Electronic Supplementary Information

Ethanol-Mediated N-Formylation of Amines with CO_2/H_2 over Cobalt Catalysts

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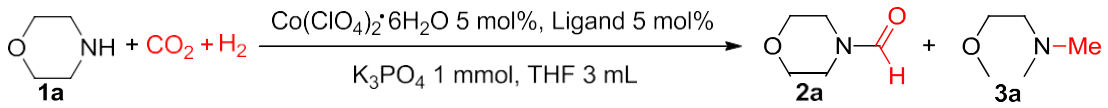
1. Reaction conditions screening for the reaction of 1a with CO_2/H_2

Table S1 Effect of ligands in THF[a]



Entry	Ligand	**2a** Yield/%[b]	**3a** Yield/%[b]
1	PP_3	69	28
2	triphos	3	4
3	dpp-BINAP	1	1
4	dpp-OPh	1	0
5	dppb	25	5
6	dppe	6	2
7	$P(PhF_5)_3$	1	0
8	$P(4\text{-}FPh)_3$	0	0
9	Cydpp	3	0
10	PPh_3	1	2
11	Bipy	1	0
12	DBU	1	1
13	Im	1	3

[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2 \cdot 6H_2O$ 5 mol%, ligand 5 mol%, K_3PO_4 1 mmol, CO_2 3 MPa, H_2 3 MPa, THF 3 mL, oil bath 140 °C, 24 h. [b] Determined by GC using dodecane as an internal standard.

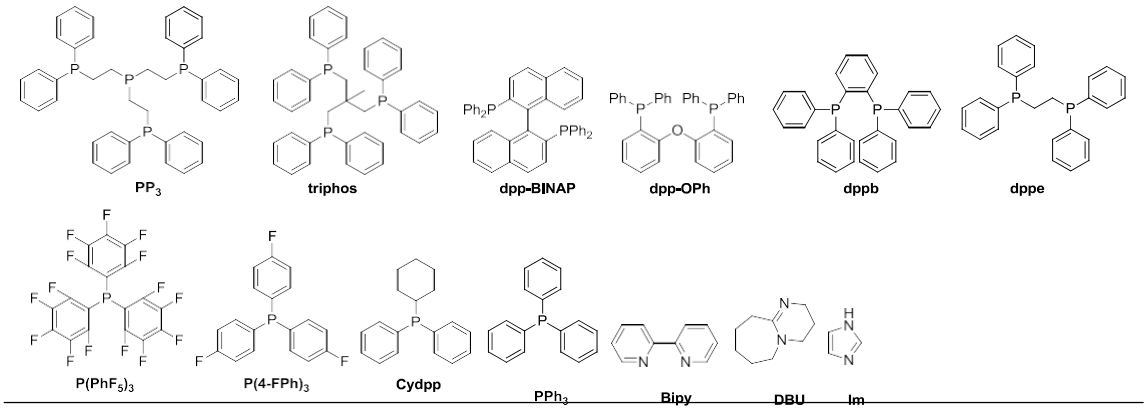
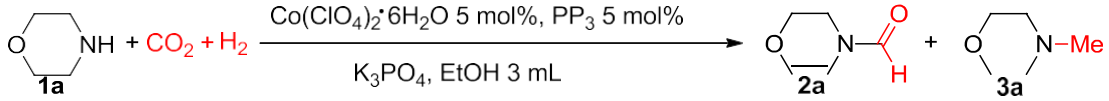


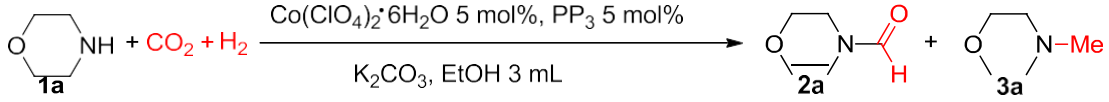
Table S2 Effect of Co species in EtOH[a]



Entry	Co	**2a** Yield/%[b]	**3a** Yield/%[b]
1	$Co(ClO_4)_2·6H_2O$	80	15
2	$Co(BF_4)_2·6H_2O$	71	15
3	$Co(NO_3)_2·6H_2O$	68	10
4	$Co(OAc)_2·4H_2O$	62	18
5	$Co(acac)_2$	48	32
6	$CoCl_2·6H_2O$	70	17

[a] Reaction conditions: **1a** 1 mmol, Co species 5 mol%, PP_3 5 mol%, K_3PO_4 1.5 mmol, EtOH 3 mL, CO_2 3 MPa, H_2 3 MPa, 140 °C, 24 h. [b] Determined by GC using dodecane as an internal standard.

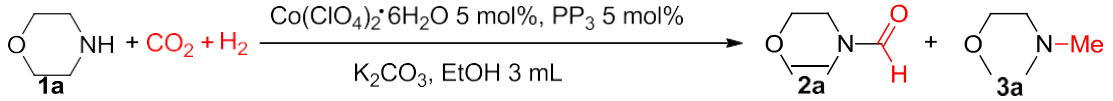
Table S3 Effect of base in EtOH[a]



Entry	Base	**2a** Yield/%[b]	**3a** Yield/%[b]
1	K_3PO_4	80	15
2	Na_3PO_4	64	10
3	K_2HPO_4	66	15
4	KH_2PO_4	28	15
5	KOH	58	22
6	KOBu-*t*	63	17
7	KF	48	30
8	K_2CO_3	95	<1
9	KOAc	62	23
10	$KClO_4$	10	13

[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, Base 1.5 mmol, EtOH 3 mL, CO_2 3 MPa, H_2 3 MPa, 140 °C, 24 h. [b] Determined by GC using dodecane as an internal standard.

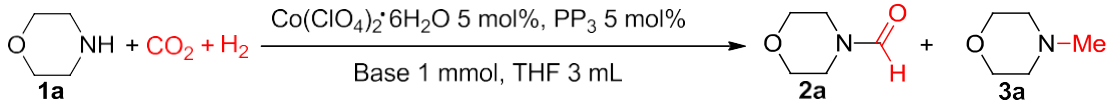
Table S4 Effect of temperature in EtOH[a]



Entry	T/°C	**2a** Yield/%[b]	**3a** Yield/%[b]
1	140	95	<1
2	120	79	10
3	100	57	16
4	80	39	5
5	60	16	2

[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, K_2CO_3 1.5 mmol, EtOH 3 mL, CO_2 3 MPa, H_2 3 MPa, 24 h. [b] Determined by GC using dodecane as an internal standard.

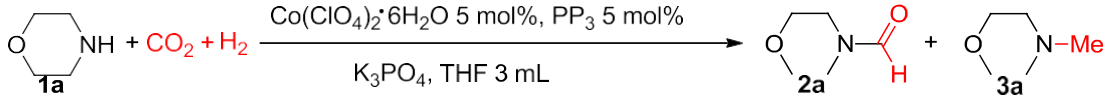
Table S5 Effect of base in THF[a]



Entry	Base	**2a** Yield/%[b]	**3a** Yield/%[b]
1	K_3PO_4	28	69
2	K_2HPO_4	29	15
3	KH_2PO_4	0	20
4	KOH	0	40
5	KO*t*-Bu	2	24
6	KF	0	26
7	K_2CO_3	39	16
8	KOAc	20	45
9	KNO_3	16	11
10	$KClO_4$	17	11
11	KBr	14	14
12	Na_3PO_4	17	37
13	NaOH	23	25
14	LiOH	19	13
15	CsOH	21	38
16	Li_2CO_3	4	33
17	Na_2CO_3	20	15
18	Cs_2CO_3	18	36
19	NaOAc	23	44
20	LiOAc	16	19
21	CsOAc	28	45

[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, Base 1 mmol, CO_2 3 MPa, H_2 3 MPa, THF 3 mL, oil bath 140 °C, 24 h. [b] Determined by GC using dodecane as an internal standard.

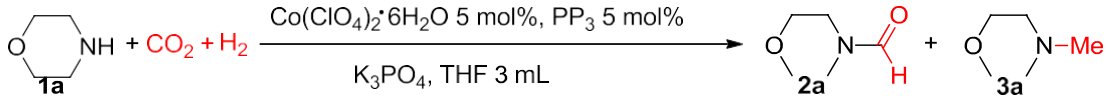
Table S6 Effect of base amount and reaction temperature in THF[a]



Entry	K_3PO_4/mmol	T/°C	**2a** Yield/%[b]	**3a** Yield/%[b]
1	1.5	140	22	24
2	1	140	28	69
3	0.5	140	15	43
4	0.25	140	14	26
5	0.1	140	5	23
6	1	160	14	30
7	1	120	21	30
8	1	100	36	3

[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, K_3PO_4, CO_2 3 MPa, H_2 3 MPa, THF 3 mL, 24 h. [b] Determined by GC using dodecane as an internal standard.

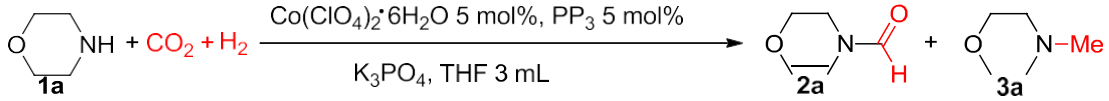
Table S7 Effect of CO_2 and H_2 pressure and reaction time in THF[a]



Entry	CO_2 pressure/MPa	Total pressure/MPa	Time/h	**2a** Yield/%[b]	**3a** Yield/%[b]
1	5	6	24	2	35
2	4	6	24	37	36
3	3	6	24	28	69
4	2	6	24	20	26
5	1	6	24	4	13
6	2	4	24	19	9
7	4	8	24	68	3
8	5	10	24	35	1
9	3	6	3	17	9
10	3	6	6	27	16
11	3	6	12	21	38
12	3	6	48	27	68
13	3	6	72	29	69

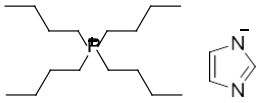
[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, K_3PO_4 1 mmol, THF 3 mL. [b] Determined by GC using dodecane as an internal standard.

Table S8 Effect of additives in THF[a]



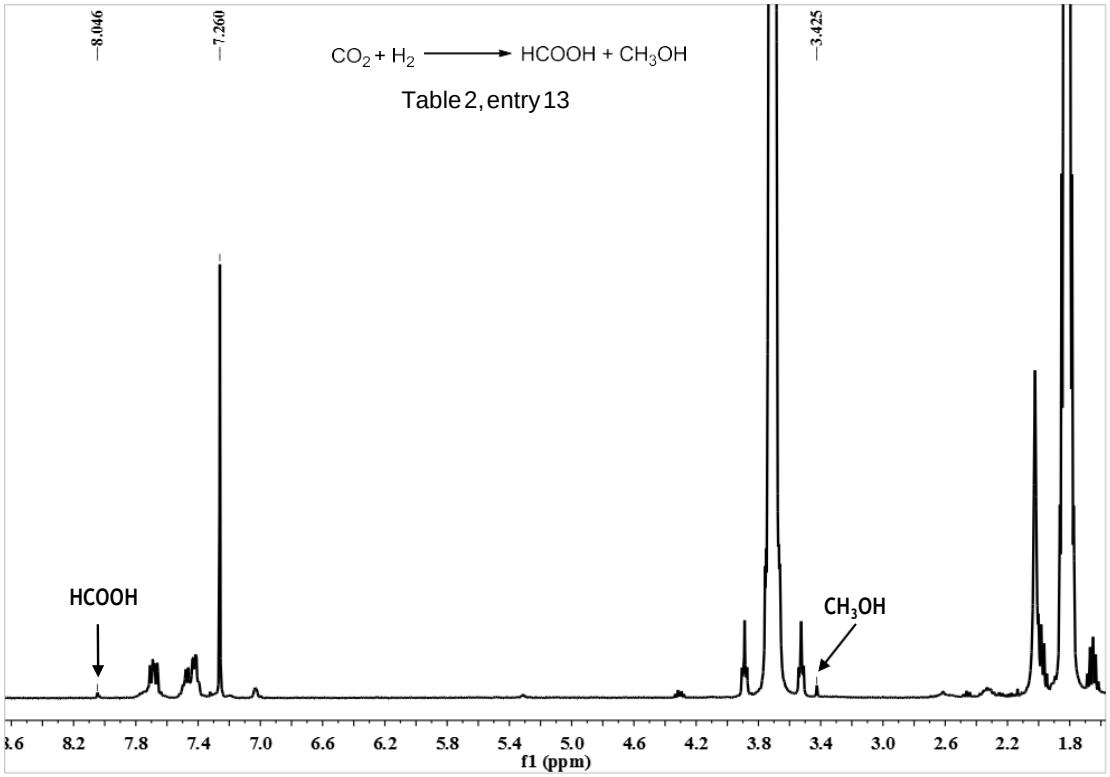
Entry	Additive/mmol	**2a** Yield/%[b]	**3a** Yield/%[b]
1	DBU/1	42	22
2	$Yb(OTf)_3·H_2O$/0.1	43	<1
3	triphos/0.05	29	13
4	$RuCl_3·3H_2O$/0.05	37	4
5	BMImBr/1	51	4
6	Mn power/1.2	52	27
7	Zn power/1.2	71	14
8	$B(PhF_5)_3$/0.1	52	16
9[c]	$[P_{4444}][Im]$/1	90	1
10[c]	n-Bu_4NF/1	89	12
11	Pd/C/0.05	67	<1
12	$PhSiH_3$/0.2	21	5
13	betaine	28	9

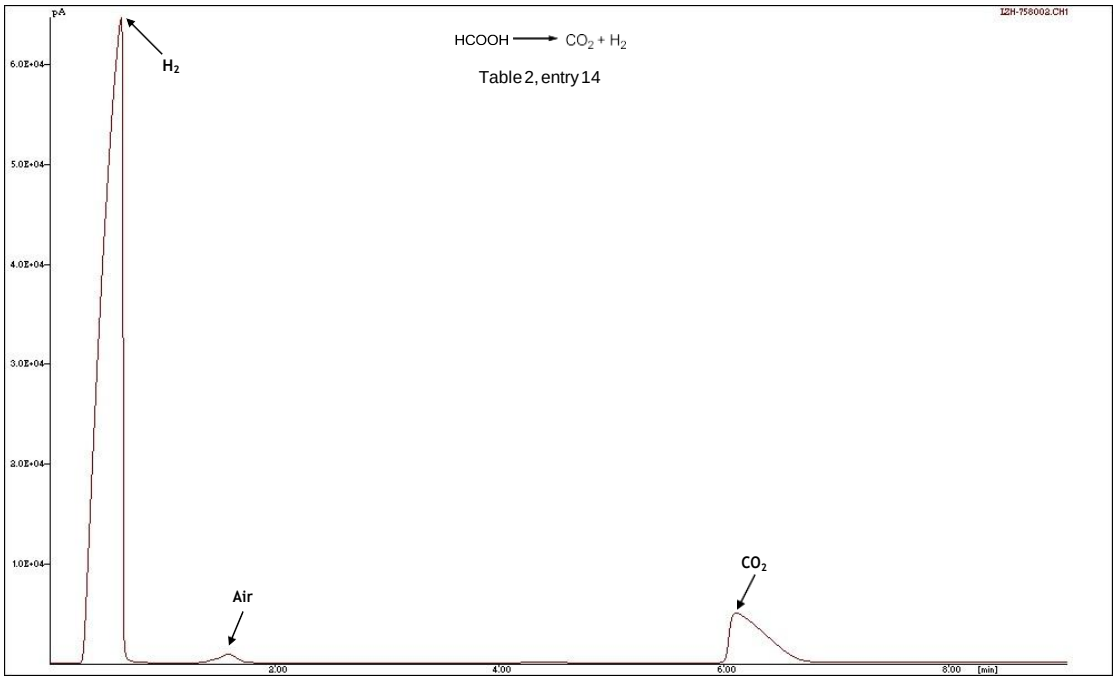
[a] Reaction conditions: **1a** 1 mmol, $Co(ClO_4)_2·6H_2O$ 5 mol%, PP_3 5 mol%, K_3PO_4 1 mmol, THF 3 mL, CO_2 3 MPa, H_2 3 MPa, 140 °C, 24 h. [b] Determined by GC using dodecane as an internal standard. [c] No base. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene, triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane, BMImBr = 1-butyl-3-methylimidazolium bromide,

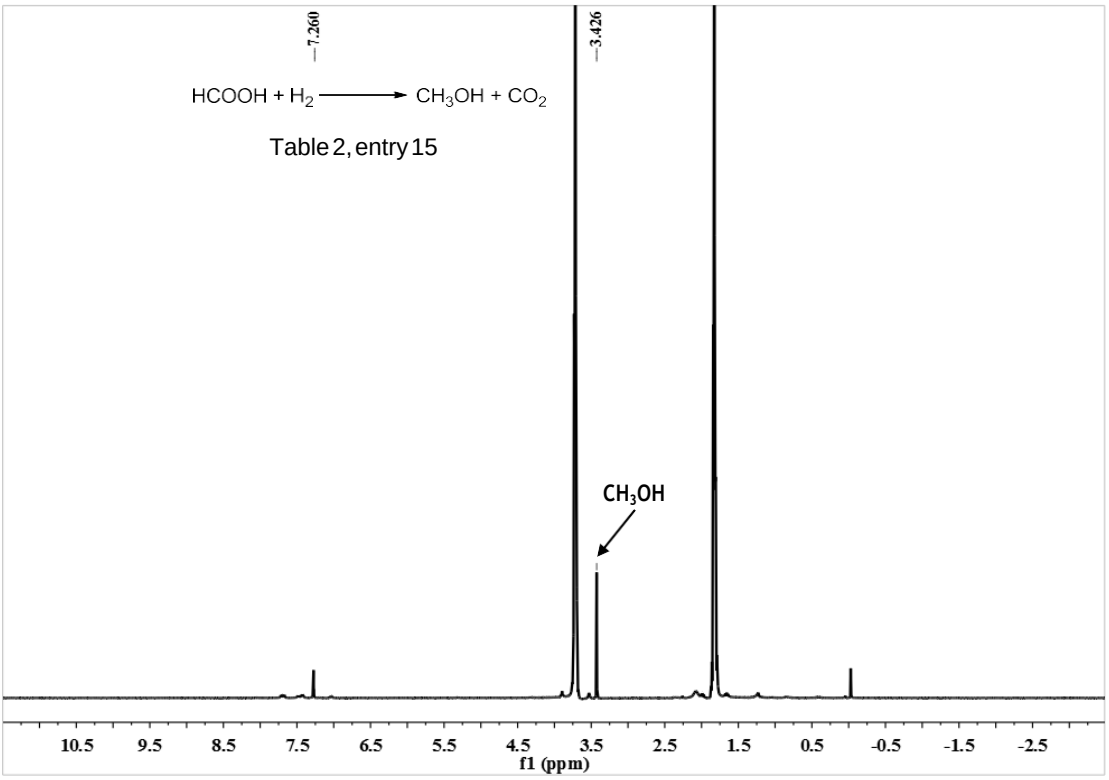


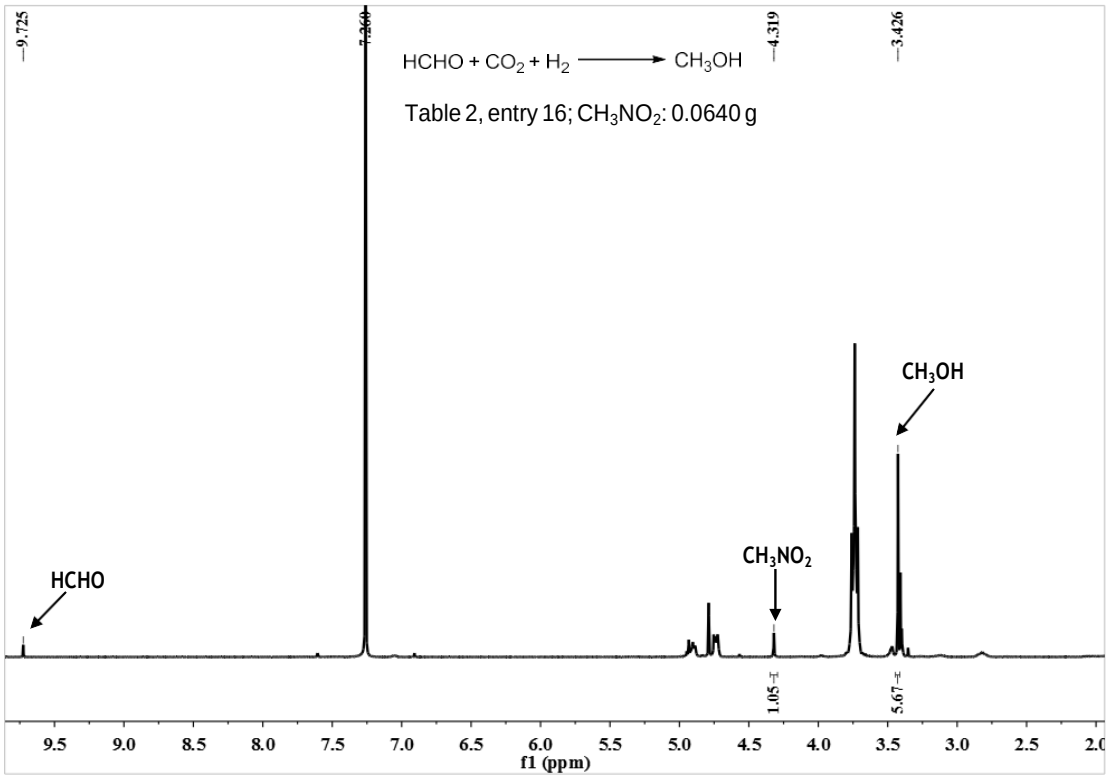
$[P_{4444}][Im]$

2. NMR spectra for the determination of HCOOH, CH_3OH and GC spectra for the determination of CO_2 and H_2

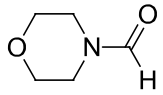




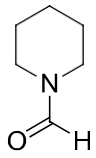

7.260
3.426
HCOOH + H2 → CH3OH + CO2
Table 2, entry 15
CH3OH
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2.5
f1 (ppm)


9.725
7.260
4.319
3.426
HCHO + CO2 + H2 → CH3OH
Table 2, entry 16; CH3NO2: 0.0640 g
CH3OH
CH3NO2
HCHO
1.05
5.67
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
f1 (ppm)

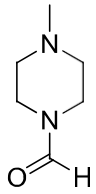
3. Yields determination and characterization of the formamide products from amines and CO_2/H_2



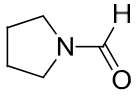
2a; N-Formylmorpholine; CAS No. 4394-85-8;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.17 (t, ^3J = 5.2 Hz, 2H), 3.31 (t, ^3J = 5.2 Hz, 2H), 3.41 (t, ^3J = 4.4 Hz, 2H), 3.45 (t, ^3J = 4.4 Hz, 2H), 7.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 38.89, 44.11, 64.75, 65.68, 159.39. M ($C_5H_9NO_2$) = 115.1, EI-MS found 115.0 [M], 86.0 [M-CHO].



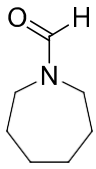
2b; N-Formylpiperidine; CAS No. 2591-86-8;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40-1.50 (m, 4H), 1.55-1.61 (m, 2H), 3.21 (t, ^3J = 5.2 Hz, 2H), 3.37 (t, ^3J = 5.6 Hz), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 24.41, 24.81, 26.30, 40.34, 46.56, 160.56. M ($C_6H_{11}NO$) = 113.1, EI-MS found 113.0 [M], 84.0 [M-CHO].



2c; 1-Formyl-4-methylpiperazine; CAS No. 7556-55-0;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.34 (t, ^3J = 4.8 Hz, 2H), 2.38 (t, ^3J = 4.8 Hz, 2H), 3.37 (t, ^3J = 4.4 Hz, 2H), 3.54 (s, 2H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 39.80, 45.47, 46.07, 54.17, 55.34, 160.66. M ($C_6H_{12}N_2O$) = 128.1, EI-MS found 128.0 [M], 113.0 [M-CH_3], 99.0 [M-CHO].

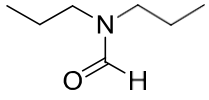


2d; N-Formylpyrrolidine; CAS No. 3760-54-1;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65-1.70 (m, 4H), 3.16 (t, ^3J = 6.4 Hz, 2H), 3.27 (t, ^3J = 6.4 Hz, 2 H), 8.01 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 22.07, 22.77, 40.71, 43.58, 158.31. M (C_5H_9NO) = 99.1, EI-MS found 99.0 [M], 71.0 [M-C=O].

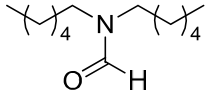


2e; N-formylhexamethyleneimine; CAS No. 25114-81-2;[2] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR

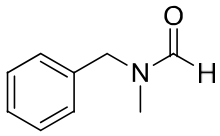
($CDCl_3$, 400 MHz) δ 1.56 (s, 4H), 1.69-1.72 (m, 4H), 3.35 (t, ^3J = 6 Hz, 2H), 3.43 (t, ^3J = 6 Hz, 2H), 8.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.81, 26.91, 27.89, 30.21, 43.35, 47.64, 162.81. M ($C_7H_{13}NO$) = 127.1, EI-MS found 127.0 [M], 98.0 [M-CHO].



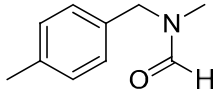
2f; N,N-di-n-propylformamide; CAS No. 6282-00-4;[3] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (10:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.72-0.76 (m, 6H), 1.38-1.45 (m, 4H), 3.02 (t, ^3J = 7.2 Hz, 2H), 3.10 (t, ^3J = 7.6 Hz, 2H), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.51, 10.92, 20.17, 21.45, 43.35, 48.76, 162.39. M ($C_7H_{15}NO$) = 129.2, EI-MS found 129.1 [M], 100.0 [M-CHO].



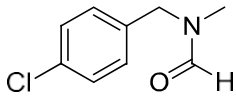
2g; N,N-dihexylformamide; CAS No. 14287-94-6;[4] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84-0.86 (m, 6H), 1.25 (s, 12H), 1.47-1.48 (m, 4H), 3.14 (t, ^3J = 7.2 Hz, 2H), 3.23 (t, ^3J = 7.2 Hz, 2H), 7.99 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.83, 13.87, 22.41, 22.44, 26.04, 26.51, 27.17, 28.54, 31.27, 31.42, 42.02, 47.34, 162.54. M ($C_{13}H_{27}NO$) = 213.2, EI-MS found 213.1 [M], 198.1 [M-CH_3], 184.1 [M-CHO].



