A Convenient Pinacol Coupling of Diaryl Ketones with B_2pin_2 via Pyridine Catalysis

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Electronic Supplementary Information

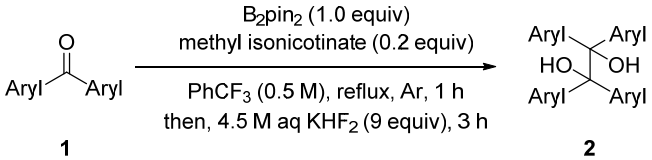
1. General Experimental

CH_2Cl_2 (Fisher, HPLC grade), 1,4-dioxane (Fisher, HPLC grade), and THF (Fisher, HPLC grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. α,α,α-Trifluorotoluene (Acros, 99+%) was dried with CaH_2 (Acros, 93%) and distilled under argon. The solvents which were used for pyridine-boryl radical-promoted pinacol coupling were degassed by freeze-pump-thaw. Methyl *tert*-butyl ether (MTBE) (J.T. Baker, HPLC grade) and 1,4-dioxane (Fisher, HPLC grade) were dried with Na (Alfa, 99%) in the presence of benzophenone (Alfa, 99%) and distilled under argon. 4-Bromobenzotrifluoride (Alfa, 99%) was dried with CaH_2 (Acros, 93%) and distilled under argon. Benzaldehyde (**3a**, Acros, 98%), acetophenone (**3b**, Alfa, 99%), methyl isonicotinate (TCI, >99%), and *p*-anisaldehyde (Alfa, 98%) were distilled under argon. Filtration and column chromatography were performed using Merck 230–400-mesh silica gel 60 Å (0.040-0.063 mm). The following reagents were recrystallized from the indicated solvents prior to use: benzophenone (**1a**, Alfa, petroleum ether), 4,4'-dimethylbenzophenone (**1b**, Alfa, petroleum ether), 4,4'-dimethoxybenzophenone (**1c**, TCI, Et_2O), 4,4'-difluorobenzophenone (**1d**, Alfa, EtOH), 4,4'-dichlorobenzophenone (**1e**, TCI, Et_2O), 4,4'-dibromobenzophenone (**1f**, Alfa, CH_2Cl_2/hexanes), 2,2'-dichlorobenzophenone (**1g**, Alfa, MeOH), 4-fluoro-4'-methoxybenzophenone (**1h**, Alfa, CH_2Cl_2/hexanes), di-2-thienylketone (**1j**, Alfa, CH_2Cl_2/hexanes), 9-fluorenone (**1k**, TCI, MeOH/CH_2Cl_2), 2,7-dibromo-9-fluorenone (**1l**, TCI, CH_2Cl_2/hexanes), xanthone (**1m**, TCI, EtOH), 4-cyanopyridine (TCI, Et_2O), and 4-phenylpyridine (Acros, Et_2O). B_2pin_2 (Alfa, 98+%), KHF_2 (Alfa, 98%), and Mg (Junsei, 98%) were used without further purification. Solvents and reagents for recrystallization, work-up and chromatography were petroleum ether (Daejung, Extra Pure), MeOH (Duksan, Extra Pure), EtOH (Duksan, Extra Pure), CH_2Cl_2 (Duksan, Extra Pure), EtOAc (Duksan, Extra Pure), Et_2O (Daejung, Extra Pure), hexanes (Duksan, Extra Pure), $MgSO_4$ (Duksan, 99.0%), and Na_2SO_4 (Duksan, 99.0%). ^1H and ^{13}C NMR spectra were recorded on a JEOL ECS400 spectrometer (400 MHz, ^1H; 100 MHz, ^{13}C). Chemical shifts are referenced to residual chloroform (7.26 ppm, ^1H; 77.23 ppm, ^{13}C), dichloromethane (5.32 ppm, ^1H; 53.84 ppm, ^{13}C), acetone (2.05 ppm, ^1H), and acetonitrile (1.94 ppm, ^1H; 1.32 ppm, ^{13}C). Chemical shifts are reported in ppm, and multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, *J*, are reported in Hertz. Analytical thin-layer chromatography was conducted on Merck silica gel 60 F_{254} TLC plates. Visualization was accomplished with UV (254 nm and 365 nm) and a $KMnO_4$ staining solution. High resolution electrospray ionization mass spectrometry (ESI-HRMS) was performed on a Thermo Scientific LTQ Orbitrap XL spectrometer at Environmental OMICS Laboratory, GIST. High resolution fast atom bombardment mass spectrometry (FAB-HRMS) was performed on a JEOL JMS-700 spectrometer at Korea Basic Science Institute (KBSI), Daegu Center. High resolution field desorption mass spectrometry (FD-HRMS) was performed on a JEOL JMS-T200GC spectrometer at CNU Center for Research Facilities at Chonnam National University. Data are reported in the form of *m/z*.

2. Experimental Procedures

2.1. Boryl Radical-Promoted Pinacol Coupling of Diaryl Ketones

2.1.1. Homocoupling



1 **2**

To a solution of ketone (**1**, 1.00 mmol) and B_2pin_2 (254 mg, 1.00 mmol) in $PhCF_3$ (1 mL) was added methyl isonicotinate (24 μL, 0.20 mmol) at room temperature under argon, and the mixture was refluxed for 1 hour. The reaction mixture was cooled to room temperature, transferred to a vial with CH_2Cl_2 (3 mL), and stirred with 4.5 M aq KHF_2 (2 mL) at room temperature under air. After 3 hours, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL) four times. The combined organic layers were dried over Na_2SO_4 (6-12 g), filtered, and concentrated under reduced pressure. The crude material was adsorbed to SiO_2 and purified by column chromatography (SiO_2, ϕ: 2.5 cm, l: 15 cm) to afford the diol (**2**). **2a-e** and **2m** have been fully characterized in the literature.[1] Copies of ^1H NMR spectra are attached at the end of the ESI.

Data for **2f**:

^1H NMR: (400 MHz, $CDCl_3$) δ 7.34–7.30 (m, 8H), 7.15–7.12 (m, 8H), 2.82 (brs, 2H).

$^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 142.6, 130.9, 130.4, 122.0, 82.7.

HRMS (ESI): $[M–OH]^+$ calcd for $C_{26}H_{17}Br_4O$: 660.8013; found: 660.8010.

Data for **2h**:

HRMS (ESI): $[M–OH]^+$ calcd for $C_{28}H_{23}F_2O_3$: 445.1615; found: 445.1631.

(^1H and $^{13}C\{^1H\}$ NMR data were reported in the literature.[2])

Data for **2i**:

^1H NMR: (400 MHz, CD_3Cl) δ 7.50–7.43 (m, 8H), 7.12–7.10 (m, 4H), 6.73–6.70 (m, 4H), 3.76 (s, 6H), 2.91 (brs, 2H); the other diastereomer: δ 7.68–7.66 (m, 4H), 7.43–7.40 (m, 4H), 6.95–6.92 (m, 4H), 6.75–6.73 (m, 4H), 3.78 (s, 6H), 2.96 (brs, 2H)

$^{13}C\{^1H\}$ NMR: (100 MHz, CD_3Cl) δ 158.9, 148.7, 135.4, 129.7, 129.213, 129.209 (q, J = 32.2), 124.34 (q, J = 3.6), 124.33 (q, J = 272.0), 113.2, 83.0, 55.4; the other diastereomer: δ 159.2, 148.5, 134.9, 129.8, 129.1, 129.0 (q, J = 32.4), 124.5 (q, J = 3.6), 124.3 (q, J = 272.0), 113.2, 82.9, 55.4.

HRMS (FD): $[M]^+$ calcd for $C_{30}H_{24}F_6O_4$: 562.1579; found: 562.1577.

Data for **2j**:

$^{13}C\{^1H\}$ NMR: (100 MHz, CD_3CN) δ 148.8, 127.9, 126.9, 126.7, 83.0.

HRMS (FAB): $[M–OH]^+$ calcd for $C_{18}H_{13}OS_4$: 372.9849; found: 372.9851.

(^1H NMR data were reported in the literature.[3])

Data for **2k**:

HRMS (FAB): $[M\text{-}OH]^+$ calcd for $C_{26}H_{17}O$: 345.1279; found: 345.1277.

(^1H and $^{13}C\{^1H\}$ NMR data were reported in the literature.[4])

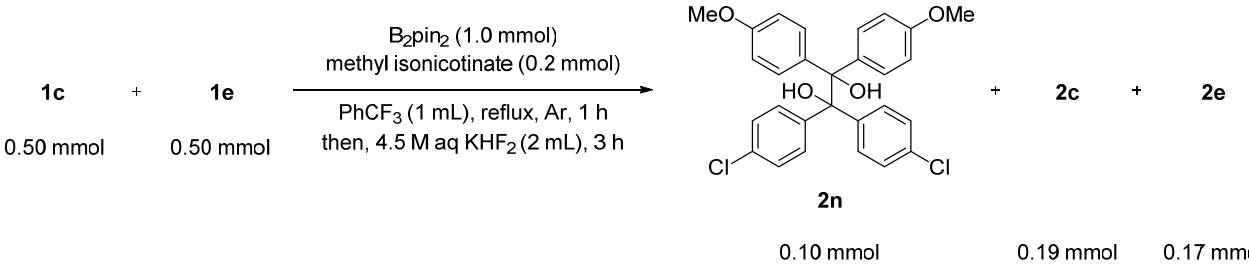
Data for **2l**:

^1H NMR: (400 MHz, CD_2Cl_2) δ 7.45–7.29 (m, 10H), 3.35 (s, 2H).

$^{13}C\{^1H\}$ NMR: (100 MHz, CD_2Cl_2) δ 146.5, 138.9, 133.0, 129.0, 121.6, 121.3, 86.5.

HRMS (ESI): $[M–OH]^+$ calcd for $C_{26}H_{13}Br_4O$: 656.7700; found: 656.7702.

2.1.2. Heterocoupling



To a solution of **1c** (121 mg, 0.500 mmol), **1d** (126 mg, 0.500 mmol), and B_2pin_2 (254 mg, 1.00 mmol) in $PhCF_3$ (1 mL) was added methyl isonicotinate (24 μL, 0.20 mmol) at room temperature under argon, and the mixture was refluxed for 1 hour. The reaction mixture was cooled to room temperature, transferred to a vial with CH_2Cl_2 (3 mL), and stirred with 4.5 M aq KHF_2 (2 mL) at room temperature under air. After 3 hours, the mixture was poured into water (20 ml) and extracted with CH_2Cl_2 (20 mL) four times. The combined organic layers were dried over Na_2SO_4 (6 g), filtered, and concentrated under reduced pressure. The crude material was adsorbed to SiO_2 and purified by column chromatography (SiO_2, ϕ: 2.5 cm, l: 18 cm, EtOAc:haxanes = 1:15→1:6→1:3) to afford the diols, **2n** (R_f = 0.2 in EtOAc/hexanes = 1:7, off-white solid, 47 mg, 0.10 mmol), **2c** (R_f = 0.1 in EtOAc/hexanes = 1:7, off-white solid, 93 mg, 0.19 mmol), and **2e** (R_f = 0.5 in EtOAc/hexanes = 1:7, white solid, 87 mg, 0.17 mmol).

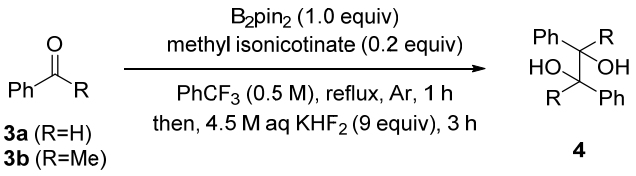
Data for **2n**:

^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 4H), 7.15–7.09 (m, 8H), 6.72 (m, 4H), 3.77 (s, 6H), 2.86 (m, 2H).

$^{13}C\{^1H\}$ NMR: (100 MHz, $CDCl_3$) δ 158.8, 142.9, 136.1, 133.0, 130.1, 130.0, 127.5, 113.0, 83.2, 82.3, 55.4.

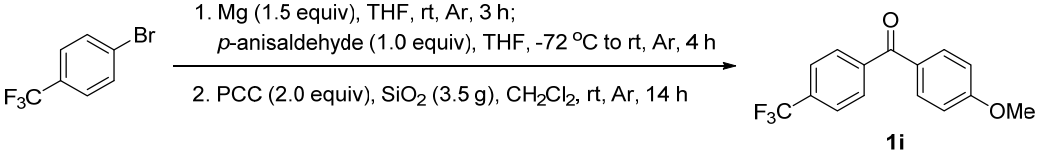
HRMS (FAB): $[M\text{-}OH]^+$ calcd for $C_{28}H_{23}{}^{35}Cl_2O_3$, $C_{28}H_{23}{}^{35}Cl^{37}ClO_3$: 477.1024, 479.0995; found: 477.1028, 479.0921.

2.2. Boryl Radical-Promoted Pinacol Coupling of Benzaldehyde and Acetophenone



To a solution of carbonyl compound (**3**, 1.00 mmol) and B_2pin_2 (254 mg, 1.00 mmol) in $PhCF_3$ (1 mL) was added methyl isonicotinate (24 μL, 0.20 mmol) at room temperature under argon, and the mixture was refluxed for 48 hours. The reaction mixture was cooled to room temperature, transferred to a vial with CH_2Cl_2 (3 mL), and stirred with 4.5 M aq KHF_2 (2 mL) at room temperature under air. After 3 hours, the mixture was poured into water (20 mL) and extracted with CH_2Cl_2 (20 mL) four times. The combined organic layers were dried over Na_2SO_4 (6 g), filtered, and concentrated under reduced pressure. The crude material was adsorbed to SiO_2 and purified by column chromatography (SiO_2, ϕ: 2 cm, l: 15 cm) to afford the diol (**4a**: yellow solid, 52 mg, 49%; **4b**: white solid, 9 mg, 7%) as a mixture of diastereomers.

2.3. Preparation of 4-Methoxy-4'-(trifluoromethyl)benzophenone[5]



To a mixture of Mg (365 mg, 15.0 mmol) in THF (20 mL) was added 4-bromobenzotrifluoride (1.4 mL, 10 mmol) at room temperature under argon. After 3 hours, the solution was added to a solution of *p*-anisaldehyde (1.2 mL, 10 mmol) in THF (10 mL) dropwise at –72 °C, and the reaction mixture was stirred at room temperature. After 4 hours, the reaction mixture was quenched by sat. aq NH_4Cl (45 mL), diluted with Et_2O (45 mL), and the organic layer was separated. The aqueous layer was extracted with Et_2O (45 mL). The combined organic layers were dried over $MgSO_4$ (6 g), filtered, and concentrated under reduced pressure. To a mixture of PCC (4.3 g, 20 mmol) and SiO_2 (3.5 g) in CH_2Cl_2 (10 mL) was added a solution of the crude material (3.0 g) in CH_2Cl_2 (3 mL). The flask containing the remaining crude material was rinsed twice with CH_2Cl_2 (3mL and 4 mL). The reaction mixture was stirred at room temperature for 14 hours. The reaction mixture was filtered by SiO_2 (ϕ: 2.5 cm, l: 3 cm, CH_2Cl_2) and concentrated under reduced pressure. The crude material was purified by precipitation from CH_2Cl_2/hexanes to afford 4-methoxy-4'-(trifluoromethyl)benzophenone (**1i**) as a white solid in 79% yield (2.2 g, 7.9 mmol).

Data for **1i**:

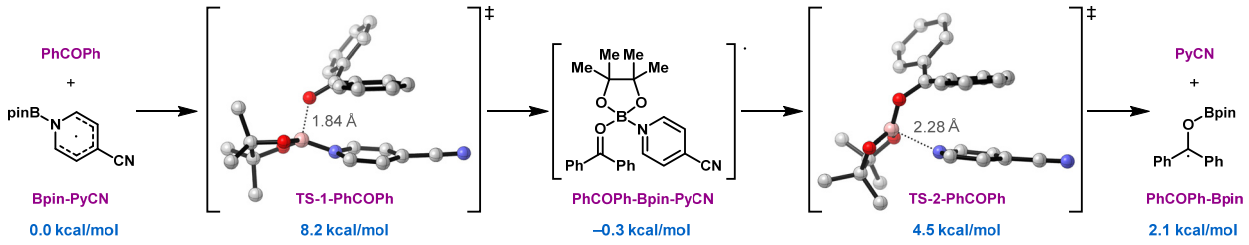
HRMS (FD): $[M]^+$ calcd for $C_{15}H_{11}F_3O_2$: 280.0711; found: 280.0703.

(^1H and $^{13}C\{^1H\}$ NMR data were reported in the literature.[5])

3. DFT Calculation

Conformation around the B–O(carbonyl) bond in the PhCOPh-Bpin-PyCN complex was analyzed, and then approximate transition structures for the benzophenone ketyl radical formation were obtained by the PM6 semi-empirical Hamiltonian using MOPAC 2016.[6] These saddle points were refined by DFT calculation at the UM062X/6-31G(d,p) level of theory[7] using the Gaussian 16 suite of programs[8]. A phenyl ring in these structures were replaced by a methyl group, and then saddle point optimizations were performed for the acetophenone ketyl radical formation. These transition structures were verified by the presence of a single negative frequency as well as the Intrinsic Reaction Coordinate (IRC) calculation at the same level of theory. The reactant and the product from the IRC calculation were further optimized to give the ground state structures which have no imaginary frequency. All the reported energy values are obtained after thermal free energy correction. The 3-D illustrations were produced using CYLview 1.0b.[9]

3.1. Benzophenone Ketyl Radical Formation



- computed data for **PhCOPh** + **Bpin-PyCN**

: total free energy = –1327.535200 Hartree

: relative free energy = 0.00 kcal/mol

: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	-1.76615900	-0.82630100	-0.57247300
N	-0.43931900	-1.15944800	-1.04063900
O	-0.52830600	0.73168500	1.33888800
C	0.65227300	0.97126500	1.12894200
C	1.03138000	2.29704600	0.54931900
C	1.68507300	-0.06290400	1.43907700
C	0.18898100	-2.33935600	-0.64757400
C	1.45713600	-2.63207900	-1.02611500
C	2.19733700	-1.72177900	-1.84152600
C	0.27245900	-0.26195400	-1.83388200
C	1.54360800	-0.51743800	-2.23437300
H	2.06291400	0.21148300	-2.84553600
H	-0.26391900	0.63805100	-2.10579700
H	-0.40670000	-2.98531300	-0.01541700
H	1.91616900	-3.55127200	-0.68289500
O	-2.53556300	-1.69784100	0.14172000
O	-2.37475500	0.35437600	-0.89371600
C	-3.75548900	0.22642500	-0.48115900
C	-3.71010700	-0.95761300	0.55581700
C	-3.46870200	-0.49827300	1.99103000
H	-2.59648300	0.15424100	2.05241900
H	-3.28293300	-1.38124200	2.60797200
H	-4.34372000	0.02295300	2.38922600
C	-4.91035500	-1.88973300	0.49724500
H	-5.01423500	-2.35215100	-0.48517300
H	-5.82904000	-1.34265000	0.73084100
H	-4.78782500	-2.68288900	1.23854300
C	-4.19997200	1.55633400	0.10469500
H	-3.51672900	1.87752800	0.89267500
H	-5.21204400	1.47984400	0.51400400
H	-4.20515800	2.31631200	-0.68094700
C	-4.55461700	-0.10794000	-1.73807300
H	-4.22221700	-1.05551600	-2.17138300
H	-4.39250000	0.68040100	-2.47672900
H	-5.62516000	-0.17480700	-1.52723000
C	3.55631300	-1.95521500	-2.15293800
N	4.68398900	-2.13546600	-2.38118100
C	0.08403300	2.93481600	-0.26047300
C	0.36076900	4.18286500	-0.80240300
C	1.57150900	4.81447700	-0.51660400
C	2.50333500	4.19694500	0.31266500
C	2.23848700	2.93664900	0.84208400

