Supporting Information

A Bifunctional Iridium Catalyst Modified for Persistent Hydrogen Generation from Formic Acid: Understanding Deactivation via Cyclometalation of a 1,2-Diphenylethylenediamine Motif

Asuka Matsunami[1], Shigeki Kuwata[1,2], and Yoshihito Kayaki*[1]

[1]Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, 2-12-1-E4-1 O-okayama, Meguro-ku Tokyo 152-8552, Japan
[2]PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
*E-mail for Y. K.: ykayaki@o.cc.titech.ac.jp.

Contents

General information

All manipulations of oxygen and moisture-sensitive materials were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents and formic acid were purchased from Kanto Chemical Co., Inc. and dried by refluxing over sodium benzophenone ketyl (1,2-dimethoxyethane) or B_2O_3 (formic acid), and distilled under argon before use. Deionized water was produced by a Millipore Elix 3 system. THF-d_8 was degassed by three freeze-pump-thaw cycles and purified by trap-to-trap distillation after being dried with CaH_2. The Ir (**1a**, **1b**) complexes derived from TfDPEN were prepared according to our previous paper[1]. [1]H (399.8 MHz), [19]F (376.2 MHz), and [13]C{[1]H} (100.5 MHz) NMR were recorded on a JEOL JNM-ECX400 spectrometer at 25 ˚C. The NMR chemical shifts were referenced to an external tetramethylsilane signal (0.0 ppm) by using the signals of residual proton impurities in the deuterated solvents for ^{1}H and ^{13}C, and referenced to an external CF_3CO_2H signal (-76.5 ppm) for ^{19}F NMR. Abbreviations for NMR are as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, or br = broad.

Representative procedures for the catalytic evolution of hydrogen from formic acid

A syringe pump
0.3 mL/min
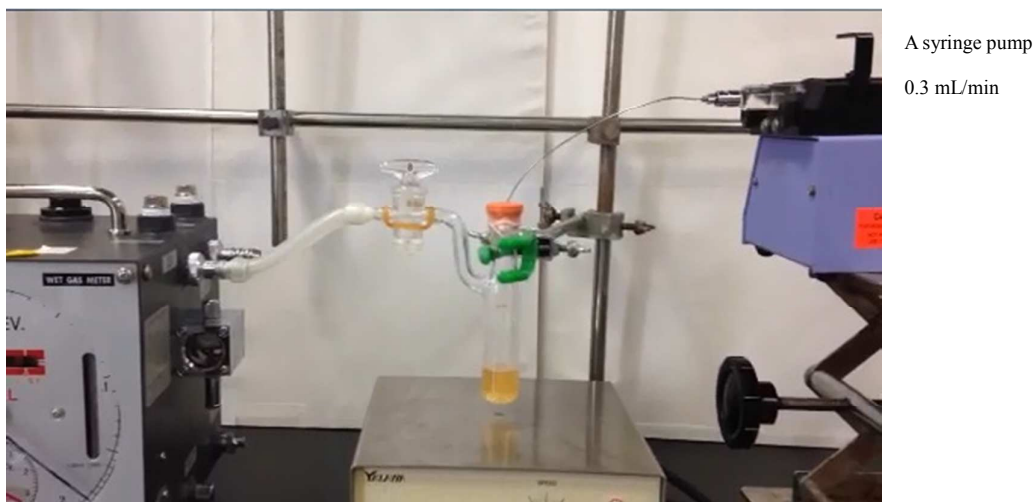
Figure S1. The experimental set up

To a solution of the iridium catalyst **1b** (20.9 mg, 0.030 mmol) in DME (3 mL) and degassed water (3 mL), formic acid was added for 10 min by using a syringe pump (0.3 mL/min). Using a mass-flowmeter, the rate of the gas evolution amount was measured.
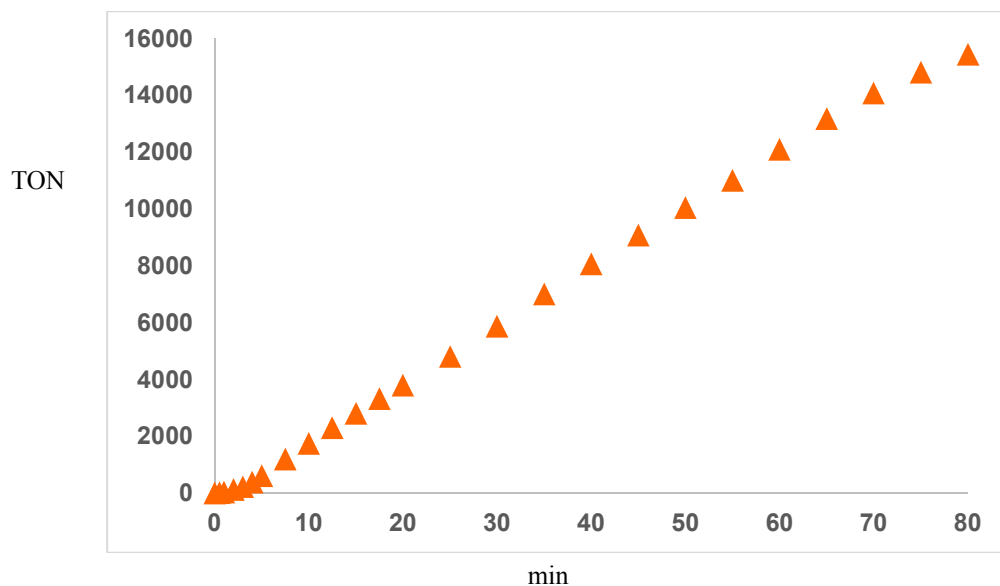
$S/C = 1.59 \times 10^4$ (**5a** 0.01 mmol, HCOOH 6 mL (0.075 mL/min), DME 6 mL, H_2O 6 mL)

Figure S2. Time versus TON plots for the catalytic acceptorless dehydrogenation from formic acid using complex **5b** at 60 °C.

Preparation and characterization data for Ir complexes

Thermal transformation of the hydridoiridium complex 1b to iridacycles 2 and 3

<in DME>

A solution of the hydridoiridium complex **1b** (139.3 mg, 0.207 mmol) in DME (10 mL) was stirred under reflux conditions for 38 h. After the removal of the solvent, the crude product (**2**:**3** = 82:18, determined by ^{1}H NMR) was purified by silica gel flash column chromatography (eluted with hexane and diethyl ether (1:2); TLC information: R_f = 0.33 for **2**, and R_f = 0.22 for **3**) to give the pure complexes **2** (56.5 mg, 0.084 mmol, 41% isolated yield).

<in DME/H$_2$O mixed solvent>

A solution of the hydridoiridium complex **1b** (149.8 mg, 0.223 mmol) in DME and water mixed solvent (each 5 mL) was stirred at 80 °C for 50 min. After the removal of the DME, dichloromethane (15 mL) was introduced and water layer was separated. The crude product (129.3 mg, 0.193 mmol, 87% crude yield; **2**:**3** = 14:86, determined by ^{1}H NMR) was purified by silica gel flash column chromatography (eluted with hexane and diethyl ether (1:2)) to give the pure complexes **3** (98.4 mg, 0.147 mmol, 66% isolated yield).

Cp*Ir[κ³(N,N',C)-(S,S)-NH₂CHPhCHNTfC₆H₄] (2)
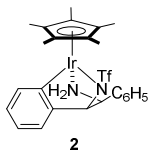
^{1}H NMR (THF–d_8, r.t.): δ 1.85 (s, 15H; C$_5$(CH_3)$_5$), 3.13 (d, $^3J_{HH}$ = 8.4 Hz, 1H; NH$_2$CHPhCHNTfC$_6$H$_4$), 3.78 (d, $^3J_{HH}$ = 10.6 Hz, 1H; NH_2CHPhCHNTfC$_6$H$_4$), 4.75 (s, 1H; NH$_2$CHPhCHNTfC$_6$H$_4$), 4.97 (br, 1H; NH_2CHPhCHNTfC$_6$H$_4$), 6.80-6.85 (m, 2H; aryl) , 7.14-7.17 (m, 1H; aryl), 7.21-7.25 (m, 1H; aryl), 7.29-7.32 (m, 2H; aryl), 7.36-7.38 (m, 2H; aryl), 7.74-7.76 (m, 1H; aryl); ^{19}F NMR (THF–d_8, r.t.): δ -76.2 (s, CF_3); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, r.t.): δ 9.02 (C$_5$(CH$_3$)$_5$), 54.4 (NH$_2$CHC$_6$H$_5$CHNTfC$_6$H$_4$), 78.0 (NH$_2$CHC$_6$H$_5$CHNTfC$_6$H$_4$), 86.9 (C$_5$(CH$_3$)$_5$), 120.7 (q, $^1J_{CF}$ = 327.8 Hz; CF_3), 120.3, 123.2, 125.9, 126.9, 128.4, 128.7, 132.5, 139.5, 151.2, 152.0 (NH$_2$CHC$_6$H$_5$CHNTfC_6H$_4$). Elemental analysis calcd(%) for C$_{25}$H$_{28}$F$_3$IrN$_2$O$_2$S: C, 44.83; H, 4.21; N, 4.18; found: C, 44.45; H, 4.35; N, 4.20.