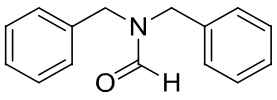
2h; N-methyl-N-benzylformamide; CAS No. 17105-71-4;[5] Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (50:1) as eluent. Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.78, 2.84 (s, 3H), 4.39 (s, 1H), 4.52 (s, 1H), 7.19-7.37 (m, 5H), 8.16, 8.28 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.42, 33.98, 47.75, 53.45, 127.36, 127.60, 128.06, 128.22, 128.66, 128.87, 135.77, 136.03, 162.52, 162.69. M ($C_9H_{11}NO$) = 149.1, EI-MS found 149.1 [M], 134.0 [M-CH_3], 120.1 [M-CHO].



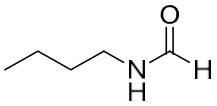
2i; N-methyl-N-[(4-methylphenyl)methyl]formamide; CAS No. 54410-77-4; Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32, 2.34 (s, 3H), 2.76, 2.82 (s, 3H), 4.34, 4.47 (s, 2H), 7.07-7.17 (m, 4H), 8.13, 8.26 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.01, 29.28, 33.88, 47.42, 53.18, 127.33, 128.21, 129.28, 129.49, 132.65, 132.97, 137.27, 137.81, 162.44, 162.61. M ($C_{10}H_{13}NO$) = 163.2, EI-MS found 163.0 [M], 148.0 [M-CH_3], 134.0 [M-CHO].



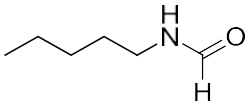
2j; N-methyl-N-[(4-chlorophenyl)methyl]formamide; CAS No. 104936-73-4; Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.69, 2.77 (s, 3H), 4.29, 4.41 (s, 2H), 7.06-7.29 (m, 4H), 8.07, 8.20 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 29.37, 33.96, 47.11, 52.76, 128.70, 128.82, 129.07, 129.57, 133.49, 133.99, 134.26, 134.57, 162.52, 162.59. M ($C_9H_{10}ClNO$) = 183.0, EI-MS found 182.9 [M], 167.8 [M-CH_3], 147.9 [M-Cl], 139.9 [M-CH_3-CO].



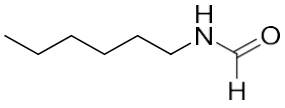
2k; N,N-dibenzylformamide; CAS No. 5464-77-7;[6] Purification by column chromatography on silica gel using petroleum ether/ethyl acetate (100:1) as eluent. Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.26 (s, 2H), 4.41 (s, 2H), 7.16-7.39 (m, 10 H), 8.42 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 44.67, 50.24, 127.63, 127.68, 128.11, 128.50, 128.66, 128.89, 135.65, 136.03, 162.78. M ($C_{15}H_{15}NO$) = 225.1, EI-MS found 225.1 [M], 134.0 [M-C_7H_7].



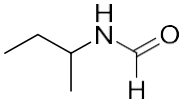
2l; N-butylformamide; CAS No. 871-71-6;[7] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.89-0.93 (m, 3H), 1.30-1.39 (m, 2H), 1.46-1.53 (m, 2H), 3.25-3.30 (m, 2H), 5.74 (s, 1H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 21.66, 31.30, 39.88, 46.11, 160.71. M ($C_5H_{11}NO$) = 101.1, EI-MS found 101.1 [M], 100.1 [M-H], 86.0 [M-CH_3], 72.0 [M-CHO].



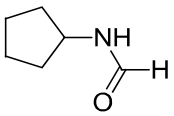
2m; N-pentylformamide; CAS No. 2591-79-9;[8] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.82-0.86 (m, 3H), 1.26-1.28 (m, 4H), 1.44-1.51 (m, 2H), 3.19-3.25 (m, 2H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.80, 22.15, 28.86, 29.02, 38.03, 161.26. M ($C_6H_{11}NO$) = 115.2, EI-MS found 115.0 [M], 100.0 [M-CH_3], 86.0 [M-CHO].



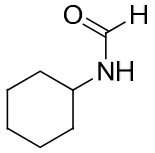
2n; N-hexylformamide; CAS No. 2591-78-8;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.85-0.89 (m, 3H), 1.24-1.34 (m, 6H), 1.46-1.53 (m, 2H), 3.24-3.31 (m, 2H), 5.71 (s, 1H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 13.93, 22.48, 26.46, 29.44, 31.36, 38.16, 161.12. M ($C_7H_{15}NO$) = 129.2, EI-MS found 129.0 [M], 114.0 [M-CH_3], 100.0 [M-CHO].



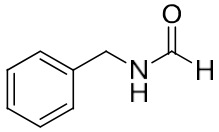
2o; N-*sec*-butylformamide; CAS No. 53798-89-3;[9] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.91 (t, ^{3}J = 6.8 Hz, 3H), 1.14 (d, ^{3}J = 6.4 Hz, 3H), 1.40-1.55 (m, 2H), 3.96-4.03 (m, 1H), 5.44 (s, 1H), 8.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 10.22, 20.37, 29.54, 45.47, 160.52. M ($C_5H_{11}NO$) = 101.1, EI-MS found 101.0 [M], 86.0 [M-CH_3], 72.0 [M-CHO].



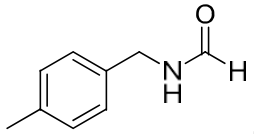
2p; N-cyclopentylformamide; CAS No. 41215-40-1;[5] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (20:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38-1.44 (m, 2H), 1.58-1.70 (m, 4H), 1.95-2.01 (m, 2H), 4.23-4.31 (m, 1H), 5.65 (s, 1H), 8.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 23.60, 33.01, 34.05, 49.91, 53.53, 160.76. M ($C_6H_{11}NO$) = 113.1, EI-MS found 113.0 [M], 83.9 [M-CHO].



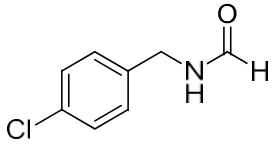
2q; N-cyclohexylformamide; CAS No. 766-93-8;[5] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (20:1) as eluent. Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.11-1.40 (m, 6H), 1.68-1.73 (m, 2H), 1.86-1.94 (m, 2H), 3.81-3.89 (m, 1H), 5.54 (s, 1H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 24.70, 25.40, 33.02, 34.68, 47.05, 50.90, 160.23. M ($C_7H_{13}NO$) = 127.1, EI-MS found 127.0 [M], 97.9 [M-CHO], 84.0 [M-NCHO].



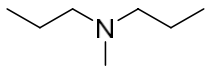
2r; N-benzylformamide; CAS No. 6343-54-0;[10] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.42 (d, ^3J = 8 Hz, 2H), 6.39 (s, 1H), 7.24-7.32 (m, 5H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 42.11, 127.63, 127.75, 128.75, 137.67, 161.22. M (C_8H_9NO) = 135.1, EI-MS found 135.0 [M], 106.0 [M-CHO].



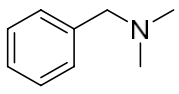
2s; N-(4-methylbenzyl)formamide; CAS No. 90609-66-8;[1] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 4.38 (d, ^3J = 5.6 Hz, 2H), 7.11-7.16 (m, 4H), 8.17 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 20.96, 41.76, 127.64, 129.28, 134.54, 137.20, 161.02. M ($C_9H_{11}NO$) = 149.2, EI-MS found 148.9 [M], 133.9 [M-CH_3], 119.9 [M-CHO].



2t; N-(4-chlorobenzyl)formamide; CAS No. 86386-67-6;[10] Purification by column chromatography on silica gel using CH_2Cl_2/CH_3OH (50:1) as eluent. Light yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.43 (d, ^3J = 8.0 Hz, 2H), 6.04 (s, 1H), 7.19-7.22 (m, 2H), 7.28-7.32 (m, 2H), 8.25 (s, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 41.44, 128.87, 129.09, 133.50, 136.15, 160.95. M (C_8H_8ClNO) = 169.0, EI-MS found 169.0 [M], 140.0 [M-CHO] 134.0 [M-Cl].



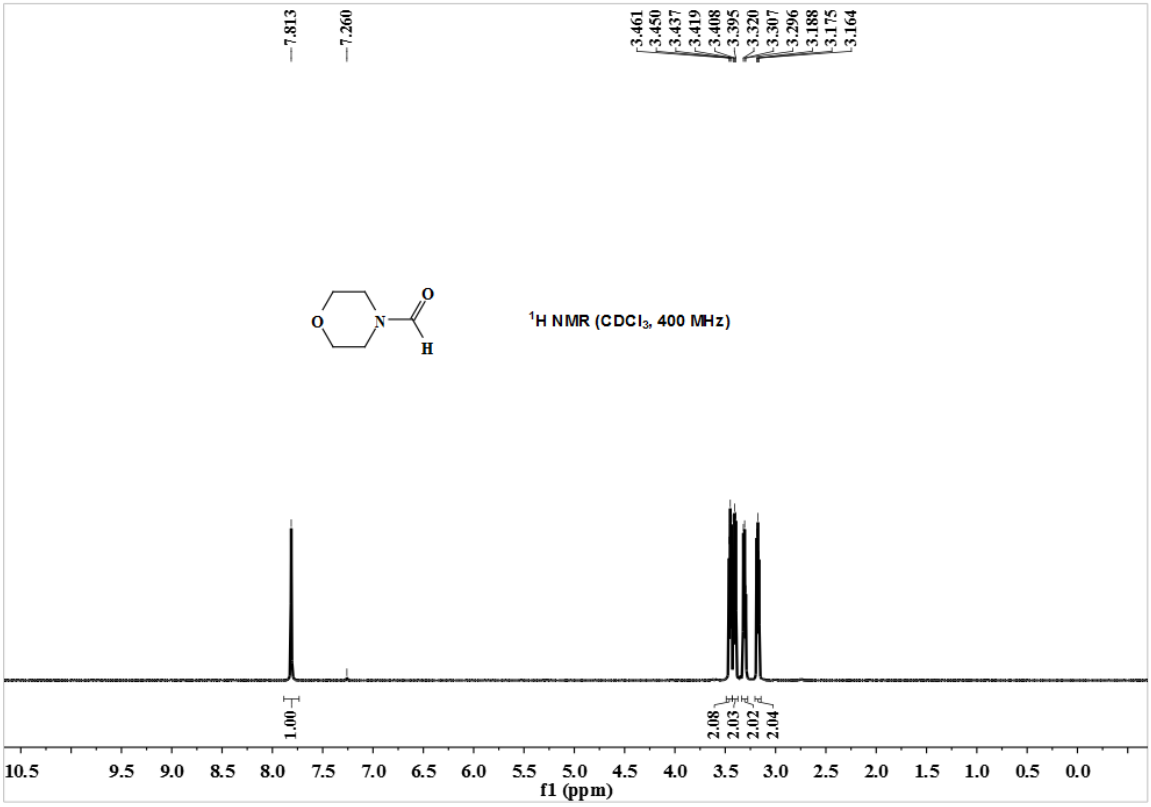
3f; N-methyl-N-propylpropan-1-amine; CAS No. 3405-42-3;[12] Purification by column chromatography on silica gel using petroleum ether/ethyl acetate/triethylamine (10:1:0.05) as eluent. Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.84-0.88 (t, 6H), 1.40-1.50 (m, 4H), 2.17 (s, 3H), 2.22-2.27 (t, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 11.90, 20.45, 42.30, 59.87.
EI-MS found 115.2 [M], 86.1 [M-CHO].

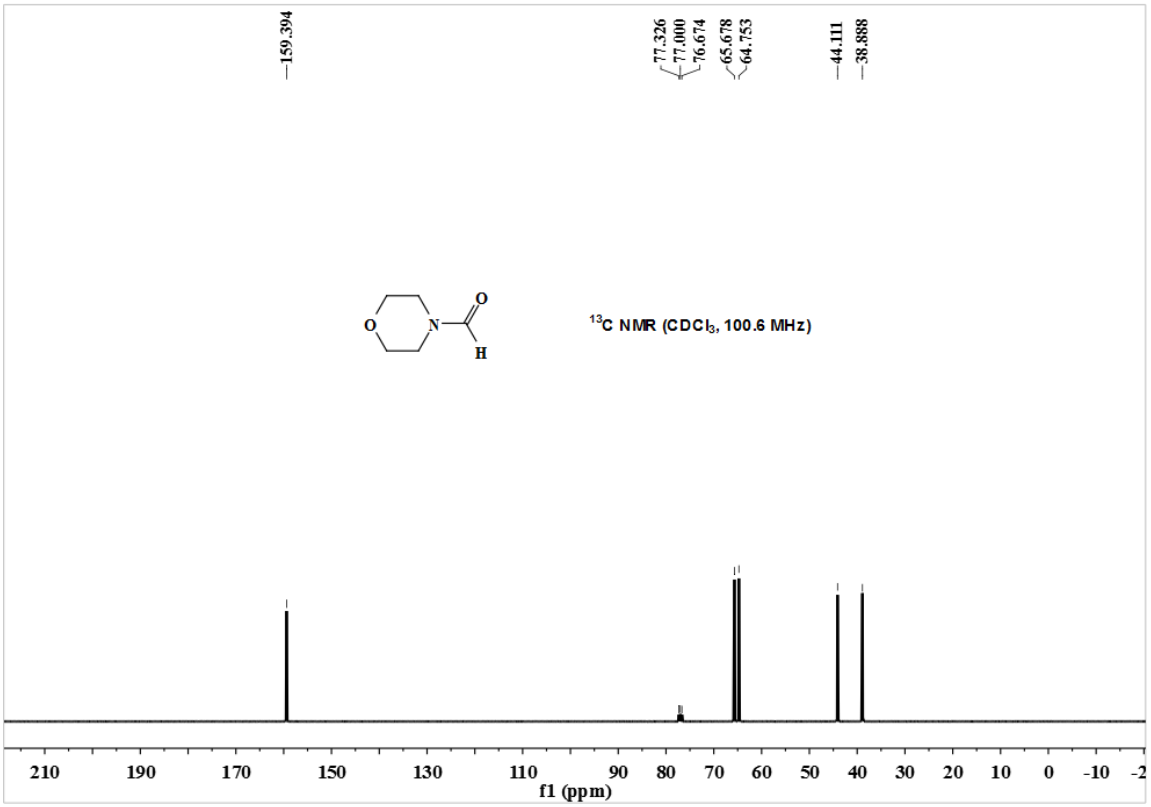


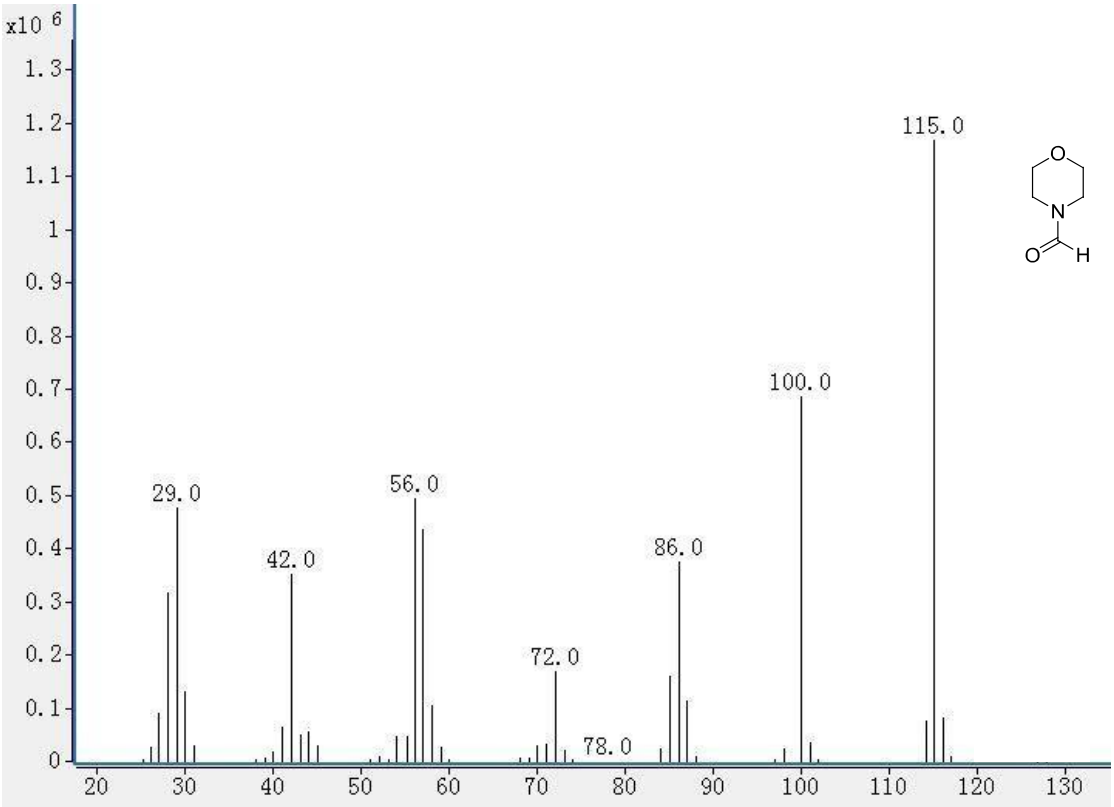
3h; N,N-dimethylbenzylamine; CAS No. 103-83-3;[12] Purification by column chromatography on silica gel using petroleum ether/ethyl acetate/triethylamine (10:1:0.05) as eluent. Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 6H), 3.45 (s, 2H), 7.29-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 45.31, 64.36, 126.98,128.17, 129.05, 138.80. EI-MS found

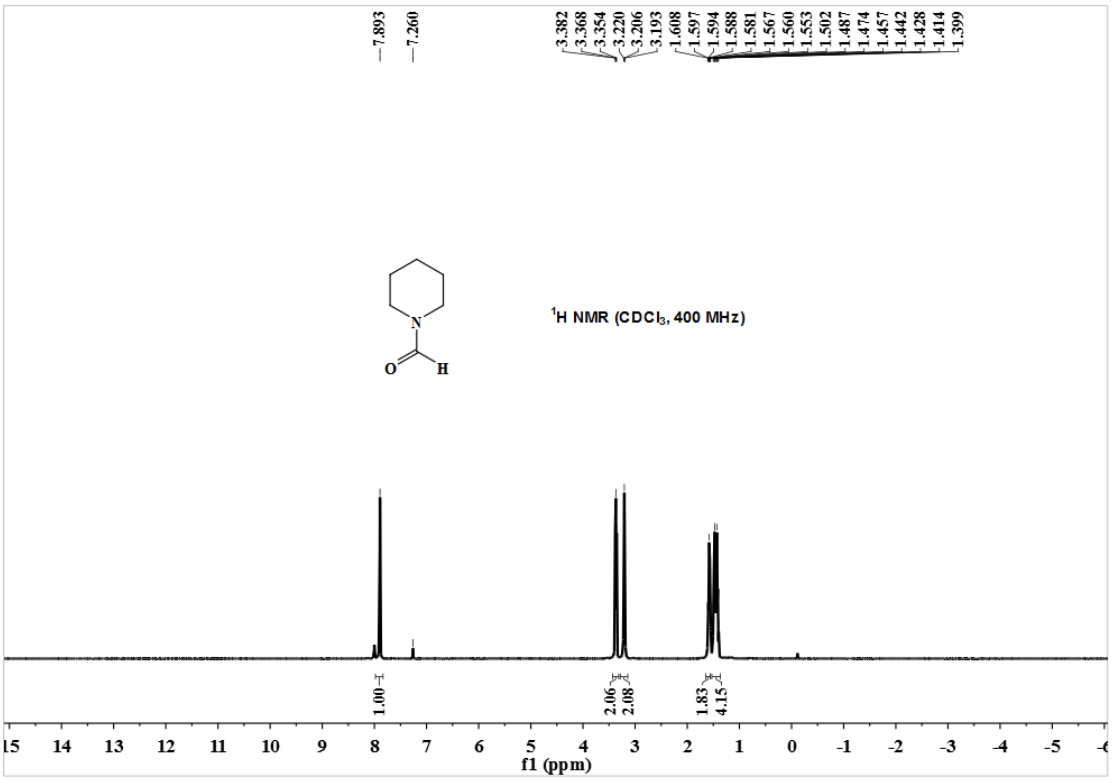
135.1 [M], 91.0 [M-N(CH_3)$_2$].

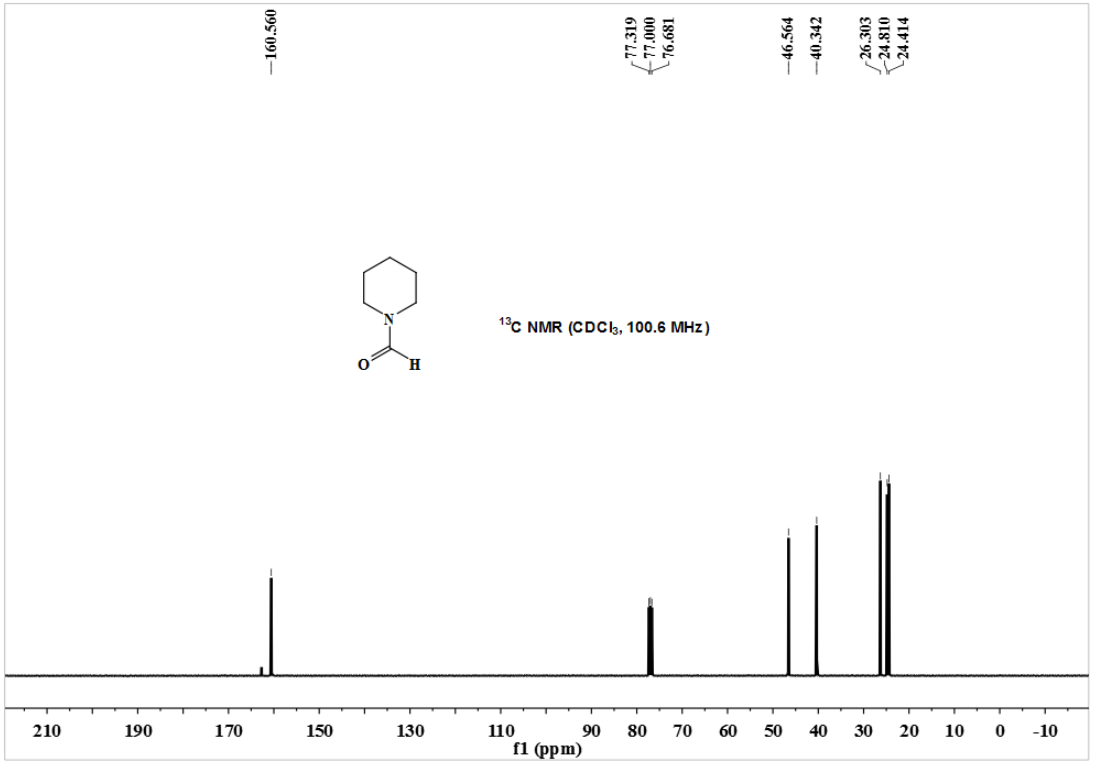
4. NMR and EI-MS spectra of the formamide products from amines and CO_2/H_2

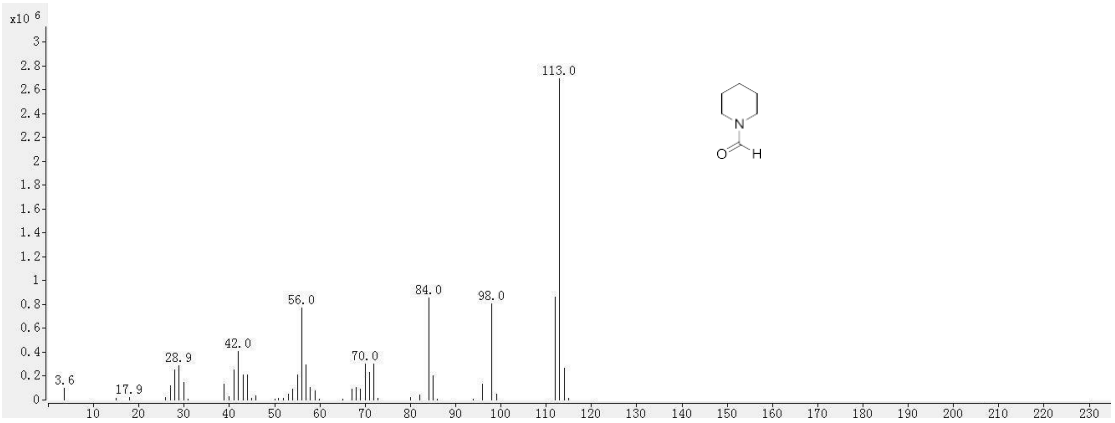


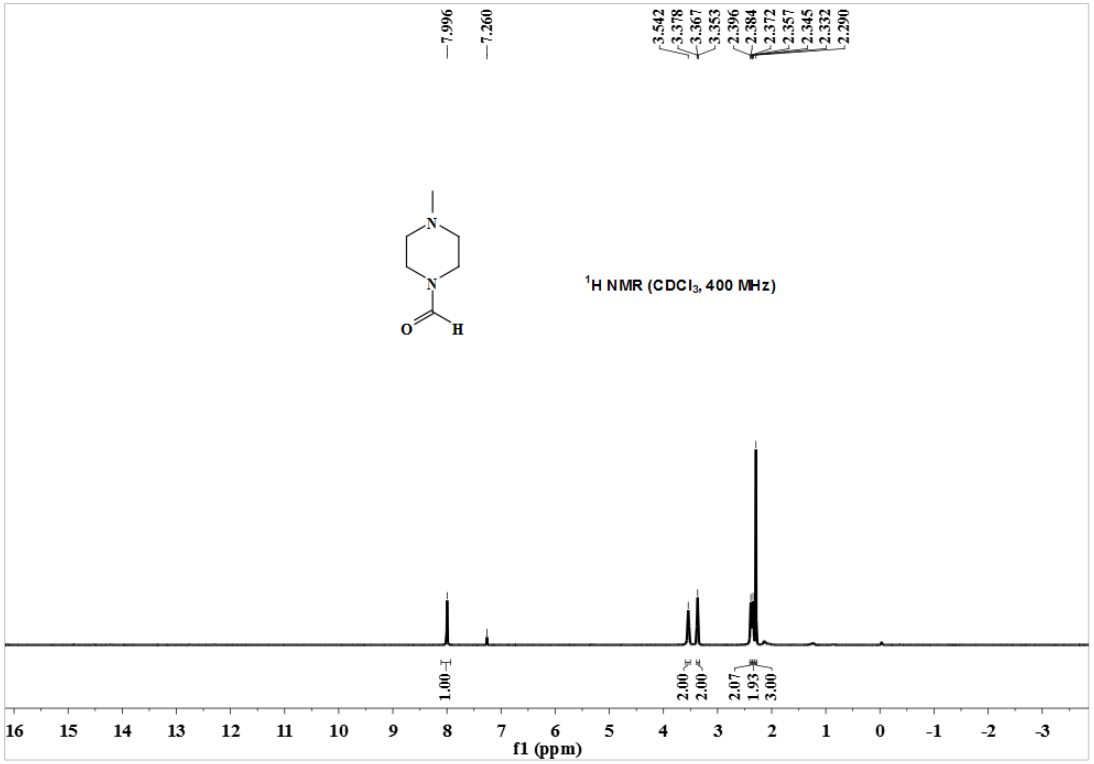

159.394
77.326
77.000
76.674
65.678
64.753
44.111
38.888
^{13}C NMR (CDCl$_3$, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)

