Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

Practical Catalytic Cleavage of C(sp^3)–C(sp^3) Bonds in Amines

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Supporting Information

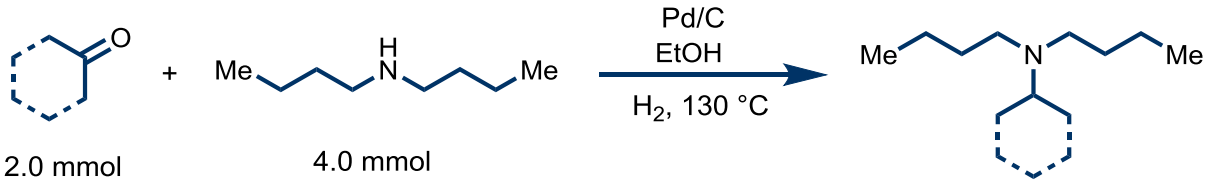
Contents

1. General Remarks

Deuterated solvents were ordered from Deutero GmbH. NMR spectra were received using Bruker 300 Fourier, Bruker AV 300 and Bruker AV 400 spectrometers. Chemical shifts are reported in ppm relative to the deuterated solvent. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet and m = multiplet. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.26 ppm, δC = 77.12 ppm; DMSO-d_6: δH = 2.50 ppm, δC = 39.52 ppm). All measurements were carried out at room temperature unless otherwise stated. Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector. Gas chromatography was performed on a HP 7890A chromatography with a HP5 column. High resolution mass spectra (HRMS) were obtained either from a MAT 95 XP from Thermo (EI) or from an HPLC system 1200 and downstream ESI-TOF-MS 6210 from Agilent (ESI). Thin layer chromatography was performed on Merck TLC-plates with fluorescence indication (silica type 60, F_{254}), spots were visualized using UV-light or vanilline. Column chromatography was performed using silica with a grain size of 40–63 µm from Macherey-Nagel. Solvents were used directly without further purification. HPLC grade MeCN supplier is Fisher Chemical. Linezolid supplier is Gute Chemie–abcr Services**.** Substrates **23a, 24a, 33a, 35a, 37a, 38a, 40a, 41a, 42a, 44a, 45a, 46a, 47a, 48a, 49a, 50a, 51a, 52a, 53a, 57a, 58a, 59a, 68a** were prepared following the method or modified method published by Ma and co-workers (Ma, D., *et al*. *Org. Lett.*, **2003**, *5*, 2453–2455.) Other chemicals were obtained from commercial sources and were used without further purification. Unless otherwise mentioned, all catalytic reactions were carried out in 4 mL or 8 mL glass vials, which were set in an alloy plate and placed inside 300 mL autoclave (PARR Instrument Company).

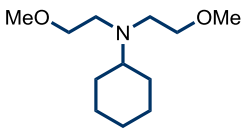
EPR spectra were recorded on a Bruker EMX-micro cw-EPR spectrometer (X-band, $\nu \approx 9.7$ GHz) at different temperature with a microwave power of 6.9 mW, a modulation frequency of 100 kHz and modulation amplitude up to 5G. The EPR spectrometer is equipped with a variable temperature control unit including a liquid N_2 cryostat and a temperature controller. UV-Vis spectra were recorded on an AvaSpec-2048 UV-vis spectrometer (Avantes). To monitor the Cu^{II} signal and detect radical intermediates might be formed upon the catalytic reaction, the reaction was stopped at different time intervals and 50 µL of the reaction mixture were transferred into a glass microcapillary tube (Hirschmann) to record immediately the EPR spectra at room temperature.

2. General Procedure for Substrates Preparation (GR I)

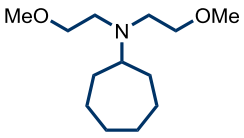


2.0 mmol 4.0 mmol

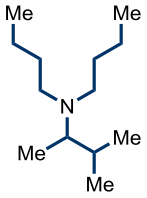
In a 8 mL vial fitted with magnetic stirring bar and septum cap, Pd/C (Palladium on activated charcoal 10% Pd basis (Sigma-Aldrich)) (40 mg) and ketones (2.0 mmol) were added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. EtOH (3.0 mL) was added. The vials (up to seven) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with air 3 times at 5 bar and finally pressurized to the desired value (50 bar). Then it was placed into an aluminium block and heated to the desired temperature (130 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and diluted with acetone. The reaction mixture was analyzed by GC or as isolated product (column chromatograpy: chromatography: *n*-heptane/ethyl acetate) by NMR, GC-MS and HRMS.



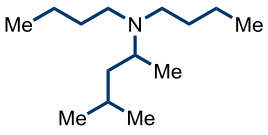
9a 90%



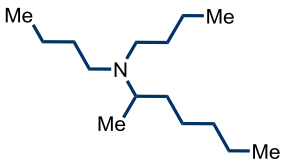
10a 58%



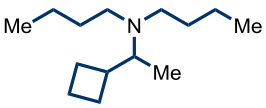
11a 25%



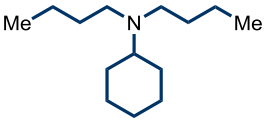
12a 24%



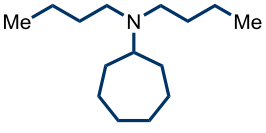
13a 53%



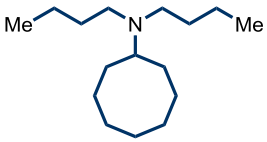
14a 38%



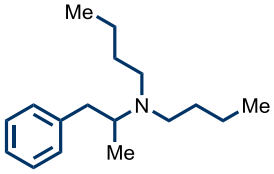
15a 72%



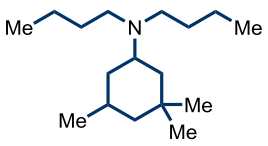
16a 42%



17a 51%

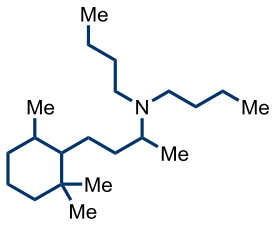


19a 39%



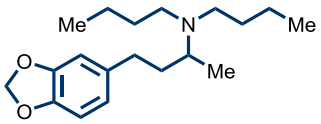
65a 63%

from **Isophorone**



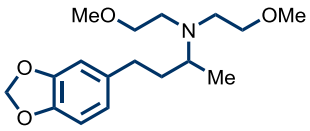
66a 28%

from **α-Ionone**



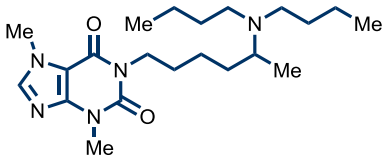
67a 99%

from **Piperonylacetone**



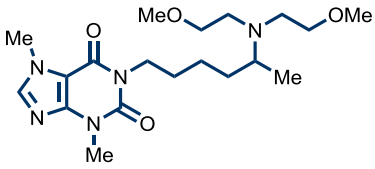
68a 43%

from **Piperonylacetone**



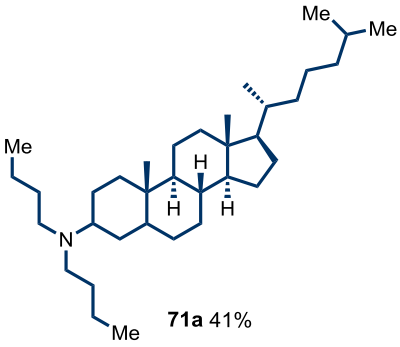
69a 88%

from **Pentoxifylline**



70a 26%

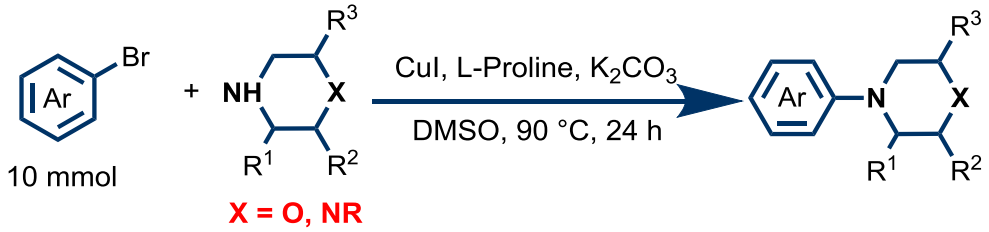
from **Pentoxifylline**



71a 41%

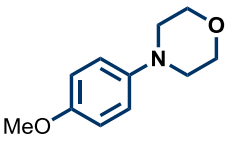
from **5-Cholesten-3-one**

3. General Procedure for Substrates Preparation (GR II)

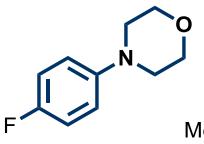


General procedure for the synthesis of substrates (GR I): A mixture of aryl bromide (10 mmol), morpholines (20 mmol), K_2CO_3 (20 mmol), CuI (1.0 mmol) and L-proline (2.0 mmol) in 10 mL of DMSO was heated at 90 °C and for 24 h. The cooled mixture was partitioned between water and ethyl acetate. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, and concentrated in vacuo. The desired products were isolated by silica gel column

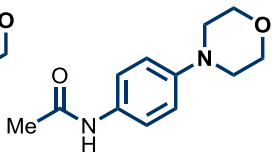
chromatography (*n*-heptane/ethyl acetate mixtures). (Ma, D., *et al*. *Org. Lett.*, **2003**, *5*, 2453–2455.)



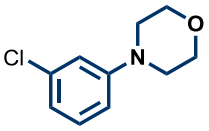
23a 18%



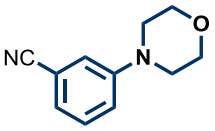
24a 26%



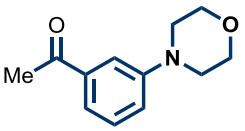
33a 40%



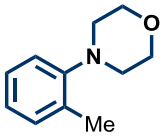
35a 51%



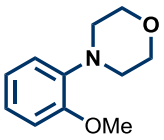
37a 40%



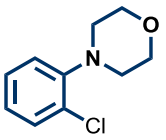
38a 40%



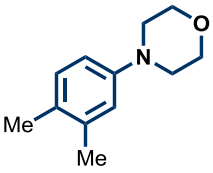
40a 7%



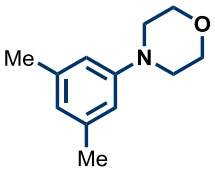
41a 19%



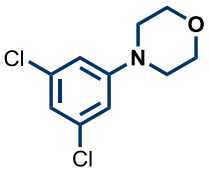
42a 5%



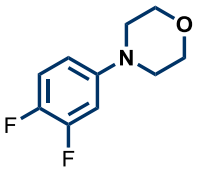
44a 25%



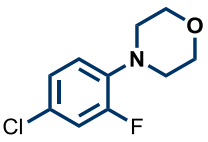
45a 56%



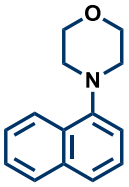
46a 58%



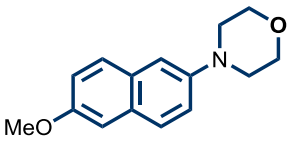
47a 52%



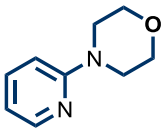
48a 13%



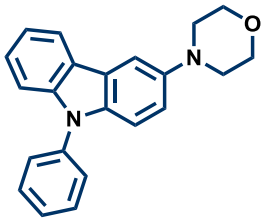
49a 11%



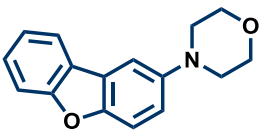
50a 51%



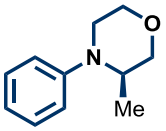
51a 36%



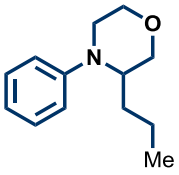
52a 57%



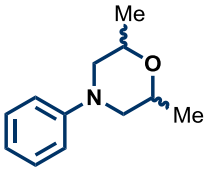
53a 62%



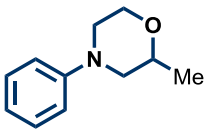
57a 5%



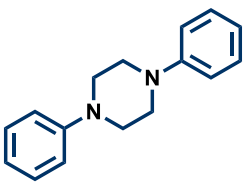
58a 1%



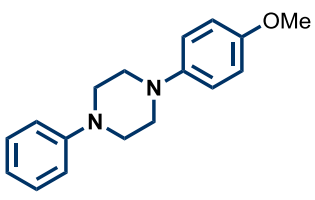
59a 42%



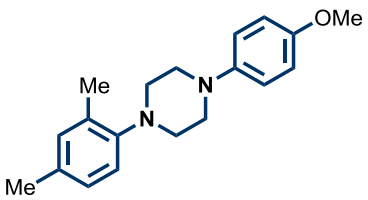
60a 31%



62a 30%

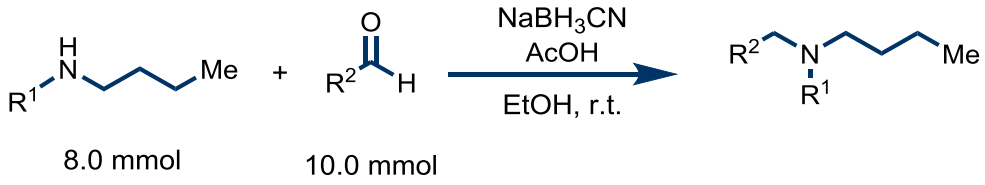


63a 12%

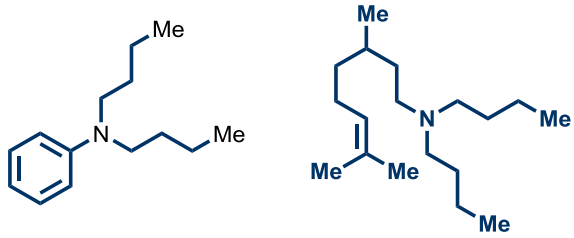


64a 32%

Substrates Preparation (20a and 72a)



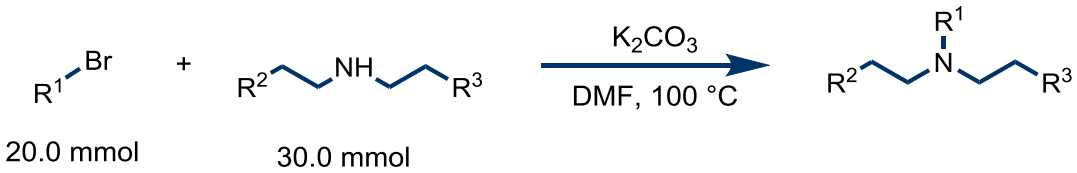
To a 100 mL round bottom flask equipped with magnetic stir bar was added amine (8.0 mmol, 1 equiv.) and methanol (20 mL). Next, aldehyde (10.0 mmol, 1.25 equiv.) was added, followed by $NaBH_3CN$ (10.0 mmol, 1.25 equiv.). After completion (monitored by TLC or GC-FID), the reaction was quenched with saturated $NaHCO_3$ (20 mL) and methanol was removed by evaporation under reduced pressure. The mixture was diluted with H_2O and extracted with ethyl acetate (50 mL x 3). The extracts were combined and washed with brine and dried over anhydrous Na_2SO_4 and filtered. Lastly, the solvent was removed by evaporation under reduced pressure.



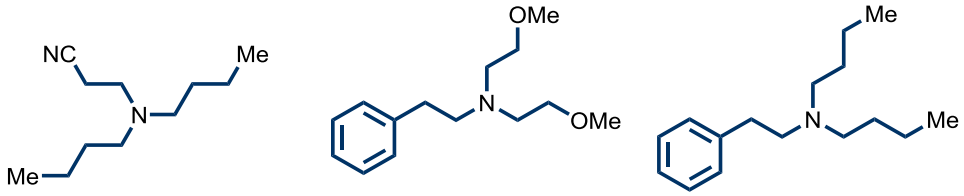
20a 45%

72a 86%

Substrates Preparation (5a, 8a and 18a)



To a 100 mL round bottom flask equipped with magnetic stir bar was added dimethylformamide (20 mL), bromide (20.0 mmol, 1 equiv.) and amine (30.0 mmol, 2.0 equiv.). The reaction mixture was heated to 100 °C. After completion (monitored by TLC or GC-FID), the reaction mixture was filtered to remove K_2CO_3. The mixture was diluted with H_2O and extracted with ethyl acetate (50 mL x 3). The extracts were combined and washed with brine and dried over anhydrous Na_2SO_4 and then filtered. Lastly, solvent and amine was removed by evaporation under reduced pressure.



5a 59% **8a** 73% **18a** 65%

4. General Procedure for the Oxidation Reaction (GR III)

General Procedure for the Oxidative Cleavage of Carbon–Carbon Single Bonds (GR III)
In an 8 mL vial fitted with magnetic stirring bar and septum cap, CuCl (2.5 mg, 0.025 mmol) was added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. MeCN (2.0 mL), pyridine (80 mg) and substrates (tertiary amine, 0.5 mmol) were added, independently. The vials (up to seven) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with air 2 times at 10 bar and finally pressurized to the desired value (30 bar). Then it was placed into an aluminium block and heated to the desired temperature (100 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and diluted with acetone. The reaction mixture was analyzed by GC or as isolated product (column chromatograpy: chromatography: *n*-heptane/ethyl acetate) by NMR, GC-MS and HRMS.

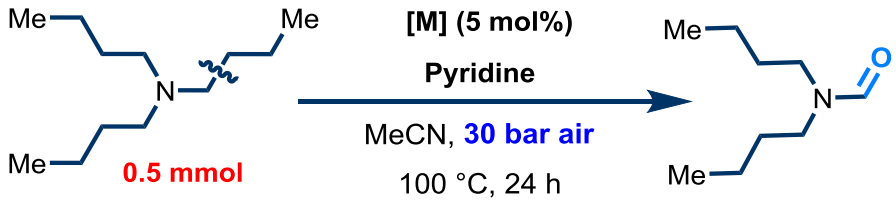
5. General Procedure for the Oxidation Reaction (GR VI)

General Procedure for the Oxidative Cleavage of Carbon–Carbon Single Bonds (GR II)
In a 4 mL vial fitted with magnetic stirring bar and septum cap, $Cu(CF_3SO_3)_2$ (6.0 mg) and *N*-phenylmorpholine were added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. MeCN (2.0 mL) and pyridine (8.0 mg) were added, independently. The vials (up to eight) were set in an alloy plate and then placed into a 300 mL steel Parr autoclave. The autoclave was flushed with air 2 times at 10 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heated to the desired temperature (80 °C) from room temperature. At the end of the reaction,

the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and diluted with acetone. The reaction mixture was analyzed by GC or as isolated product (column chromatography: chromatography: *n*-heptane/ethyl acetate) by NMR, GC-MS and HRMS.

6. Catalytic Experiments

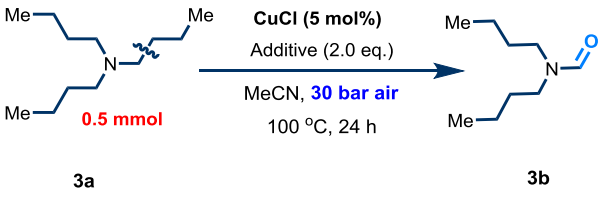
Table S1. Conditions optimisation



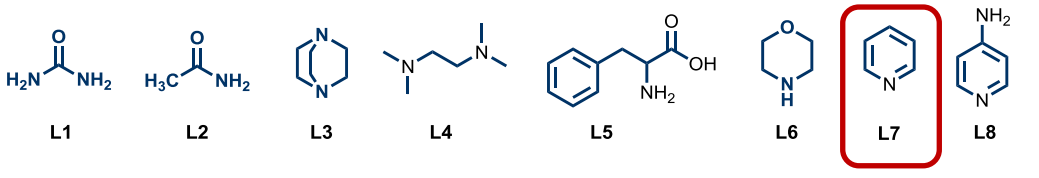
Entry	Catalyst (5 mol%)	Additive	Yield (%)[i]
1	$Pd(OAc)_2$	-	20
2	$RuCl_3$	-	11
3	$Ru(acac)_3$	-	trace
4	$AgCF_3SO_3$	-	trace
5	Ag_2CO_3	-	19
6	$Co(OAc)_2{\cdot}4H_2O$	-	20
7	$Cu(OAc)_2$	-	60
8	CuCl	-	74
9	$CuBr_2$	-	70
10	CuBr	-	70
11	CuI	-	72
12	$Cu(CF_3SO_3)_2$	-	64
13	Copper(II) Phthalocyanine	-	trace
14	CuCl	**L1**	80
15	CuCl	**L2**	78
16	CuCl	**L3**	48

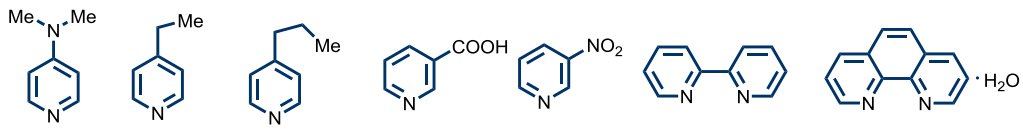
17	CuCl	**L4**	0
18	CuCl	**L5**	0
19	CuCl	**L6**	44
20	**CuCl**	**L7**	**90**
21	CuCl	**L8**	38
22	CuCl	**L9**	53
23	CuCl	**L10**	67
24	CuCl	**L11**	67
25	CuCl	**L12**	72
26	CuCl	**L13**	60
27	CuCl	**L14**	33
28	CuCl	**L15**	trace
29	CuCl	**L7** (20 mol%)	74
30	CuCl	**L7** (40 mol%)	80
31	CuCl	**L7** (1.0 eq.)	84
32	CuCl	**L7** (2.0 eq.)	72[‡]
33	CuCl	**L7** (2.0 eq.)	74*
34	-	**L7** (2.0 eq.)	trace

Reaction conditions: Tri-*n*-butylamine **3a** (0.5 mmol), catalyst (5 mol%) and additive (y mol%), 30 bar air, MeCN, 100 °C. [‡]Yield determined by GC using *n*-dodecane as the standard. [‡]20 bar air, 80 °C. *CuCl (3 mol%).



3a 3b

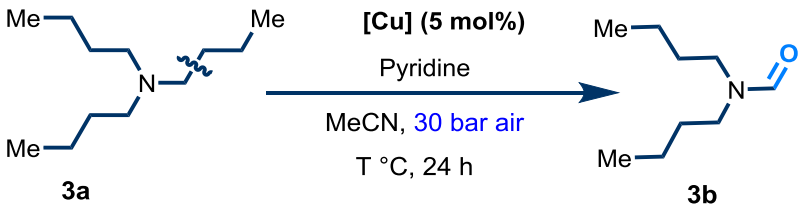




Reaction conditions: Tri-*n*-butylamine **3a** (0.5 mmol), catalyst (5 mol%) and additive (2.0 eq.), 30 bar air, MeCN (2.0 mL), 100 °C, 24 h.

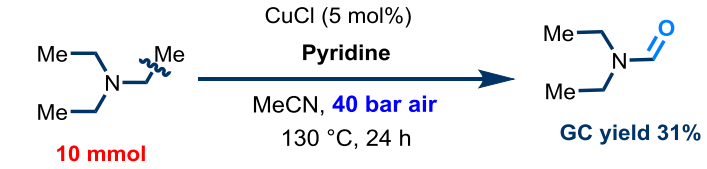
As part of a program to develop new catalysts for the oxidation of amines, recently we investigated the reaction of tributylamine (**3a**, 0.5 mmol) with molecular oxygen in the presence of different potential metal catalysts (5 mol%). In general, the reactions of the benchmark substrate were performed in aerobic atmosphere (30 bar) at 100 °C using acetonitrile as solvent due to its stability against oxidation. Among the tested catalysts trace or only low activity was observed in the presence of $Pd(OAc)_2$, $RuCl_3$, $Ru(acac)_3$, $AgCF_3SO_3$, Ag_2CO_3 $Co(OAc)_2{\cdot}4H_2O$ (Table S1, entries 1-6). Surprisingly, using $Cu(OAc)_2$ *N,N*-dibutylformamide was obtained in 60% yield (Table S1, entry 7). Apparently, in this case a selective cleavage of the C-C bond took place. Consequently, other copper salts, such as CuCl, $CuBr_2$, CuBr, CuI, $Cu(CF_3SO_3)_2$ and copper(II) phthalocyanine were examined as the catalyst (Table S1, entries 8-13), and CuCl gave the highest yield. As nitrogen-containing additives are known to improve the efficiency of aerobic oxidation reactions, urea and acetamide were added to the model substrate using CuCl due to the stability (Table S1, entries 14 and 15).[1] Notably, in the presence of urea, the product yield increased to 80% (Table S1, entry 14). Decreased yields or no desired C-C bond cleavage product was observed using DABCO (1,4-diazabicyclo[2.2.2]octane), TMEDA (N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine), L-phenylalanine and morpholine (Table S1, entries 6-19), which have been mostly relied on in aerobic oxidation reactions. To our delight, in the presence of pyridine, the product yield increased to 90% (Table S1, entry 20). More expensive pyridines with electron-rich as well as electron-poor substituents gave no improvement (Table S1 entries 21-26). From a mechanistic point it is interesting that the bidentate ligand 2,2'-bipyridine and 1,10-phenanthroline monohydrate (Table S1 entries 27 and 28) gave much lower yields of product. Decreased amounts of pyridine and catalyst loading as well as lower temperature lead to less *N,N*-dibutylformamide (Table S1 entries 29-32). Finally, the efficiency and selectivity of the reaction dramatically decreased in the absence of a copper catalyst (Table S1, entry 34). Notably, dehydrogenated product *N,N*-dibutylbut-1-en-1-amine was observed by GC-MS (Fig. S2 and Scheme S2). Interestingly, *N,N*-dibutylformamide formed and dehydrogenated intermediate disappeared while CuCl catalyst was added. This dehydrogenated product could be an intermediate of this C-C bond cleavage reaction.

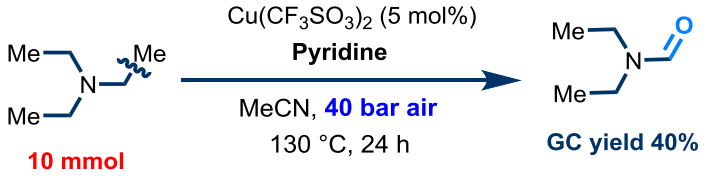
Table S2. Catalytic Experiments: tri-n-butylamine

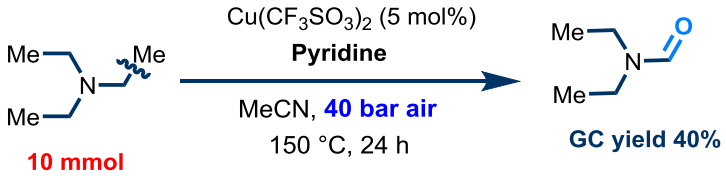


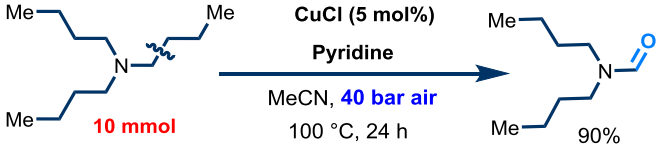
Catalyst	Additive (200 mol%)	Temperature (°C)	Yield (%)
Cu_2O	-	80	trace
	-	120	42
	Pyridine	80	trace
		100	34
CuO	-	80	trace
	-	120	10
	Pyridine	80	0
		100	trace
Reaction conditions: Tri-*n*-butylamine **3a** (0.5 mmol), catalyst (5 mol%) and additive (y mol%), 30 bar air, MeCN, T °C. [t]Yield determined by GC using *n*-dodecane as the standard.			

Upscale reactions









Control experiments.

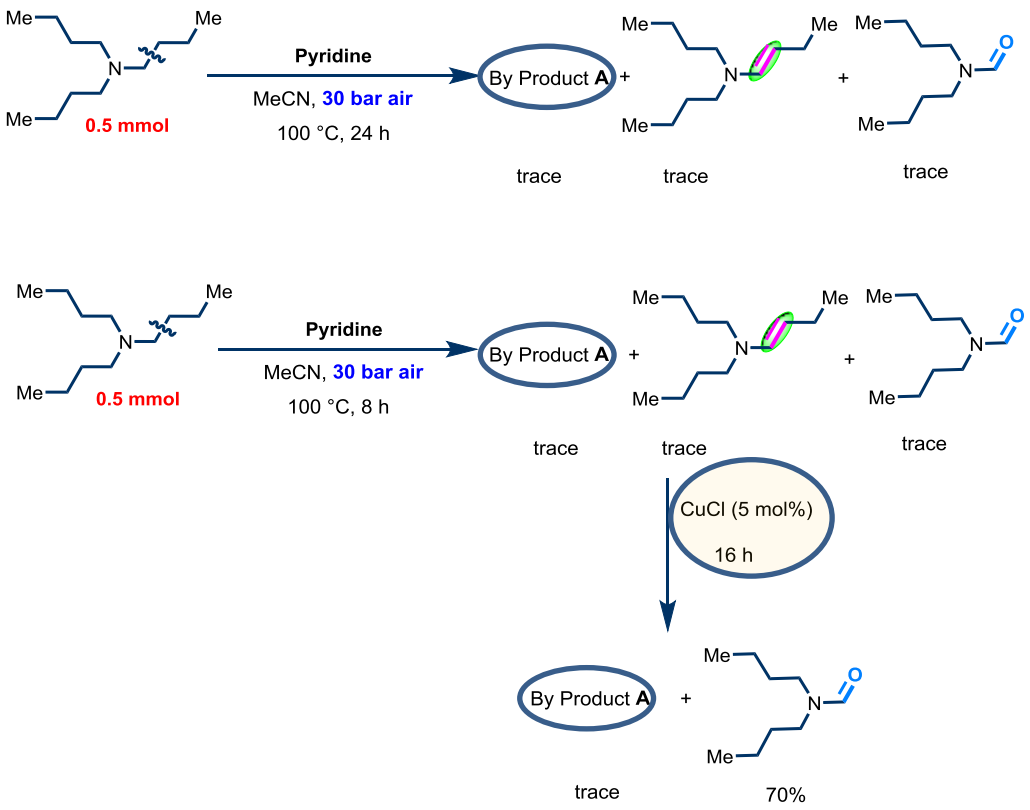
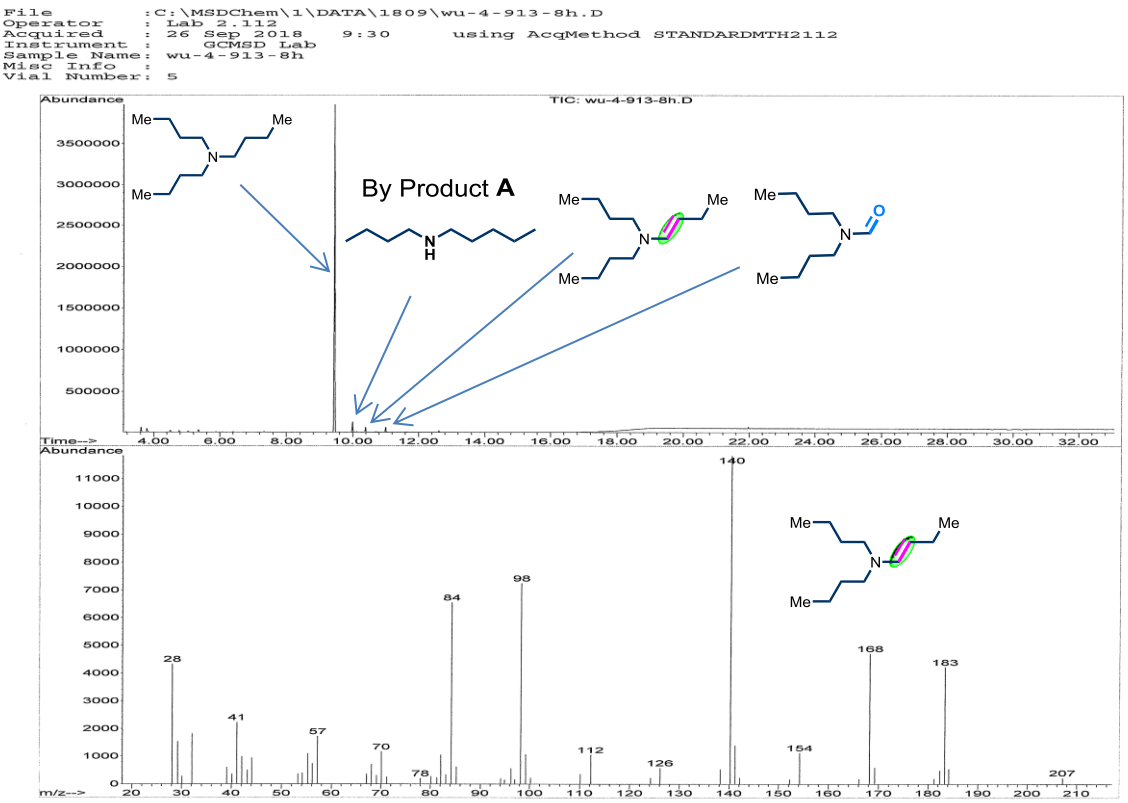
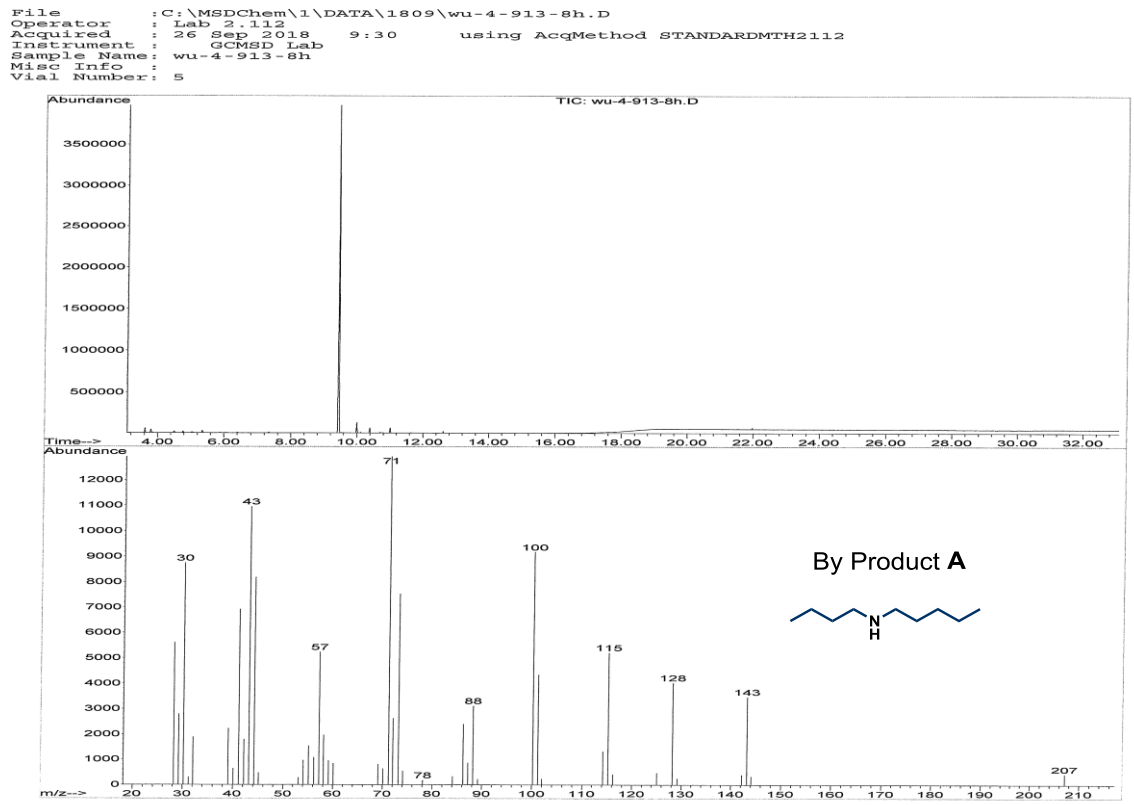
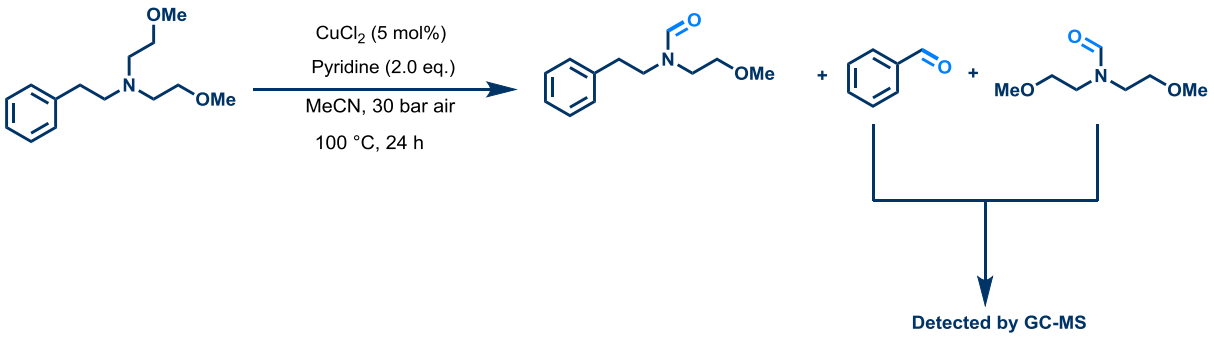


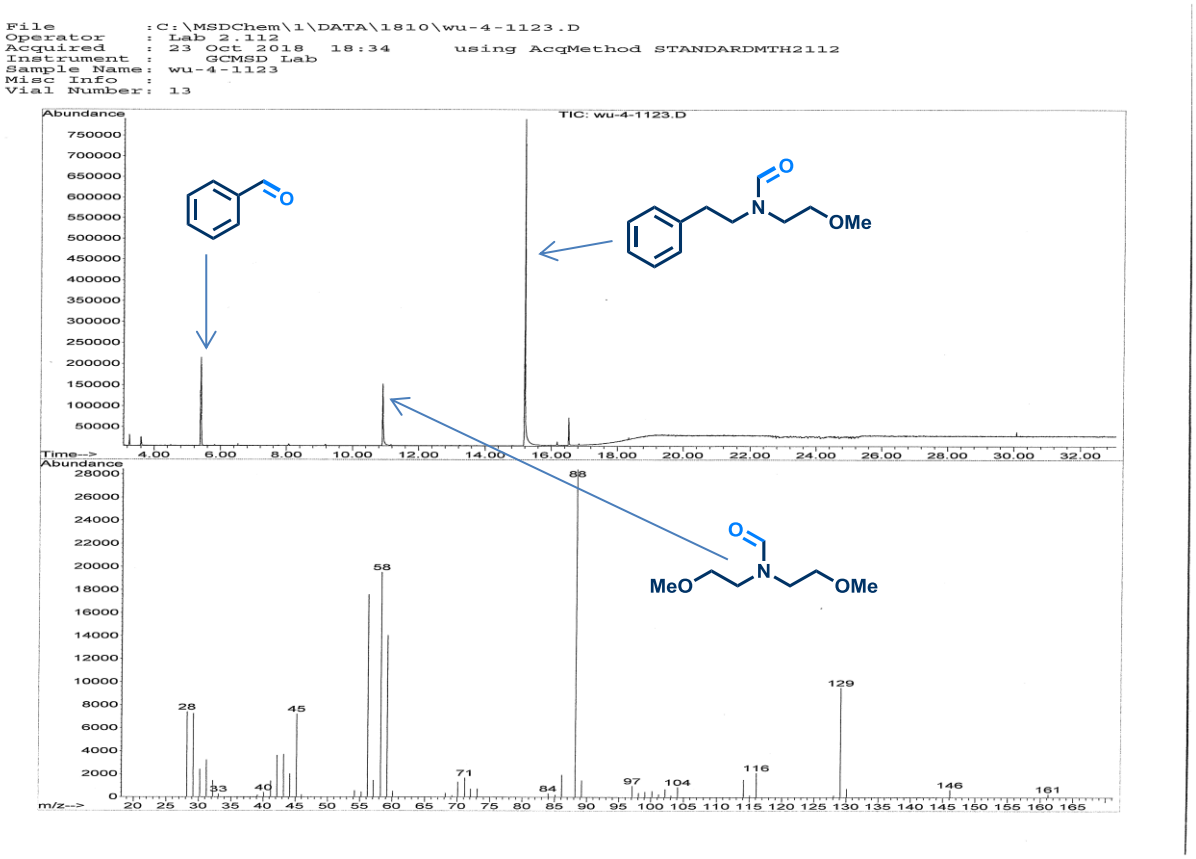
Figure S1. Putative intermediate of C-C bond cleavage reaction.





Scheme S1. GC-MS spectra of control experiments.

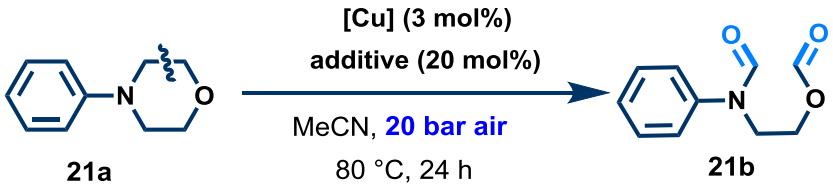




Scheme S2. GC-MS spectra of **18b**.

Table S3. Conditions optimisation

Selective cleavage C-C single bond of *N*-phenylmorpholine use different catalysts.



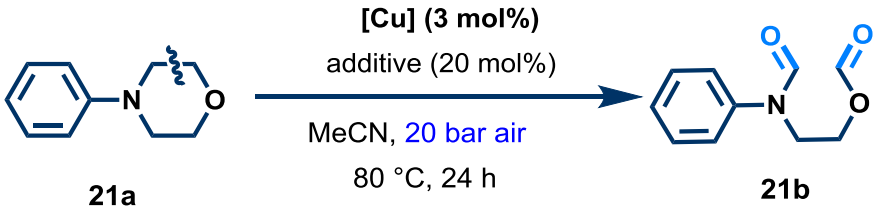
21a 21b

Entry	Catalyst	Ligand	Yield (%)[t]
1	CuCl	pyridine	63
2	$Cu(OAc)_2$	pyridine	66
3	$CuBr_2$	pyridine	43
4	CuBr	pyridine	55
5	**$Cu(CF_3SO_3)_2$**	**pyridine**	**90**
6	CuI	pyridine	0

Reaction conditions: Substrates **21a** (0.5 mmol), catalyst (3 mol%) and additive (20 mol%), 20 bar air, MeCN, 80 °C. [t]Yield determined by GC using *n*-dodecane as the standard.

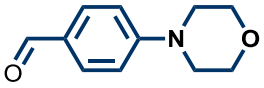
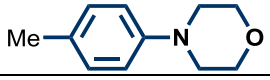
When *N*-phenylmorpholine (0.5 mmol) was chosen as the benchmark substrate, only 63% 2-(N-phenylformamido)ethyl formate was obtained using CuCl (3 mol%) as the catalyst under milder conditions (20 bar air at 80 °C) (Table S3, entry 1). Consequently, other copper salts, such as $Cu(OAc)_2$, $CuBr_2$, CuBr, $Cu(CF_3SO_3)_2$ and CuI were examined as the catalyst (Table S3, entries 2-5). To our delight, using $Cu(CF_3SO_3)_2$ C-C bond cleavage product was obtained in 90% yield (Table S3, entry 5). Only trace amount of C-C bond cleavage product was detected when the reaction was performed under 1 atmosphere air or O_2 (eq. S1).

Table S4. Conditions comparison

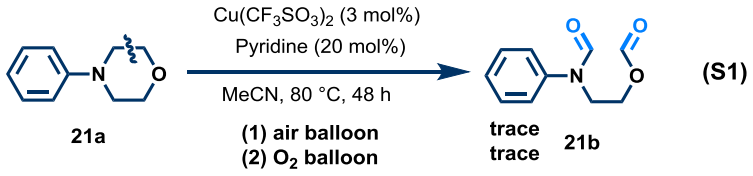


Catalyst	Additive (20 mol%)	Temperature (°C)	Yield (%)
Cu_2O	Pyridine	80	52
		100	28
	-	120	48
CuO	Pyridine	80	33
		100	55
	-	120	trace
Reaction conditions: Substrate **21a** (0.5 mmol), catalyst (3 mol%) and additive (20 mol%), 20 bar air, MeCN, 80 °C. [t]Yield determined by GC using *n*-dodecane as the standard.			

Table S5. Substrates comparison

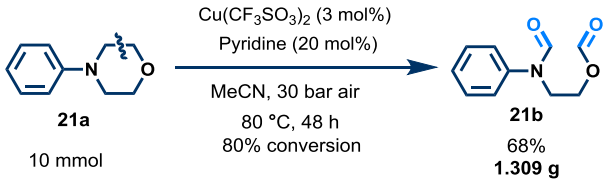
Substrate	Catalyst	Additive (20 mol%)	Temperature (°C)	Yield (%)
	Cu_2O	Pyridine	100	trace
		-	120	0
	CuO	Pyridine	100	trace
		-	120	0
	Cu_2O	Pyridine	80	27
		Pyridine	100	32
	Cu_2O	Pyridine	80	trace
		-	120	0
	CuO	Pyridine	80	trace
		-	120	0
Reaction conditions: Substrates **a** (0.5 mmol), catalyst (3 mol%) and additive (20 mol%), 20 bar air, MeCN, T °C. Isolated yields.				

1 Atmosphere air or O_2 experiment (eq. S1):



(S1)

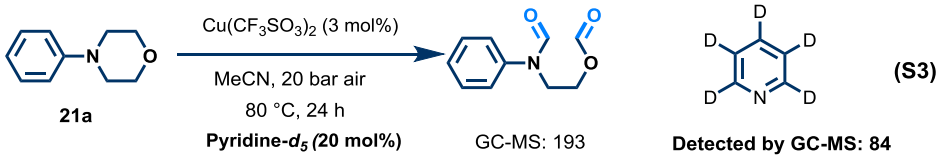
Gram scale reaction (eq. S2):



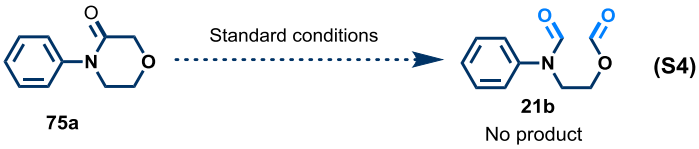
(S2)

7. Mechanistic Studies

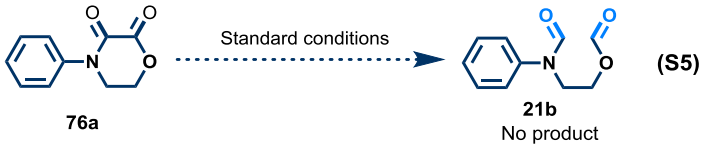
Pyridine-d_5 experiment (eq. S3):



(S3)



(S4)

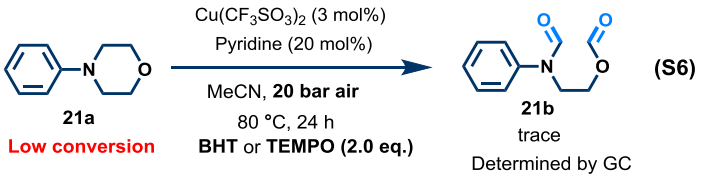


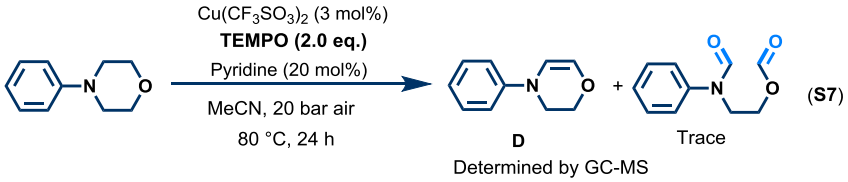
(S5)

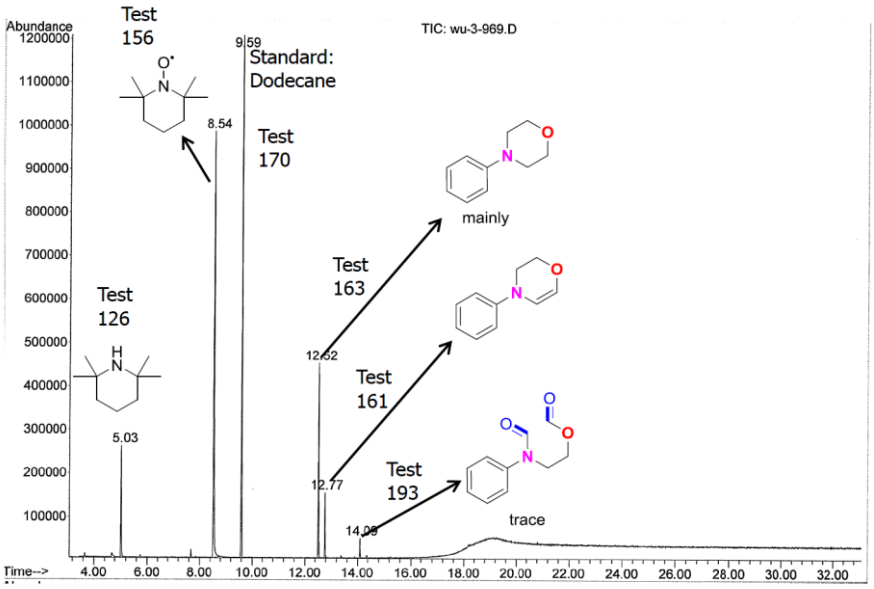
Radical-trapping Experiments and GC-MS Resuts

In a 4 mL vial fitted with magnetic stirring bar and septum cap, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-phenylmorpholine, TEMPO (or BHT) were added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. Solvent MeCN (2.0 mL) and pyridine (8.0 mg) were added, independently. The vial (up to eight) was set in an alloy plate and then placed into a

300 mL steel Parr autoclave. The autoclave was flushed with air 2 times at 10 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heated to the desired temperature (80 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the sample was removed from the autoclave, and diluted with acetone. *n*-Dodecane 90 mg was added for GC and GC-MS measurement (eq. S6).

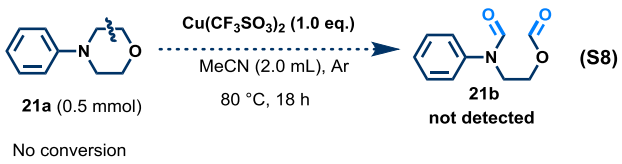






Scheme S3. GC-MS spectra of radical-trapping experiment.

Stoichiometric amounts of Cu(OTf)$_2$ (eq. S8)



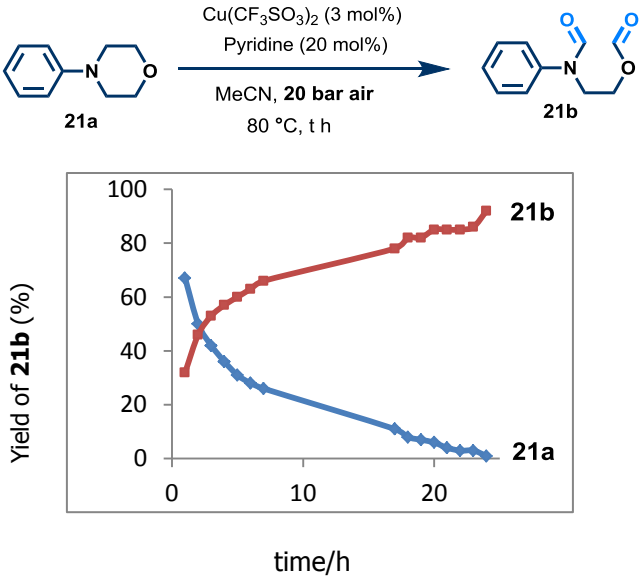
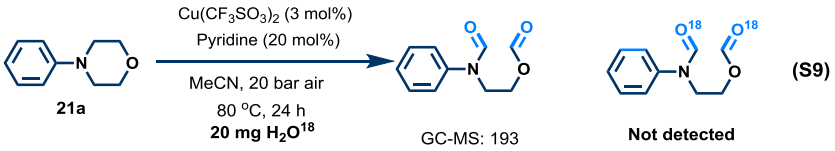


Figure S2. Kinetic data of the C-C bonds cleavage reaction

^{18}O-labeled water and control experiment (eq. S9)



(S9)

EPR and UV-Vis Investigation

To get deeper insight into the catalytic process, the interaction of the different components in the reaction mixture was investigated in a consecutive manner by EPR and UV-vis spectroscopy. A solution of 0.016 mmol $Cu(OTf)_2$ in 2.0 mL acetonitrile shows an EPR signal at g = 2.165 with a poorly resolved hyperfine structure (hfs) (Figure S3) arising from the coupling of the unpaired electron of Cu^{II} with its nuclear spin (d^9, S = 1/2, I = 3/2). The reason for unresolved hfs is due to the fast exchange between the CH_3CN and Cu-coordinated solvent molecules[2]. Upon addition of pyridine, the four hfs lines become more resolved at g_{iso} = 2.123 with a coupling constant of A = 80 G, indicating that the pyridine ligand is coordinated to the Cu^{II} site. However, addition of *N*-phenylmorpholine (**21a**) to $Cu(OTf)_2$ at 20 °C and ambient pressure caused a quick vanish of the Cu^{II} signal and a rise of a temporary radical signal with unresolved hfs at g = 2.004 which disappeared within less than one minute, pointing to its high reactivity. We attribute these changes to the reduction of Cu^{II} by **21a** to Cu^{I} which is accompanied by the formation of an EPR-active radical intermediate

(Figure S3e). Samples taken from the catalytic reactor after 30 and 80 min (Figure S3c and d) showed only a very weak Cu^{II} signal, indicating that oxidation of Cu^{I} by O_2 under these conditions is very slow in comparison to fast reduction of Cu^{II} by **21a**.

The in situ-UV-vis spectrum of $Cu(OTf)_2$ in CH_3CN shows bands below 300 nm and around 750 nm arising from a ligand-to-metal charge transfer (LMCT) and a d-d transition of Cu^{II}. When pyridine is added, the LMCT band increases and the d-d band shifts to lower wavelength (565 nm), indicating the coordination of pyridine to Cu^{II}, yet without any change of its divalent valence state as evident, too, from the EPR spectrum in Figure S3. When **21a** is added to $Cu(OTf)_2$ in CH_3CN without pyridine, the LMCT and d-d bands of Cu^{II} disappear and new metal-to-ligand (MLCT) bands of Cu^{I} appear around 320 and 466 nm (Figure S4c), indicating fast reduction of Cu^{II} to Cu^{I}, in agreement with EPR results. Subsequent addition of pyridine to this solution changes the spectrum only slightly, probably due to coordination of pyridine to Cu^{I} (Figure S4d).

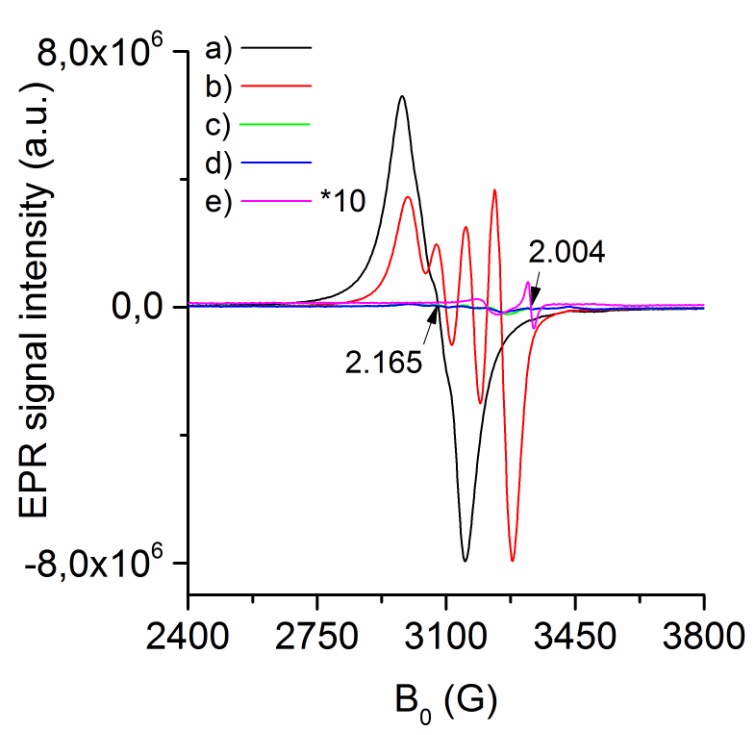


Figure S3. EPR spectra of a) $Cu(OTf)_2$; b) $Cu(OTf)_2$ + pyridine; and after catalytic test under standard conditions for c) 30 min; d) 180 min; e) $Cu(OTf)_2$ + **21a**; recorded at 20 °C.

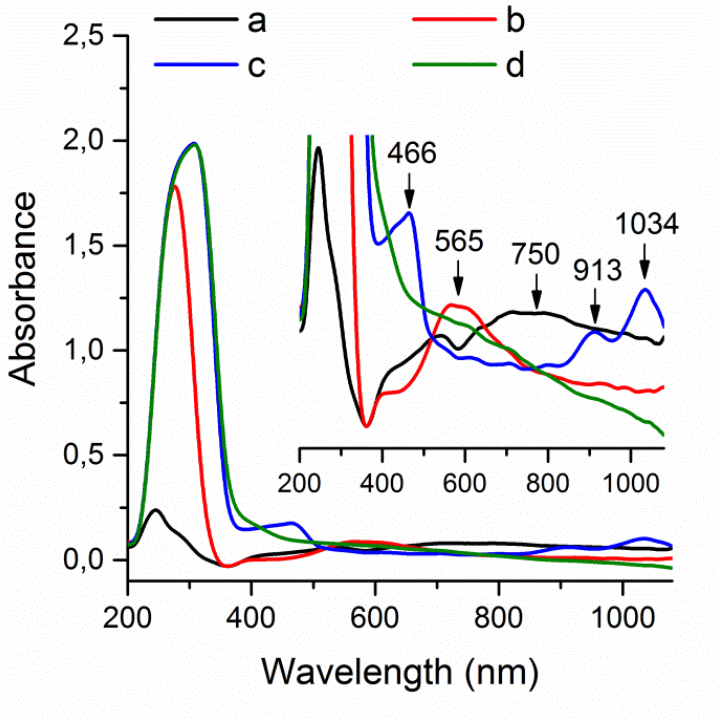
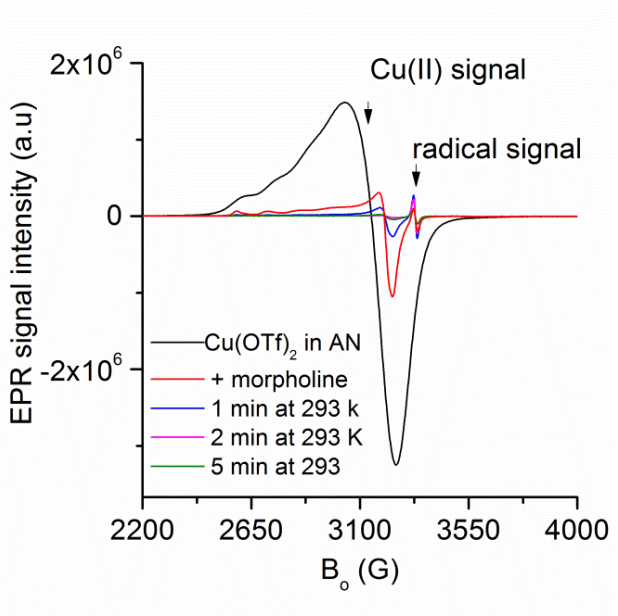
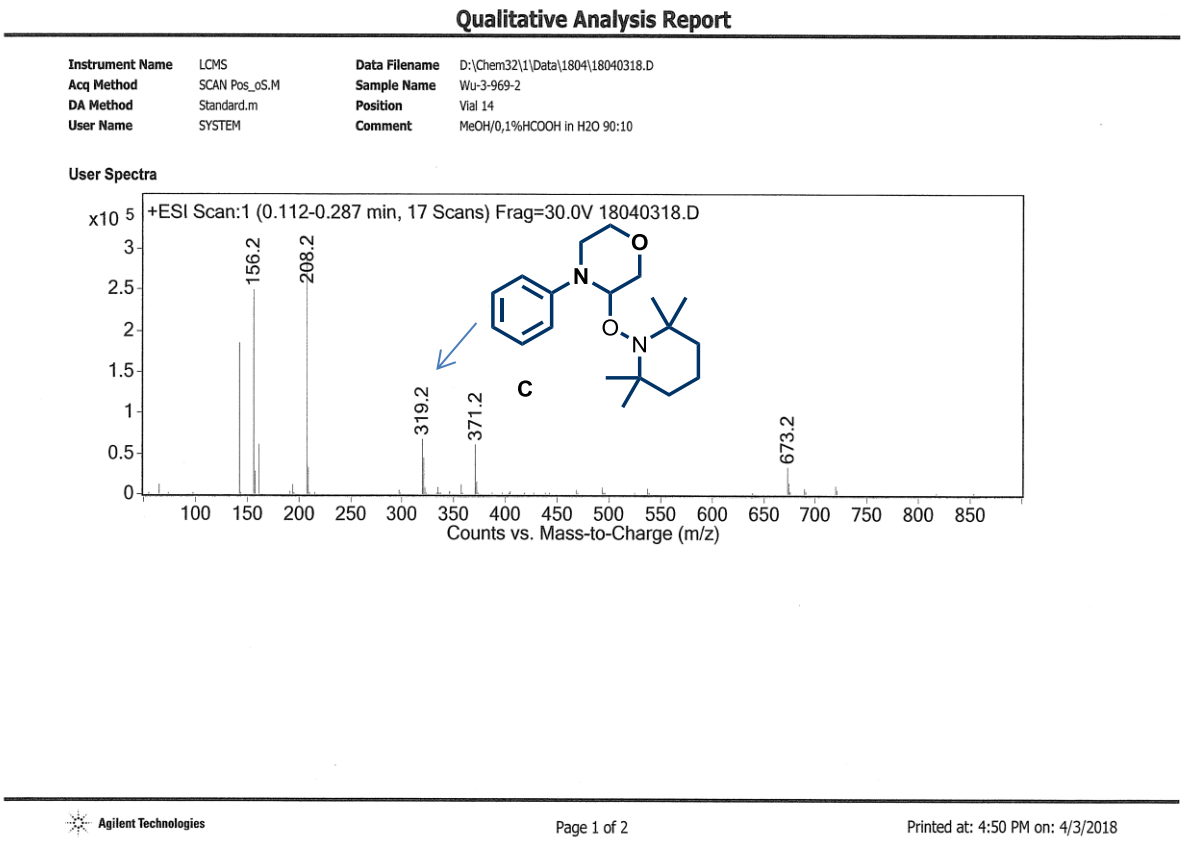


Figure S4. UV-Vis spectra of a) $Cu(OTf)_2$; b) $Cu(OTf)_2$ + pyridine; c) $Cu(OTf)_2$ + **21a**; d) $Cu(OTf)_2$ + **21a** then pyridine. recorded at 20 °C.

The EPR and UV-vis experiments in the above were conducted under argon atmosphere. We did some in situ EPR investigation with a frozen solution under Ar, too. Firstly, we measured EPR spectra of $Cu(OTf)_2$ in MeCN at 200 K, then we added *N*-phenylmorpholine at 293 K to Cu(II) solution and frozen again rapidly. The drop of the Cu(II) signal was attributed to its reduction to Cu(I). Heating the sample at 293 for different periods decreased the Cu(II) signal again (see below) suggesting that reaction of *N*-phenylmorpholine with Cu(II) is very fast. Additionally, we conducted some EPR investigations at 90 K, which did not provide any evidence for the formation of Cu(II) antiferromagnetic species. Such dimer, if they formed, should have a d-d transition band in the Vis region (see for example, Solomon, E. I.; Sundaram, U. M.; Machonkin, T. E., Multicopper Oxidases and Oxygenases. *Chem. Rev.* **1996**, *96*, 2563-2605 and Mirica, L. M.; Ottenwaelder, X.; Stack, T. D. P., Structure and Spectroscopy of Copper-Dioxygen Complexes. *Chem. Rev*. **2004**, *104*, 1013-1045.) Of course, we aware that solvents with a high dielectric constant will lower signal sensitivity or eliminate the signals completely when conducted at room temperature. Therefore, all the EPR investigations at RT were conducted using EPR capillary tubes (ID 0.5 mm) to prevent absorption of the microwave energy by the solvents. Clearly, the lack of the EPR signal seen in some of the EPR spectra cannot be due to this effect.


2x10^6
0
-2x10^6
EPR signal intensity (a.u)
Cu(II) signal
radical signal
Cu(OTf)2 in AN
+ morpholine
1 min at 293 k
2 min at 293 K
5 min at 293
2200
2650
3100
3550
4000
Bo (G)

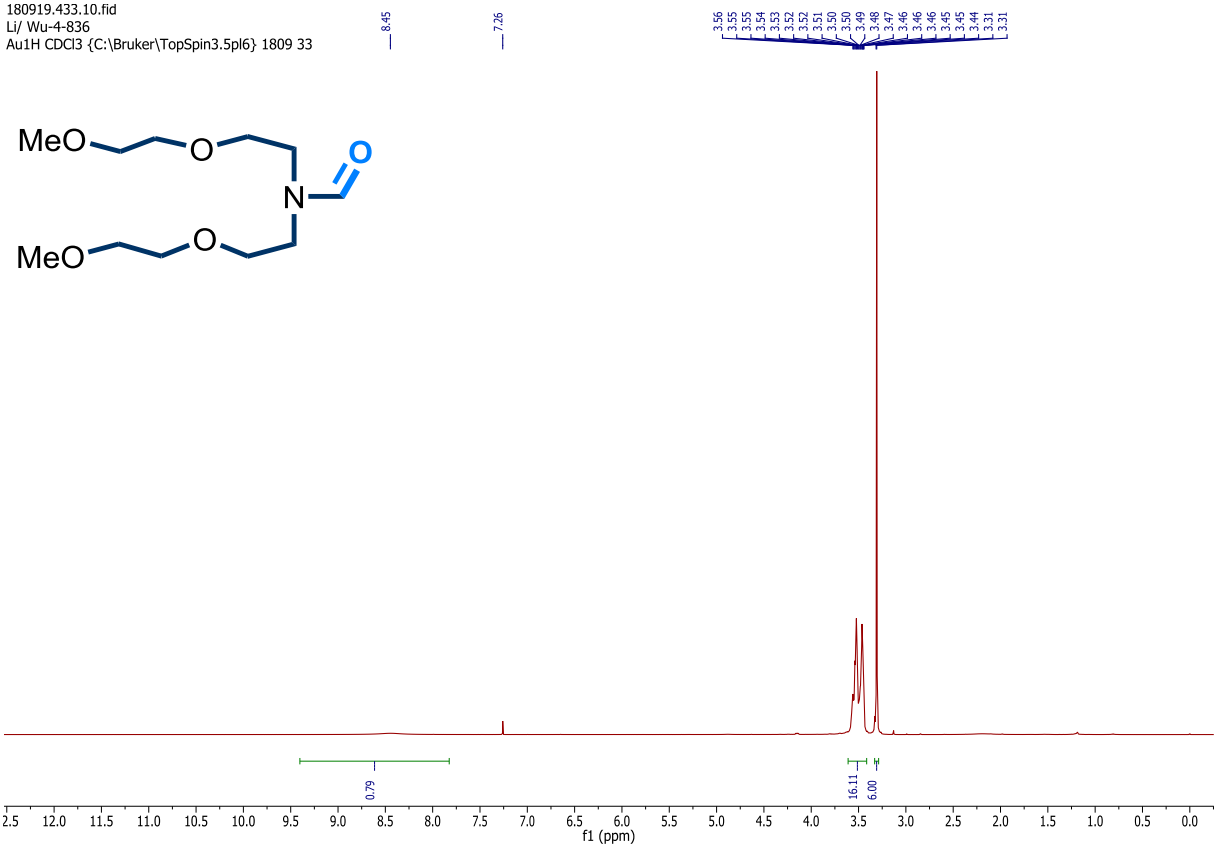


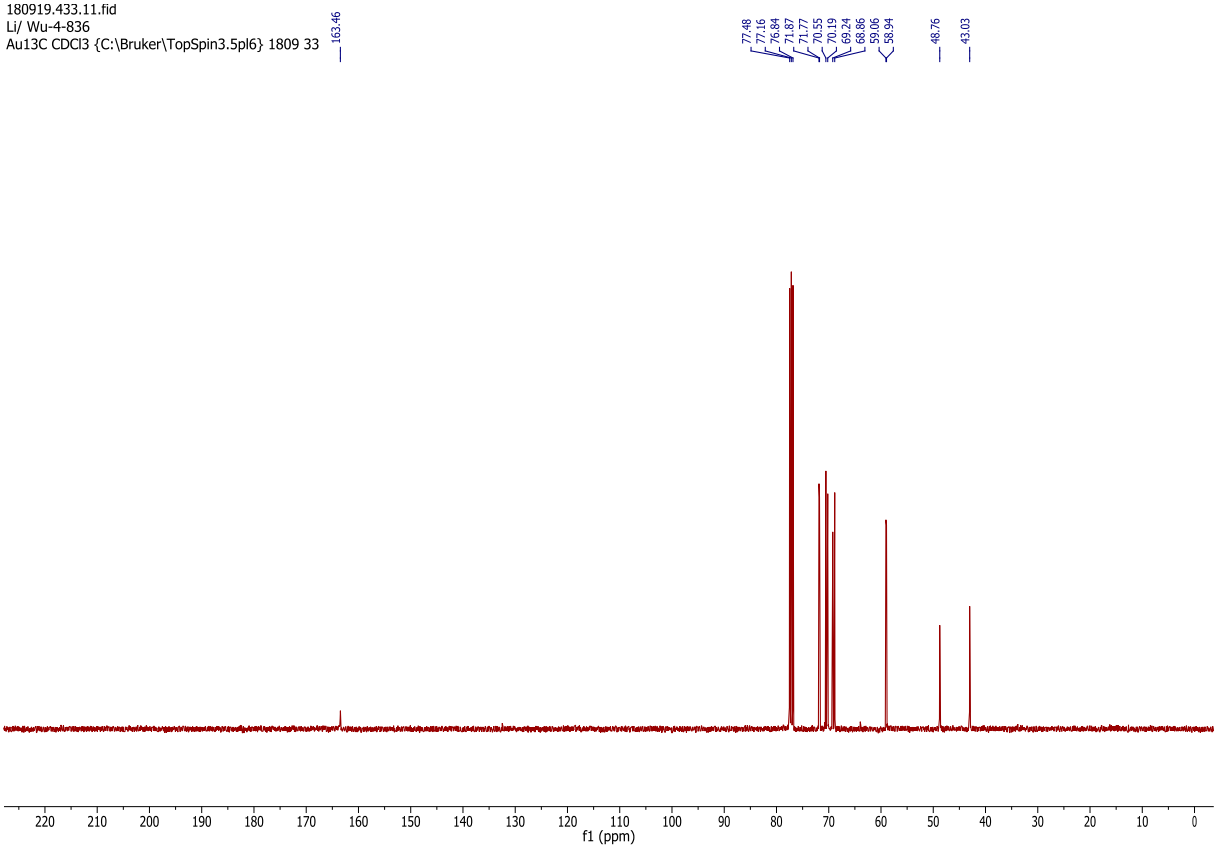
Scheme S4. The formation of α-amino radical was detected by LC-MS

When 2 equivalents of TEMPO (2,2,6,6-Tetramethyl-1-piperidinyloxy) was added into the reaction system, the reaction was totally shut down, along with the dehydrogenation product 4-phenyl-3,4-dihydro-*2H*-1,4-oxazine detected by GC-MS. A colorless liquid mixture was isolated by silica gel column chromatography.

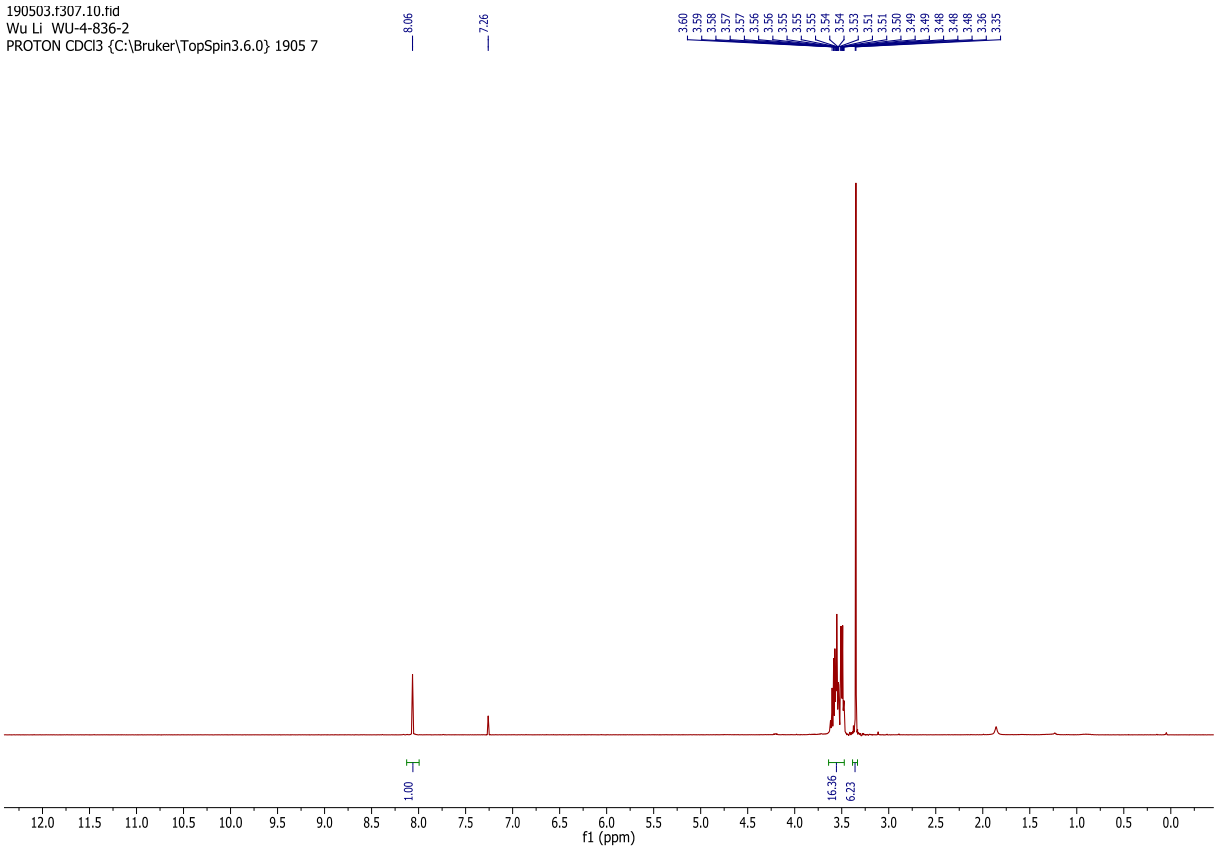
8. NMR Experiments for 7b and 37b.

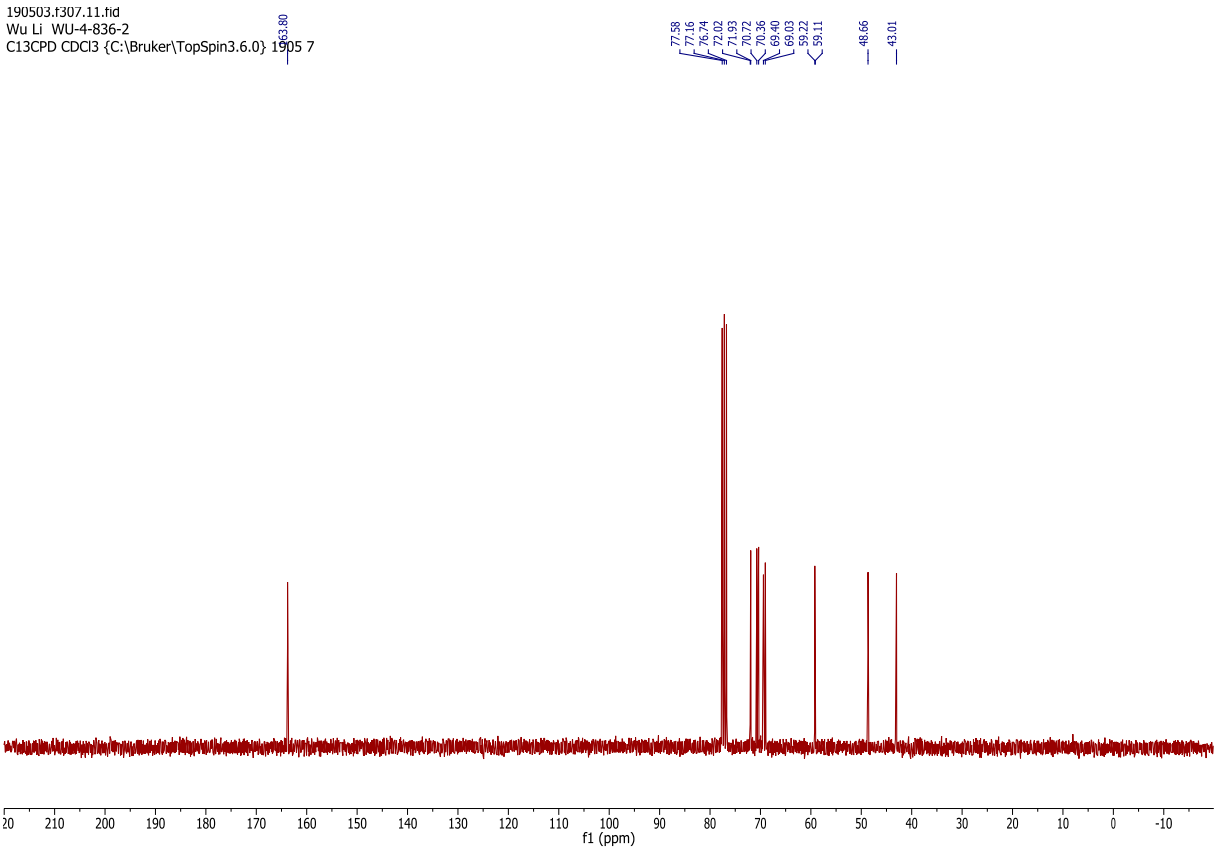
Original spectra for **7b**:



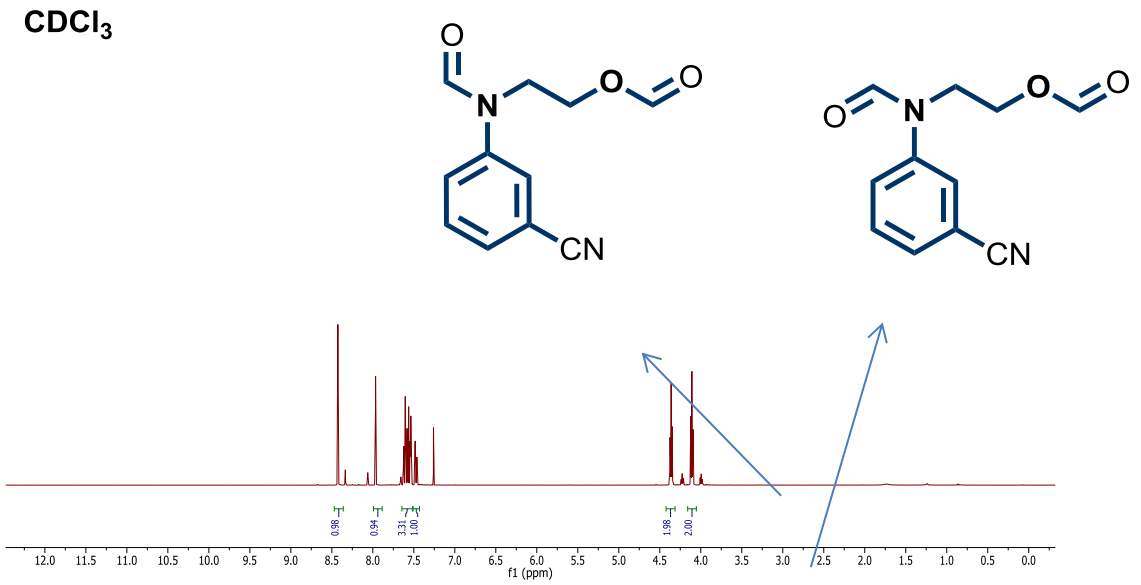


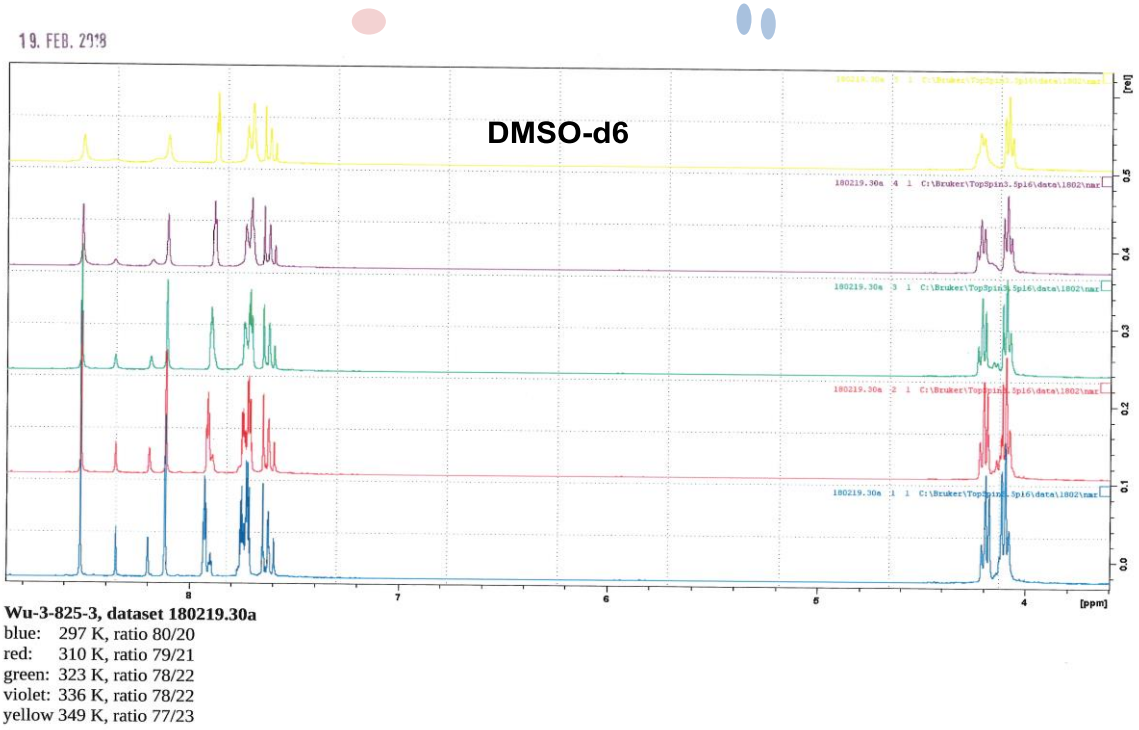
Original spectra for **7b** (The $CDCl_3$ was filtered through K_2CO_3.)