Cp*Ir[κ³(N,N',C)-(S,S)-NTfCHPhCHNH₂C₆H₄] (3)
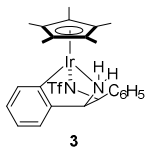
^{1}H NMR (CD$_2$Cl$_2$, r.t.): δ 1.83 (s, 15H; C$_5$(CH_3)$_5$), 3.00 (br, 1H; NTfCHC$_6$H$_5$CHNH_2C$_6$H$_4$), 3.26 (br, 1H; NTfCHC$_6$H$_5$CHNH_2C$_6$H$_4$), 4.14 (s, 1H; NTfCHC$_6$H$_5$CHNH$_2$C$_6$H$_4$), 4.57 (s, 1H, NTfCHC$_6$H$_5$CHNH$_2$C$_6$H$_4$), 6.99-7.03 (m, 2H; aryl), 7.32-7.35 (m, 2H; aryl), 7.42-7.46 (m, 2H; aryl), 7.51-7.53 (m, 2H; aryl), 7.80-7.82 (m, 1H; aryl); ^{19}F NMR (CD$_2$Cl$_2$, r.t.): δ -76.0 (s, CF_3); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, r.t.): δ 9.32 (C$_5$(CH$_3$)$_5$),

62.7 (NTf*C*H*C$_6$H$_5$*C*HNH$_2$C$_6$H$_4$), 71.5 (NTfCH*C$_6$H$_5$*CHNH$_2$C$_6$H$_4$), 87.4 (C_5(CH$_3$)$_5$), 119.8 (q, $^1J_{CF}$ = 332.7 Hz; CF$_3$), 121.5, 123.0, 126.0, 126.8, 127.7, 129.1, 133.6, 142.0, 148.0, 150.2 (NTfCH*C$_6$H$_5$*CHNH$_2$*C$_6$H$_4$*). Elemental analysis calcd(%) for C$_{25}$H$_{28}$F$_3$IrN$_2$O$_2$S: C, 44.83; H, 4.21; N, 4.18; found: C, 45.01; H, 4.48; N, 4.29.

*Cp*IrCl[κ^2(N,N') –NTfCH$_2$CH$_2$NH$_2$]*
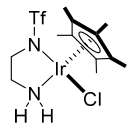
^{1}H NMR (CD$_2$Cl$_2$, r.t.): δ 1.64 (s, 15H; C$_5$(C*H$_3$*)$_5$), 2.96 (br, 4H; NTfC*H$_2$*C*H$_2$*NH$_2$), 3.80 (br, 1H; NTfCH$_2$CH$_2$N*H$_2$*), 3.99 (br, 1H; NTfCH$_2$CH$_2$N*H$_2$*); ^{19}F NMR (CD$_2$Cl$_2$, r.t.): δ -74.2 (s, C*F$_3$*); ^{13}C{^{1}H} NMR (DMSO–d_6): δ 9.19 (C$_5$(*C*H$_3$)$_5$), 47.7 (NTfCH$_2$*C*H$_2$NH$_2$), 51.8 (NTf*C*H$_2$CH$_2$NH$_2$), 85.3 (C_5(CH$_3$)$_5$), 121.1 (q, $^1J_{CF}$ = 329.7 Hz; CF$_3$). Elemental analysis calcd(%) for C$_{14}$H$_{23}$Cl$_3$F$_3$IrN$_2$O$_2$S: C, 26.32; H, 3.63; N, 4.38; found: C, 26.66; H, 3.43; N, 4.41.

*Cp*IrH[κ^2(N,N') - NTfCH$_2$CH$_2$NH$_2$]*
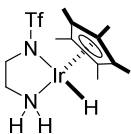
^{1}H NMR (THF–d_8, r.t.): δ -11.3 (s, 1H; Ir*H*), 1.70 (s, 15H; C$_5$(C*H$_3$*)$_5$), 2.42 (m, 2H; NTfCH$_2$C*H$_2$*NH$_2$) , 2.82 (br, 2H; NTfC*H$_2$*CH$_2$NH$_2$), 4.43 (br, 1H; NTfCH$_2$CH$_2$N*H$_2$*), 5.05 (br, 1H; NTfCH$_2$CH$_2$N*H$_2$*); ^{19}F NMR (THF–d_8, r.t.): δ -72.6 (s, C*F$_3$*); ^{13}C{^{1}H} NMR (THF–d_8, r.t.): δ = 9.28 (C$_5$(C*H$_3$)$_5$), 49.1 (NTfCH$_2$*C*H$_2$NH$_2$), 54.0 (NTf*C*H$_2$CH$_2$NH$_2$), 85.7 (C_5(CH$_3$)$_5$), 122.6 (q, $^1J_{CF}$ = 331.6 Hz; CF$_3$). Elemental analysis calcd(%) for C$_{13}$H$_{22}$F$_3$IrN$_2$O$_2$S: C, 30.05; H, 4.27; N, 5.39; found: C, 30.28; H, 4.48; N, 5.46.

X-ray structure determination

All measurements were made on a Rigaku Saturn CCD area detector equipped with graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.71070 Å) under nitrogen stream at 123 K. Indexing was performed from eighteen images. The crystal-to-detector distance was 45.05 mm. The data were collected to a maximum 2θ value of 55.0°. A total of 720 oscillation images were collected. A sweep of data was carried out using ω scans from –110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 0.0°. A second sweep was performed using ω scans from –110.0 to 70.0° in 0.5° steps, at χ = 45.0° and ϕ = 90.0°. Intensity data were collected for Lorentz-polarization effects as well as absorption. Structure solution and refinements were performed with the CrystalStructure program package. The heavy atom positions were determined by Direct methods (SIR2002), and the remaining non-hydrogen atoms were found by subsequent Fourier techniques. An empirical absorption correction based on equivalent reflections was applied to all data. All non-hydrogen atoms other than solvent molecules were refined anisotropically by full-matrix least-square techniques based on F^2. The low-temperature data collection enabled hydrogens attached to the primary amine in **2**, **3**, **4**, and **5b** to be located from the Fourier difference map and refined isotropically. All other hydrogens either were not refined or were constrained to ride on their parent atom. Relevant crystallographic data are compiled in Tables S3 and S4.

Table S1. Comparison of selected bond lengths and angles of **2** and **3**.

Complex	Ir1-N1	Ir-N2	Ir-Cp*(av.)	∠N1-Ir1-N2
2[a]	2.1595 Å	2.139 Å	2.1886 Å	75.95°
3	2.120(4) Å	2.166(4) Å	2.1926 Å	76.20(15) °

a) Mean value.

Table S2. Comparison of selected bond lengths and angles of **5b** and **1b**[1].