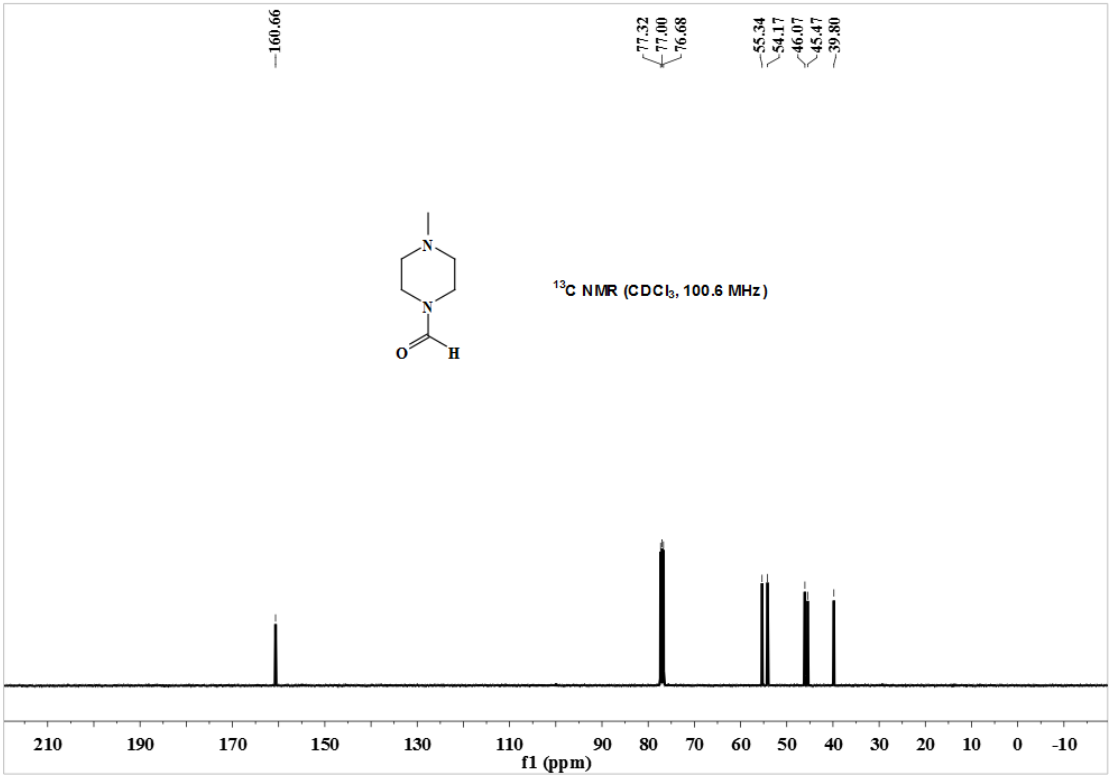

x10 6
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
115.0
100.0
86.0
56.0
42.0
29.0
72.0
78.0
20 30 40 50 60 70 80 90 100 110 120 130

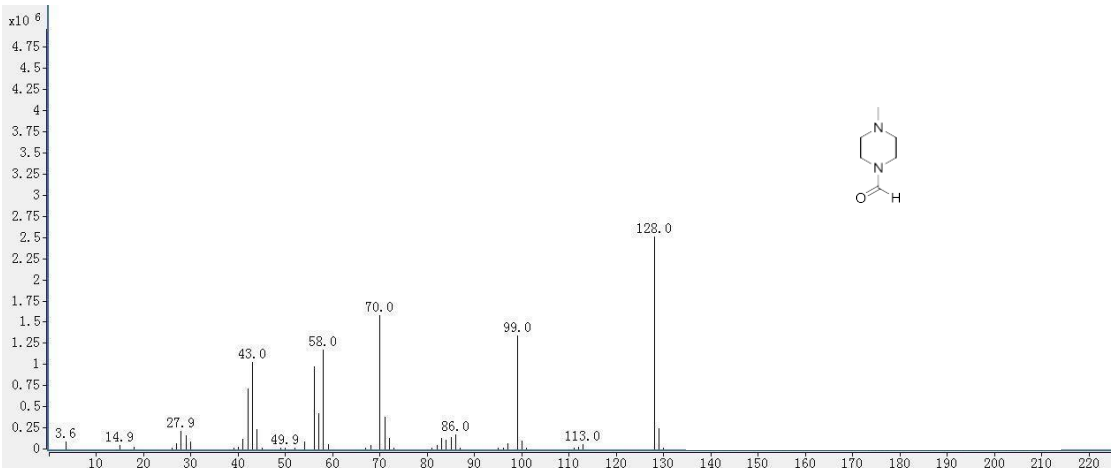

7.893
7.260
3.382
3.368
3.354
3.220
3.206
3.193
1.608
1.597
1.594
1.588
1.581
1.567
1.560
1.553
1.502
1.487
1.474
1.457
1.442
1.428
1.414
1.399
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
2.06
2.08
1.83
4.15
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

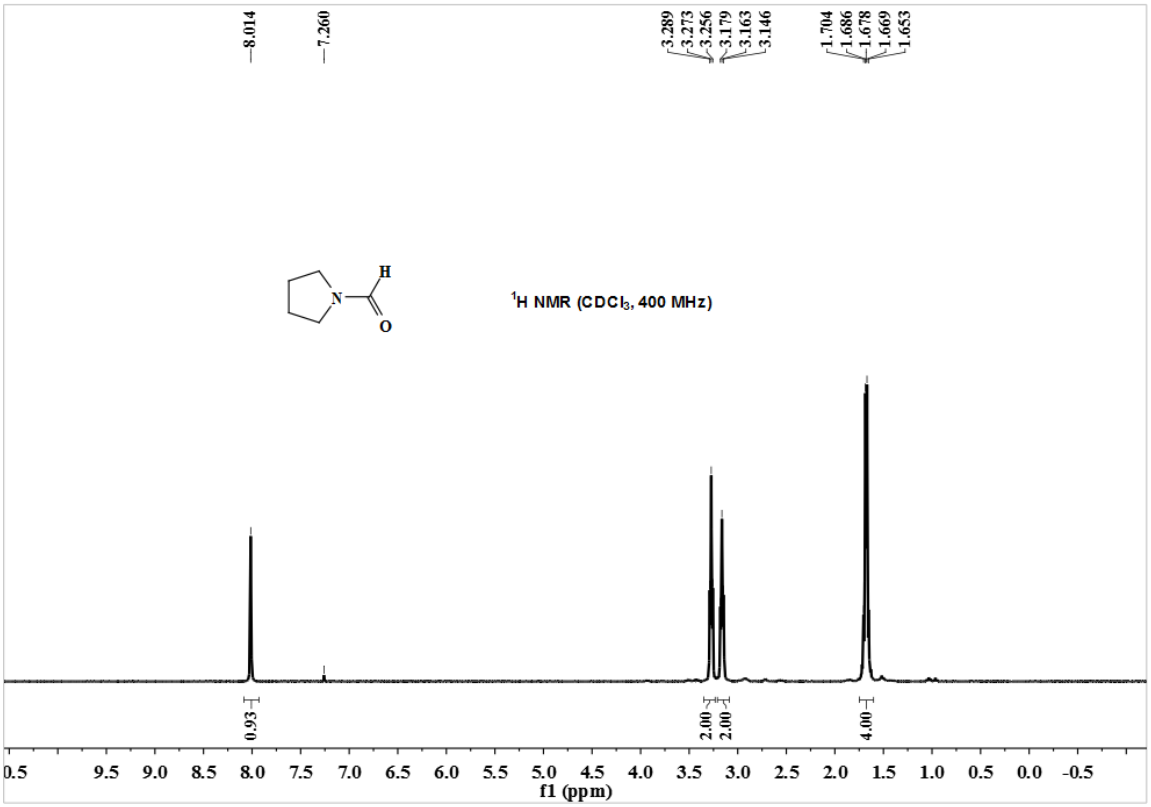

160.560
77.319
77.000
76.681
46.564
40.342
26.303
24.810
24.414
N
O
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

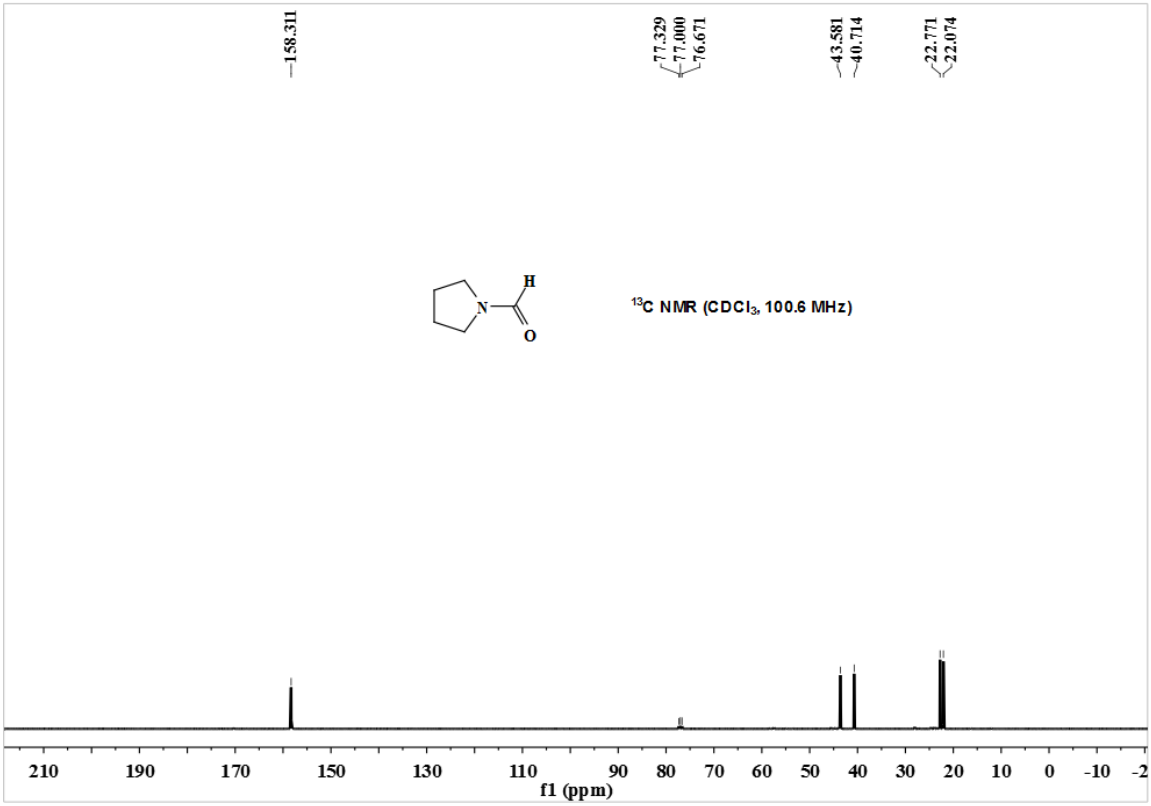

x10 6
113.0
84.0
98.0
56.0
42.0
28.9
70.0
3.6
17.9

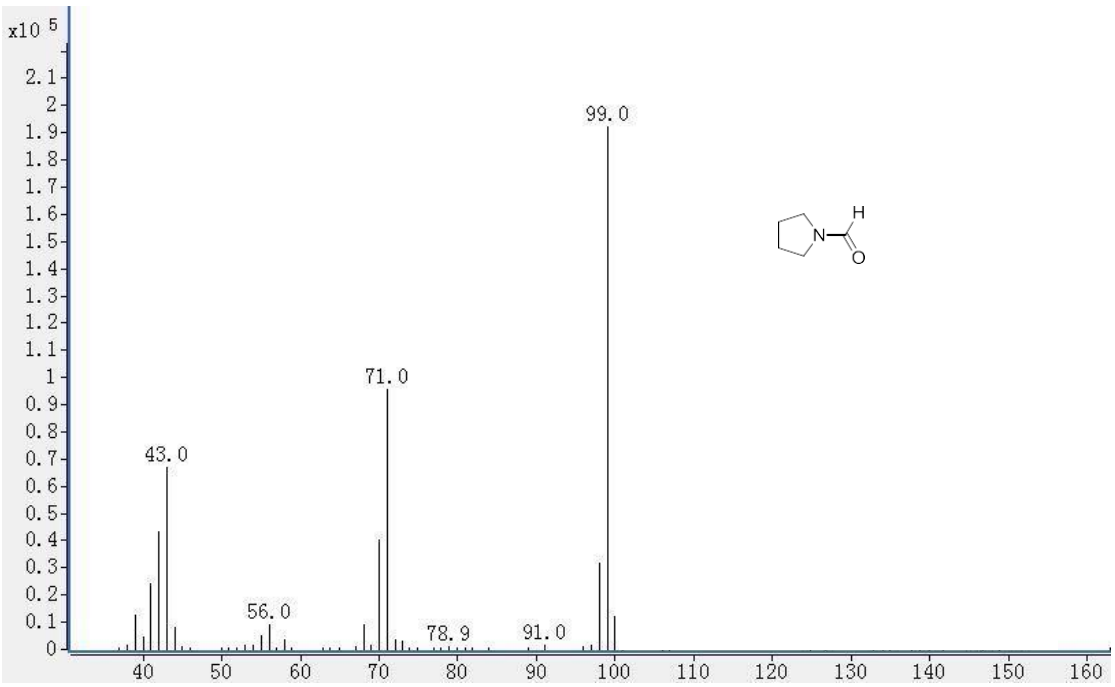

7.996
7.260
3.542
3.378
3.367
3.353
2.396
2.384
2.372
2.357
2.345
2.332
2.290
^{1}H NMR (CDCl$_3$, 400 MHz)
1.00
2.00
2.00
2.07
1.93
3.00
f1 (ppm)

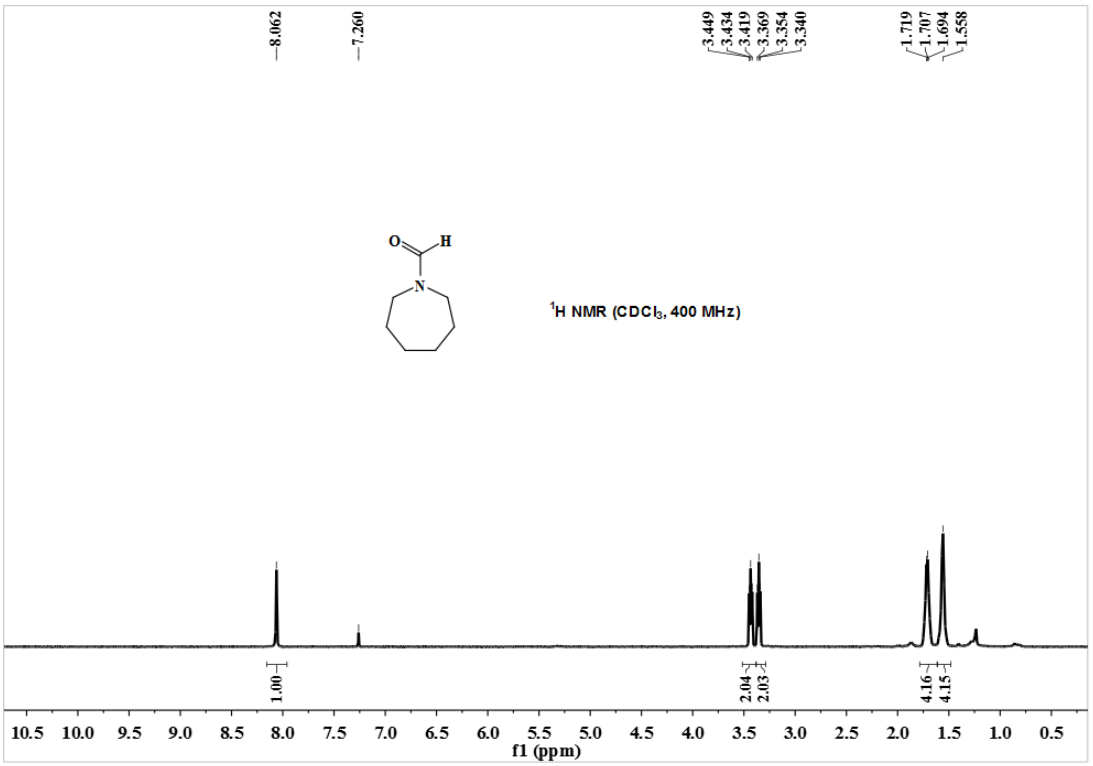

160.66
77.32
77.00
76.68
55.34
54.17
46.07
45.47
39.80
^{13}C NMR (CDCl$_3$, 100.6 MHz)
f1 (ppm)

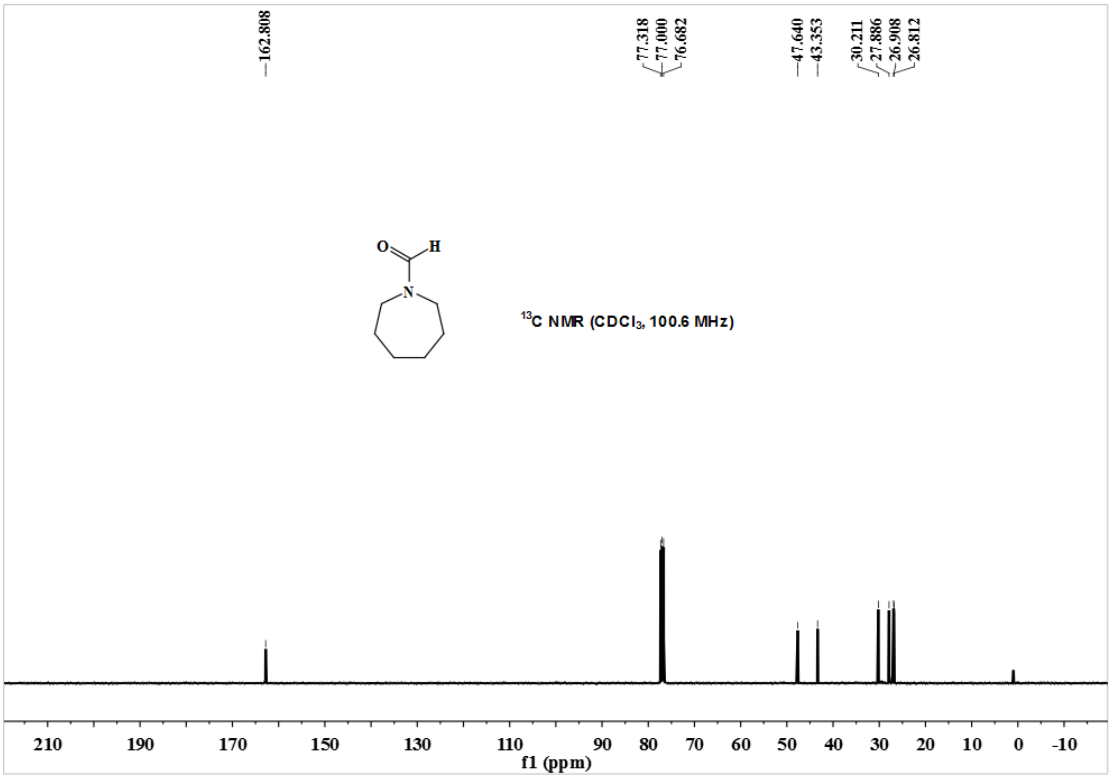

x10 6
128.0
70.0
99.0
58.0
43.0
27.9
3.6
14.9
49.9
86.0
113.0

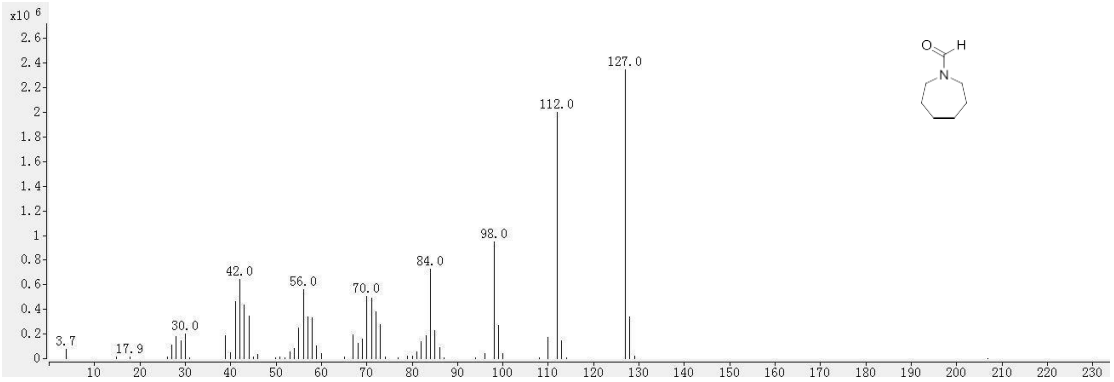

8.014
7.260
3.289
3.273
3.256
3.179
3.163
3.146
1.704
1.686
1.678
1.669
1.653
^{1}H NMR (CDCl$_3$, 400 MHz)
0.93
2.00
2.00
4.00
f1 (ppm)

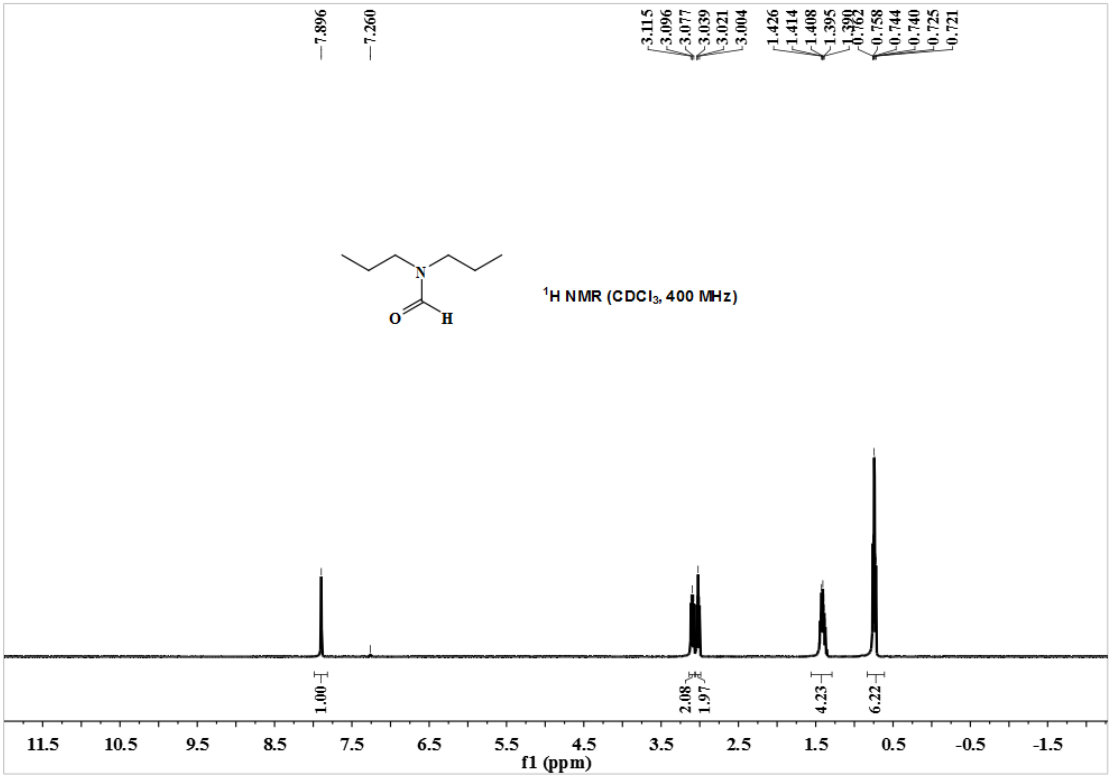

158.311
77.329
77.000
76.671
43.581
40.714
22.771
22.074
^{13}C NMR (CDCl$_3$, 100.6 MHz)
f1 (ppm)

