

Electronic Supplementary Information (ESI)

Tetracoordinate Borates as Catalysts for Reductive Formylation of Amines with Carbon Dioxide

Xiaolin Jiang^{†,‡}, Zijun Huang^{†,§}, Mohamed Makha[†], Chen-Xia Du[†], Dongmei Zhao^{*,‡},
Fang Wang^{*,†}, and Yuehui Li^{*,†}

[†] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Suzhou Research Institute of LICP, Center for Excellence in Molecular Synthesis, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences, Lanzhou 730000, P.R. China

[‡] Key Laboratory of Structure-based Drug Design & Discovery of Ministry of Education, Shenyang Pharmaceutical University, Shenyang 110016, P. R. China

[§] University of Chinese Academy of Sciences, Beijing 100049, P.R. China

[†] College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450001, P.R. China

1. General information	S2
2. Reaction procedures and condition optimization	S2 - S5
3. Control experiments	S6 - S7
4. DFT calculation experiments	S8 - S11
5. Crystallographic data	S12
6. Characterization data	S13 - S21
7. References	S22
8. Copies of spectra	S23 - S87

1. General information

Unless otherwise stated, all the materials were purchased from commercial suppliers (Adamas, TCI) and were used as received. CO₂ (99.99%) was purchased from Messer (Wujiang, China). Solvents were dried by solvent purification system from LC Technology Solution Inc. Flash chromatography was performed on silica gel. The products were characterized by ¹H NMR and ¹³C NMR spectroscopy. ¹H and ¹³C NMR spectra were recorded on Bruker 400 MHz spectrometer. The NMR chemical shift values refer to CDCl₃ (δ (¹H), 7.26 ppm; δ (¹³C), 77.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br. = broad singlet), coupling constants (Hz) and integration. GC-MS data were obtained shimadzu GCMS-QP 2010 SE, GC data were obtained shimadzu GC-2010 Plus, HRMS data were obtained on Agilent 6530 spectrometer. All measurements were carried out at room temperature unless otherwise stated.

2.1 General Procedure for the reactions in (Table S1, 2)

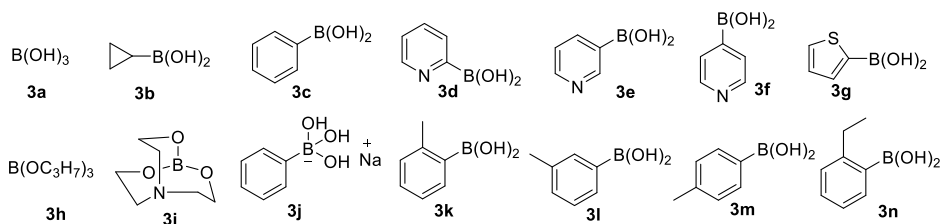
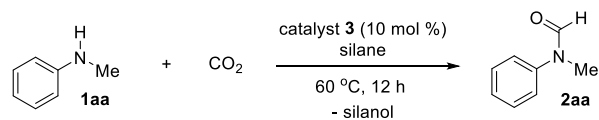
To a 4 mL sealing tube in an nitrogen-filled glove box, the *N*-methylaniline (0.2 mmol), sodium aromatic borate catalyst and silane reductant were added followed by addition of solvent (1 mL). Then the tube was sealed, taken out of the glove box, and placed into the autoclave. The autoclave was sealed and purged three times with CO₂ gas, then pressurized to 2.5 atm. At last, the autoclave was stirred at 60 °C for 12 h. The yield was determined by GC analysis using *n*-hexadecane as an internal standard.

2.2 General Procedure for the reactions in (Table S3, 4, 5)

To a 4 mL sealing tube in an nitrogen-filled glove box, the different kinds of substrate (0.2 mmol), sodium (trihydroxy)phenylborate (10 mol%) and phenylsilane were added followed by addition of solvent (1 mL) under N₂ atmosphere. Then the tube was sealed, taken out of the glove box, and placed into the autoclave. The autoclave was sealed and purged three times with CO₂ gas, then pressurized to 2.5 atm. At last, the autoclave was stirred at 60 °C for 12 h. The yield was determined by GC analysis or the product was purified by silica gel to give the isolated yield.

2.3 Conditions optimization for the reaction of *N*-methylaniline and carbon dioxide.

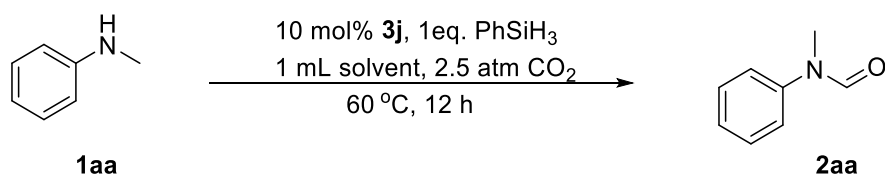
Table S1 Investigation of different catalyst for the reaction of *N*-methylaniline and carbon dioxide.^a



Entry	[B]10 mol%	[Si]1 eq.	Solvent	Yield (%) ^b
1	-	PhSiH ₃	DGDE	none
2	3a	PhSiH ₃	DGDE	none
3	3b	PhSiH ₃	DGDE	none
4	3c	PhSiH ₃	DGDE	none
5	3d	PhSiH ₃	DGDE	9
6	3e	PhSiH ₃	DGDE	3
7	3f	PhSiH ₃	DGDE	none
8	3g	PhSiH ₃	DGDE	none
9	3h	PhSiH ₃	DGDE	none
10	3i	PhSiH ₃	DGDE	none
11	3j	PhSiH ₃	DGDE	45
12	3k	PhSiH ₃	DGDE	none
13	3l	PhSiH ₃	DGDE	none
14	3m	PhSiH ₃	DGDE	none
15	3n	PhSiH ₃	DGDE	none

^aReaction conditions: **1aa** (0.2 mmol, 1 eq.), catalyst **3** (0.02 mmol, 10 mol%), phenylsilane (0.2 mmol, 1eq.), CO_2 (0.25 MPa) in DGDE (1 mL) at 60 °C for 12 h. ^bDetermined by GC analysis using n-hexadecane as an internal standard. DGDE = Diethylene glycol dimethyl ether.

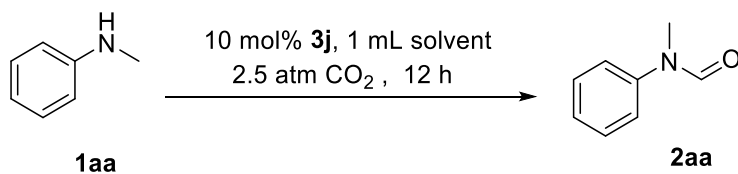
Table S2 Investigation of different solvents for the reaction of *N*-methylaniline and carbon dioxide.^a



Entry	[B]10 mol%	[Si]1 eq.	Solvent	Yield (%) ^b
1	3j	PhSiH ₃	CH ₃ CN	trace
2	3j	PhSiH ₃	THF	trace
3	3j	PhSiH ₃	DGDE	43
4	3j	PhSiH ₃	NMP	8
5	3j	PhSiH ₃	1,4-dioxane	3
6	3j	PhSiH ₃	mesitylene	none
7	3j	PhSiH ₃	heptane	none
8	3j	PhSiH ₃	DCE	none
9	3j	PhSiH ₃	toluene	none
10	3j	PhSiH ₃	CPME	none

^aReaction conditions: **1aa** (0.2 mmol, 1 eq.), catalyst **3j** (0.02 mmol, 10 mol%), phenylsilane (0.2 mmol, 1 eq.), CO₂ (0.25 MPa) in different solvents (1 mL) at 60 °C for 12 h. ^bDetermined by GC analysis using *n*-hexadecane as an internal standard. THF = Tetrahydrofuran. NMP = *N*-methylpyrrolidone. DCE = 1,2-Dichloroethane. CPME = Cyclopentyl methyl ether.

Table S3 Investigation of different silicanes and temperature for the reaction of *N*-methylaniline and carbon dioxide.^a

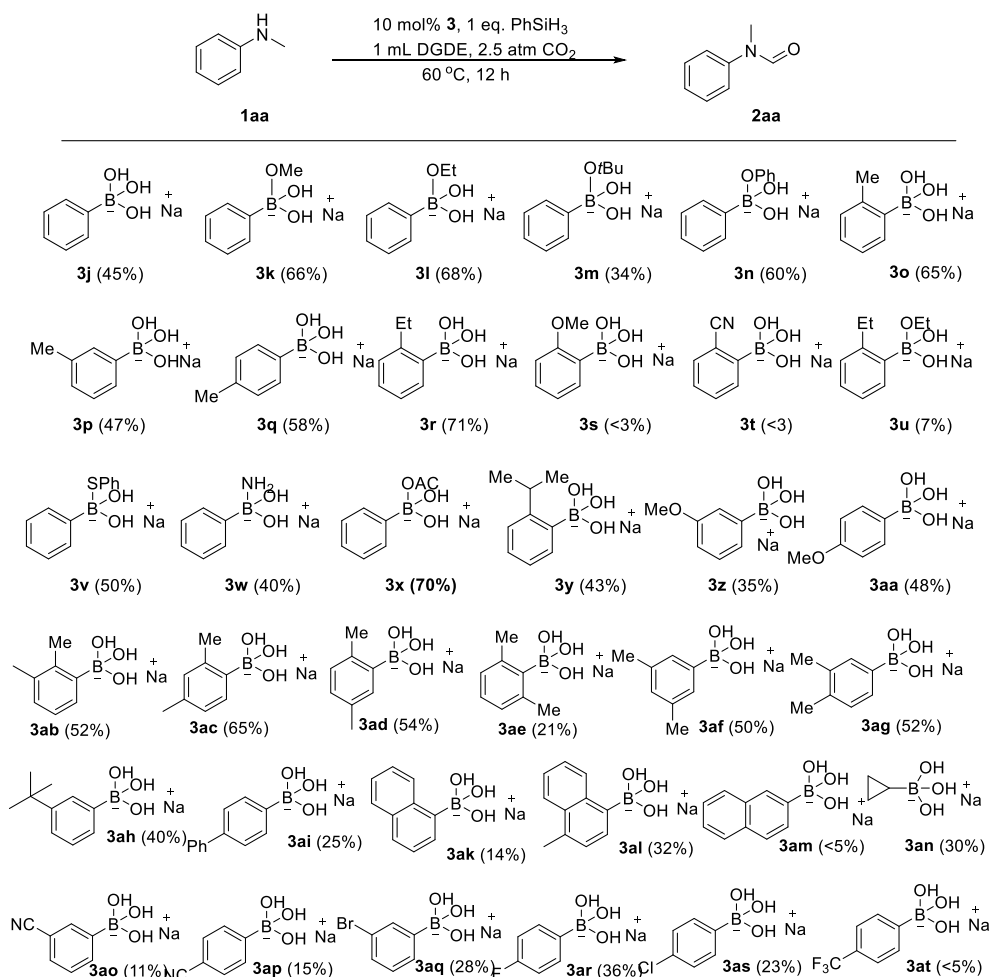


Entry	[B]10 mol%	[Si]1 eq.	Solvent	T(°C)	Yield (%) ^b
1	3j	PhSiH ₃	DGDE	60	45
2	3j	PhSiH ₃ (2 eq.)	DGDE	60	68
3	3j	PhSiH ₃	DGDE	100	78

4	3j	PhSiH ₃	THF	100	25
5	3j	PhSiH ₃ (2 eq.)	DGDE	60	88
6	3j	TMDS	DGDE	60	<3
7	3j	PMHS(5 eq.)	DGDE	60	<3
8	3j	PMHS(5 eq.)	DGDE	100	22

^aReaction conditions: **1aa** (0.2 mmol, 1 eq.), catalyst **3j** (0.02 mmol, 10 mol%), silane, CO₂ (0.25 MPa) in DGDE (1 mL) for 12 h. ^bDetermined by GC analysis using *n*-hexadecane as an internal standard.

Table S4 Investigation of different sodium aromatic borates prepared by in-situ mixing aromatic boronic acids with NaOH or sodium alkoxides for the reaction of *N*-methylaniline and carbon dioxide.^a



^aReaction conditions: **1aa** (0.2 mmol, 1 eq.), catalyst **3** (0.04 mmol, 20 mol%), phenylsilane (0.2 mmol, 1 eq.), CO₂ (0.25 MPa) in DGDE (1 mL) at 60 °C for 12 h. ^bDetermined by GC analysis using *n*-hexadecane as an internal standard.

3. Control Experiments

3.1 Procedure for reaction in Figure. S1--Eq. 1^{1a}

To a Schlenk tube in an nitrogen-filled glove box, the sodium phenyltrihydroxyborate (0.2 mmol), PdCl₂ (1 mol%) and PPh₃(1 mol%), were added followed by addition of degassed toluene (1.0 mL) under N₂ atmosphere. Finally, benzoyl chloride(0.22 mmol) was added dropwisely. The Schlenk tube was taken out of the glove box. The reaction mixture was stirred at 60 °C for 3 h. The yield was determined by GC analysis using *n*-tetradecane as an internal standard.

3.2 Procedure for reaction in Figure. S1--Eq. 2^{1a}

To a Schlenk tube in an nitrogen-filled glove box, the sodium phenyltrihydroxyborate (0.2 mmol), PdCl₂ (1 mol%) and PPh₃(1 mol%) and phenylsilane (1 mmol) were added followed by addition of degassed toluene (1.0 mL) under N₂ atmosphere. Finally, benzoyl chloride(0.22 mmol) was added dropwisely. The Schlenk tube was taken out of the glove box. The reaction mixture was stirred at 60 °C for 3 h. The yield was determined by GC analysis using *n*-tetradecane as an internal standard.

3.3 Procedure for reaction in Figuer. S1--Eq. 3^{1b}

To a Schlenk tube in an nitrogen-filled glove box, the 4-iodoanisole (0.2 mmol), sodium phenyltrihydroxyborate (0.22 mmol) and Pd(OAc)₂ (1 mol%) were added followed by addition of degassed dioxane (1.0 mL) under N₂ atmosphere. Finally the Schlenk tube was taken out of the glove box. The reaction mixture was stirred at 60 °C for 3 h. The yield was determined by GC analysis using *n*-tetradecane as an internal standard.

3.4 Procedure for reaction in Figuer. S1--Eq. 4^{1b}

To a Schlenk tube in an nitrogen-filled glove box, the 4-iodoanisole (0.2 mmol), sodium phenyltrihydroxyborate (0.22 mmol), Pd(OAc)₂ (1 mol%) and phenylsilane (1 mmol) were added followed by addition of degassed dioxane (1.0 mL) under N₂ atmosphere. Finally the Schlenk tube was taken out of the glove box. The reaction mixture was stirred at 60 °C for 3 h. The yield was determined by GC analysis using *n*-tetradecane as an internal standard.

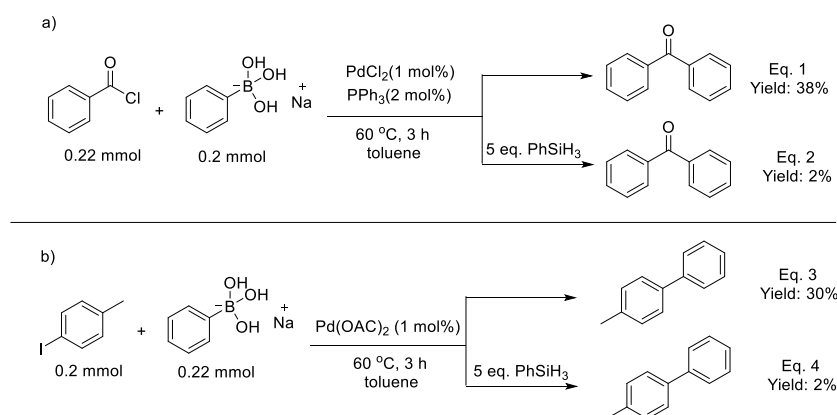


Figure S1. The silane effect in Pd-catalyzed Suzuki reactions.

3.5 Non-catalytic methods²

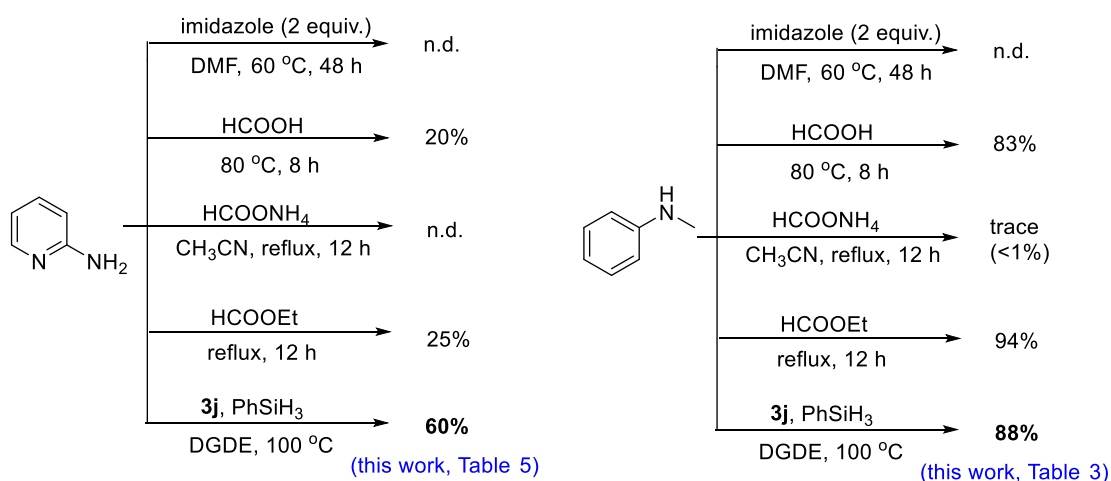
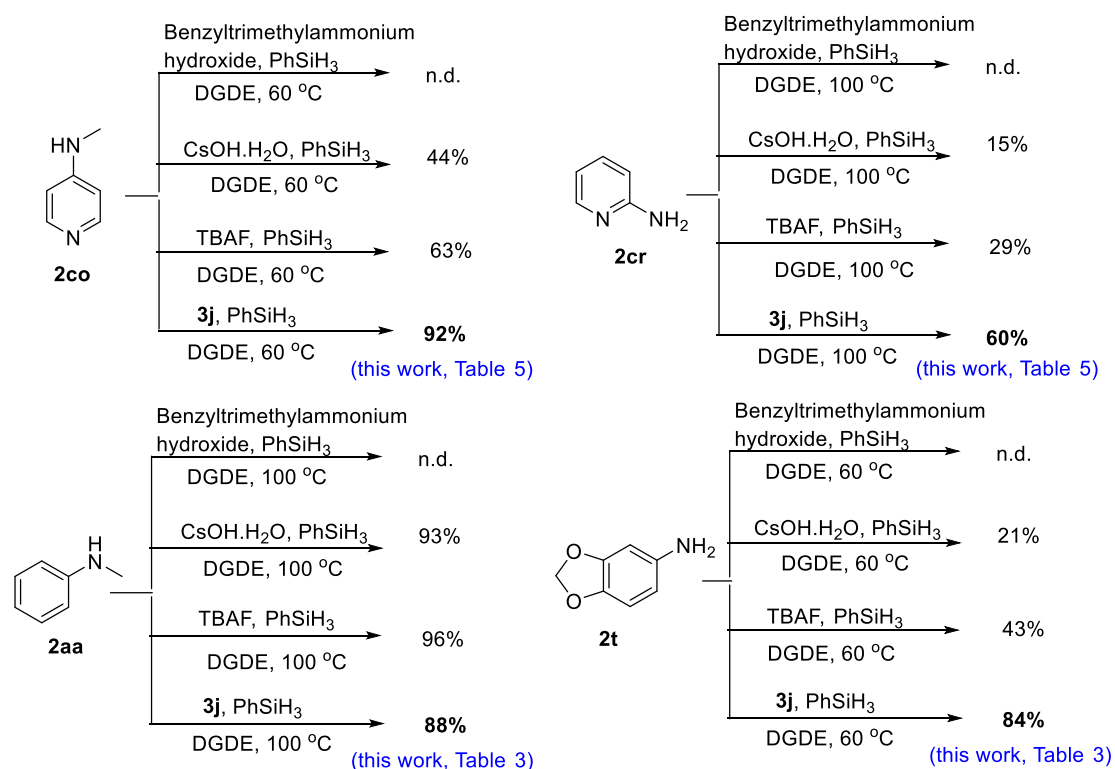


Figure S2. Control experiments using non-catalytic methods.

3.6 Different kinds of catalyst that activates silane



Reaction conditions: substrate (0.2 mmol, 1 eq.), catalyst (0.02 mmol, 10 mol%), phenylsilane (0.2 mmol, 1 eq.), CO₂ (0.25 MPa) in DGDE (1 mL) at 60 °C or 100 °C for 12 h. Yields were determined by GC analysis.

Figure S3. Control experiments using different kinds of catalyst that activates silane.

4. DFT calculation experiments

4.1. DFT calculation details

All DFT calculations were carried out employing the Gaussian 16 program.³ The M06-2X^{4a} corrected with Grimme's D3 dispersion^{4b} correction combined with 6-311g(d,p) basis set for C, H, O, B, Na, Si atoms was used for geometry optimization. Dispersion-corrected, spin-component scaled doubly-hybrid functional DSD-PBEP86 was confirmed working well on thermochemical, weak interaction and so on and approaching the accuracy of composite *ab initio* schemes.^{4c,4d} Therefore, the optimized geometries obtained at the M06-2X-D3/6-311G(d,p) level were further verified by a single point energy calculation based on DSD-PBEP86 in conjunction with def2-TZVPP basis set.^{4e} All geometries were fully optimized without any symmetry constraints. Solvent effects (tetrahydrofuran) were considered in all calculations using the polarizable continuum model (PCM)⁵ implemented in Gaussian 16. Vibrational frequency analysis was performed to confirm the minima nature of the stationary points. If not specified, the energies are discussed based on DSD-PBEP86/def2-TZVPP level.

4.2 DFT-Calculated Interaction Modes

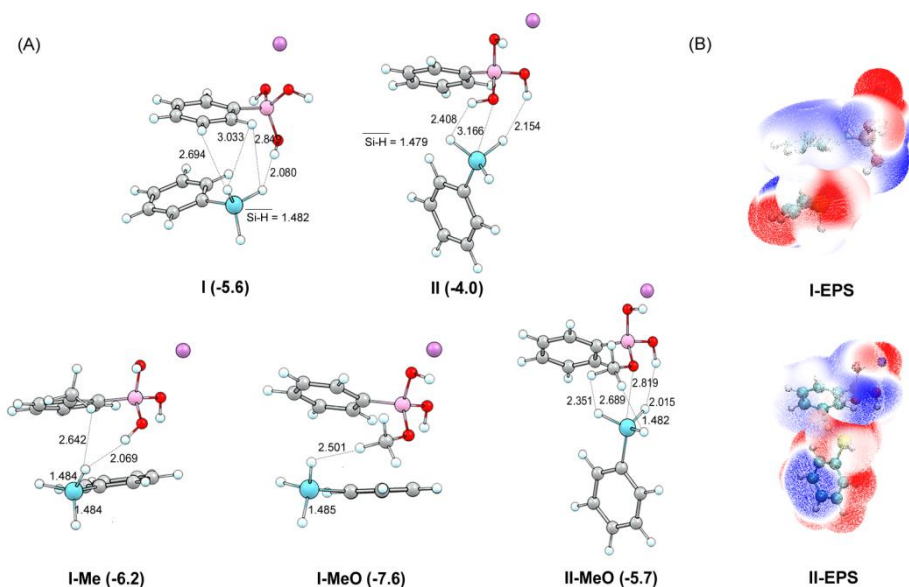


Figure S4. (A) Optimized complex structures of sodium aryl borates (**3j**, **3k**, **3o**) with phenylsilane at the M06-2X-D3/6-311G(d, p) level of theory. Values in parenthesis denote the binding energies (in kcal mol⁻¹) calculated at DSD-PBEP86/def2-TZVPP level. Bond lengths are in Å. (B) Electrostatic potential map for the catalyst-silane interaction.

Table S5. Energies of I, II, I-Me, I-MeO, II-MeO, and sodium aromatic borates (**3j**, **3k**, **3o**) calculated at M06-2X-D3/6-311G(d,p) level and DSD-PBEP86/def2-TZVPP level in solvent.

Complexes	M06-2X-D3/6-311G(d,p)		DSD-PBEP86/def2-TZVPP	
	E ^a	ΔE ^b	E	ΔE
I	-1169.294935	-7.4	-1167.890408	-5.6
II	-1169.293489	-6.5	-1167.887991	-4.0
I-Me	-1208.603744	-8.2	-1207.143507	-6.2
I-MeO	-1208.583317	-10.5	-1207.120437	-7.6
II-MeO	-1208.580002	-8.4	-1207.117401	-5.7
PhSiH₃	-522.8713551		-522.2928466	
3j	-646.4117964		-645.5886984	
3o	-685.7193318		-684.840776	
3k	-685.6952477		-684.8154567	

^a The energies E and ΔE are in a.u. and kcal mol⁻¹, respectively.

^b ΔE = E(complex) – E(PhSiH₃) – E(**3**), (**3** = **3j**, **3k**, or **3o**)

Table S6. Mulliken charges for the optimized PhSiH₃, **3j**, **3k**, **3o** and complexes **I**, **II**, **I-Me**, **I-MeO**, **II-MeO** calculated at DSD-PBEP86/def2-TZVPP level.

	H(Si)	Si	Ph(Si)	H(OH)	O	B	Na	Ph(B)	Me
PhSiH ₃	-0.26	0.42	-0.16						
3j				0.67	-1.81	0.56	0.91	-0.32	
3o				0.65	-1.83	0.61	0.92	-0.33	-0.01
3k				0.42	-1.70	0.51	0.92	-0.32	0.18
I	-0.28	0.39	-0.13	0.65	-1.78	0.56	0.91	-0.31	
II	-0.31	0.43	-0.16	0.65	-1.80	0.58	0.91	-0.30	
I-Me	-0.27	0.40	-0.12	0.64	-1.85	0.59	0.92	-0.30	-0.01
I-MeO	-0.28	0.39	-0.13	0.44	-1.73	0.56	0.91	-0.29	0.13
II-MeO	-0.32	0.51	-0.23	0.44	-1.71	0.56	0.91	-0.29	0.14

The coordinates of all stationary points calculated at M062X-D3/6-311g(d,p) level of theory

I				B	-2.43021400	0.38884200	-0.59573300
C	0.09820300	-2.21290800	0.97556300	O	-1.78969700	1.24204100	-1.60142200
C	-0.90086100	-1.64058900	0.19020000	H	-1.08934100	1.75283400	-1.18955500
C	-1.34394500	-0.32836200	0.39147400	O	-3.38274400	1.16404100	0.25380700
C	-0.74922100	0.38177100	1.44449600	H	-3.66785100	1.91833500	-0.26924900
C	0.24858200	-0.17633400	2.24052700	O	-3.27350800	-0.60521800	-1.32204800
C	0.68073000	-1.47915200	2.00388700	H	-2.77812800	-1.01577600	-2.03166600
H	0.42801300	-3.22858700	0.78268900	C	4.19382800	-0.86838900	-0.28631200
H	-1.34485600	-2.23203900	-0.60651100	C	3.71004000	0.35782000	0.15420600
H	-1.08540500	1.39588900	1.64647200	C	2.47062700	0.84369900	-0.28510900
H	0.69161700	0.40245500	3.04451000	C	1.72948400	0.06584500	-1.17991600
H	1.46297400	-1.91614700	2.61445000	C	2.21450700	-1.16064800	-1.62725100

C	3.44517000	-1.62883600	-1.18234400	H	0.29555500	-1.62046700	0.42015200
H	5.15272500	-1.23107700	0.06553200	H	0.45866000	-0.11991300	-1.50700000
H	4.30591200	0.93984700	0.85140100	Na	-4.65410300	-0.99394400	1.59453600
H	0.75270000	0.40099400	-1.51532200				
H	1.62248200	-1.75477800	-2.31406300	I-Me			
H	3.82074800	-2.58516000	-1.52763900	C	0.65563000	0.91651500	2.35956200
Si	1.82785700	2.49980700	0.30863300	C	-0.18542500	0.12554300	1.57899700
H	0.49829600	2.75482300	-0.29373300	C	-0.93365400	0.63706500	0.51365500
H	1.71577200	2.55179600	1.78414500	C	-0.82089800	2.02296900	0.26003900
H	2.74727800	3.58566700	-0.11203700	C	0.03445600	2.81345400	1.03027900
Na	-4.89883100	-0.54645500	0.18628700	C	0.77494700	2.27065600	2.07822300
				H	1.22562800	0.47256200	3.16915600
II				H	-0.25198200	-0.93564700	1.80004500
C	-0.30198000	2.14884300	1.08535800	H	0.11713200	3.87438800	0.81118600
C	-1.05661900	0.97909000	1.00437300	H	1.43272800	2.90251700	2.66500300
C	-1.87668700	0.69865500	-0.09462000	B	-1.89453900	-0.34791600	-0.38650700
C	-1.93433200	1.67302100	-1.10103200				
C	-1.18659200	2.84594900	-1.03847700	O	-1.52610900	-0.32776200	-1.80992300
C	-0.35733400	3.08457600	0.05589900	H	-0.69198300	0.12943900	-1.92392300
H	0.33332600	2.32872700	1.94654100	O	-3.33832000	0.02480300	-0.27145700
H	-0.99384100	0.25568600	1.81250900	H	-3.56218500	0.56154300	-1.03312500
H	-2.57765800	1.50406900	-1.96155800	O	-1.87832200	-1.74262700	0.14674900
H	-1.24646100	3.57489500	-1.83976500	H	-0.99182200	-2.10242500	0.07416500
H	0.23186300	3.99324000	0.10899400	C	2.99003300	-1.58936600	1.12883000
B	-2.63513700	-0.73688600	-0.28841100	C	2.96773100	-0.42730300	0.36281100
O	-2.02503700	-1.52825400	-1.36631500	C	2.22419300	-0.35498300	-0.81934100
H	-1.73282400	-0.94382100	-2.06942300	C	1.50549900	-1.48937300	-1.21958900
O	-4.08190200	-0.48512900	-0.56048700	C	1.52159200	-2.65245300	-0.45579800
H	-4.36474800	-1.16057200	-1.18281700	C	2.26191300	-2.70217800	0.72354600
O	-2.60994400	-1.55808000	0.95387400	H	3.56711700	-1.62181400	2.04578700
H	-1.72658800	-1.89612100	1.11001300	H	3.52098300	0.44099500	0.7065090
C	4.32828900	1.05296000	0.41950800	H	0.91240700	-1.47135900	-2.12831900
C	3.07029600	0.63841000	-0.00908900	H	0.96333000	-3.52265300	-0.78423000
C	2.79972000	-0.71433500	-0.25490700	H	2.27296500	-3.60698600	1.32015700
C	3.83478200	-1.63856400	-0.06478700	Si	2.18226700	1.23390200	-1.81610100
C	5.09473100	-1.22960000	0.36196200	H	0.81668400	1.48294600	-2.33996300
C	5.34231100	0.11830900	0.6060790	H	2.61188400	2.36465700	-0.96489300
H	4.51843000	2.10403700	0.6042110	H	3.09279300	1.14562800	-2.98420900
H	2.28751300	1.37796100	-0.15459600	Na	-4.05097000	-1.95234600	0.47598000
H	3.65910000	-2.69312900	-0.25516400	C	-1.65647500	2.69450700	-0.80828200
H	5.88341800	-1.96003800	0.50103200	H	-1.67535700	2.11492600	-1.73204900
H	6.32318700	0.43912700	0.9371340	H	-2.69268400	2.79103800	-0.47001500
Si	1.07361000	-1.24977100	-0.7821100	H	-1.28124900	3.69538800	-1.02965200
H	1.18691700	-2.44126500	-1.65674800				

I-MeO							
				C	2.54541500	2.75516300	1.10534500
C	0.43042900	1.79177300	1.7286200	C	1.74659000	3.41742600	0.17679800
C	-0.15826500	0.65113000	1.18398100	H	0.51362900	3.19427900	-1.57083500
C	-1.21284200	0.72135600	0.26518000	H	0.82871600	0.75786300	-1.71093300
C	-1.66428700	2.00722400	-0.06846900	H	3.34769500	0.87000100	1.74397300
C	-1.09010900	3.15809800	0.46681800	H	3.03463200	3.31595400	1.89479900
C	-0.03406700	3.05361800	1.36916900	H	1.60884000	4.49101700	0.23953900
H	1.25366800	1.69502400	2.4298380	B	2.24366600	-1.01967300	-0.02809500
H	0.22970500	-0.32148700	1.47758800	O	1.29093400	-1.70856200	0.85591400
H	-2.49485100	2.10397300	-0.76210200	O	3.65259300	-1.35134400	0.30995400
H	-1.46403800	4.13626800	0.18289100	H	3.67932400	-2.27947600	0.56292800
H	0.42037000	3.94478900	1.7878630	O	2.02338400	-1.54972800	-1.40135000
B	-1.88399700	-0.62370500	-0.38883500	H	1.08949300	-1.55709900	-1.61816200
O	-1.40911700	-0.95276700	-1.73384300	C	-4.75701900	1.39629500	-0.31361200
O	-3.36454900	-0.42649800	-0.38247400	C	-3.45819800	0.95995500	-0.06838000
O	-1.63381500	-1.82014200	0.46383800	C	-3.16434100	-0.40207400	0.08011100
H	-0.70413200	-2.05758600	0.42966400	C	-4.22312300	-1.31377800	-0.01748700
C	3.06821500	-1.81630400	1.28441800	C	-5.52500400	-0.88525600	-0.26122000
C	3.19226500	-0.53016700	0.76487200	C	-5.79330100	0.47223800	-0.41100000
C	2.50637000	-0.15187600	-0.39445500	H	-4.96183100	2.45504000	-0.42415100
C	1.69556500	-1.10167700	-1.02594100	H	-2.66113300	1.69401200	0.01246100
C	1.57189800	-2.38992700	-0.51484500	H	-4.03209600	-2.37631600	0.10188400
C	2.25556000	-2.74856200	0.64526900	H	-6.32984000	-1.60807800	-0.33107500
H	3.60137500	-2.08970500	2.18765300	H	-6.80624400	0.80895200	-0.59877300
H	3.81688200	0.19093200	1.2832190	Si	-1.38433300	-0.96895700	0.36351600
H	1.11179400	-0.83325700	-1.89996500	H	-1.43795800	-2.23425600	1.12706000
H	0.93285900	-3.10730800	-1.01814000	H	-0.78409300	-1.19405000	-0.97206700
H	2.15490300	-3.74962700	1.04864400	H	-0.70772900	0.12160700	1.09160300
Si	2.55237600	1.61138000	-1.03520500	C	1.38843200	-1.43096300	2.22924900
H	1.17979000	2.07478200	-1.33901900	H	1.13857900	-0.38599800	2.45547200
H	3.18379400	2.48343600	-0.01704000	H	0.68673200	-2.07422200	2.76707800
H	3.35941900	1.68977200	-2.27940100	H	2.39876400	-1.62506400	2.61011900
Na	-3.49216600	-1.48994400	1.63963000	Na	4.15589900	-1.13856400	-1.93852300
C	-1.42774000	0.07217200	-2.68980900				
H	-0.68865200	0.85458600	-2.46877200				
H	-1.19618700	-0.35389000	-3.67006800				
H	-2.41204700	0.55708600	-2.75375500				
H	-3.72220900	-0.97509100	-1.08700900				

II-MeO

C	1.13165800	2.68748800	-0.83709000
C	1.31309700	1.30763500	-0.90832400
C	2.09812200	0.60982000	0.01952900
C	2.71545100	1.37453100	1.01907300

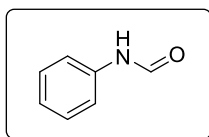
5. Crystallographic data

5.1 Crystallographic data of *N*-(3,5-difluorophenyl)formamide (**2q**)

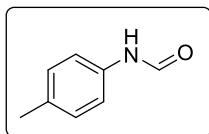
Empirical formula	C ₇ H ₅ F ₂ NO
Formula weigh	157.12
Crystal system	monoclinic
Space group	P21/c
<i>a</i> (Å)	4.3520(8)
<i>b</i> (Å)	10.590(2)
<i>c</i> (Å)	14.532(3)
α (°)	90
β (°)	98.269(2)
γ (°)	90
<i>V</i> (Å ³)	662.8(2)
<i>Z</i>	4
Temperature/K	296(2)
<i>F</i> (000)	320
θ min, θ max (deg)	2.39, 29.19
R(int)	0.0210
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0425, 0.1107
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0407, 0.1345

CCDC 1971981 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

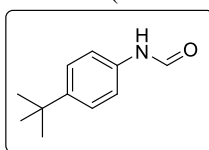
6. Characterization data



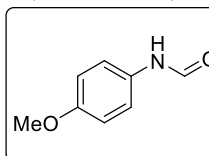
N-phenylformamide (**2a**)⁶, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.70, 8.37 (d, *J* = 11.4 Hz and *J* = 1.5 Hz, total 1H), 8.50, 7.61 (br., total 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.36 - 7.31 (m, 2H), 7.19 - 7.06 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.8, 136.9, 129.8, 129.8, 125.3, 120.1, 120.1.



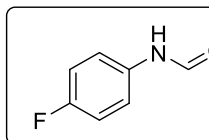
N-*p*-tolylformamide (**2b**)⁷, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.73, 8.58 (d, *J* = 10.6 Hz and *J* = 8.0 Hz, total 1H), 8.26, 7.82 (s, and br., total 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 9.4 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 1H), 2.32 (d, *J* = 8.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 135.2, 134.5, 130.3, 130.3, 120.2, 120.2, 21.0.



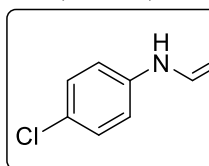
N-(4-(*tert*-butyl)phenyl)formamide (**2e**)⁸, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.65, 8.35 (d, *J* = 11.5 Hz and *J* = 1.7 Hz, total 1H), 8.17 (s, 1H), 7.46 (d, *J* = 11.2 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.03 (d, *J* = 11.3 Hz, 1H), 1.30 (d, *J* = 4.7 Hz, total 9H). ¹³C NMR (100 MHz, CDCl₃) δ 162.5, 148.6, 134.3, 126.6, 126.6, 119.9, 119.9.



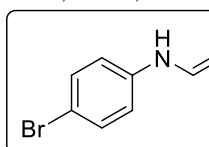
N-(4-methoxybenzyl)formamide (**2f**)⁸, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.51, 8.30 (d, *J* = 11.5 Hz and *J* = 1.6 Hz, total 1H), 8.34, 7.66 (d, *J* = 9.8 Hz and br., total 1H), 7.44 (d, *J* = 9.0 Hz, 1H), 7.04 (d, *J* = 8.9 Hz, 1H), 6.87 (dd, *J* = 13.0, 9.0 Hz, 2H), 3.79 (d, *J* = 6.6 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 157.6, 130.0, 121.9, 121.9, 114.9, 114.9, 55.6.



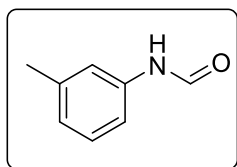
N-(4-fluorophenyl)formamide (**2g**)⁸, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.58, 8.35 (d, *J* = 11.3 Hz and *J* = 1.5 Hz, total 1H), 7.57 - 7.44, 7.08 - 6.98 (m, total 4H). ¹³C NMR (100 MHz, CDCl₃; due to the complexity, C-F coupling is not shown) δ 162.9, 160.06, 132.8, 121.9, 121.3, 116.7, 115.9.



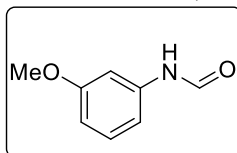
N-(4-chlorophenyl)formamide (**2h**)⁹, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.71, 8.63 (d, *J* = 11.1 Hz and br., total 1H), 8.41, 7.62 (s, total 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.41 - 7.29 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.5, 159.0, 135.4, 135.3, 130.8, 129.9, 129.2, 121.2, 120.1.



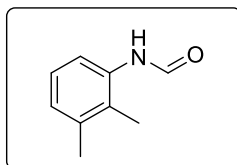
N-(4-bromophenyl)formamide (**2i**)⁸, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.66, 8.38 (d, *J* = 11.3 Hz and *J* = 1.6 Hz, total 1H), 8.34 (br., 1H), 7.47, 6.98 (d, *J* = 6.7 Hz and *J* = 8.8 Hz, total 2H), 7.44 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 135.9, 132.1, 132.1, 121.5, 121.5, 117.5.



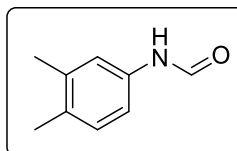
N-*m*-tolylformamide (**2k**)⁹, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.06, 8.74 (d, *J* = 11.2 Hz, and br, total 1H), 8.37, 8.02 (s, 1H, and bs, 1H, total 1H), 7.48 - 7.34 (m, 1H), 7.33 - 7.20 (m, 1H), 7.04 - 6.95 (m, 2H), 2.37 (s, *J* = 10.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 159.5, 139.9, 139.1, 137.0, 136.8, 129.6, 129.0, 126.1, 125.6, 120.8, 119.5, 117.2, 115.7, 21.5.



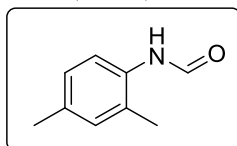
N-(3-methoxyphenyl)formamide (**2l**)¹⁰, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.70, 8.45 (d, *J* = 11.6 Hz, 1H and br., total 1H), 8.36, 7.60 (d, *J* = 7.9 Hz, and br., total 1H), 7.30 - 7.20, 6.75 - 6.67 (m, 3H), 7.02, 6.63 (d, *J* = 8.0 Hz and t, *J* = 2.2 Hz total 1H), 3.81, 3.79 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 160.7, 137.9, 130.6, 110.9, 110.4, 104.9, 55.4.



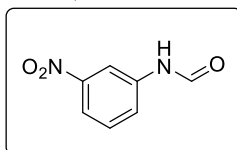
N-(2,3-dimethylphenyl)formamide (**2m**)¹¹, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.46, 8.44 (d, *J* = 12.0 Hz and *J* = 4.0 Hz, total 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.14 - 6.98 (m, 3H), 2.32, 2.31 (s, total 3H), 2.20, 2.18 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 138.4, 128.9, 127.9, 126.3, 121.9, 119.6, 20.5, 13.6.



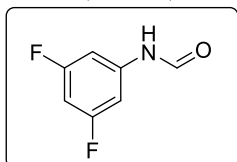
N-(3,4-dimethylphenyl)formamide (**2n**)¹¹, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.61, 8.34 (d, *J* = 11.5 Hz and *J* = 1.7 Hz, total 1H), 7.88, 7.20 (br., total 1H), 7.33, 7.25, 7.23 (d, *J* = 1.8 Hz, total 1H), 7.09 (t, *J* = 8.3 Hz, 1H), 6.87 - 6.80 (m, 1H), 2.26 - 2.22 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 138.2, 134.3, 133.9, 130.7, 121.4, 117.5, 19.8, 19.2.



N-(2,4-dimethylphenyl)formamide (**2o**)¹², 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.46, 8.40 (d, *J* = 12.0 Hz and *J* = 1.6 Hz, total 1H), 7.78, 7.10 (br., total 1H), 7.71 - 7.65, 7.05 - 7.01 (m, total 3H), 2.31, 2.29 (s, total 3H), 2.26, 2.24 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 136.0, 132.4, 131.9, 129.9, 127.5, 123.4, 20.8, 17.6.

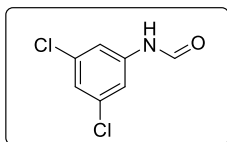


N-(3-nitrophenyl)formamide (**2p**)⁹, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 10.66, 10.46 (s and d, *J* = 10.3 Hz, total 1H), 8.95, 8.61 (d, *J* = 10.7 Hz and *J* = 1.9 Hz, total 1H), 8.38, 8.02 (s, total 1H), 7.91, 7.69 (dd, *J* = 16.0, 8.4 Hz and d, *J* = 7.9 Hz, total 2H), 7.62 (t, *J* = 7.1 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.6, 153.2, 144.5, 135.6, 130.2, 123.3, 118.6.



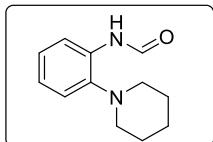
N-(3,5-difluorophenyl)formamide (**2q**)¹³, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.72, 8.39 (d, *J* = 11.1 Hz and s total 1H), 8.46, 7.60 (br., total 1H), 7.20 - 7.12, 6.72 - 6.45 (m, total 3H). ¹³C NMR (100 MHz, CDCl₃) 164.5, 162.0, 159.2, 138.9, 103.0, 101.4, 100.2.

HRMS: C₇H₅F₂NO[M⁺H⁺]; calculated: 158.0412, found: 158.0422.



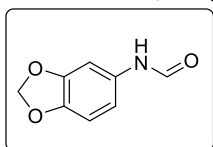
N-(3,5-dichlorophenyl)formamide (**2r**)¹⁴, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.70, 8.38 (d, *J* = 11.1 Hz and *J* = 0.8 Hz, total 1H), 8.25, 7.40 (d, *J* = 8.0 Hz and br. total 1H), 7.51, 7.01 (d, *J* = 1.6 Hz, total 2H), 7.19 - 7.13 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 138.5, 135.5, 124.9, 124.9, 118.2, 118.2.

HRMS: C₇H₅Cl₂NO[M⁺H⁺]; calculated: 189.9821, found: 189.9829.

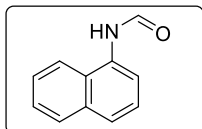


N-(2-(piperidin-1-yl)phenyl)formamide (**2s**)¹⁵, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.92, 8.55 (d, *J* = 12.0 Hz and s, total 1H), 8.60, 8.25 (br., total 1H), 8.41, 7.25 (d, *J* = 6.8 Hz, *J* = 7.8 Hz, total 1H), 7.25 - 7.10 (m, 3H), 2.87 - 2.79 (m, 4H), 1.83 - 1.74 (m, 4H), 1.69 - 1.56 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 142.6, 132.7, 125.2, 124.2, 120.8, 120.1, 53.9, 53.6, 26.9, 26.6, 24.0.

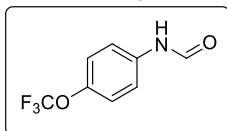
HRMS: C₁₂H₁₆N₂O[M⁺H⁺]; calculated: 205.1335, found: 205.1335.



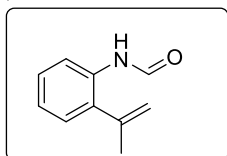
N-(benzo[*d*][1,3]dioxol-5-yl)formamide (**2t**)¹⁶, 84% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.53, 8.33 (d, *J* = 11.4 Hz and s, total 1H), 8.06, 7.39 (br., total 1H), 7.27, 6.66 (d, *J* = 1.9 Hz, total 1H), 6.88, 6.58 (dd, *J* = 8.2, 1.9 Hz, total 1H), 6.79 (dd, *J* = 11.5, 8.3 Hz, 1H), 6.00 (d, *J* = 12.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 148.7, 145.7, 131.0, 113.3, 108.7, 102.9, 101.7.



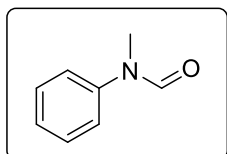
N-(naphthalen-1-yl)formamide (**2w**)⁹, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.64, 8.62 (br. and s, total 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.91 - 7.86, 7.31 (m and d, *J* = 8.0 Hz, 2H), 7.79, 7.72 (d, *J* = 8.0 Hz, 1H), 7.62 - 7.42 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 134.3, 132.0, 128.6, 127.8, 127.0, 126.5, 126.2, 125.6, 121.3, 119.1.



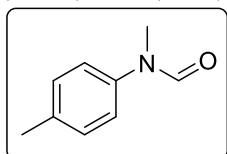
N-(4-(trifluoromethoxy)phenyl)formamide (**2y**)⁹, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.67, 8.39 (d, *J* = 11.3 Hz and *J* = 1.5 Hz, total 1H), 8.37, 7.55 (br., total 1H), 7.61 - 7.56, 7.16 - 7.10 (m, total 2H), 7.21 (dd, *J* = 16.5, 8.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃; due to the complexity, C-F coupling is not shown) δ 162.4, 146.5, 135.5, 122.6, 121.8, 121.2, 120.1, 120.45.



