SUPPORTING INFORMATION

Ultra-High Surface Area Silica Material and its Application for Selective N-Formylation of Amines Using CO_2 Surrogate

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1 Chemicals and Material Characterisation

Tetraethyl orthosilicate (TEOS), β-cyclodextrin (β-CD), cetyltrimethylammonium bromide (CTAB), aqueous NH3 (28% v/v), absolute ethanol, anilines and formic acid were purchased from Sigma-Aldrich, and Alfa Aesar. All chemicals were of analytical research grade and used without further purification. All manipulations were performed under standard atmosphere using oven dried glassware at 100 °C for 24 hours.

1.1 Solid State ^{29}Si CP/MAS NMR

NMR data was collected were performed using a Bruker Avance III 600 MHz NMR spectrometer at resonance frequency of 119.2 MHz. A LT-MAS 3.2 mm triply (HXY) tuned probe was used with 3.2 mm ZrO_2 rotor spinning the sample at rate of 10 KHz. The π/2-pulse length was 2.5 μs, and the recycle delay of 3.0 secs with accumulation of 5120 scans spectrum. The solid-state NMR measurements were carried out at room temperature and NMR spectrum was referenced against the Si signal of tetramethylsilane (TMS) at 0 ppm.

1.2 ^{1}H and ^{13}C{^{1}H} Solution State NMR

NMR spectra were acquired on Bruker Avance Neo NB 400 MHz and Bruker Avance III HD SB 800 MHz NMR spectrometers. Chemical shifts (δ) are reported in ppm downfield of tetramethylsilane. Samples were dissolved in deuterated chloroform ($CDCl_3$) or deuterated d_6-DMSO. The residual solvent signals were used as references for ^{1}H and ^{13}C{1H} NMR spectra ($CDCl_3$: δH = 7.26 ppm, δC = 77.12 ppm; DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm. Coupling constants (J) are quoted in Hz.

1.3 Powder X-ray Diffraction Spectrometry

XRD spectra were recorded using Bruker D8 Advance X-Ray diffractometer with Cu Kα radiation (1.54 Å), at 40 kV, 40 mA passing through a Ni filter, equipped with a 2θ compensating slit. The sample was mounted on polymethylmethacrylate (PMMA) sample holder, and analysed in the 2θ range of 10-80° with step size of 0.01° and step time of 1.0 s.

1.4 Transmission Electron Microscopy (TEM)

Bright-field TEM imaging was performed using a Thermo Scientific Talos F200X operated at 200 kV. Samples were prepared by dispersing the silica powder in isopropyl alcohol and sonicating for ~5 min. A ~10 μL aliquot of the suspension was drop-cast onto 300-mesh Cu lacey carbon grids and allowed to air-dry at room temperature. Imaging was performed under low-dose conditions to minimise beam damage, as the silica was sensitive to prolonged electron exposure.

1.5 Focused Ion Beam (FIB)-TEM

SEM lamellae were prepared using an FEI Versa 3D DualBeam system equipped with a Ga^+ ion source. The sample was first coated with a protective Pt layer via gas injection, followed by trench milling and lift-out using an Easylift micromanipulator. The lamellae were then mounted onto TEM grids for imaging and analysis. Final thinning to electron transparency (~50 nm) was performed at low ion beam currents to minimise damage.

1.6 Scanning Electron Microscopy (SEM)

SEM images were recorded using on a Quanta 650 Schottky Field Emission Scanning Electron Microscope at an acceleration voltage of 10 kV. Sample powder was coated with carbon for conductivity and dispersed on the adhesive carbon tape.

The specific BET surface areas were determined using Micromeritics ASAP 2420, which involved the degassing at 350 °C for 6 h under vacuum to eliminate contaminants and moisture. The specific surface area calculations were based on the BET equation, and pore size distribution was analysed using BJH desorption. Measurements were carried out at 77 K.

2 General Experimental Conditions

2.1 Preparation of the Silica Materials

β-Cyclodextrin (β-CD) and cetyltrimethylammonium bromide (CTAB) were dissolved in 100 mL of 1:1 (v/v) mixture of deionised water and Ethanol. The mixture was stirred at 300 rpm and 15 mL of aqueous NH_3 (28-30%) was added dropwise. After 60 minutes, tetraethyl orthosilicate (TEOS) was added dropwise. The resulting solution was aged at room temperature for 2 hours with continuous stirring at 400 rpm. The product was isolated by centrifugation at 10,000 rpm for 10 minutes, washed three times with water (25 mL) and ethanol (20 mL), air dried, and calcined in a furnace at 550 ℃ for 6 hours to obtain mesoporous silica nanoparticles.

2.2 N-formylation of Amines

Typically, the amine (1.0 mmol), formic acid (5.0 mmol), and QSM-2 (2 mg) were charged into a 10 mL glass vial with tightly closed cap. Then, the mixture was stirred at 70-100 ^oC for 1-1.5 h. The reaction progress was monitored by TLC using ethyl acetate/n-hexane (1 : 3) as the mobile phase. After completion of the reaction, the reaction mixture was diluted with EtOAc (10 mL) and filtered. Water (10 mL) was added to the filtrate, and the product was extracted with ethyl acetate (2 x 10 mL). The organic layer containing the product was dried over anhydrous Na_2SO_4. The solvent was evaporated *in vacuo,* and the residue was purified by flash chromatography to obtain the pure N-formylated products.

2.3 Reaction Monitoring and Purification

Thin layer chromatography (TLC) was carried out using Aluminum baked TLC plates containing F_{254} UV indicator (SiliCycle). Purification of compounds by silica column chromatography were performed using an automated Combiflash® Rf+ Lumen system with pre-packaged silica cartridges (12 g, 18 g PuriFlash® columns).

3 Synthetic Procedure for the Scaled-up Silica (QSM-2-SU)

The β-cyclodextrin (3.25 g) was dissolved in warm water (250 mL), followed by the addition of CTAB (12 g) under sonication. Subsequently, NH_3 (28%; 75 mL) and ethanol (250 mL) were added dropwise with overhead stirring at 500 rpm. After 15 min, TEOS (18.5 mL) was added dropwise with continuous stirring. The resulting solution was aged for 2 hours at room temperature with stirring at 650 rpm. The final product was centrifuged at 10,000 rpm for 10 mins, washed three times with water and ethanol, and dried in air. The air-dried powder was then calcined in a furnace at 550 ^oC for 6 hours to obtain spherical silica.

Table 1. Modified processes for improvement of physical properties of MCM-48 type and analogue silica

SN	Surfactant / Additive	Reaction composition	Time: Temp	Comments
1	Mixed surfactant CTAB/ SDS[1]	1.0 SiO_2: 0.152 CTAB: 0.025 SDS: 0.5 NaOH: 62 H_2O	72 h: 100 °C	BET surface area = 861.8 $m^2.g^{-1}$ Pore volume = 0.862 cm^3 g^{-1}. Pore size = 27.2 Å Calcination Temperature: 600 ^oC for 6 h.
2	Mixed surfactant Pluronic P123/CTAB[2]	1.0 SiO_2: 0.125 CTAB: x P123: 0.50 NaOH: 61 H_2O (x=0.000625–0.01875)	48 h: 100 °C	BET surface area = 1500 $m^2.g^{-1}$ Pore volume = 1.5 $cm^3.g^{-1}$ Pore size = 40 Å Calcination Temperature: 550 ^oC for 5 h. Exceptional hydrothermal stability.
3	PVP/CTAB as mixed templates[3]	1.05 g NaOH: 55 mL H_2O: PVP (PVP/CTAB= 1:7, 1:5, 1:3, 1:2): 4.00 g CTAB: 11.55 TEOS	3 days: 100 °C	BET surface Area = 1870 $m^2.g^{-1}$ Pore size = 23.2 Å Calcination Temperature: 550 ^oC for 6 h. Silanol-Rich MCM-48
4	Mixed templates(o-C_nPOC_m / CTAB)[4]	1CTAB: x TEOS: y o-C_2POC_{14}: 1208 H_2O: 150 NH_3 Co-template: N-alkyl-2-[p-(N,N-diethylamino)-o-(alkyloxy)]pyridiniumBromide	4h: RT	BET surface area = 980 $m^2.g^{-1}$ Pore volume = 0.44 $cm^3.g^{-1}$ Pore size = <20 Å Calcination Temperature: 900 ^oC for 5 h. Unusually high thermal stability;
5	Triton X-100 as nonionic co-surfactant[5]	1 SiO_2:1.25 Na_2O: 0.92 C_{20}TMABr: 0.08 Triton X-100: 300 H_2O	4 days: 100 °C	BET surface area = 1150 m^2 g^{-1}. Pore volume = 1.25 $cm^3.g^{-1}$ Pore size = 40.1 Å

				Calcination Temperature: 600 °C. Broad distribution of average pore sizes;
6	Gemini surfactant[6, 7]	0.513 g surfactant: 33.3 g water: 0.296 g NaOH: 2.08 g silica source. Surfactant: p-phenylenedimethylenebis(nhexadecyl dimethylammonium) dibromide	0.5h to 2 days: 100 °C	BET surface area = 1164 m^2 g^{-1} Pore volume = 0.58 $cm^3.g^{-1}$ Pore size = 25 Å Calcination Temperature: 550 °C for 5 h. Narrow pore size distribution
7	Pluronic F127used to tailor particle size[8]	x:0.4:12.5y:54y:417y:z TEOS: CTAB: NH_3: EtOH: H_2O: F127 with x = 1-4.25, y = 1-9, and z = 0-0.094.	Post hydrothermal at 130 °C and 150 °C.	BET surface area= 1248 $m^2.g^{-1}$ Pore volume = 0.96 $cm^3.g^{-1}$. Pore size = 23-33 Å; Calcination Temperature: 600 °C. Monodisperse Spherical MCM-48
8	CTAB with Fluoride ion[9]	1 SiO_2: 0.25Na_2O: xCTAB: 70H_2O: yNaF, where x=0-0.65 and y=0-1.0	72 h: 100 °C	BET surface area = 1281 m^2. g^{-1}. Pore size = 24 Å Calcination Temperature: 600 °C for 6 h. Reduction of CTAB Template Amount
9	Additive: Citric acid (CA)[10]	1 TEOS: 4 H_2O: 6 ethanol: x CA: 0.072 HNO_3 (x=0.1-1.2)	6 days: 50 °C	BET surface area = 1015 $m^2.g^{-1}$. Pore volume = 1.48 $cm^3.g^{-1}$. Pore size = 58 Å Calcination Temperature: 500 °C for 2 h.
10	CTAB with Fluoride ion as a counterion[11]	n(CnTAB): n(TEOS): n(HNO_3): n(NaF): n(H_2O) (NaF-0 to 1)	2 days: 30-50 °C	BET surface area = 1262 $m^2.g^{-1}$. Pore volume = 1.08 $cm^3.g^{-1}$. Pore size = 63.0 Å Calcination Temperature: 550 °C for 6 h. Ordered earthworm-like mesoporous silica
11	CTAB[12]	2.6g CTAB: 120mL H_2O: 50mL ethanol: 12 mL NH_4OH: 3.6mL TEOS	16h: RT	BET surface area = 1855 $m^2.g^{-1}$. Pore volume = 0.824 $cm^3.g^{-1}$. Pore size = 21.8 Å Calcination Temperature: 540 °C for 9 h.
12	Gemini Surfactant[13]	06 GEM: 0.6 NaOH: 150 H_2O: 1TEOS GEM 18-12-18 and GEM 16-12-16	2 days: 100 °C	BET surface area = 1600 $m^2.g^{-1}$. Pore volume = 1.4 $cm^3.g^{-1}$. Pore size = 13.1 Å Calcination Temperature: 550 °C. Improved material quality
13	CTAB[14]	1M TEOS:12.5 M: NH_3: 54 M EtOH: 0.4 M CTAB: 417 M H_2O.	2-24h: RT	BET surface area = 1010 $m^2.g^{-1}$. Pore volume = 0.8 $cm^3.g^{-1}$. Pore size = 33 Å Calcination Temperature: 600 °C for 6 h. Highly ordered uniform spheres of size

o-C_nPOC_m = N-alkyl-2-[p-(N,N-diethylamino)-o-(alkyloxy)]pyridinium bromide

4 *SEM Images of QSM Materials*

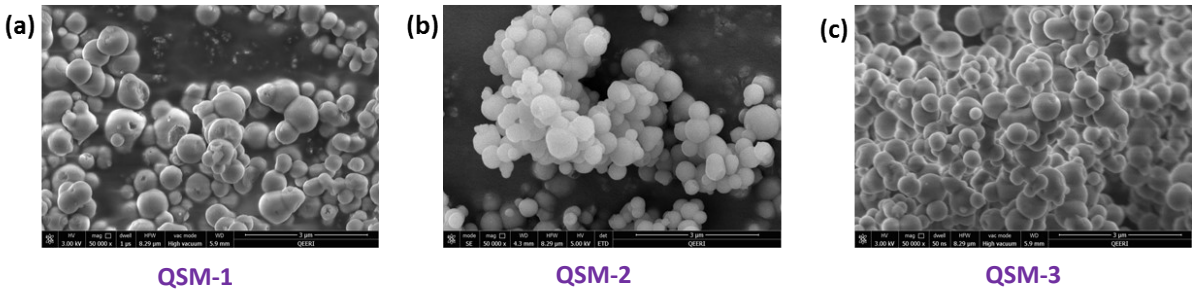


Figure 1. SEM images for silica synthesised using β-CD amount a) 0.3 g, b) 0.65 g, and c) 0.9 g

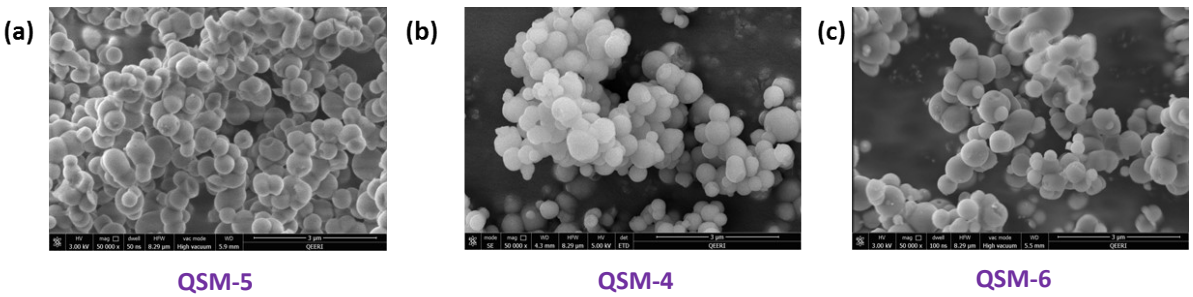
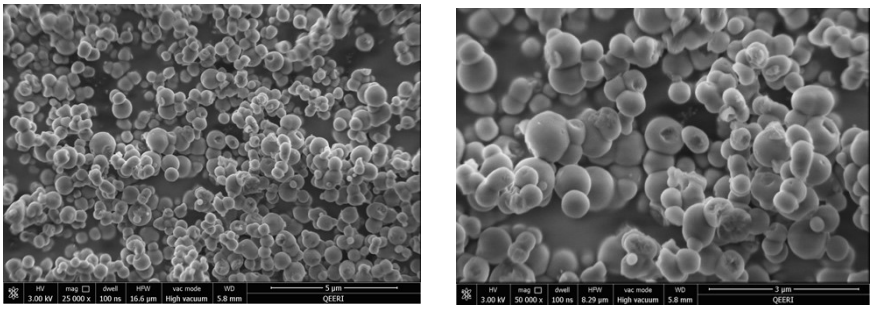


Figure 2. SEM images for silica synthesised at a) 0 ℃, b) RT, c) 50 ℃



QSM-2-SU

Figure 3. SEM of scale-up silica (QSM-2-SU)

5 TEM Images

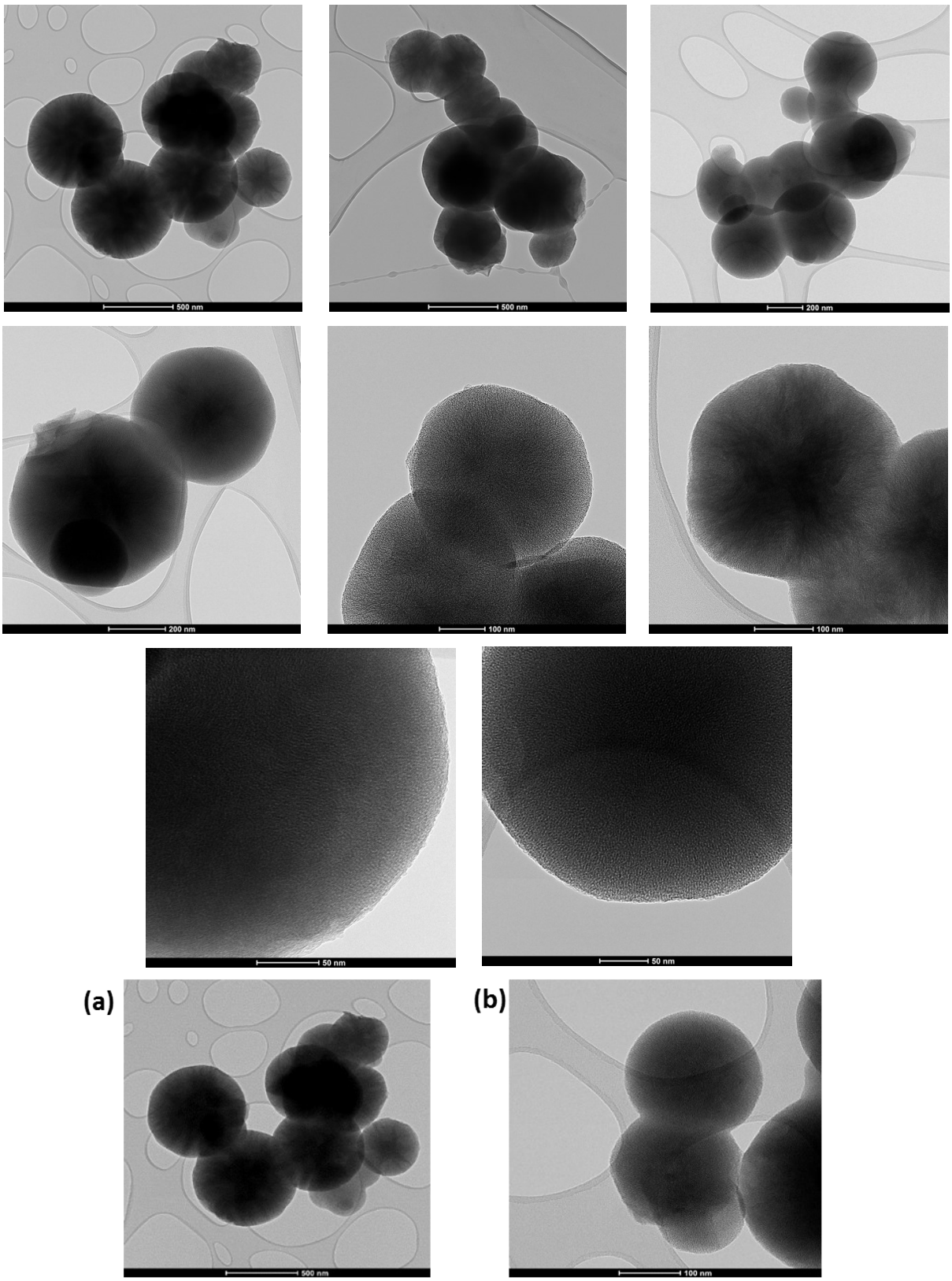


Figure 4. TEM of silica; a) optimized condition (QSM-2), b) scale-up, 5x (QSM-2-SU)

6 FIB-TEM

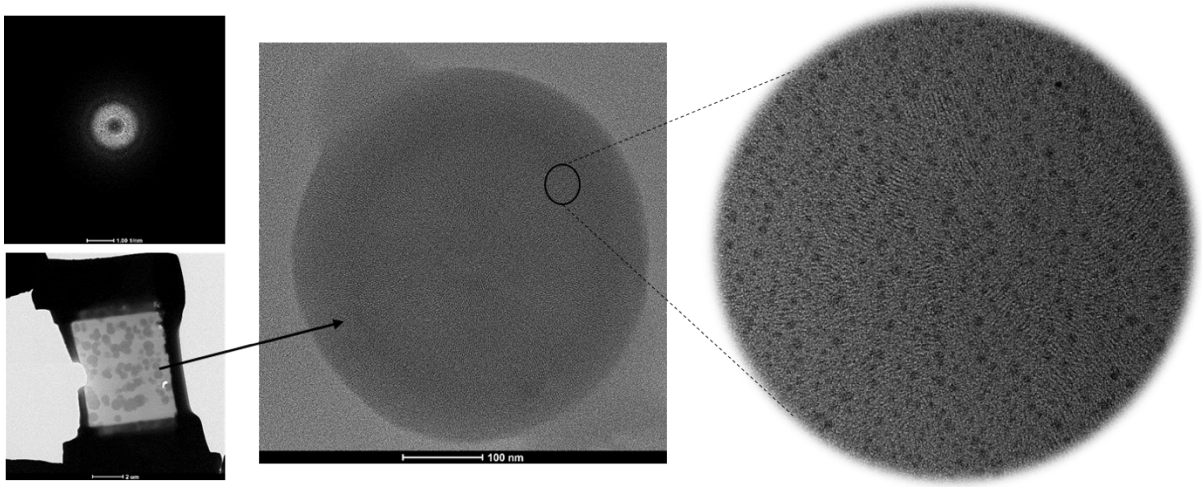
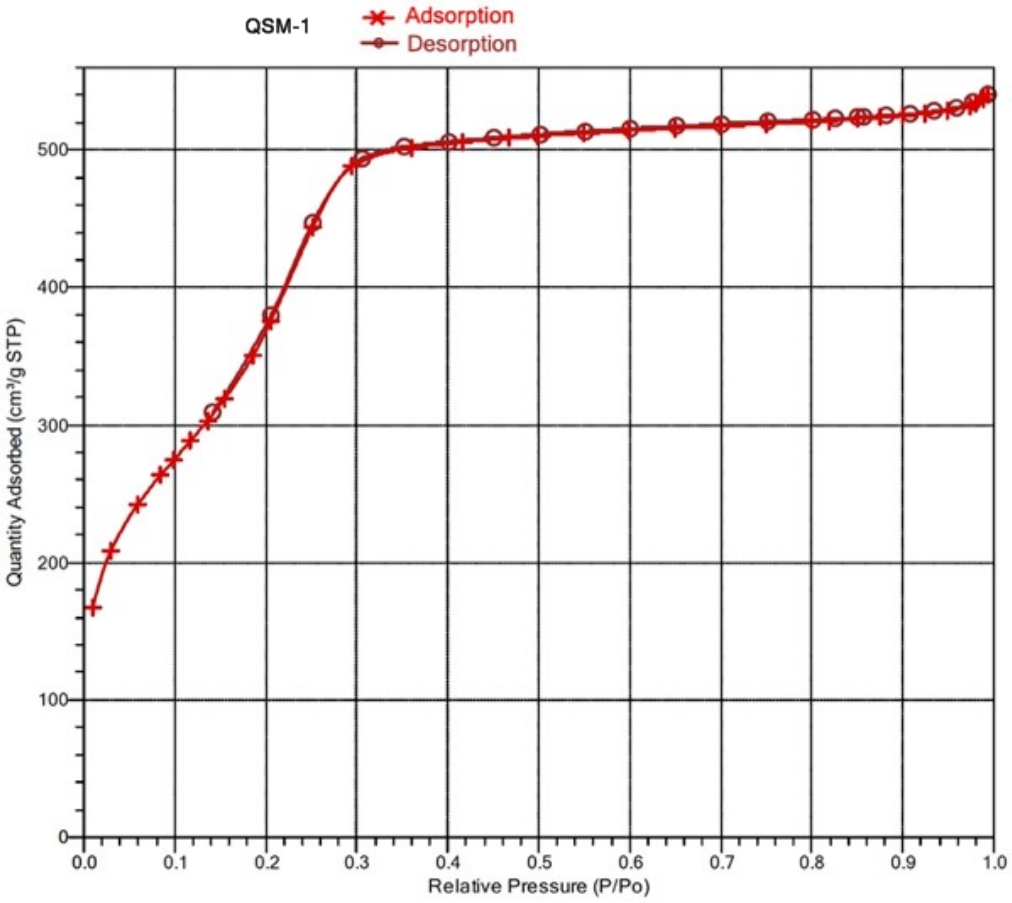
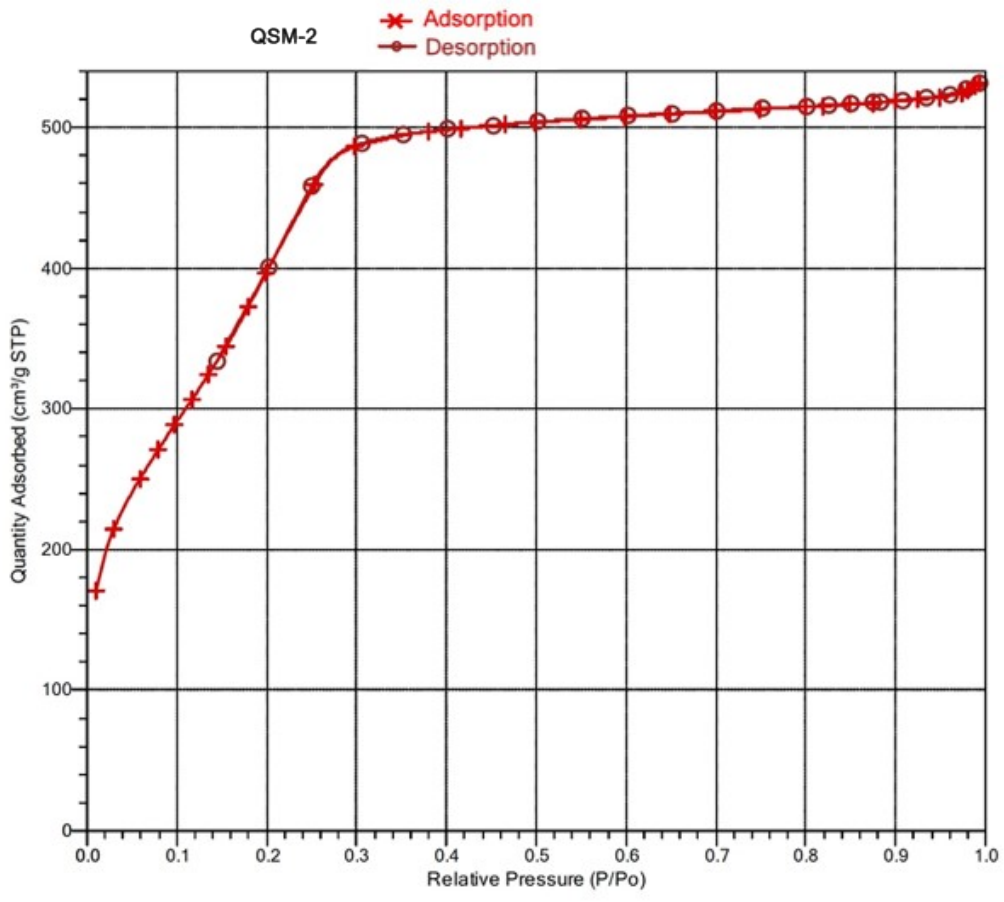
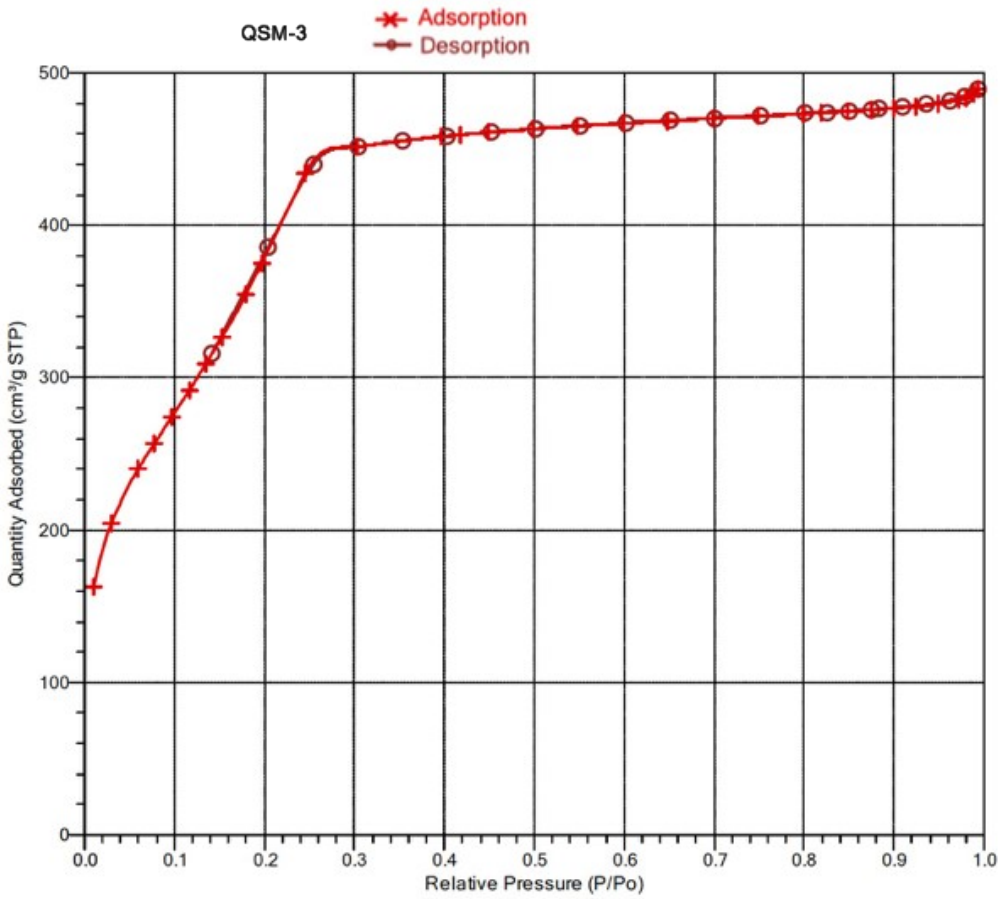


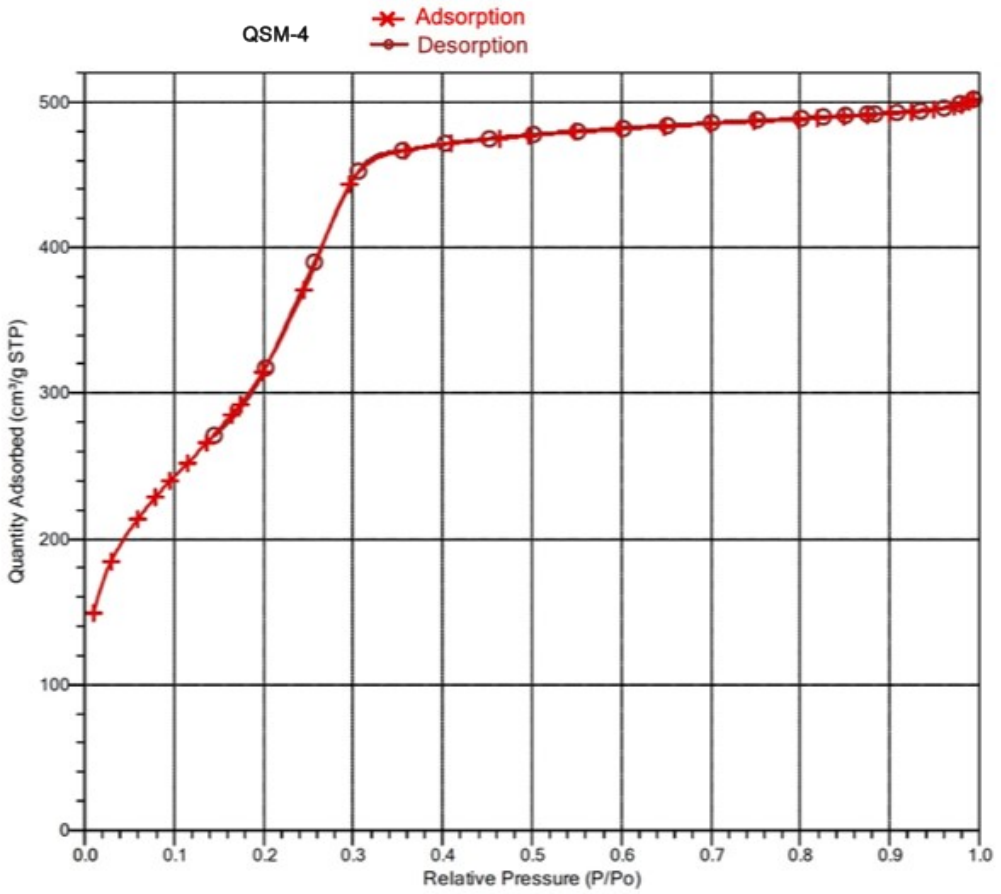
Figure 5. FIB-TEM images for scaled-up silica (QSM-2-SU)

7 BET Isotherms






QSM-3
Adsorption
Desorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (P/Po)
0
100
200
300
400
500
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0


QSM-4
Adsorption
Desorption
Quantity Adsorbed (cm³/g STP)
Relative Pressure (P/Po)
0
100
200
300
400
500
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

