Supporting Information For

Catalyst-free selective *N*-formylation and *N*-methylation of amines using CO_2 as a sustainable C1 source

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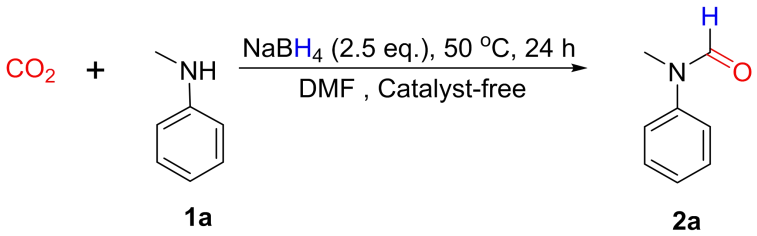
1. General information

All amines are analytically pure agents purchased from TCI Chemical and are used without further purification unless otherwise indicated. The deuterated solvents are purchased from CIL (Cambridge Isotope Laboratories). All the solvents used for reactions were distilled after drying over an appropriate drying agent. CO_2 (99.99 vt.%) and N_2 (99.999%) are purchased from Guiyang Shengjian Gas Center, Guizhou University. The products were determined using Shimadzu GC2014 gas chromatograph and Shimadzu GC-MS-QP2010. The NMR spectra were recorded on a Bruker AV 400 spectrometer at 400 MHz (^{1}H NMR) and 101 MHz (^{13}C NMR). The NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (^{1}H and ^{13}C) and $BF_3{\cdot}Et_2O$ (^{11}B NMR).

2. Typical procedure for selective *N*-formylation of amine



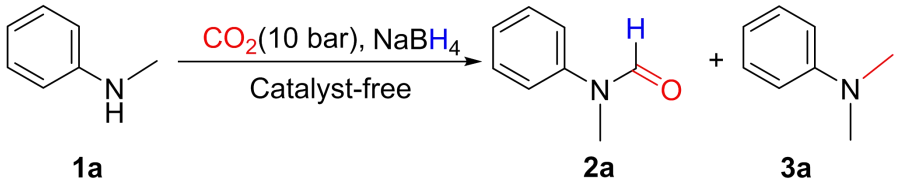
1a **2a**

A stainless autoclave (25 mL teflon inner tube) was charged with 2.5 mmol of $NaBH_4$, 1 mmol of substrate **1a**, and solvent of DMF. The reactor was pressurized with 10 bar of CO_2 gas at ambient temperature. The reactor was heated and stirred at 50 °C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of **2a** was determined by GC/MS using dodecane as the internal standard. The isolated **2a** was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. Particularly, all formylated products were identified through comparisons with the corresponding ^{1}H NMR, ^{13}C NMR data reported in the literatures.[1-5]

The solvent effect on selective *N*-formylation and *N*-methylation of amine is shown in Table S1. We found that both water and methanol (CH_3OH) are ineffective (Entry 1 and 2). Diglyme, acetonitrile (CH_3CN), and tetrahydrofuran (THF) afforded moderate yields of **2a** (Entry 3-5), but

they are not optimal due to the inferior selectivity. To our delight, both DMSO and DMF are effective for the selective *N*-formylation of amines (Entry 7 and 8).

Table S1. The solvent effect on selective *N*-formylation and *N*-methylation of amine.

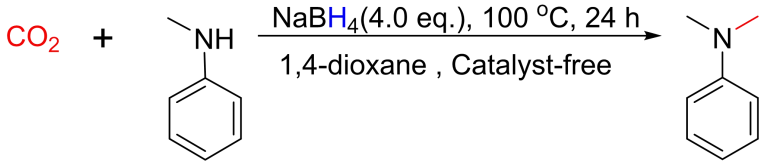


1a **2a** **3a**

Entry	Solvent	Yield of **2a** (%)[a]	Yield of **3a** (%)[a]
1	H_2O	0	0
2	CH_3OH	0	0
3	Diglyme	81	13
4	CH_3CN	74	26
5	THF	75	18
6	1,4-dioxane	47	33
7	DMSO	90	10
8	DMF	94	6

Reaction conditions: amine **1a** (1.0 mmol), solvent (3 mL), CO_2 (10 bar), $NaBH_4$ (2.5 mmol), 50 °C, 24 h. [a]The yields were determined by GC/MS using dodecane as the internal standard.

3. Typical procedure for selective *N*-methylation of amine

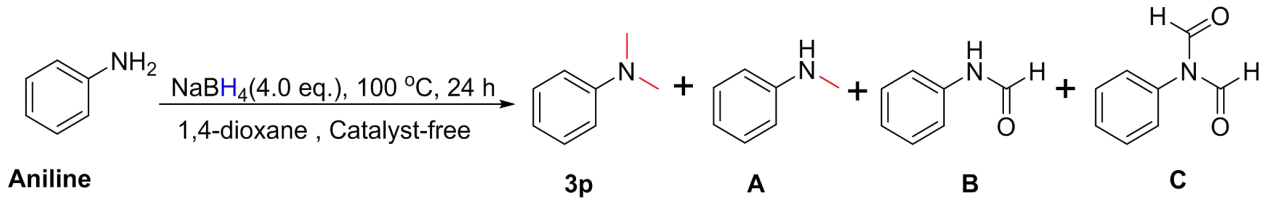


1a **3a**

A stainless autoclave (25 mL teflon inner tube) was charged with 4 mmol of $NaBH_4$, 1 mmol of substrate **1a**, and solvent of 1,4-dioxane. The reactor was pressurized with 10 bar of CO_2 gas at ambient temperature. The reactor was heated and stirred at 100 °C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of **3a** was determined by GC/MS using dodecane as the internal standard. The isolated **3a** was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent. All methylated products were identified through comparisons with the corresponding ^1H NMR, ^{13}C NMR data reported in the literatures.[1-5]

4. Selective *N*-methylation of aniline

For the selective N-methylation of aniline, we performed the kinetic control experiments and analyzed the yields of various potential products (**3q**, **A**, **B**, and **C**) in the reaction system. The mole fraction of aniline, **3q** and **A** in reaction system was determined at the desired time by GC using dodecane as the internal standard. As shown in illustration, most of the aniline did not react, and the reaction produces methylated products of **3q** as major and **A** as minor. No formylation products (**B** or **C**) was formed. The yield of **3q** increases over time in the first 48 h, followed by reaching equilibrium after 48 h.



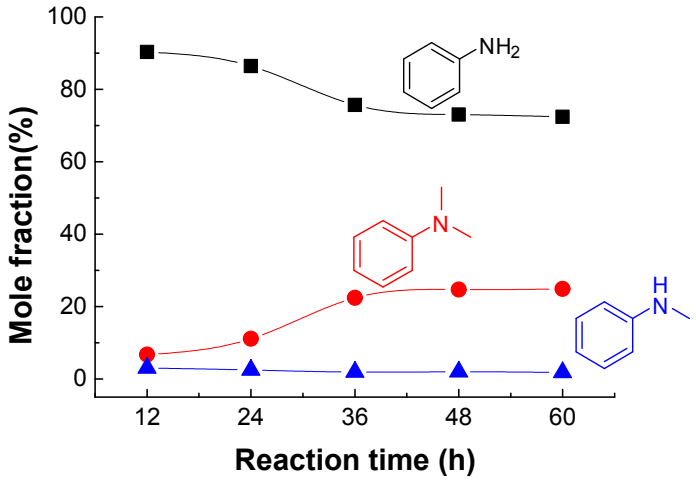
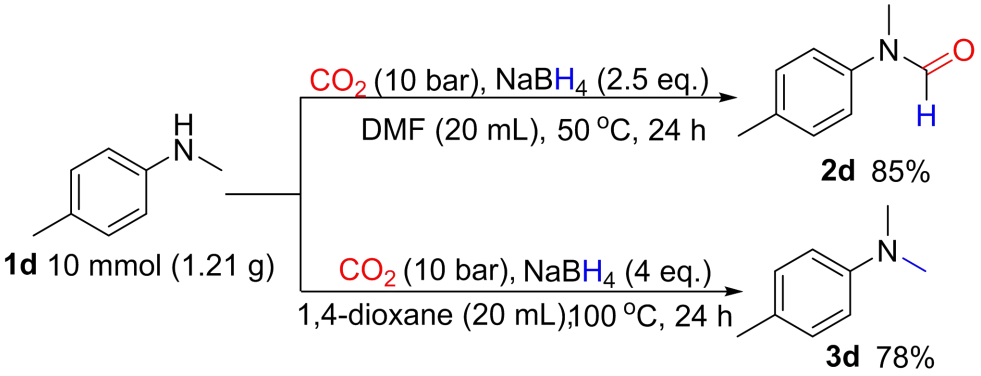


Illustration: The change of mole fraction of aniline, **3q** and **A** in reaction system over reaction time.

5. Gram scale reaction

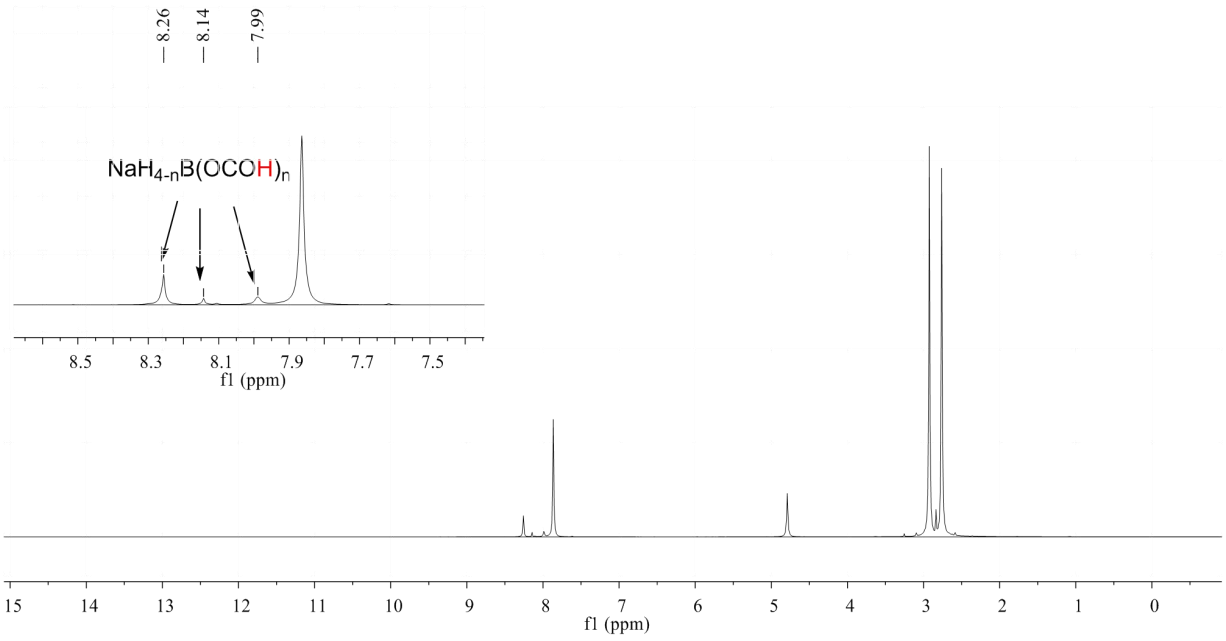
A stainless autoclave reactor coupled with a magnetic stirrer was charged with **1d** (10 mmol, 1.21 g), quantitative $NaBH_4$, and solvent (20 mL). The resulting mixture was stirred for 24 h at stated temperature under 10 bar of CO_2. After the reaction, excess CO_2 was vented discreetly. The reaction mixture was quenched by water and extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The

product of **2d** and **3d** was obtained respectively in yield of 85% and 78% after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.



6. Reaction of $NaBH_4$ and CO_2 in DMF

A stainless autoclave reactor coupled with a magnetic stirrer was charged with $NaBH_4$ (3 mmol) and DMF (3 mL). The reactor was pressurized with 10 bar of CO_2 at ambient temperature, and then was heated and stirred at 50 °C for 24 h. After the reaction, excess CO_2 was vented discreetly, about 0.1 mL of mixture was dissolved in 0.4 mL of D_2O for NMR experiment analysis. The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra are measured at 298.15 K and shown in Fig. S1.



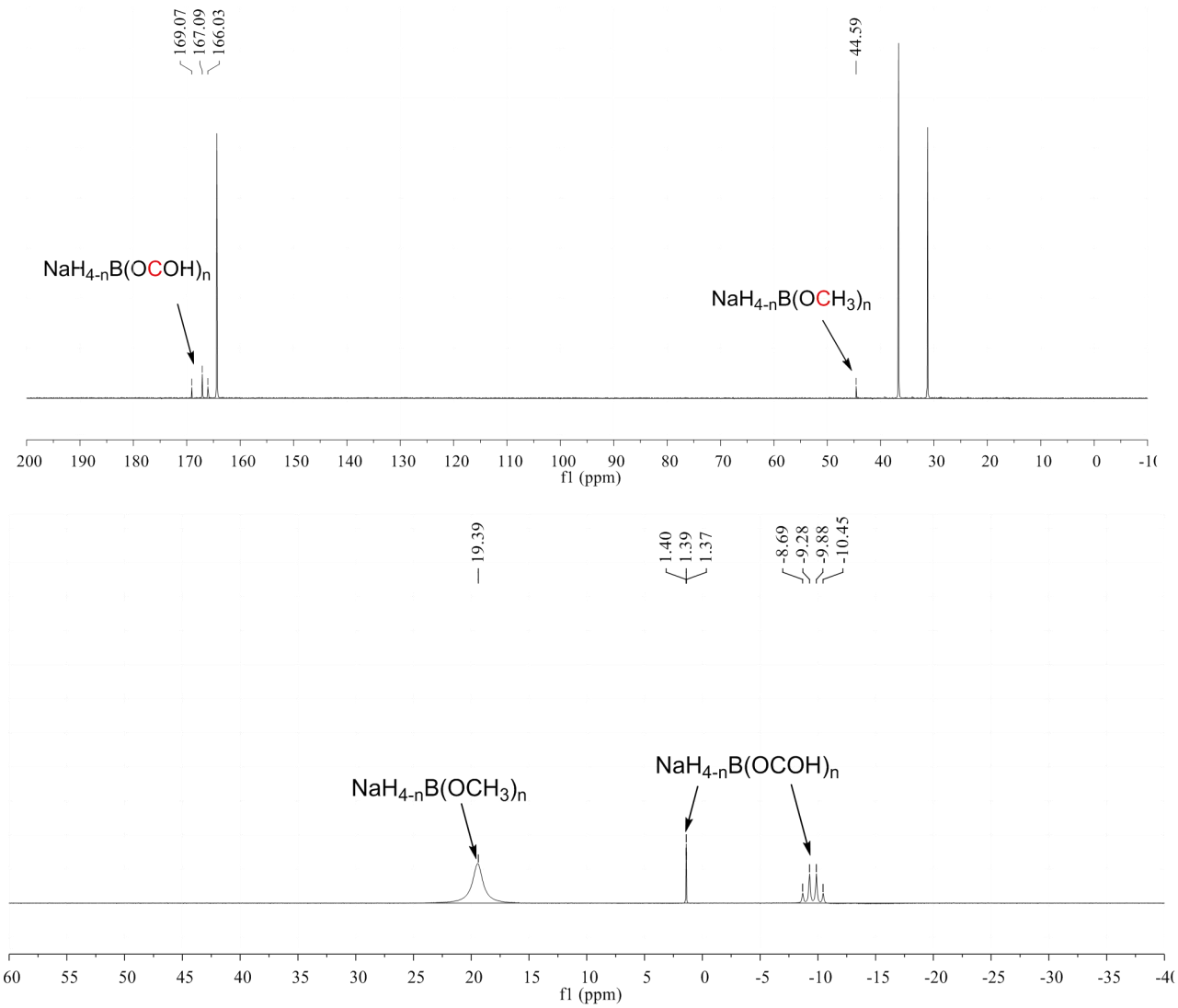


Fig. S1 The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF.

In addition, the effects of the amount of the $NaBH_4$, solvent, reaction temperature and time were examined, respectively. The specific experimental conditions and products **Int.1** and **Int. 2** are shown in Table S2.

