Supporting Information

One-Pot Selective N-Formylation of Nitroarenes to Formamides Catalyzed by Core-Shell Structured Cobalt Nanoparticles

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1. General considerations

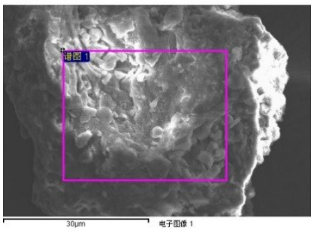
Unless otherwise noted, all reagents were purchased commercially from Sigma-Aldrich, or Aladdin and used as received without further purification. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. All operations were carried out in an argon atmosphere using glovebox and Schlenk techniques unless otherwise specified. Anhydrous tetrahydrofuran (THF), hexanes and toluene were freshly distilled over sodium/benzophenone ketyl prior to use. Gas chromatography analysis was performed on an Agilent HP-7890 instrument with a flame ionization detector (FID) and an HP-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm film thicknesses) using helium as the carrier gas. Gas chromatography-mass spectrometry analysis was carried out on an Agilent HP-7890 instrument with an Agilent HP-5975 with triple-axis detector and HP-5 capillary column using helium carrier gas. High-resolution mass data were recorded on Bruker Maxis UHR TOF mass spectrometers in ESI mode.

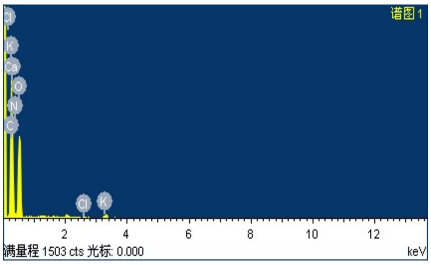
2. Characterization

The X-ray diffraction (XRD) patterns of all the catalysts were obtained on a Bruker D8 Advance X-ray diffraction diffractometer equipped with Cu Ka radiation (λ= 1.5147 Å). The morphology of catalysts was examined by a H-7600 transmission electron microscopy (TEM), a Tecnai G2 F30 high-resolution TEM (HRTEM) and a FEI Tecnai G2 F20 scanning transmission electron microscopy (STEM). Nitrogen adsorption–desorption data were obtained on a Micromeritics ASAP 2020 static volumetric sorption analyzer. The specific surface area of the samples was calculated by the Brunauer-Emmet-Teller (BET) method. The micropore volume was calculated by t-plot method. The pore size distributions were determined by non-local density functional theory (NLDFT). The X-ray photoelectron spectroscopy (XPS) data was collected on an ESCALAB 250Xi (Thermo Scientific, UK) instrument equipped with a monochromatized Al Ka line source. All the binding energies obtained were calibrated based on the C 1s peak at 284.8 eV. The elemental composition analysis of the catalysts was conducted on Vario El elemental analyzer. Ion Chromatography was conducted on a Thermo Scientific Dionex ICS-5000 equipped with CS-12 column with methanesulfonic acid (20 mM) as an eluent. Raman spectra were obtained on a Horiba Jobin Yvon LabRAM HR800 Raman spectrometer system using a 532 nm wavelength laser at room temperature. Magnetic measurement was carried out using a SQUID MPMS-XL5 from Quantum Design with the field range of -3 to 3 T in hysteresis mode. The sample was prepared in a gelatine capsule held in a plastic straw under protective atmosphere. The raw data were corrected for the diamagnetic part of the sample holder. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on a PerkinElmer Optima 5300 DV instrument.

3. Properties of bamboo shoots

The elemental compositions of dried bamboo-shoots were determined by EDX and C/H/N elemental analysis.





EDX analysis result:

Element	weight%	Atom%
C K	42.86	49.43
N K	14.39	14.23
O K	41.44	35.88
Cl K	0.10	0.04
K K	1.03	0.36
Ca K	0.18	0.06
Total	100.00	

Elemental analysis result for the dried bamboo shoots:

Element	C	N
Atom%	41.7	4.27

4. Preparation of the catalysts Co@NPC-x

The cobalt nanoparticles coated by N,P-codoped carbon shell was prepared in two-steps including hydrothermal treatment and carbonization process. The fresh bamboo shoots were obtained from Anhui Taiping Test Centre, International Centre for Bamboo and Rattan, Anhui Province, China. The Bamboo shoots were firstly cut into slices and dried at 70 °C for 24 h. The dried bamboo shoots (2 g) were then ground into powders and transferred in a 100 mL Teflon-inner stainless-steel autoclave coupled with 18 ml of deionized water. The autoclave was then heated to 180 °C and maintained for 5.5 h. The resulting brown solids were filtered, washed by distilled water thoroughly to remove any residual of soluble metal ions such as Ca^{2+} or K^{+} (detected by ion chromatography), dried at room temperature under vacuum for 24 h. After that, 0.5 g of the brown hydrochars were added to 15 mL H_2O involved 0.2 mmol of

$Co(NO_3)_2.6H_2O$ with 0.1 g of PPh_3, and stirred evenly at 60 ^oC for 2h, then the resultant mixture was dried at 100 ^oC for 10 h, and calcined at 700, 800, and 900^oC for 2 h in N_2 flow with a heating rate of 5 °C min^{-1}. The black powder heteroatom doped porous carbons were obtained and denoted as Co@NPC-x, where x represents the pyrolysis temperature.

For comparison, the catalyst Co@NC-800 was prepared by pyrolysis of the mixture of brown chars with $Co(NO_3)_2$ without addition of PPh_3 at 800^oC under N_2 flow, other conditions were kept completely same as Co@NPC-800. The catalyst Co@C-800 was prepared by pyrolysis of the mixture of commercially available activated carbon with $Co(NO_3)_2$ under otherwise identical conditions same to Co@NPC-800. The bare support NC-800 was prepared by pyrolysis of the obtained brown chars at 800^oC under N_2 flow. The bare support NPC-800 was prepared by pyrolysis of the obtained brown chars mixed physically with PPh_3 (20 wt% loading) at 800^oC under N_2 flow.

5. One-pot direct N-formylation of nitroarenes

In a typical procedure, to a sealable Schlenk reaction tube equipped with a magnetic stir bar was charged with 20 mg (4.8 mol% of Co) of Co@NPC-800 catalyst and 158 mg (2.5 mmol) of $HCOONH_4$. The tube was then sealed with a rubber septum and was evacuated for a while to remove air followed by filling with nitrogen. 2.5 mL anhydrous THF, 0.25 mmol of nitrobenzene were injected via syringe into the tube and the reaction was stirred under N_2 balloon at 120^oC. After completion of the reaction, the reaction mixture was filtered or separated using external magnet or centrifugation. The liquid was analysed by GC and GC-MS to determine the conversion and selectivity using dodecane as an internal standard. The verification of each aniline was done by comparing with the corresponding authentic sample by GC and GC-MS.

6. Catalyst recycling

The model reaction was chosen to investigate the recyclability of the novel cobalt nanocomposite catalyst. A 25 mL sealed tube was charged with a magnetic stirring bar, 20 mg Co@NPC-800 (4.8 mol% of Co) catalyst and 158 mg (2.5 mmol) of $HCOONH_4$. The tube was then sealed with a rubber septum and was evacuated for a while to remove air, then 0.25 mmol nitrobenzene, 2.5 mL anhydrous THF were injected via syringe into the tube and the reaction was stirred at 120 ^{o}C for 12 h. After completion of the reaction, tube was cooled to room temperature and the yield was determined by GC using dodecane as an internal standard, the reaction mixture was centrifuged (10000 rpm and 15 min) and the liquid was carefully decanted out. 5 mL of THF were added and the resulting mixture was stirred for 10 min by followed by centrifugation again to remove any residuals on the catalyst. Such operation was repeated for 3 times. Finally, the obtained black solid was dried under vacuum at 40^{o}C overnight for successive use.

7. Characterization results for core-shell structured Co@NPC-800.

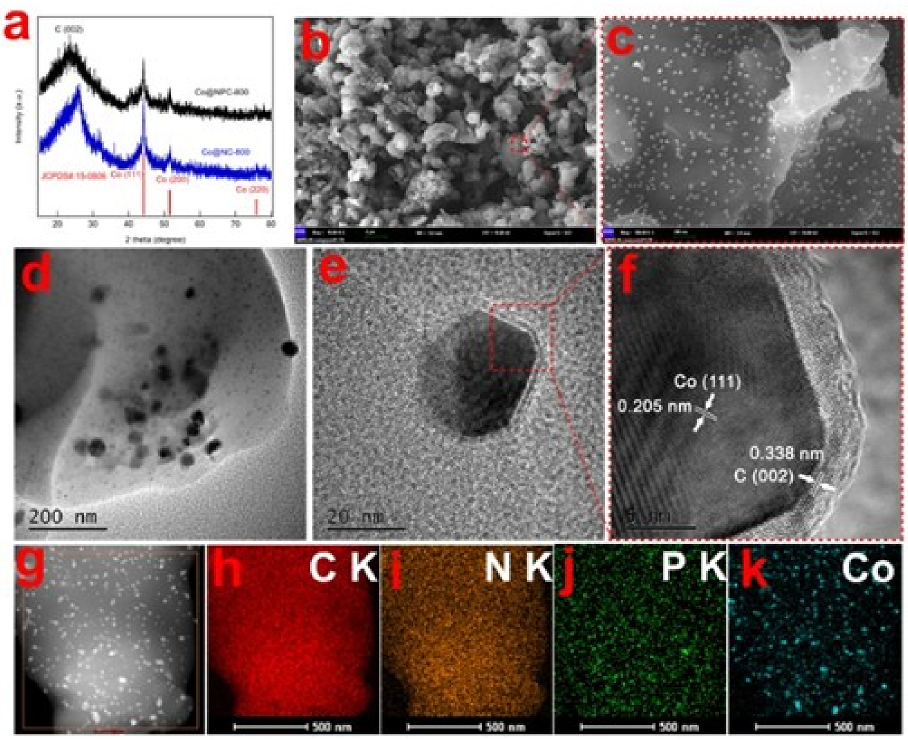
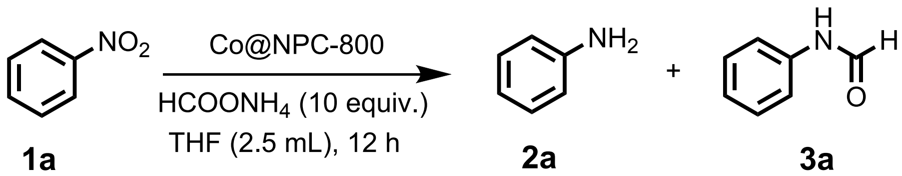


Figure S1. a) X-ray diffraction patterns for the catalysts Co@NC-800 and Co@NPC-800; b, c) SEM images of Co@NPC-800. The magnified image in (c) clearly reveals the uniformly sized nanospheres. d, e, f) HR-TEM image of Co@NPC-800 with different maganitute, showing the carbon shells and coated metal nanoparticles. Inset (f): cystal (111) plane of the metallic Co and (002) plane of the carbon. g-k) HAADF-STEM image and corresponding EDX maps of Co@NPC-800 for C (h), N (i), P (j), and Co (k).

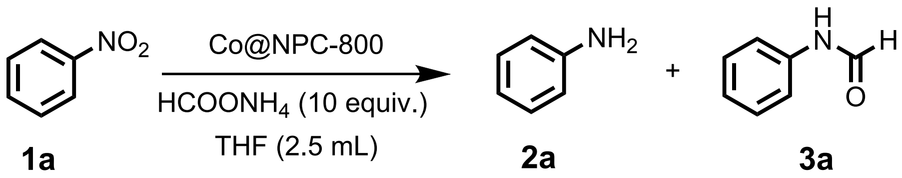
Table S1. The effect of reaction temperature on N-formylation of nitrobenzene with $HCOONH_4$.[a]



Entry	Catalyst loading (mg)	Temperature (°C)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	20	120	100	<1	>99
2	20	110	100	7	93
3	20	100	92	35	65

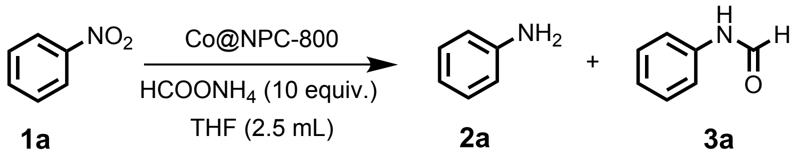
[a]Reaction condtions: nitrobenzene (0.25 mmol), $HCOONH_4$ (2.5 mmol), Co@NPC-800 (4.8 mol% of Co),THF (2.5 mL). [b]Conversion and selectivity were determined by GC using dodecane as an internal standard.

Table S2. The effect of catalyst loadings on N-formylation of nitrobenzene with $HCOONH_4$.[a]



Entry	Catalyst loading (mg)	Temperature (°C)	Reaction time (h)	Conversion (%)[b]	Selectivity (%)[b]	
					2a	**3a**
1	10	120	1	5	100	0
			2	15	100	0
			3	26	92	8
			4	42	82	18
			12	100	14	86
2	20	120	0.5	18	100	0
			2	73	48	2
			3	95	25	75
			4	100	15	85
			12	100	<1	>99

[a]Reaction conditions: nitrobenzene (0.25 mmol), $HCOONH_4$ (2.5 mmol), Co@NPC-800 (4.8 or 2.4 mol% of Co), THF (2.5 mL), 120°C. [b]Conversion and selectivity were determined by GC using dodecane as an internal standard.



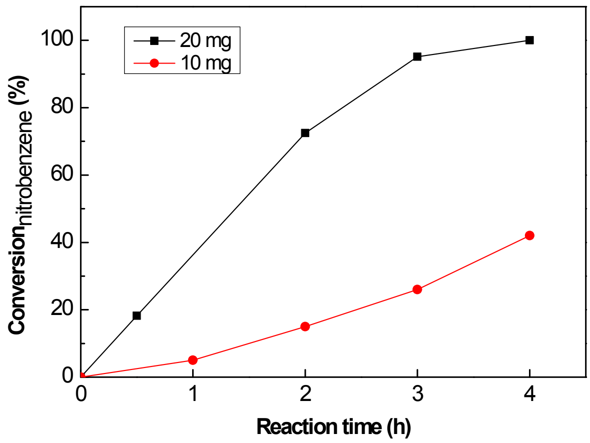
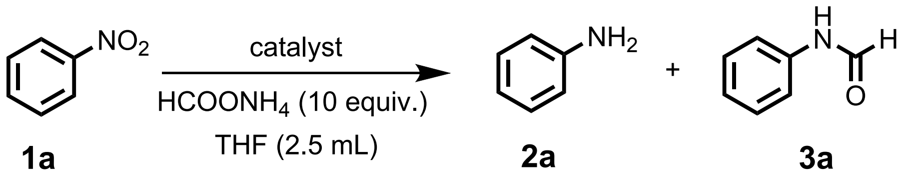


Figure S2. The reaction efficiency for the catalyst Co@NPC-800 with different loading under the standard conditions.

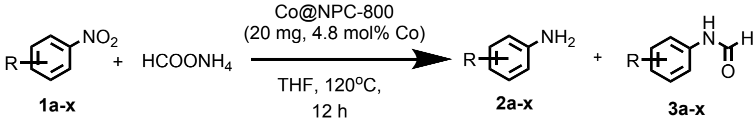
Table S3. Comparison of the reaction efficiency for N-formylation of nitrobenzene with $HCOONH_4$ over different catalysts.[a]

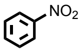
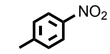
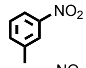
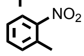
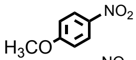
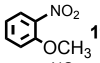
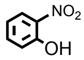
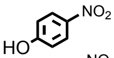
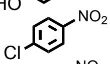
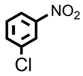
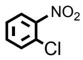
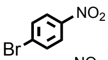
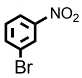
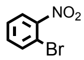
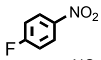
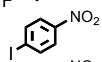
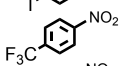
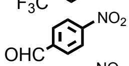
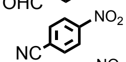
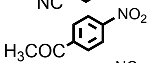
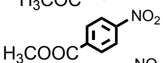
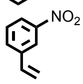
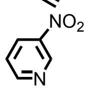
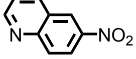


Entry	Catalyst	Reaction time (h)	Conversion (%)[b]	Selectivity (%)[b]	
				2a	**3a**
1	Co@NPC-700	4	37	35	65
2	Co@NPC-800	4	100	15	85
3	Co@NPC-900	4	79	26	74
4	Co@NC-800	4	34	31	69
5	Co@C-800	4	27	37	63

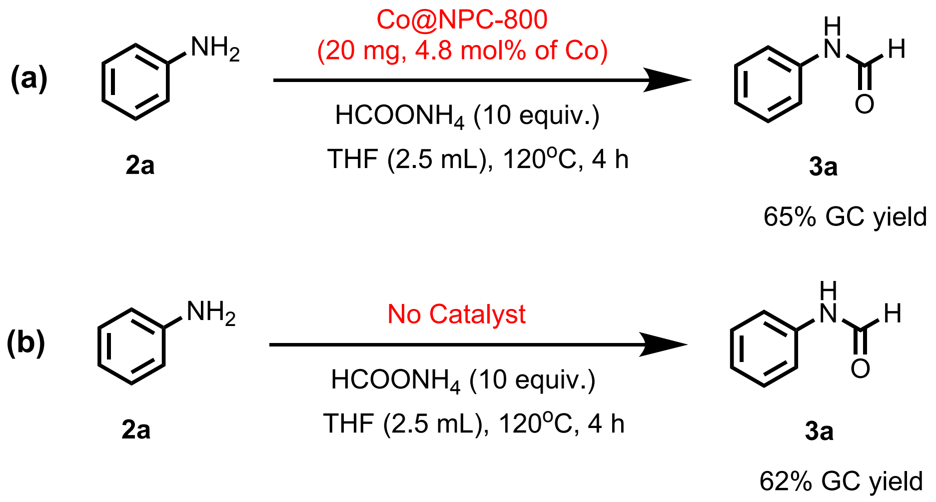
[a]Reaction conditions: nitrobenzene (0.25 mmol), $HCOONH_4$ (2.5 mmol), catalyst (4.8 mol% of Co), THF (2.5 mL), 120°C. [b]Conversion and selectivity were determined by GC using dodecane as an internal standard.

Table 4. Substrate scope[a]



Substrate		Conversion (%)[b]	Selectivity (%)[b]		Yield3 (%)[c]
			2	3	
	**1a**	100	<1	>99	98
	**1b**	100	<1	>99	98
	**1c**	100	<1	>99	94
	**1d**	100	15	85	80
	**1e**	100	<1	>99	98
	**1f**	100	6	94	89
	**1g**	100	<1	>99	95
	**1h**	100	<1	>99	96
	**1i**	100	7	93	89
	**1j**	100	27	73	68
	**1k**	100	82	18	12
	**1l**	100	14	86	82
	**1m**	100	28	72	67
	**1n**	100	77	23	16
	**1o**	100	13	87	82
	**1p**	100	20	80	75
	**1q**	100	55	45	39
	**1r**	100	47	53	46
	**1s**	100	62	38	31
	**1t**	100	54	46	39
	**1u**	100	57	43	37
	**1v**	100	50	50	45
	**1w**	100	43	57	50
	**1x**	100	26	74	67

[a]Reaction conditions: nitroarenes (0.25 mmol), Co@NPC-800 (20 mg, 4.8 mol% of Co), $HCOONH_4$ or HCOOH (2.5 mmol), THF (2.5 mL); 120 °C, 12 h. Yields of isolated products are reported.



Scheme S1. Comparison of reactivity of N-formylation of aniline with $HCOONH_4$ in the presence and absence of catalyst.

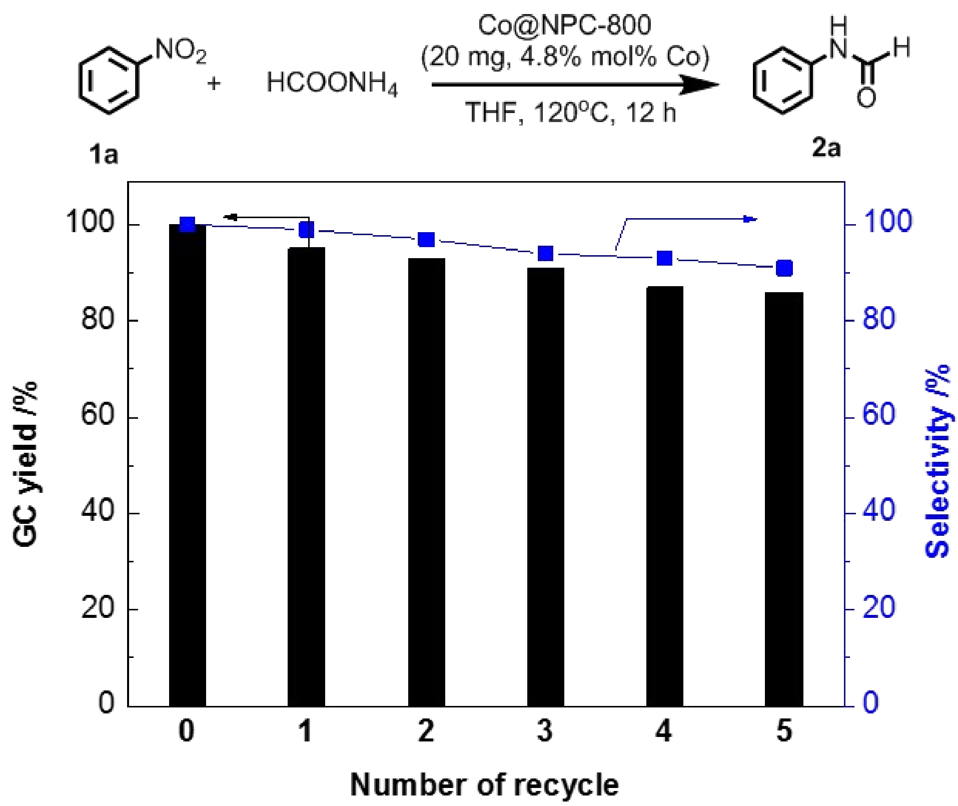


Figure S3. Recyclability of the Co@NPC-800 catalyst for N-formylation of nitrobenzene with $HCOONH_4$ under standard conditions.