H	2.95826500	2.46110100	1.50055700
H	-0.85845000	2.42675900	-0.45102600
H	-0.36738800	4.66988500	-1.44286700
H	1.78466900	5.79262200	-0.93592400
H	3.43680400	4.69642500	0.54970700
C	1.33716900	-1.06195900	2.35771600
C	2.92460100	-0.11921000	0.79623500
C	3.80899400	-1.16012900	1.07119300
C	2.22418100	-2.08933100	2.64202600
C	3.46081200	-2.14017300	1.99534500
H	4.75158300	-1.21992200	0.53703100
H	4.15080600	-2.95084500	2.20754800
H	0.35957300	-1.01433500	2.82658600
H	1.95423300	-2.85674600	3.36028000
H	3.18134500	0.61981600	0.04387700

- computed data for **TS-1-PhCOPh**

: total free energy = –1327.522067 Hartree

: relative free energy = 8.2 kcal/mol

: a single imaginary frequency at –231.60 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	1.57472300	0.30384500	-0.30861100
N	0.46660300	1.06145000	-0.98551100
O	0.55998000	-0.98214100	0.53305000
C	-0.67731700	-1.03861400	0.70960100
C	-1.36861500	-2.29093400	0.33943100
C	-1.38390300	0.11012000	1.30650400
C	0.07505100	2.30532100	-0.53625700
C	-1.11897200	2.85594600	-0.88135500
C	-2.02441900	2.12573600	-1.71001500
C	-0.36339500	0.38621400	-1.85854600
C	-1.58075900	0.88123700	-2.22454900
H	-2.20934800	0.31100500	-2.89866700
H	0.02170600	-0.55822900	-2.22552200
H	0.77967600	2.78982600	0.12843100
H	-1.39298000	3.83078800	-0.49733700
O	2.30510100	0.99747100	0.65434600
O	2.38151800	-0.54041500	-1.07858300
C	3.73850600	-0.23458800	-0.71845500
C	3.58269200	0.33692100	0.72962700
C	3.48510700	-0.76509400	1.78454700
H	2.75288400	-1.52139500	1.49127100
H	3.16110900	-0.31752900	2.72823000
H	4.45327800	-1.24784000	1.94589400
C	4.63531800	1.35951300	1.12669100
H	4.60688000	2.23054900	0.47020400

H	5.63594300	0.91734500	1.08597000
H	4.45222700	1.69541300	2.15067700
C	4.57345000	-1.50169000	-0.81239400
H	4.12633100	-2.30954000	-0.23119900
H	5.59077100	-1.32250200	-0.44945300
H	4.63443600	-1.82235600	-1.85553900
C	4.24786900	0.81667700	-1.70476800
H	3.66496500	1.73857800	-1.61908400
H	4.12860900	0.42988700	-2.71953400
H	5.30372100	1.04999700	-1.54035200
C	-3.33729100	2.59926200	-1.95594100
N	-4.42334300	2.97941300	-2.12973300
C	-0.72808100	-3.14687000	-0.56985900
C	-1.32564900	-4.34257400	-0.93830100
C	-2.55559500	-4.70731000	-0.38795300
C	-3.18214200	-3.87629000	0.53723800
C	-2.59387200	-2.67041600	0.90261400
H	-3.07009200	-2.03571900	1.64214000
H	0.23772300	-2.84900100	-0.96794800
H	-0.83434000	-4.99624700	-1.65126500
H	-3.02034100	-5.64512900	-0.67473200
H	-4.12767700	-4.17032400	0.98017800
C	-0.66777100	0.91954900	2.20363600
C	-2.69151800	0.45809100	0.94412800
C	-3.27343200	1.60849900	1.46637000
C	-1.26426500	2.04846300	2.74292800
C	-2.56320000	2.39839900	2.36714600
H	-4.26821000	1.90031100	1.14632800
H	-3.02068200	3.29477200	2.77385700
H	0.35905300	0.65726200	2.44058300
H	-0.71518100	2.66871000	3.44362800
H	-3.22649200	-0.13662700	0.21010300

- computed data for **PhCOPh-Bpin-PyCN**

: total free energy = –1327.535659 Hartree

: relative free energy = –0.3 kcal/mol

: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	-1.40465400	-0.10703500	0.27907900
N	-0.23430600	-0.94456600	-0.58154600
O	-0.64918400	0.82334700	1.11256000
C	0.64177600	1.17354500	0.97036800
C	0.91663400	2.45682600	0.36776400
C	1.62705000	0.21185100	1.43258500
C	0.21457600	-2.11710300	-0.12406800
C	1.34272800	-2.71732600	-0.66330800

C	2.00379200	-2.05819800	-1.69970500
C	0.37340600	-0.31872200	-1.59718900
C	1.50622900	-0.84877900	-2.19179000
H	2.00197300	-0.32721300	-3.00060100
H	-0.07412200	0.62288300	-1.90046800
H	-0.35598000	-2.53858700	0.69596500
H	1.71447000	-3.65300600	-0.26620300
O	-2.16321500	-1.08384700	0.98665200
O	-2.25046900	0.54859200	-0.66884600
C	-3.46067000	-0.20818500	-0.74352400
C	-3.54058200	-0.83524000	0.68641300
C	-4.07178800	0.15942200	1.71949400
H	-3.53518200	1.10937700	1.64379300
H	-3.89947000	-0.25108400	2.71738800
H	-5.14332800	0.34206200	1.59561900
C	-4.31184200	-2.14401200	0.76357200
H	-3.84983000	-2.91247300	0.14066700
H	-5.34826300	-2.00339800	0.43980100
H	-4.32310000	-2.50238300	1.79628300
C	-4.60607200	0.73141300	-1.08994900
H	-4.62485000	1.58601100	-0.41201700
H	-5.56767300	0.21073600	-1.03383700
H	-4.47938400	1.10611000	-2.10936900
C	-3.30778700	-1.27342500	-1.83278300
H	-2.54080700	-2.00525200	-1.56163400
H	-3.00589100	-0.78305600	-2.76250700
H	-4.24562100	-1.80766200	-2.01040000
C	3.21206300	-2.61732300	-2.25092000
N	4.18510700	-3.06300200	-2.68835900
C	-0.10401100	3.09734700	-0.37244000
C	0.12952200	4.32209900	-0.97981200
C	1.36764900	4.95400500	-0.85653000
C	2.37089900	4.35031200	-0.09800400
C	2.15316600	3.12379700	0.51174700
H	2.92641000	2.69173100	1.13773900
H	-1.07158500	2.61038900	-0.45720000
H	-0.66374300	4.79364500	-1.55185600
H	1.54359400	5.91342000	-1.33159800
H	3.32636100	4.84893800	0.03243800
C	1.23912600	-0.74613100	2.39623700
C	2.91287400	0.09321300	0.86333300
C	3.76389200	-0.93810900	1.23934800
C	2.10294000	-1.76253100	2.77767100
C	3.36793800	-1.87203900	2.19770700
H	4.73900000	-1.02409900	0.76910100
H	4.03907400	-2.67278400	2.49040900
H	0.24217500	-0.67373100	2.82030100
H	1.78709900	-2.47971100	3.52945500
H	3.21823500	0.78231400	0.08243100

- computed data for **TS-2-PhCOPh**

: total free energy = –1327.528030 Hartree

: relative free energy = 4.5 kcal/mol

: a single imaginary frequency at –103.80 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	-1.49764700	-0.36442300	0.66270900
N	0.26599300	-1.45766100	-0.27136800
O	-0.70537500	0.56237900	1.32406300
C	0.24379700	1.37108100	0.77117000
C	-0.15726400	2.59790800	0.13713200
C	1.61417600	0.97972100	1.08864800
C	1.17285600	-2.10652900	0.45735800
C	2.45430000	-2.38073700	-0.00598800
C	2.78546600	-1.95250400	-1.29150400
C	0.58209500	-1.06252100	-1.50568800
C	1.83189700	-1.29145500	-2.06831400
H	2.06867700	-0.94818500	-3.06818600
H	-0.20097500	-0.52769300	-2.03750400
H	0.86109400	-2.39469800	1.45762500
H	3.18217700	-2.88126300	0.62062600
O	-2.12733000	-1.33114200	1.41553000
O	-2.10710200	-0.15529900	-0.56843400
C	-3.35061700	-0.88069400	-0.53678600
C	-3.09378500	-1.96965100	0.56523100
C	-4.31730600	-2.31832600	1.40106600
H	-4.69203300	-1.44666400	1.93914300
H	-4.04905300	-3.08231900	2.13500700
H	-5.11647400	-2.71702900	0.76789700
C	-2.46994200	-3.24930700	0.00890700
H	-1.61367100	-3.02785500	-0.63030200
H	-3.20008400	-3.82989700	-0.56220500
H	-2.12281700	-3.85741600	0.84845800
C	-4.43279700	0.12128100	-0.13431200
H	-4.23338100	0.52589500	0.86288200
H	-5.42789500	-0.33182700	-0.13560900
H	-4.42511600	0.94882800	-0.84888800
C	-3.63539600	-1.43481100	-1.92355700
H	-2.80151100	-2.03824200	-2.28679500
H	-3.79234800	-0.60857700	-2.62165300
H	-4.53902500	-2.05249800	-1.91415900
C	4.11898800	-2.15706300	-1.79793600
N	5.19288900	-2.31018300	-2.19917900
C	-1.52001600	2.84525600	-0.15044400
C	-1.91813800	4.02920200	-0.74929800
C	-0.98547900	5.01487700	-1.07248800
C	0.35804400	4.80512800	-0.76142800
C	0.76962800	3.62671900	-0.15992400

H	1.80986500	3.51221500	0.12019200
H	-2.25518000	2.09057800	0.09327700
H	-2.97064900	4.18772600	-0.96392900
H	-1.30247600	5.93948100	-1.54307000
H	1.09119600	5.57701800	-0.97367700
C	1.87524900	0.31521900	2.30352100
C	2.68396900	1.17244500	0.19564300
C	3.96411700	0.73174300	0.51289800
C	3.15807500	-0.10888000	2.62073800
C	4.21060500	0.09388500	1.72729100
H	4.77083700	0.87095000	-0.20054800
H	5.21195400	-0.24472100	1.97239000
H	1.05083000	0.14617800	2.98834900
H	3.33986000	-0.60226600	3.57075500
H	2.49559300	1.62987700	-0.77069900

- computed data for **PhCOPh-Bpin** + **PyCN**

: total free energy = –1327.531922 Hartree

: relative free energy = 2.1 kcal/mol

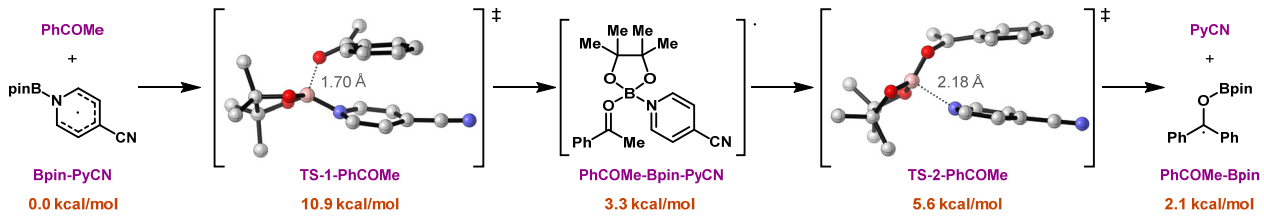
: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	-1.78140200	-0.17949700	0.79059700
N	0.45615400	-1.73925200	-0.27949600
O	-0.87621100	0.61722300	1.43241800
C	0.16401500	1.31316200	0.88084900
C	-0.11496700	2.54948400	0.19216100
C	1.47480800	0.82648700	1.27938600
C	1.47655100	-2.35731300	0.31755600
C	2.75660500	-2.42363900	-0.22090300
C	2.97481400	-1.81063100	-1.45481000
C	0.67898100	-1.15474200	-1.45951200
C	1.91686600	-1.16527700	-2.09484200
H	2.05987100	-0.67362500	-3.04982300
H	-0.17307000	-0.64178200	-1.89682500
H	1.26582300	-2.81096000	1.28209800
H	3.56321200	-2.91523700	0.30926000
O	-2.64157100	-0.96102500	1.51372300
O	-2.02956100	-0.18786500	-0.56189700
C	-3.27357800	-0.89555900	-0.74803700
C	-3.38478500	-1.75045500	0.56393900
C	-4.80392900	-1.93011500	1.08042600
H	-5.27015000	-0.97177400	1.31309100
H	-4.78322500	-2.53020000	1.99318000
H	-5.41738400	-2.45353900	0.34017500
C	-2.68412300	-3.10288500	0.45691900
H	-1.65970100	-2.97495500	0.09819300

H	-3.22306000	-3.78015100	-0.21162600
H	-2.64887000	-3.55251700	1.45232800
C	-4.36596000	0.16613400	-0.86029000
H	-4.43761200	0.74821200	0.06387300
H	-5.34260300	-0.27925700	-1.06768400
H	-4.11064000	0.84681700	-1.67670500
C	-3.18271000	-1.70888300	-2.02855100
H	-2.30631500	-2.35969600	-2.01628400
H	-3.10306700	-1.03463000	-2.88549100
H	-4.07860700	-2.32386400	-2.15900000
C	4.29199100	-1.80848800	-2.03886100
N	5.35328900	-1.79605500	-2.49890700
C	-1.42124700	2.85145200	-0.25587800
C	-1.69704800	4.04476500	-0.90402300
C	-0.69313900	4.98831200	-1.11863700
C	0.59348800	4.72631000	-0.64960300
C	0.88088600	3.53670800	0.00104300
H	1.87326600	3.38463000	0.40734900
H	-2.21723000	2.13424800	-0.10807500
H	-2.70897400	4.24221800	-1.24415700
H	-0.91386300	5.92057700	-1.62742900
H	1.37823700	5.46581900	-0.77404700
C	1.60430000	0.08345100	2.47100100
C	2.62771000	1.02208100	0.49380600
C	3.86155400	0.53396900	0.90614000
C	2.84143600	-0.39437400	2.87919300
C	3.97952600	-0.16812900	2.10468500
H	4.73320500	0.68515900	0.27608000
H	4.94605500	-0.54223500	2.42624200
H	0.71909800	-0.09490900	3.07118400
H	2.92024500	-0.94523800	3.81153800
H	2.54275100	1.52389900	-0.46452000

3.2. Acetophenone Ketyl Radical Formation



- computed data for **PhCOMe** + **Bpin-PyCN**

: total free energy = –1135.917877 Hartree

: relative free energy = 0.00 kcal/mol

: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	1.39722900	-0.67889200	-0.38357700
N	0.02591200	-1.12166900	-0.50732900
O	0.46291700	0.87922600	1.91015000
C	-0.75326800	0.86226500	1.98643500
C	-1.43959900	0.29868100	3.20987900
C	-1.59405400	1.40055500	0.87311400
C	-0.76881500	-0.71362100	-1.57734700
C	-2.08768900	-1.01589200	-1.64298300
C	-2.71164000	-1.76149800	-0.59590000
C	-0.55764800	-1.89187200	0.49602100
C	-1.87773500	-2.20849800	0.47186500
H	-2.29553000	-2.80307800	1.27645500
H	0.11469600	-2.19478500	1.28917500
H	-0.25716800	-0.12588900	-2.32863300
H	-2.67365500	-0.66138500	-2.48216900
O	1.97294100	0.17661600	-1.28158900
O	2.22726200	-1.13203300	0.59787900
C	3.55201300	-0.66571500	0.25453700
C	3.25938100	0.53485500	-0.71605400
C	3.06799800	1.86060300	0.01561900
H	2.33489700	1.75713300	0.81986800
H	2.70128100	2.60131600	-0.70058200
H	4.01188900	2.22347400	0.43152800
C	4.26065500	0.69111900	-1.84889000
H	4.29744700	-0.19909200	-2.47820500
H	5.26085200	0.88339500	-1.44824800
H	3.97352700	1.54112500	-2.47246700
C	4.27005500	-0.27823100	1.53643700
H	3.66827800	0.41928100	2.12070700
H	5.23919700	0.17854600	1.31252000
H	4.44369900	-1.17220600	2.14026700
C	4.26103300	-1.82883900	-0.43467900
H	3.74322400	-2.11240800	-1.35553600
H	4.25766500	-2.68936800	0.23810600
H	5.29715200	-1.57869700	-0.67769800
C	-4.11006200	-1.96686900	-0.57648300
N	-5.26538100	-2.11020500	-0.55130700
C	-0.96225600	2.12493100	-0.14422100
C	-2.97113000	1.17757400	0.80939400
C	-3.70964400	1.66196600	-0.26711000
C	-1.70214300	2.62697200	-1.20584100
C	-3.07611400	2.39093500	-1.26985200
H	-4.77356000	1.45731900	-0.32509400
H	-3.65338300	2.77365000	-2.10582400
H	0.11243200	2.27028100	-0.08840900
H	-1.21050600	3.19381100	-1.98998100
H	-3.47252300	0.60066700	1.58058400

H	-0.68013300	0.01700100	3.93794400
H	-2.02672700	-0.58234700	2.93464600
H	-2.12389600	1.03284700	3.64419800

- computed data for **TS-1-PhCOMe**

: total free energy = –1135.900509 Hartree

: relative free energy = 10.9 kcal/mol

: a single imaginary frequency at –279.01 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	1.25535500	-0.28260300	0.20850100
N	0.01515300	-1.09770400	-0.18605000
O	0.61183600	0.63779900	1.48529800
C	-0.59184200	0.89123500	1.76331000
C	-1.02158000	0.76536000	3.19624700
C	-1.51139300	1.39435900	0.74324500
C	-0.66017800	-0.83882600	-1.35350200
C	-1.97174200	-1.16318700	-1.52764700
C	-2.69543300	-1.76278600	-0.45397200
C	-0.65042300	-1.76962900	0.81594100
C	-1.97300100	-2.10472800	0.71025800
H	-2.46372300	-2.61912400	1.52899000
H	-0.05115600	-2.01103400	1.68696900
H	-0.07781500	-0.32001700	-2.10565300
H	-2.46778200	-0.92766900	-2.46083200
O	1.75410600	0.52767400	-0.82957900
O	2.29948700	-0.97587400	0.85045700
C	3.46809500	-0.78514200	0.04482000
C	3.17702500	0.59071300	-0.63546000
C	3.47533300	1.76907900	0.29206000
H	3.02120200	1.61053500	1.27410200
H	3.04880600	2.67628900	-0.14500600
H	4.55148900	1.91898800	0.41787400
C	3.84614800	0.79126100	-1.98560900
H	3.51329600	0.04083800	-2.70462500
H	4.93488700	0.73027300	-1.88874600
H	3.59360100	1.77949100	-2.37916300
C	4.69572500	-0.80095900	0.94227500
H	4.58608500	-0.09489900	1.76679400
H	5.59615400	-0.54791900	0.37288400
H	4.82761800	-1.80073200	1.36392500
C	3.53350900	-1.92751600	-0.97023800
H	2.67030900	-1.89574500	-1.64200600
H	3.51001600	-2.87612400	-0.42860400
H	4.44819500	-1.88834800	-1.56894300
C	-4.09784000	-1.97069500	-0.53503800
N	-5.25016500	-2.11436700	-0.59372300

C	-0.97674500	2.07274700	-0.36822200
C	-2.89647100	1.19047700	0.83316000
C	-3.72893500	1.61138600	-0.19705200
C	-1.81780300	2.51943700	-1.37365900
C	-3.19095700	2.27176800	-1.29961500
H	-4.79280600	1.40559900	-0.14713500
H	-3.84441500	2.60018100	-2.10155000
H	0.09777800	2.21344000	-0.43229900
H	-1.40625400	3.04827900	-2.22697600
H	-3.31973700	0.65790600	1.67902700
H	-0.20044900	0.35132600	3.78005800
H	-1.89724200	0.11692700	3.28603700
H	-1.30212000	1.74615600	3.59357900