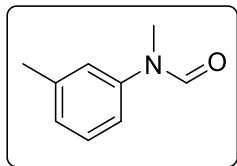
N-(2-(prop-1-en-2-yl)phenyl)formamide (**2z**)¹⁷, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.76 - 8.71, 8.40 - 8.31 (m, total 1H), 8.50 - 8.40, 7.37 - 7.27 (m, total 2H), 7.25 - 7.11 (m, 2H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.07 (d, *J* = 8.5 Hz, 1H), 2.14 - 2.08 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 142.7, 134.8, 133.0, 129.1, 128.0, 125.1, 121.3, 117.6, 24.5.



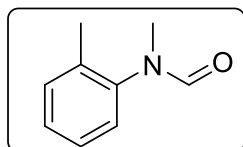
N-methyl-*N*-phenylformamide (**2aa**)¹⁸, 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.45 (s, 1H), 7.45 - 7.27 (m, 4H), 7.19 - 7.16 (m, 1H), 3.31 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 142.2, 129.7, 129.7, 126.0, 122.8, 122.8, 31.9.



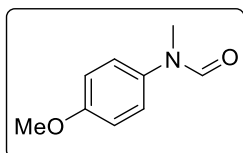
N-methyl-*N*-(*p*-tolyl)formamide (**2ab**)⁷, 91% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 3.31 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 139.7, 136.3, 130.2, 122.5, 32.2, 20.9.



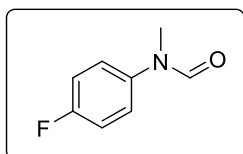
N-methyl-*N*-(*m*-tolyl)formamide (**2ac**)⁶, 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.46 (s, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 2H), 3.30 (s, 3H), 2.38 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 142.1, 139.6, 129.4, 127.1, 123.0, 119.4, 32.0, 21.4.



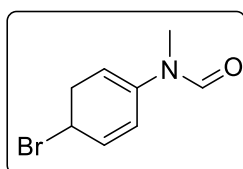
N-methyl-*N*-(*o*-tolyl)formamide (**2ad**)¹⁸, 68% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.31, 8.13 (s, total 1H), 7.31 - 7.26, 7.25 - 7.22 (m, total 3H), 7.11 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.27, 3.20 (s, total 3H), 2.27, 2.22 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 140.8, 135.5, 131.5, 128.4, 127.8, 127.2, 33.1, 17.7.



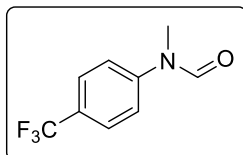
N-(4-methoxyphenyl)-*N*-methylformamide (**2ae**)⁷, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.33 (s, 1H), 7.09 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.6, 158.7, 135.0, 124.8, 114.9, 55.7, 32.8.



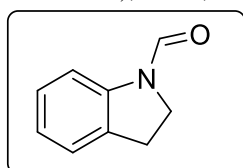
N-(4-fluorophenyl)-*N*-methylformamide (**2af**)⁶, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.20 - 7.05 (m, 4H), 3.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 159.8, (d, *J* = 250 Hz) 138.3, 124.6 (d, *J* = 8.4 Hz), 116.5 (d, *J* = 22.8 Hz), 32.5.



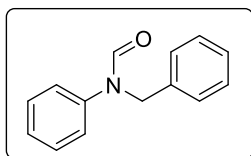
N-(4-bromophenyl)-*N*-methylformamide (**2ah**)¹⁹, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.46, 8.36 (s, total 1H), 7.56 - 7.51 (m, 2H), 7.37 - 7.33, 7.08 - 7.04 (m, total 2H), 3.34, 3.30 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 141.2, 132.7, 132.7, 123.8, 123.8, 119.7, 31.8.



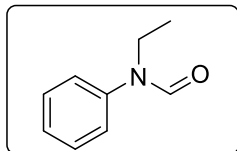
N-methyl-*N*-(4-(trifluoromethyl)phenyl)formamide (**2ai**)⁶, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 7.82 - 7.61 (m, 2H), 7.35 (t, *J* = 13.9 Hz, 2H), 3.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 145.2, 128.2 (d, *J* = 33.1 Hz), 124.0 (d, *J* = 244.2 Hz), 121.5, 31.7.



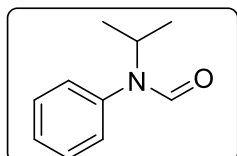
Indoline-1-carbaldehyde (**2aj**)⁹, 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.93, 8.52, (s, total 1H), 7.28 - 7.13 (m, 3H), 7.07 (t, *J* = 7.1 Hz, 1H), 4.11 - 4.04 (m, 2H), 3.19 - 3.13 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 157.6, 141.0, 131.9, 127.5, 126.0, 124.8, 124.5, 124.2, 116.6, 109.4, 46.9, 44.6, 27.7, 27.1.



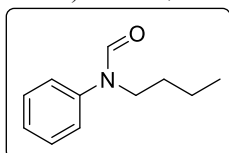
N-benzyl-*N*-phenylformamide (**2am**)⁸, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (s, 1H), 7.36 - 7.26, 7.25 - 7.20 (m, total 8H), 7.13 - 7.07 (m, 2H), 5.00 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 141.1, 136.7, 129.6, 129.6, 128.6, 128.6, 127.9, 127.9, 127.5, 126.9, 124.1, 124.1, 48.9.



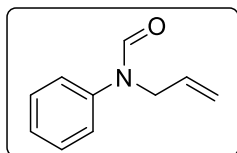
N-ethyl-*N*-phenylformamide (**2an**)⁹, 73% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.38 (s, 1H), 7.46 - 7.43 (m, 2H), 7.37 - 7.28 (m, 1H), 7.20 (d, *J* = 7.8 Hz, 2H), 3.92 - 3.87 (m, 2H), 1.21 - 1.17 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 140.8, 129.7, 126.9, 124.3, 40.1, 13.1.



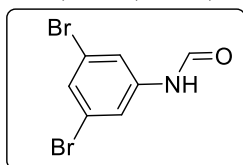
N-isopropyl-*N*-phenylformamide (**2ao**)¹¹, 67% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.42, 8.17 (s, total 1H), 7.59 - 7.33 (m, 3H), 7.17 - 7.14 (m, 2H), 4.85 - 4.74, 4.14 - 4.07 (m, total 1H), 1.27, 1.20 (d, *J* = 6.8 Hz, total 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.5, 138.4, 129.2, 129.2, 128.9, 128.9, 128.1, 45.8, 20.9, 20.9.



N-butyl-*N*-phenylformamide (**2aq**)⁶, 72% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.37, 8.33 (s, total 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 8.6 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 3.92 - 3.70 (m, 2H), 1.64 - 1.45 (m, 2H), 1.34 - 1.28 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 140.9, 129.6, 126.7, 124.1, 44.6, 29.6, 19.9, 13.6.

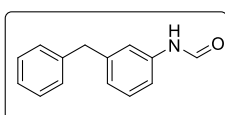


N-allyl-*N*-phenylformamide (**2at**)⁶, 44% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.51 (s, 1H), 7.44 - 7.41 (m, 2H), 7.32 - 7.29 (m, 1H), 7.23 - 7.21 (m, 2H), 5.93 - 5.83 (m, 1H), 5.24 - 5.19 (m, 2H), 4.45 (d, *J* = 5.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.0, 141.1, 132.5, 129.6, 126.7, 123.5, 117.6, 47.9.



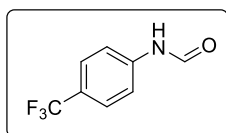
N-(3,5-dibromophenyl)formamide (**2au**)²⁰, 76% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.68, 8.37 (d, *J* = 11.1 Hz and s, total 1H), 7.80, 7.24 (br., total 1H), 7.71, 7.19 (d, *J* = 1.5 Hz, total 2H), 7.49 - 7.44 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 145.8, 133.4, 133.4, 127.7, 125.8, 125.8.

HRMS: C₇H₅Br₂NO[M⁺H⁺]; calculated: 279.8790, found: 279.8800.

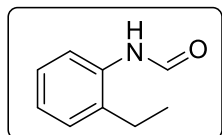


N-(3-benzylphenyl)formamide (**2aw**), 89% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.63, 8.32 (d, *J* = 11.4 Hz and *J* = 1.5 Hz, total 1H), 8.00, 7.42 (d, *J* = 9.8 Hz and *J* = 8.0 Hz, total 1H), 7.32 - 6.86 (m, 9H), 3.96 (d, *J* = 4.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.9, 143.3, 140.6, 137.0, 129.8, 129.0, 129.0, 128.7, 128.7, 126.4, 126.0, 120.4, 117.8, 41.8.

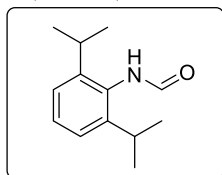
HRMS: C₁₄H₁₄NO[M⁺H⁺]; calculated: 212.1070, found: 212.1080.



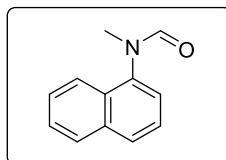
N-(4-(trifluoromethyl)phenyl)formamide (**2ax**)⁹, 72% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.69, 8.37 (d, *J* = 11.4 Hz and *J* = 1.6 Hz, 1H), 7.54 (dd, *J* = 8.5, 0.9 Hz, 1H), 7.39 - 7.28, 7.21 - 7.08 (m, total 2H). ¹³C NMR (100 MHz, CDCl₃; due to the complexity, C-F coupling is not shown) δ 162.7, 139.2, 133.8, 129.8, 129.8, 125.3, 120.0, 120.0, 37.0.



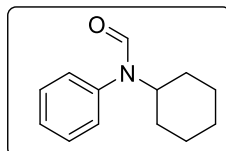
N-(2-ethylphenyl)formamide (**2ay**)²¹, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.50, 8.42 (d, *J* = 11.2 Hz, *J* = 1.6 Hz, total 1H), 7.85, 7.28 - 7.26 (d, *J* = 8.0 Hz and m, total 1H), 8.36, 7.49 (br. total 1H), 7.23 - 7.11 (m, 3H), 2.64 (dq, *J* = 15.1, 7.6 Hz, 2H), 1.23 (td, *J* = 7.6, 2.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 136.2, 134.4, 129.4, 127.0, 126.5, 121.6, 24.2, 14.2.



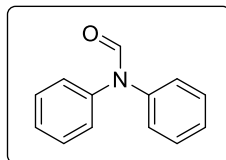
N-(2,6-diisopropylphenyl)formamide (**2az**)⁸, 70% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.45, 8.03 (s and *J* = 11.9 Hz, total 1H), 7.32 (dd, *J* = 15.4, 7.7 Hz, 1H), 7.20 (dd, *J* = 7.7, 5.5 Hz, 2H), 3.26 - 3.08 (m, 2H), 1.21 (dd, *J* = 6.9, 3.8 Hz, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 146.8, 130.0, 130.0, 128.9, 123.8, 123.8, 28.4, 23.6.



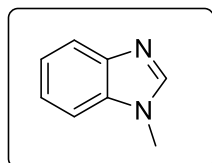
N-methyl-*N*-(naphthalen-1-yl)formamide (**2bb**)⁶, 83% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (s, 1H), 7.98 - 7.79 (m, 3H), 7.62 - 7.43 (m, 3H), 7.35 (d, *J* = 7.1 Hz, 1H), 3.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 138.2, 134.5, 130.4, 128.9, 128.6, 127.4, 126.7, 125.5, 125.1, 122.3, 34.2.



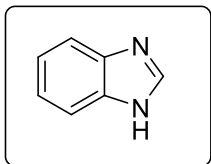
N-cyclohexyl-*N*-phenylformamide (**2bc**), 40% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.42, 8.15 (s, total 1H), 7.41-7.38 (m, 3H), 7.17 - 7.14 (m, 2H), 4.47 - 4.33 (m, 1H), 1.87 (d, *J* = 13.9 Hz, 2H), 1.77 (d, *J* = 13.9 Hz, 2H), 1.66 - 1.57 (m, 1H), 1.43 - 1.27 (m, 4H), 1.05 - 0.95 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.5 (s), 138.8, 129.3, 129.3, 129.1, 129.1, 128.2, 53.8, 31.4, 31.4, 25.8, 25.8, 25.3.



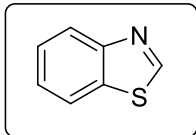
N,N-diphenylformamide (**2bd**)⁹, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (s, 1H), 7.44 - 7.35 (m, 4H), 7.34 - 7.23 (m, 4H), 7.21 - 7.12 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 161.80, 141.9, 139.7, 129.6, 129.6, 129.2, 129.2, 127.0, 126.9, 126.1, 126.1, 125.1, 125.1.



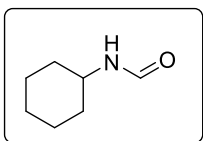
1-methyl-1*H*-benzo[*d*]imidazole (**2bf**)²², 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.34 - 7.27 (m, 2H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 143.8, 143.5, 134.6, 122.9, 122.1, 120.3, 109.3, 31.0.



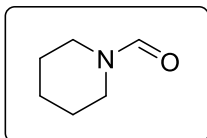
1*H*-benzo[*d*]imidazole (**2bg**)²², 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.68 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.34 - 7.27 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 140.6, 137.6, 123.2, 115.7.



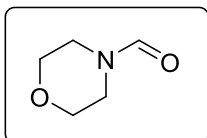
benzo[*d*]thiazole (**2bh**)²², 52% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.96 (s, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.53 - 7.47 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 153.9, 153.2, 126.2, 125.5, 123.7, 121.9.



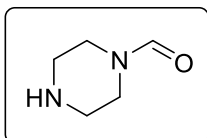
N-cyclohexylformamide (**2bi**)²¹, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.23, 8.19 (d, *J* = 4 Hz and s, total 1H), 6.04 - 5.79 (m, 1H), 4.06 - 3.87, 3.45 - 3.30 (m, total 1H), 2.05 - 1.95 (m, 2H), 1.89 - 1.77 (m, 2H), 1.76 - 1.68 (m, 1H), 1.53 - 1.21 (m, 5H). ¹³C NMR (100 MHz, CDCl₃) δ 160.3, 47.3, 33.1, 33.1, 25.5, 24.9, 24.9.



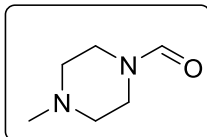
Piperidine-1-carbaldehyde (**2bj**)⁷, 78% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.02 - 8.07 (m, 1H), 3.50 - 3.53 (m, 2H), 3.31 - 3.35 (m, 2H), 1.76 - 1.54 (m, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 46.9, 40.7, 26.6, 25.2, 24.8.



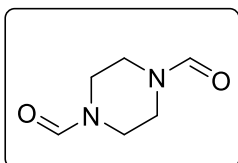
Morpholine-4-carbaldehyde (**2bk**)²³, 77% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 3.69 (t, *J* = 4.8, 2H), 3.65 (t, *J* = 4.6, 2H), 3.56 (t, *J* = 4.8, 2H), 3.39 (t, *J* = 4.6, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 67.2, 66.4, 45.8, 40.6.



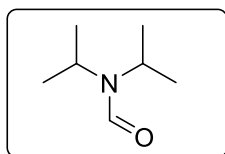
Piperazine-1-carbaldehyde (**2bl**)⁷, 74% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (t, *J* = 11.2 Hz, 1H), 3.54 (t, *J* = 4.6 Hz, 2H), 3.36 (t, *J* = 4.2 Hz, 2H), 2.88 - 2.80 (m, 4H), 1.86 (br., 1H). ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 47.3, 46.8, 45.5, 41.3.



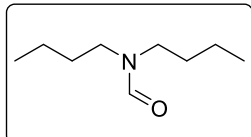
4-methylpiperazine-1-carbaldehyde (**2bm**)²³, 80% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.21, 8.03 (s, total 1H), 3.59 (d, *J* = 4.3 Hz, 2H), 3.42 (dd, *J* = 10.2, 5.6 Hz, 2H), 2.48 - 2.37 (m, 4H), 2.34 (m, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.7, 55.3, 54.1, 45.9, 45.4, 39.7.



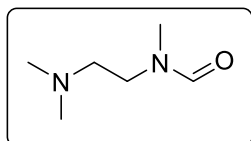
Piperazine-1,4-dicarbaldehyde (**2bn**)¹⁸, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.12, 8.10 (s and br. total 2H), 3.65 - 3.54 (m, 4H), 3.48 - 3.36 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 161.0, 160.8, 46.1, 45.0, 40.5, 39.5.



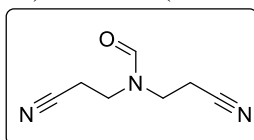
N,N-diisopropylformamide (**2bp**)²⁴, 75% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.24, 8.22 (br. and d, *J* = 4.4 Hz, total 1H), 4.25 - 4.17 (m, 1H), 3.67 - 3.59 (m, 1H), 1.34 - 1.26 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 46.5, 44.1, 23.6, 23.6, 20.30, 20.3.



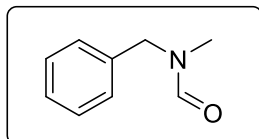
N,N-dibutylformamide (**2bq**)²³, 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 1H), 3.31 (t, *J* = 7.2 Hz, 2H), 3.21 (t, *J* = 7.2 Hz, 2H), 1.60 - 1.45 (m, 4H), 1.40 - 1.26 (m, 4H), 0.95 (td, *J* = 7.3, 2.7 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 47.2, 41.9, 30.7, 29.4, 20.2, 19.6, 13.8, 13.6.



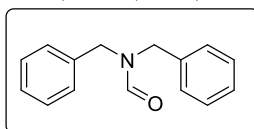
N-(2-(dimethylamino)ethyl)-*N*-methylformamide (**2br**)²⁴, 90% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 2.3 Hz, 1H), 3.45 (t, *J* = 6.7 Hz, 1H), 3.31 (t, *J* = 6.7 Hz, 1H), 2.97, 2.89 (s, total 3H), 2.44 (dt, *J* = 10.0, 6.7 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 56.7, 45.6, 45.2, 32.4.



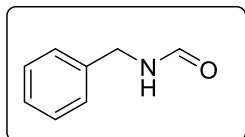
N,N-bis(2-cyanoethyl)formamide (**2bs**)²³, 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.27, 8.25 (br. and s, total 1H), 3.80 - 3.65 (m, 4H), 2.80 - 2.71 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 118.2, 116.8, 44.5, 40.3, 19.2, 16.5.



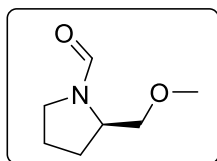
N-benzyl-*N*-methylformamide (**2bt**)⁷, 86% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.29, 8.16 (s, total 1H), 7.49 - 6.85 (m, 5H), 4.52, 4.39 (s, total 2H), 2.85, 2.78 (s, total 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.7, 136.1, 135.80 (s), 128.9, 128.9, 128.3, 127.4, 127.4, 53.6, 33.9.



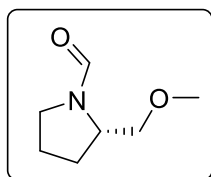
N,N-dibenzylformamide (**2ce**)⁷, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 7.40 - 7.28 (m, 6H), 7.21 - 7.16 (m, 4H), 4.42 (s, 2H), 4.26 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 136.1, 135.7, 128.9, 128.9, 128.7, 128.7, 128.5, 128.5, 128.2, 127.7, 127.7, 127.6, 50.28, 44.71.



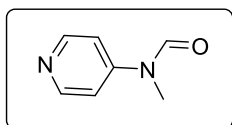
N-benzylformamide (**2cj**)⁷, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.26, 8.19 (s, and d, *J* = 11.9 Hz, total 1H), 7.40 - 7.24 (m, 5H), 5.86 (br., 1H), 4.49, 4.41 (d, *J* = 5.9 Hz and *J* = 6.5 Hz, total 2H). ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 137.6, 128.8, 128.8, 127.8, 127.8, 126.9, 42.1.



(*R*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde (**2cm**)²⁵, 94% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.33, 8.26 (s, total 1H), 4.19 - 3.93 (m, total 1H), 3.65 - 3.50 (m, 2H), 3.40 - 3.27 (m, 5H), 2.09 - 1.75 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 161.7, 75.4, 58.9, 56.4, 43.6, 27.4, 22.8.

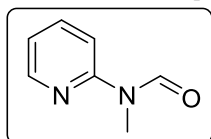


(*S*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde (**2cn**)²⁵, 96% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.33, 8.26 (s, total 1H), 4.16 - 3.95 (m, total 1H), 3.68 - 3.49 (m, 2H), 3.41 - 3.26 (m, 5H), 2.02 - 1.72 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 161.9, 75.4, 59.1, 56.8, 43.7, 27.8, 22.2.

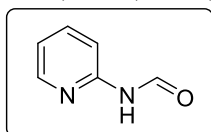


N-methyl-*N*-(pyridin-4-yl)formamide (**2co**), 92% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.82 (s, 1H), 8.59 (d, *J* = 6.3 Hz, 2H), 7.10 (d, *J* = 4.8 Hz, 2H), 3.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 151.2, 151.2, 148.9, 113.7, 113.7, 30.2.

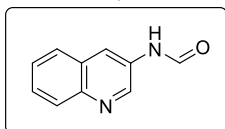
HRMS: C₇H₉N₂O[M⁺H⁺]; calculated: 137.0709, found: 137.0709.



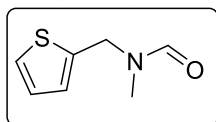
N-methyl-*N*-(pyridin-2-yl)formamide (**2cq**)²⁶, 58% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.35 (s, 1H), 8.40 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.81 - 7.63 (m, 1H), 7.17 - 7.07 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 3.35 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 154.0, 148.6, 138.5, 120.1, 111.3, 28.8.



N-(pyridin-2-yl)formamide (**2cr**)²⁶, 60% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.47, 9.28 (br., total 1H), 9.32, 8.52 (d, *J* = 10.3 Hz, s total 1H), 8.33 (d, *J* = 6.0 Hz, 1H), 8.25, 6.91 (d, *J* = 8.4 Hz, total 1H), 7.71 (dt, *J* = 17.2, 8.1 Hz, 1H), 7.08 (dd, *J* = 13.0, 8.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.3, 150.7, 147.6, 138.8, 120.2, 115.0.



N-(quinolin-3-yl)formamide (**2cu**)²⁷, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ (equilibrium mixture of E/Z isomers) 9.84, 9.51 (br., total 1H), 9.17, 8.75 (d, *J* = 11.7 Hz and s, total 1H), 8.86 (dd, *J* = 4.1, 1.2 Hz, 1H), 8.81 - 8.78 (m, 1H), 8.22 (d, *J* = 6.9 Hz, 1H), 7.64 - 7.56 (m, 2H), 7.51 (dd, *J* = 8.2, 4.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 148.5, 138.3, 136.4, 133.8, 127.9, 127.3, 122.2, 121.8, 117.6.



N-methyl-*N*-(thiophen-2-ylmethyl)formamide (**2cz**)²⁸, 85% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.24, 8.06 (s, total 1H), 7.25 (dd, *J* = 16.4, 5.0 Hz, 1H), 7.00 - 6.92 (m, 2H), 4.66 (s, 1H), 4.55 (s, 1H), 2.90, 2.83 (s, total 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.4, 138.9, 127.2, 126.8, 125.9, 48.4, 33.8.

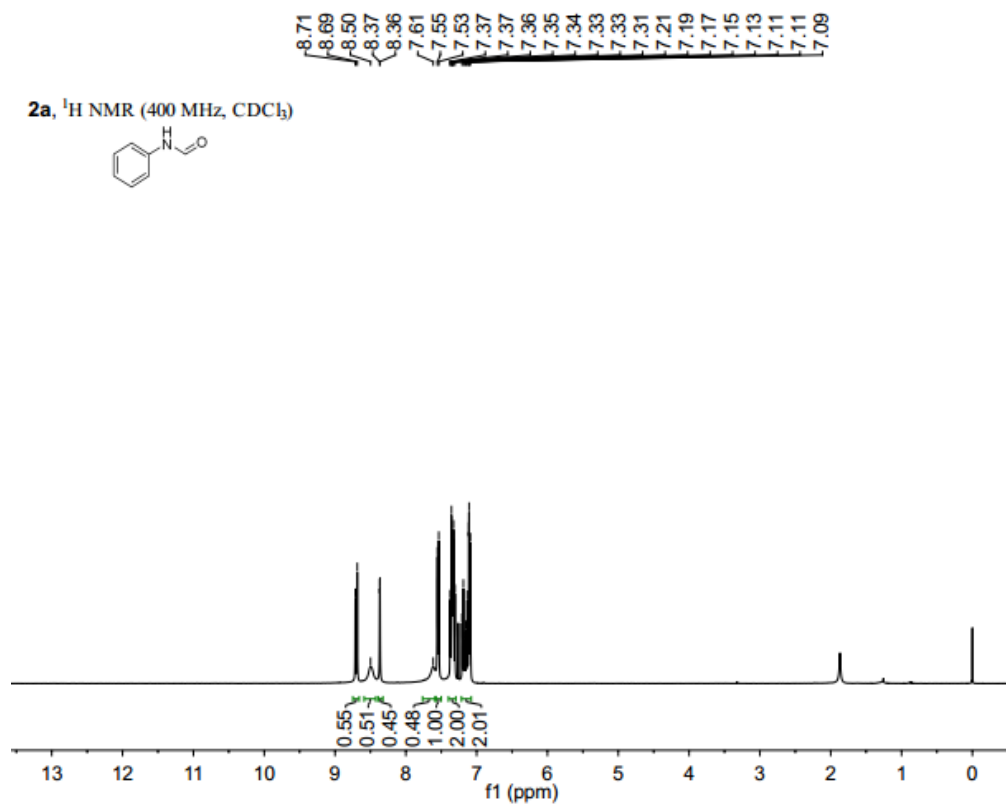
7. References

- (1) a) S. Sithebe, P. Molefe, *J. Organomet. Chem.*, 2017, **846**, 305; b) B. Basu, K. Biswas, S. Kundu and S. Ghosh, *Green Chem.*, 2010, **12**, 1734.
- (2) C. J. Gerack, L. McElwee-White, *Molecules* 2014, **19**, 7689.

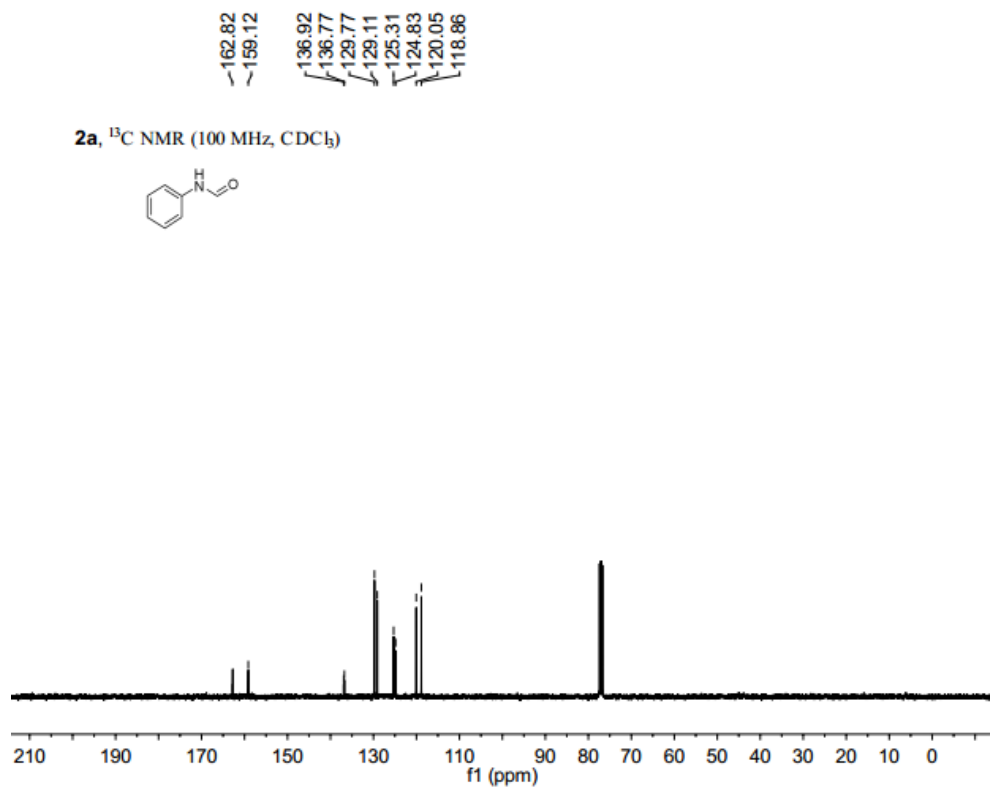
- (3) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford CT, 2016.
- (4) a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215. b) S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104. c) S. Kozuch and J. M. L. Martin, *Phys. Chem. Chem. Phys.*, 2011, **13**, 20104. d) Kozuch, Sebastian; Martin, Jan M.L. *J. Comp. Chem.*, 2013, **34**, 2327. e) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
- (5) S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.*, 55 (1981) 117-29; S. Miertuš and J. Tomasi, *Chem. Phys.*, 65 (1982) 239-45; J. L. Pascual-Ahuir, E. Silla, and I. Tuñón, *J. Comp. Chem.*, 15 (1994) 1127-38. (5) S. Miertuš, E. Scrocco, and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117; S. Miertuš and J. Tomasi, *Chem. Phys.*, 1982, **65**, 239; J. L. Pascual-Ahuir, E. Silla, and I. Tuñón, *J. Comp. Chem.*, 1994, **15**, 1127.
- (6) Z. Huang, et al. and Y. Li, *ChemSusChem* 2019, **12**, 3054.
- (7) L. Hao, Y. Zhao, et al., X. Gao, and Z. Liu, *ACS Catal.* 2015, **5**, 4989.
- (8) H. Li, T. P. Gonçalves, et al. and K.-W. Huang, *Chem. Commun.*, 2018, **54**, 11395.
- (9) J. Yin, J. Zhang, et al. and H. Gong, *Org. Lett.*, 2019, **21**, 387.
- (10) X.-F. Li, X.-G. Zhang, et al. and X. Zhang, *J. Org. Chem.*, 2018, **83**, 12815.
- (11) X. Ma, S. Deng and Q. Song, *Org. Chem. Front.*, 2018, **5**, 3505.
- (12) M. R. Mutra, G. K. Dhandabani, J. Wang, *Adv. Synth. Catal.*, 2018, **360**, 3960.
- (13) H. Tumma, N. Nagaraju and K. - V Reddy, *J. Mol. Catal. A.*, 2009, **310**, 121.
- (14) G.- R. Pettit, et al. and K. Parent, *J. Org. Chem.*, 1961, **26**, 2563.
- (15) O. Meth-Cohn H. Suschitzky *J. Chem. Soc.*, 1963, 4666.
- (16) L. Becerra-Figueroa, A. Ojeda-Porras et al. and D. Gamba-Sanchez, *J. Org. Chem.* 2014, **79**, 4544.
- (17) B. Li, Y. Park and S. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 1125.
- (18) Z. Ke, Y. Zhang, X. Cui and F. Shi, *Green Chem*, 2016, **18**, 808.
- (19) C. Fang, C. Lu, et al. and B.-L. Lin, *ACS Catal.*, 2016, **6**, 7876.
- (20) F. D. Chattaway, K. J. P. Orton, *Chem. Ber.* 1900, **33**, 2399.
- (21) Z. Tan, Z. Li, Y. Ma, J. Qin and C. Yu, *Eur. J. Org. Chem*, 2019, **28**, 4538.
- (22) Z. Zhang, Q. Sun, C. Xia and W. Sun, *Org. Lett.*, 2016, **18**, 6316.
- (23) H. Liu, Q. Mei, et al. and B. Han, *Green Chem*, 2017, **19**, 196.
- (24) J. Dale, T. Sigvartsen, *Acta Chem. Scand.*, 1991, **45**, 1064.
- (25) L. A. G. M. van den Broek, et al. and B. Zwanenburg, *J. Org. Chem*, 1984, **49**, 1691.
- (26) S. Ko, H. Han and S. Chang, *Org. Lett.*, 2003, **5**, 2687.
- (27) T. Ikawa, T. Barder, et al. and S. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 13001.
- (28) F. Barba, J. Recio and B. Batanero, *Tetrahedron Lett.*, 2013, **54**, 1835.

8. Copies of product NMR

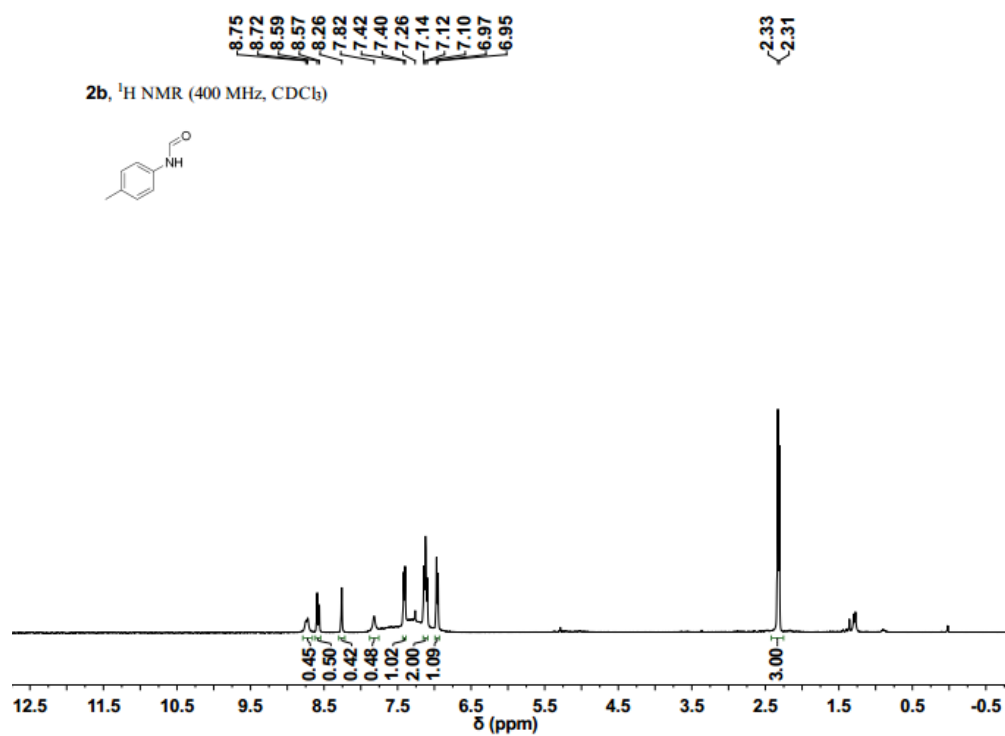
^1H NMR for *N*-phenylformamide, **2a**



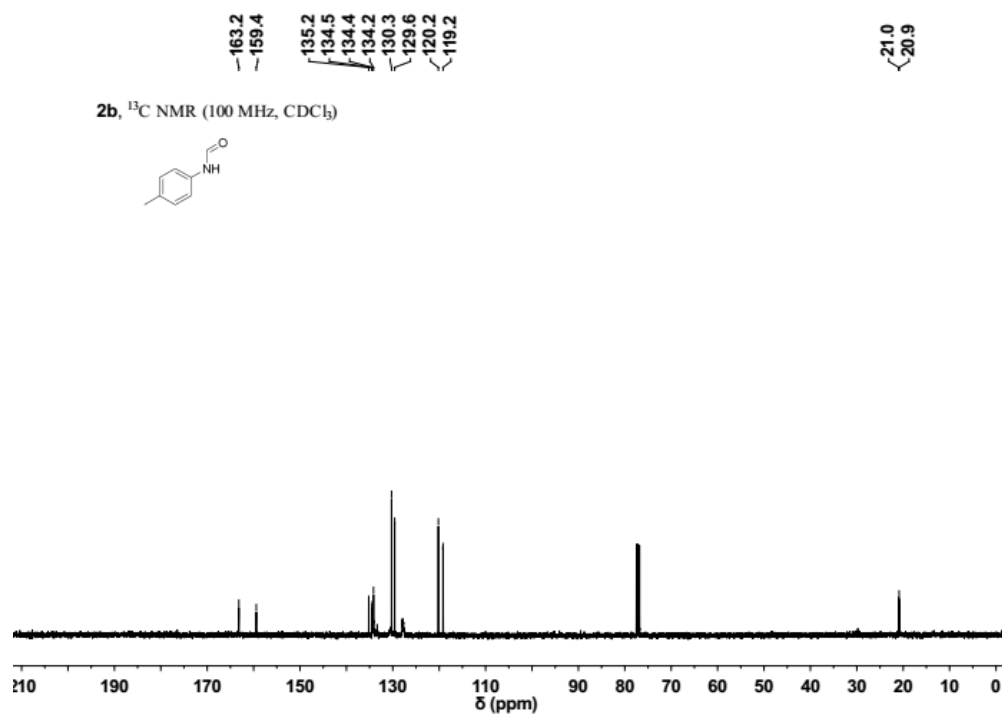
^{13}C NMR for *N*-phenylformamide, **2a**



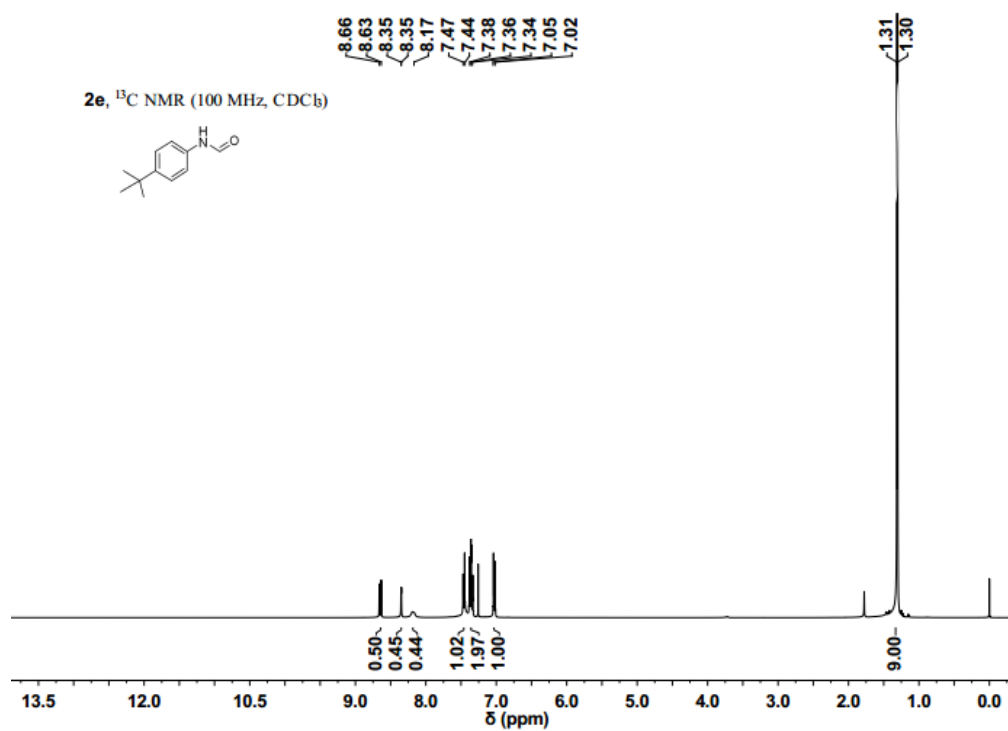
^1H NMR for *N*-p-tolylformamide, **2b**



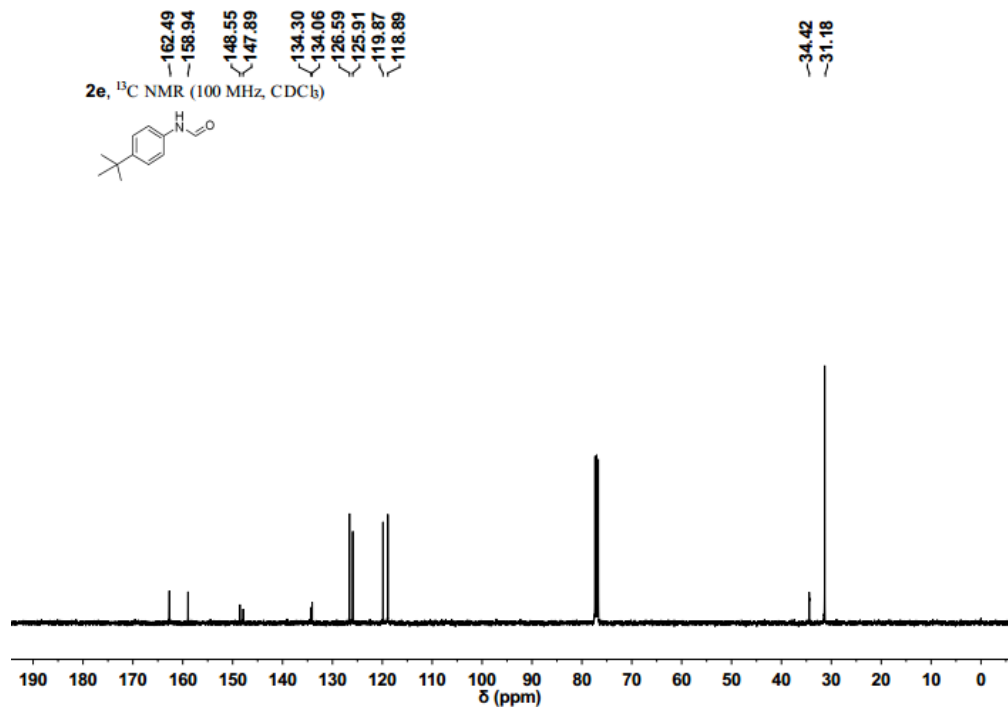
^{13}C NMR for *N*-p-tolylformamide, **2b**



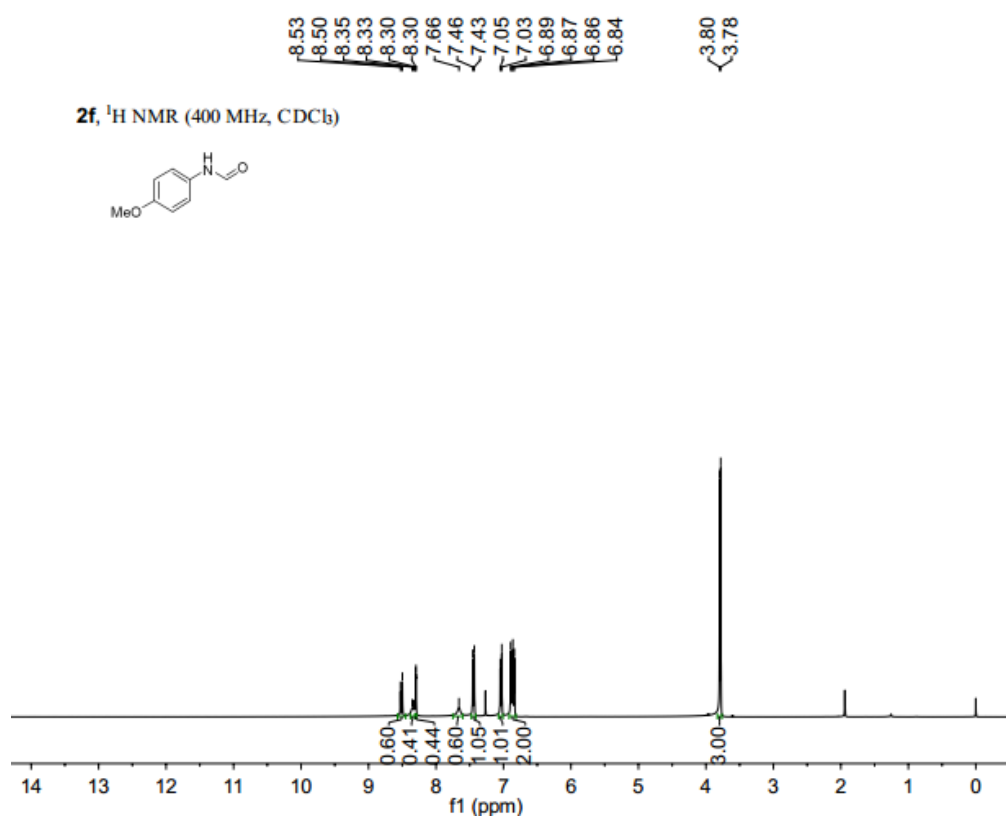
^1H NMR for *N*-(4-(tert-butyl)phenyl)formamide, **2e**



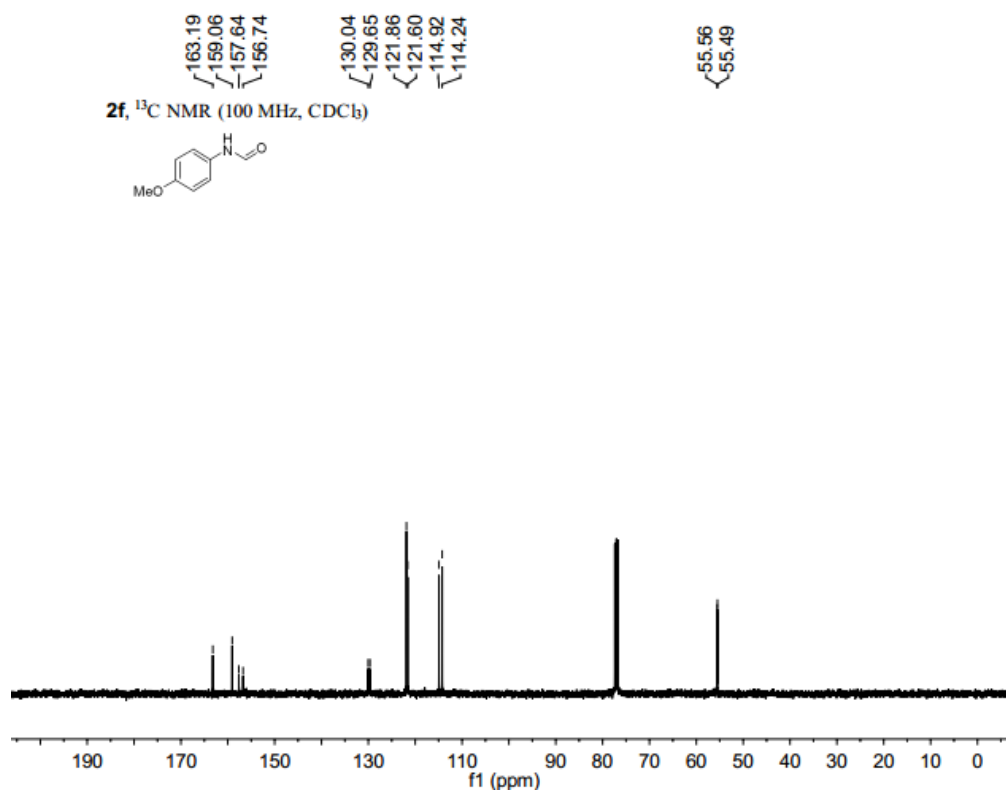
^{13}C NMR for *N*-(4-(tert-butyl)phenyl)formamide, **2e**



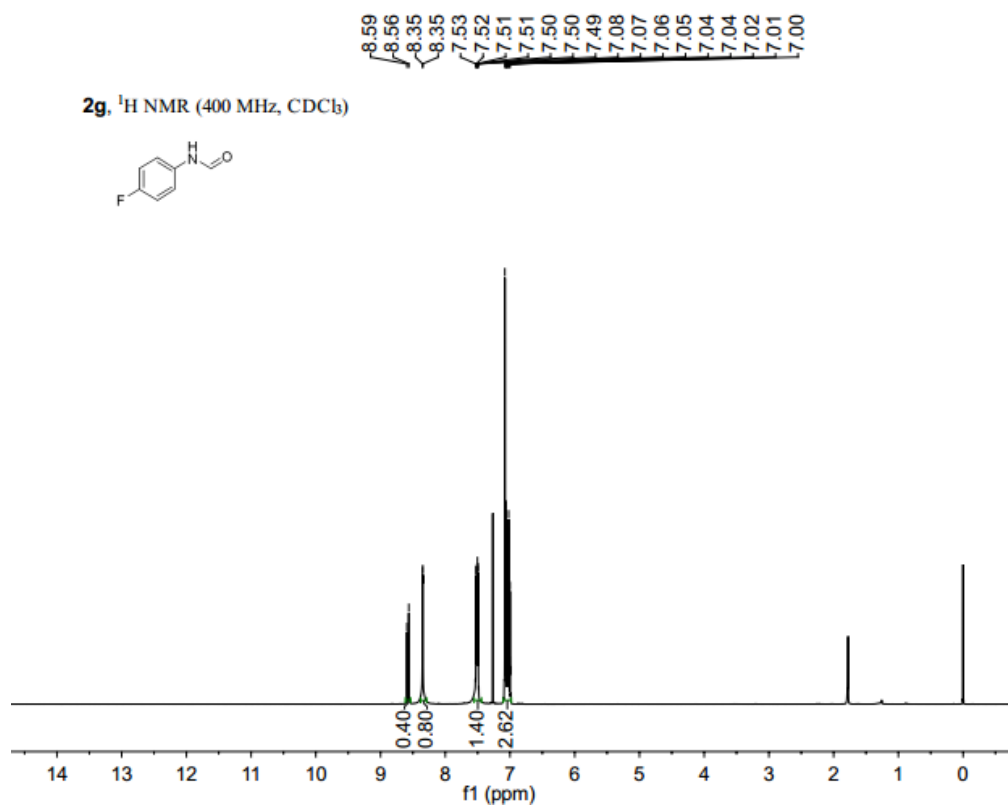
^1H NMR for *N*-(4-methoxybenzyl)formamide, **2f**



