N-Methylation of Amine and Nitro Compound with CO_2/H_2 Catalyzed by Pd/CuZrOx under Mild Reaction Conditions

Xinjiang Cui, Yan Zhang, Youquan Deng and Feng Shi*
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000, China

1. Experimental

All solvents and chemicals were obtained commercially and were used as received.

Mass spectra were in general recorded on an HP 6890/5973 GC-MS. High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 KeV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at room temperature. A part of solution was dropped on the grid for the measurement of TEM images. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2θ range of 10-80°. For the data interpretation the software WinXpow (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar^+ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The palladium loadings of the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

Typical procedure for catalyst preparation: 639 g $Cu(NO_3)_2 \cdot 3H_2O$, 307 mg $ZrOCl_2 \cdot 8H_2O$ and suitable amount of H_2PdCl_4 were added into 50 mL deionized water and agitated till complete dissolution. Then, 20 mL Na_2CO_3 solution (0.354 M) was dropwise added and the mixture was further stirred for 3 h at room temperature. The reaction mixture was centrifuged and washed by water to remove the base till the pH value of the aqueous solution was ~7.0. Subsequently, the

solid was dried at 100 ^{o}C for 4 h, calcined in static air at 350 ^{o}C for 12 h and reduced under hydrogen flow at 300 ^{o}C for 3 h. The catalyst was denoted as PdCuZrOx. All the other catalysts were prepared with the same method by using different metal salts.

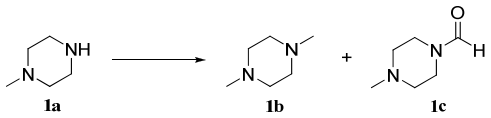
Typical reaction procedure for the N-methylation of primary amines: 1.0 mmol amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into an 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^{o}C for 30 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Typical reaction procedure for the N-methylation of secondary amines: 1.0 mmol amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into an 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^{o}C for 30 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

Typical reaction procedure for the N-formylation of amines: 1.0 mmol amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into an 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^{o}C for 15 h under magnetic stirring. Subsequently, the autoclave was cooled to room temperature, and 40 mg biphenyl and 10 mL ethanol were added for quantitative analysis by GC-FID (Agilent 6890A).

2. Catalysts screening and characterization of the catalysts

Table S1. Catalyst screening and reaction conditions optimization[a]



Entry	Catalysts	Conv./(%)[b]	Yield of **1b** /(%)[b]	Yield of **1c** /(%)[b]
1	Pd/CuOx	5	0	100
2	Pd/ZrOx	30	30	70
3	Pd/CuAlOx	50	2	47
4	Pd/CuZrOx	95	86(81[c])	7
5	Pd/CuZnOx	2	2	0
6	Pd/CuFeOx	4	0	3
7	Pd/CuMgOx	0	0	0
8	Pd/CuNiOx	0	0	0
9	Pd/AlZrOx	30	1	26
10	Pd/ZnZrOx	73	1	68
11	Pd/NiZrOx	85	5	57
12	Pt/CuZrOx	89	73	16
13	Rh/CuZrOx	42	3	39
14	Ru/CuZrOx	18	3	15
15	4%Pd/CuZrOx	97	87	10
16	1%Pd/CuZrOx	75	64	11
17	0.5%/PdCuZrOx	48	36	12
18	CuZrOx	85	42	43

[a]Reaction conditions: 1.0 mmol amine, 40 mg catalyst (2wt% Pd, 0.75 mol% Pd to 1a), 2 mL octane, 1.0 MPa CO_2, 2.5 MPa H_2, 150 ^oC, 24 h. [b]The numbers were determined by GC-FID using biphenyl as external standard material. [c]The catalysts was reused at the 3rd run.

Table S2. Physicochemical properties of the catalyst samples

Catalyst	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
Pd/ZrOx	25.7	0.03	3.50
Pd/CuOx	1.20	0.01	183.6
Pd/CuZrOx	89.3	0.31	10.21

