MOFs Come up to Scratch: An Environmentally Benign Route to Oxidative [4+2] Cycloaddition on Maleimides Solely via MOF in Water

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Abstract: The first Diels-Alder reaction of vinyl arenes with ene systems catalyzed by MOFs is reported. Maleimides and maleic anhydride were annulated/dehydrogenated on styrenes in the presence of a mixed-metal (FeNi)MIL-88A catalyst. Neither additional oxidant nor a source of halogen is needed to drive this oxidative [4+2] cyclization reaction. Kinetic evidence such as activation entropy corroborates the proposed concerted mechanism. The reaction proceeds merely through a cost-effective catalyst in water as the greenest solvent. The product of annulation of styrene with maleic anhydride was used for the first L-selective annulative π-extension on naphthalene.

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Experimental Procedures

I-General Information

All commercially available reagents were used without further purification. Unless noted otherwise, all reagents were purchased from Acros Organics and Merck Millipore. TLC was conducted on silica gel 250 micron, F254 plates. ^{1}HNMR spectra were recorded at room temperature on a Bruker 400 and 500 MHz spectrometers, using $CDCl_3$ as solvent. Chemical shifts are reported in ppm with TMS as an internal standard (TMS: δ 0.0 ppm). ^{13}C NMR spectra are referenced from the solvent central peak. Chemical shifts are given in ppm. *N*-benzylmaleimide, *N*-cyclohexylmaleimide and *N*-phenethylmaleimide were prepared using the instructions given in previous papers.

II-The synthesis of nickel-exchanged MIL-88A ((FeNi)MIL-88A)

$FeCl_3.6H_2O$ (2.8 mmol, 0.757 g) and $Ni(NO_3)_2.6H_2O$ (1.4 mmol, 0.4 g) were added to a vessel and 30 mL deionized water was added. Then fumaric acid (4.2 mmol, 0.487 g) was added and the resulted mixture stirred for 15 minutes. The mixture was transferred into a Teflon-lined autoclave and heated at 100 °C for 15 h. After filtration and washing with hot water, 0.35 g mustard color powder was obtained. The product was analyzed by various spectroscopic methods.

III-The synthesis of silver-deposited on MIL-88A

MIL-88A was prepared according to literature. Fumaric acid (4.2 mmol, 0.487 g) and $FeCl_3.6H_2O$ (4.2 mmol, 1.13 g) were added to a vessel containing 21 mL deionized water. The mixture stirred for 1 h at room temperature and then transferred into a 70 mL Teflon-lined autoclave. The autoclave put in an oven and heated to 70 ^oC for 8 h. After cooling to room temperature and centrifuge, the resulted solid was washed thoroughly with hot water and ethanol and dried at 100 ^oC to yield MIL-88A. $AgNO_3$ (0.25 mmol, 37 mg) was dissolved in a 35 mL 1:1 solution of deionized water and ethanol. 0.25 g of the as-prepared MIL-88A was added to the resulting solution and heated to 85 ^oC for 1 day. The solid was washed with water and ethanol and dried at room temperature (led to 0.2 g yellowish-orange powder).

IV-General procedure for the synthesis of Benzo[e]isoindole-1,3-diones

In a vial equipped with a stir bar, vinyl arene (3 mmol), maleimide (1 mmol) and (FeNi)MIL-88A (0.2 g, 0.017 mol%) were dissolved in water (5 mL) and capped. The resulting mixture was heated in an oil bath at 100 ^oC for 20 h. After extraction with dichloromethane and drying the organic layer over sodium sulfate, the solution was evaporated under reduced pressure. The organic residue was purified by column chromatography. Pure benzo[e]isoindole-1,3-dione was obtained after recrystallization of the product from n-hexane.

V-General procedure for the synthesis of Naphtho[1,2-c]furan-1,3-diones

Vinyl arene (1 mmol), maleic anhydride (5 mmol, 0.49 g) and (FeNi)MIL-88A (0.2 g, 0.017 mol%) in acetonitrile (5 mL), was stirred at 100 ^oC for 20 h in a capped vessel. After extraction with dichloromethane and drying over sodium sulfate, the organic layer evaporated under reduced pressure. The organic residue was purified by a silica loaded column chromatography. Recrystallization of the product using n-hexane gave pure products.

VI-The synthesis of 1,2,3,4-tetraphenylphenanthrene (7)

Naphtho[1,2-c]furan-1,3-dione **3p** (1mmol), diphenyl acetylene **6** (2 equiv), $PdCl_2$ (20 mol%), *tetra*-butylammonium iodide (40 mol%), triphenylphosphine (20 mol%) and K_2CO_3 (2 equiv) were dissolved in DMF (5 mL) and capped. The mixture was heated at 140 ^oC for 20 h. The resulted mixture was extraction with dichloromethane and the organic layer dried over sodium sulfate. The solution was evaporated under reduced pressure and the organic residue was purified by column chromatography.

VII-Hot filtration test of the catalyst

To study the homogeneous or heterogeneous type of the catalyst, the reaction of styrene **1** and *N*-benzyl maleimide **2** in the optimal condition was quenched after 6 h when it gained 32% yield of **3a**. The catalyst (FeNi)MIL-88A was filtered from the hot reaction solution and the reaction was allowed to continue for further 14 h by the filtrate. The reaction led to 35% yield at the end of 20 h. Experiment confirms that the reaction proceeds inside the (FeNi)MIL-88A as a heterogeneous catalyst not by the homogeneous solution.

Results and Discussion

XRD patterns of the Ag-deposited MIL-88A and (FeNi)MIL-88A in Co anode have been shown in Figure S1. In the case of MIL-88A and (FeNi)MIL-88A, diffraction patterns can be clearly seen at 2Θ: 12.6°, 14.0° which are related to the pure MIL-88A structure regarding literature reports on Cu anode.[1] No detectable difference was observed between XRD of Ni modified structure and that of the parent compound confirming that the structure of MIL-88A remained intact (Figure S1a-b). When Ag was deposited on MIL-88A, a different scenario happened due to the presence of Cl^- anions in the pores of MIL-88A which was consistent with Liu's report.[2] In its XRD, there were three additional diffractions at 32.4°, 37.6° and 54.2° related to 111, 200 and 220 patterns of AgCl (JCPDS no. 31-1238) confirming the precipitation of AgCl in the pores of MIL-88A (Figure S1c).

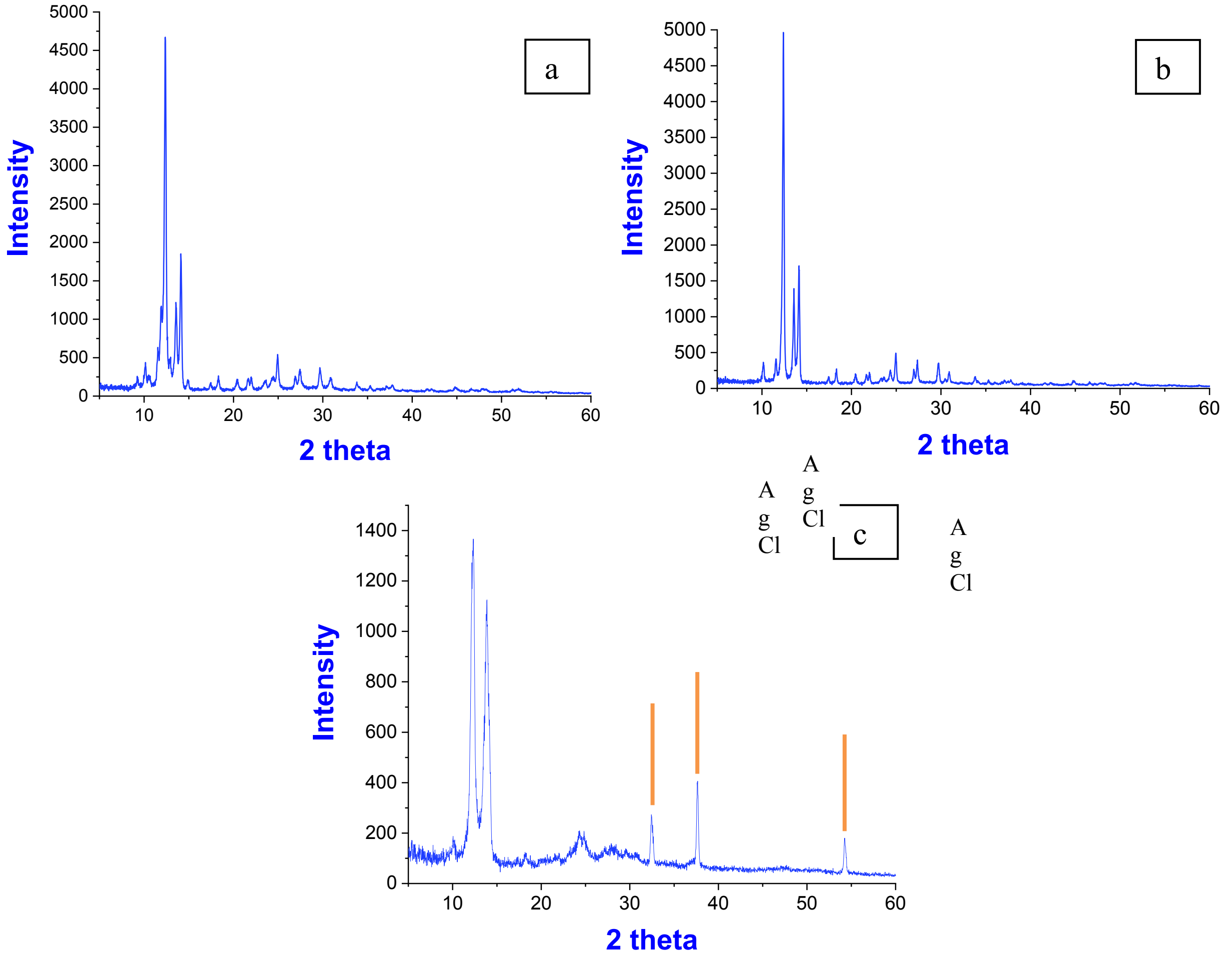


Figure S1. XRD patterns of (a) as-prepared MIL-88A, (b) (FeNi)MIL-88A and (c) Ag-deposited MIL-88A.

Figure S2 depicts the FTIR spectra of the prepared compounds. The bands at 1394 cm^{-1} and 1601 cm^{-1} are generated by the symmetric and asymmetric stretching of the C=O bonds of carboxylate groups of the fumarate linkers. The bands at 1219 cm^{-1} can be assigned to the C-O vibration of the fumarate groups. Broad band at around 3000-3600 cm^{-1} indicates O-H stretching mode of adsorbed water which overlaps with stretching of C-H bonds. In addition, forming Fe-Oxo clusters can be proved by the band at around 577 cm^{-1}, the characteristic band of Fe-O bonds. The bands at 644 cm^{-1} and 677 cm^{-1} are related to the carbonyl group [1b,3] and C-H bending mode, respectively.

As is clear, no detectable changes were found in the FTIR spectrum of mixed-metal FeNi nor in that of the Ag-deposited MIL-88A proving that the structures did not change considerably after introducing Ag(I) and Ni(II) into the parent compound.

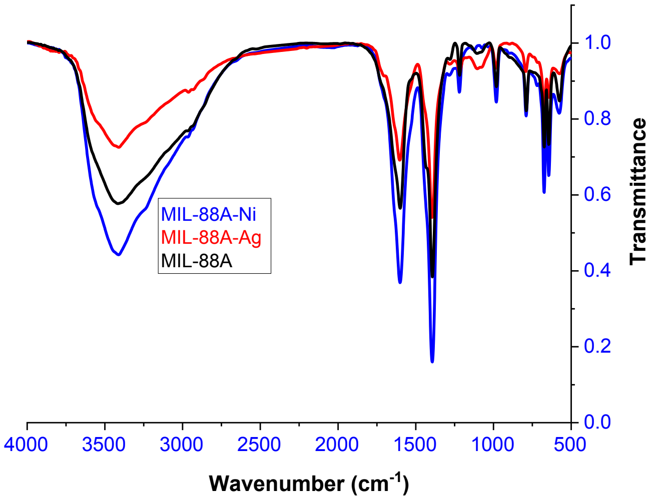
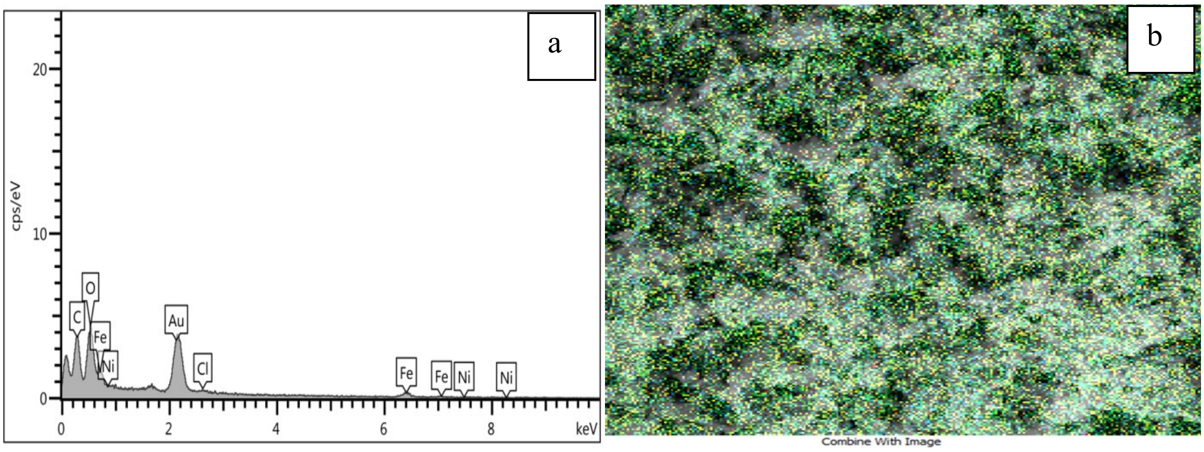


Figure S2. The FTIR of MIL-88A, (FeNi)MIL-88A and Ag-deposited MIL-88A

The quantitative amounts of the metal content were measured by the energy dispersive X-ray spectroscopy (EDAX) and elemental mapping (Figure S3-S4). EDAX indicated the presence of Fe, C, Ni and Cl for the (FeNi)MIL-88A; and Fe, C, Ag, and Cl and for Ag-deposited MIL-88A; the presence of Cl$^-$ in the structure of (FeNi)MIL-88A confirmed the partial exchanging of Ni in the structure. Elemental mapping demonstrates the uniform distribution of all elements (O, Cl, Fe and Ni in the case of (FeNi)MIL-88A and O, Cl, Fe and Ag) within the MOF structures.



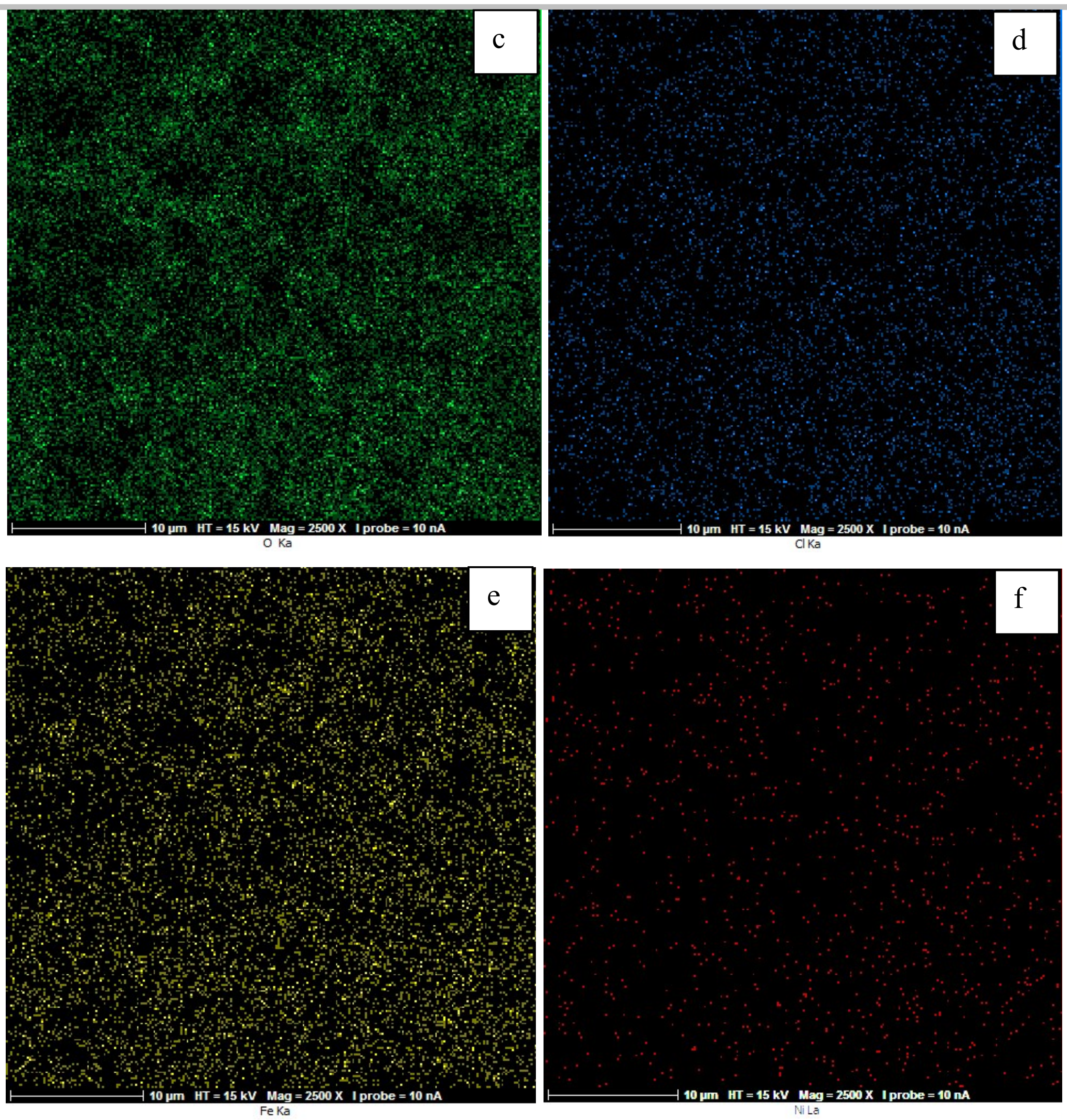


Figure S3. EDAX elemental analyses-elemental mapping of the prepared (FeNi)MIL-88A (a) EDAX analysis of (FeNi)MIL-88A; (b) elemental mapping of (FeNi)MIL-88A showing all elements; (c) mapping of oxygen; (d) mapping of Cl; (e) mapping of Fe; (f) mapping of Ni.

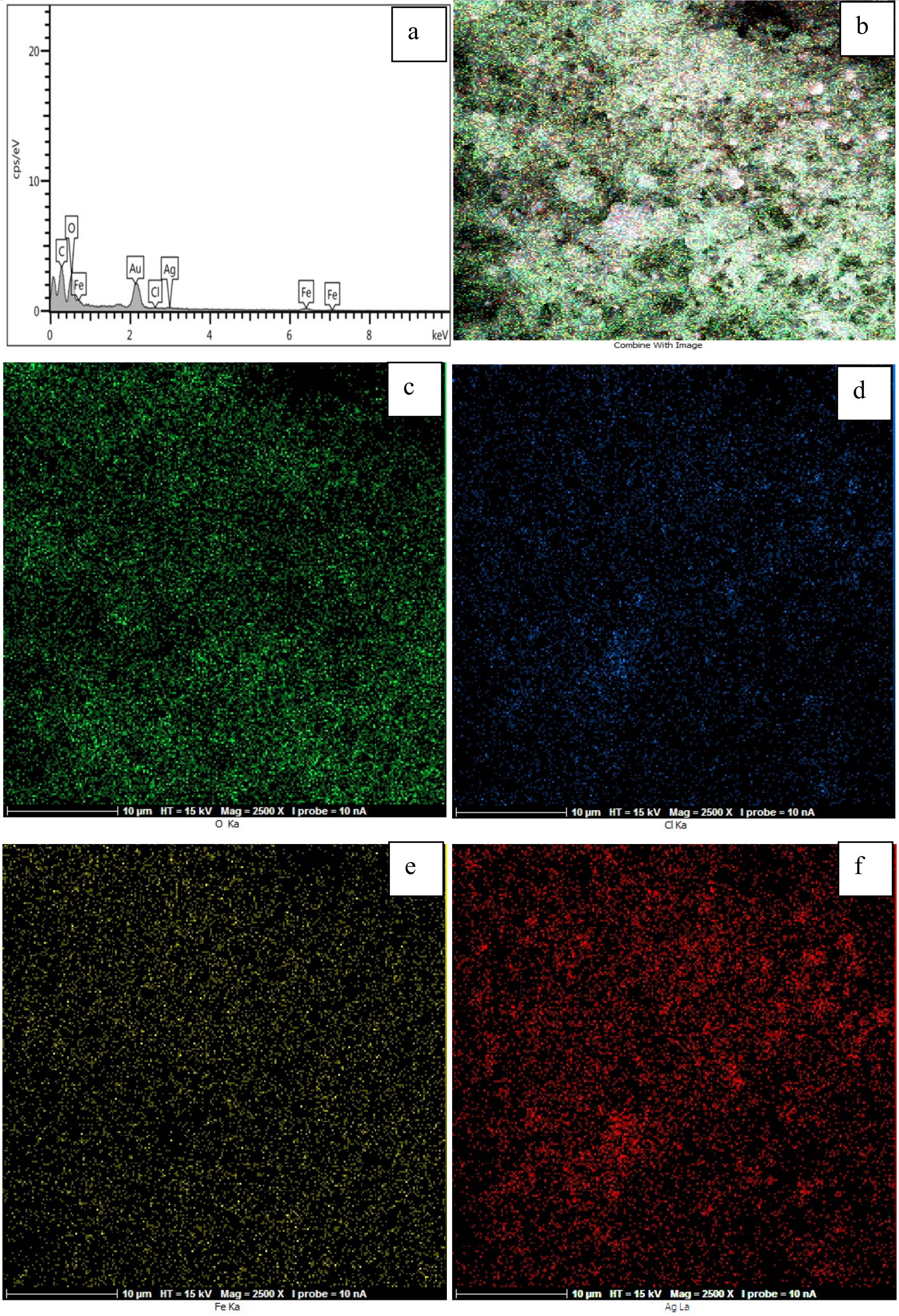


Figure S4. EDAX elemental analyses-elemental mapping of the prepared Ag-deposited MIL-88A (a) EDAX analysis of Ag-deposited MIL-88A; (b) elemental mapping of Ag-deposited MIL-88A showing all elements; (c) mapping of oxygen; (d) mapping of Cl; (e) mapping of Fe; (f) mapping of Ag.

The catalyst could be recovered and reused in successive runs with slight loss of activity (Figure S5). This is due to the stability of chemical structure in the reaction medium which is confirmed by TGA-DTA and providing its potential to be used in practical applications.

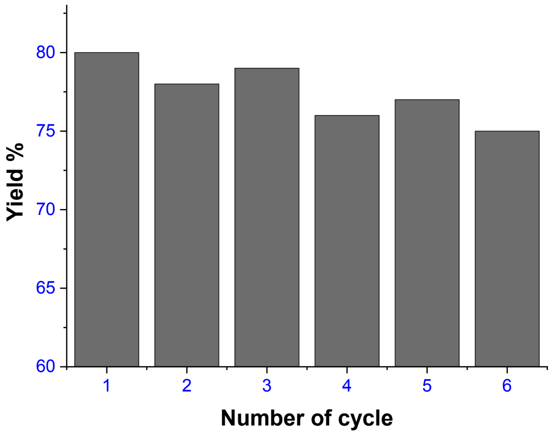


Figure S5. Plot of **3a** yield at various runs; recovery test of (Fe-Ni)MIL-88A in the reaction of styrene and *N*-methyl maleimide

Mechanistic Studies

Study on the reaction kinetic

In a reaction of styrene 1 and *N*-benzyl maleimide at the optimal reaction conditions, aliquots (0.05 mL) were removed every 90 min hour and continue this to 360 min. HPLC was used to determine the concentration of *N*-benzyl maleimide at each time by using a calibration plot. Two plots were recorded. The first was recorded to check the fist-order kinetic and another for second-order kinetic reaction. The ln[maleimide] and l/[maleimide] were plotted against time (Figure S6a-b). The figure shows a straighter line with a correlation value of 0.989, in the case of the later indicate a second-order reaction. From the slope of the line, a rate constant of 2.9×10^{-3} L.mol^{-1} sec^{-1} is obtained at 100 ^{o}C. In contrast, when the data is plotted in a first-order manner a much lower correlation value (= 0.964) is obtained. From the plot of Figure S6b it is easily seen that the reaction demonstrates simple second-order reaction kinetics.

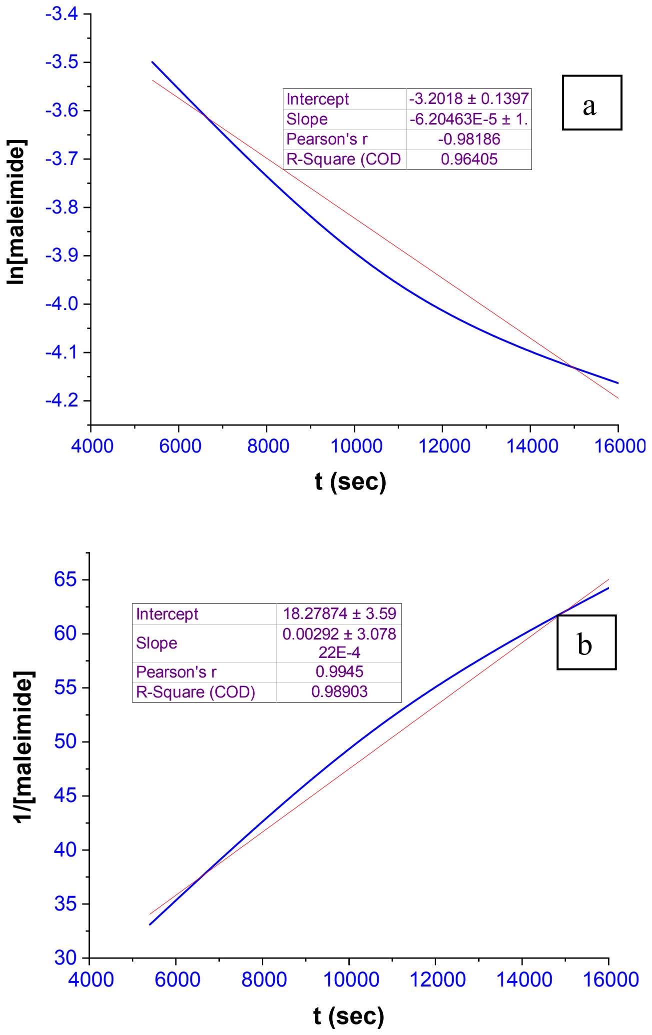


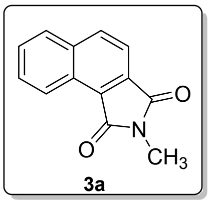
Figure S6. The plots of reaction kinetic of styrene and *N*-benzyl maleimide at 100 ^{o}C, a) first-order plot for the reaction; b) second-order plot for the reaction

The presence of ionic/polar transition state(s) was checked by determination of rate constant of reaction in various solvents (Table S1). Investigation showed that the reaction constant changed only slightly over the change of solvent.