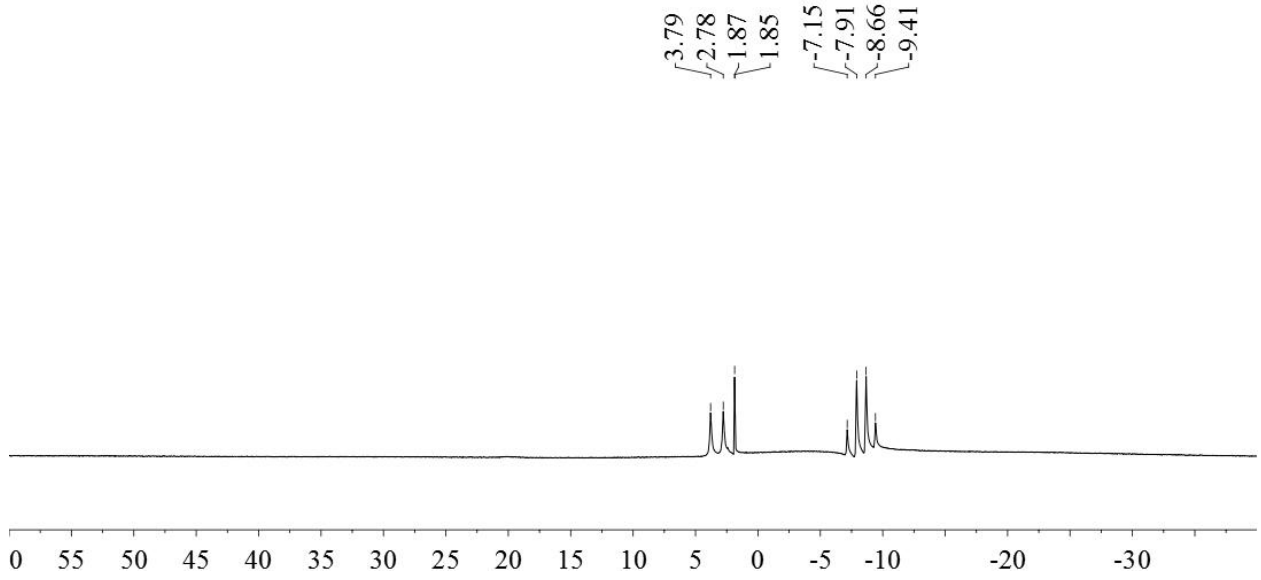
$$CO_2 + NaBH_4 \xrightarrow[T,\ t]{\text{Solvent (3 mL)}} NaH_{4-n}B(OCOH)_n + NaH_{4-n}B(OCH_3)_n$$

Int. 1 **Int. 2**

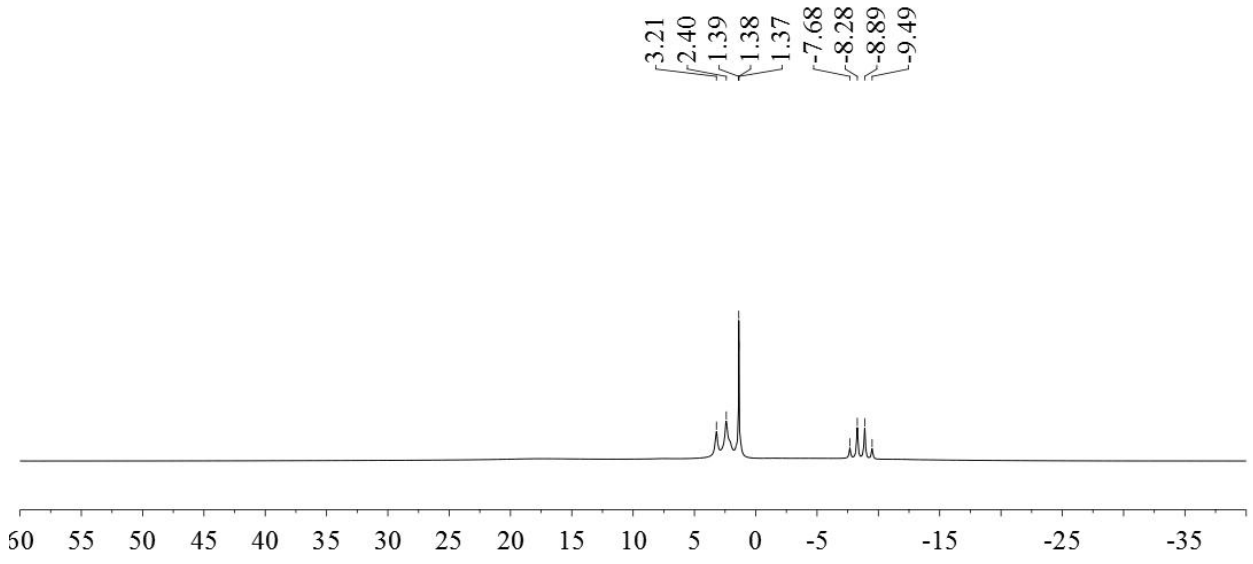
Table S2 Control experiment on formation of I**nt. 1** and **Int.** under different conditions.

Entry	$NaBH_4$ (mmol)	Solvent (mL)	*T* (°C)	*t* (h)	**Int.1**[a]	**Int.2**[a]
1	1.0	DMF (3 mL)	50	24	major	trace
2	2.0	DMF (3 mL)	50	5	major	trace
3	2.0	DMF (3 mL)	50	24	moiety	moiety
4	2.0	DMF (3 mL)	100	24	moiety	moiety
5	2.5	1,4-dioxane (3 mL)	100	24	trace	major
6	4.0	1,4-dioxane (3 mL)	100	24	trace	major
7	4.0	1,4-dioxane (3 mL)	50	24	minor	major

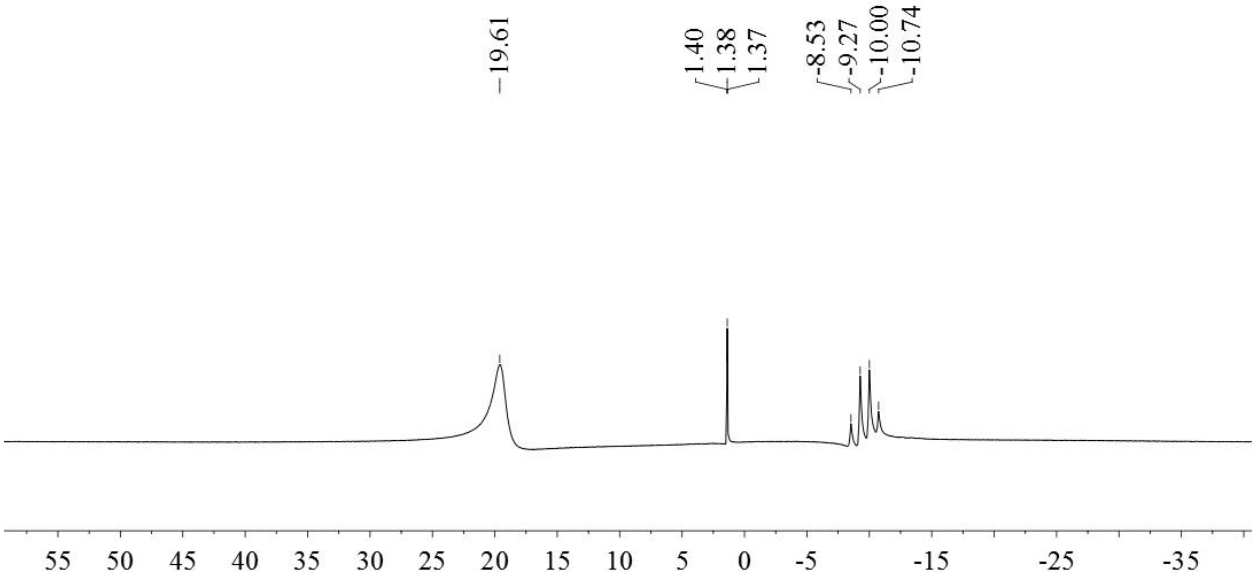
[a]Determined by the ^{11}B NMR.



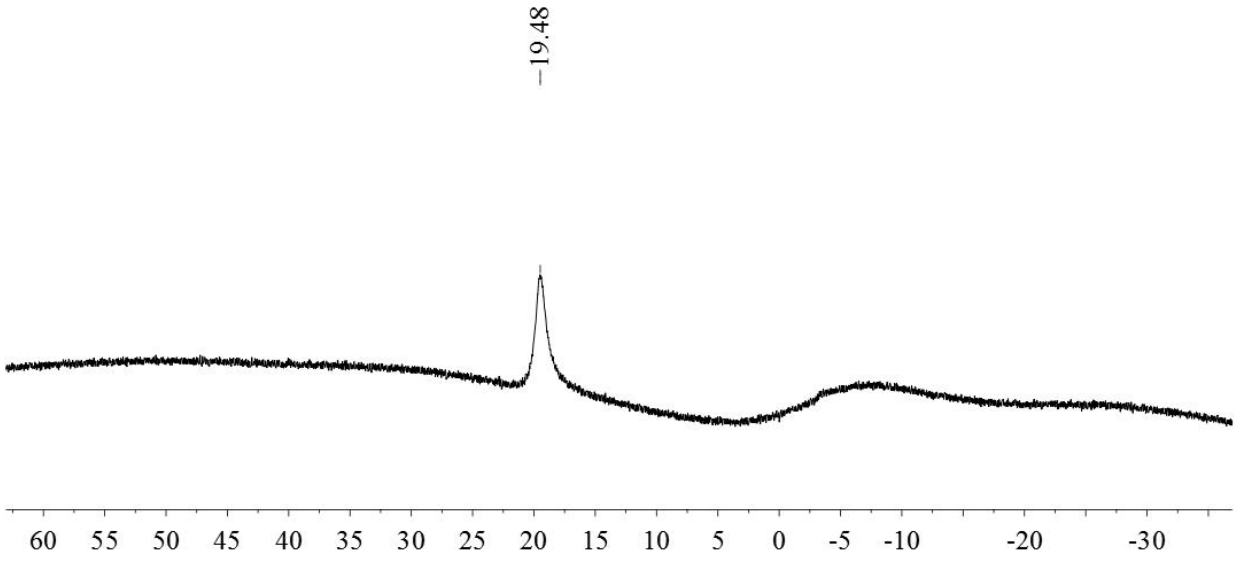
The ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF (The experimental conditions are shown in Table S2, Entry 1).



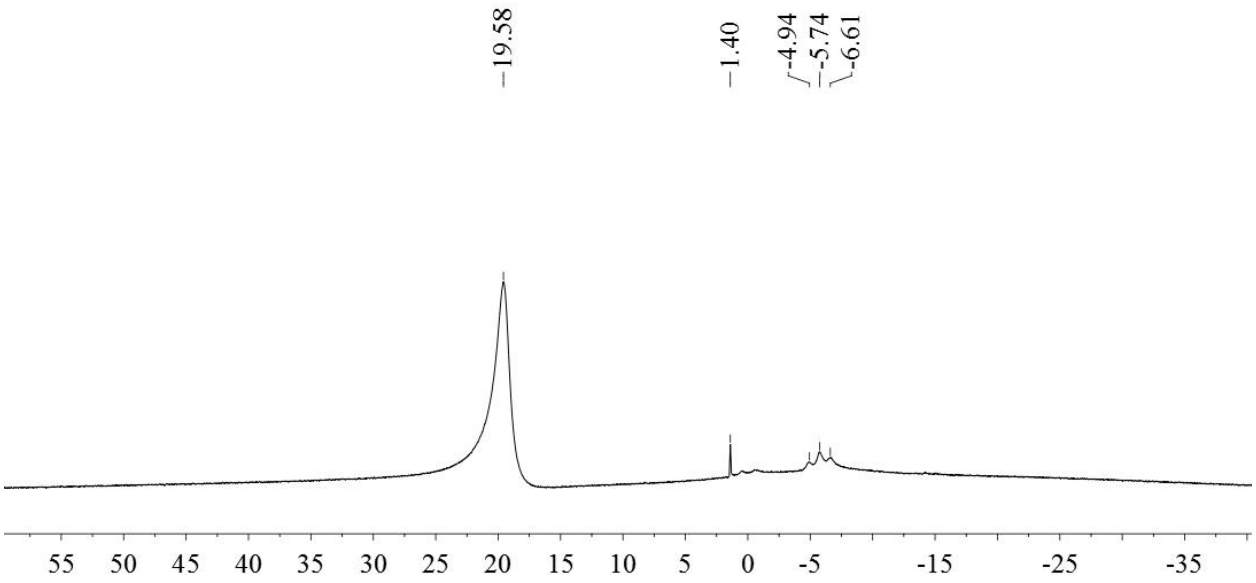
The ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF (The experimental conditions are shown in Table S2, Entry 2).



The ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF (The experimental conditions are shown in Table S2, Entry 4).

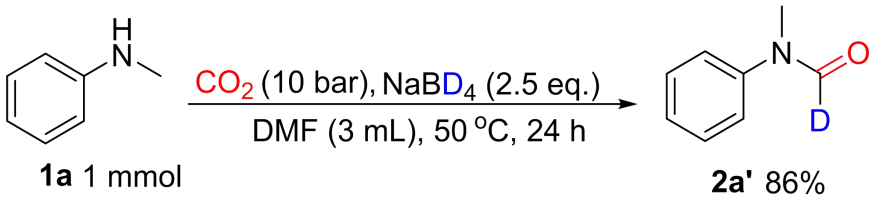


The ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF (The experimental conditions are shown in Table S2, Entry 5).



The ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in DMF (The experimental conditions are shown in Table S2, Entry 7).

7. Isotope labeling experiment with $NaBD_4$



A stainless autoclave (25 mL teflon inner tube) was charged with 2.5 mmol of $NaBD_4$, 1 mmol of substrate **1a**, and solvent of DMF (3 mL). The reactor was pressurized with 10 bar of CO_2 gas at ambient temperature. The reactor was heated and stirred at 50 °C for 24 h. After the reaction, the reactor was cooled to room temperature and the pressure was vented laxly. The mixture was quenched with water and extracted with ethyl acetate. The yield of **2a'** was determined by GC/MS using dodecane as the internal standard. The isolated **2a'** was obtained after purification by flash chromatography on silica gel using petroleum ether/ethyl acetate as the eluent, and the structure confirmed by NMR (Fig. S2).

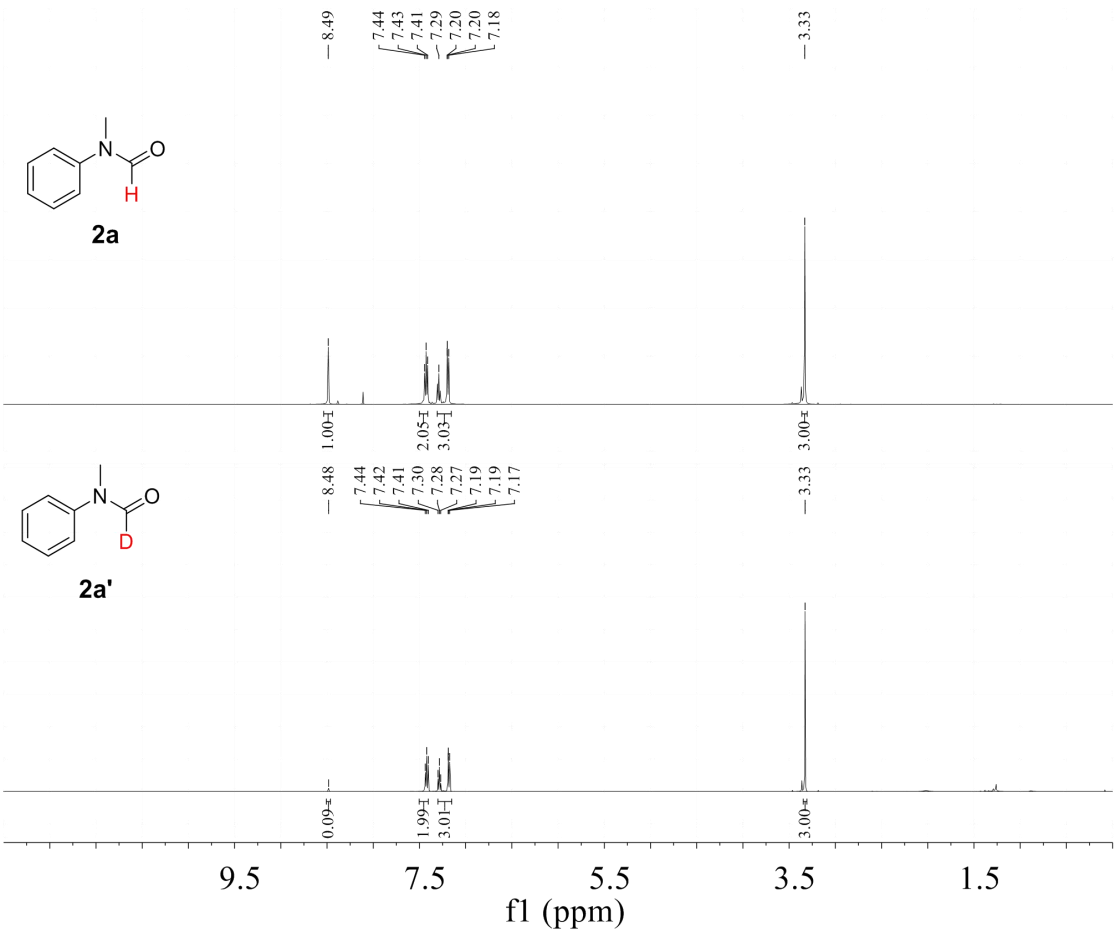


Fig. S2 The ^{1}H NMR spectra of **2a** and **2a'**.

