Electronic Supplementary information

Palladium nanoparticles immobilized on an amine-functionalized MIL-101(Cr) as a highly active catalyst for oxidative amination of aldehydes

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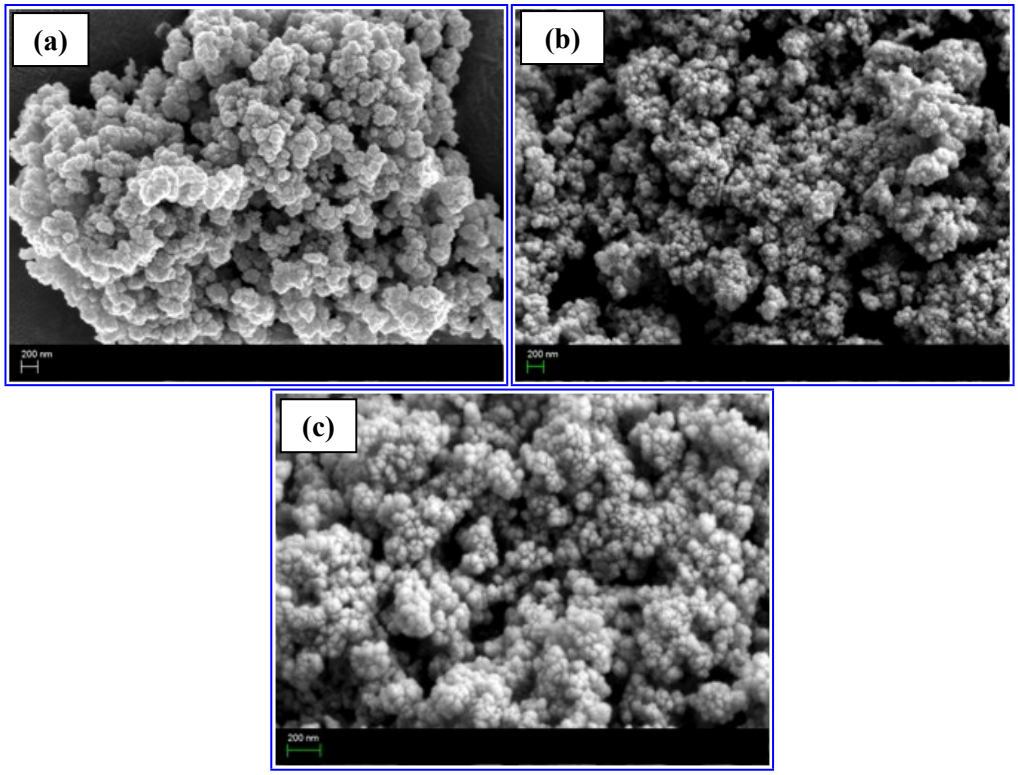


Fig. S1 FE-SEM images of (a) NH_2-MIL-101(Cr), (b) Fresh Pd/NH_2-MIL-101(Cr), (C) Recovered Pd/NH_2-MIL-101(Cr)

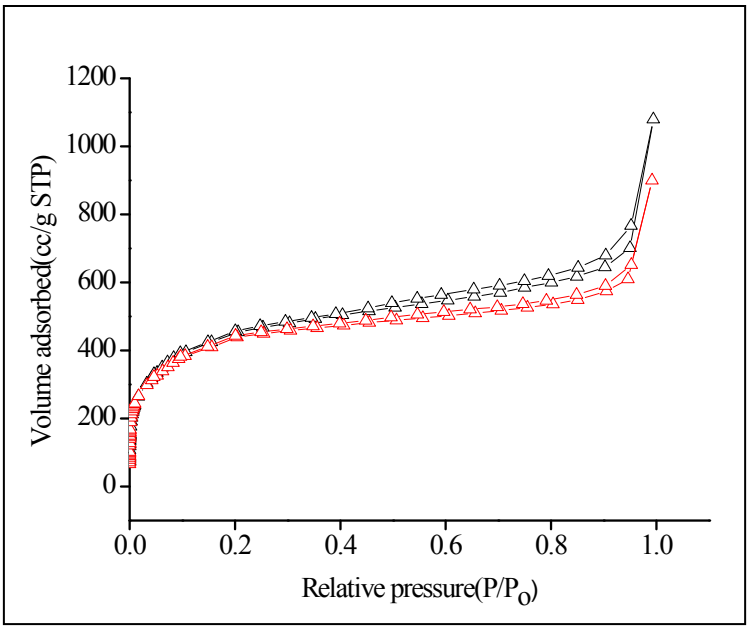


Fig. S2 N_2 adsorption isotherm of NH_2-MIL-101(Cr) (black) and Pd/NH_2-MIL-101(Cr) (red)

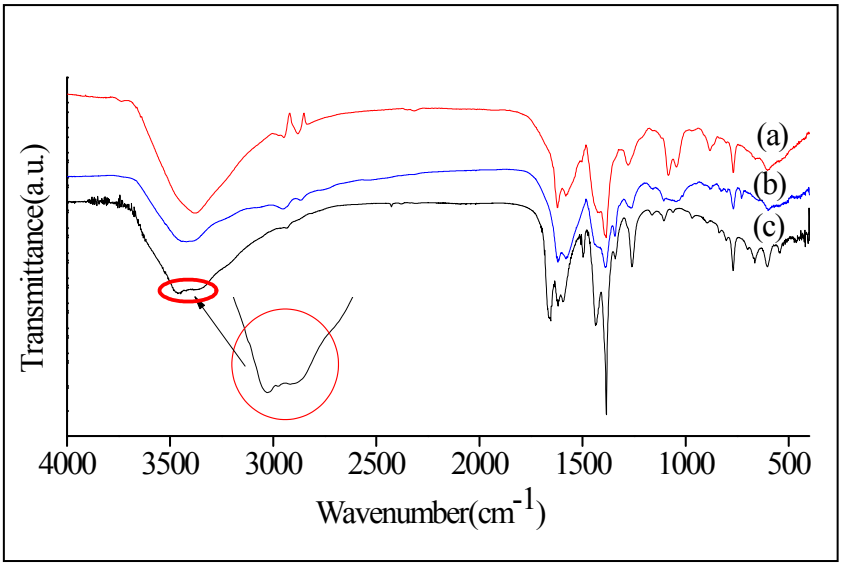


Fig. S3 FT-IR spectra of (a) Fresh Pd/NH_2-MIL-101(Cr), (b) Recovered Pd/NH_2-MIL-101(Cr) and (c) NH_2-MIL-101(Cr)

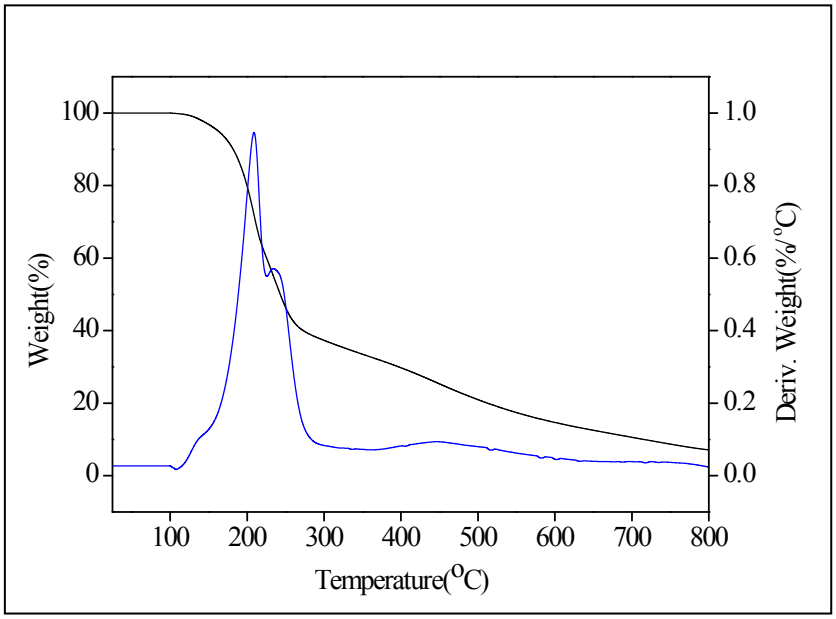


Fig. S4 Thermogravimetric (black) and derivative curve (blue) of Pd/NH_2-MIL-101(Cr)

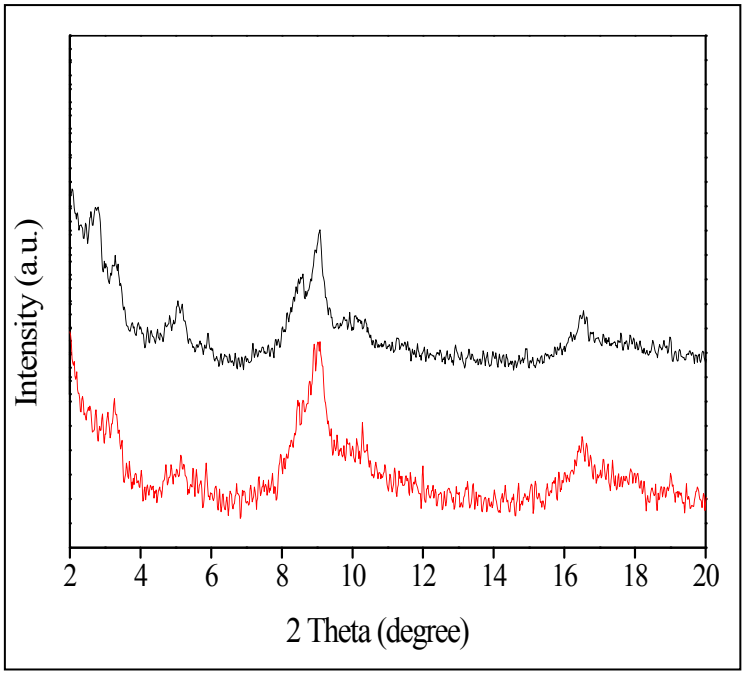


Fig. S5 PXRD pattern of Fresh catalyst (Black), Recovered catalyst (Red)

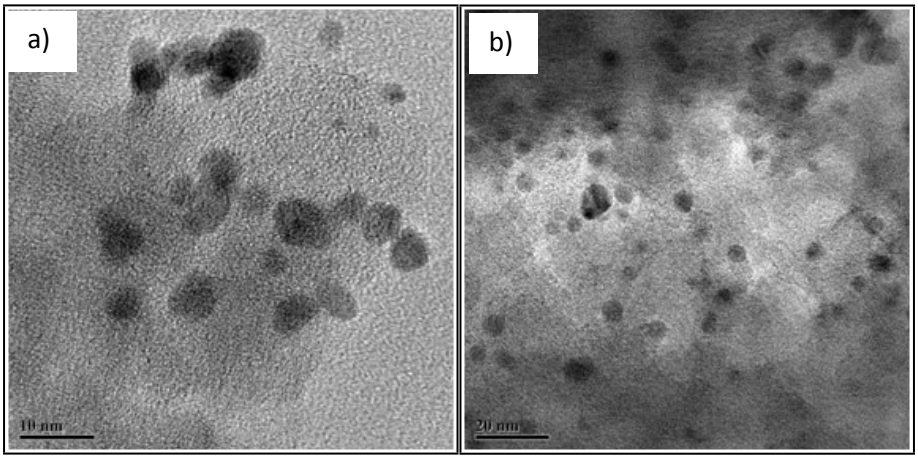


Fig. S6 TEM images of the recovered Pd/NH_2-MIL-101(Cr)

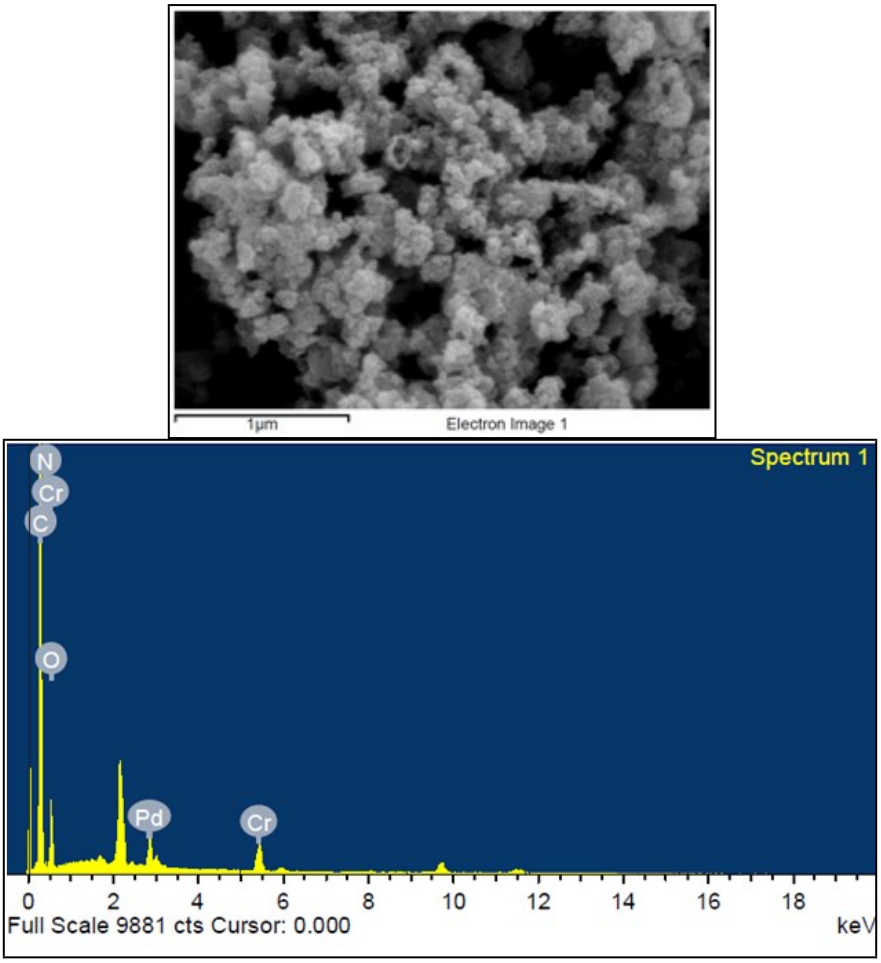
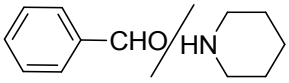
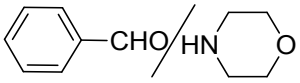
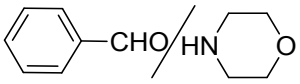
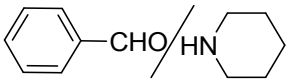
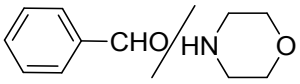
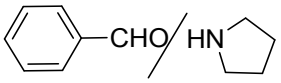
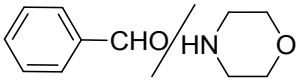
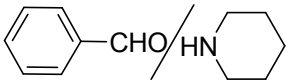
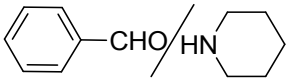


Fig. S7 EDS spectrum of the recovered Pd/NH_2-MIL-101(Cr)

Table S1: Oxidative amination of benzaldehyde with different amines catalyzed by other reported catalyst in the literature

Entry	Aldehydes/Amines	Reaction conditions	Yield[a] (%)	TON	Ref.
1		$[Rh(COD)_2]BF_4$/Toluene/140°C/8h	78	31	25
2		$CuSO_4.5H_2O$/MeCN/60°C/6h/TBHP/$CaCO_3$	78	15	27
3		$FeSO_4.7H_2O$/MeCN/60°C/6h/TBHP/$CaCO_3$	74	14	28
4		$RuH_2(PPh_3)_4$/NHC precursor/NaH/MeCN/Toluene/Reflux/24h	66	13	29
5		NBS/NHC catalyst/Et_3N/CH_3CN/25°C/ 18 h	77	7	A
6		La[N(TMS)2]/C_6D_6/25°C/24h	38	22	B
7		KI/TBHP/H_2O/80°C/15h	63	12	C
8[b]		SiO_2@APTES@Pd-FFR/H_2O_2/reflux at 70°C	-	414	77
9		Pd/NH_2−MIL-101(Cr)/solvent free/ H_2O_2/60°C/2h	85	904	This study

[a]Isolated yield

[b]Conversion=97% ,was determined through GC-MS

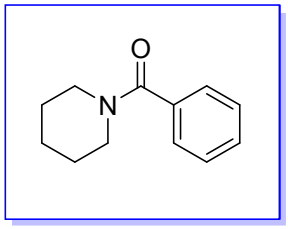
A. A. Alanthadka and C. U. Maheswari, *Adv. Synth. Catal.,* 2015, **357,** 1199–1203.

