Electronic Supplementary Information

Oxy-Tethered Cp*Ir(III) Complex as a Competent Catalyst for Selective Dehydrogenation from Formic Acid

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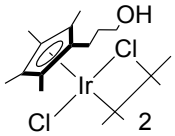
1. General Information

All experiments were conducted under an argon atmosphere following standard Schlenk techniques unless otherwise noted. Solvents and some reagents were distilled under argon after refluxing over CaH_2 (*n*-hexane and NEt_3), P_2O_5 (CH_2Cl_2, CH_3CN), $CaSO_4$ (DMF), Na/benzophenone ketyl (1,2-dimethoxyethane, Et_2O) or B_2O_3 (formic acid), and stored under an argon atmosphere. Water was deionised by using a Merck-Millipore Direct-Q 3 UV system and degassed by bubbling argon. All deuterated NMR solvents were purified by trap-to-trap distillation after being dried by appropriate methods and degassed by three freeze-pump-thaw cycles. FsDPEN was prepared according to the procedures described in the literature with modifications.[S1] The Rh complex **1b**,[S2] $C_5(CH_3)_4C_3H_6OH$[S2] and Cp*Ir(FsDPEN)[S3] were prepared according to the literatures. Other reagents were purchased from Tokyo Chemical Industry Co. Ltd., Sigma-Aldrich Co. LLC., Kanto Chemical Co. Inc. and Nacalai Tesque Ltd. used as delivered. ^{1}H (399.8 MHz), ^{19}F (376.2 MHz) and ^{13}C{^{1}H} (100.5 MHz) NMR spectra were recorded on a JNM-ECX400 spectrometers and 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.

2. Preparation and Characterization Data for Rh and Ir Complexes

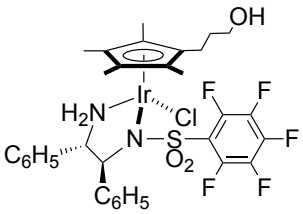
Synthesis of 1a.



To a solution of $IrCl_3 \cdot nH_2O$ (3.00 g, 6.78 mmol/51.73% Ir) in methanol (50 mL) was added $C_5(CH_3)_4C_3H_6OH$ (5.78 g. 32.0 mmol), Na_2CO_3 (0.935 g, 8.82 mmol) under argon atmosphere. The reaction mixture was refluxed for 24 h and then cooled. The solution was removed under reduced pressure and washed with diethyl ether and methanol to afford **1a** as a yellow powder (2.54 g, 5.73 mmol/Ir, 71% yield).

^{1}H NMR (399.8 MHz, $CDCl_3$, δ/ppm) 1.60, 1.63 (s, each 6H, $C_5(CH_3)_4$), 1.71 (tt, $^3J_{HH}$ = 6.3 Hz, 7.8 Hz, 2H, $CH_2CH_2CH_2OH$), 2.36 (t, $^3J_{HH}$ = 7.9, 2H, $CH_2CH_2CH_2OH$), 3.66 (t, $^3J_{HH}$ = 6.1, 2H, $CH_2CH_2CH_2OH$). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, δ/ppm): 9.27, 9.27 ($CpCH_3$), 20.8 ($CpCH_2$), 30.3 (CH_2CH_2OH), 62.2 (CH_2CH_2OH), 86.3, 86.8, 87.2 (CCH_3). Anal. Calcd for $C_{24}H_{38}Cl_4Ir_2O_2$: C, 32.58; H, 4.33. Found: C, 32.45; H, 4.24.

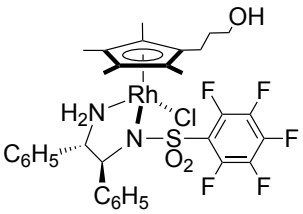
Synthesis of 2a.



A mixture of **1a** (442.0 mg, 0.999 mmol) and (*S*,*S*)-FsDPEN (442.5 mg, 1.00 mmol) in CH_2Cl_2 (20 mL), K_3PO_4 (237.2 mg, 1.12 mmol) was added and stirred at room temperature for 24 h. After filtration of the reaction mixture through a glass membrane filter, the yellow solution was concentrated under reduced pressure. Yellow crystals of the desired product were obtained by slow diffusion of hexane into the CH_2Cl_2 solution (788.8 mg, 0.930 mmol, 93% yield).

^{1}H NMR (399.8 MHz, CD_2Cl_2, δ/ppm) 1.74 (m, 2H, $CH_2CH_2CH_2OH$), 1.79 (m, 12H, $C_5(CH_3)_4$), 2.32 (t, $^3J_{HH}$ = 7.3, 2H, $CH_2CH_2CH_2OH$), 3.68 (t, $^3J_{HH}$ = 7.3, 2H, $CH_2CH_2CH_2OH$), 3.75 (br, t, $^3J_{HH}$ = 12.0 Hz, 1H, FsNCHC*H*NH_2), 4.35 (m, 1H, N*H*$_2$), 4.45 (m, 1H, N*H*$_2$), 4.64 (d, $^3J_{HH}$ = 11.0 Hz, 1H, FsNC*H*CHNH_2), 6.90–7.23 (m, 10H, Ph). ^{19}F NMR (376.2 MHz, CD_2Cl_2, δ/ppm) −134.8 (d, $^3J_{FF}$ = 23 Hz, 2H), −154.0 (t, $^3J_{FF}$ = 23 Hz, 1H), −163.6 (t, $^3J_{FF}$ = 20 Hz, 2H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, δ/ppm): 9.2, 9.3 (Cp*C*H_3), 20.8 (*C*H_2CH_2OH), 30.1 (Cp*C*H_2), 61.9 (CH_2*C*H_2OH), 68.4, 73.4 (FsNH*C*H*C*HNH_2), 86.4, 86.9, 87.2 (*C*CH_3), 121.7 (m, C_6F_5), 127.1, 127.3, 127.4, 128.2, 128.9 (Ph), 135.8 (m, C_6F_5), 138.2, 139.2 (Ph_{ipso}), 142.8 (m, C_6F_5), 145.3 (m, C_6F_5). Anal. Calcd for $C_{33}H_{37}ClF_5IrN_2O_3S\cdot$ 0.5 CH_2Cl_2: C, 42.95; H, 3.99; N 3.08. Found: C, 43.07; H, 3.93; N 3.02.

Synthesis of 2b.

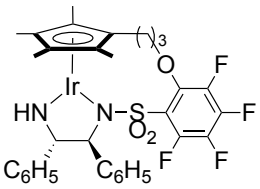


A mixture of **1b** (168.7 mg, 0.498 mmol) and (*S*,*S*)-FsDPEN (220.4 mg, 0.498 mmol) in THF (20 mL), $N(CH_2CH_3)_3$ (48.3 mg, 0.477 mmol) was added and stirred at room temperature for 16 h. After evaporation, extracted with CH_2Cl_2, washed with water (1 mL×3), the organic layer was dried over Na_2SO_4. After removal of the solvent under reducer pressure, the residue was recrystallized with CH_3CN/Et_2O to afford **2b** as orange crystals (0.184 g, 0.247 mmol, 50% yield).

^{1}H NMR (399.8 MHz, CD_2Cl_2, δ/ppm) 1.75 (tt, $^3J_{HH}$ = 7.3 Hz, 2H, $CH_2CH_2CH_2OH$), 1.81, 1.81, 1.82, 1.84 (s, each 3H, Cp*C*H_3), 2.46 (dt, $^3J_{HH}$ = 4.3 Hz, 7.3 Hz, 2H, $CH_2CH_2CH_2OH$), 3.65 (m, 1H, N*H*$_2$), 3.69 (t, $^3J_{HH}$ = 6.1 Hz, 2H, $CH_2CH_2CH_2OH$), 3.79 (dd, $^3J_{HH}$ = 11.3 Hz, FsNCHC*H*NH_2), 3.91 (br, t, $^3J_{HH}$ = 11.9 Hz, 1H, N*H*$_2$), 4.26 (d, $^3J_{HH}$ = 10.7 Hz, 1H, FsNC*H*CHNH_2), 6.89–7.19 (m, 10H,

Ph). ^{19}F NMR (376.2 MHz, CD_2Cl_2, δ/ppm) −135.1 (d, $^3J_{FF}$ = 23 Hz, 2F), −154.5 (t, $^3J_{FF}$ = 20 Hz, 1F), −163.9 (t, $^3J_{FF}$ = 20 Hz, 2F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, δ/ppm): 9.4, 9.5 (Cp*C*H$_3$), 20.9 (*C*H$_2$CH$_2$OH), 30.7 (Cp*C*H$_2$), 61.7 (CH$_2$*C*H$_2$OH), 68.1, 71.2 (FsNH*C*H*C*HNH$_2$), 94.36, 94.43, 95.05, 95.14, 95.8 (*C*CH$_3$), 121.8 (m, C_6F_5), 127.1, 127.2, 127.3, 128.2, 128.6, 128.7 (Ph), 135.7 (m, C_6F_5), 139.0, 139.2 (Ph$_{ipso}$), 142.6 (m, C_6F_5), 145.2 (m, C_6F_5). Anal. Calcd for $C_{32}H_{32}ClF_4N_2O_3RhS$: C, 51.14; H, 4.81; N 3.61. Found: C, 51.66; H, 4.49; N 3.70.

Synthesis of 3.

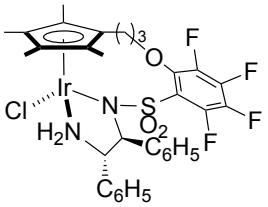


Method A: A mixture of **2a** (66.3 mg, 7.82×10^{-2} mmol) and K_2CO_3 (27.5 mg, 0.199 mmol) in dehydrated DMF (5.0 mL) was stirred at room temperature for 24 h. After evaporation of the resulting red purple solution, washed with hexane (10 mL×3) to afford **3** as a red purple powder (18.6 mg, 2.35×10^{-2} mmol, 30% yield).

Method B: A mixture of **1a** (442.1 mg, 0.999 mmol), (*S*,*S*)-FsDPEN (444.0 mg, 1.00 mmol) and K_2CO_3 (280.8 mg, 2.03 mmol) in dehydrated DMF was stirred at room temperature for 24 h. After evaporation of the resulting red purple solution, washed with hexane (10 mL×3) to afford **3** as a red purple powder (201.3 mg, 27% yield).

^{1}H NMR (399.8 MHz, CD_2Cl_2, δ/ppm) 1.75, 1.83, 2.14, 2.24 (s, each 3H, Cp*C*H$_3$), 2.56 (m, 2H, -C*H*$_2$C*H*$_2$CH$_2$O-), 3.11 (m, 1H, -C*H*$_2$CH$_2$CH$_2$O-), 4.07 (s, 1H, FsCHC*H*NH), 4.13 (t, $^3J_{HH}$ = 7.3 Hz, 1H, -CH$_2$CH$_2$C*H*$_2$O-), 4.30 (s, 1H, FsNC*H*CHNH), 4.79 (t, $^3J_{HH}$ = 7.6 Hz, 1H, -CH$_2$CH$_2$C*H*$_2$O-), 5.59 (br, 1H, N*H*), 7.1−7.6 (m, 10H, Ph). ^{19}F NMR (376.2 MHz, CD_2Cl_2, δ/ppm) −140.0 (dt, $^3J_{FF}$ = 26 Hz, 8.6 Hz, 1F), −154.5 (dt, $^3J_{FF}$ = 20 Hz, 8.6 Hz, 1F), −154.6 (dt, $^3J_{FF}$ = 20 Hz, 5.8 Hz, 1F), −162.5 (t, $^3J_{FF}$ = 20 Hz, 1F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, δ/ppm): 8.5, 9.6, 11.4, 13.3 (Cp*C*H$_3$), 22.4 (*C*H$_2$CH$_2$O), 25.3 (Cp*C*H$_2$), 74.2 (CH$_2$*C*H$_2$O), 72.7, 78.7 (FsNH*C*H*C*HNH), 78.6, 86.3, 86.9, 87.9, 89.1 (*C*CH$_3$), 123.2 (m, C_6F_4), 126.0, 126.3, 126.6, 127.0, 127.5, 127.7 (Ph), 136.8, 140.4, 141.6, 142.7, 144.1 (m, C_6F_4) 145.6, 147.5 (Ph$_{ipso}$). Anal. Calcd for $C_{32}H_{31}F_4IrN_2O_3S$: C, 48.54; H, 3.95; N 3.54. Found: C, 48.88; H, 4.14; N 3.78.

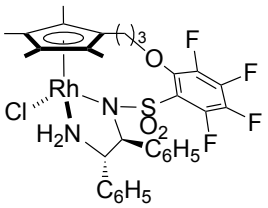
Synthesis of 4a.



A mixture of **3** (76.0 mg, 0.100 mmol) and aqueous NH_4Cl in CH_2Cl_2 (5 mL) were stirred at room temperature for 24 h. After evaporation of the resulting yellow solution, washed with hexane (10 mL×3) to afford **4a** as a yellow powder (82.9 mg, 99% yield).

^{1}H NMR (399.8 MHz, CD_2Cl_2, δ/ppm) 1.56, 1.69, 1.79, 1.85 (s, each 3H, Cp*C*H$_3$), 2.23–2.31 (m, 2H, -C*H*$_2$CH$_2$CH$_2$O-), 2.80–2.90 (m, 1H, -C*H*$_2$CH$_2$O-), 3.20–3.26 (m, 1H, -C*H*$_2$CH$_2$O-), 3.79 (ddd, $^3J_{HH}$ = 3.4 Hz, 12.5 Hz, 12.5 Hz, 1H, NH$_2$C*H*), 4.29 (br, d, $^3J_{HH}$ = 9.5 Hz, N*H*$_2$), 4.40 (t, $^3J_{HH}$ = 9.2 Hz, 1H, -C*H*$_2$O-), 4.53 (br, t, $^3J_{HH}$ = 11.4 Hz, 1H, N*H*$_2$), 4.61 (d, $^3J_{HH}$ = 11.3 Hz, 1H, C*H*Fs), 4.61–4.66 (m, 1H, -C*H*$_2$O-), 6.83–7.27 (m, 10H, Ph). ^{19}F NMR (376.2 MHz, CD_2Cl_2, δ/ppm) −133.3 (dt, $^3J_{FF}$ = 8.7 Hz, 8.7 Hz, 26.0 Hz, 1F), −155.6–155.7 (m, 1F), −157.7 (dd, $^3J_{FF}$ = 8.7 Hz, 20.2 Hz, 1F), −164.8 (dd, $^3J_{FF}$ = 26.0 Hz, 26.0 Hz, 1F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, δ/ppm): 9.4, 9.5, 9.8, 11.2 (Cp*C*H$_3$), 22.2 (*C*H$_2$CH$_2$OH), 27.6 (Cp*C*H$_2$), 69.9, 73.1 (FsNH*C*H*C*HNH$_2$), 74.3 (CH$_2$*C*H$_2$OH), 75.3, 82.6, 83.7, 91.7, 102.7 (*C*CH$_3$), 127.4, 127.5, 127.6, 129.1, 129.2, 129.3 (Ph), 137.4, 138.7 (Ph$_{ipso}$). Anal. Calcd for $C_{32}H_{32}ClF_4IrN_2O_3S$: C, 46.40; H, 3.89; N 3.38. Found: C, 46.26; H, 3.80; N 3.21.

Synthesis of 4b.



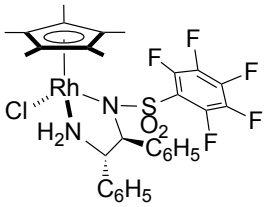
Method A: A mixture of **2b** (140.8 mg, 0.186 mmol) and K_2CO_3 (30.8 mg, 0.223 mmol) in CH_3CN (5.0 mL) was stirred at room temperature for 18 h. The resulting brown solution was evaporated under reduced pressure, and the product was dissolved to CH_2Cl_2 (10 mL) and washed with water (2 mL×3). After dried over anhydrous Na_2SO_4, the organic layer was filtrated. After removal of the solvent under reducer pressure, the residue was recrystallized with CH_2Cl_2/Et_2O to afford **4b** as orange crystals (90.3 mg, 0.122 mmol, 66% yield).

Method B: A mixture of **1b** (179.7 mg, 0.509 mmol), (*S*,*S*)-FsDPEN (222.8 mg, 0.504 mmol) and K_2CO_3 (162.8 mg, 1.18 mmol) in CH_3CN (15 mL) was stirred at room temperature for 24 h. The resulting brown solution was evaporated under reduced pressure, and the product was dissolved to CH_2Cl_2 (10 mL) and washed with water (2 mL×3). After dried over anhydrous Na_2SO_4, the organic

layer was filtrated. Removal of the solvent under reducer pressure, the residue was recrystallized with CH_2Cl_2/Et_2O to afford **4b** as orange crystals (98.1 mg, 0.130 mmol, 25% yield).