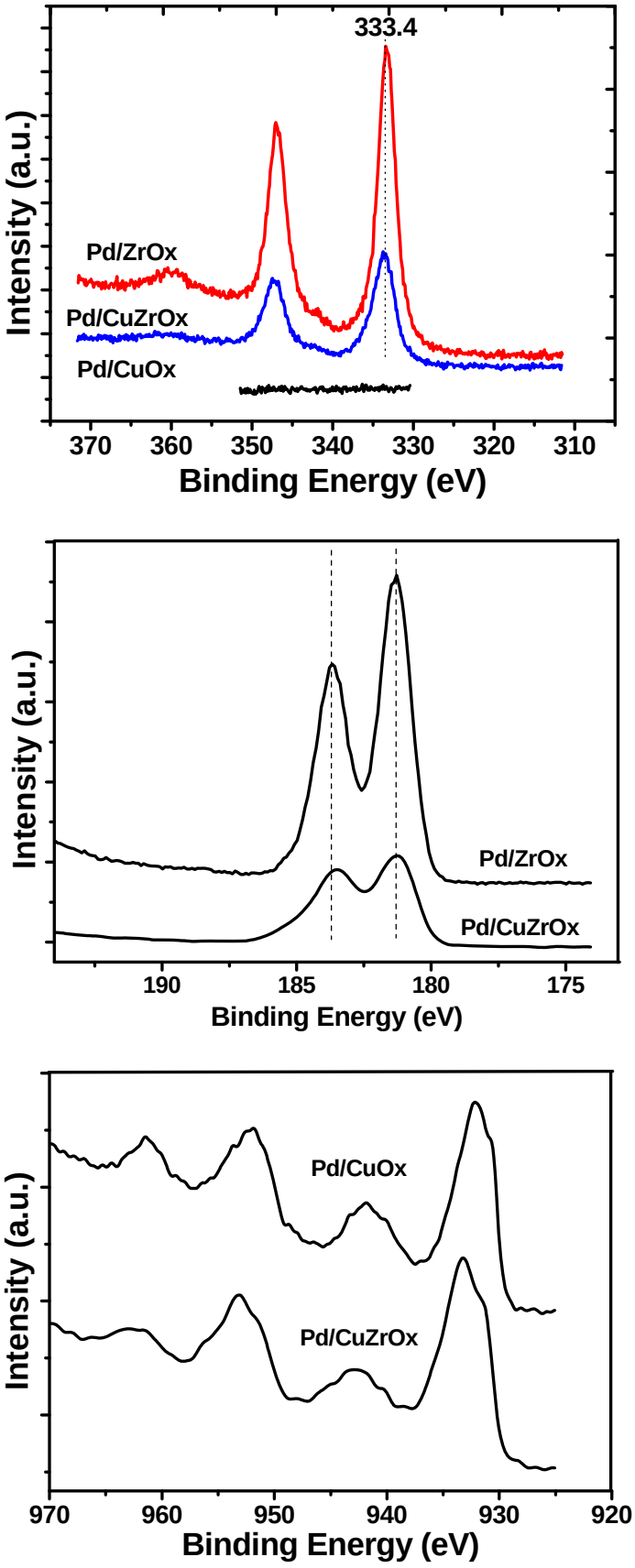


Figure S1. XPS spectra of Pd_{3d}, Zr_{3d} and Cu_{2p}

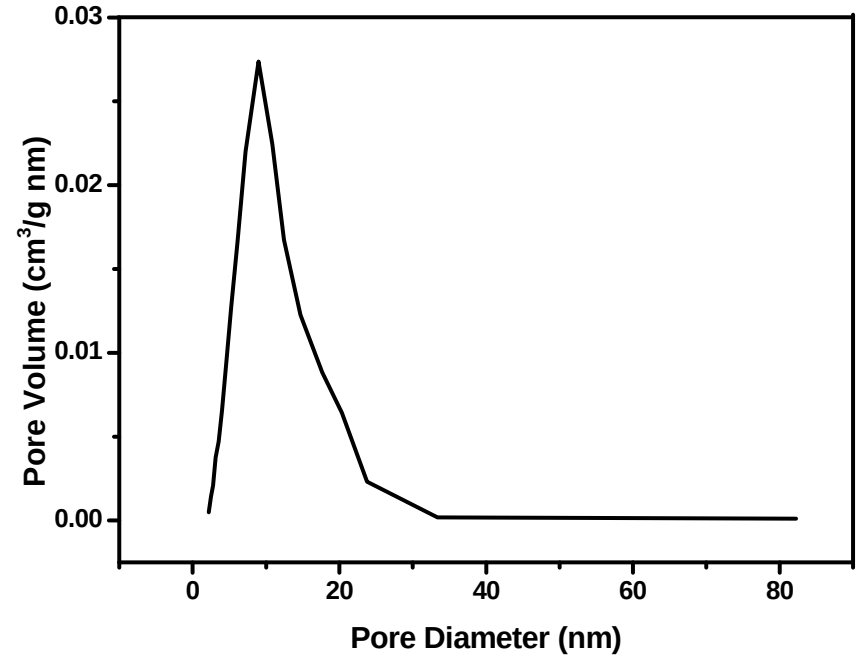


Figure S2. Picture of BJH desorption dV/dD pore volume of catalyst Pd/ZrCuOx

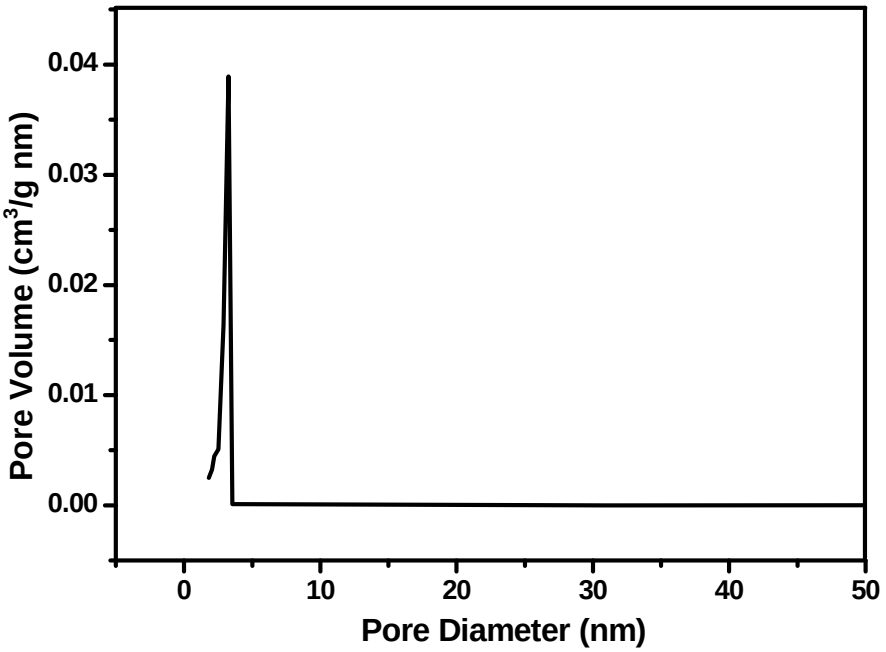


Figure S3. Picture of BJH desorption dV/dD pore volume of catalyst Pd/ZrOx

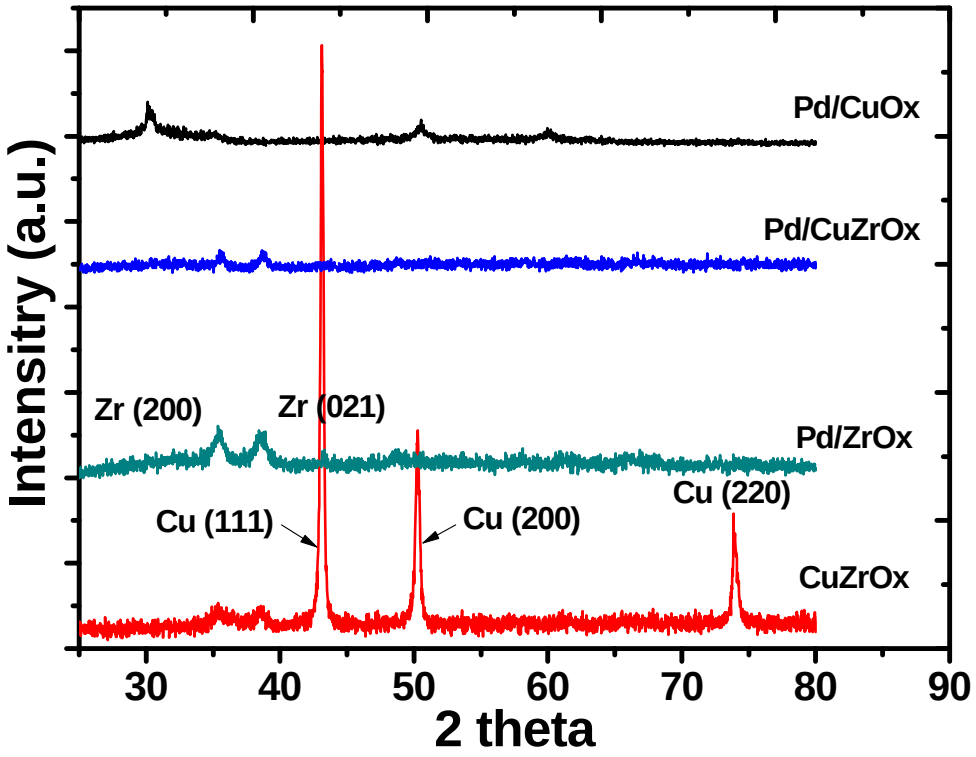


Figure S4. XRD diffraction patterns of the catalyst samples

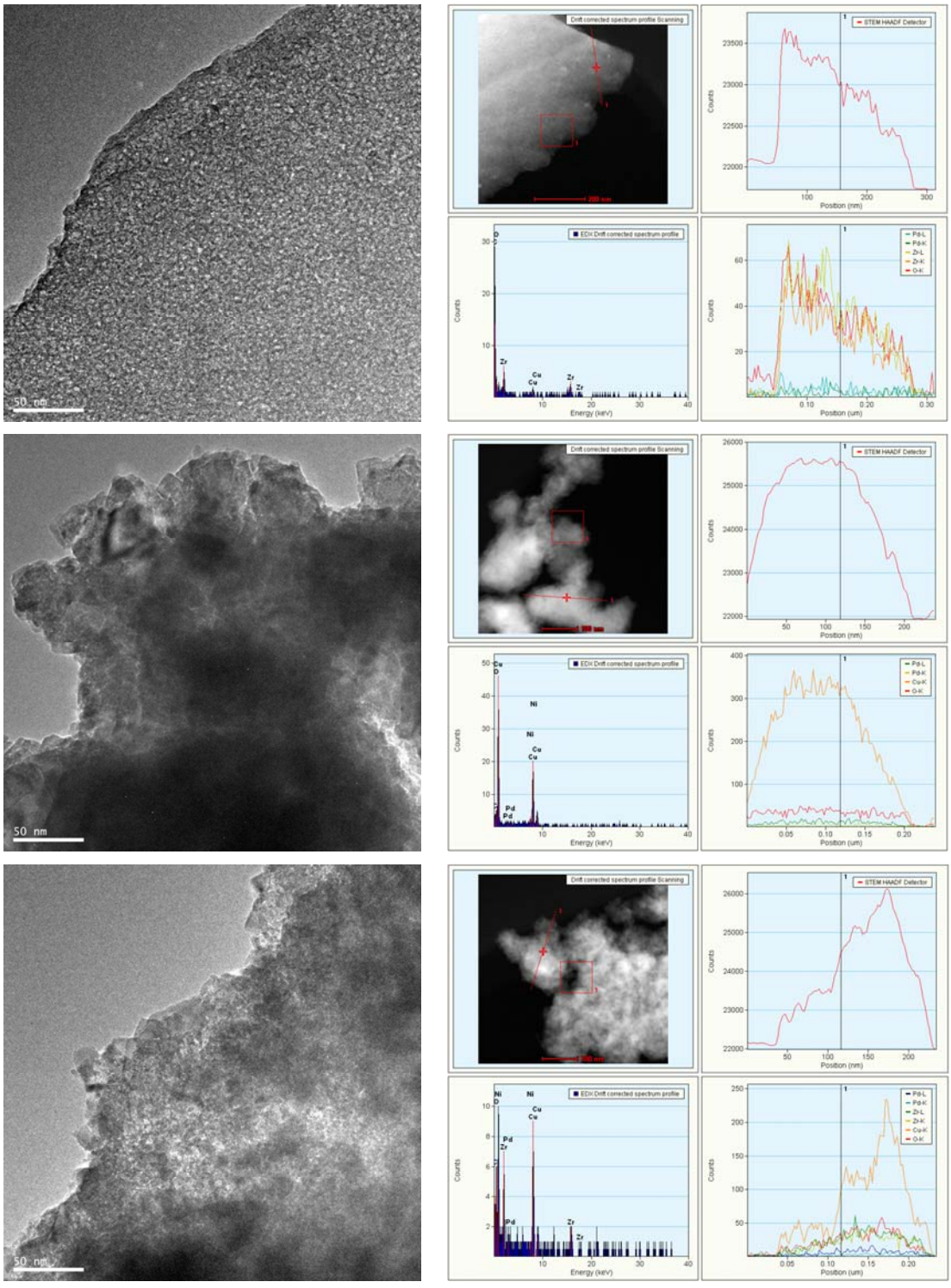


Figure S5. TEM and HAADF-STEM images of catalyst Pd/ZrOx, Pd/CuOx and Pd/CuZrOx (from the topside)

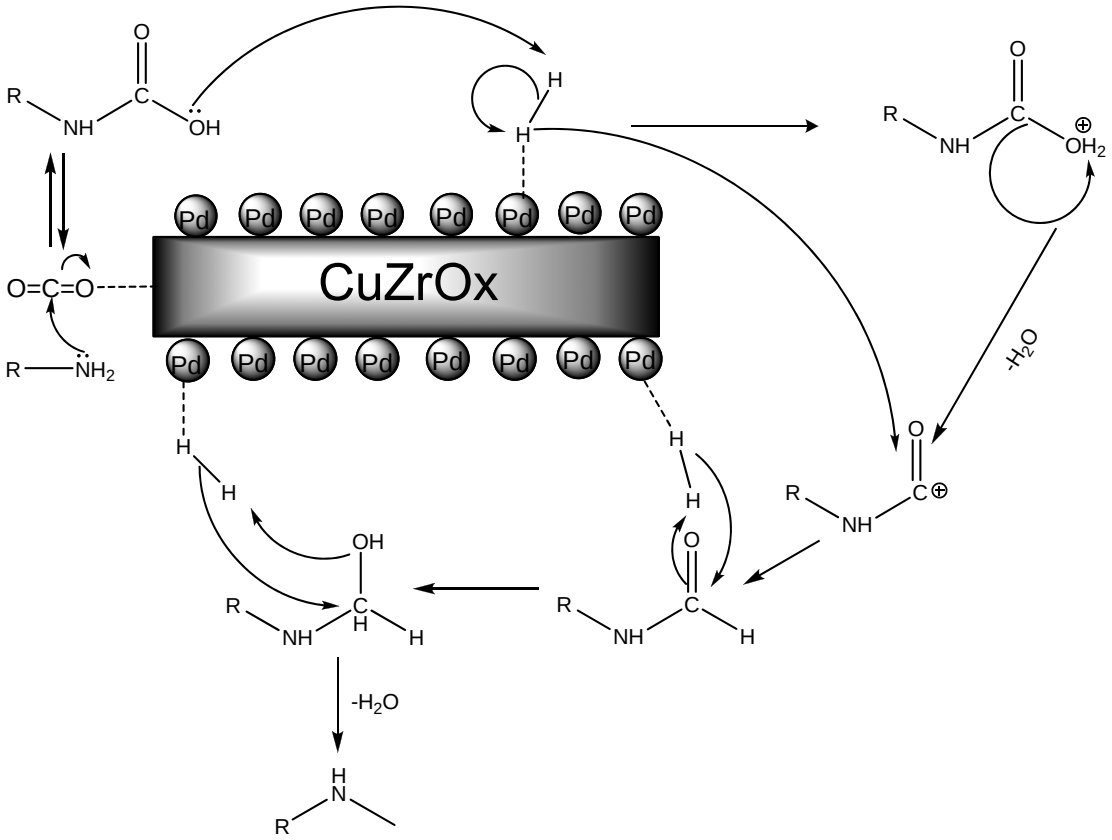
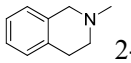
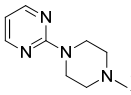


Figure S6. A possible reaction mechanism about eh N-methylation reaction

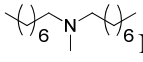
3. Characterization of the products



2-methyl-1,2,3,4-tetrahydroisoquinoline: (Table 2, Entry 9); The typical procedure for the reaction of 1,2,3,4-tetrahydroisoquinoline was followed: 133 mg 1,2,3,4-tetrahydroisoquinoline, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (20:1) to give isolated yields (121 mg, 83%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.46 (s, 3H), 2.69-2.72 (t, 2H), 2.91-2.95 (t, 2H), 3.59 (s, 2H), 7.00-7.02 (t, 1H), 7.09-7.14 (m, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.12, 46.01, 52.87, 57.91, 125.62, 126.15, 126.43, 128.65, 133.76, 134.59; MS (E.I., 70 eV) *m*/*z* (rel. int.) 146 (100), 144 (11), 131 (7), 130 (6), 118 (5), 115 (6), 105 (7), 104 (48), 103 (16), 78 (12), 77 (9), 42 (7).

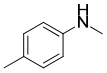


2-(4-methylpiperazin-1-yl)pyrimidine (Table 2, Entry 10); The typical procedure for the reaction of 2-(piperazin-1-yl)pyrimidine was followed: 164 mg 2-(piperazin-1-yl)pyrimidine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (120:1) to give isolated yields (135 mg, 76%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.37 (s, 3H), 2.53-2.56 (t, 4H), 3.86-3.89 (t, 4H), 6.49-6.52 (t, 1H), 8.30-8.31 (d,2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 45.25, 45.78, 54.59, 110.00, 157.72, 161.62; MS (E.I., 70 eV) *m*/*z* (rel. int.) 178 (69), 134 (21), 122 (8), 121 (41), 120 (23), 109 (8), 108 (100), 83 (16), 81 (6), 80 (36), 79 (13), 71 (34), 70 (33), 58 (8), 56 (8), 54 (5), 53 (12), 43 (21), 42 (21).

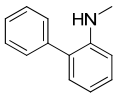


N-methyl-N-octyloctan-1-amine (Table 2, Entry 11); The typical procedure for the N-methylation of dioctylamine was followed: 241 mg dioctylamine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0

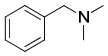
MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (15:1) to give a brown solid (189 mg, 74%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.86-0.90 (t, 6H), 1.28 (t, 20H), 1.41-1.47 (t, 4H), 2.21 (s, 3H), 2.29-2.33 (t, 4H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.08, 22.66, 27.30, 29.29, 29.59, 31.86, 42.34, 57.93; MS (E.I., 70 eV) *m*/*z* (rel. int.) 255 (3), 157 (11), 156 (100), 58 (16).



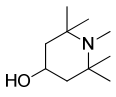
N,4-dimethylbenzenamine (Table 3, Entry 2); The typical procedure for the N-methylation of p-toluidine was followed: 106 mg p-toluidine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (100:1) to give a brown solid (88.3 mg, 73%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.24 (s, 3H), 2.81 (s, 3H), 3.44 (s, 1H), 6.54-6.57 (t, 2H), 6.99-7.00 (d, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.39, 30.17, 112.72, 126.61, 129.72, 147.08; MS (E.I., 70 eV) *m*/*z* (rel. int.) 121 (71), 120 (100), 106 (7), 91 (14), 77 (8).



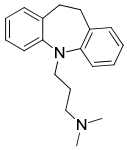
N-methylbiphenyl-2-amine: (Table 3, Entry 7); The typical procedure for the reaction of biphenyl-2-amine was followed: 169 mg biphenyl-2-amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (120:1) to give isolated yields (144.6 mg, 79%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.78 (s, 3H), 3.96 (s, 1H), 6.68-6.70 (d, 1H), 6.75-6.80 (d, 1H), 7.07-7.10 (d,1H), 7.23-7.45 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 30.80, 109.85, 116.85, 127.21, 127.64, 128.80, 128.89, 129.45, 130.05, 139.56, 146.19; MS (E.I., 70 eV) *m*/*z* (rel. int.) 183 (100), 182 (51), 180 (21), 168 (14), 167 (30), 166 (11), 165 (17), 152 (10), 139 (5), 83 (5).