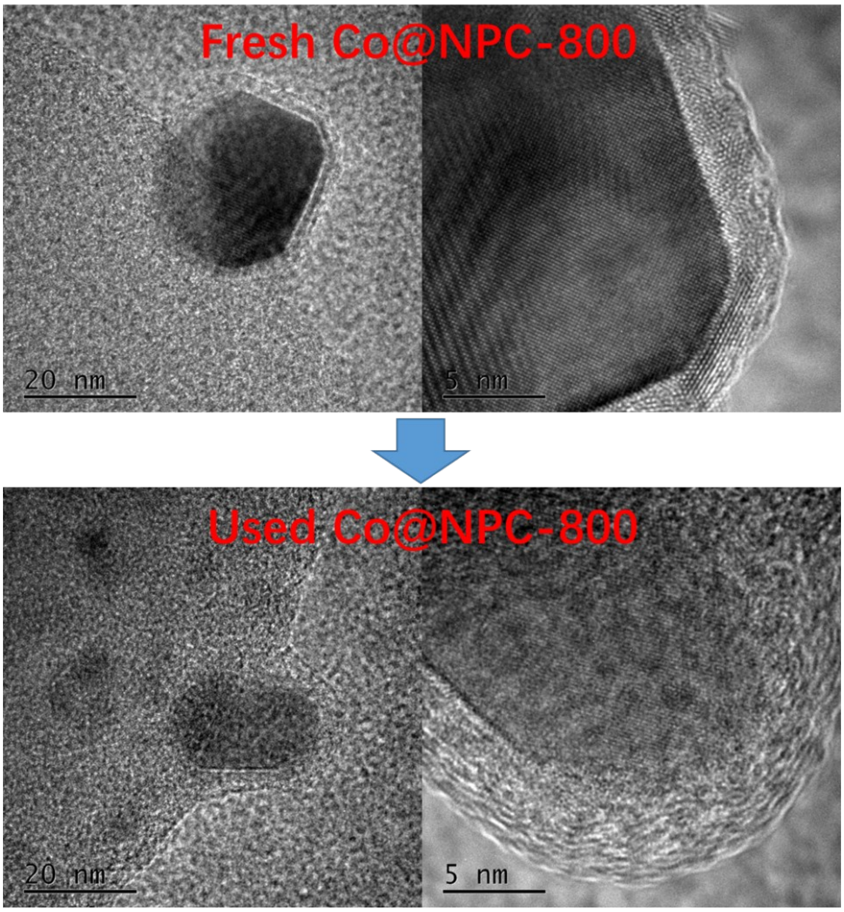


Figure S4. HR-TEM images for the catalyst Co@NPC-800 before and after use.

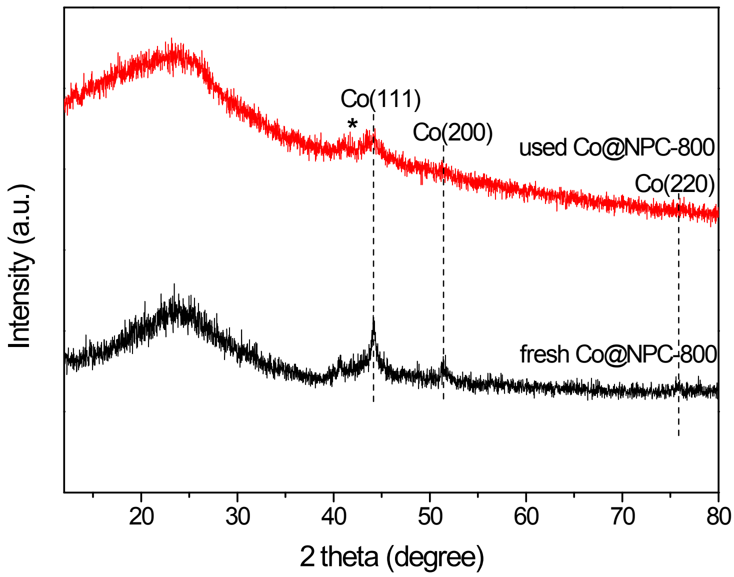
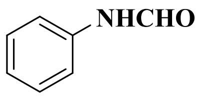
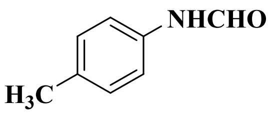


Figure S5. XRD pattern for the catalyst Co@NPC-800 before and after use.

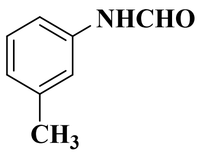
8. ^{1}H and ^{13}C NMR analysis data for all N-formamides



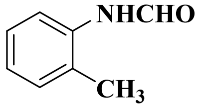
***N*-Phenyl formamide (2a)**, ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.63 (d, *J* = 11.4 Hz, 1H, *trans*), 8.31 (d, *J* = 1.2 Hz, 1H, *cis*), 8.04 (brs, 1H, *cis*), 7.47 (d, 2H), 7.33-7.23 (m, 4H),7.16-7.05 (m, 2H), 7.04-6.99 (d, H);^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5, 159.0, 136.8, 136.7, 129.8, 129.2, 125.4, 124.9,120.0, 118.9; The spectroscopic data matched that previously reported[2].



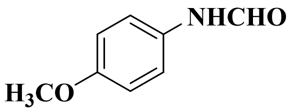
***N*-(4-Methylphenyl) formamide (2b)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 11.5 Hz, 1H, *trans*), 8.27 (d, J = 1.6 Hz, 0.89H, *cis*), 8.18 (brs, 0.88H, *trans*), 7.41 (brs, 0.60H, *cis*), 7.35 (d, 1.80H), 7.07 (m, 3.67H), 6.91 (d, 1.99H), 2.25 (d, 5.59H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.0, 135.2, 134.5, 134.3, 134.1, 130.3, 129.6, 120.1, 119.2, 20.9, 20.8; The spectroscopic data matched that previously reported[4].



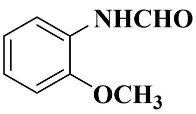
***N*-(3-Methylphenyl) formamide (2c)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 11.4 Hz, 1H, *trans*), 8.41 (brs, J = 22.3 Hz, 0.88H, *trans*), 8.28 (d, J = 1.2 Hz, 0.75H, *cis*), 7.44 (brs, 0.71H, *cis*), 7.33 (s, 0.74H), 7.24 (d, 0.73H), 7.18-7.10 (m, 1.71H), 6.95 – 6.80 (m, 3.63H), 2.27 (d, 5.13H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 159.1, 139.9, 139.1, 136.8, 129.6, 128.9, 126.1, 125.6, 120.7, 119.5, 117.1, 115.8, 21.4; The spectroscopic data matched that previously reported[2].



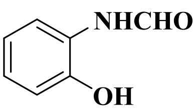
***N*-(2-Methylphenyl) formamide (2d)**, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, J = 11.3 Hz, 1H, *trans*), 8.36 (d, J = 1.2 Hz, 0.55H, *cis*), 7.98 (brs, 0.87H, *cis*), 7.81 (d, J = 7.9 Hz, 0.58H, *trans*), 7.18-6.99 (m, 6.22H), 2.22 (d, 4.79H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.4, 159.2, 135.0, 134.6, 131.3, 130.6, 129.7, 128.6, 127.2, 126.9, 126.1, 125.6, 123.1, 120.7, 17.7; The spectroscopic data matched that previously reported[1].



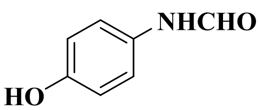
***N*-(4-Methoxyphenyl) formamide (2e)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 11.5 Hz, 1H, *trans*), 8.24 (d, *J* = 1.2 Hz, 1.07H, *cis*), 7.96 (brs, 0.92H, *trans*), 7.46-7.32 (m, 3.05H), 7.00-6.91 (m, 2.05H), 6.85-6.74 (m, 4.11H), 3.72 (d, 6.05H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.2, 159.8, 159.1, 158.9, 157.7, 156.8, 129.9, 129.5, 121.9, 121.7, 114.9, 114.3, 106.5, 104.0, 55.6, 55.5; The spectroscopic data matched that previously reported[4].



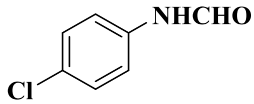
***N*-(2-Methoxyphenyl) formamide (2f)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 11.6 Hz, 0.47H, *trans*), 8.38 (d, *J* = 1.3 Hz, 1H, *cis*), 8.29 (dd, *J* = 8.0, 1.3 Hz, 1H, *trans*), 7.70 (brs, 1.32H, *cis*), 7.22-6.96 (m, 2.29H), 6.93-6.78 (m, 2.99H), 3.81 (d, 4.55H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 158.8, 148.7, 147.8, 126.7, 126.2, 125.2, 124.3, 121.1, 121.0, 120.5, 116.7, 111.3, 110.1, 55.7; The spectroscopic data matched that previously reported[6].



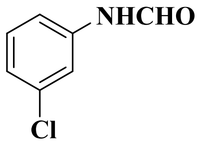
***N*-(2-Hydroxyphenyl) formamide (2g)**, ^{1}H NMR (400 MHz, DMSO) δ 9.94 (s, 0.98H, *trans*), 9.79 (s, 0.22H, *cis*), 9.57 (brs, 0.99H, *trans*), 9.26 (d, *J* = 10.8 Hz, 0.21H, *cis*), 8.52 (d, *J* = 11.2 Hz, 0.16H, *trans*), 8.29 (d, *J* = 1.9 Hz, 1H, *cis*), 8.03 (dd, *J* = 7.9, 1.1 Hz, 1.98H), 7.18-6.54 (m, 4.08H); ^{13}C NMR (101 MHz, DMSO) δ 163.9, 160.5, 149.4, 147.2, 126.5, 125.9, 125.8, 124.6, 122.2, 121.3, 119.9, 119.4, 116.5, 115.5; The spectroscopic data matched that previously reported[2].



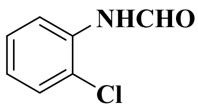
***N*-(4-Hydroxyphenyl) formamide (2h)**, ^{1}H NMR (400 MHz, DMSO) δ 9.95-9.79 (m, 1.27H), 9.26 (d, 1.31H), 8.51 (d, *J* = 11.2 Hz, 0.30H, *trans*), 8.17 (d, *J* = 1.9 Hz, 1.00H, *cis*), 7.38 (m, 1.98H), 7.02-6.94 (m, 0.63H), 6.71 (m, 2.64H); ^{13}C NMR (151 MHz, DMSO) δ 163.0, 159.3, 154.7, 154.0, 130.4, 130.1, 121.3, 120.7, 116.3, 115.7; The spectroscopic data matched that previously reported[2].



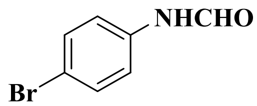
***N*-(4-Chlorophenyl) formamide (2i)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (brs, 0.62H, *trans*), 8.58 (d, J = 11.2 Hz, 0.76H, *trans*), 8.28 (s, 1H, *cis*), 7.77 (brs, 0.87H, *cis*), 7.47-7.38 (m, 2.03H), 7.30-7.15 (m, 3.59H), 7.02-6.93 (m, 1.47H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4, 159.1, 138.0, 137.9, 135.5, 134.8, 130.9, 130.2, 125.4, 124.9, 120.1, 118.8, 117.9, 116.7. The spectroscopic data matched that previously reported[3].



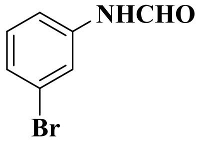
***N*-(3-Chlorophenyl) formamide (2j)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J = 11.2 Hz, 1H, *trans*), 8.42 (brs, 0.88H, *trans*), 8.30 (s, 1.26H, *cis*), 7.59 (t, 1.29H), 7.52 (brs, 0.94H, *cis*), 7.32 (dd, 1.28H), 7.25-7.13 (m, 2.57H), 7.13-7.00 (m, 3.11H), 6.92 (dd, 0.99H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 159.3, 138.0, 137.9, 135.5, 134.7, 130.9, 130.1, 125.4, 124.9, 120.1, 118.8, 118.0, 116.7; The spectroscopic data matched that previously reported[2].



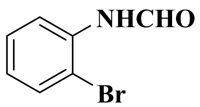
***N*-(2-Chlorophenyl) formamide (2k)**, ^{1}H NMR (400 MHz, DMSO) δ 9.87 (brs, 1.24H), 8.48 (d, J = 10.7 Hz, 0.26H, *trans*), 8.36 (s, 1H, *cis*), 8.11 (d, 1H), 7.58-7.08 (m, 4.19H); ^{13}C NMR (101 MHz, DMSO) δ 164.0, 160.9, 135.4, 134.7, 130.5, 130.0, 128.6, 128.1, 127.1, 126.0, 124.0, 123.7; The spectroscopic data matched that previously reported[2].



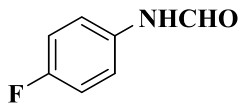
***N*-(4-Bromophenyl) formamide (2l)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J = 11.2 Hz, 0.74H, *trans*), 8.49 (brs, 0.64H, *trans*), 8.30 (s, 1H, *cis*), 7.56 (brs, 0.91H, *cis*), 7.43-7.32 (m, 5.43H), 6.91 (d, 1.44H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 159.1, 135.9, 135.8, 132.8, 132.1, 121.6, 120.3, 118.3, 117.5. The spectroscopic data matched that previously reported[2].



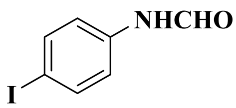
***N*-(3-Bromophenyl) formamide (2m)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 11.1 Hz, 0.83H, *trans*), 8.57 (brs, 0.67H, *trans*), 8.29 (d, *J* = 1.2 Hz, 1H, *cis*), 7.73 (t, *J* = 1.8 Hz, 1.01H), 7.64 (brs, 0.85H, *cis*), 7.38 (d, *J* = 8.0 Hz, 1.01H), 7.28-7.20 (m, 1.9H), 7.19-7.08 (m, 2.37H), 6.97 (dd, 0.80H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 159.2, 138.1, 131.1, 130.4, 128.3, 127.9, 123.4, 123.0, 122.7, 121.7, 118.5, 117.2. The spectroscopic data matched that previously reported[2].



***N*-(2-Bromophenyl) formamide (2n)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 11.1 Hz, 0.51H, *trans*), 8.43 (s, 1H, *cis*), 8.32 (dd, *J* = 8.2, 1.3 Hz, 0.98H), 7.72-7.43 (m, 2.89H), 7.30-7.16 (m, 2.53H), 7.05-6.90 (m, 1.54H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.6, 158.8, 135.1, 134.8, 133.5, 132.4, 128.7, 128.5, 126.4, 125.7, 122.2, 118.9, 114.5, 113.0. The spectroscopic data matched that previously reported[2].

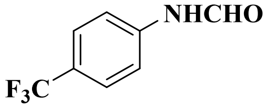


***N*-(4-Fluorophenyl) formamide (2o)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 11.3 Hz, 1H, *trans*), 8.28 (s, 1.42H, *cis*), 8.21 (brs, 0.84H, *trans*), 7.50-7.31 (m, 3.93H), 7.05-6.90 (m, 6.77H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 161.7, 160.9, 159.3, 159.0, 158.4, 132.8, 132.7, 121.9, 121.8, 121.3, 121.2, 116.7, 116.5, 115.9, 115.7; The spectroscopic data matched that previously reported[2] .

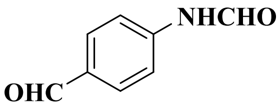


***N*-(4-Iodophenyl) formamide (2p)**, ^{1}H NMR (400 MHz, DMSO) δ 10.29 (brs, 0.98H, *cis*), 10.19 (d, *J* = 10.8 Hz, 0.30H, *trans*), 8.79 (d, *J* = 10.9 Hz, 0.29H, *trans*), 8.30 (d, *J* = 1.8 Hz, 1H, *cis*), 7.70-7.60 (m, 2.63H), 7.48-7.37 (m, 2.17H), 7.04 (d, 0.61H); ^{13}C

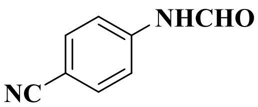
NMR (101 MHz, DMSO) δ 162.9, 160.2, 138.8, 138.5, 138.4, 138.0, 121.8, 120.1, 87.6. The spectroscopic data matched that previously reported[5] .



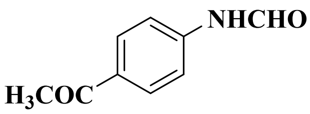
***N*-(4-(Trifluoromethyl)phenyl) formamide (2q)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (m, 1.45H), 8.36 (s, 1H, *cis*), 7.77 (brs, 1H, *cis*), 7.61 (d, 2.10H), 7.57-7.47 (m, 3.48H), 7.13 (d, 1.44H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 159.3, 139.9, 127.1, 126.4, 119.7, 117.9. HRMS (ESI): calcd. for $C_8H_7F_3NO^+$ $[M+H]^+$ 189.0401, found 189.0410.



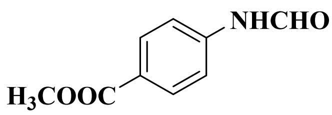
***N*-(4-Formylphenyl) formamide (2r)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (d, 1.57H), 8.98 (brs, 0.61H, *trans*), 8.85 (d, J = 11.0 Hz, 0.63H, *trans*), 8.40 (s, 1H, *cis*), 8.28 (brs, 0.98H, *cis*), 7.93-7.56 (m, 5.63H), 7.21 (d, 0.73H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 190.7, 161.7, 159.2, 142.4, 133.1, 132.7, 131.8, 131.2, 119.6, 117.5. HRMS (ESI): calcd. for $C_8H_8NO_2^+$ $[M+H]^+$ 150.1490, found 150.1498.



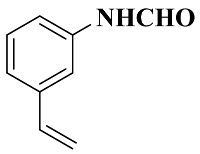
***N*-(4-Cyanophenyl) formamide (2s)**, ^{1}H NMR (400 MHz, DMSO) δ 10.69 (brs, 0.97H, *cis*), 10.57 (d, J = 10.5 Hz, 0.35H, *trans*), 9.04 (d, J = 10.6 Hz, 0.32H, *trans*), 8.42 (d, J = 1.6 Hz, 1H, *cis*), 7.88-7.74 (m, 4.76H), 7.42 (d, 0.67H); ^{13}C NMR (101 MHz, DMSO) δ 163.2, 160.9, 143.4, 142.8, 134.3, 133.9, 119.8, 119.4, 117.5, 105.9, 105.7. HRMS (ESI): calcd. for $C_8H_7N_2O^+$ $[M+H]^+$ 147.0480, found 147.0505.



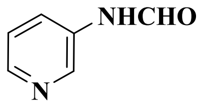
***N*-(4-Acetylphenyl) formamide (2t)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 10.6 Hz, 0.96H, *trans*), 8.81 (d, J = 11.1 Hz, 1H, *trans*), 8.42 (brs, 1.44H, *cis*), 8.37 (s, 1.64H, *cis*), 7.96-7.80 (m, 5.35H), 7.61 (d, 3.25H), 7.12 (d, 1.98H), 2.51 (d, 7.76H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 197.0, 162.2, 159.6, 141.5, 141.3, 133.6, 133.2, 130.5, 129.8, 119.3, 117.3, 26.5. The spectroscopic data matched that previously reported[2].



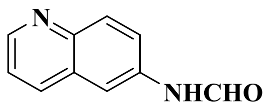
Methyl 4-formamidobenzoate (2u), ^{1}H NMR (400 MHz, DMSO) δ 10.54 (s, 0.95H, *cis*), 10.47 (d, *J* = 10.6 Hz, 0.34H, *trans*), 8.97 (d, *J* = 10.7 Hz, 0.31H, *trans*), 8.35 (d, *J* = 1.5 Hz, 1H, *cis*), 8.02-7.84 (m, 2.69H), 7.72 (d, 2.06H), 7.32 (d, 0.68H), 3.82 (s, 3.91H); ^{13}C NMR (101 MHz, DMSO) δ 166.2, 163.0, 160.6, 143.4, 143.0, 131.3, 130.9, 124.8, 124.7, 119.1, 116.9, 52.4. HRMS (ESI): calcd. for $C_9H_{10}NO_3^+$ $[M+H]^+$ 180.0582, found 150.0600.



***N*-(3-Vinylphenyl) formamide (2v)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 11.3 Hz, 1H, *trans*), 8.32 (s, 0.99H, *cis*), 7.78 (brs, 1.04H, *trans*), 7.55 (s, 1H, *cis*), 7.40-7.20 (m, 3.34H), 7.19-6.86 (m, 4.67H), 6.62 (dd, 1.97H), 5.70 (dd, 1.99H), 5.23 (dd, 2.05H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3, 157.8, 138.4, 137.7, 136.1, 135.8, 135.2, 134.9, 128.9, 128.2, 122.3, 121.7, 118.2, 117.1, 116.7, 115.6, 114.4, 113.8; HRMS (ESI): calcd. for $C_9H_{10}NO^+$ $[M+H]^+$ 148.0684, found 148.0692.



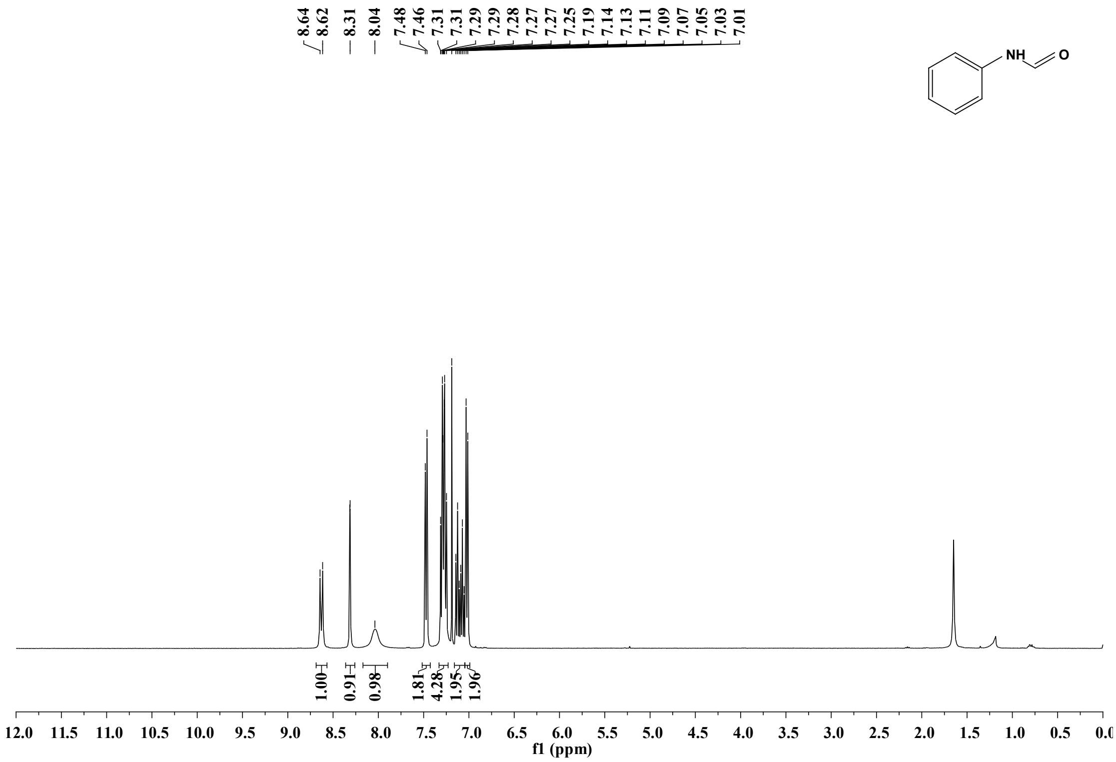
***N*-(Pyridin-3-yl) formamide (2w)**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (brs, 0.37H, *trans*), 8.88 (brs, 0.93H, *cis*), 8.65 (d, *J* = 11.1 Hz, 0.36H, *trans*), 8.59 (d, *J* = 2.3 Hz, 1H, *cis*), 8.42 (d, 0.34H), 8.41-8.35 (m, 1.33H), 8.29 (dd, 0.98H), 8.20-8.12 (m, 1.01H), 7.46-7.38 (m, 035H), 7.30-7.21 (m, 1.35H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 159.7, 146.4, 145.3, 140.9, 140.7, 134.4, 133.8, 127.7, 126.1, 124.3, 124.0. The spectroscopic data matched that previously reported[7] .

