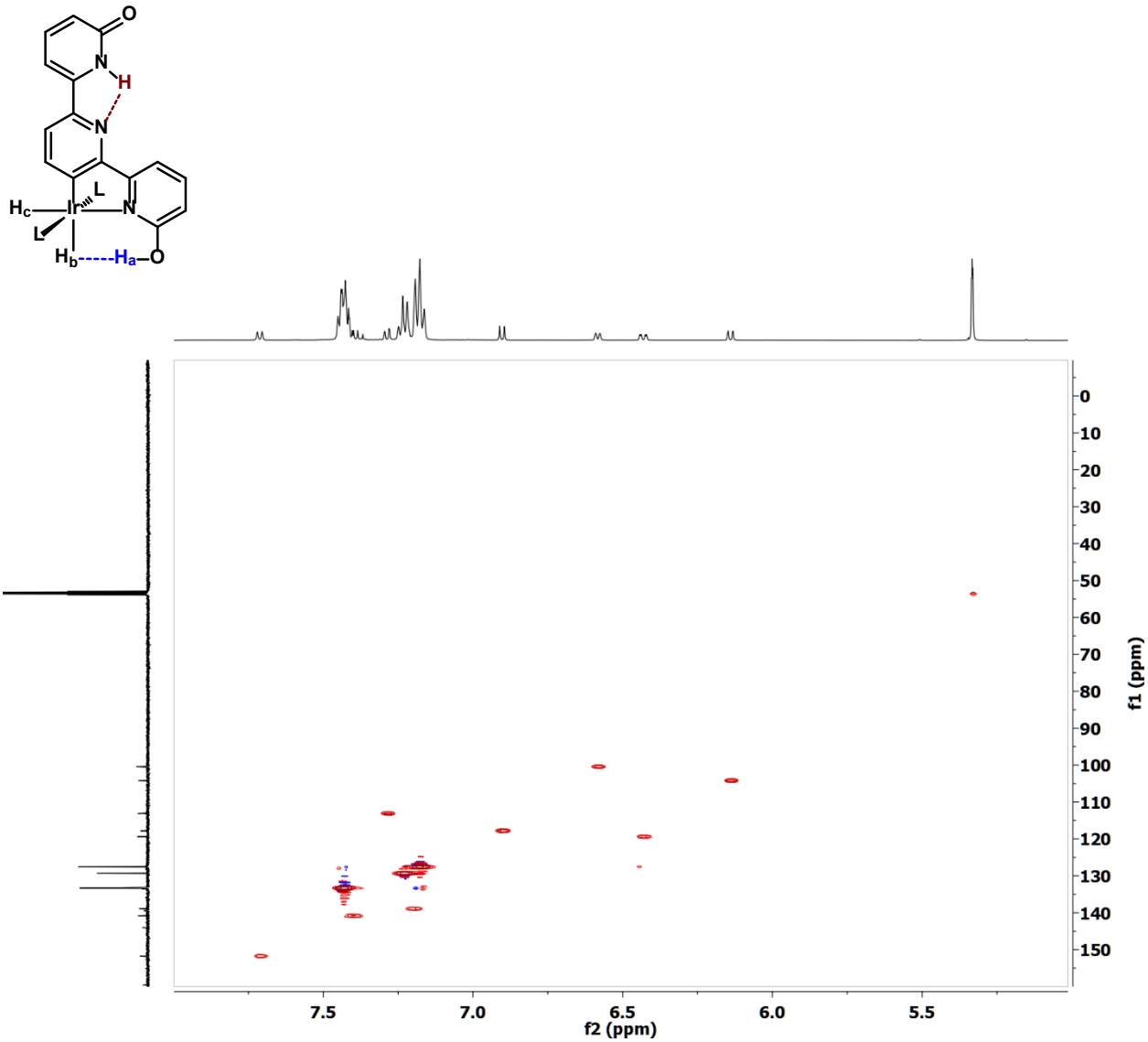


Figure S12. ^{1}H HSQC NMR spectrum (CD_2Cl_2, 25 °C) of **1**.

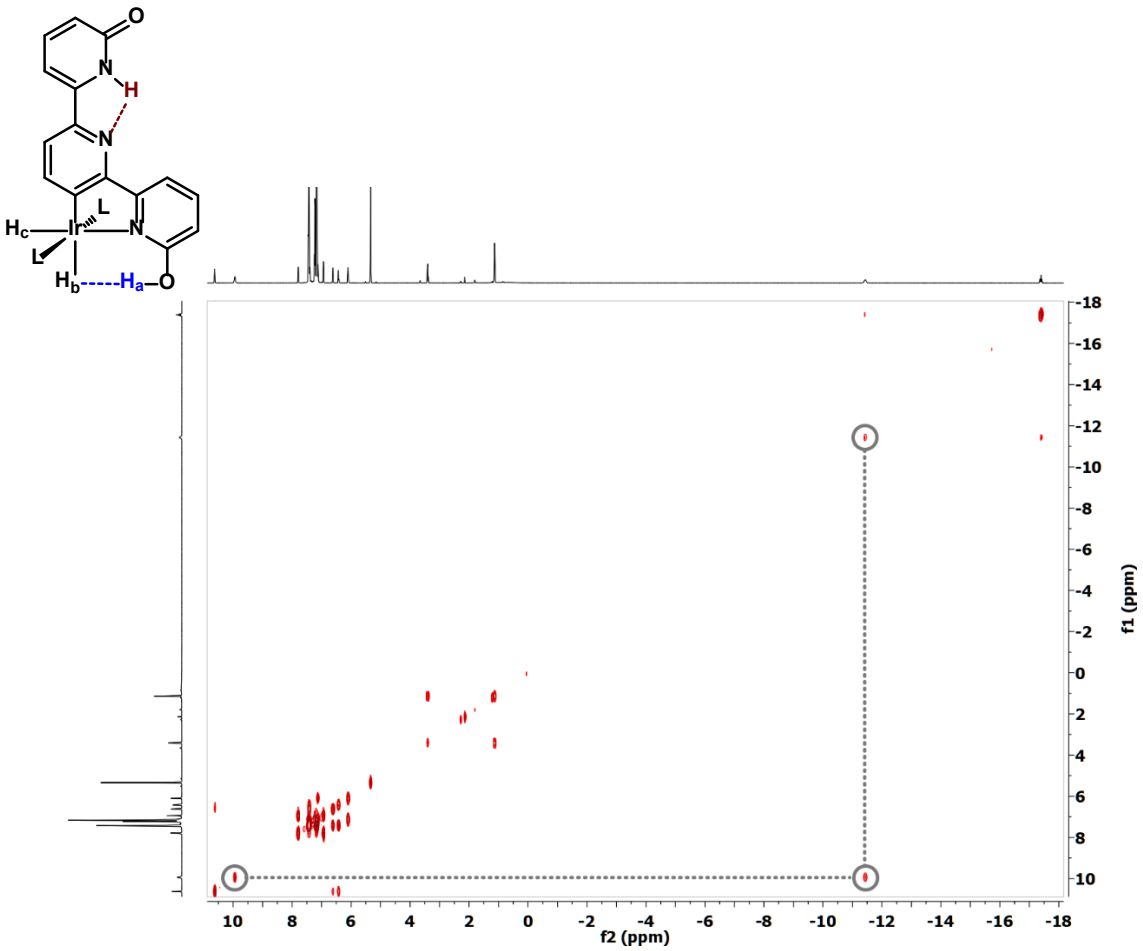


Figure S13. ^{1}H g-COSY NMR spectrum (CD_2Cl_2, 500 MHz,-65 °C) of **1**. Cross peak between H_a and H_b is highlighted.

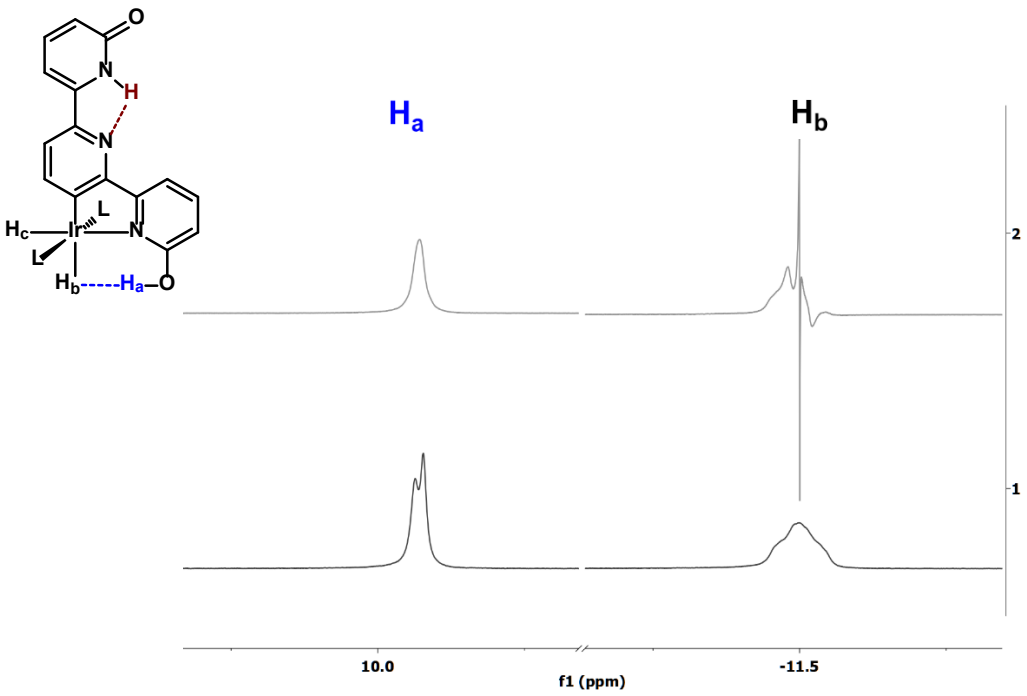


Figure S14. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, -65 °C) of **1** selective decoupling of H_b with resulting loss of multiplicity of H_a.

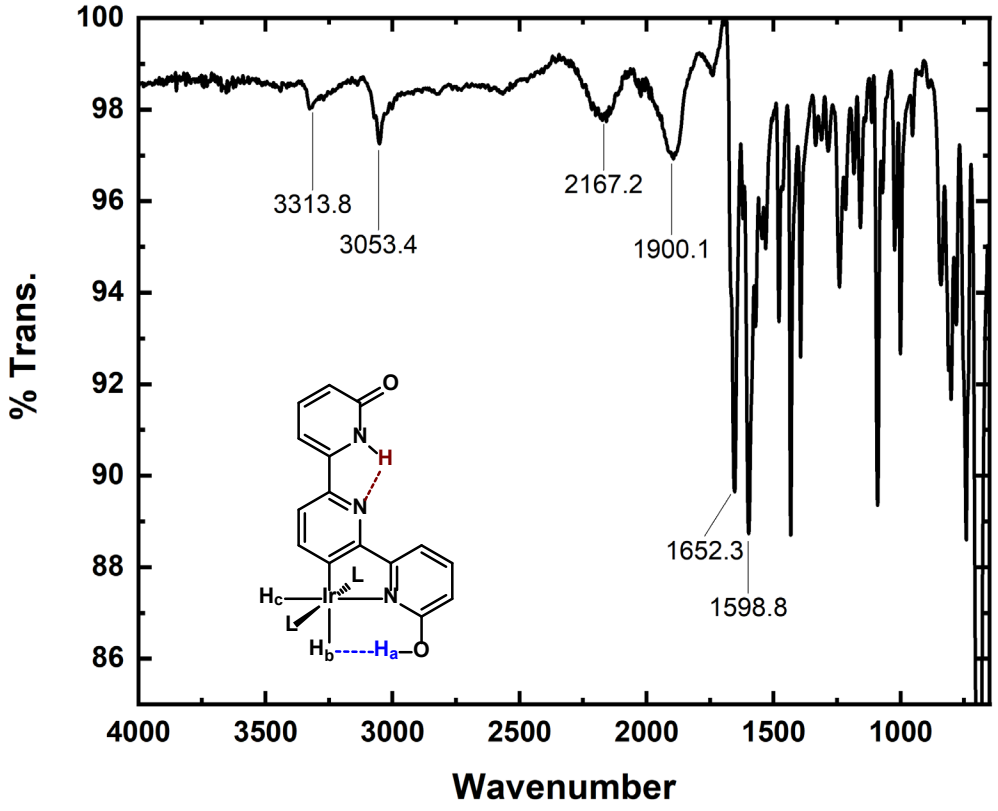


Figure S15. Infrared spectrum (ATIR) of **1**.

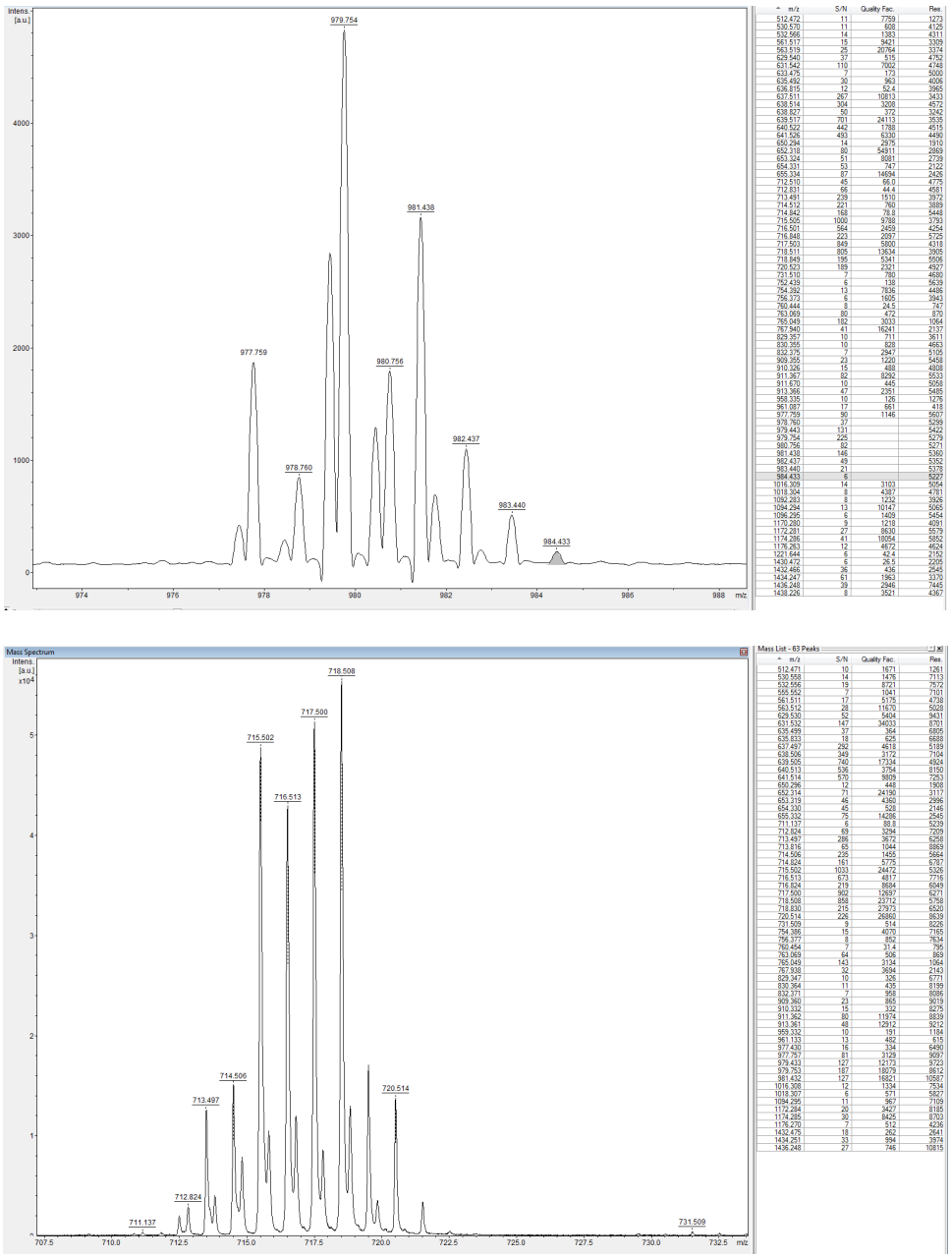


Figure S16. MALDI-TOF analysis of **1.**

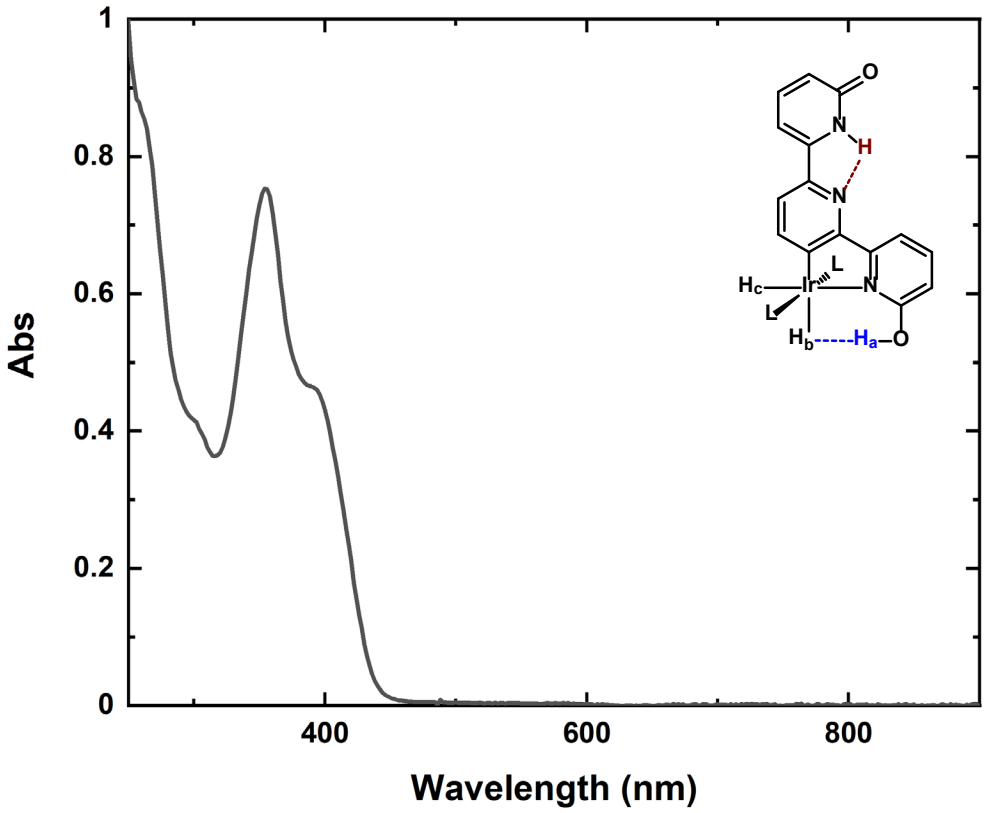


Figure S17. Electronic absorption spectrum of **1** recorded in CH_2Cl_2 at ambient temperature.

