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Electronic Supplementary Information

Direct transformation of 2-acetylpyridine oxime esters into α-oxygenated imines in an Ir(III) complex

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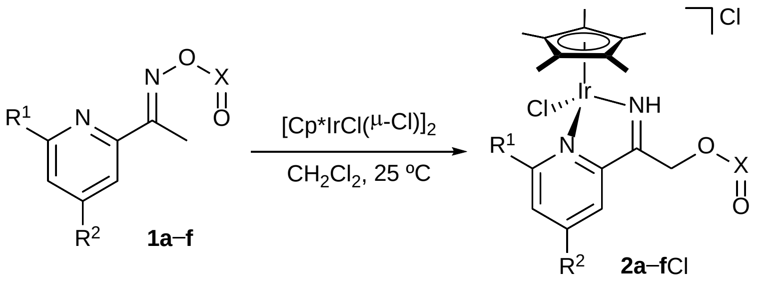
Contents

General considerations

All experimental manipulations for air and water sensitive reagents were carried out in dried glass vessels under an argon or a nitrogen atmosphere by standard Schlenk techniques. Dichloromethane was distilled over P_4O_{10}; methanol was distilled over Mg. They were degassed and stored under an argon atmosphere. The other solvents (anhydrous grade) were purchased from Sigma-Aldrich and purged with argon before use. ^{1}H (500 MHz) and ^{13}C{^{1}H} (126 MHz) NMR spectra were recorded on a JEOL ECA-500 spectrometer. Chemical shifts are reported in δ, referenced to residual ^{1}H and ^{13}C signals of deuterated solvents as internal standards. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer using KBr pellets. Elemental analyses were performed on a Perkin Elmer 2400 series II CHN analyzer.

Transformation of 1 into 2



	R_1	R_2	X=O
a:	H	H	COMe
b:	H	Me	COMe
c:	H	H	COMe
d:	Br	H	CO_2Et
e:	H	H	SO_2Me
f:	H	H	$SO_2(4\text{-}MeC_6H_4)$

General procedure

A mixture of [Cp*IrCl(μ-Cl)]$_2$ and oxime ester **1** in dichloromethane was stirred at 25 °C for an appropriate reaction time (3–6 h). After the completion of the reaction, the mixture was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–hexane or dichloromethane–methanol–diethyl ether to give **2**Cl.

Synthesis of 2aCl: This compound was obtained from $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (31.9 mg, 0.040 mmol) and oxime acetate **1a** (14.4 mg, 0.081 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–hexane. Dark red crystals (38.2 mg, 83% yield). ^{1}H NMR (CD_2Cl_2) δ 15.7 (br s, 1H), 8.78 (d, *J* = 6.0 Hz, 1H), 8.06 (m, 2H), 7.73 (m, 1H), 5.88 (d, *J* = 14 Hz, 1H), 5.61 (d, *J* = 14 Hz, 1H), 2.13 (s, 3H), 1.89 (s, 15H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 174.4, 170.3, 155.5, 151.8, 140.1, 129.7, 127.7, 90.8, 61.9, 21.0, 9.49; IR (KBr, cm^{-1}) 1750 ($\nu_{C=O}$), 1598 ($\nu_{C=N}$), 1235 ($\nu_{C–O}$); Anal. Calcd for $C_{19}H_{25}Cl_2IrN_2O_2$: C, 39.58; H, 4.37; N, 4.86. Found: C, 39.33; H, 4.45; N, 4.72.

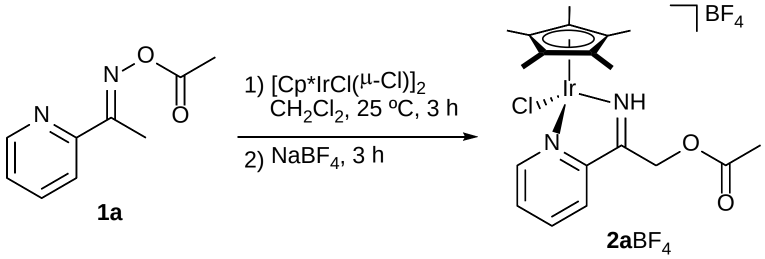
Synthesis of 2bCl: This compound was obtained from $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (59.6 mg, 0.075 mmol) and oxime acetate **1b** (39.4 mg, 0.205 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Dark red crystals (43.6 mg, 49% yield). ^{1}H NMR ($CDCl_3$) δ 15.2 (br s, 1H), 8.63 (d, *J* = 6.0 Hz, 1H), 7.82 (s, 1H), 7.57 (dd, *J* = 6.0, 1.0 Hz, 1H), 5.88 (d, *J* = 14 Hz, 1H), 5.61 (d, *J* = 14 Hz, 1H), 2.63 (s, 3H), 2.12 (s, 3H), 1.90 (s, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 174.4, 170.1, 154.9, 152.7, 150.8, 130.3, 128.2, 90.3, 61.5, 21.7, 21.0, 9.53; IR (KBr, cm^{-1}) 1749 ($\nu_{C=O}$), 1622 ($\nu_{C=N}$), 1225 ($\nu_{C–O}$); Anal. Calcd for $C_{20}H_{27}Cl_2IrN_2O_2$: C, 40.68; H, 4.61; N, 4.74. Found: C, 40.44; H, 4.59; N, 4.61.

Synthesis of 2dCl: This compound was obtained from $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (15.8 mg, 0.020 mmol) and oxime carbonate **1d** (9.6 mg, 0.046 mmol) according to *general procedure*. The reaction time was 3 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Orange crystals (15.6 mg, 65% yield). ^{1}H NMR ($CDCl_3$) δ 15.5 (br s, 1H), 8.78 (d, *J* = 5.0 Hz, 1H), 8.11 (d, *J* = 7.0 Hz, 1H), 8.06 (td, *J* = 7.8, 1.4 Hz, 1H), 7.74 (ddd, *J* = 7.3, 5.9, 1.4 Hz, 1H), 6.15 (d, *J* = 14 Hz, 1H), 5.54 (d, *J* = 14 Hz, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 1.91 (s, 15H), 1.30 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 173.6, 155.1, 153.9, 151.6, 140.0, 129.8, 127.7, 90.6, 65.3, 64.9, 14.3, 9.53; IR (KBr, cm^{-1}) 1755 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$), 1260 ($\nu_{C–O}$); Anal. Calcd for $C_{20}H_{27}Cl_2IrN_2O_3$: C, 39.60; H, 4.49; N, 4.62. Found: C, 39.23; H, 4.24; N, 4.53.