B. S. Seo and T. J. Marks, *Org. Lett.,* 2008, **10,** 317–319.

C. K. R. Reddy, C. U. Maheswari, M. Venkateshwar and M. L. Kantam, *Eur. J. Org. Chem.,* 2008, **21,** 3619–3622.

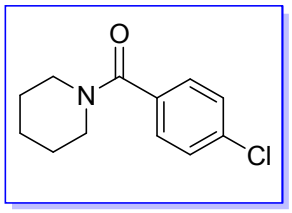
1. ^{1}H and ^{13}C NMR data of the synthesized compounds:

(i) phenyl(piperidin-1-yl)methanone (entry 1)



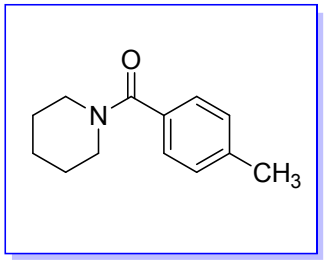
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39 (s, 5H), 3.71 (s, 2H), 3.34 (s, 2H), 1.68-1.51 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 170.2, 136.3, 129.2, 128.2, 126.6, 48.6, 43.0, 26.4, 25.5, 24.4; MS m/z 189.1 (M^+).

(ii) (4-chlorophenyl)(piperidin-1-yl)methanone (entry 2)



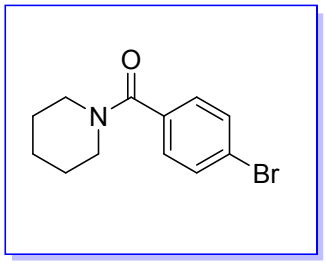
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.39-7.36 (m, 2H), 7.35-7.33 (m, 2H) 3.69 (s, 2H), 3.33 (s, 2H), 1.67-1.51 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.1, 135.2, 134.6, 128.2, 48.7, 43.1, 26.4, 25.4, 24.4; MS m/z 223 (M^+).

(iii) piperidin-1-yl(p-tolyl)methanone (entry 3)



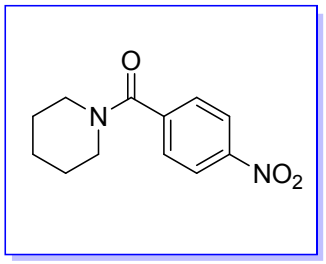
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.29-7.28 (m, 2H), 7.20-7.18 (m, 2H) 3.69 (s, 2H), 3.36 (s, 2H), 2.37(s,3H), 1.67-1.51 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 170.4, 139.3, 133.3, 128.8, 126.7,48.7, 40.8, 29.5, 24.4, 21.2; MS m/z 203.1 (M^+).

(iv) (4-bromophenyl)(piperidin-1-yl)methanone (entry 4)



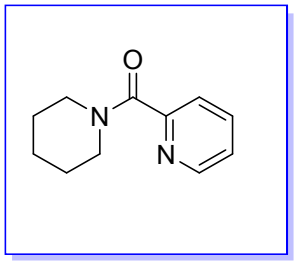
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.55-7.52 (m, 2H), 7.29-7.26 (m, 2H) 3.69 (s, 2H), 3.32 (s, 2H), 1.67-1.51 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.1, 135.1, 131.5, 128.4, 123.5, 48.6, 40.8, 29.5, 25.4, 24.3; MS m/z 267 (M^+).

(v) (4-nitrophenyl)(piperidin-1-yl)methanone (entry 5)



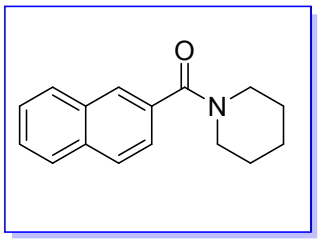
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.29-8.27 (m, 2H), 7.58-7.56 (m, 2H) 3.74-3.72 (m, 2H), 3.30-3.28 (m, 2H), 1.72-1.52 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 167.7, 148.0, 142.5, 127.6, 123.7,48.5, 43.0, 26.3, 25.3, 24.2; MS m/z 234 (M^+).

(vi) piperidin-1-yl(pyridin-2-yl)methanone (entry 6)



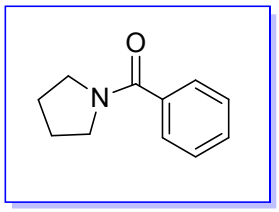
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.60-8.59 (d, J= 5Hz, 1H), 7.80-7.77 (m, 1H), 7.58-7.56 (d, J=10 Hz, 1H), 7.34-7.31(m, 1H), 3.75-3.73 (m, 2H), 3.44-3.42 (m, 2H), 1.69-1.57 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 167.5, 154.6, 148.3, 136.8, 124.0, 123.1,48.1, 43.1, 26.3, 25.4, 24.4; MS m/z 190.1 (M^+).

(vii) naphthalen-2-yl(piperidin-1-yl)methanone(entry 7)



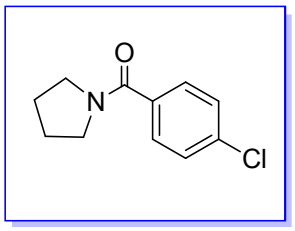
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.07-8.01 (m, 2H), 7.93-7.91(m, 1H), 7.85-7.79 (m, 2H), 7.55-7.49 (m, 2H), 3.72 (s, 2H), 2.85-2.82 (m, 2H), 1.63-1.56 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ163.8, 136.3, 133.0, 128.9, 128.1, 127.8, 127.5, 126.9, 126.5, 49.3, 29.5, 24.9; MS m/z 239.1 (M^+).

(viii) phenyl(pyrrolidin-1-yl)methanone (entry 8)



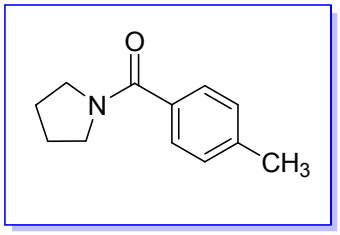
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.52-7.50 (m, 2H), 7.41-7.38 (m, 3H), 3.66-3.63 (t, J= 15 Hz, 2H), 3.43-3.40 (t, J= 15 Hz, 2H), 1.98-1.94 (m, 2H), 1.89-1.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.5, 137.0, 129.6, 128.0, 126.9, 49.4, 46.0, 26.2, 24.3; MS m/z 175.1 (M^+).

(ix) (4-chlorophenyl)(pyrrolidin-1-yl)methanone (entry 9)



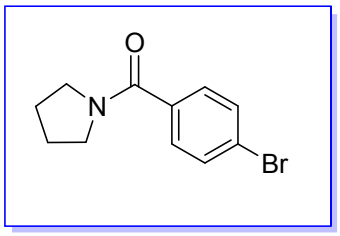
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.49-7.46 (m, 2H), 7.39-7.36 (m, 2H), 3.65-3.62 (t, J= 15 Hz, 2H), 3.43-3.40 (t, J= 15 Hz, 2H), 1.99-1.95 (m, 2H), 1.91-1.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 168.4, 135.7, 129.7, 128.5, 128.3, 49.5, 46.1, 26.3, 24.2; MS m/z 209 (M^+).

(x) pyrrolidin-1-yl(p-tolyl)methanone (entry 10)



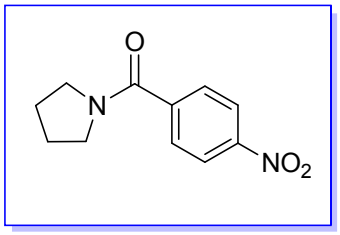
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.43-7.41 (m, 2H), 7.20-7.18 (m, 2H), 3.64-3.62 (t, J= 10 Hz, 2H), 3.45-3.42 (t, J= 15 Hz, 2H), 2.37 (s, 3H), 1.96-1.93 (m, 2H), 1.87-1.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.6, 139.7, 134.1, 128.6, 127.0, 53.3, 49.5, 46.0, 26.2, 24.3, 21.2; MS m/z 189 (M^+).

(xi) (4-bromophenyl)(pyrrolidin-1-yl)methanone (entry 11)



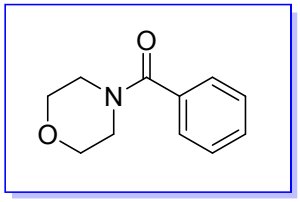
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.54-7.52 (m, 2H), 7.42-7.39 (m, 2H), 3.64-3.61 (t, J= 15 Hz, 2H), 3.42-3.39 (t, J= 15 Hz, 2H), 1.97-1.93 (m, 2H), 1.91-1.86 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 168.4, 135.8, 131.3, 128.7, 123.9, 49.4, 46.1, 26.2, 24.2; MS m/z 252.9 (M^+).

(xii) (4-nitrophenyl)(pyrrolidin-1-yl)methanone (entry 12)



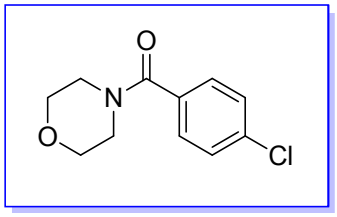
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.20-8.18 (m, 2H), 7.62-7.60 (m, 2H), 3.60-3.57 (t, J= 15 Hz, 2H), 3.33-3.30 (t, J= 15 Hz, 2H), 1.94-1.91 (m, 2H), 1.87-1.84 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 167.2, 148.2, 142.9, 128.0, 123.5, 49.3, 46.2, 26.2, 24.2; MS m/z 220 (M^+).

(xiii) morpholino(phenyl)methanone (entry 13)



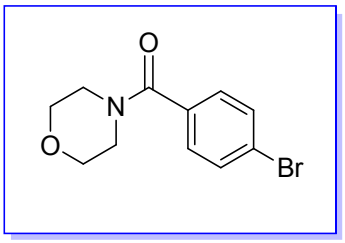
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41 (s, 5H), 3.79-3.45 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 170.3, 135.1, 129.7, 128.4, 126.9, 66.7, 48.3, 42.4; MS m/z 191 (M^+).

(xiv) (4-chlorophenyl)(morpholino)methanone (entry 14)



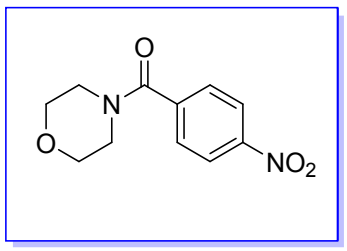
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.41-7.38 (m, 2H), 7.37-7.35 (m, 2H), 3.71-3.40 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.2, 135.9, 133.4, 128.7, 128.5, 66.7, 47.1, 43.1; MS m/z 225 (M^+).

(xv) (4-bromophenyl)(morpholino)methanone (entry 15)



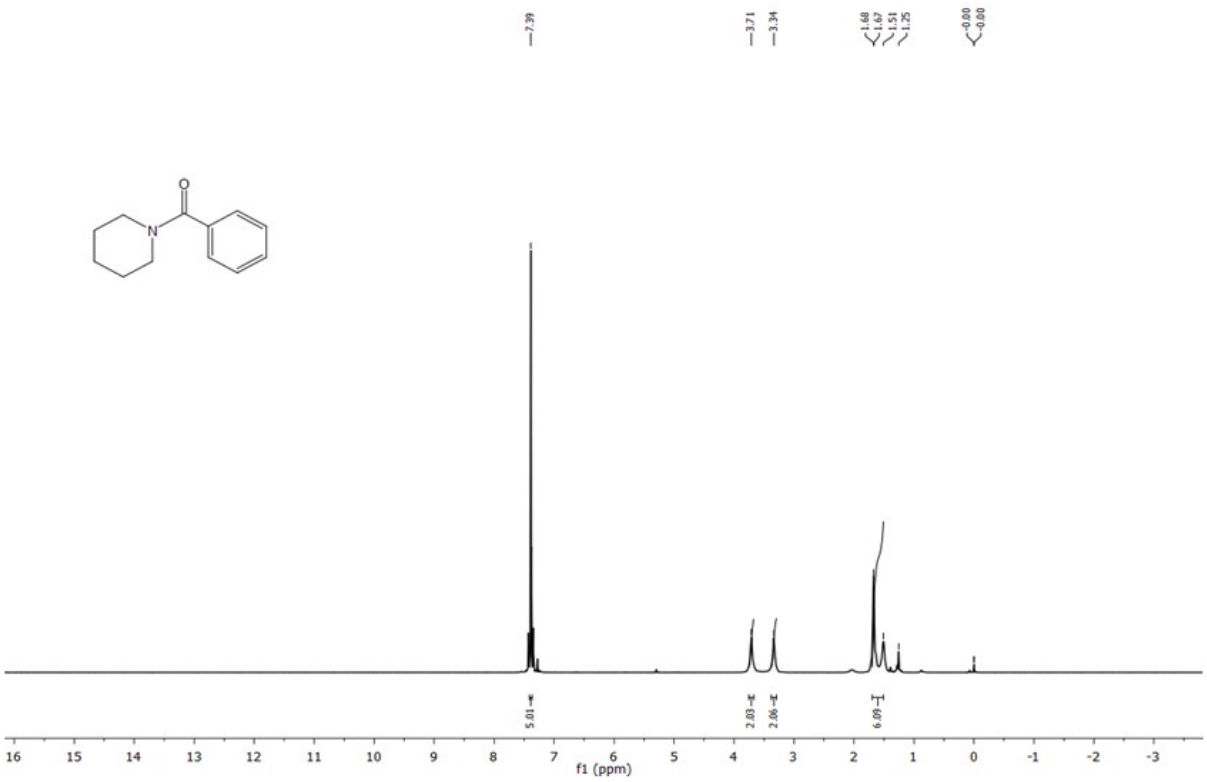
^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.58-7.55 (m, 2H), 7.31-7.27 (m, 2H), 3.77-3.45 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 169.2, 133.9, 131.7, 128.7, 124.1, 66.7, 47.4, 42.7; MS m/z 269 (M^+).

(xvi) morpholino(4-nitrophenyl)methanone (entry 15)



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.30-8.28 (m, 2H), 7.61-7.58 (m, 2H), 3.70-3.39 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 167.9, 148.3, 141.2, 128.0, 123.8, 66.6, 47.9, 42.4; MS m/z 236 (M^+).