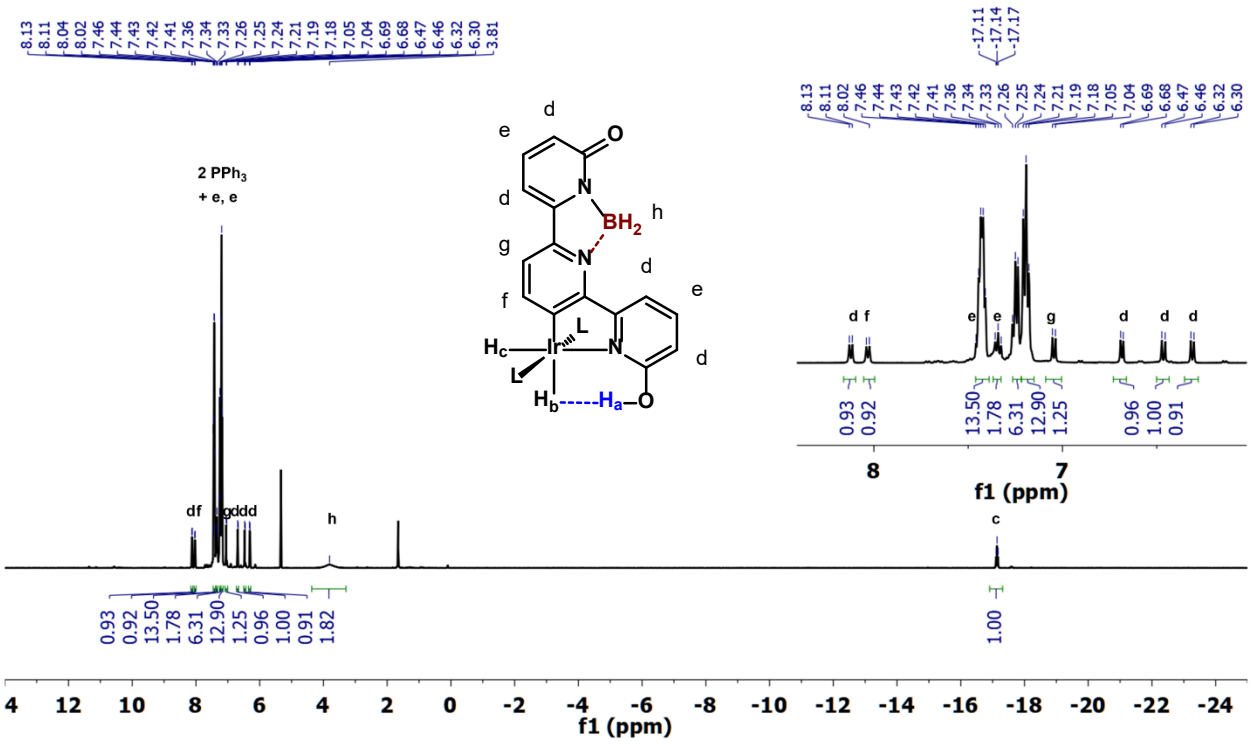


Figure S18. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, 25 °C) of **2**.

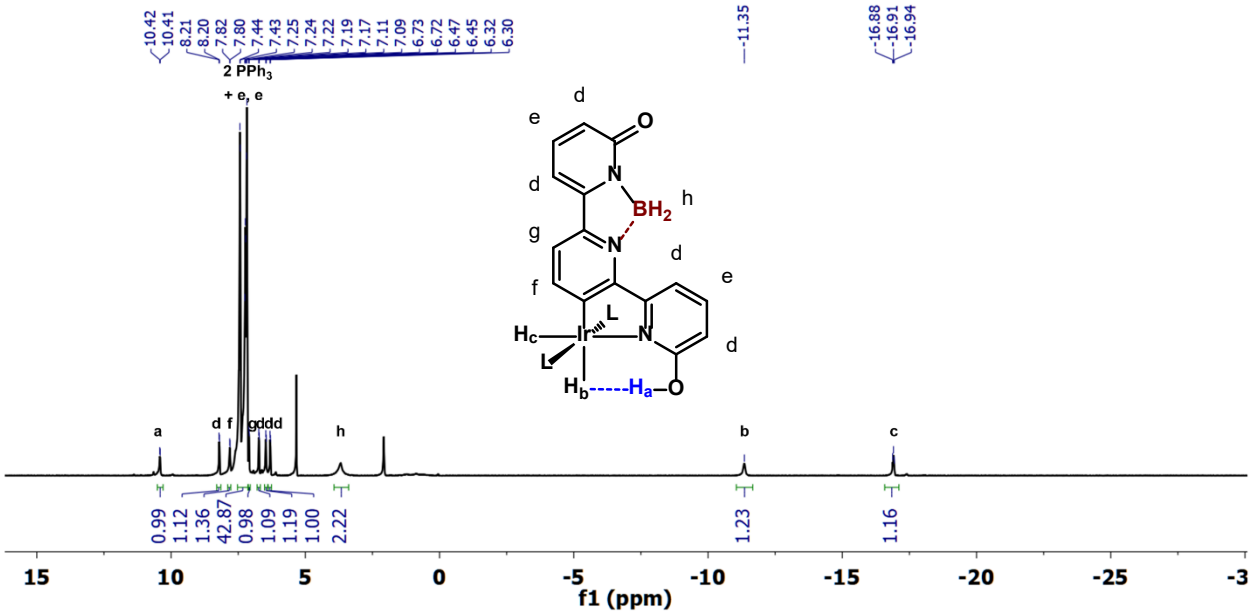


Figure S19. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, -35 °C) of **2**.

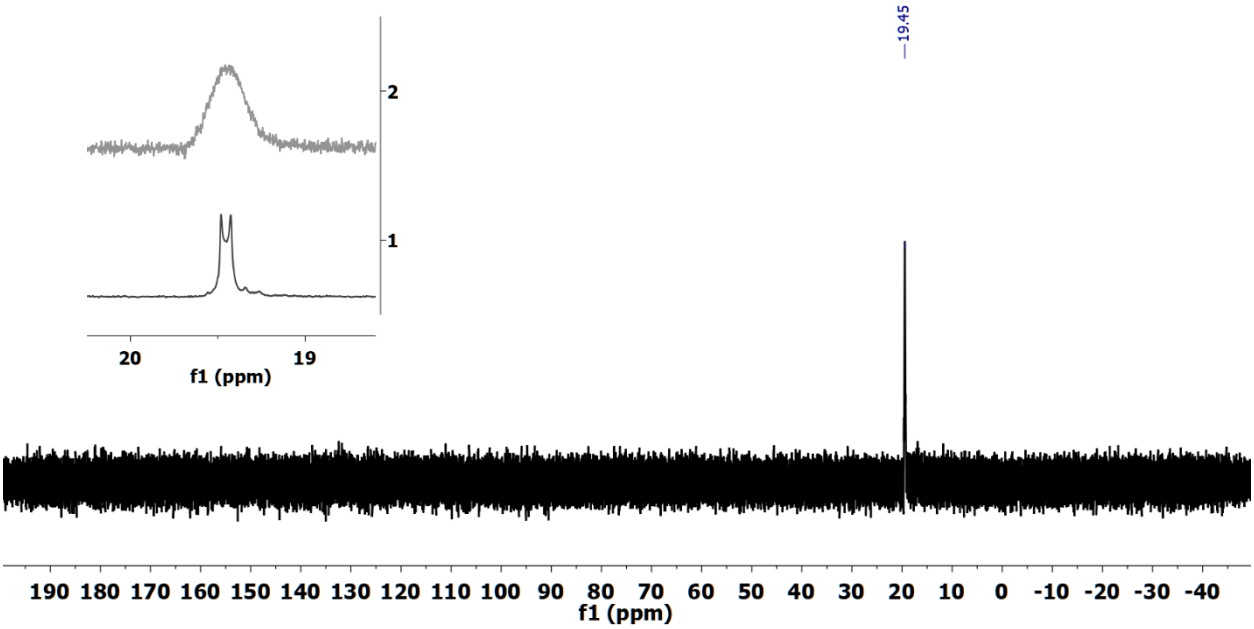


Figure S20. ^{31}P NMR spectrum (CD_2Cl_2, 162 MHz, 25 °C) of **2** with inset of $^{31}P\{^1H\}$ (top) and ^{31}P NMR (bottom) spectra.

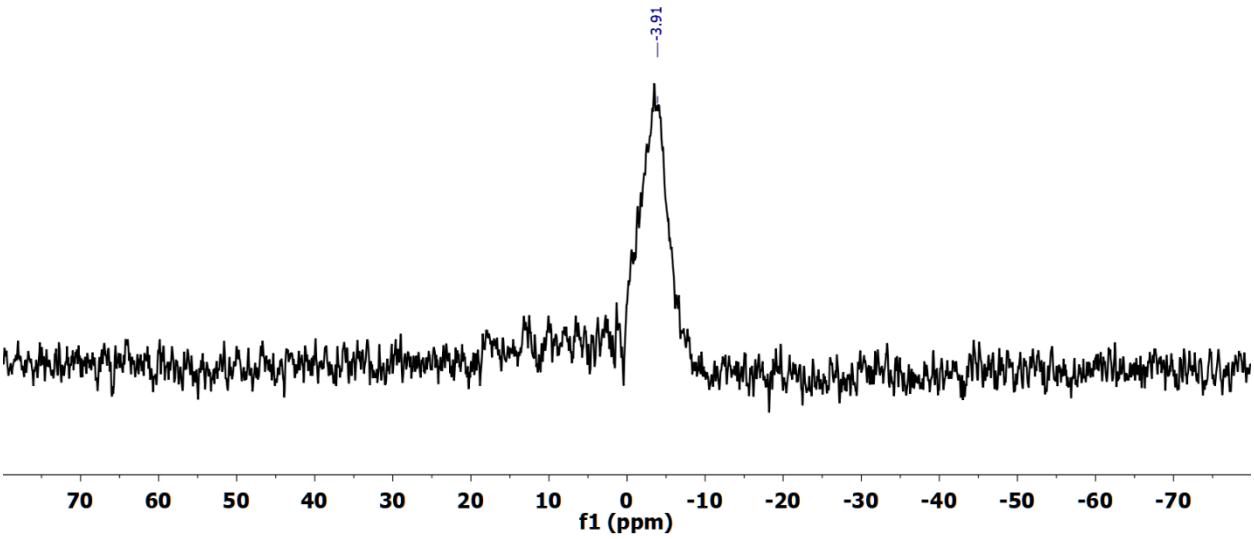


Figure S21. ^{11}B NMR spectrum (CD_2Cl_2, 128 MHz, 25 °C) of **2**.

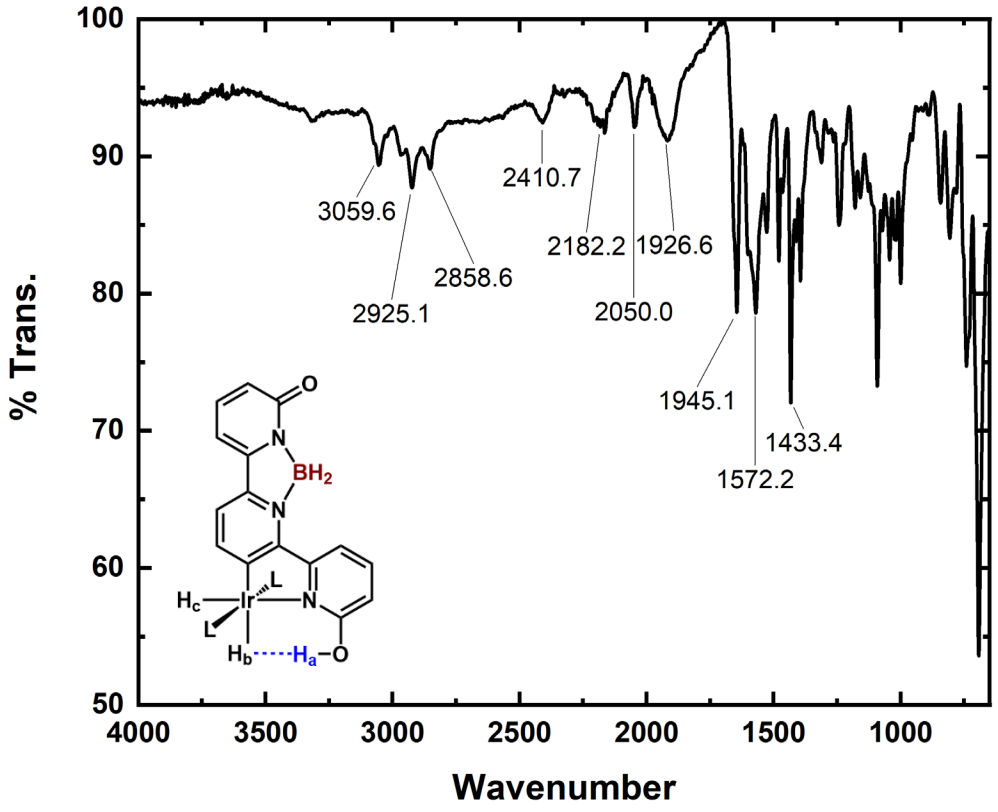


Figure S22. Infrared spectrum (ATIR) of **2**.

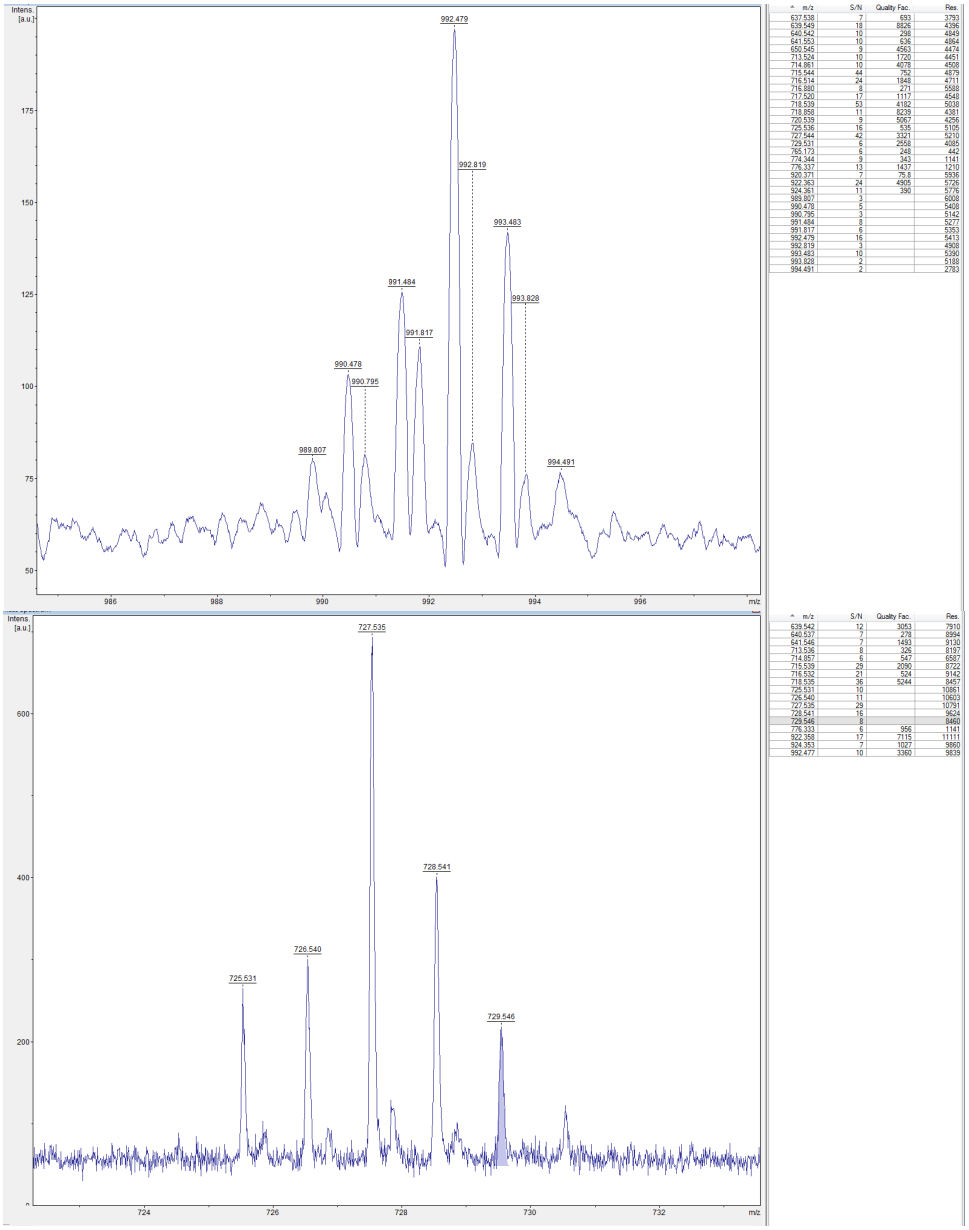


Figure S23. MALDI-TOF analysis of **2**.

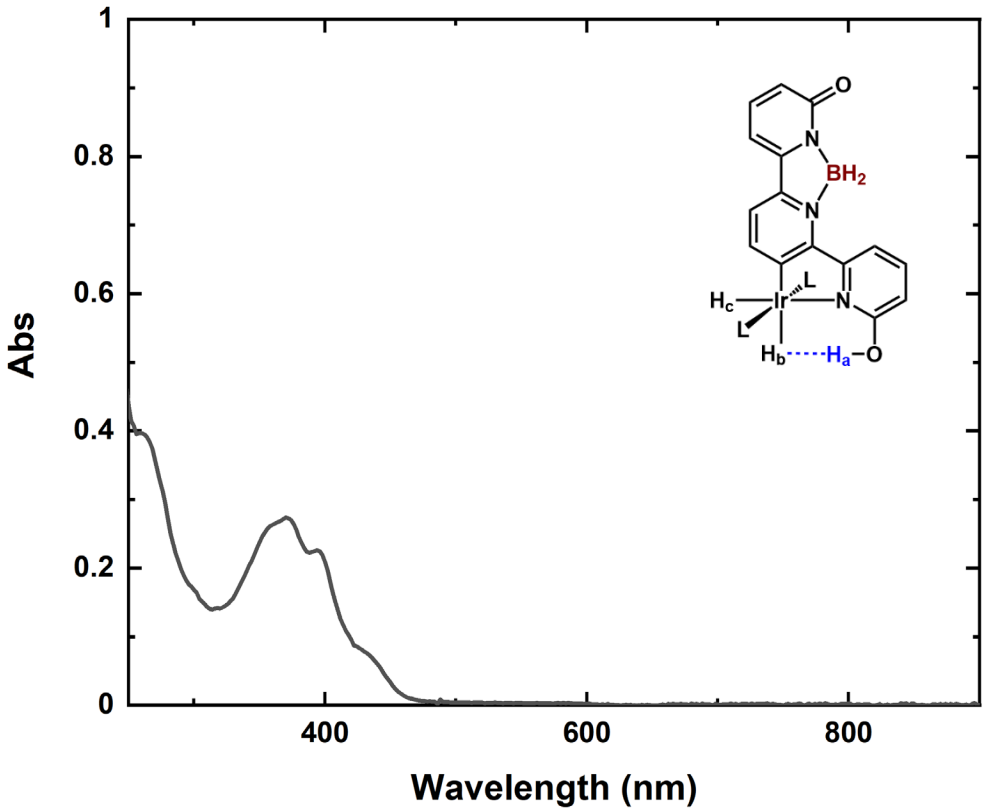


Figure S24. Electronic absorption spectrum of **2** recorded in CH_2Cl_2 at ambient temperature.

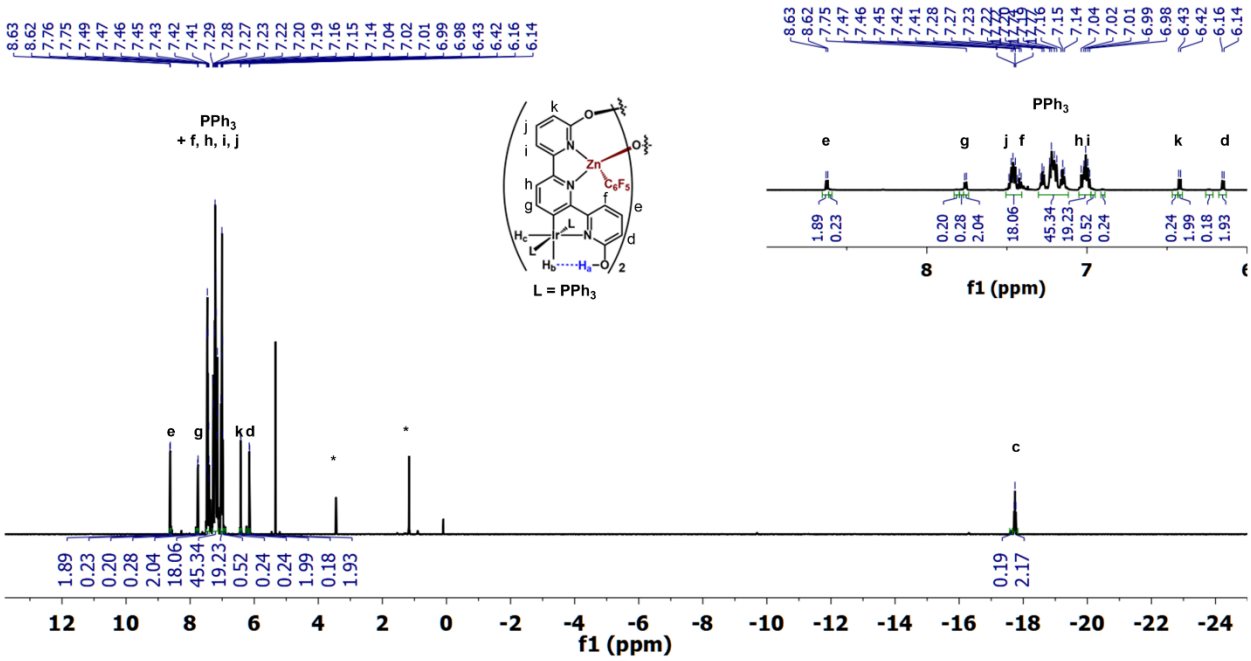


Figure S25. ^{1}H NMR spectrum (CD_2Cl_2, 700 MHz, 25 °C) of **3**. Residual Et_2O is denoted by (*). Additional integrals of an inseparable compound proposed to be the diastereomer of **3** is present at 20% yield and accounts for the excess integration of the PPh_3 region.