Synthesis of 2eCl: This compound was obtained from $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (31.4 mg, 0.039 mmol) and oxime sulfonate **1e** (18.2 mg, 0.085 mmol) according to *general procedure*. The reaction time was 6 h. The product was purified by recrystallization from dichloromethane–methanol–diethyl ether. Orange crystals (40.5 mg, 84% yield). ^1H NMR ($CDCl_3$) δ 14.4 (br s, 1H), 8.79 (d, J = 4.5 Hz, 1H), 8.25 (d, J = 7.5 Hz, 1H), 8.13 (td, J = 7.8, 1.2 Hz, 1H), 7.79 (ddd, J = 7.3, 5.6, 1.6 Hz, 1H), 5.28 (d, J = 13 Hz, 1H), 5.10 (d, J = 13 Hz, 1H), 2.84 (s, 3H), 1.87 (s, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 174.8, 154.6, 151.6, 140.0, 129.7, 128.2, 90.6, 39.9, 39.6, 9.28; IR (KBr, cm^{-1}) 1599 ($\nu_{C=N}$), 1187 ($\nu_{S=O}$); Anal. Calcd for $C_{18}H_{25}Cl_2IrN_2O_3S$: C, 35.29; H, 4.11; N, 4.57 Found: C, 35.33; H, 4.01; N, 4.53.

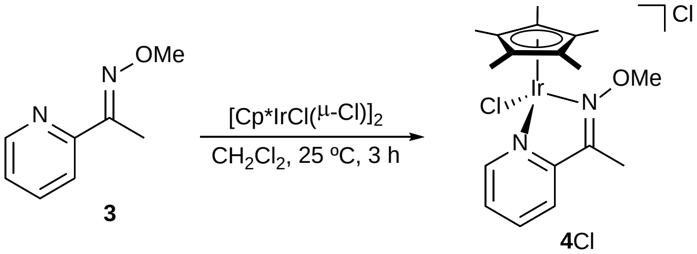
Synthesis of 2fCl: This compound was obtained from $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (62.9 mg, 0.079 mmol) and oxime sulfonate **1f** (60.8 mg, 0.209 mmol) according to *general procedure*. The reaction time was 6 h. The product was purified by precipitation from dichloromethane–methanol–diethyl ether. Red oil (52.4 mg, 48% yield). ^1H NMR ($CDCl_3$) δ 14.3 (br s, 1H), 8.78 (d, J = 5.0 Hz, 1H), 8.23 (d, J = 7.0 Hz, 1H), 8.09 (t, J = 7.3, 1H), 7.81 (d, J = 8.0 Hz, 2H), 7.77 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 5.27 (d, J = 13 Hz, 1H), 5.10 (d, J = 13 Hz, 1H), 2.35 (s, 3H), 1.83 (s, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 175.2, 154.3, 151.8, 142.5, 140.1, 140.1, 130.0, 128.9, 128.4, 126.3, 90.6, 39.8, 21.5, 9.27; IR (KBr, cm^{-1}) 1600 ($\nu_{C=N}$), 1184 ($\nu_{S=O}$); Anal. Calcd for $C_{24}H_{29}Cl_2IrN_2O_3S$: C, 41.86; H, 4.24; N, 4.07. Found: C, 41.47; H, 4.25; N, 4.14.

Synthesis of 2aBF$_4$

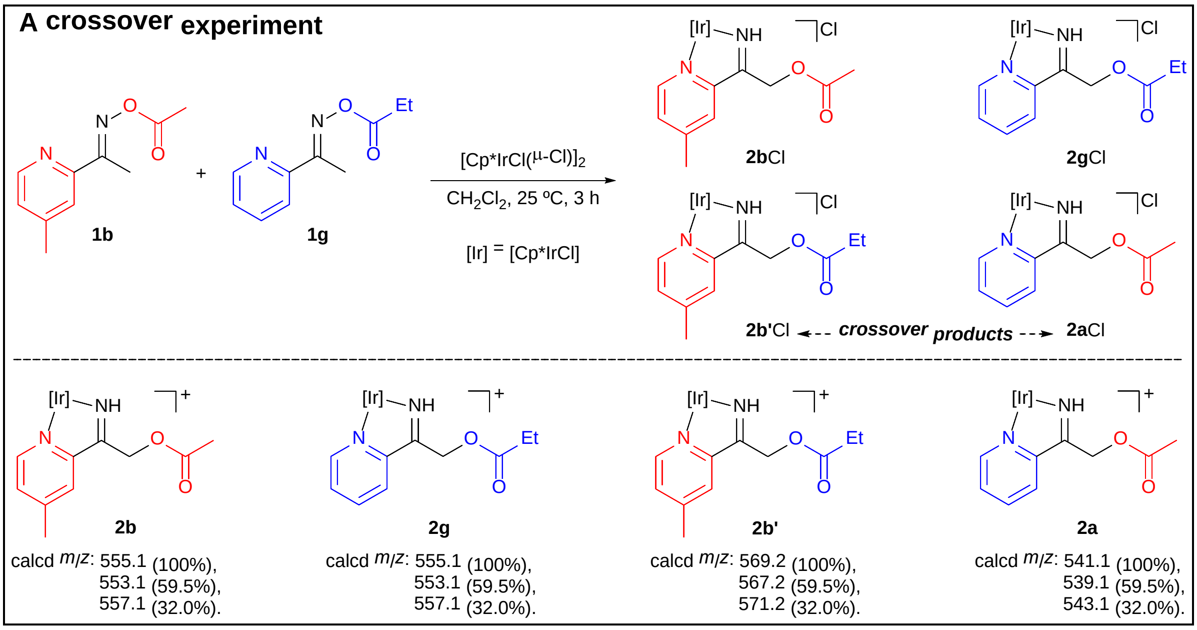


A mixture of [Cp*IrCl(μ-Cl)]$_2$ (31.9 mg, 0.040 mmol) and oxime acetate **1a** (15.1 mg, 0.085 mmol) in dichloromethane (7 mL) was stirred at 25 °C for 3 h. $NaBF_4$ (11.0 mg, 0.100 mmol) was added to the resulting mixture and stirred for additional 3 h. Then, the mixture was filtered through a Celite pad, and the filtrate was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–methanol–diethyl ether to give **2a**BF_4 as orange crystals (31.0 mg, 62% yield). ^1H NMR (CD_2Cl_2) δ 11.6 (br s, 1H), 8.82 (d, *J* = 5.5 Hz, 1H), 8.16 (td, *J* = 7.6, 1.2 Hz, 1H), 8.10 (br d, *J* = 7.5 Hz, 1H), 7.83 (ddd, *J* = 7.3, 5.8, 1.5 Hz, 1H), 5.53 (d, *J* = 16 Hz, 1H), 5.44 (d, *J* = 17 Hz, 1H), 2.25 (s, 3H), 1.82 (s, 15H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 176.0, 170.1, 154.0, 152.2, 140.5, 130.8, 127.9, 90.8, 62.9, 20.8, 9.13; IR (KBr, cm^{-1}) 1751 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$), 1234 ($\nu_{C–O}$), 1084 ($\nu_{B–F}$); Anal. Calcd for $C_{19}H_{25}BClF_4IrN_2O_2$: C, 36.35; H, 4.01; N, 4.46. Found: C, 36.46; H, 3.86; N, 4.44.

