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Supporting Information For

Catalyst-free *N*-formylation of amines using BH_3NH_3 and CO_2 at mild conditions

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Index:

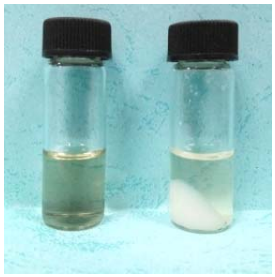
1. General information. All solvents and chemicals are analytically pure agents purchased from Energy Chemical, Inc and are used without further purification unless otherwise indicated. The BH_3NH_3 is purchased from Aladdin reagent Chemical Company. The deuterated solvents are purchased from TCI Chemical Company. CO_2 (99.99 vt.%) is purchased from Nanjing Tianze Gas Center, Nanjing. 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, ^{13}C). The yields were determined using a Shimadzu GC2014 gas chromatograph with a flame-ionization detector. The conversion and yield of the product were resolved by ^{1}H NMR using 1,3,5-trimethyoxybenzene as an internal standard or GC/MS analysis using dodecane as the internal standard, meanwhile, the substrates and their corresponding products also were decided by a Shimadzu GC-MS-QP2010. To isolate the products, the corresponding formamides were obtained after purification by flash chromatography on silica gel.

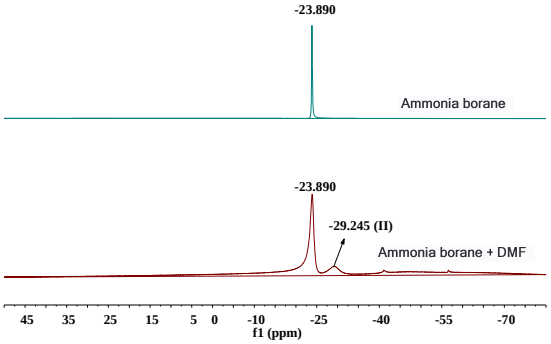
2. Typical procedure for the synthesis of 1a. A stainless autoclave reactor coupled with a magnetic stirrer was charged with *N*-methylaniline (1 mmol), BH_3NH_3 (3 mmol), and DMF (5 mL). The reactor was pressurized with 1 MPa of CO_2 at ambient temperature, and then was heated and stirred at 50 ^{o}C for 24 h. After the reaction, excess CO_2 was vented discreetly. The conversion and yield of the product were resolved by ^{1}H NMR using 1,3,5-trimethyoxybenzene as an internal standard or GC/MS analysis using dodecane as the

internal standard. The desired products were obtained in the corresponding isolated yields after purification by flash chromatography on silica gel with petroleumether and ethyl acetate. Other substrates are performed using the same method unless otherwise specified.

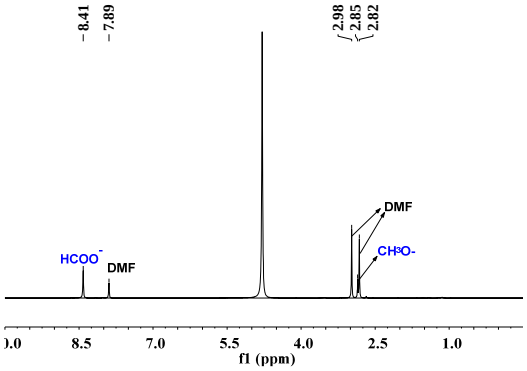
3. Gram scale synthesis of 15a. A stainless autoclave reactor coupled with a magnetic stirrer was charged with dibenzylamine (6 mmol, 1.18 g), BH_3NH_3 (18 mmol, 0.56 g), and DMF (15 mL). The resulting mixture was stirred for 24 h at 50°C under 1 MPa of CO_2. After the reaction, excess CO_2 was vented 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 *N,N′*-dibenzylformamide **(15a)** was obtained in a yield of 81% after purification by flash chromatography on silica gel with petroleumether/ethyl acetate.

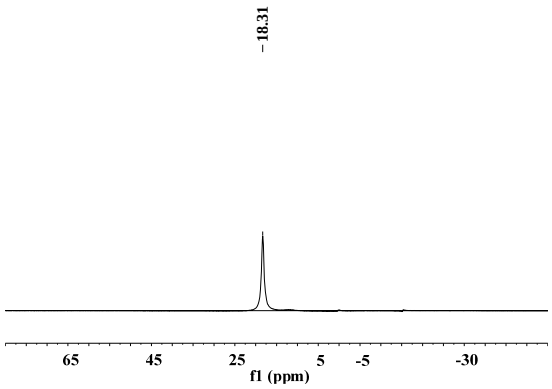
4. Stepwise reaction of BH_3NH_3, CO_2 and morpholine. A stainless autoclave reactor coupled with a magnetic stirrer was charged with BH_3NH_3 (3 mmol), and DMF (5 mL). The reactor was pressurized with 1 MPa of CO_2 at ambient temperature, then heated and stirred at 50°C for 24 h. After the reaction, excess CO_2 was vented discreetly (The active intermediate III can be isolated as white solid by adding ethyl acetate to the reaction mixture). Then, the morpholine (1 mmol) was added to reactor. It was heated and stirred at 50°C for another 24 h. After the reaction, the conversion and yield of the product were resolved by GC/MS analysis using dodecane as the internal standard.



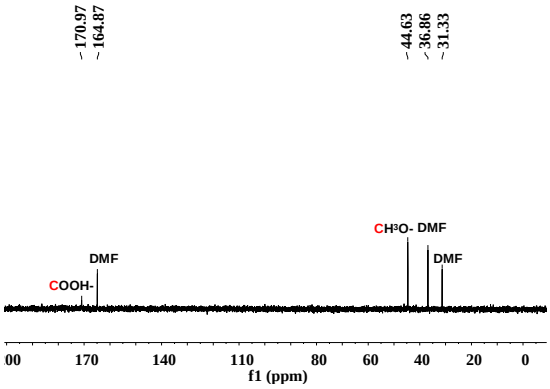


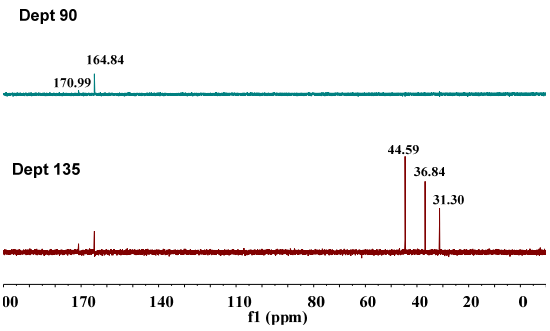
(a) (b)





(c) (d)





(e) (f)

Figure S1 (a): The reaction mixtures before (left) and after (right) addition of ethyl acetate (active species as white solid); (b): The ^{11}B-NMR of BH_3NH_3 and BH_3NH_3 + DMF in D_2O; (c) The ^{1}H-NMR of compound **III**; (d) The ^{11}B{^{1}H} NMR of compound **III**; (e) The ^{13}C-NMR of

compound **III**; and (f) The dept-90 and dept-135 of compound **III**.

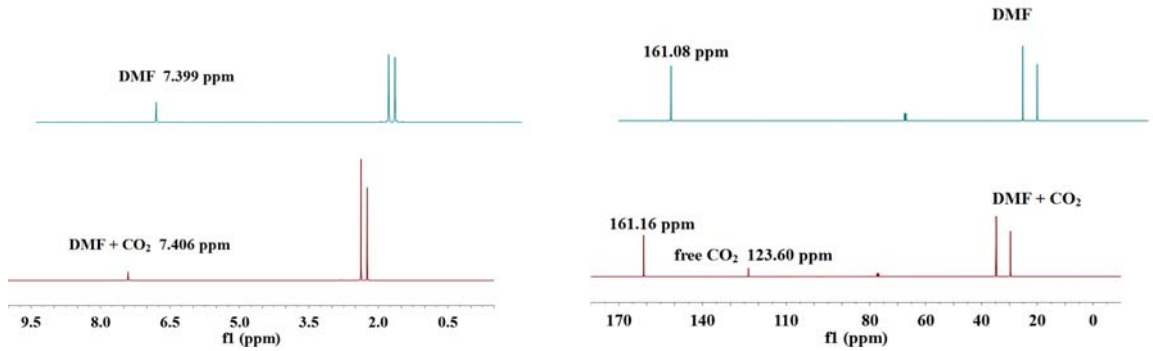
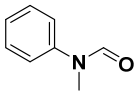
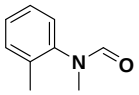


Figure S2 ^{1}H- and ^{13}C-NMR spectra of DMF and DMF + CO_2 in $CDCl_3$. (Chemical shift at 124.60 ppm derives from free CO_2 (see *Angew. Chem. Int. Ed.* **2009**, *48*, 9839 -9843), suggesting that CO_2 can dissolve in DMF well).

5. Detailed descriptions for products

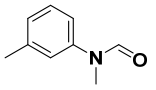


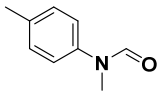
(**1a**) ***N*-methylformanilide:** light yellow oil, 91 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H, -CHO), 7.42 (t, J = 7.9 Hz, 2H, -CH-ar), 7.29 (d, J = 7.5 Hz, 1H, -CH-ar), 7.22 - 7.10 (m, 2H, -CH-ar), 3.33 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.56 (s, -CHO), 142.10 (s, -C-ar), 129.65 (s, -CH-ar), 126.50 (s, -CH-ar), 122.41 (s, -CH-ar), 32.14 (s, -CH_3).

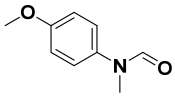


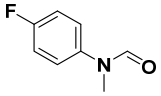
(**2a**) ***N*-methyl-*N*-(2-methylphenyl)formamide:** yellow oil, 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H, -CHO), 7.35 - 7.24 (m, 3H, -CH-ar), 7.14 - 6.99 (m, 1H, -CH-ar), 3.20 (s, 3H, -CH_3), 2.27 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.01 (s, -CHO), 140.72 (s, -C-ar), 135.44 (s, -C-ar), 131.47 (s, -CH-ar), 128.44 (s, -CH-ar), 127.81 (s,

-CH-ar), 127.20 (s, -CH-ar), 33.05 (s, -CH_3), 17.70 (s, -CH_3).

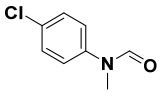
 (**3a**) ***N*-Methyl-*N*-(3-methylphenyl)formamide:** yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H, -CHO), 7.35 - 7.24 (m, 3H, -CH-ar), 7.14 - 6.99 (m, 1H, -CH-ar), 3.20 (s, 3H, -CH_3), 2.27 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.31 (s, -CHO), 142.15 (s, -C-ar), 139.65 (s, -C-ar), 129.39 (s, -CH-ar), 127.15 (s, -CH-ar), 123.05 (s, -CH-ar), 119.42 (s, -CH-ar), 32.02 (s, -CH_3), 21.40 (s, -CH_3).

 (**4a**) ***N*-methyl-*N*-(4-methylphenyl)formamide:** light yellow oil, 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H, -CHO), 7.35 - 7.24 (m, 3H, -CH-ar), 7.14 - 6.99 (m, 1H, -CH-ar), 3.20 (s, 3H, -CH_3), 2.27 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.14 (s, -CHO), 139.64 (s, -C-ar), 136.12 (s, -C-ar), 130.07 (s, -CH-ar), 122.33 (s, -CH-ar), 31.98 (s, -CH_3), 20.75 (s, -CH_3).

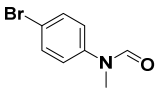
 (**5a**) ***N*-(4-methoxyl)-*N*-methylformamide**: brown oil, 95% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H, -CHO), 7.10 (d, J = 9.0 Hz, 2H, -CH-ar), 6.93 (d, J = 9.0 Hz, 2H, -CH-ar), 3.81 (s, 3H, O-CH_3), 3.29 - 3.22 (m, 3H, N-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.40 (s, -CHO), 158.23 (s, -CHO), 135.14 (s, -C-ar), 124.53 (s, -CH-ar), 114.71 (s, -CH-ar), 55.46 (s, O-CH_3), 32.57 (s, N-CH_3).

 (**6a**) ***N*-(4-fluorophenyl)-*N*-methylformamide:** claybank oil, 71% yield. ^{1}H

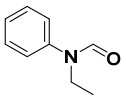
NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H, -CHO), 7.09 - 6.93 (m, 4H, -CH-ar), 3.21 (s, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.19 (s, -CHO), 159.80 (s, -C-ar), 138.33 (s, -CH-ar), 124.59 (s, -CH-ar), 116.57 (s, -CH-ar), 116.35 (s, -CH-ar), 32.44 (s, $-CH_3$).



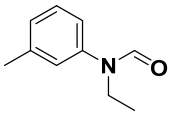
(**7a**) ***N*-(4-chlorophenyl)-*N*-methylformamide**: claybank oil, 75% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H, -CHO), 7.30 - 7.21 (m, 2H, -CH-ar), 7.04 - 6.97 (m, 2H, -CH-ar), 3.19 (s, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.95 (s, -CHO), 140.73 (s, -C-ar), 131.87 (s, -C-ar), 129.71 (s, -CH-ar), 123.44 (s, -CH-ar), 31.97 (s, $-CH_3$).



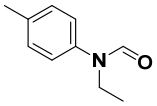
(8a) *N*-(4-bromophenyl)-*N*-methylformamide: brown solid 83% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H, -CHO), 7.57 - 7.50 (m, 2H, -CH-ar), 7.08 - 6.99 (m, 2H, -CH-ar), 3.30 (s, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.91 (s, -CHO), 141.25 (s, -C-ar), 132.72 (s, -CH-ar), 123.75 (s, -CH-ar), 119.67 (s, -C-ar), 31.96 (s, $-CH_3$).



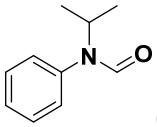
(**10a**) ***N*-Ethylformanilide:** light yellow oil, 77 % yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H, -CHO), 7.42 (t, J = 7.7 Hz, 2H, -CH-ar), 7.31 (d, J = 7.4 Hz, 1H, -CH-ar), 7.17 (d, J = 7.5 Hz, 2H, -CH-ar), 3.87 (q, J = 7.2 Hz, 2H, $-CH_2-$), 1.16 (t, J = 7.2 Hz, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.01 (s, -CHO), 140.81 (s, -C-ar), 129.63 (s, -CH-ar), 126.85 (s, -CH-ar), 124.23 (s, -CH-ar), 40.06 (s, $-CH_2-$), 13.04 (s, $-CH_3$).



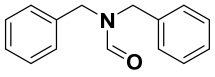
(**11a**) ***N*-ethyl-*N*-(3-methylphenyl)formamide:** light yellow oil, 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H, -CHO), 7.29 (t, *J* = 7.7 Hz, 1H, -CH-ar), 7.11 (d, *J* = 7.5 Hz, 1H, -CH-ar), 6.97 (d, *J* = 7.8 Hz, 2H, -CH-ar), 3.85 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 2.38 (s, 3H, $-CH_3$), 1.16 (dd, *J* = 8.6, 5.7 Hz, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.98 (s, -CHO), 140.73 (s, -C-ar), 139.63 (s, -C-ar), 129.37 (s, -CH-ar), 127.61 (s, -CH-ar), 124.90 (s, -CH-ar), 121.28 (s, -CH-ar), 40.02 (s, -CH-ar), 21.34 (s, $-CH_2-$), 13.04 (s, $-CH_3$).