8. Reaction of $NaBH_4$ and CO_2 in 1,4-dioxane

Analogously, a stainless autoclave reactor coupled with a magnetic stirrer was charged with $NaBH_4$ (3 mmol) and 1,4-dioxane (3 mL). The reactor was pressurized with 10 bar of CO_2 at ambient temperature, and then was heated and stirred at 100^{o}C for 24 h. After the reaction, excess CO_2 was vented discreetly, about 0.1 mL of mixture was dissolved in 0.4 mL of D_2O for NMR experiment analysis. The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra are measured at 298.15 K and shown in Fig. S3.

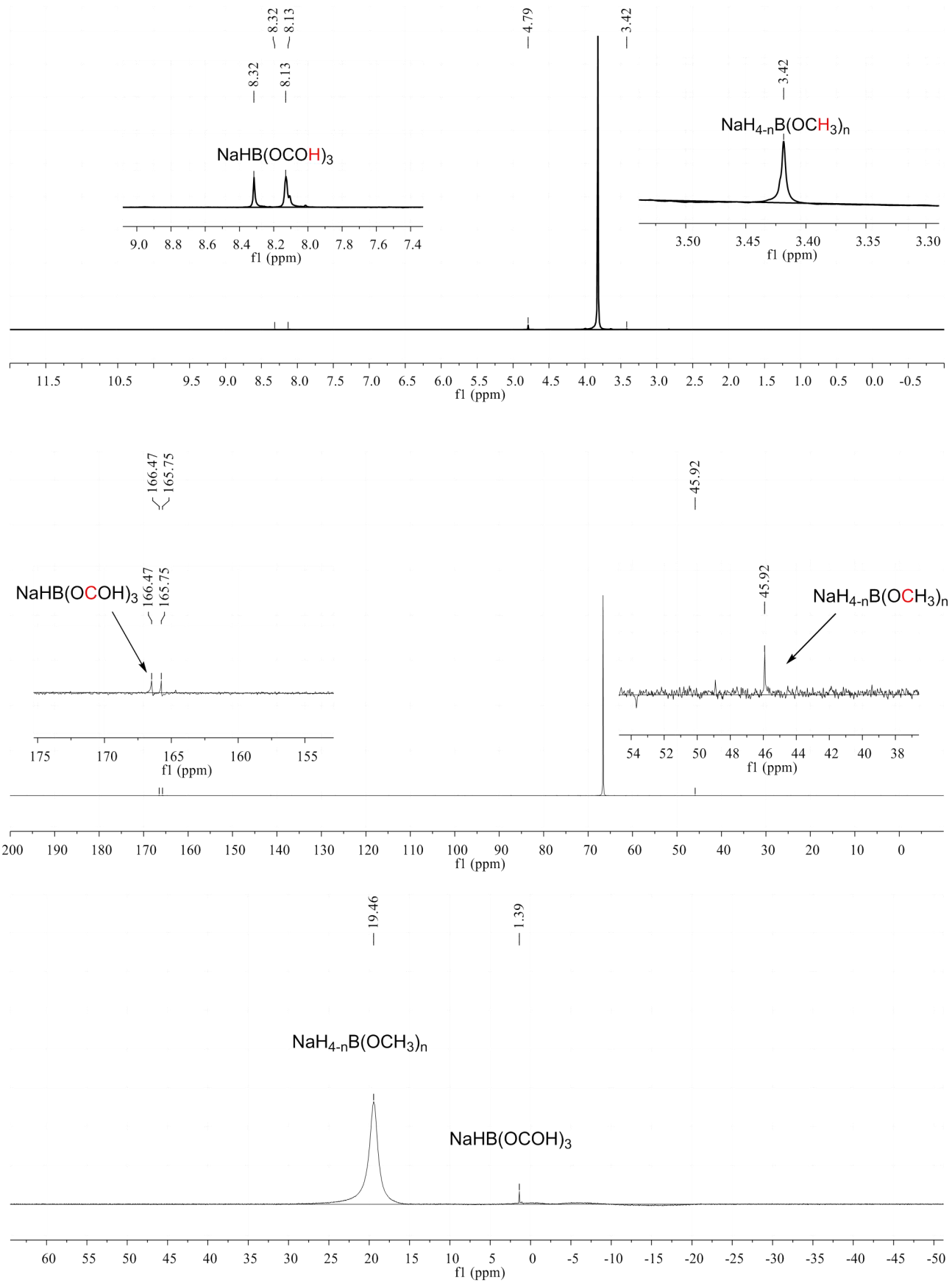
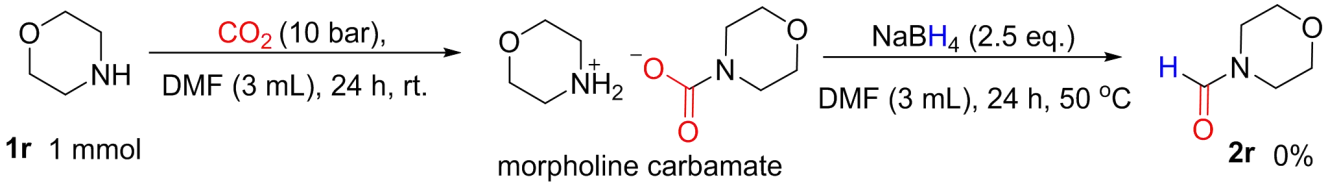


Fig. S3 The ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra for the reaction of $NaBH_4$ and CO_2 in 1,4-dioxane.

9. Details on stepwise reaction of 1r, CO_2 and $NaBH_4$

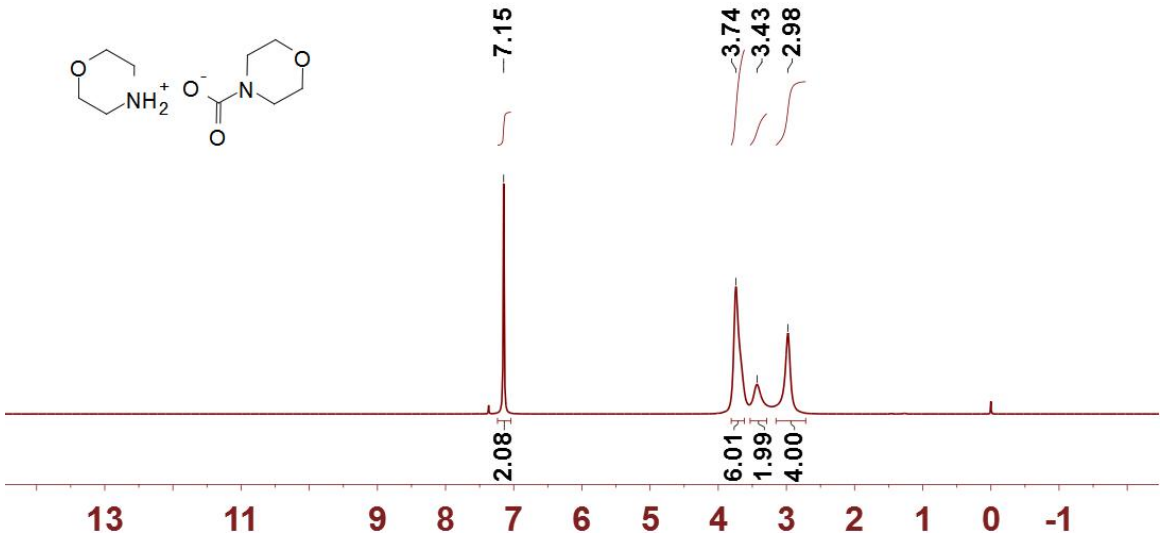
A stainless autoclave reactor coupled with a magnetic stirrer was charged with **1r** (1 mmol), DMF (3 mL), and 10 bar of CO_2. The resulting mixture was stirred for 24 h at room temperature. After the reaction, residual CO_2 was completely removed through the pump at low temperature (ice-salt baths), and 2.5 eq. $NaBH_4$ (2.5 mmol) and 1 bar of N_2 were introduced into the reactor. Then, it was heated and stirred at 50°C for another 24 h. After the reaction, the conversion and yield of the **2r** was resolved by GC/MS analysis using dodecane as the internal standard.

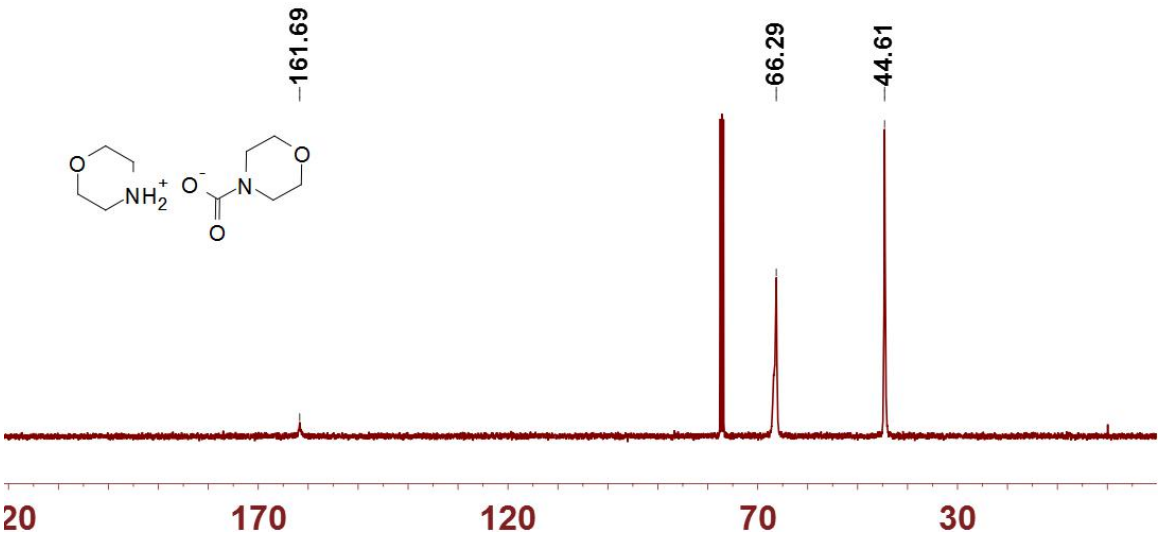


1r 1 mmol

morpholine carbamate

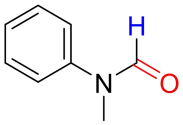
2r 0%



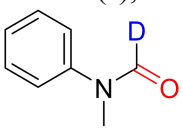


The ^{1}H NMR and ^{13}C NMR of morpholine carbamate.

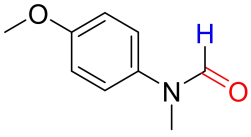
10. The NMR information of formamides and methylamines



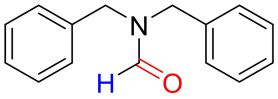
2a: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.41 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 – 7.07 (m, 2H), 3.25 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.46 (s), 142.04 (s), 129.59 (s), 126.41 (s), 122.28 (s), 32.02 (s) ppm.



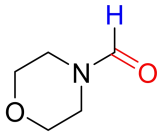
2a': ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 (t, *J* = 7.9 Hz, 2H), 7.28 (s, 1H), 7.22 – 7.15 (m, 2H), 3.33 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 162.37 (s), 142.15 (s), 129.63 (s), 126.40 (s), 122.32 (s), 32.00 (s) ppm.



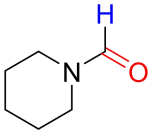
2e: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (s, 1H), 6.94 – 6.87 (m, 2H), 6.77 – 6.69 (m, 2H), 3.60 (s, 3H), 3.06 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.24 (s), 158.05 (s), 135.02 (s), 124.29 (s), 114.57 (s), 55.29 (s), 32.32 (s) ppm.



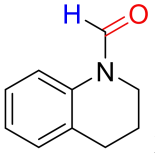
2n: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 (s, 1H), 7.44 – 7.28 (m, 6H), 7.26 – 7.16 (m, 4H), 4.43 (s, 2H), 4.28 (s, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.90 (s), 136.04 (s), 135.66 (s), 77.50 (s), 77.18 (s), 76.86 (s), 50.28 (s), 44.66 (s) ppm.



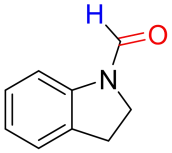
2q: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (s, 1H), 3.52 (ddd, *J* = 16.4, 7.2, 3.8 Hz, 4H), 3.43 – 3.36 (m, 2H), 3.26 (dd, *J* = 6.4, 3.3 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.75 (s), 67.09 (s), 66.26 (s), 45.64 (s), 40.42 (s) ppm.



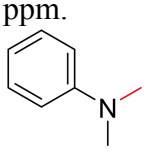
2r: ^{1}H NMR (400 MHz, $CDCl_3$) 7.83 (s, 1H), 3.35 – 3.27 (m, 2H), 3.20 – 3.12 (m, 2H), 1.60 – 1.45 (m, 2H), 1.45 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 160.75 (s), 46.72 (s), 40.47 (s), 26.43 (s), 24.95 (s), 24.52 (s) ppm.



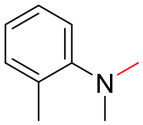
2s: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.77 (s, 1H), 7.22 – 7.07 (m, 4H), 3.83 – 3.75 (m, 2H), 2.81 (dd, *J* = 18.8, 12.4 Hz, 2H), 2.01 – 1.87 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 161.06 (s), 137.19 (s), 129.60 (s), 128.85 (s), 127.06 (s), 124.50 (s), 116.97 (s), 40.24 (s), 27.08 (s), 22.22 (s) ppm.



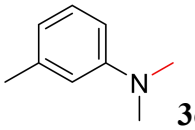
2t: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.94 (s, 1H), 8.53 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.11 (m, 3H), 7.12 – 6.99 (m, 1H), 4.20 – 3.96 (m, 2H), 3.24 – 3.06 (m, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 159.35 (s), 157.57 (s), 141.06 (s), 131.93 (s), 127.56 (d, *J* = 2.4 Hz), 126.06 (s), 124.87 (s), 124.56 (s), 124.25 (s), 116.60 (s), 109.40 (s), 46.95 (s), 44.64 (s), 27.74 (s), 27.17 (s) ppm.



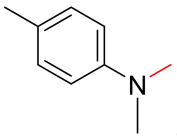
3a (colourless liquid, 80% yield, 97 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 8.9, 7.2 Hz, 2H), 6.74 (dd, *J* = 4.9, 3.7 Hz, 3H), 2.94 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.58 (s), 129.00 (s), 116.54 (s), 112.57 (s), 40.56 (s).



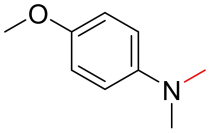
3b (colourless liquid, 85% yield, 115 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 – 7.22 (m, 2H), 7.20 – 7.02 (m, 2H), 2.82 (s, 6H), 2.46 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.80 (s), 132.19 (s), 131.25 (s), 126.53 (s), 122.67 (s), 118.44 (s), 44.32 (s), 18.47 (s) ppm.



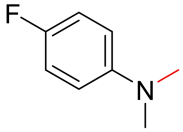
3c (colourless liquid, 82% yield, 110 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 2.0 Hz, 1H), 6.70 (dd, *J* = 4.7, 3.5 Hz, 3H), 3.06 (s, 6H), 2.46 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 150.87 (s), 138.79 (s), 129.05 (s), 117.78 (s), 113.59 (s), 110.07 (s), 40.79 (s), 22.02 (s) ppm.



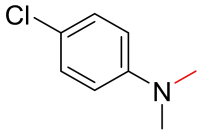
3d (colourless liquid, 93% yield, 125 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.95 (dt, *J* = 4.9, 1.4 Hz, 2H), 6.70 – 6.52 (m, 2H), 2.78 (s, 6H), 2.16 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.95 (s), 129.72 (s), 126.21 (s), 113.35 (s), 41.17 (s), 20.39 (s) ppm.



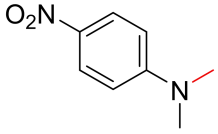
3e (white solid, 78% yield, 118 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 – 6.65 (m, 4H), 3.68 (s, 3H), 2.79 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.13 (s), 145.66 (s), 115.03 (s), 114.66 (s), 55.77 (s), 41.93 (s).



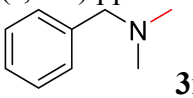
3f (light yellow solid, 64% yield, 89 mg): ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.76 (t, *J* = 8.8 Hz, 2H), 6.57 – 6.38 (m, 2H), 2.70 (s, 6H) ppm.^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.84 (s), 154.50 (s), 147.57 (s), 115.53 (s), 115.31 (s), 113.99 (d, *J* = 7.4 Hz), 41.35 (s) ppm.



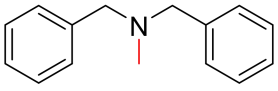
3g: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (d, *J* = 9.2 Hz, 2H), 6.69 (d, *J* = 9.1 Hz, 2H), 2.97 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 149.21 (s), 128.85 (s), 121.39 (s), 113.69 (s), 40.67 (s) ppm.



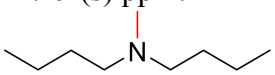
3h: ^{1}H NMR (400 MHz, DMSO) δ = 8.17 – 8.05 (m, 2H), 6.66 – 6.54 (m, 2H), 3.11 (s, 6H) ppm. ^{13}C NMR (101 MHz, DMSO) δ = 149.46 (s), 121.34 (s), 105.50 (s), 35.52 (s) ppm.