Synthesis of 4Cl



A mixture of [Cp*IrCl(μ-Cl)]$_2$ (47.8 mg, 0.060 mmol) and oxime ether **3** (18.9 mg, 0.126 mmol) in dichloromethane was stirred at 25 °C for 3 h. After the completion of the reaction, the mixture was concentrated in vacuo. The crude product was purified by recrystallization from dichloromethane–methanol–diethyl ether to give **4**Cl as orange crystals (48.8 mg, 74% yield). ^1H NMR ($CDCl_3$) δ 8.84 (d, *J* = 4.5 Hz, 1H), 8.62 (d, *J* = 8.0 Hz, 1H), 8.27 (t, *J* = 7.5 Hz, 1H), 7.93 (t, *J* = 6.3 Hz, 1H), 3.95 (s, 3H), 2.98 (s, 3H), 1.80 (s, 15H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.6, 153.2, 151.8, 141.0, 130.5, 129.2, 90.8, 63.3, 14.5, 9.14; IR (KBr, cm^{-1}) 1610 ($\nu_{C=N}$); Anal. Calcd for $C_{18}H_{25}Cl_2IrN_2O$: C, 39.41; H, 4.59; N, 5.11. Found: C, 39.31; H, 4.68; N, 4.83.



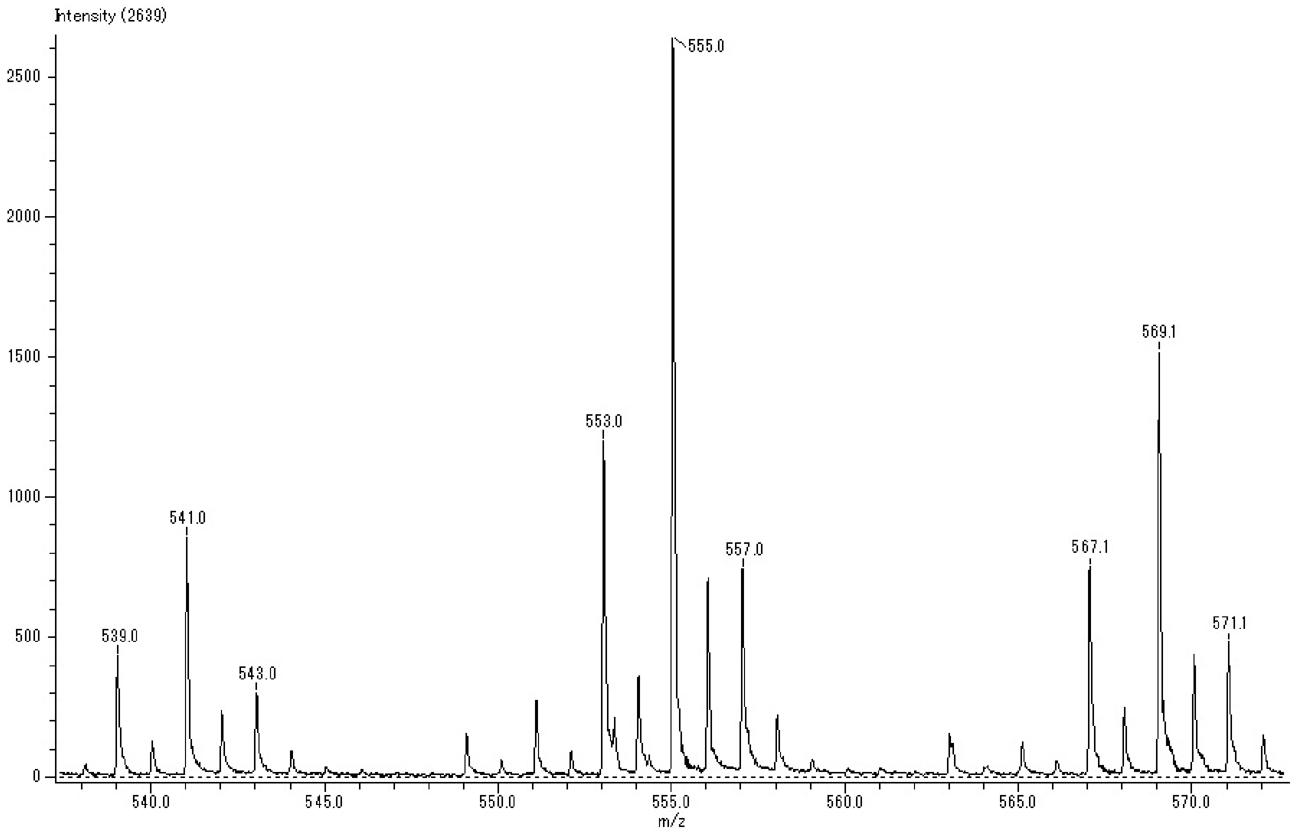


Fig. S1. ESI-MS spectrum (positive ion mode) for the reaction mixture in Scheme 3 (A crossover experiment).

X-ray diffraction studies

Diffraction data were collected on a Rigaku VariMax Saturn CCD diffractometer with graphite monochromated Mo-Ka radiation (λ = 0.71075 Å) at −180 °C. Intensity data were corrected for Lorentz and polarization effects and for an empirical absorption.[S1] All calculations were performed using the *CrystalStructure*[S2] crystallographic software package except for refinements, which was performed using SHELXL-97.[S3] The structures were solved by direct methods (SIR-97 for **2a**BF_4[S4] and SIR-2011 for **4**Cl[S5]) and expanded using Fourier techniques. Non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least-squares techniques. Hydrogen atoms were placed at the calculated positions with fixed isotropic parameters. Details of the X-ray diffraction study are summarized in Table S1.