^{1}H and ^{13}C spectra of the synthesized compounds



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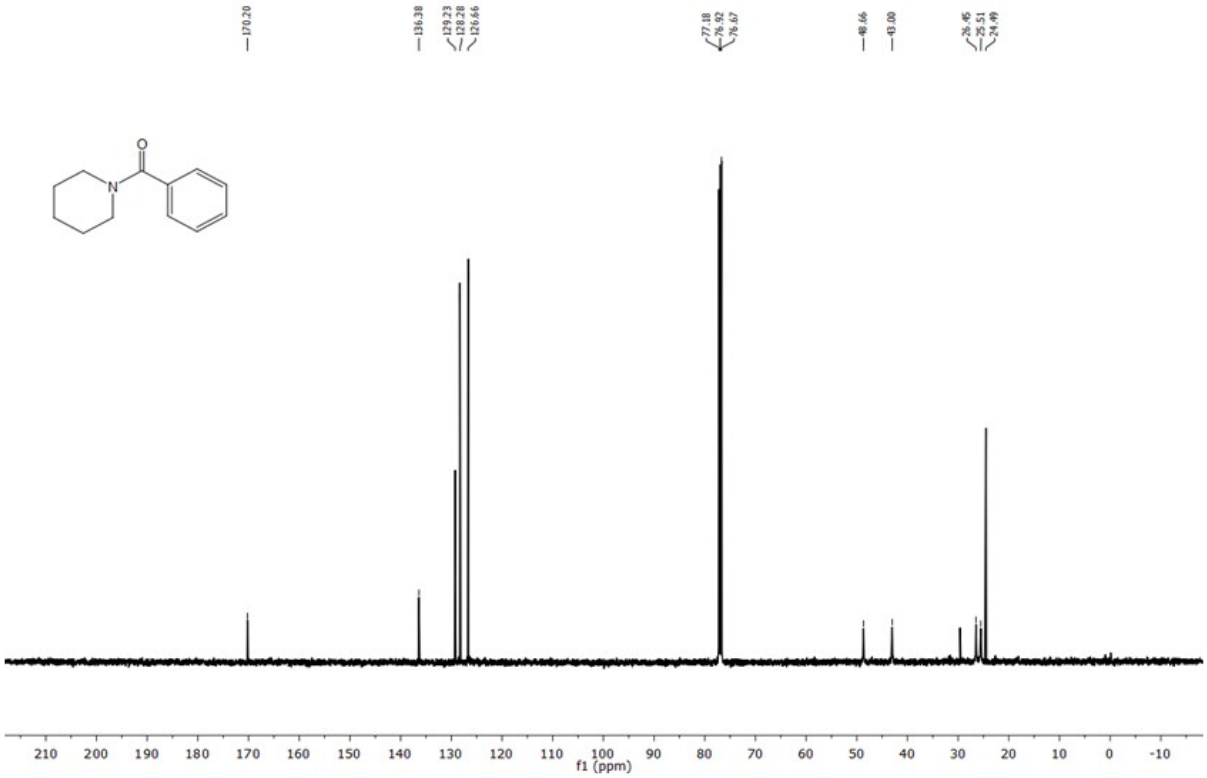
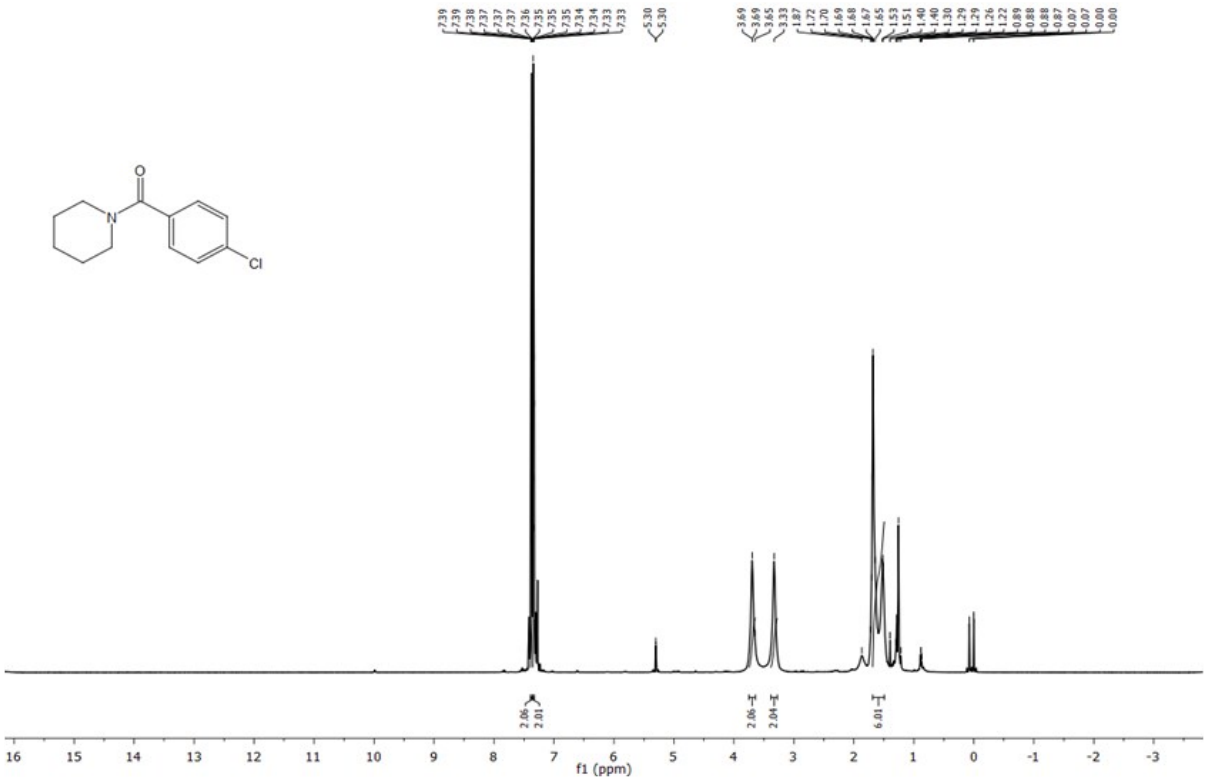
200

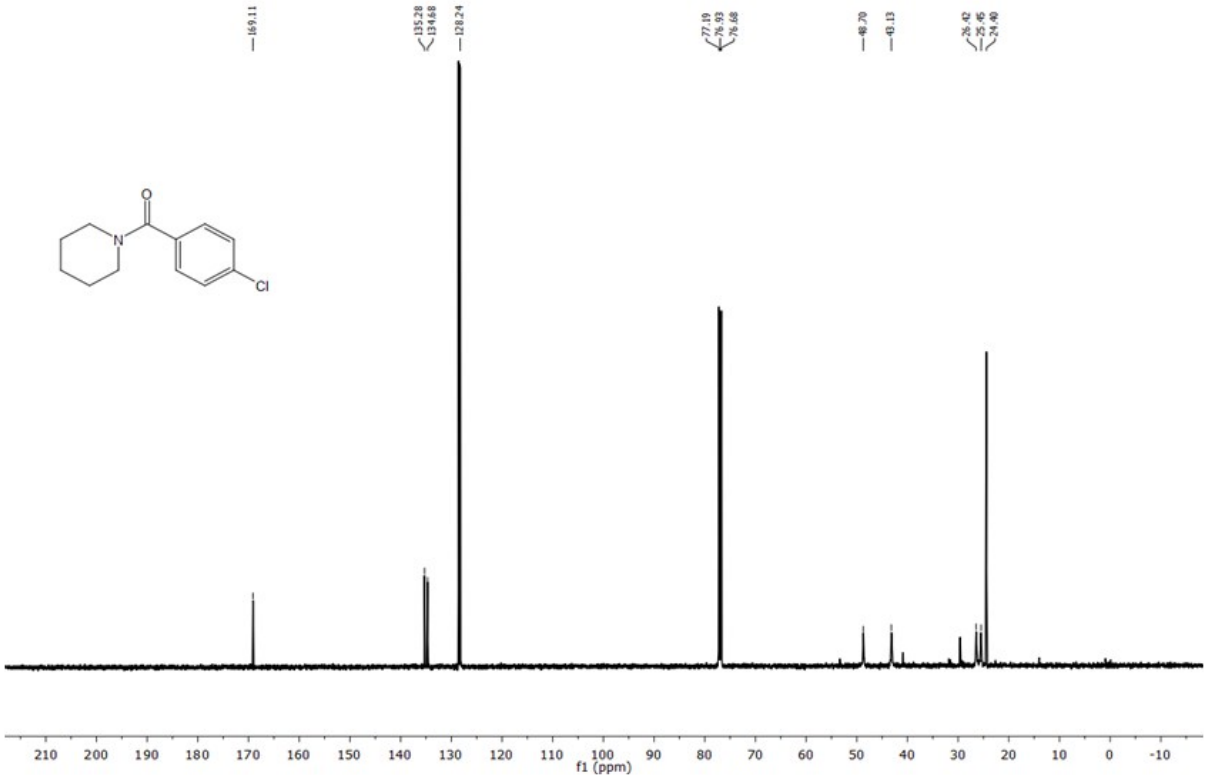
201



202



203



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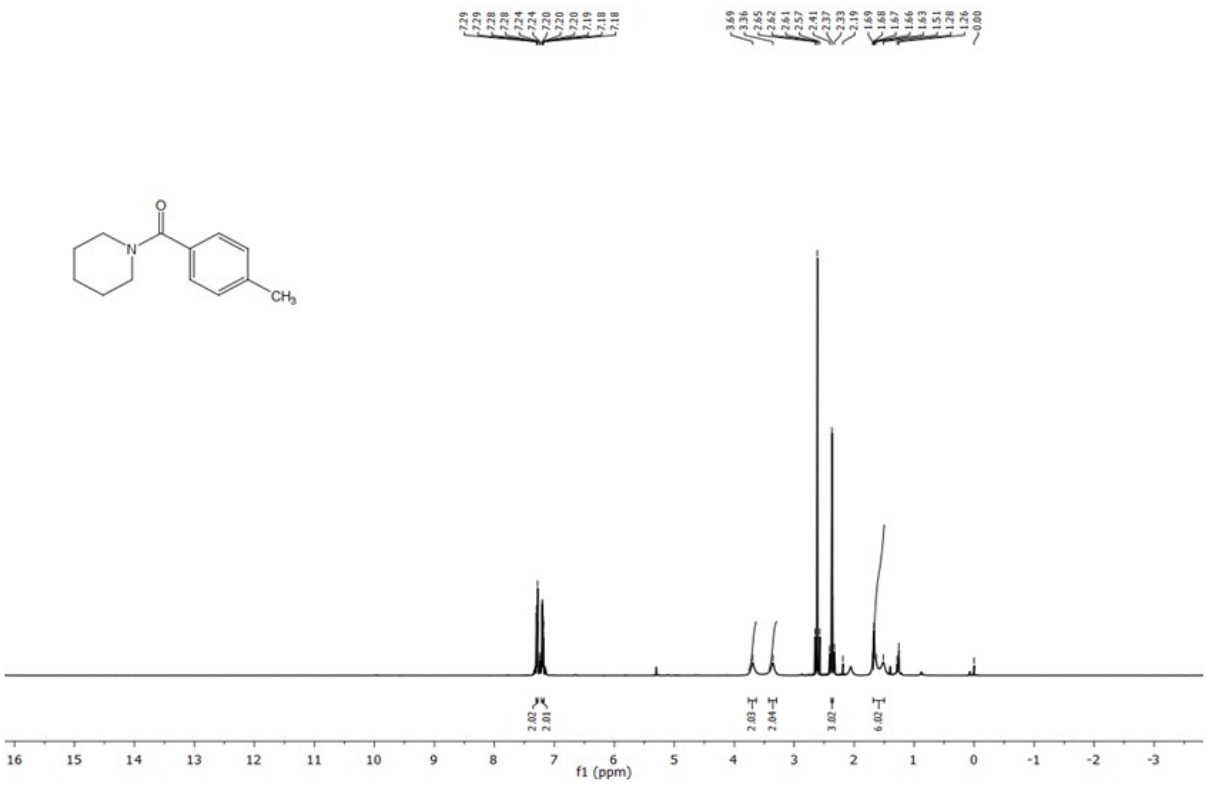

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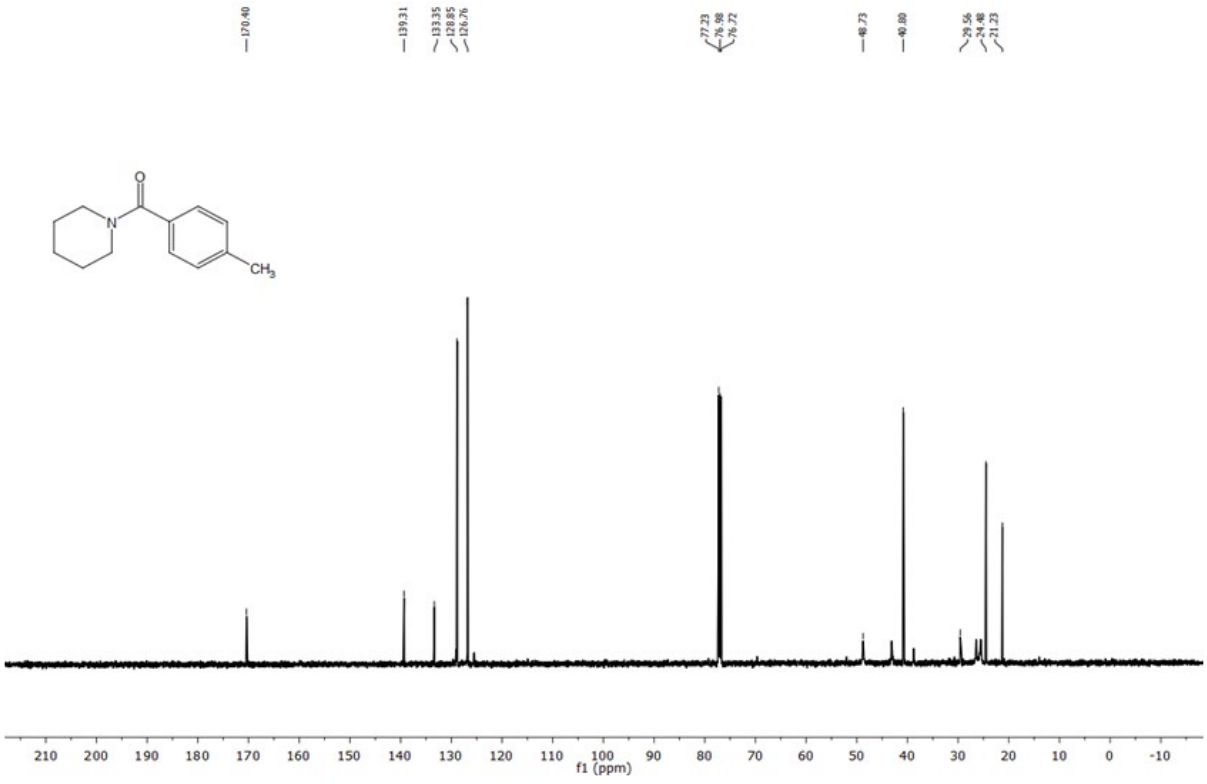
206