^{1}H NMR (399.8 MHz, CD_2Cl_2, δ/ppm) 1.60, 1.74, 1.81, 1.88 (s, each 3H, Cp*C*H$_3$), 2.03–2.10 (m, 1H, -C*H*$_2$CH$_2$CH$_2$O-), 2.25–2.34 (m, 1H, -C*H*$_2$CH$_2$O-), 2.96–3.06 (m, 1H, -C*H*$_2$CH$_2$O-), 3.36 (ddd, $^3J_{HH}$ = 6.1 Hz, 6.1 Hz, 17.7 Hz,-C*H*$_2$CH$_2$CH$_2$O-), 3.57 (br, d, $^3J_{HH}$ = 9.2 Hz, 1H, N*H*$_2$), 3.81 (ddd, $^3J_{HH}$ = 3.1 Hz, 12.4 Hz, 12.4 Hz, 1H, -C*H*$_2$O-), 4.04 (br, t, $^3J_{HH}$ = 10.4 Hz, N*H*$_2$), 4.27 (d, $^3J_{HH}$ = 11.0 Hz, 1H, C*H*NFs), 4.41 (dt, $^3J_{HH}$ = 2.8 Hz, 9.2 Hz, 1H, NH$_2$C*H*), 4.71–4.76 (m, 1H, -C*H*$_2$O-), 6.82–7.24 (m, 10H, Ph). ^{19}F NMR (376.2 MHz, CD_2Cl_2, δ/ppm) −132.3 (dt, $^3J_{FF}$ = 8.7 Hz, 26.0 Hz, 1F), −155.8 (dt, $^3J_{FF}$ = 5.8 Hz, 20.2 Hz, 1F), −157.8 (dd, $^3J_{FF}$ = 8.7 Hz, 23.1 Hz, 1F), −164.7 (t, $^3J_{FF}$ = 26.0 Hz, 1F). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.5 MHz, δ/ppm): 9.1, 9.5, 9.7, 10.6 (Cp*C*H$_3$), 22.2 (*C*H$_2$CH$_2$OH), 26.9 (Cp*C*H$_2$), 69.1, 70.5 (FsNH*C*H*C*HNH$_2$), 73.9 (CH$_2$*C*H$_2$OH), 83.6 (d, $^1J_{CRh}$ = 8.6 Hz, *C*CH$_3$), 91.5 (d, $^1J_{CRh}$ = 8.6 Hz, *C*CH$_3$), 92.6 (d, $^1J_{CRh}$ = 8.6 Hz, *C*CH$_3$), 98.2 (d, $^1J_{CRh}$ = 8.6 Hz, *C*CH$_3$), 110.2 (d, $^1J_{CRh}$ = 8.6 Hz, *C*CH$_3$), 125.8 (m, C_6F_4), 126.9, 127.1, 128.5, 128.6, 128.7, 128.8 (C_6F_4), 129.8, 137.6 (m, C_6F_4), 138.1, 139.1 (Ph$_{ipso}$), 140.3, 141.0, 142.6 (m, C_6F_4). Anal. Calcd for $C_{32}H_{32}ClF_4N_2O_3RhS\cdot H_2O$: C, 51.27; H, 4.95; N 3.62. Found: C, 51.14; H, 4.72; N 3.70.

Synthesis of Cp*RhCl(FsDPEN) 5.



A mixture of [Cp*RhCl(μ-Cl)]$_2$ (74.7 mg, 0.241 mmol), FsDPEN (107.5 mg, 0.243 mmol) and K_2CO_3 (41.0 mg, 0.297 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 60 h. The resulting orange solution was filtered and washed with water. The water layer was exracted with CH_2Cl_2 and the combined organic layer was evaporated under reduced pressure. Then the resultant orange solid was washed with Et_2O (10 mL) and recrystallized with CH_2Cl_2/Et_2O to afford **5** as orange crystals in 66% yield (113.0 mg, 0.158 mmol).

^{1}H NMR (399.8 MHz, CD_2Cl_2, *δ*/ppm): 1.77 (s, C$_5$(C*H*$_3$)$_5$, 15H), 3.53 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 3.76 (t, $^3J_{HH}$ = 11.3 Hz, 1H), 3.88 (t, $^3J_{HH}$ = 11.9 Hz, 1H), 4.23 (d, $^3J_{HH}$ = 10.7 Hz, 1H, C*H*NFs), 6.87–6.93 (m, aryl, 7H), 7.13–7.16 (m, aryl, 3H). ^{19}F NMR (376.17 MHz, CD_2Cl_2, *δ*/ppm): –135.1–135.1 (m, 2F), –154.6 (vt, $^3J_{FF}$ = 20.2 Hz, 1F), –163.9 (vt, $^3J_{FF}$ = 20.2 Hz, 1F). ^{13}C{^{1}H} NMR (CD_2Cl_2, r.t., *δ*/ppm): 9.2 (C$_5$(*C*H$_3$)$_5$, 5C), 68.5, 71.4 (FsNH*C*H*C*HNH$_2$), 95.0 (d, $^1J_{CRh}$ = 8.6 Hz, *C*$_5$(CH$_3$)$_5$), 122.2 (m, Pf), 127.4, 127.5, 127.6, 128.5, 128.9, 129.0 (Ph), 136.0 (C_6F_5), 138.5 (C_6F_5), 139.2, 139.6 (Ph$_{ipso}$), 140.4, 142.9, 145.4 (C_6F_5). Anal. Calcd for $C_{30}H_{29}ClF_5RhN_2O_2S$: C, 50.40; H, 4.09; N, 3.92. Found: C,50.00; H, 4.21; N, 4.01.

3. General Procedure of the Catalytic Dehydrogenation from Formic Acid

A 20-mL Schlenk flask was charged with an appropriate catalyst (0.030 mmol) in DME (3 mL) and degassed water (3 mL) under an argon atmosphere. To the solution maintained, formic acid was added for 10 min by using a syringe pump (0.3 mL/min). The rate of the gas evolution amount was measured with a mass-flowmeter (Shinagawa Corporation, W-NK-0.5A) and was analyzed by gas chromatography.

4. X-ray Structure Determination for 1a, 2a, 2b, 4a, 4b and 5.

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.[S4] The heavy-atom positions were determined by a direct method program (SHELXT[S5]) and the remaining non-hydrogen atoms were found by subsequent Fourier syntheses and refined by full-matrix least-squares techniques against F^2 using the SHELXL-2014/7 program.[S6] The hydrogen atoms were placed at calculated positions; these hydrogen atoms were included in the refinements with a riding model. Relevant crystallographic data are compiled in Tables S1–S3.

Table S1. Crystallographic data for **1a** and **2a·CH_2Cl_2**

	1a	**2a·CH_2Cl_2**
Empirical Formula	$C_{24}H_{38}Cl_4Ir_2O_2$	$C_{33}H_{35}Cl_3F_5IrN_2O_3S$
Formula Weight	884.81	933.28
Crystal Color, Habit	orange, prism	yellow, prism
Crystal System	monoclinic	orthorhombic
Space Group	$P2_1/n$ (#14)	$P2_12_12_1$ (#19)
Lattice Parameters	a = 8.496(3) Å	a = 8.170(2) Å
	b = 14.455(5) Å	b = 15.036(4) Å
	c = 23.136(3) Å	c = 27.939(7) Å
	β = 95.660(6) °	
	V = 1350.6(8) $Å^3$	V = 3432.0(16) $Å^3$
Z value	2	4
D_{calc}	2.176 g/cm^3	1.806 g/cm^3
F_{000}	840.00	1840.00
μ(MoKα)	102.853 cm^{-1}	42.599 cm^{-1}
Exposure Rate	10.0 sec./°	10.0 sec./°
No. of Reflections Measured	10858	28362
No. of unique reflections	3068	3436
No. Variables	163	478
$R1$ (I>2.00σ(I))	0.0353	0.0353
w$R2$ (All reflections)	0.0923	0.0856
GOF on F^2	1.003	1.000

$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$

Table S2. Crystallographic data for **2b** and **4a**

	2b	**4a**
Empirical Formula	$C_{32}H_{33}ClF_5N_2O_3RhS$	$C_{32}H_{32}ClF_4IrN_2O_3S$
Formula Weight	759.03	826.33
Crystal Color, Habit	orange, prism	yellow, prism
Crystal System	orthorhombic	orthorhombic
Space Group	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)
Lattice Parameters	a = 8.3245(11) Å	a = 7.8860(16) Å
	b = 19.219(3) Å	b = 19.686(4) Å
	c = 20.158(3) Å	c = 20.376(4) Å
	V = 3225.2(7) Å^3	V = 3163.3(11) Å^3
Z value	4	4
D_{calc}	1.563 g/cm^3	1.735 g/cm^3
F_{000}	1544.00	1624.00
μ(MoKα)	7.406 cm^{-1}	44.422 cm^{-1}
Exposure Rate	16.0 sec./°	10.0 sec./°
No. of Reflections Measured	26837	26180
No. of unique reflections	7331	7239
No. Variables	439	429
$R1$ (I>2.00σ(I))	0.0396	0.0402
w$R2$ (All reflections)	0.1008	0.1083
GOF on F^2	1.000	1.007

$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$

Table S3. Crystallographic data for **4b·CH_2Cl_2** and **5**

	4b·CH_2Cl_2	**5**
Empirical Formula	$C_{33}H_{34}Cl_3F_4N_2O_3RhS$	$C_{30}H_{29}ClF_5N_2O_2RhS$
Formula Weight	823.96	714.98
Crystal Color, Habit	orange, prism	orange, prism
Crystal System	orthorhombic	orthorhombic
Space Group	$P2_12_12_1$ (#19)	$P2_12_12_1$ (#19)
Lattice Parameters	a = 8.051(2) Å	a = 7.9971(11) Å
	b = 20.321(6) Å	b = 11.5082(19) Å
	c = 20.535(6) Å	c = 32.026(5) Å
	V = 3359.7(17) $Å^3$	V = 2947.4(8) $Å^3$
Z value	4	4
D_{calc}	1.629 g/cm^3	1.611 g/cm^3
F_{000}	1672.00	1448.00
μ(MoKα)	8.675 cm^{-1}	8.026 cm^{-1}
Exposure Rate	16.0 sec./°	32.0 sec./°
No. of Reflections Measured	27121	24450
No. of unique reflections	7643	6736
No. Variables	459	379
$R1$ (I>2.00σ(I))	0.0760	0.0471
w$R2$ (All reflections)	0.1633	0.1137
GOF on F^2	1.000	1.016

$R1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$, $wR2 = [\Sigma (w (F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$

Table S4. Comparison of selected bond lengths and angles of **4a**, **4b** and **5**.

Complex	**4a**	**4b**	**5**
∠Cp*(centroid)–M–N2	136.27(16)°	135.7(2)°	133.88(16)°
Cp*(centroid)–M	1.791(3) Å	1.801(3) Å	1.778(3) Å
M–N1	2.125(5) Å	2.128(7) Å	2.129(5) Å
M–N2	2.165(5) Å	2.161(6) Å	2.164(5) Å
M–Cl	2.235(6) Å	2.432(2) Å	2.4148(17) Å
∠N1–M–N2	77.7(2)°	78.5(2)°	78.44(19)°
∠N1–M–Cl	81.83(16)°	81.6(2)°	85.00(14)°
∠N2–M–Cl	87.36(14)°	89.34(17)°	89.38(13)°

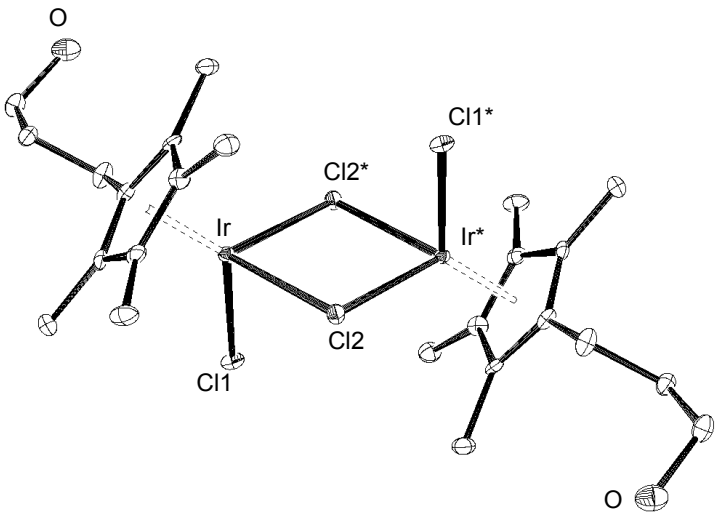


Fig. S1. Crystal structure of **1a**. All hydrogen atoms are omitted for clarity, and the ellipsoids represent 30% probability.

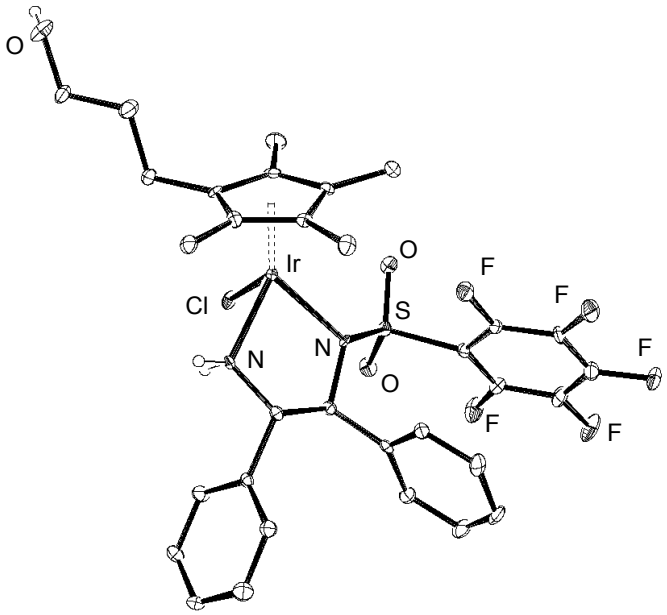


Fig. S2. Crystal structure of **2a·CH_2Cl_2**. All hydrogen atoms and CH_2Cl_2 solvent molecules are omitted for clarity, and the ellipsoids represent 30% probability.

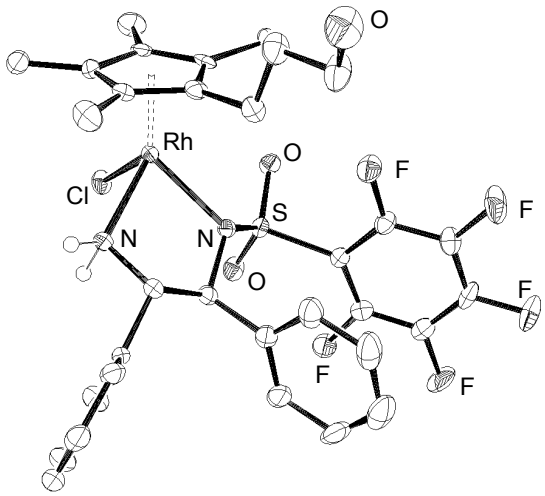


Fig. S3. Crystal structure of **2b**. All hydrogen atoms are omitted for clarity, and the ellipsoids represent 30% probability.

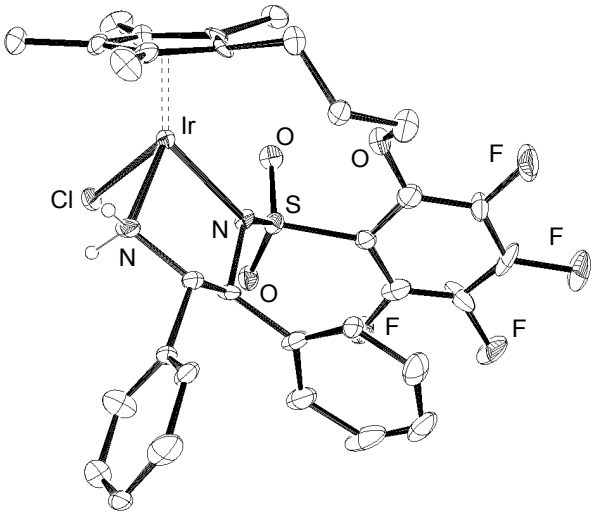


Fig. S4. Crystal structure of **4a**. All hydrogen atoms are omitted for clarity, and the ellipsoids represent 30% probability.

5. References

S1) J. E. D. Martins, M. Wills, *Tetrahedron*, 2009, **65**, 5782.

S2) S. J. Lucas, R. M. Lord, A. M. Basri, S. J. Allison, R. M. Phillips, A. J. Blacker, P. C. McGowan, *Dalton Trans*., 2016, **45**, 6812.

S3) A. Matsunami, Y. Kayaki, S. Kuwata, T. Ikariya, *Organometallics,* 2018, **37**, 1958.