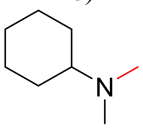
3i: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 4.4 Hz, 4H), 7.28 (ddd, *J* = 8.7, 5.0, 3.8 Hz, 1H), 3.46 (s, 2H), 2.28 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.96 (s), 129.11 (s), 128.27 (s), 127.07 (s), 64.47 (s), 45.41 (s) ppm.



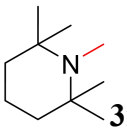
3j: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.80 – 6.65 (m, 4H), 3.68 (s, 3H), 2.79 (s, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 138.38 (s), 127.97 (s), 127.28 (s), 125.99 (s), 60.93 (s), 41.29 (s) ppm.



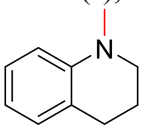
3k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (dd, *J* = 8.7, 6.6 Hz, 4H), 2.14 (s, 3H), 1.44 – 1.32 (m, 4H), 1.24 (dq, *J* = 14.3, 7.2 Hz, 4H), 0.85 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 57.62 (s), 42.31 (s), 29.43 (s), 20.77 (s), 14.06 (s).



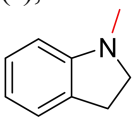
3l: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.29 (s, 6H), 2.16 (dt, *J* = 14.0, 6.9 Hz, 1H), 1.83 (dd, *J* = 37.9, 12.3 Hz, 4H), 1.63 (d, *J* = 12.9 Hz, 1H), 1.30 – 1.10 (m, 5H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ = 63.76 (s), 41.48 (s), 28.85 (s), 26.21 (s), 25.70 (s) ppm.



3m: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.16 (s, 3H), 1.45 (tdd, *J* = 7.1, 3.4, 1.5 Hz, 2H), 1.38 (dd, *J* = 6.6, 3.6 Hz, 4H), 0.97 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 53.73 (s), 41.21 (s), 31.46 (s), 28.48 (s), 26.29 (s), 17.90 (s) ppm.



3n: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.24 (t, *J* = 7.7 Hz, 1H), 7.12 (d, *J* = 7.0 Hz, 1H), 6.84 – 6.69 (m, 2H), 3.42 – 3.32 (m, 2H), 3.04 (s, 3H), 2.93 (t, *J* = 6.4 Hz, 2H), 2.14 (tt, *J* = 10.1, 5.0 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 146.90 (s), 128.96 (s), 127.21 (s), 122.98 (s), 116.37 (s), 111.11 (s), 51.43 (s), 39.26 (s), 27.97 (s), 22.65 (s) ppm.



3o: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.20 – 7.05 (m, 2H), 6.71 (dd, *J* = 11.0, 3.7 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 1H), 3.32 (dd, *J* = 11.0, 5.3 Hz, 2H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.80 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.42 (s), 130.36 (s), 127.37 (s), 124.32 (s), 117.85 (s), 107.31 (s), 56.21 (s), 36.35 (s), 28.79 (s) ppm.

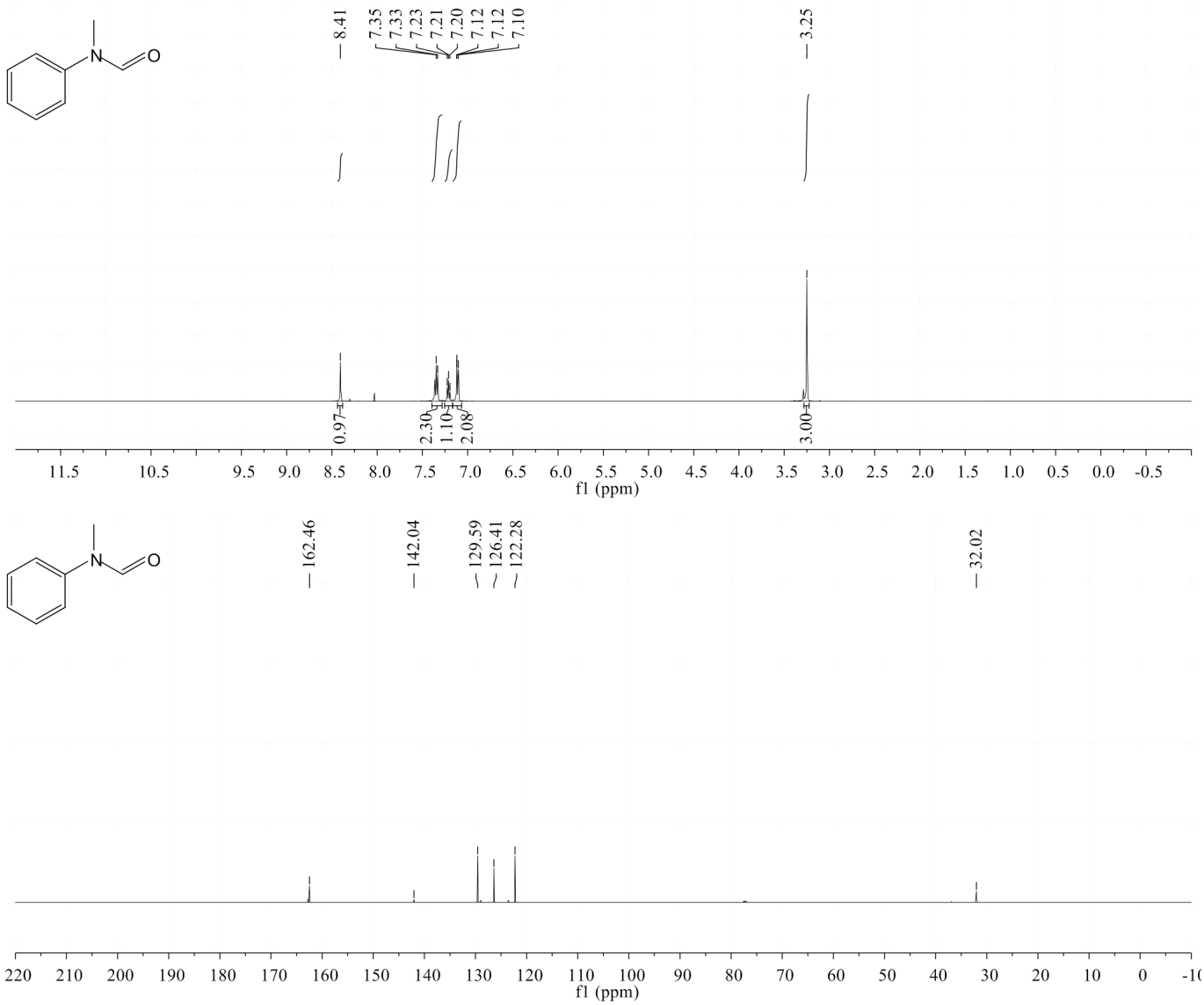


Fig.S4 The ^{1}H NMR and ^{13}C NMR spectra of **2a**.

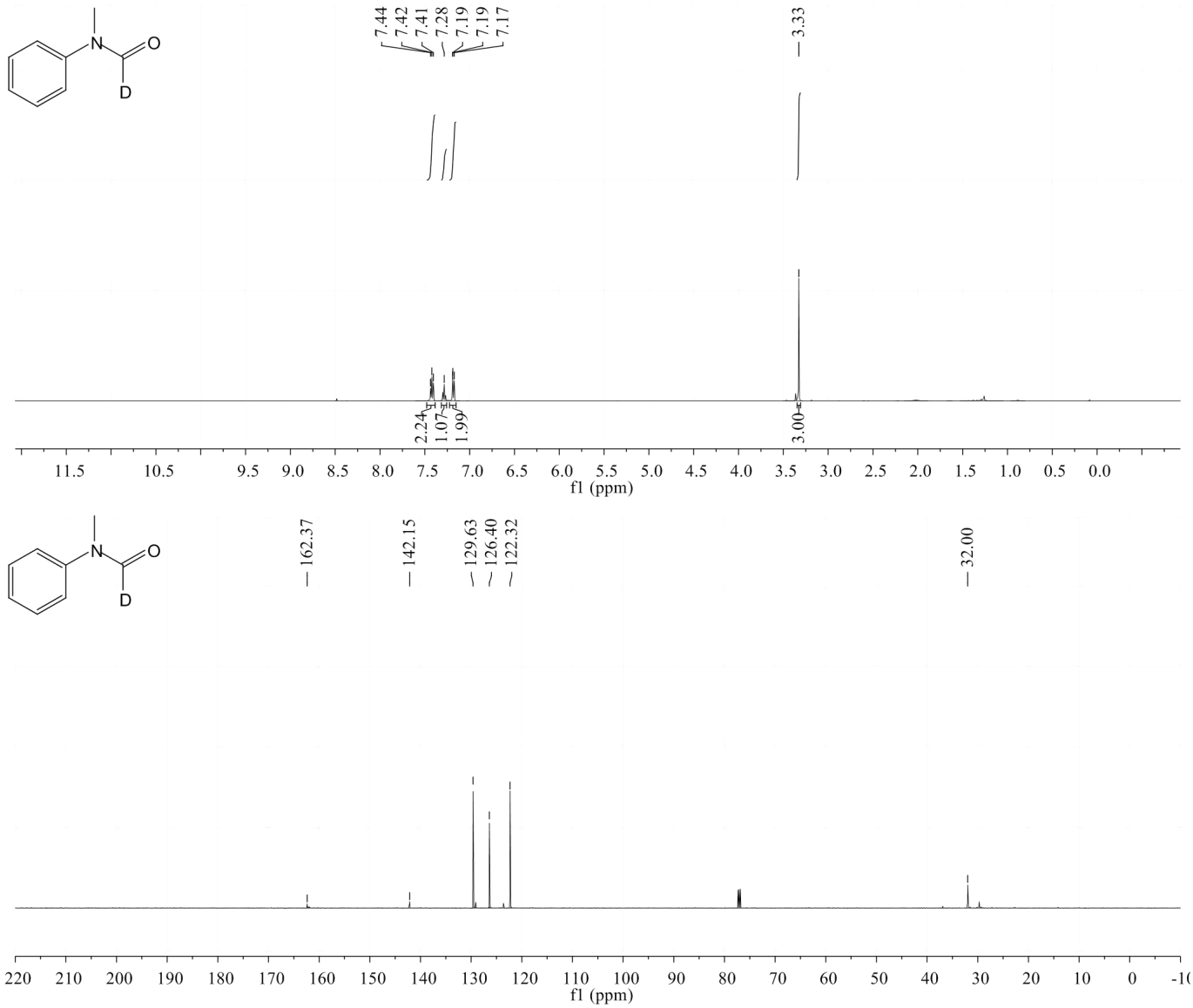


Fig.S5 The ^{1}H NMR and ^{13}C NMR spectra of **2a'**.

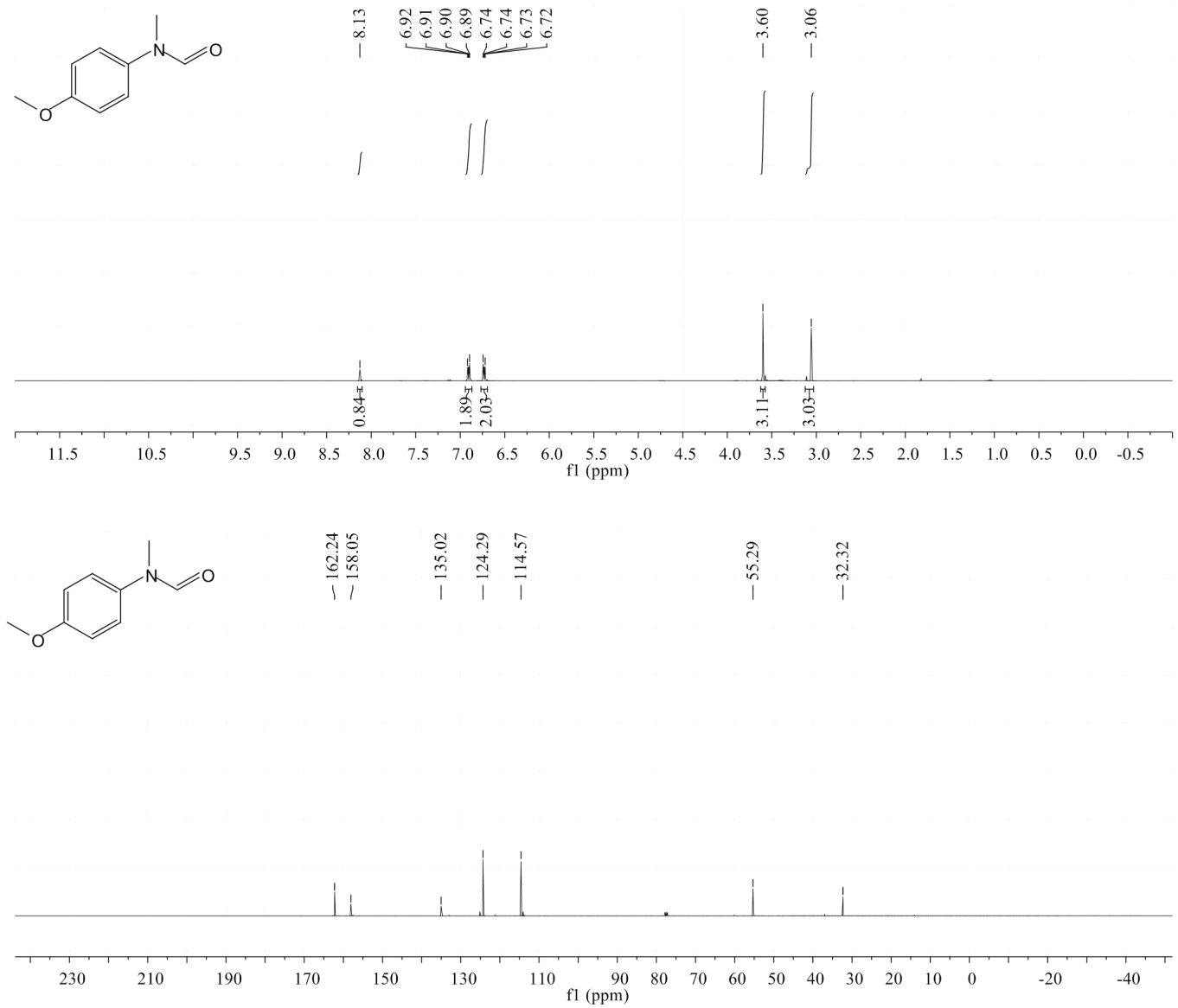


Fig.S6 The ^{1}H NMR and ^{13}C NMR spectra of **2e**.

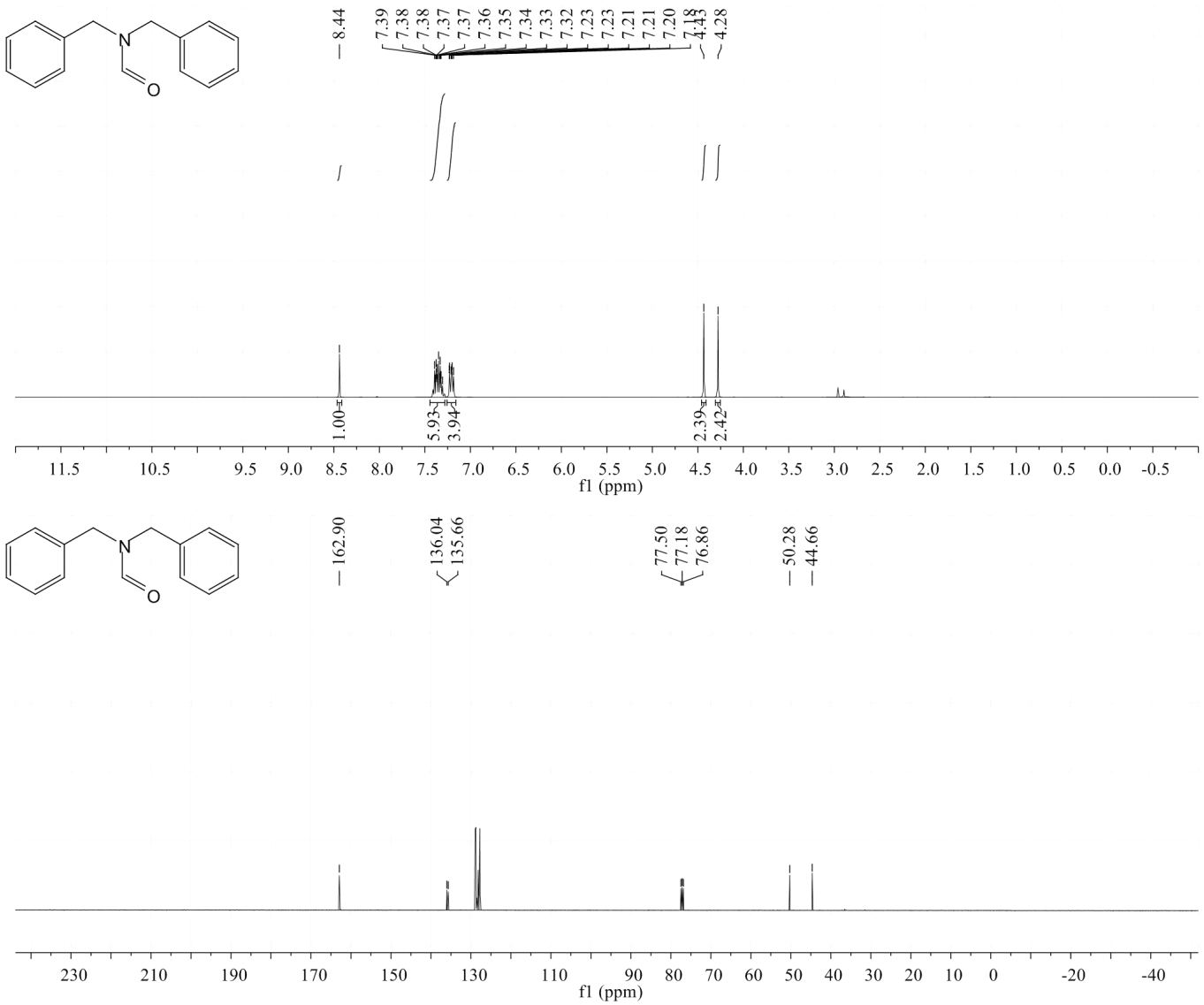


Fig.S7 The ^{1}H NMR and ^{13}C NMR spectra of **2n**.