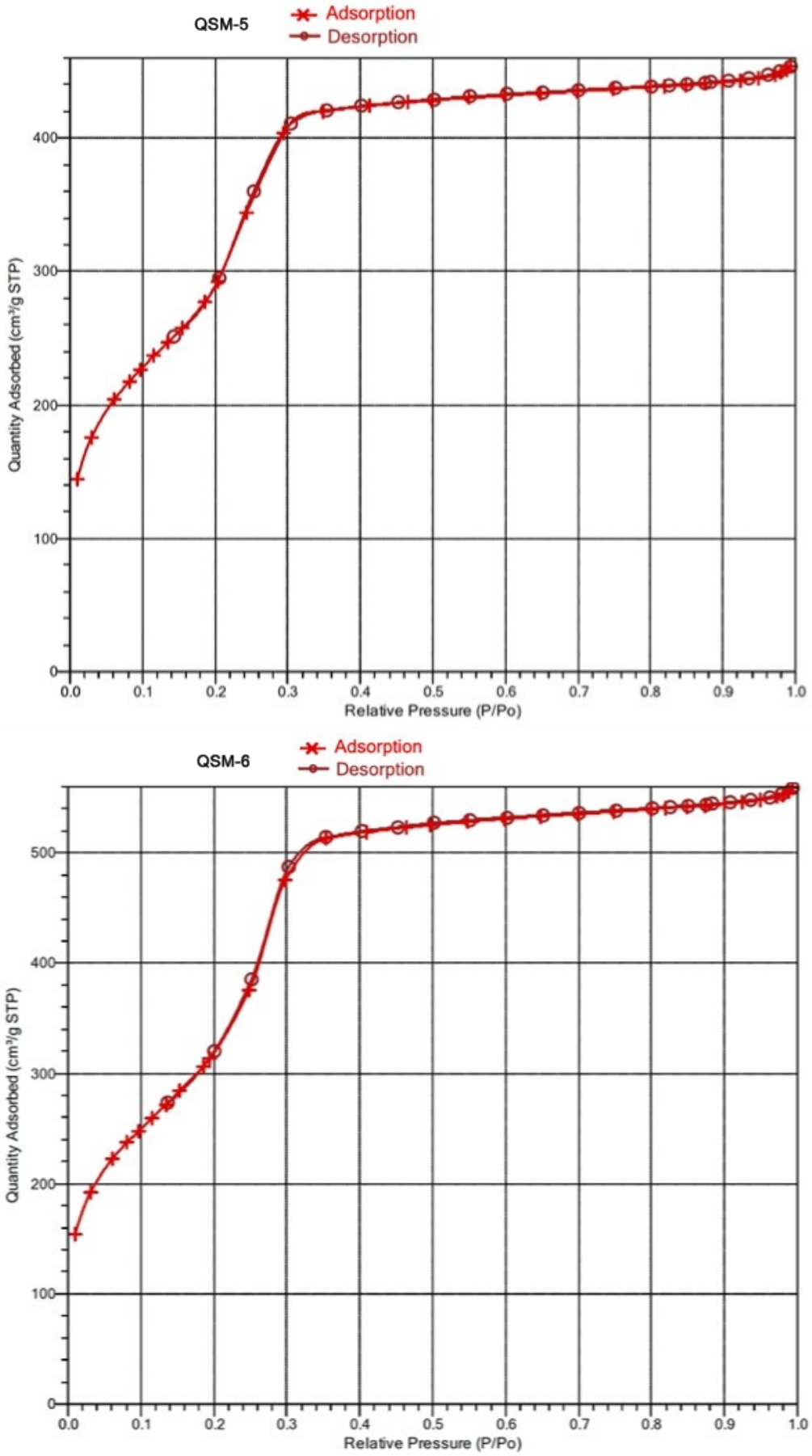


Figure 6. BET isotherms of QSM-1 to QSM-6 materials

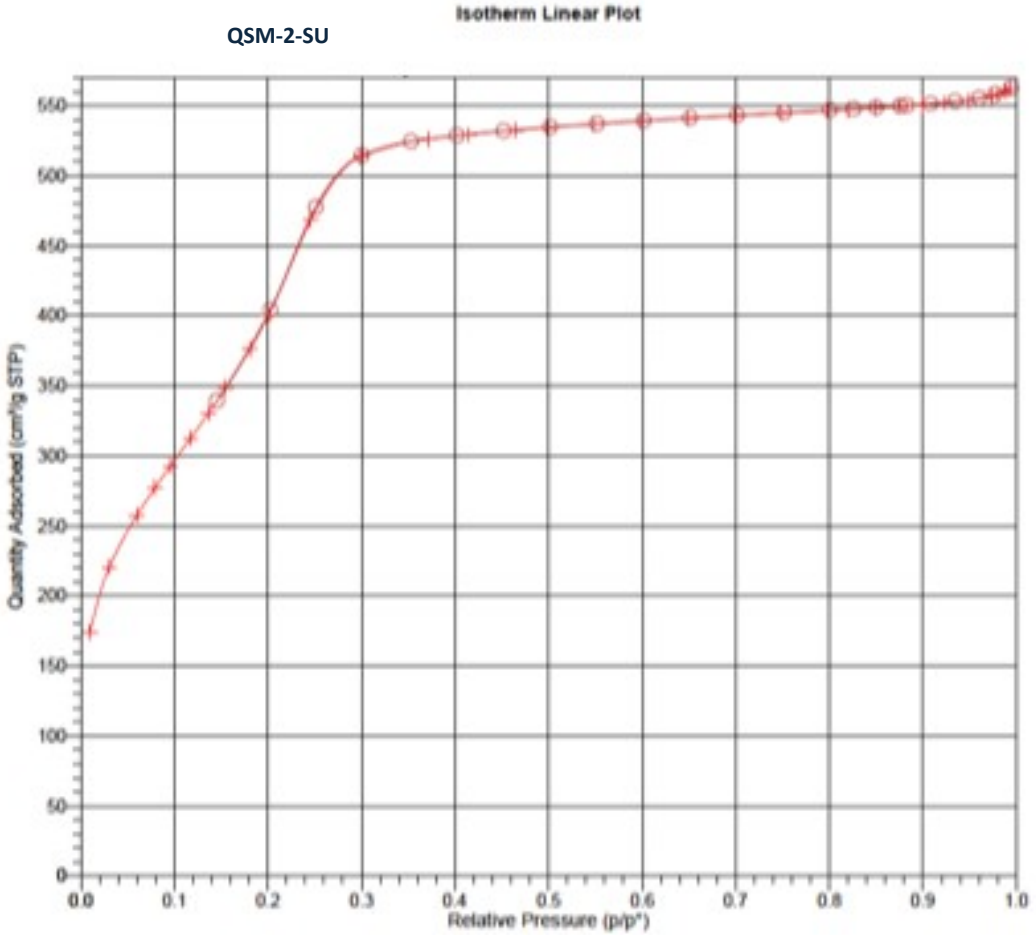


Figure 7. BET isotherm of QSM-2-SU (SA: 1680 m^2 g^{-1})

8 FTIR Spectrum

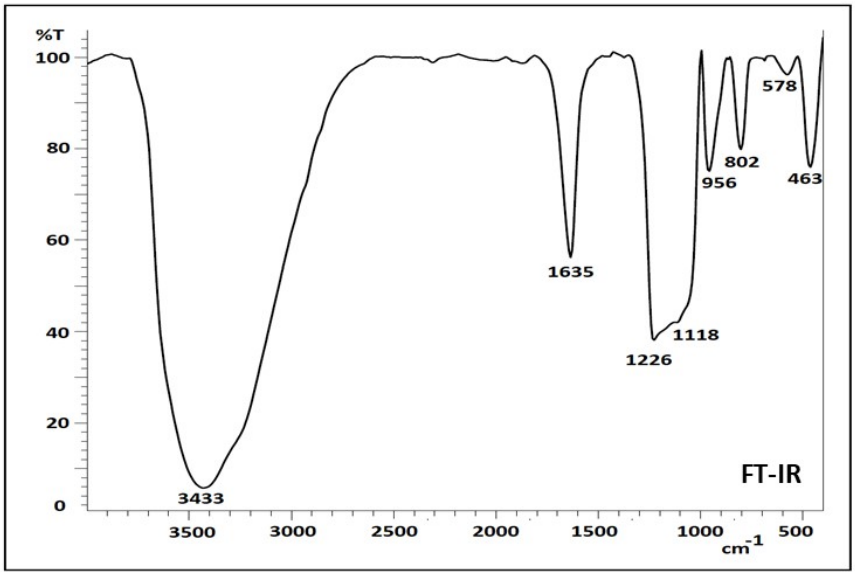


Figure 8. FTIR spectrum of scaled up silica (QSM-2-SU)

9 ^{29}Si CP/MAS NMR Spectra

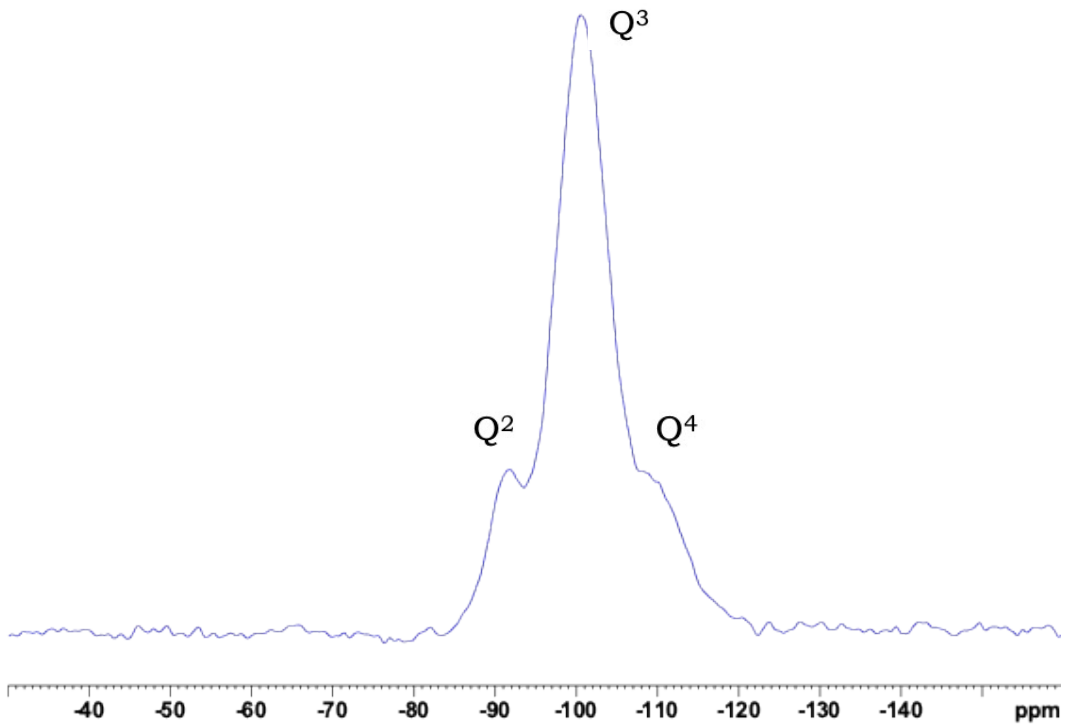


Figure 9. ^{29}Si CP/MAS NMR spectrum of QSM-1

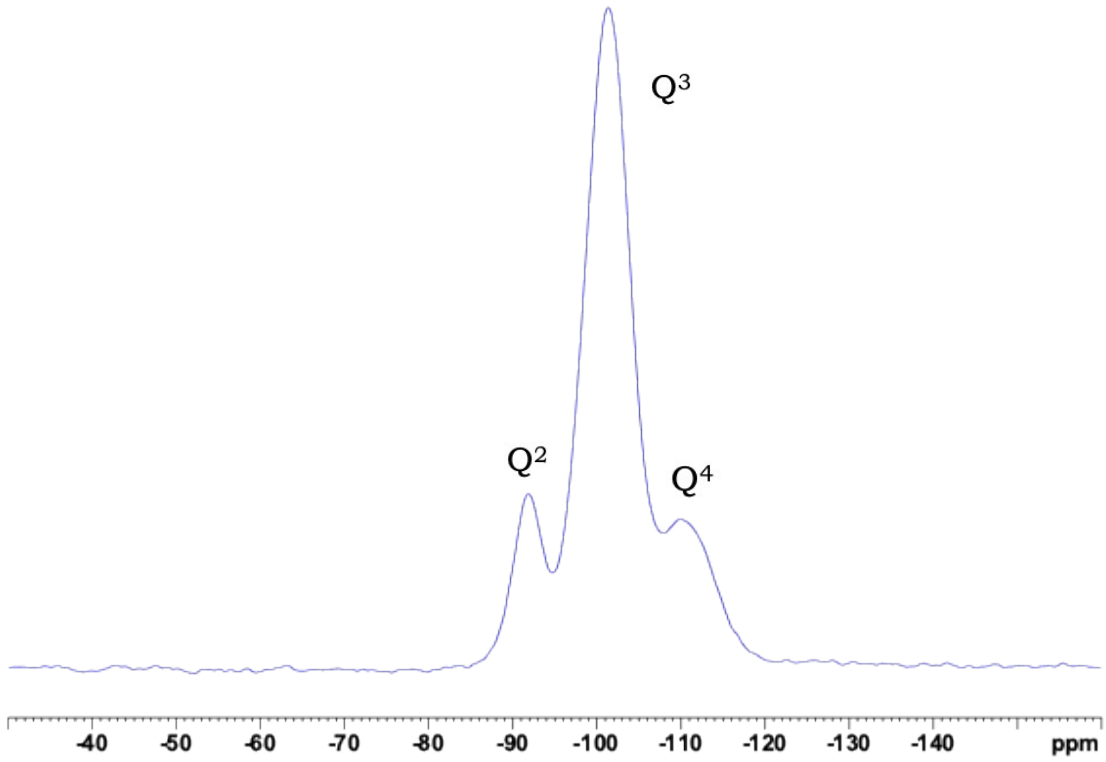


Figure 10. ^{29}Si CP/MAS NMR spectrum of QSM-2

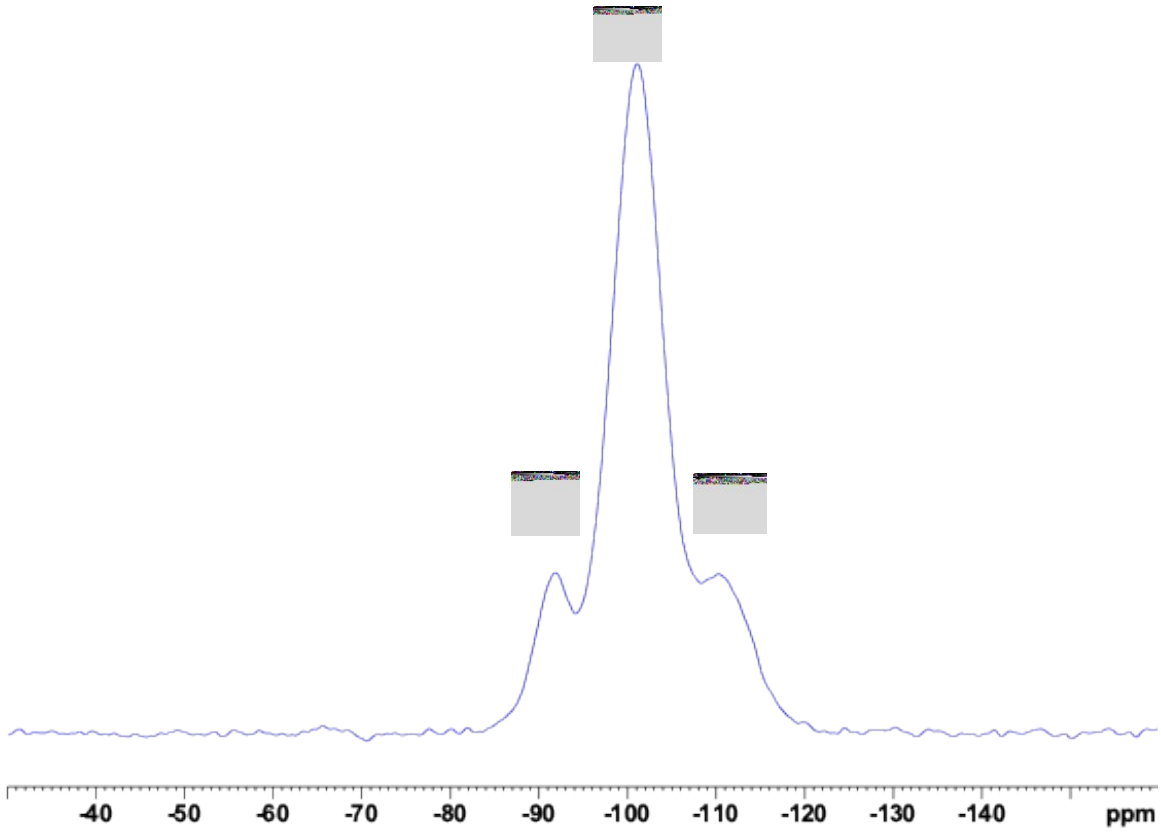


Figure 11. ^{29}Si CP/MAS NMR spectrum of QSM-3

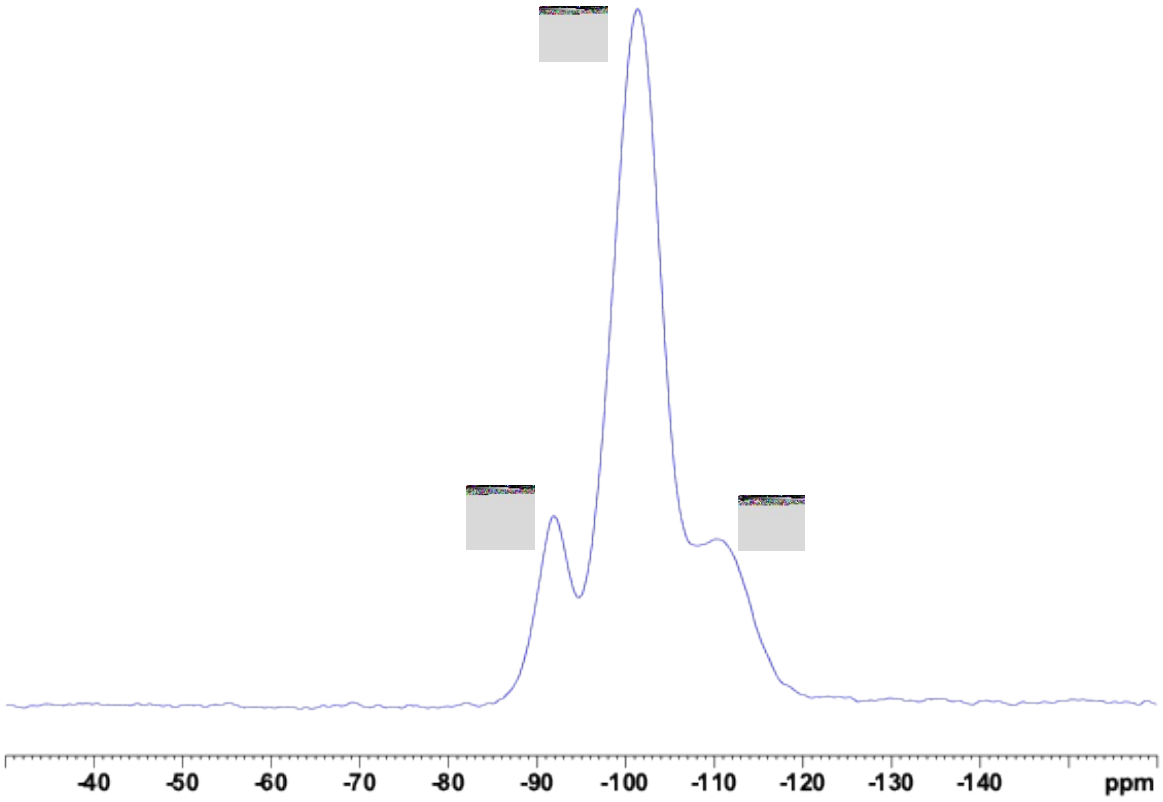


Figure 12. ^{29}Si CP/MAS NMR spectrum of QSM-4

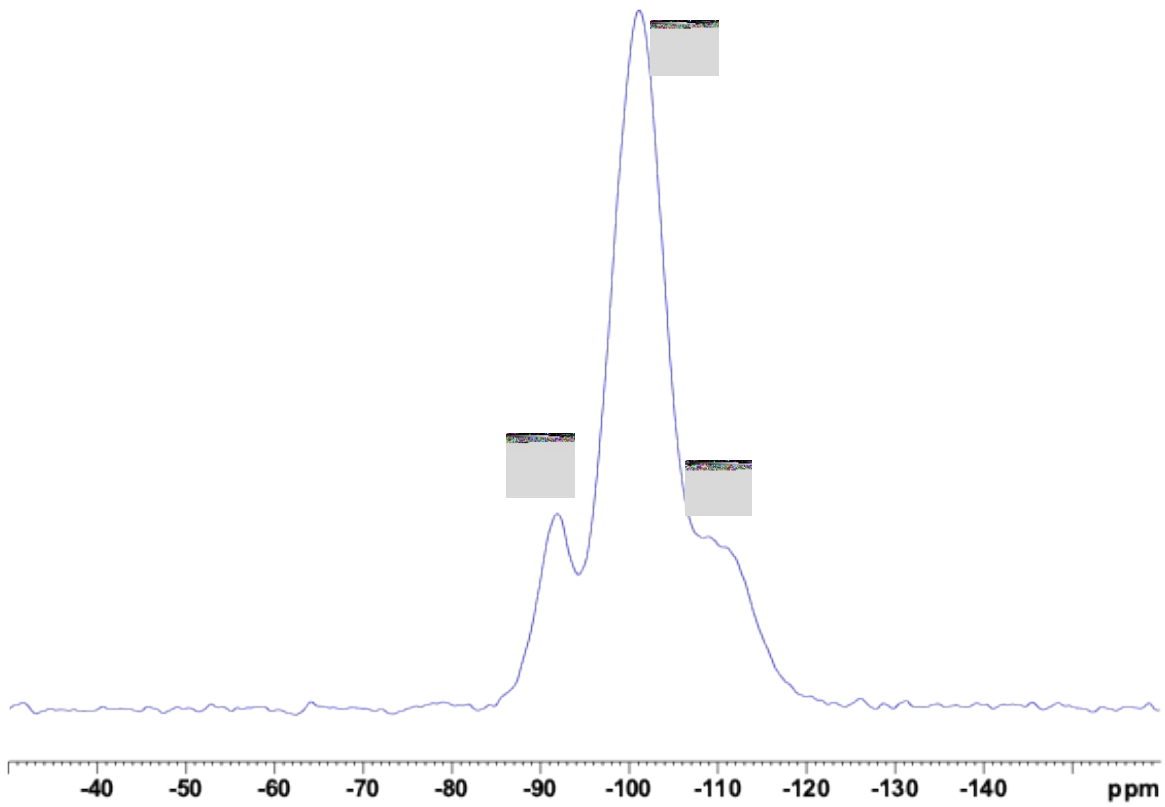


Figure 13. ^{29}Si CP/MAS NMR spectrum of QSM-5

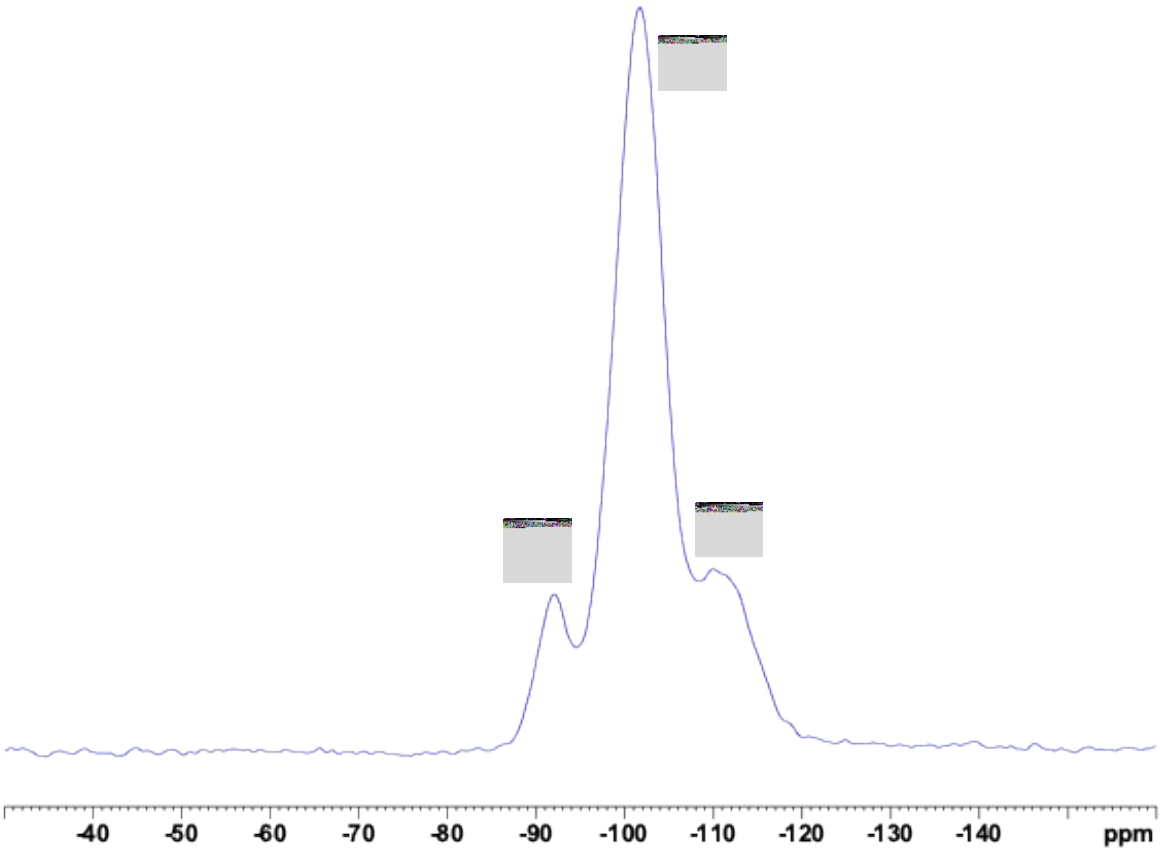


Figure 14. ^{29}Si CP/MAS NMR spectrum of QSM-6

10 Synthesis of Formamides

Table 2. Comparison of QSM-2 with various catalysts for N-formylation of amines

S. No.	Catalyst	Catalyst Load	Solvent	T (°C)	Time (min)	Yield	Ref.
1	DES/SBA-15	20 mg	Solvent-free	RT	40-120	72-98	[15]
2	$[PVP\text{-}SO_3H]HSO_4$	5 mg	Solvent-free	60	2-20	85-97	[16]
3	Nano-Al_2O_3	5 mol%	Solvent-free	40–70	5-300	43-98	[17]
4	Co_3O_4 NPs	15 mg	Solvent-free	40	4-20	89-95	[18]
5	$Pd(OAC)_2$/bpy,PivOH/ $BF_3.Et_2O$ (0.01 mmol)	5 mol%	Toluene	120	1440	55-93	[19]
6	$Cr^{III}Mo_6\text{-}CH_3$ & Na_2SO_3	1 mol% & (0.05 eq.)	1,4-Dioxane	80	240	89-99	[20]
7	FSG-Hf(NPf2)4 (1 mol%)	1 mol%	Solvent free	70	60-240	86	[21]
8	$(NH_4)_3[FeMo_6O_{18}(OH)_6]$ & Na_2SO_3	1 mol% & (0.05 eq.)	Solvent-free	80	120	89-99	[22]
9	ZIF-9/GO	10 mg	Solvent-free	r.t	5-45	86-98	[23]
10	Catalyst free	-	THF	150	180	17-99	[24]
11	QSM-2	2 mg	Solvent-free	70-100	60-90		This work

11 Substrate Scope for N-Formylation of Amines

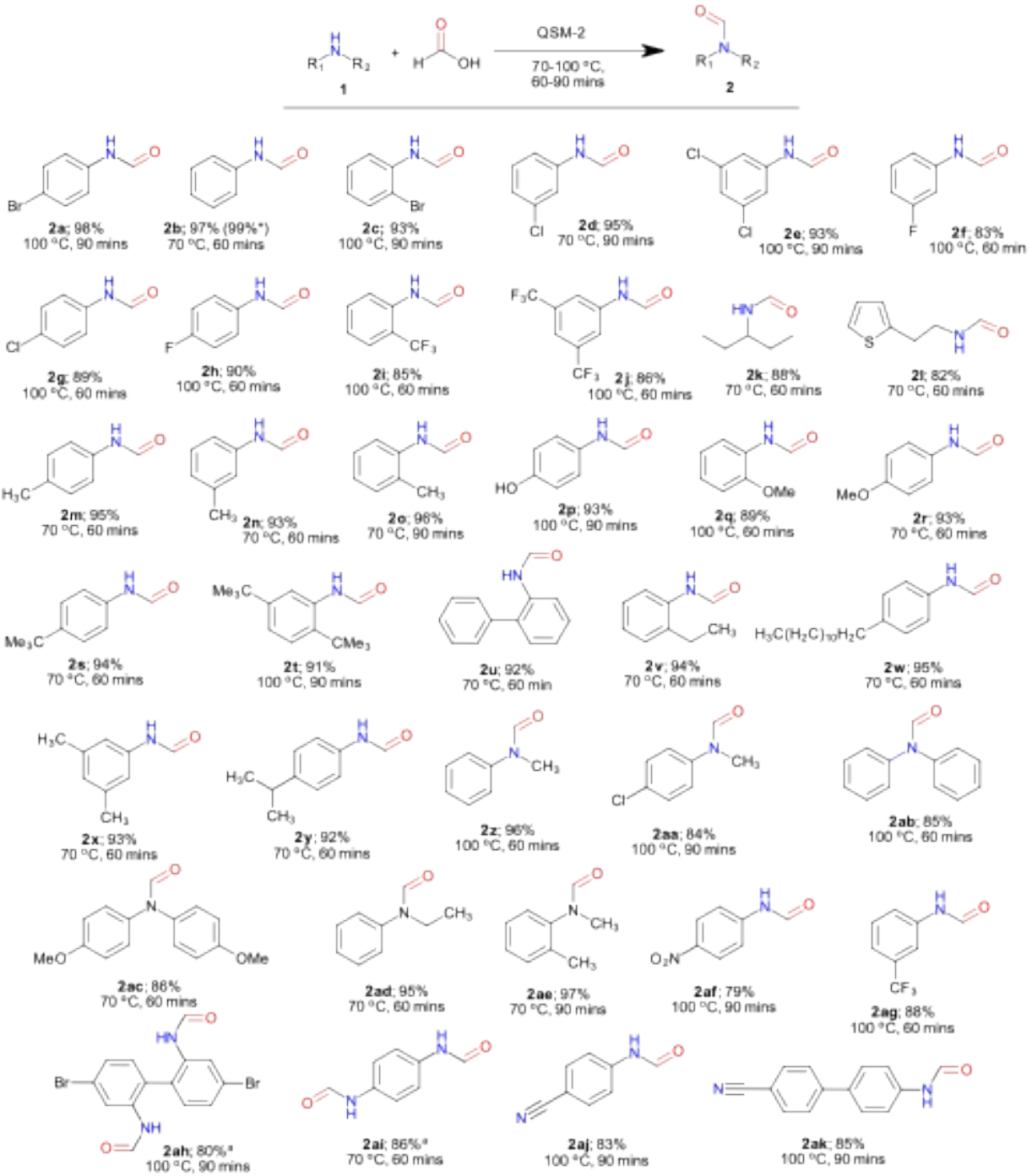
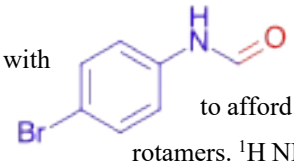


Figure 15. N-Formylation of amines with formic acid in presence of QSM-2 catalyst

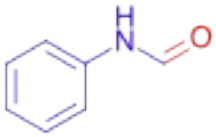
12 ^{1}H and $^{13}C\{^{1}H\}$ NMR Data of Formamides

12.1 N-(4-bromophenyl)formamide (2a)



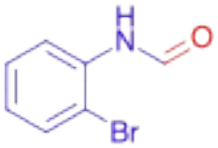
Following the general procedure 2.2, 4-bromoaniline **1a** (172 mg, 1 mmol) was reacted with formic acid (189 µL, 5 mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford *N*-(4-bromophenyl)formamide **2a** as an off-white solid (196 mg, 98% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 11.2 Hz, 0.7H), 8.49 (br s, 0.6H), 8.30 (s, 1H), 7.56 (br s, 0.91H, cis), 7.43-7.32 (m, 5.4H), 6.91 (d, J = 8.6 Hz, 1.4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 159.1, 17 135.9, 135.8, 132.8, 132.1, 121.6, 120.3, 118.3, 117.5.

12.2 N-phenyl formamide (2b)



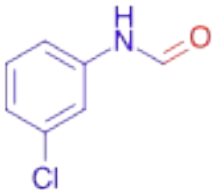
Following the general procedure 2.2, aniline **1b** (93 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-phenyl formamide **2b** as a white solid (117 mg, 97% yield). Mixture of rotamers. ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.90 (br s, 1H), 8.74 (d, J = 11.2 Hz, 1H), 8.38 (s, 1H), 8.00 (br s, 1H), 7.47 (d, J = 7.76 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.33-7.23 (m, 4H),7.16-7.05 (m, 2H), 7.04-6.99 (m, H); ^{13}C NMR (201 MHz, $CDCl_3$) δ 163.0, 159.5, 137.0,136.8, 129.8, 129.1, 125.3, 124.8,120.1, 118.8.

12.3 N-(2-bromophenyl)formamide (2c)



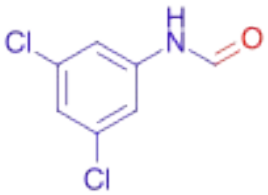
Following the general procedure 2.2, 2-bromoaniline **1c** (172 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(2-bromophenyl)formamide **2c** as an off-white solid (186 mg, 93% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, J = 11.1 Hz, 1H), 8.50 (s, 2H), 8.39 (d, J = 8.2 Hz, 2H), 7.72 (br s, 2H), 7.60 (d, J = 8.0 Hz, 1H),7.55 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.01 (td, J = 7.7, 1.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 158.9, 135.1, 134.8, 133.5, 132.4, 128.7, 128.5, 126.4, 125.7, 122.3, 118.9, 114.5, 113.0.

12.4 N-(3-chlorophenyl)formamide (2d)



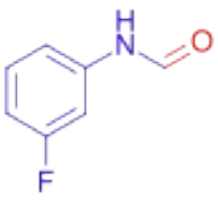
Following the general procedure 2.2, 3-Chloroaniline **1d** (127 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 70 °C to afford product *N*-(3-chlorophenyl)formamide **2d** as a pale yellow solid (147 mg, 95% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.61 (m, 1H), 8.36 (d, J = 1.3 Hz, 1H), 7.77 (br s, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.32 (dd, J = 8.7, 7.3 Hz, 3.6H), 7.07- 7.01 (m, 1.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 159.2, 135.4, 130.8, 129.9, 129.1, 121.3, 120.1.

12.5 N-(3,5-dichlorophenyl)formamide (2e)



Following the general procedure 2.2,3,5-dichloroaniline **1e** (160 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(3,5-dichlorophenyl)formamide **2e** as a white solid (175 mg, 93% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.62 (d, J = 10.9 Hz, 0.4H), 8.27 (s, 1H), 8.20 (s, 0.4H), 7.41 (s, 2H), 7.72 (s, 1H), 7.46 (d, J = 1.7 Hz, 2H), 7.10 (s, 0.4H), 7.06 (d, J = 1.7 Hz, 1H), 6.95 (d, J = 1.5 Hz, 0.8H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 161.7, 159.2, 139.1, 138.9, 135.9, 135.2, 124.8, 124.4, 118.1, 116.7.

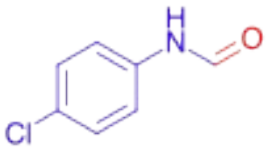
12.6 N-(3-fluorophenyl)formamide (2f)



Following the general procedure 2.2, 3-fluoroaniline **1f** (111 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-(3-fluorophenyl)formamide **2f** as a brown solid (115 mg, 83% yield). Mixture of

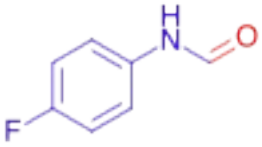
rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (d, J = 10.2 Hz, 1H), 8.72 (d, J = 11.2 Hz, 2.6H), 8.35 (d, J = 1.6 Hz, 1.7H), 7.50 (d, J = 10.7 Hz, 1.7H), 7.33-7.19 (m, 4.5H), 6.92-6.77 (m, 4.7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 164.1, 162.8, 162.1, 161.7, 159.6, 138.5, 138.4, 131.2, 130.3, 115.3, 114.1, 112.1, 11.9, 111.7, 111.5, 107.8, 107.5, 106.0, 105.8.

12.7 N-(4-chlorophenyl)formamide (2g)



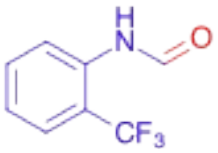
Following the general procedure 2.2, 4-chloroaniline **1g** (127mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-(4-chlorophenyl)formamide **2g** as an off-white solid (140 mg, 89% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.3 (s, 1H). 10.22 (d, J = 8.8 Hz, 0.3H), 8.78 (d, J = 10.9 Hz, 0.3H), 8.28 (d, J = 1.7 Hz, 1H), 7.64-7.56 (m, 2H,), 7.40-7.37 (m, 2.6H), 7.25-7.19 (m, 0.6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.0, 160.2, 137.9, 137.6, 129.7, 129.2, 127.9, 127.7, 121.2, 119.5.

12.8 N-(4-fluorophenyl)formamide (2h)



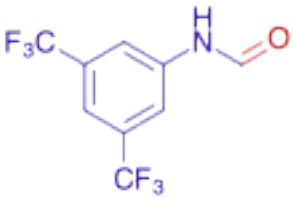
Following the general procedure 2.2, 4-fluoroaniline **1h** (111 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-(4-fluorophenyl)formamide **2h** as an off-white solid (125 mg, 90% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (d, J = 9.3 Hz, 1H), 8.59 (d, J = 11.3 Hz, 1H) 8.32 (s, 1.6H), 8.17 (s, 1.3H), 7.13-7.04 (m, 3H), 7.53-7.46 (m, 3.4H), 6.92-7.03 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 161.7, 160.8, 159.5, 159.2, 158.4, 133.0, 132.8, 122.2, 121.9, 116.6, 116.4, 115.9, 115.6.

