Supplementary Information

Electrochemically Enabled Decyanative C(sp^3)–H Oxygenation of *N*-Cyanomethylamines to Formamides

Mu-Jia Luo,*[a] Wei Zhou,[a] Ruchun Yang,[a] Haixin Ding[a], Xian-Rong Song[a] and Qiang Xiao*[a]

[a] *Key Laboratory of Organic Chemistry of Jiangxi Province, Jiangxi Science & Technology Normal University, Nanchang, 330013, China. E-mail: luomjchem@163.com; E-mail: xiaoqiang@tsinghua.org.cn.*

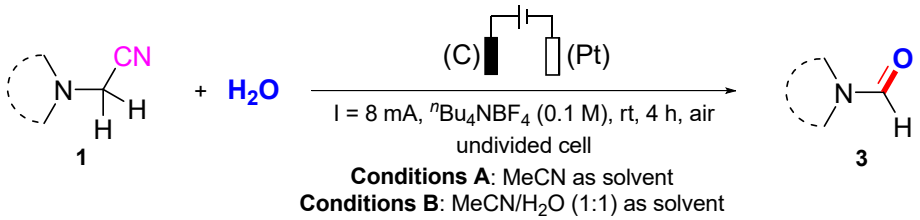
List of Contents

(A) Typical Experimental Procedure

(a) General

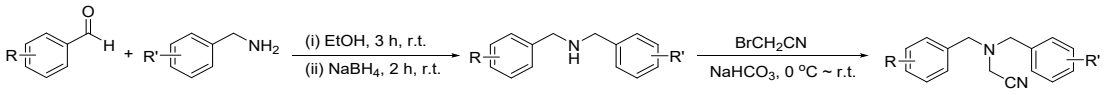
The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected. The instrument for electrolysis is DC power source (PM3005B) (made in China). Cyclic voltammograms were obtained on a CHI 605E potentiostat. The anode electrode is graphite rod (Φ6 mm×80 mm) and cathode electrode is platinum electrodes (1.0×1.0 cm^2).

(b) General procedures for electrochemical decyanative C(sp^3)–H oxygenation of *N*-cyanomethylamines for the synthesis of *N*,*N*-disubstituted formamides.



To an undivided three-necked bottle (10 mL) were added **1** (0.5 mmol), **H_2O** (4.0 equiv.), $^{n}Bu_4NBF_4$ (0.1 M) and MeCN (6 mL)/ or MeCN/H_2O (1:1, 6 mL). The bottle was equipped with platinum plate (1.0×1.0 cm^2) electrodes as cathode and graphite rod (Φ = 6 mm) electrode as anode under air. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at room temperture for 4 h until complete consumption of **1** as monitored by TLC analysis. After the reaction was finished, added H_2O (5 mL) and the solution was extracted with EtOAc (3×10 mL). The combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired *N*,*N*-disubstituted formamides.

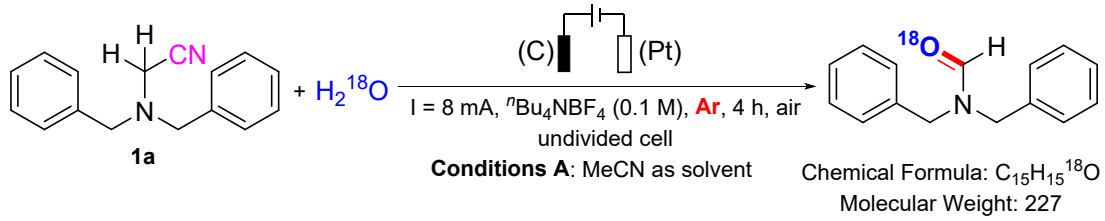
(c) General procedures for the synthesis of starting materials[1,2]



To a mixture of aryl aldehyde (10 mmol), benzylamine (10 mmol), and 3Å MS (2 g, powdered) was added absolute EtOH (30mL). After 3 h, $NaBH_4$ (0.57 g, 15 mmol) was added slowly, and the mixture was stirred for another 2 h. After the reaction was finished, added H_2O (20 mL) and the solution was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine (3×50 mL), and dried over Na_2SO_4, filtered and concentrated in vacuum to give a crude product. The crude product was used directly in the next step without further purification.

α-Bromoacetonitrile (10 mmol) was added dropwise to a solution of crude dibenzylamine or commercial triethylamine (10 mmol) in acetonitrile (30 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature, and stirred for 14 h. The reaction was quenched with sat. $NaHCO_3$ (20 mL), and the solution was extracted with EtOAc (3×50 mL). The combined organic layers were washed with brine (3×50 mL), and dried over Na_2SO_4. After concentration, the obtained crude product was purified by column chromatography (petroleum ether/EtOAc) to afford corresponding derivative.

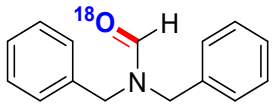
(d) Procedures for electrochemical isotope labeling experiment.



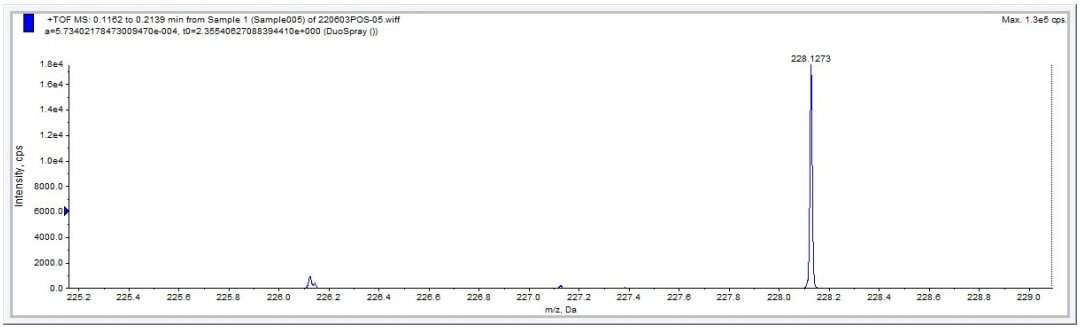
To an undivided three-necked bottle (10 mL) were added **1a** (0.5 mmol), **$H_2{}^{18}O$** (4.0 equiv.), $^nBu_4NBF_4$ (0.1 M) and MeCN (6 mL). The bottle was equipped with platinum plate (1.0×1.0 cm^2) electrodes as cathode and graphite rod electrode (Φ = 6 mm) as anode under argon. The reaction mixture was stirred and electrolyzed at a constant current of 8 mA at room temperture for 4 h. After the reaction was finished, added H_2O (5 mL) and the solution was extracted with EtOAc (3×10 mL). The

combined organic layer was dried with Na_2SO_4, filtered and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired *N*,*N*-disubstituted formamides.

HRMS dates:



HRMS *m/z* (ESI) calcd for $C_{15}H_{16}N^{18}O$ $[M+H]^+$ 228.1269, found 228.1273.



(e) Cyclic voltammogram analysis

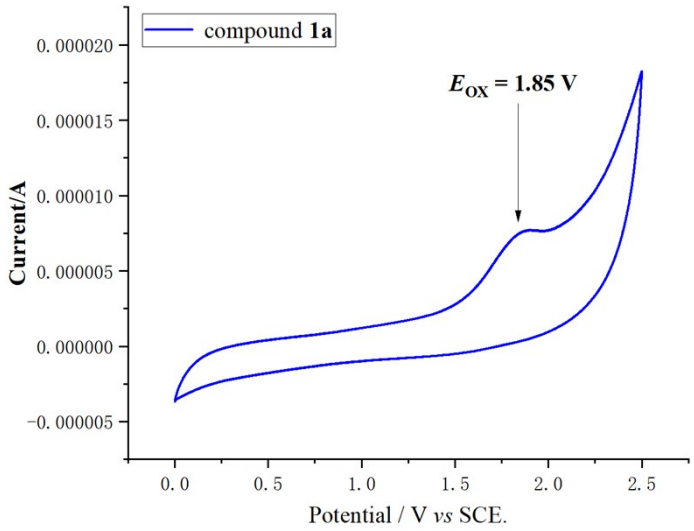


Figure S1. Cyclic voltammogram curves (0-2.5 V). Using GC disk as working electrode, Pt net, and SCE as counter and reference electrode at 100 mV/s scan rate. **1a** (0.083 M), $^nBu_4NPF_6$ (0.1 M) and MeCN (6 mL).

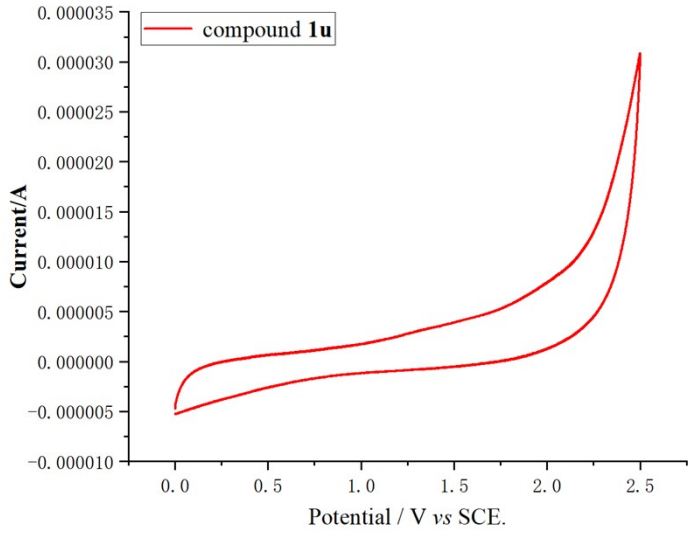
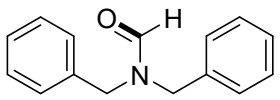


Figure S2. Cyclic voltammogram curves (0-2.5 V). Using GC disk as working electrode, Pt net, and SCE as counter and reference electrode at 100 mV/s scan rate. **1u** (0.083 M), $^{n}Bu_4NPF_6$ (0.1 M) and MeCN (6 mL).

Scanning range: 0 – 2.5 V (compound **1u** has no oxidative potential peak in the range of 0-2.5 V).

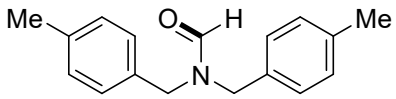
(B) Analytical data

***N*,*N*-Dibenzylformamide (2a)[3]:**



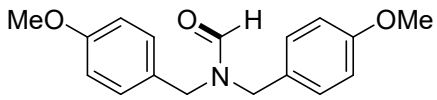
86% yield; 96.8 mg (0.5 mmol scale); Whilte solid; mp 52-53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.40-7.23 (m, 6H), 7.19-7.15 (m, 4H), 4.40 (s, 2H), 4.23 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 135.9, 135.5, 128.7, 128.5, 128.3, 128.0, 127.5, 127.5, 50.0, 44.4; LRMS (EI, 70 eV) *m/z* (%): 225 (M^+, 8), 134 (100), 106 (28), 91 (78), 79 (42), 65 (33); HRMS *m/z* (ESI) calcd for $C_{15}H_{16}NO$ $[M+H]^+$ 226.1226, found 226.1234. The analytical data are in accordance with those reported in the literature.

***N*,*N*-Bis(4-methylbenzyl)formamide (2b):**



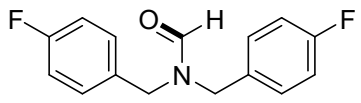
88% yield; 111.3 mg (0.5 mmol scale); Whilte solid; mp 56-57 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.18-7.12 (m, 4H), 7.09-7.04 (m, 4H), 4.35 (s, 2H), 4.19 (s, 2H), 2.35 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 137.7, 137.2, 132.9, 132.5, 129.4, 129.2, 128.4, 127.6, 49.7, 44.0, 21.0; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 7), 207 (6), 148 (100), 120 (47), 93(38), 77 (29); HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1538.

***N*,*N*-Bis(4-methoxybenzyl)formamide (2c):**



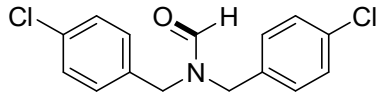
92% isolated yield; 131.1 mg (0.5 mmol scale); Light yellow solid; mp 61-63 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.19-7.10 (m, 6H), 7.03-6.95 (m, 2H), 4.45 (s, 2H), 4.21 (s, 2H), 2.14 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 136.4, 135.9, 133.1, 133.0, 130.5, 130.3, 128.3, 127.7, 127.4, 127.3, 126.1, 125.8, 47.5, 42.4, 18.8, 18.7; LRMS (EI, 70 eV) *m/z* (%): 285 (M^+, 15), 164 (100), 121 (68); HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO_3$ $[M+H]^+$ 286.1438, found 286.1442.

***N*,*N*-Bis(4-fluorobenzyl)formamide (2d):**



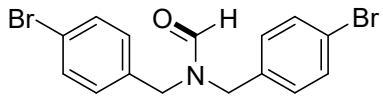
80% isolated yield; 104.4 mg (0.5 mmol scale); Light yellow solid; mp 53-54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.17-7.13 (m, 4H), 7.07-6.96 (m, 4H), 4.36 (s, 2H), 4.25 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 26.9 Hz), 162.5, 160.9 (d, *J* = 26.0 Hz), 131.5 (d, *J* = 3.1 Hz), 131.1 (d, *J* = 3.1 Hz), 129.9 (d, *J* = 8.0 Hz), 129.2 (d, *J* = 8.2 Hz), 115.6 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.3 Hz), 49.3, 43.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.77, -114.48; LRMS (EI, 70 eV) *m/z* (%): 261 (M^+, 3), 152 (100), 124 (57), 109 (87), 97 (48), 83 (34); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}F_2NO$ $[M+H]^+$ 262.1038, found 262.1042.

***N,N*-Bis(4-chlorobenzyl)formamide (2e):**



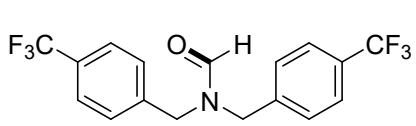
83% isolated yield; 121.6 mg (0.5 mmol scale); Light yellow solid; mp 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.11-7.08 (m, 4H), 4.35 (s, 2H), 4.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 134.2, 134.0, 133.8, 133.5, 129.7, 129.0, 128.9, 128.7, 49.5, 43.9; LRMS (EI, 70 eV) *m/z* (%): 293 (M^+, 4), 207 (20), 168 (100), 140 (48), 125 (53); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}Cl_2NO$ $[M+H]^+$ 294.0447, found 294.0454.

***N,N*-Bis(4-bromobenzyl)formamide (2f):**



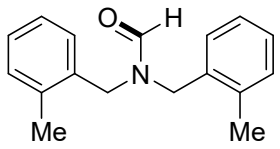
85% isolated yield; 161.9 mg (0.5 mmol scale); Whilte solid; mp 118-119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.48 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.05-7.02 (m, 4H), 4.33 (s, 2H), 4.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 134.6, 134.2, 131.9, 131.6, 130.0, 129.2, 122.0, 121.5, 49.5, 43.9; LRMS (EI, 70 eV) *m/z* (%): 381 (M^+, 10), 225 (24), 169 (100); HRMS *m/z* (ESI) calcd for $C_{15}H_{14}Br_2NO$ $[M+H]^+$ 381.9437, found 381.9443.

***N,N*-Bis(4-(trifluoromethyl)benzyl)formamide (2g):**



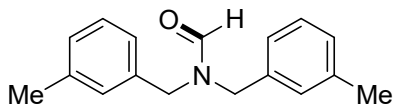
80% isolated yield; 144.4 mg (0.5 mmol scale); Whilte solid; mp 62-63 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.31-7.29 (m, 4H), 4.49 (s, 2H), 4.39 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 139.8, 139.4, 130.5 (q, *J* = 32.4 Hz), 130.0 130.5 (q, *J* = 32.4 Hz), 128.5, 127.9, 125.9 (q, *J* = 3.6 Hz), 125.6 (q, *J* = 3.6 Hz), 125.3, 125.1, 122.5, 122.4, 50.0, 44.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6, -62.7; LRMS (EI, 70 eV) *m/z* (%): 361 (M^+, 7), 342 (10), 202 (100), 174 (83), 159 (48); HRMS *m/z* (ESI) calcd for $C_{17}H_{14}F_6NO$ $[M+H]^+$ 362.0974, found 362.0978.

***N,N*-Bis(2-methylbenzyl)formamide (2h):**



76% yield; isolated yield; 96.1 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.13-7.07 (m, 4H), 6.90-6.84 (m, 4H), 4.32 (s, 2H), 4.17 (s, 2H), 3.81 (s, 3H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 159.3, 159.0, 129.7, 128.9, 128.0, 127.4, 114.1, 113.9, 55.2, 55.1, 49.4, 43.7; LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 8), 207 (6), 148 (100), 120 (32), 93 (44), 77 (31); HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1544.

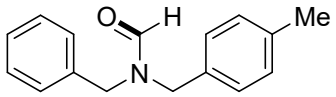
***N,N*-Bis(3-methylbenzyl)formamide (2i):**



87% isolated yield; 110.1 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.25-7.17 (m, 2H), 7.12-7.06 (m, 2H), 7.00-6.94 (m, 4H), 4.36 (s, 2H), 4.19 (s, 2H), 2.33 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 138.4, 138.1, 135.7, 135.4, 128.9, 128.6, 128.5, 128.3, 128.1, 128.1, 125.3, 124.5, 49.9, 44.3, 21.1;

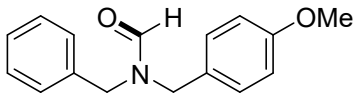
LRMS (EI, 70 eV) *m/z* (%): 253 (M^+, 10), 148 (100), 120 (53), 105 (33), 93 (36); HRMS *m/z* (ESI) calcd for $C_{17}H_{20}NO$ $[M+H]^+$ 254.1539, found 254.1543.

***N*-Benzyl-*N*-(4-methylbenzyl)formamide (2j):**



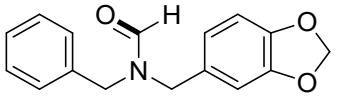
88% isolated yield; 105.2 mg (0.5 mmol scale); Whilte solid; mp 54-55 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 0.5H), 8.38 (s, 0.5H), 7.36-7.29 (m, 3H), 7.20-7.04 (m, 6H), 4.39 (s, 1H), 4.36 (s, 1H), 4.23 (s, 1H), 4.20 (s, 1H), 2.35 (s, 1.5H), 2.33 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 137.8, 137.2, 136.0, 135.6, 132.8, 132.4, 129.5, 129.2, 128.8, 128.5, 128.4, 128.4, 128.0, 127.6, 127.5, 50.0, 49.8, 44.4, 44.2, 21.0; LRMS (EI, 70 eV) *m/z* (%): 239 (M^+, 10), 148 (100), 134 (40), 120 (47), 106 (38), 91 (70); HRMS *m/z* (ESI) calcd for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383, found 240.1387.

***N*-Benzyl-*N*-(4-methoxybenzyl)formamide (2k):**



90% isolated yield; 114.8 mg (0.5 mmol scale); Whilte solid; mp 57-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 0.5H), 8.35 (s, 0.5H), 7.33-7.25 (m, 3H), 7.19-7.14 (m, 2H), 7.12-7.05 (m, 2H), 6.88-6.82 (m, 2H), 4.37 (s, 1H), 4.32 (s, 1H), 4.21 (s, 1H), 4.16 (s, 1H), 3.77 (s, 1.5H), 3.76 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.4, 159.2, 158.8, 135.8, 135.5, 129.6, 128.8, 128.6, 128.4, 128.2, 127.8, 127.4, 127.3, 127.2, 114.0, 113.8, 55.0, 54.9, 49.73, 49.4, 44.1, 43.7; LRMS (EI, 70 eV) *m/z* (%): 255 (M^+, 8), 164 (100), 137 (34), 121 (33), 109 (33), 91 (40); HRMS *m/z* (ESI) calcd for $C_{16}H_{18}NO_2$ $[M+H]^+$ 256.1332, found 256.1334.

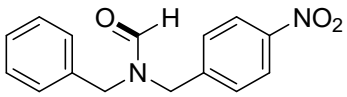
***N*-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-*N*-benzylformamide (2l):**



91% isolated yield; 122.4 mg (0.5 mmol scale); Light yellow solid; mp 64-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.38-7.27 (m, 3H), 7.20-7.16 (m, 2H), 6.78-6.60 (m, 3H), 5.94 (s, 1H),

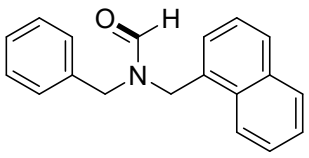
5.92 (s, 1H), 4.39 (s, 1H), 4.29 (s, 1H), 4.24 (s, 1H), 4.14 (s, 1H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.5, 148.0, 147.8, 147.3, 146.9, 135.8, 135.4, 129.6, 129.1, 128.7, 128.5, 128.3, 127.9, 127.5, 127.4, 121.8, 121.1, 108.7, 108.2, 108.0, 107.8, 101.1, 100.9, 49.9, 44.2, 44.2; LRMS (EI, 70 eV) *m/z* (%): 269 (M^+, 17), 178 (100), 150 (41), 135 (30), 91 (36); HRMS *m/z* (ESI) calcd for $C_{16}H_{16}NO_3$ $[M+H]^+$ 270.1125, found 270.1103.

***N*-Benzyl-*N*-(4-nitrobenzyl)formamide (2m):**



72% yield; 97.2 mg (0.5 mmol scale); Whilte solid; mp 55-56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 0.6H), 8.45 (s, 0.4H), 8.23-8.14 (m, 2H), 7.38-7.28 (m, 5H), 7.18-7.16 (m, 2H), 4.51 (s, 1.3H), 4.44 (s, 0.7H), 4.40 (s, 0.7H), 4.34 (s, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 162.81 147.7, 147.3, 143.6, 143.2, 135.2, 134.9, 129.0, 128.9, 128.7, 128.4, 128.3, 127.9, 127.6, 124.0, 123.7, 50.8, 49.6, 45.1, 44.4; LRMS (EI, 70 eV) *m/z* (%): 270 (M^+, 4), 207 (8), 179 (11), 134 (100), 106 (45), 91 (53); HRMS *m/z* (ESI) calcd for $C_{15}H_{15}N_2O_3$ $[M+H]^+$ 271.1077, found 271.1080.

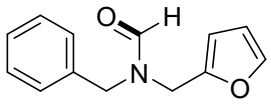
***N*-Benzyl-*N*-(naphthalen-1-ylmethyl)formamide (2n):**



83% yield; 114.1 mg (0.5 mmol scale); Whilte solid; mp 64-66 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 0.3H), 8.39 (s, 0.7H), 8.06-8.04 (m, 0.6H), 7.86-7.72 (m, 2.4H), 7.51-7.42 (m, 2H), 7.38-7.24 (m, 4.2H), 7.18-7.09 (m, 2.8H), 4.86 (s, 1.3H), 4.69 (s, 0.7H), 4.45 (s, 0.7H), 4.08 (s, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.5, 136.0, 135.5, 133.7, 131.5, 131.0, 130.9, 130.7, 128.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.5, 127.3, 126.5, 125.9, 125.7, 125.1, 124.8, 123.7, 122.3, 49.8, 47.7, 45.1, 42.5; LRMS (EI, 70 eV) *m/z* (%): 275 (M^+, 17), 184 (100), 156 (54), 141 (54), 129

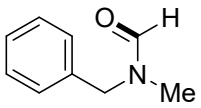
(86), 115 (48); HRMS *m/z* (ESI) calcd for $C_{19}H_{18}NO$ $[M+H]^+$ 276.1383, found 276.1390.

_N_-Benzyl-_N_-(furan-2-ylmethyl)formamide (2o):



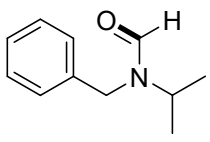
81% isolated yield; 87.1 mg (0.5 mmol scale); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 0.5H), 8.31 (s, 0.5H), 7.37-7.24 (m, 4H), 7.24-7.19 (m, 2H), 6.33-6.19 (m, 2H), 4.45 (s, 1H), 4.39 (s, 1H), 4.33 (s, 1H), 4.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.3, 149.5, 149.0, 142.8, 142.3, 135.8, 135.4, 128.7, 128.5, 128.2, 127.9, 127.5, 127.5, 110.3, 110.2, 109.0, 108.9, 50.4, 44.7, 43.1, 37.4; LRMS (EI, 70 eV) *m/z* (%): 215 (M^+, 12), 134 (35), 124 (100), 96 (88), 81 (35); HRMS *m/z* (ESI) calcd for $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1019, found 216.1024.

_N_-Benzyl-_N_-methylformamide (2p)[3]:



86% isolated yield; 64.1 mg (0.5 mmol scale); colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 0.6H), 8.14 (s, 0.4H), 7.38-7.19 (m, 5H), 4.51 (s, 0.9H), 4.38 (s, 1.1H), 2.83 (s, 1.3H), 2.76 (s, 1.7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.4, 135.8, 135.6, 128.6, 128.4, 128.0, 127.8, 127.4, 127.2, 53.2, 47.5, 33.8, 29.2; LRMS (EI, 70 eV) *m/z* (%): 149 (M^+, 100), 134 (14), 106 (33), 91 (95), 79 (42), 65 (35). The analytical data are in accordance with those reported in the literature.

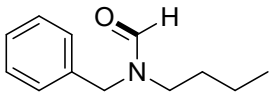
_N_-Benzyl-_N_-isopropylformamide (2q)[4]:



75% isolated yield; 66.4 mg (0.5 mmol scale); Light yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 0.7H), 8.22 (s, 0.3H), 7.36-7.21 (m, 5H), 4.52 (s, 1.4H), 4.47-4.36 (m, 0.3H), 4.36 (s, 0.6H), 3.76-3.69 (m, 0.7H), 1.18 (d, J = 6.8 Hz, 4.1H), 1.09 (d, J = 6.8 Hz, 1.9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.2, 138.0, 137.9, 128.5, 128.3, 127.6, 127.4, 127.0, 126.9,

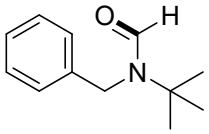
49.8, 48.1, 44.8, 43.9, 22.1, 20.0; LRMS (EI, 70 eV) *m/z* (%): 177 (M^+, 22), 134 (31), 106 (28), 91 (100), 79 (19); The analytical data are in accordance with those reported in the literature.

***N*-Benzyl-*N*-butylformamide (2r)[5]:**



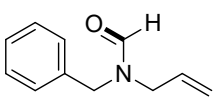
81% isolated yield; 77.4 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 0.4H), 8.18 (s, 0.6H), 7.36-7.19 (m, 5H), 4.52 (s, 1.1H), 4.37 (s, 0.9H), 3.21 (t, *J* = 7.6 Hz, 0.9H), 3.11 (t, *J* = 7.2 Hz, 1H), 1.49-1.42 (m, 2H), 1.29-1.23 (m, 2H), 0.90-0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.5, 136.3, 136.0, 128.5, 128.3, 127.9, 127.7, 127.2, 127.2, 50.9, 46.2, 44.8, 41.4, 29.9, 28.7, 19.8, 19.3, 13.5, 13.3; LRMS (EI, 70 eV) *m/z* (%): 191 (M^+, 11), 134 (12), 106 (9), 91 (100); The analytical data are in accordance with those reported in the literature.

***N*-Benzyl-*N*-(*tert*-butyl)formamide (2s)[6]:**



71% isolated yield; 67.8 mg (0.5 mmol scale); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.31-7.27 (m, 2H), 7.22-7.21 (m, 3H), 4.64 (s, 2H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 138.8, 128.4, 126.7, 126.7, 7 55.9, 44.0, 30.0; LRMS (EI, 70 eV) *m/z* (%): 191 (M^+, 8), 134 (46), 106 (36), 91 (100); The analytical data are in accordance with those reported in the literature.