207



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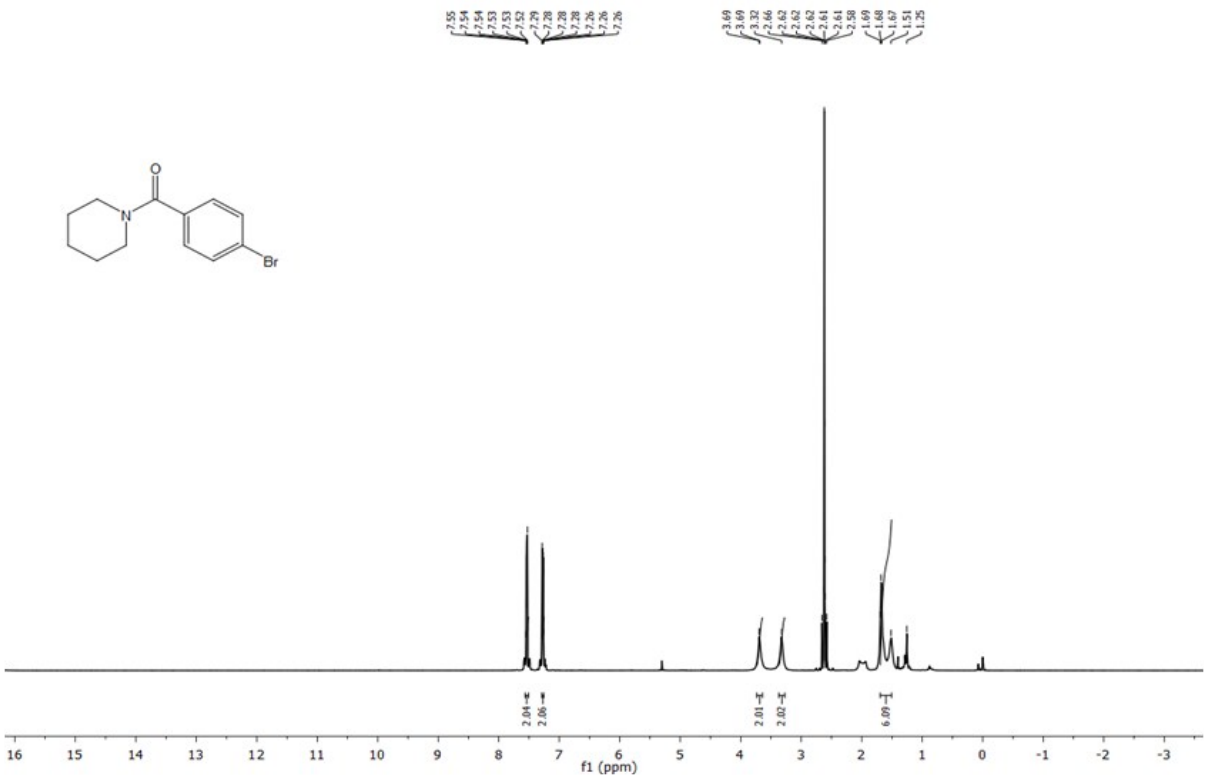
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7.54
7.54
7.53
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7.52
7.29
7.28
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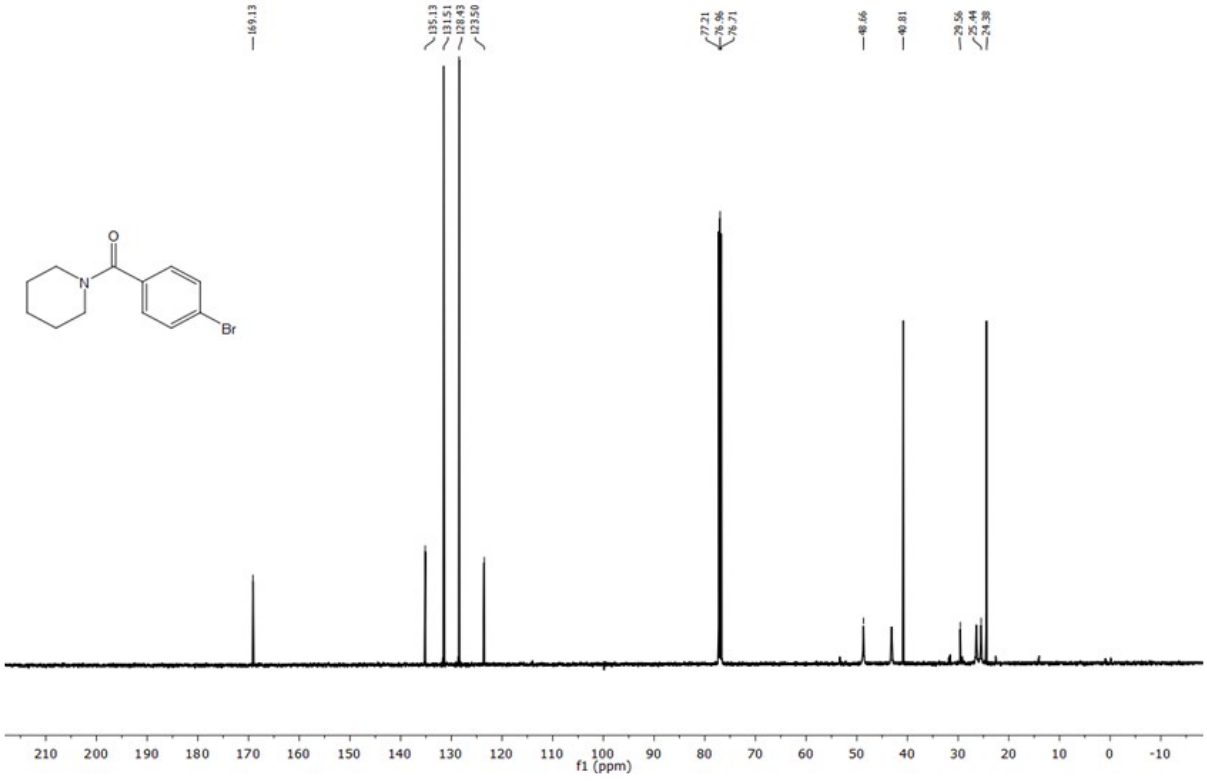
7.28
7.26
7.26
7.26
3.69
3.69
3.32
2.66
2.62
2.62
2.62
2.61
2.61
2.58
1.69
1.68
1.67
1.51
1.25
O
N
Br
2.04
2.06
2.01
2.02
6.09
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

209

210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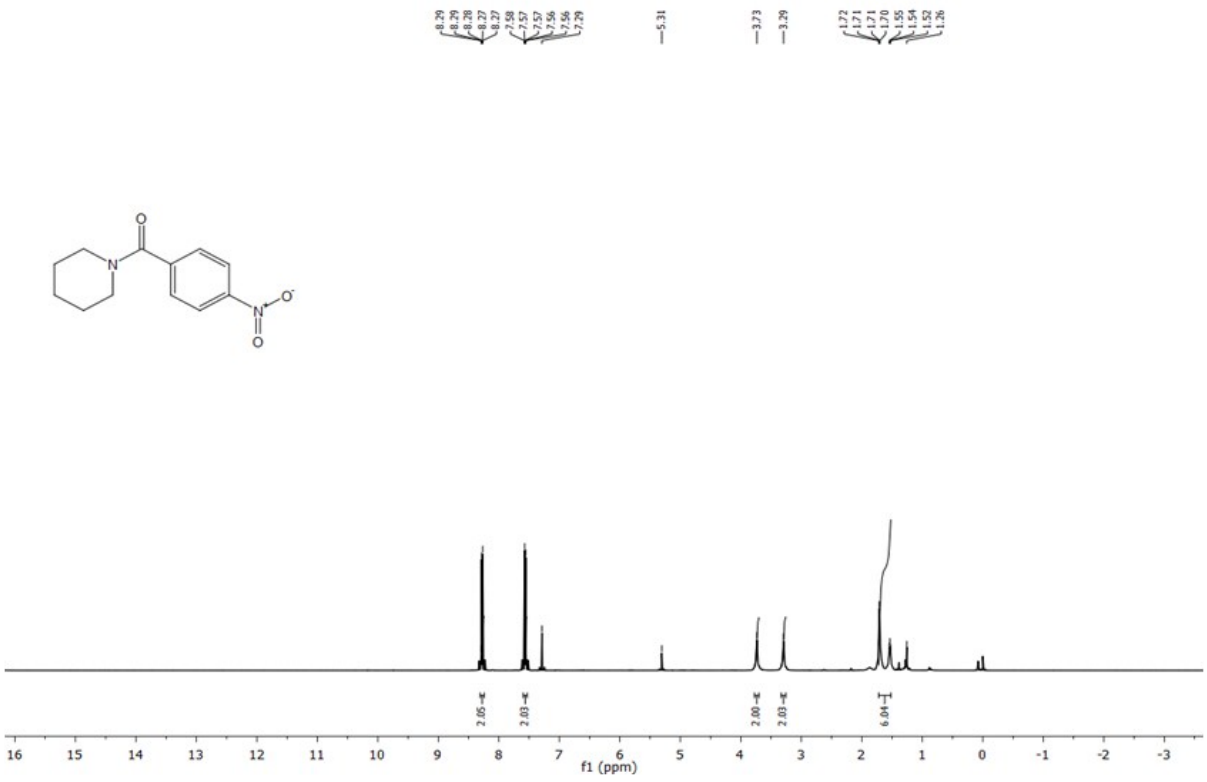
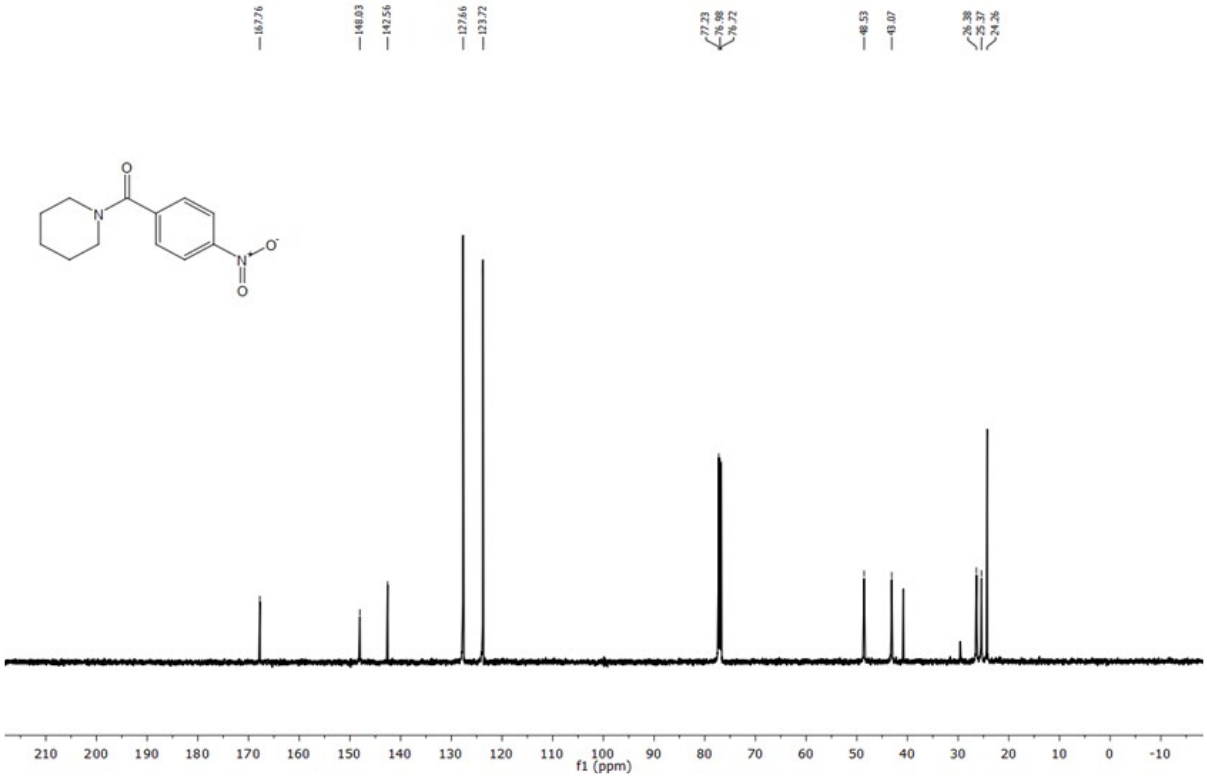
135.13
131.51
128.43
123.50
77.21
76.96
76.71
48.66
40.81
29.56
25.44
24.38
O
N
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

211

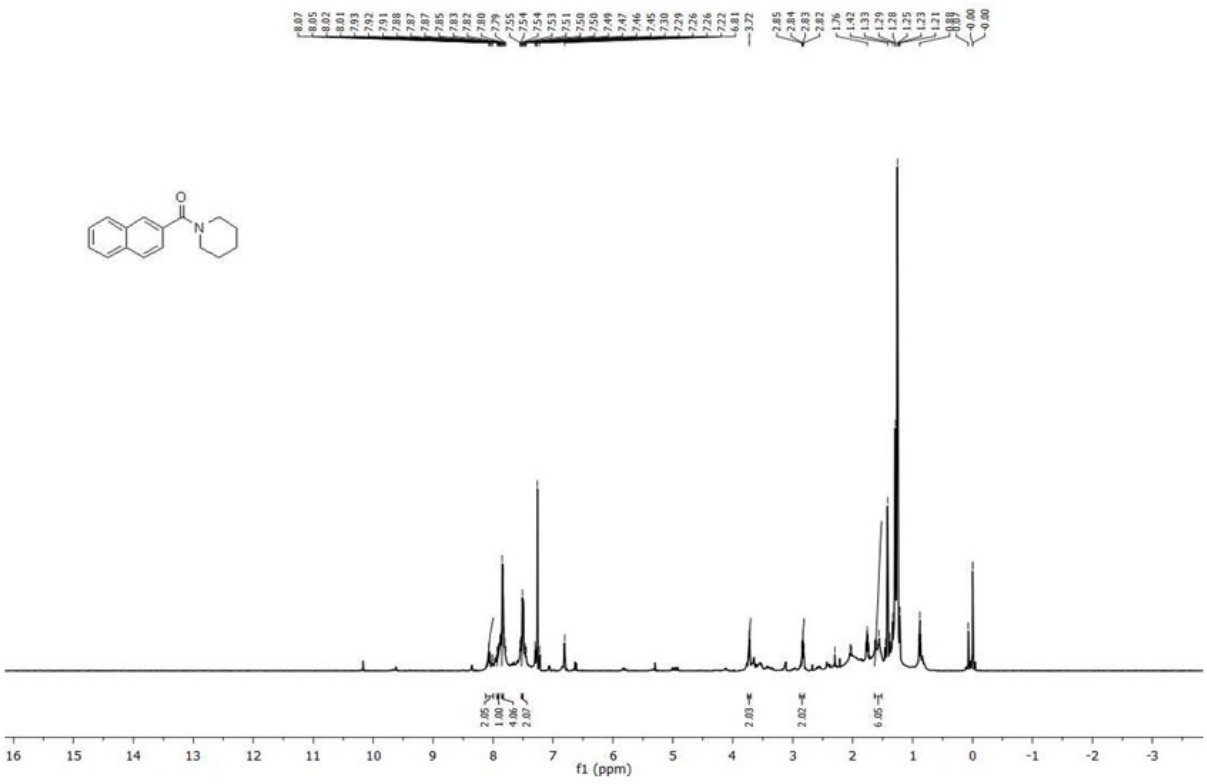

8.29
8.29
8.28
8.27
8.27
7.58
7.57
7.57
7.56
7.56
7.29
5.31
3.73
3.29
1.72
1.71
1.71
1.70
1.55
1.54
1.52
1.26
2.05
2.03
2.00
2.03
6.04
f1 (ppm)

212

213


165.76
148.03
142.56
127.66
123.72
77.23
76.98
76.72
48.53
43.07
26.38
25.37
24.26
f1 (ppm)