Those peaks marked in the spectra are from the same product. When we increased the temperature for **37b** during NMR experiment, the lower peaks disappeared regularly. As you can see, in the spectra in DMSO-d6, two lower peaks at chemical shift 8.2 and 8.4 are disappeared regularly. The lower peak at 8.4 is from formamide which coalesces to peak at 8.5. And the peak at about 8.2 is from formate which coalesces to peak at 8.1.

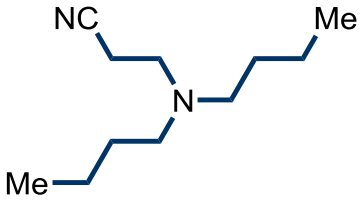




Wu-3-825-3, dataset 180219.30a
blue: 297 K, ratio 80/20
red: 310 K, ratio 79/21
green: 323 K, ratio 78/22
violet: 336 K, ratio 78/22
yellow 349 K, ratio 77/23

9. Characterization Data for the Substrates and Products

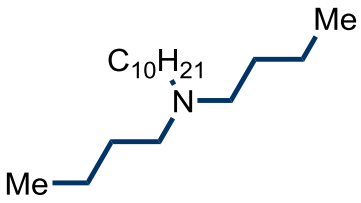
3-(Dibutylamino)propanenitrile (5a)



^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.85–2.69 (m, 2H), 2.51–2.30 (m, 6H), 1.54–1.22 (m, 9H), 0.91 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 119.34, 53.69, 49.73, 29.63, 20.63, 16.29, 14.17.

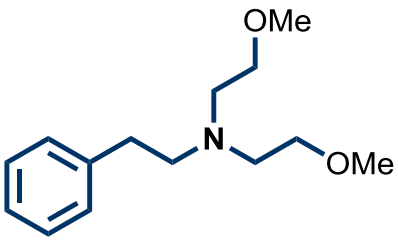
N,N-Dibutyldecan-1-amine (6a)



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.46–2.33 (m, 6H), 1.48–1.35 (m, 6H), 1.33–1.21 (m, 18H), 0.96–0.82 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 54.36, 54.05, 32.06, 29.82, 29.79, 29.77, 29.69, 29.49, 29.25, 27.81, 27.07, 22.84, 20.96, 14.26.

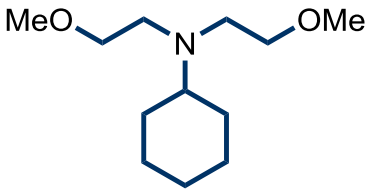
2-Methoxy-*N*-(2-methoxyethyl)-*N*-phenethylethan-1-amine (8a)



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28–7.17 (m, 2H), 7.15–7.08 (m, 3H), 3.42 (t, *J* = 6.0 Hz, 4H), 3.28 (s, 6H), 2.73 (t, *J* = 6.0 Hz, 8H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 140.58, 128.85, 128.44, 126.02, 71.21, 58.98, 57.38, 53.97, 33.41.

***N,N*-Bis(2-methoxyethyl)cyclohexanamine (9a)**

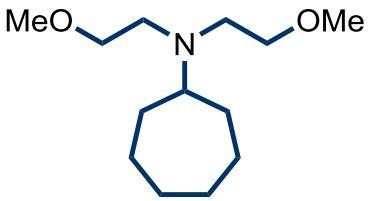


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.34 (s, 10H), 2.71 (s, 4H), 2.45 (s, 1H), 1.77 (d, J = 9.0 Hz, 4H), 1.61 (d, J = 12.2 Hz, 1H), 1.17 (d, J = 10.0 Hz, 5H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 72.79, 62.09, 59.00, 51.05, 29.23, 26.45, 26.27.

HR-MS (ESI) m/z calcd for $[C_{12}H_{26}NO_2]^+$ ($[M+H]^+$): 216.1958, found: 216.1966.

***N,N*-Bis(2-methoxyethyl)cycloheptanamine (10a)**

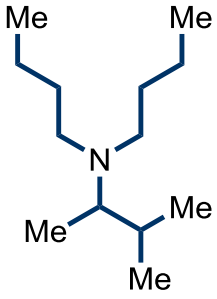


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.40 (t, J = 6.5 Hz, 4H), 3.34 (s, 6H), 2.74–2.55 (m, 5H), 1.82 (s, 2H), 1.66 (dd, J = 6.9, 4.1 Hz, 2H), 1.55–1.35 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 72.56, 63.45, 58.85, 51.10, 30.56, 27.83, 25.94.

HR-MS (ESI) m/z calcd for $[C_{13}H_{28}NO_2]^+$ ($[M+H]^+$): 230.2115, found: 230.2123.

***N*-Butyl-*N*-(3-methylbutan-2-yl)butan-1-amine (11a)**

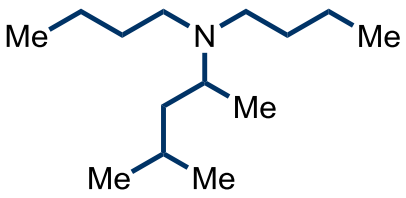


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.75–2.70 (m, 1H), 2.51–2.34 (m, 4H), 1.70–1.57 (m, 1H), 1.42–1.28 (m, 8H), 1.00–0.93 (m, 3H), 0.90 (td, J = 7.3, 3.3 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 55.29, 49.06, 35.85, 30.55, 20.80, 20.51, 20.34, 14.37, 14.20, 14.09, 13.97.

HR-MS (ESI) m/z calcd for $[C_{13}H_{30}N]^+$ ($[M+H]^+$): 200.2373, found: 200.2380.

***N,N*-Dibutyl-4-methylpentan-2-amine (12a)**

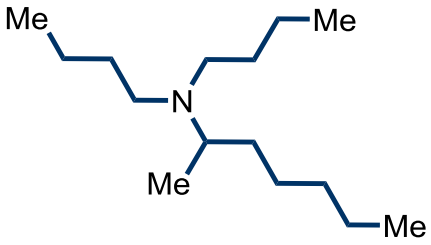


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.68–2.64 (m, 1H), 2.48–2.20 (m, 4H), 1.56 (dddd, *J* = 7.7, 6.7, 2.5, 0.9 Hz, 1H), 1.42–1.23 (m, 10H), 0.91–0.84 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 52.66, 49.90, 49.47, 35.85, 31.41, 25.04, 23.25, 20.81, 14.27.

HR-MS (ESI) m/z calcd for $[C_{14}H_{32}N]^+$ ($[M+H]^+$): 214.2529, found: 214.2531.

***N,N*-Dibutylheptan-2-amine (13a)**

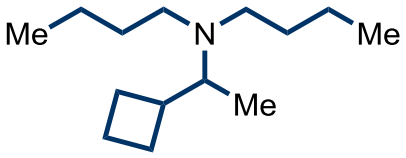


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.73–2.66 (m, 1H), 2.50–2.28 (m, 4H), 1.48–1.38 (m, 4H), 1.37–1.18 (m, 12H), 0.95–0.85 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 55.47, 50.03, 32.17, 30.96, 26.90, 22.82, 20.81, 20.55, 14.22, 14.15, 14.01.

HR-MS (ESI) m/z calcd for $[C_{15}H_{34}N]^+$ ($[M+H]^+$): 228.2686, found: 228.2691.

***N*-Butyl-*N*-(1-cyclobutylethyl)butan-1-amine (14a)**

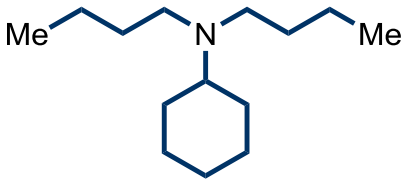


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.67–2.52 (m, 1H), 2.46–2.15 (m, 5H), 1.99–1.88 (m, 2H), 1.85–1.48 (m, 4H), 1.46–1.13 (m, 8H), 0.97–0.84 (m, 6H), 0.77 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 60.96, 50.18, 39.80, 31.50, 27.67, 27.00, 20.72, 18.17, 14.28, 9.76.

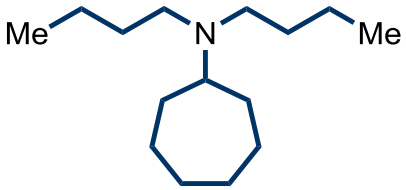
HR-MS (ESI) m/z calcd for $[C_{14}H_{30}N]^+$ ($[M+H]^+$): 212.2373, found: 212.2377.

***N,N*-Dibutylcyclohexanamine (15a)**



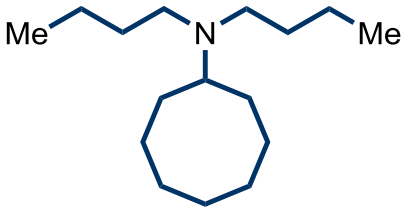
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.43 (t, J = 7.6 Hz, 5H), 1.87–1.69 (m, 4H), 1.40 (td, J = 8.4, 4.1 Hz, 4H), 1.35–1.25 (m, 4H), 1.25–1.14 (m, 4H), 0.90 (t, J = 7.3 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 60.33, 50.61, 31.39, 29.18, 26.62, 26.42, 20.89, 14.28.

***N,N*-Dibutylcycloheptanamine (16a)**



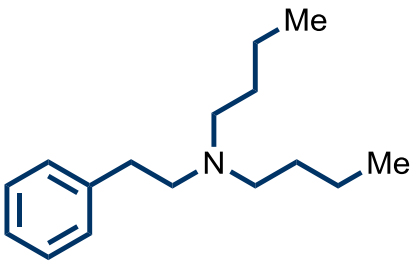
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.66 (s, 1H), 2.36 (t, J = 7.4 Hz, 4H), 1.85–1.60 (m, 4H), 1.57–1.22 (m, 16H), 0.90 (t, J = 7.2 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 61.55, 50.78, 31.73, 30.33, 28.11, 26.30, 20.93, 14.30.
HR-MS (ESI) m/z calcd for $[C_{15}H_{32}N]^+$ ($[M+H]^+$): 226.2529, found: 226.2532.

***N,N*-Dibutylcyclooctanamine (17a)**



^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 2.76 (s, 1H), 2.33 (dd, J = 8.5, 6.3 Hz, 4H), 1.75–1.22 (m, 22H), 0.90 (t, J = 7.2 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 59.63, 50.78, 31.75, 30.18, 26.80, 26.75, 26.14, 20.93, 14.30.
HR-MS (ESI) m/z calcd for $[C_{16}H_{34}N]^+$ ($[M+H]^+$): 240.2686, found: 240.2687.

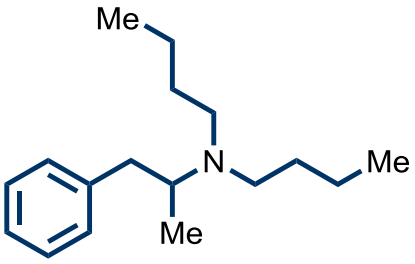
***N*-Butyl-*N*-phenethylbutan-1-amine (18a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.38–7.26 (m, 2H), 7.25–7.18 (m, 3H), 2.85–2.67 (m, 4H), 2.58–2.44 (m, 4H), 1.55–1.42 (m, 4H), 1.39–1.27 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.04, 128.85, 128.44, 125.97, 56.28, 53.97, 33.59, 29.45, 20.92, 14.27.

***N*-Butyl-*N*-(1-phenylpropan-2-yl)butan-1-amine (19a)**

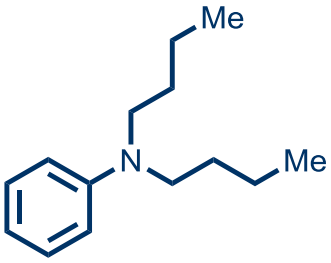


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35–7.15 (m, 2H), 7.09 (td, *J* = 6.6, 1.7 Hz, 3H), 3.02–2.75 (m, 2H), 2.49–2.14 (m, 5H), 1.33 (ddt, *J* = 13.8, 8.8, 4.3 Hz, 4H), 1.27–1.17 (m, 4H), 0.96–0.70 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 141.35, 129.38, 128.25, 125.74, 57.61, 50.17, 39.67, 31.55, 20.81, 14.77, 14.30.

HR-MS (ESI) m/z calcd for $[C_{17}H_{30}N]^+$ ($[M+H]^+$): 348.2373, found: 348.2380.

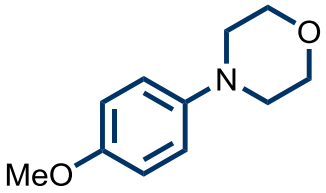
***N,N*-Dibutylaniline (20a)**



^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25–7.16 (m, 2H), 6.73–6.49 (m, 3H), 3.35–3.13 (m, 4H), 1.63–1.52 (m, 4H), 1.36 (dq, *J* = 14.7, 7.4 Hz, 4H), 0.96 (t, *J* = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 148.31, 129.31, 115.17, 111.80, 50.91, 29.55, 20.52, 14.18.

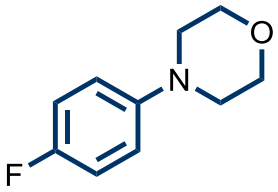
4-(4-Methoxyphenyl)morpholine (23a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.99–6.71 (m, 4H), 3.91–3.82 (m, 4H), 3.77 (s, 3H), 3.11–2.99 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.20, 145.57, 118.02, 114.64, 67.12, 55.70, 51.03.

4-(4-Fluorophenyl)morpholine (24a)

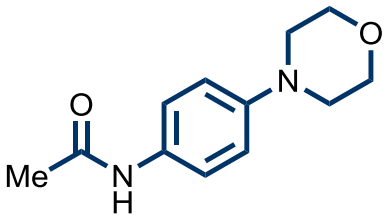


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.05–6.91 (m, 2H), 6.91–6.76 (m, 2H), 3.90–3.74 (m, 4H), 3.14–2.99 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.32 (d, J = 239.0 Hz), 147.94 (d, J = 2.3 Hz), 117.49 (d, J = 7.6 Hz), 115.63 (d, J = 22.0 Hz), 66.93, 50.34.

^{19}F-NMR (282 MHz, $CDCl_3$): δ (ppm) 124.18.

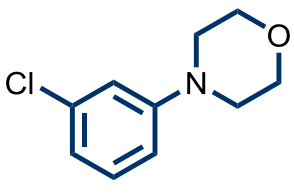
***N*-(4-Morpholinophenyl)acetamide (33a)**



^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 9.71 (s, 1H), 7.44 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 3.82–3.61 (m, 4H), 3.12–2.91 (m, 4H), 2.00 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 167.61, 147.03, 131.75, 120.12, 115.44, 66.14, 49.00, 23.82.

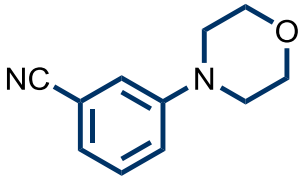
4-(3-Chlorophenyl)morpholine (35a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.22–7.11 (m, 1H), 6.91–6.70 (m, 3H), 3.90–3.77 (m, 4H), 3.24–3.07 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.41, 135.10, 130.17, 119.74, 115.56, 113.66, 66.80, 48.93.

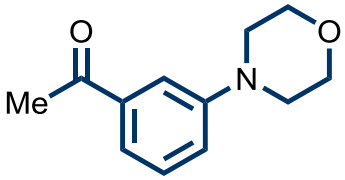
3-Morpholinobenzonitrile (37a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33 (dd, J = 9.2, 7.4 Hz, 1H), 7.17–7.03 (m, 3H), 3.94–3.74 (m, 4H), 3.26–3.09 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.41, 130.05, 123.02, 119.70, 119.35, 118.23, 113.12, 66.67, 48.52.

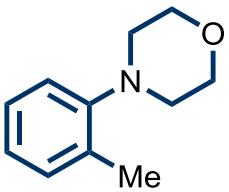
1-(3-Morpholinophenyl)ethan-1-one (38a)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48–7.45 (m, 1H), 7.40 (ddd, J = 7.6, 1.6, 1.0 Hz, 1H), 7.31 (ddd, J = 8.1, 7.6, 0.5 Hz, 1H), 7.07 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 3.86–3.75 (m, 4H), 3.23–3.10 (m, 4H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 198.31, 151.41, 137.93, 129.27, 120.19 (d, J = 1.3 Hz), 114.32, 66.71, 48.97, 26.71.

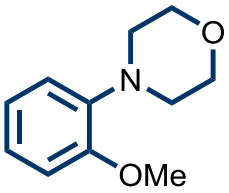
4-(*o*-Tolyl)morpholine (40a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.19 (m, 2H), 7.07–6.90 (m, 2H), 3.90–3.79 (m, 4H), 3.02–2.83 (m, 4H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.38, 132.76, 131.31, 126.79, 123.55, 119.08, 67.59, 52.39, 18.02.

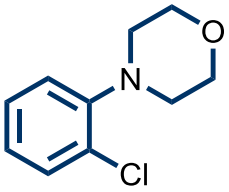
4-(2-Methoxyphenyl)morpholine (41a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.08–6.77 (m, 4H), 3.87 (m, 7H), 3.08 (t, J = 4.6 Hz, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.37, 123.32, 121.18, 118.16, 111.44, 67.30, 55.50, 51.31.

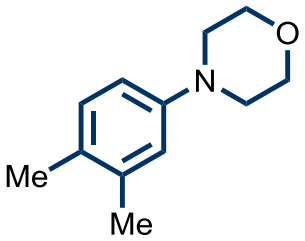
4-(2-Chlorophenyl)morpholine (42a)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37 (dd, J = 7.9, 1.5 Hz, 1H), 7.26–7.21 (m, 1H), 7.12–7.03 (m, 1H), 7.00 (ddd, J = 7.9, 7.3, 1.6 Hz, 1H), 3.94–3.80 (m, 4H), 3.14–2.99 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 148.98, 130.92, 128.89, 127.82, 124.19, 120.50, 67.26, 51.82.

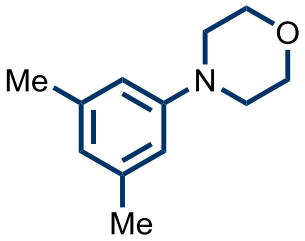
4-(3,4-Dimethylphenyl)morpholine (44a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.12–7.00 (m, 1H), 6.81–6.74 (m, 1H), 6.71 (dd, J = 8.2, 2.7 Hz, 1H), 3.98–3.83 (m, 4H), 3.22–3.06 (m, 4H), 2.31–2.26 (s, 3H), 2.25–2.19 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 149.70, 137.27, 130.31, 128.43, 117.76, 113.53, 67.10, 50.08, 20.32, 18.88.

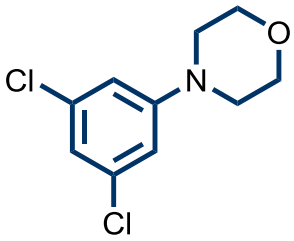
4-(3,5-Dimethylphenyl)morpholine (45a)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.60 (s, 3H), 4.00–3.77 (m, 4H), 3.31–3.06 (m, 4H), 2.33 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 151.49, 138.75, 122.08, 113.79, 67.06, 49.64, 21.73.

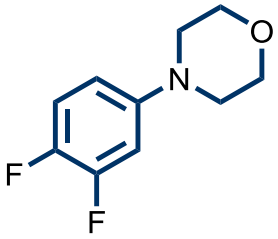
4-(3,5-Dichlorophenyl)morpholine (46a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 6.82 (t, J = 1.7 Hz, 1H), 6.73 (d, J = 1.8 Hz, 2H), 3.90–3.73 (m, 4H), 3.21–3.03 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.74, 135.59, 119.32, 113.62, 66.61, 48.46.

4-(3,4-Difluorophenyl)morpholine (47a)



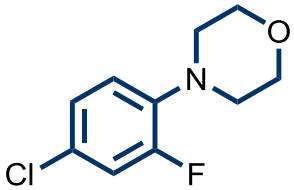
^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.08-7.01 (m, 1H), 6.72-6.65 (m, 1H), 6.60–6.54 (m, 1H), 3.87–3.78 (m, 4H), 3.11–3.01 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 152.27 (d, J = 13.3 Hz), 149.02 (d, J = 13.3 Hz), 148.51 (dd, J = 7.5, 2.4 Hz), 146.06 (d, J = 12.9 Hz), 142.88 (d, J = 13.0 Hz), 117.33 (dd, J = 17.7, 1.8 Hz), 111.15 (dd, J = 5.6, 3.1 Hz), 105.01 (d, J = 20.3 Hz), 66.77, 49.65.

HR-MS (EI) m/z calcd for [$C_{10}H_{11}NOF_2^+$] [M^+]: 199.0803, found: 199.0801.

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) -125.98– -139.29 (m), -142.50– -153.86 (m).

4-(4-Chloro-2-fluorophenyl)morpholine (48a)



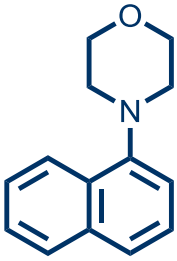
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14–6.99 (m, 2H), 6.90–6.75 (m, 1H), 3.96–3.76 (m, 4H), 3.10–2.95 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 155.45 (d, *J* = 249.8 Hz), 138.92 (d, *J* = 8.4 Hz), 127.21 (d, *J* = 10.0 Hz), 124.69 (d, *J* = 3.6 Hz), 119.48 (d, *J* = 3.8 Hz), 117.08 (d, *J* = 24.3 Hz). 67.02, 50.98 (d, *J* = 3.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) 120.00.

HR-MS (EI) m/z calcd for [$C_{10}H_{11}NOClF^+$] [M^+]: 215.0508, found: 215.0504.

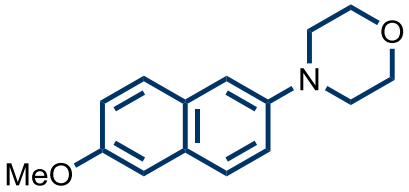
4-(Naphthalen-1-yl)morpholine (49a)



^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.33–8.05 (m, 1H), 7.90–7.73 (m, 1H), 7.58 (dt, *J* = 8.6, 1.0 Hz, 1H), 7.54–7.32 (m, 3H), 7.18–6.97 (m, 1H), 4.06–3.89 (m, 4H), 3.20–2.96 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 134.93, 128.61, 126.05, 125.98, 125.62, 124.01, 123.52, 114.84, 67.60, 53.65.

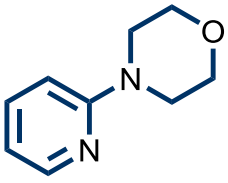
4-(6-Methoxynaphthalen-2-yl)morpholine (50a)



^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 7.73–7.59 (m, 2H), 7.32–7.22 (m, 1H), 7.20–7.07 (m, 3H), 4.01–3.88 (m, 7H), 3.33–3.14 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 156.30, 147.70, 129.86, 129.69, 128.41, 127.75, 119.75, 119.01, 110.82, 105.90, 67.08, 55.38, 50.33.

4-(Pyridin-2-yl)morpholine (51a)

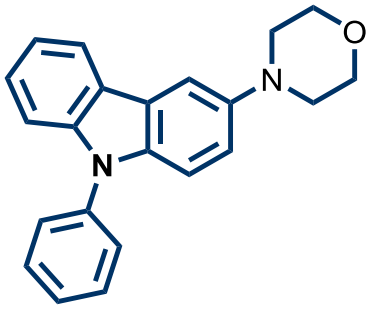


^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.19 (ddd, *J* = 5.0, 2.0, 0.9 Hz, 1H), 7.49 (ddd, *J* = 8.6, 7.2, 2.0 Hz, 1H), 6.73–6.51 (m, 2H), 3.92–3.70 (m, 4H), 3.54–3.41 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 159.65, 147.98, 137.70, 113.93, 107.10, 66.88, 45.74.

HR-MS (ESI): m/z calculated for $[C_9H_{13}N_2O]^+$ ($[M+H]^+$): 165.1022, found: 165.1023.

4-(9-Phenyl-*9H*-carbazol-3-yl)morpholine (52a)

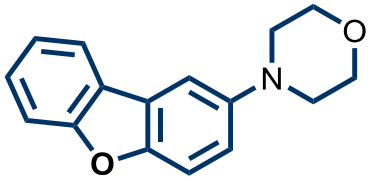


^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02 (dt, J = 7.8, 1.0 Hz, 1H), 7.66–7.58 (m, 1H), 7.54–7.43 (m, 4H), 7.40–7.24 (m, 4H), 7.21–7.14 (m, 1H), 7.07 (dd, J = 9.0, 2.4 Hz, 1H), 4.01–3.74 (m, 4H), 3.26–3.08 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 141.37, 138.00, 136.52, 129.95, 127.32, 127.00, 126.04, 123.95, 123.40, 120.30, 119.75, 117.94, 110.51, 109.96, 107.92, 67.25, 52.07.

HR-MS (ESI): m/z calculated for $[C_{22}H_{21}N_2O]^+$ ($[M+H]^+$): 329.1648, found: 329.1648.

4-(Dibenzo[b,d]furan-2-yl)morpholine (53a)



^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (ddd, J = 7.7, 1.4, 0.7 Hz, 1H), 7.46 (dt, J = 8.3, 0.9 Hz, 1H), 7.43–7.32 (m, 3H), 7.29–7.20 (m, 1H), 7.04 (dd, J = 9.0, 2.5 Hz, 1H), 4.07–3.73 (m, 4H), 3.28–3.01 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.92, 151.44, 127.18, 124.80, 124.57, 122.57, 120.60, 117.98, 112.06, 111.84, 107.92, 67.18, 51.51.

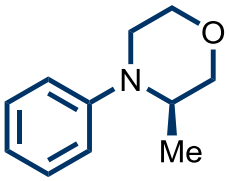
HR-MS (ESI): m/z calculated for $[C_{16}H_{16}NO_2]^+$ ($[M+H]^+$): 254.1176, found: 254.1176.

4-Decylmorpholine (56a)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.79–3.62 (m, 4H), 2.42 (dd, J = 5.7, 3.7 Hz, 4H), 2.36–2.24 (m, 2H), 1.56–1.39 (m, 2H), 1.26 (q, J = 3.1 Hz, 14H), 0.92–0.78 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 67.12, 59.40, 53.93, 32.03, 29.71, 29.46, 27.67, 26.69, 22.82, 14.25.

(*R*)-3-Methyl-4-phenylmorpholine (57a)

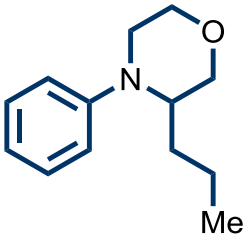


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33–7.22 (m, 2H), 6.95–6.76 (m, 3H), 3.97 (dtd, *J* = 11.2, 3.4, 0.9 Hz, 1H), 3.91–3.78 (m, 1H), 3.80–3.58 (m, 3H), 3.23–3.05 (m, 2H), 1.07 (dd, *J* = 6.5, 0.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 150.10, 129.34, 119.97, 116.87, 72.20, 67.36, 51.16, 44.59, 11.81.

HR-MS (EI) m/z calcd for [$C_{11}H_{15}NO^{+}$] [M^{+}]: 177.1148, found: 177.1146.

4-Phenyl-3-propylmorpholine (58a)

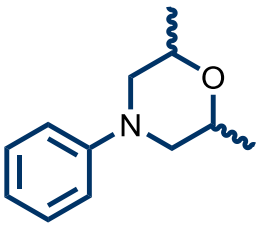


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.30–7.22 (m, 2H), 6.91–6.75 (m, 3H), 4.03–3.84 (m, 2H), 3.80–3.65 (m, 2H), 3.54 (dd, *J* = 10.2, 2.7 Hz, 1H), 3.23–3.10 (m, 2H), 1.90–1.68 (m, 1H), 1.44–1.12 (m, 3H), 0.91–0.83 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.00, 129.38, 119.11, 115.71, 68.82, 67.14, 55.56, 44.67, 27.42, 20.26, 14.22.

HR-MS (EI) m/z calcd for [$C_{13}H_{19}NO^{+}$] [M^{+}]: 205.1461, found: 205.1460.

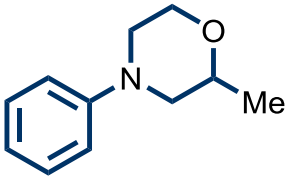
2,6-Dimethyl-4-phenylmorpholine (59a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37–7.26 (m, 2.67H), 7.05–6.74 (m, 3.54H), 4.19 (td, *J* = 6.3, 3.3 Hz, 0.43H), 3.84 (dqd, *J* = 10.4, 6.3, 2.4 Hz, 2H), 3.48 (ddd, *J* = 11.1, 2.3, 1.2 Hz, 2H), 3.33–3.12 (m, 0.42H), 2.91 (ddd, *J* = 11.8, 6.1, 1.0 Hz, 0.40H), 2.60–2.25 (m, 2H), 1.29 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 150.69, 128.89, 119.49, 115.59, 115.49, 71.38, 66.20, 54.58, 54.04, 18.81, 17.79.

2-Methyl-4-phenylmorpholine (60a)

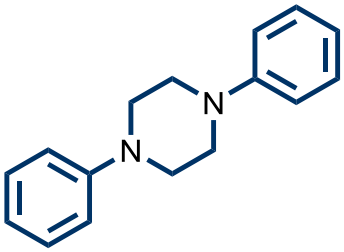


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40–7.23 (m, 2H), 7.05–6.87 (m, 3H), 4.05 (ddd, J = 11.4, 3.5, 1.6 Hz, 1H), 3.89–3.68 (m, 2H), 3.56–3.30 (m, 2H), 2.86 (td, J = 11.8, 3.5 Hz, 1H), 2.52 (dd, J = 11.8, 10.2 Hz, 1H), 1.29 (d, J = 6.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.24, 129.29, 120.05, 115.89, 71.90, 66.85, 55.73, 48.71, 19.19.

HR-MS (EI) m/z calcd for [$C_{11}H_{15}NO^{+}$] [M^{+}]: 177.1148, found: 177.1149.

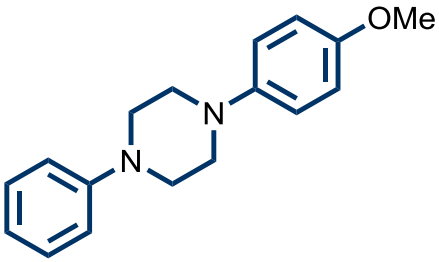
1,4-Diphenylpiperazine (62a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41–7.27 (m, 4H), 7.07–6.97 (m, 4H), 6.97–6.83 (m, 2H), 3.37 (s, 8H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 151.34, 129.32, 120.22, 116.48, 49.56.

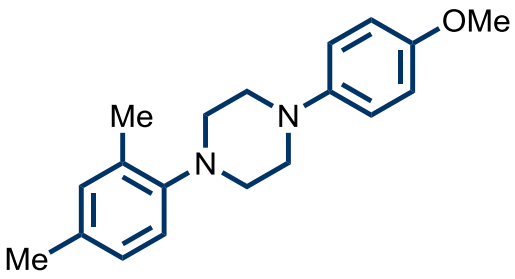
1-(4-Methoxyphenyl)-4-phenylpiperazine (63a)



^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.26–7.15 (m, 2H), 6.93–6.87 (m, 3H), 6.84–6.75 (m, 3H), 6.65–6.50 (m, 1H), 3.70 (s, 3H), 3.37–3.23 (m, 4H), 3.20–3.06 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 154.18, 151.38, 145.71, 129.28, 120.10, 118.62, 116.42, 114.60, 55.69, 51.04, 49.62.

1-(2,4-Dimethylphenyl)-4-(4-methoxyphenyl)piperazine (64a)

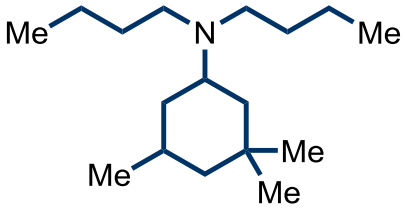


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.10–6.96 (m, 5H), 6.90 (d, J = 9.1 Hz, 2H), 3.81 (s, 3H), 3.36–3.19 (m, 4H), 3.14–2.94 (m, 4H), 2.40–2.26 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 153.92, 149.07, 145.98, 132.82, 132.67, 131.95, 127.17, 119.05, 118.34, 114.55, 55.67, 52.23, 51.35, 20.84, 17.85.

HR-MS (EI) m/z calcd for $[C_{19}H_{24}N_2O^+]$ $[M^+]$: 296.1883, found: 296.1882.

***N,N*-Dibutyl-3,3,5-trimethylcyclohexan-1-amine (65a)**

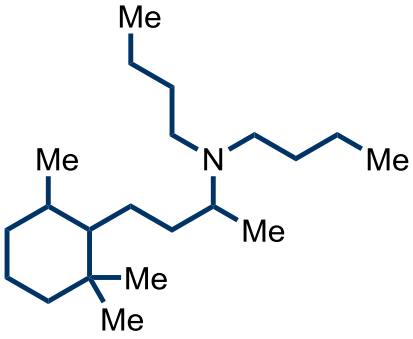


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.76–2.58 (m, 1H), 2.53–2.41 (m, 4H), 1.58–1.54 (m, 1H), 1.47–1.23 (m, 14H), 0.98–0.89 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 53.40, 50.31, 45.97, 40.32, 35.10, 32.57, 31.65, 30.40, 26.73, 22.05, 20.91, 14.25.

HR-MS (ESI) m/z calcd for $[C_{17}H_{36}N]^+$ ($[M+H]^+$): 254.2842, found: 254.2854.

***N*-Butyl-*N*-(4-(2,2,6-trimethylcyclohexyl)butan-2-yl)butan-1-amine (66a)**

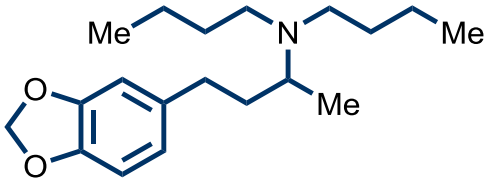


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.64 (d, J = 7.0 Hz, 1H), 2.48–2.16 (m, 4H), 1.94–1.80 (m, 1H), 1.55–1.22 (m, 14H), 1.21–1.01 (m, 4H), 1.02–0.75 (m, 19H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 55.75, 53.95, 50.08, 42.45, 36.84, 35.29, 31.51, 30.58, 28.68, 27.70, 23.08, 22.34, 21.35, 20.90, 14.49, 14.32.

HR-MS (ESI) m/z calcd for $[C_{21}H_{44}N]^+$ ($[M+H]^+$): 310.3468, found: 310.3474.

_N_-(4-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl)-_N_-butylbutan-1-amine (67a)

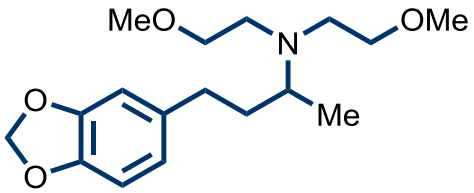


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.78–6.53 (m, 3H), 5.91 (s, 2H), 2.84–2.20 (m, 7H), 1.71 (s, 2H), 1.44–1.22 (m, 8H), 1.01–0.81 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.56, 145.47, 137.09, 121.13, 109.01, 108.16, 100.79, 54.48, 49.86, 33.27, 31.53, 20.84, 14.30, 13.96.

HR-MS (ESI) m/z calcd for $[C_{19}H_{32}NO_2]^+$ ($[M+H]^+$): 306.2428, found: 306.2429.

4-(Benzo[d][1,3]dioxol-5-yl)-_N,N_-bis(2-methoxyethyl)butan-2-amine (68a)

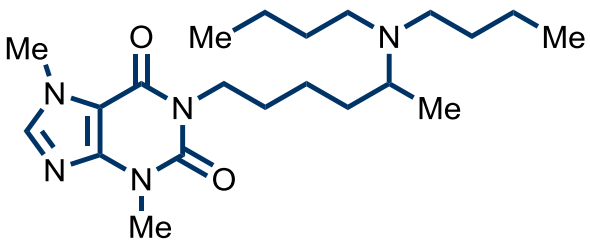


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.74–6.66 (m, 2H), 6.65–6.55 (m, 1H), 5.89 (s, 2H), 3.38 (td, J = 6.8, 1.9 Hz, 4H), 3.33 (s, 6H), 2.68 (dt, J = 13.5, 6.8 Hz, 3H), 2.62–2.47 (m, 4H), 1.71 (dddd, J = 13.3, 9.8, 5.7, 3.6 Hz, 1H), 1.47 (ddt, J = 13.5, 9.7, 6.5 Hz, 1H), 0.96 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 147.51, 145.45, 136.75, 121.09, 108.98, 108.09, 100.73, 72.74, 58.86, 56.31, 50.42, 36.50, 32.96, 14.37.

HR-MS (ESI) m/z calcd for $[C_{17}H_{28}NO_4]^+$ ($[M+H]^+$): 310.2013, found: 310.2021.

1-(5-(Dibutylamino)hexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (69a)

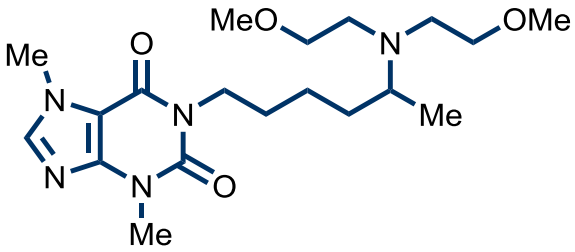


^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 (d, J = 0.7 Hz, 1H), 4.05–3.91 (m, 5H), 3.56 (s, 3H), 2.74–2.53 (m, 1H), 2.44–2.18 (m, 4H), 1.70–1.57 (m, 2H), 1.45–1.18 (m, 12H), 0.88 (t, J = 7.2 Hz, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 155.30, 151.47, 148.70, 141.29, 107.69, 54.87, 49.75, 41.47, 33.58, 29.66, 28.24, 24.62, 20.67, 14.14.

HR-MS (ESI) m/z calcd for $[C_{21}H_{38}N_5O_2]^+$ ($[M+H]^+$): 392.3020, found: 392.3018.

1-(5-(Bis(2-methoxyethyl)amino)hexyl)-3,7-dimethyl-3,7-dihydro-1H-purine-2,6-dione (70a)



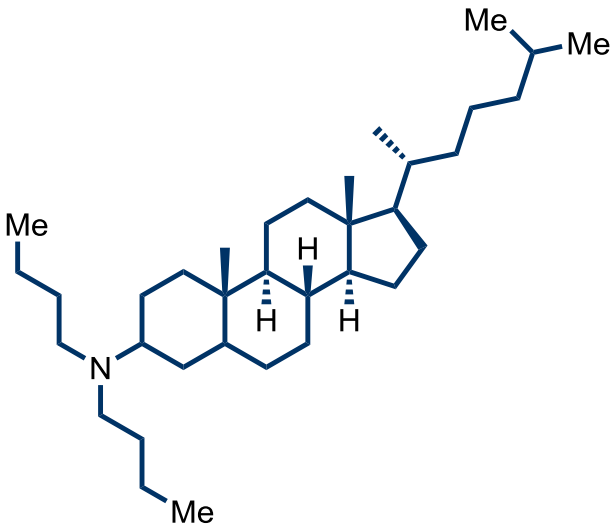
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 (q, J = 0.6 Hz, 1H), 4.04–3.93 (m, 5H), 3.56 (s, 3H), 3.32 (s, 9H), 2.77–2.52 (m, 5H), 1.76 (s, 1H), 1.62 (q, J = 7.6 Hz, 2H), 1.50 (s, 1H), 1.41–1.33 (m, 2H), 1.25 (d, J = 6.9 Hz, 1H), 0.93 (d, J = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 155.28, 151.46, 148.71, 141.33, 107.68, 72.71, 58.82, 56.93, 50.34, 41.40, 33.58, 29.67, 28.12, 24.49, 14.64.

HR-MS (ESI) m/z calcd for $[C_{19}H_{34}N_5O_4]^+$ ($[M+H]^+$): 396.2605, found: 396.2604.

HR-MS (ESI): m/z calculated for $[C_{19}H_{33}N_5O_4Na]^+$ ($[M+Na]^+$): 418.2425, found: 418.2426.

(*8R,9S,10S,13R,14S,17R*)-*N,N*-Dibutyl-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-*1H*-cyclopenta[a]phenanthren-3-amine (71a)

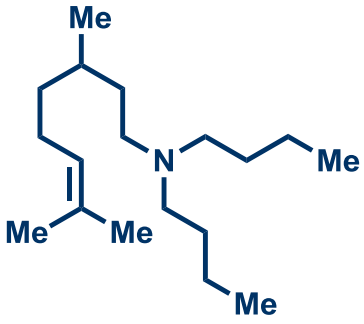


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 2.46 (m, 5H), 1.91–0.82 (m, 57H), 0.64 (d, *J* = 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 61.04, 56.67, 56.45, 54.66, 50.64, 46.32, 43.35, 42.85, 40.83, 40.38, 39.68, 36.88, 36.33, 36.04, 35.95, 35.23, 32.33, 31.00, 29.62, 28.49, 28.17, 27.77, 26.77, 24.42, 23.96, 23.88, 22.98, 22.72, 20.93, 18.84, 14.32, 12.20.

HR-MS (ESI) m/z calcd for $[C_{35}H_{66}N]^+$ ($[M+H]^+$): 500.5190, found: 500.5198.

***N,N*-Dibutyl-3,7-dimethyloct-6-en-1-amine (72a)**

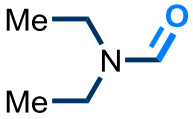


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.09 (ddt, *J* = 8.6, 5.7, 1.4 Hz, 1H), 2.51–2.30 (m, 6H), 2.10–1.90 (m, 2H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.61–1.58 (m, 3H), 1.52–1.36 (m, 6H), 1.35–1.22 (m, 6H), 1.19–1.11 (m, 1H), 0.94–0.86 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 131.20, 125.05, 54.01, 52.15, 37.40, 33.92, 31.17, 29.24, 25.87, 25.66, 20.96, 19.89, 17.77, 14.26.

HR-MS (ESI) m/z calcd for $[C_{18}H_{38}N]^+$ ($[M+H]^+$): 268.2999, found: 268.3004.

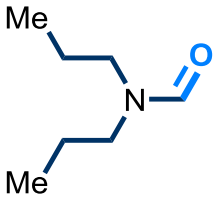
***N,N*-diethylformamide (1b)**



10 mmol scale

In a 300 mL steel Parr autoclave, $Cu(OTf)_2$ (180 mg, 0.5 mmol) was added, MeCN (30.0 mL), pyridine (1.60 g) and tertiary amine (1.01 g, 10 mmol) were added, independently. The autoclave was flushed with air 2 times at 10 bar and finally pressurized to the desired value (30 bar). Then it was placed into an aluminium block and heat to the desired temperature (130 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the yield of **1b** was determined by GC using *n*-dodecan as the standard. Safety statement: The scaling up reactions performed with a flammable solvent (MeCN) under high pressures of air (40 bar) with a substrate capable of autoxidation (*n*-tributylamine), so the explosion hazard should be taken in consideration.

***N,N*-Dipropylformamide (2b)**

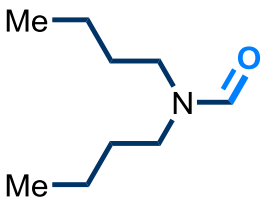


According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), tripropylamine **2a** (66 mg, 0.46 mmol), air (30 bar), room temperature to 130 °C and then at 130 °C for 24 h. The product **2b** (44 mg, 0.34 mmol, 73%) was obtained by column chromatography (*n*-Heptane/EtOAc: 4:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (s, 1H), 3.25–3.18 (m, 2H), 3.13 (dd, J = 7.7, 6.6 Hz, 2H), 1.62–1.44 (m, 4H), 0.85 (td, J = 7.4, 2.0 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.03, 49.32, 43.87, 21.85, 20.56, 11.36, 10.97.

***N,N*-Dibutylformamide (3b)**

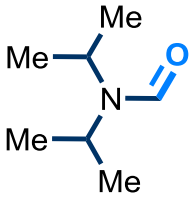


According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), tributylamine **3a** (92 mg, 0.50 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The yield of **3b** was determined by GC using *n*-dodecan as the standard.

10 mmol scale

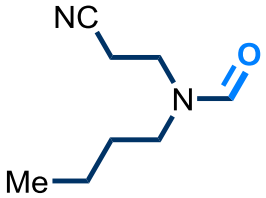
In a 300 mL steel Parr autoclave, CuCl (55 mg, 0.56 mmol) was added, MeCN (30.0 mL), pyridine (1.60 g) and tributylamine **3a** (1.85 g, 10 mmol) were added, independently. The autoclave was flushed with air 2 times at 10 bar and finally pressurized to the desired value (40 bar). Then it was placed into an aluminium block and heat to the desired temperature (100 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the yield of **3b** was determined by GC using *n*-dodecan as the standard (90%). Safety statement: The scaling up reactions performed with a flammable solvent (MeCN) under high pressures of air (40 bar) with a substrate capable of autoxidation (*n*-tributylamine), so the explosion hazard should be taken in consideration.

***N,N*-Diisopropylformamide (4b)**



According to **GP III**, CuCl (2.6 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-ethyl-*N*-isopropylpropan-2-amine **4a** (74 mg, 0.57 mmol), air (40 bar), room temperature to 130 °C and then at 130 °C for 24 h. The the yield of **4b** was determined by GC using *n*-dodecan as the standard.

***N*-Butyl-*N*-(2-cyanoethyl)formamide (5b)**



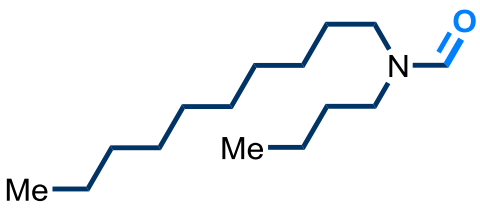
According to **GP III**, CuCl (2.6 mg), acetonitrile (2.0 mL), pyridine (80 mg), 3-(dibutylamino)propanenitrile **5a** (100 mg, 0.55 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **5b** (65 mg, 0.42 mmol, 76%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (s, 1H), 3.85–3.01 (m, 4H), 2.89–2.28 (m, 2H), 1.42 (dtd, J = 92.8, 14.9, 7.3 Hz, 4H), 0.94 (h, J = 10.0, 8.0 Hz, 3H).

^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm) 163.70, 163.38, 119.52, 119.43, 46.75, 42.85, 37.97, 30.71, 29.42, 20.05, 19.60, 18.01, 16.02, 14.19, 14.05.

HR-MS (EI) m/z calcd for [$C_8H_{14}N_2O^+$] [M^+]: 154.1101, found: 154.1104.

***N*-Butyl-*N*-decylformamide (6b)**



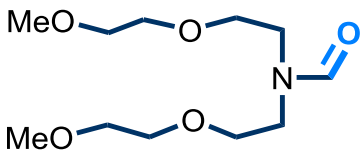
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutyldecan-1-amine **6a** (136 mg, 0.51 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **6b** (119 mg, 0.49 mmol, 96%) was by column chromatography (*n*-Heptane/EtOAc: 3:1) obtained as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38 (s, 1H), 3.41–3.10 (m, 4H), 1.47 (q, J = 7.6 Hz, 5H), 1.39–1.08 (m, 15H), 0.90–0.81 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.44, 47.43, 42.07, 31.86, 30.72, 29.49, 29.37, 29.19, 26.48, 22.66, 20.14, 19.65, 14.09, 13.78, 13.62.

HR-MS (EI) m/z calcd for [$C_{15}H_{31}NO^+$] [M^+]: 241.2400, found: 241.2400.

***N,N*-Bis(2-(2-methoxyethoxy)ethyl)formamide (7b)**



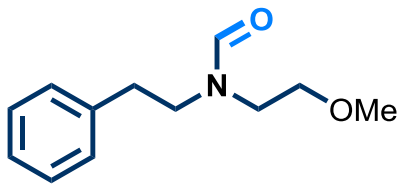
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), tris(2-(2-methoxyethoxy)ethyl)amine **7a** (170 mg, 0.53 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **7b** (99 mg, 0.40 mmol, 75%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.45 (s, 1H), 3.61–3.41 (m, 16H), 3.31 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.46, 71.87, 71.77, 70.55, 70.19, 69.24, 68.86, 59.06, 58.94, 48.76, 43.03.

HR-MS (EI) m/z calcd for [$C_{11}H_{23}NO_5^+$] [M^+]: 249.1571, found: 249.1570.

***N*-(2-Methoxyethyl)-*N*-phenethylformamide (8b)**



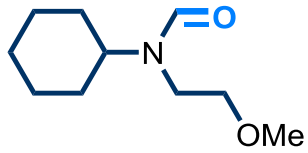
According to **GP III**, CuCl (2.7 mg), acetonitrile (2.0 mL), pyridine (80 mg), 2-methoxy-*N*-(2-methoxyethyl)-N-phenethylethan-1-amine **8a** (132 mg, 0.56 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **8b** (91 mg, 0.44 mmol, 79%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29–8.17 (m, 1H), 7.39–7.04 (m, 5H), 3.54 (dd, *J* = 20.8, 12.7 Hz, 5H), 3.38–3.28 (m, 4H), 2.85 (t, *J* = 6.8 Hz, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) *δ* (ppm) 163.25, 139.02, 129.09, 128.82, 126.65, 69.78, 58.49, 49.12, 44.02, 34.90.

HR-MS (EI) m/z calcd for [$C_{12}H_{17}NO_2^+$] [M^+]: 207.1254, found: 207.1257.

***N*-Cyclohexyl-*N*-(2-methoxyethyl)formamide (9b)**



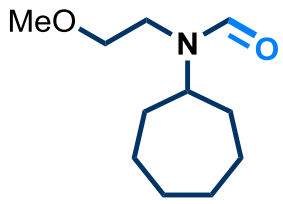
According to **GP III**, CuCl (2.6 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-bis(2-methoxyethyl)cyclohexanamine **9a** (104 mg, 0.48 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **9b** (89 mg, 0.48 mmol, 99%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) 8.38 (s, 1H), 3.47–3.10 (m, 8H), 1.87–1.68 (m, 3H), 1.68–1.52 (m, 2H), 1.49–1.33 (m, 2H), 1.32–1.17 (m, 2H), 1.12–0.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) *δ* (ppm) 163.16, 72.26, 70.44, 58.69, 41.73, 32.76, 25.80, 25.36.

HR-MS (EI) m/z calcd for [$C_{10}H_{19}NO_2^+$] [M^+]: 185.1410, found: 185.1412.

***N*-Cycloheptyl-*N*-(2-methoxyethyl)formamide (10b)**



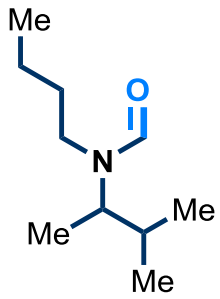
According to **GP III**, CuCl (2.8 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-bis(2-methoxyethyl)cycloheptanamine **10a** (146 mg, 0.64 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **10b** (123 mg, 0.62 mmol, 97%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.48 (s, 1H), 3.52–3.20 (m, 8H), 1.86–1.33 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.90, 71.89, 70.36, 58.61, 42.28, 34.96, 27.13, 24.87.

HR-MS (EI) m/z calcd for $[C_{11}H_{21}NO_2^+]$ $[M^+]$: 199.1567, found: 199.1574.

***N*-Butyl-*N*-(3-methylbutan-2-yl)formamide (11b)**



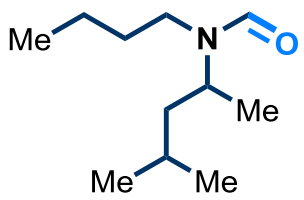
According to **GP III**, CuCl (2.6 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-butyl-*N*-(3-methylbutan-2-yl)butan-1-amine **11a** (80 mg, 0.40 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **11b** (66 mg, 0.39 mmol, 98%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15 (s, 1H), 3.56–3.37 (m, 1H), 3.22–2.92 (m, 2H), 1.62–1.37 (m, 4H), 1.35–1.12 (m, 7H), 0.93–0.86 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.62, 54.51, 41.00, 37.54, 31.06, 20.79, 20.65, 19.71, 14.02, 13.87.

HR-MS (EI) m/z calcd for $[C_{10}H_{21}NO^+]$ $[M^+]$: 171.1617, found: 171.1609.

***N*-Butyl-*N*-(4-methylpentan-2-yl)formamide (12b)**



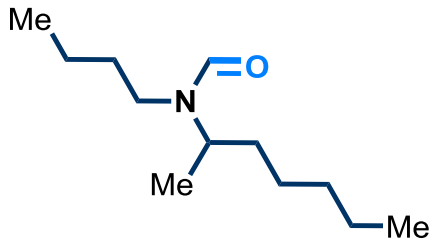
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutyl-4-methylpentan-2-amine **12a** (68 mg, 0.32 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **12b** (56 mg, 0.30 mmol, 94%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.61 (s, 1H), 3.68–3.41 (m, 1H), 3.16 (ddt, J = 34.6, 15.0, 7.3 Hz, 2H), 1.66–1.39 (m, 4H), 1.36–1.08 (m, 6H), 0.98–0.78 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 161.92, 52.72, 44.41, 41.07, 31.14, 24.63, 22.92, 22.09, 21.05, 20.65, 13.87.

HR-MS (ESI) m/z calcd for $[C_{11}H_{24}NO]^+$ ($[M+H]^+$): 186.1852, found: 186.1860.

***N*-Butyl-*N*-(heptan-2-yl)formamide (13b)**



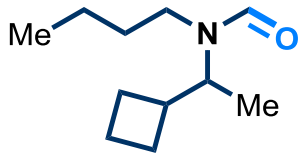
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutylheptan-2-amine **13a** (95 mg, 0.42 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **13b** (81 mg, 0.40 mmol, 95%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.41 (s, 1H), 3.42 (dt, J = 8.6, 6.6 Hz, 1H), 3.25–2.97 (m, 2H), 1.58–1.39 (m, 4H), 1.31–1.13 (m, 11H), 0.92–0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.26, 54.92, 41.07, 35.36, 31.55, 31.05, 26.21, 22.56, 20.73, 14.03, 13.85, 13.74.

HR-MS (EI) m/z calcd for $[C_{12}H_{25}NO^+]$ $[M^+]$: 199.1931, found: 199.1927.

***N*-Butyl-*N*-(1-cyclobutylethyl)formamide (14b)**



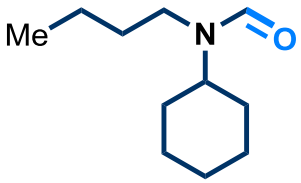
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-butyl-*N*-(1-cyclobutylethyl)butan-1-amine **14a** (94 mg, 0.45 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **14b** (76 mg, 0.42 mmol, 93%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.55 (s, 1H), 3.30 (dq, J = 10.0, 6.5 Hz, 1H), 3.20–2.88 (m, 2H), 2.56–2.31 (m, 1H), 2.11–1.96 (m, 1H), 1.96–1.70 (m, 3H), 1.69–1.55 (m, 2H), 1.48 (p, J = 7.5 Hz, 2H), 1.34–1.21 (m, 2H), 1.10 (d, J = 6.6 Hz, 2H), 1.03 (d, J = 6.3 Hz, 1H), 0.91–0.86 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.95, 60.64, 41.31, 30.98, 26.28, 26.09, 20.56, 17.16, 17.04, 15.74, 13.84.

HR-MS (EI) m/z calcd for [$C_{11}H_{21}NO^+$] [M^+]: 183.1618, found: 183.1614.

N-Butyl-*N*-cyclohexylformamide (15b)



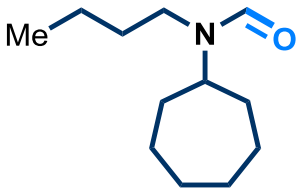
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutylcyclohexanamine **15a** (90 mg, 0.43 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **15b** (75 mg, 0.41 mmol, 95%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.90 (s, 1H), 3.33–3.01 (m, 3H), 1.79 (ddd, J = 27.4, 9.5, 3.5 Hz, 3H), 1.71–1.58 (m, 2H), 1.56–1.39 (m, 4H), 1.35–1.20 (m, 4H), 1.16–1.02 (m, 1H), 0.89 (td, J = 7.3, 4.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.39, 59.00, 42.14, 32.92, 30.72, 25.97, 25.24, 20.47, 13.85.

HR-MS (EI) m/z calcd for [$C_{11}H_{21}NO^+$] [M^+]: 183.1618, found: 183.1612.

N-Butyl-*N*-cycloheptylformamide (16b)



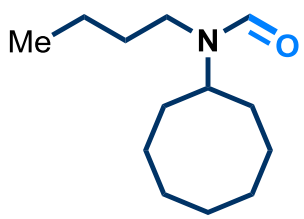
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutylcycloheptanamine **16a** (117 mg, 0.52 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **16b** (100 mg, 0.51 mmol, 98%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.73 (s, 1H), 3.29 (dd, J = 9.7, 4.2 Hz, 1H), 3.21–3.02 (m, 2H), 1.82–1.24 (m, 16H), 0.88 (td, J = 7.2, 4.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.30, 61.18, 42.42, 35.06, 30.93, 27.13, 24.90, 20.36, 13.68.

HR-MS (EI) m/z calcd for [$C_{12}H_{23}NO^+$] [M^+]: 197.1774, found: 197.1780.

***N*-Butyl-*N*-cyclooctylformamide (17b)**



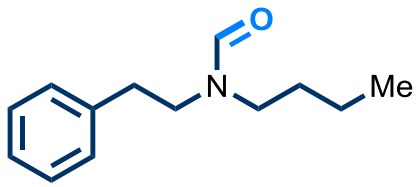
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutylcyclooctanamine **17a** (129 mg, 0.54 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **17b** (112 mg, 0.53 mmol, 98%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a light yellow liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.04 (d, J = 75.4 Hz, 1H), 3.90–3.40 (m, 1H), 3.23–2.99 (m, 2H), 1.93–1.14 (m, 18H), 0.93–0.82 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 162.41, 58.48, 41.71, 33.63, 33.32, 31.85, 26.40, 25.91, 20.42, 14.14.

HR-MS (EI) m/z calcd for [$C_{13}H_{25}NO^{+}$] [M^{+}]: 211.1931, found: 211.1929.

***N*-Butyl-*N*-phenethylformamide (18b)**



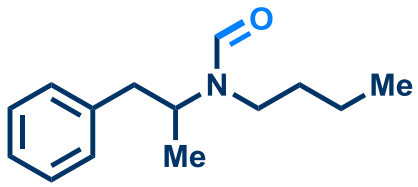
According to **GP III**, CuCl (1.7 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-butyl-*N*-phenethylbutan-1-amine **18a** (75 mg, 0.32 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **18b** (37 mg, 0.18 mmol, 56%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (s, 1H), 7.41–6.85 (m, 5H), 3.51–3.32 (m, 2H), 3.31–3.17 (m, 1H), 3.04 (t, J = 7.1 Hz, 1H), 2.88–2.68 (m, 2H), 1.52–1.35 (m, 2H), 1.30–1.14 (m, 2H), 0.86 (dd, J = 8.5, 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 162.97, 138.89, 133.11, 129.01, 126.93, 49.18, 44.36, 35.60, 30.84, 20.28, 13.93.

HR-MS (EI) m/z calcd for [$C_{13}H_{19}NO^{+}$] [M^{+}]: 205.1461, found: 205.1460.

***N*-Butyl-*N*-(1-phenylpropan-2-yl)formamide (19b)**

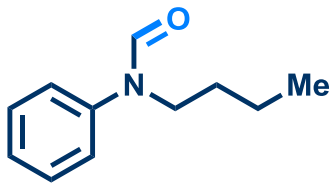


According to **GP III**, CuCl (2.6 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-butyl-*N*-(1-phenylpropan-2-yl)butan-1-amine **19a** (113 mg, 0.46 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **19b** (100 mg, 0.46 mmol, 99%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a light yellow liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 7.83 (s, 1H), 7.31–7.24 (m, 2H), 7.23–7.13 (m, 3H), 3.83 (q, J = 7.1 Hz, 1H), 3.21–2.95 (m, 2H), 2.80 (d, J = 7.4 Hz, 2H), 1.50–1.31 (m, 2H), 1.27–1.13 (m, 5H), 0.89–0.82 (m, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 162.69, 139.33, 129.51, 128.70, 126.67, 55.51, 46.47, 41.24, 32.80, 19.72, 18.22, 14.03.

***N*-Butyl-*N*-phenylformamide (20b)**



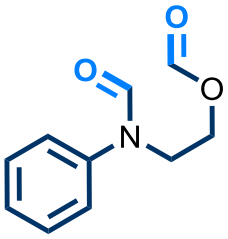
According to **GP III**, CuCl (2.7 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutylaniline **20a** (106 mg, 0.52 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **20b** (65 mg, 0.37 mmol, 71%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a yellow liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.39 (s, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.35–7.22 (m, 3H), 3.77 (t, J = 7.1 Hz, 2H), 1.38 (ddd, J = 8.7, 6.3, 2.1 Hz, 2H), 1.22 (td, J = 9.3, 8.3, 6.0 Hz, 2H), 0.82 (td, J = 7.3, 3.3 Hz, 3H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 162.43, 141.19, 129.99, 126.58, 123.80, 43.38, 29.56, 19.77, 14.00.

HR-MS (EI) m/z calcd for [$C_{11}H_{15}NO^{+}$] [M^{+}]: 177.1148, found: 177.1154.

2-(*N*-Phenylformamido)ethyl formate (21b)[3]



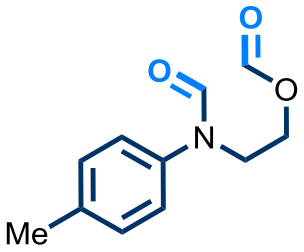
According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 4-phenylmorpholine **21a** (80 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (20 bar), room temperature to 80 °C and then at 80 °C for 24 h. The product **21b** (84 mg, 0.44 mmol, 90%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.40 (s, 1H), 8.02–7.92 (m, 1H), 7.47–7.38 (m, 2H), 7.36–7.24 (m, 1H), 7.27–7.14 (m, 2H), 4.34 (t, *J* = 5.5 Hz, 2H), 4.11 (t, *J* = 5.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.73, 160.61, 140.65, 129.86, 127.36, 124.49, 60.65, 44.22.

HR-MS (EI) m/z calcd for $[C_{10}H_{11}NO_3^+]$ $[M^+]$: 193.0733, found: 193.0738.

2-(*N*-*p*-Tolylformamido)ethyl formate (22b)



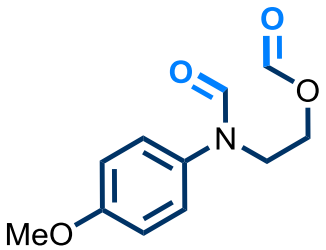
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(*p*-tolyl)morpholine **22a** (86 mg, 0.49 mmol), acetonitrile (2.0 mL), air (20 bar), pyridine (8.0 mg), room temperature to 80 °C and then at 80 °C for 24 h. The product **22b** (86 mg, 0.42 mmol, 86%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.33 (s, 1H), 7.95 (p, *J* = 0.7 Hz, 1H), 7.25–7.15 (m, 2H), 7.10–7.01 (m, 2H), 4.30 (td, *J* = 5.7, 0.9 Hz, 2H), 4.05 (dd, *J* = 6.0, 5.3 Hz, 2H), 2.41–2.28 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.77, 160.65, 138.04, 137.43, 130.42, 124.65, 60.65, 44.25, 21.00.

HR-MS (EI) m/z calcd for $[C_{11}H_{13}NO_3^+]$ $[M^+]$: 207.0890, found: 207.0894.

2-(*N*-(4-Methoxyphenyl)formamido)ethyl formate (23b)



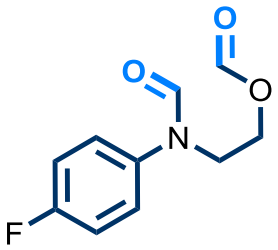
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(4-methoxyphenyl)morpholine **23a** (97 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **23b** (91 mg, 0.41 mmol, 82%) was obtained by column chromatography (*n*-Heptane/EtOAc: 4:1) as yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.26 (s, 1H), 7.96 (t, *J* = 0.7 Hz, 1H), 7.16–7.03 (m, 2H), 6.96–6.81 (m, 2H), 4.28 (td, *J* = 5.7, 0.9 Hz, 2H), 4.01 (td, *J* = 5.6, 0.6 Hz, 2H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 162.87, 160.65, 158.91, 133.37, 126.72, 114.94, 60.63, 55.59, 44.54.

HR-MS (EI) m/z calcd for $[C_{11}H_{13}NO_4^+]$ $[M^+]$: 223.0839, found: 223.0836.

2-(*N*-(4-Fluorophenyl)formamido)ethyl formate (24b)



According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 4-(4-fluorophenyl)morpholine **24a** (95 mg, 0.52 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **24b** (94 mg, 0.45 mmol, 87%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

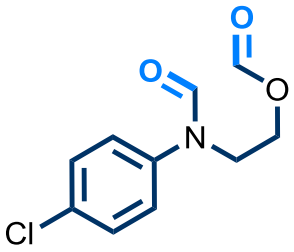
^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.30 (s, 1H), 7.95 (t, *J* = 0.7 Hz, 1H), 7.22–7.14 (m, 2H), 7.13–7.04 (m, 2H), 4.31 (td, *J* = 5.6, 0.8 Hz, 2H), 4.04 (ddd, *J* = 6.0, 5.2, 0.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 162.78, 161.50 (d, *J* = 202.8 Hz), 160.32, 136.77 (d, *J* = 3.2 Hz), 126.86 (d, *J* = 8.6 Hz), 116.71 (d, *J* = 23.0 Hz), 60.65, 44.64.

^{19}F NMR (282 MHz, $CDCl_3$): *δ* (ppm) -113.98.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}FNO_3^+]$ $[M^+]$: 211.0639, found: 211.0639.

2-(*N*-(4-Chlorophenyl)formamido)ethyl formate (25b)



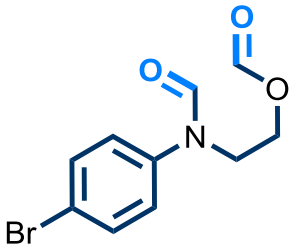
According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 4-(4-chlorophenyl)morpholine **25a** (99 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (20 bar), room temperature to 80 °C and then at 80 °C for 24 h. The product **25b** (85 mg, 0.37 mmol, 74%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.35 (s, 1H), 7.95 (t, *J* = 0.7 Hz, 1H), 7.43–7.31 (m, 2H), 7.19–7.05 (m, 2H), 4.36–4.26 (m, 2H), 4.05 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.38, 160.57, 139.33, 133.13, 130.05, 125.76, 60.67, 44.40.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}ClNO_3^+]$ $[M^+]$: 227.0344, found: 227.0340.

2-(*N*-(4-Bromophenyl)formamido)ethyl formate (26b)



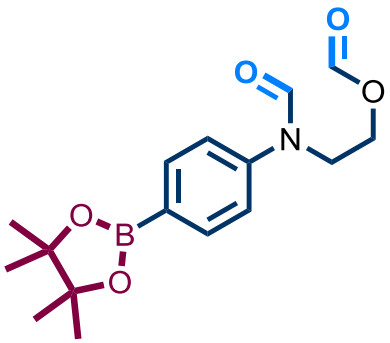
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(4-bromophenyl)morpholine **26a** (124 mg, 0.51 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **26b** (51 mg, 0.19 mmol, 37%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.37 (s, 1H), 7.96 (t, *J* = 0.7 Hz, 1H), 7.58–7.51 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.33 (m, 2H), 4.12–4.02 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.36, 160.60, 139.88, 133.08, 126.03, 120.99, 60.72, 44.40.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}BrNO_3^+]$ $[M^+]$: 270.9839, found: 270.9841.

2-(*N*-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)formamido)ethyl formate (27b)



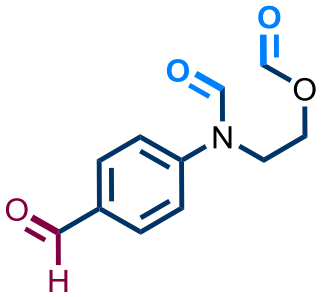
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.3 mg), 4-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine **27a** (145 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (20 bar), room temperature to 80 °C and then at 80 °C for 24 h. The product **27b** (92 mg, 0.29 mmol, 58%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.43 (s, 1H), 7.92 (t, J = 0.7 Hz, 1H), 7.89–7.73 (m, 2H), 7.22–7.10 (m, 2H), 4.42–4.24 (m, 2H), 4.11 (dd, J = 5.9, 5.3 Hz, 2H), 1.33 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.57, 160.61, 143.17, 136.45, 122.96, 84.17, 60.74, 43.92, 24.94.

HR-MS (EI) m/z calcd for $[C_{16}H_{22}BNO_5^+]$ $[M^+]$: 319.1586, found: 319.1590.

2-(*N*-(4-Formylphenyl)formamido)ethyl formate (28b)



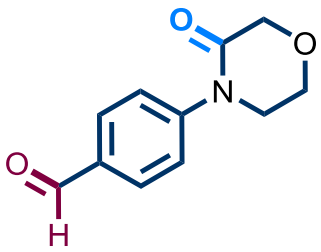
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-morpholinobenzaldehyde **28a** (96 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **28b** (71 mg, 0.32 mmol, 64%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.99 (s, 1H), 8.56 (s, 1H), 7.99–7.85 (m, 3H), 7.45–7.32 (m, 2H), 4.44–4.31 (m, 2H), 4.16 (tt, J = 5.8, 0.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 190.77, 162.14, 160.54, 146.06, 134.49, 131.47, 123.11, 60.70, 43.99.

HR-MS (EI) m/z calcd for $[C_{11}H_{11}NO_4^+]$ $[M^+]$: 221.0683, found: 221.0678.

4-(3-Oxomorpholino)benzaldehyde (28c)



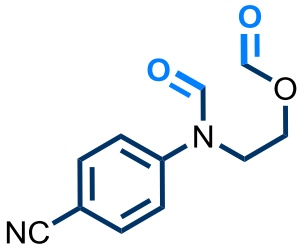
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-morpholinobenzaldehyde **28a** (96 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **28c** (15 mg, 0.07 mmol, 14%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 10.00 (s, 1H), 8.01–7.84 (m, 2H), 7.69–7.50 (m, 2H), 4.37 (s, 2H), 4.12–4.02 (m, 2H), 3.94–3.76 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 191.19, 166.86, 146.62, 134.42, 130.75, 125.10, 68.77, 64.15, 49.12.

HR-MS (EI) m/z calcd for $[C_{11}H_{11}NO_3^+]$ $[M^+]$: 205.0733, found: 205.0738.

2-(*N*-(4-Cyanophenyl)formamido)ethyl formate (29b)



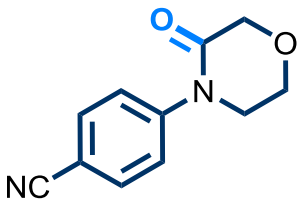
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-morpholinobenzonitrile **29a** (95 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **29b** (52 mg, 0.24 mmol, 48%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.52 (s, 1H), 8.00–7.88 (m, 1H), 7.78–7.66 (m, 2H), 7.39–7.29 (m, 2H), 4.37 (td, *J* = 5.5, 0.9 Hz, 2H), 4.13 (dd, *J* = 5.8, 5.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 161.90, 160.49, 144.85, 133.98, 123.34, 118.03, 110.47, 60.68, 44.08.

HR-MS (EI) m/z calcd for $[C_{11}H_{10}N_2O_3^+]$ $[M^+]$: 218.0686, found: 218.0685.

4-(3-Oxomorpholino)benzonitrile (29c)



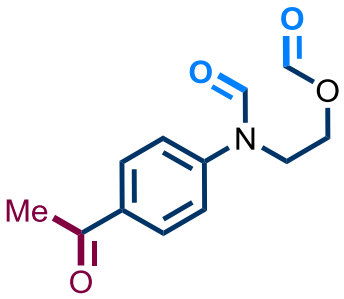
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-morpholinobenzonitrile **29a** (95 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **29c** (13 mg, 0.06 mmol, 12%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 7.76–7.67 (m, 2H), 7.60–7.47 (m, 2H), 4.36 (s, 2H), 4.10–4.00 (m, 2H), 3.88–3.75 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 166.85, 145.21, 133.20, 125.18, 118.44, 110.24, 68.75, 64.09, 48.96.

HR-MS (EI) m/z calcd for $[C_{11}H_{10}N_2O_2^+]$ $[M^+]$: 202.0737, found: 202.0734.

2-(*N*-(4-Acetylphenyl)formamido)ethyl formate (30b)



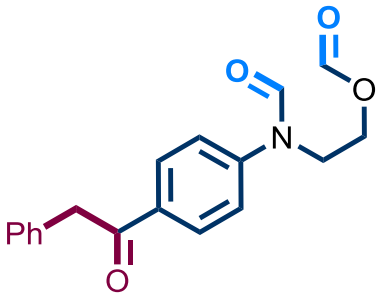
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 1-(4-morpholinophenyl)ethan-1-one **30a** (101 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 120 °C and then at 120 °C for 24 h. The product **30b** (90 mg, 038 mmol, 78%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.45 (s, 1H), 8.00–7.89 (m, 2H), 7.87 (t, *J* = 0.7 Hz, 1H), 7.28–7.09 (m, 2H), 4.36–4.22 (m, 2H), 4.07 (dd, *J* = 5.9, 5.2 Hz, 2H), 2.52 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 196.67, 162.16, 160.52, 144.81, 135.26, 130.14, 122.83, 60.64, 43.87, 26.62.

HR-MS (EI) m/z calcd for $[C_{12}H_{13}NO_4^+]$ $[M^+]$: 235.0839, found: 235.0838.

2-(*N*-(4-(2-Phenylacetyl)phenyl)formamido)ethyl formate (31b)



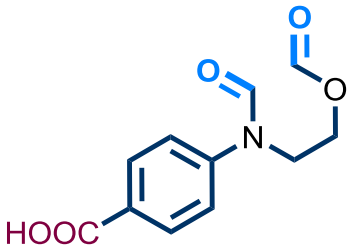
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.5 mg), 1-(4-morpholinophenyl)-2-phenylethan-1-one **31a** (143 mg, 0.54 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **31b** (73 mg, 0.25 mmol, 46%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 8.04–7.95 (m, 2H), 7.87 (t, J = 0.7 Hz, 1H), 7.33–7.07 (m, 7H), 4.33–4.25 (m, 2H), 4.20 (s, 2H), 4.06 (dd, J = 5.9, 5.3 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 196.27, 162.18, 160.56, 144.89, 134.72, 134.25, 130.54, 129.45, 128.87, 127.15, 122.86, 60.69, 45.66, 43.93.

HR-MS (EI) m/z calcd for $[C_{18}H_{17}NO_4^+]$ $[M^+]$: 311.1152, found: 311.1154.

4-(*N*-(2-(Formyloxy)ethyl)formamido)benzoic acid (32b)



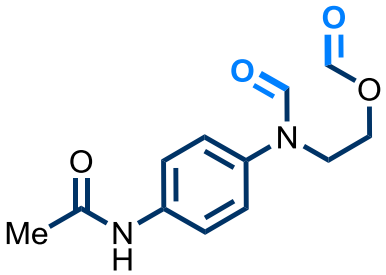
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.3 mg), 4-morpholinobenzoic acid **32a** (104 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 120 °C and at 120 °C for 24 h. The product **32b** (71 mg, 0.30 mmol, 60%) was obtained by column chromatography (*n*-Heptane/EtOAc: 3:1) as a white solid.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 12.99 (s, 1H), 8.62 (s, 1H), 8.17–8.07 (m, 1H), 8.08–7.87 (m, 2H), 7.54–7.41 (m, 2H), 4.28–4.18 (m, 2H), 4.14–4.05 (m, 2H).

^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 166.71, 162.59, 161.87, 144.52, 130.73, 128.06, 22.15, 60.17, 42.48.

HR-MS (EI) m/z calcd for $[C_{11}H_{11}NO_5^+]$ $[M^+]$: 237.0631, found: 237.0632.

2-(*N*-(4-Acetamidophenyl)formamido)ethyl formate (33b)



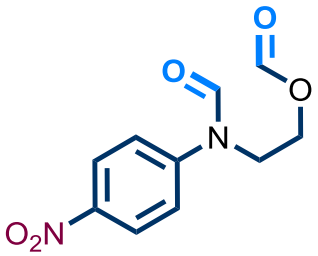
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.5 mg), *N*-(4-morpholinophenyl)acetamide **33a** (111 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **33b** (89 mg, 0.36 mmol, 72%) was obtained by column chromatography (*n*-Heptane/EtOAc: 4:1) as a light brown liquid.

^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 10.03 (s, 1H), 8.34 (s, 1H), 8.14 (t, J = 0.7 Hz, 1H), 7.73–7.55 (m, 2H), 7.32–7.19 (m, 2H), 4.17 (dd, J = 5.9, 5.0 Hz, 2H), 4.03–3.94 (m, 2H), 2.05 (s, 3H).

^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 168.37, 162.46, 161.87, 137.88, 135.29, 124.50, 119.78, 60.10, 43.11, 23.98.

HR-MS (EI) m/z calcd for [$C_{12}H_{14}N_2O_4^+$] [M^+]: 250.0948, found: 250.0947.

2-(*N*-(4-Nitrophenyl)formamido)ethyl formate (34b)[4]

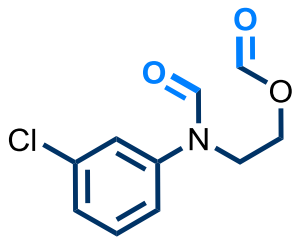


According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 4-(4-nitrophenyl)morpholine **34a** (105 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **34b** (51 mg, 0.21 mmol, 42%) was obtained by column chromatography (*n*-Heptane/EtOAc: 4:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.59 (s, 1H), 8.35–8.21 (m, 2H), 7.95 (q, J = 0.7 Hz, 1H), 7.44–7.31 (m, 2H), 4.44–4.33 (m, 2H), 4.17 (dd, J = 5.9, 5.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.84, 160.49, 146.57, 145.81, 125.60, 122.84, 60.71, 44.18.

2-(*N*-(3-Chlorophenyl)formamido)ethyl formate (35b)



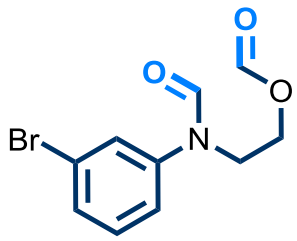
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.5 mg), 4-(3-chlorophenyl)morpholine **35a** (125 mg, 0.64 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **35b** (47 mg, 0.21 mmol, 33%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.40 (s, 1H), 7.98 (p, *J* = 0.7 Hz, 1H), 7.41–7.27 (m, 2H), 7.23 (td, *J* = 2.0, 0.5 Hz, 1H), 7.10 (ddd, *J* = 7.7, 2.2, 1.3 Hz, 1H), 4.35 (td, *J* = 5.6, 0.9 Hz, 2H), 4.09 (dd, *J* = 5.9, 5.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.38, 160.61, 142.07, 135.58, 130.95, 127.55, 124.54, 122.43, 60.72, 44.39.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}ClNO_3^+]$ $[M^+]$: 227.0344, found: 227.0343.

2-(*N*-(3-Bromophenyl)formamido)ethyl formate (36b)



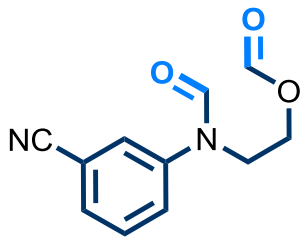
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.1 mg), 4-(3-bromophenyl)morpholine **36a** (117 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **36b** (59 mg, 0.22 mmol, 45%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.33 (s, 1H), 7.91 (p, *J* = 0.7 Hz, 1H), 7.39 (ddd, *J* = 8.0, 1.8, 1.0 Hz, 1H), 7.34–7.29 (m, 1H), 7.24–7.19 (m, 1H), 7.08 (ddd, *J* = 8.0, 2.2, 1.0 Hz, 1H), 4.34–4.19 (m, 2H), 4.06 – 3.98 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.35, 160.59, 142.15, 131.17, 130.45, 127.41, 123.37, 122.92, 60.68, 44.38.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}BrNO_3^+]$ $[M^+]$: 270.9839, found: 270.9841.

2-(*N*-(3-Cyanophenyl)formamido)ethyl formate (37b)



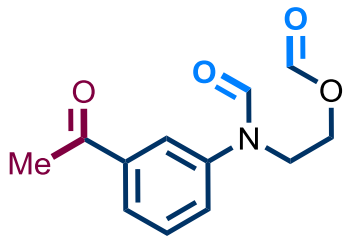
According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 3-morpholinobenzonitrile **37a** (85 mg, 0.45 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **37b** (59 mg, 0.27 mmol, 60%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.43 (s, 1H), 7.97 (t, *J* = 0.8 Hz, 1H), 7.65–7.52 (m, 3H), 7.47 (ddd, *J* = 7.9, 2.3, 1.3 Hz, 1H), 4.36 (ddd, *J* = 5.7, 5.1, 0.8 Hz, 2H), 4.11 (td, *J* = 5.4, 0.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 162.01, 160.49, 141.91, 131.01, 130.67, 128.37, 127.26, 117.71, 114.24, 60.72, 44.53.

HR-MS (EI) m/z calcd for $[C_{11}H_{10}N_2O_3^+]$ $[M^+]$: 218.0686, found: 218.0686.

2-(*N*-(3-Acetylphenyl)formamido)ethyl formate (38b)



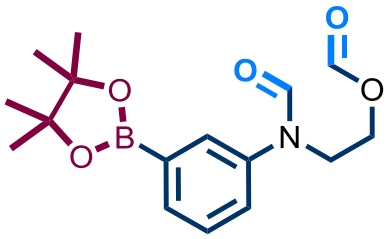
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 1-(3-morpholinophenyl)ethan-1-one **38a** (100 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **38b** (82 mg, 0.35 mmol, 71%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.41 (s, 1H), 7.94 (m, 1H), 7.87 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.80 (ddd, *J* = 2.2, 1.7, 0.5 Hz, 1H), 7.53 (td, *J* = 7.8, 0.5 Hz, 1H), 7.40 (ddd, *J* = 8.0, 2.3, 1.1 Hz, 1H), 4.37–4.26 (m, 2H), 4.12 (dd, *J* = 5.8, 5.2 Hz, 2H), 2.61 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 196.96, 162.41, 160.56, 141.35, 138.71, 130.26, 128.58, 127.19, 123.55, 60.69, 44.28, 26.79.

HR-MS (EI) m/z calcd for $[C_{12}H_{13}NO_4^+]$ $[M^+]$: 235.0839, found: 235.0838.

2-(*N*-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)formamido)ethyl formate (39b)



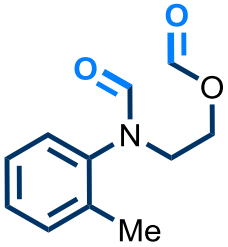
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine **39a** (150 mg, 0.52 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (20 bar), room temperature to 80 °C and then at 80 °C for 24 h. The product **39b** (94 mg, 0.30 mmol, 58%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.30 (s, 1H), 7.88 (q, J = 0.7 Hz, 1H), 7.66 (dt, J = 7.3, 1.2 Hz, 1H), 7.52 (ddd, J = 2.5, 1.1, 0.5 Hz, 1H), 7.34 (ddd, J = 7.9, 7.4, 0.5 Hz, 1H), 7.25–7.15 (m, 1H), 4.30–4.15 (m, 2H), 4.03 (ddd, J = 5.9, 5.2, 0.6 Hz, 2H), 1.26 (s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.82, 160.67, 140.16, 133.73, 130.57, 129.34, 127.42, 84.33, 60.73, 44.14, 24.96.

HR-MS (EI) m/z calcd for [$C_{16}H_{22}BNO_5^+$] [M^+]: 319.1586, found: 319.1591.

