Supporting Information

The Efficient LED-Driven MOF-Catalysis for Aerobic C-H and C-C Bond Oxidation

Mehdi Sheykhan*[,a,b] Mona Bahmani,[b] Masoumeh Abbasnia[a]

[a]Department of Organic Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, P.O. Box 14155-4838, Tehran, Iran

[b]Chemistry Department, University of Guilan, P.O. Box 41335-1914, Rasht, Iran

Table of contents:

1. Experimental section

1.1. Materials and instruments

All of the chemicals were purchased from commercial sources. Fe_3O_4, SiO_2 supported on Fe_3O_4, linked to APTMS as well as MIL-88A were prepared according to the literature. SiO_2 used in mechanistic study is commercial silicagel 60 (0.015-0.040 mm, 115111 merck catalog no.). Maghemite was synthesized by calcination of magnetite at 300 ^oC, 3h. FT-IR spectra were recorded on an Agilent Cary 630 ATR-FTIR spectrophotometer. Thermogravimetric analyses (TGA) were carried out under N_2 atmosphere on a NETZSCH STA 409PC/PG instrument at a heating rate of 10 °C min^{-1}. 1H NMR spectra were recorded on Bruker 500 MHz NMR spectrometers and the chemical shifts were reported relative to TMS. Powder X-ray diffractions were studied by Philips X'Pert MBD on Co Kα (1.789 Å) tube. N_2 adsorption/desorption isotherms were analyzed by Micromeritics ASAP 2020 surface area analyzer.

1.2. Synthesis of magnetic support

Magnetic support of the catalyst was prepared according to the literature.[1] Briefly, after dissolving $FeCl_2$ (2.5 mmol) and $FeCl_3$ (2 equiv) in 20 mL water, 35 mL aq. NH_3 was added drop-wise under vigorous stirring. 20 mL TEOS was added slowly at 90 ◦C, stirring was continued for 12 h. The resulting silica supported magnetite was decanted by a magnet and washed with water and EtOH. The resulted dark-brownish solid was dried at 70 ◦C. 1 g of the prepared solid was dispersed in 15 mL toluene and then 4.5 mL APTMS was added to the suspension and refluxed for 8 h under N_2 gas. Finally, the product was decanted by magnetic, washed thoroughly with DCM, and dried at 50 ◦C.

1.3. Synthesis of magnetic MIL-88A

Magnetic MIL-88A was synthesized according literature by some modifications. In the presence of 0.1 g magnetic support, 4.2 mmol fumaric acid (0.485 g) and 4.2 mmol $FeCl_3.6H_2O$ (1.13g) were dissolved in 20 mL water and stirred at r.t for 1 h. Resulted suspension transferred into a Teflon-lined steel autoclave 70 ^oC for 8 h. After cooling to rt. washing with hot water and EtOH, the product dried at 100 ^oC to gain magnetic MIL-88A.

2. Characterization

2.1. Powder XRD of the magnetic MIL-88A

To determine the phases that is present in the synthesized compound, PXRD analysis used. The data were collected in Co radiation (λ = 1.789 Å) at 293 K. Patterns at 2Θ: 12.7^o, 14.0^o are clearly appeared showing the presence of MIL-88A. Patterns at around 35.1^o, 41.0^o, 50.1^o are related to cubic crystals of magnetite and broad peak at 20-30 is due to amorphous SiO_2 (Figure S1).

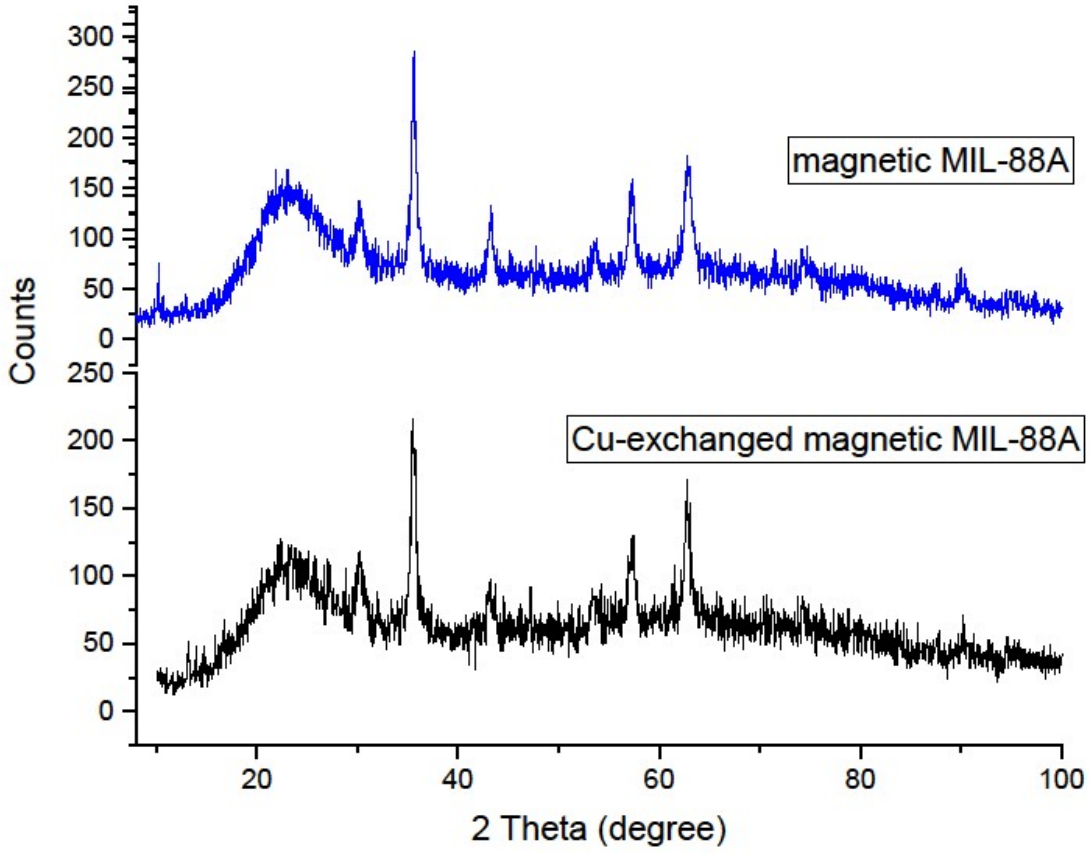


Figure S1. Powder XRD of the magnetic MIL-88A; and Cu-exchanged magnetic MIL-88A

2.2. FTIR spectrum on the magnetic MIL-88A

As shown in FTIR of MIL-88A, bands at 1397 cm^{-1} and 1608 cm^{-1} are related to the symmetric and asymmetric C=O stretching vibrations of fumarate linkers. The characteristic band of Fe-oxo group is clear at 585 cm^{-1} whereas bands related to the carbonyl and C-H bending appeared at 645 cm^{-1} and 677 cm^{-1}, respectively. Stretching mode of O-H bonds of adsorbed water caused a broad band around 2500-3500 cm^{-1}. In FTIR of magnetic support 815 cm^{-1} and 1109 cm^{-1} are caused by symmetric and asymmetric stretching of Si-OSi bonds, respectively. Bands at 2945 cm^{-1} and 2956 cm^{-1} are related to C-H stretching of APTMS linker.

As it is clear, most intense bands of magnetic support and MIL-88A are appeared in the prepared magnetic MIL-88A.

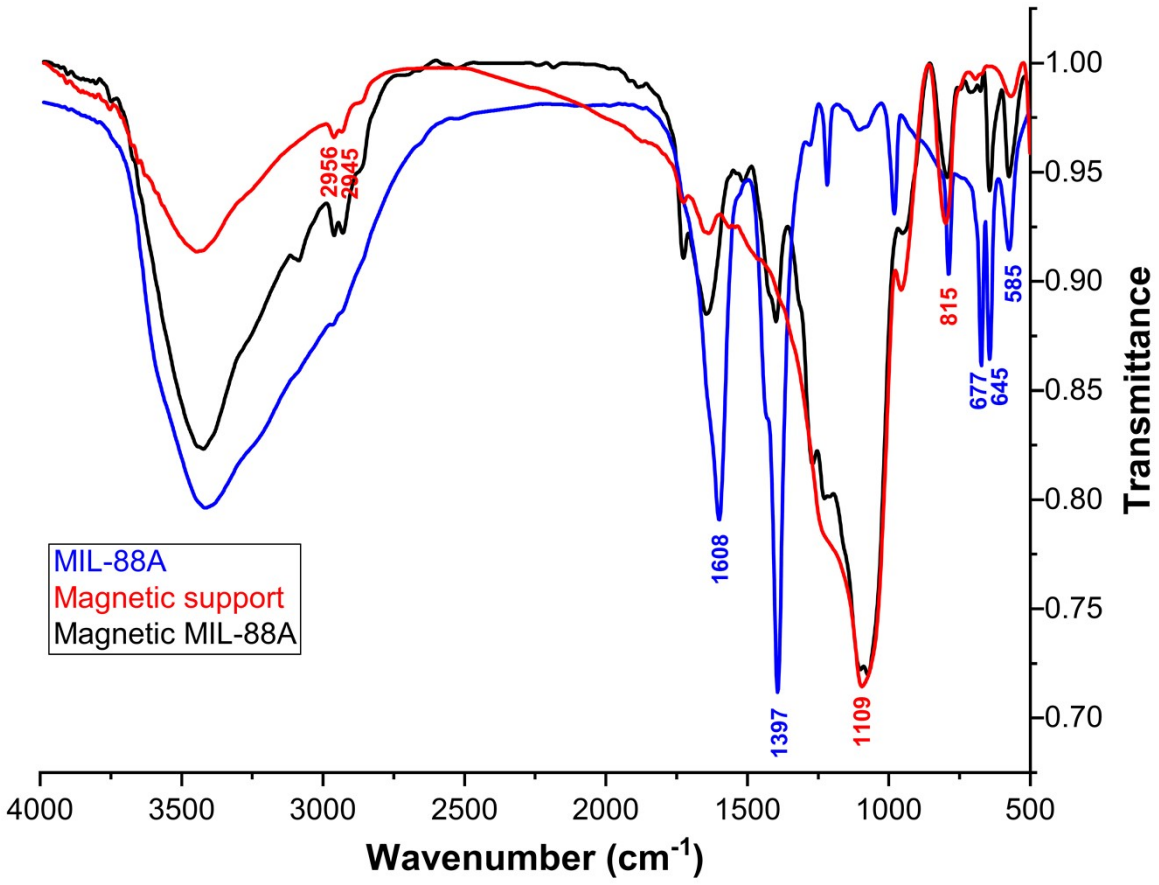
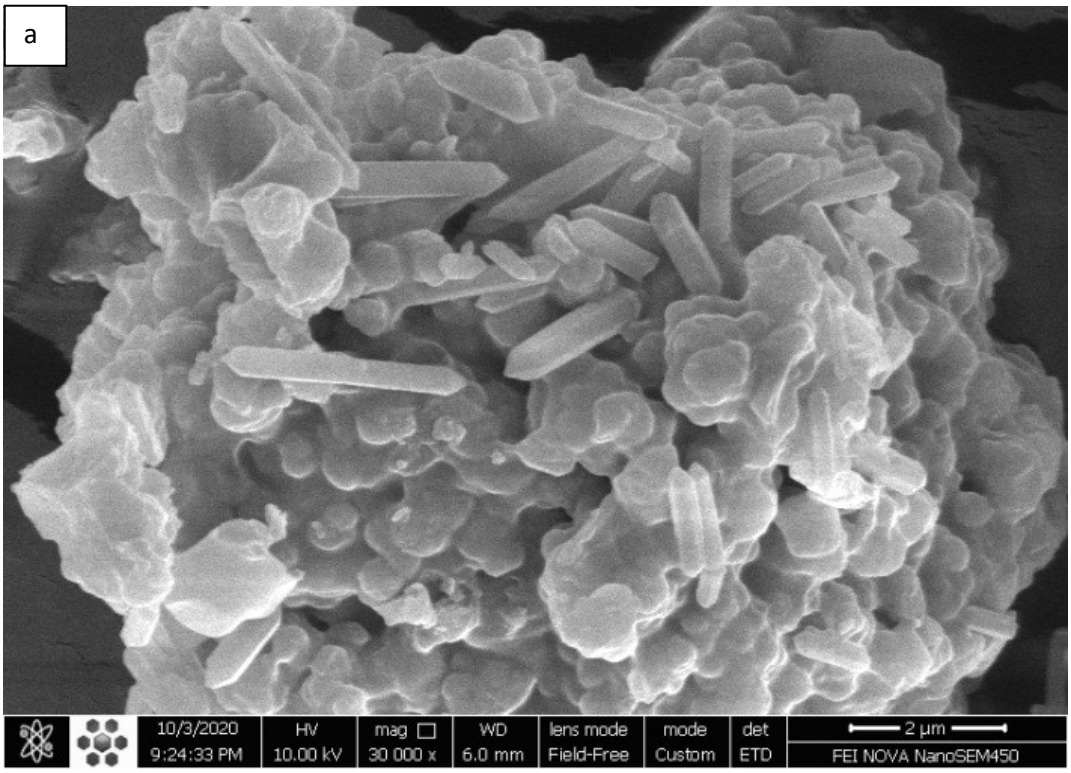