- computed data for **PhCOMe-Bpin-PyCN**

: total free energy = –1135.912639 Hartree

: relative free energy = 3.3 kcal/mol

: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	1.28647000	0.19690600	-0.39105000
N	-0.00840900	-0.82709500	0.02557800
O	0.59487000	1.27846400	-1.06452700
C	-0.18916400	2.09623400	-0.32375500
C	0.49783000	3.10803200	0.53647500
C	-1.60131200	1.91605600	-0.38729500
C	-0.44282700	-1.71514100	-0.87439500
C	-1.64900800	-2.37464900	-0.71258600
C	-2.42356700	-2.06466300	0.40889700
C	-0.71505900	-0.56453700	1.12887800
C	-1.94899400	-1.15598200	1.35427200
H	-2.53414600	-0.90044100	2.22841400
H	-0.26539000	0.14803600	1.81211000
H	0.21111500	-1.85620600	-1.72911700
H	-1.99473600	-3.08889200	-1.44916400
O	2.15991700	-0.51975500	-1.24592400
O	1.94172100	0.47749200	0.84996600
C	3.33244900	0.22106200	0.62868200
C	3.29098700	-0.90239600	-0.45815700
C	4.51610400	-0.96052300	-1.35820300
H	4.62482000	-0.03478500	-1.92502900
H	4.41198400	-1.78480100	-2.06895200
H	5.42406300	-1.12836800	-0.76957800
C	3.01900000	-2.27977900	0.15226000
H	2.18318000	-2.23602300	0.85717000
H	3.89501100	-2.66995800	0.67836700
H	2.76153500	-2.97550200	-0.65160300

C	3.97056500	1.50658000	0.09906100
H	3.52162000	1.78763200	-0.85835900
H	5.05165500	1.40182600	-0.03133600
H	3.78317600	2.30932500	0.81755800
C	3.97888400	-0.18901800	1.94297800
H	3.43624100	-1.01344400	2.40910600
H	3.97291200	0.65786000	2.63438600
H	5.01869300	-0.49368200	1.78559300
C	-3.71643100	-2.67668200	0.58214800
N	-4.75348000	-3.16948300	0.71778100
C	-2.17338300	1.04258300	-1.34930700
C	-2.47886100	2.52305500	0.54864600
C	-3.83296100	2.22988600	0.54609800
C	-3.52887400	0.76325600	-1.34077700
C	-4.37289400	1.34048600	-0.38679600
H	-4.47933400	2.69436600	1.28489400
H	-5.43275700	1.11092300	-0.37886500
H	-1.52046700	0.60618200	-2.09764400
H	-3.94069600	0.08898300	-2.08700200
H	-2.07924700	3.19604100	1.30069300
H	-0.11964000	3.99671400	0.68718300
H	1.42916000	3.40459200	0.04733300
H	0.77516100	2.69836900	1.51671300

- computed data for **TS-2-PhCOMe**

: total free energy = –1135.908922 Hartree

: relative free energy = 5.6 kcal/mol

: a single imaginary frequency at –133.23 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	1.51725300	-0.39918800	0.50765000
N	-0.00998300	1.01082300	-0.13349500
O	0.57628400	-1.23928500	1.09708800
C	-0.20684900	-2.04675200	0.32733300
C	0.46339900	-3.06095600	-0.54143100
C	-1.61410800	-1.85203400	0.40694000
C	-0.53030600	1.84761900	0.76538700
C	-1.81093100	2.36916700	0.64664700
C	-2.58037500	1.96656100	-0.44813000
C	-0.73249200	0.65962000	-1.19614700
C	-2.03513200	1.10234900	-1.39671200
H	-2.61809900	0.76486900	-2.24477900
H	-0.24780800	-0.02415600	-1.88896000
H	0.10863300	2.07911500	1.61411900
H	-2.21543400	3.04131600	1.39372900
O	2.31815200	0.38130000	1.31951200
O	2.08351900	-0.64288800	-0.74162900

C	3.44718700	-0.19124200	-0.65518900
C	3.38720700	0.87482800	0.49381200
C	4.64953800	0.96065400	1.33929700
H	4.85526500	0.01347200	1.83960800
H	4.52298600	1.73006400	2.10513600
H	5.51110300	1.23149500	0.72045700
C	3.00508000	2.26641600	-0.01039500
H	2.12591100	2.22438500	-0.65639100
H	3.82912200	2.72820200	-0.56173700
H	2.77172400	2.89678400	0.85223100
C	4.29240400	-1.40862200	-0.27995600
H	3.99297100	-1.79831300	0.69770500
H	5.35930300	-1.17060900	-0.25151400
H	4.12814300	-2.19035000	-1.02598900
C	3.87712200	0.35493000	-2.00715100
H	3.18816200	1.12447900	-2.35904100
H	3.89099700	-0.45518800	-2.74080100
H	4.88386900	0.78079700	-1.94887400
C	-3.94314300	2.41688100	-0.57786400
N	-5.03777100	2.77684500	-0.67616700
C	-2.17285300	-0.98114400	1.37588500
C	-2.49741000	-2.45903300	-0.52153200
C	-3.85278900	-2.17198200	-0.50184800
C	-3.53067000	-0.71148800	1.38708700
C	-4.38346100	-1.28994300	0.44284100
H	-4.50625000	-2.63447200	-1.23543700
H	-5.44357300	-1.06131200	0.44749900
H	-1.51149100	-0.52978000	2.10714500
H	-3.93534800	-0.03559300	2.13550300
H	-2.10284400	-3.12737600	-1.28049500
H	-0.13789700	-3.97113800	-0.61296000
H	1.43568100	-3.31458600	-0.11315200
H	0.65074600	-2.68784100	-1.55664100

- computed data for **PhCOMe-Bpin** + **PyCN**

: total free energy = –1135.914516 Hartree

: relative free energy = 2.1 kcal/mol

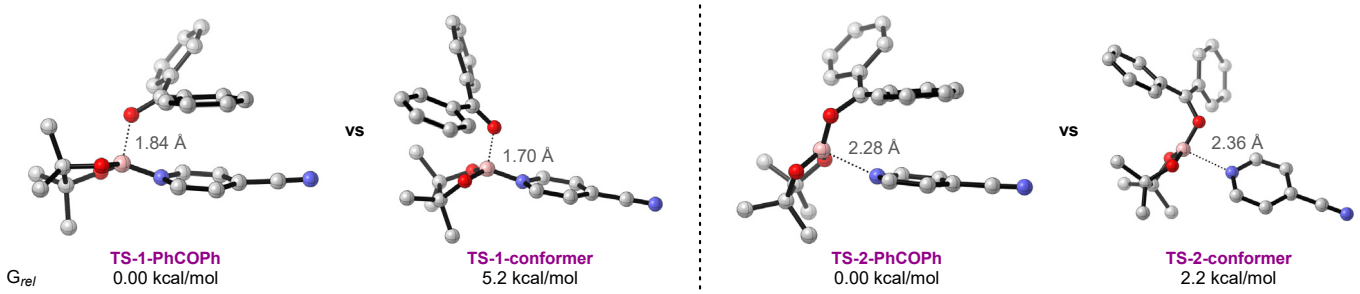
: no imaginary frequency

: Cartesian coordinates

Atom	X	Y	Z
B	1.79839000	0.68014900	-0.55875900
N	-0.12151900	-1.53822100	0.01990700
O	0.68943200	1.35119300	-0.99524000
C	-0.18888800	1.94814000	-0.13549000
C	0.36222700	2.80338700	0.95769400
C	-1.56988400	1.72792900	-0.38141400
C	-0.92697000	-2.22411600	-0.79604400

C	-2.29375900	-2.35913100	-0.59164900
C	-2.85202000	-1.73022100	0.52360600
C	-0.66471300	-0.96058000	1.09191900
C	-2.02386700	-1.02105900	1.39067900
H	-2.43042800	-0.51287100	2.25663500
H	0.02344500	-0.40683900	1.72623500
H	-0.45373300	-2.68405700	-1.65995000
H	-2.91333100	-2.91640800	-1.28419400
O	2.75000100	0.23034500	-1.42995100
O	2.09907400	0.45869400	0.76457700
C	3.45748900	-0.02914900	0.79827400
C	3.66445600	-0.57706600	-0.65913300
C	5.06842100	-0.38403200	-1.21048800
H	5.34281800	0.67112200	-1.24833700
H	5.11668000	-0.78622500	-2.22514800
H	5.79815700	-0.91918000	-0.59458200
C	3.22521900	-2.03057500	-0.81877000
H	2.21123700	-2.16771700	-0.43423900
H	3.90776300	-2.71180400	-0.30279000
H	3.22978400	-2.27604000	-1.88382200
C	4.34362600	1.17397600	1.11358500
H	4.26428700	1.93095800	0.32747500
H	5.39322200	0.88613200	1.21651800
H	4.00900700	1.61951400	2.05367800
C	3.56653900	-1.07994800	1.89046400
H	2.81242200	-1.85762800	1.75704000
H	3.41280700	-0.61156400	2.86611600
H	4.55919500	-1.54085200	1.88444700
C	-4.27151100	-1.79964600	0.76347300
N	-5.41080800	-1.86091300	0.95411300
C	-1.99631100	0.98009000	-1.50722200
C	-2.56199000	2.19449000	0.51803200
C	-3.90051200	1.90768800	0.30711300
C	-3.34049700	0.71777700	-1.71192500
C	-4.30504500	1.16726000	-0.80672400
H	-4.64118100	2.25880700	1.01893800
H	-5.35361900	0.93660500	-0.95908600
H	-1.24870700	0.61712100	-2.20346100
H	-3.64448300	0.14262900	-2.58192700
H	-2.26947200	2.75650400	1.39939700
H	-0.28613600	3.66352900	1.14236600
H	1.35029600	3.17374200	0.67291200
H	0.48420500	2.25457900	1.90045100

3.3. Comparison between Transition State Conformers



- computed data for **TS-1-conformer**

: total free energy = –1327.513830 Hartree

: relative free energy = 5.2 kcal/mol

: a single imaginary frequency at –654.30 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	-0.79736700	-0.37108500	0.52344500
N	-2.22746800	-0.00009100	0.19345200
O	0.01463700	0.80115300	-0.40913800
C	1.24325500	0.78584200	-0.69950100
C	2.07303600	1.88293700	-0.18458000
C	1.79175000	-0.28998600	-1.53556400
C	-2.82701900	-0.53323300	-0.92527800
C	-4.01377800	-0.06168500	-1.40261300
C	-4.66293700	1.02097300	-0.74936200
C	-2.83987600	1.05376500	0.83181100
C	-4.02702200	1.56580600	0.40196900
H	-4.48448100	2.38710400	0.94004100
H	-2.31526100	1.42840700	1.70214100
H	-2.30004200	-1.36928700	-1.36940600
H	-4.46277600	-0.52014100	-2.27550800
O	-0.36228400	-1.64307600	0.10223000
O	-0.42757000	-0.14321400	1.86959400
C	0.35037000	-1.26791100	2.30344400
C	-0.06972500	-2.38889400	1.28936700
C	1.02307600	-3.39646500	0.96427900
H	1.87650500	-2.90636000	0.48949600
H	0.63264700	-4.14357100	0.26833000
H	1.36153500	-3.91280800	1.86846300
C	-1.35269200	-3.10562700	1.71353900
H	-2.13844100	-2.38275400	1.95273500
H	-1.19142000	-3.75149000	2.58123900
H	-1.69882900	-3.72151900	0.87961100
C	1.83255500	-0.90729200	2.20143200
H	2.13593500	-0.75869500	1.16191800
H	2.46347000	-1.69196300	2.62943700

H	2.01077700	0.02174600	2.74957700
C	-0.00072300	-1.56799000	3.75444000
H	-1.07838300	-1.67618900	3.88411000
H	0.33912700	-0.74601800	4.39006500
H	0.49197800	-2.48633100	4.09025200
C	-5.89517600	1.53536600	-1.22471300
N	-6.90686400	1.95667600	-1.61517400
C	1.67780000	2.48727600	1.02020600
C	2.41910800	3.53802700	1.54109600
C	3.53754900	4.01278200	0.85500600
C	3.91931200	3.43258300	-0.35371700
C	3.19605100	2.36638300	-0.87256900
H	3.47668500	1.92802500	-1.82473700
H	0.80689900	2.09114400	1.53510500
H	2.12506600	3.99357300	2.48071700
H	4.10927900	4.84138100	1.26037200
H	4.77743600	3.81687500	-0.89462100
C	3.13453200	-0.69046900	-1.44555700
C	0.92684100	-0.96257900	-2.41175000
C	1.40142400	-1.99859400	-3.20062400
C	3.59883900	-1.74517800	-2.22169200
C	2.73615900	-2.39376500	-3.10381800
H	0.73244500	-2.50732600	-3.88623900
H	3.10318100	-3.21302300	-3.71366800
H	3.79803800	-0.19932300	-0.74067800
H	4.63193300	-2.06448600	-2.13612500
H	-0.11066200	-0.64897900	-2.46078700

- computed data for **TS-2-conformer**

: total free energy = –1327.524611 Hartree

: relative free energy = 2.2 kcal/mol

: a single imaginary frequency at –59.71 cm^{-1}

: Cartesian coordinates

Atom	X	Y	Z
B	-0.04315500	-0.70757400	0.11340900
N	-2.29722700	-0.04104300	-0.13919600
O	0.25981800	0.44184100	-0.60959500
C	1.50304400	0.99767800	-0.47833200
C	1.56691500	2.25321700	0.23855600
C	2.60173300	0.29606800	-1.09097000
C	-3.19400000	-0.94188800	-0.53928600
C	-4.48256300	-0.60378300	-0.93548300
C	-4.83685000	0.74627000	-0.91608400
C	-2.63281100	1.24926100	-0.14690600
C	-3.89495400	1.69727200	-0.52002400
H	-4.13924100	2.75259700	-0.51084500
H	-1.85038200	1.94651700	0.14103800

H	-2.84579100	-1.97199900	-0.55593300
H	-5.18888700	-1.36042800	-1.25500400
O	-0.29802200	-1.94867100	-0.44230000
O	0.25011800	-0.77518300	1.45794000
C	0.00284100	-2.12670700	1.88293400
C	0.12162500	-2.92181300	0.53683000
C	1.56517800	-3.29635600	0.20293700
H	2.22552500	-2.42747800	0.28538700
H	1.60623300	-3.64701400	-0.83141600
H	1.93610100	-4.08858700	0.85928300
C	-0.77662400	-4.14413500	0.44008800
H	-1.82936400	-3.88016400	0.56110500
H	-0.51278700	-4.87577600	1.21028300
H	-0.64820300	-4.61495800	-0.53771400
C	1.03650300	-2.50537300	2.93277100
H	2.04960400	-2.31959200	2.57419900
H	0.94186000	-3.56232500	3.20169300
H	0.87715400	-1.90710500	3.83324800
C	-1.39846600	-2.17358400	2.48819300
H	-2.15848600	-1.92046000	1.74549900
H	-1.45466200	-1.43686900	3.29315700
H	-1.62141400	-3.16104500	2.90196100
C	-6.16117500	1.15493000	-1.31184600
N	-7.22476700	1.48133400	-1.62734700
C	0.63532500	2.51610400	1.26403900
C	0.65487200	3.72431100	1.94569600
C	1.59490400	4.70328000	1.62324400
C	2.51857600	4.45853400	0.60787900
C	2.50799700	3.25259000	-0.07914600
H	3.20420400	3.08808500	-0.89506900
H	-0.06403200	1.73455100	1.54510300
H	-0.05962200	3.90133900	2.74380200
H	1.60665300	5.64778900	2.15692700
H	3.24333000	5.22050100	0.33874500
C	3.94567600	0.52451900	-0.71675400
C	2.34285000	-0.70578400	-2.05457100
C	3.38261300	-1.42044000	-2.62978500
C	4.97507400	-0.19868500	-1.29888000
C	4.70495800	-1.17163800	-2.26237200
H	3.16020000	-2.17931300	-3.37379400
H	5.51510700	-1.73427300	-2.71404300
H	4.16764600	1.24637900	0.06169100
H	5.99848400	-0.01339200	-0.98789300
H	1.31573000	-0.90813800	-2.33738800