 N,N-dimethyl-1-phenylmethanamine: (Table 2, Entry 9); The typical procedure for the reaction of phenylmethanamine was followed: 106 mg phenylmethanamine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ diethyl ether (3:1) to give isolated yields (121 mg, 83%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 2.24 (s, 6H), 3.43 (s, 2H), 7.31-7.36 (m, 5H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 45.25, 64.31, 127.11, 128.26; MS (E.I., 70 eV) *m*/*z* (rel. int.) 135 (100), 134 (82), 118 (8), 92 (13), 91 (80), 89 (170, 77 (6), 65 (20), 63 (6), 58 (84), 51 (6), 44 (7), 42 (16), 39 (6).

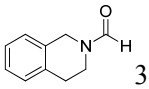
 N,N-dimethyldodecan-1-amine (Table 2, Entry 11); The typical procedure for the N,N-dimethylation of dodecan-1-amine was followed: 185 mg dodecan-1-amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (10:1) to give a brown solid (147 mg, 69%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.85-0.90 (t, 3H), 1.25-1.32 (t, 20H), 1.41-1.47 (t, 2H), 2.22 (s, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09, 22.63, 27.58, 27.64, 27.78, 29.35, 29.63, 29.67, 31.92, 45.90, 59.99, 35.22, 45.16, 48.72, 57.50, 119.96, 122.48, 126.39, 129.81, 134.21, 148.21; MS (E.I., 70 eV) *m*/*z* (rel. int.) 213 (3), 58 (100).

 1,2,2,6,6-pentamethylpiperidin-4-ol (Scheme 1); The typical procedure for the N-methylation of 2,2,6,6-tetramethylpiperidin-4-ol was followed: 157 mg 2,2,6,6-tetramethylpiperidin-4-ol, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 160 ^oC for 48 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether to give a

brown solid (147 mg, 69%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.04 (s, 3H), 1.18 (s, 3H), 1.40-1.47 (t, 2H), 1.54-1.55 (d, 1H), 1.83-1.86 (t, 2H); 2.26 (s, 3H); 3.90-3.96 (m, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 20.65, 28.06, 33.14, 49.83, 55.74, 63.66; MS (E.I., 70 eV) *m*/*z* (rel. int.) 157 (10), 156 (100), 138 (9), 100 (28), 85 (6), 72 (40), 56 (27), 41 (5).

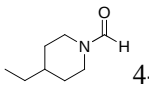


3-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-N,N-dimethylpropan-1-amine (Scheme 1); The typical procedure for the N-dimethylation of 3-(10,11-dihydro-5H-dibenzo[b,f]azepin-5-yl)-N-methylpropan-1-amine was followed: 266 mg dodecan-1-amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^{o}C for 30 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (10:1) to give a brown solid (249 mg, 89%); ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 1.77-1.80 (t, 2H), 2.21 (s, 6H), 2.39-2.42 (t, 2H), 3.18 (s, 4H), 3.78-3.82 (t, 2H), 6.92-6.97 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 25.7, 35.22, 45.16, 48.72, 57.50, 119.96, 122.48, 126.39, 129.81, 134.21, 148.21; MS (E.I., 70 eV) *m*/*z* (rel. int.) 281 (6), 280 (24), 236 (13), 235 (83), 234 (100), 222 (6), 221 (6), 220 (19), 209 (6), 208 (21), 207 (13), 206 (14), 204 (7), 195 (31), 194 (26), 193 (36), 192 (13), 191 (7), 180 (6), 179 (8), 178 (8), 167 (5), 165 (7), 130 (14), 91 (5), 85 (6), 84 (7), 70 (6), 58 (39).

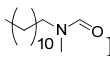


3,4-dihydroisoquinoline-2(1H)-carbaldehyde (Scheme 2); The typical procedure for the reaction of 1,2,3,4-tetrahydroisoquinolinewas followed: 133 mg dodecan-1-amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^{o}C for 15 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (6:1) to give isolated yields (109 mg, 68%). ^{1}H NMR (400.1 MHz, $CDCl_3$): δ = 2.87-2.91 (t, 2H), 3.65-3.67 (d, 2H), 4.55 (s, 2H), 7.14-7.21 (t, 4H), 8.21(s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.95, 29.76, 38.11, 42.40,

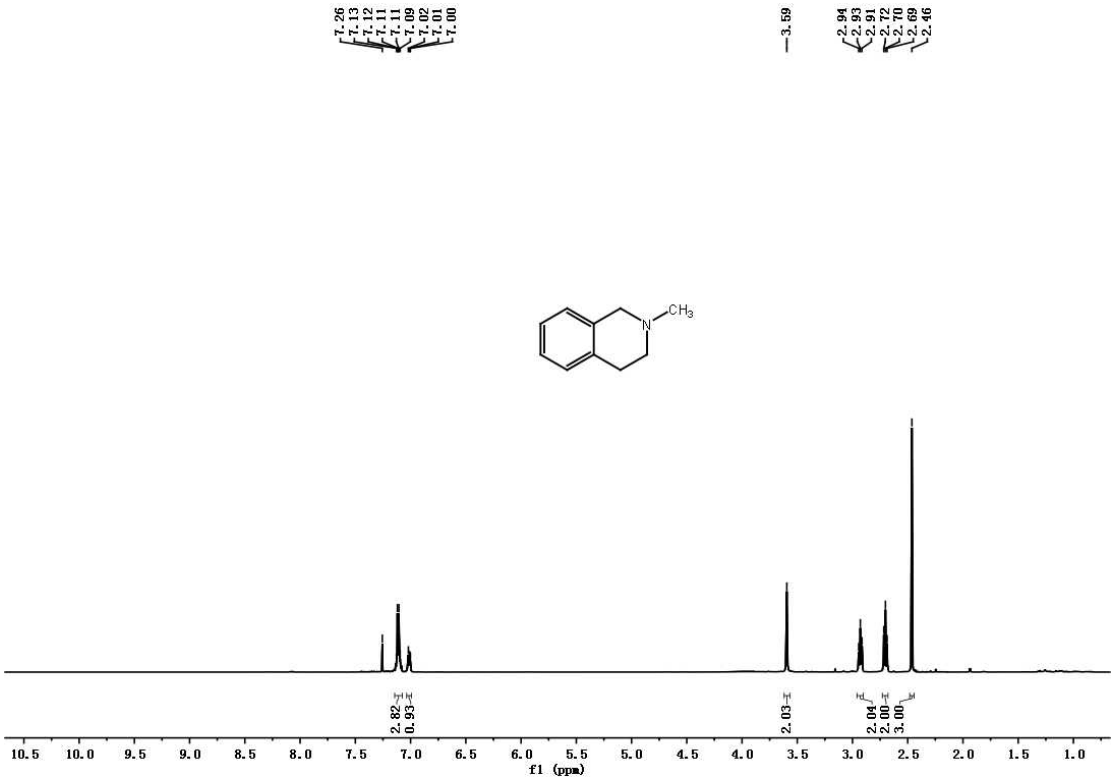
43.32, 47.38, 125.89, 126.53, 126.66, 126.68, 126.78, 127.16, 128.91, 129.20, 131.77, 132.23, 133.55, 134.47, 161.30, 161.79.



4-ethylpiperidine-1-carbaldehyde (Scheme 2); The typical procedure for the reaction of dodecan-1-amine was followed: 116 mg 4-ethylpiperidine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 15 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 30-60ºC)/ethyl acetate (6:1) to give isolated yields (93 mg, 65%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 1.10 (s, 3H), 2.24-2.27 (m, 6H), 2.26 (s, 2H), 3.58 (s, 2H), 8.03 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 39.91, 45.57, 51.95, 52.25, 53.17, 160.70.