Figure S2. FTIR spectra of the magnetic support, MIL-88A and magnetic MIL-88A

2.3. SEM photographs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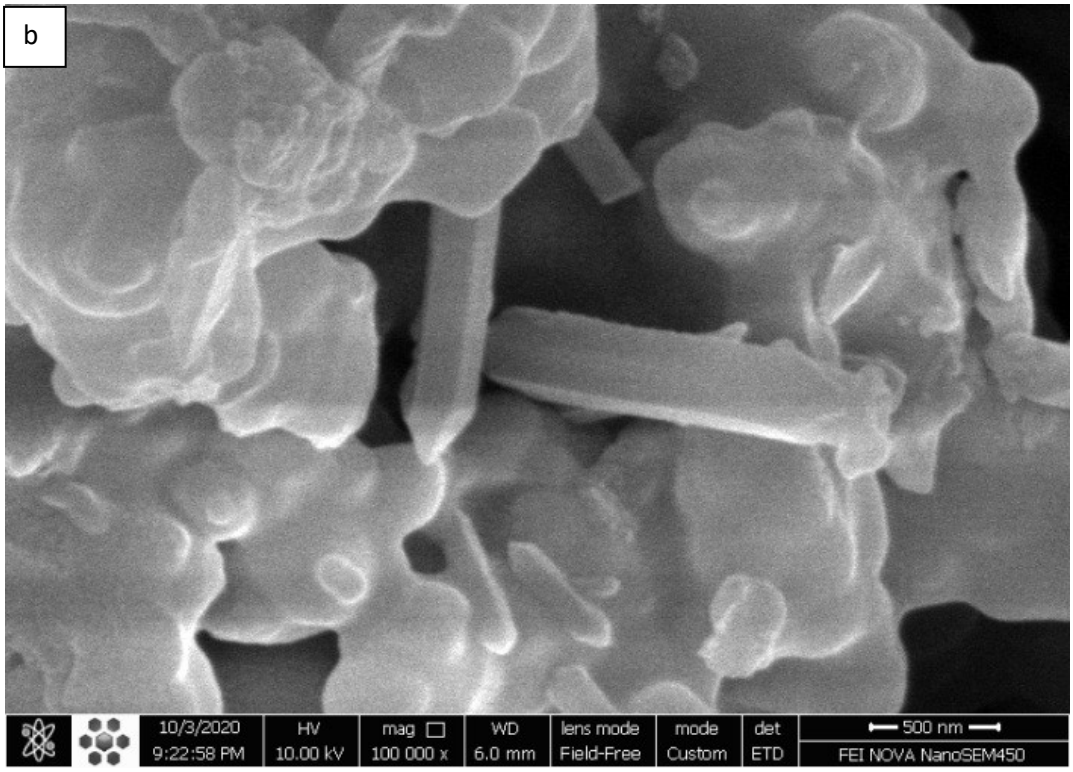
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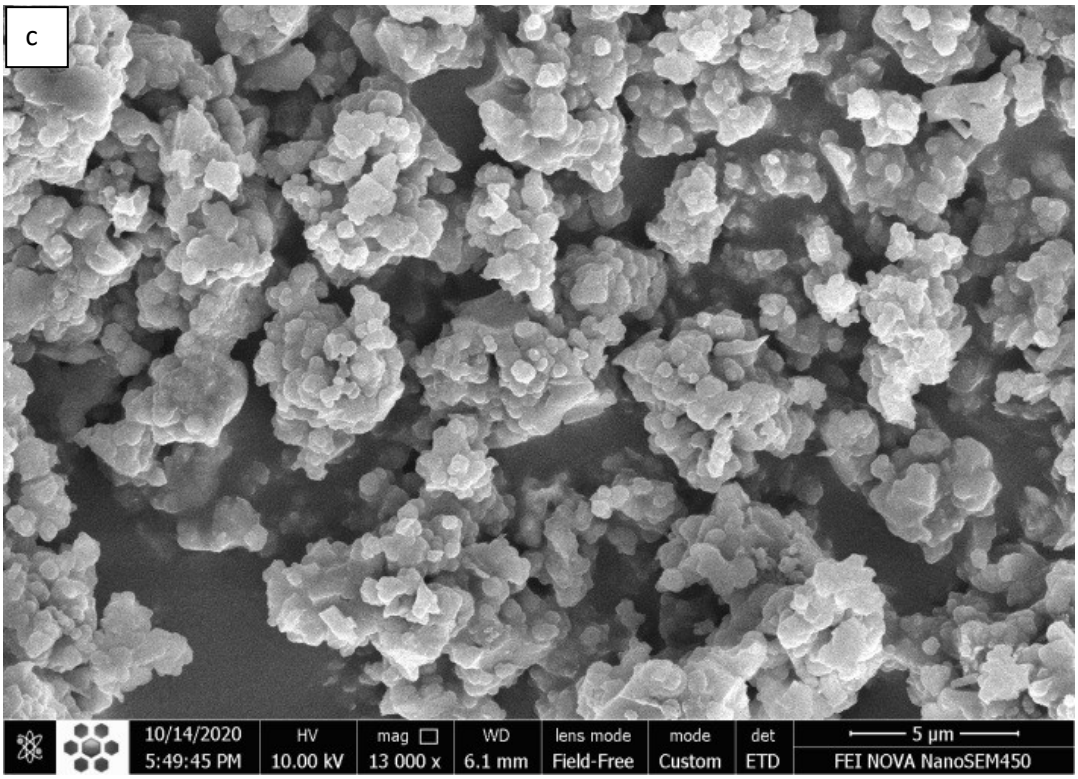
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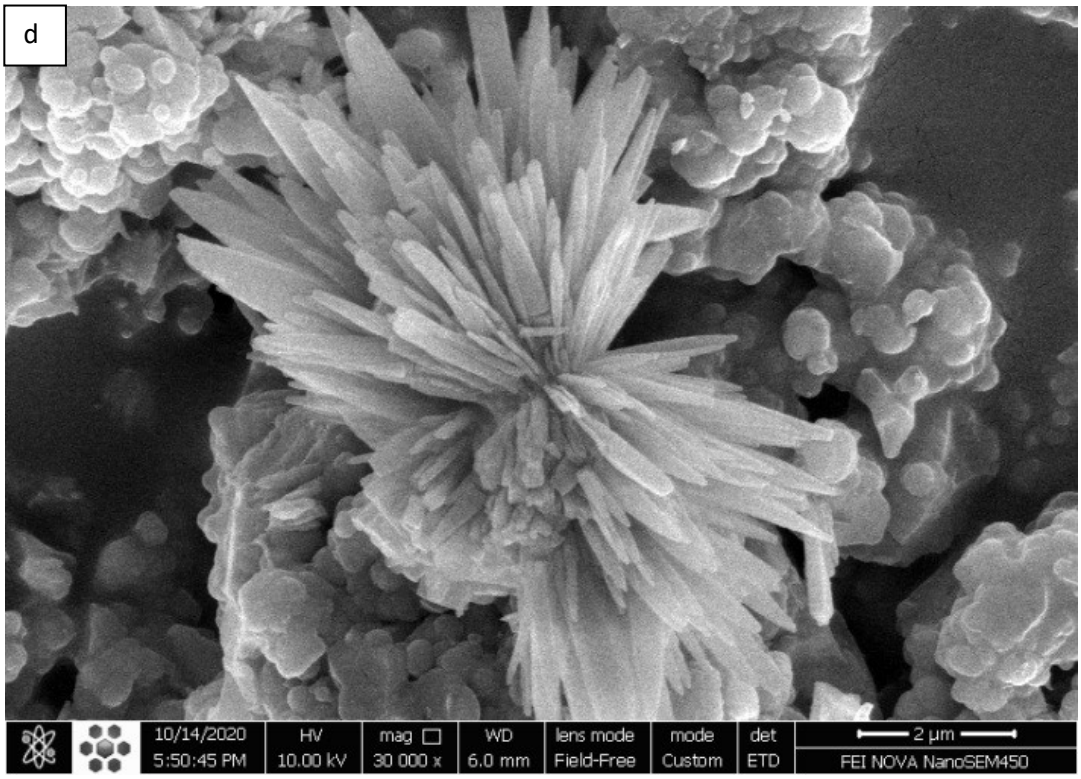
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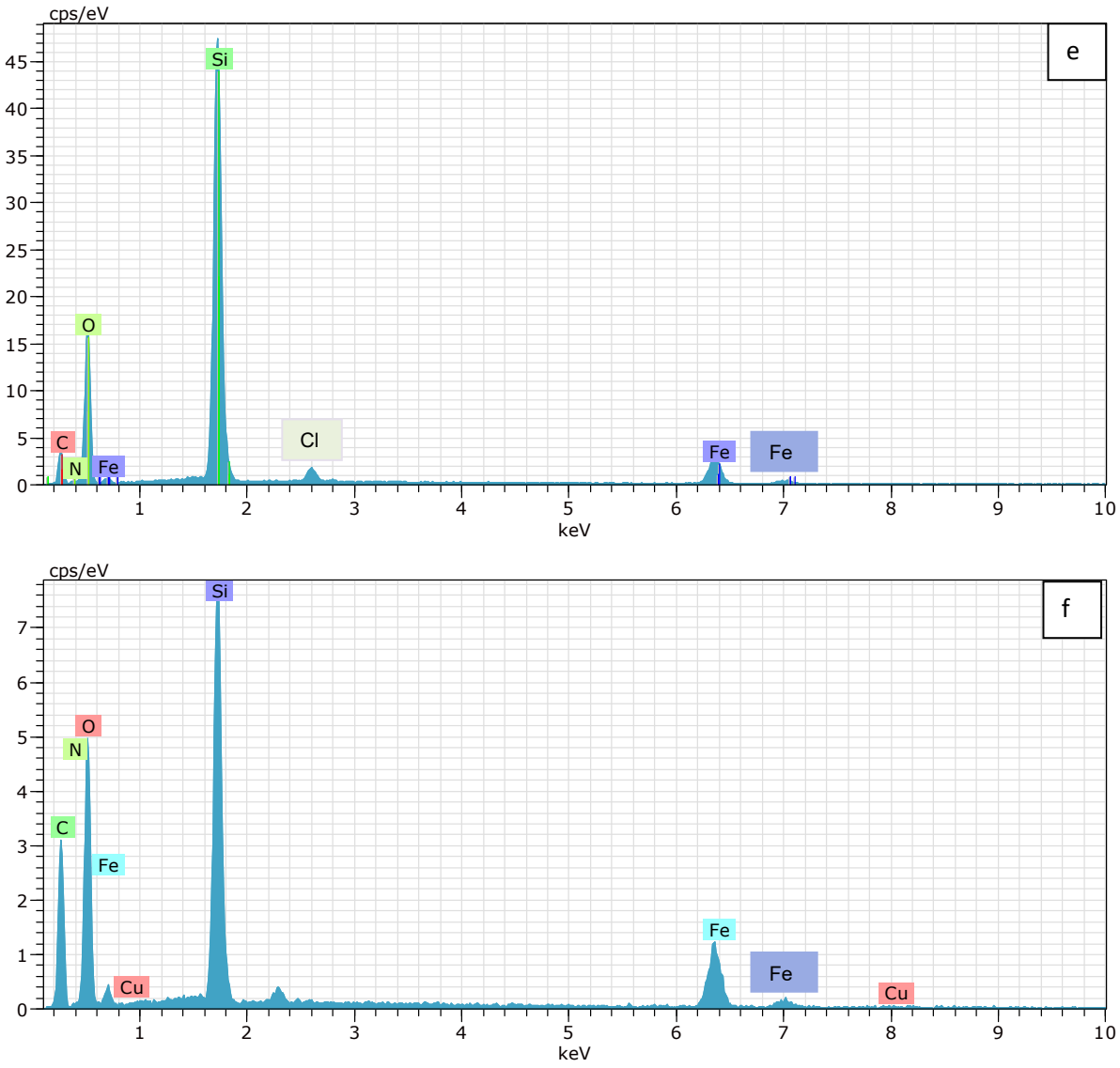


Figure S3. SEM micrograph of the prepared catalysts (a-b) magnetic MIL-88A; (c-d) Cu-exchanged magnetic MIL-88A and (e-f) elemental analyses EDS of the synthesized compounds

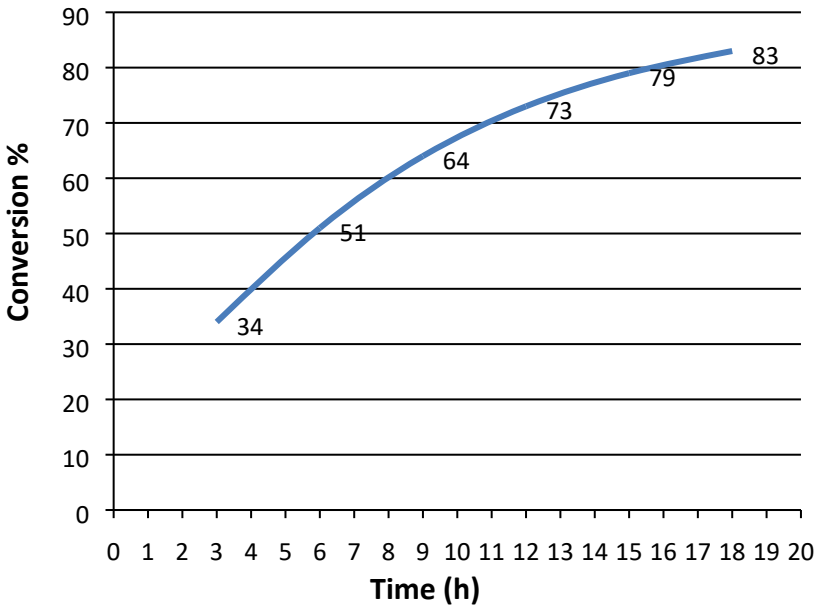
3. Reaction analyses

3.1. A typical method for the photo-induced aerobic oxidation

Substrate (0.3 mmol) and magnetic MIL-88A (15 mg, 0.7 mol%) in acetonitrile (0.6 mL) were stirred at room temperature and 7w blue LED under O_2 balloon for 20 h. The catalyst was recovered by using an external magnet, washed twice with CH_3CN and was reused in a new run. Crude product was purified by column chromatography without need to aqueous workup. ^{1}HNMR was used to determine purity of the products by comparison of results with the literature while the conversion of substrate, the yield and selectivity of product were obtained by GC analysis.