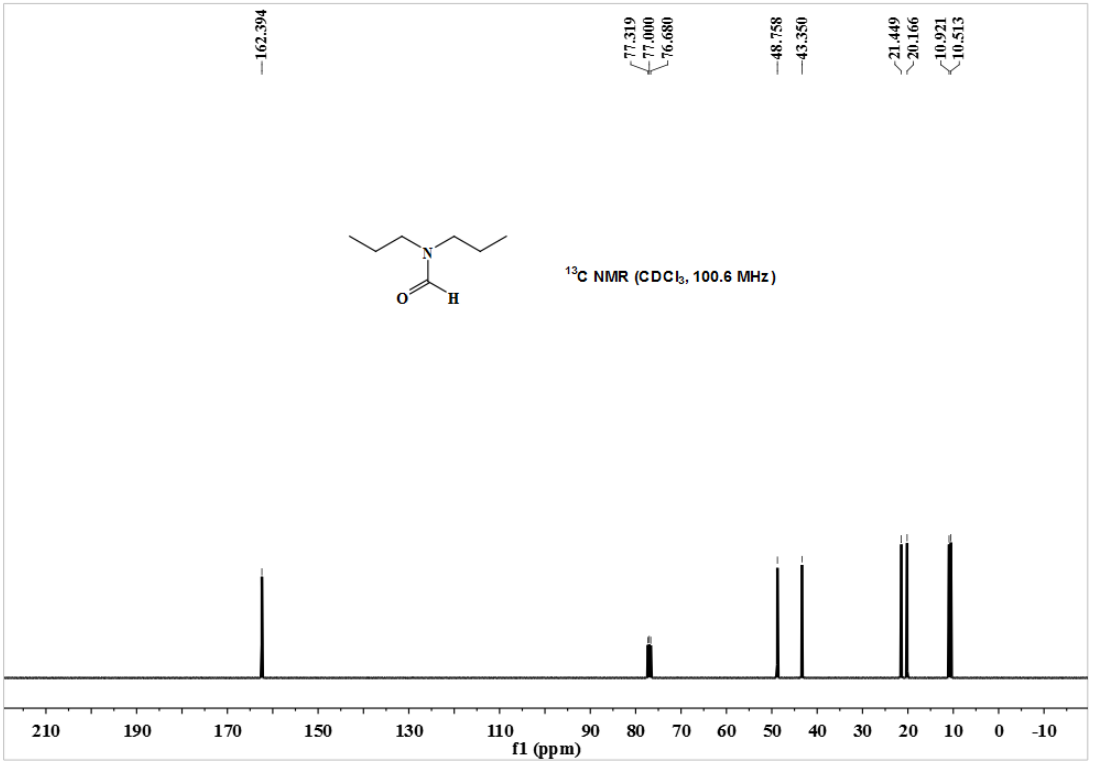

x10 5
99.0
71.0
43.0
56.0
78.9
91.0
H
N
O

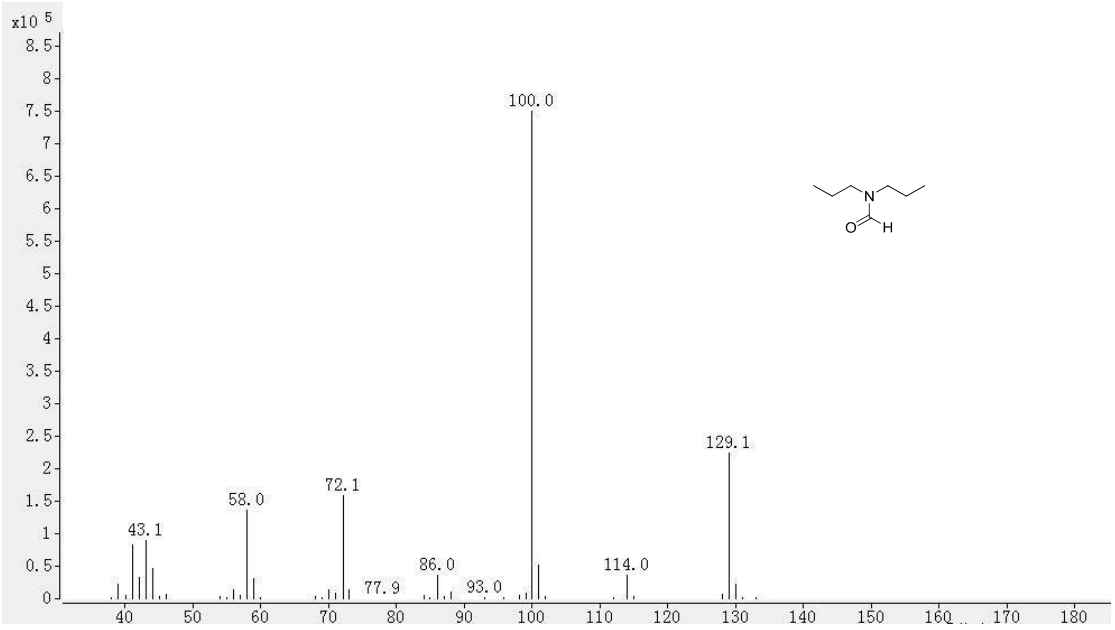

8.062
7.260
3.449
3.434
3.419
3.369
3.354
3.340
1.719
1.707
1.694
1.558
O
H
N
1H NMR (CDCl3, 400 MHz)
1.00
2.04
2.03
4.16
4.15
f1 (ppm)

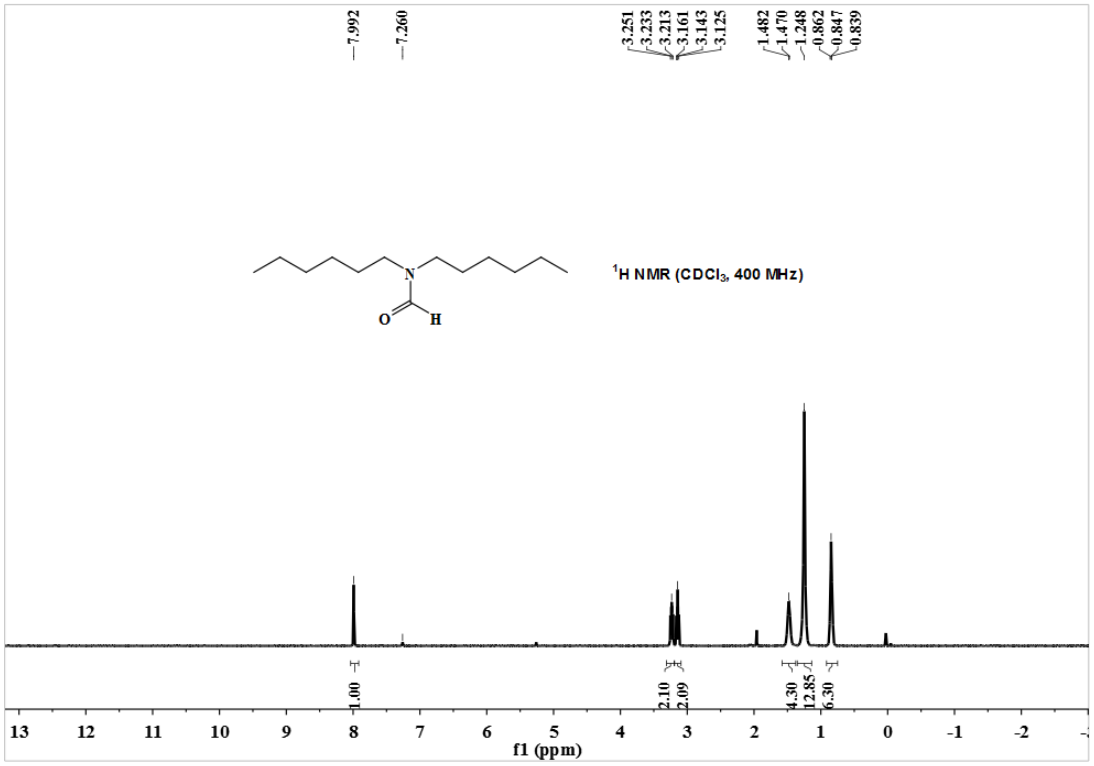

162.808
77.318
77.000
76.682
47.640
43.353
30.211
27.886
26.908
26.812
O
H
N
13C NMR (CDCl3, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

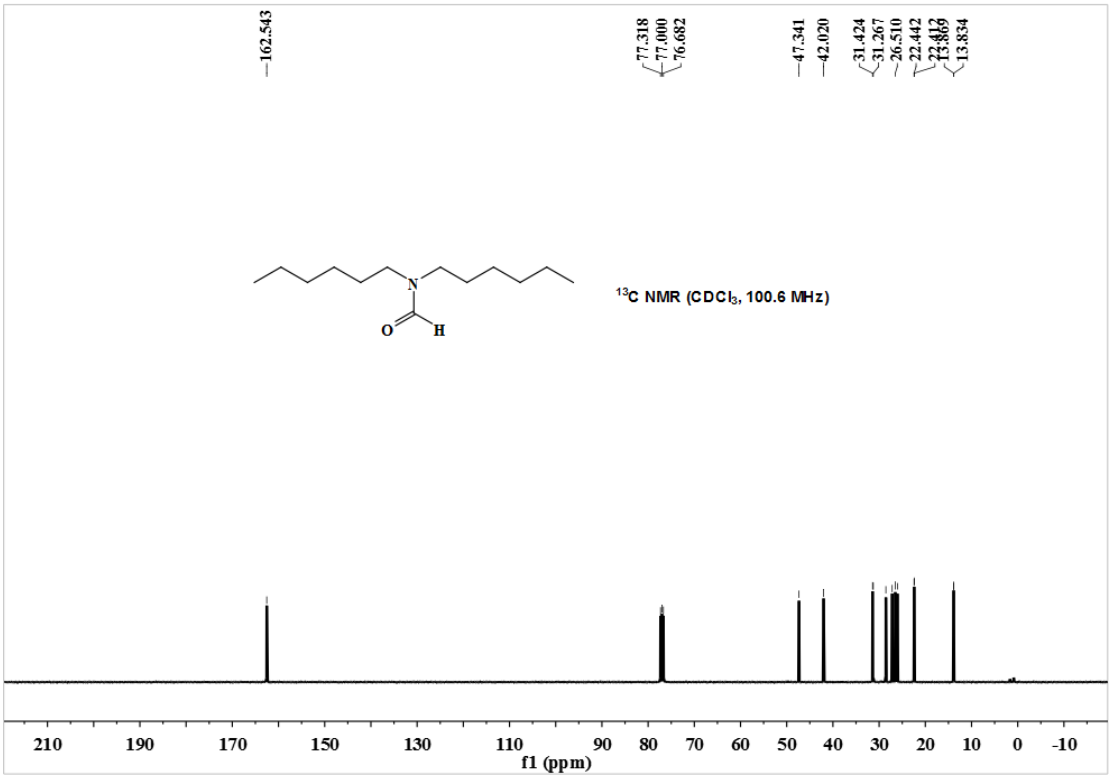

x10 6
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
3.7
17.9
30.0
42.0
56.0
70.0
84.0
98.0
112.0
127.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
O
H
N

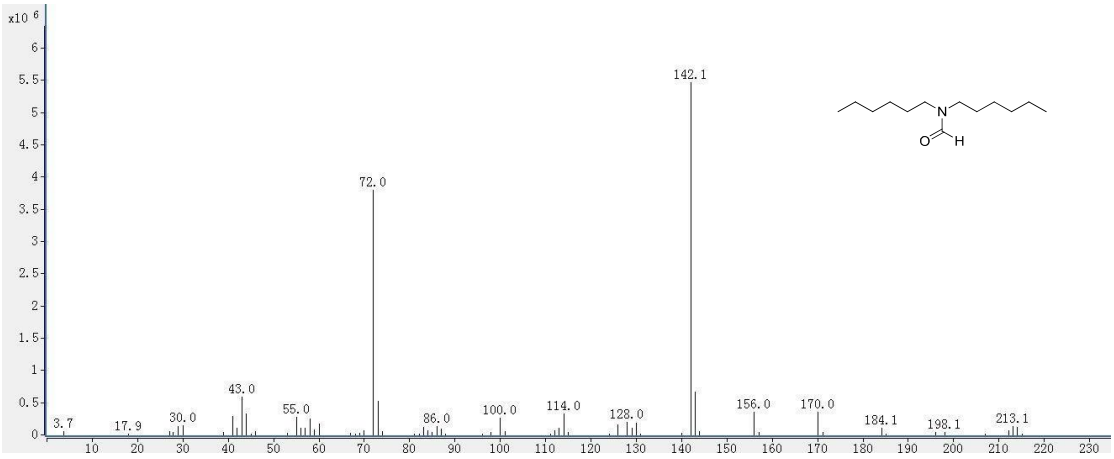

7.896
7.260
3.115
3.096
3.077
3.039
3.021
3.004
1.426
1.414
1.408
1.395
1.390
0.762
0.758
0.744
0.740
0.725
0.721
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
2.08
1.97
4.23
6.22
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

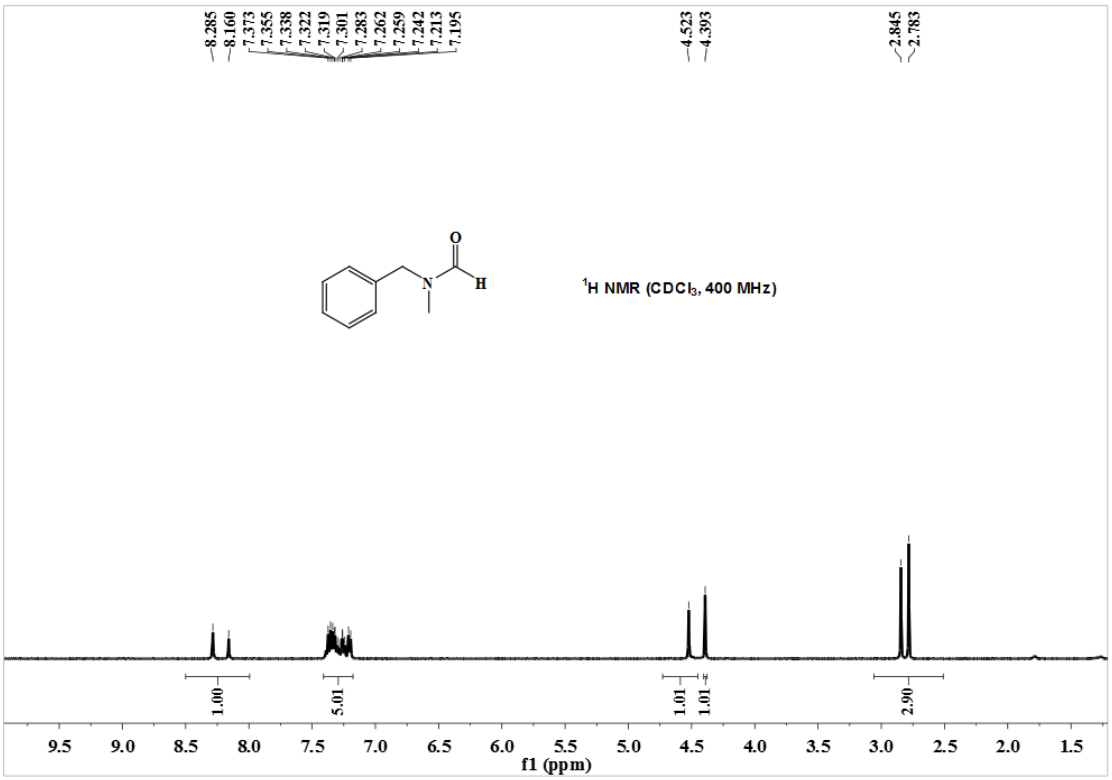

162.394
77.319
77.000
76.680
48.758
43.350
21.449
20.166
10.921
10.513
N
O
H
13C NMR (CDCl3, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

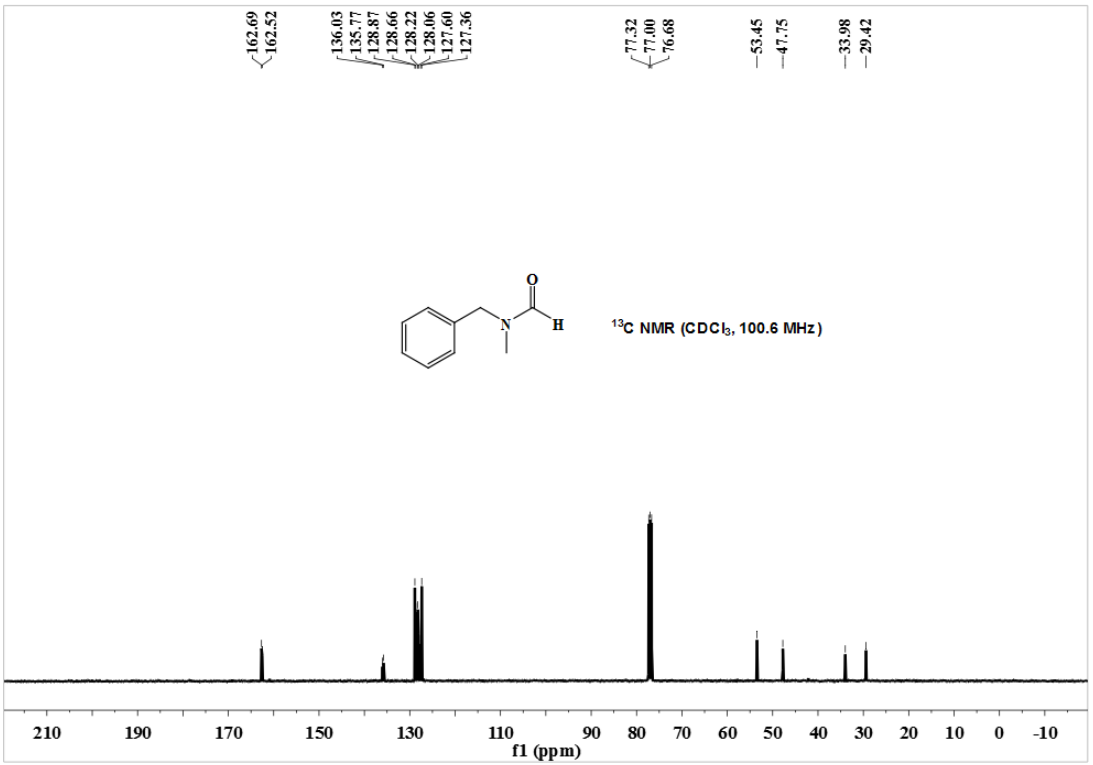

x10 5
100.0
129.1
72.1
58.0
43.1
86.0
77.9
93.0
114.0
N
O
H

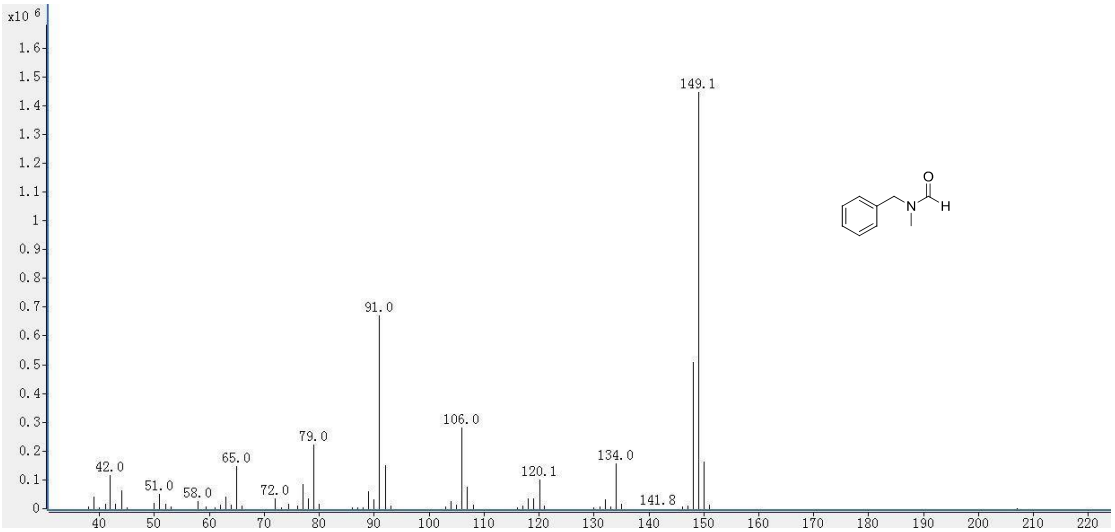

7.992
7.260
3.251
3.233
3.213
3.161
3.143
3.125
1.482
1.470
1.248
0.862
0.847
0.839
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
2.10
2.09
4.30
12.85
6.30
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

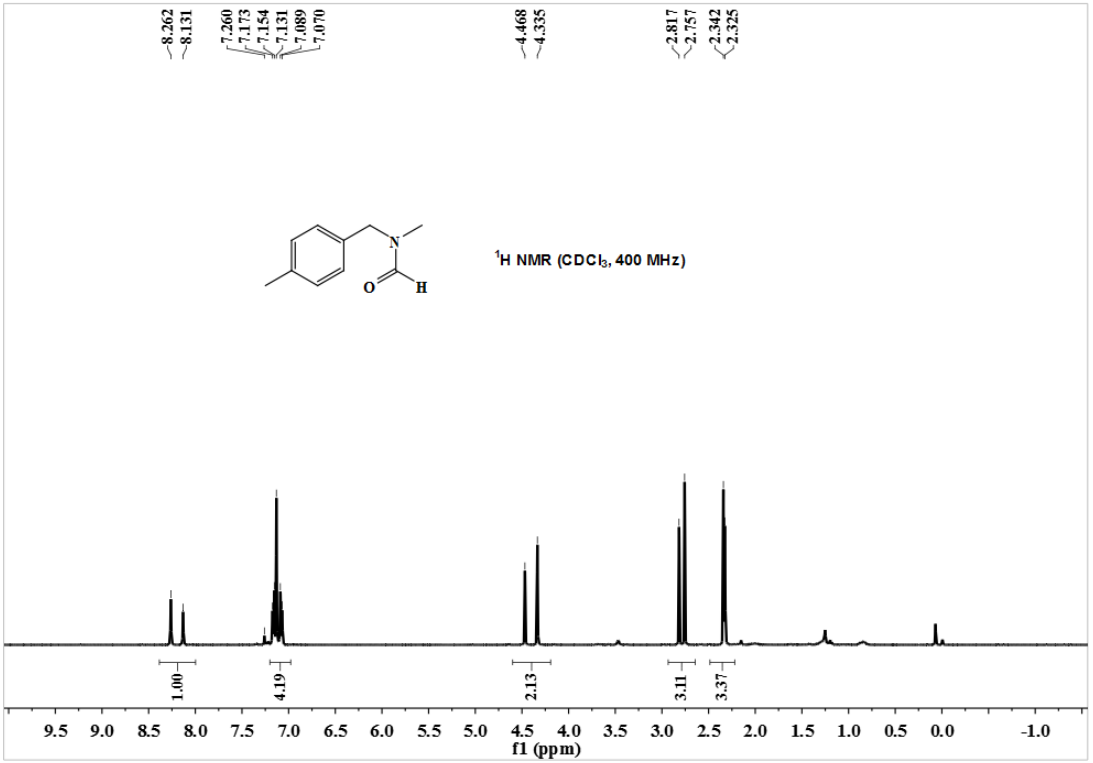

162.543
77.318
77.000
76.682
47.341
42.020
31.424
31.267
26.510
22.442
22.412
13.869
13.834
N
O
H
^{13}C NMR (CDCl$_3$, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

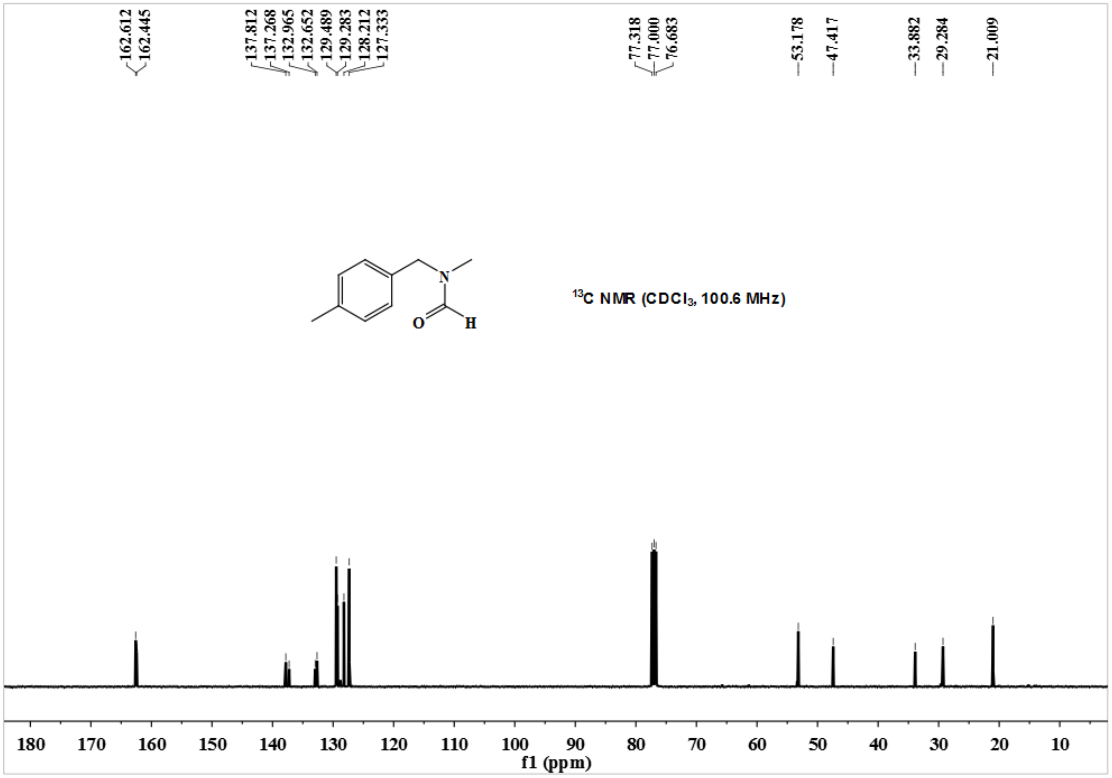

x10 6
142.1
72.0
43.0
55.0
3.7
17.9
30.0
86.0
100.0
114.0
128.0
156.0
170.0
184.1
198.1
213.1
N
O
H