N-dodecyl-N-methylformamide (Scheme 2) (GC purity 98%); The typical procedure for the reaction of dodecan-1-amine was followed: 185 mg dodecan-1-amine, 40 mg PdCuZrOx catalyst and 2 mL octane were added into a 80 mL autoclave. Then it was exchanged with CO_2, and 1.0 MPa CO_2 and 2.5 MPa H_2 were introduced. The reaction was reacted at 150 ^oC for 15 h under magnetic stirring. The title compound was obtained and purified by column chromatography using petroleum ether (b.p. 60-90ºC)/ethyl acetate (4:1) to give isolated yields (152 mg, 56%). ^1H NMR (400.1 MHz, $CDCl_3$): δ = 0.85-0.90 (t, 3H), 1.26 (s, 18H), 1.53-1.56 (m, 2H), 2.85 (s, 3H), 8.04 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.09, 22.67, 26.32, 28.00, 29.32, 29.49, 29.54, 29.59, 29.61, 31.90, 44.20, 49.61, 162.63; MS (E.I., 70 eV) *m*/*z* (rel. int.) 227 (13), 226 (23), 212 (16), 210 (10), 156 (7), 142 (8), 128 (10), 115 (5), 114 (9), 100 (13), 87 (7), 86 (14), 73 (53), 72 (100), 60 (11), 57 (5), 55 (10), 44 (42), 43 (11), 42 (7), 41 (14).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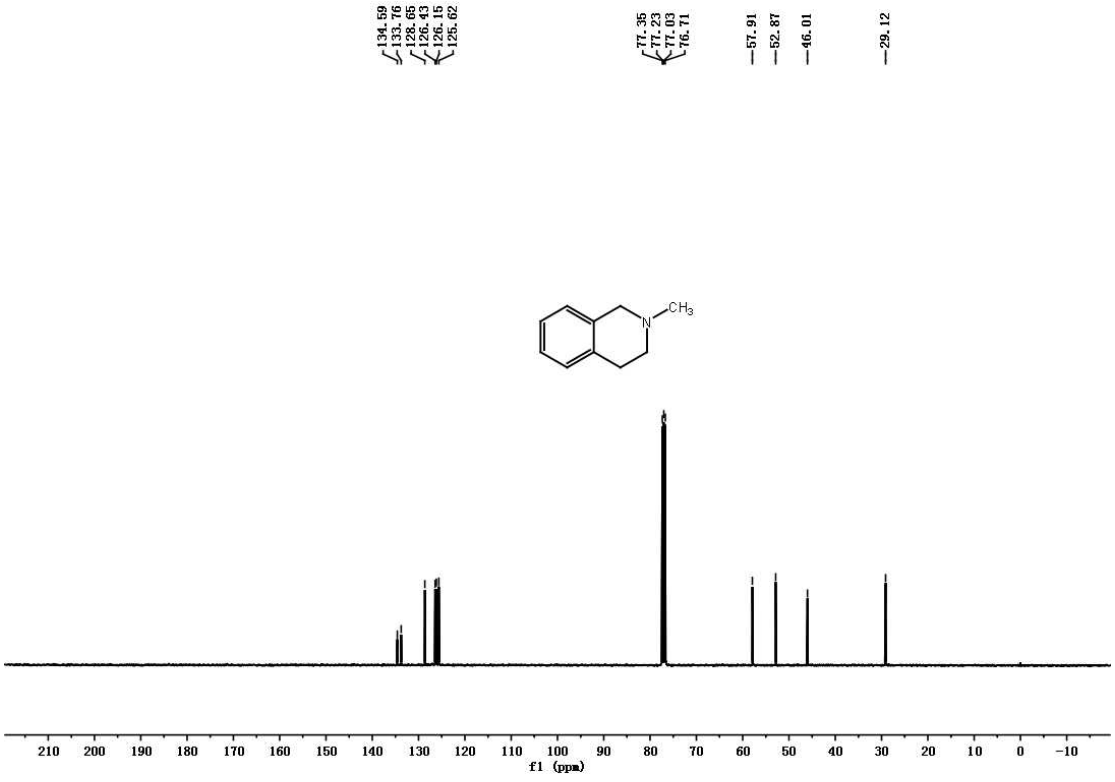
7.12
7.11
7.11
7.09
7.02
7.01
7.00
3.59
2.94
2.93
2.91
2.72
2.70
2.69
2.46
N
CH3
2.82
0.93
2.03
2.04
2.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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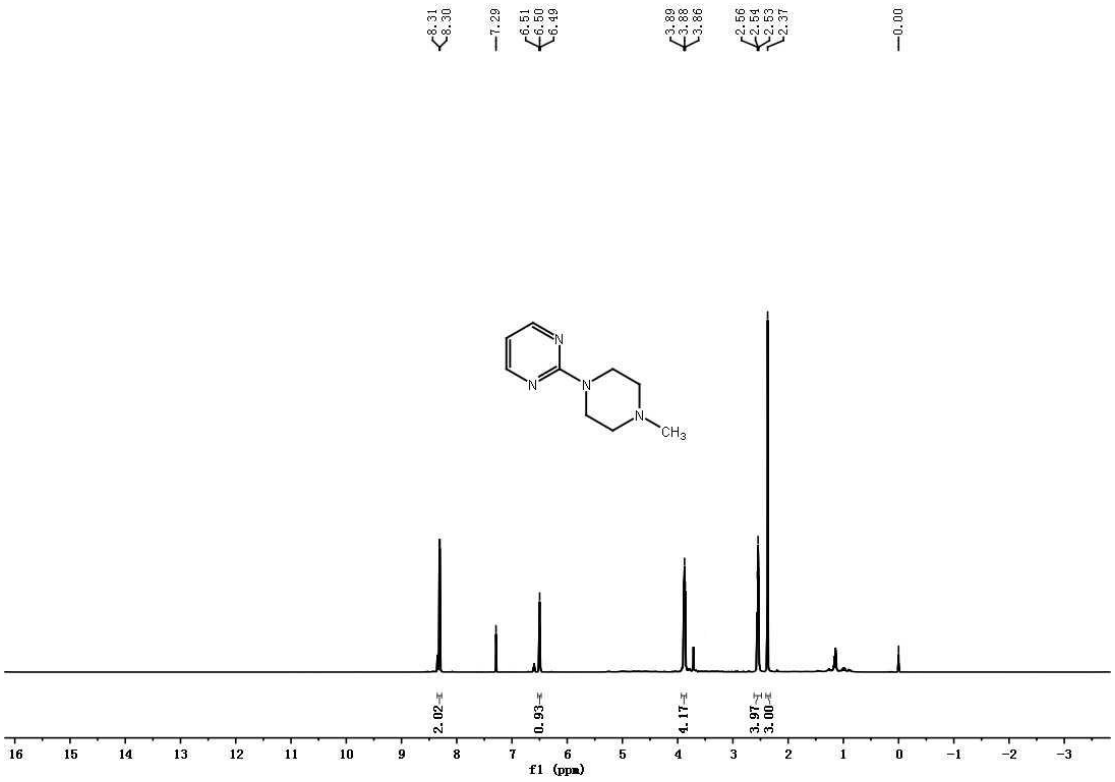
133.76
128.65
126.43
126.15
125.62
77.35
77.23
77.03
76.71
57.91
52.87
46.01
29.12