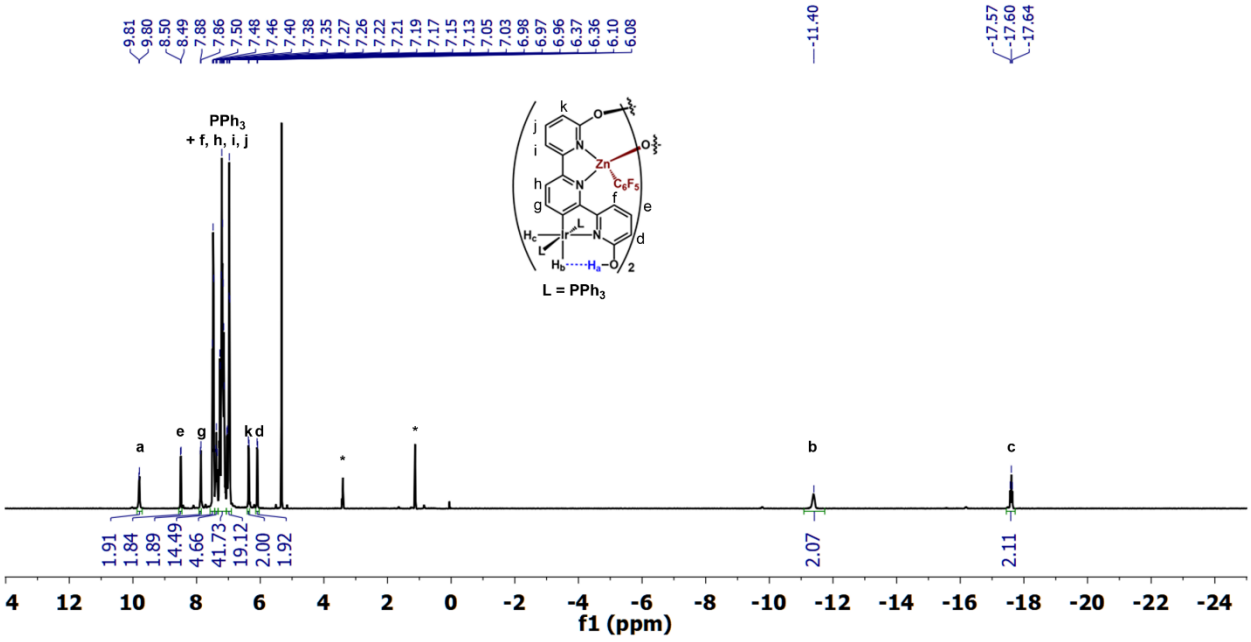


Figure S26. ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, -35°C) of **3**. Residual Et_2O is denoted by (*).

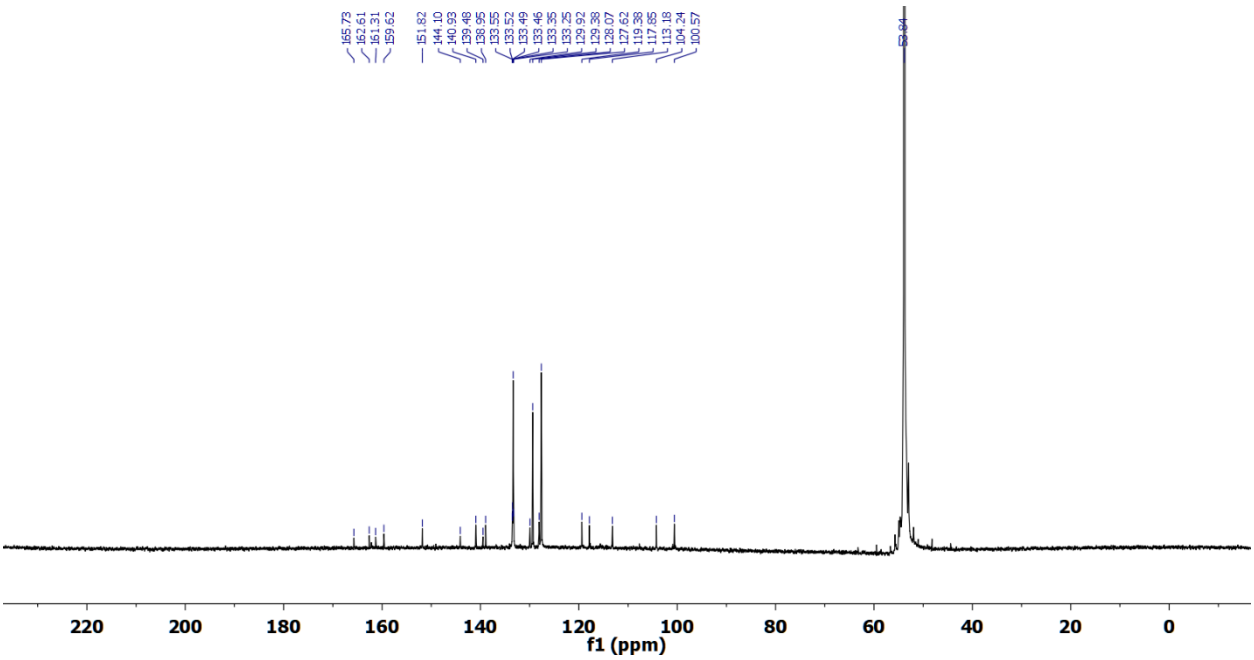


Figure S27. ^{13}C NMR spectrum (CH_2Cl_2, 176 MHz, 25 °C) of **3**. Note peaks for the perfluoro phenyl groups are not observed which we attribute to multiple C-F coupling interactions.

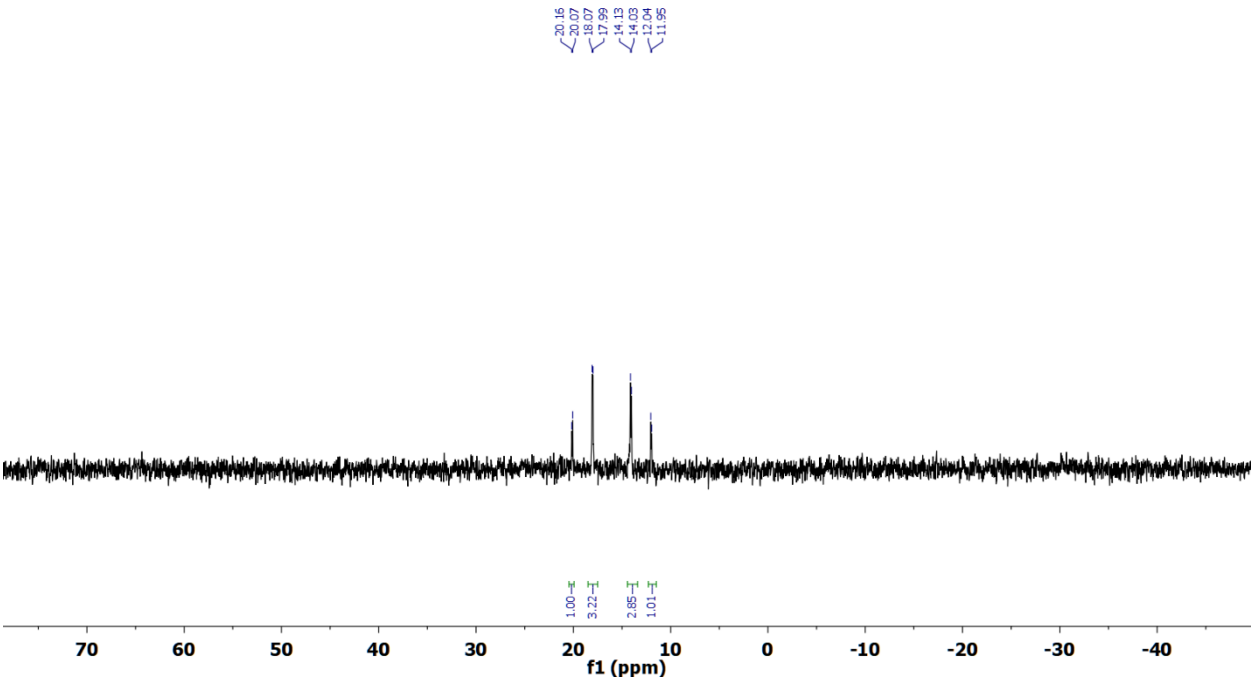


Figure S28. ^{31}P NMR spectrum (CD_2Cl_2, 162 MHz, 25 °C) of **3**.

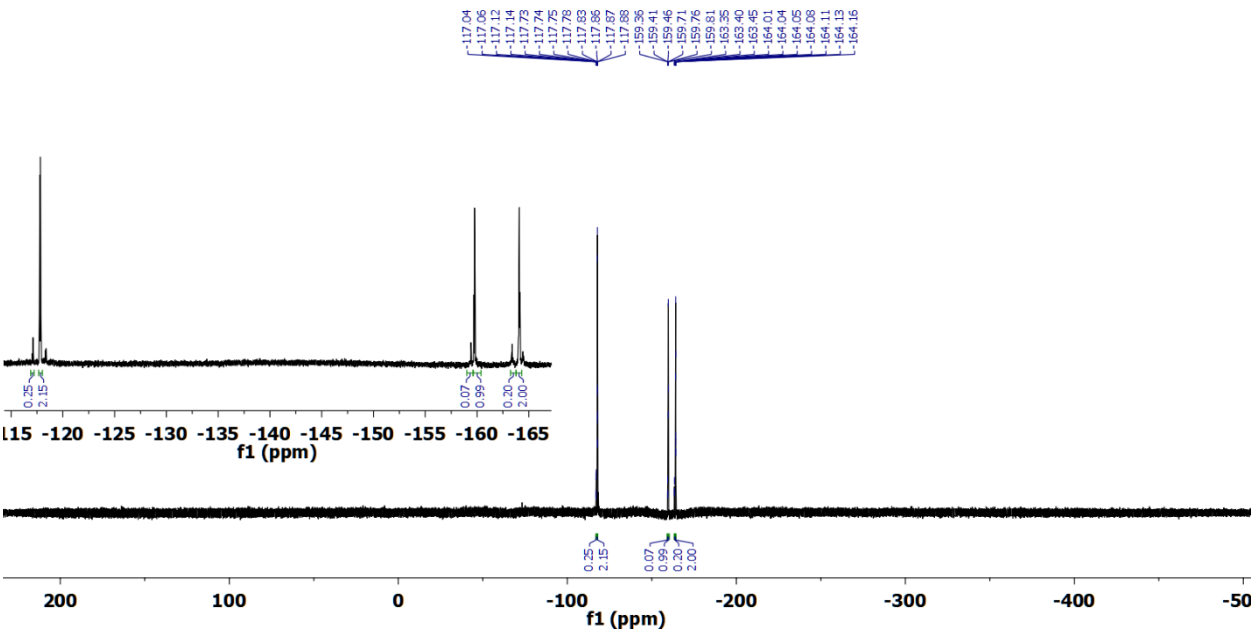


Figure S29. ^{19}F NMR spectrum (CD_2Cl_2, 376 MHz, 25 °C) of **3** with inset.

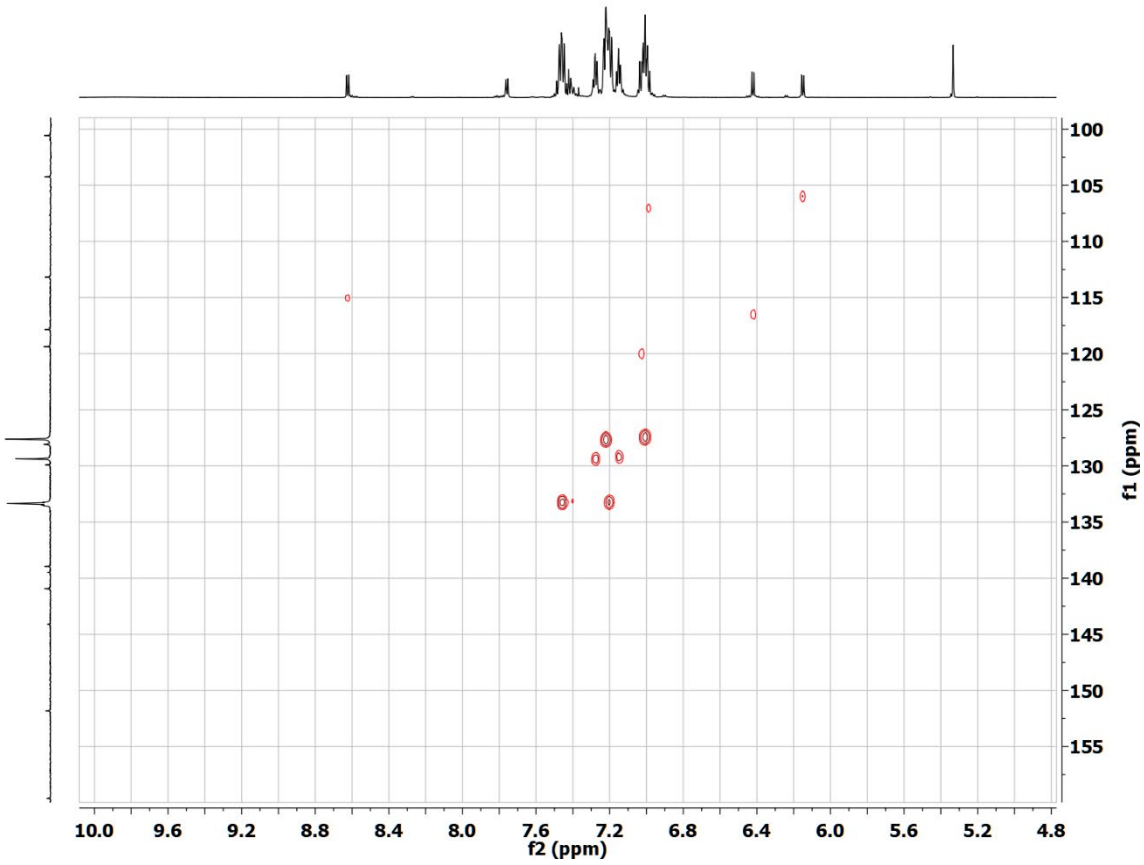


Figure S30. ^{1}H HSQC NMR spectrum (CD_2Cl_2, 25 °C) of **3**.

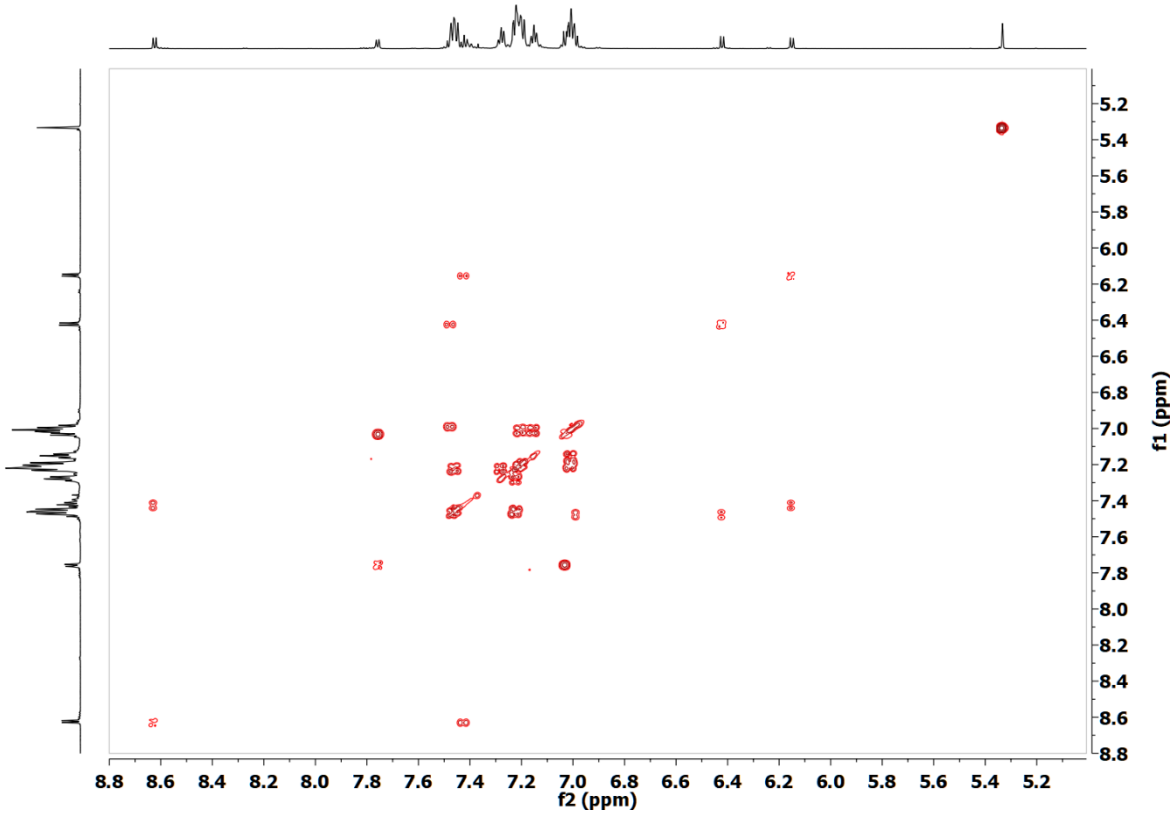


Figure S31. ^{1}H g-COSY NMR spectrum (CD_2Cl_2, 700 MHz, 25 °C) of **3**.

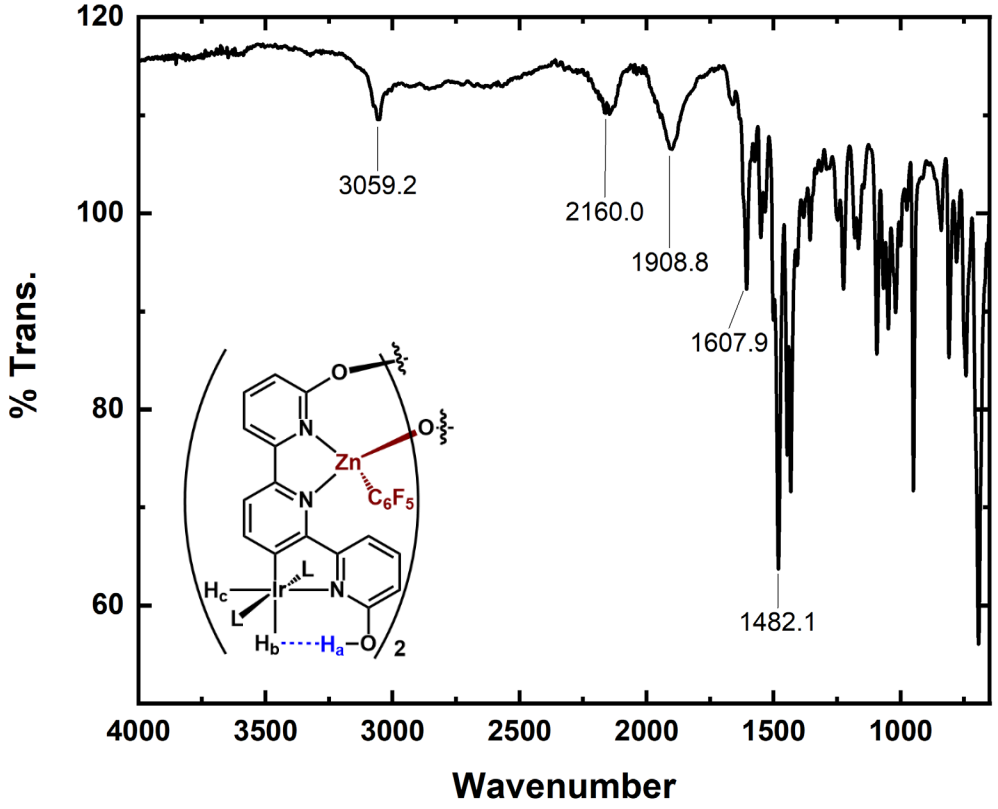


Figure S32. Infrared spectrum (ATIR) of **3**.