12.9 N-(2-trifluoromethylphenyl) formamide (2i)



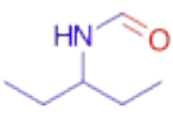
Following the general procedure 2.2, 2-(trifluoromethyl)aniline **1i** (161 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-(2-trifluoromethylphenyl) formamide **2i** as an off-white solid (160 mg, 85% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 10.7 Hz, 0.6H), 8.47 (s, 1H), 8.30 (d, J = 8.3 Hz, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.9 Hz, 1.3H), 7.58 (q, J = 7.8 Hz, 2H), 7.35 (t, J = 8.2 Hz, 1.4H), 7.26 (t, J = 7.8 Hz, 1.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 159.1, 134.5, 134.1, 133.4, 133.0, 126.2, 125.8, 124.9, 124.4, 122.6, 121.8.

12.10 N-[3,5-bis(trifluoromethyl)phenyl]formamide (2j)



Following the general procedure 2.2, 3,5-bis(trifluoromethyl)aniline **1j** (229mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-[3,5-bis(trifluoromethyl)phenyl]formamide **2j** as an off-white solid (221 mg, 86% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.8 (s, 1H), 10.6 (s, 0.2H), 9.1 (s, 0.2H), 8.4 (s, 1H), 8.2 (s, 2H), 7.9 (s, 0.4H), 7.8 (br s 1.2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 161.3, 141.3, 140.5, 131.3 (q, $J_{C\text{-}F}$ 30.8 Hz), 127.6, 124.9, 122.2, 119.5, 119.4, 117.6, 116.9.

12.11 N-(Pentan-3-yl)formamide (2k)



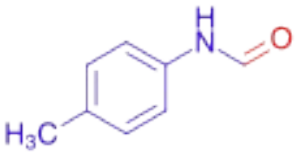
Following the general procedure 2.2, pentane-3-amine **1k** (87 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(pentan-3-yl)formamide **2k** as a colourless oil (101 mg, 88% yield). ^{1}H NMR (800

MHz, $CDCl_3$) δ 8.30 (s, 1H), 3.06-3.03 (m, 1H, -*CH*-), 1.69-1.63 (m, 4H, -CH_2-), 0.98 (t, J = 8.0 Hz, 6H, -CH_3). ^{13}C NMR (201 MHz, $CDCl_3$) δ 167.3, 54.5, 24.9. 9.4.

12.12 N-[2-(thiophen-2-yl)ethyl]formamide (2l)

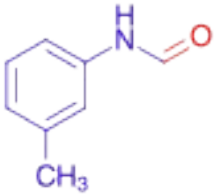
Following the general procedure 2.2, 2-(thiophen-2-yl)ethan-1-amine **1l** (127 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-[2-(thiophen-2-yl)ethyl]formamide **2l** as a pale yellow oil (127 mg, 82% yield). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.17-7.16 (m, 1H), 6.92-6.91 (m, 1H), 6.87 (d, J = 2.4 Hz 1H), 3.22 (t, J = 8.0 Hz, 2H, -CH_2), 3.18 (t, J = 8.0 Hz, 2H, -CH_2). ^{13}C NMR (201 MHz, $CDCl_3$) δ 166.9, 138.1127.4, 126.5, 124.9, 41.0, 27.7.

12.13 N-(4-methylphenyl)formamide (2m)



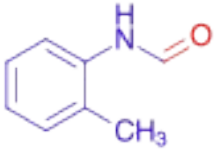
Following the general procedure 2.2, 4-methylaniline **1m** (107 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(4-methylphenyl)formamide **2m** as a white solid (128 mg, 95% yield). Mixture of rotamers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (d, J = 10.4 Hz, 1H), 8.63 (d, J = 11.6 Hz, 1H), 8.29 (s, 1H), 8.21 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 8.0, 2H), 2.32 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.3, 159.6, 135.1, 134.5, 134.4, 134.3, 130.2, 129.5, 120.2, 120.2, 119.1, 20.9, 20.8.

12.14 N-(3-methylphenyl)formamide (2n)



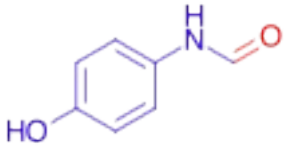
Following the general procedure 2.2, 3-methylaniline **1n** (107 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(3-methylphenyl)formamide **2n** an off-white solid (125 mg, 93% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (d, J = 9.9 Hz, 1H), 8.60 (d, J = 11.4 Hz, 1H), 8.23 (d, J = 1.8 Hz, 1H), 8.09 (s, 1H), 7.31 (s, H), 7.24 (d, J = 8.1 Hz, 1H), 7.18-7.06 (m, 2H), 6.89 (d, J = 7.7 Hz, 1H), 6.87-6.78 (m, 3H), 2.24 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2, 159.6, 139.8, 139.0, 137.0, 136.8, 129.5, 128.9, 126.1, 125.6, 120.8, 119.5, 117.2, 115.7, 21.5, 21.4.

12.15 N-(2-methylphenyl)formamide (2o)



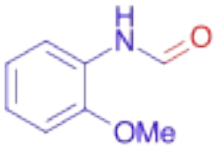
Following the general procedure 2.2, 2-methylaniline **1o** (107 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 70 °C to afford product *N*-(2-methylphenyl)formamide **2o** a an off-white solid (129 mg, 96% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, J = 7.9 Hz, 1H), 8.42 (d, J =11.2 Hz, 1H), 8.28 (d, J = 1.5 Hz, 0.6H), 7.72 (d, J = 7.8 Hz, 0.6H), 7.64 (br s, 1H), 7.18-6.93 (m, 6H), 2.22 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 159.7, 135.2, 134.7, 131.3, 130.6, 130.1, 129.1, 127.4, 127.1, 126.7, 125.6, 124.8, 123.3, 120.9, 17.8.

12.16 N-(4-hydroxyphenyl)formamide (2p)



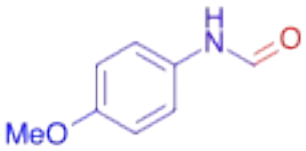
Following the general procedure 2.2, 4-aminophenol **1p** (107 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product N-(4-hydroxyphenyl)formamide **2p** as a white solid (127 mg, 93% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.89 (s, 1H), 9.84 (d, J = 11.2 Hz, 0.3H), 9.27 (s, 0.3H), 9.24 (s, 1H), 8.51 (d, J = 11.2 Hz, 0.3H), 8.16 (d, J = 1.6 Hz, 1H), 7.37 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 0.6H), 6.76-6.67 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.0, 159.2, 154.7, 153.9, 130.4, 130.1, 121.2, 120.6, 116.3, 115.6.

12.17 N-(2-methoxyphenyl)formamide (2q)



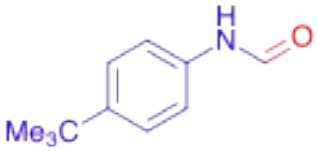
Following the general procedure 2.2, 2-methoxyaniline **1q** (123 mg, 1 mmol) a was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-(2-methoxyphenyl)formamide **2q** as pale-yellow solid (134 mg, 89% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 11.6 Hz, 0.4H), 8.45 (d, *J* = 1.5 Hz, 1H), 8.36 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.85 (br s, 1H), 7.19 (d, *J* = 7.9 Hz, 0.4H), 7.13 (dt, *J* = 7.9 Hz, 1.3 Hz, 0.6H), 7.07 (dt, *J* =7.9, 1.6 Hz, 1H), 6.99-6.86 (m, 3H), 3.88 (s, 3H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 158.7, 148.7, 147.8, 126.7, 126.2, 125.2, 124.3, 121.1, 120.5, 116.6, 111.3, 110.0, 55.7.

12.18 N-(4-methoxyphenyl) formamide (2r)



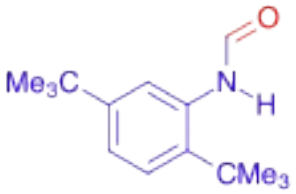
Following the general procedure 2.2, 4-methoxyaniline **1r** (123 mg 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(4-methoxyphenyl)formamide **2r** as a light yellow oil (140 mg, 93% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 10.6 Hz, 0.7H), 8.54 (s, 1H), 8.51 (s, 0.7H), 8.24 (s, 1H), 7.44 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 1.5H), 6.83 (dd, *J* = 16.6, 8.9 Hz, 3H), 3.77 (s, 2H), 3.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 159.7, 157.5, 156.6, 130.2, 129.8, 121.9, 121.4, 114.9, 114.1, 55.5, 55.4.

12.19 N-(4-tert-butylphenyl)formamide (2s)



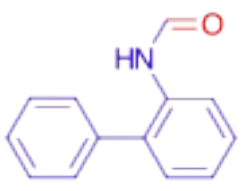
Following the general procedure 2.2, 4-(*tert*-butyl)aniline **1s** (149 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product -(4-tert-butylphenyl)formamide **2s** as a white solid (166 mg, 94% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (br s, 2H), 8.64 (s, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 7.85 (br s, 1H), 7.49-7.44 (m, 2H), 7.39-7.31 7.31 (m, 4H), 7.06-7.01 (m, 2H), 1.31 (s, 9H), 1.29 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 159.3, 148.5, 147.8, 134.4, 134.2, 126.6, 125.9, 119.9, 118.8, 34.5, 34.4, 31.3.

12.20 N-(2,5-di-tert-butylphenyl)formamide (2t)



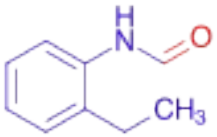
Following the general procedure 2.2, 2,5-di-*tert*-butylaniline **1t** (205 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product N-(2,5-di-tert-butylphenyl)formamide **2t** as a white solid (212 mg, 91% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 1.6 Hz, 0.2H), 8.78 (d, *J* = 11.3 Hz, 1H), 7.68 (d, *J* = 1.9 Hz. O.2H), 7.52 (s, 1H), 7.37 (s, 1.3H). 7.35 (s, 1.2H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.2 Hz, 0.3H), 7.08 (d, *J* = 2.1 Hz, 1H), 1.42 (s, 2H), 1.41 (s. 9H). 1.32 (s, 9H), 1.31 (s. 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 159.4, 150.5, 149.8, 140.3, 139.3, 134.0, 133.4, 126.9, 126.4, 124.9, 123.9, 123.5, 123.2, 34.5, 34.3, 31.2, 30.8.

12.21 N-[(1,1'-biphenyl)-2-yl]formamide (2u)



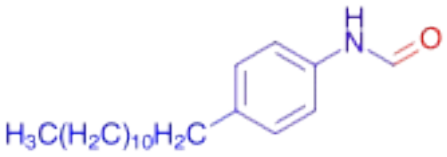
Following the general procedure 2.2, [1,1'-biphenyl]-2-amine **1u** (169 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-[(1,1'-biphenyl)-2-yl]formamide **2u** as an off-white solid (181 mg, 92% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 11.3 Hz, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 8.28 (s, 1H), 7.52-7.39 (m, 6H), 7.39-7.29 (m, 7H), 7.28-7.23 (m, 3H), 7.22-7.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 158.7, 137.8, 137.3, 133.9, 133.8, 132.9, 131.9, 131.2, 130.2, 129.3, 129.2, 128.8, 128.6, 128.2, 125.3, 124.6, 121.5, 118.2.

12.22 N-(2-ethylphenyl)formamide (2v)



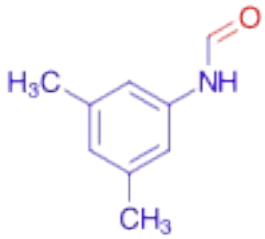
Following the general procedure 2.2, 2-ethylaniline **1v** (121 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(2-ethylphenyl)formamide **2v** as a white solid (140 mg, 94% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 11.2 Hz, 1H), 8.43 (d, J = 1.4 Hz, 0.5H), 8.34 (br s, 1H), 7.86 (d, J = 7.4 Hz, 0.5H), 7.28-7.23 (m, 1H), 7.23-7.17 (m, 3H), 7.17-7.11 (m, 1.5H), 2.66 (q, J = 7.6 Hz, 2H), 2.62 (q, J = 7.6 Hz, 2H minor), 1.23 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 159.5, 136.1, 134.8, 134.4, 133.9, 129.5, 128.7, 127.6, 127.0, 126.7, 126.5, 125.9, 123.7, 121.6, 119.1, 24.2, 24.0, 14.2, 14.0.

12.23 N-(4-dodecylphenyl)formamide (2w)



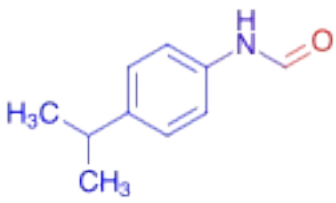
Following the general procedure 2.2, 4-dodecylaniline **1w** (261 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product N-(4-dodecylphenyl)formamide **2w** as a white solid (274 mg, 95% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, J = 11.4 Hz, 1H), 8.64 (d, J = 11.4 Hz, 1H), 8.32 (d, J = 1.6 Hz, 1H), 7.83 (br s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.13 (dd, J = 8.4, 3.2 Hz, 4H), 7.01 (d, J = 8.3 Hz, 2H), 2.56 (q, J = 7.7 Hz, 4H, -CH_2-Ar), 1.64-1.51 (m, 4H, -CH_2-CH_2-Ar), 1.36-1.18 (m, 4H), 0.88 (t, J = 6.8 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 159.2, 140.2, 139.6, 134.6, 134.4, 129.6, 128.9, 120.1, 119.1, 35.4, 35.3, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4, 29.3, 22.7, 14.2.

12.24 N-(3,5-dimethylphenyl)formamide (2x)



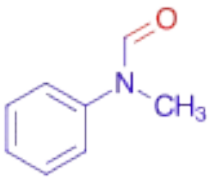
Following the general procedure 2.2, 3,5-dimethyl aniline **1x** (121 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(3,5-dimethylphenyl)formamide **2x** as a white solid (138 mg, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 11.4 Hz, 1H), 8.29 (d, J = 9.4 Hz, 0.5H), 8.24 (s, 0.5H), 7.33 (s, 0.5H), 7.08 (s, 1H), 6.74 (s, 1H), 6.70 (s, 0.7H), 6.63 (s, 2H), 2.23 (s, 6H), 2.2 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.1, 139.6, 138.9, 136.7, 136.6, 126.9, 126.6, 117.7, 116.5, 21.3.

12.25 N-(4-propan-2-yl-phenyl)formamide (2y)



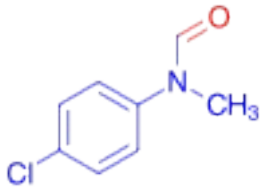
Following the general procedure 2.2, 4-isopropylaniline **1y** (135 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(4-propan-2-yl-phenyl)formamide **2y** as a white solid (150 mg, 92% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 11.0 Hz, 1H), 8.55 (d, J =11.4 Hz, 1H), 8.21 (d, J = 1.6 Hz, 1H), 8.02 (d, J = 4.7 Hz, 1H), 7.38 (d J = 8.5 Hz, 2H, Ar-H), 7.08 (dd, J = 8.4, 5.6 Hz, 4H), 6.94 (d, J = 8.4 Hz, 2H), 2.78 (m, 1H, -CH-Ar), 1.13 (t, J = 7.2 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 159.6, 146.1, 145.5, 134.8, 134.6, 127.6, 126.9, 120.4, 119.2, 33.6, 24.0.

12.26 N-Methyl-N-phenylformanilide (2z)



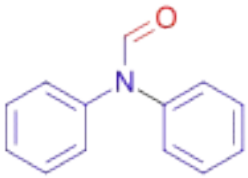
Following the general procedure 2.2, *N*-methylaniline **1z** (107 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*-Methyl-*N*-phenylformanilide **2z** as yellow oil (129 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H, -CHO), 7.42 (t, J = 7.6 Hz, 2H), 7.28 (dd, J = 7.9, 3.4 Hz, 1H), 7.18 (d, J = 8.4 Hz, 2H), 3.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 142.1, 129.9, 129.1, 126.6, 123.6, 122.4, 32.1.

12.27 N-(4-chlorophenyl)-N-methylformamide (2aa)



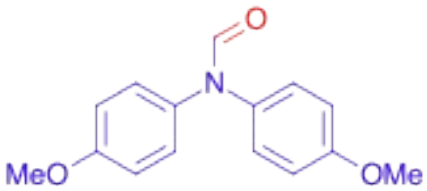
Following the general procedure 2.2, 4-chloro-*N*-methylaniline **1aa** (141 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(4-chlorophenyl)-*N*-methylformamide **2aa** as a yellow solid (142 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.32 (d, J = 8.7 Hz, 2H, Ar-H), 7.08 (d, J = 8.7 Hz, 2H, Ar-H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 140.7, 131.8, 129.7, 129.0, 124.5, 123.4, 31.9.

12.28 N,N-Diphenylformamide (2ab)



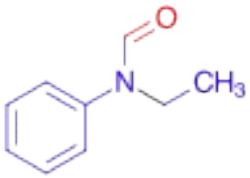
Following the general procedure 2.2, diphenylamine **1ab** (169 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 100 °C to afford product *N*,*N*-Diphenylformamide **2ab** as a yellow solid (167 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.32-7.22 (m, 4H), 7.22-7.11 (m, 4H), 7.08-7.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 141.8, 139.7, 129.8,3 129.2, 126.9, 126.2, 125.1.

12.29 N,N-bis(4-methoxyphenyl)formamide (2ac)



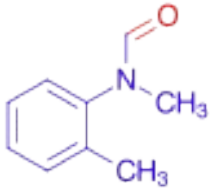
Following the general procedure 2.2, bis(4-methoxyphenyl)amine **1ac** (229 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*,*N*-bis(4-methoxyphenyl)formamide **2ac** as an off-white solid (221 mg, 86% yield). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.56 (s, 1H, -CHO), 7.23-7.22 (m, 2H, -CH-Ar), 7.12-7.11 (m, 2H, -CH-Ar), 6.94 – 6.91 (m, 4H, -CH-Ar), 3.84 (s, 3H, -OCH3), 3.82 (s, 3H, -OCH3). ^{13}C NMR (201 MHz, $CDCl_3$) δ 161.9, 158.6, 158.0, 134.9, 132.9, 127.0, 126.6, 114.8, 55.6, 55.4.

12.30 N-Ethyl-N-phenylformamide (2ad)



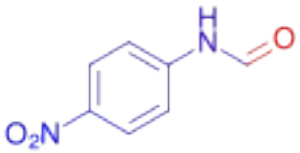
Following the general procedure 2.2, *N*-ethylaniline **1ad** (121 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-ethyl-*N*-phenylformamide **2ad** as a colourless oil (141 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.42 (t, J = 7.8 Hz, 2H), 7.33-7.27 (m, 1 H) 7.20-7.15 (m, 2H), 3.87 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 140.8, 129,6, 129.3, 126.9, 126.1, 124.3, 40.1, 13.1.

12.31 N-Methyl-N-(2-methylphenyl)formamide (2ae)



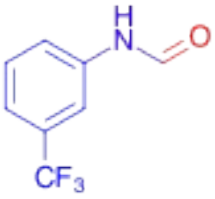
Following the general procedure 2.2, *N*-ethyl-2-methylaniline **1ae** (135 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) at for 90 min at 70 °C to afford product *N*-methy-*N*-(2-methylphenyl)formamide **2ae** as a pale-yellow oil (158 mg, 97% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 0.1H), 8.14 (s, 1H), 7.33-7.21 (m, 4H), 7.16 (d, J = 7.2 Hz, 1.2H), 3.27 (s, 0.3H), 3.20 (s, 3H), 2.27 (s, 3H), 2.22 (s, 0.3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 161.9, 140.7, 135.4, 131.4, 131.2, 128.4, 128.3, 127.8, 127.2, 126.9, 37.2, 33.1, 17.7.

12.32 N-(4-nitrophenyl)formamide (2af)



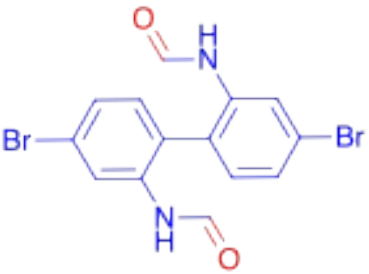
Following the general procedure 2.2, 4-nitroaniline **1af** (138 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(4-nitrophenyl)formamide **2af** as a yellow solid (131 mg, 79% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.84 (s, 1H), 10.72 (s, 0.3H), 9.06 (d, J = 7.3Hz, 0.3H), 8.41 (s, 1H), 8.24 (d, J = 8.9Hz, 2H), 7.83 (d, J = 8.9 Hz, 2H), 7.33 (d, J = 8.2 Hz, 0.6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.3, 161.0, 145.4, 144.7, 142.9, 126.9, 125.9, 125.6, 119.5, 117.0, 112.8.

12.33 N-(3-trifluoromethyphenyl) formamide (2ag)



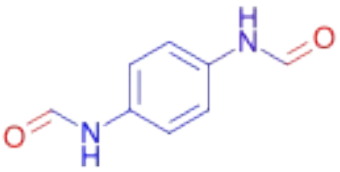
Following the general procedure 2.2, 3-(trifluoromethyl)aniline **1ag** (161 mg, 1 mmol) was reacted with formic acid (189 µL, 5mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(3-trifluoromethyphenyl) formamide **2ag** as a white solid (166 mg, 88% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 7.9 Hz, 0.4H), 8.79 (s, 0.4H), 8.77 (d, J = 11.3, 1H), 8.41 (d, J = 1.6 Hz, 1H, Ar-H), 7.91 (s, 1H, Ar-H), 7.72 (d, J = 7.9 Hz, 1H), 7.49-7.33 (m 3H, Ar-H), 7.31 (d, J = 7.6 Hz, 0.5H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 160.1, 137.5, 131.5, 130.4, 129.6, 125.1, 123.2, 122.4, 121.9, 121.4, 116.9, 115.3.

12.34 N,N'-(4,4'-dibromo-[1,1'-biphenyl]-2,2'-diyl)diformamide (2ah)



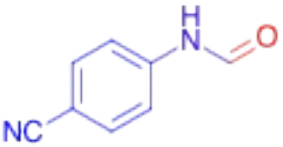
Following the general procedure 2.2, 4,4'-dibromo-[1,1'-biphenyl]-2,2'-diamine **1ah** (339 mg, 1 mmol) was reacted with formic acid (378 µL, 10 mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*,*N*'-(4,4'-dibromo-[1,1'-biphenyl]-2,2'-diyl)diformamide **2ah** as white solid (316 mg, 80% yield). Mixture of rotamers. Major ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 2H), 8.46 (d, J = 1.8 Hz, 2H), 8.12 (s, 2H), 7.41 (dd, J = 8.0, 4.0 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.2, 137.7, 133.1, 127.5, 127.1, 124.6, 122.2.

12.35 N-(4-formylamino-phenyl)formamide (2ai)



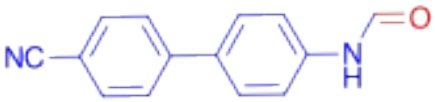
Following the general procedure 2.2, benzene-1,4-diamine **1ai** (108 mg, 1 mmol) was reacted with formic acid (378 µL, 10 mmol) in the presence of QSM-2 (2 mg) for 60 min at 70 °C to afford product *N*-(4-formylamino-phenyl)formamide **2ai** as a brown solid (141 mg, 86% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.15 (s, 2H), 10.08 (d, J = 11.0 Hz, 0.6H), 8.70 (d, J = 11.0 Hz, 0.6H), 8.24 (d, J = 1.8 Hz, 2H), 7.57-7.51 (m, 4H), 7.18-7.12 (m, 1.2H), 3.33 (s, 3H, -CH3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 159.8, 134.8, 134.5, 12.7, 120.1, 119.4, 118.8.

12.36 N-(4-cyanophenyl)formamide (2aj)



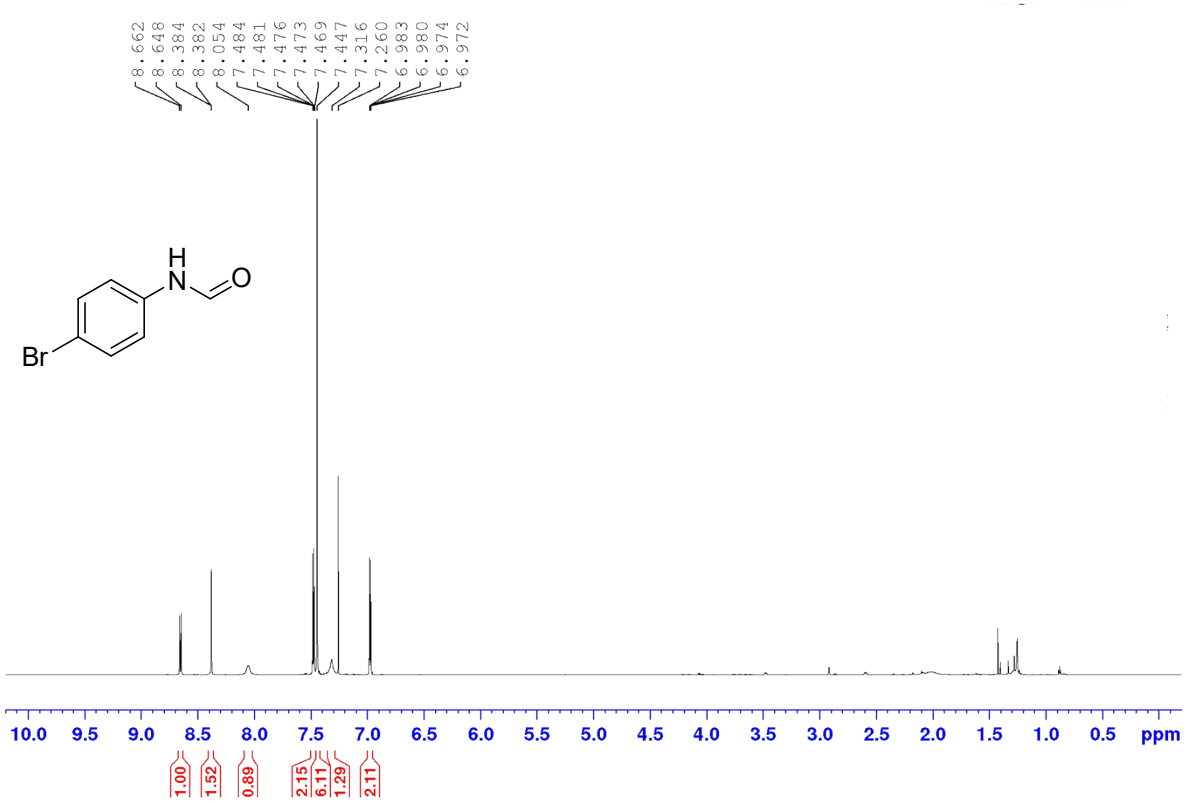
Following the general procedure 2.2, 4-aminobenzonitrile **1aj** (118 mg, 1 mmol) was reacted with formic acid (189 µL, 5 mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(4-cyanophenyl)formamide **2aj** as an off-white solid (121 mg, 83% yield). Mixture of rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 0.5H), 8.24 (s, 2H), 7.67 (d, J = 8.7 Hz, 5H, Ar-H), 7.61-7.55 (m, 6H, Ar-H), 7.23 (d J = 8.6 Hz, 1H, Ar-H), ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.5, 141.9, 133.6, 132.9, 119.6, 118.3, 117.4, 106.7.

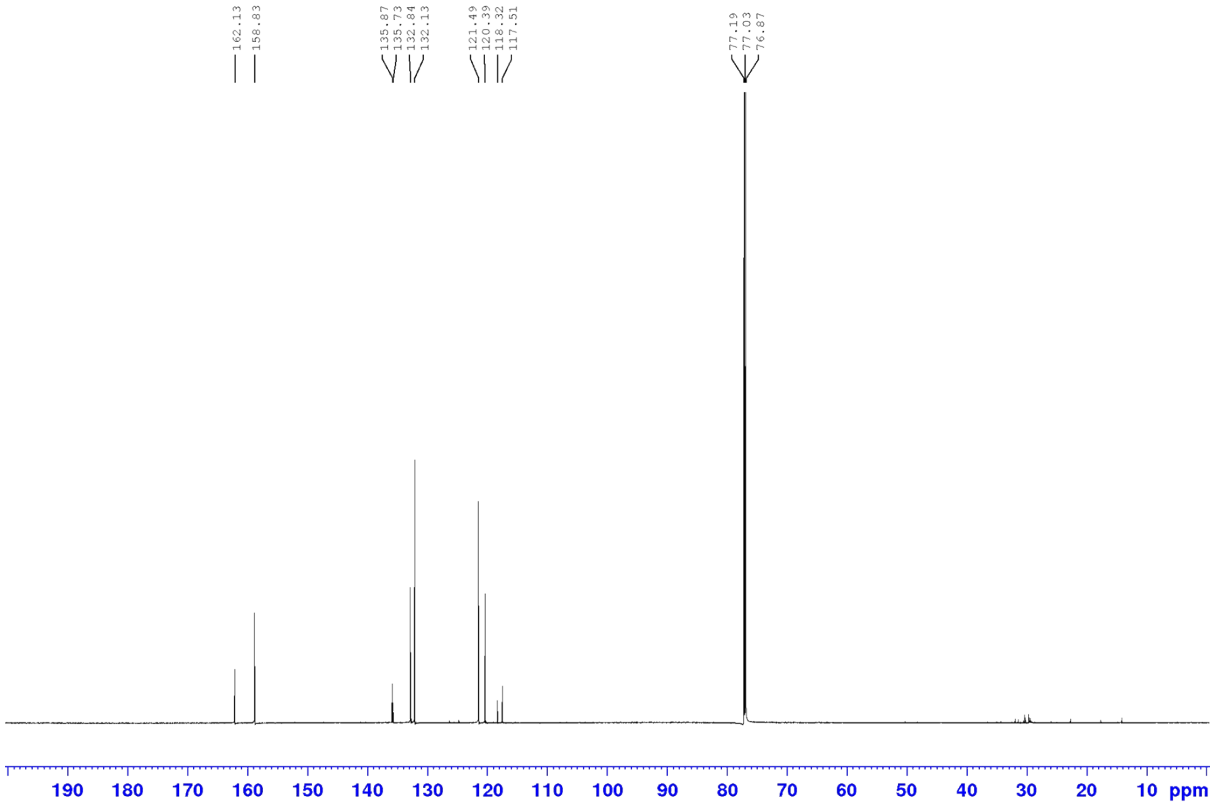
12.37 N-(4'-cyano[1,1'-biphenyl]-4-yl)formamide (2ak)

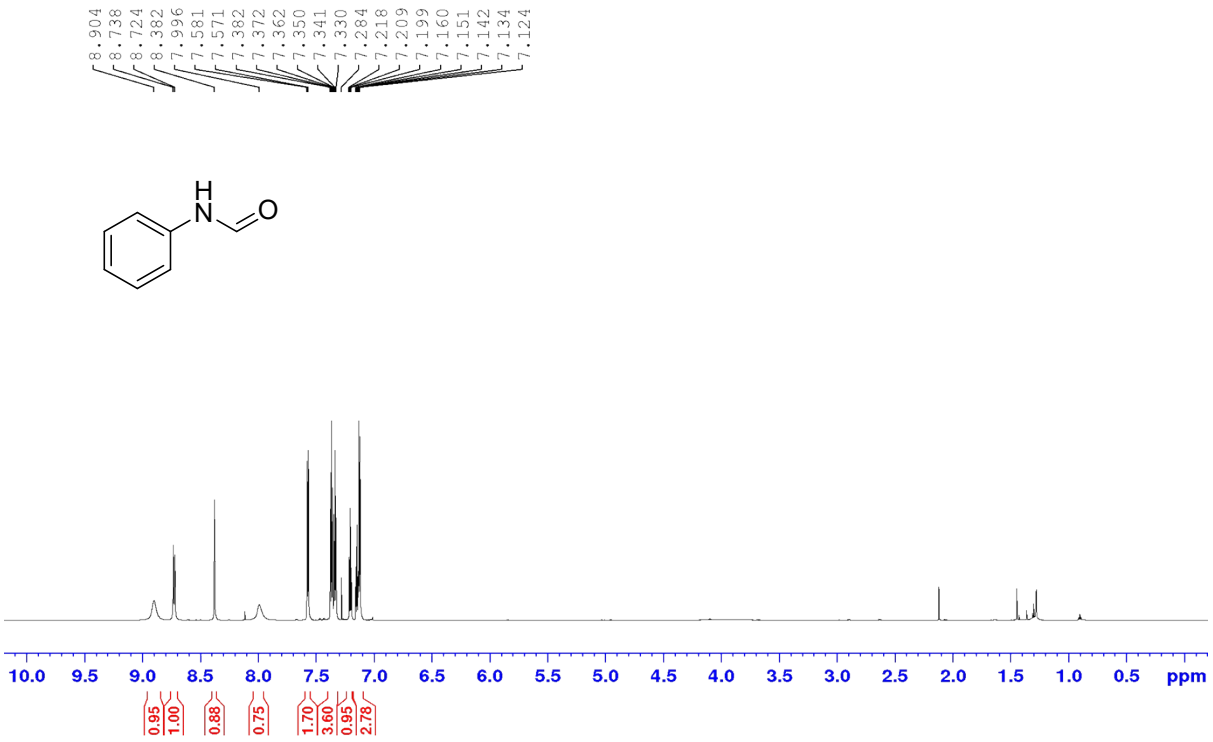


Following the general procedure 2.2, 4'-amino-[1,1'-biphenyl]-4-carbonitrile **1ak** (194 mg, 1 mmol) was reacted with formic acid (189 µL, 5 mmol) in the presence of QSM-2 (2 mg) for 90 min at 100 °C to afford product *N*-(4'-cyano[1,1'-biphenyl]-4-yl)formamide **2ak** as a white solid (188 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 10.3 (d, J = 10.9 Hz, 0.3H), 8.91 (d, J = 10.9 Hz, 0.3H), 8.34 (d, J = 1.7 Hz, 1H) 7.88 (q, J = 8.3 Hz, 5H, Ar-H), 7.76-7.71 (m, 5H, Ar-H), 7.34 (d, J = 8.6 Hz, 0.6H, Ar-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 160.3, 144.5, 144.4, 139.6, 139.4, 133.6, 133.3, 128.6, 128.1, 127.5, 127.4.