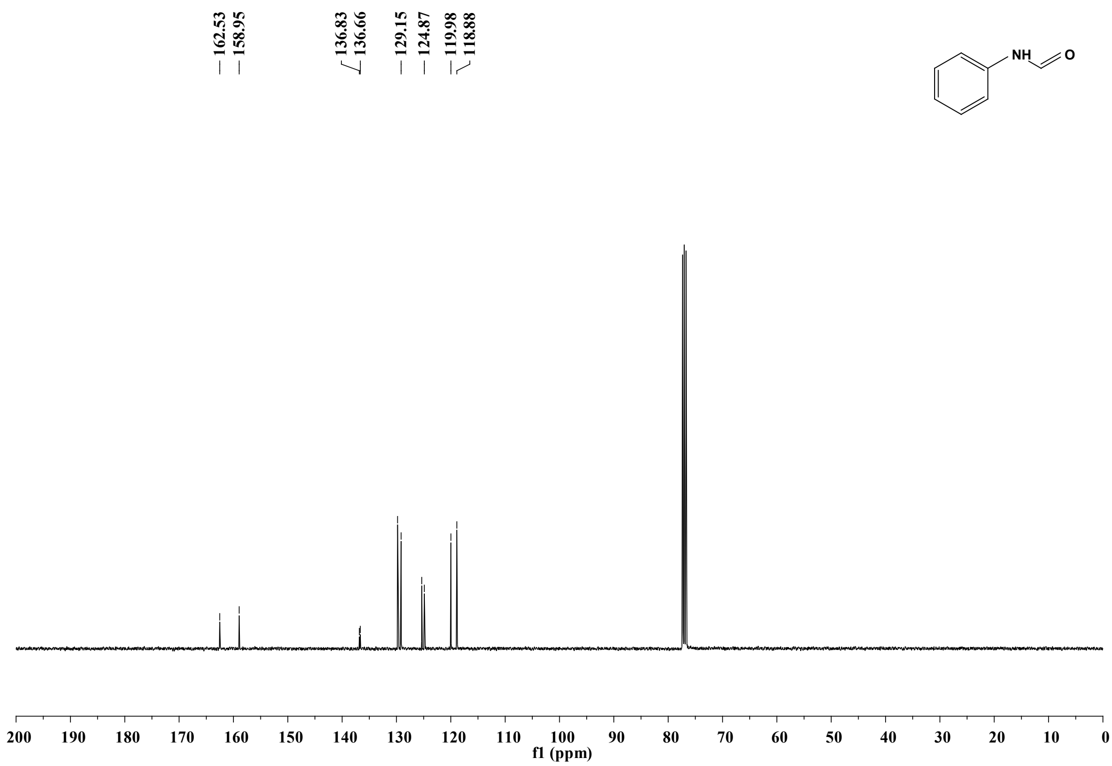


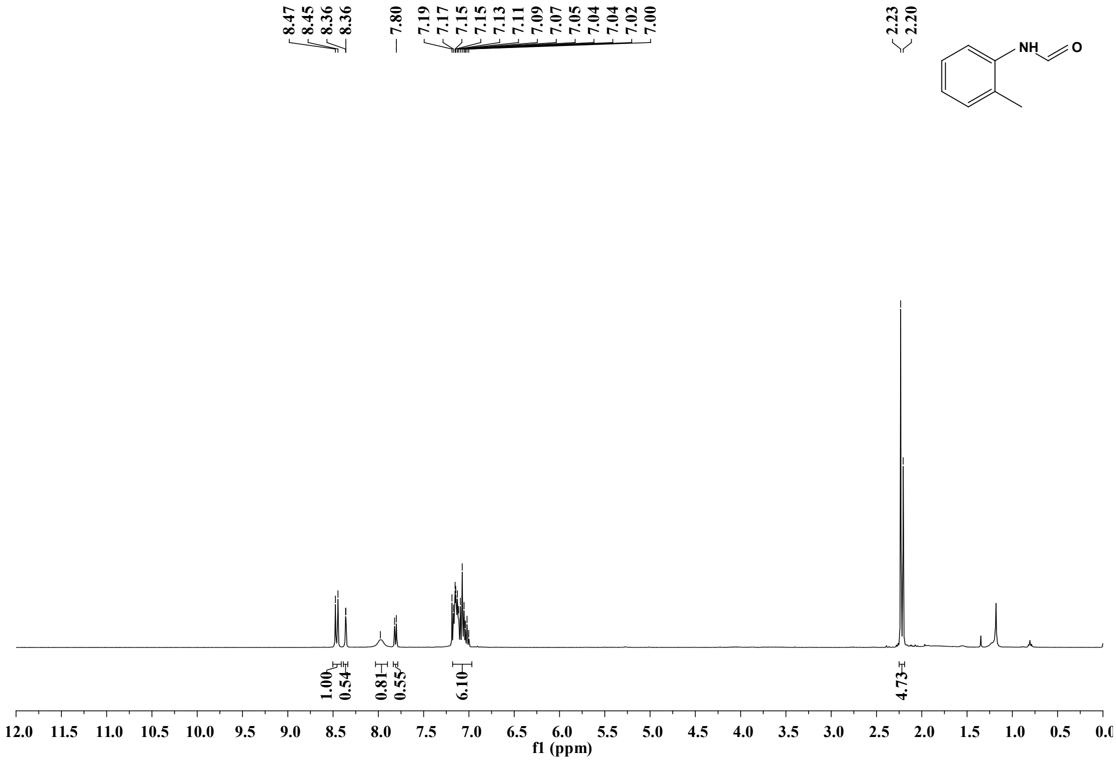
***N*-(Quinolin-6-yl) formamide (2x)**, ^{1}H NMR (400 MHz, DMSO) δ 10.55 (s, 0.74H, *cis*), 10.48 (d, *J* = 10.8 Hz, 0.24H, *trans*), 8.99 (d, *J* = 10.8 Hz, 0.24H, *trans*), 8.79 (dd, *J* = 4.1, 1.6 Hz, 1H, *cis*), 8.40 (dd, 1.66H), 8.32-8.11 (m, 1.28H), 7.99 (d, 1.02H), 7.79

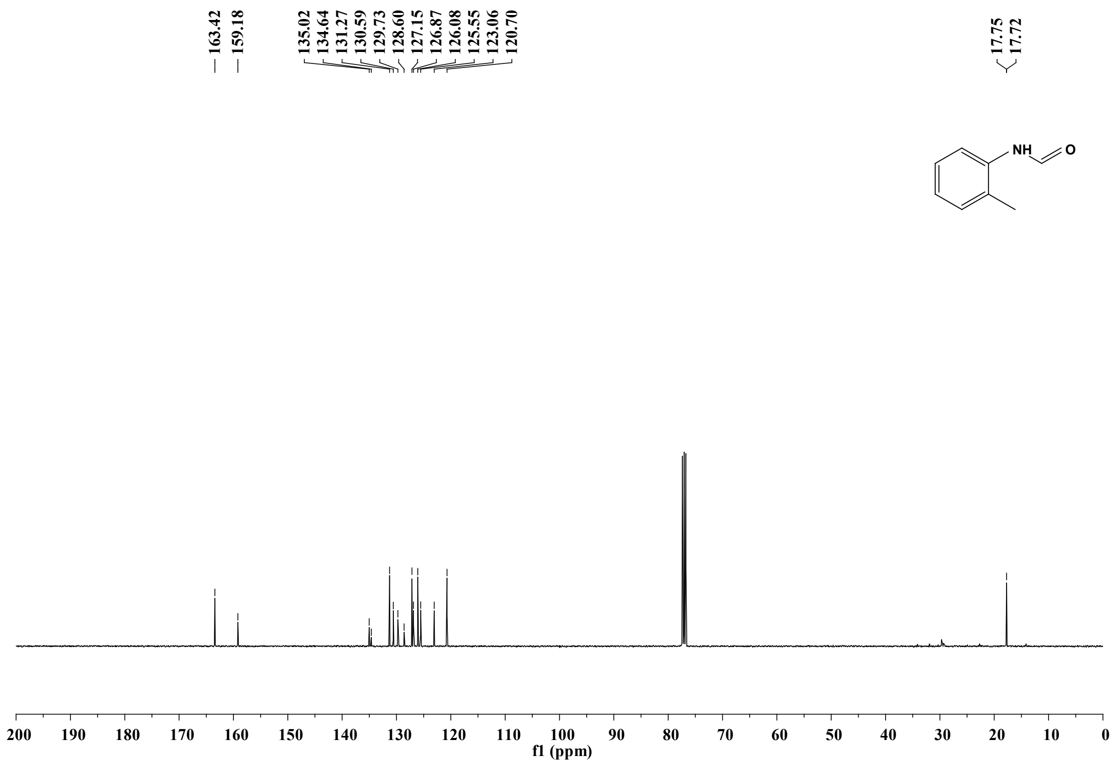
(dd, 0.81H), 7.76-7.61 (m, 0.56H), 7.52-7.43 (m, 1.02H); ^{13}C NMR (101 MHz, DMSO) δ 163.3, 160.6, 149.7, 149.5, 145.4, 145.3, 136.9, 136.6, 136.0 135.6, 130.8, 130.2, 129.0, 128.8, 123.5, 122.5, 122.4, 122.3, 115.8, 113.0. HRMS (ESI): calcd. for $C_{10}H_9N_2O^+$ $[M+H]^+$ 173.0637, found 173.0646.