Complex	Ir1-N1	Ir-N2	Ir-Cp*(av.)	∠N1-Ir1-N2
5b	2.143(4) Å	2.136(5) Å	2.1908 Å	79.63(17)°
1b	2.126(2) Å	2.149(3) Å	2.195 Å	76.58(10) °
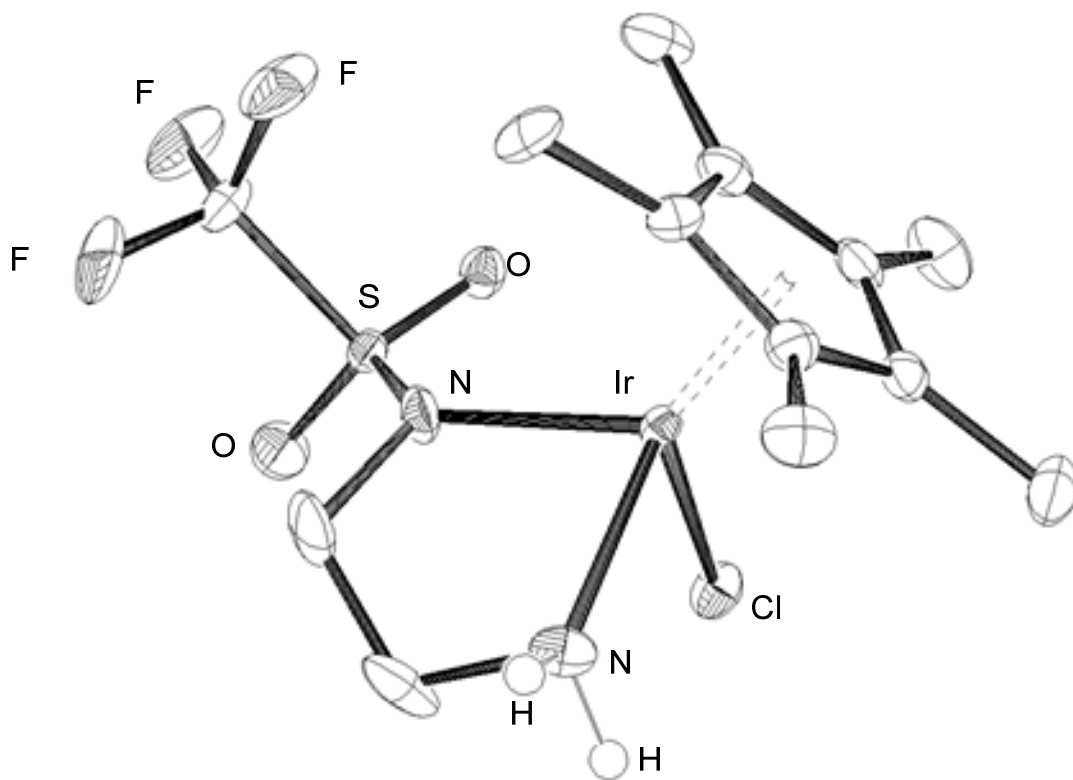
Figure S3. ORTEP drawing of a chloroiridium complex **4** derived from TfEN.
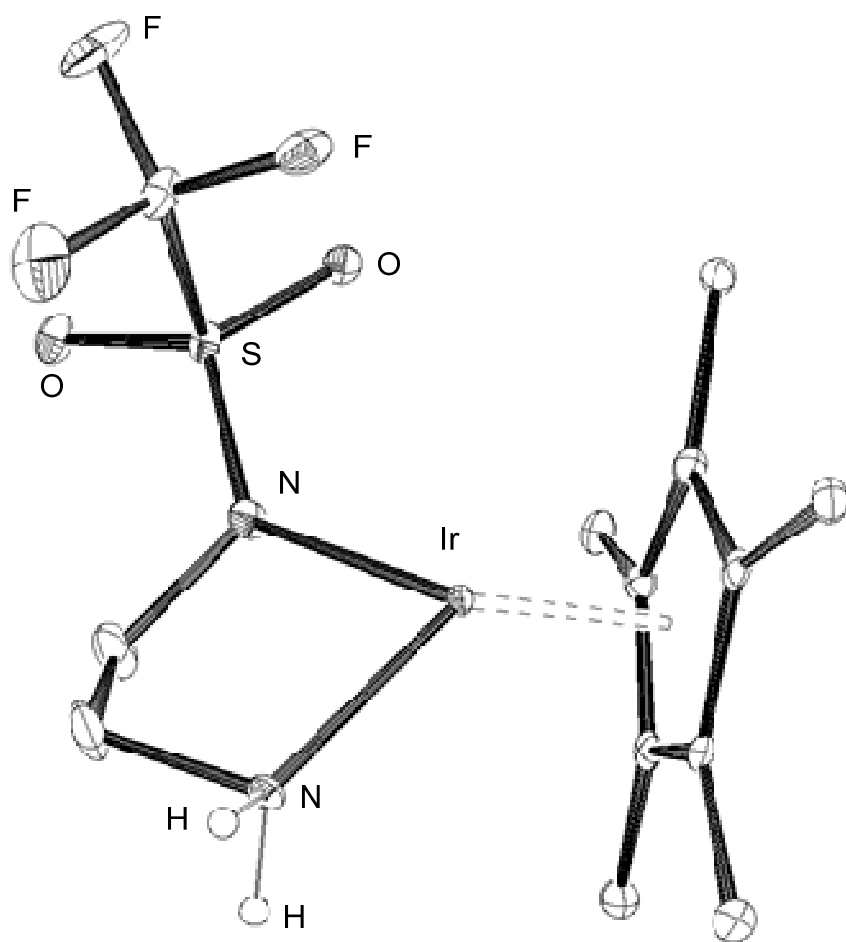
Figure S4. ORTEP drawing of a hydridoiridium complex **5b** derived from TfEN.

Table S3.   Crystallographic data for **2** and **3**

	2	3
Empirical Formula	$C_{25}H_{28}F_3IrN_2O_2S$	$C_{25}H_{28}F_3IrN_2O_2S$
Formula Weight	669.78	669.78
Crystal Color, Habit	yellow, prism	yellow, prism
Crystal System	monoclinic	orthohombic
Space Group	$C2$ (#5)	$P2_12_12_1$ (#19)
Lattice Parameters	$a = 20.77760$ Å	$a = 11.1945(10)$ Å
	$b = 14.35170$ Å	$b = 12.8348(11)$ Å
	$c = 18.81300$ Å	$c = 17.138(2)$ Å
		$\beta = 114.794(2)$ °
	$V = 5234.74710$ Å^3	$V = 2462.4(4)$ Å^3
Z value	8	4
D_{calc}	1.700 g/cm^3	1.807 g/cm^3
F$_{000}$	2624.00	1312.00
μ(MoKα)	52.401 cm^{-1}	55.699 cm^{-1}
Exposure Rate	10.0 sec./°	10.0 sec./°
No. of Reflections Measured	21609	20326
No. of unique reflections	9804	5646
No. Variables	670	336
$R1$ (I>2.00σ(I))	0.0359	0.0253
w$R2$ (All reflections)	0.0935	0.0647
GOF on F^2	1.000	1.000

$R1 = \Sigma \,||F_o| - |F_c|| \,/\, \Sigma \,|F_o|$, w$R2 = [\, \Sigma \,(\, w\,(F_o^2 - F_c^2)^2 \,)/ \Sigma \,w(F_o^2)^2 \,]^{1/2}$

Table S4. Crystallographic data for **4·CH$_2$Cl$_2$** and **5b**

	4·CH$_2$Cl$_2$	5b
Empirical Formula	C$_{14}$H$_{23}$Cl$_3$F$_3$IrN$_2$O$_2$S	C$_{13}$H$_{22}$F$_3$IrN$_2$O$_2$S
Formula Weight	638.98	519.60
Crystal Color, Habit	yellow, prism	orange, prism
Crystal System	monoclinic	tetragonal
Space Group	$P2_1/c$ (#14)	$I4_1cd$ (#110)
Lattice Parameters	a = 11.168(3) Å	a = 16.724(2) Å
	b = 11.884(3) Å	c = 23.136(3) Å
	c = 16.488(4)Å	
	β = 104.162(3) °	
	V = 2121.7(9) Å^3	V = 6470.7(12) Å^3
Z value	4	16
D_{calc}	2.000 g/cm^3	2.133 g/cm^3
F$_{000}$	1232.00	4000.00
μ(MoKα)	68.226 cm^{-1}	84.433 cm^{-1}
Exposure Rate	6.0 sec./°	2.0 sec./°
No. of Reflections Measured	17038	25200
No. of unique reflections	4866	3673
No. Variables	258	221
$R1$ (I>2.00σ(I))	0.0381	0.0234
w$R2$ (All reflections)	0.1014	0.0574
GOF on F^2	1.000	1.000

$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$, w$R2 = [\, \Sigma \, (\, w \, (F_o^2 - F_c^2)^2 \,)/ \Sigma \, w(F_o^2)^2 \,]^{1/2}$

2

Filename   = 1847-TfIrC-Tf-1H-5.jd
Author   = delta
Experiment   = single_pulse.ex2
Sample_id   = 1
Solvent   = TETRAHYDROFURAN-
Creation_time   = 26-JAN-2017 11:06:03
Revision_time   = 28-JAN-2017 18:38:32
Current_time   = 28-JAN-2017 18:38:57