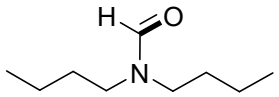
***N*-Allyl-*N*-benzylformamide (2t)[7]:**



88% isolated yield; 77.0 mg (0.5 mmol scale); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 0.5H), 8.20 (s, 0.5H), 7.37-7.26 (m, 3H), 7.24-7.18 (m, 2H), 5.76-5.63 (m, 1H), 5.26-5.08 (m, 2H), 4.51 (s, 1H), 4.36 (s, 1H), 3.84 (d, *J* = 6.0 Hz, 1H), 3.71 (d, *J* = 6.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 162.3, 136.1, 135.7, 132.7, 131.7, 128.7, 128.474, 128.2, 127.9,

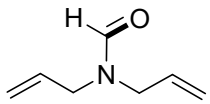
127.4, 127.4, 118.6, 118.1, 7 50.2, 48.9, 44.8, 43.8; LRMS (EI, 70 eV) *m/z* (%): 175 (M^+, 12), 134 (68), 106 (42), 91 (100), 79 (48); The analytical data are in accordance with those reported in the literature.

***N*,*N*-Dibutylformamide (2w)**[8]**:**



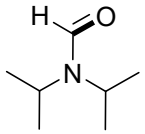
78% isolated yield; 122.5 mg (1.0 mmol scale); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 3.29 (t, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 7.2 Hz, 2H), 1.57-1.48 (m, 4H), 1.37-1.26 (m, 4H), 0.96-0.91 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 46.6, 41.3, 30.3, 28.9, 19.7, 19.2, 13.3, 13.2; LRMS (EI, 70 eV) *m/z* (%): 157 (M^+, 4), 114 (52), 72 (100). The analytical data are in accordance with those reported in the literature.

***N*,*N*-Diallylformamide (2x)**[8]**:**



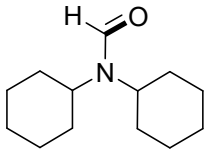
80% isolated yield; 100.0 mg (1.0 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 5.80-5.66 (m, 2H), 5.26-5.14 (m, 4H), 3.94 (d, *J* = 6.0 Hz, 2H), 3.83 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 132.8, 131.8, 118.2, 117.7, 48.9, 43.9; LRMS (EI, 70 eV) *m/z* (%): 125 (M^+, 11), 110 (26), 84 (35), 56 (47), 41 (100); The analytical data are in accordance with those reported in the literature.

***N*,*N*-Diisopropylformamide (2y)**[9]**:**



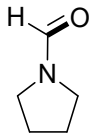
77% isolated yield; colorless oil; 99.3 mg (1.0 mmol scale); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 4.18-4.12 (m, 1H), 3.68-3.61 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 6H), 1.27 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 46.1, 43.3, 22.7, 19.6; LRMS (EI, 70 eV) *m/z* (%): 129 (M^+, 18), 114 (14), 86 (23), 72 (100), 58 (24), 44 (68). The analytical data are in accordance with those reported in the literature.

***N*,*N*-Dicyclohexylformamide (2z)[10]:**



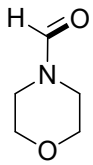
72% isolated yield; 150.5 mg (1.0 mmol scale); Light yellow solid; mp 59-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 3.98-3.90 (m, 1H), 3.10-3.02 (m, 1H), 1.85-1.77 (m, 6H), 1.69-1.63 (m, 6H), 1.54-1.44 (m, 2H), 1.38-1.24 (m, 4H), 1.83-1.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 54.7, 52.1, 34.4, 30.2, 26.0, 25.7, 25.1, 25.0; LRMS (EI, 70 eV) *m/z* (%): 209 (M^+, 27), 166 (25), 128 (94), 84 (63), 55 (77), 46 (100); HRMS *m/z* (ESI) calcd for $C_{13}H_{24}NO$ $[M+H]^+$ 210.1852, found 210.1855. The analytical data are in accordance with those reported in the literature.

Pyrrolidine-1-carbaldehyde (2aa)[9]:



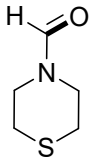
76% isolated yield; 75.2 mg (1.0 mmol scale); Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 3.51 (t, *J* = 6.4 Hz, 2H), 3.42 (t, *J* = 6.4 Hz, 2H), 1.95-1.89 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 45.9, 43.0, 24.7, 24.1; LRMS (EI, 70 eV) *m/z* (%): 99 (M^+, 100), 71 (62), 43 (94); The analytical data are in accordance with those reported in the literature.

Morpholine-4-carbaldehyde (2ab)[9]:



80% isolated yield; 92.0 mg (1.0 mmol scale); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.71 (t, *J* = 4.8 Hz, 2H), 3.67 (t, *J* = 4.8 Hz, 2H), 3.58 (t, *J* = 4.8 Hz, 2H), 3.41 (t, *J* = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 67.0, 66.2, 45.6, 40.4; LRMS (EI, 70 eV) *m/z* (%): 115 (M^+, 90), 100 (75), 86 (42), 72 (21), 56 (100), 42 (89); The analytical data are in accordance with those reported in the literature.

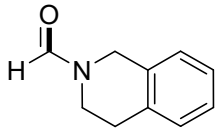
Thiomorpholine-4-carbaldehyde (2ac)[11]:



76% yield; 99.6 mg (1.0 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.80 (t, *J* = 5.2 Hz, 2H), 3.64 (t, *J* = 5.2 Hz, 2H),

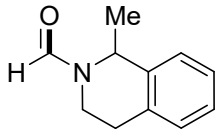
2.65 (t, J = 5.2 Hz, 2H), 2.60 (t, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 47.9, 41.9, 27.9, 26.7; LRMS (EI, 70 eV) *m/z* (%): 131 (M^+, 100), 116 (21), 103 (134), 72 (31), 56 (59), 42 (78); The analytical data are in accordance with those reported in the literature.

3,4-Dihydroisoquinoline-2(1*H*)-carbaldehyde (2ad)[9]:



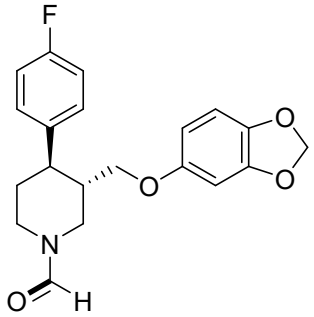
85% yield; 68.4 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.19 (s, 1H), 7.27-7.09 (m, 4H), 4.68 (s, 1.3H), 4.53 (s, 0.7H), 3.78 (t, J = 6.0 Hz, 0.7H), 3.64 (t, J = 6.0 Hz, 1.3H), 2.91-2.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 161.0, 134.3, 133.4, 132.1, 131.6, 129.0, 128.8, 126.9, 126.6, 126.5, 126.3, 125.7, 47.1, 43.0, 42.1, 37.8, 29.6, 27.8; LRMS (EI, 70 eV) *m/z* (%): 161 (M^+, 100), 146 (12), 132 (27), 117 (55), 104 (78), 77 (33); The analytical data are in accordance with those reported in the literature.

1-Methyl-3,4-dihydroisoquinoline-2(1*H*)-carbaldehyde (2ae)[12]:



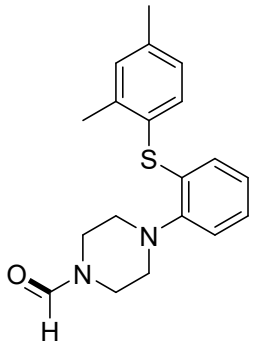
83% isolated yield; 72.6 mg (0.5 mmol scale); Light yellow solid; mp 48-49 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 0.4H), 8.13 (s, 0.6H), 7.22-7.09 (m, 4H), 5.45 (q, J = 6.8 Hz, 0.6H), 4.77 (q, J = 6.8 Hz, 0.4H), 4.46-4.41 (m, 0.4H), 3.71-3.86 (m, 0.6H), 3.57-3.50 (m, 0.6H), 3.20-3.03 (m, 0.4H), 2.99-2.76 (m, 2H), 1.55 (d, J = 6.8 Hz, 1H), 1.47 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 137.1, 137.0, 133.5, 132.6, 129.1, 128.8, 126.9, 126.9, 126.5, 126.5, 126.3, 52.5, 46.9, 39.7, 33.8, 29.7, 28.0, 24.2, 21.5; LRMS (EI, 70 eV) *m/z* (%): 175 (M^+, 42), 160 (100), 132 (83), 117 (44), 77 (24); The analytical data are in accordance with those reported in the literature.

(3S,4R)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbaldehyde (2af)[3]:



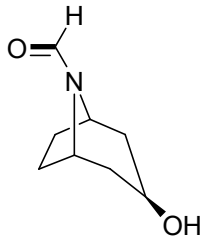
75% isolated yield; 133.9 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 0.5H), 8.16 (s, 0.5H), 7.19-7.16 (m, 2H), 7.06-7.00 (m, 2H), 6.69-6.55 (m, 1H), 6.41-6.40 (m, 1H), 6.20-6.17 (m, 1H), 5.92 (s, 1H), 5.91 (s, 1H), 4.79-4.75 (m, 0.5H), 4.63-4.59 (m, 0.5H), 4.03-3.99 (m, 0.5H), 3.80-3.76 (m, 0.5H), 3.68-3.64 (m, 1H), 3.54-3.50 (m, 1H), 3.29-3.16 (m, 1H), 2.94-2.72 (m, 2H), 2.16-1.91 (m, 2H), 1.81-1.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 160.8, 160.7, 160.4, 154.0, 153.8, 148.1, 148.1, 141.8, 141.7, 138.3, 138.2, 128.7, 128.6, 128.5, 115.7, 115.6, 115.5, 115.4, 107.8, 107.7, 105.5, 105.4, 101.0, 101.0, 97.9, 97.8, 68.5, 68.4, 49.0, 46.0, 44.4, 44.0, 42.7, 41.4, 40.0, 34.4, 33.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.54, -115.65; HRMS *m/z* (ESI) calcd for $C_{20}H_{21}FNO_4$ $[M+H]^+$ 358.1449, found 358.1436. The analytical data are in accordance with those reported in the literature.

4-(2-((2,4-dimethylphenyl)thio)phenyl)piperazine-1-carbaldehyde (2ag):



73% isolated yield; 119.0 mg (0.5 mmol scale); Light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.15 (s, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.01 (t, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 3.73 (t, *J* = 4.8 Hz, 2H), 3.53 (t, *J* = 4.8 Hz, 2H), 3.05 (t, *J* = 4.8 Hz, 2H), 3.02 (t, *J* = 4.8 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 148.4, 141.96, 139.1, 135.8, 134.5, 131.6, 127.7, 126.4, 125.5, 124.8, 119.9, 52.3, 51.0, 46.0, 40.4, 21.0, 20.4; HRMS *m/z* (ESI) calcd for $C_{19}H_{23}N_2OS$ $[M+H]^+$ 327.1526, found 327.1503.

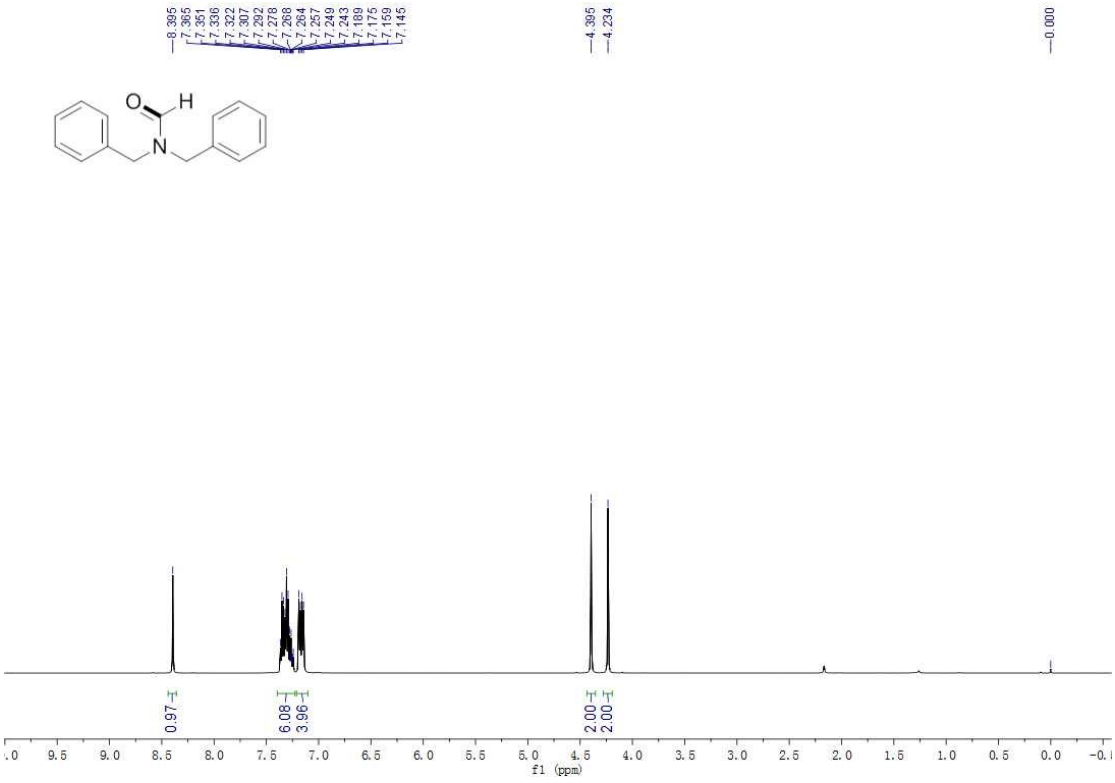
(1R,3S,5S)-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carbaldehyde (2ah)[13]:



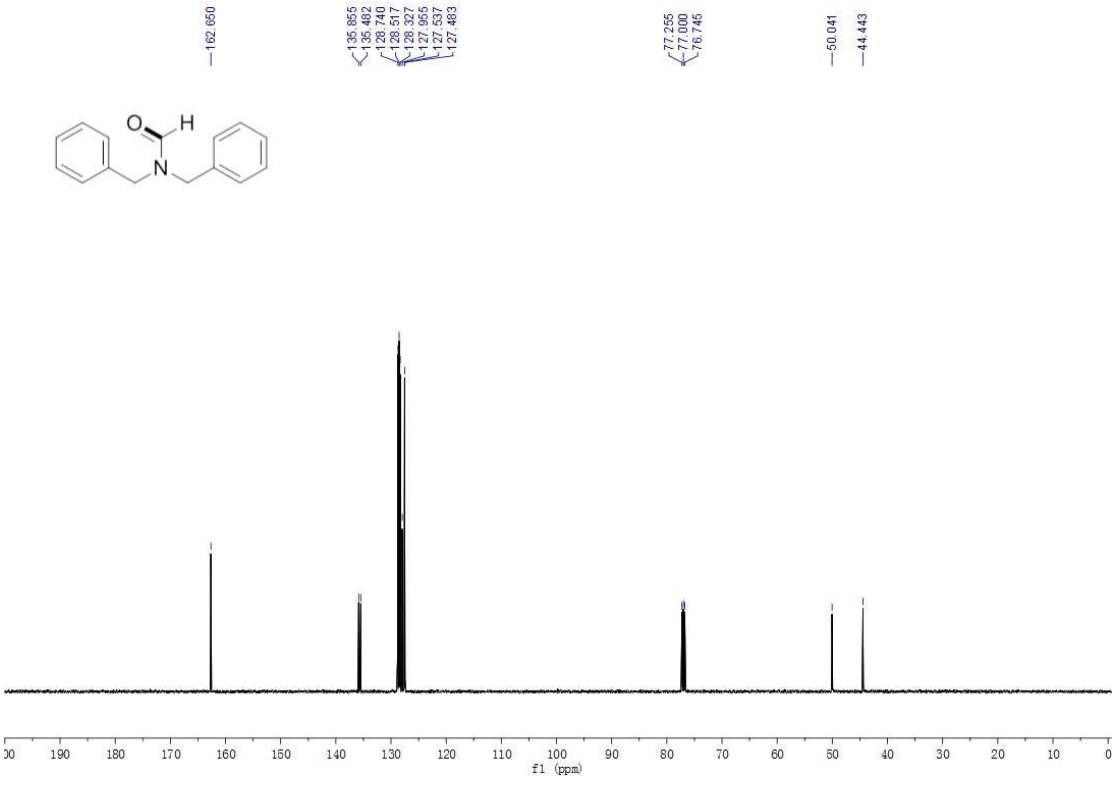
68% isolated yield; 105.4 mg (1.0 mmol scale); White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 4.56-4.52 (m, 1H), 4.16-4.13 (m, 1H), 4.04-4.02 (m, 1H), 3.35 (s, 1H), 2.33-2.28 (m, 2H), 2.09-2.03 (m, 1H), 1.99-1.96 (m, 2H), 1.94-1.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 64.4, 54.0, 49.1, 41.1, 38.5, 28.0, 27.3; HRMS *m/z* (ESI) calcd for $C_8H_{14}NO_2$ $[M+H]^+$ 156.1019, found 156.0994. The analytical data are in accordance with those reported in the literature.

(C) Spectra (NMR Spectra)

N,*N*-Dibenzylformamide (2a):

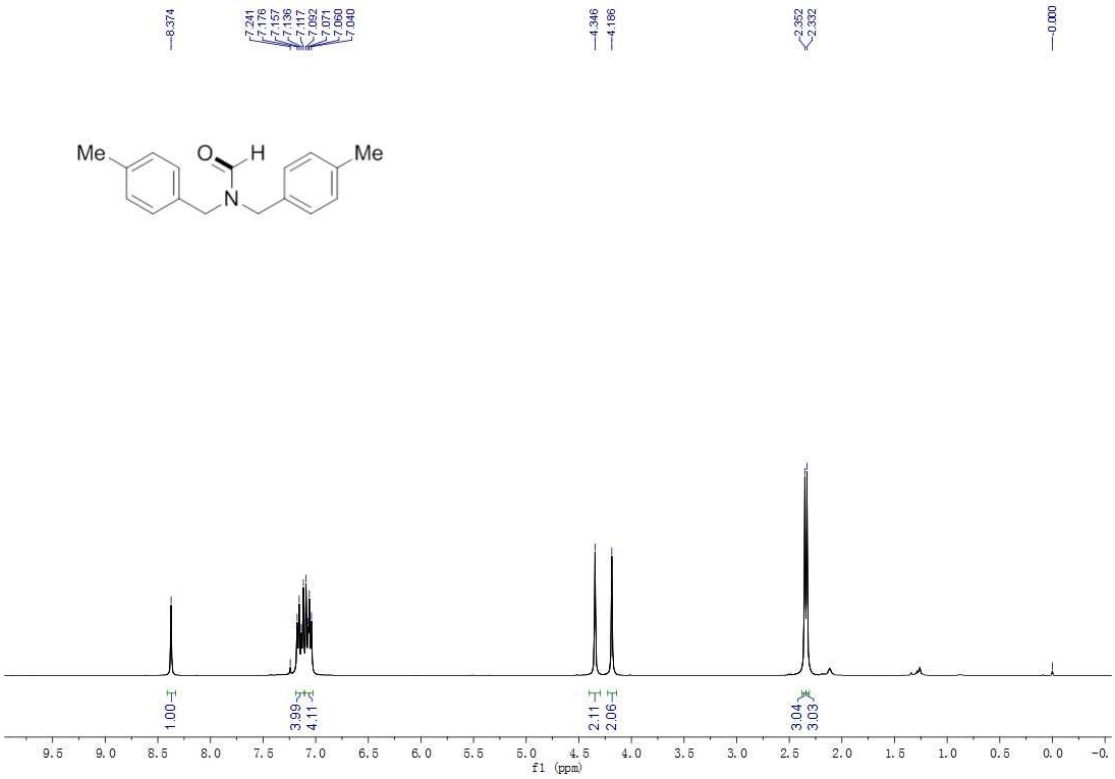


^{1}H NMR (500 MHz, $CDCl_3$)

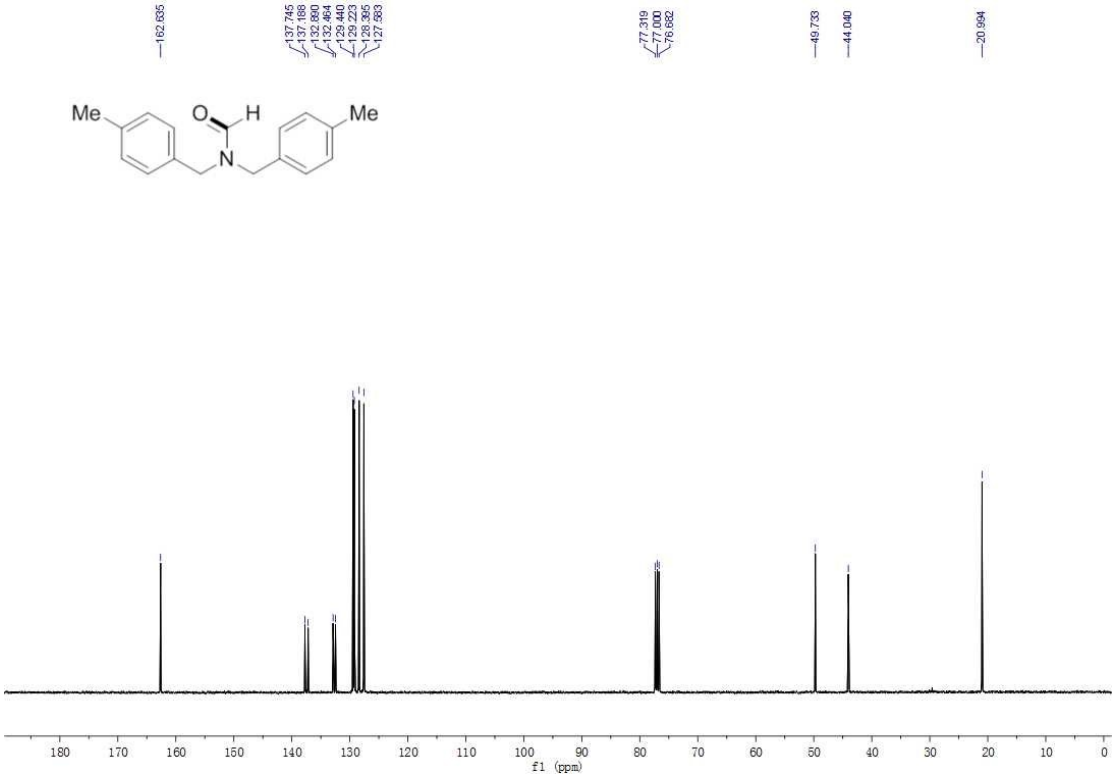


^{13}C NMR (125 MHz, $CDCl_3$)

***N,N*-Bis(4-methylbenzyl)formamide (2b):**

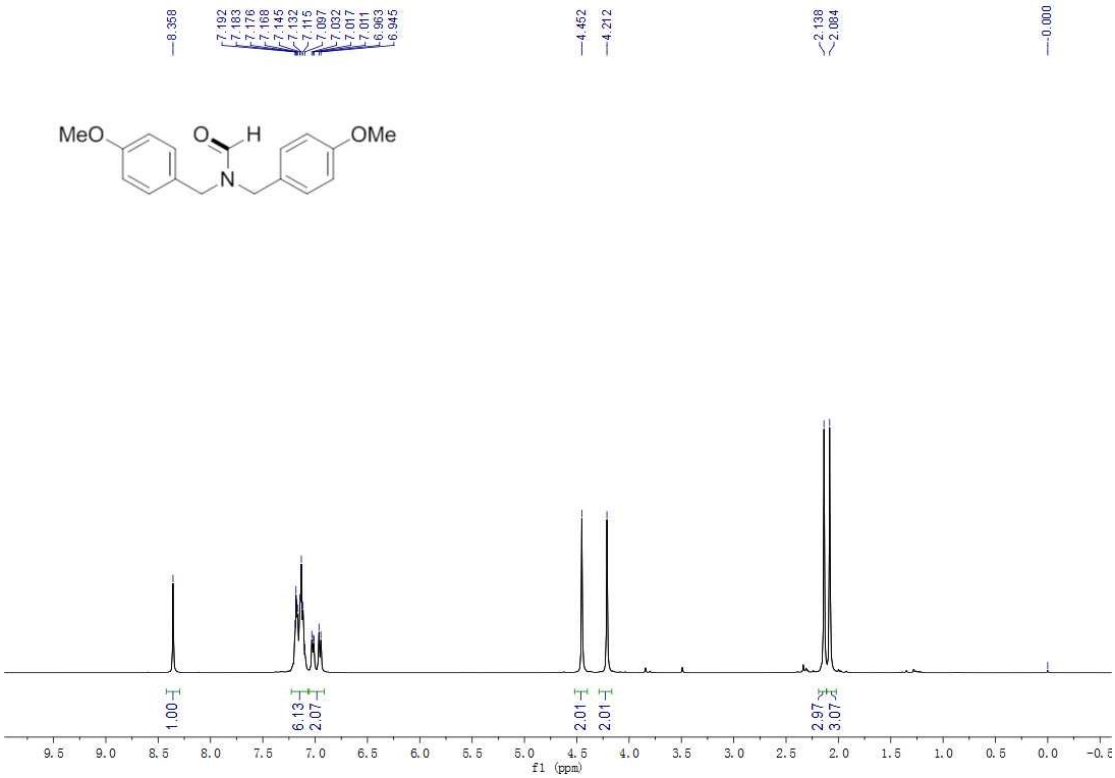


^{1}H NMR (400 MHz, $CDCl_3$)

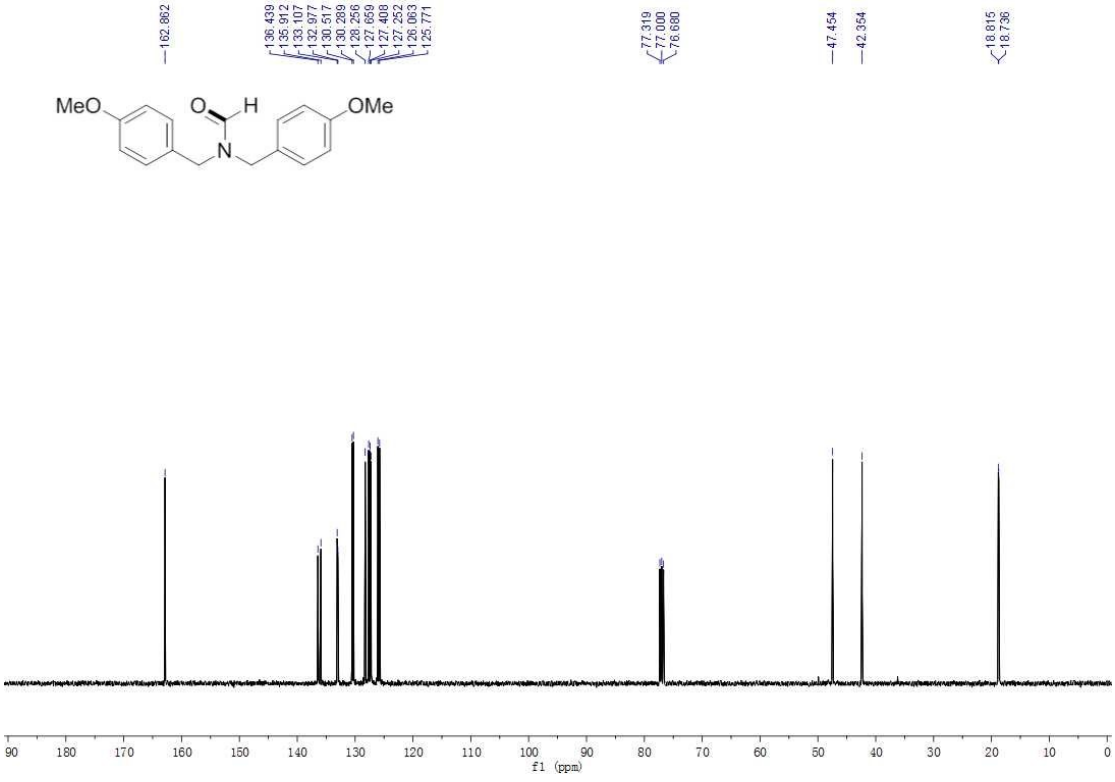


^{13}C NMR (100 MHz, $CDCl_3$)