3.2. Study of the turnover number for the aerobic oxidation of toluene catalyzed by magnetic MIL-88A

Toluene (0.1 mmol) and magnetic MIL-88A (5 mg, 0.7 mol%) in acetonitrile (0.2 mL) were stirred under blue light (7w) under O_2 balloon at rt. The reaction was analyzed by GC to determine the conversion of toluene and TON.



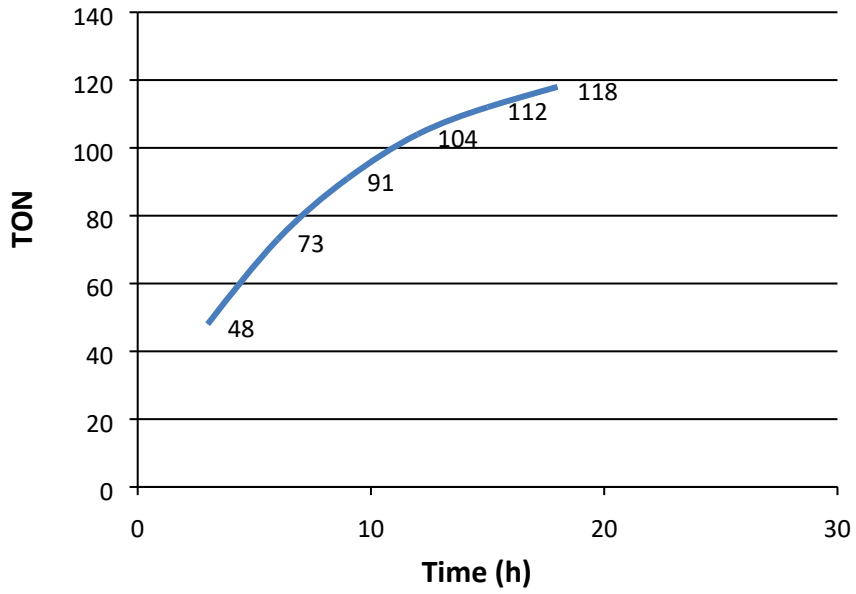
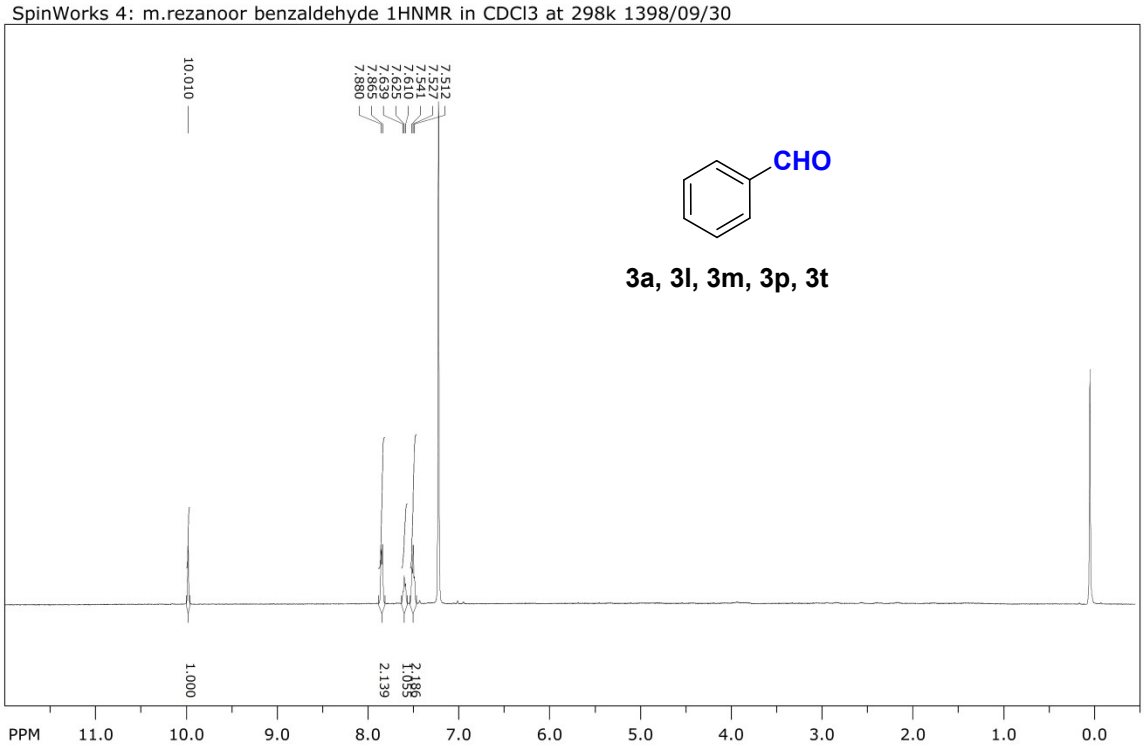


Figure S4. Reaction profile under optimized conditions

4. Copies of ^{1}HNMR



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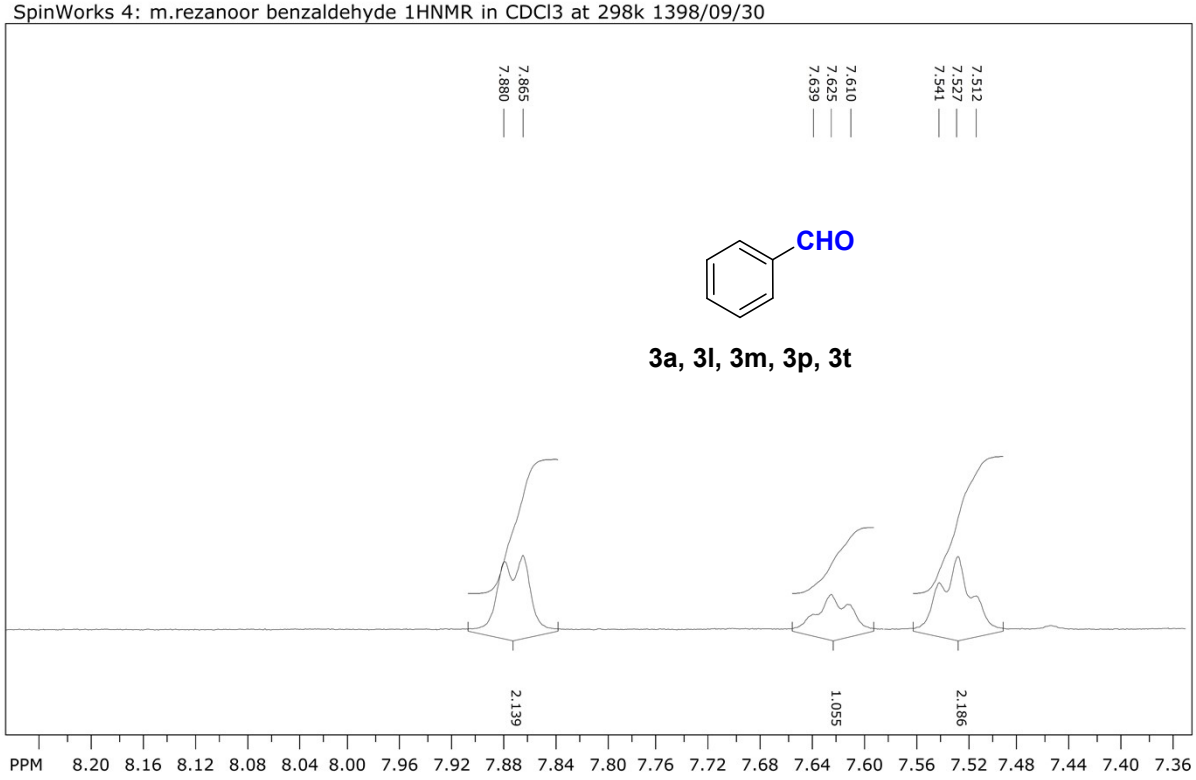

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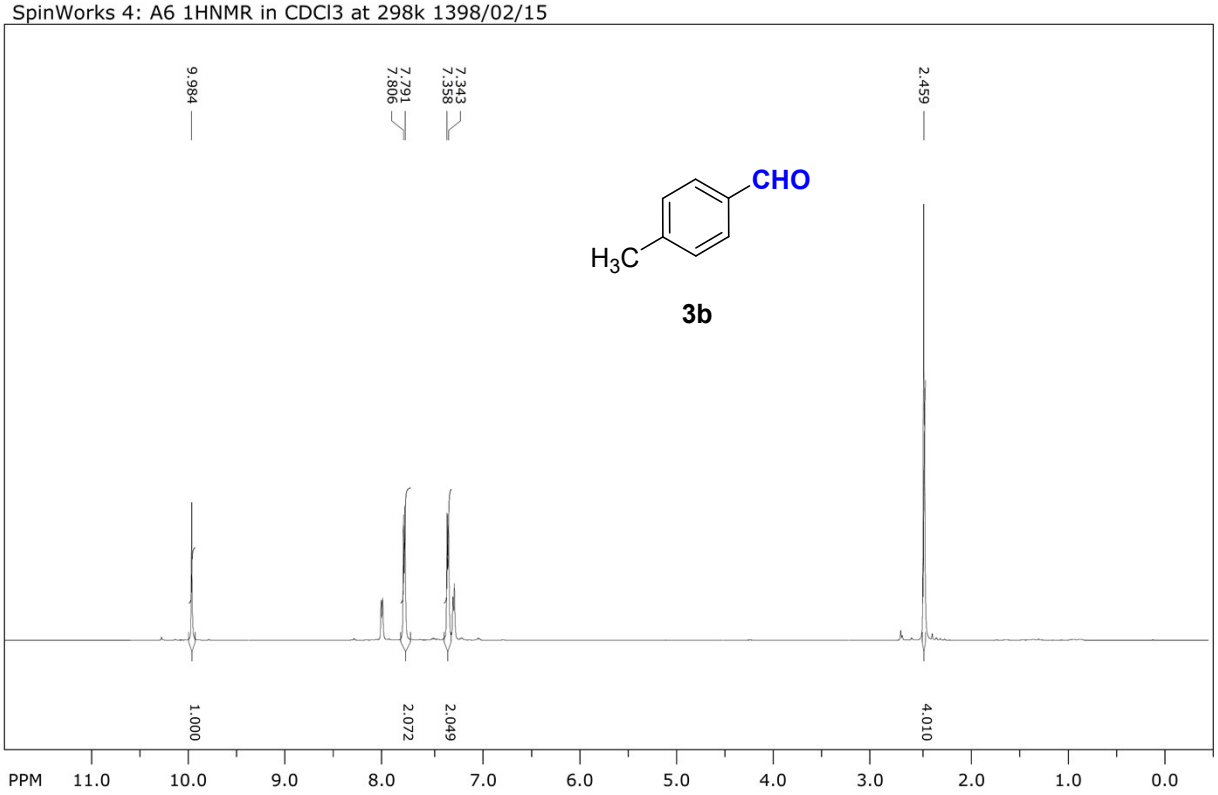

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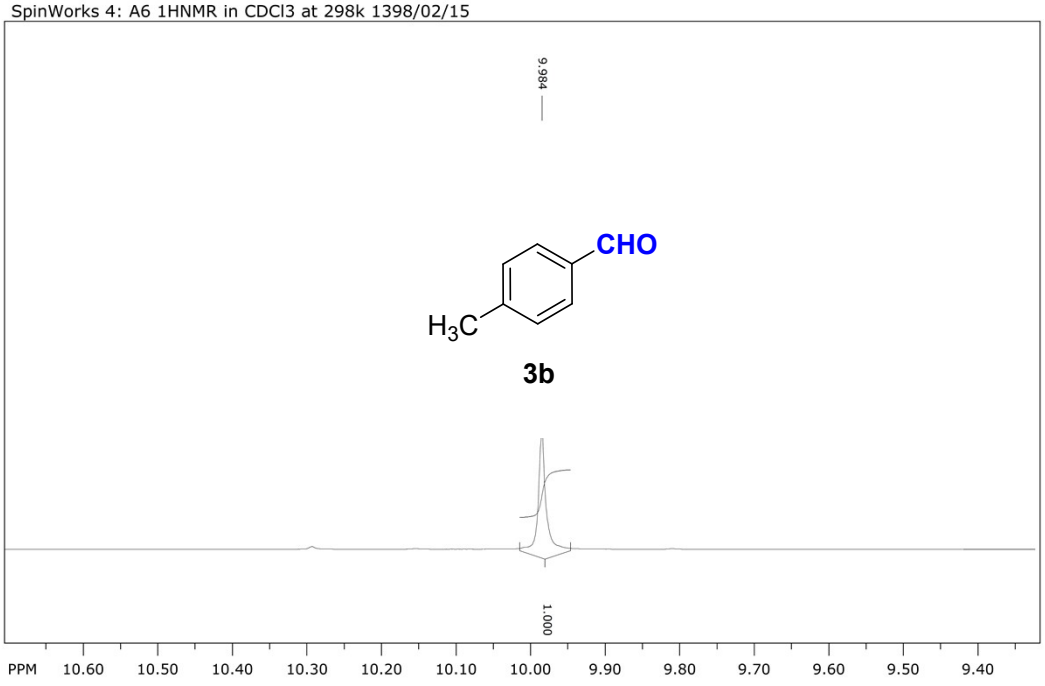