Comment   = single_pulse
Data_format   = 1D COMPLEX
Dim_size   = 52428
Dim_title   = 1H
Dim_units   = [ppm]
Dimensions   = X
Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength   = 9.389766[T] (400[MHz])
X_acq_duration   = 2.84164096[s]
X_domain   = 1H
X_freq   = 399.78219838[MHz]
X_offset   = -7[ppm]
X_points   = 65536
X_prescans   = 1
X_resolution   = 0.35190934[Hz]
X_sweep   = 23.06273063[kHz]
Irr_domain   = 1H
Irr_freq   = 399.78219838[MHz]
Irr_offset   = 5[ppm]
Tri_domain   = 1H
Tri_freq   = 399.78219838[MHz]
Tri_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 16
Total_scans   = 16

X_90_width   = 13.68[us]
X_acq_time   = 2.84164096[s]
X_angle   = 45[deg]
X_atn   = 2.1[dB]
X_pulse   = 6.84[us]
Irr_mode   = Off
Tri_mode   = Off
Dante_presat   = FALSE
Initial_wait   = 1[s]
Recvr_gain   = 44
Relaxation_delay = 6[s]
Repetition_time   = 8.84164096[s]
Temp_get   = 23.8[dC]

X : parts per Million : 1H

S12

2

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
phase : 80 : 0 : 50[%]
phase : 0 : 0 : 50[%]
phase : -70 : 0 : 50[%]
base_correct : None : 0 : Smooth

Derived from: 1847-TfIrC-Tf-19F-1.jdf

Filename   = 1847-TfIrC-Tf-19F-5.j
Author   = delta
Experiment   = single_pulse.ex2
Sample_id   = 1
Solvent   = TETRAHYDROFURAN-
Creation_time   = 26-JAN-2017 11:10:26
Revision_time   = 28-JAN-2017 18:39:37
Current_time   = 28-JAN-2017 18:39:50

Comment   = single_pulse
Data_format   = 1D REAL
Dim_size   = 52428
Dim_title   = 19F
Dim_units   = [ppm]
Dimensions   = X
Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength = 9.389766[T] [400[MHz]
X_acq_duration = 0.34603008[s]
X_domain   = 19F
X_freq   = 376.17105393[MHz]
X_offset   = 0[ppm]
X_points   = 65536
X_prescans   = 1
X_resolution   = 2.88992217[Hz]
X_sweep   = 189.39393939[kHz]
Irr_domain   = 19F
Irr_freq   = 376.17105393[MHz]
Irr_offset   = 5[ppm]
Tri_domain   = 19F
Tri_freq   = 376.17105393[MHz]
Tri_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 32
Total_scans   = 32

X_90_width   = 16.1[us]
X_acq_time   = 0.34603008[s]
X_angle   = 45[deg]
X_atn   = 3[dB]
X_pulse   = 8.05[us]
Irr_mode   = Off
Tri_mode   = Off
Dante_presat   = FALSE
Initial_wait   = 1[s]
Recvr_gain   = 52
Relaxation_delay = 5[s]
Repetition_time = 5.34603008[s]
Temp_get   = 23.7[dC]

abundance

−76.2178

X : parts per Million : 19F

2

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
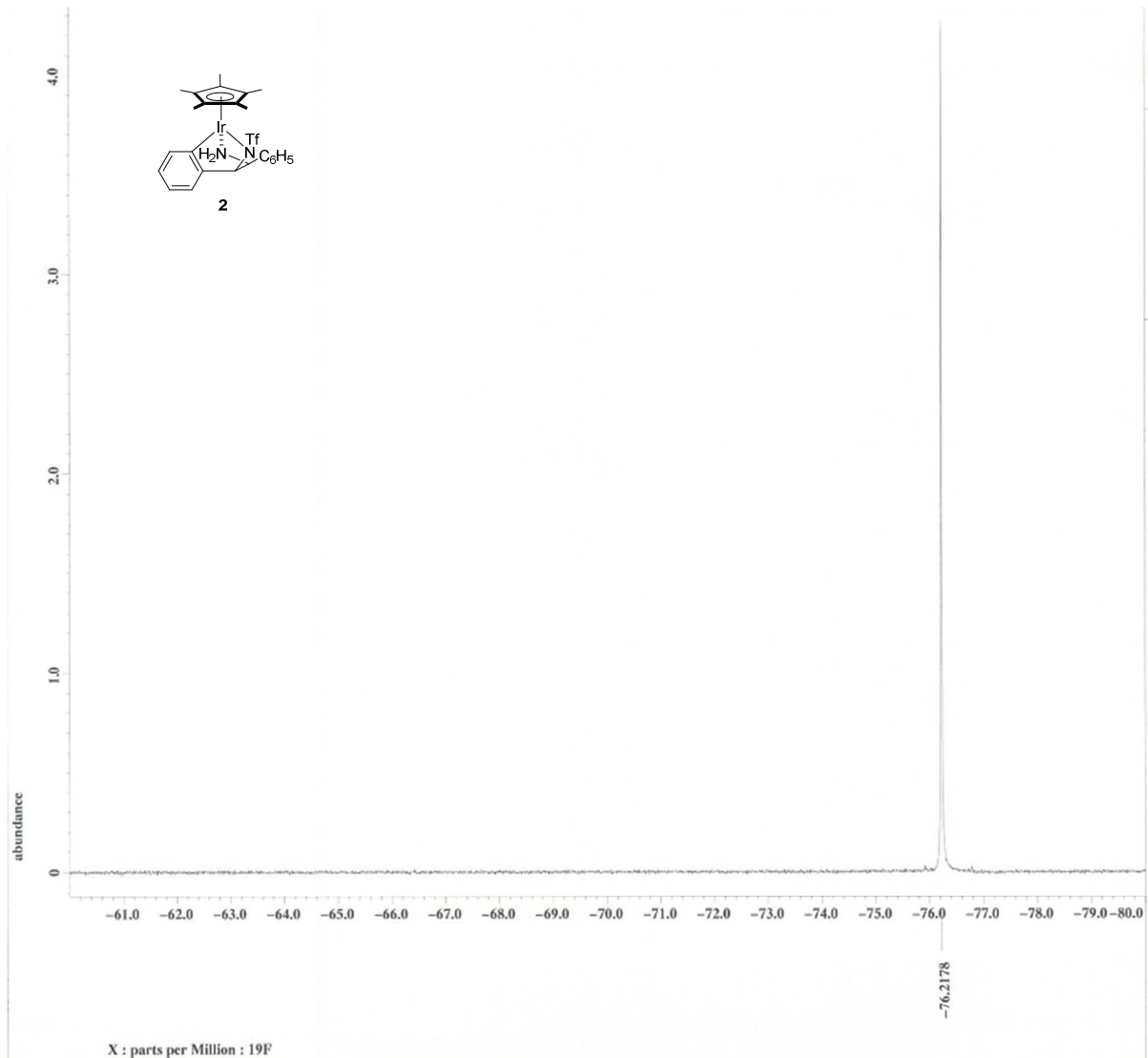zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 2417-TfIrC-NTf-1.jdf

Filename   = 2417-TfIrC-NTf-3.jdf
Author   = delta
Experiment   = single_pulse_dec
Sample_id   = 1
Solvent   = METHYLENE-CHLORI
Creation_time   = 20-AUG-2016 07:52:19
Revision_time   = 20-AUG-2016 09:14:41
Current_time   = 20-AUG-2016 09:16:09