S4) *CrystalStructure 4.1: Crystal Structure Analysis Package*; Rigaku Coorporation, Tokyo 196-8666, Japan, 2000–2015.

S5) G. M. Sheldrick, *Acta Crystallogr., Sect. C* 2014, **70**, 1437.

S6) G. M. Sheldrick, *Acta Crystallogr., Sect. C* 2015, **71**, 3.

6. NMR Spectra

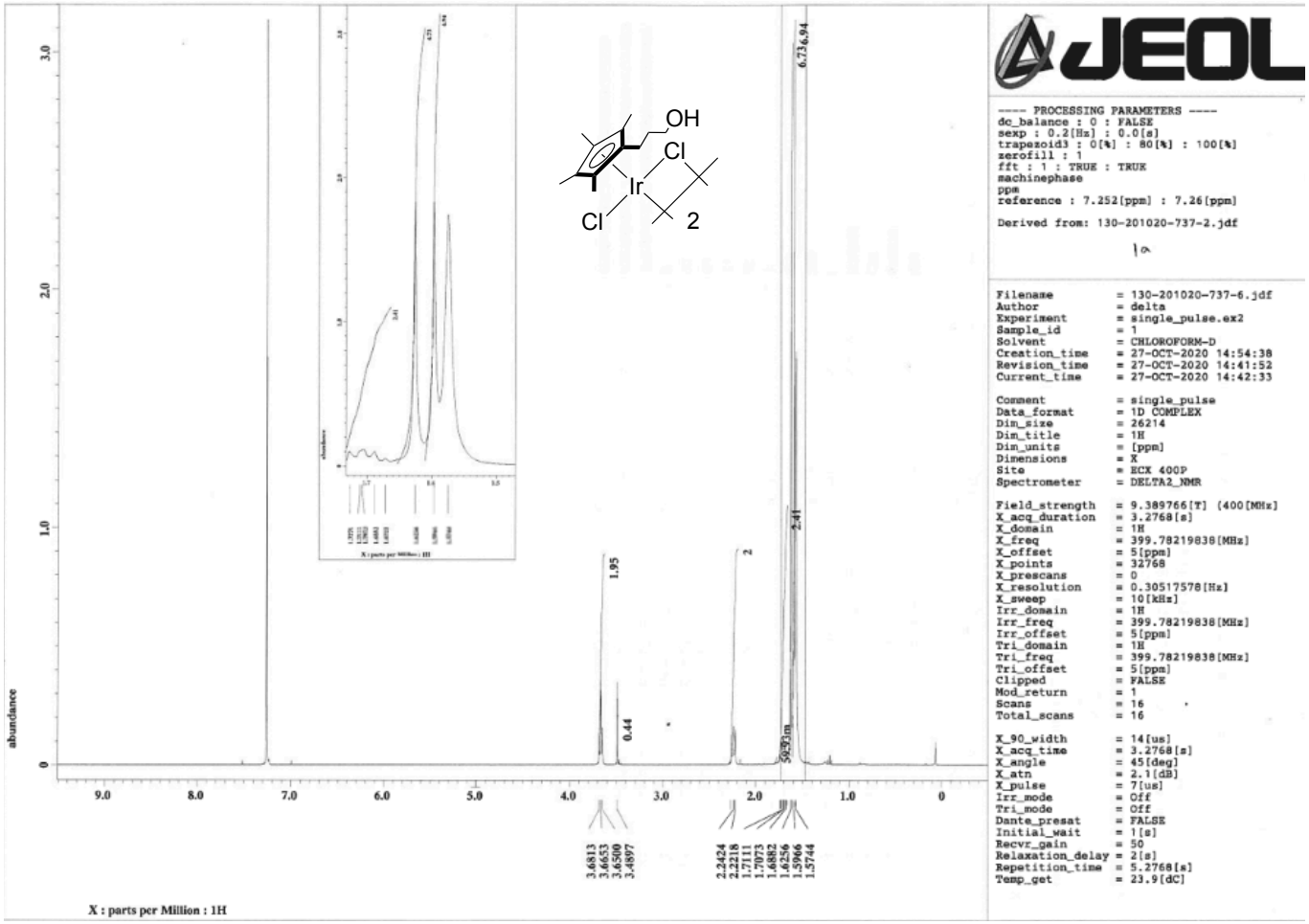


Fig. S5. ^{1}H NMR spectrum (399.78 MHz, $CDCl_3$, rt) of **1a**.

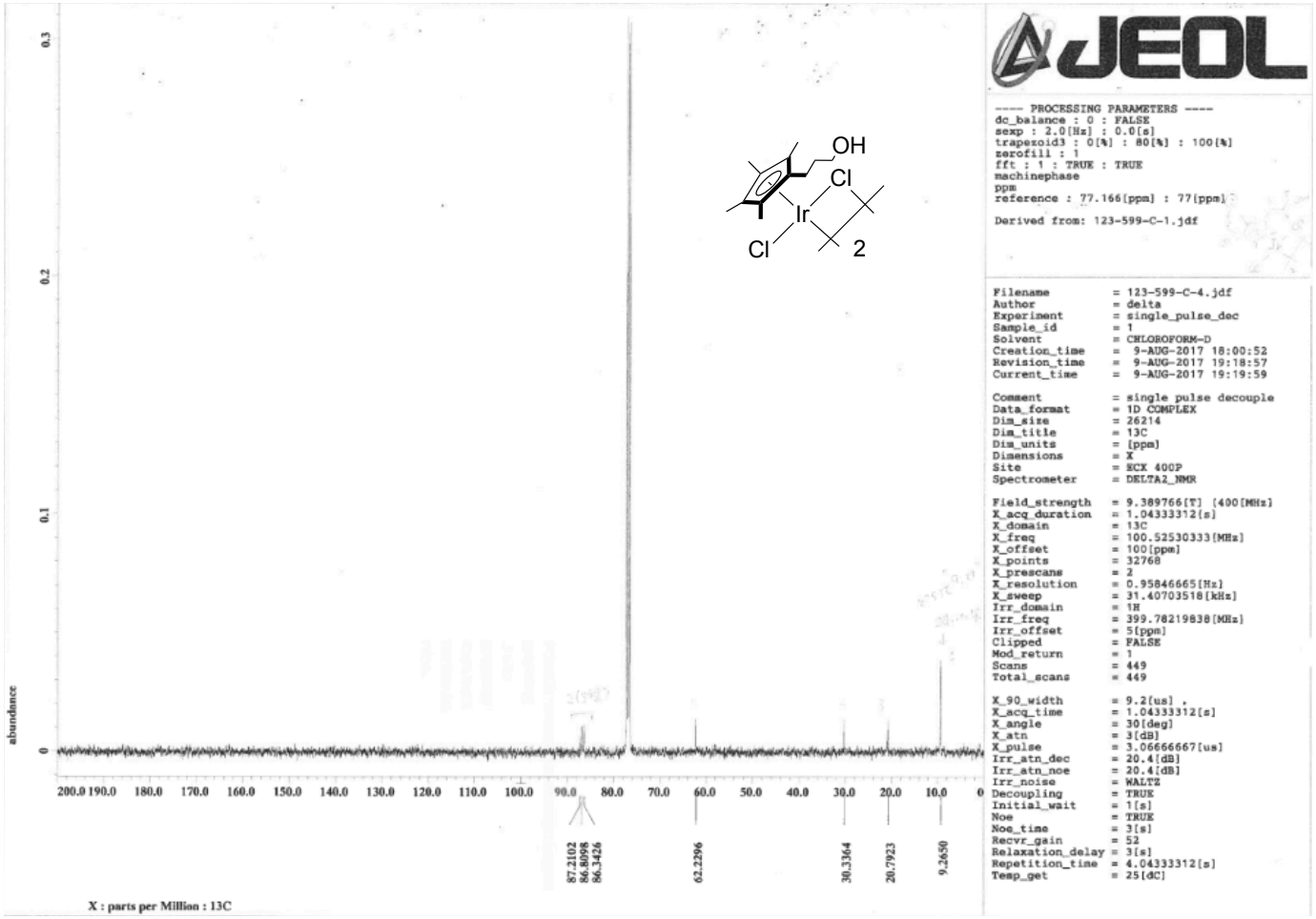


Fig. S6. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, $CDCl_3$, rt) of **1a**.

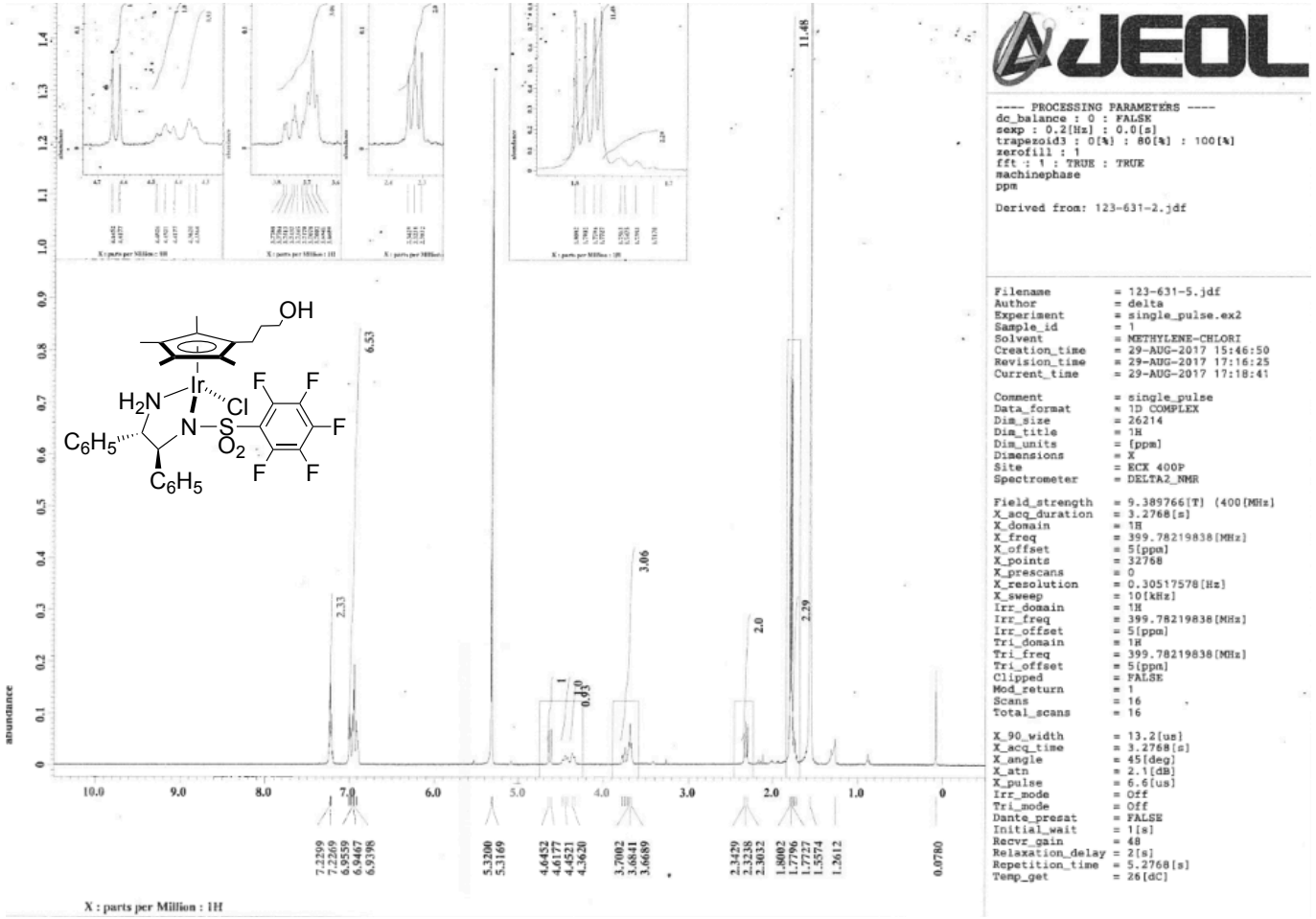


Fig. S7. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **2a**.

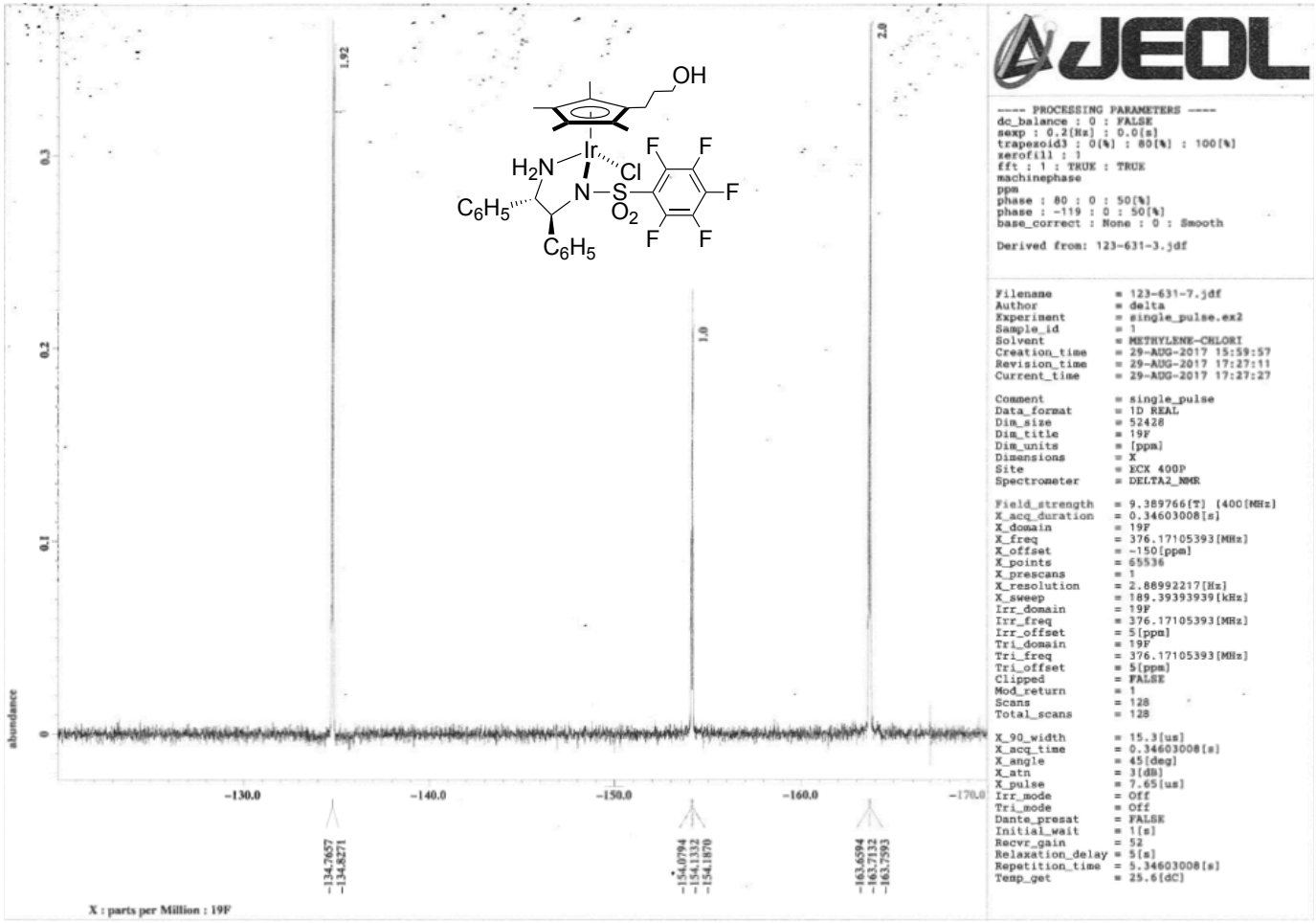


Fig. S8. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **2a**.