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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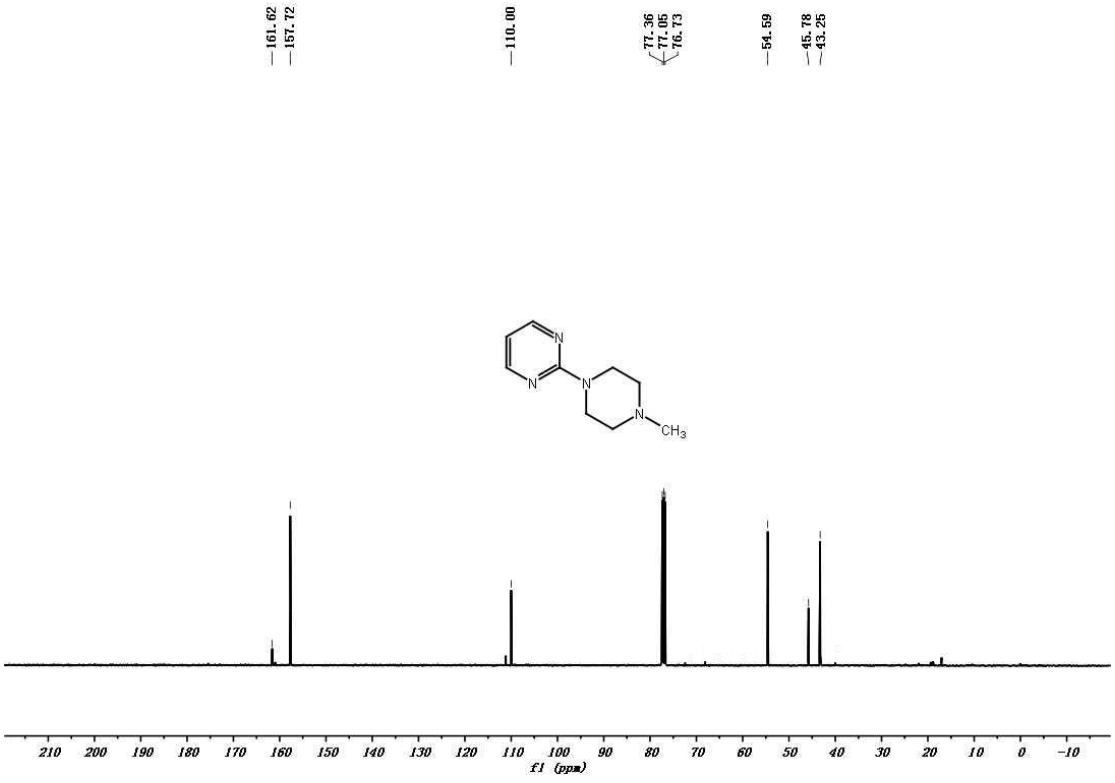
8.30
7.29
6.51
6.50
6.49
3.89
3.88
3.86
2.56
2.54
2.53
2.37
0.00
N
N
N
N
CH3
2.02
0.93
4.17
3.97
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)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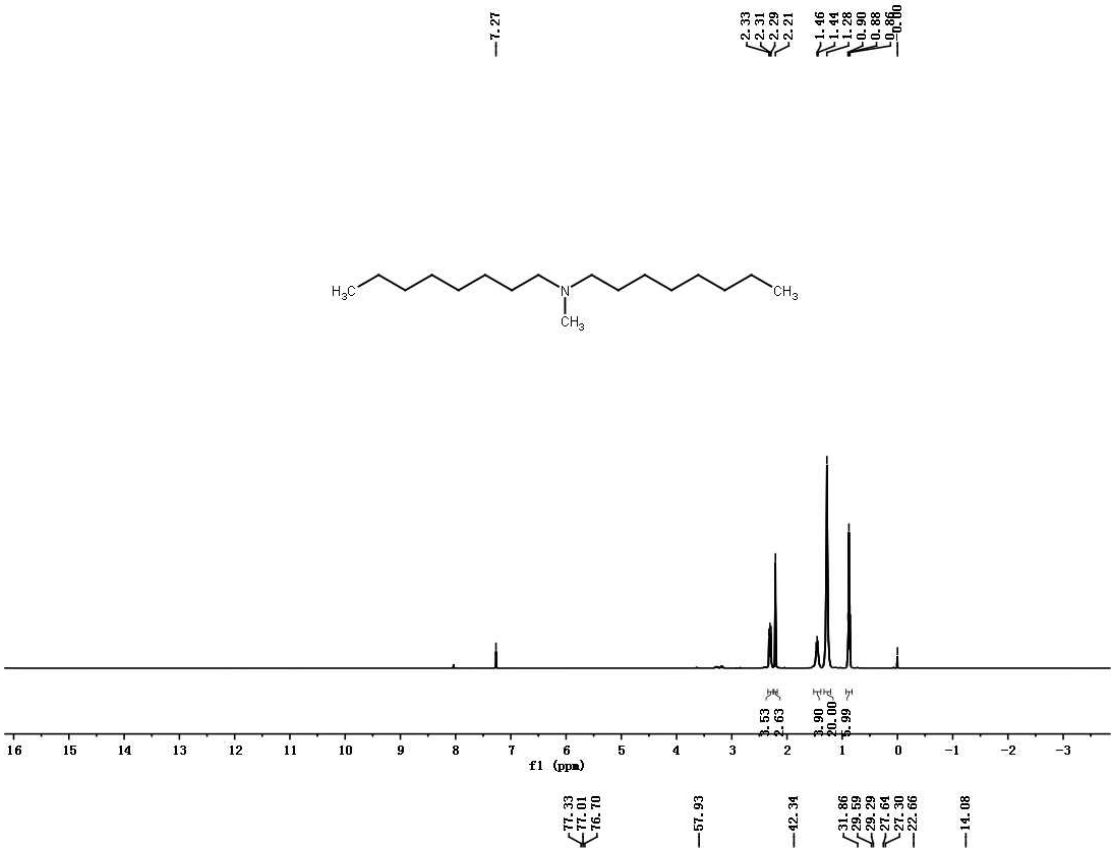
157.72
110.00
77.36
77.05
76.73
54.59
45.78
43.25
N
N
N
N
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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1.44
1.28
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H3C
N
CH3
CH3
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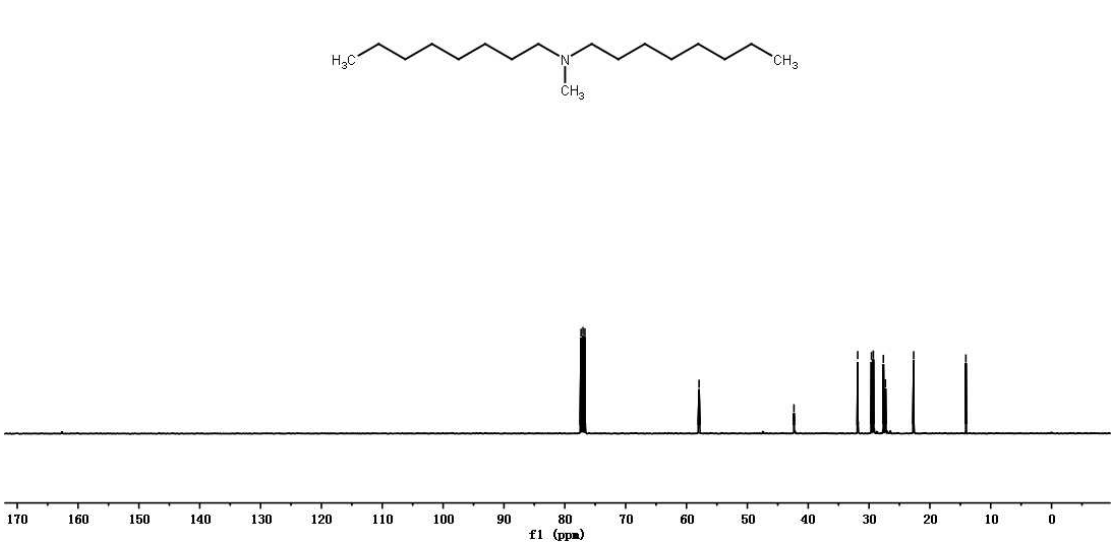
3.90
20.00
5.99
f1 (ppm)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27.30
22.66
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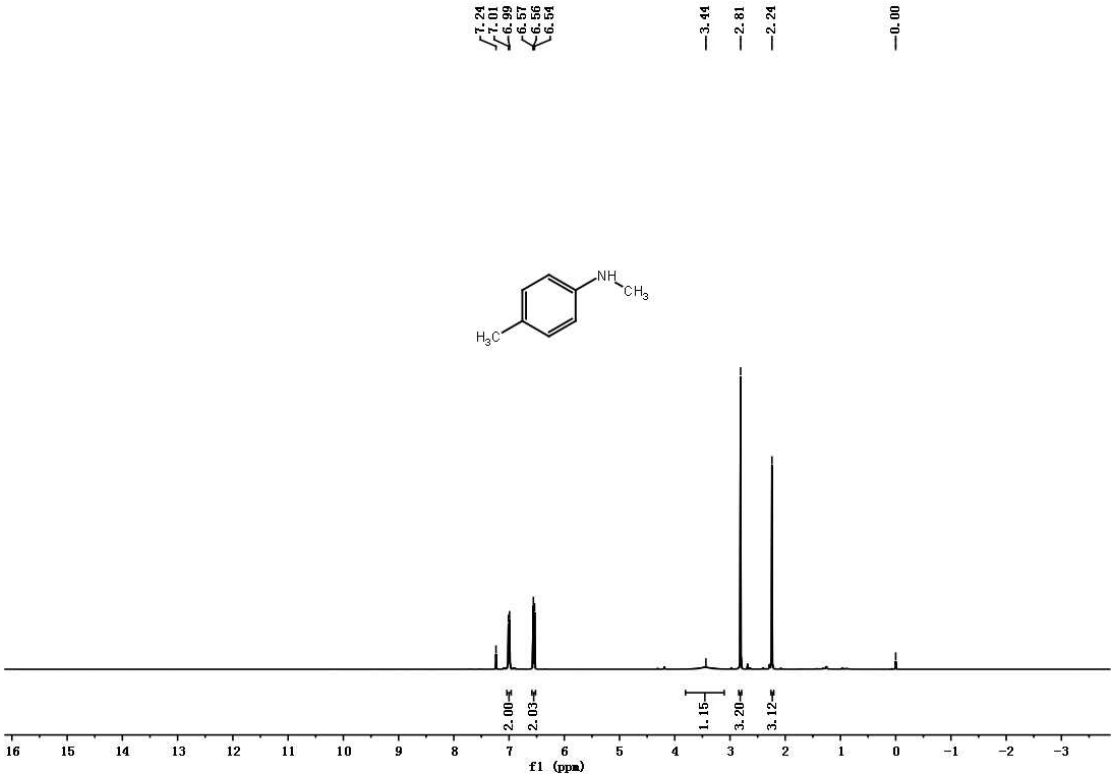
H3C
N
CH3
CH3
f1 (ppm)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6.56
6.54
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CH3
H3C
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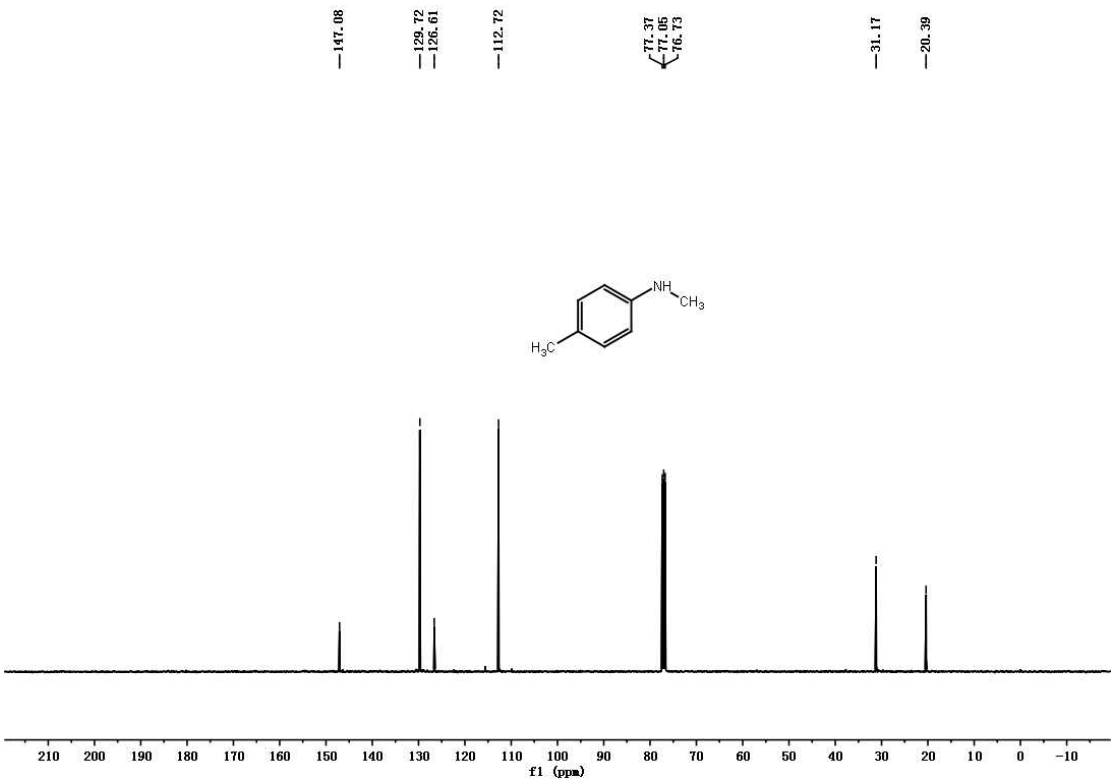
2.03
1.15
3.20
3.12
f1 (ppm)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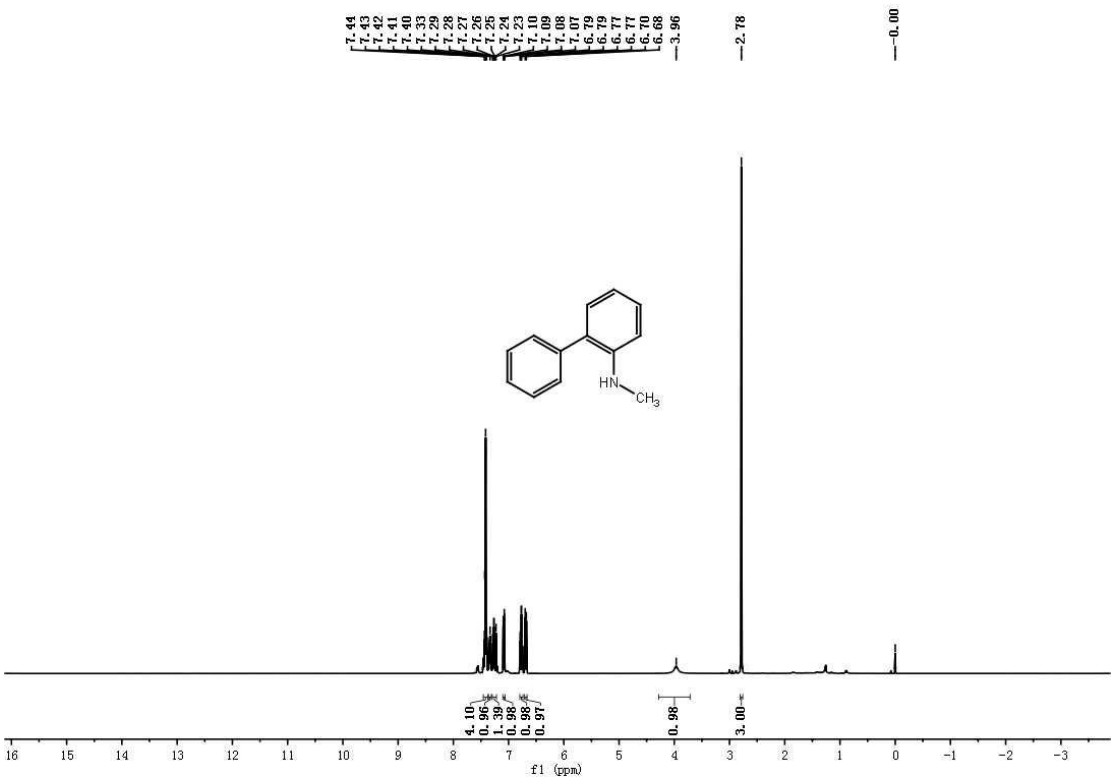
77.05
76.73
31.17
20.39
NH
CH3
H3C
f1 (ppm)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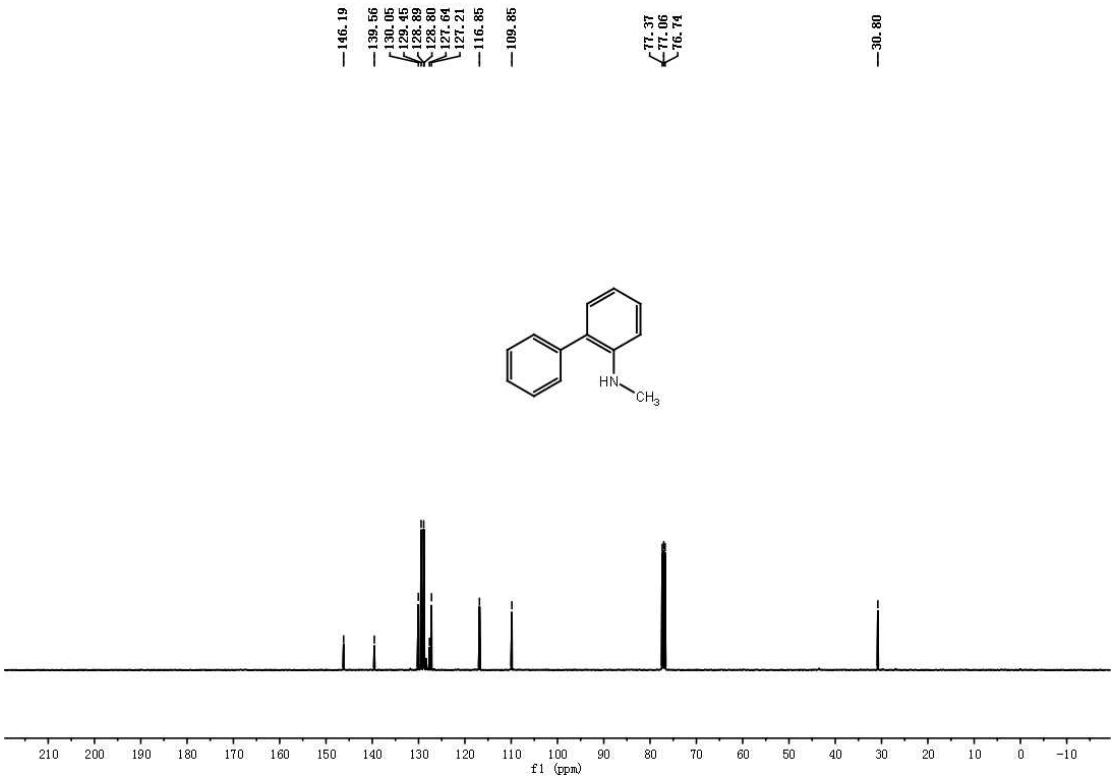
7.42
7.41
7.40
7.33
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.10
7.09
7.08
7.07
6.79
6.79
6.77
6.77
6.70
6.68
3.96
2.78
0.00
HN
CH3
4.10
0.96
1.39
0.98
0.97
0.98
3.00
f1 (ppm)