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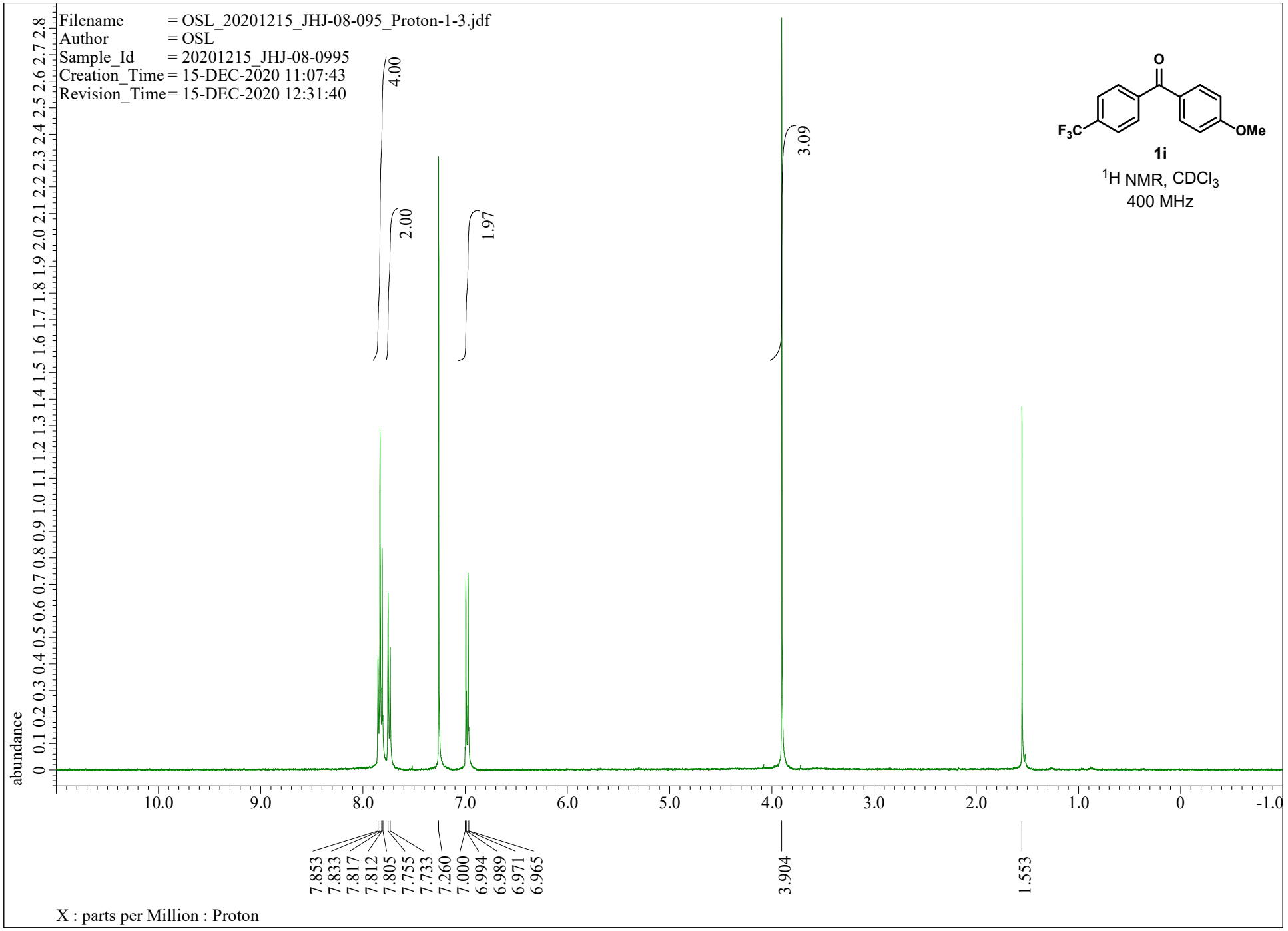
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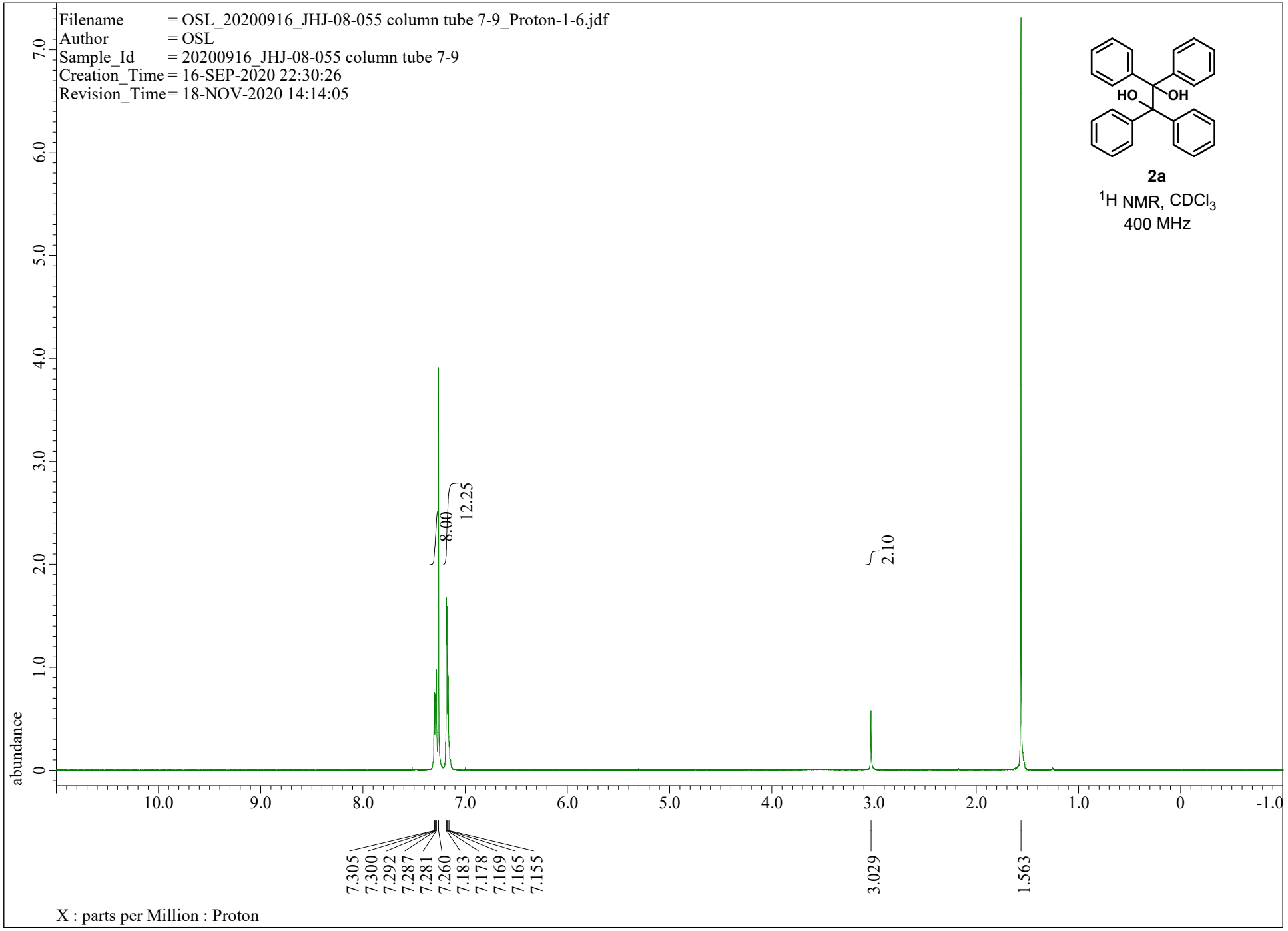
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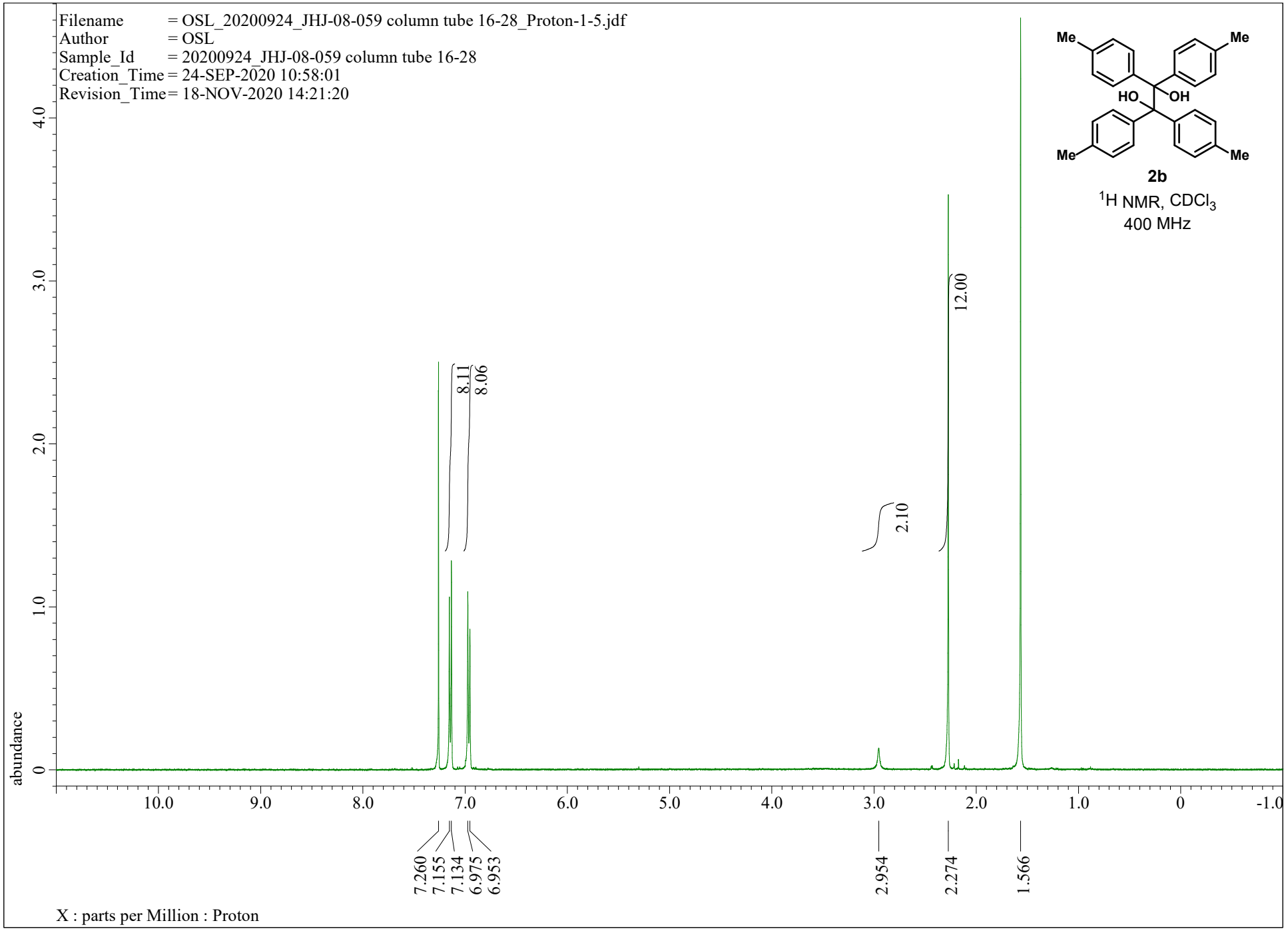
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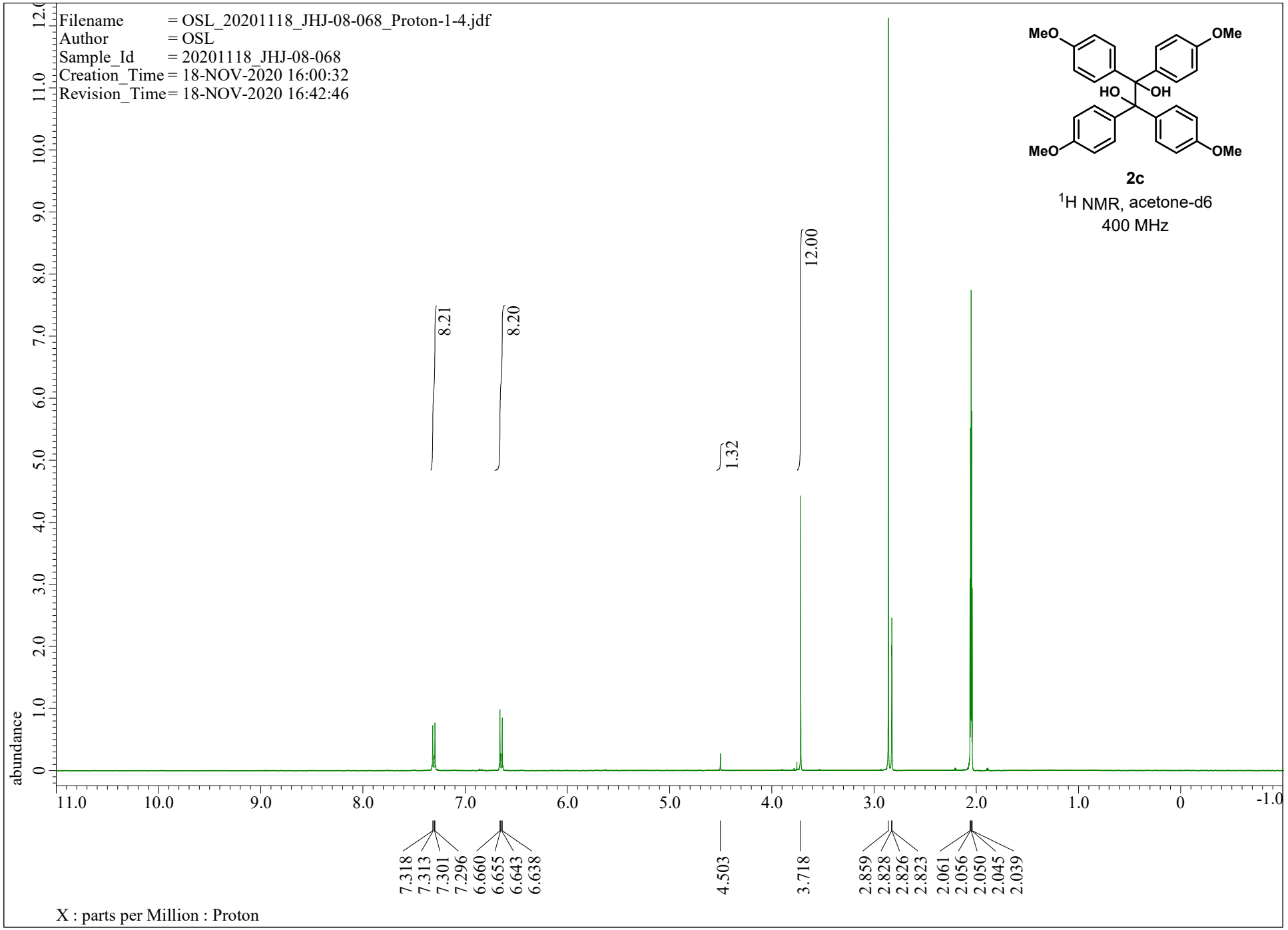
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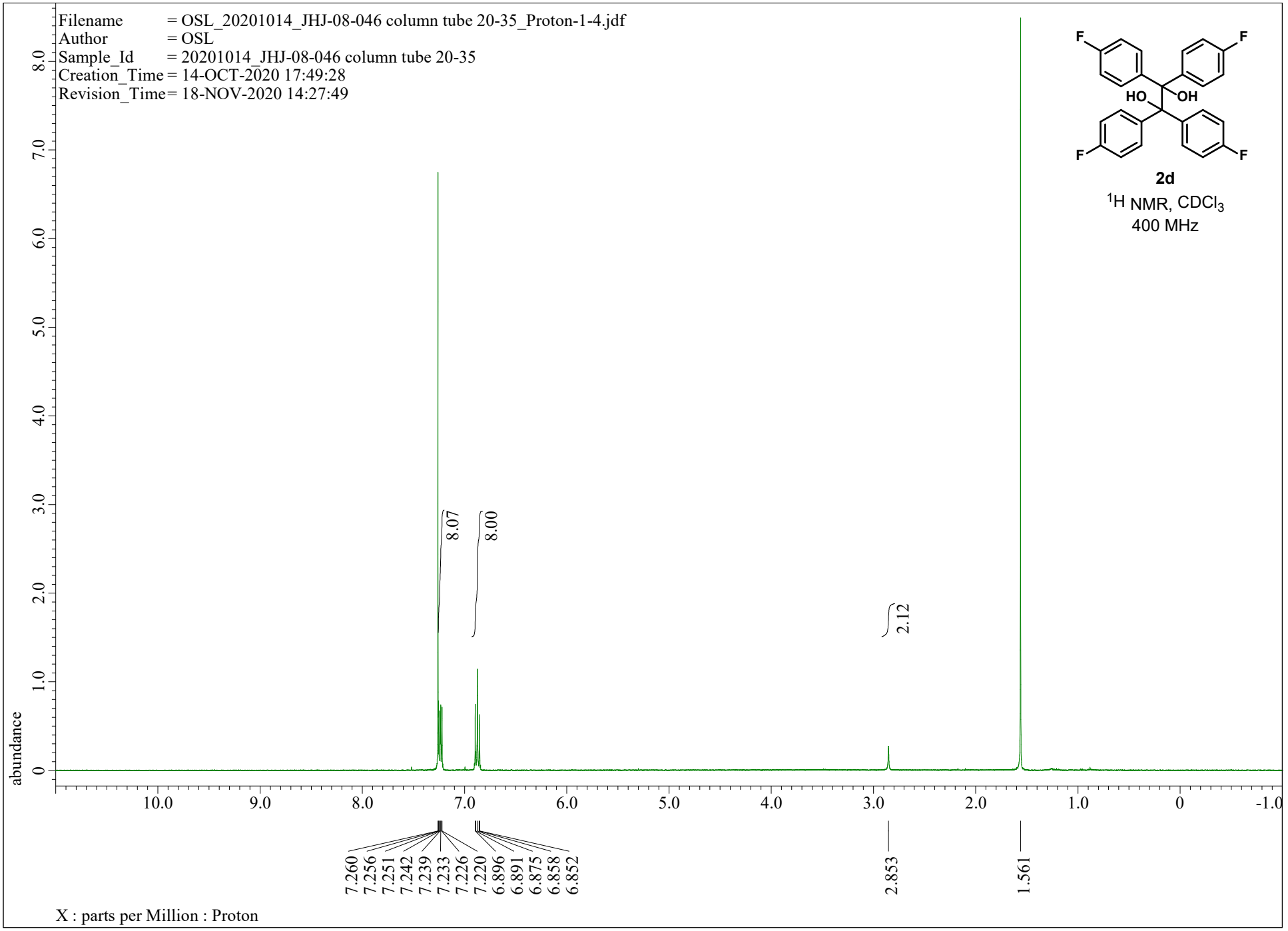
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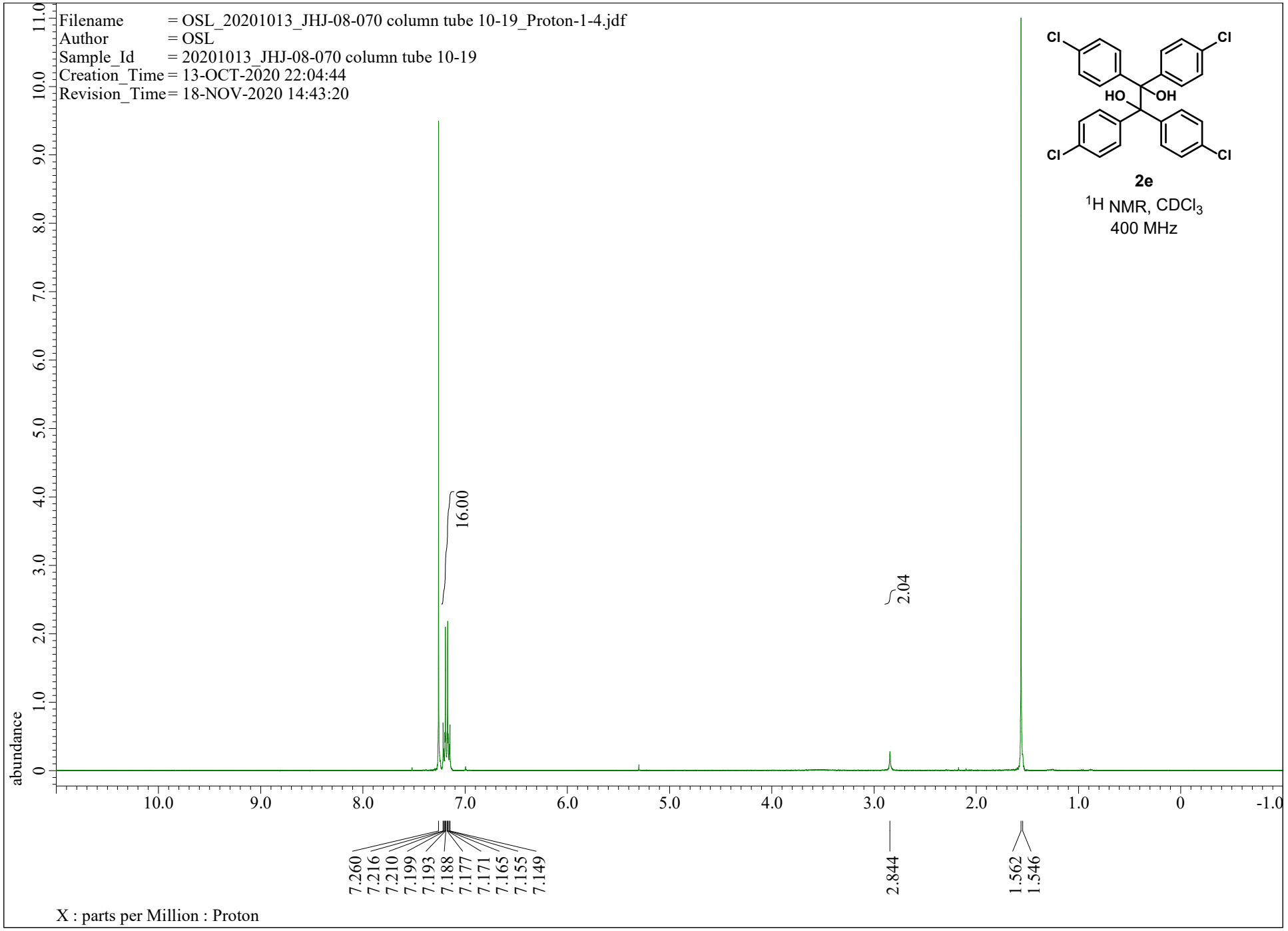
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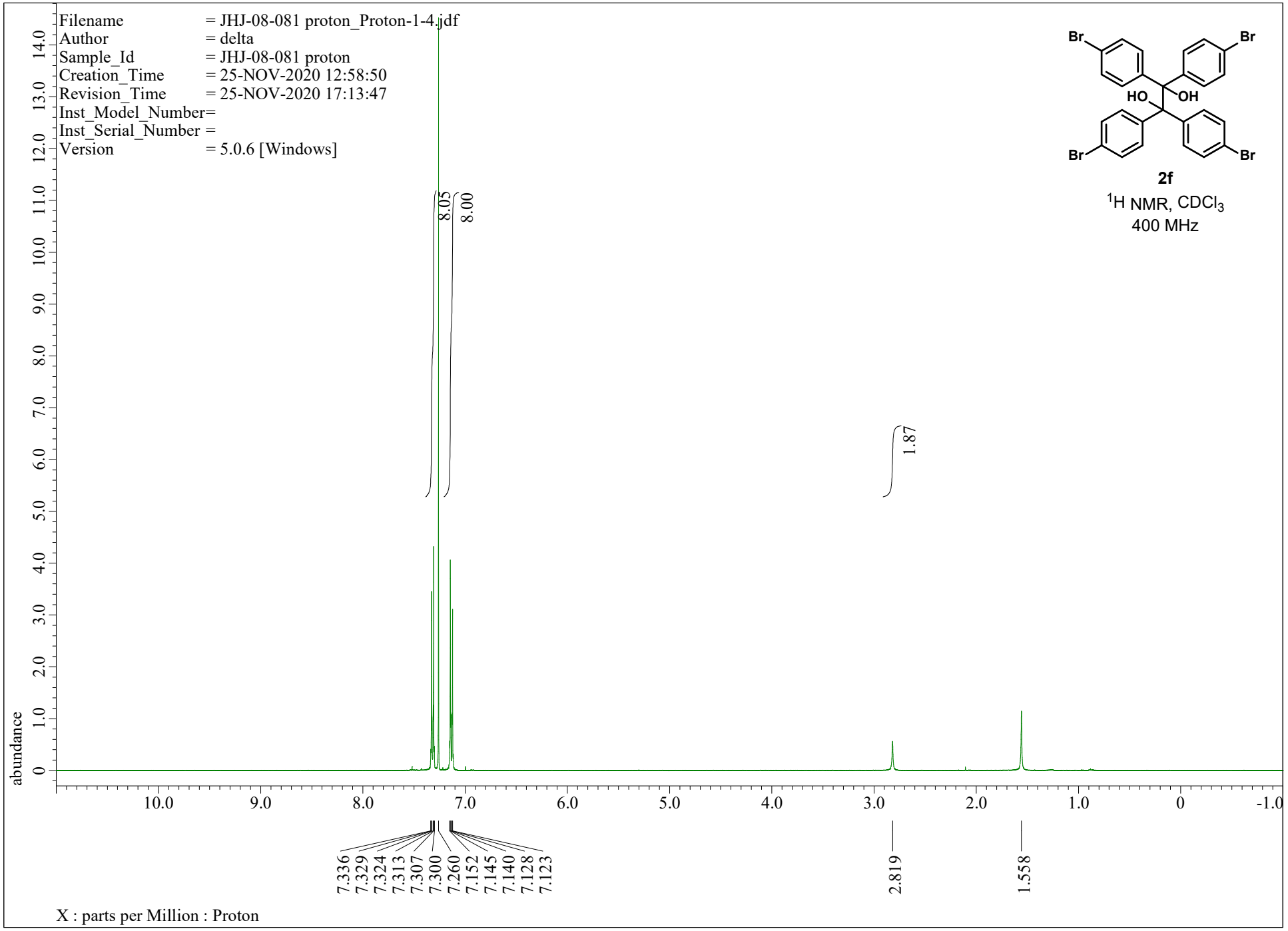
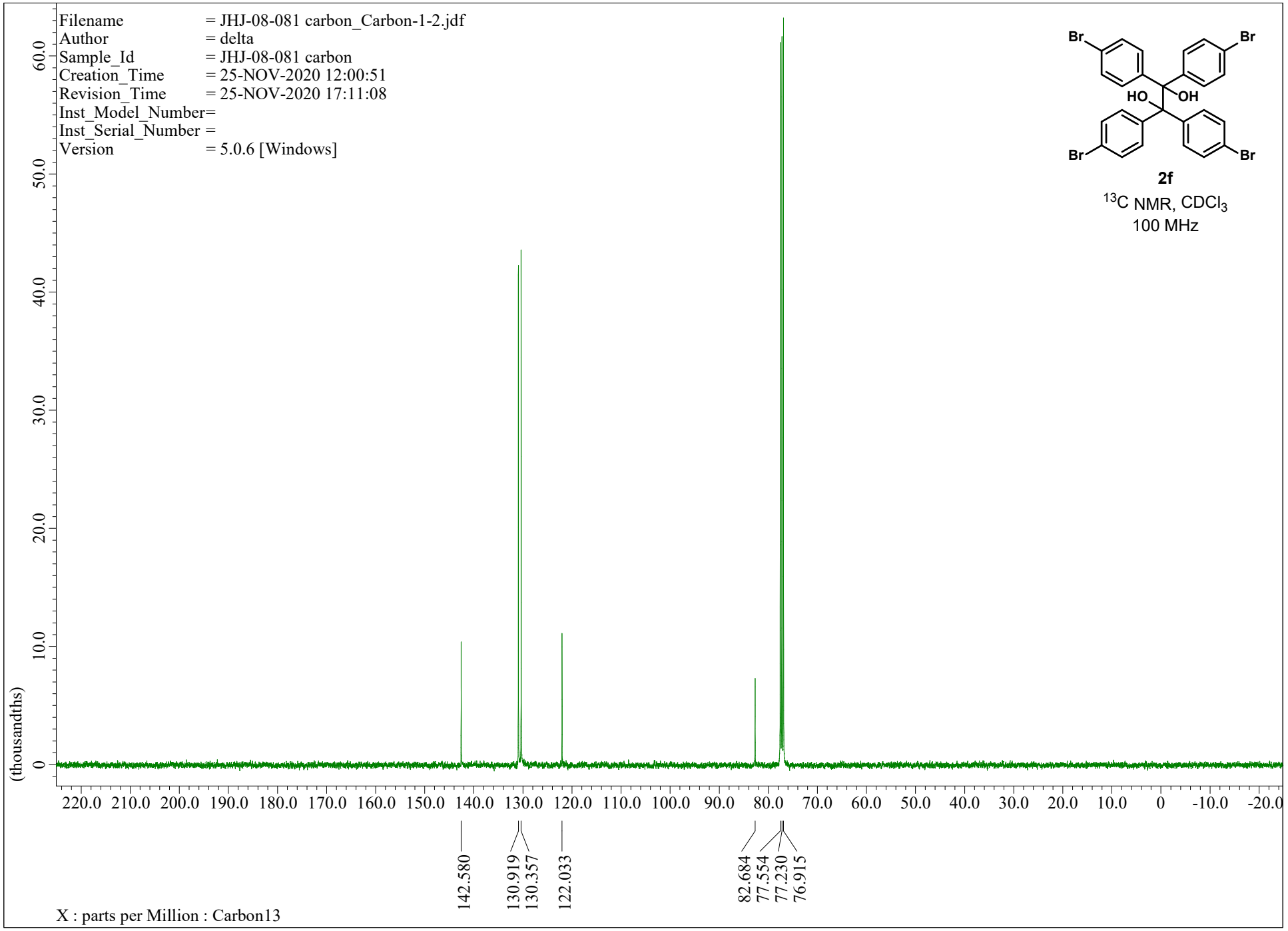
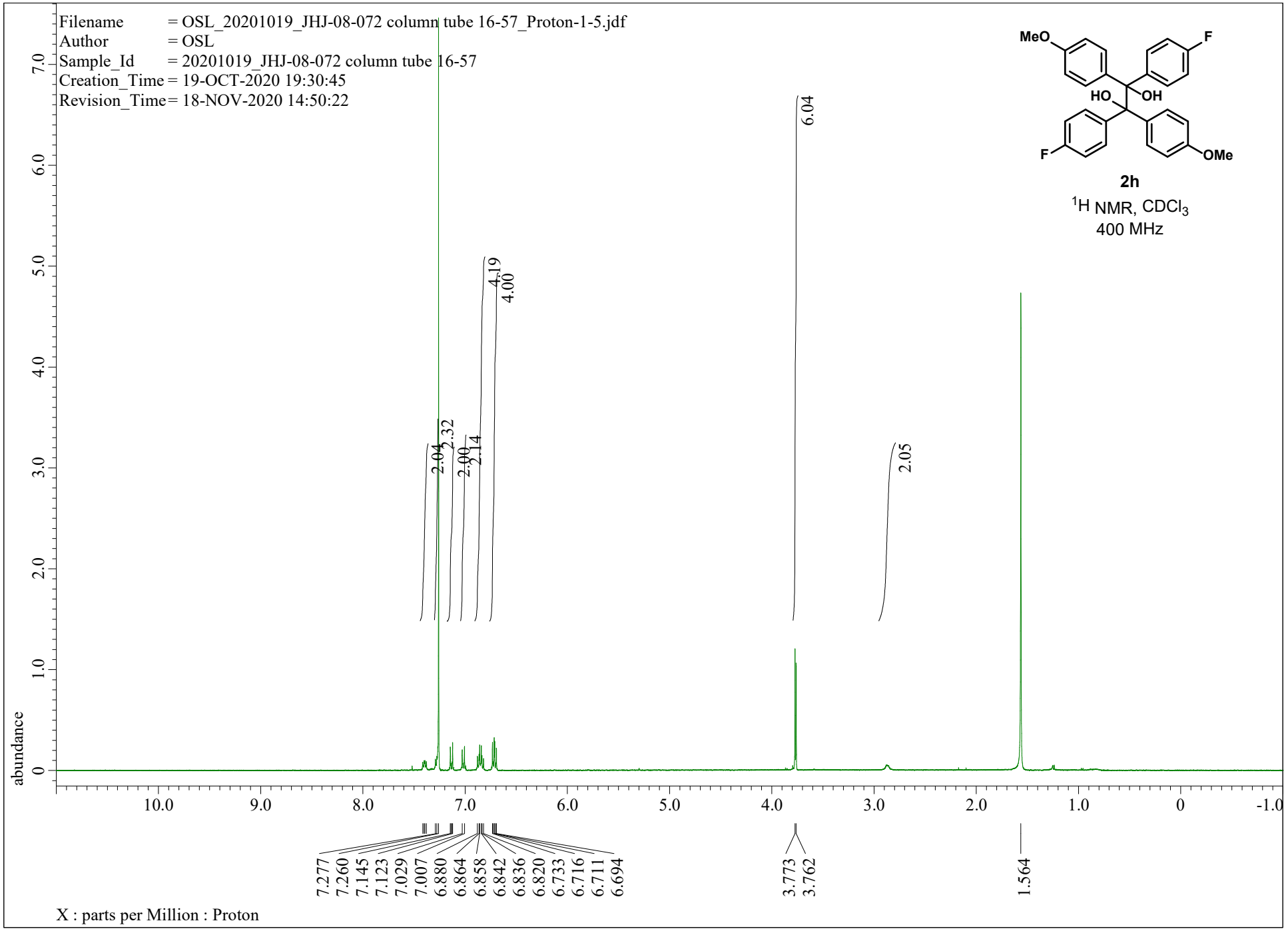
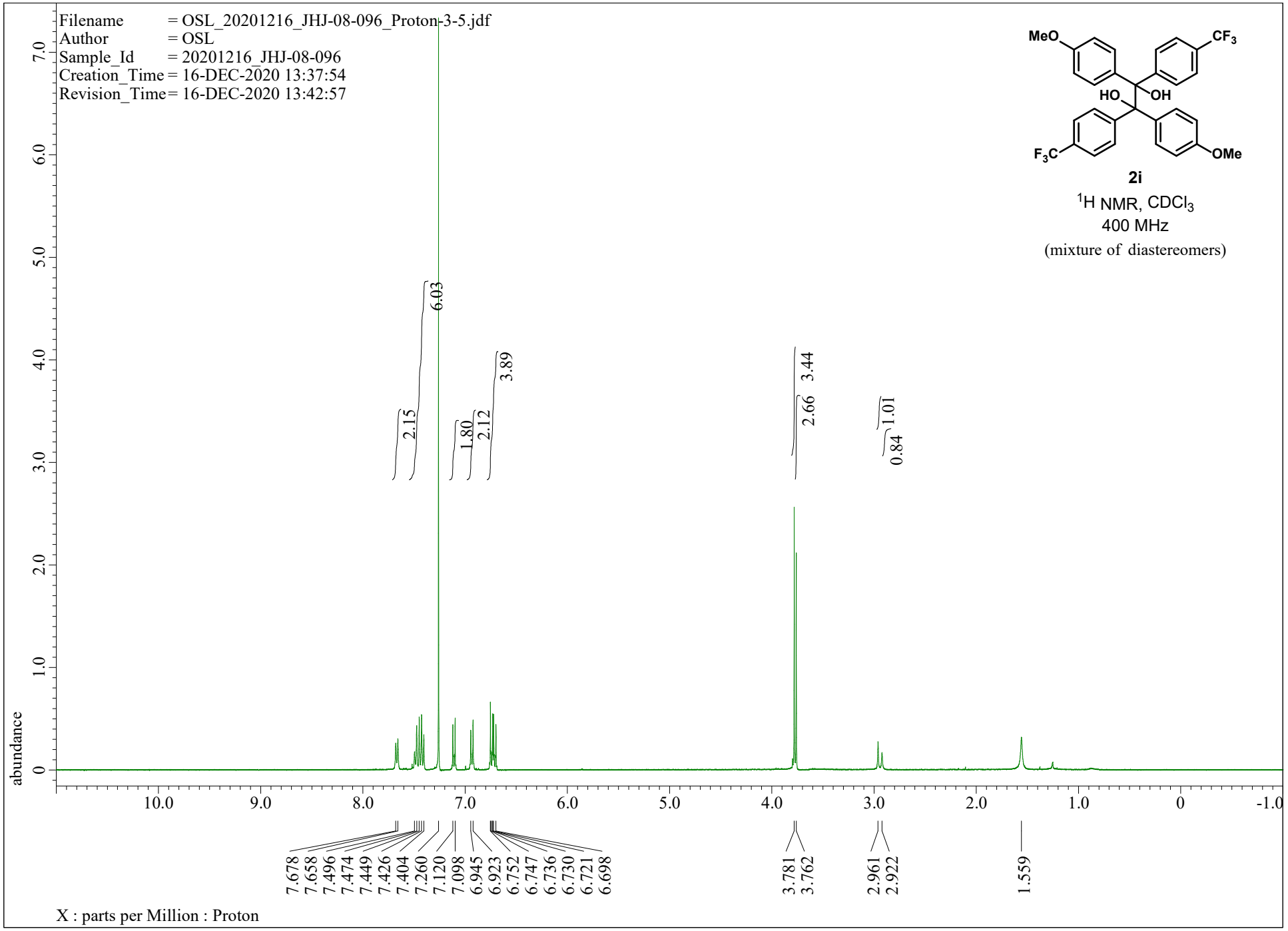
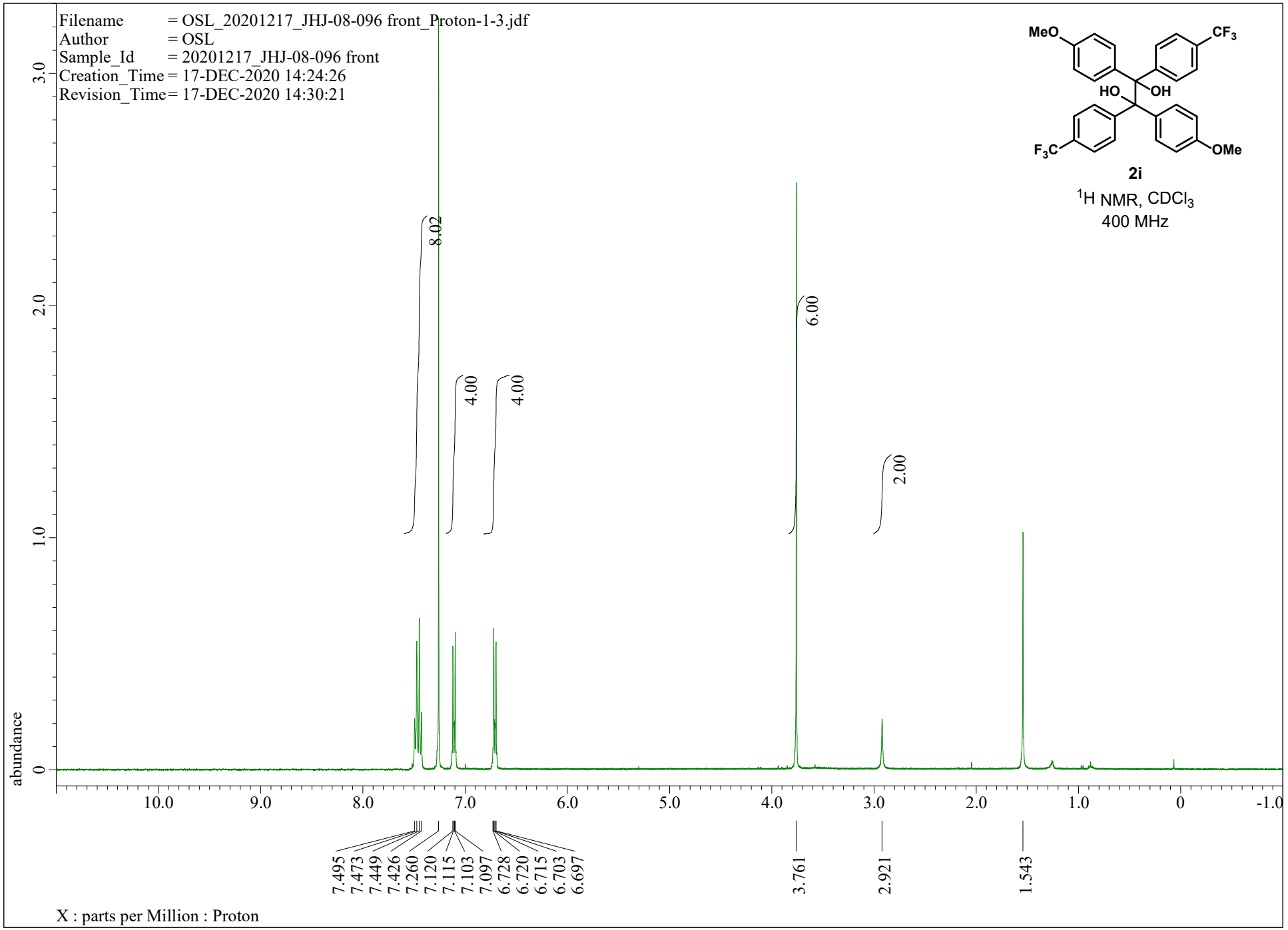
2.04
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.260
7.216
7.210
7.199
7.193
7.188
7.177
7.171
7.165
7.155
7.149
2.844
1.562
1.546
X : parts per Million : Proton