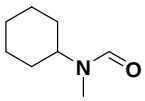
(1**2a**) ***N*-ethyl-*N*-(4-methylphenyl)formamide:** light yellow oil, 85 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H, -CHO), 7.21 (d, *J* = 8.1 Hz, 2H, -CH-ar), 7.05 (dd, *J* = 8.6, 2.1 Hz, 2H, -CH-ar), 3.83 (q, *J* = 7.2 Hz, 2H, $-CH_2-$), 2.35 (d, *J* = 7.9 Hz, 3H, $-CH_3$), 1.22 - 1.08 (m, 3H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.97 (s, -CHO), 138.17 (s, -C-ar), 136.77 (s, -C-ar), 130.14 (s, -CH-ar), 124.37 (s, -CH-ar), 40.06 (s, $-CH_2-$), 20.85 (s, $-CH_3$), 12.96 (s, $-CH_3$).



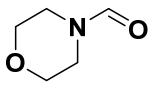
(**13a**) ***N*-isopropy-*N*-phenylformamide:** light yellow oil, 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H, -CHO), 7.47 - 7.36 (m, 3H, -CH-ar), 7.18 - 7.08 (m, 2H, -CH-ar), 4.80 (dt, *J* = 13.7, 6.8 Hz, 1H, -CH-), 1.20 (d, *J* = 6.8 Hz, 6H, $-CH_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.55 (s, -CHO), 138.40 (s, -C-ar), 129.24 (s, -CH-ar), 128.97 (s, -CH-ar), 128.15 (s, -CH-ar), 45.77 (s, -CH-), 20.93 (s, $-CH_3$).



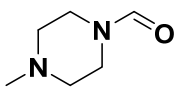
(**15a**) ***N,N'*-dibenzylformamide:** colorless solid, 96 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H, -CHO), 7.41 - 7.20 (m, 6H, -CH-ar), 7.20 - 7.03 (m, 4H, -CH-ar), 4.36 (s, 2H, -CH_2-), 4.19 (s, 2H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89 (s, -CHO), 136.13 (s, -C-ar), 135.77 (s, -C-ar), 128.96 (s, -CH-ar), 128.75 (s, -CH-ar), 128.54 (s, -CH-ar), 128.16 (s, -CH-ar), 127.74 (d, -CH-ar), 50.21 (s, -CH_2-), 44.62 (s, -CH_2-).



(16a) *N*-cyclohexyl-*N*-methylformamide: light yellow oil, 93 % yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H, -CHO), 7.95 (s, 1H, -CHO), 4.12 (d, *J* = 3.7 Hz, 1H, -CH-), 3.22 (dd, *J* = 7.8, 4.0 Hz, 1H, -CH-), 2.83 - 2.69 (m, 3H, -CH_3), 1.77 - 1.11 (m, 10H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.38 (d, -CHO), 62.96 (s, -CH-), 58.18 (s, -CH-), 50.79 (s, -CH_2-), 38.05 (s, -CH_2-), 31.31 (s, -CH_2-), 30.25 (s, -CH_2-), 29.46 (s, -CH_2-), 29.20 (s, -CH_2-), 27.88 (s, -CH_2-), 25.95 (s, -CH_2-), 25.49 (s,-CH_3), 25.13 (s,-CH_3).

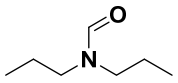


(17a) *N*-formylmorpholine: colourless liquid 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H, -CHO), 3.69 (ddd, *J* = 15.5, 7.3, 3.8 Hz, 4H, -CH_2-), 3.59 - 3.55 (m, 2H, -CH_2-), 3.42 (dd, *J* = 6.3, 3.4 Hz, 2H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$, -CHO) δ 160.79 (s, -CH_2-), 67.16 (s, -CH_2-), 66.34 (s, -CH_2-), 45.71 (s, -CH_2-), 40.50 (s, -CH_2-).

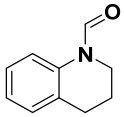


(18a) 1-formyl-4-methylpiperazine: light yellow oil, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H, -CHO), 3.50 -3.37 (m, 2H, -CH_2-), 3.33 - 3.19 (m, 2H,

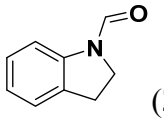
-CH_2-), 2.34 - 2.21 (m, 4H, -CH_2-), 2.20 (s, 3H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.63 (s, -CHO), 55.25 (s, -CH_2-), 54.09 (s, -CH_2-), 46.02 (s, -CH_2-), 45.38 (s, -CH_2-), 39.68 (s, -CH_3).



(19a) *N'N*-dipropylformamide: colourless liquid 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H, -CHO), 3.25 - 3.14 (m, 2H, -CH_2-), 3.13 - 3.02 (m, 2H, -CH_2-), 1.55 - 1.37 (m, 4H, -CH_2-), 0.83 (td, *J* = 7.4, 2.6 Hz, 6H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.87 (s, -CHO), 49.17 (s, -CH_2-), 43.73 (s, -CH_2-), 21.79 (s, -CH_2-), 20.50 (s, -CH_2-), 11.30 (s, -CH_3), 10.90 (s, -CH_3).

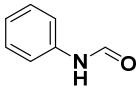


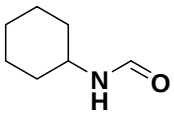
(**22a**) **3,4-dihydroquinoline-1(2H)-carbaldehyde**: yellow oil, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H, -CHO), 7.22 - 7.02 (m, 4H, -CH-ar), 3.85 - 3.69 (m, 2H, -CH_2-), 2.80 (t, *J* = 6.4 Hz, 2H, -CH_2-), 1.94 (dt, *J* = 12.5, 6.3 Hz, 2H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.06 (s, -CHO), 137.19 (s, -C-ar), 129.60 (s, -CH-ar), 128.85 (s, -C-ar), 127.06 (s, -CH-ar), 124.50 (s, -CH-ar), 116.97 (s, -CH-ar), 40.24 (s, -CH_2-), 27.08 (s, -CH_2-), 22.22 (s, -CH_2-).

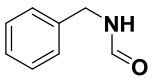


(**23a**) **Indoline-1-carbaldehyde:** claybank oil, 95% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H, -CHO), 8.53 (s, 1H, -CHO), 8.08 (d, *J* = 8.5 Hz, 1H, -CHO), 7.31 - 7.11 (m, 3H, -CH-ar), 7.12 - 6.99 (m, 1H, -CH-ar), 4.20 - 3.96 (m, 2H, -CH_2-), 3.24 - 3.06 (m, 2H, -CH_2-). ^{13}C NMR (101 MHz, CDCl3) δ 159.35 (s, -CHO),

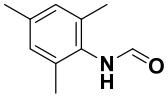
157.57 (s, -CHO), 141.06 (s, -C-ar), 131.93 (s, -C-ar), 127.56 (d, -CH-ar), 126.06 (s, -CH-ar), 124.87 (s, -CH-ar), 124.56 (s, -C-ar), 116.60 (s, -C-ar), 109.40 (s, -CH-ar), 46.95 (s, -CH_2-), 44.64 (s, -CH_2-), 27.74 (s, -CH_2-), 27.17 (s, -CH_2-).

 **(26a) *N*-phenylformamide**: colorless solid, 74% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (b, 1H, -NH-), 8.70 (d, *J* = 11.4 Hz, 1H, -CHO), 8.32 (d, *J* = 1.5 Hz, 2H, -CHO), 7.55 (dt, *J* = 8.7, 1.7 Hz, 2H, -CH-ar), 7.41 - 7.24 (m, 4H -CH-ar), 7.24 - 7.03 (m, 4H, -CH-ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.22 (s, -CHO), 159.73 (s, -CHO), 137.09 (s, -C-ar), 136.89 (s, -C-ar), 130.03 (s, -CH-ar), 129.75 (s, -CH-ar), 129.36 (s, -CH-ar), 129.09 (s, -CH-ar), 125.28 (s, -CH-ar), 124.80 (s, -CH-ar), 120.21 (s, -CH-ar), 118.79 (s, -CH-ar).

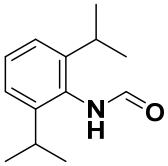
 (**27a**) ***N*-cyclohexylformamide**: light yellow oil, 83% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 12.0 Hz, 1H, -CHO), 6.54 (d, *J* = 70.7 Hz, 1H, -NH-), 3.92 - 3.71 (m, 1H, -CH-), 3.29 (s, 1H, -CH-), 2.03 - 1.56 (m, 6H, -CH_2-), 1.38 - 1.13 (m, 6H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.95 (s, -CHO), 160.73 (s, -CHO), 51.26 (s, -CH-), 47.08 (s, -CH-), 34.48 (s, -CH_2-), 32.84 (s, -CH_2-), 25.36 (s, -CH_2-), 24.71 (s, -CH_2-).

 **(28a) *N*-benzylformamide:** light yellow oil, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H, -CHO), 7.21 (dt, *J* = 13.4, 7.7 Hz, 5H, -CH-ar), 6.36 (s, 1H, N-H), 4.34 (d, *J* = 5.9 Hz, 2H, -CH_2-). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.27 (s, -CHO), 137.67 (s,

-C-ar), 128.74 (s), 127.67 (s, -C-ar), 127.61 (s, -C-ar), 42.10 (s, -CH_2-).



(29a) *N*-mesitylformamide: colorless solid, 86% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 1.2 Hz, 1H, -CHO), 8.04 (d, *J* = 11.9 Hz, 1H, -CHO), 6.90 (d, *J* = 21.4 Hz, 2H, -CH-ar), 2.24 (t, *J* = 22.0 Hz, 9H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30 (s, -CHO), 159.97 (s, -CHO), 137.51 (s, -C-ar), 135.17 (s, -C-ar), 134.93 (s, -CH-ar), 130.52 (s, -CH-ar), 129.71 (s, -CH-ar), 129.33 (s, -C-ar), 128.96 (s, -C-ar), 20.92 (d, -CH_3), 18.63 (s, -CH_3), 18.42 (s, -CH_3).



(30a) *N*-(2,6-diisopropylphenyl)formamide: colorless solid, 81% yield. Mixture of cis and trans rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H, -CHO), 8.03 (d, *J* = 11.9 Hz, 1H, -CHO), 7.51 (d, *J* = 11.4 Hz, 1H, -CH-ar), 7.33 (dd, *J* = 15.1, 7.2 Hz, 1H, -CH-ar), 7.20 (dd, *J* = 7.7, 4.9 Hz, 2H, -CH-ar), 7.06 (s, 1H, -CH-ar), 3.22 (dt, *J* = 13.7, 6.9 Hz, 1H, -CH-), 3.11 (dt, *J* = 13.7, 6.9 Hz, 1H, -CH-), 1.21 (d, *J* = 2.7 Hz, 12H, -CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.43 (s, -CHO), 160.83 (s, -CHO), 146.78 (s, -C-ar), 146.10 (s, -C-ar), 130.02 (s, -CH-ar), 129.47 (s, -CH-ar), 128.95 (s, -C-ar), 128.83 (s, -C-ar), 123.83 (s, -CH-ar), 123.59 (s, -CH-ar), 28.81 (s, -CH-), 28.43 (s, -CH-), 23.66 (s, -CH_3).

6. Original NMR spectra

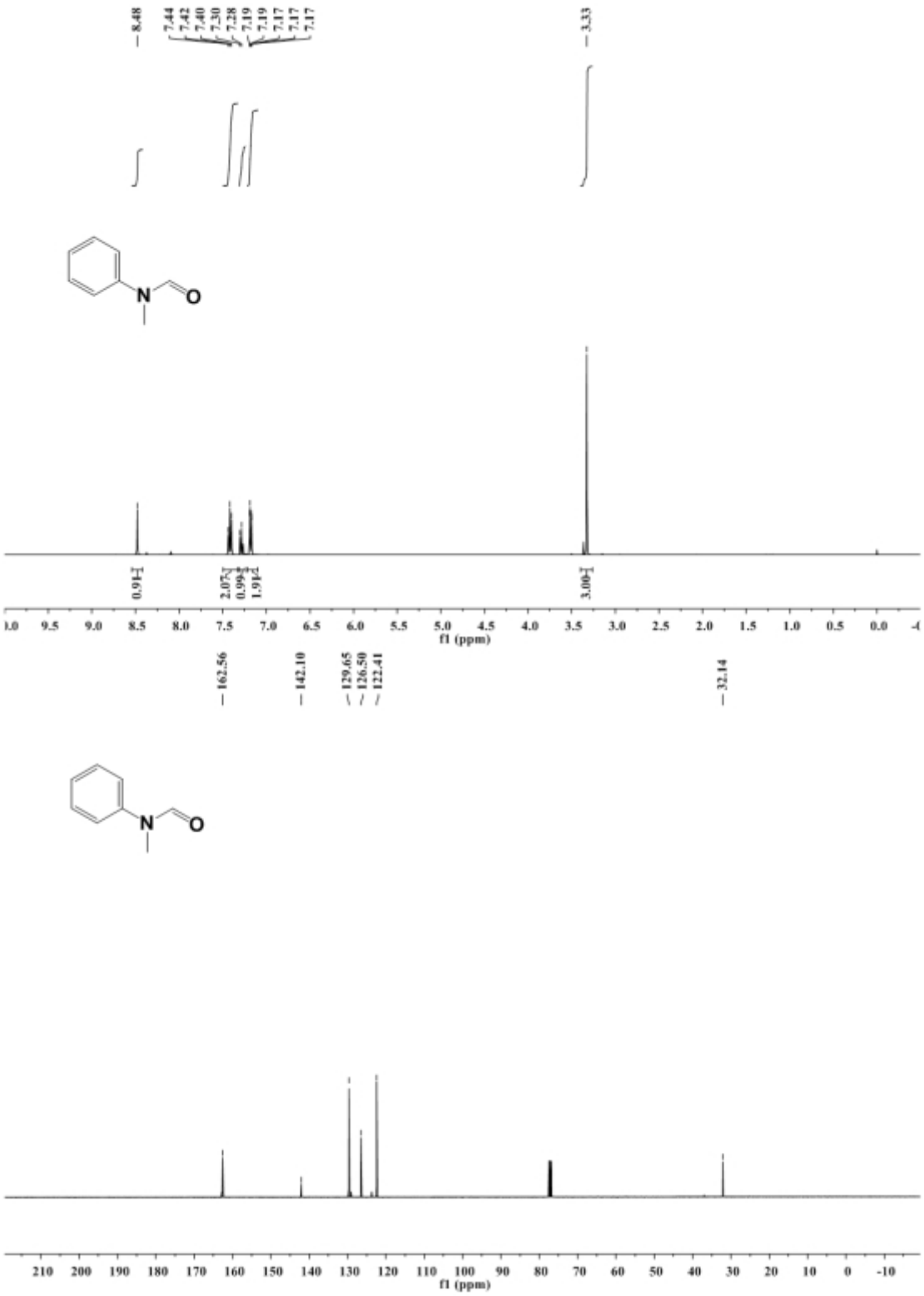


Fig. S3 The ^{1}H NMR and ^{13}C NMR spectra of **1a**.