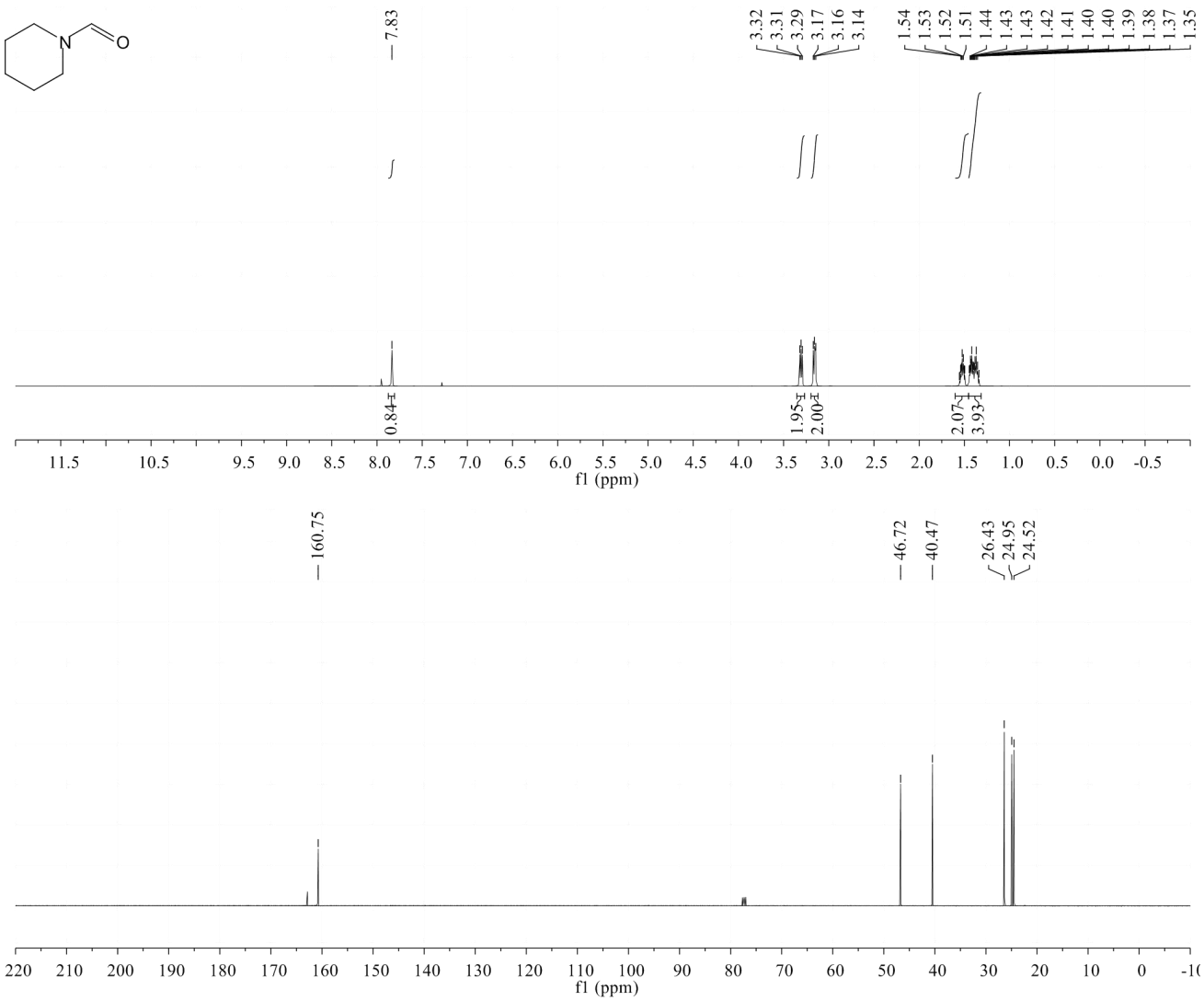


Fig.S8 The ^{1}H NMR and ^{13}C NMR spectra of **2q**.

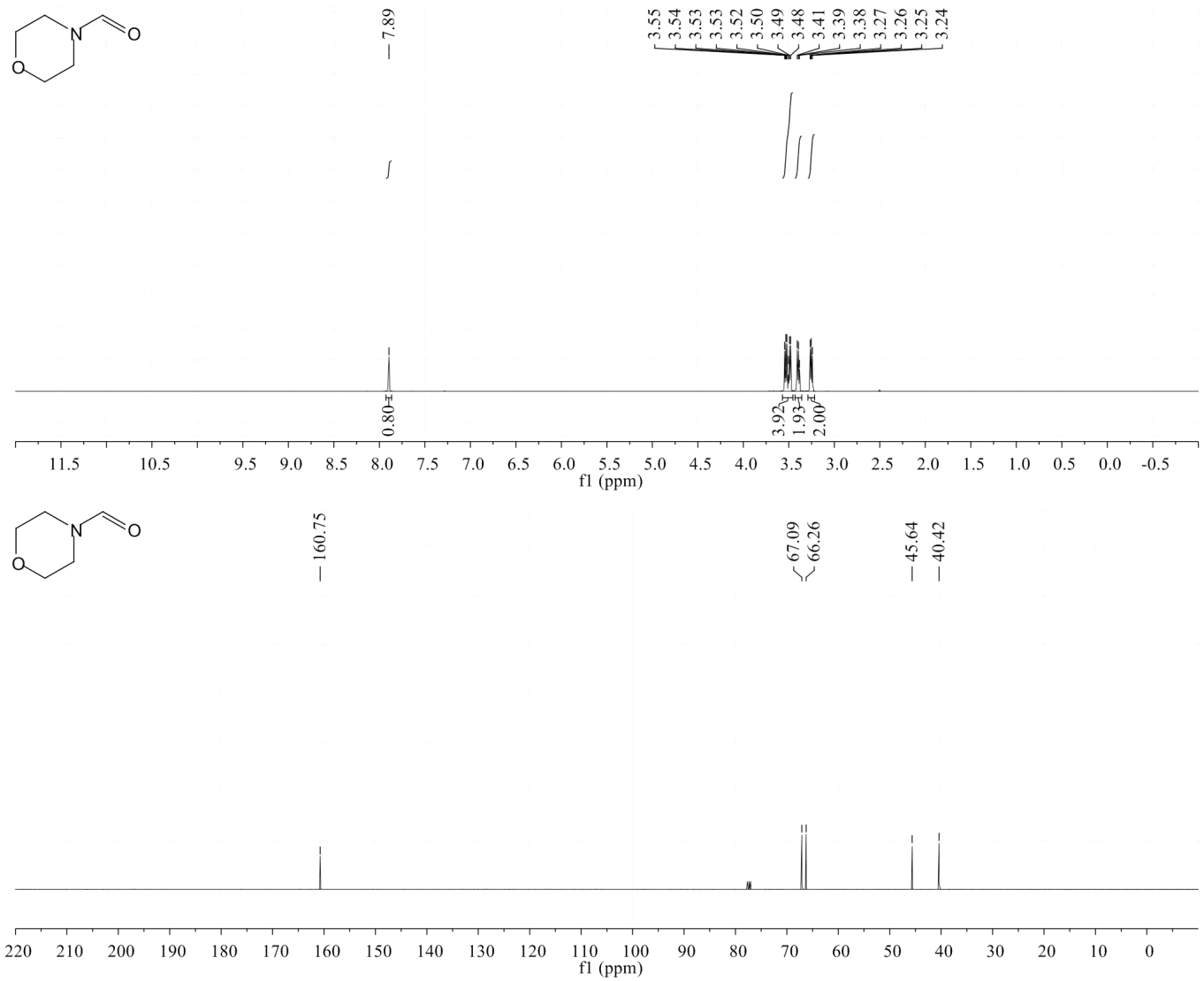


Fig.S9 The ^{1}H NMR and ^{13}C NMR spectra of **2r**.

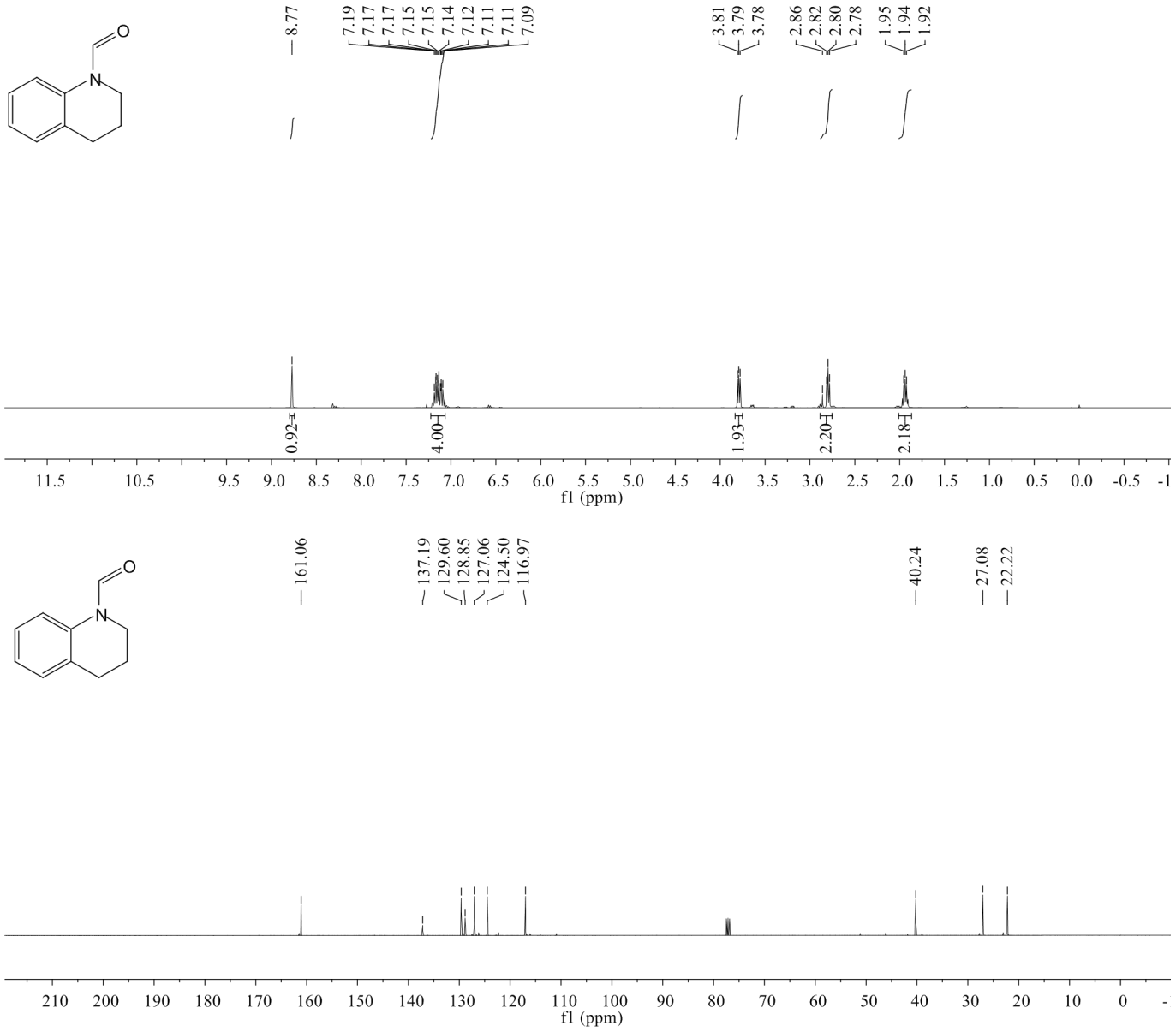


Fig.S10 The ^{1}H NMR and ^{13}C NMR spectra of **2s**.

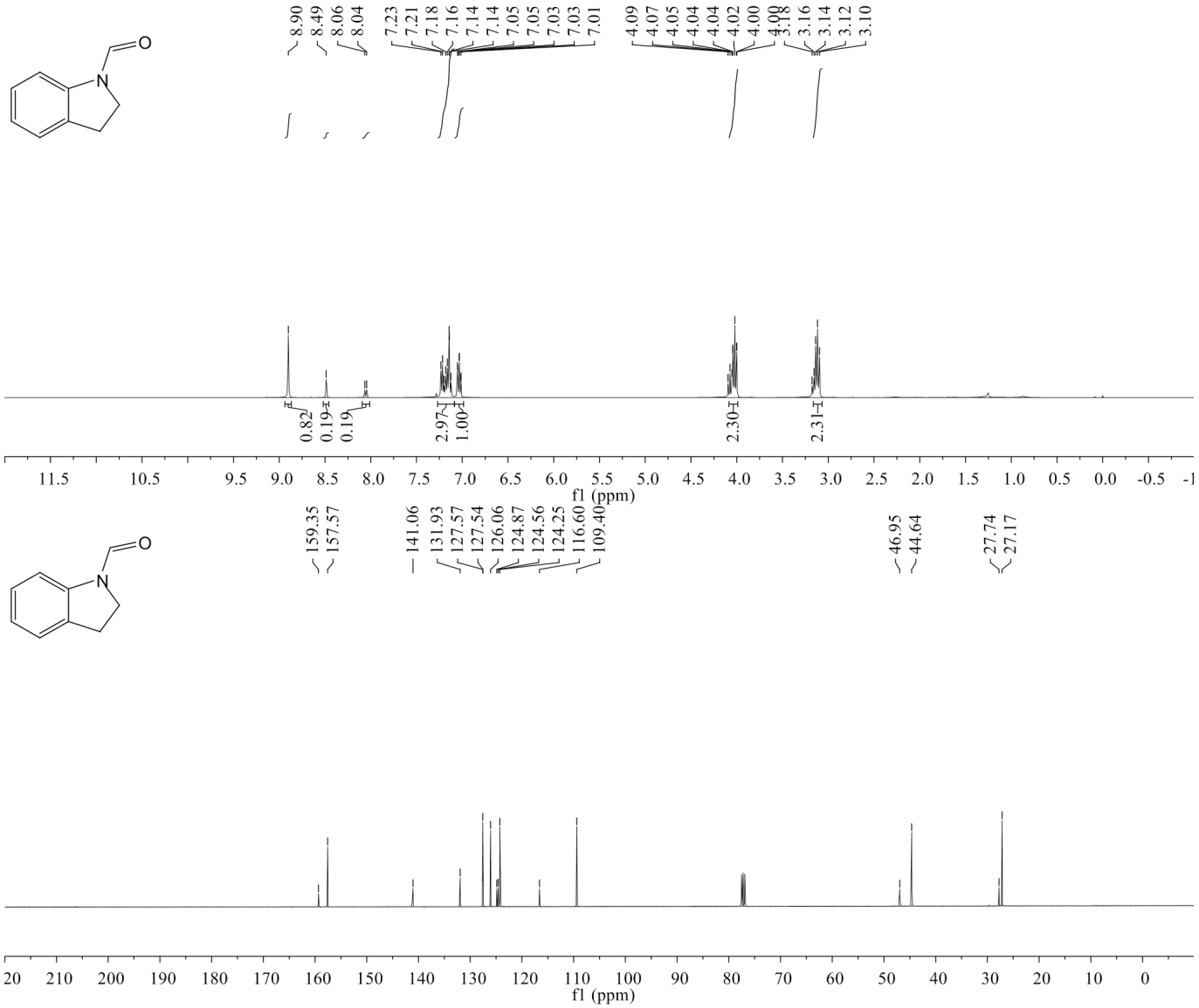


Fig.S11 The ^{1}H NMR and ^{13}C NMR spectra of **2t**.