Table S1. Solvent effect in the reaction of *N*-benzyl maleimide with styrene on the optimal conditions

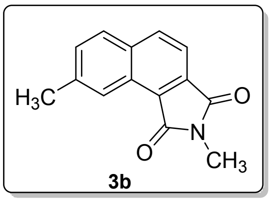
entry	solvent	10^3× second-order rate constant k, L/mol.sec
1	H_2O	2.9
2	ethanol	2.4
3	toluene	2.1
4	ethyl acetate	1.9
5	acetonitrile	1.6

Spectral data



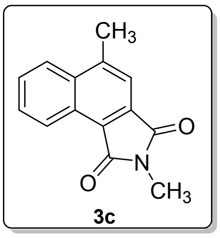
3a

2-Methyl-2H-benzo[e]isoindole-1,3-dione (3a); Off-white solid, mp. 156-157 °C, ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.98 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.67-7.78 (m, 2H), 3.26 (s, 3H). Known compound.[6]



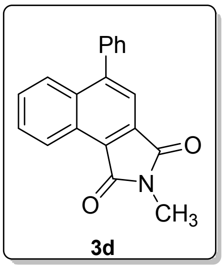
3b

2,8-Dimethyl-2H-benzo[e]isoindole-1,3-dione (3b); White solid, mp. 171-173 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 8.0 Hz, 1.5 Hz, 1H), 3.18 (s, 3H), 2.56 (s, 3H). Known compound.[6]



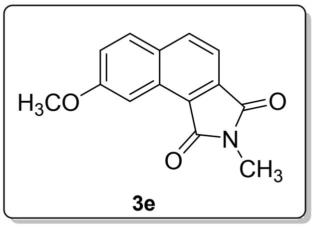
3c

2,5-Dimethyl-2H-benzo[e]isoindole-1,3-dione (3c); Off-white solid, mp. 161-162 °C, ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.99 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 8.12 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.69-7.77 (m, 3H), 3.24 (s, 3H), 2.86 (s, 3H). Known compound.[6]



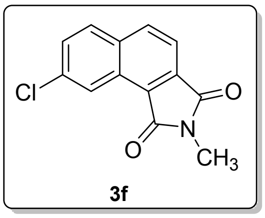
3d

2-Methyl-5-phenyl-2H-benzo[e]isoindole-1,3-dione (3d); Greenish white, mp. 191-192 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.99 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.78 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.44-7.51 (m, 5H), 3.20 (s, 3H). Known compound.[6]



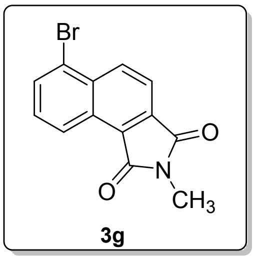
3e

8-Methoxy-2-methyl-2H-benzo[e]isoindole-1,3-dione (3e); Green solid, mp. 162-163 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.5 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 9.0 Hz, 2.5 Hz, 1H), 3.98 (s, 3H), 3.20 (s, 3H). Known compound.[6]



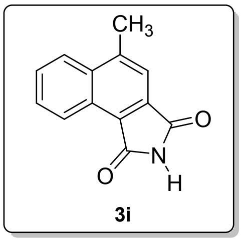
3f

8-Chloro-2-methyl-2H-benzo[e]isoindole-1,3-dione (3f); Greenish white solid, mp. 201-203 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.91 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.0 Hz, 1H), 3.20 (s, 3H). Known compound.[6]



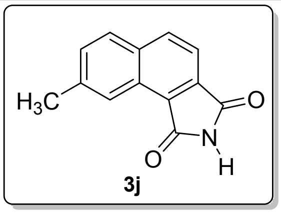
3g

6-Bromo-2-methyl-2H-benzo[e]isoindole-1,3-dione (3g); White solid, mp. 166-168 °C, ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 7.6 Hz, 1H), 8.59 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 8.4 Hz, 0.8 Hz, 1H), 3.20 (s, 3H). Known compound.[6]



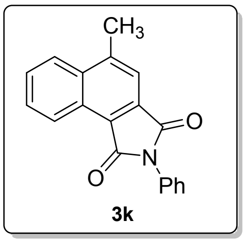
3i

5-Methyl-2H-benzo[e]isoindole-1,3-dione (3i); Green-yellow solid, Decomposed at 231 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.0 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.64-7.70 (m, 4H), 2.80 (s, 3H). Known compound.[6]



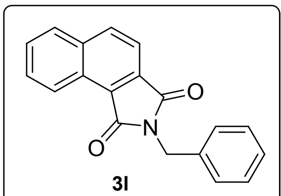
3j

8-Methyl-2H-benzo[e]isoindole-1,3-dione (3j); Green-yellow solid, Decomposed at 221 °C. ^{1}HNMR (500 MHz, CDCl$_3$) δ 8.68 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.47-7.50 (m, 2H), 2.57 (s, 3H). ^{13}CNMR (100 MHz, CDCl$_3$) δ 169.4, 168.5, 140.3, 135.2, 132.0, 131.3, 130.9, 128.8, 128.5, 127.0, 123.8, 117.7, 22.1. Known compound.[6]



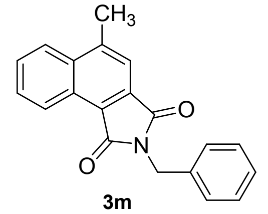
3k

5-Methyl-2-phenyl-2H-benzo[e]isoindole-1,3-dione (3k); Pale-yellow solid, mp. 176-178 °C, ^{1}HNMR (500 MHz, CDCl$_3$) δ 8.99 (dd, *J* = 7.5 Hz, 1.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 7.78 (s, 1H), 7.65-7.73 (m, 2H), 7.43-7.49 (m, 4H), 7.36 (tt, *J* = 7.0 Hz, 1.5 Hz, 1H), 2.83 (s, 3H). Known compound.[6]



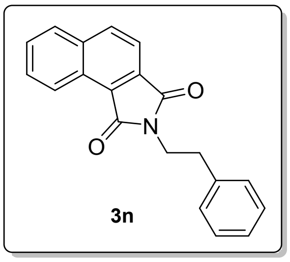
3l

2-Benzyl-2H-benzo[e]isoindole-1,3-dione (3l); Green solid, mp. 147-148 °C, ^{1}HNMR (400 MHz, CDCl$_3$) δ 8.88 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.65-7.69 (m, 1H), 7.59 (td, *J* = 7.6 Hz, 1.2 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.24-7.30 (m, 3H), 4.85 (s, 2H). Known compound.[6]



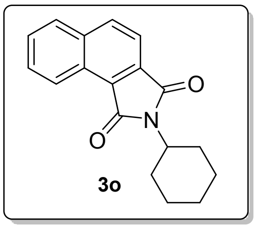
3m

2-Benzyl-5-methyl-1H-benzo[e]isoindole-1,3(2H)-dione (3m); ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H), 8.11 (dd, *J* = 7.5 Hz, 2.0 Hz, 1H), 7.69-7.73 (m, 3H), 7.55 (m, 1H), 7.47 (d, *J* = 6.5 Hz, 2H), 7.32-7.35 (m, 2H), 4.89 (s, 2H), 2.84 (s, 3H). FT-IR (cm^{-1}) ν: 3081, 2967, 2933, 2858, 1721, 1624, 1466, 1373, 1262, 1128, 1088, 955, 823, 735, 711. Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.67; H, 4.99; N, 4.61.



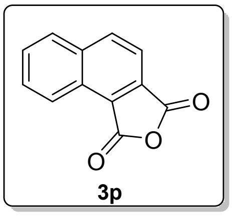
3n

2-Phenethyl-1H-benzo[e]isoindole-1,3(2H)-dione (3n); ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.94 (d, *J* = 7.0 Hz, 1H), 8.17 (d, *J* = 7.0 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.74 (t, *J* = 7.0 Hz, 1H), 7.67 (t, *J* = 7.0 Hz, 1H), 7.48 (s, 1H), 7.29-7.33 (m, 4H), 3.98 (t, *J* = 9.0 Hz, 2H), 3.05 (t, *J* = 9.0 Hz, 2H). FT-IR (cm^{-1}) ν: 3073, 2955, 2928, 2880, 1725, 1630, 1469, 1378, 1258, 1120, 1082, 967, 829, 742, 718. Anal. Calcd for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.70; H, 5.04; N, 4.59.



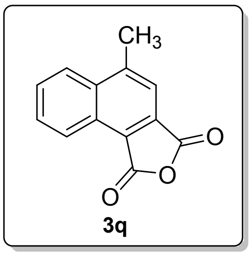
3o

2-Cyclohexyl-2H-benzo[e]isoindole-1,3-dione (3o); Pale green solid, mp. 141-143 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 4.10 (tt, *J* = 12.5 Hz, 4.0 Hz, 1H), 2.21 (dq, *J* = 12.5 Hz, 4.0 Hz, 2H), 1.85 (d, *J* = 13.5 Hz, 2H), 1.74 (d, *J* = 12.0 Hz, 3H), 1.61-1.70 (m, 3H). Known compound.[6]



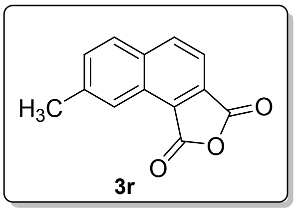
3p

Naphtho[1,2-c]furan-1,3-dione (3p); White solid, mp. 144-145 °C, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.84 (d, *J* = 8.0 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (td, *J* = 7.0, 1.5 Hz, 1H), 7.77 (td, J = 7.0, 1.5 Hz, 1H). Known compound.[6]



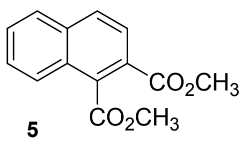
3q

5-Methylnaphtho[1,2-c]furan-1,3-dione (3q); Greenish white solid, mp. 148-151 ºC, ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 5.6 Hz, 2.4 Hz, 1H), 8.21 (dd, *J* = 5.6 Hz, 2.4 Hz, 1H), 7.75-7.78 (m, 3H), 2.82 (s, 3H). Known compound.[6]



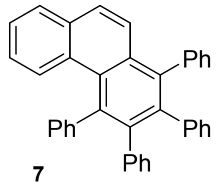
3r

8-Methylnaphtho[1,2-c]furan-1,3-dione (3r); Green solid, mp. 146-147 ºC, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.60 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 2.62 (s, 3H). Known compound.[6]



5

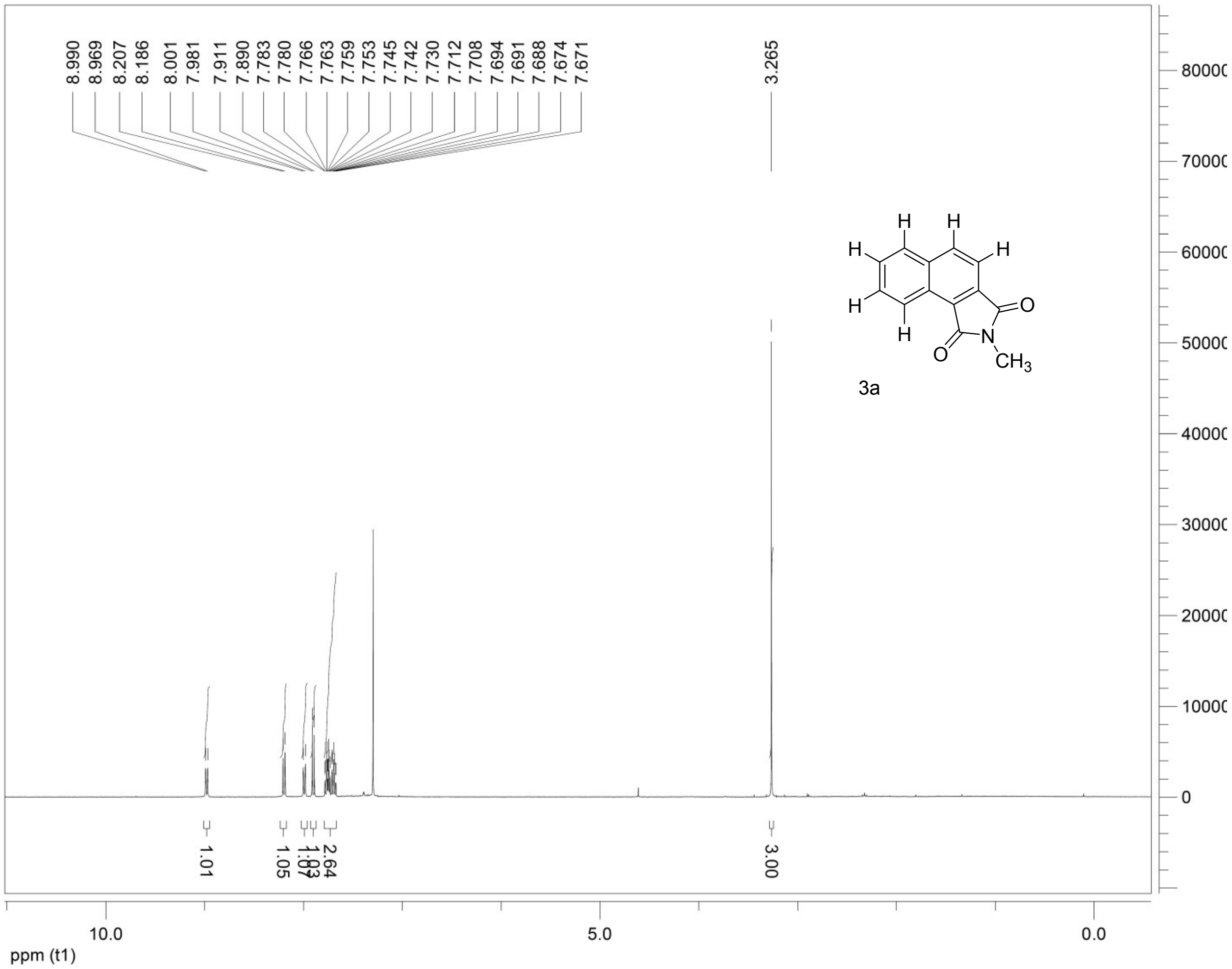
8-Methylnaphtho[1,2-c]furan-1,3-dione (5); Yellow solid, mp. 84-85 ºC, ^{1}HNMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.5 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.87-7.91 (m, 2H), 7.58-7.64 (m, 2H), 4.09 (s, 3H), 3.97 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 169.7, 166.4, 135.2, 131.0, 129.7, 128.8, 128.6, 128.2, 127.9, 126.2, 126.1, 125.1, 53.0, 52.8. Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.79; H, 4.92. known compound.[7]

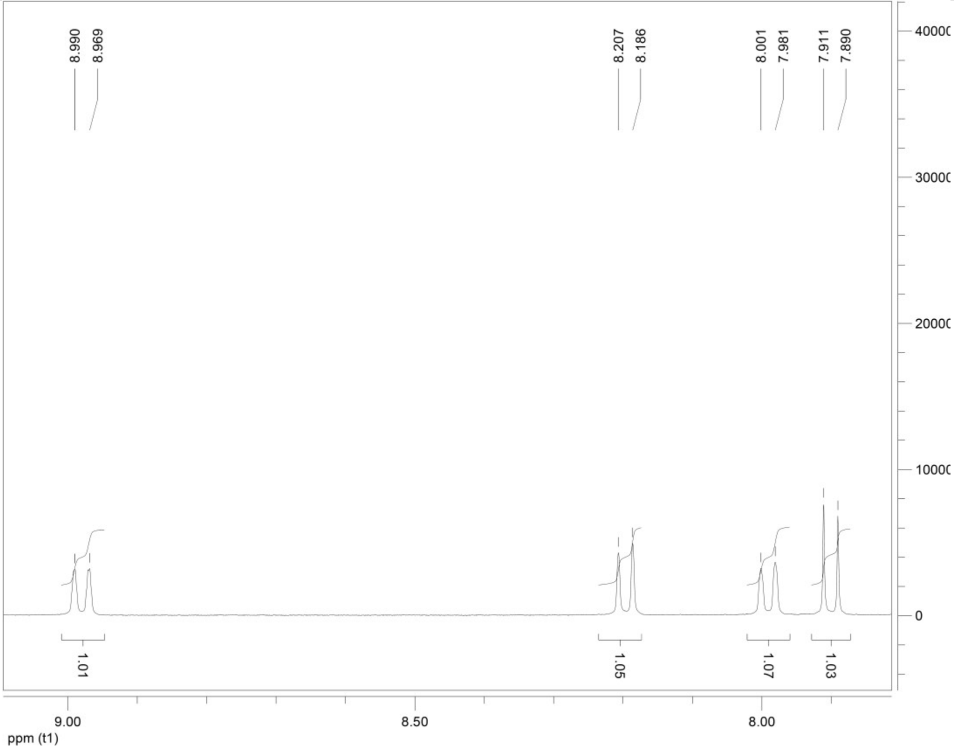


7

1,2,3,4-Tetraphenylphenanthrene (7); Yellow solid, mp. 150-152 ºC, ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.5 Hz, 1H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.13-7.20 (m, 8H), 7.07-7.11 (m, 3H), 6.97 (td, *J* = 7.0 Hz, 1.5 Hz, 1H), 6.76-6.81 (m, 8H), 6.72-6.74 (dd, *J* = 7.5 Hz, 1.5 Hz, 2H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 143.3, 140.6, 140.5, 140.4, 140.0, 139.5, 139.0, 138.5, 138.5, 138.2, 138.2, 138.0, 137.9, 137.9, 133.3, 132.3, 132.3, 131.5, 131.4, 131.3, 131.0, 130.7, 130.6, 128.7, 128.5, 128.1, 128.0, 127.4, 127.3, 126.4, 126.3, 126.3, 126.2, 125.7, 125.1, 125.1, 125.0, 124.6. MS (70 eV): m/z= 482 [M^+].

Copies of ¹H, ¹³CNMR

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1.05
1.07
1.03
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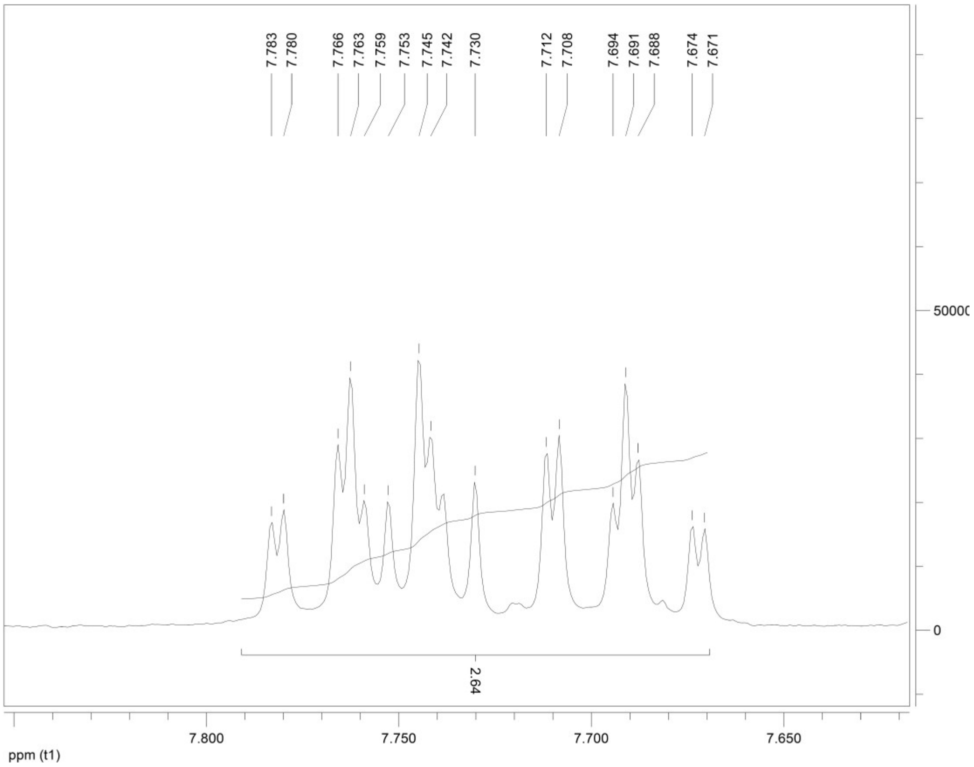
8.00
ppm (t1)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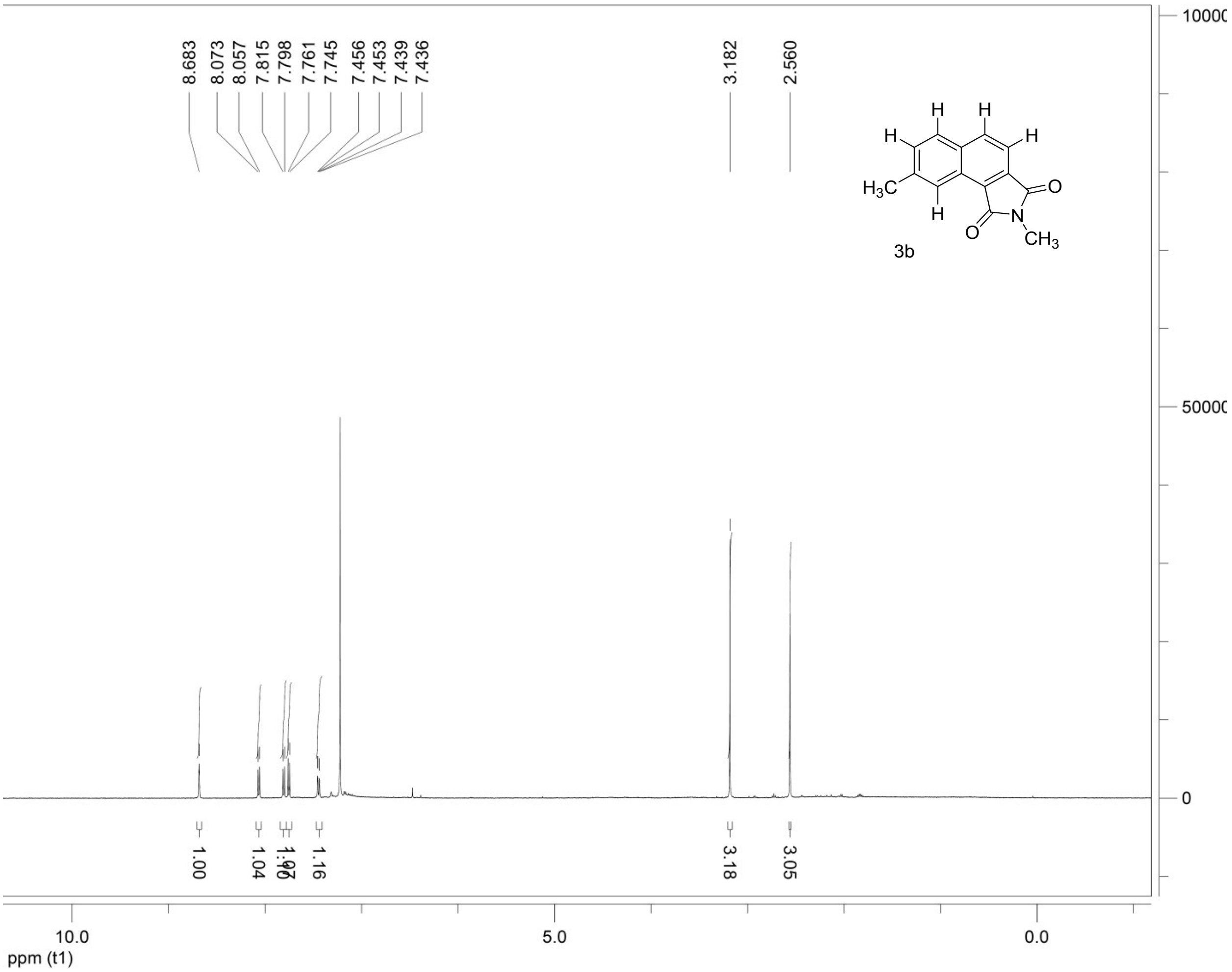
ppm (t1)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8.057
7.815
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7.745
7.456
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7.439
7.436
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2.560
H
H
H
H
H_3C
H
O
N
O
CH_3
3b
1.00
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1.10
1.07
1.16
3.18
3.05
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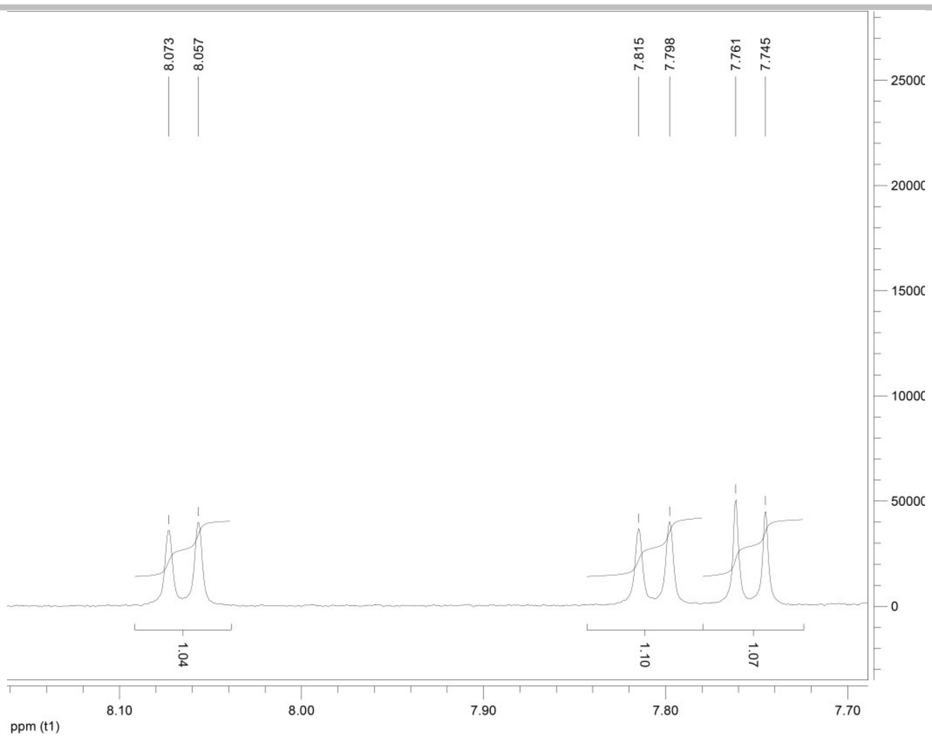
0.0
ppm (t1)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1.10
1.07
8.10
8.00
7.90
7.80
7.70
ppm (t1)