***N,N*-Bis(4-methoxybenzyl)formamide (2c):**

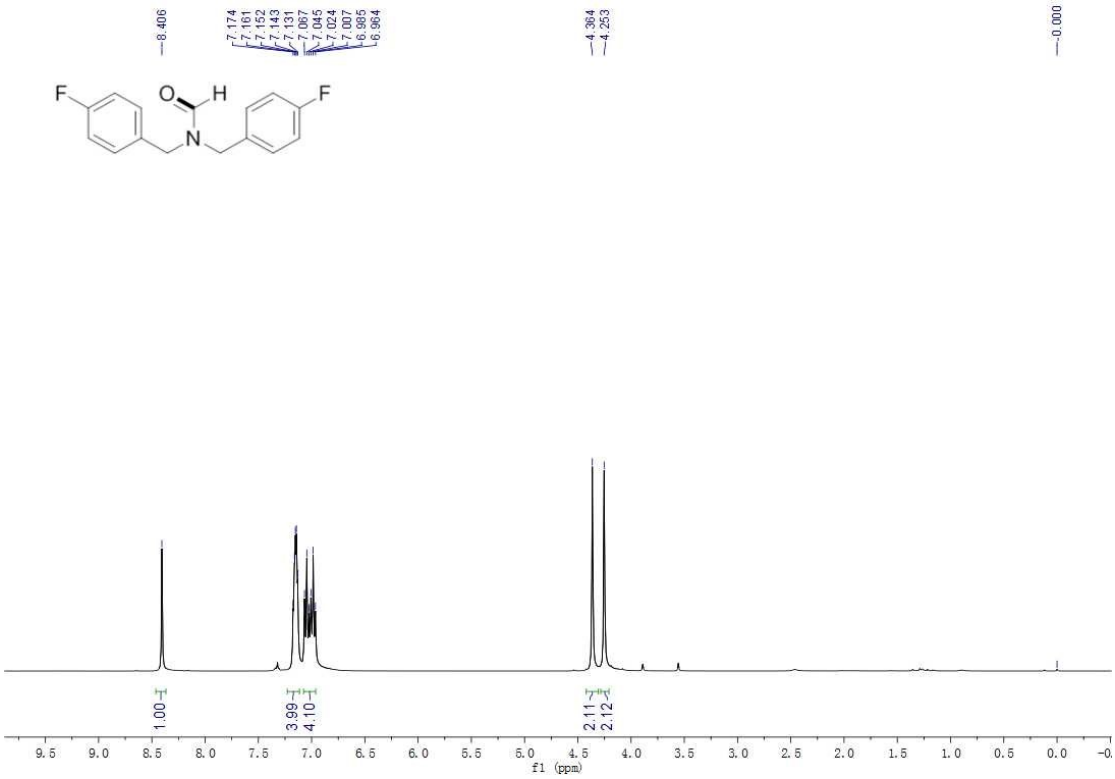


^{1}H NMR (400 MHz, $CDCl_3$)

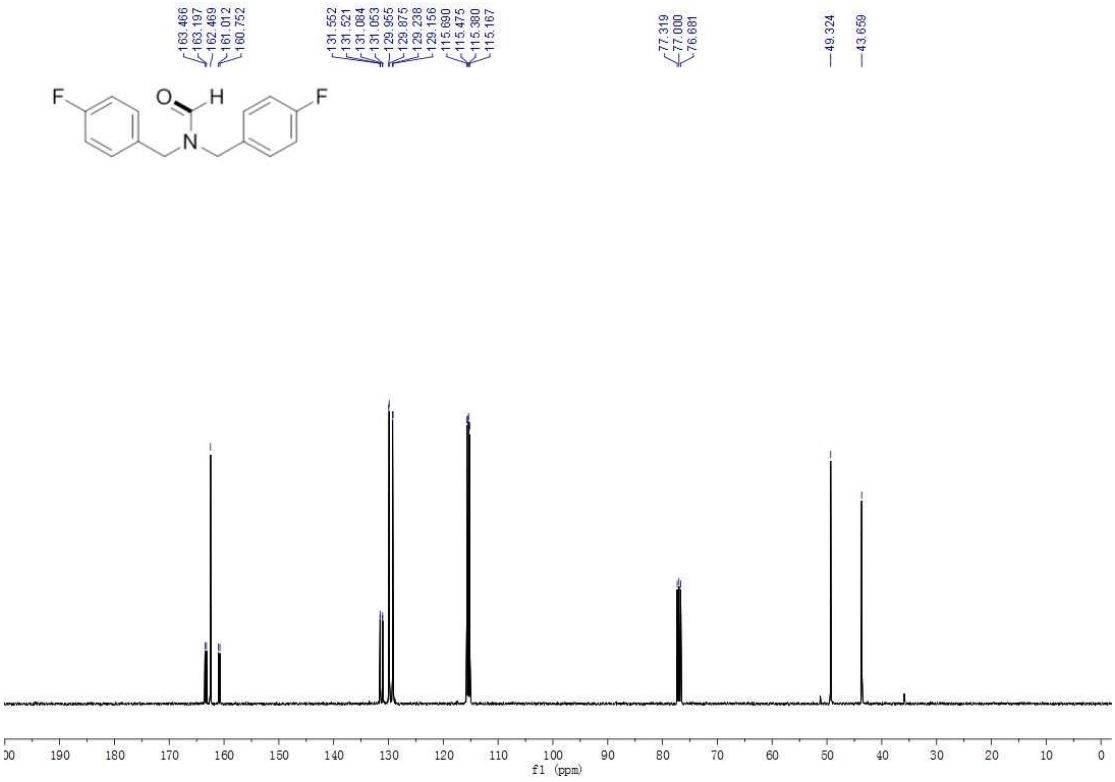


^{13}C NMR (100 MHz, $CDCl_3$)

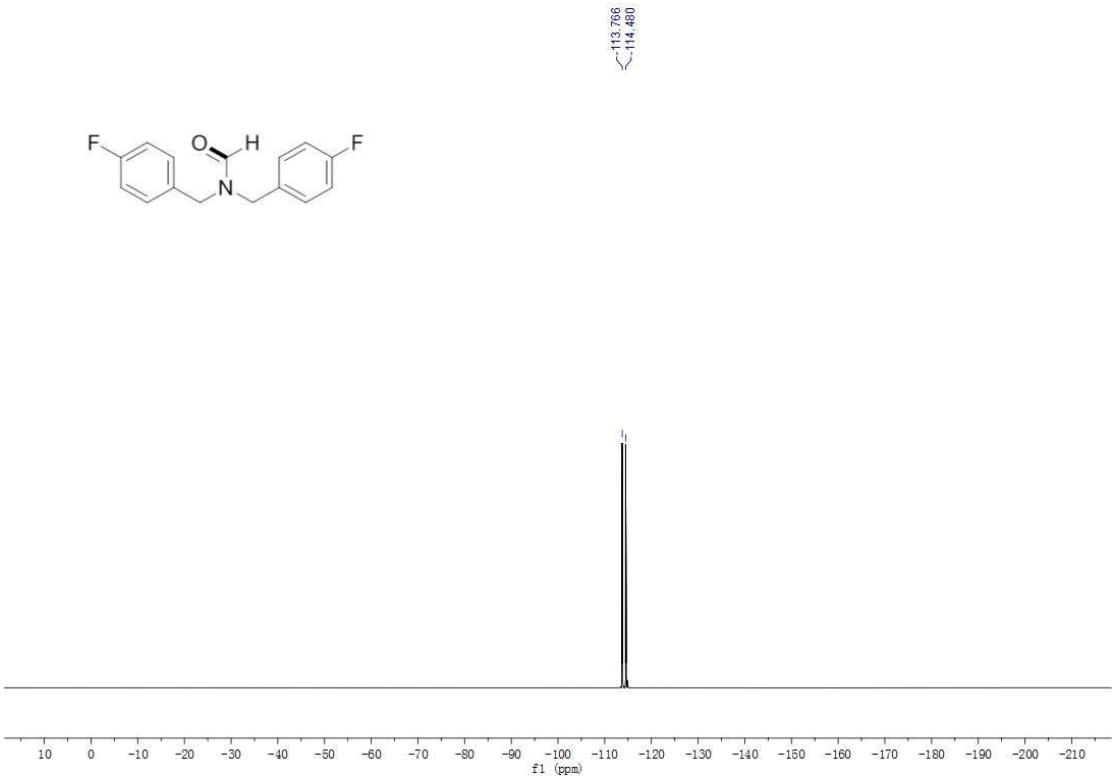
***N,N*-Bis(4-fluorobenzyl)formamide (2d):**



^{1}H NMR (400 MHz, $CDCl_3$)

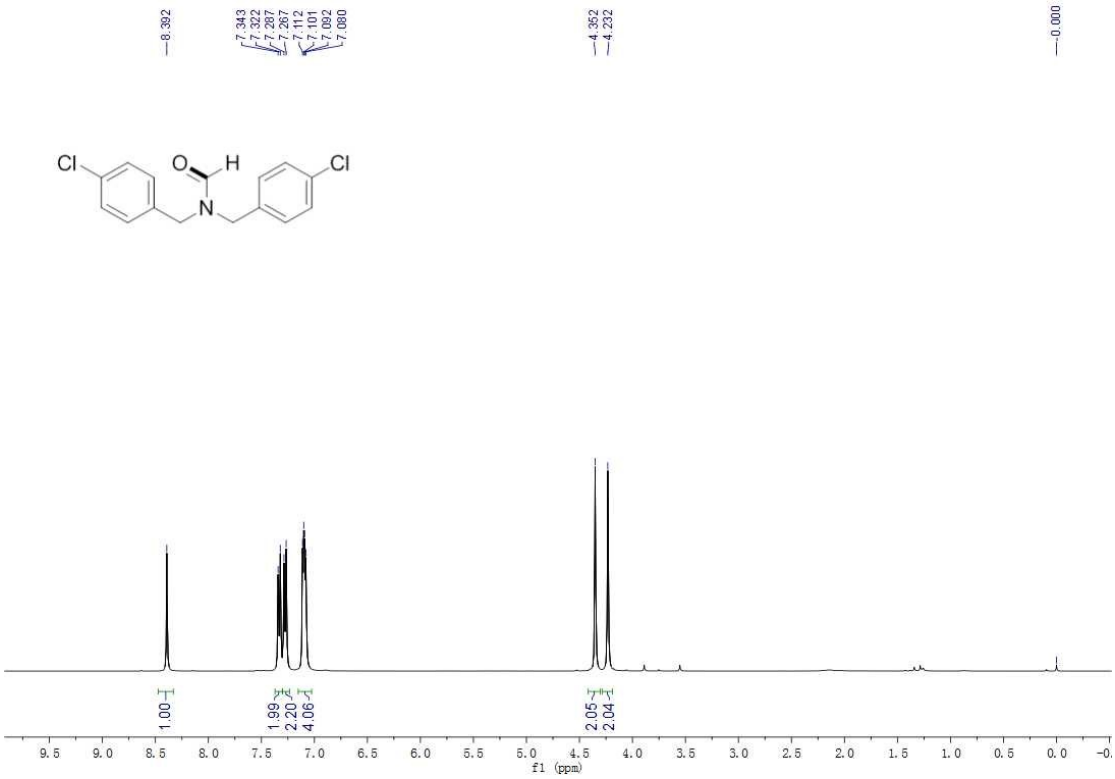


^{13}C NMR (100 MHz, $CDCl_3$)

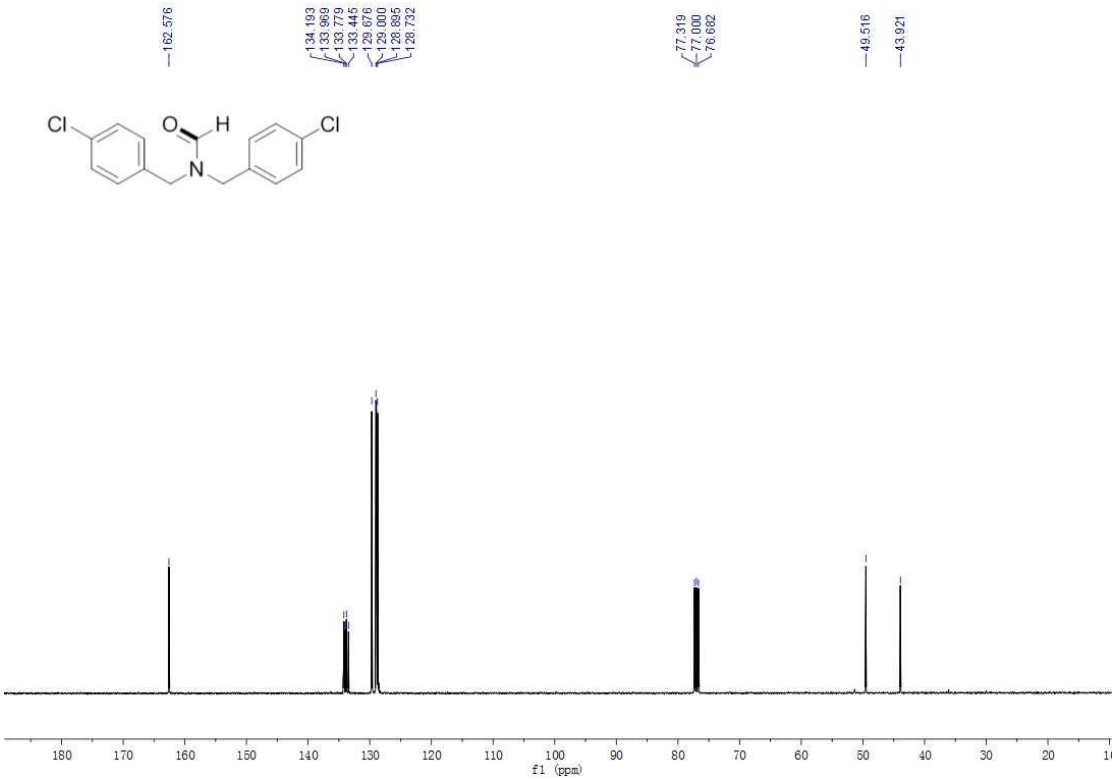


^{19}F NMR (376 MHz, $CDCl_3$)

***N,N*-Bis(4-chlorobenzyl)formamide (2e):**

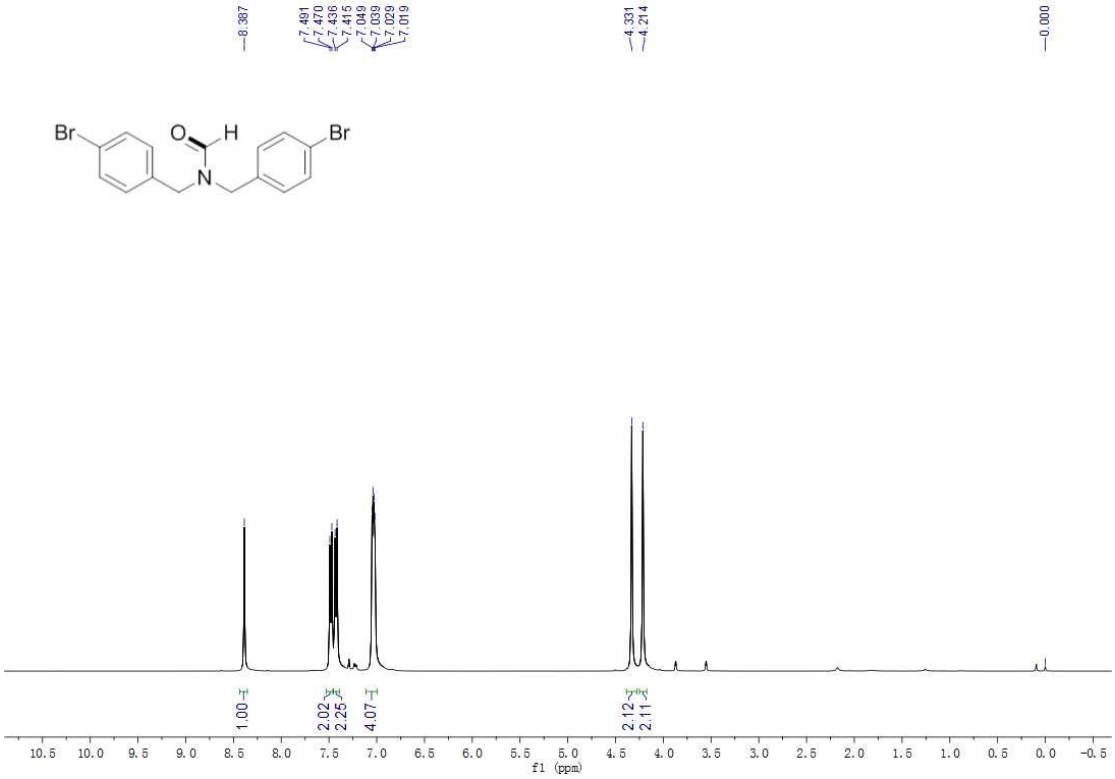


^{1}H NMR (400 MHz, $CDCl_3$)

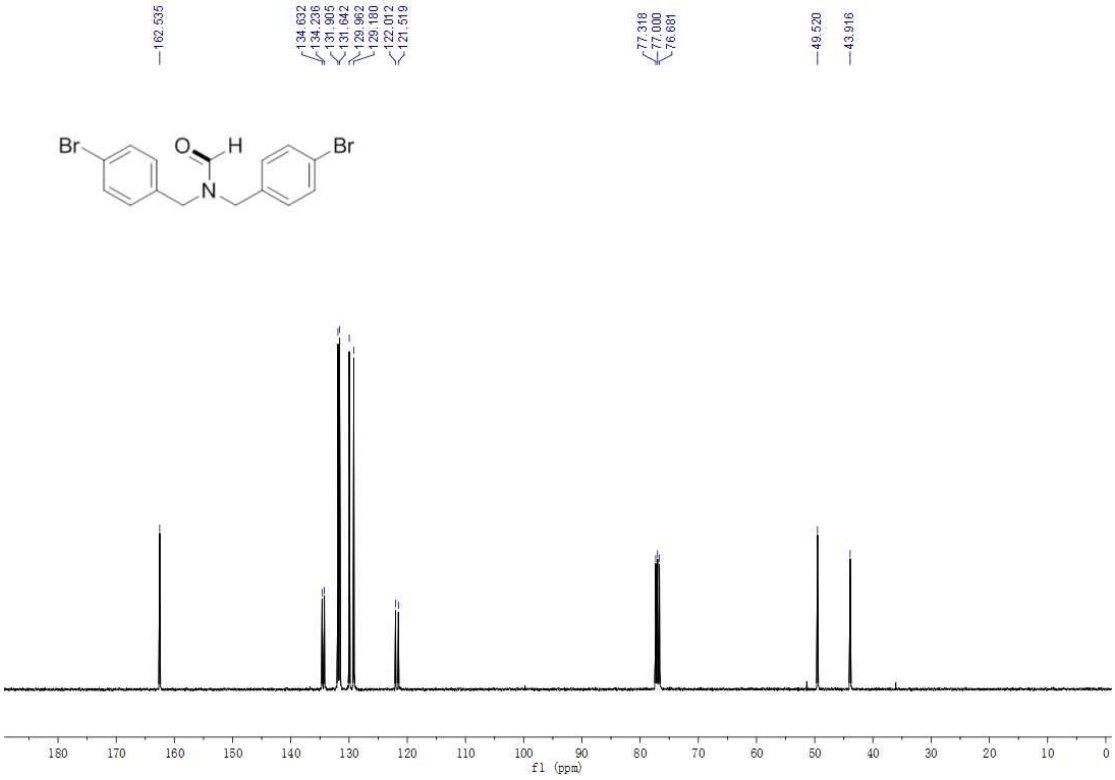


^{13}C NMR (100 MHz, $CDCl_3$)

***N,N*-Bis(4-bromobenzyl)formamide (2f):**

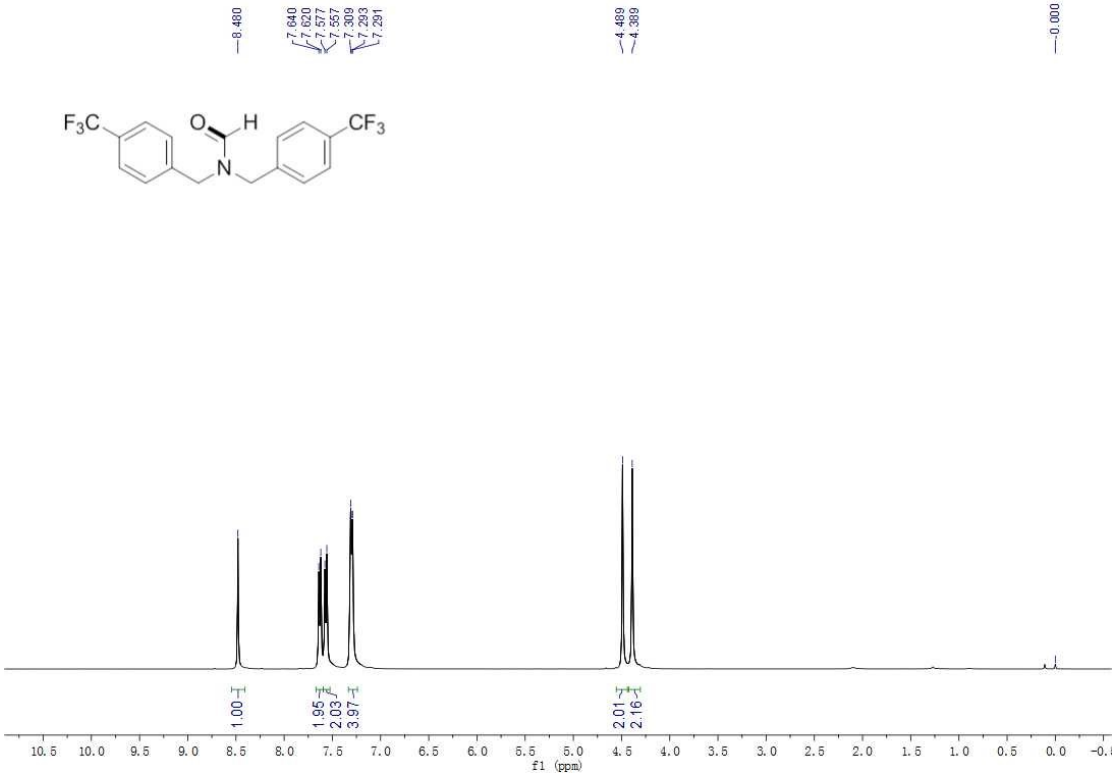


^{1}H NMR (400 MHz, $CDCl_3$)

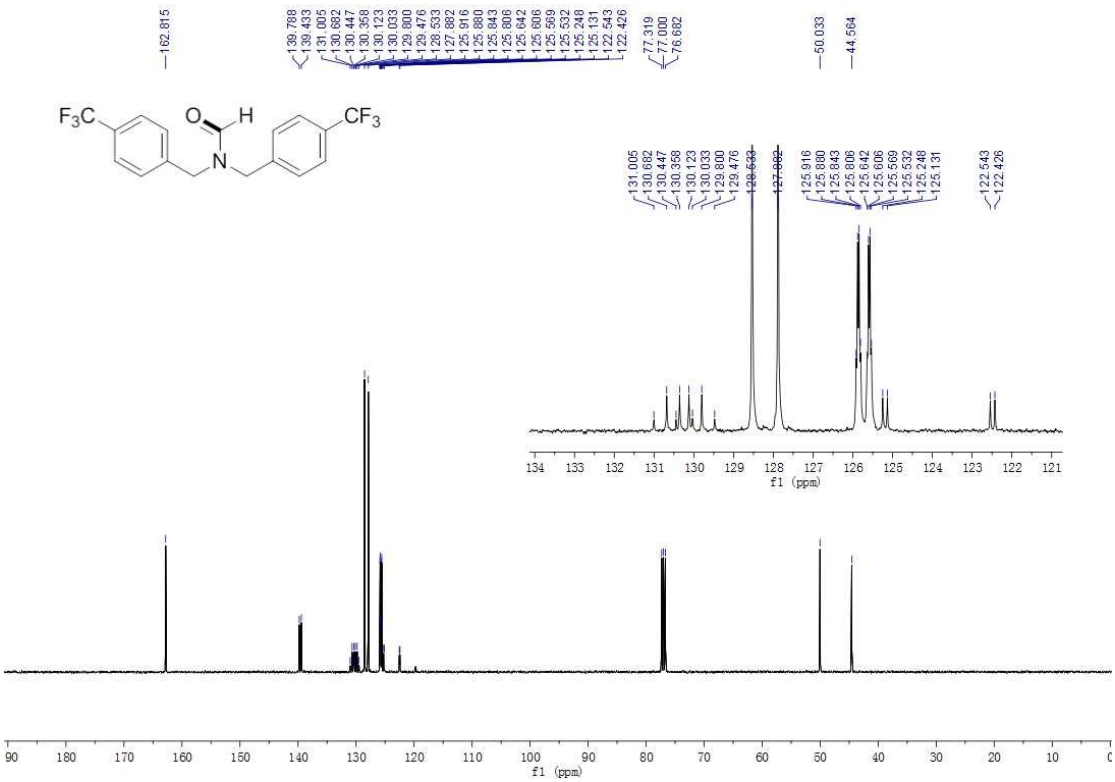


^{13}C NMR (100 MHz, $CDCl_3$)

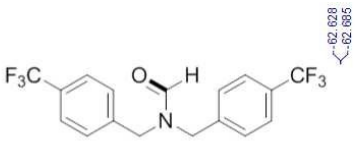
***N,N*-Bis(4-(trifluoromethyl)benzyl)formamide (2g):**

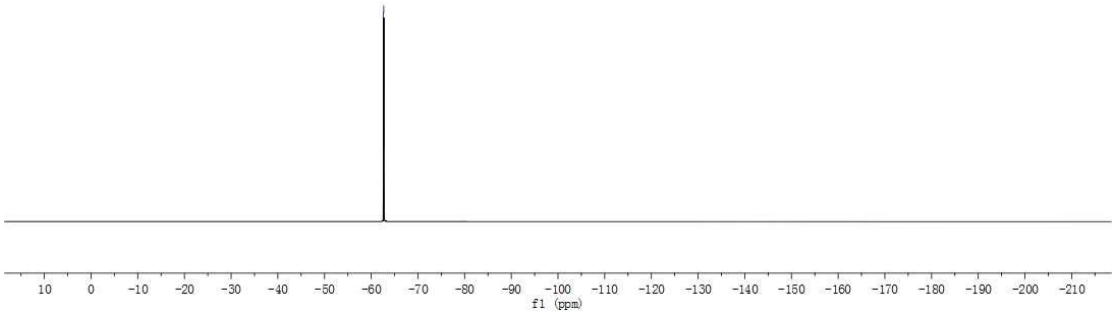


^{1}H NMR (400 MHz, $CDCl_3$)



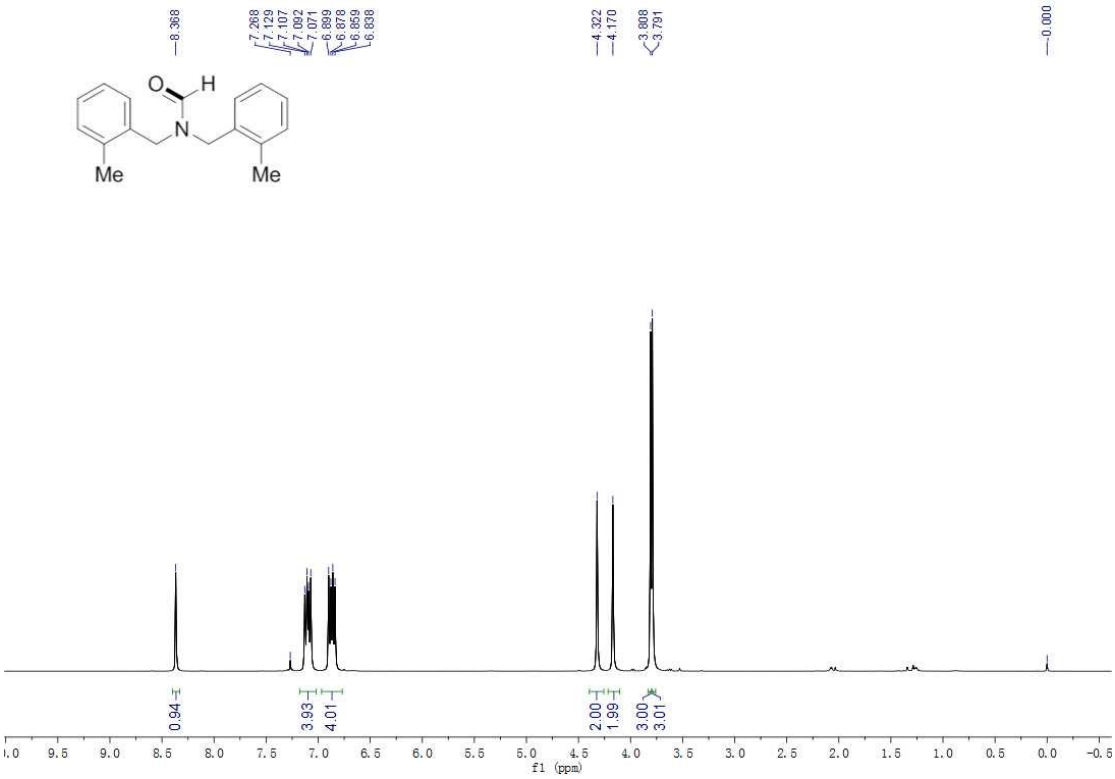
^{13}C NMR (100 MHz, $CDCl_3$)