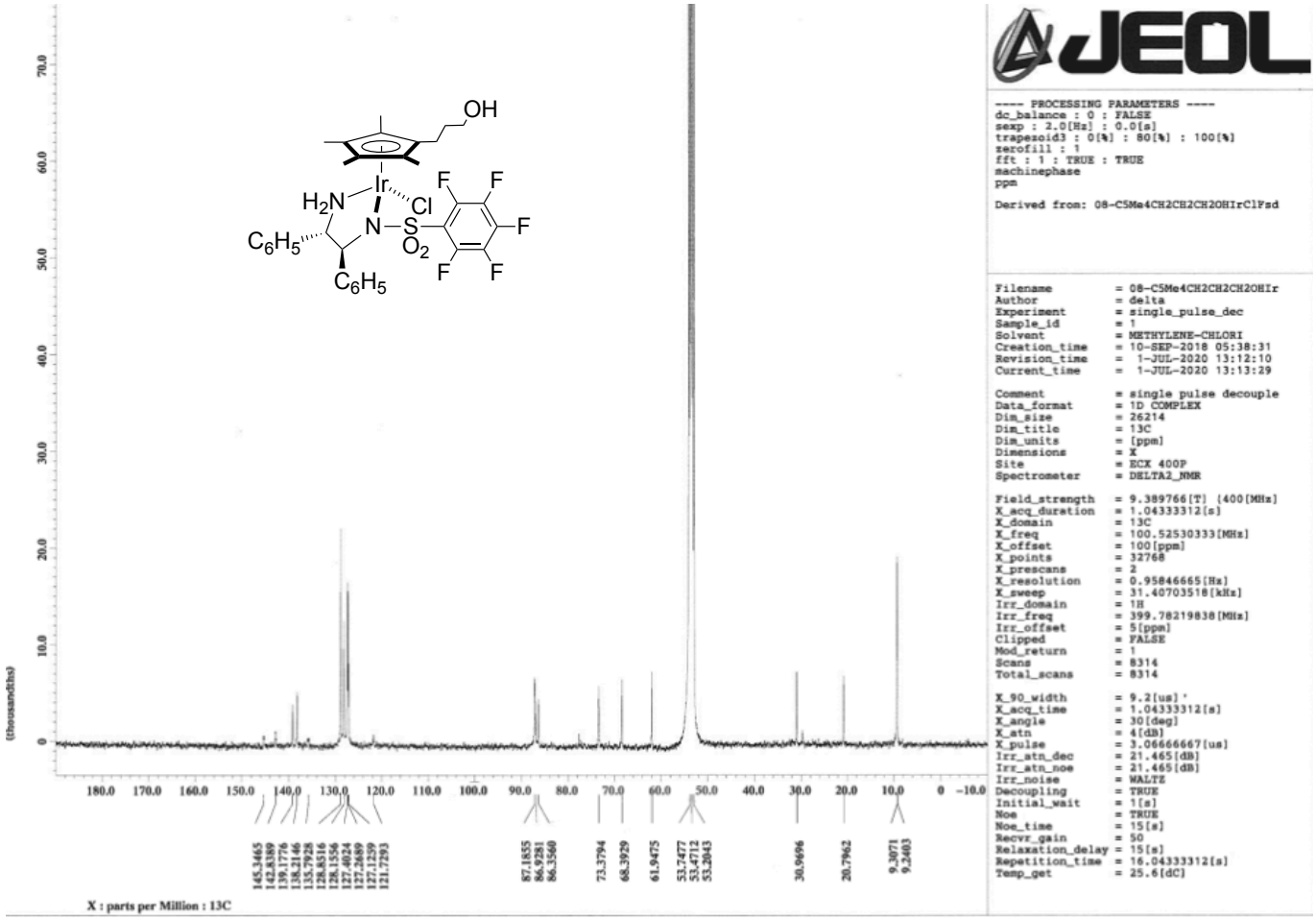


Fig. S9. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **2a**.

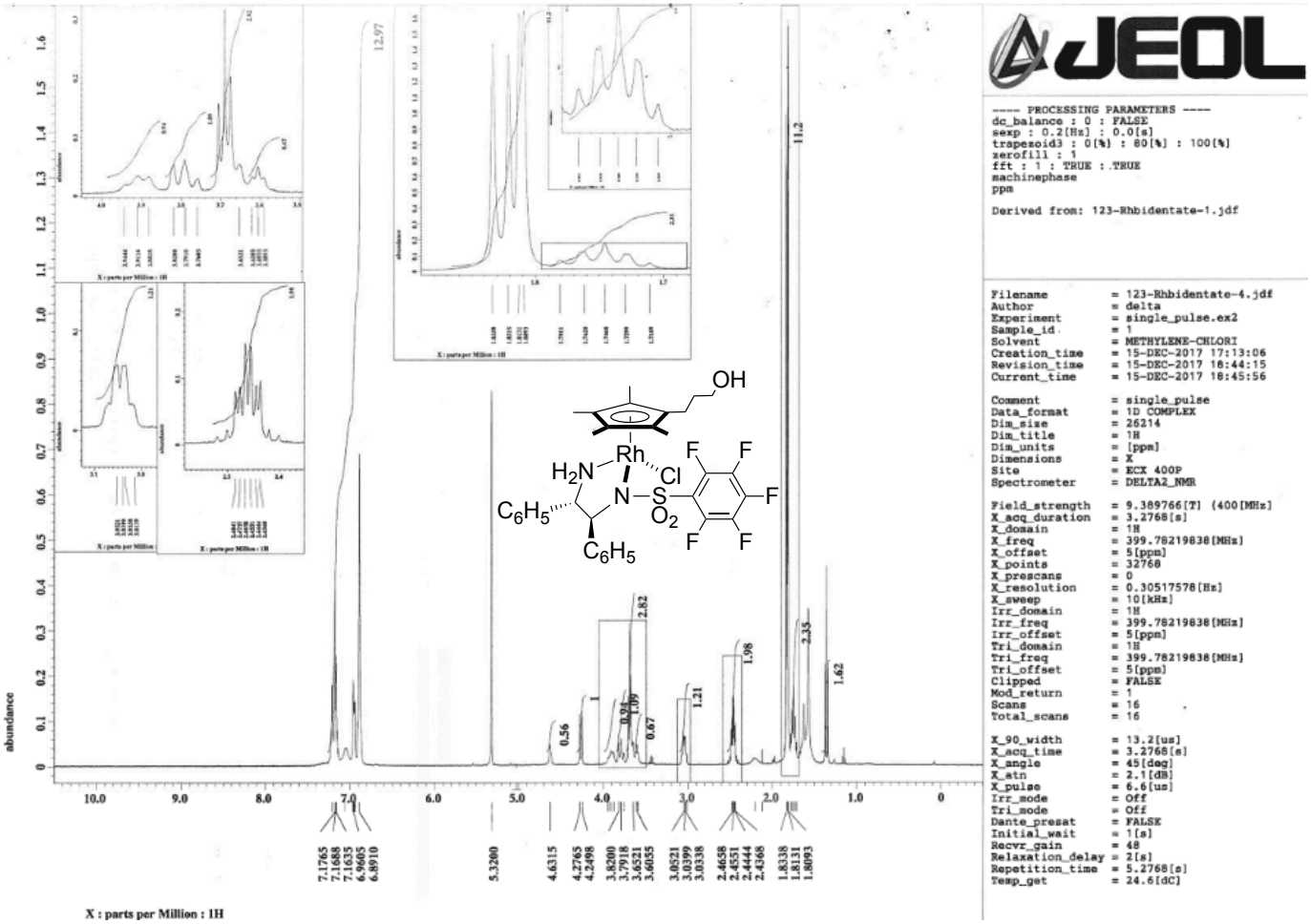


Fig. S10. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **2b**.

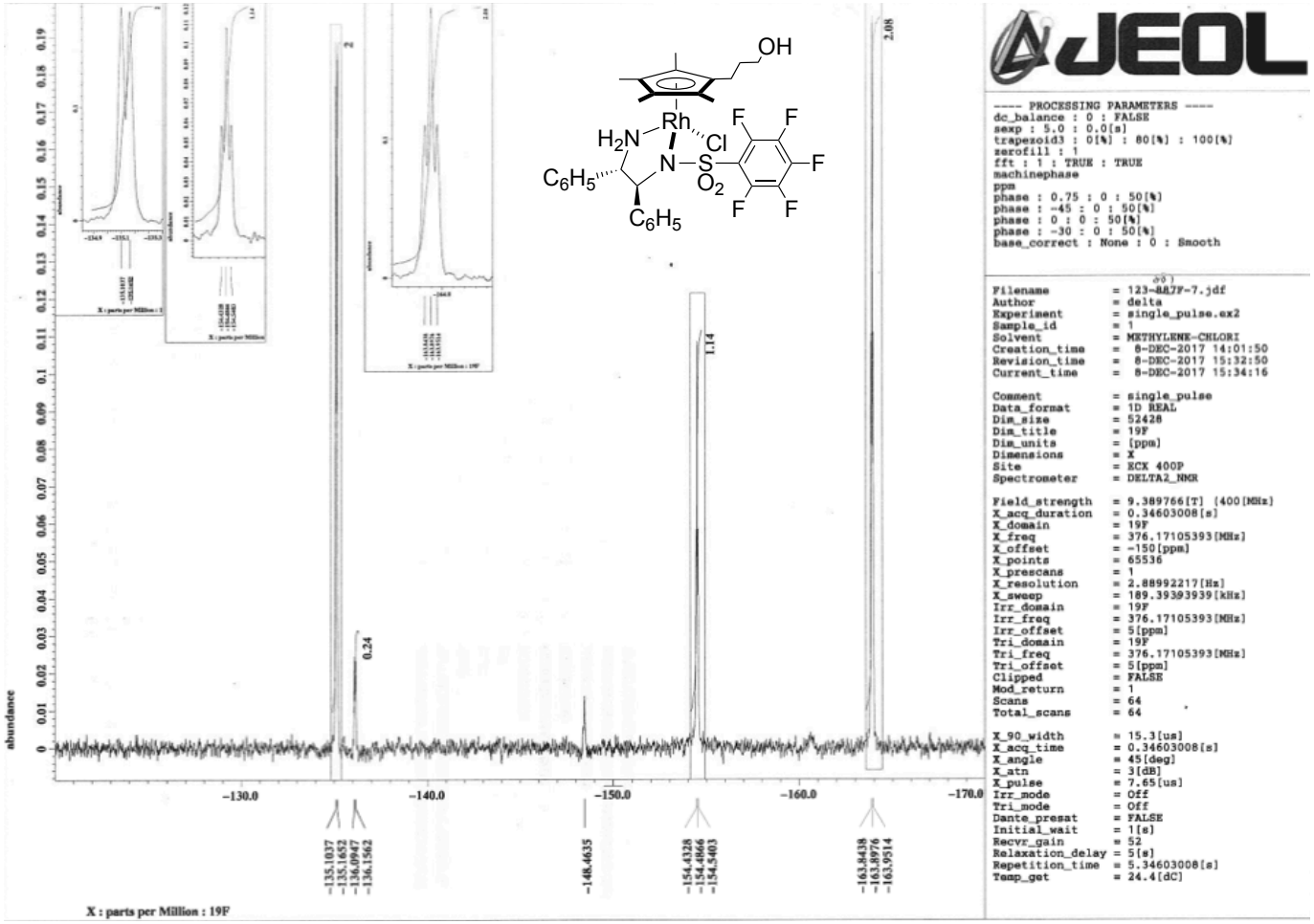


Fig. S11. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **2b**.

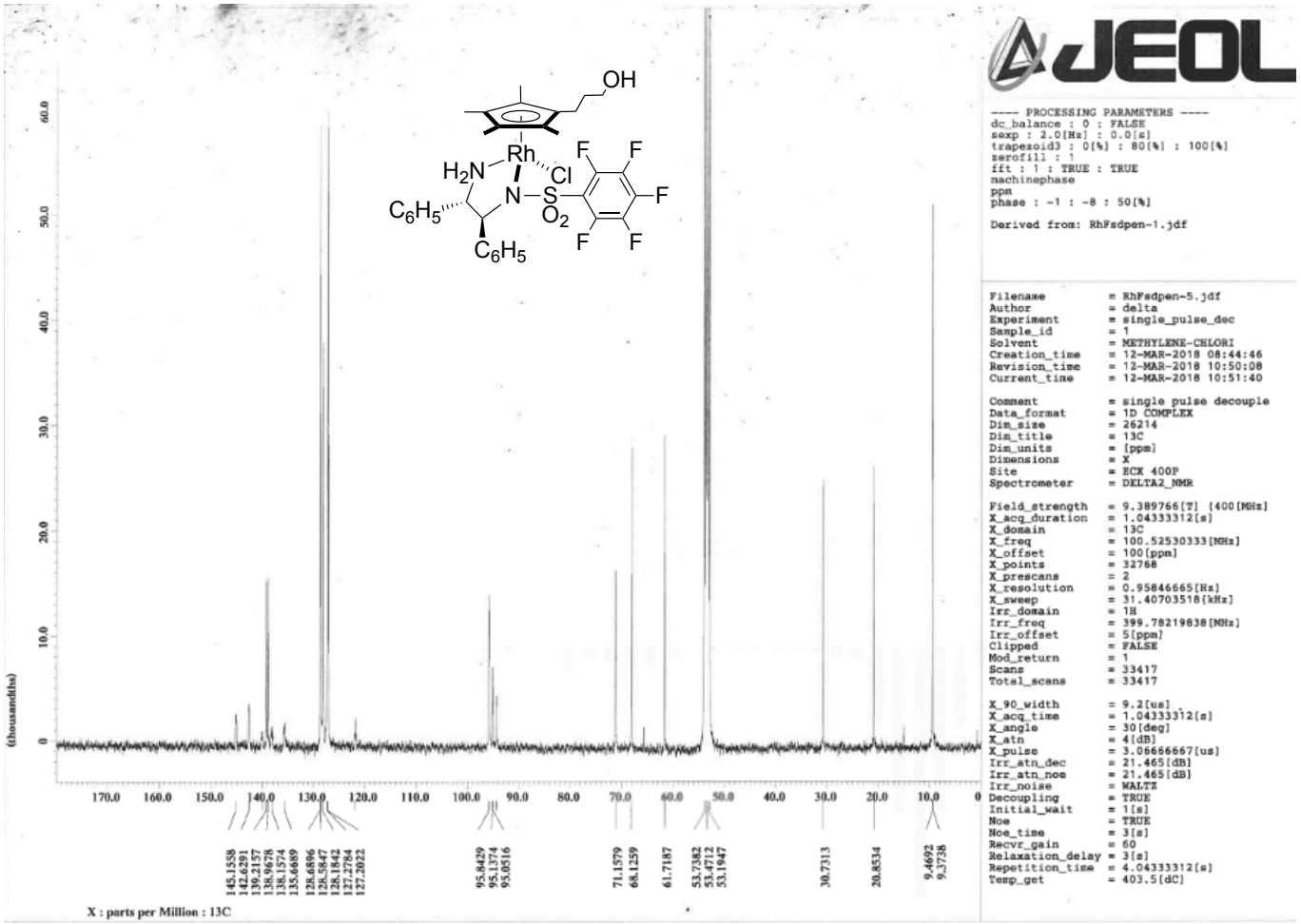


Fig. S12. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **2b**.

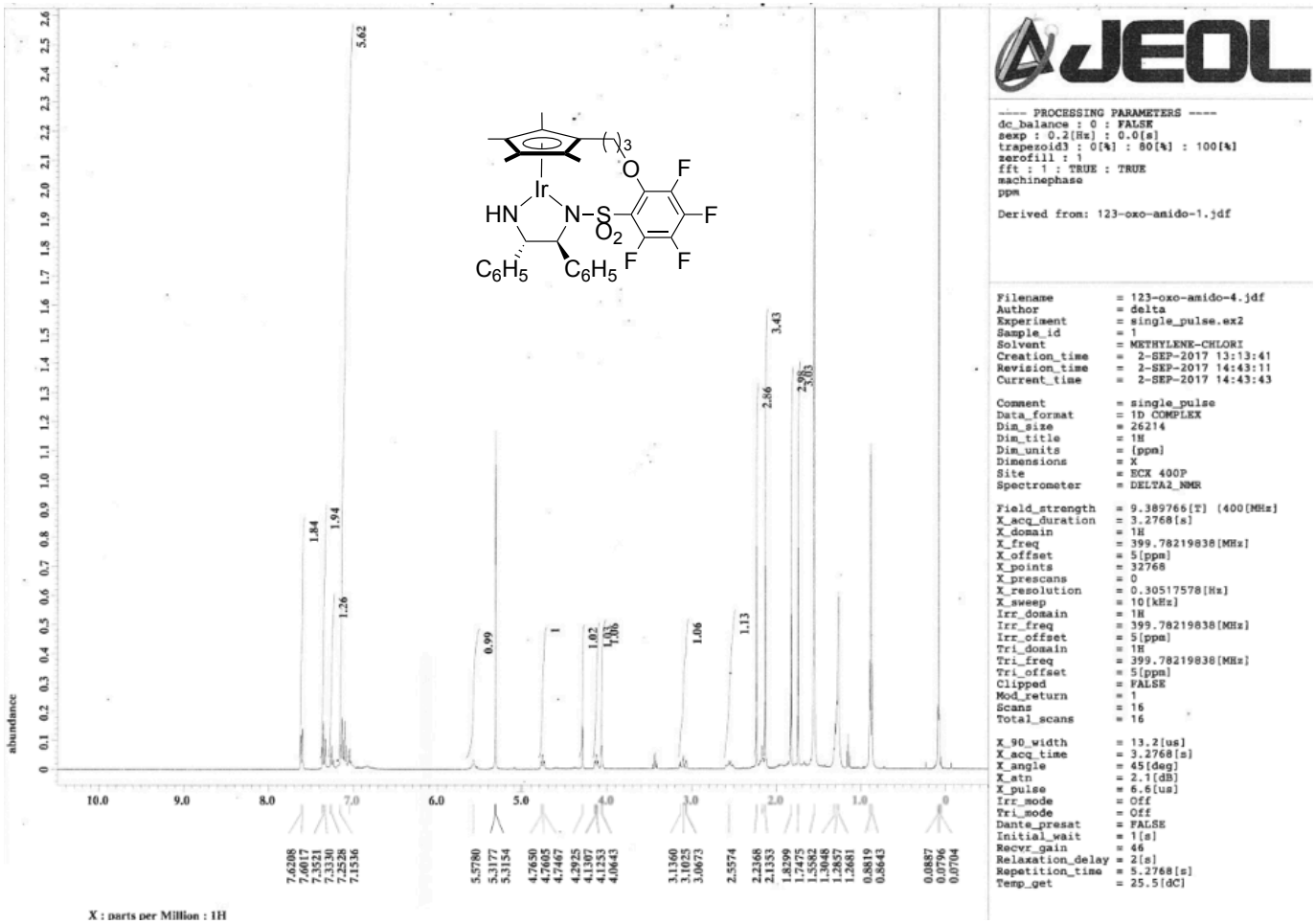


Fig. S13. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **3**.