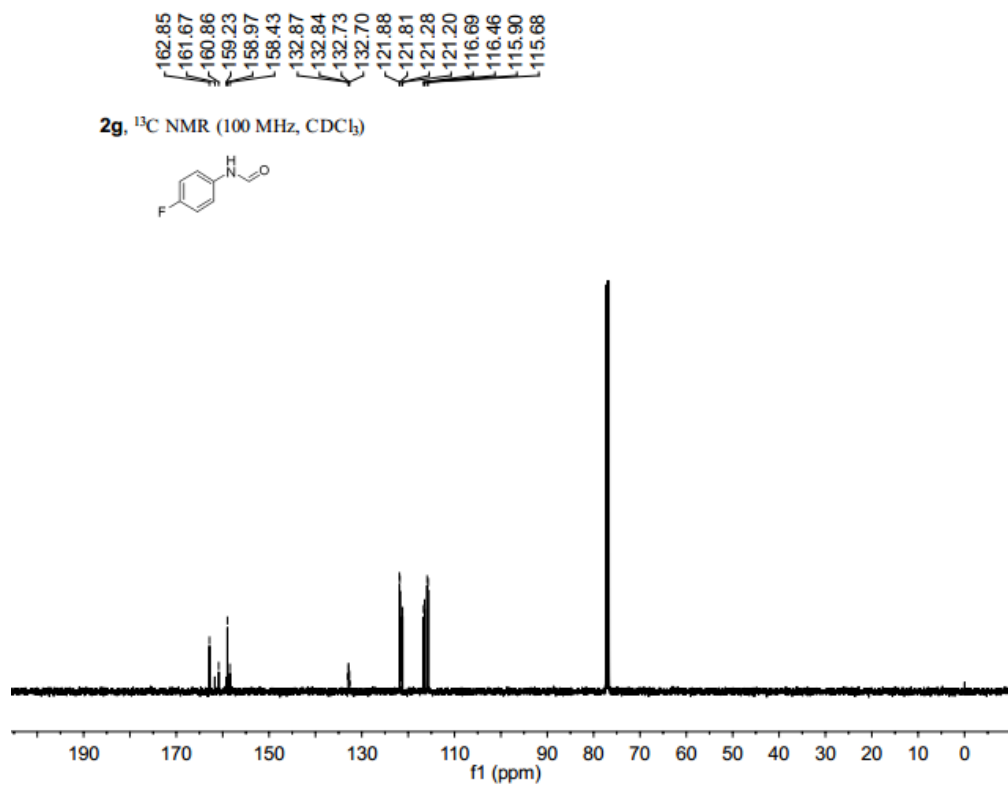
^{13}C NMR for *N*-(4-methoxybenzyl)formamide, **2f**



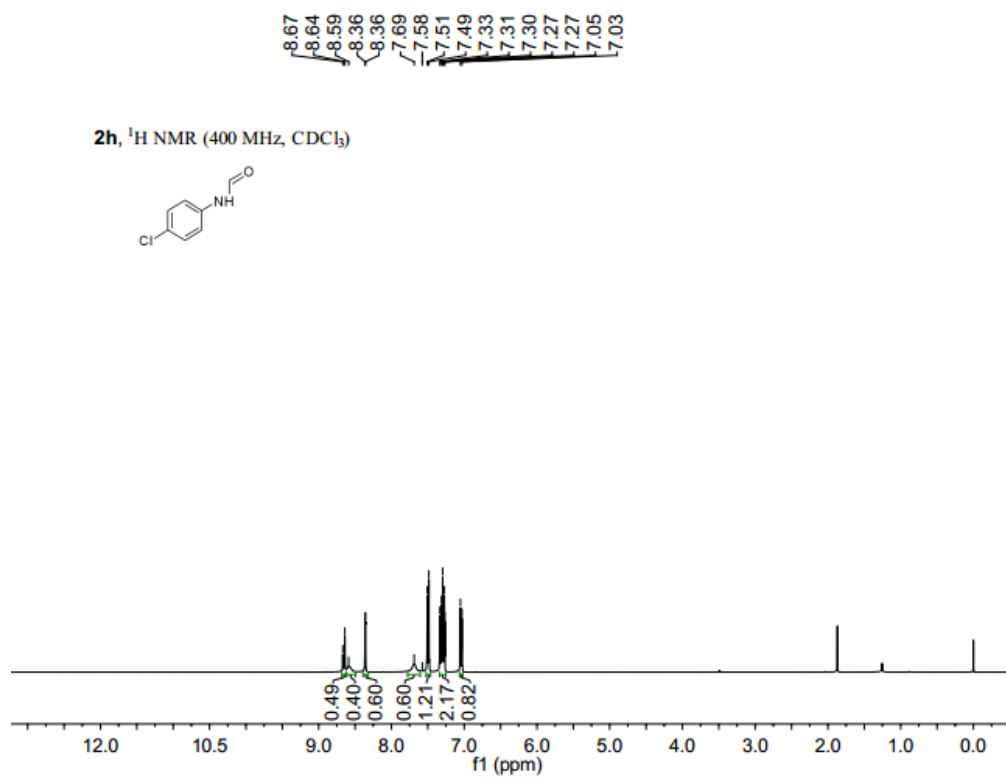
¹H NMR for *N*-(4-fluorophenyl)formamide, **2g**



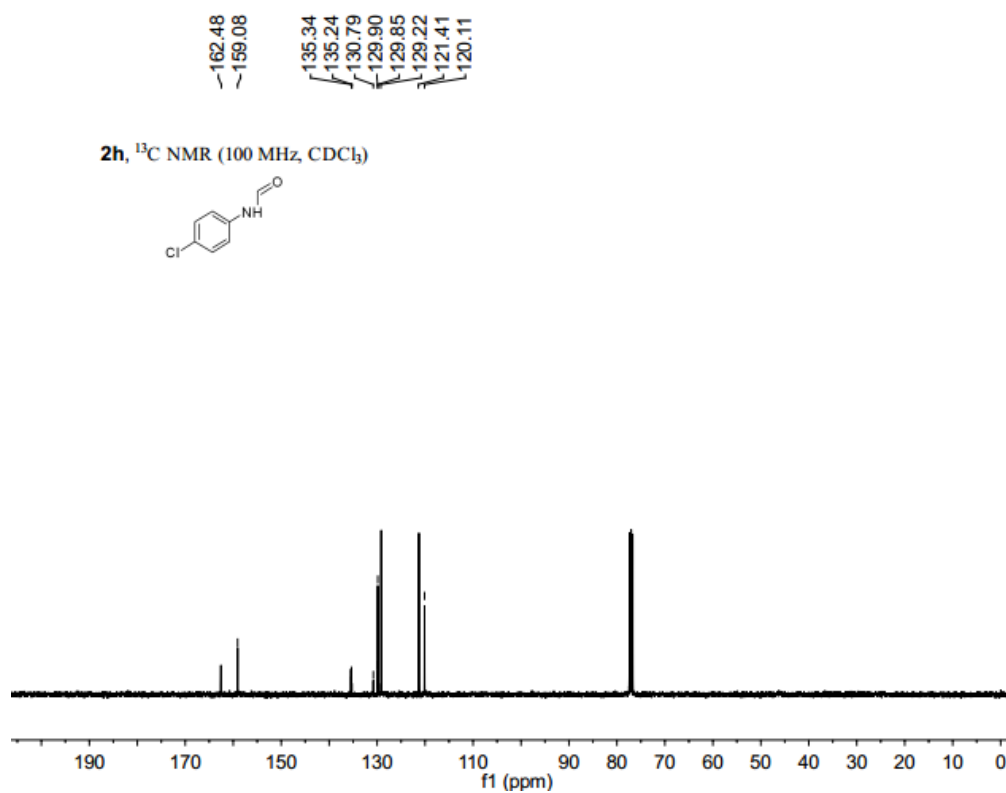
¹³C NMR for *N*-(4-fluorophenyl)formamide, **2g**



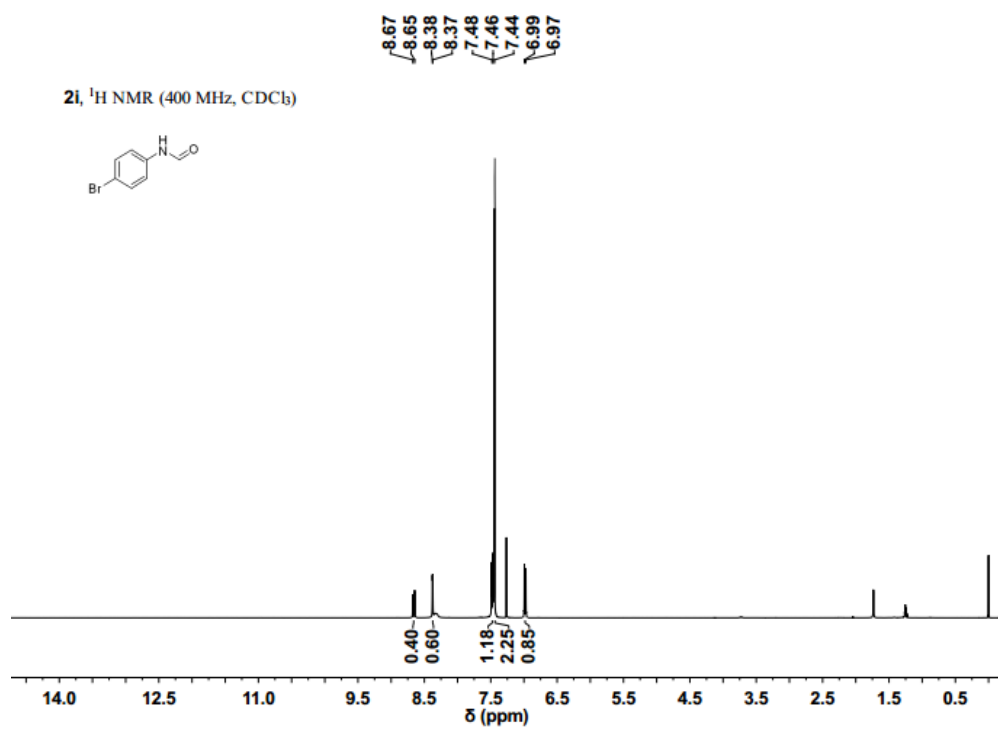
¹H NMR for *N*-(4-chlorophenyl)formamide, **2h**



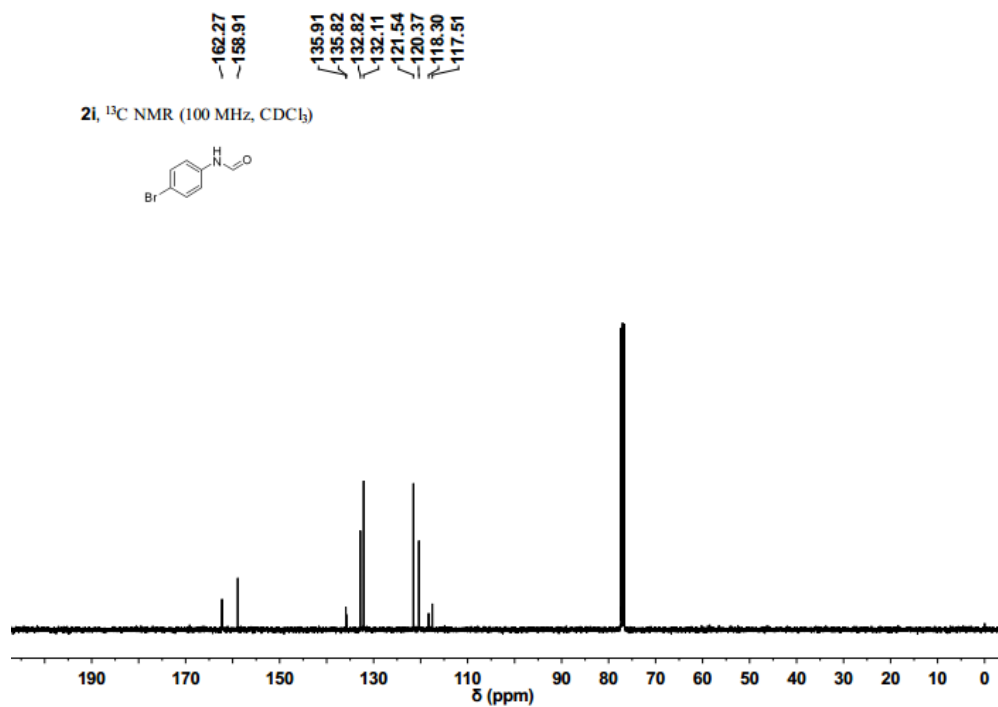
¹³C NMR for *N*-(4-chlorophenyl)formamide, **2h**



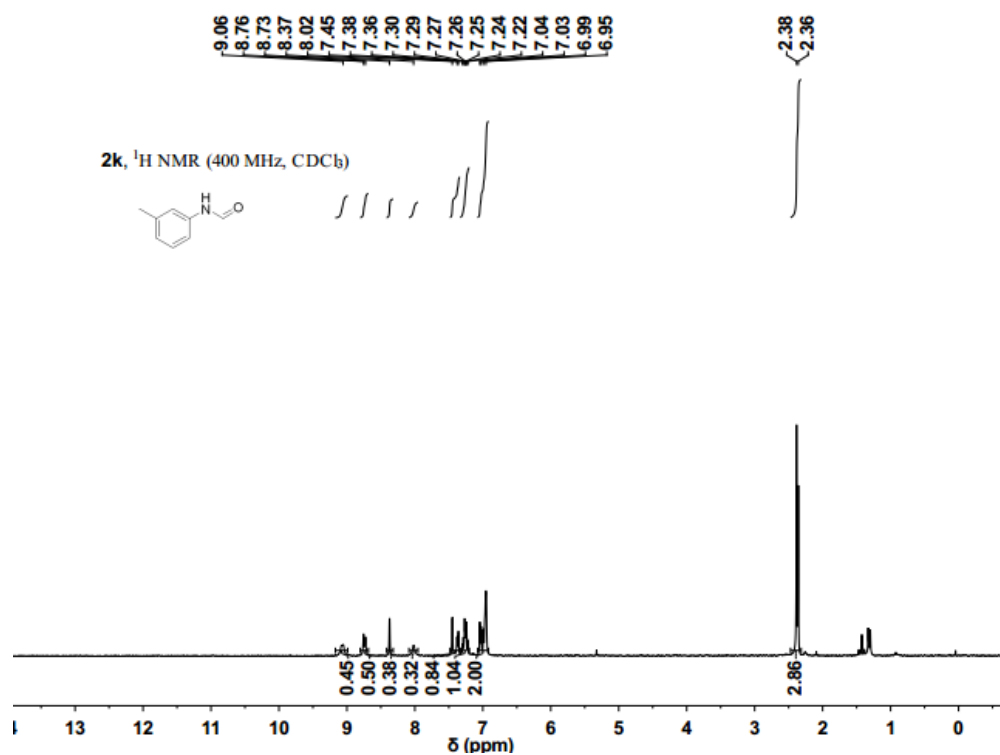
^1H NMR for *N*-(4-bromophenyl)formamide, **2i**



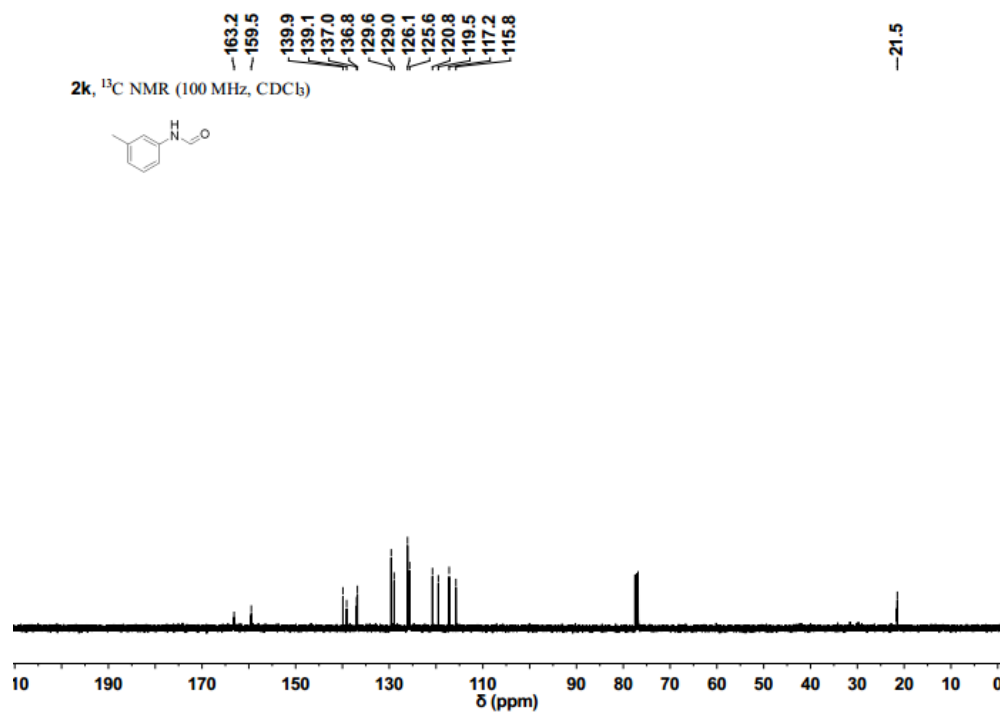
^{13}C NMR for *N*-(4-bromophenyl)formamide, **2i**



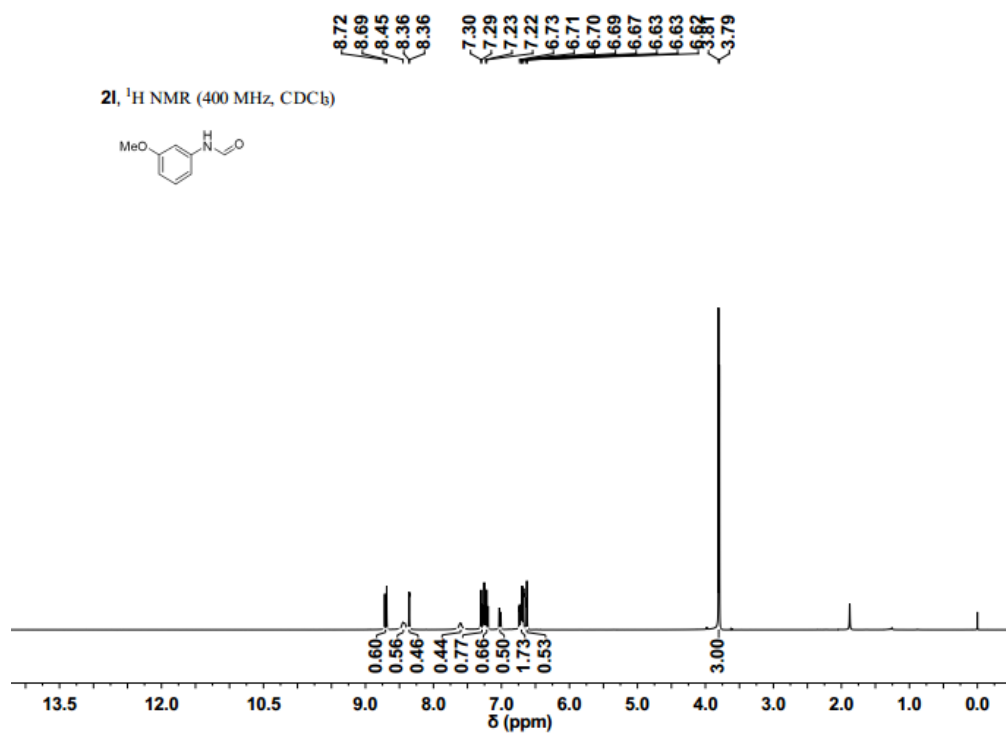
^1H NMR for *N*-m-tolylformamide, **2k**



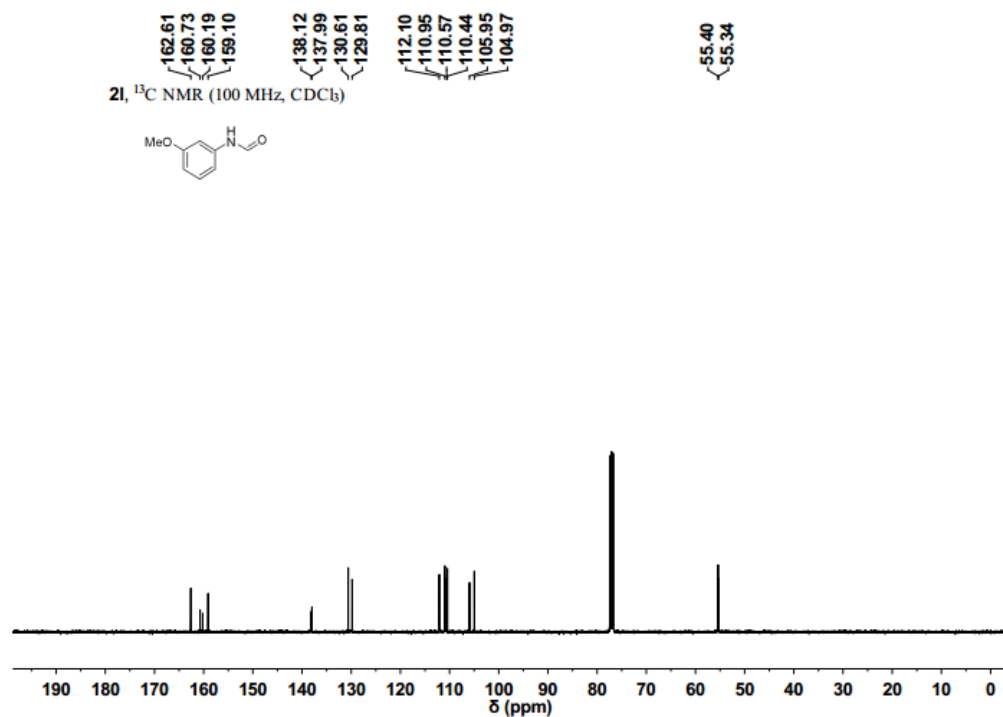
^{13}C NMR for *N*-m-tolylformamide, **2k**



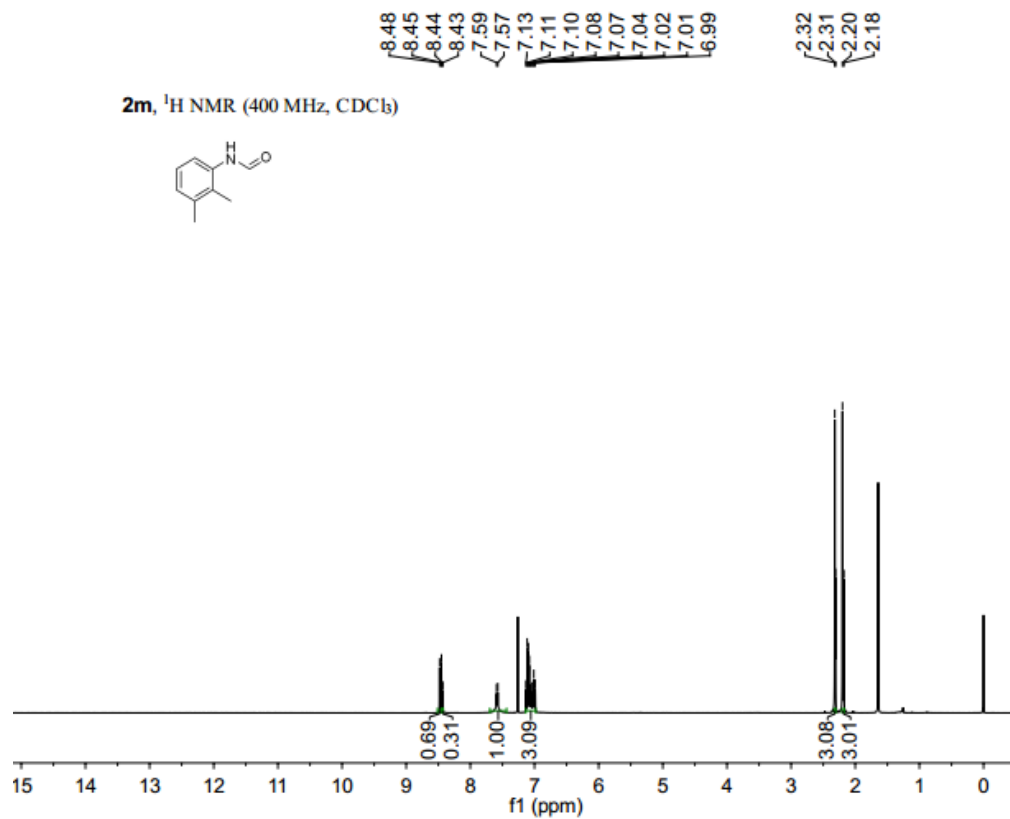
^1H NMR for *N*-(2,3-dimethylphenyl)formamide, **21**



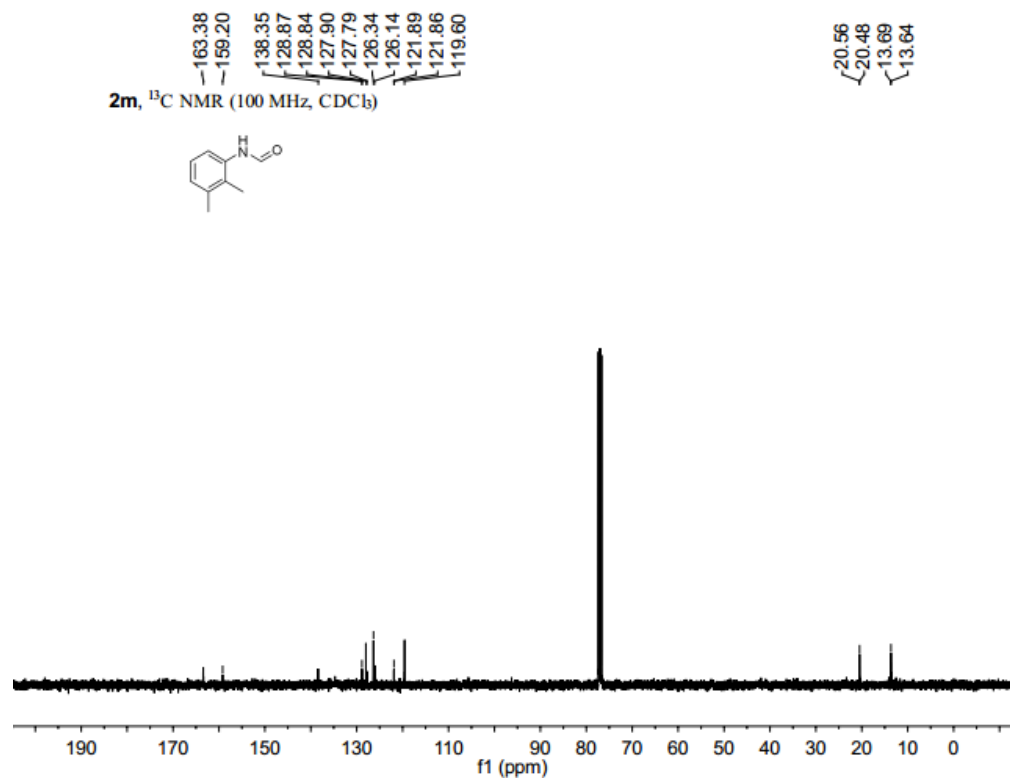
^{13}C NMR for *N*-(4-chlorophenyl)formamide, **21**



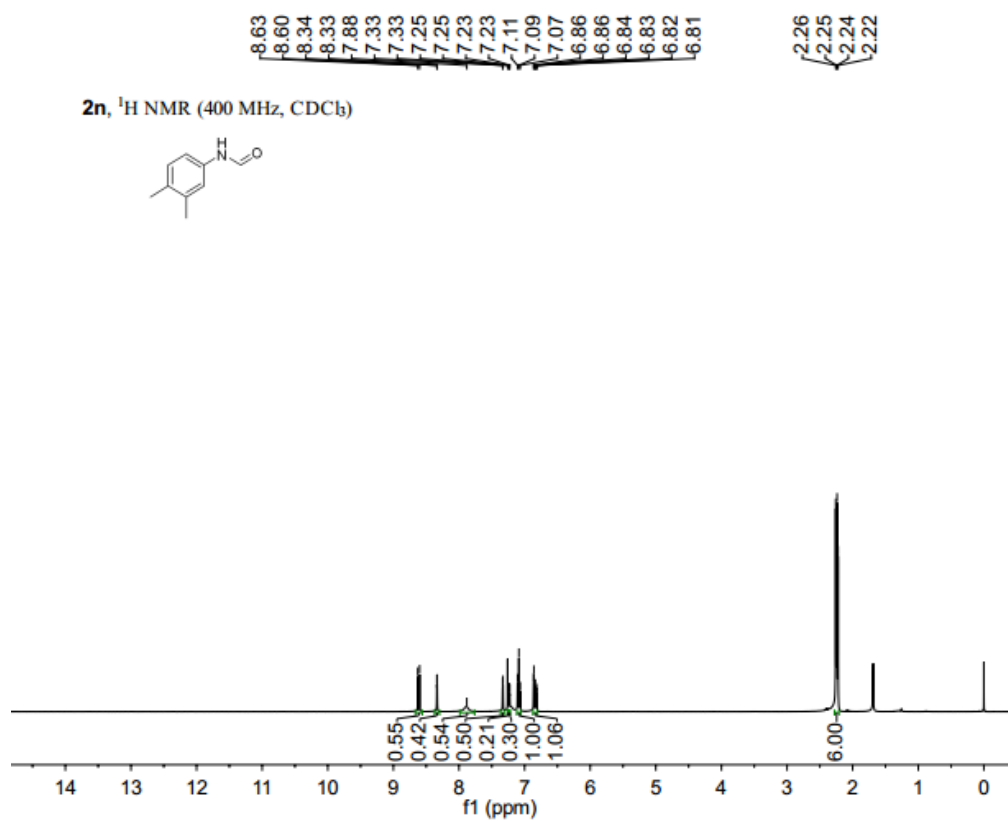
^1H NMR for *N*-(2,3-dimethylphenyl)formamide, **2m**



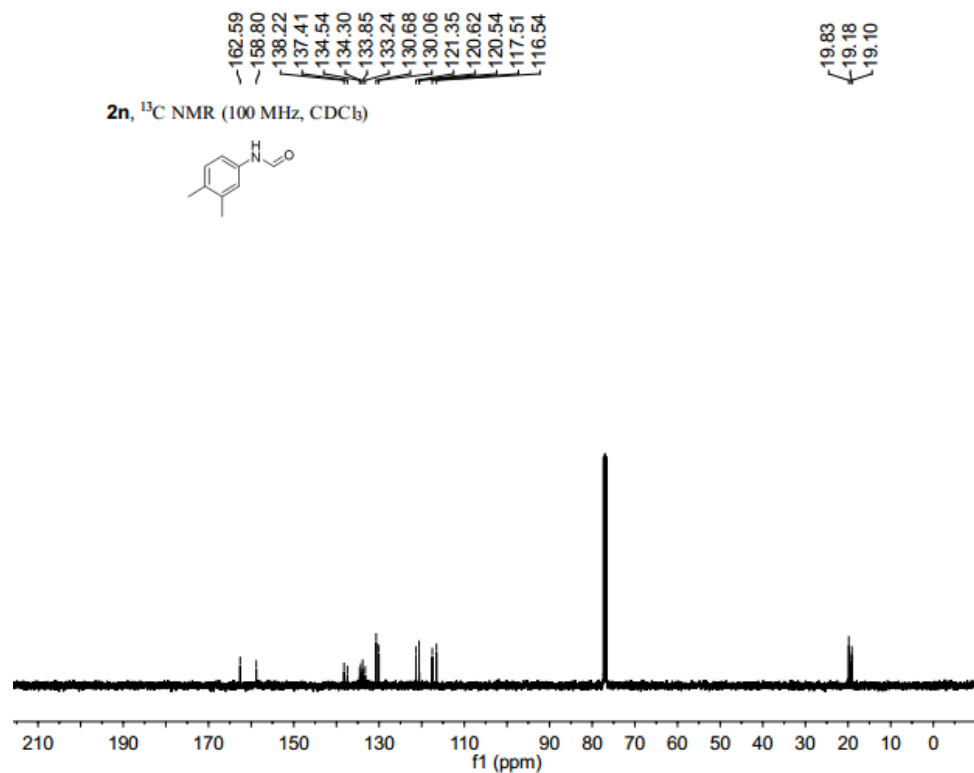
^{13}C NMR for *N*-(2,3-dimethylphenyl)formamide, **2m**



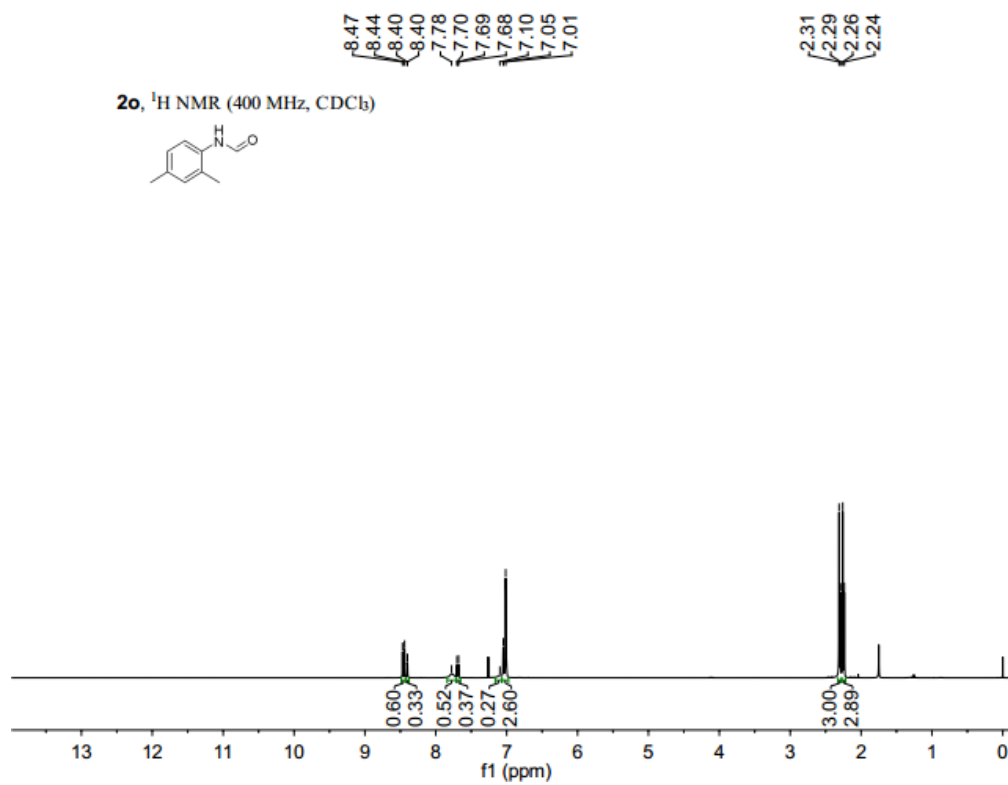
¹H NMR for *N*-(3,4-dimethylphenyl)formamide, **2n**



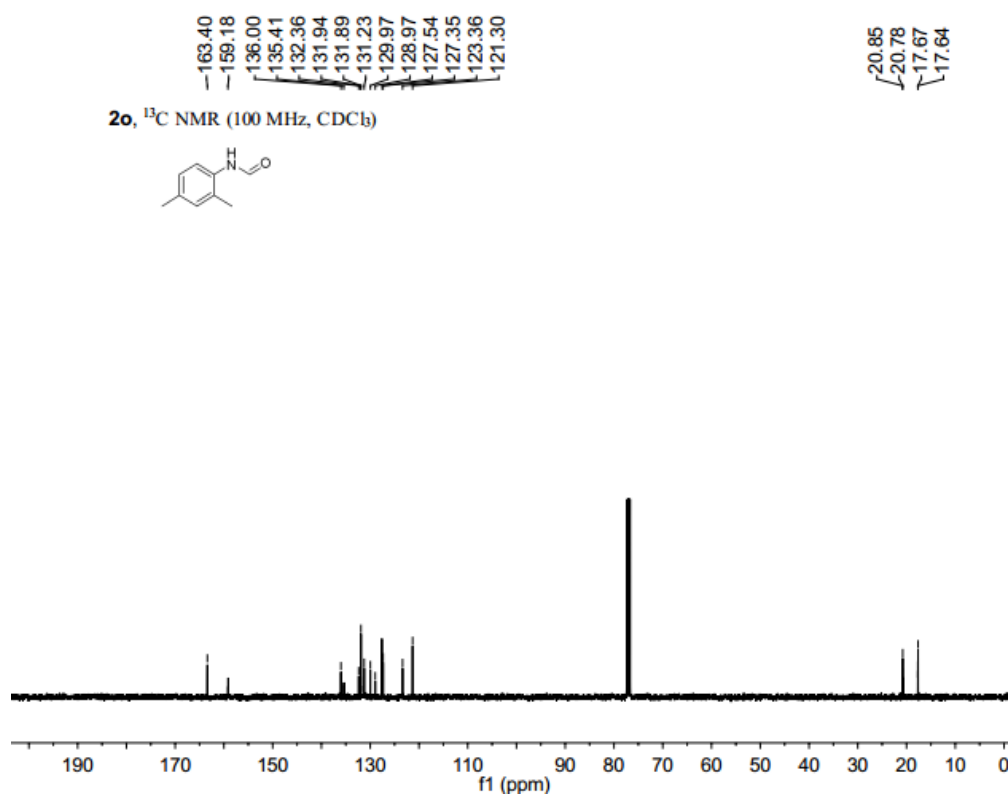
¹³C NMR for *N*-(3,4-dimethylphenyl)formamide, **2n**



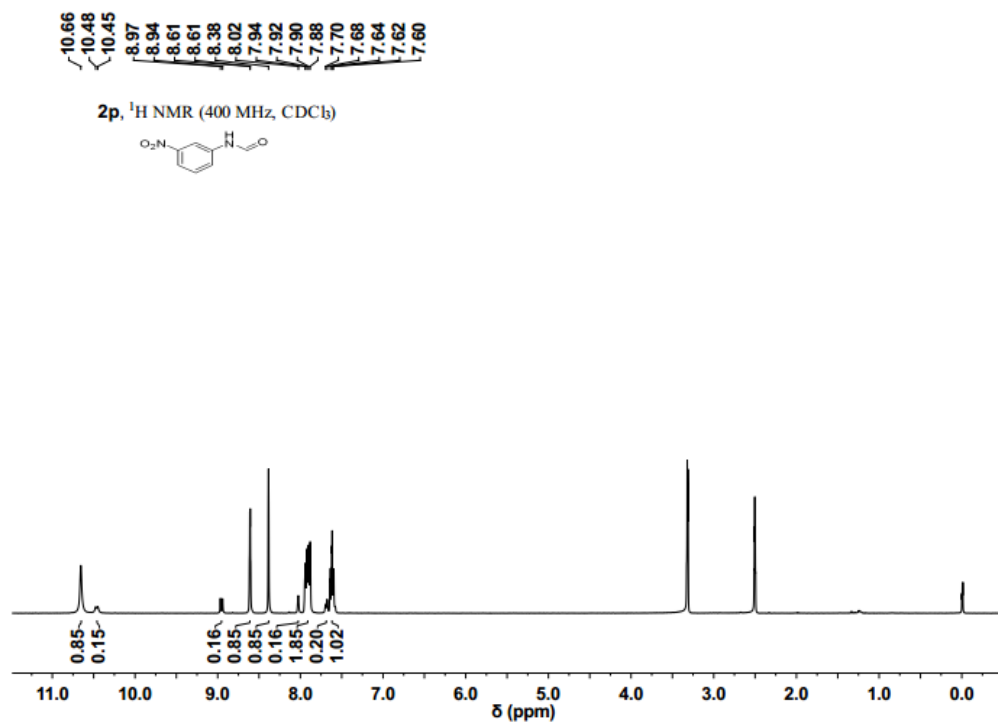
¹H NMR for *N*-(2,4-dimethylphenyl)formamide, **2o**



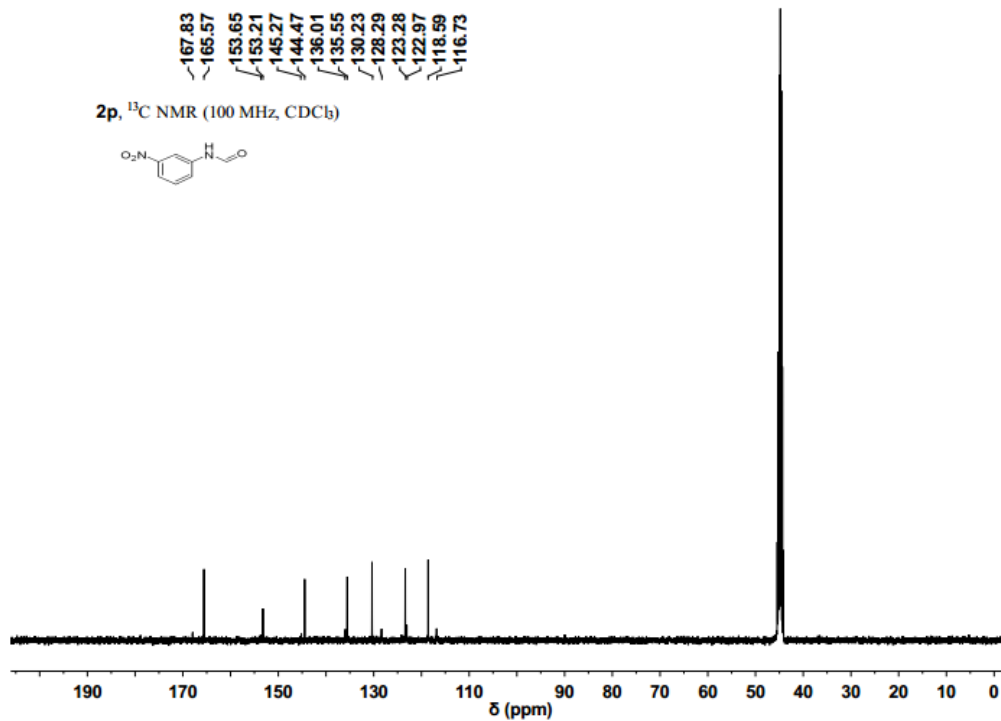
¹³C NMR for *N*-(2,4-dimethylphenyl)formamide, **2o**



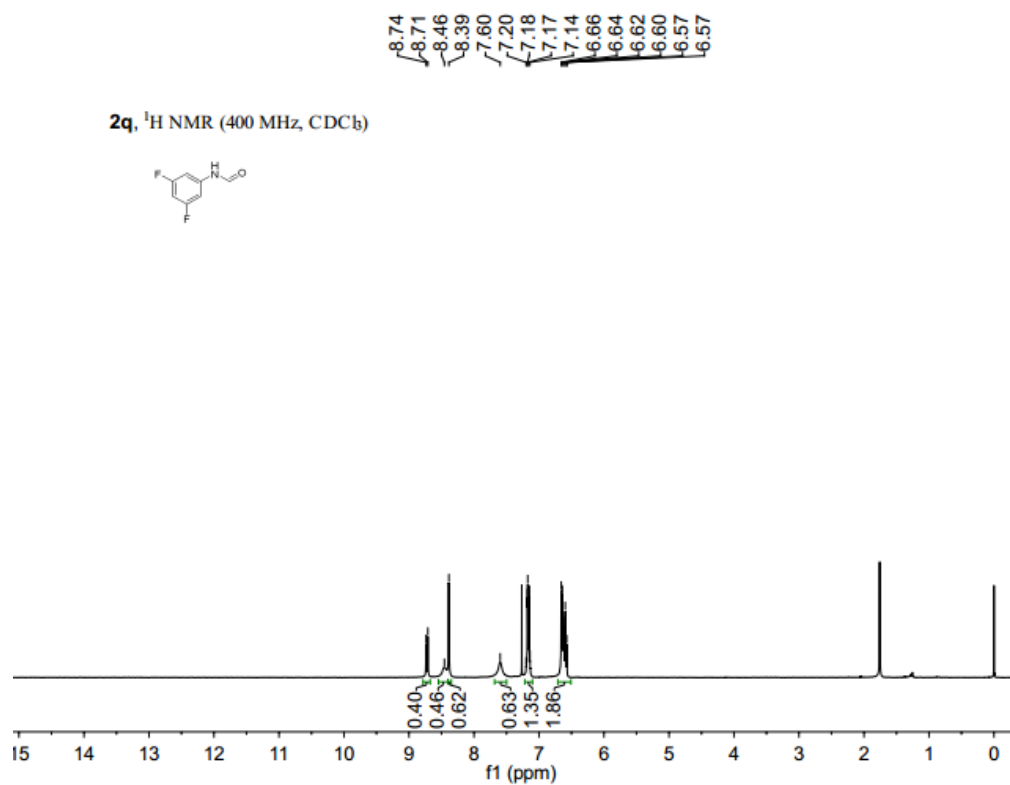
^1H NMR for *N*-(3-nitrophenyl)formamide, **2p**



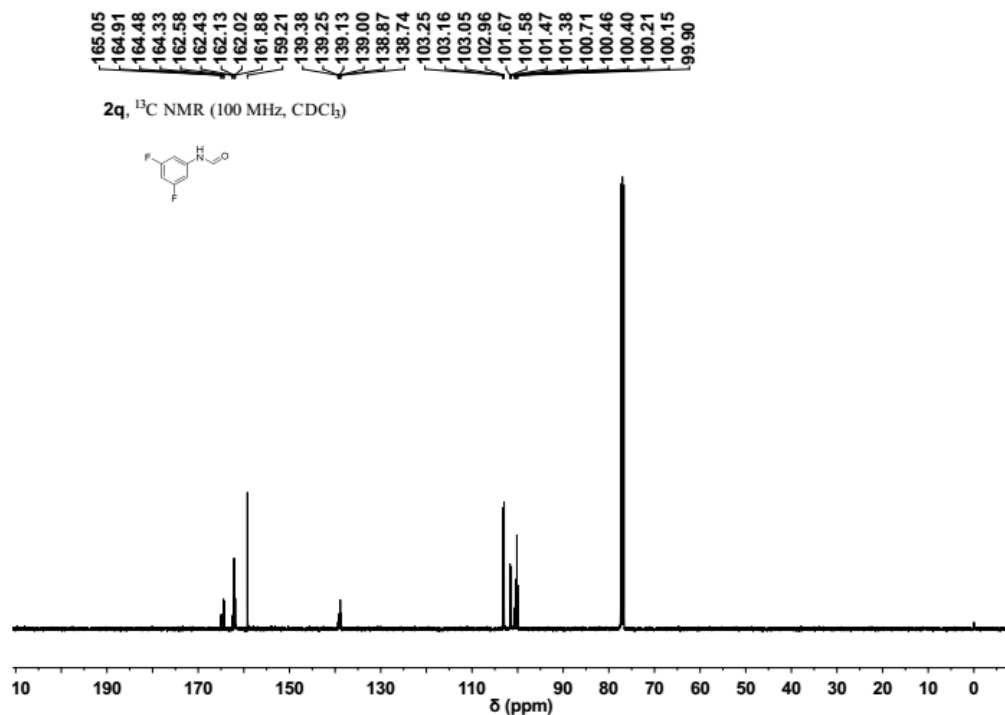
^{13}C NMR for *N*-(3-nitrophenyl)formamide, **2p**