Table S1. X-ray crystallographic data for 2aBF$_4$ and 4Cl.

	2aBF$_4$	**4**Cl·CH$_3$OH
CCDC	1555548	1555549
empirical formula	$C_{19}H_{25}BClF_4IrN_2O_2$	$C_{19}H_{29}Cl_2IrN_2O_2$
formula weight	627.90	580.58
dimension of crystals	0.23×0.08×0.07	0.186×0.171×0.089
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$ (#19)	$P2_1/c$ (#14)
a [Å]	7.5430(10)	11.7603(11)
b [Å]	12.7445(17)	12.1239(12)
c [Å]	22.732(3)	15.2286(15)
α [°]	90.0000	90.0000
β [°]	90.0000	91.3973(15)
γ [°]	90.0000	90.0000
V [Å^3]	2185.2(6)	2170.7(4)
Z	4	4
ρ_{calcd} [g cm^{-3}]	1.908	1.776
F(000)	1216	1136
μ [cm^{-1}]	63.005	64.289
trans. factors range	0.444–0.643	0.362–0.564
index ranges	$-9 \leq h \leq 9$	$-15 \leq h \leq 13$
	$-16 \leq k \leq 12$	$-15 \leq k \leq 15$
	$-29 \leq l \leq 29$	$-19 \leq l \leq 19$
no. rflns measured	17827	17299
no. unique rflns	8521	8138
R_{int}	0.0385	0.0330
no. rflns ($I > 2\sigma(I)$)	5000	4889
no. params refined	271	347
$R1$ ($I > 2\sigma(I)$)[a]	0.0269	0.0253
R (All cata)	0.0315	0.0296
$wR2$ (All cata)[b]	0.0545	0.0622
GOF[c]	0.994	1.098
max diff peak/hole [e Å^{-3}]	1.70/–2.09	0.76/–2.15

[a] $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma w(F_o^2)^2]^{1/2}$, $w = 1 / [\sigma^2 F_o^2 + (aP)^2 + bP]$ (a and b are constants suggested by the refinement program; $P = [\max(F_o^2,0) + 2F_c^2] / 3$). [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2 / (N_{\text{obs}} - N_{\text{params}})]^{1/2}$.

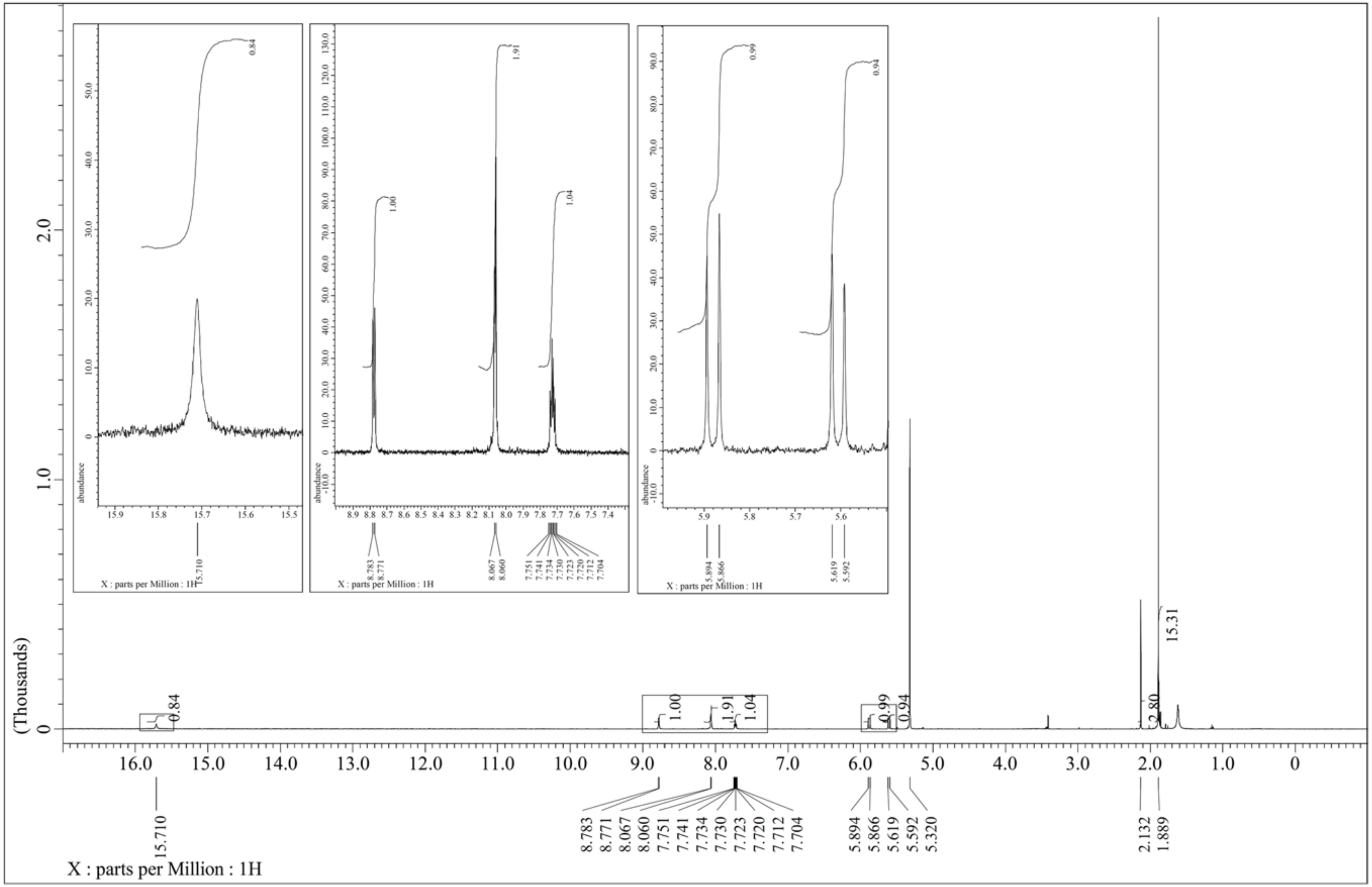


Fig. S2. ^{1}H NMR (CD_2Cl_2) spectrum of 2aCl.