13 NMR Spectra



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8.738
8.724
8.382
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7.362
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7.330
7.284
7.218
7.209
7.199
7.160
7.151
7.142
7.134
7.124
H
N
O
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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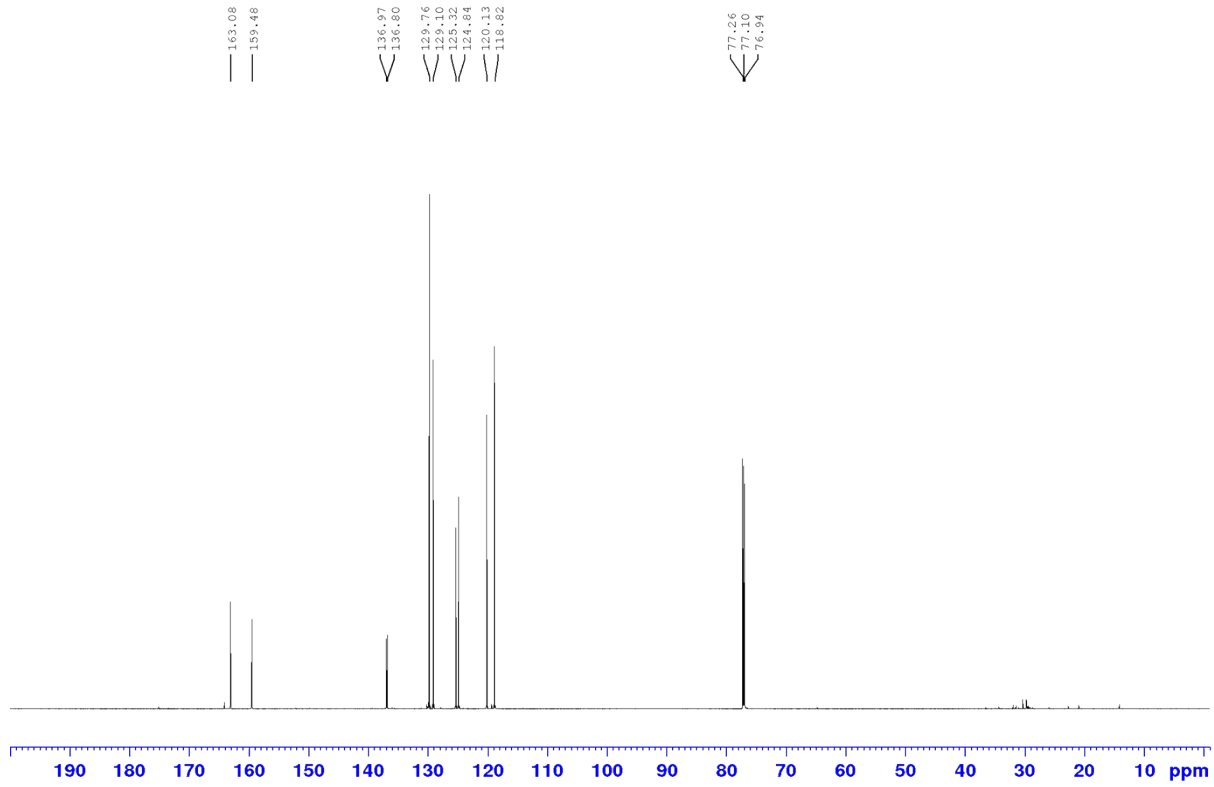
1.00
0.88
0.75
1.70
3.60
0.95
2.78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77.10
76.94
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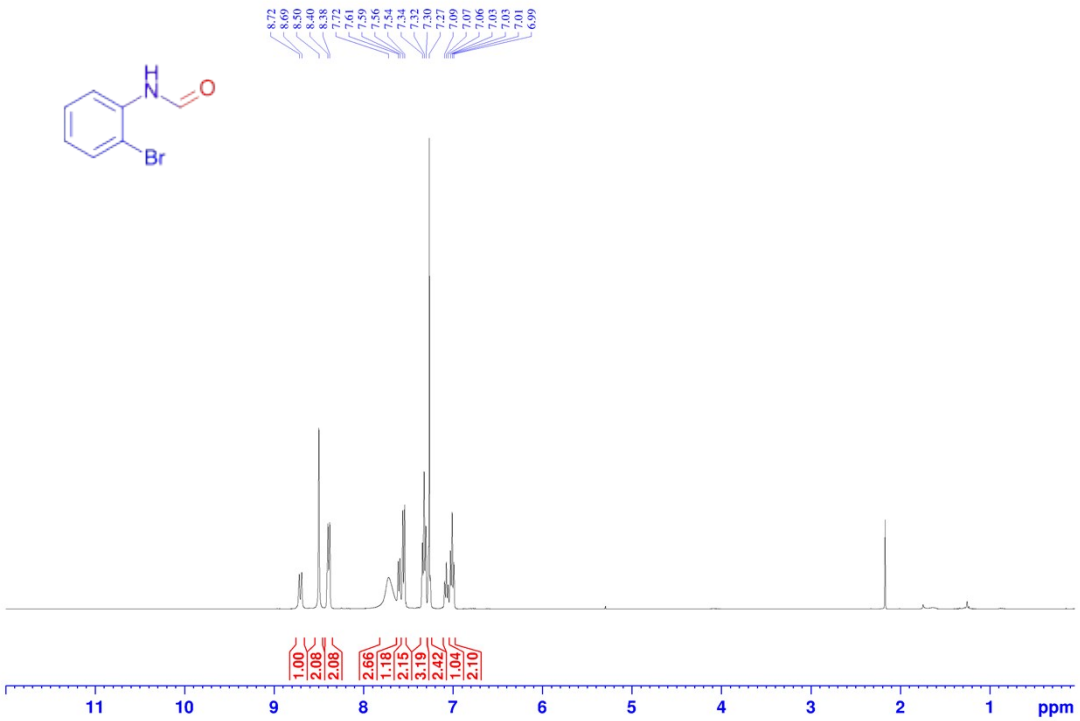
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7.27
7.09
7.07
7.06
7.03
7.01
6.99
H
N
O
Br
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2.08
2.66
1.18
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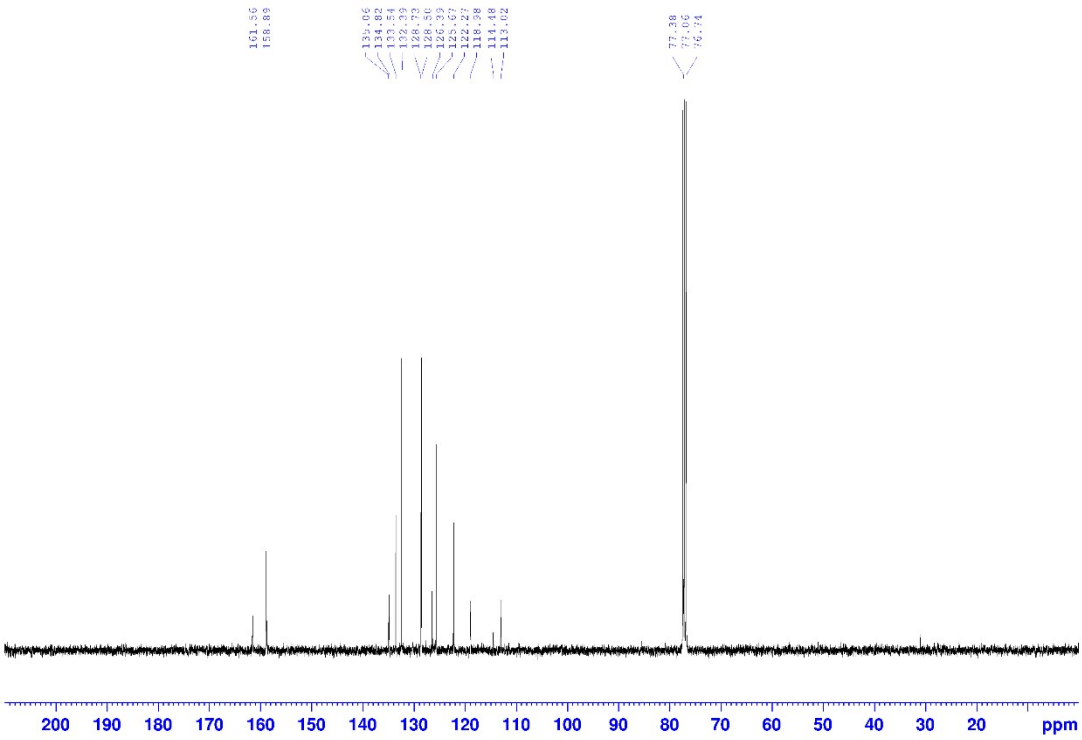
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122.27
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113.02
77.38
77.06
76.74
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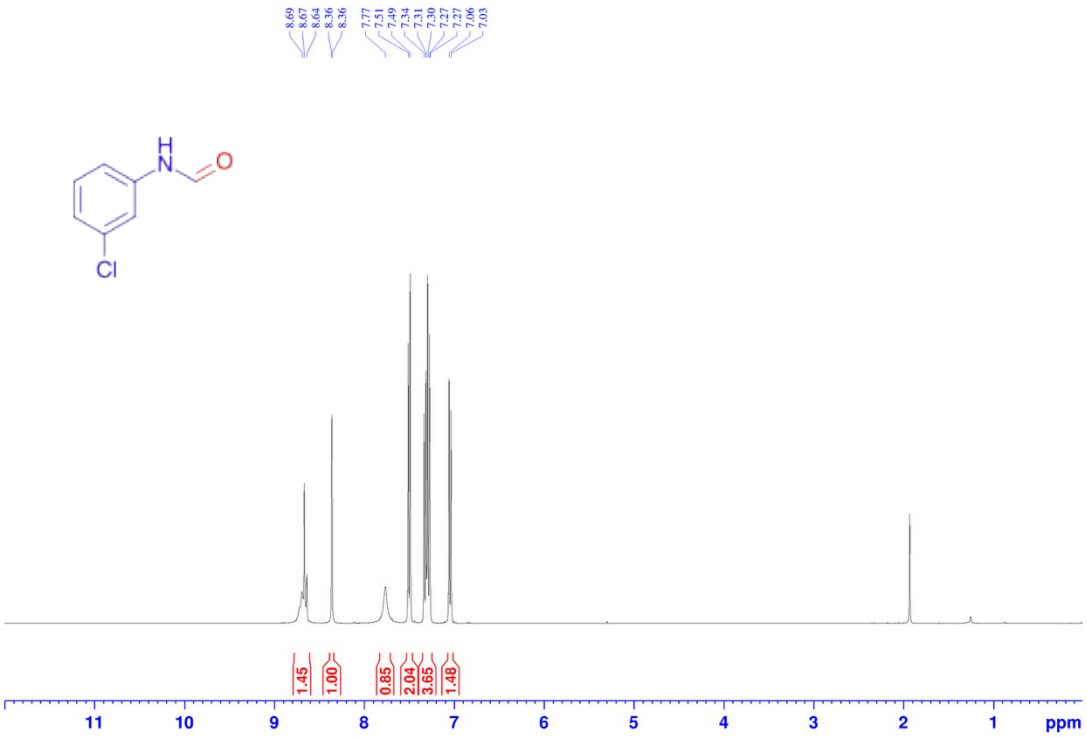
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7.27
7.06
7.03
H
N
O
Cl
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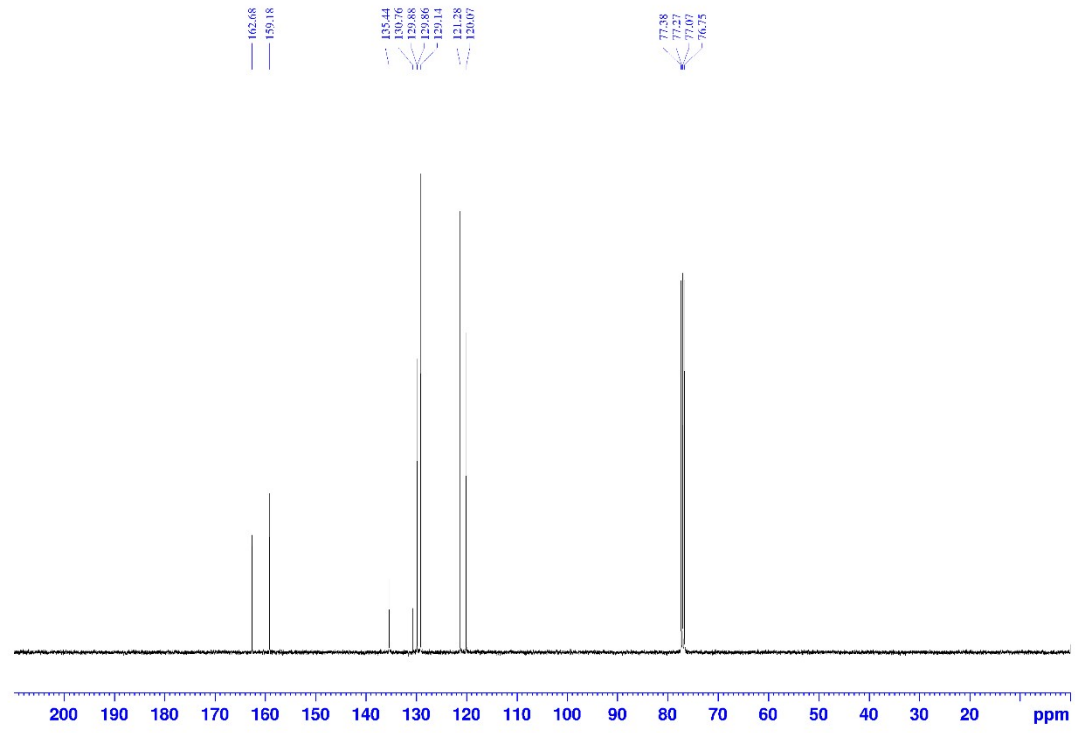
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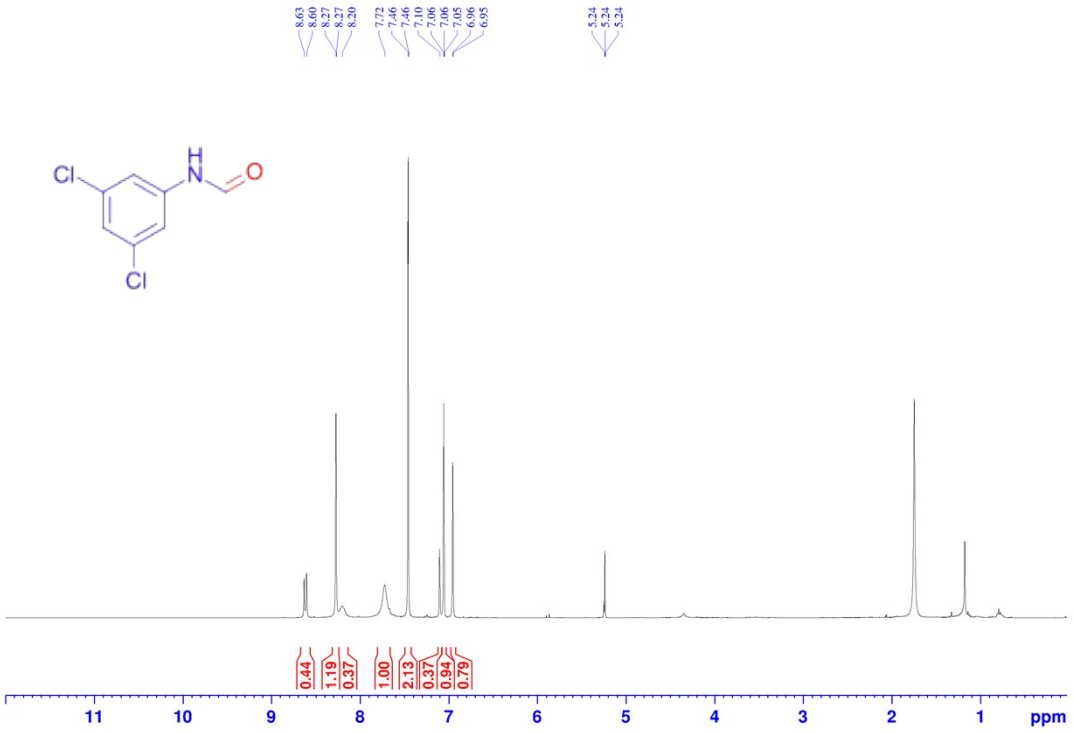
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7.46
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6.95
5.24
5.24
5.24
Cl
H
N
O
Cl
0.44
1.19
0.37
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3
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1
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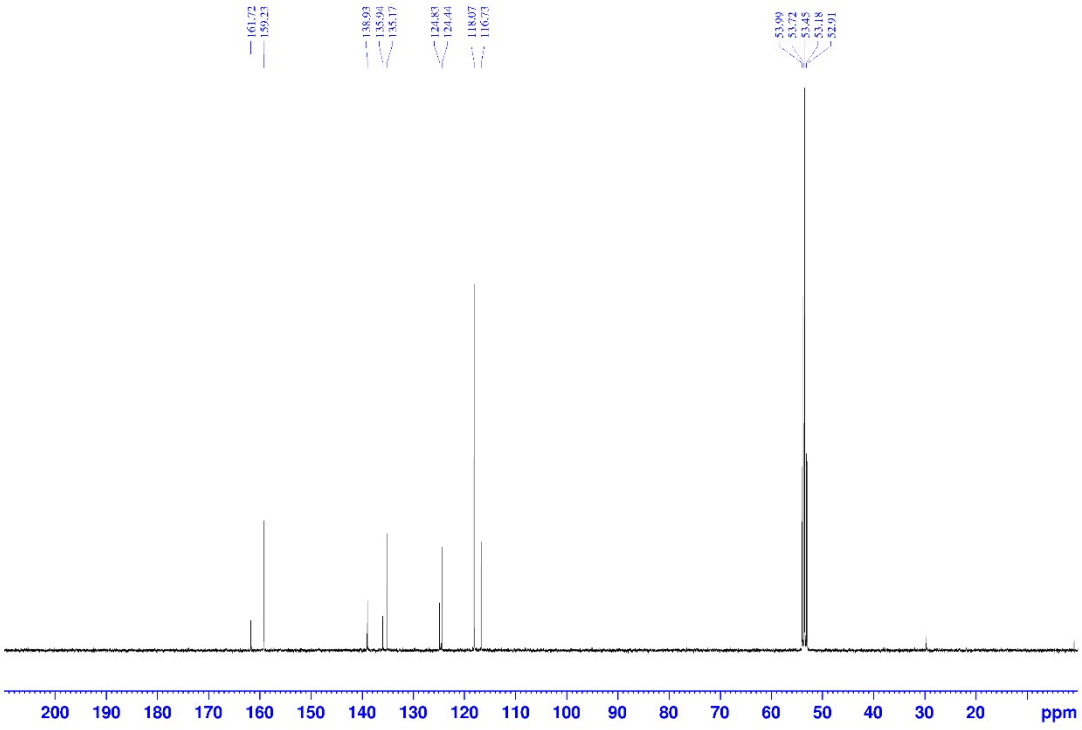
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52.91
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150
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80
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40
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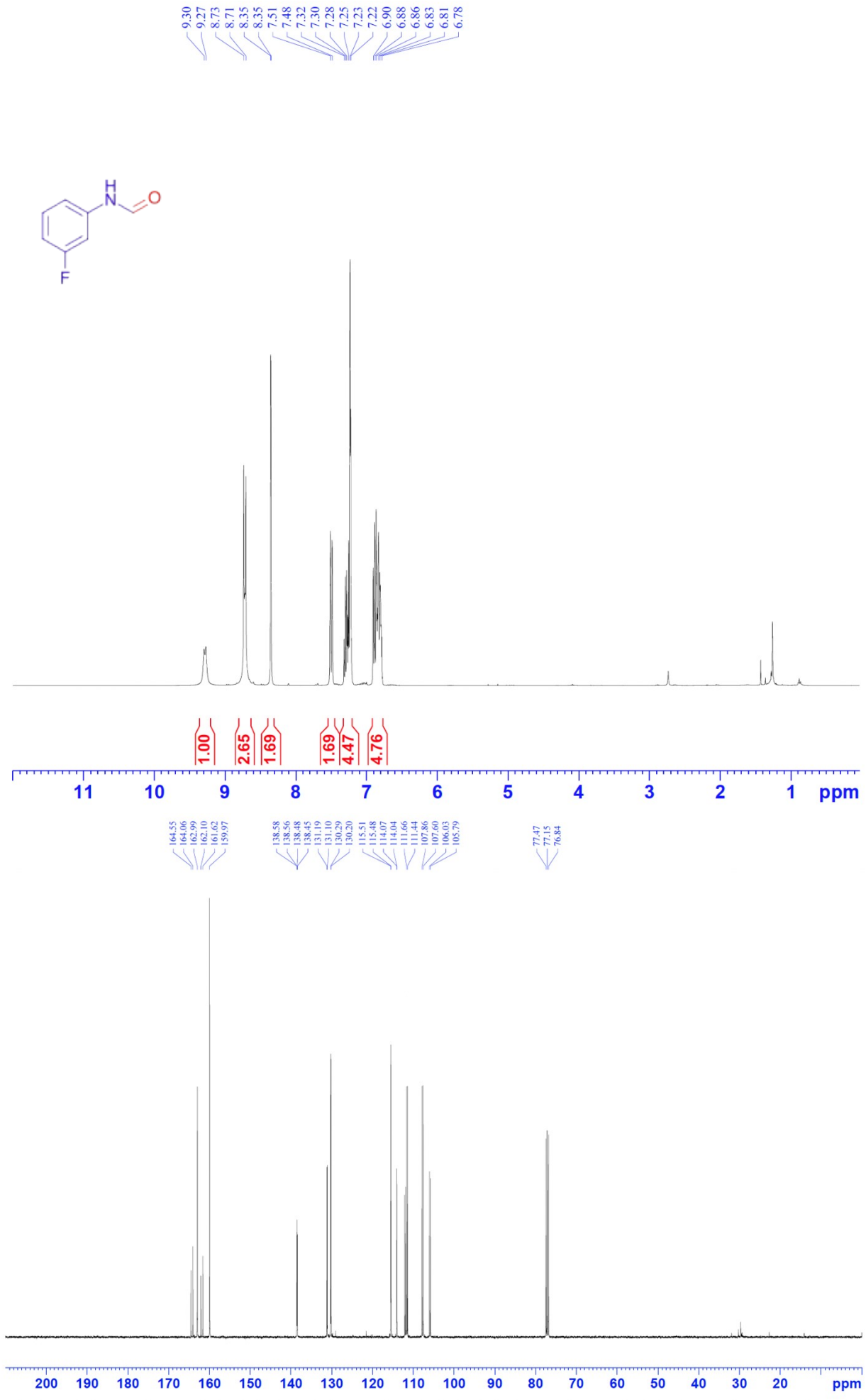
20
ppm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7.28
7.25
7.23
7.22
6.90
6.88
6.86
6.83
6.81
6.78
H
N
O
F
1.00
2.65
1.69
1.69
4.47
4.76
11
10
9
8
7
6
5
4
3
2
1
ppm
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164.06
162.99
162.10
161.62
159.97
138.58
138.56
138.48
138.45
131.19
131.10
130.29
130.20
115.51
115.48
114.07
114.04
111.66
111.44
107.86
107.60
106.03
105.79
77.47
77.15
76.84
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160
150
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130
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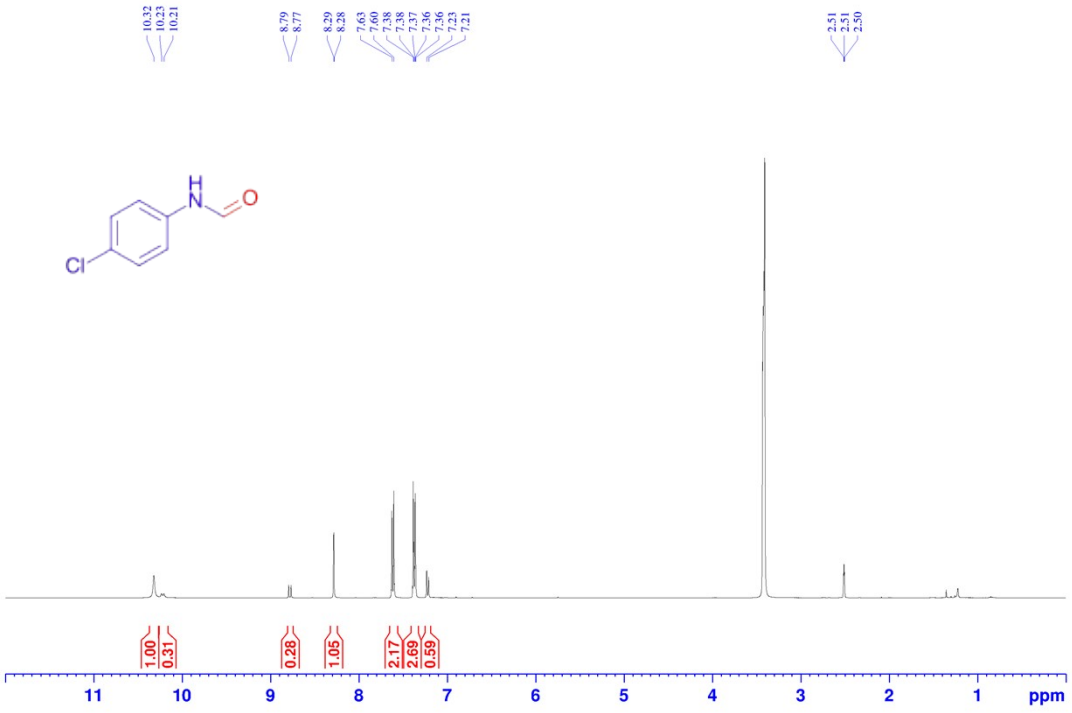
40
30
20
ppm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7.63
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7.38
7.38
7.37
7.36
7.36
7.23
7.21
2.51
2.51
2.50
Cl
H
N
O
1.00
0.31
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1.05
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2.69
0.59
11
10
9
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7
6
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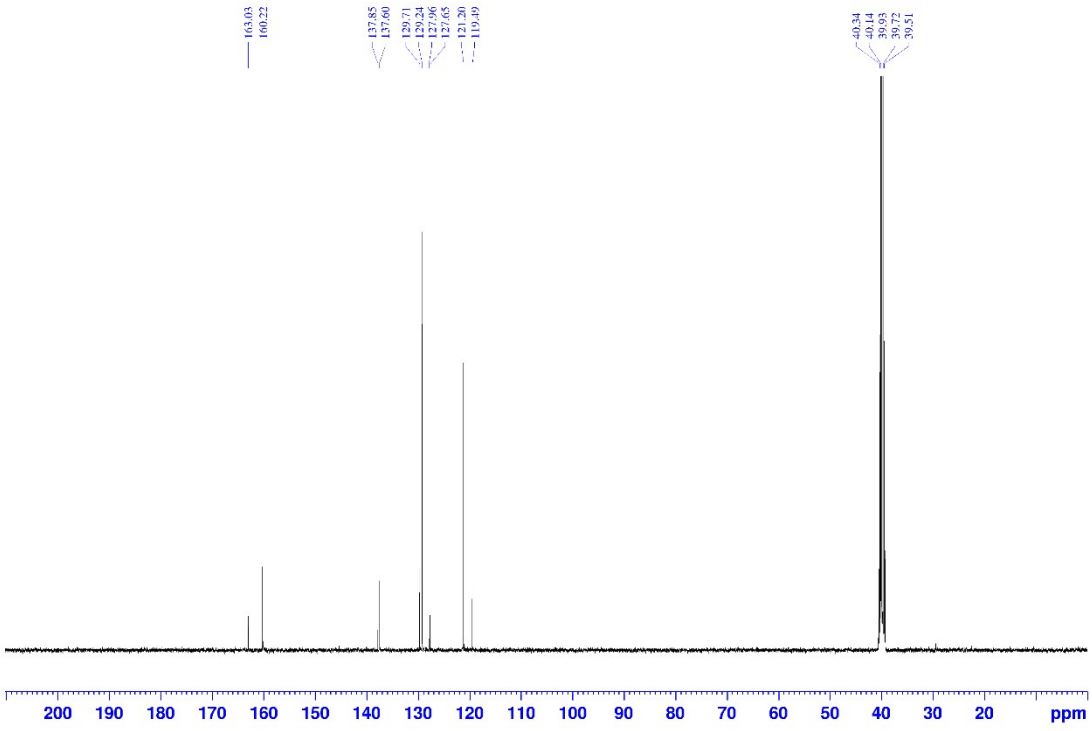
3
2
1
ppm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137.85
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129.24
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127.65
121.20
119.49
40.34
40.14
39.93
39.72
39.51
200
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170