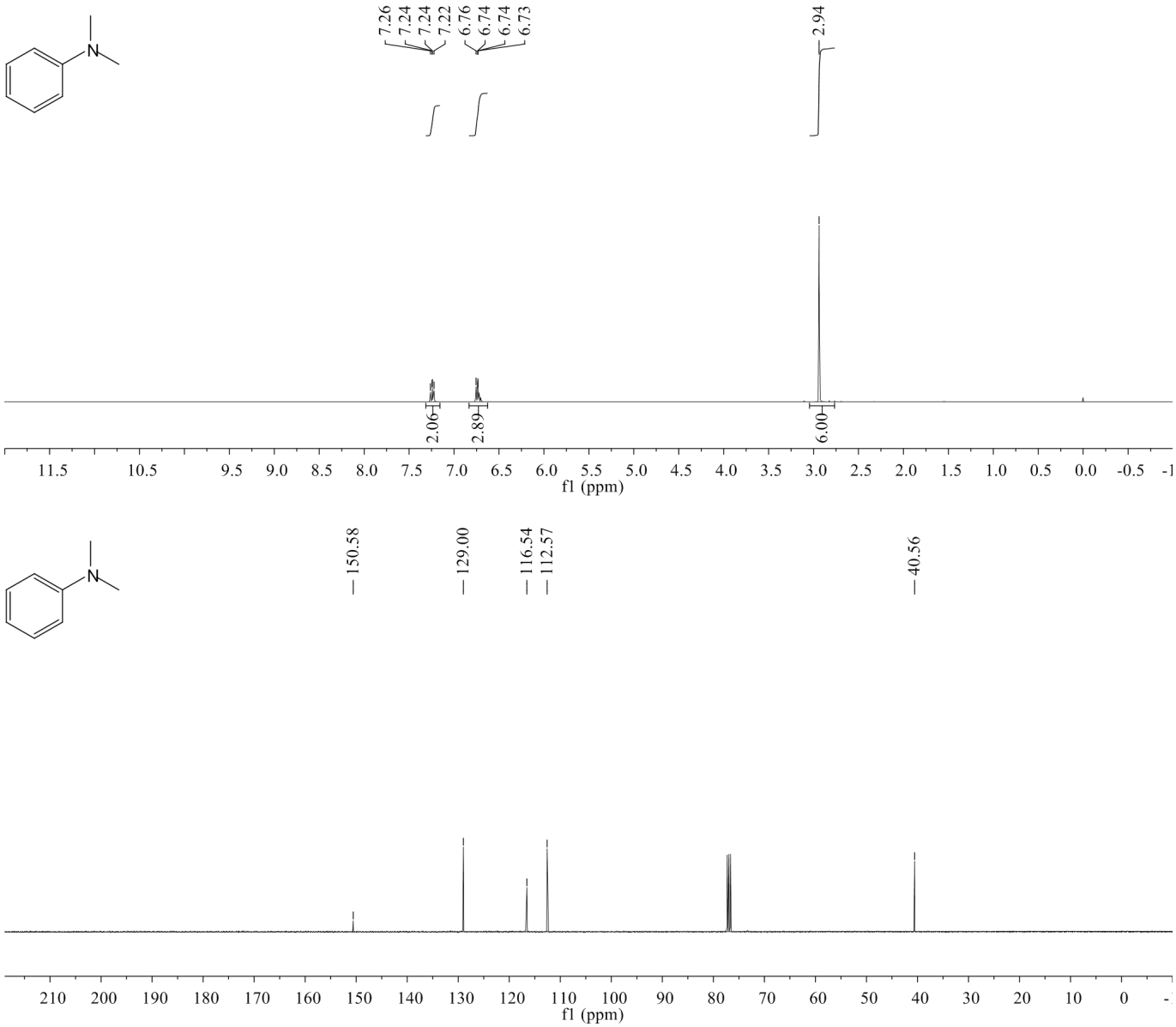


Fig.S12 The ^{1}H NMR and ^{13}C NMR spectra of **3a**.

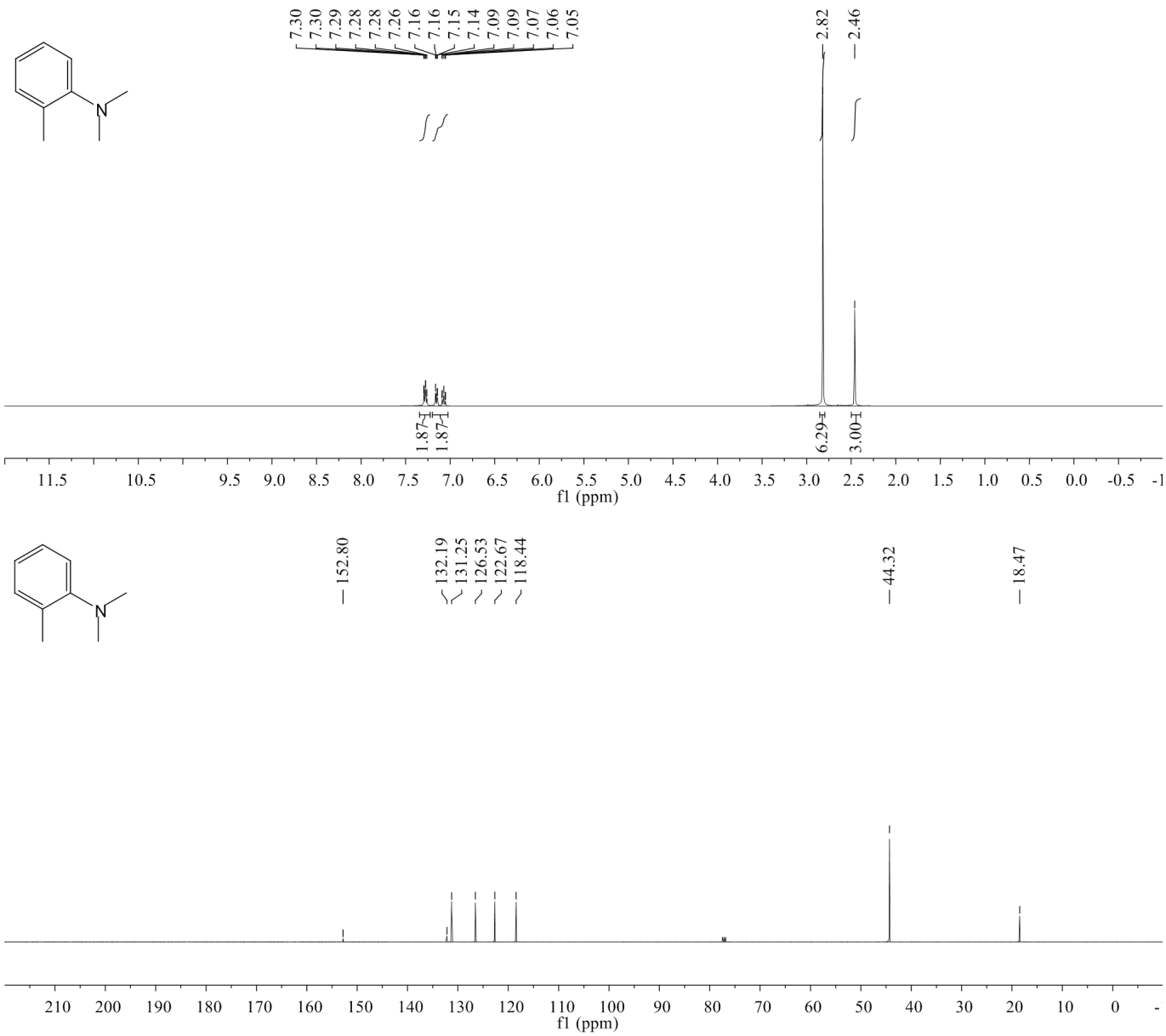


Fig.S13 The ^{1}H NMR and ^{13}C NMR spectra of **3b**.

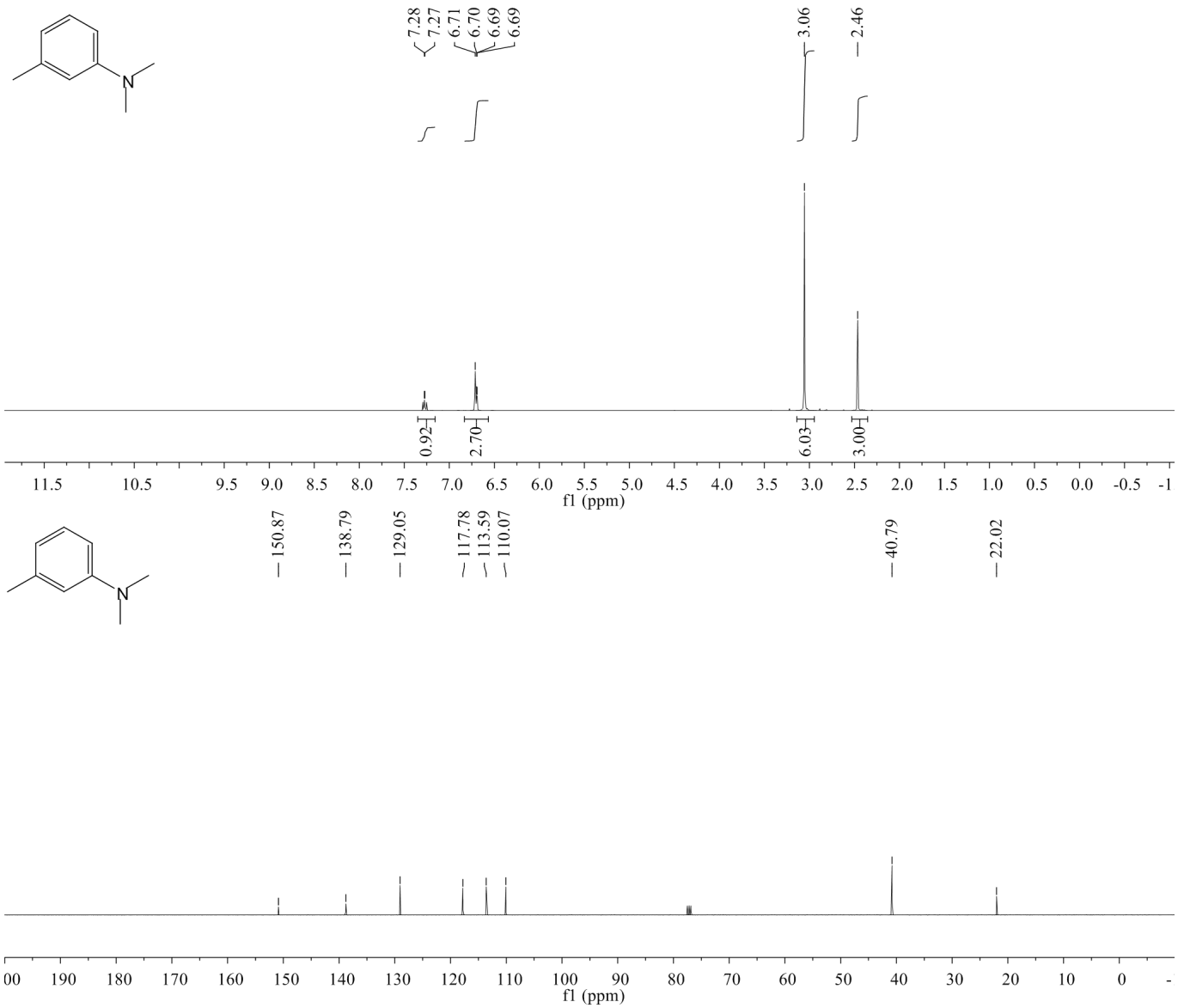


Fig.S14 The ^{1}H NMR and ^{13}C NMR spectra of **3c**.

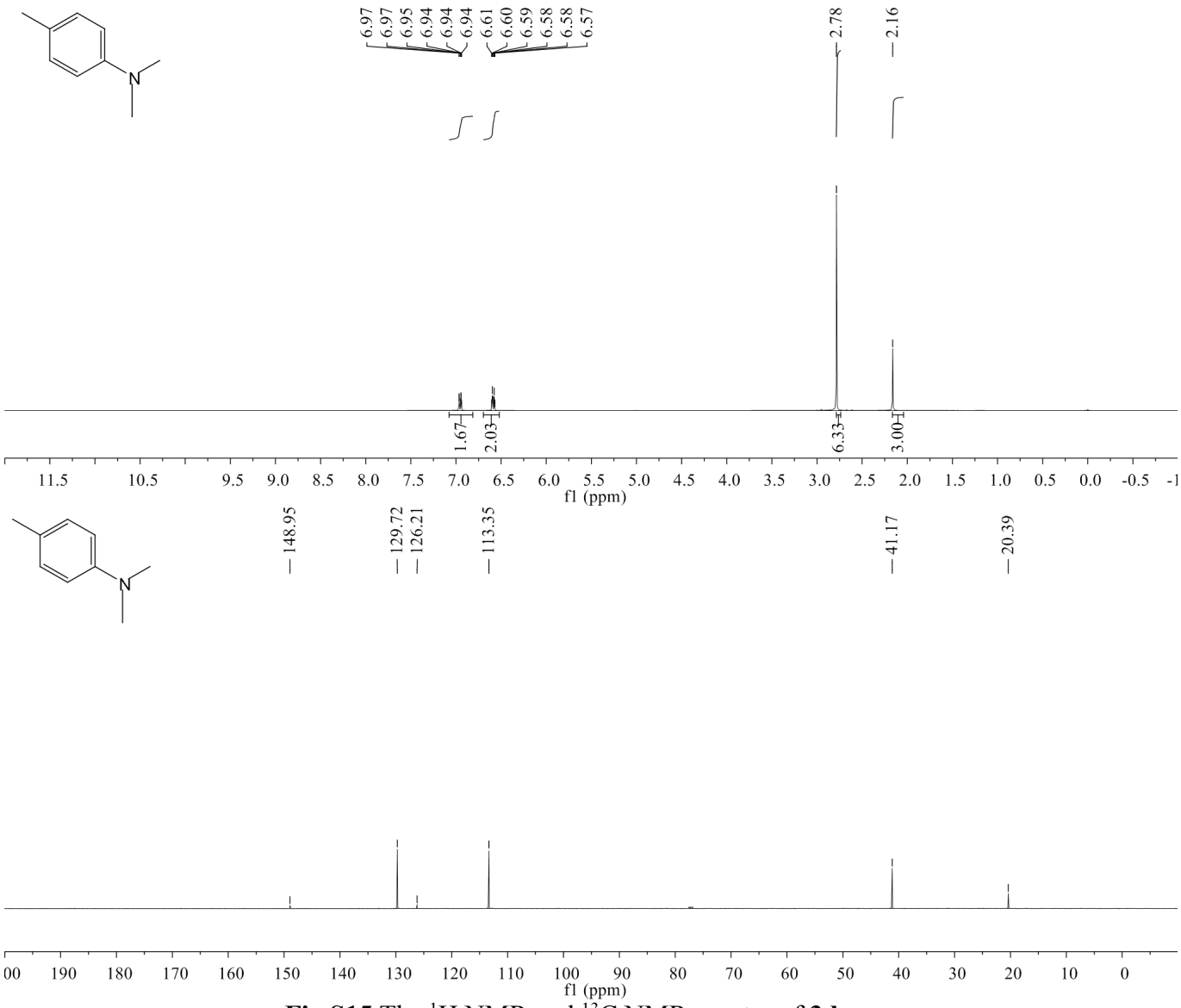


Fig.S15 The ^{1}H NMR and ^{13}C NMR spectra of **3d**.