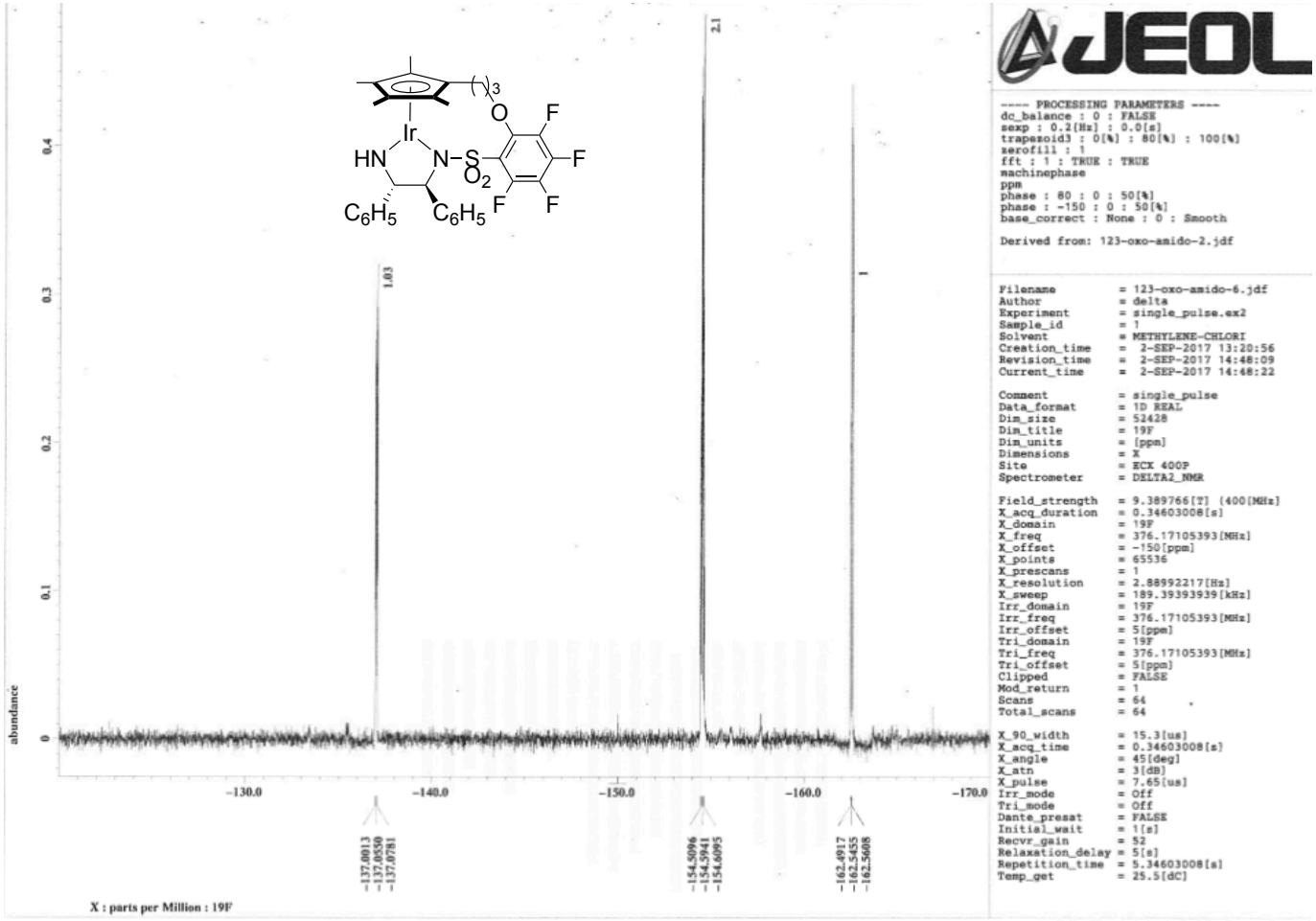


Fig. S14. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **3**.

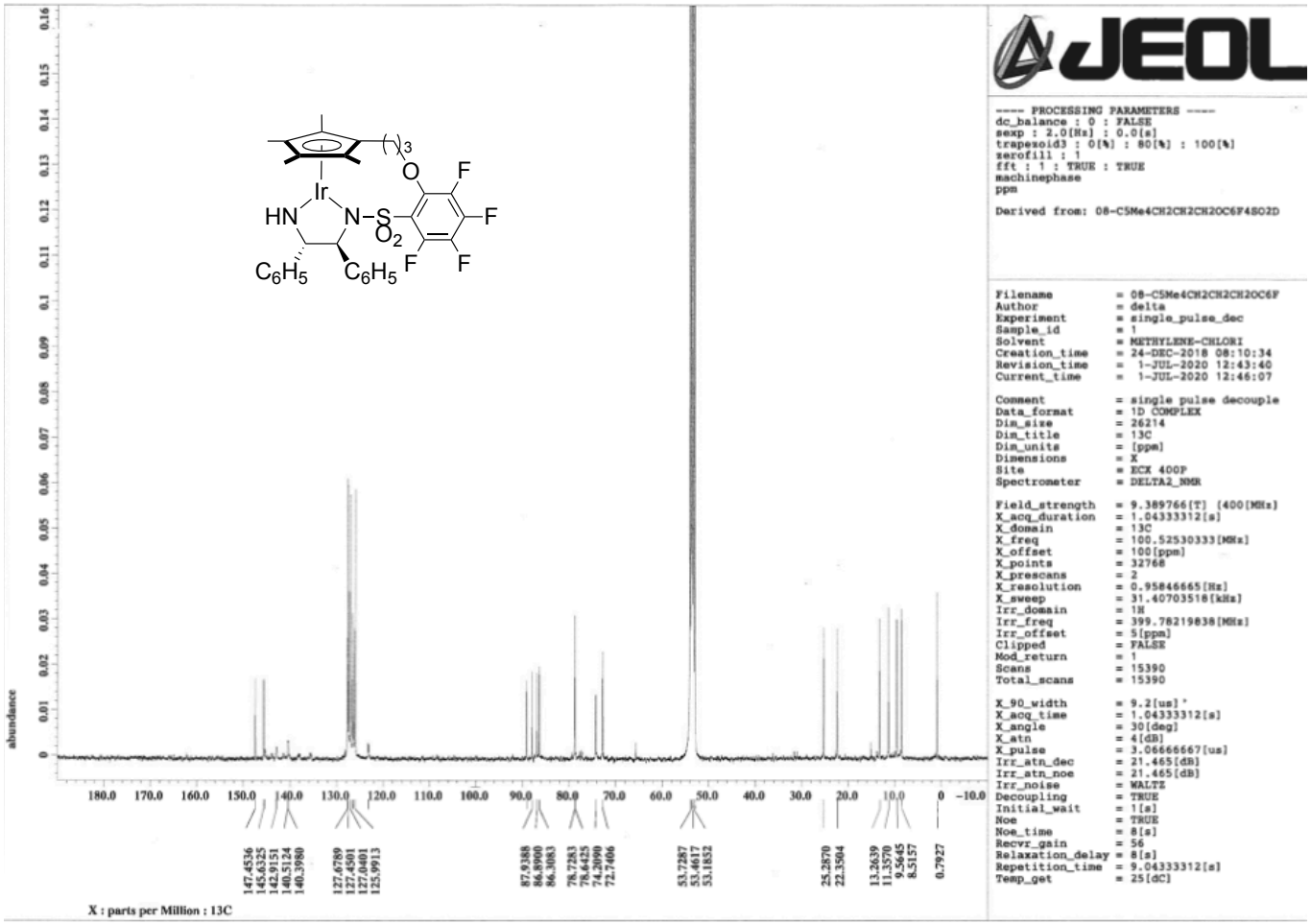


Fig. S15. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **3**.

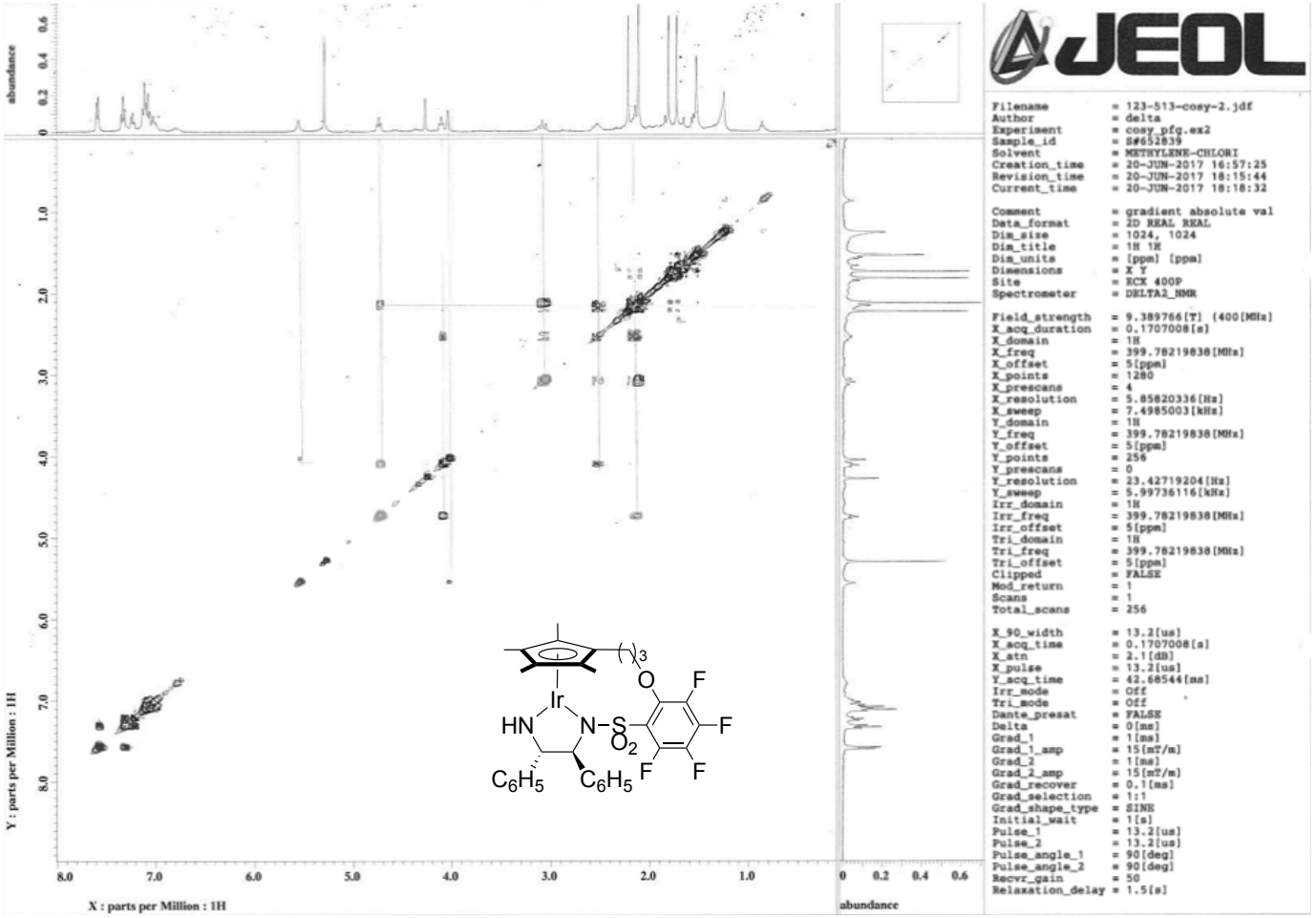


Fig. S16. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, rt) of **3**.

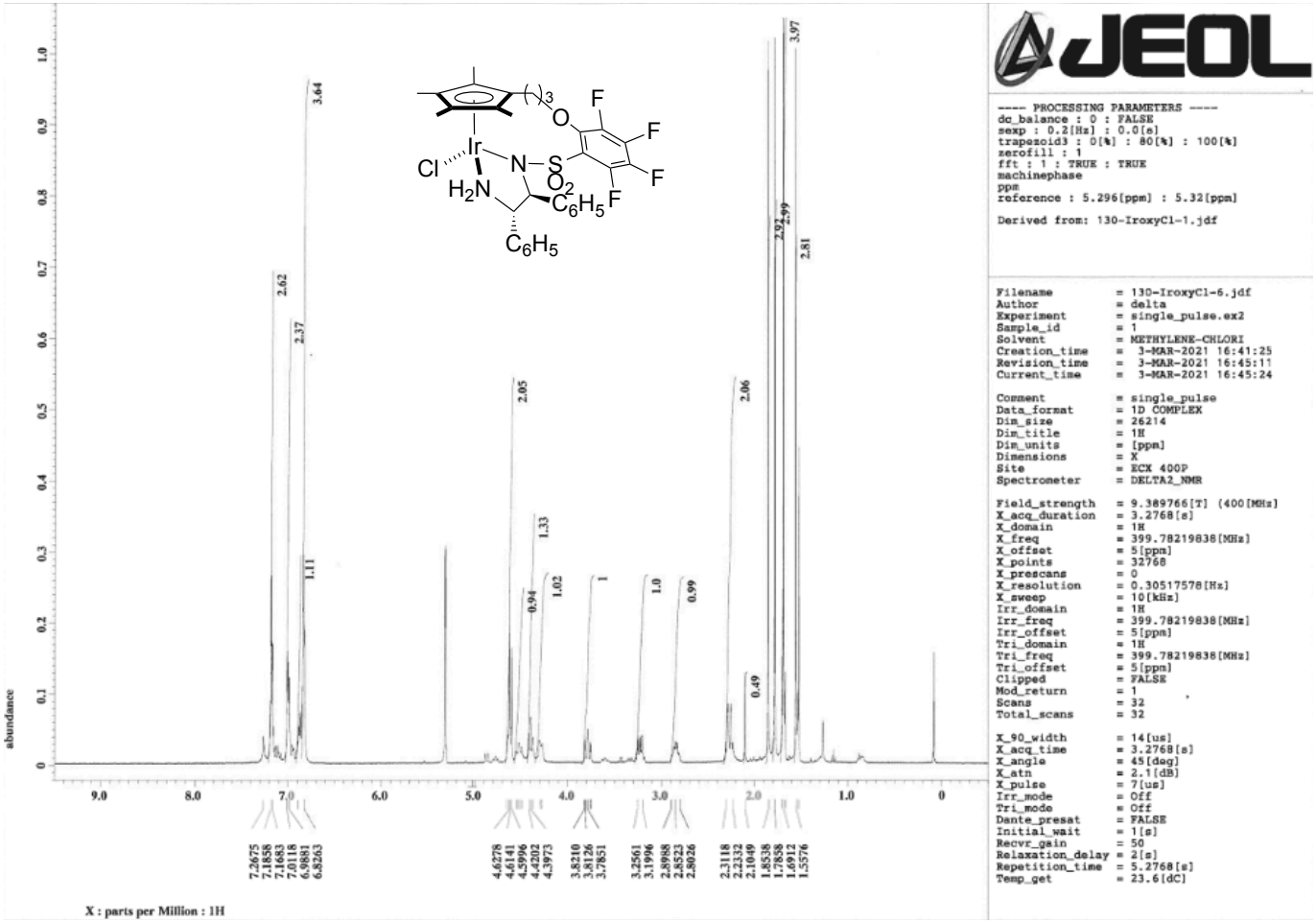


Fig. S17. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **4a**.