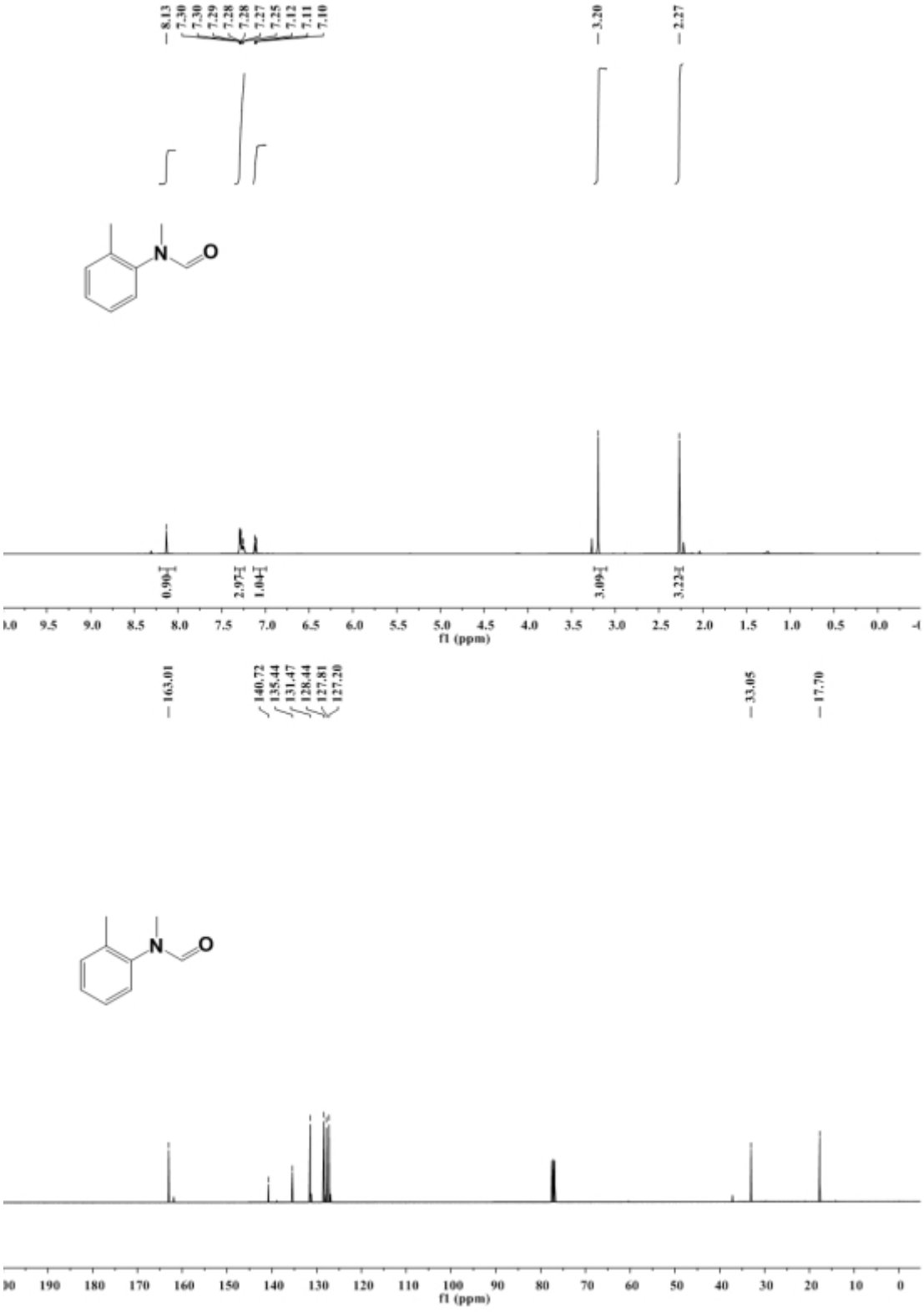


Fig. S4 The ^{1}H NMR and ^{13}C NMR spectra of **2a**.

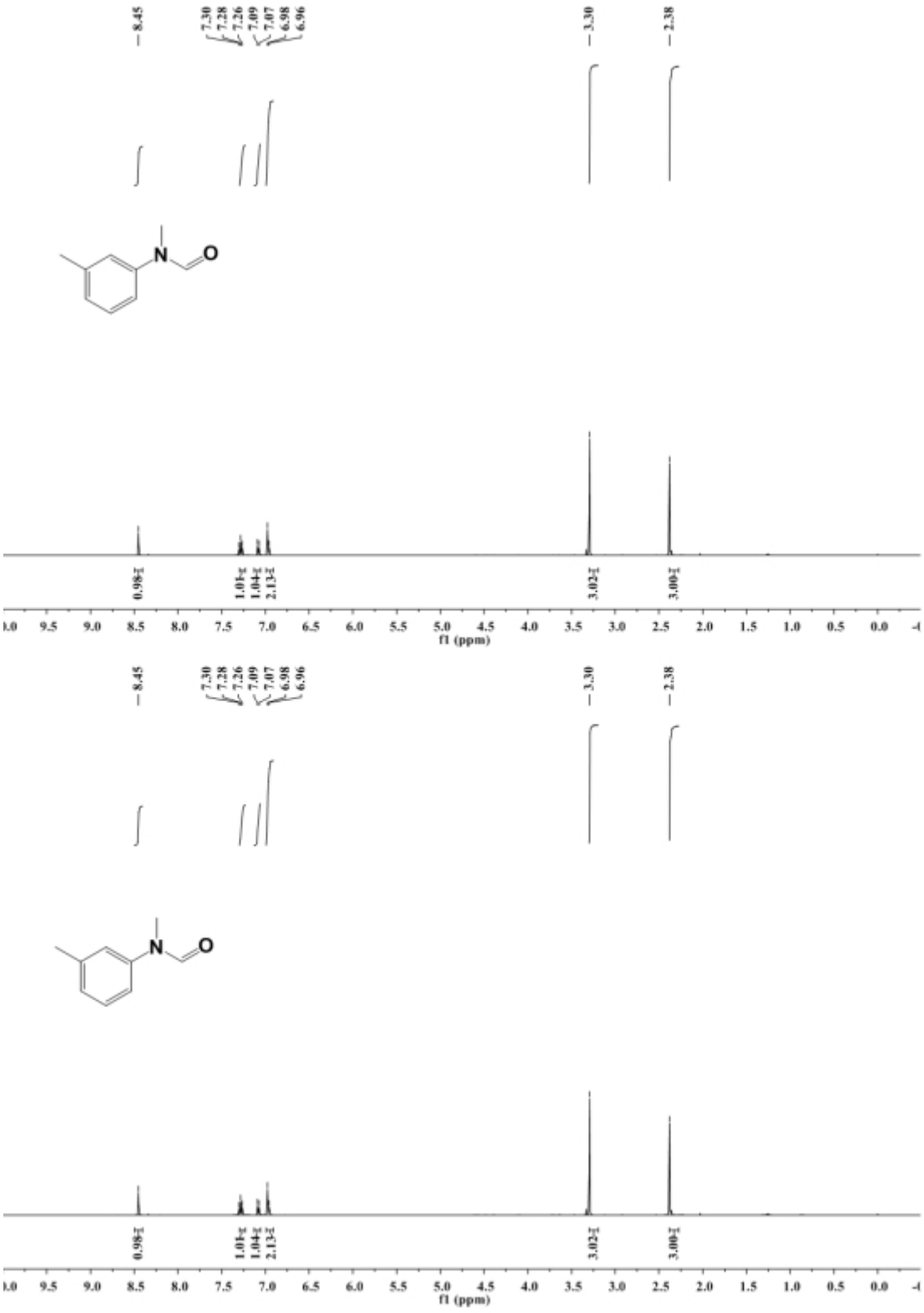


Fig. S5 The ^{1}H NMR and ^{13}C NMR spectra of **3a**.

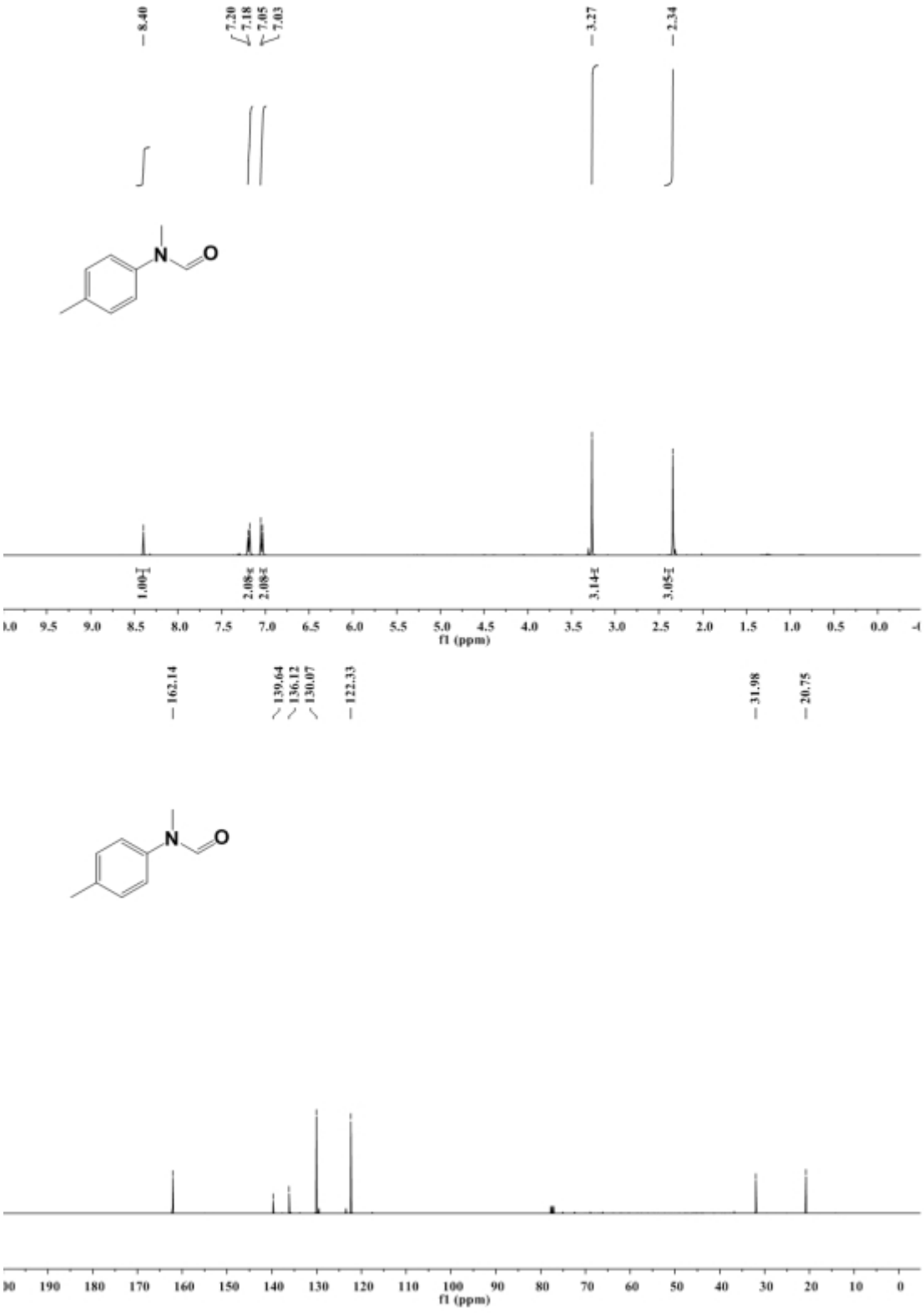


Fig. S6 The ^{1}H NMR and ^{13}C NMR spectra of **4a**.

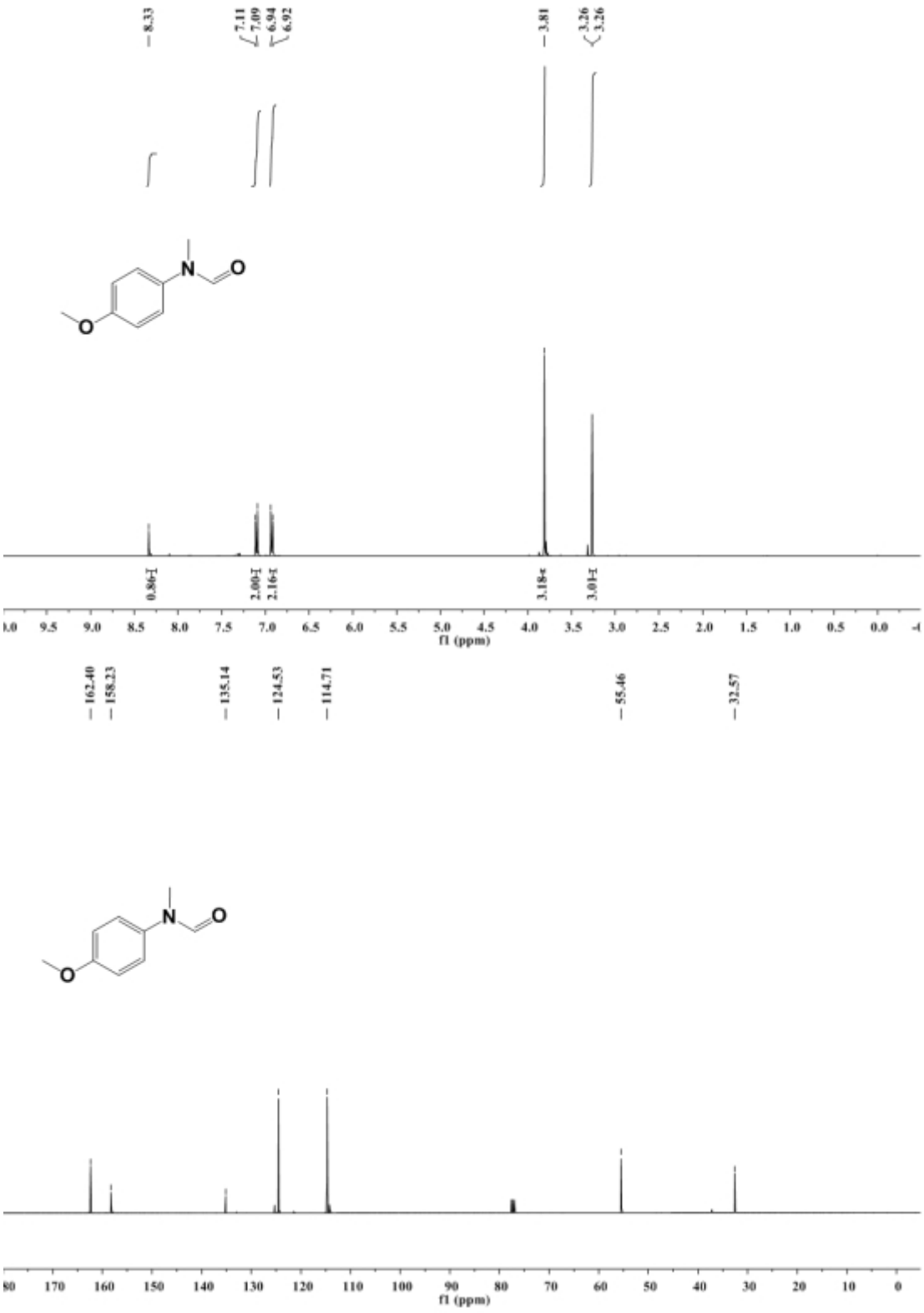


Fig. S7 The ^{1}H NMR and ^{13}C NMR spectra of **5a**.