2-(*N*-*o*-Tolylformamido)ethyl formate (40b)



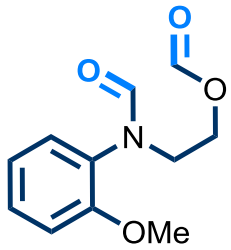
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 4-(o-tolyl)morpholine **40a** (95 mg, 0.54 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **40b** (53 mg, 0.26 mmol, 48%) was obtained by column chromatography (*n*-Heptane/EtOAc: 10:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.15 (s, 1H), 7.98 (t, J = 0.8 Hz, 1H), 7.33–7.27 (m, 2H), 7.26 (s, 1H), 7.20–7.11 (m, 1H), 4.30 (td, J = 5.6, 0.9 Hz, 2H), 3.98 (t, J = 5.6 Hz, 2H), 2.27 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.48, 160.69, 138.97, 135.94, 131.76, 128.90, 127.36, 60.77, 44.26, 17.87.

HR-MS (EI) m/z calcd for [$C_{11}H_{13}NO_3^+$] [M^+]: 207.0890, found: 207.0890.

2-(*N*-(2-Methoxyphenyl)formamido)ethyl formate (41b)



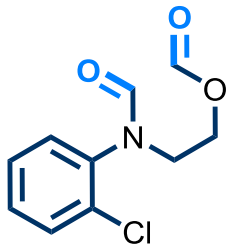
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(2-methoxyphenyl)morpholine **41a** (95 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **41b** (76 mg, 0.34 mmol, 69%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.94 (p, J = 0.7 Hz, 1H), 7.33 (ddd, J = 8.3, 7.5, 1.7 Hz, 1H), 7.14 (dd, J = 8.0, 1.7 Hz, 1H), 7.02–6.90 (m, 2H), 4.32–4.16 (m, 2H), 3.99 (td, J = 5.7, 0.6 Hz, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.78, 160.72, 155.36, 129.72, 129.13, 128.80, 121.03, 111.99, 60.98, 55.67, 43.69.

HR-MS (EI) m/z calcd for $[C_{11}H_{13}NO_4^+]$ $[M^+]$: 223.0839, found: 223.0834.

2-(*N*-(2-Chlorophenyl)formamido)ethyl formate (42b)



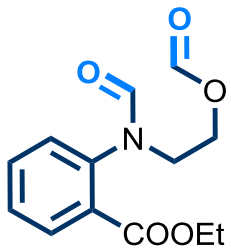
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(2-chlorophenyl)morpholine **42a** (76 mg, 0.39 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **42b** (42 mg, 0.19 mmol, 49%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.10 (s, 1H), 7.90 (t, J = 0.7 Hz, 1H), 7.51–7.42 (m, 1H), 7.33–7.22 (m, 3H), 4.25 (td, J = 5.6, 0.9 Hz, 2H), 3.98 (t, J = 5.5 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.20, 160.66, 137.81, 133.07, 130.97, 130.37, 130.05, 128.21, 60.96, 44.29.

HR-MS (EI) m/z calcd for $[C_{10}H_{10}ClNO_3^+]$ $[M^+]$: 227.0344, found: 227.0343.

Ethyl 2-(*N*-(2-(Formyloxy)ethyl)formamido)benzoate (43b)



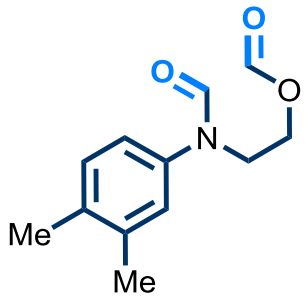
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.9 mg), ethyl 2-morpholinobenzoate **43a** (116 mg, 0.49 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **43b** (41 mg, 0.15 mmol, 31%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (s, 1H), 8.02 (ddd, J = 7.8, 1.7, 0.4 Hz, 1H), 7.94 (p, J = 0.7 Hz, 1H), 7.60 (ddd, J = 7.9, 7.5, 1.6 Hz, 1H), 7.49–7.44 (m, 1H), 7.31 (ddd, J = 8.0, 1.2, 0.4 Hz, 1H), 4.39–4.23 (m, 4H), 4.00 (t, J = 5.6 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 165.59, 162.96, 160.67, 140.48, 133.43, 132.22, 129.94, 129.31, 128.68, 61.95, 61.29, 45.69, 14.29.

GC-MS (EI) (70 eV): m/z (%) = 265 (M^+).

2-(*N*-(3,4-Dimethylphenyl)formamido)ethyl formate (44b)



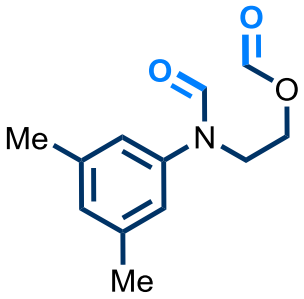
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.4 mg), 4-(3,4-dimethylphenyl)morpholine **44a** (96 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **44b** (82 mg, 0.37 mmol, 74%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.33 (s, 1H), 7.97 (t, J = 0.7 Hz, 1H), 7.15 (dq, J = 7.9, 0.6 Hz, 1H), 6.99–6.82 (m, 2H), 4.37–4.24 (m, 2H), 4.05 (dd, J = 6.0, 5.4 Hz, 2H), 2.26 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.82, 160.69, 138.38, 138.25, 136.12, 130.82, 125.91, 122.12, 60.65, 44.18, 19.98, 19.36.

HR-MS (EI) m/z calcd for [$C_{12}H_{15}NO_3^+$] [M^+]: 221.1046, found: 221.1043.

2-(*N*-(3,5-Dimethylphenyl)formamido)ethyl formate (45b)



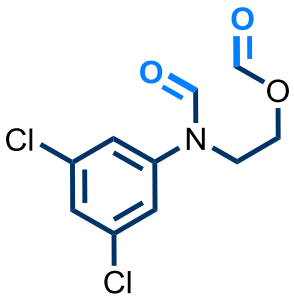
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.5 mg), 4-(3,5-dimethylphenyl)morpholine **45a** (95 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **45b** (72 mg, 0.33 mmol, 66%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.35 (s, 1H), 7.97 (t, J = 0.7 Hz, 1H), 6.94 (dt, J = 1.5, 0.7 Hz, 1H), 6.79 (tt, J = 1.3, 0.6 Hz, 2H), 4.38–4.24 (m, 2H), 4.06 (t, J = 5.7 Hz, 2H), 2.33 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.79, 160.70, 140.48, 139.72, 129.08, 122.30, 60.67, 44.08, 21.36.

HR-MS (EI) m/z calcd for $[C_{12}H_{15}NO_3^+]$ $[M^+]$: 221.1046, found: 221.1042.

2-(*N*-(3,5-Dichlorophenyl)formamido)ethyl formate (46b)



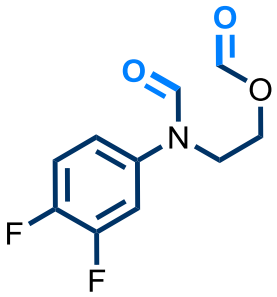
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 4-(3,5-dichlorophenyl)morpholine **46a** (115 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **46b** (57 mg, 0.22 mmol, 44%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.41 (s, 1H), 7.98 (p, J = 0.7 Hz, 1H), 7.31 (t, J = 1.8 Hz, 1H), 7.13 (d, J = 1.8 Hz, 2H), 4.34 (td, J = 5.5, 0.9 Hz, 2H), 4.06 (ddd, J = 6.0, 5.1, 0.6 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 161.95, 160.52, 142.88, 136.21, 127.37, 122.47, 60.65, 44.43.

HR-MS (EI) m/z calcd for $[C_{10}H_9Cl_2NO_3^+]$ $[M^+]$: 260.9954, found: 260.9958.

2-(*N*-(3,4-Difluorophenyl)formamido)ethyl formate (47b)



According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 4-(3,4-difluorophenyl)morpholine **47a** (100 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **47b** (78 mg, 0.34 mmol, 68%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a brown liquid.

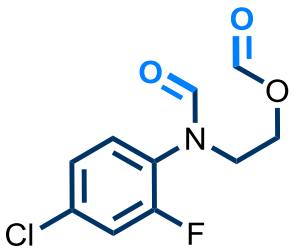
^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.43 (s, 1H), 8.06 (t, *J* = 0.7 Hz, 1H), 7.37–7.28 (m, 1H), 7.18 (ddd, *J* = 10.8, 6.8, 2.7 Hz, 1H), 7.04 (dddd, *J* = 8.8, 3.7, 2.7, 1.7 Hz, 1H), 4.42 (ddd, *J* = 5.7, 5.1, 0.8 Hz, 2H), 4.12 (ddd, *J* = 6.0, 5.1, 0.6 Hz, 2H).

13C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.21, 160.45, 150.61 (dd, *J* = 252.1, 14.1 Hz), 149.50 (dd, *J* = 250.1, 12.5 Hz), 137.23 (dd, *J* = 7.5, 3.6 Hz), 120.83 (dd, *J* = 6.4, 3.6 Hz), 118.26 (dd, *J* = 18.4, 1.4 Hz), 114.23 (dd, *J* = 19.0, 0.9 Hz), 60.68, 44.76.

^{19}F NMR (282 MHz, $CDCl_3$): *δ* (ppm) -132.93– -134.53 (m), -138.20 (d, *J* = 21.3 Hz).

HR-MS (EI) m/z calcd for [$C_{10}H_9F_2NO_3^+$] [M^+]: 229.0545, found: 229.0544.

2-(*N*-(4-Chloro-2-fluorophenyl)formamido)ethyl formate (48b)



According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.3 mg), 4-(4-chloro-2-fluorophenyl)morpholine **48a** (109 mg, 0.51 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **48b** (72 mg, 0.29 mmol, 57%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a light yellow liquid.

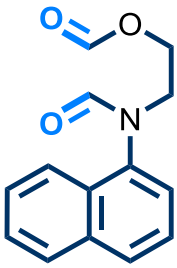
^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.29 (d, *J* = 1.9 Hz, 1H), 8.03 (t, *J* = 0.7 Hz, 1H), 7.37–7.27 (m, 3H), 4.40 (td, *J* = 5.4, 0.7 Hz, 2H), 4.16 – 4.07 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.73 (d, *J* = 1.9 Hz), 160.53, 159.42, 156.06, 134.89 (d, *J* = 9.7 Hz), 130.78 (d, *J* = 2.2 Hz), 129.59 (d, *J* = 1.6 Hz), 127.10 (d, *J* = 12.0 Hz), 125.65 (d, *J* = 3.9 Hz), 118.09, 117.78, 60.89, 44.35 (d, *J* = 2.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) *δ* (ppm) -118.98.

HR-MS (EI) m/z calcd for [$C_{10}H_9ClFNO_3^+$] [M^+]: 245.0250, found: 245.0252.

2-(*N*-(Naphthalen-1-yl)formamido)ethyl formate (49b)



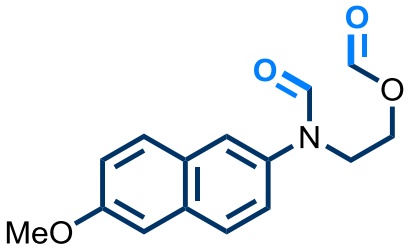
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 4-(naphthalen-1-yl)morpholine **49a** (106 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **49b** (68 mg, 0.28 mmol, 56%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.30 (s, 1H), 7.98–7.89 (m, 3H), 7.84–7.77 (m, 1H), 7.61–7.48 (m, 3H), 7.41 (dd, *J* = 7.2, 1.2 Hz, 1H), 4.59–4.42 (m, 1H), 4.32 (td, *J* = 5.5, 0.8 Hz, 2H), 3.90–3.73 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 163.80, 160.67, 136.31, 134.74, 130.79, 129.50, 128.83, 127.69, 126.98, 126.52, 125.58, 122.19, 60.85, 45.01.

HR-MS (EI) m/z calcd for [$C_{14}H_{13}NO_3^+$] [M^+]: 243.0890, found: 243.0890.

2-(*N*-(6-Methoxynaphthalen-2-yl)formamido)ethyl formate (50b)



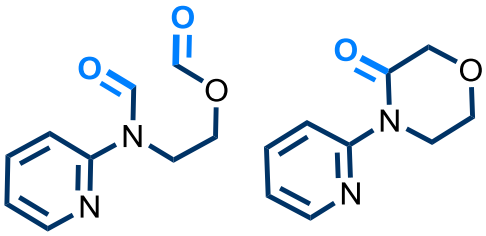
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(6-methoxynaphthalen-2-yl)morpholine **50a** (111 mg, 0.46 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **50b** (79 mg, 0.29 mmol, 63%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.37 (s, 1H), 7.88 (t, *J* = 0.7 Hz, 1H), 7.73–7.61 (m, 2H), 7.47 (dd, *J* = 2.3, 0.7 Hz, 1H), 7.24–7.18 (m, 1H), 7.13 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 4.35–4.22 (m, 2H), 4.08 (dd, *J* = 5.9, 5.3 Hz, 2H), 3.84 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.95, 160.67, 158.28, 135.95, 133.49, 129.25, 128.92, 128.70, 123.46, 123.09, 120.17, 105.75, 60.76, 55.46, 44.35.

HR-MS (EI) m/z calcd for [$C_{15}H_{15}NO_4^+$] [M^+]: 273.0996, found: 273.0998.

2-(*N*-(Pyridin-2-yl)formamido)ethyl formate (51b) and 4-(pyridin-2-yl)morpholin-3-one (51c)



According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(pyridin-2-yl)morpholine **51a** (82 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **51b** and **51c** (32 mg) were obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a colorless liquid.

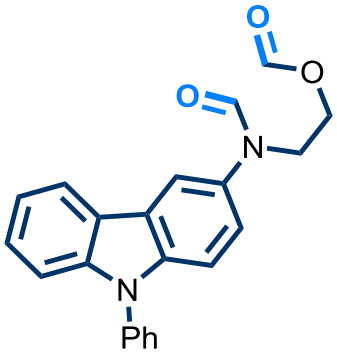
^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 9.05 (s, 1H), 8.40–8.33 (m, 1H), 8.05–7.96 (m, 0.64H), 7.91 (t, *J* = 0.8 Hz, 1H), 7.66 (dddd, *J* = 9.8, 8.4, 7.4, 1.9 Hz, 1.66H), 7.14–6.99 (m, 2.62H), 4.35 (tt, *J* = 5.7, 0.8 Hz, 2H), 4.29 (s, 1H), 4.28–4.21 (m, 2H), 4.07–4.01 (m, 1H), 4.01–3.94 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): *δ* (ppm) 162.35, 160.86, 148.98, 147.76, 138.80, 137.63, 120.83, 119.39, 112.88, 68.73, 64.49, 61.15, 45.78, 40.80.

HR-MS (ESI): m/z calculated for (**51b**) $[C_9H_{11}N_2O_3]^+$ ($[M+H]^+$): 195.0764, found: 195.0762.

HR-MS (ESI): m/z calculated for (**51c**) $[C_9H_{11}N_2O_2]^+$ ($[M+H]^+$): 179.0815, found: 179.0811.

2-(*N*-(9-Phenyl-*9H*-carbazol-3-yl)formamido)ethyl formate (52b)



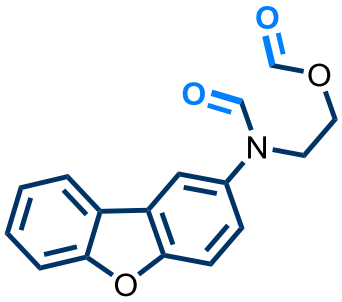
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 4-(9-phenyl-*9H*-carbazol-3-yl)morpholine **52a** (149 mg, 0.45 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **52b** (122 mg, 0.34 mmol, 76%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ* (ppm) 8.52 (s, 1H), 8.16 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.03 (s, 1H), 7.99 (d, *J* = 2.1 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 2H), 7.59–7.42 (m, 6H), 7.39–7.32 (m, 1H), 7.30–7.21 (m, 1H), 4.42 (t, *J* = 5.6 Hz, 2H), 4.22 (t, *J* = 5.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.39, 160.76, 141.74, 139.95, 137.23, 133.09, 130.15, 128.03, 127.16, 126.97, 124.11, 123.76, 122.66, 120.58, 120.54, 117.80, 60.79, 45.10.

HR-MS (ESI): m/z calculated for $[C_{22}H_{19}N_2O_3]^+$ ($[M+H]^+$): 359.1390, found: 359.1389.

2-(*N*-(Dibenzo[b,d]furan-2-yl)formamido)ethyl formate (53b)



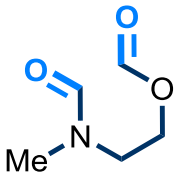
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-(dibenzo[b,d]furan-2-yl)morpholine **53a** (98 mg, 0.51 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **53b** (98 mg, 0.35 mmol, 74%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.45 (s, 1H), 8.01 (t, *J* = 0.7 Hz, 1H), 7.96 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1H), 7.79 (dd, *J* = 2.3, 0.6 Hz, 1H), 7.60 (dt, *J* = 8.3, 0.7 Hz, 2H), 7.52 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.43–7.35 (m, 1H), 7.30 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.39 (ddd, *J* = 5.8, 5.3, 0.8 Hz, 2H), 4.24–4.13 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.07, 160.67, 157.02, 154.94, 135.79, 128.19, 125.50, 124.56, 123.46, 123.23, 120.95, 117.83, 112.76, 112.03, 60.72, 45.01.

HR-MS (ESI): m/z calculated for $[C_{16}H_{14}NO_4]^+$ ($[M+H]^+$): 284.0917, found: 284.0919.

2-(*N*-methylformamido)ethyl formate (54b)



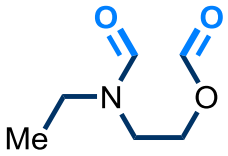
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-methylmorpholine **54a** (100 mg, 1.0 mmol), acetonitrile (2.0 mL), pyridine (40 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **54b** (44 mg, 0.34 mmol, 34%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a colorless yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–7.94 (m, 2H), 4.28 (dtd, *J* = 13.8, 5.3, 0.8 Hz, 2H), [3.63–3.57 (m), 3.50 (t, *J* = 5.3 Hz), 2H], [3.01 (s)–2.89 (d), (3H)].

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 163.03, 162.99, 160.72, 160.48, 60.96, 60.04, 48.19, 43.29, 35.54, 29.86.

HR-MS (ESI): m/z calculated for $[C_5H_9NO_3Na]^+$ ($[M+Na]^+$): 154.0475, found: 154.0473.

2-(*N*-Ethylformamido)ethyl formate (55b)



According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-ethylmorpholine **55a** (91 mg, 0.79 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **55b** (63 mg, 0.43 mmol, 54%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29–7.92 (m, 2H), 4.25 (dtd, *J* = 13.8, 5.6, 0.8 Hz, 2H), 3.60–3.27 (m, 4H), 1.15 (dt, *J* = 20.1, 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.98, 160.50, 61.15, 43.12, 40.93, 14.86.

HR-MS (EI) m/z calcd for $[C_6H_{11}NO_3^+]$ $[M^+]$: 145.0733, found: 145.0733.

2-(*N*-Decylformamido)ethyl formate (56b)

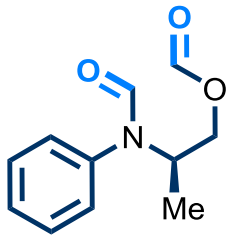
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.0 mg), 4-decylmorpholine **56a** (130 mg, 0.57 mmol), acetonitrile (2.0 mL), pyridine (40 mg), air (40 bar), room temperature to 130 °C and then at 130 °C for 24 h. The product **56b** (120 mg, 0.47 mmol, 82%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27–7.85 (m, 2H), 4.25 (dt, *J* = 20.3, 5.5 Hz, 2H), 3.55 (t, *J* = 5.7 Hz, 1H), 3.47 (t, *J* = 5.4 Hz, 1H), 3.35–3.19 (m, 2H), 1.51 (dt, *J* = 13.1, 4.3 Hz, 2H), 1.35–1.14 (m, 14H), 0.87–0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.34, 160.72, 61.09, 48.43, 41.26, 31.89, 29.53, 29.30, 29.21, 28.75, 27.35, 26.89, 26.44, 22.71, 14.15.

HR-MS (EI) m/z calcd for $[C_{14}H_{27}NO_3^+]$ $[M^+]$: 257.1986, found: 257.1985.

(*R*)-2-(*N*-Phenylformamido)propyl formate (57b)



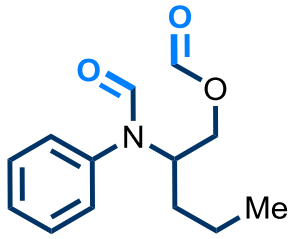
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), (*R*)-3-methyl-4-phenylmorpholine **57a** (75 mg, 0.38 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **57b** (52 mg, 0.25 mmol, 66%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.23 (s, 1H), 8.06 (t, *J* = 0.8 Hz, 1H), 7.46–7.36 (m, 3H), 7.22–7.15 (m, 2H), 4.85 (ddd, *J* = 8.8, 7.0, 5.1 Hz, 1H), 4.30 (dddd, *J* = 11.5, 5.2, 1.0, 0.5 Hz, 1H), 4.19 (ddd, *J* = 11.4, 8.8, 0.8 Hz, 1H), 1.25 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 163.22, 160.62, 138.30, 129.69, 128.55, 128.49, 64.20, 49.54, 15.58.

HR-MS (EI) m/z calcd for $[C_{11}H_{13}NO_3^+]$ $[M^+]$: 207.0890, found: 207.0889.

2-(*N*-Phenylformamido)pentyl formate (58b)



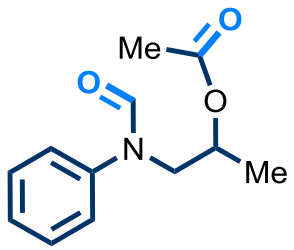
According to **GR VI**, $Cu(CF_3SO_3)_2$ (1.2 mg), 4-phenyl-3-propylmorpholine **58a** (13 mg, 0.06 mmol), acetonitrile (1.0 mL), pyridine (4.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **58b** (9.0 mg, 0.04 mmol, 67%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.31 (s, 1H), 8.09–8.05 (m, 1H), 7.48–7.34 (m, 3H), 7.23–7.17 (m, 2H), 4.78–4.62 (m, 1H), 4.40–4.30 (m, 1H), 4.25–4.12 (m, 1H), 1.72–1.30 (m, 4H), 0.99–0.91 (m, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 163.65, 160.69, 139.01, 129.76, 128.38, 128.09, 63.43, 54.46, 31.65, 19.69, 14.00.

HR-MS (EI) m/z calcd for $[C_{13}H_{17}NO_3^+]$ $[M^+]$: 235.1203, found: 235.1201.

1-(*N*-Phenylformamido)propan-2-yl acetate (59b)



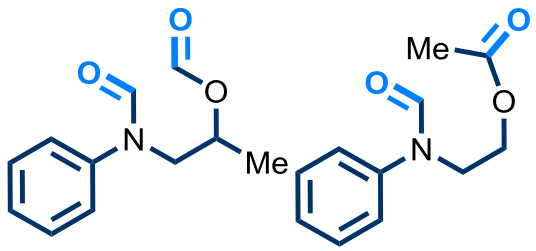
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.2 mg), 2,6-dimethyl-4-phenylmorpholine **59a** (98 mg, 0.51 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **59b** (61 mg, 0.28 mmol, 55%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.38 (s, 1H), 7.50–7.37 (m, 2H), 7.33–7.23 (m, 1H), 7.23–7.11 (m, 2H), 5.21–5.04 (m, 1H), 4.07–3.88 (m, 2H), 1.77 (s, 3H), 1.24 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 170.40, 162.83, 141.32, 129.76, 127.03, 124.33, 68.85, 48.88, 20.97, 17.88.

HR-MS (EI) m/z calcd for $[C_{12}H_{15}NO_3^+]$ $[M^+]$: 221.1046, found: 221.1044.

1-(*N*-Phenylformamido)propan-2-yl formate (60b) 2-(*N*-phenylformamido)ethyl acetate (60c)



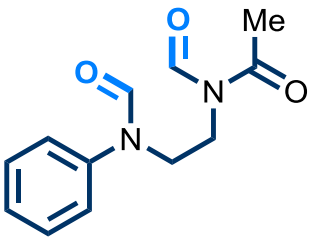
According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 2-methyl-4-phenylmorpholine **60a** (82 mg, 0.46 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (20 bar), room temperature to 80 °C and then at 80 °C for 24 h. The product **60b** and **60c** (66 mg, 0.32 mmol, 70%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.40 (d, *J* = 3.8 Hz, 1H), 7.89 (dq, *J* = 1.0, 0.5 Hz, 1H), 7.49–7.36 (m, 3H), 7.36–7.25 (m, 2H), 7.25–7.13 (m, 3H), 5.27 (dddd, *J* = 7.5, 6.5, 4.4, 1.0 Hz, 1H), 4.32–4.20 (m, 0.72H), 4.12–4.05 (m, 0.93H), 4.04–3.96 (m, 1.67H), 1.91 (s, 1H), 1.29 (dd, *J* = 6.4, 0.5 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 170.79, 162.91, 160.41, 140.98, 129.86, 127.27, 124.37, 68.41, 61.44, 9.11, 44.35, 20.73, 17.90.

HR-MS (EI) m/z calcd for $[C_{11}H_{13}NO_3^+]$ $[M^+]$: 207.0890, found: 207.0890.

***N*-Formyl-*N*-(2-(*N*-phenylformamido)ethyl)acetamide (61b)**



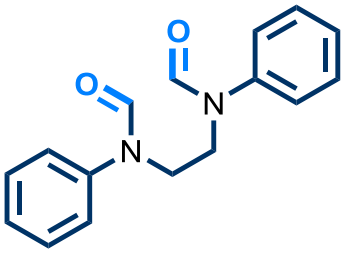
According to **GR VI**, $Cu(CF_3SO_3)_2$ (6.5 mg), 1-(4-phenylpiperazin-1-yl)ethan-1-one **61a** (80 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **61b** (43 mg, 0.18 mmol, 36%) was obtained as a light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 9.04 (s, 1H), 8.33 (s, 1H), 7.49–7.38 (m, 2H), 7.36–7.27 (m, 1H), 7.25–7.19 (m, 2H), 4.10–3.89 (m, 4H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 171.44, 163.02, 162.93, 141.02, 129.84, 127.13, 124.06, 43.45, 8.23, 22.83.

HR-MS (EI) m/z calcd for $[C_{12}H_{14}N_2O_3^+]$ $[M^+]$: 234.0999, found: 234.0997.

***N*,*N*′-(Ethane-1,2-diyl)bis(*N*-phenylformamide) (62b)**



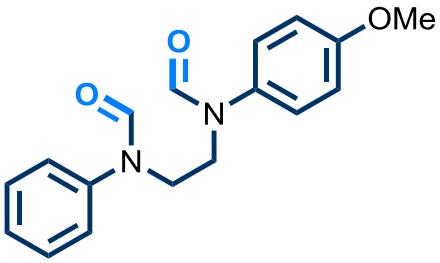
According to **GR VI**, $Cu(CF_3SO_3)_2$ (5.8 mg), 1,4-diphenylpiperazine **62a** (119 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (160 mg), air (30 bar), room temperature to 100 °C and at 100 °C for 24 h. The product **62b** (53 mg, 0.20 mmol, 40%) was obtained by column chromatography (*n*-Heptane/EtOAc: 8:1) as a yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$): *δ* (ppm) 8.35 (s, 2H), 7.44–7.37 (m, 4H), 7.35–7.29 (m, 2H), 7.11–7.05 (m, 4H), 4.07 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): *δ* (ppm) 162.74, 140.80, 129.81, 126.96, 123.60, 43.39.

HR-MS (EI) m/z calcd for $[C_{16}H_{16}N_2O_2^+]$ $[M^+]$: 268.1206, found: 268.1202.

***N*-(4-Methoxyphenyl)-*N*-(2-(*N*-phenylformamido)ethyl)formamide (63b)**



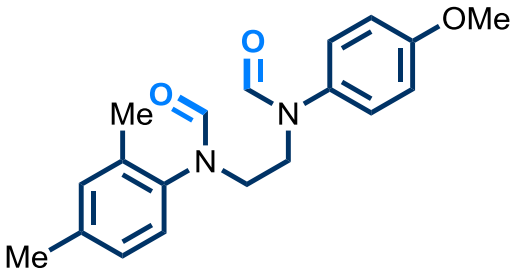
According to **GR VI**, $Cu(CF_3SO_3)_2$ (12 mg), 1-(4-methoxyphenyl)-4-phenylpiperazine **63a** (144 mg, 0.54 mmol), acetonitrile (2.0 mL), pyridine (160 mg), air (30 bar), room temperature to 100 ^oC and then at 100 ^oC for 24 h. The product **63b** (42 mg, 0.14 mmol, 26%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a yellow solid.

^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.33 (s, 1H), 8.21 (s, 1H), 7.45–7.33 (m, 3H), 7.13–7.07 (m, 2H), 7.00–6.93 (m, 2H), 6.92–6.85 (m, 2H), 4.06–3.94 (m, 4H), 3.82 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 162.88, 162.73, 158.69, 140.88, 133.67, 129.83, 127.02, 125.87, 123.82, 114.91, 55.69, 43.77, 43.35.

HR-MS (EI) m/z calcd for $[C_{17}H_{18}N_2O_3^+]$ $[M^+]$: 298.1312, found: 298.1309.

***N*-(2,4-Dimethylphenyl)-*N*-(2-(*N*-(4-methoxyphenyl)formamido)ethyl)formamide (64b)**



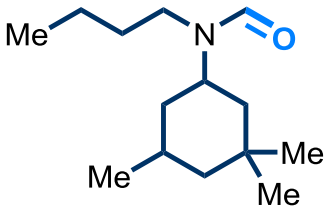
According to **GR VI**, $Cu(CF_3SO_3)_2$ (12 mg), 1-(3,4-dimethylphenyl)-4-(4-methoxyphenyl)piperazine **64a** (147 mg, 0.50 mmol), acetonitrile (2.0 mL), pyridine (160 mg), air (30 bar), room temperature to 100 ^oC and then at 100 ^oC for 24 h. The product **64b** (39 mg, 0.12 mmol, 24%) was obtained by column chromatography (*n*-Heptane/EtOAc: 5:1) as a yellow solid.

^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 8.05 (s, 1H), 7.12–7.06 (m, 3H), 7.02–6.95 (m, 2H), 6.91 (d, J = 8.9 Hz, 2H), 3.92 (d, J = 6.5 Hz, 2H), 3.83–3.77 (m, 5H), 2.34 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.52, 162.81, 158.75, 138.71, 136.60, 135.33, 133.57, 132.29, 128.74, 127.85, 126.12, 114.94, 55.67, 43.44, 43.23, 21.11, 17.82.

HR-MS (EI) m/z calcd for $[C_{19}H_{22}N_2O_3^+]$ $[M^+]$: 326.1625, found: 326.1625.

***N*-Butyl-*N*-(3,3,5-trimethylcyclohexyl)formamide (65b)**



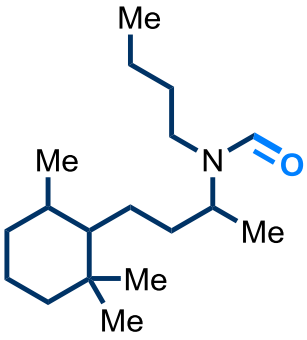
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutyl-3,3,5-trimethylcyclohexan-1-amine **65a** (138 mg, 0.55 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **65b** (115 mg, 0.51 mmol, 93%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1) as a light yellow liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.28–7.90 (m, 1H), 3.26–3.04 (m, 3H), 1.73 (s, 1H), 1.47–1.18 (m, 10H), 1.07–1.00 (m, 5H), 0.91–0.86 (m, 7H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 162.76, 50.55, 44.42, 43.88, 42.66, 37.27, 33.87, 32.08, 31.27, 28.99, 27.65, 21.51, 20.34, 14.18.

HR-MS (EI) m/z calcd for [$C_{14}H_{27}NO^{+}$] ([M^{+}]): 225.2093, found: 225.2089.

***N*-Butyl-*N*-(4-(2,2,6-trimethylcyclohexyl)butan-2-yl)formamide (66b)**



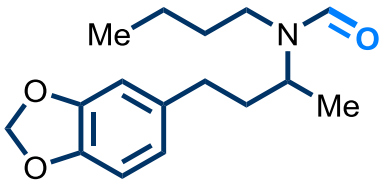
According to **GP III**, CuCl (2.8 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-butyl-*N*-(4-(2,2,6-trimethylcyclohexyl)butan-2-yl)butan-1-amine **66a** (80 mg, 0.26 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **66b** (74 mg, 0.26 mmol, 99%) was obtained by column chromatography (*n*-Heptane/EtOAc: 1:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.86–8.22 (m, 1H), 4.23–2.68 (m, 3H), 1.59–0.74 (m, 31H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 161.46, 55.76, 53.47, 49.74, 42.14, 36.53, 36.07, 34.29, 31.18, 30.34, 28.56, 27.77, 22.31, 20.92, 20.62, 20.61, 18.53, 13.85.

HR-MS (EI) m/z calcd for [$C_{18}H_{35}NO^{+}$] [M^{+}]: 281.2713, found: 281.2716.

***N*-(4-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl)-*N*-butylformamide (67b)**



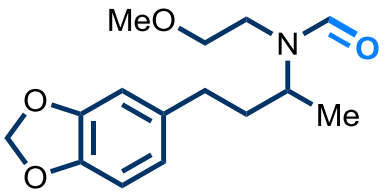
According to **GP III**, CuCl (2.7 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N*-(4-(benzo[d][1,3]dioxol-5-yl)butan-2-yl)-*N*-butylbutan-1-amine **67a** (130 mg, 0.43 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **67b** (109 mg, 0.39 mmol, 91%) was obtained by column chromatography (*n*-Heptane/EtOAc: 1:1) as a yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (s, 1H), 6.69–6.40 (m, 3H), 5.83 (s, 2H), 3.39 (ddd, *J* = 9.1, 6.9, 5.4 Hz, 1H), 3.24–2.95 (m, 2H), 2.41 (dtdd, *J* = 22.9, 14.0, 9.1, 6.4 Hz, 2H), 1.88–1.64 (m, 2H), 1.57–1.42 (m, 2H), 1.29–1.13 (m, 5H), 0.86 (td, *J* = 7.4, 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 163.34, 147.74, 145.85, 135.41, 121.03, 108.71, 108.24, 100.84, 53.64, 40.73, 36.79, 33.48, 32.21, 31.05, 20.73, 18.73.

HR-MS (EI) m/z calcd for [$C_{16}H_{23}NO_3^+$] [M^+]: 277.1673, found: 277.1672.

***N*-(4-(Benzo[d][1,3]dioxol-5-yl)butan-2-yl)-*N*-(2-methoxyethyl)formamide (68b)**



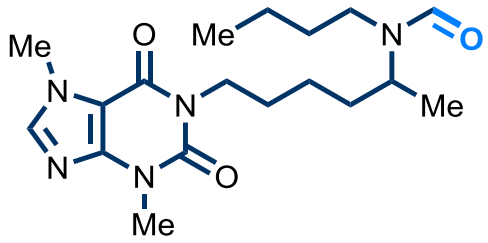
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL), pyridine (80 mg), 4-(benzo[d][1,3]dioxol-5-yl)-*N,N*-bis(2-methoxyethyl)butan-2-amine **68a** (172 mg, 0.56 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **68b** (149 mg, 0.53 mmol, 95%) was obtained by column chromatography (*n*-Heptane/EtOAc: 1:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.40 (s, 1H), 6.75–6.51 (m, 3H), 5.89 (s, 2H), 3.65–3.19 (m, 8H), 2.69–2.26 (m, 2H), 1.96–1.67 (m, 2H), 1.23 (dd, *J* = 13.8, 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.86, 147.73, 145.64, 134.63, 121.04, 108.57, 108.23, 100.85, 70.25, 58.74, 54.02, 40.96, 36.80, 32.22, 20.65.

HR-MS (EI) m/z calcd for [$C_{15}H_{21}NO_4^+$] [M^+]: 279.1465, found: 279.1465.

***N*-Butyl-*N*-(6-(3,7-dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-1H-purin-1-yl)hexan-2-yl)formamide (69b)**



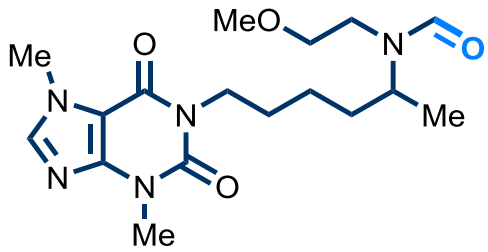
According to **GP III**, CuCl (2.8 mg), acetonitrile (2.0 mL), pyridine (80 mg), 1-(5-(dibutylamino)hexyl)-3,7-dimethyl-3,7-dihydro-*1H*-purine-2,6-dione **69a** (130 mg, 0.33 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **69b** (115 mg, 0.32 mmol, 97%) was obtained by column chromatography (*n*-Heptane/EtOAc: 1:1) as a light yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.14 (s, 1H), 7.77–7.41 (s, 1H), 3.93 (s, 5H), 3.48 (d, J = 37.7 Hz, 4H), 3.07 (ddt, J = 38.2, 17.6, 11.9 Hz, 2H), 1.75–1.40 (m, 6H), 1.35–1.10 (m, 7H), 0.92–0.82 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.52, 155.31, 151.32, 141.52, 54.49, 48.92, 44.79, 40.83, 34.79, 34.04, 30.89, 29.54, 27.74, 23.83, 20.64, 19.96, 18.68, 13.66.

HR-MS (ESI) m/z calcd for $[C_{18}H_{30}N_5O_3]^+$ ($[M+H]^+$): 364.2343, found: 364.2351.

***N*-(6-(3,7-Dimethyl-2,6-dioxo-2,3,6,7-tetrahydro-*1H*-purin-1-yl)hexan-2-yl)-*N*-(2-methoxyethyl)formamide (70b)**



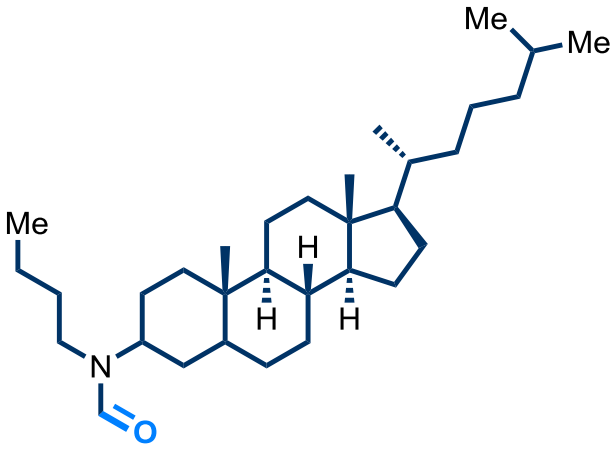
According to **GP III**, CuCl (2.8 mg), acetonitrile (2.0 mL), pyridine (80 mg), 1-(5-(bis(2-methoxyethyl)amino)hexyl)-3,7-dimethyl-3,7-dihydro-*1H*-purine-2,6-dione **70a** (102 mg, 0.26 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **70b** (69 mg, 0.19 mmol, 73%) was obtained by column chromatography (*n*-Heptane/EtOAc: 1:1) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.31 (s, 1H), 7.78 (s, 1H), 3.96 (d, J = 7.1 Hz, 5H), 3.68–3.25 (m, 11H), 1.70–1.45 (m, 4H), 1.38–1.07 (m, 5H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 164.10, 163.33, 154.85, 151.23, 143.40, 71.78, 69.96, 58.44, 53.77, 48.44, 44.11, 33.64, 29.81, 27.54, 23.65, 20.69, 18.88.

HR-MS (ESI) m/z calcd for $[C_{17}H_{28}N_5O_4]^+$ ($[M+H]^+$): 366.2136, found: 366.2144.

***N*-Butyl-*N*-((*8R,9S,10S,13R,14S,17R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-*1H*-cyclopenta[a]phenanthren-3-yl)formamide (71b)**



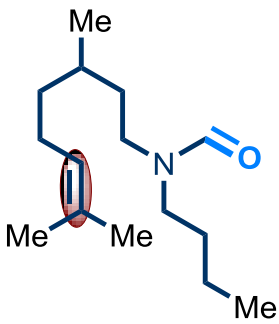
According to **GP III**, CuCl (2.5 mg), acetonitrile (2.0 mL) and DMF (2.0 mL), pyridine (80 mg), (*8R,9S,10S,13R,14S,17R*)-*N,N*-dibutyl-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-amine **71a** (90 mg, 0.18 mmol), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **71b** (82 mg, 0.17 mmol, 94%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1 to 1:5) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 3.24 (m, 3H), 2.44–0.29 (m, 53H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 156.46, 60.51, 56.54, 56.35, 54.21, 46.18, 43.21, 42.84, 40.82, 39.44, 37.83, 36.49, 35.70, 34.51, 33.71, 32.89, 31.88, 30.37, 28.61, 27.94, 27.04, 26.40, 24.88, 23.55, 22.76, 21.08, 20.75, 19.93, 18.61, 13.81, 12.31, 12.01.

HR-MS (EI) m/z calcd for $[C_{32}H_{57}NO]^+$ $[M]^+$: 471.4435, found: 471.4435.

***N*-Butyl-*N*-(3,7-dimethyloct-6-en-1-yl)formamide (72b)**



According to **GP III**, CuCl (2.8 mg), acetonitrile (2.0 mL), pyridine (80 mg), *N,N*-dibutyl-3,7-dimethyloct-6-en-1-amine **72a** (131 mg, 0.49 mmol), air (30 bar), room temperature to 100 °C

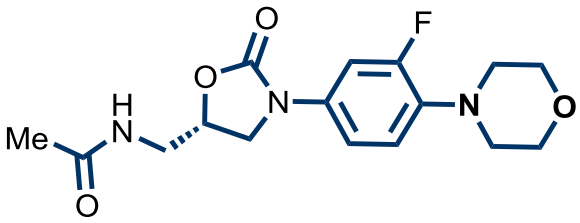
and then at 100 °C for 24 h. The product **72b** (72 mg, 0.30 mmol, 72%) was obtained by column chromatography (*n*-Heptane/EtOAc: 4:1) as a light yellow liquid.

^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 8.00 (s, 1H), 5.19–4.98 (m, 1H), 3.27–3.09 (m, 4H), 2.04–1.86 (m, 2H), 1.69–1.62 (m, 3H), 1.60–1.54 (m, 3H), 1.48–1.19 (m, 8H), 1.18–1.07 (m, 1H), 0.93–0.85 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ (ppm) 162.85, 131.00, 124.97, 46.42, 44.81, 41.16, 36.87, 35.72, 34.10, 30.69, 29.62, 25.95, 20.04, 19.74, 17.93, 13.98.

HR-MS (ESI) m/z calcd for $[C_{15}H_{30}NO]^+$ ($[M+H]^+$): 240.2322, found: 240.2331.

Linezolid (73a) (Supplier: Gute Chemie–abcr Services)

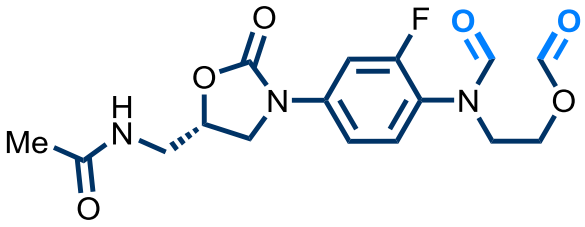


^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.24 (t, *J* = 5.9 Hz, 1H), 7.49 (dd, *J* = 15.0, 2.5 Hz, 1H), 7.18 (ddd, *J* = 8.8, 2.6, 0.9 Hz, 1H), 7.06 (dd, *J* = 9.8, 8.8 Hz, 1H), 4.79–4.58 (m, 1H), 4.08 (t, *J* = 9.0 Hz, 1H), 3.79–3.63 (m, 5H), 3.40 (t, *J* = 5.5 Hz, 2H), 3.03–2.89 (m, 4H), 1.83 (s, 3H).

^{13}C NMR (101 MHz, DMSO-d_6): δ (ppm) 170.43, 156.24, 154.51, 153.82, 135.98 (d, *J* = 8.8 Hz), 133.90 (d, *J* = 10.5 Hz), 119.71 (d, *J* = 4.2 Hz), 114.53 (d, *J* = 3.3 Hz), 107.08 (d, *J* = 26.2 Hz), 72.01, 66.62, 51.17 (d, *J* = 2.8 Hz), 47.75, 41.87, 22.91.

^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm) -119.93.

(*S*)-2-(*N*-(4-(5-(Acetamidomethyl)-2-oxooxazolidin-3-yl)-2-fluorophenyl)formamido)ethyl formate (73b)



According to **GP II**, $Cu(CF_3SO_3)_2$ (6.0 mg), Linezolid **73a** (174 mg, 0.52 mmol), acetonitrile (2.0 mL), pyridine (8.0 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **73b** (160 mg, 0.44 mmol, 85%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1 to 1:5) as yellow solid.

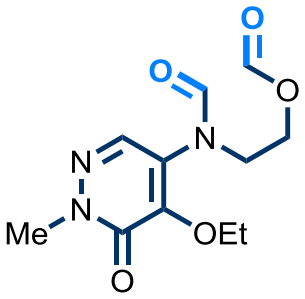
^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 8.43–8.00 (m, 3H), 7.77–7.30 (m, 3H), 4.86–4.68 (m, 1H), 4.25–4.03 (m, 3H), 3.95 (t, J = 5.4 Hz, 2H), 3.78 (ddd, J = 9.4, 6.4, 1.1 Hz, 1H), 3.44 (t, J = 5.5 Hz, 2H).

^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm) 170.08, 166.60–162.15 (m), 161.80, 158.89, 155.63, 154.01, 139.23 (d, J = 10.7 Hz), 131.42–127.22 (m), 122.73 (d, J = 12.2 Hz), 120.71 (d, J = 13.3 Hz), 114.10 (d, J = 3.1 Hz), 105.90 (dd, J = 26.1, 13.0 Hz), 71.78 (d, J = 3.3 Hz), 60.59, 60.35, 47.73, 47.23, 43.50, 41.37, 22.45.

^{19}F NMR (282 MHz, DMSO-d_6): δ (ppm) -118.13 (dt, J = 12.8, 6.7 Hz), -121.61 (dd, J = 12.7, 8.9 Hz).

HR-MS (EI) m/z calcd for [$C_{16}H_{18}FN_3O_6^+$] [M^+]: 367.1174, found: 367.1173.

2-(*N*-(5-Ethoxy-1-methyl-6-oxo-1,6-dihydropyridazin-4-yl)formamido)ethyl formate (74b)



According to **GP II**, $Cu(CF_3SO_3)_2$ (3.6 mg), Emorfazone **74a** (41 mg, 0.17 mmol), acetonitrile (2.0 mL), pyridine (32 mg), air (30 bar), room temperature to 100 °C and then at 100 °C for 24 h. The product **74b** (31 mg, 0.12 mmol, 71%) was obtained by column chromatography (*n*-Heptane/EtOAc: 2:1 to 5:1) as colorless liquid.

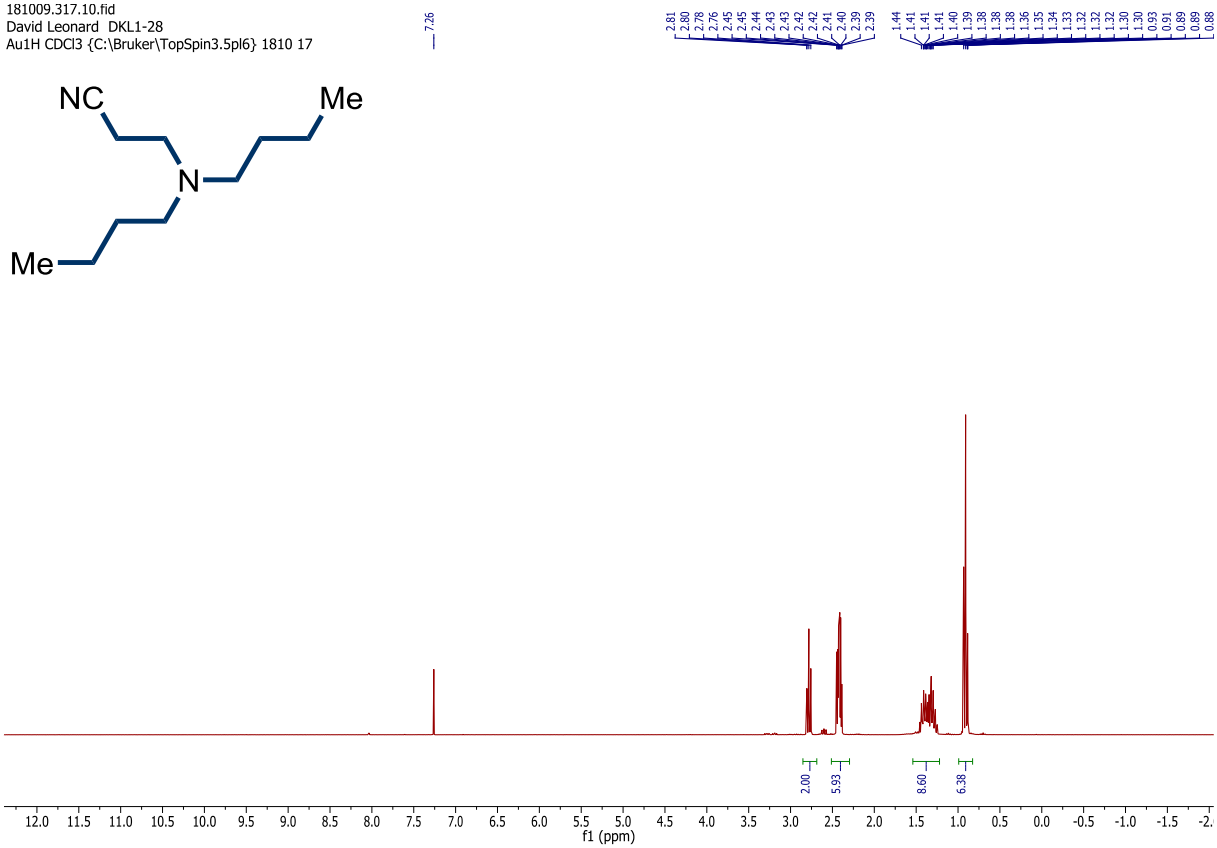
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.22 (s, 1H), 8.01 (s, 1H), 7.63 (d, J = 6.9 Hz, 1H), 4.63 (t, J = 7.1 Hz, 2H), 4.32 (td, J = 5.5, 0.9 Hz, 2H), 3.98 (td, J = 5.4, 0.6 Hz, 2H), 3.77 (d, J = 8.3 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H).

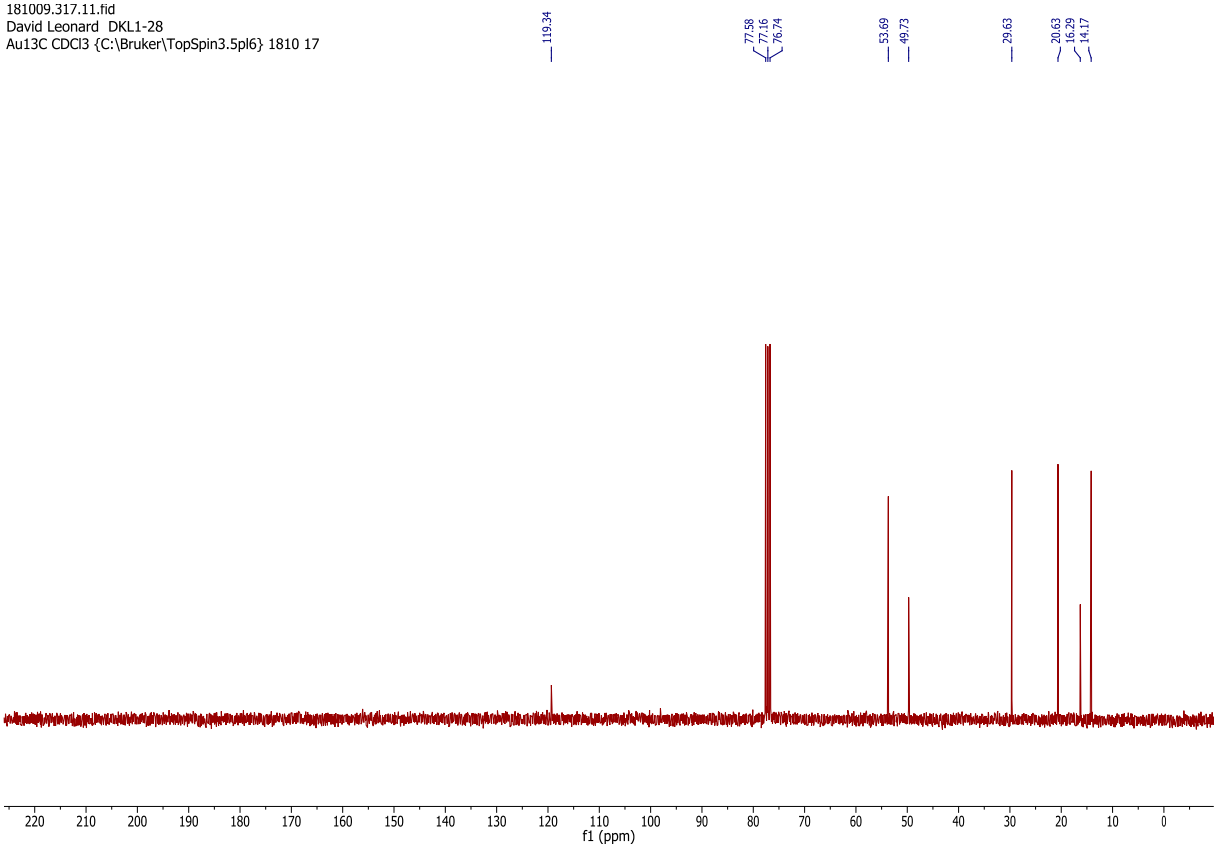
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 162.45, 160.33, 158.14, 148.41, 135.44, 128.87, 69.18, 61.09, 43.62, 40.33, 15.84.

HR-MS (ESI) m/z calcd for $[C_{11}H_{16}N_3O_5]^+$ ($[M+H]^+$): 270.1084, found: 270.1088.

10. ^{1}H NMR and ^{13}C NMR and Spectra for Substrates and Products

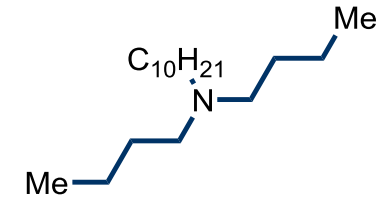
Original spectra for **5a**:

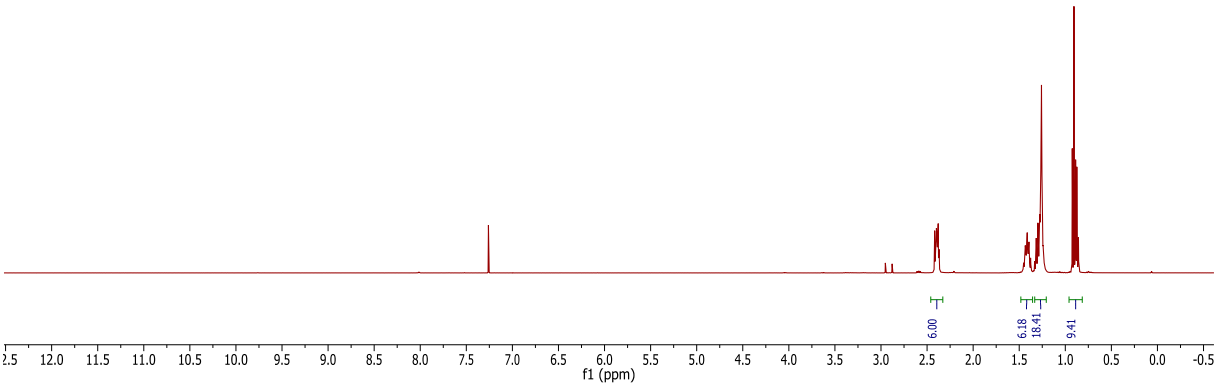




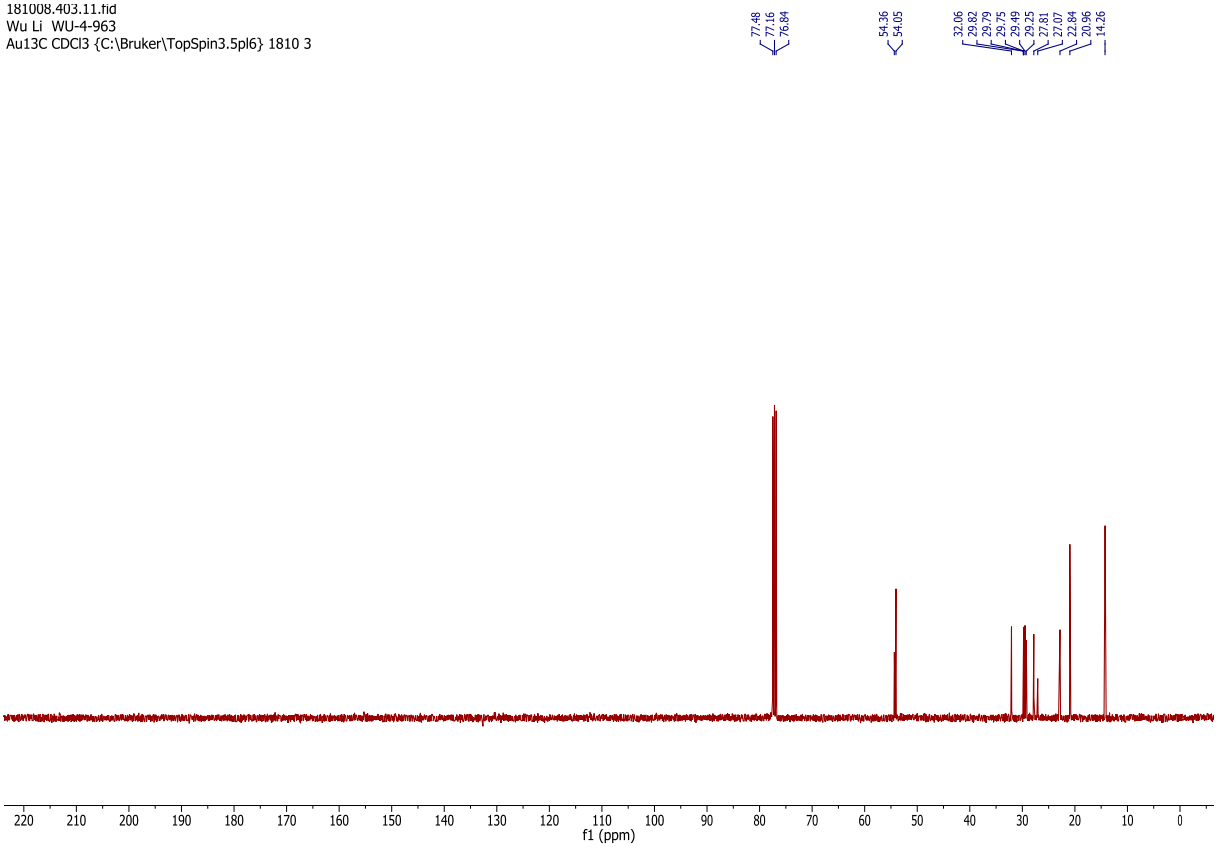
Original spectra for **6a**:

181008.403.10.fid
Wu Li WU-4-963
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 3





181008.403.11.fid
Wu Li WU-4-963
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 3



Data File C:\CHEM32\1\DATA\201810\2018-10-04 07-45-42\WU-4-963-COL.D
Sample Name: WU-4-963-col

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Acq. Instrument : GC Lab.133                      Location : Vial 2
Injection Date  : 10/4/2018 7:51:26 AM                 Inj :   1
                                                 Inj Volume : 1 µl
Acq. Method     : C:\CHEM32\1\DATA\201810\2018-10-04 07-45-42\STANDARDMTH 20.M
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Analysis Method : C:\CHEM32\1\METHODS\SW KAL CYCLOPROPYLMETHYLKETON 0519.M
Last changed    : 4/27/2019 1:13:56 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
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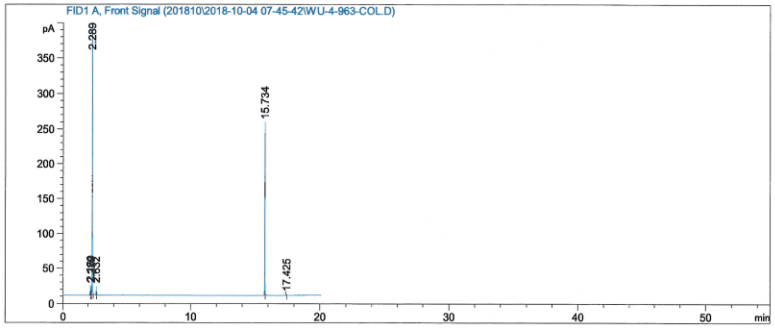


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======================================================================
                        Internal Standard Report
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Sorted By             :      Signal
Calib. Data Modified  :      4/27/2019 1:09:40 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
Sample ISTD Information:
ISTD  ISTD Amount   Name
  #     [ng/ul]
----|------------|-------------------------
  1     27.80000   C16


Signal 1: FID1 A, Front Signal

RetTime  Type  ISTD    Area     Amt/Area    Amount   Grp   Name
 [min]         used  [pA*s]      ratio     [ng/ul]
-------|------|----|----------|----------|----------|--|------------------
  3.205          1     -          -          -         Cyclopropylethanol
  3.279          1     -          -          -         Cyclopropylmethylketon
 14.572          1     -          -          -         C16

Totals without ISTD(s) :               0.00000
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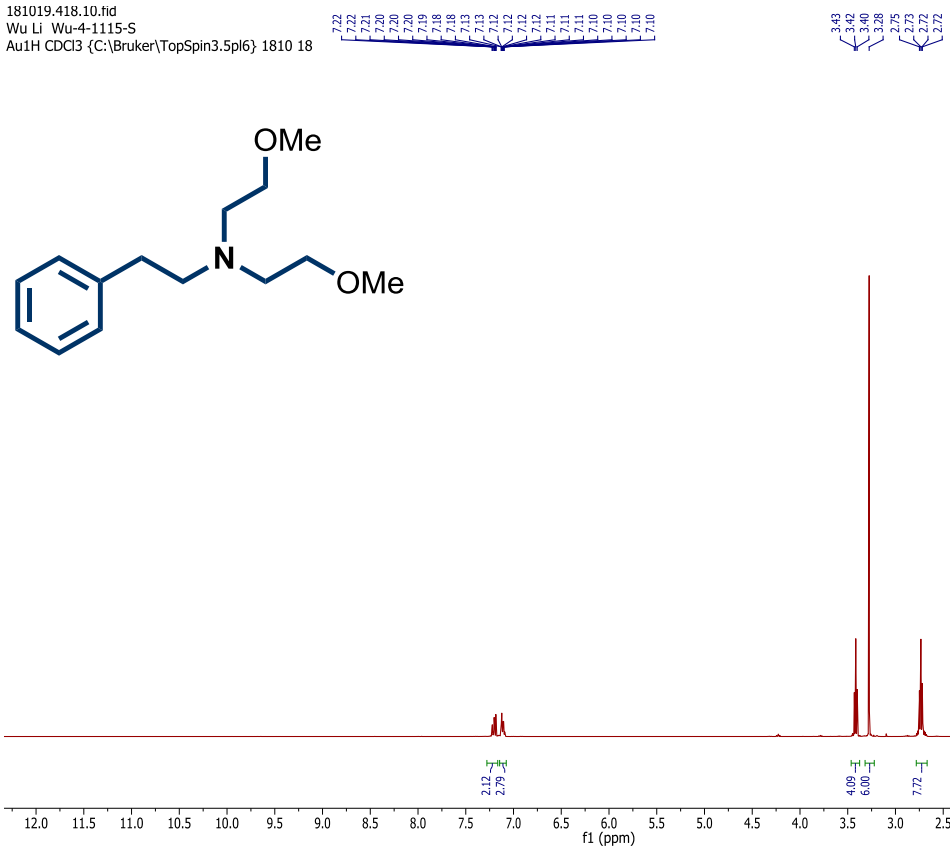
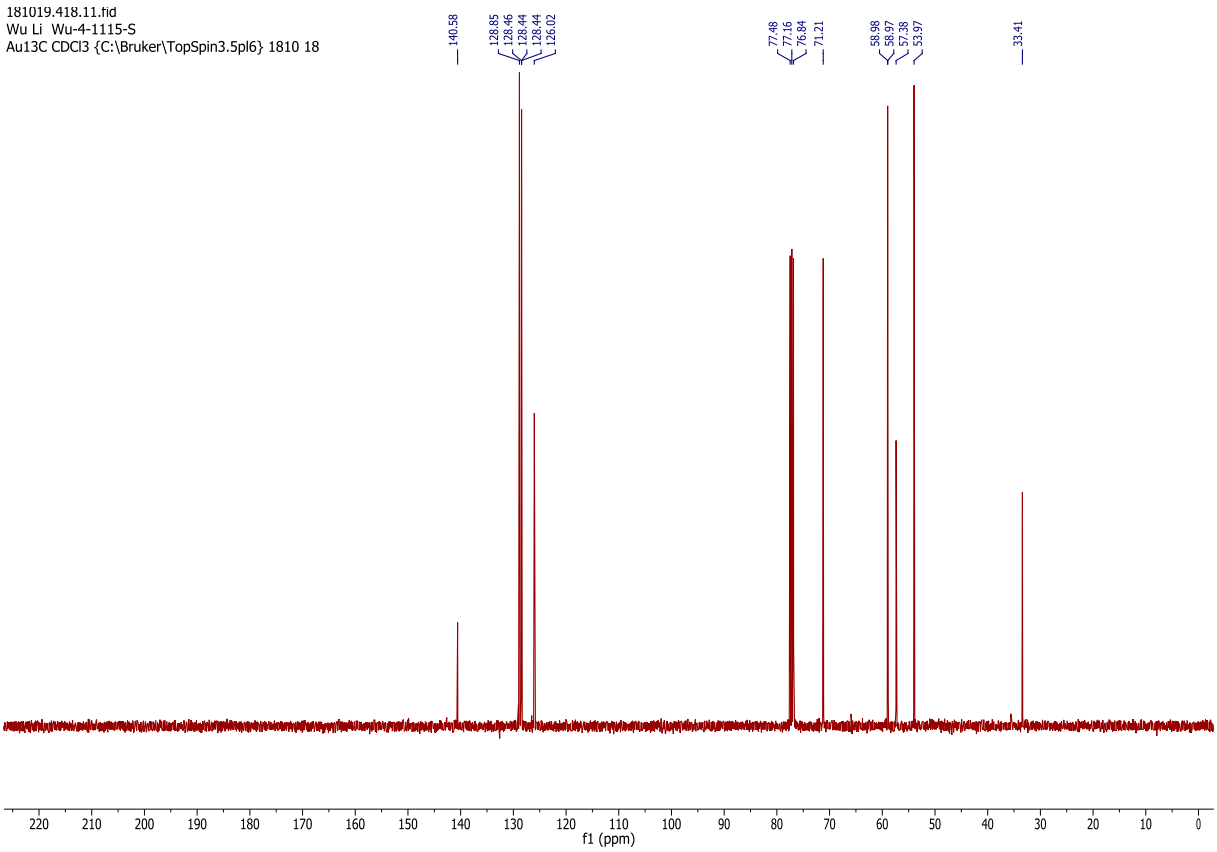
Original spectra for **8a**:





Data File C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\WU-4-988-COL-25.D
Sample Name: WU-4-988-col-25

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Acq. Instrument : GC Lab.133                   Location : Vial 28
Injection Date  : 10/11/2018 7:47:02 AM            Inj :   1
                                              Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d

Additional Info : Peak(s) manually integrated
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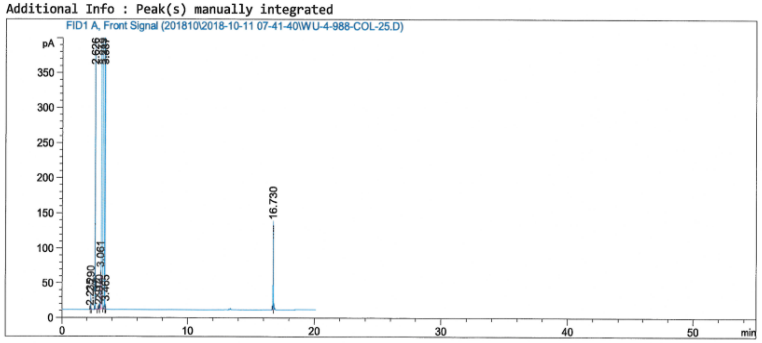


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==================================================================
                        Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal
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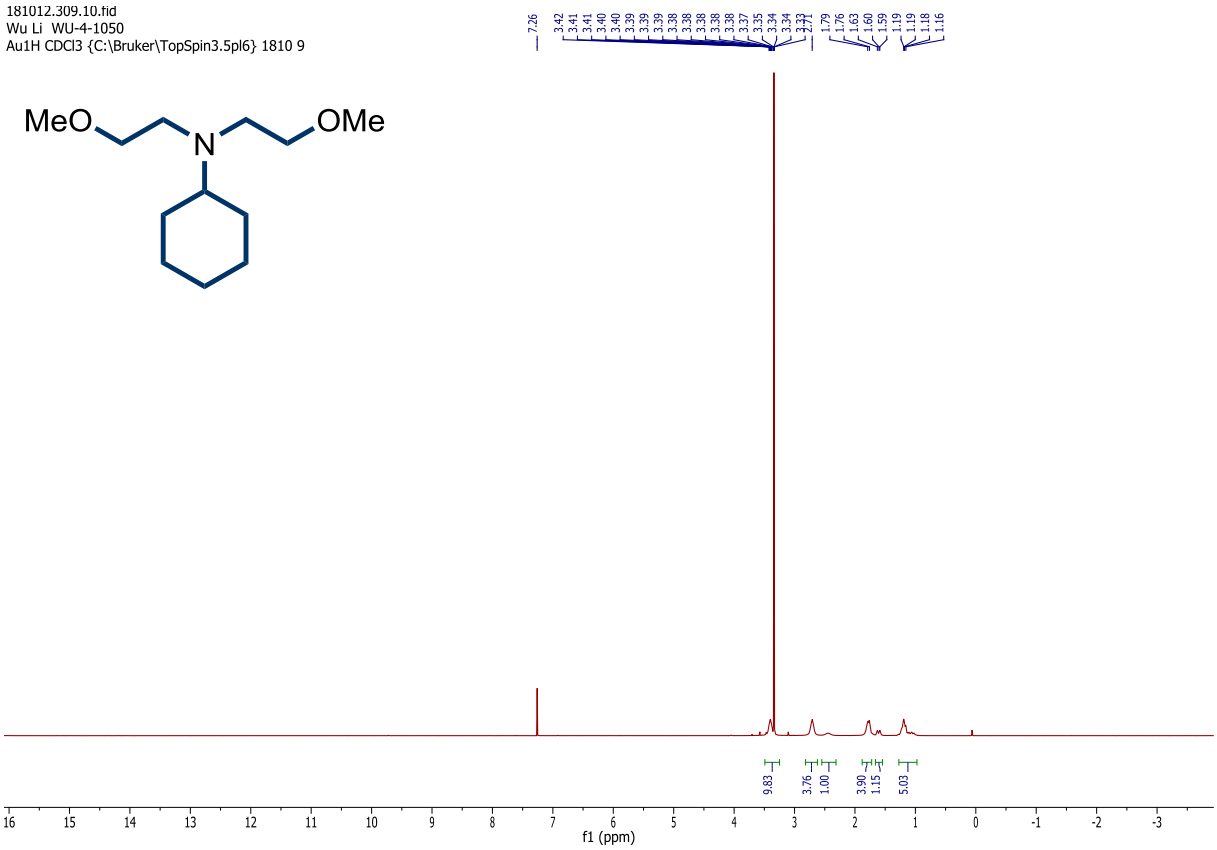
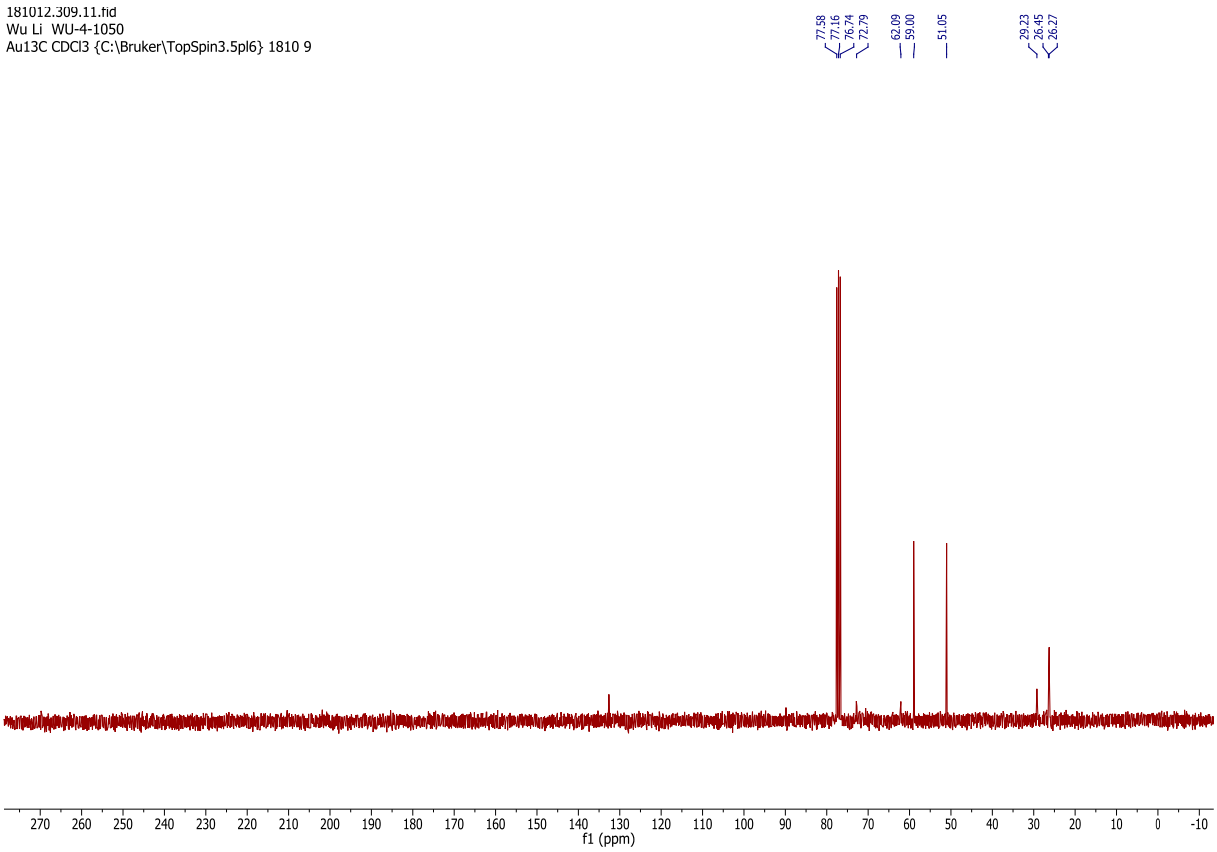
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.235	BV	0.0163	2.22059	1.97778	0.00157
2	2.290	VB	0.0140	19.83987	21.35296	0.01399
3	2.626	BB	0.0150	662.59399	705.14691	0.46708
4	2.912	BV	0.0349	5.95006	2.74135	0.00419
5	2.970	VV	0.0372	18.04052	8.09644	0.01272
6	3.061	BV	0.0460	163.16457	56.04660	0.11502
7	3.219	VB S	0.0462	1.36945e5	3.71963e4	96.53644
8	3.387	BV	0.0214	3803.53198	2553.25464	2.68122
9	3.465	VB	0.0167	8.24082	7.57881	0.00581
10	16.730	VV	0.0294	229.76047	125.22737	0.16196
Totals :				1.41858e5	4.06777e4	

Original spectra for **9a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-1050.D
Sample Name: WU-4-1050

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Acq. Instrument : GC Lab.133                    Location : Vial 4
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                                               Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
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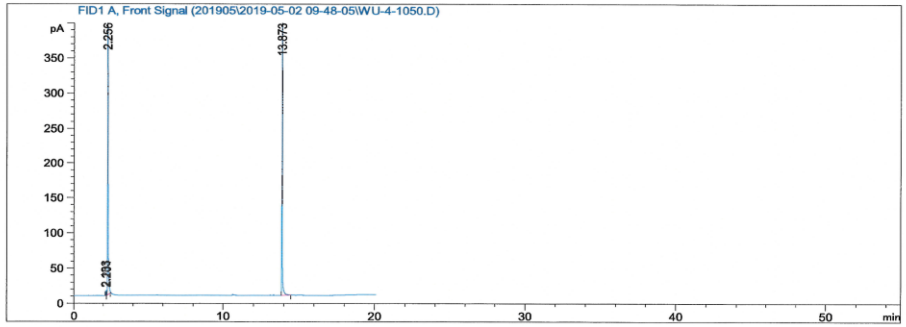


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==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

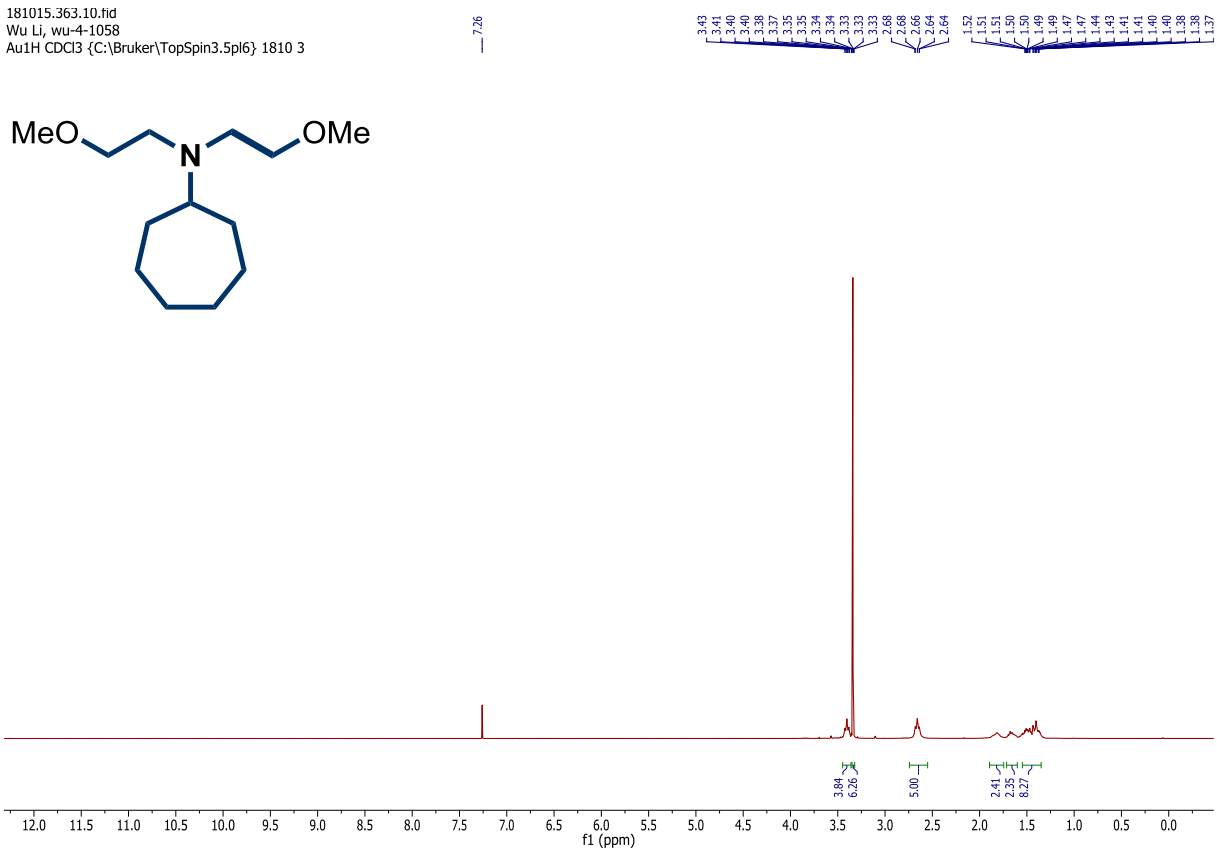

Signal 1: FID1 A, Front Signal

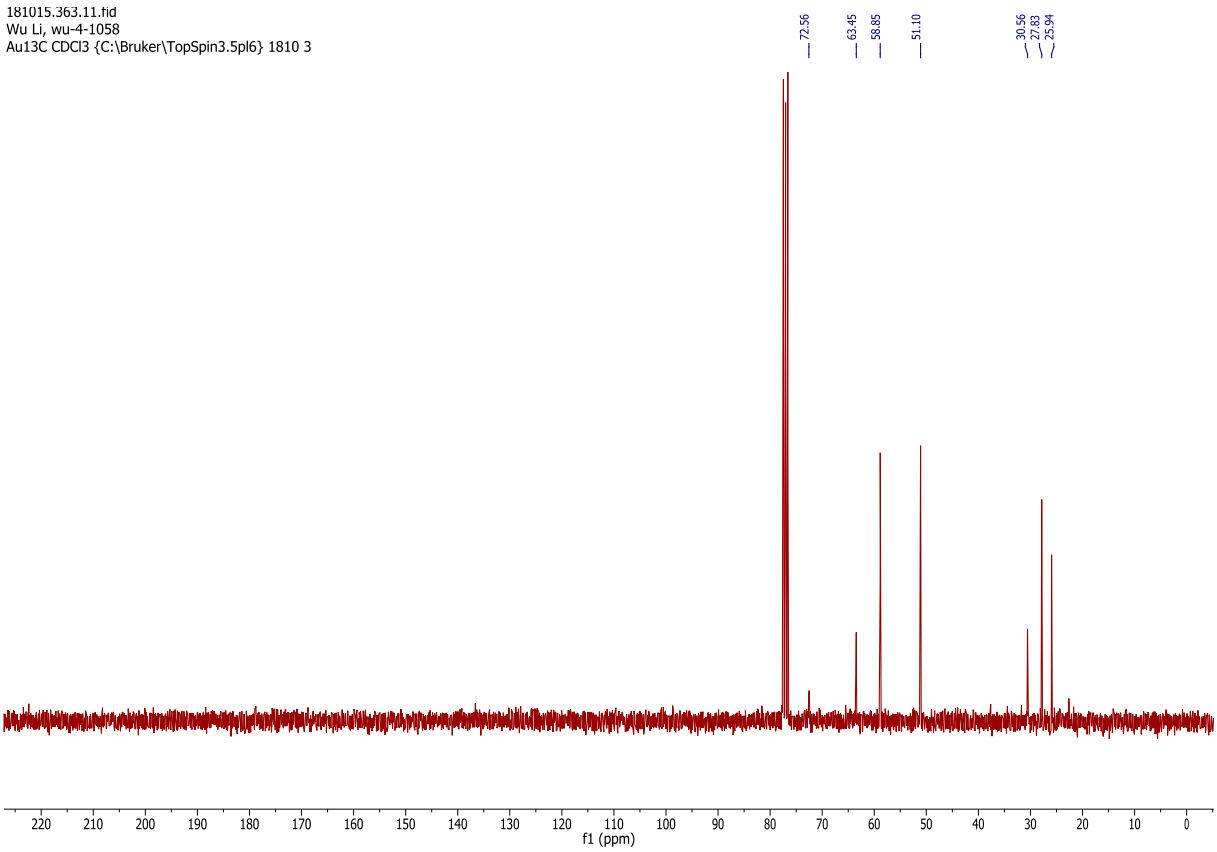
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BV    0.0170    8.09186    7.26236  0.01087
   2   2.201 BB    0.0195    8.94929    7.51857  0.01202
   3   2.256 VB S  0.0179 7.33688e4  6.84150e4  98.58112
   4  13.873 BB    0.0304 1038.95996  523.36066  1.39599