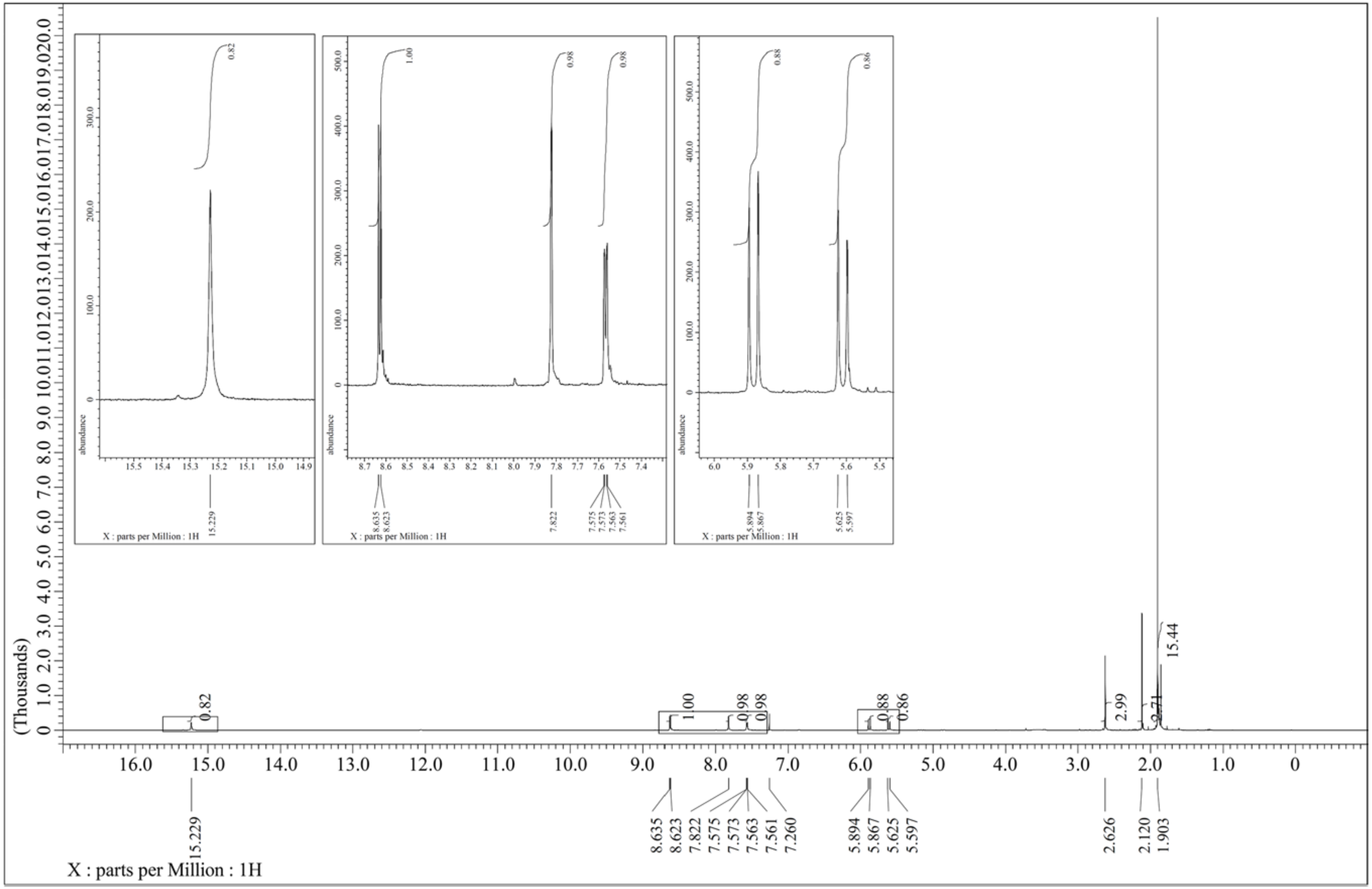


Fig. S3. ¹H NMR (CDCl₃) spectrum of 2bCl.