160
150
140
130
120
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100
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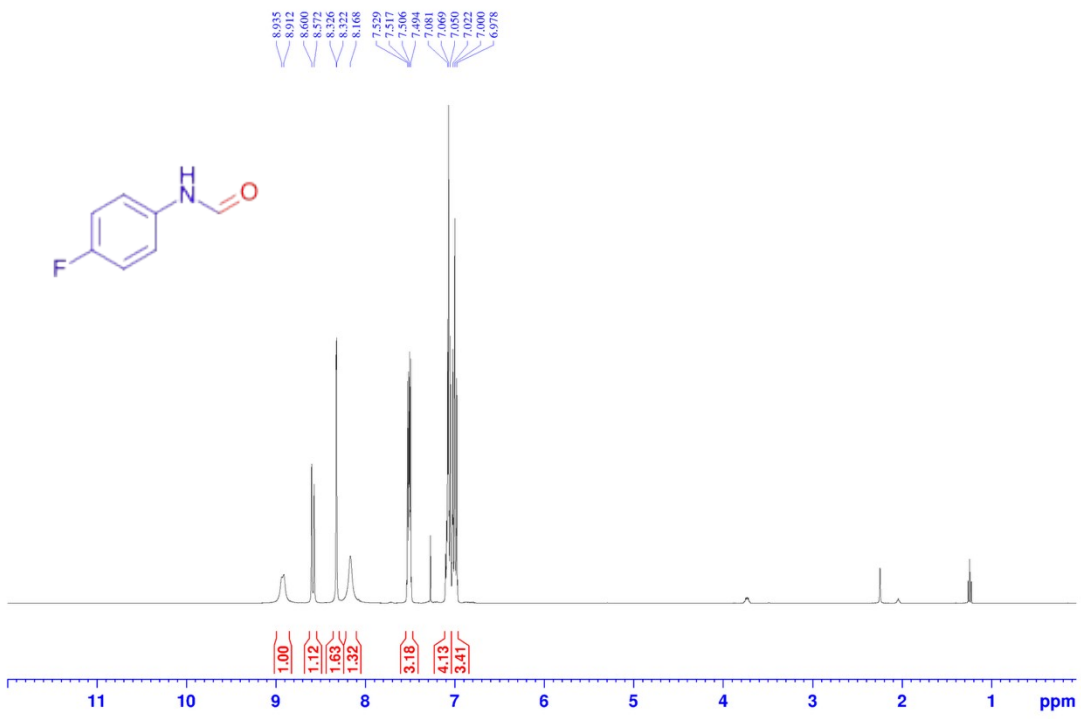
80
70
60
50
40
30
20
ppm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8.322
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7.506
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7.050
7.022
7.000
6.978
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N
O
F
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1.12
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4.13
3.41
11
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9
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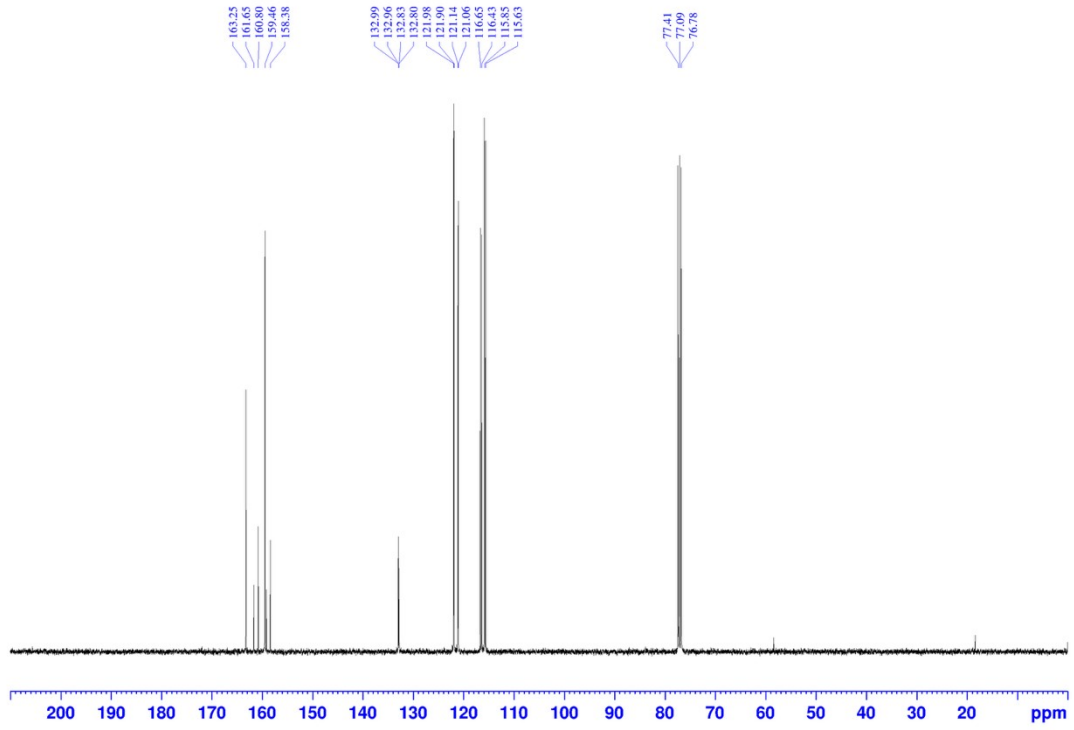
7
6
5
4
3
2
1
ppm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121.90
121.14
121.06
116.65
116.43
115.85
115.63
77.41
77.09
76.78
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160
150
140
130
120
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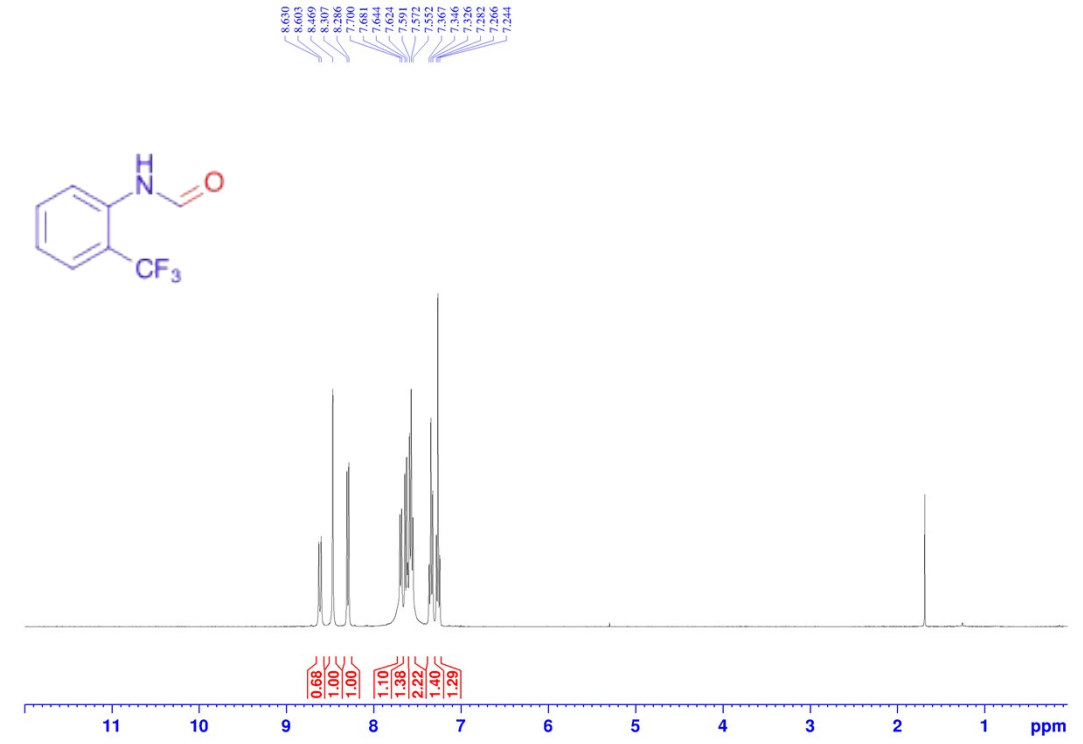
40
30
20
ppm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7.644
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7.591
7.572
7.553
7.367
7.346
7.326
7.282
7.266
7.244
H
N
O
CF3
0.68
1.00
1.00
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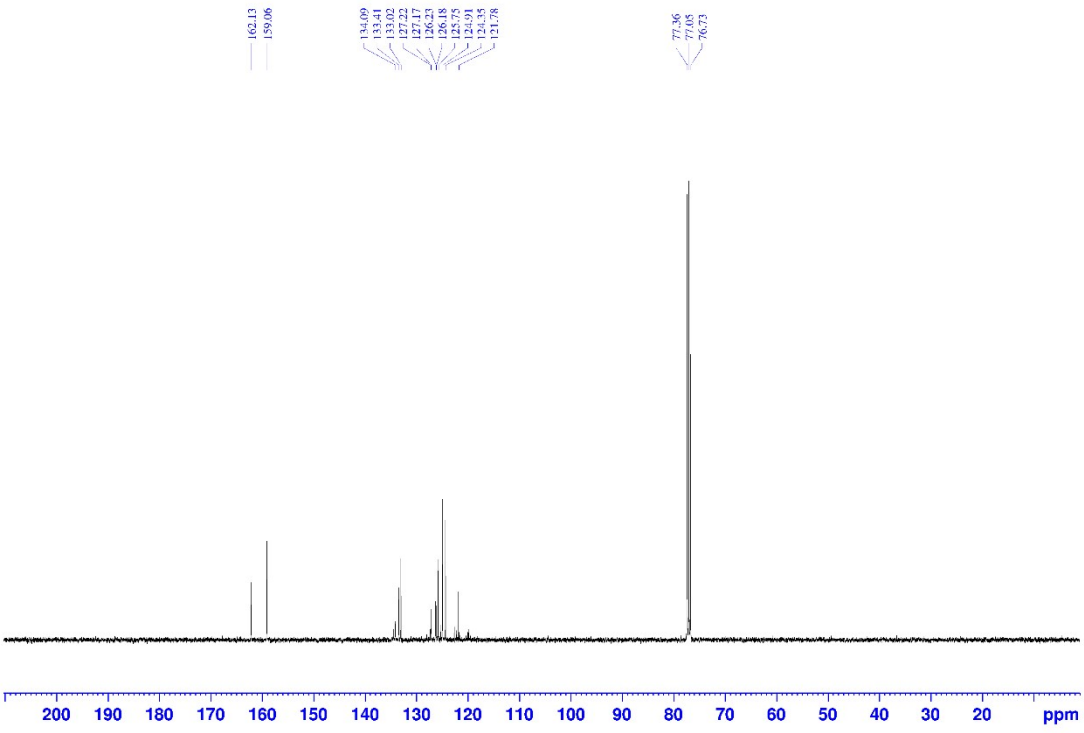
2.22
1.40
1.29
11
10
9
8
7
6
5
4
3
2
1
ppm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132.72
127.17
126.23
126.18
125.75
124.91
124.35
121.78
77.36
77.05
76.73
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160
150
140
130
120
110
100
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80
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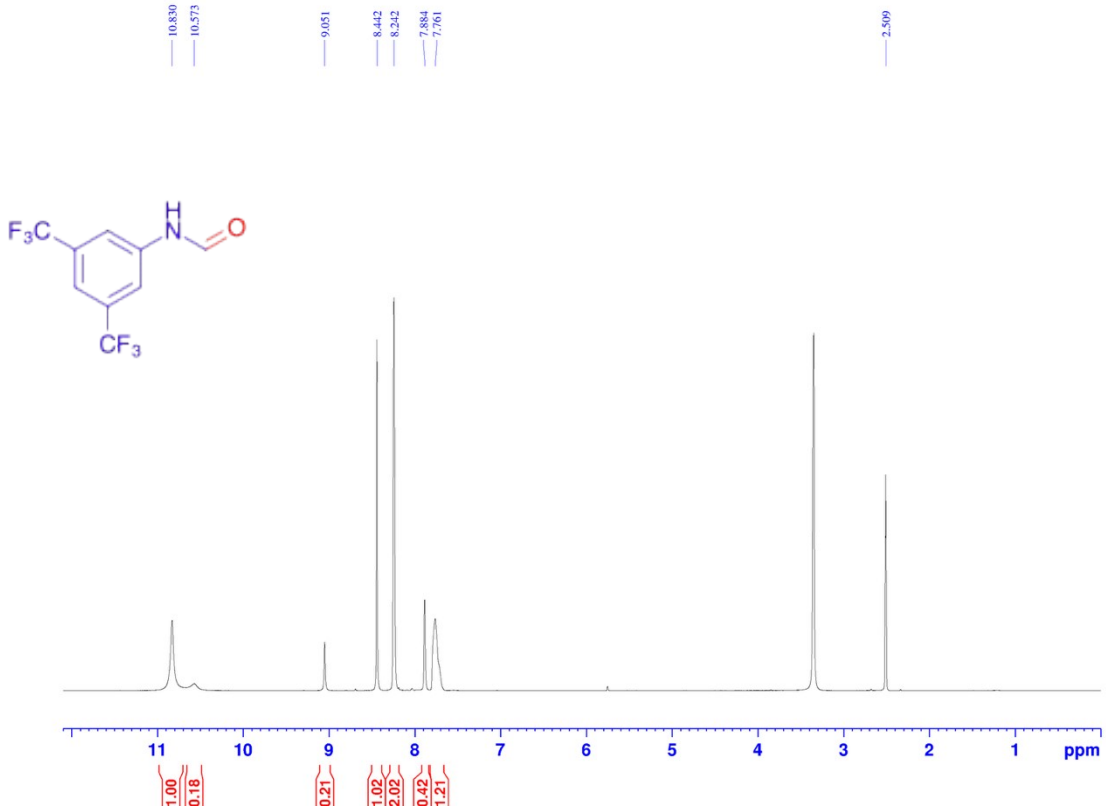
50
40
30
20
ppm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7.761
2.509
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H
N
O
CF3
11
10
9
8
7
6
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4
3
2
1
ppm
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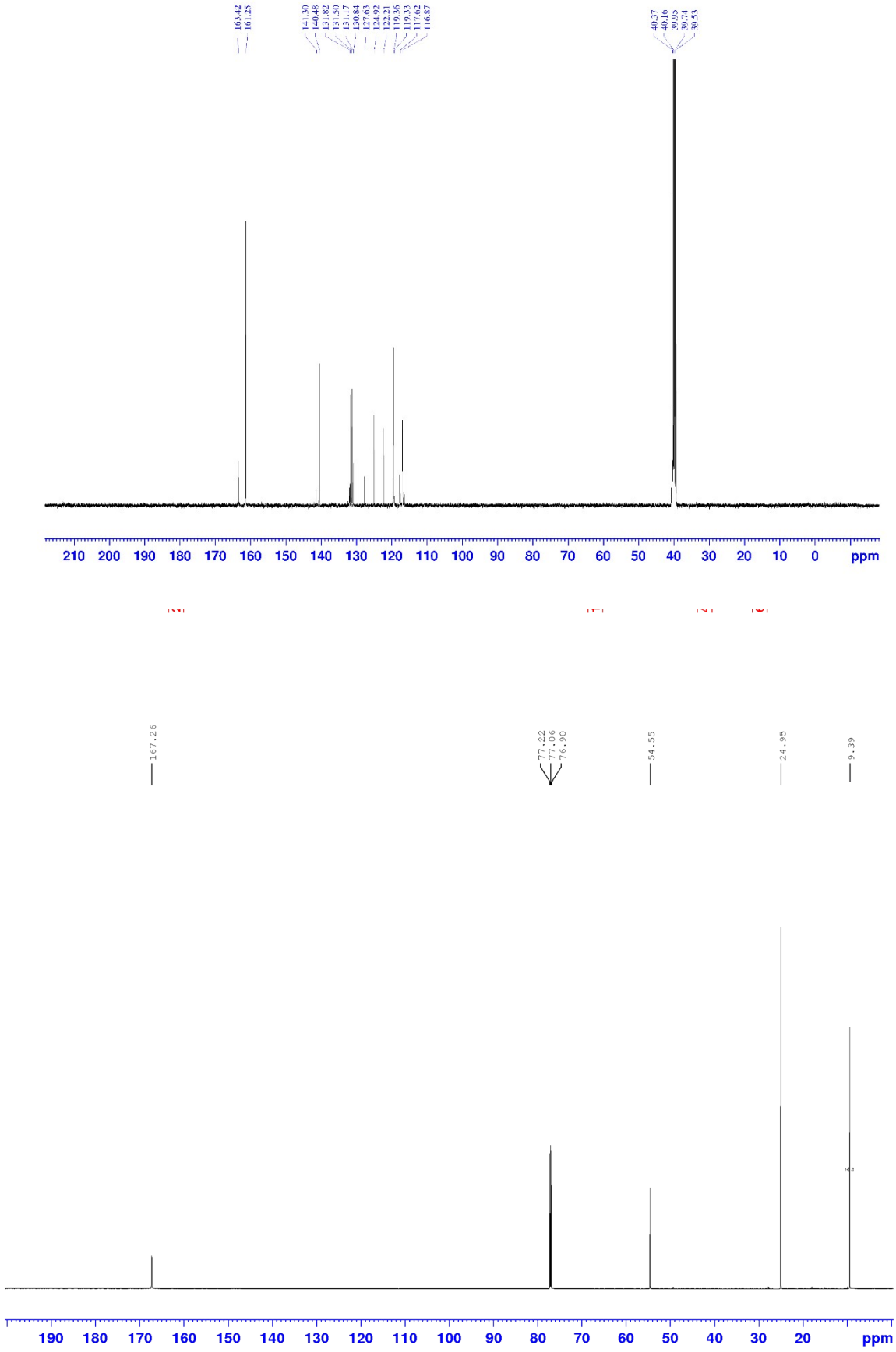
0.42
1.21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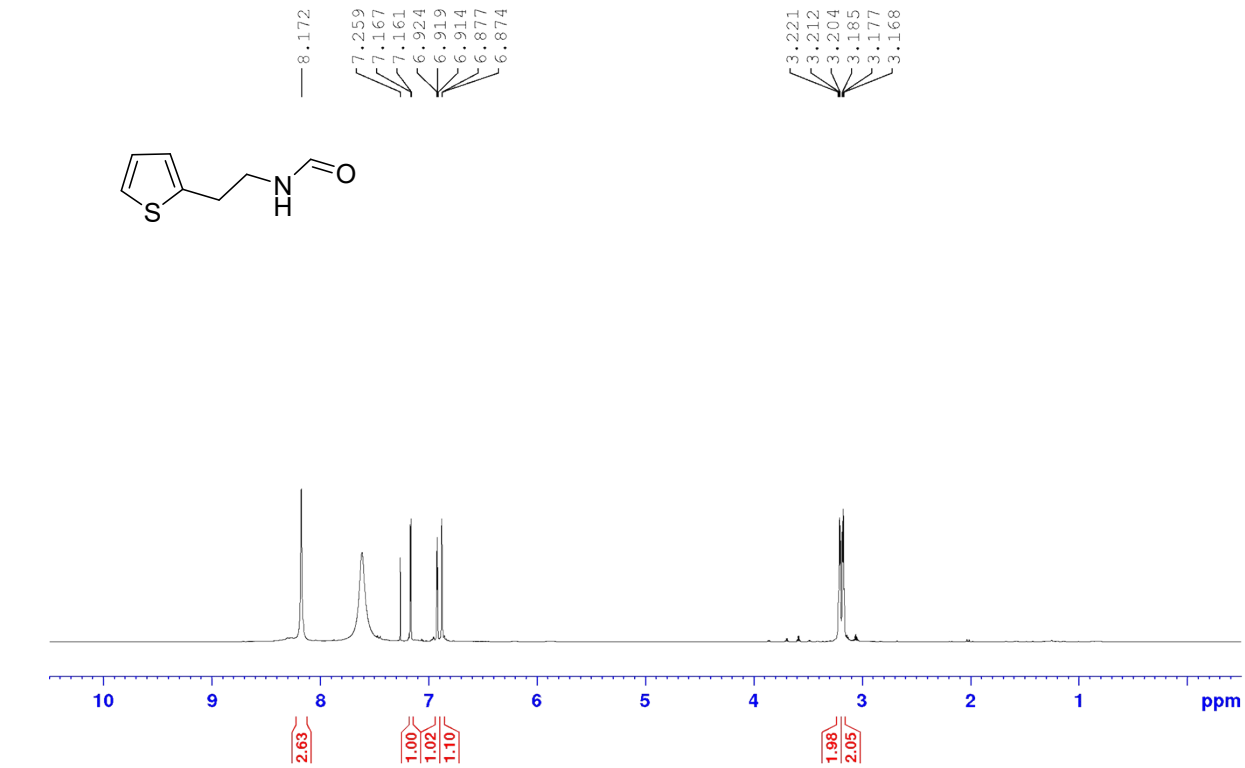
131.50
131.17
130.84
127.63
124.92
122.21
119.36
119.33
117.62
116.87
40.37
40.16
39.95
39.74
39.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
167.26
77.22
77.06
76.90
54.55
24.95
9.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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6.877
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3.212
3.204
3.185
3.177
3.168
S
N
H
O
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8
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5
4
3
2
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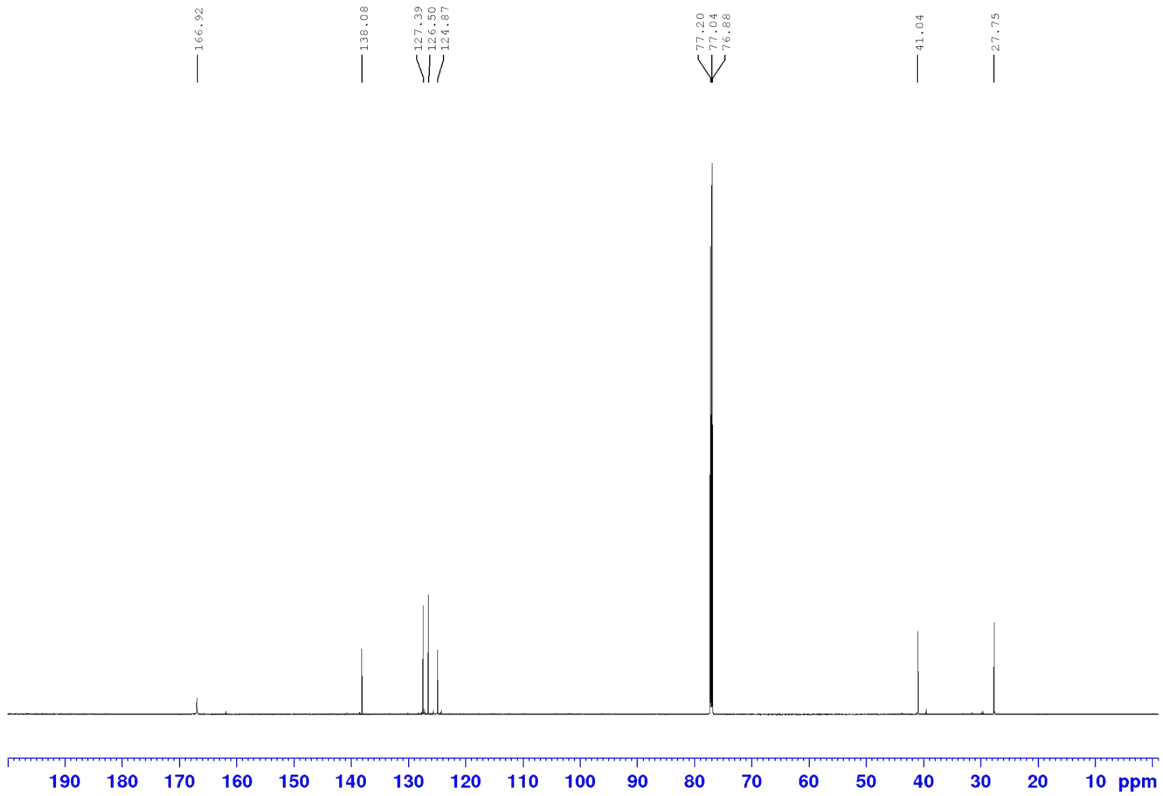
1.10
1.98
2.05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76.88
41.04
27.75
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150
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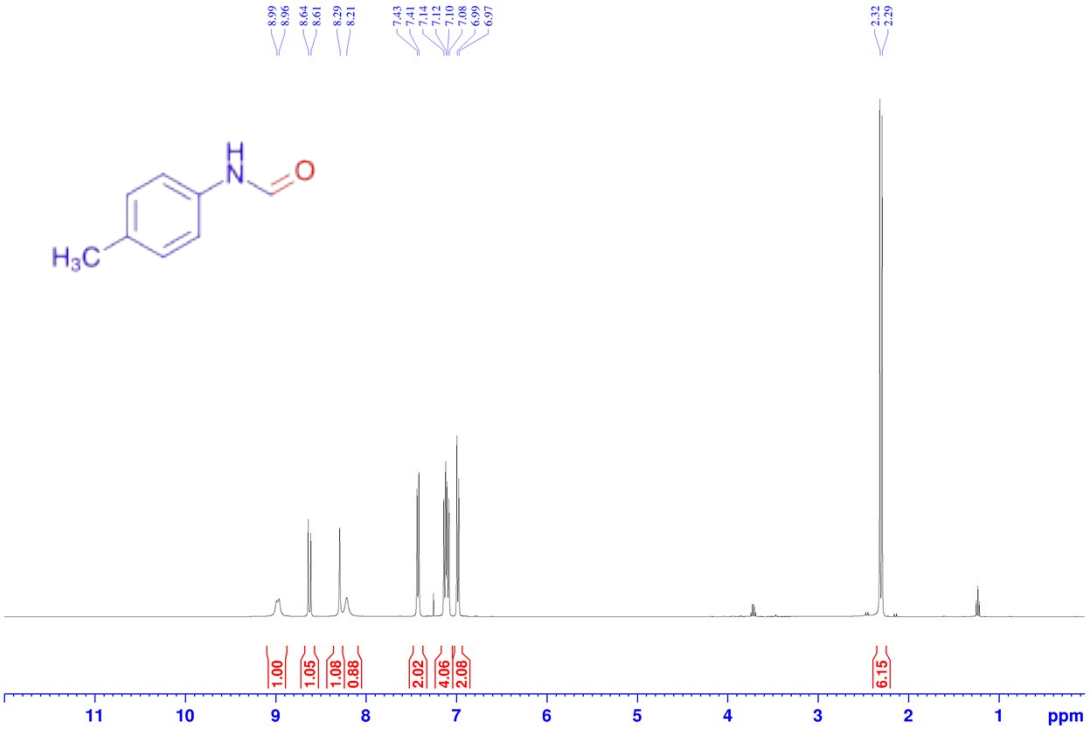
30
20
10
ppm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7.12
7.10
7.08
6.99
6.97
2.32
2.29
H
N
O
H3C
1.00
1.05
1.08
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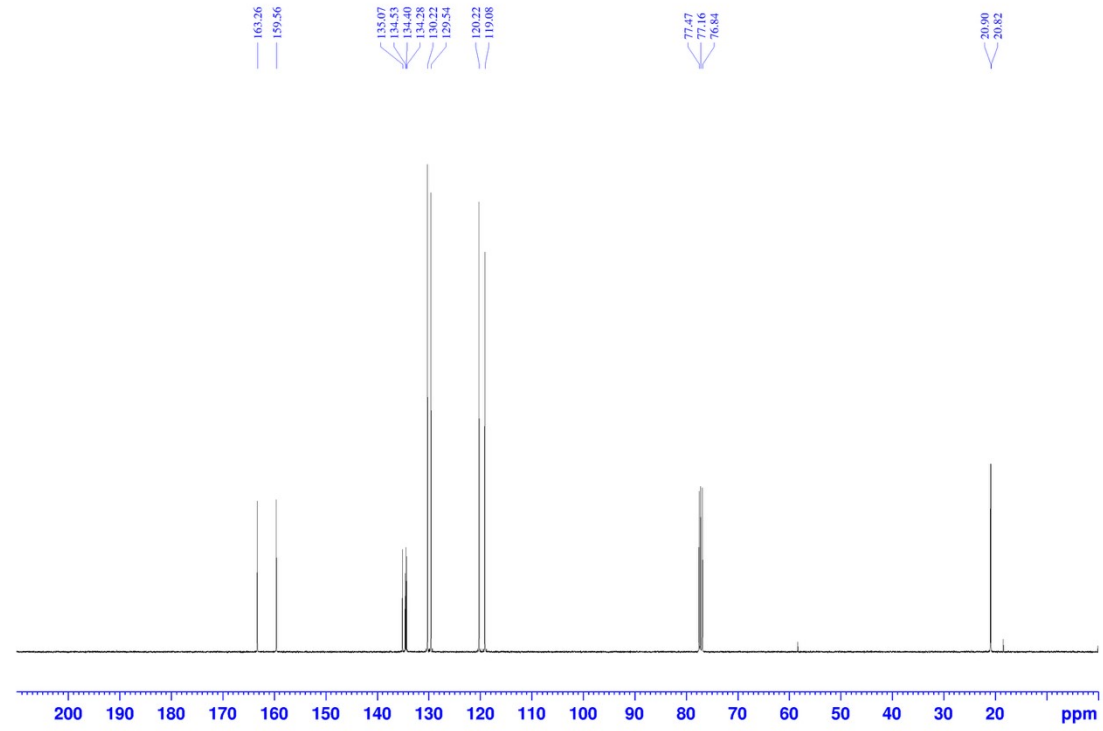
2.08
6.15
11
10
9
8
7
6
5
4
3
2
1
ppm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119.08
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77.16
76.84
20.90
20.82