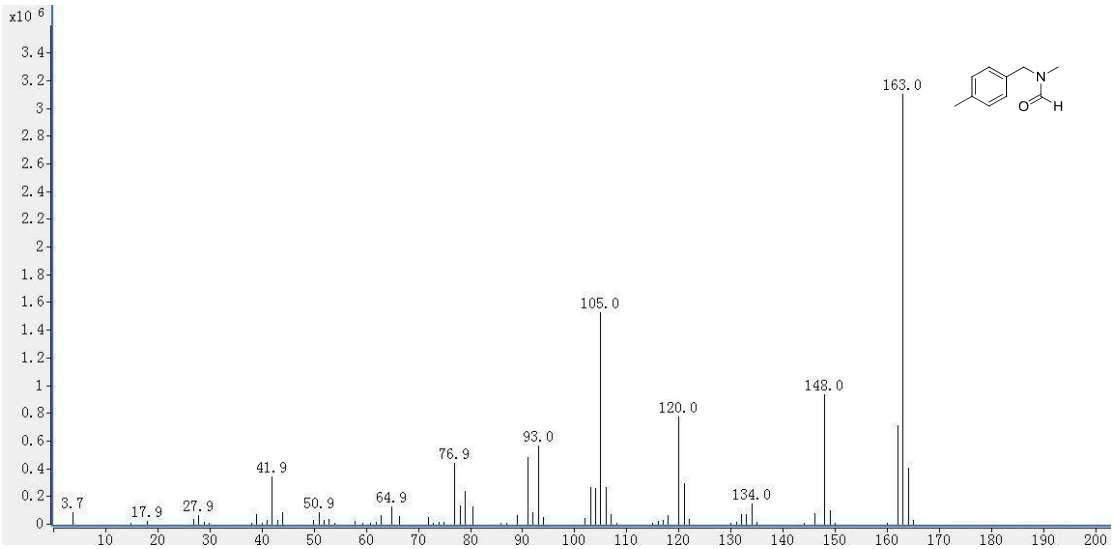

8.285
8.160
7.373
7.355
7.338
7.322
7.319
7.301
7.283
7.262
7.259
7.242
7.213
7.195
4.523
4.393
2.845
2.783
O
N
H
1H NMR (CDCl3, 400 MHz)
1.00
5.01
1.01
1.01
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

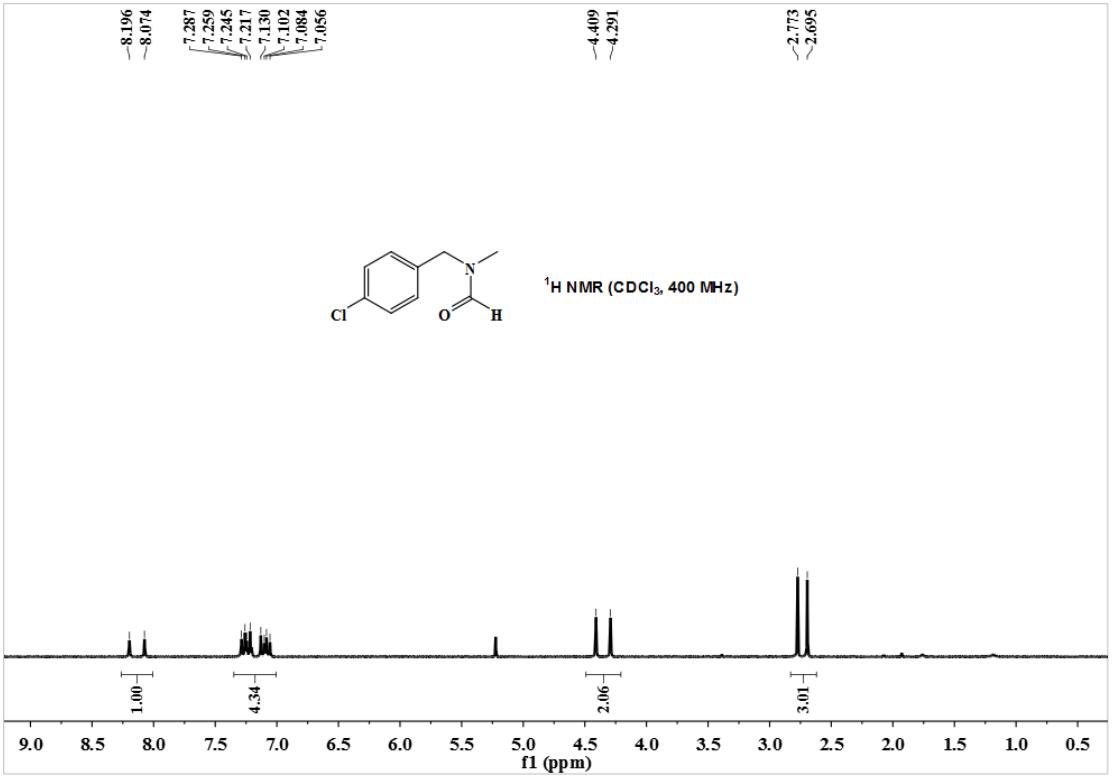

162.69
162.52
136.03
135.77
128.87
128.66
128.22
128.06
127.60
127.36
77.32
77.00
76.68
53.45
47.75
33.98
29.42
O
N
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

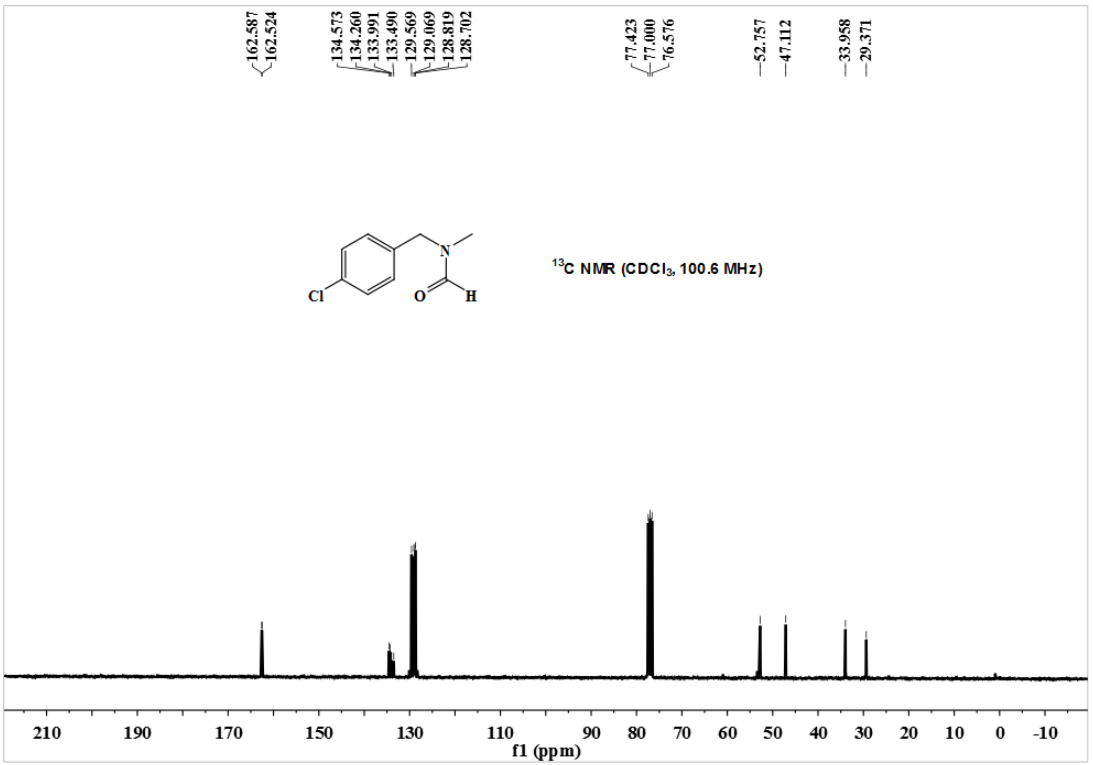

x10 6
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
149.1
91.0
106.0
79.0
65.0
42.0
51.0
58.0
72.0
120.1
134.0
141.8
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
O
N
H

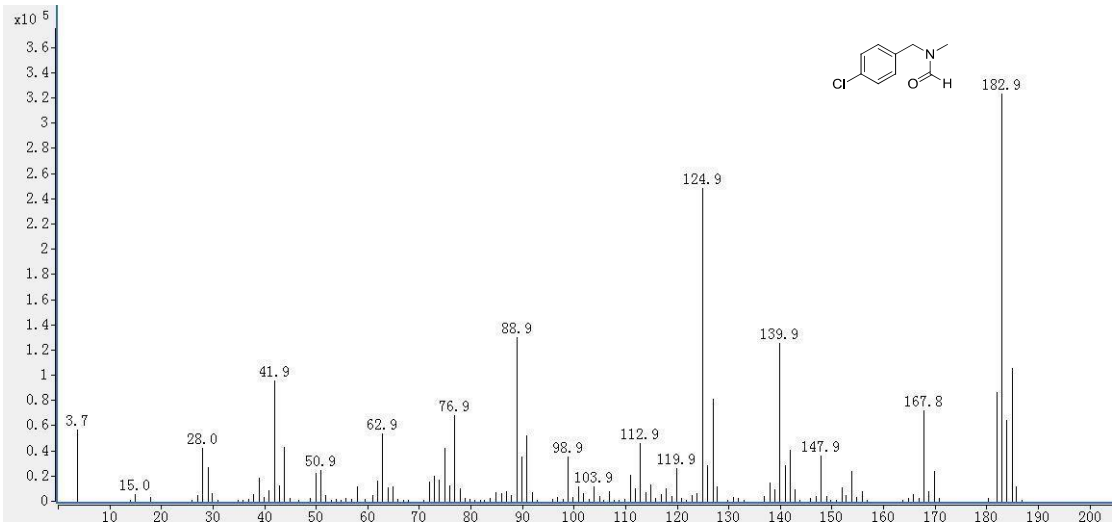

8.262
8.131
7.260
7.173
7.154
7.131
7.089
7.070
4.468
4.335
2.817
2.757
2.342
2.325
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
4.19
2.13
3.11
3.37
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)

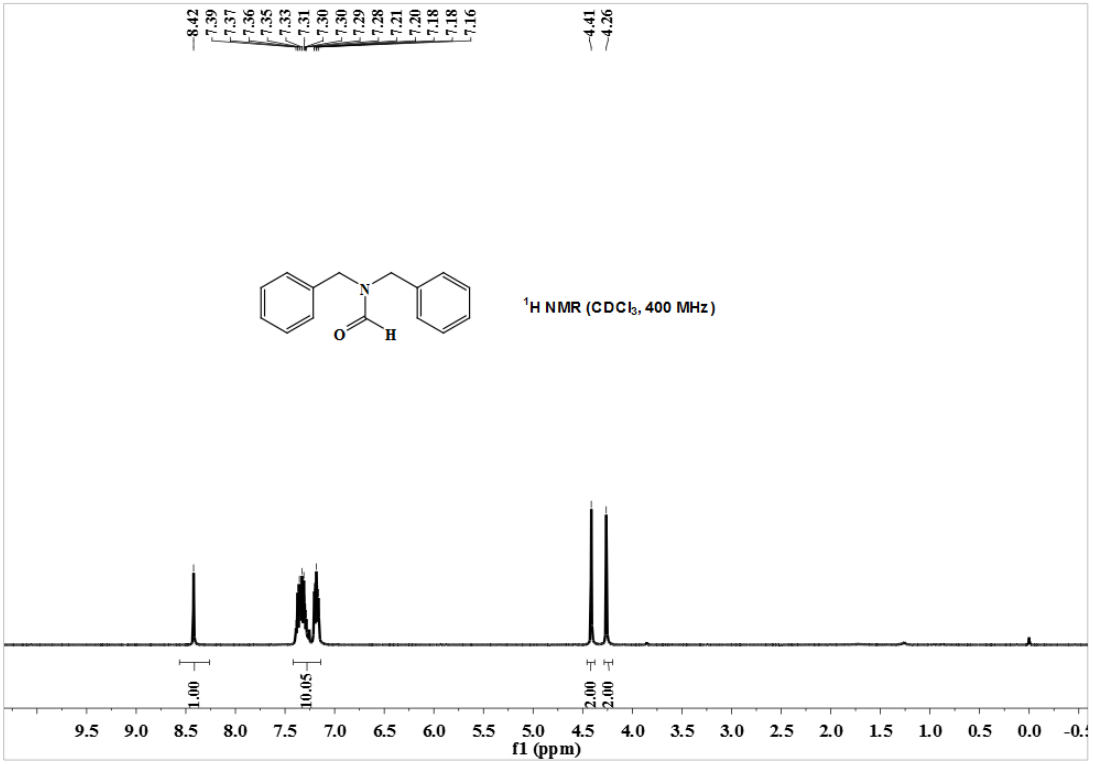

162.612
162.445
137.812
137.268
132.965
132.652
129.489
129.283
128.212
127.333
77.318
77.000
76.683
53.178
47.417
33.882
29.284
21.009
N
O
H
13C NMR (CDCl3, 100.6 MHz)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

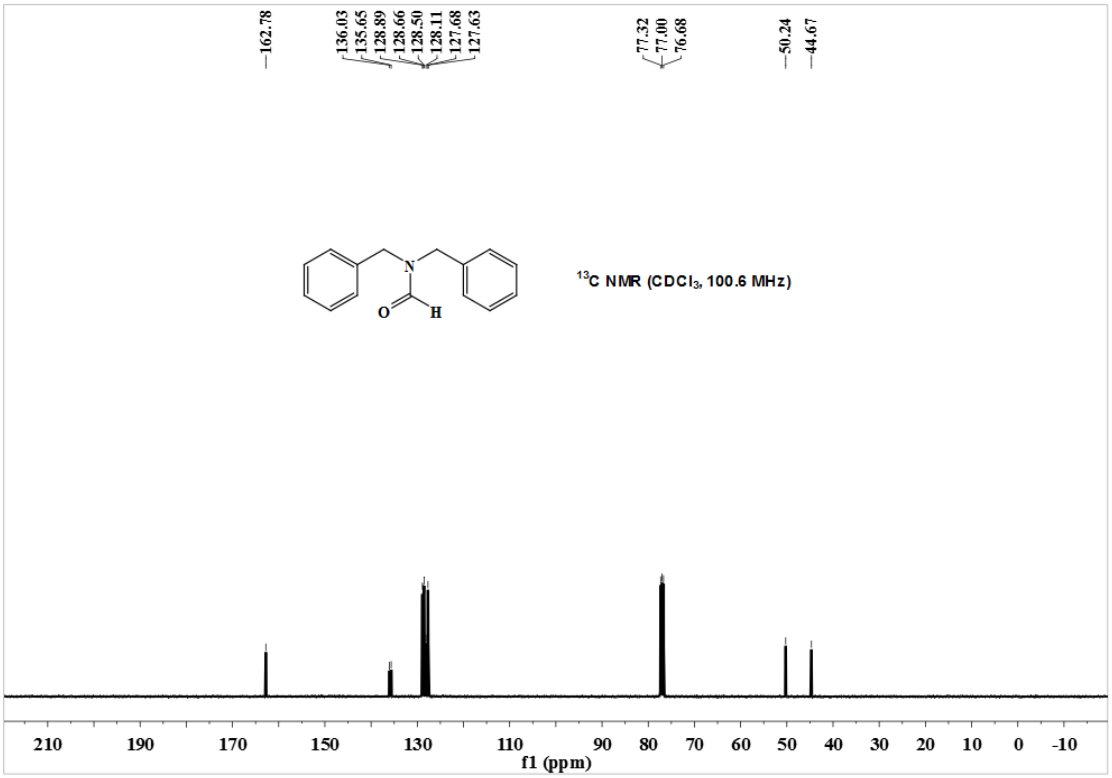

x10 6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
163.0
105.0
148.0
120.0
93.0
76.9
41.9
3.7
17.9
27.9
50.9
64.9
134.0
N
O
H
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

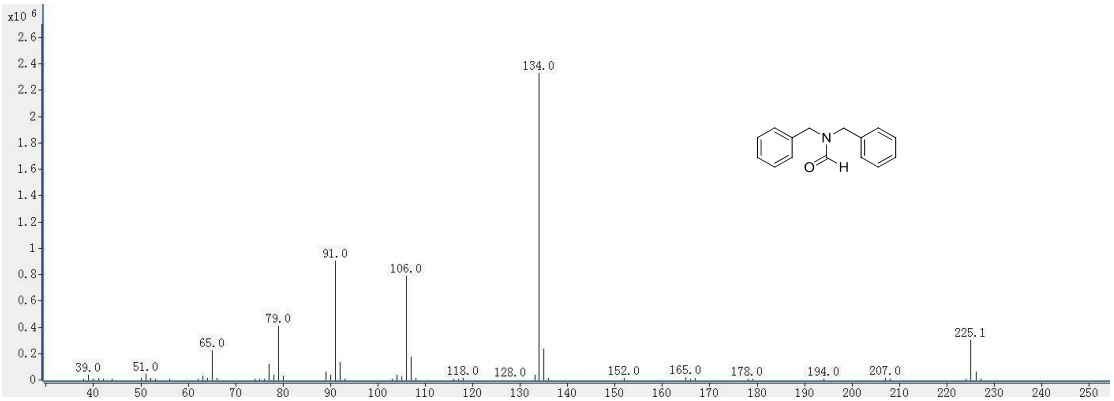

8.196
8.074
7.287
7.259
7.245
7.217
7.130
7.102
7.084
7.056
4.409
4.291
2.773
2.695
Cl
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
4.34
2.06
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

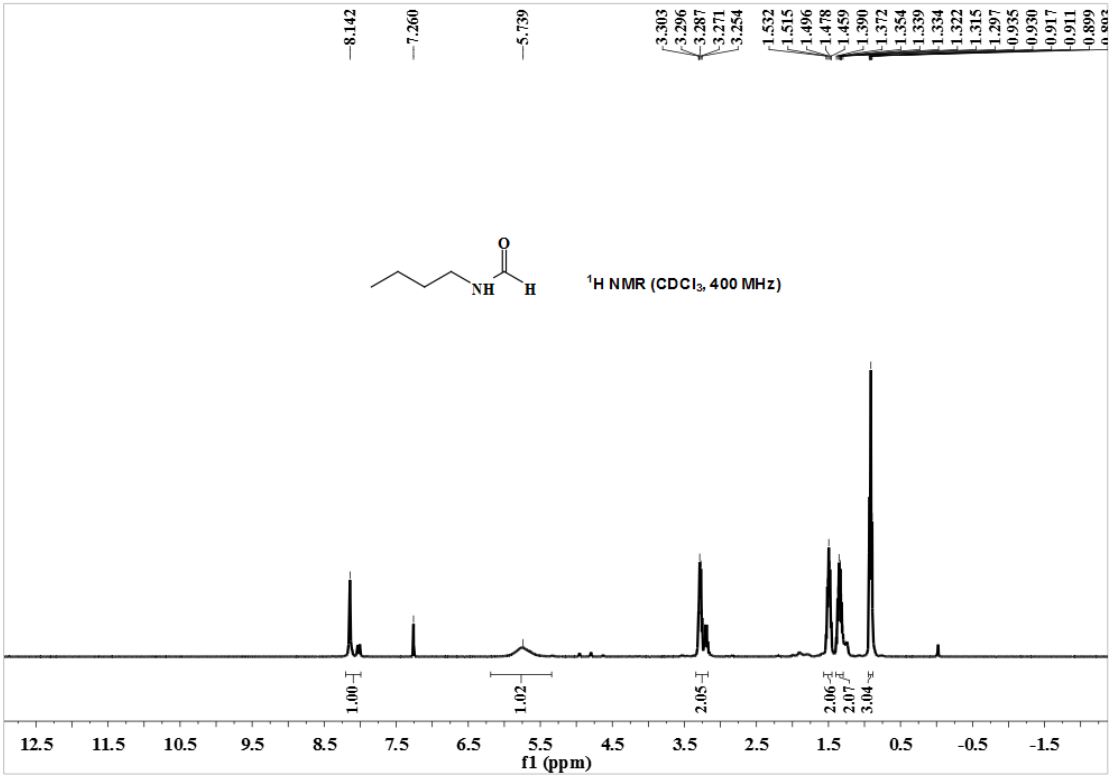

162.587
162.524
134.573
134.260
133.991
133.490
129.569
129.069
128.819
128.702
77.423
77.000
76.576
52.757
47.112
33.958
29.371
Cl
N
O
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

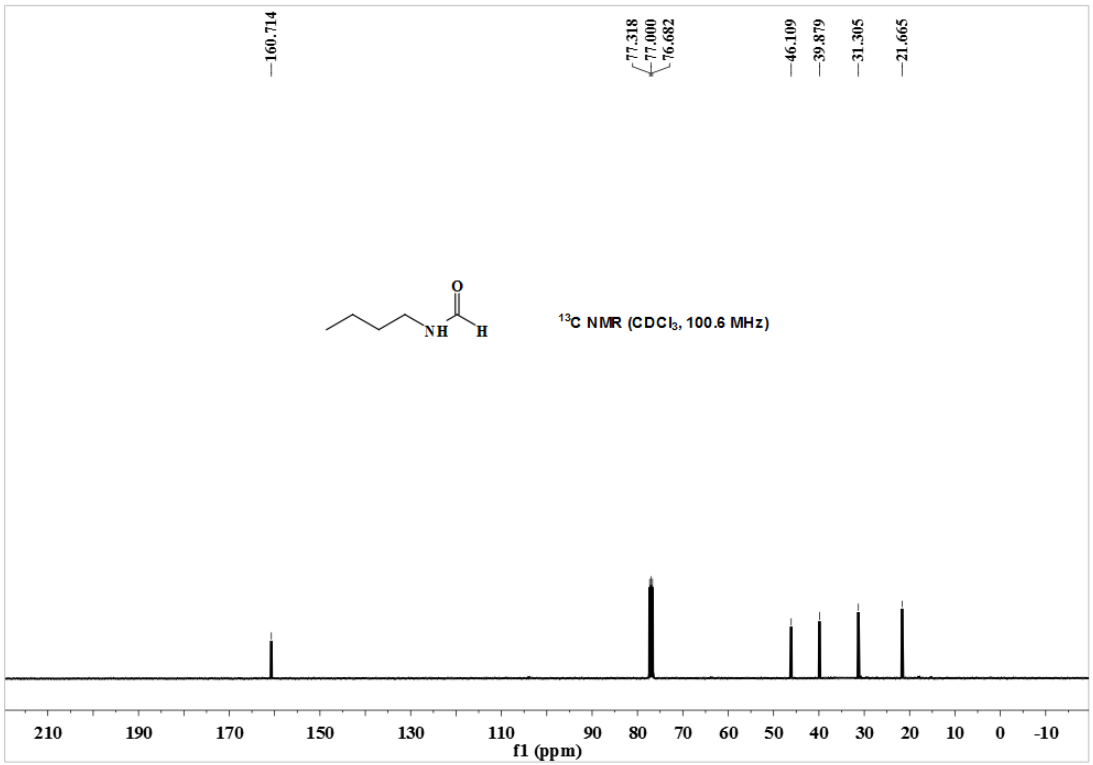

x10 5
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
3.7
15.0
28.0
41.9
50.9
62.9
76.9
88.9
98.9
103.9
112.9
119.9
124.9
139.9
147.9
167.8
182.9
Cl
N
O
H

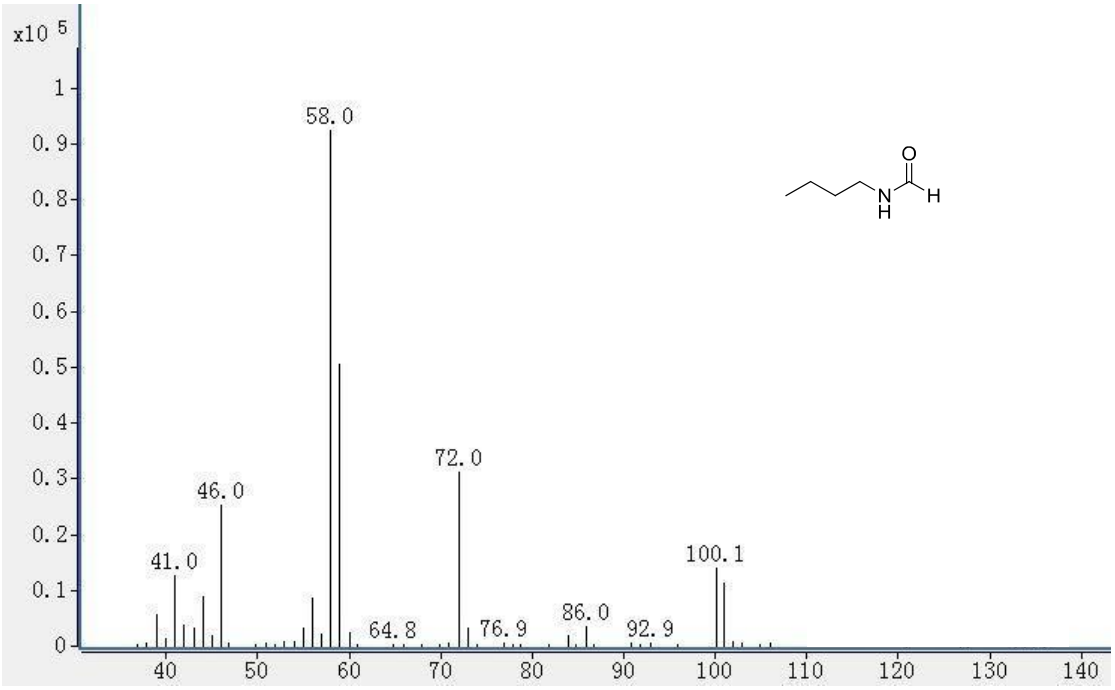

8.42
7.39
7.37
7.36
7.35
7.33
7.31
7.30
7.30
7.29
7.28
7.21
7.20
7.18
7.18
7.16
4.41
4.26
N
O
H
1H NMR (CDCl3, 400 MHz)
1.00
10.05
2.00
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