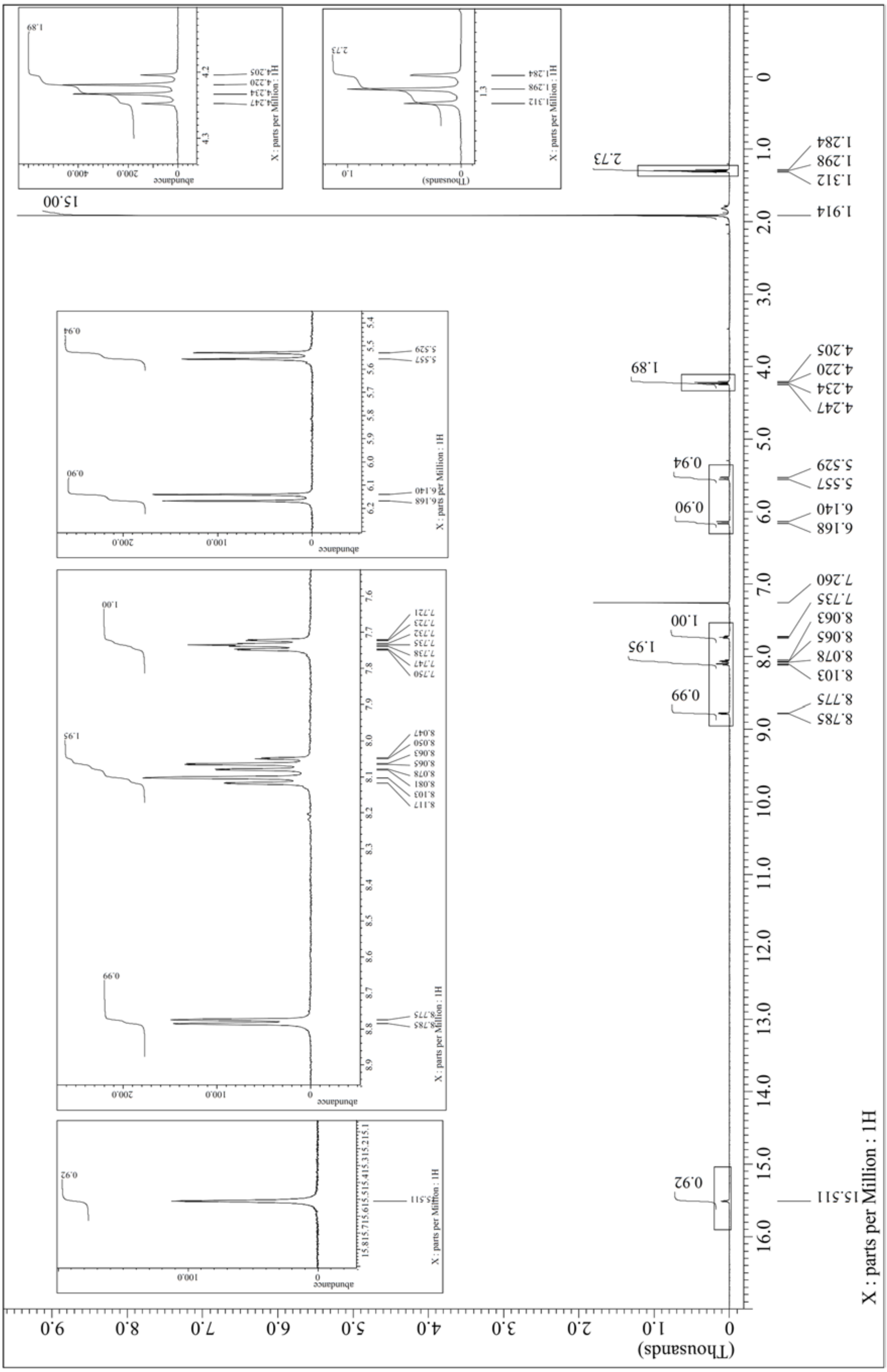


Fig. S4. ¹H NMR ($CDCl_3$) spectrum of 2dCl.

Fig. S5. **^{1}H NMR (CDCl$_3$) spectrum of 2eCl.**

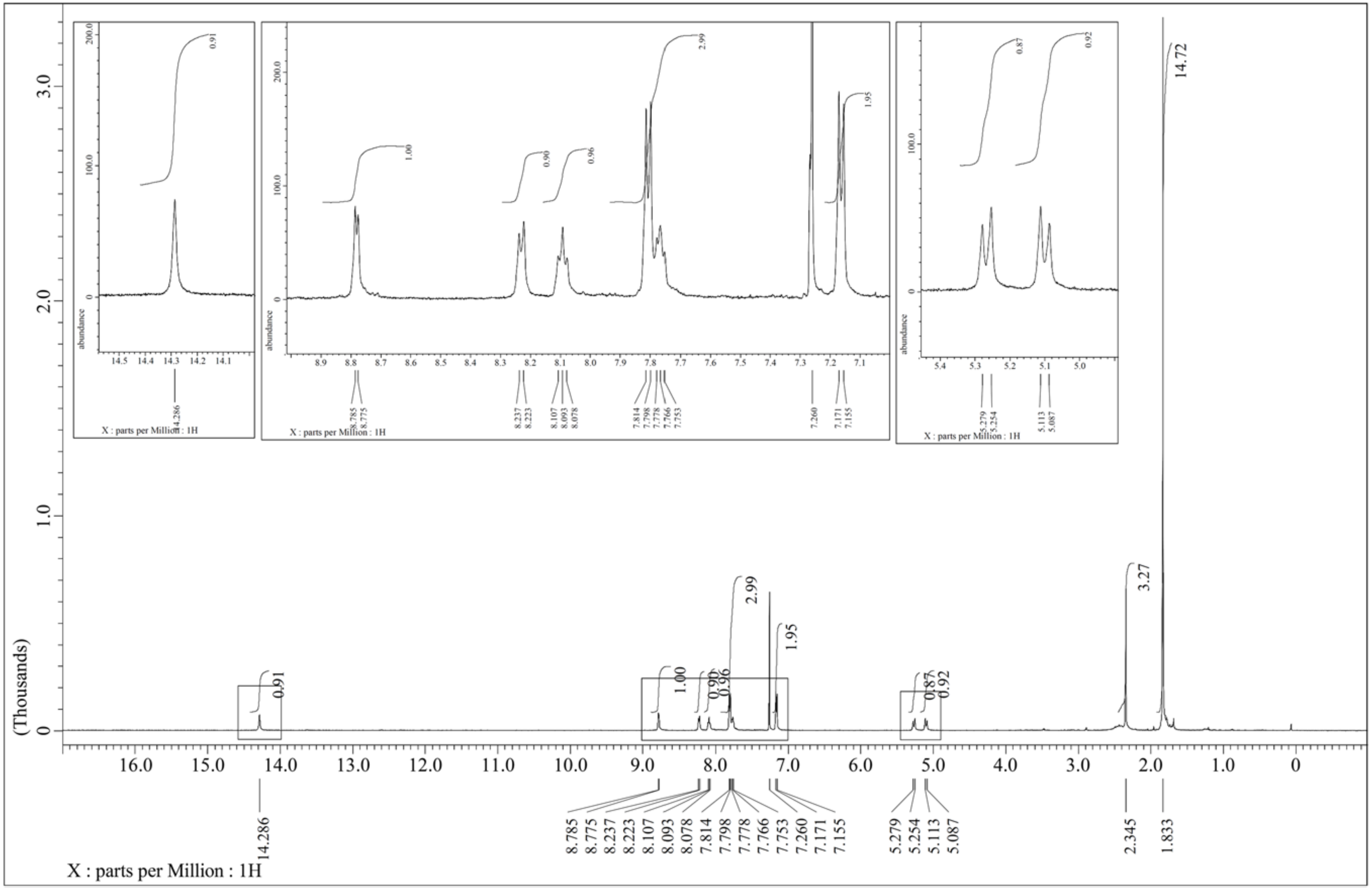


Fig. S6. ^{1}H NMR (CDCl$_3$) spectrum of 2fCl.