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160
150
140
130
120
110
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80
70
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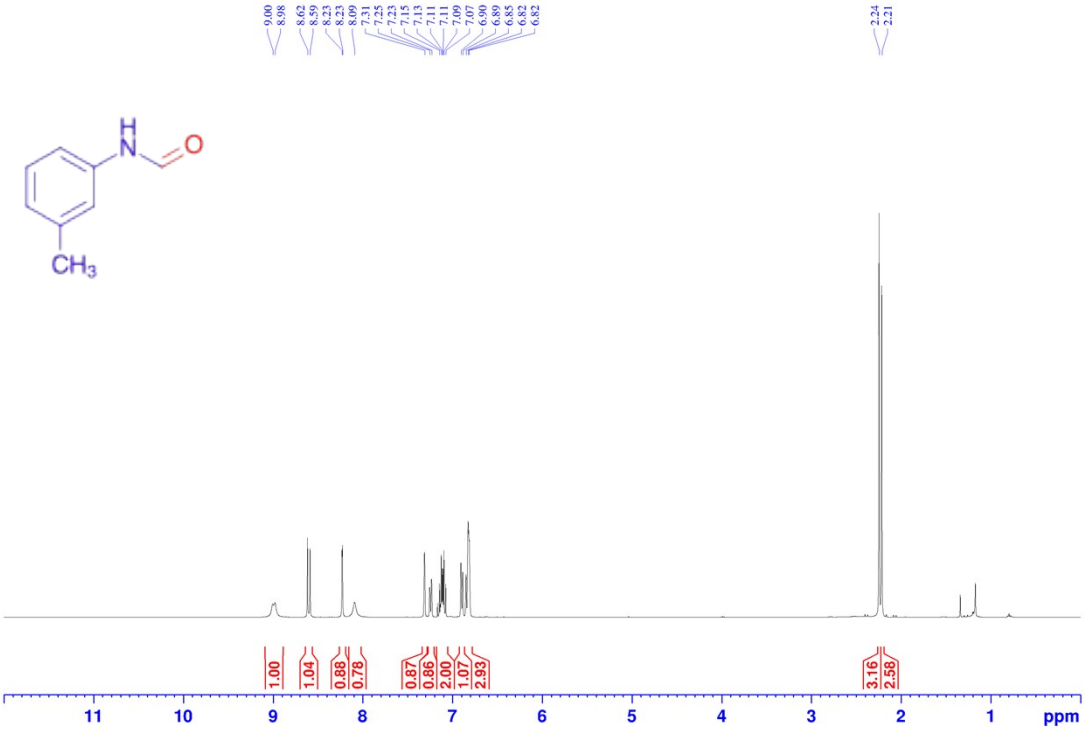
50
40
30
20
ppm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7.23
7.15
7.13
7.11
7.09
7.07
6.90
6.89
6.85
6.82
6.82
2.24
2.21
H
N
O
CH3
1.00
1.04
0.88
0.78
0.87
0.86
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11
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7
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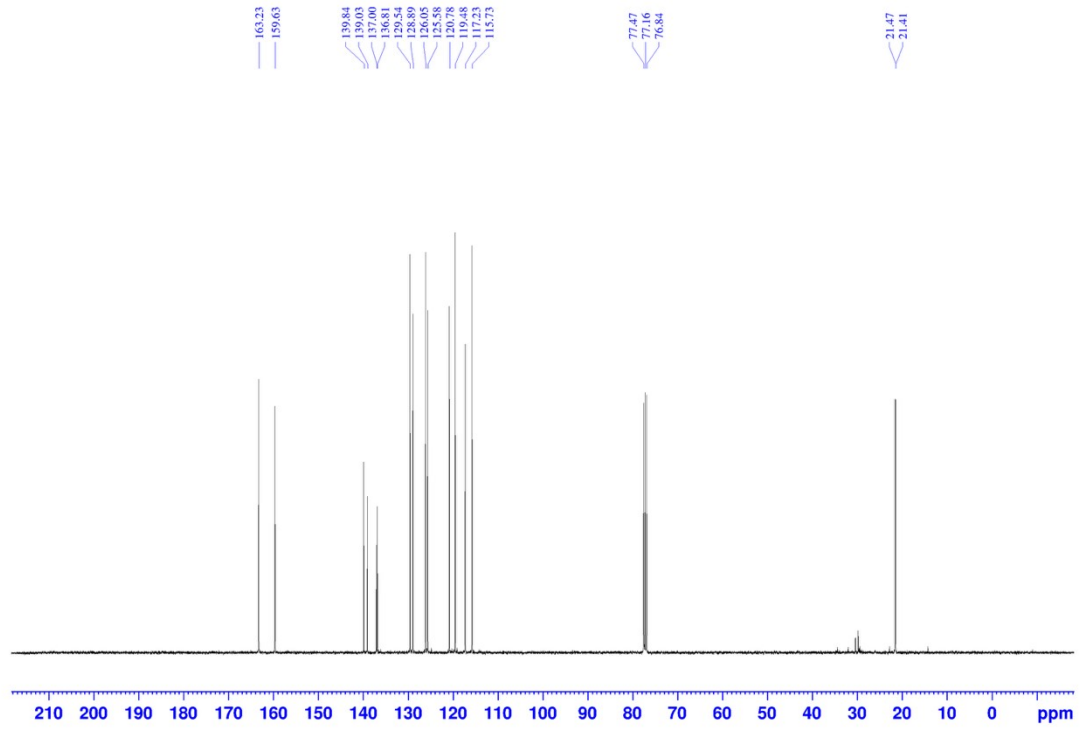
3
2
1
ppm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128.89
126.05
125.58
120.78
119.48
117.23
115.73
77.47
77.16
76.84
21.47
21.41
210
200
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140
130
120
110
100
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60
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30
20
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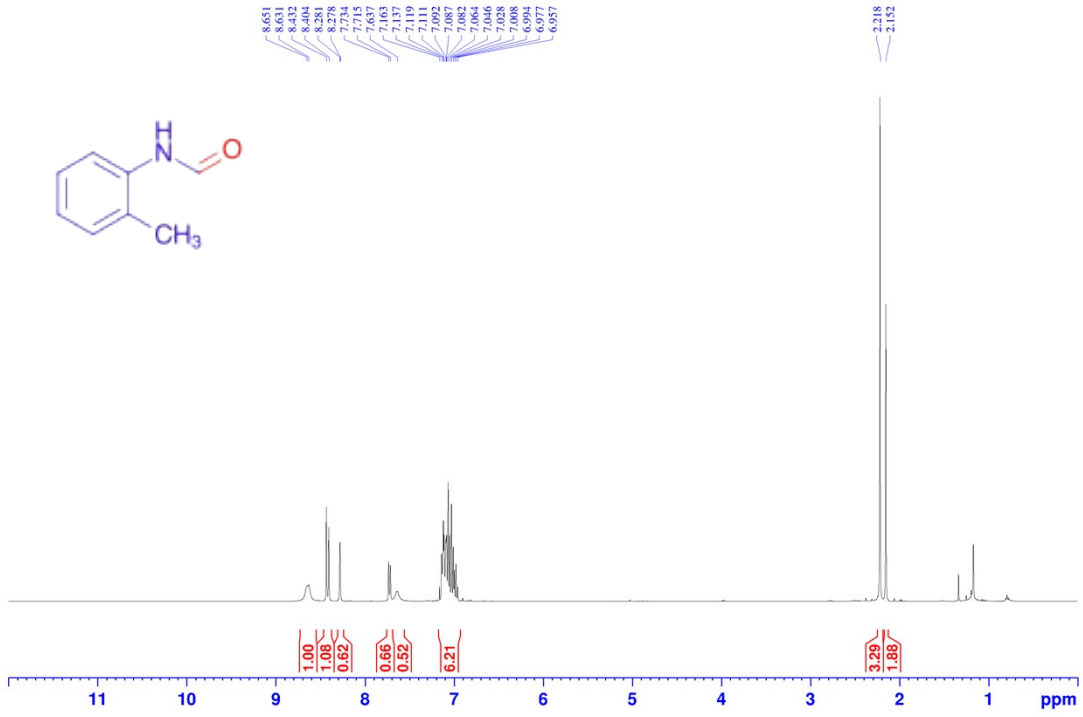
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7.119
7.111
7.092
7.087
7.082
7.064
7.046
7.028
7.008
6.994
6.977
6.957
2.218
2.152
H
N
O
CH3
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1.08
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11
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7
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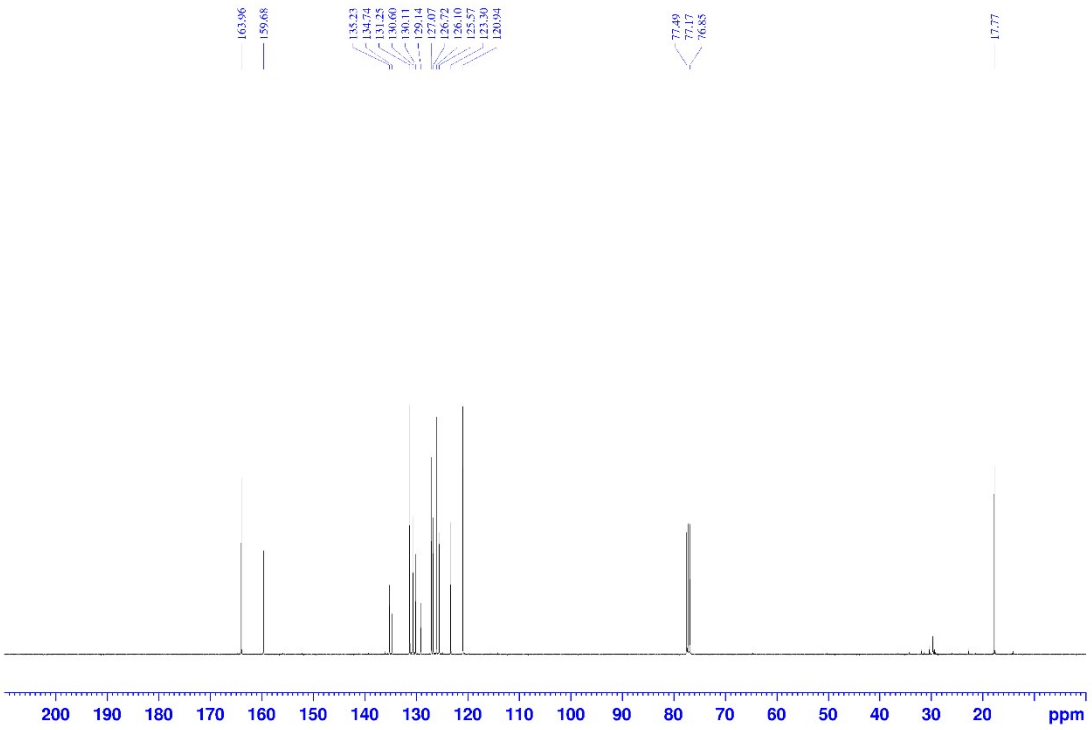
ppm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129.14
127.07
126.72
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125.57
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120.94
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76.85
17.77
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80
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40
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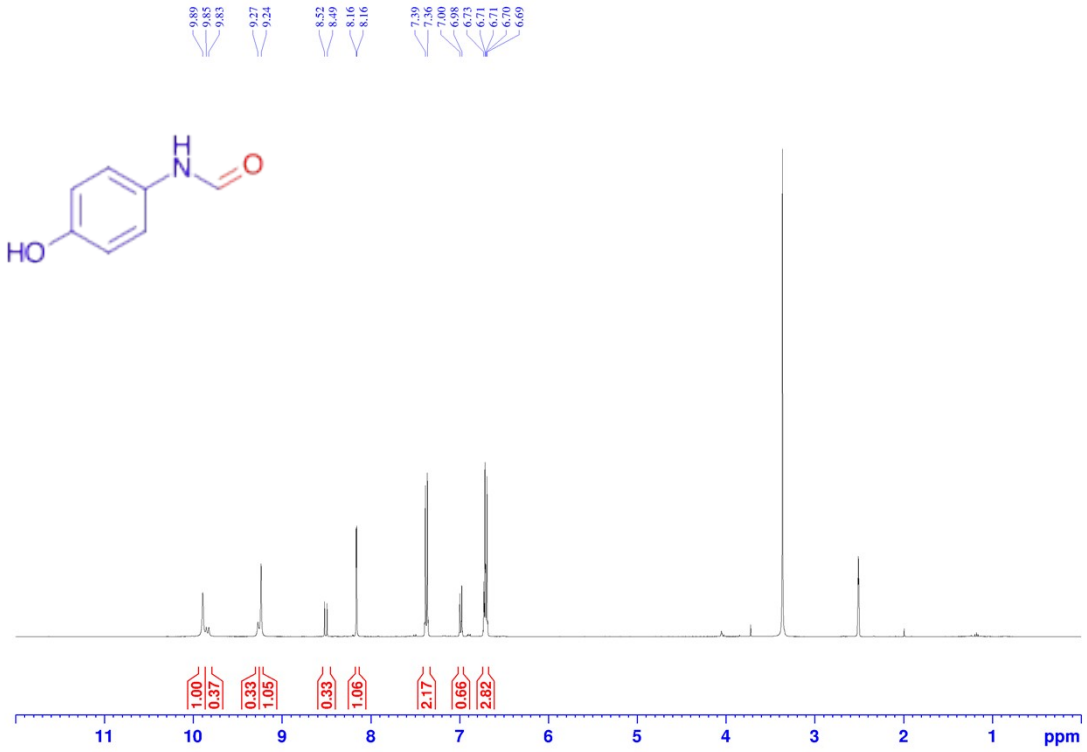
20
ppm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8.16
7.39
7.36
7.00
6.98
6.73
6.71
6.71
6.70
6.69
H
N
O
HO
1.00
0.37
0.33
1.05
0.33
1.06
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0.66
2.82
11
10
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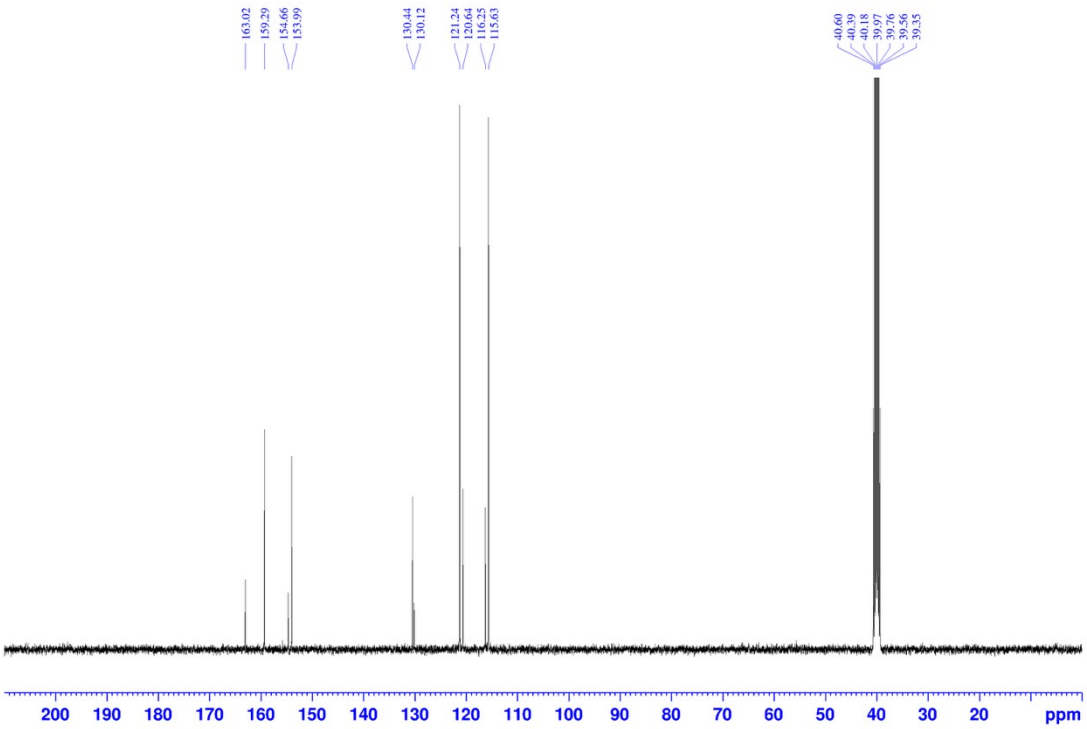
7
6
5
4
3
2
1
ppm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116.25
115.63
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40.18
39.97
39.76
39.56
39.35
200
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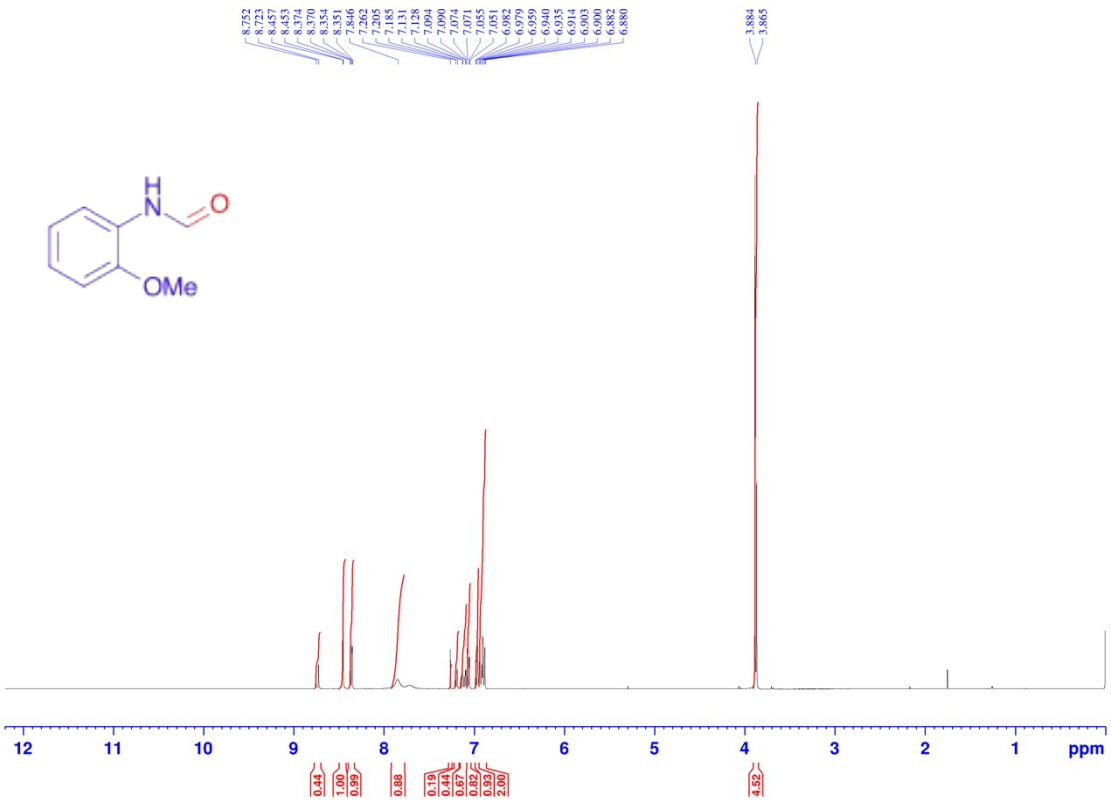
20
ppm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7.090
7.074
7.071
7.055
7.051
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6.979
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6.940
6.935
6.914
6.903
6.900
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6.880
3.884
3.865
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N
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6
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ppm
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0.44
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0.82
0.93
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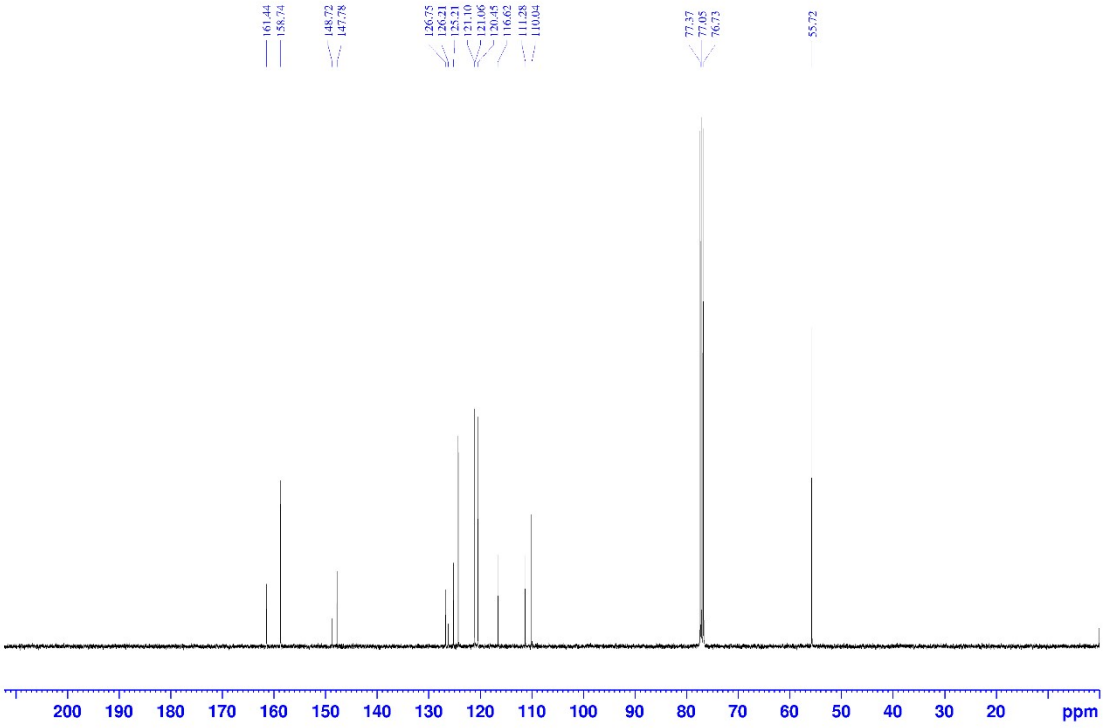
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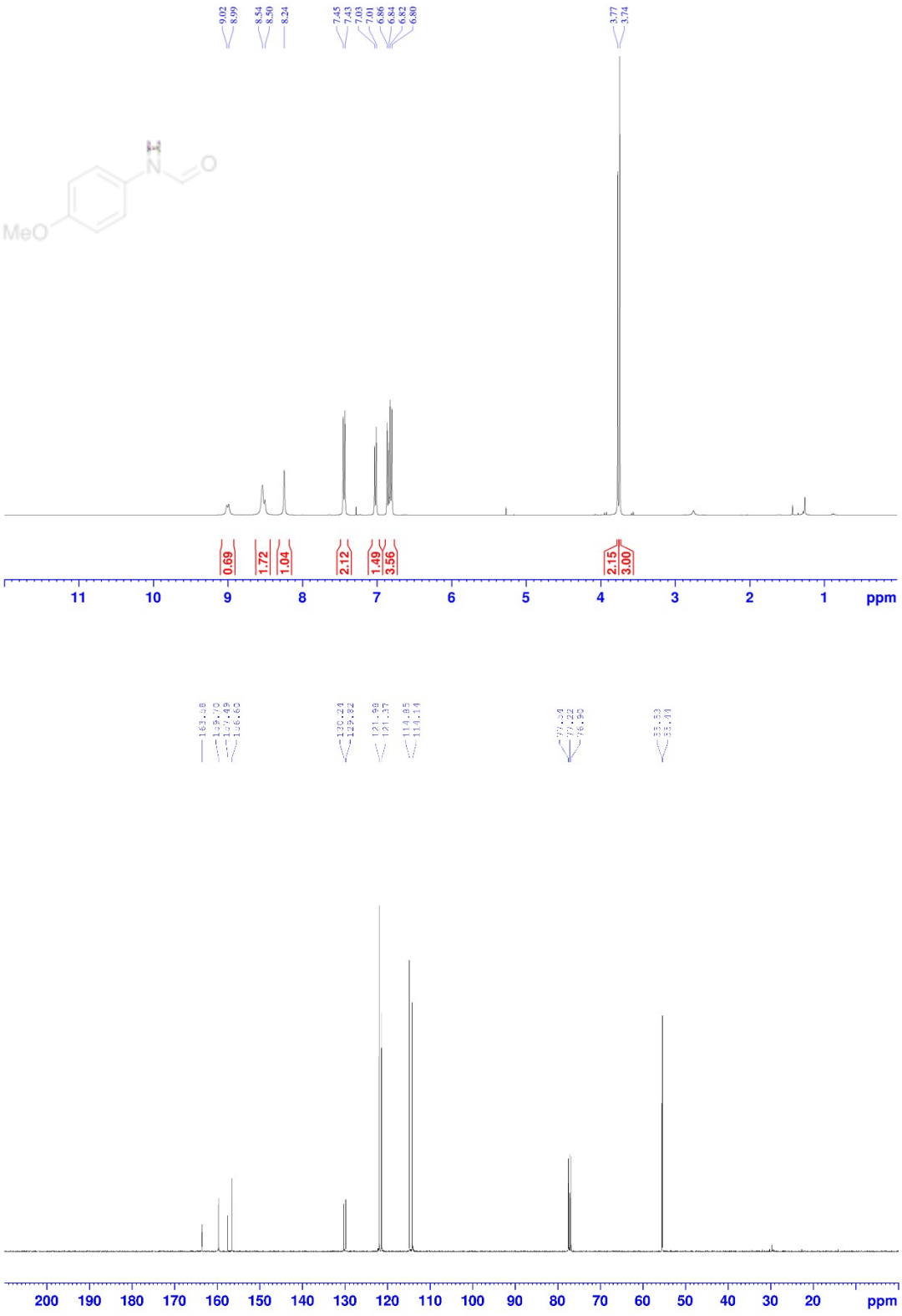
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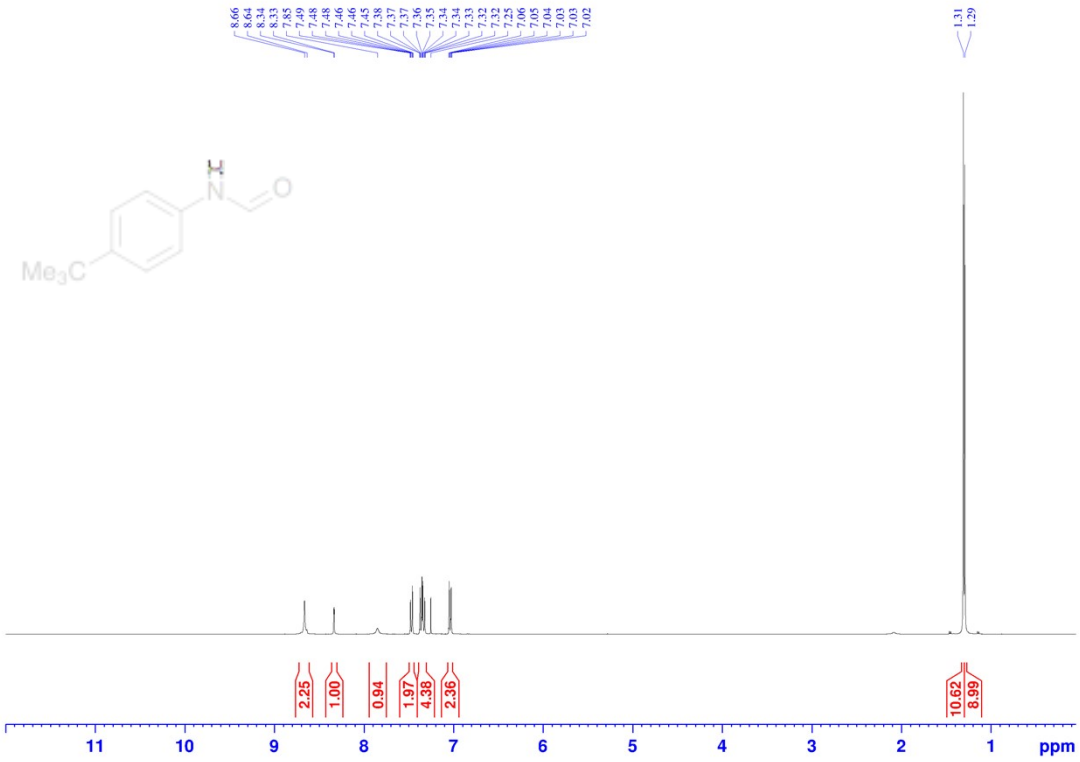
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7.04
7.03