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7.439
7.436
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1.16
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7.500
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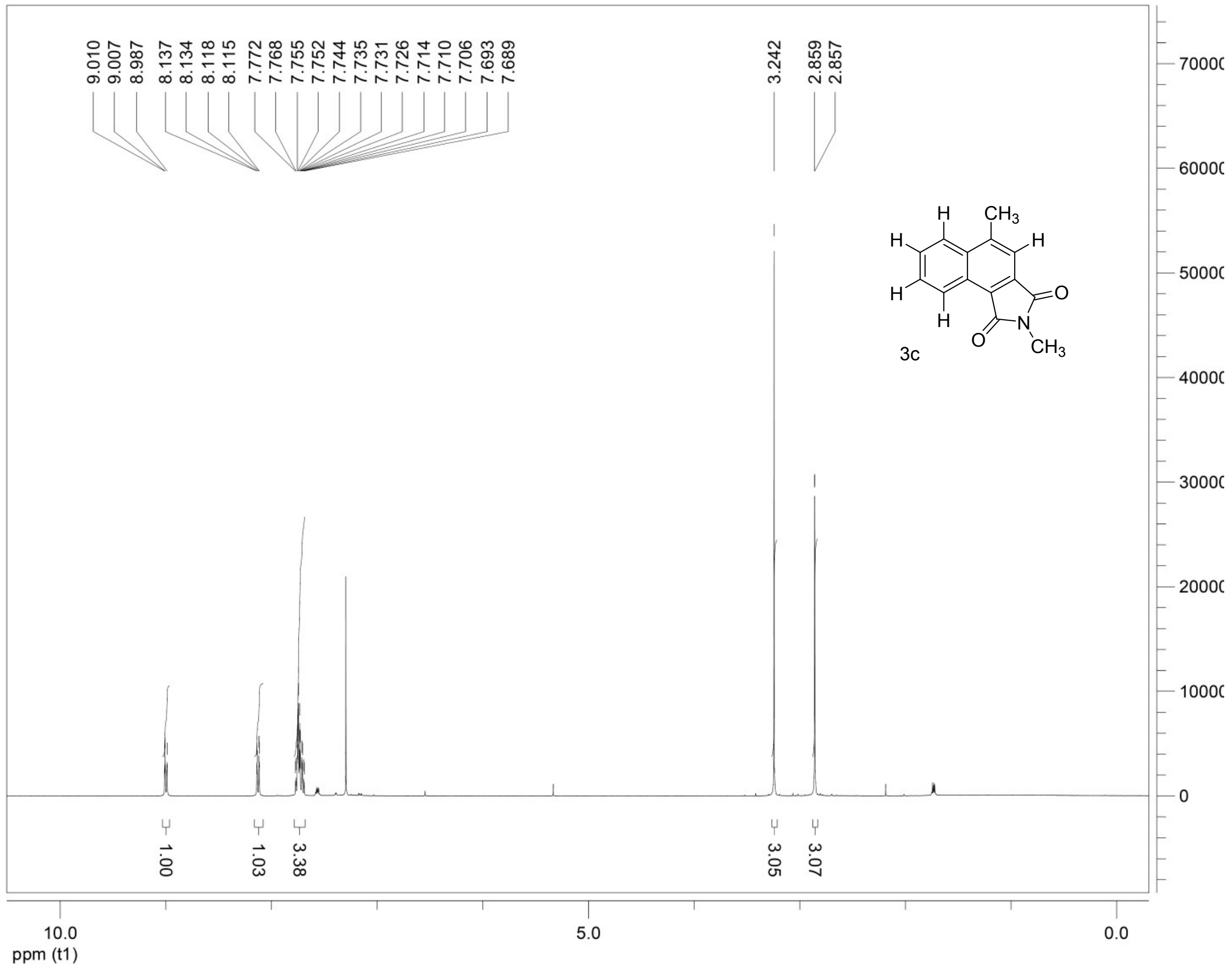
7.400
ppm (t1)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8.118
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7.744
7.735
7.731
7.726
7.714
7.710
7.706
7.693
7.689
3.242
2.859
2.857
H
CH3
H
H
H
H
O
O
N
CH3
3c
1.00
1.03
3.38
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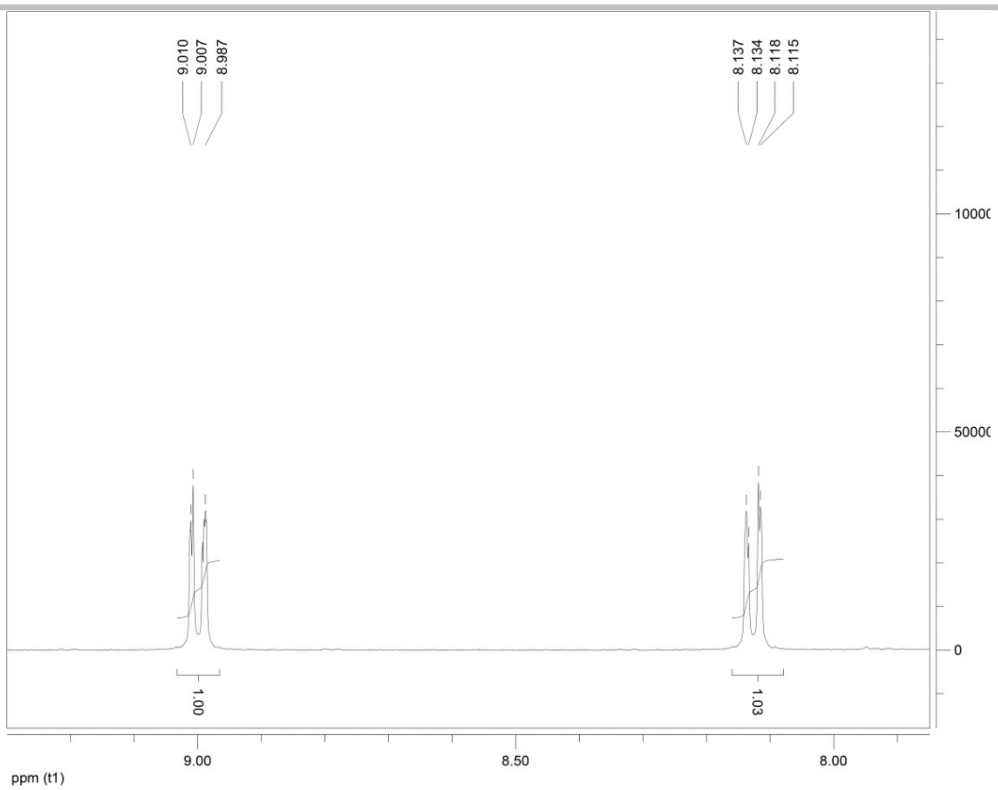
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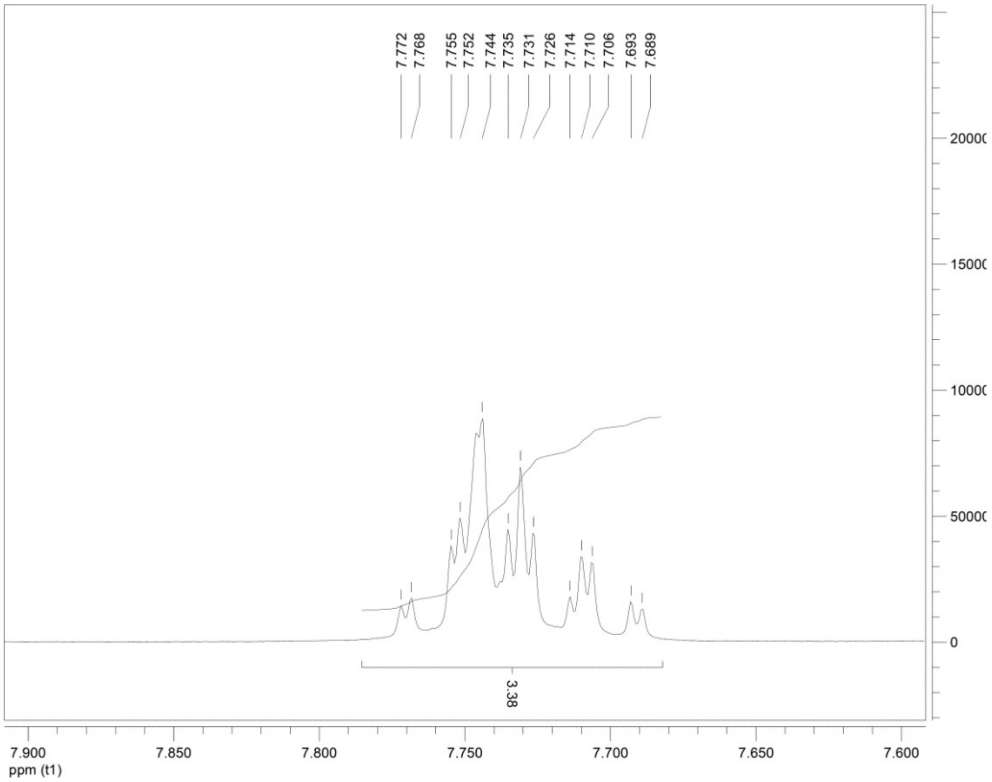
ppm (t1)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7.735
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7.710
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7.689
200000
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100000
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0
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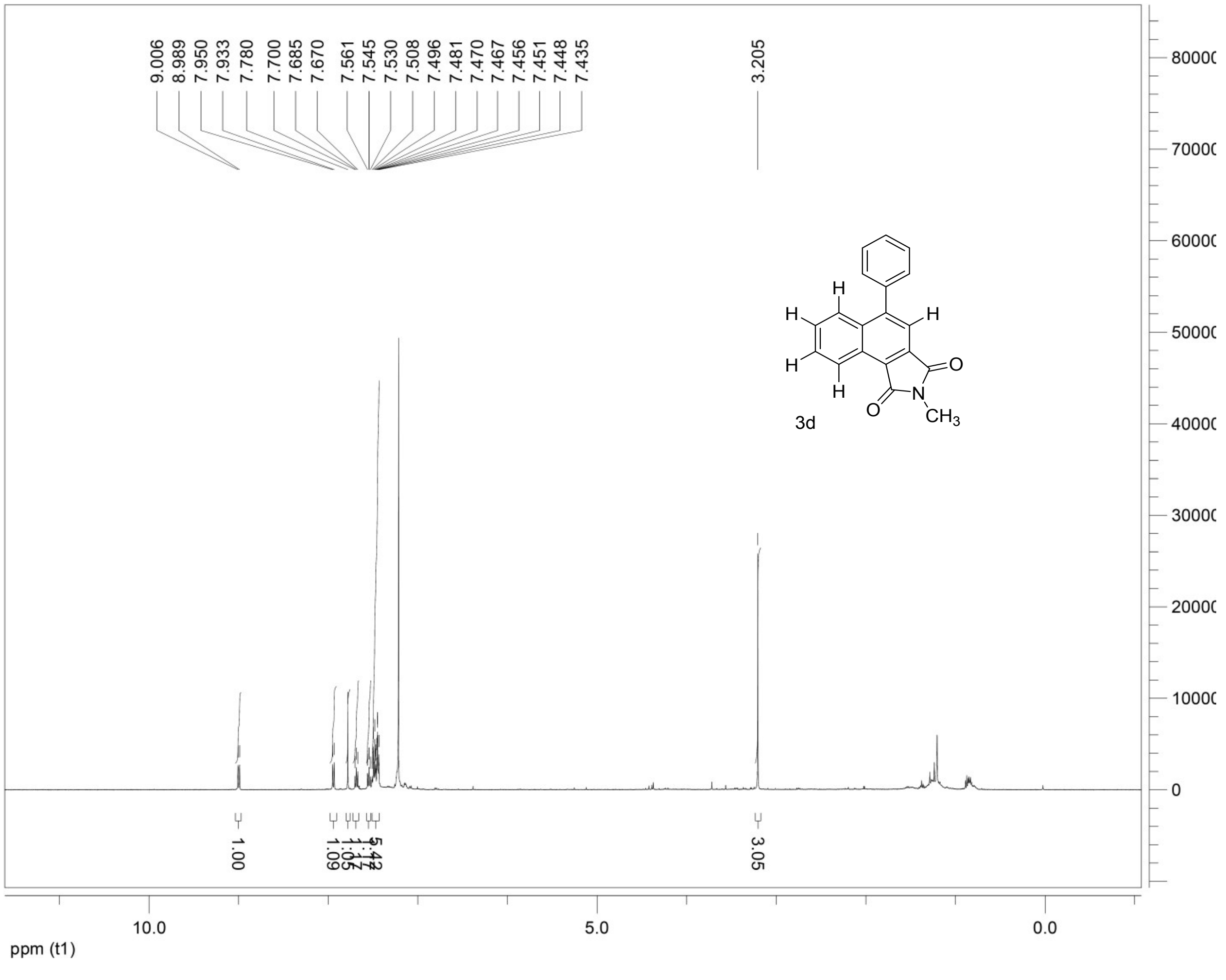
7.600
ppm (t1)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7.670
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7.545
7.530
7.508
7.496
7.481
7.470
7.467
7.456
7.451
7.448
7.435
3.205
H
H
H
H
H
O
N
O
CH3
3d
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1.17
5.42
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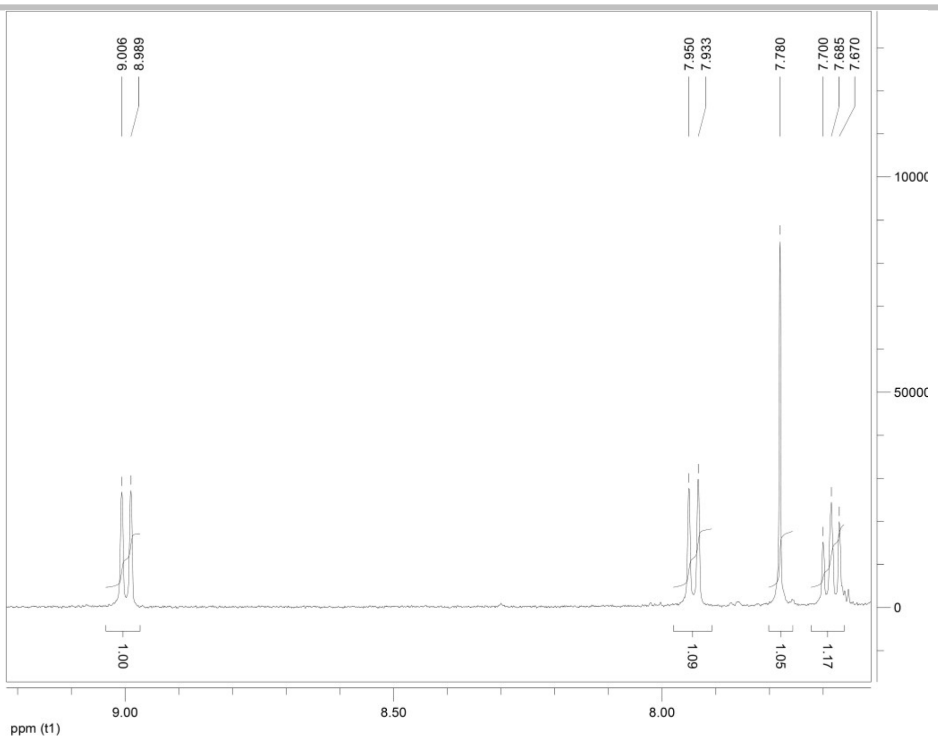
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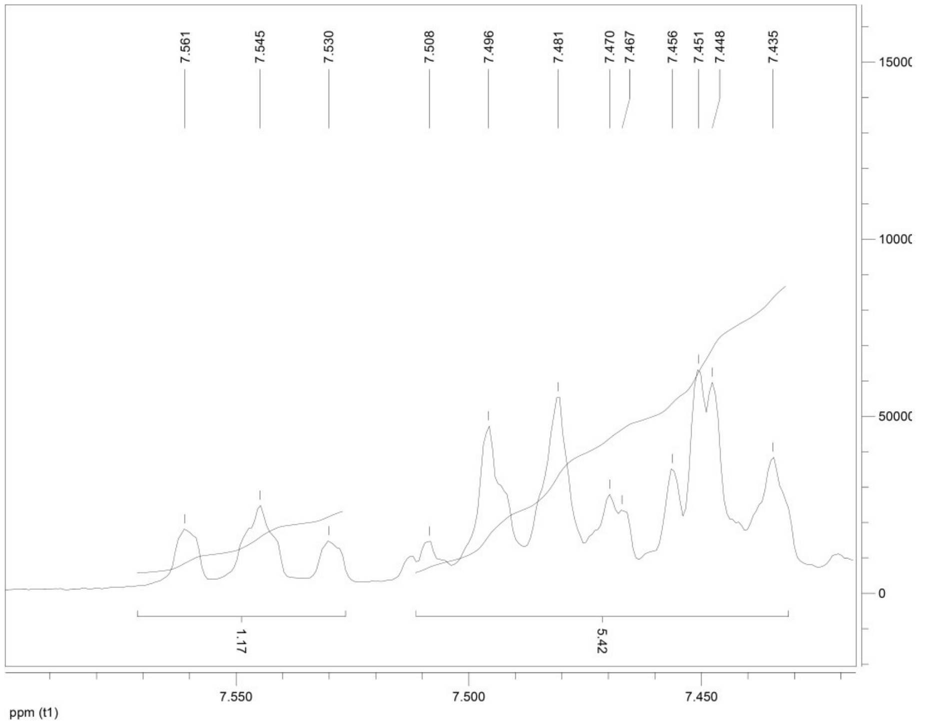
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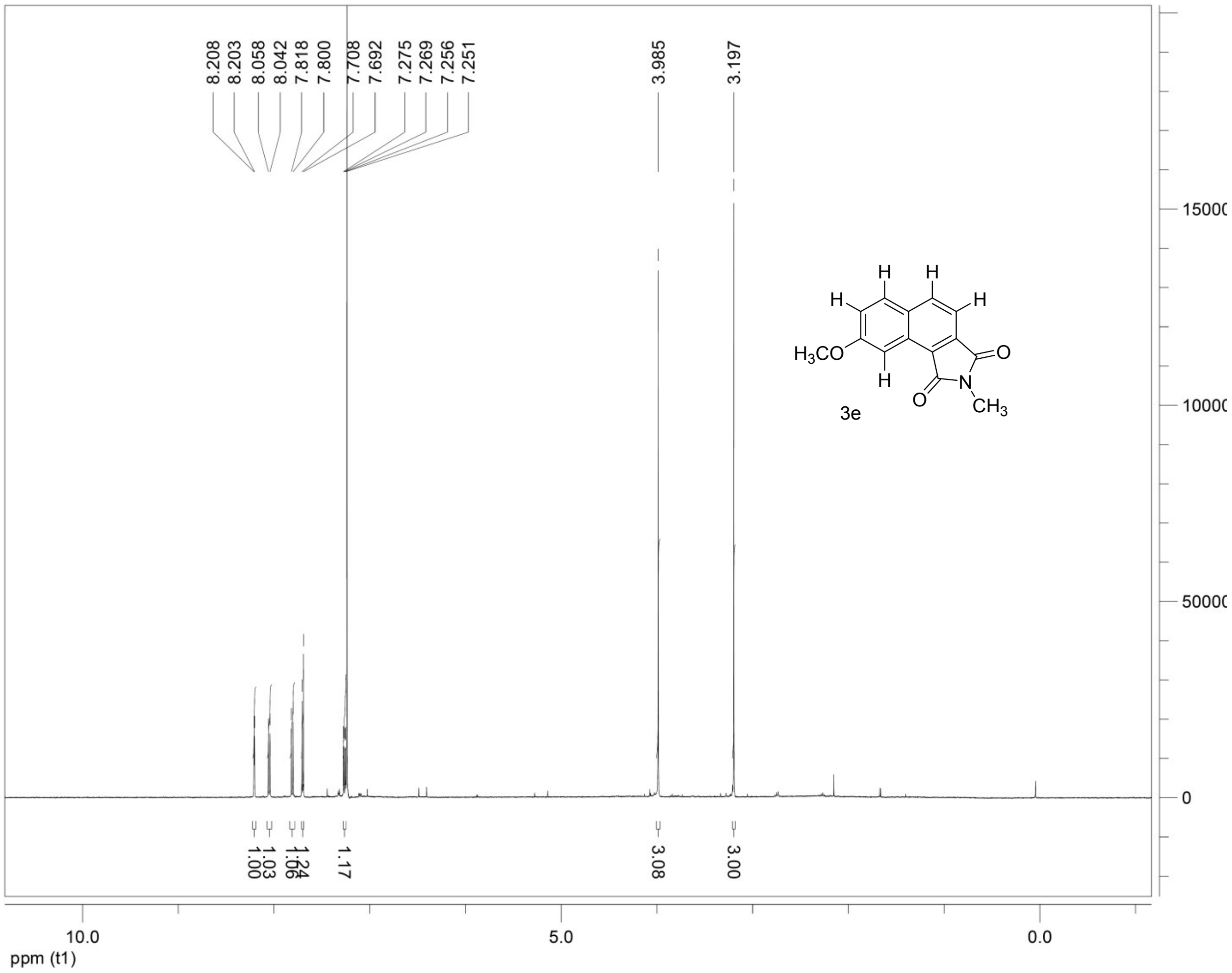