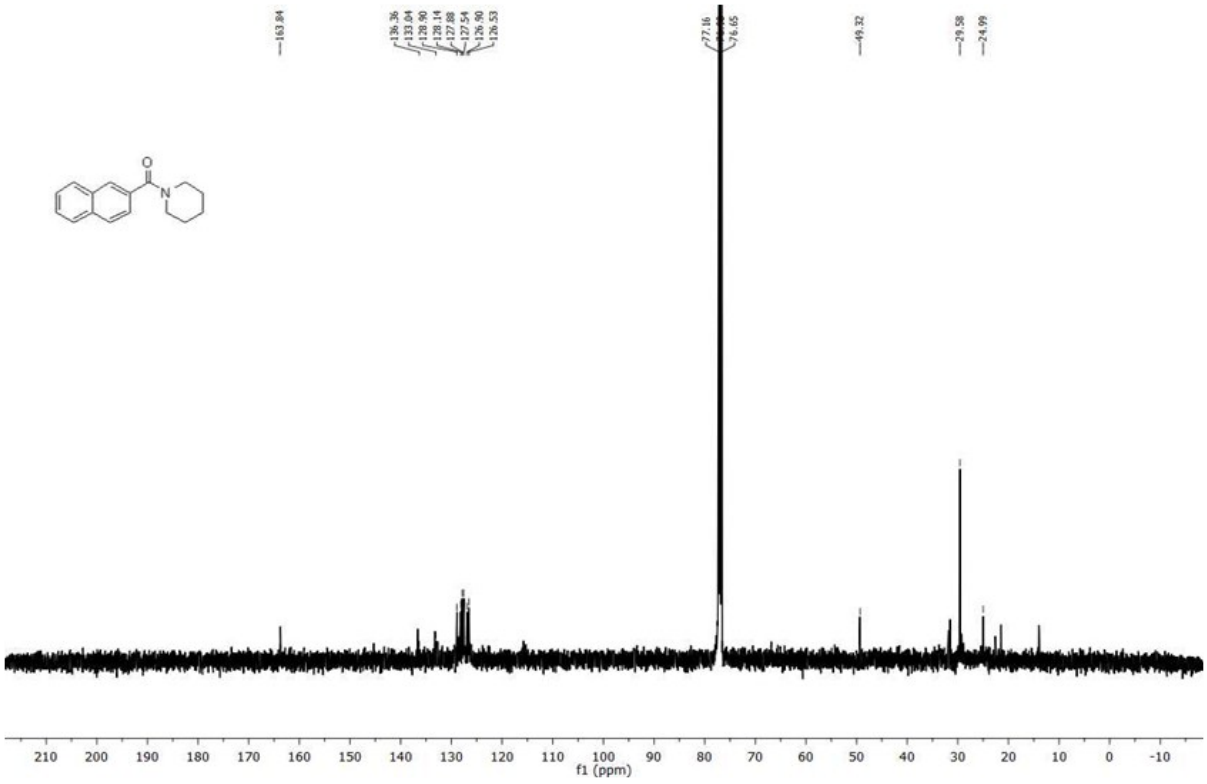
214



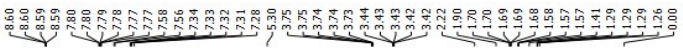
215

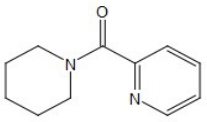
216

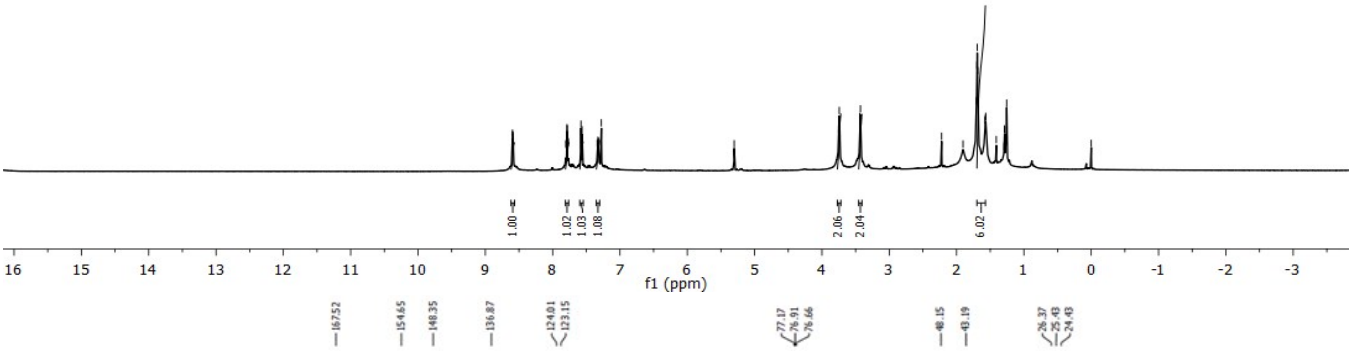
217

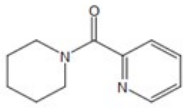


218

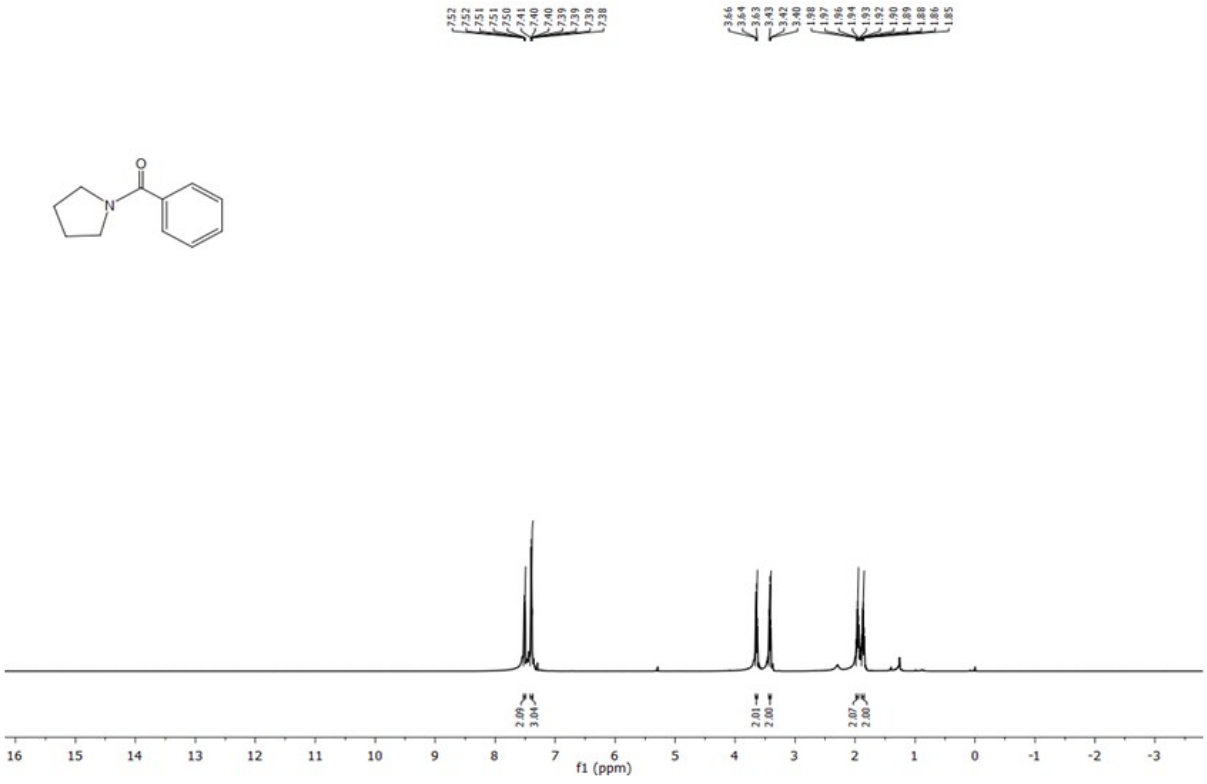








220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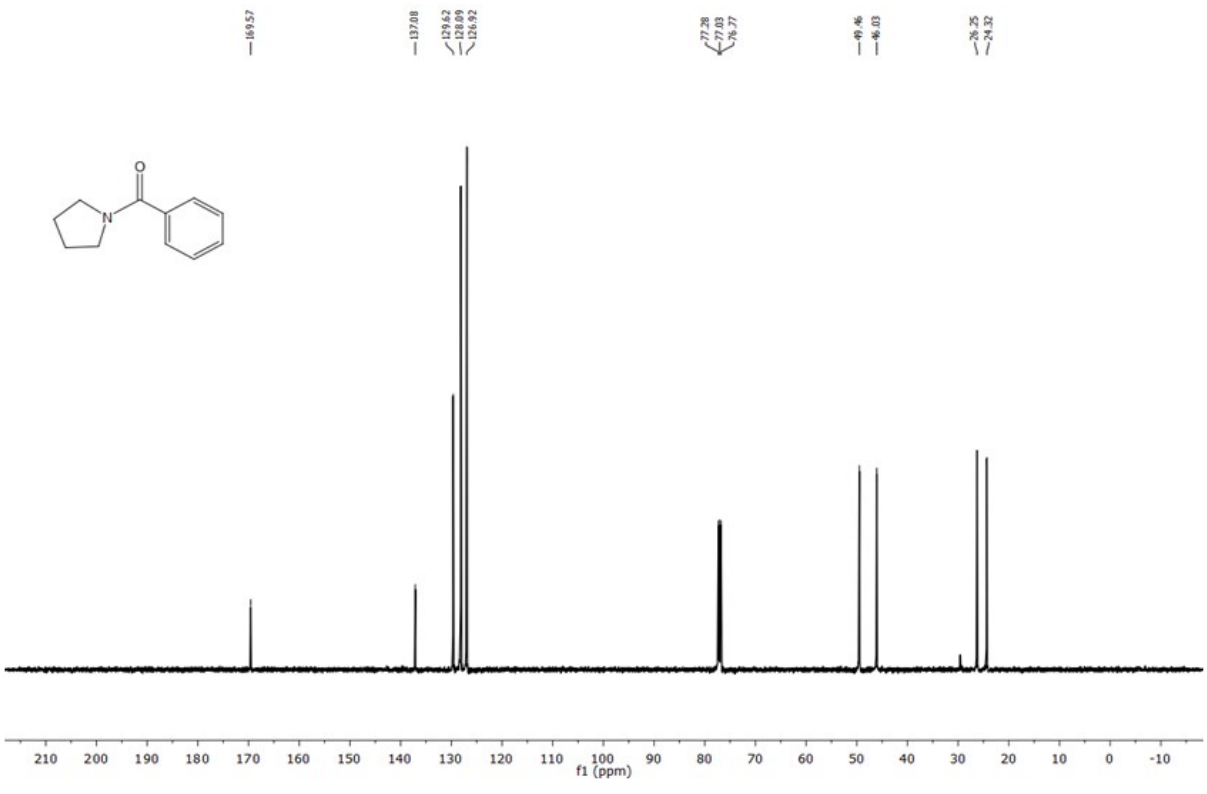
7.40
7.40
7.39
7.39
7.39
7.38
3.66
3.64
3.63
3.43
3.42
3.40
1.98
1.97
1.96
1.94
1.93
1.92
1.90
1.89
1.88
1.86
1.85
O
N
2.09
3.04
2.01
2.00
2.07
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

221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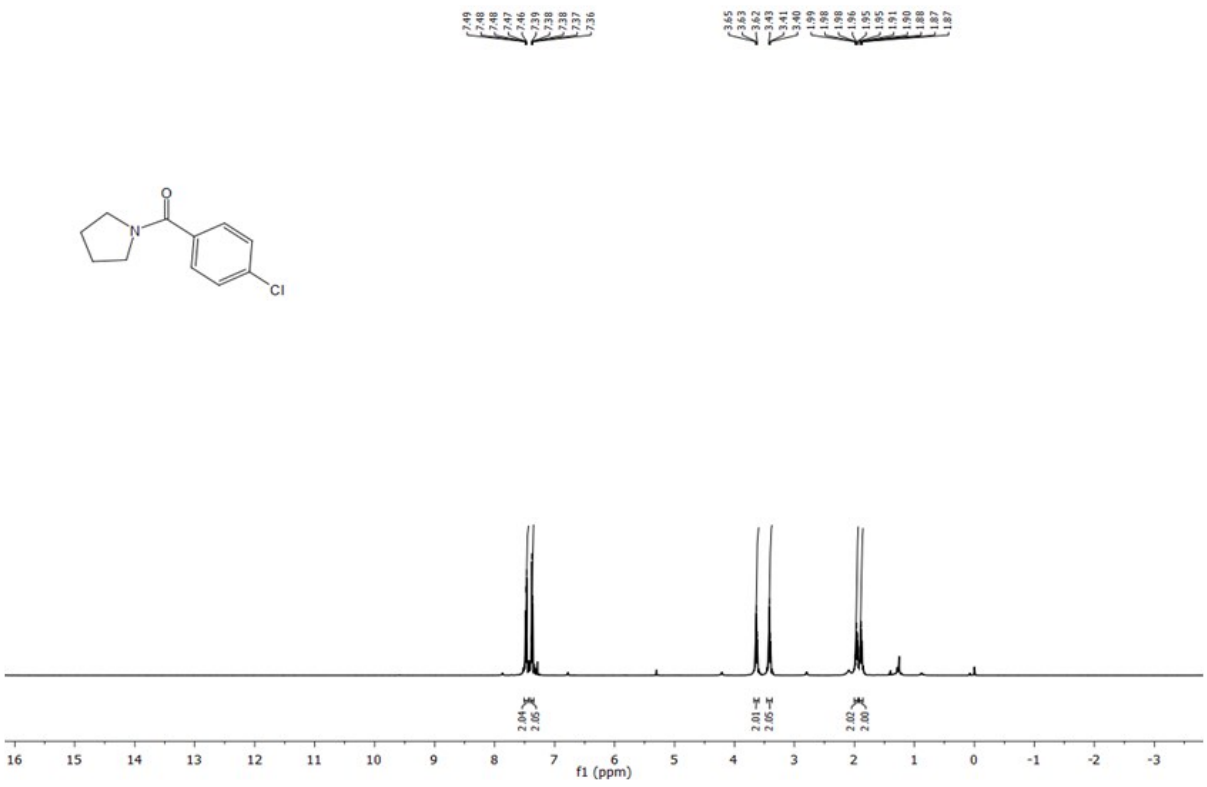
137.08
129.62
128.09
126.92
77.28
77.03
76.77
49.46
46.03
26.25
24.32
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