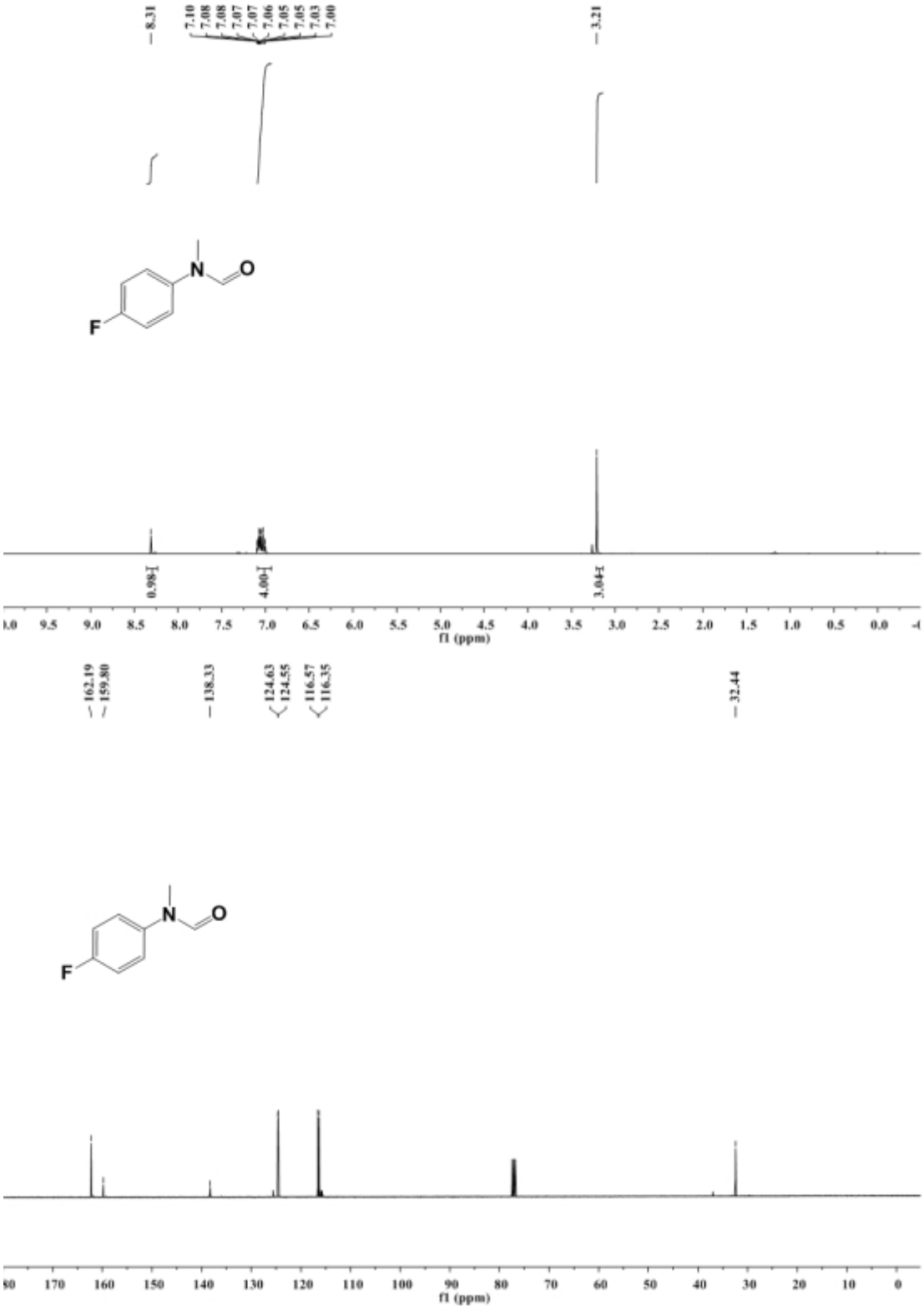


Fig. S8 The ^{1}H NMR and ^{13}C NMR spectra of **6a**.

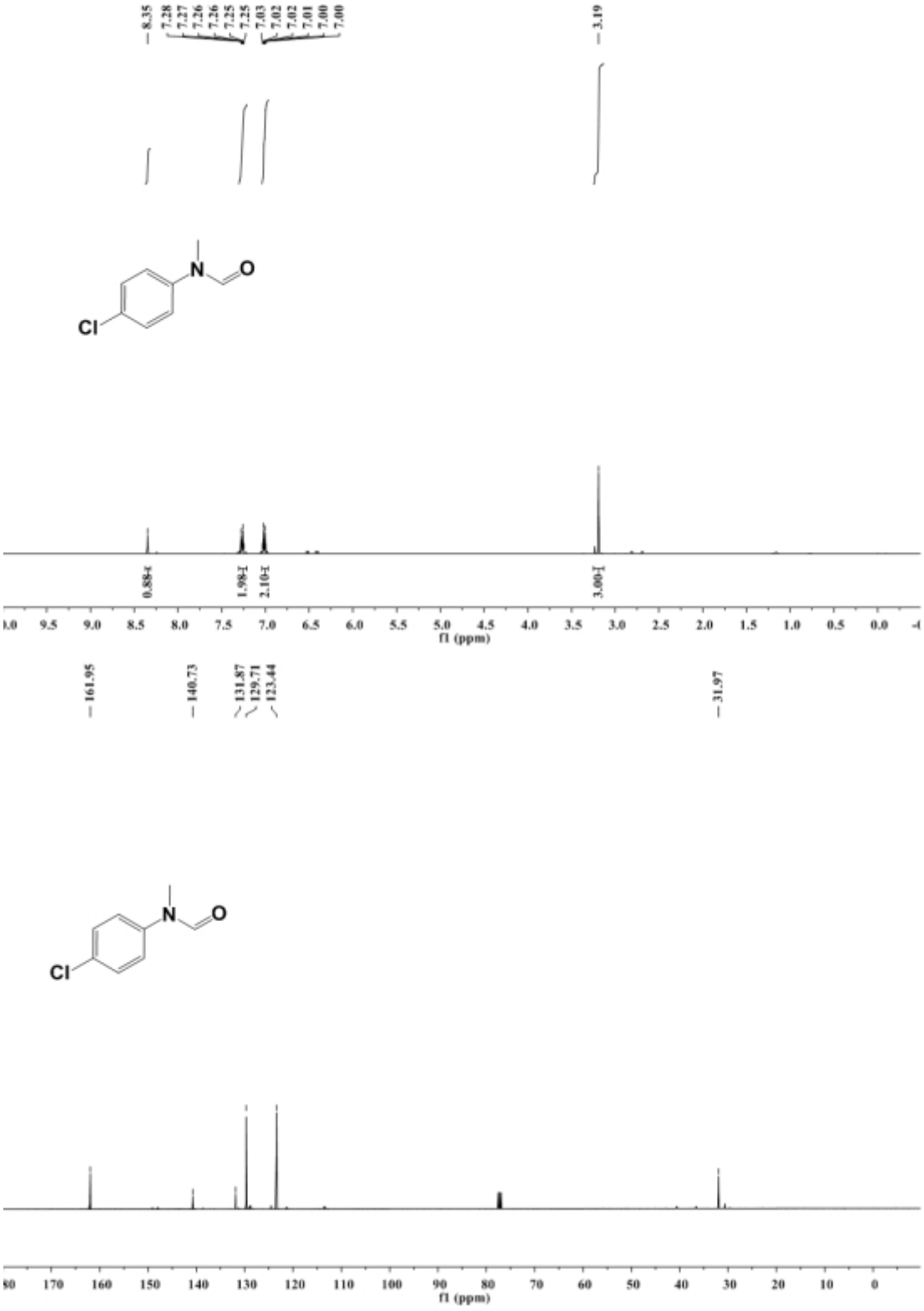


Fig. S9 The ^{1}H NMR and ^{13}C NMR spectra of **7a**.

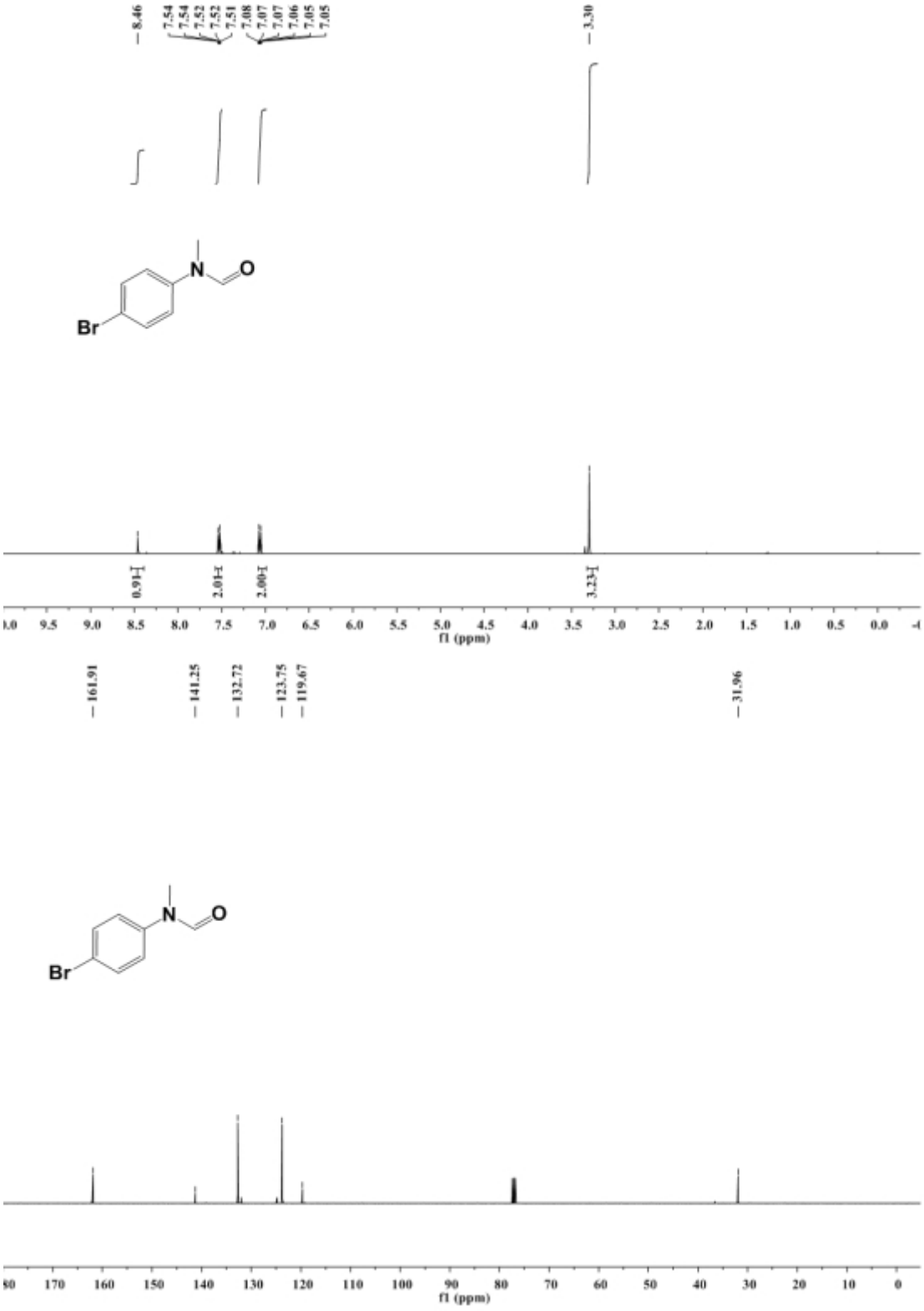


Fig. S10 The ^{1}H NMR and ^{13}C NMR spectra of **8a**.

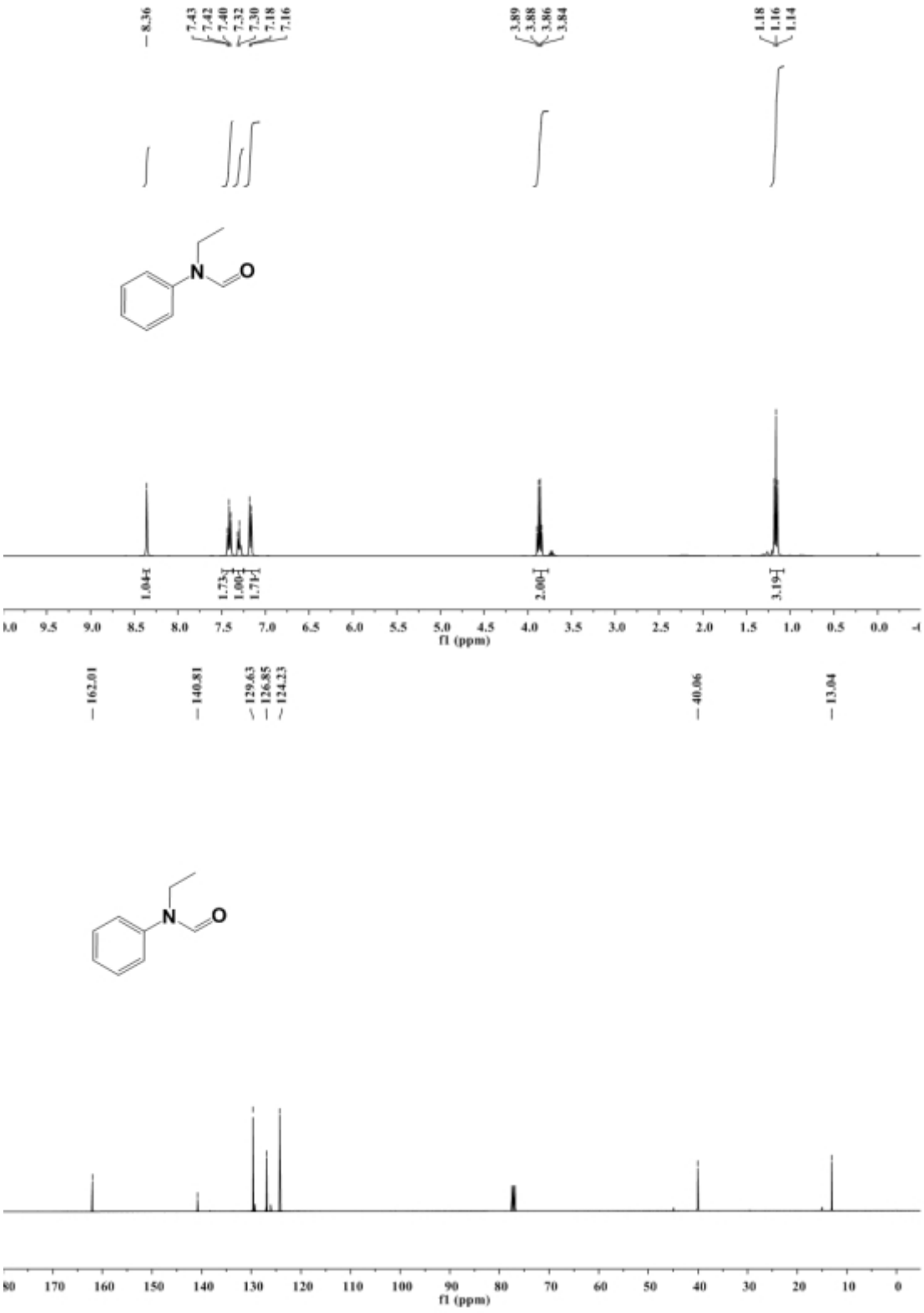


Fig. S11 The ^{1}H NMR and ^{13}C NMR spectra of **10a**.