Comment   = single pulse decouple
Data_format   = 1D COMPLEX
Dim_size   = 26214
Dim_title   = 13C
Dim_units   = [ppm]
Dimensions   = X
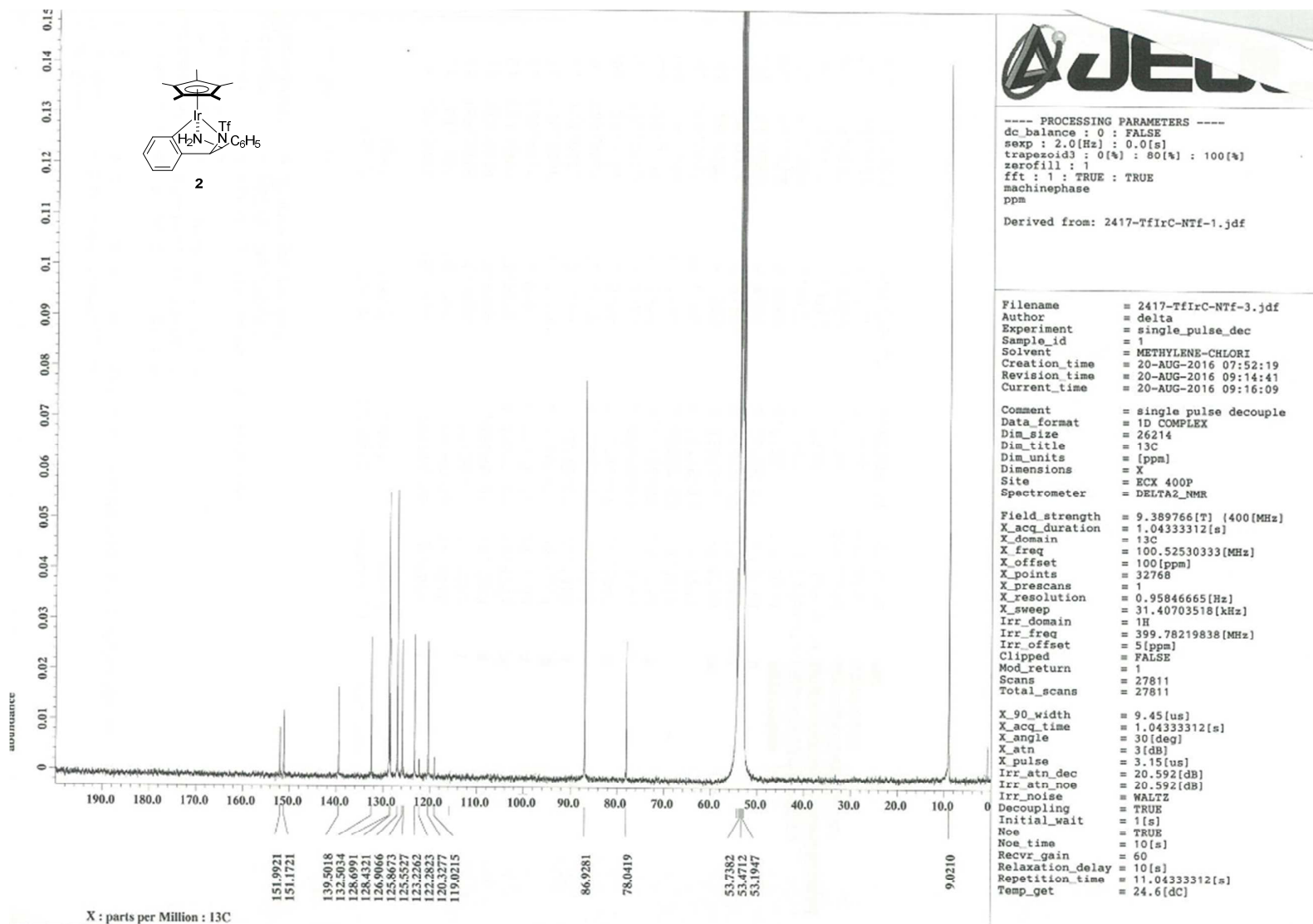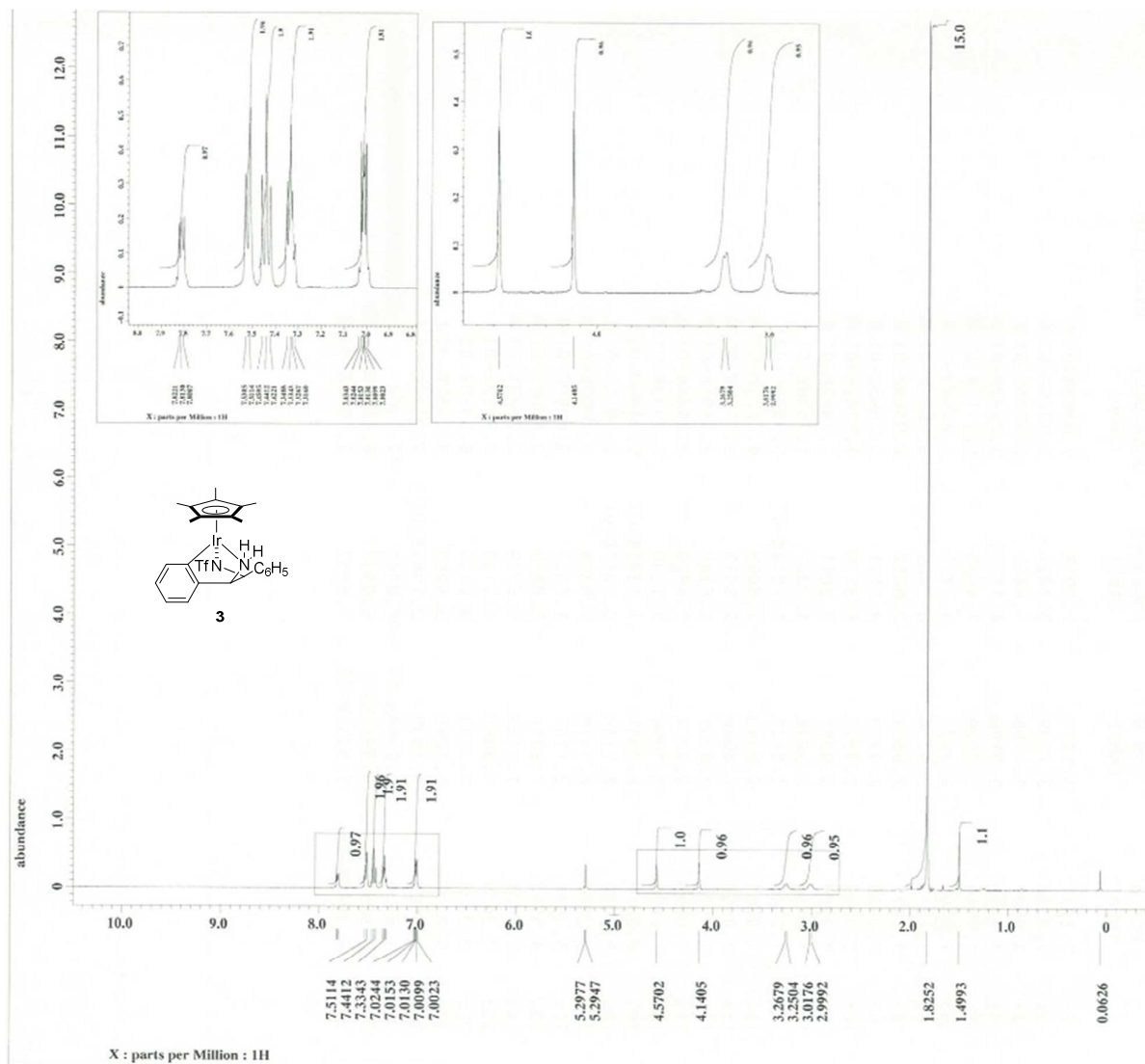Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 1.04333312[s]
X_domain   = 13C
X_freq   = 100.52530333[MHz]
X_offset   = 100[ppm]
X_points   = 32768
X_prescans   = 1
X_resolution   = 0.95846665[Hz]
X_sweep   = 31.40703518[kHz]
Irr_domain   = 1H
Irr_freq   = 399.78219838[MHz]
Irr_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 27811
Total_scans   = 27811

X_90_width   = 9.45[us]
X_acq_time   = 1.04333312[s]
X_angle   = 30[deg]
X_atn   = 3[dB]
X_pulse   = 3.15[us]
Irr_atn_dec   = 20.592[dB]
Irr_atn_noe   = 20.592[dB]
Irr_noise   = WALTZ
Decoupling   = TRUE
Initial_wait   = 1[s]
Noe   = TRUE
Noe_time   = 10[s]
Recvr_gain   = 60
Relaxation_delay = 10[s]
Repetition_time = 11.04333312[s]
Temp_get   = 24.6[dC]

151.9921
151.1721
139.5018
132.5034
128.6991
128.4321
126.9066
125.8673
125.5527
123.2262
122.2823
120.3377
119.0215
86.9281
78.0419
53.7382
53.4712
53.1947
9.0210

X : parts per Million : 13C

X : parts per Million : 19F

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 1847-13C-1.jdf

Filename   = 1847-13C-25.jdf
Author   = delta
Experiment   = single_pulse_dec
Sample_id   = 1
Solvent   = METHYLENE-CHLORI
Creation_time   = 22-JAN-2017 14:44:19
Revision_time   = 27-JAN-2017 14:22:04
Current_time   = 27-JAN-2017 14:24:12

Comment   = single pulse decouple
Data_format   = 1D COMPLEX
Dim_size   = 26214
Dim_title   = 13C
Dim_units   = [ppm]
Dimensions   = X
Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength = 9.389766[T] (400[MHz])
X_acq_duration = 1.04333312[s]
X_domain   = 13C
X_freq   = 100.52530333[MHz]
X_offset   = 100[ppm]
X_points   = 32768
X_prescans   = 2
X_resolution   = 0.95846665[Hz]
X_sweep   = 31.40703518[kHz]
Irr_domain   = 1H
Irr_freq   = 399.78219838[MHz]
Irr_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 16131
Total_scans   = 16131