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7.692
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3.197
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1.03
1.24
1.06
1.17
3.08
3.00
15000
10000
50000
0
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ppm (t1)
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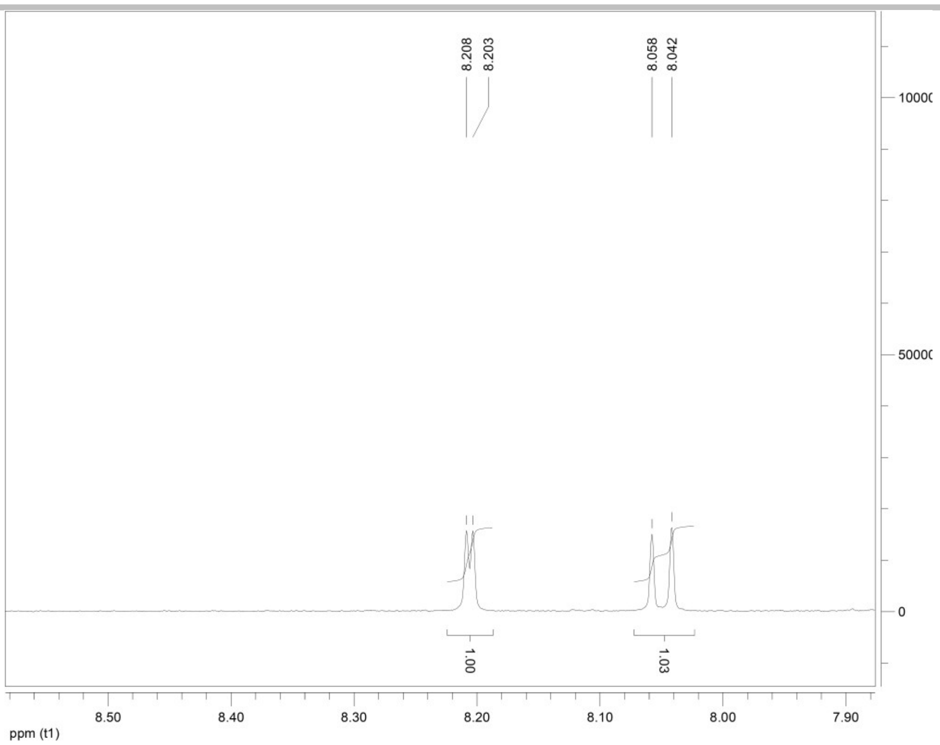
H
H
H
H
H$_3$CO
O
O
N
CH$_3$
3e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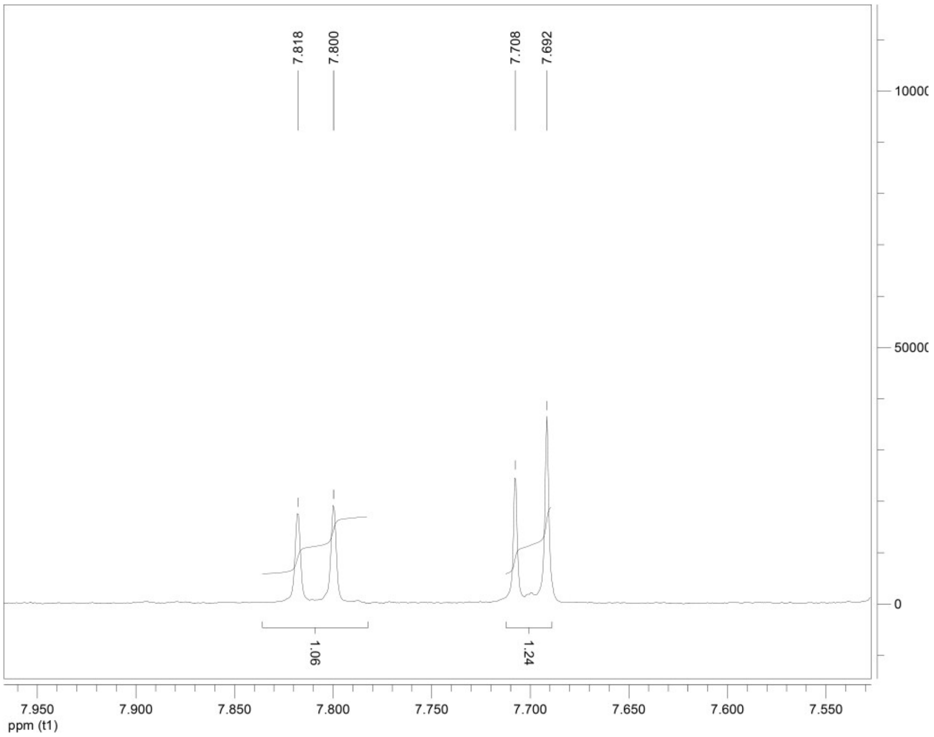
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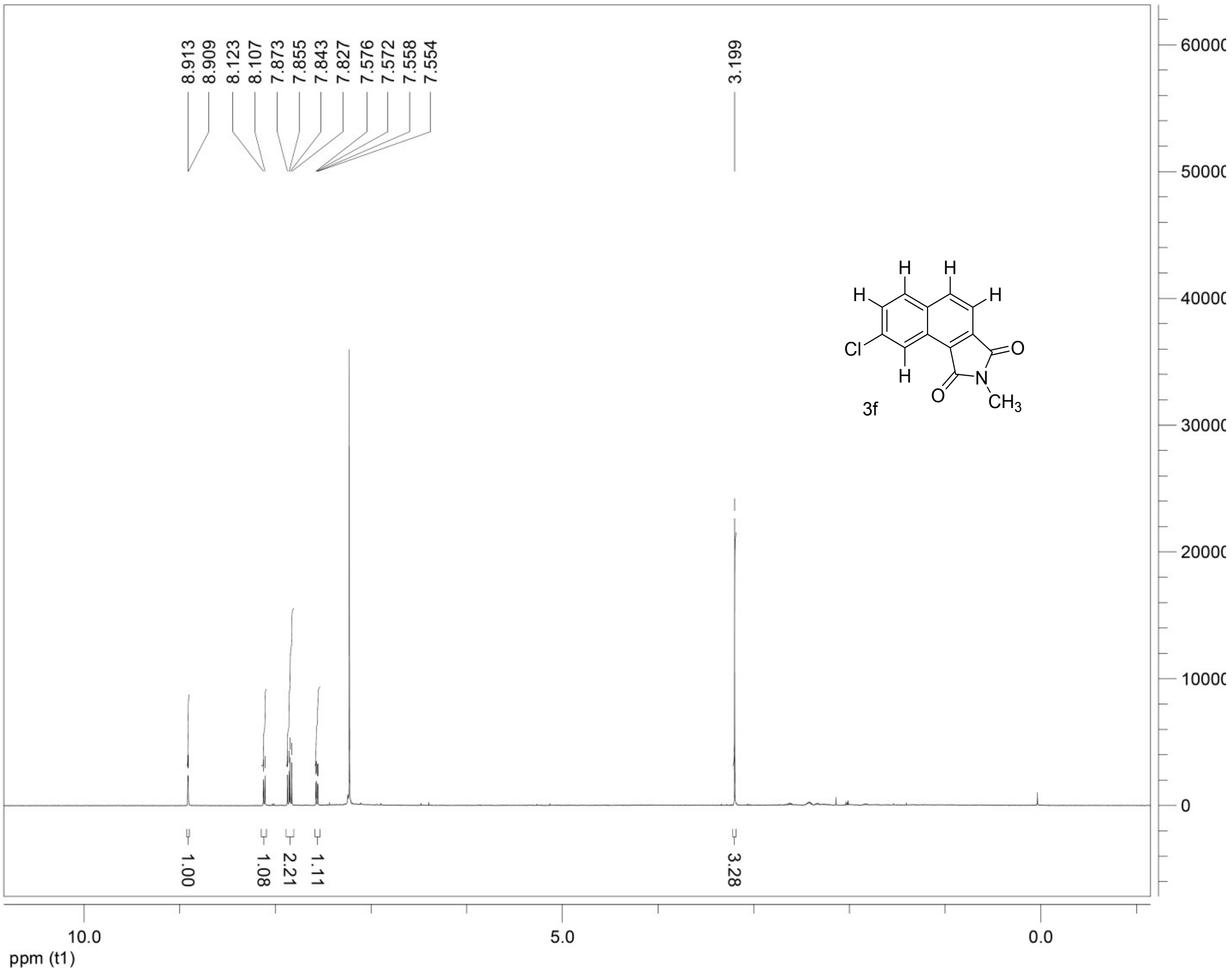
7.550
ppm (t1)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7.827
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7.554
3.199
1.00
1.08
2.21
1.11
3.28
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50000
40000
30000
20000
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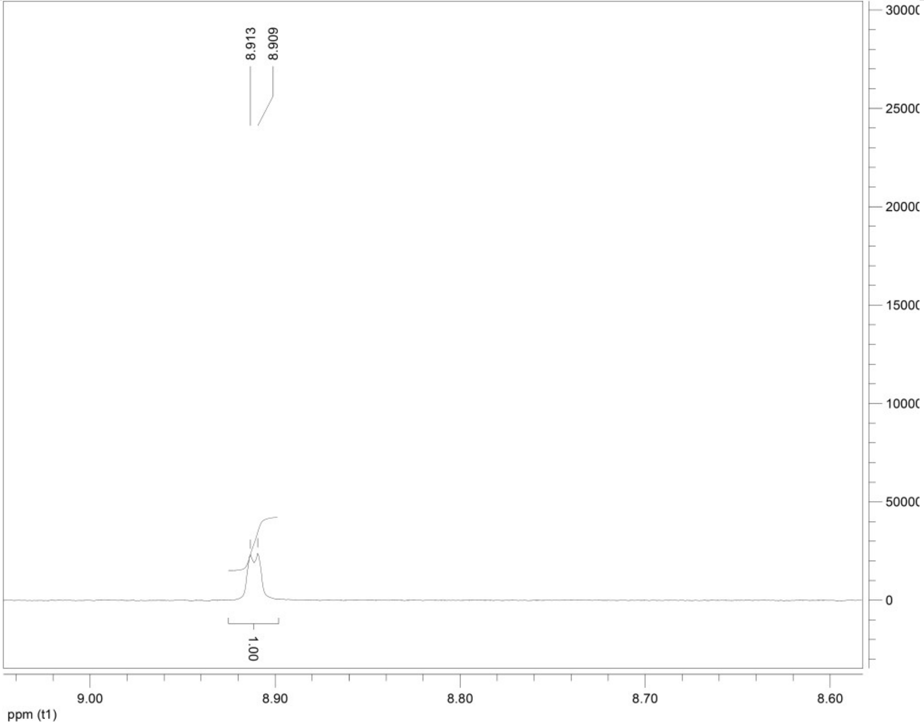
H
Cl
H
O
O
N
CH3
3f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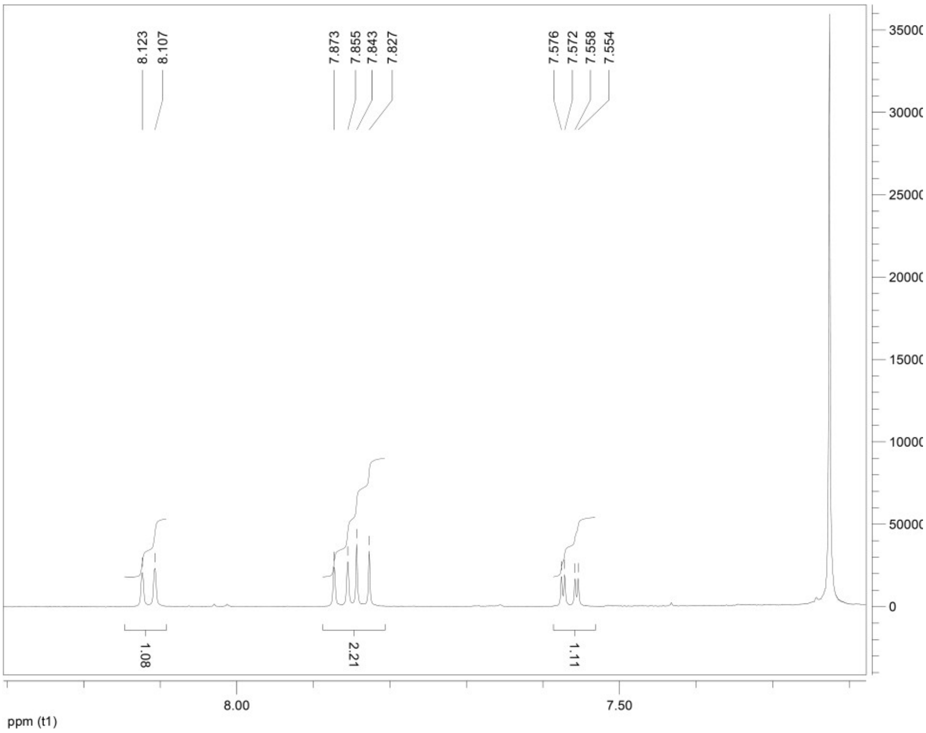
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7.873
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7.827
7.576
7.572
7.558
7.554
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1.11
8.00
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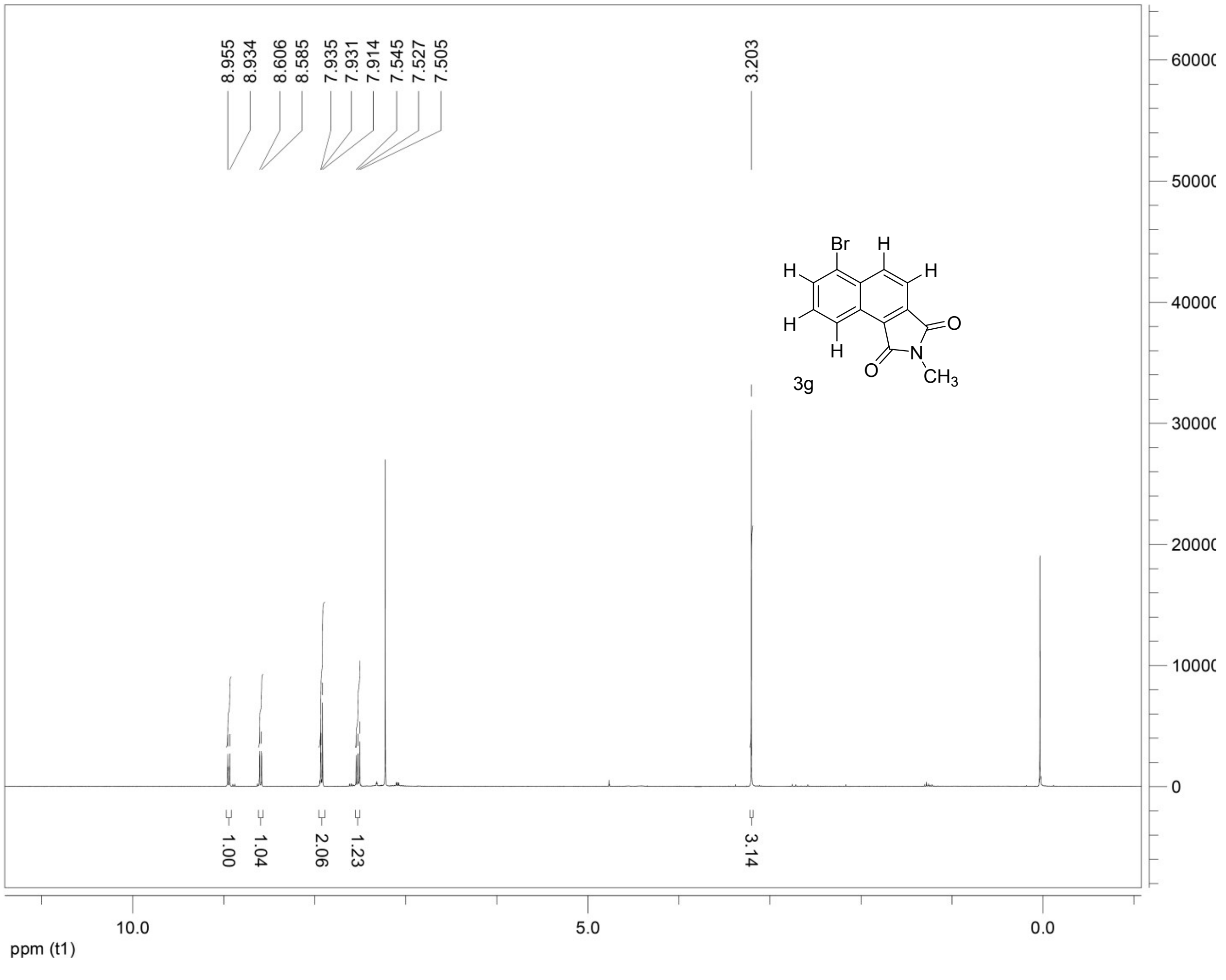
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7.527
7.505
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H
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H
H
H
O
O
N
CH_3
3g
60000
50000
40000
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2.06
1.23
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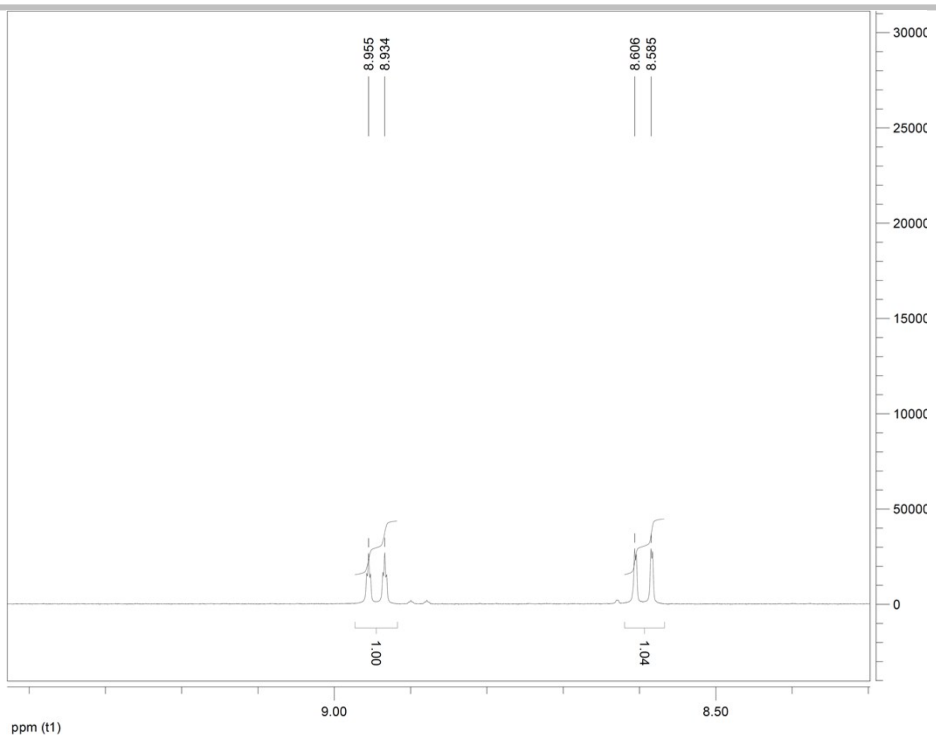
ppm (t1)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8.585
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8.50
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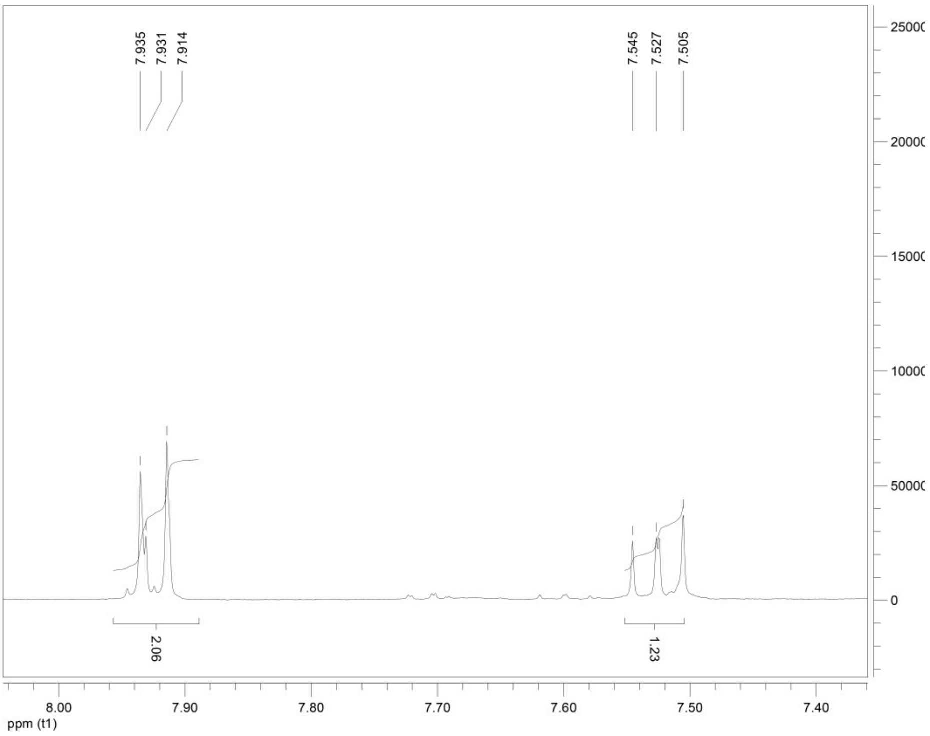
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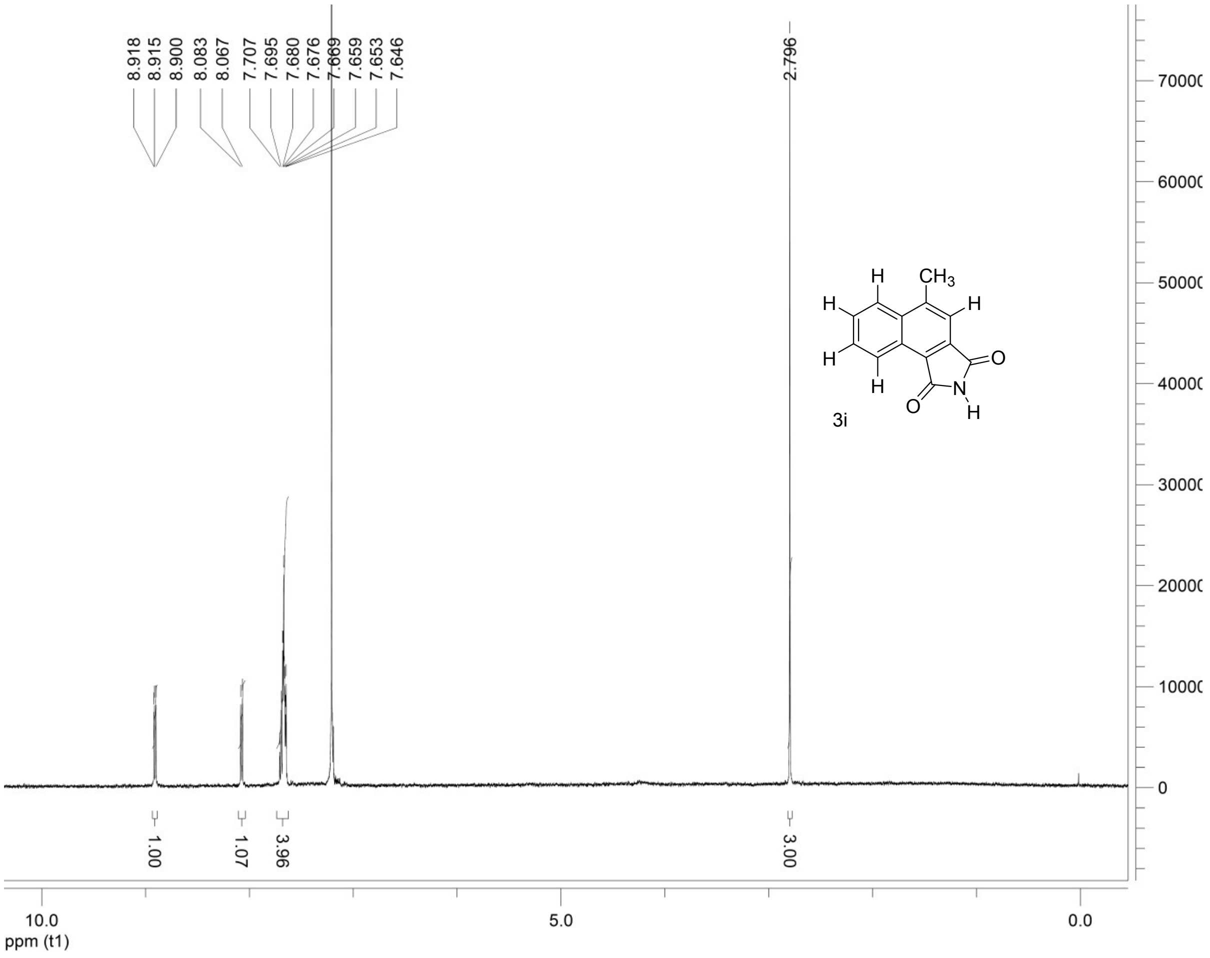
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7.653
7.646
2.796
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1.07
3.96
3.00
10.0
5.0
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10000
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N
O
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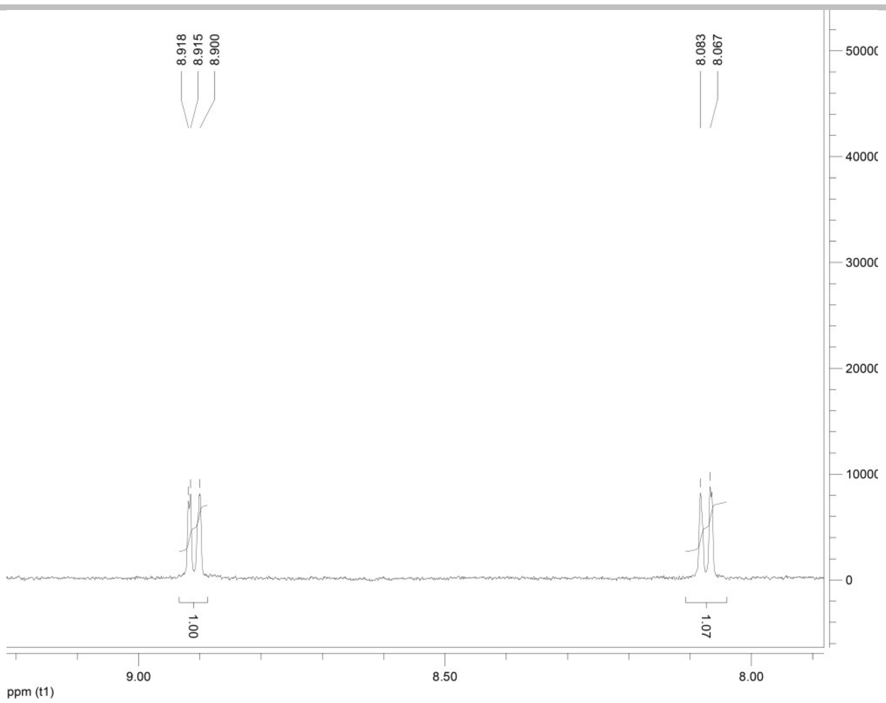
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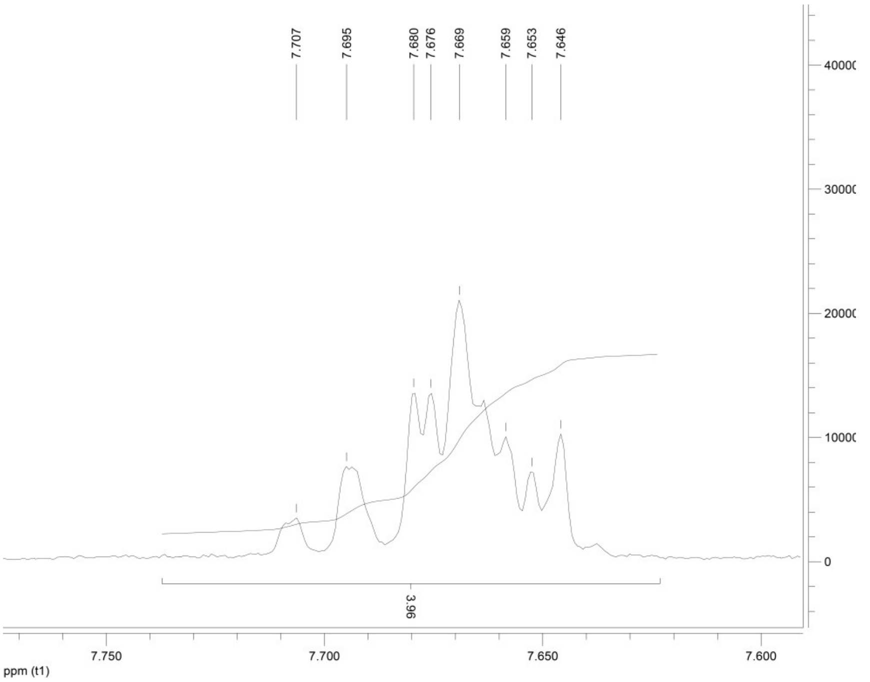
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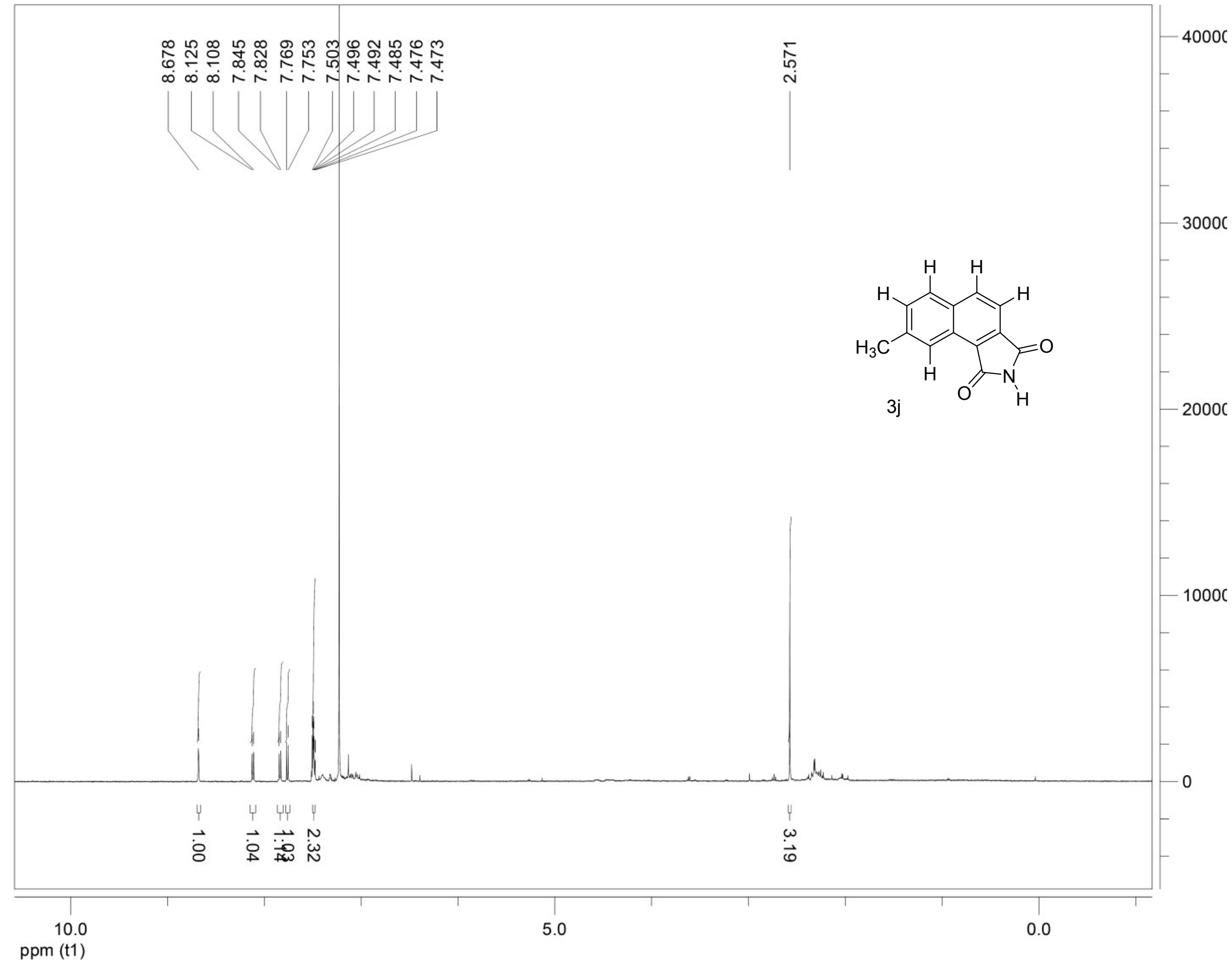
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8.108
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7.492
7.485
7.476
7.473
2.571
40000
30000
20000
10000
0
1.00
1.04
1.04
1.03
2.32
3.19
10.0
5.0
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ppm (t1)
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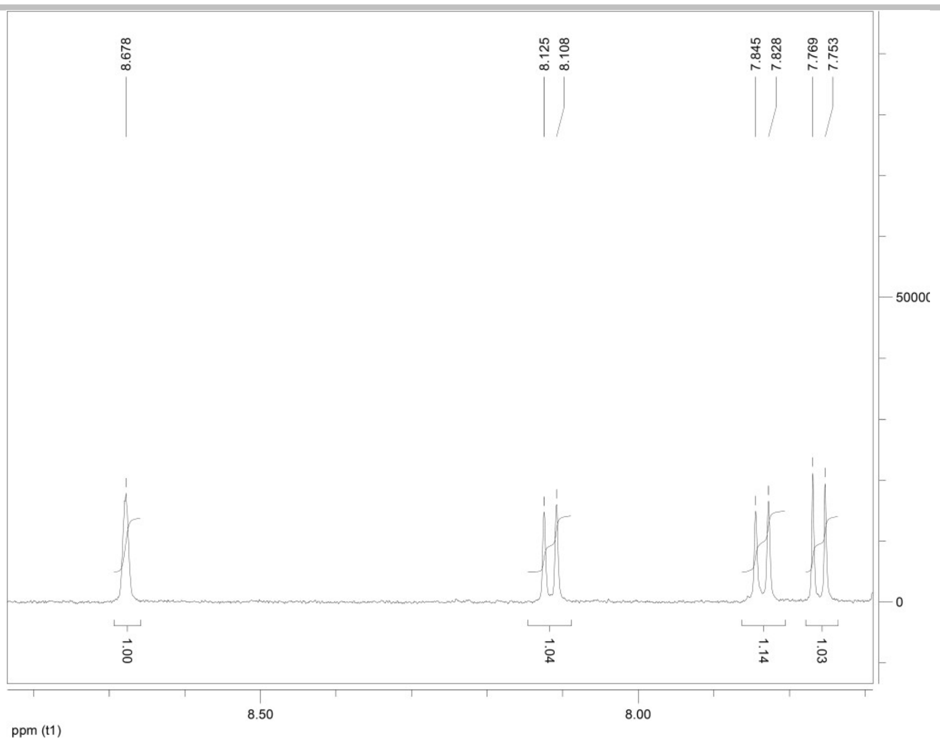
H
H
H
H$_3$C
H
O
N
O
H
3j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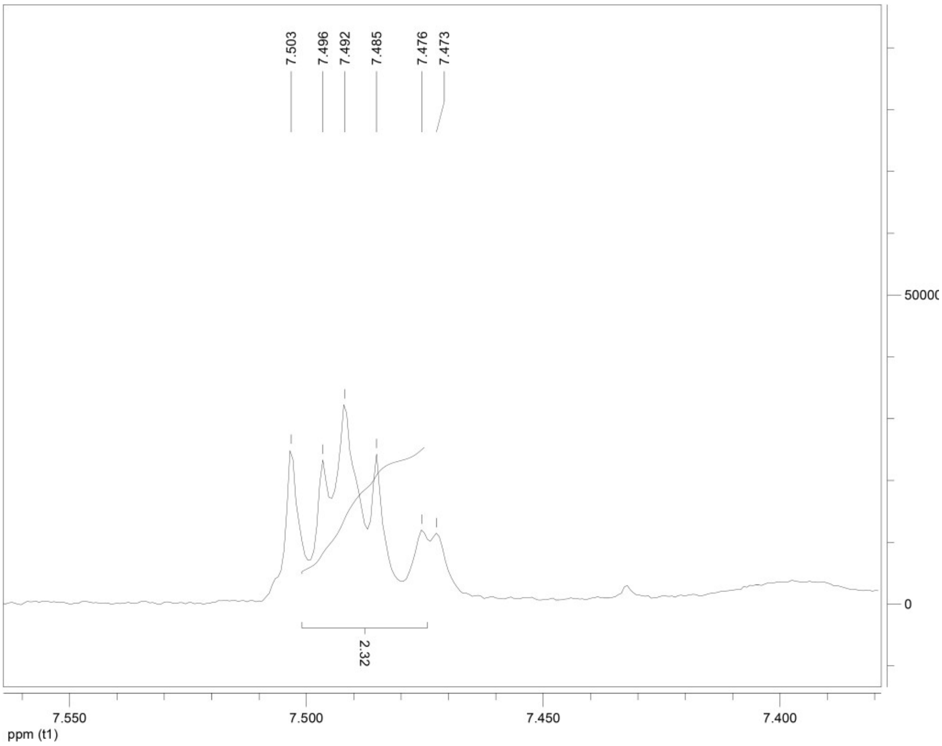
1.03
8.50
8.00
ppm (t1)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2.32
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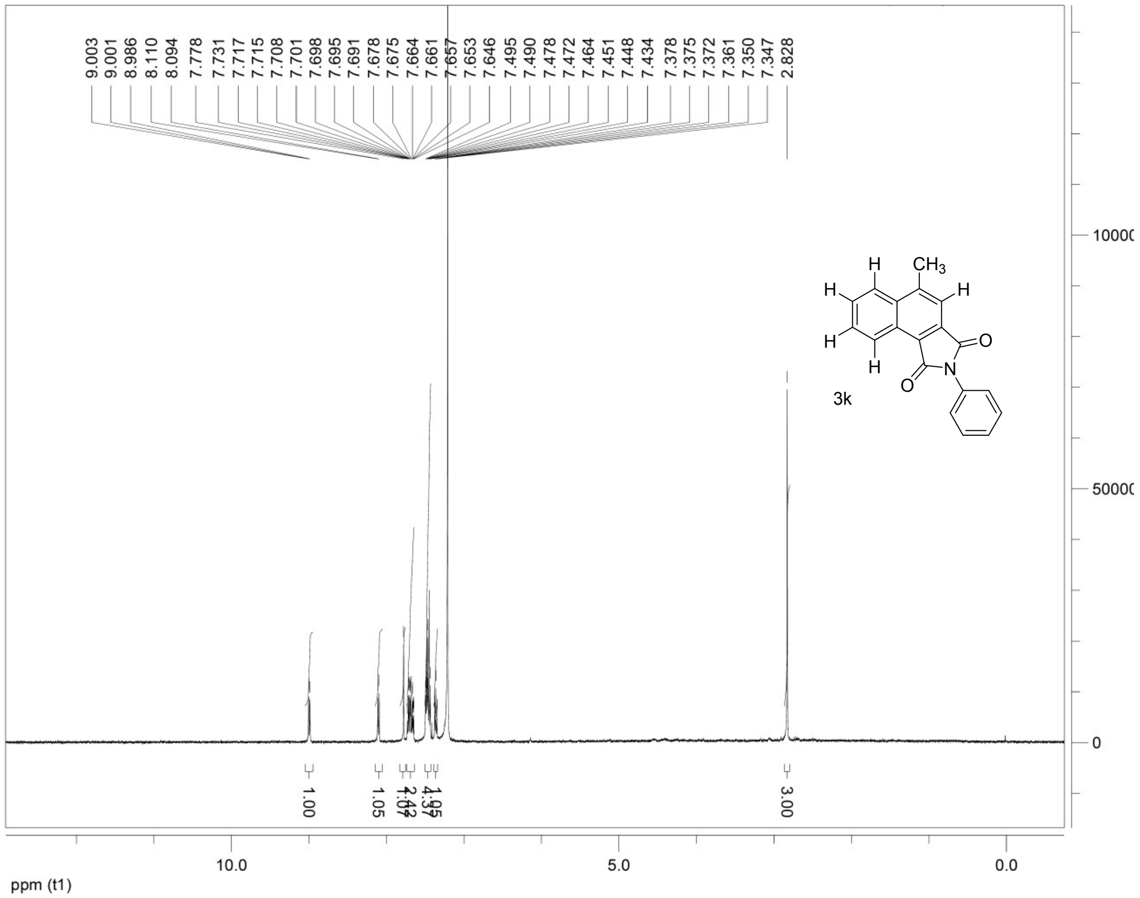
7.500
7.450
7.400
ppm (t1)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7.698
7.695
7.691
7.678
7.675
7.664
7.661
7.657
7.653
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7.490
7.478
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7.375
7.372
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7.347
2.828
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1.05
1.07
2.12
4.37
1.05
3.00
3.00
10.0
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ppm (t1)
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O
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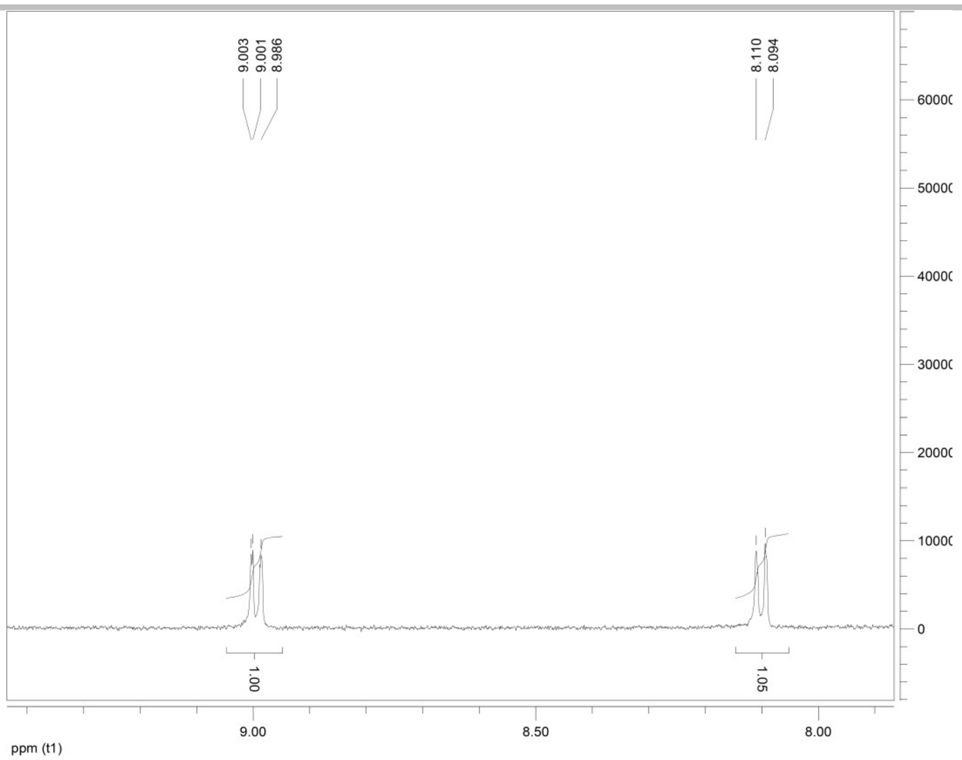
3k