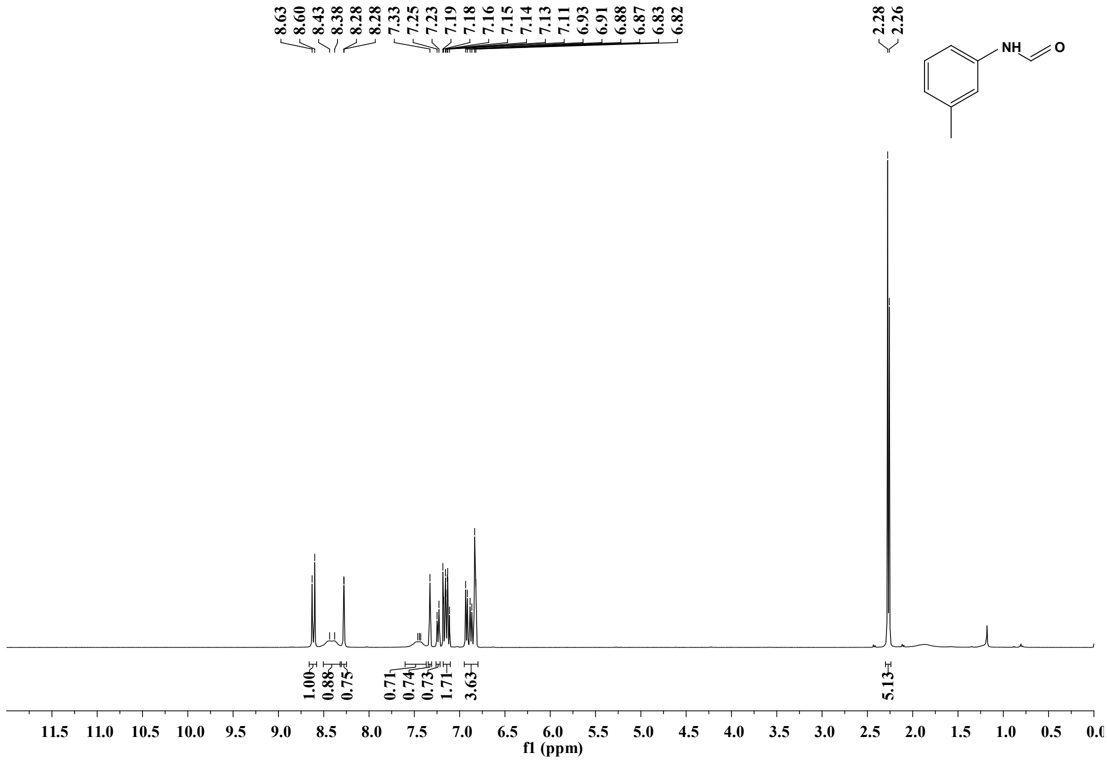
9. ¹H and ¹³C NMR spectra of products







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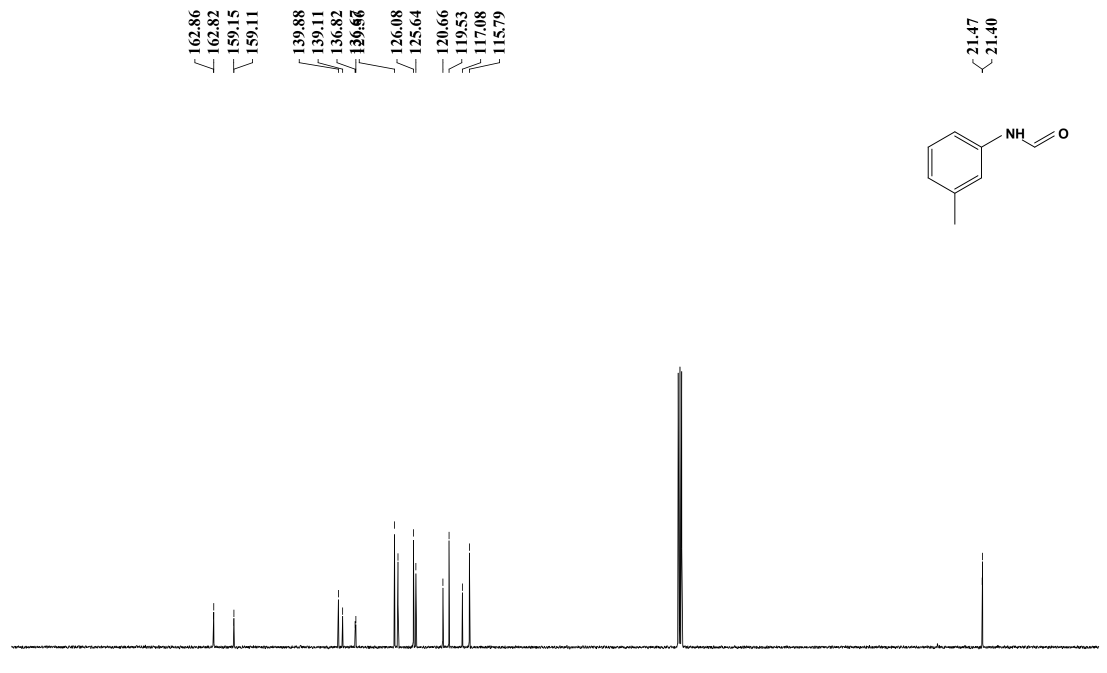
2.28 2.26
NH
O
1.00 0.88 0.75 0.71 0.74 0.73 1.71 3.63 5.13
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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21.47 21.40
NH
O
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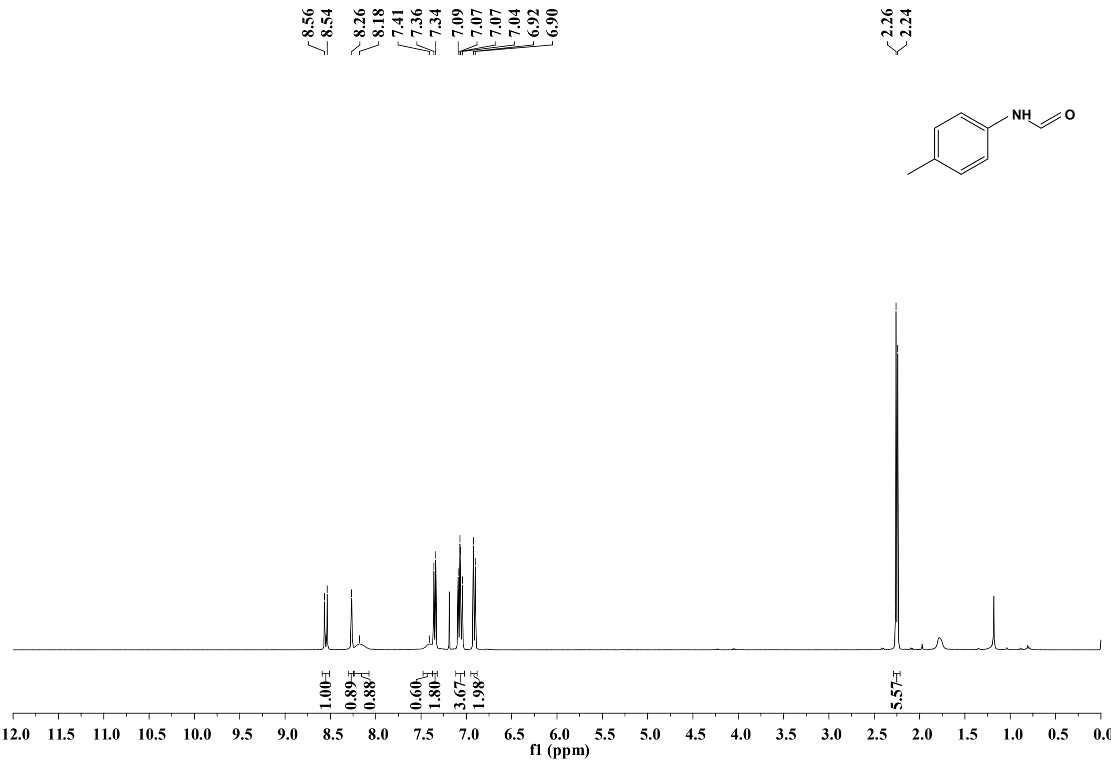
f1 (ppm)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7.07
7.07
7.04
6.92
6.90
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3.67
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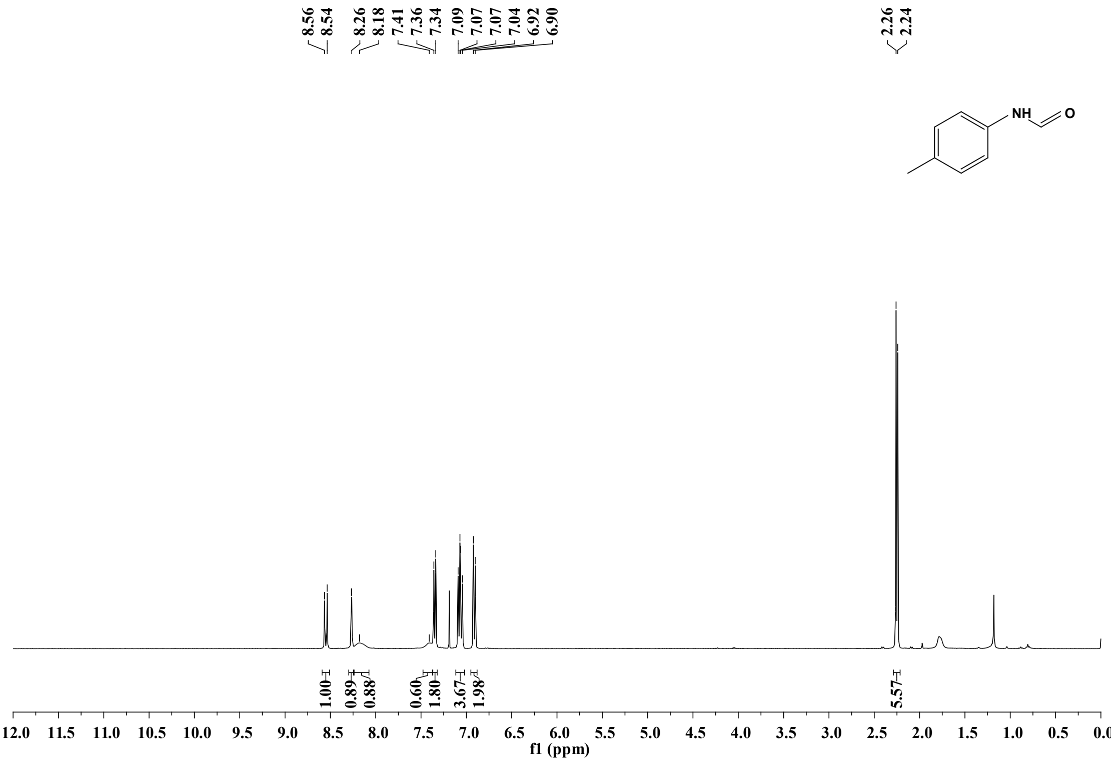
5.57
f1 (ppm)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6.90
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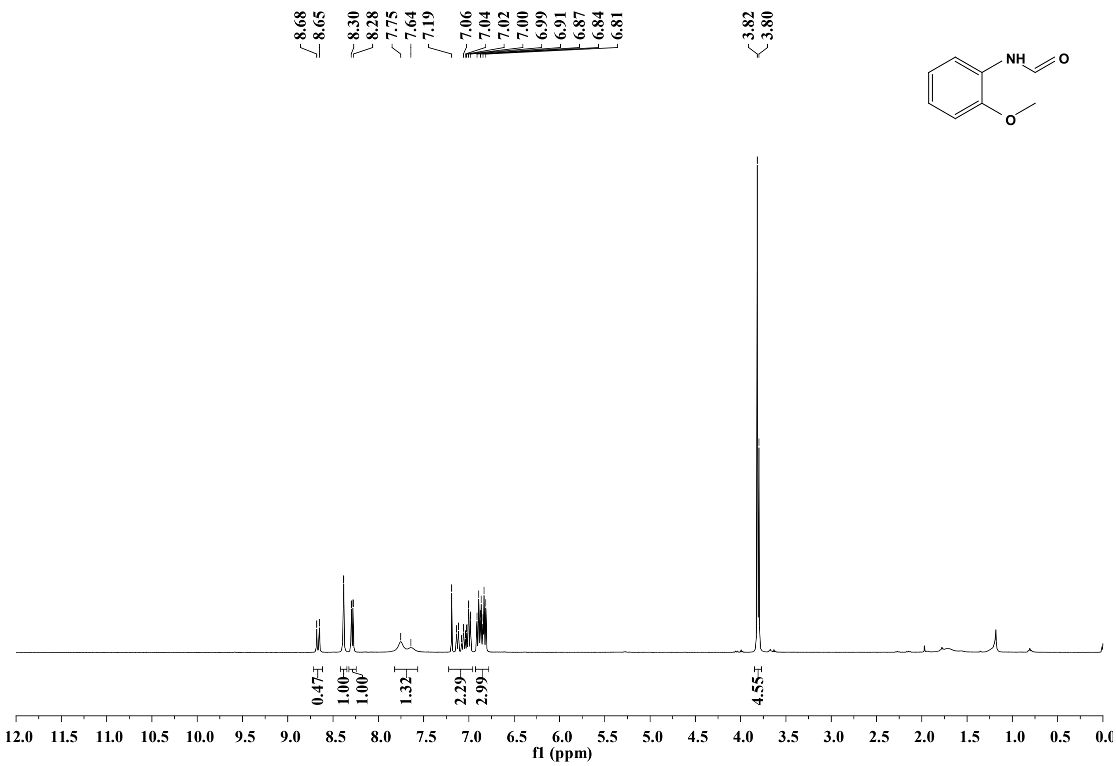
5.57
f1 (ppm)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7.02
7.00
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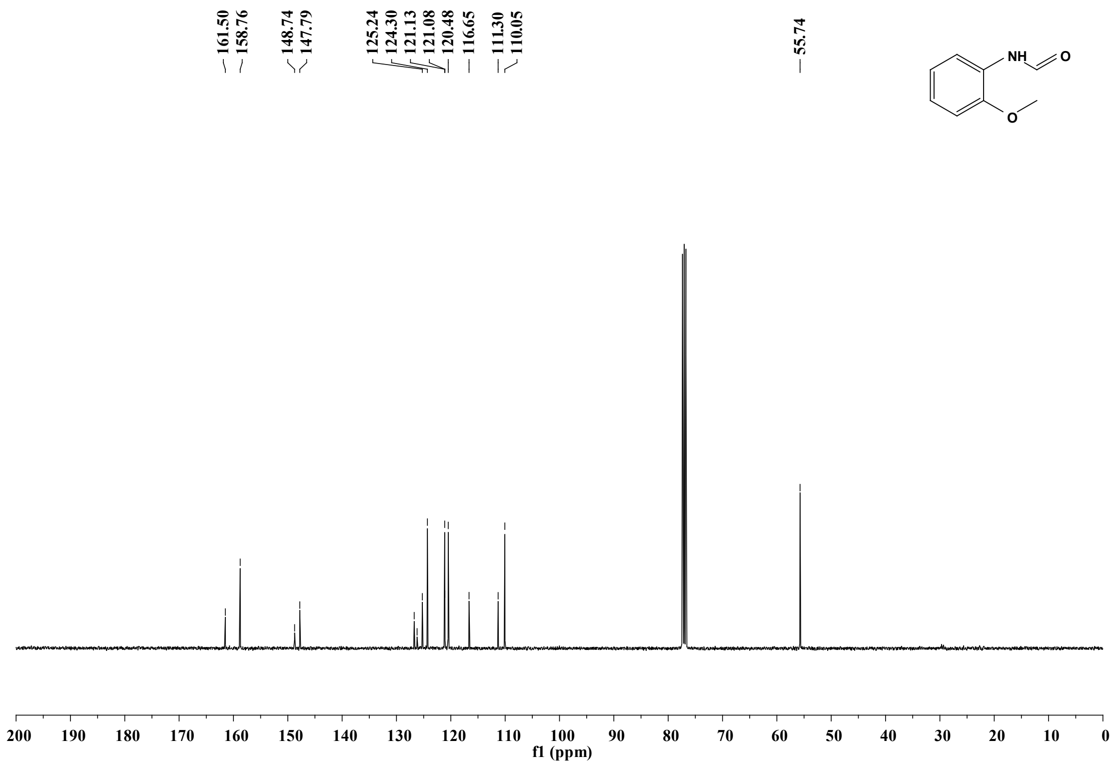
6.91
6.87
6.84
6.81
3.82
3.80
NH
O
O
0.47
1.00
1.00
1.32
2.29
2.99
4.55
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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121.08
120.48
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110.05
55.74
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O
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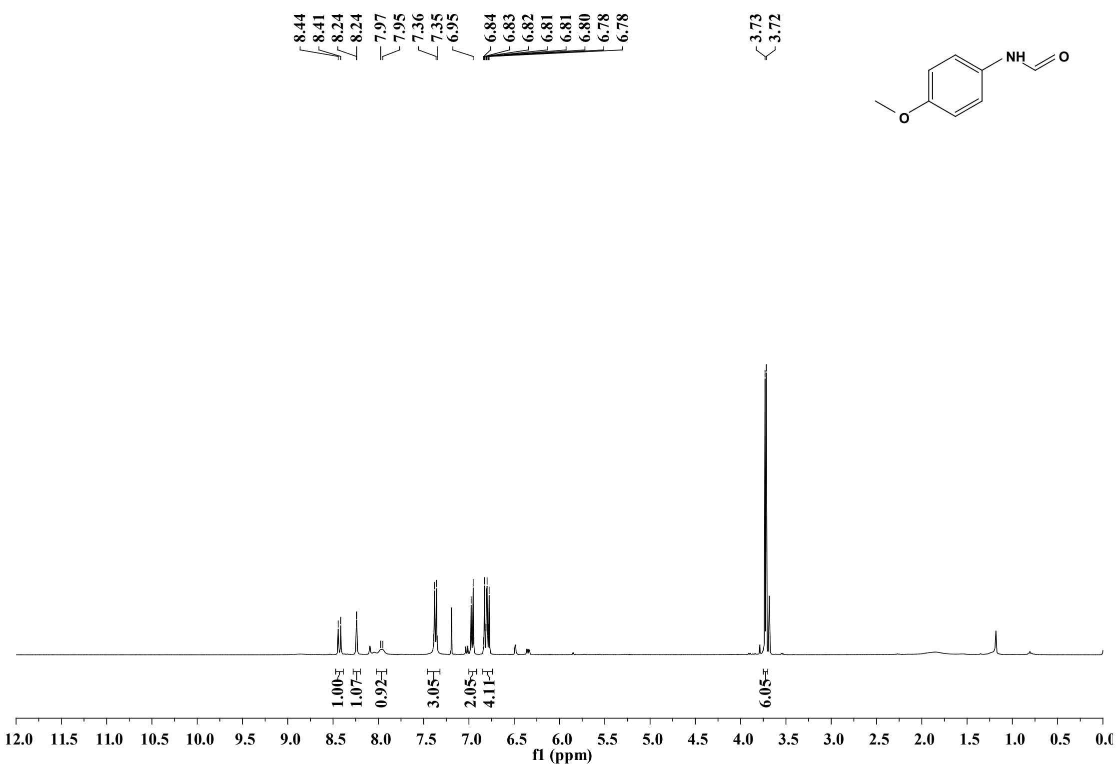
f1 (ppm)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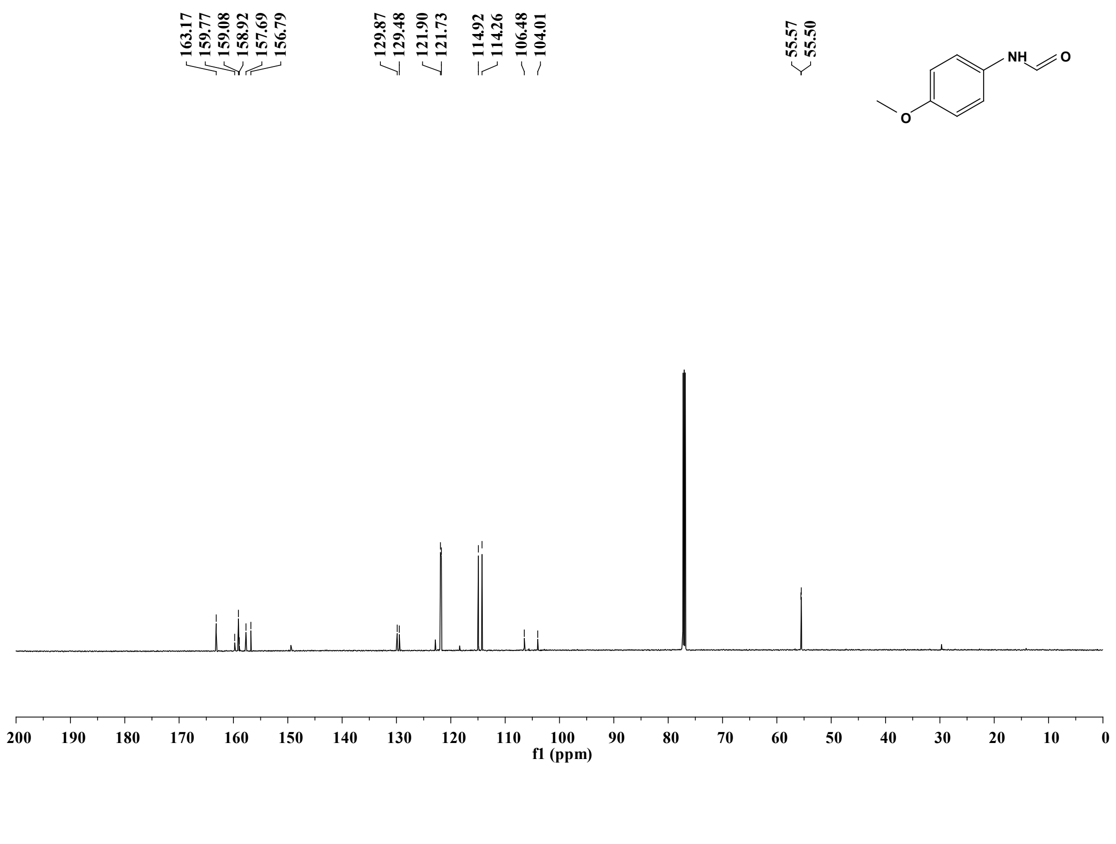
6.82
6.81
6.81
6.80
6.78
6.78
3.73
3.72
NH
O
O
1.00
1.07
0.92
3.05
2.05
4.11
6.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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55.50
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O
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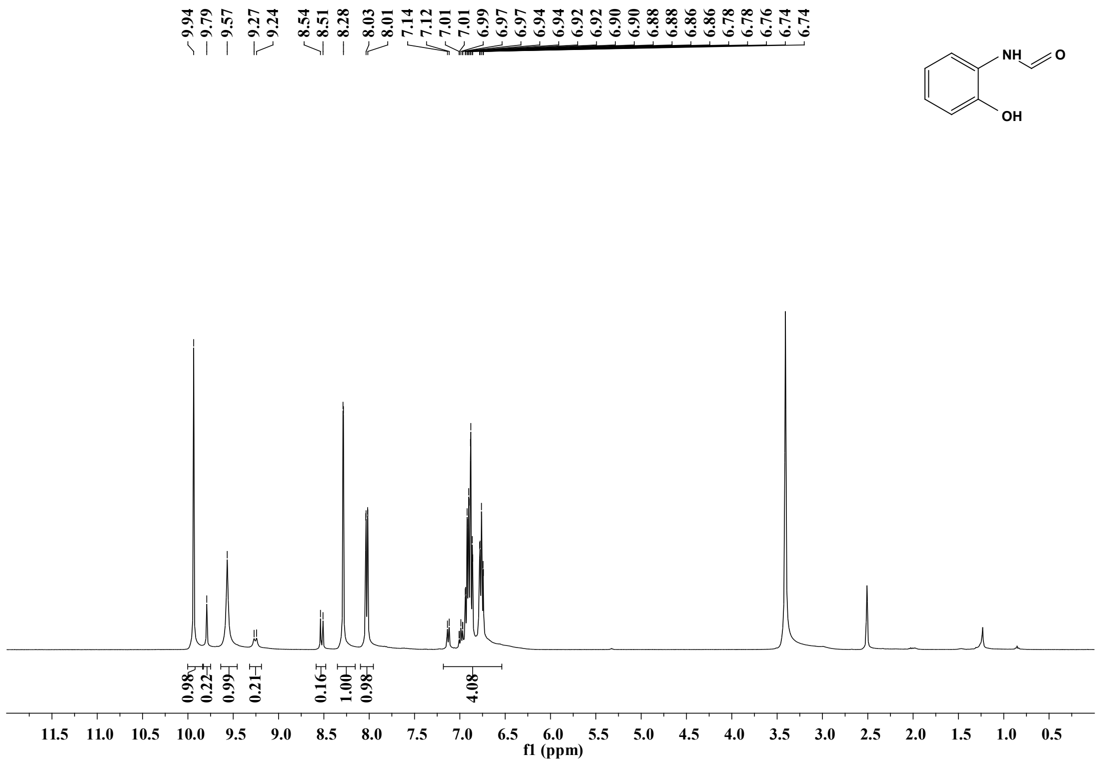
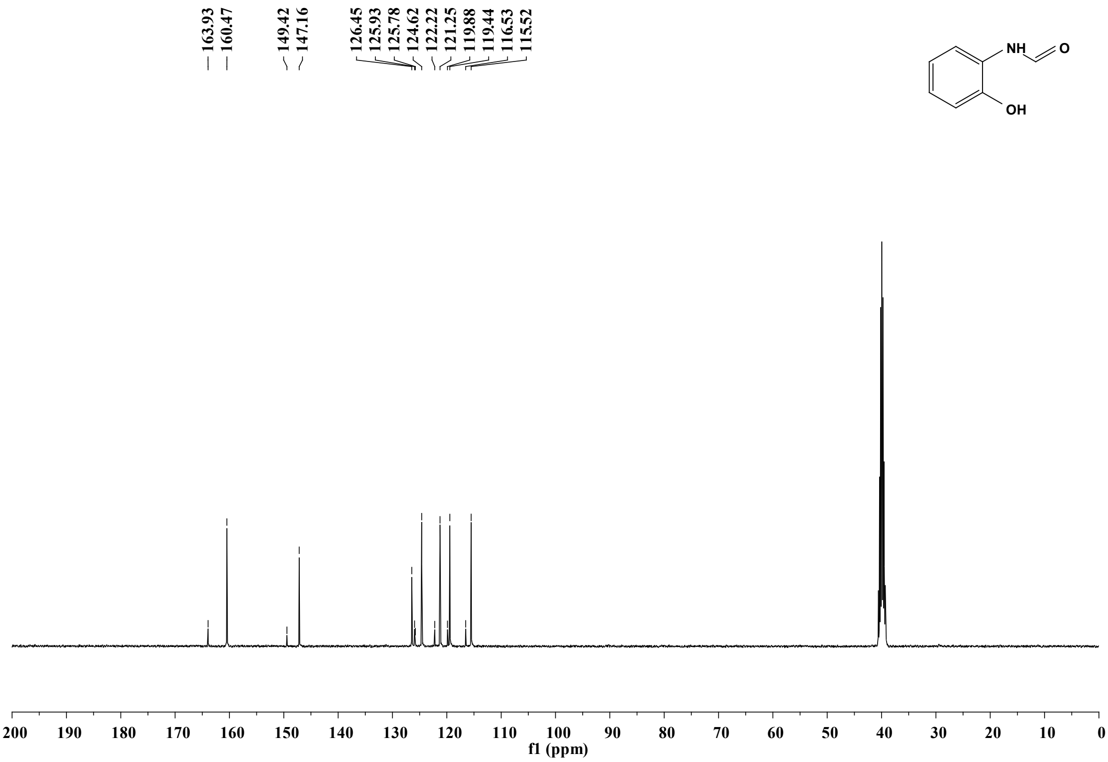
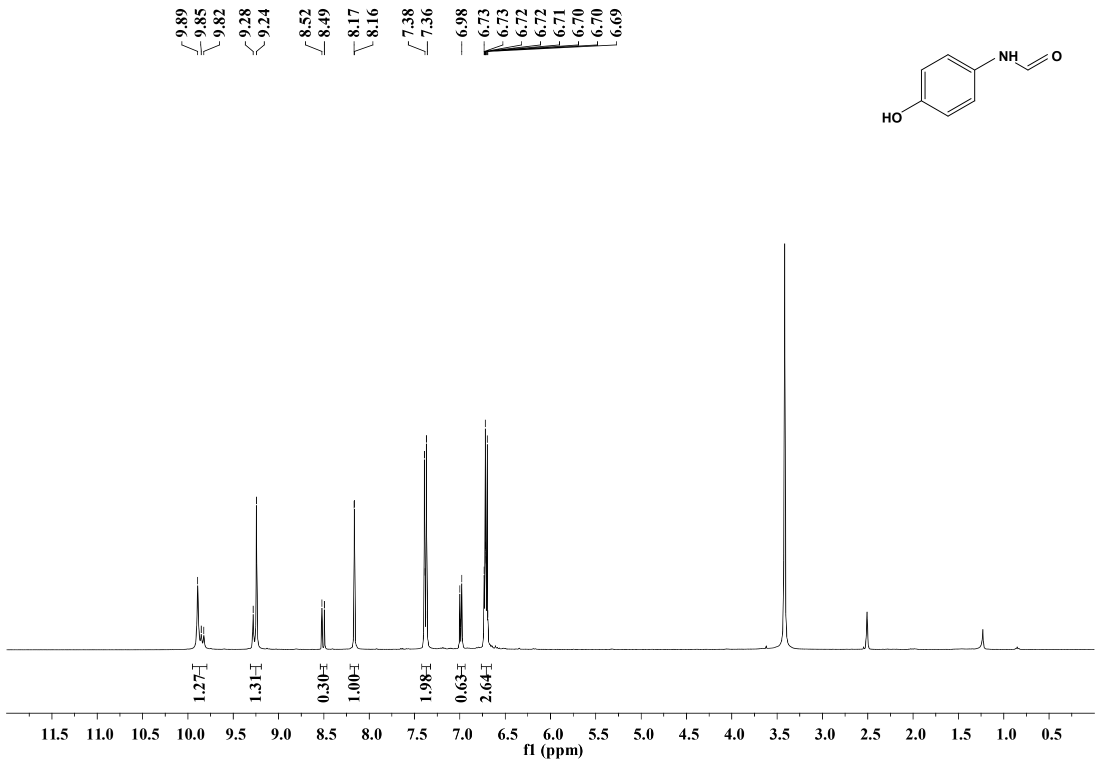
f1 (ppm)