222


7.49
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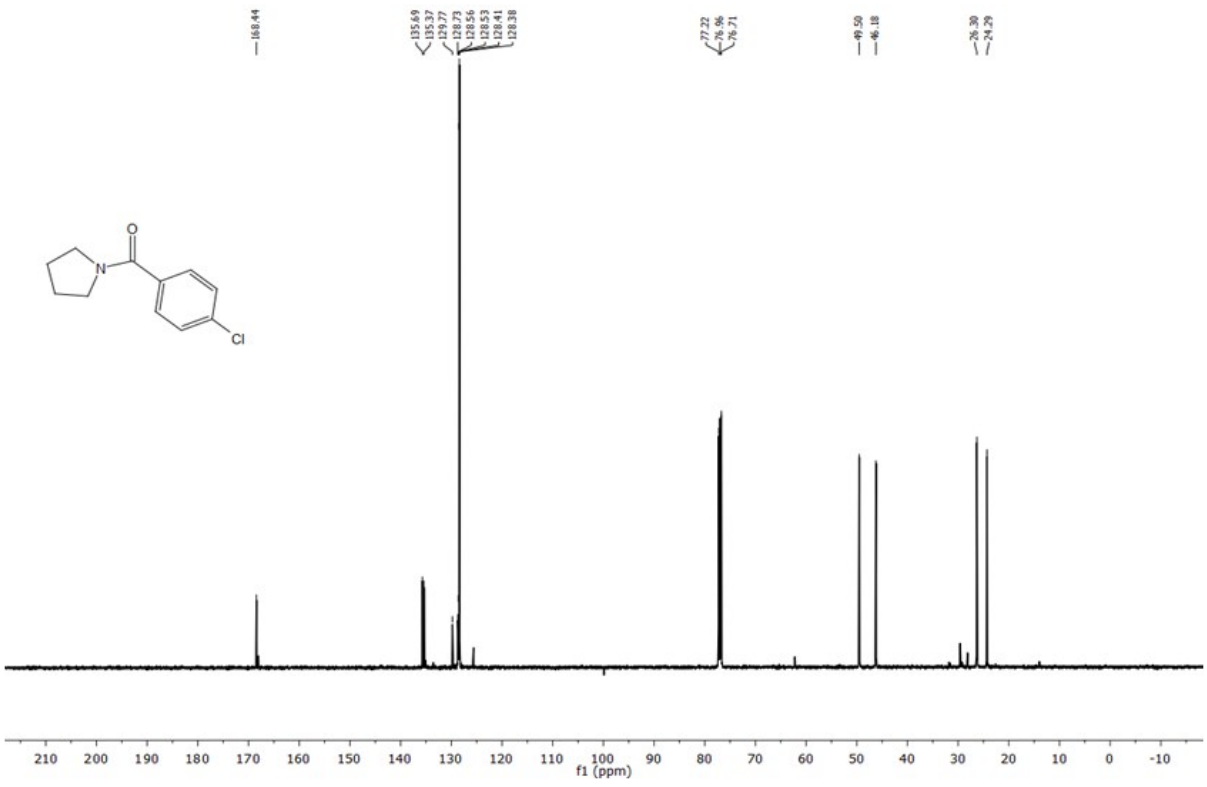
7.48
7.48
7.47
7.46
7.39
7.38
7.38
7.37
7.36
3.65
3.63
3.62
3.43
3.41
3.40
1.99
1.98
1.98
1.96
1.95
1.95
1.91
1.90
1.88
1.87
1.87
O
N
Cl
2.04
2.05
2.01
2.05
2.02
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

223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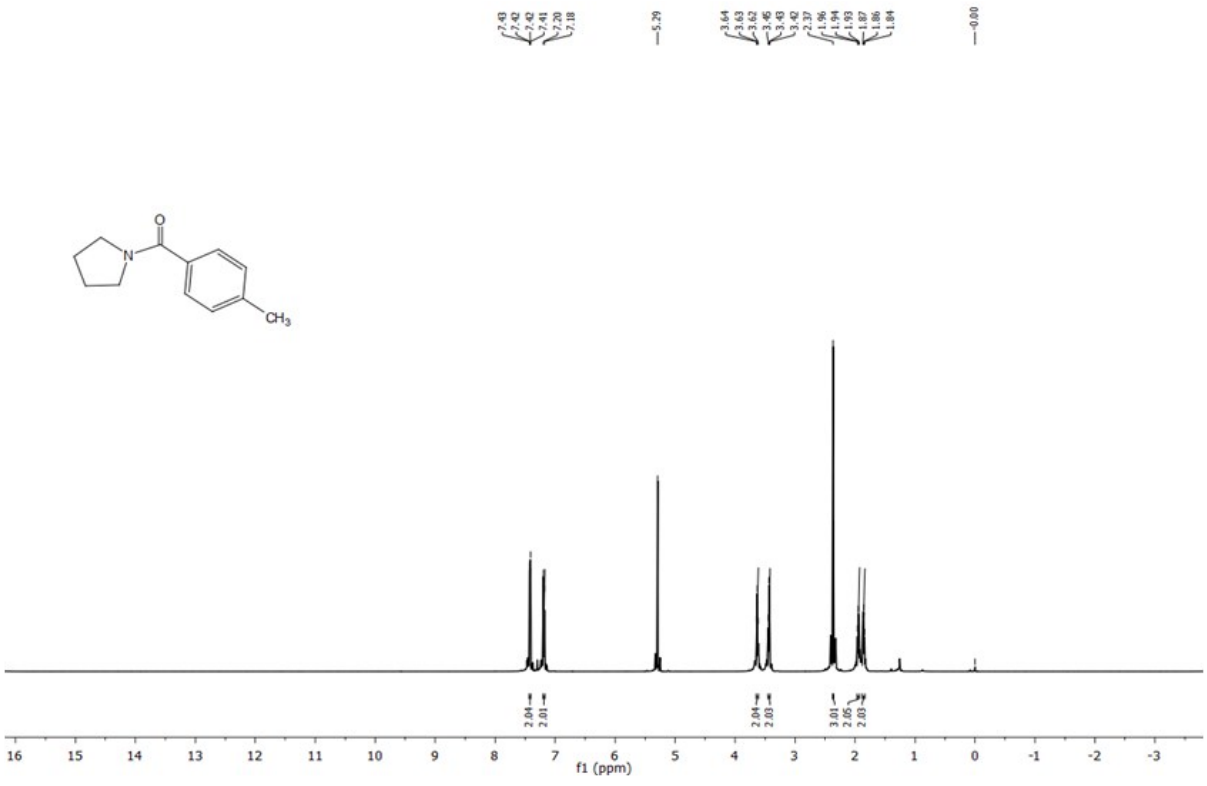
135.69
135.37
129.77
128.73
128.56
128.53
128.41
128.38
77.22
76.96
76.71
49.50
46.18
26.30
24.29
O
N
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

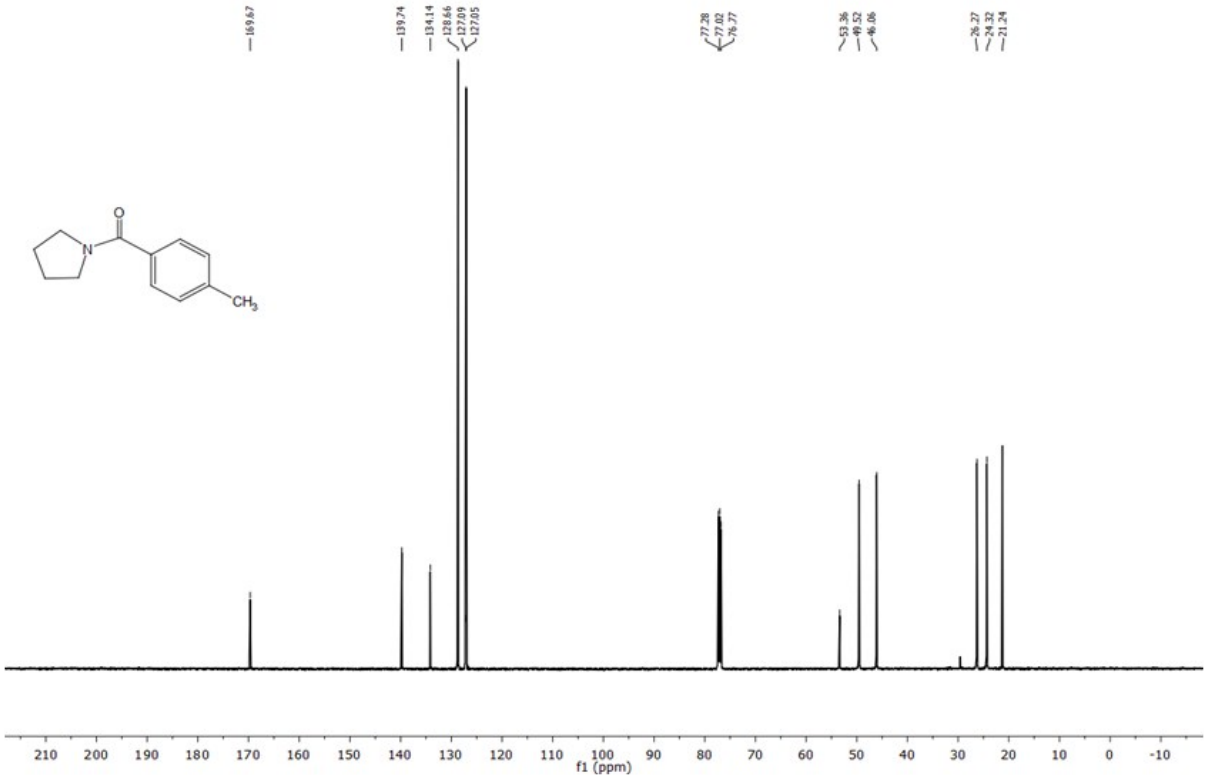
224

225



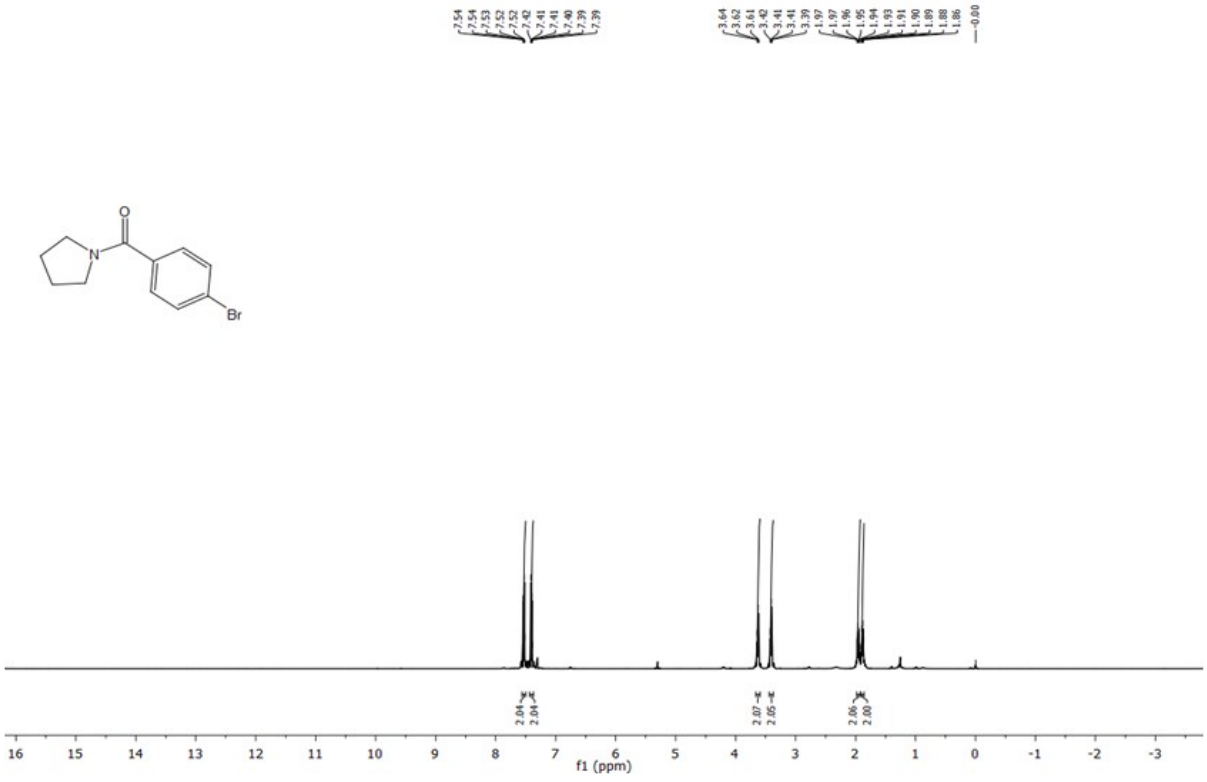
226

227



228

229



230

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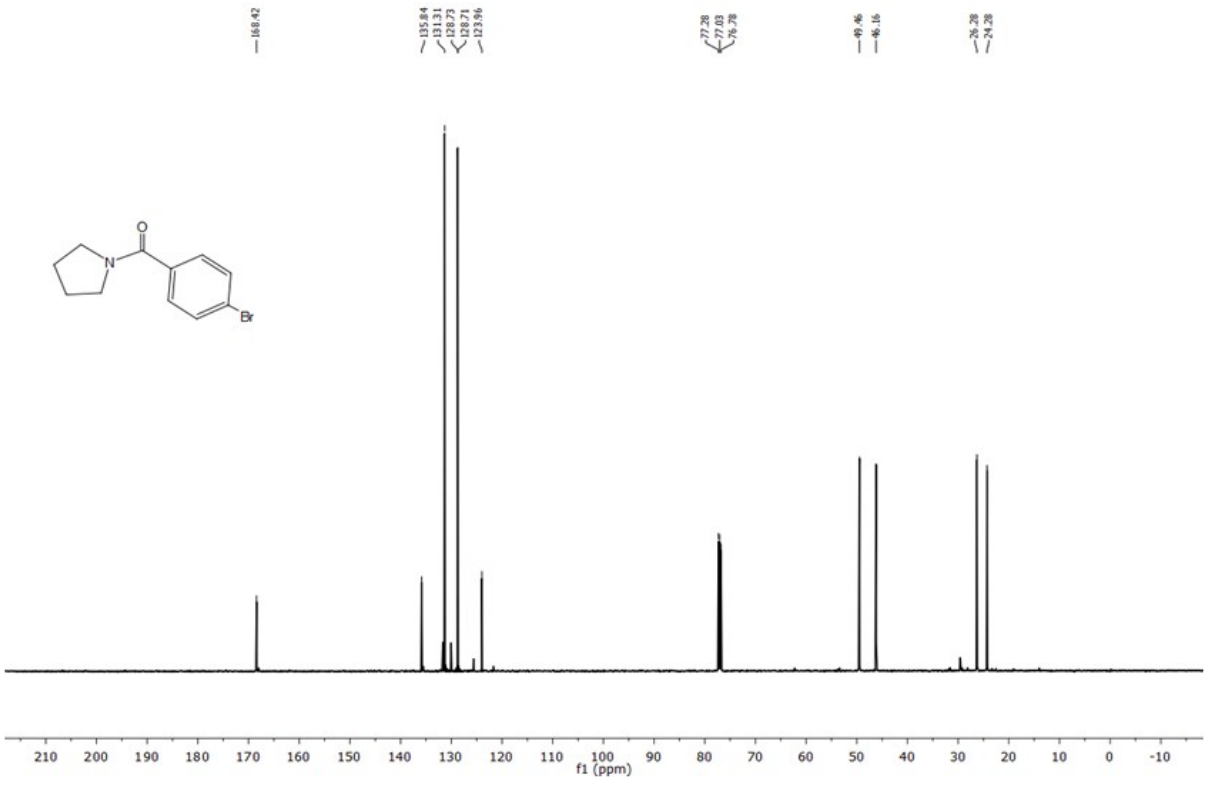
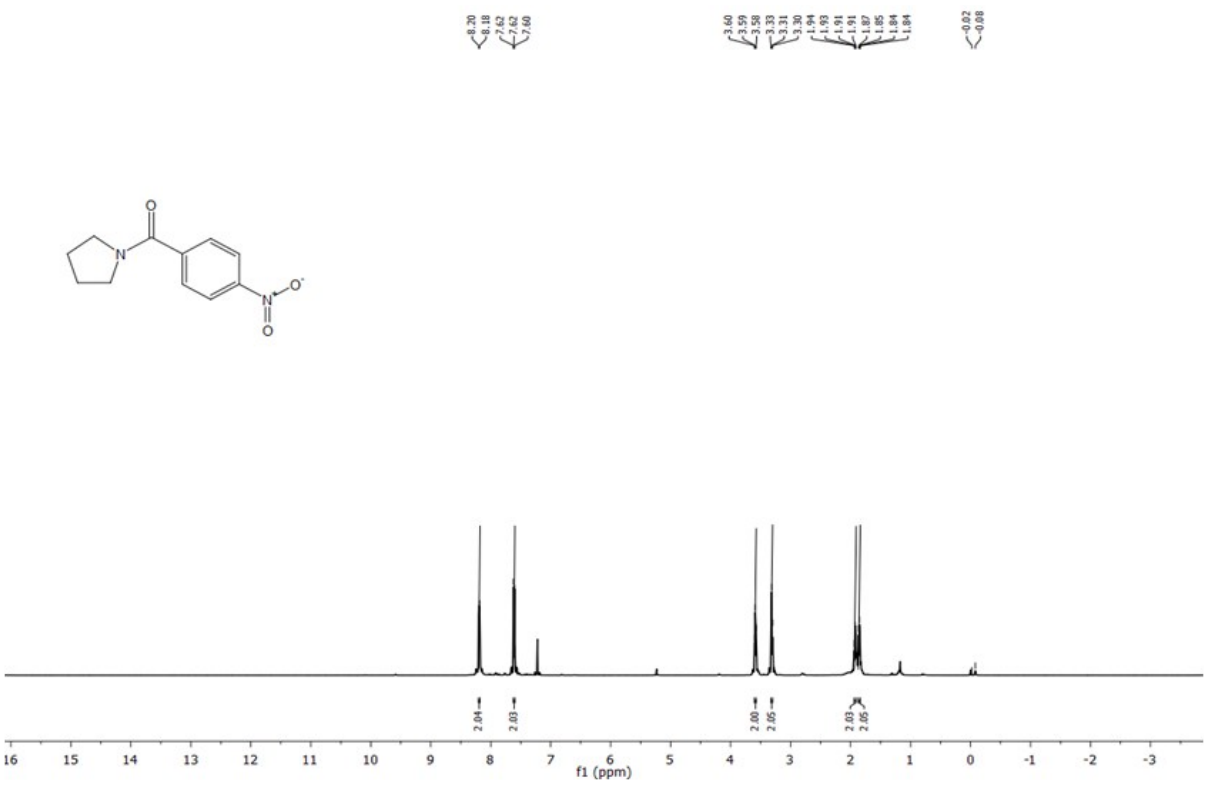