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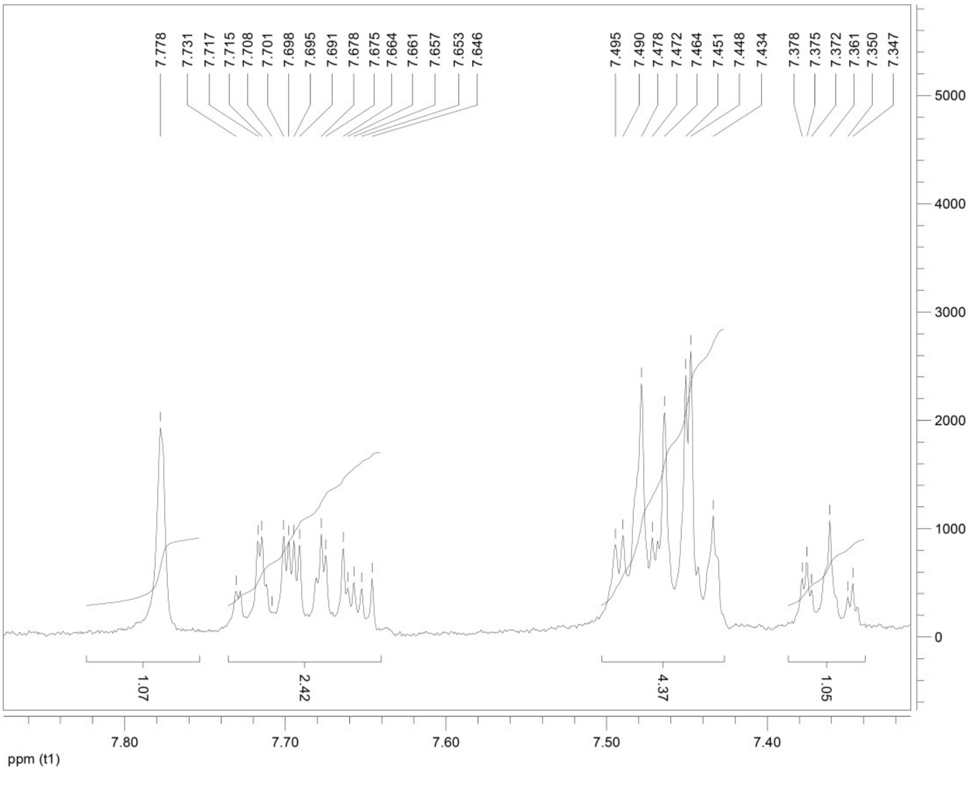
ppm (t1)



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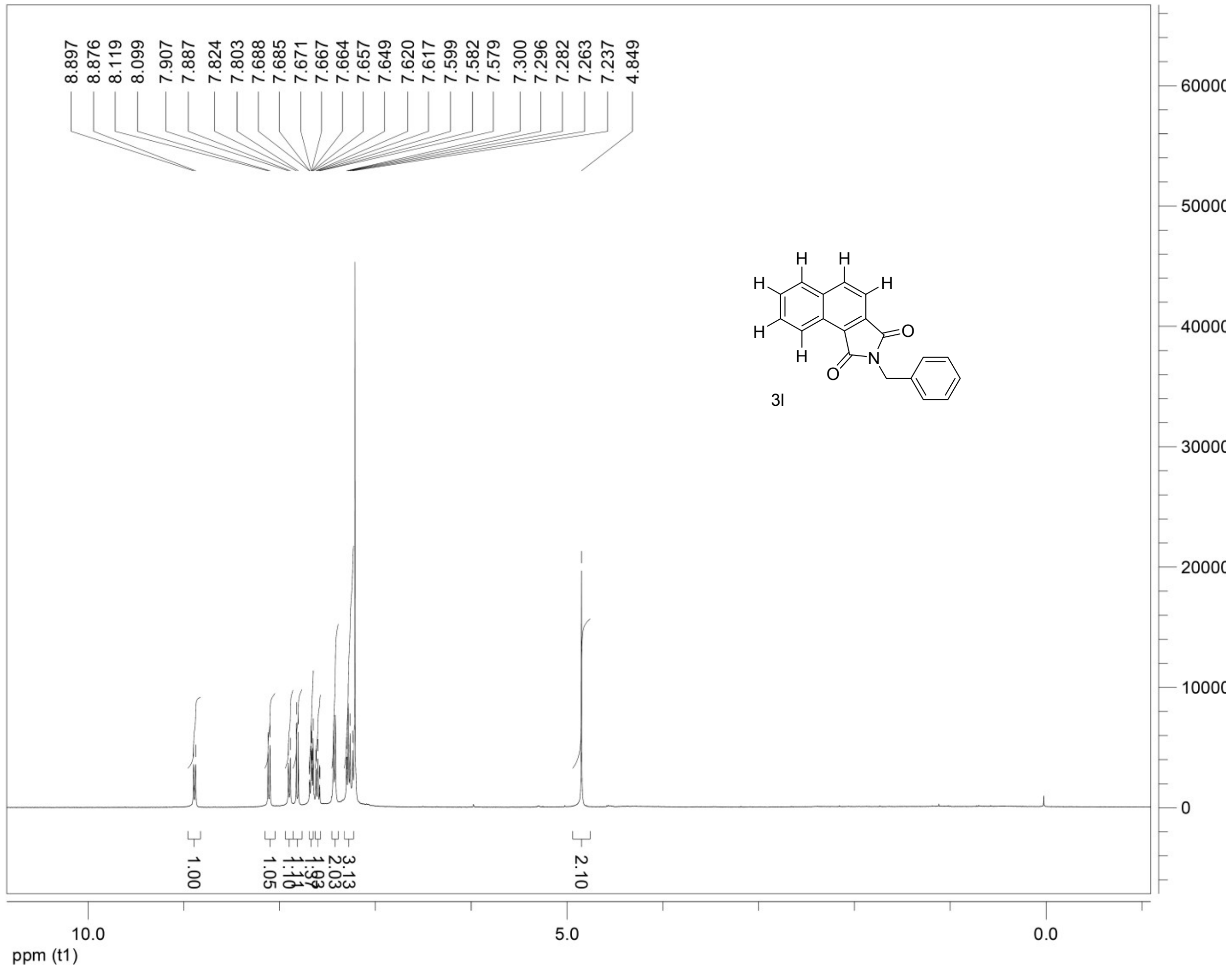
ppm (t1)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7.664
7.657
7.649
7.620
7.617
7.599
7.582
7.579
7.300
7.296
7.282
7.263
7.237
4.849
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H
H
H
H
H
O
N
O
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50000
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30000
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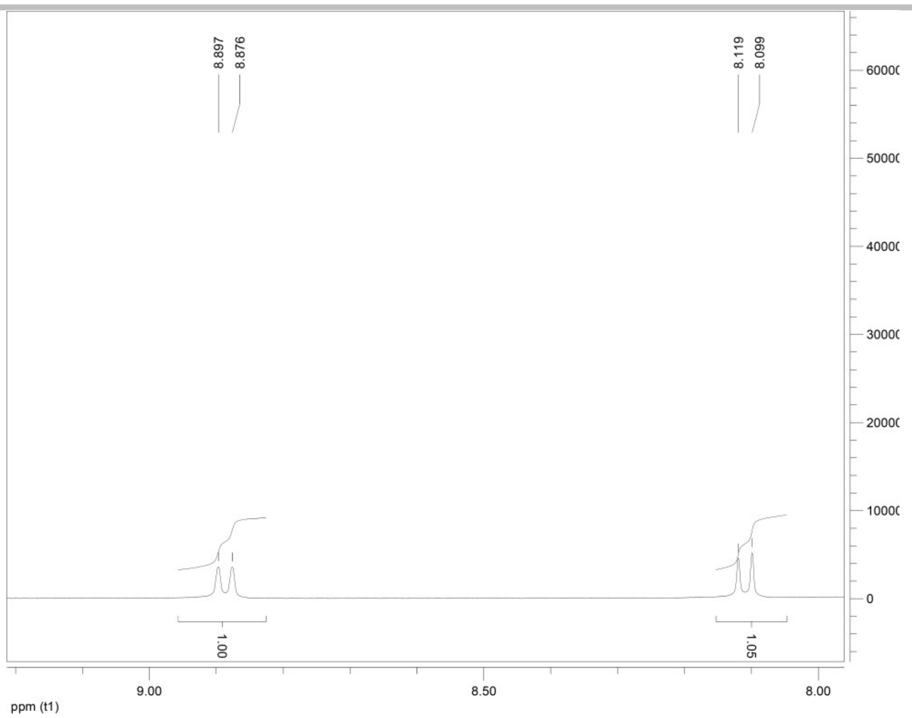
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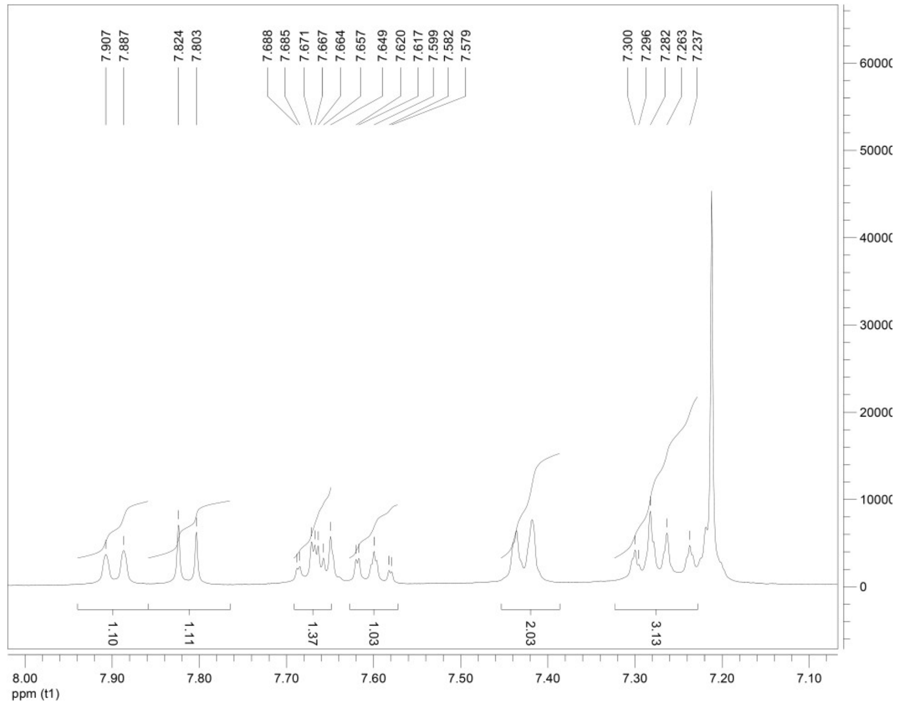
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7.296
7.282
7.263
7.237
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1.11
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1.03
2.03
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20000
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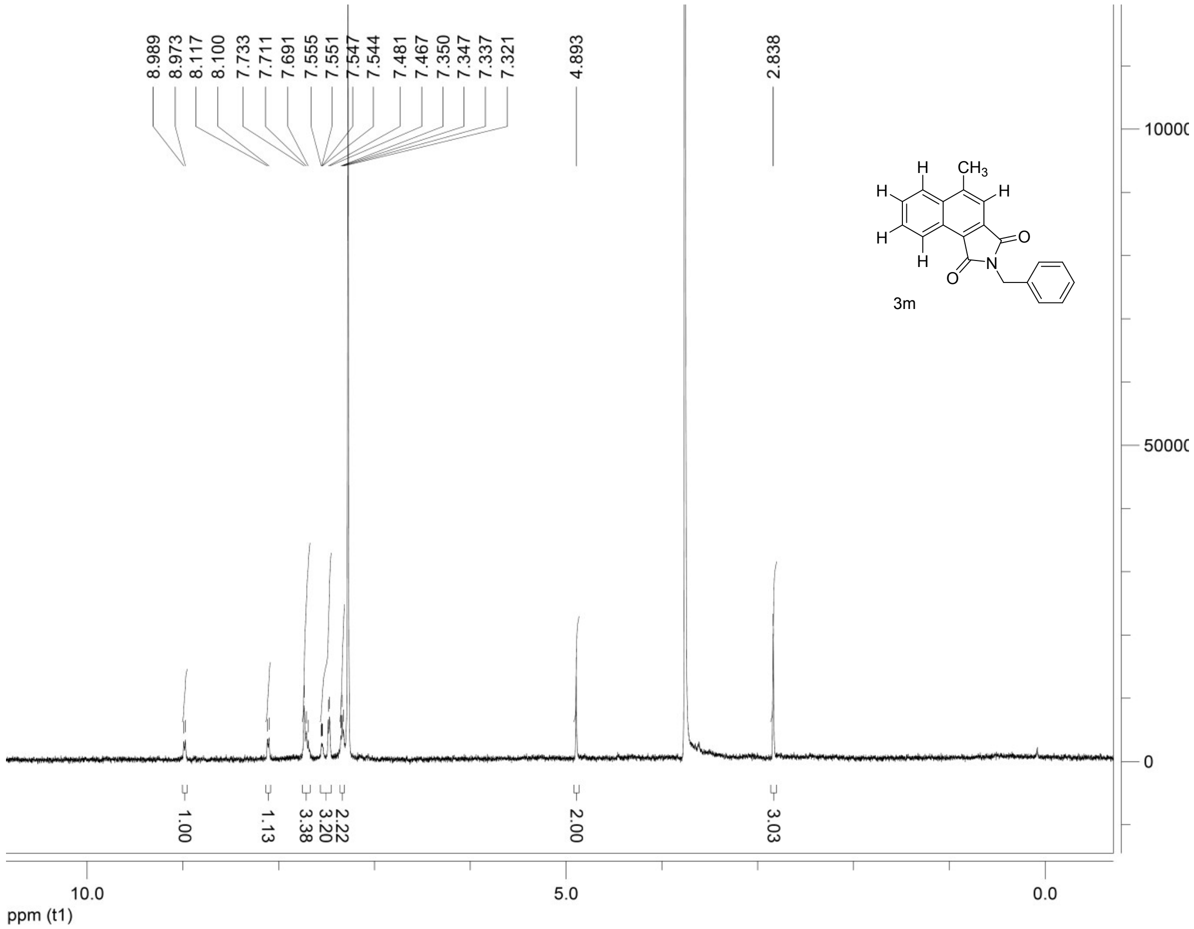
7.10
ppm (t1)