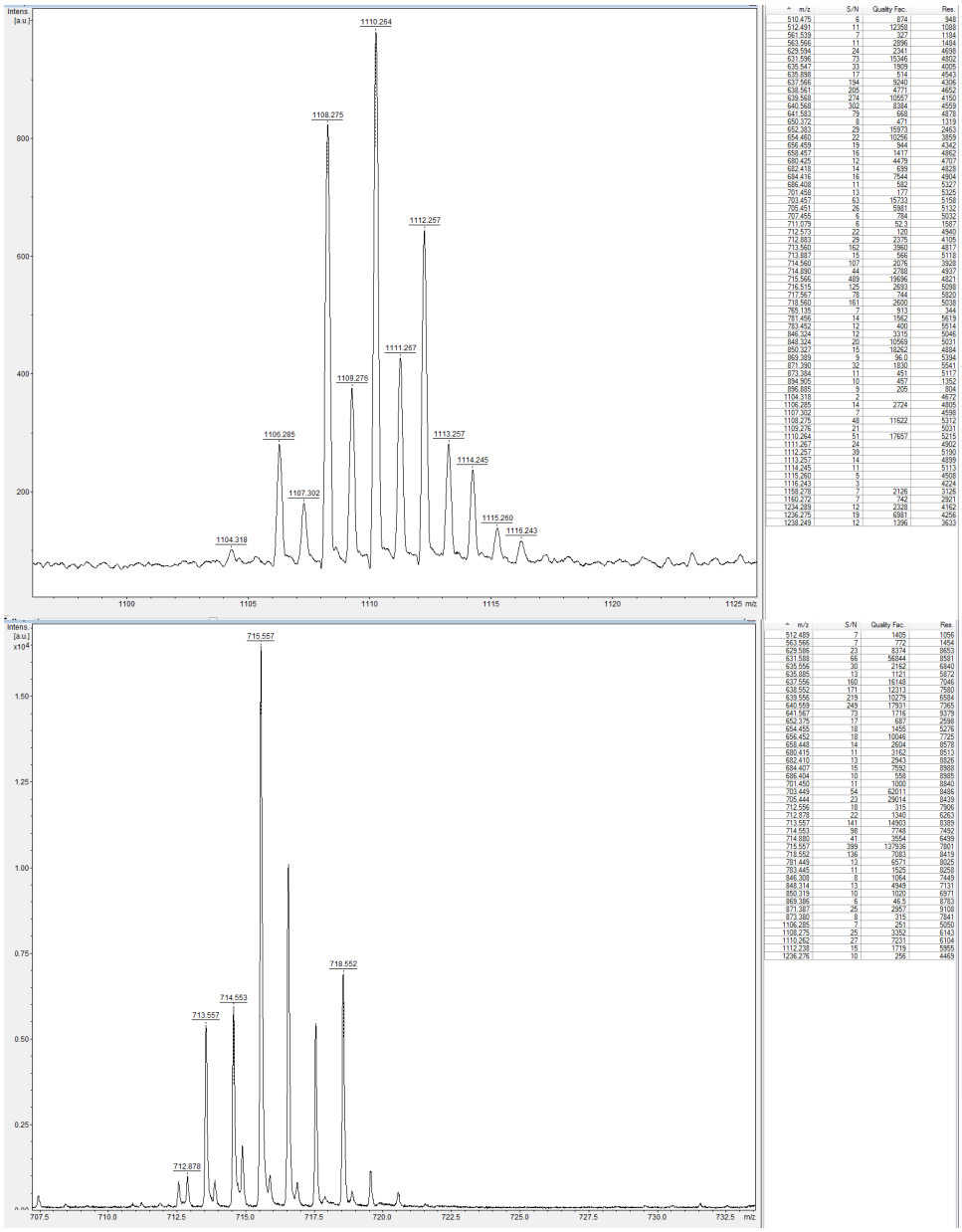


Figure S33. MALDI-TOF analysis of **3**.

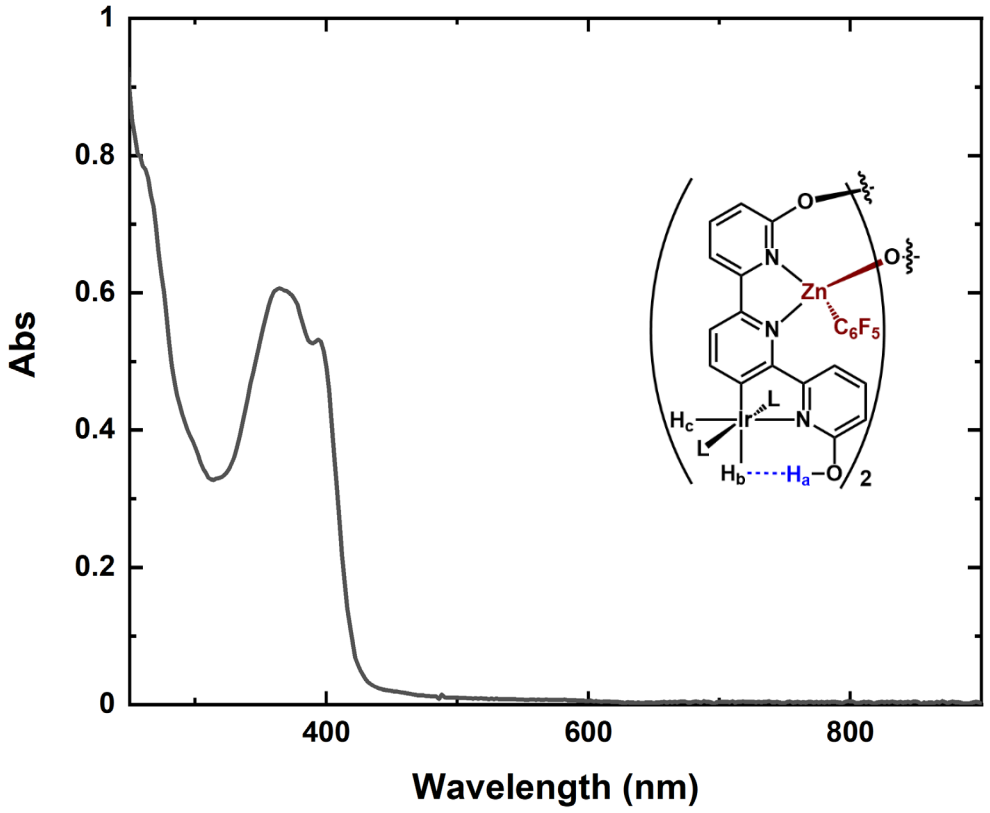


Figure S34. Electronic absorption spectrum of **3** recorded in CH_2Cl_2 at ambient temperature.

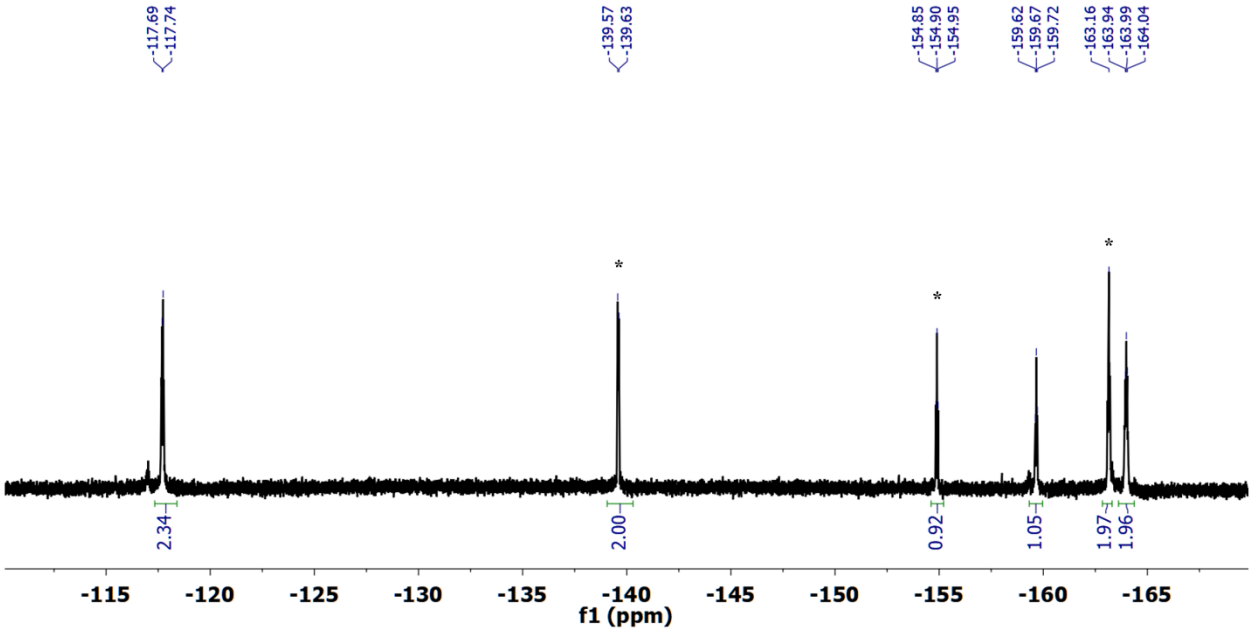


Figure S35. ^{19}F NMR (CH_2Cl_2, 376 MHz, 25 °C) spectrum of a reaction aliquot of **3**. Denoted (*) peaks are consistent with literature[6] values for HC_6F_5.

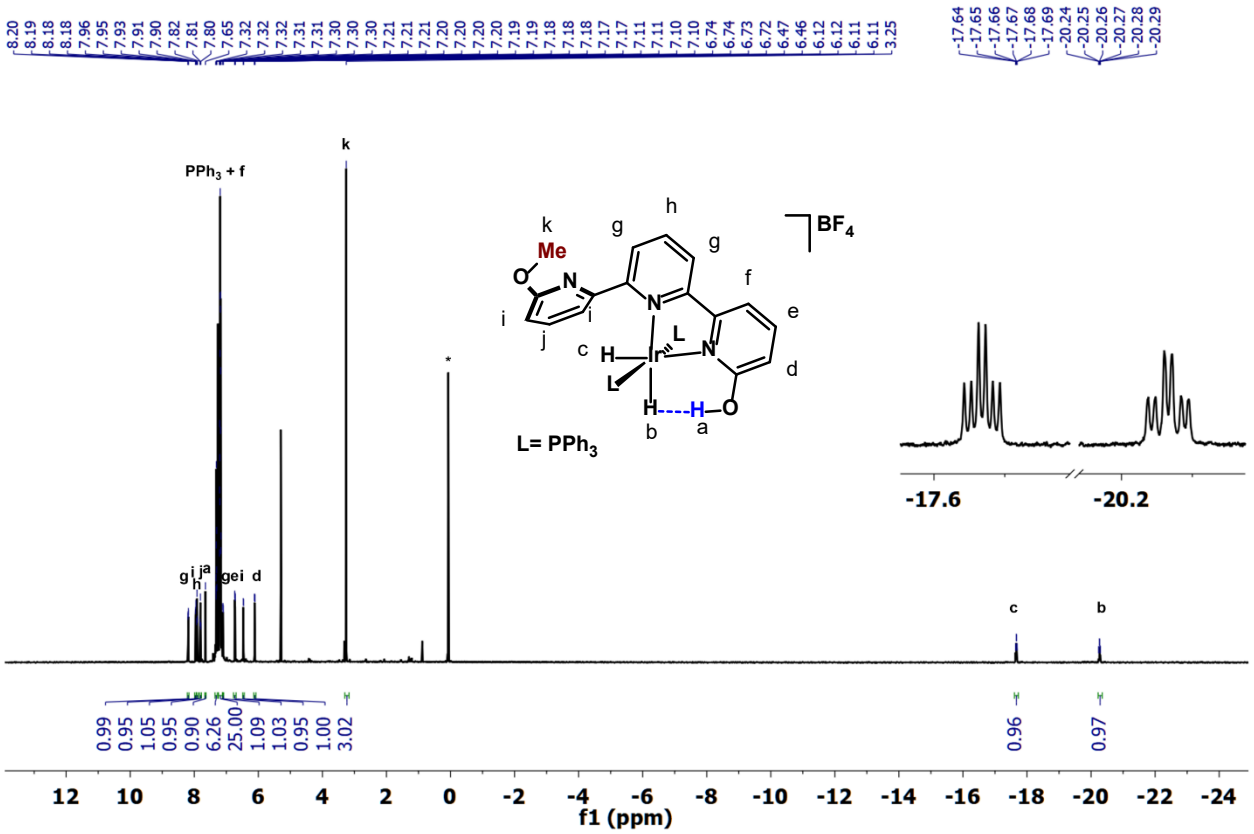


Figure S36. ^{1}H NMR spectrum ($CDCl_3$, 700 MHz, 25 °C) of **4**.

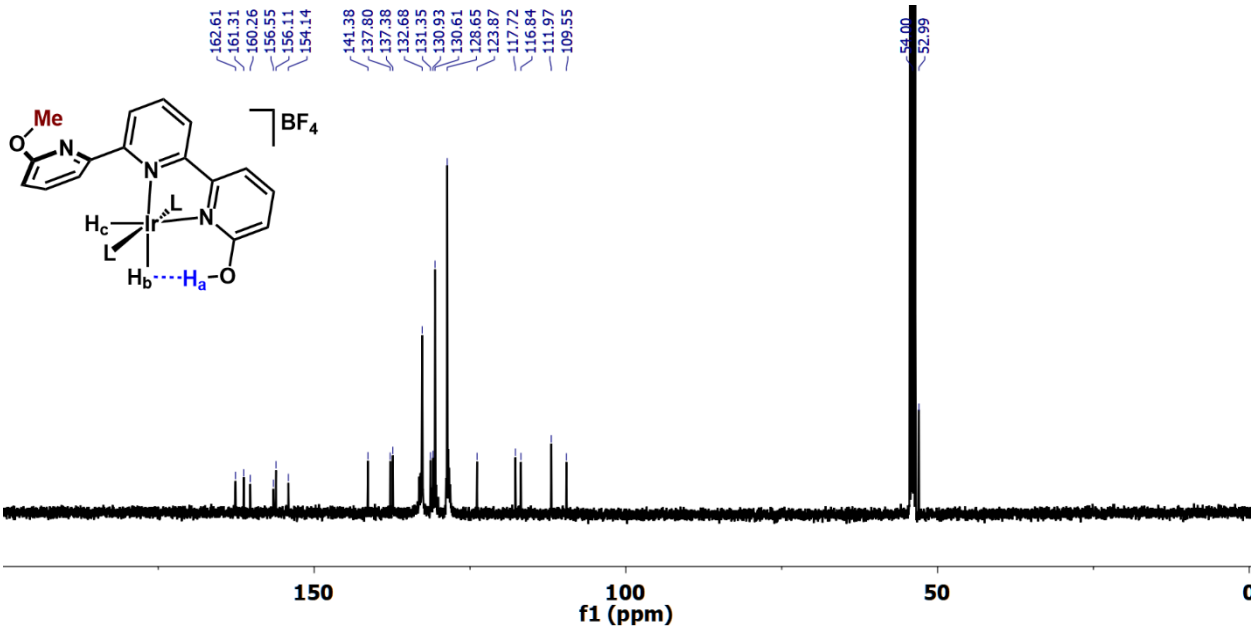


Figure S37. ^{13}C NMR spectrum (CD_2Cl_2, 126 MHz, 25 °C) of **4**.

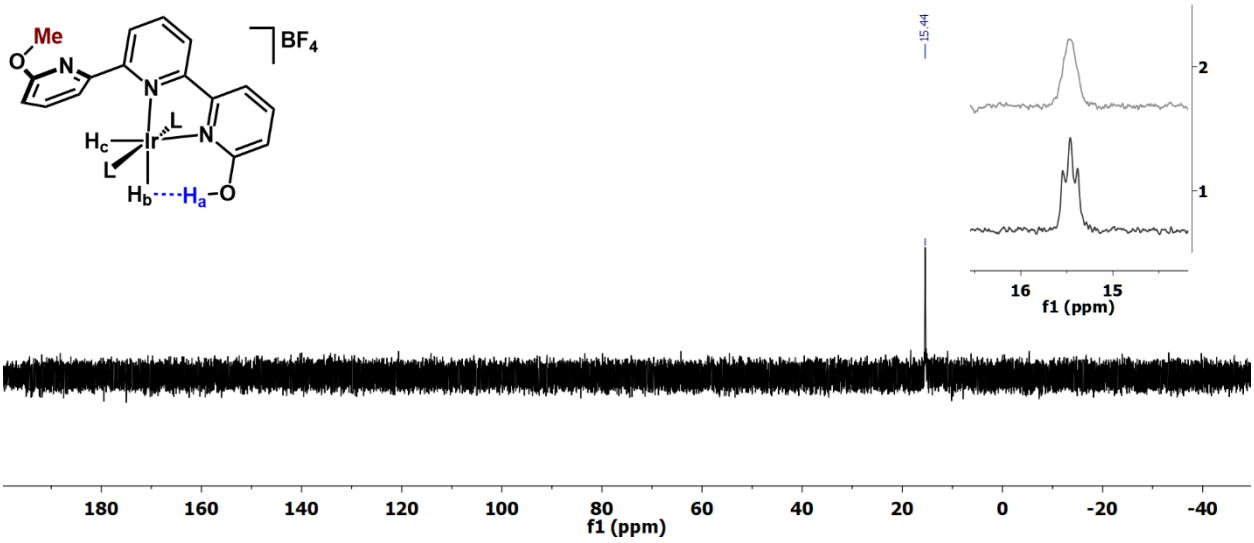


Figure S38. $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 162 MHz, 25 °C) of **4** with inset comparison of $^{31}P\{^1H\}$ (top) and ^{31}P (bottom) coupling.

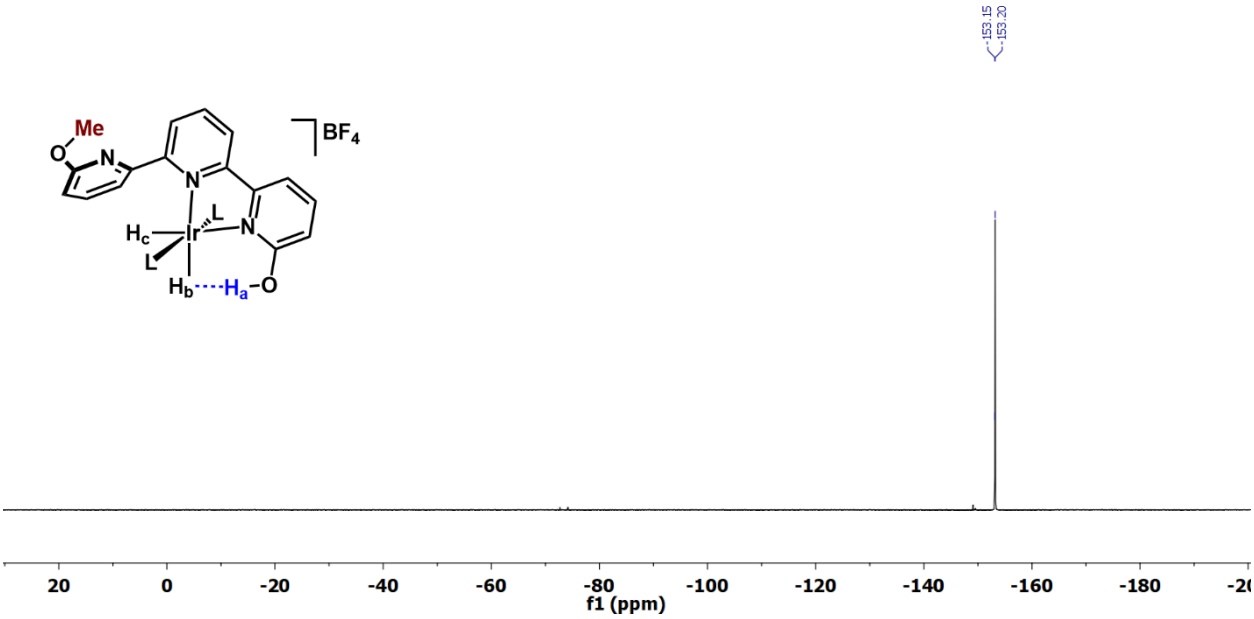


Figure S39. ^{19}F NMR spectrum (CD_2Cl_2, 471 MHz, 25 °C) of **4**.