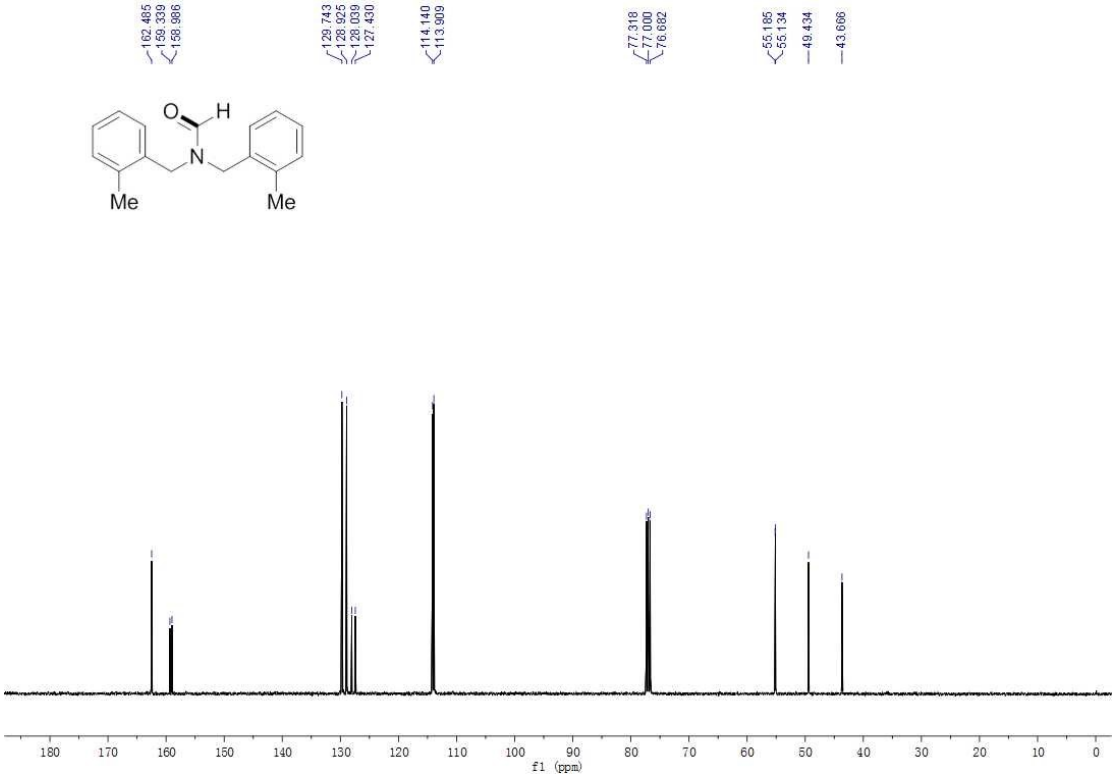


^{19}F NMR (376 MHz, $CDCl_3$)

***N,N*-Bis(2-methylbenzyl)formamide (2h):**

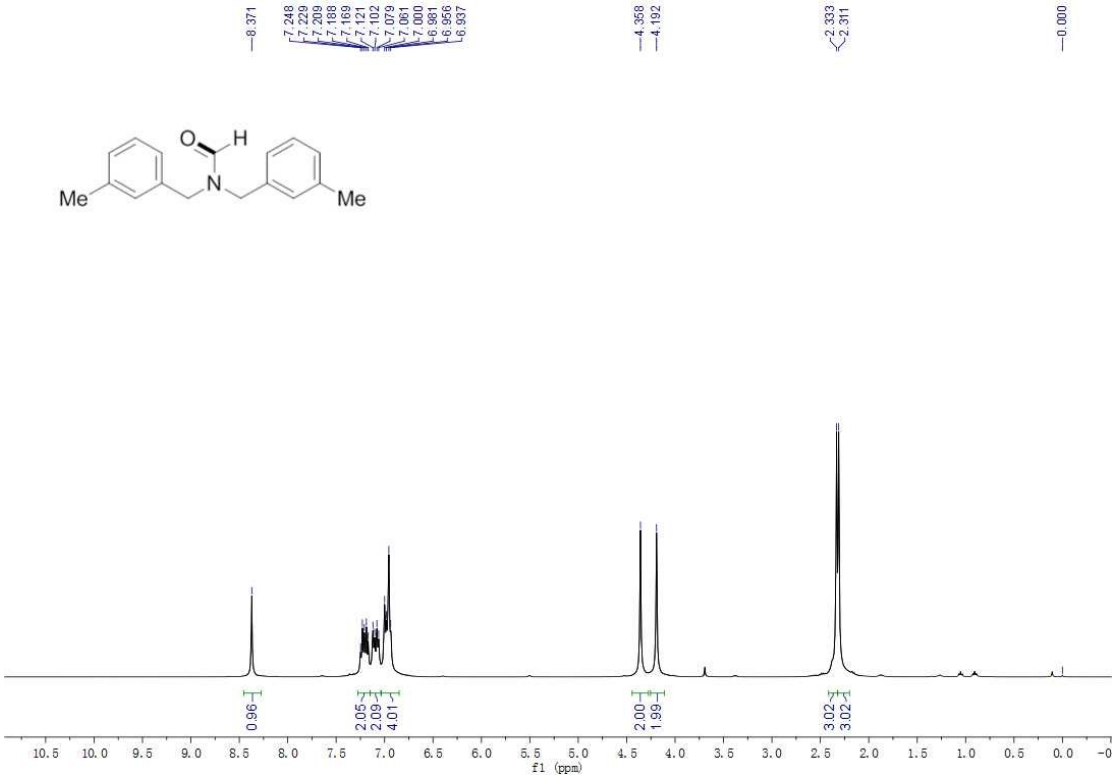


^{1}H NMR (400 MHz, $CDCl_3$)

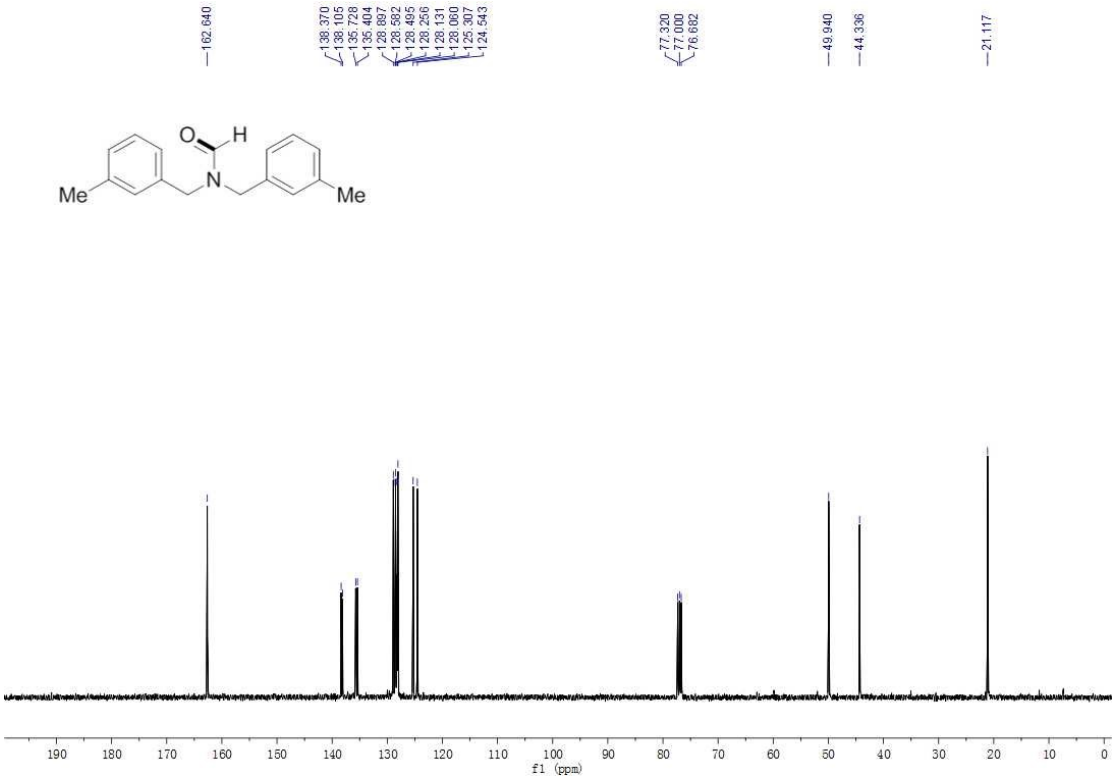


^{13}C NMR (100 MHz, $CDCl_3$)

***N,N*-Bis(3-methylbenzyl)formamide (2i):**

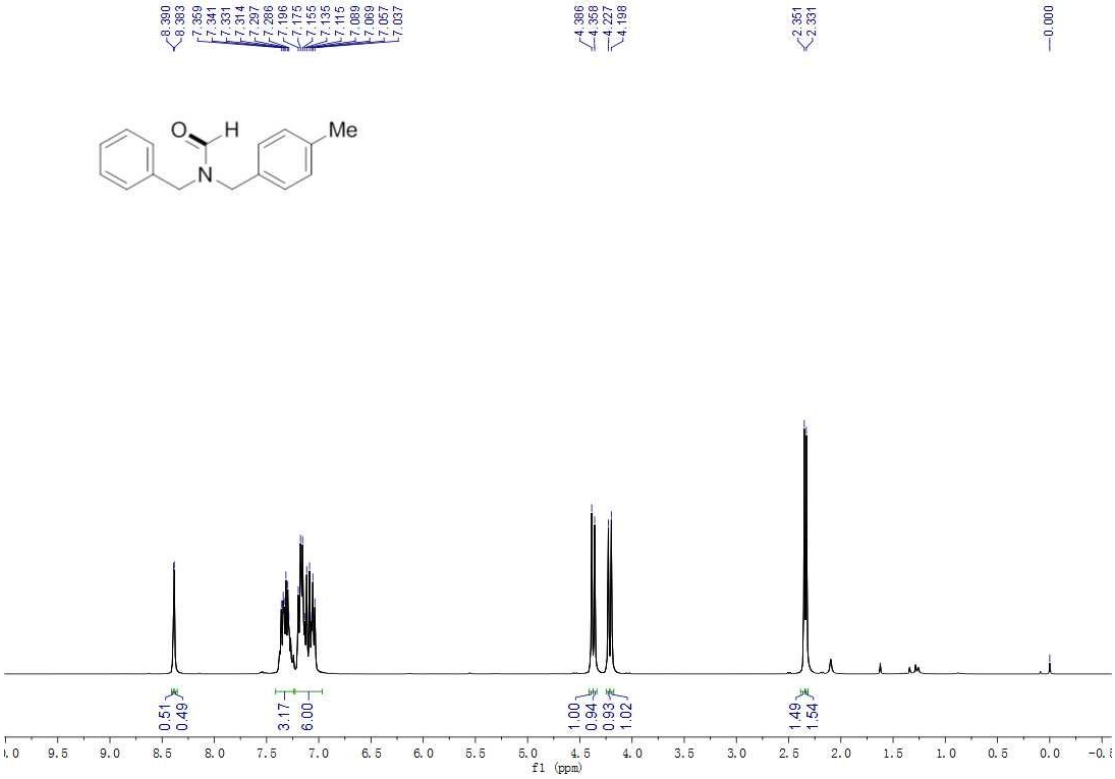


^{1}H NMR (400 MHz, $CDCl_3$)

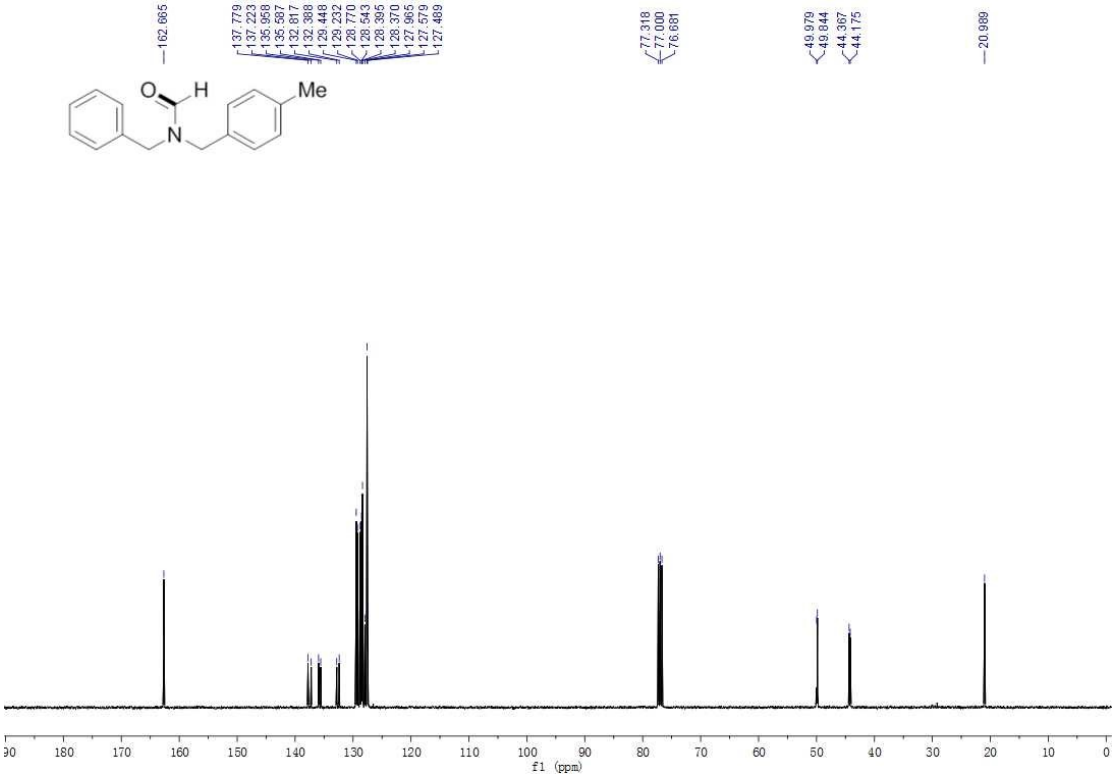


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(4-methylbenzyl)formamide (2j):**

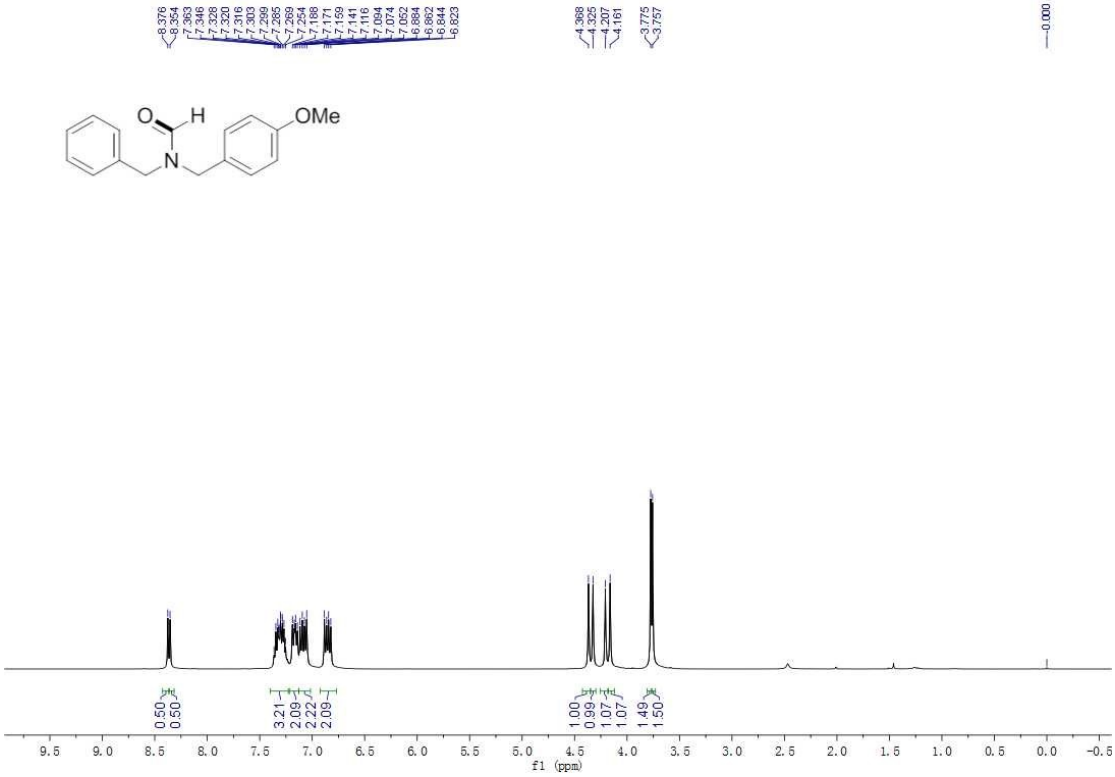


^{1}H NMR (400 MHz, $CDCl_3$)

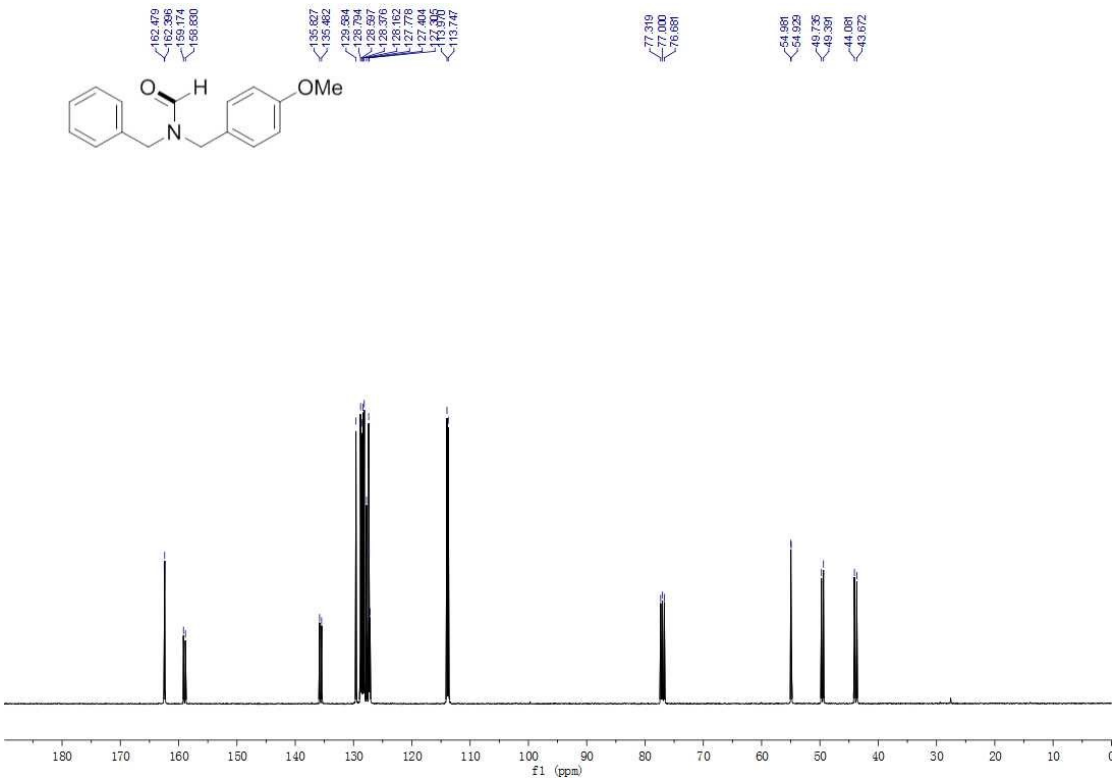


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(4-methoxybenzyl)formamide (2k):**

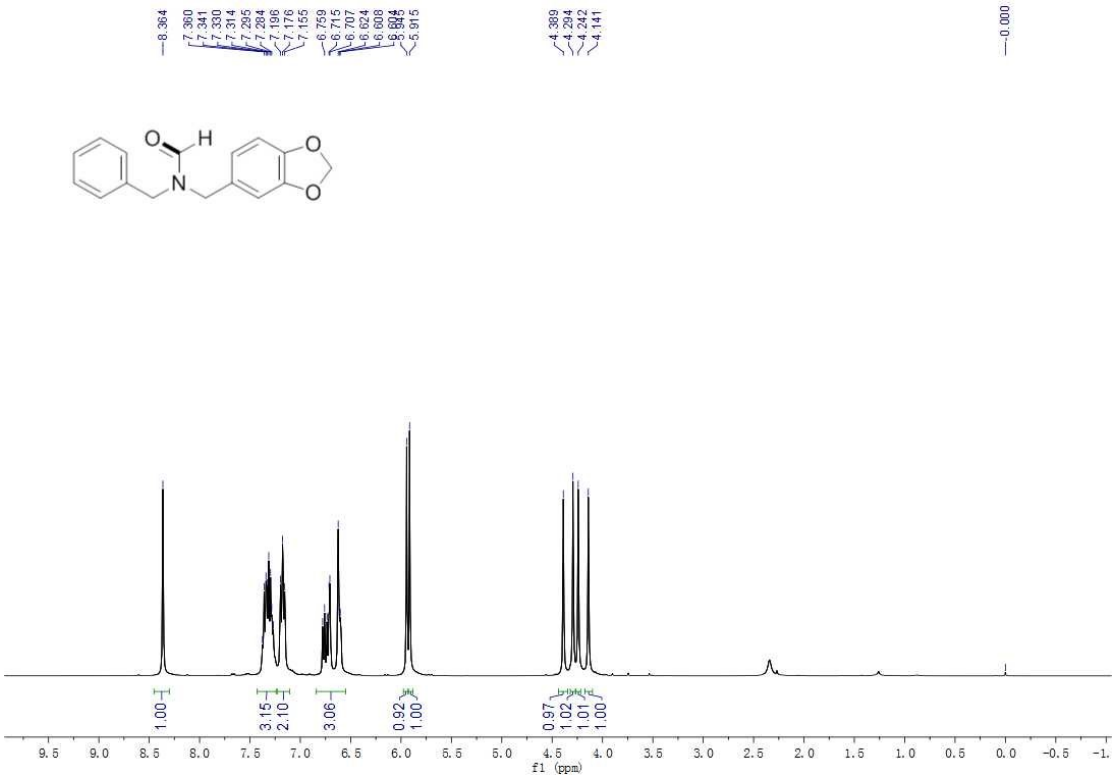


^{1}H NMR (400 MHz, $CDCl_3$)

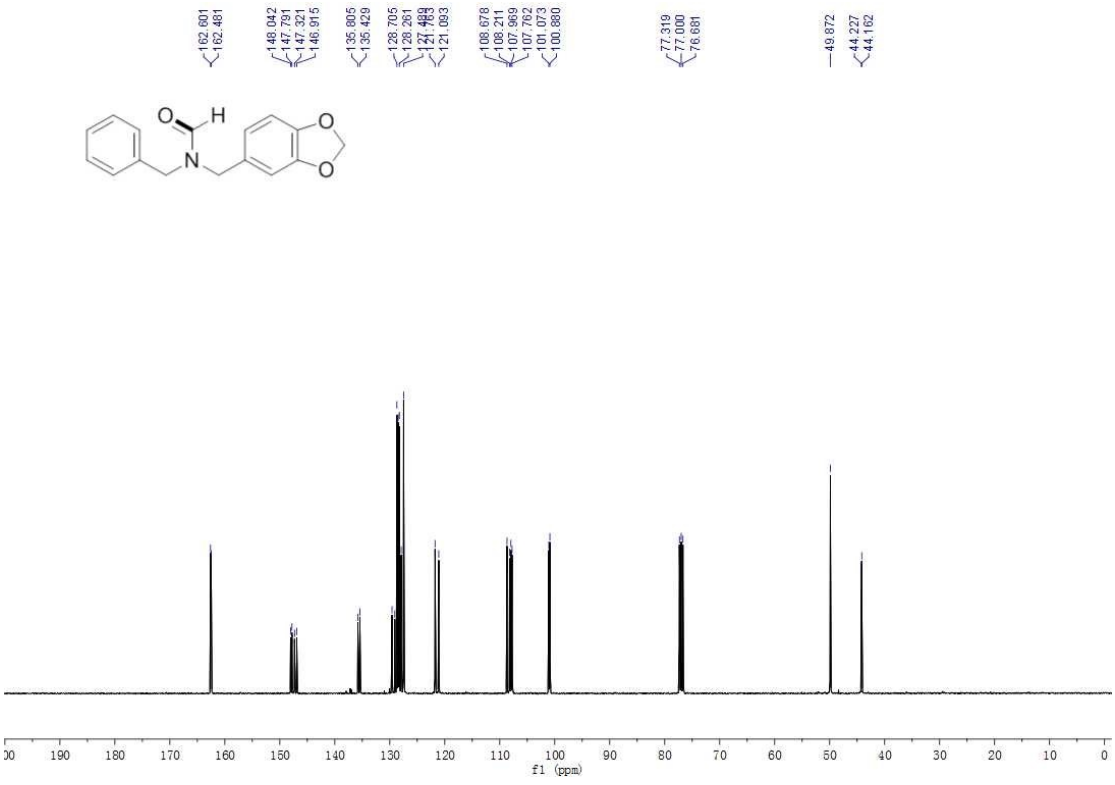


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-(Benzo[*d*][1,3]dioxol-5-ylmethyl)-*N*-benzylformamide (2l):**

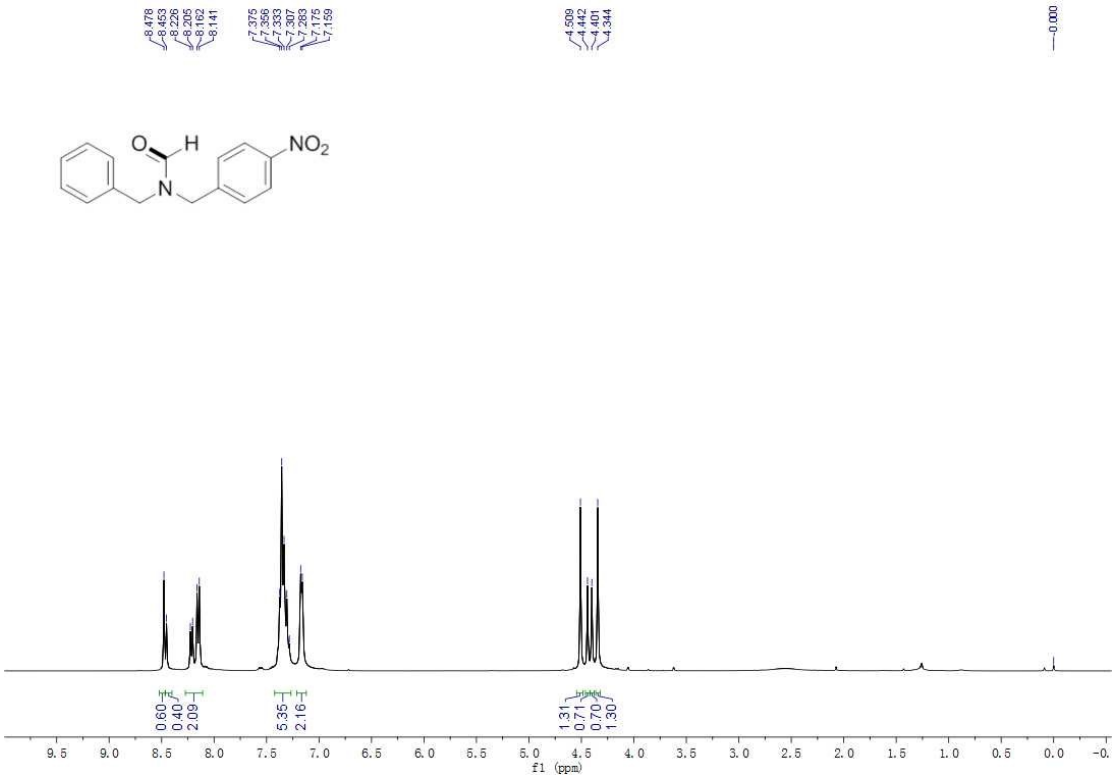


^{1}H NMR (400 MHz, $CDCl_3$)