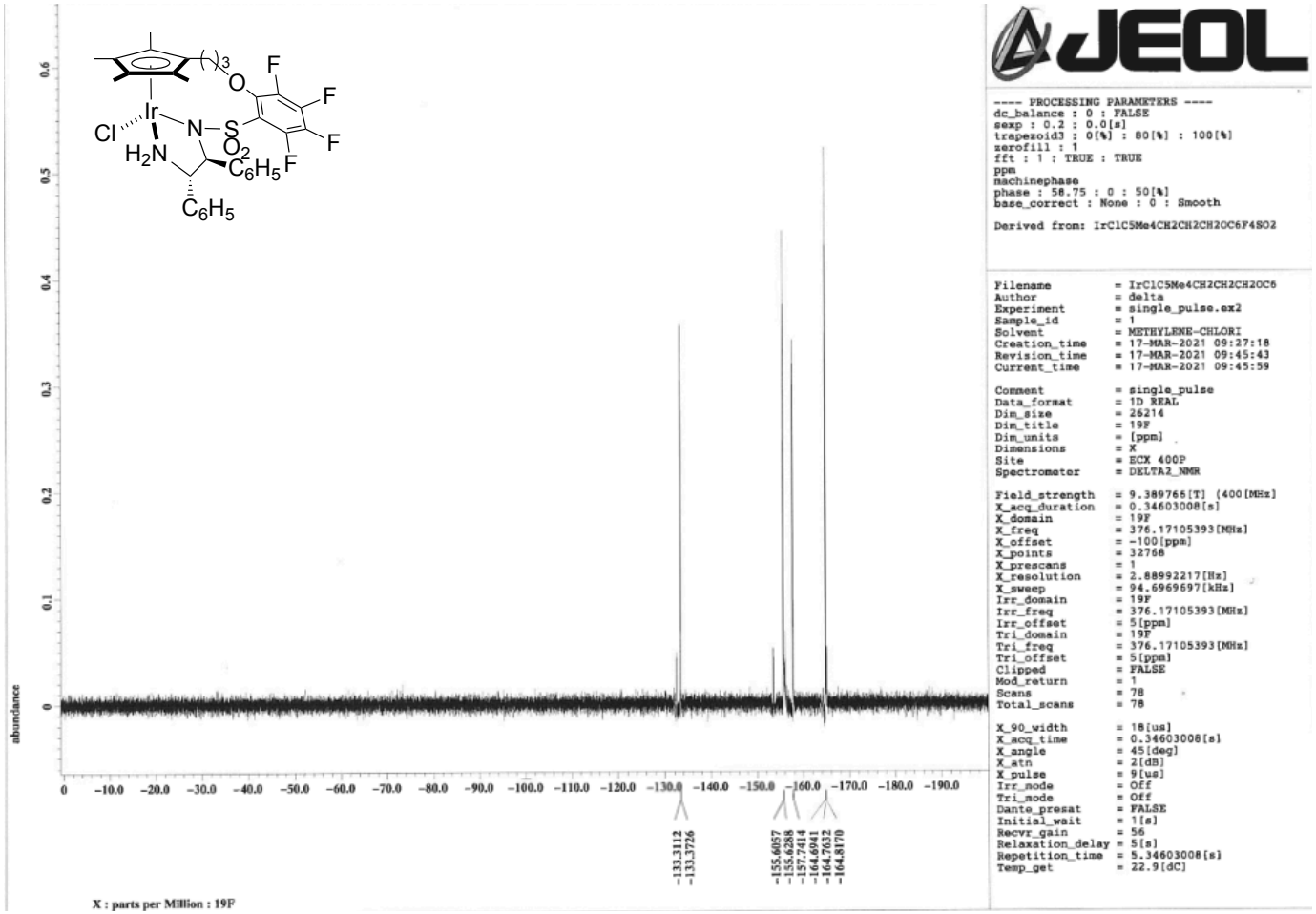


Fig. S18. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **4a**.

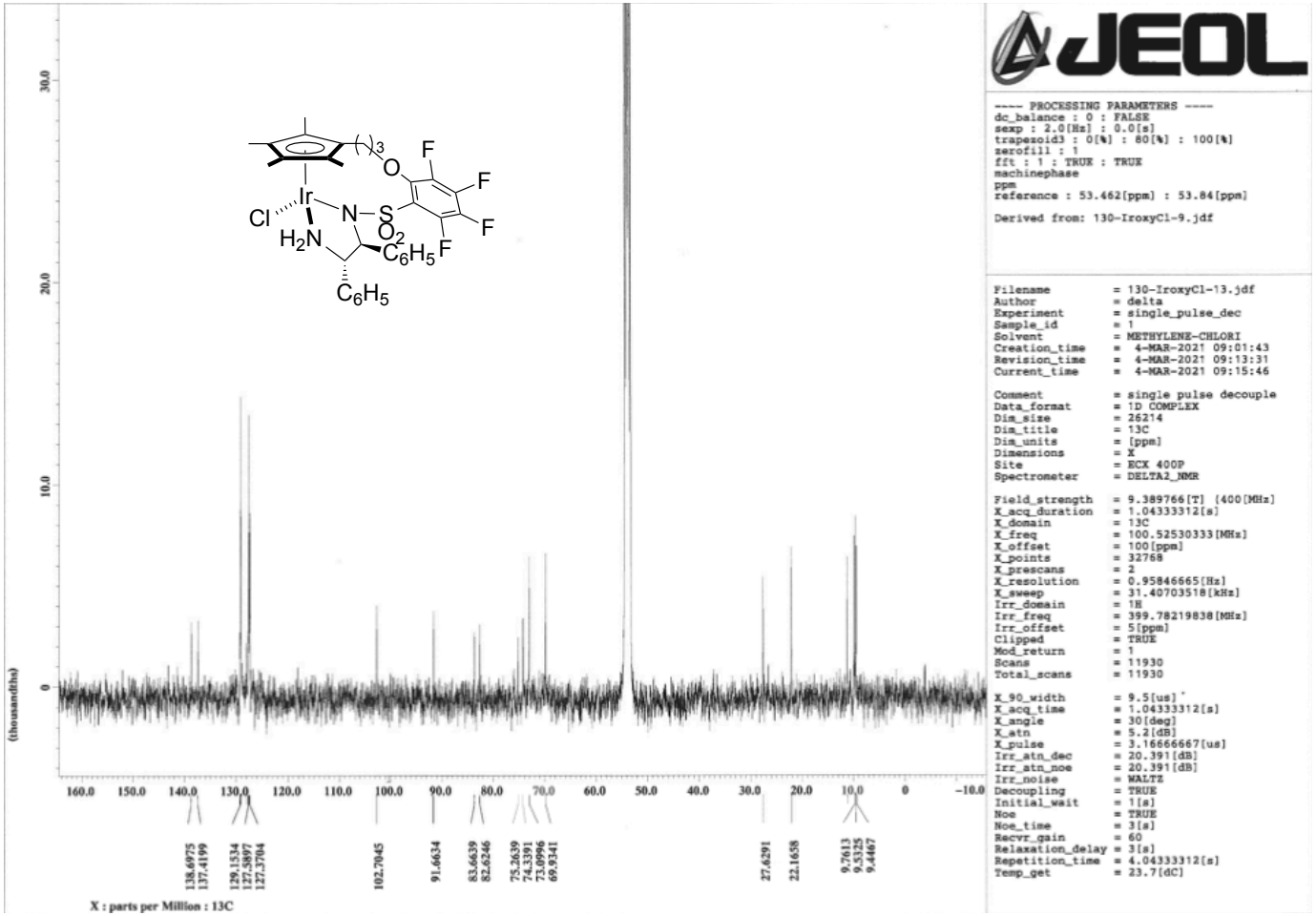


Fig. S19. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **4a**.

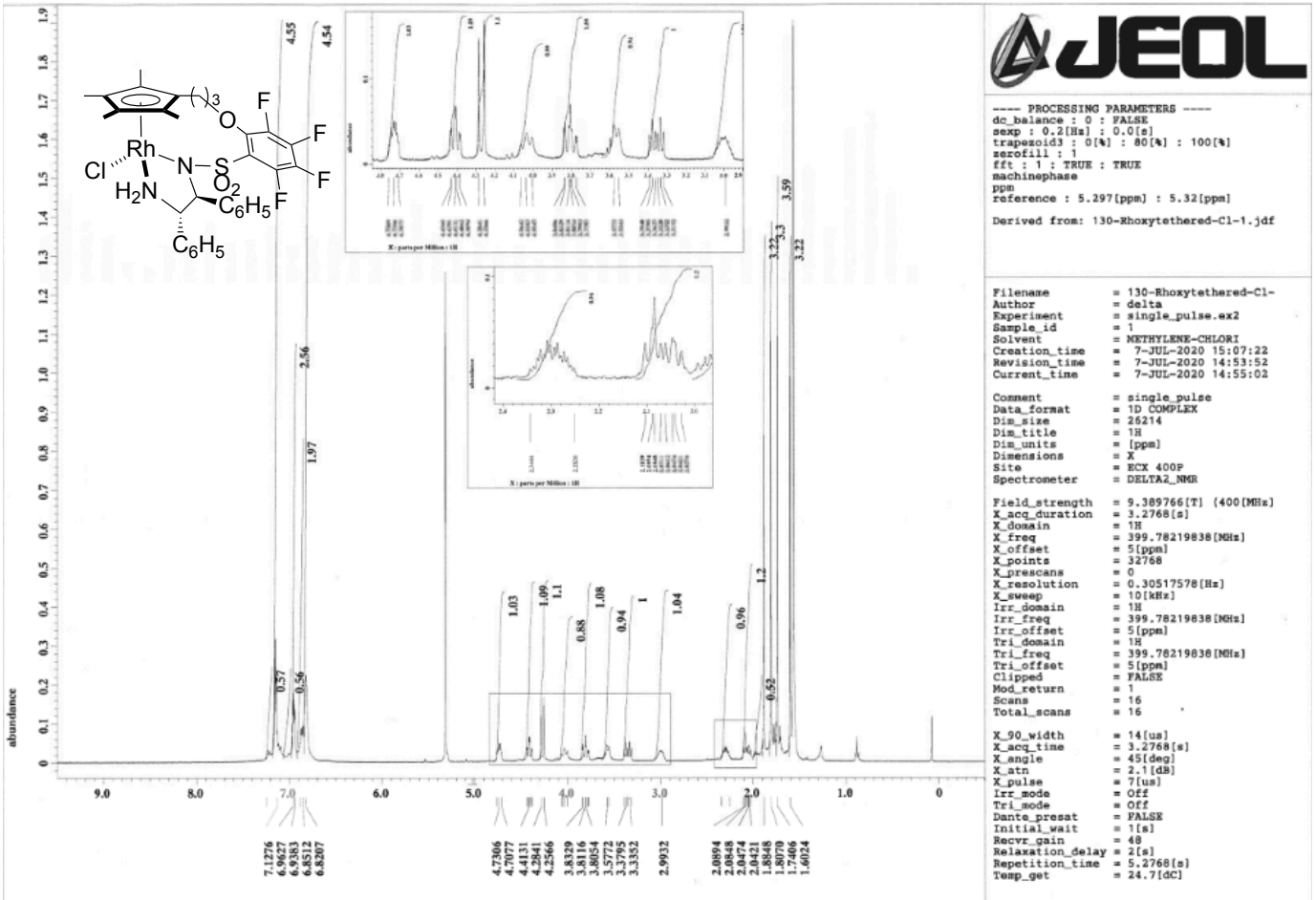


Fig. S20. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **4b**.

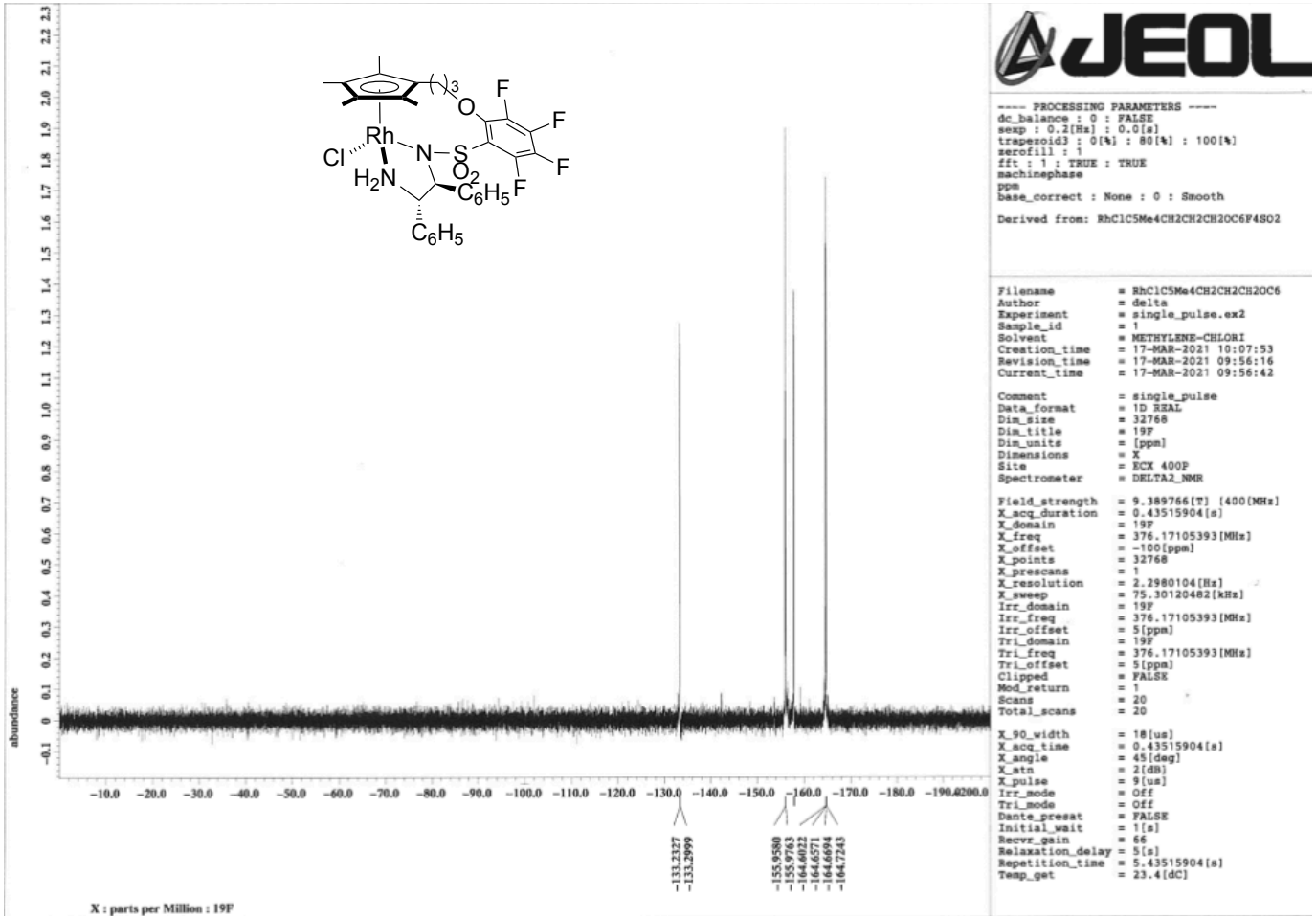


Fig. S21. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **4b**.