7.03
7.02
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1.29
Me3C
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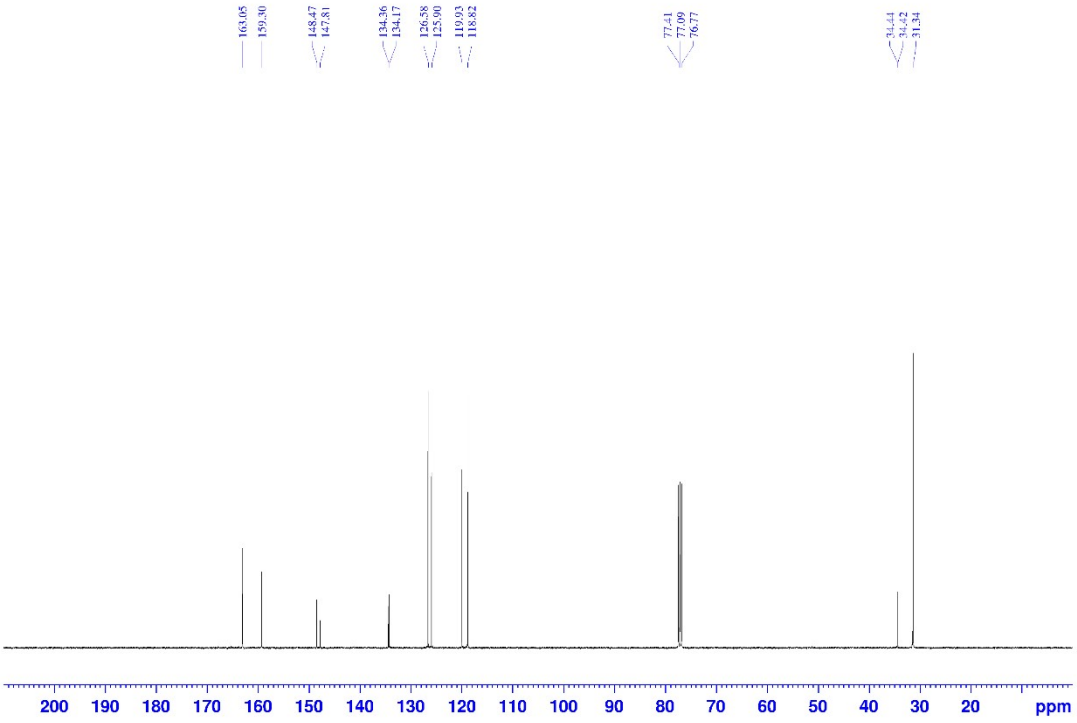
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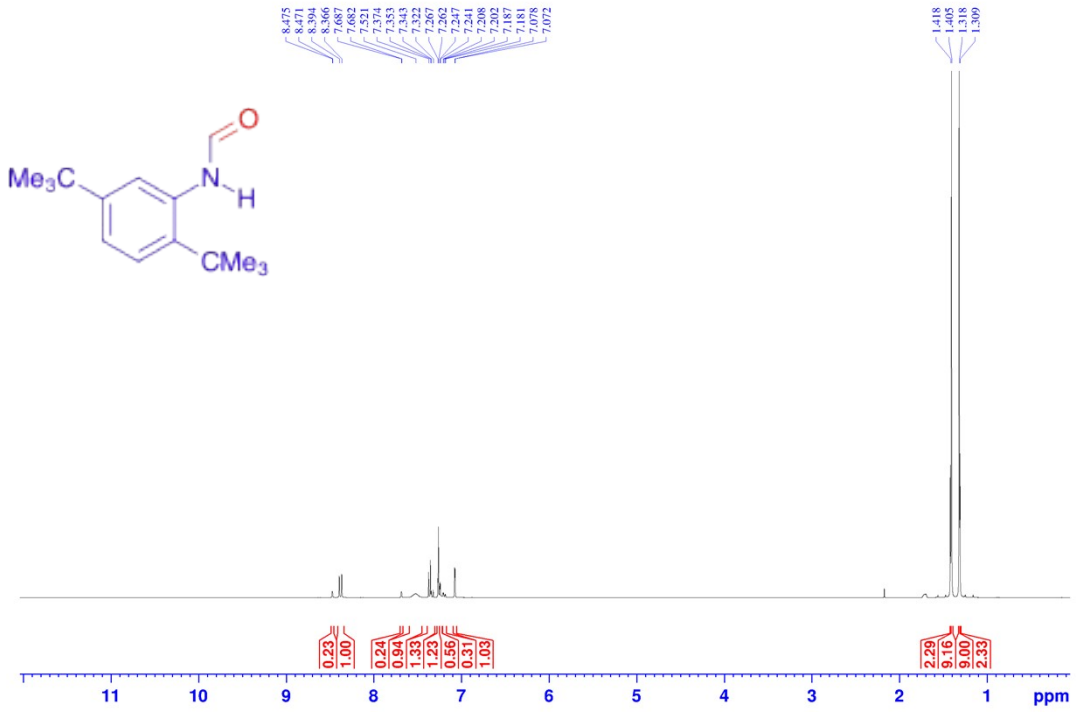
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7.202
7.187
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1.405
1.318
1.309
O
N
H
Me3C
CMe3
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0.24
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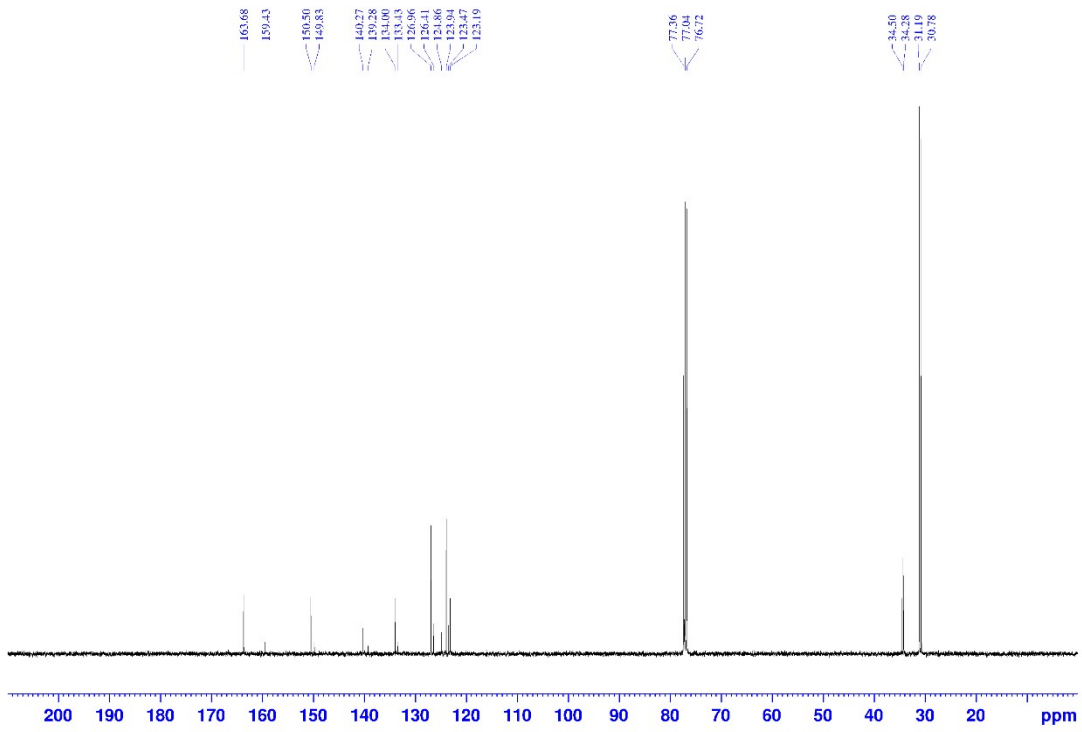
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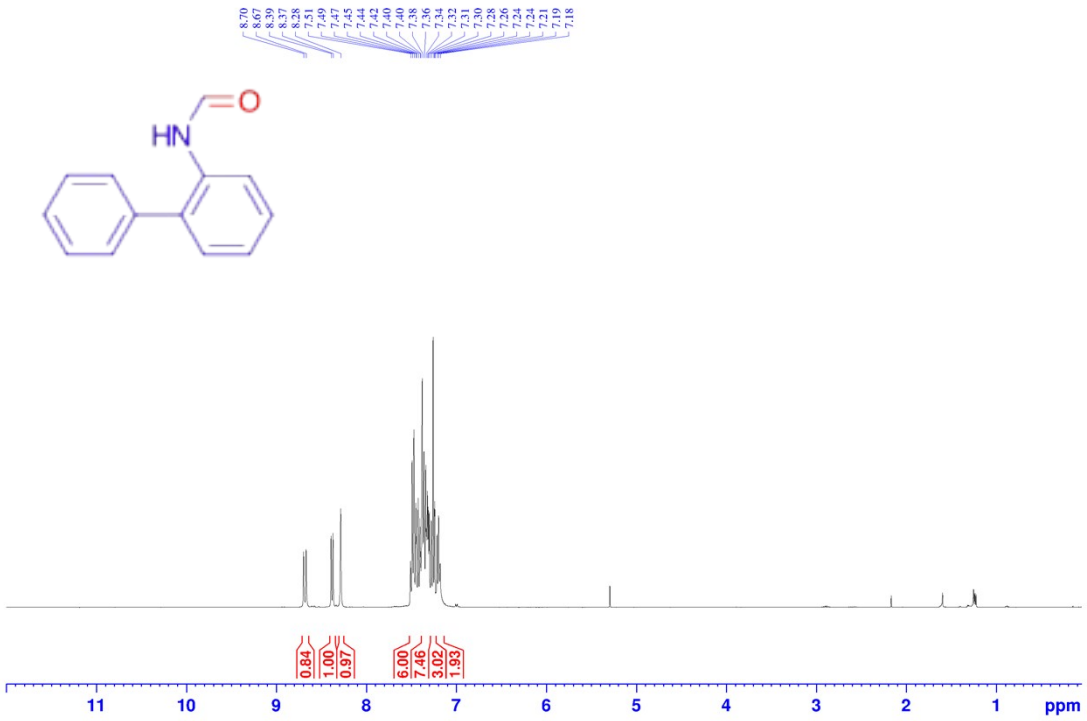
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7.36
7.34
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7.31
7.30
7.28
7.26
7.24
7.24
7.21
7.19
7.18
O
HN
0.84
1.00
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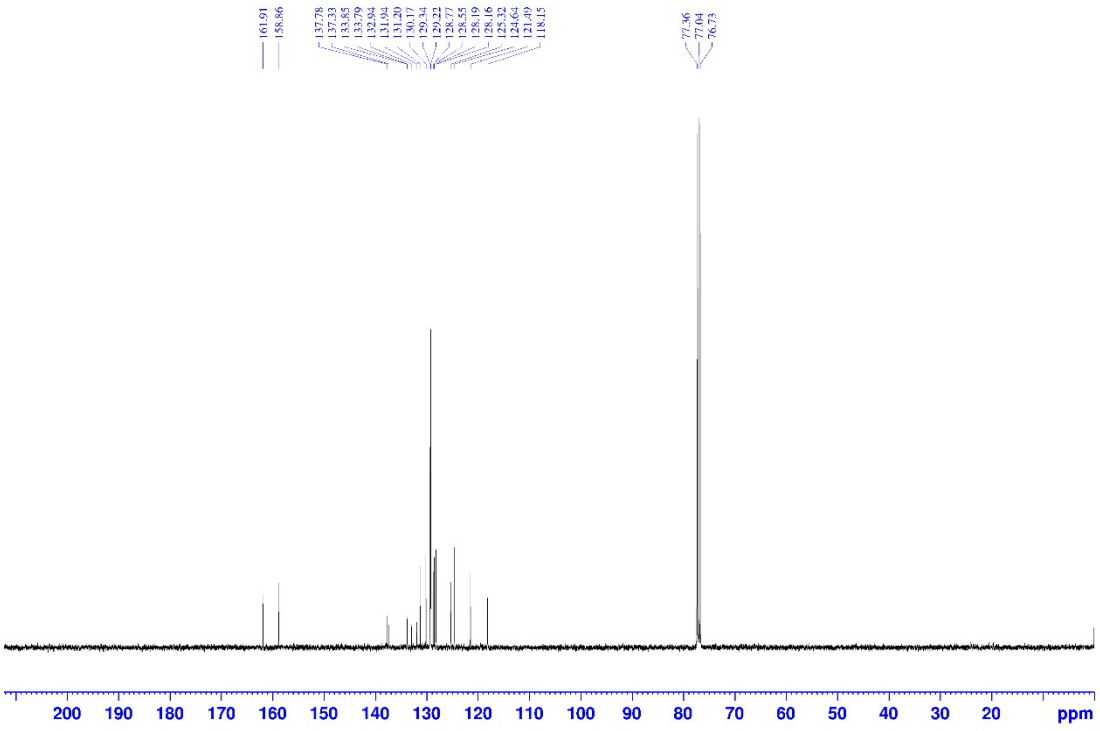
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128.19
128.16
125.32
124.64
121.49
118.15
77.36
77.04
76.73
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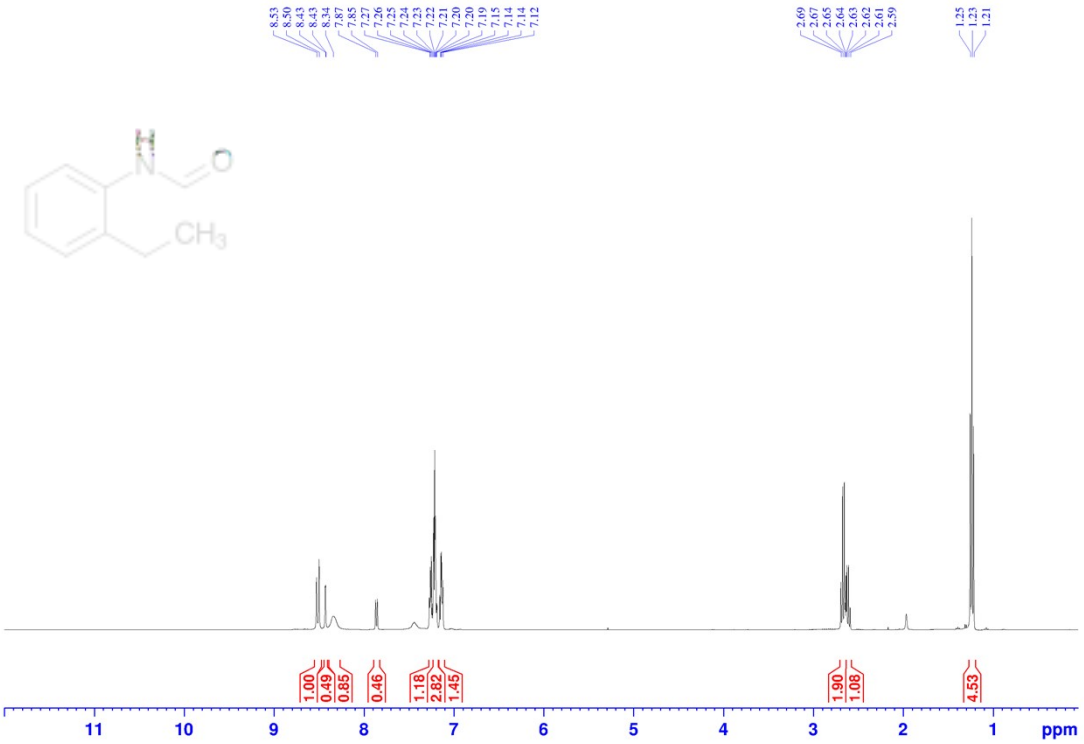
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7.20
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7.15
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7.14
7.12
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2.65
2.64
2.63
2.62
2.61
2.59
1.25
1.23
1.21
H
N
O
CH3
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0.85
0.46
1.18
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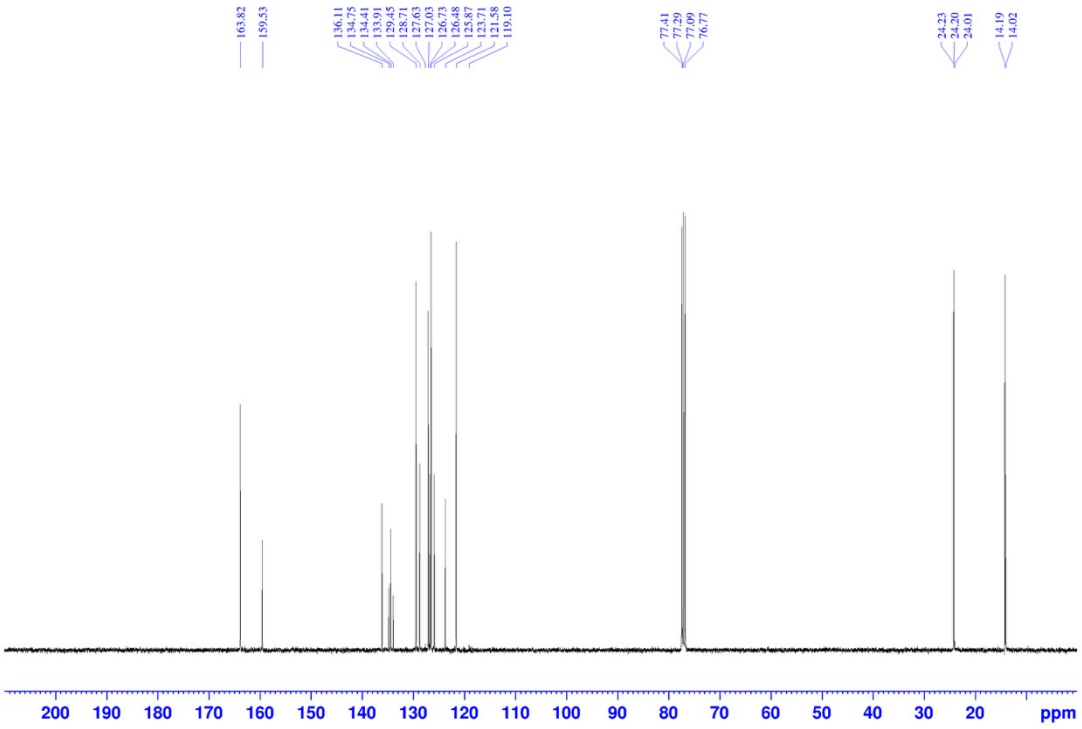
ppm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77.29
77.09
76.77
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24.20
24.01
14.19
14.02
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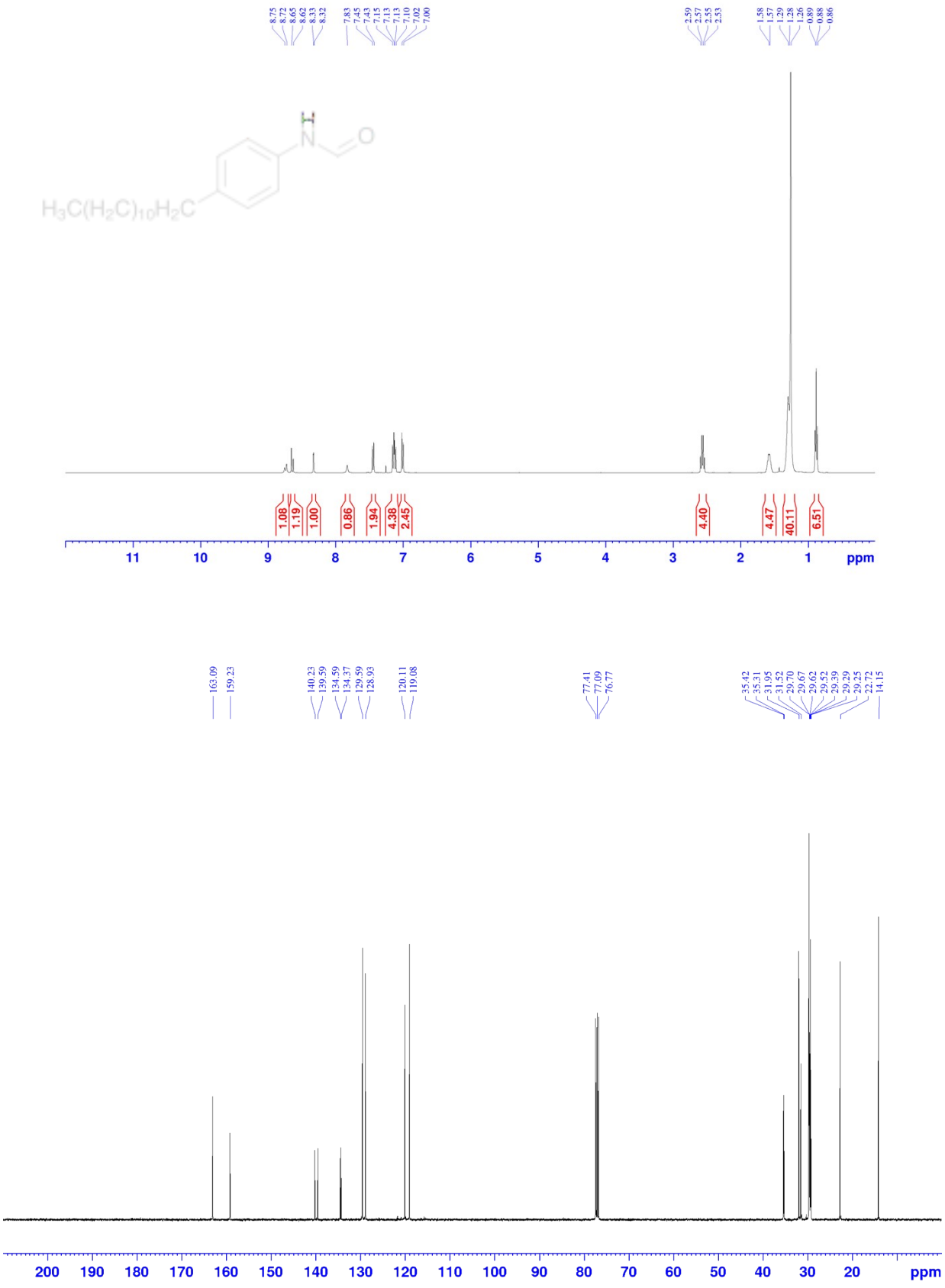
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2.55
2.53
1.58
1.57
1.29
1.28
1.26
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0.88
0.86
H3C(H2C)10H2C
1.08
1.19
1.00
0.86
1.94
4.38
2.45
4.40
4.47
40.11
6.51
11 10 9 8 7 6 5 4 3 2 1 ppm
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129.59
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119.08
77.41
77.09
76.77
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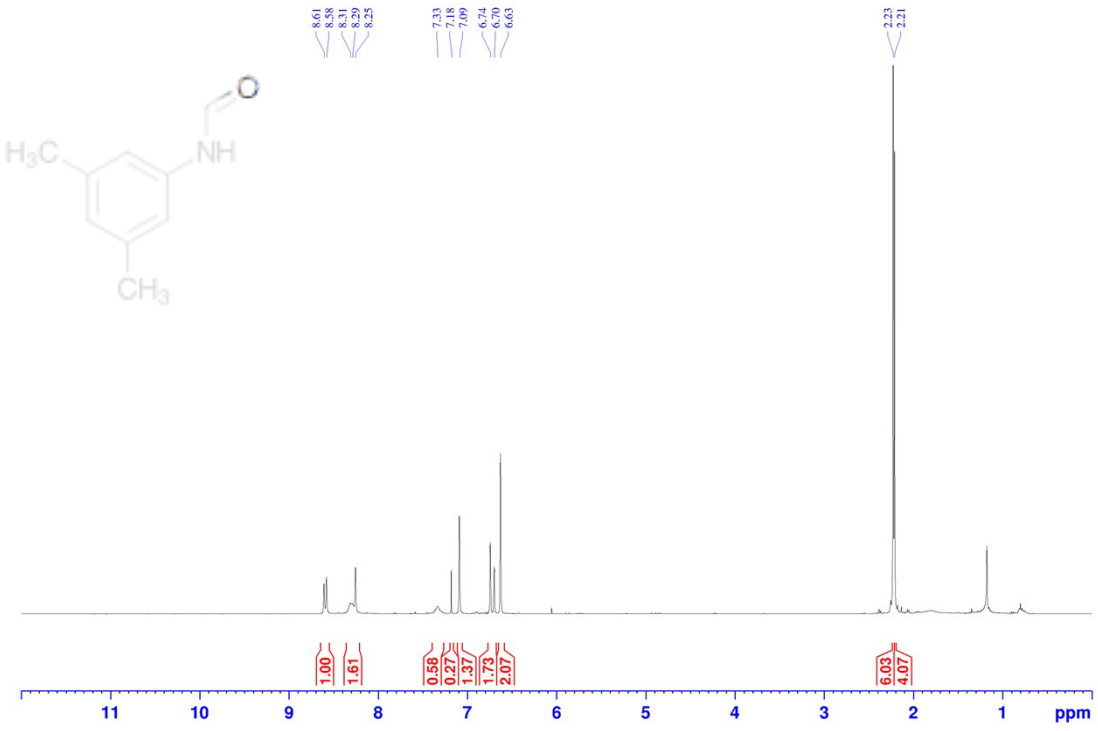
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O
NH
H3C
CH3
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0.58
0.27
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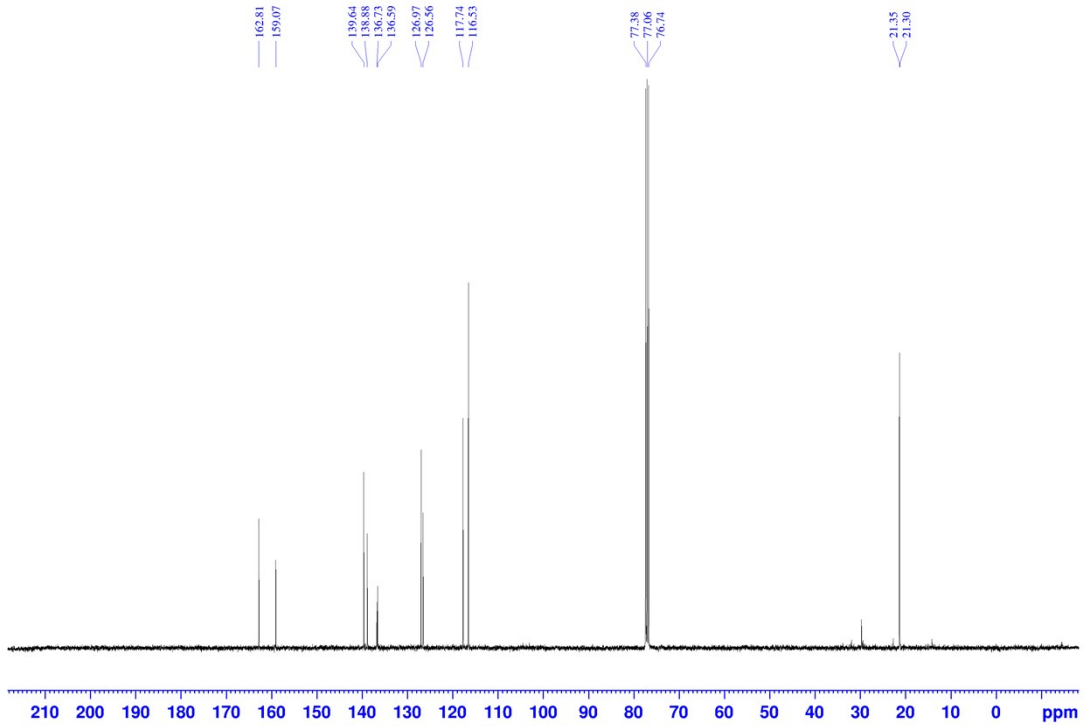
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21.30
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200
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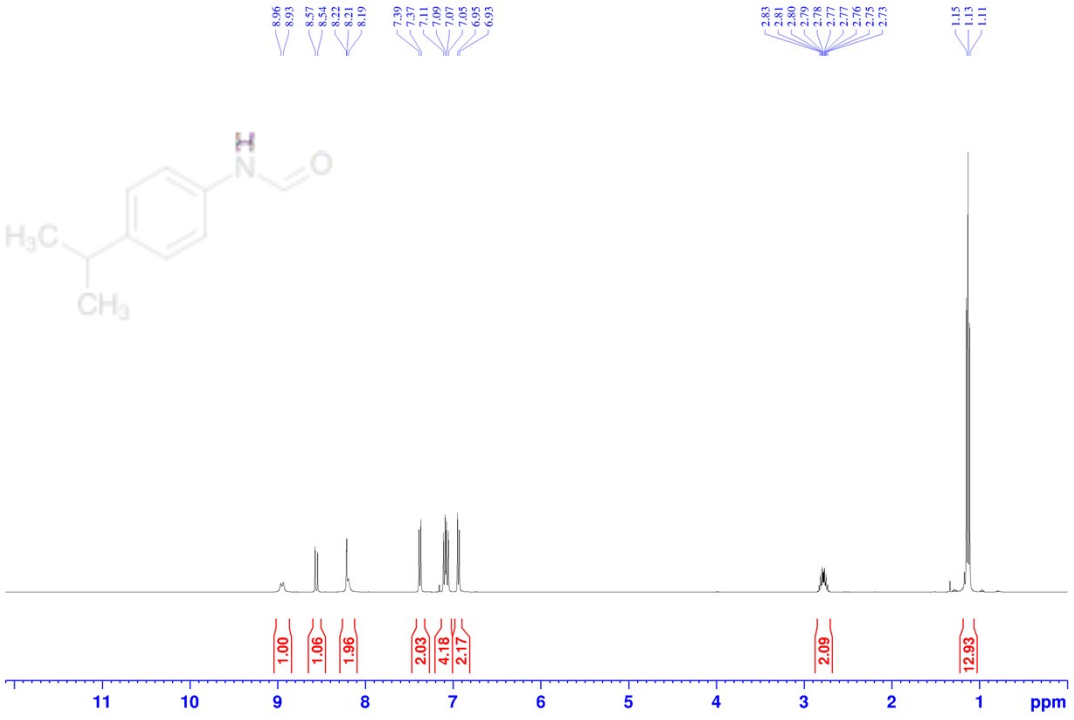
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6.93
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2.80
2.79
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2.77
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2.76
2.75
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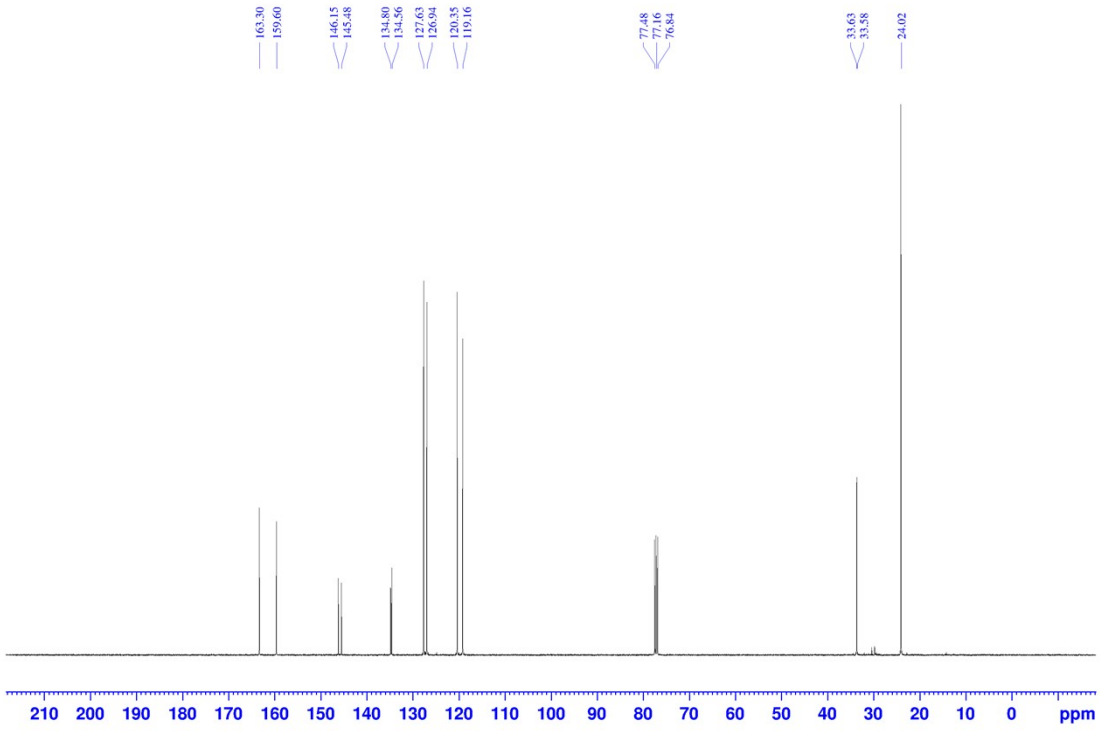
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76.84
33.63
33.58
24.02
210
200
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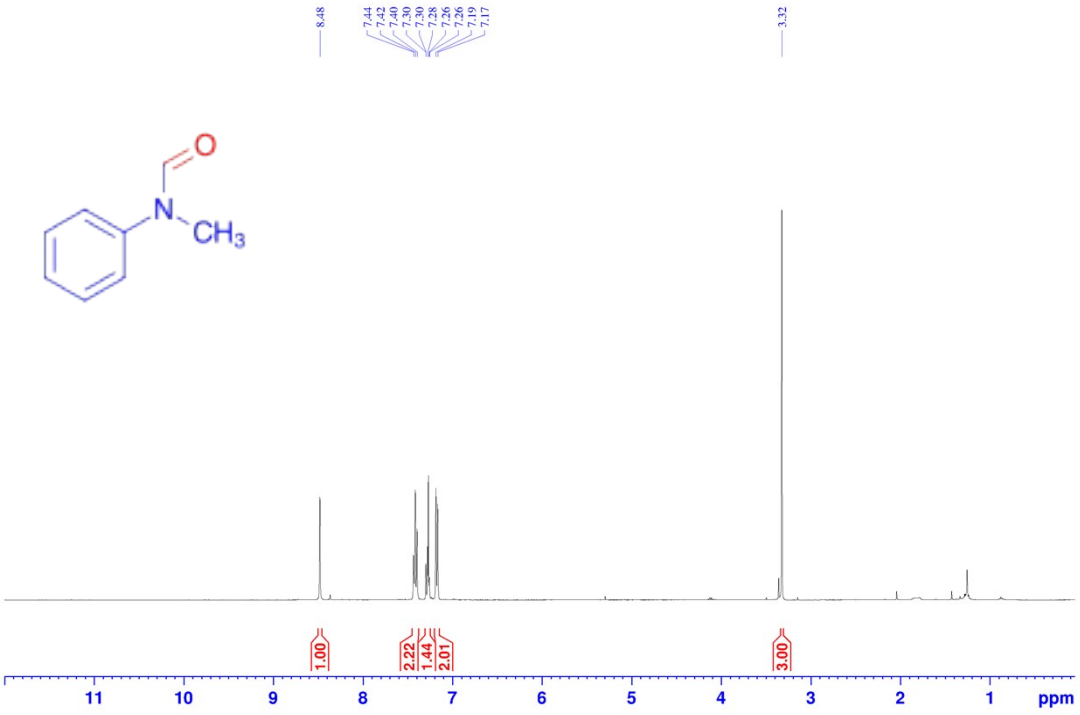
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N
CH3
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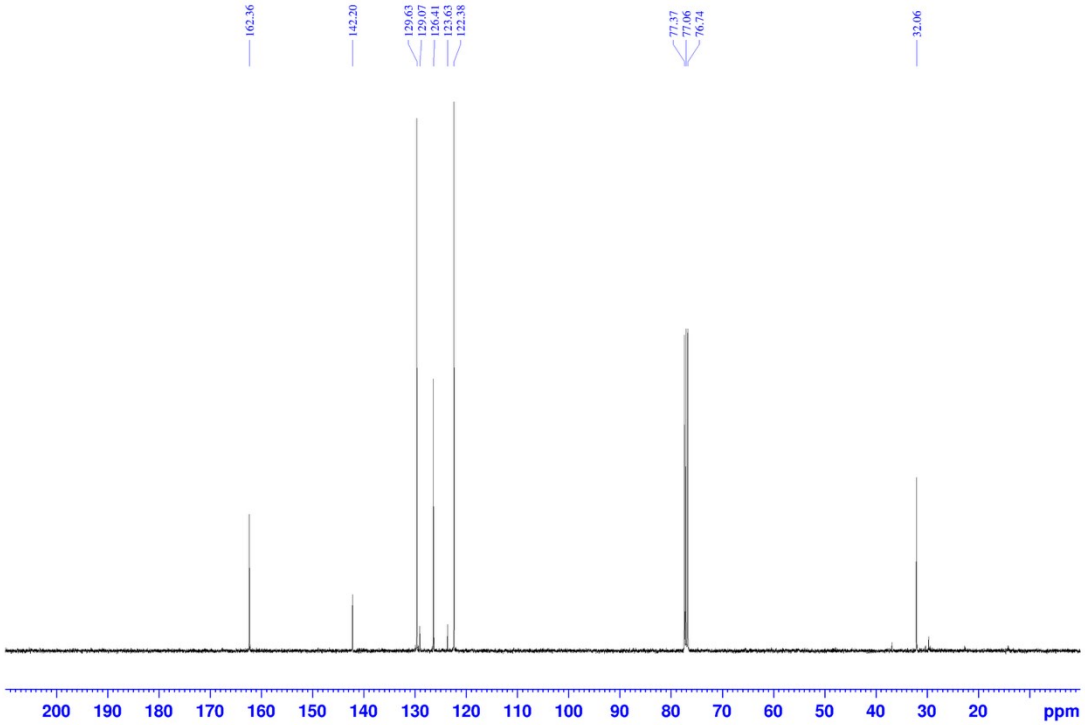