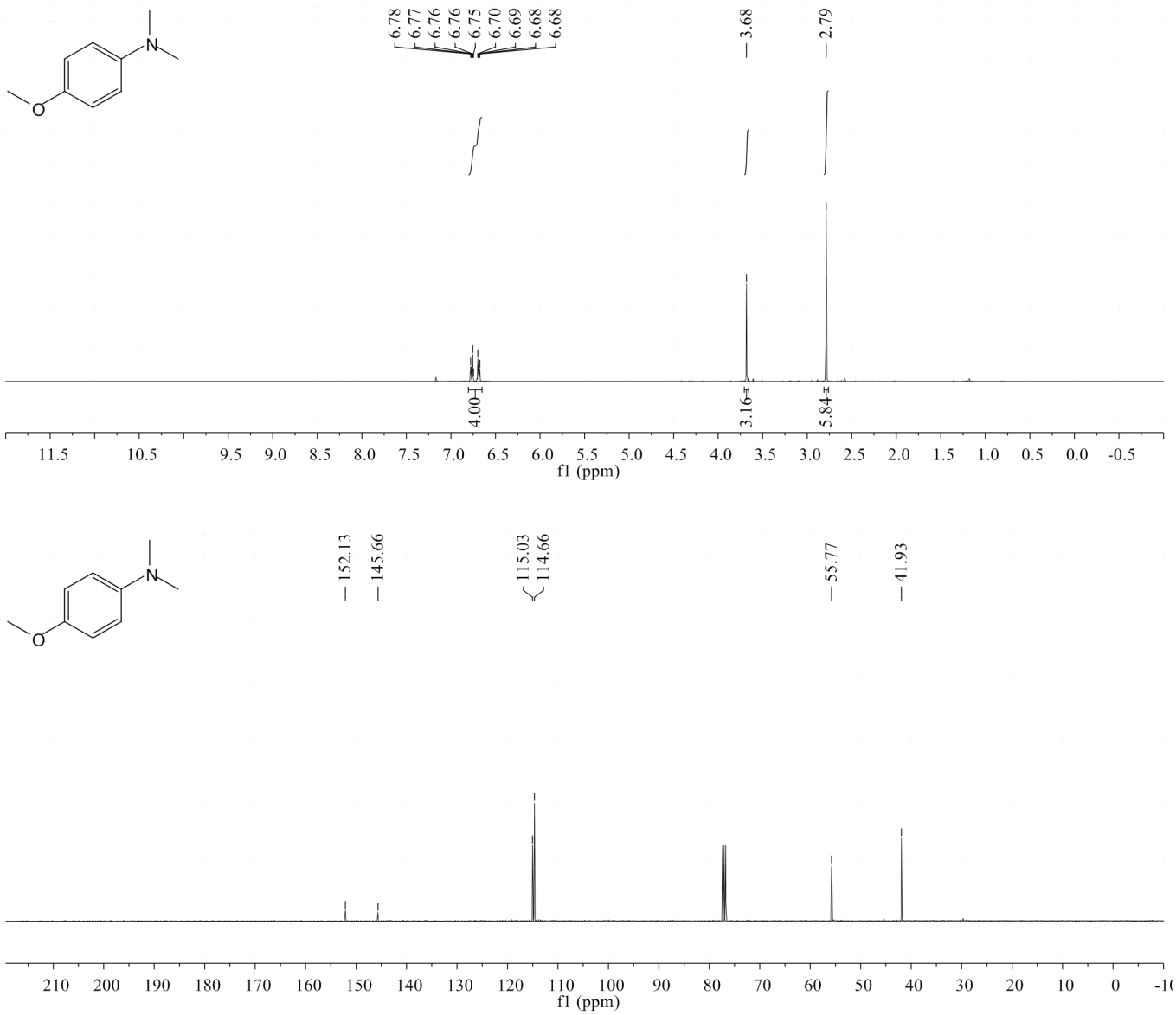


Fig.S16 The ^{1}H NMR and ^{13}C NMR spectra of **3e**.

Fig.S17 The ^{1}H NMR and ^{13}C NMR spectra of **3f**.

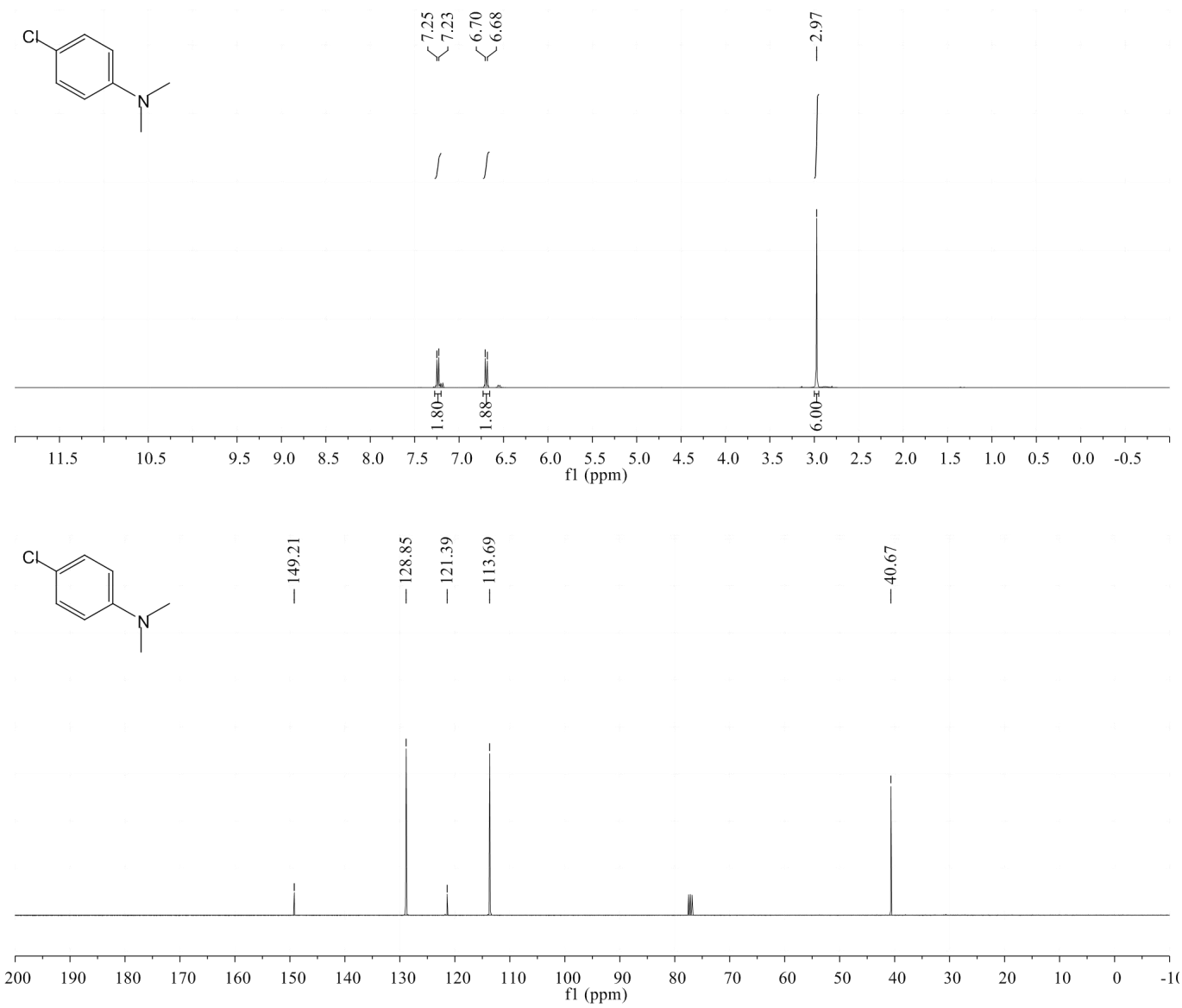


Fig.S18 The ^{1}H NMR and ^{13}C NMR spectra of **3g**.

Fig.S19 The ^{1}H NMR and ^{13}C NMR spectra of **3h**.

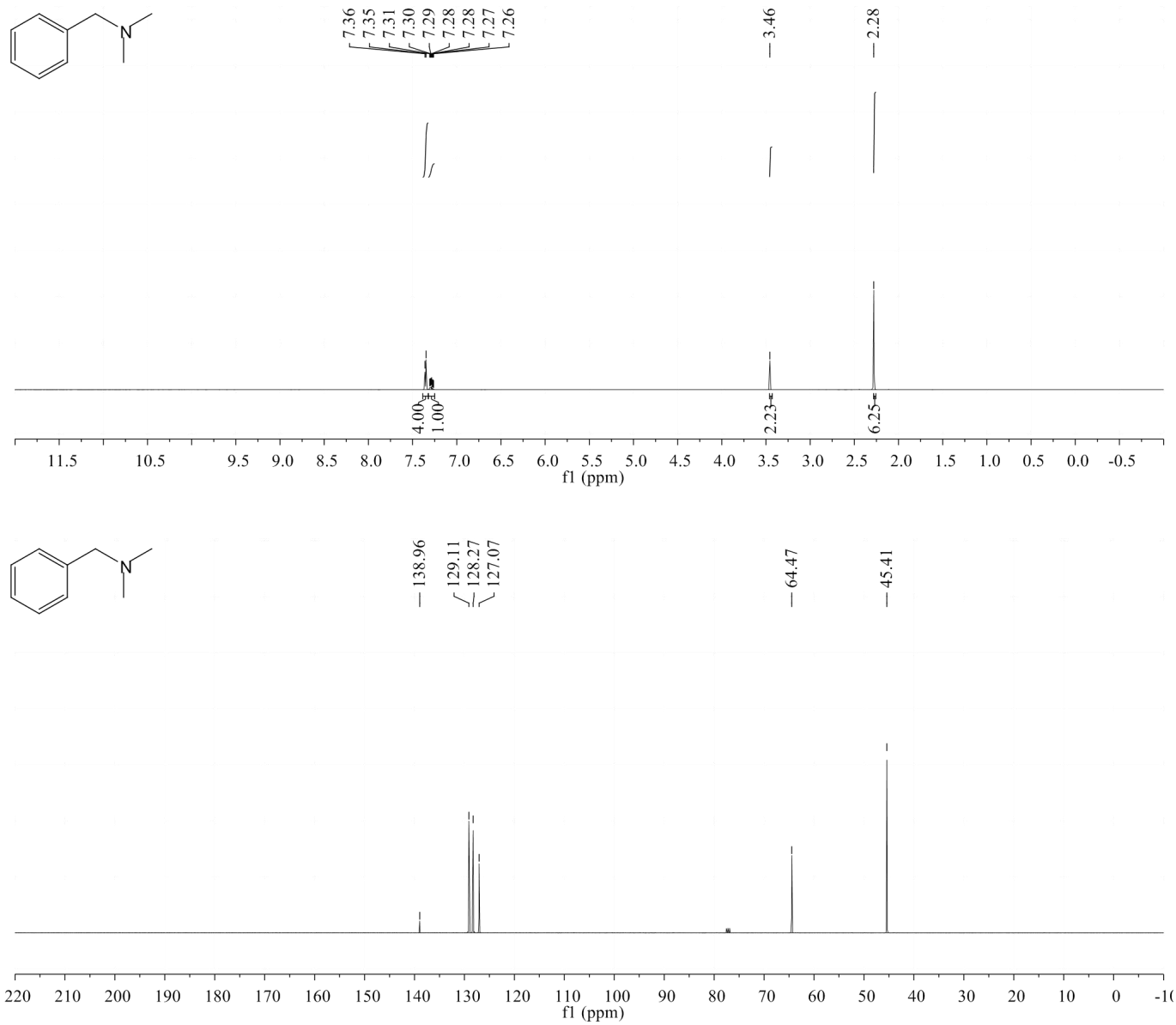


Fig.S20 The ^{1}H NMR and ^{13}C NMR spectra of **3i**.

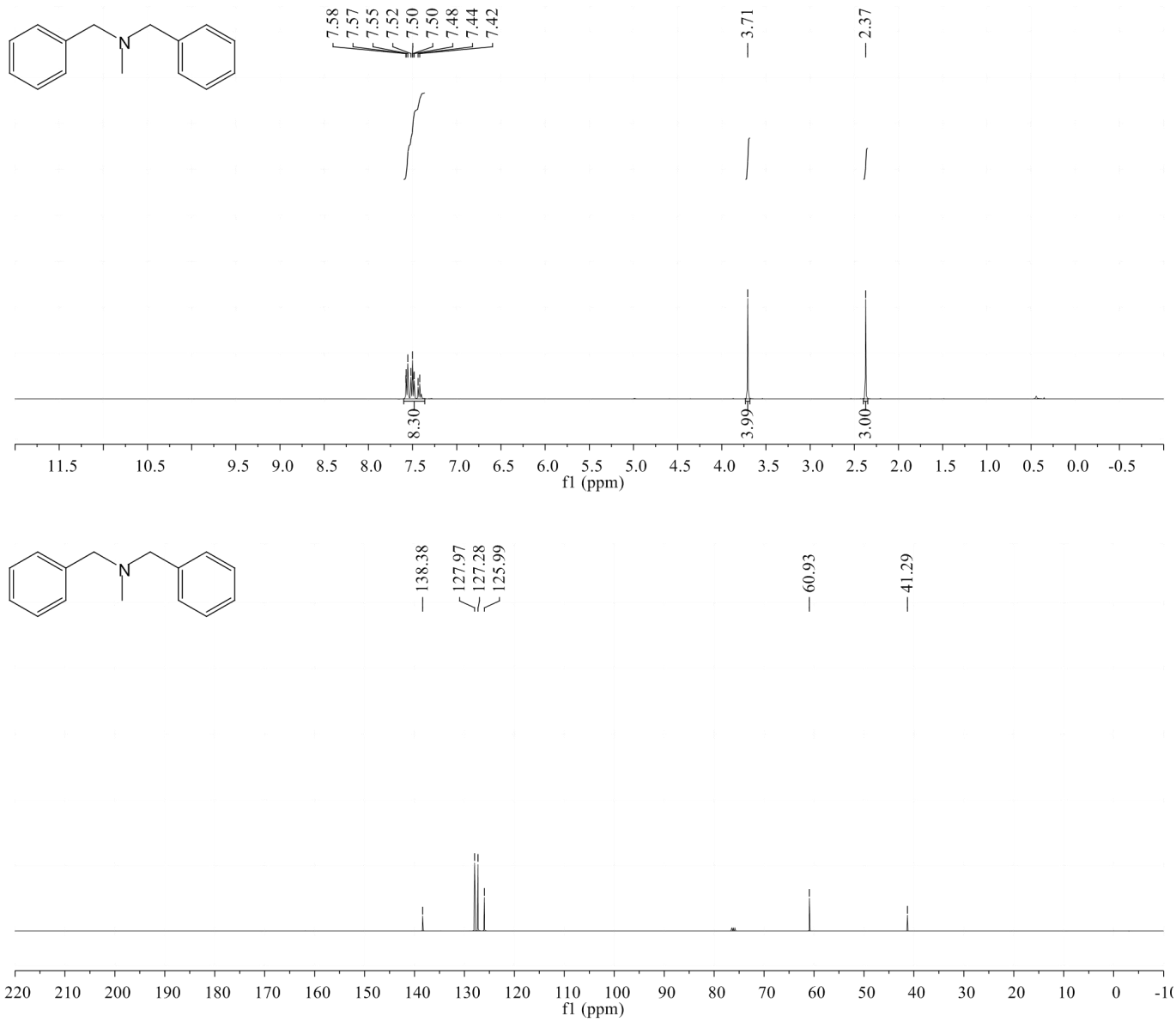


Fig.S21 The ^{1}H NMR and ^{13}C NMR spectra of **3j**.

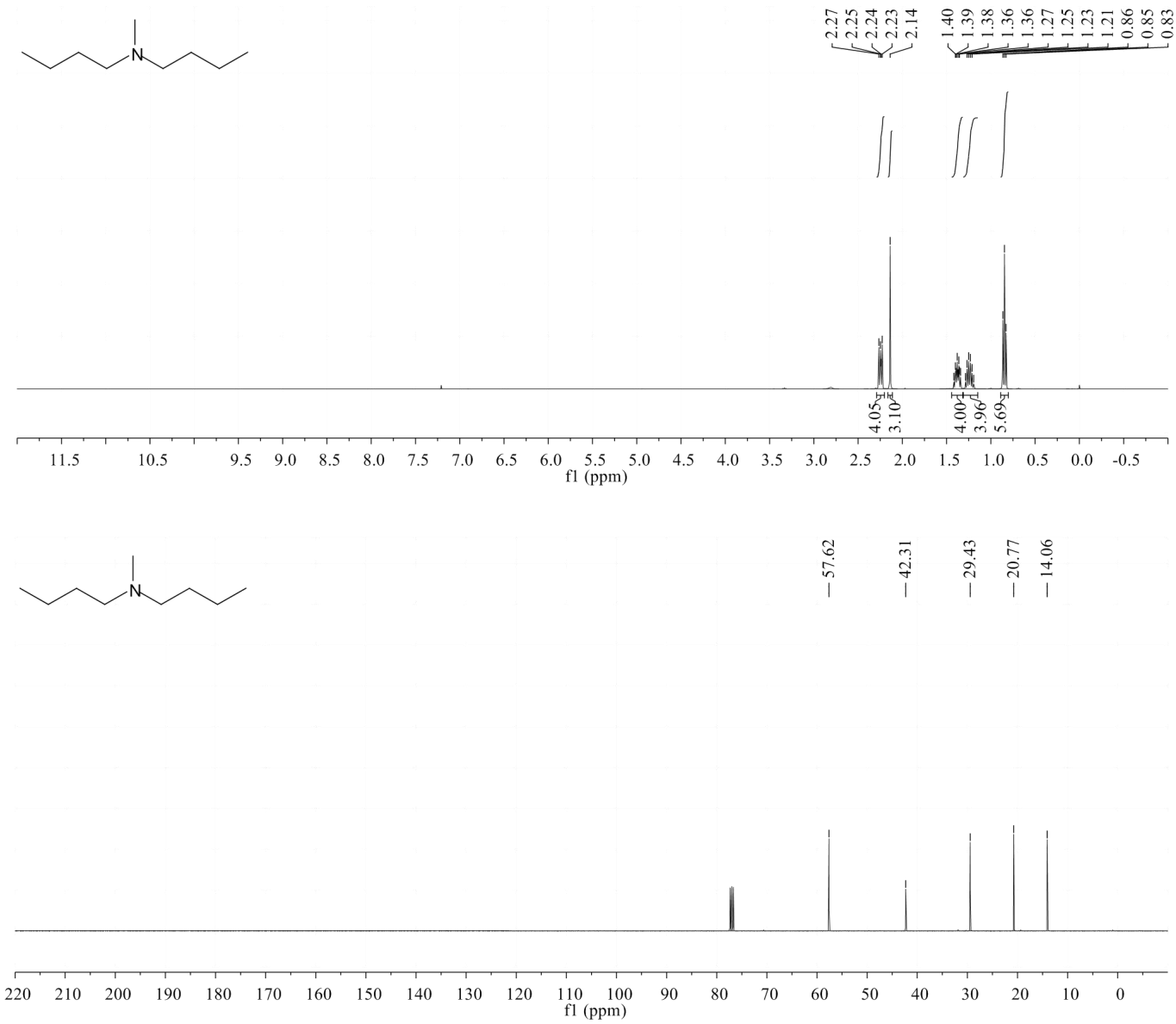


Fig.S22 The ^{1}H NMR and ^{13}C NMR spectra of **3k**.