X_90_width   = 9.45[us]
X_acq_time   = 1.04333312[s]
X_angle   = 30[deg]
X_atn   = 3[dB]
X_pulse   = 3.15[us]
Irr_atn_dec   = 20.592[dB]
Irr_atn_noe   = 20.592[dB]
Irr_noise   = WALTZ
Decoupling   = TRUE
Initial_wait   = 1[s]
Noe   = TRUE
Noe_time   = 3[s]
Recvr_gain   = 54
Relaxation_delay = 3[s]
Repetition_time = 4.04333312[s]
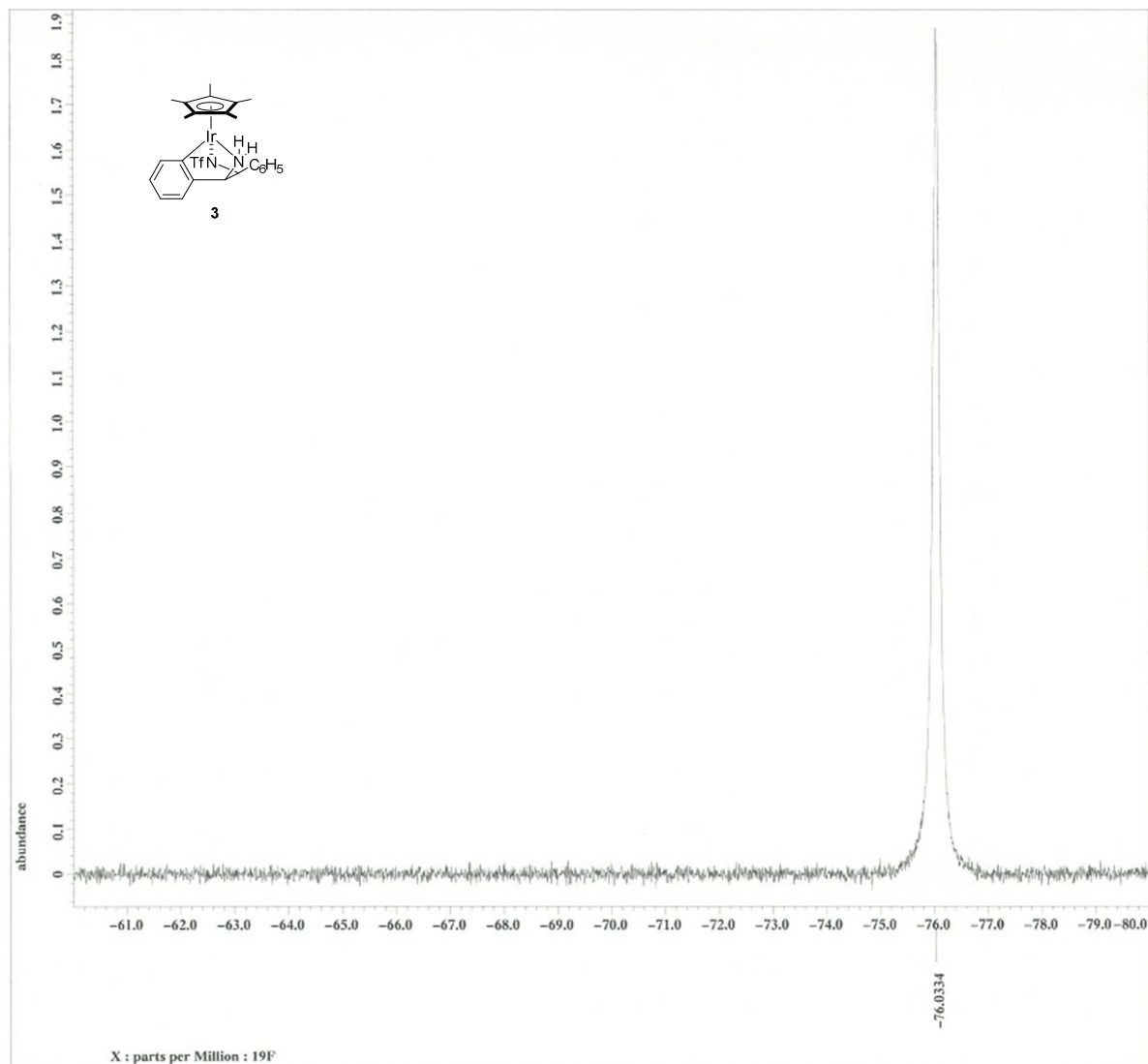Temp_get   = 42[dC]

X : parts per Million : 13C

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
phase : 0 : 0 : 50[%]

Derived from: 1695-1H-1.jdf

Filename	= 1695-1H-5.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= 1
Solvent	= METHYLENE-CHLORI
Creation_time	= 8-JUN-2015 12:22:58
Revision_time	= 8-JUN-2015 13:02:06
Current_time	= 8-JUN-2015 13:02:45
Comment	= single_pulse
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 400P
Spectrometer	= DELTA2_NMR
Field_strength	= 9.389766[T] (400[MHz])
X_acq_duration	= 3.2768[s]
X_domain	= 1H
X_freq	= 399.78219838[MHz]
X_offset	= 5[ppm]
X_points	= 32768
X_prescans	= 0
X_resolution	= 0.30517578[Hz]
X_sweep	= 10[kHz]
Irr_domain	= 1H
Irr_freq	= 399.78219838[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 1H
Tri_freq	= 399.78219838[MHz]
Tri_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 16
Total_scans	= 16
X_90_width	= 14[us]
X_acq_time	= 3.2768[s]
X_angle	= 45[deg]
X_atn	= 2.1[dB]
X_pulse	= 7[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 48
Relaxation_delay	= 2[s]
Repetition_time	= 5.2768[s]
Temp_get	= 25.8[dC]

X : parts per Million : 1H

abundance

0.97

31.13m

−73.5970
−74.1502

X : parts per Million : 19F

5.0 4.0 3.0 2.0 1.0 0

−10.0 −20.0 −30.0 −40.0 −50.0 −60.0 −70.0 −80.0 −90.0 −100.0

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
reference : −77.638[ppm] : −76.5[ppm]
phase : 0 : 0 : 50[%]
phase : 0 : 0 : 50[%]
phase : −4 : 0 : 50[%]
base_correct : None : 0 : Smooth

Filename   = 1695-19F-4.jdf
Author   = delta
Experiment   = single_pulse.ex2
Sample_id   = 1
Solvent   = METHYLENE-CHLORI
Creation_time   = 8-JUN-2015 12:20:10
Revision_time   = 8-JUN-2015 12:57:28
Current_time   = 8-JUN-2015 12:57:52