146.19
139.56
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127.21
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109.85
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77.06
76.74
30.80
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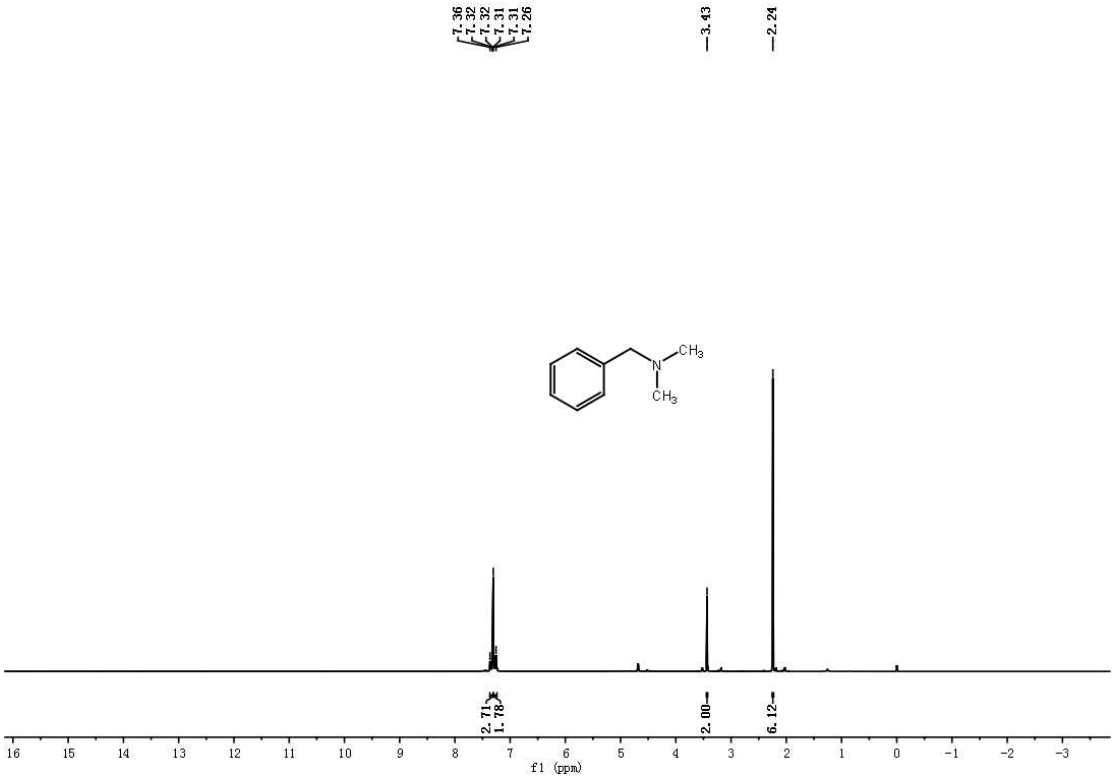
CH3
f1 (ppm)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7.32
7.31
7.31
7.26
3.43
2.24
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CH3
CH3
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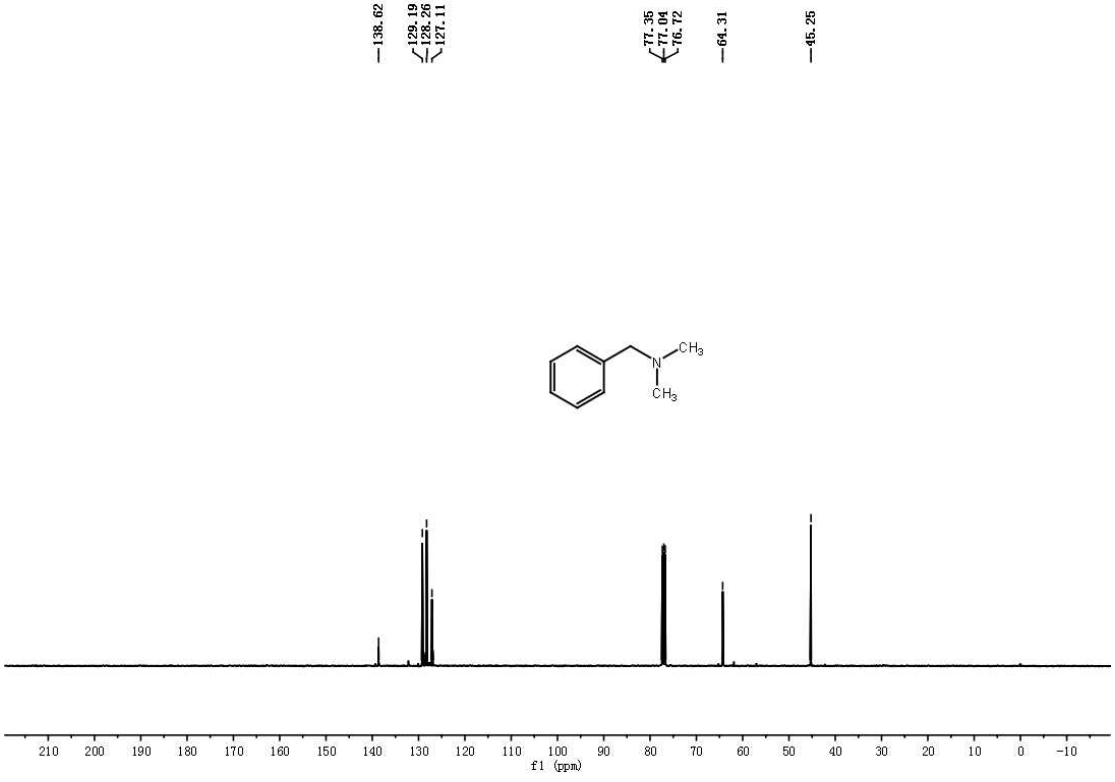
1.78
2.00
6.12
f1 (ppm)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64.31
45.25
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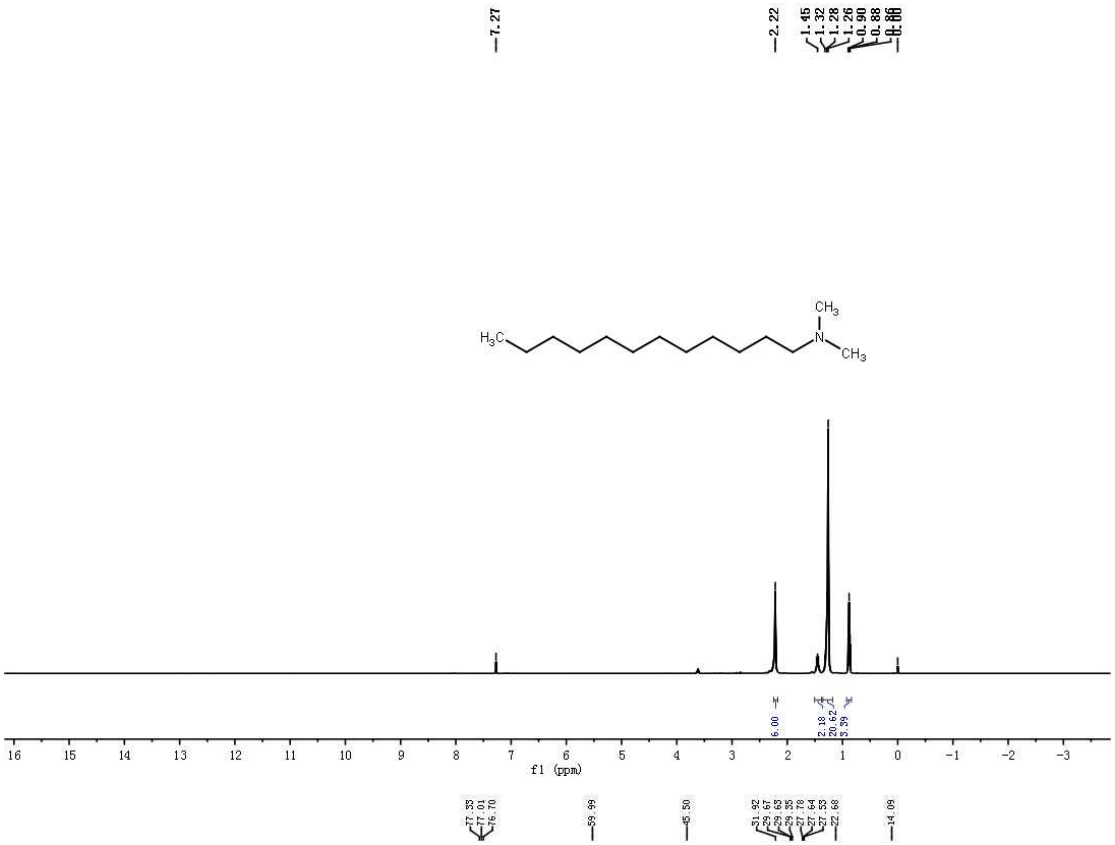
CH3
CH3
f1 (ppm)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1.32
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0.88
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N
CH3
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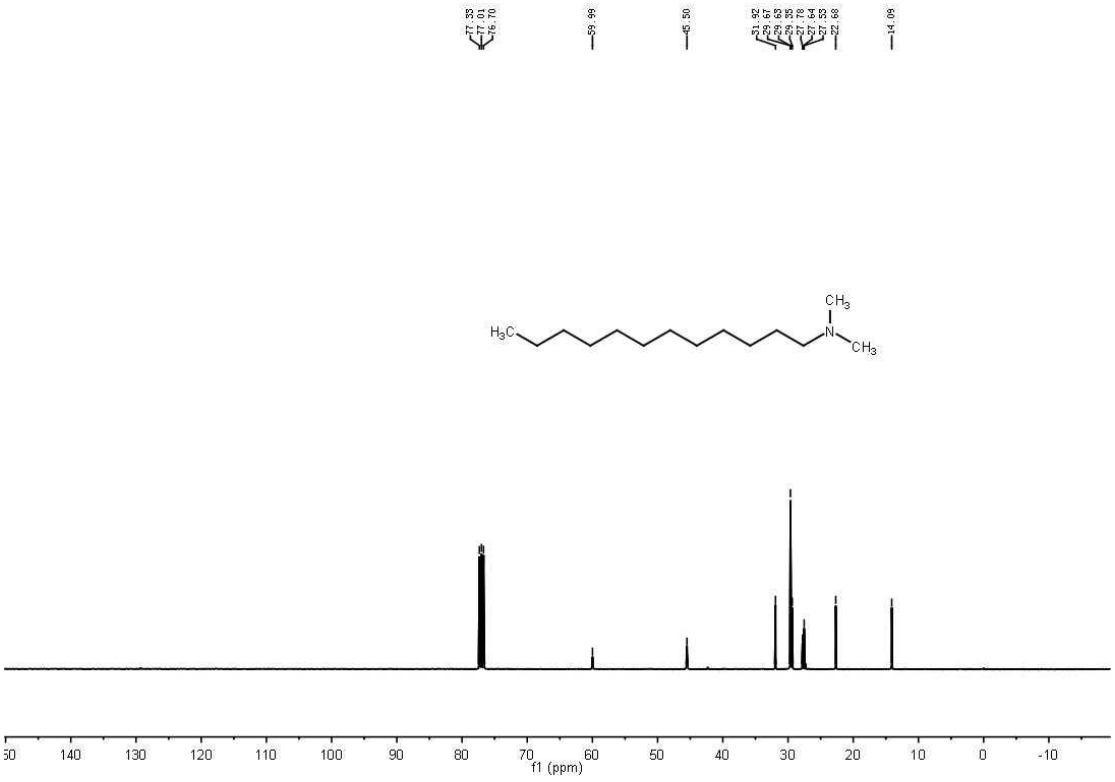
2.18
20.62
3.39
f1 (ppm)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29.19
27.64
27.53
22.68
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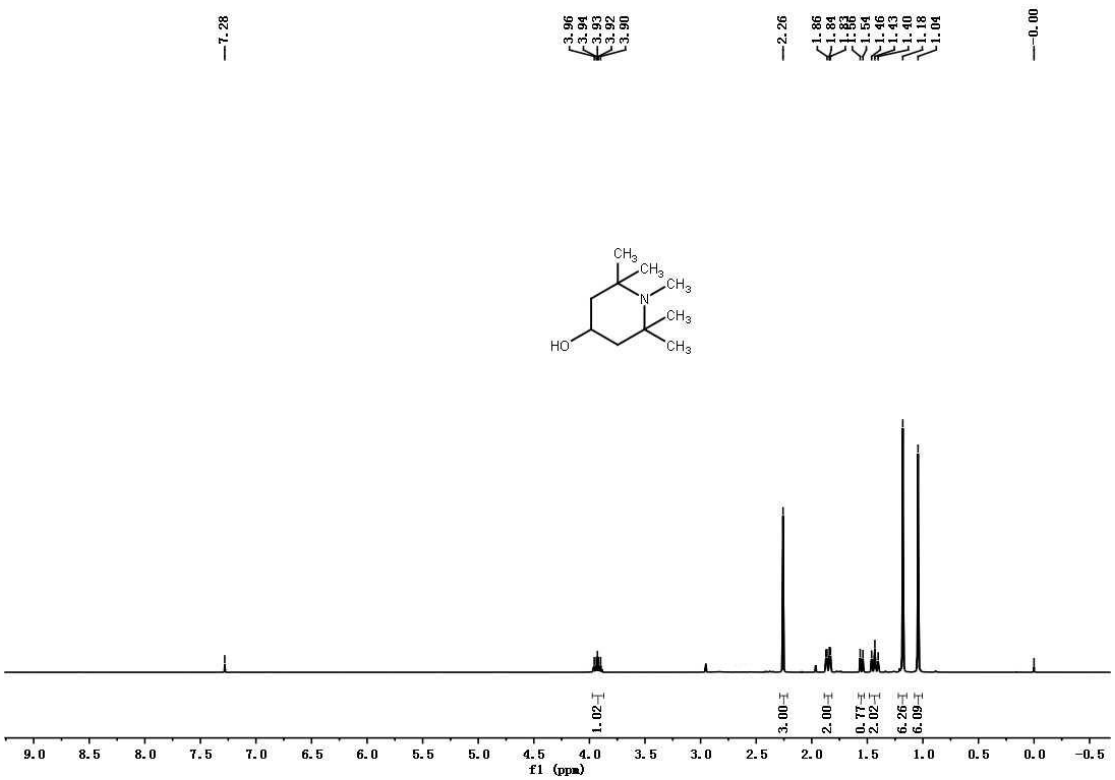
H3C
N
CH3
f1 (ppm)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3.93
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3.90
2.26
1.86
1.84
1.83
1.54
1.46
1.43
1.40
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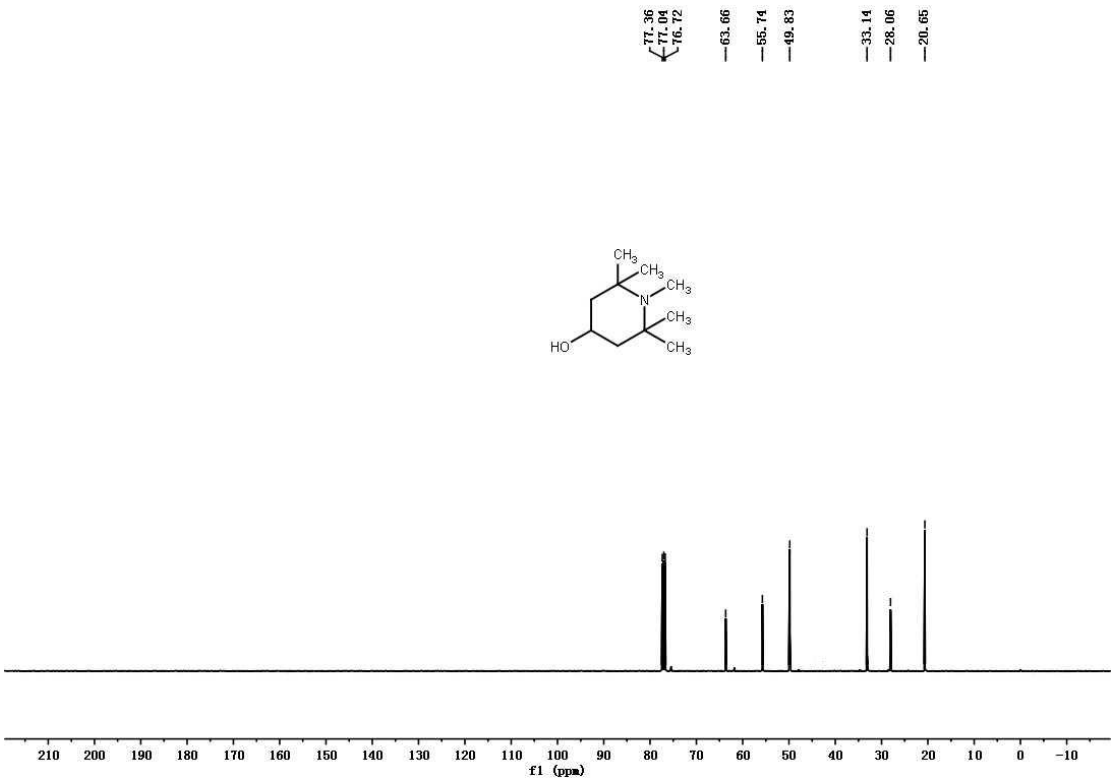
0.00
HO
1.02
3.00
2.00
0.77
2.02
6.26
6.09
f1 (ppm)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76.72
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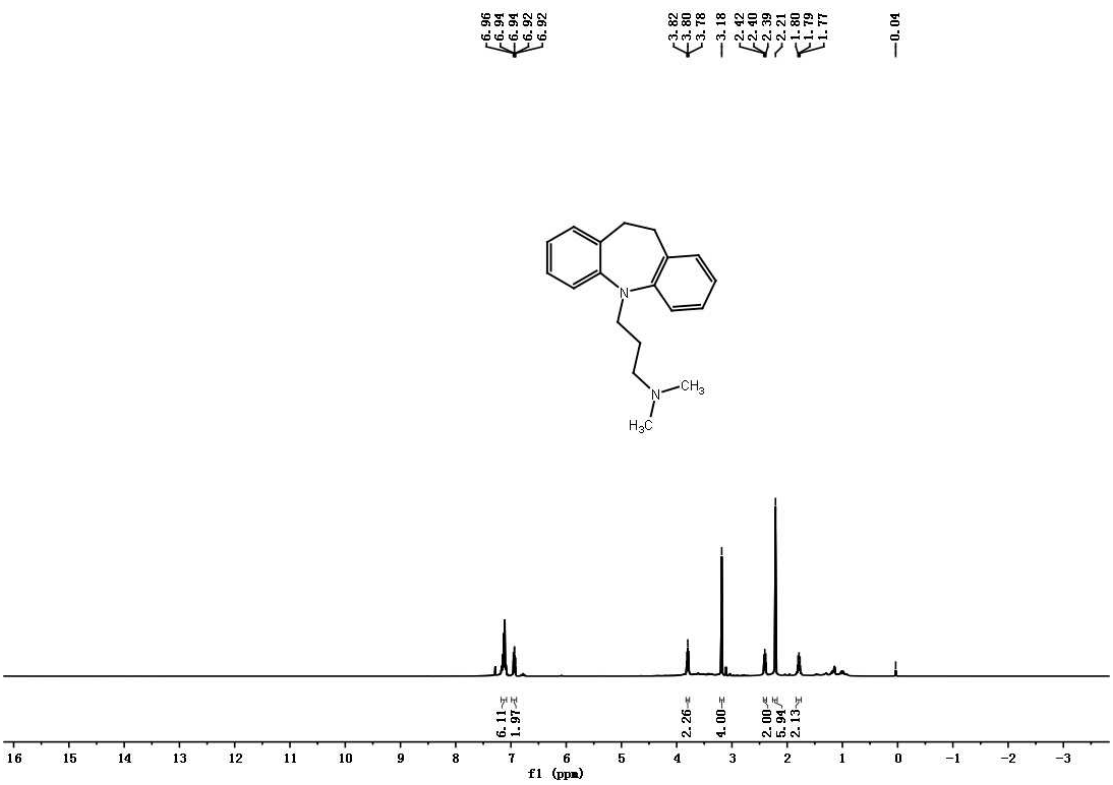