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9.28
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8.17
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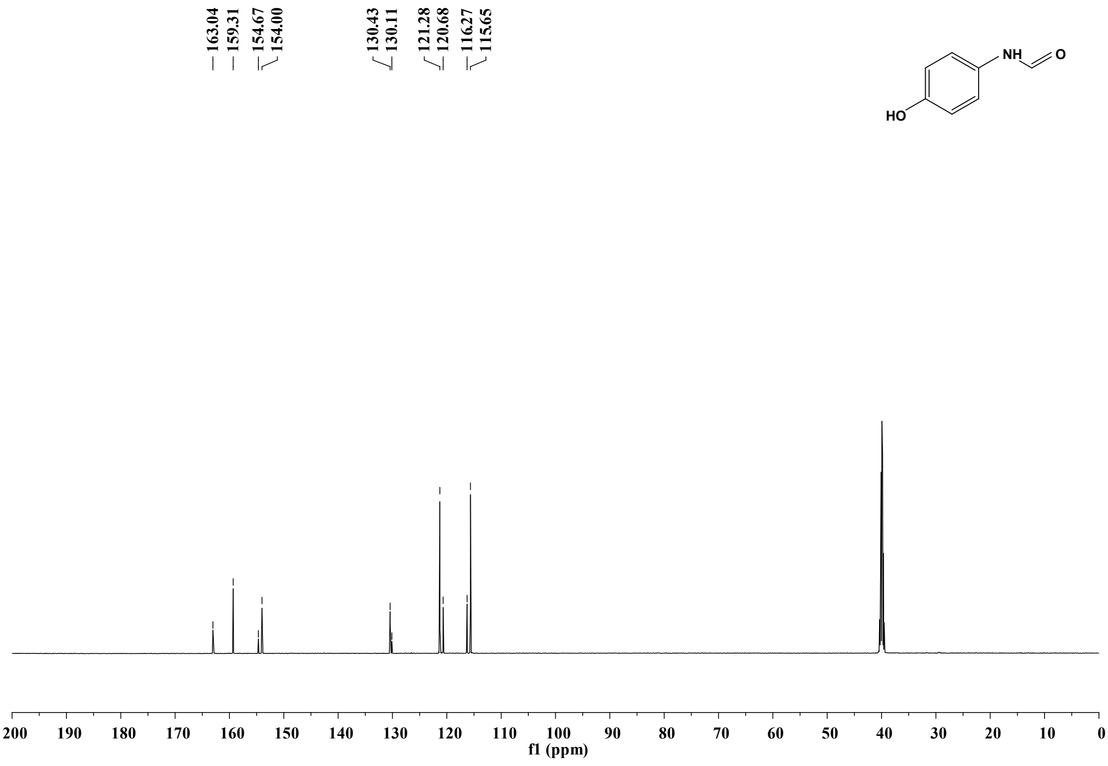
7.38
7.36
6.98
6.73
6.73
6.72
6.72
6.71
6.70
6.70
6.69
NH
O
HO
1.27
1.31
0.30
1.00
1.98
0.63
2.64
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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130.11
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115.65
NH
O
HO
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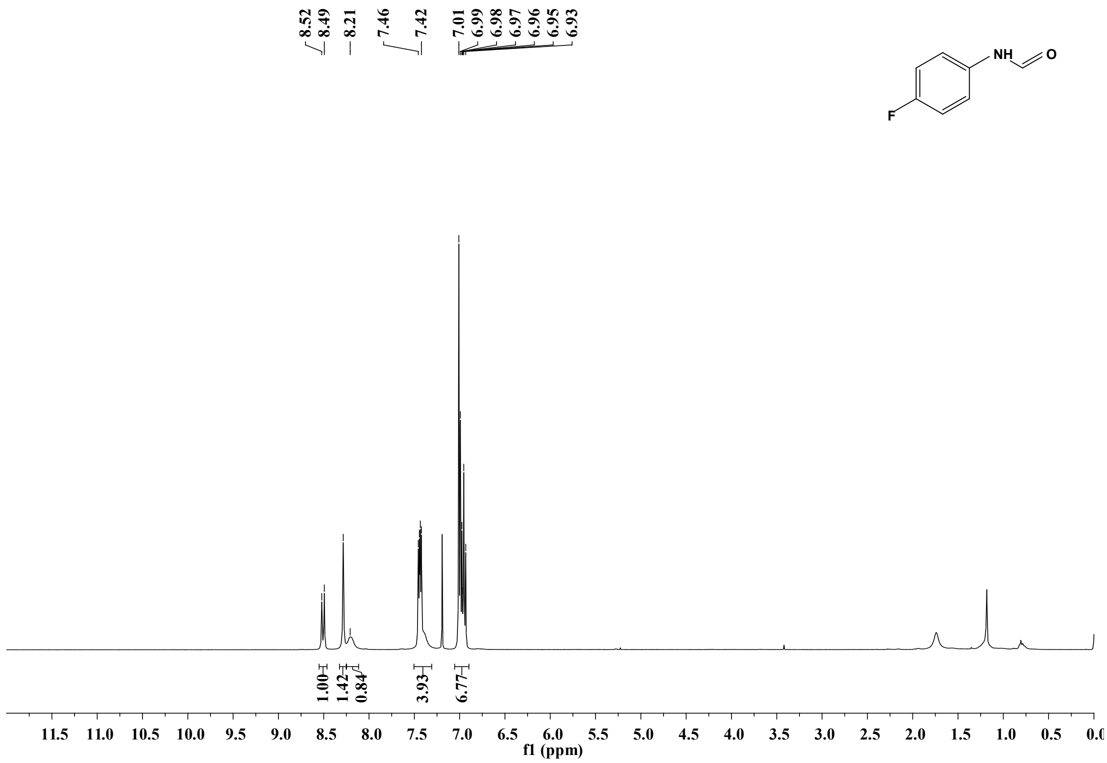
f1 (ppm)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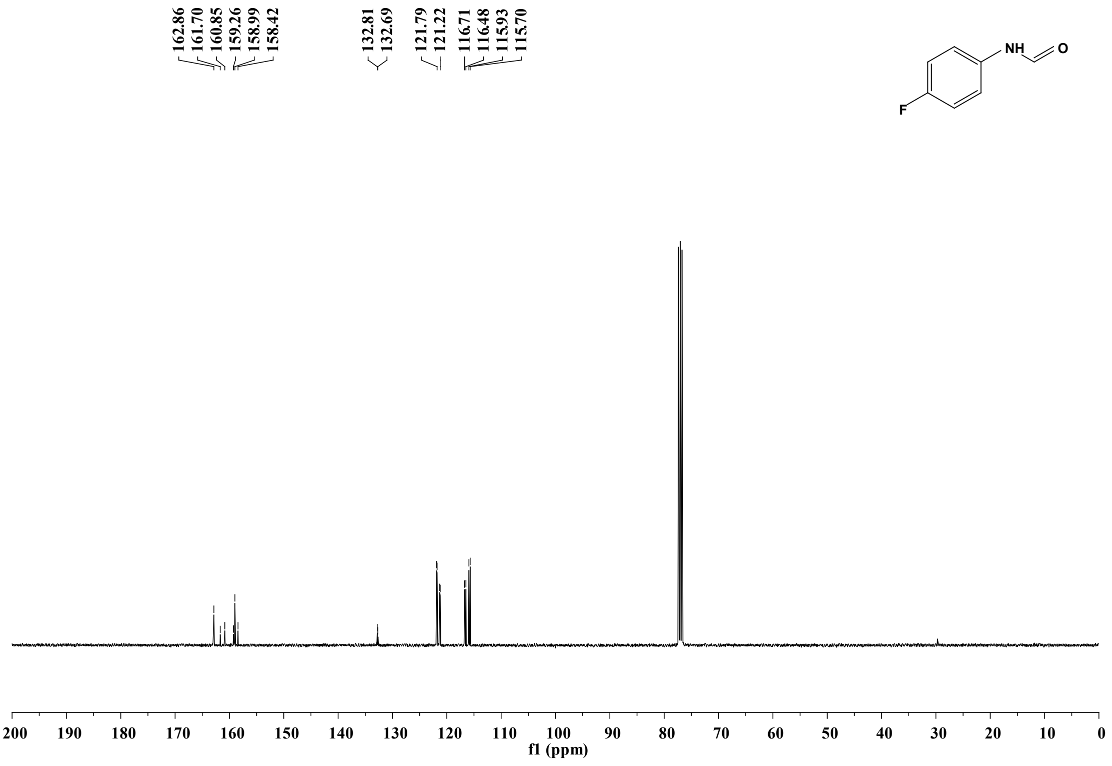
7.01
6.99
6.98
6.97
6.96
6.95
6.93
NH
O
F
1.00
1.42
0.84
3.93
6.77
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.70
NH
O
F
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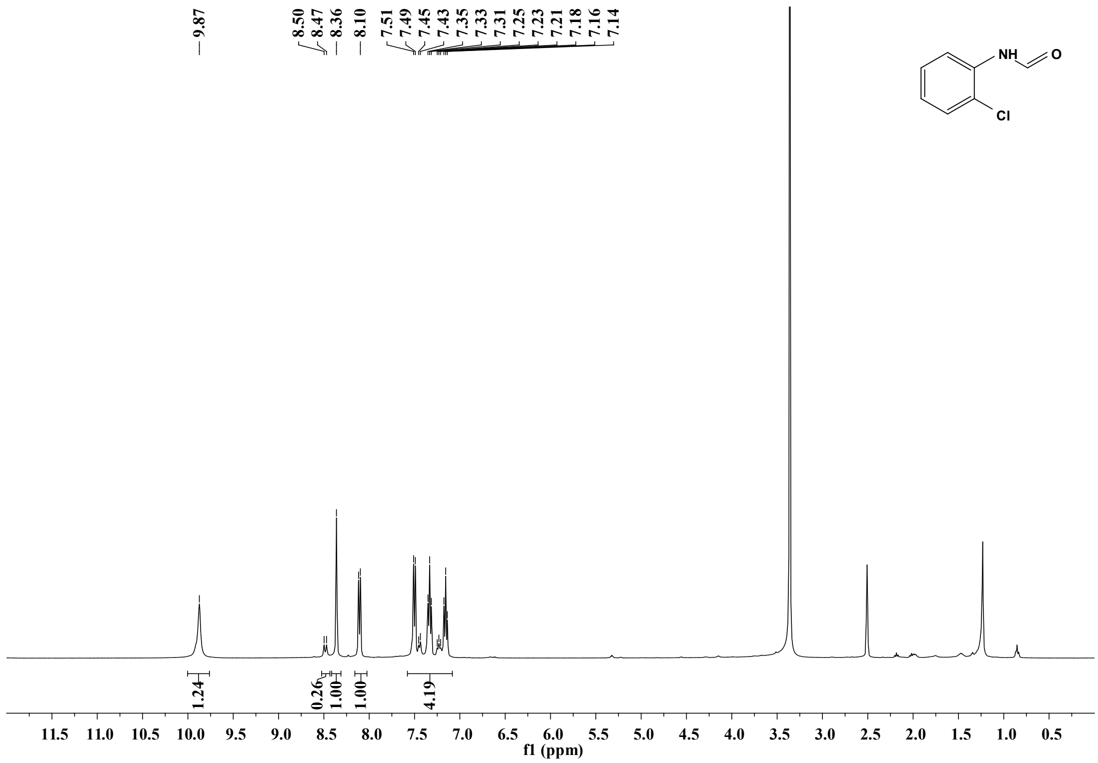
f1 (ppm)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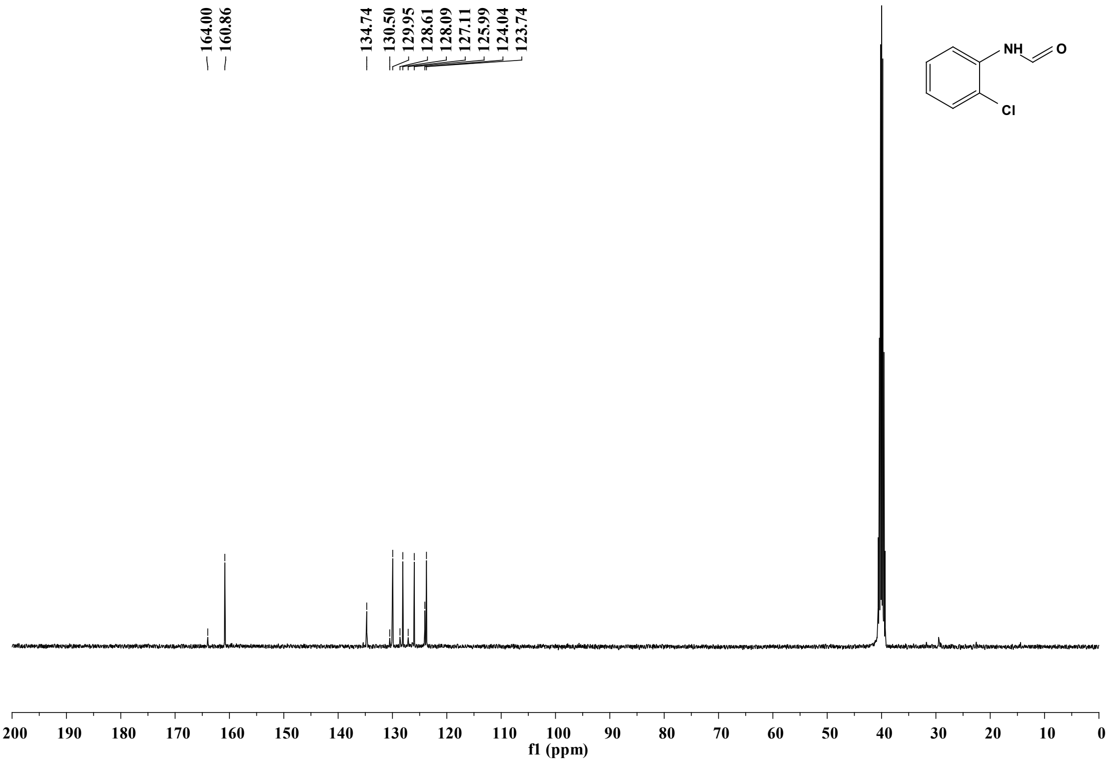
7.25
7.23
7.21
7.18
7.16
7.14
NH
O
Cl
1.24
0.26
1.00
1.00
4.19
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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O
Cl
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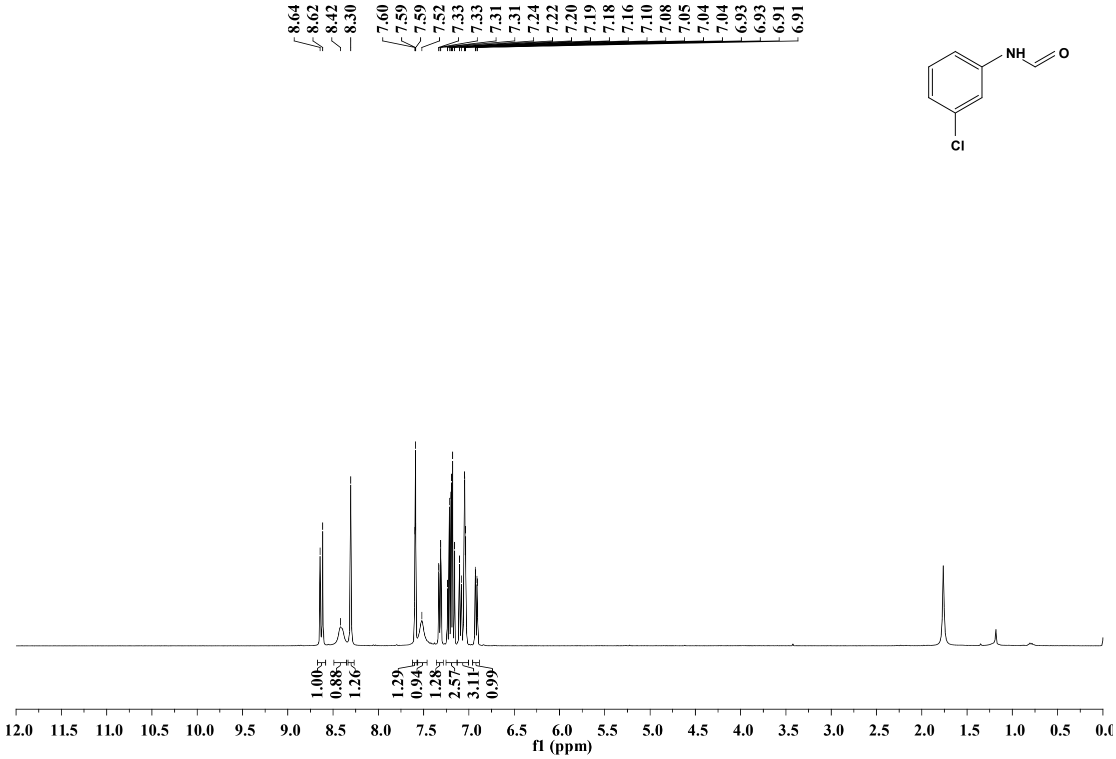
f1 (ppm)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7.22