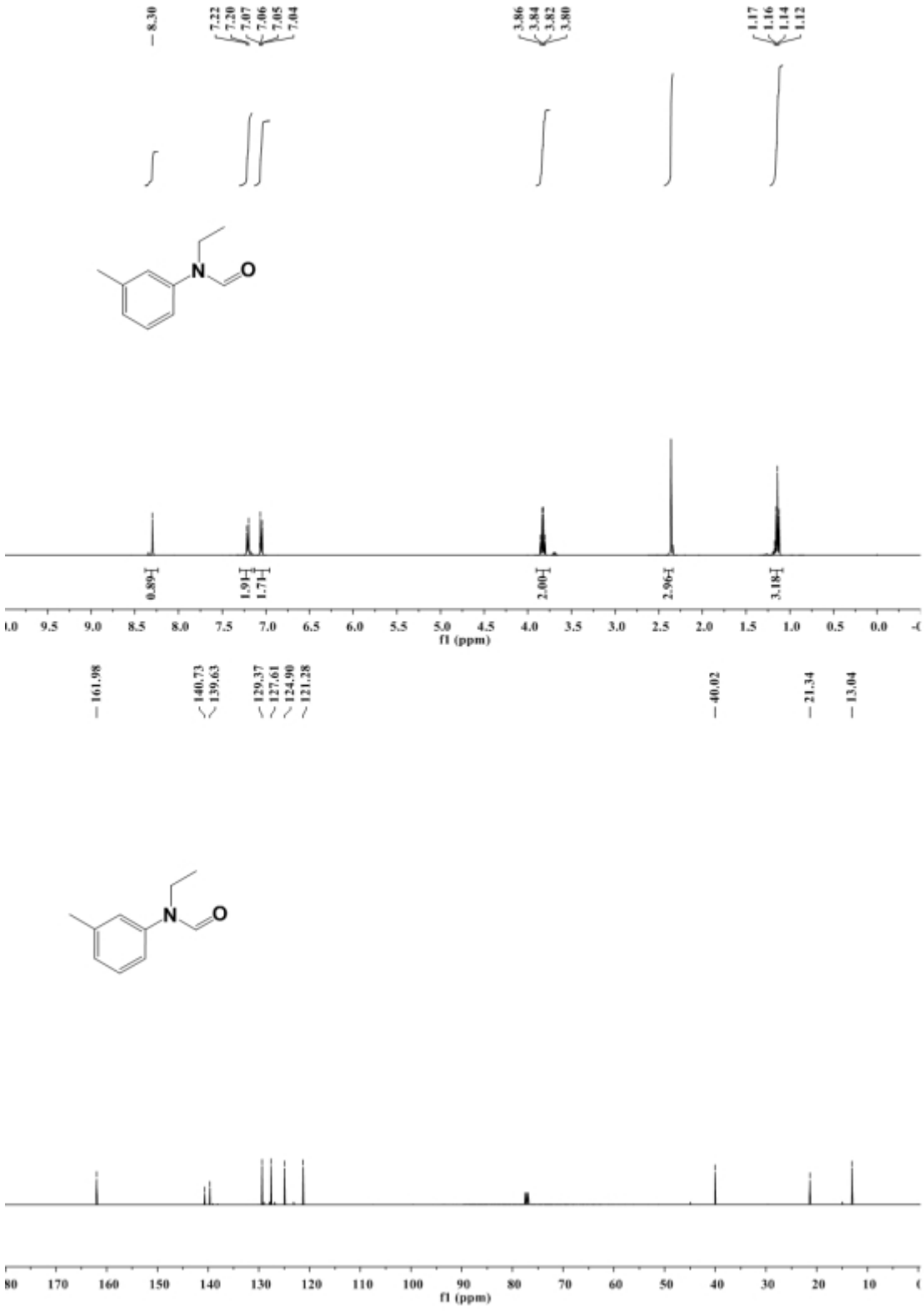


Fig. S12 The ^{1}H NMR and ^{13}C NMR spectra of **11a**.

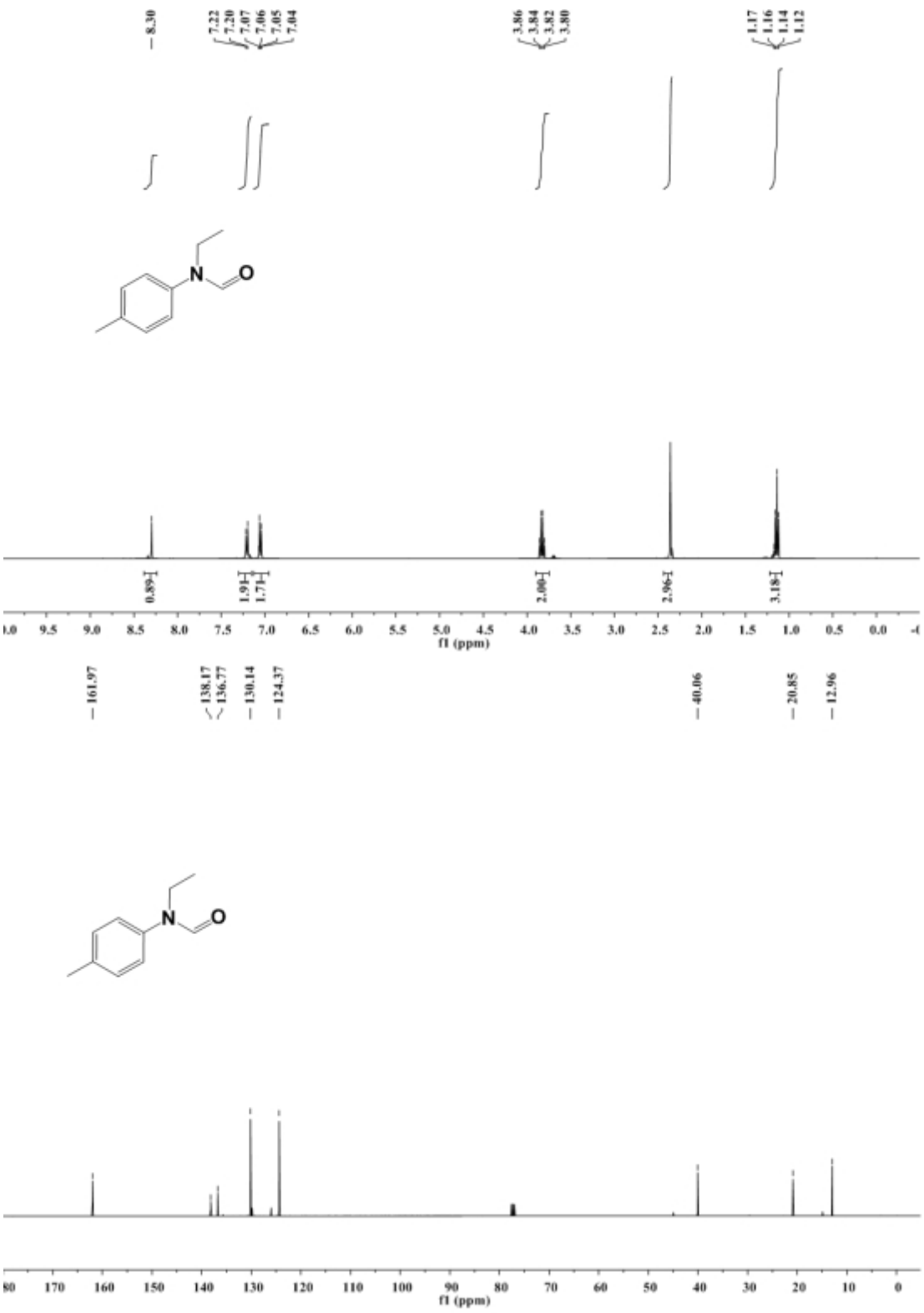


Fig. S13 The ^{1}H NMR and ^{13}C NMR spectra of **12a**.

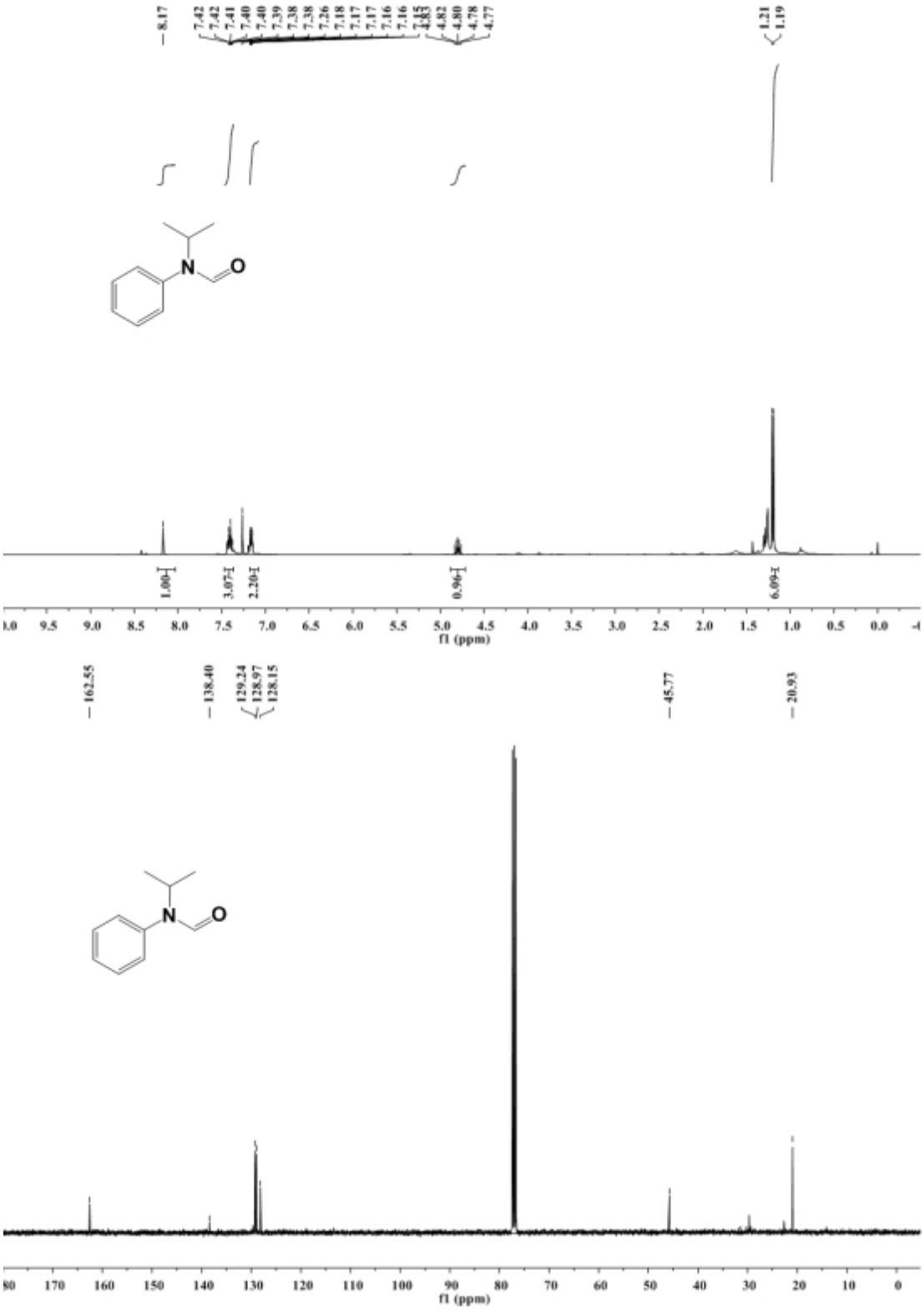


Fig. S14 The ^{1}H NMR and ^{13}C NMR spectra of **13a**.