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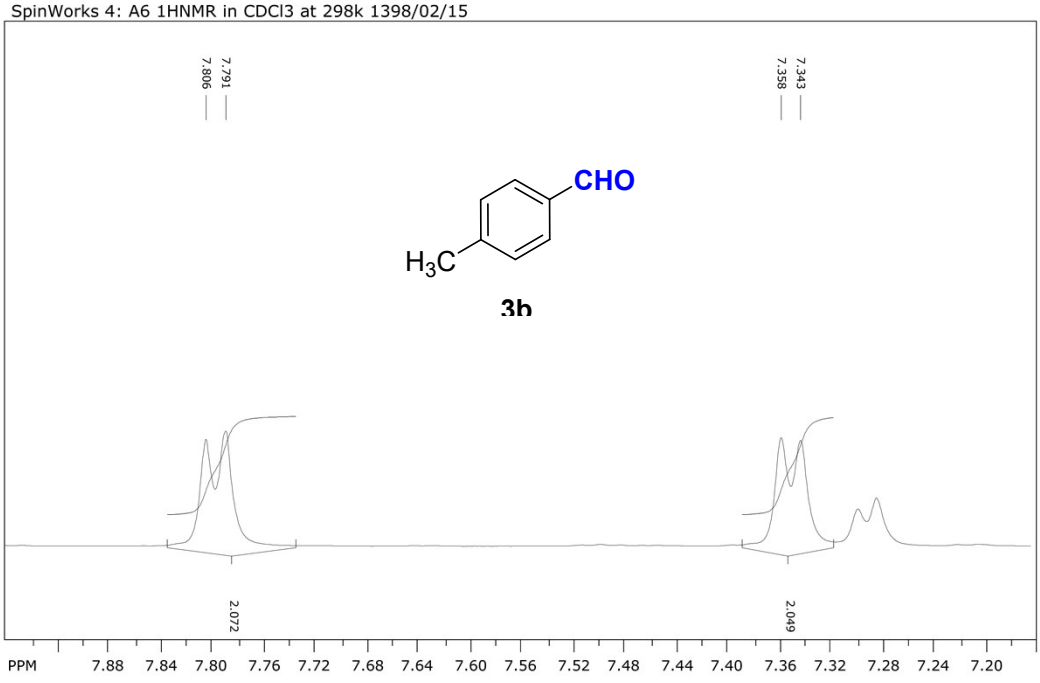

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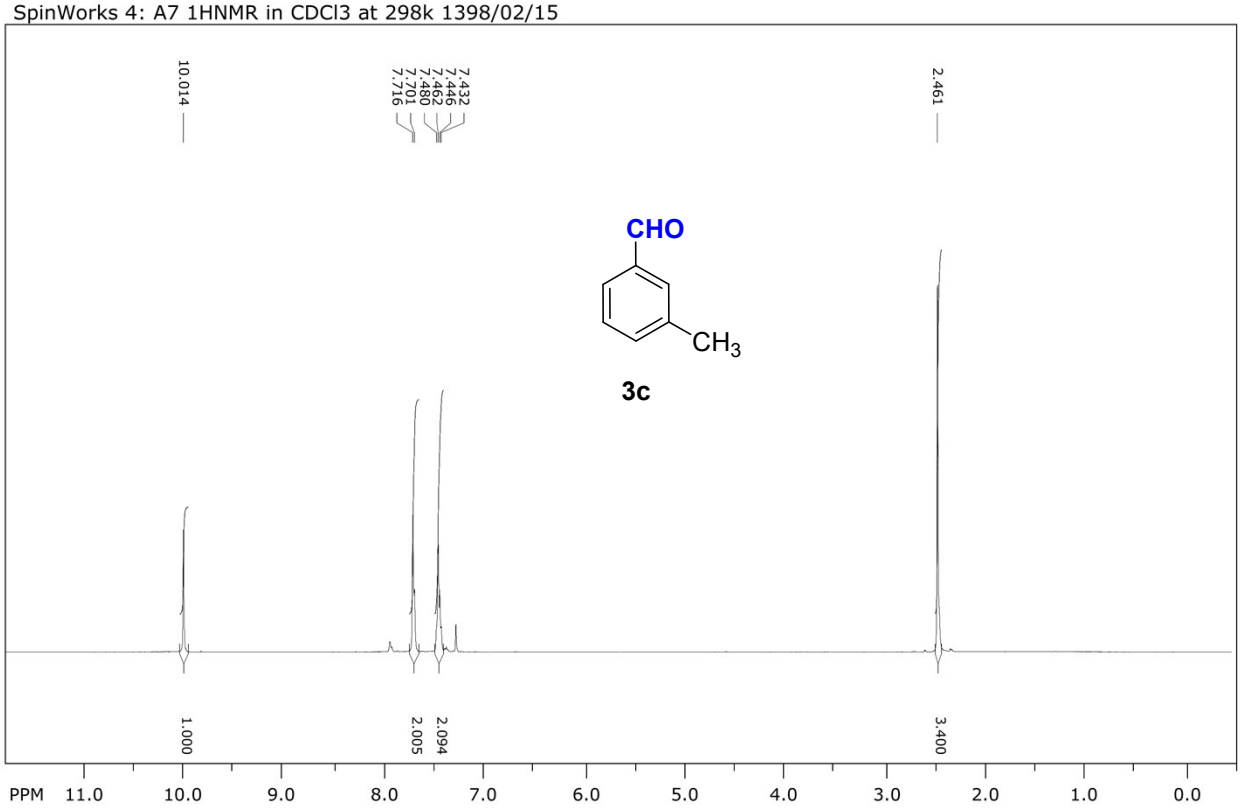

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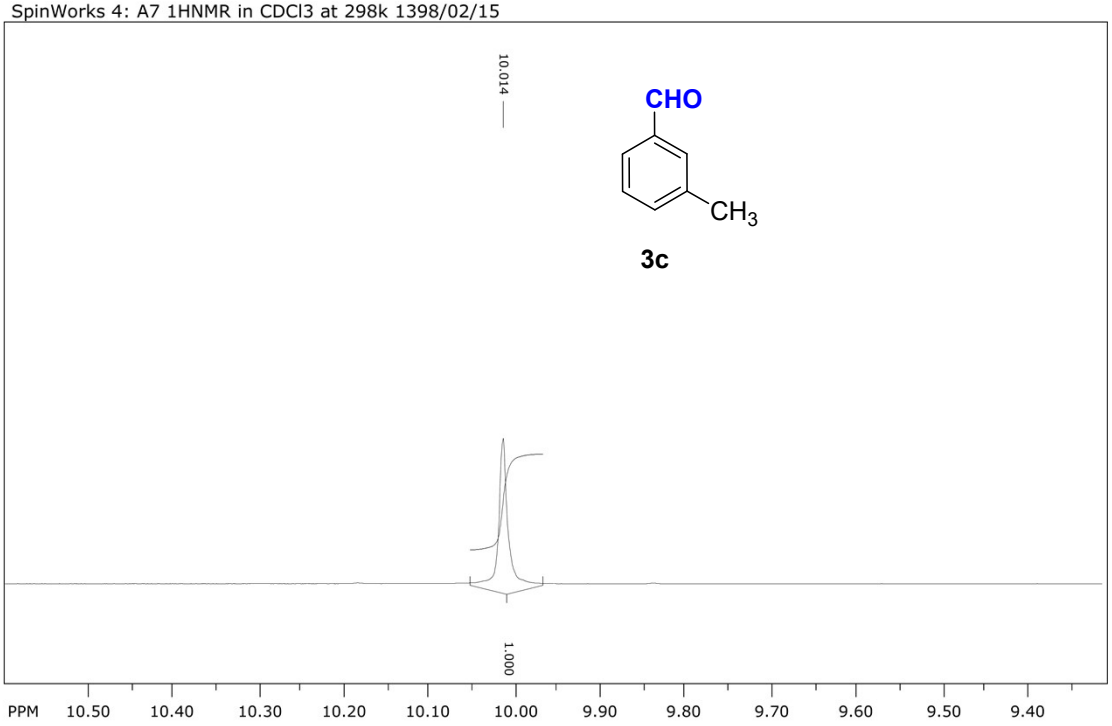

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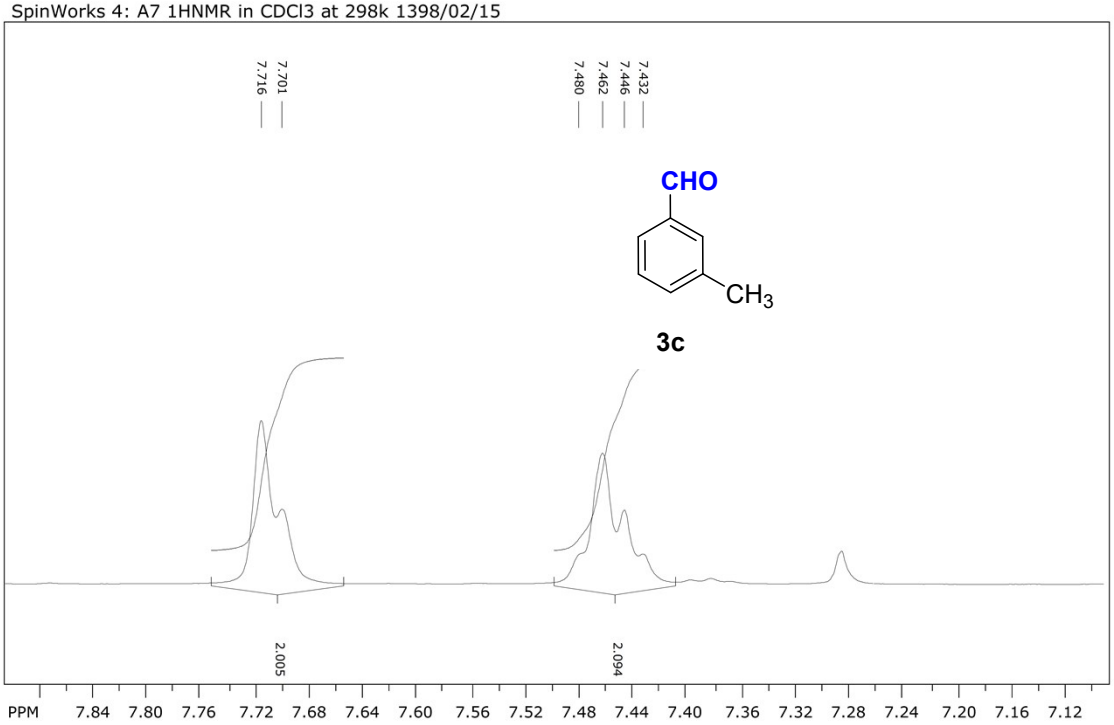

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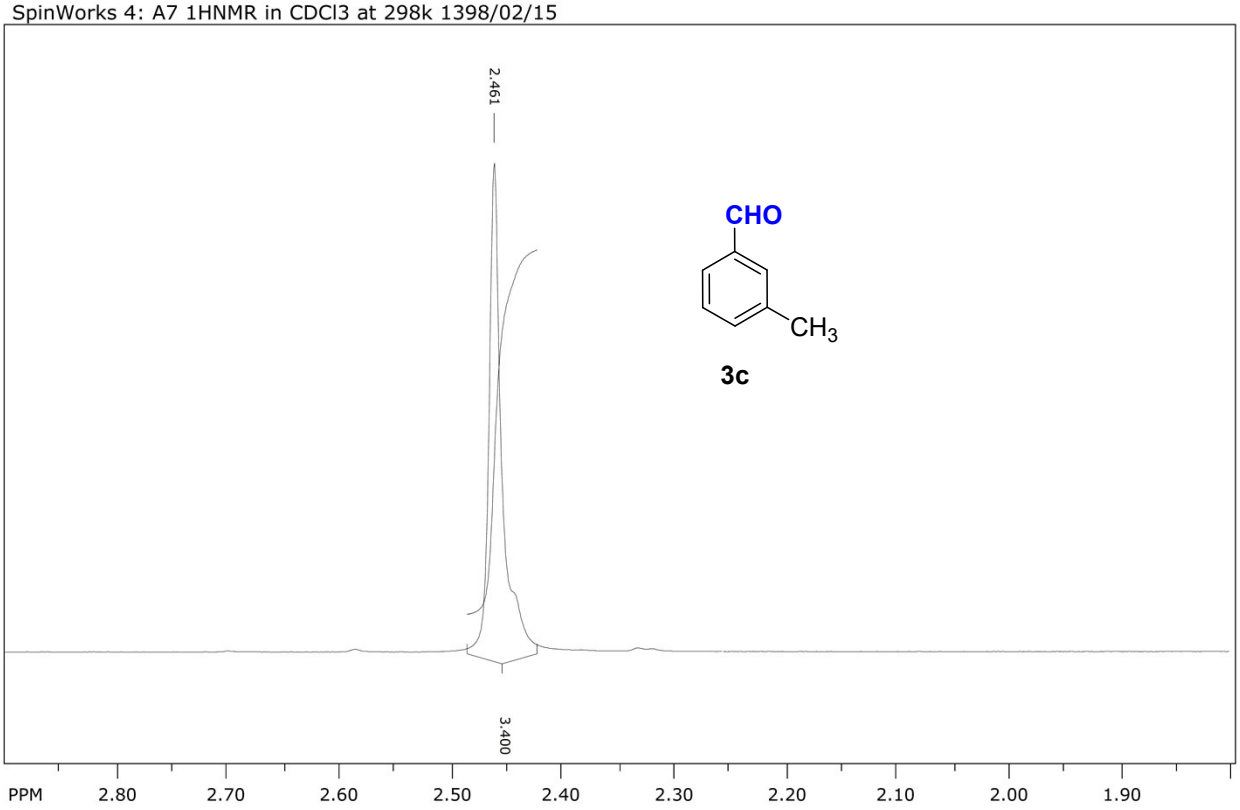