Totals :                  7.44248e4  6.89531e4


==================================================================
                      *** End of Report ***
```

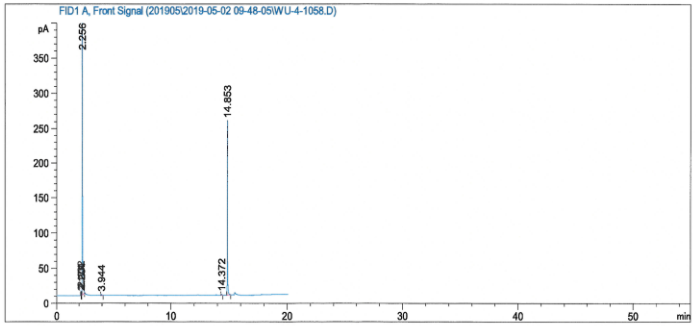
Original spectra for **10a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-1058.D
Sample Name: WU-4-1058

```
==================================================================
Acq. Operator   : Lab 2.112                    Seq. Line :   7
Acq. Instrument : GC Lab.133                    Location : Vial 7
Injection Date  : 5/2/2019 12:46:37 PM             Inj :   1
                                                Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

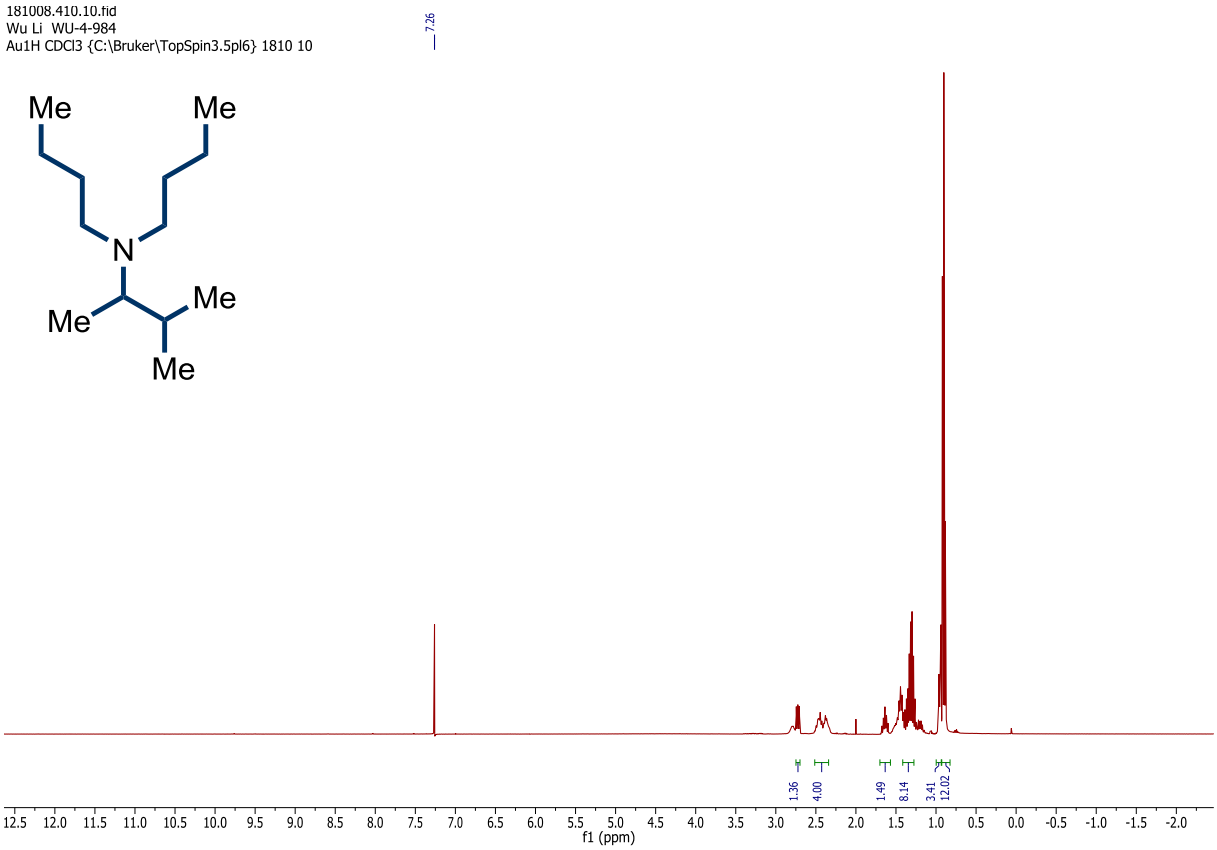

Signal 1: FID1 A, Front Signal

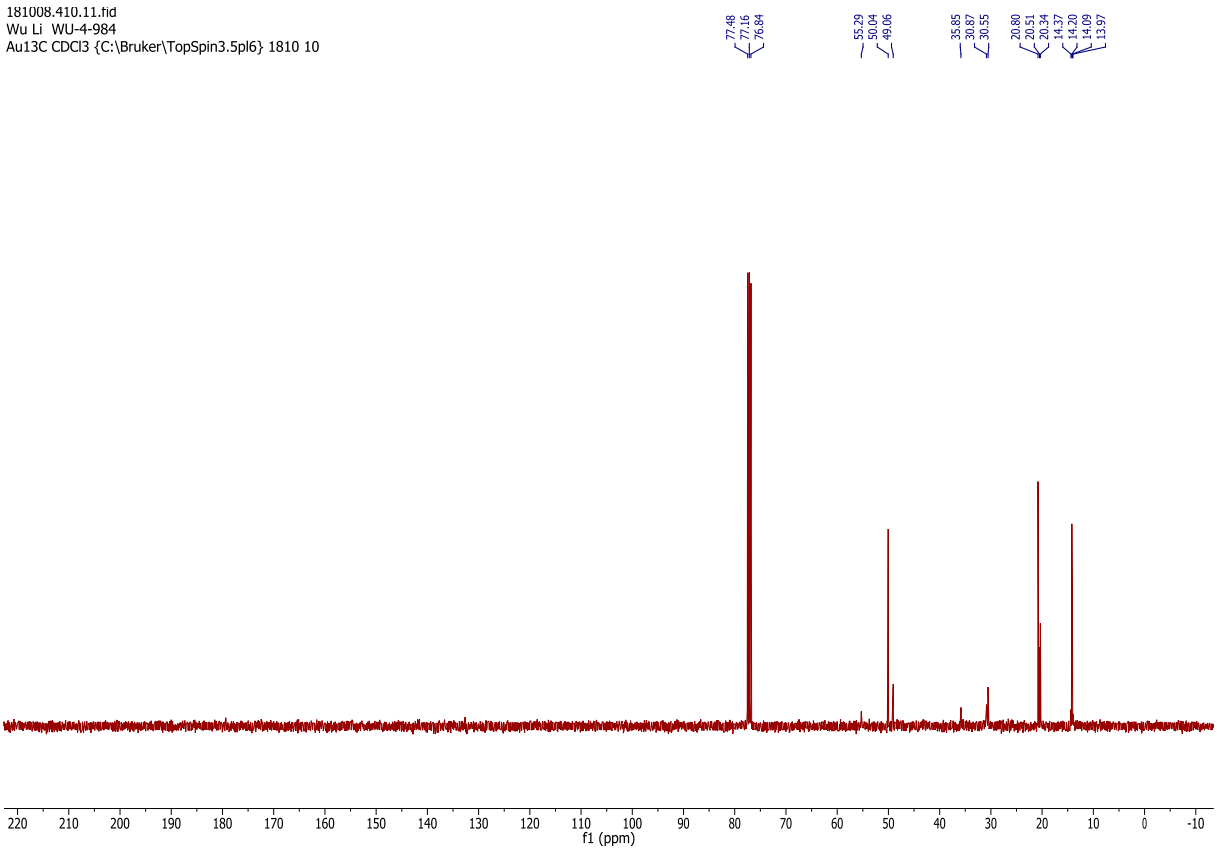
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.132 BV    0.0162    7.89442    7.54467  0.01079
   2   2.171 VV    0.0129    2.03822    2.45142  0.00279
   3   2.201 VB    0.0185    5.71871    4.87688  0.00782
   4   2.256 VB S  0.0173 7.26184e4  6.80473e4  99.29088
   5   3.944 BB    0.0300    3.31291    1.58433  0.00453
   6  14.372 BB    0.0298    3.81358    1.90257  0.00521
   7  14.853 BB    0.0296  495.85077  249.56918  0.67797

Totals :                  7.31371e4  6.83152e4

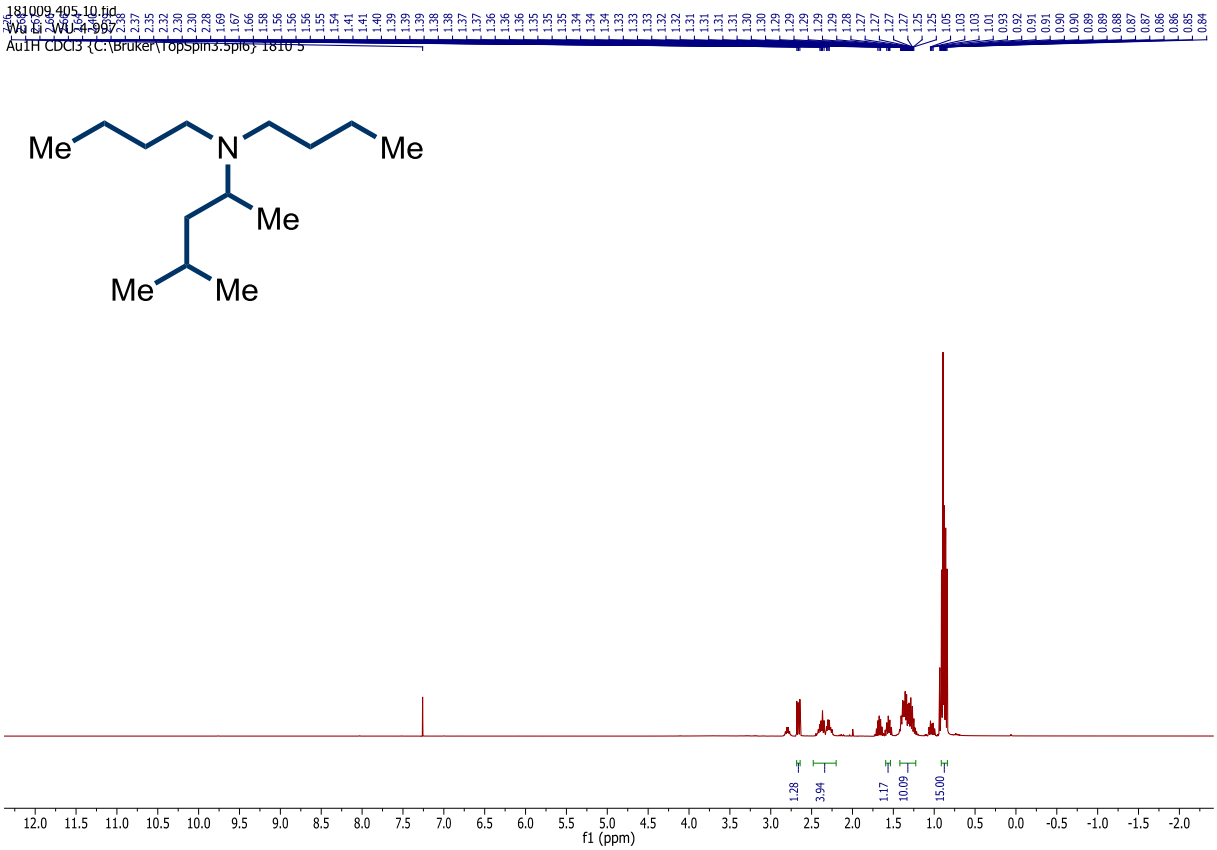
==================================================================
                        *** End of Report ***
```

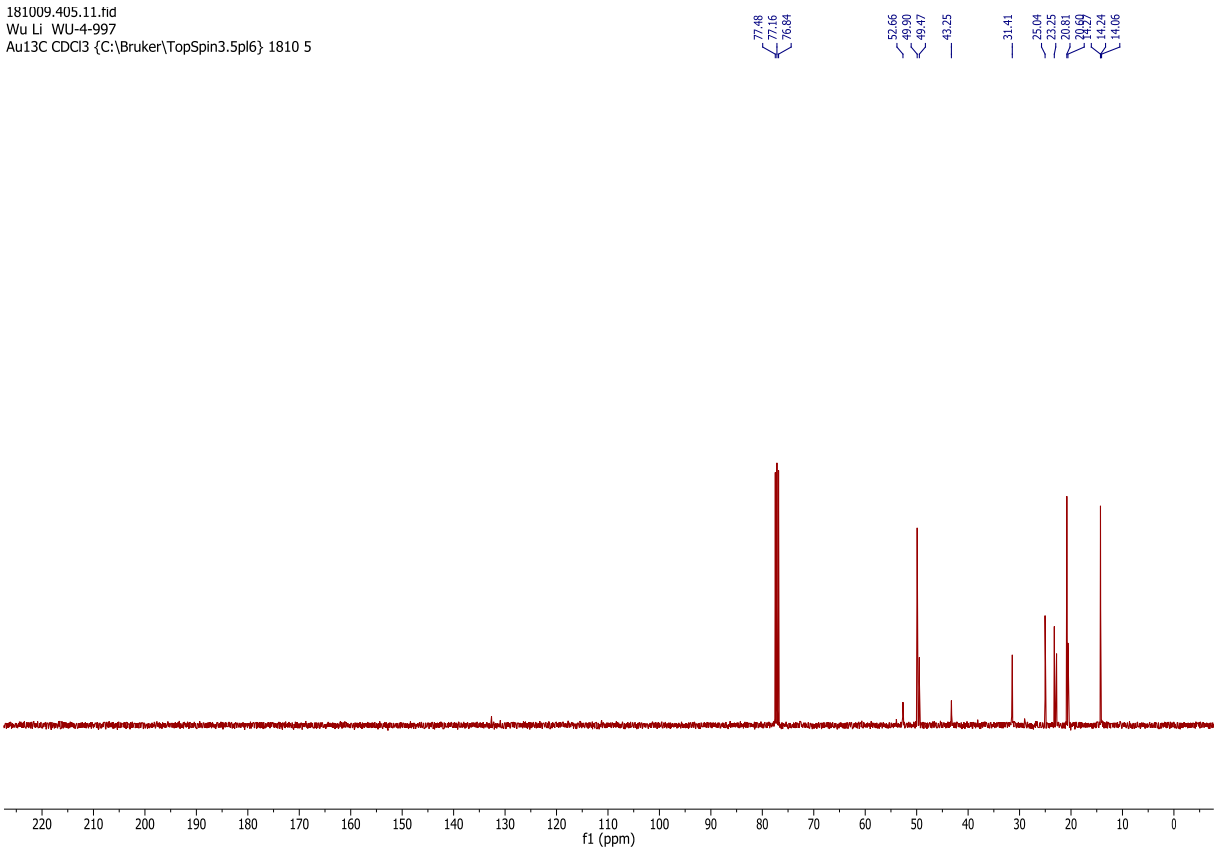
Original spectra for **11a**:



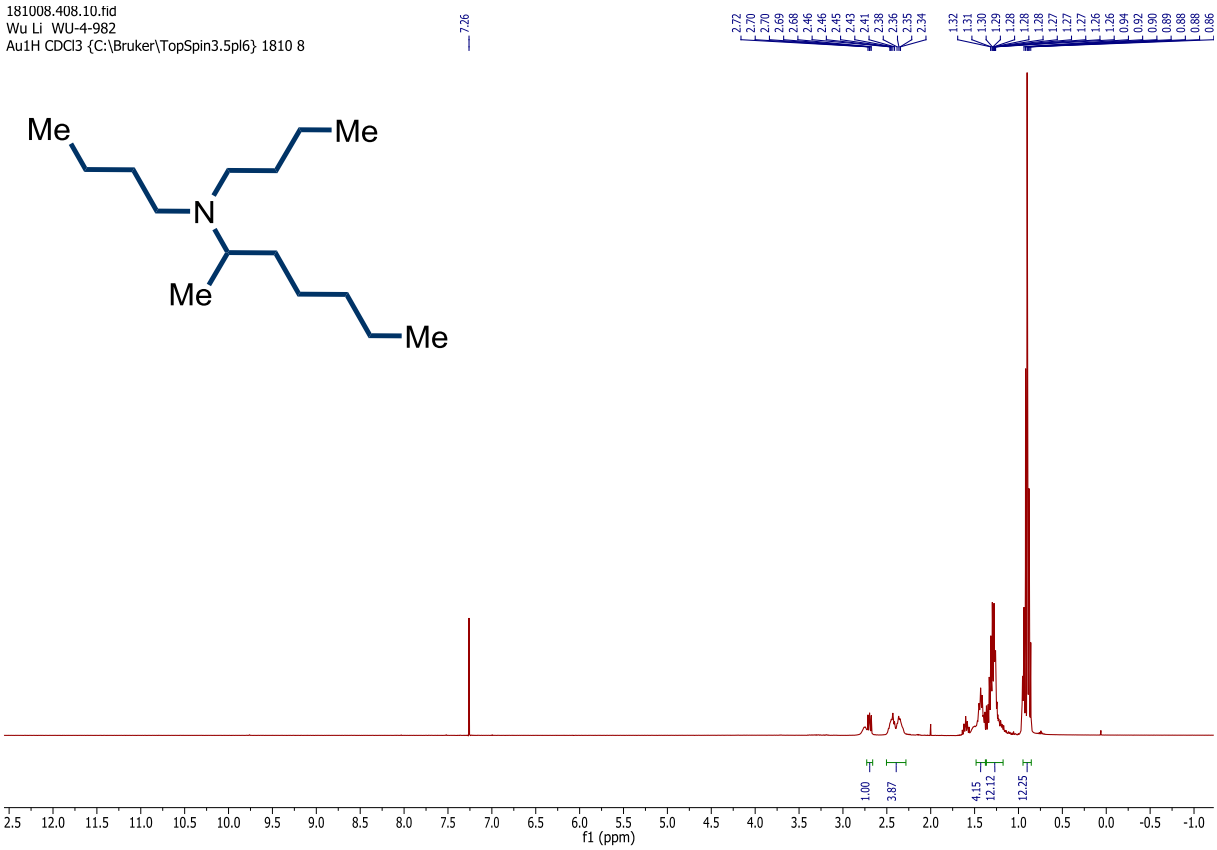


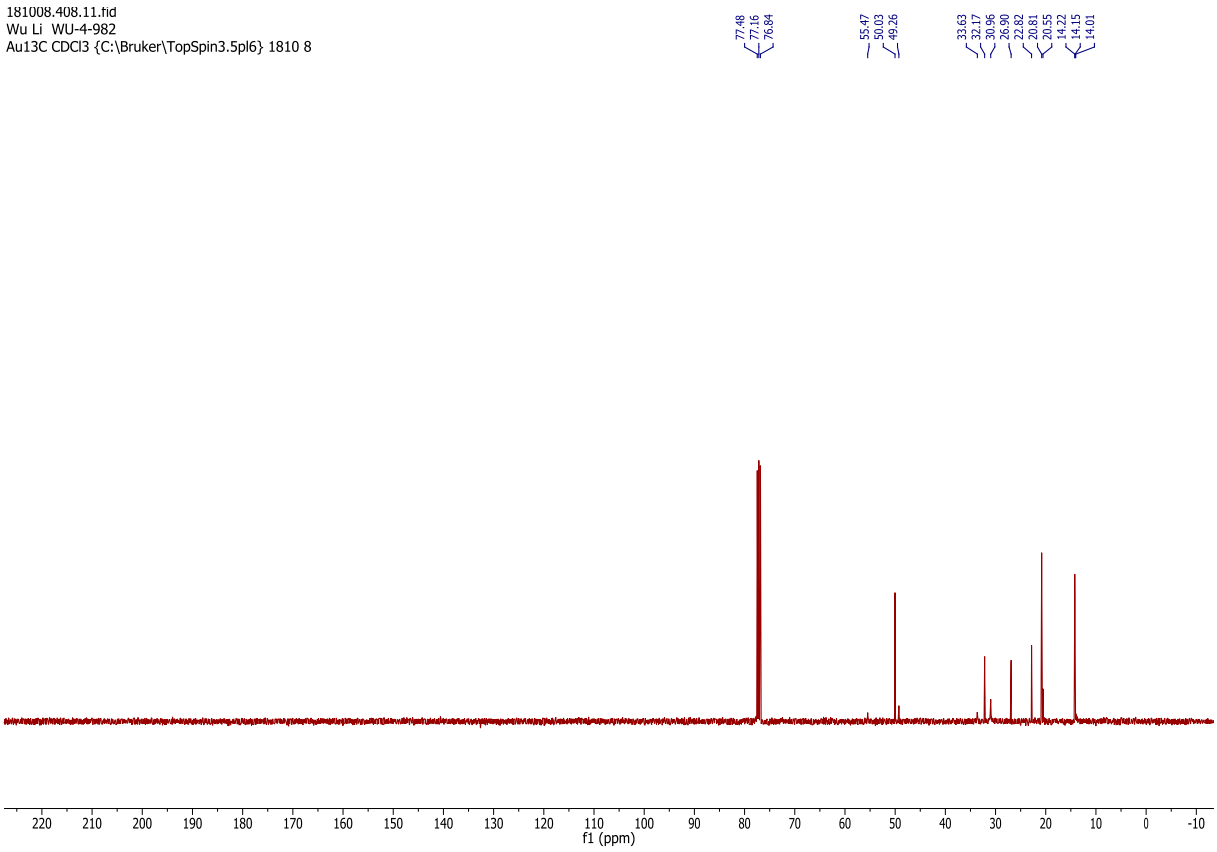
Original spectra for **12a**:





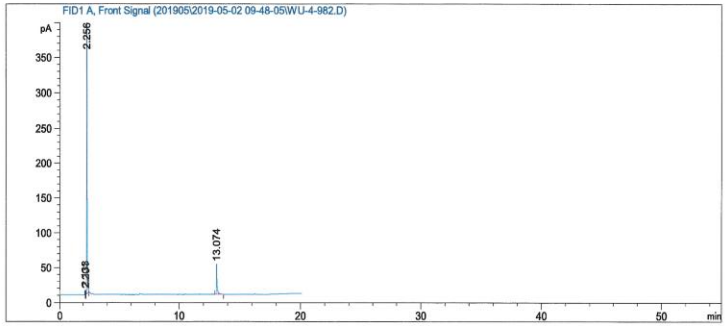
Original spectra for **13a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-982.D
Sample Name: WU-4-982

```
======================================================================
Acq. Operator   : Lab 2.112                    Seq. Line :   8
Acq. Instrument : GC Lab.133                   Location : Vial 8
Injection Date  : 5/2/2019 1:13:15 PM             Inj :   1
                                               Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

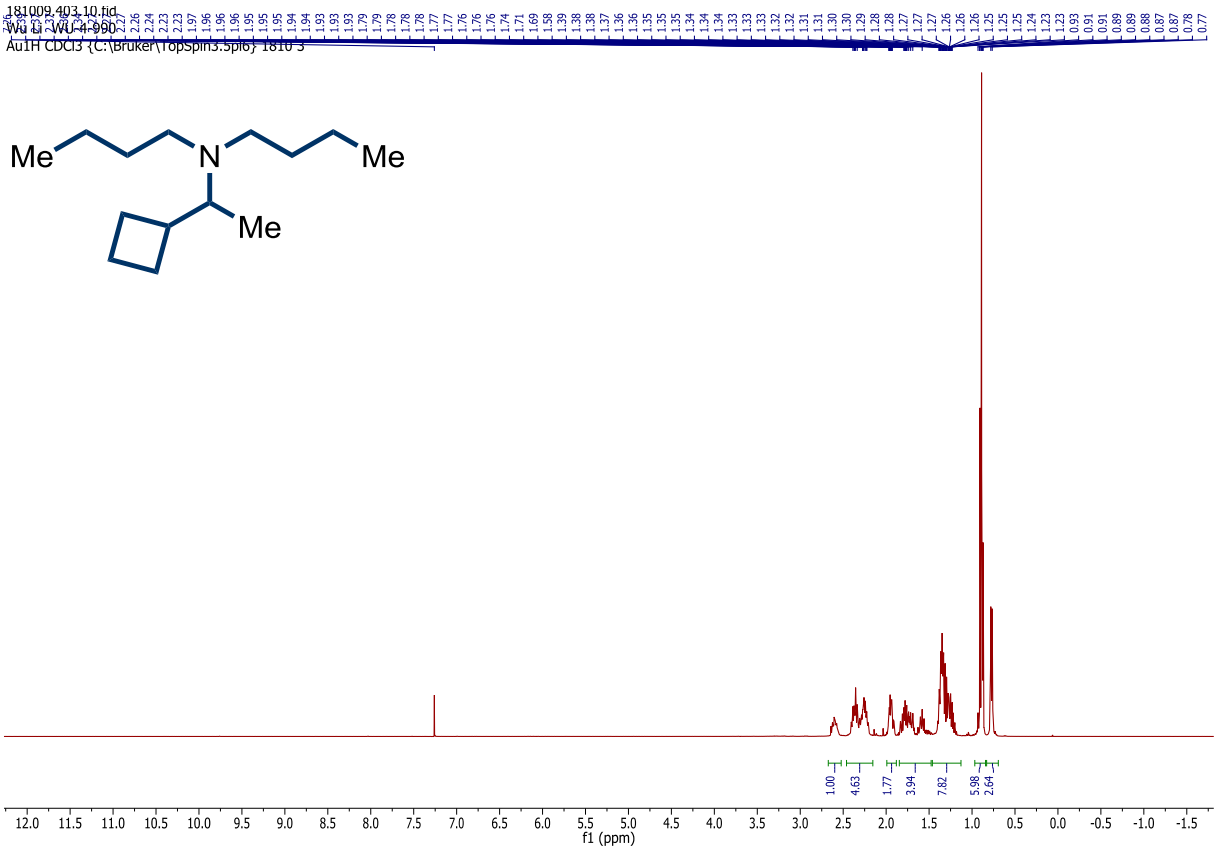

Signal 1: FID1 A, Front Signal

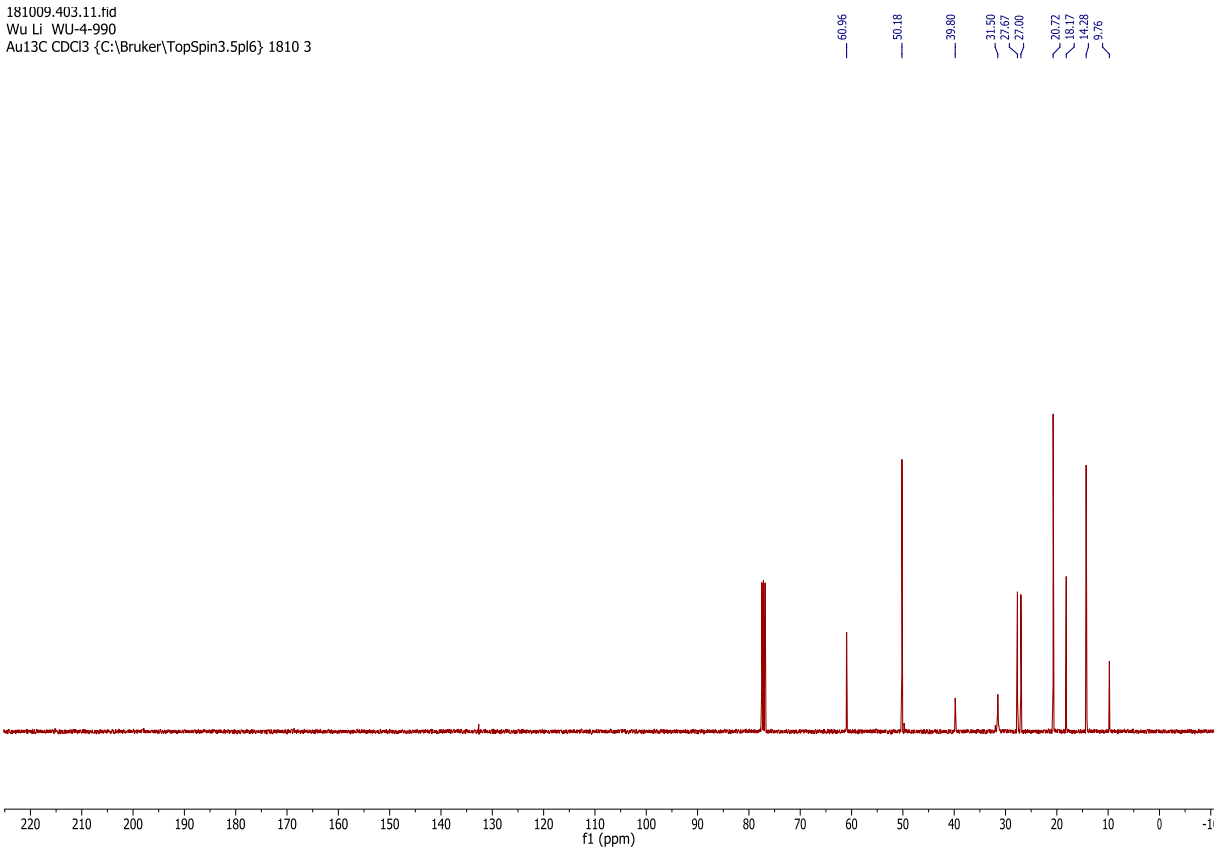
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BB    0.0163    7.33834    6.52669  0.00988
   2   2.201 BB    0.0183    4.87632    4.20943  0.00657
   3   2.256 VB S  0.0178 7.40721e4  6.92267e4  99.76906
   4  13.074 BB    0.0487  159.24245   43.93989  0.21449

Totals :                  7.42436e4  6.92813e4

======================================================================
                        *** End of Report ***
```

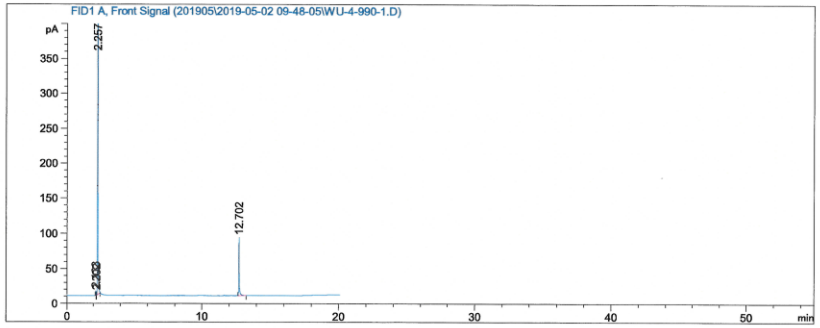
Original spectra for **14a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-990-1.D
Sample Name: WU-4-990-1

```
======================================================================
Acq. Operator   : Lab 2.112                      Seq. Line :  20
Acq. Instrument : GC Lab.133                     Location : Vial 2
Injection Date  : 5/2/2019 6:32:43 PM               Inj :   1
                                                 Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

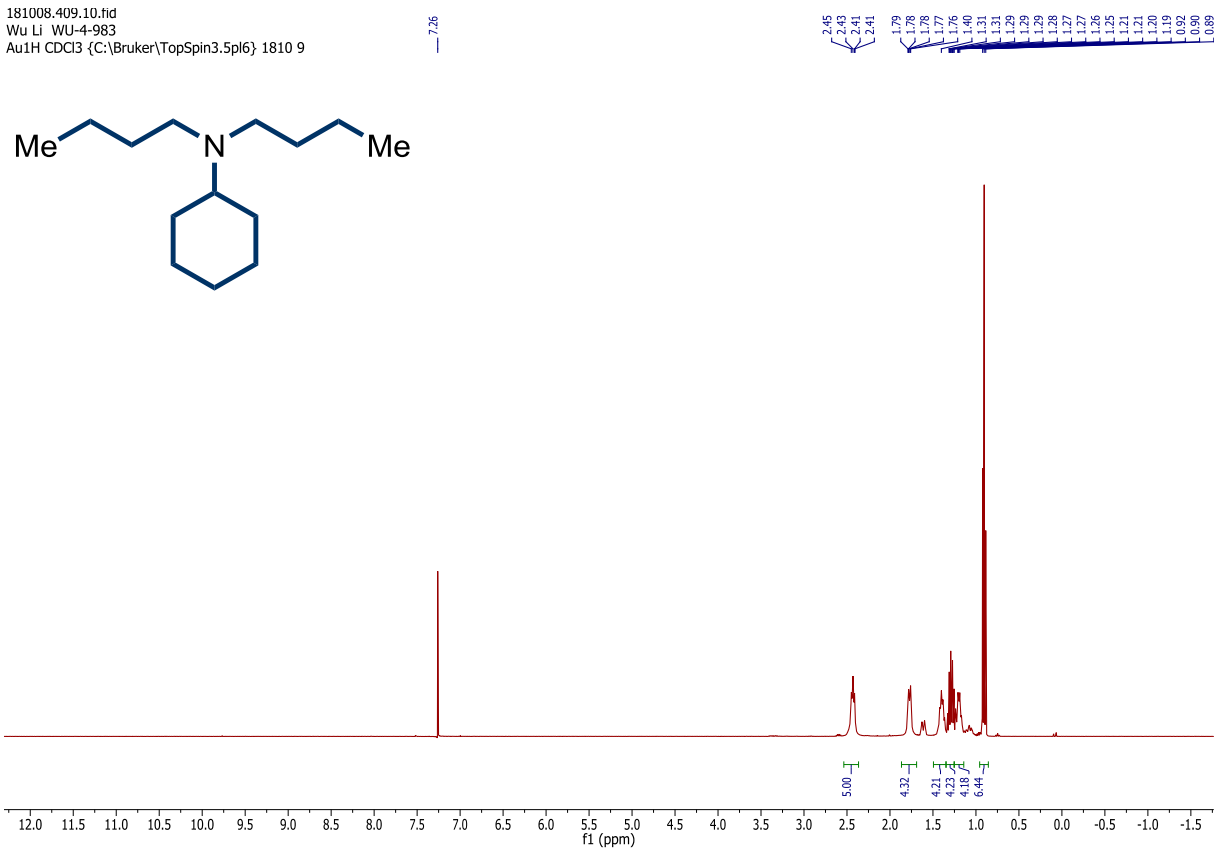

Signal 1: FID1 A, Front Signal

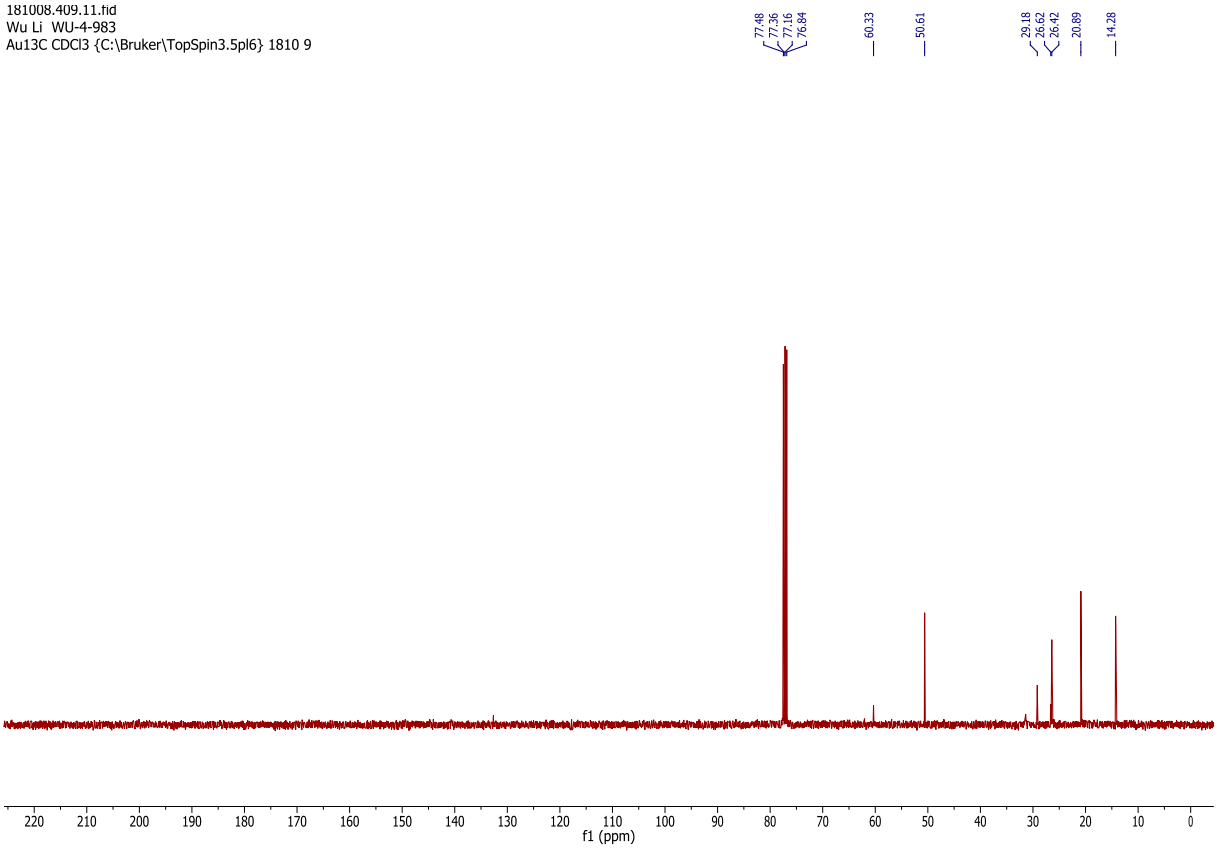
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BB    0.0163    7.79851    6.97088  0.01004
   2   2.202 BV    0.0199    4.62243    3.78133  0.00595
   3   2.257 VB S  0.0176 7.74383e4  7.05899e4  99.70252
   4  12.702 BB    0.0380  218.62764   82.75813  0.28148

Totals :                  7.76694e4  7.06834e4

======================================================================
                        *** End of Report ***
```

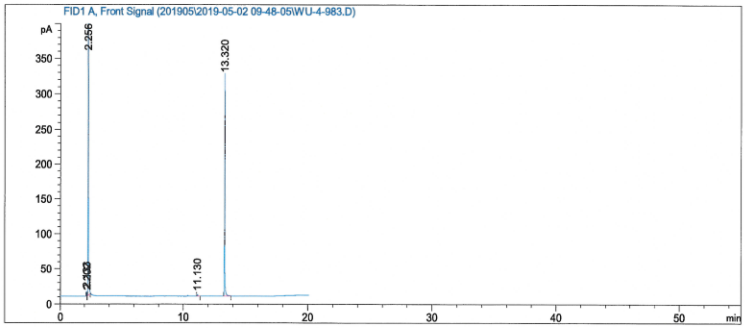
Original spectra for **15a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-983.D
Sample Name: WU-4-983

```
=====================================================================
Acq. Operator   : Lab 2.112                    Seq. Line :   3
Acq. Instrument : GC Lab.133                    Location : Vial 3
Injection Date  : 5/2/2019 11:00:03 AM             Inj :   1
                                                Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

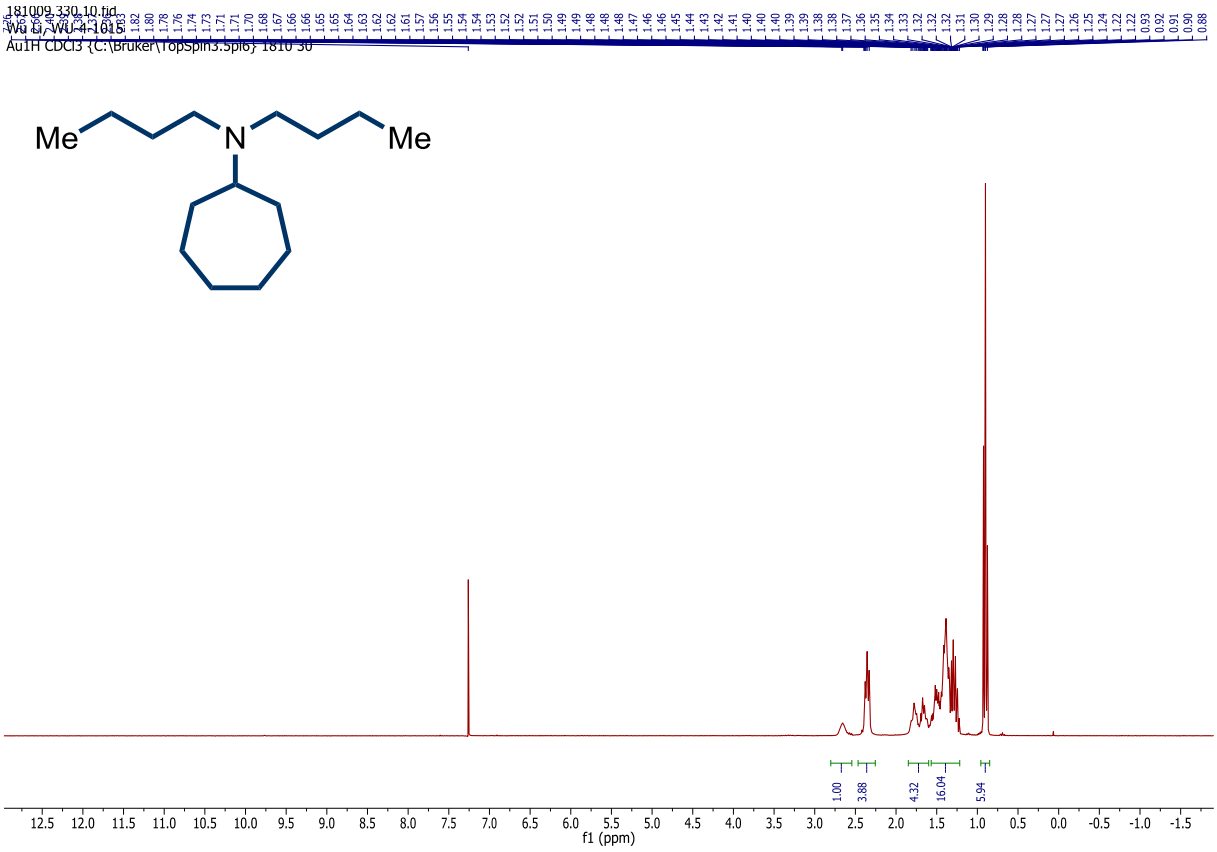

Signal 1: FID1 A, Front Signal

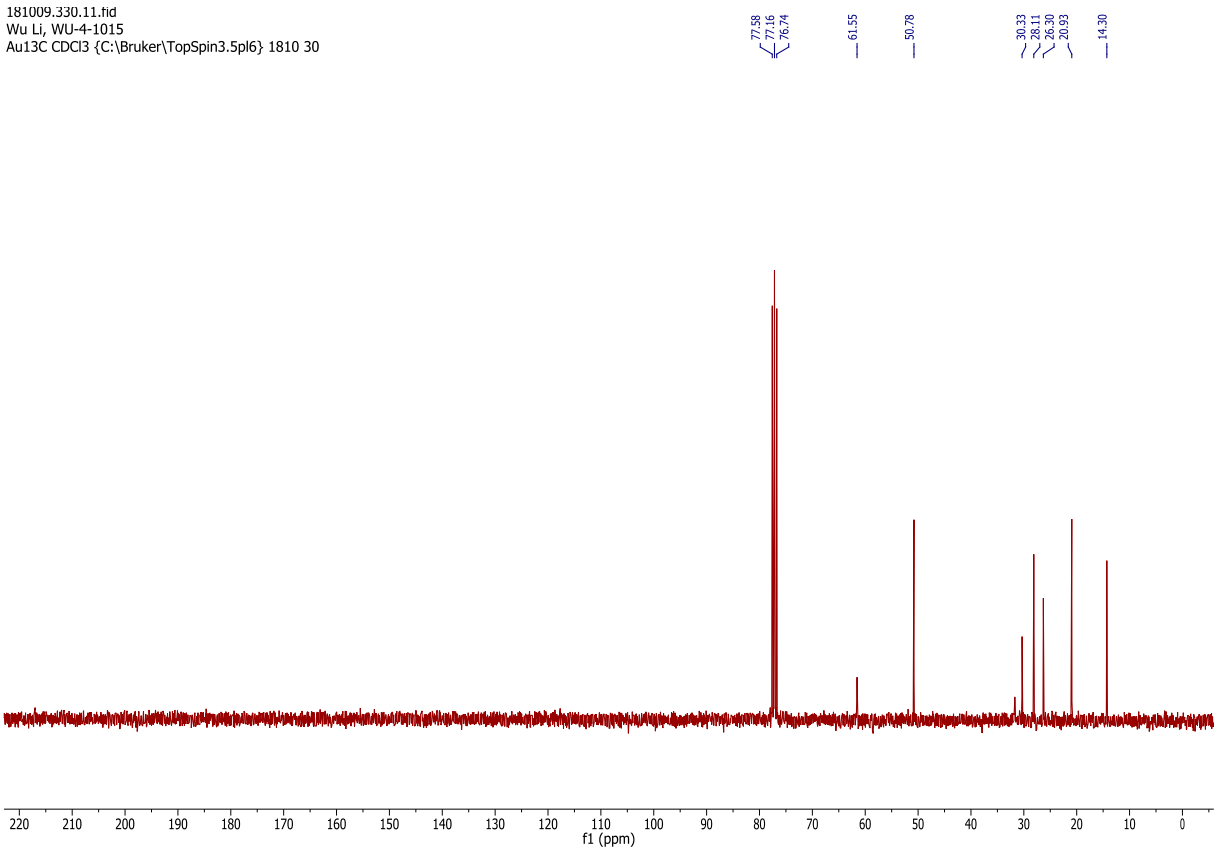
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BB    0.0169    7.87409    7.11071  0.01046
   2   2.202 BV    0.0183    5.10283    4.42283  0.00678
   3   2.256 VB S  0.0173 7.46134e4  6.93702e4  99.11974
   4  11.130 BB    0.0396    7.86597    2.82916  0.01045
   5  13.320 BB    0.0310  641.78119  314.83890  0.85257

Totals :                  7.52760e4  6.96994e4

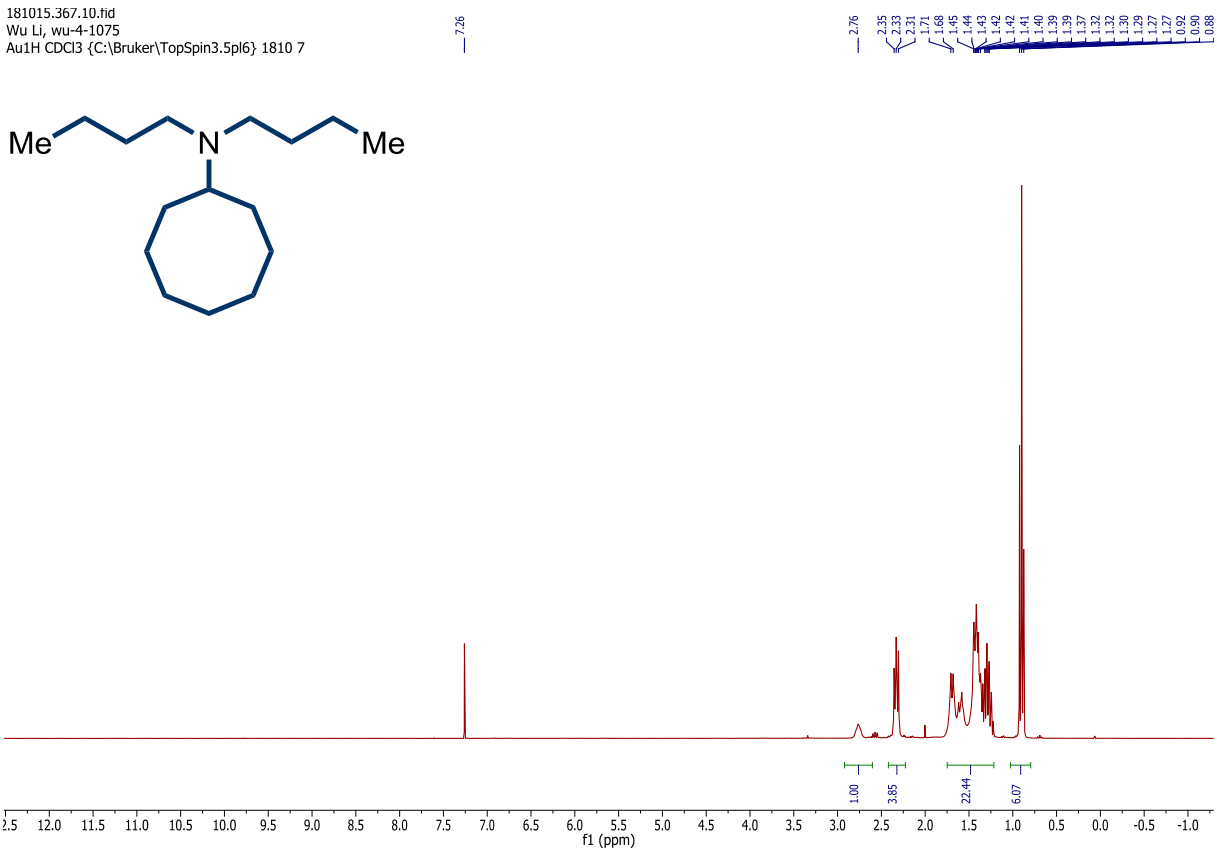

=====================================================================
                        *** End of Report ***
```

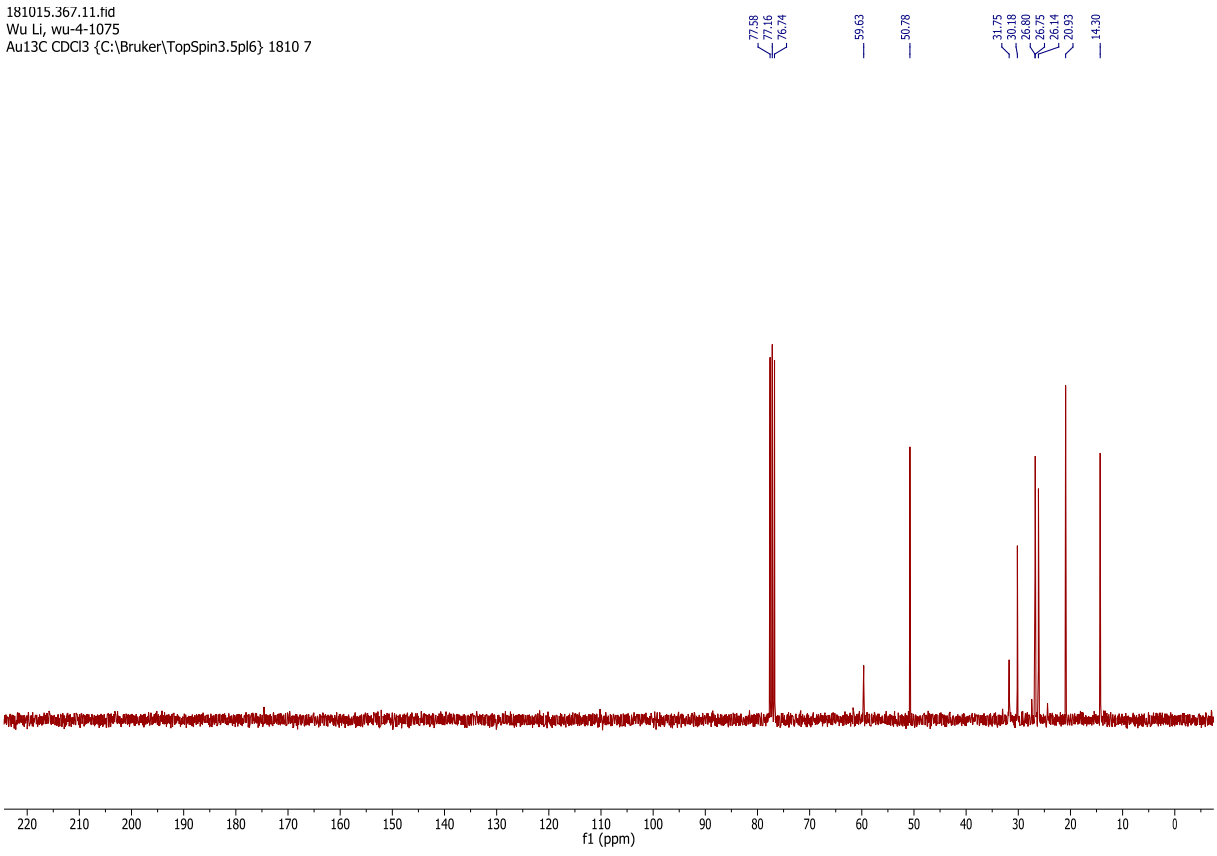
Original spectra for **16a**:





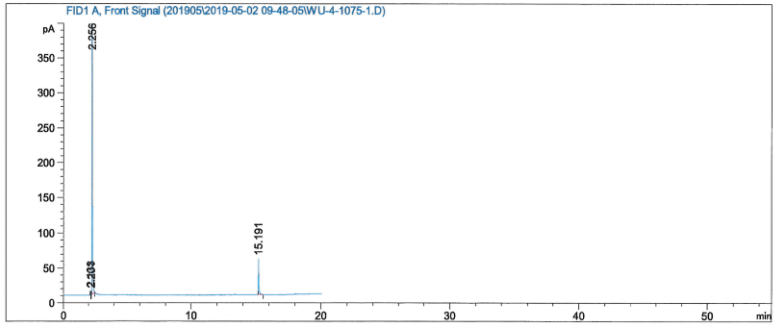
Original spectra for **17a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-1075-1.D
Sample Name: WU-4-1075-1

```
======================================================================
Acq. Operator   : Lab 2.112                      Seq. Line :  19
Acq. Instrument : GC Lab.133                      Location : Vial 5
Injection Date  : 5/2/2019 6:06:10 PM                 Inj :   1
                                                 Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

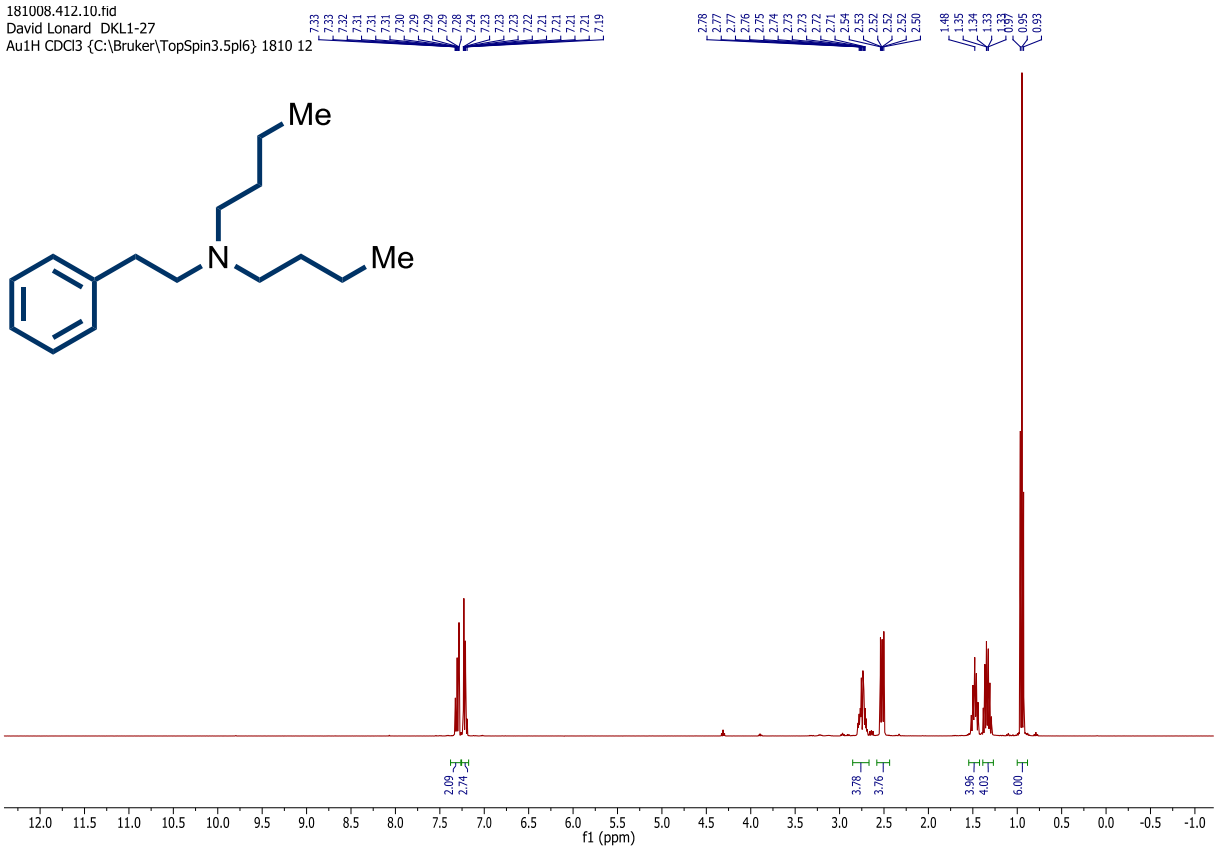

Signal 1: FID1 A, Front Signal

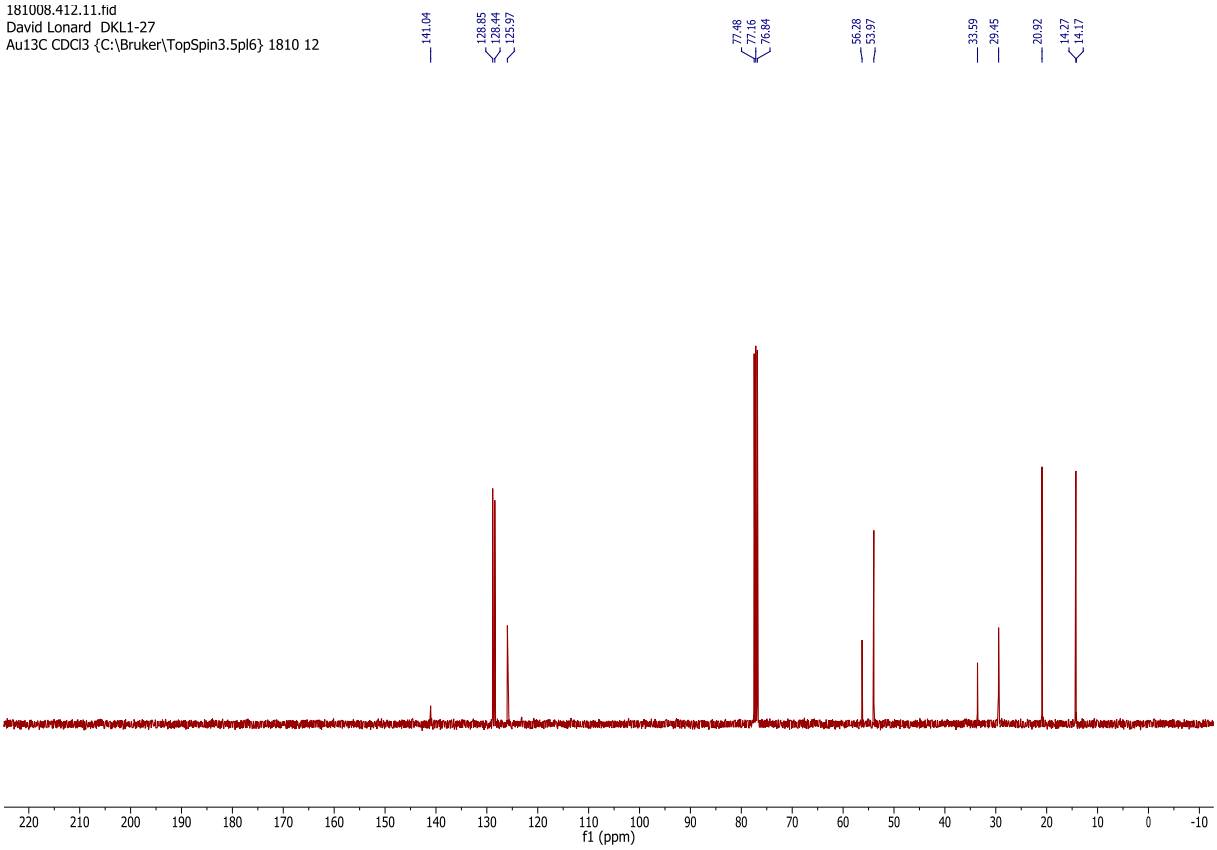
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BB    0.0167    7.35947    6.74832  0.01014
   2   2.201 BV    0.0196    7.17888    5.99652  0.00989
   3   2.256 VB S  0.0172 7.24261e4  6.79581e4  99.80103
   4  15.191 BB    0.0351  129.85249   52.76576  0.17893

Totals :                  7.25705e4  6.80236e4

======================================================================
                        *** End of Report ***
```

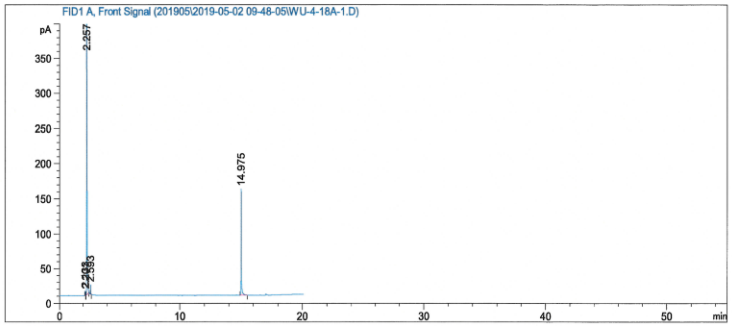
Original spectra for **18a**:





Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-18A-1.D
Sample Name: WU-4-18a-1

```
==================================================================
Acq. Operator   : Lab 2.112                    Seq. Line :  25
Acq. Instrument : GC Lab.133                    Location : Vial 17
Injection Date  : 5/2/2019 9:28:20 PM               Inj :   1
                                               Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

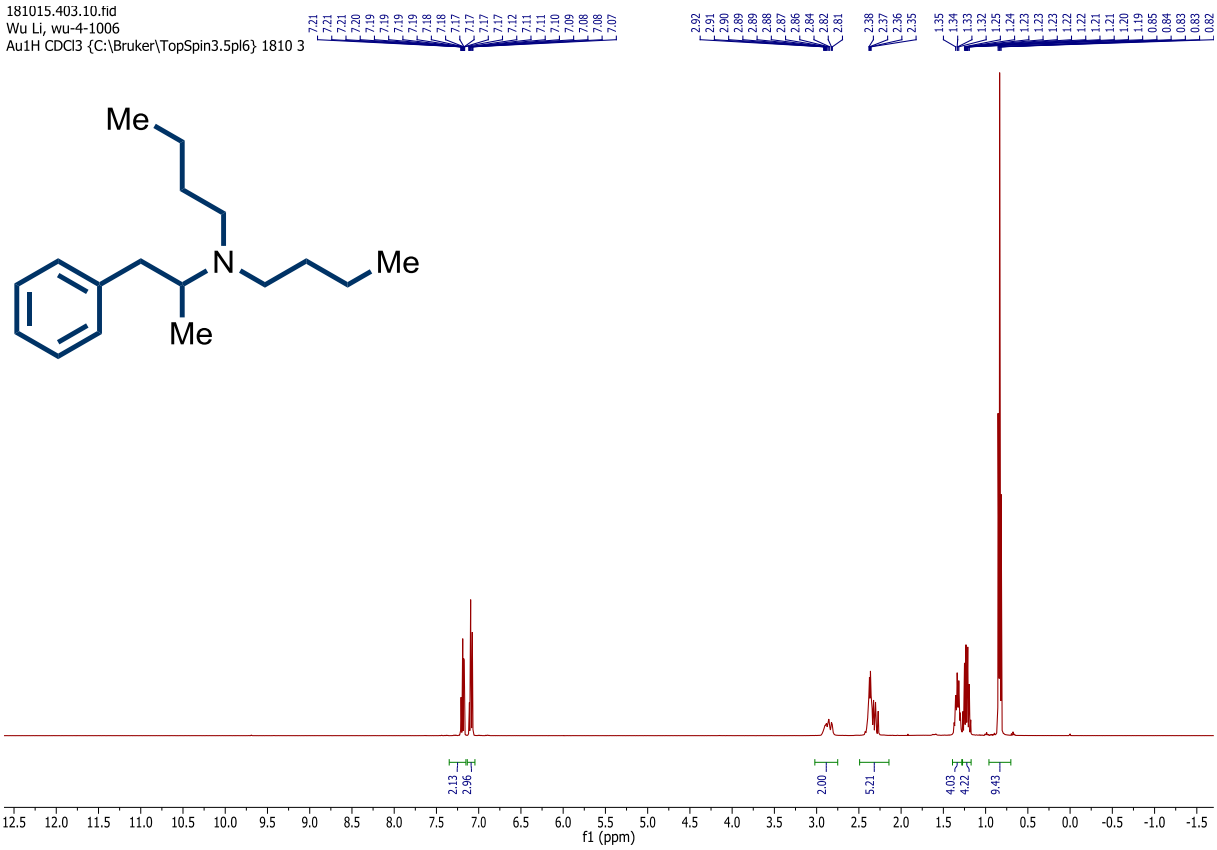

Signal 1: FID1 A, Front Signal

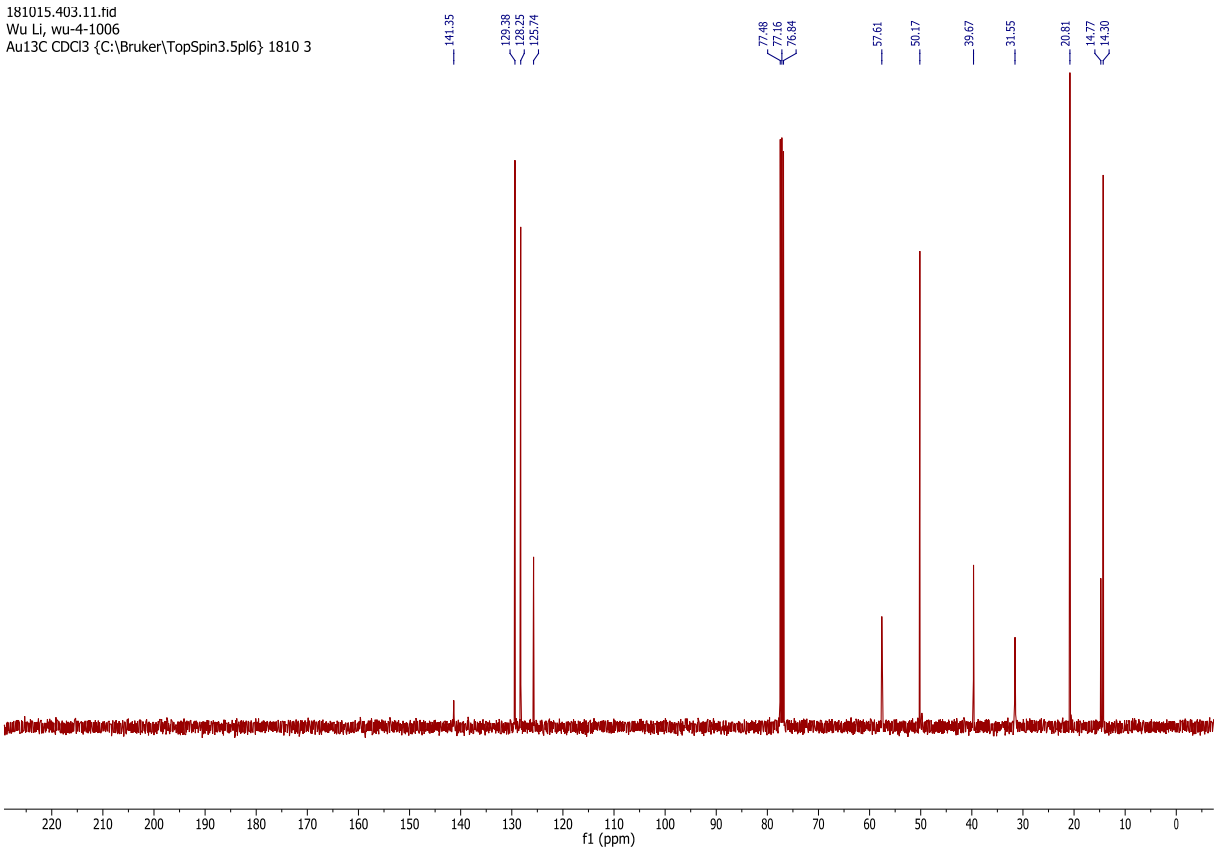
Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BV    0.0165    7.64779    6.71610  0.00990
   2   2.201 BB    0.0189    6.15275    5.08335  0.00797
   3   2.257 VB S  0.0183 7.68151e4  7.01430e4  99.46024
   4   2.593 BB    0.0167   15.85004   13.66284  0.02052
   5  14.975 BB    0.0375  387.22055  153.12811  0.50137