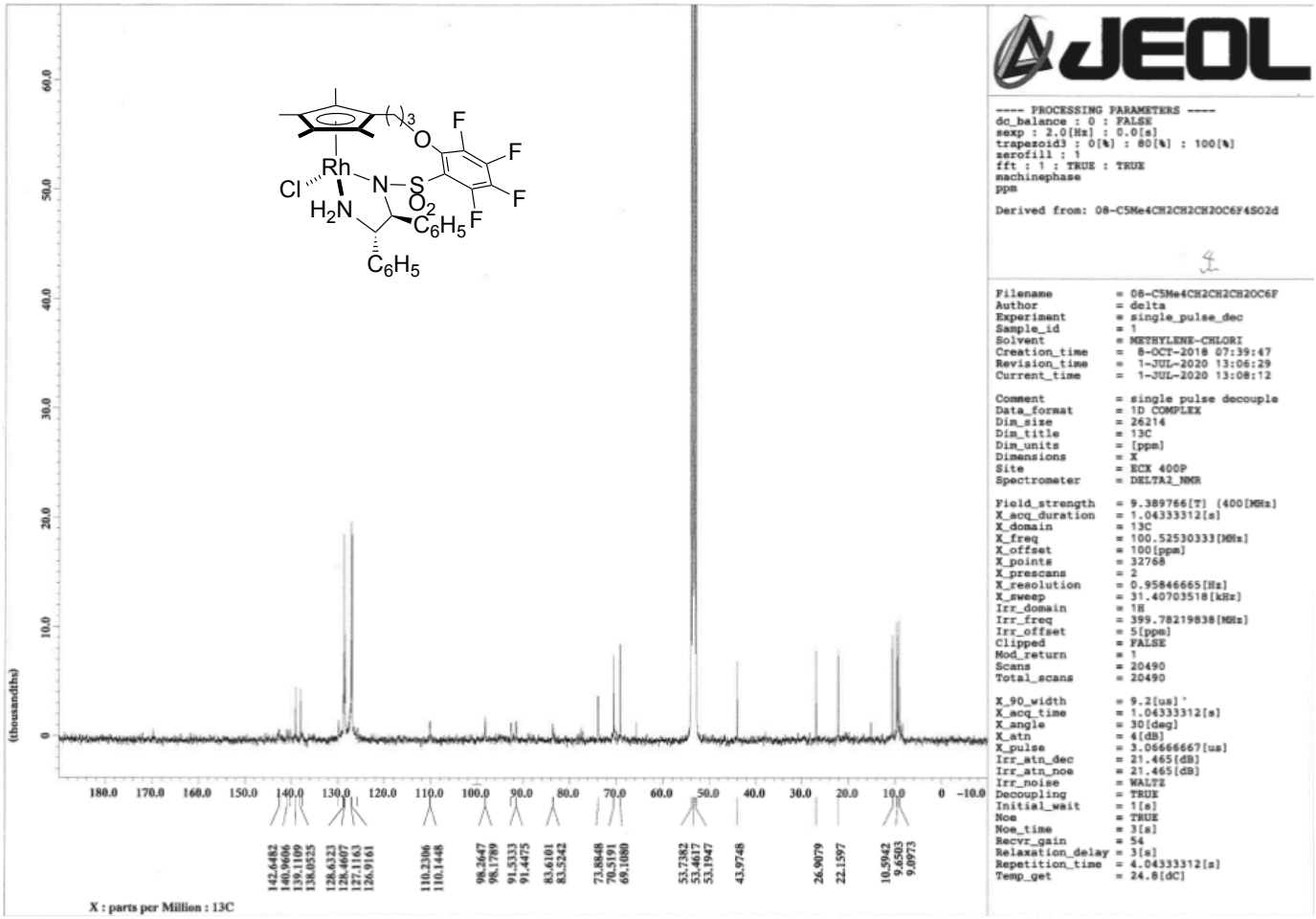


Fig. S22. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **4b**.

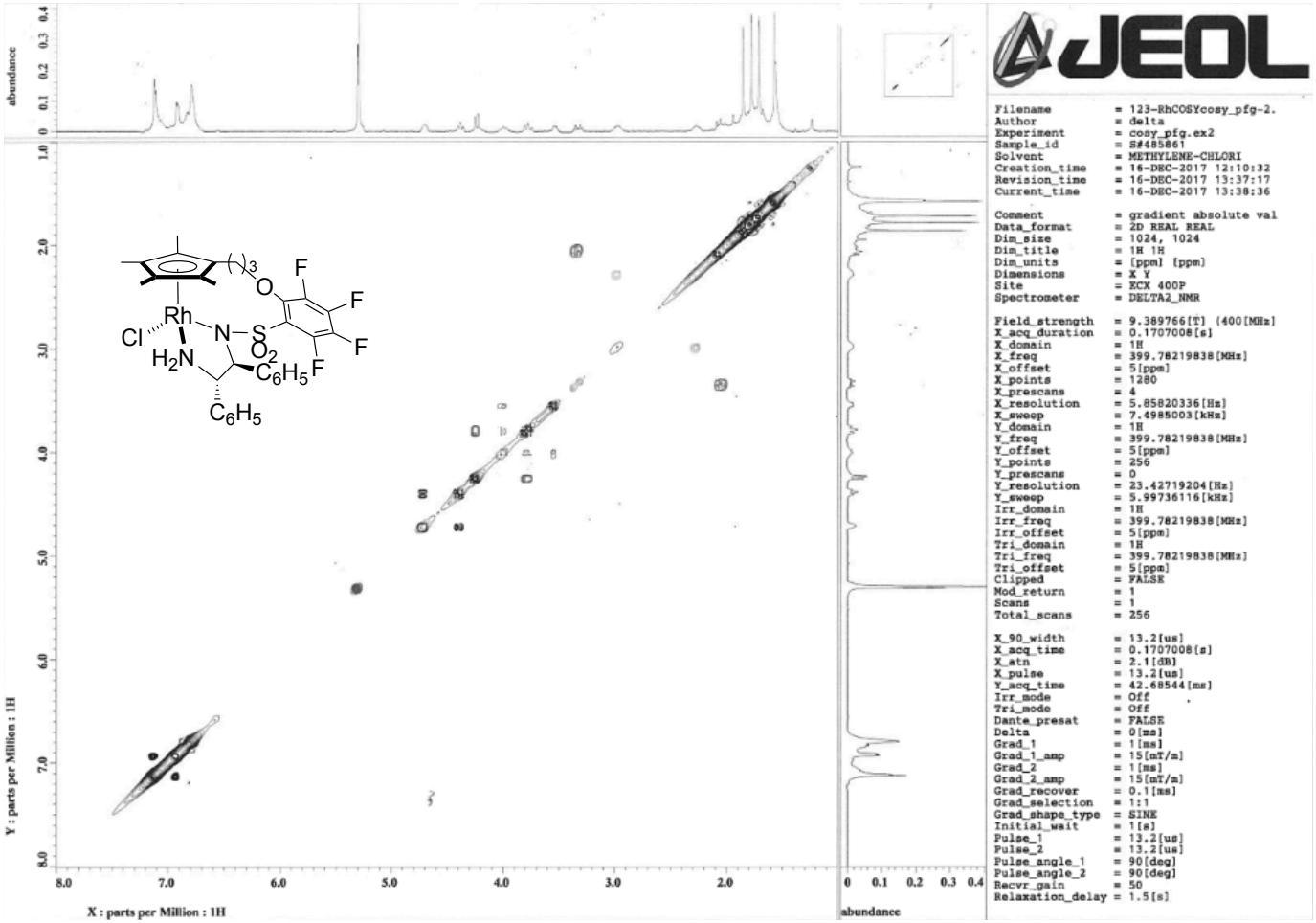


Fig. S23. ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, rt) of **4b**.

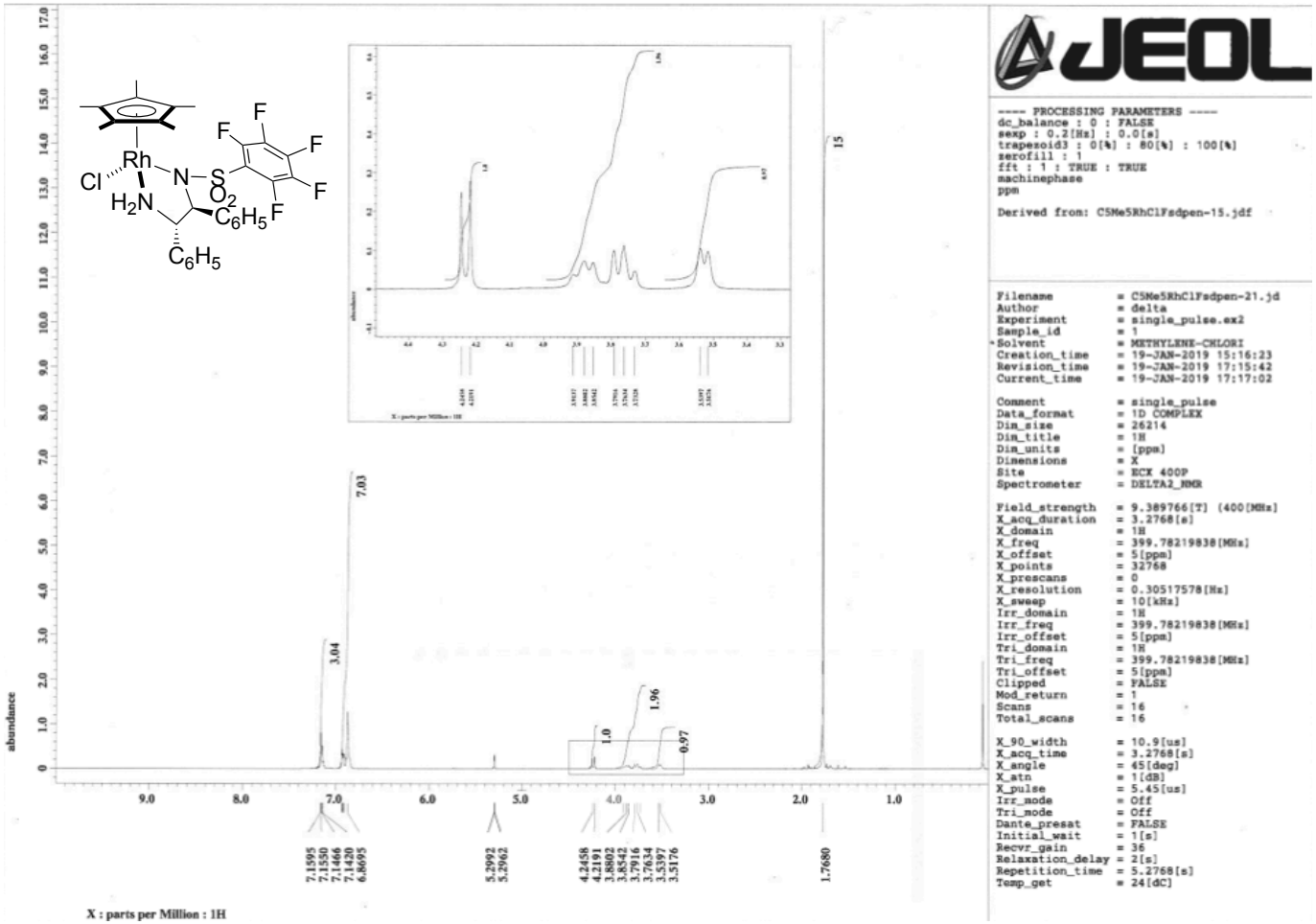


Fig. S24. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, rt) of **5**.

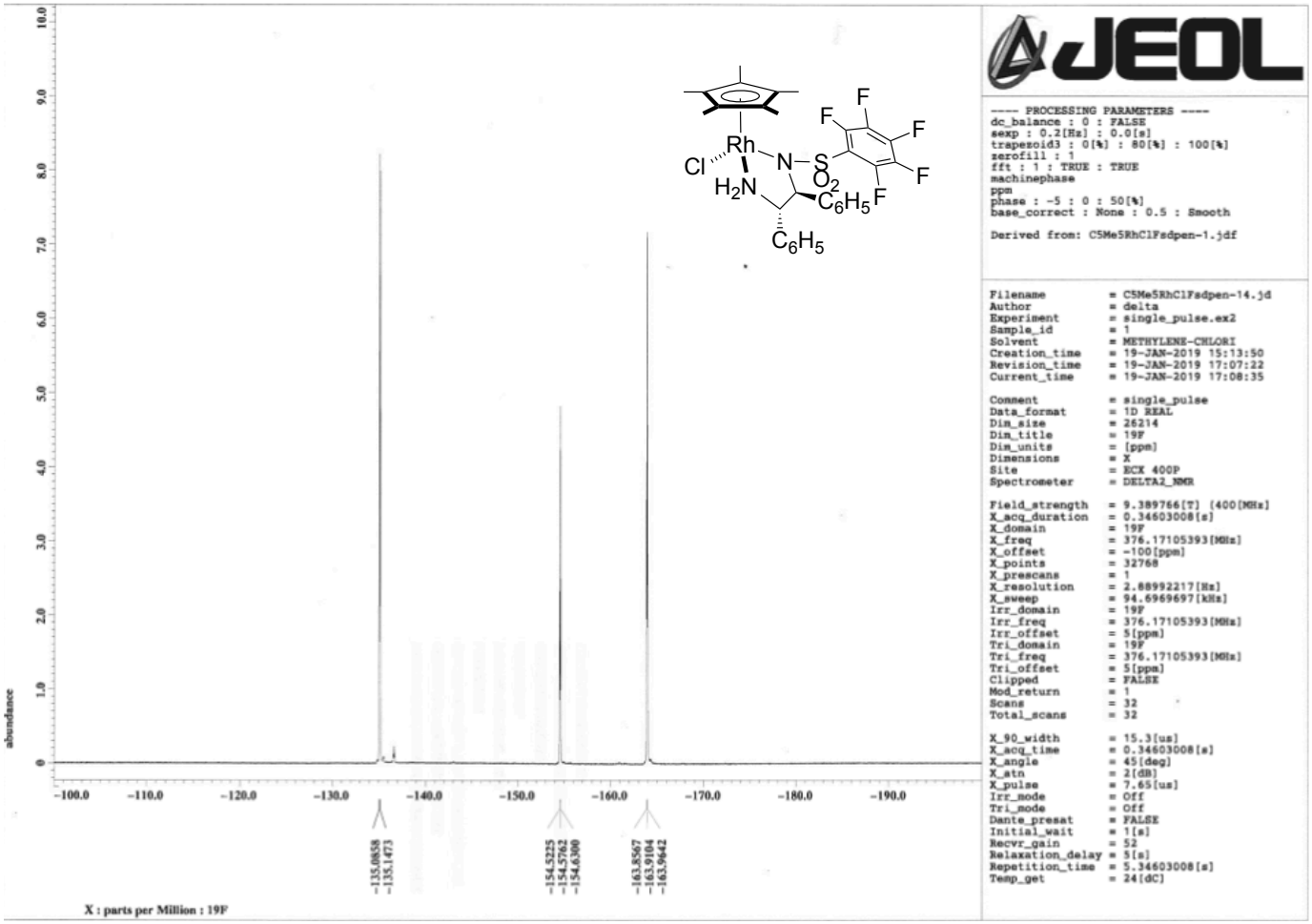


Fig. S25. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **5**.

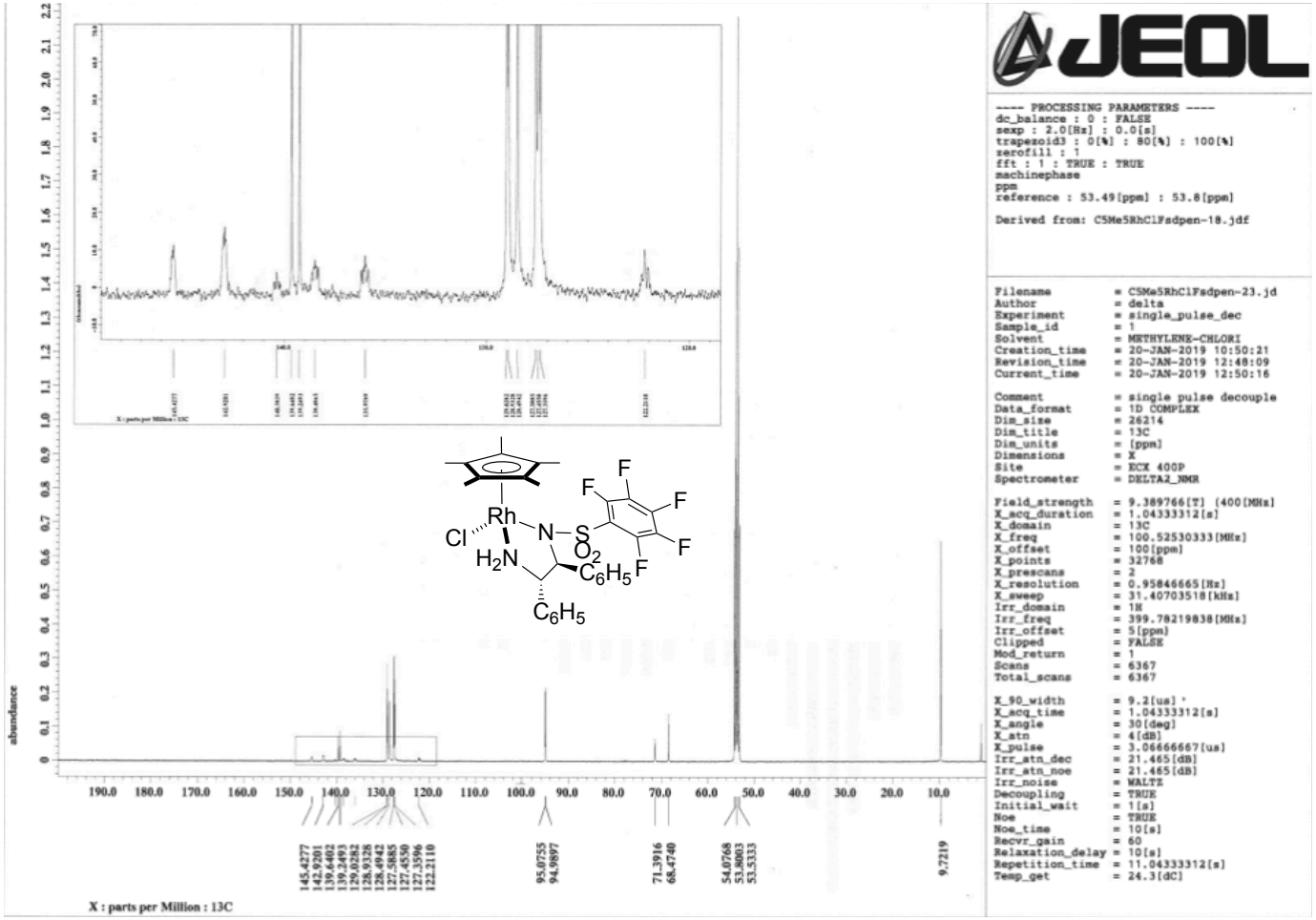


Fig. S26. $^{13}C\{^{1}H\}$ NMR spectrum (100.5 MHz, CD_2Cl_2, rt) of **5**.