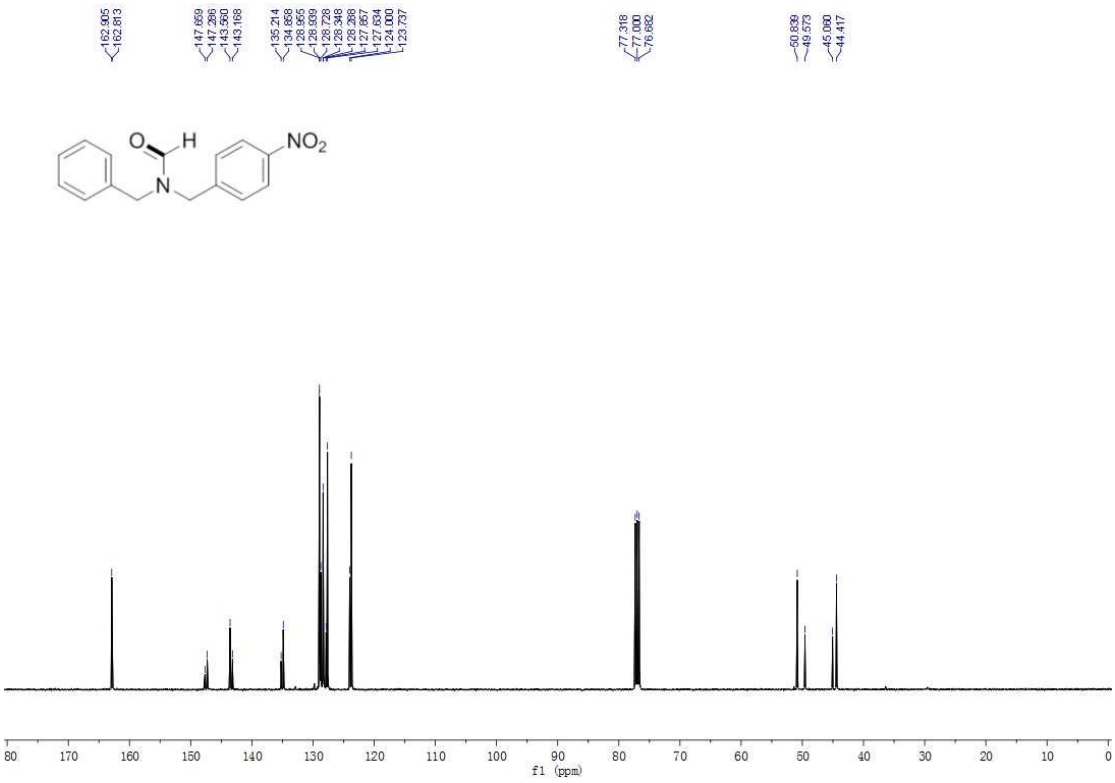


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(4-nitrobenzyl)formamide (2m):**

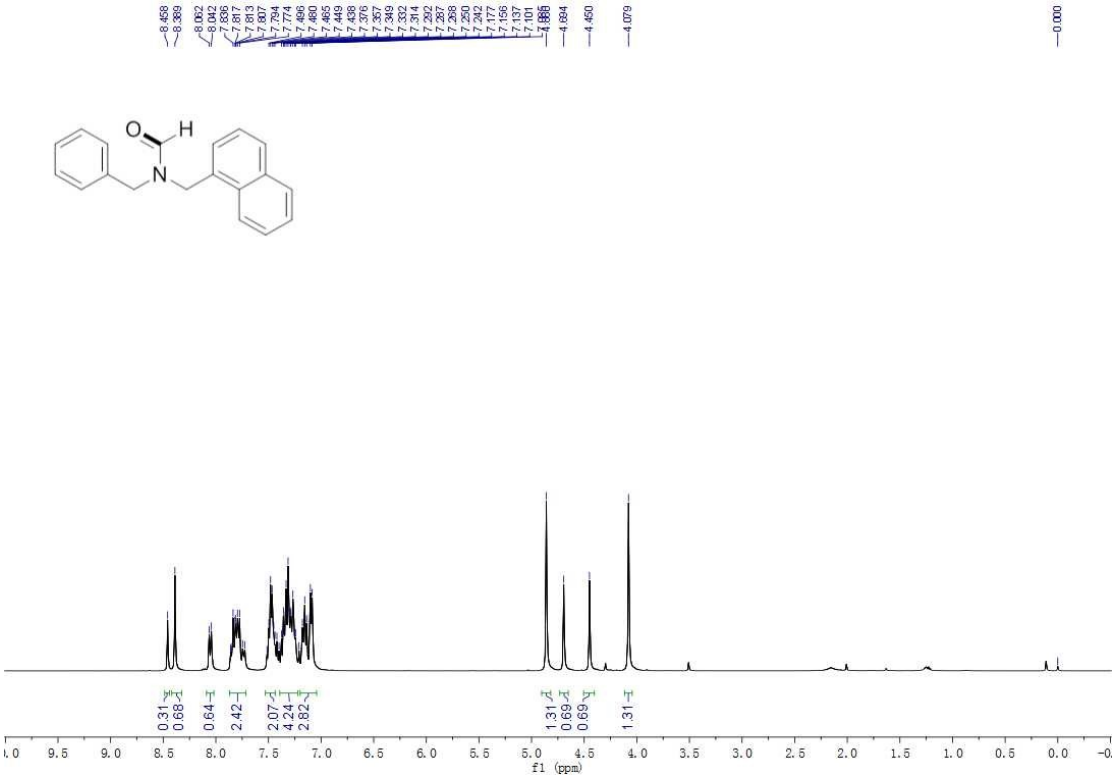


^{1}H NMR (400 MHz, $CDCl_3$)

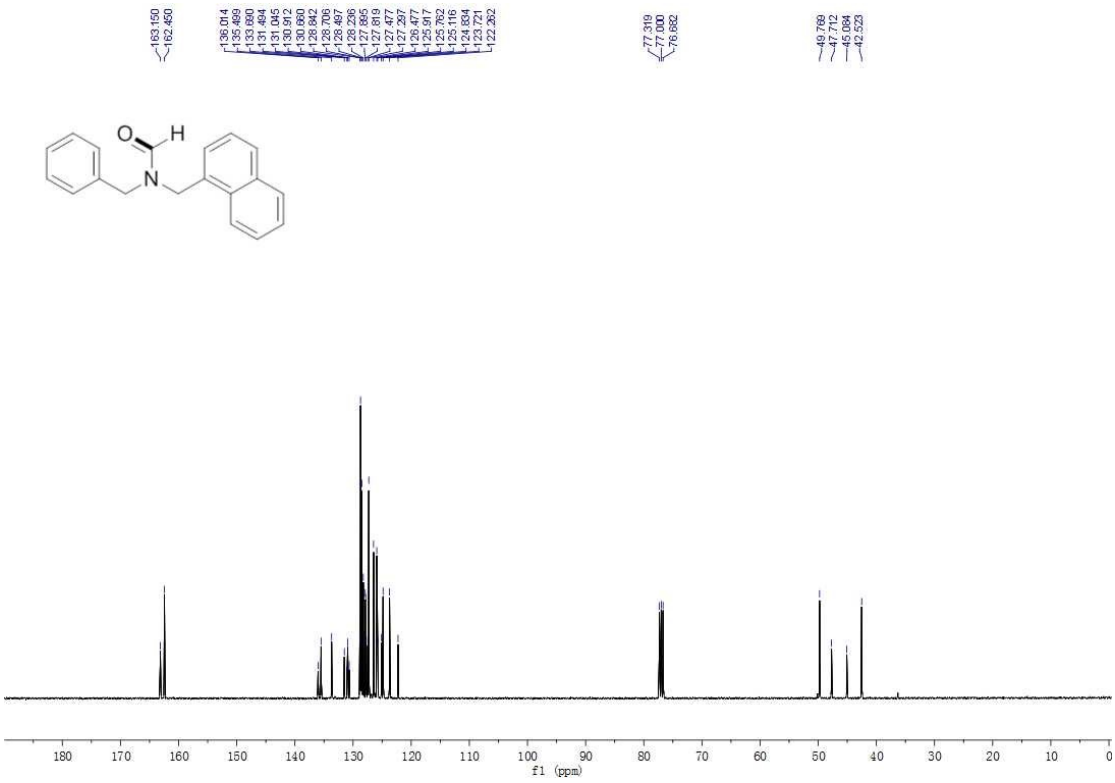


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(naphthalen-1-ylmethyl)formamide (2n):**

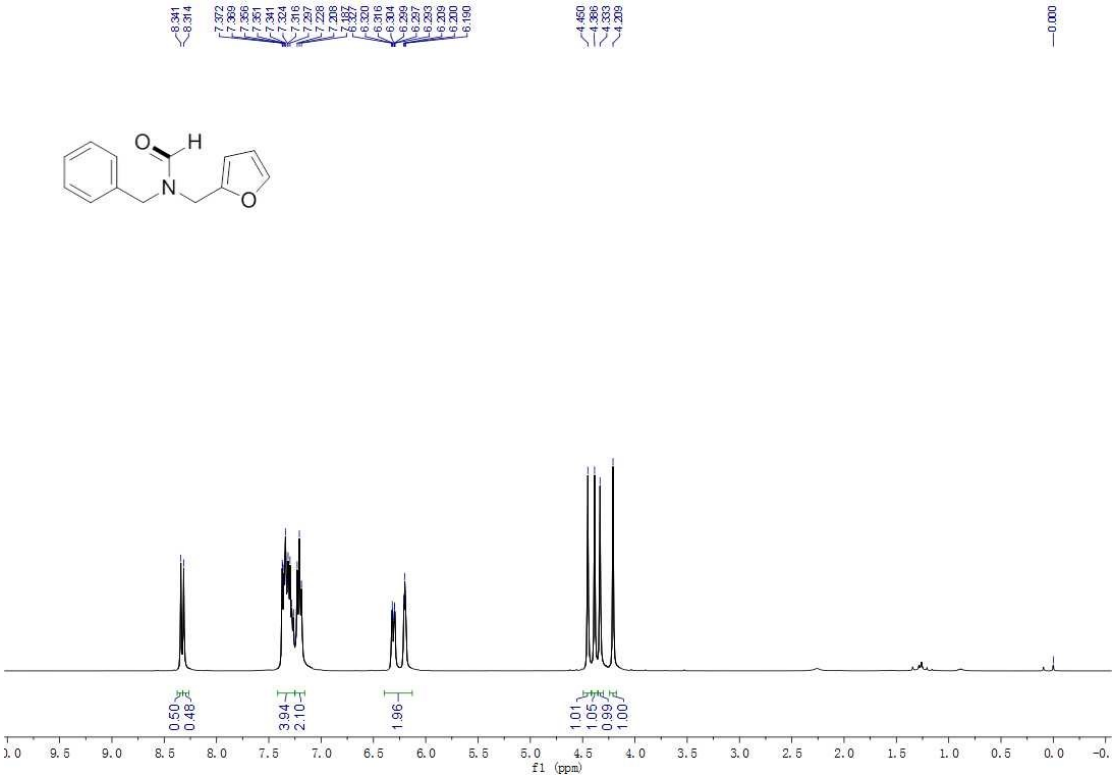


^{1}H NMR (400 MHz, $CDCl_3$)

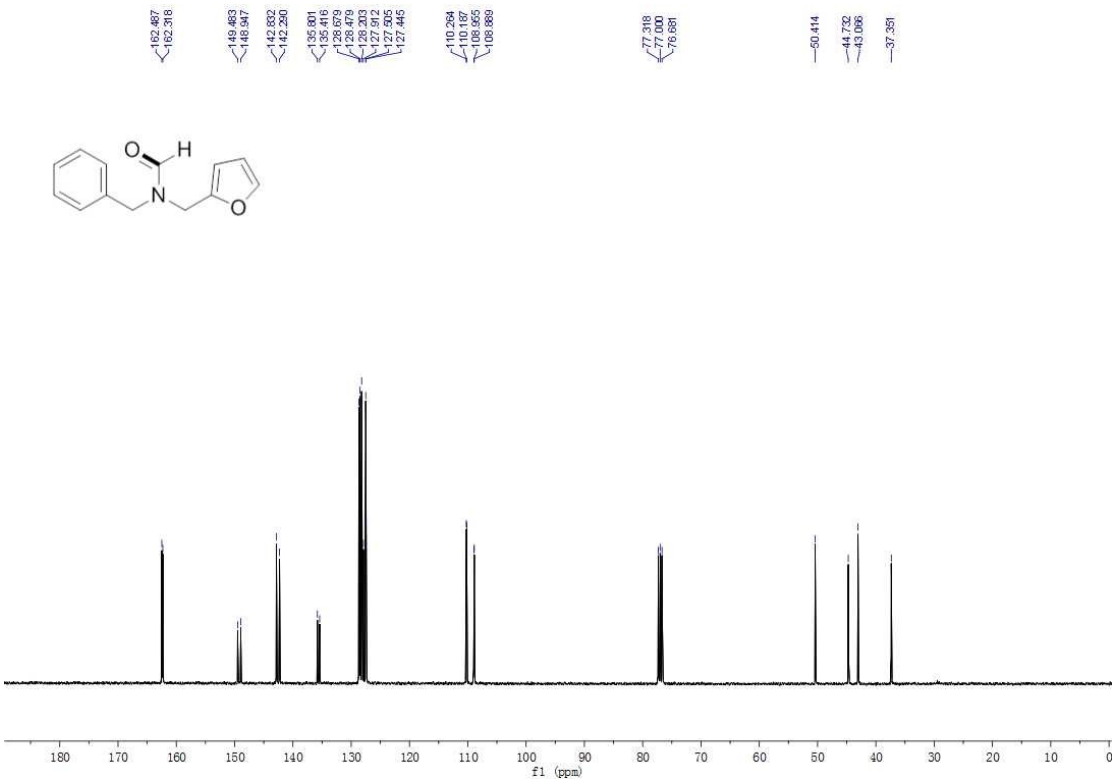


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(furan-2-ylmethyl)formamide (2o):**

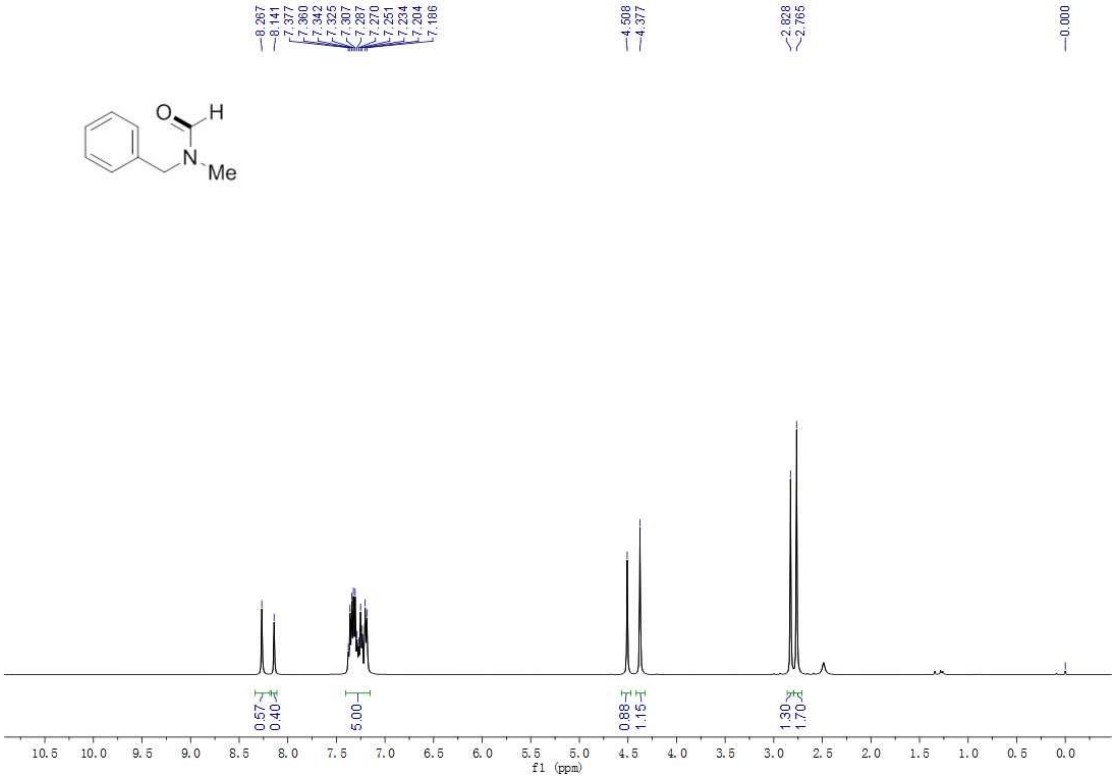


^{1}H NMR (400 MHz, $CDCl_3$)

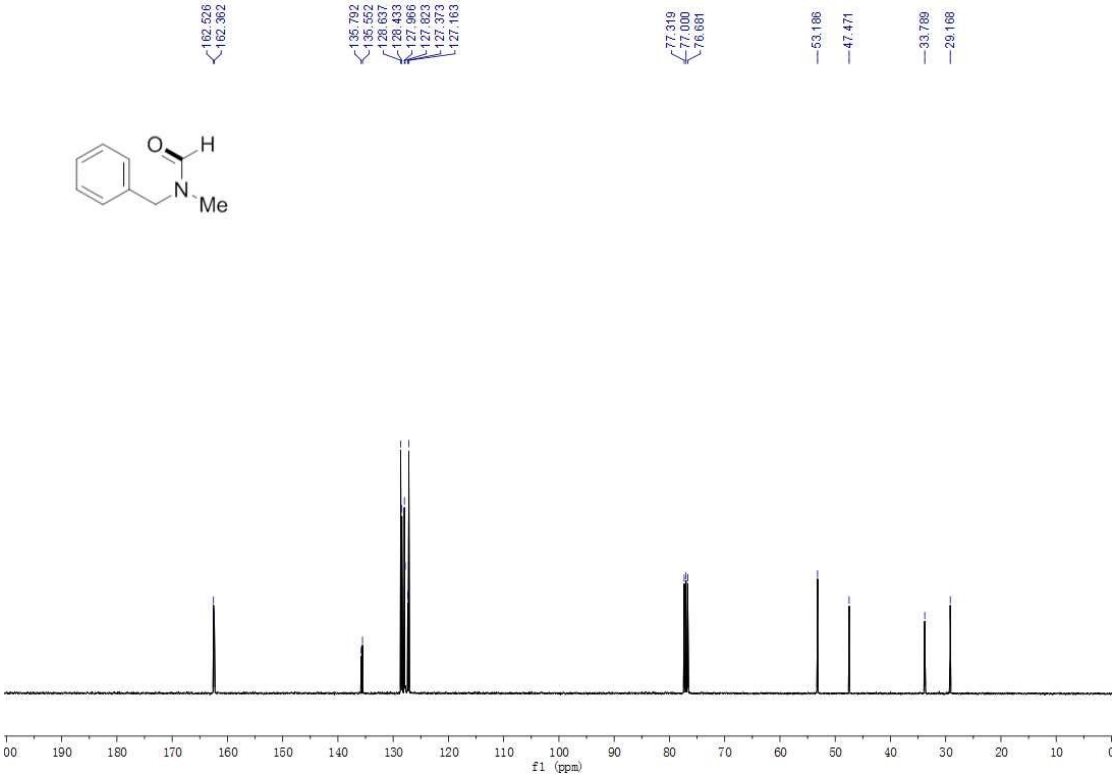


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-methylformamide (2p):**

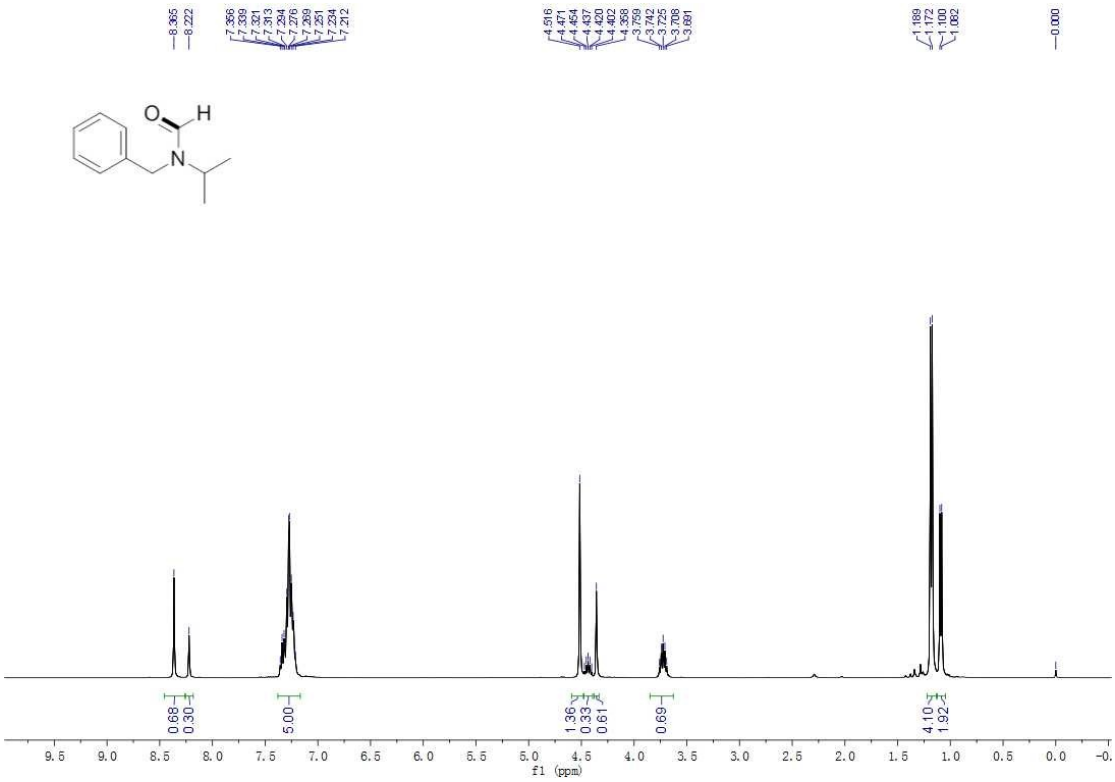


^{1}H NMR (400 MHz, $CDCl_3$)

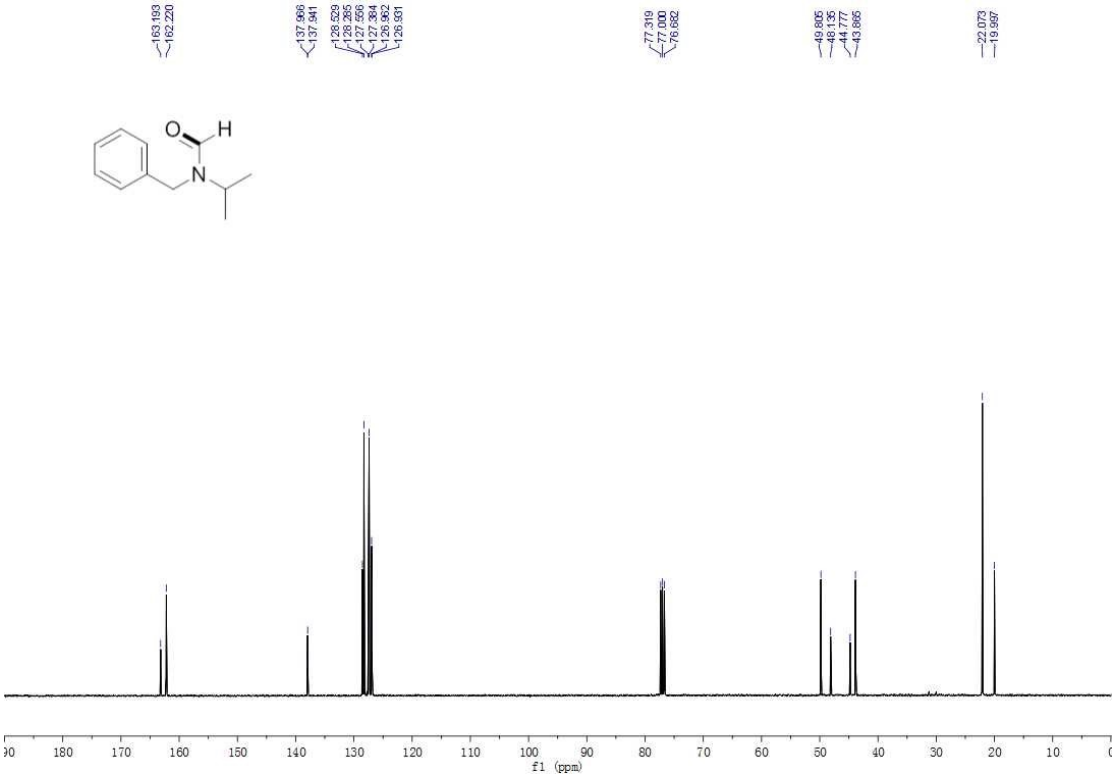


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-isopropylformamide (2q):**

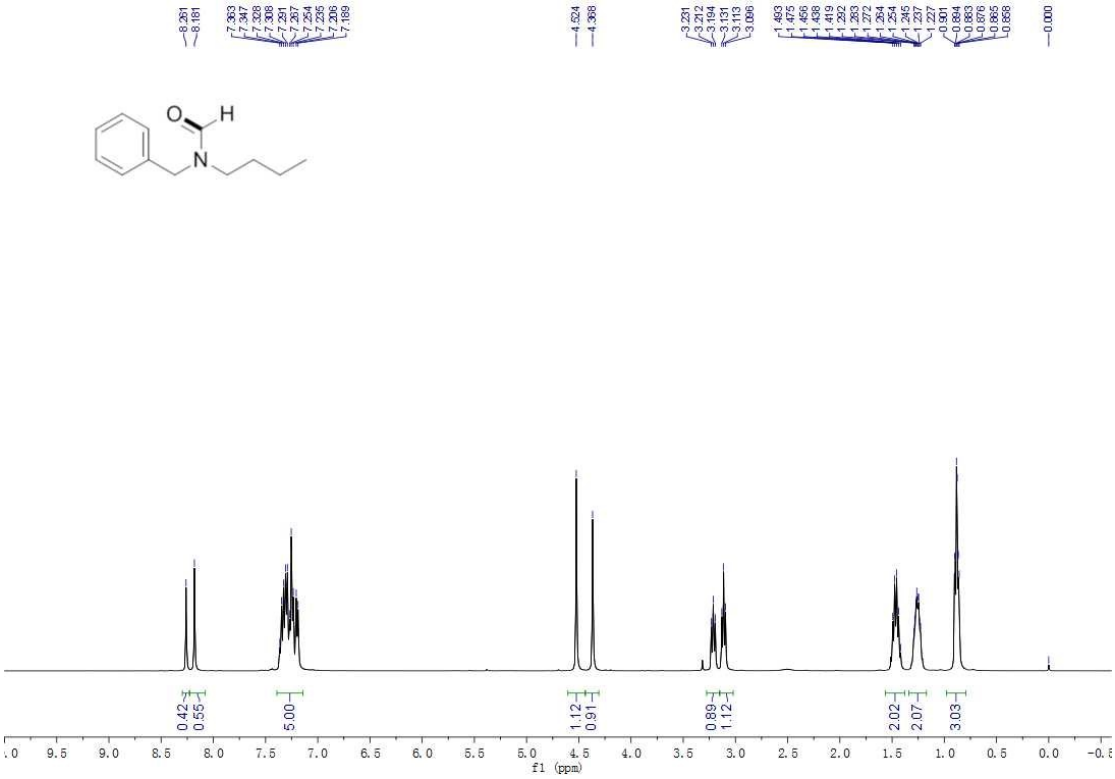


^{1}H NMR (400 MHz, $CDCl_3$)