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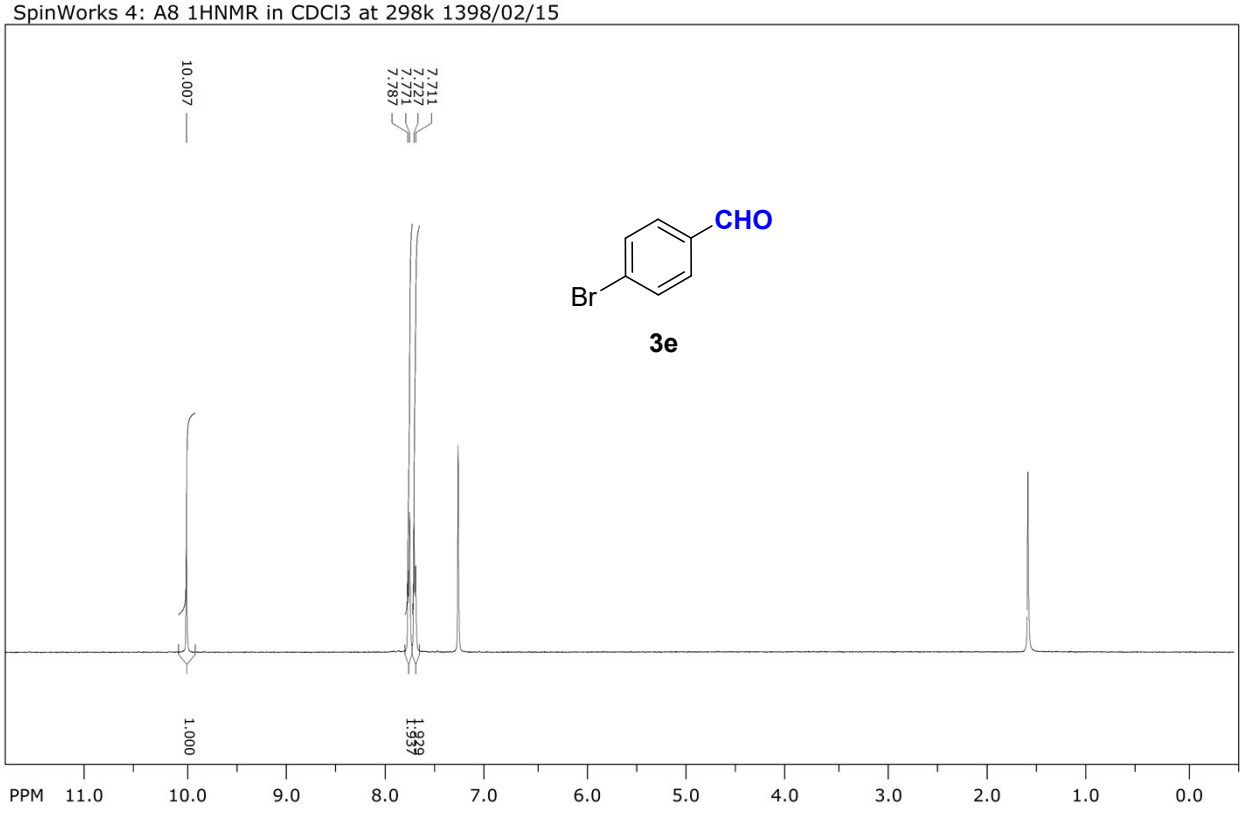

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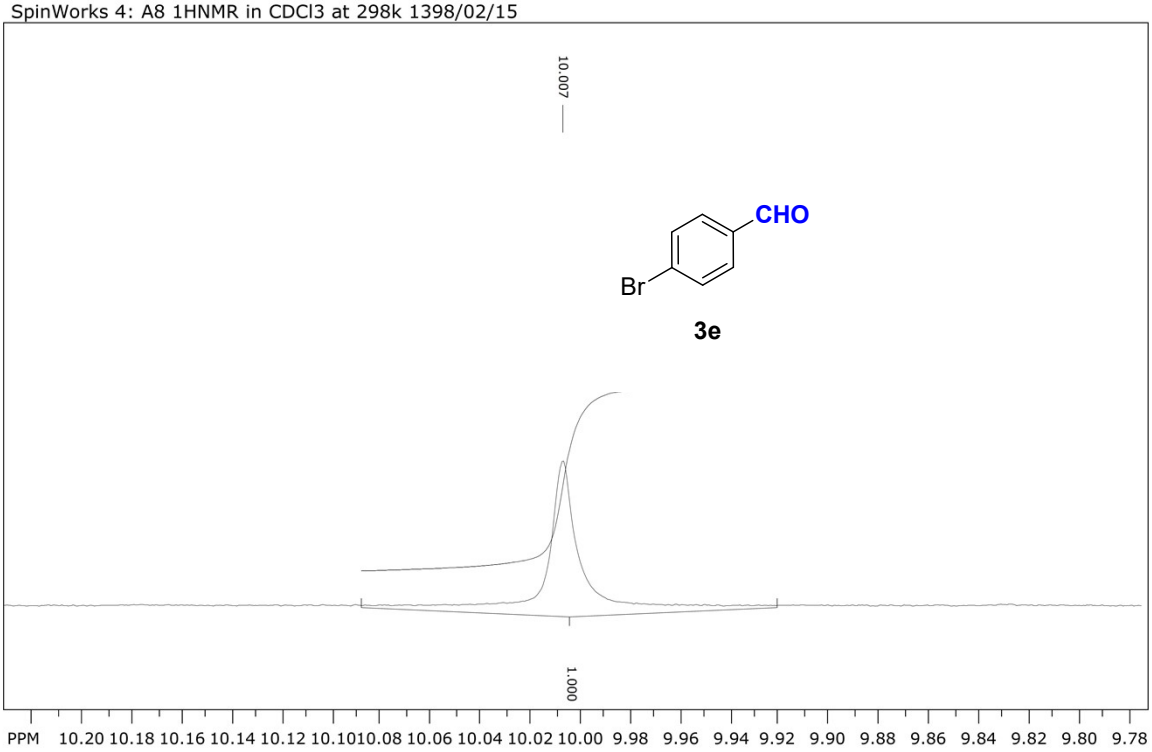

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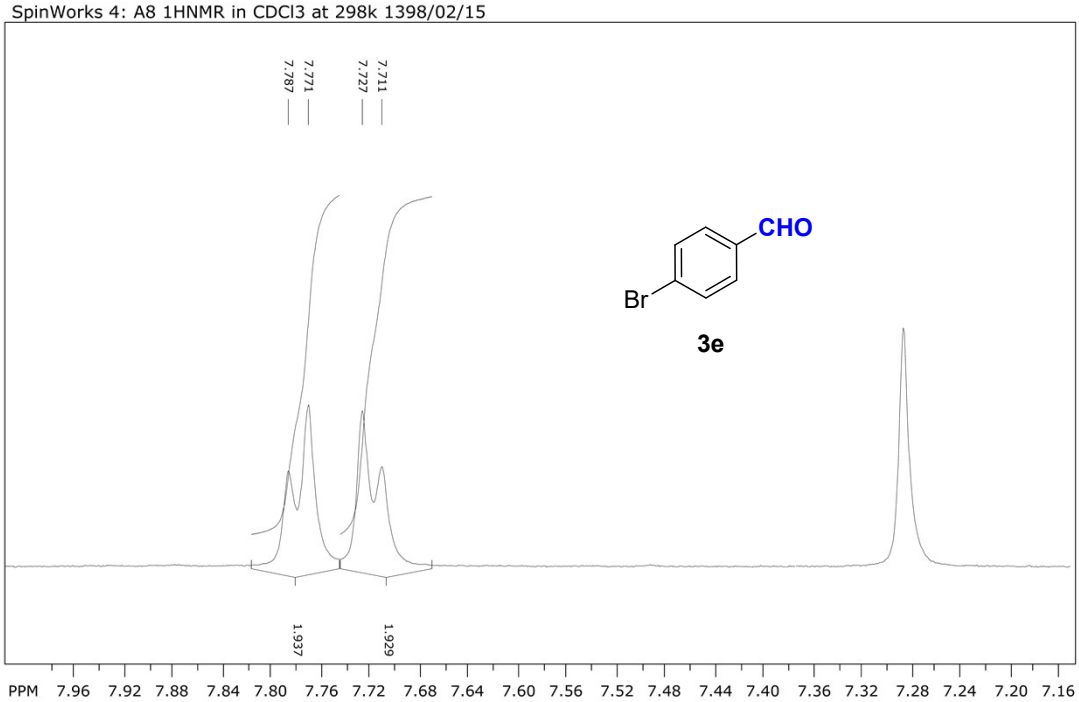

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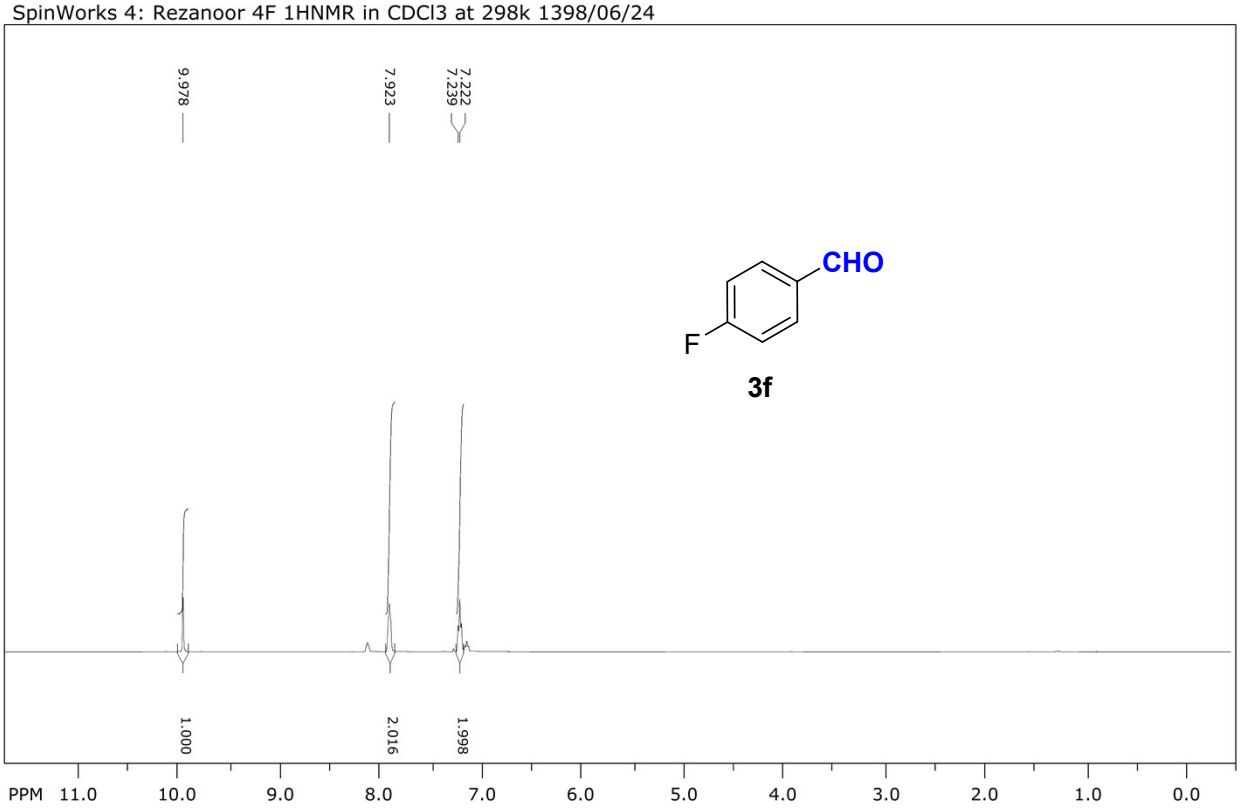

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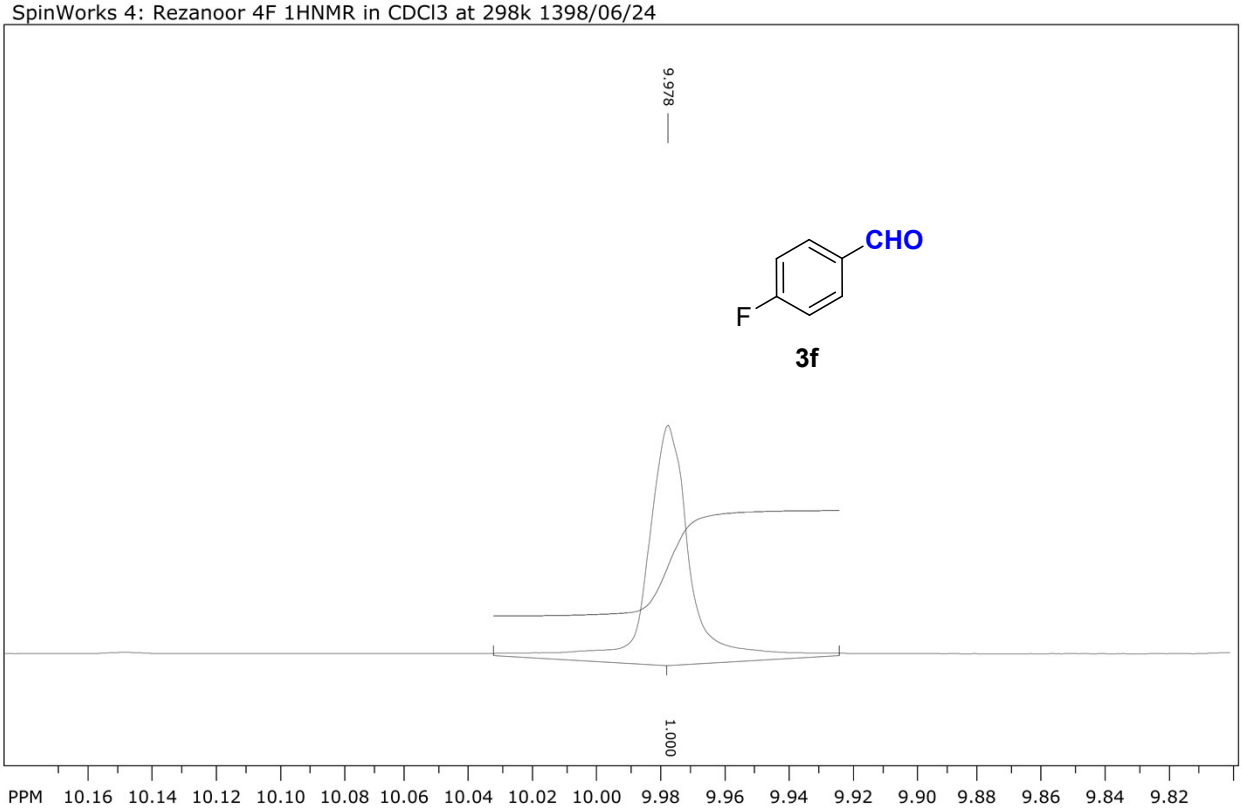