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20
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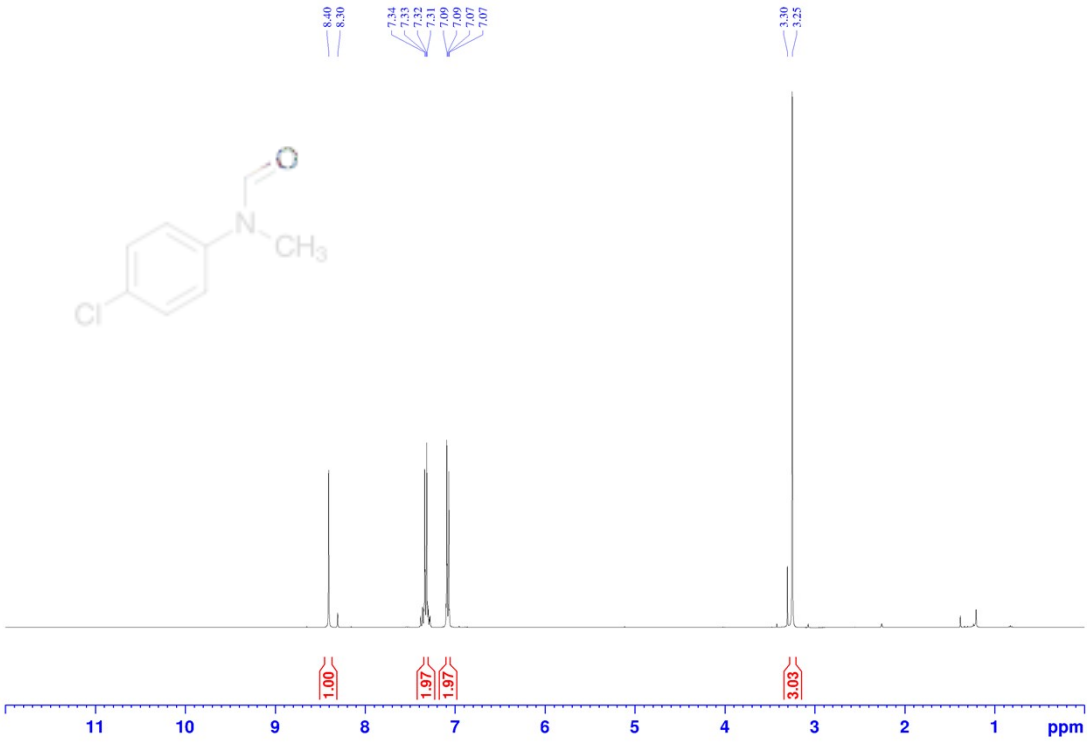
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7.09
7.07
7.07
3.30
3.25
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N
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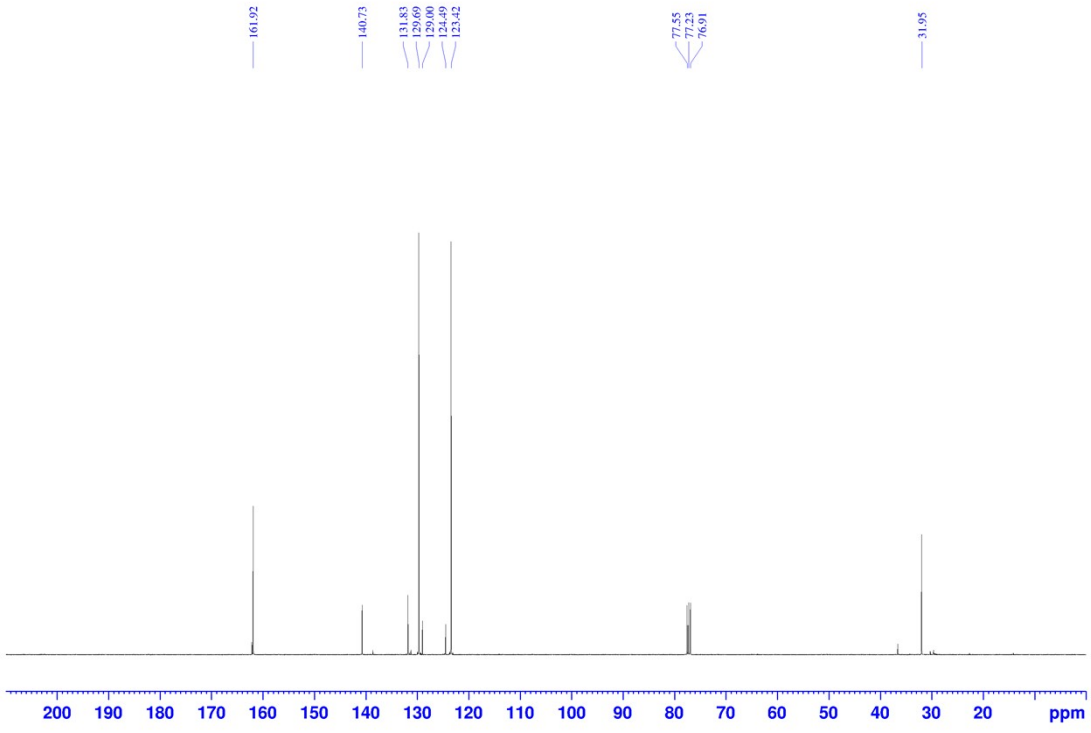
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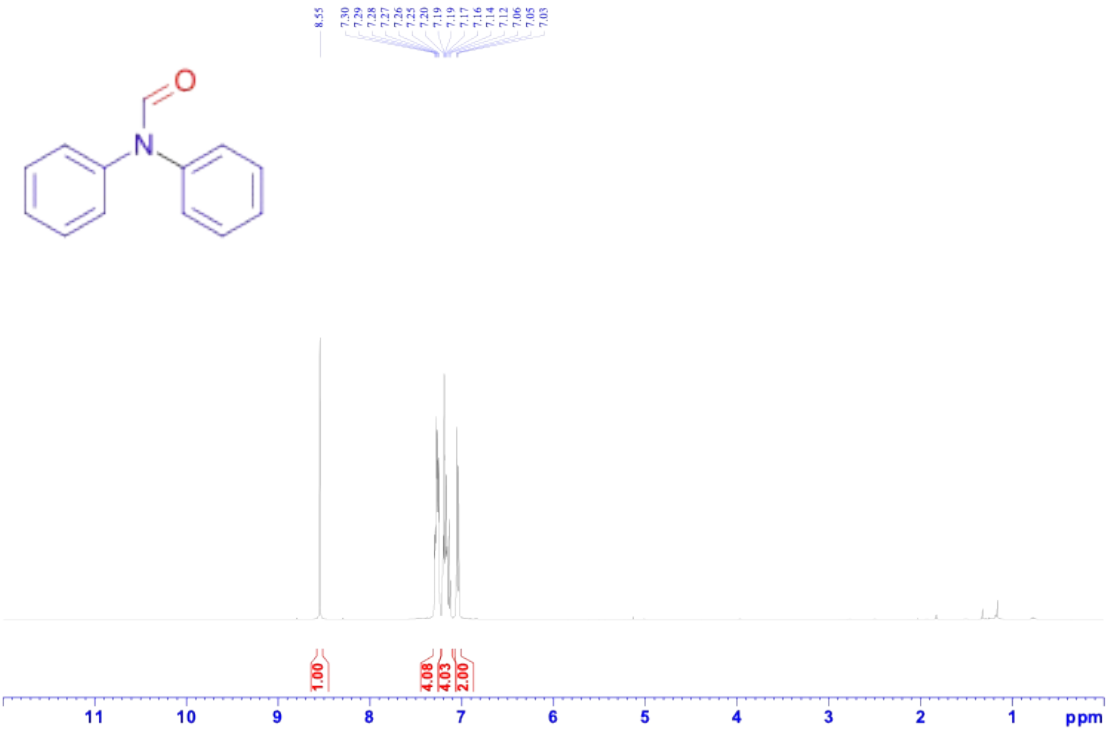
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7.05
7.03
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7
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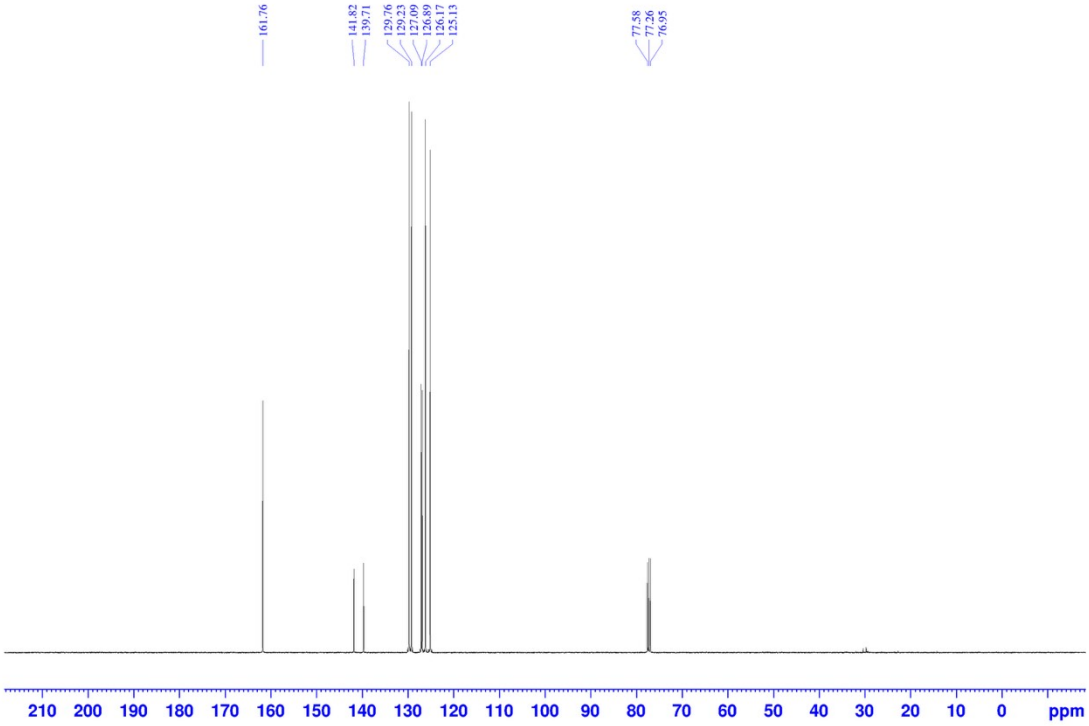
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200
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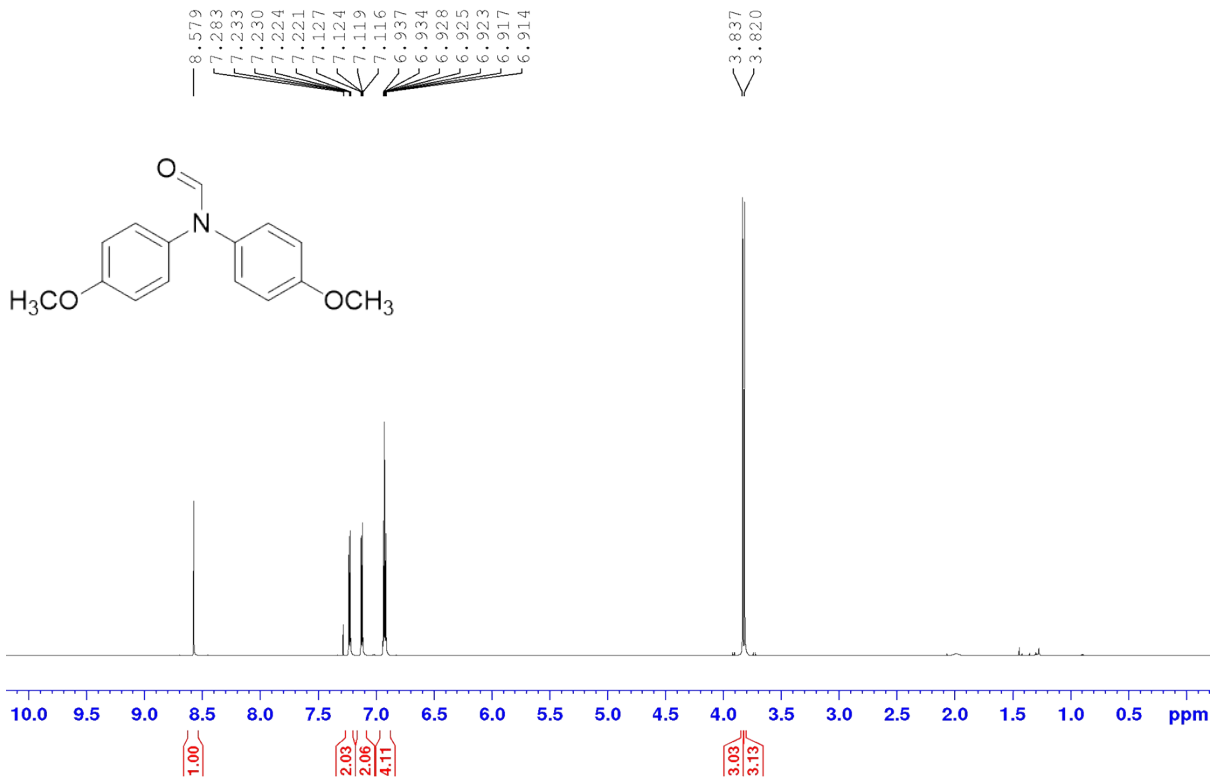
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6.925
6.923
6.917
6.914
3.837
3.820
O
N
H3CO
OCH3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
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2.03
2.06
4.11
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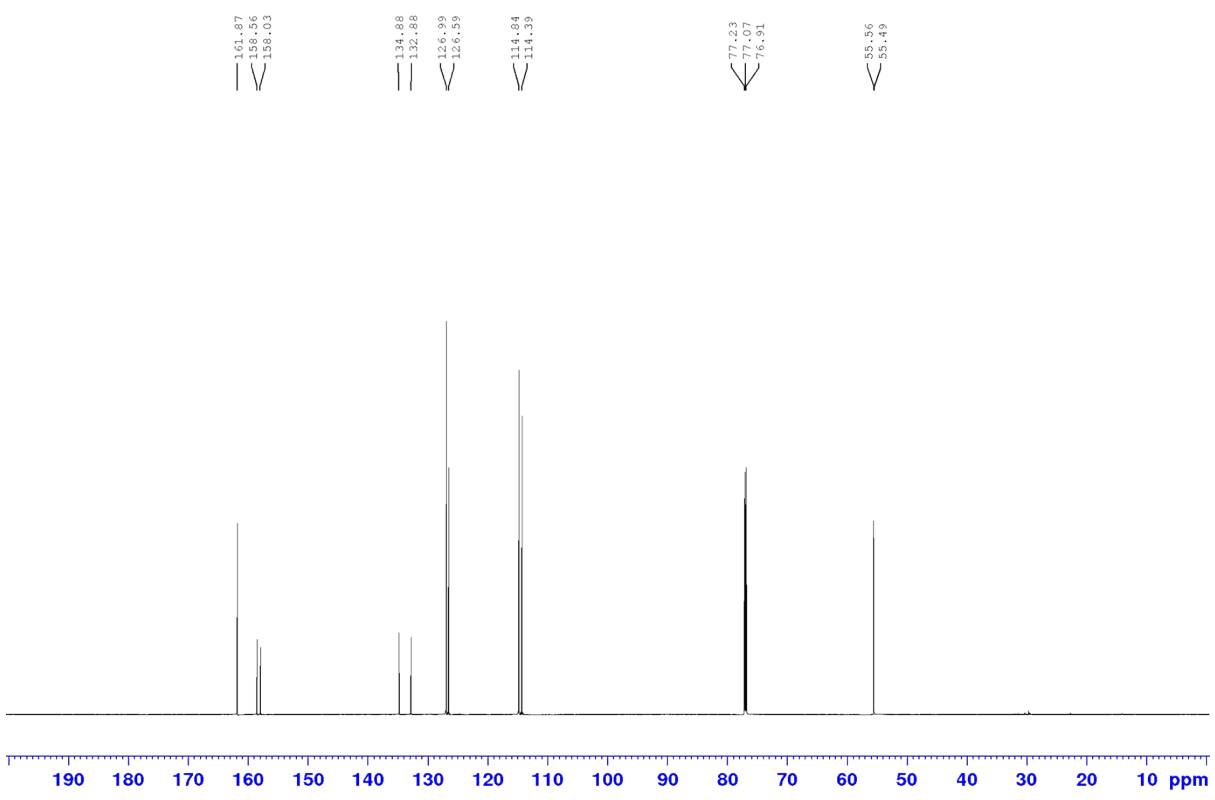
3.13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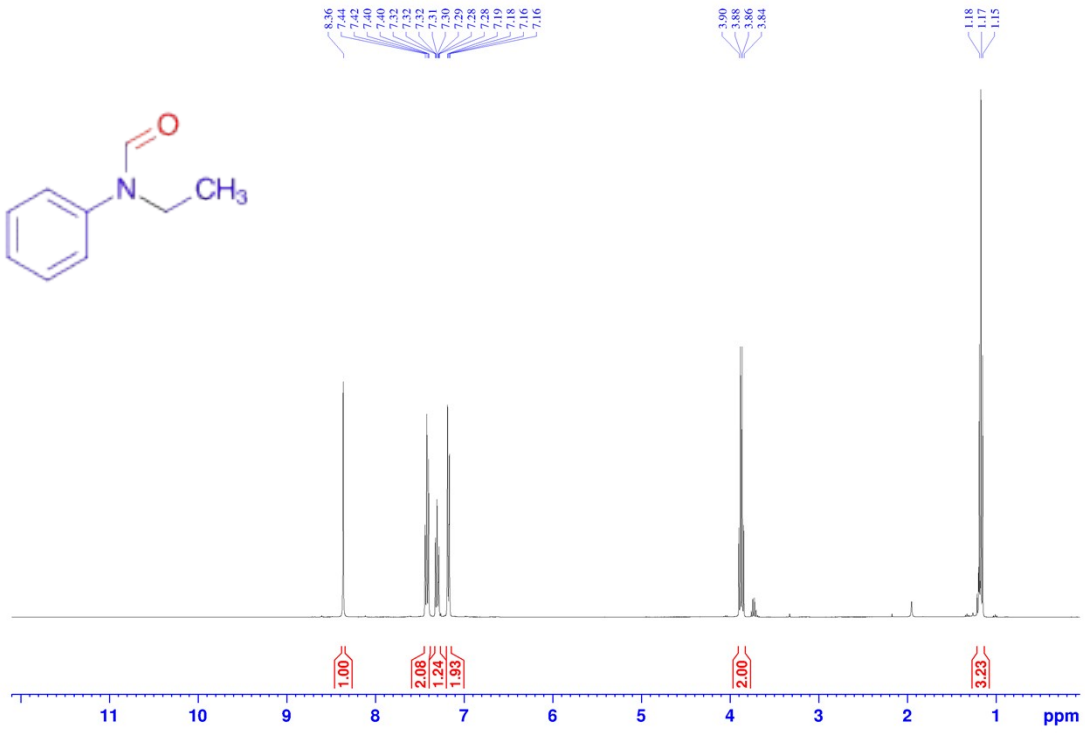
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7.16
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3.88
3.86
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1.17
1.15
O
N
CH3
1.00
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7
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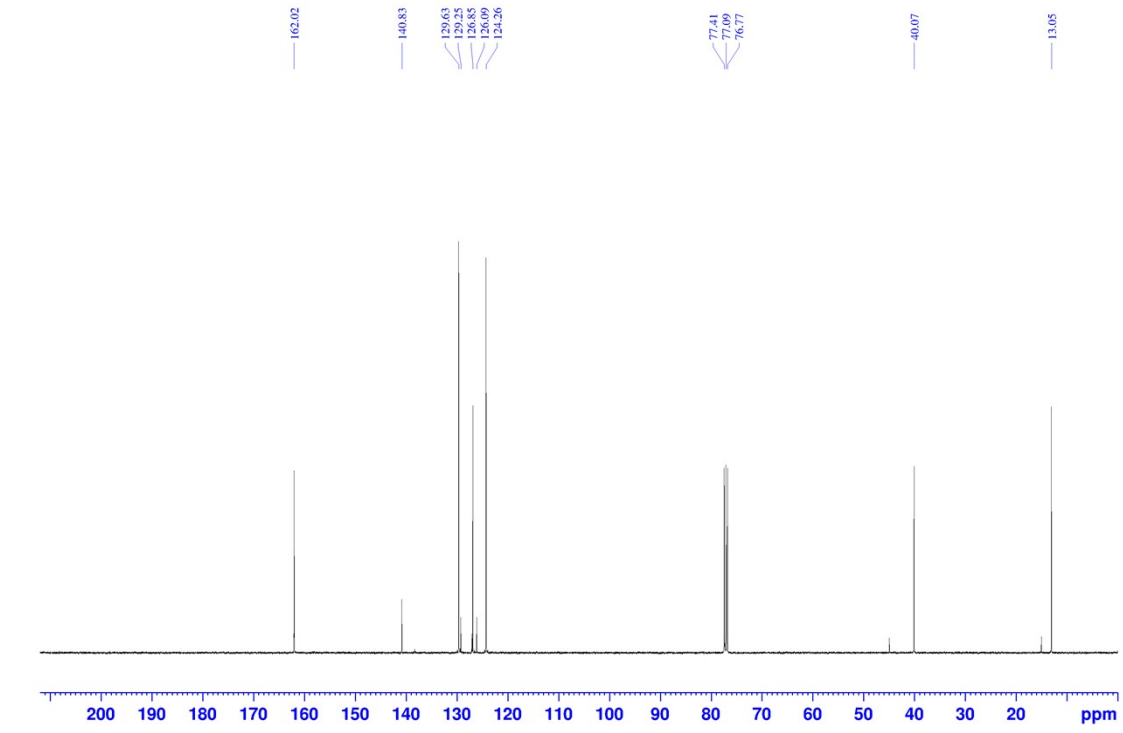
ppm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20
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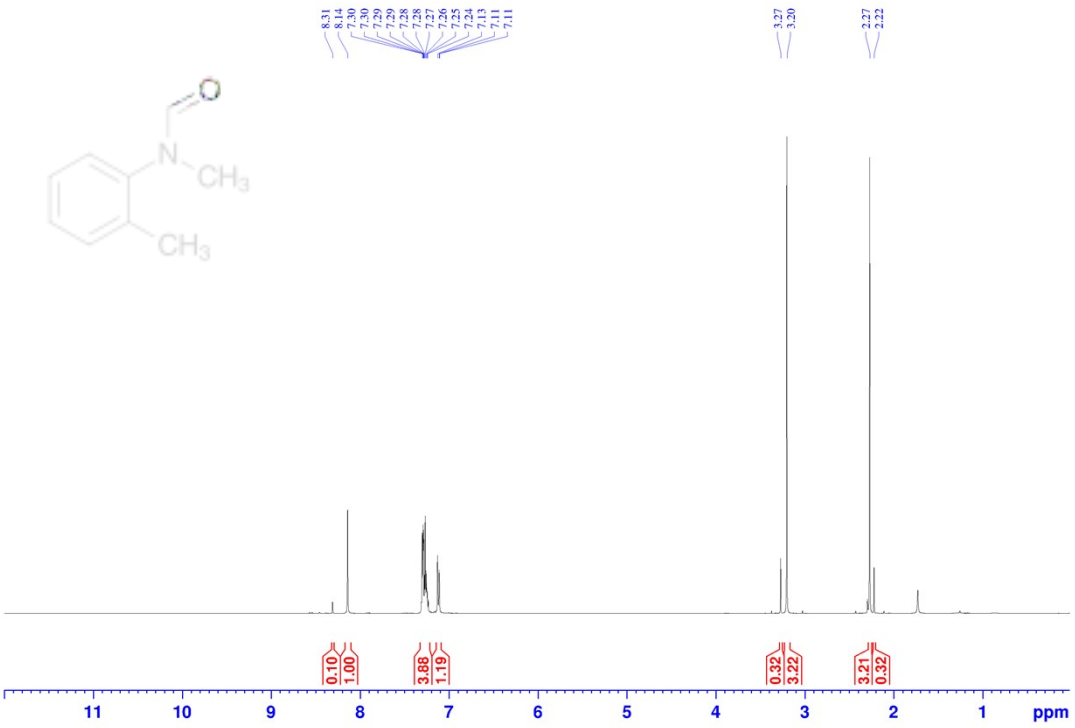
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7.11
7.11
3.27
3.20
2.27
2.22
O
N
CH3
CH3
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1.19
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3.22
3.21
0.32
11
10
9
8
7
6
5
4
3
2
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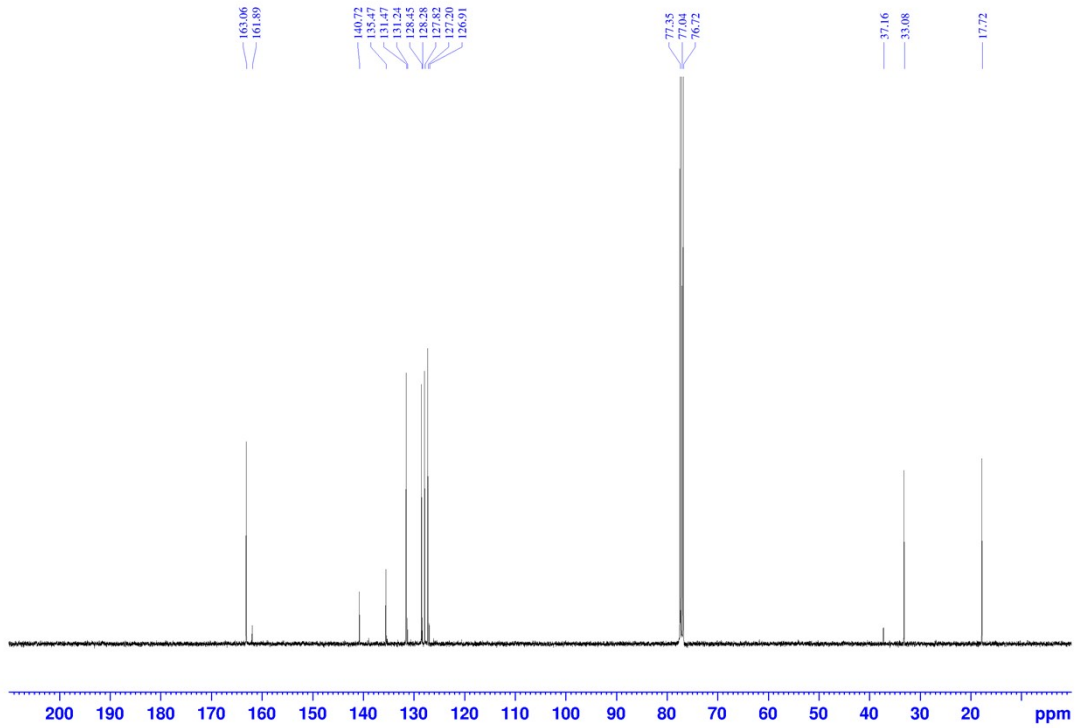
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76.72
37.16
33.08
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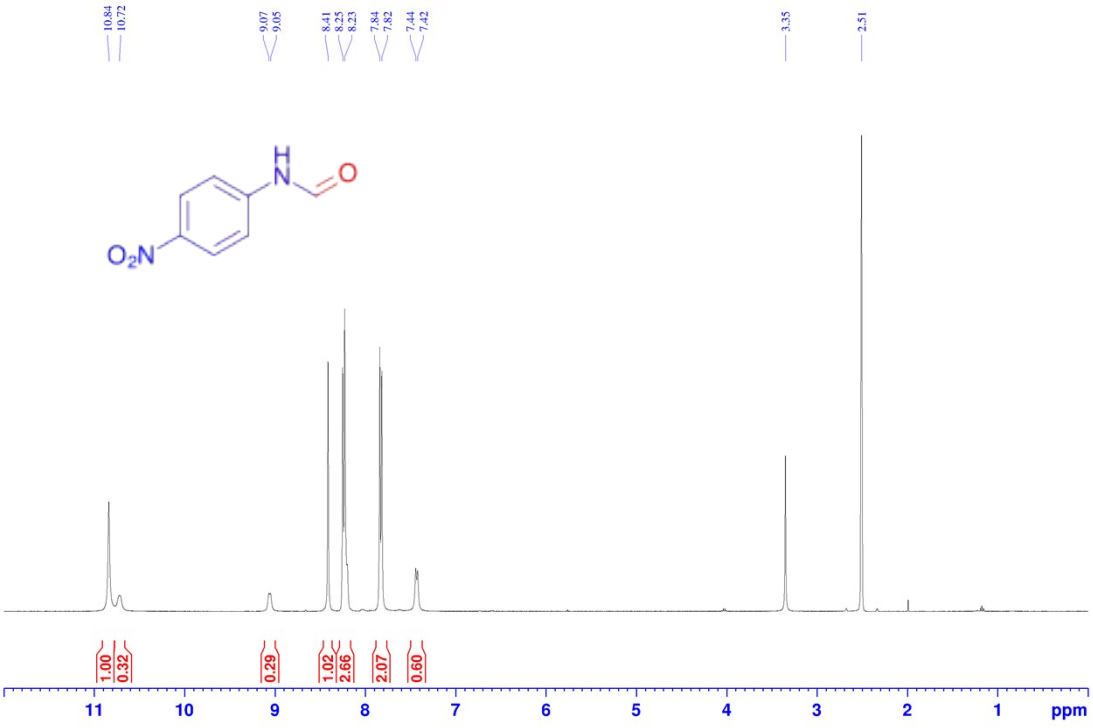
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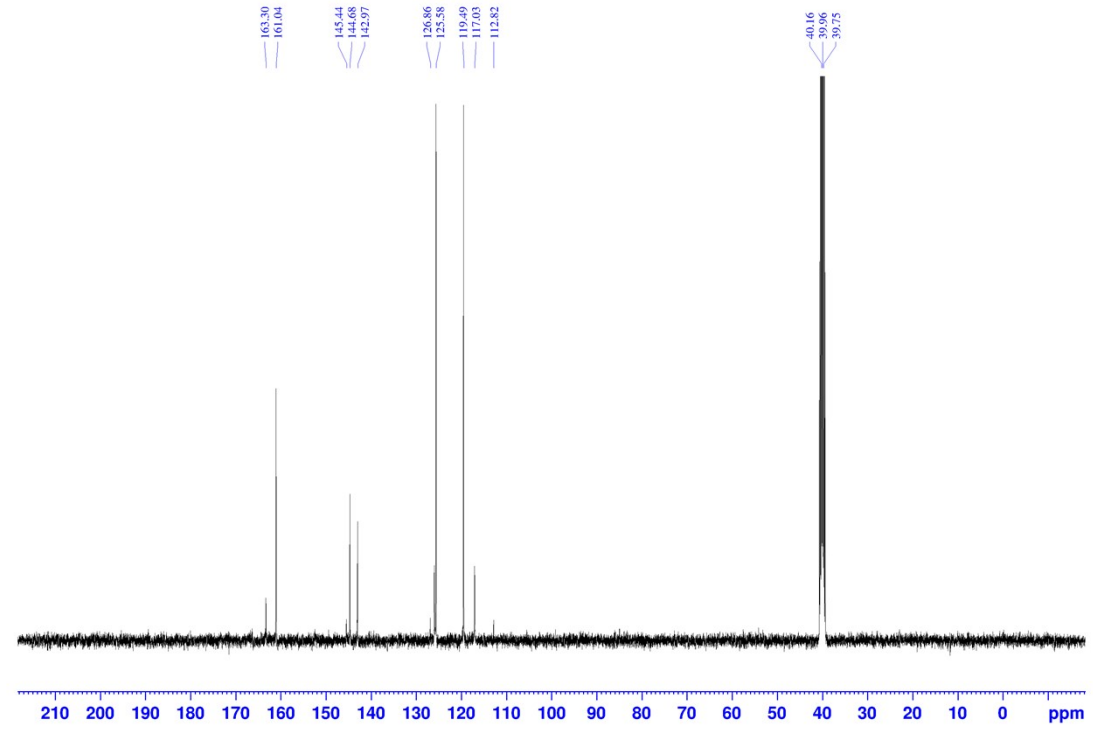
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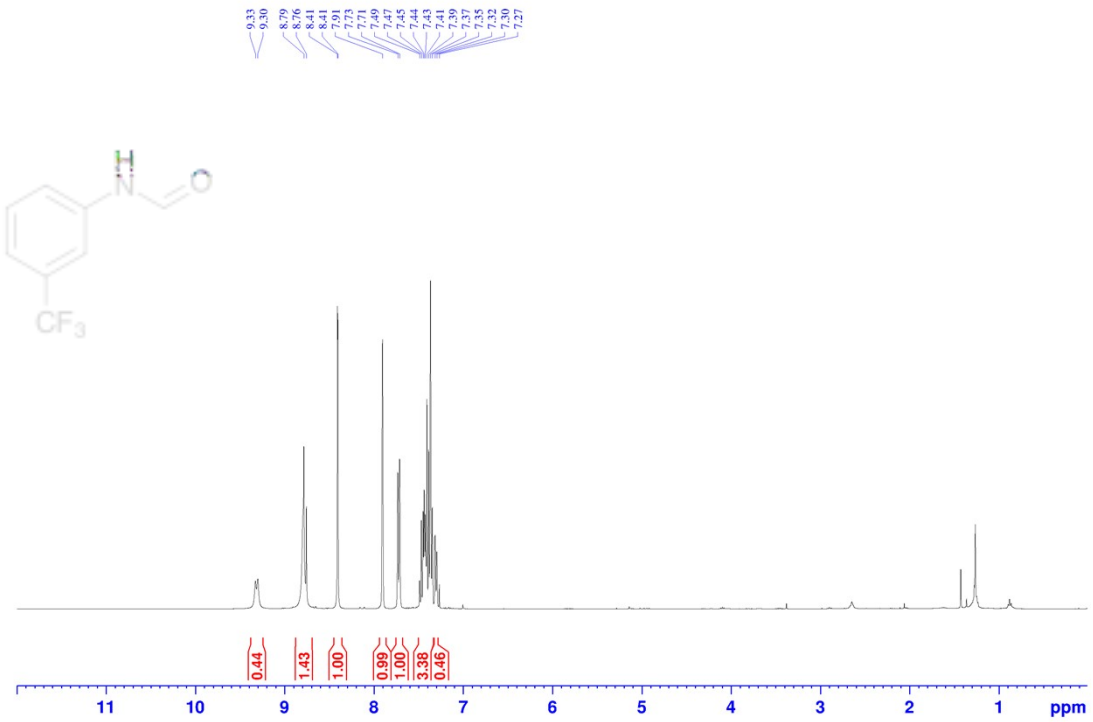
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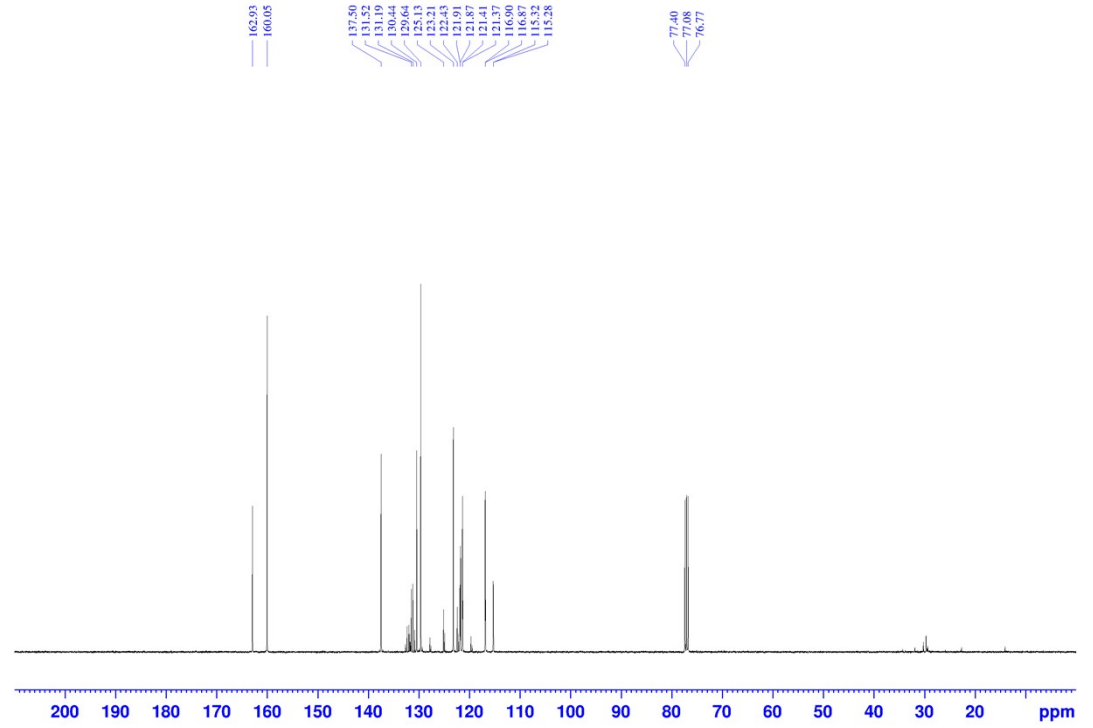
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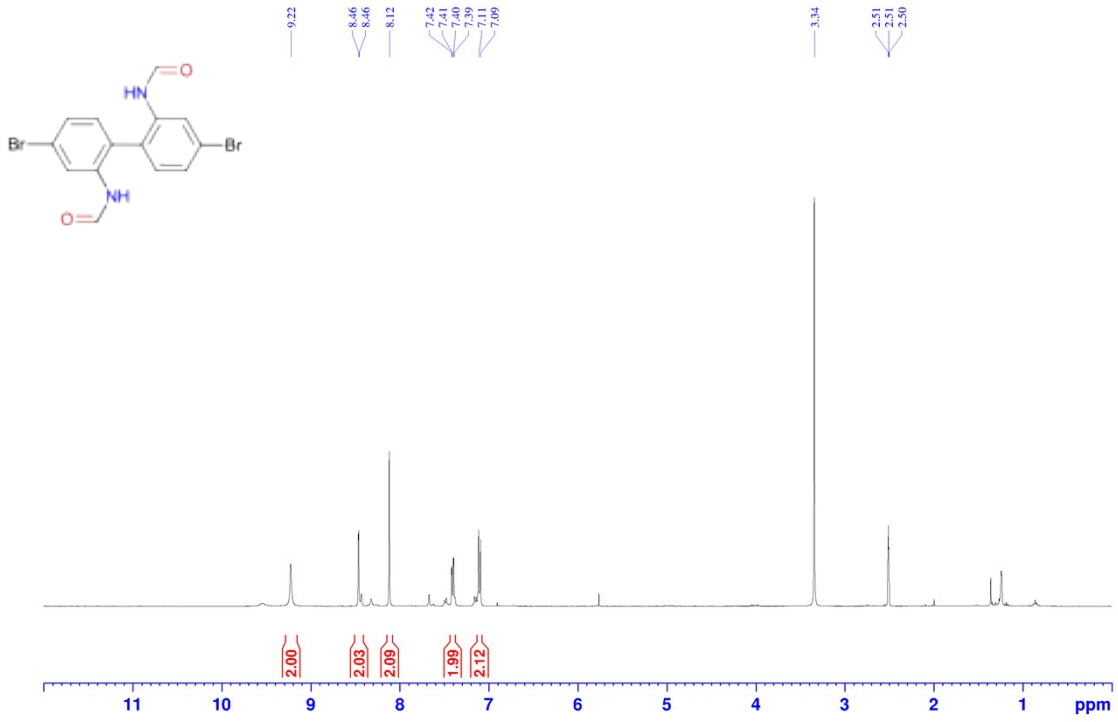
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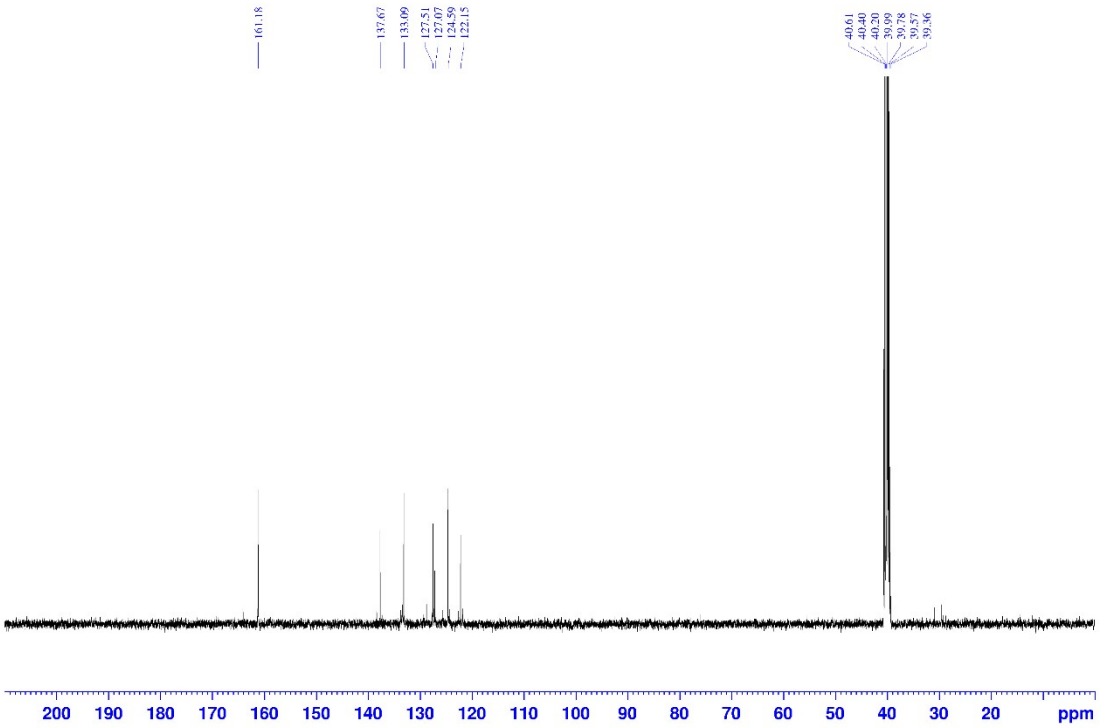
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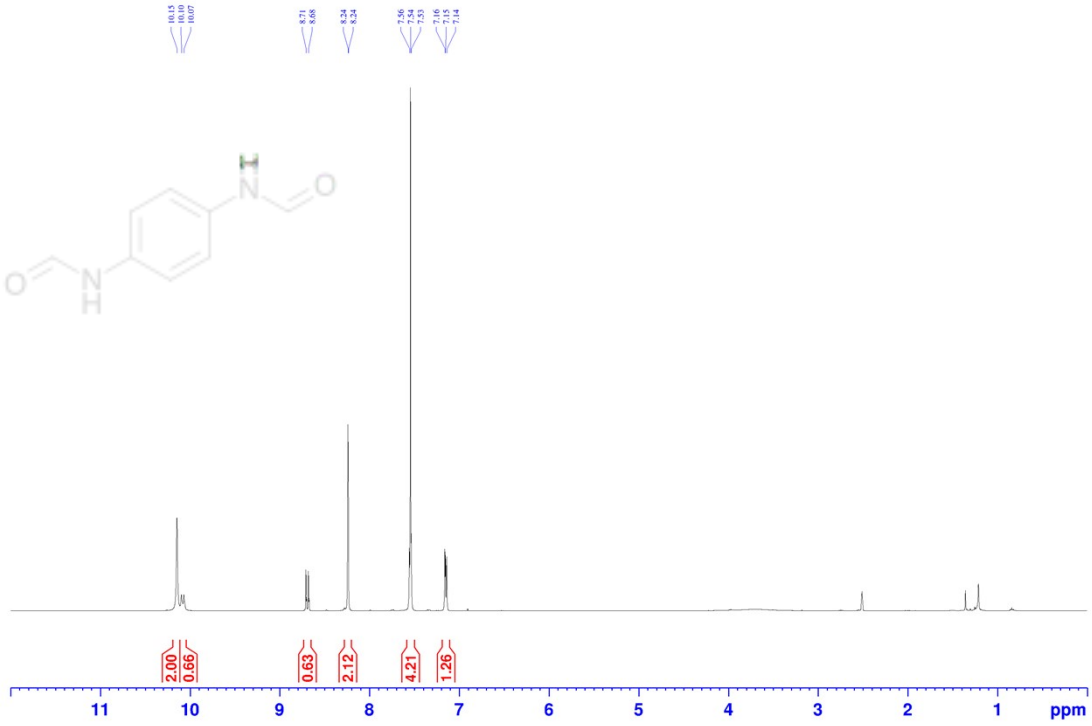
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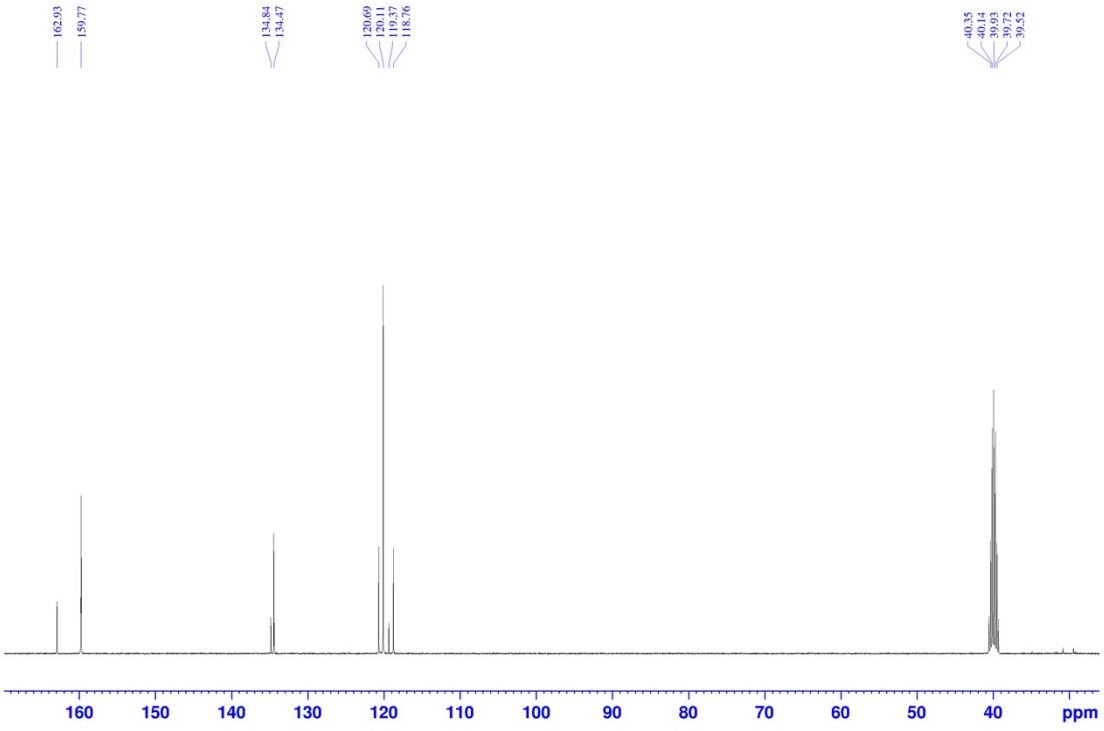
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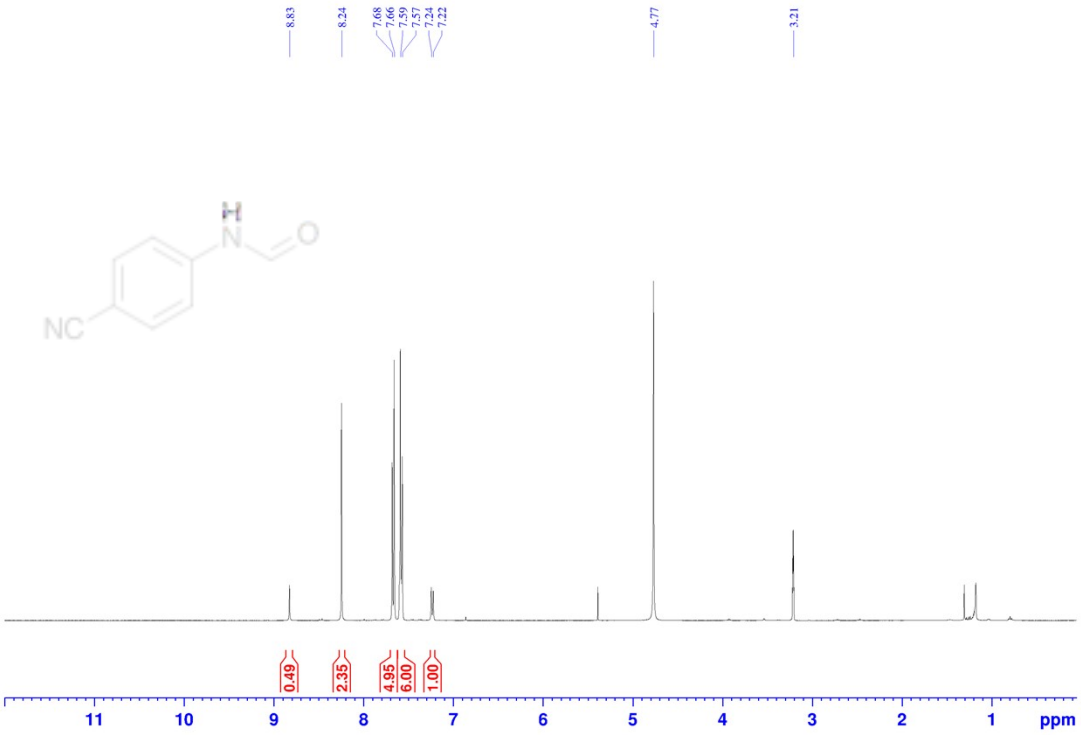
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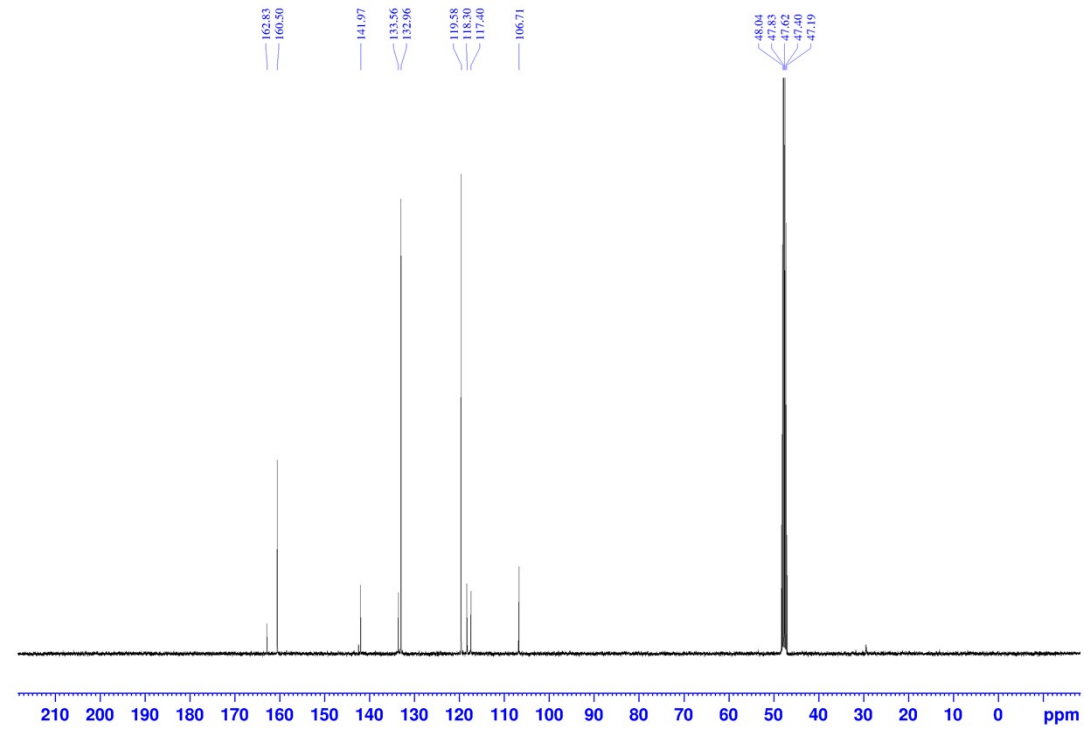
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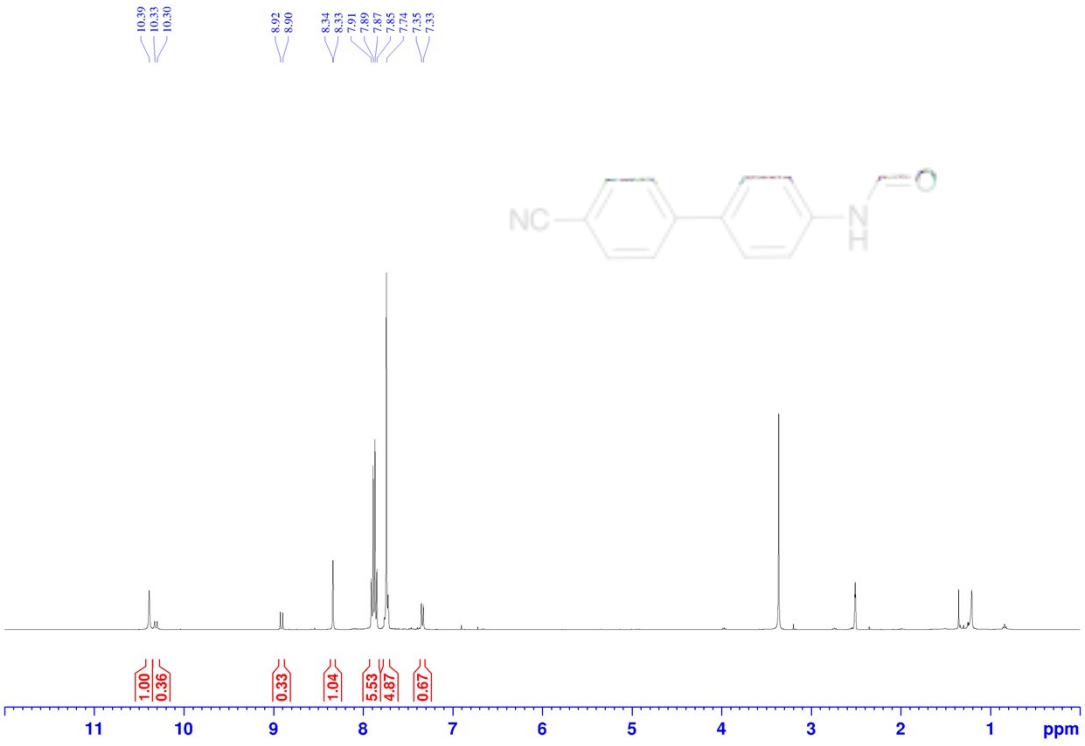
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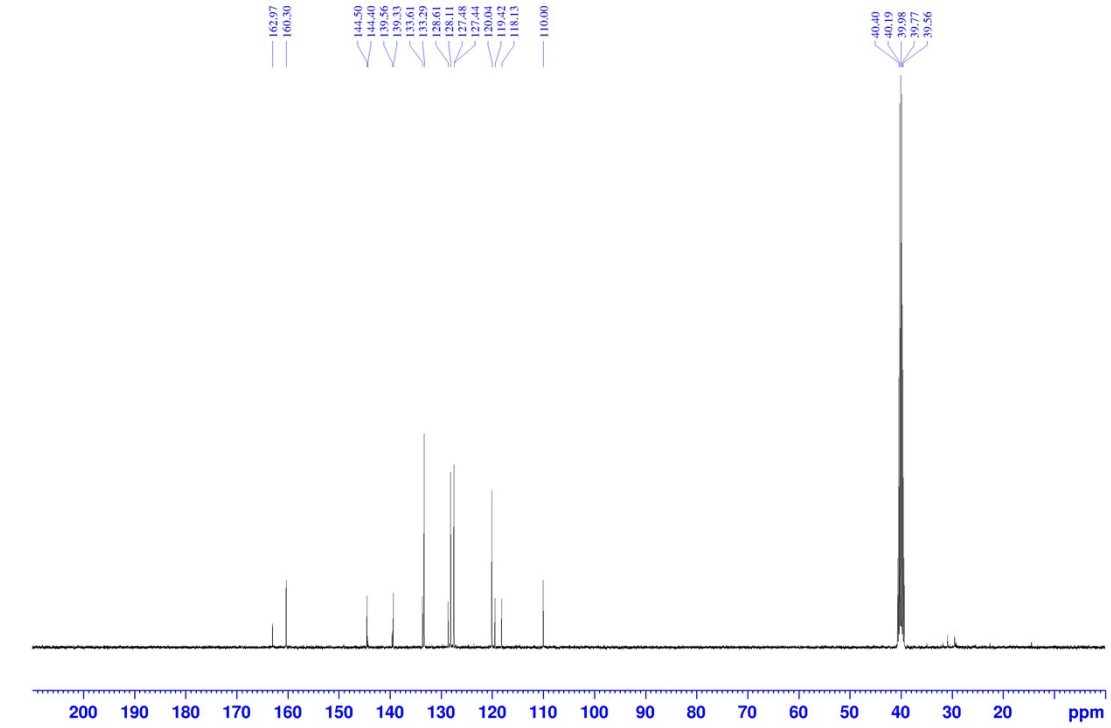
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ppm

14 References

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