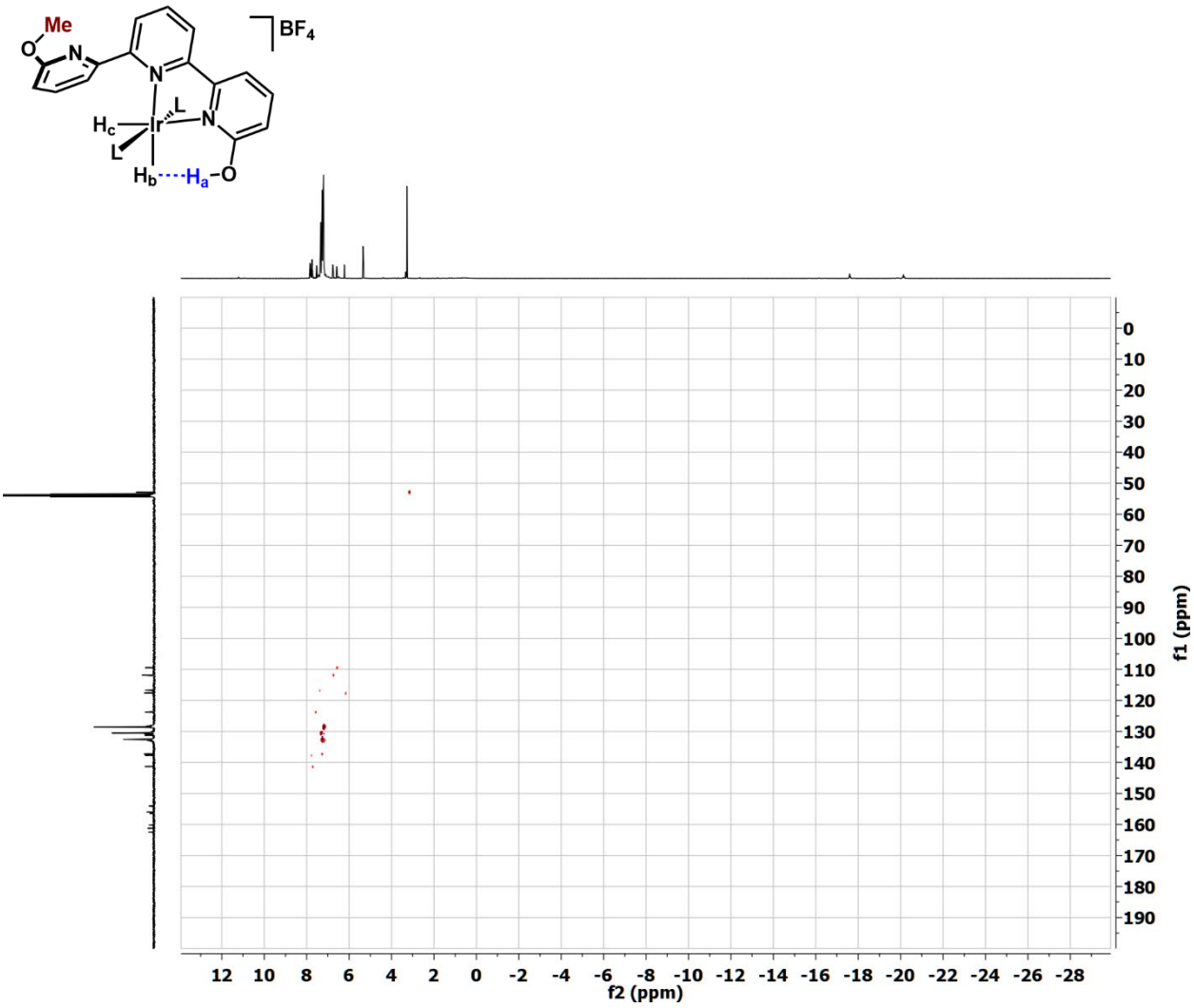


Figure S40. ^{1}H HSQC NMR spectrum (CD_2Cl_2, 25 °C) of **4**.

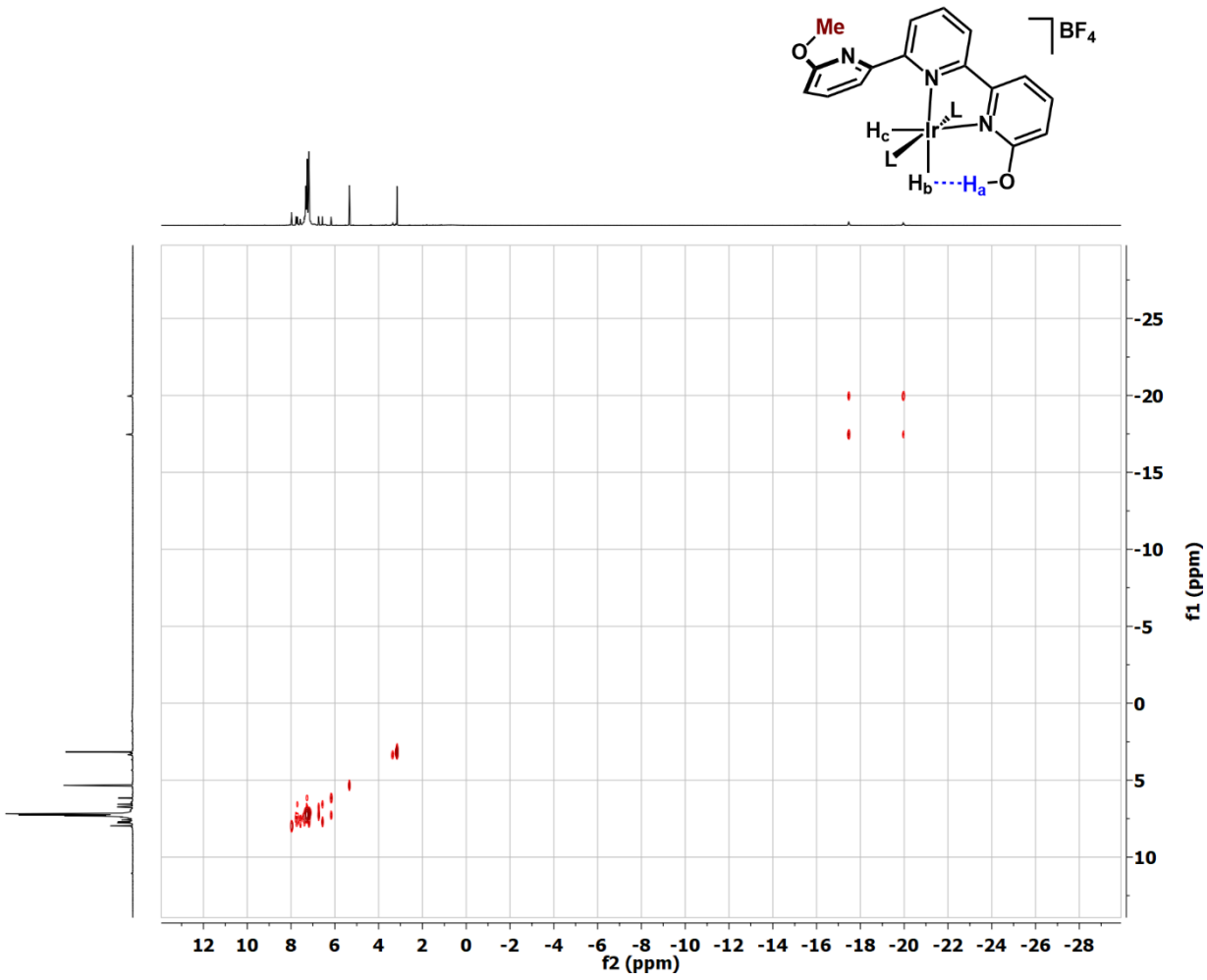


Figure S41. ^{1}H g-COSY NMR spectrum (CD_2Cl_2, 700 MHz, 25 °C) of **4**.

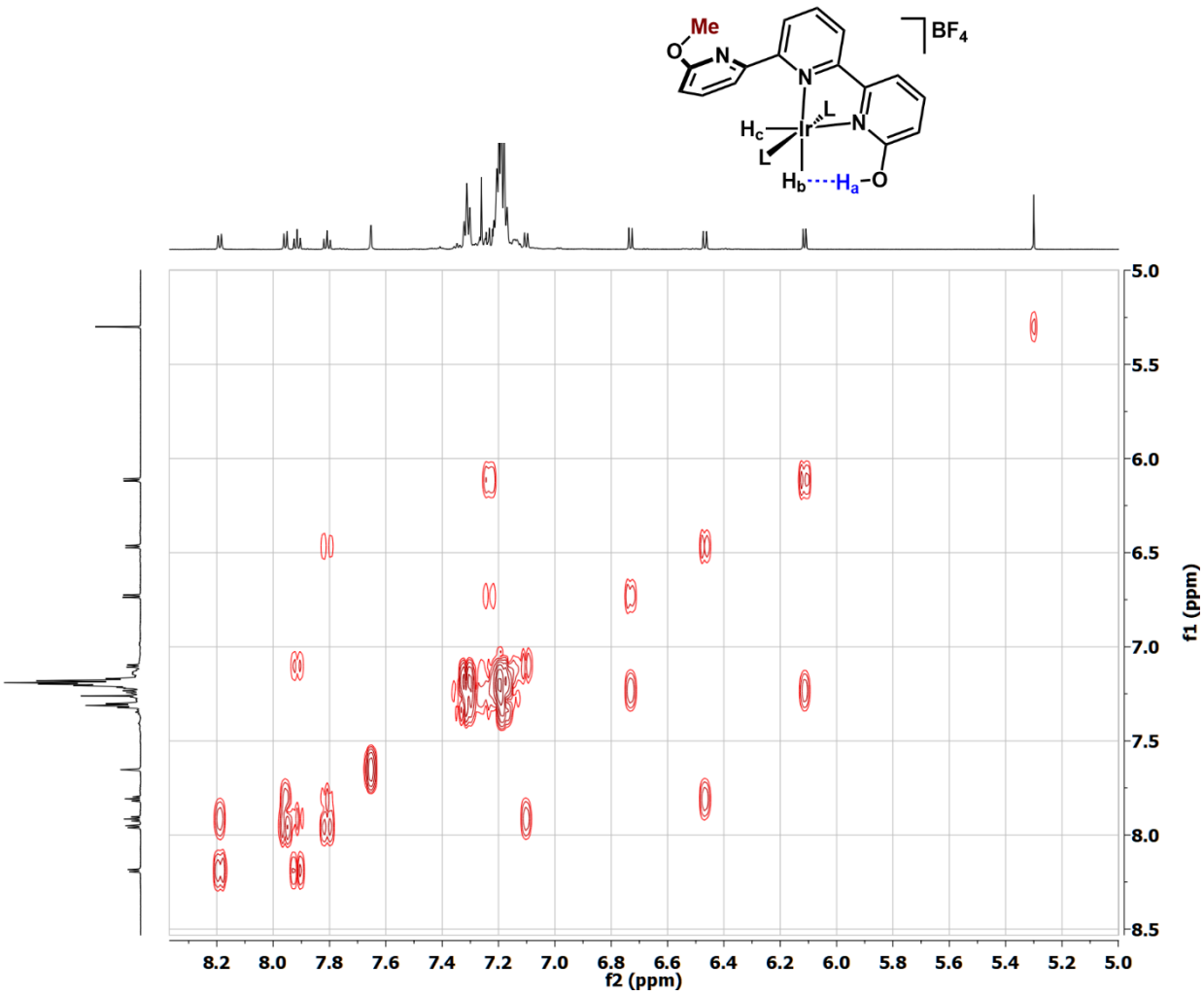


Figure S42. ^{1}H g-COSY NMR spectrum ($CDCl_3$, 700 MHz, 25 °C) of **4** of aromatic region.

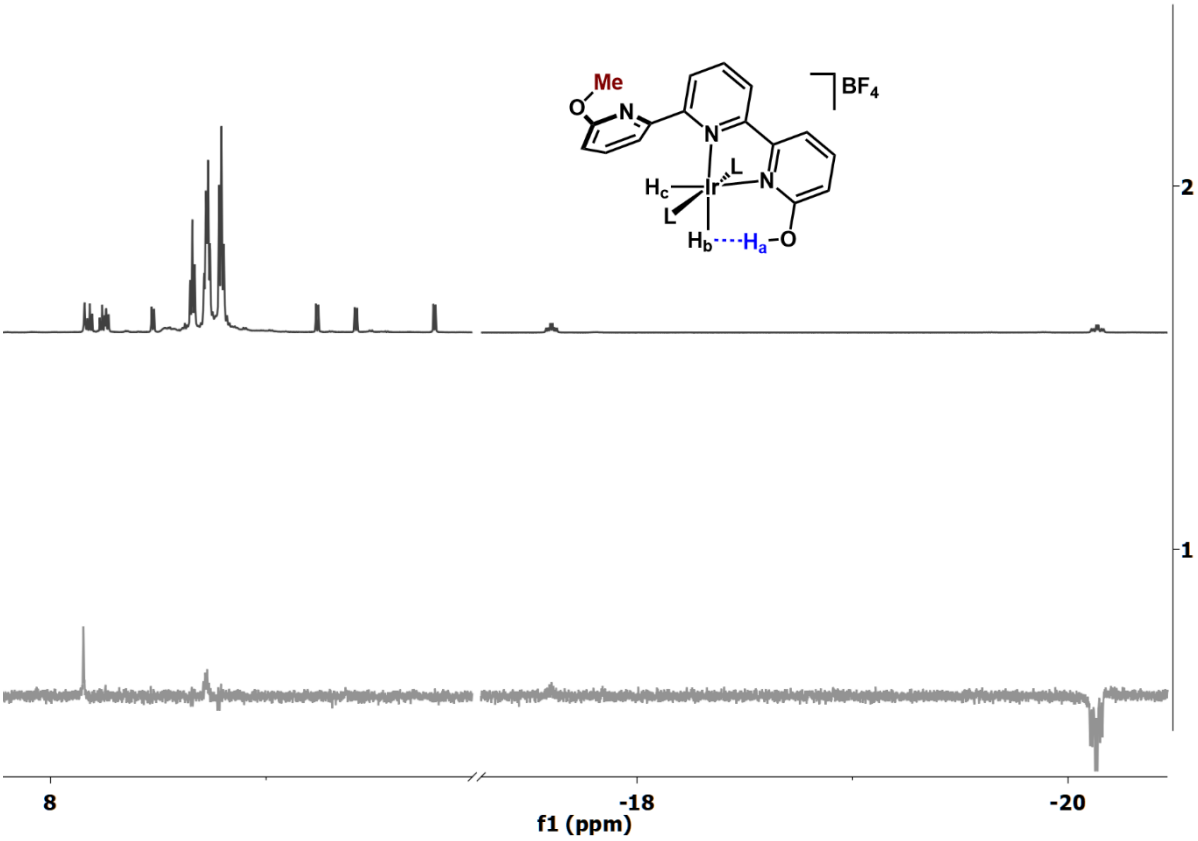


Figure S43. ^{1}H NMR spectra (CD_2Cl_2, 700 MHz, 35 °C) of **4** (top) and corresponding NOESY spectrum (bottom) with a selective irradiation pulse (63 Hz) centered at -20.6 ppm.

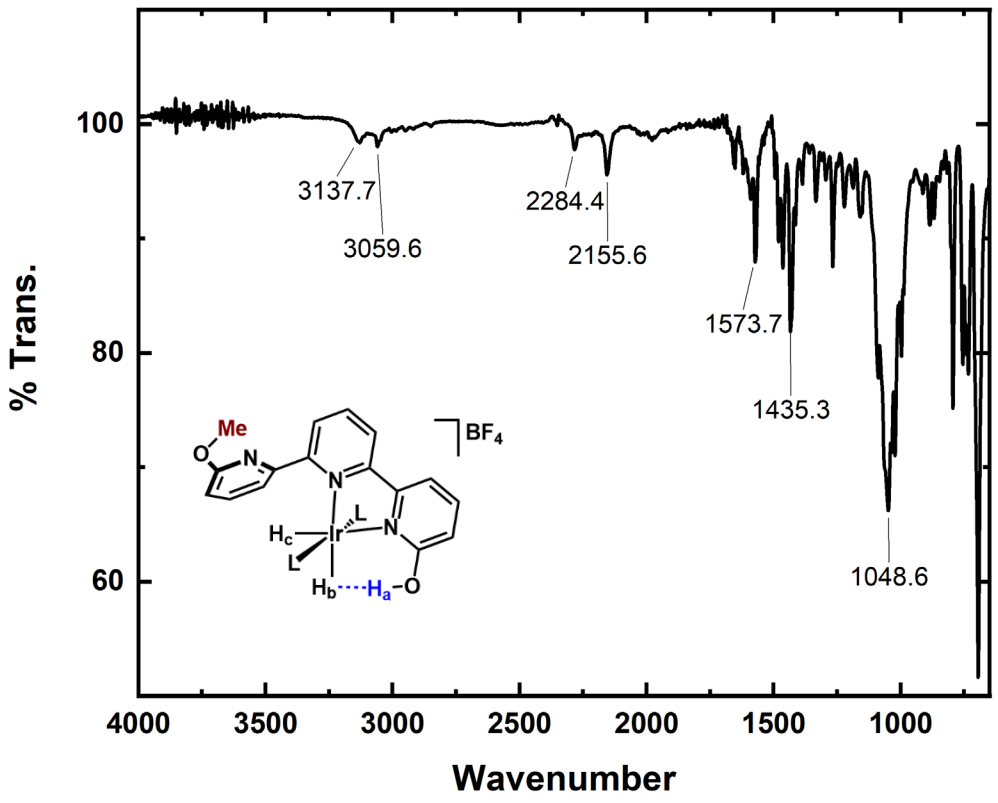


Figure S44. Infrared spectrum (ATIR) of **4**.

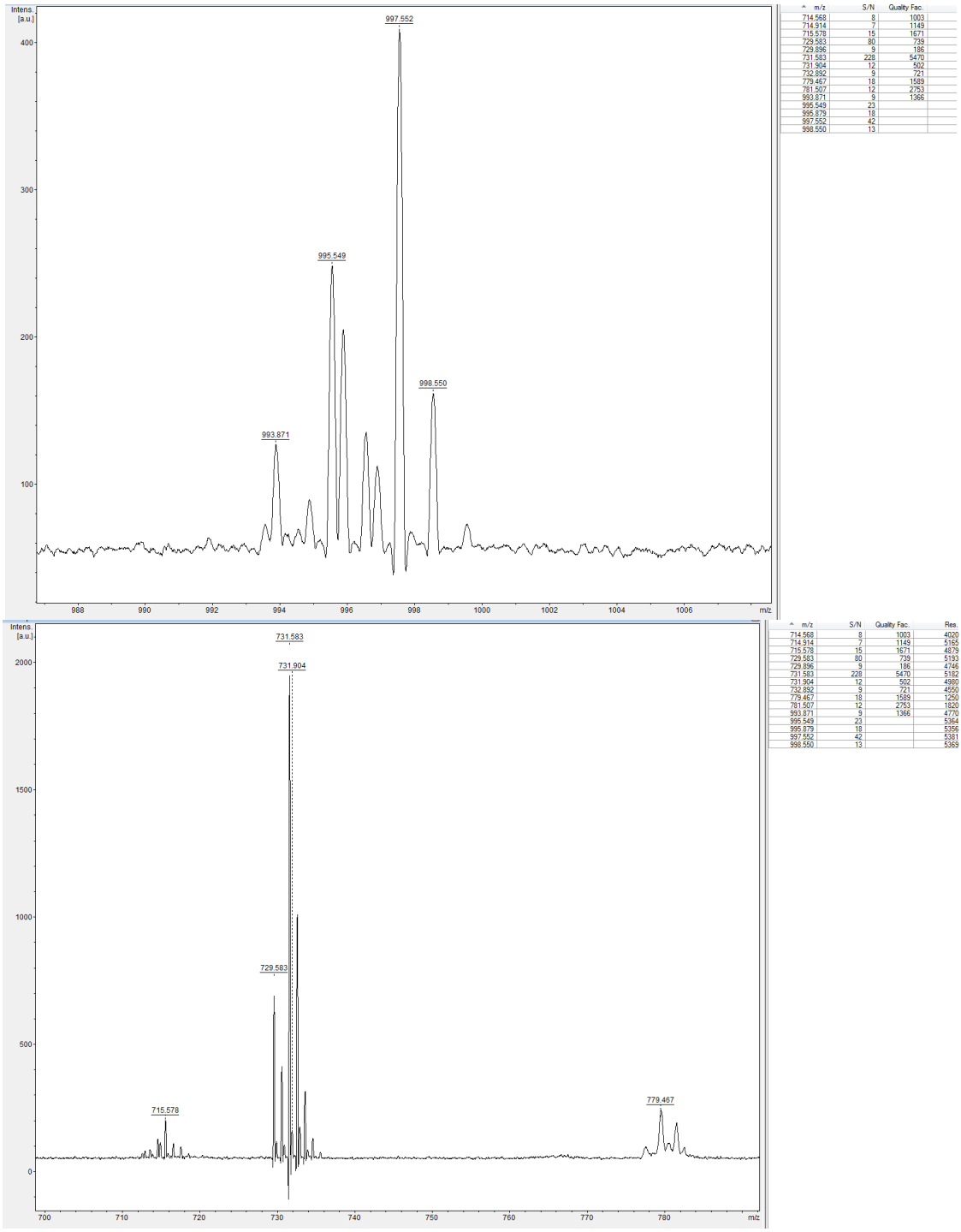


Figure S45. MALDI-TOF analysis of **4**.