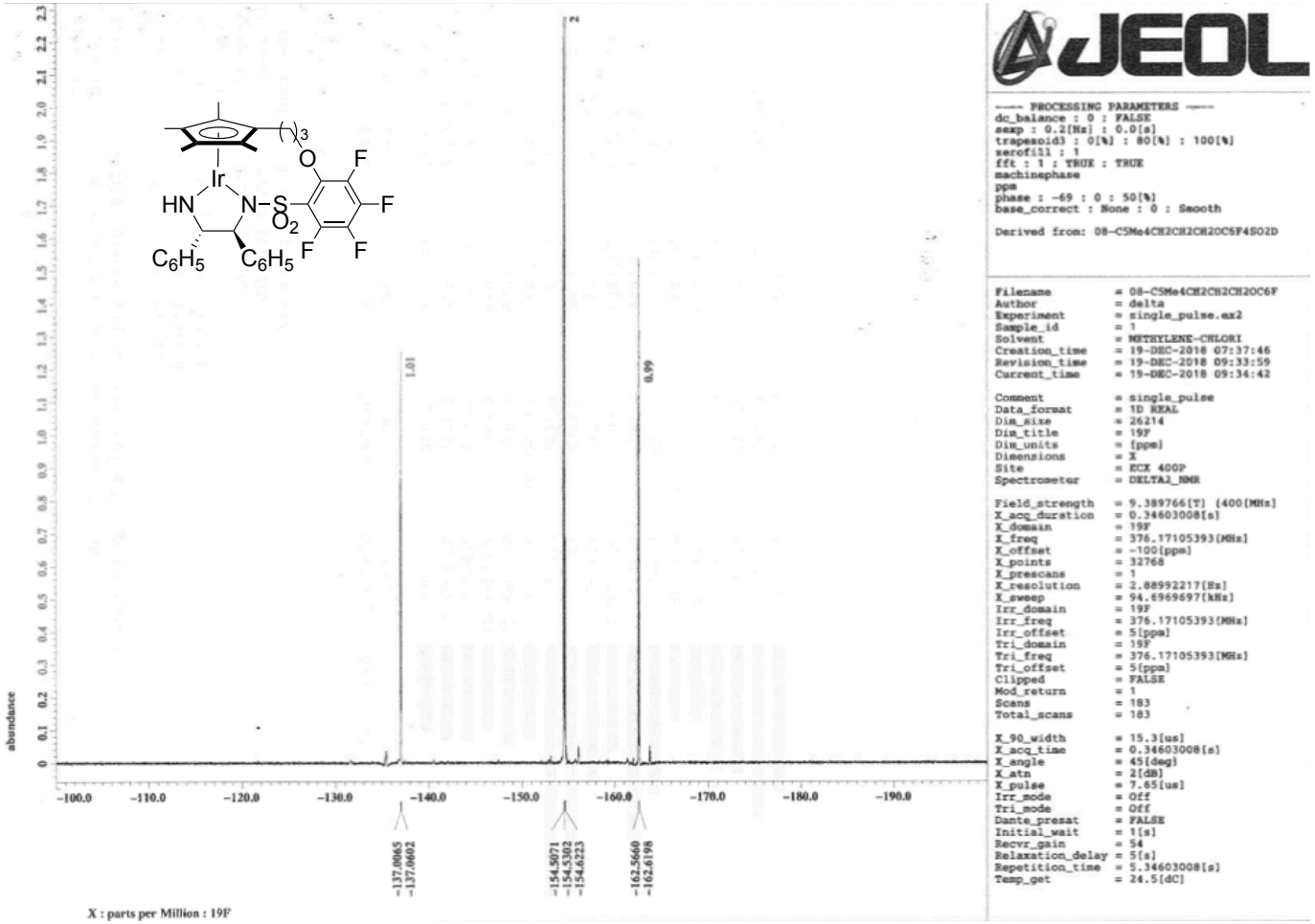


Fig. S27. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of **3**.

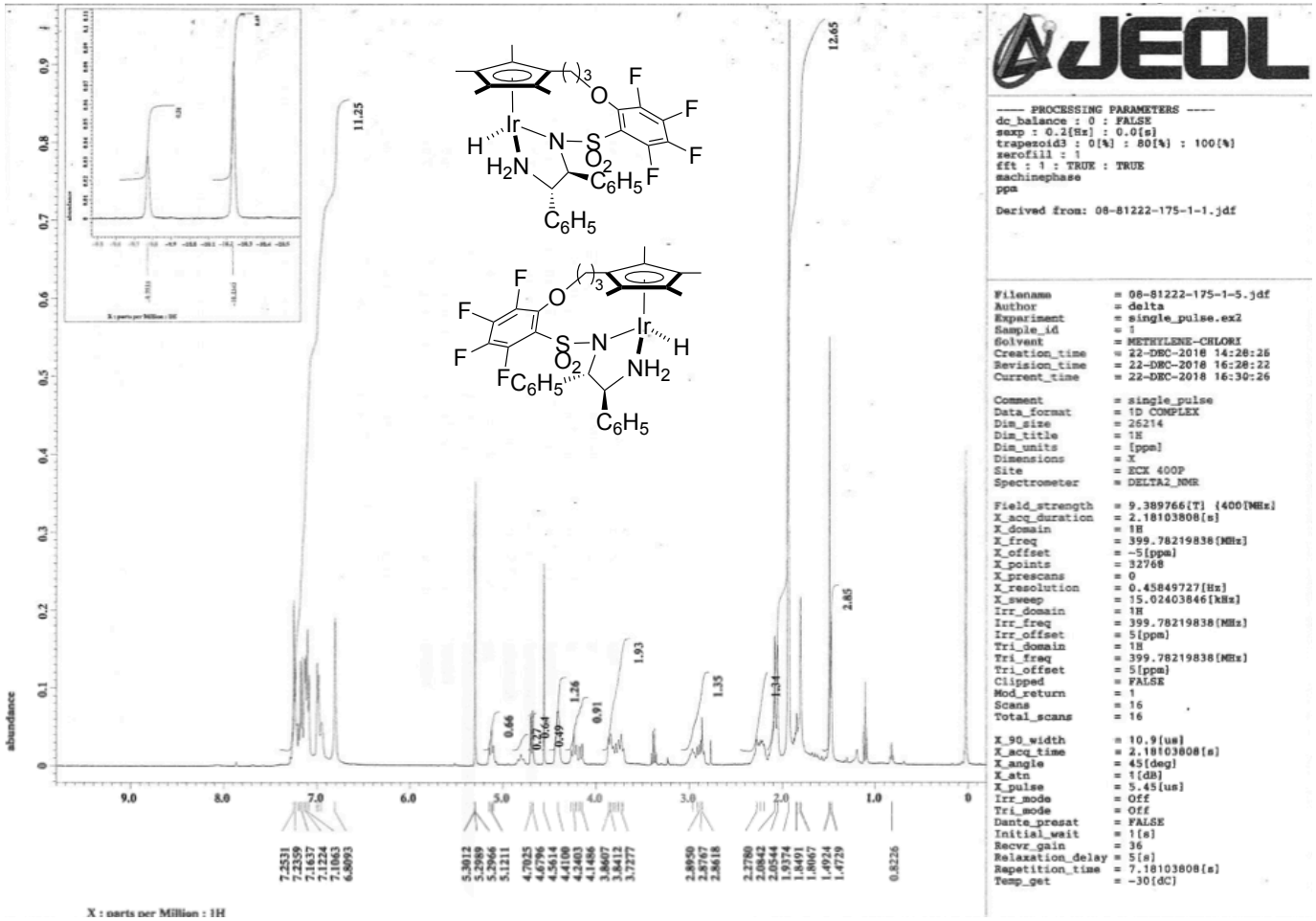


Fig. S28. ^{1}H NMR spectrum (399.78 MHz, CD_2Cl_2, –30 °C) of a reaction mixture of **3** and 1.15 equiv. of HCOOH.

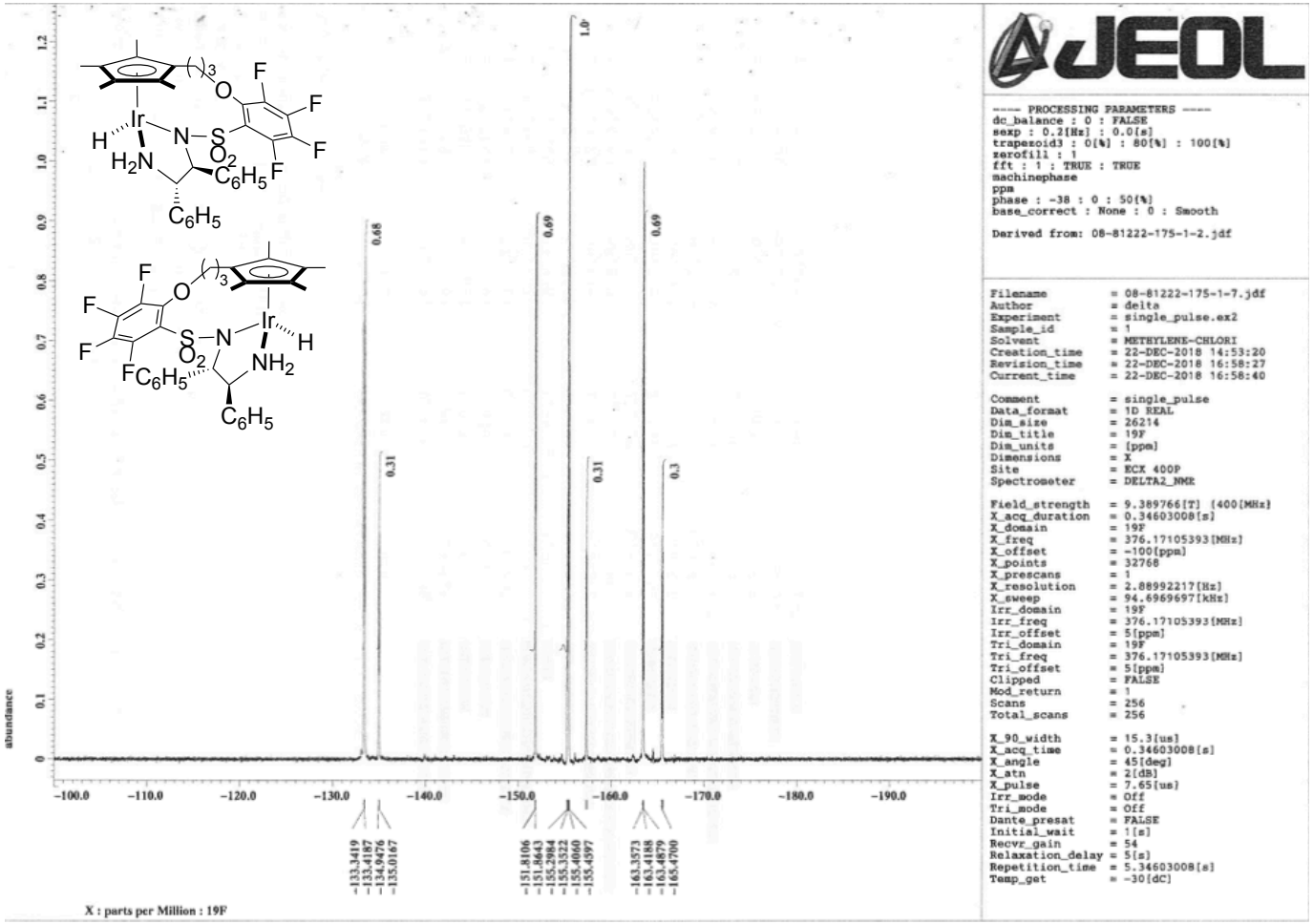


Fig. S29. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, –30 °C) of a reaction mixture of **3** and 1.15 equiv. of HCOOH after 1 h.

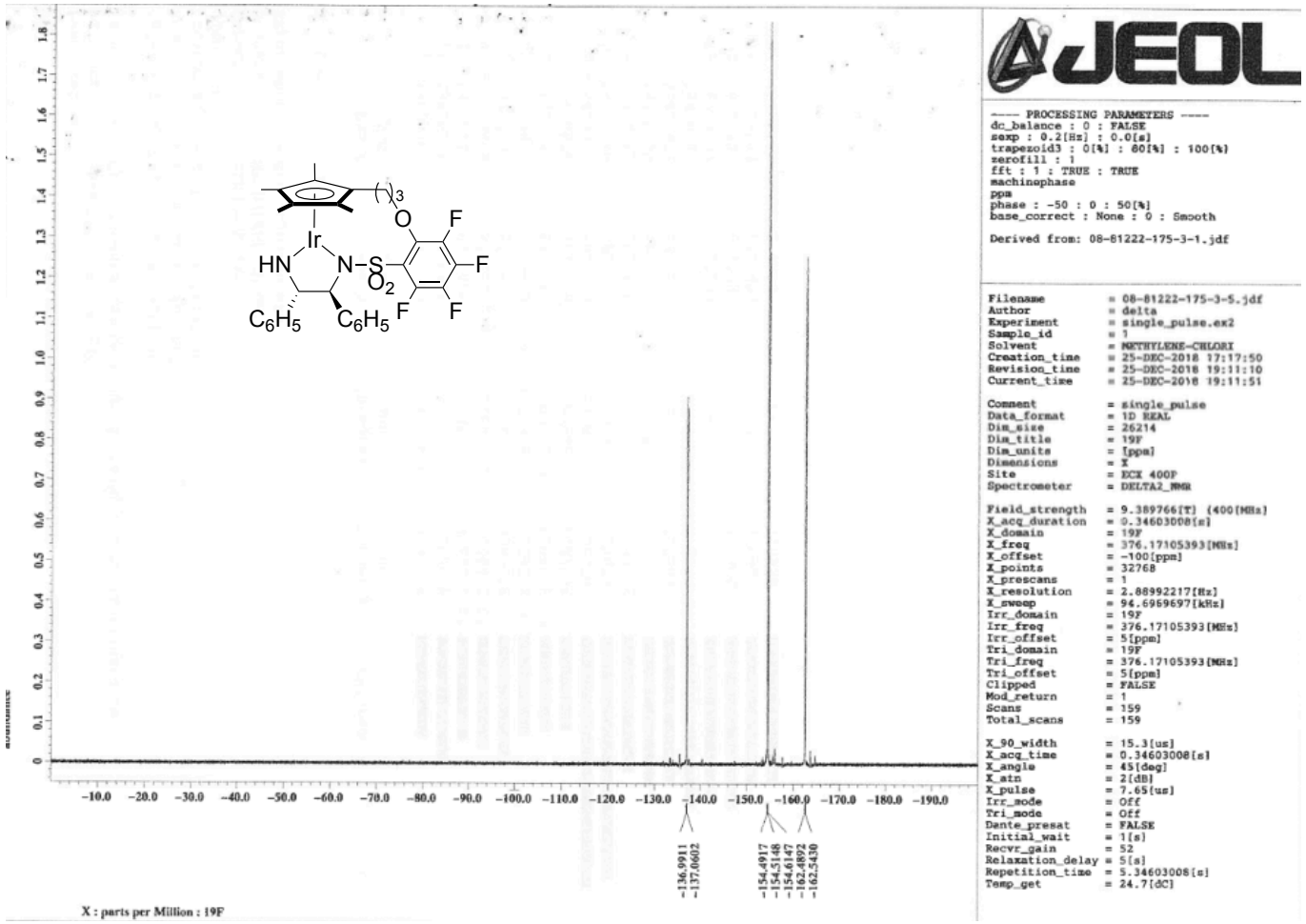


Fig. S30. ^{19}F NMR spectrum (376.2 MHz, CD_2Cl_2, rt) of a reaction mixture of **3** and 1.15 equiv. of HCOOH after 3 d.