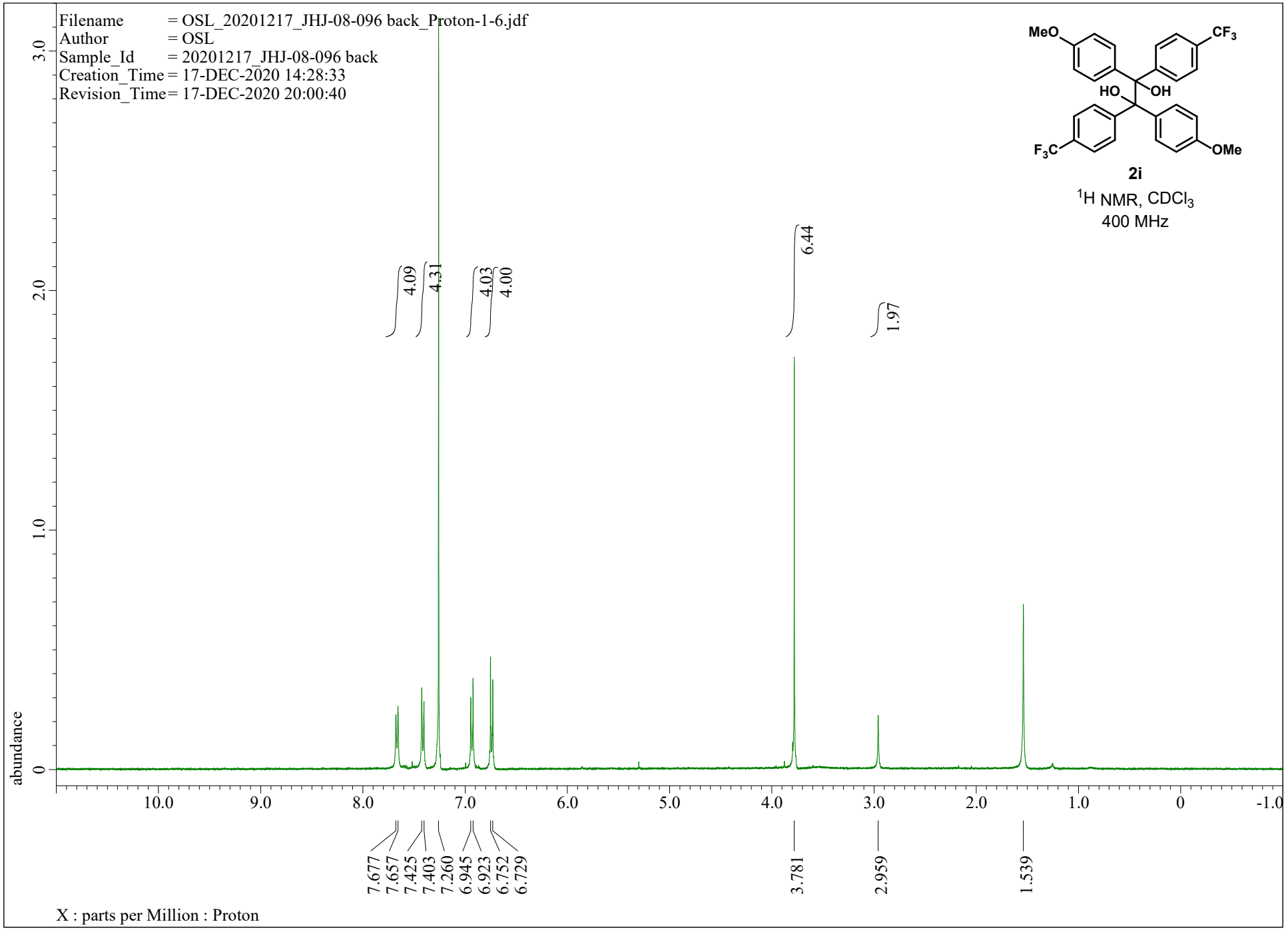

Filename = JHJ-08-081 proton_Proton-1-4.jdf
Author = delta
Sample_Id = JHJ-08-081 proton
Creation_Time = 25-NOV-2020 12:58:50
Revision_Time = 25-NOV-2020 17:13:47
Inst_Model_Number=
Inst_Serial_Number =
Version = 5.0.6 [Windows]
Br
Br
HO
OH
Br
Br
2f
1H NMR, CDCl3
400 MHz
8.05
8.00
1.87
abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.336
7.329
7.324
7.313
7.307
7.300
7.260
7.152
7.145
7.140
7.128
7.123
2.819
1.558
X : parts per Million : Proton