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7.481
7.467
7.350
7.347
7.337
7.321
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2.838
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H
H
O
N
H
O
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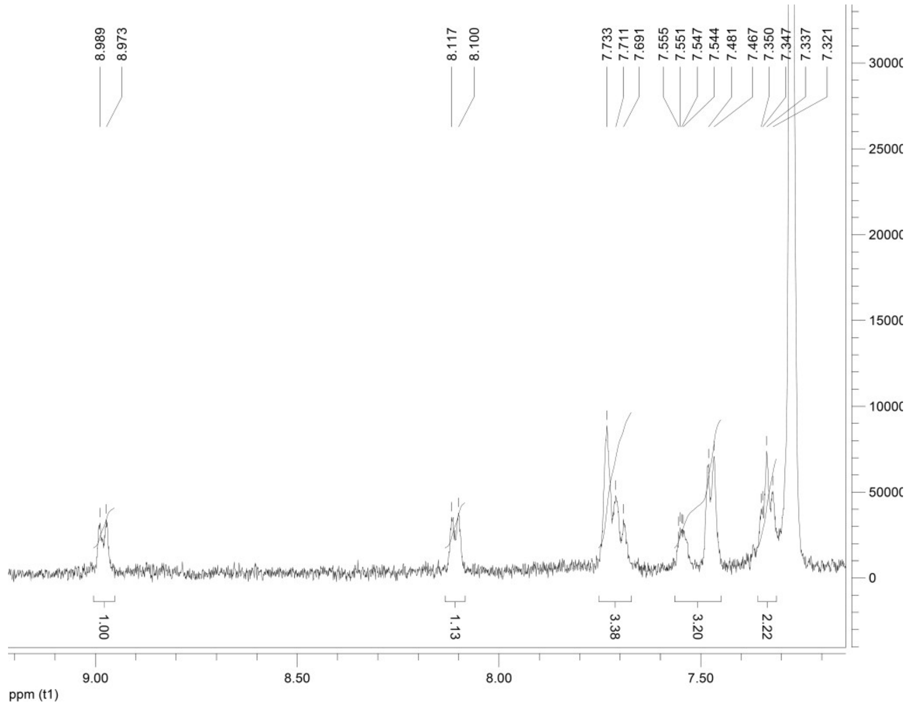
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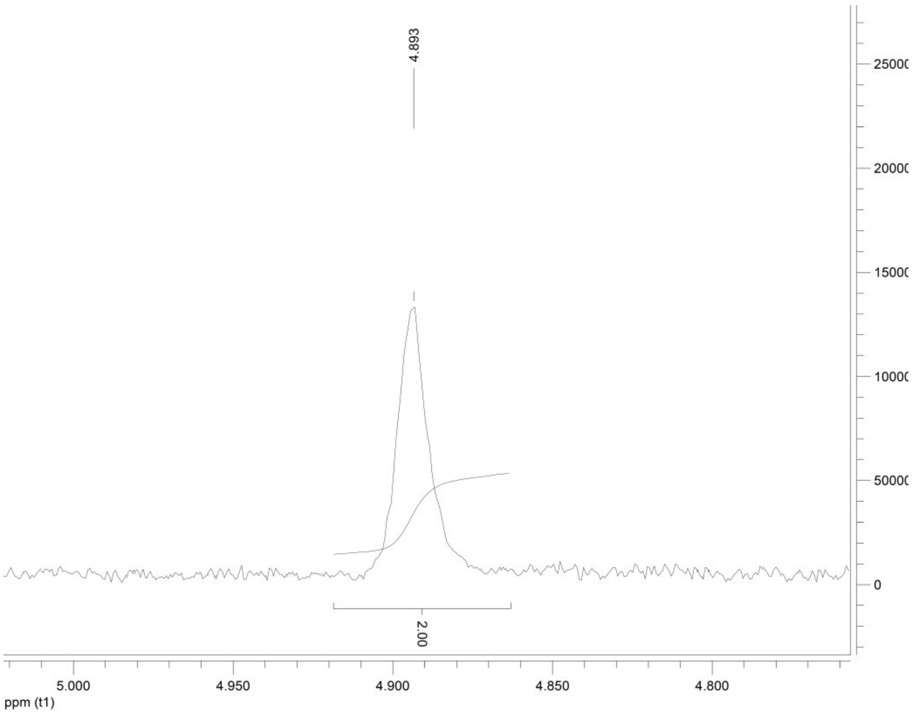
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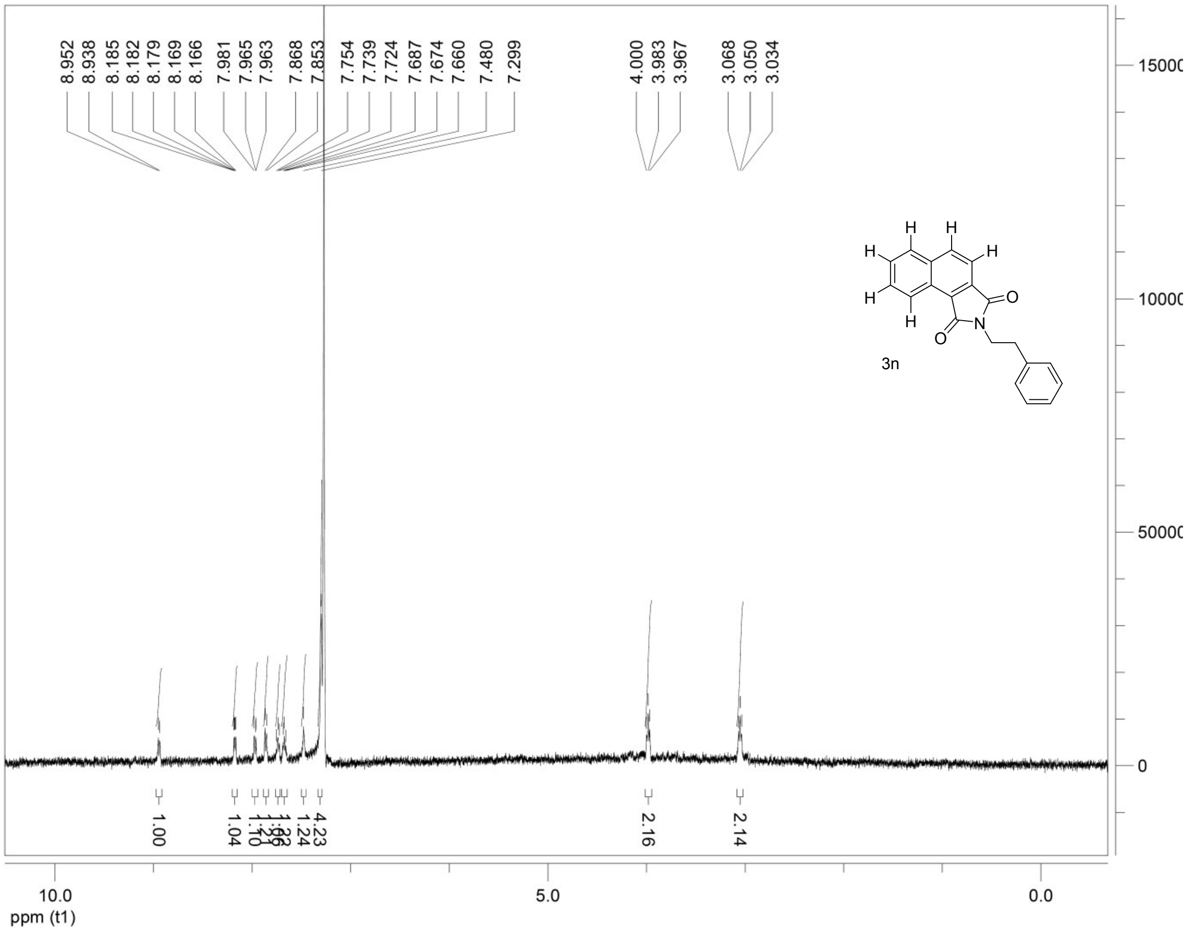8.952
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7.754
7.739
7.724
7.687
7.674
7.660
7.480
7.299
4.000
3.983
3.967
3.068
3.050
3.034
H
H
H
H
H
H
O
N
O
3n
1.00
1.04
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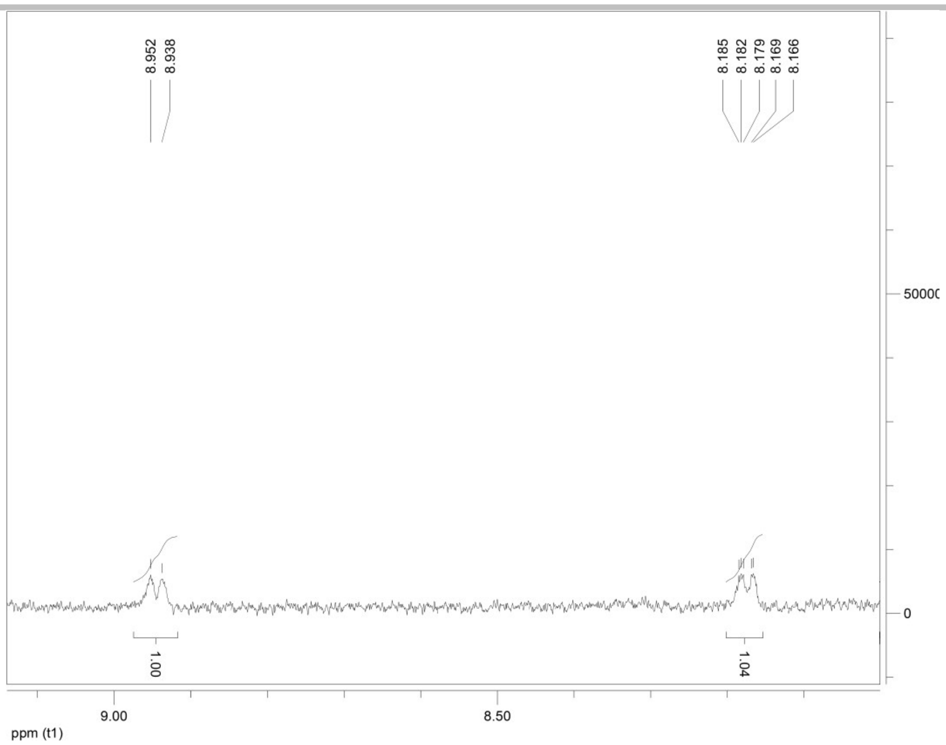
ppm (t1)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8.169
8.166
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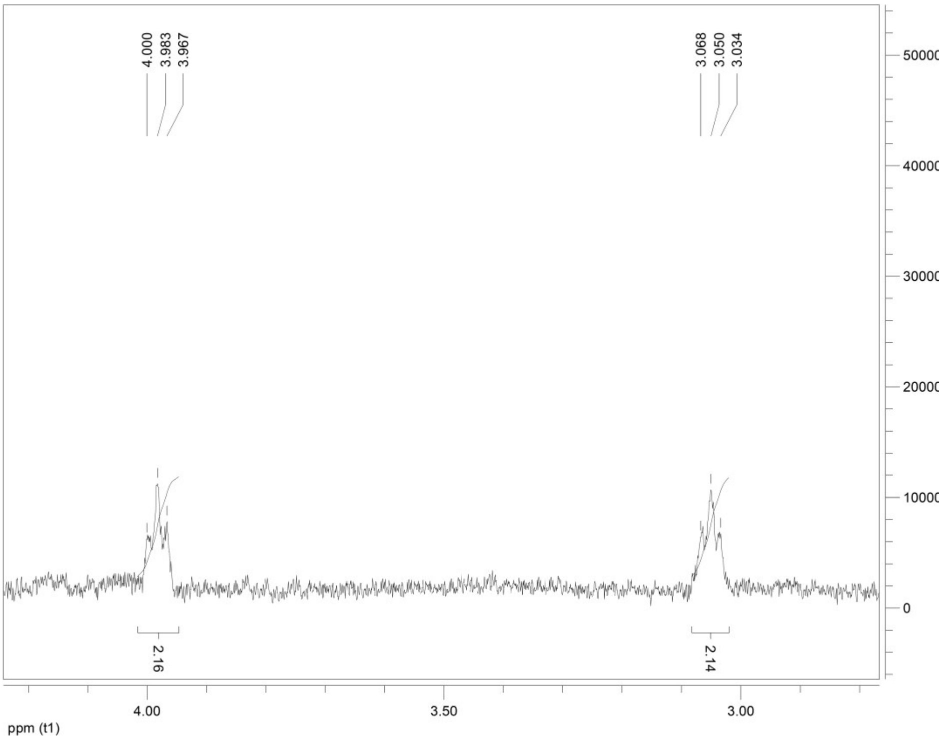
ppm (t1)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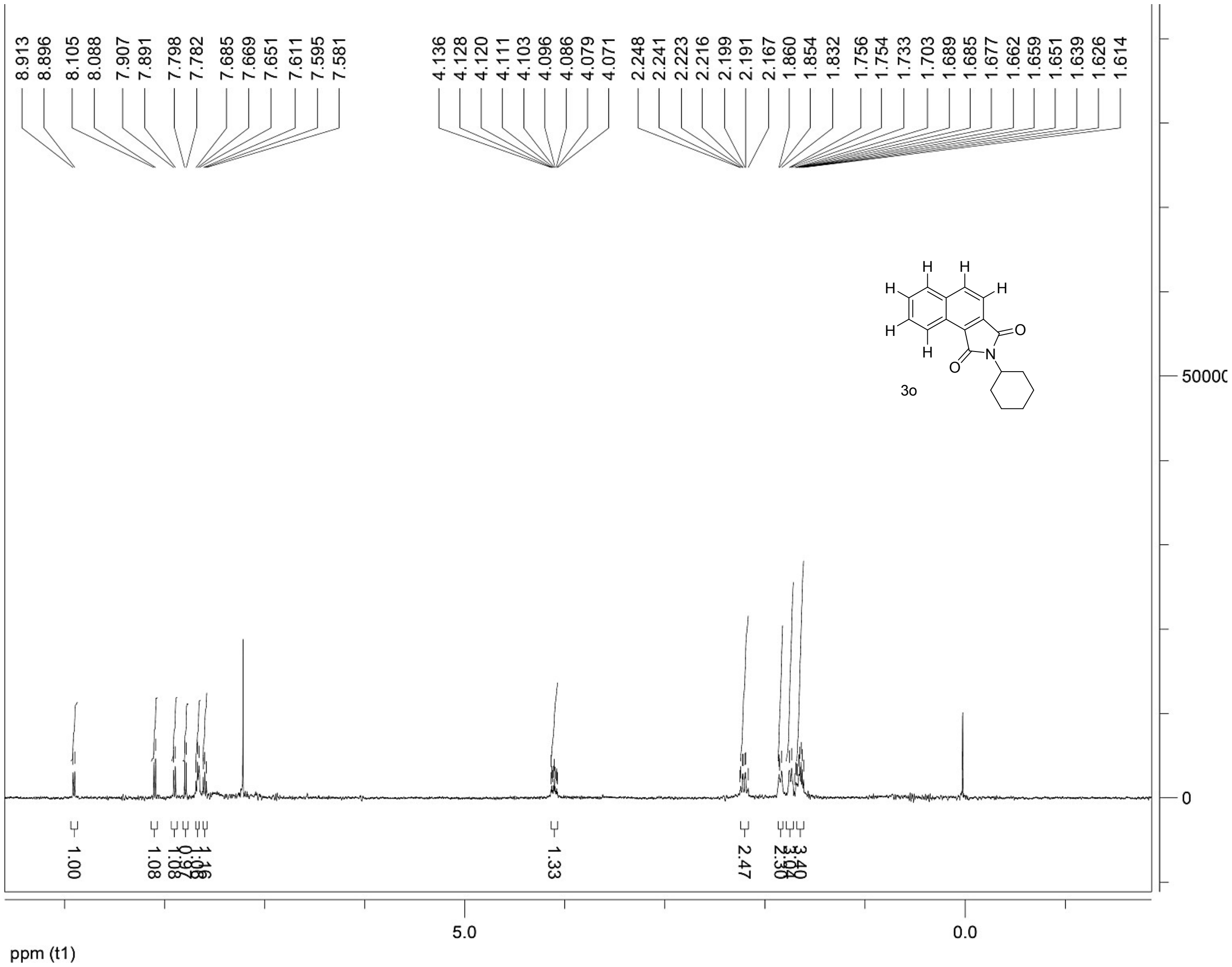
ppm (t1)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7.611
7.595
7.581
4.136
4.128
4.120
4.111
4.103
4.096
4.086
4.079
4.071
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2.241
2.223
2.216
2.199
2.191
2.167
1.860
1.854
1.832
1.756
1.754
1.733
1.703
1.689
1.685
1.677
1.662
1.659
1.651
1.639
1.626
1.614
H
H
H
H
H
H
O
N
O
3o
50000
0
1.00
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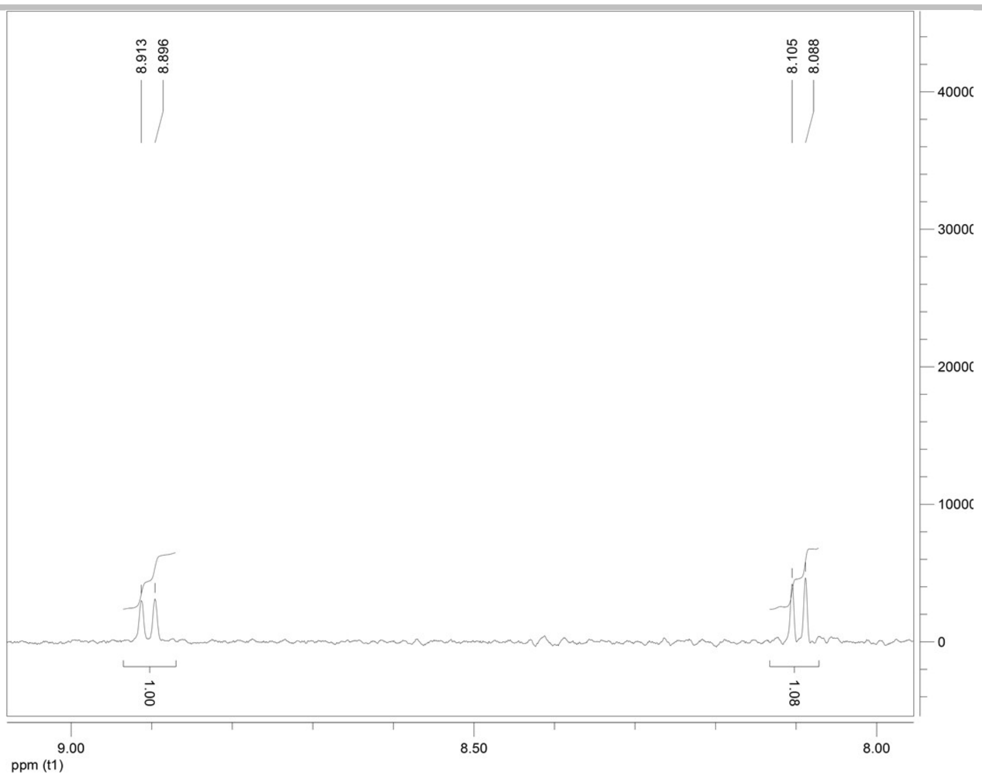
ppm (t1)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1.08
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8.50
8.00
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10000
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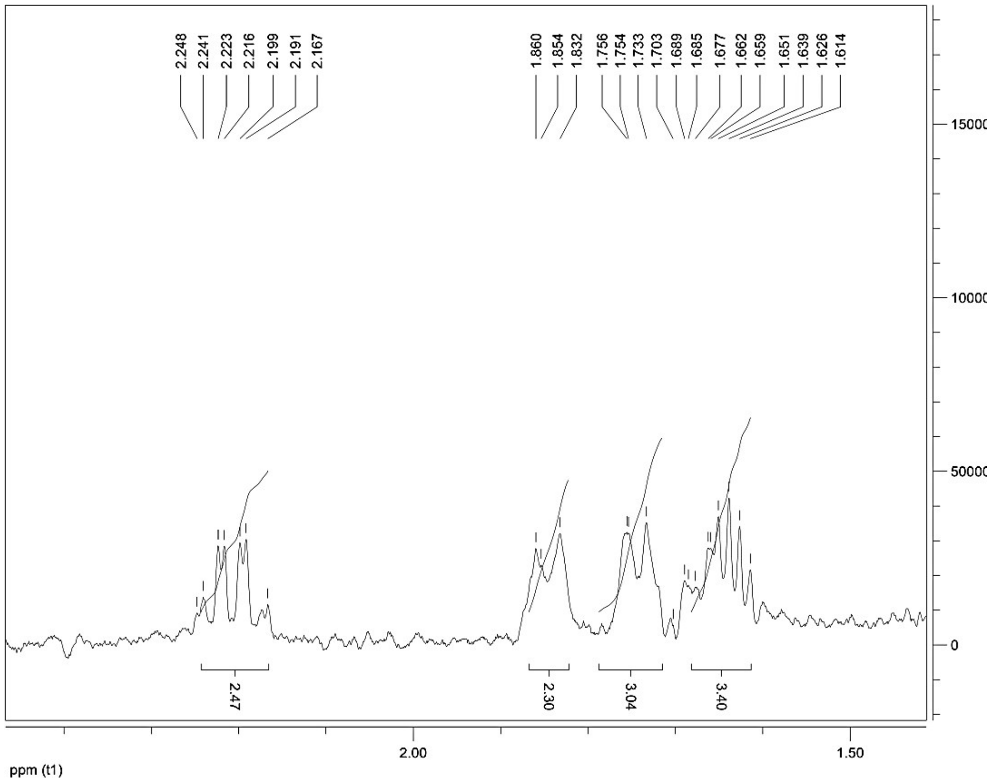
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1.662
1.659
1.651
1.639
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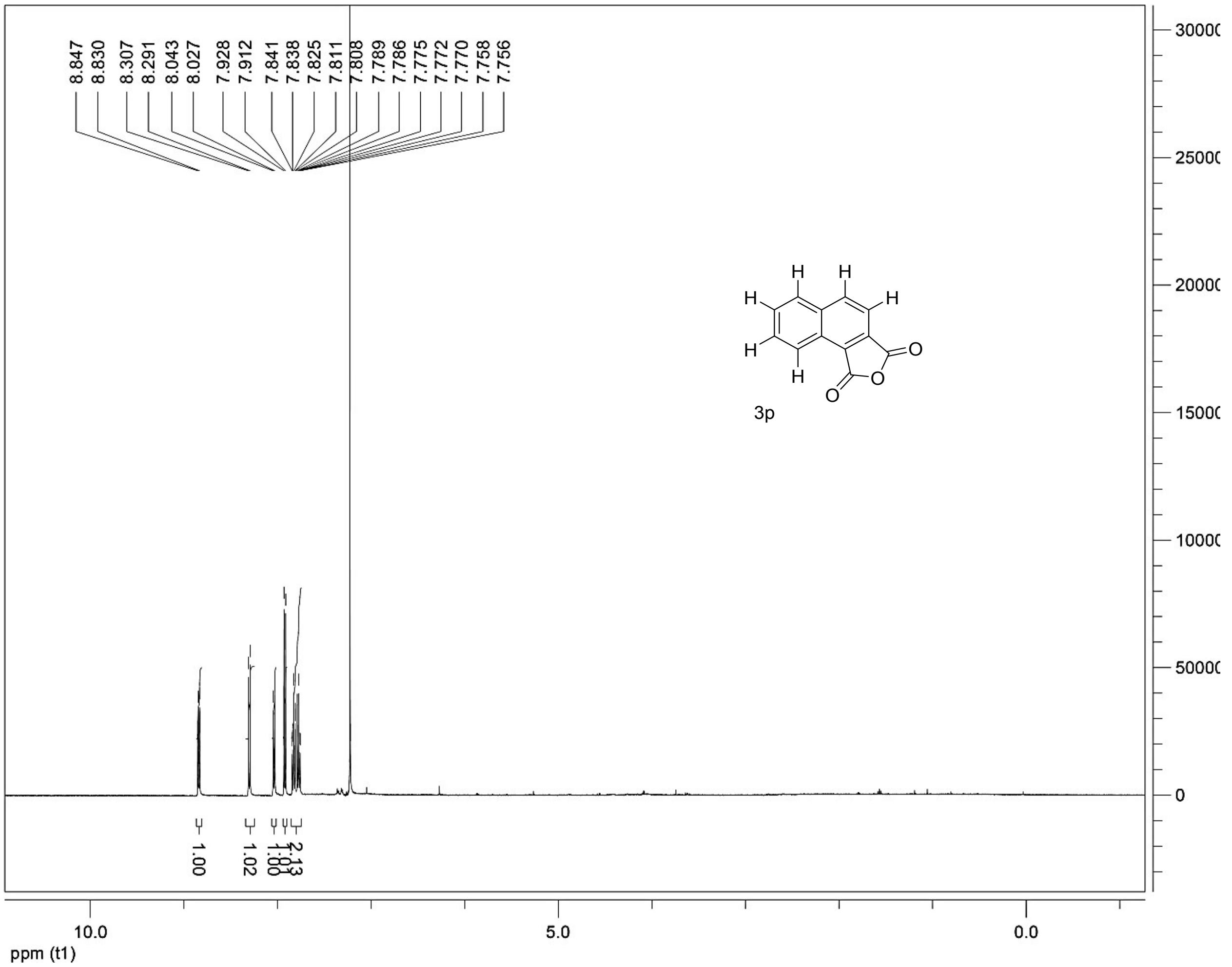
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8.291
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8.027
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7.912
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7.838
7.825
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7.808
7.789
7.786
7.775
7.772
7.770
7.758
7.756
H
H
H
H
H
H
O
O
O
3p
30000
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20000
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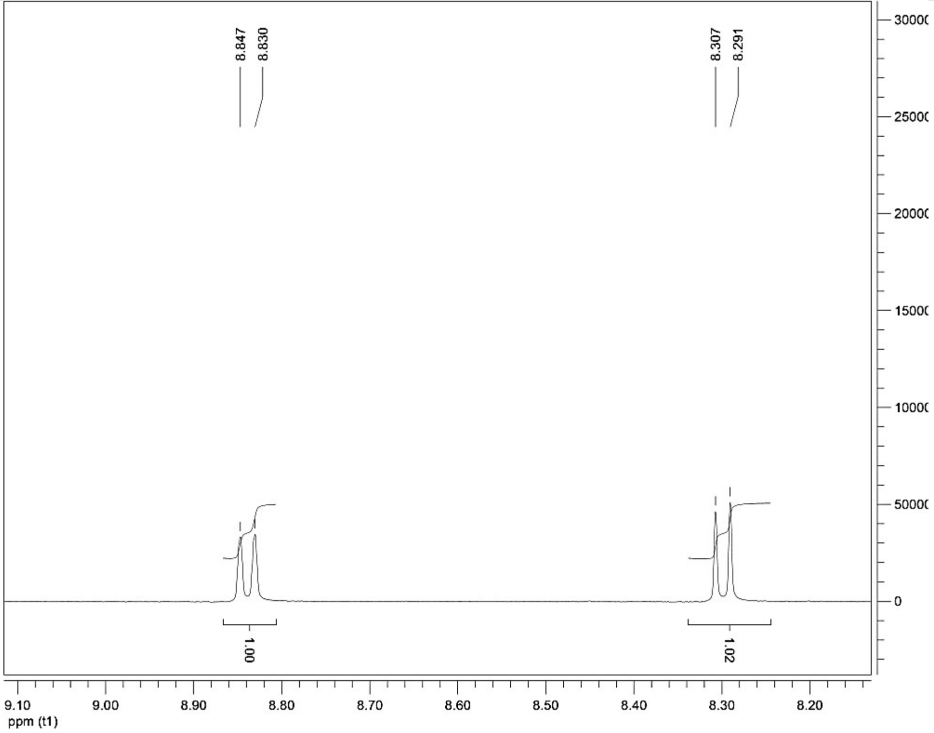
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8.307
8.291
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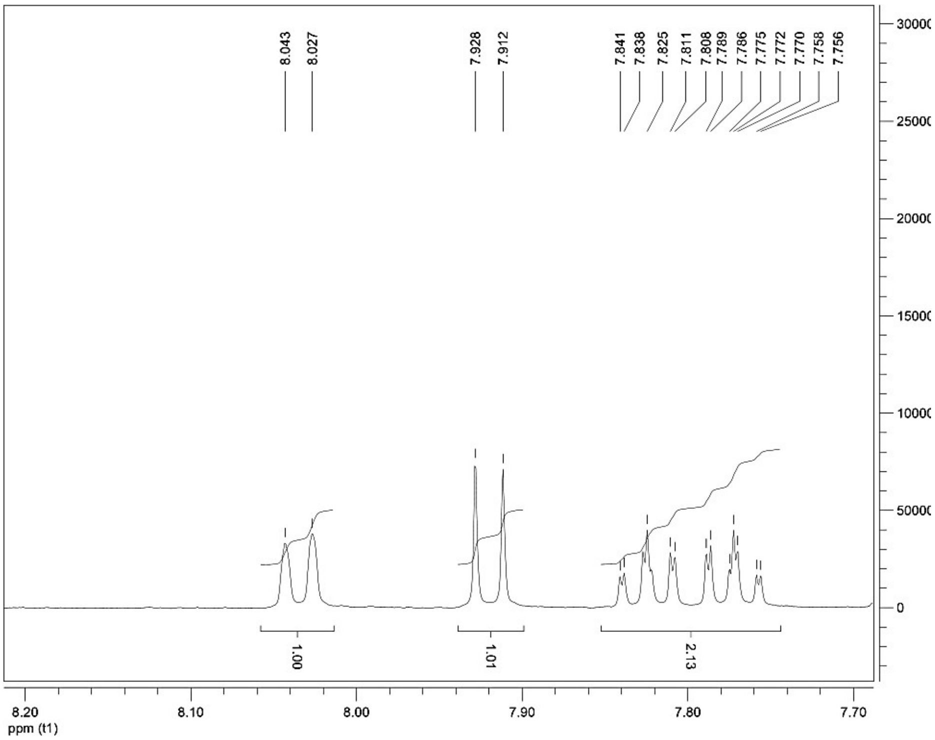
ppm (t1)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7.772
7.770
7.758
7.756
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1.01
2.13
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10000
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7.70
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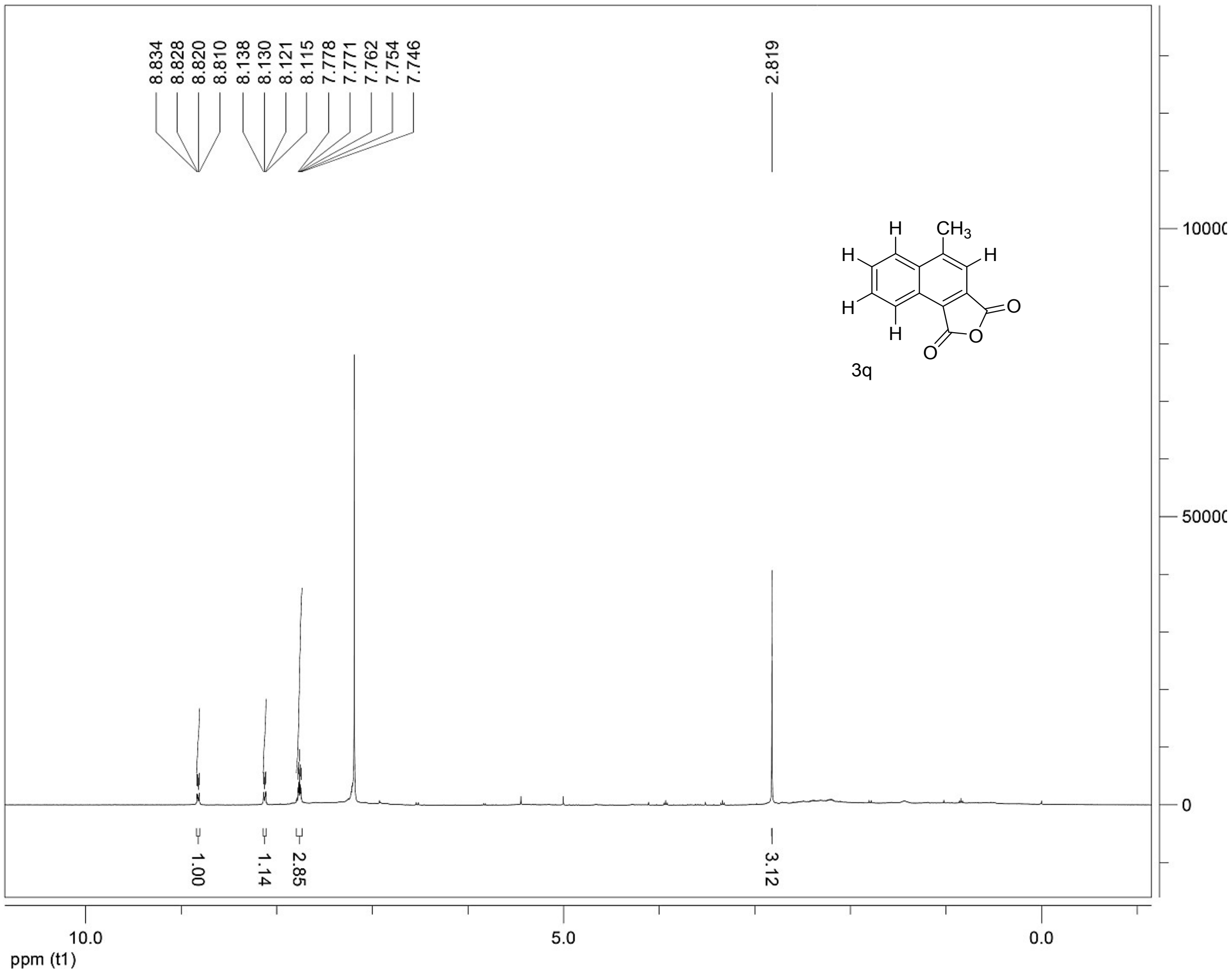
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8.115
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7.754
7.746
2.819
H
CH3
H
H
H
H
O
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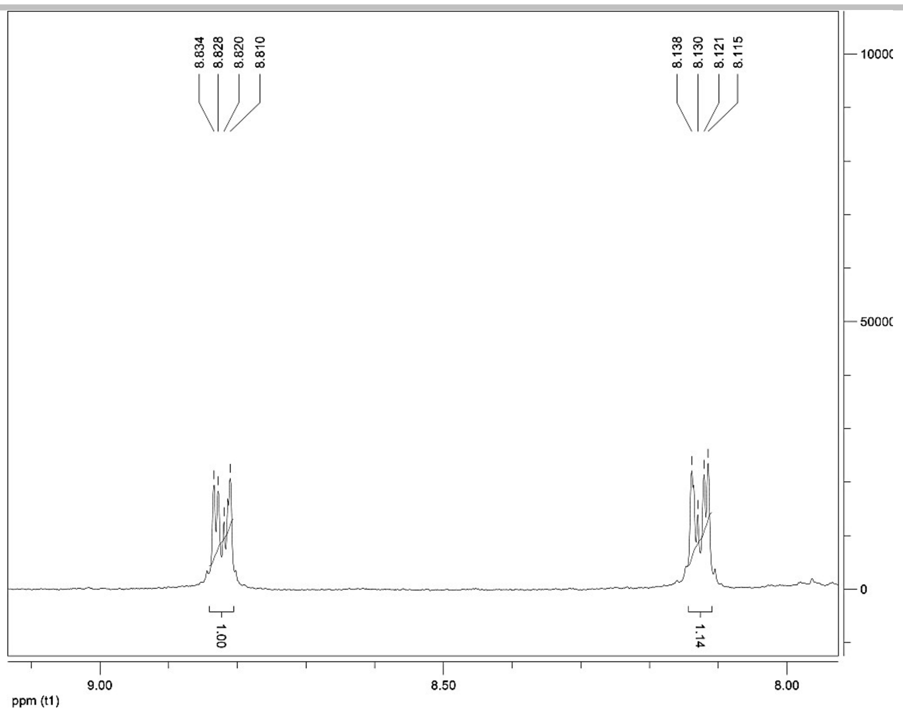