55.74
49.83
33.14
28.06
20.65
HO
f1 (ppm)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6.94
6.92
6.92
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3.80
3.78
3.18
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2.40
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2.21
1.80
1.79
1.77
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H3C
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1.97
2.26
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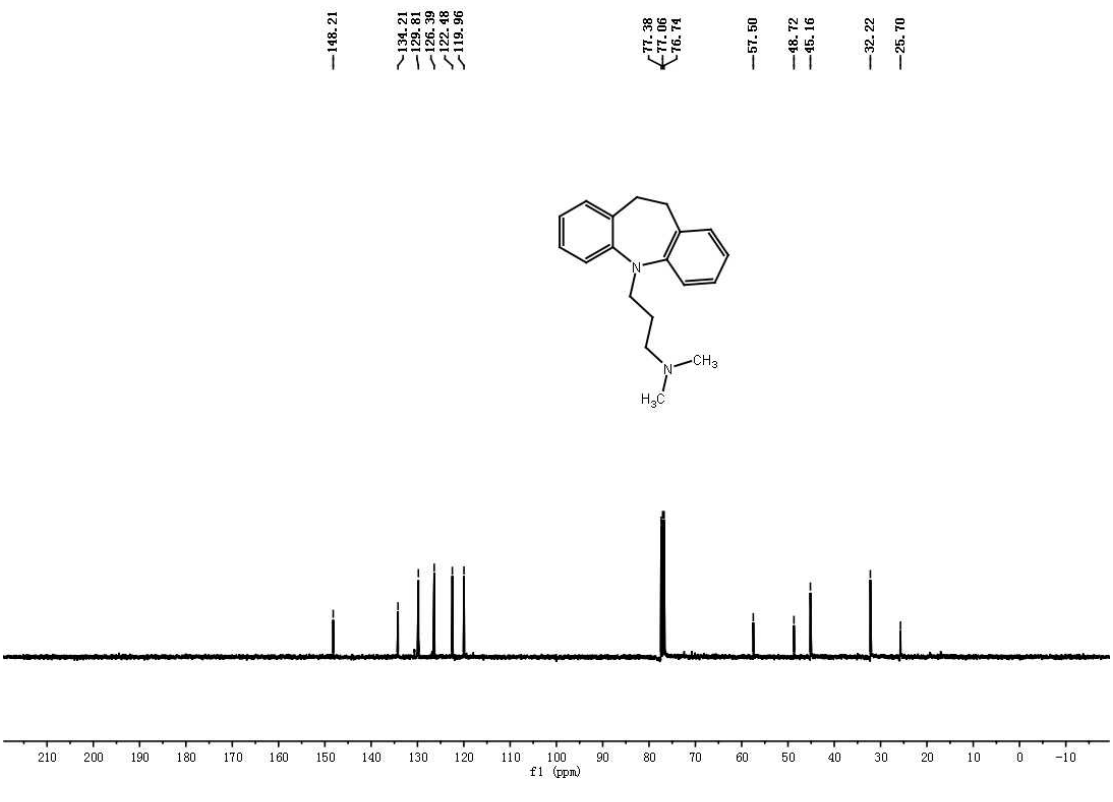
2.00
5.94
2.13
f1 (ppm)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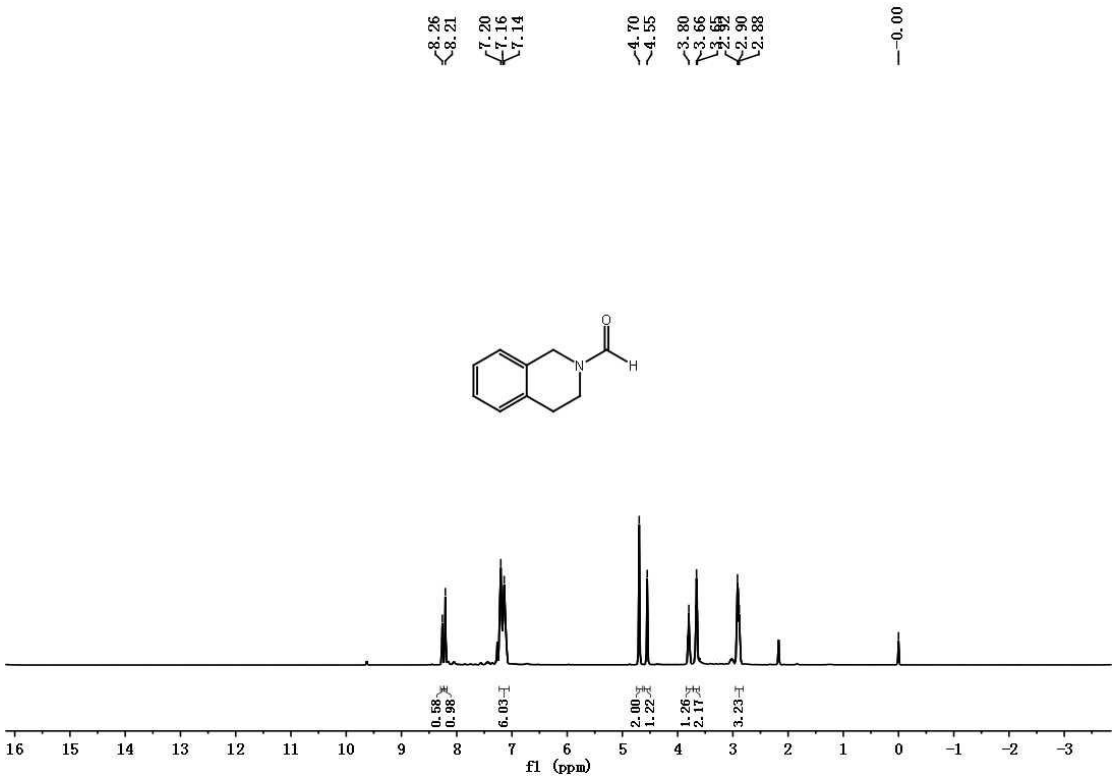
48.72
45.16
32.22
25.70
N
N
CH3
H3C
f1 (ppm)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7.14
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4.55
3.80
3.66
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2.88
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H
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0.98
6.03
2.00
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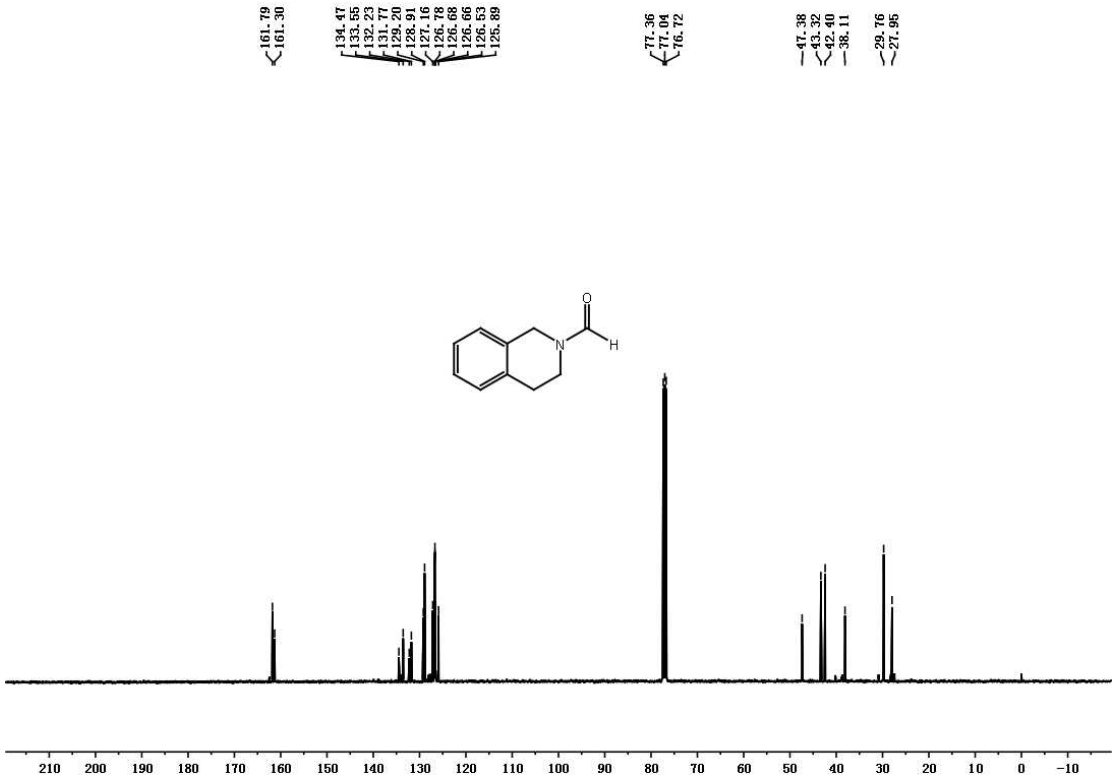
1.26
2.17
3.23
f1 (ppm)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38.11
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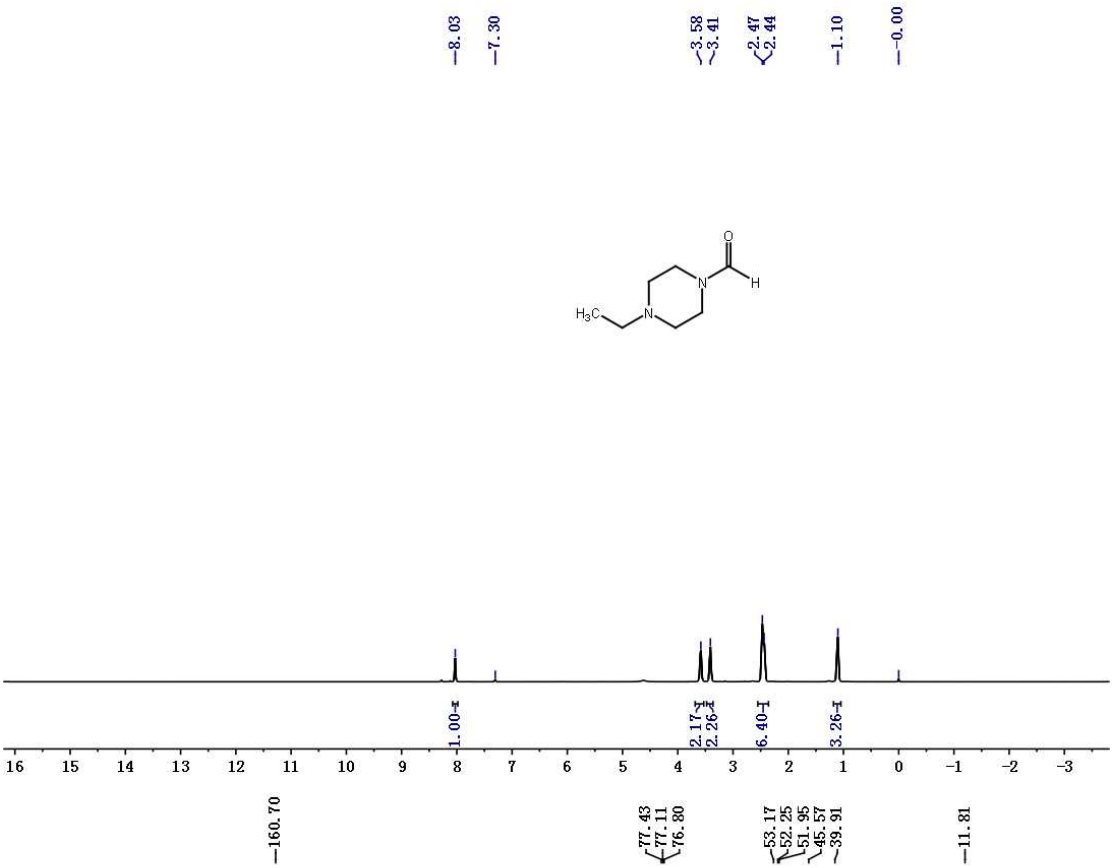
27.95
O
N
H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H
N
N
H3C
1.00
2.17
2.26
6.40
3.26
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
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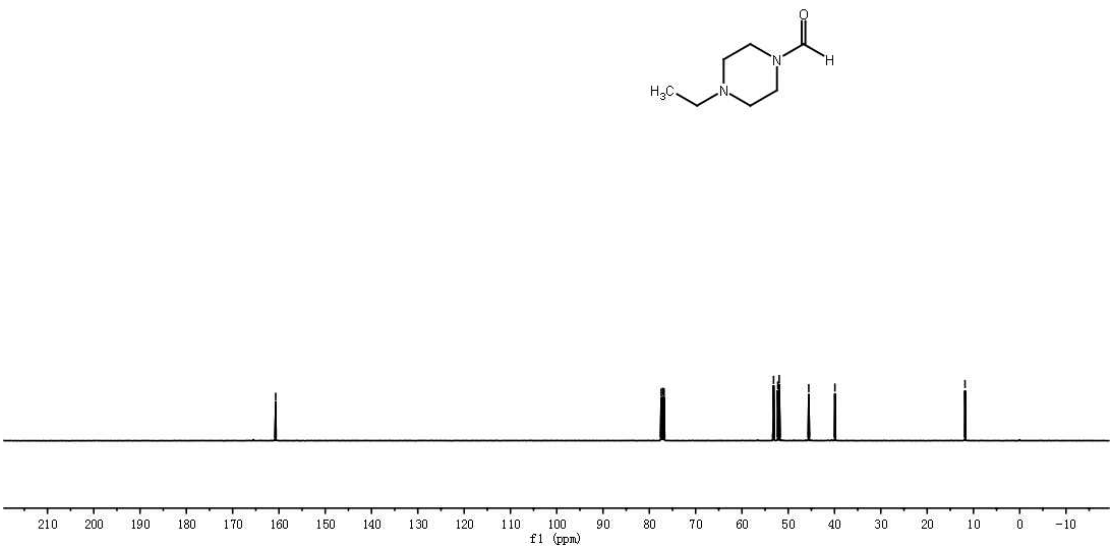
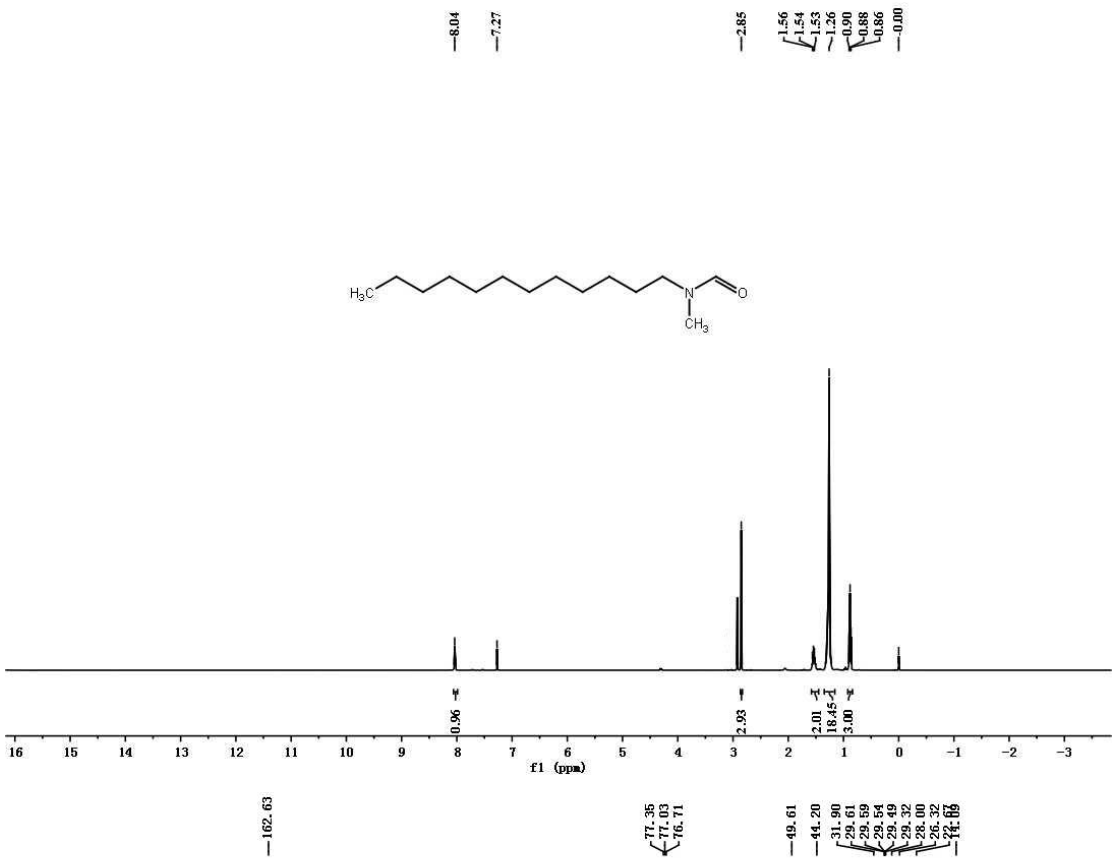
77.43
77.11
76.80
53.17
52.25
51.95
45.57
39.91
11.81