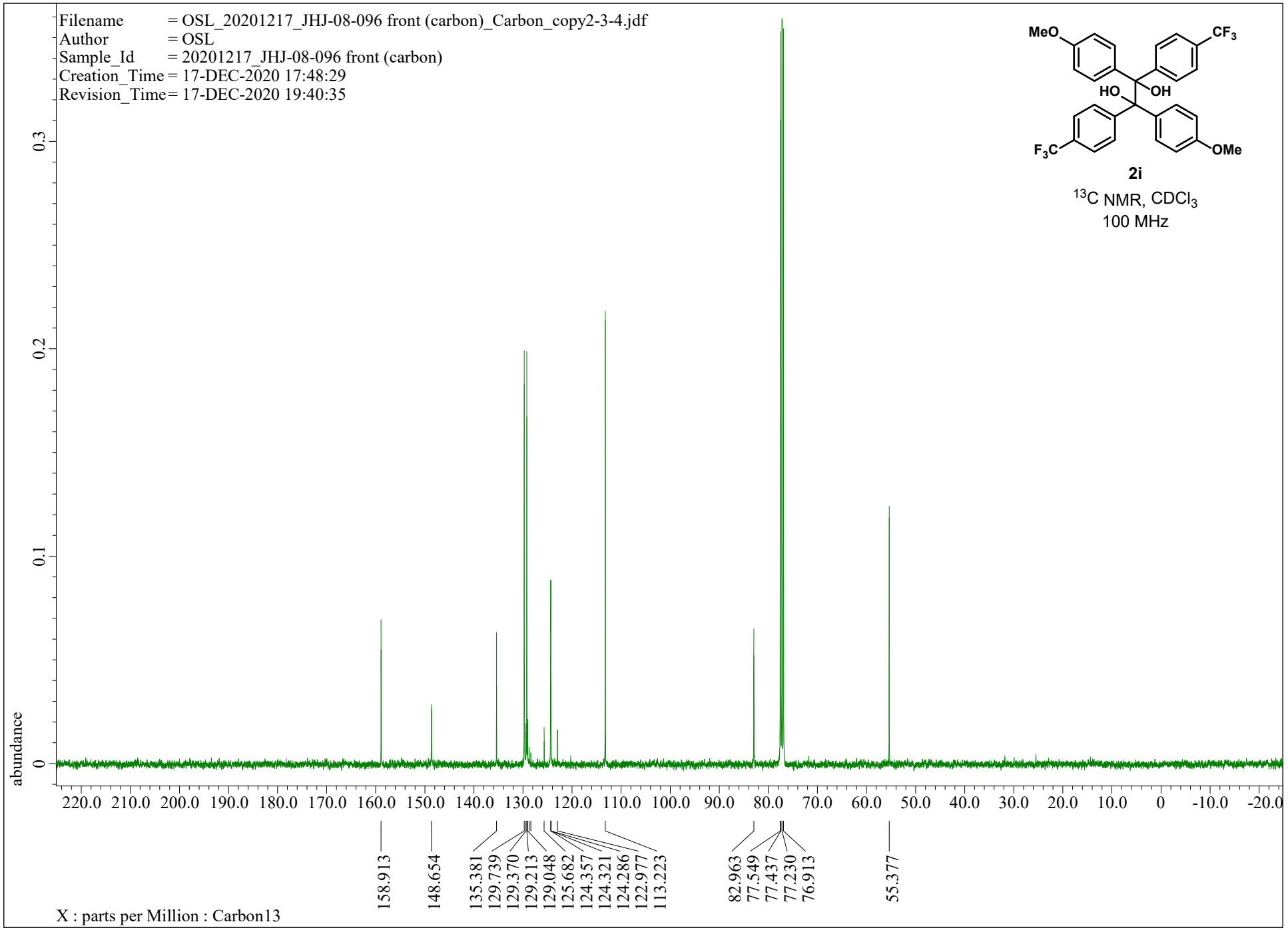

Filename = JHJ-08-081 carbon_Carbon-1-2.jdf
Author = delta
Sample_Id = JHJ-08-081 carbon
Creation_Time = 25-NOV-2020 12:00:51
Revision_Time = 25-NOV-2020 17:11:08
Inst_Model_Number=
Inst_Serial_Number =
Version = 5.0.6 [Windows]
Br
Br
HO
OH
Br
Br
2f
13C NMR, CDCl3
100 MHz
(thousandths)
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
142.580
130.919
130.357
122.033
82.684
77.554
77.230
76.915
X : parts per Million : Carbon13

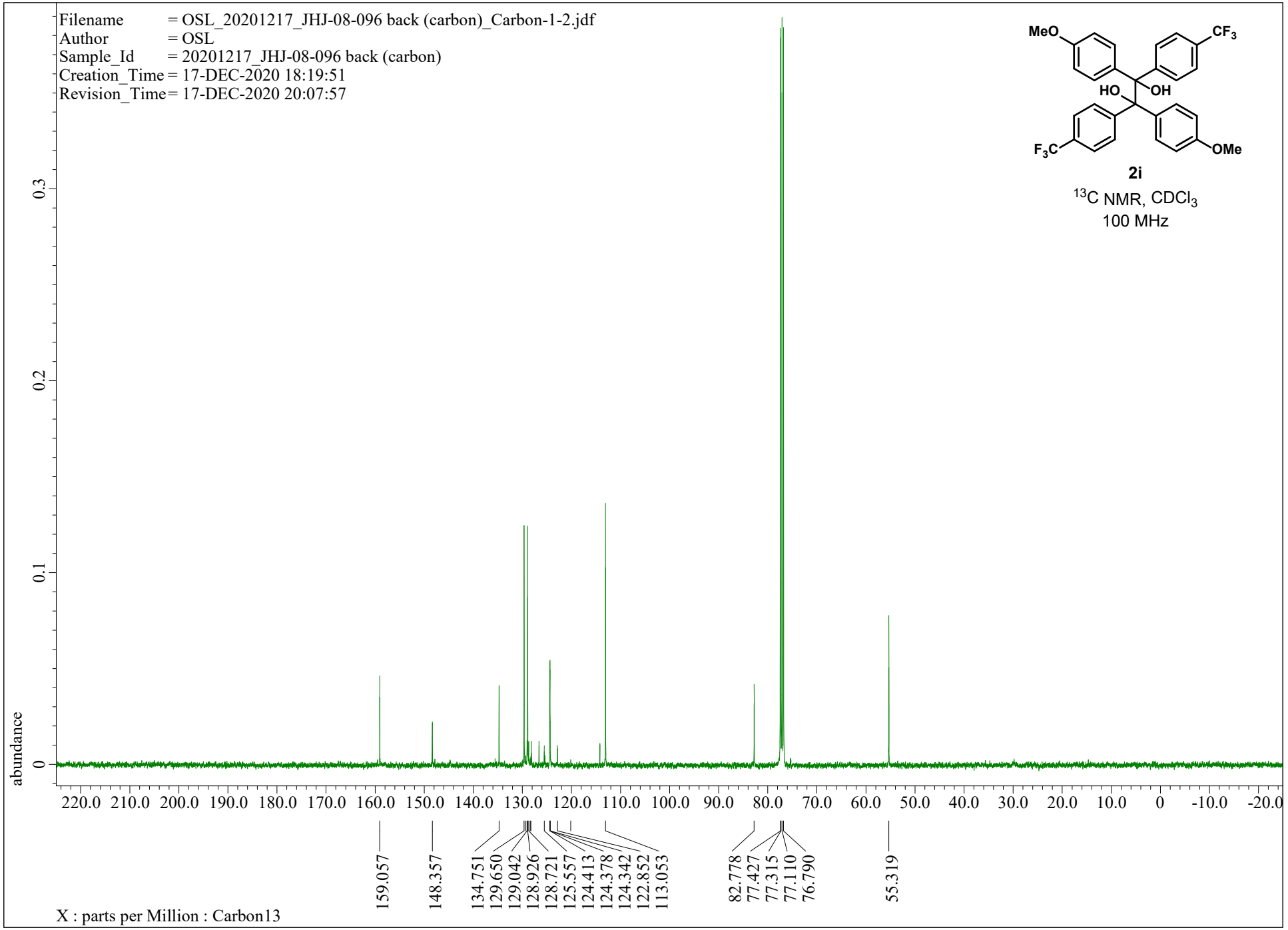

Filename = OSL_20201019_JHJ-08-072 column tube 16-57_Proton-1-5.jdf
Author = OSL
Sample_Id = 20201019_JHJ-08-072 column tube 16-57
Creation_Time = 19-OCT-2020 19:30:45
Revision_Time = 18-NOV-2020 14:50:22
MeO
F
HO
OH
F
OMe
2h
1H NMR, CDCl3
400 MHz
6.04
4.19
4.00
2.32
2.04
2.00
2.14
2.05
abundance
7.277
7.260
7.145
7.123
7.029
7.007
6.880
6.864
6.858
6.842
6.836
6.820
6.733
6.716
6.711
6.694
3.773
3.762
1.564
X : parts per Million : Proton

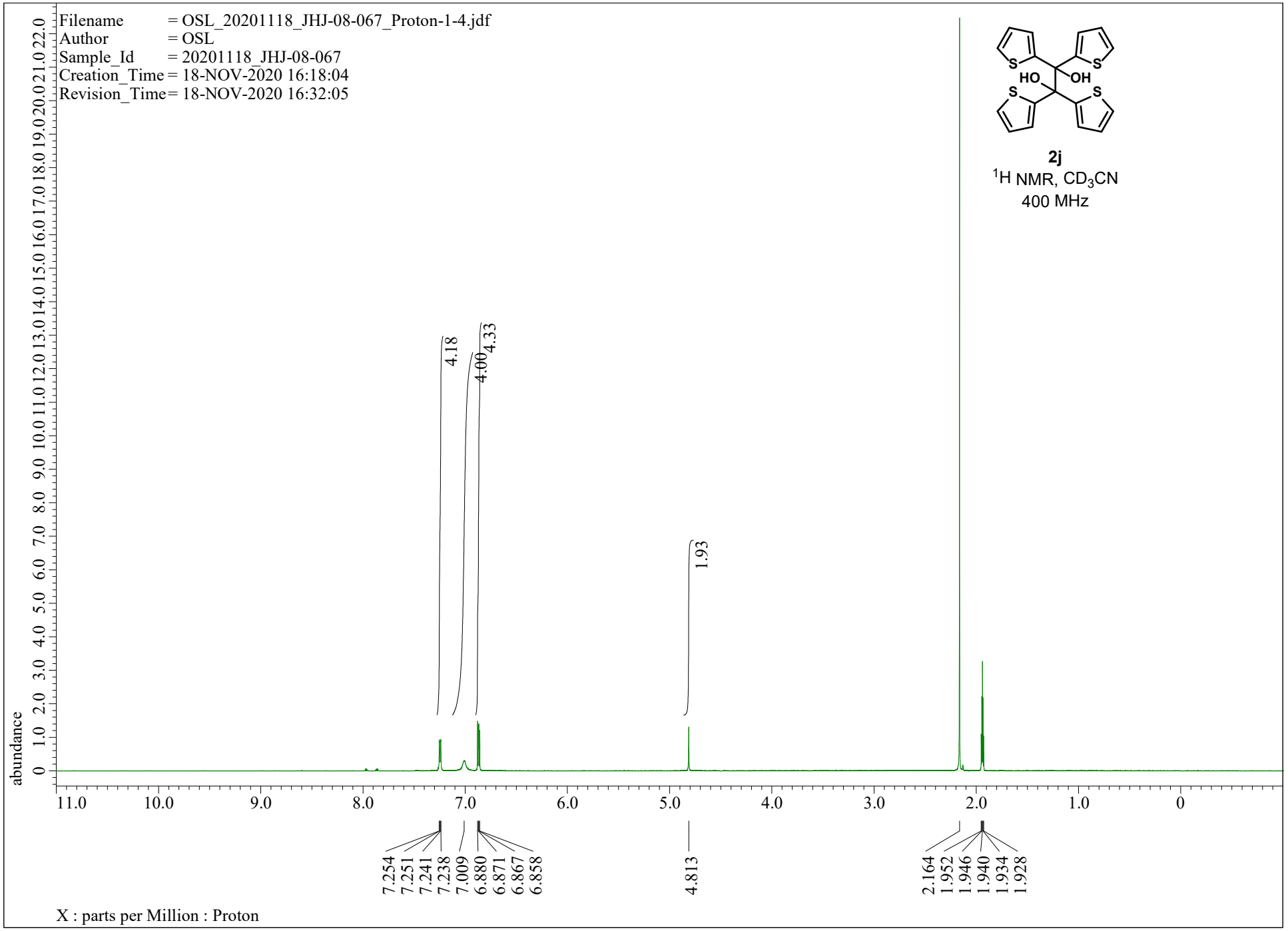

Filename = OSL_20201216_JHJ-08-096_Proton-3-5.jdf
Author = OSL
Sample_Id = 20201216_JHJ-08-096
Creation_Time = 16-DEC-2020 13:37:54
Revision_Time = 16-DEC-2020 13:42:57
MeO
CF3
HO
OH
F3C
OMe
2i
1H NMR, CDCl3
400 MHz
(mixture of diastereomers)
abundance
X : parts per Million : Proton
2.15
6.03
1.80
2.12
3.89
3.44
2.66
1.01
0.84
7.678
7.658
7.496
7.474
7.449
7.426
7.404
7.260
7.120
7.098
6.945
6.923
6.752
6.747
6.736
6.730
6.721
6.698
3.781
3.762
2.961
2.922
1.559

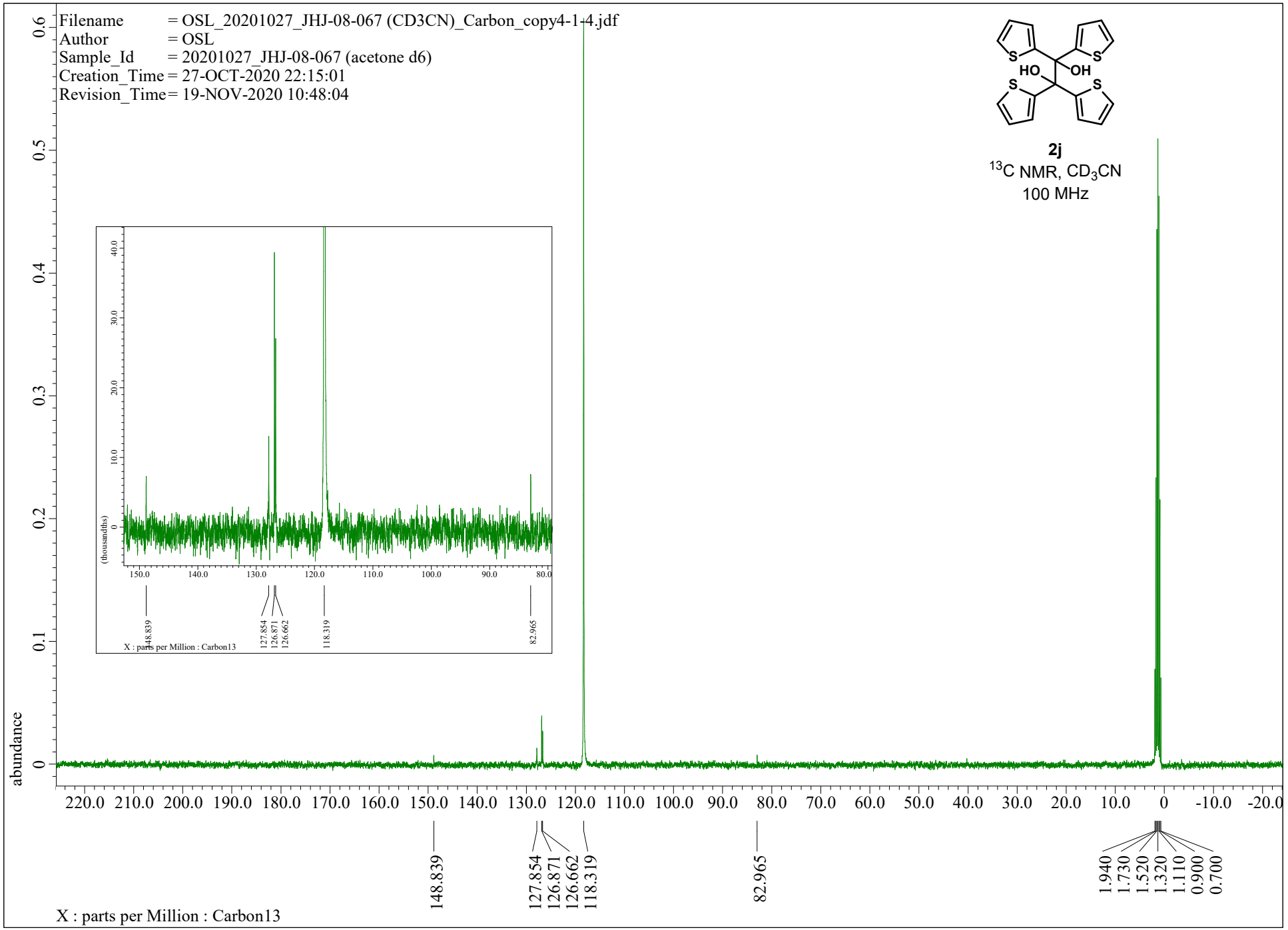

Filename = OSL_20201217_JHJ-08-096 front_Proton-1-3.jdf
Author = OSL
Sample_Id = 20201217_JHJ-08-096 front
Creation_Time = 17-DEC-2020 14:24:26
Revision_Time = 17-DEC-2020 14:30:21
MeO
CF3
HO
OH
F3C
OMe
2i
1H NMR, CDCl3
400 MHz
8.02
4.00
4.00
6.00
2.00
abundance
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.495
7.473
7.449
7.426
7.260
7.120
7.115
7.103
7.097
6.728
6.720
6.715
6.703
6.697
3.761
2.921
1.543
X : parts per Million : Proton