7.20
7.19
7.18
7.16
7.10
7.08
7.05
7.04
7.04
6.93
6.93
6.91
6.91
NH
O
Cl
1.00
0.88
1.26
1.29
0.94
1.28
2.57
3.11
0.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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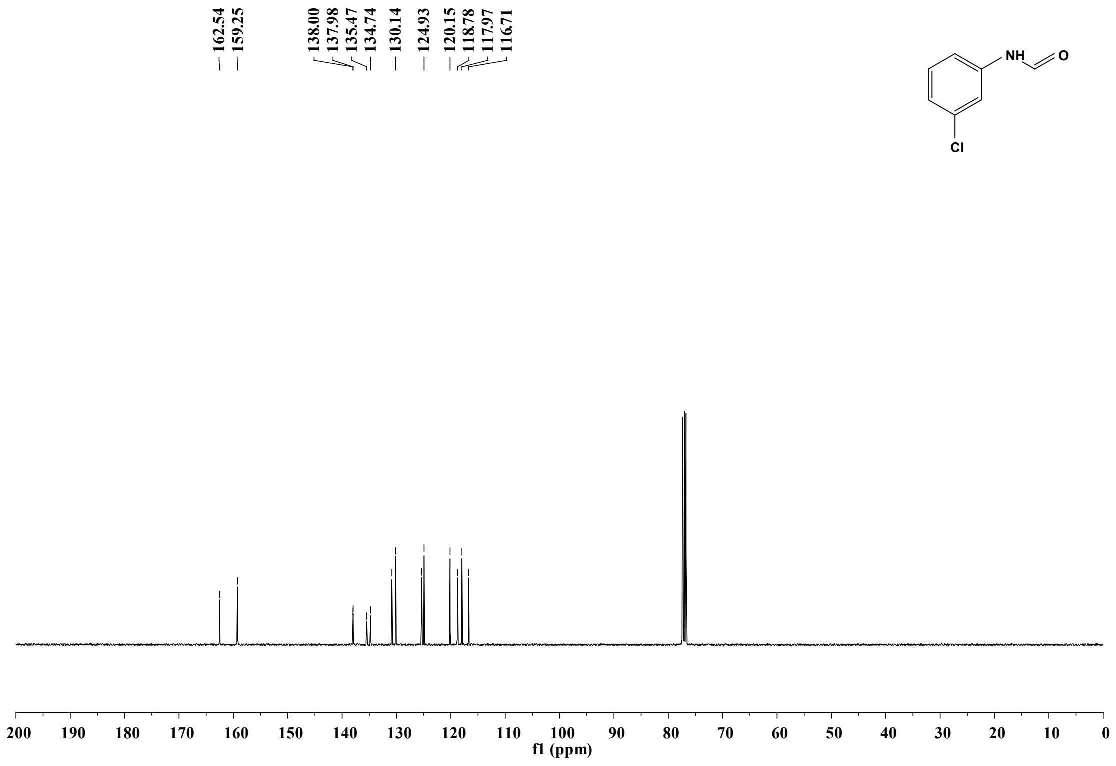
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Cl
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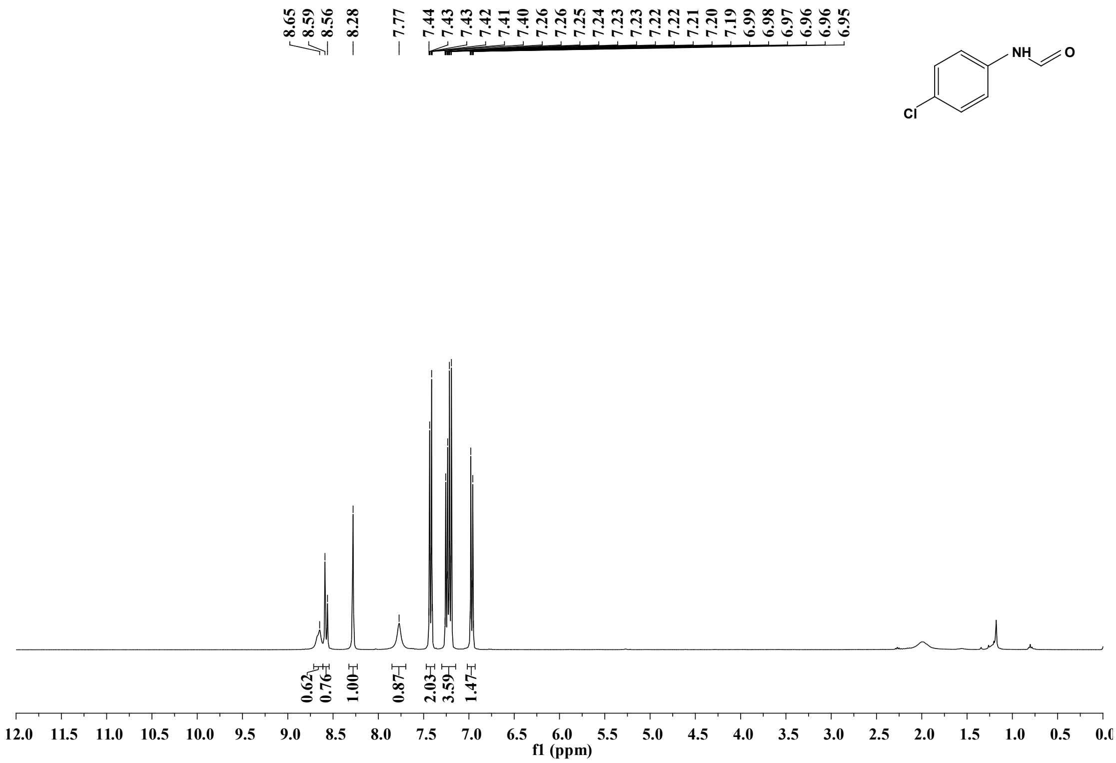
f1 (ppm)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7.24
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7.19
6.99
6.98
6.97
6.96
6.96
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Cl
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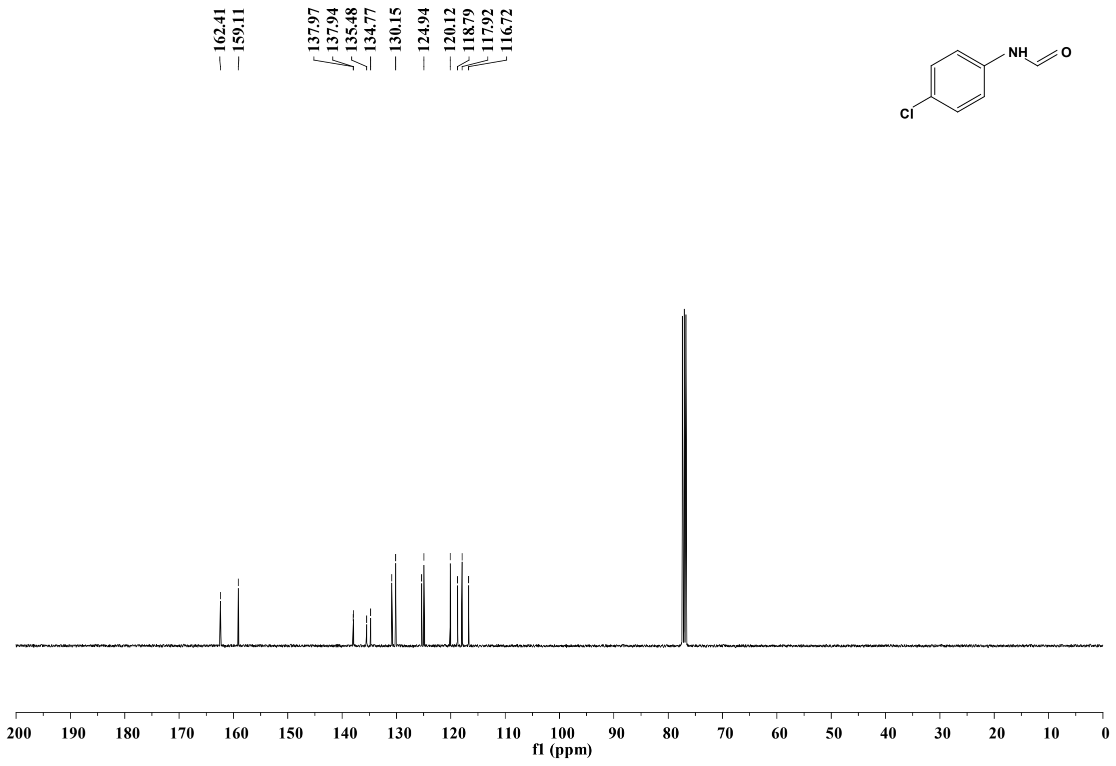
1.47
f1 (ppm)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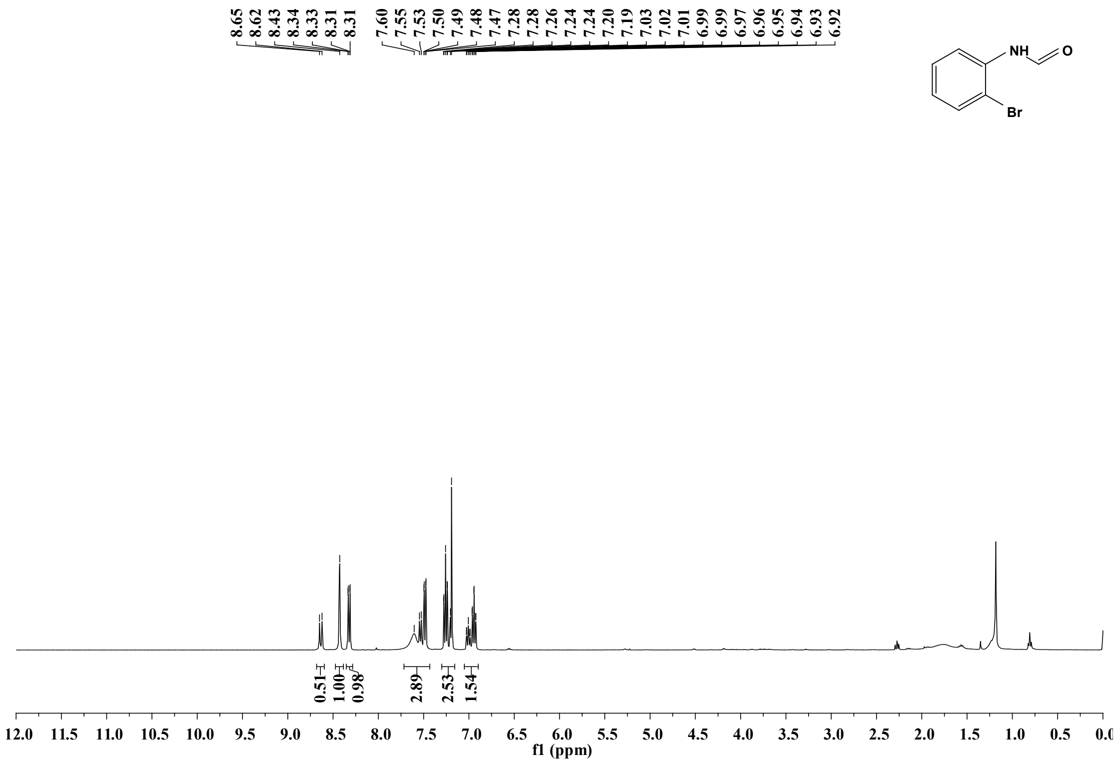
Cl
f1 (ppm)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7.48
7.47
7.28
7.28
7.26
7.24
7.24
7.20
7.19
7.03
7.02
7.01
6.99
6.99
6.97
6.96
6.95
6.94
6.93
6.92
NH
O
Br
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1.00
0.98
2.89
2.53
1.54
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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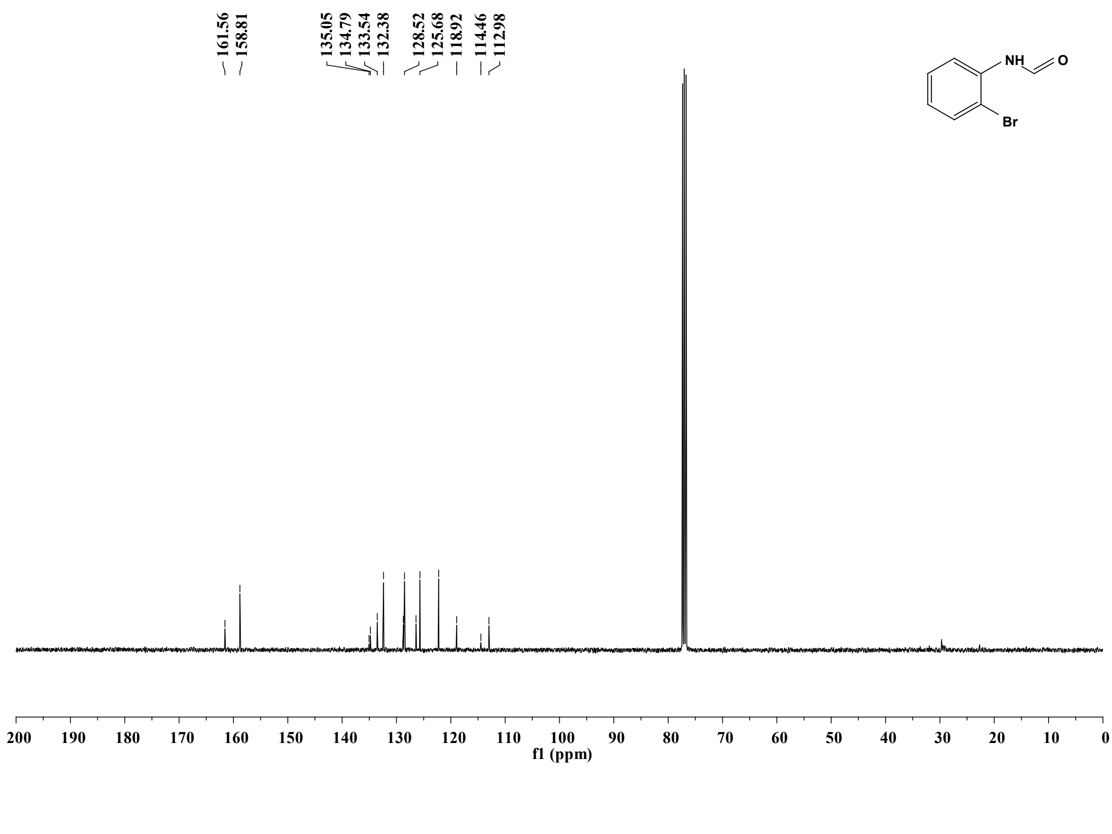
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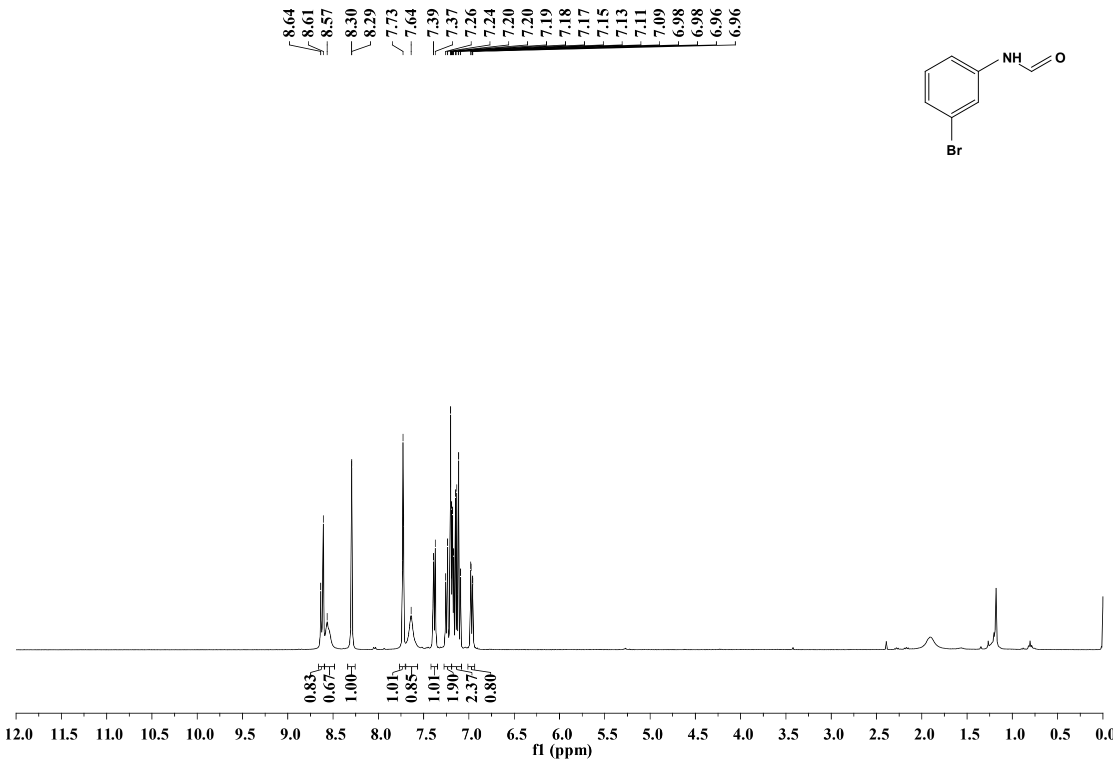