232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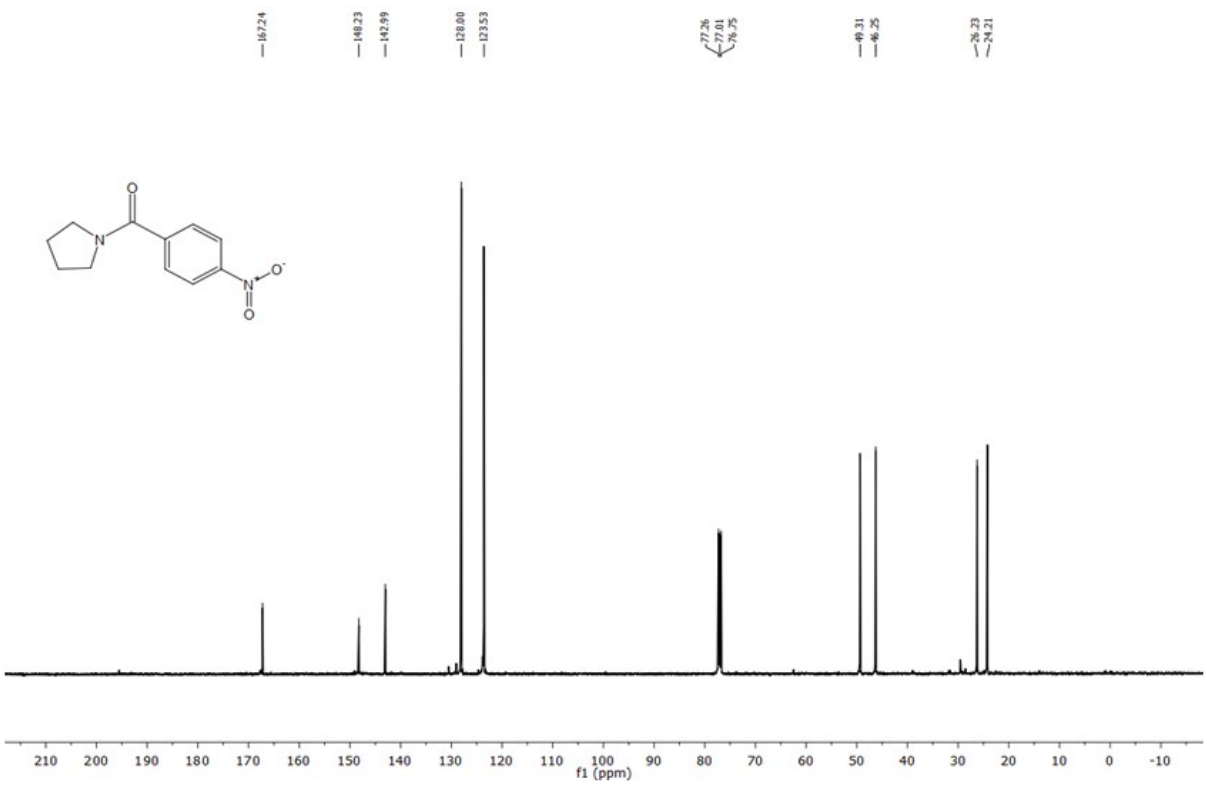
8.18
7.62
7.62
7.60
7.60
3.60
3.59
3.58
3.33
3.31
3.30
1.94
1.93
1.91
1.91
1.87
1.85
1.84
1.84
-0.02
-0.08
2.04
2.03
2.00
2.05
2.03
2.05
f1 (ppm)

233

234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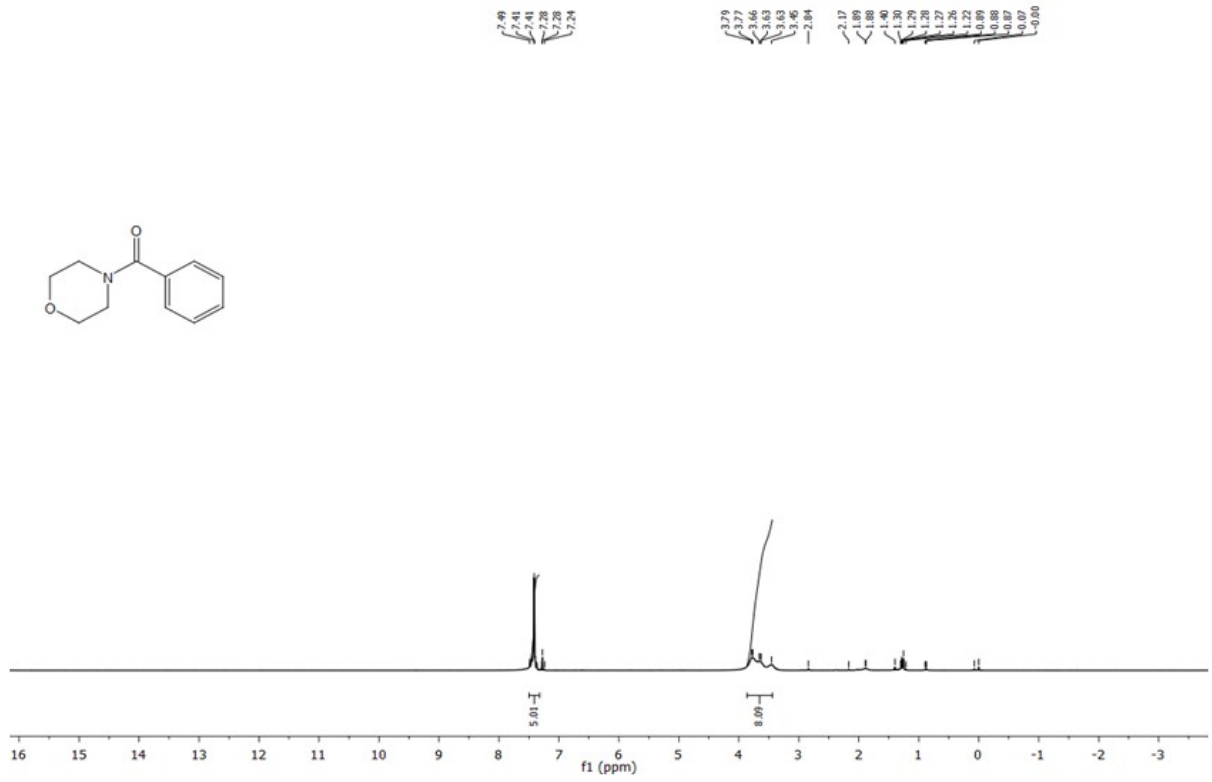
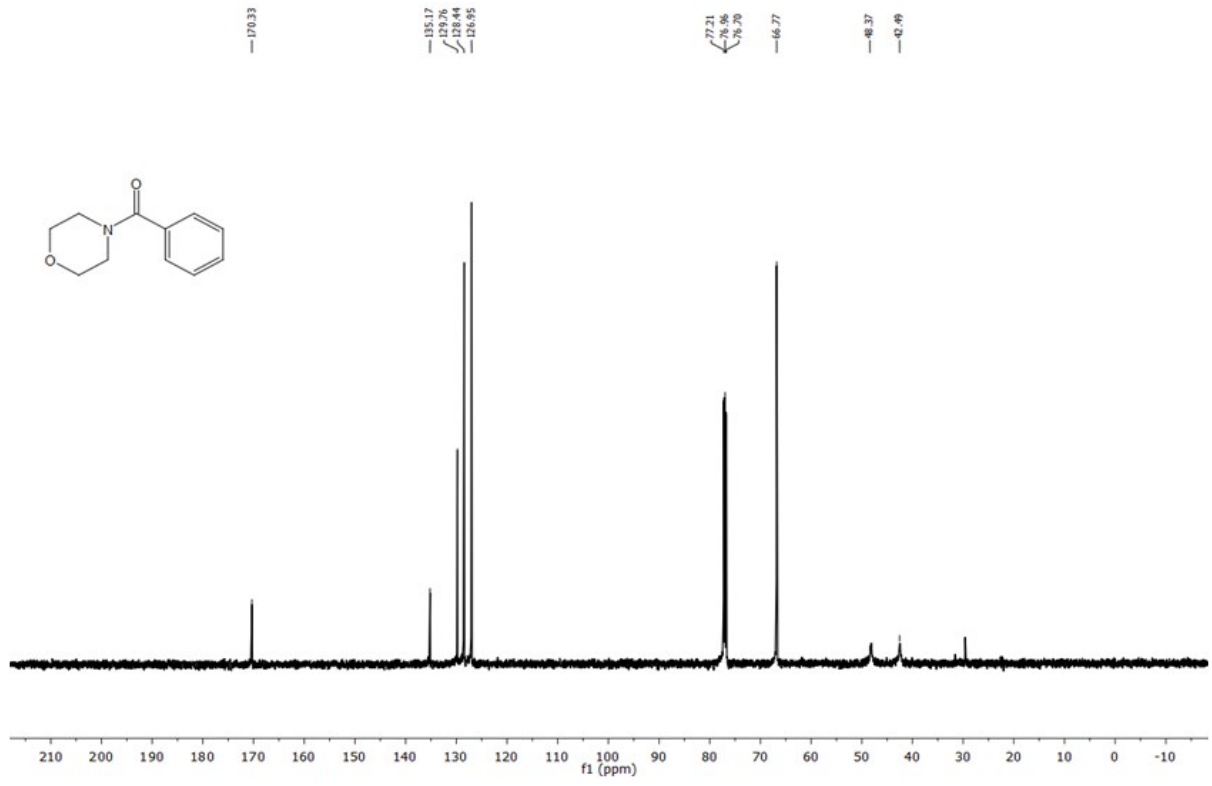
123.53
77.26
77.01
76.75
49.31
46.25
26.23
24.21
f1 (ppm)