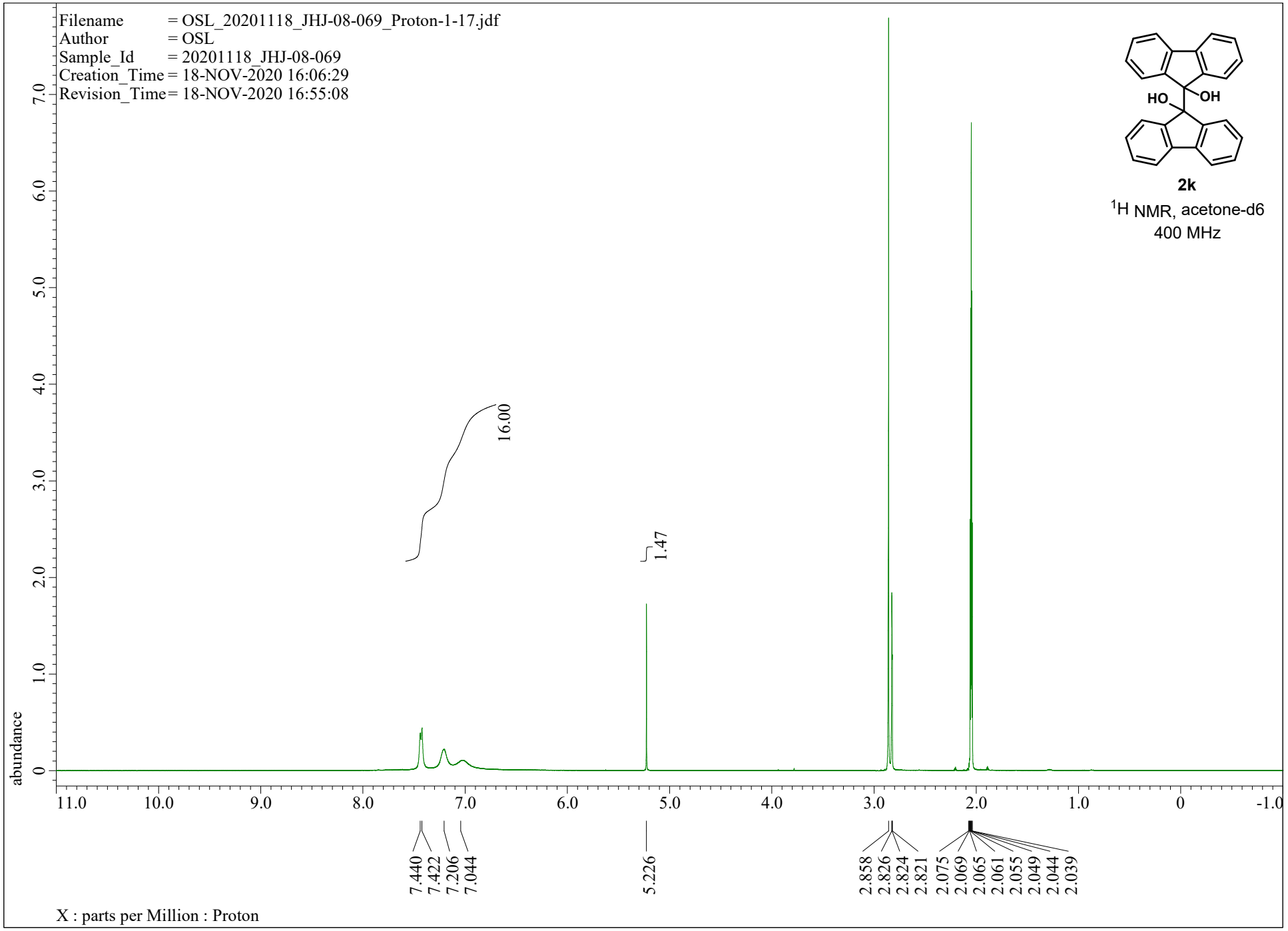

Filename = OSL_20201217_JHJ-08-096 back_Proton-1-6.jdf
Author = OSL
Sample_Id = 20201217_JHJ-08-096 back
Creation_Time = 17-DEC-2020 14:28:33
Revision_Time = 17-DEC-2020 20:00:40
MeO
CF3
HO
OH
F3C
OMe
2i
1H NMR, CDCl3
400 MHz
4.09
4.31
4.03
4.00
6.44
1.97
abundance
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.677
7.657
7.425
7.403
7.260
6.945
6.923
6.752
6.729
3.781
2.959
1.539
X : parts per Million : Proton

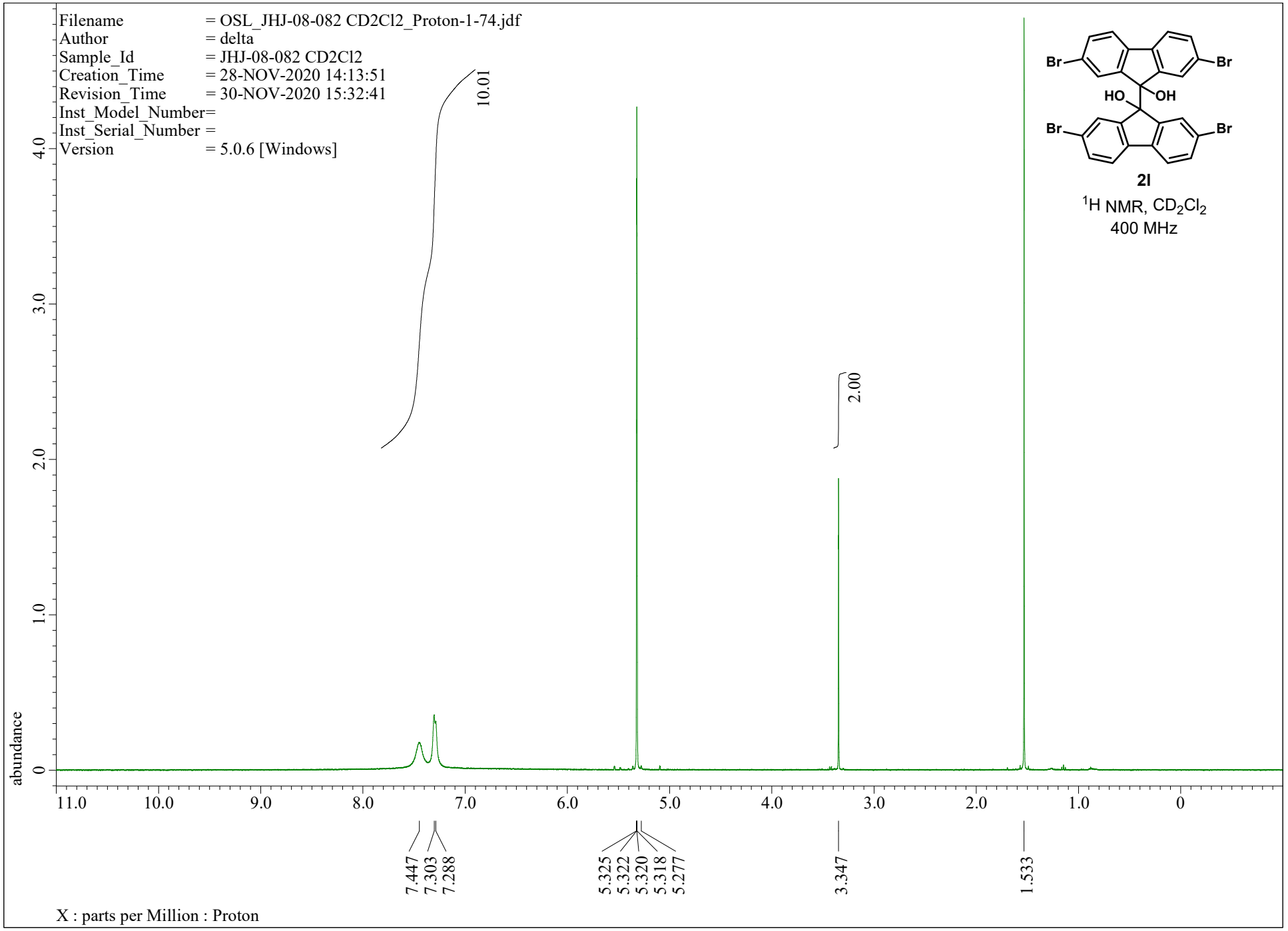

Filename = OSL_20201217_JHJ-08-096 front (carbon)_Carbon_copy2-3-4.jdf
Author = OSL
Sample_Id = 20201217_JHJ-08-096 front (carbon)
Creation_Time = 17-DEC-2020 17:48:29
Revision_Time = 17-DEC-2020 19:40:35
MeO
CF3
HO
OH
F3C
OMe
2i
13C NMR, CDCl3
100 MHz
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
158.913
148.654
135.381
129.739
129.370
129.213
129.048
125.682
124.357
124.321
124.286
122.977
113.223
82.963
77.549
77.437
77.230
76.913
55.377
X : parts per Million : Carbon13

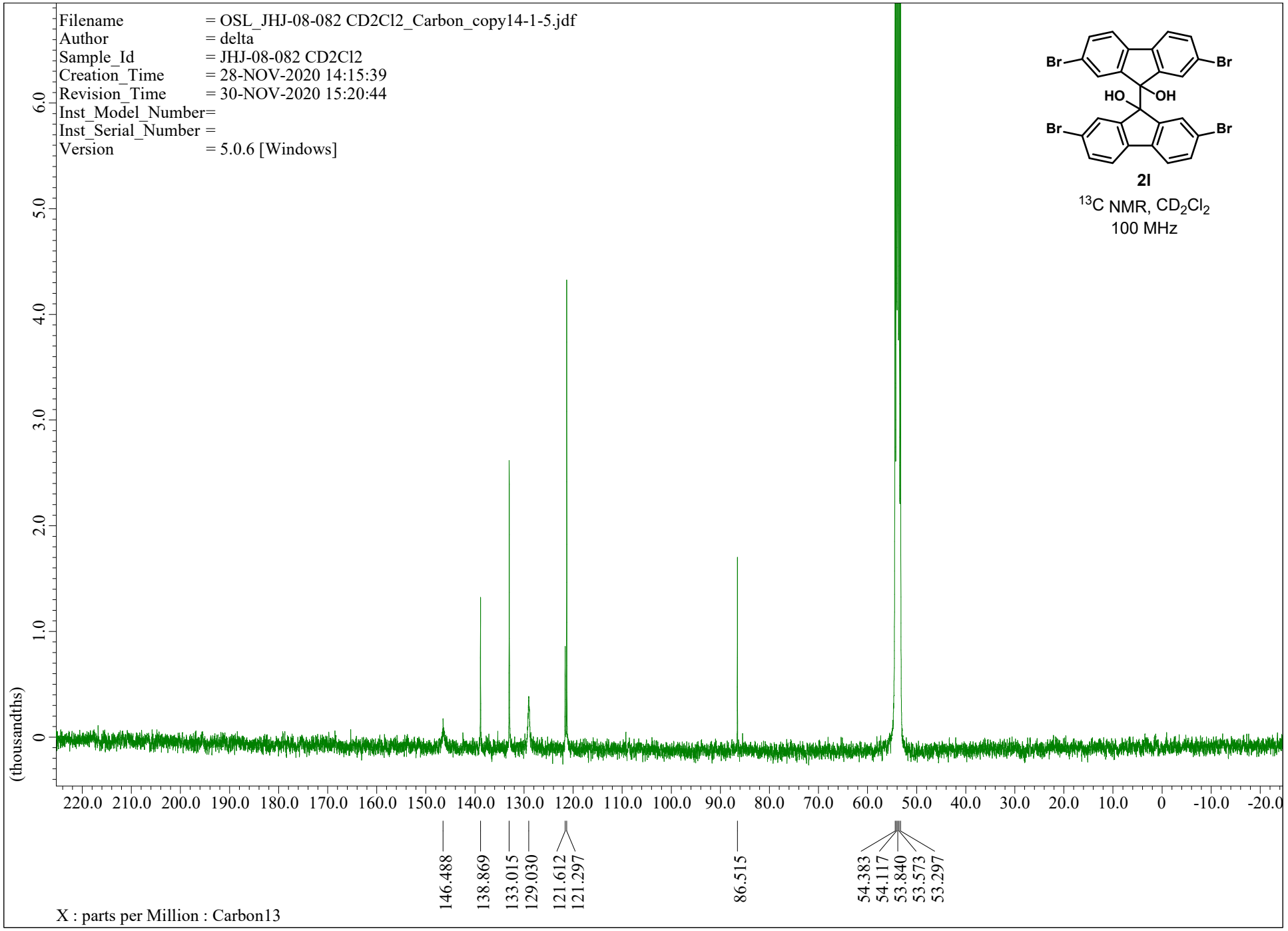

Filename = OSL_20201217_JHJ-08-096 back (carbon)_Carbon-1-2.jdf
Author = OSL
Sample_Id = 20201217_JHJ-08-096 back (carbon)
Creation_Time = 17-DEC-2020 18:19:51
Revision_Time = 17-DEC-2020 20:07:57
MeO
CF3
HO
OH
F3C
OMe
2i
13C NMR, CDCl3
100 MHz
abundance
0
0.1
0.2
0.3
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
159.057
148.357
134.751
129.650
129.042
128.926
128.721
125.557
124.413
124.378
124.342
122.852
113.053
82.778
77.427
77.315
77.110
76.790
55.319
X : parts per Million : Carbon13

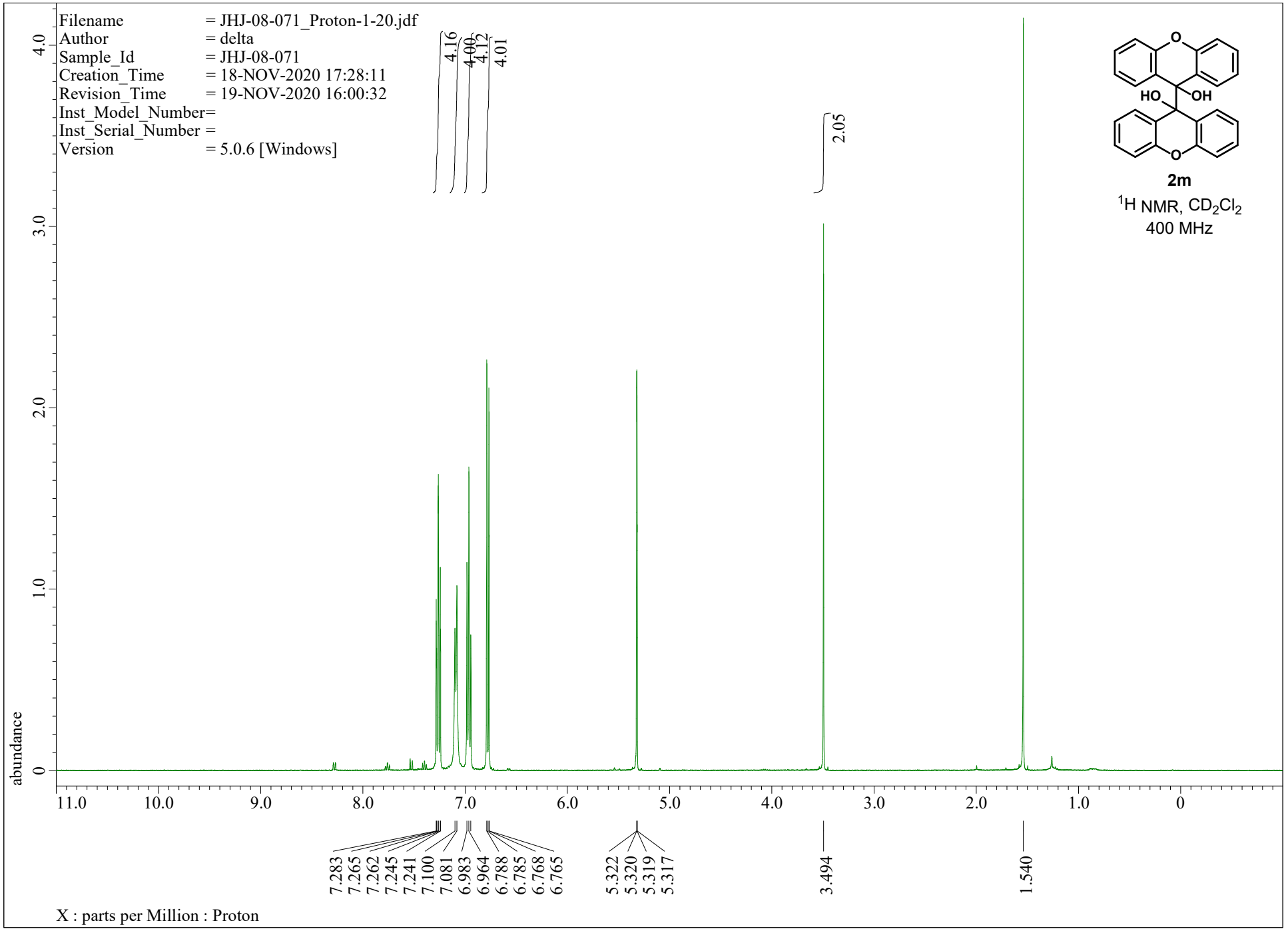

Filename = OSL_20201118_JHJ-08-067_Proton-1-4.jdf
Author = OSL
Sample_Id = 20201118_JHJ-08-067
Creation_Time = 18-NOV-2020 16:18:04
Revision_Time = 18-NOV-2020 16:32:05
HO
OH
S
2j
1H NMR, CD3CN
400 MHz
4.18
4.00
4.33
1.93
abundance
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.254
7.251
7.241
7.238
7.009
6.880
6.871
6.867
6.858
4.813
2.164
1.952
1.946
1.940
1.934
1.928
X : parts per Million : Proton