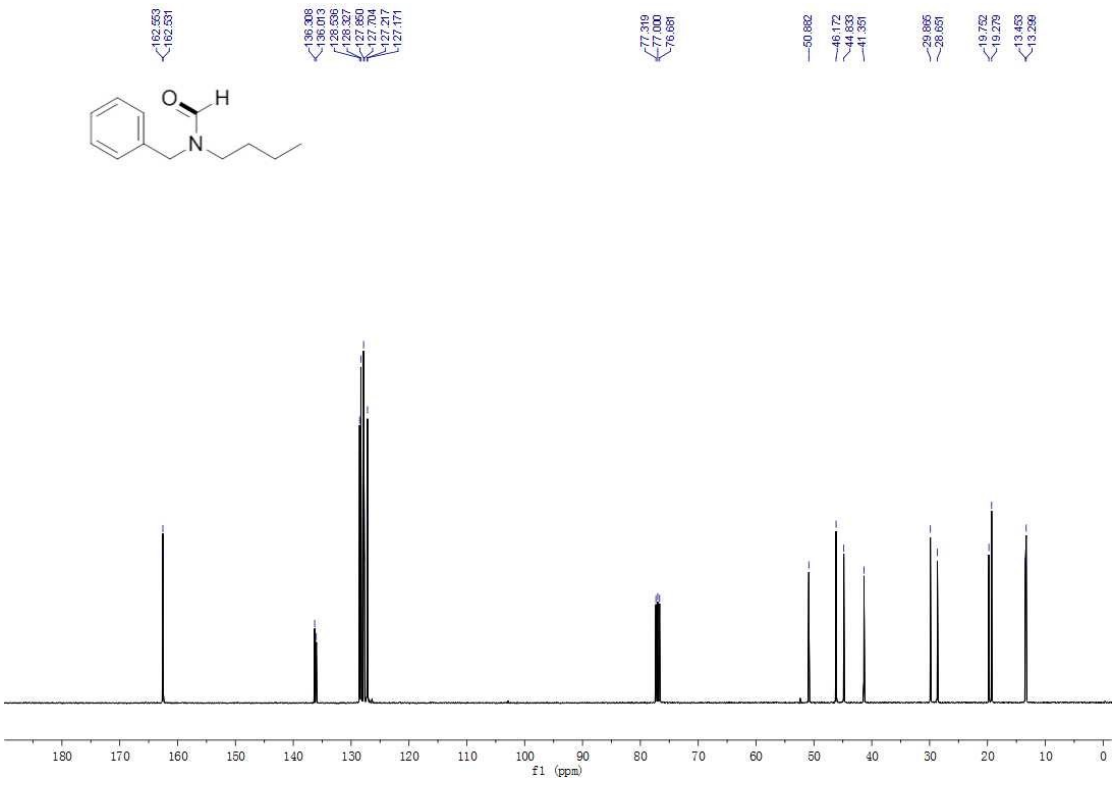


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-butylformamide (2r):**

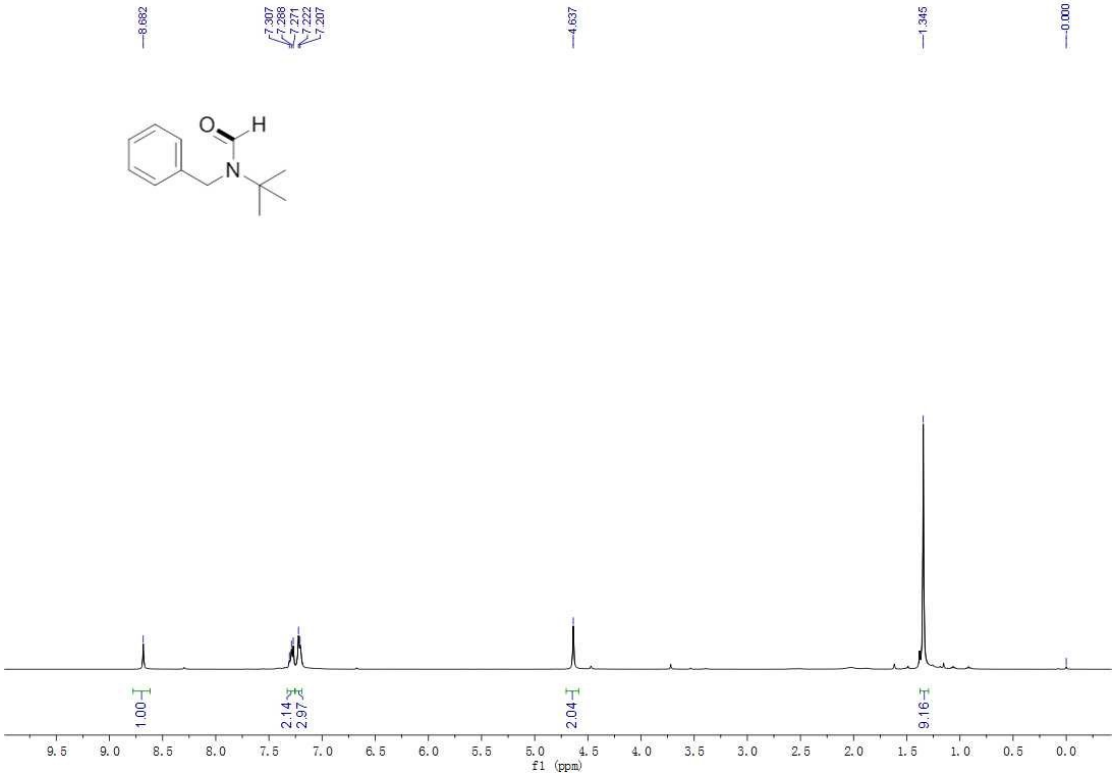


^{1}H NMR (400 MHz, $CDCl_3$)

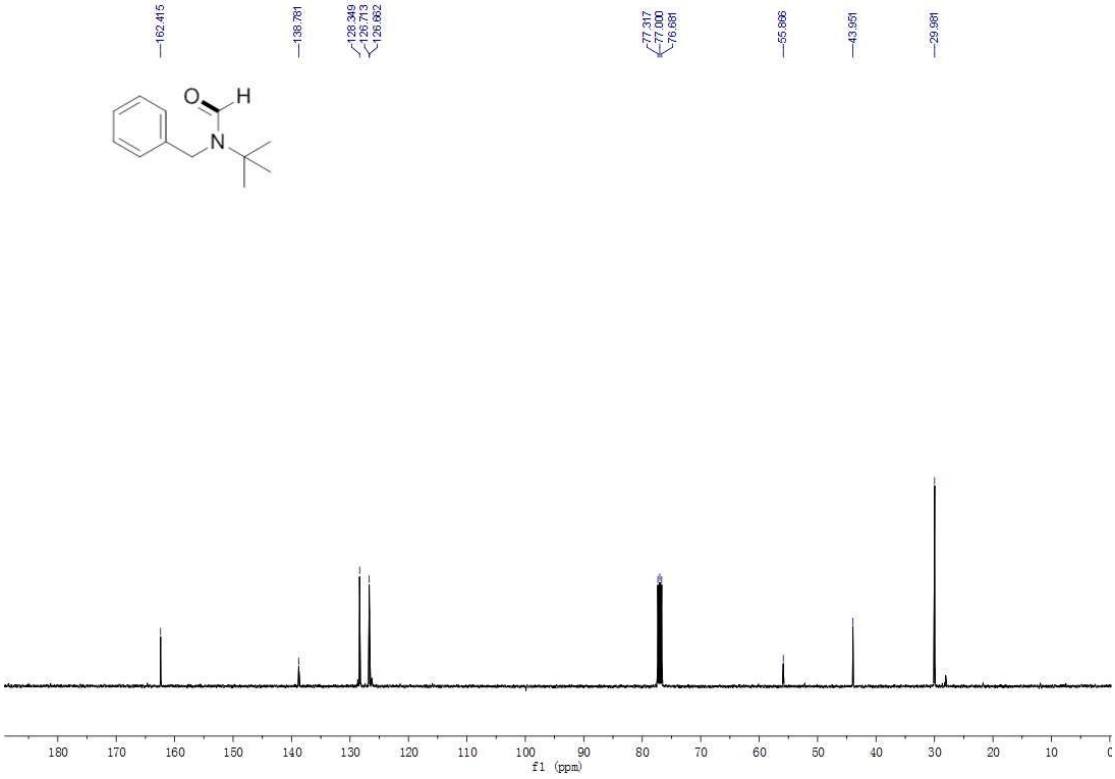


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Benzyl-*N*-(*tert*-butyl)formamide (2s):**

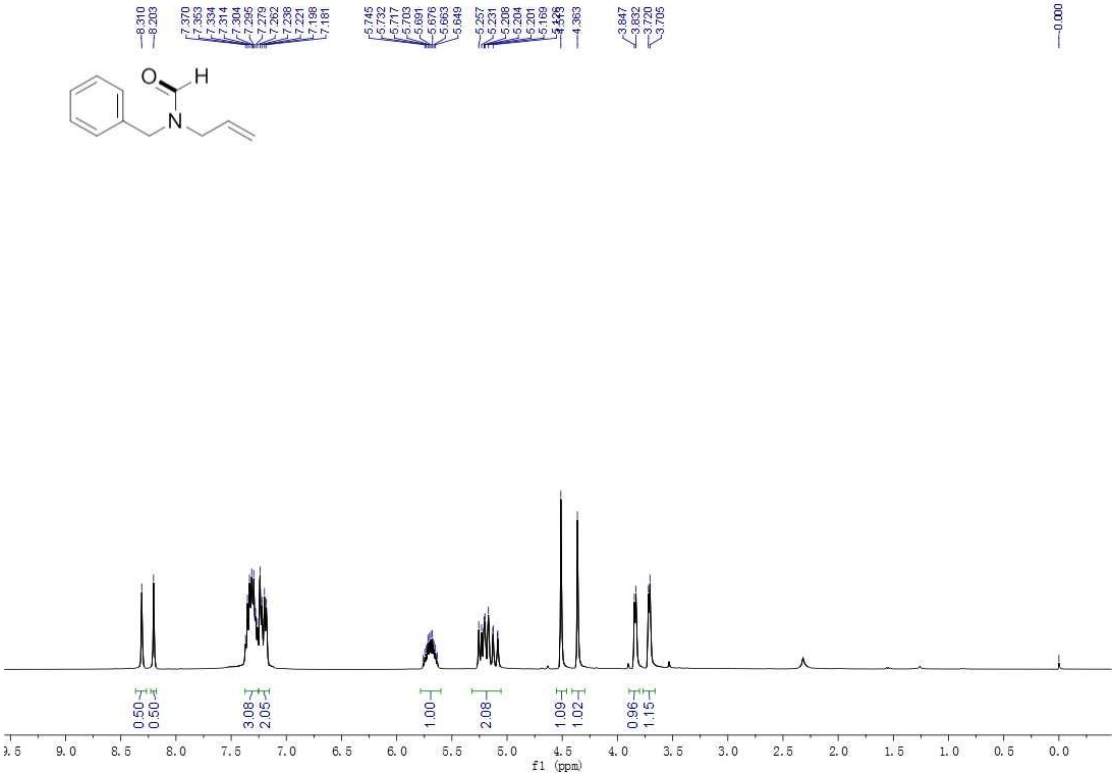


^{1}H NMR (400 MHz, $CDCl_3$)

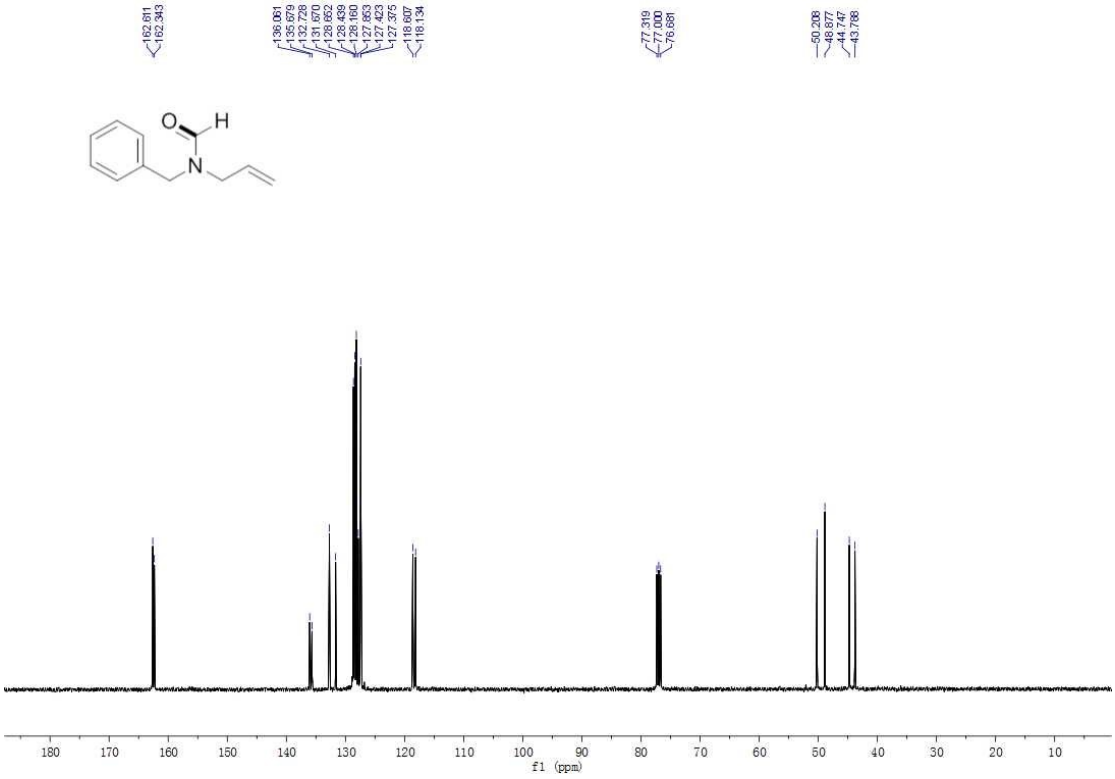


^{13}C NMR (100 MHz, $CDCl_3$)

***N*-Allyl-*N*-benzylformamide (2t):**

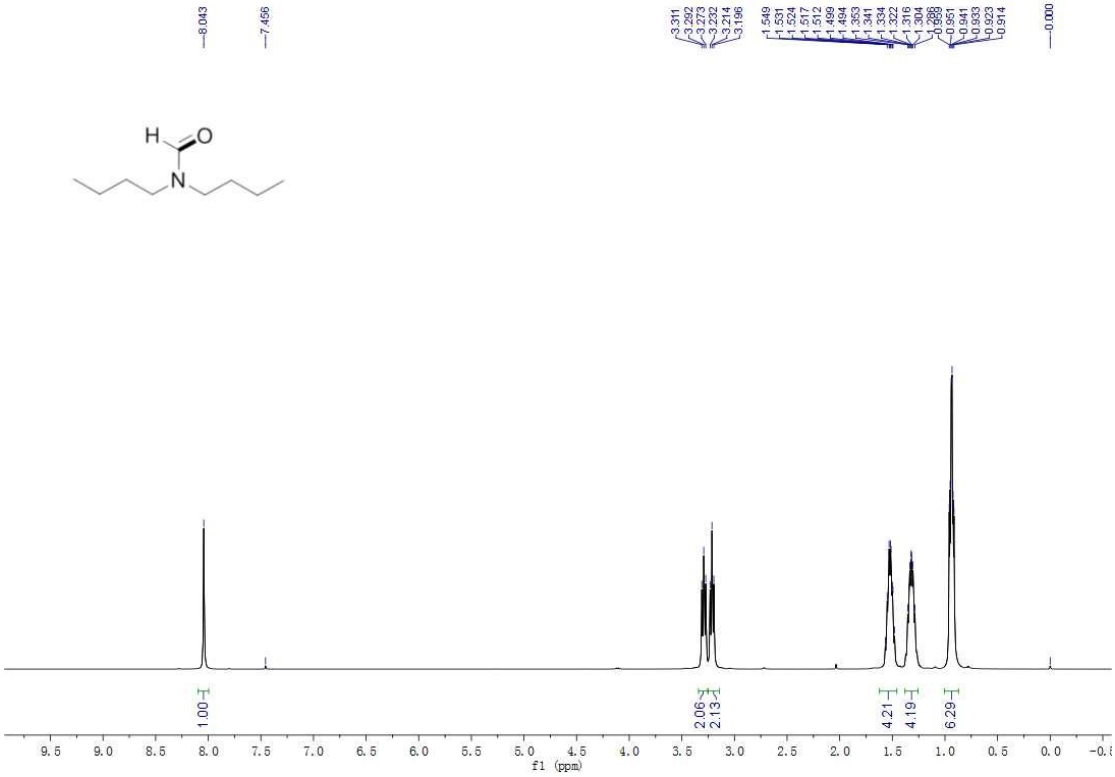


^{1}H NMR (400 MHz, $CDCl_3$)

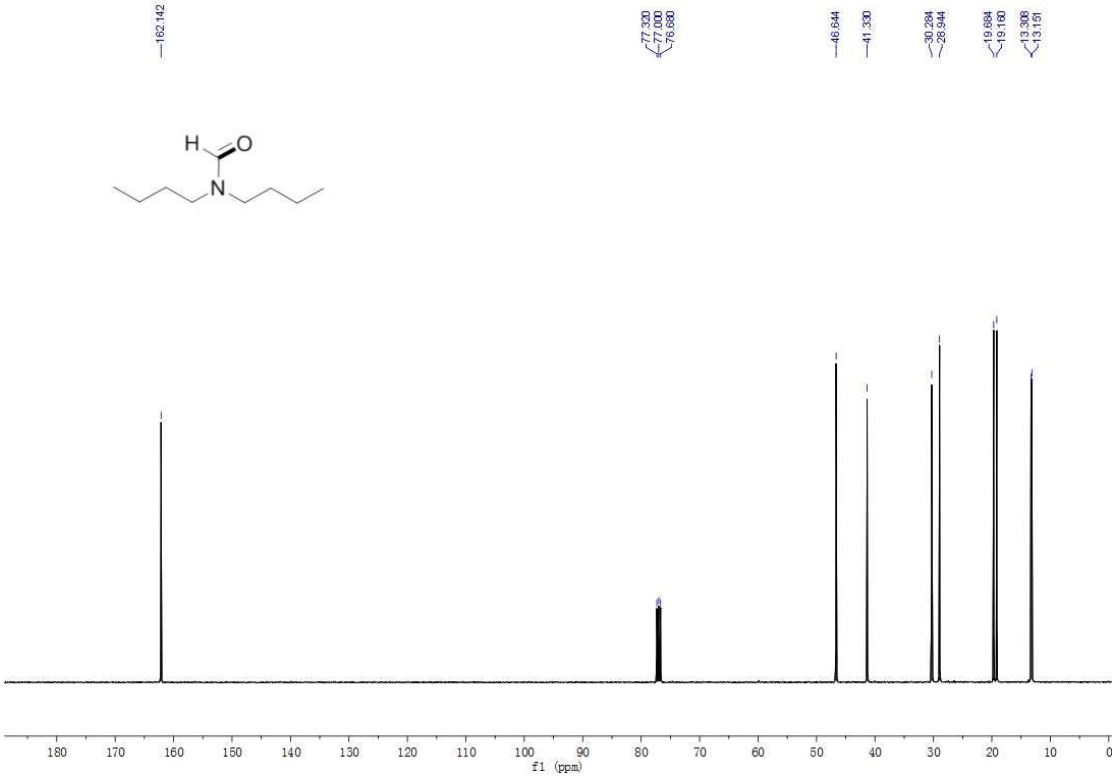


^{13}C NMR (100 MHz, $CDCl_3$)

***N,N*-Dibutylformamide (2w):**

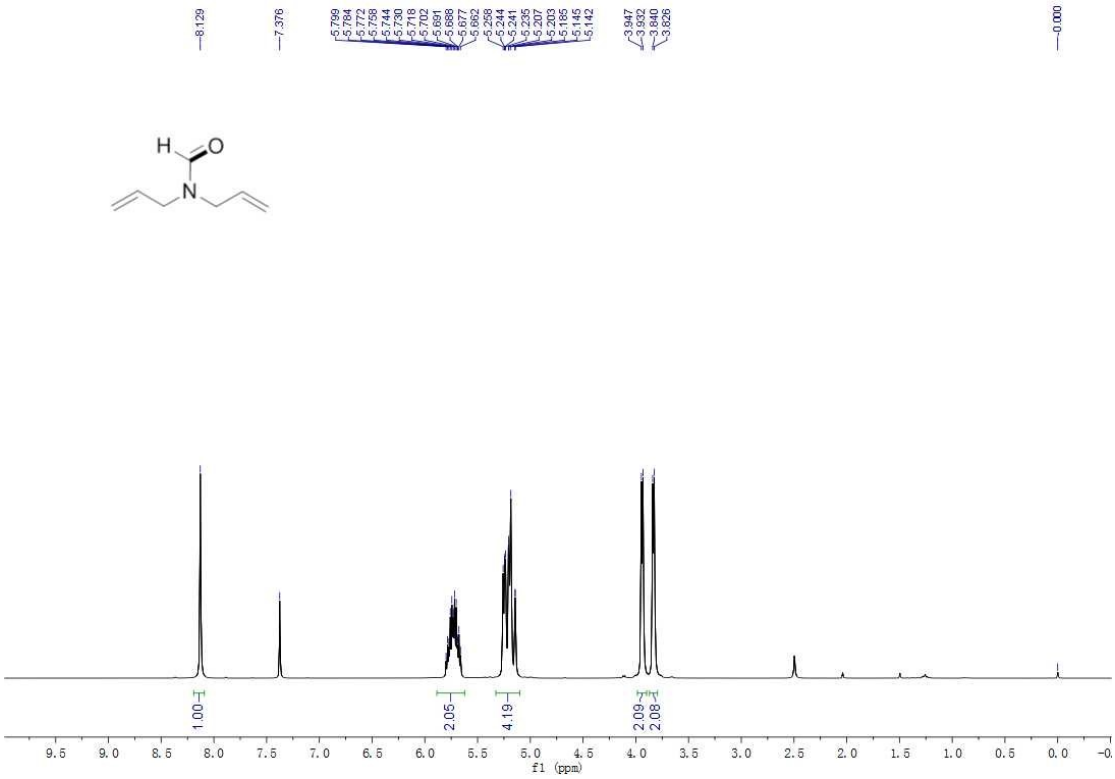


^{1}H NMR (400 MHz, $CDCl_3$)

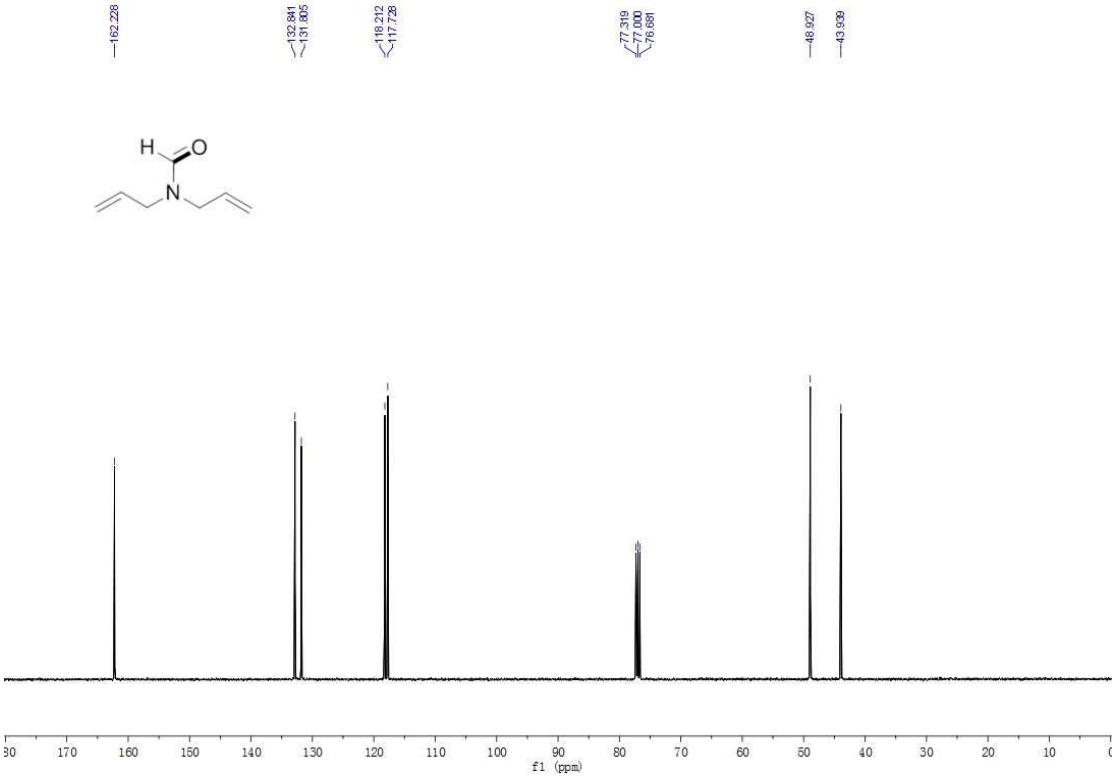


^{13}C NMR (100 MHz, $CDCl_3$)

***N*,*N*-Diallylformamide (2x):**

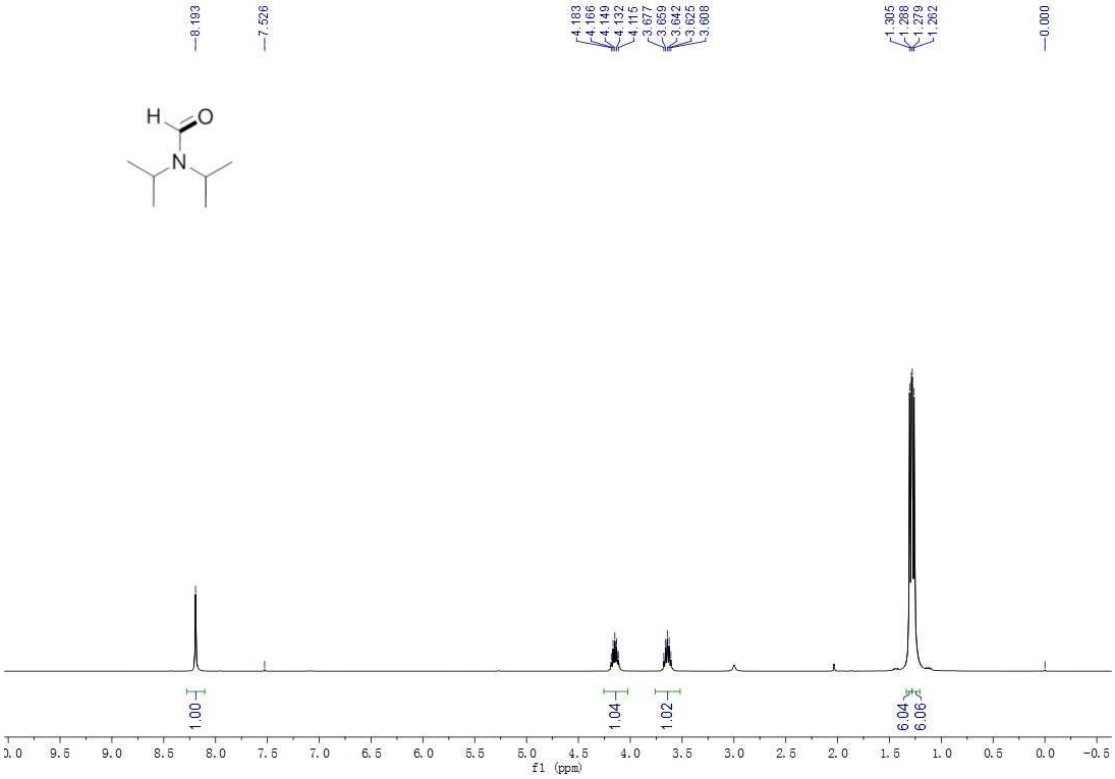


^{1}H NMR (400 MHz, $CDCl_3$)