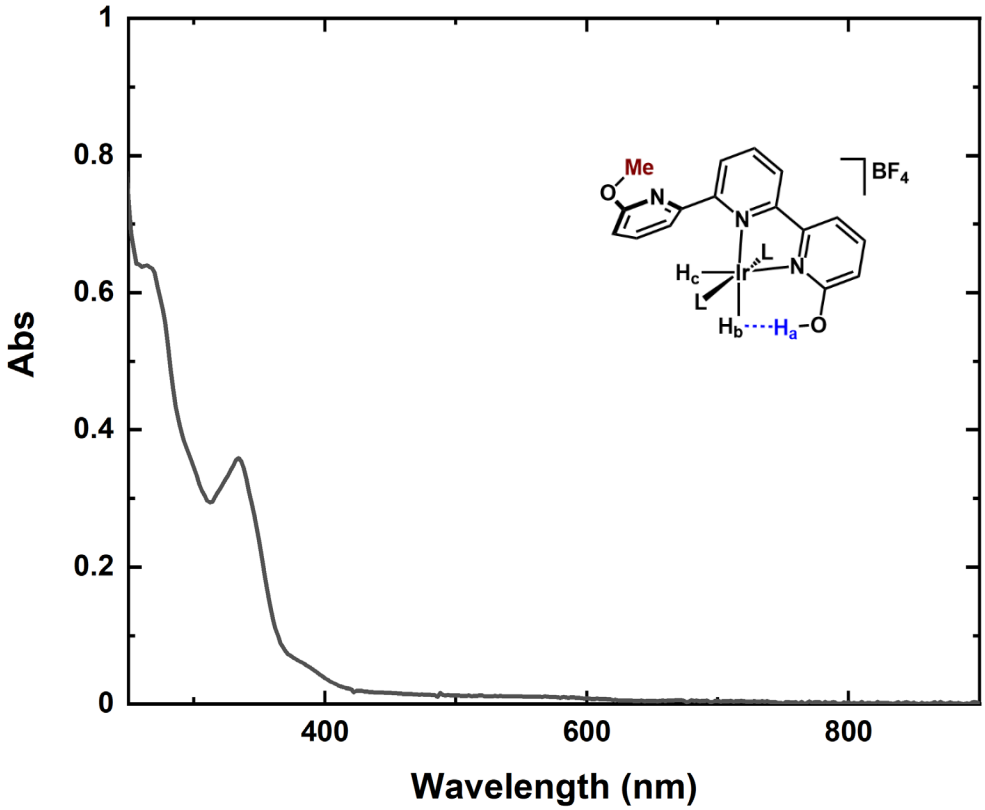


Figure S46. Electronic absorption spectrum of **4** recorded in CH_2Cl_2 at ambient temperature.

Crystallographic analysis:

Compound: $Ir(H)_2(PPh_3)_2(dhtp)$
Local Name: cm4119_sq
CCDC: 2103821

Table S3. Crystallographic parameters for **1**.

Crystal data	
Chemical formula	$2(C_{51}H_{42}IrN_3O_2P_2)\cdot(C_4H_{10}O)\cdot1.5(CH_2Cl_2)$[+solvent]
M_r	1083.77
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	85
a, b, c (Å)	15.9510 (1), 27.4111 (2), 23.7638 (1)
β (°)	103.551 (1)
V (Å^3)	10101.10 (11)
Z	8
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.78
Crystal size (mm)	0.06 × 0.02 × 0.02
Data collection	
Diffractometer	Rigaku Saturn 944+ CCD
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.586, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	302176, 20398, 17811
R_{int}	0.106
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.049, 0.141, 1.04
No. of reflections	20398
No. of parameters	1194
No. of restraints	45
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 36.524P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.05, −1.94

Computer programs: *CrystalClear*-SM Expert 2.0 r16 (Rigaku, 2014), *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2008), Bruker *SHELXTL*.

Refinement details:

Yellow needles of **cm4119_sq** were grown from a dichloromethane/diethyl ether solution of the compound at 20 deg. C. A crystal of dimensions 0.06 x 0.02 x 0.02 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 4159 images were collected with an oscillation width of 1.0° in ω. The exposure times were 4 sec. for the low angle images, 16 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 302176 reflections to a maximum 2θ value of 148.26° of which 20398 were independent and 17811 were greater than 2σ(I). The final cell constants (Table S3) were based on the xyz centroids of 66886 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P2(1)/n with Z = 8 for the formula $C_{51}H_{42}N_3O_2P_2Ir$, $(C_4H_{10}O)$, $1.5(CH_2Cl_2)$, [+ solvent]. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0485 and wR2 = 0.1341 [based on I > 2sigma(I)], R1 = 0.0550 and wR2 = 0.1406 for all data. The SQUEEZE subroutine of the PLATON program suite[7] was used to address the disordered solvent contained in solvent accessible voids present in the structure. Additional details are presented in Table S3 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

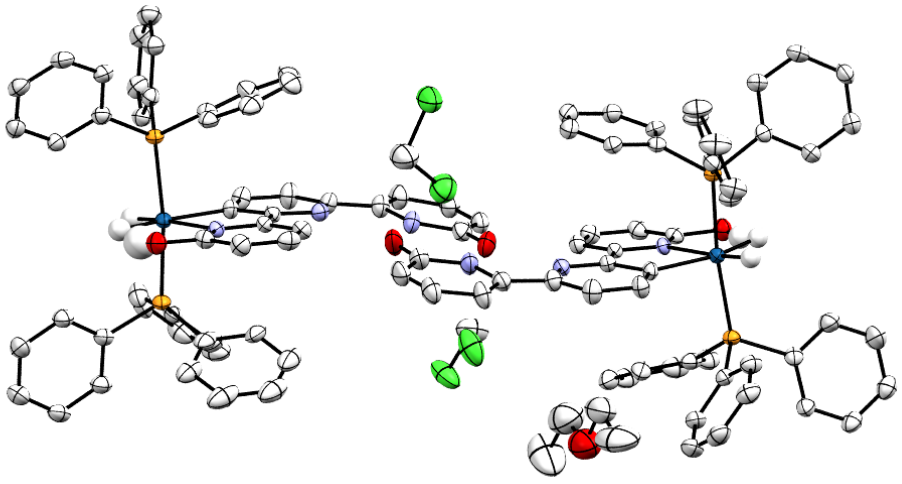


Figure S47. Molecular structure of **1 CH_2Cl_2 Et_2O** with 50% probability ellipsoids. Hydrogen atoms not bound to iridium or engaged in hydrogen bonds are omitted for clarity.

Compound: $Ir(H)_2(PPh_3)_2(dhtp\text{-}BH_2)$
Local Name: CM4189
CCDC: 2103820

Table S4. Crystallographic parameters for **2**.

Crystal data	
Chemical formula	$C_{51}H_{42}BIrN_3O_2P_2 \cdot 2(C_4H_{10}O)$
M_r	1142.06
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	85
a, *b*, *c* (Å)	15.63118 (7), 23.44856 (10), 14.12898 (8)
V (Å^3)	5178.68 (4)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	5.97
Crystal size (mm)	0.12 × 0.07 × 0.07
Data collection	
Diffractometer	Rigaku Saturn 944+ CCD
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.716, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	158777, 5373, 5327
R_{int}	0.063
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.624
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.092, 1.06
No. of reflections	5373
No. of parameters	362
No. of restraints	22
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2 + 11.3361P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.26, −1.30

Computer programs: *CrystalClear*-SM Expert 2.0 r12 (Rigaku, 2011), *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2008), Bruker *SHELXTL*.

Refinement details:

Yellow needles of **cm4189** were grown from a dichloromethane/diethyl ether solution of the compound at 22 deg. C. A crystal of dimensions 0.12 x 0.07 x 0.07 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 4281 images were collected with an oscillation width of 1.0° in ω. The exposure times were 2 sec. for the low angle images, 10 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 15877 reflections to a maximum 2θ value of 148.08° of which 5373 were independent and 5327 were greater than 2σ(I). The final cell constants (Table S4) were based on the xyz centroids of 79038 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P_{nma} with Z = 4 for the formula $C_{59}H_{62}BN_3O_4P_2Ir$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0355 and wR2 = 0.0920 [based on I > 2sigma(I)], R1 = 0.0357 and wR2 = 0.0921 for all data. Additional details are presented in Table S4 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

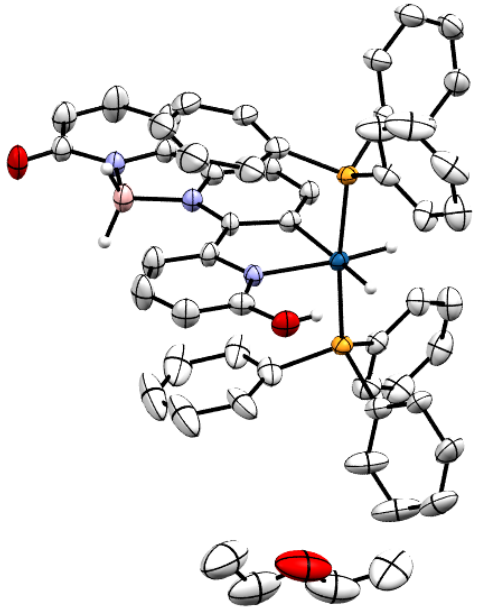


Figure S48. Molecular structure of **2 Et_2O** with 50% probability ellipsoids. Hydrogen atoms not bound to iridium, boron or engaged in hydrogen bonds are omitted for clarity.

Compound: $[Ir(H)_2(PPh_3)_2(dhtp\text{-}ZnAr^F)]_2$
Local Name: jps1089
CCDC: 2103819

Table S5. Crystallographic parameters for **3**.

Crystal data	
Chemical formula	$'(C_{114}H_{82}F_{10}Ir_2N_6O_4P_4Zn_2)\cdot 1.5(C_5H_{12})\cdot(CH_2Cl_2)'$
M_r	2622.01
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	85
a, b, c (Å)	15.0726 (4), 19.6116 (6), 20.9592 (6)
α, β, γ (°)	74.069 (3), 71.860 (2), 80.182 (2)
V (Å^3)	5636.9 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	6.52
Crystal size (mm)	0.08 × 0.07 × 0.06
Data collection	
Diffractometer	Rigaku Saturn 944+ CCD
Absorption correction	Multi-scan
T_{min}, T_{max}	0.851, 1.000
No. of measured, independent	84816, 20413, 17789
R_{int}	0.093
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.608
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.163, 1.02
No. of reflections	20413
No. of parameters	1580
No. of restraints	538
H-atom treatment	H atoms treated by a mixture of independent and constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.25, −2.21

Computer programs: *CrystalClear*-SM Expert 2.0 r16 (Rigaku, 2014), *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2008), Bruker *SHELXTL*.

Refinement details:

Yellow blocks of **jps1089** were grown layering pentane on a concentrated dichloromethane solution of the compound at 20 deg. C. A crystal of dimensions 0.08 x 0.07 x 0.06 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating

anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 3 sec. for the low angle images, 25 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 84816 reflections to a maximum 2θ value of 139.39° of which 20413 were independent and 17789 were greater than 2σ(I). The final cell constants (Table S5) were based on the xyz centroids of 32621 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P1bar with Z = 2 for the formula $C_{122.5}H_{102}N_6O_4P_4Cl_2Zn_2Ir_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. One triphenylphosphine ligand is disordered in two orientations. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0559 and wR2 = 0.1529 [based on I > 2sigma(I)], R1 = 0.0628 and wR2 = 0.1629 for all data. Additional details are presented in Table S5 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

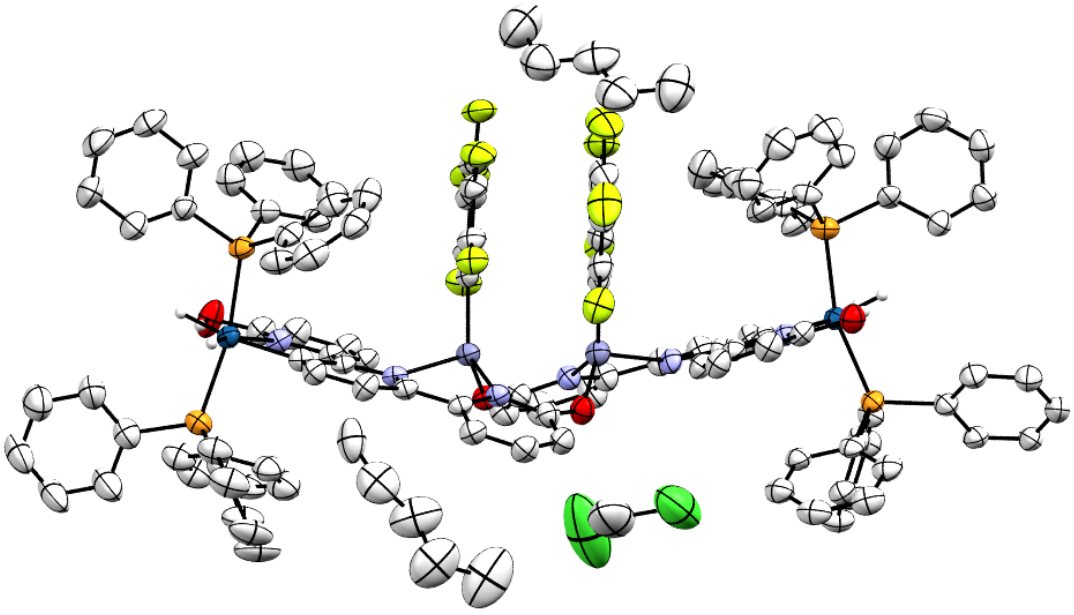


Figure 49. Molecular structure of **3** CH_2Cl_2 $2C_5H_{12}$ with 50% probability ellipsoids. Hydrogen atoms not bound to iridium or engaged in hydrogen bonds are omitted for clarity. Disordered positions of one triphenyl phosphine ligand have been omitted for clarity.

Compound: $[Ir(H)_2(PPh_3)_2(tpy^{OHOCH3})][BF_4]$
Local Name: jps2254
CCDC 2103818

Table S6. Crystallographic parameters for **4**.

Crystal data	
Chemical formula	$C_{52}H_{45}IrN_3O_2P_2 \cdot BF_4 \cdot CH_2Cl_2$
M_r	1169.78
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	85
a, b, c (Å)	11.0219 (1), 22.6904 (1), 19.9096 (1)
β (°)	105.642 (1)
V (Å^3)	4794.81 (6)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	7.56
Crystal size (mm)	0.24 × 0.19 × 0.16
Data collection	
Diffractometer	Rigaku Saturn 944+ CCD
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.363, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	71360, 8949, 8941
R_{int}	0.074
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.607
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.097, 1.13
No. of reflections	8949
No. of parameters	701
No. of restraints	99
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2 + 12.7248P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.99, −2.13

Computer programs: *CrystalClear*-SM Expert 2.0 r16 (Rigaku, 2014), *CrysAlis PRO* 1.171.40.53 (Rigaku OD, 2019), *SHELXT* (Sheldrick, 2014), *SHELXL2018*/3 (Sheldrick, 2008), Bruker *SHELXTL*.

Refinement details:

Yellow plates of **jps2254** were grown from a dichloromethane/diethyl ether solution of the compound at 20 deg. C. A crystal of dimensions 0.24 x 0.19 x 0.16 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 A) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 2028 images were collected with an oscillation width of 1.0° in ω. The exposure times were 1 sec. for the low angle images, 6 sec. for high angle. Rigaku d*trek images were exported to CrysAlisPro for processing and corrected for absorption. The integration of the data yielded a total of 71360 reflections to a maximum 2θ value of 138.90° of which 8949 were independent and 8941 were greater than 2σ(I). The final cell constants (Table S6) were based on the xyz centroids of 59657 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection. The structure was solved and refined with the Bruker SHELXTL (version 2018/3) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{53}H_{47}BN_3O_2F_4P_2Cl_2Ir$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of idealized and refined positions. The dichloromethane solvate and tetrafluoroborate anion are both disordered. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0362 and wR2 = 0.0970 [based on I > 2sigma(I)], R1 = 0.0363 and wR2 = 0.0970 for all data. Additional details are presented in Table S6 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

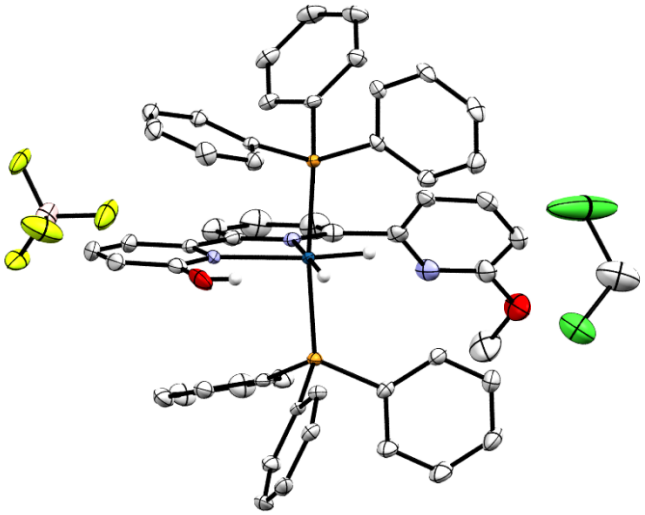


Figure S50. Molecular structure of **4** $\mathbf{CH_2Cl_2}$ with 50% probability ellipsoids Hydrogen atoms not bound to iridium or engaged in hydrogen bonds are omitted for clarity. A single set of atomic positions for the disordered BF_4^- and CH_2Cl_2 groups are shown for clarity.

Table S7. Key bond lengths from the XRD analysis of **1-4**.

Compound	Ir-E (Å)	Ir-E[a] (Å)	Ir-N (Å)	Ir-N[a] (Å)
1	2.018(5)	2.098(5)	2.155(4)	2.149(4)
2	2.081(4)		2.133(3)	
3	2.062(6)	2.073(6)	2.148(4)	2.150(4)
4	2.184(3)		2.150(3)	

a) Denotes secondary coordinate from a second molecule in the unit cell (**1**) or from a dimeric structural unit (**3**).

H_a-H_b distance from dipolar relaxation criteria and crystallographic distances

H_a/H_b distances were determined from dipolar relaxation in accordance with the literature.[8] Interatomic distances were determined from the crystallographic distances for all atoms with the Ir-H_b contacts approximated to be 1.590 Å. This value was selected as the average terminal Ir-H distance as determined by neutron diffraction iridium hydride complexes.[9] K_x values for the calculations at 500 MHz were found in Desrosiers and Halpern et al.

The internuclear separation from these Ir-H corrected distances were used in accordance with equation 2 to solve for the average internuclear separation of H_a and H_b (r_{HH}).

$$\frac{1}{T_1(min)} = \sum_{H-H} \frac{K_H}{{r_{HH}}^6} + \sum_{other\ atoms} \frac{K_x}{r^6} \qquad (2)$$

T_1(min) values for **1**-**4** were established as described in the general considerations. Due to decomposition upon warming, the T_1(min) of compound **3** reflects the minimum value we could experimentally observe but may not reflect a global minimum as higher temperatures would be necessary to verify. When the observed T_1(min) for **3** is used in the expression above a larger than expected H-H distance is obtained and is consistent with not obtaining a global T_1(min) value for **3**. This value provides an upper bound for the distance but is not structurally meaningful as the average H_a-H_b distance.

Table S8. H_a and H_b distances by T_1 criterion method for **1-4**.