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8.115
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1.14
10000
50000
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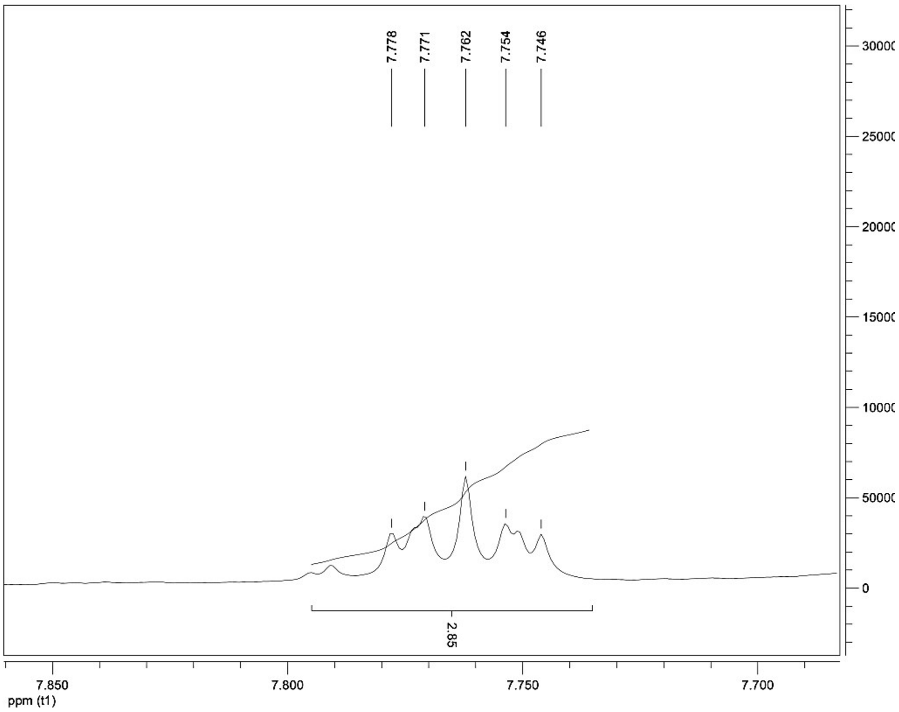
8.00
ppm (t1)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7.762
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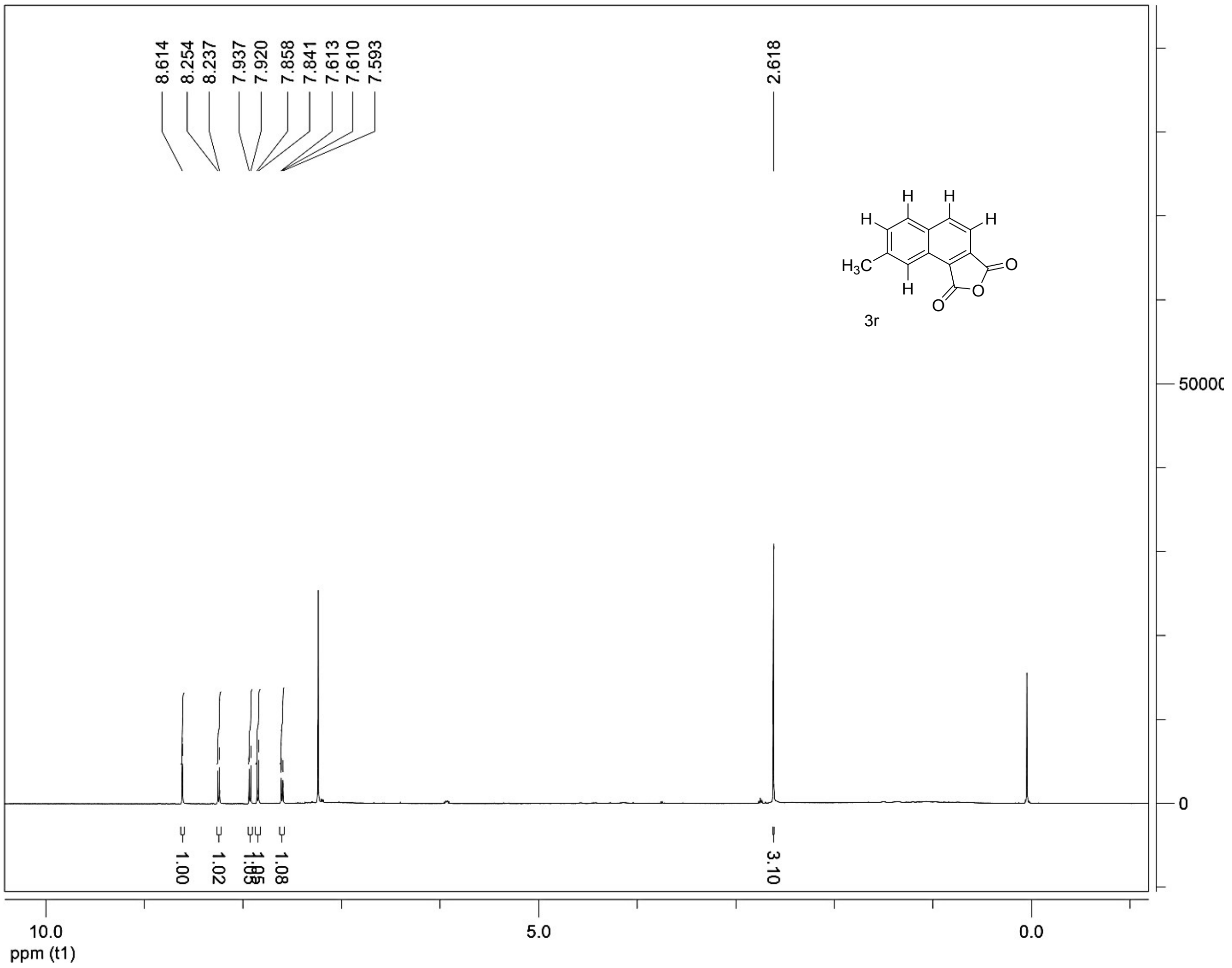
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7.613
7.610
7.593
2.618
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H
H
H
H
H_3C
O
O
O
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1.05
1.08
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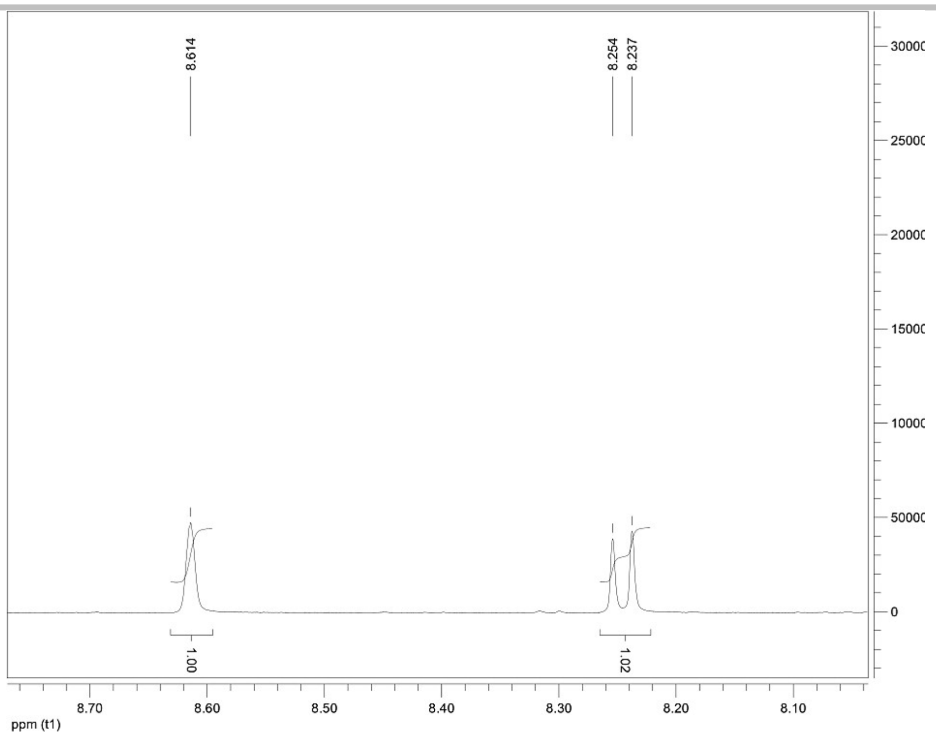
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8.20
8.10
ppm (t1)
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20000
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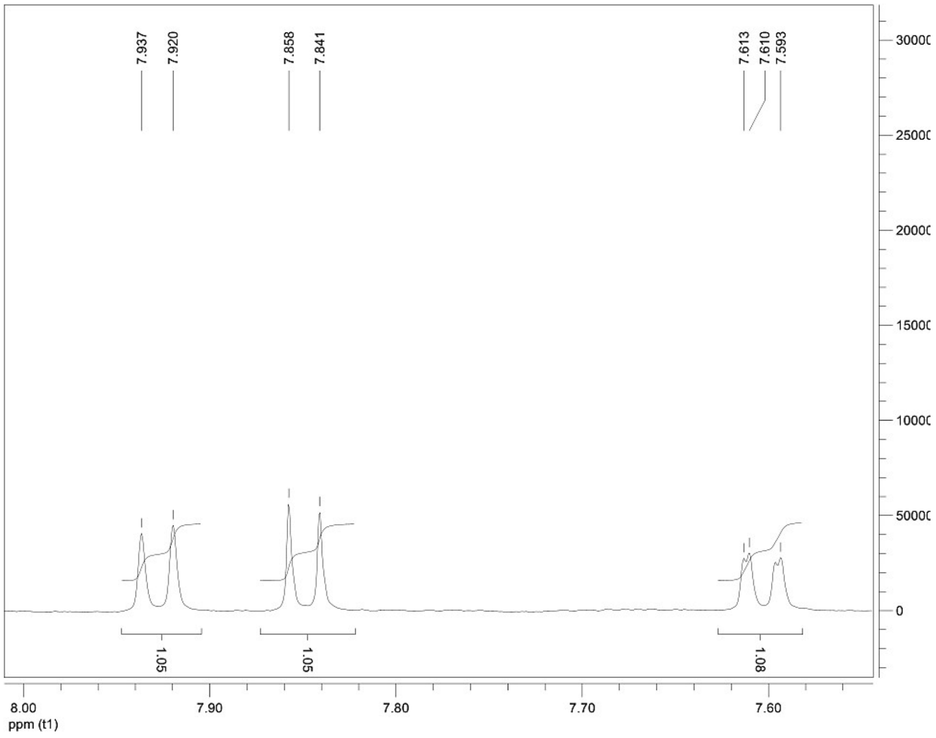
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7.841
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7.610
7.593
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1.05
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7.70
7.60
ppm (t1)
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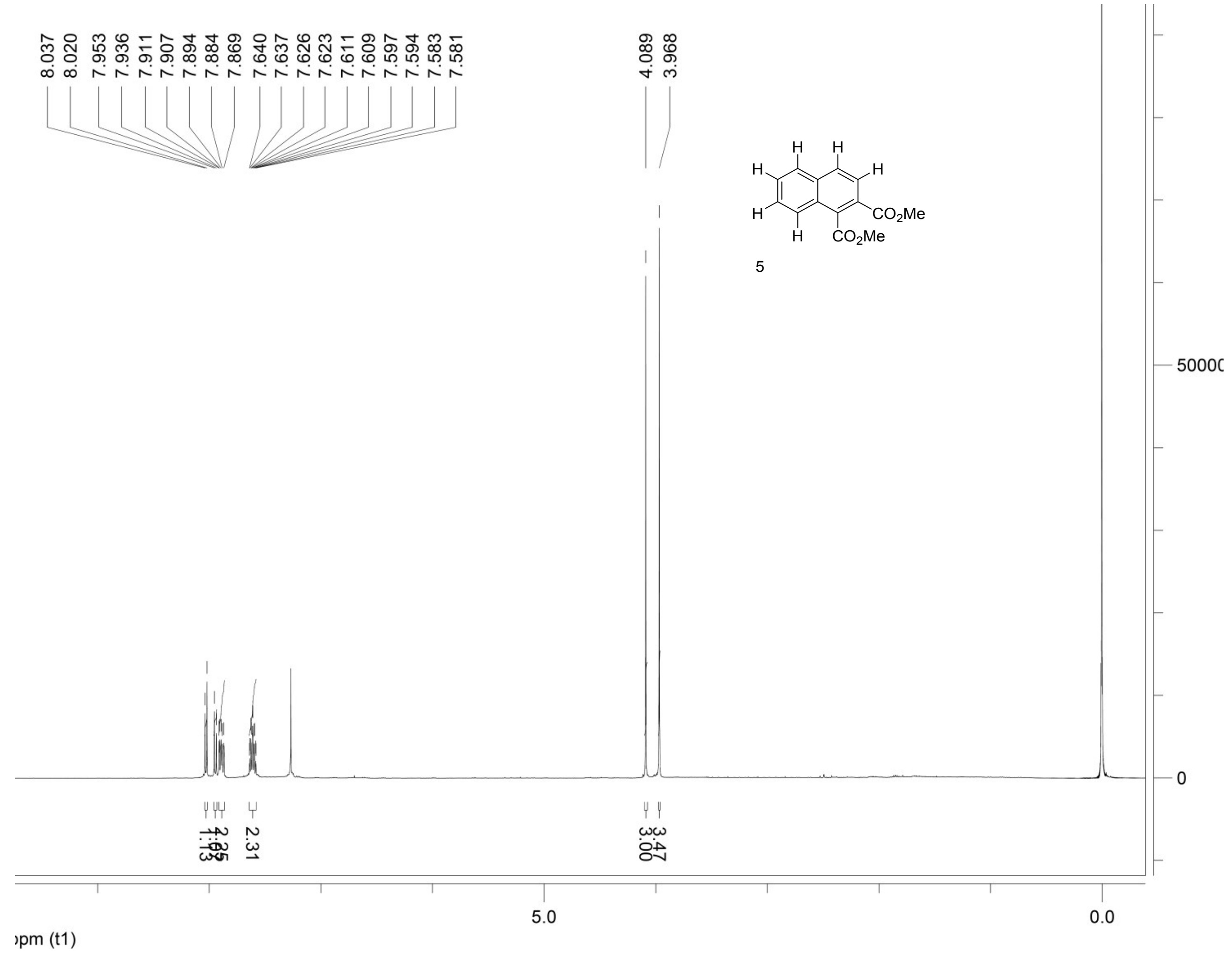
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7.626
7.623
7.611
7.609
7.597
7.594
7.583
7.581
4.089
3.968
H
H
H
H
CO2Me
H
H
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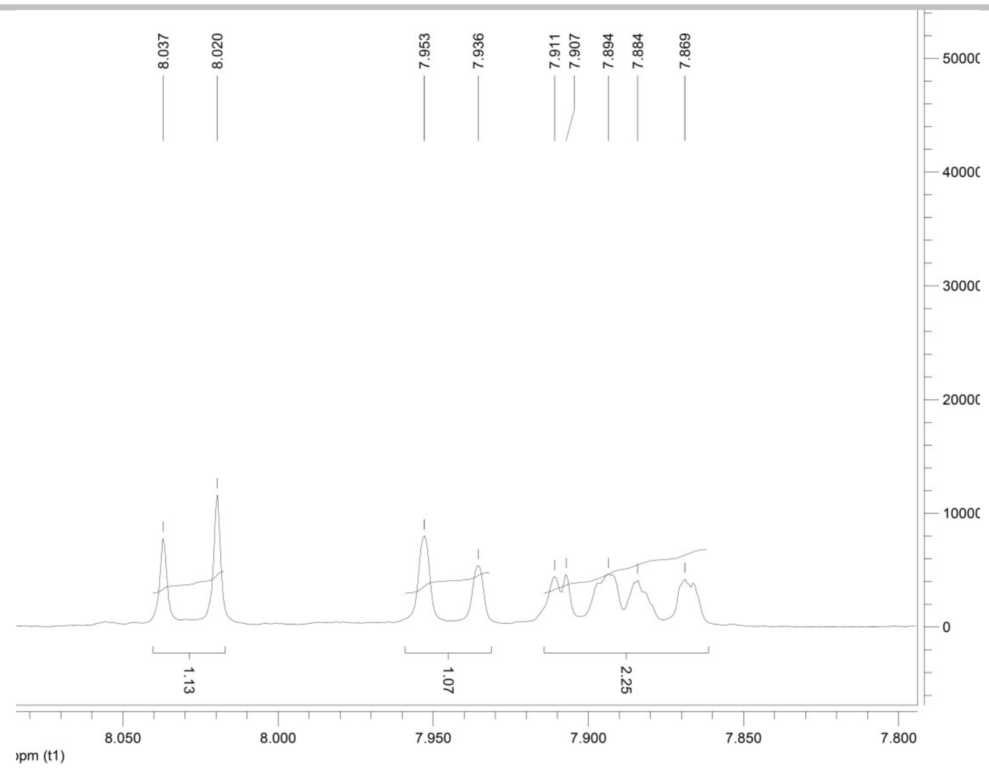
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7.907
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4000C
3000C
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1000C
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1.07
2.25
8.050
8.000
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7.900
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7.800
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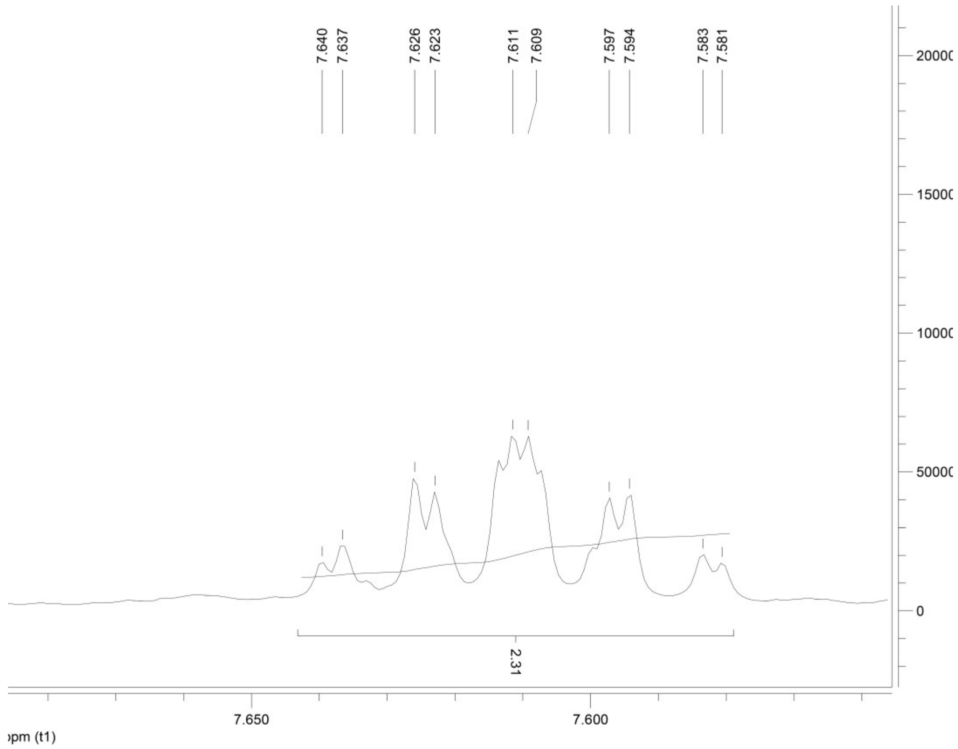
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7.623
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7.609
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1000C
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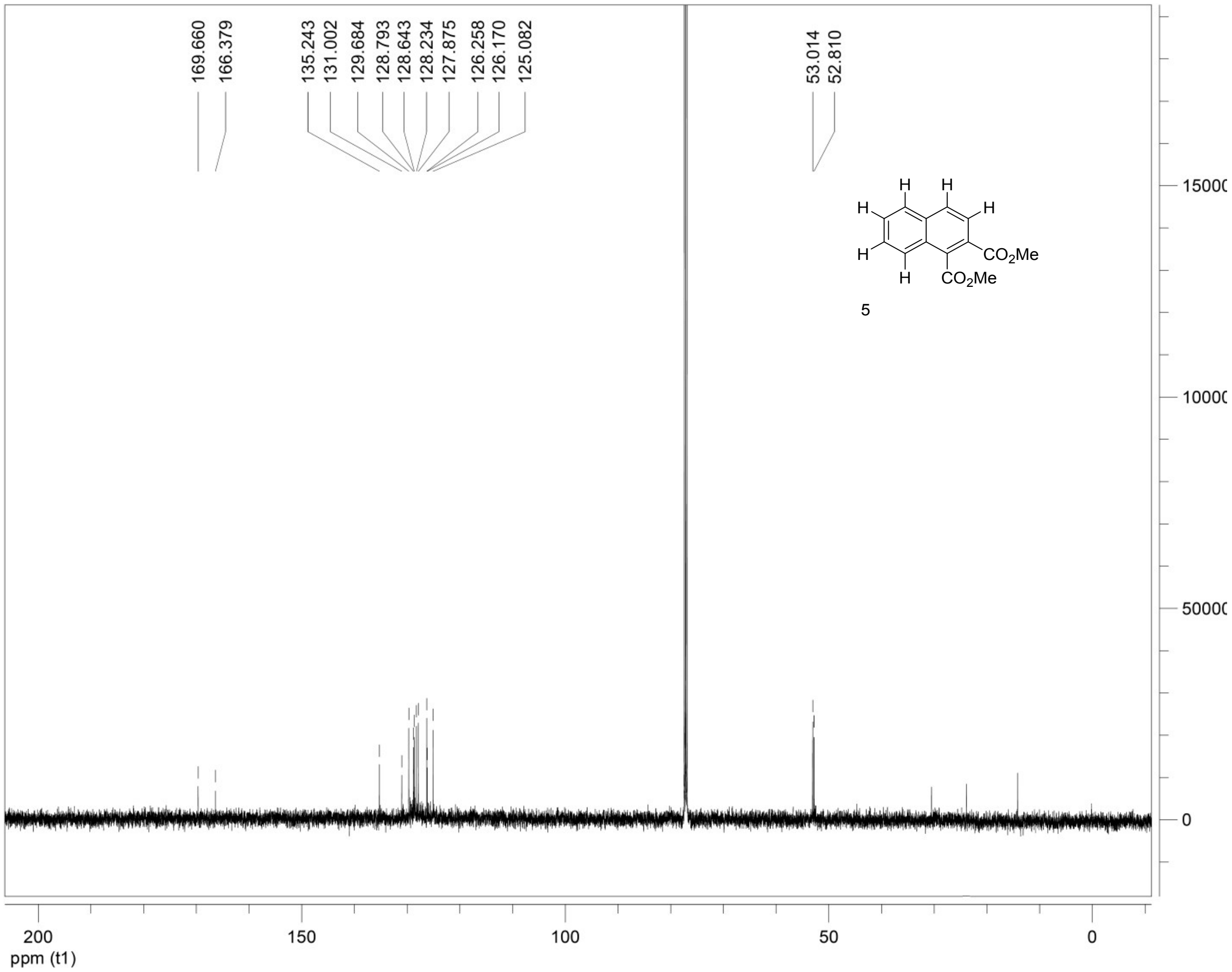
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53.014
52.810
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H
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CO_2Me
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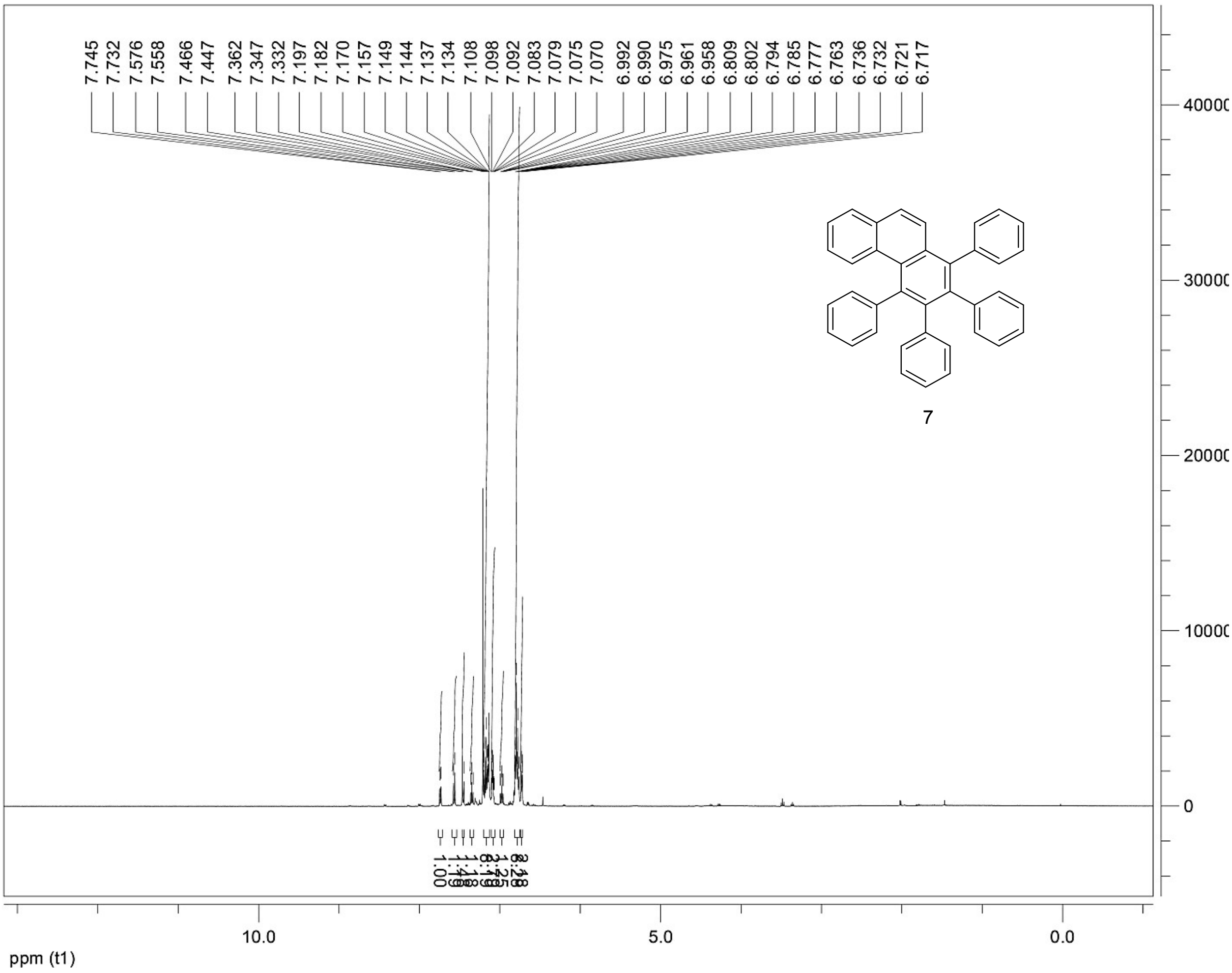7.745
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7.157
7.149
7.144
7.137
7.134
7.108
7.098
7.092
7.083
7.079
7.075
7.070
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6.990
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6.961
6.958
6.809
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6.794
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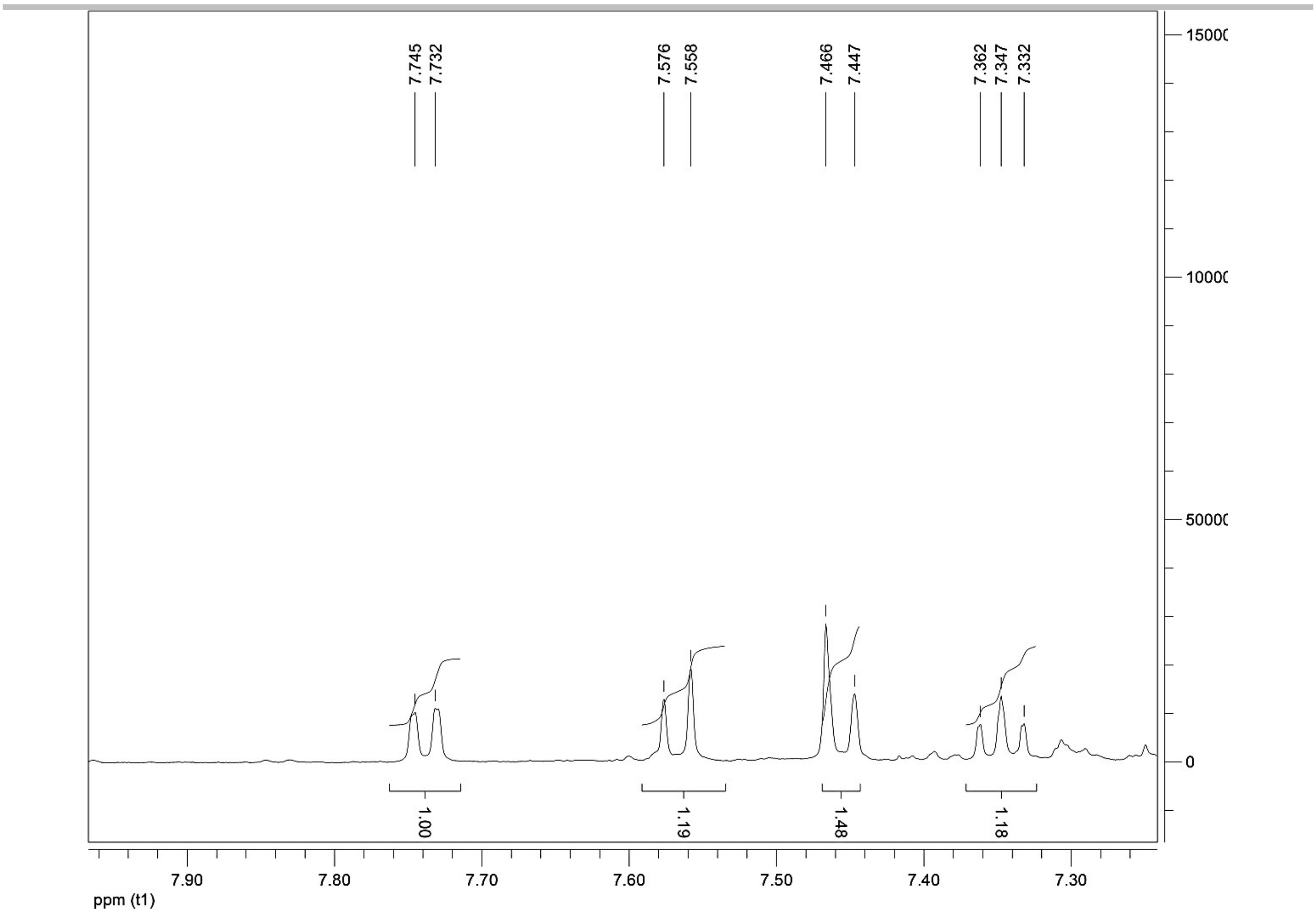
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1.19
1.48
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7.80
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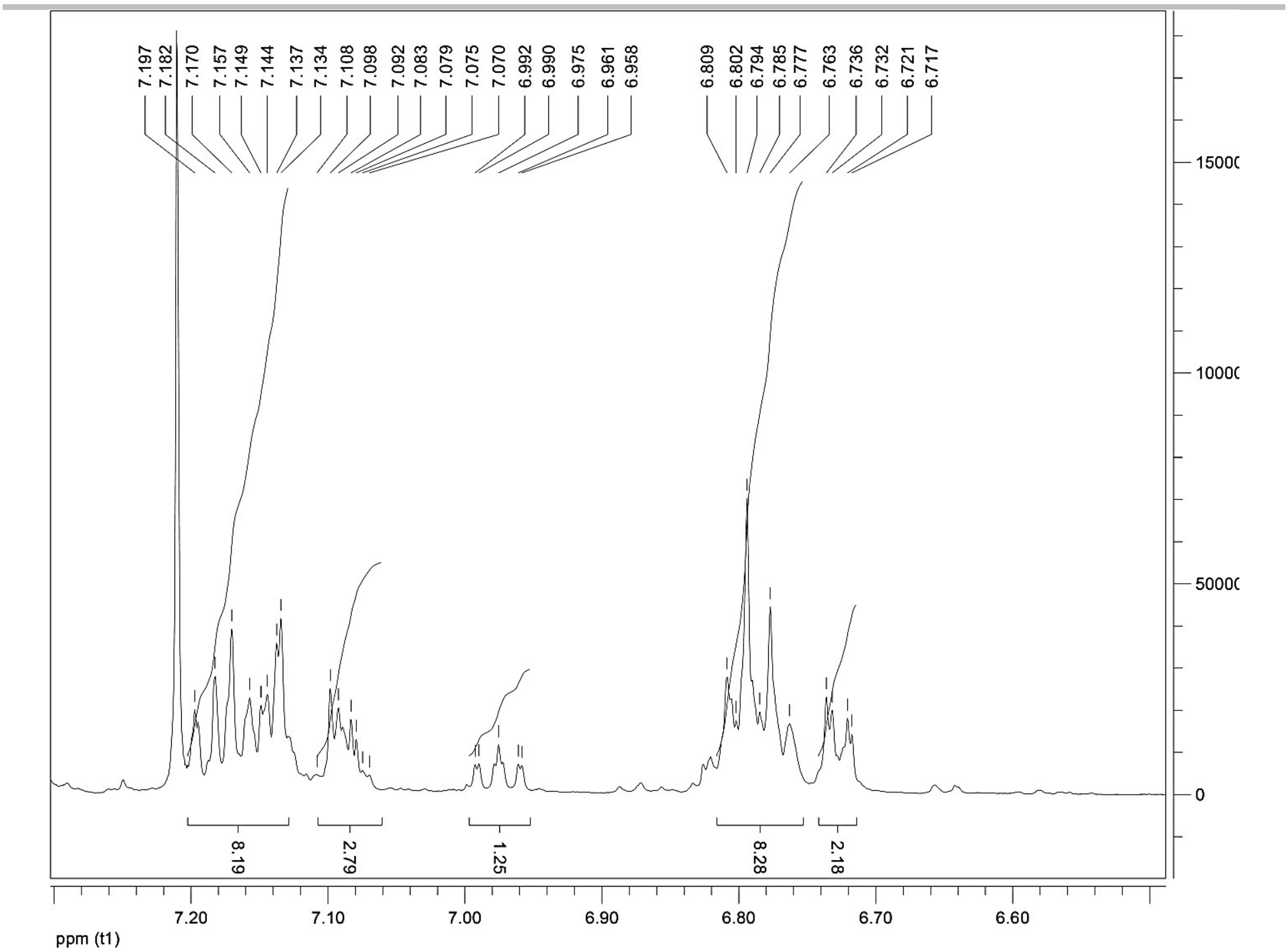
7.50
7.40
7.30
ppm (t1)