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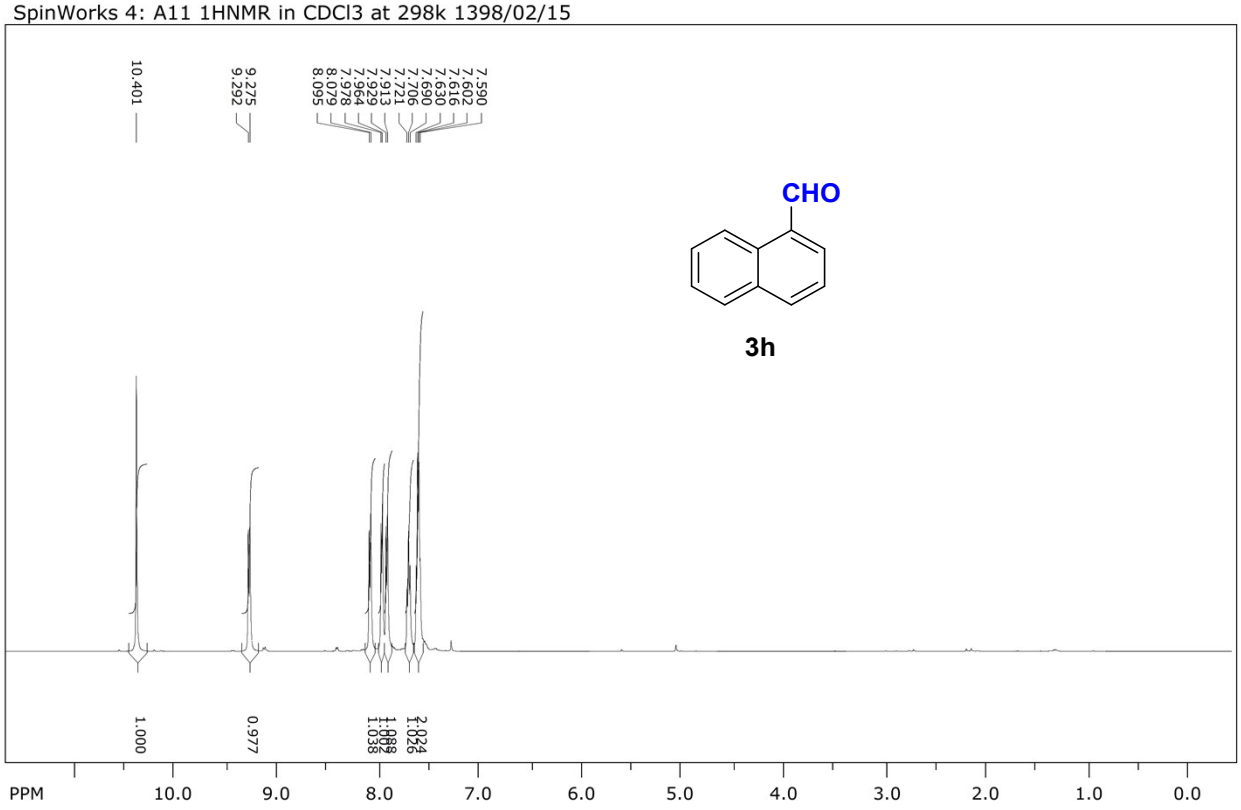

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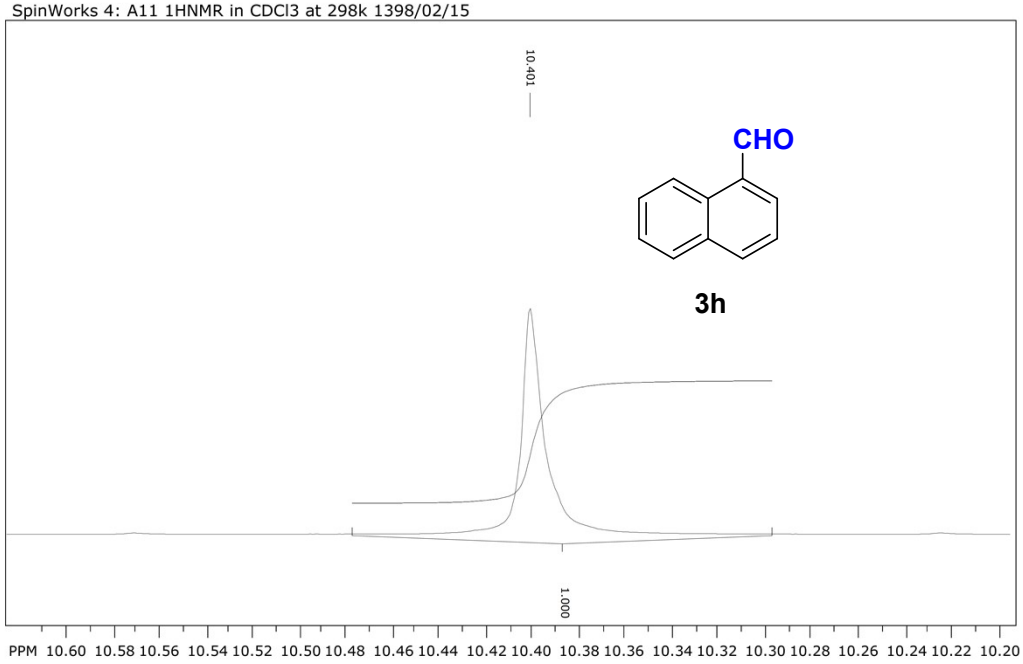

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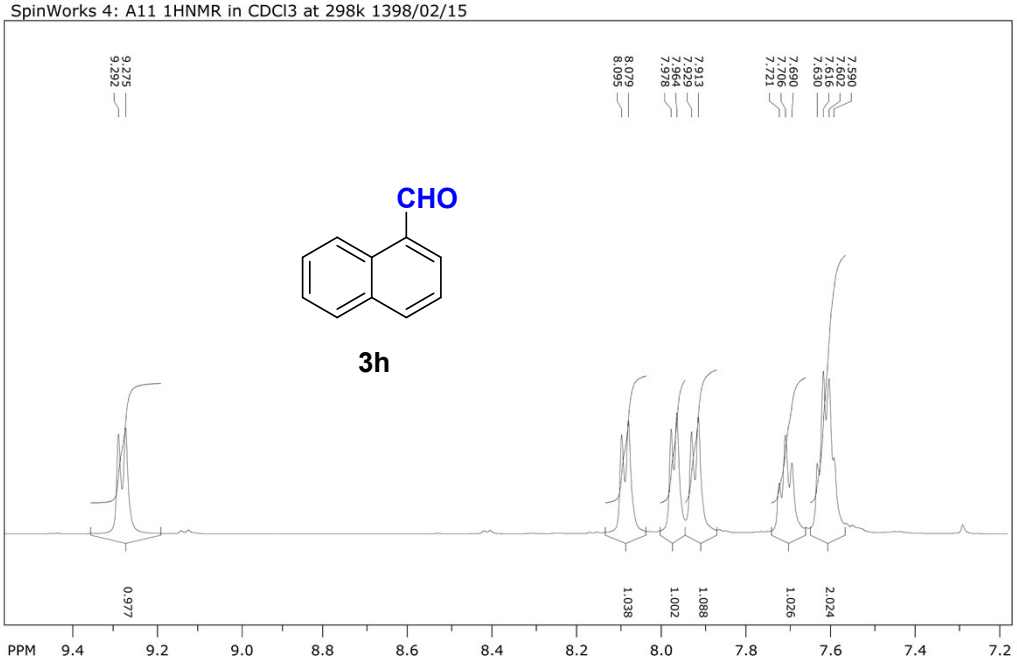

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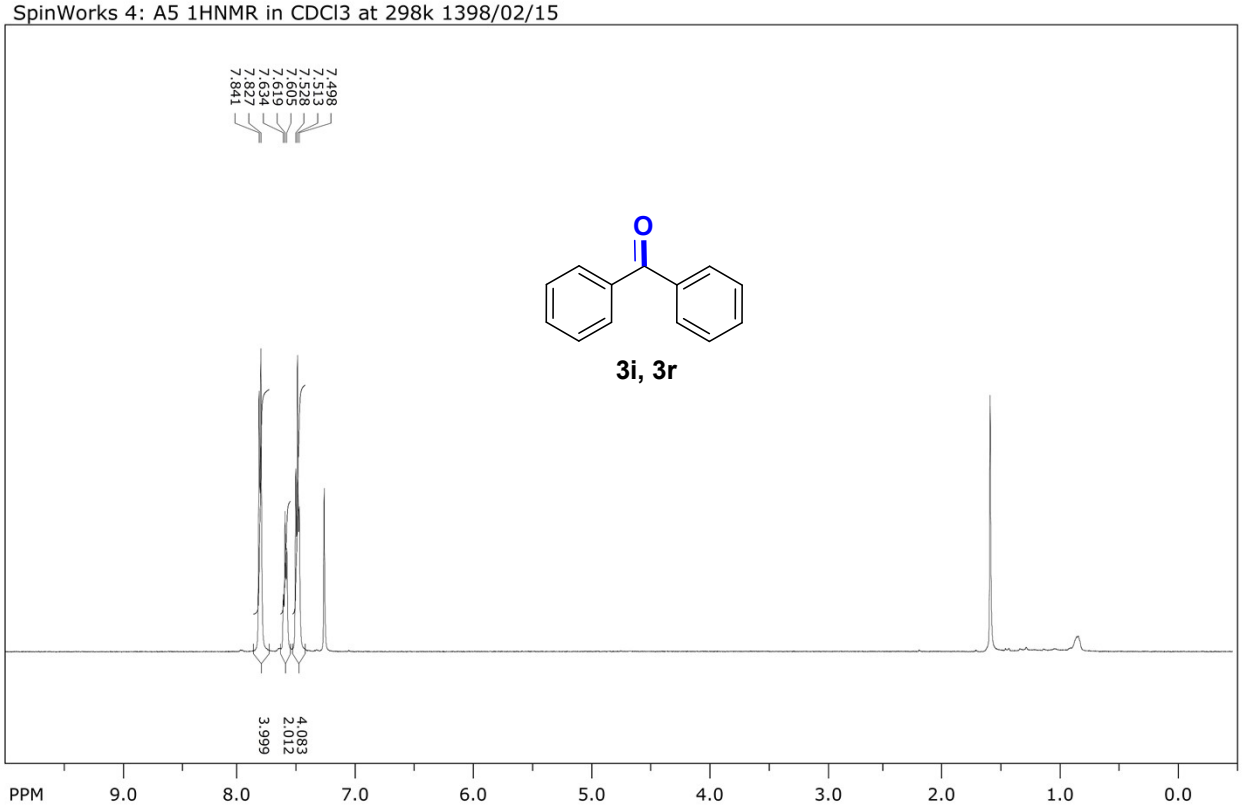

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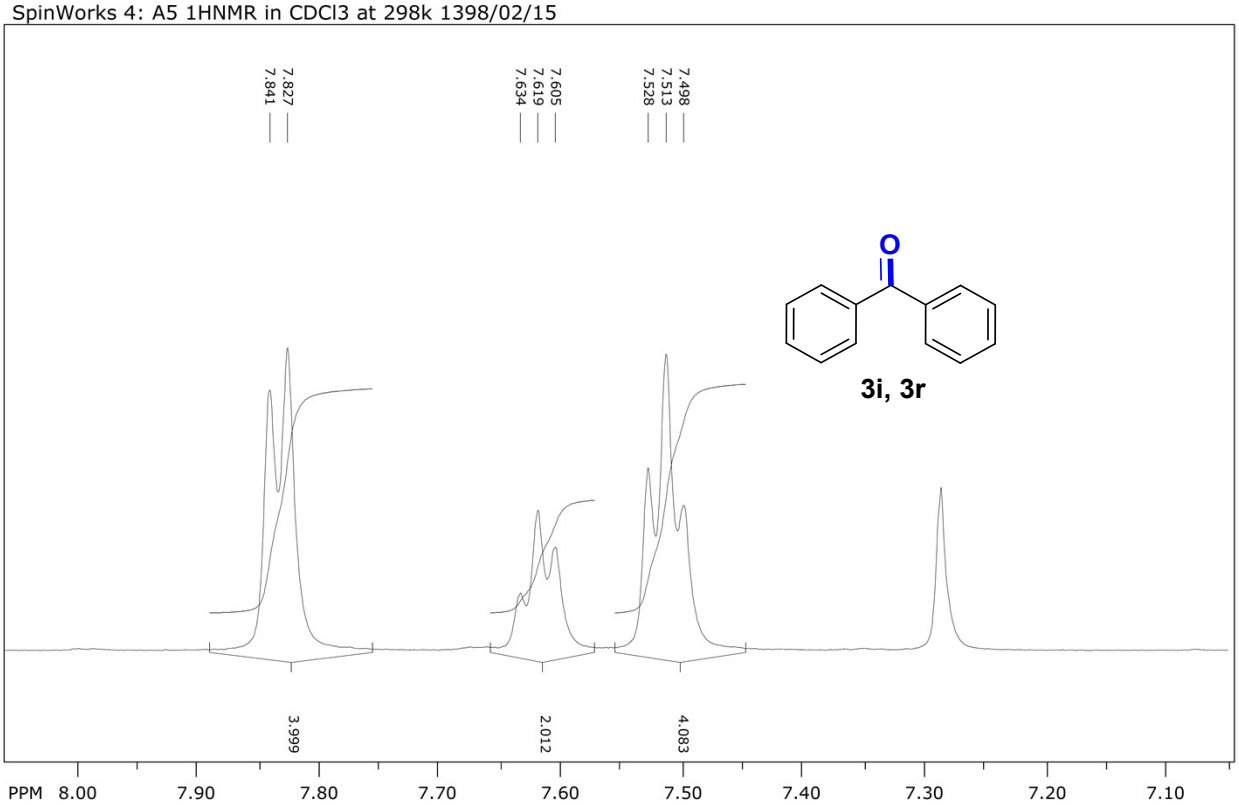
Hz/cm: 210.007 ppm/cm: 0.41990