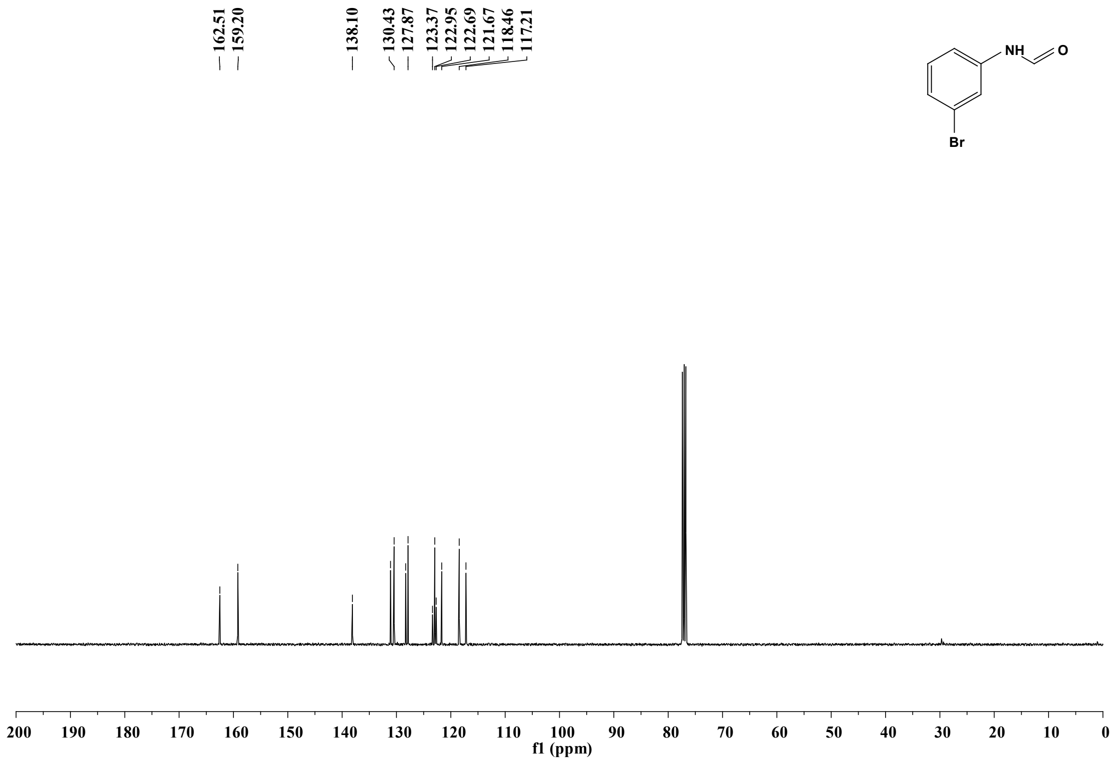

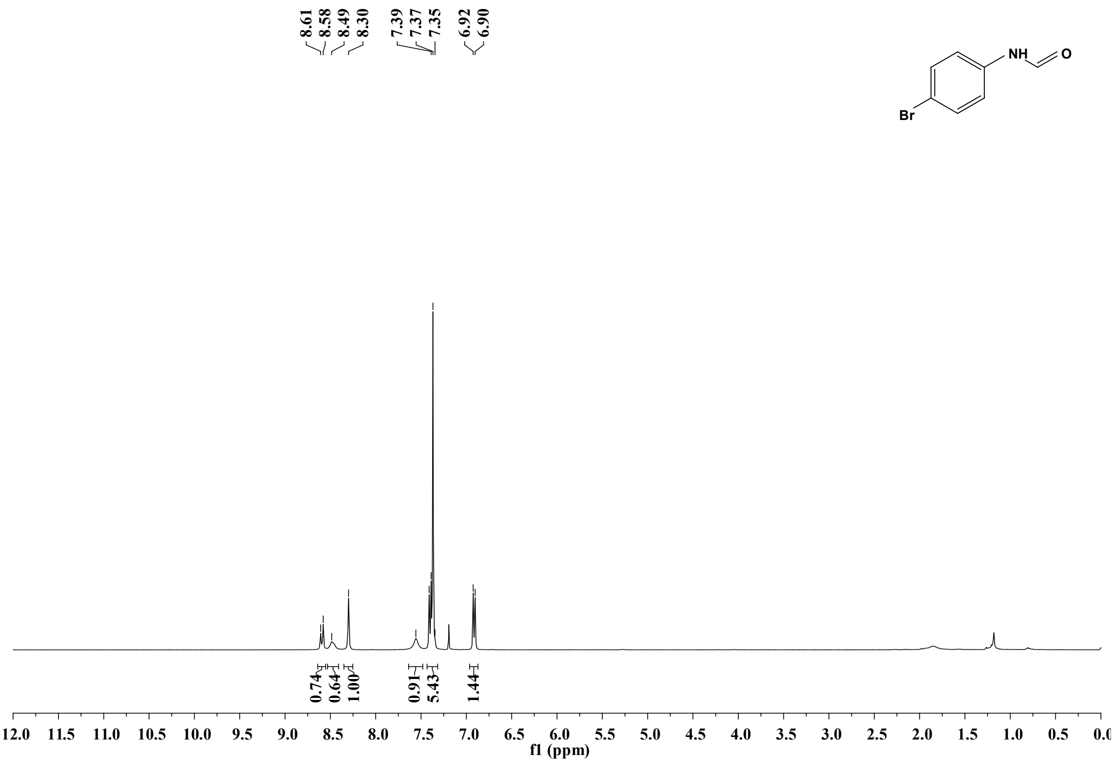
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7.37
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6.92
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NH
O
Br
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0.64
1.00
0.91
5.43
1.44
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 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 0.0
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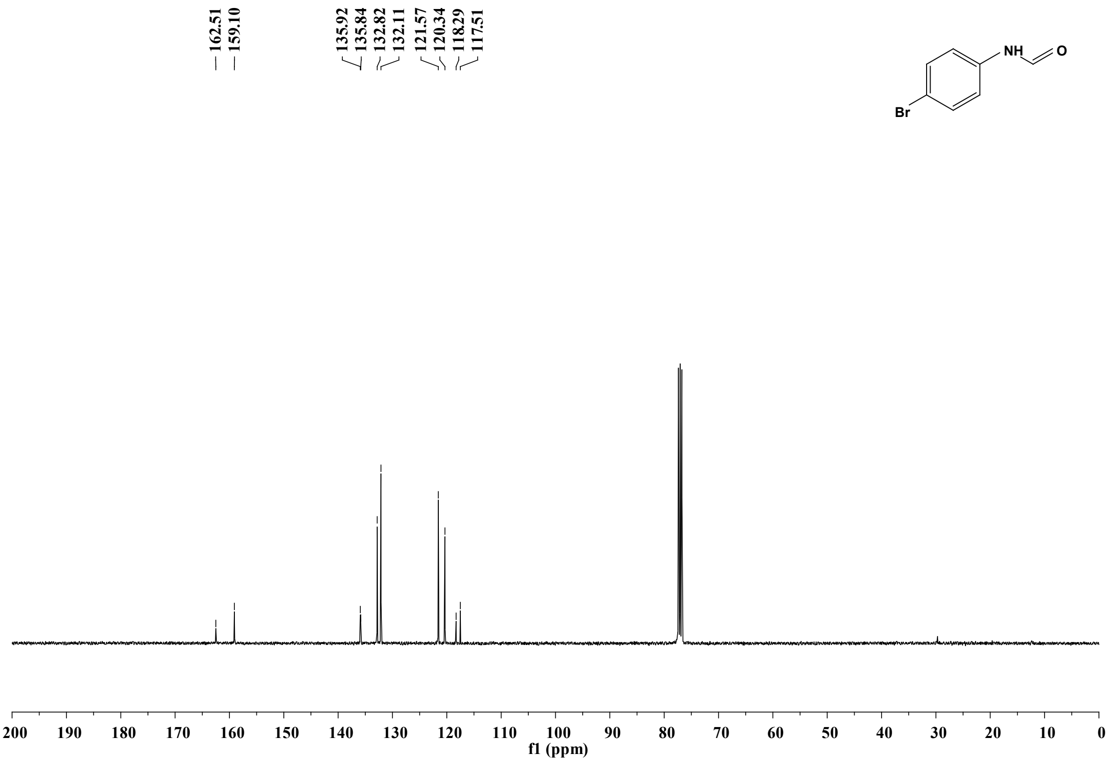
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132.11
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118.29
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NH
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Br
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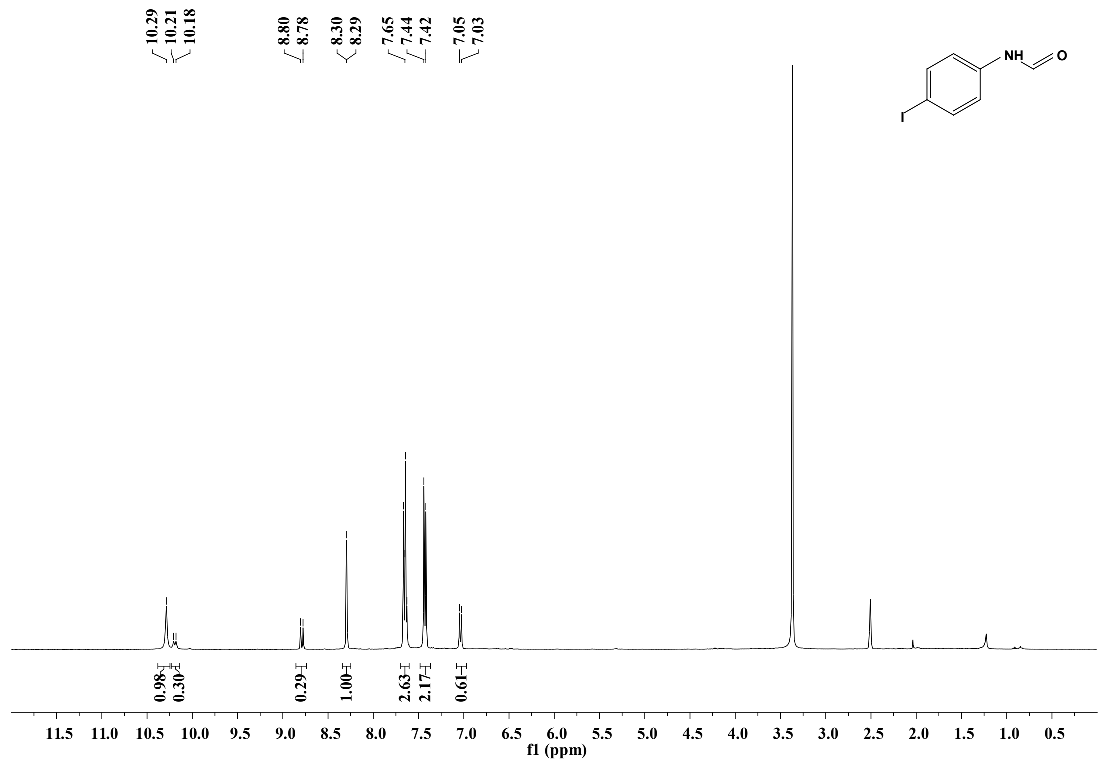
f1 (ppm)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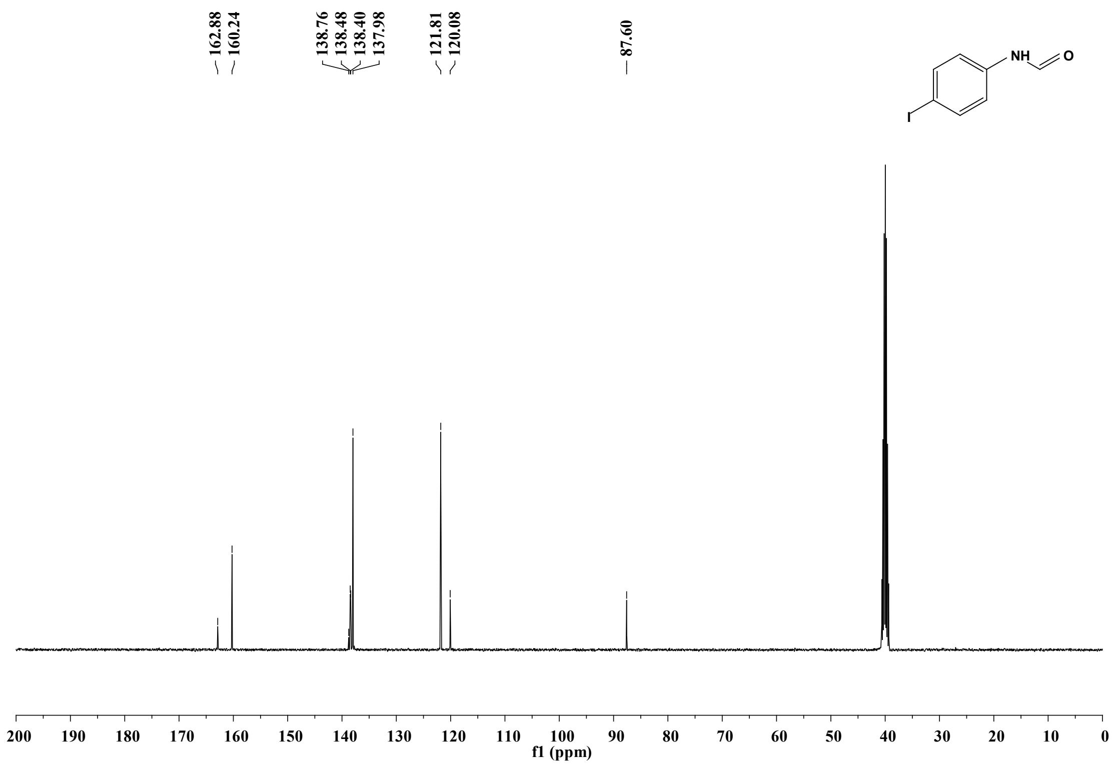
7.65
7.44
7.42
7.05
7.03
NH
O
I
0.98
0.30
0.29
1.00
2.63
2.17
0.61
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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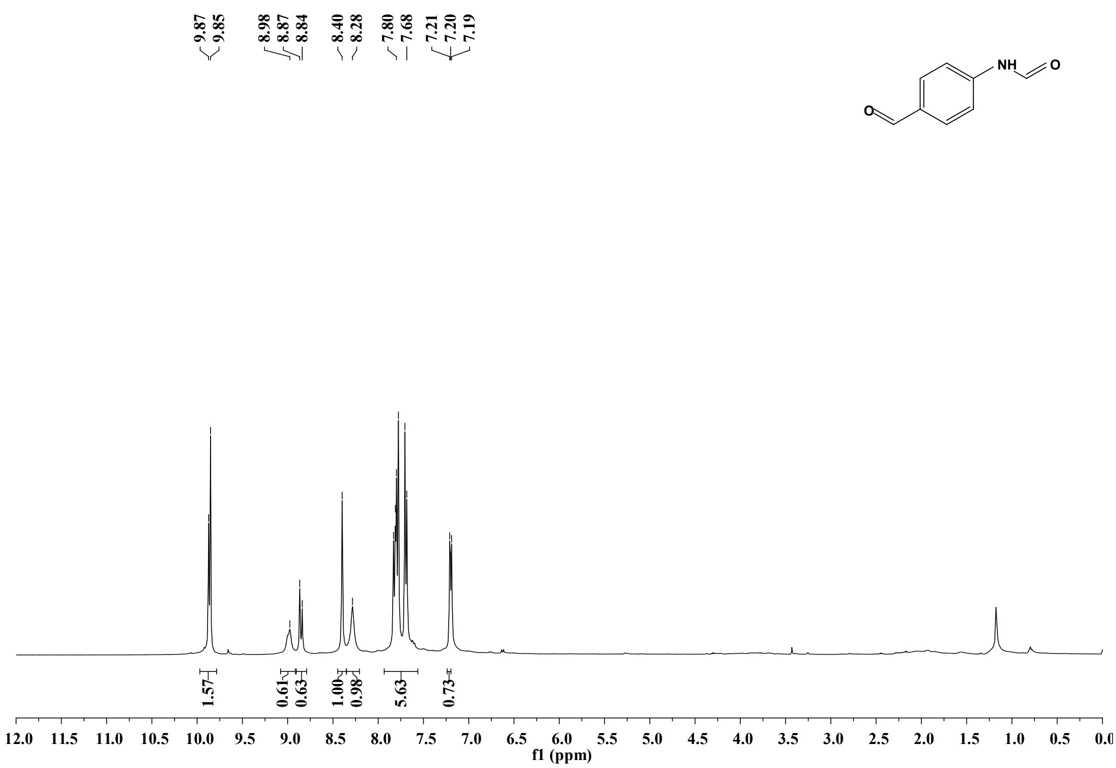
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7.19
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O
O
1.57
0.61
0.63
1.00
0.98
5.63
0.73
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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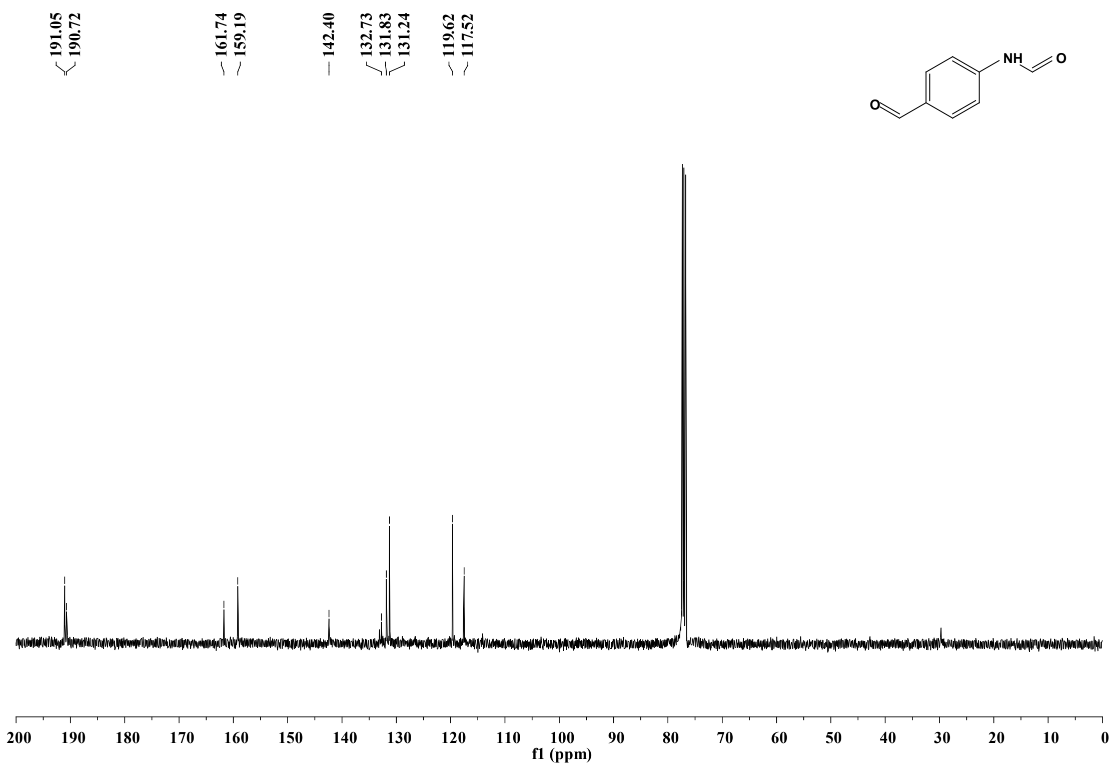
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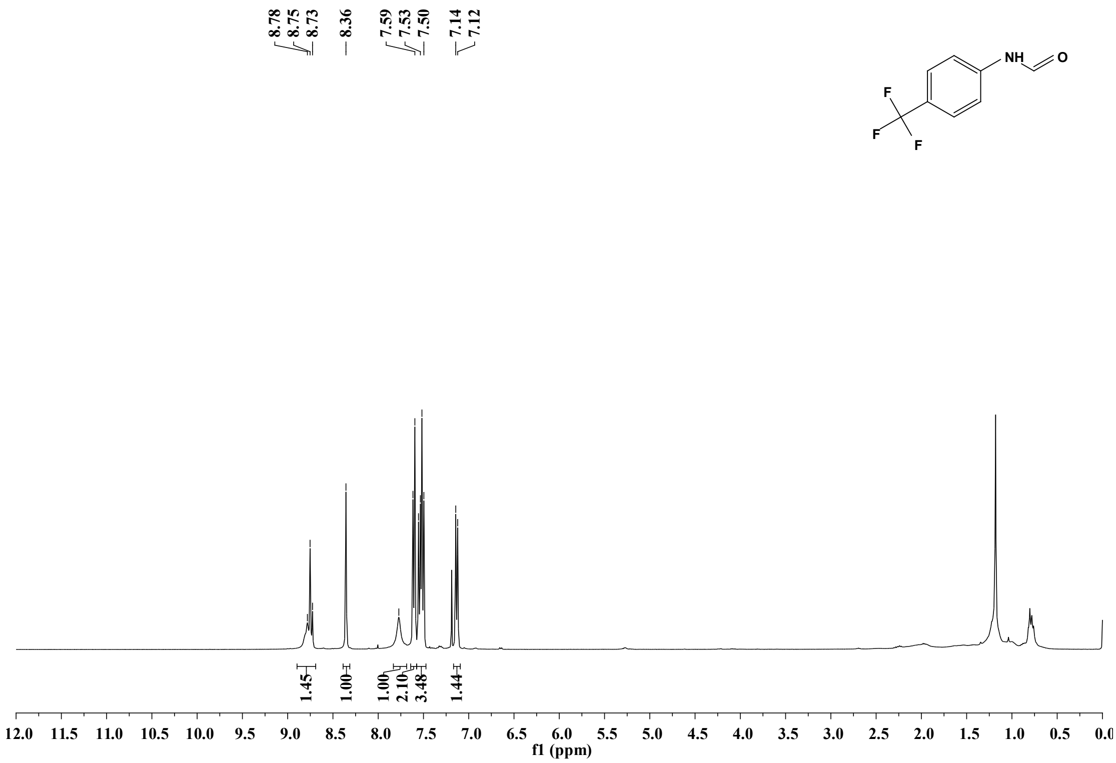
f1 (ppm)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7.50
7.14
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O
F
F
F
1.45
1.00
1.00
2.10
3.48
1.44
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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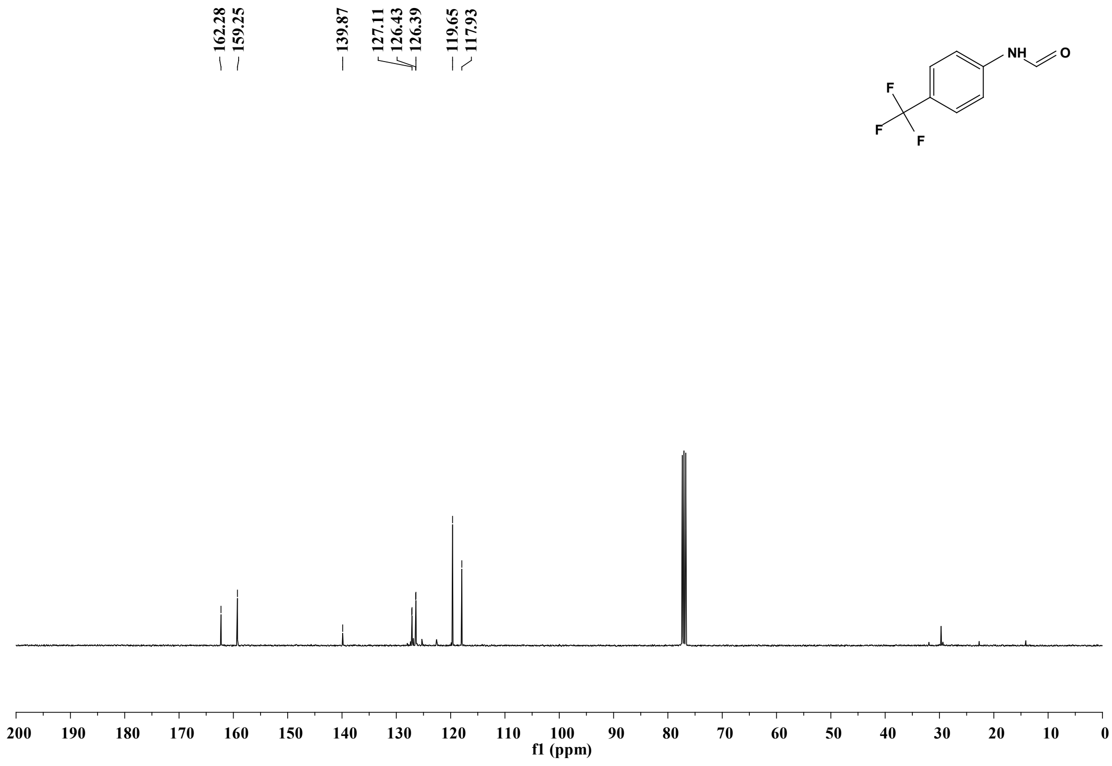
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F
F
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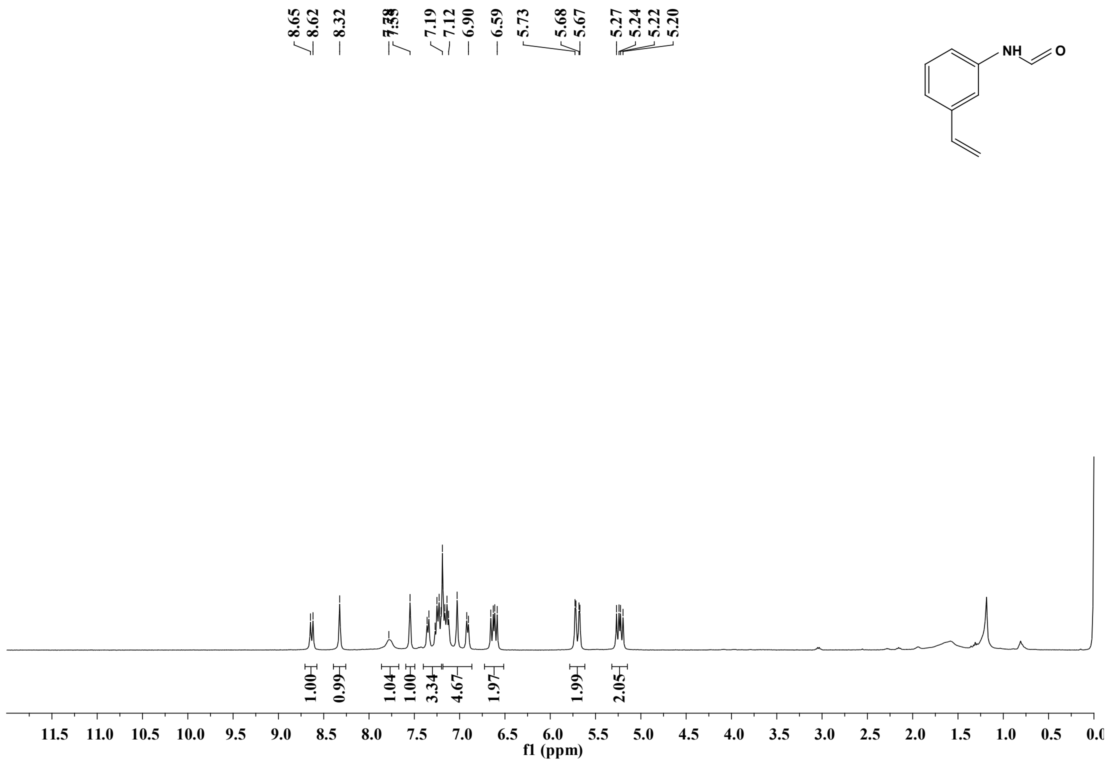
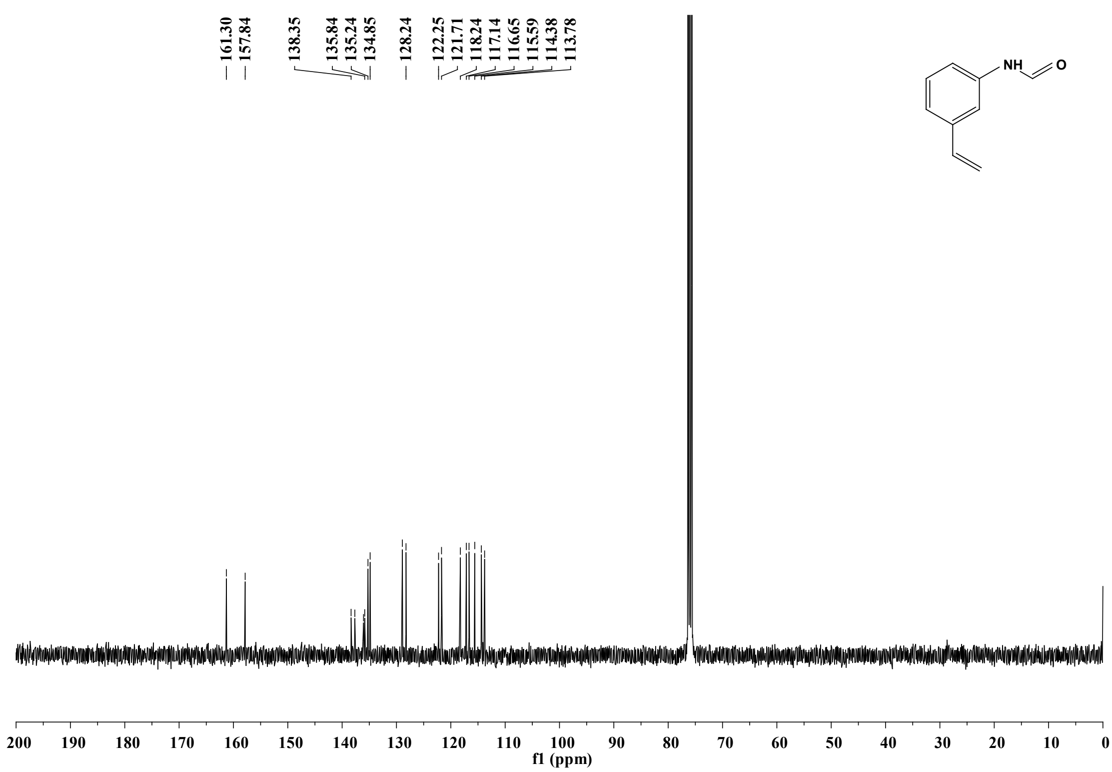
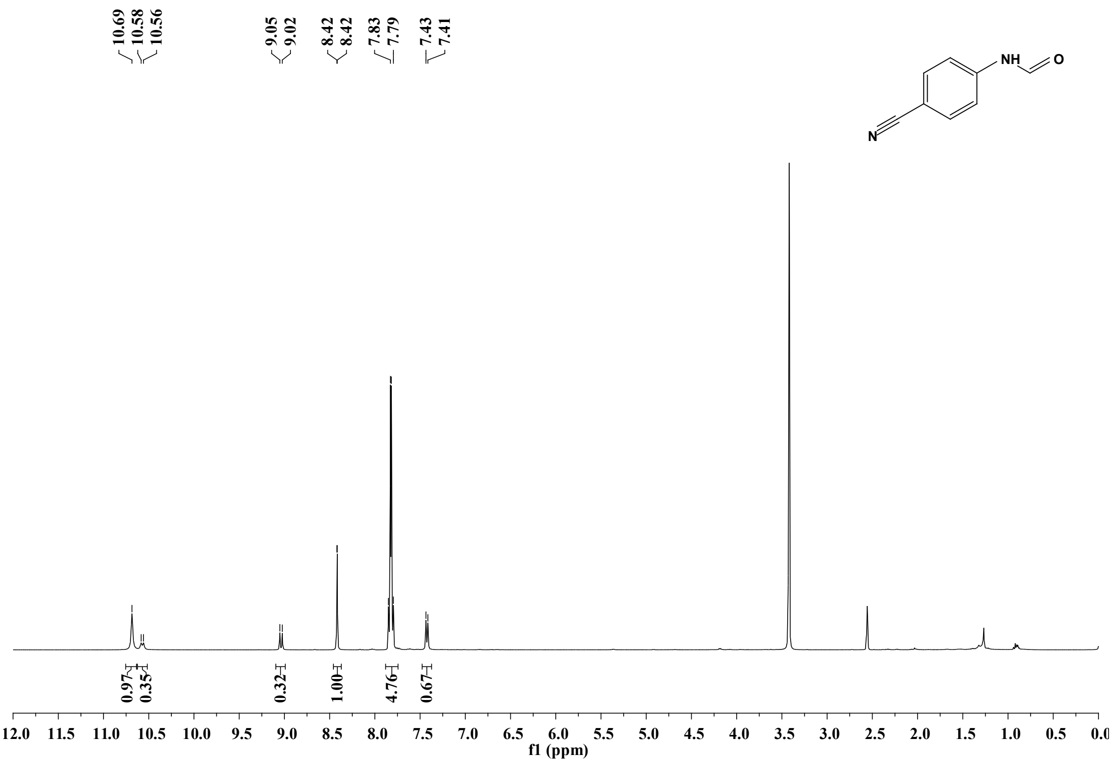
f1 (ppm)