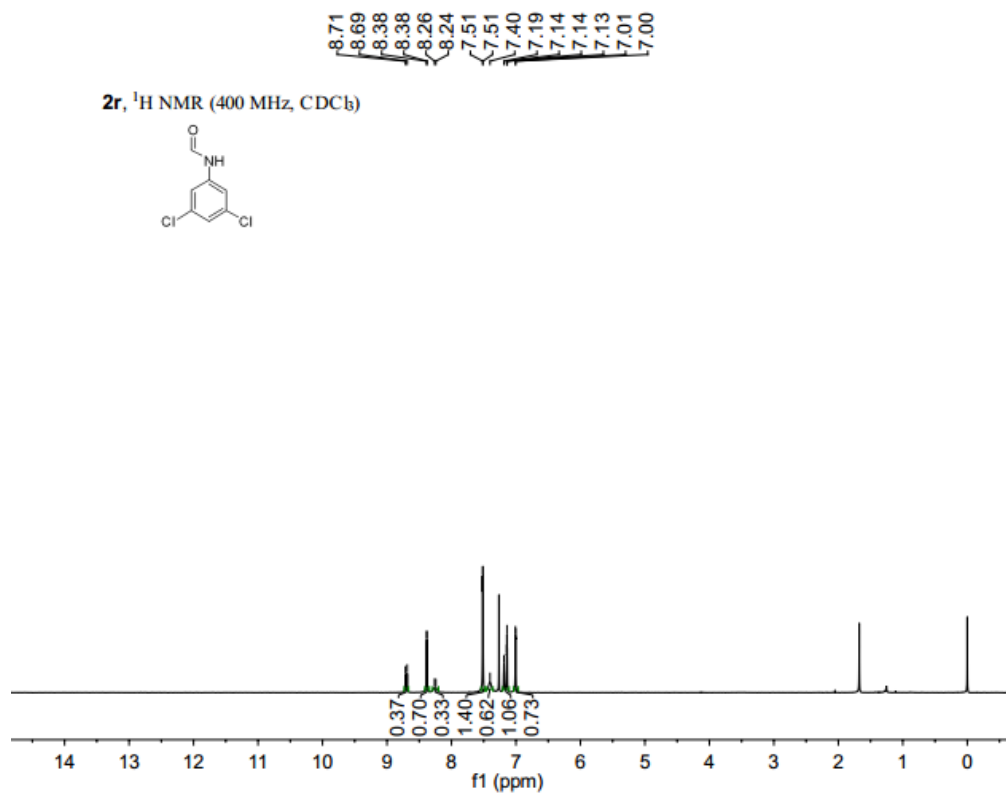
^1H NMR for *N*-(3,5-difluorophenyl)formamide, **2q**



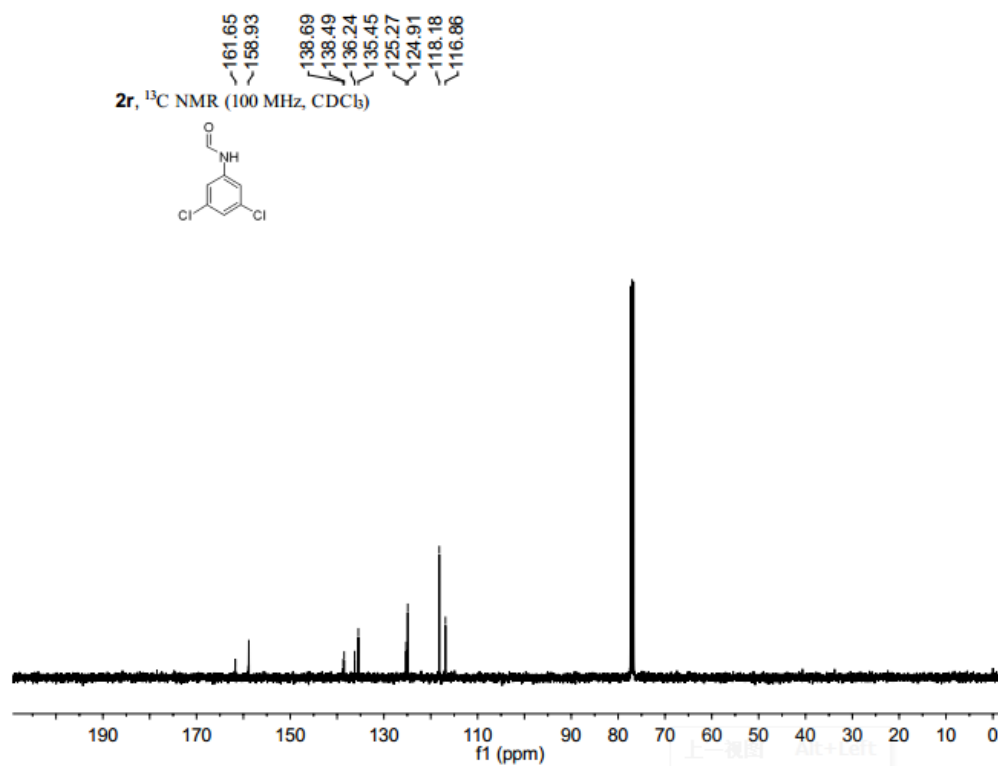
^{13}C NMR for *N*-(3,5-difluorophenyl)formamide, **2q**



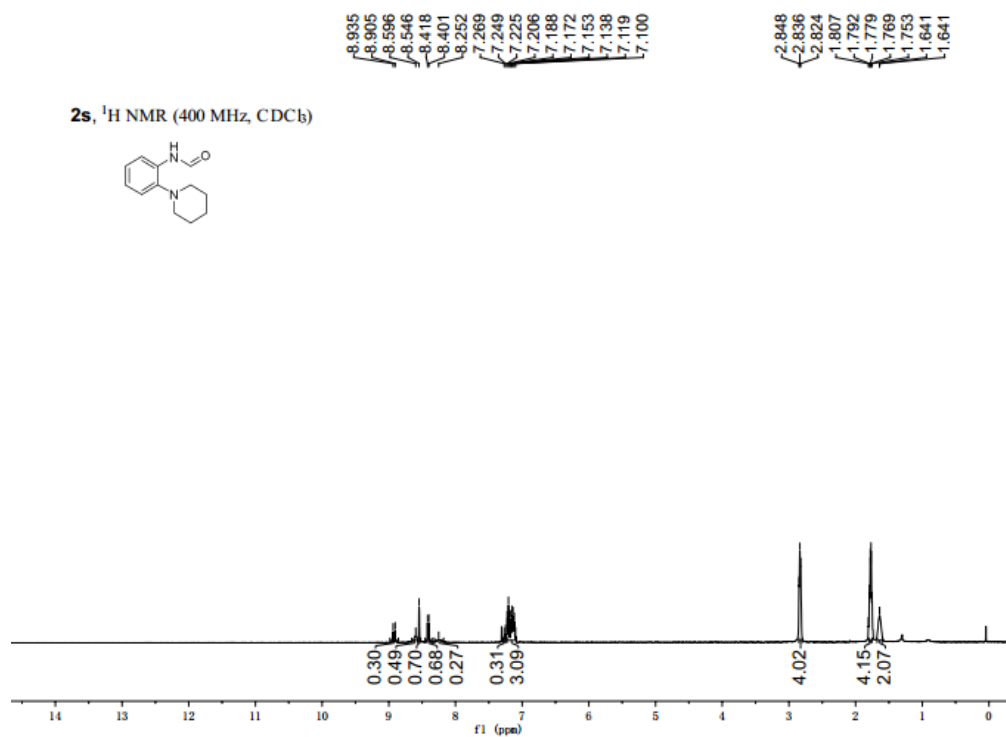
^1H NMR for *N*-(3,5-dichlorophenyl)formamide, **2r**



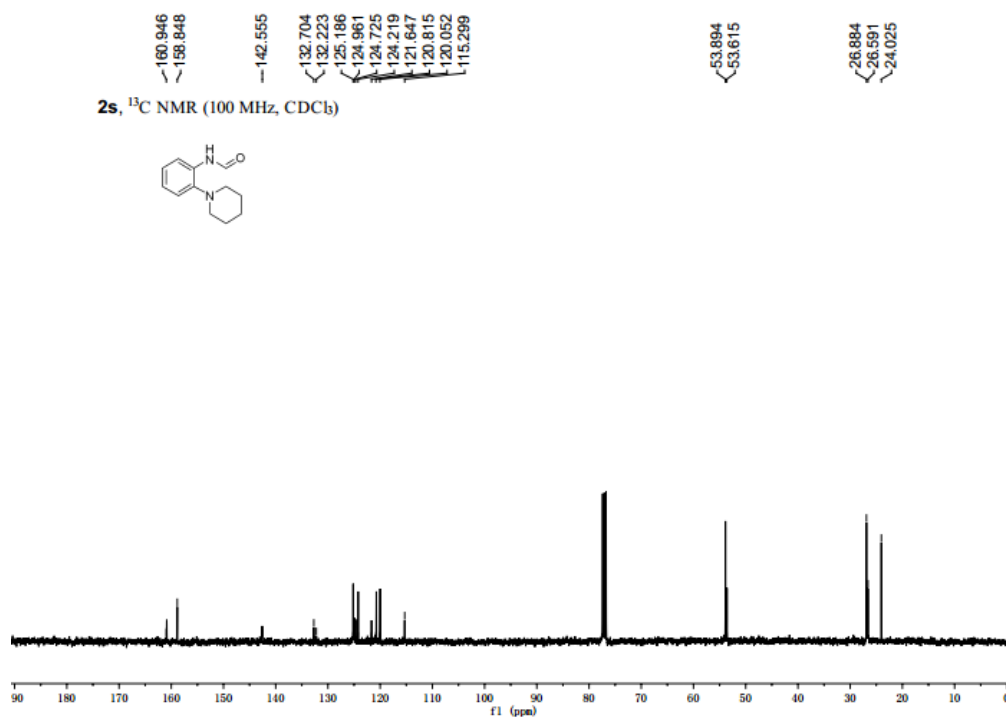
^{13}C NMR for *N*-(3,5-dichlorophenyl)formamide, **2r**



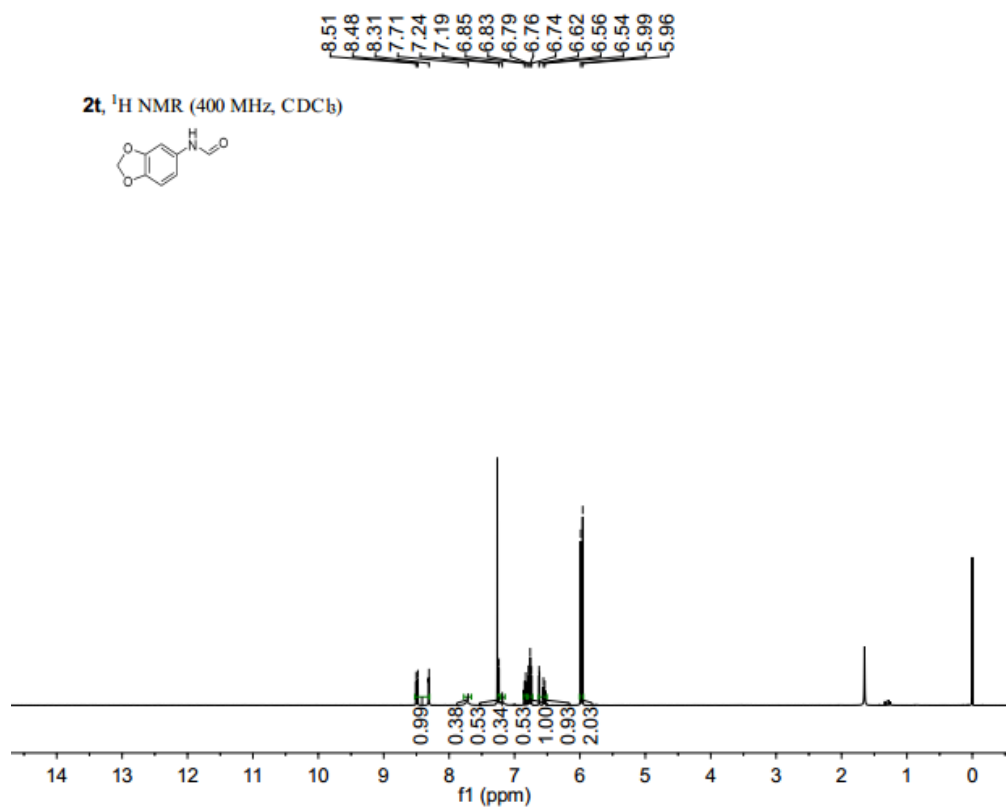
^1H NMR for *N*-(2-(piperidin-1-yl)phenyl)formamide, **2s**



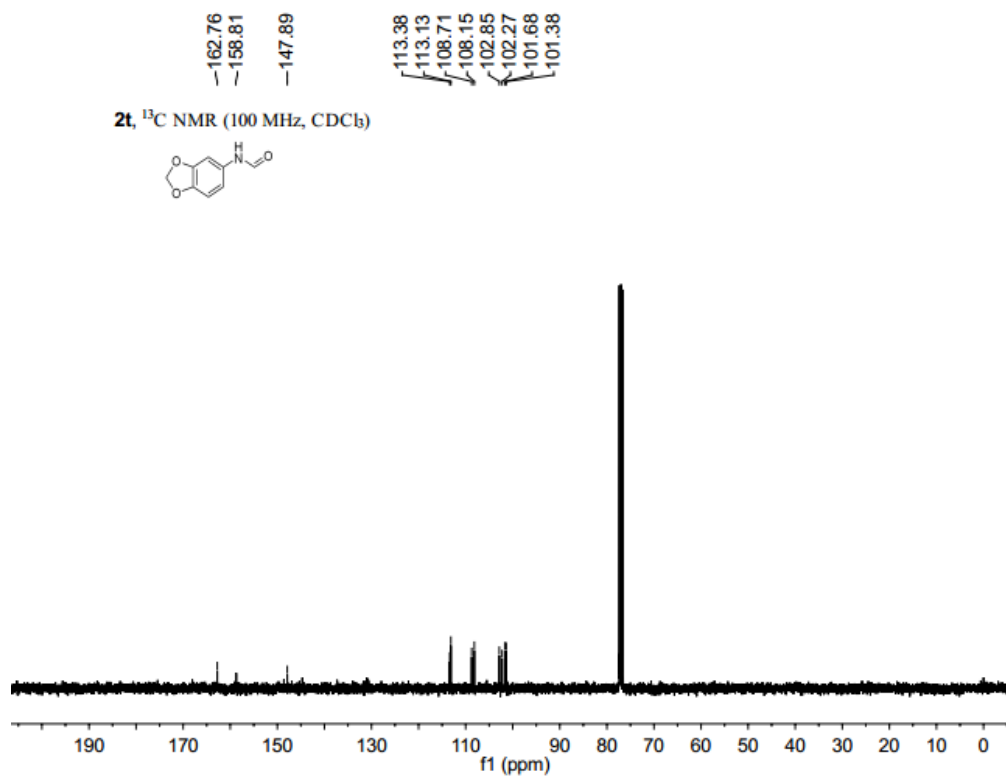
^{13}C NMR for *N*-(2-(piperidin-1-yl)phenyl)formamide, **2s**



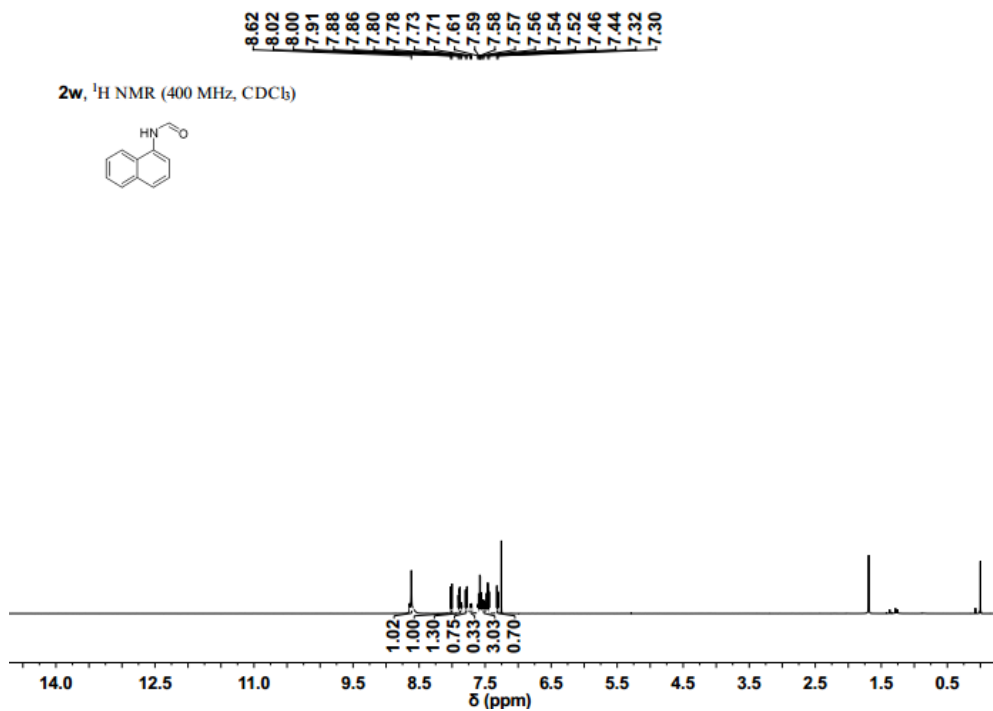
¹H NMR for *N*-(benzo[*d*][1,3]dioxol-5-yl)formamide, **2t**



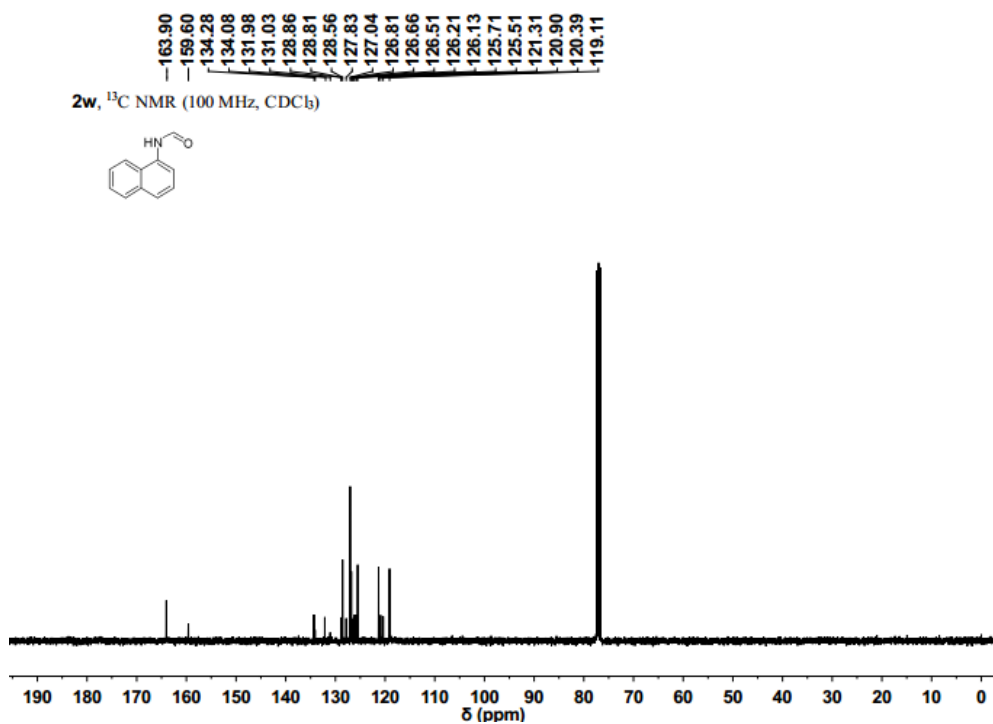
¹³C NMR for *N*-(benzo[*d*][1,3]dioxol-5-yl)formamide, **2t**



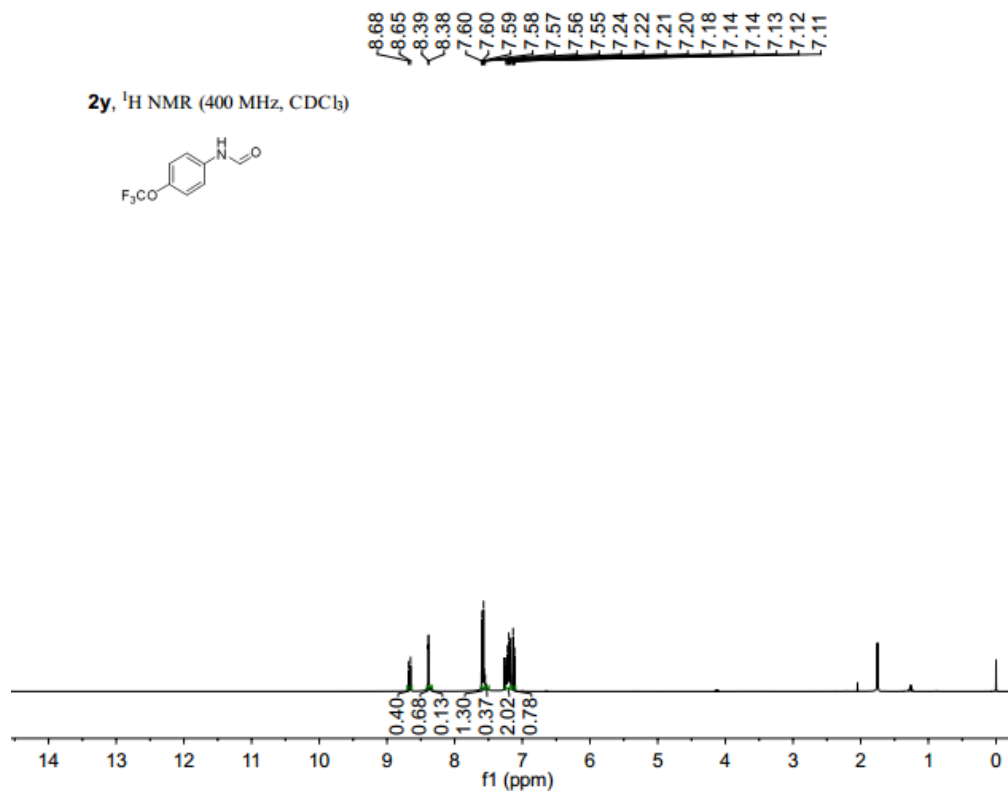
¹H NMR for *N*-(naphthalen-1-yl)formamide, **2w**



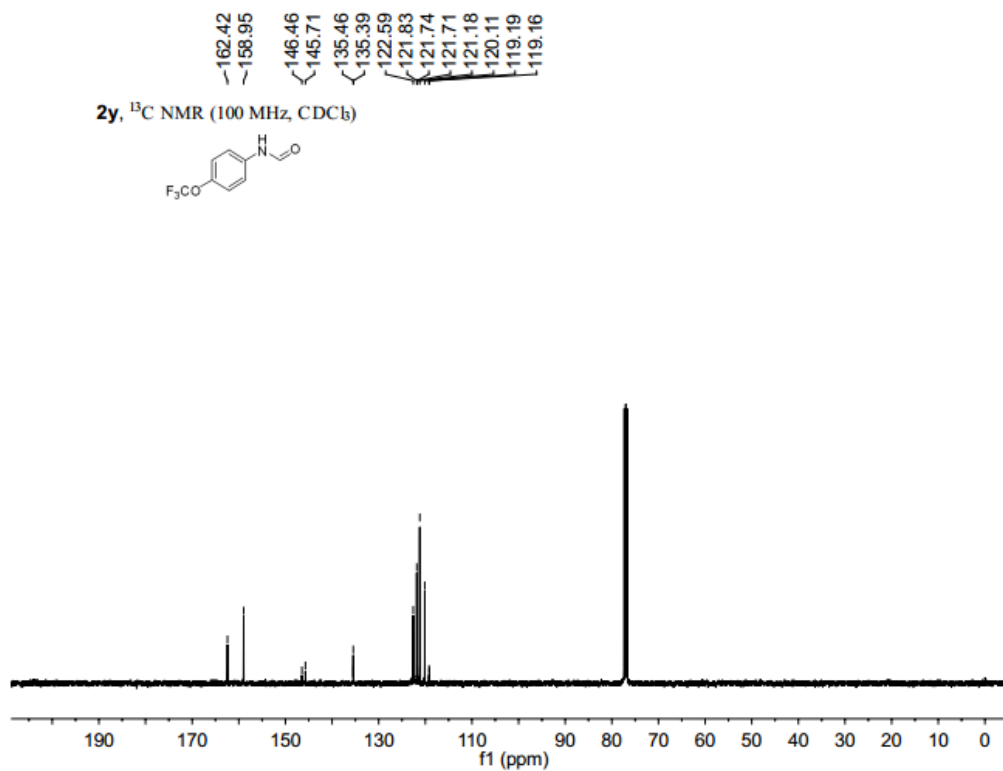
¹³C NMR for *N*-(naphthalen-1-yl)formamide, **2w**



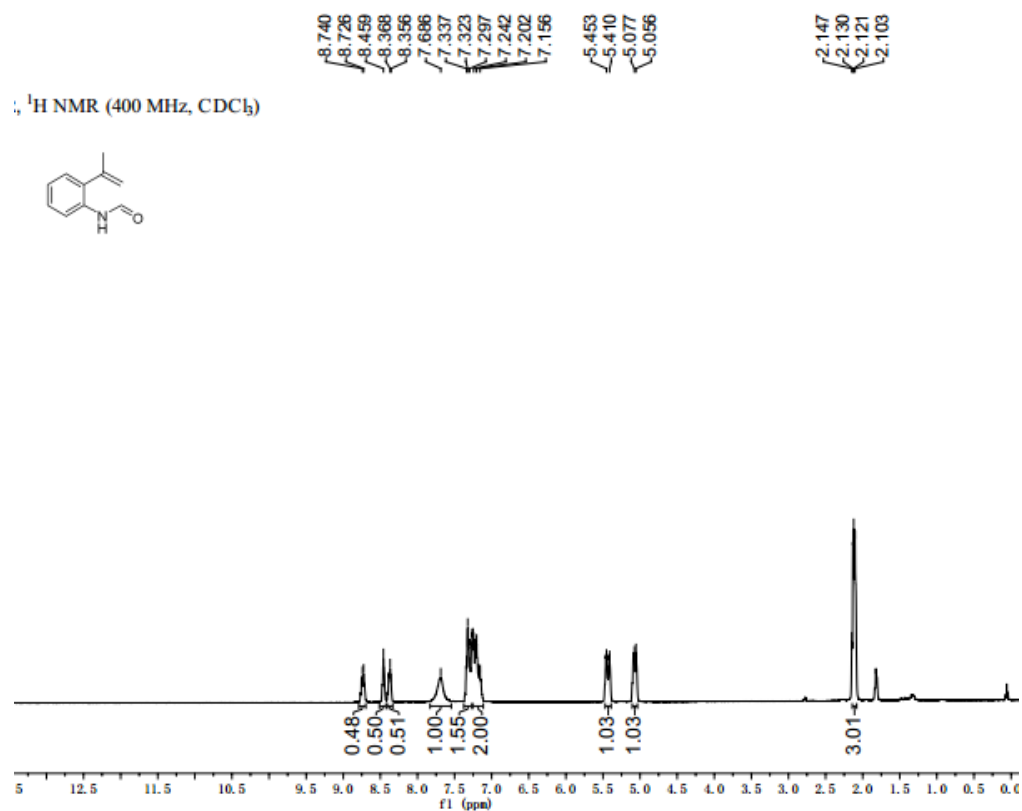
¹H NMR for *N*-(4-(trifluoromethoxy)phenyl)formamide, **2y**



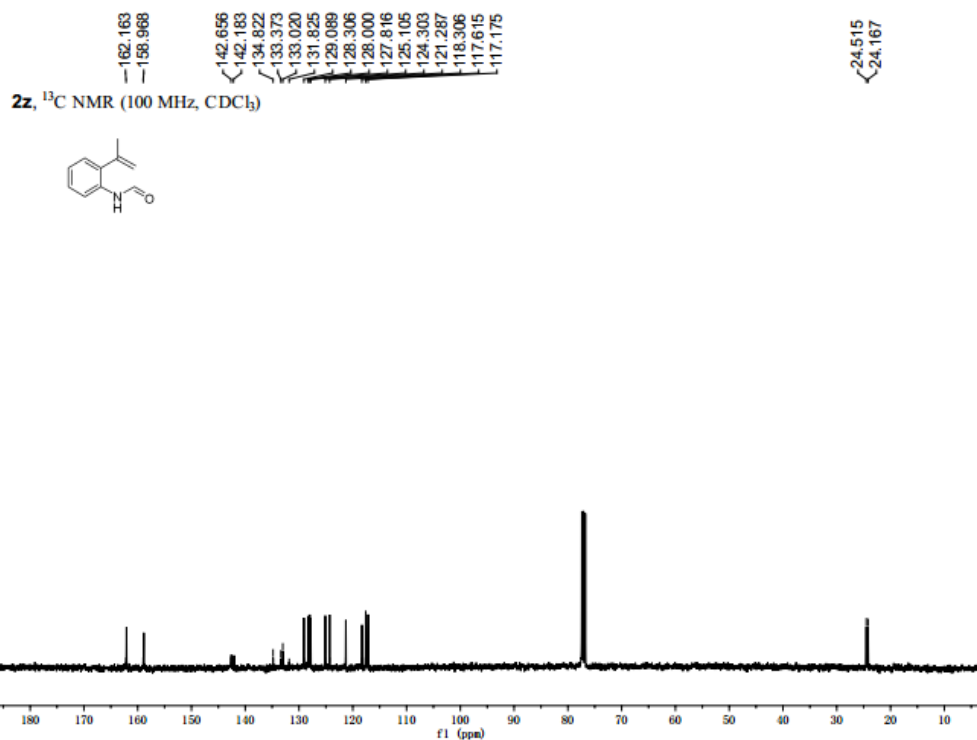
¹³C NMR for *N*-(4-(trifluoromethoxy)phenyl)formamide, **2y**



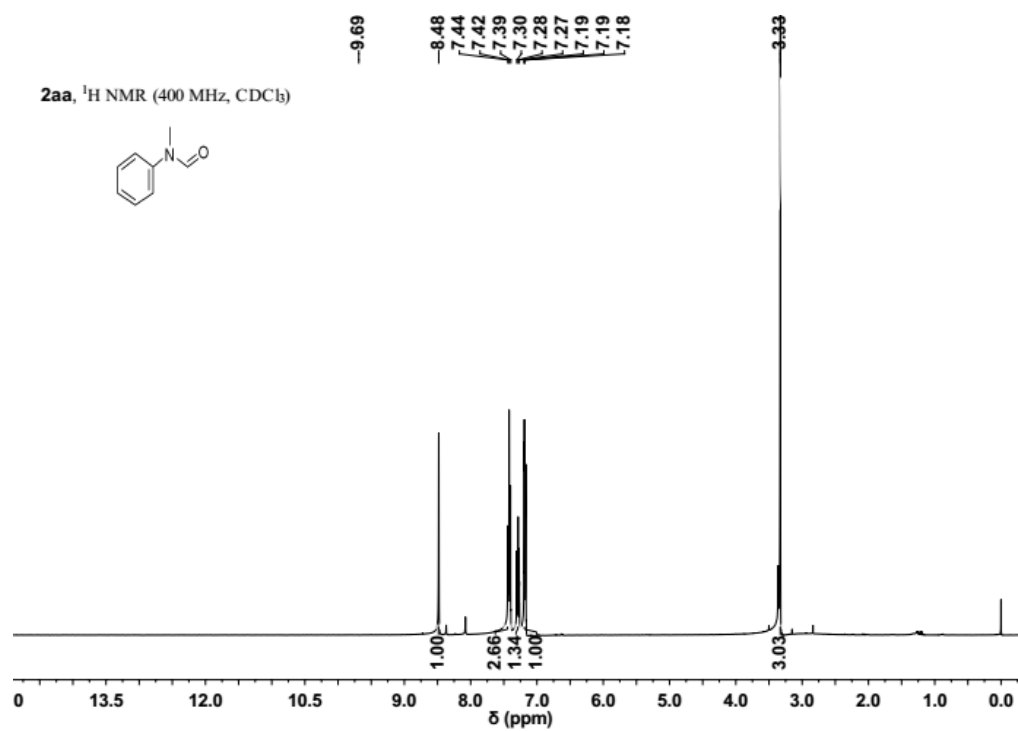
^1H NMR for *N*-(2-(prop-1-en-2-yl)phenyl)formamide, **2z**



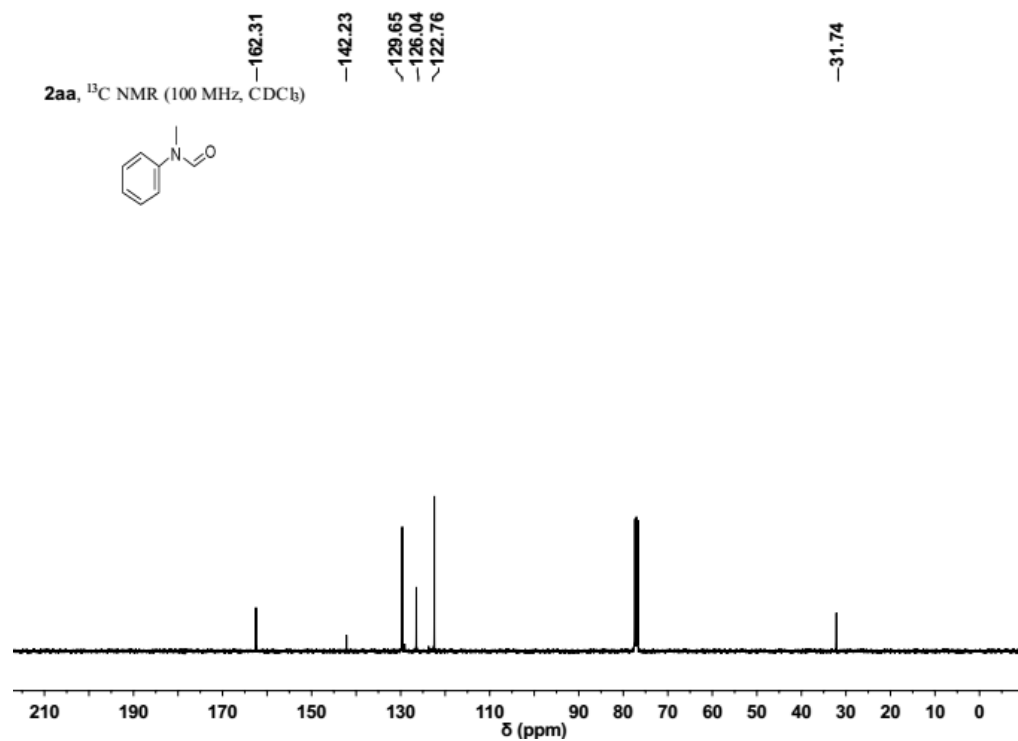
^{13}C NMR for *N*-(2-(prop-1-en-2-yl)phenyl)formamide, **2z**



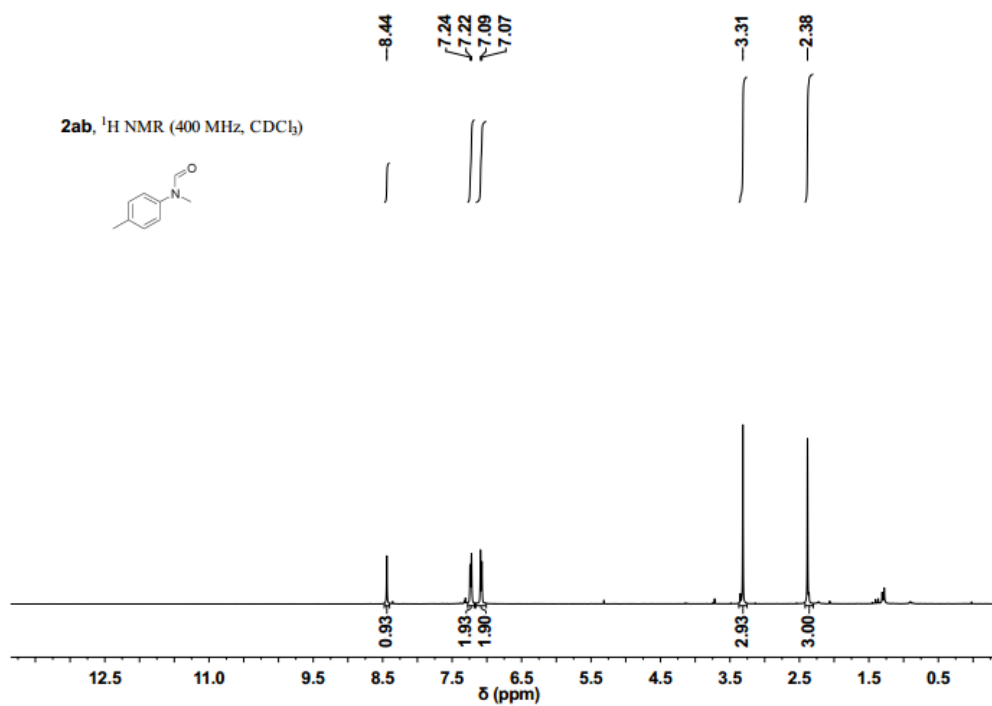
¹H NMR for *N*-methyl-*N*-phenylformamide, **2aa**



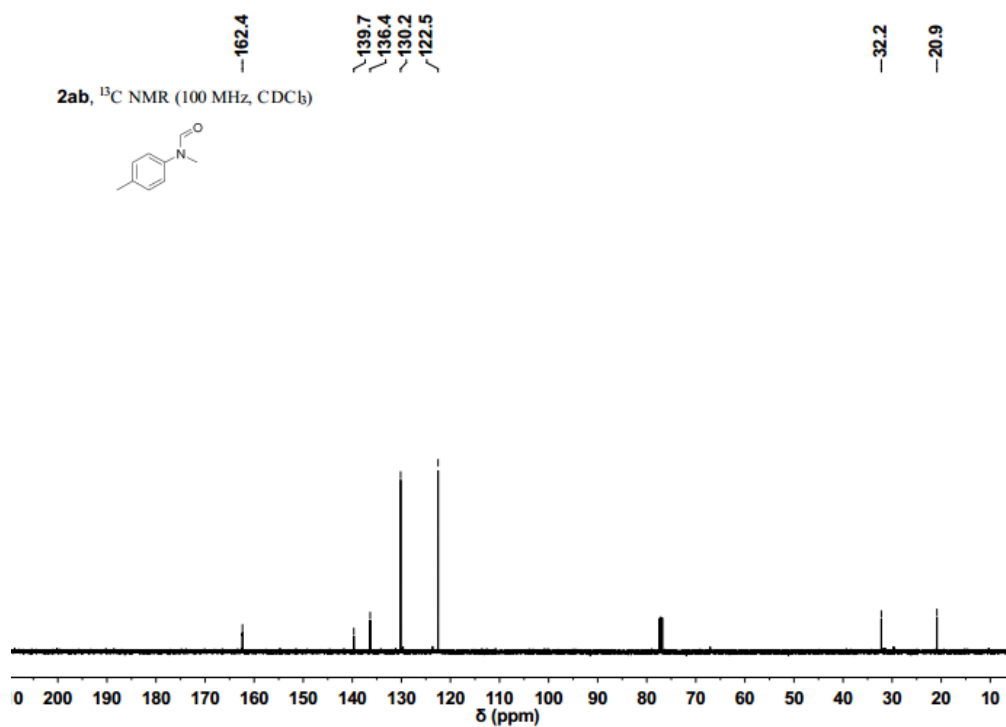
¹³C NMR for *N*-methyl-*N*-phenylformamide, **2aa**



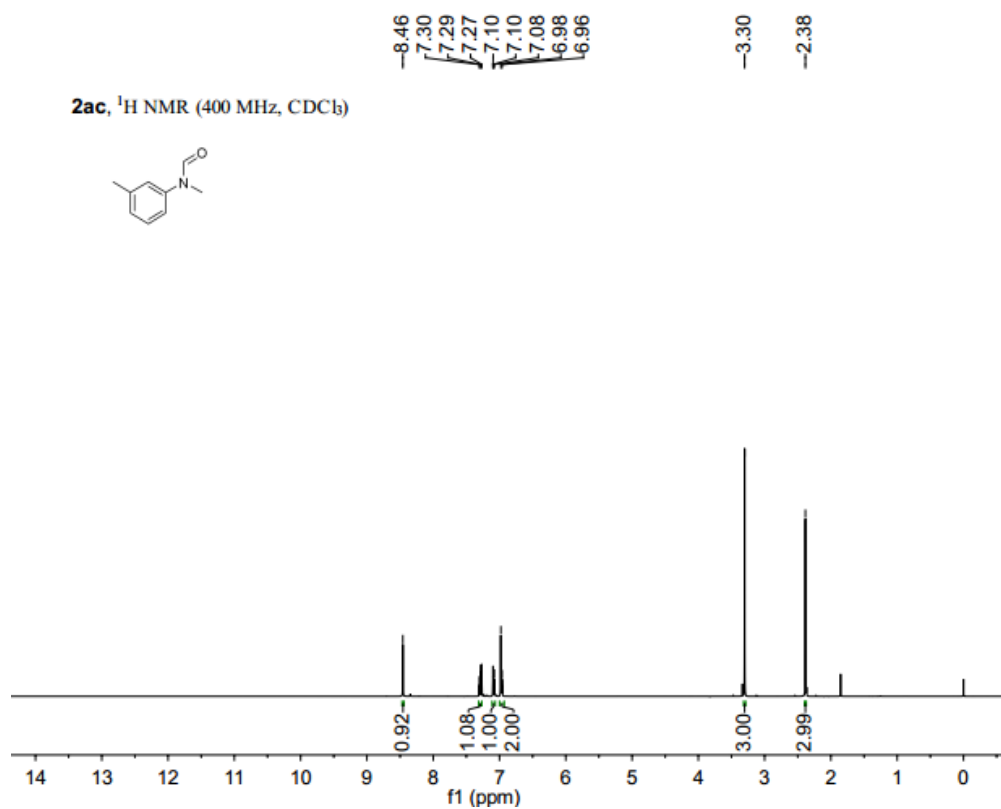
^1H NMR for *N*-methyl-*N*-(*p*-tolyl)formamide, **2ab**



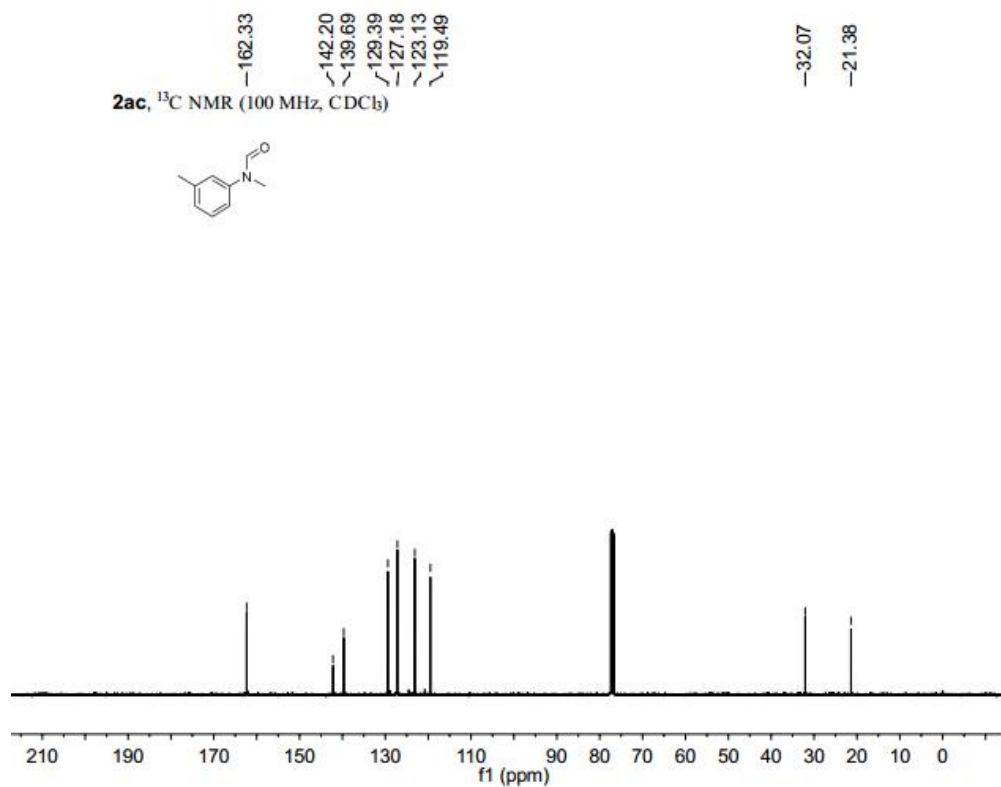
^{13}C NMR for *N*-methyl-*N*-(*p*-tolyl)formamide, **2ab**



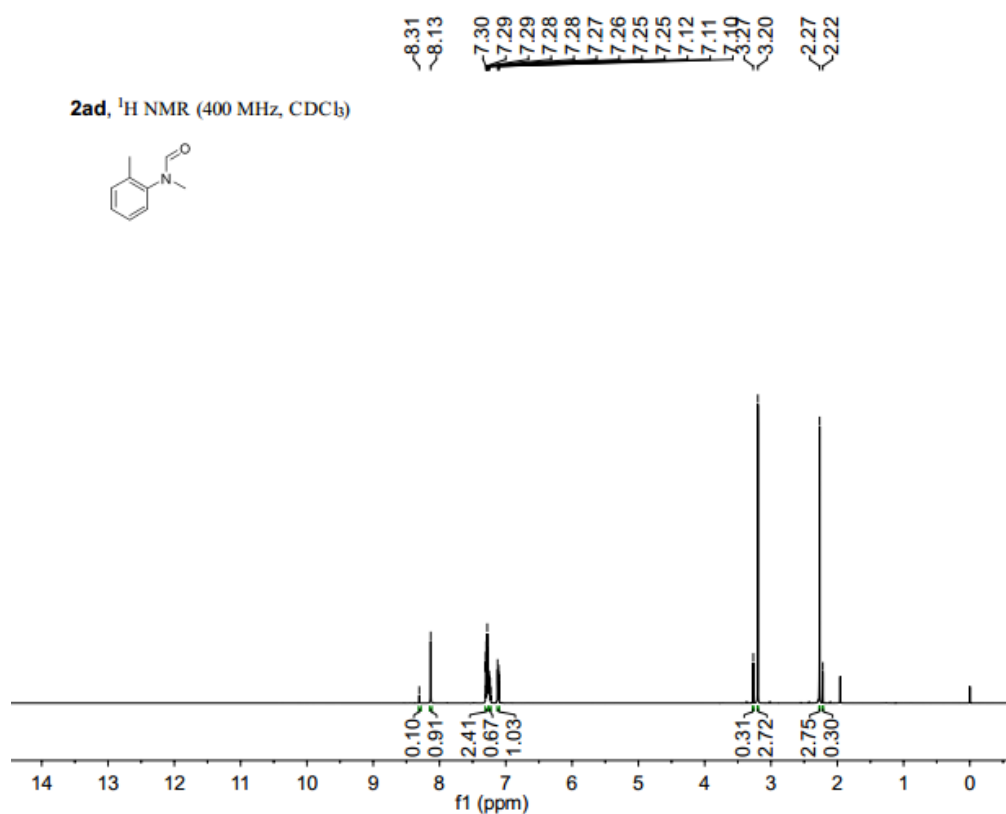
¹H NMR for *N*-methyl-*N*-(*m*-tolyl)formamide, **2ac**