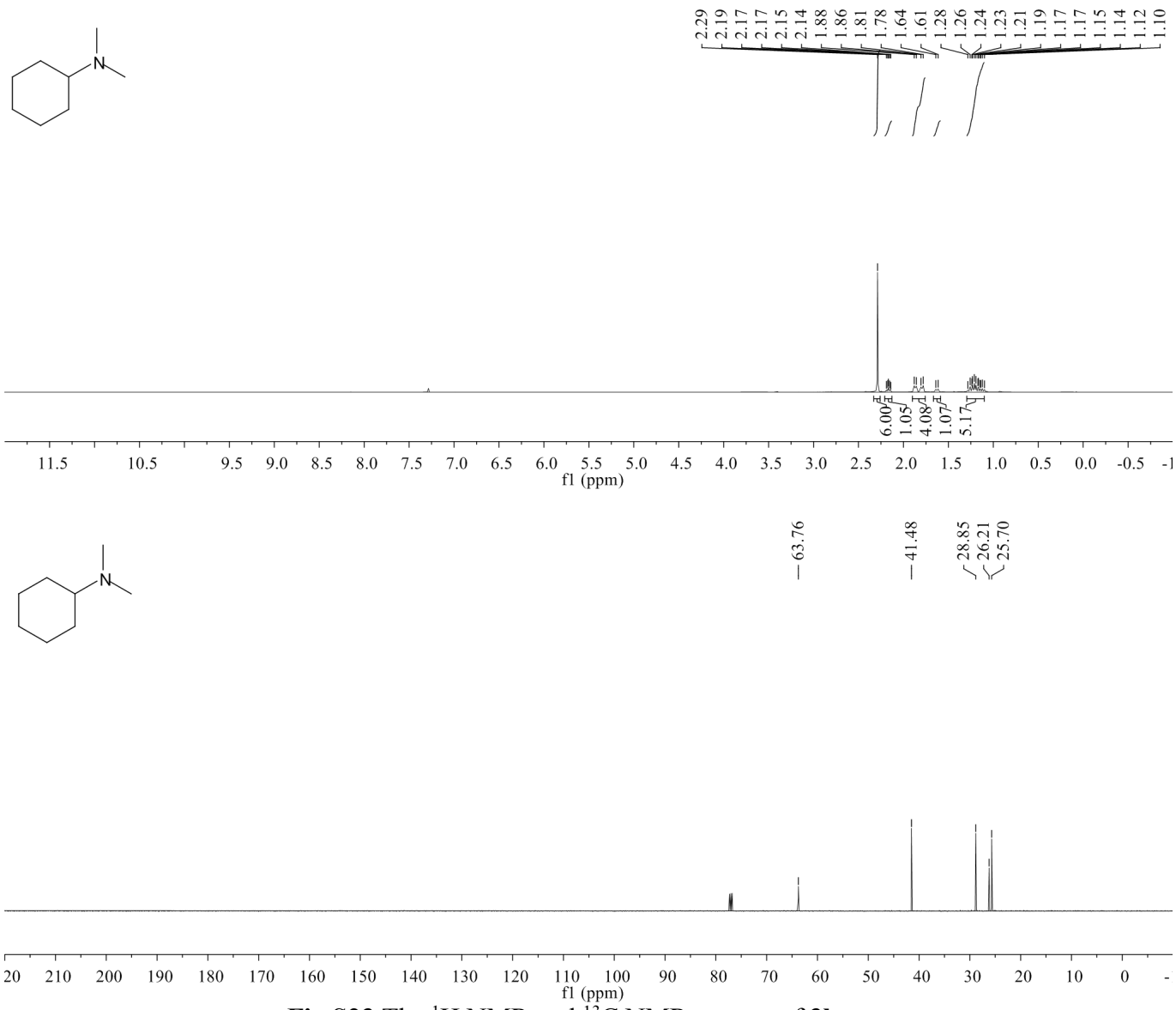


Fig.S23 The ^{1}H NMR and ^{13}C NMR spectra of **3l**.

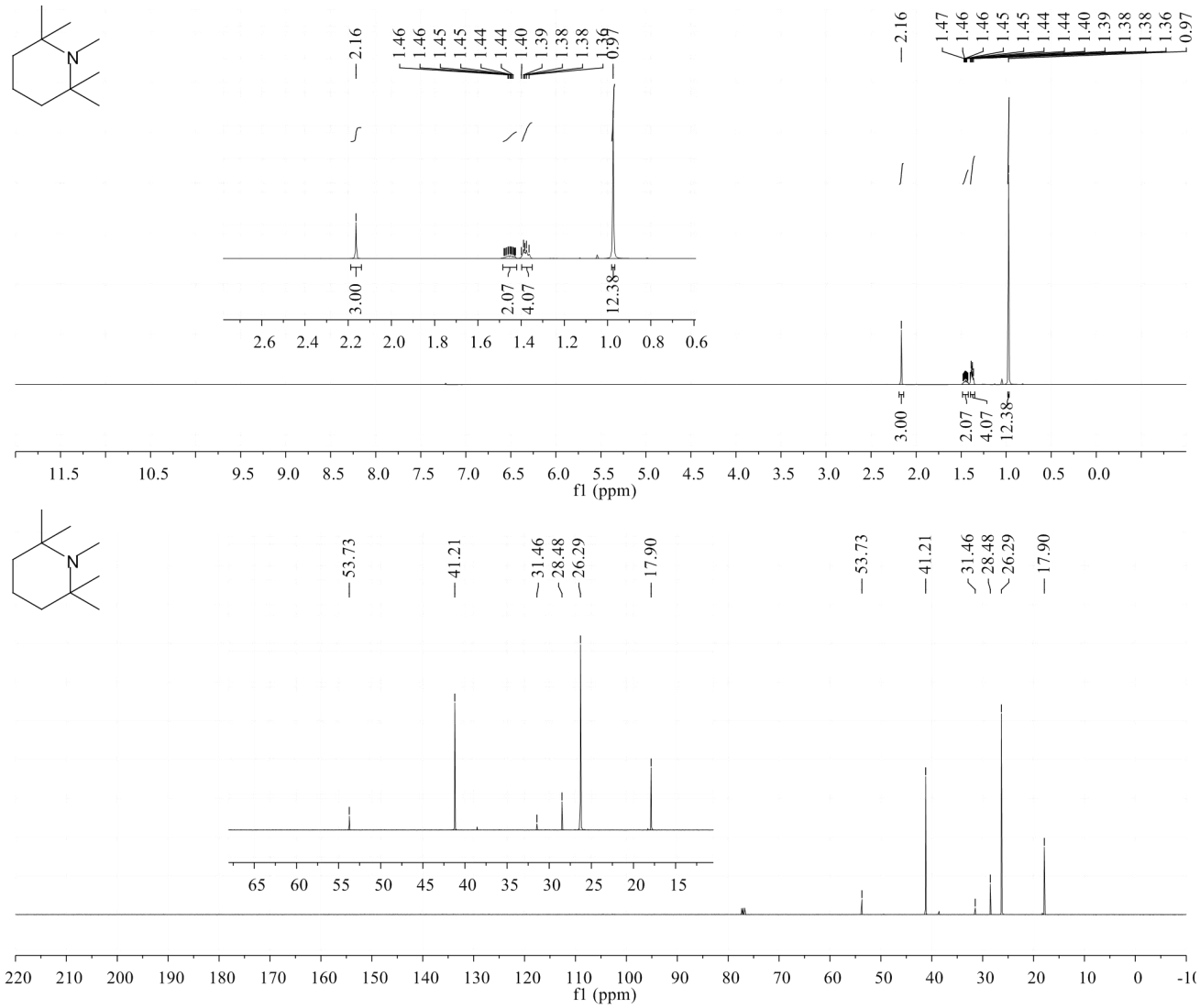


Fig.S24 The ^{1}H NMR and ^{13}C NMR spectra of **3m**.

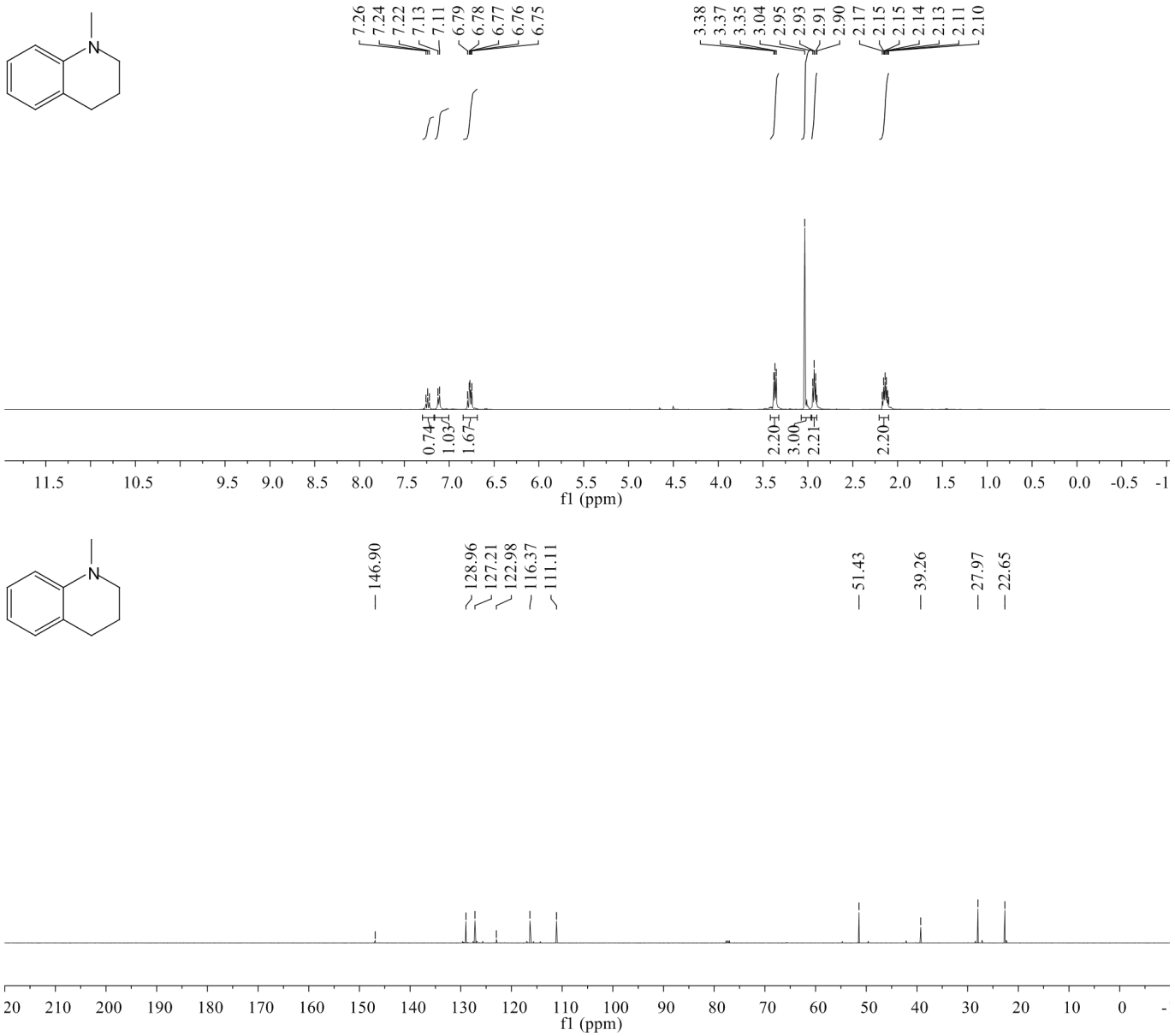


Fig.S25 The ^{1}H NMR and ^{13}C NMR spectra of **3n**.

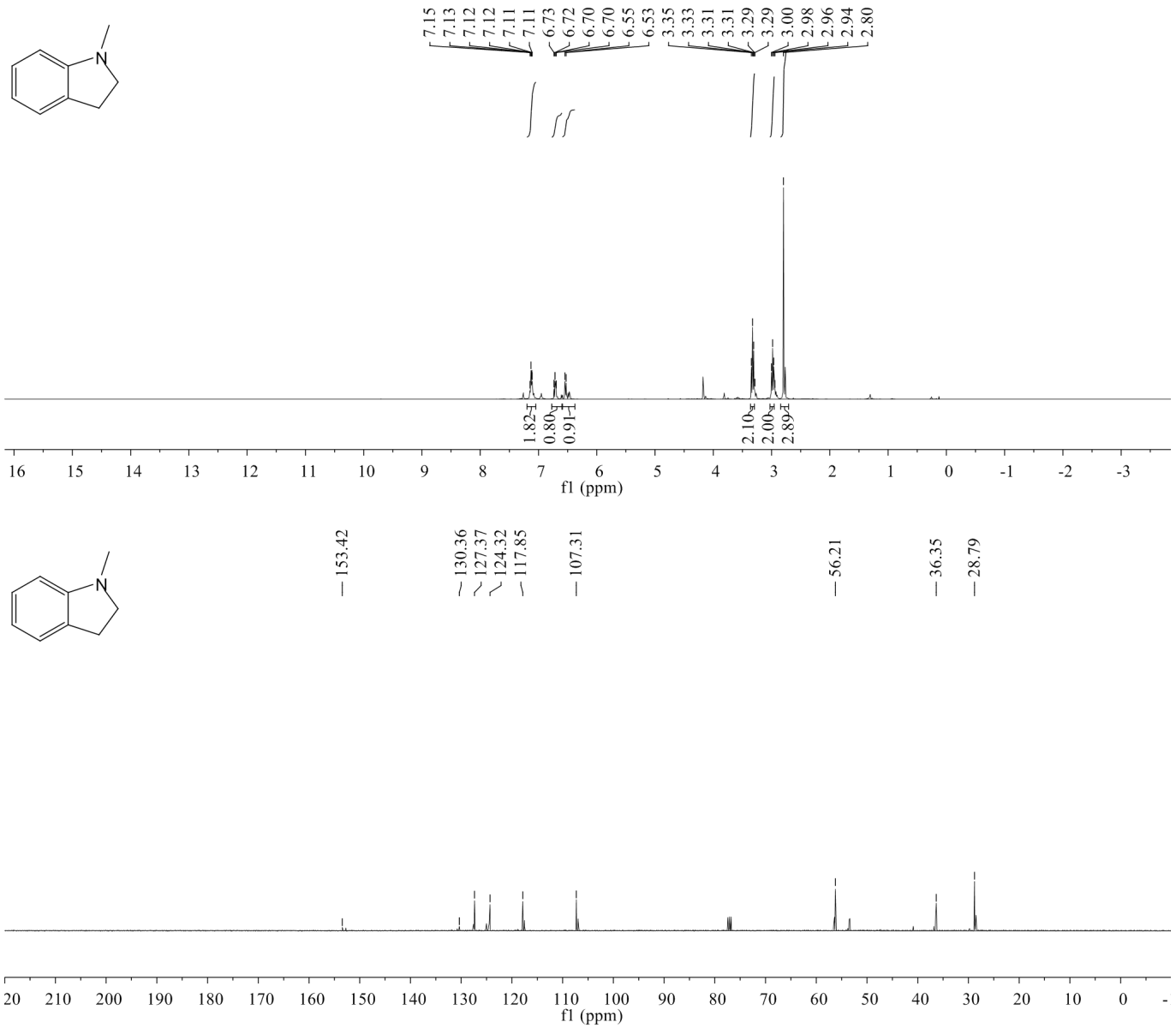


Fig.S26 The ^{1}H NMR and ^{13}C NMR spectra of **3o**.

11. References

1. C. Fang, C. Lu, M. Liu, Y. Zhu, Y. Fu and B. Lin, *ACS Catal.*, 2016, **6**, 7876-7881.
2. X. Liu, X. Li, C. Qiao, H. Fu and L. He, *Angew. Chem. Int. Ed.*, 2017, **56**, 7425-7429.
3. C. Xie, J. Song, H. Wu, B. Zhou, C. Wu, B. Han, *ACS Sustainable Chem. Eng*., 2017, **5**, 7086-7092.
4. G. Li, J. Chen, D. Zhu, Y. Chen and J. Xia, *Adv. Synth. Catal*., 2018, **360**, 2364-2369.
5. M. Wang, N. Wang, X. Liu, C. Qiao and L. He, *Green Chem*., 2018, **20**, 1564-1570.