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7.43
7.41
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N
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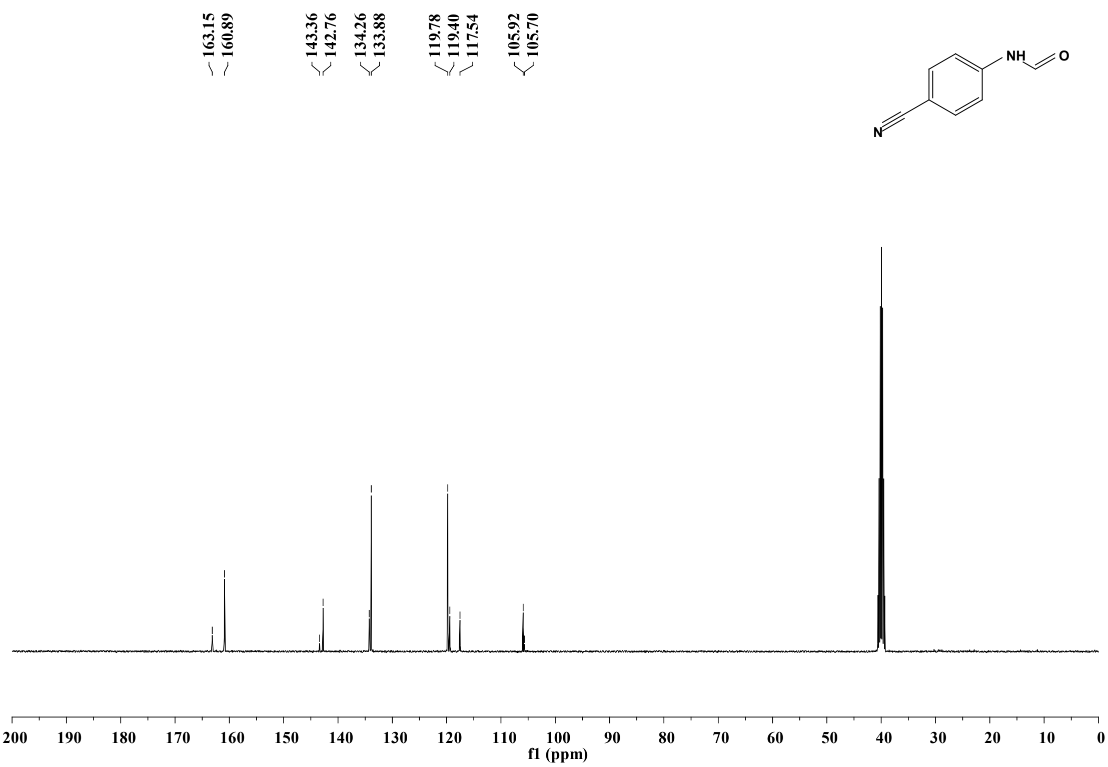
0.35
0.32
1.00
4.76
0.67
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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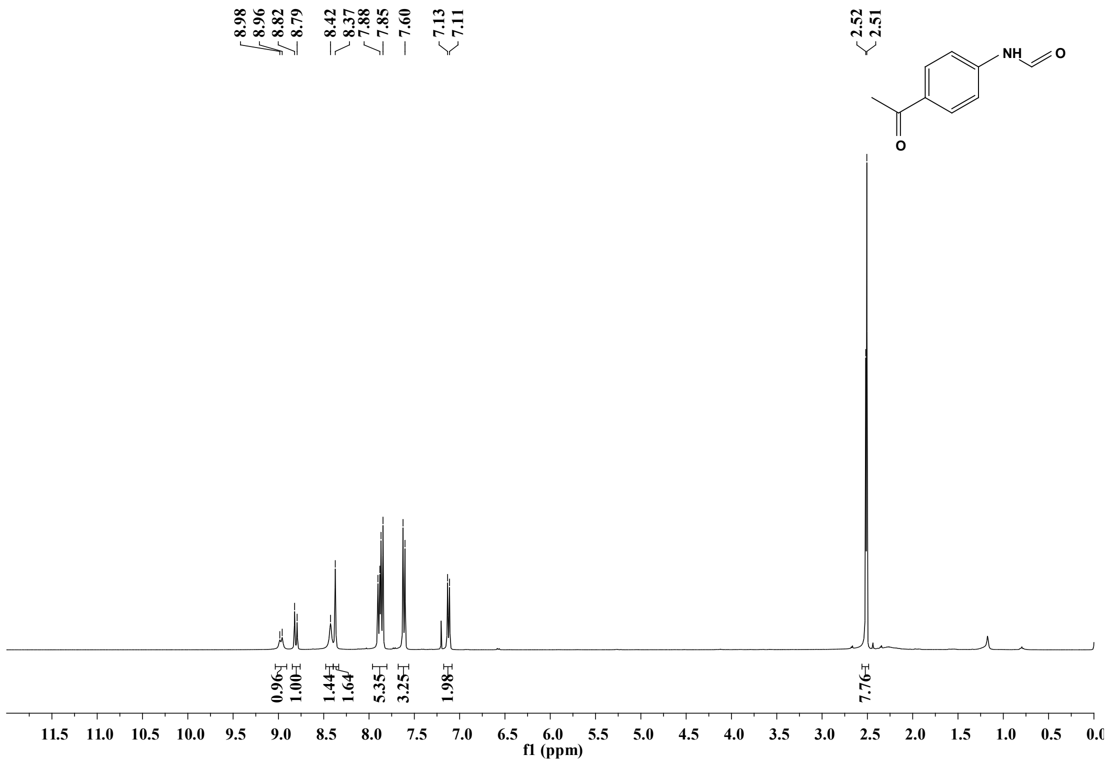
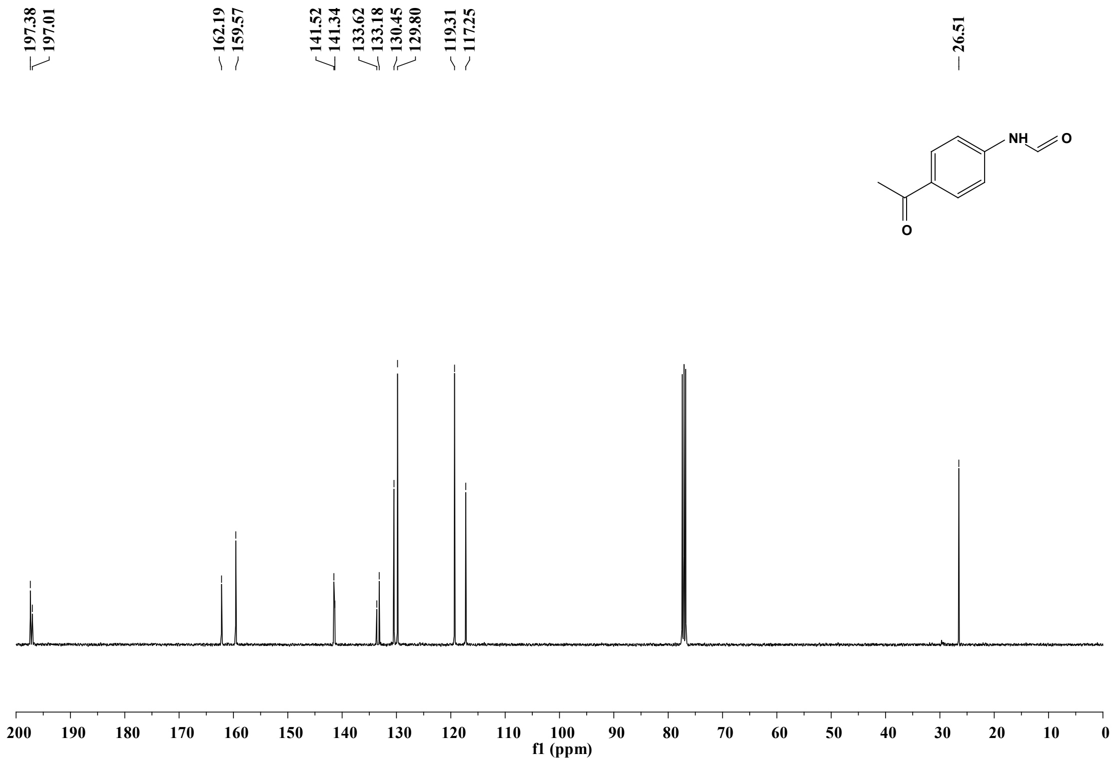
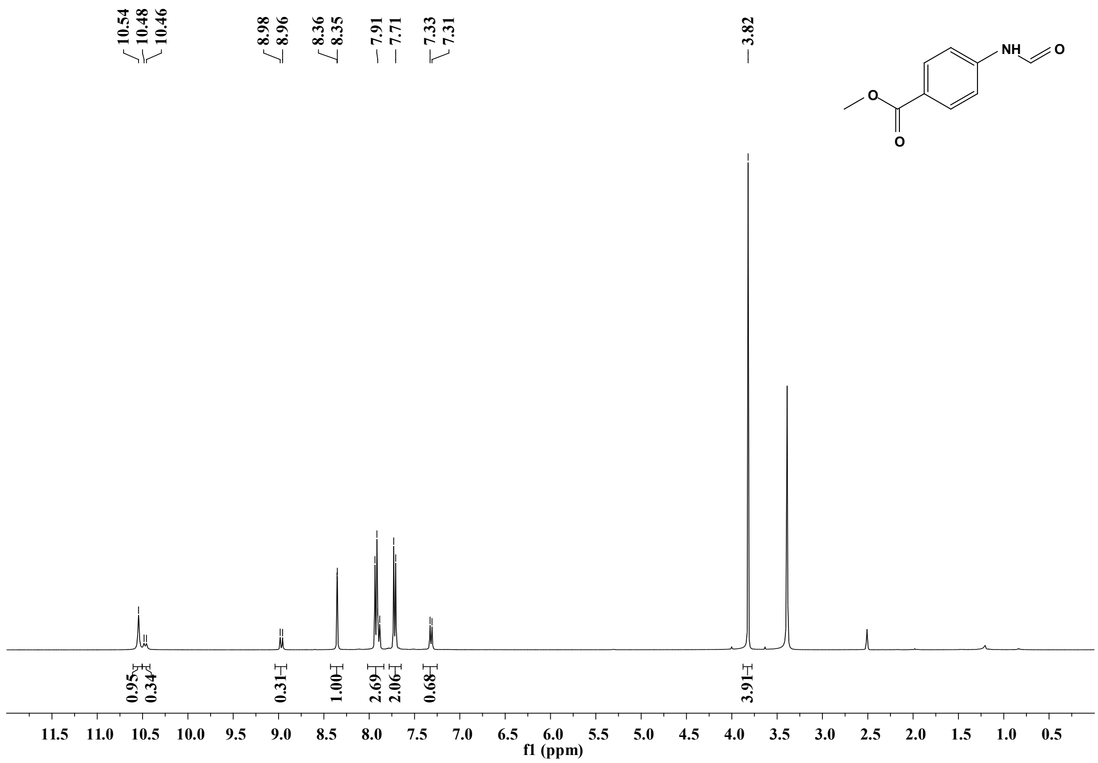
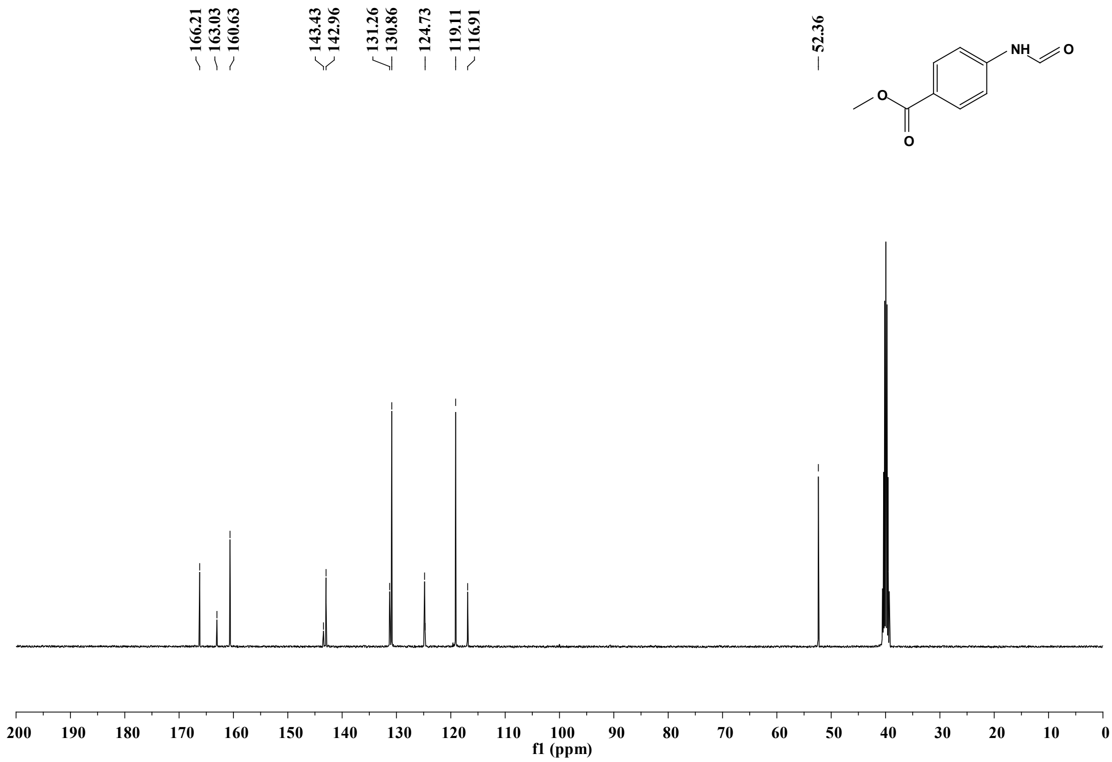
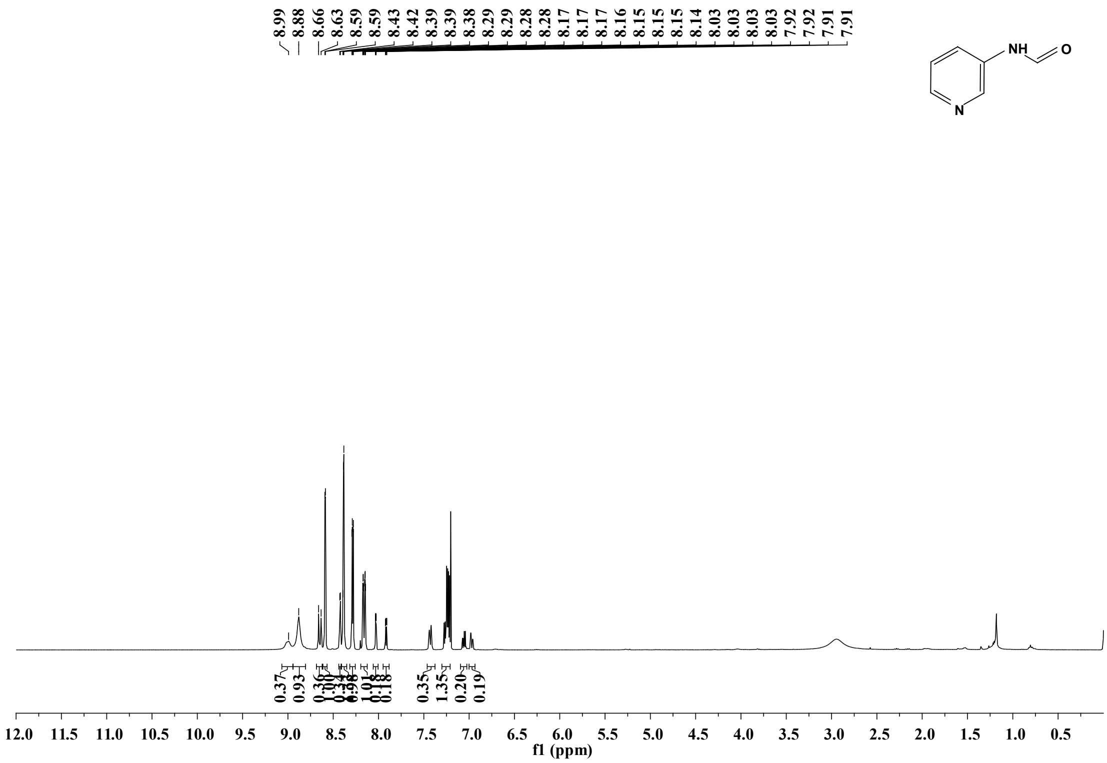
160.89
143.36
142.76
134.26
133.88
119.78
119.40
117.54
105.92
105.70
NH
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

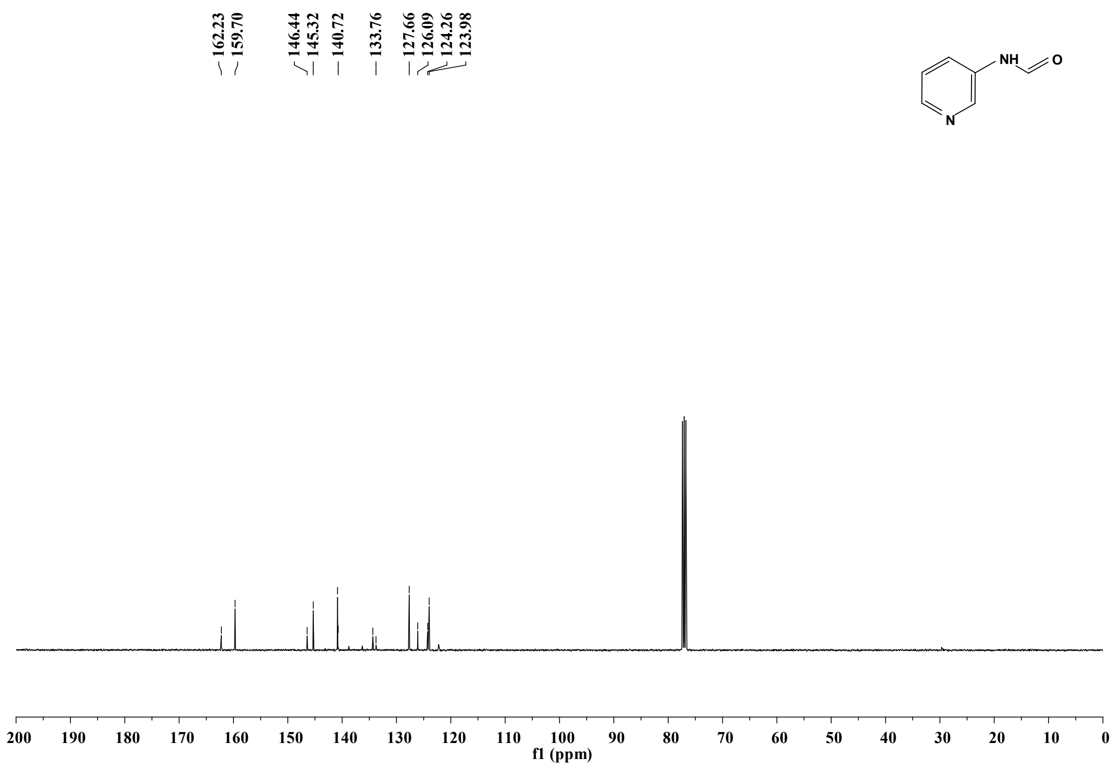

8.98
8.96
8.82
8.79
8.42
8.37
7.88
7.85
7.60
7.13
7.11
2.52
2.51
NH
O
O
0.96
1.00
1.44
1.64
5.35
3.25
1.98
7.76
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.38
197.01
162.19
159.57
141.52
141.34
133.62
133.18
130.45
129.80
119.31
117.25
26.51
NH
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.54
10.48
10.46
8.98
8.96
8.36
8.35
7.91
7.71
7.33
7.31
3.82
NH
O
O
O
0.95
0.34
0.31
1.00
2.69
2.06
0.68
3.91
11.5 11.0 10.5 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
f1 (ppm)


166.21
163.03
160.63
143.43
142.96
131.26
130.86
124.73
119.11
116.91
52.36
NH
O
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.99
8.88
8.66
8.63
8.59
8.59
8.59
8.43
8.42
8.39
8.39
8.38
8.29
8.29
8.28
8.28
8.17
8.17
8.17
8.16
8.15
8.15
8.15
8.14
8.03
8.03
8.03
8.03
7.92
7.92
7.91
7.91
NH
O
N
0.37
0.93
1.01
1.35
0.35
0.20
0.19
12.0 11.5 11.0 10.5 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
f1 (ppm)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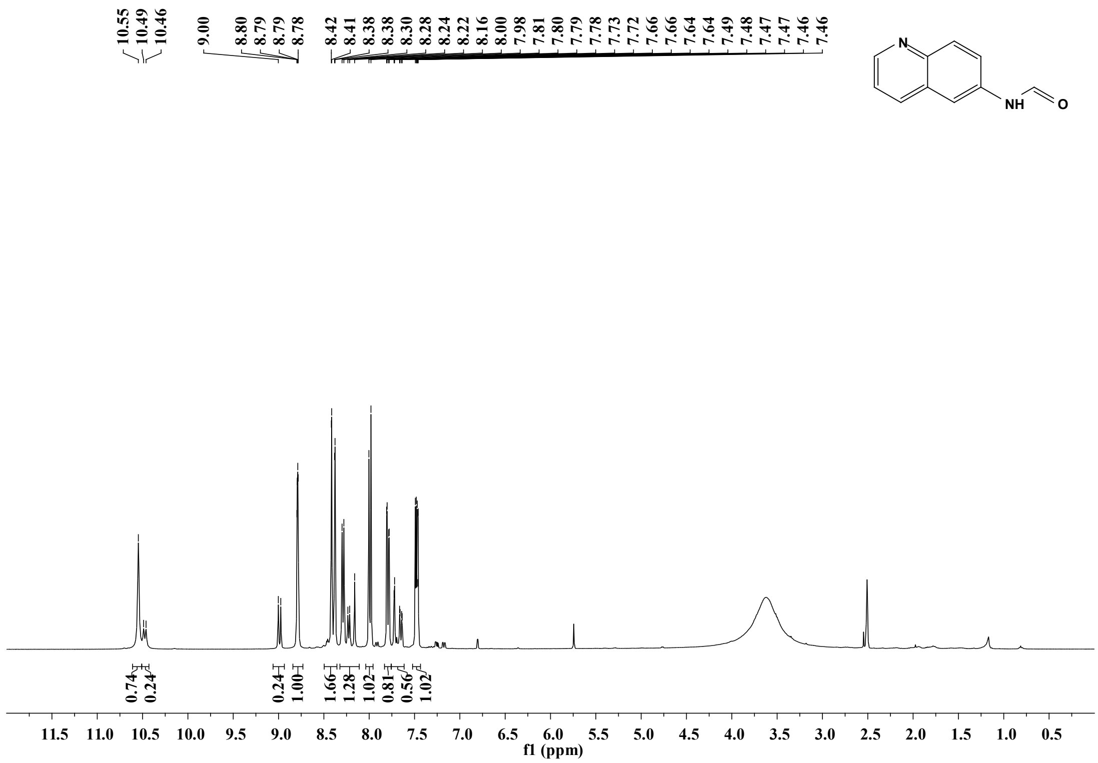
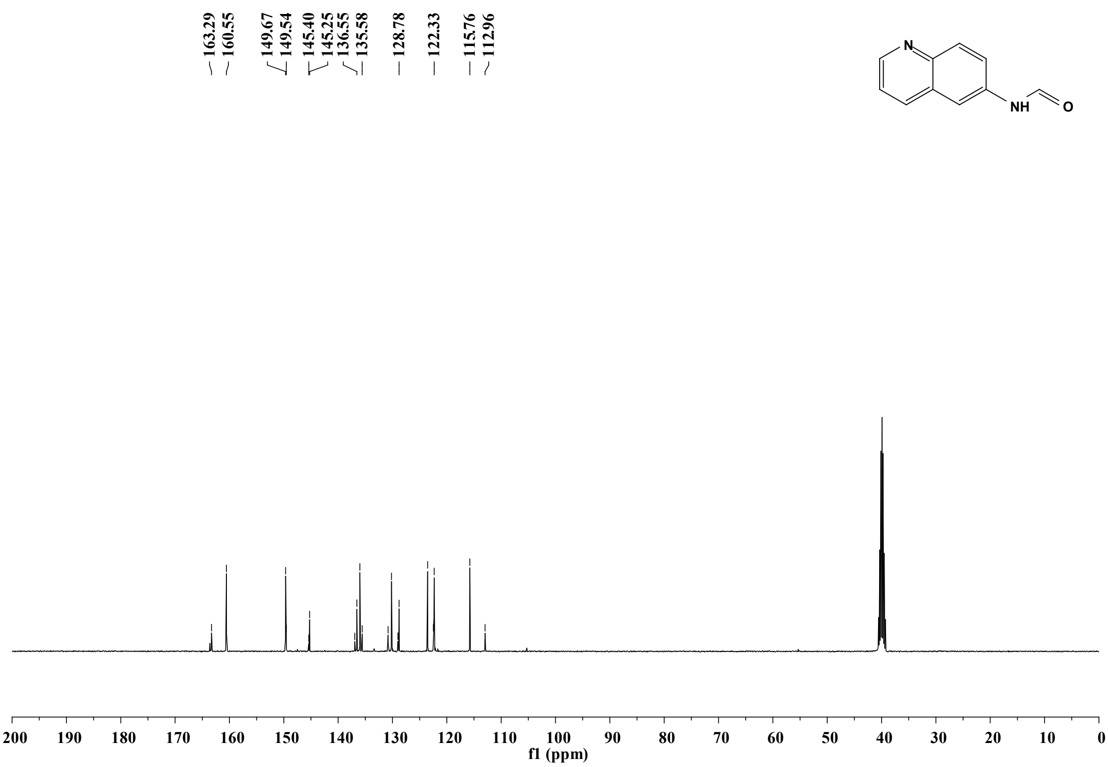
159.70
146.44
145.32
140.72
133.76
127.66
126.09
124.26
123.98
NH
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


10.55
10.49
10.46
9.00
8.80
8.79
8.79
8.78
8.42
8.41
8.38
8.38
8.30
8.28
8.24
8.22
8.16
8.00
7.98
7.81
7.80
7.79
7.78
7.73
7.72
7.66
7.66
7.64
7.49
7.48
7.47
7.47
7.46
7.46
N
NH
O
0.74
0.24
0.24
1.00
1.66
1.28
1.02
0.81
0.56
1.02
11.5 11.0 10.5 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
f1 (ppm)


163.29
160.55
149.67
149.54
145.40
145.25
136.55
135.58
128.78
122.33
115.76
112.96
N
NH
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

10.Reference

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