Compound	T1(min) H_b (s)	*Other atom contribution*	H_a-H_b distance (Å)
1	0.170	4.70088	2.00
2	0.158	4.05033	1.80
3	0.254	3.98607	< 3.26
4	0.200	3.64503	1.96

Structural Comparison of H_a H_b distances upon measurement method

Table S9. H_a and H_b distances by method for **1-4**.

Compound	XRD (Å)	XRD[a] (Å)	T_1 correction (Å)	DFT (Å)
1	1.7(1)	1.6(1)	2.00	1.5590
2	1.81		1.80	1.5449
3	1.9(1)	2.09(9)	< 3.26	1.5446[b]
4	2.13(7)		1.96	1.7622

a) Denotes secondary coordinate from a second molecule in the unit cell (**1**) or from a dimeric structural unit (**3**).
b) Reported for truncated model **3'**

Computational Details

Structure optimization and frequency analysis was performed using Gaussian 16 revA03-avx2.[10] In accordance with optimized methods for iridium complexes,[11] and appropriate for hydrogen bond interactions,[12] structures were optimized using the PBE functional[13] with atoms H-Zn were treated with the basis set 6-311G(d,p),[14] while LANL2DZ[15] with included ECP augmented with one f-polarization function (0.938) was used for Ir.[16] Calculations were performed with a PCM of dichloromethane.[17] Structures were confirmed minima by the absence of imaginary frequencies. Charge analysis was performed using NBO version 3.0.230 NonCovalent Interaction analysis[18] and AIM[19] were performed using Multiwfn 3.6.[20] NCI isosurfaces are presented at s = 0.5. NCI plots rendered using VMD.[21]

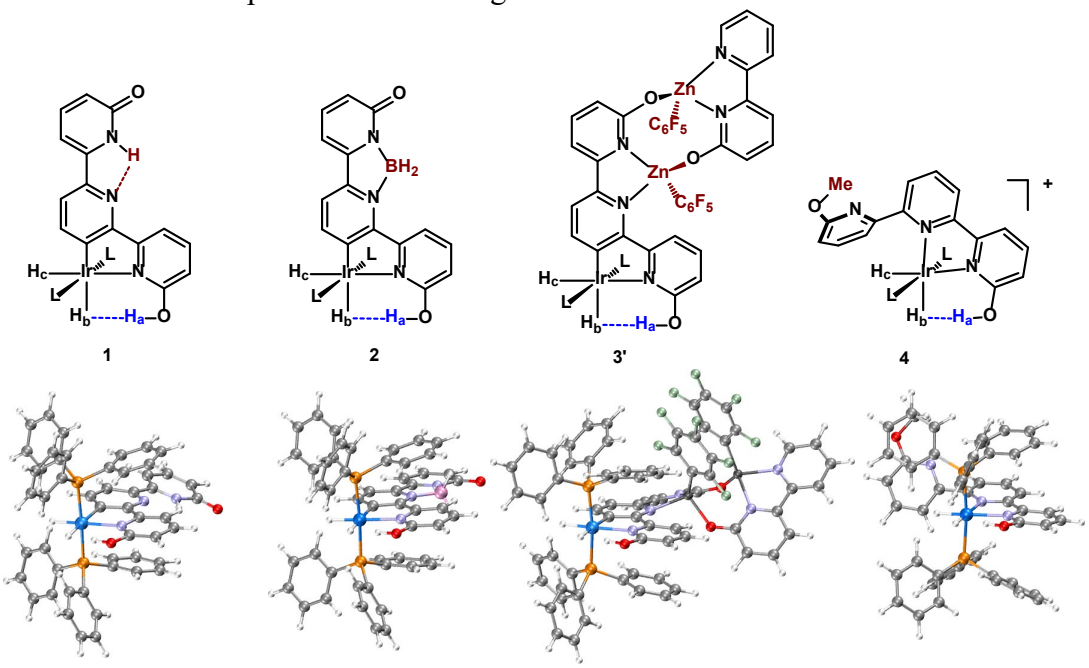
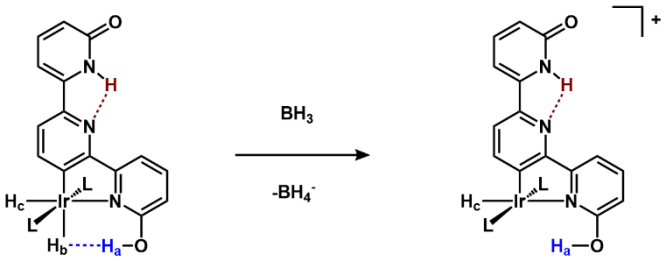


Figure S51. Optimized structures of **1**, **2**, truncated **3** (**3'**), and **4**.

Calculation of Relative Hydricity

Hydride transfer to BH_3 was used to model a molecular partner upon Ir-H_b dissociation with a PCM of dichloromethane. Due to large structural reorganization of **4** upon modeling hydride transfer to a trigonal bipyramidal structure, a simplified hydride transfer model was used in which H_b was removed from the optimized structure and the corresponding single point energy of the resulting hydride transfer complex was used. This approximation may exacerbate the relative difference in energy calculated for this instance. Relaxed optimizations of **1** and **2** afforded a relative difference of 2.9 kcal/mol; a total 0.5 kcal/mol difference between the two procedures. The values are best used as a qualitative description of the similarity of hydricities for the series, where **2** and **3** have are observed to have minimal influence on the hydricities, while the primary sphere perturbation of **4** provides a larger contribution.

Table S10. Energies of compounds for the determination of the relative ΔG_H for hydride transfer to BH_3 ($\Delta\Delta G_H$) with representative reaction scheme for **1**.



Compound	G (Hartree)	BH_3 G (Hartree)	G (Hartree)	BH_4^- (Hartree)	ΔG (kcal/mol)	ΔΔG (kcal/mol)
1	-3067.8864	-26.543593	-3067.11314	-27.277951	24.4	0.0
2	-3093.3370	-26.543593	-3092.55986	-27.277951	26.8	2.4
3'	-8649.3916	-26.543593	-8648.61833	-27.277951	24.4	0.0
4	-3107.5619	-26.543593	-3106.71943	-27.277951	67.8	43.4

Computational dihydrogen bond analysis

Hydrogen bond energies were calculated from the electron density potential energy ($V(r_{CP})$) at the bond critical point in accordance with equation 3.[22] The H-bond energy of **1**, was found to be comparable (within 1 kcal/mol) with the energy difference from a relaxed potential energy surface calculation of a bond rotation isomer of **1** (**1-180°**) where the O-H_a bond is rotated 180° out of plane and disengaged from the dihydrogen bond interaction to H_b (Figure S52).

$$E_{HB} = \frac{V(r_{CP})}{2} \qquad (3)$$

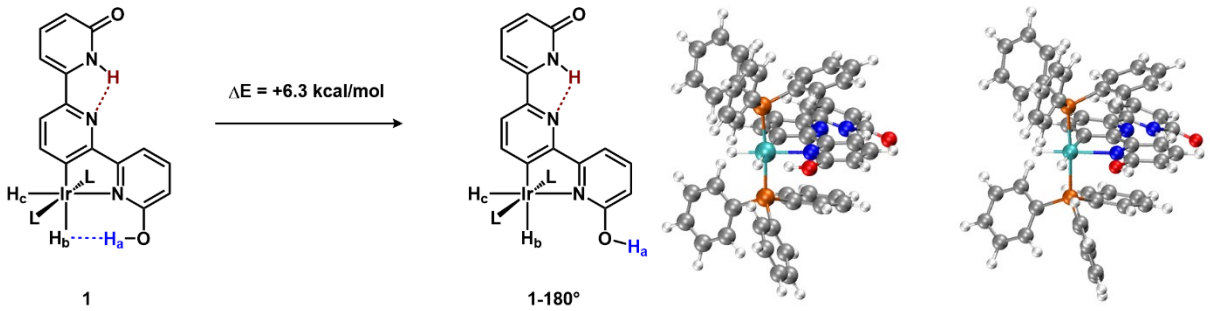


Figure S52. Relative energies of H-bond conformers of **1** (left) with 3-D renders for comparisons (right).

Table S11. Bond critical point analysis of **1-4**.

Compound	$V(r_{CP})$ (Hartree)	E_{HB} (kcal/mol)	$\nabla^2\rho_{CP}$	H_{CP}
1	-0.02289	-7.2	0.051576	-0.004945
2	-0.02473	-7.8	0.052353	-0.005824
3'	-0.02381	-7.5	0.051775	-0.005434
4	-0.01615	-5.1	0.054181	-0.001350

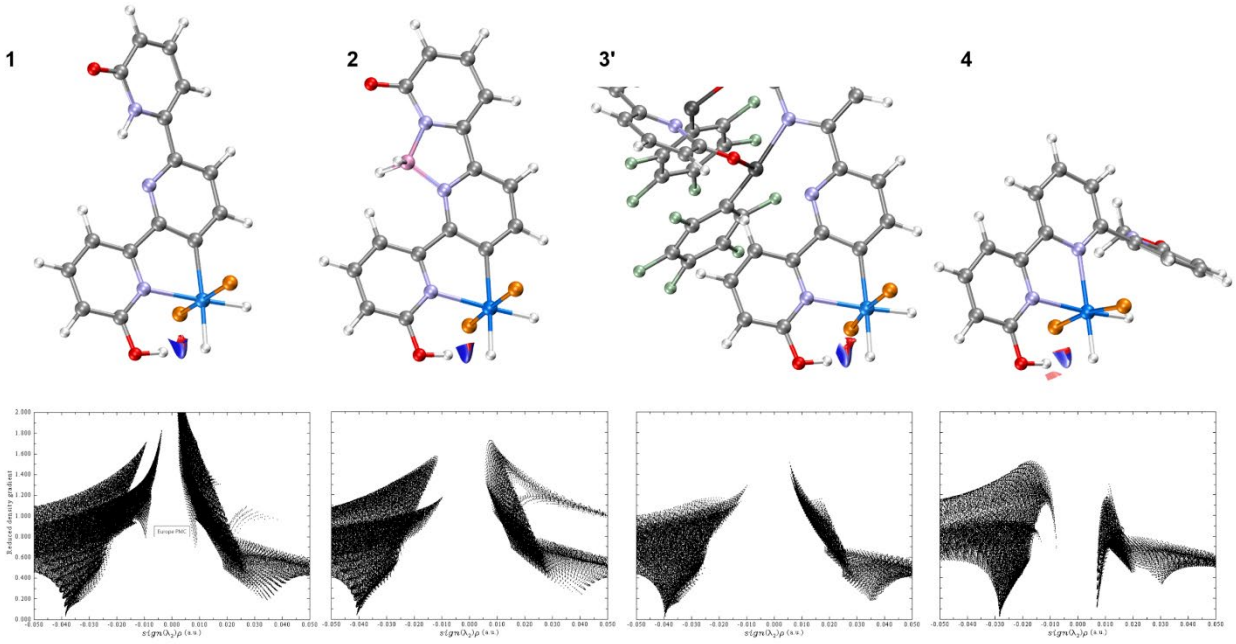


Figure S53. NCI plots of the H-bond interaction between with corresponding RDG scatter plot for defined spatial regions between H_a and H_b of compounds **1-4**.

Table S12. Natural charge analysis of **1-4**.

Compound	Ir	H_a	H_b	H_c
1	-1.22	0.51	-0.03	0.11
2	-1.21	0.51	-0.02	0.12
3'	-1.23	0.51	-0.03	0.12
4	-1.01	0.52	0.09	0.11

Optimized Coordinates:

1

Ir	-1.16460300	0.44393900	0.18259400
H	-1.70790500	0.69600900	1.65827700
N	-0.34790400	0.10822200	-1.78579900
C	0.82361800	-0.39882800	-4.24749700
C	0.87928900	-0.48144100	-1.84666500
C	-0.99902100	0.44008300	-2.92337500
C	-0.43025700	0.20910200	-4.18694900
C	1.48940600	-0.75617000	-3.07086100
H	-0.98351300	0.49777500	-5.08065600
H	2.47069100	-1.22877700	-3.07306800
H	1.28158100	-0.59610700	-5.21932000
C	1.46158800	-0.77152200	-0.52679100
C	2.52963600	-1.39951400	1.89735600
C	0.64551500	-0.50865700	0.61918400
C	1.22798000	-0.89825400	1.84054000
C	3.26185200	-1.52020700	0.70214500
H	0.66498100	-0.79012900	2.77062700
H	2.98696400	-1.65532100	2.85566000
C	4.69399200	-1.87930400	0.67942300
C	7.43120500	-2.38236200	0.34435600
N	5.33817700	-1.61902200	-0.49898400
C	5.41899700	-2.41364600	1.73125500
C	6.80245200	-2.66285500	1.53922100
C	6.70465400	-1.81836200	-0.77572000
H	4.93024900	-2.64516200	2.67587800
H	7.38178000	-3.08849400	2.36325900
H	8.49612800	-2.56699100	0.19764800
P	-2.16224700	-1.62562000	0.23931600
P	-0.09768100	2.49525600	0.33608700
O	-2.21046700	0.99454100	-2.80473800
H	-2.38118800	1.06174000	-1.80240800
H	-2.59342600	1.18557300	-0.26285500
C	-1.99591000	-2.53903500	1.83229500
C	-1.85160400	-3.90665100	4.28381600
C	-1.80276300	-1.83044400	3.02817600
C	-2.12505000	-3.93964500	1.87234900
C	-2.04858900	-4.61940400	3.09280100
C	-1.73270700	-2.51174900	4.24958700
H	-1.70591700	-0.74340000	2.98661900
H	-2.27225400	-4.50040600	0.94676100
H	-2.14216600	-5.70773500	3.11348700
H	-1.58019600	-1.95062000	5.17472100
H	-1.79118400	-4.43908600	5.23596700
C	-1.38863500	-2.73783900	-0.99588400

C	0.02126600	-4.12625300	-2.98834500
C	-0.21829100	-3.44641600	-0.67181800
C	-1.83770800	-2.71320300	-2.32820900
C	-1.13585800	-3.40785800	-3.31841900
C	0.47758600	-4.14487600	-1.66467700
H	0.15199500	-3.44243900	0.35541100
H	-2.73269600	-2.14351400	-2.59050500
H	-1.48954000	-3.38067300	-4.35159000
H	1.38601100	-4.69277000	-1.40392500
H	0.56983400	-4.66548800	-3.76415900
C	-3.96699300	-1.75183200	-0.09882500
C	-6.74392900	-1.93739700	-0.45888900
C	-4.78262700	-0.63265400	0.12618100
C	-4.54706800	-2.96882300	-0.50186700
C	-5.93106200	-3.05722200	-0.68630900
C	-6.16887300	-0.72735900	-0.05033000
H	-4.31151600	0.30668900	0.42627100
H	-3.91674500	-3.84215900	-0.68514600
H	-6.37580400	-4.00166800	-1.00877000
H	-6.79921200	0.14754200	0.12627500
H	-7.82465200	-2.00918700	-0.60274600
C	0.10373200	3.15433200	2.04513900
C	0.56566600	4.08487200	4.65447800
C	0.06690500	2.26383800	3.13030900
C	0.37192400	4.51532100	2.27262700
C	0.59749700	4.97750200	3.57430100
C	0.30145300	2.72759100	4.43054400
H	-0.15351100	1.21258300	2.93885800
H	0.39548200	5.21583700	1.43473700
H	0.79642800	6.03813100	3.74515300
H	0.27283000	2.02767800	5.26920800
H	0.74264200	4.44858100	5.66942500
C	-0.78620300	3.91423900	-0.61284800
C	-1.91221700	6.10653800	-1.96347400
C	0.03998000	4.93380400	-1.12234400
C	-2.17773300	4.00409200	-0.78078000
C	-2.73810900	5.09794100	-1.44967600
C	-0.52345400	6.02280800	-1.79854000
H	1.12320300	4.86935500	-0.99943100
H	-2.80956500	3.20227400	-0.39120600
H	-3.82161300	5.15804300	-1.57684600
H	0.12537200	6.80576200	-2.19808600
H	-2.34952500	6.95556600	-2.49415100
C	1.64347200	2.37131700	-0.25134800
C	4.22770100	1.76397800	-1.17778700
C	2.67445000	2.07953900	0.66021900

C	1.91928000	2.36438100	-1.62966400
C	3.20879200	2.07013100	-2.08771100
C	3.95812800	1.77434400	0.19741300
H	2.46547600	2.07151200	1.73191300
H	1.12271600	2.56900200	-2.34900600
H	3.40826600	2.05633300	-3.16158900
H	4.74707600	1.52932200	0.91238600
N	2.71810000	-1.23918000	-0.49677400
O	7.16575400	-1.51105200	-1.88726300
H	5.22701100	1.50844900	-1.53913000
H	4.74775500	-1.23535100	-1.24655900

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Ir	-1.25594200	0.14436300	0.17823000
H	-1.88446000	0.24538700	1.63757700
N	-0.31900400	0.00040800	-1.75362800
C	0.92485300	-0.28640800	-4.20979400
C	1.03399300	-0.22859300	-1.79718000
C	-1.04074500	0.07668700	-2.89306900
C	-0.44076900	-0.04227700	-4.15869700
C	1.67268000	-0.39225200	-3.02976500
H	-1.05959100	0.03985600	-5.05210000
H	2.73517200	-0.59661600	-3.07542900
H	1.42220800	-0.40408000	-5.17466500
C	1.64086100	-0.27083000	-0.45391800
C	2.69406600	-0.36510600	2.11977700
C	0.74682500	-0.16608400	0.65568700
C	1.32110000	-0.25425200	1.93938100
C	3.50974500	-0.41245900	0.99030800
H	0.67223500	-0.22818300	2.81607400
H	3.14722000	-0.40799100	3.11169400
C	4.96083700	-0.49067200	0.95579000
C	7.64791300	-0.62880100	0.38291200
N	5.36651000	-0.54630300	-0.34569400
C	5.84969000	-0.50208800	2.01917100
C	7.22596400	-0.57182200	1.69766000
C	6.71828600	-0.62588200	-0.73098200
H	5.49468300	-0.45659600	3.04773500
H	7.96538500	-0.58021400	2.50334600
H	8.70775900	-0.68299900	0.12814700
P	-1.56997000	-2.13735700	0.29101700
P	-0.93733100	2.43966000	0.26178200
O	-2.35877600	0.26113500	-2.78770000
H	-2.54937500	0.30567500	-1.78511400
H	-2.84292900	0.38885600	-0.27064500
C	-1.20175600	-2.91027300	1.92220200

C	-0.73156700	-4.10232200	4.42271300
C	-1.23352500	-2.13633200	3.09197900
C	-0.93914300	-4.28992200	2.01192700
C	-0.70159500	-4.88104800	3.25706900
C	-1.00075200	-2.73089500	4.33852400
H	-1.44123800	-1.06728300	3.00981900
H	-0.90754900	-4.89997300	1.10637400
H	-0.49210400	-5.95155700	3.31724300
H	-1.02627700	-2.11939500	5.24365800
H	-0.54513100	-4.56578700	5.39433700
C	-0.42830900	-2.98604500	-0.86387500
C	1.46243700	-3.87990800	-2.73800300
C	0.88532400	-3.28371100	-0.45891800
C	-0.78467800	-3.12588300	-2.21687700
C	0.15791300	-3.57435700	-3.14773400
C	1.82379100	-3.73620500	-1.39289900
H	1.17454100	-3.15273500	0.58610400
H	-1.79804000	-2.87742200	-2.54156900
H	-0.12532900	-3.67394400	-4.19792800
H	2.84328000	-3.95921300	-1.07123800
H	2.19968300	-4.22111000	-3.46825800
C	-3.23104200	-2.81515600	-0.11499900
C	-5.79526900	-3.84992700	-0.59185100
C	-4.36271900	-2.00709700	0.07391100
C	-3.38703700	-4.14759900	-0.53904600
C	-4.66641400	-4.65936400	-0.78170500
C	-5.64206200	-2.52592800	-0.16082000
H	-4.22236000	-0.97106700	0.39186700
H	-2.50898400	-4.77839100	-0.69521900
H	-4.78173800	-5.69122300	-1.12170100
H	-6.51969600	-1.89211100	-0.01298400
H	-6.79320300	-4.25173100	-0.78261400
C	-1.13450500	3.21216500	1.92167000
C	-1.27030100	4.37317000	4.47588600
C	-0.94484200	2.42441900	3.06875500
C	-1.39506700	4.58669200	2.05981900
C	-1.46668500	5.16166600	3.33401000
C	-1.00771300	3.00377200	4.34148500
H	-0.76067200	1.35593100	2.94708600
H	-1.55213400	5.20628200	1.17403200
H	-1.67935600	6.22856000	3.43438800
H	-0.85799200	2.38298200	5.22807800
H	-1.32733800	4.82516900	5.46887400
C	-1.95235400	3.49829000	-0.84785100
C	-3.58480100	5.13928100	-2.44085100
C	-1.44431400	4.69614500	-1.38521100