Comment   = single_pulse
Data_format   = 1D REAL
Dim_size   = 26214
Dim_title   = 19F
Dim_units   = [ppm]
Dimensions   = X
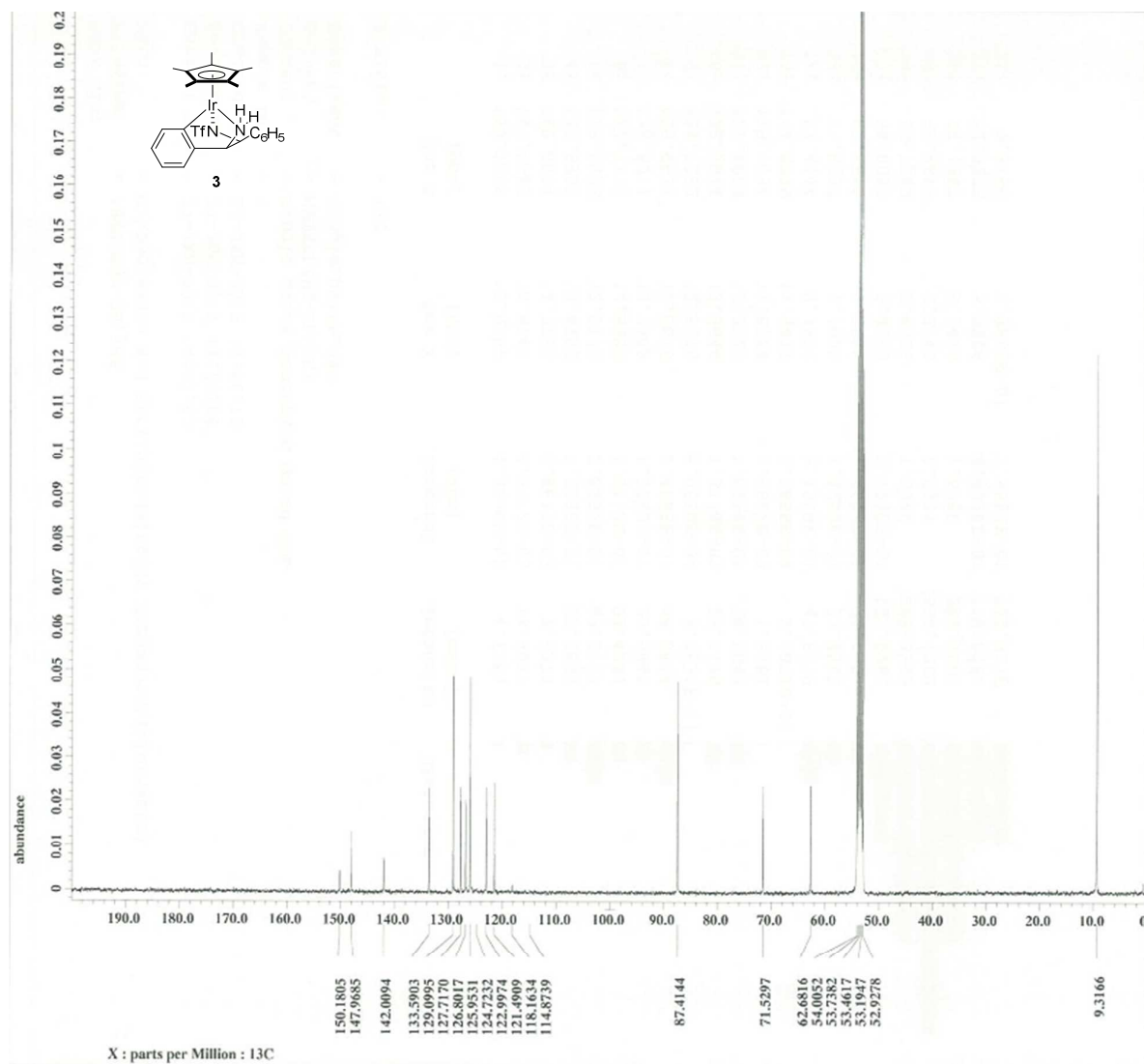Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength   = 9.389766[T] (400[MHz])
X_acq_duration   = 0.17301504[s]
X_domain   = 19F
X_freq   = 376.17105393[MHz]
X_offset   = 0[ppm]
X_points   = 32768
X_prescans   = 1
X_resolution   = 5.77984434[Hz]
X_sweep   = 189.39393939[kHz]
Irr_domain   = 19F
Irr_freq   = 376.17105393[MHz]
Irr_offset   = 5[ppm]
Tri_domain   = 19F
Tri_freq   = 376.17105393[MHz]
Tri_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 12
Total_scans   = 12

X_90_width   = 16.1[us]
X_acq_time   = 0.17301504[s]
X_angle   = 45[deg]
X_atn   = 3[dB]
X_pulse   = 8.05[us]
Irr_mode   = Off
Tri_mode   = Off
Dante_presat   = FALSE
Initial_wait   = 1[s]
Recvr_gain   = 54
Relaxation_delay = 5[s]
Repetition_time   = 5.17301504[s]
Temp_get   = 25.9[dC]

abundance

X : parts per Million : 13C

125.9722
122.6923
119.4124
116.1325

85.3072
79.8344
79.5006
79.1669

40.6758
40.4661
40.2563
40.0466
39.8368
39.6270
39.4173

9.1926

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
phase : 0 : 0 : 50[%]

Derived from: 105-60801-2543-1H-1.jdf

Filename   = 105-60801-2543-1H-5.j
Author   = delta
Experiment   = single_pulse.ex2
Sample_id   = 1
Solvent   = TETRAHYDROFURAN-
Creation_time   = 2-AUG-2016 13:38:26
Revision_time   = 28-JAN-2017 18:13:20
Current_time   = 28-JAN-2017 18:13:45

Comment   = single_pulse
Data_format   = 1D COMPLEX
Dim_size   = 52428
Dim_title   = 1H
Dim_units   = [ppm]
Dimensions   = X
Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength   = 9.389766[T] [400[MHz]
X_acq_duration   = 2.84164096[s]
X_domain   = 1H
X_freq   = 399.78219838[MHz]
X_offset   = -7[ppm]
X_points   = 65536
X_prescans   = 1
X_resolution   = 0.35190934[Hz]
X_sweep   = 23.06273063[kHz]
Irr_domain   = 1H
Irr_freq   = 399.78219838[MHz]
Irr_offset   = 5[ppm]
Tri_domain   = 1H
Tri_freq   = 399.78219838[MHz]
Tri_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 16
Total_scans   = 16

X_90_width   = 13.68[us]
X_acq_time   = 2.84164096[s]
X_angle   = 45[deg]
X_atn   = 2.1[dB]
X_pulse   = 6.84[us]
Irr_mode   = Off
Tri_mode   = Off
Dante_presat   = FALSE
Initial_wait   = 1[s]
Recvr_gain   = 44
Relaxation_delay = 6[s]
Repetition_time   = 8.84164096[s]
Temp_get   = 23.7[dC]

X : parts per Million : 1H

0.94

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
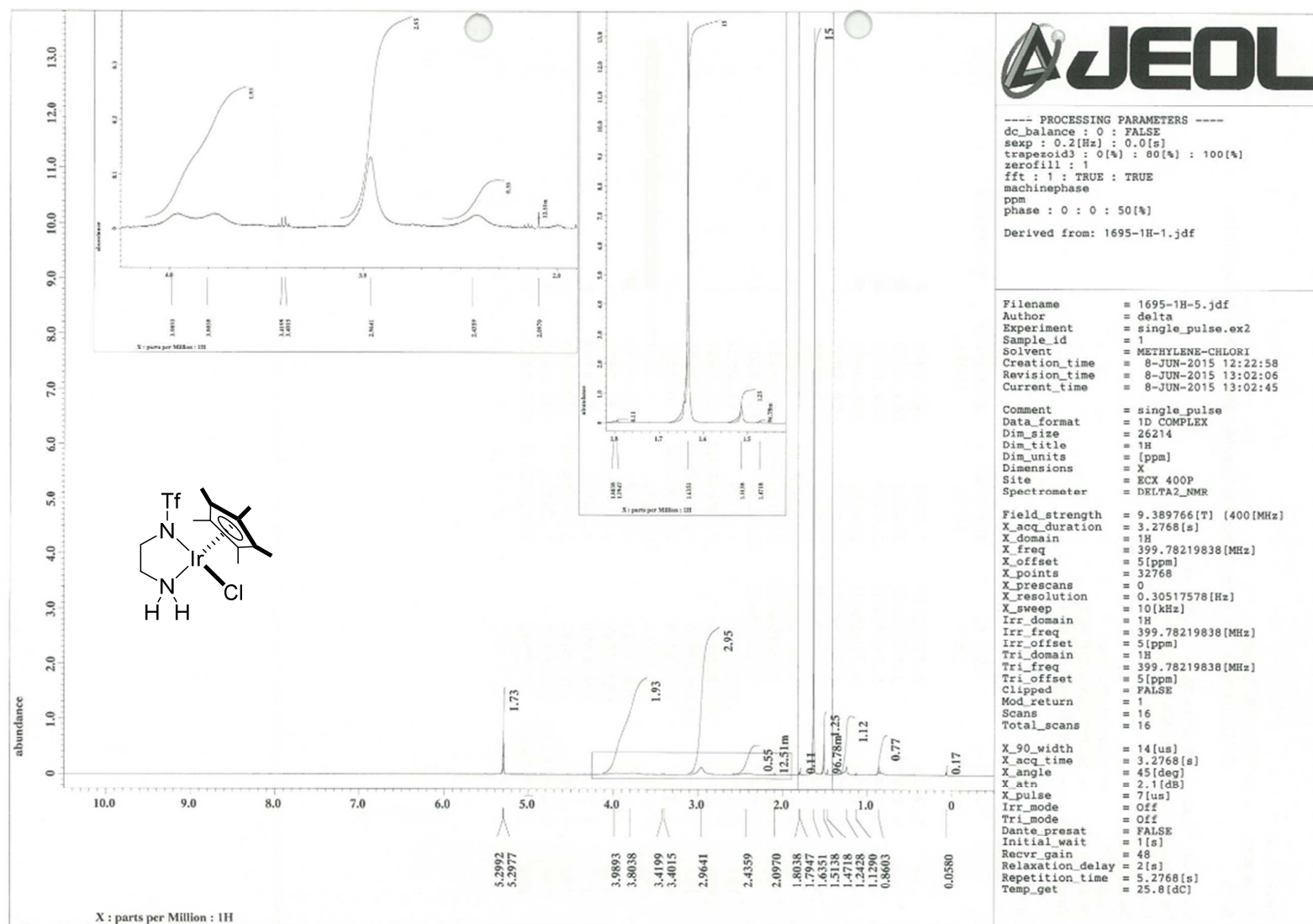zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm
phase : 80 : 0 : 50[%]
phase : 0 : 0 : 50[%]
phase : -47 : 0 : 50[%]
base_correct : None : 0 : Smooth