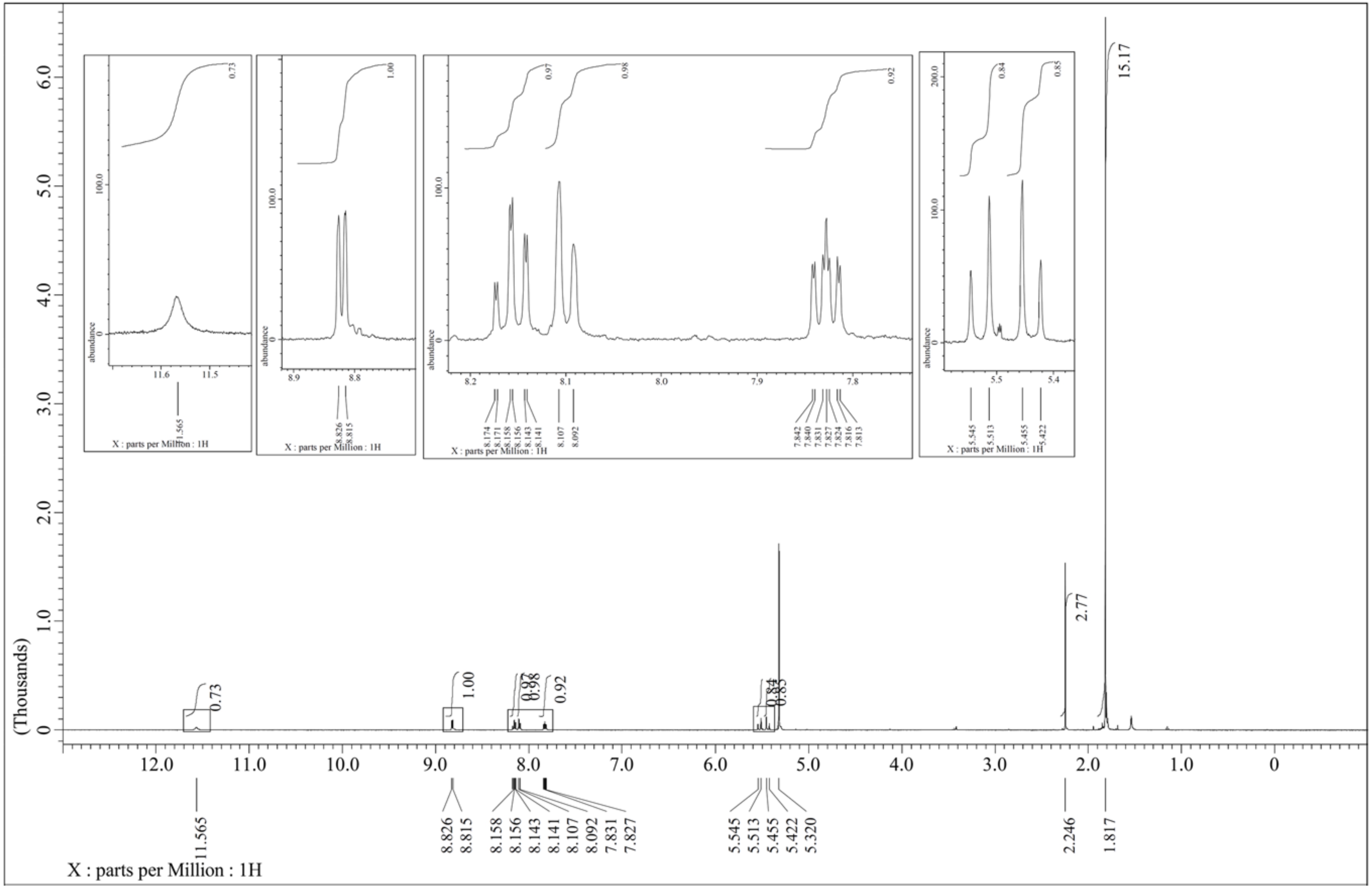


Fig. S7. ^1H NMR (CD_2Cl_2) spectrum of 2aBF$_4$.