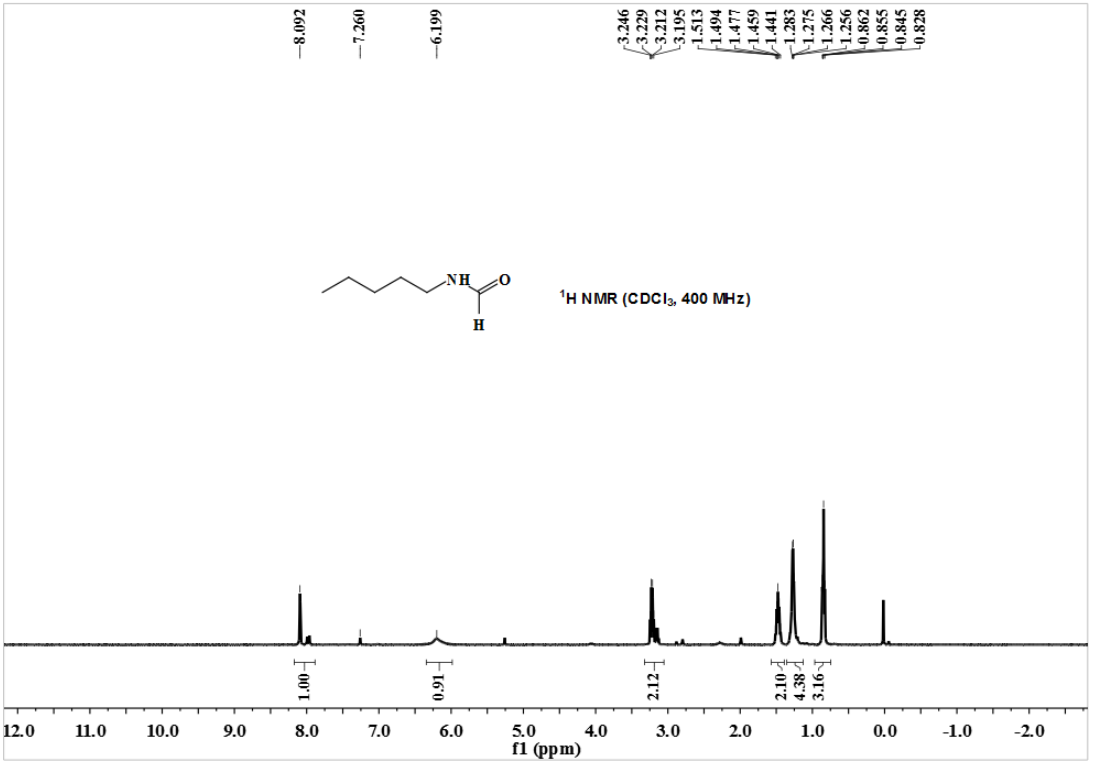

162.78
136.03
135.65
128.89
128.66
128.50
128.11
127.68
127.63
77.32
77.00
76.68
50.24
44.67
N
O
H
13C NMR (CDCl3, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

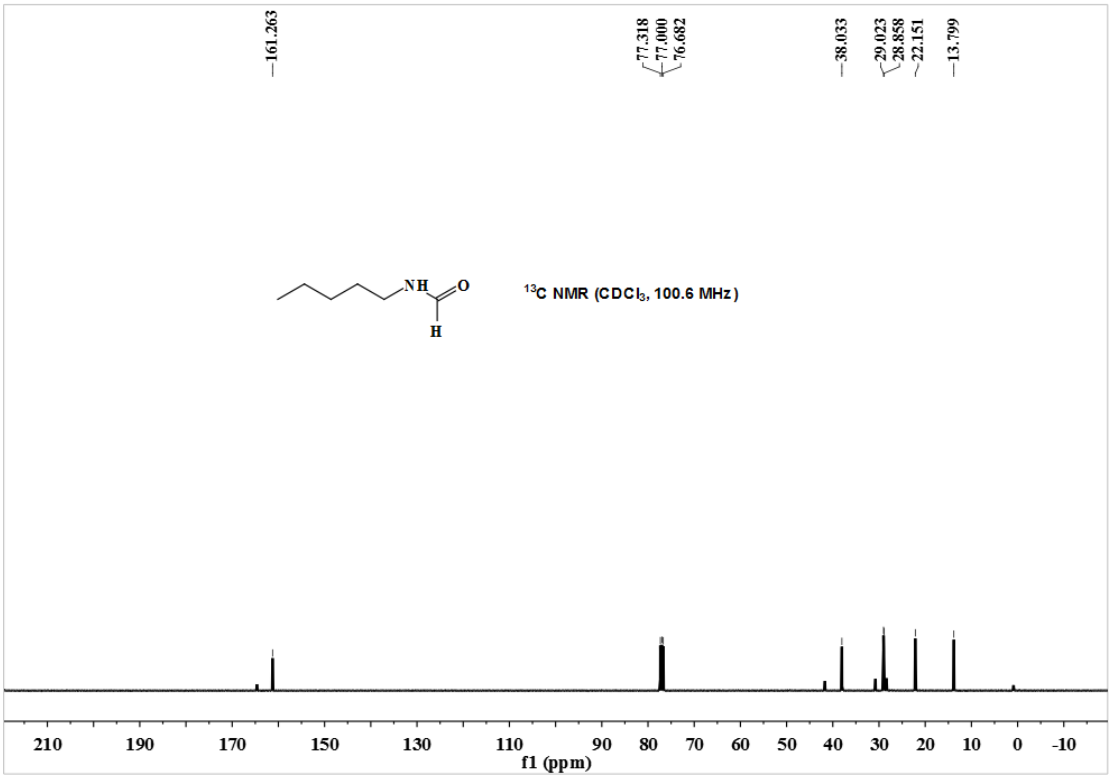

x10 6
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
134.0
91.0
106.0
79.0
65.0
39.0
51.0
118.0
128.0
152.0
165.0
178.0
194.0
207.0
225.1
N
O
H
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250

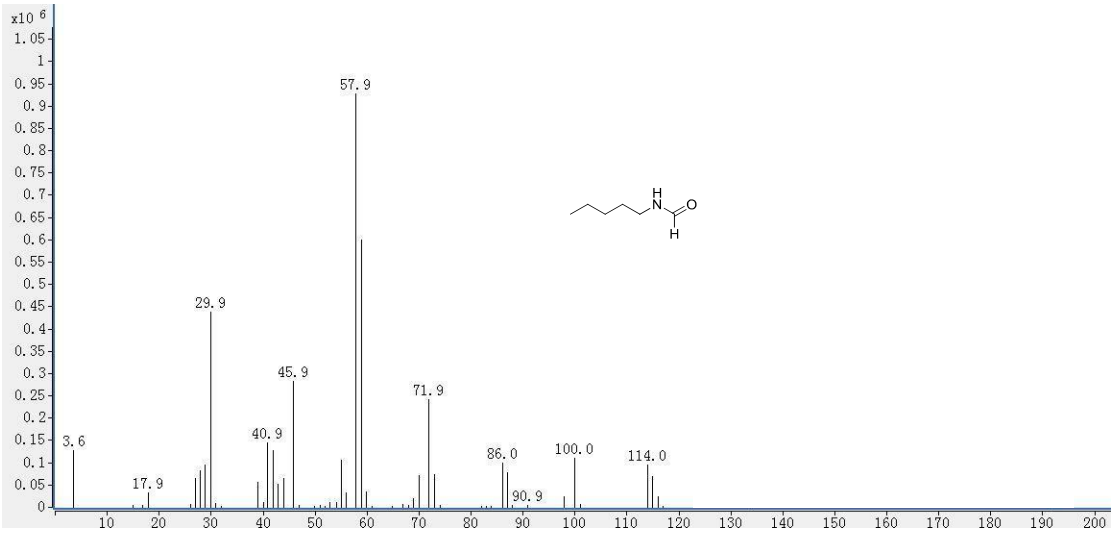

8.142
7.260
5.739
3.303
3.296
3.287
3.271
3.254
1.532
1.515
1.496
1.478
1.459
1.390
1.372
1.354
1.339
1.334
1.322
1.315
1.297
0.935
0.930
0.917
0.911
0.899
O
NH
H
1H NMR (CDCl3, 400 MHz)
1.00
1.02
2.05
2.06
2.07
3.04
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

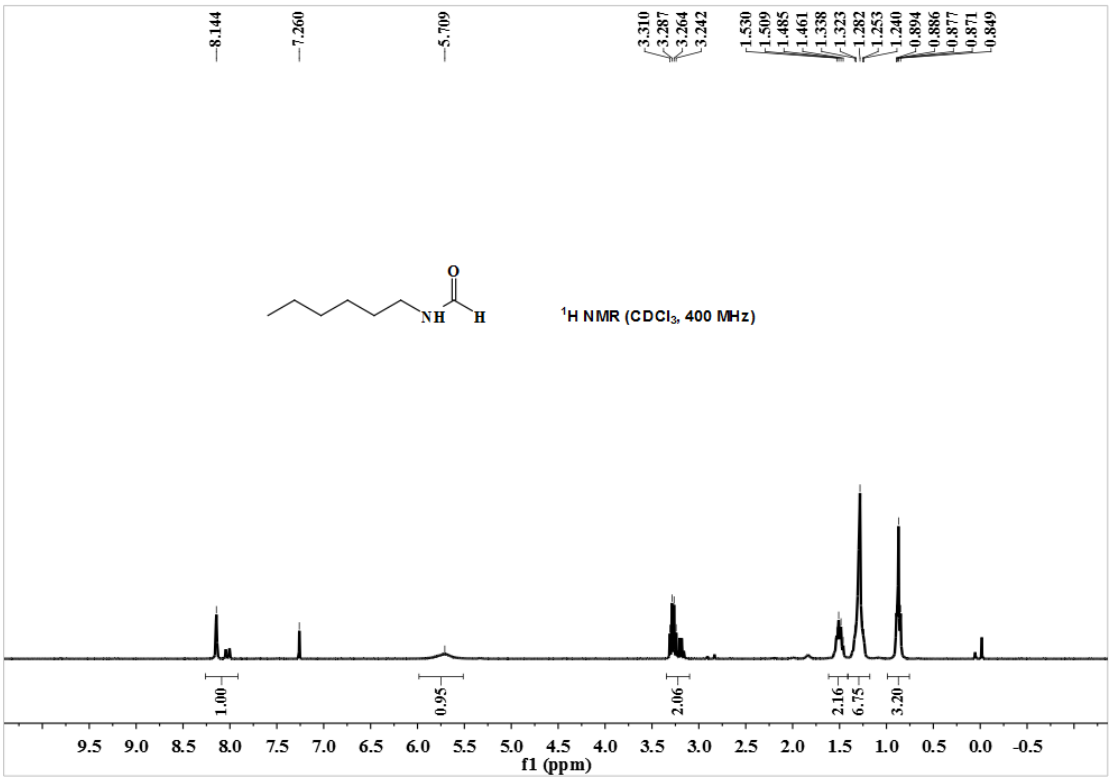

160.714
77.318
77.000
76.682
46.109
39.879
31.305
21.665
O
NH
H
13C NMR (CDCl3, 100.6 MHz)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

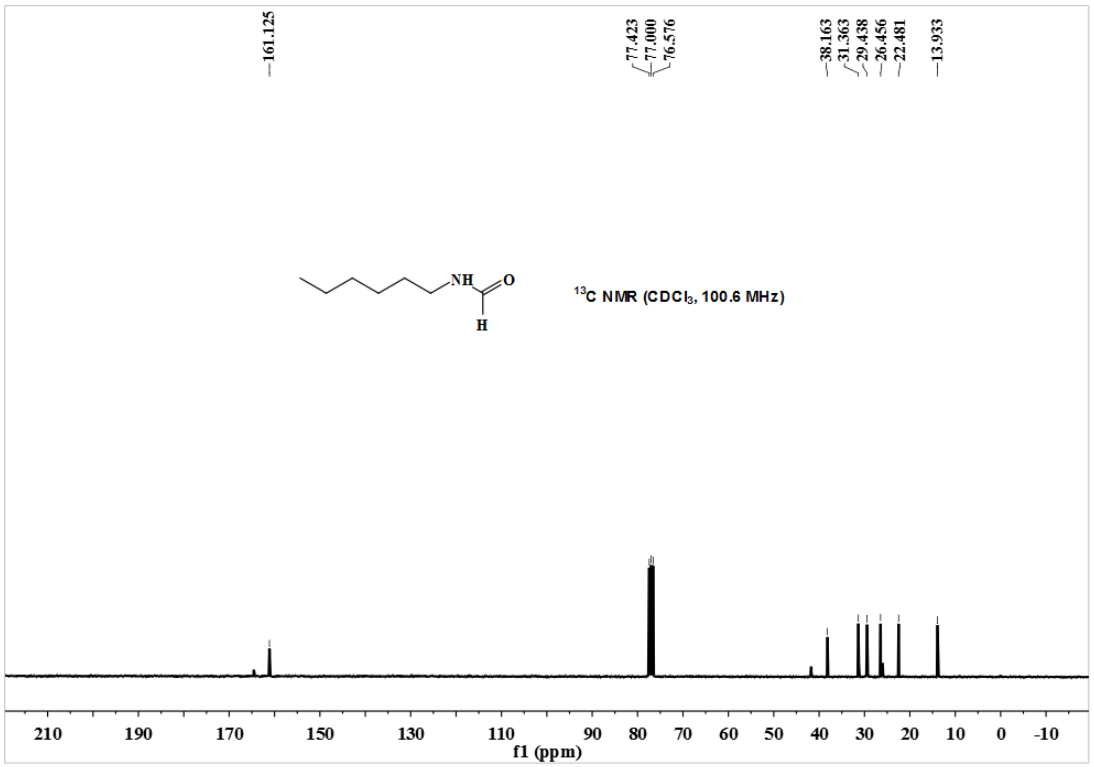

x10 5
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
58.0
72.0
46.0
41.0
100.1
64.8
76.9
86.0
92.9
40
50
60
70
80
90
100
110
120
130
140
O
N
H
H

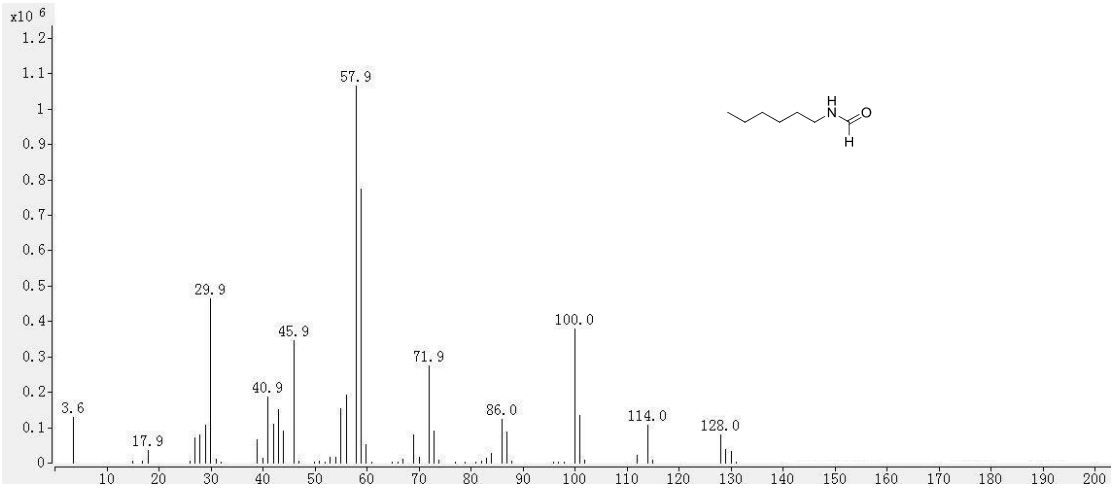

8.092
7.260
6.199
3.246
3.229
3.212
3.195
1.513
1.494
1.477
1.459
1.441
1.283
1.275
1.266
1.256
0.862
0.855
0.845
0.828
NH
O
H
1H NMR (CDCl3, 400 MHz)
1.00
0.91
2.12
2.10
4.38
3.16
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

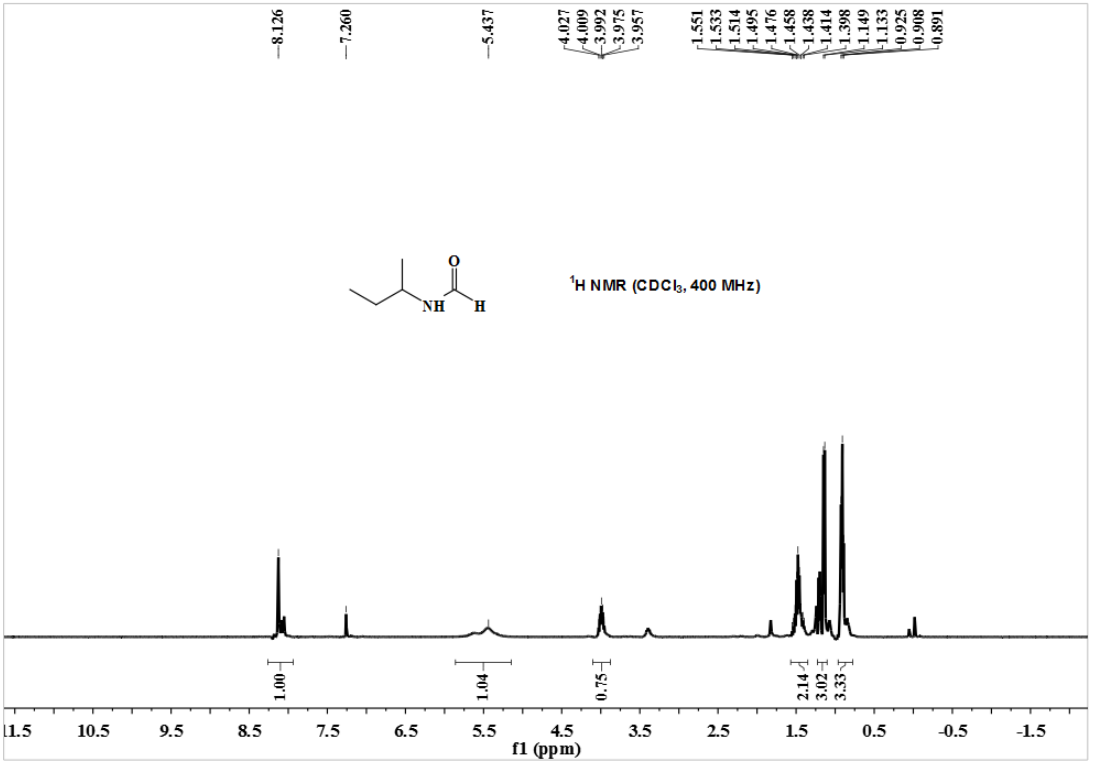

161.263
77.318
77.000
76.682
38.033
29.023
28.858
22.151
13.799
NH
O
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

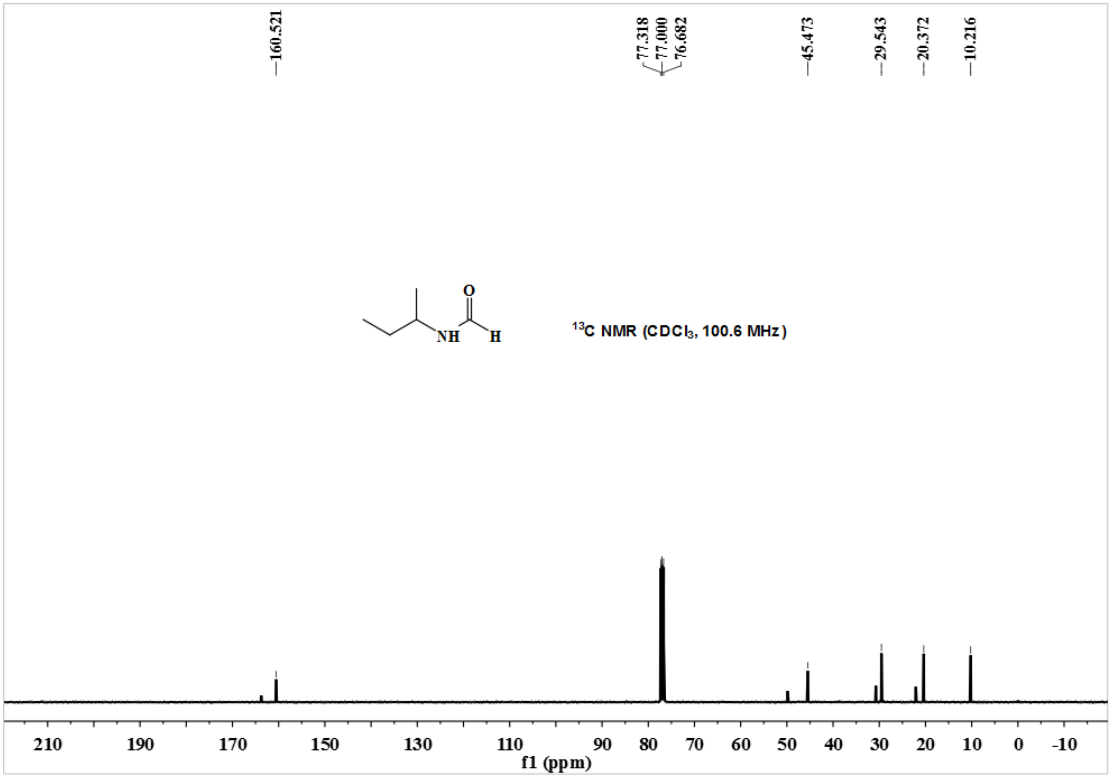

x10 6
1.05
1
0.95
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
57.9
29.9
45.9
71.9
40.9
3.6
17.9
86.0
90.9
100.0
114.0
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200

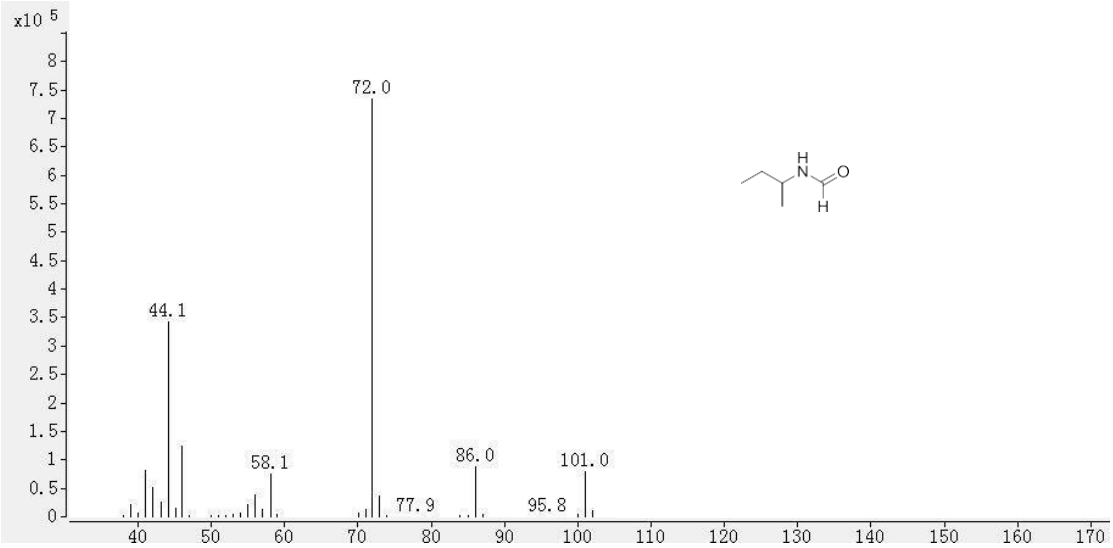

8.144
7.260
5.709
3.310
3.287
3.264
3.242
1.530
1.509
1.485
1.461
1.338
1.323
1.282
1.253
1.240
0.894
0.886
0.877
0.871
0.849
NH
O
H
1H NMR (CDCl3, 400 MHz)
1.00
0.95
2.06
2.16
6.75
3.20
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

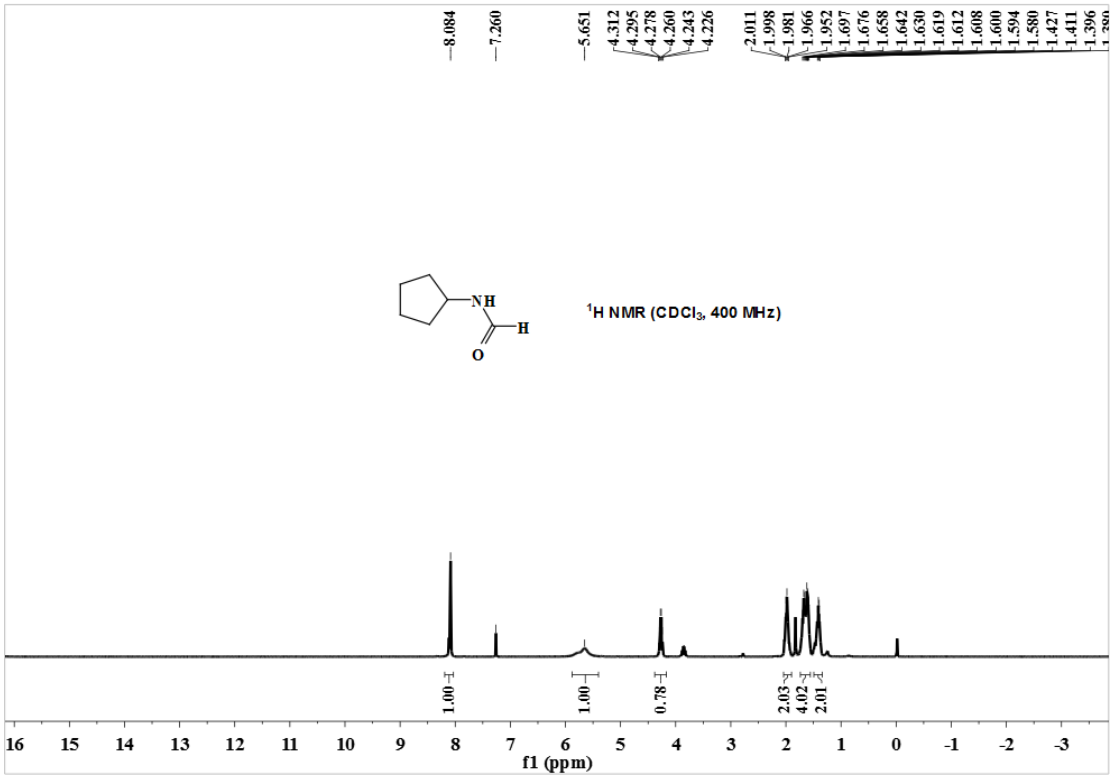

161.125
77.423
77.000
76.576
38.163
31.363
29.438
26.456
22.481
13.933
NH
O
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