Derived from: TfenIrH-ka-19F-1.jdf

Filename   = TfenIrH-ka-19F-6.jdf
Author   = delta
Experiment   = single_pulse.ex2
Sample_id   = 1
Solvent   = TETRAHYDROFURAN-
Creation_time   = 31-MAR-2017 21:00:53
Revision_time   = 31-MAR-2017 22:22:34
Current_time   = 31-MAR-2017 22:22:41

Comment   = single_pulse
Data_format   = 1D REAL
Dim_size   = 52428
Dim_title   = 19F
Dim_units   = [ppm]
Dimensions   = X
Site   = ECX 400P
Spectrometer   = DELTA2_NMR

Field_strength = 9.389766[T] (400[MHz]
X_acq_duration = 0.34603008[s]
X_domain   = 19F
X_freq   = 376.17105393[MHz]
X_offset   = 0[ppm]
X_points   = 65536
X_prescans   = 1
X_resolution   = 2.88992217[Hz]
X_sweep   = 189.39393939[kHz]
Irr_domain   = 19F
Irr_freq   = 376.17105393[MHz]
Irr_offset   = 5[ppm]
Tri_domain   = 19F
Tri_freq   = 376.17105393[MHz]
Tri_offset   = 5[ppm]
Clipped   = FALSE
Mod_return   = 1
Scans   = 42
Total_scans   = 42

X_90_width   = 16.1[us]
X_acq_time   = 0.34603008[s]
X_angle   = 45[deg]
X_atn   = 3[dB]
X_pulse   = 8.05[us]
Irr_mode   = Off
Tri_mode   = Off
Dante_presat   = FALSE
Initial_wait   = 1[s]
Recvr_gain   = 54
Relaxation_delay = 5[s]
Repetition_time = 5.34603008[s]
Temp_get   = 23.2[dC]

−72.6301

−76.6326

abundance

−10.0   −20.0   −30.0   −40.0   −50.0   −60.0   −70.0   −80.0   −90.0   −100.0
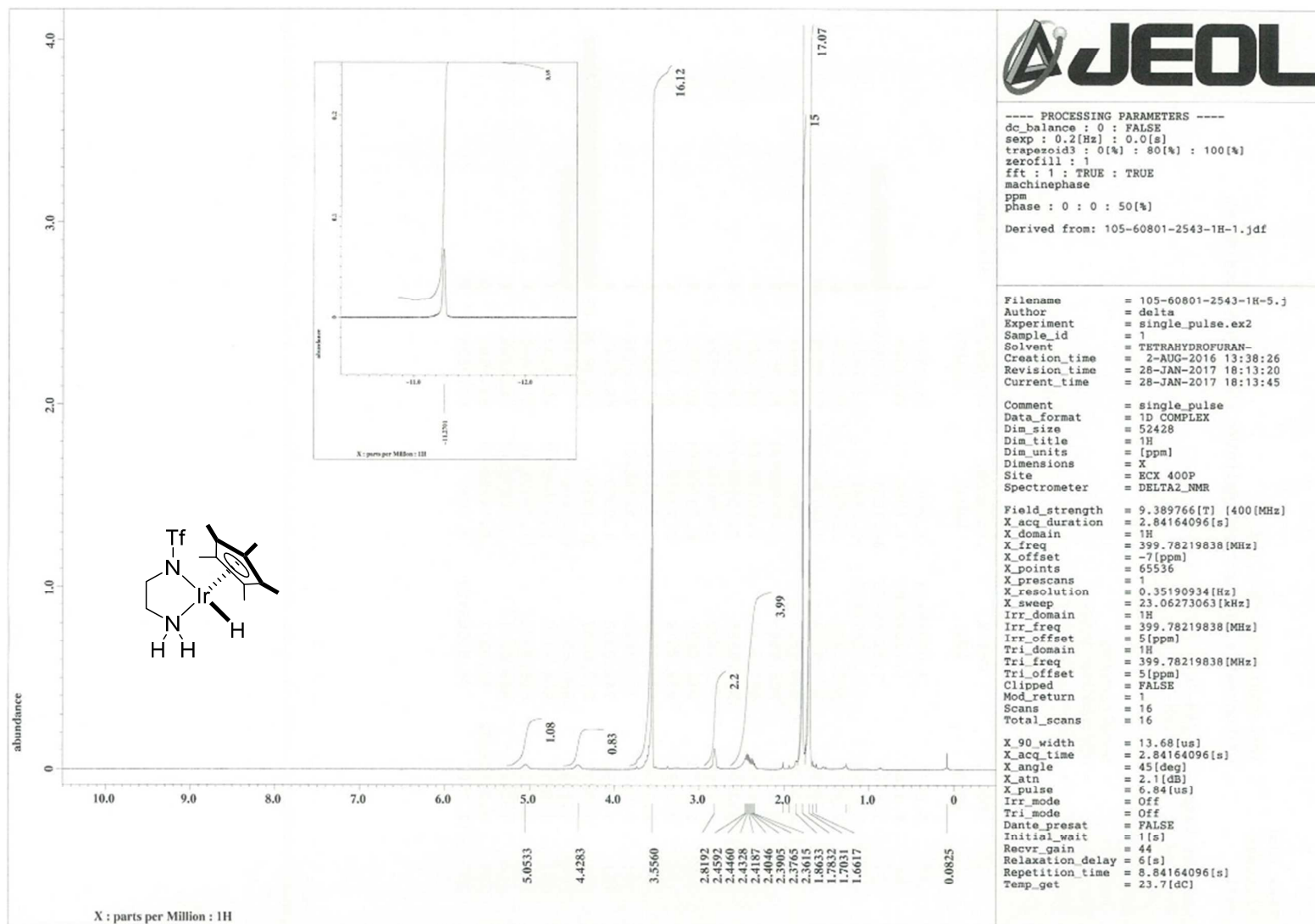
X : parts per Million : 19F

---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 2.0[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: 2543-TfenIrH-13C-1.jdf

Filename	= 2543-TfenIrH-13C-7.jd
Author	= delta
Experiment	= single_pulse_dec
Sample_id	= 1
Solvent	= TETRAHYDROFURAN-
Creation_time	= 11-AUG-2016 12:29:47
Revision_time	= 11-AUG-2016 13:57:34
Current_time	= 11-AUG-2016 14:06:38
Comment	= single pulse decouple
Data_format	= 1D COMPLEX
Dim_size	= 26214
Dim_title	= 13C
Dim_units	= [ppm]
Dimensions	= X
Site	= ECX 400P
Spectrometer	= DELTA2_NMR
Field_strength	= 9.389766[T] (400[MHz]
X_acq_duration	= 1.04333312[s]
X_domain	= 13C
X_freq	= 100.52530333[MHz]
X_offset	= 100[ppm]
X_points	= 32768
X_prescans	= 2
X_resolution	= 0.95846665[Hz]
X_sweep	= 31.40703518[kHz]
Irr_domain	= 1H
Irr_freq	= 399.78219838[MHz]
Irr_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 2999
Total_scans	= 2999
X_90_width	= 9.45[us]
X_acq_time	= 1.04333312[s]
X_angle	= 30[deg]
X_atn	= 3[dB]
X_pulse	= 3.15[us]
Irr_atn_dec	= 20.592[dB]
Irr_atn_noe	= 20.592[dB]
Irr_noise	= WALTZ
Decoupling	= TRUE
Initial_wait	= 1[s]
Noe	= TRUE
Noe_time	= 3[s]
Recvr_gain	= 46
Relaxation_delay	= 3[s]
Repetition_time	= 4.04333312[s]
Temp_get	= 23.9[dC]

X : parts per Million : 13C

Reference

1 A. Matsunami, Y. Kayaki, T. Ikariya, *Chem. Eur. J.* **2015**, *21*, 13513.