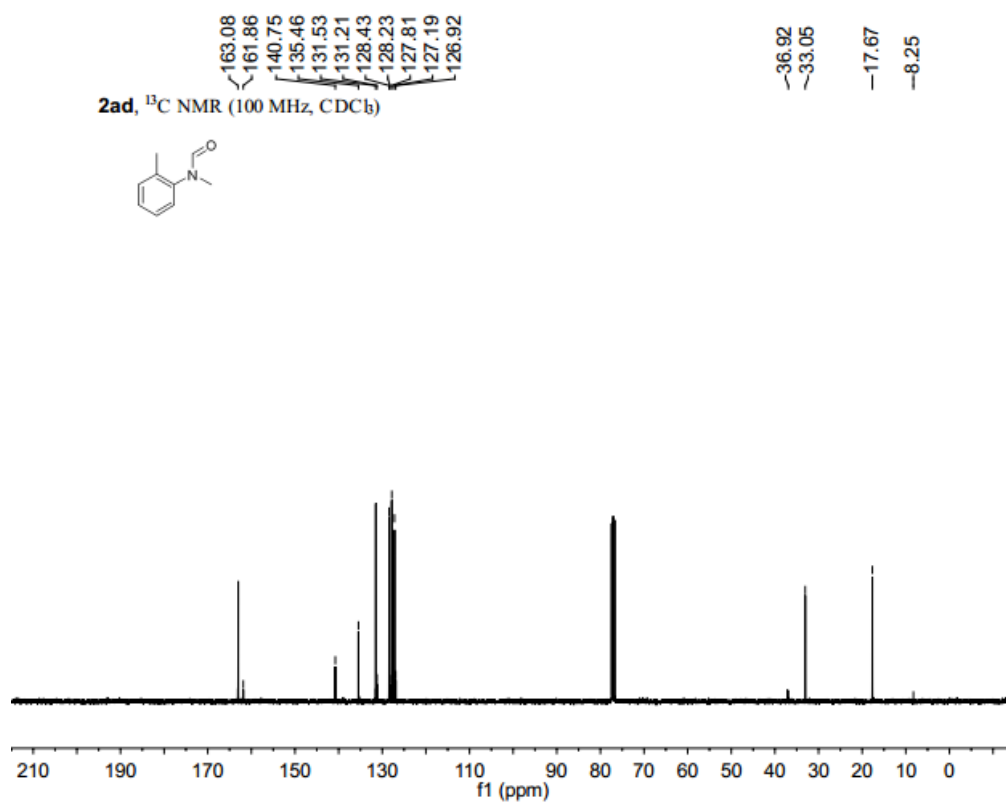
¹³C NMR for *N*-methyl-*N*-(*m*-tolyl)formamide, **2ac**



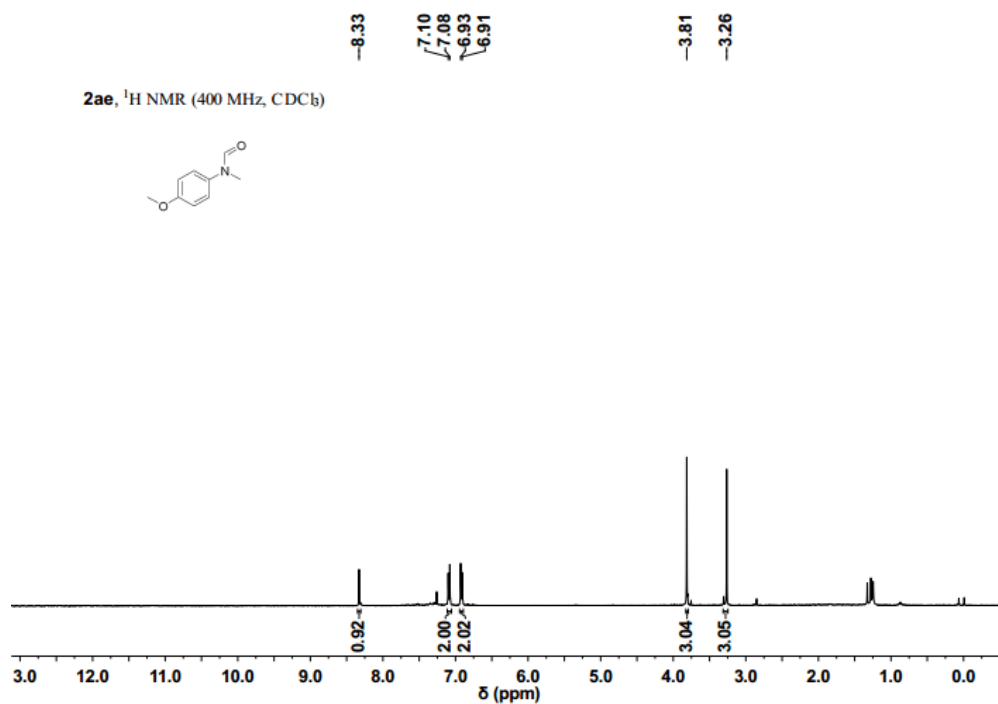
¹H NMR for *N*-methyl-*N*-(*o*-tolyl)formamide, **2ad**



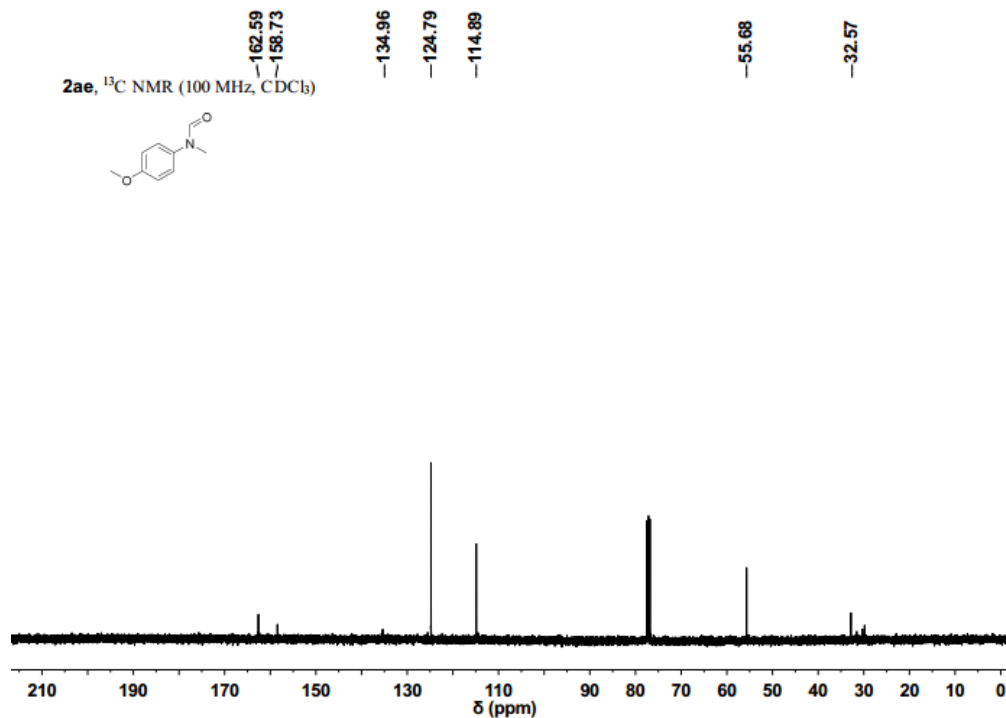
¹³C NMR for *N*-methyl-*N*-(*o*-tolyl)formamide, **2ad**



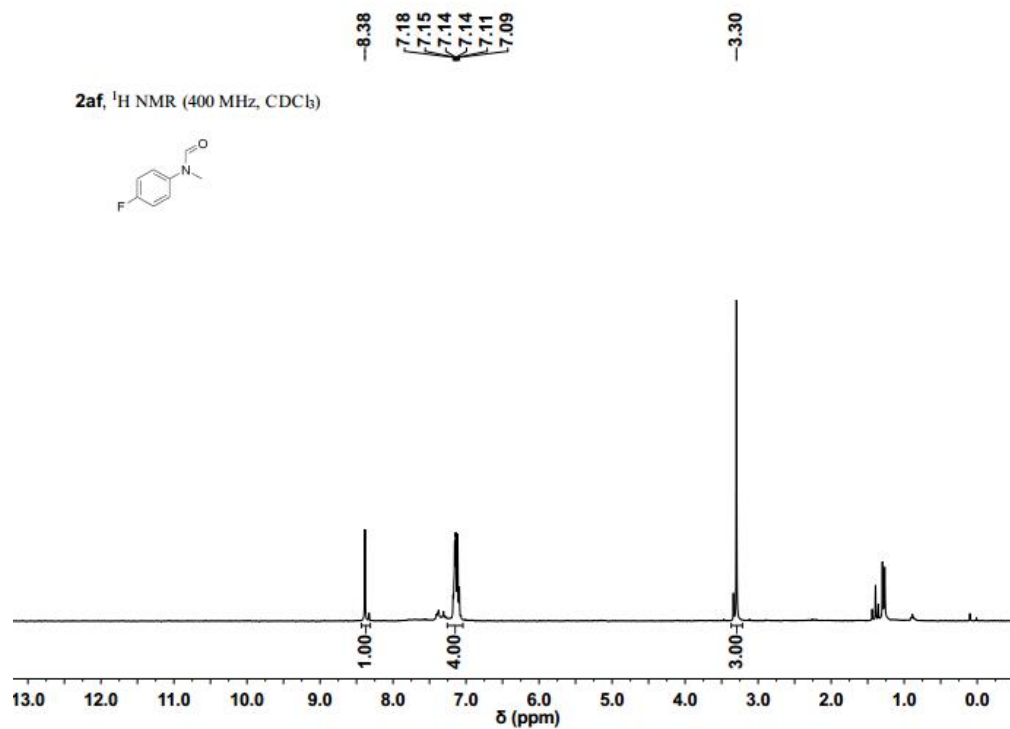
^1H NMR for *N*-(4-methoxyphenyl)-*N*-methylformamide, **2ae**



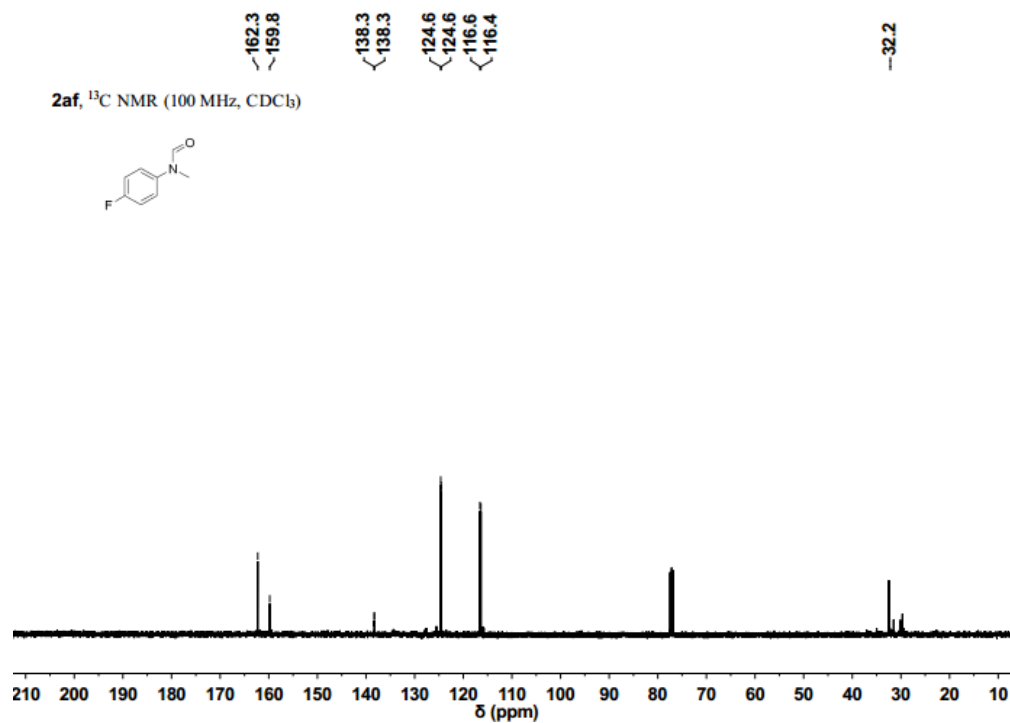
^{13}C NMR for *N*-(4-methoxyphenyl)-*N*-methylformamide, **2ae**



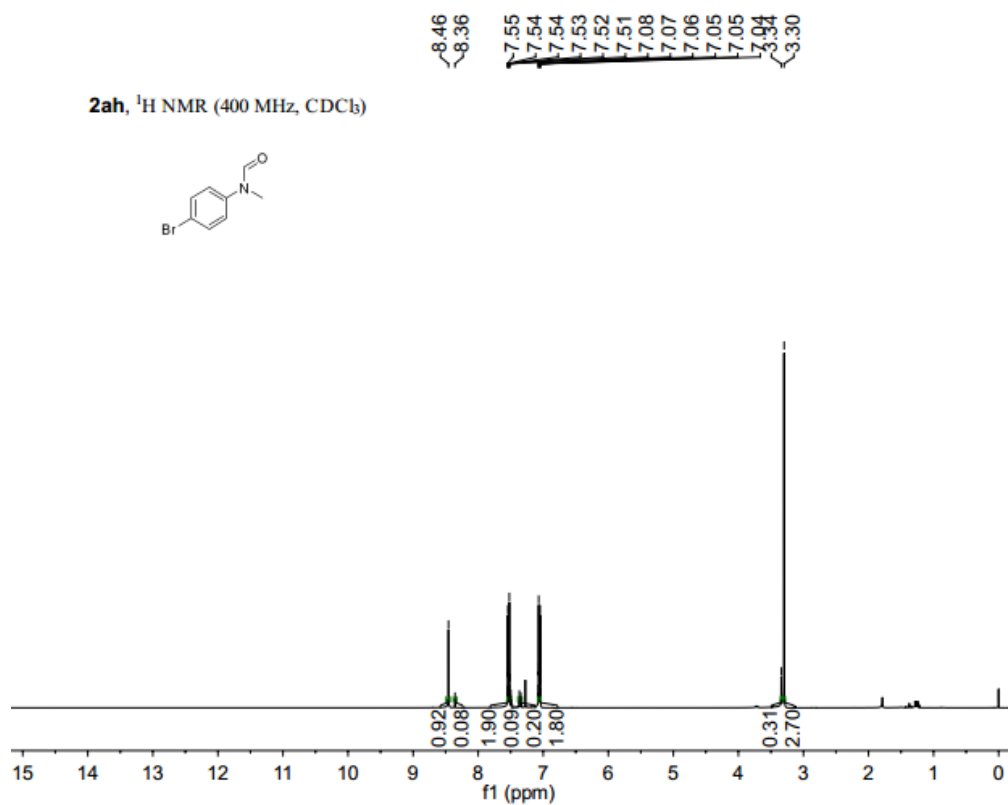
^1H NMR for *N*-(4-fluorophenyl)-*N*-methylformamide, **2af**



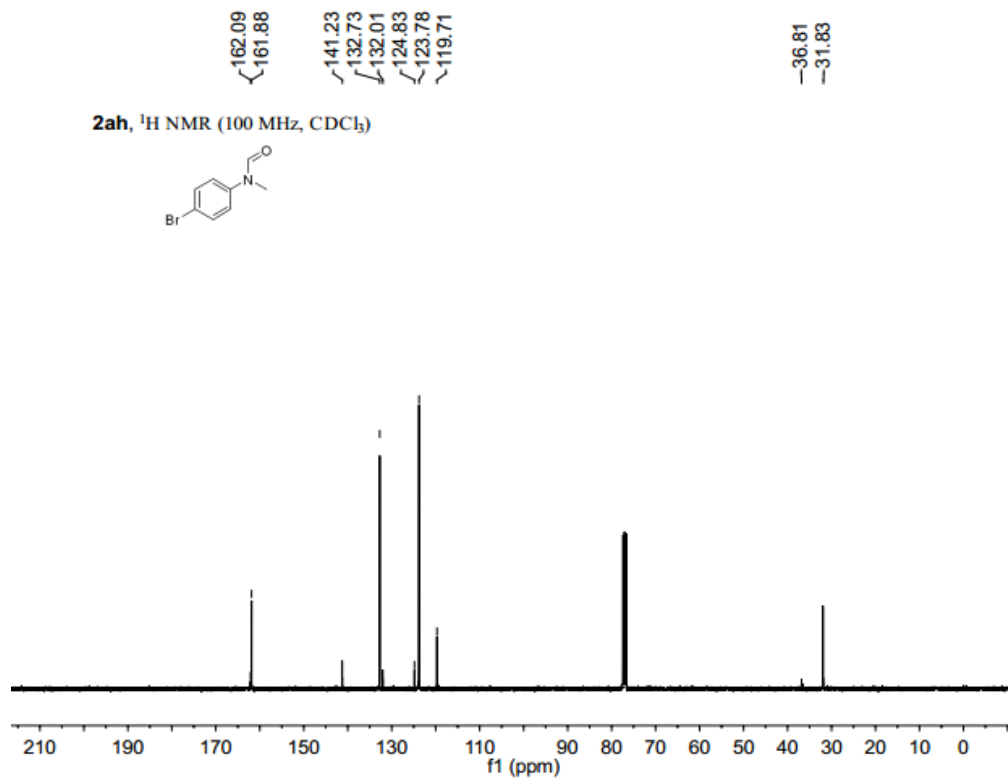
^{13}C NMR for *N*-(4-fluorophenyl)-*N*-methylformamide, **2af**



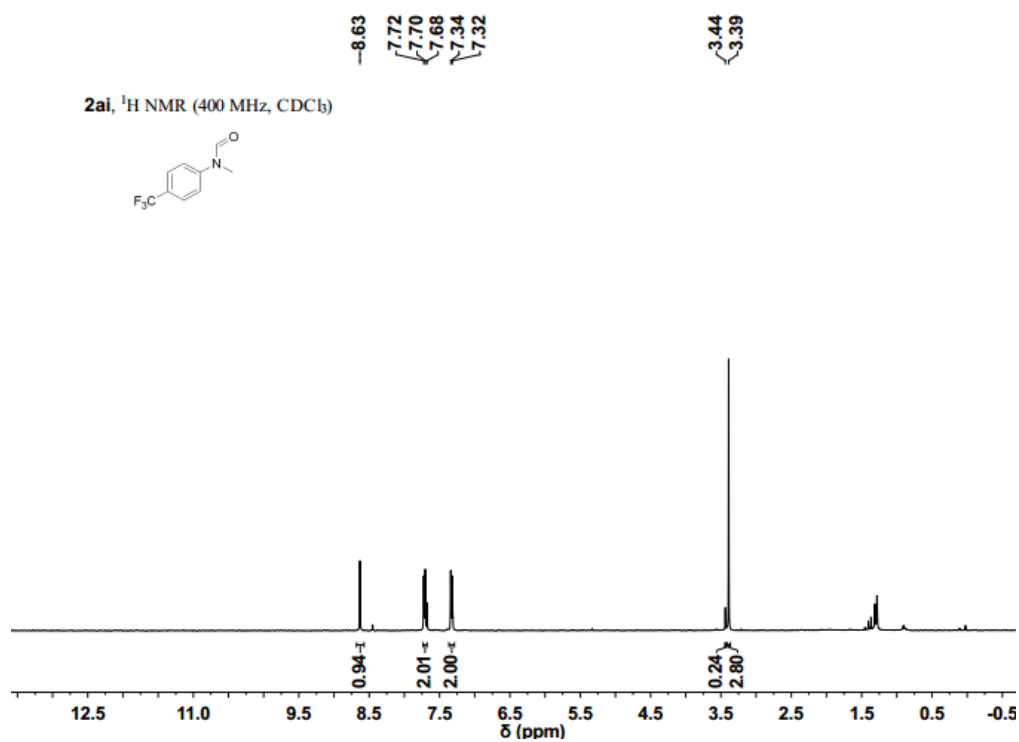
^1H NMR for *N*-(4-bromophenyl)-*N*-methylformamide, **2ah**



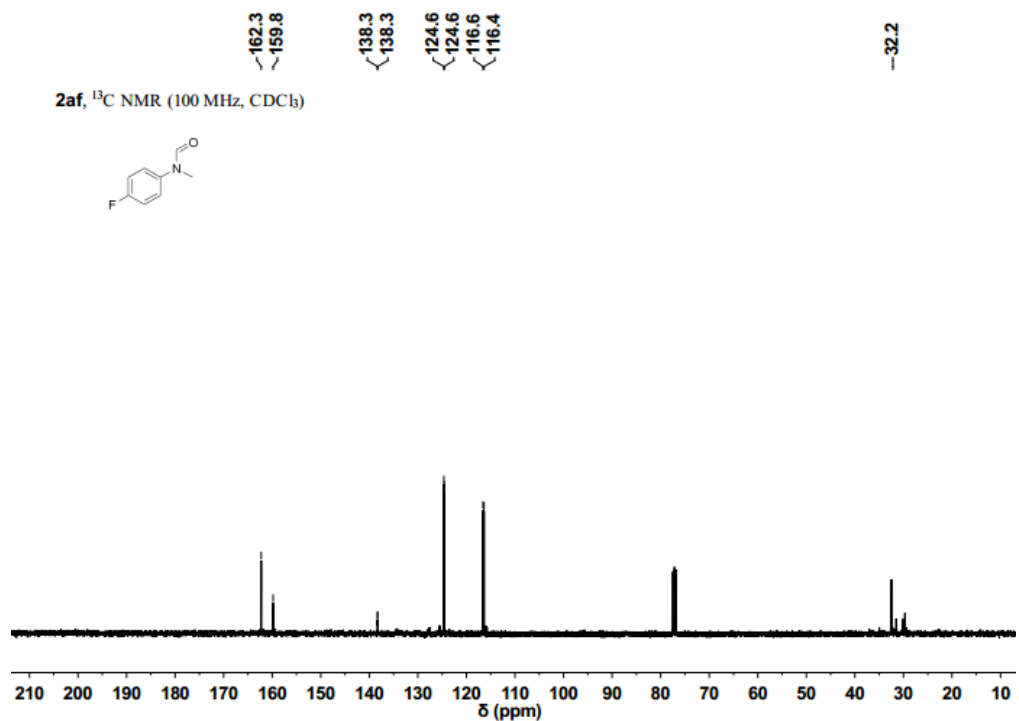
^{13}C NMR for *N*-(4-bromophenyl)-*N*-methylformamide, **2ah**



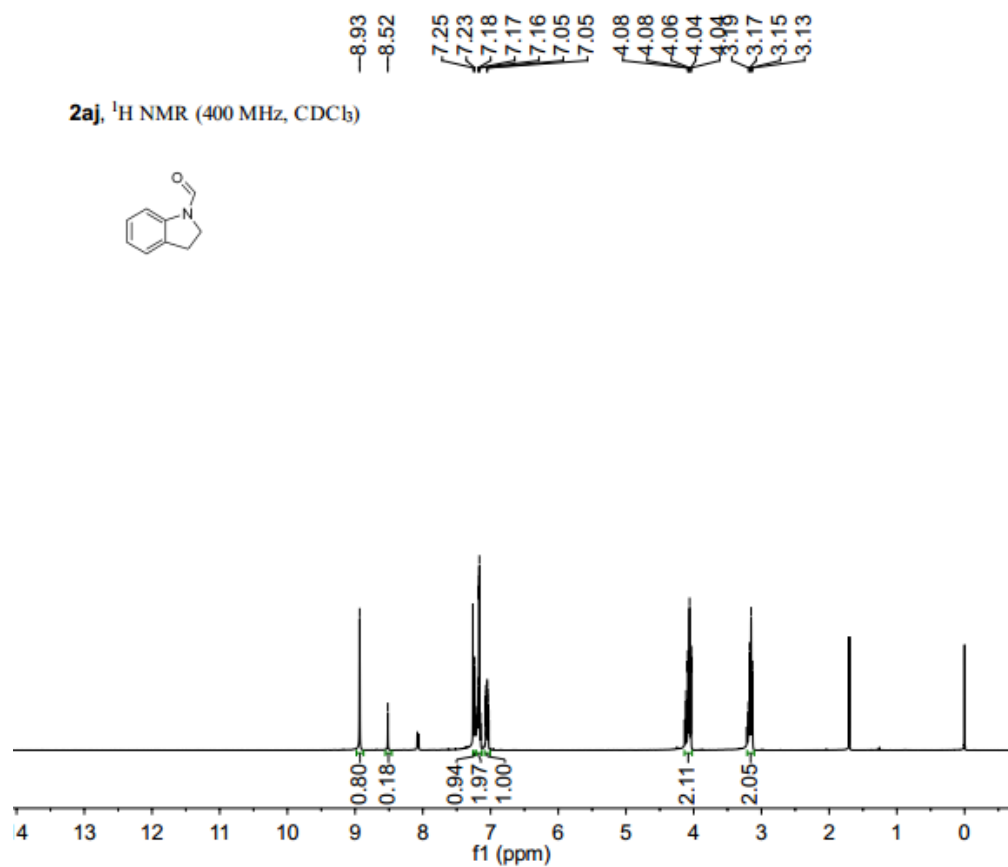
^1H NMR for *N*-methyl-*N*-(4-(trifluoromethyl)phenyl)formamide, **2ai**



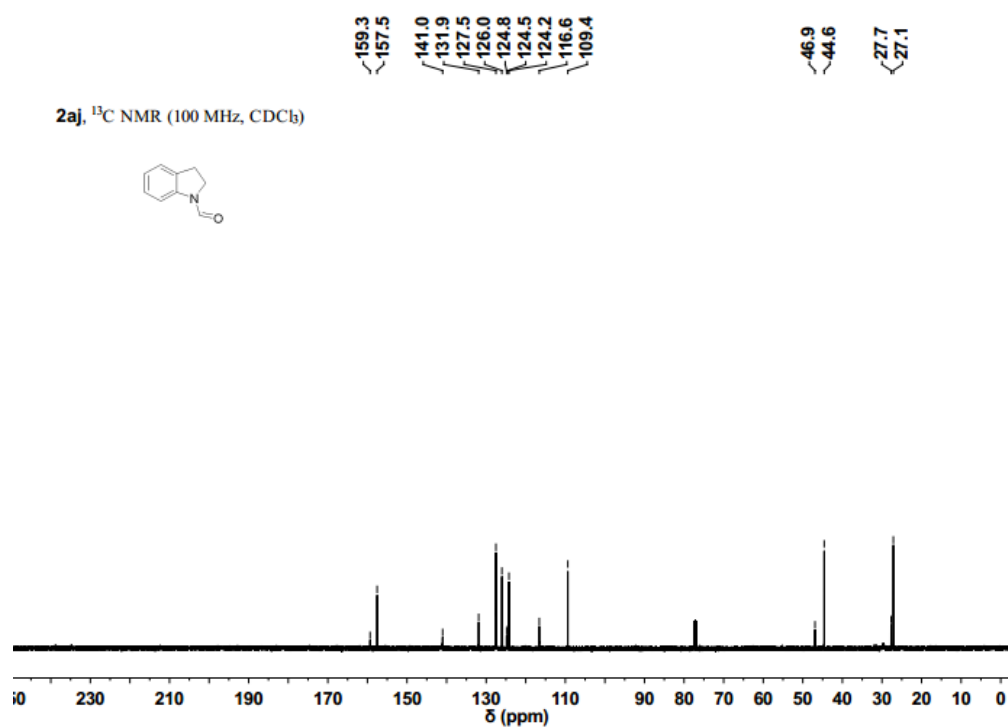
^{13}C NMR for *N*-methyl-*N*-(4-(trifluoromethyl)phenyl)formamide, **2ai**



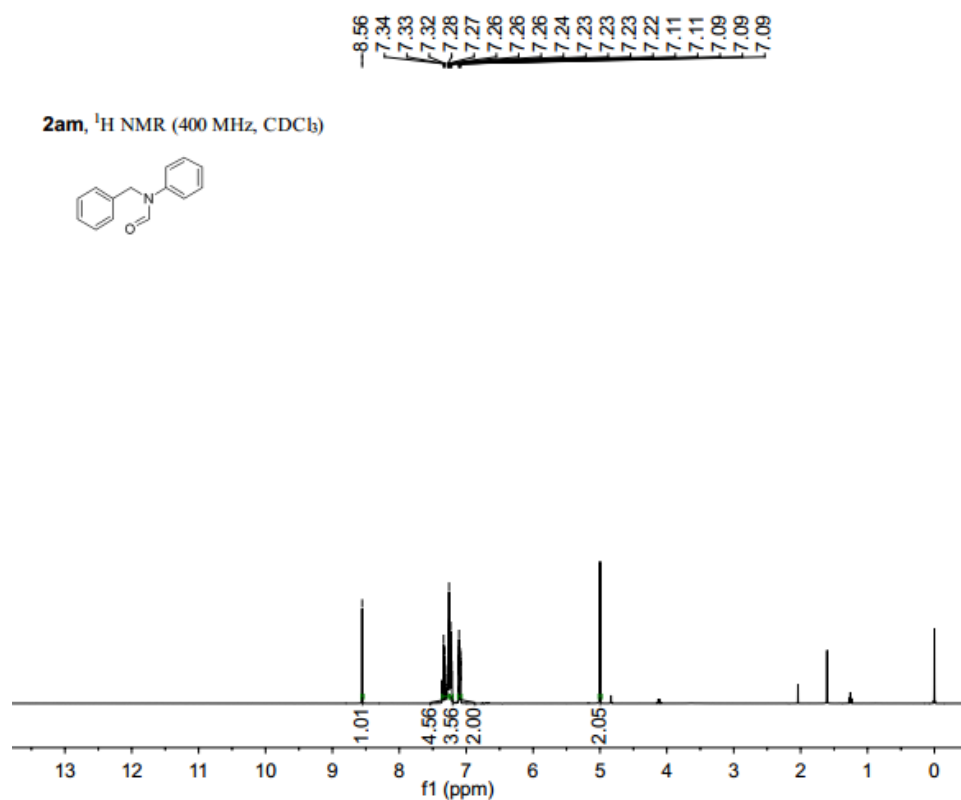
^1H NMR for indoline-1-carbaldehyde, **2aj**



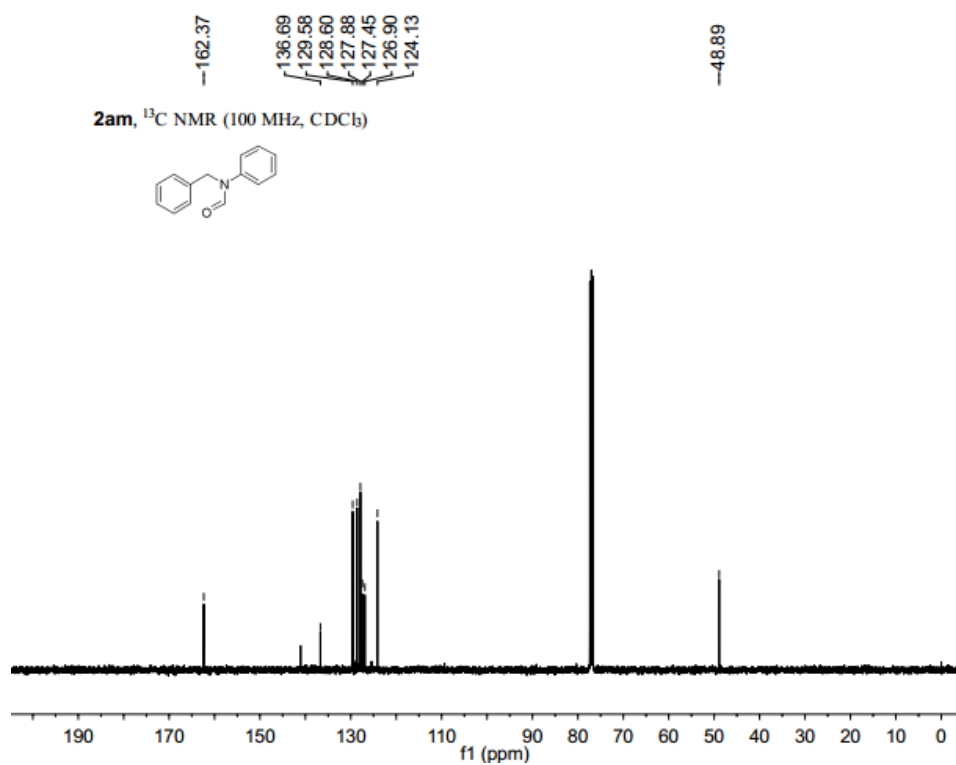
^{13}C NMR for indoline-1-carbaldehyde, **2aj**



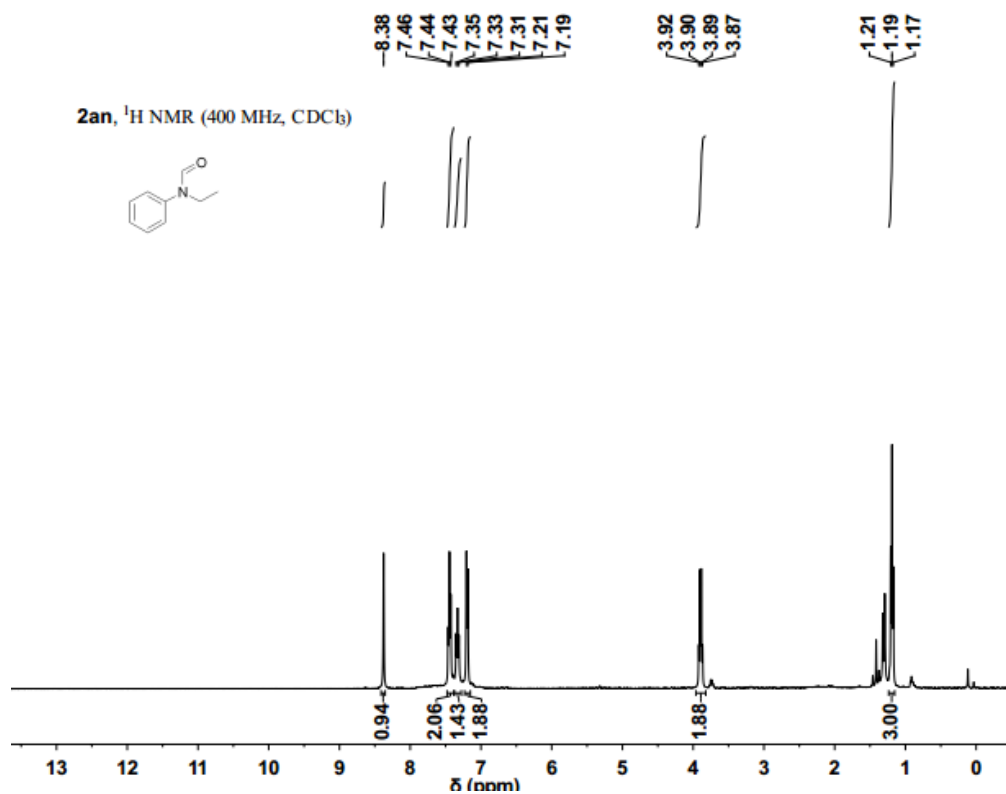
^1H NMR for *N*-benzyl-*N*-phenylformamide, **2am**



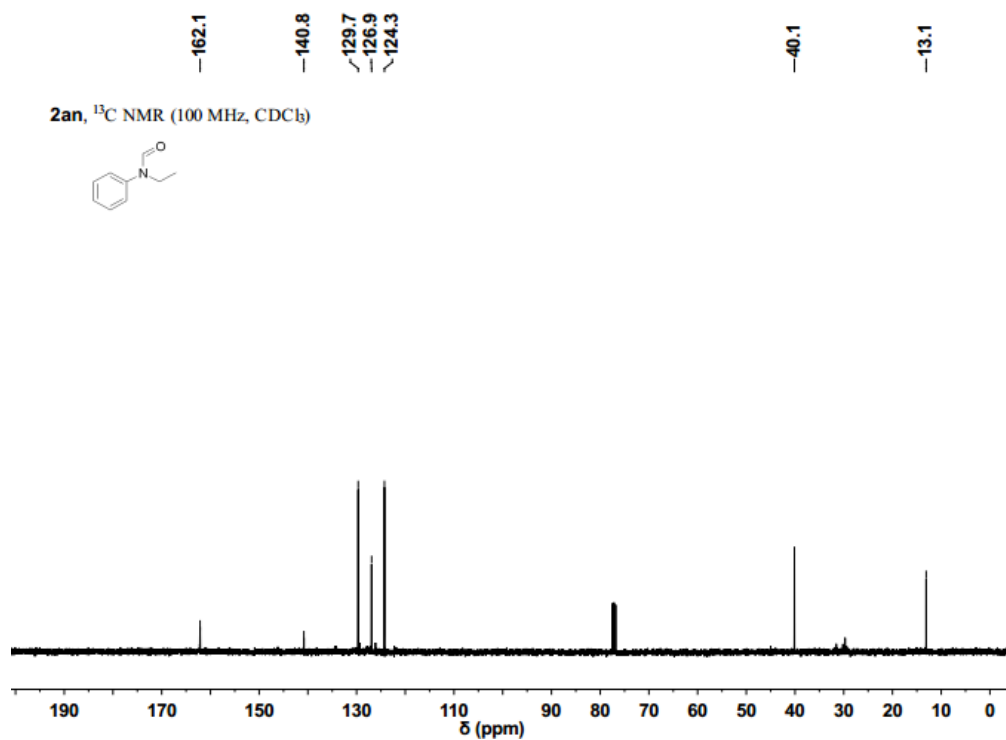
^{13}C NMR for *N*-benzyl-*N*-phenylformamide, **2am**



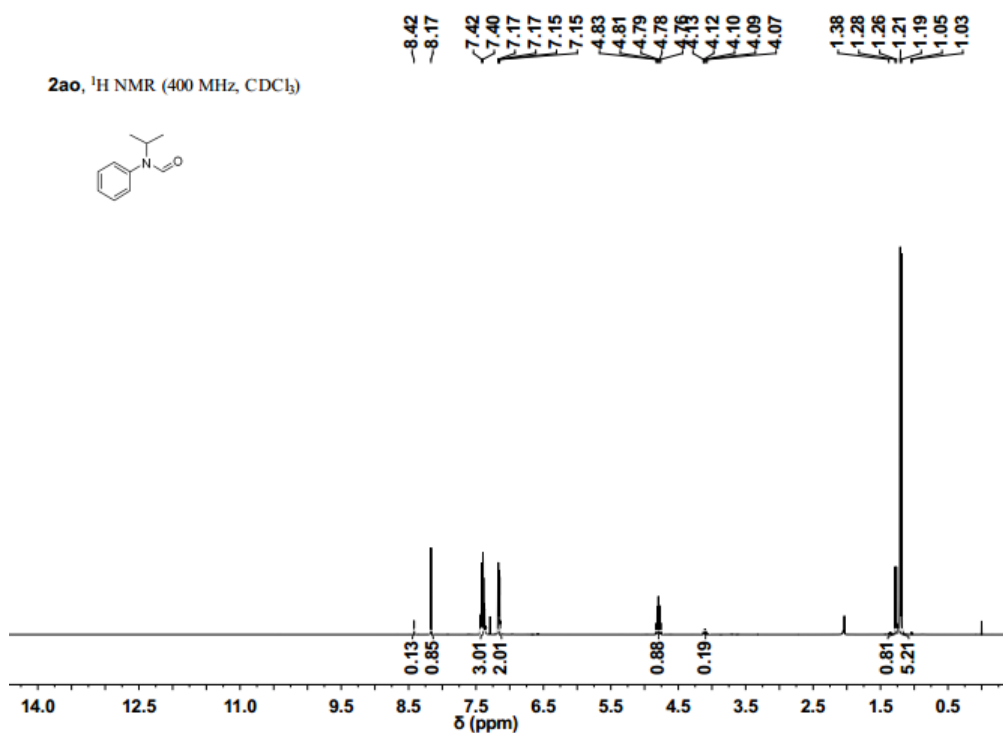
^1H NMR for *N*-ethyl-*N*-phenylformamide, **2an**



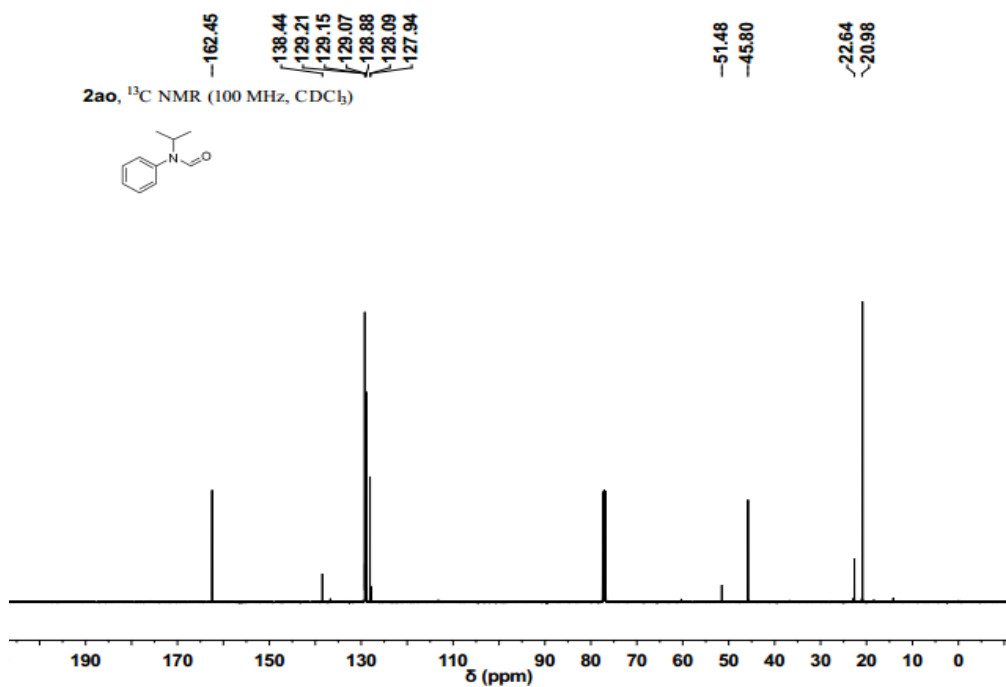
^{13}C NMR for *N*-ethyl-*N*-phenylformamide, **2an**



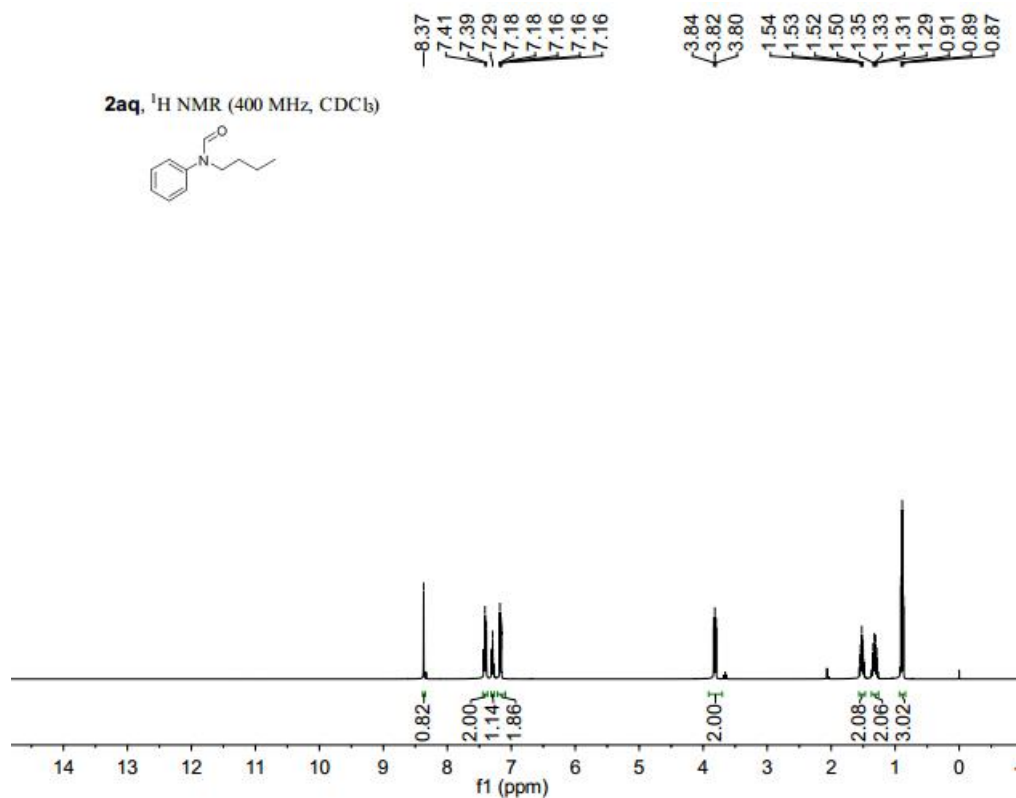
^1H NMR for *N*-isopropyl-*N*-phenylformamide, **2ao**



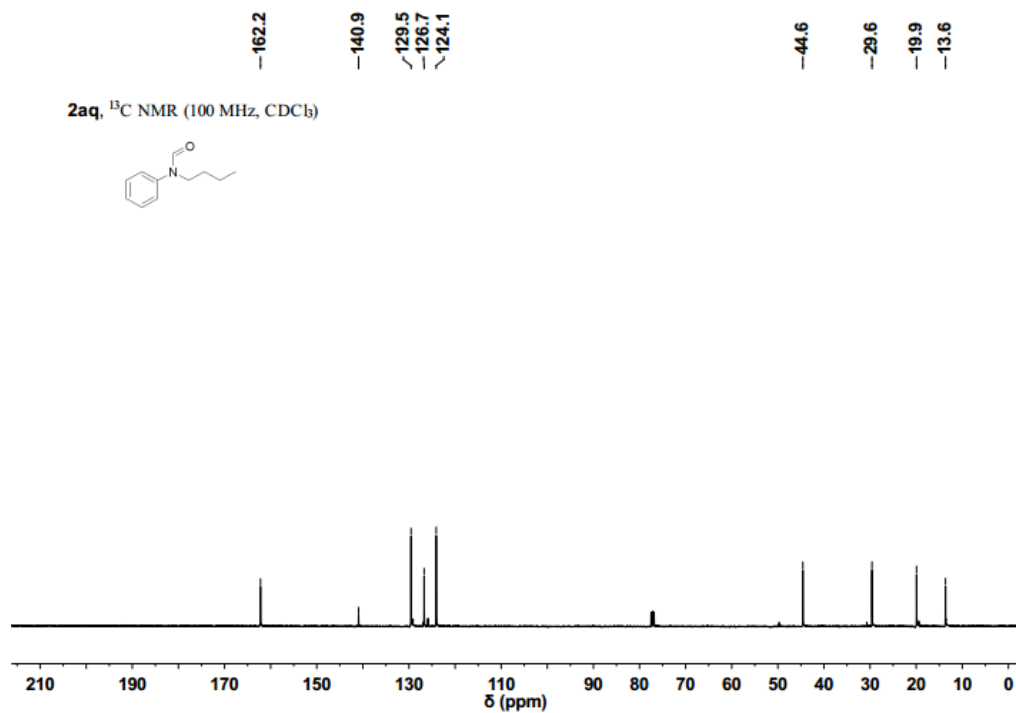
^{13}C NMR for *N*-isopropyl-*N*-phenylformamide, **2ao**



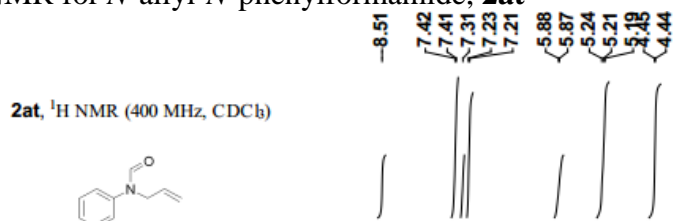
¹H NMR for *N*-butyl-*N*-phenylformamide, **2aq**



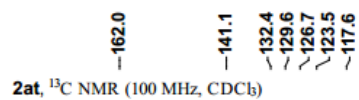
¹³C NMR for *N*-butyl-*N*-phenylformamide, **2aq**