Totals :                 7.72320e4  7.03216e4

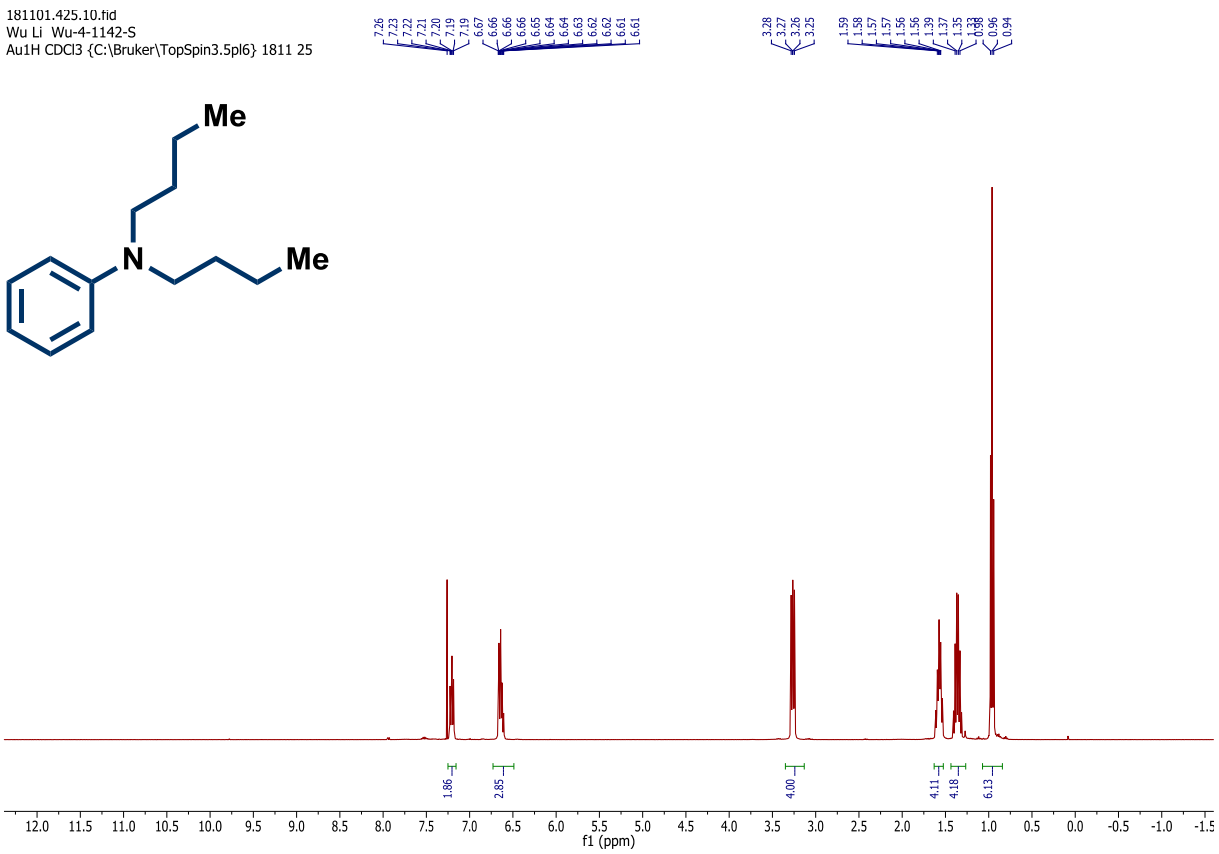

==================================================================
                      *** End of Report ***
```

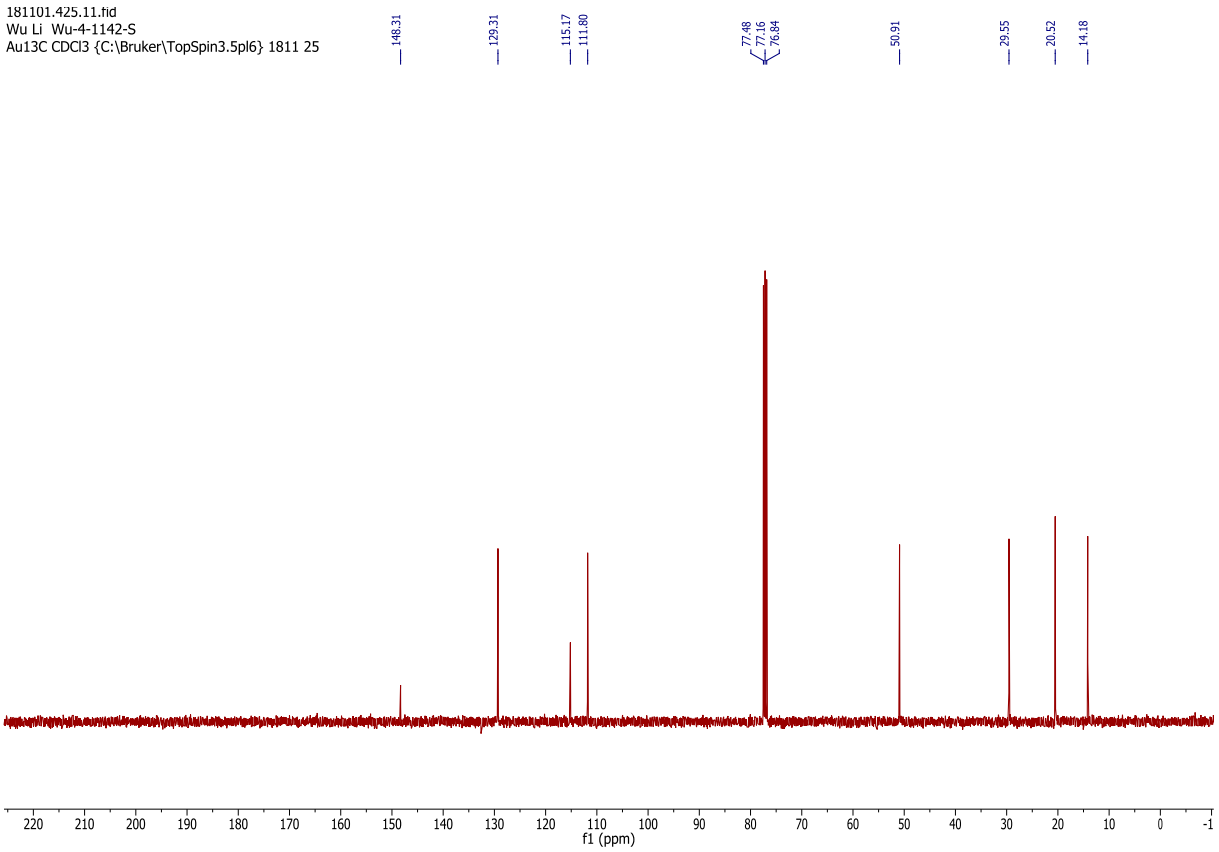
Original spectra for **19a**:



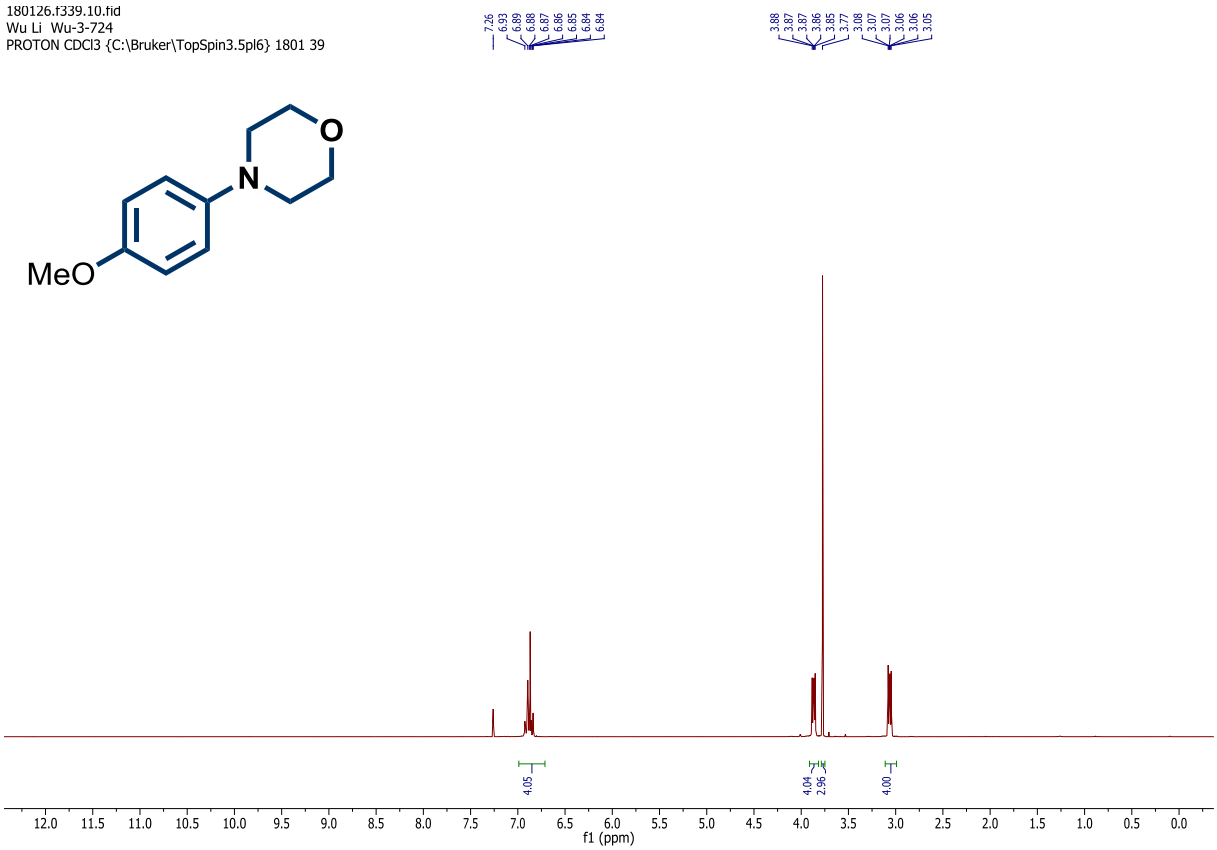


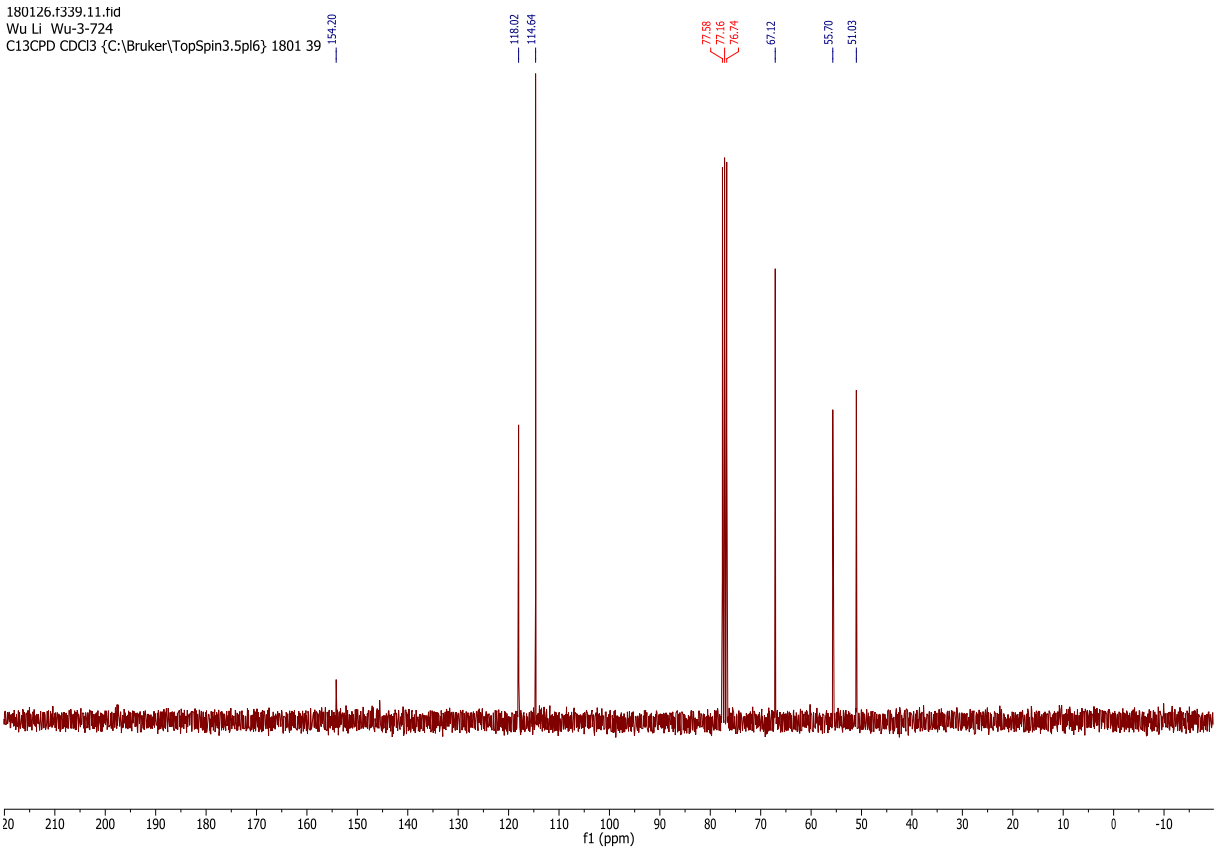
Original spectra for **20a**:





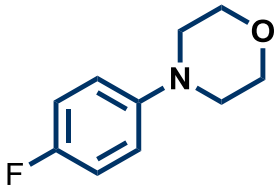
Original spectra for **23a**:

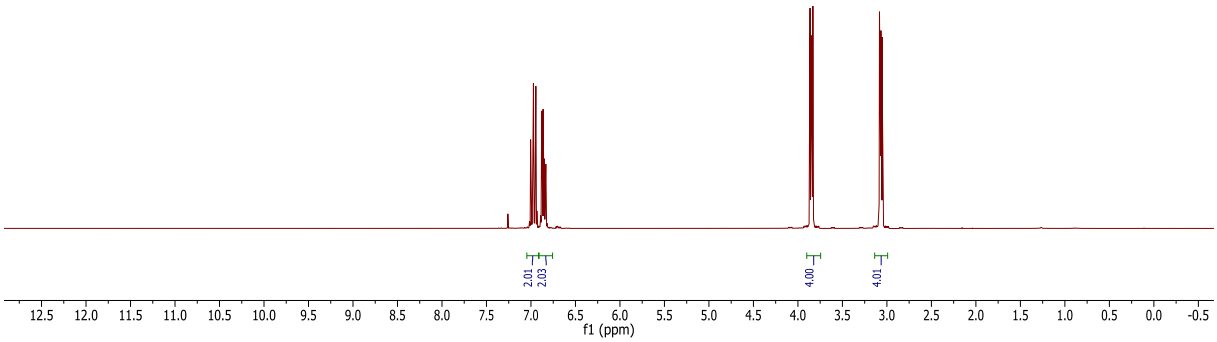




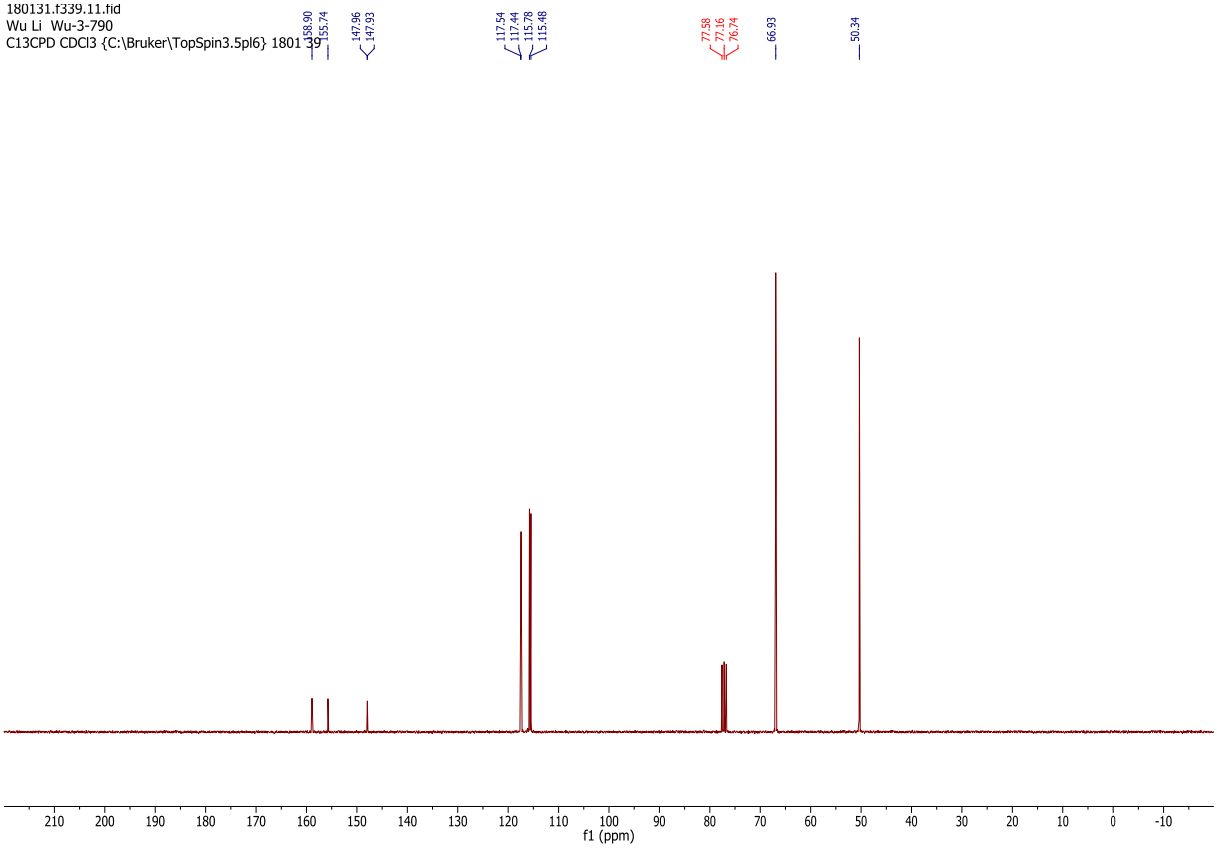
Original spectra for **24a**:

180131.f339.10.fid
Wu Li Wu-3-790
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1801 39

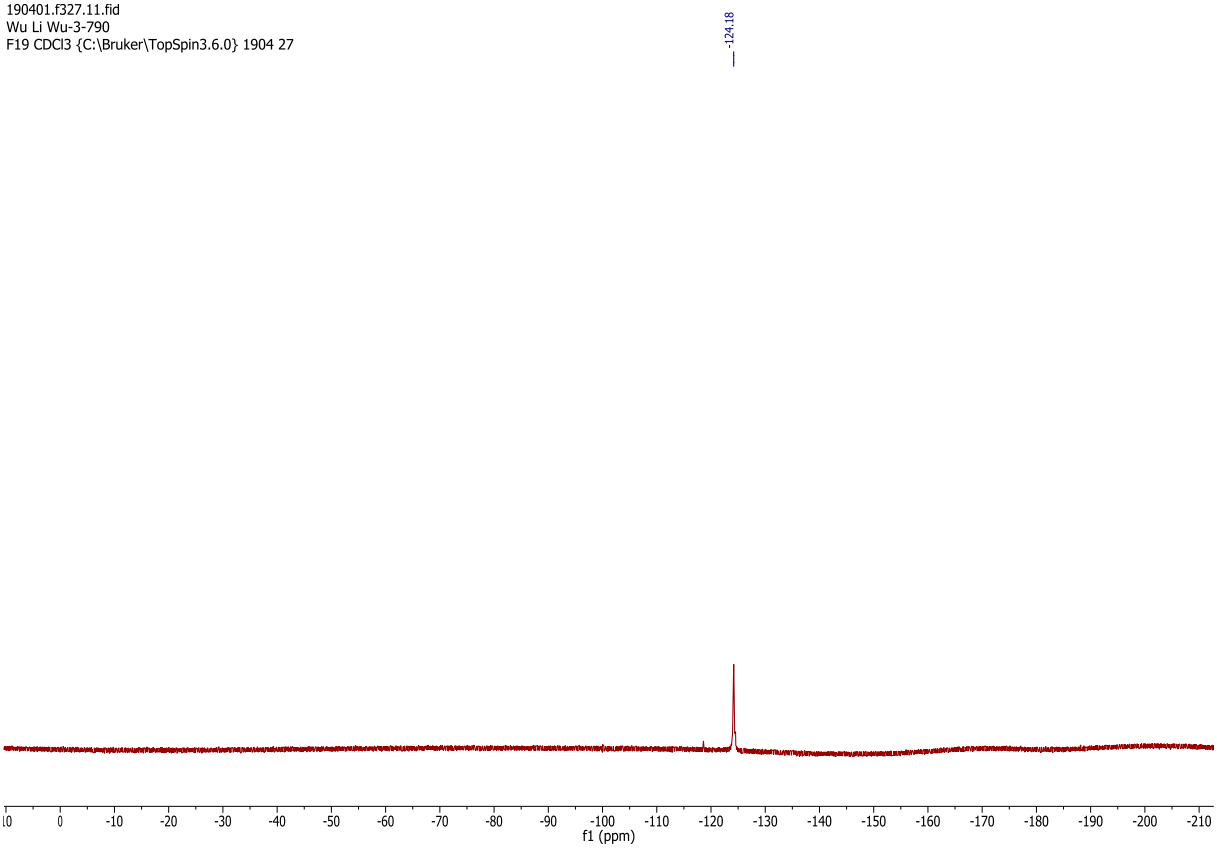




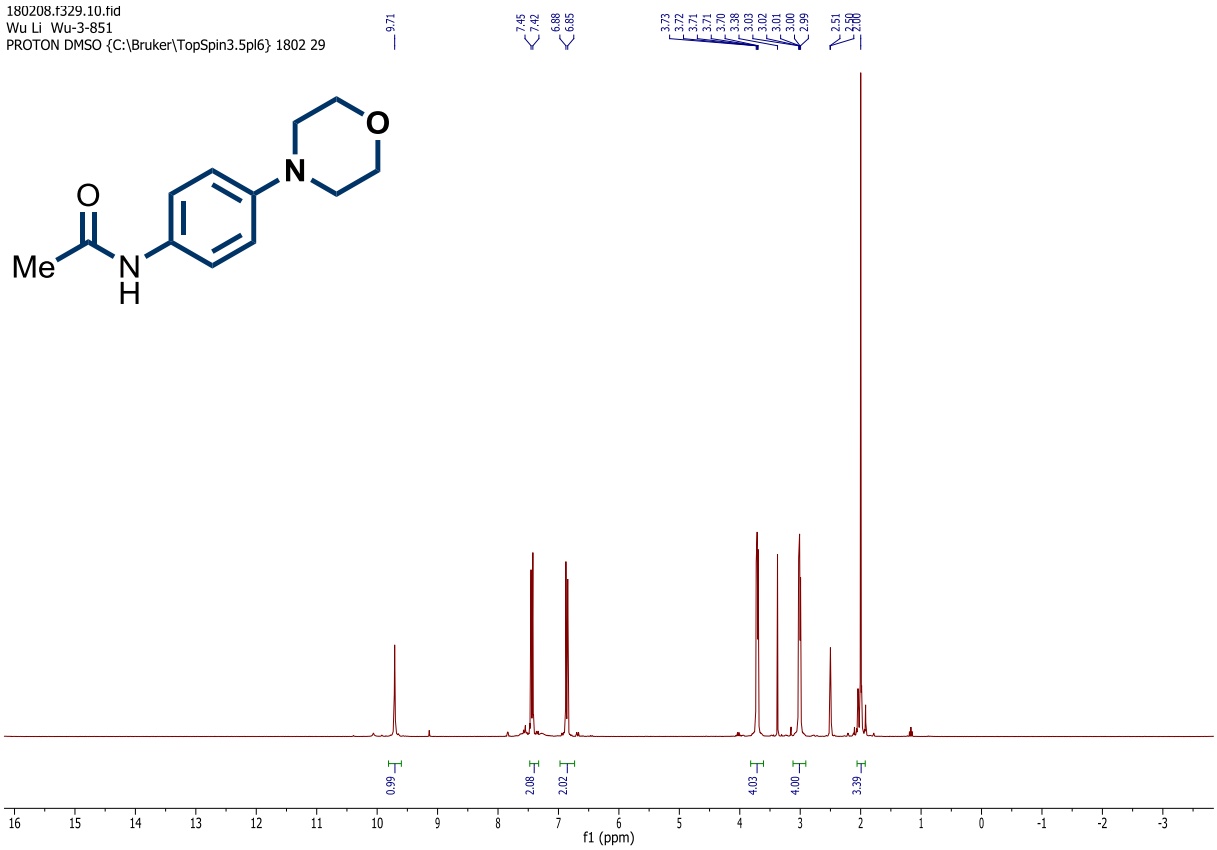
180131.f339.11.fid
Wu Li Wu-3-790
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1801 39

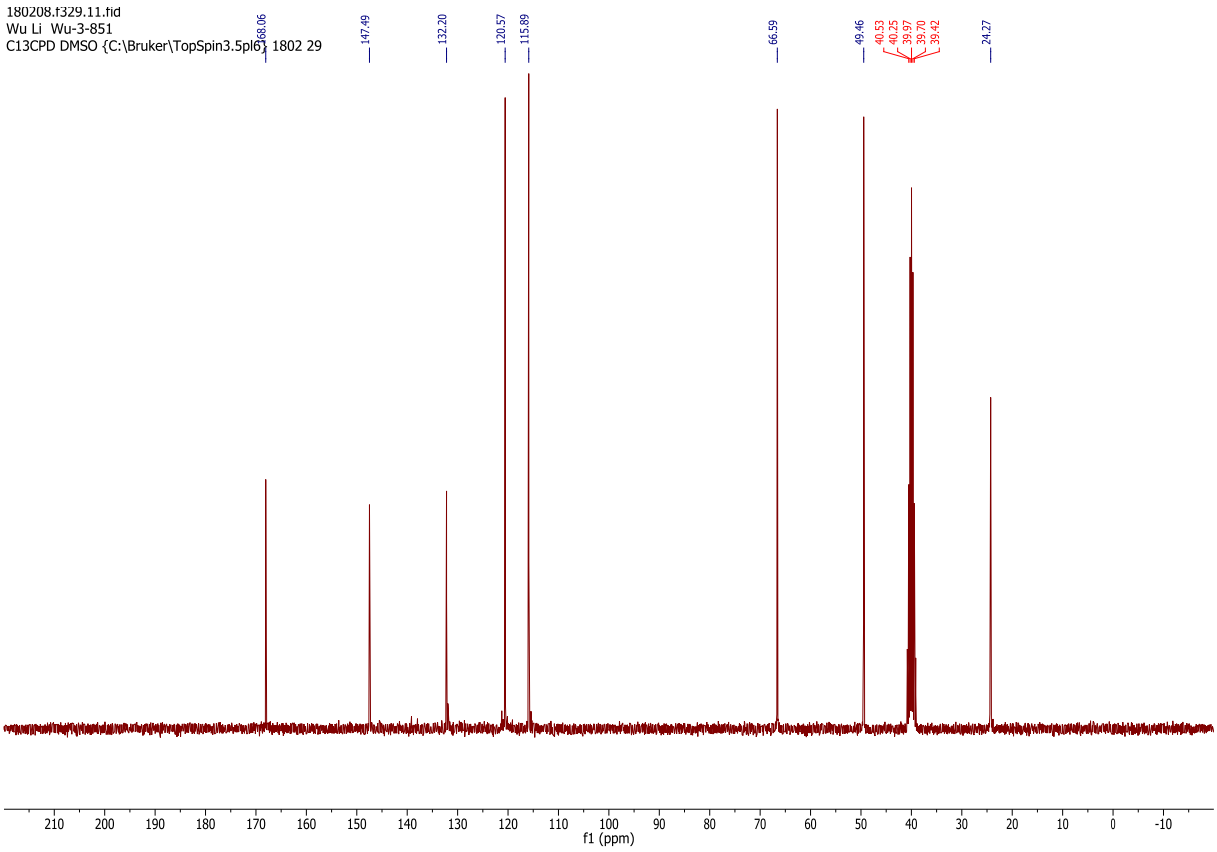


190401.f327.11.fid
Wu Li Wu-3-790
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 27

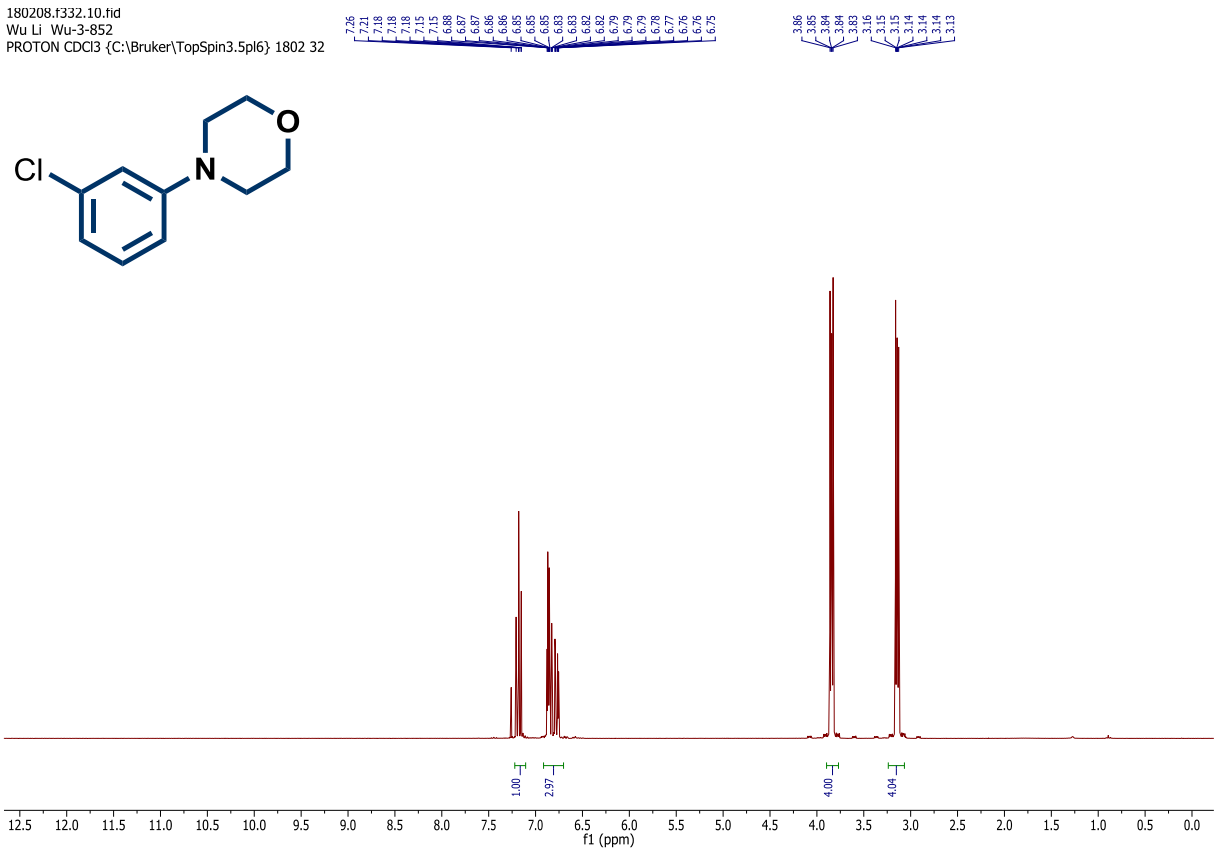


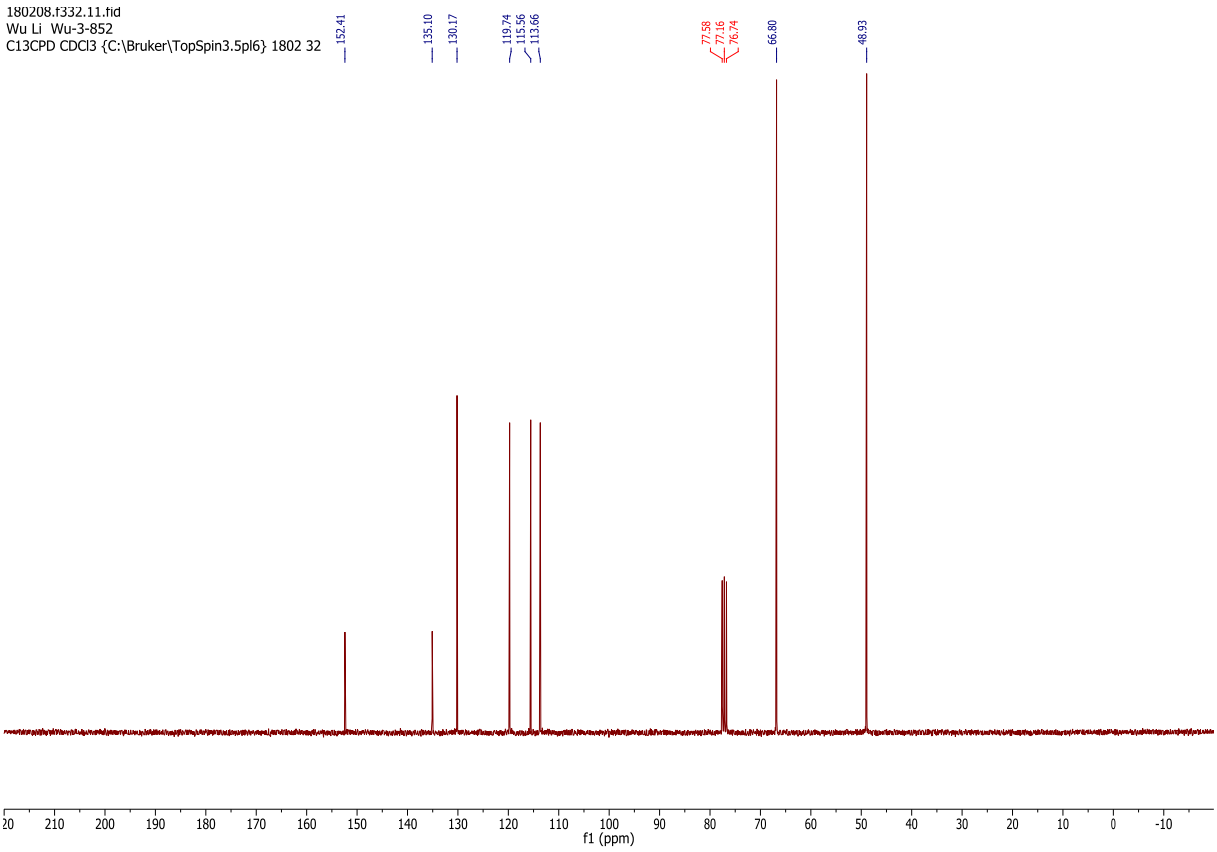
Original spectra for **33a**:



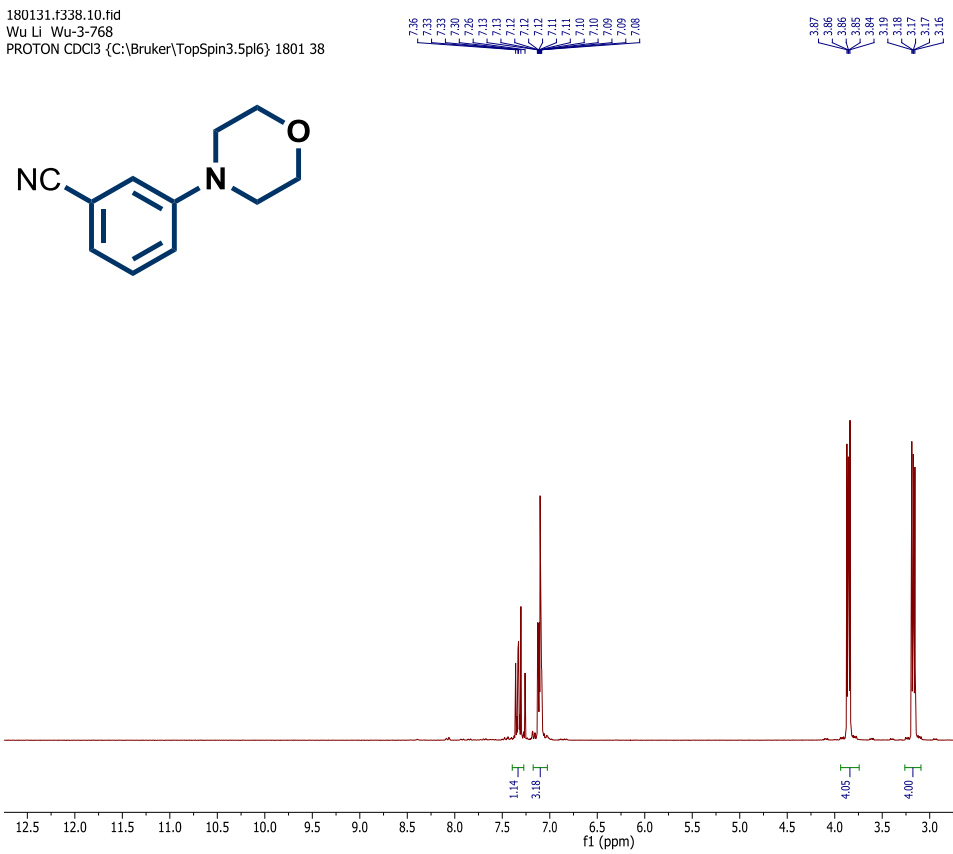


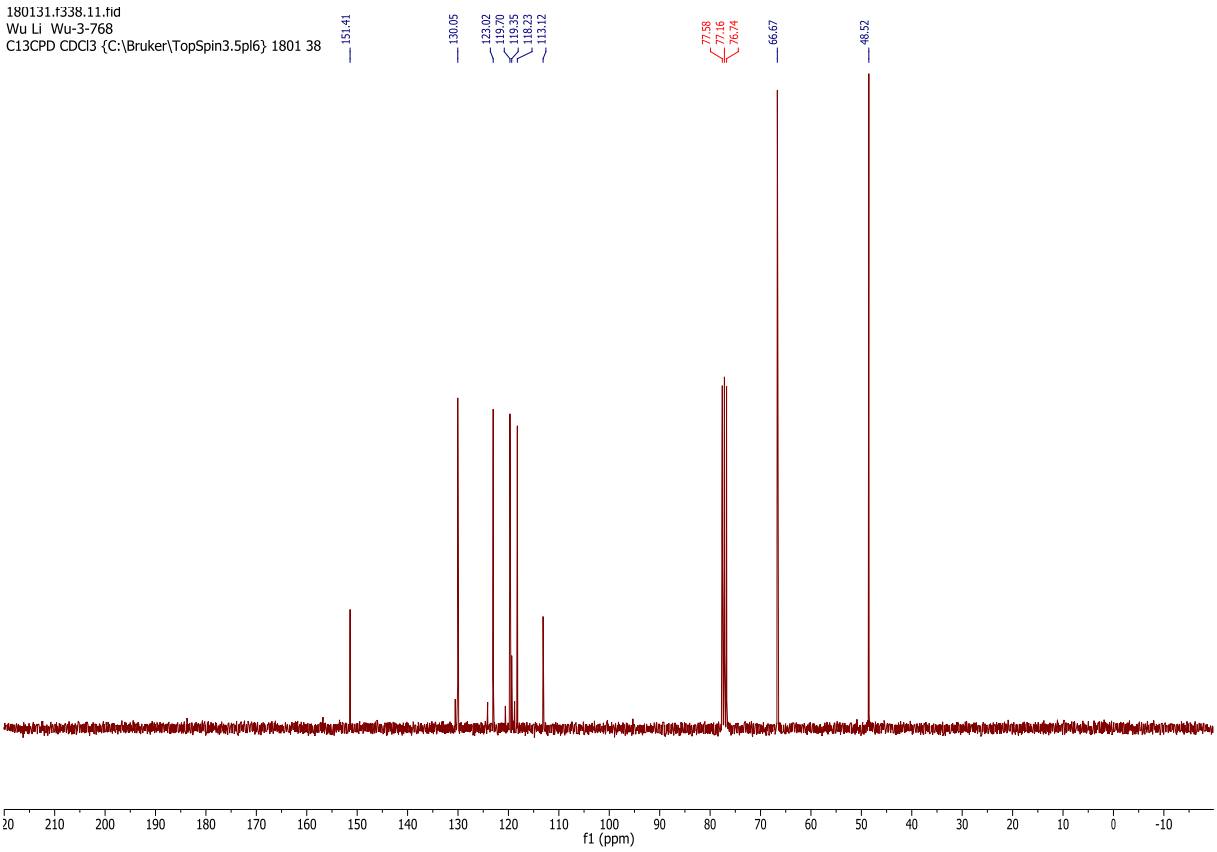
Original spectra for **35a**:



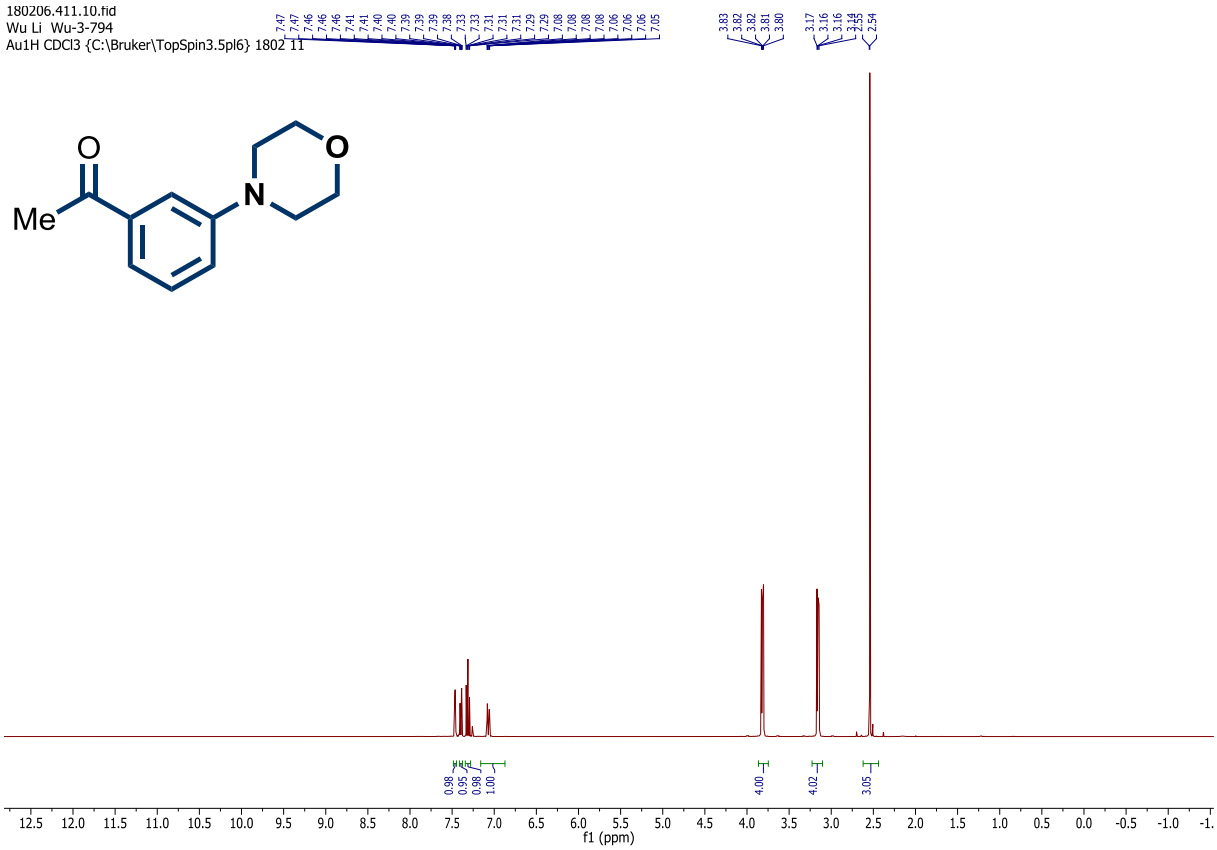


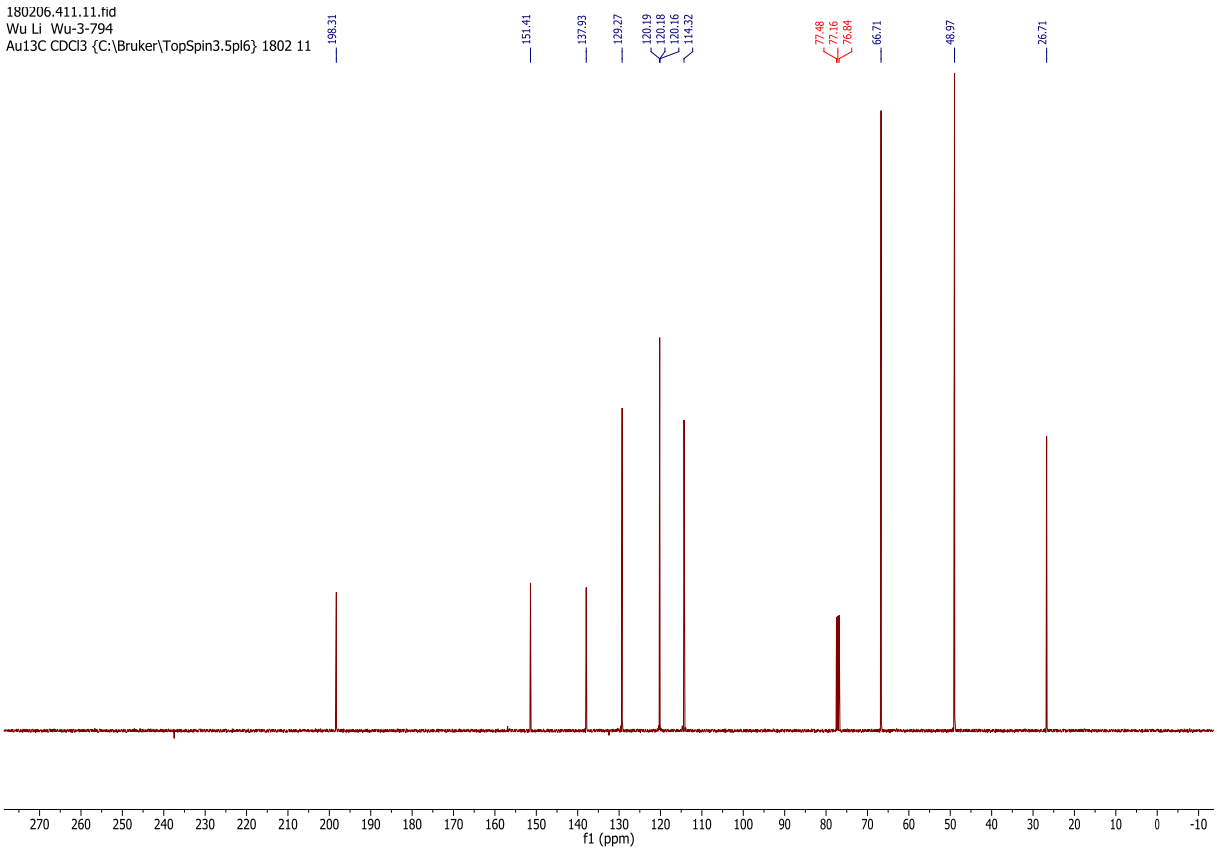
Original spectra for **37a**:



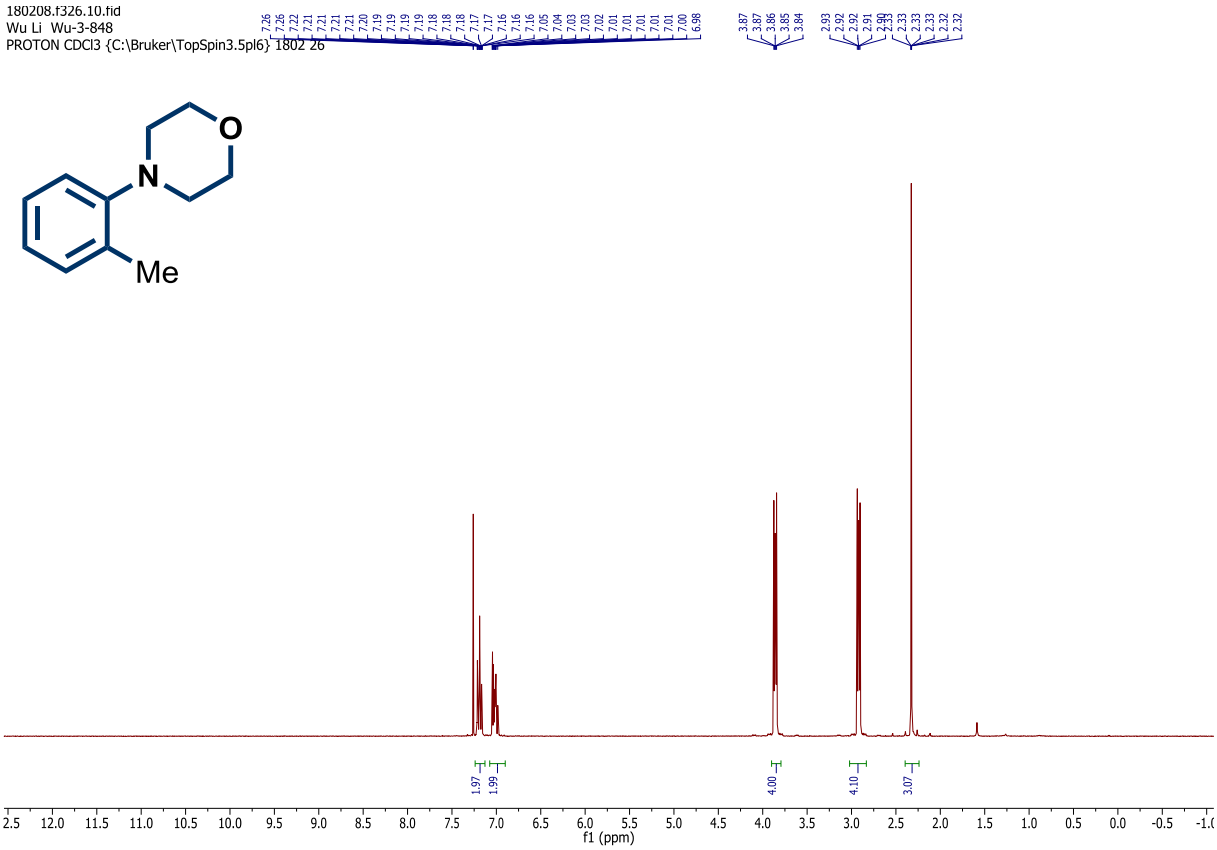


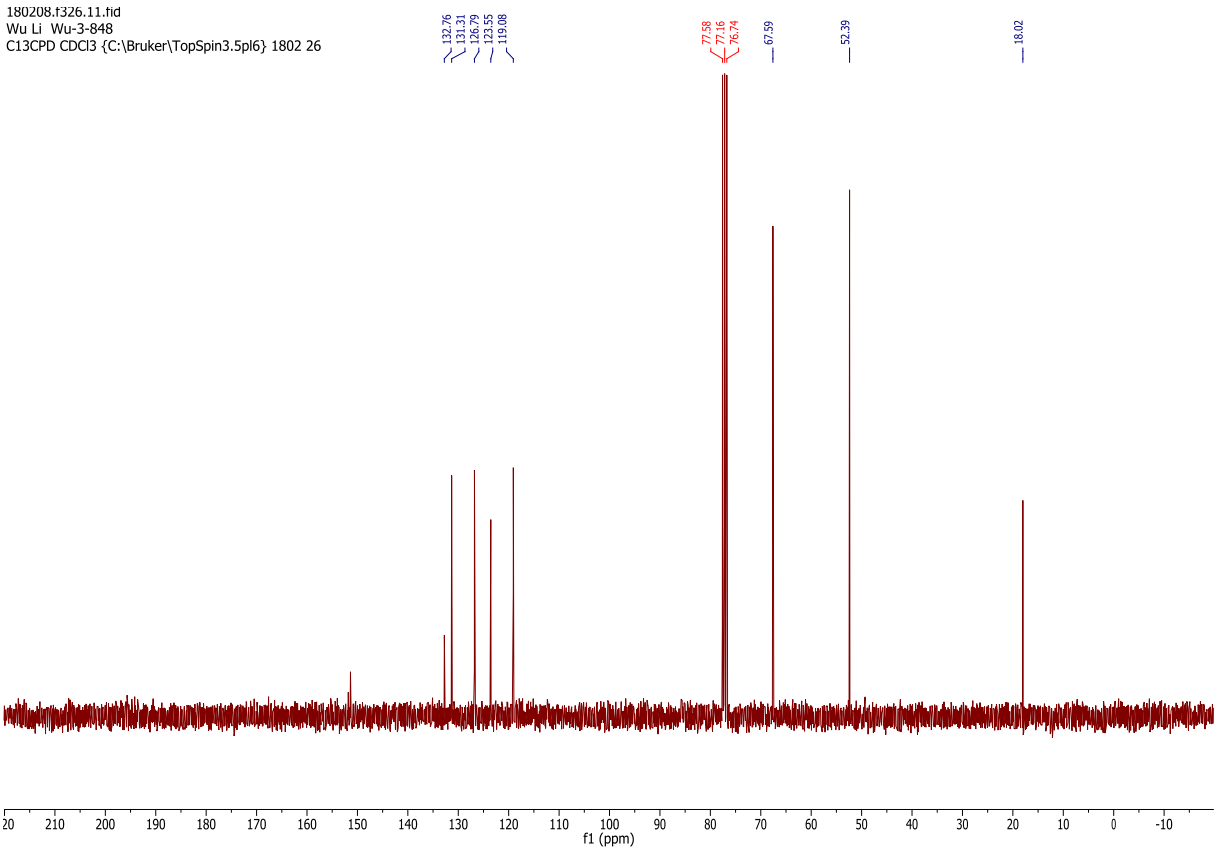
Original spectra for **38a**:



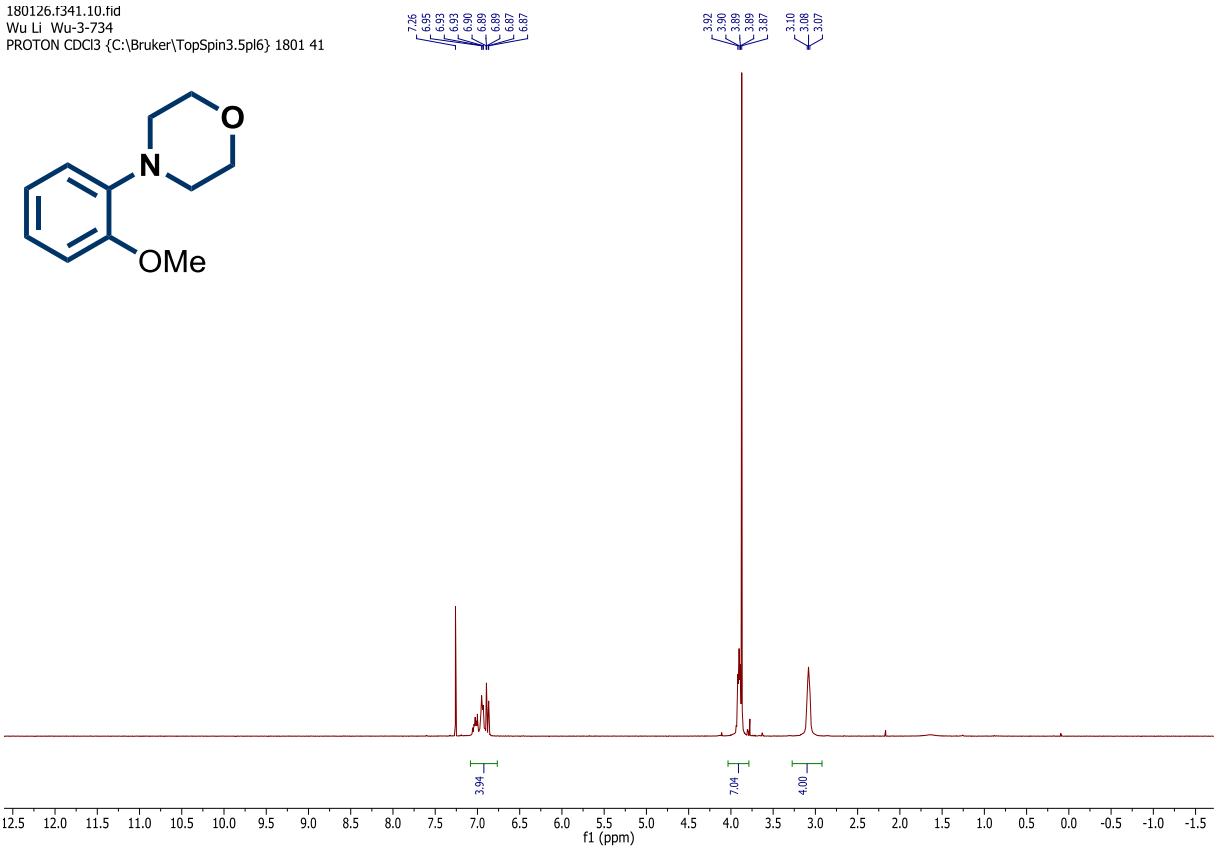


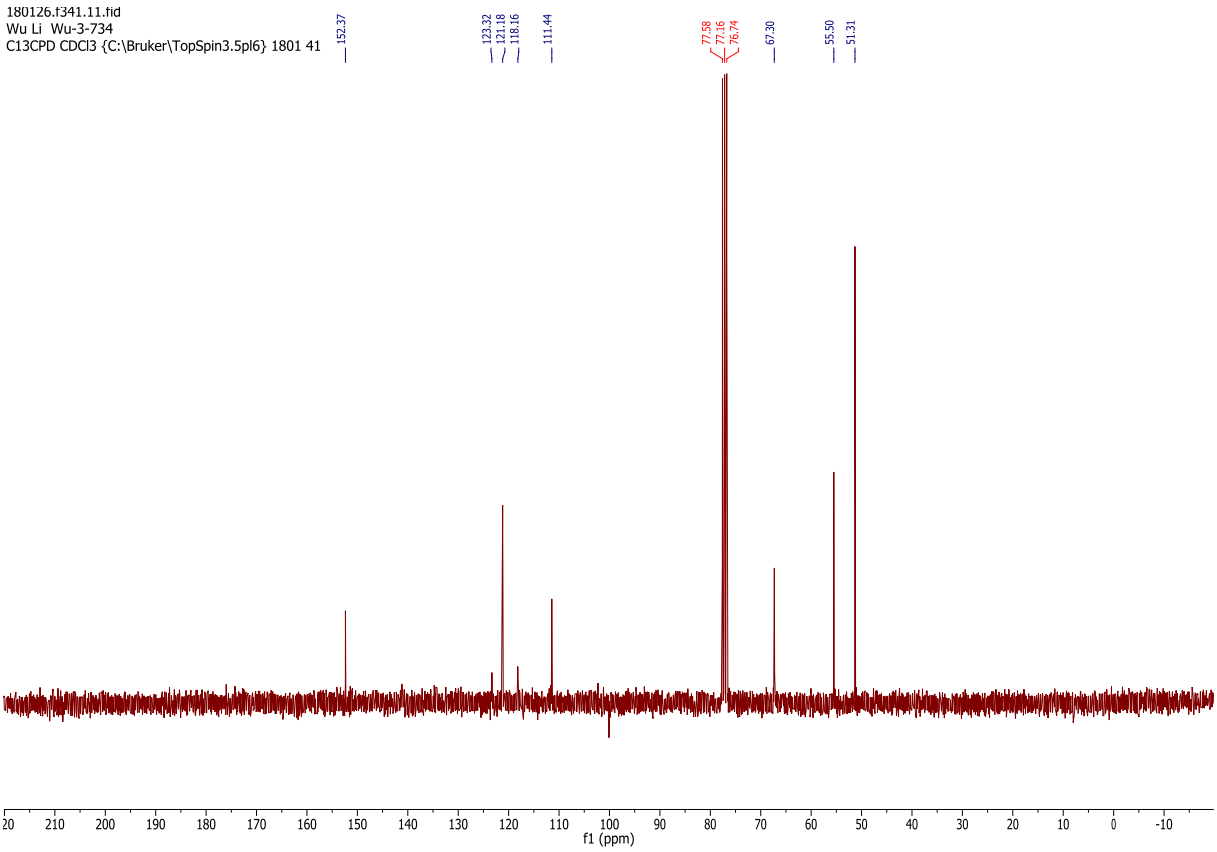
Original spectra for **40a**:



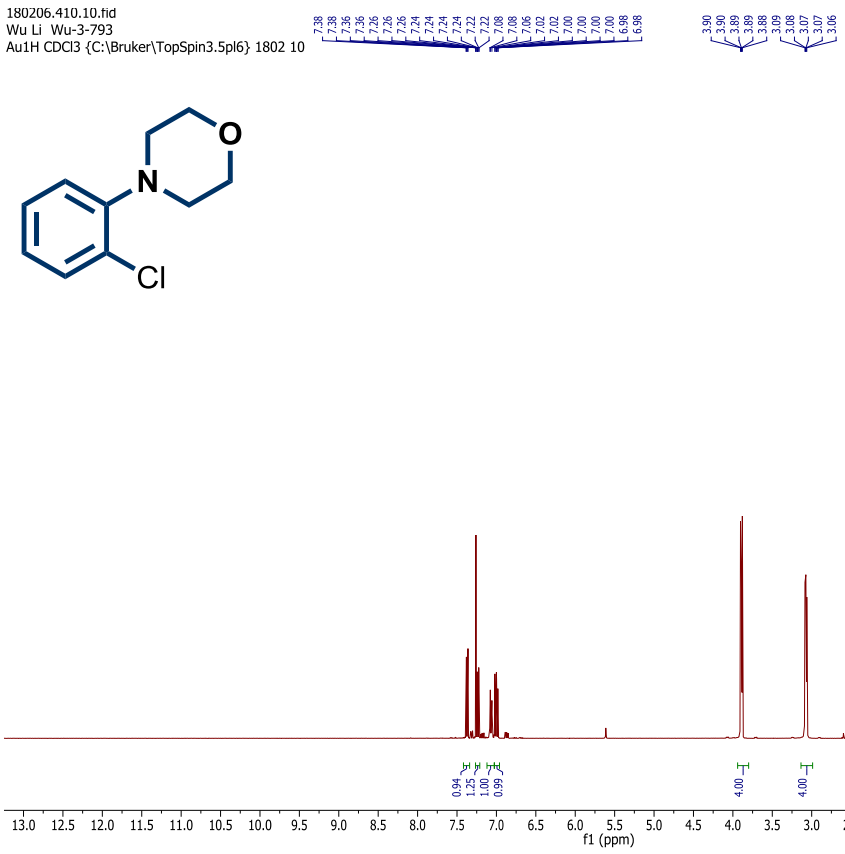


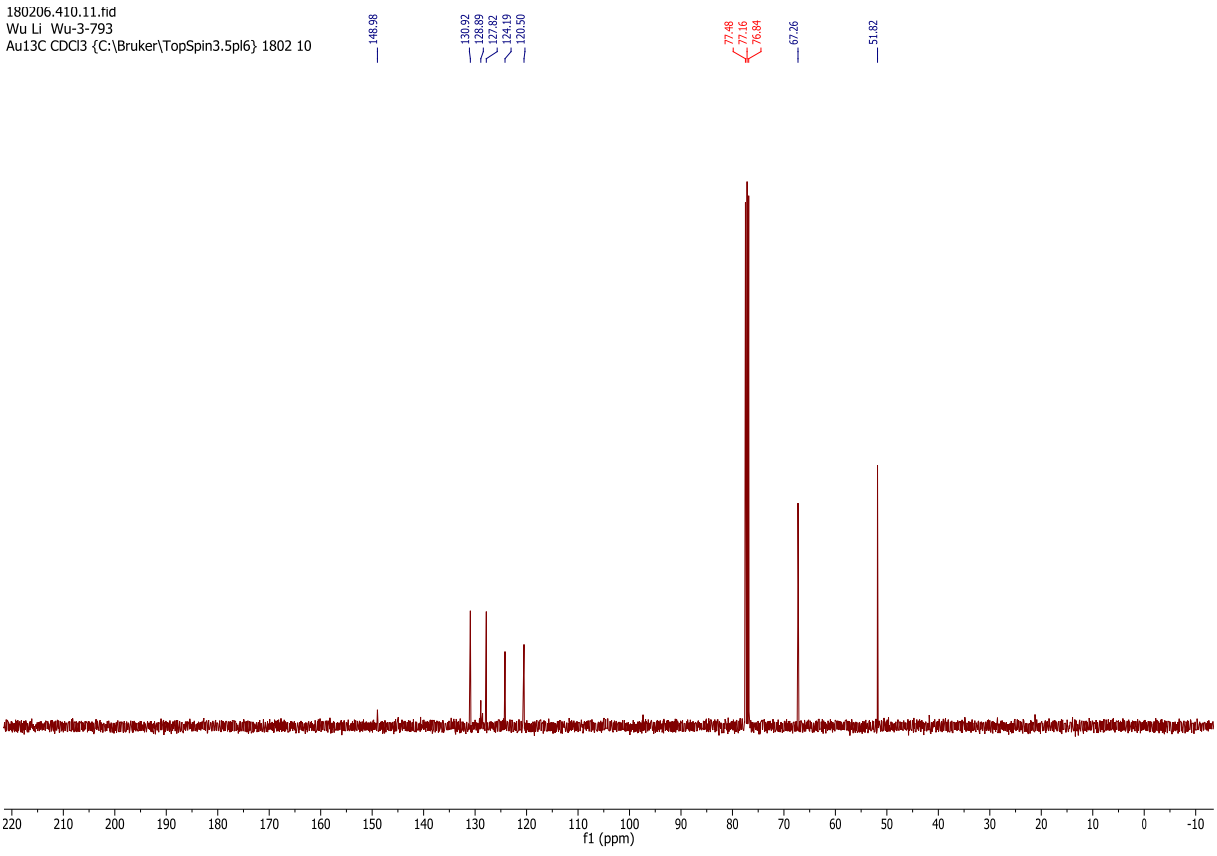
Original spectra for **41a**:



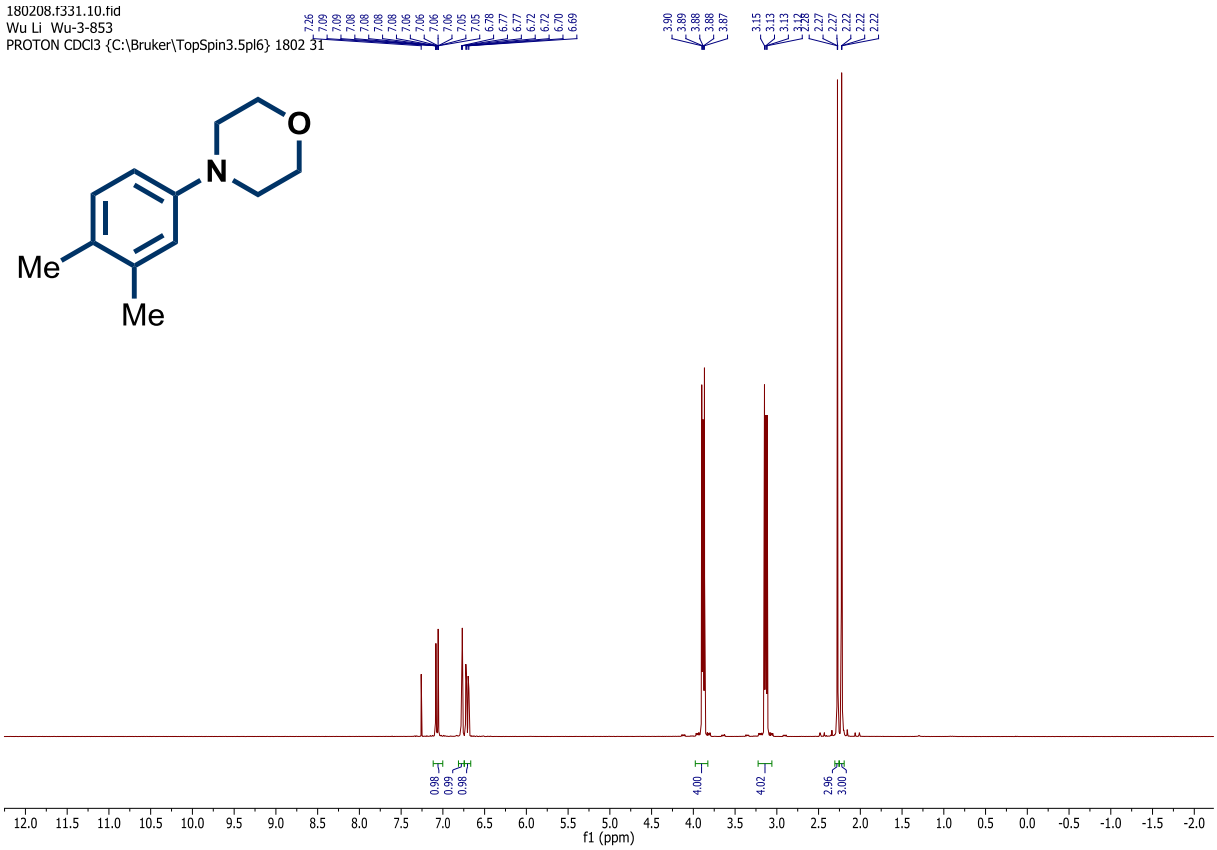


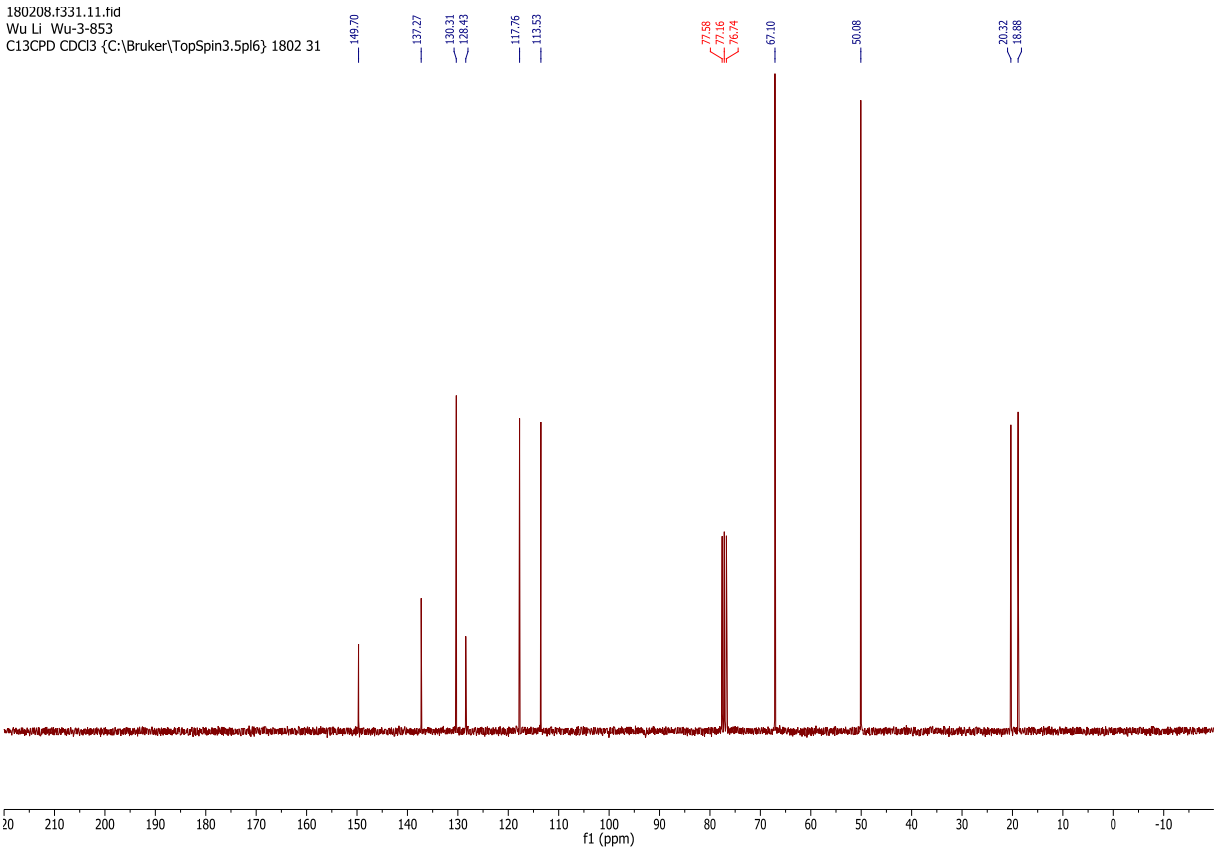
Original spectra for **42a**:



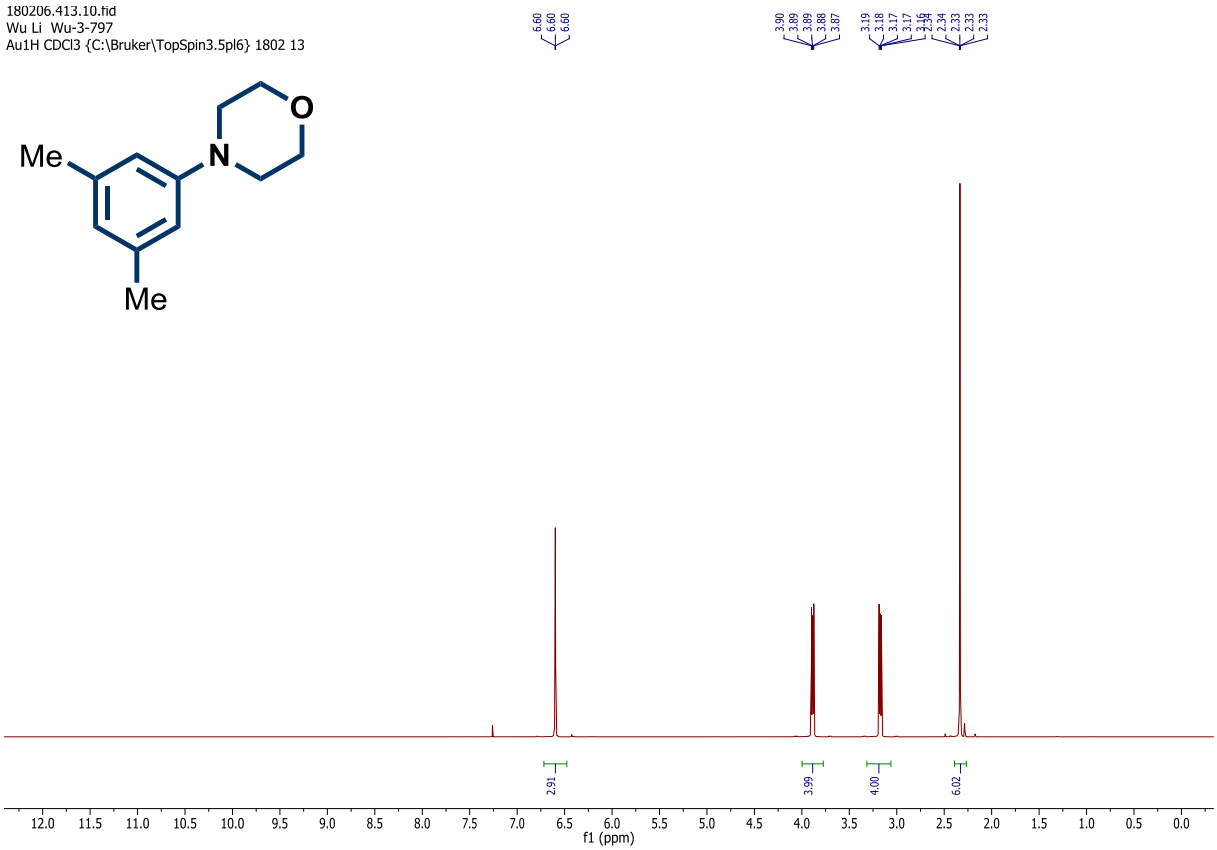


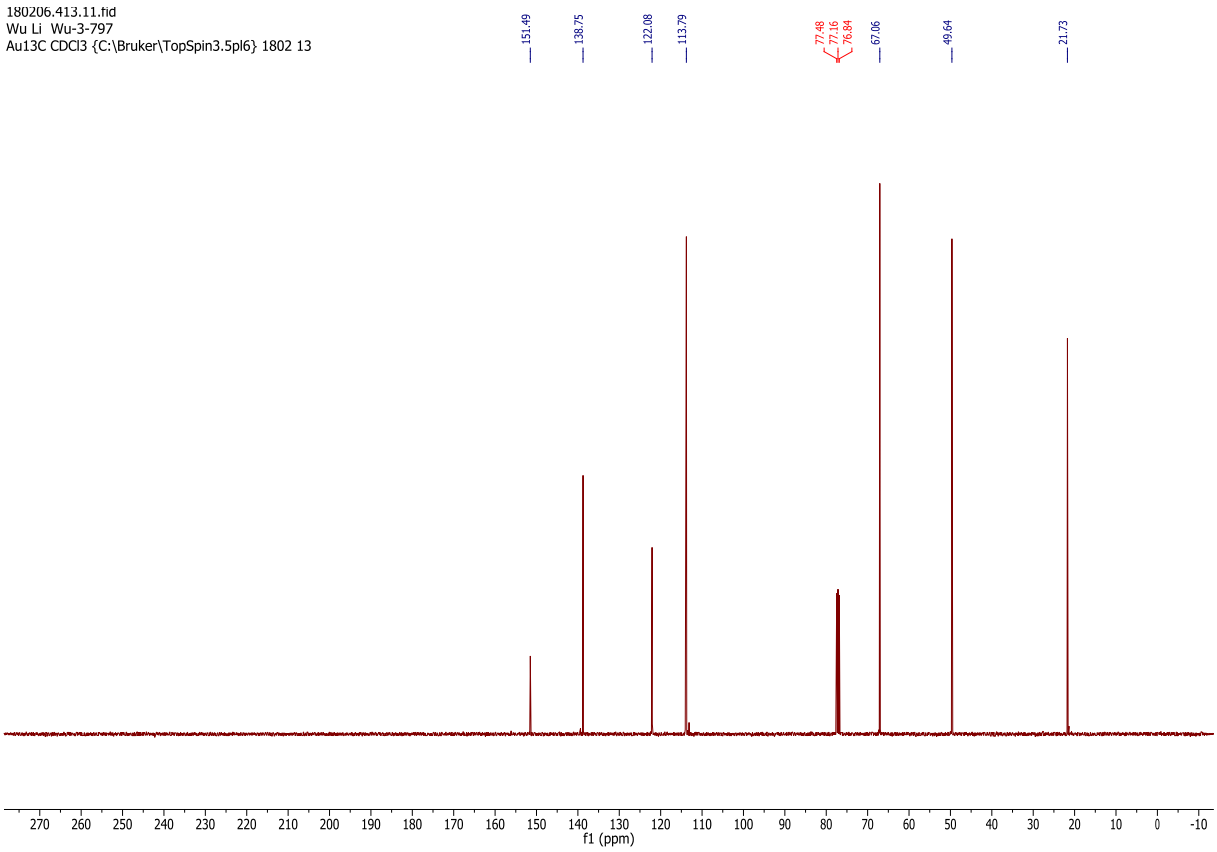
Original spectra for **44a**:



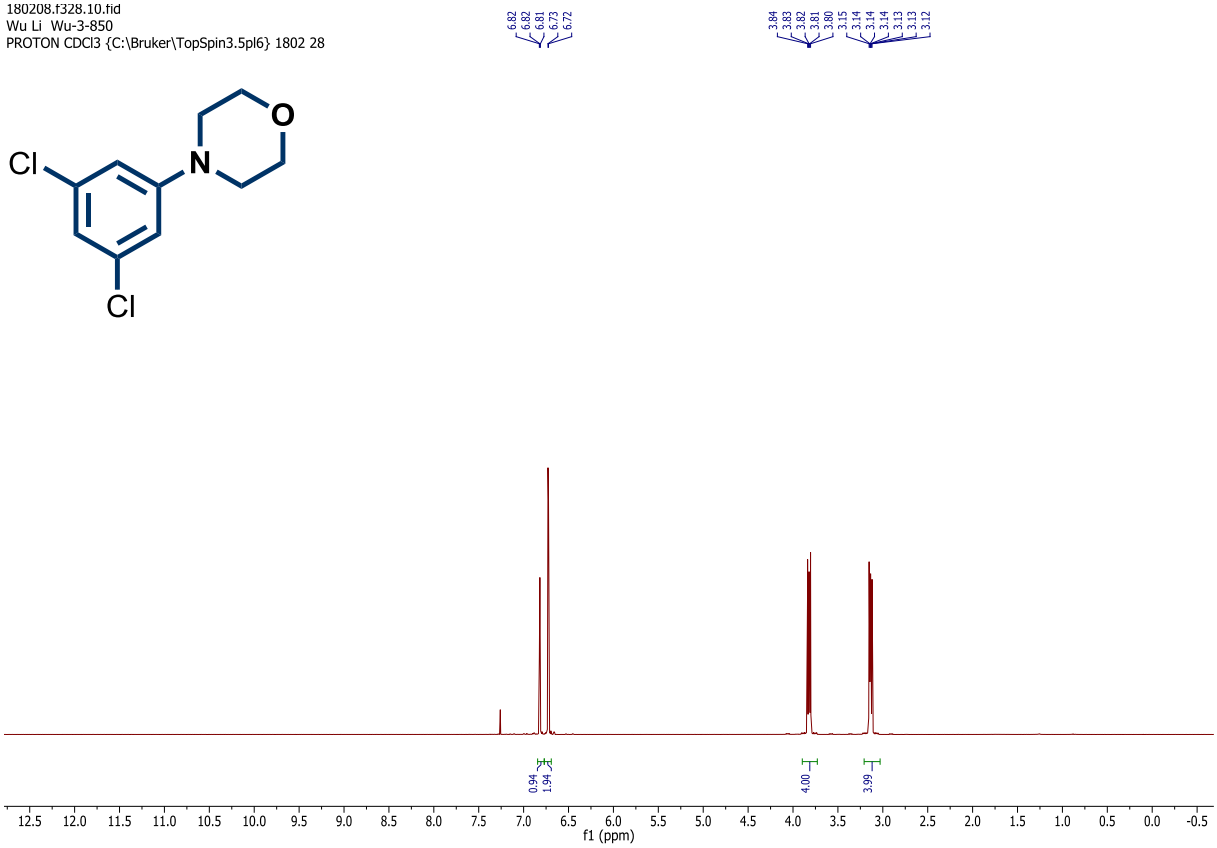


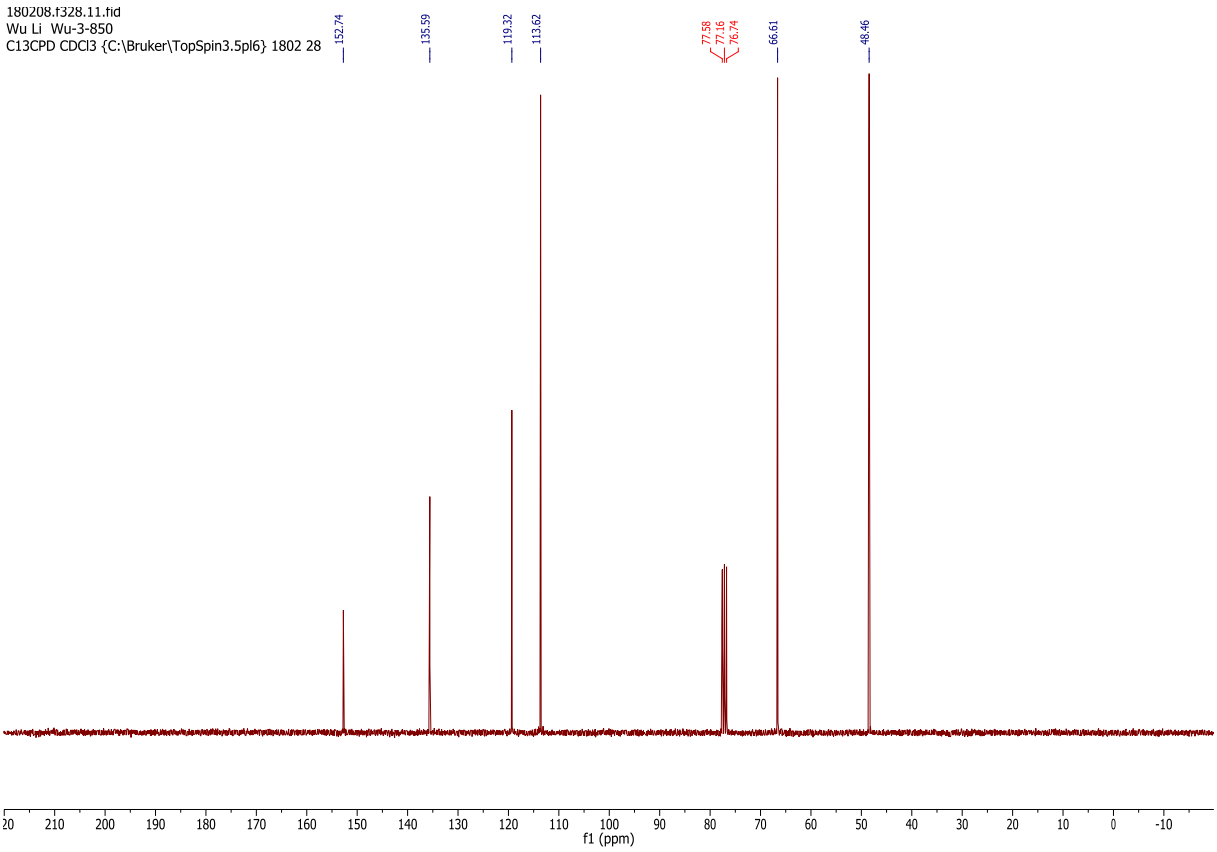
Original spectra for **45a**:



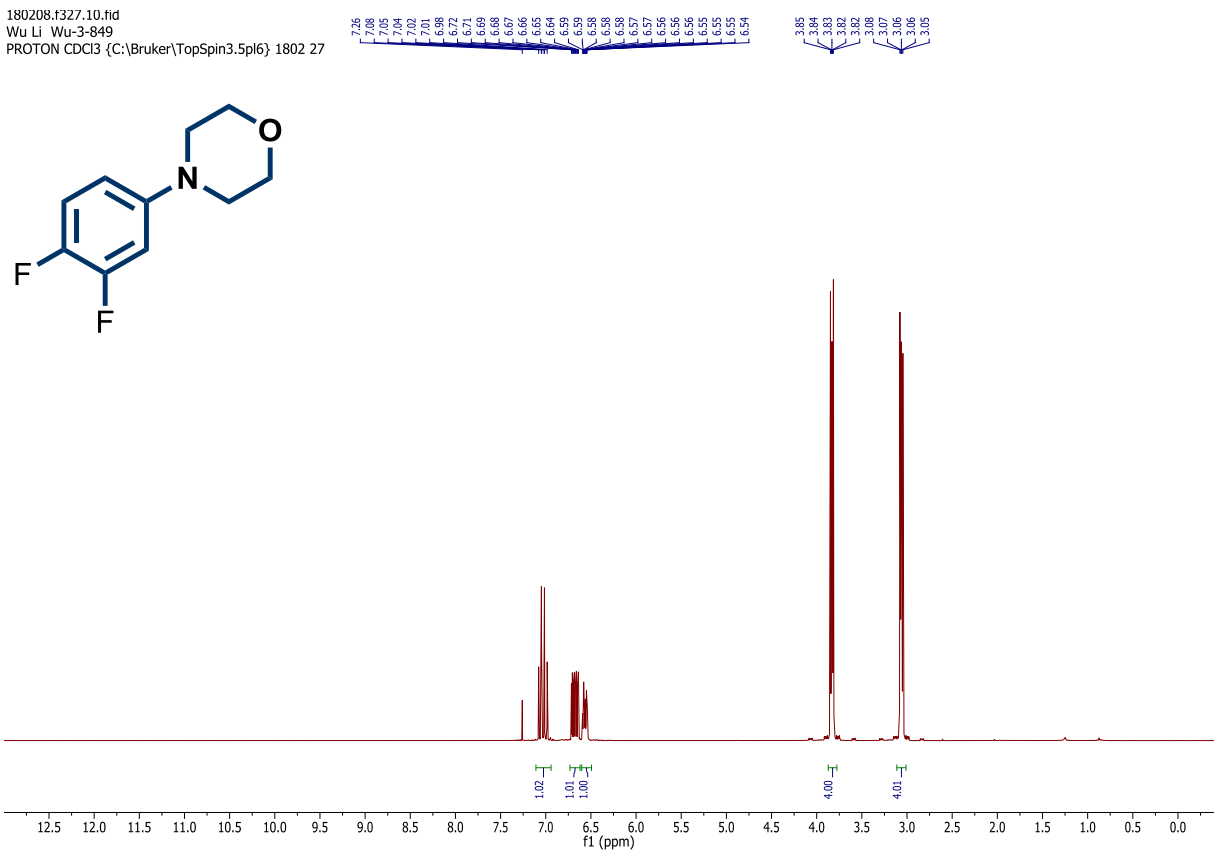


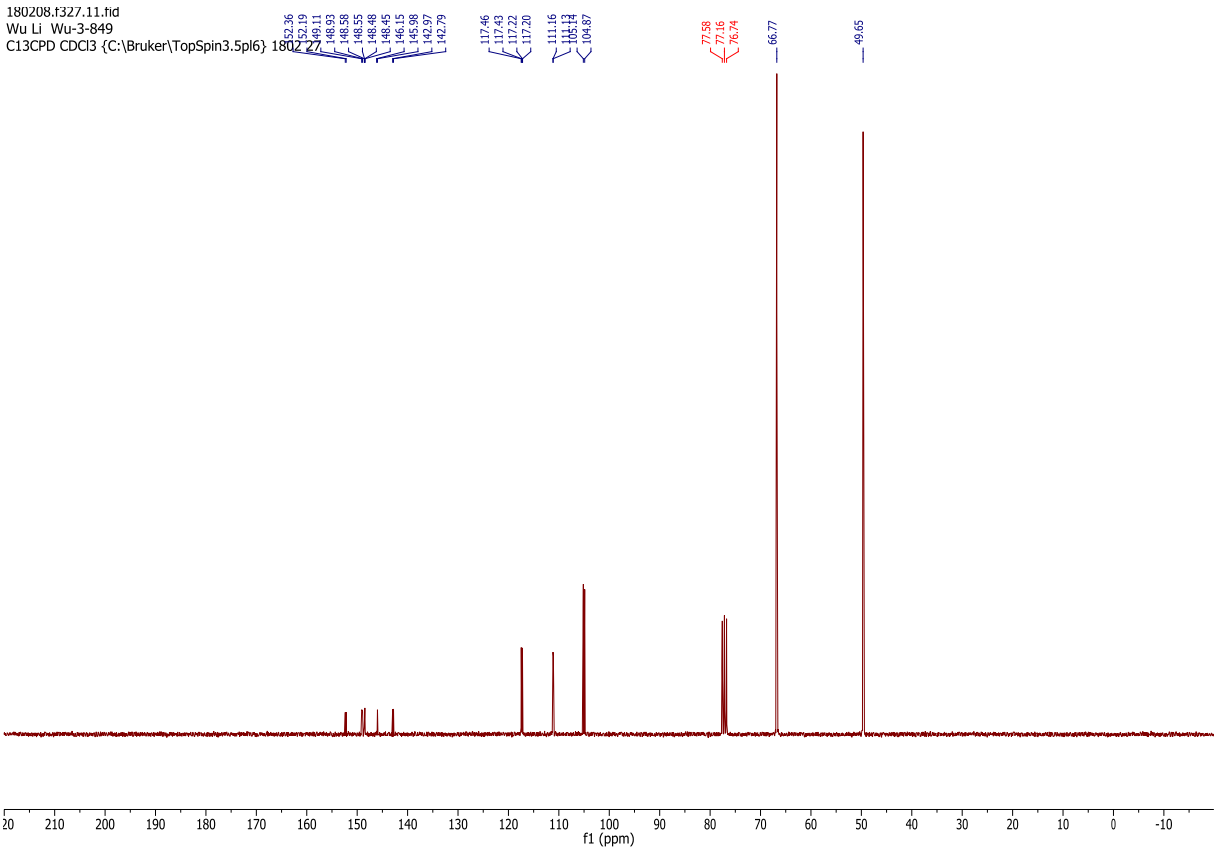
Original spectra for **46a**:



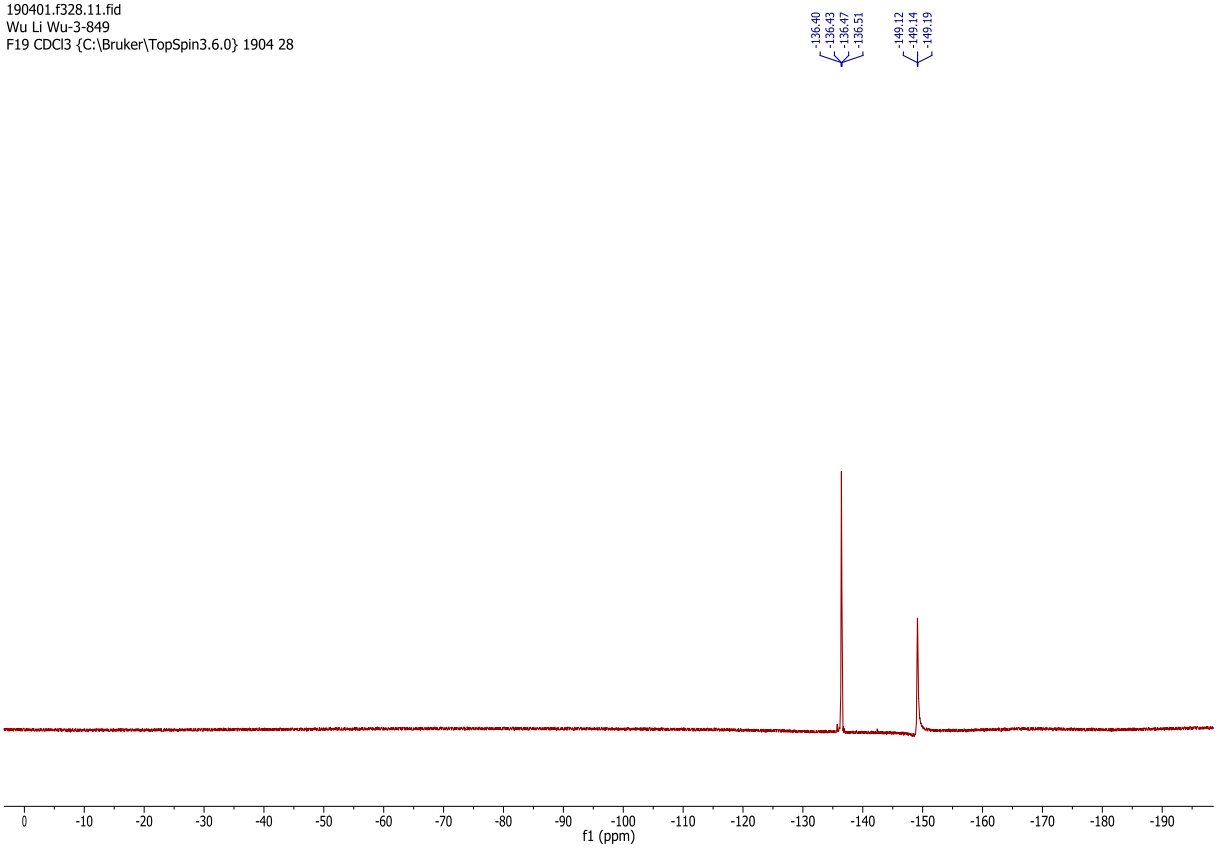


Original spectra for **47a**:



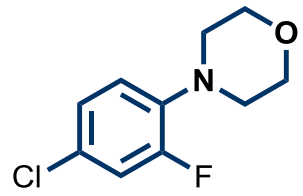


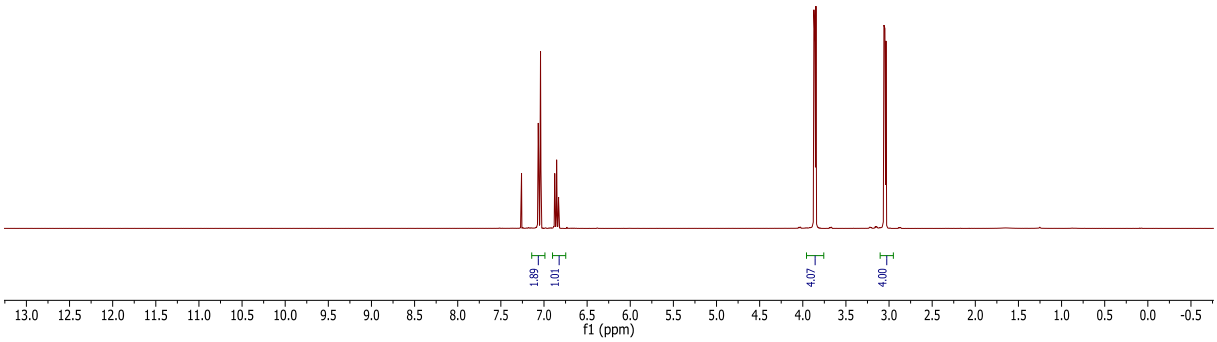
190401.f328.11.fid
Wu Li Wu-3-849
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 28



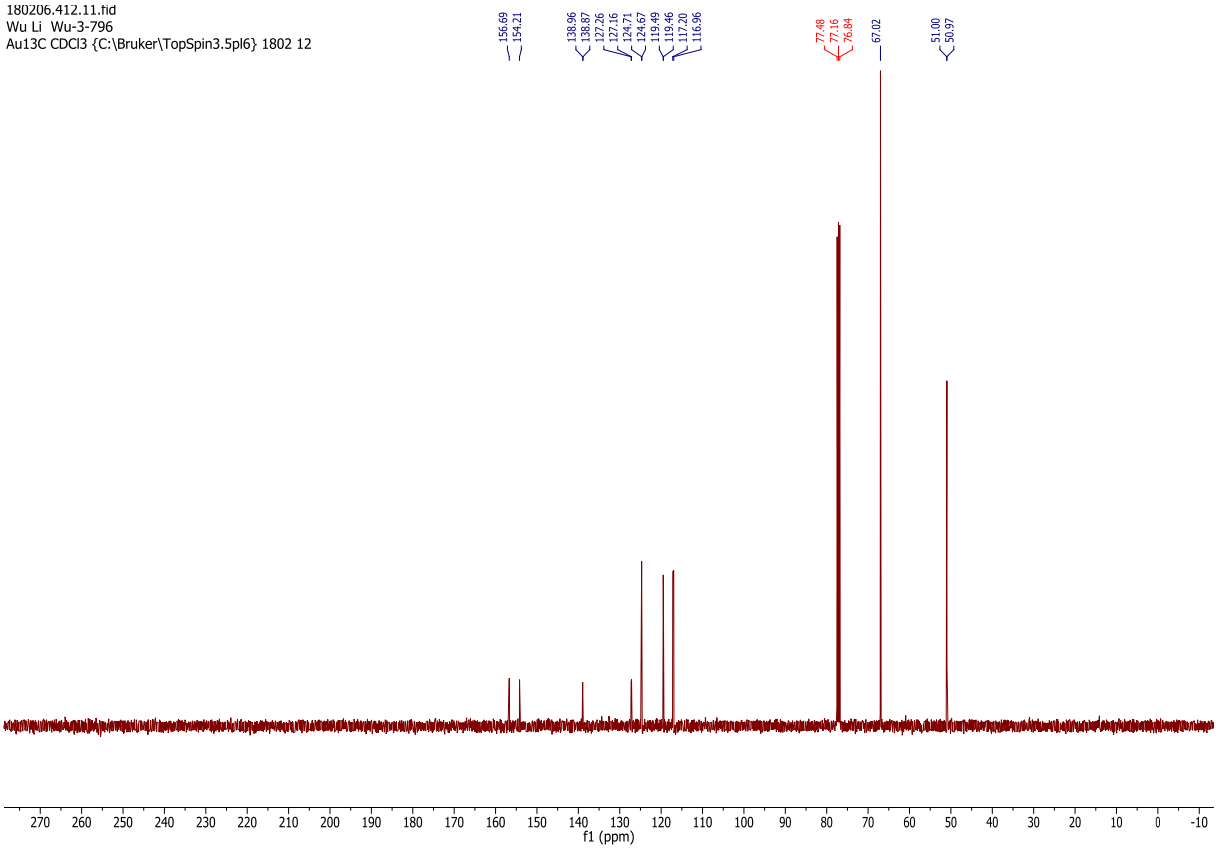
Original spectra for **48a**:

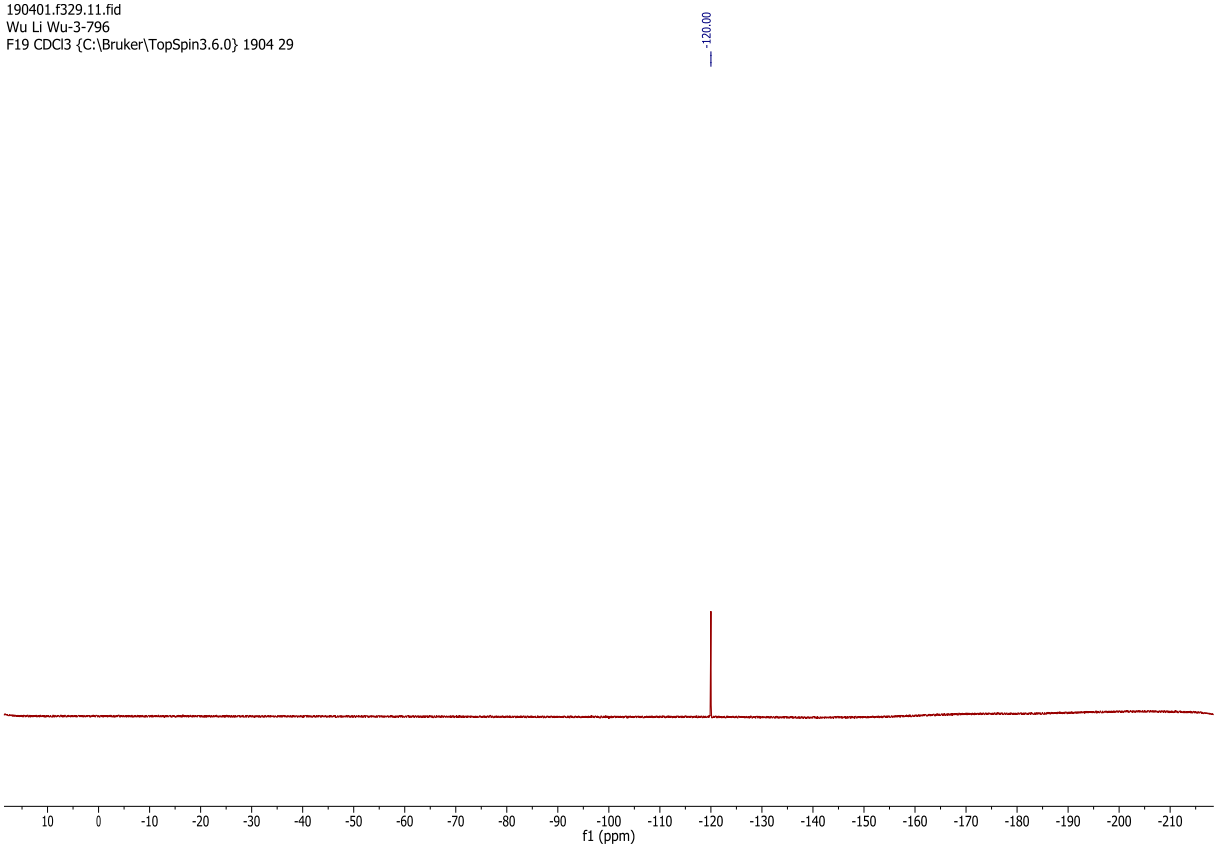
180206.412.10.fid
Wu Li Wu-3-796
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1802 12



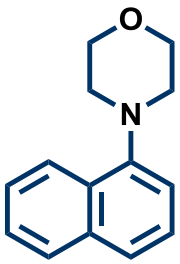


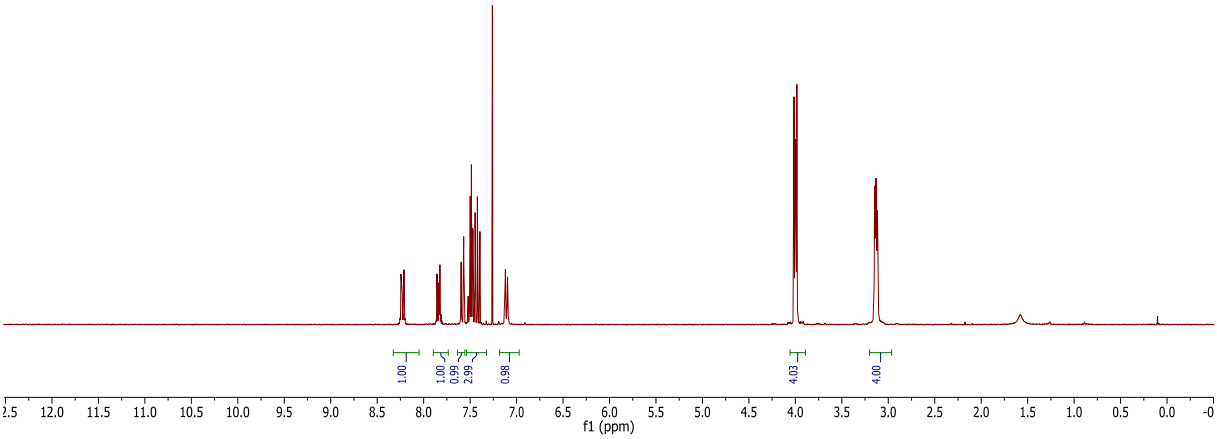
180206.412.11.fid