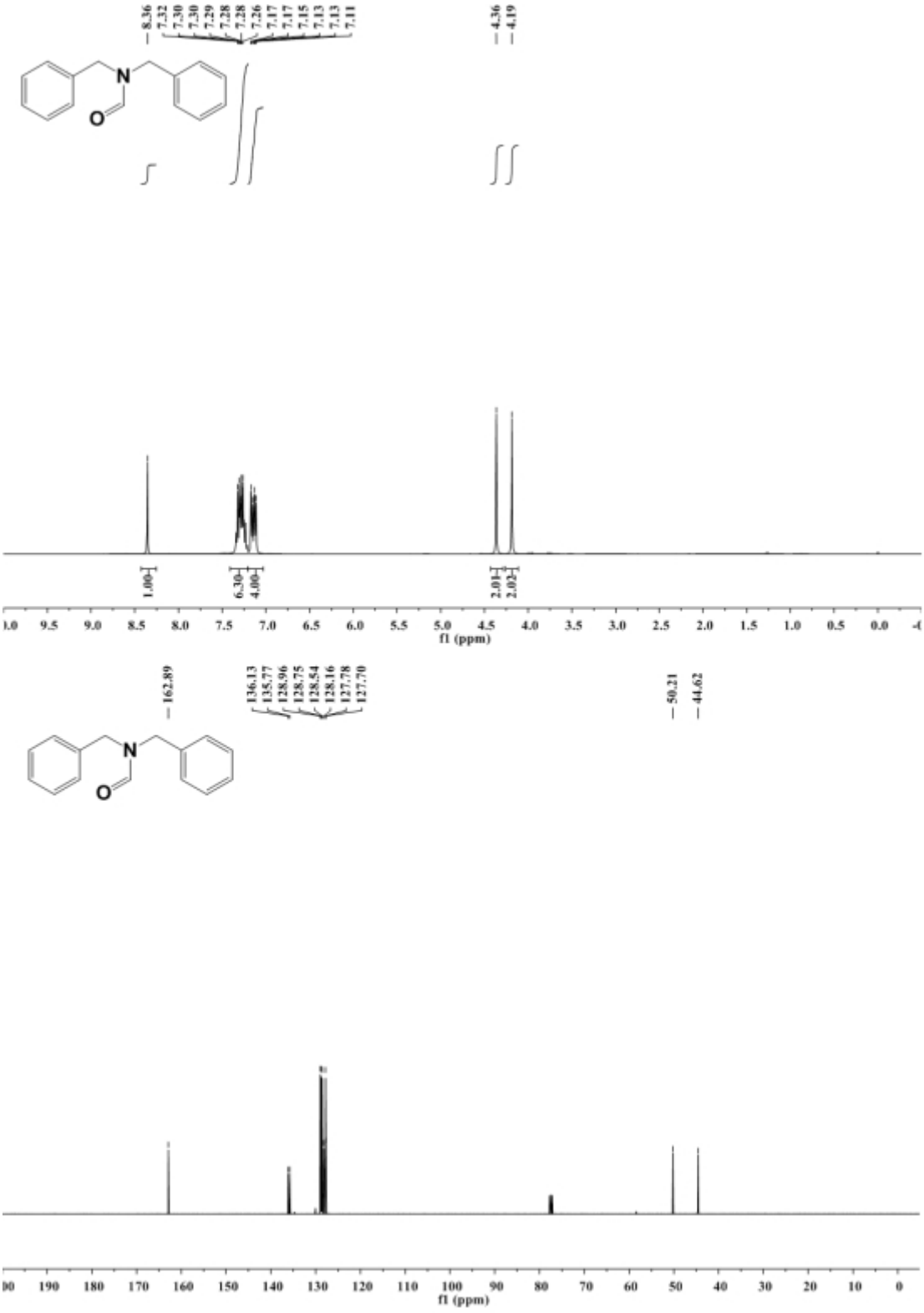


Fig. S15 The ^{1}H NMR and ^{13}C NMR spectra of **15a**.

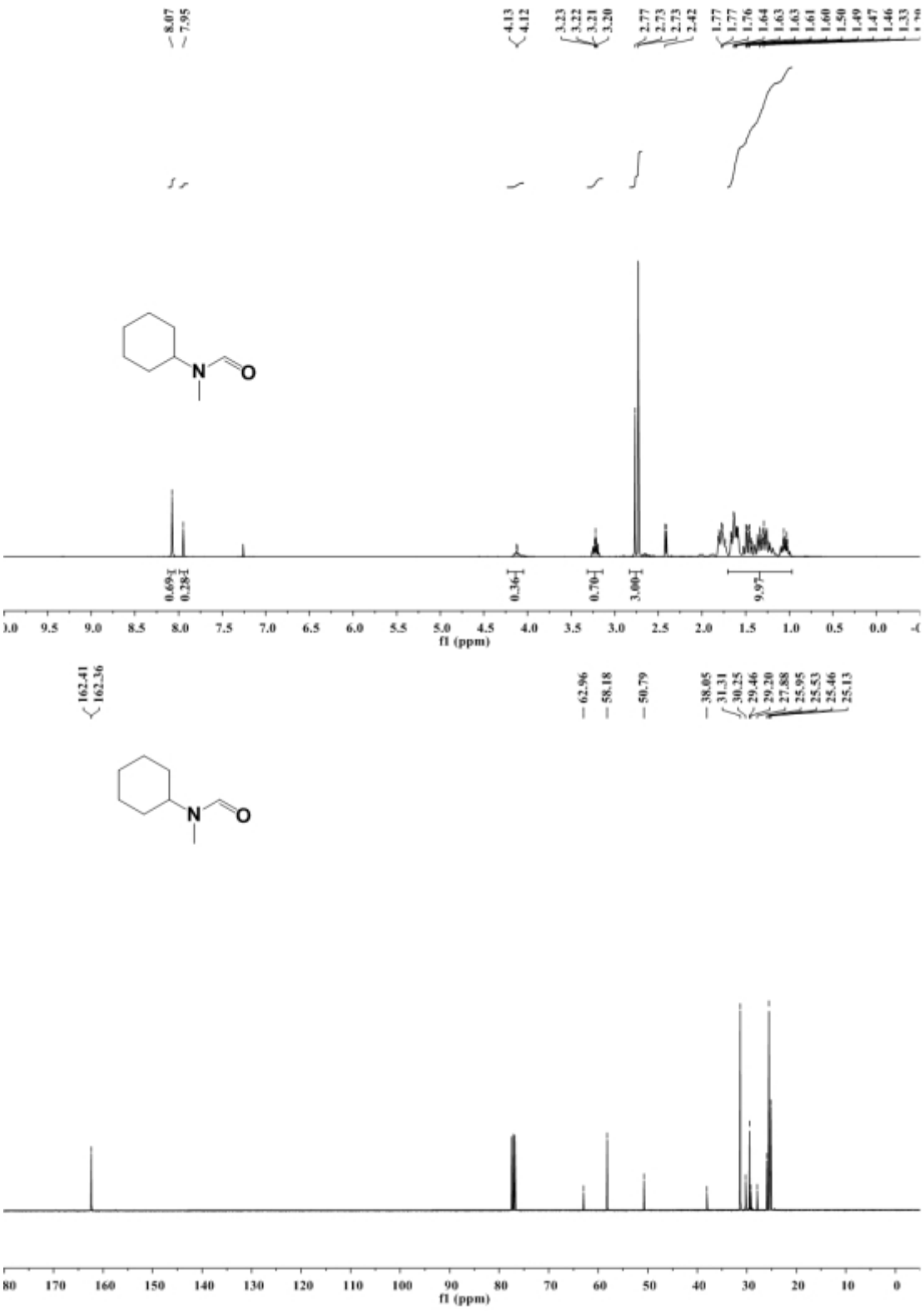


Fig. S16 The ^{1}H NMR and ^{13}C NMR spectra of **16a**.

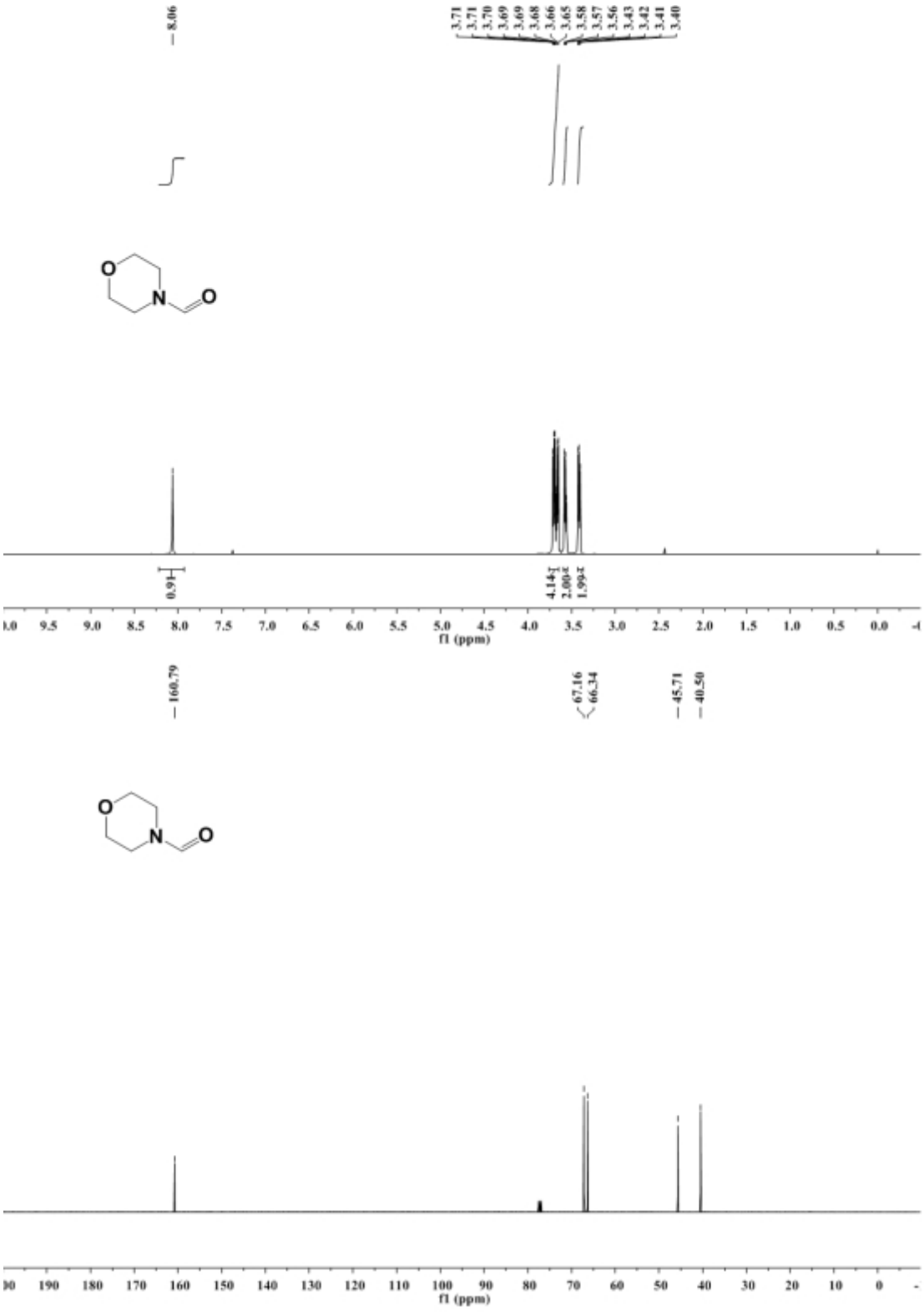


Fig. S17 The ^{1}H NMR and ^{13}C NMR spectra of **17a**.

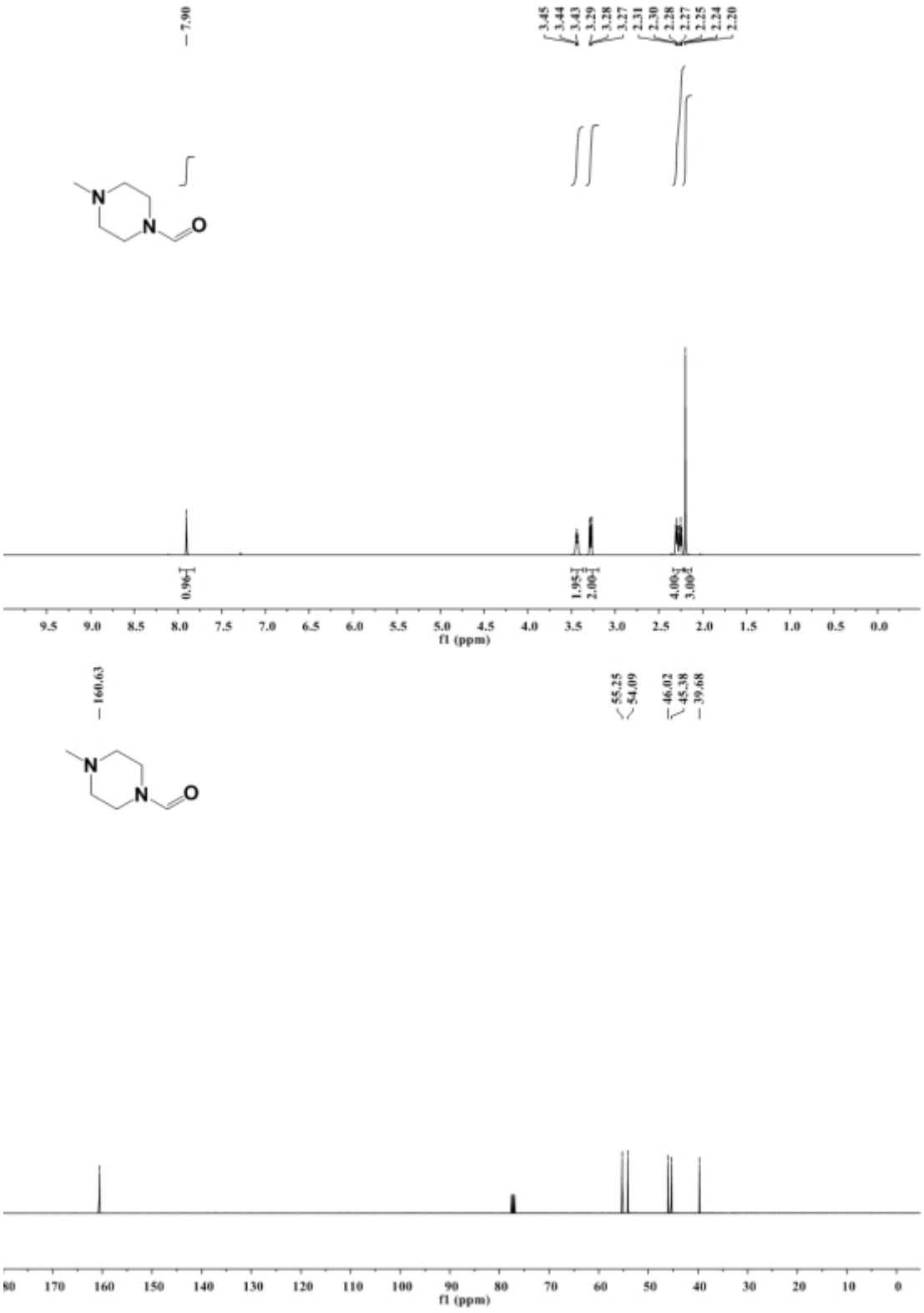


Fig. S18 The ^{1}H NMR and ^{13}C NMR spectra of **18a**.