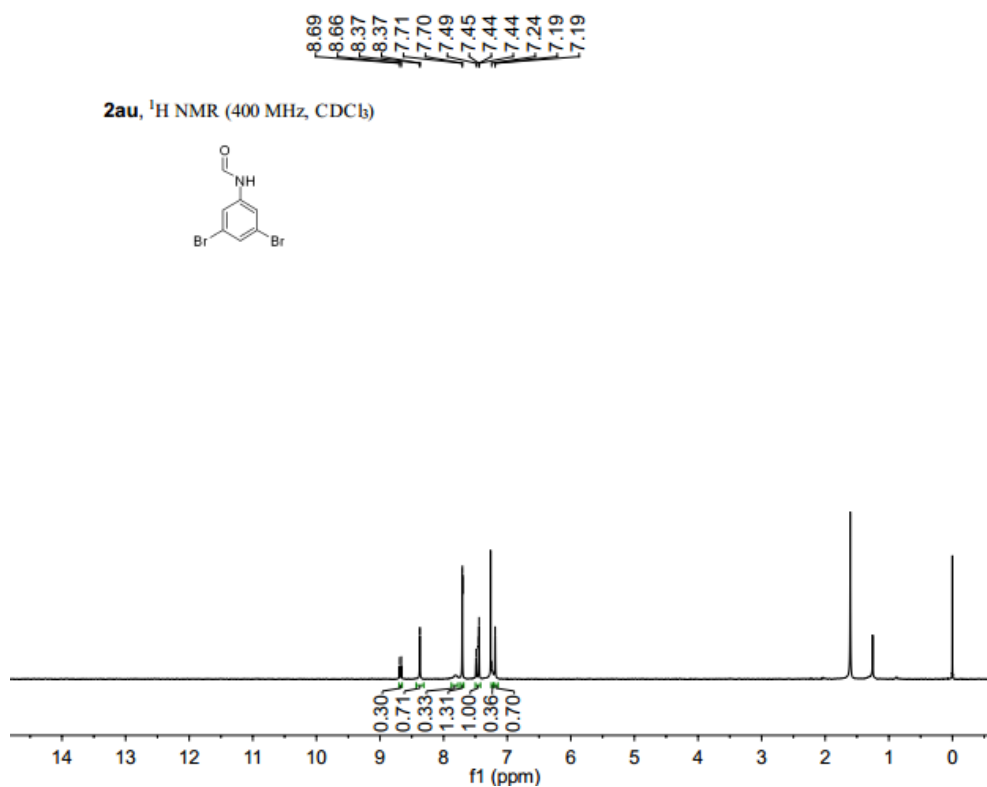
¹H NMR for *N*-allyl-*N*-phenylformamide, **2at**



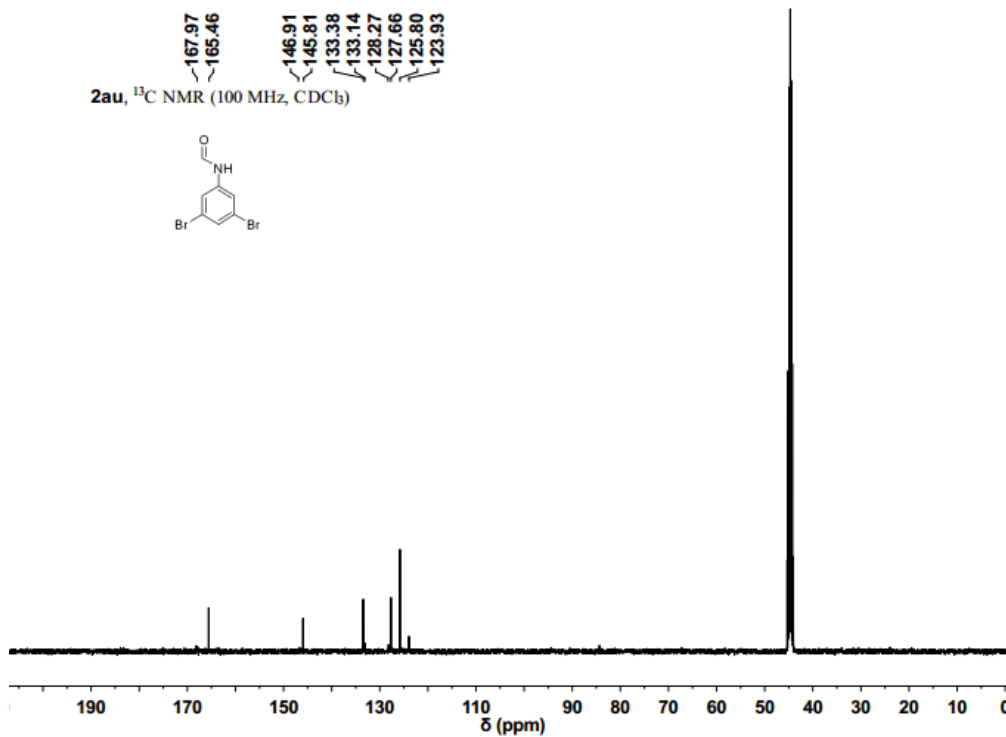
¹³C NMR for *N*-allyl-*N*-phenylformamide, **2at**



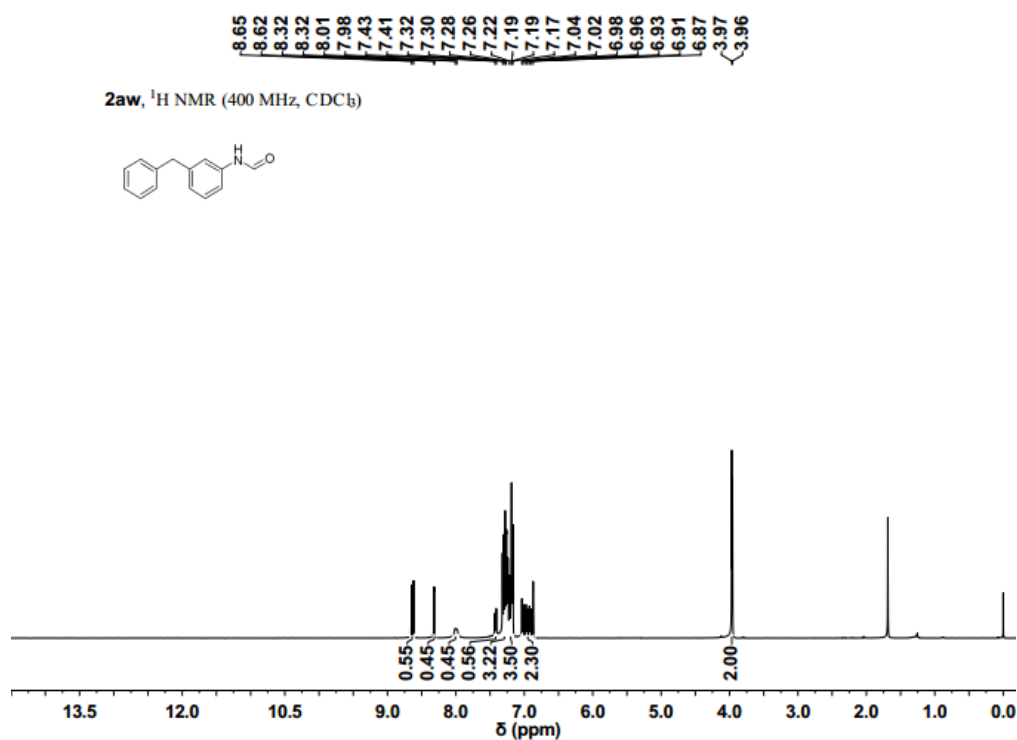
^1H NMR for *N*-(3,5-dibromophenyl)formamide, **2au**



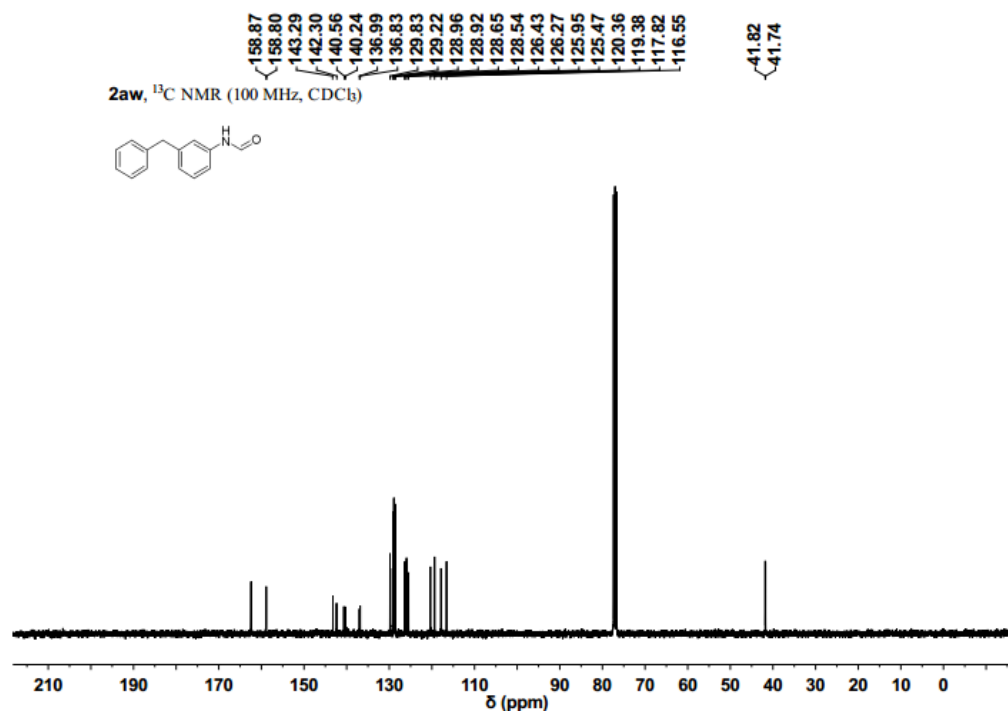
^{13}C NMR for *N*-(3,5-dibromophenyl)formamide, **2au**



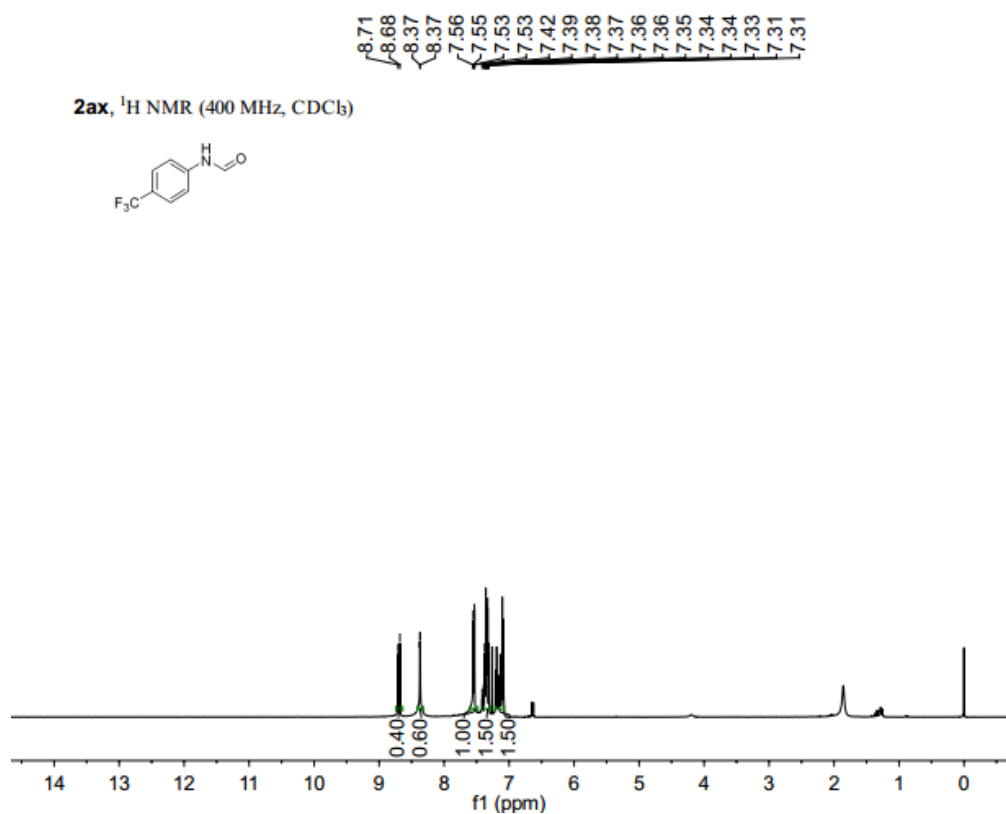
¹H NMR for *N*-(3-benzylphenyl)formamide, **2aw**



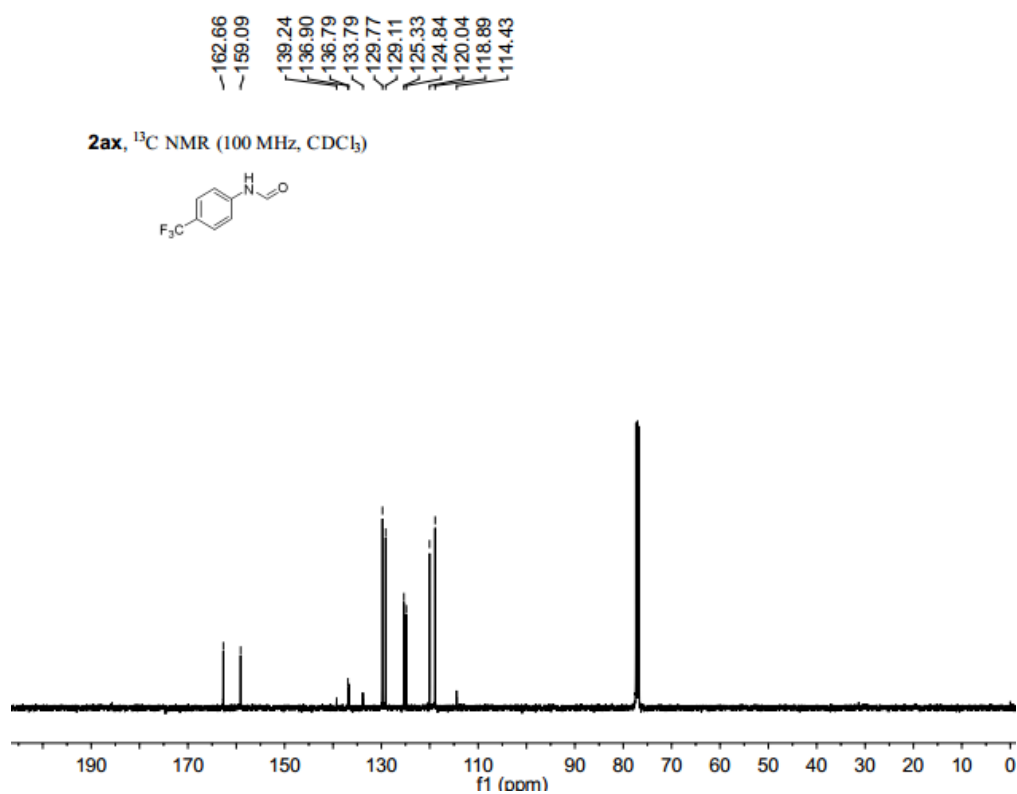
¹³C NMR for *N*-(3-benzylphenyl)formamide, **2aw**



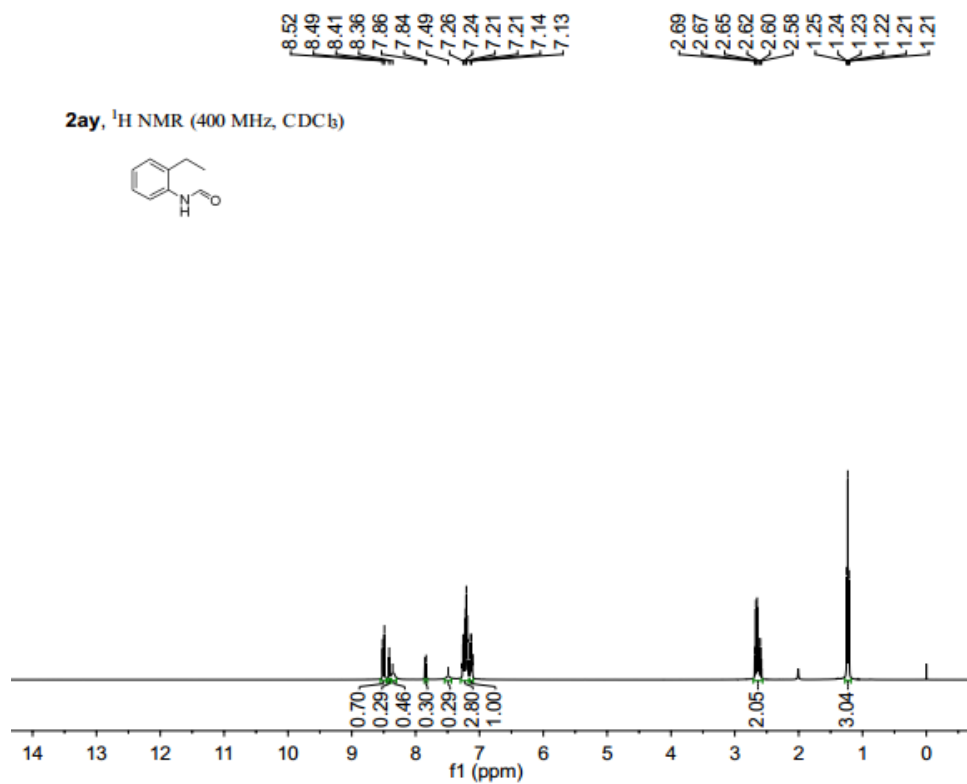
^1H NMR for *N*-(4-(trifluoromethyl)phenyl)formamide, **2ax**



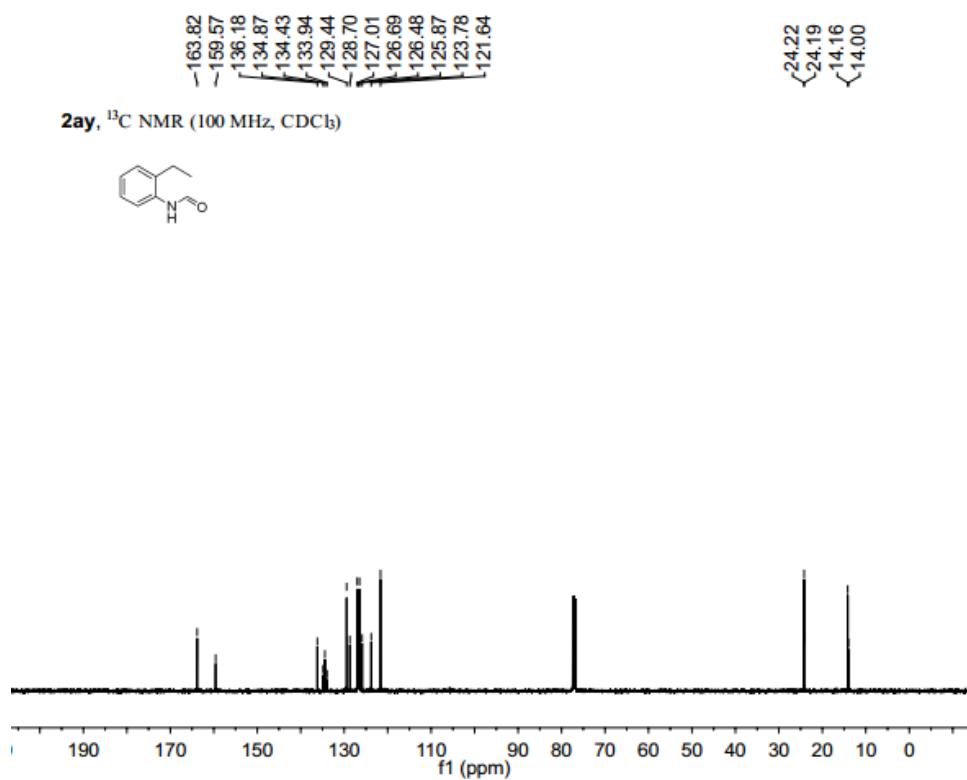
^{13}C NMR for *N*-(4-(trifluoromethyl)phenyl)formamide, **2ax**



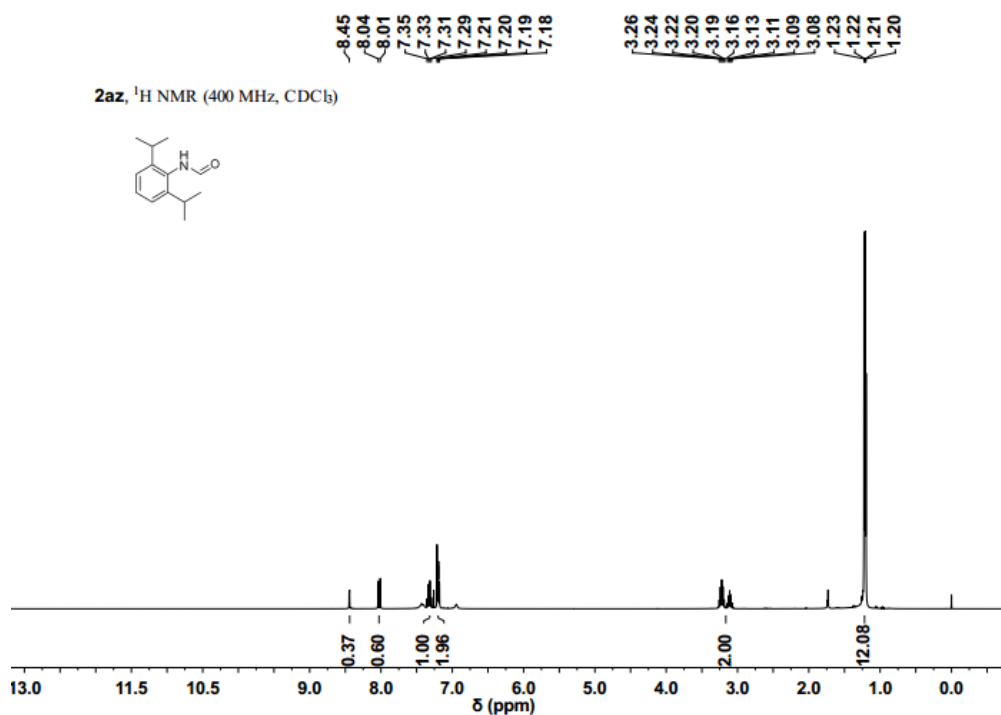
^1H NMR for *N*-(2-ethylphenyl)formamide, **2ay**



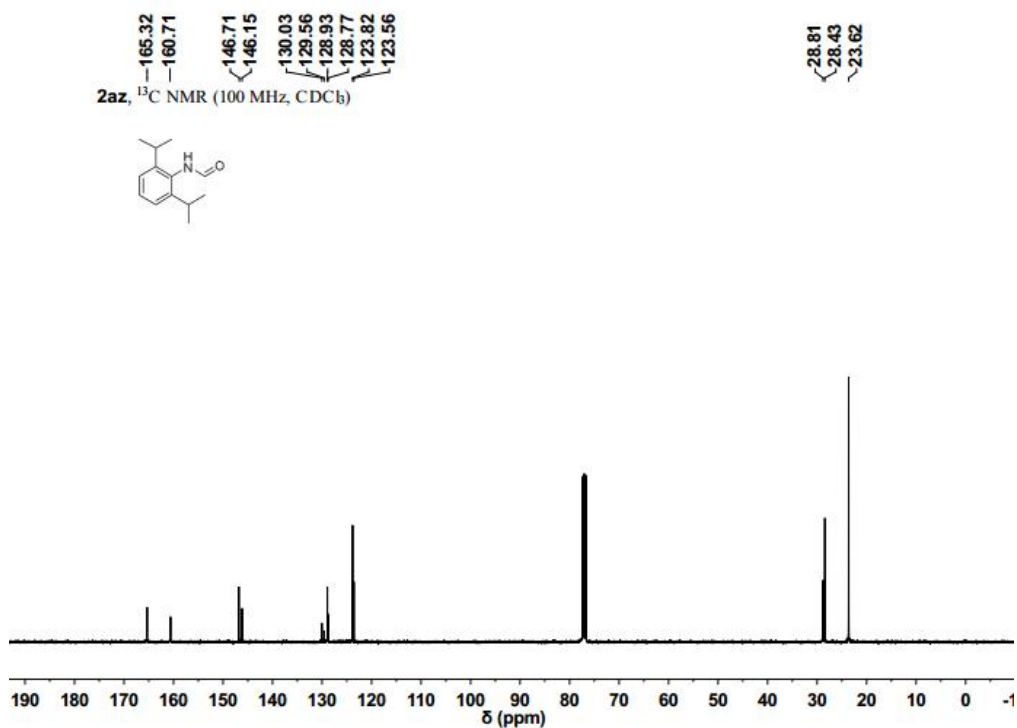
^{13}C NMR for *N*-(2-ethylphenyl)formamide, **2ay**



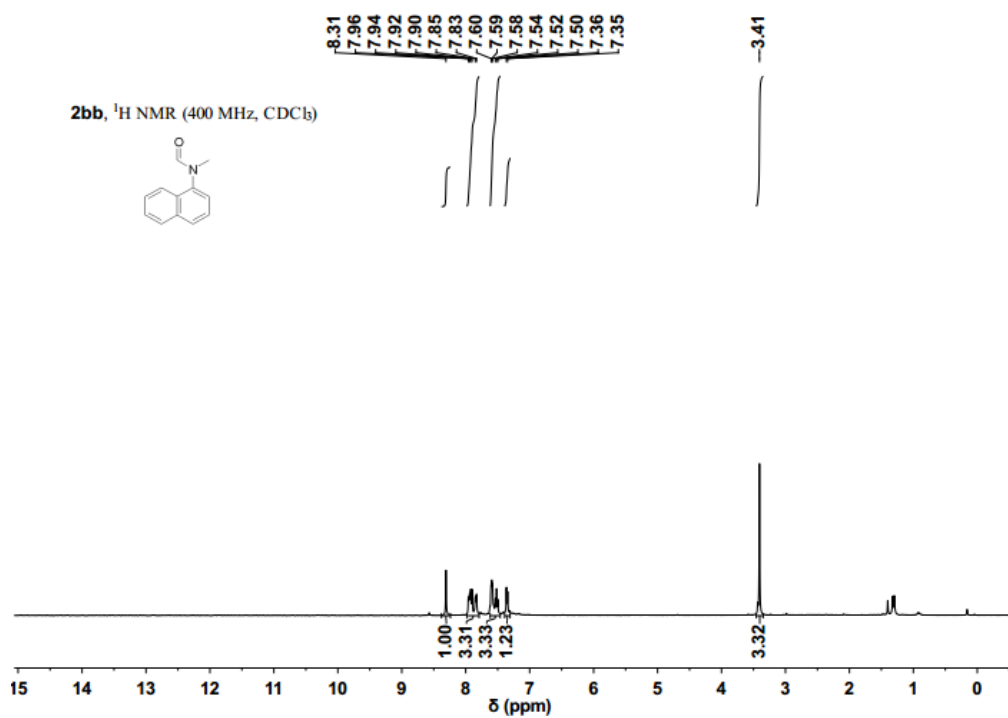
^1H NMR for *N*-(2,6-diisopropylphenyl)formamide, **2az**



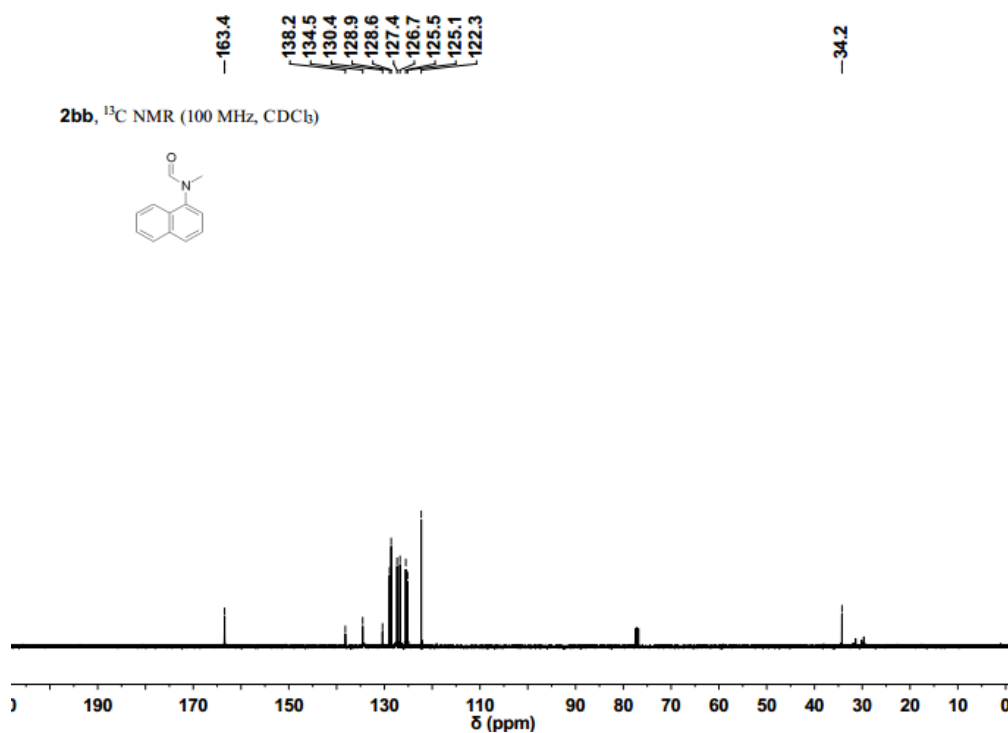
^{13}C NMR for *N*-(2,6-diisopropylphenyl)formamide, **2az**



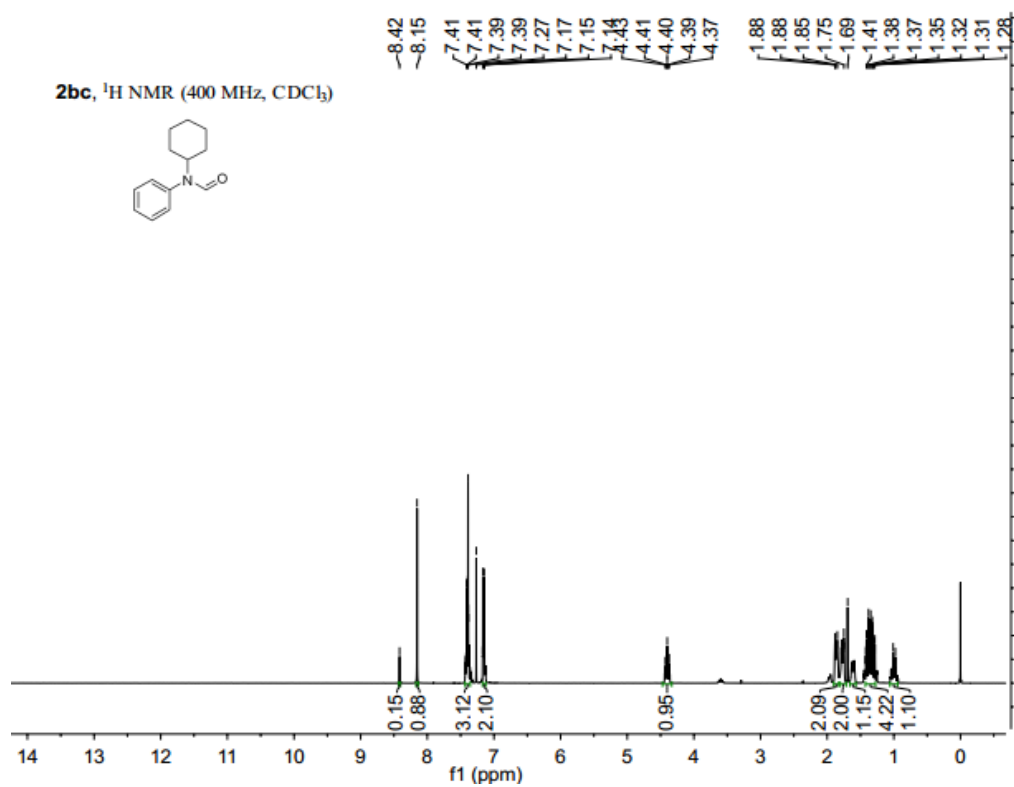
^1H NMR for *N*-methyl-*N*-(naphthalen-1-yl)formamide, **2bb**



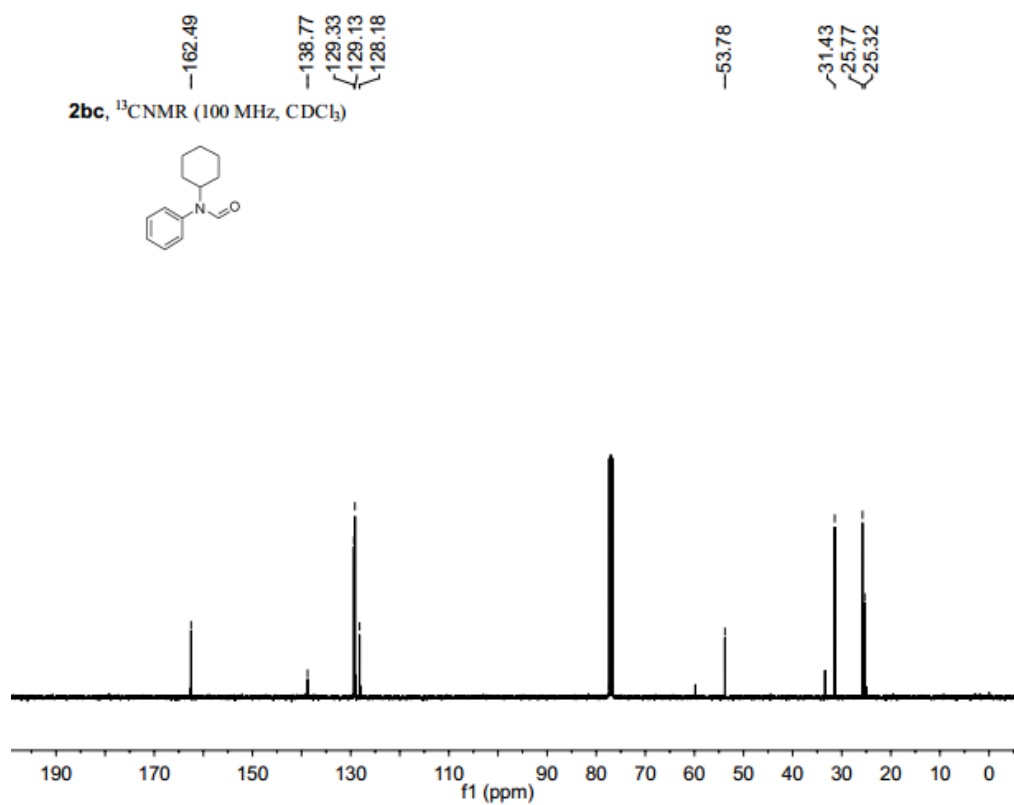
^{13}C NMR for *N*-methyl-*N*-(naphthalen-1-yl)formamide, **2bb**



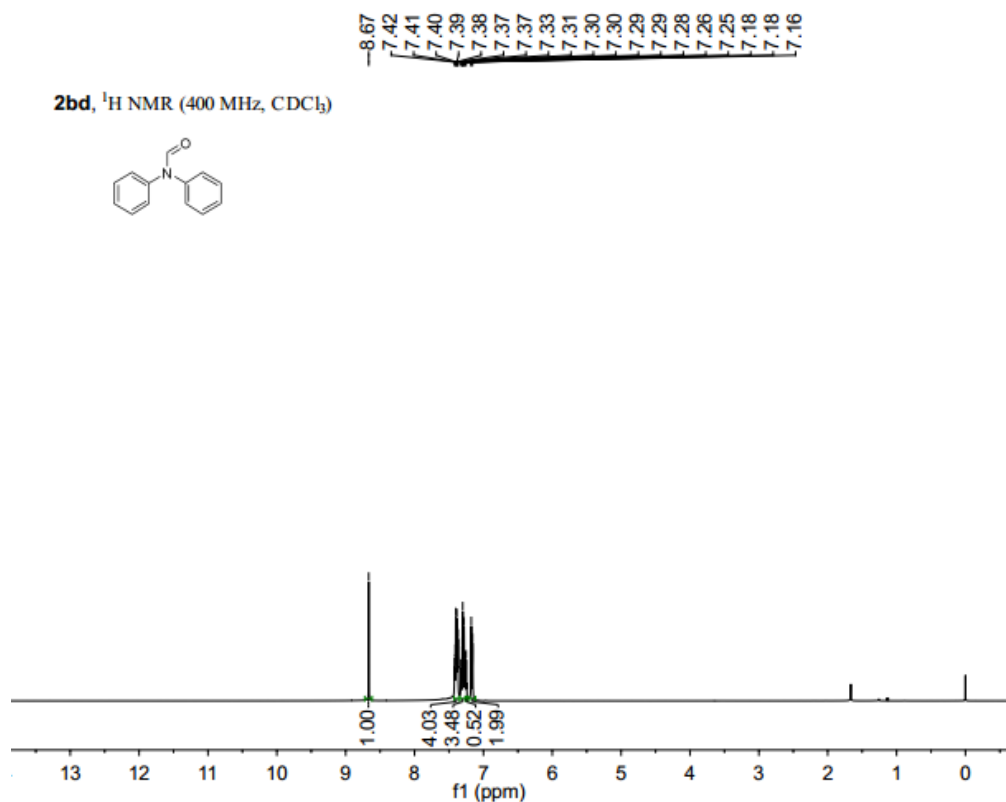
^1H NMR for *N*-cyclohexyl-*N*-phenylformamide, **2bc**



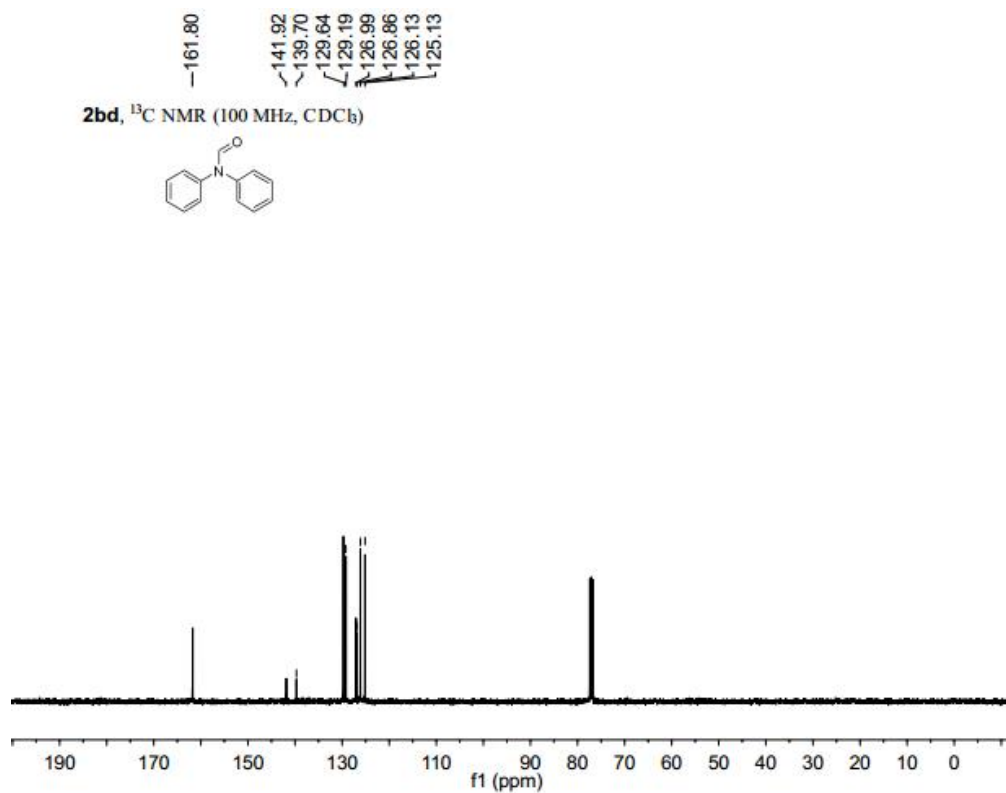
^{13}C NMR for *N*-cyclohexyl-*N*-phenylformamide, **2bc**



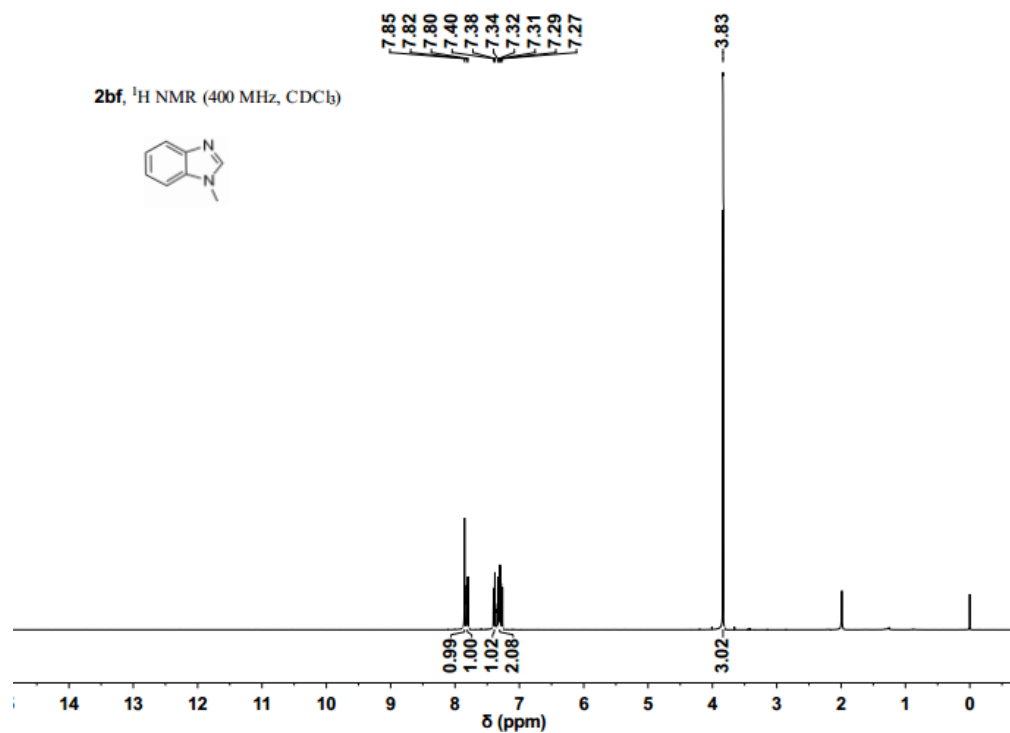
^1H NMR for *N,N*-diphenylformamide, **2bd**



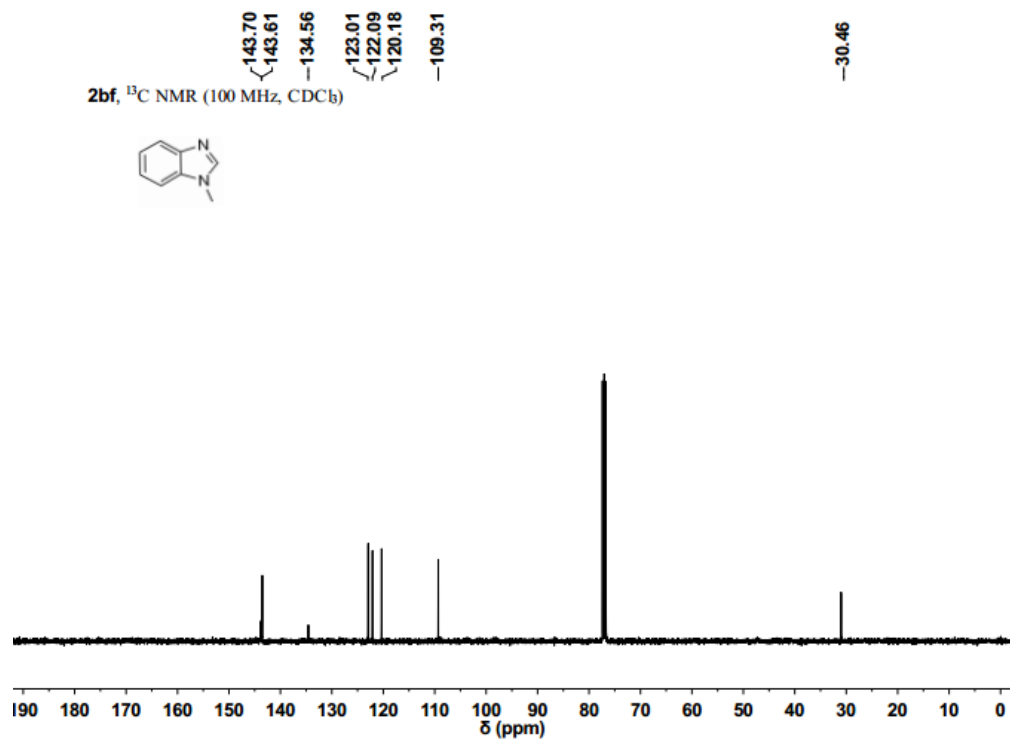
^{13}C NMR for *N,N*-diphenylformamide, **2bd**



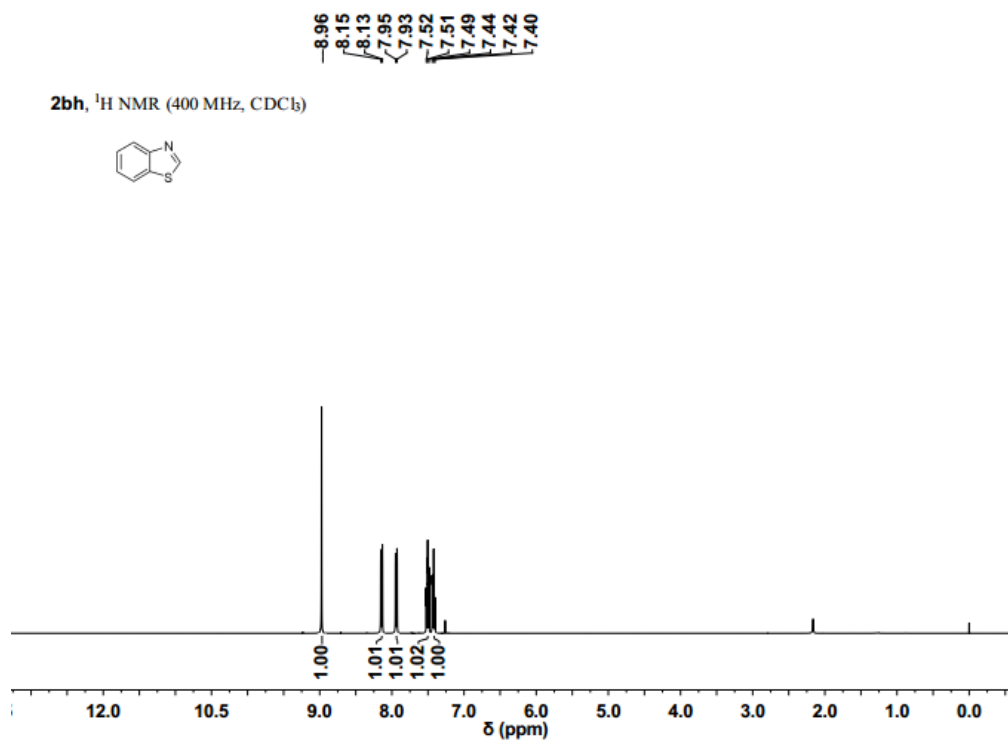
^1H NMR for 1-methyl-1*H*-benzo[*d*]imidazole, **2bf**