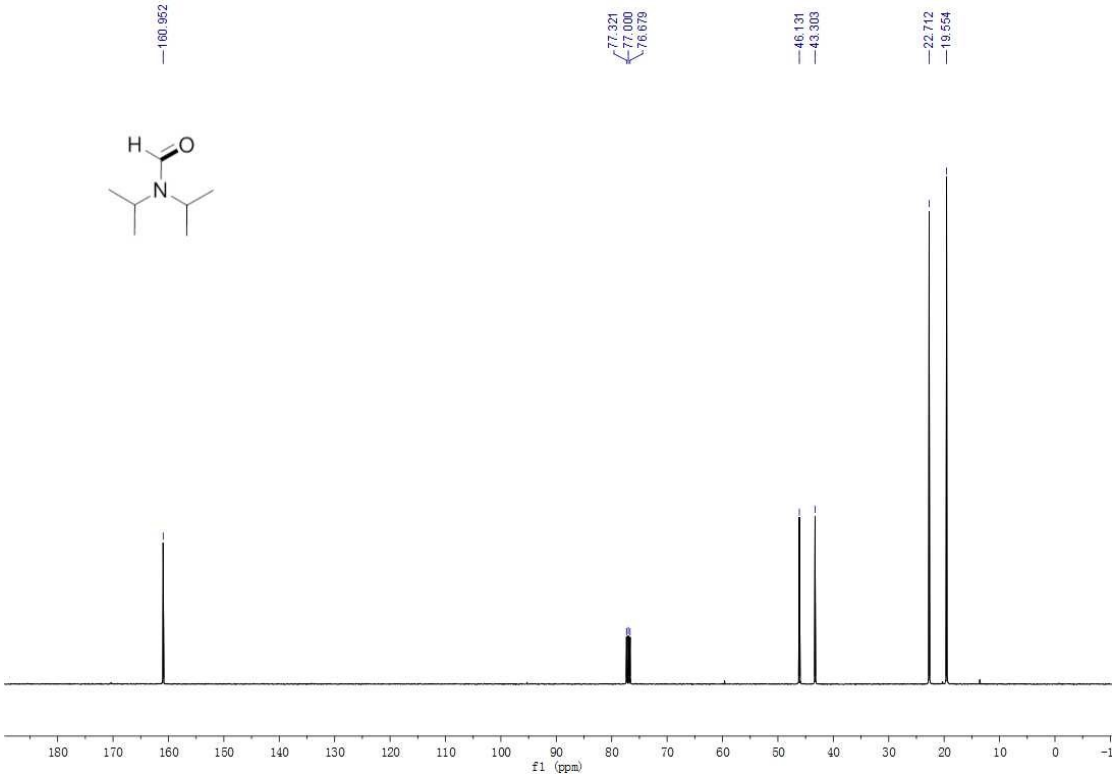


^{13}C NMR (100 MHz, $CDCl_3$)

***N*,*N*-Diisopropylformamide (2y):**

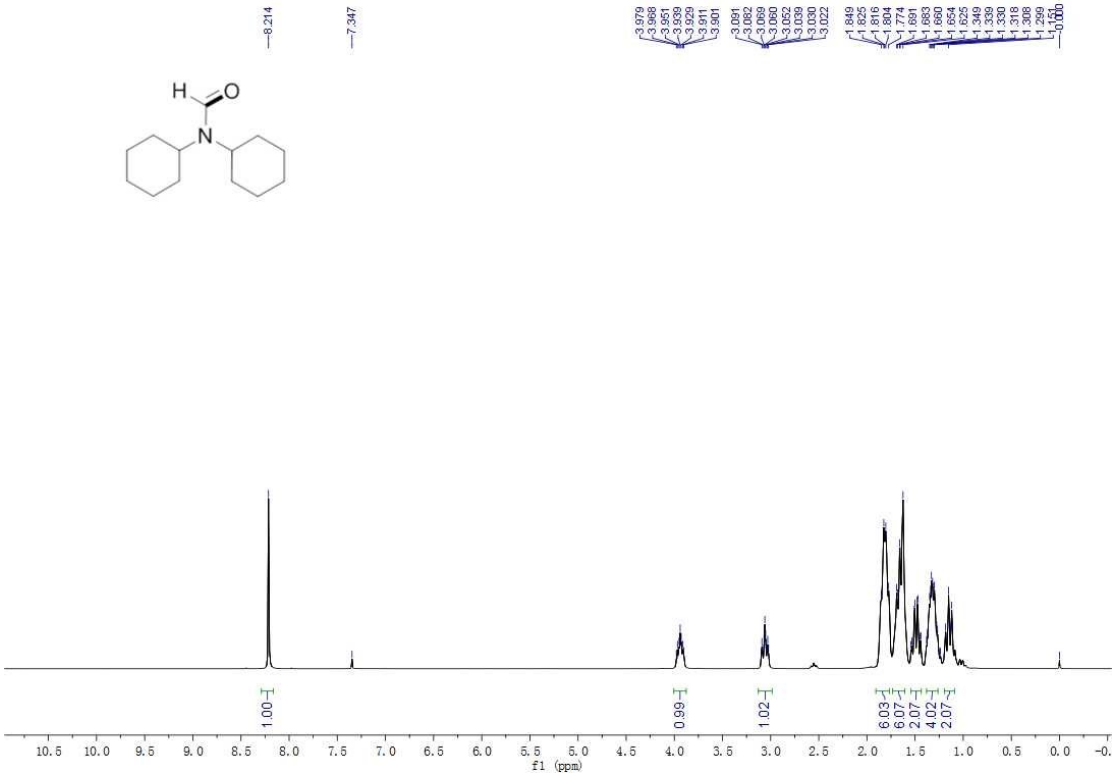


^{1}H NMR (400 MHz, $CDCl_3$)

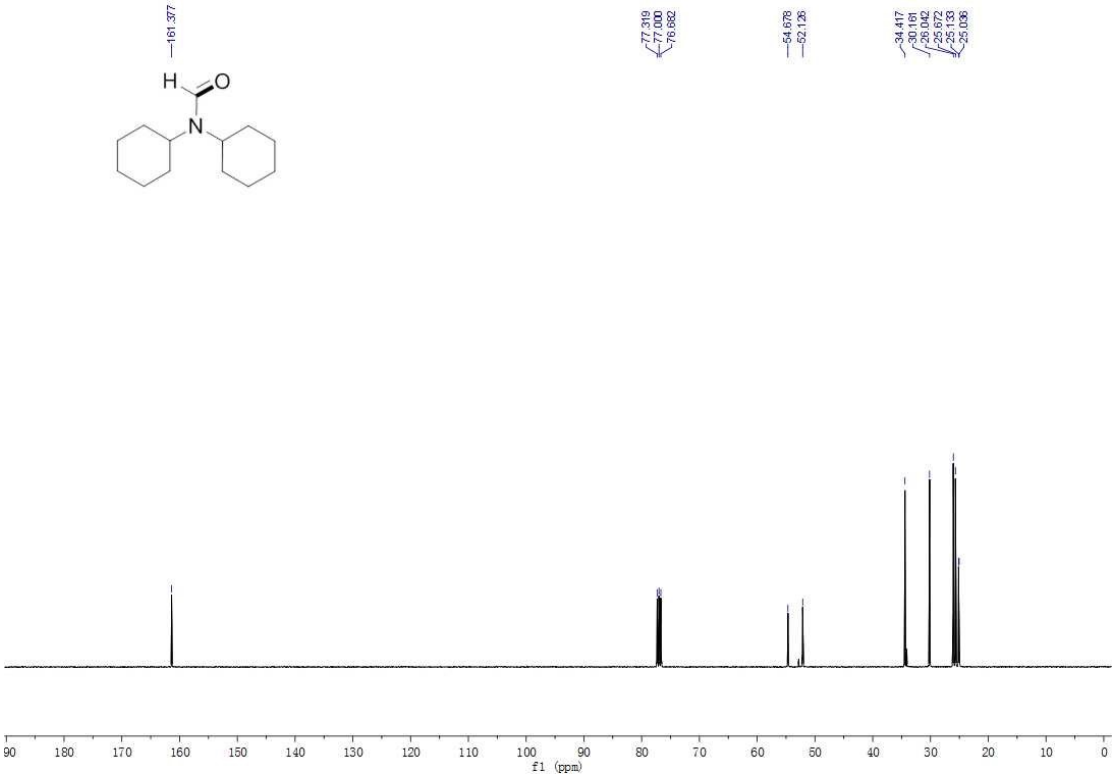


^{13}C NMR (100 MHz, $CDCl_3$)

***N*,*N*-Dicyclohexylformamide (2z):**

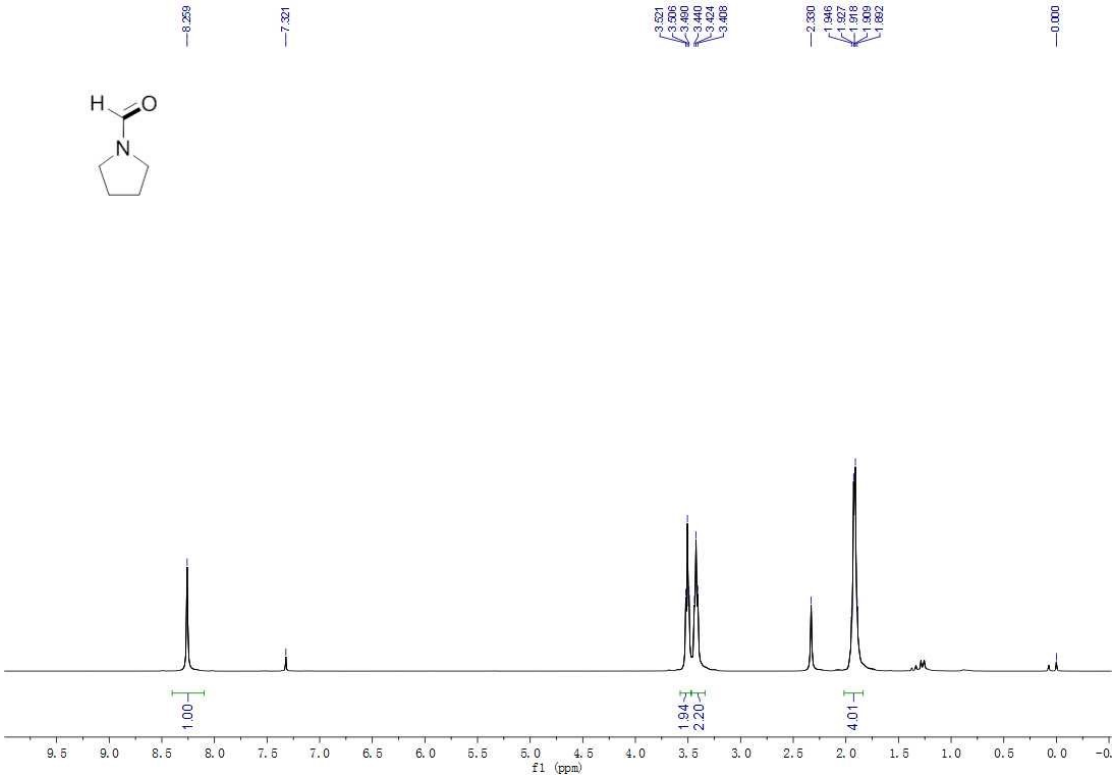


^{1}H NMR (400 MHz, $CDCl_3$)

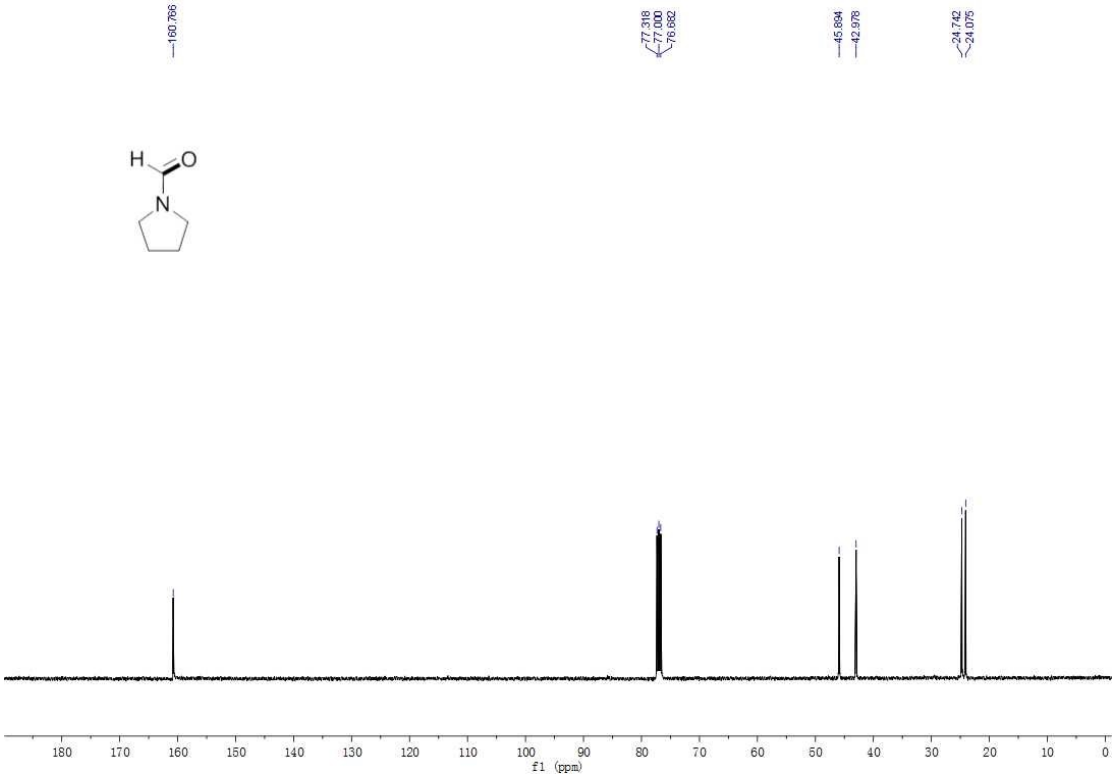


^{13}C NMR (100 MHz, $CDCl_3$)

Pyrrolidine-1-carbaldehyde (2aa):

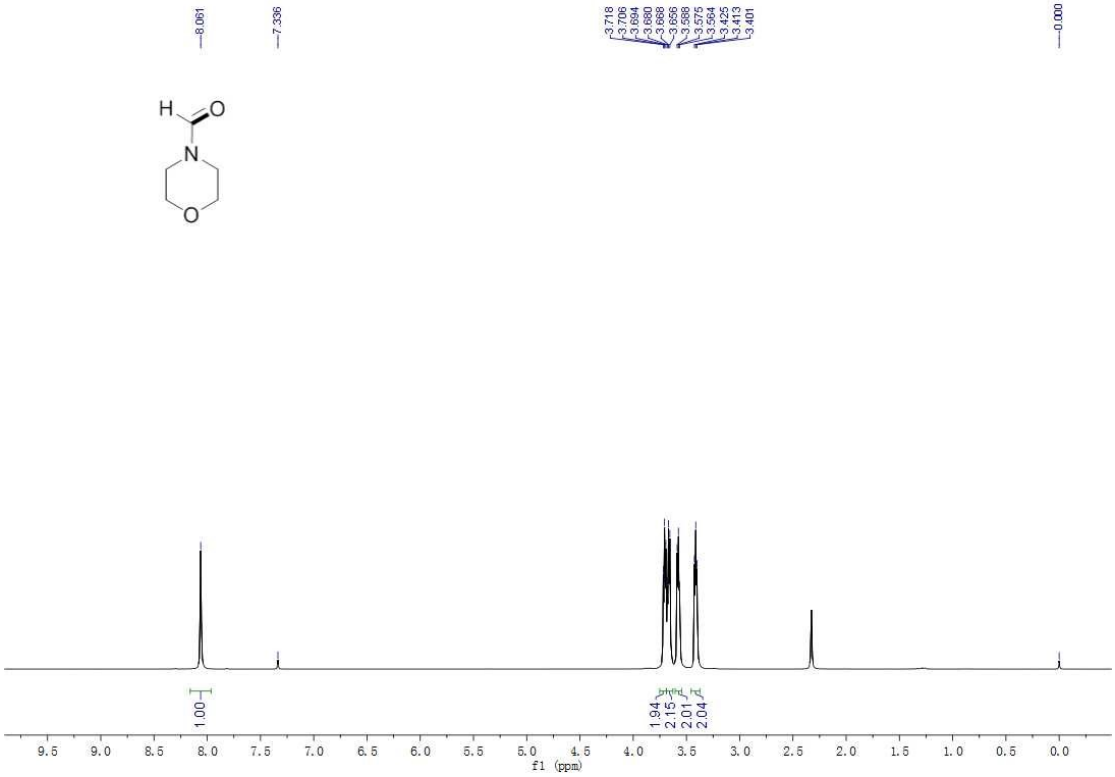


^{1}H NMR (400 MHz, $CDCl_3$)

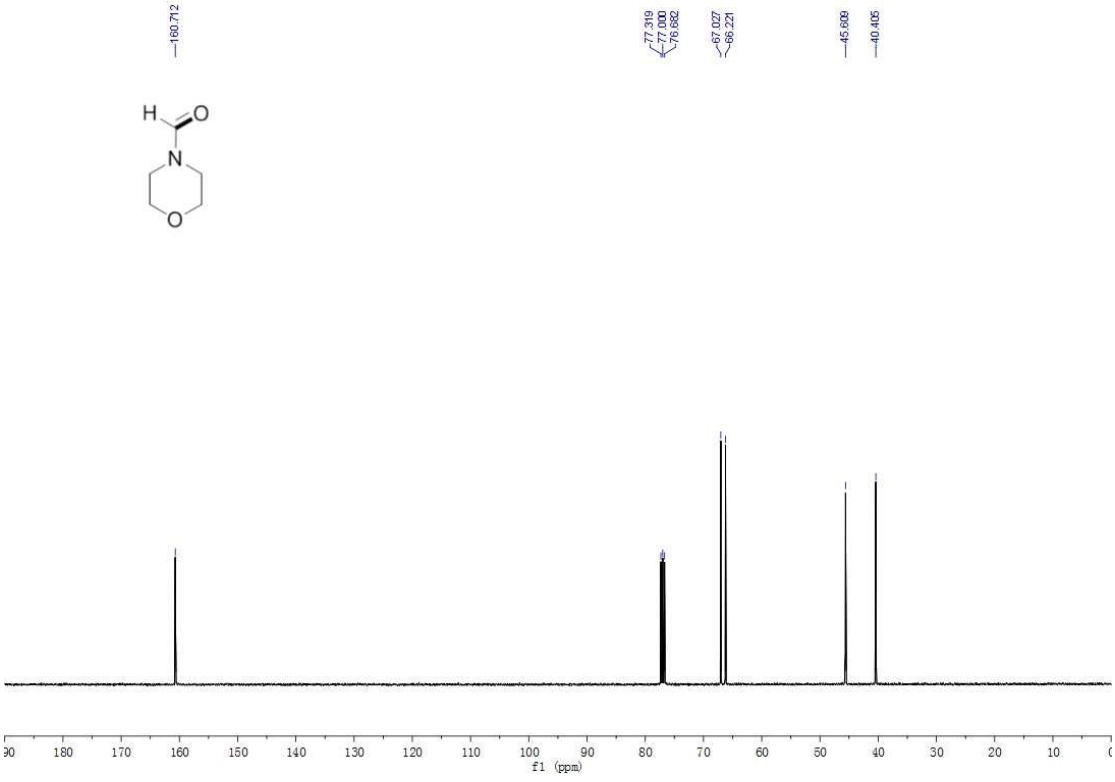


^{13}C NMR (100 MHz, $CDCl_3$)

Morpholine-4-carbaldehyde (2ab):

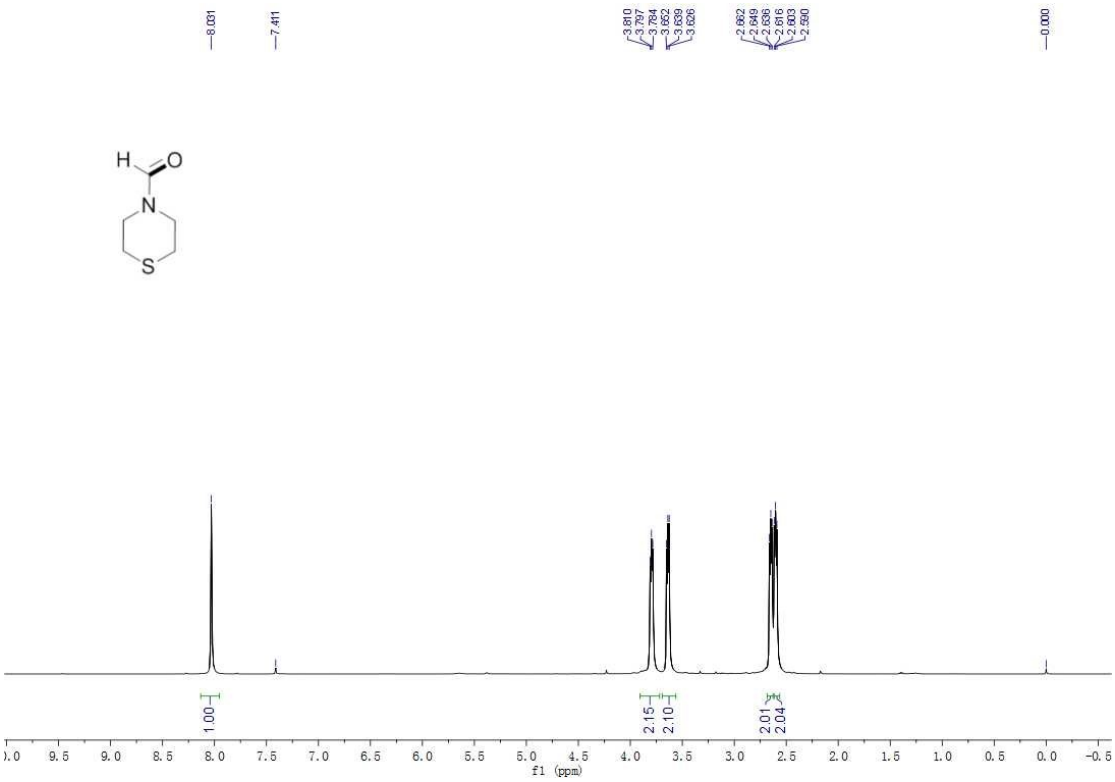


^{1}H NMR (400 MHz, $CDCl_3$)

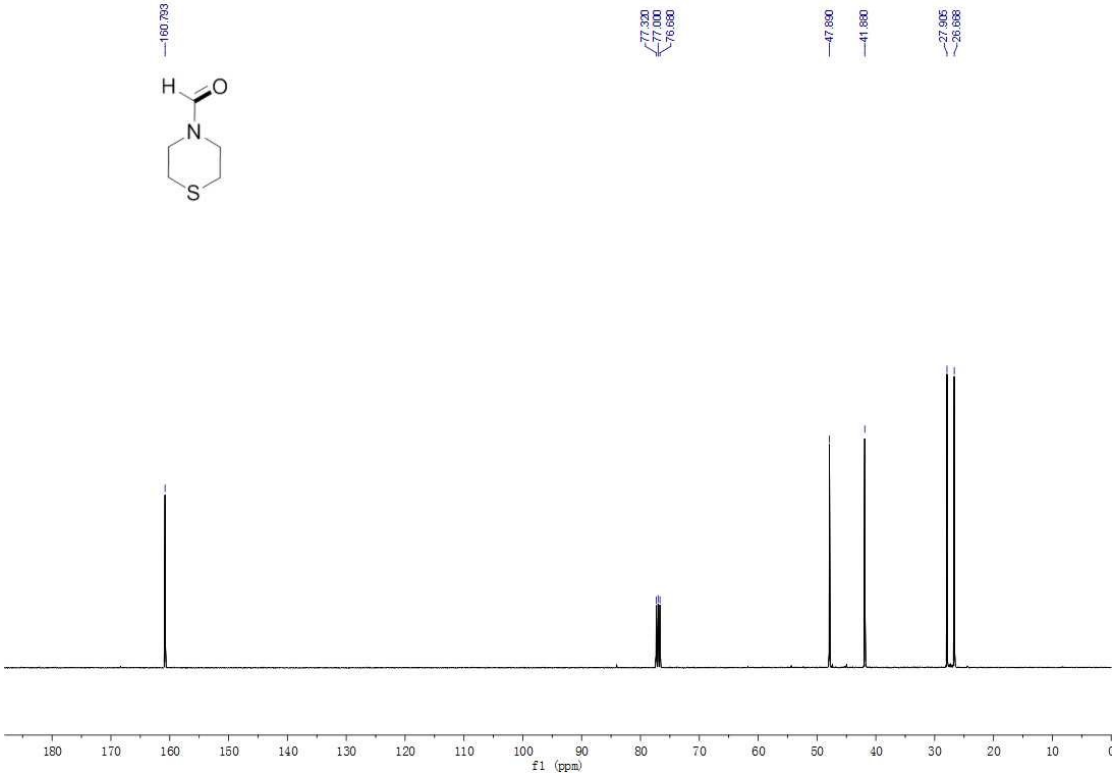


^{13}C NMR (100 MHz, $CDCl_3$)

Thiomorpholine-4-carbaldehyde (2ac):

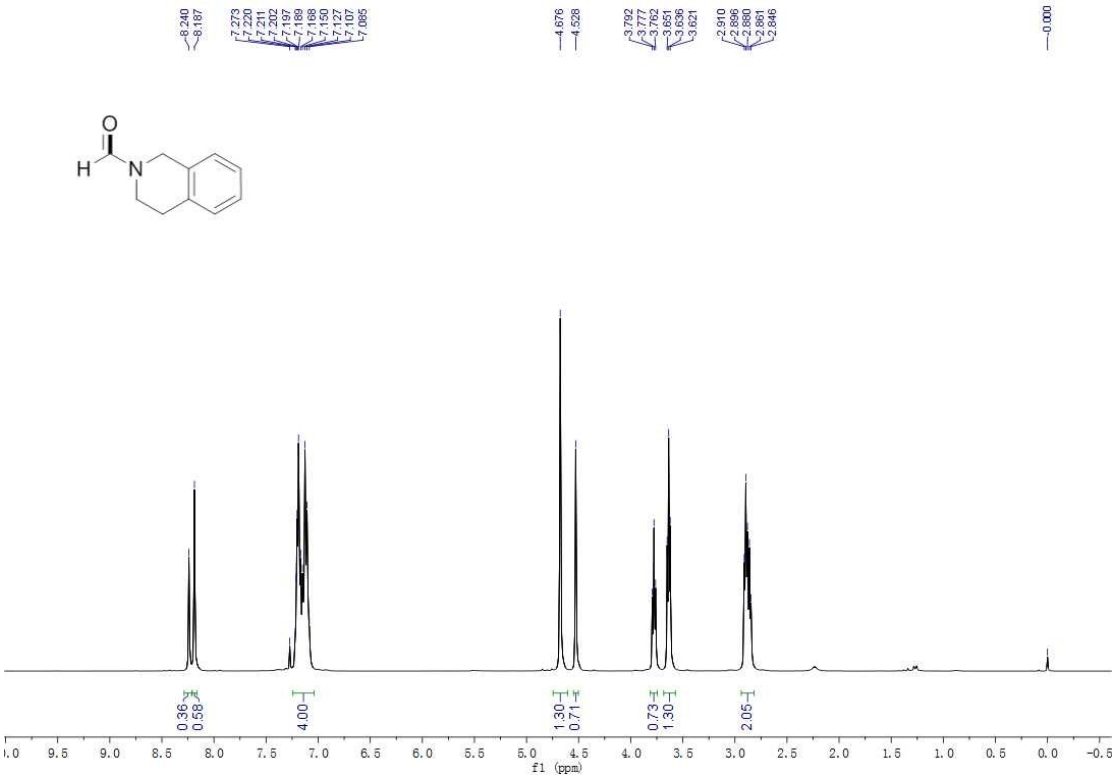


^{1}H NMR (400 MHz, $CDCl_3$)