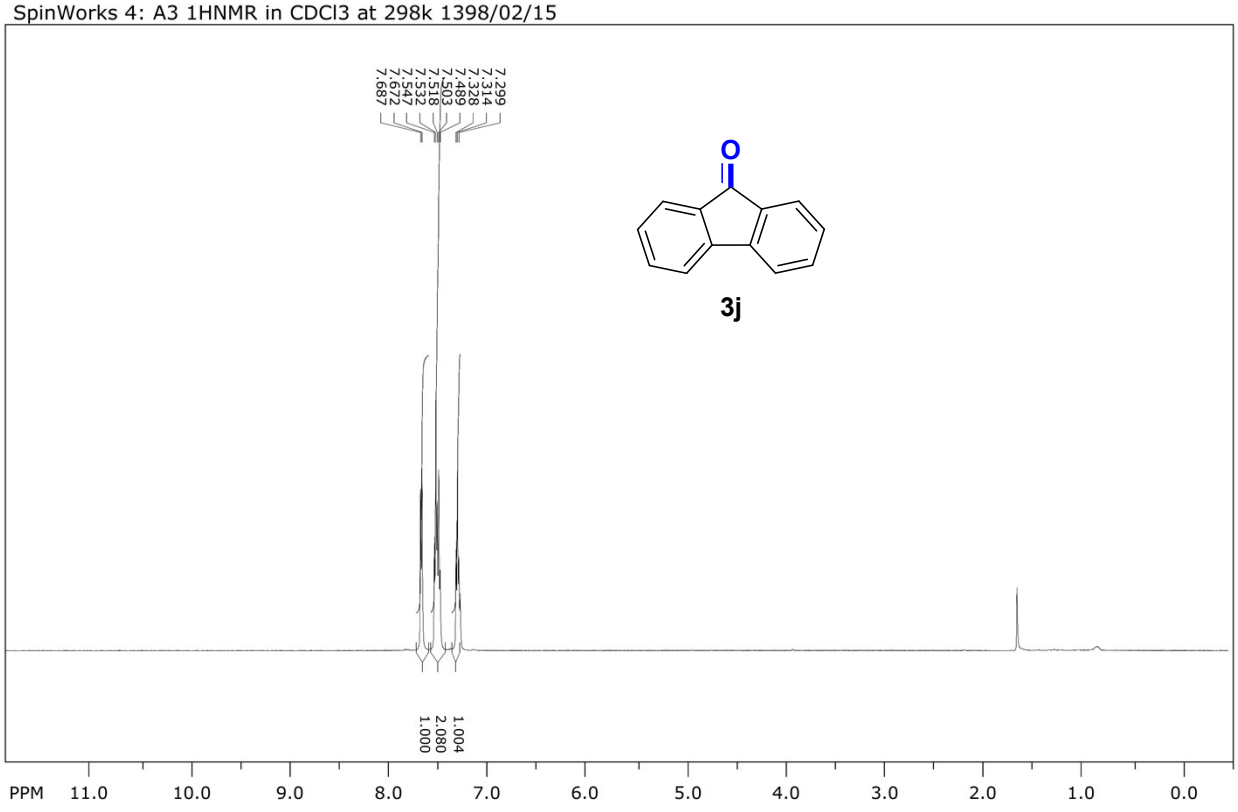
SpinWorks 4: A5 1HNMR in CDCl3 at 298k 1398/02/15



file: ...zanoor\MIL-88a\74 Benzophenone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 20.311 ppm/cm: 0.04061

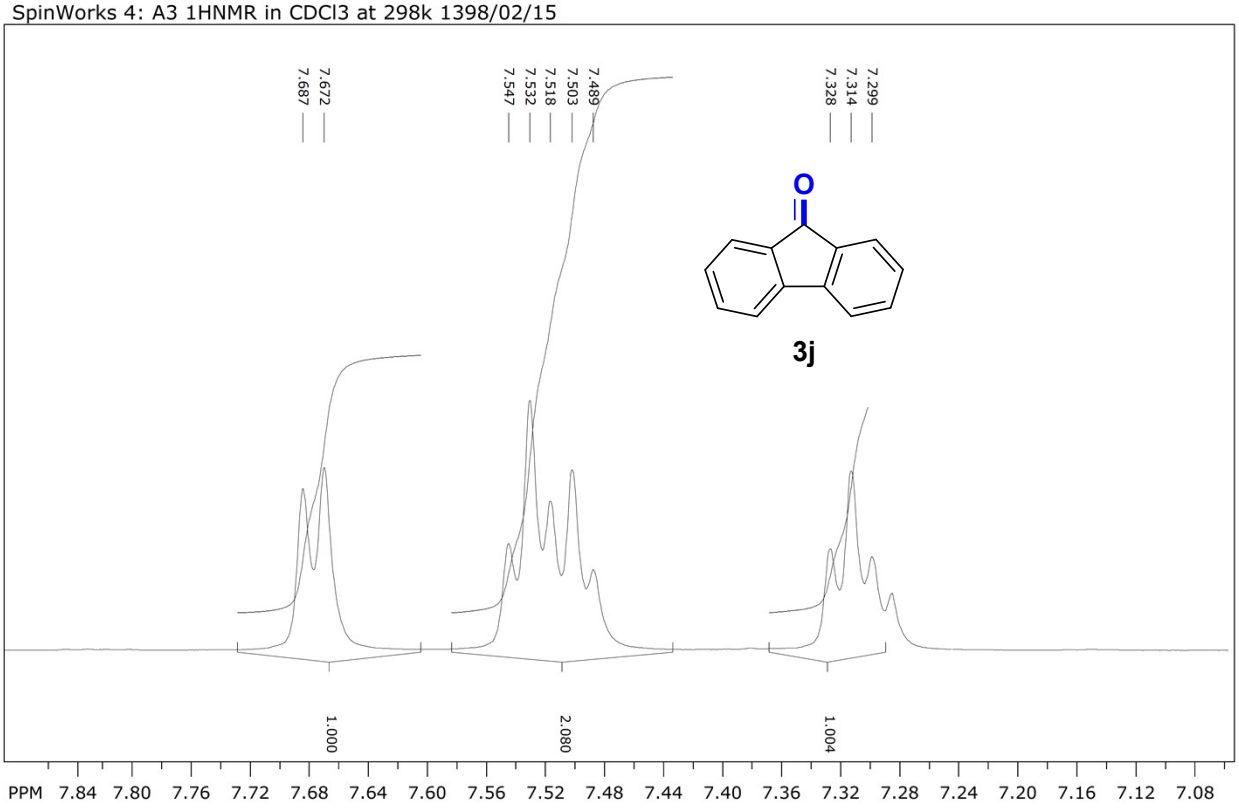
SpinWorks 4: A3 1HNMR in CDCl3 at 298k 1398/02/15



file: ...rezanoor\MIL-88a\72 Fluorenone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 247.496 ppm/cm: 0.49486

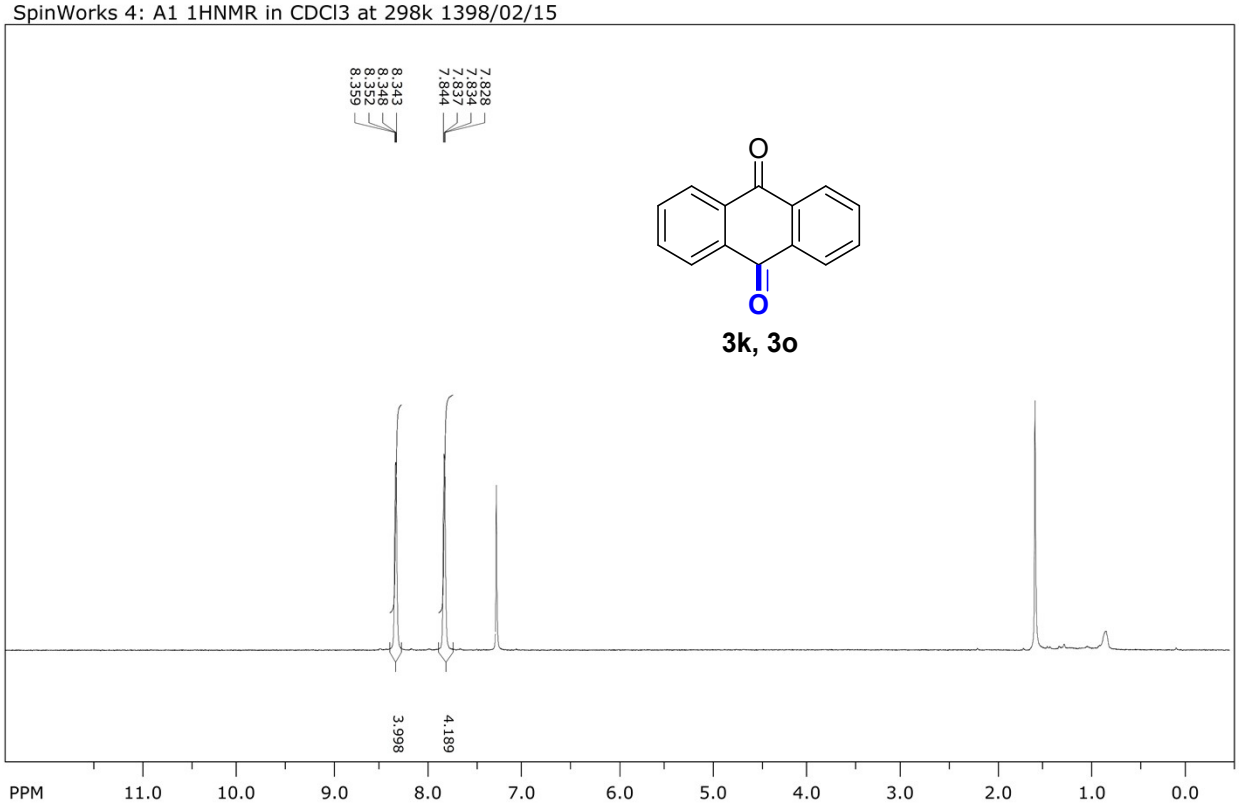
SpinWorks 4: A3 1HNMR in CDCl3 at 298k 1398/02/15



file: ...rezanoor\MIL-88a\72 Fluorenone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 16.688 ppm/cm: 0.03337

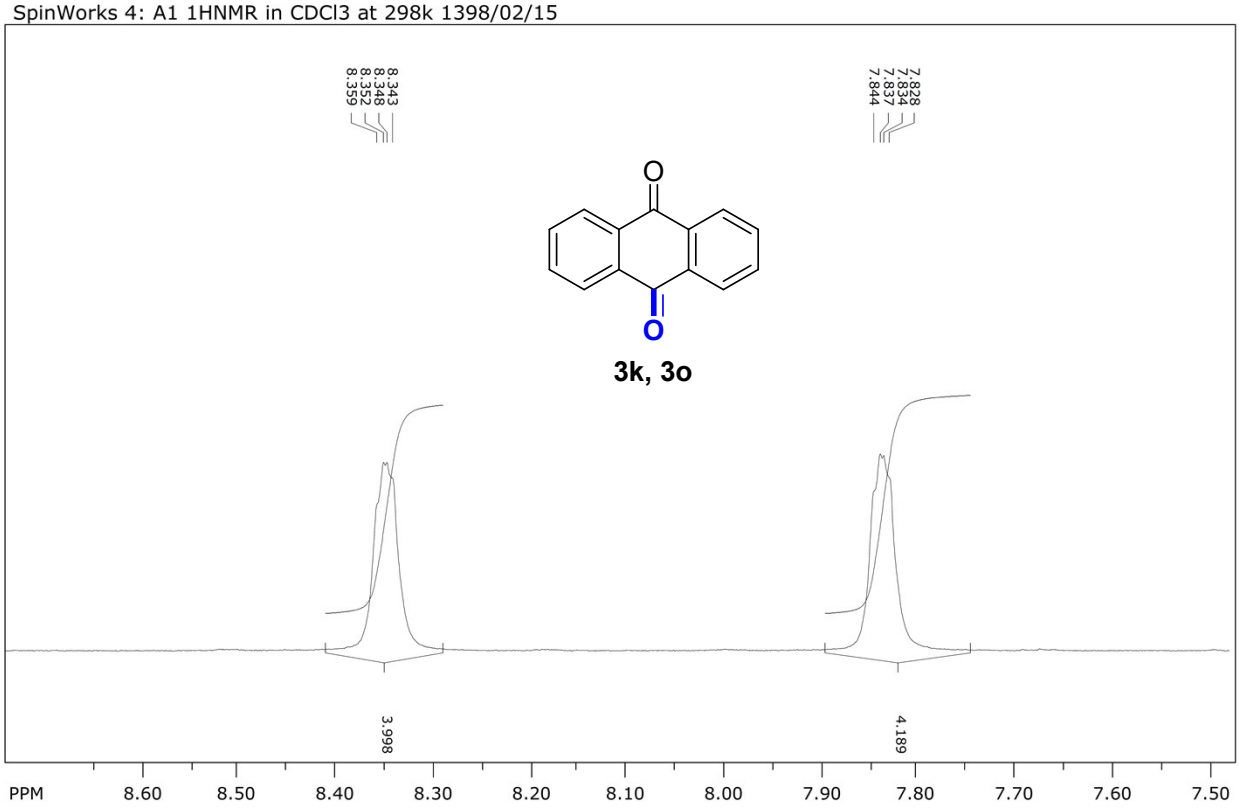
SpinWorks 4: A1 1HNMR in CDCl3 at 298k 1398/02/15



file: ...anoor\MIL-88a\70 Anthraquinone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 259.105 ppm/cm: 0.51807