O
H
N
N
H3C
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)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H3C
N
O
CH3
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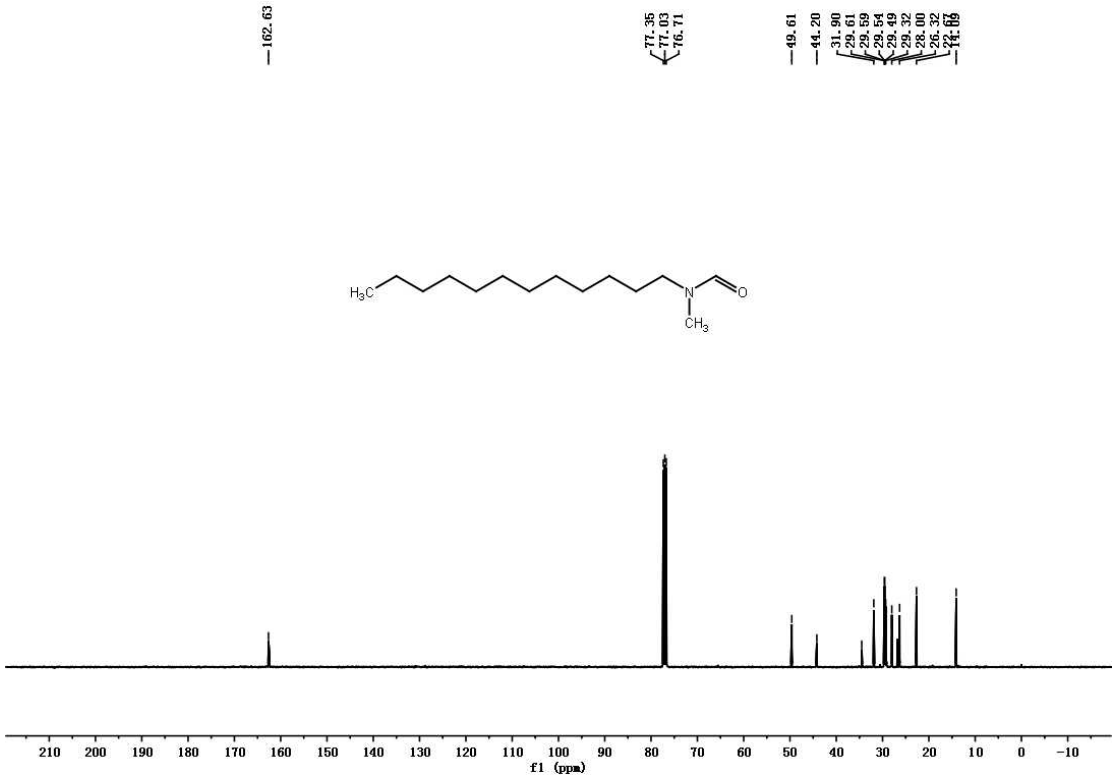
2.93
2.01
18.45
3.00
f1 (ppm)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76.71
49.61
44.20
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29.61
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29.54
29.49
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28.00
26.32
22.67
14.09
H3C
N
O
CH3
f1 (ppm)