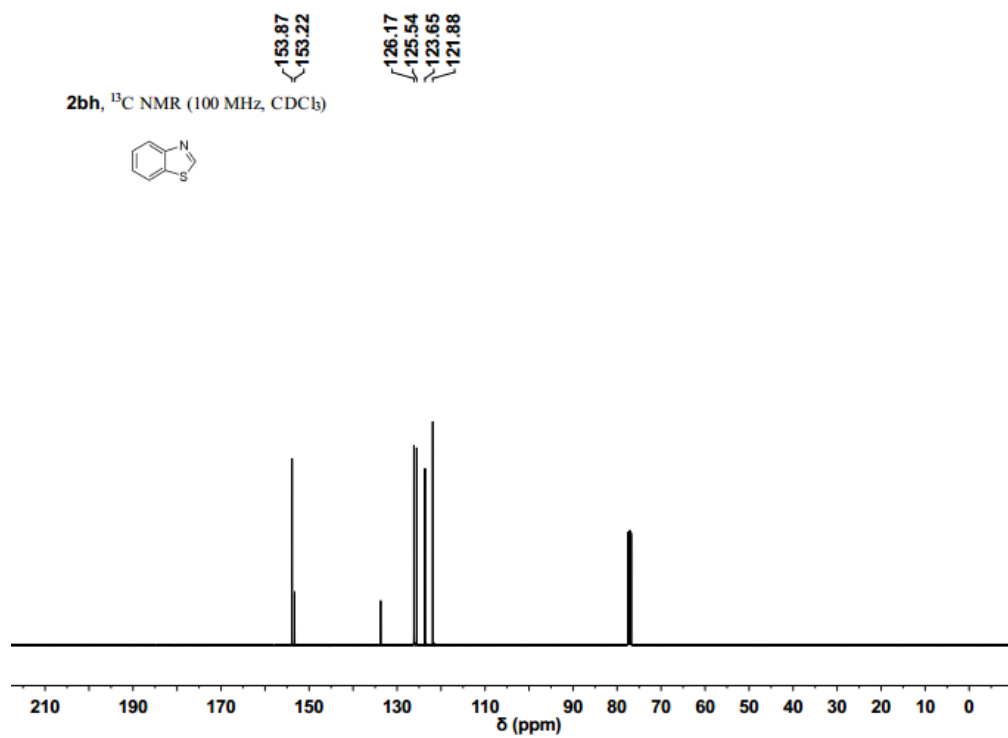
^{13}C NMR for 1-methyl-1*H*-benzo[*d*]imidazole, **2bf**



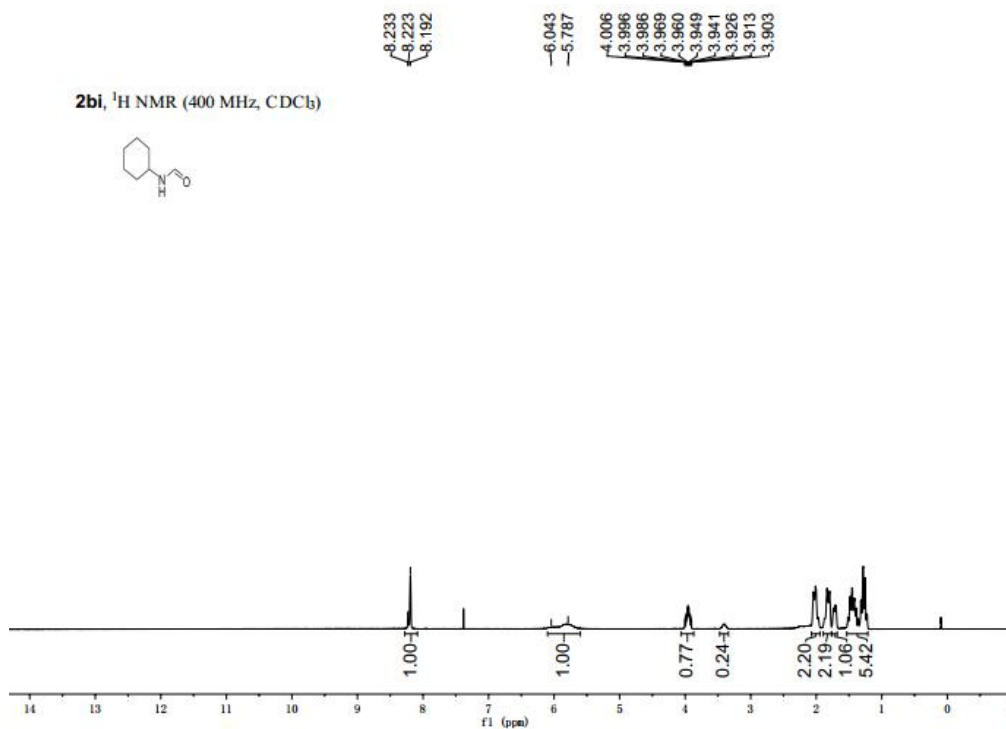
^1H NMR for benzo[*d*]thiazole, **2bh**



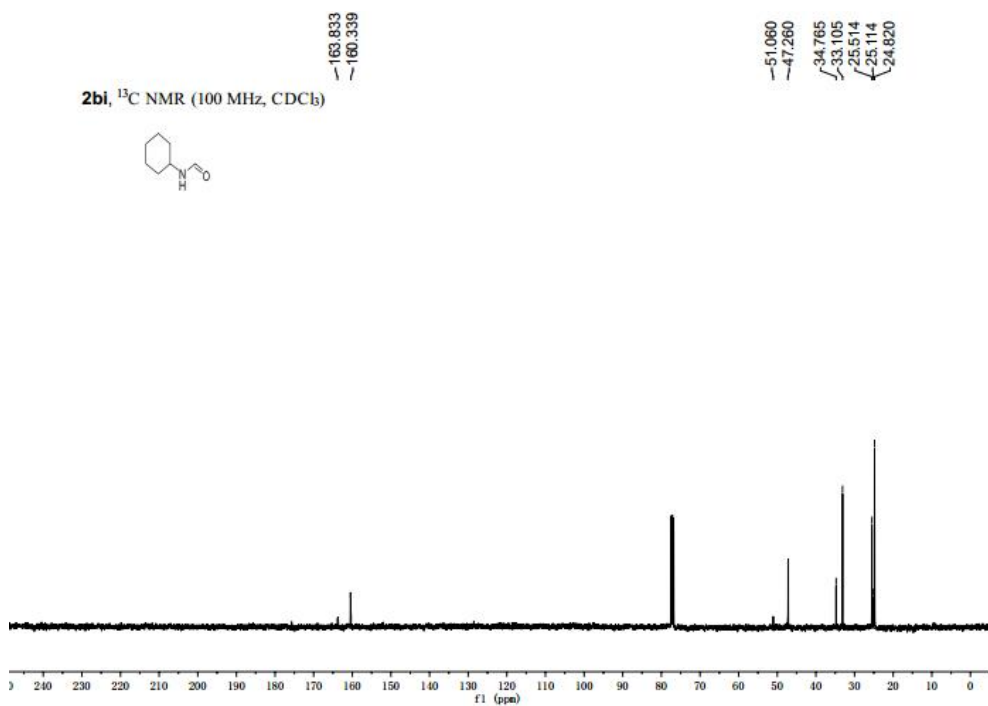
^{13}C NMR for benzo[*d*]thiazole, **2bh**



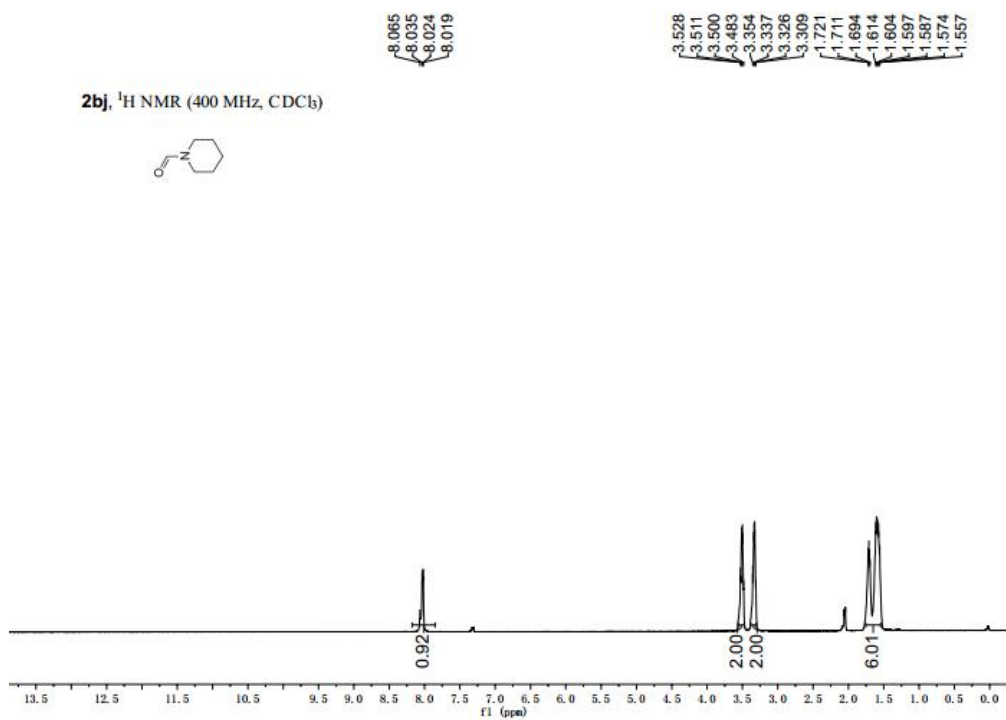
^1H NMR for *N*-cyclohexylformamide, **2bi**



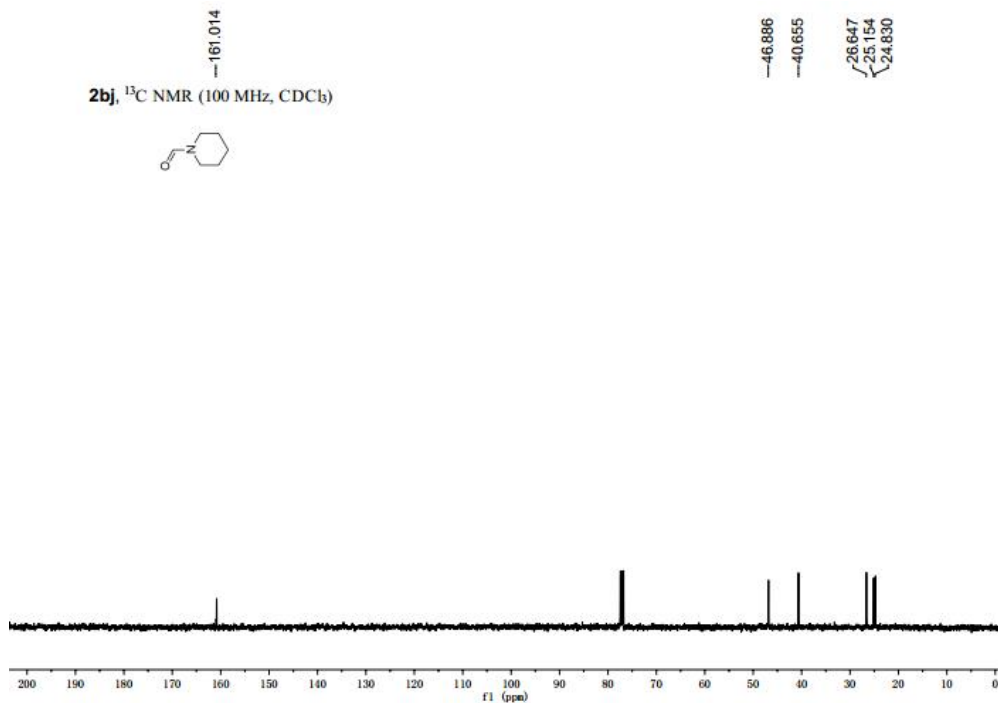
^{13}C NMR for *N*-cyclohexylformamide, **2bi**



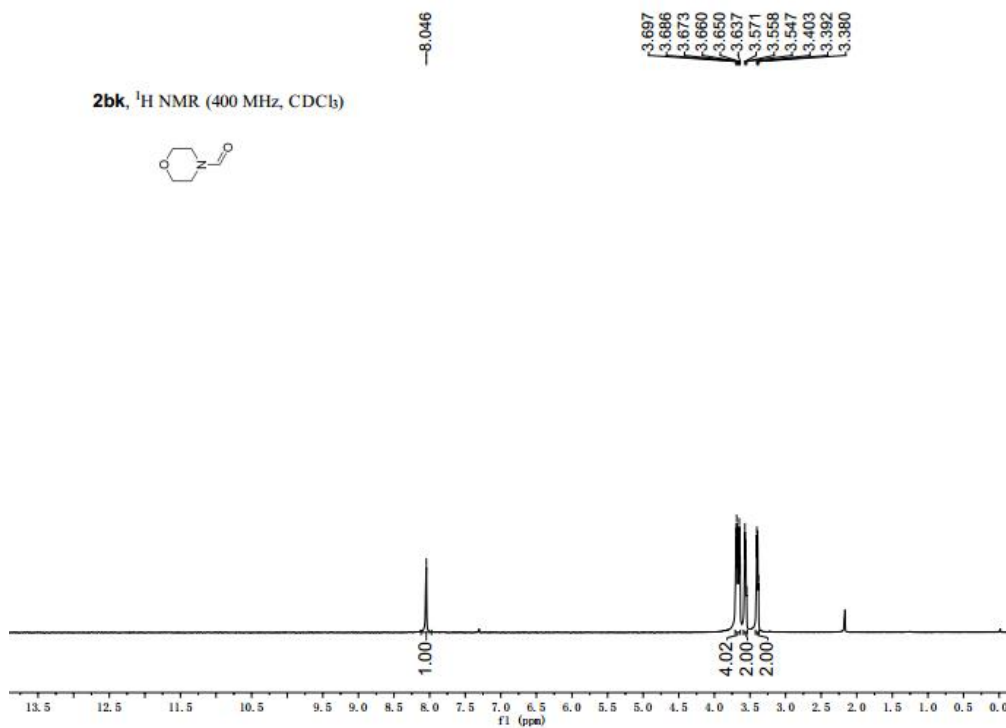
¹H NMR for piperidine-1-carbaldehyde, **2bj**



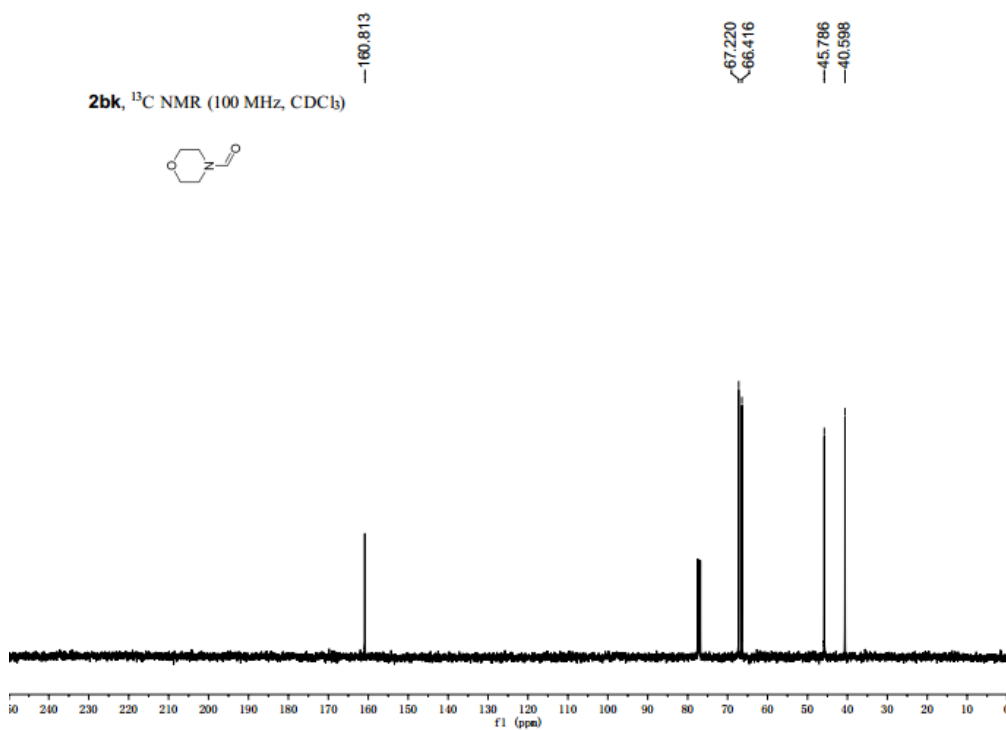
¹³C NMR for piperidine-1-carbaldehyde, **2bj**



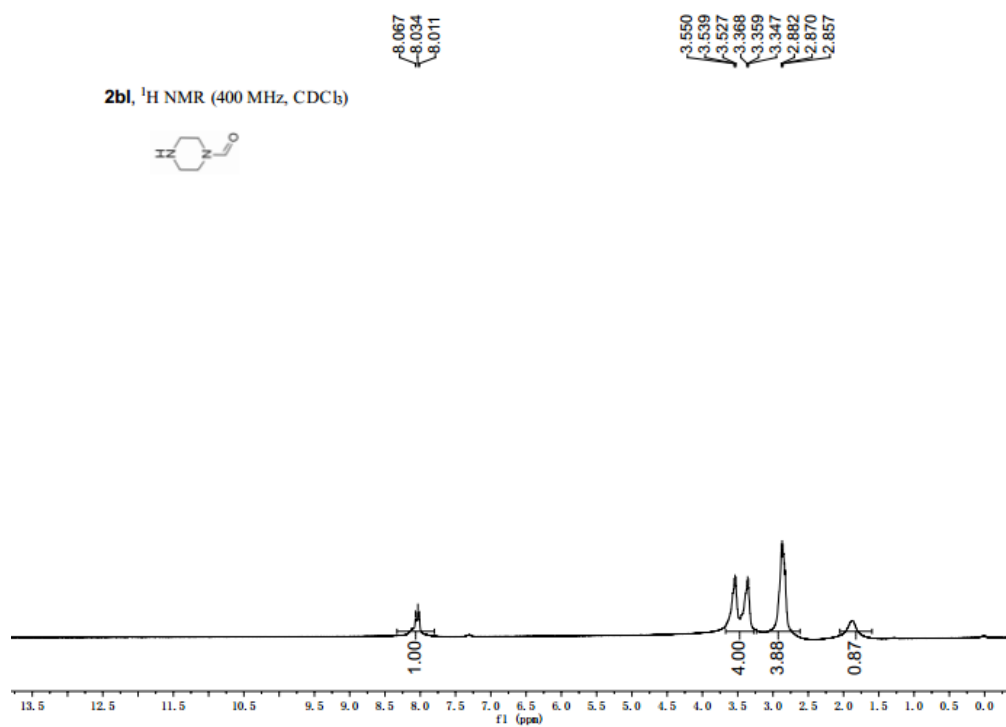
^1H NMR for morpholine-4-carbaldehyde, **2bk**



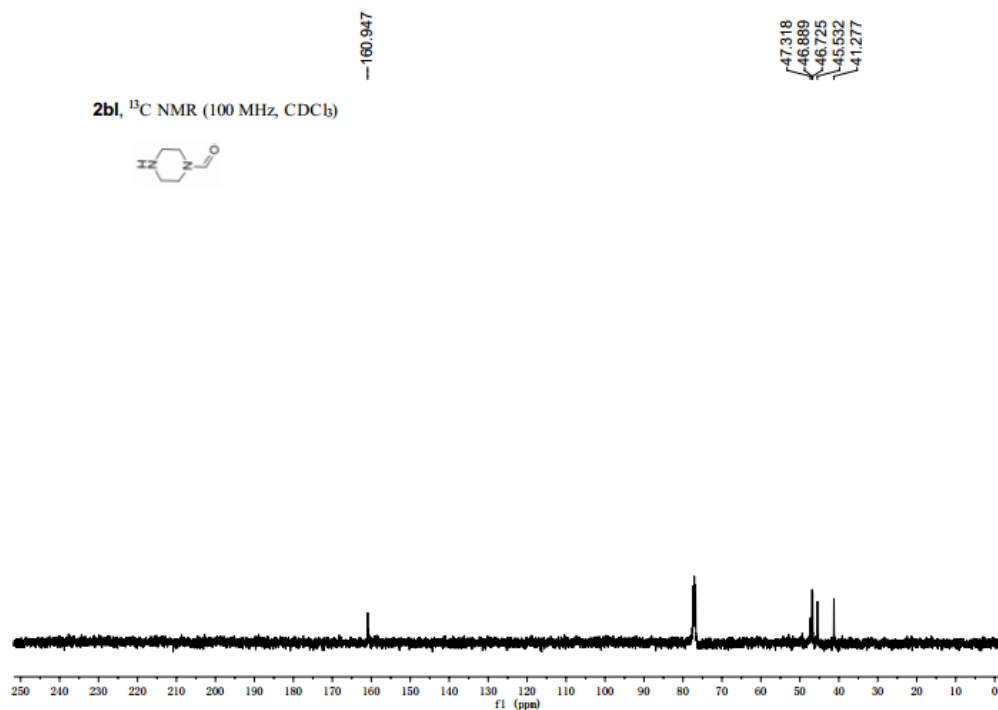
^{13}C NMR for morpholine-4-carbaldehyde, **2bk**



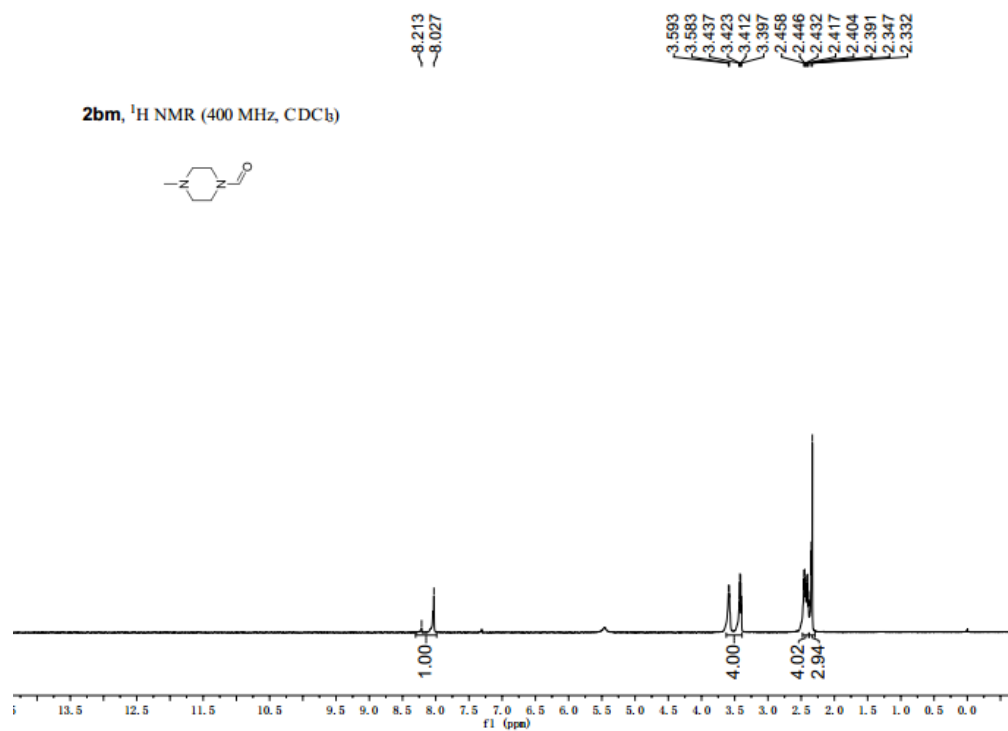
^1H NMR for piperazine-1-carbaldehyde, **2bl**



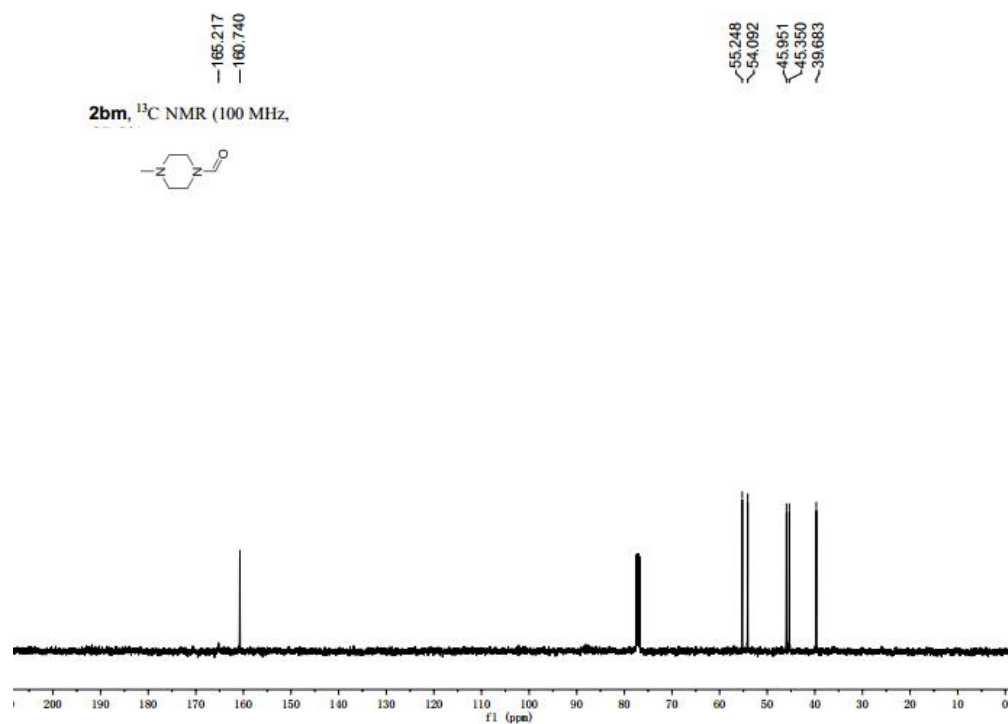
^{13}C NMR for piperazine-1-carbaldehyde, **2bl**



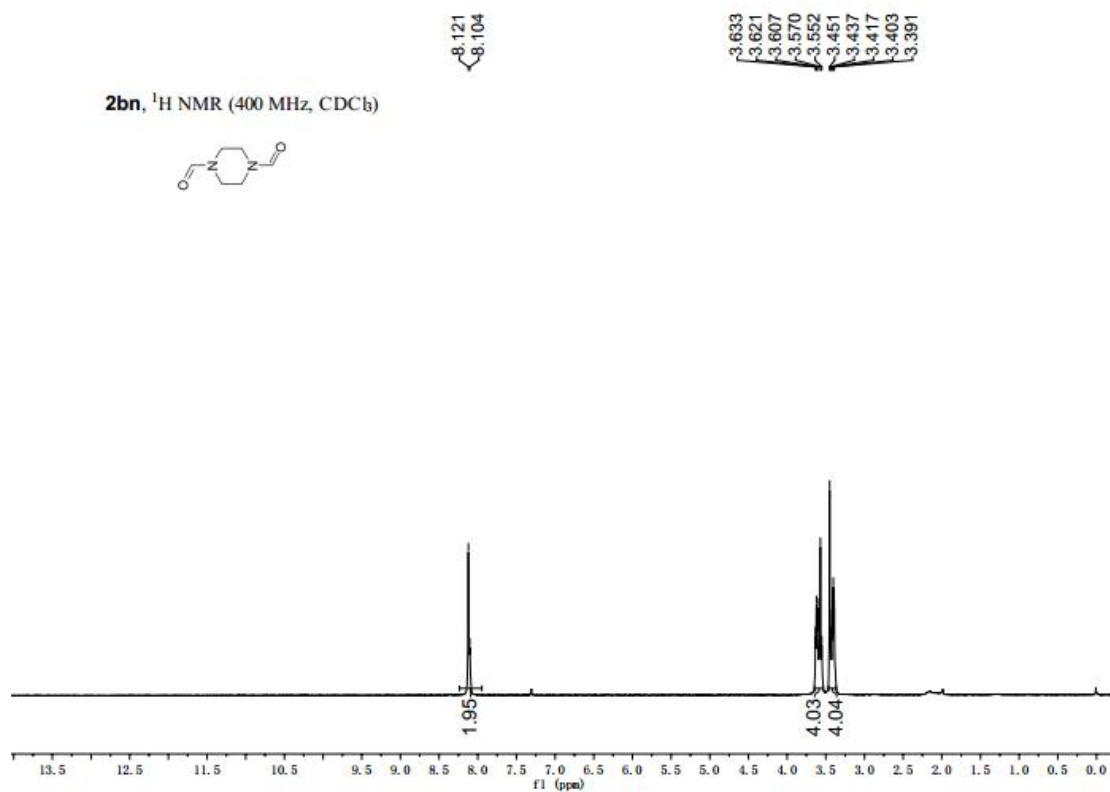
^1H NMR for 4-methylpiperazine-1-carbaldehyde, **2bm**



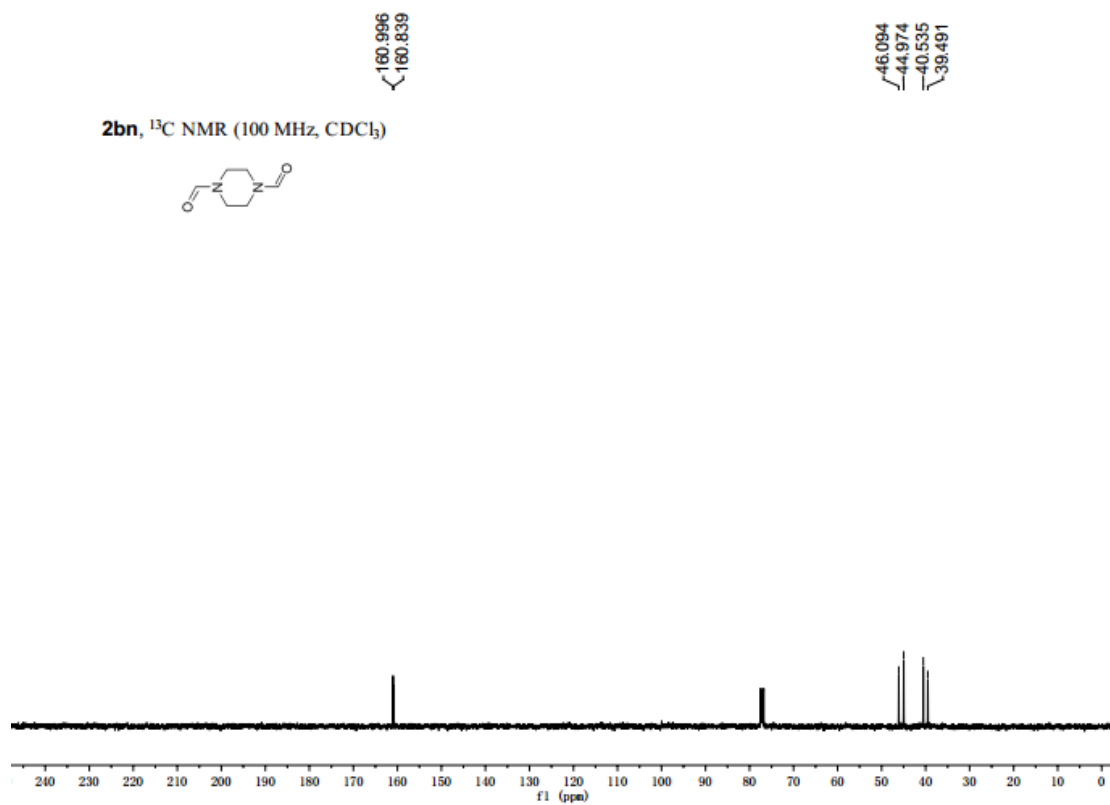
^{13}C NMR for 4-methylpiperazine-1-carbaldehyde, **2bm**



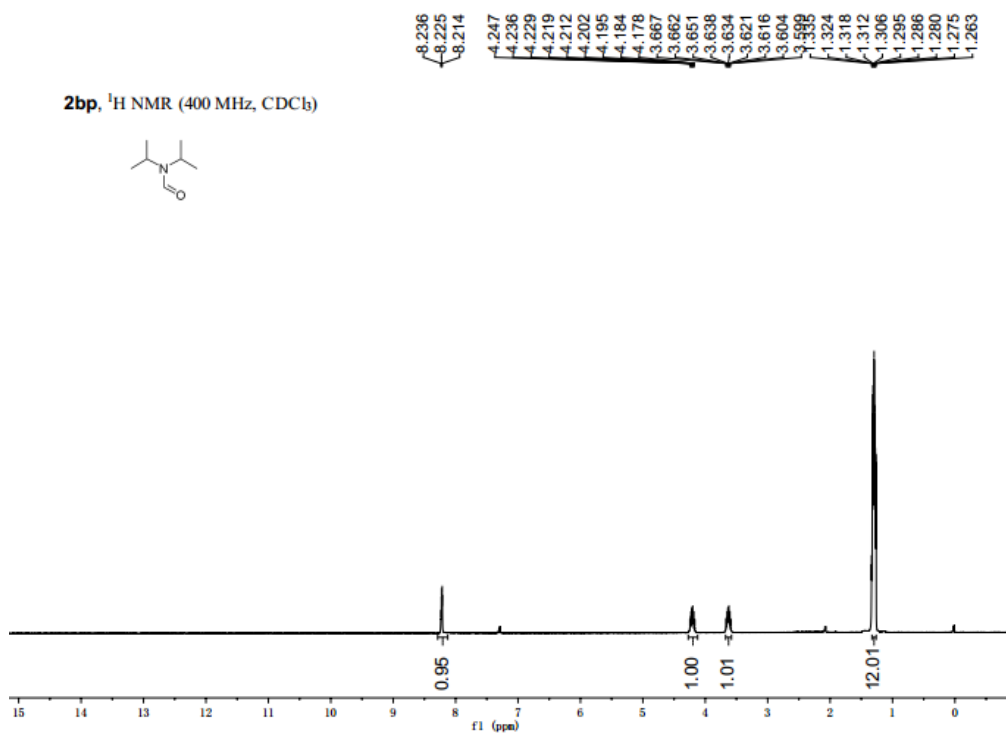
^1H NMR for piperazine-1,4-dicarbaldehyde, **2bn**



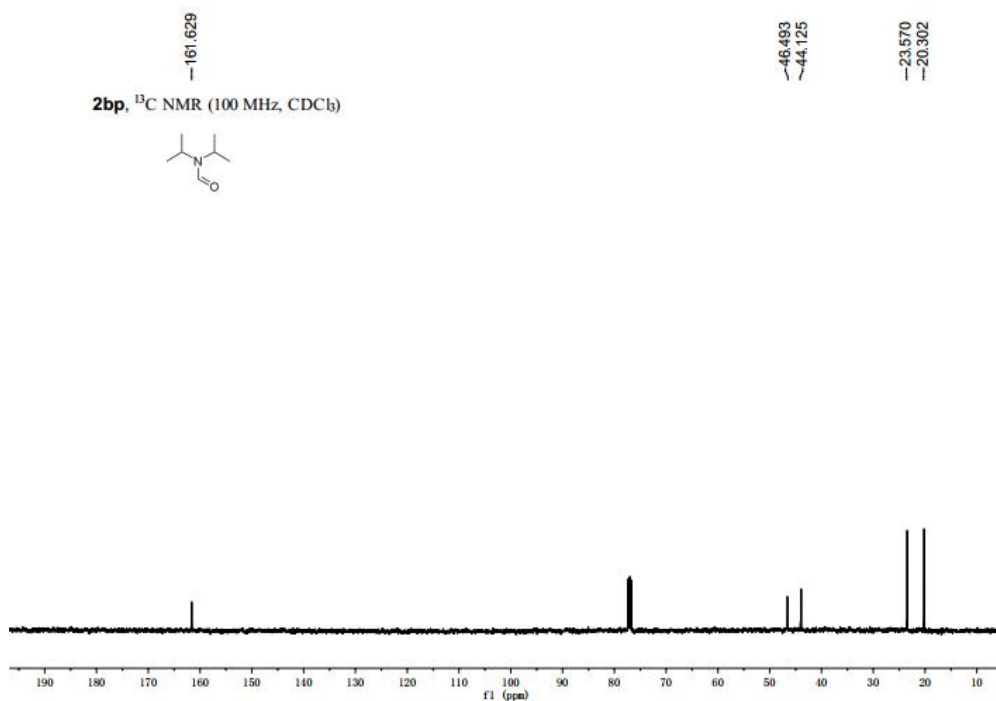
^{13}C NMR for piperazine-1,4-dicarbaldehyde, **2bn**



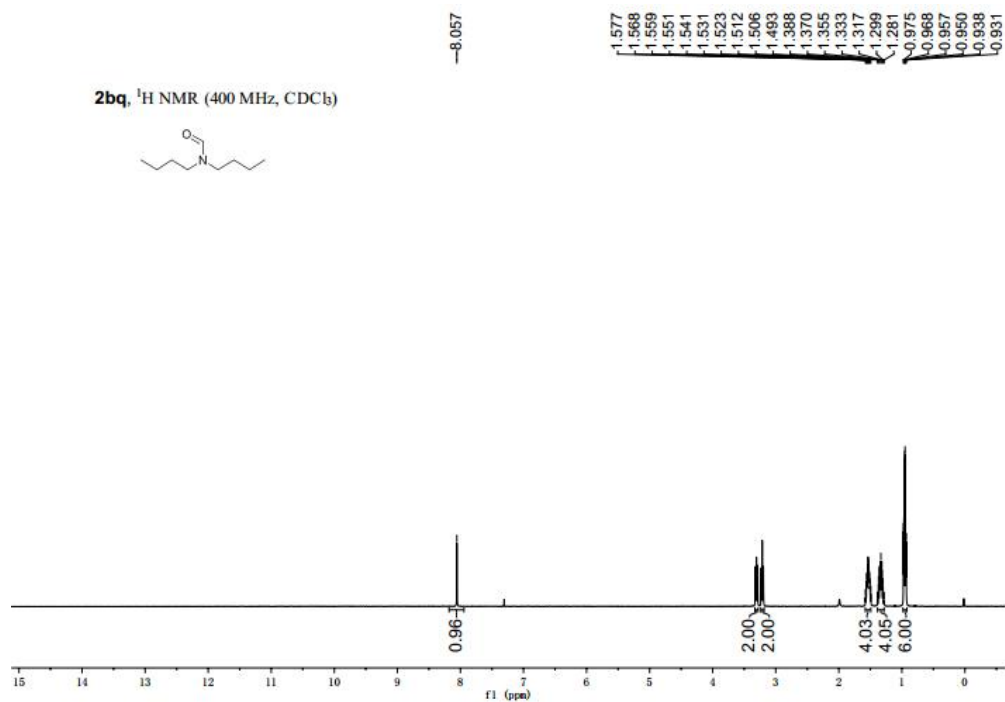
^1H NMR for *N,N*-diisopropylformamide, **2bp**



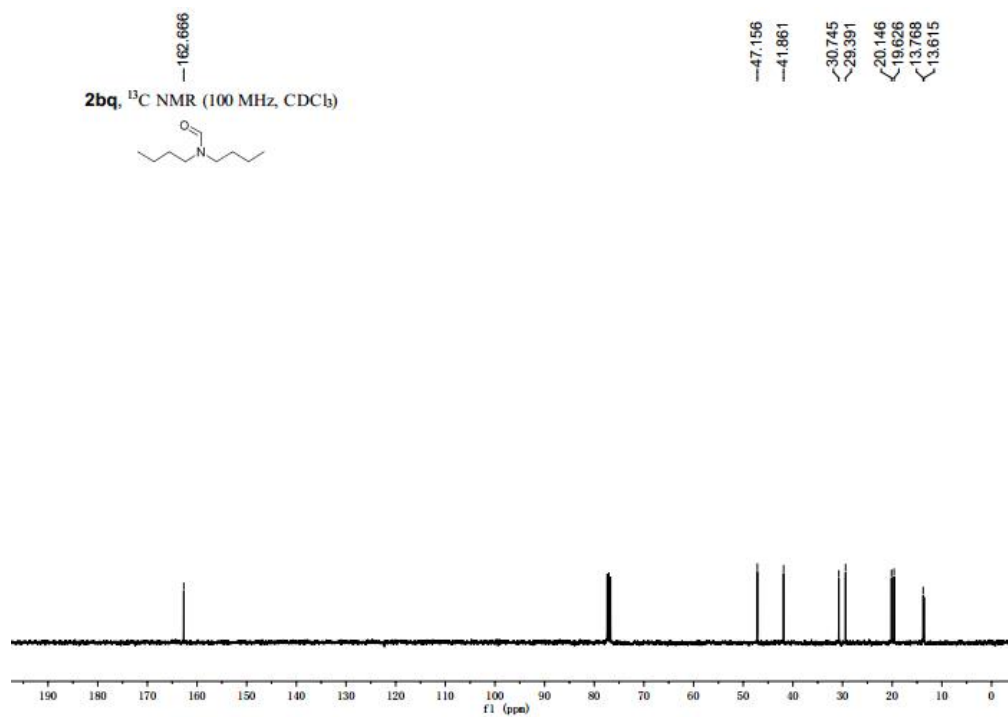
^{13}C NMR for *N,N*-diisopropylformamide, **2bp**



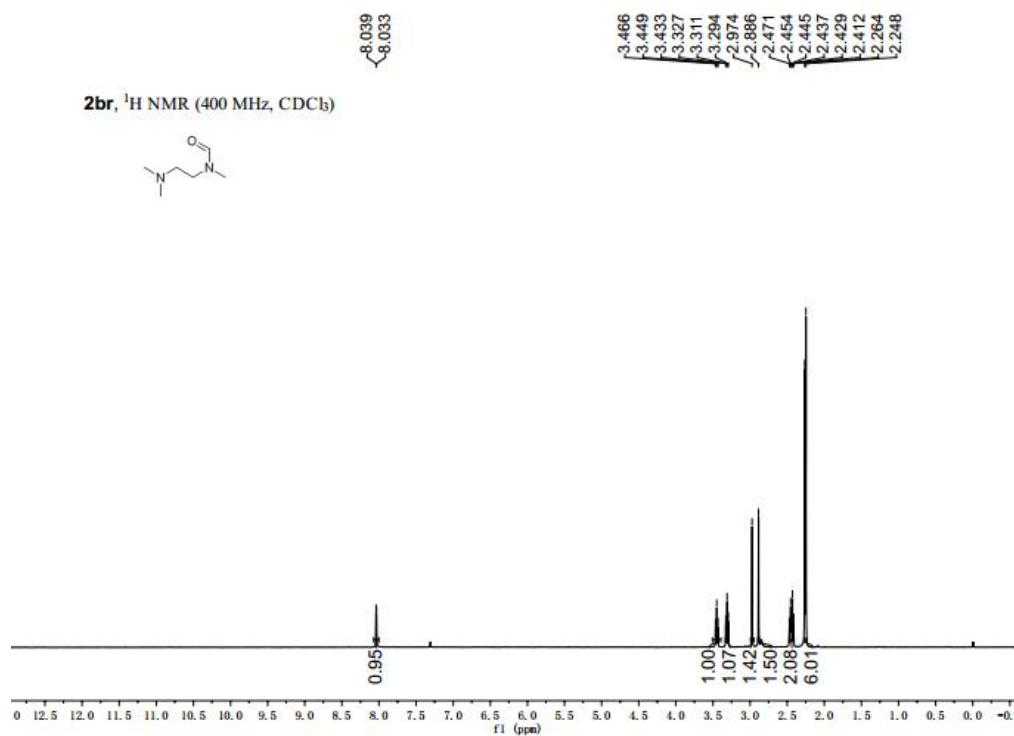
^1H NMR for *N,N*-dibutylformamide, **2bq**



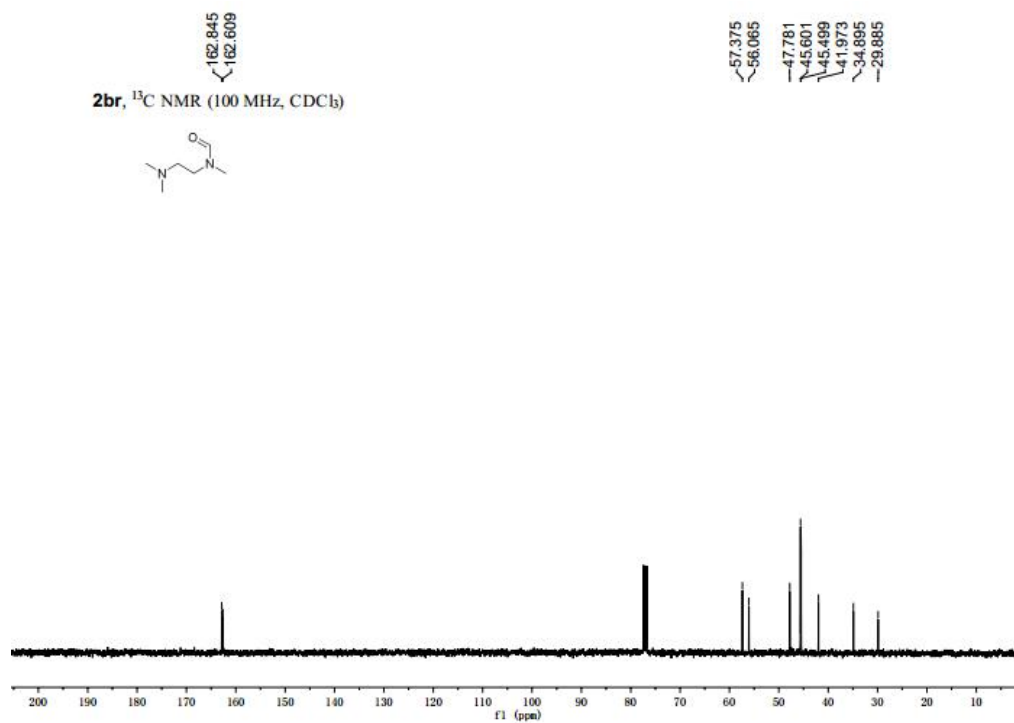
^{13}C NMR for *N,N*-dibutylformamide, **2bq**



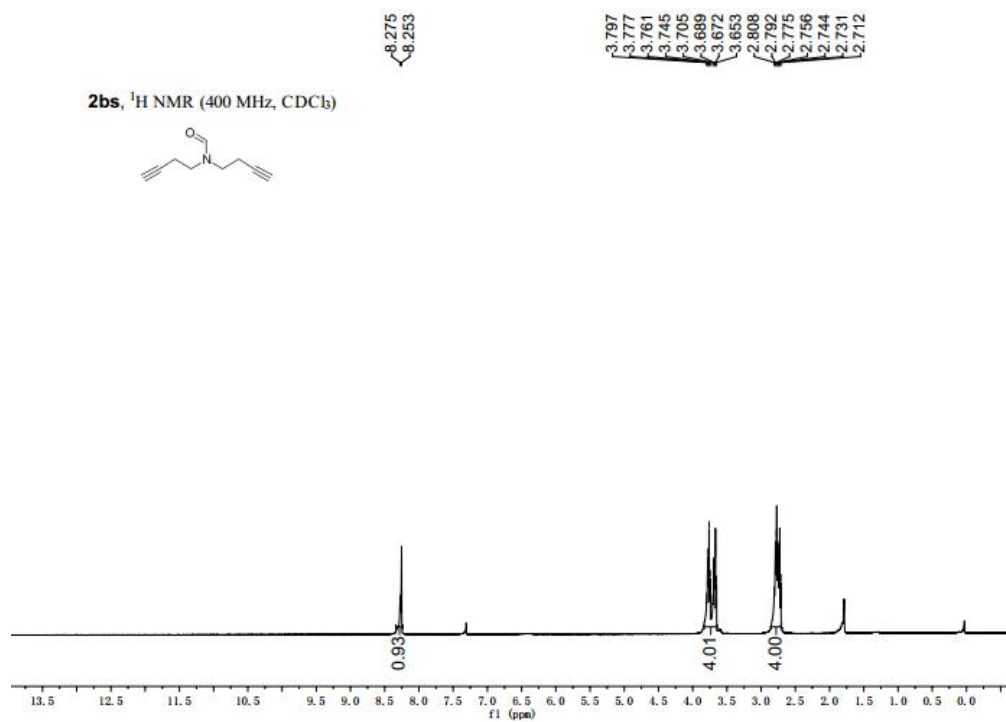
^1H NMR for *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide, **2br**