Wu Li Wu-3-796
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1802 12

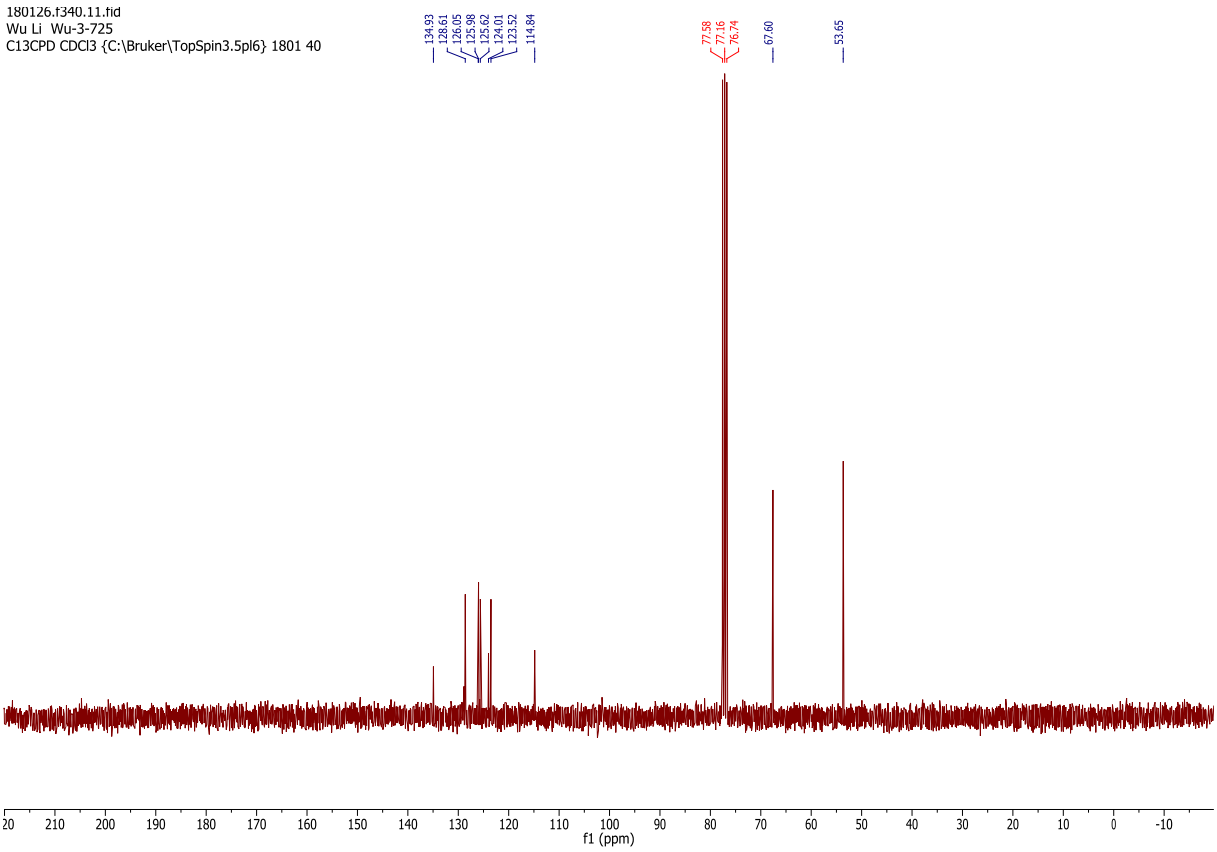



190401.f329.11.fid
Wu Li Wu-3-796
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 29
-120.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

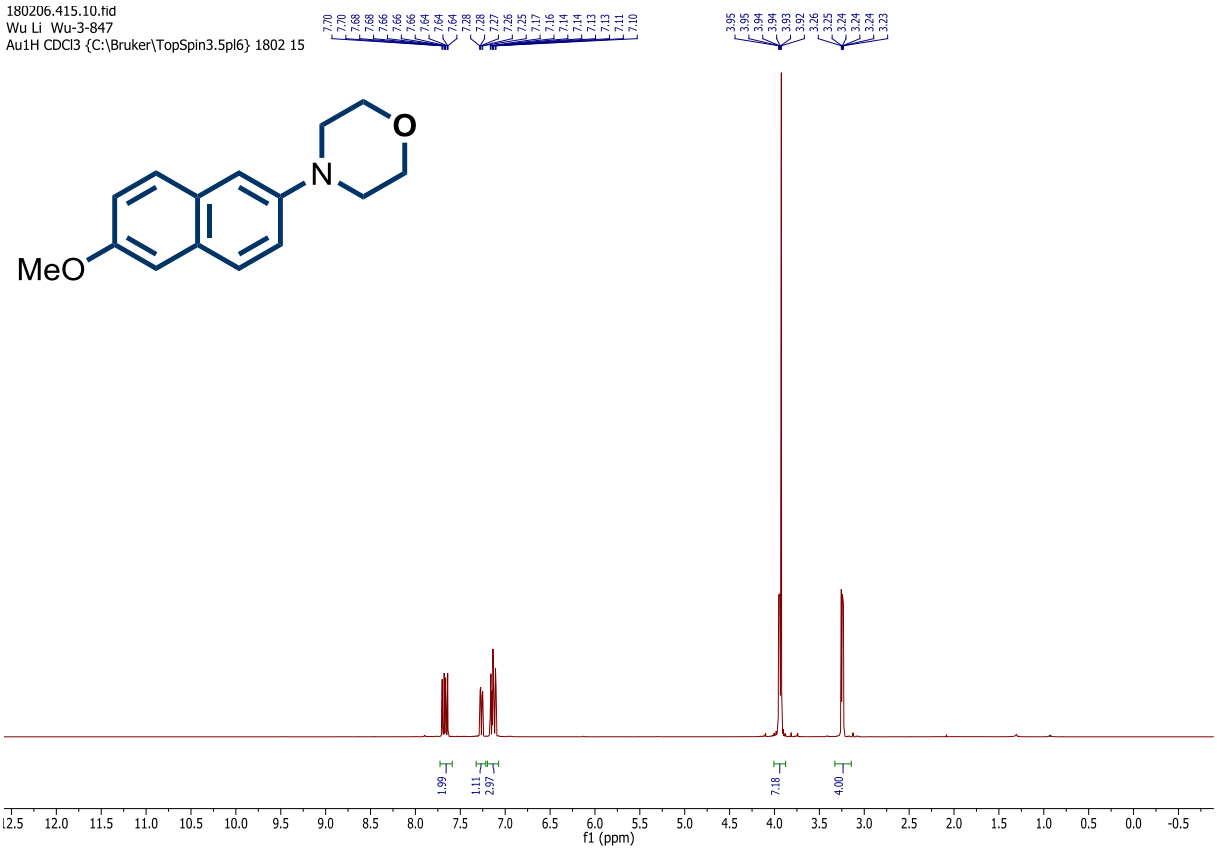
Original spectra for **49a**:

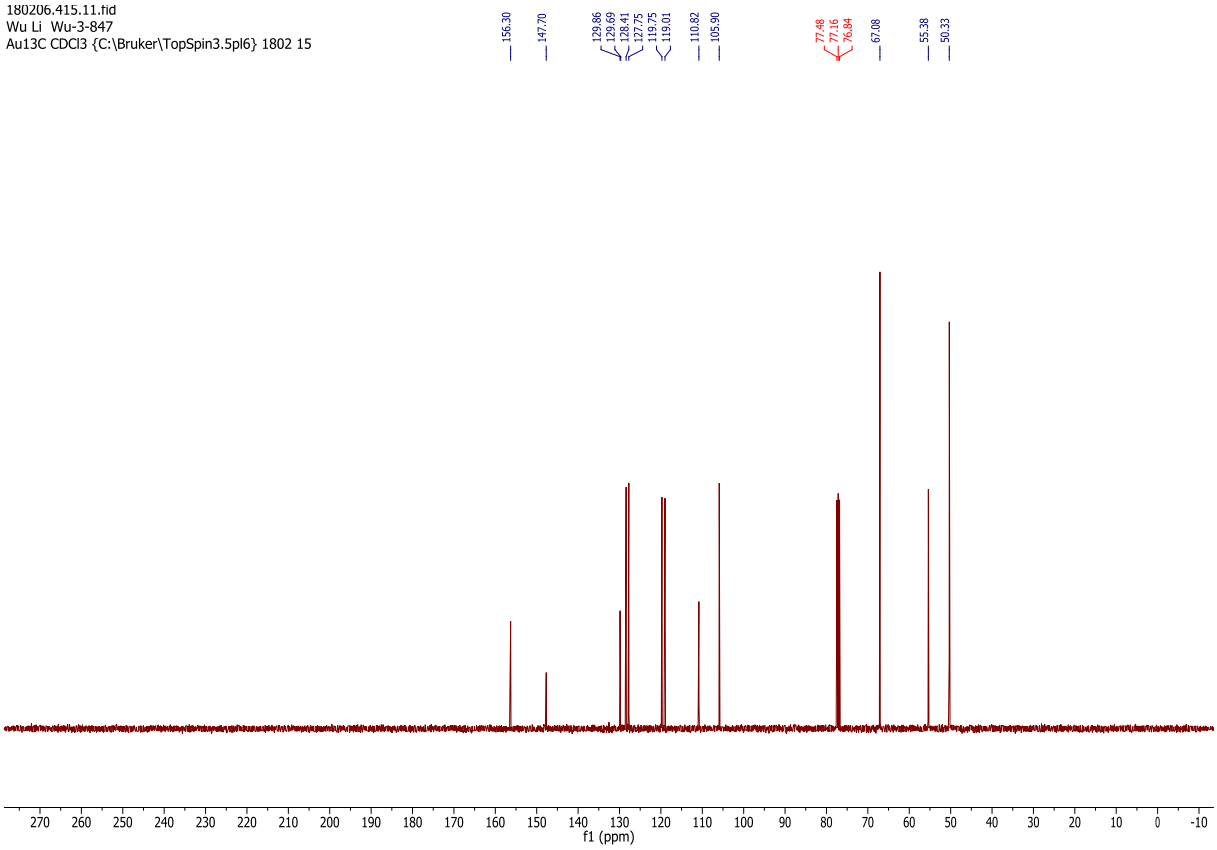




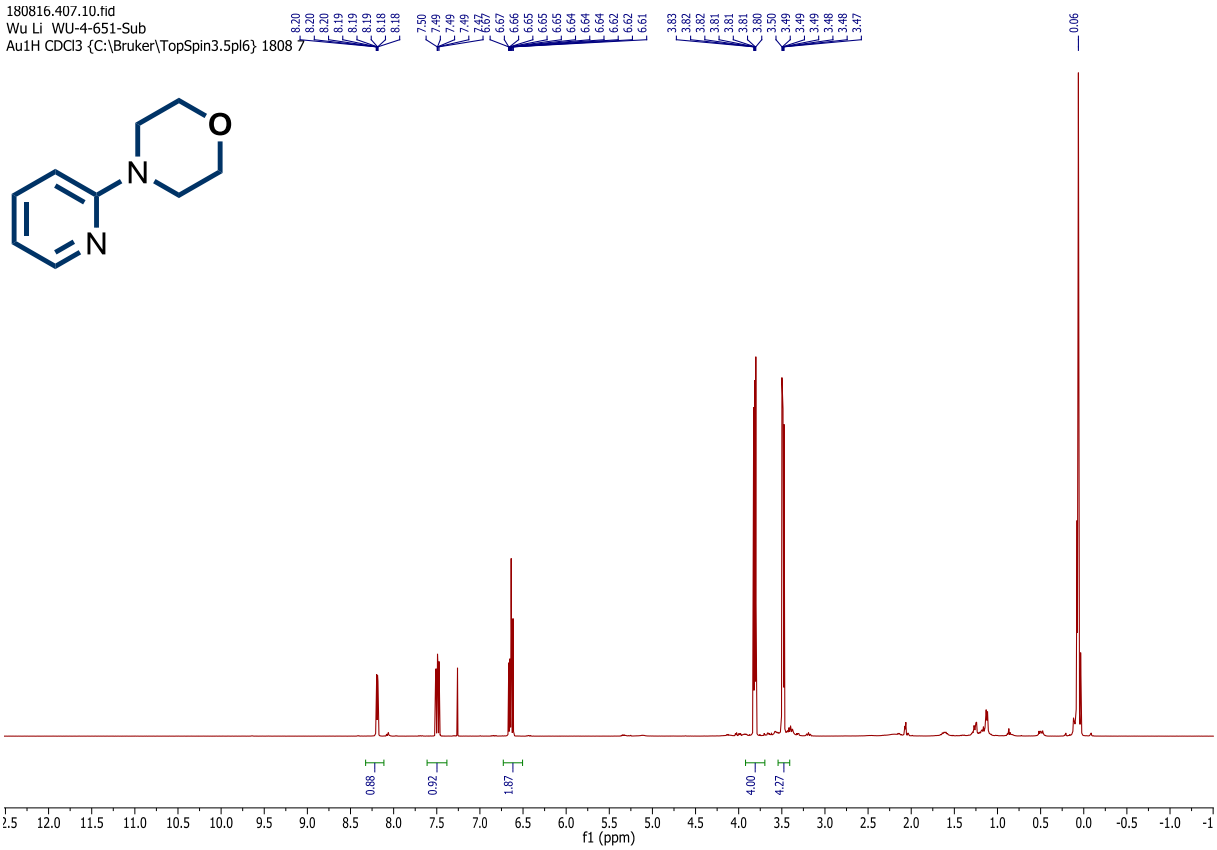


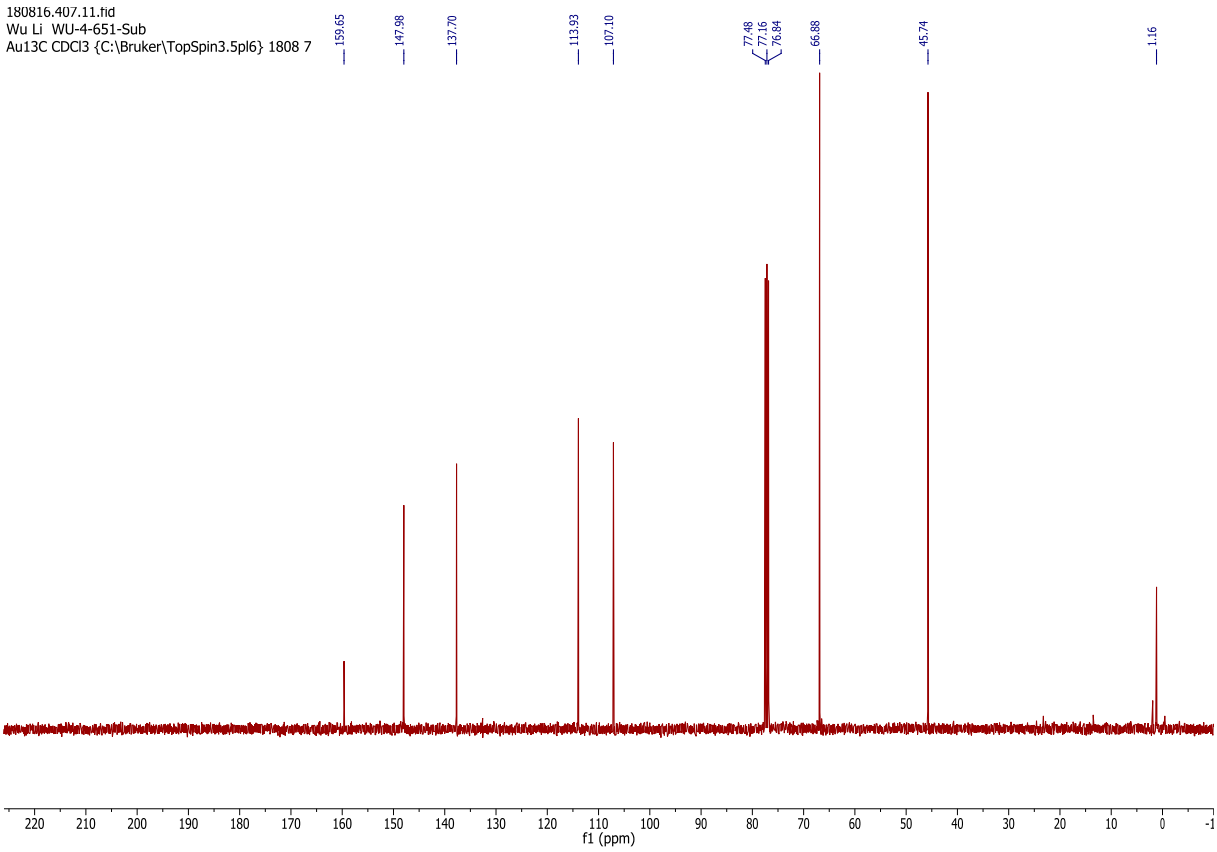
Original spectra for **50a**:



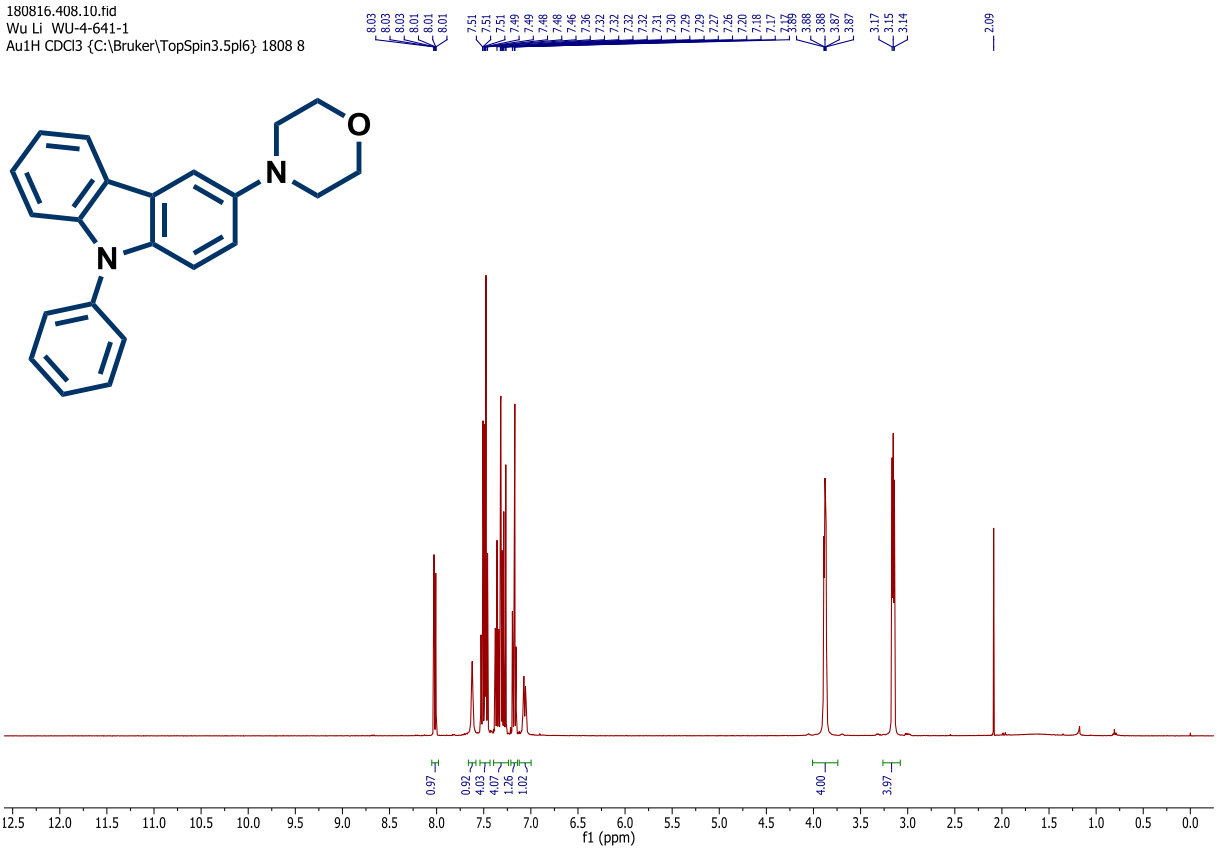


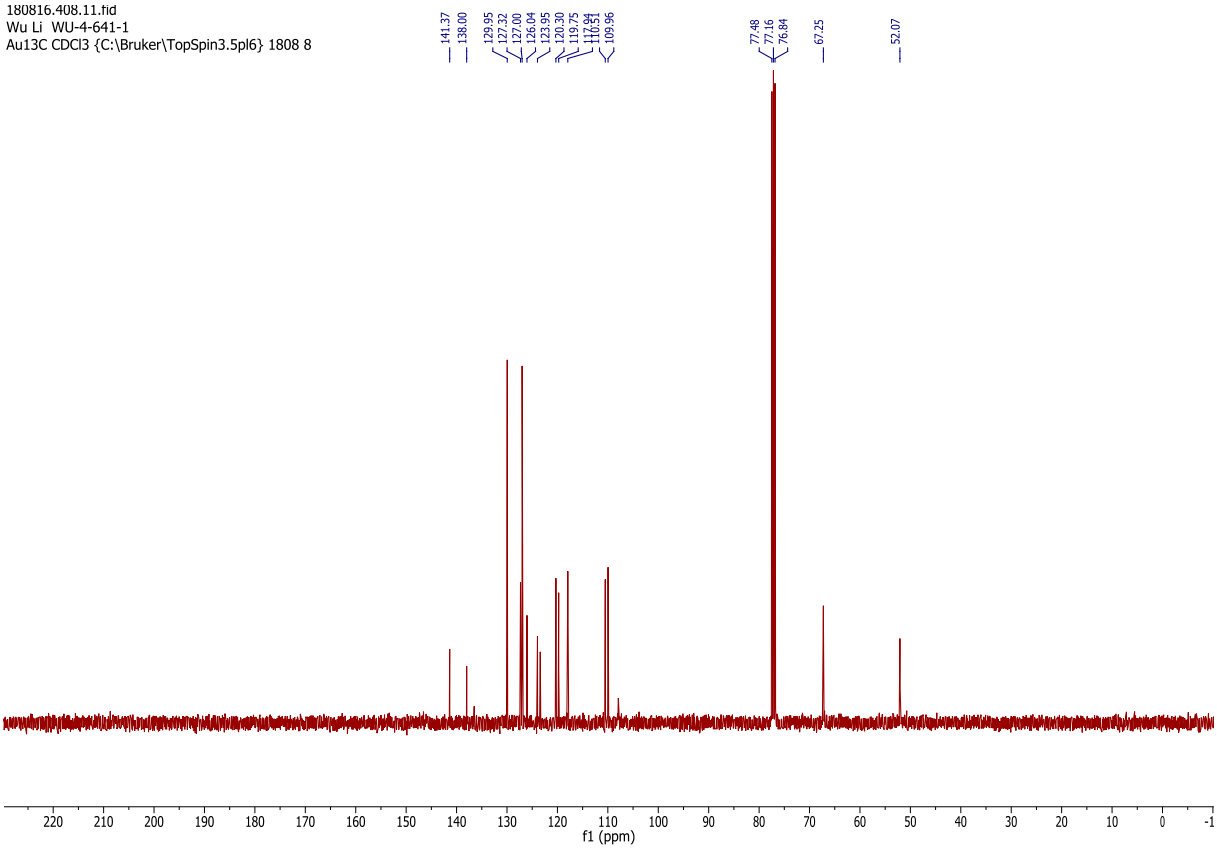
Original spectra for **51a**:



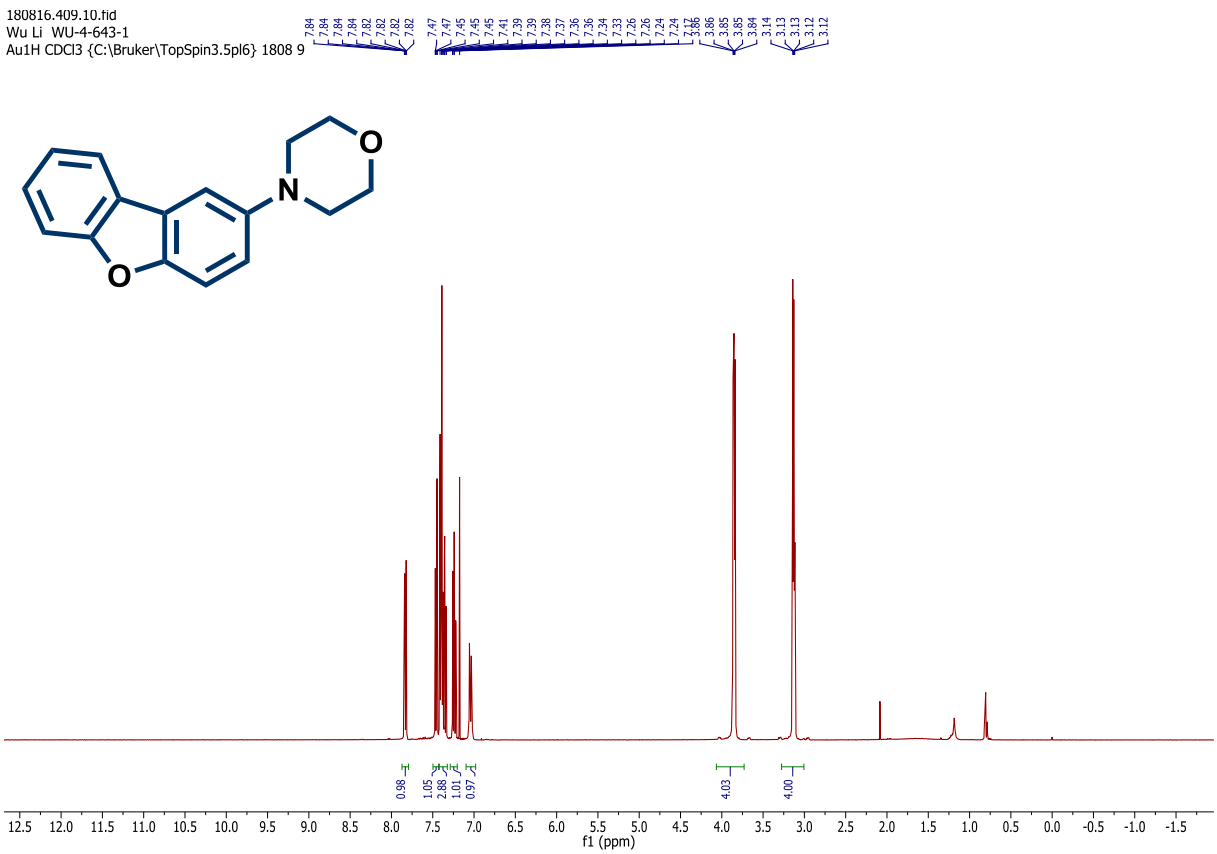


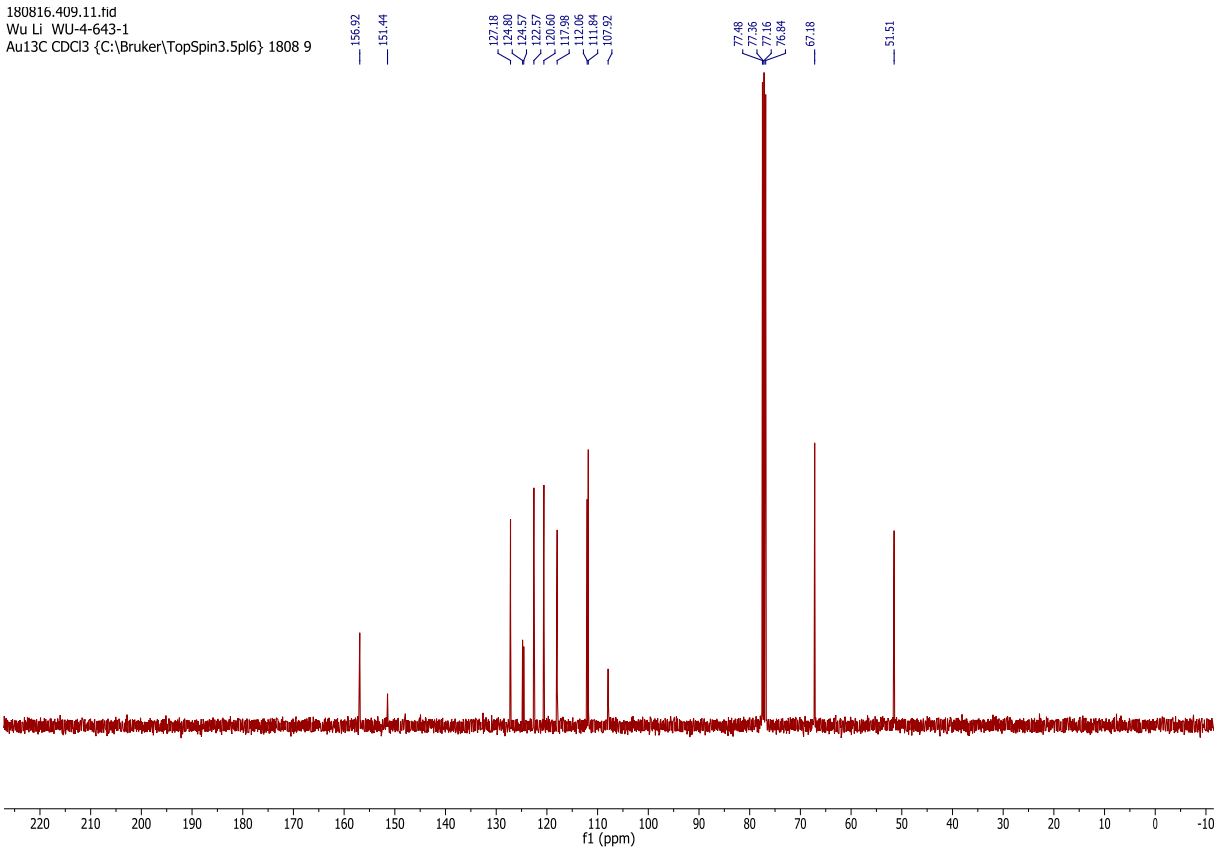
Original spectra for **52a**:



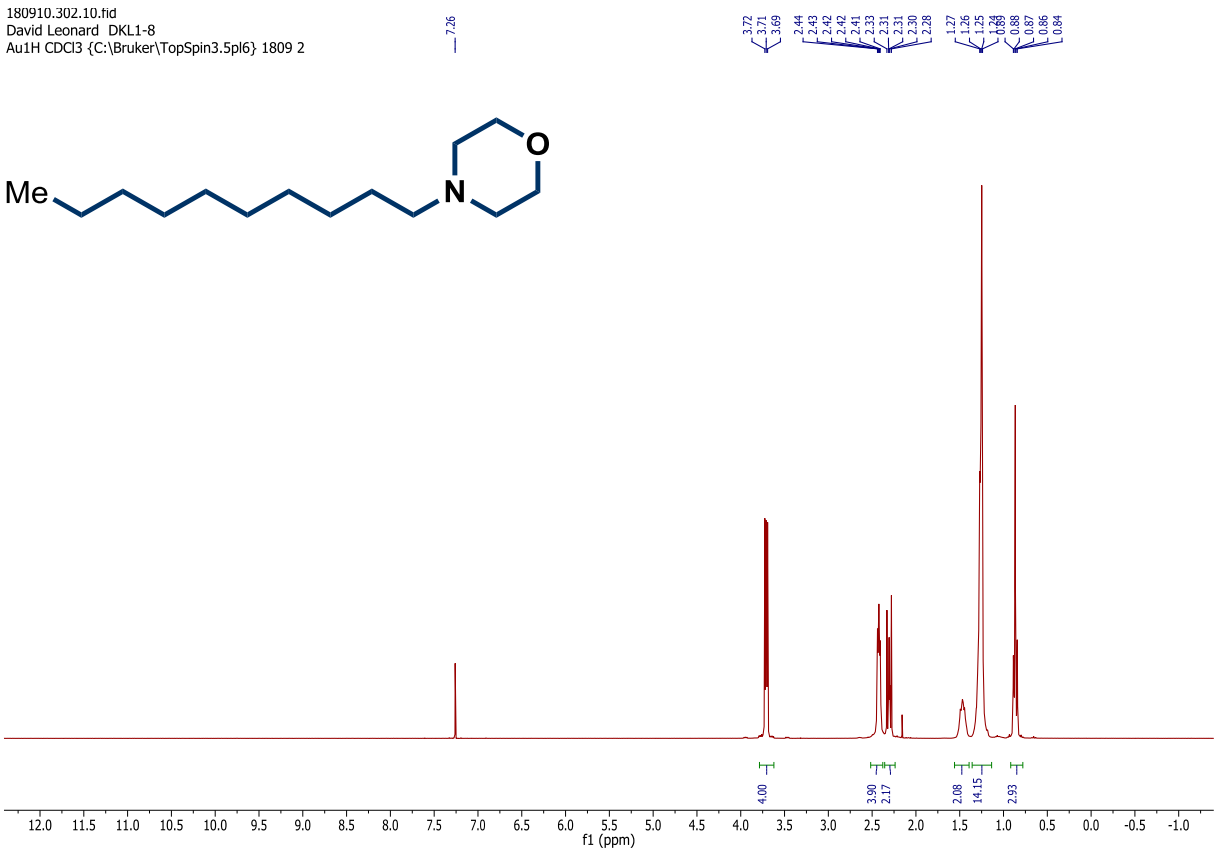


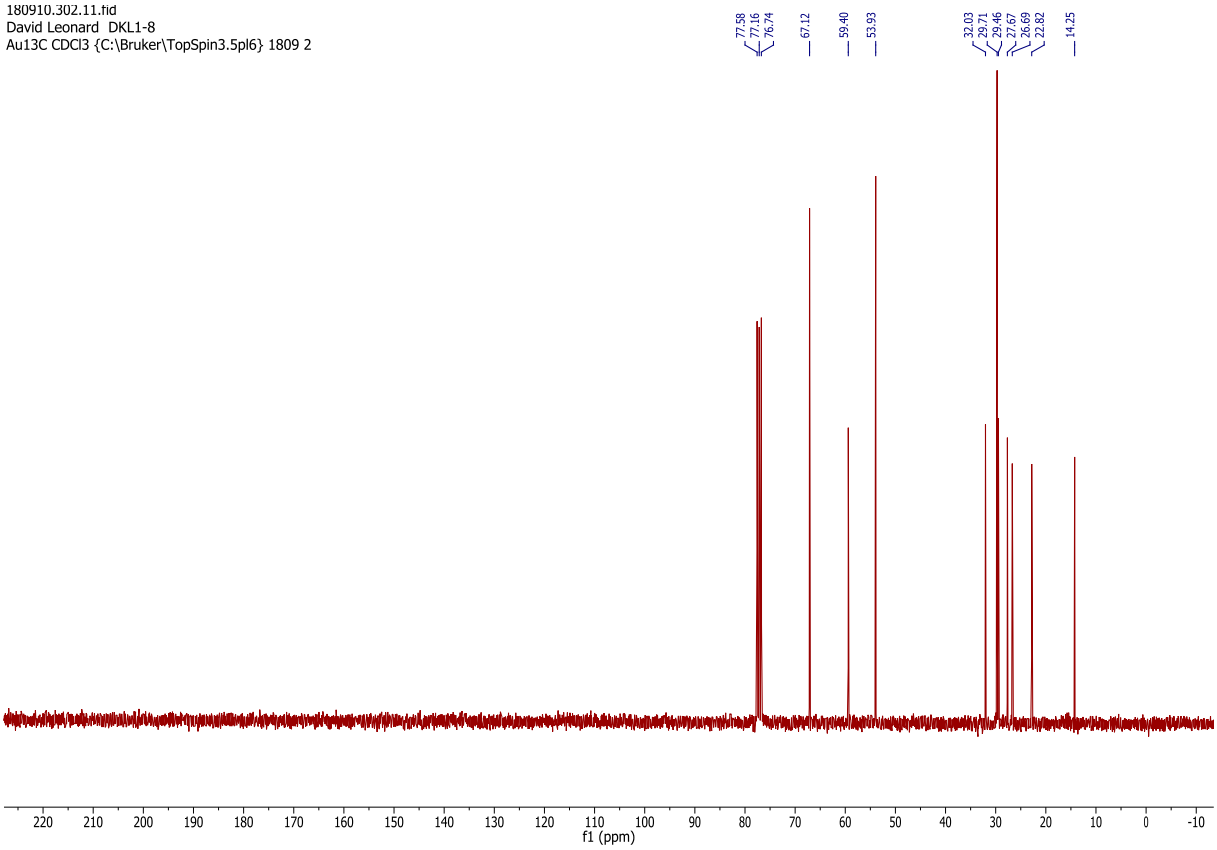
Original spectra for **53a**:



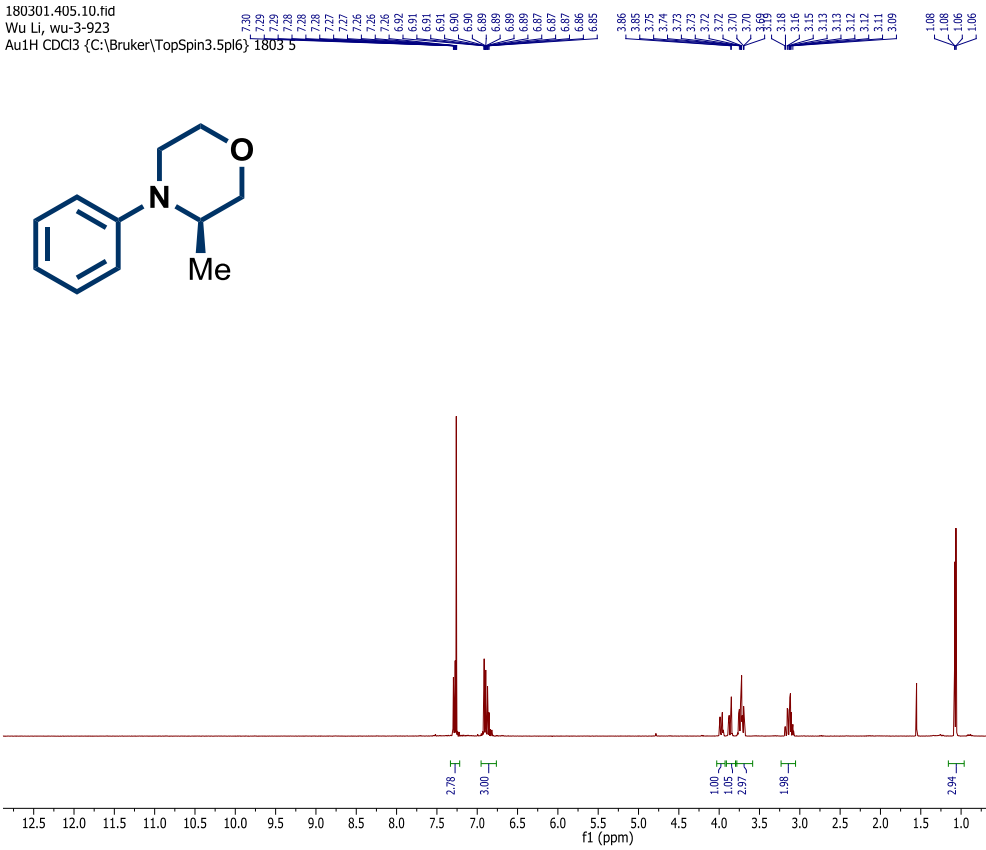


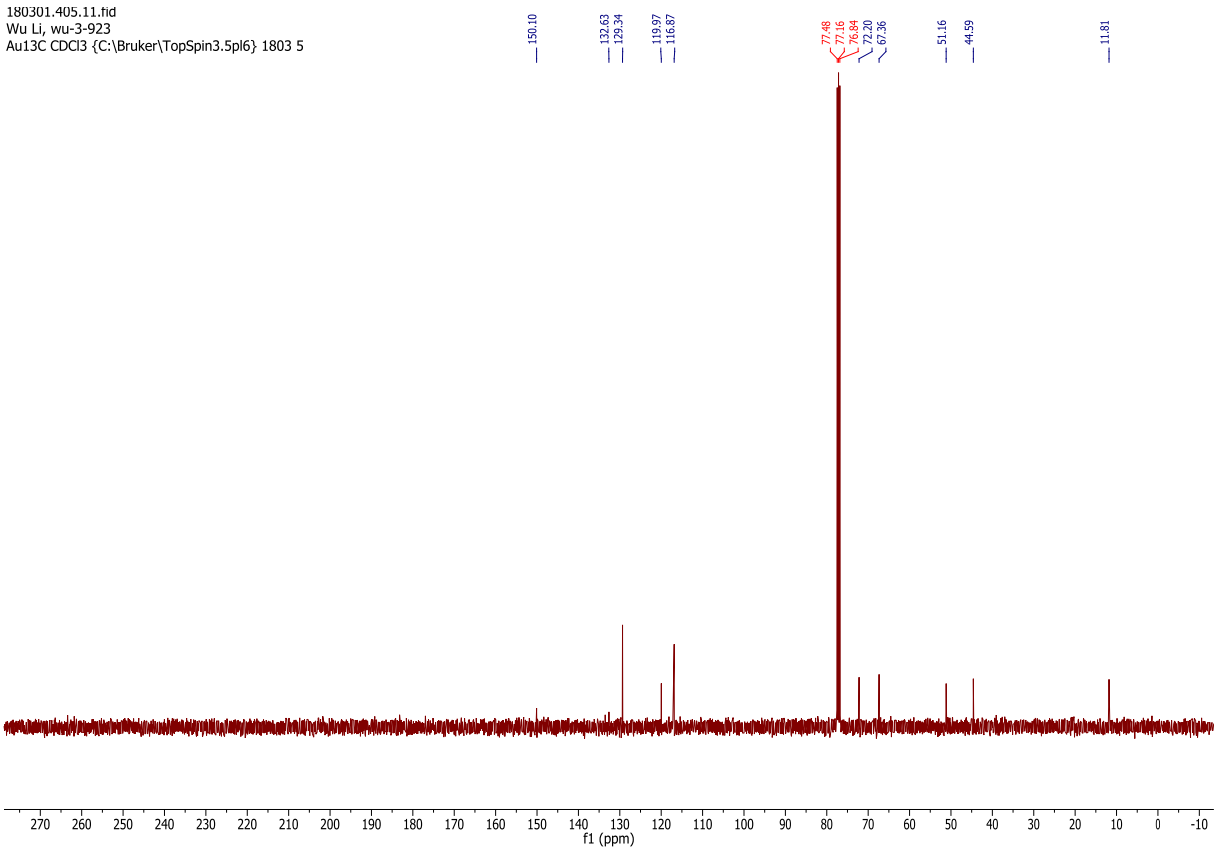
Original spectra for **56a**:



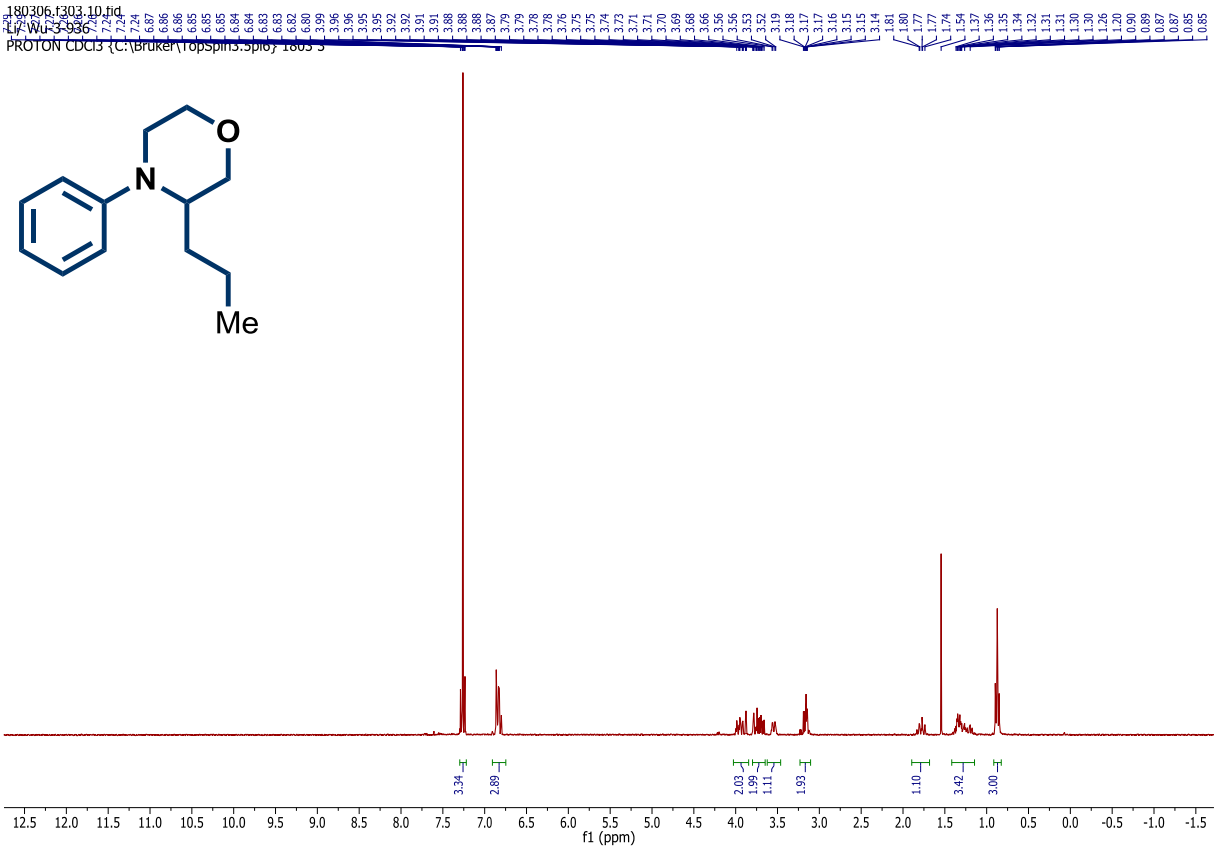


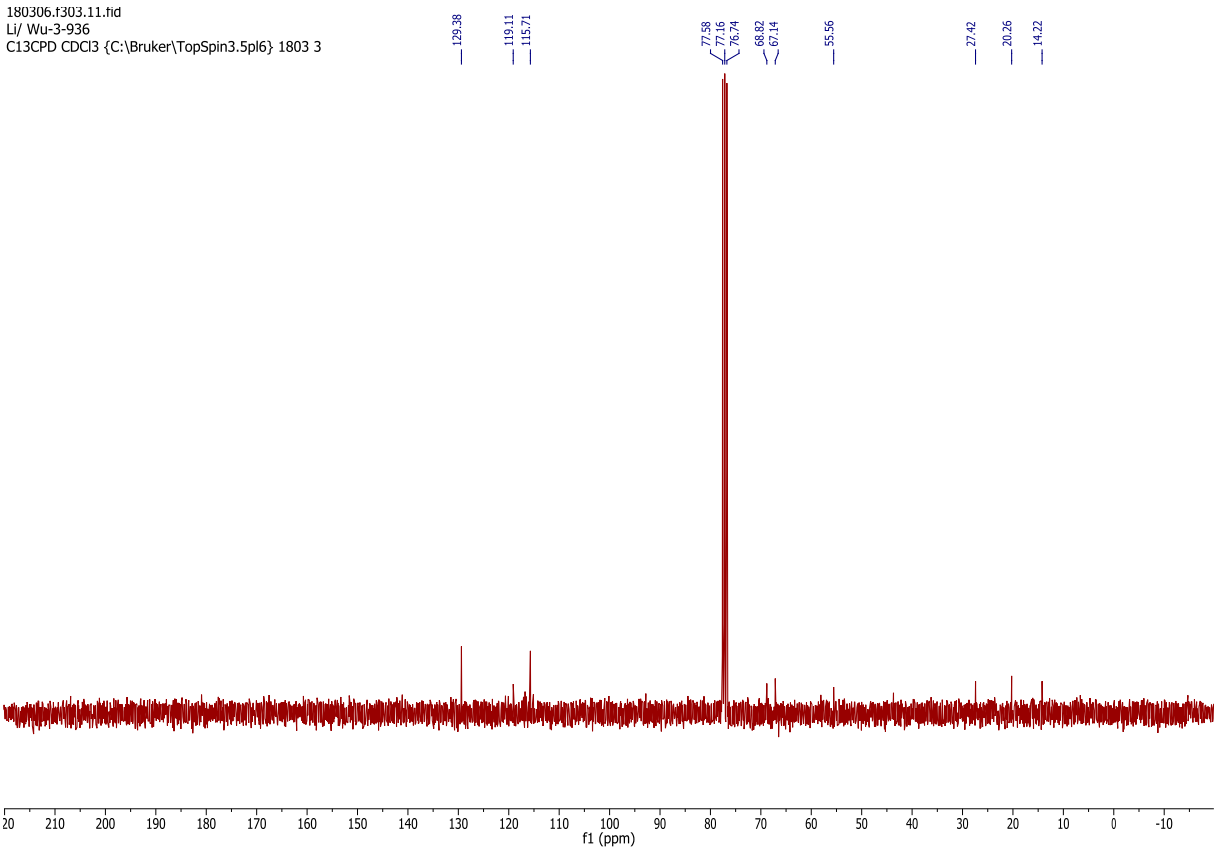
Original spectra for **57a**:



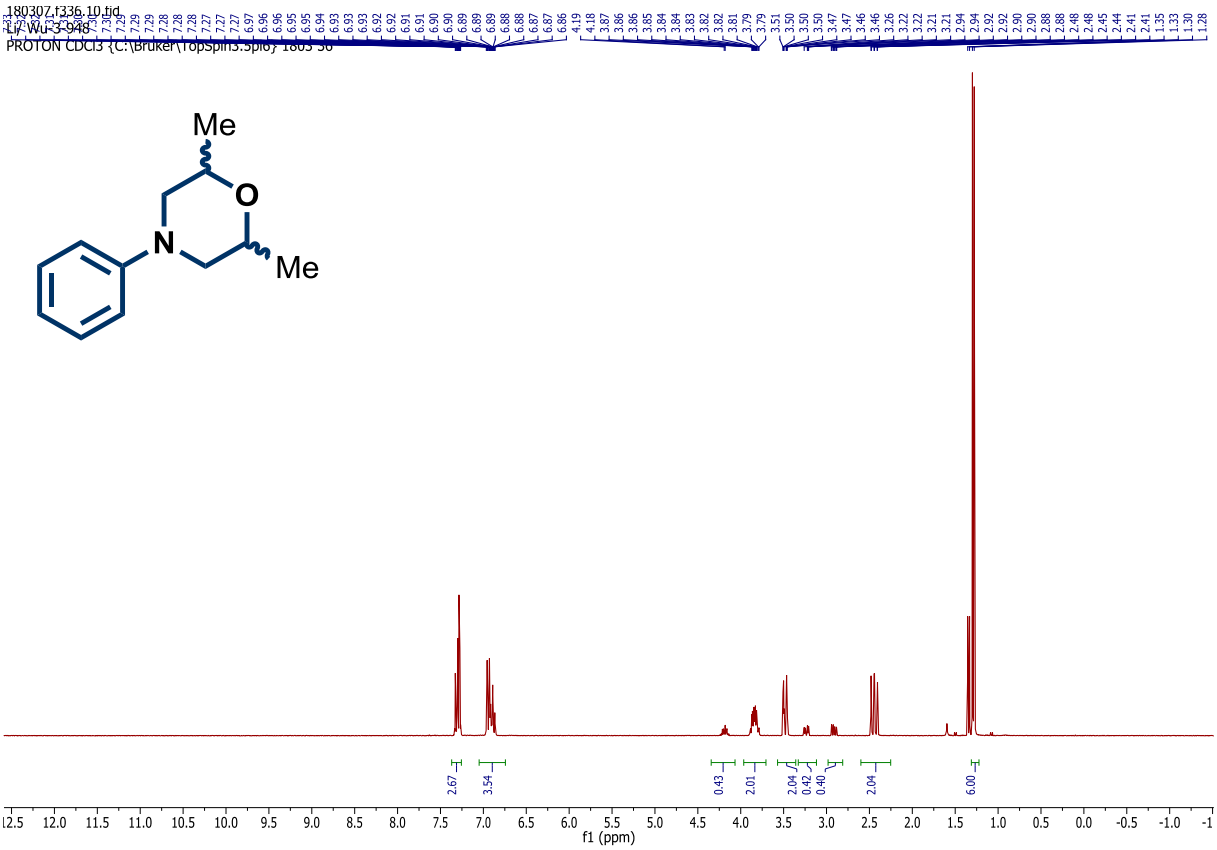


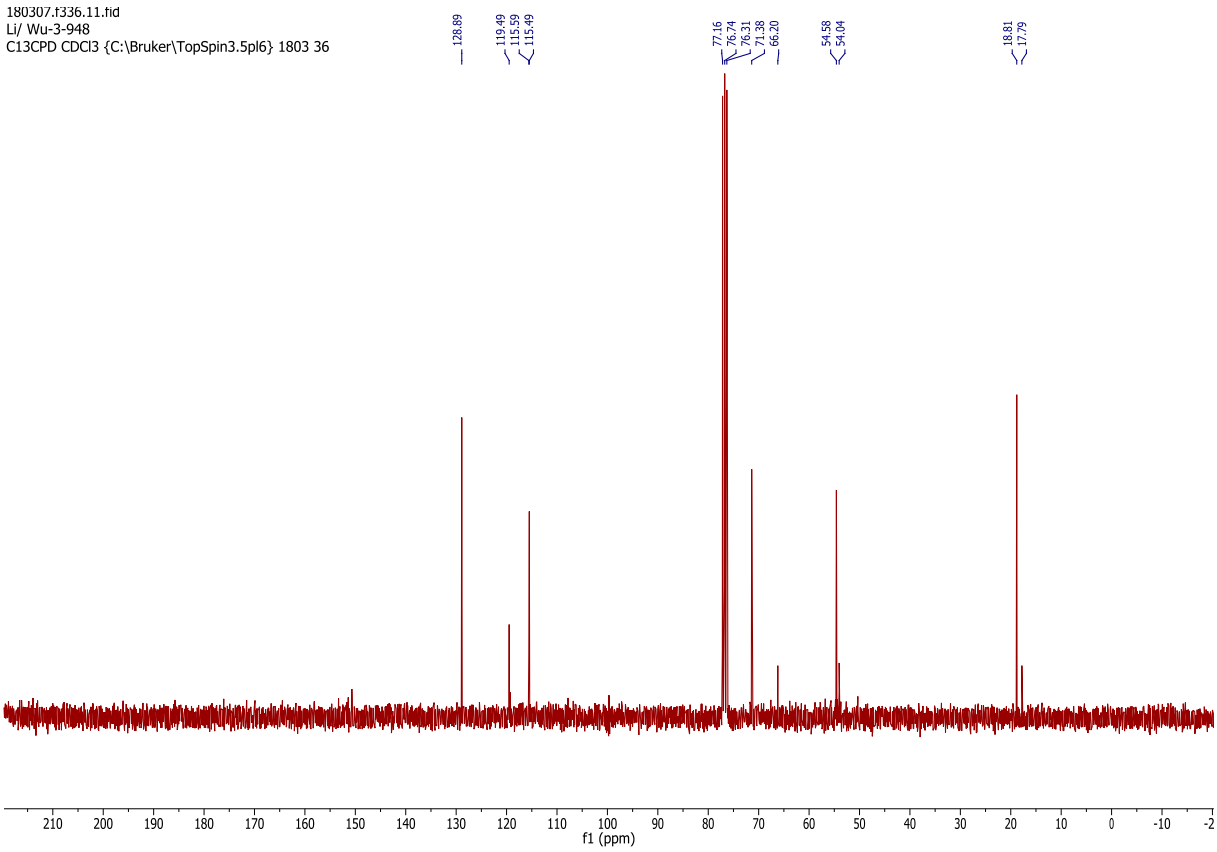
Original spectra for **58a**:



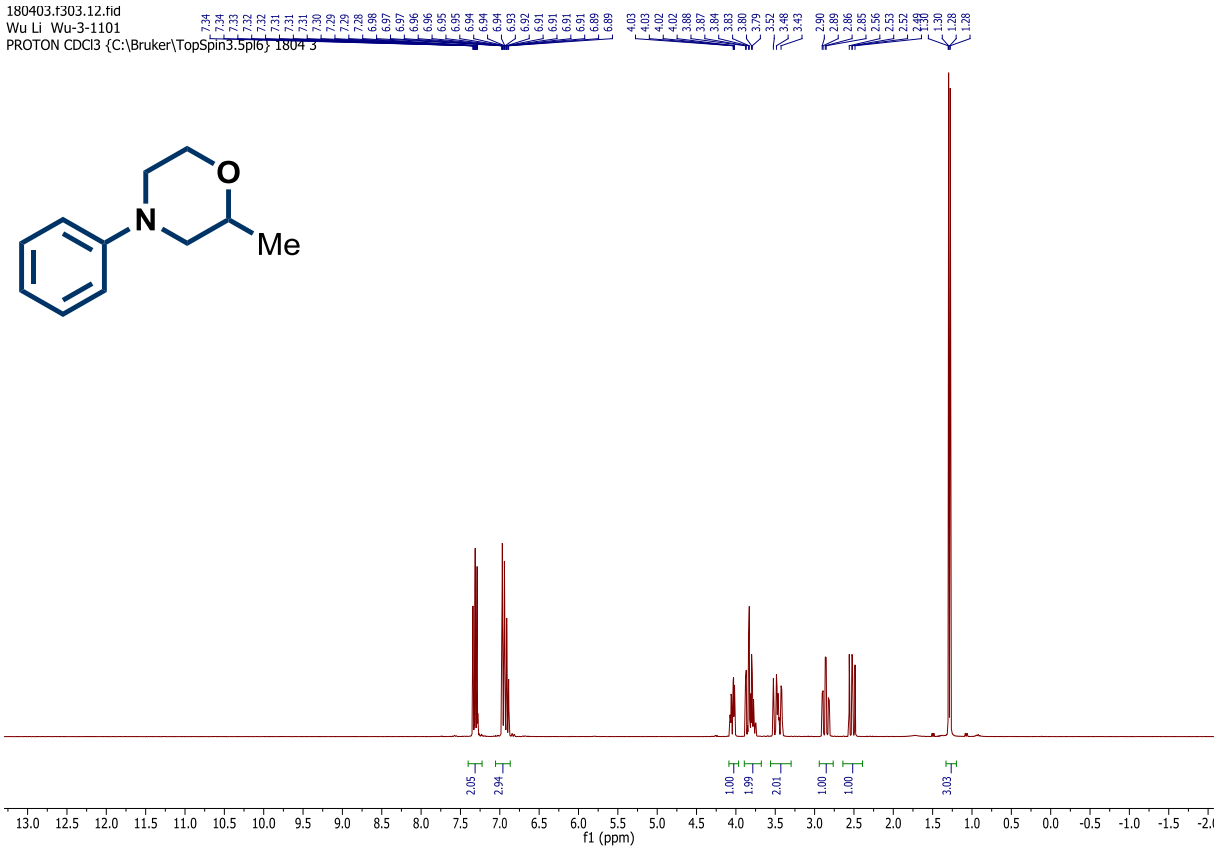


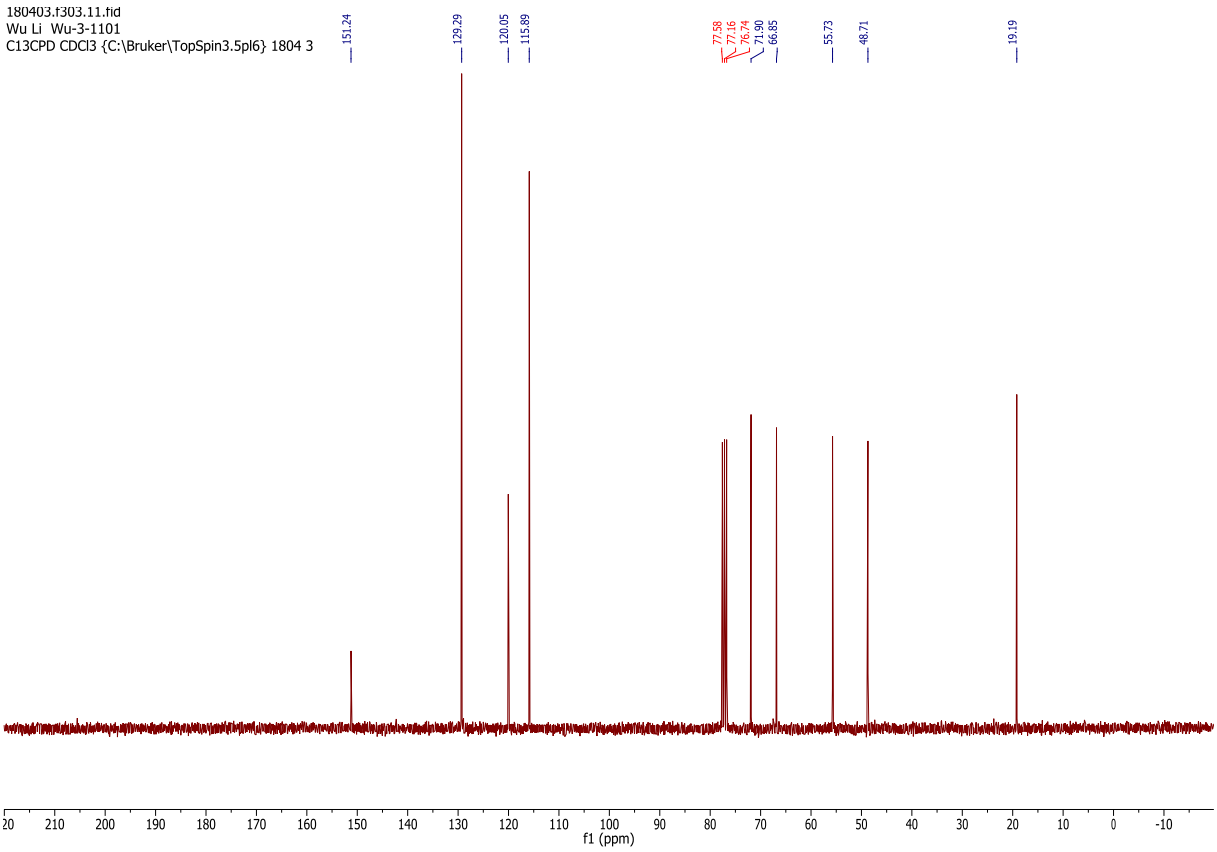
Original spectra for **59a**:



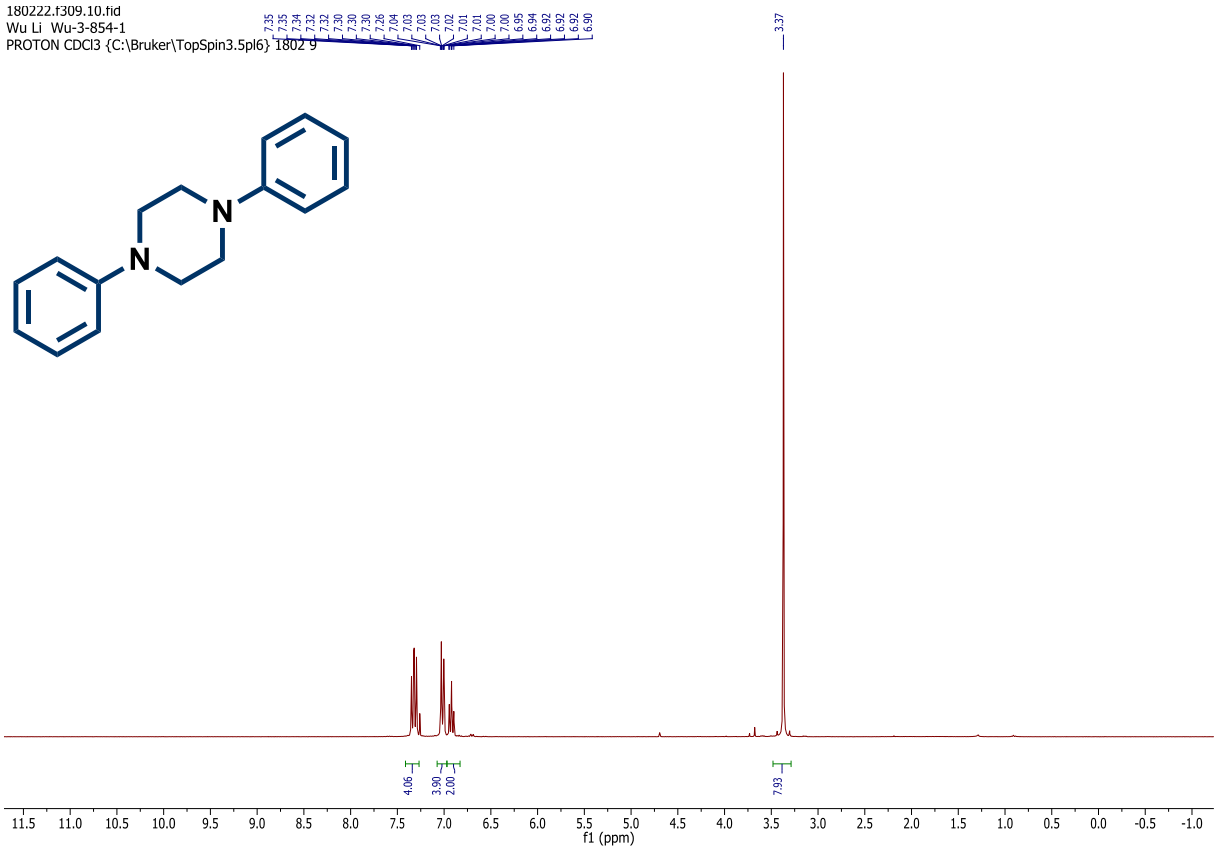


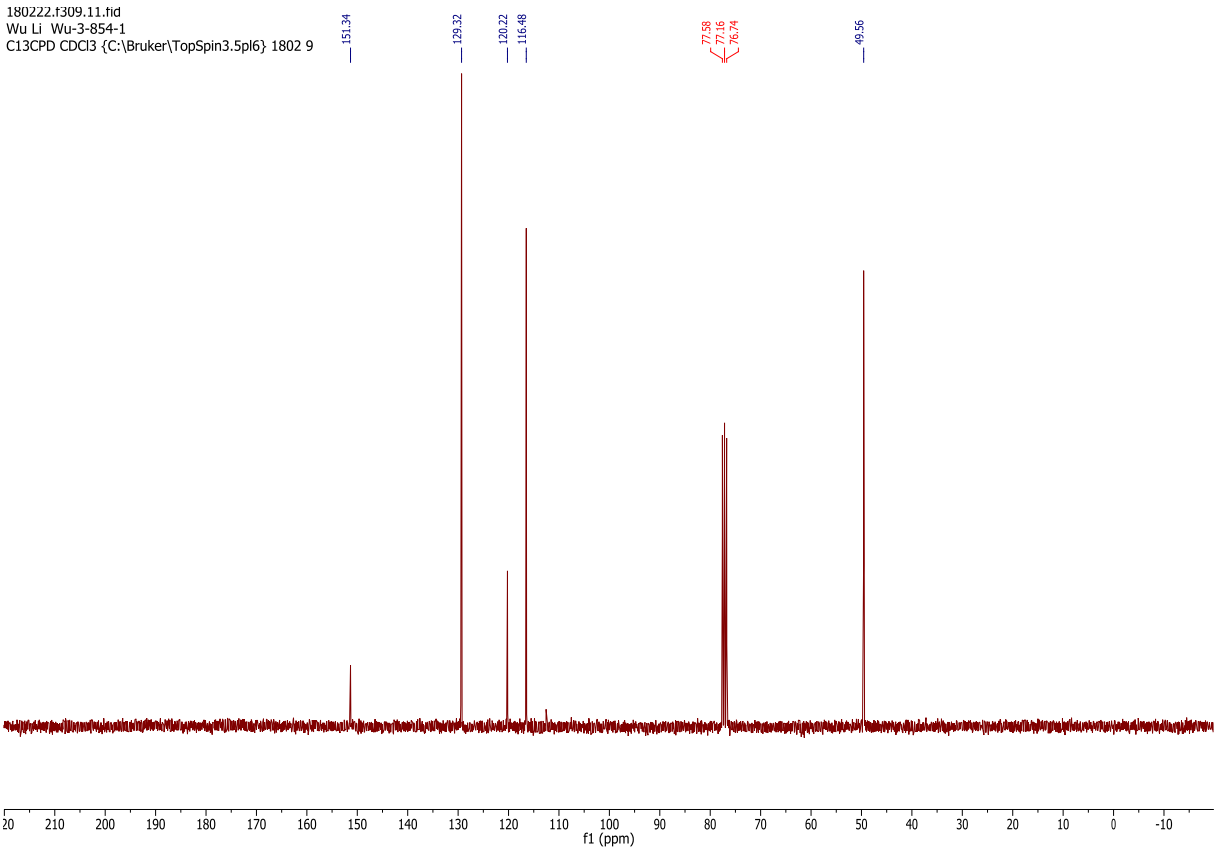
Original spectra for **60a**:



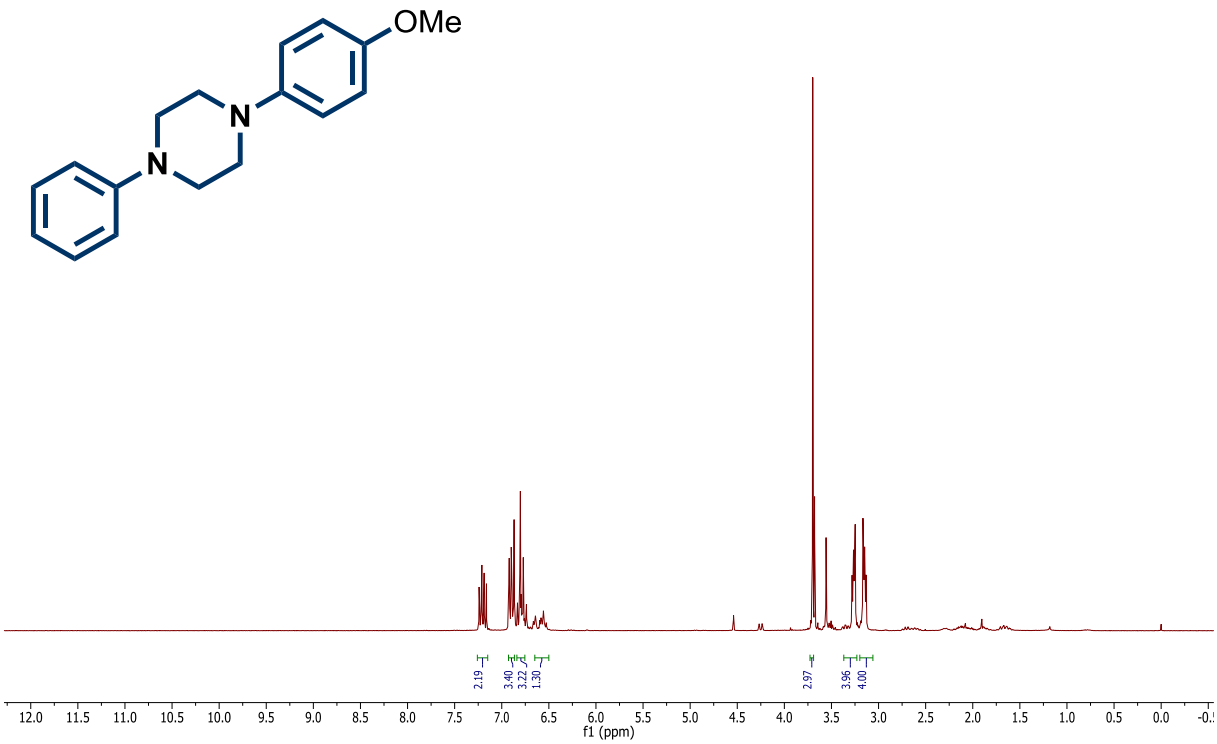


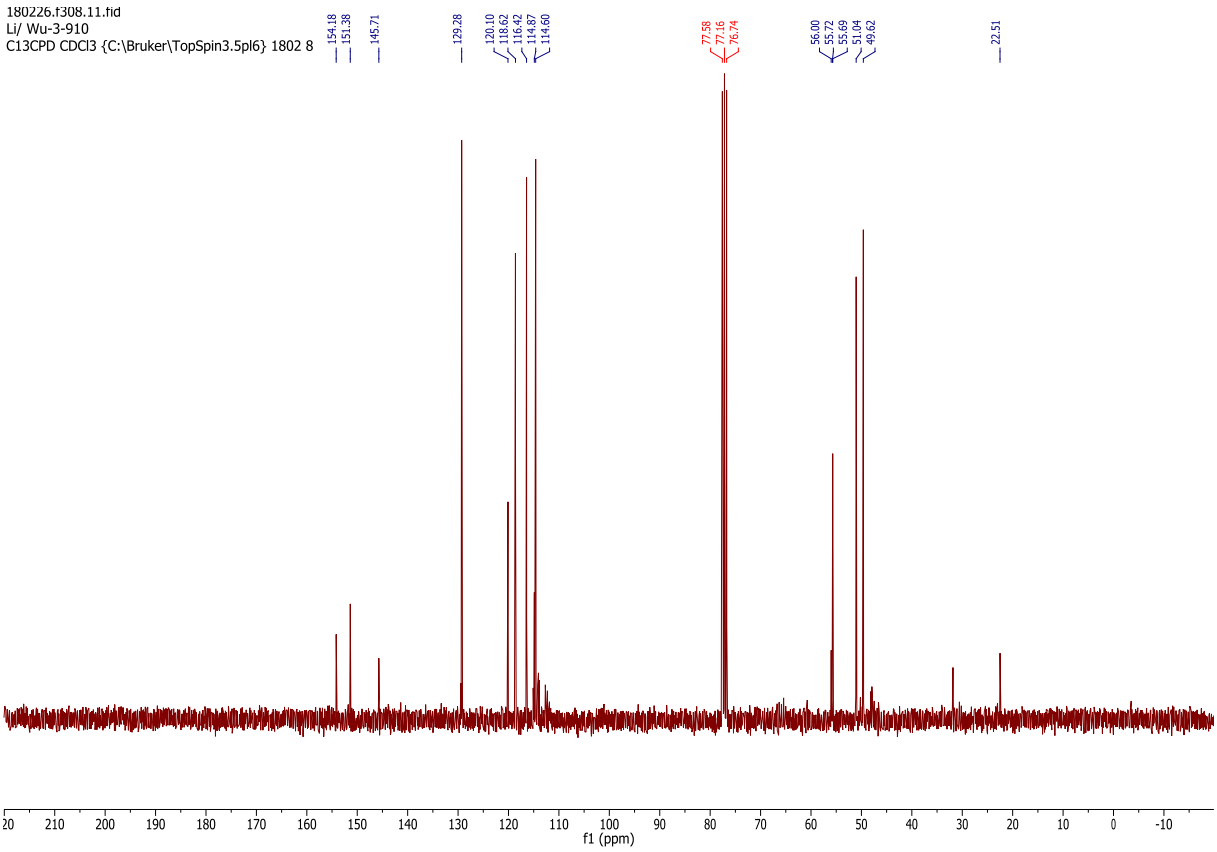
Original spectra for **62a**:



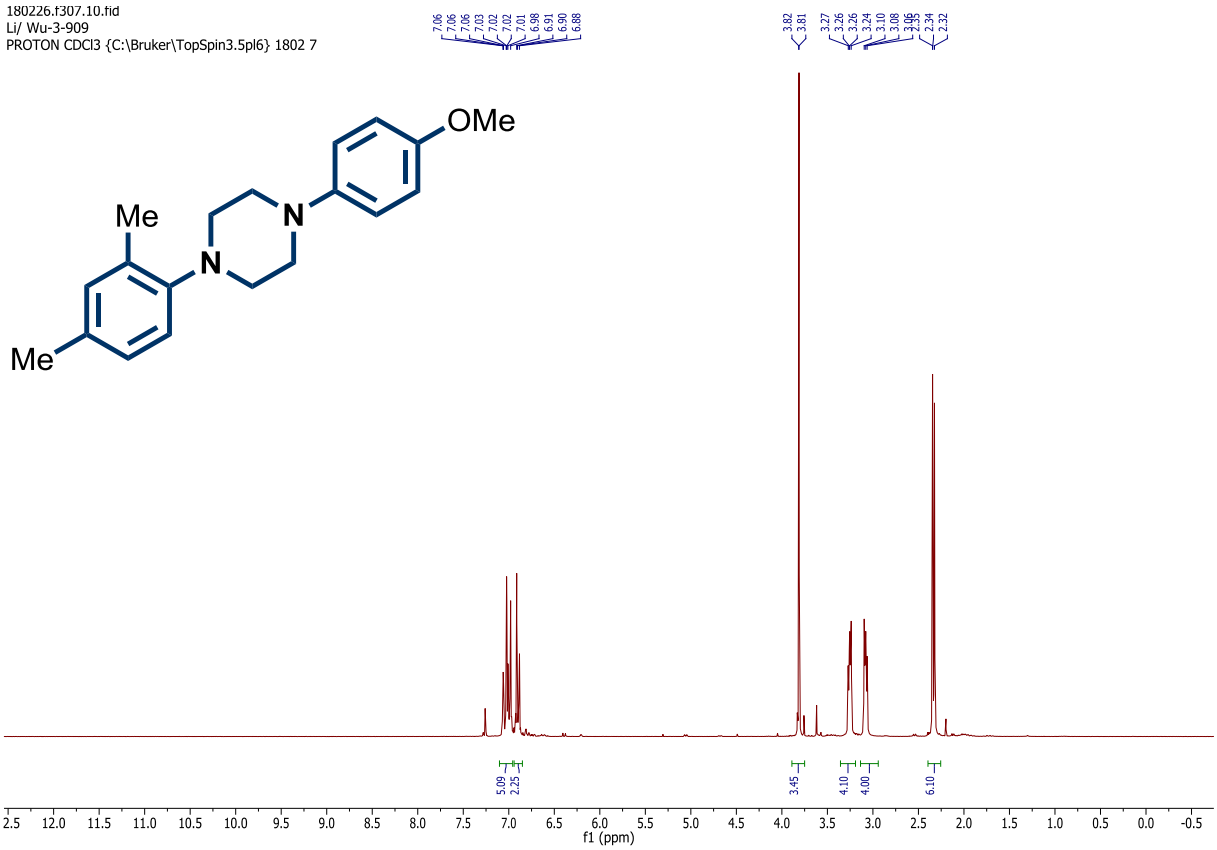


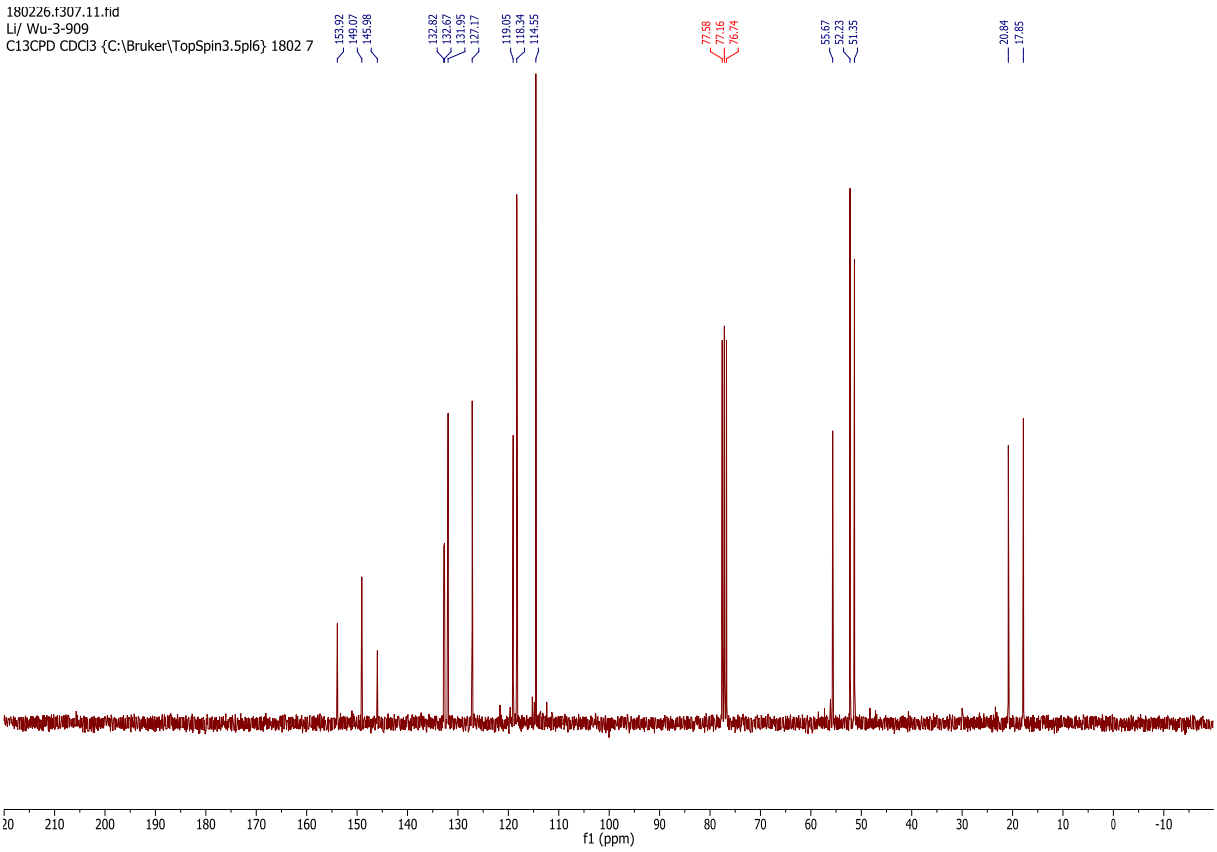
Original spectra for **63a**:





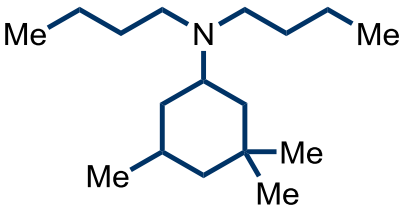
Original spectra for **64a**:

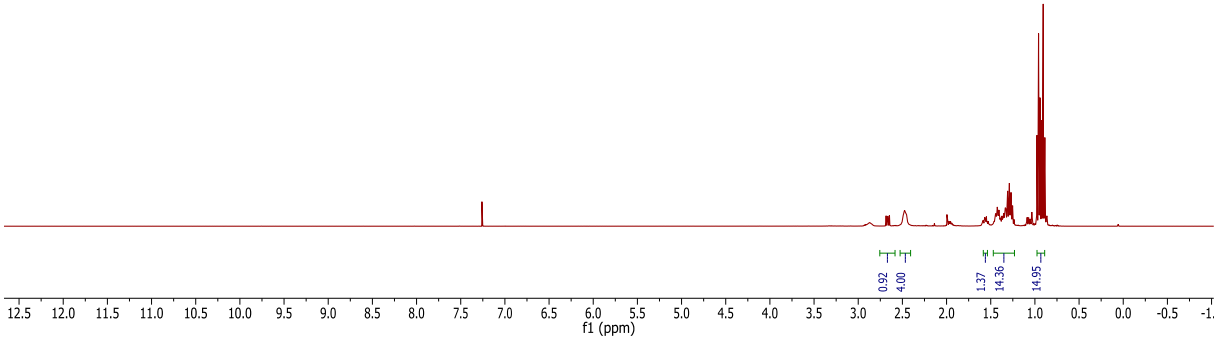




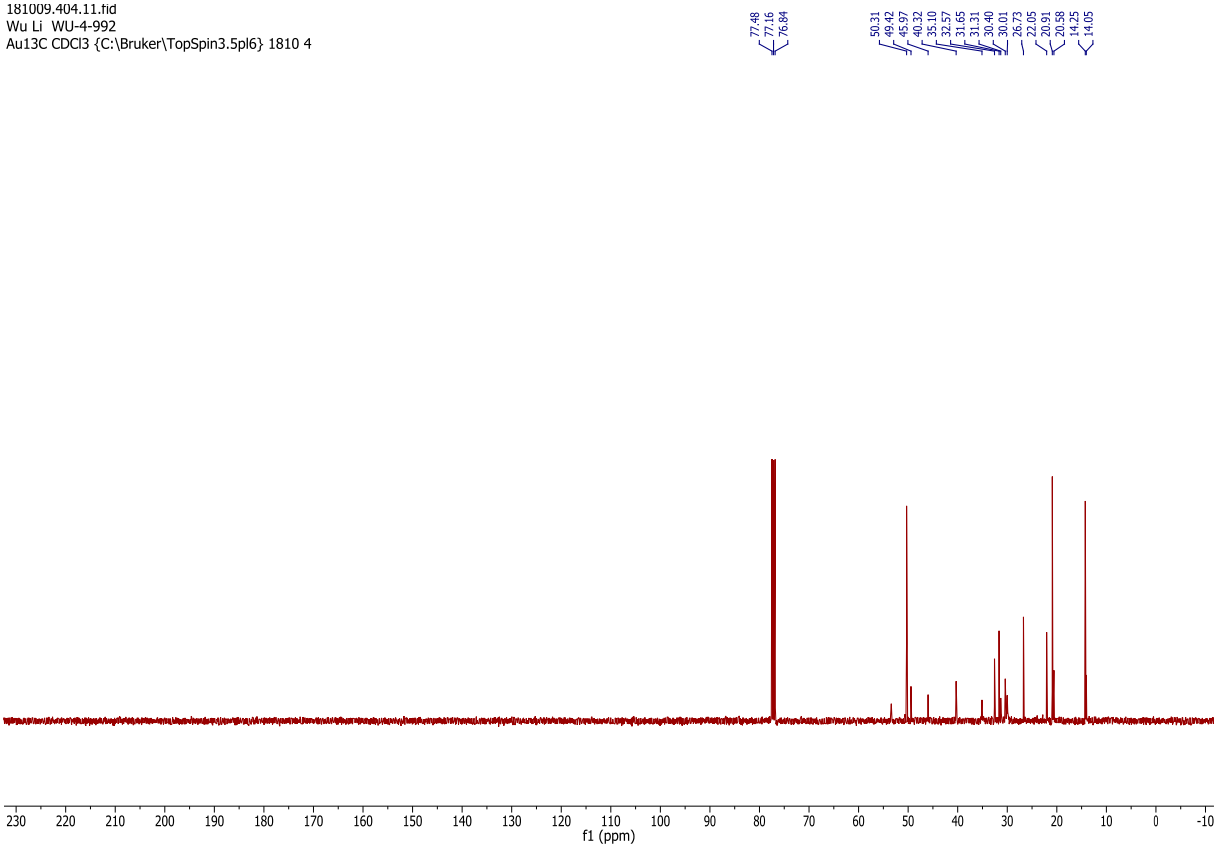
Original spectra for **65a**:

181009.404.10.fid
Wu Li WU-4-992
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 4





181009.404.11.fid
Wu Li WU-4-992
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 4



Data File C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\WU-4-992-1.D
Sample Name: WU-4-992-1

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==================================================================
Acq. Operator   : Lab 2.112                    Seq. Line :  22
Acq. Instrument : GC Lab.133                   Location : Vial 12
Injection Date  : 5/2/2019 7:25:52 PM             Inj :   1
                                               Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201905\2019-05-02 09-48-05\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```
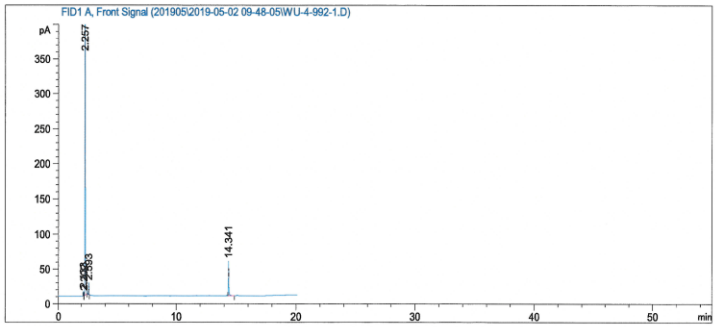
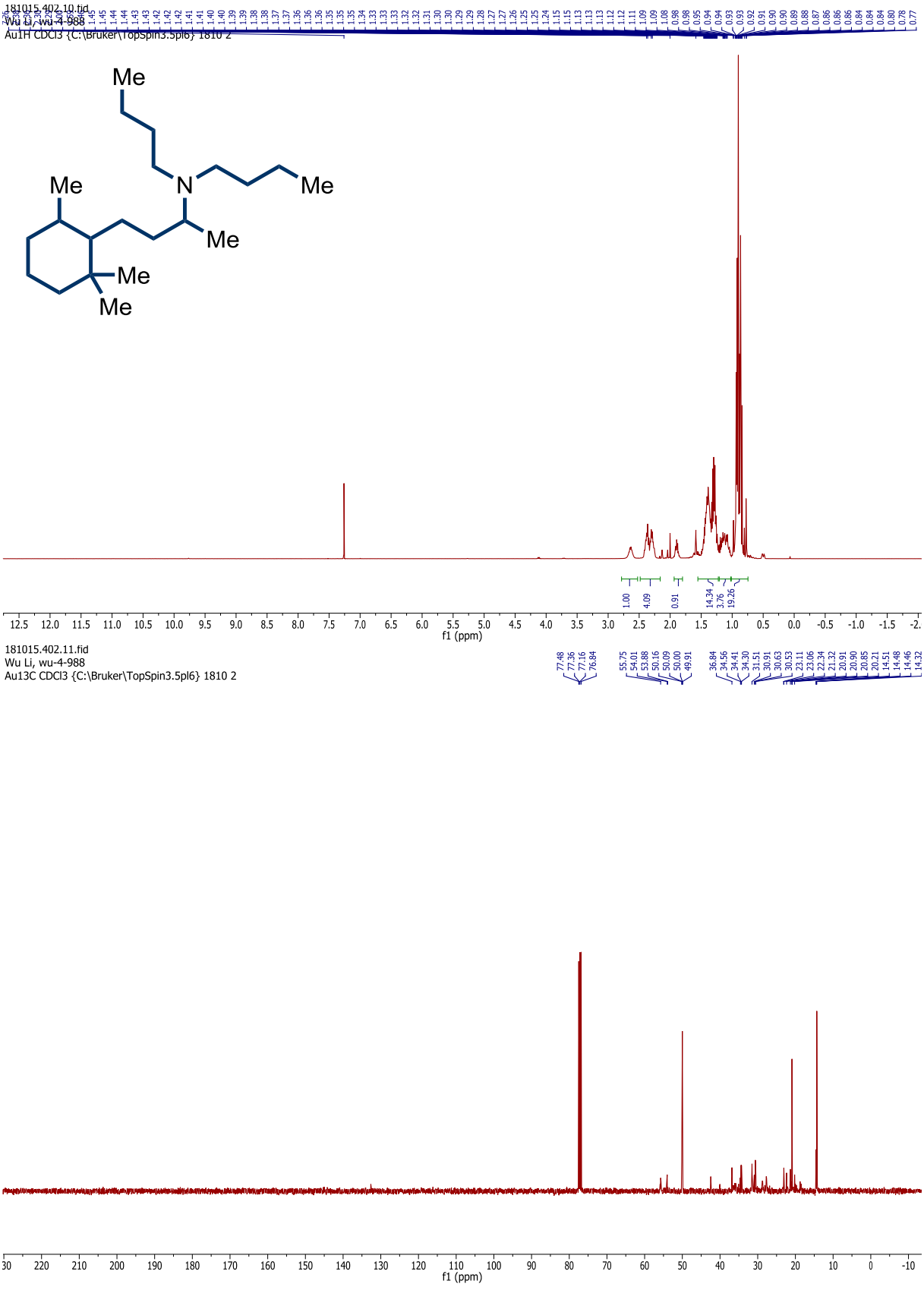