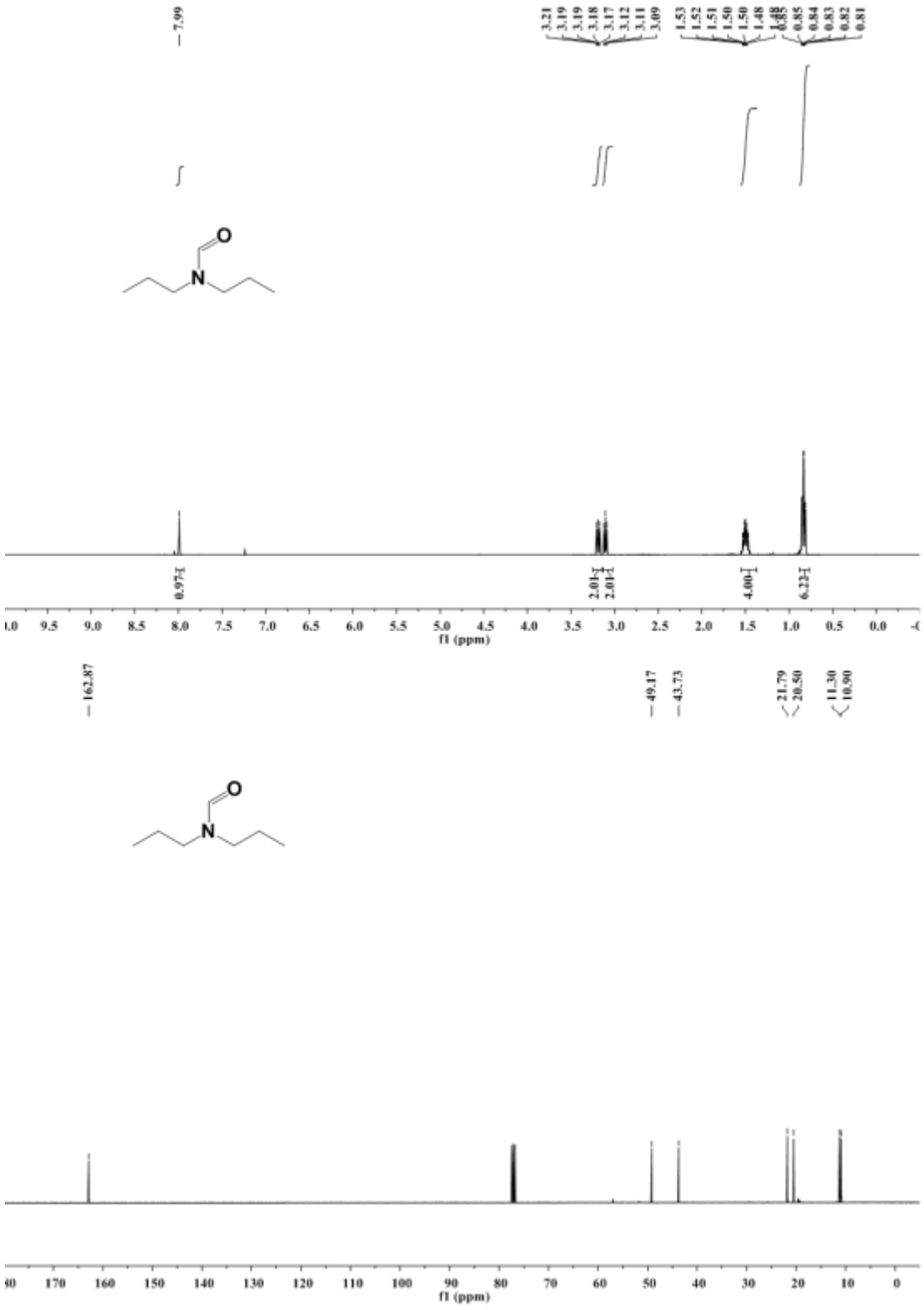


Fig. S19 The ^{1}H NMR and ^{13}C NMR spectra of **19a**.

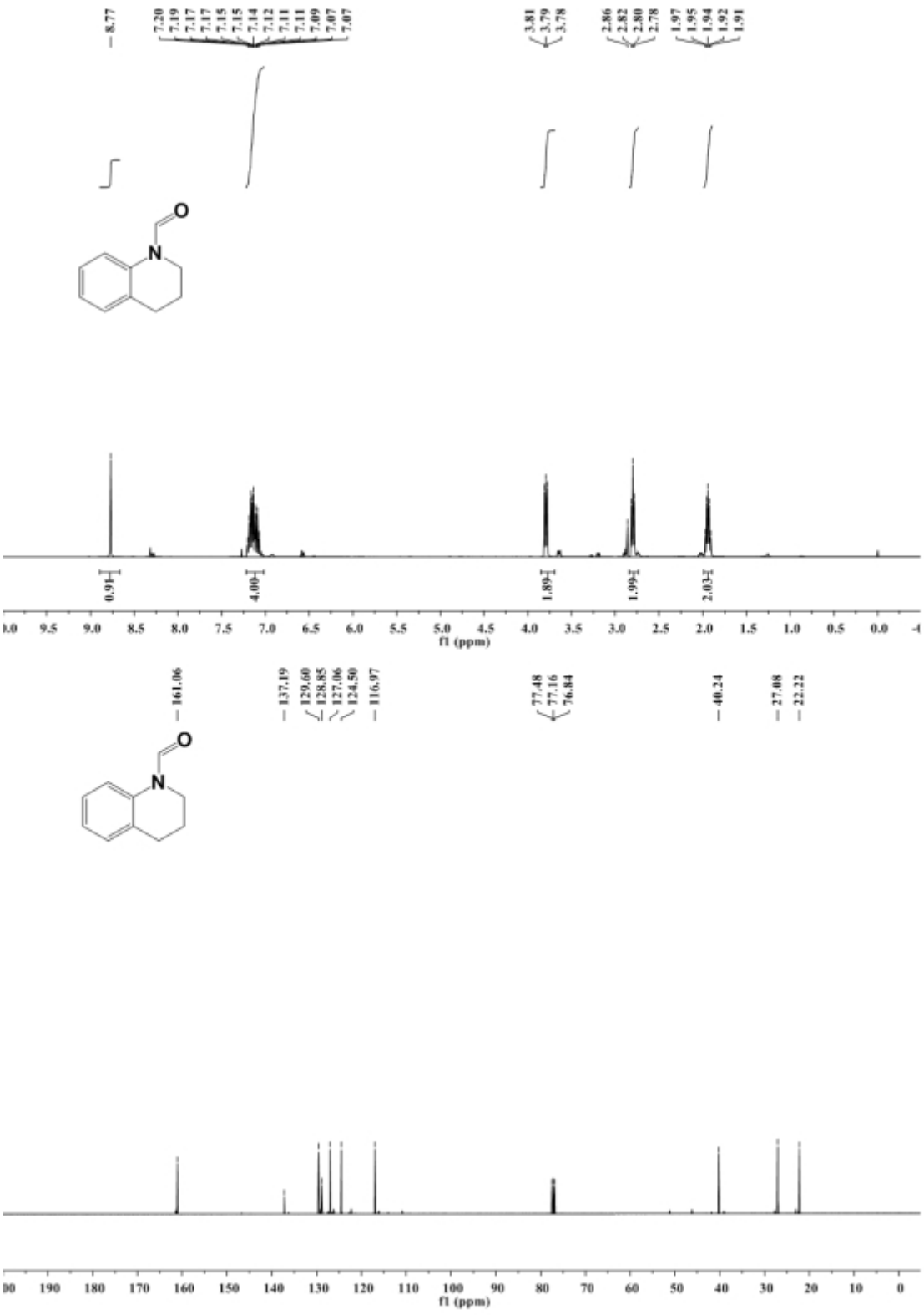


Fig. S20 The ^{1}H NMR and ^{13}C NMR spectra of **22a**.

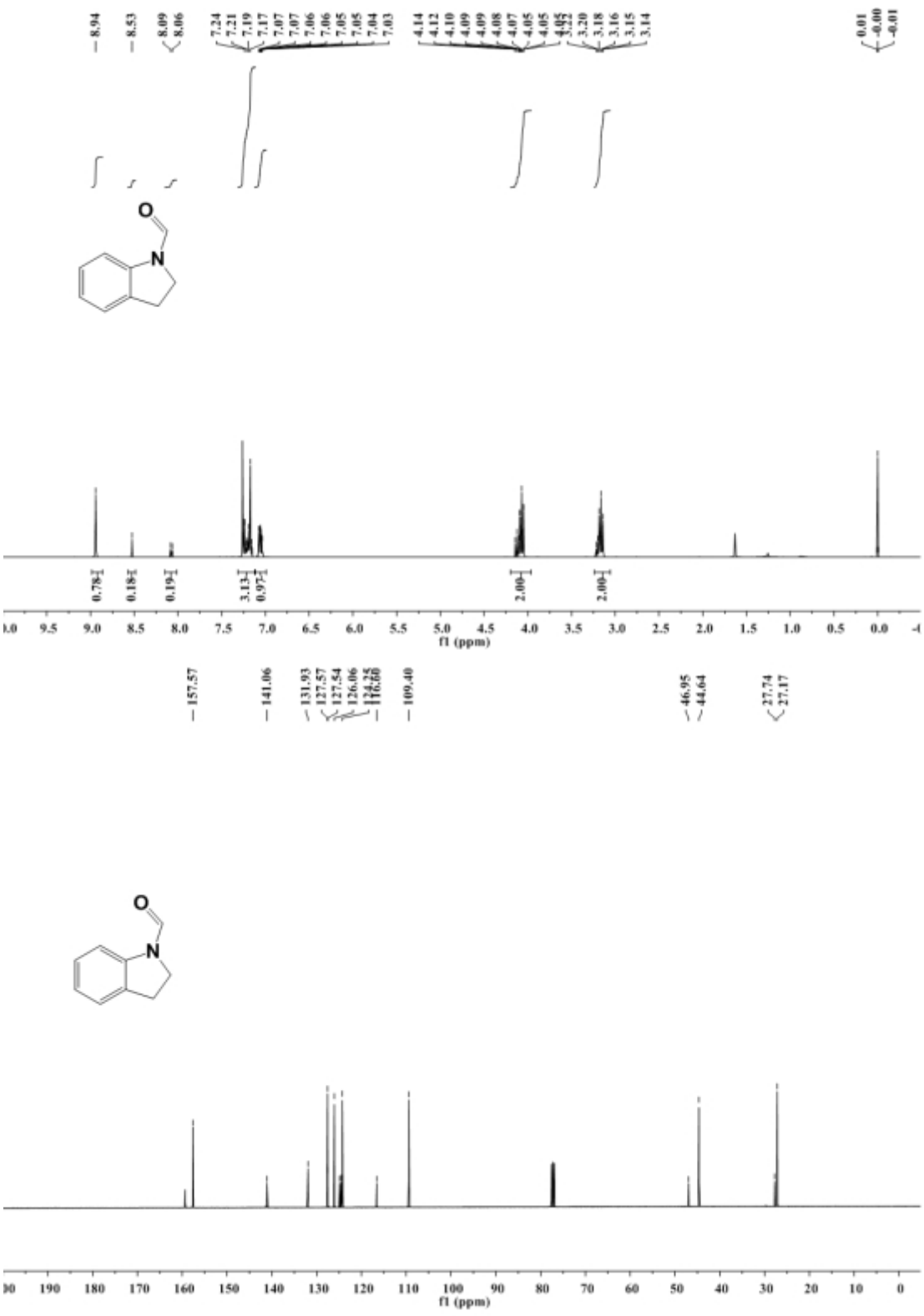


Fig. S21 The ^{1}H NMR and ^{13}C NMR spectra of **23a**.

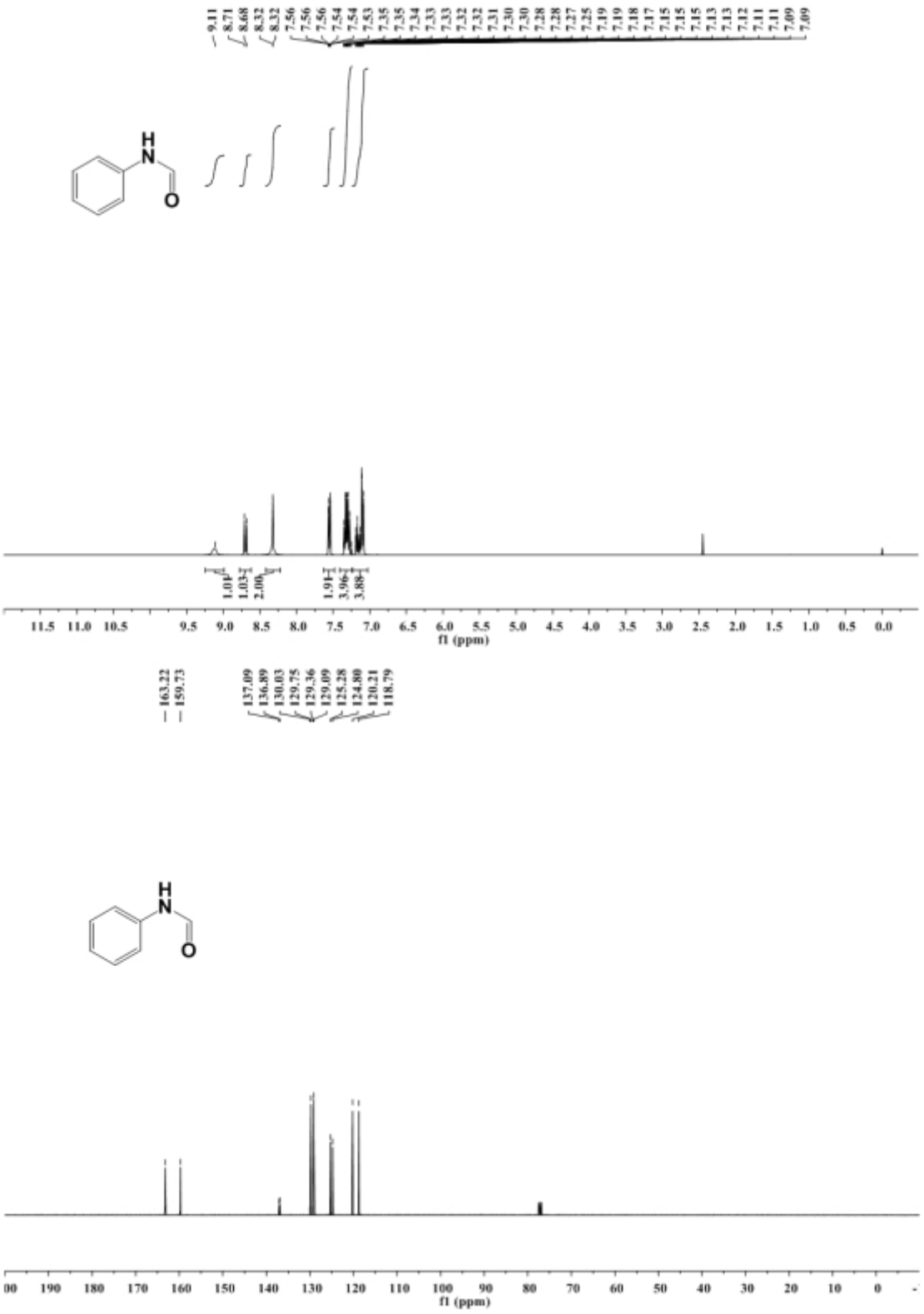


Fig. S22 The ^{1}H NMR and ^{13}C NMR spectra of **26a**.