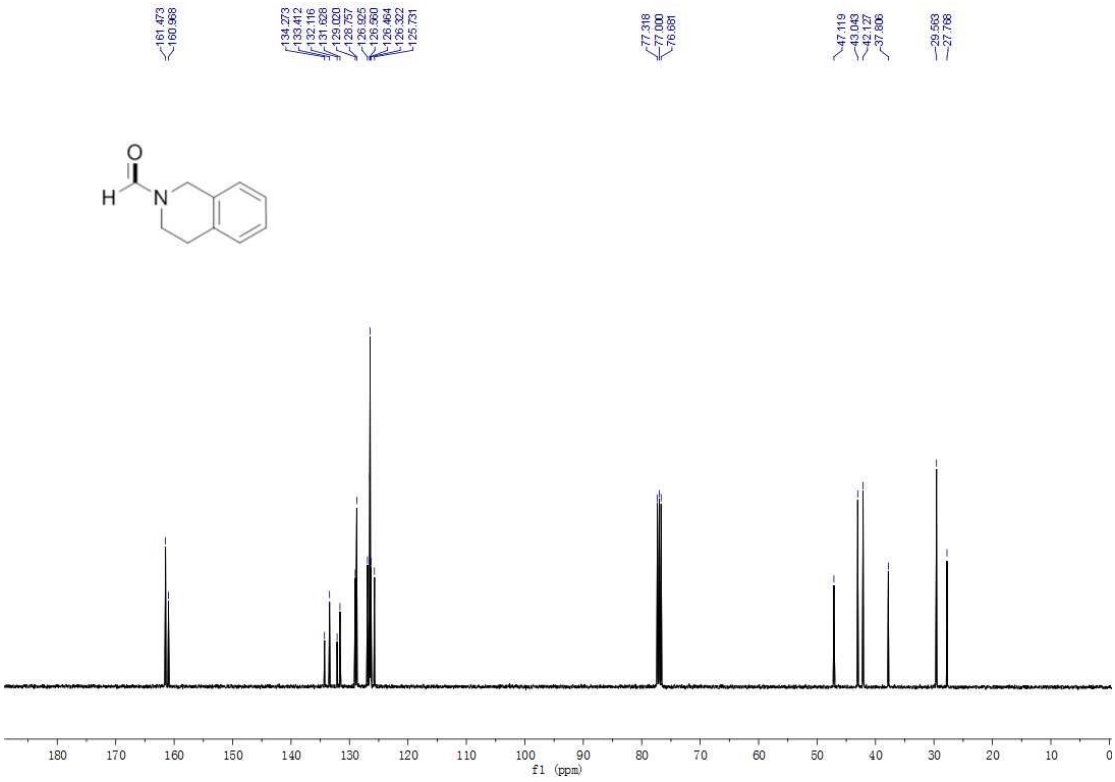


^{13}C NMR (100 MHz, $CDCl_3$)

3,4-Dihydroisoquinoline-2(1*H*)-carbaldehyde (2ad):

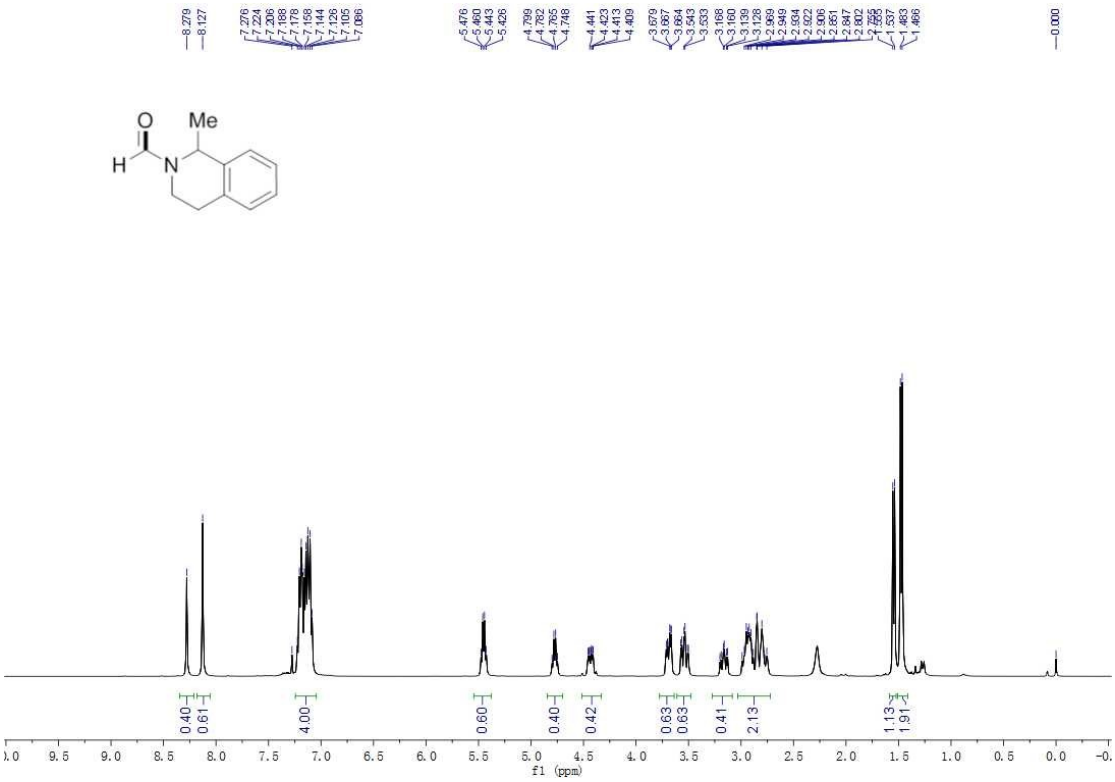


^{1}H NMR (400 MHz, $CDCl_3$)

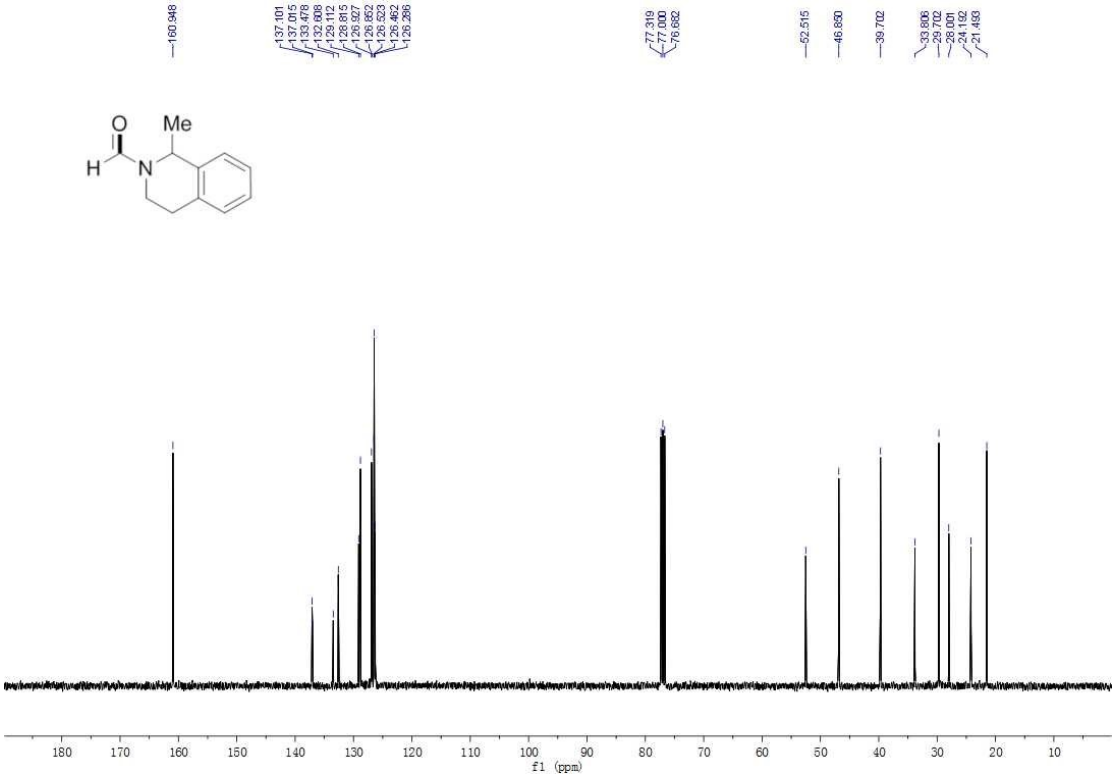


^{13}C NMR (100 MHz, $CDCl_3$)

1-Methyl-3,4-dihydroisoquinoline-2(1*H*)-carbaldehyde (2ae):

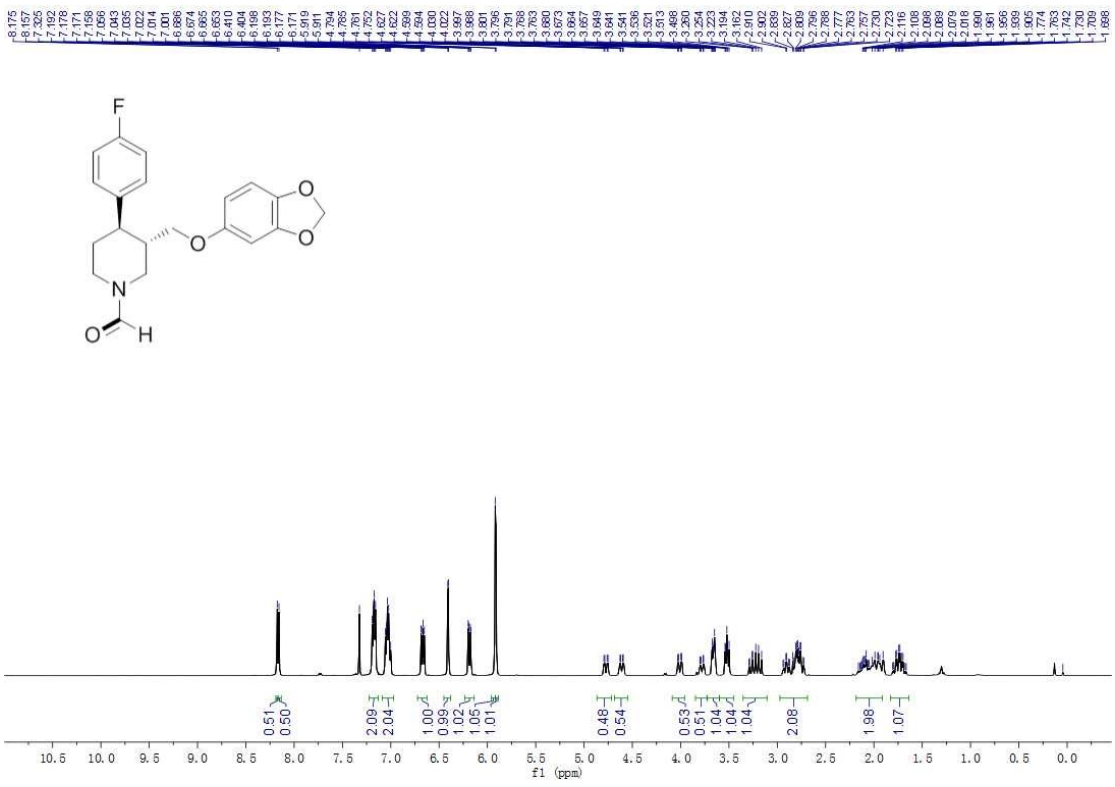


^{1}H NMR (400 MHz, $CDCl_3$)

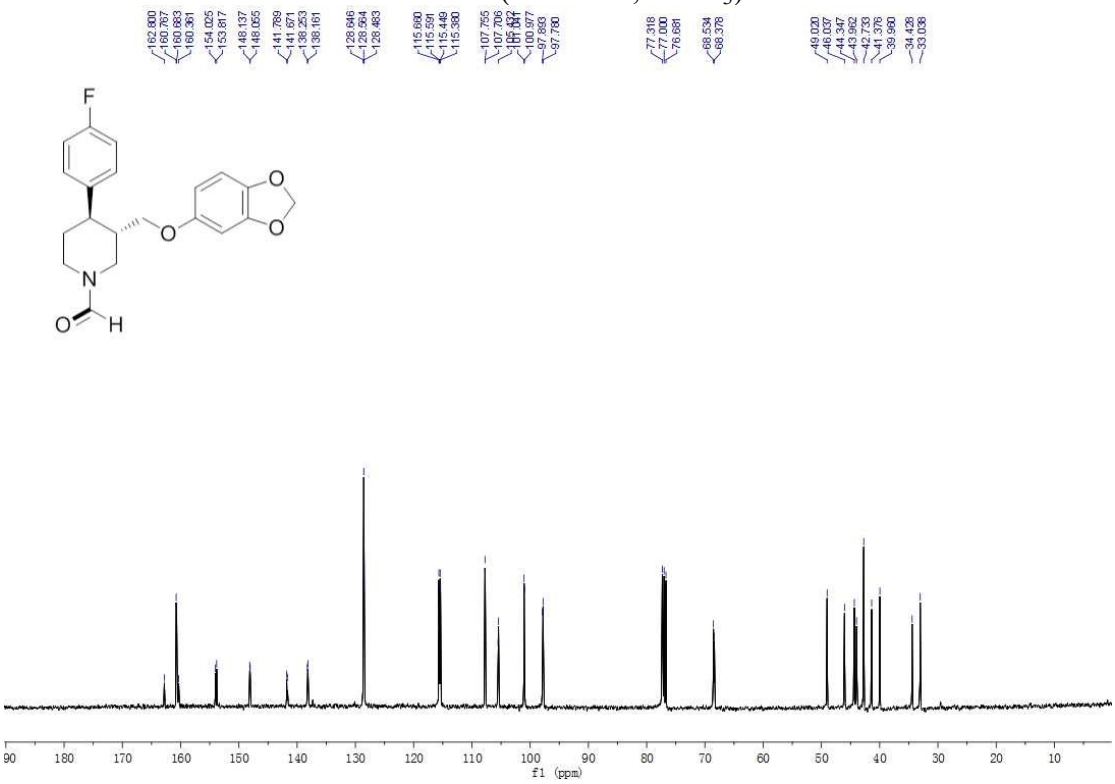


^{13}C NMR (100 MHz, $CDCl_3$)

(3S,4R)-3-((benzo[*d*][1,3]dioxol-5-yloxy)methyl)-4-(4-fluorophenyl)piperidine-1-carbaldehyde (2af):



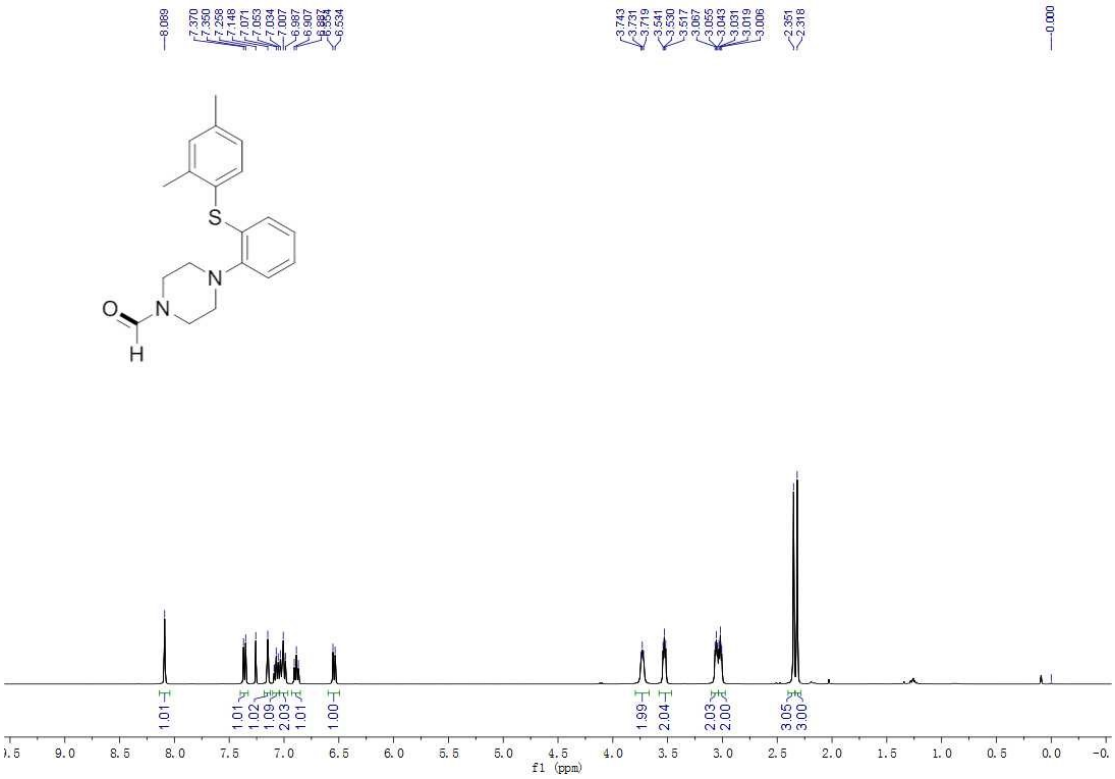
^{1}H NMR (400 MHz, $CDCl_3$)



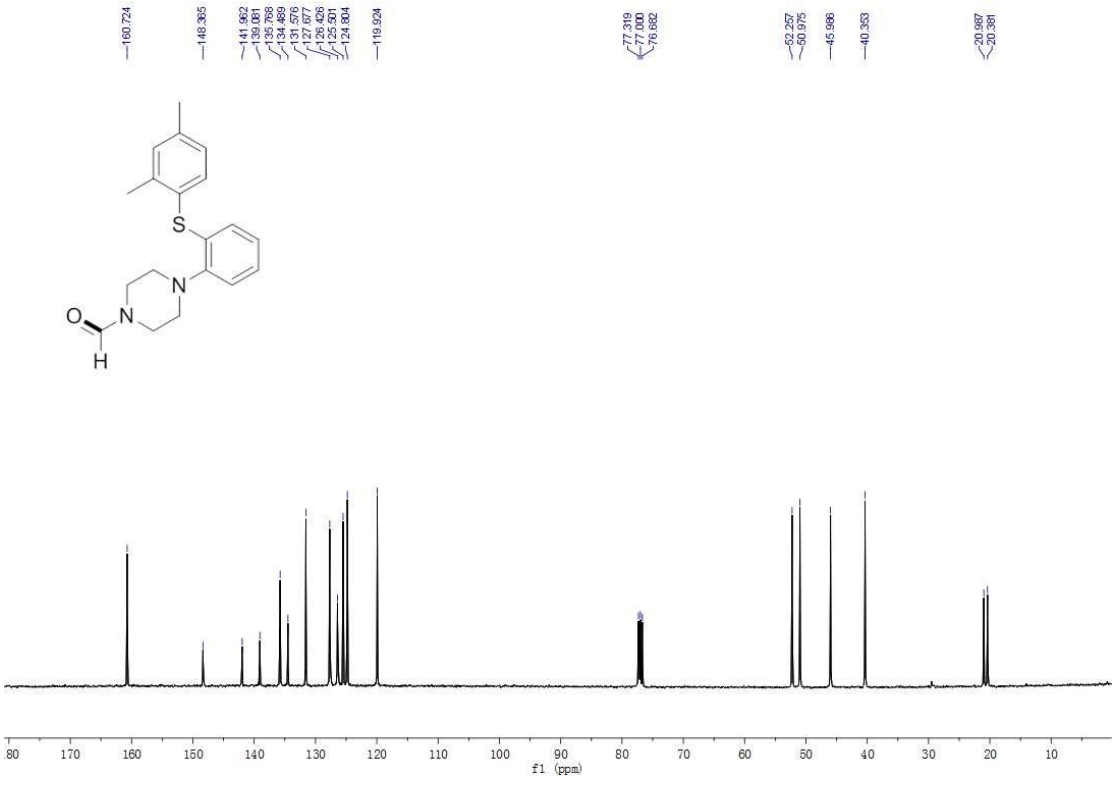
^{13}C NMR (100 MHz, $CDCl_3$)

^{19}F NMR (376 MHz, $CDCl_3$)

4-(2-((2,4-dimethylphenyl)thio)phenyl)piperazine-1-carbaldehyde (2ag):

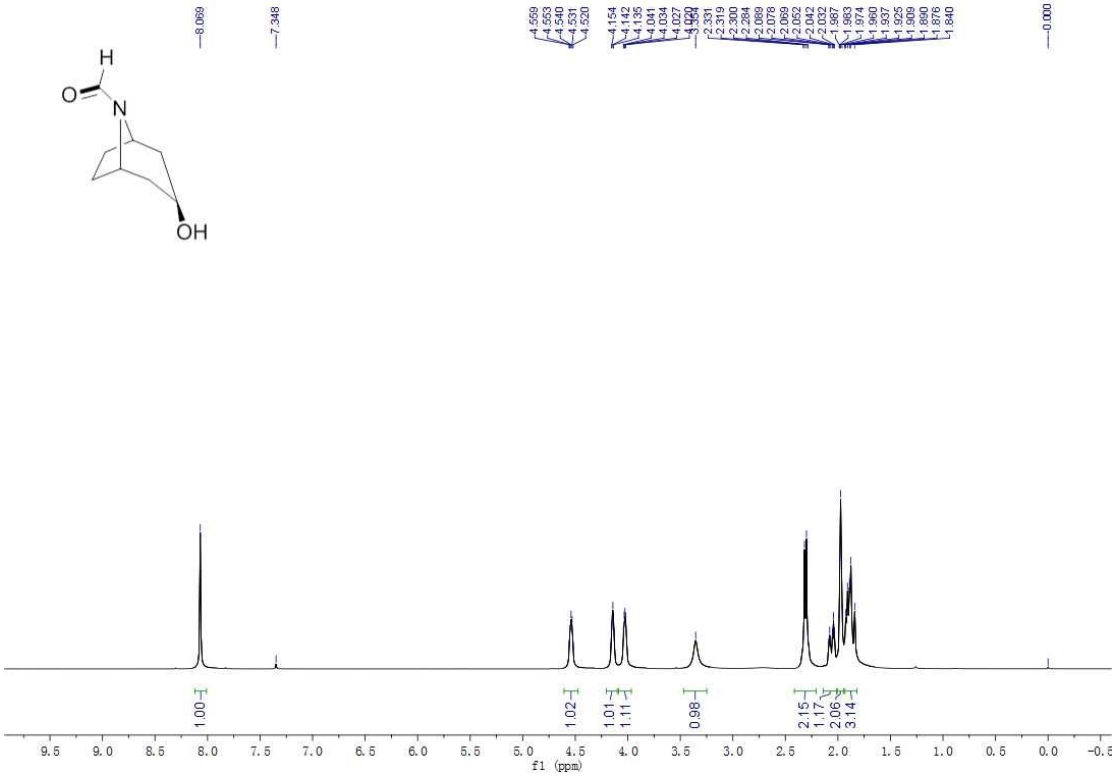


^{1}H NMR (400 MHz, $CDCl_3$)

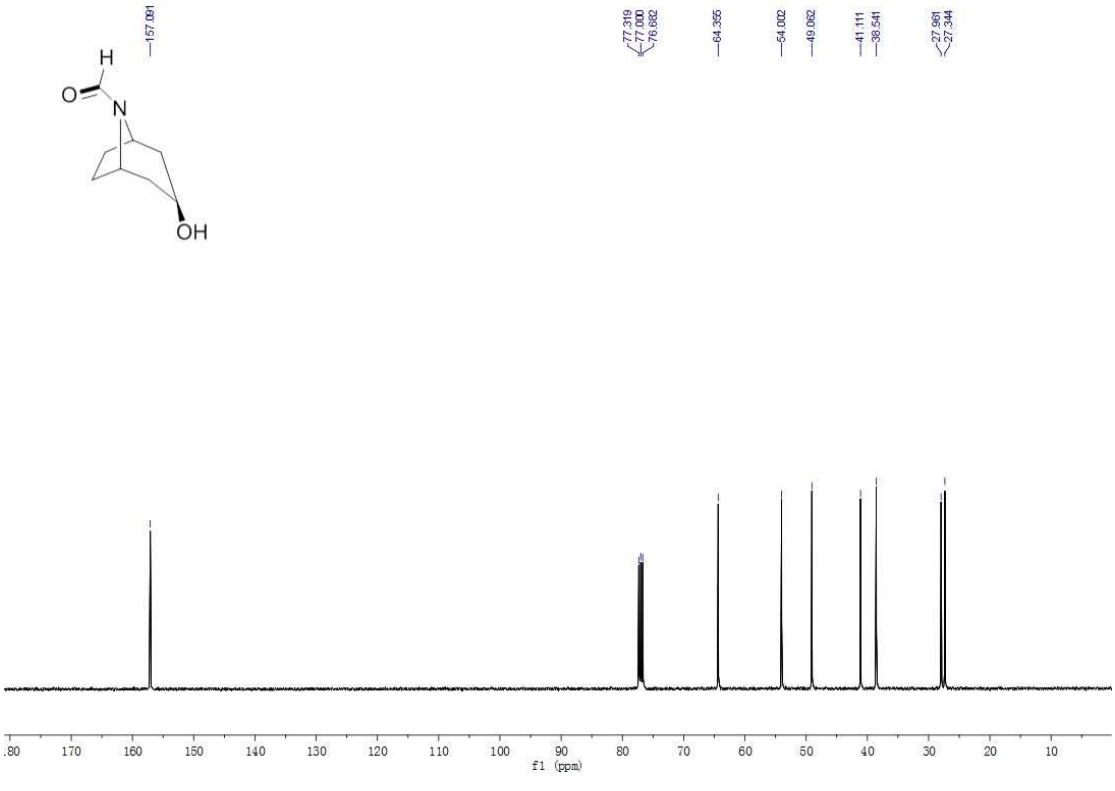


^{13}C NMR (100 MHz, $CDCl_3$)

(1R,3S,5S)-3-hydroxy-8-azabicyclo[3.2.1]octane-8-carbaldehyde (2ah)[l]:



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

(D) Reference

[1] Y.-Q. Fang and E. N. Jacobsen, *J. Am. Chem. Soc*., 2008, 130, **17**, 5660–5661.

[2] S. Kotani, M. Sakamoto, K. Osakama and M. Nakajima, *Eur. J. Org. Chem*., 2015, **2015**, 6606–6609.

[3] S. Nakai, T. Yatabe, K. Suzuki, Y. Sasano, Y. Iwabuchi, J.-y. Hasegawa, N. Mizuno and K. Yamaguchi, *Angew. Chem., Int. Ed*., 2019, **58**, 16651–16659.

[4] O. Saidi, M. J. Bamford, A. J. Blacker, J. Lynch, S. P. Marsden, P. Plucinski, R. J. Watson and J. M. J. Williams, *Tetrahedron Lett*., 2010, **51**, 5804–5806.

[5] F.-P. Wu, J.-B. Peng, X. Qi, J. Ying and X.-F. Wu, *Adv. Synth. Catal*., 2018, **360**, 3412–3417.

[6] J. Cossy, T. Cochet, V. Bellosta, A. Greiner and D. Roche, *Synlett*, 2011, 1920–1922.

[7] T.V.Q. Nguyen, W.-J. Yoo and S. Kobayashi, *Angew. Chem., Int. Ed*., 2015, **54**, 9209–9212.

[8] H. Liu, Q. Mei, Q. Xu, J. Song, H. Liu and B. Han, *Green Chem*., 2017, **19**, 196–201.

[9] Y. Shen, Q. Zheng, Z.-N. Chen, D. Wen, J. H. Clark, X. Xu and T. Tu, *Angew. Chem., Int. Ed*., 2021, **60**, 4125–4132.

[10] Q. Zhang, X.-T. Lin, N. Fukaya, T. Fujitani, K. Sato and J.-C. Choi, *Green Chem*., 2020, **22**, 8414–8422.

[11] A. Gopakumar, I. Akçok, L. Lombardo, F. Le Formal, A. Magrez, K. Sivula and P. J. Dyson, *ChemistrySelect*, 2018, **3**, 10271–10276.

[12] Z. He, H. Liu, H. Liu, Q. Qian, Q. Meng, Q. Mei, B. Han, *ChemCatChem*, 2017, **9**, 1947–1952.

[13] M. J. P. Mandigma, J. Ẑurauskas, C. I. MacGregor, L. J. Edwards, A. Shahin, L. d'Heureuse, P. Yip, D. J. S. Birch, T. Gruber, J. Heilmann, M. P. Johnb and J. P. Barham, *Chem. Sci.*, 2022, **13**, 1912–1924.