235



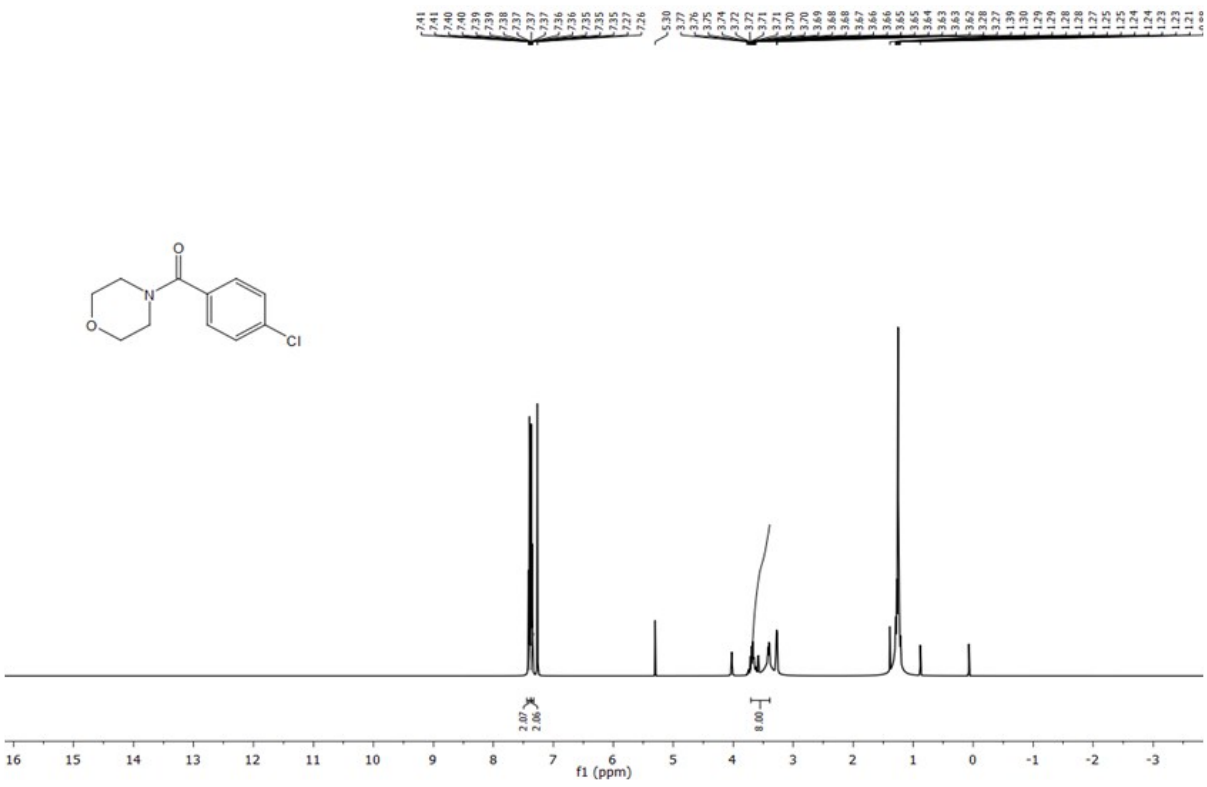
236

237



238

239


O
N
O
Cl
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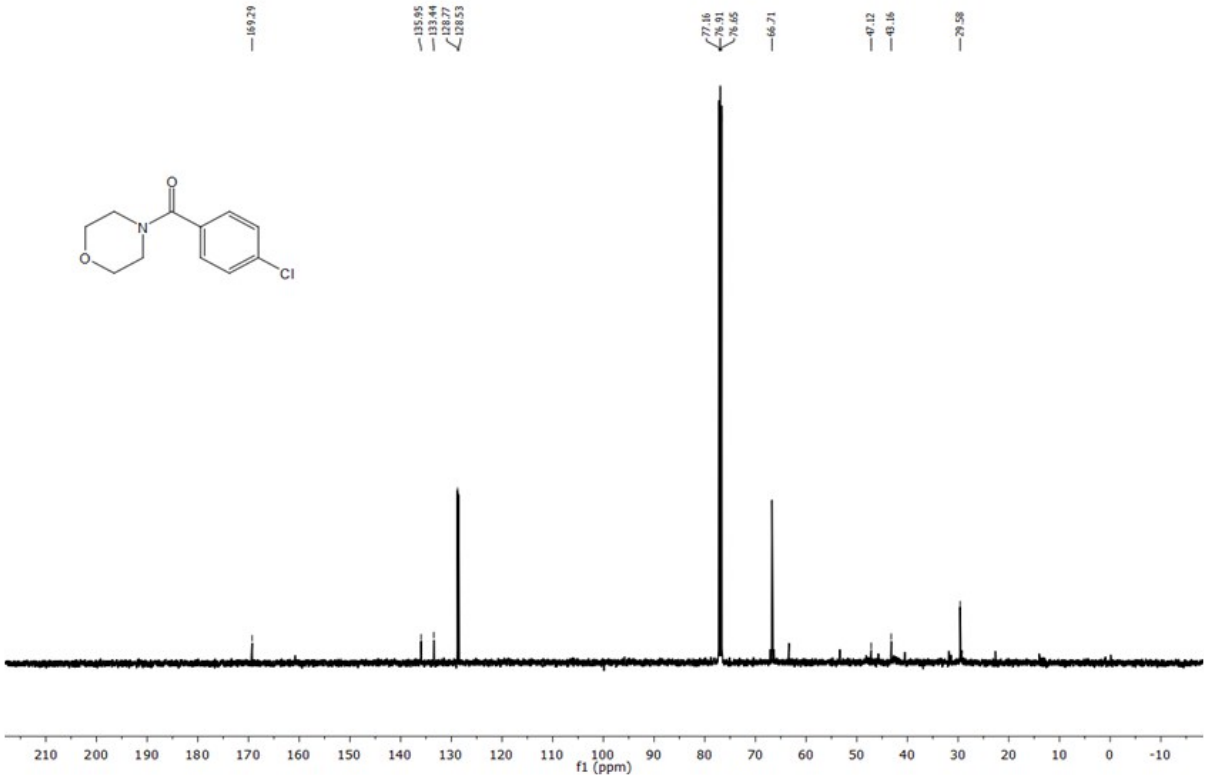
2.06
8.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

240

241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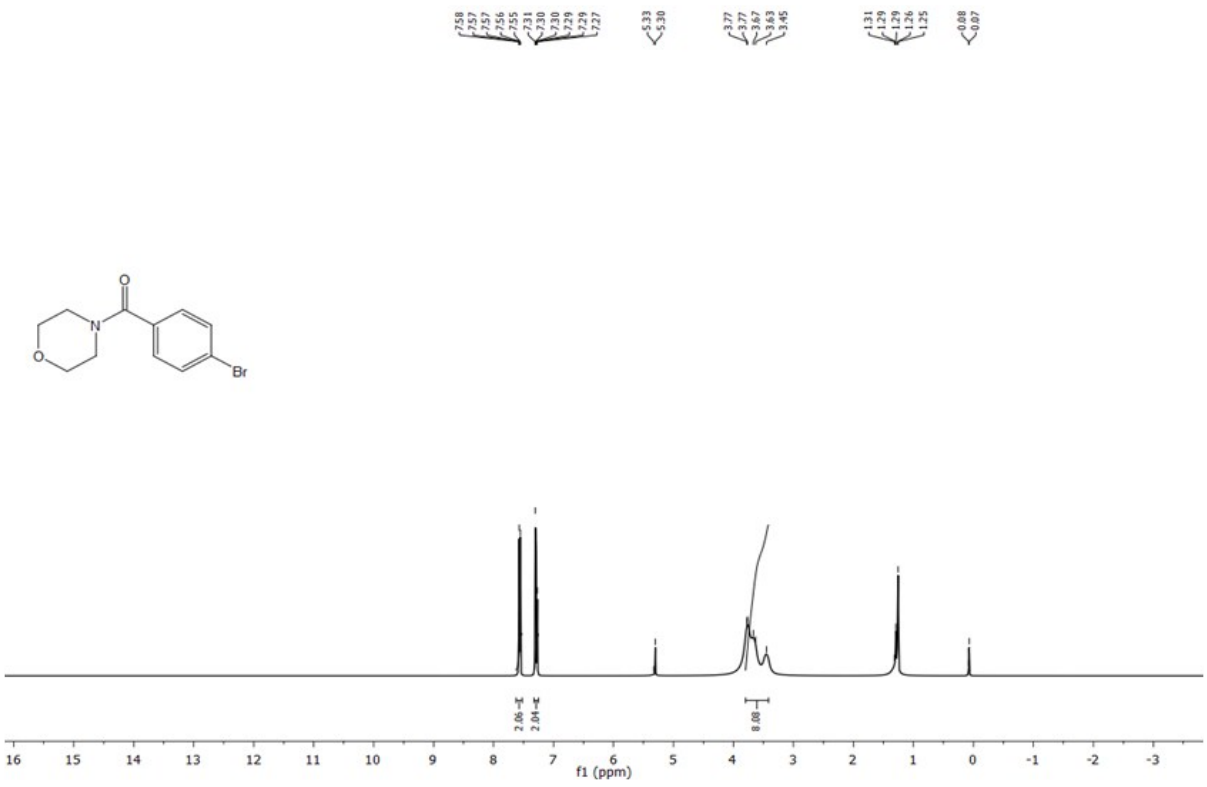
133.44
128.77
128.53
77.16
76.91
76.65
66.71
47.12
43.16
29.58
O
N
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

242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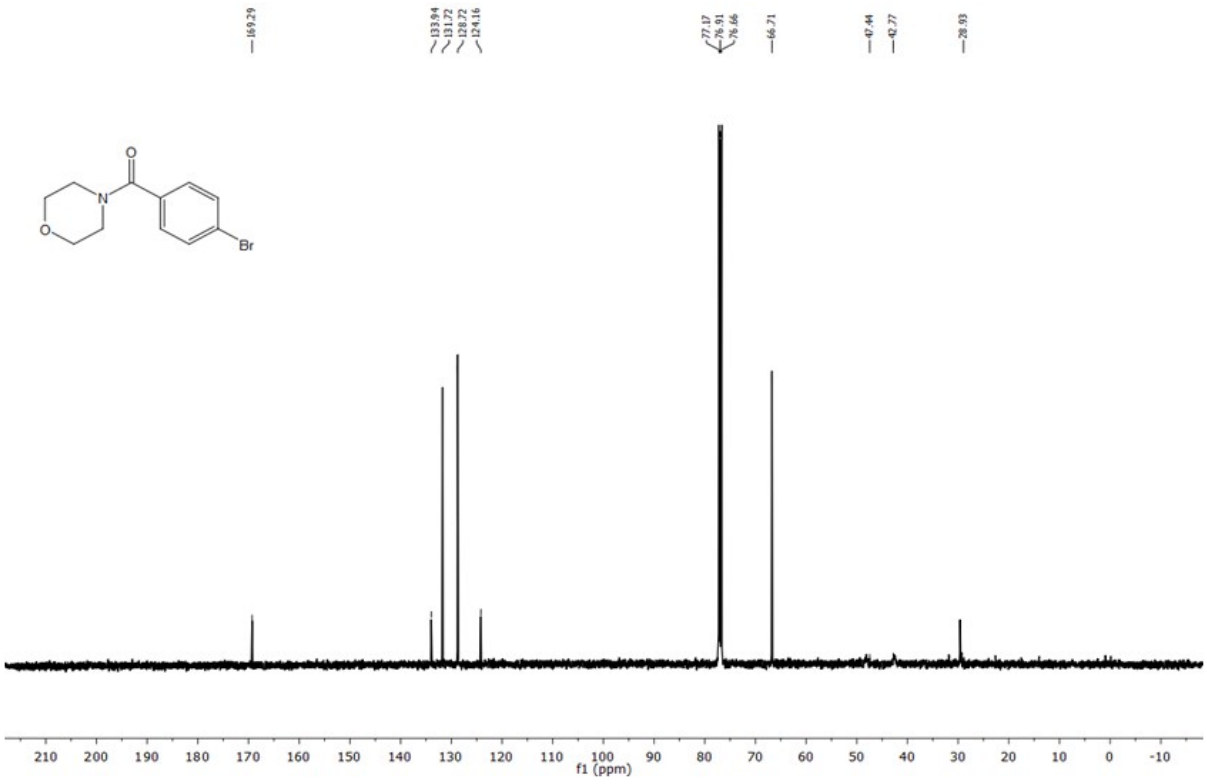
7.57
7.57
7.56
7.55
7.31
7.30
7.30
7.29
7.29
7.27
5.33
5.30
3.77
3.77
3.67
3.63
3.45
1.31
1.29
1.29
1.26
1.25
0.88
0.87
O
N
O
Br
2.06
2.04
8.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

243

244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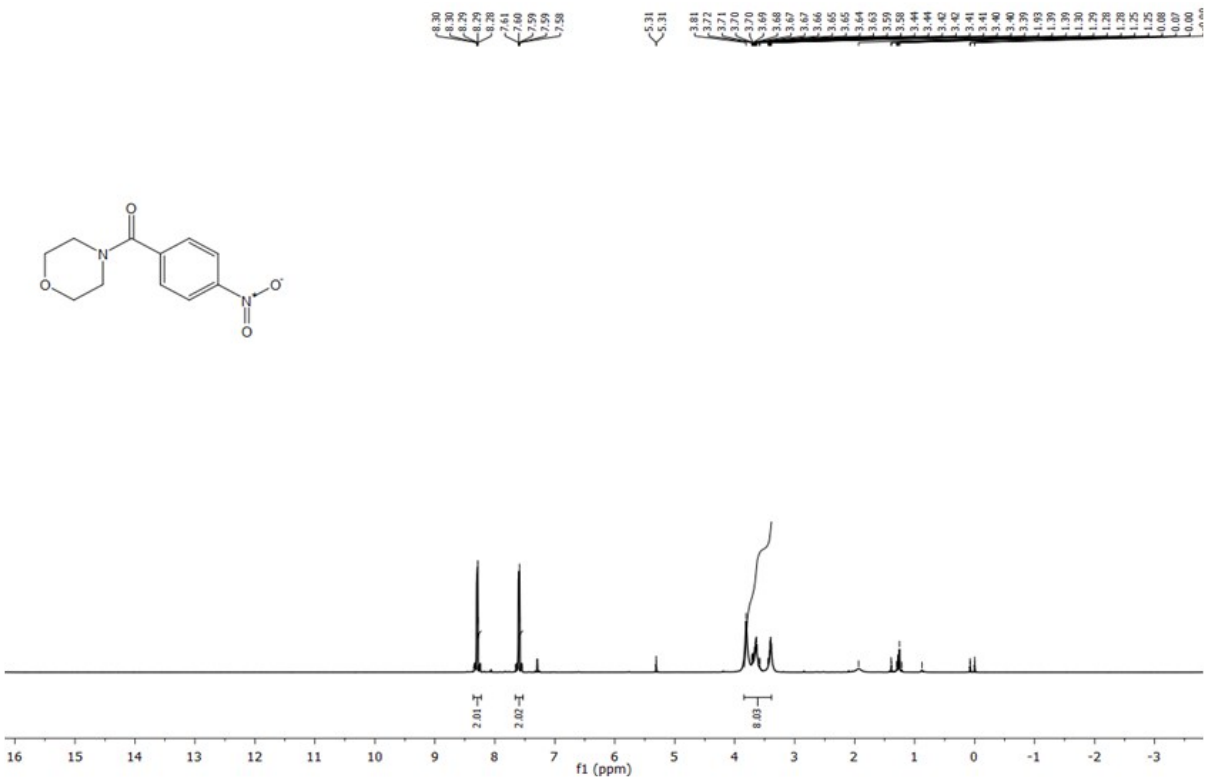
128.72
124.16
77.17
76.91
76.66
66.71
47.44
42.77
28.93
O
N
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

245



246

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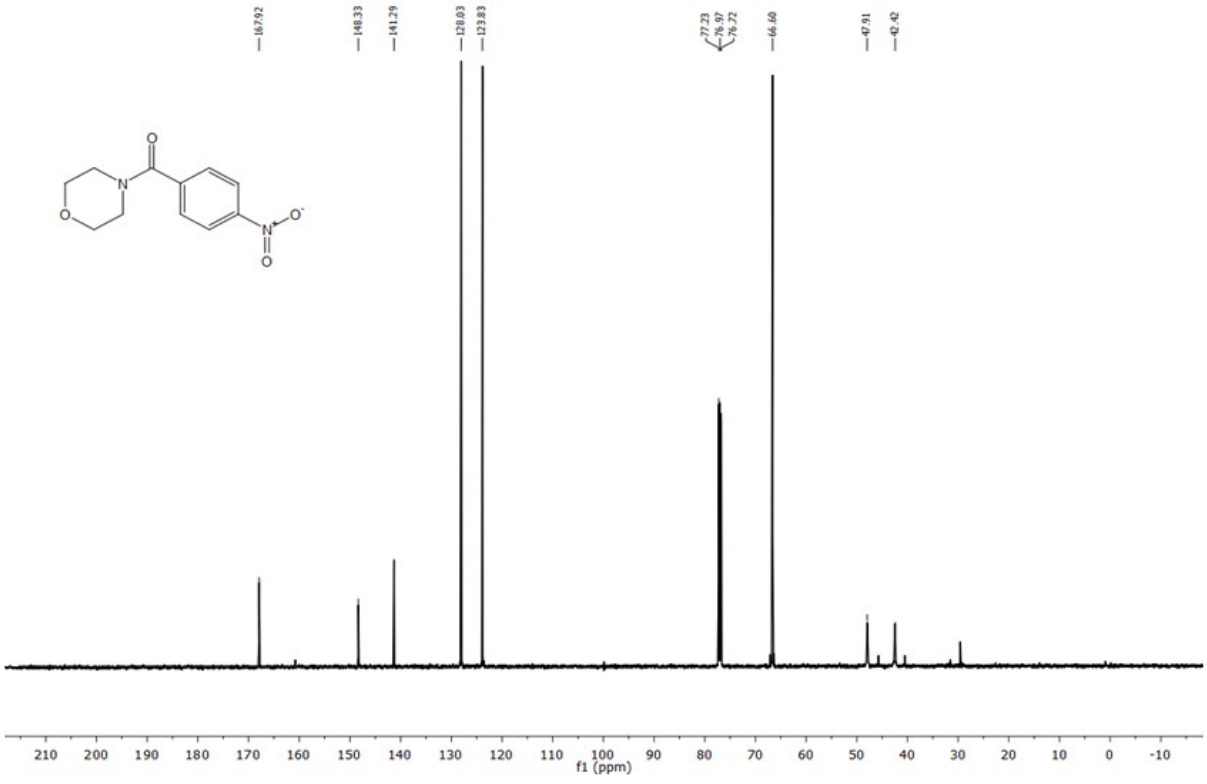

248

249