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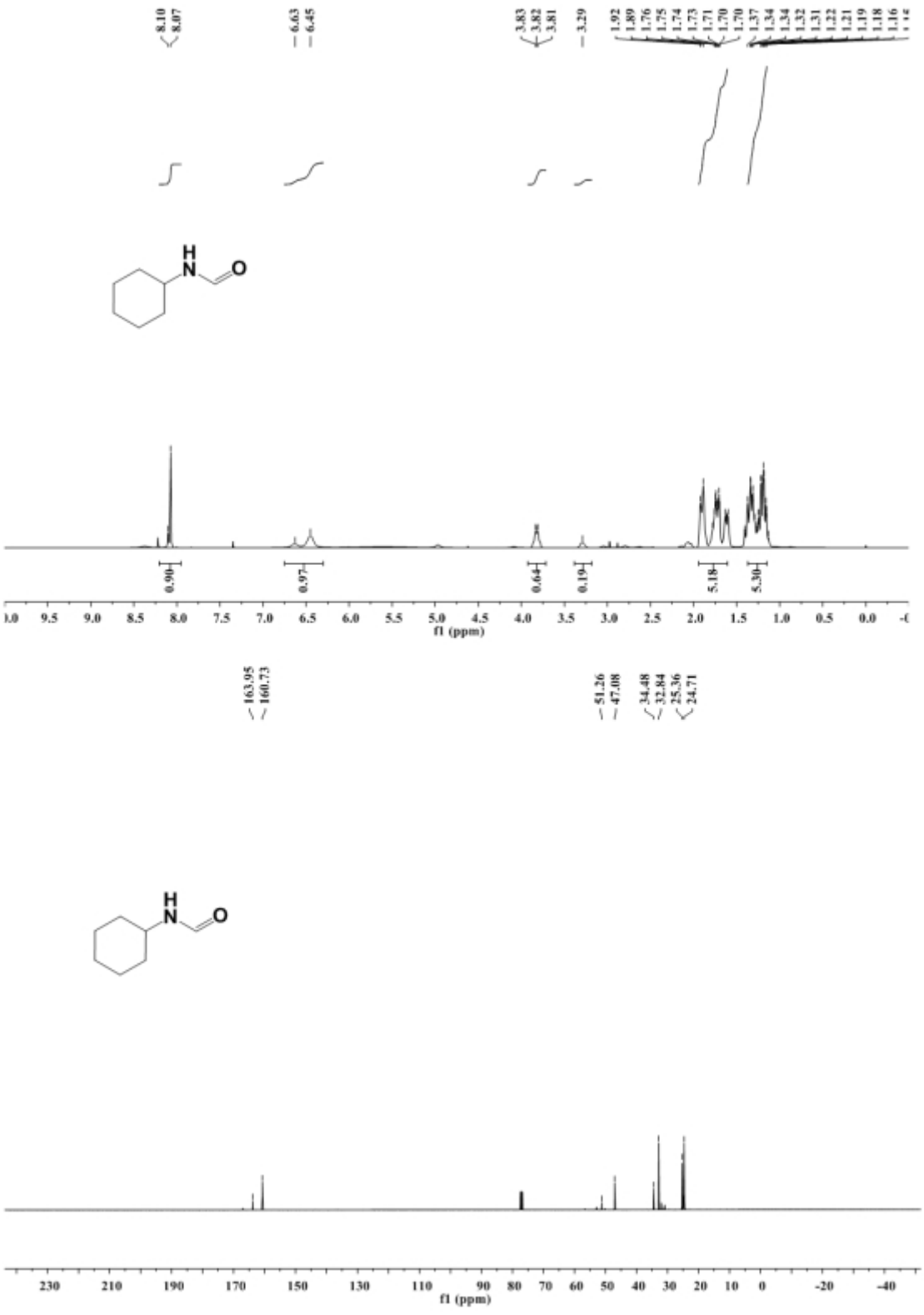

Fig. S23 The ^{1}H NMR and ^{13}C NMR spectra of **27a**.

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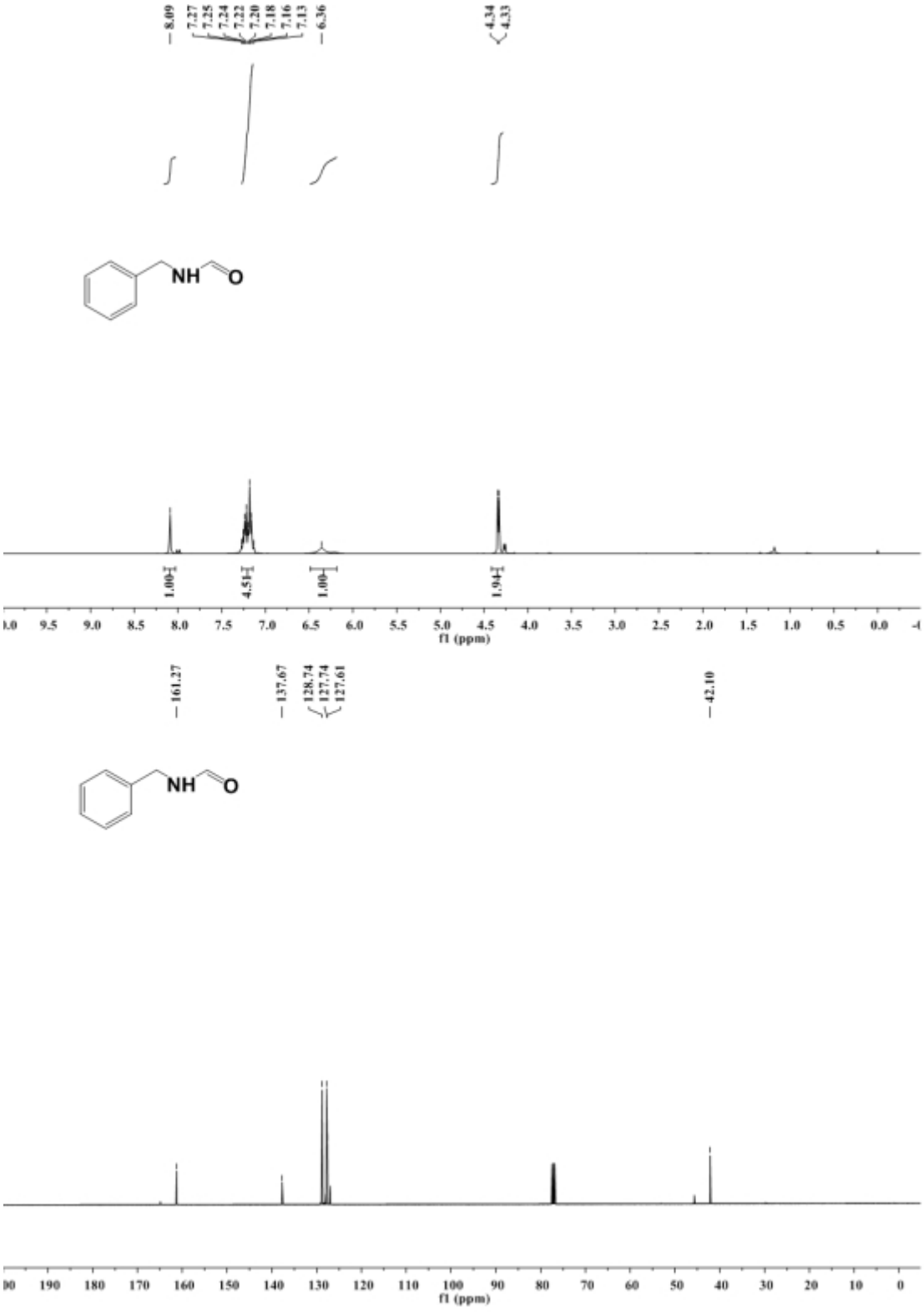

Fig. S24 The ^{1}H NMR and ^{13}C NMR spectra of **28a**.

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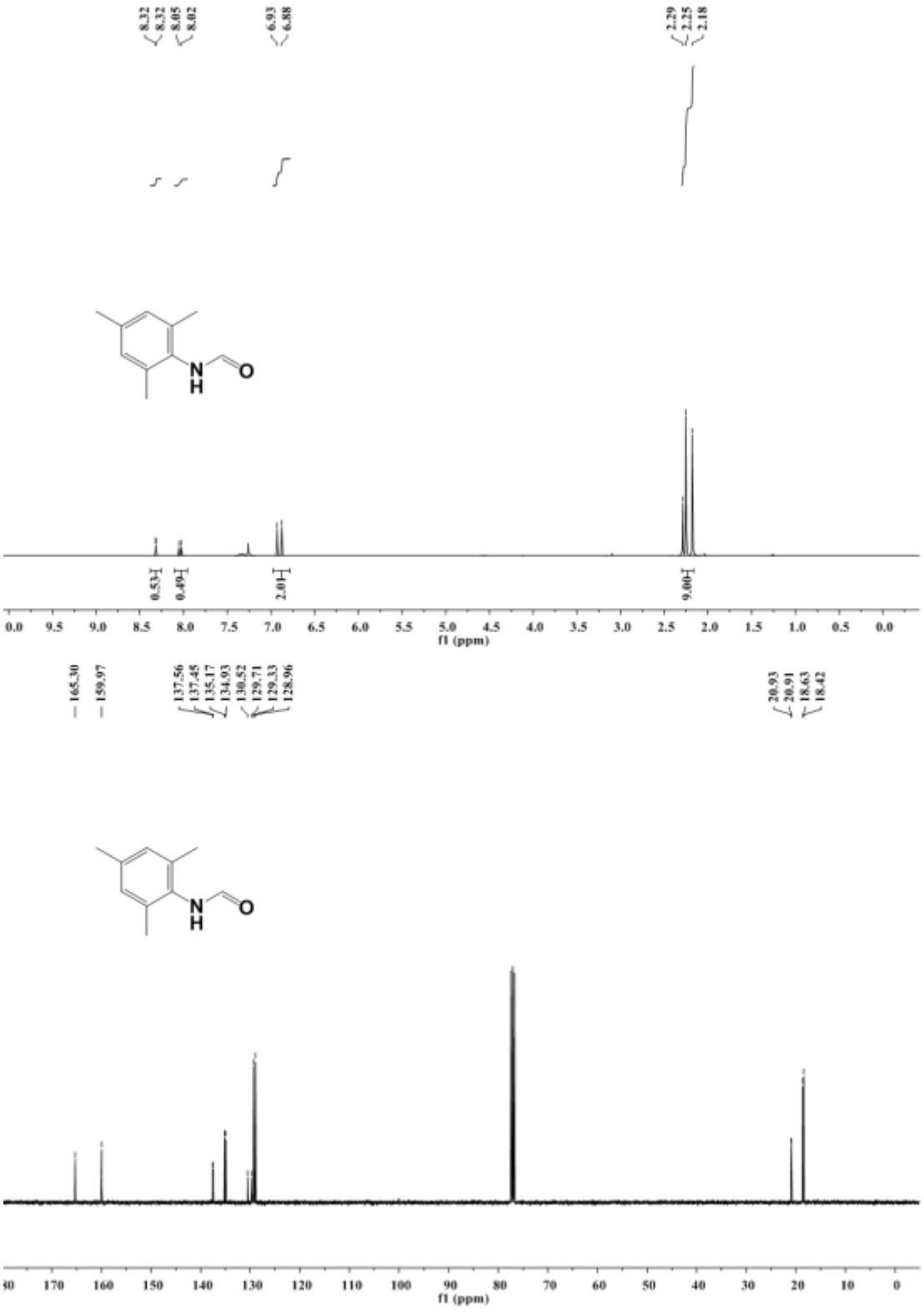

Fig. S25 The ^{1}H NMR and ^{13}C NMR spectra of **29a**.

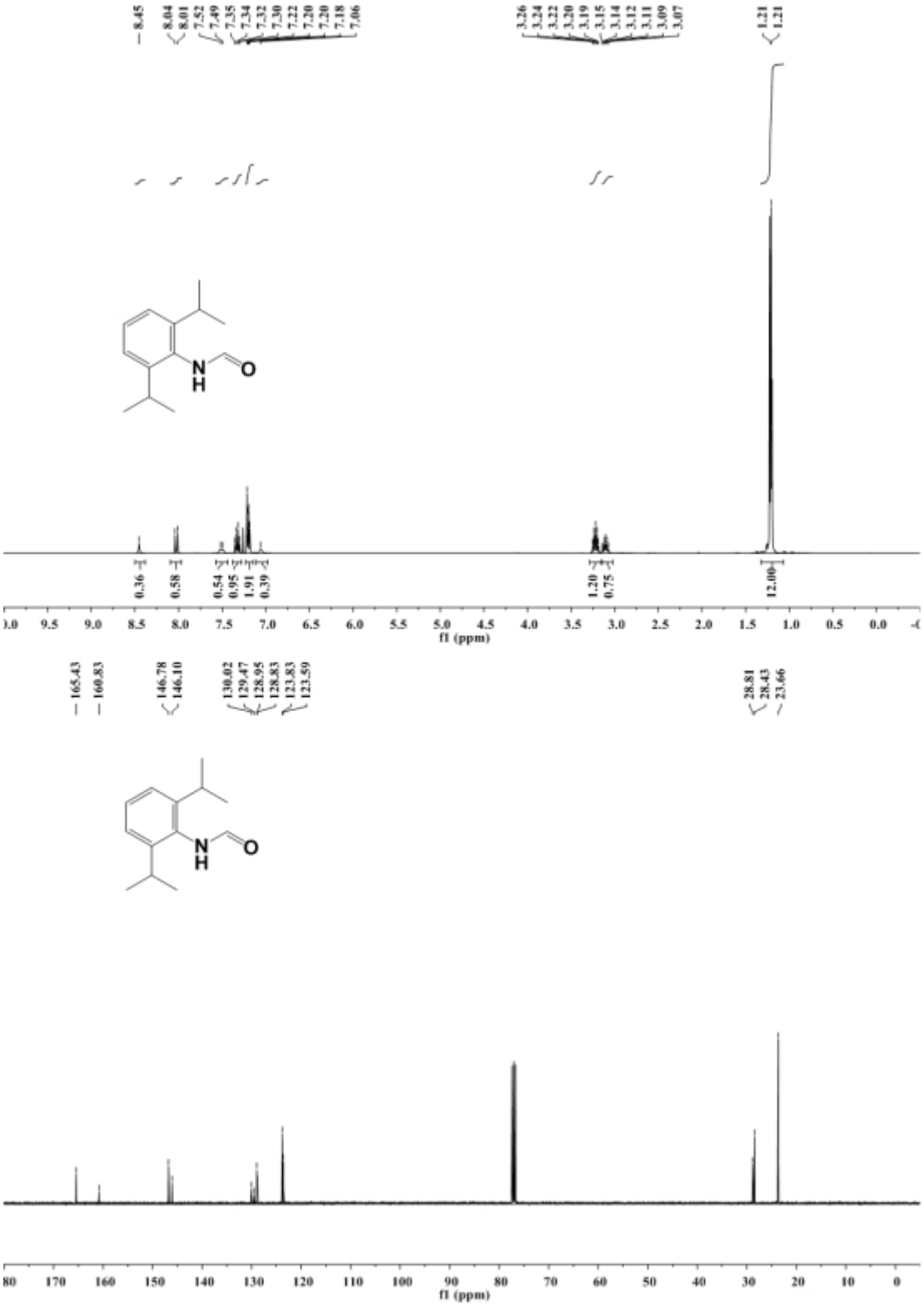

Fig. S26 The ^{1}H NMR and ^{13}C NMR spectra of **30a**.