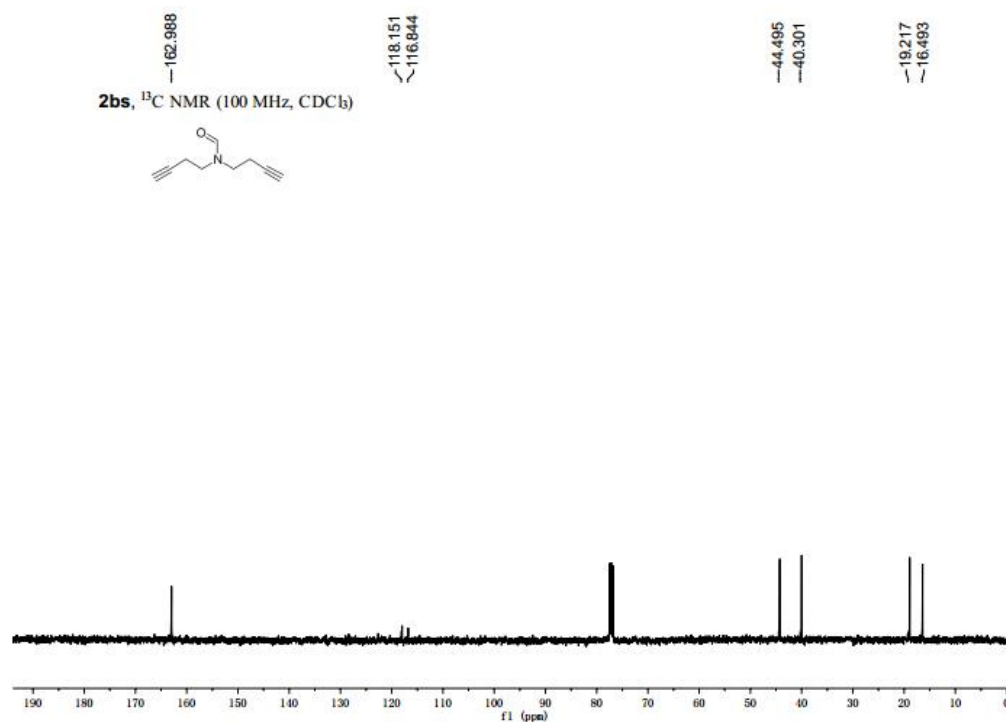
^{13}C NMR for *N*-(2-(dimethylamino)ethyl)-*N*-methylformamide, **2br**



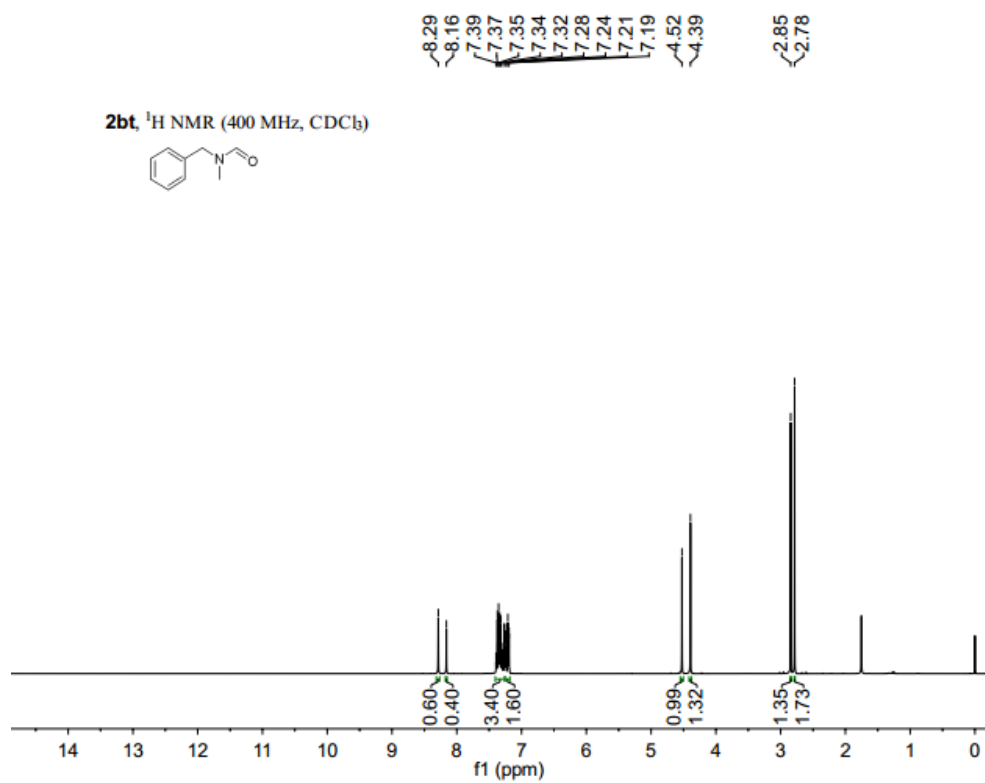
^1H NMR for *N,N*-bis(2-cyanoethyl)formamide, **2bs**



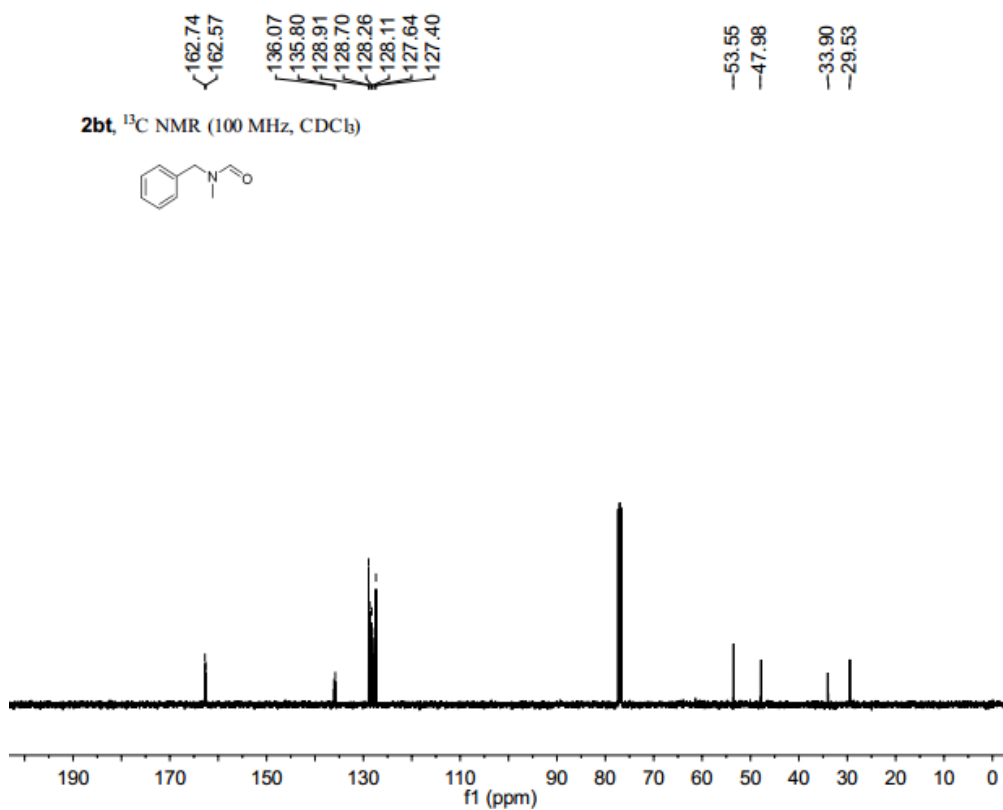
^{13}C NMR for *N,N*-bis(2-cyanoethyl)formamide, **2bs**



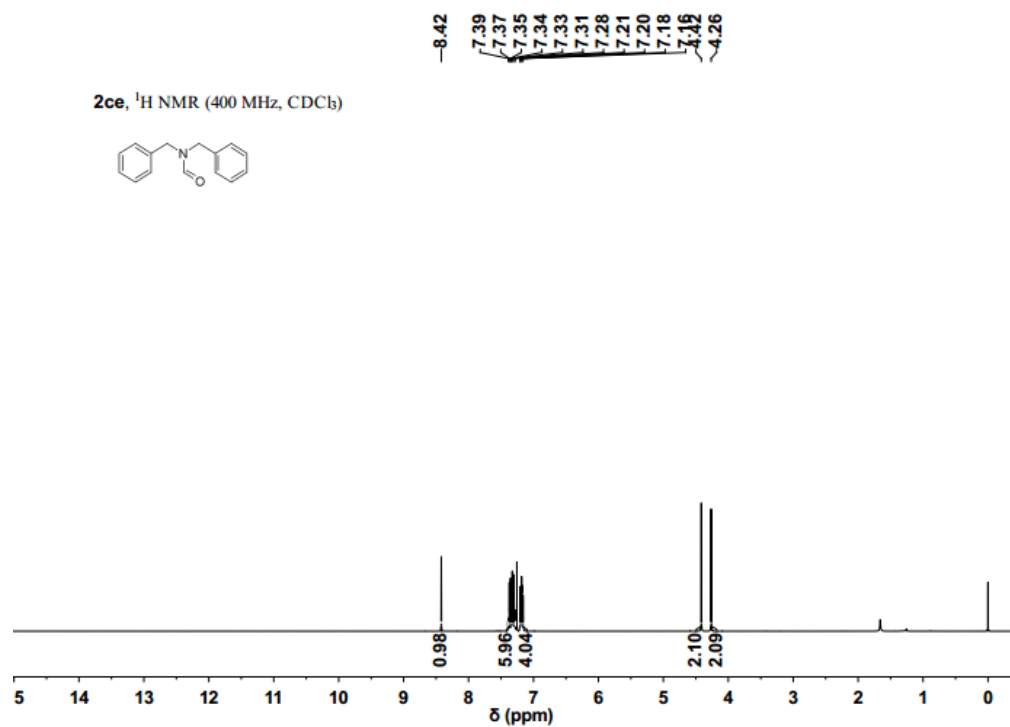
¹H NMR for *N*-benzyl-*N*-methylformamide, **2bt**



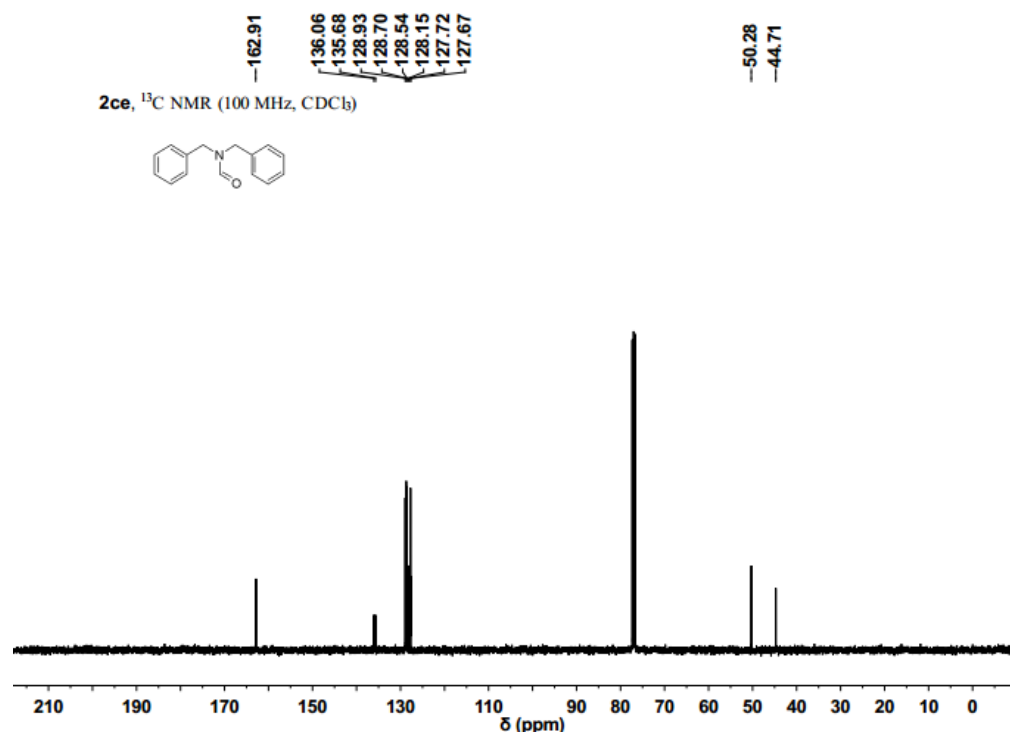
¹³C NMR for *N*-benzyl-*N*-methylformamide, **2bt**



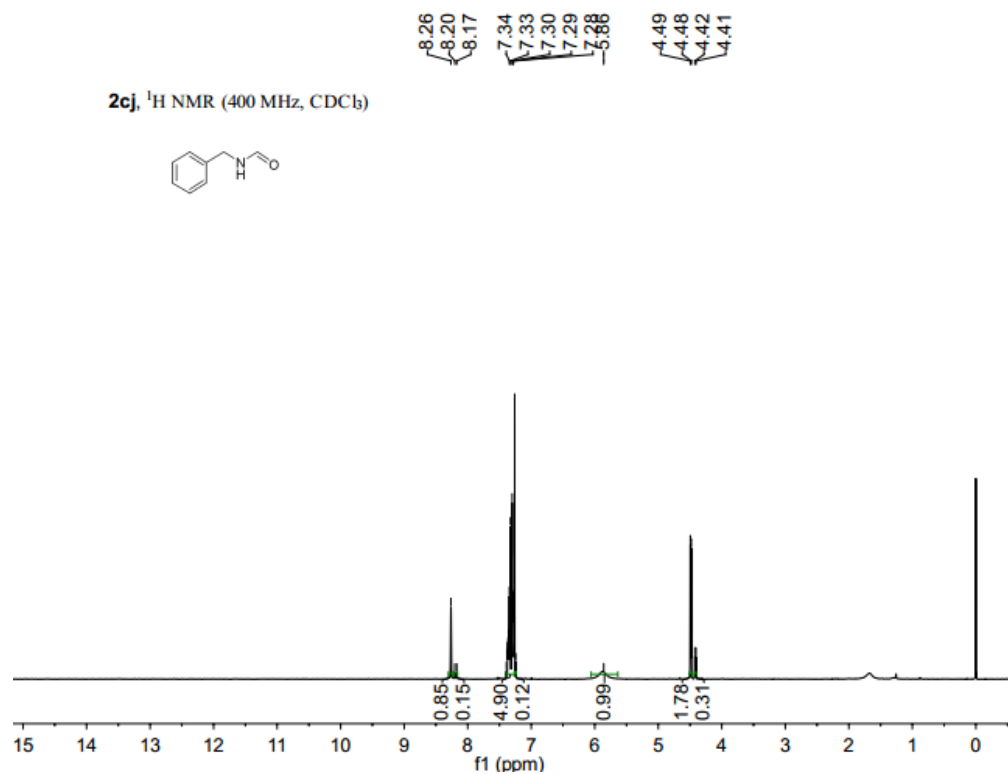
^1H NMR for *N,N*-dibenzylformamide, **2ce**



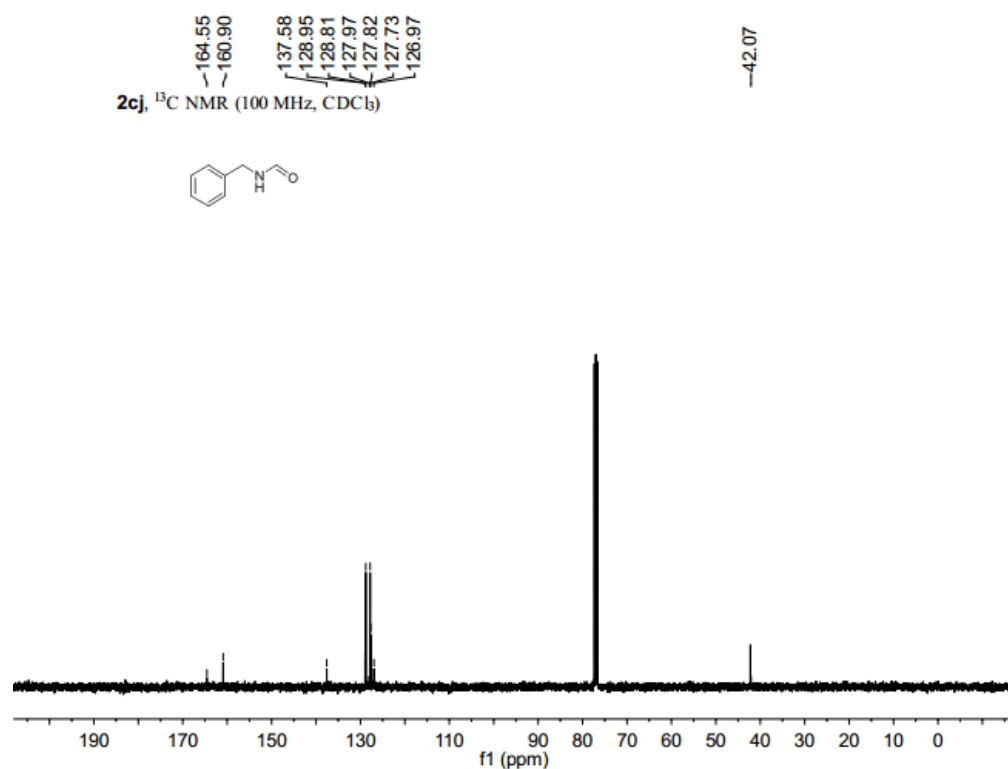
^{13}C NMR for *N,N*-dibenzylformamide, **2ce**



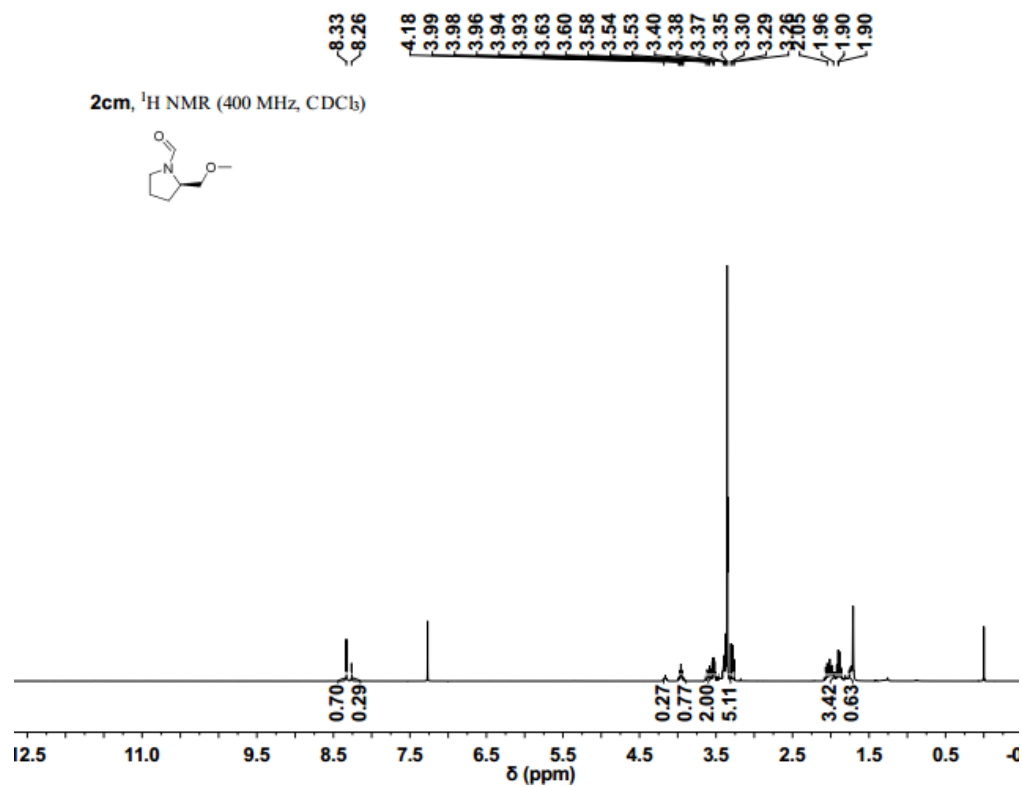
¹H NMR for *N*-benzylformamide, **2cj**



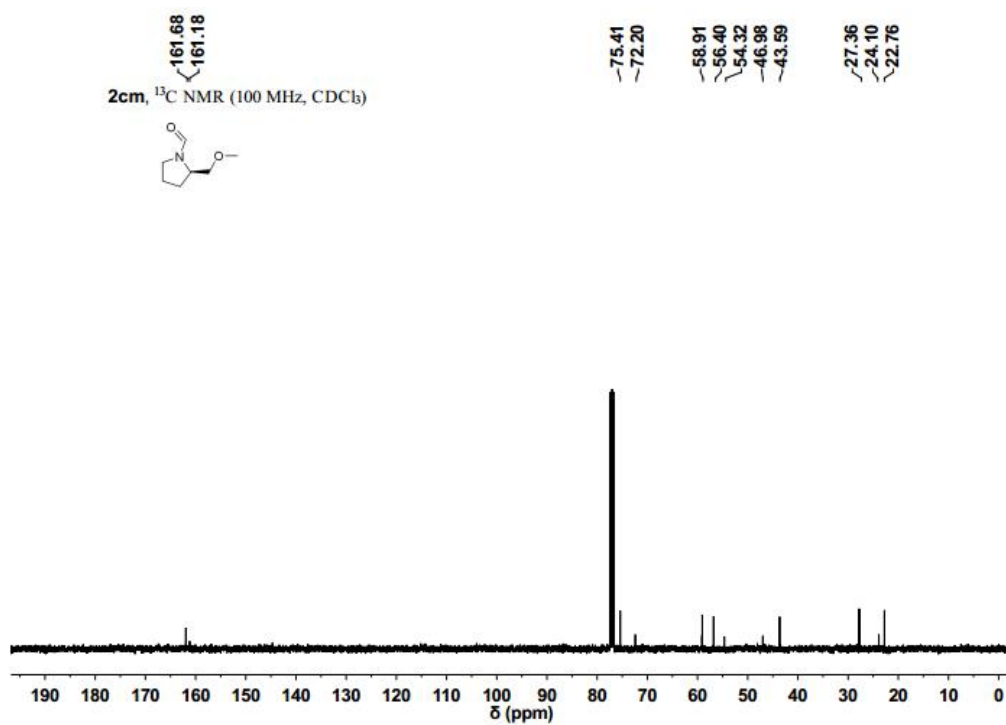
¹³C NMR for *N*-benzylformamide, **2cj**



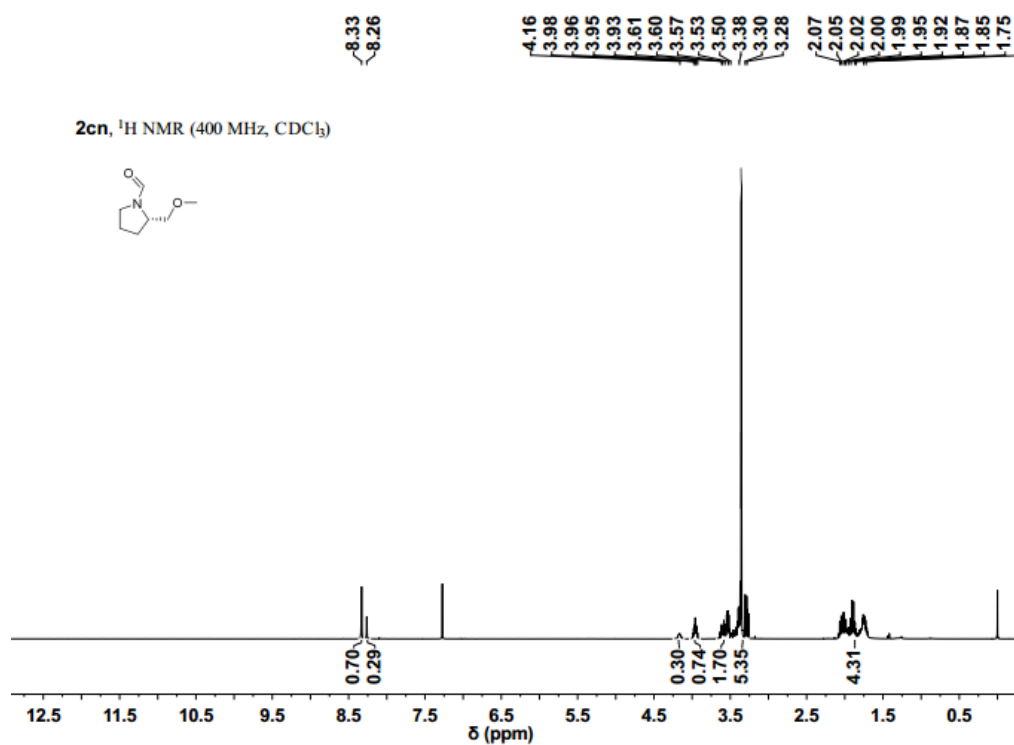
^1H NMR for (*R*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde, **2cm**



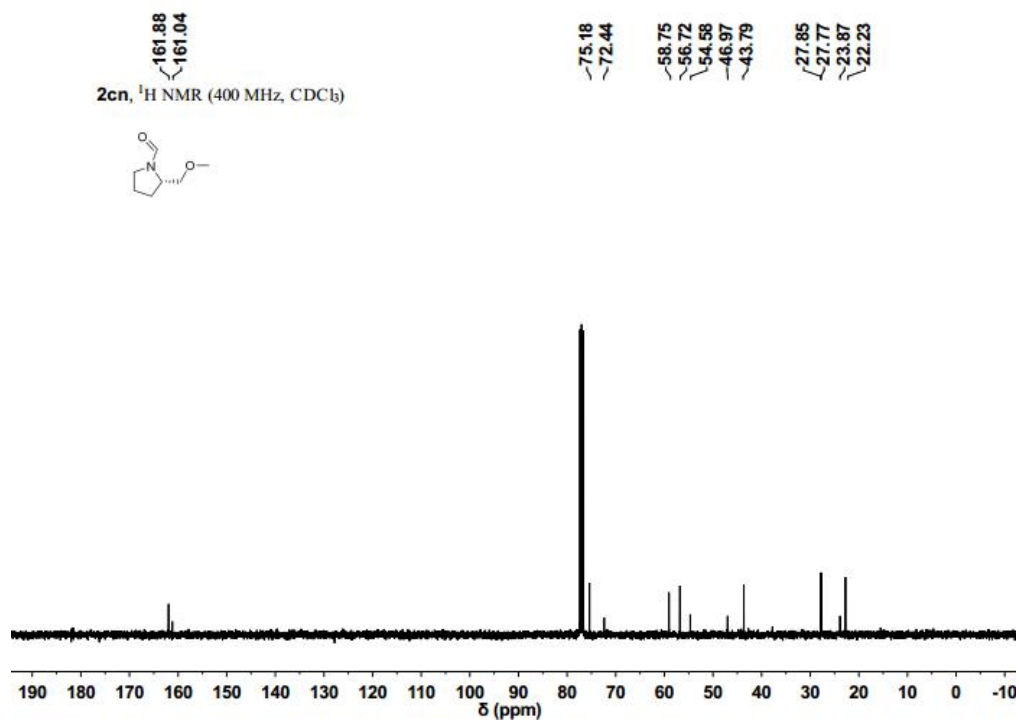
^{13}C NMR for (*R*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde, **2cm**



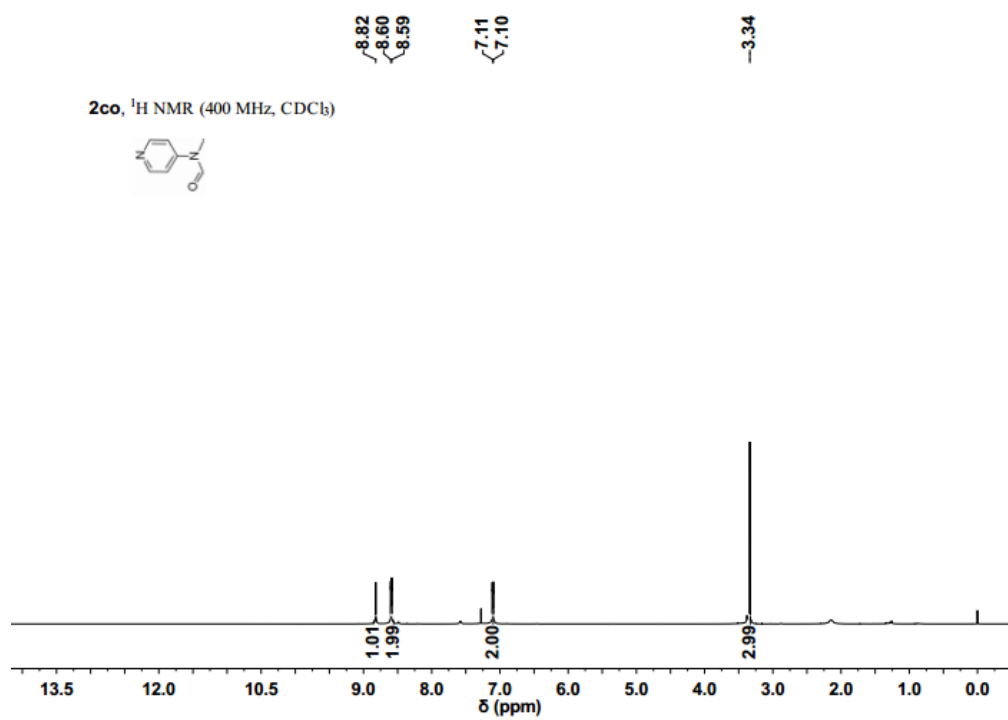
^1H NMR for (*S*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde, **2cn**



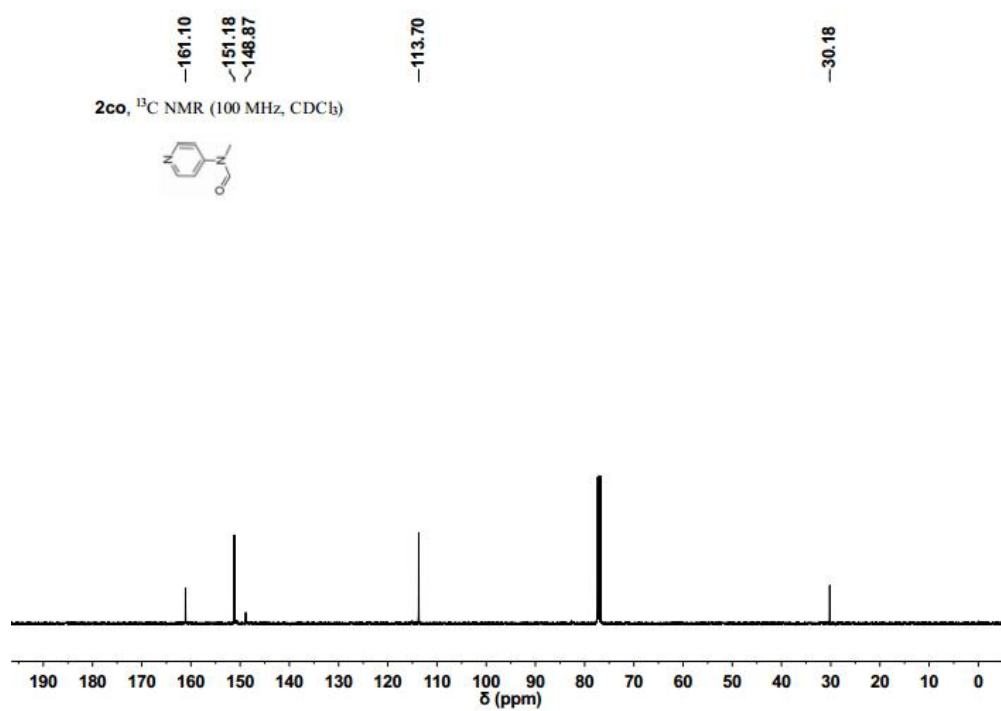
^{13}C NMR for (*S*)-2-(methoxymethyl)pyrrolidine-1-carbaldehyde, **2cn**



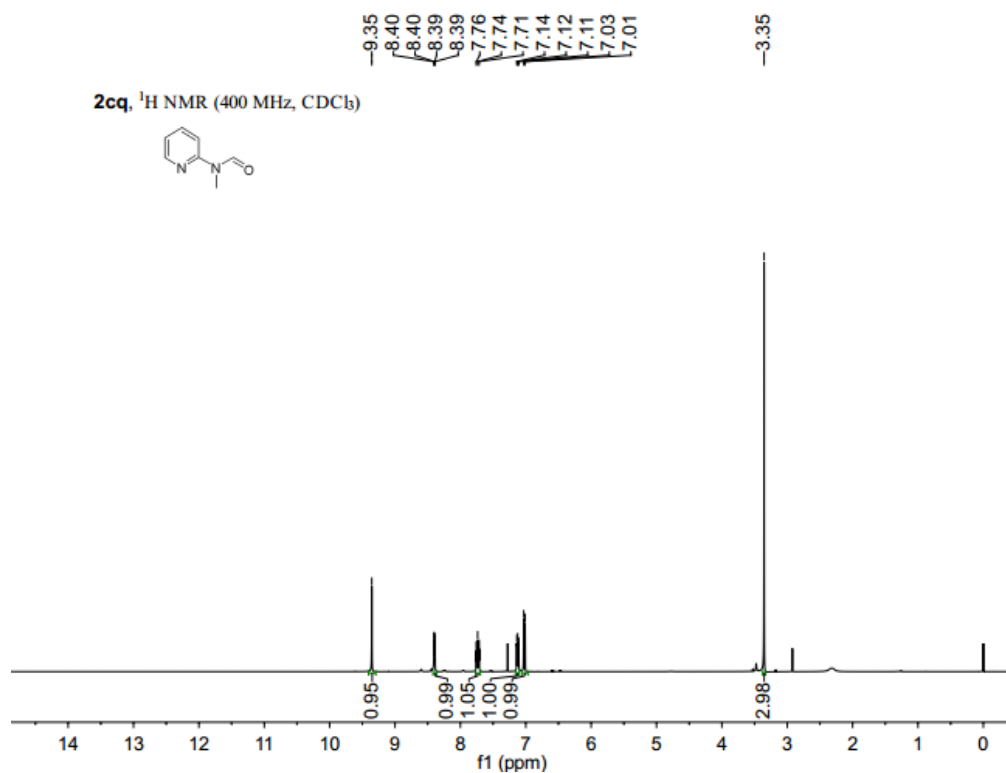
^1H NMR for *N*-methyl-*N*-(pyridin-4-yl)formamide, **2co**



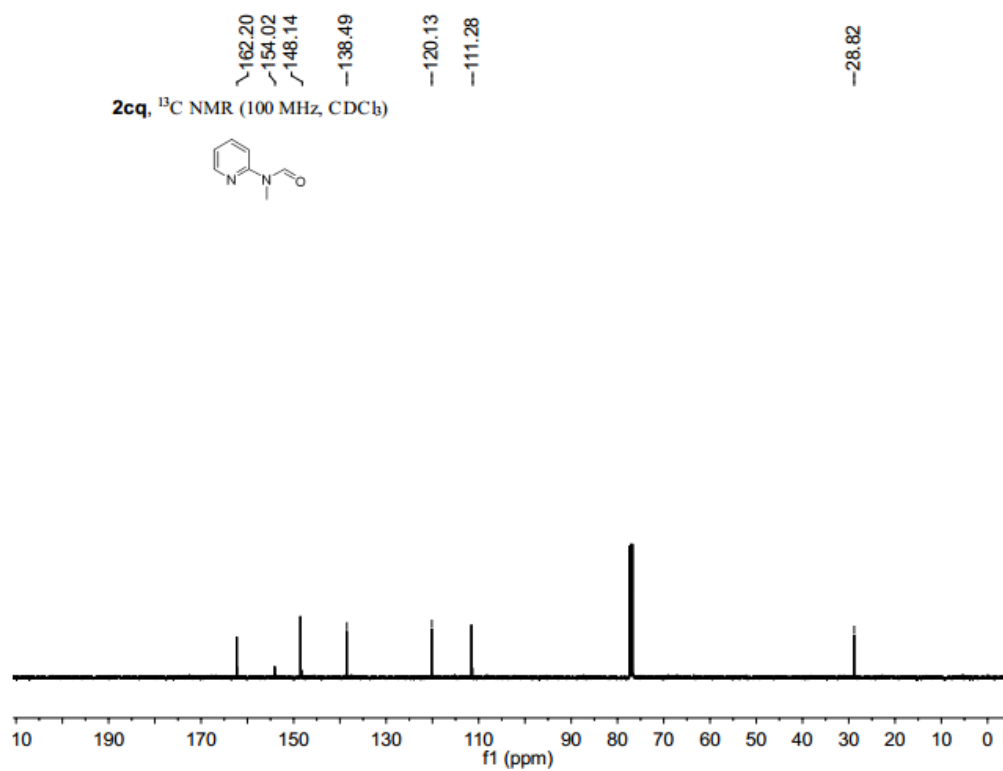
^{13}C NMR for *N*-methyl-*N*-(pyridin-4-yl)formamide, **2co**



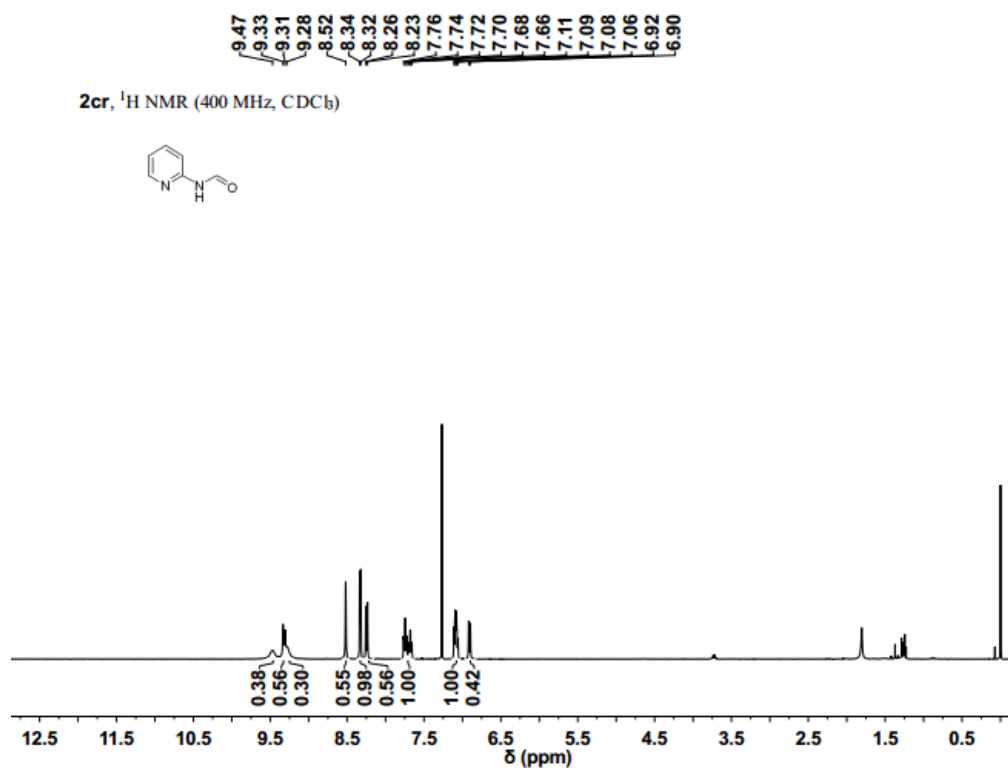
^1H NMR for *N*-methyl-*N*-(pyridin-2-yl)formamide, **2cq**



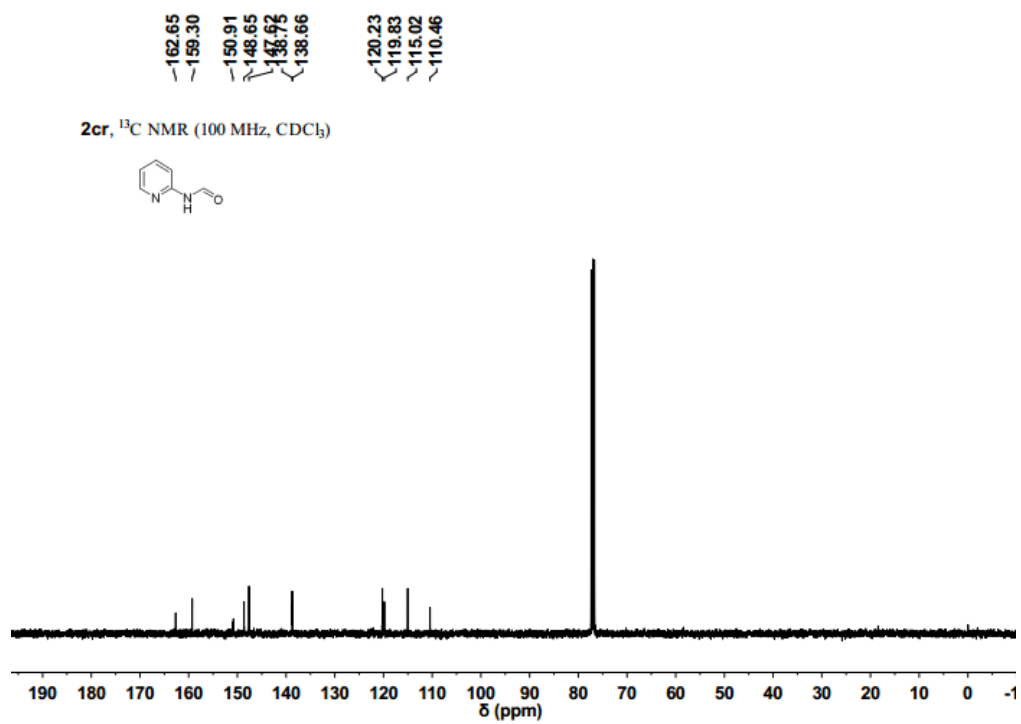
^{13}C NMR for *N*-methyl-*N*-(pyridin-2-yl)formamide, **2cq**



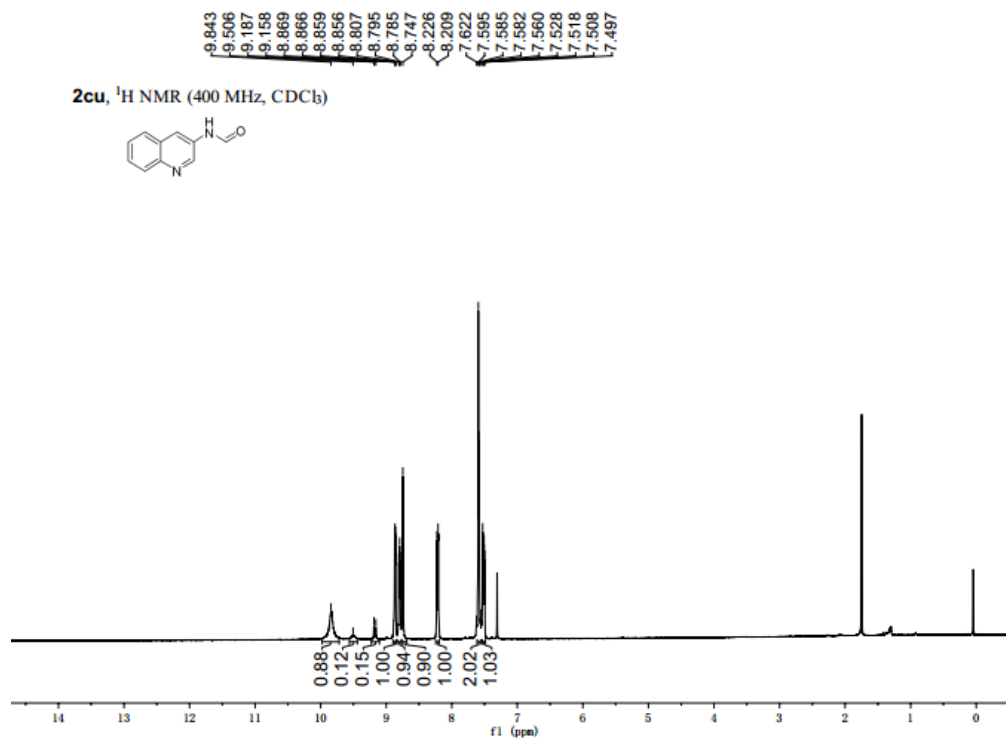
¹H NMR for *N*-(pyridin-2-yl)formamide, **2cr**



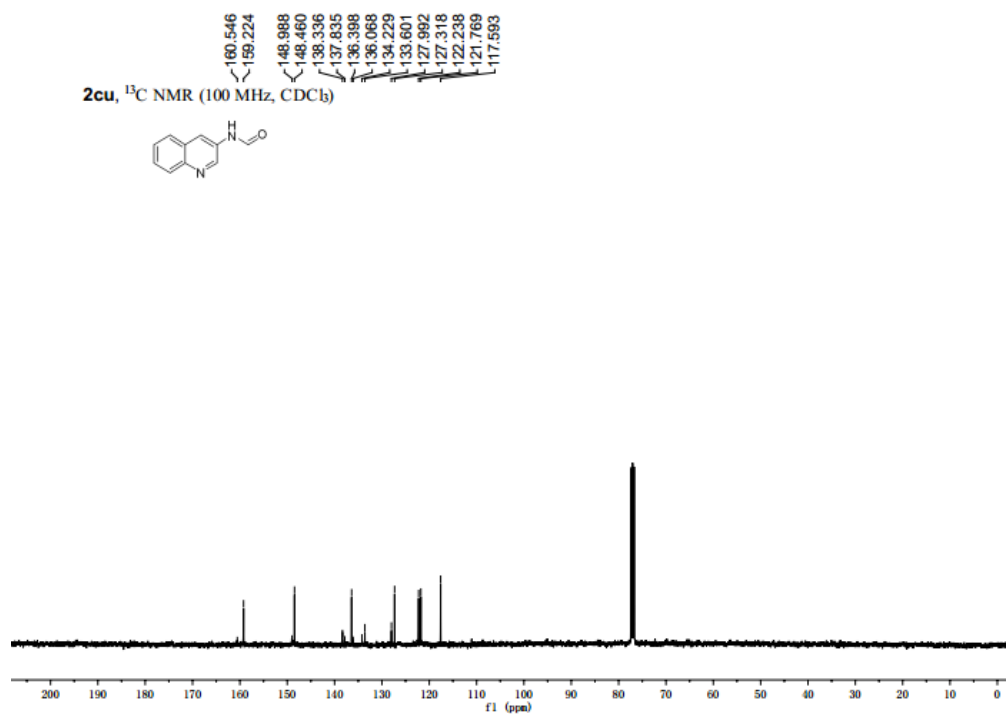
¹³C NMR for *N*-(pyridin-2-yl)formamide, **2cr**



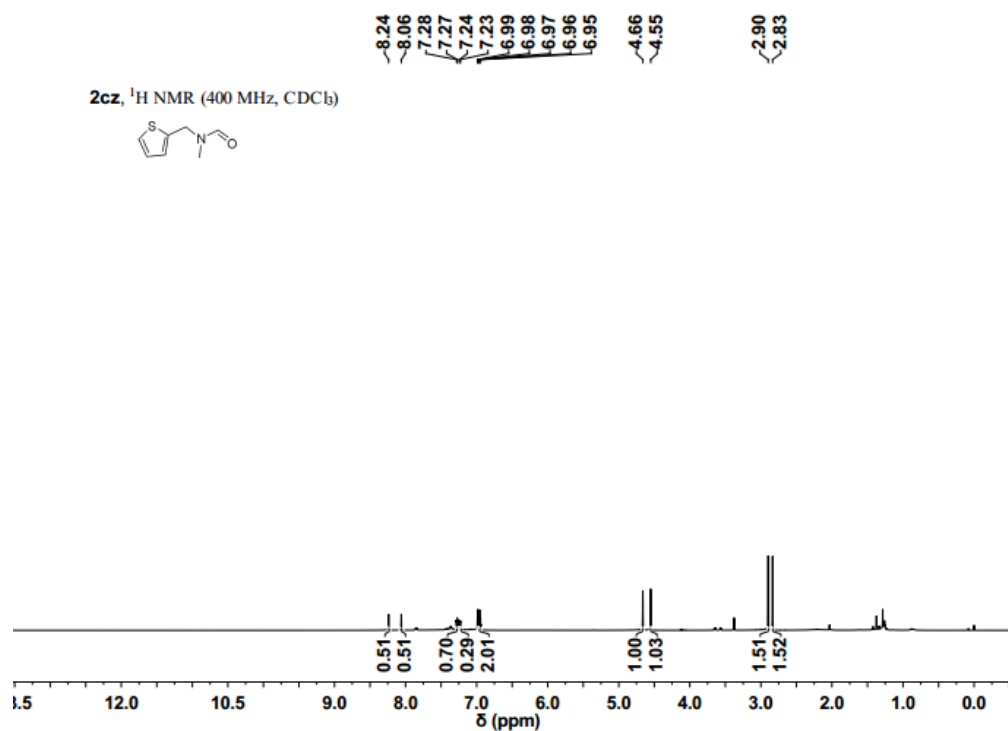
¹H NMR for *N*-(quinolin-3-yl)formamide, **2cu**



¹³C NMR for *N*-(quinolin-3-yl)formamide, **2cu**



^1H NMR for *N*-methyl-*N*-(thiophen-2-ylmethyl)formamide, **2cz**



^{13}C NMR for *N*-methyl-*N*-(thiophen-2-ylmethyl)formamide, **2cz**