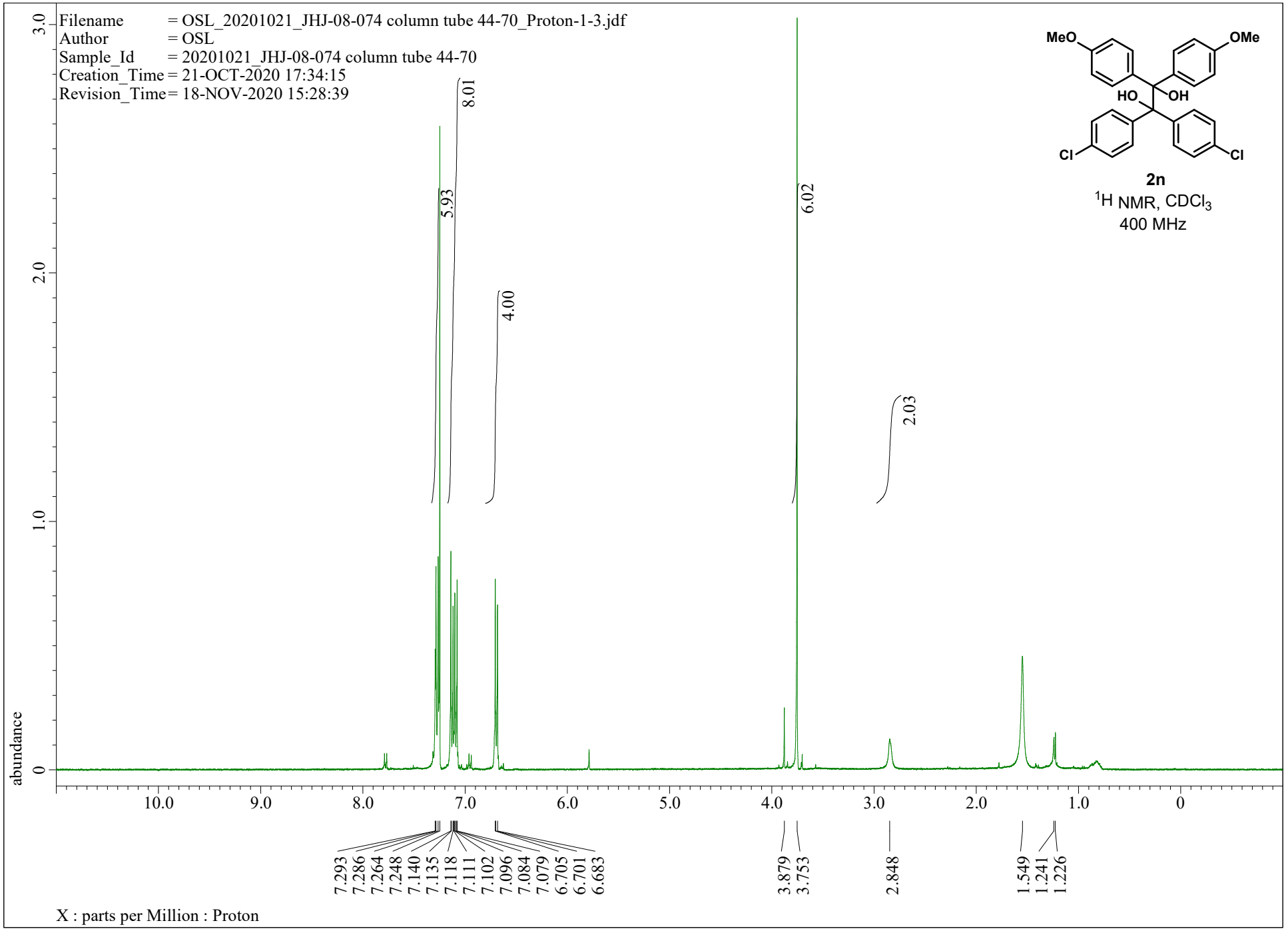

Filename = OSL_20201027_JHJ-08-067 (CD3CN)_Carbon_copy4-1-4.jdf
Author = OSL
Sample_Id = 20201027_JHJ-08-067 (acetone d6)
Creation_Time = 27-OCT-2020 22:15:01
Revision_Time = 19-NOV-2020 10:48:04
HO
OH
S
2j
13C NMR, CD3CN
100 MHz
abundance
0.6
0.5
0.4
0.3
0.2
0.1
0
(thousandths)
40.0
30.0
20.0
10.0
0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
148.839
127.854
126.871
126.662
118.319
82.965
X : parts per Million : Carbon13
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
1.940
1.730
1.520
1.320
1.110
0.900
0.700
X : parts per Million : Carbon13

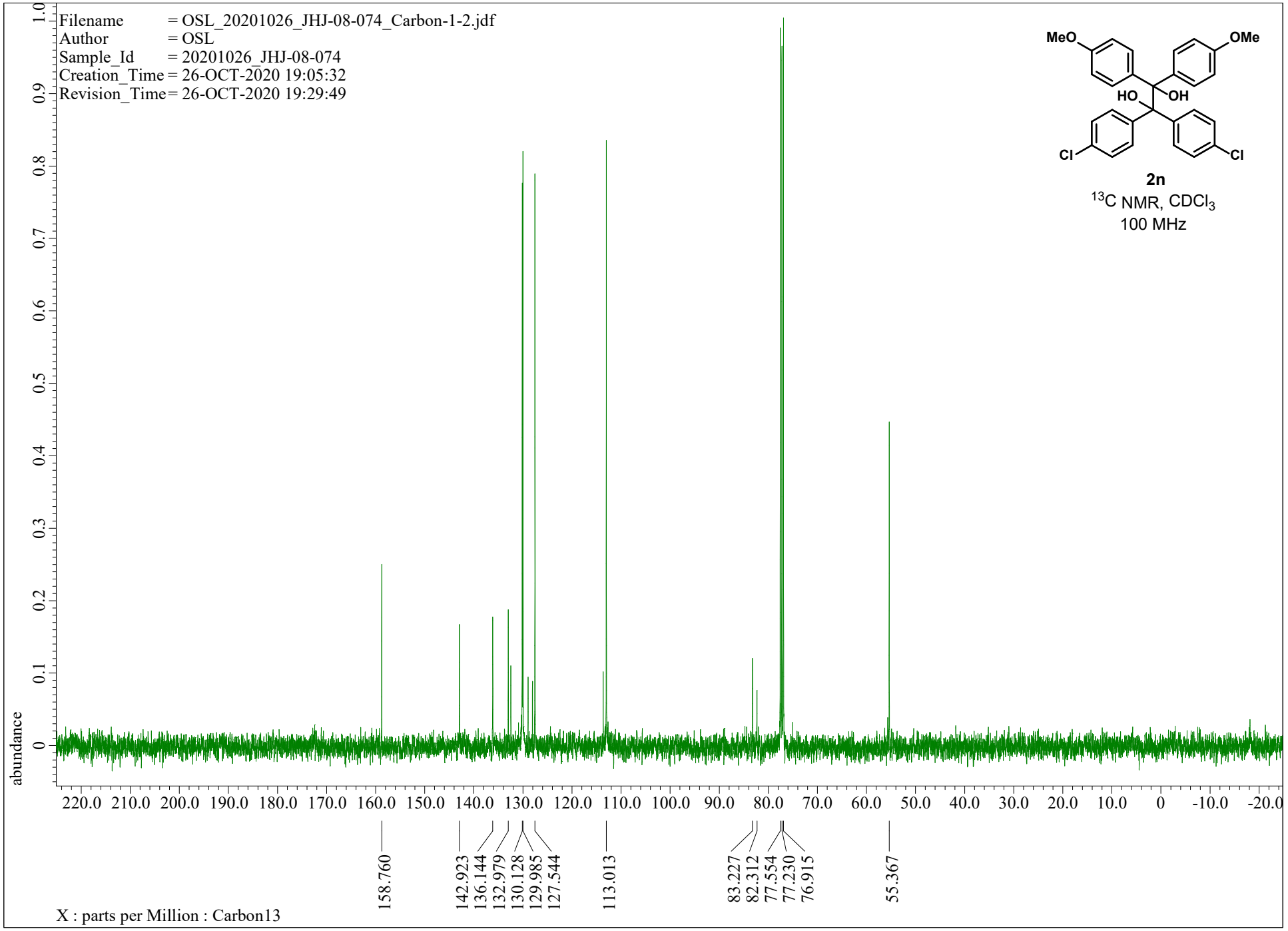

Filename = OSL_20201118_JHJ-08-069_Proton-1-17.jdf
Author = OSL
Sample_Id = 20201118_JHJ-08-069
Creation_Time = 18-NOV-2020 16:06:29
Revision_Time = 18-NOV-2020 16:55:08
HO
OH
2k
1H NMR, acetone-d6
400 MHz
16.00
1.47
abundance
X : parts per Million : Proton
7.440
7.422
7.206
7.044
5.226
2.858
2.826
2.824
2.821
2.075
2.069
2.065
2.061
2.055
2.049
2.044
2.039

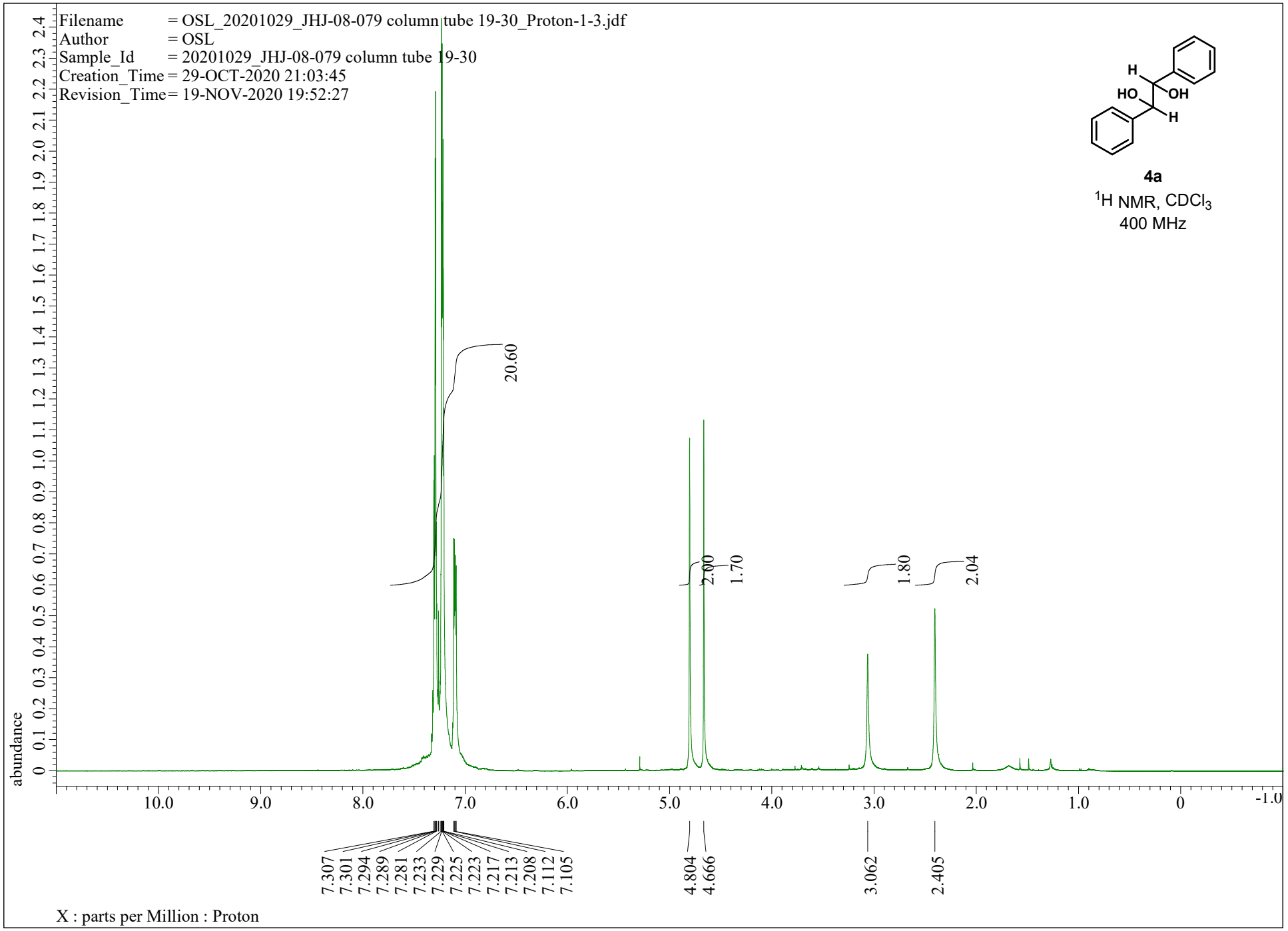

Filename = OSL_JHJ-08-082 CD2Cl2_Proton-1-74.jdf
Author = delta
Sample_Id = JHJ-08-082 CD2Cl2
Creation_Time = 28-NOV-2020 14:13:51
Revision_Time = 30-NOV-2020 15:32:41
Inst_Model_Number=
Inst_Serial_Number =
Version = 5.0.6 [Windows]
10.01
2.00
Br
Br
HO
OH
Br
Br
2l
1H NMR, CD2Cl2
400 MHz
abundance
4.0
3.0
2.0
1.0
0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.447
7.303
7.288
5.325
5.322
5.320
5.318
5.277
3.347
1.533
X : parts per Million : Proton

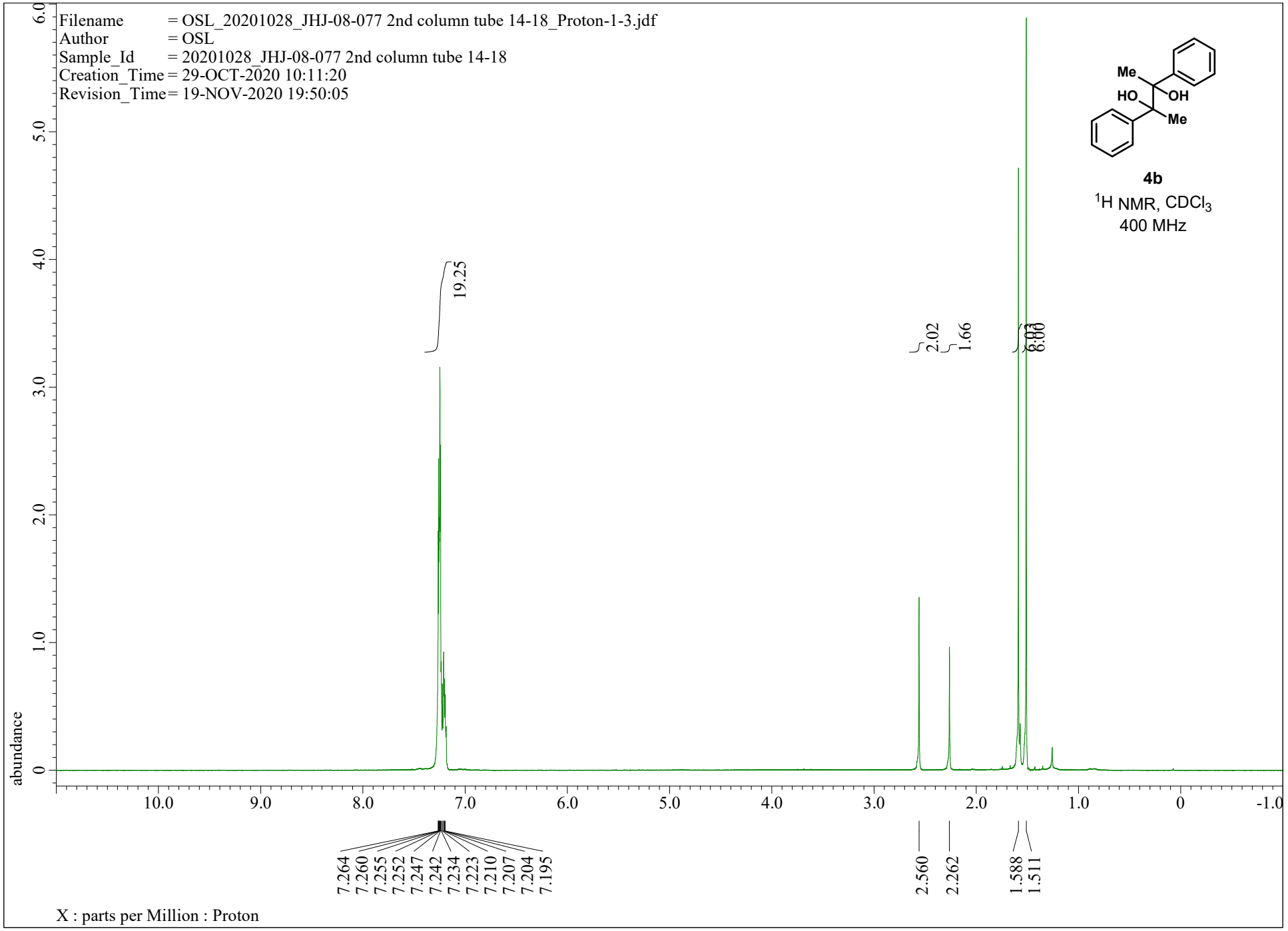

Filename = OSL_JHJ-08-082 CD2Cl2_Carbon_copy14-1-5.jdf
Author = delta
Sample_Id = JHJ-08-082 CD2Cl2
Creation_Time = 28-NOV-2020 14:15:39
Revision_Time = 30-NOV-2020 15:20:44
Inst_Model_Number=
Inst_Serial_Number =
Version = 5.0.6 [Windows]
Br
Br
HO
OH
Br
Br
2l
13C NMR, CD2Cl2
100 MHz
(thousandths)
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
146.488
138.869
133.015
129.030
121.612
121.297
86.515
54.383
54.117
53.840
53.573
53.297
X : parts per Million : Carbon13


Filename = JHJ-08-071_Proton-1-20.jdf
Author = delta
Sample_Id = JHJ-08-071
Creation_Time = 18-NOV-2020 17:28:11
Revision_Time = 19-NOV-2020 16:00:32
Inst_Model_Number=
Inst_Serial_Number =
Version = 5.0.6 [Windows]
4.16
4.00
4.12
4.01
2.05
HO
OH
O
O
2m
1H NMR, CD2Cl2
400 MHz
abundance
4.0
3.0
2.0
1.0
0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.283
7.265
7.262
7.245
7.241
7.100
7.081
6.983
6.964
6.788
6.785
6.768
6.765
5.322
5.320
5.319
5.317
3.494
1.540
X : parts per Million : Proton


Filename = OSL_20201021_JHJ-08-074 column tube 44-70_Proton-1-3.jdf
Author = OSL
Sample_Id = 20201021_JHJ-08-074 column tube 44-70
Creation_Time = 21-OCT-2020 17:34:15
Revision_Time = 18-NOV-2020 15:28:39
MeO
OMe
HO
OH
Cl
Cl
2n
1H NMR, CDCl3
400 MHz
8.01
5.93
4.00
6.02
2.03
abundance
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.293
7.286
7.264
7.248
7.140
7.135
7.118
7.111
7.102
7.096
7.084
7.079
6.705
6.701
6.683
3.879
3.753
2.848
1.549
1.241
1.226
X : parts per Million : Proton


Filename = OSL_20201026_JHJ-08-074_Carbon-1-2.jdf
Author = OSL
Sample_Id = 20201026_JHJ-08-074
Creation_Time = 26-OCT-2020 19:05:32
Revision_Time = 26-OCT-2020 19:29:49
MeO
OMe
HO
OH
Cl
Cl
2n
13C NMR, CDCl3
100 MHz
abundance
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
158.760
142.923
136.144
132.979
130.128
129.985
127.544
113.013
83.227
82.312
77.554
77.230
76.915
55.367
X : parts per Million : Carbon13


Filename = OSL_20201029_JHJ-08-079 column tube 19-30_Proton-1-3.jdf
Author = OSL
Sample_Id = 20201029_JHJ-08-079 column tube 19-30
Creation_Time = 29-OCT-2020 21:03:45
Revision_Time = 19-NOV-2020 19:52:27
4a
1H NMR, CDCl3
400 MHz
abundance
20.60
2.00
1.70
1.80
2.04
7.307
7.301
7.294
7.289
7.281
7.233
7.229
7.225
7.223
7.217
7.213
7.208
7.112
7.105
4.804
4.666
3.062
2.405
X : parts per Million : Proton


Filename = OSL_20201028_JHJ-08-077 2nd column tube 14-18_Proton-1-3.jdf
Author = OSL
Sample_Id = 20201028_JHJ-08-077 2nd column tube 14-18
Creation_Time = 29-OCT-2020 10:11:20
Revision_Time = 19-NOV-2020 19:50:05
Me
HO
OH
Me
4b
1H NMR, CDCl3
400 MHz
19.25
2.02
1.66
6.03
6.00
abundance
6.0
5.0
4.0
3.0
2.0
1.0
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.264
7.260
7.255
7.252
7.247
7.242
7.234
7.223
7.210
7.207
7.204
7.195
2.560
2.262
1.588
1.511
X : parts per Million : Proton