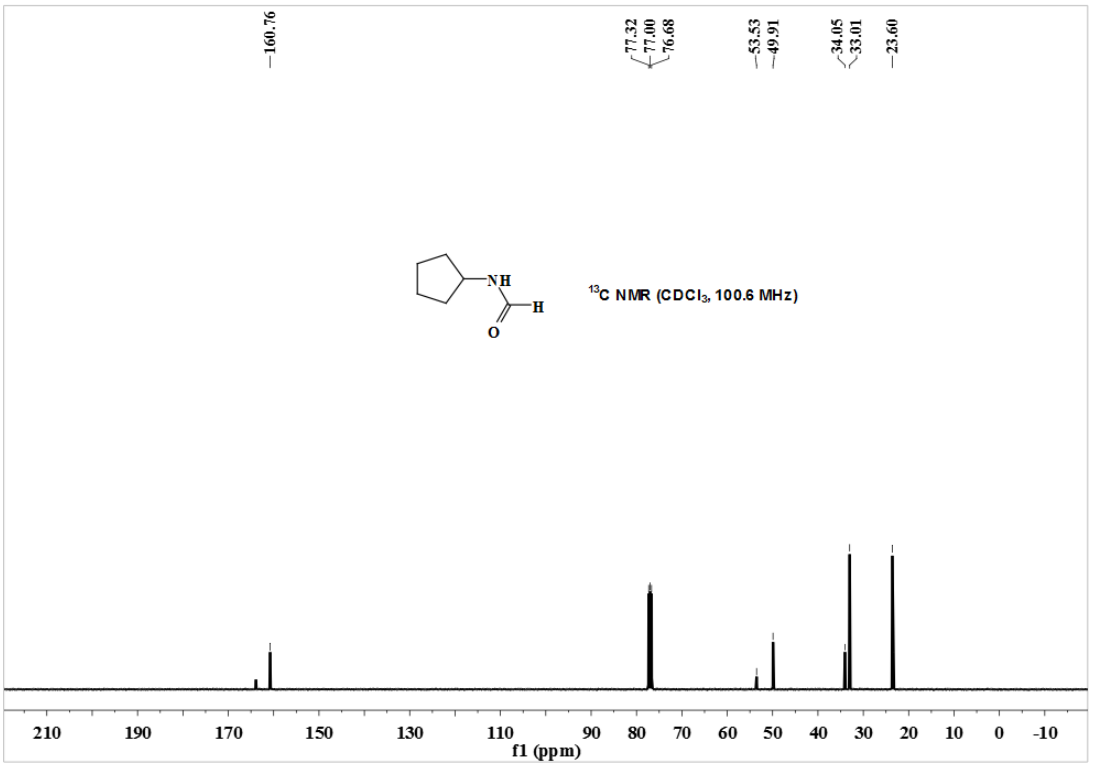

x10 6
57.9
29.9
45.9
71.9
40.9
100.0
86.0
114.0
128.0
3.6
17.9

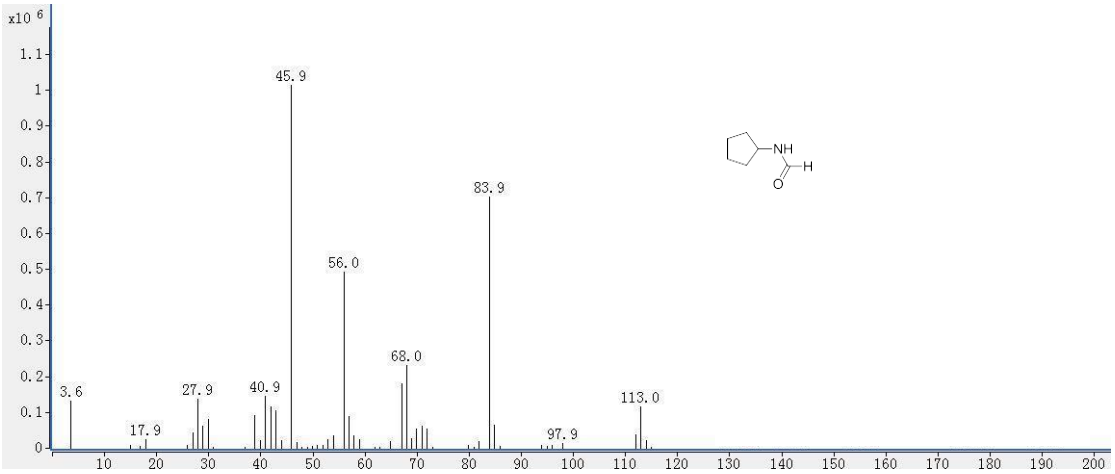

8.126
7.260
5.437
4.027
4.009
3.992
3.975
3.957
1.551
1.533
1.514
1.495
1.476
1.458
1.438
1.414
1.398
1.149
1.133
0.925
0.908
0.891
1H NMR (CDCl3, 400 MHz)
1.00
1.04
0.75
2.14
3.02
3.33
f1 (ppm)

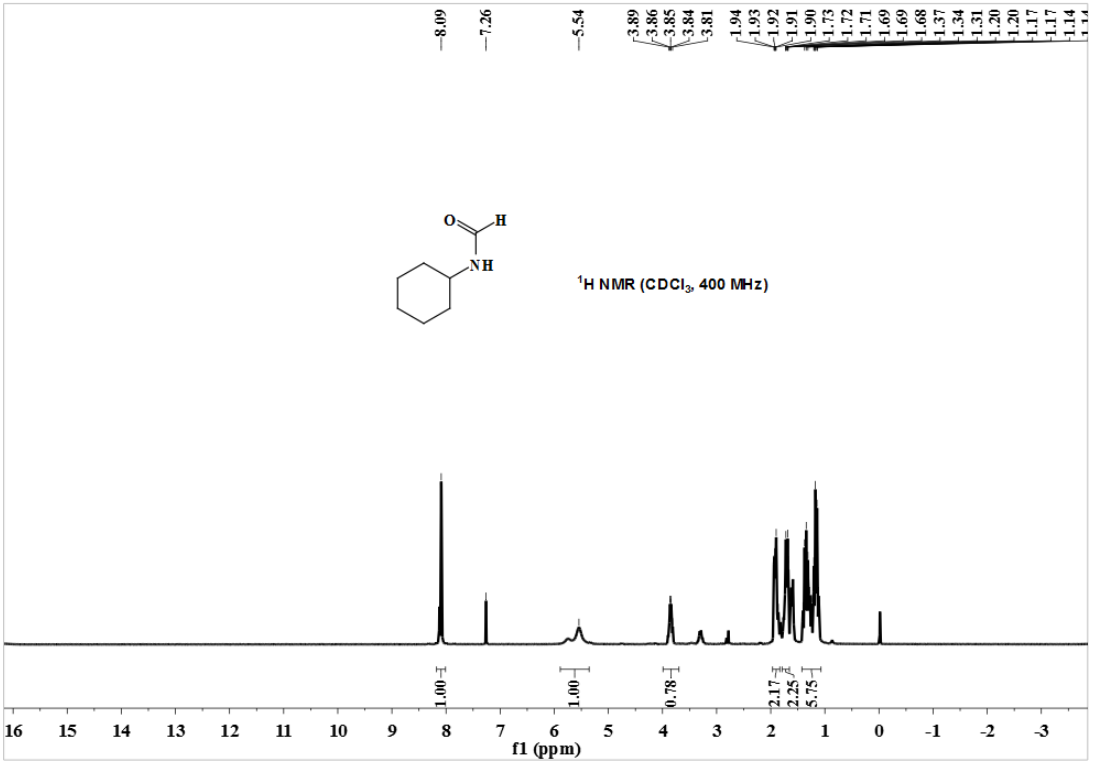

160.521
77.318
77.000
76.682
45.473
29.543
20.372
10.216
O
NH
H
^{13}C NMR (CDCl$_3$, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

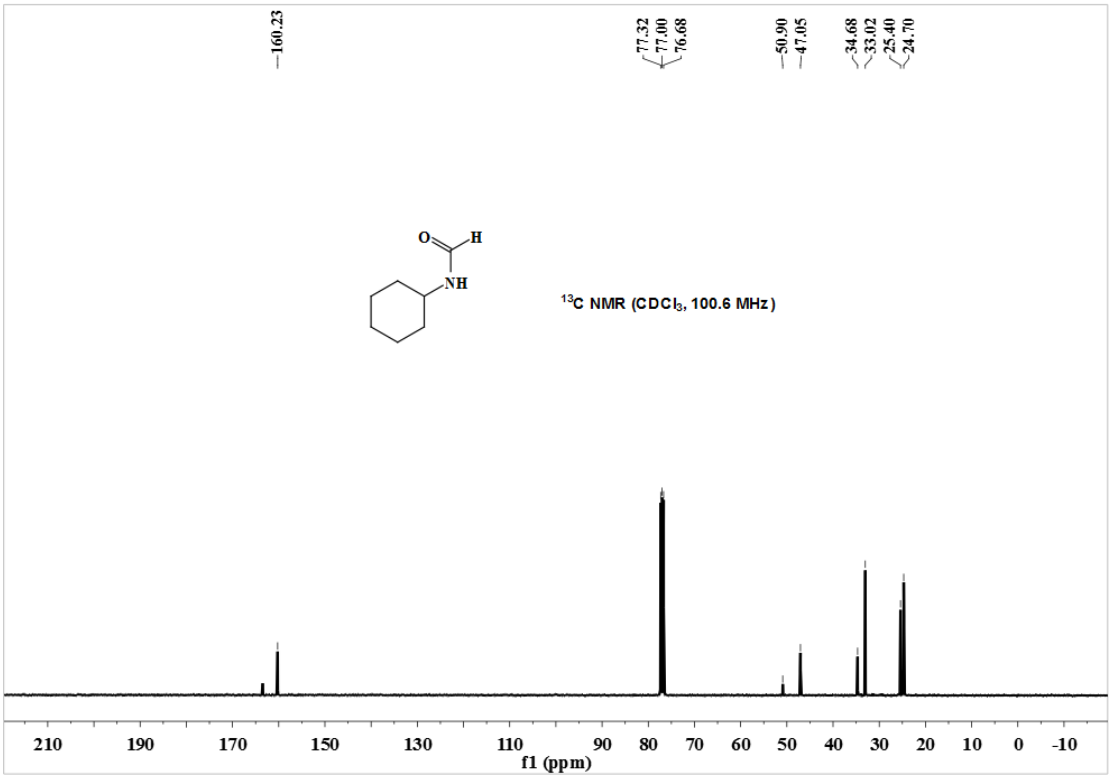

x10 5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
72.0
44.1
58.1
77.9
86.0
95.8
101.0
40 50 60 70 80 90 100 110 120 130 140 150 160 170
H
N
O
H

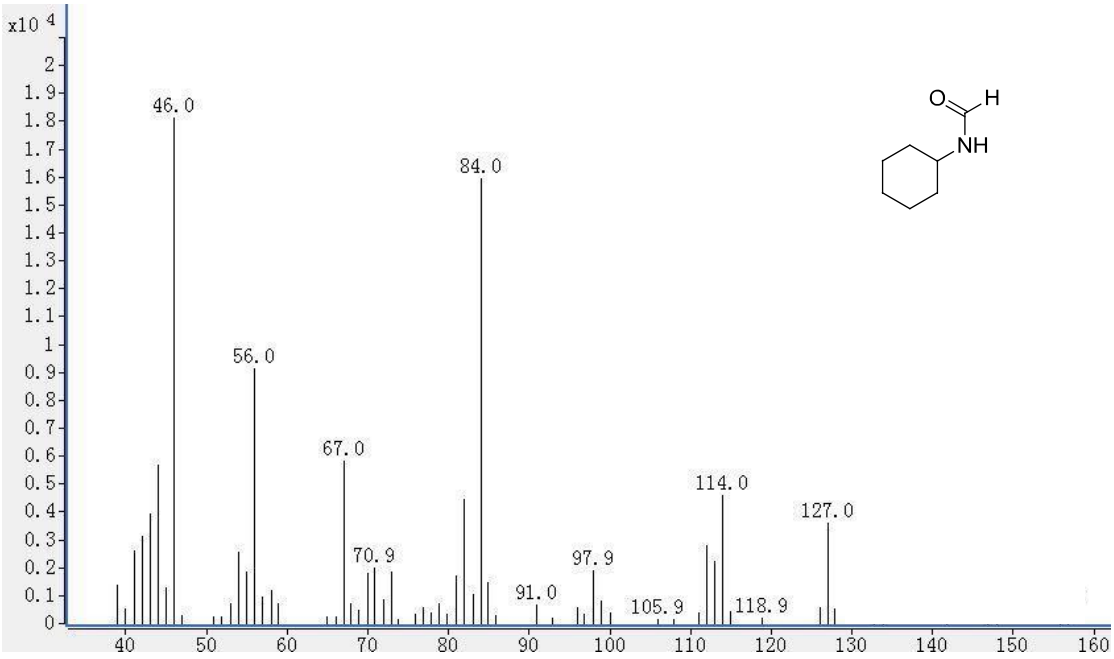

8.084
7.260
5.651
4.312
4.295
4.278
4.260
4.243
4.226
2.011
1.998
1.981
1.966
1.952
1.697
1.676
1.658
1.642
1.630
1.619
1.612
1.608
1.600
1.594
1.580
1.427
1.411
1.396
NH
H
O
1H NMR (CDCl3, 400 MHz)
1.00
1.00
0.78
2.03
4.02
2.01
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

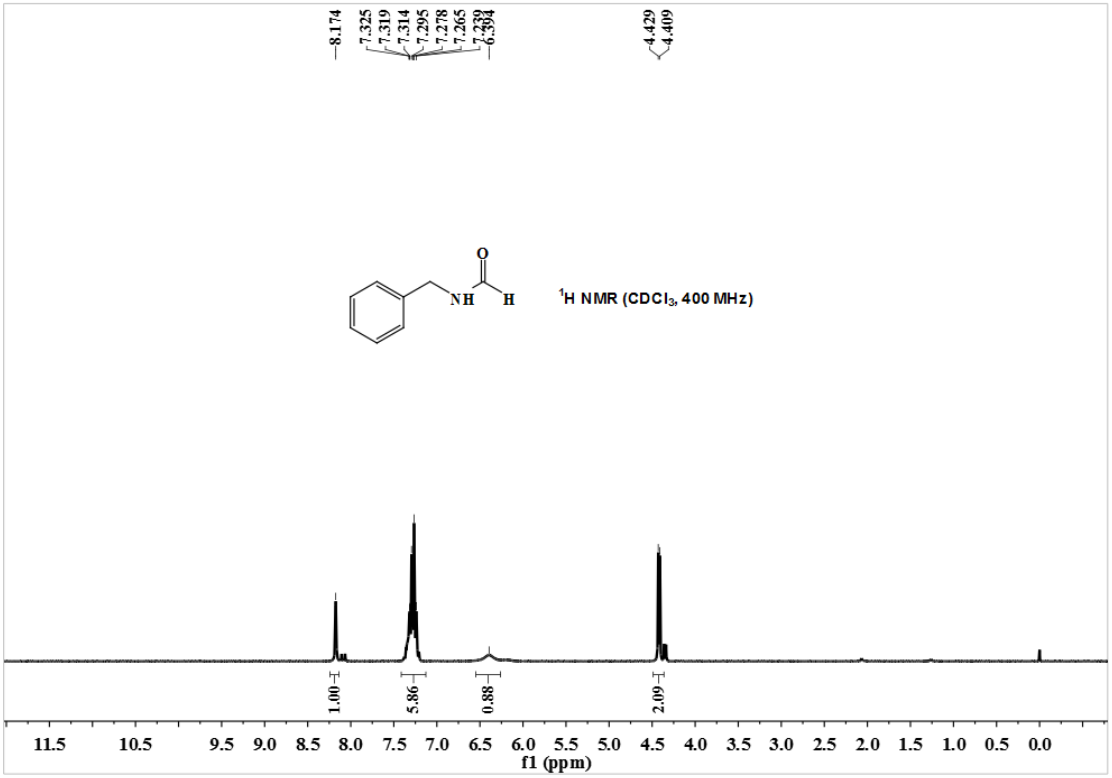

160.76
77.32
77.00
76.68
53.53
49.91
34.05
33.01
23.60
NH
H
O
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

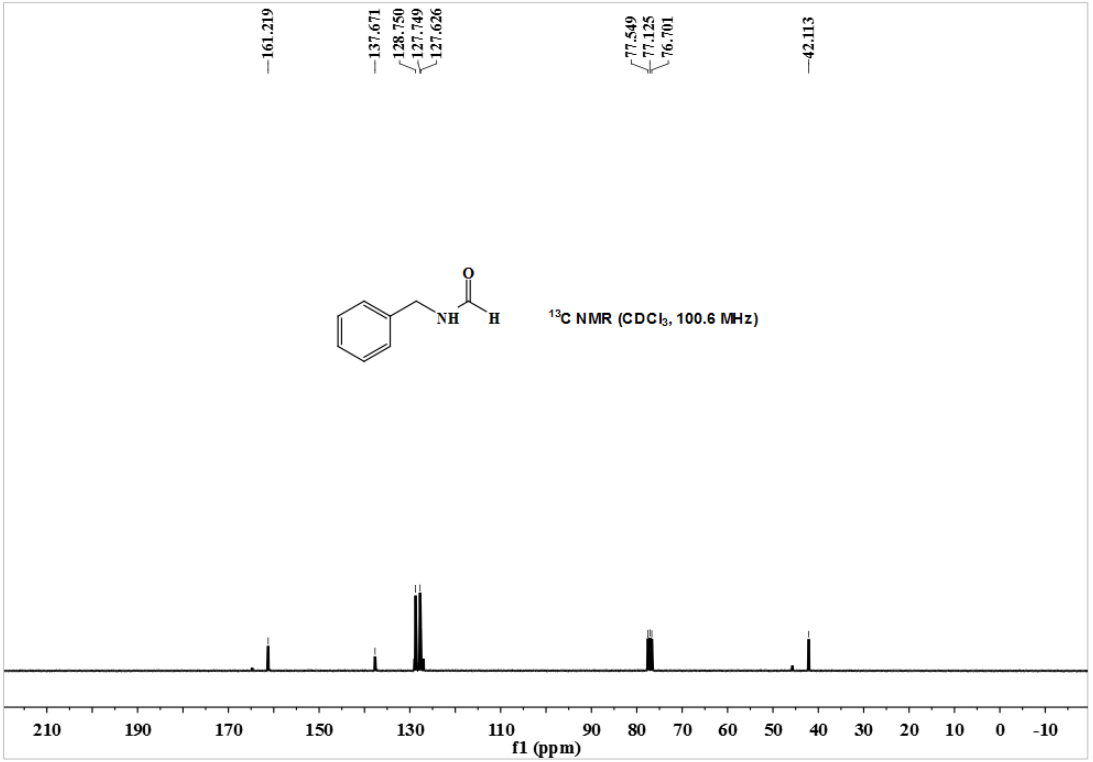

x10 6
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
45.9
83.9
56.0
68.0
3.6
27.9
40.9
17.9
97.9
113.0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
NH
H
O

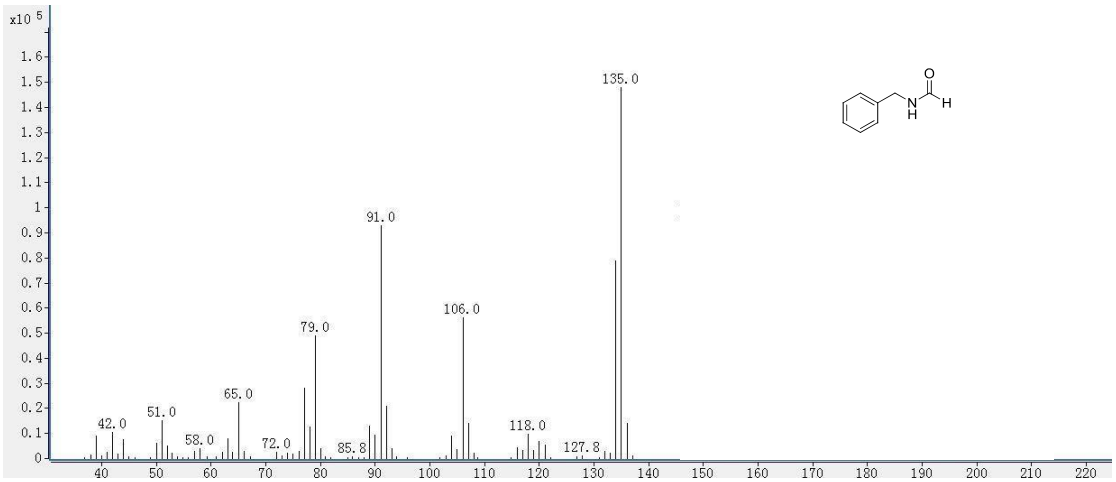

8.09
7.26
5.54
3.89
3.86
3.85
3.84
3.81
1.94
1.93
1.92
1.91
1.90
1.73
1.72
1.71
1.69
1.69
1.68
1.37
1.34
1.31
1.20
1.20
1.17
1.17
1.14
O
H
NH
1H NMR (CDCl3, 400 MHz)
1.00
1.00
0.78
2.17
2.25
5.75
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

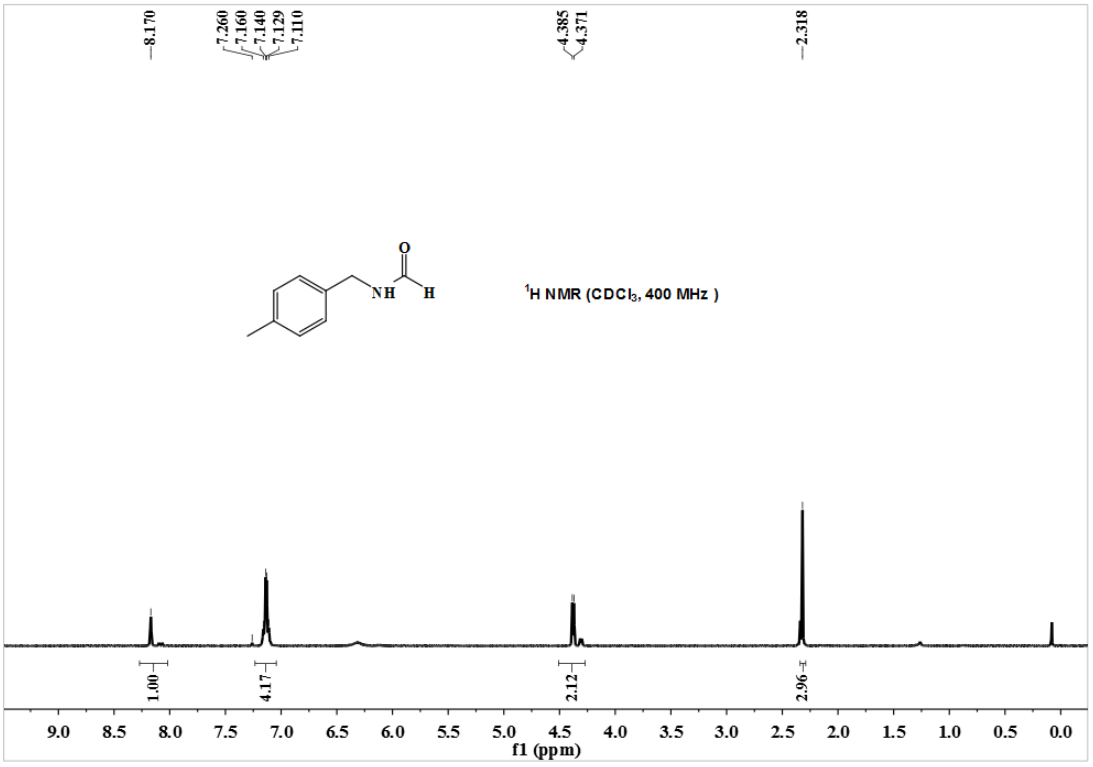

160.23
77.32
77.00
76.68
50.90
47.05
34.68
33.02
25.40
24.70
O
H
NH
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

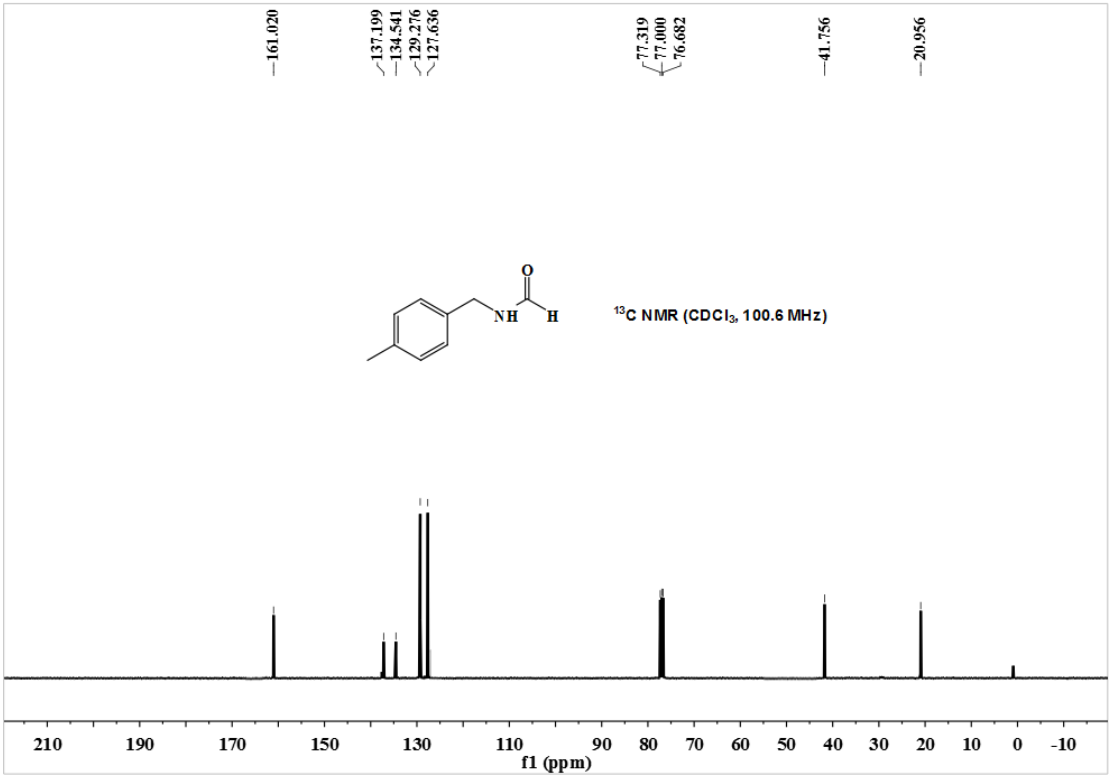

x10 4
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
46.0
84.0
56.0
67.0
114.0
127.0
70.9
97.9
91.0
105.9
118.9
40 50 60 70 80 90 100 110 120 130 140 150 160
O
H
NH