C	-3.28281200	3.13249900	-1.11003300
C	-4.09622000	3.95212300	-1.90008100
C	-2.25869800	5.50962500	-2.18230600
H	-0.41063700	4.98712200	-1.18687700
H	-3.66735100	2.19733800	-0.69608000
H	-5.12932200	3.65839200	-2.10007900
H	-1.85434700	6.43371000	-2.60193100
H	-4.21798600	5.77412900	-3.06508500
C	0.79826100	2.84711400	-0.18369500
C	3.51867300	3.01149400	-0.86743000
C	1.77686400	2.94116200	0.82068900
C	1.19145500	2.83697400	-1.53392000
C	2.54594100	2.92716600	-1.87117200
C	3.13148200	3.02014400	0.47810000
H	1.47951400	2.93616300	1.87153700
H	0.44037600	2.74128800	-2.32151100
H	2.84301000	2.90424500	-2.92185200
H	3.88623500	3.07936300	1.26585300
N	2.99256300	-0.39351100	-0.27721300
O	7.02766700	-0.68713400	-1.93587500
H	4.57665400	3.05502000	-1.13420900
B	4.17666000	-0.52975600	-1.32872400
H	4.21096800	0.42553300	-2.08007300
H	4.07876600	-1.58581900	-1.93480800

3’

Ir	3.76596800	0.12397000	-0.10479000
Zn	-2.17601000	-0.94003200	0.50541900
Zn	-5.20594400	-1.07205600	0.53196300
P	3.35652100	2.38323100	0.02215500
P	4.40357800	-2.09755000	-0.09018600
C	0.97285400	-0.75162700	0.46836100
C	-0.12796300	-1.29807100	2.45661900
C	2.19164000	-0.41829100	1.13064600
C	0.99645800	-0.70626200	-1.00616900
C	2.37311500	-0.16404900	-2.84716400
C	-1.36186600	-1.82195100	3.09256600
C	2.16165300	-0.54286800	2.53283100
H	3.05152500	-0.29158600	3.11135400
C	-0.03983700	-1.06769400	-1.86544900
H	-0.96490500	-1.48856100	-1.48410500
C	1.34203800	-0.46043600	-3.75628300
H	1.52237900	-0.33529300	-4.82385400
C	1.02997500	-1.00643900	3.19513900
H	1.02626500	-1.11267300	4.28083900
C	0.13526900	-0.92270000	-3.24775000

H	-0.68489200	-1.17808900	-3.92171700
C	-2.55737900	-2.95232700	4.84448200
H	-2.57994500	-3.42565200	5.82947600
C	-1.35261100	-2.41296900	4.35485600
H	-0.43170000	-2.48713700	4.93086000
C	-3.68021400	-2.28032900	2.78475500
C	-2.67757400	0.92006200	-1.76787300
C	-2.33079600	0.78604600	-0.43188800
C	-2.01975100	1.96686000	0.22835700
C	-2.43410300	3.31175500	-1.71777400
C	-2.74521900	2.14867800	-2.42609200
C	-2.06713500	3.22450200	-0.37342800
C	-3.57456800	-2.95473800	-1.24656400
C	-7.17435800	-2.15082300	-1.35088200
C	-8.35988200	-2.26627100	-2.09503600
H	-8.37743200	-2.83612200	-3.02375500
C	-8.24704800	-0.78440000	0.21306700
C	-5.81292900	-3.75202200	-2.73866200
H	-6.69881600	-4.06374600	-3.28944300
C	-4.55575900	-4.32636200	-3.01206700
H	-4.46026900	-5.07883300	-3.79862200
C	-5.89225300	-2.79476900	-1.73110800
C	-4.68112500	1.46020300	2.05210900
C	-5.39644300	1.77561300	-0.16113600
C	-4.49389200	2.83497600	2.22117000
C	-5.11290300	0.88345200	0.86536600
C	-5.23624300	3.15662300	-0.05744300
C	-4.77396800	3.68691100	1.15095900
F	-1.67371800	1.92664600	1.55047700
F	-2.98033800	-0.18768200	-2.51040300
F	-5.80345300	1.29825300	-1.37904400
F	-4.35747700	0.67161100	3.11988600
F	-1.77831600	4.36020600	0.30848100
F	-3.04835500	2.23654100	-3.74249100
F	-2.46018100	4.50784100	-2.33691100
F	-4.01635200	3.35321500	3.37578900
F	-5.45745200	3.98416600	-1.10608900
F	-4.56894200	5.01440100	1.26934400
N	-0.15990200	-1.13346000	1.11086900
O	-4.74253900	-2.24965800	2.05979700
O	-2.54958800	-2.61057700	-0.55243500
N	-2.49483600	-1.74683800	2.33938000
N	-4.80579600	-2.40159800	-1.00599500
O	3.56998800	0.23117800	-3.28902100
N	2.19519400	-0.27316400	-1.51302100
N	-7.13991400	-1.41743800	-0.21208800

C	1.74758000	-4.01235400	-2.57627600
H	1.63036400	-4.15983800	-3.65225400
C	2.88738400	-3.36753900	-2.08635800
H	3.65565400	-3.01460100	-2.77859800
C	2.03751700	-3.59720200	0.17805800
H	2.13798200	-3.41365300	1.25014000
C	3.04505600	-3.16629000	-0.70343700
C	0.75314400	-4.45163100	-1.69207500
H	-0.14024000	-4.94930900	-2.07661700
C	0.89879400	-4.24262500	-0.31579800
H	0.11207700	-4.55607400	0.37361300
C	4.79398600	-2.80669600	1.56586900
C	5.16870000	-1.96116700	2.62075500
H	5.18090200	-0.88262800	2.45016800
C	5.47637300	-3.88296500	4.07069800
H	5.73757500	-4.30163000	5.04551400
C	5.51062400	-2.49791300	3.86845300
H	5.79833600	-1.83078600	4.68460100
C	4.76787200	-4.19876700	1.77120400
H	4.46953400	-4.86498400	0.95876700
C	2.52248700	3.06653200	-1.46482400
C	3.22163100	3.90466000	-2.35200100
H	4.22964700	4.24126500	-2.10135000
C	1.22582500	2.63044900	-1.80377900
H	0.67232000	1.96547400	-1.13730400
C	2.63460300	4.30462500	-3.55788400
H	3.18815200	4.95602400	-4.23832200
C	0.64649600	3.03148200	-3.01306900
H	-0.35185900	2.68148300	-3.27807700
C	1.34752600	3.86707800	-3.89146000
H	0.89099900	4.17180200	-4.83596900
C	2.34824200	2.88100600	1.47384100
C	2.87901900	2.53022800	2.72948200
H	3.83416500	1.99989600	2.77735800
C	2.18472100	2.84703400	3.89874000
H	2.60347700	2.57414000	4.87050200
C	1.11382300	3.53995000	1.40013300
H	0.69118200	3.81700900	0.43311700
C	0.41027400	3.83979300	2.57621500
H	-0.56596900	4.32196500	2.50554700
C	0.94412300	3.49848100	3.82278700
H	0.39208400	3.73221100	4.73617600
C	-3.70450800	-2.89751400	4.07557300
H	-4.65250600	-3.31133900	4.42177100
C	-9.51248300	-1.62365700	-1.64257300
H	-10.44086100	-1.70243000	-2.21162700

C	4.84224400	3.44643400	0.23416900
C	-9.46299000	-0.86854400	-0.46374600
C	-3.45103100	-3.94030200	-2.27955400
H	-2.46081300	-4.35962800	-2.46295800
C	4.67689700	4.80320300	0.56981900
H	3.67247900	5.20819300	0.71952100
C	5.86275100	-2.59878400	-1.09515800
C	6.84380300	-1.64462000	-1.40393500
H	6.68015300	-0.60729300	-1.10126200
C	7.25024300	3.75201500	0.21358800
H	8.25332000	3.33927300	0.08076800
C	6.13107700	2.92272900	0.05979600
H	6.23296400	1.86359800	-0.18655100
C	7.99588600	-2.02277900	-2.10485000
H	8.75552600	-1.27459700	-2.34373900
C	6.04201800	-3.93657500	-1.49313100
H	5.27726900	-4.68233700	-1.26459000
C	5.10437000	-4.73283500	3.01936000
H	5.07455500	-5.81430800	3.17169100
C	5.79570100	5.62863900	0.71927500
H	5.66335800	6.68128700	0.98009000
C	8.16904300	-3.35347900	-2.50618500
H	9.06434500	-3.64686700	-3.05948900
C	7.08429000	5.10354800	0.54031200
H	7.95782500	5.74873400	0.66135700
C	7.18973800	-4.30933800	-2.20089300
H	7.31844900	-5.34735400	-2.51672600
H	4.99120000	0.52927000	-1.17626700
H	4.85432600	0.41014000	1.03193800
H	4.13821100	0.36949700	-2.45406100
H	-8.13413000	-0.18977600	1.12304500
H	-10.34169500	-0.34684600	-0.08314700

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Ir	-0.33294700	-0.19453700	0.36366300
P	-2.45522000	0.75073000	0.38558300
O	-1.57500900	-3.11403300	0.97256100
N	-0.96828300	-1.86190800	-0.86271400
N	0.23074200	0.38597500	-1.66022400
C	-4.33999500	-0.44769700	-1.39617800
C	-2.67514200	2.22378400	-0.69251800
C	-3.00645600	1.31508800	2.04034000
C	-5.04296300	-2.42628500	0.46100300
C	-2.06418800	1.58788000	3.04415100
C	-3.85090100	2.27944800	4.53425500
C	-3.05681100	3.46845400	-0.15922200

C	-4.12480900	-1.43300600	0.81343100
C	-3.76550800	-0.43865500	-0.11487100
C	-0.83714400	-1.71963500	-2.21319700
C	0.96703700	1.47214100	-2.00894200
C	-2.33914700	2.13463400	-2.05801000
C	-0.12740500	-0.50297200	-2.64597600
C	-4.37575400	1.52748400	2.28783500
C	-4.79426000	2.00637700	3.53348500
C	0.63251700	3.17310600	-0.16223800
C	-2.48799300	2.07109200	4.28838200
C	-1.52131200	-2.98552800	-0.35610700
C	-3.09863500	4.60273100	-0.97956900
C	-1.32364800	-2.69327500	-3.08850400
C	-1.92641600	-3.84117500	-2.55862900
C	0.19555700	-0.27906100	-3.98880300
C	-2.02251900	-4.00494400	-1.18185600
N	2.82152400	2.57601400	-1.00150500
C	-5.25544500	-1.44836900	-1.74641400
C	1.47671000	2.42489900	-0.98102700
C	-5.60494000	-2.44047400	-0.82258300
C	1.21670300	4.12888300	0.68517100
C	3.35736700	3.47059400	-0.16935100
C	1.32134800	1.72889400	-3.34137600
C	2.59650000	4.28745800	0.69505900
C	0.91597400	0.85791000	-4.34706000
O	4.69986200	3.62458100	-0.12854000
C	-2.39314300	3.26790800	-2.87499500
C	-2.76629800	4.50627900	-2.33588700
C	5.47541800	2.73541300	-0.95995700
P	1.78013900	-1.11205700	0.67909200
C	1.87735300	-2.57284100	1.79578600
C	2.75857600	1.11146700	2.10292400
C	3.76619600	1.88902700	2.68597900
C	5.11071000	1.54210700	2.51392600
C	2.85378900	-3.56671500	1.60087300
C	5.45003600	0.40500100	1.76685100
C	1.03537100	-2.64019900	2.91723500
C	2.96501900	-4.62700800	2.50724900
C	3.09507400	-0.02344400	1.35238000
C	4.44679300	-0.38182500	1.19320200
C	2.11462400	-4.69590900	3.61870700
C	1.15411600	-3.69781800	3.82574600
C	2.42573700	-1.70119700	-0.93001200
C	2.00607000	-2.94453500	-1.43648100
C	3.15393200	-0.82254300	-1.75319400
C	3.46982800	-1.19644200	-3.06352700

C	3.06469700	-2.44220900	-3.56104500
C	2.33311400	-3.31501000	-2.74547800
H	6.52091200	3.00453900	-0.76580700
H	5.28802700	1.68829500	-0.67578200
H	5.22806400	2.87883600	-2.02298900
H	0.14450700	1.09971900	1.13243600
H	-0.72836800	-0.64355800	1.84528000
H	-1.19450100	-2.26801700	1.34599500
H	6.49858300	0.13113600	1.62914300
H	5.89583000	2.15875900	2.95667800
H	3.49769800	2.77927900	3.25855200
H	1.70899300	1.39096100	2.21019200
H	4.71432400	-1.26700900	0.61148100
H	3.44731200	0.16318500	-1.38124600
H	4.02656500	-0.50522500	-3.70040600
H	3.31360600	-2.73006700	-4.58502400
H	2.00759600	-4.28445200	-3.12925300
H	1.42577200	-3.62364500	-0.80769600
H	-1.23785900	-2.57049200	-4.16618700
H	-2.31575000	-4.61020200	-3.22784400
H	-2.47190300	-4.88644000	-0.72589100
H	-0.09911400	-1.00134000	-4.74793600
H	1.17333200	1.04597000	-5.39060000
H	1.91944500	2.61426700	-3.55581100
H	3.09976500	5.01062500	1.33773000
H	0.58773500	4.74391600	1.33252800
H	-0.44413000	3.02942700	-0.20231600
H	-1.00740000	1.40440800	2.84208900
H	-1.75172100	2.27837100	5.06830500
H	-4.18042700	2.65093300	5.50732300
H	-5.85810700	2.16441700	3.72386600
H	-5.11046700	1.31138200	1.50861100
H	-3.68721100	-1.42890700	1.81419300
H	-5.31568500	-3.19242700	1.19011300
H	-6.31906500	-3.21931900	-1.09915500
H	-5.69956800	-1.44624900	-2.74444100
H	-4.09015000	0.33029300	-2.11924700
H	-2.02274600	1.18347000	-2.48574500
H	-2.13057300	3.18331500	-3.93180200
H	-2.79483900	5.39390500	-2.97164100
H	-3.38978800	5.56510200	-0.55274600
H	-3.30880800	3.55509800	0.89921300
H	3.51963400	-3.51752600	0.73670300
H	3.71859500	-5.40072700	2.34364900
H	2.20257700	-5.52569600	4.32362800
H	0.49241800	-3.74287300	4.69361700

H	0.29135700	-1.85689700	3.07924700

1-180°

Ir	-1.14370300	0.43673100	0.26091000
H	-1.60956200	0.63778400	1.76228300
N	-0.35621500	0.14642300	-1.77289700
C	0.91342000	-0.29931800	-4.22821100
C	0.89245900	-0.41261300	-1.82488300
C	-0.97162300	0.44886000	-2.93185100
C	-0.36178400	0.26157700	-4.18331600
C	1.54572200	-0.65180800	-3.03672600
H	-0.89863900	0.53838400	-5.09314200
H	2.53717700	-1.10152200	-3.01001500
H	1.40319900	-0.46513200	-5.19004800
C	1.47984200	-0.74561100	-0.51550600
C	2.55122800	-1.48583400	1.87612000
C	0.66416900	-0.54261300	0.63809900
C	1.24831200	-0.98986500	1.84145500
C	3.28544500	-1.54246600	0.67600400
H	0.67944800	-0.93021700	2.77351500
H	3.00947400	-1.78837500	2.82050100
C	4.71737000	-1.89887500	0.63919000
C	7.45448800	-2.39439200	0.28169700
N	5.35825000	-1.61052700	-0.53437300
C	5.44760900	-2.45825600	1.67527800
C	6.82979800	-2.70281100	1.47214800
C	6.72358900	-1.80348900	-0.82100300
H	4.96368400	-2.71196900	2.61655900
H	7.41210600	-3.14761100	2.28397200
H	8.51885000	-2.57546900	0.12665300
P	-2.18633700	-1.60344200	0.23939600
P	-0.10044700	2.49040100	0.40823700
O	-2.22683500	0.93854100	-2.81087600
H	-2.57149500	1.11237800	-3.70541500
H	-2.53978400	1.22225900	-0.12857700
C	-2.05038900	-2.59027500	1.79292900
C	-1.91640900	-4.05824200	4.18769800
C	-1.82063100	-1.93622000	3.01321700
C	-2.21229900	-3.98804300	1.77972400
C	-2.14234900	-4.71782000	2.97134900
C	-1.75740600	-2.66702400	4.20637600
H	-1.68289400	-0.85245400	3.00895300
H	-2.37540000	-4.50946300	0.83395100
H	-2.26248600	-5.80361900	2.94971100
H	-1.57710900	-2.14778600	5.15088400

H	-1.86141500	-4.62939700	5.11754800
C	-1.41307600	-2.68853600	-1.02359500
C	0.02451500	-4.00145400	-3.04932200
C	-0.23915200	-3.39762200	-0.71414800
C	-1.85517700	-2.63151700	-2.35681600
C	-1.13896800	-3.28650900	-3.36413200
C	0.47068800	-4.05779800	-1.72306000
H	0.12452200	-3.42034800	0.31513900
H	-2.75512000	-2.06333100	-2.60481900
H	-1.48660300	-3.23230000	-4.39848700
H	1.38314600	-4.60404100	-1.47277600
H	0.58510100	-4.50897200	-3.83791200
C	-3.98742000	-1.70104900	-0.14456300
C	-6.75210400	-1.83256600	-0.61617700
C	-4.78273500	-0.55599400	0.00543500
C	-4.58169500	-2.91572400	-0.53460600
C	-5.95870000	-2.97845900	-0.77324500
C	-6.16299900	-0.62336300	-0.22592000
H	-4.29468000	0.38189500	0.28528100
H	-3.96610300	-3.80849600	-0.66644000
H	-6.41334900	-3.92235700	-1.08368900
H	-6.77752600	0.27244700	-0.10652700
H	-7.82771000	-1.88375100	-0.80203100
C	-0.06448800	3.19321200	2.11074300
C	0.08560300	4.12835000	4.75745500
C	0.09358300	2.28801500	3.17654200
C	-0.15788800	4.56831700	2.38001800
C	-0.08930300	5.03090600	3.70105700
C	0.17879800	2.75492400	4.49244000
H	0.13000900	1.21895200	2.95585600
H	-0.29763200	5.27947500	1.56353700
H	-0.17550200	6.10125200	3.90316400
H	0.30726600	2.04460700	5.31291200
H	0.14063800	4.49321500	5.78586300
C	-0.67600300	3.85943500	-0.67830600
C	-1.57409500	5.94726500	-2.32883600
C	0.14190100	4.98363900	-0.90985100
C	-1.93647200	3.78216200	-1.28879200
C	-2.38297700	4.82509800	-2.11112200
C	-0.30876800	6.02433900	-1.72875900
H	1.13609300	5.03495600	-0.45941500
H	-2.53589600	2.88248100	-1.13009000
H	-3.36416600	4.75675400	-2.58776100
H	0.33010700	6.89339000	-1.90302000
H	-1.92310700	6.75881100	-2.97208700
C	1.68480600	2.36830400	-0.04743600

C	4.32171000	1.77609700	-0.83085300
C	2.65304700	2.03007500	0.91443800
C	2.05041900	2.41173200	-1.40409500
C	3.36382600	2.12148400	-1.79121700
C	3.96325200	1.73633600	0.52344200
H	2.37836000	1.98367600	1.97006000
H	1.30258400	2.65830600	-2.16158000
H	3.63161800	2.14679800	-2.85016700
H	4.70386400	1.46091500	1.27809800
N	2.74171800	-1.20553100	-0.50804600
O	7.18044800	-1.46925100	-1.92688900
H	5.34146200	1.52934600	-1.13672400
H	4.76507900	-1.20474600	-1.26797700

BH_3

B	0.00000000	0.00000000	0.00000000
H	0.00000000	1.20004700	0.00000000
H	-1.03927100	-0.60002400	0.00000000
H	1.03927100	-0.60002400	0.00000000

BH_4

B	0.00000000	0.00000000	0.00000000
H	0.71600800	0.71600800	0.71600800
H	-0.71600800	0.71600800	-0.71600800
H	0.71600800	-0.71600800	-0.71600800
H	-0.71600800	-0.71600800	0.71600800

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