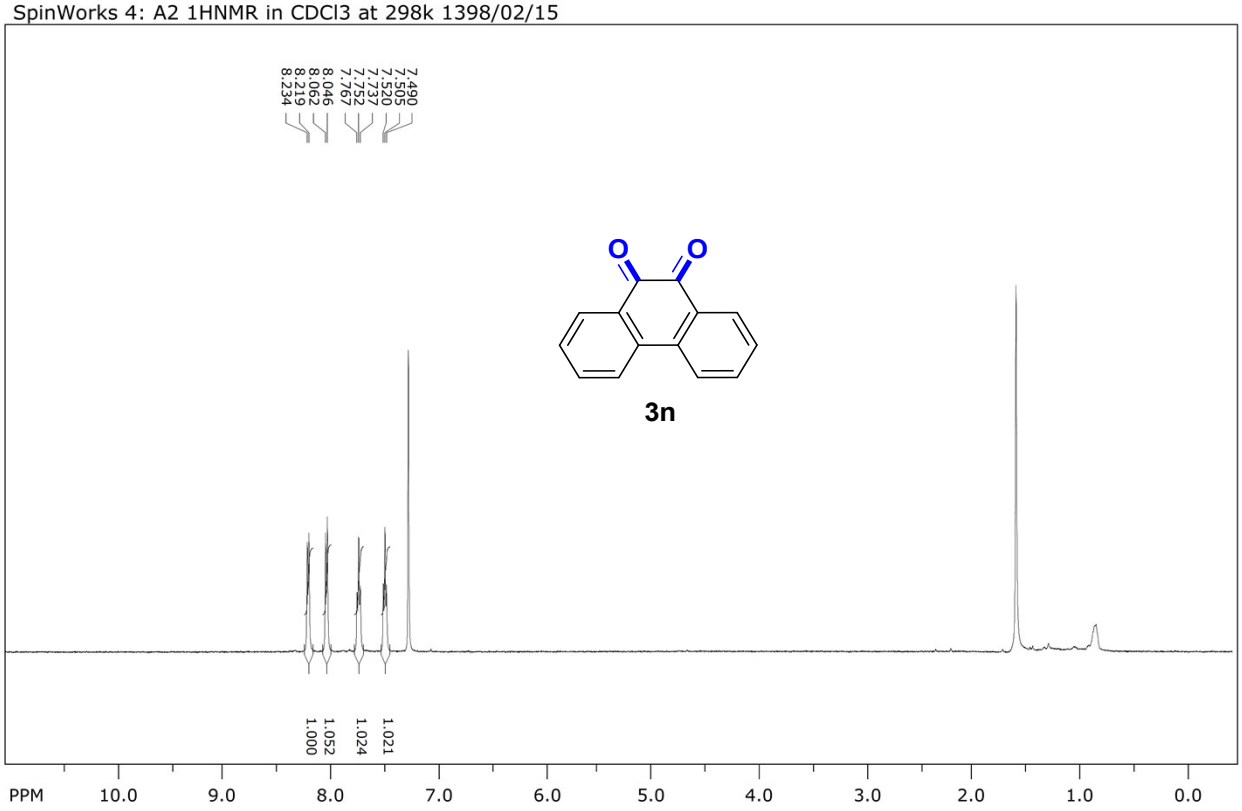
SpinWorks 4: A1 1HNMR in CDCl3 at 298k 1398/02/15



file: ...anoor\MIL-88a\70 Anthraquinone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 25.384 ppm/cm: 0.05075

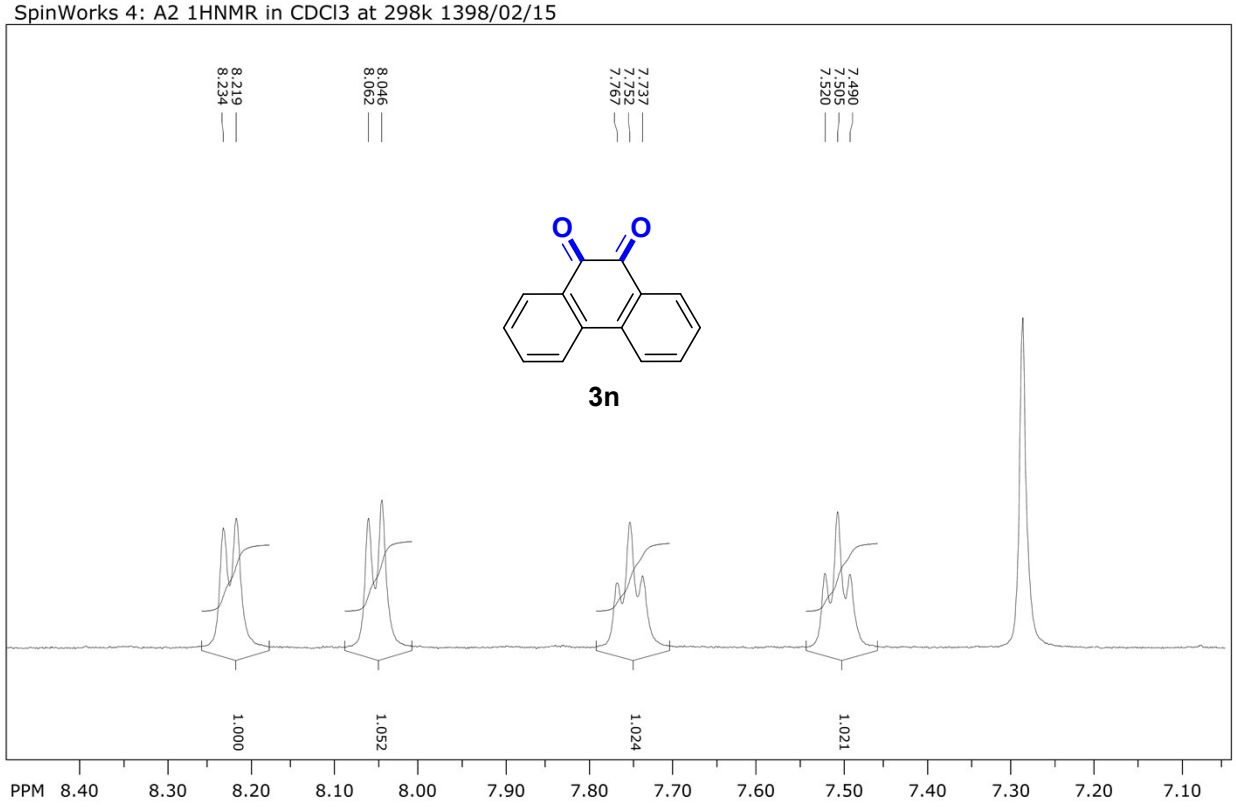
SpinWorks 4: A2 1HNMR in CDCl3 at 298k 1398/02/15



file: ...r\MIL-88a\71 Phenanthroquinone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 230.382 ppm/cm: 0.46064

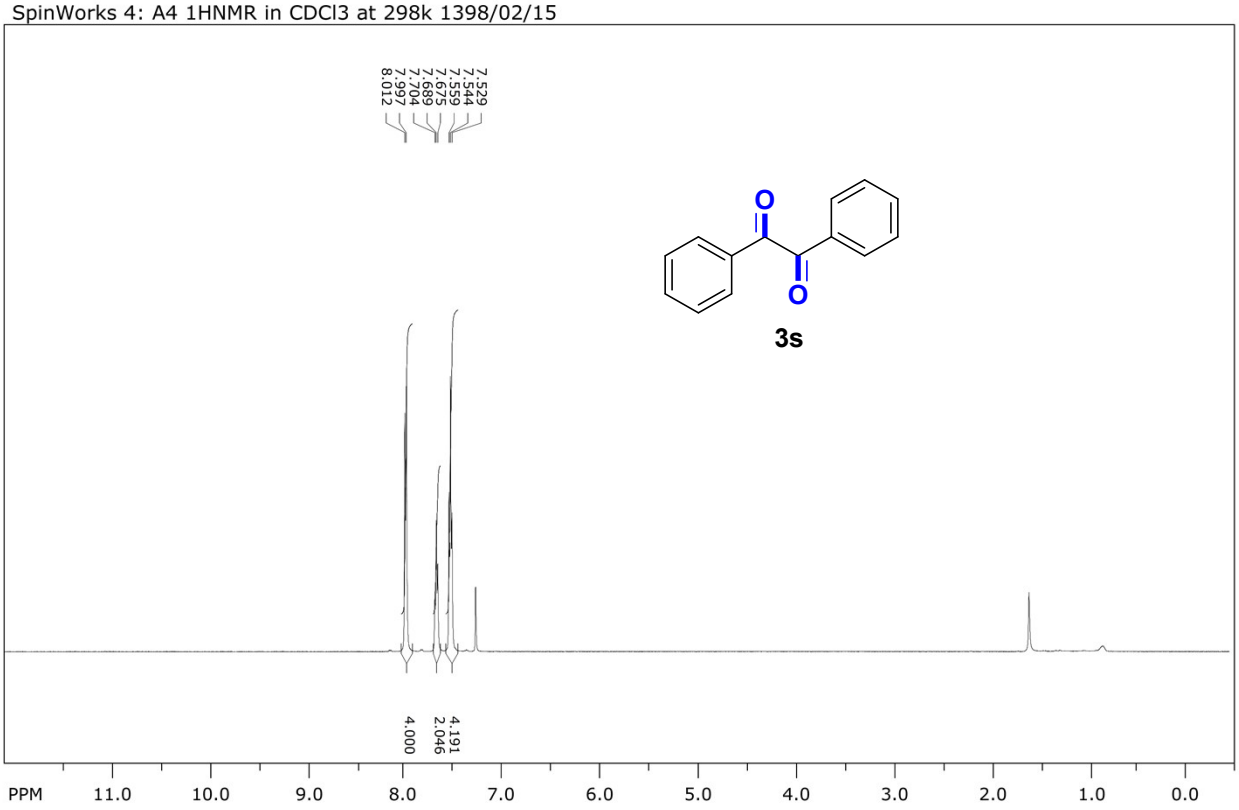
SpinWorks 4: A2 1HNMR in CDCl3 at 298k 1398/02/15



file: ...r\MIL-88a\71 Phenanthroquinone\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 28.970 ppm/cm: 0.05792

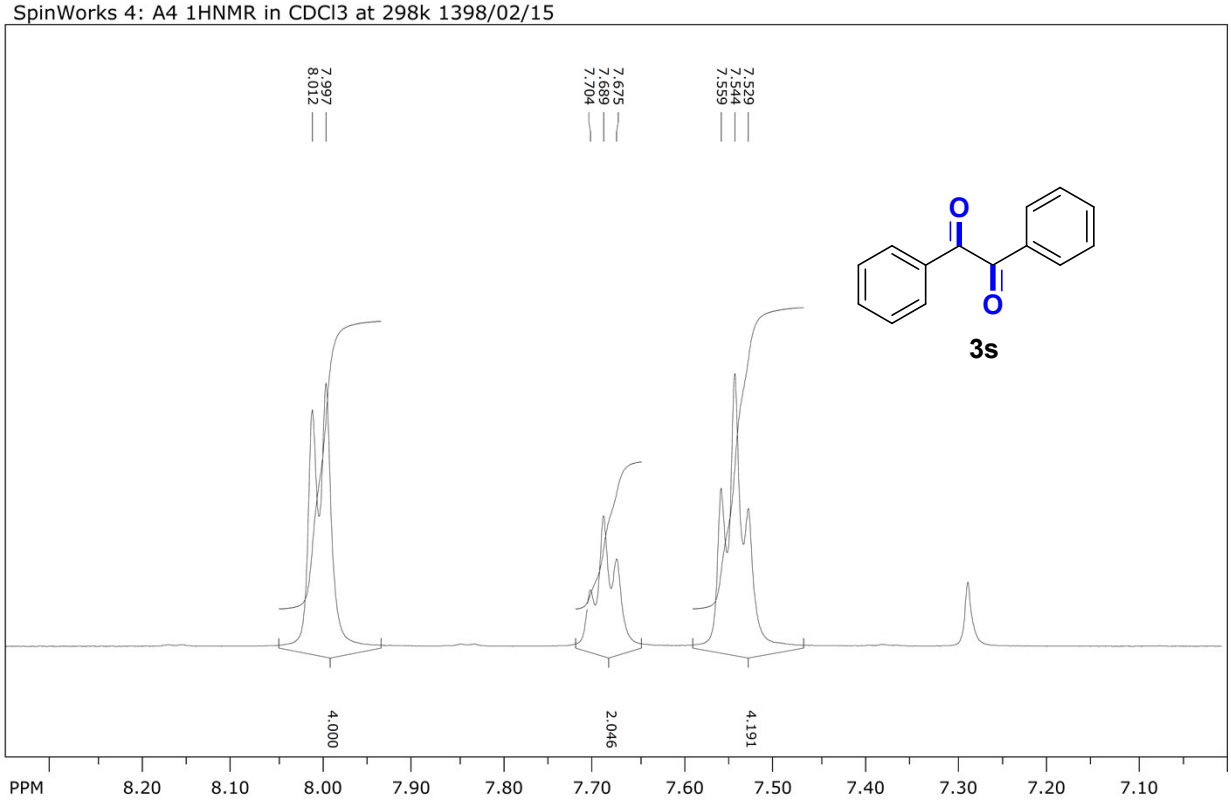
SpinWorks 4: A4 1HNMR in CDCl3 at 298k 1398/02/15



file: ...ata\rezanoor\MIL-88a\73 Benzil\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 251.855 ppm/cm: 0.50358

SpinWorks 4: A4 1HNMR in CDCl3 at 298k 1398/02/15



file: ...ata\rezanoor\MIL-88a\73 Benzil\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 30988 points
width: 10330.58 Hz = 20.6557 ppm = 0.333374 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 26.997 ppm/cm: 0.05398