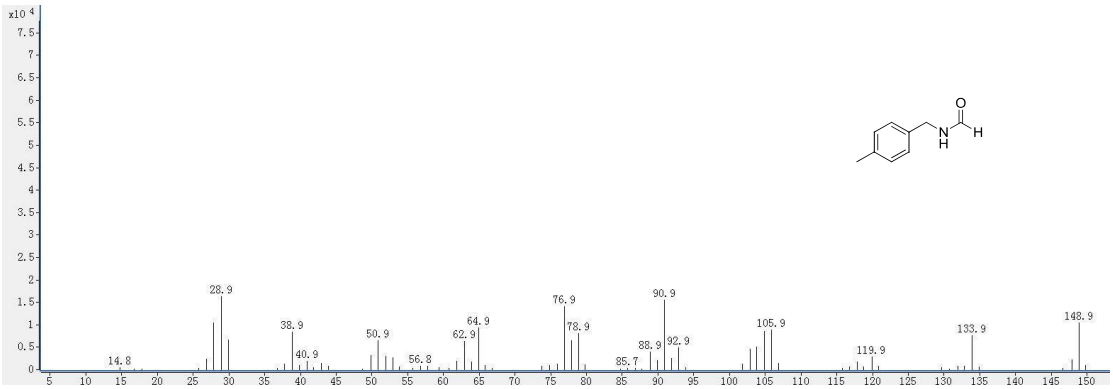

8.174
7.325
7.319
7.314
7.295
7.278
7.265
7.239
6.394
4.429
4.409
O
NH
H
1H NMR (CDCl3, 400 MHz)
1.00
5.86
0.88
2.09
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

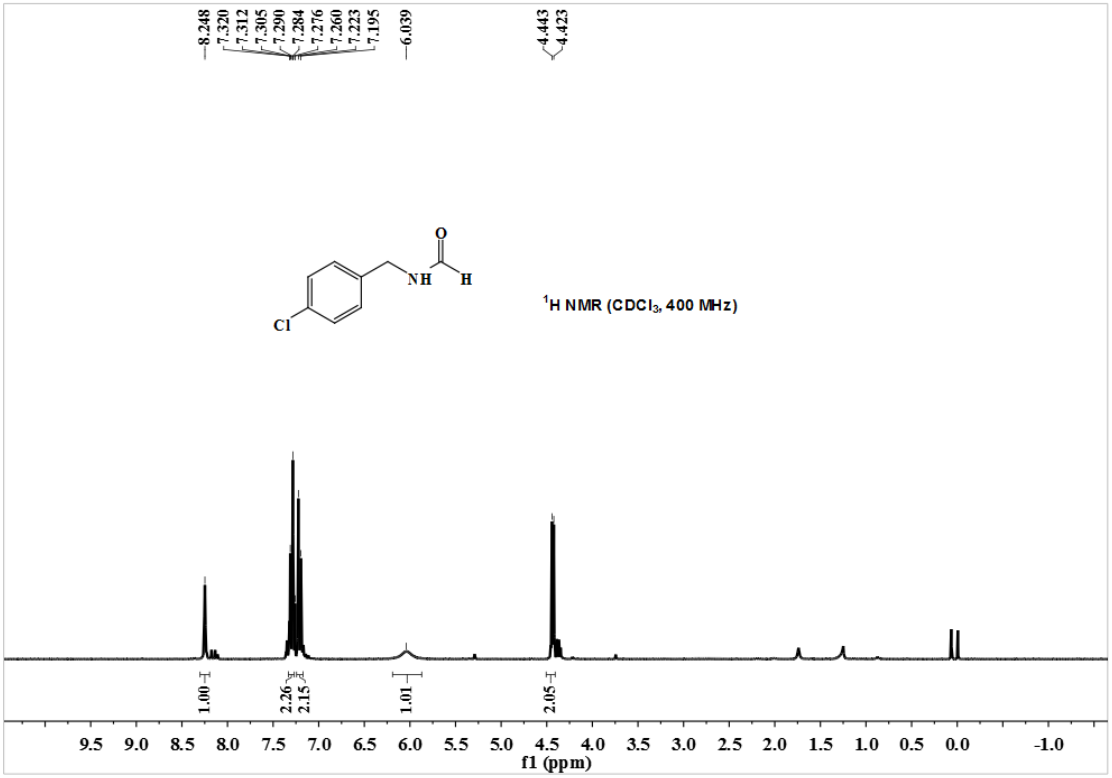

161.219
137.671
128.750
127.749
127.626
77.549
77.125
76.701
42.113
O
NH
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

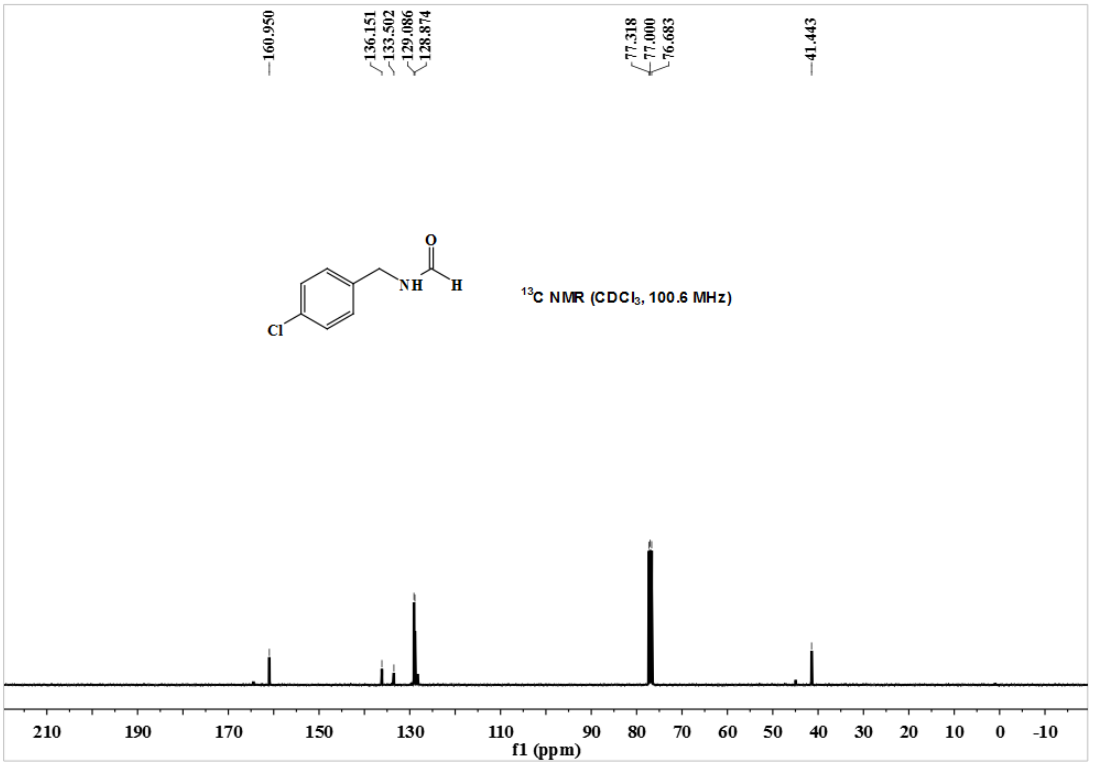

x10 5
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
135.0
91.0
106.0
79.0
65.0
51.0
42.0
58.0
72.0
85.8
118.0
127.8
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
O
N
H
H

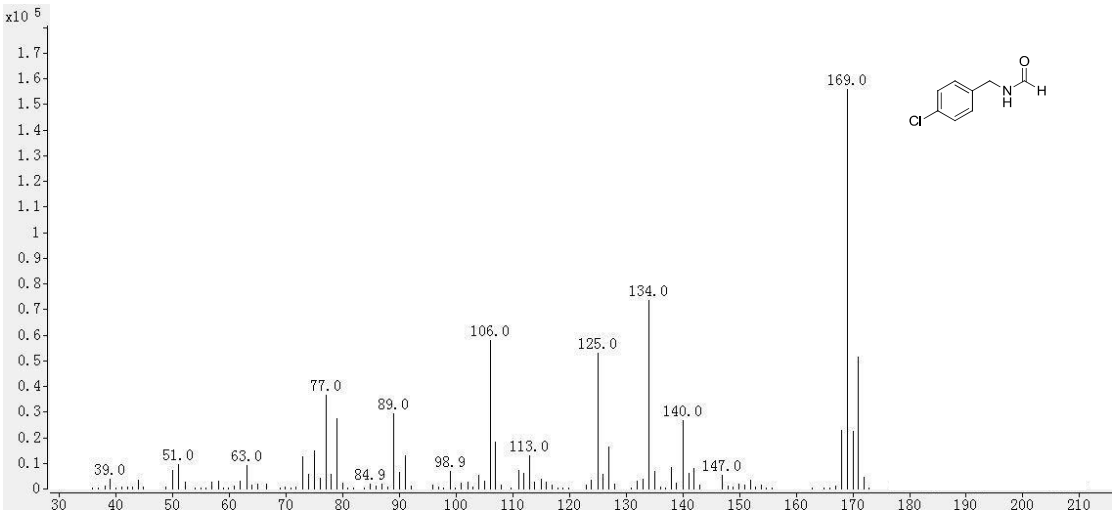

8.170
7.260
7.160
7.140
7.129
7.110
4.385
4.371
2.318
O
NH
H
1H NMR (CDCl3, 400 MHz)
1.00
4.17
2.12
2.96
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

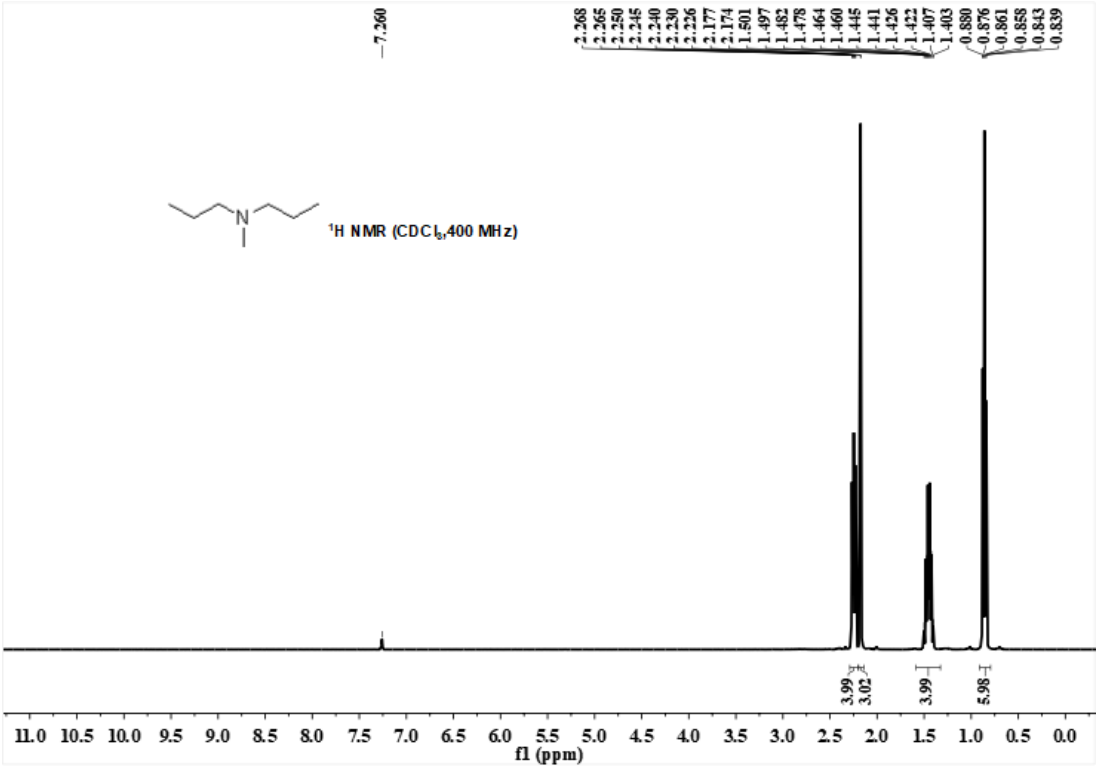

161.020
137.199
134.541
129.276
127.636
77.319
77.000
76.682
41.756
20.956
O
NH
H
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

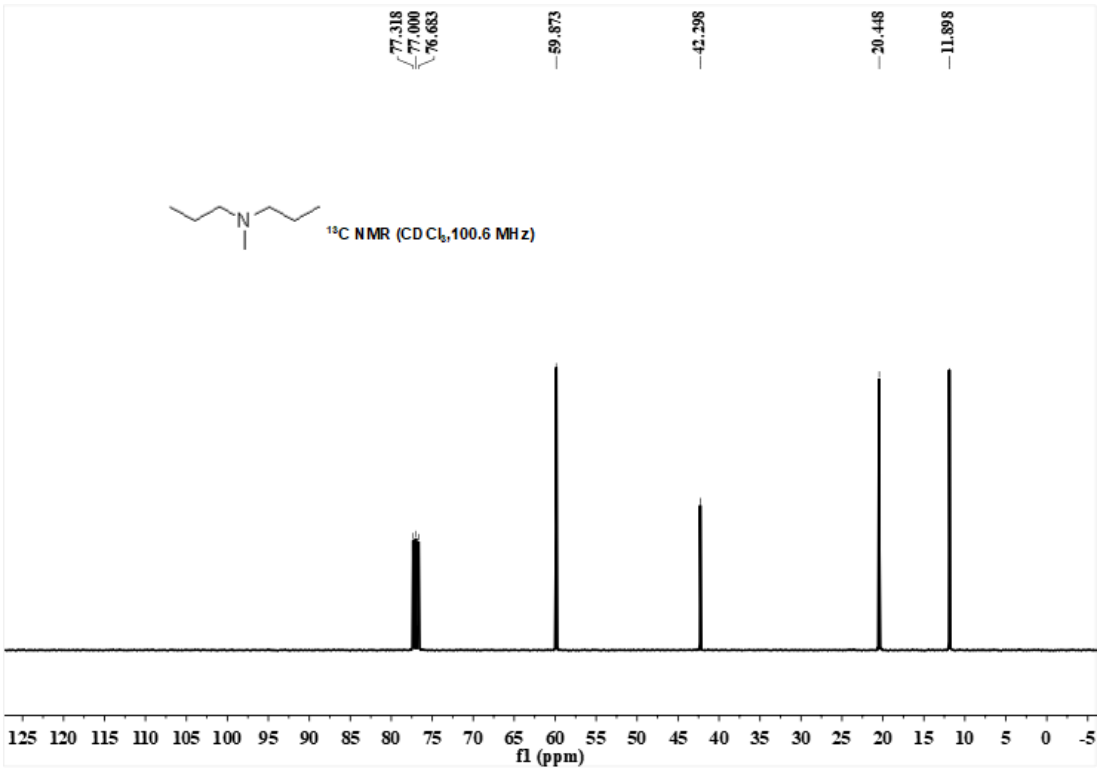

x10 4
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
O
N
H
H
14.8
28.9
38.9
40.9
50.9
56.8
62.9
64.9
76.9
78.9
85.7
88.9
90.9
92.9
105.9
119.9
133.9
148.9
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150

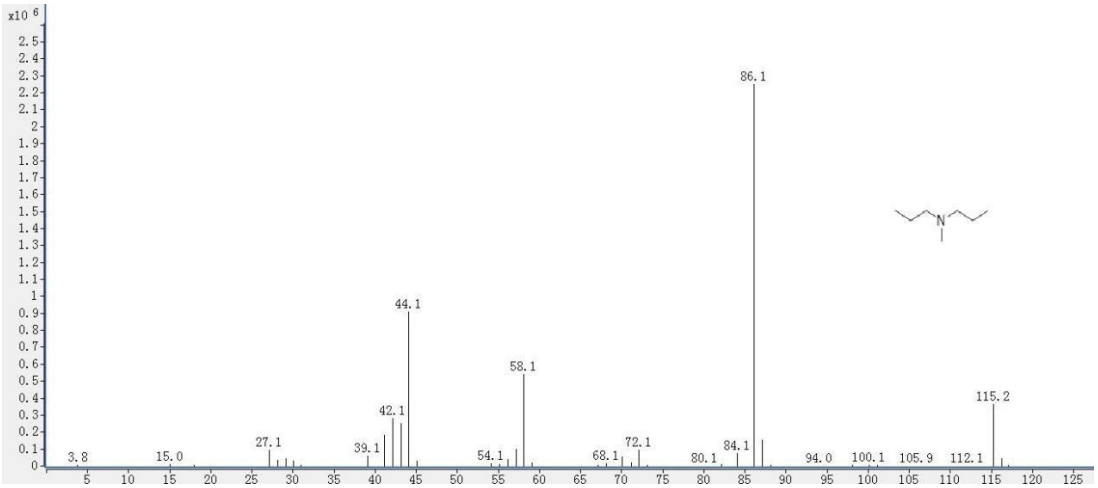

8.248
7.320
7.312
7.305
7.290
7.284
7.276
7.260
7.223
7.195
6.039
4.443
4.423
O
NH
H
Cl
1H NMR (CDCl3, 400 MHz)
1.00
2.26
2.15
1.01
2.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -1.0
f1 (ppm)

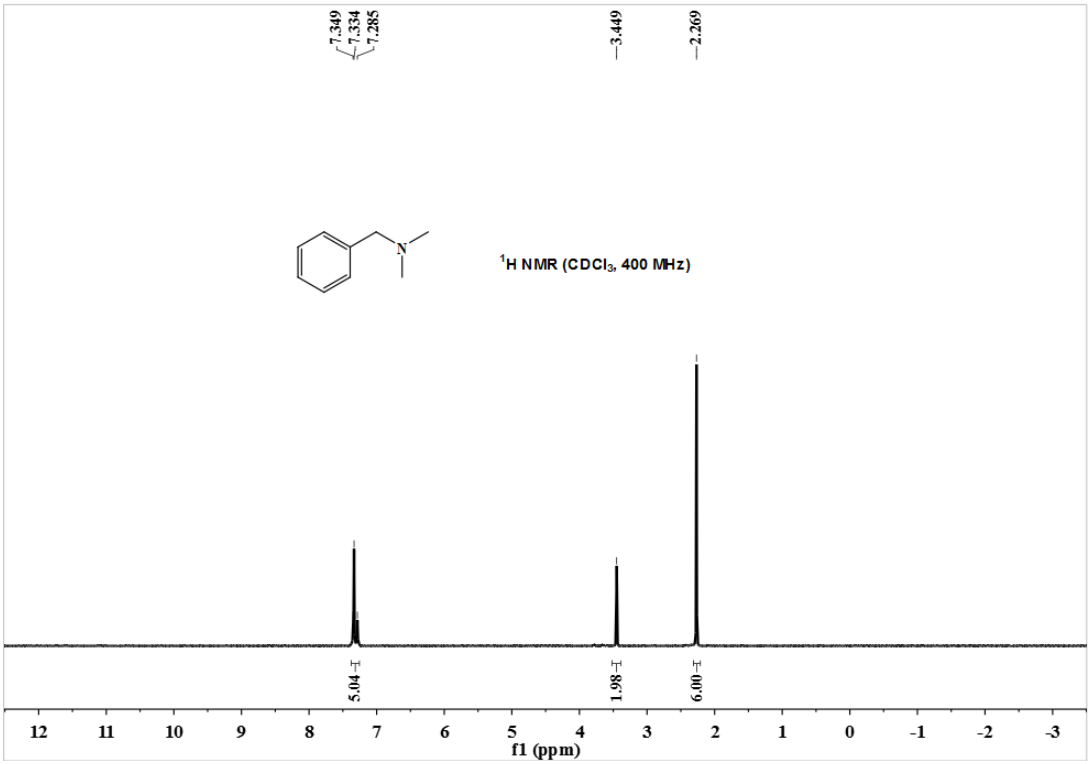

160.950
136.151
133.502
129.086
128.874
77.318
77.000
76.683
41.443
O
NH
H
Cl
13C NMR (CDCl3, 100.6 MHz)
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

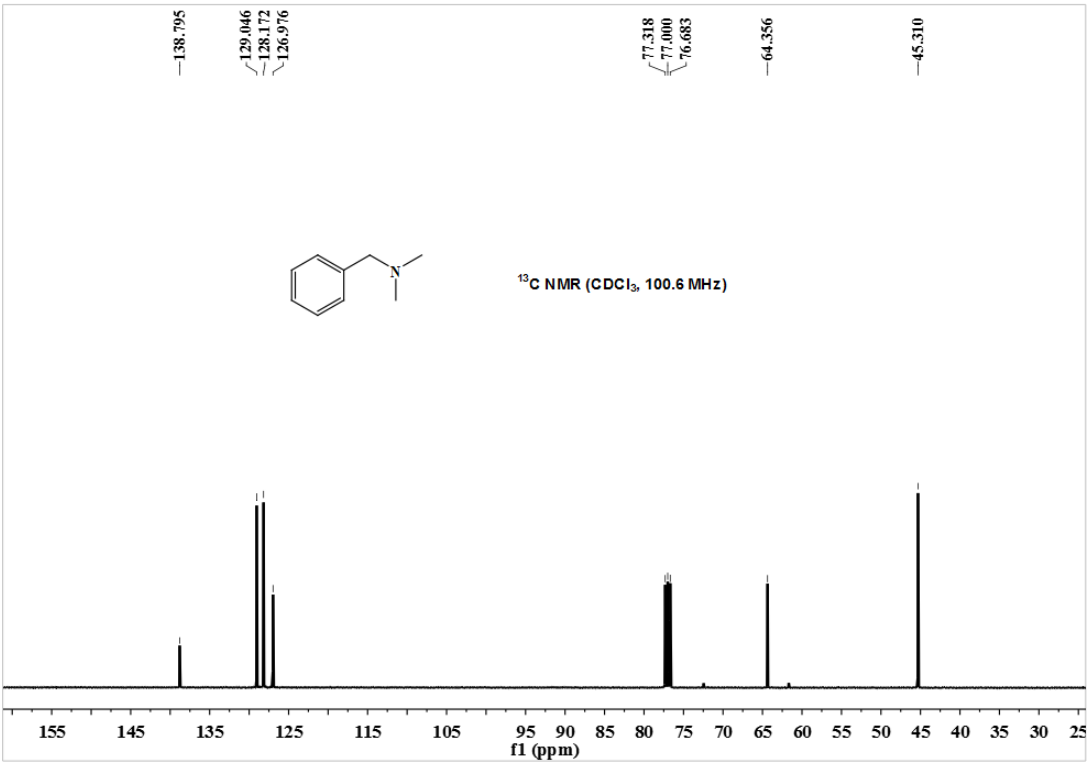

x10 5
169.0
134.0
106.0
125.0
77.0
89.0
140.0
113.0
51.0
63.0
39.0
84.9
98.9
147.0
Cl
N
H
O

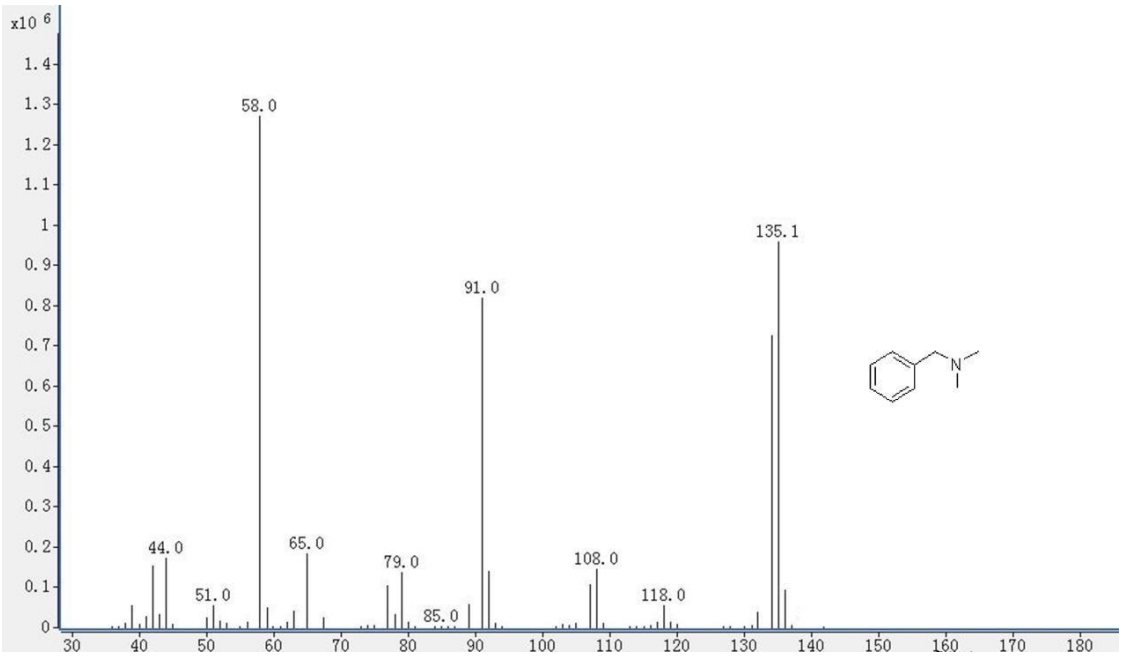

7.260
2.268
2.265
2.250
2.245
2.240
2.230
2.226
2.177
2.174
1.501
1.497
1.482
1.478
1.464
1.460
1.445
1.441
1.426
1.422
1.407
1.403
0.880
0.876
0.861
0.858
0.843
0.839
N
1H NMR (CDCl3,400 MHz)
3.99
3.02
3.99
5.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


77.318
77.000
76.683
59.873
42.298
20.448
11.898
^{13}C NMR (CDCl$_3$,100.6 MHz)
125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)


x10 6
86.1
44.1
58.1
42.1
115.2
27.1
39.1
72.1
84.1
3.8
15.0
54.1
68.1
80.1
94.0
100.1
105.9
112.1


7.349
7.334
7.285
3.449
2.269
N
^{1}H NMR (CDCl$_3$, 400 MHz)
5.04
1.98
6.00
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


138.795
129.046
128.172
126.976
77.318
77.000
76.683
64.356
45.310
N
^{13}C NMR (CDCl$_3$, 100.6 MHz)
155 145 135 125 115 105 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)



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