7.197
7.182
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6.785
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6.721
6.717
15000
10000
50000
0
8.19
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2.18
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7.00
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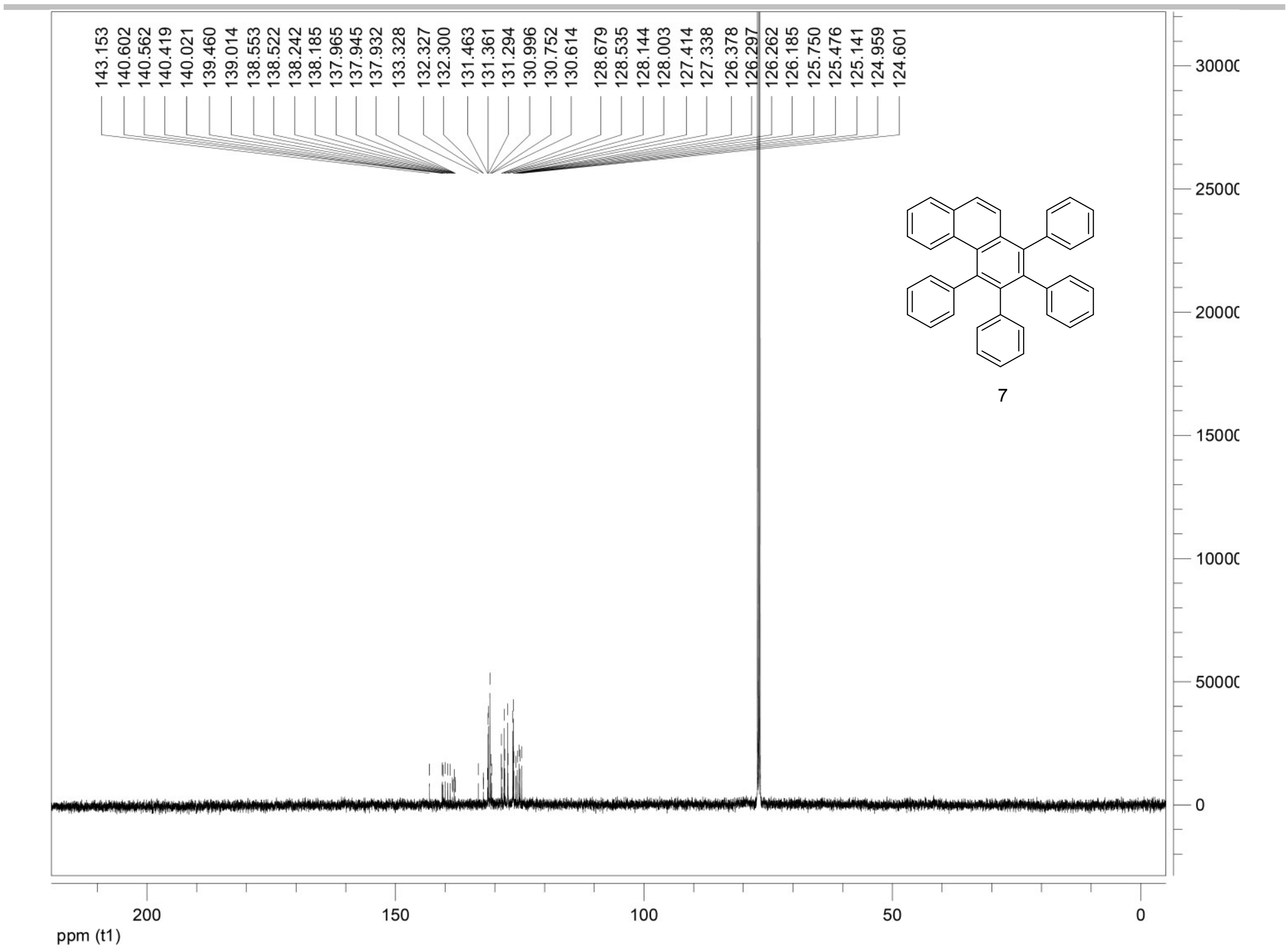
6.60
ppm (t1)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137.932
133.328
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132.300
131.463
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131.294
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130.614
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128.535
128.144
128.003
127.414
127.338
126.378
126.297
126.262
126.185
125.750
125.476
125.141
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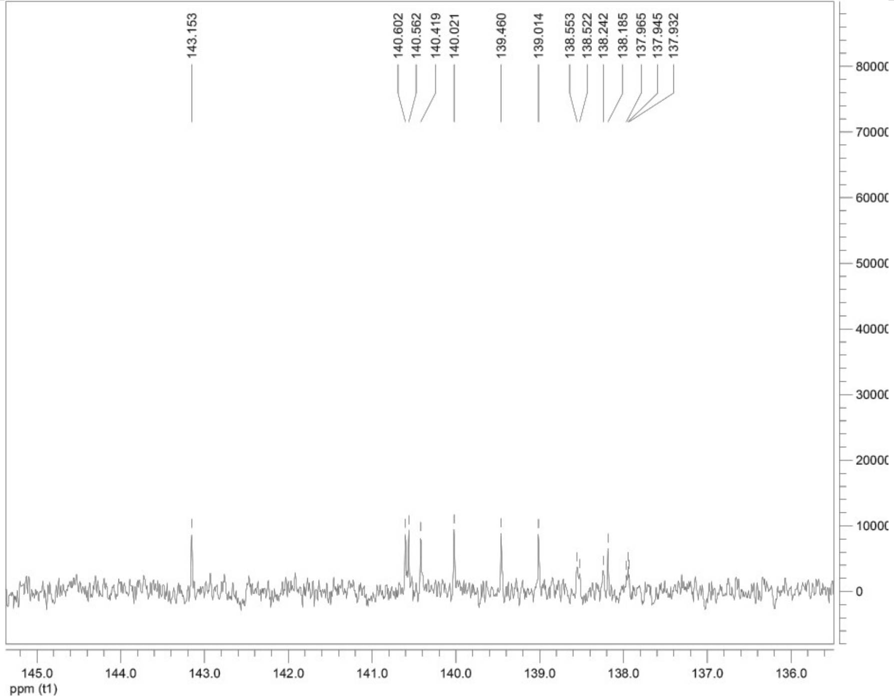
ppm (t1)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138.185
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137.945
137.932
80000
70000
60000
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40000
30000
20000
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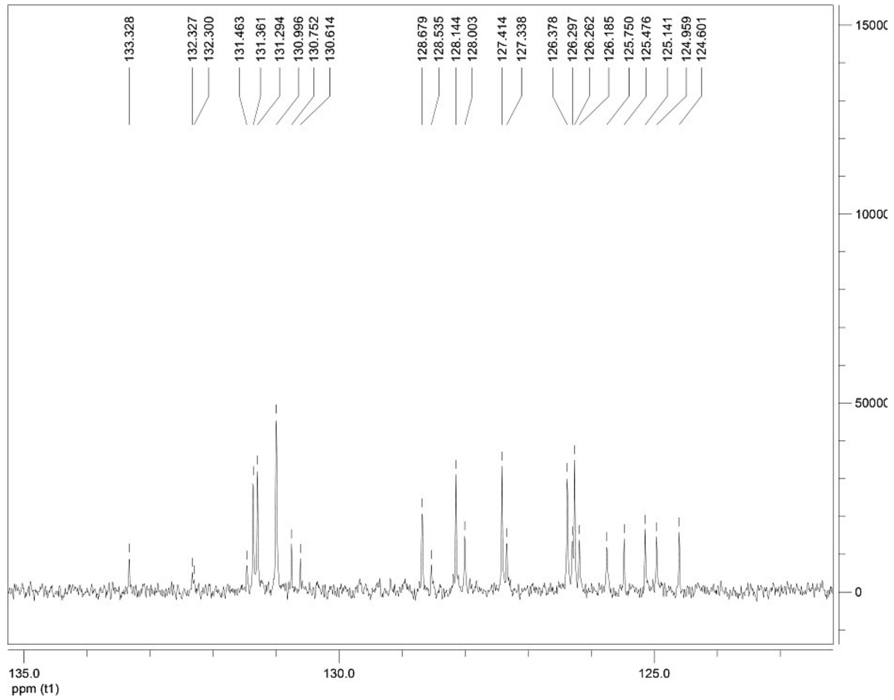
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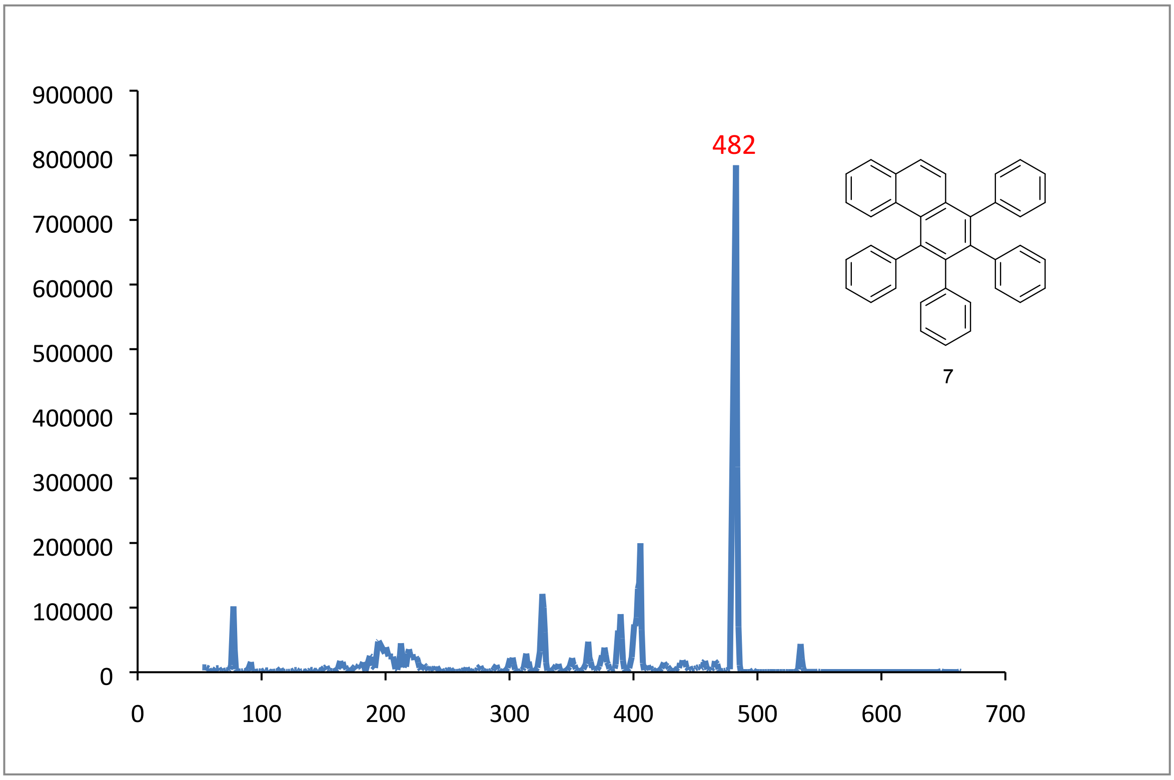
130.752
130.614
128.679
128.535
128.144
128.003
127.414
127.338
126.378
126.297
126.262
126.185
125.750
125.476
125.141
124.959
124.601
150000
100000
50000
0
135.0
130.0
125.0
ppm (t1)


900000
800000
700000
600000
500000
400000
300000
200000
100000
0
0
100
200
300
400
500
600
700
482
7

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