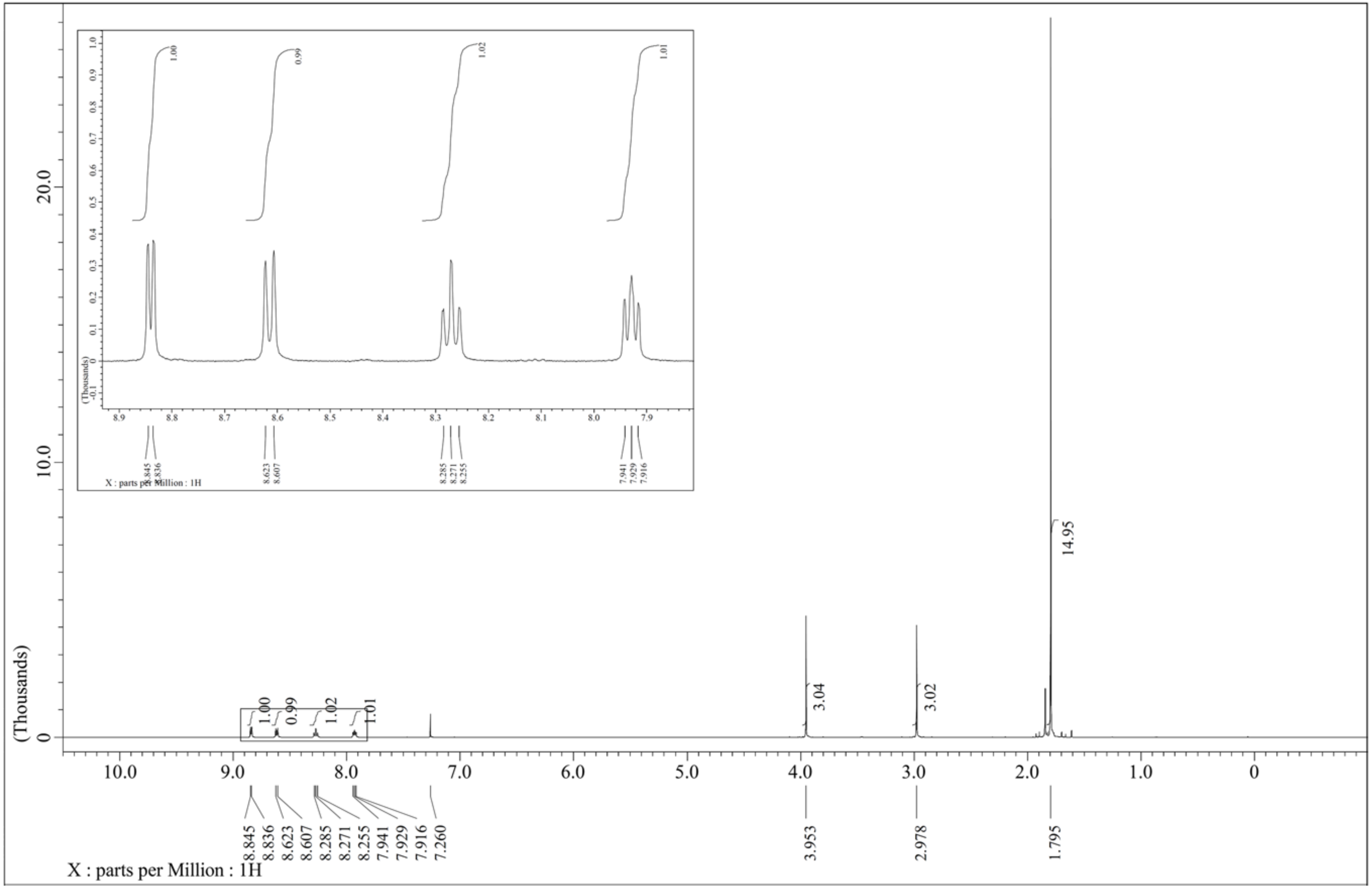


Fig. S8. ^{1}**H NMR (CDCl**$_3$**) spectrum of 4Cl.**

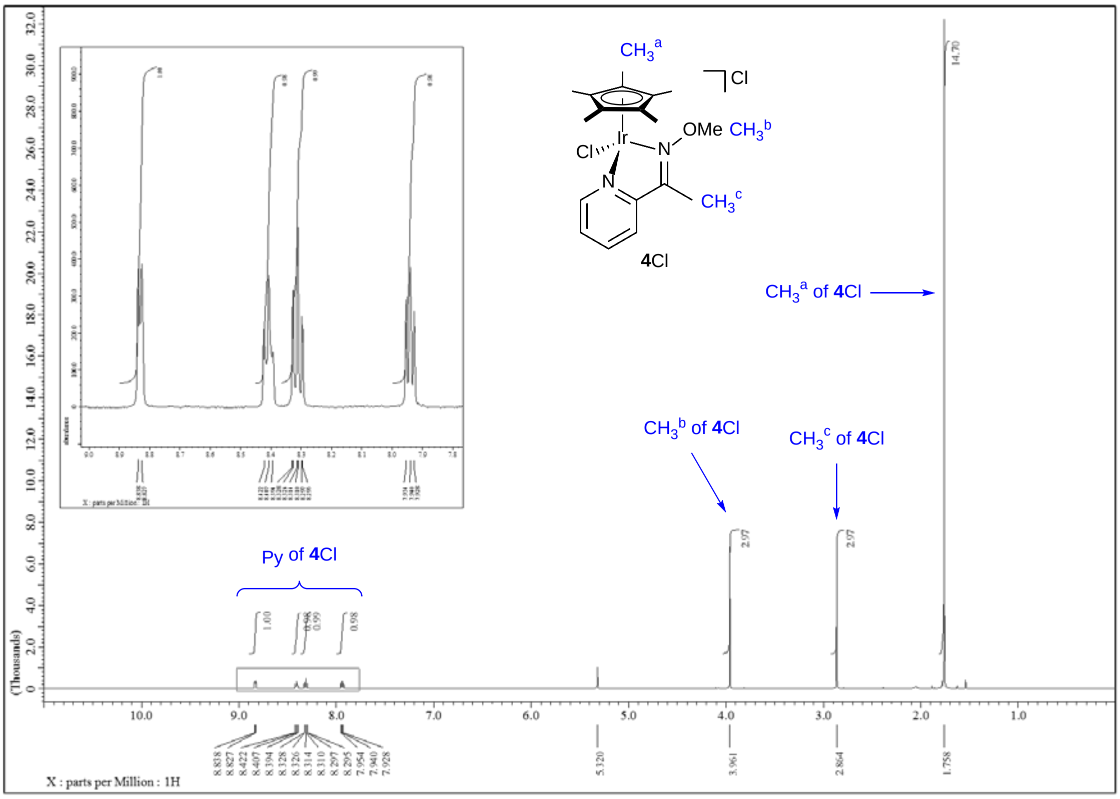


Fig. S9. Full ^{1}H NMR (CD_2Cl_2-D_2O) spectrum of 4Cl.

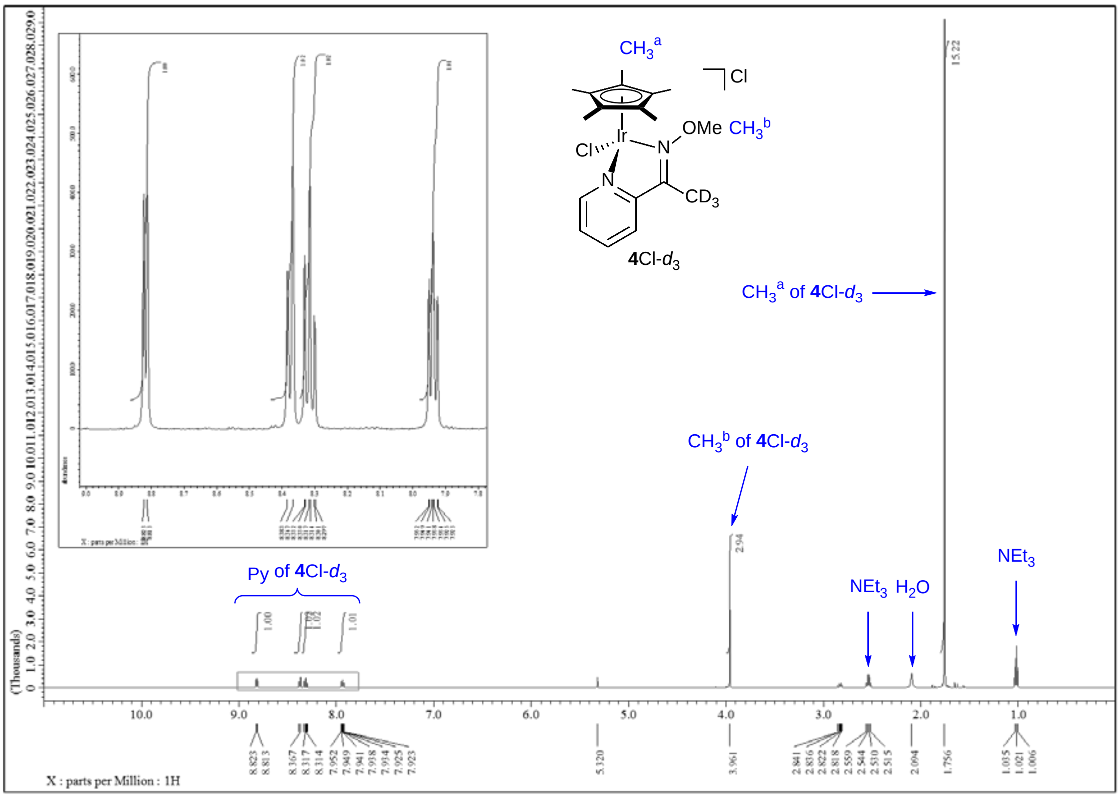


Fig. S10. Full ^{1}H NMR (CD_2Cl_2-D_2O-NEt_3) spectrum of 4Cl-d_3.

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