```
==================================================================
                      Area Percent Report
==================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.133 BB    0.0169    7.78096    6.64356  0.01001
   2   2.202 BV    0.0201    4.32213    3.47774  0.00556
   3   2.257 VB S  0.0177 7.75879e4  7.00394e4  99.78242
   4   2.593 BB    0.0170   19.99812   16.92118  0.02572
   5  14.341 BB    0.0391  137.07954   50.20229  0.17629

Totals :                  7.77570e4  7.01167e4


==================================================================
                      *** End of Report ***
```

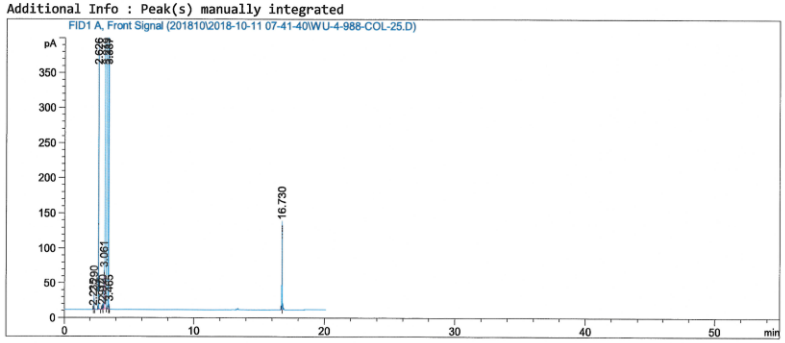
Original spectra for **66a**:



Data File C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\WU-4-988-COL-25.D
Sample Name: WU-4-988-col-25

Acq. Operator	: Lab 2.112	Seq. Line :	1
Acq. Instrument	: GC Lab.133	Location :	Vial 28
Injection Date	: 10/11/2018 7:47:02 AM	Inj :	1
		Inj Volume :	1 µl
Method	: C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\STANDARDMTH 20.M (Sequence Method)		
Last changed	: 8/28/2018 4:06:15 PM by Lab 2.112		
Method Info	: HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d		

Additional Info : Peak(s) manually integrated



Area Percent Report

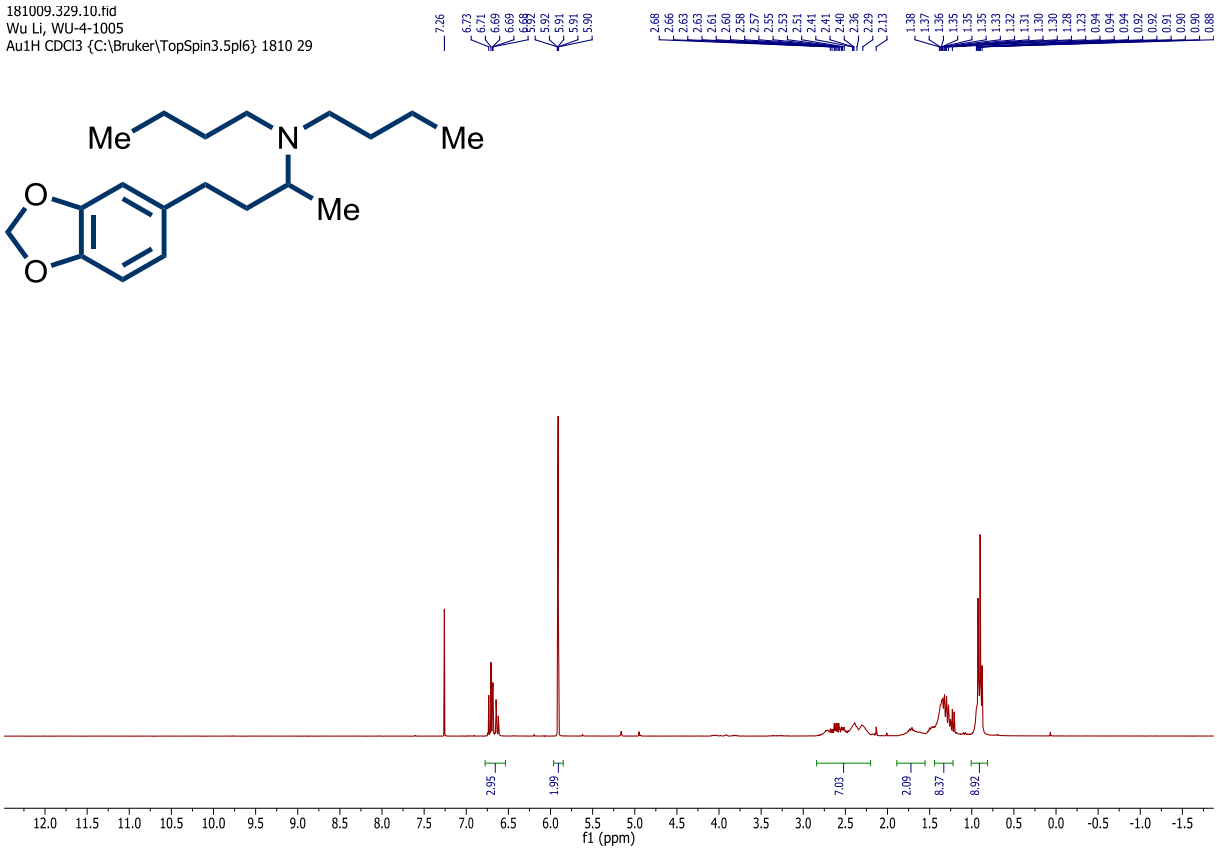
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

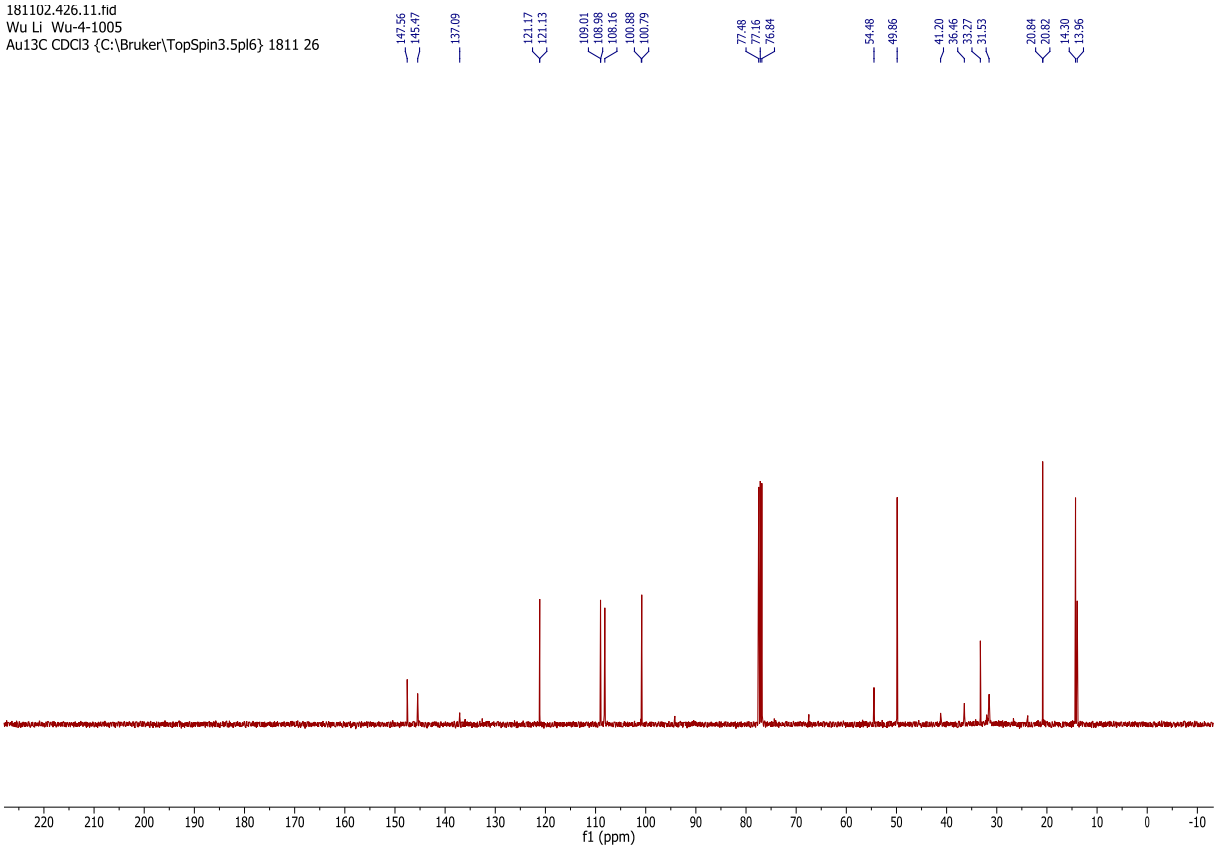
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	2.235	BV	0.0163	2.22059	1.97778	0.00157
2	2.290	VB	0.0140	19.83987	21.35296	0.01399
3	2.626	BB	0.0150	662.59399	705.14691	0.46708
4	2.912	BV	0.0349	5.95006	2.74135	0.00419
5	2.970	VV	0.0372	18.04052	8.09644	0.01272
6	3.061	BV	0.0460	163.16457	56.04660	0.11502
7	3.219	VB S	0.0462	1.36945e5	3.71963e4	96.53644
8	3.387	BV	0.0214	3803.53198	2553.25464	2.68122
9	3.465	VB	0.0167	8.24082	7.57881	0.00581
10	16.730	VV	0.0294	229.76047	125.22737	0.16196
Totals :				1.41858e5	4.06777e4	

Original spectra for **67a**:

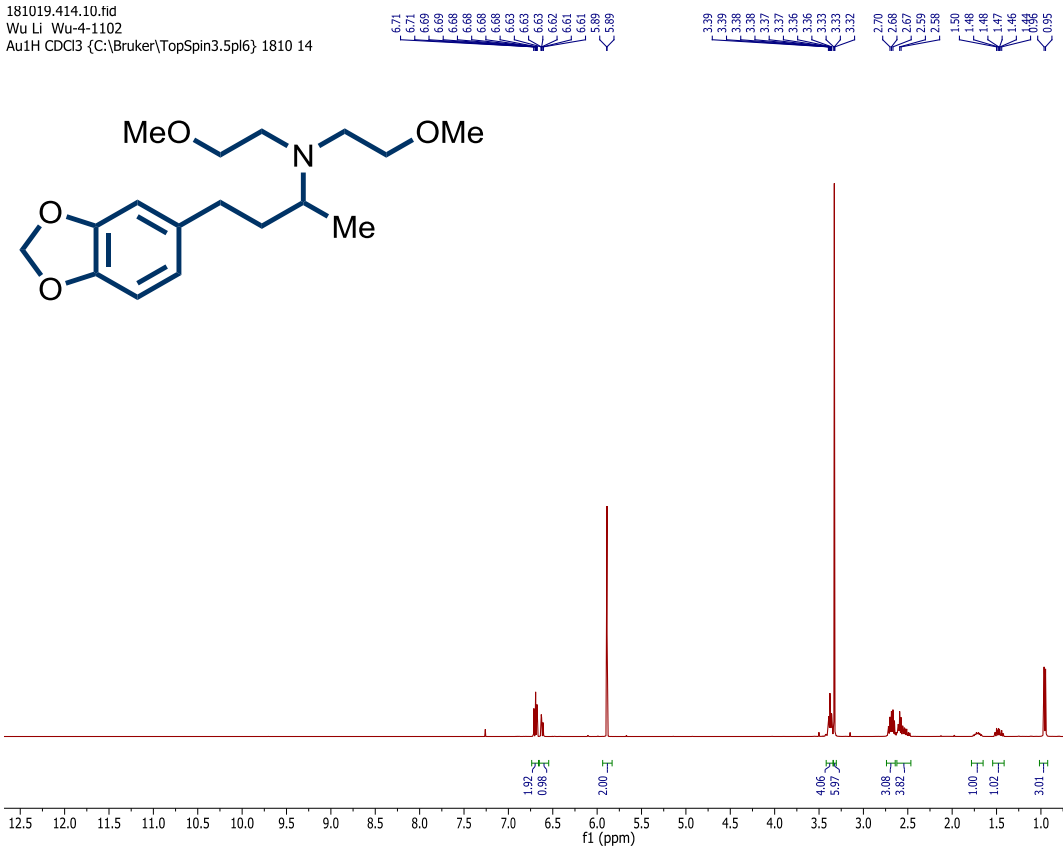
181009.329.10.fid
Wu Li, WU-4-1005
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 29

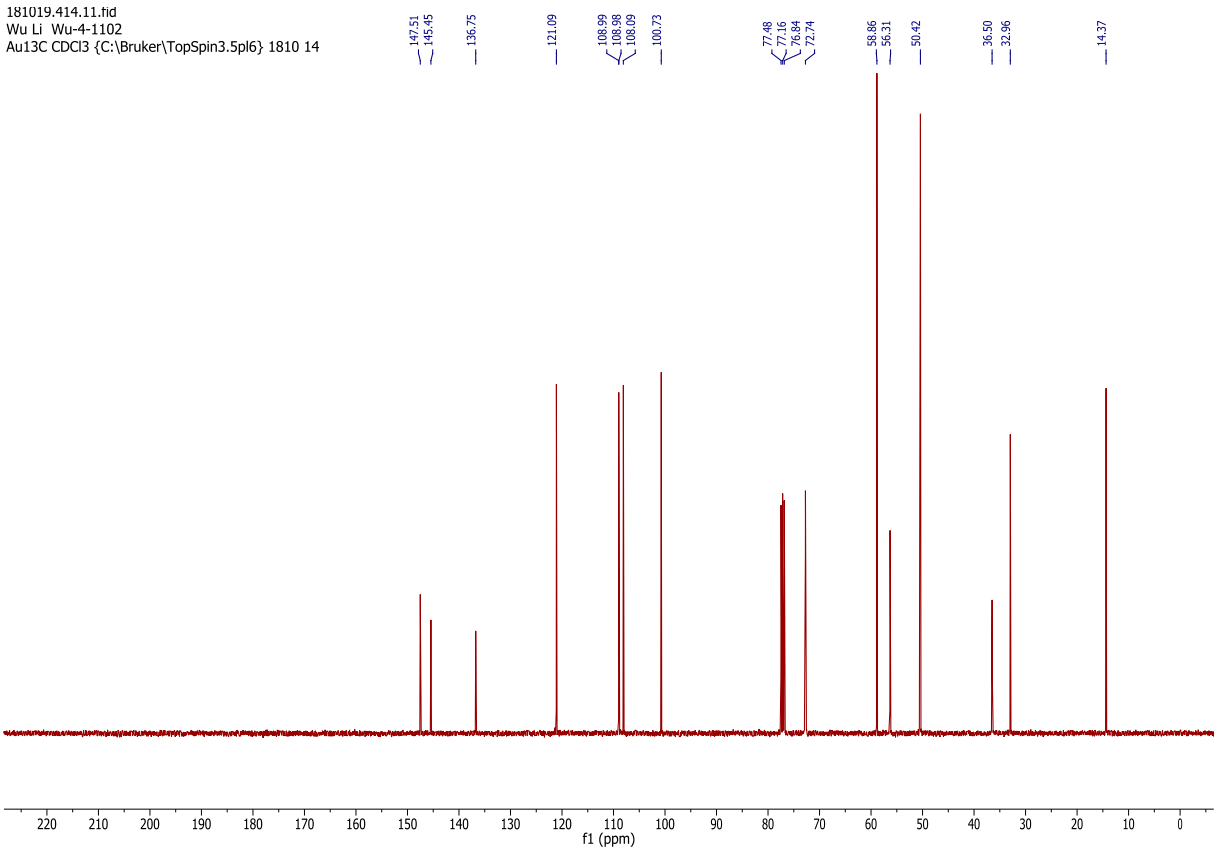


181102.426.11.fid
Wu Li Wu-4-1005
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 26



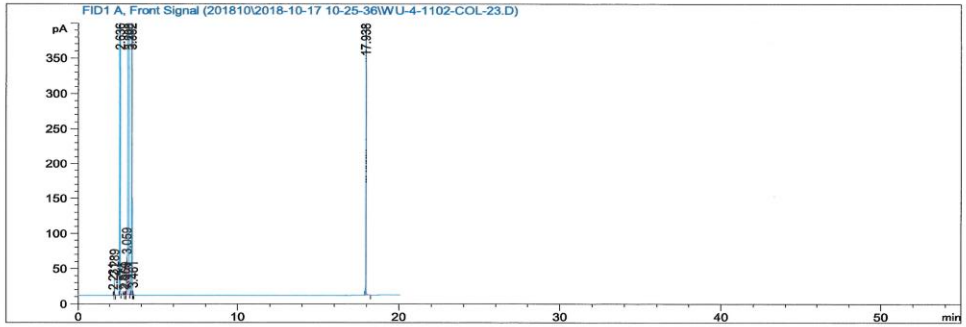
Original spectra for **68a**:





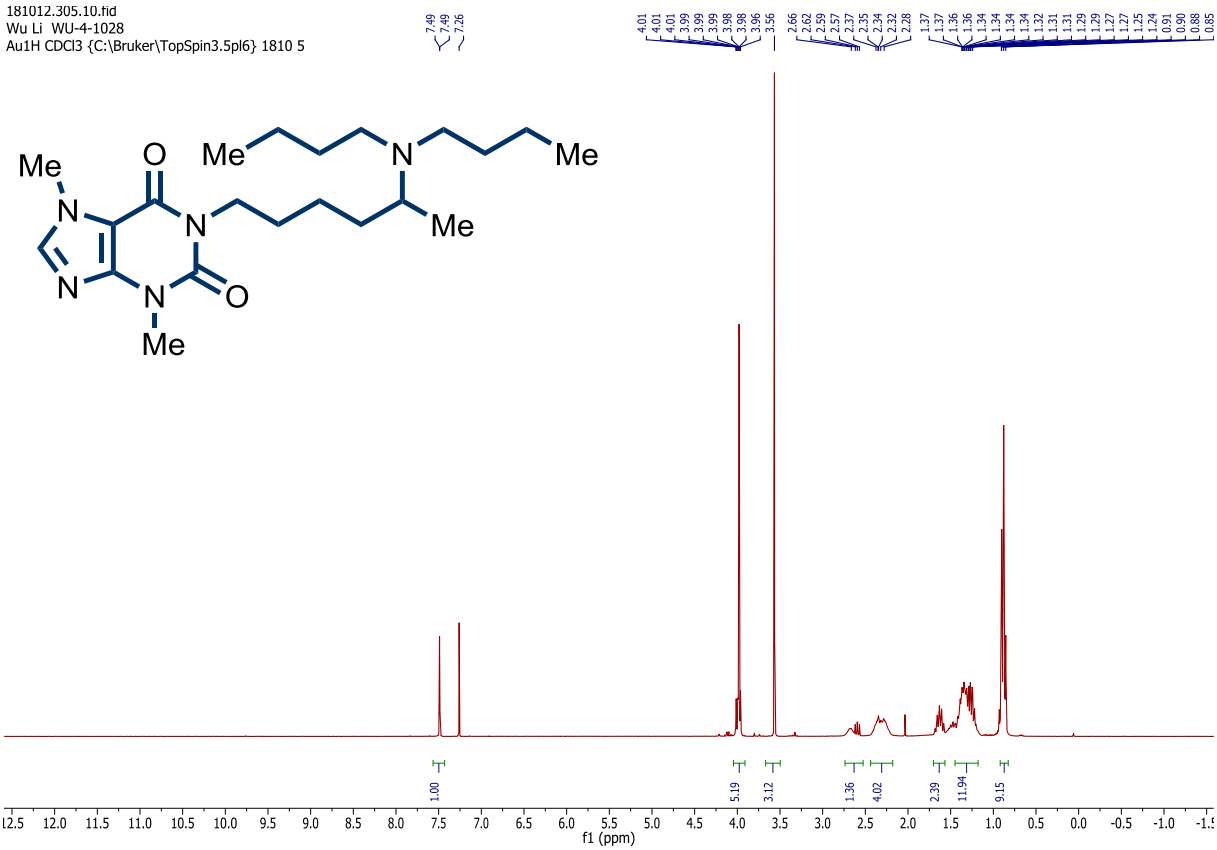
Data File C:\CHEM32\1\DATA\201810\2018-10-17 10-25-36\WU-4-1102-COL-23.D
Sample Name: Wu-4-1102-col-23

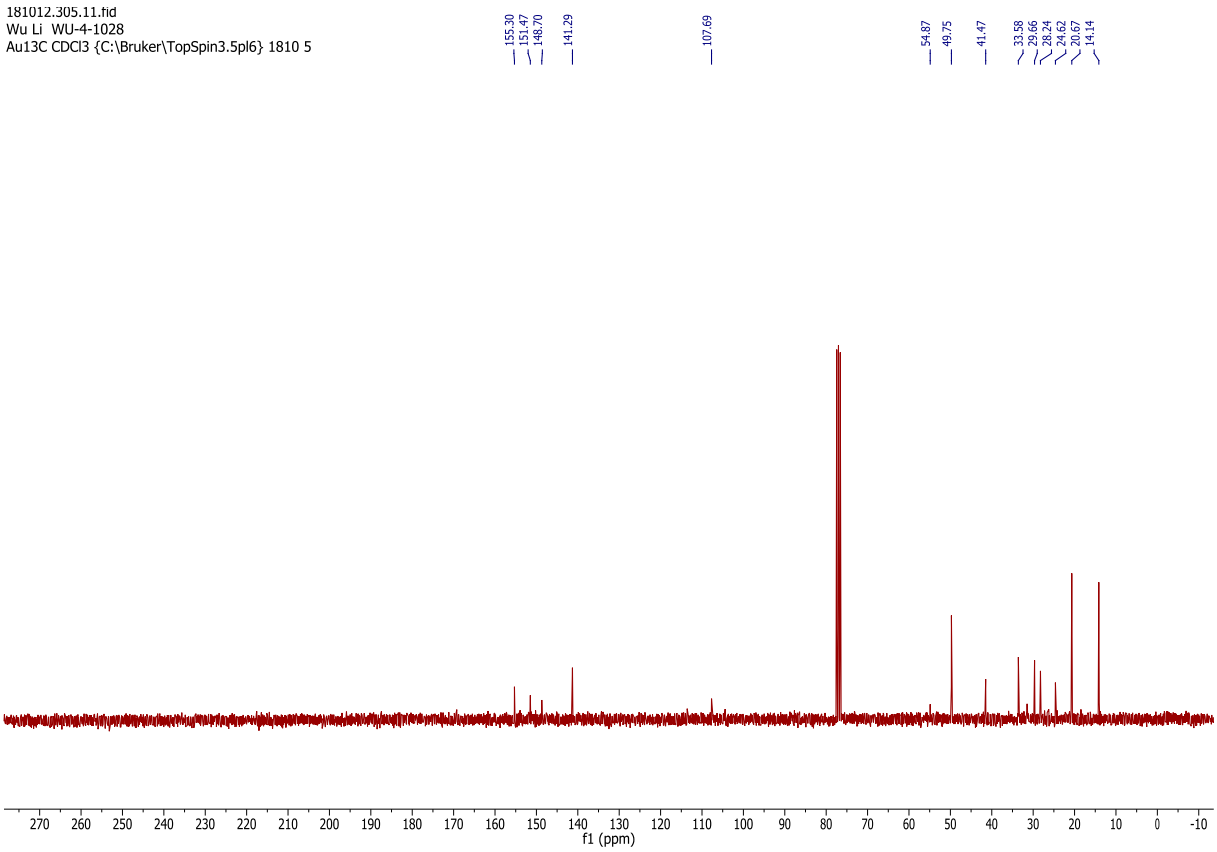
```
======================================================================
Acq. Operator   : Lab 2.112                      Seq. Line :   4
Acq. Instrument : GC Lab.133                      Location : Vial 5
Injection Date  : 10/17/2018 12:30:46 PM             Inj :   1
                                                 Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201810\2018-10-17 10-25-36\STANDARDMTH 20.M (Sequence
                  Method)
Last changed    : 8/28/2018 4:06:15 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```




```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1   2.231 BV    0.0147    3.93640    3.98874  0.00302
   2   2.289 VB    0.0134   20.26611   23.20634  0.01552
   3   2.636 BB S  0.0178 1.15812e4  1.03885e4   8.87179
   4   2.874 BV    0.0231    5.39643    3.30009  0.00413
   5   2.969 VB    0.0338    9.94167    4.95223  0.00762
   6   3.059 BV    0.0429  152.70145   53.45003  0.11698
   7   3.208 VB S  0.0432 1.14947e5  3.35641e4  88.05543
   8   3.382 BV    0.0213 3241.65405 2184.31519  2.48328
   9   3.461 VB    0.0176    6.96775    6.33958  0.00534
  10  17.938 BB    0.0198  570.31329  444.21979  0.43689

Totals :                  1.30539e5  4.66764e4
```

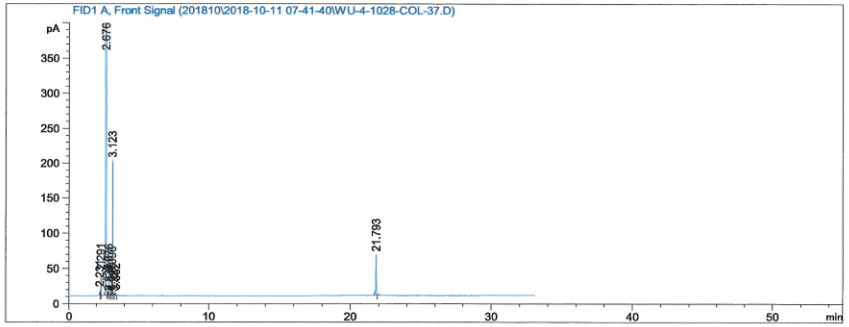
Original spectra for **69a**:





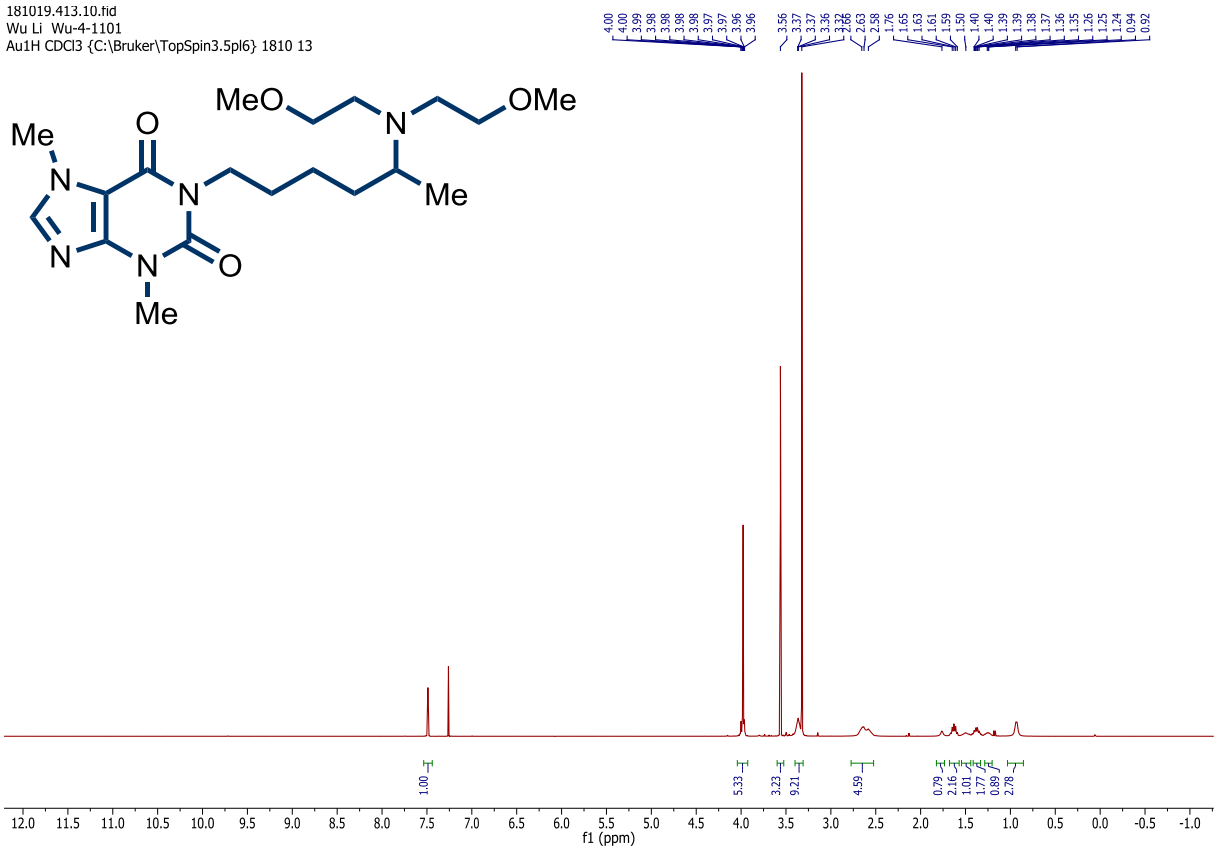
Data File C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\WU-4-1028-COL-37.D
Sample Name: WU-4-1028-col-37

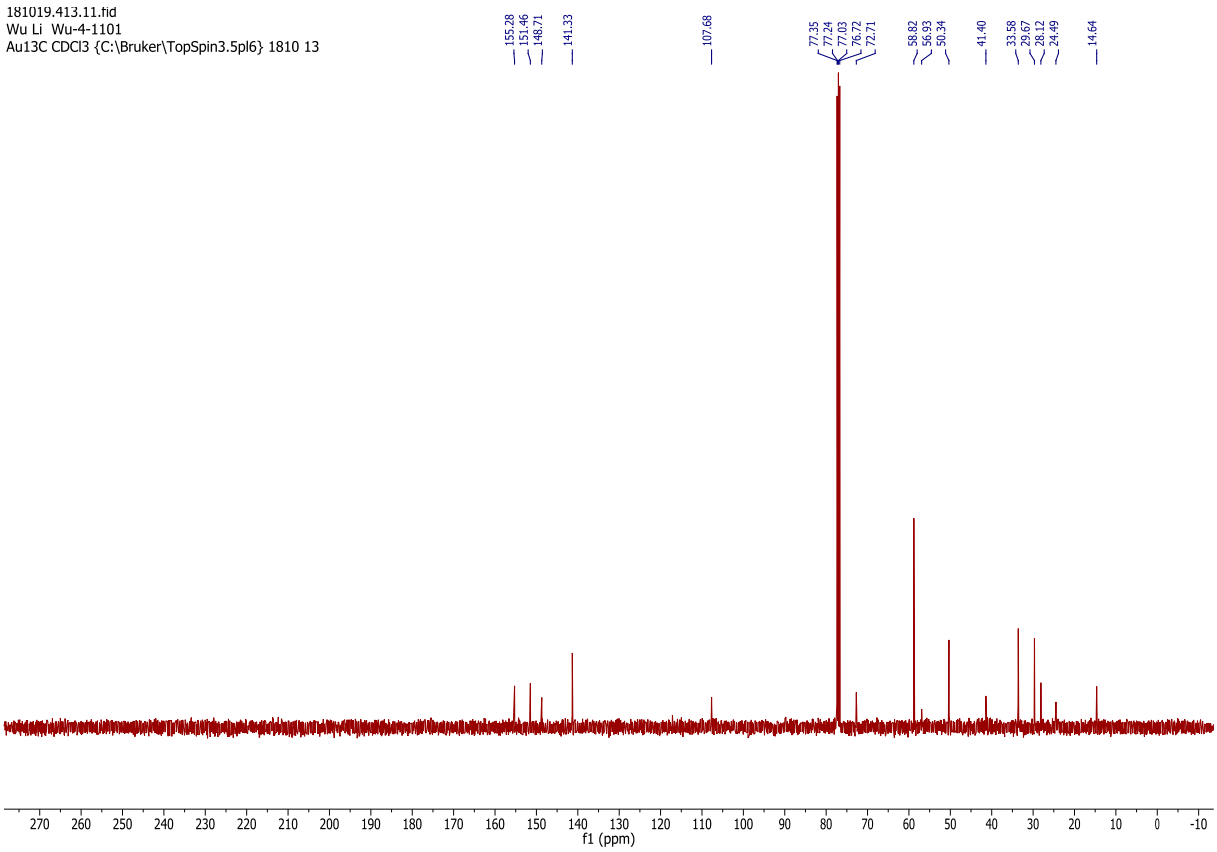
```
======================================================================
Acq. Operator   : Lab 2.112                      Seq. Line :  45
Acq. Instrument : GC Lab.133                     Location : Vial 29
Injection Date  : 10/12/2018 5:07:20 AM              Inj :   1
                                                 Inj Volume : 1 µl
Method          : C:\CHEM32\1\DATA\201810\2018-10-11 07-41-40\STANDARDMTH.M (Sequence Method)
Last changed    : 5/24/2017 4:48:45 PM by Lab 2.112
Method Info     : HP5 (30x0.25x0.25): 50/8-120/0/15-200/0/25-300/10; 1mL/min; 260i320d
```



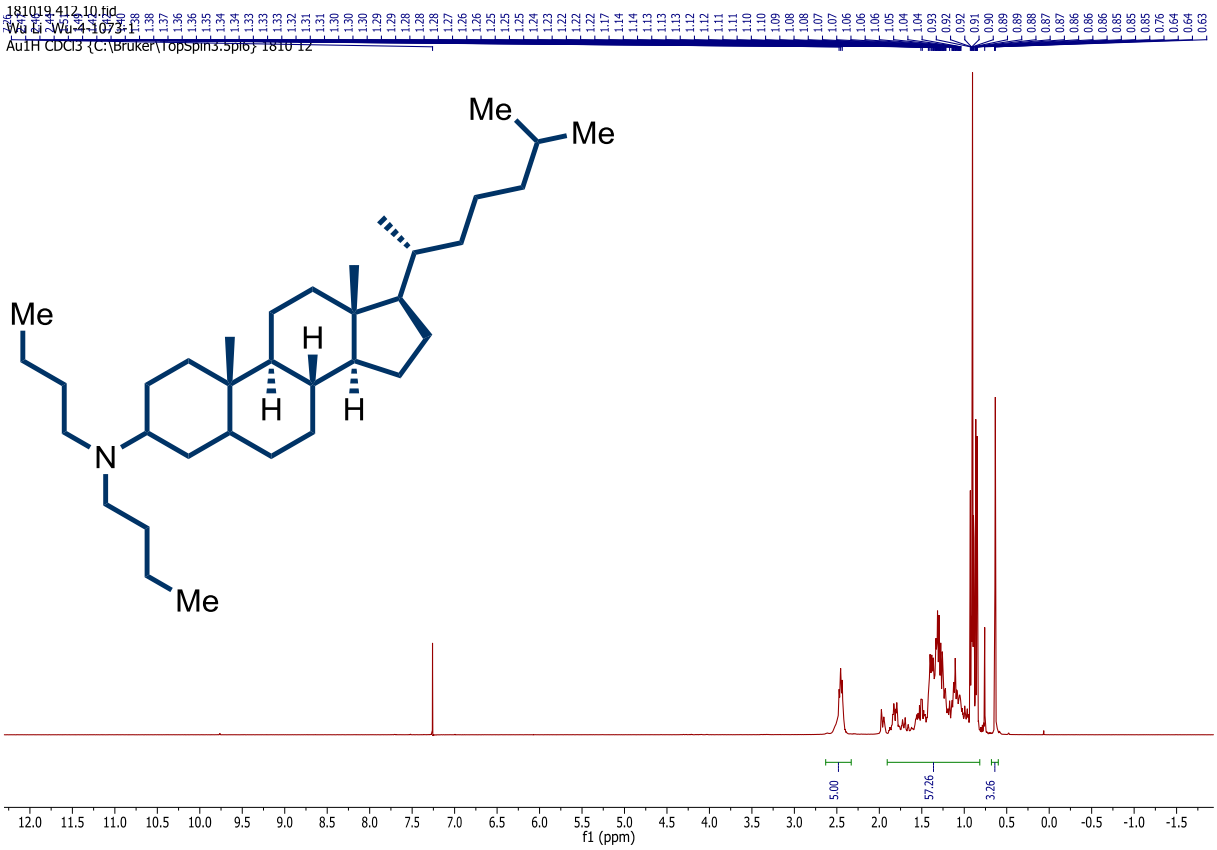

```
======================================================================
                    Internal Standard Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs
======================================================================
======================================================================
                    Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: FID1 A, Front Signal

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]        %
----|-------|----|-------|----------|----------|--------|
   1   2.231 BV    0.0172    9.58794    8.46316  0.01263
   2   2.291 VB    0.0166   34.30347   31.85532  0.04519
   3   2.676 BB S  0.0454 7.54190e4  3.08000e4  99.35167
   4   2.834 BB    0.0146    1.77279    1.94322  0.00234
   5   2.876 BB    0.0146   28.00041   30.85436  0.03689
```

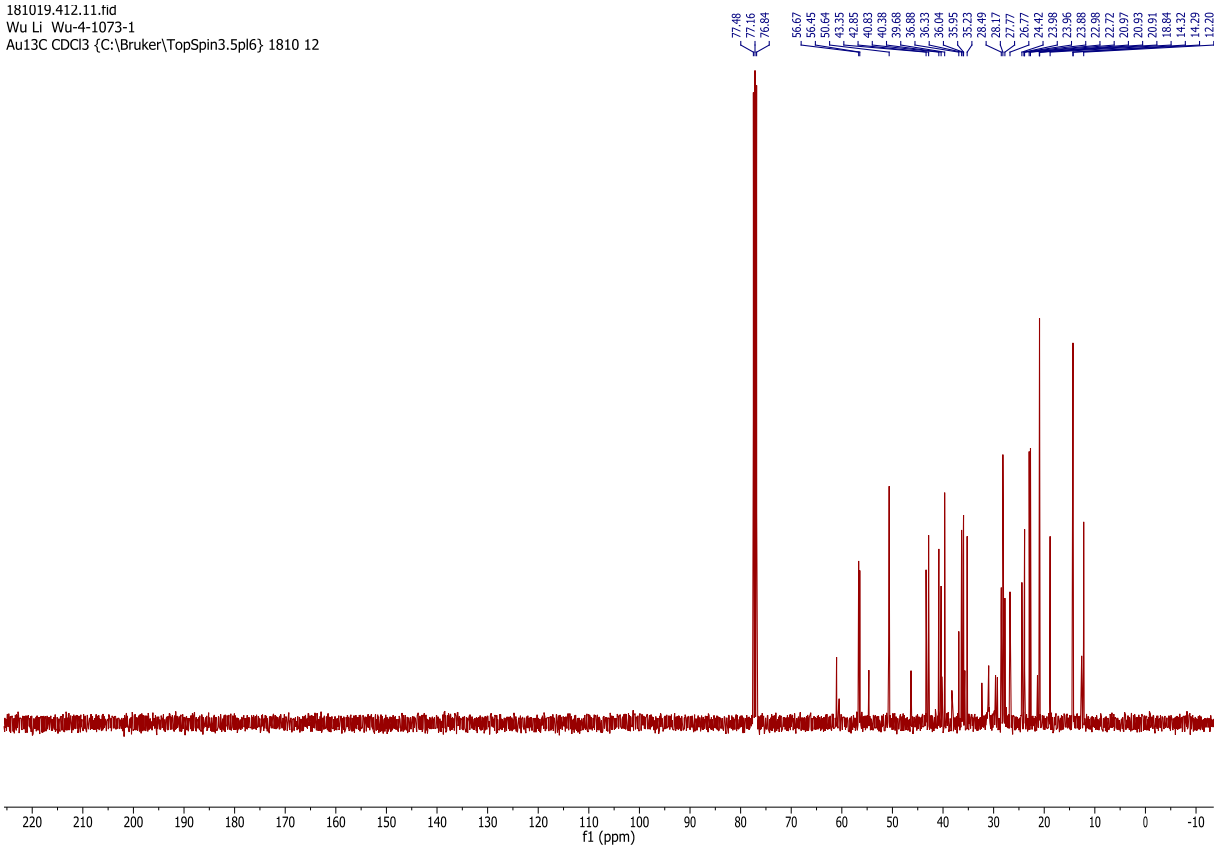
Original spectra for **70a**:



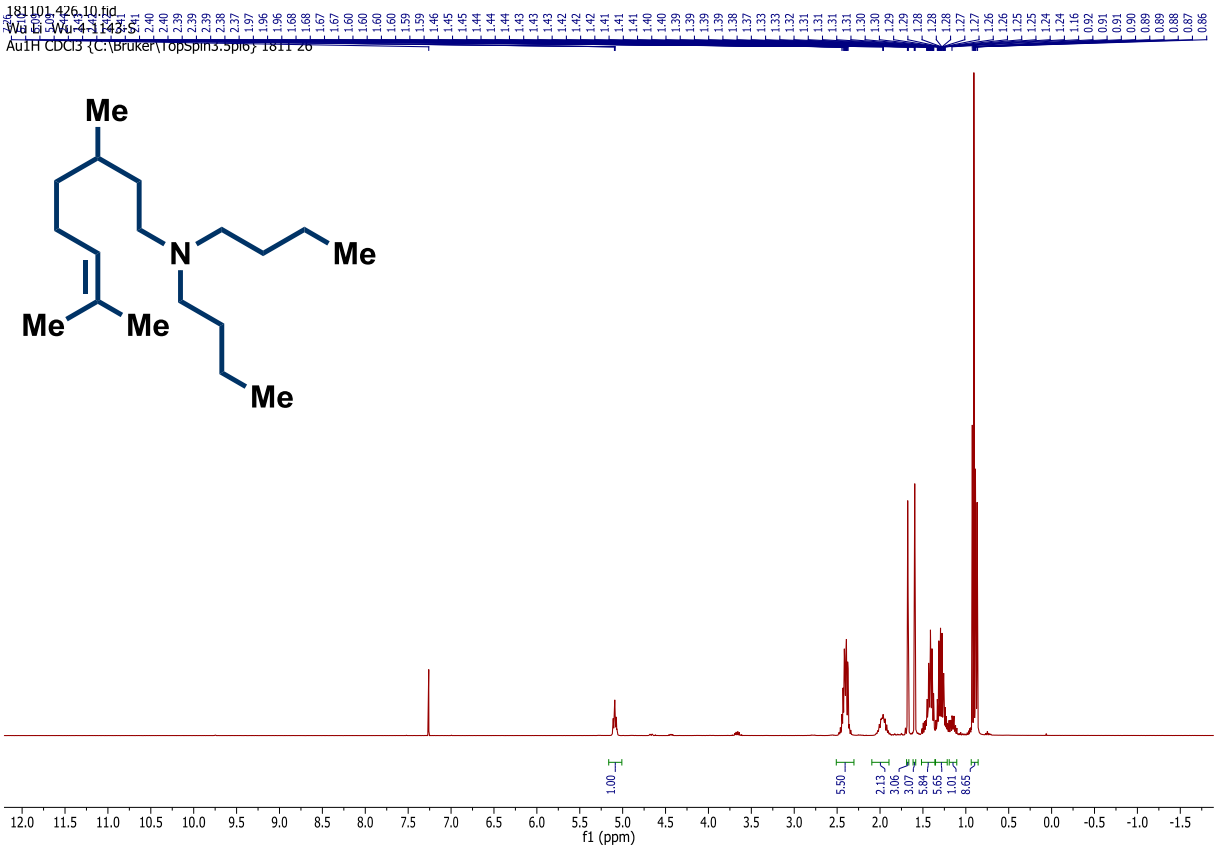


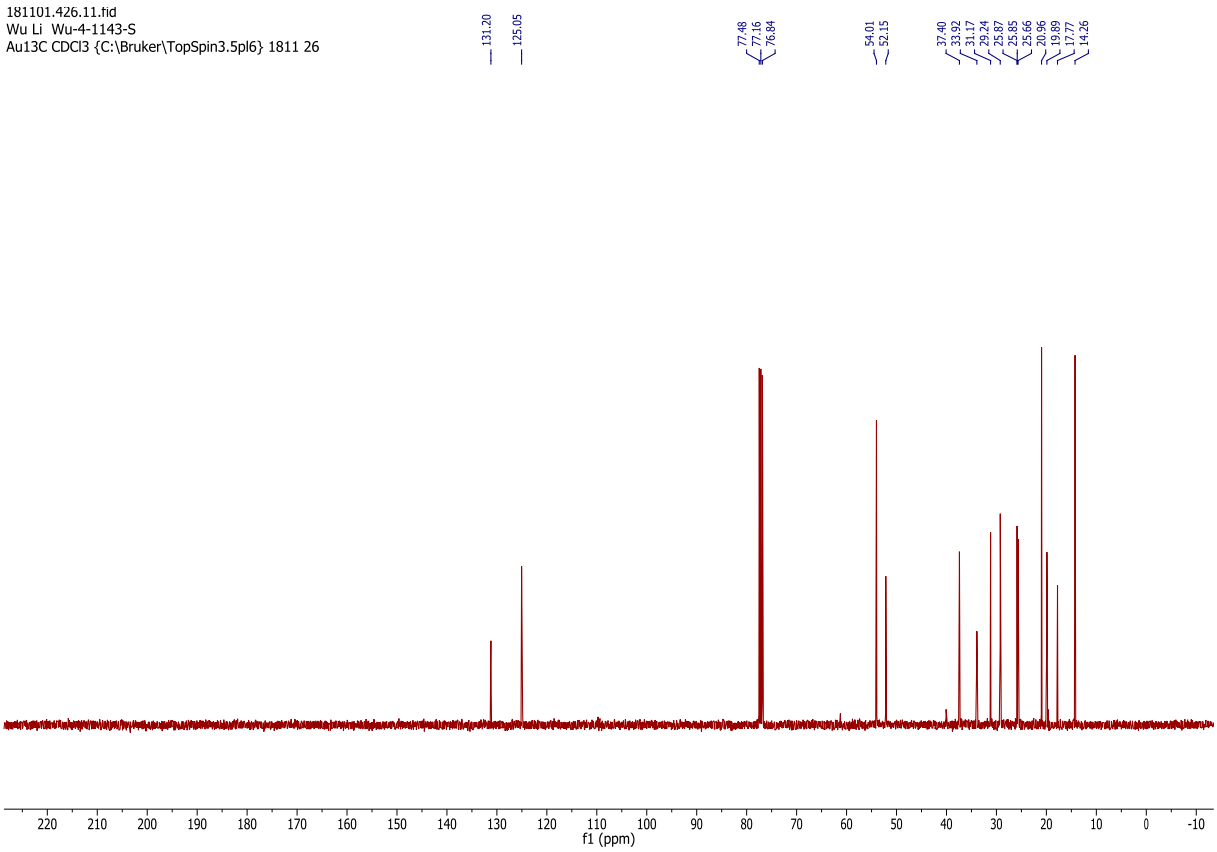
Original spectra for **71a**:



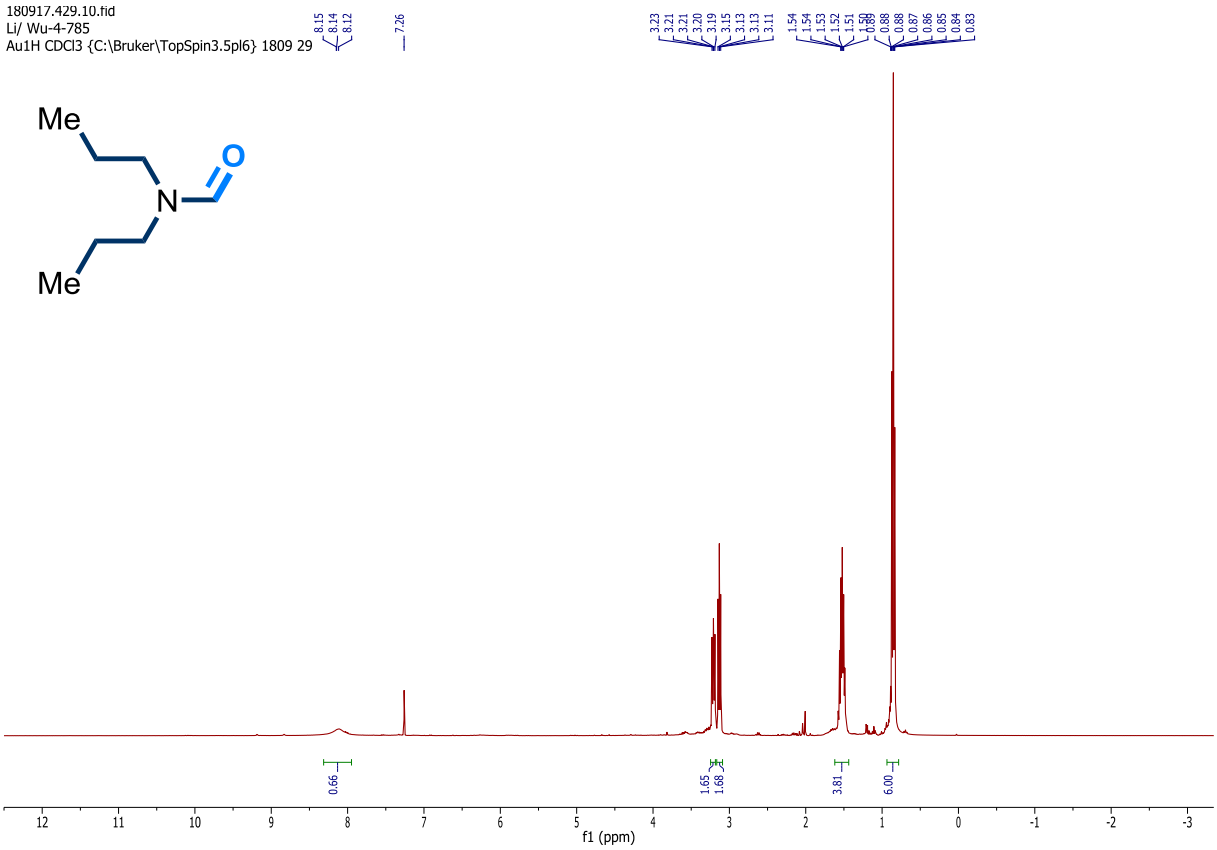


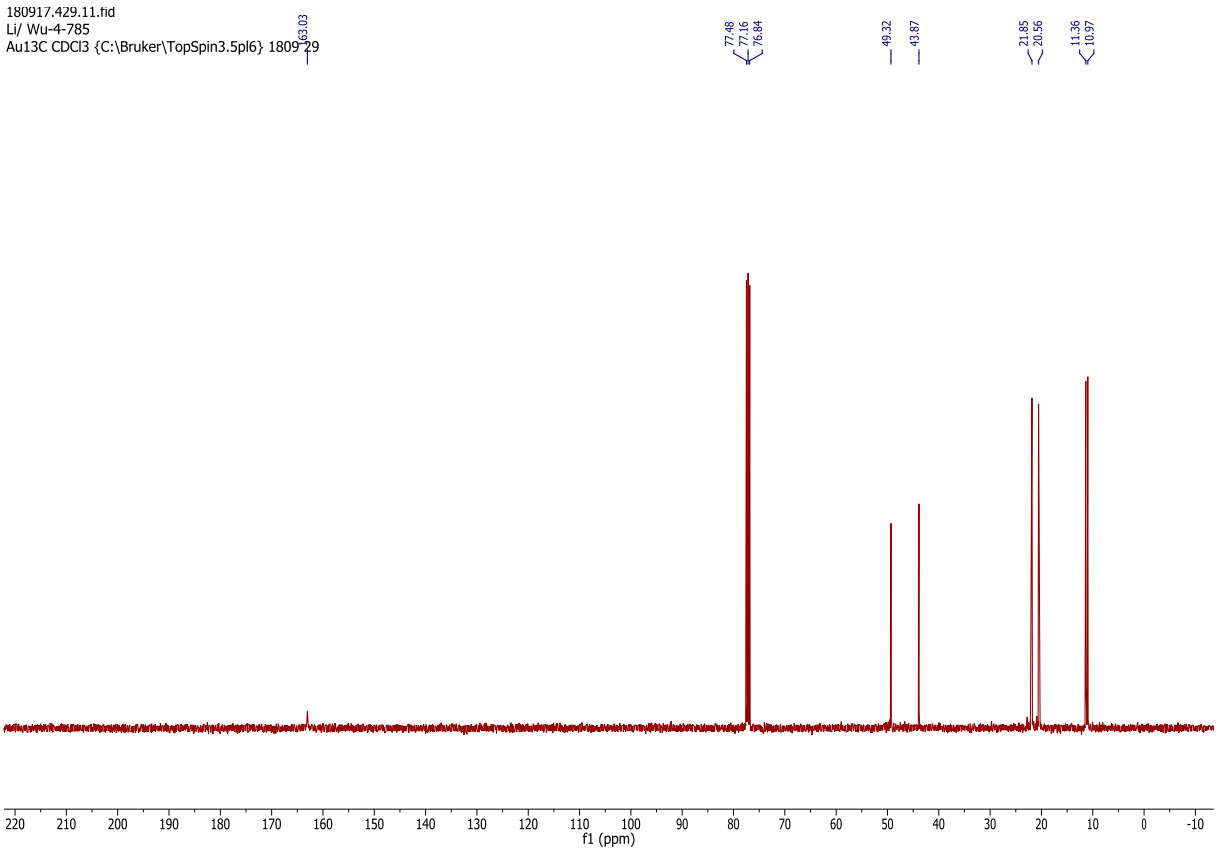
Original spectra for **72a**:



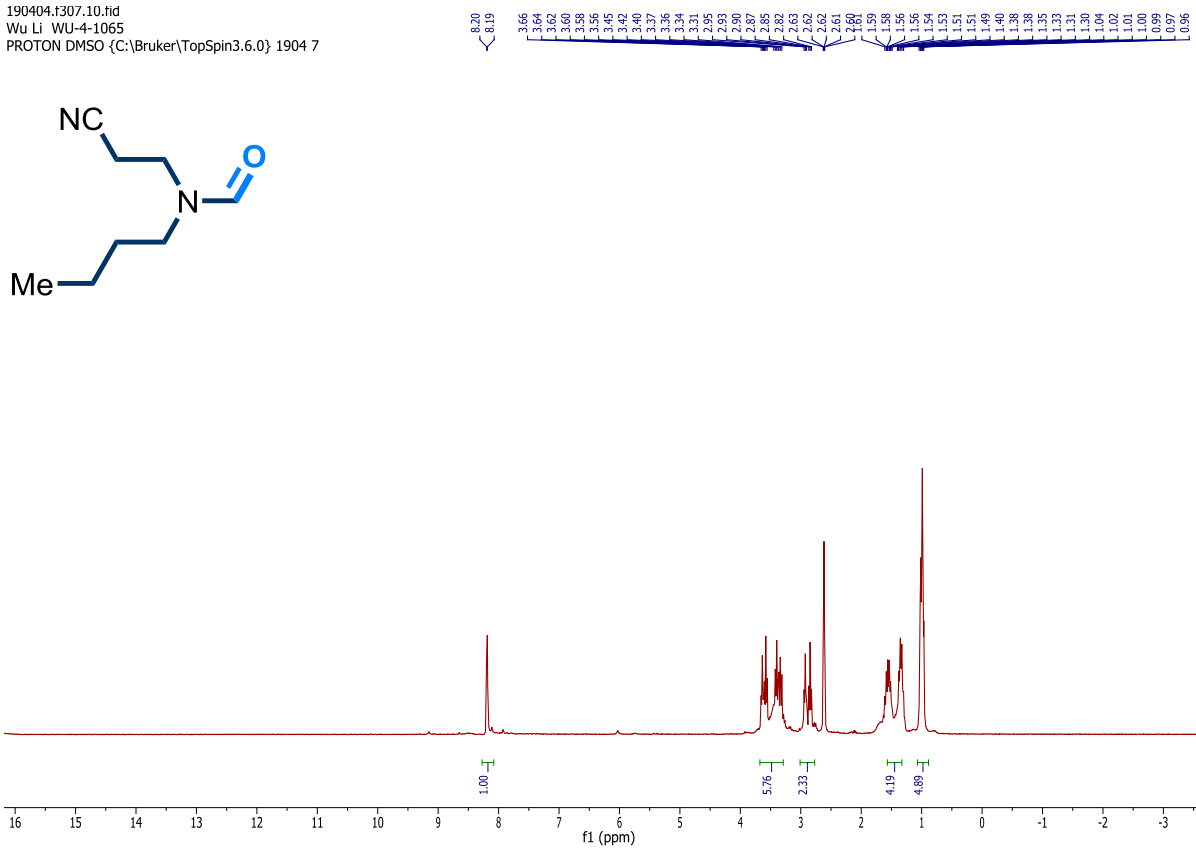


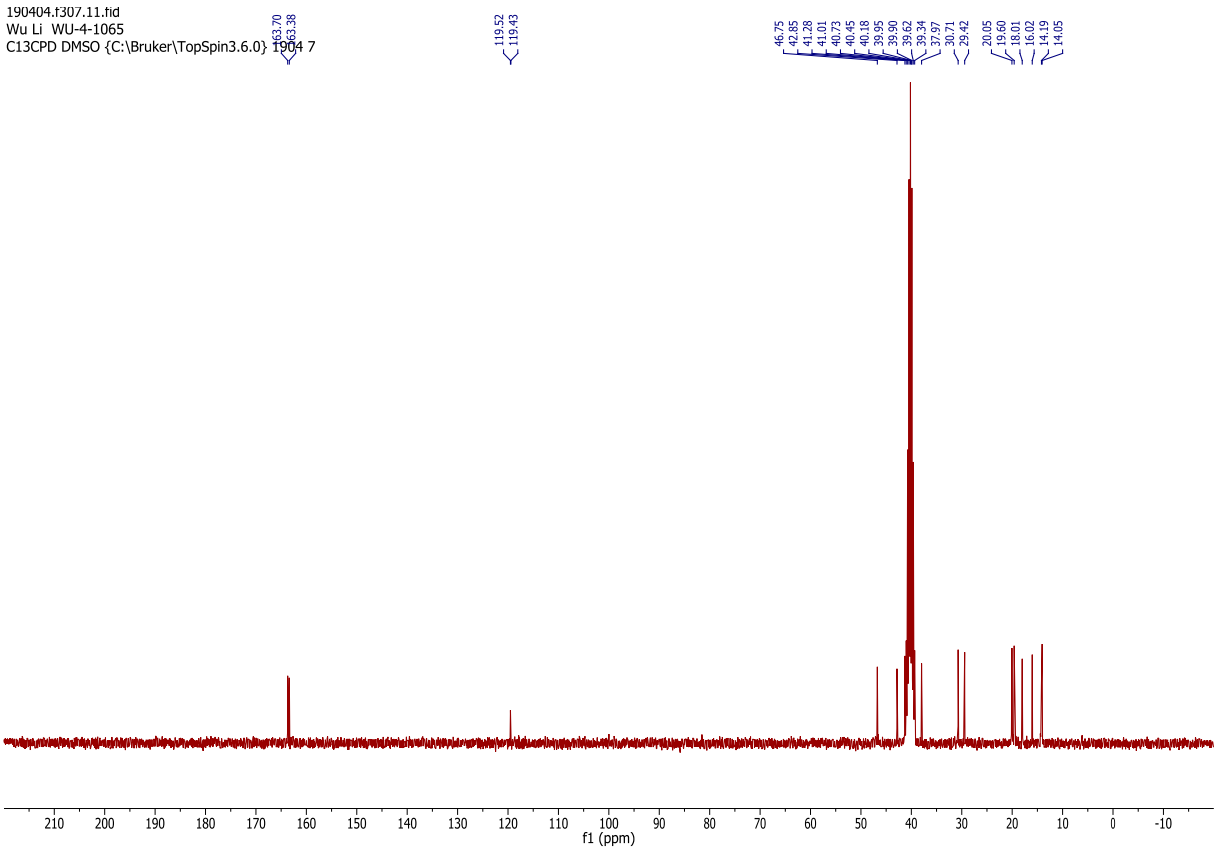
Original spectra for **2b**:



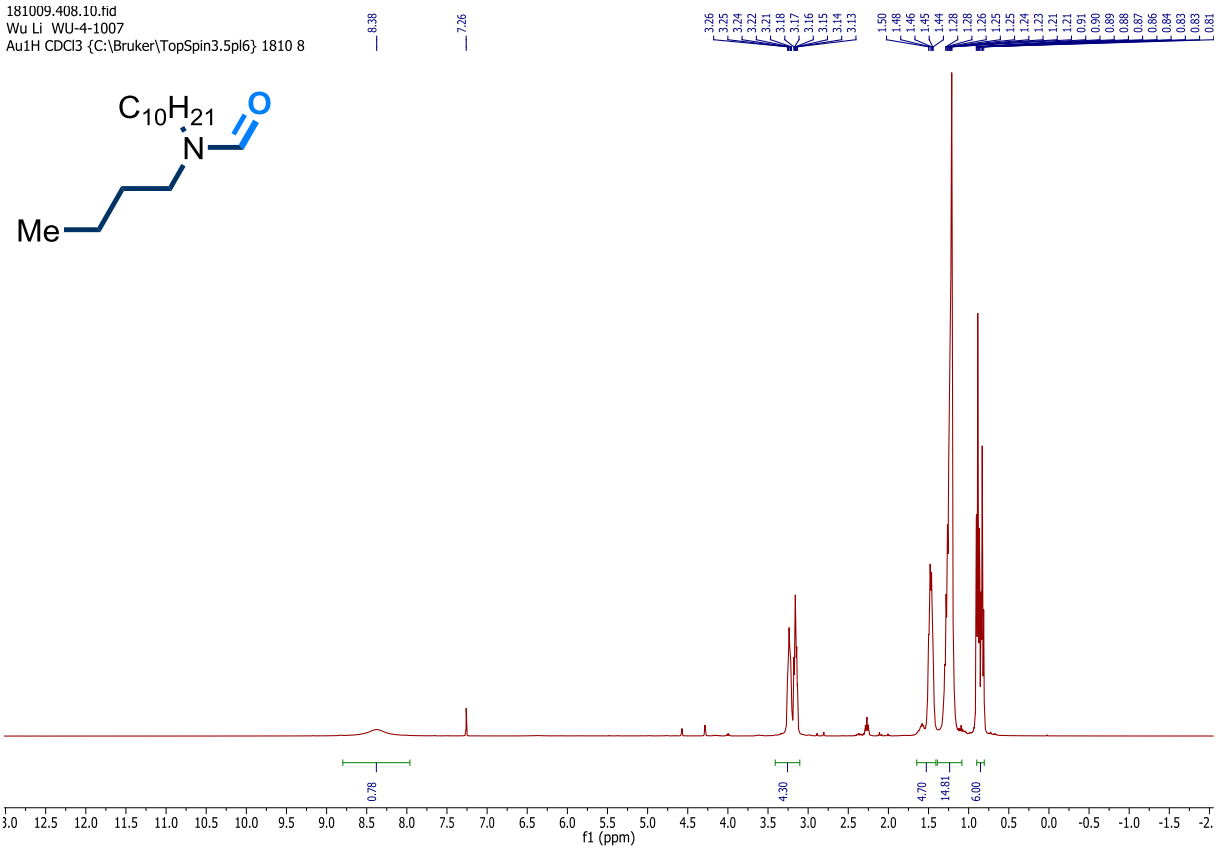


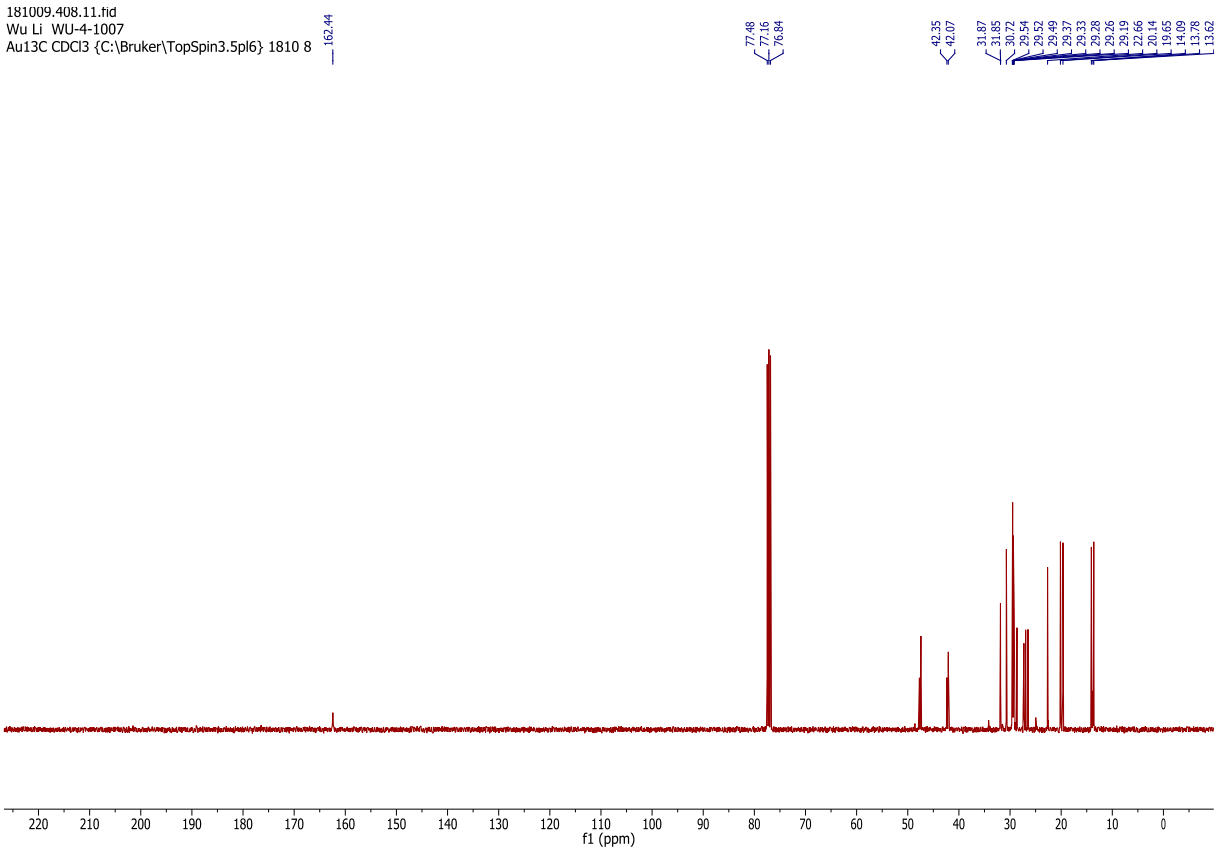
Original spectra for **5b**:



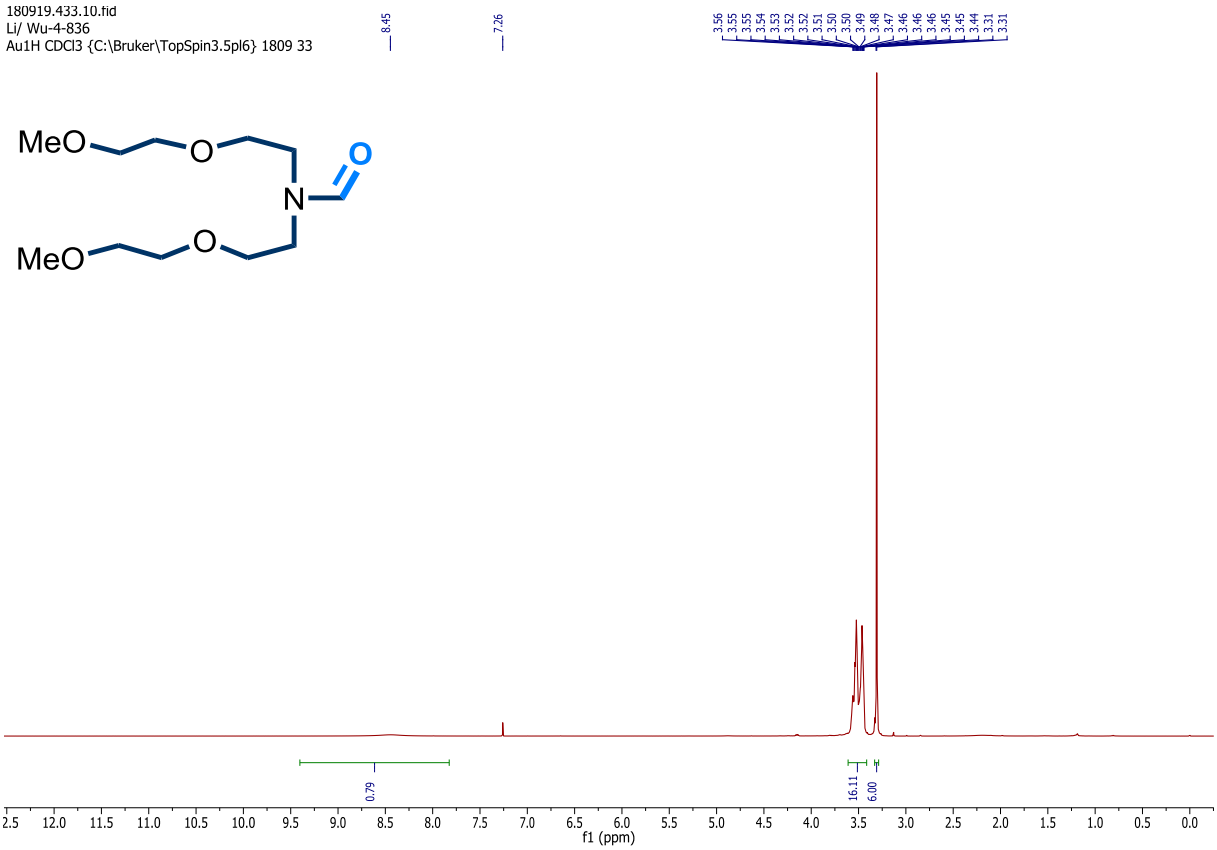


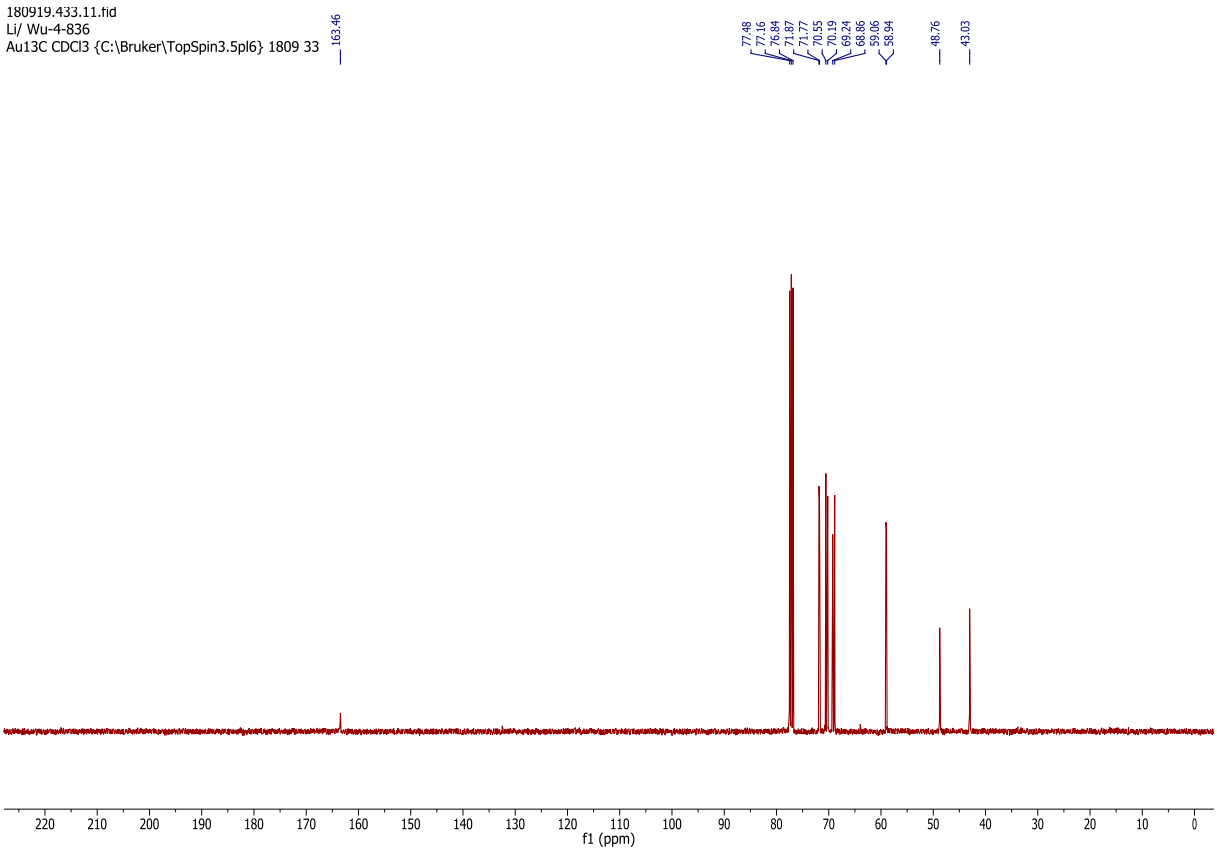
Original spectra for **6b**:



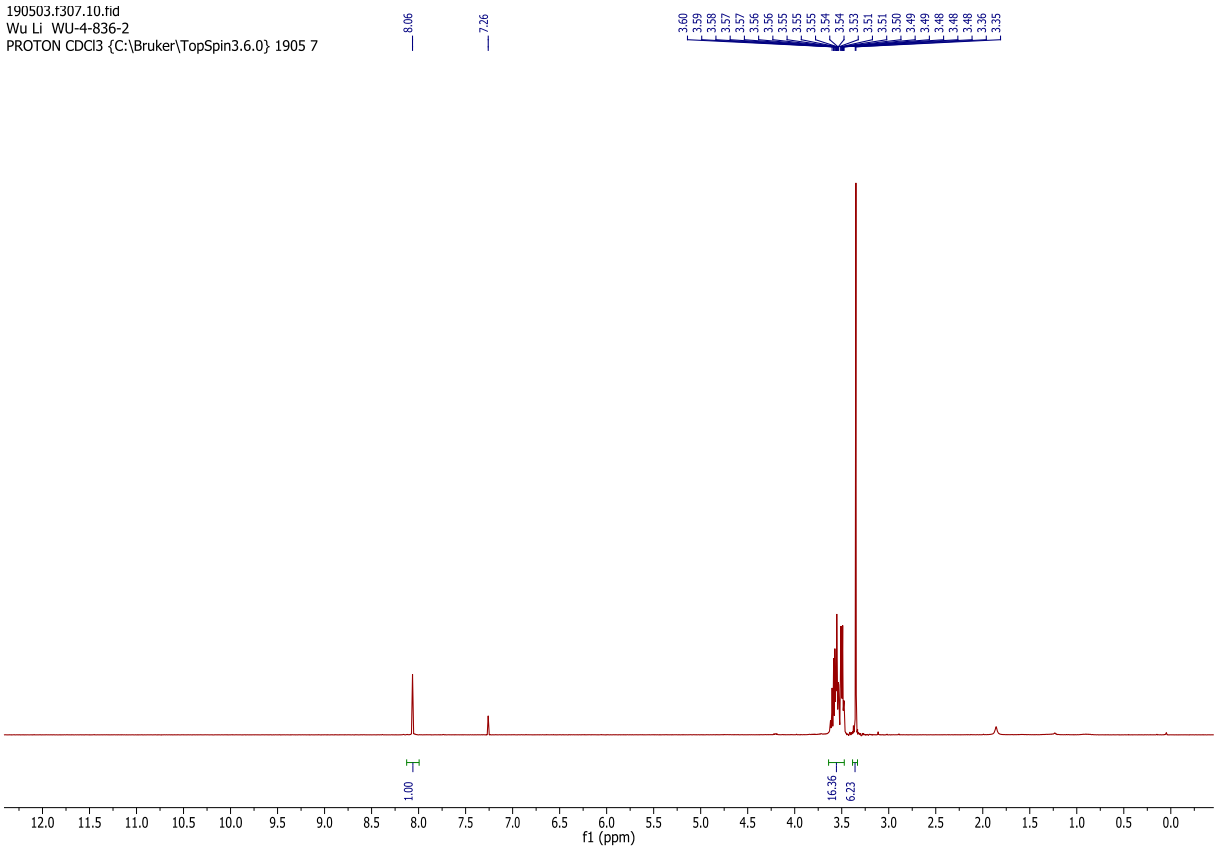


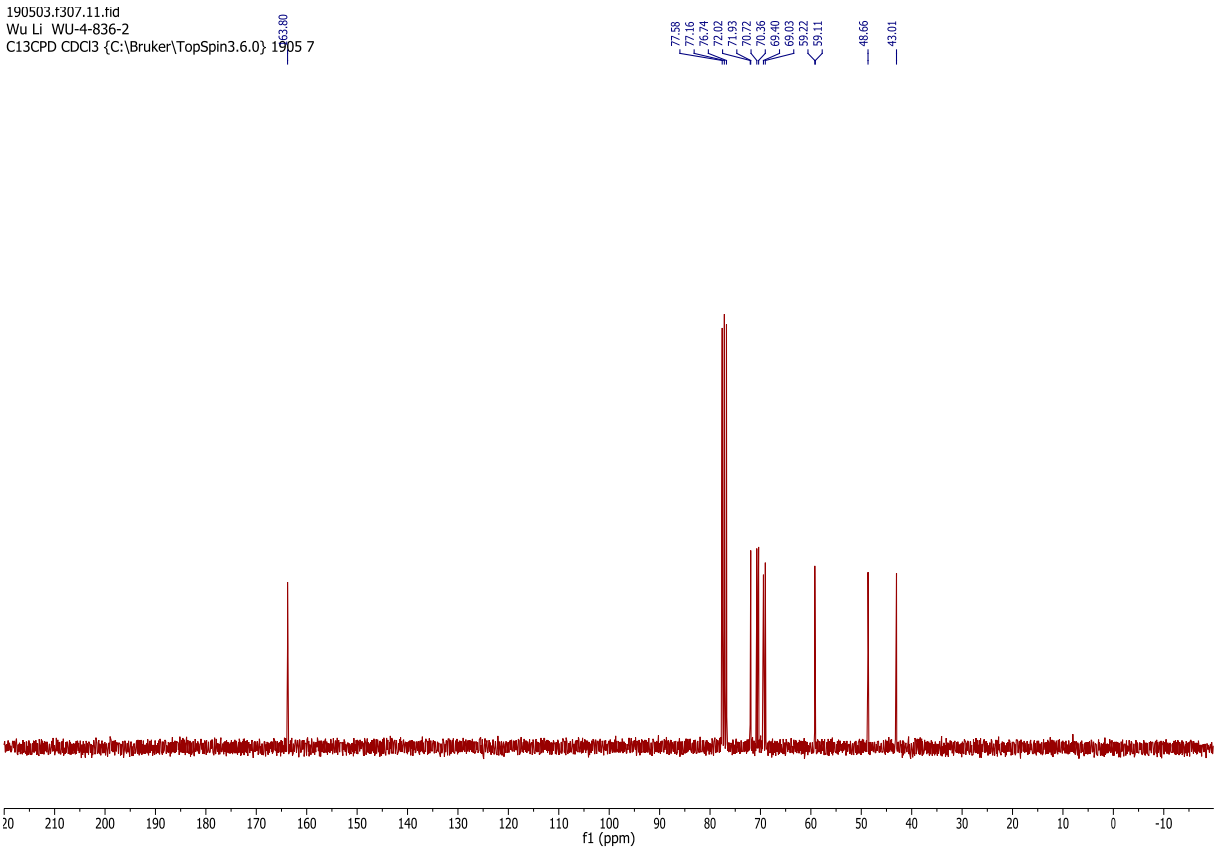
Original spectra for **7b**:



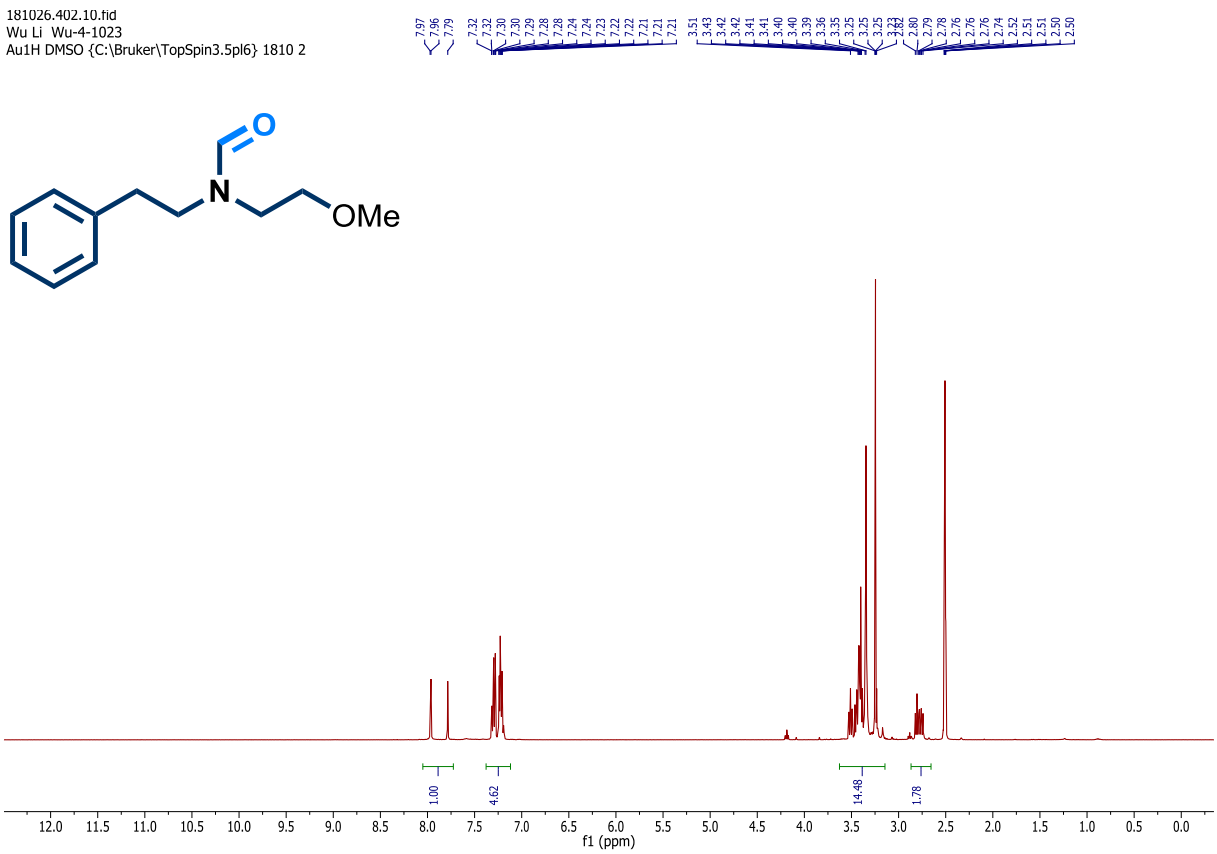


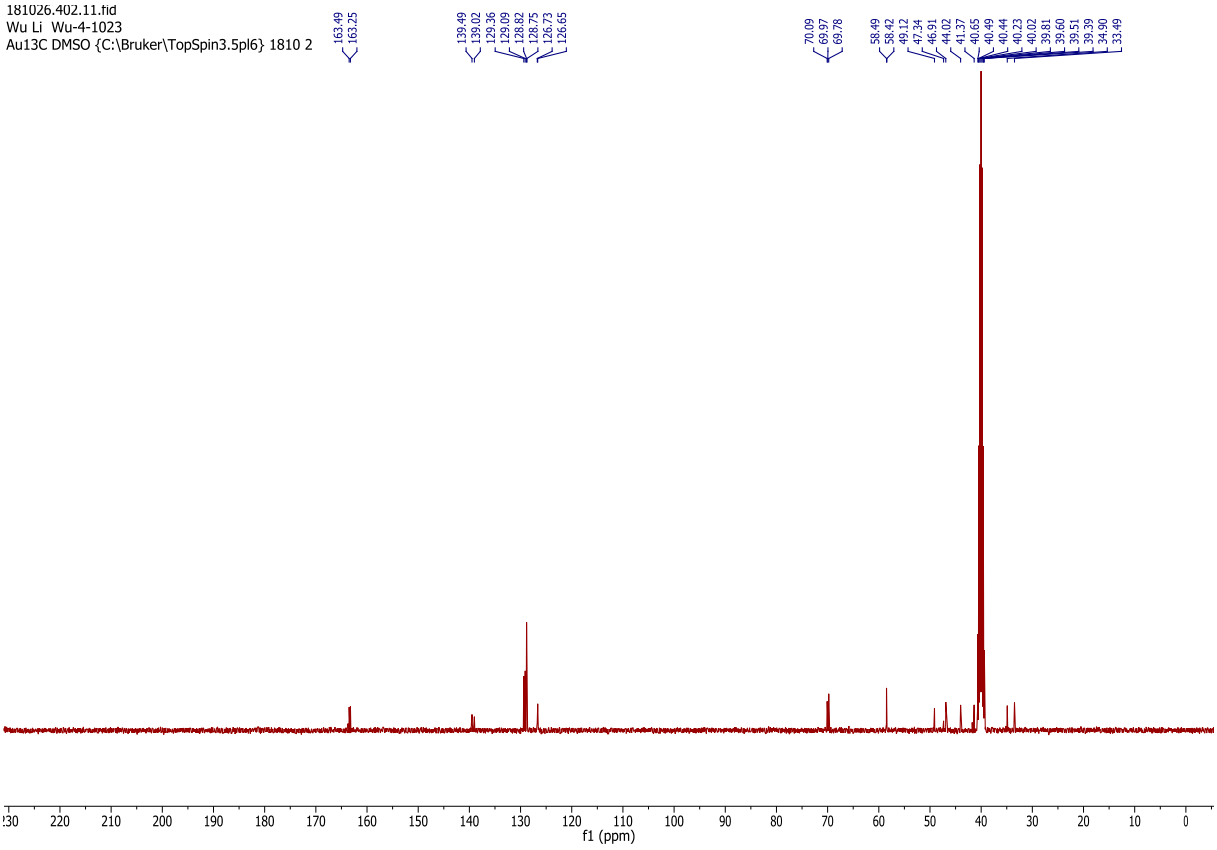
Original spectra for **7b** (The $CDCl_3$ was filtered through K_2CO_3.)



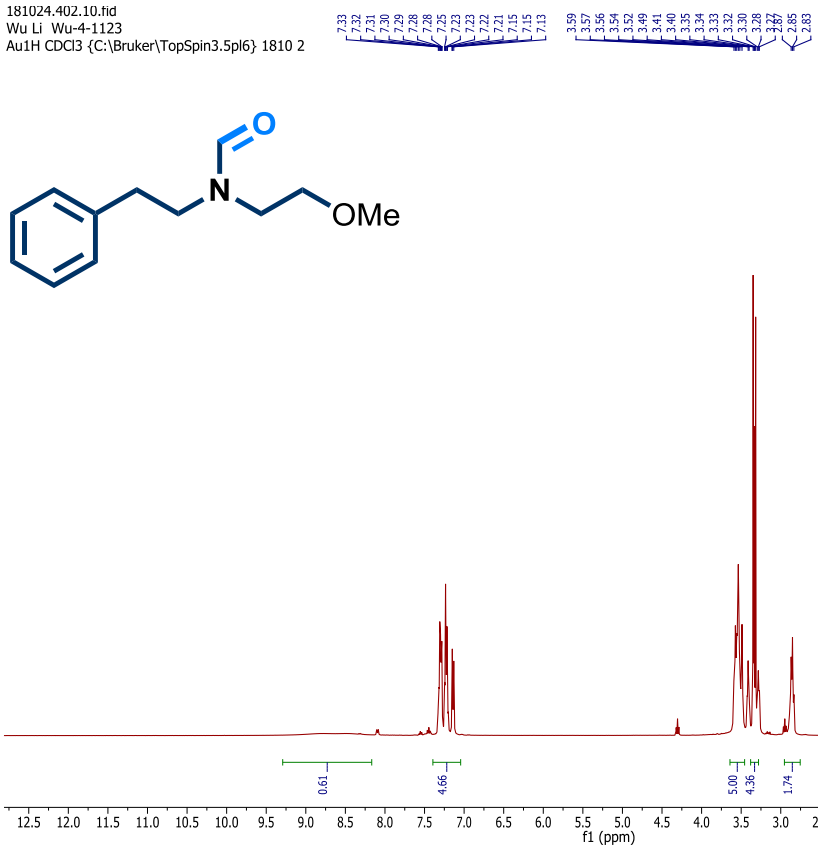


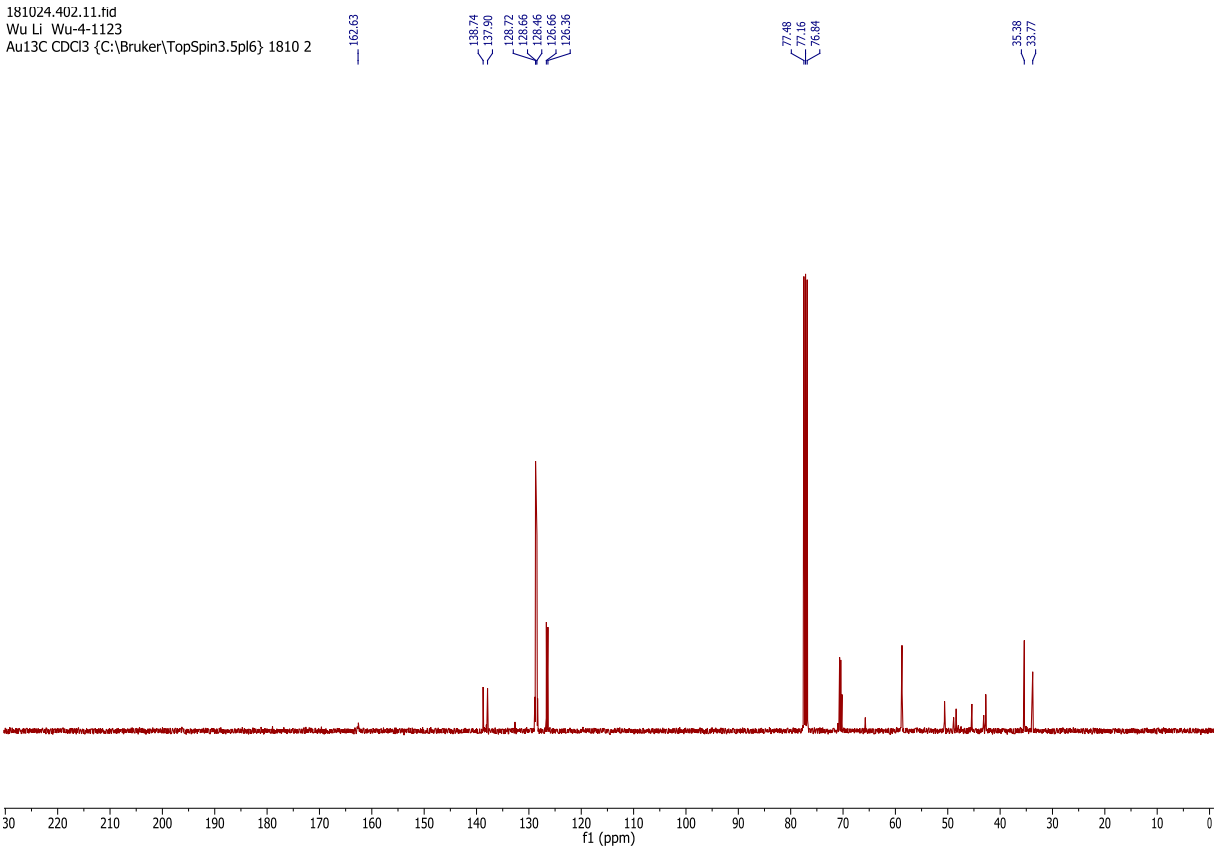
Original spectra for **8b** (in DMSO-*d6*):



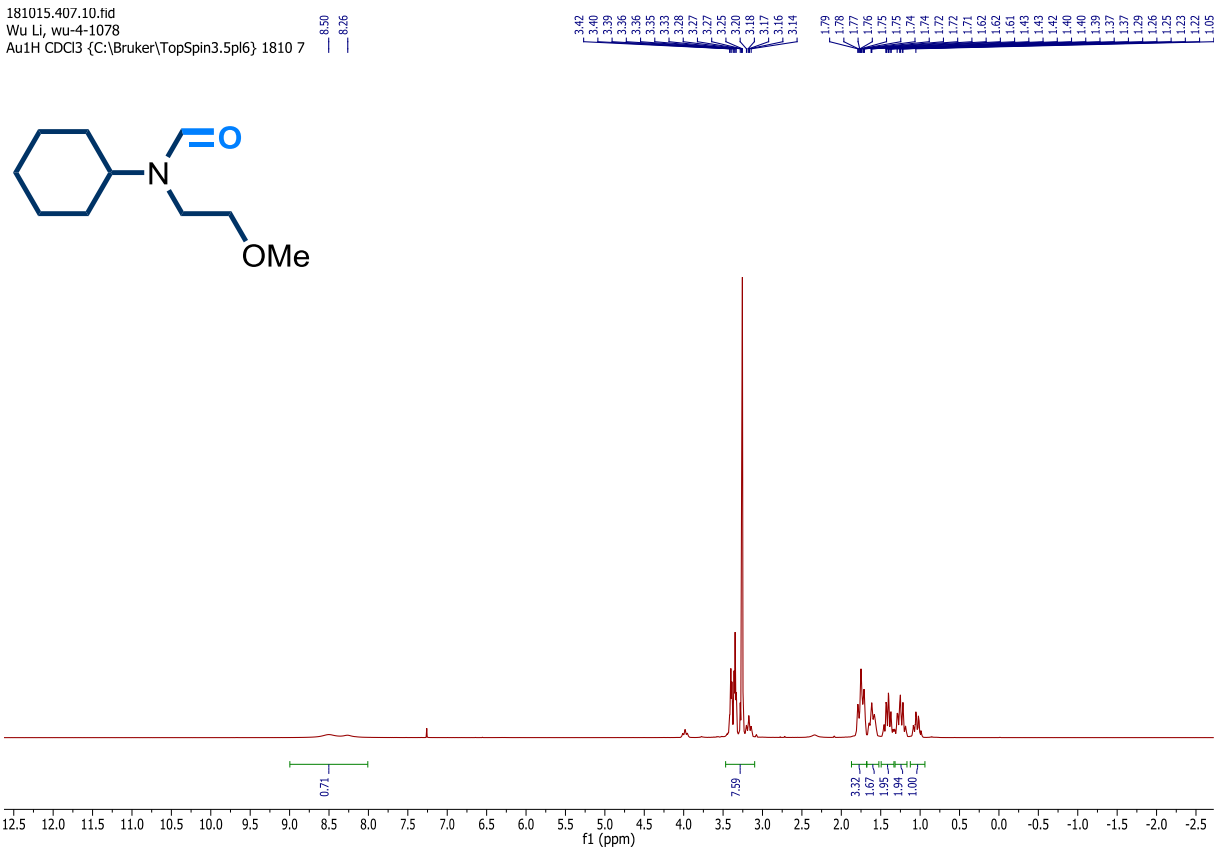


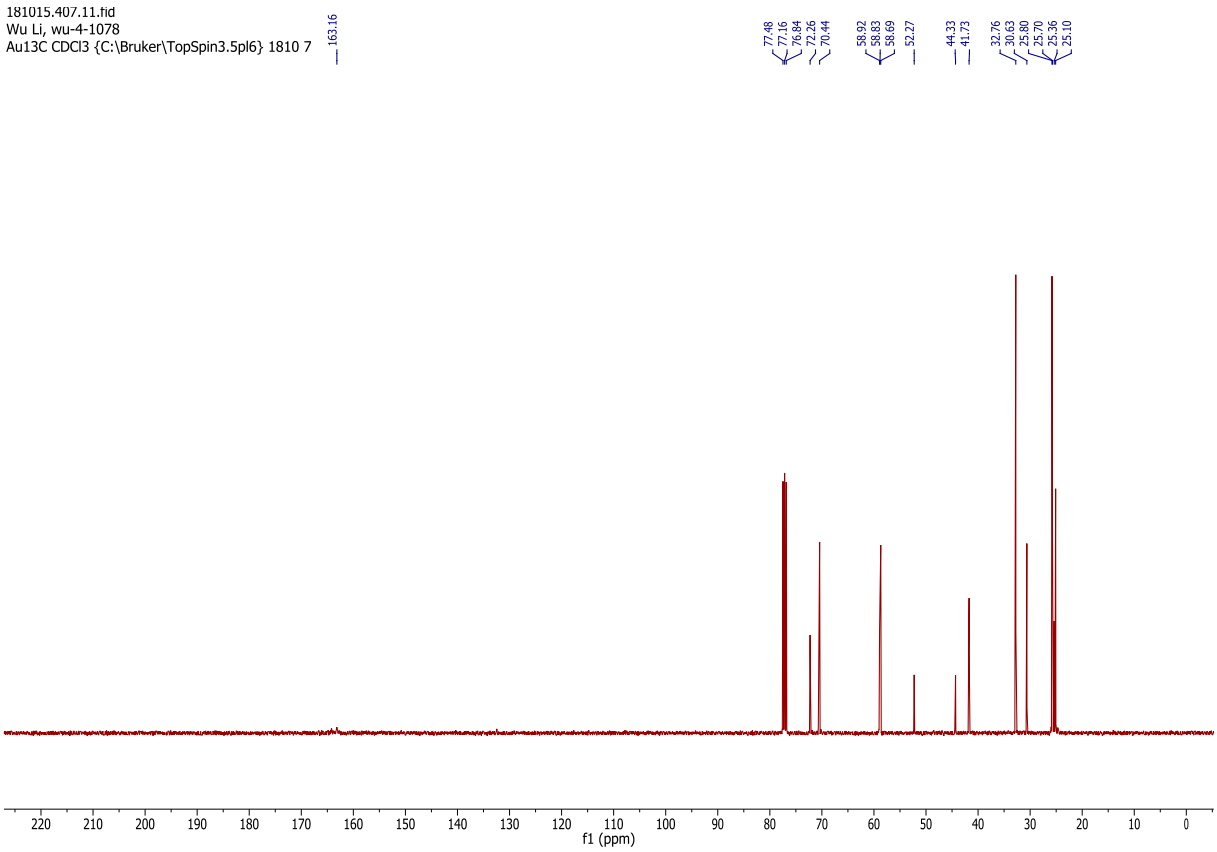
Original spectra for **8b** (in $CDCl_3$):



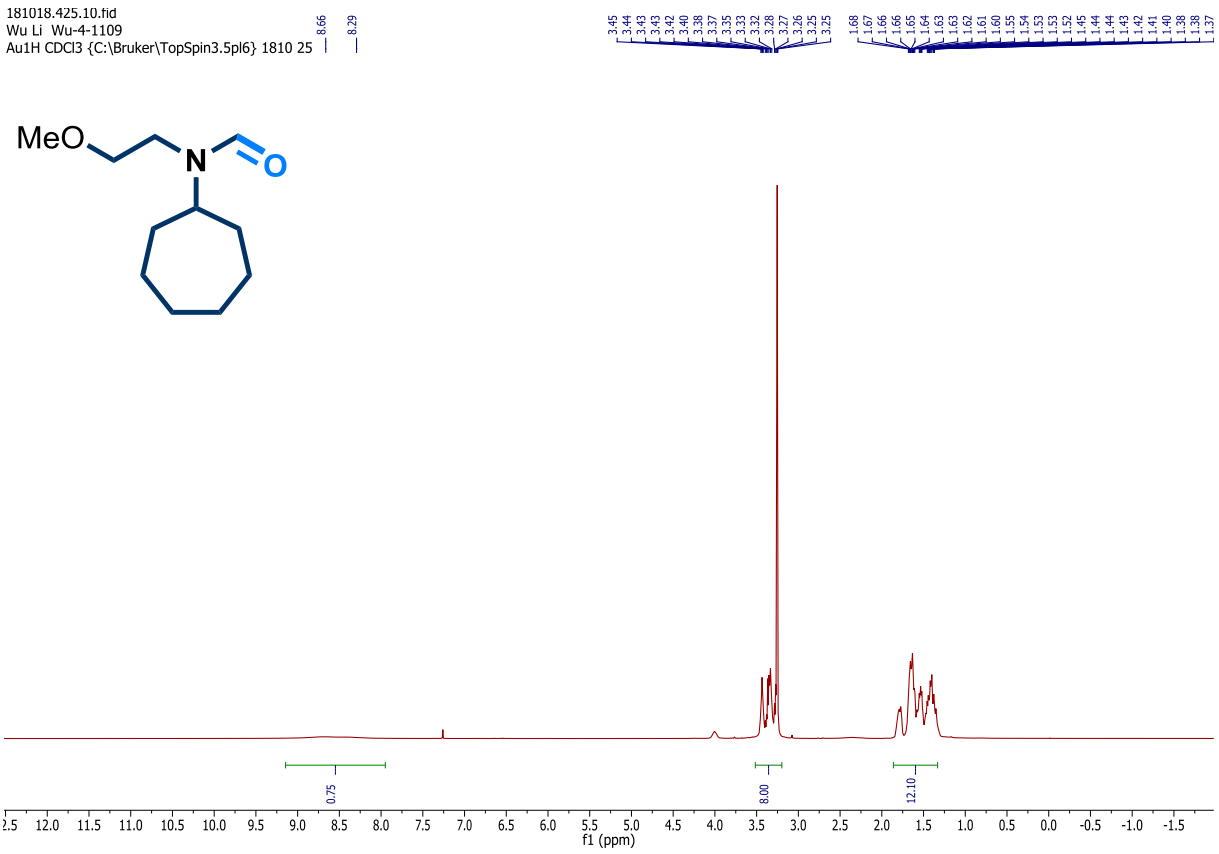


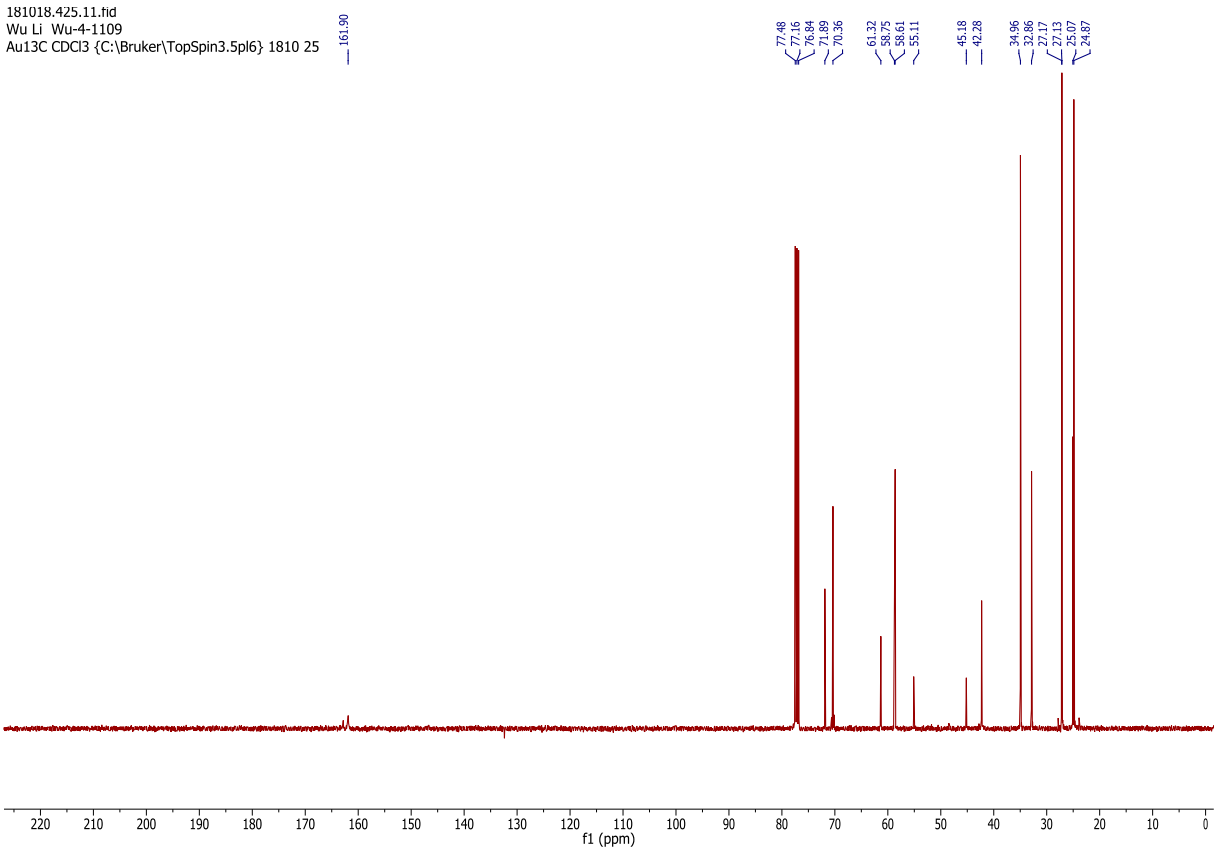
Original spectra for **9b**:



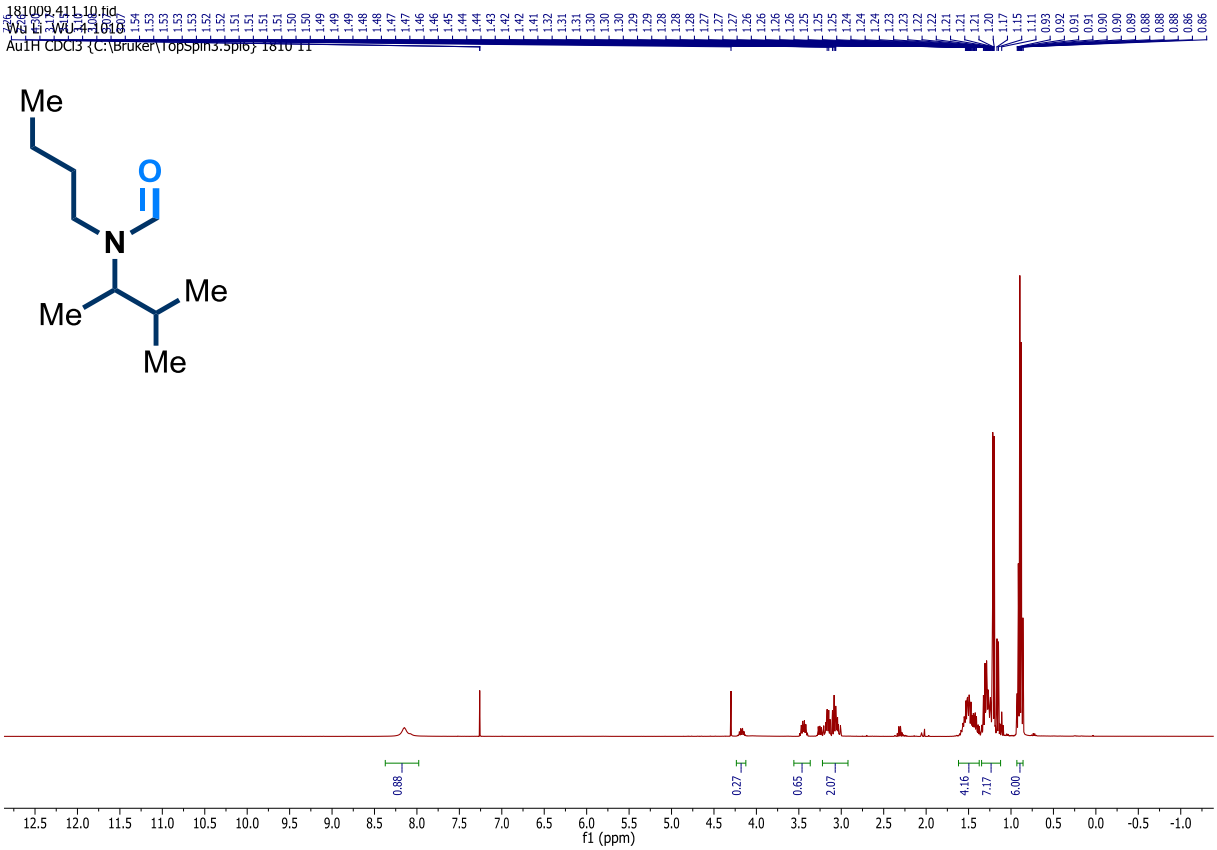


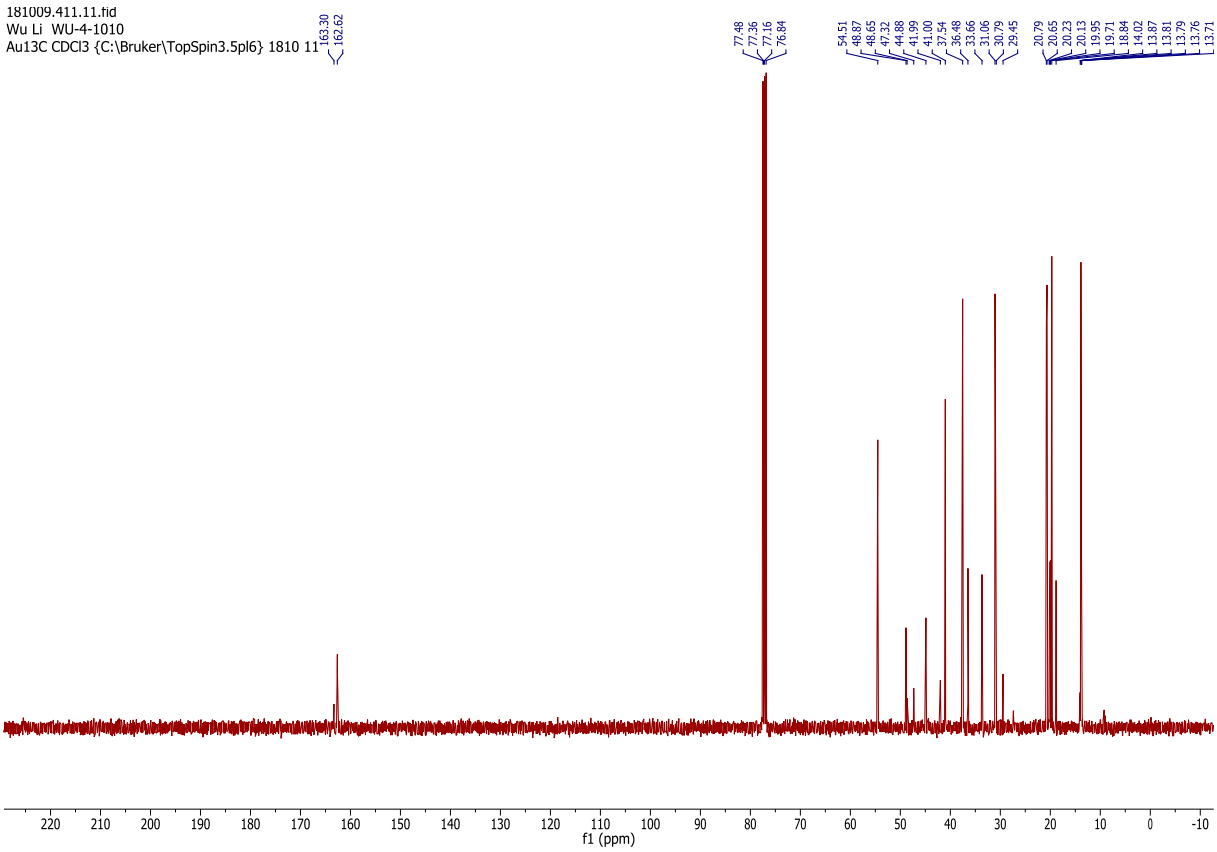
Original spectra for **10b**:



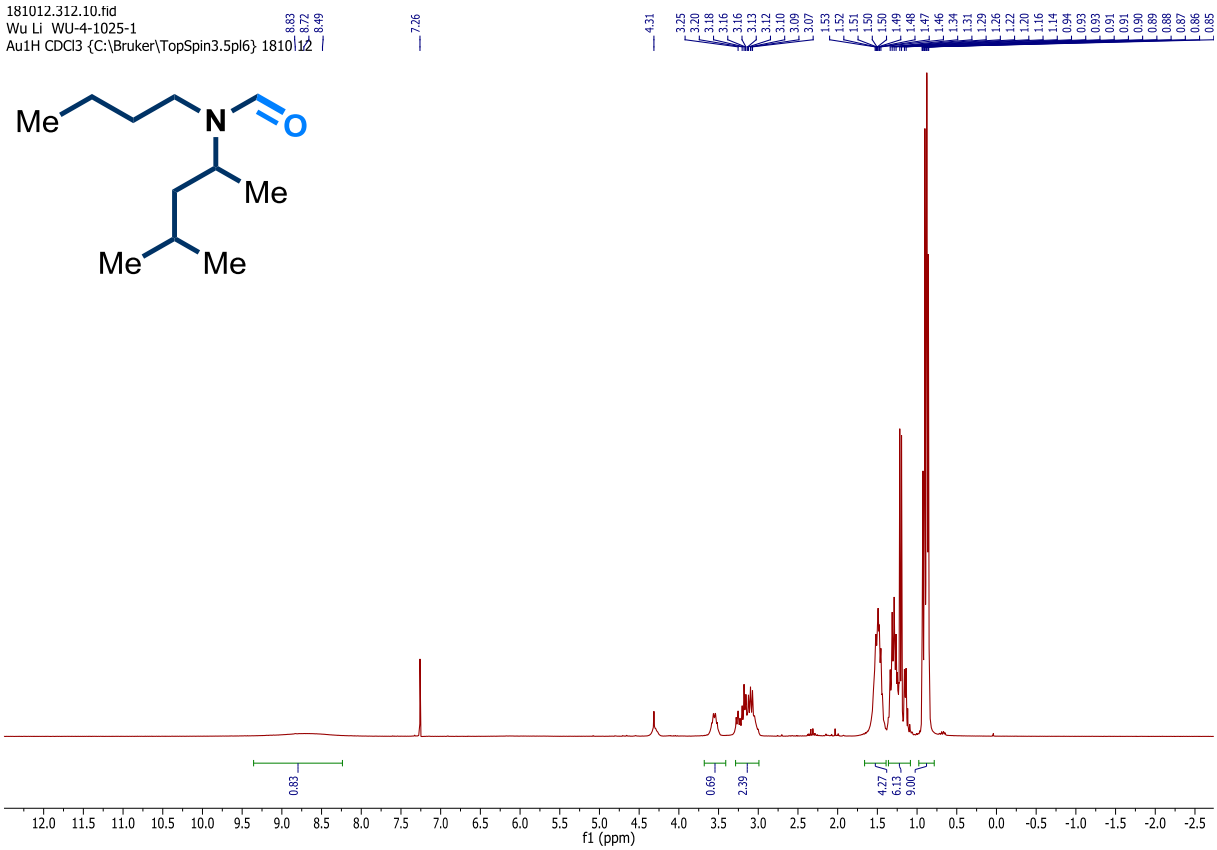


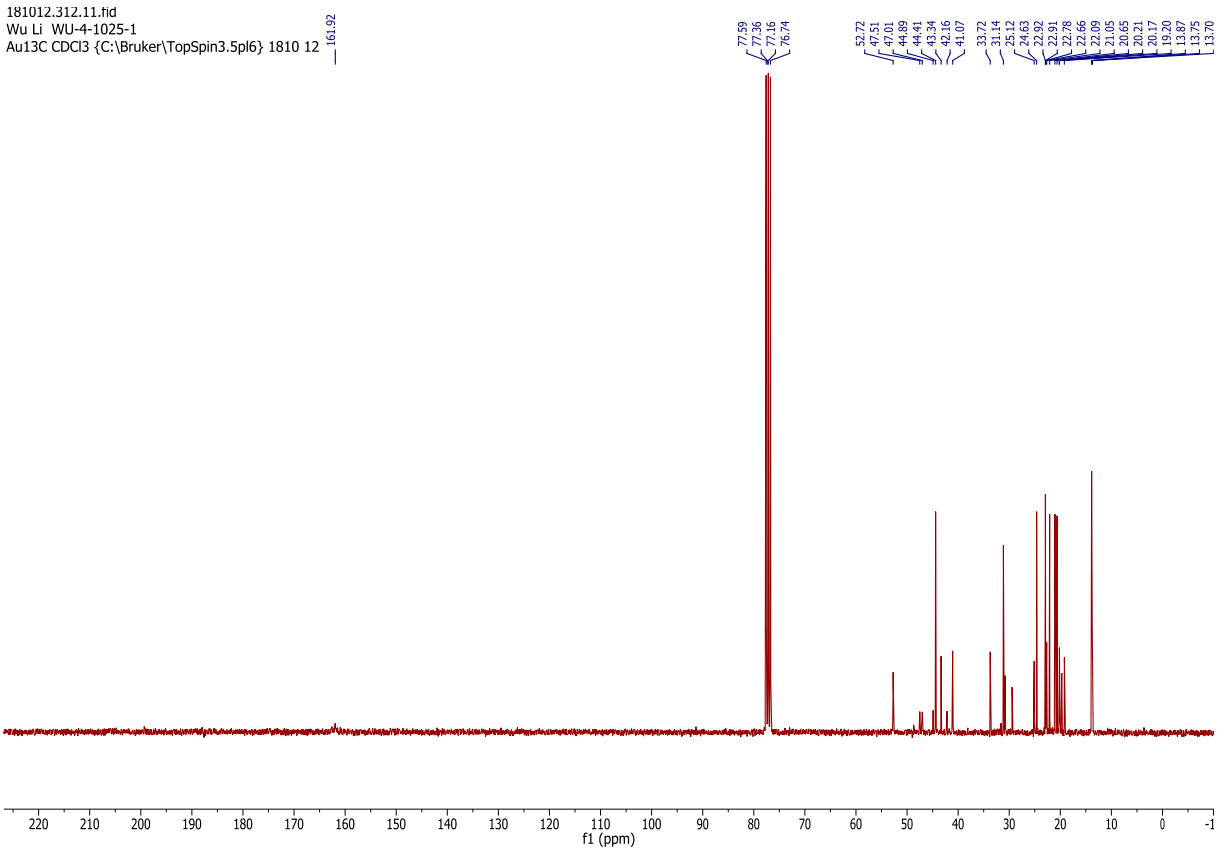
Original spectra for **11b**:



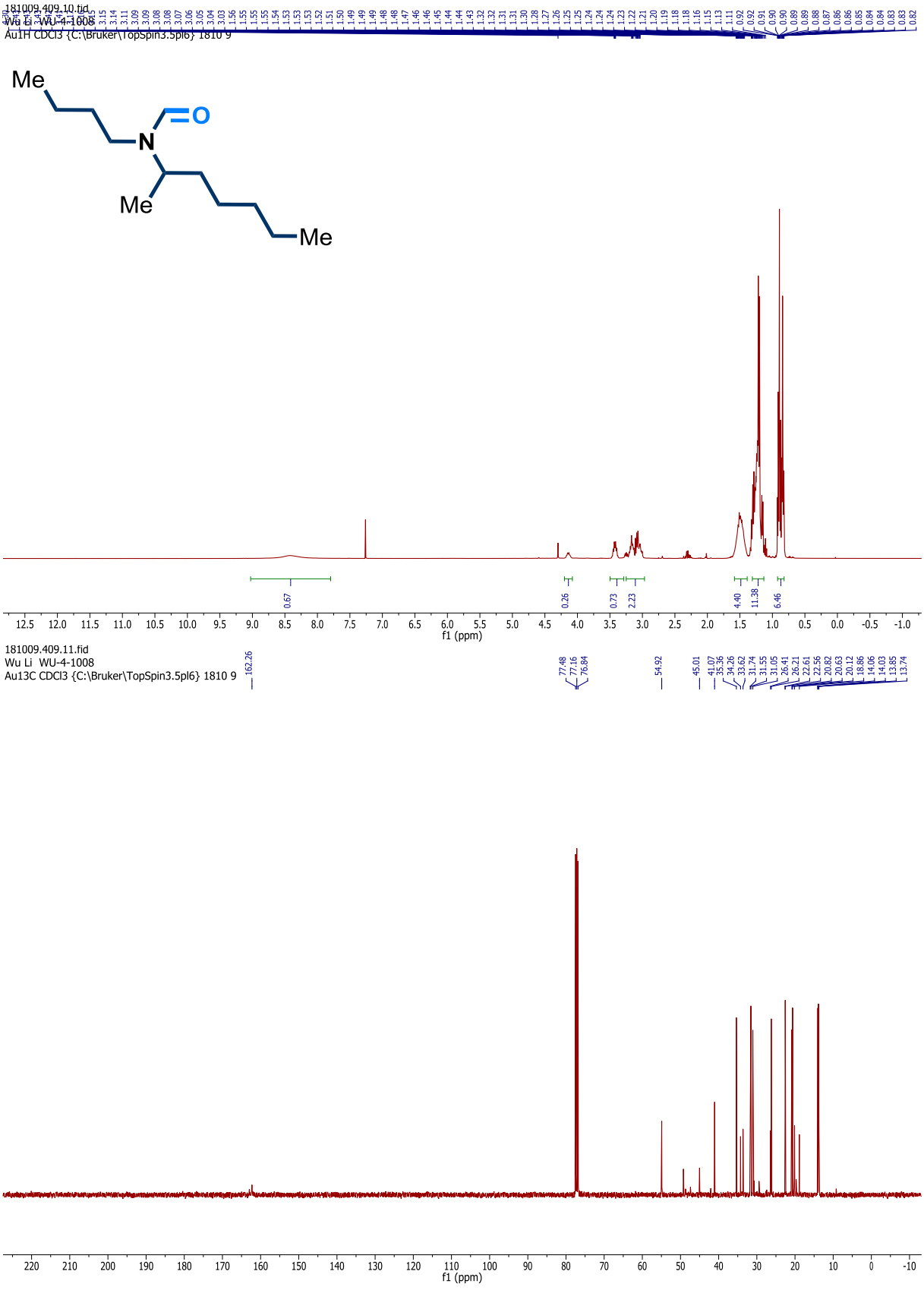


Original spectra for **12b**:

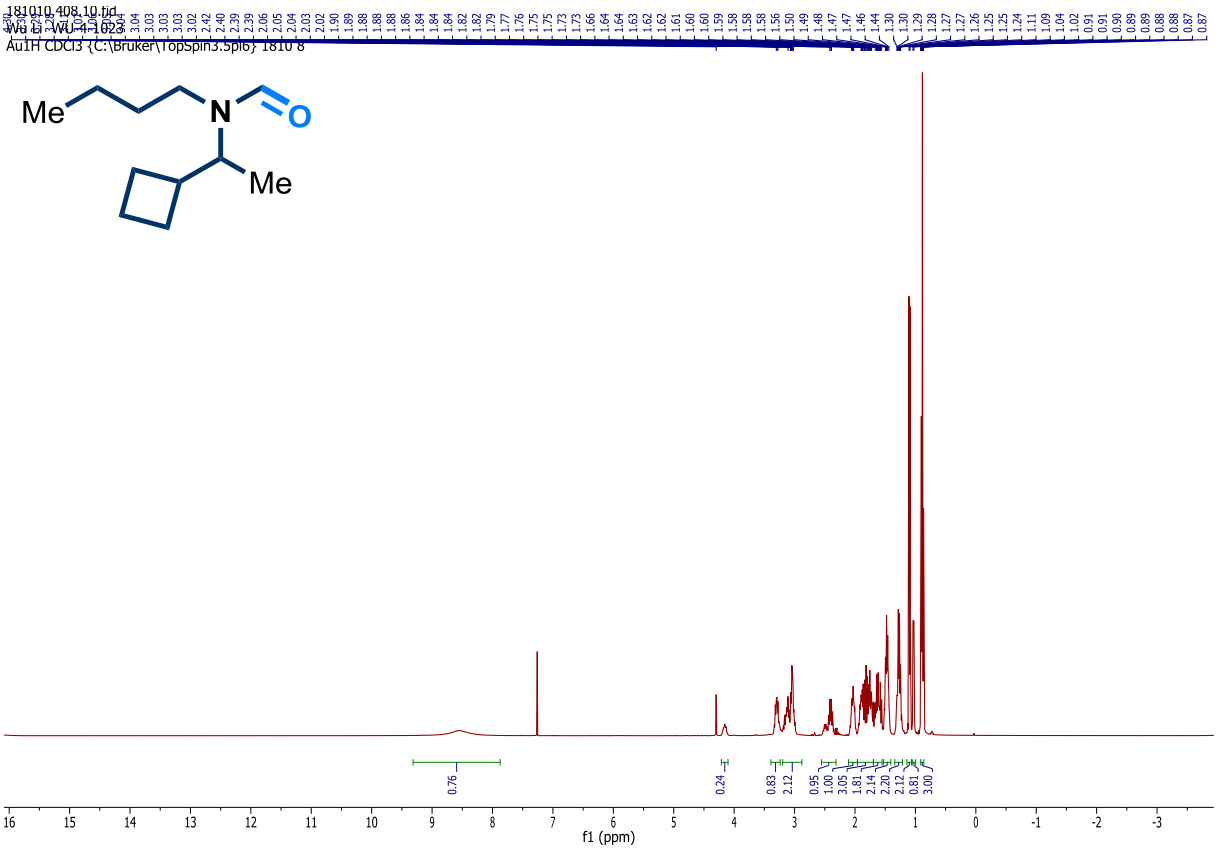


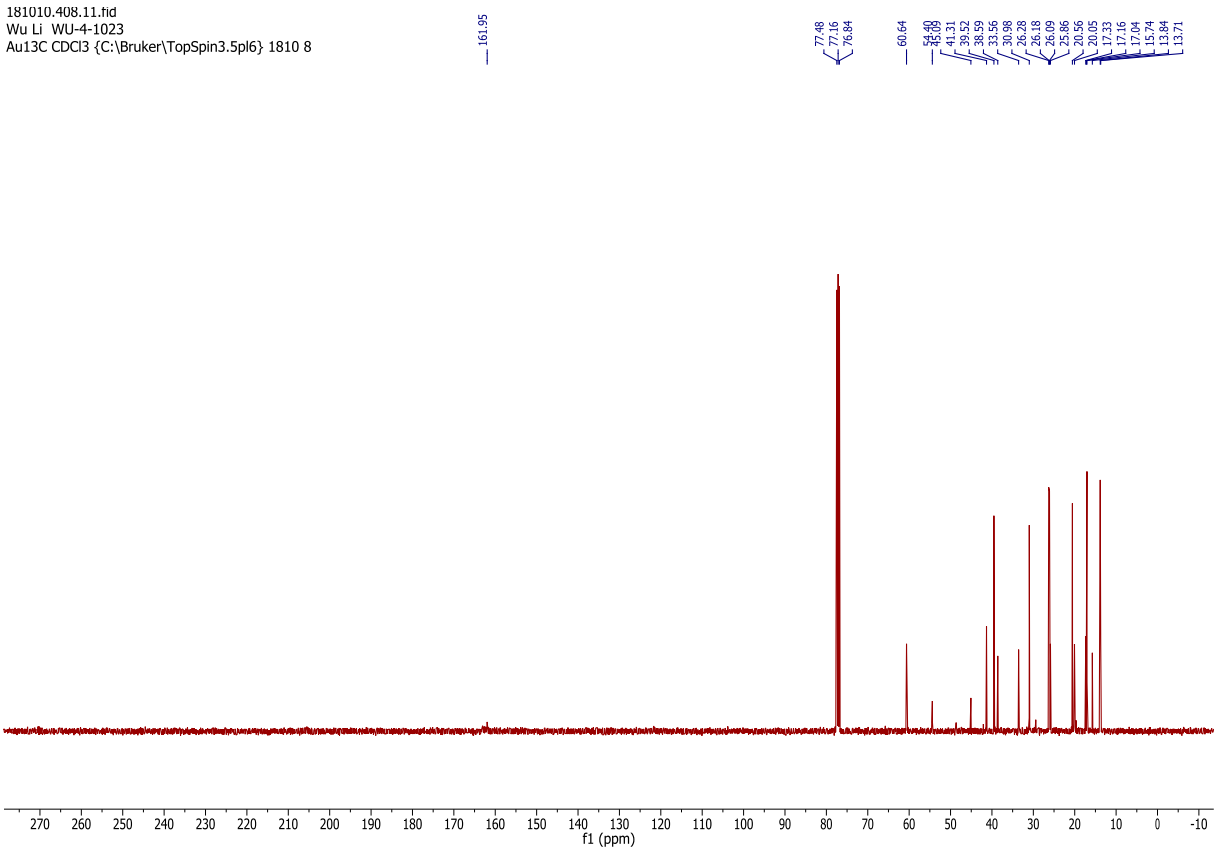


Original spectra for **13b**:

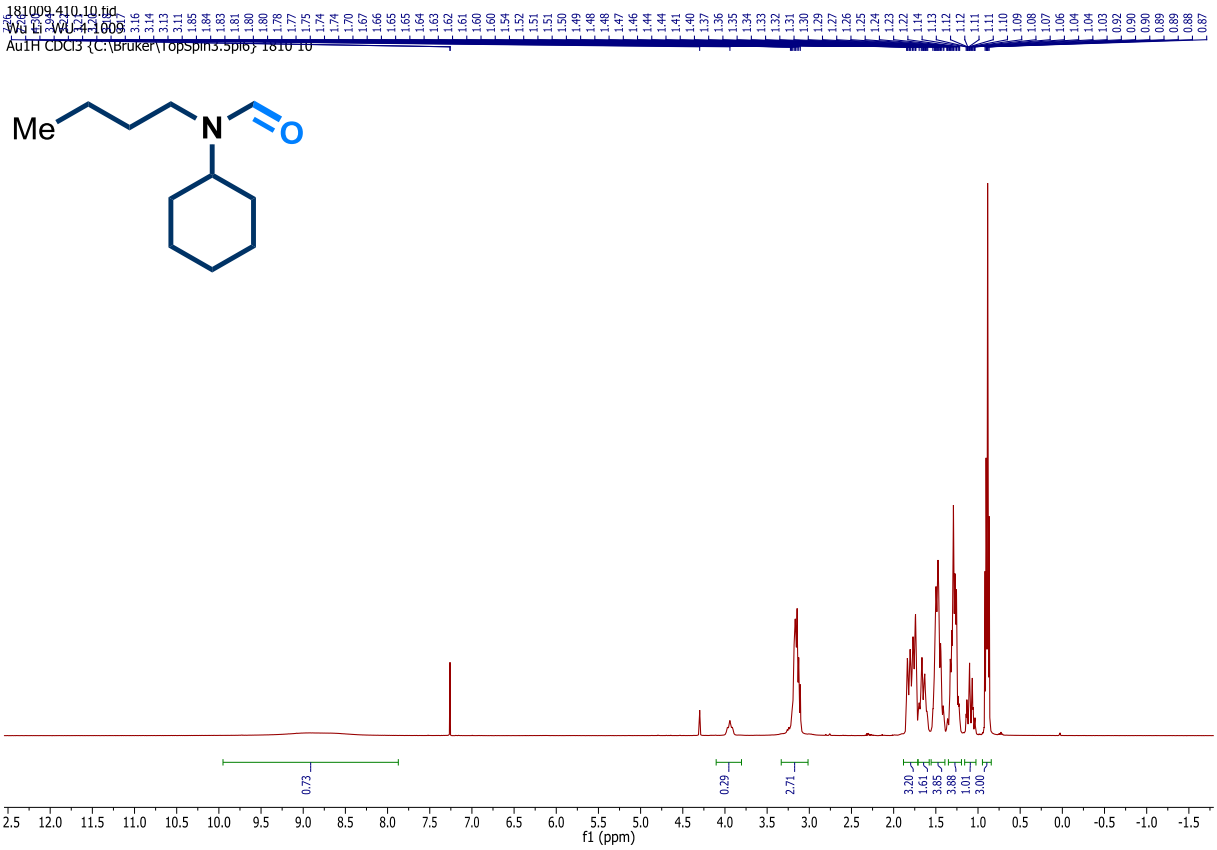


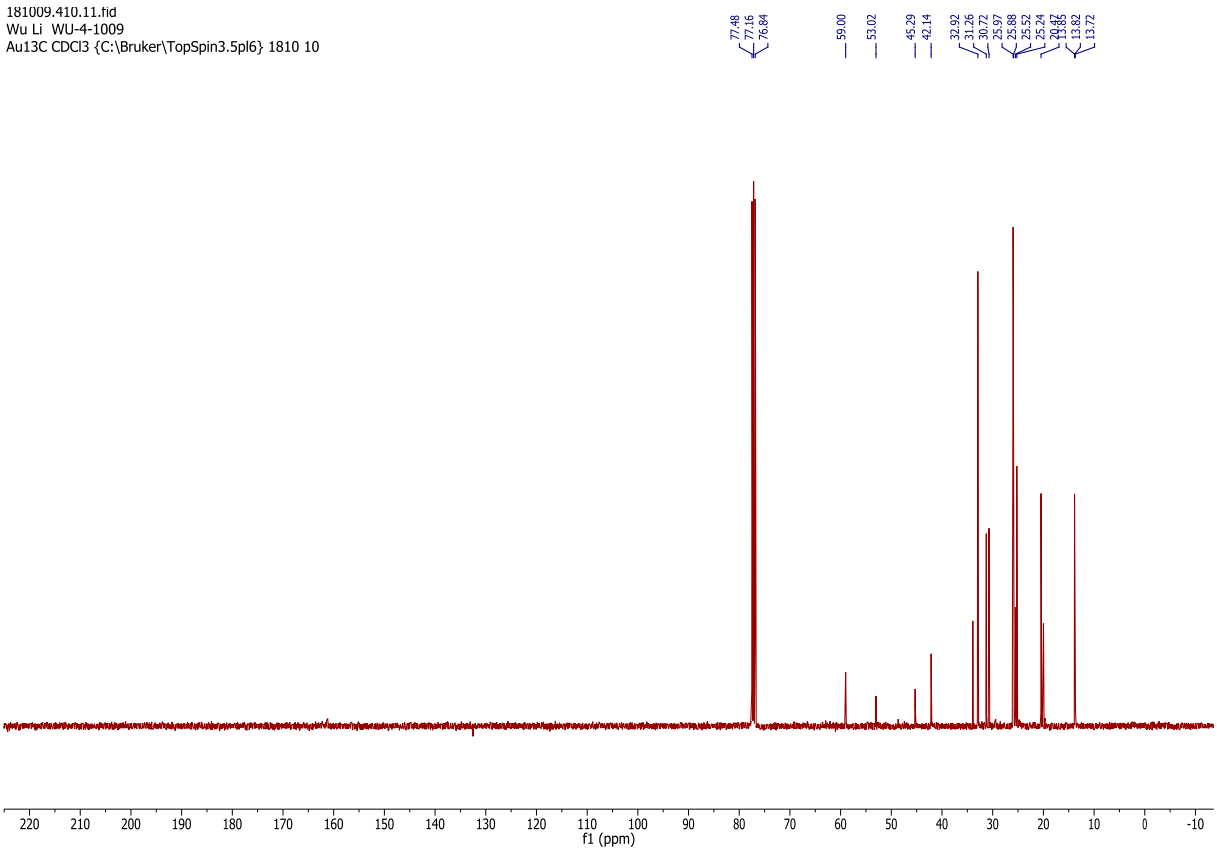
Original spectra for **14b**:



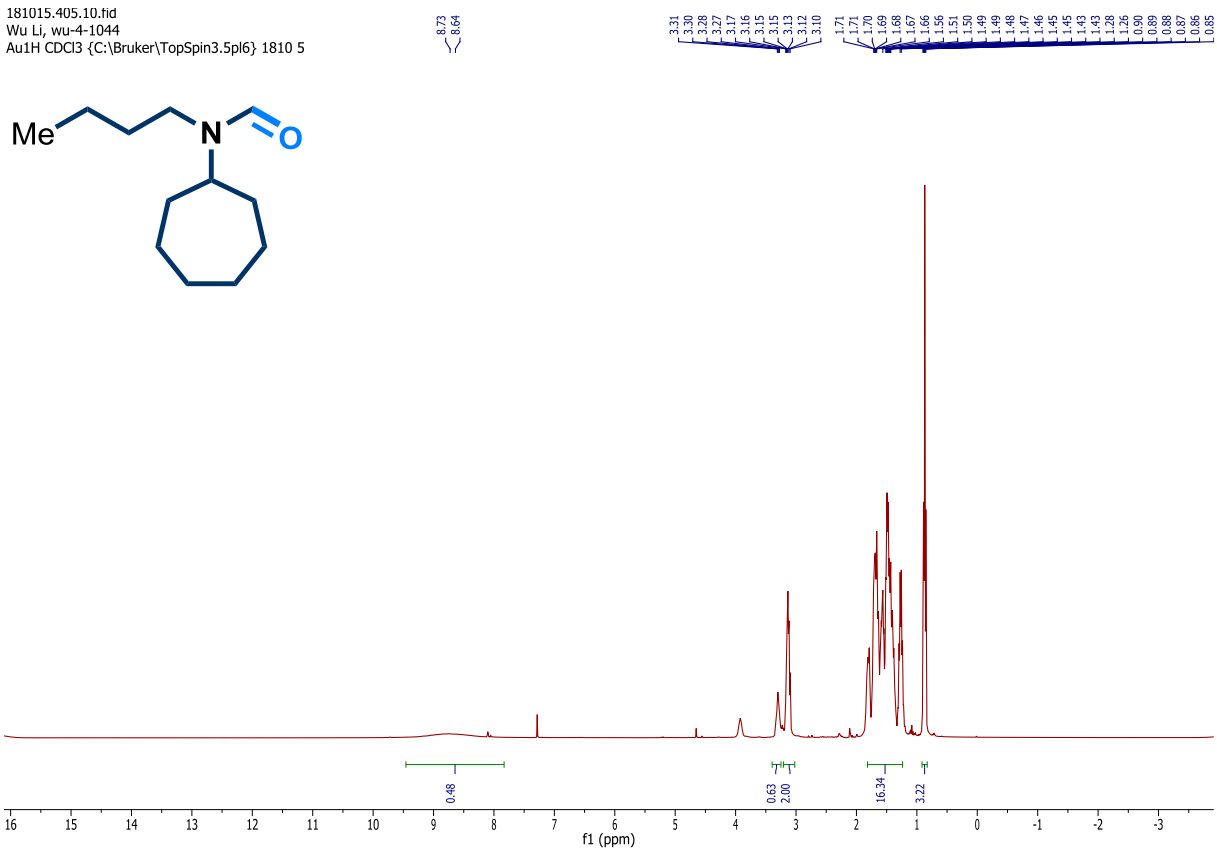


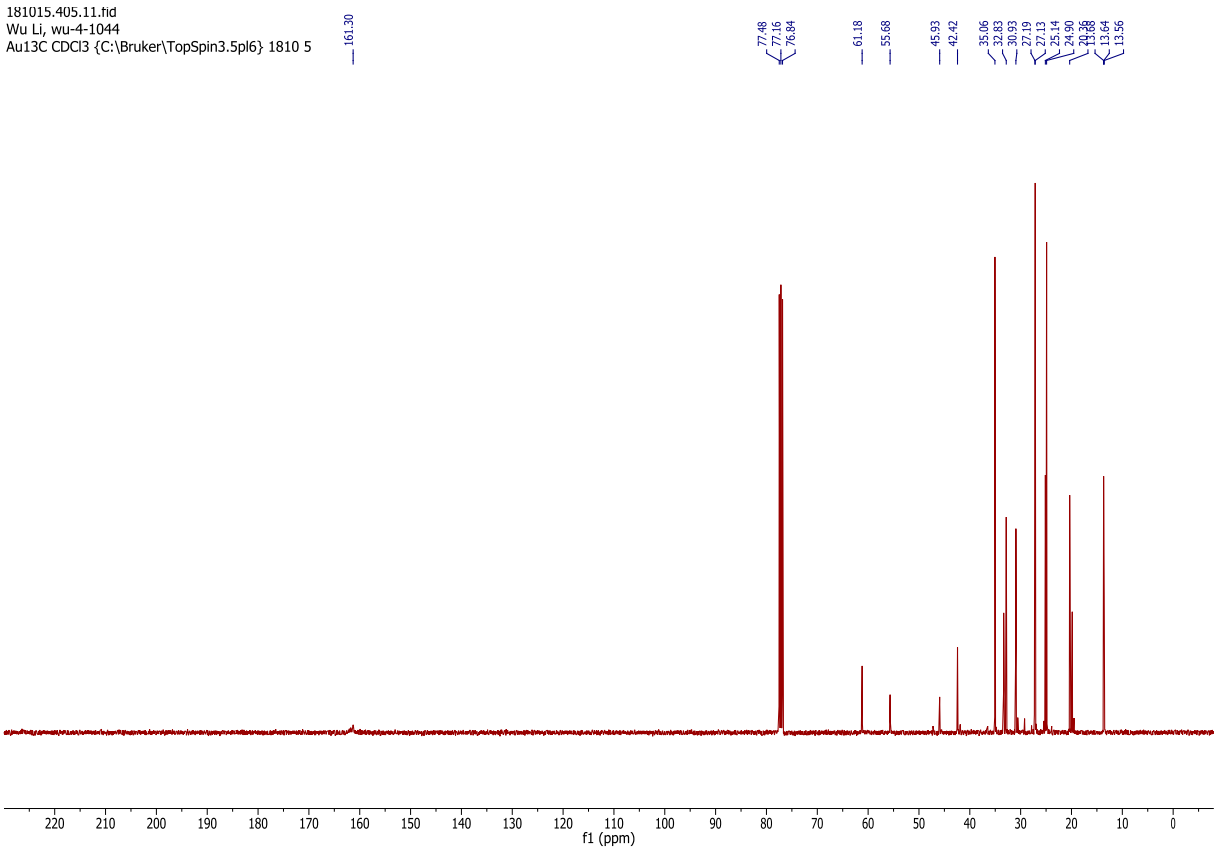
Original spectra for **15b**:





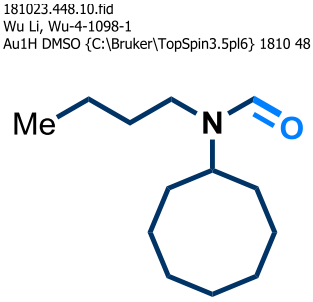
Original spectra for **16b**:



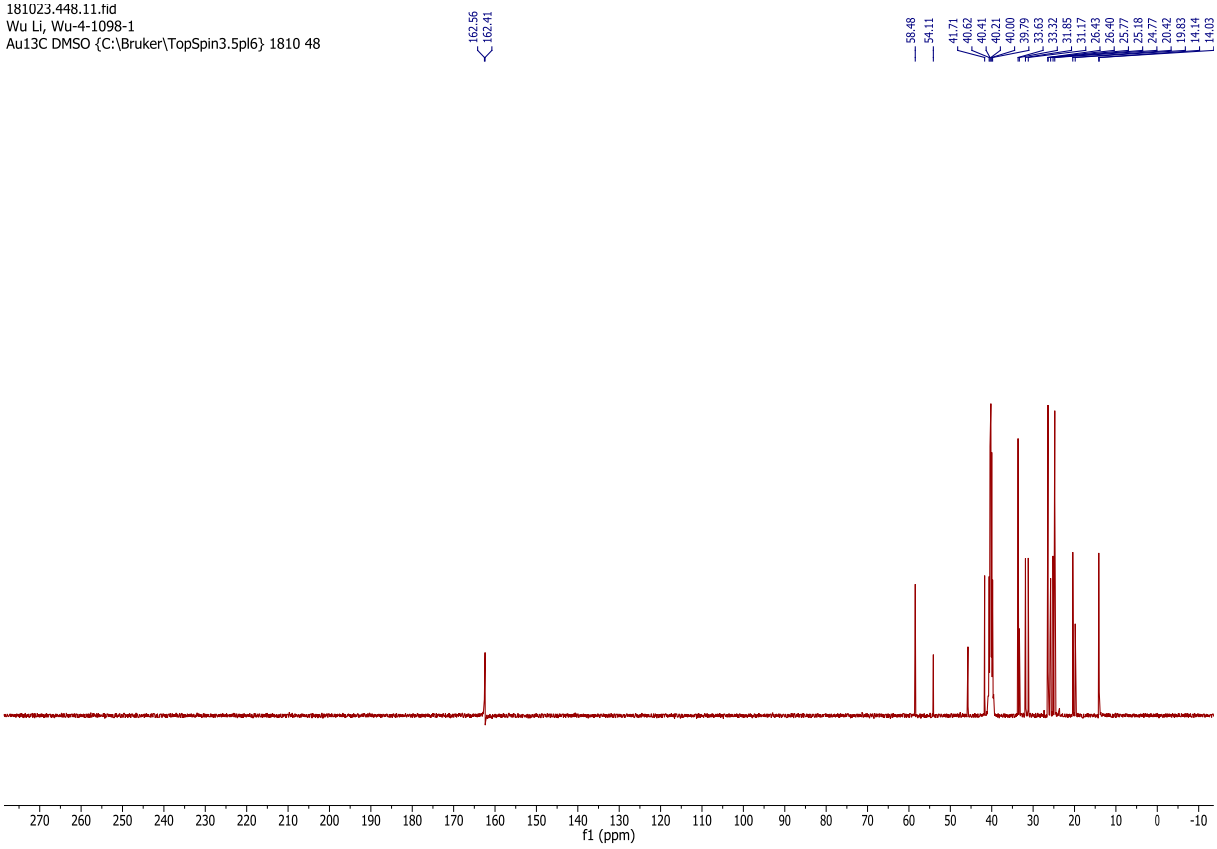


Original spectra for **17b**:

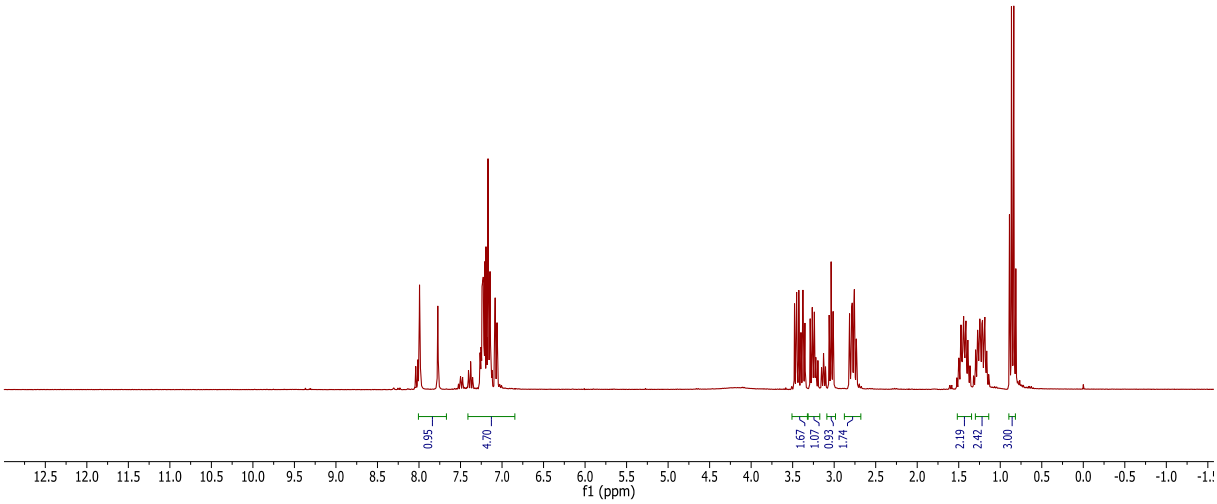
181023.448.10.fid
Wu Li, Wu-4-1098-1
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1810 48

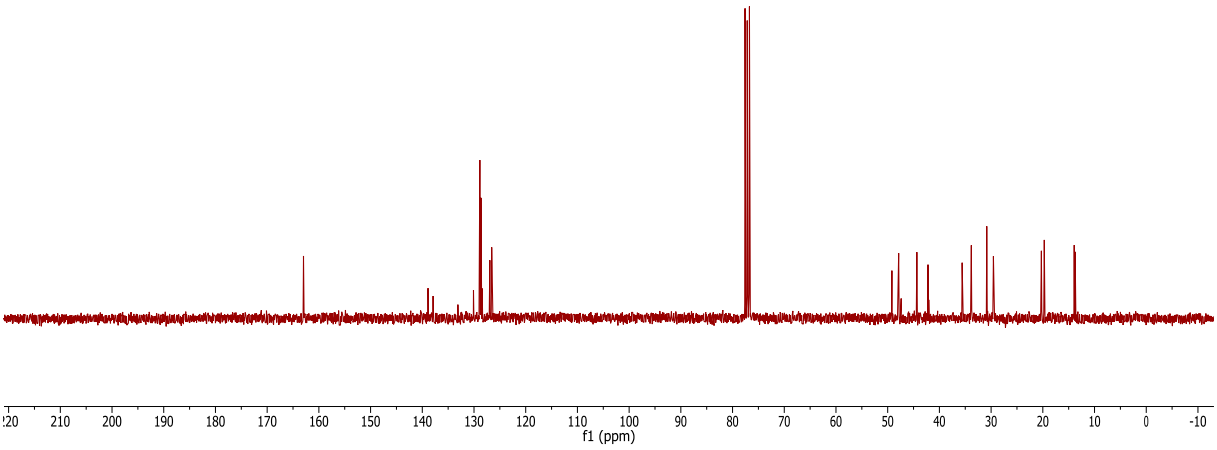


181023.448.11.fid
Wu Li, Wu-4-1098-1
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1810 48

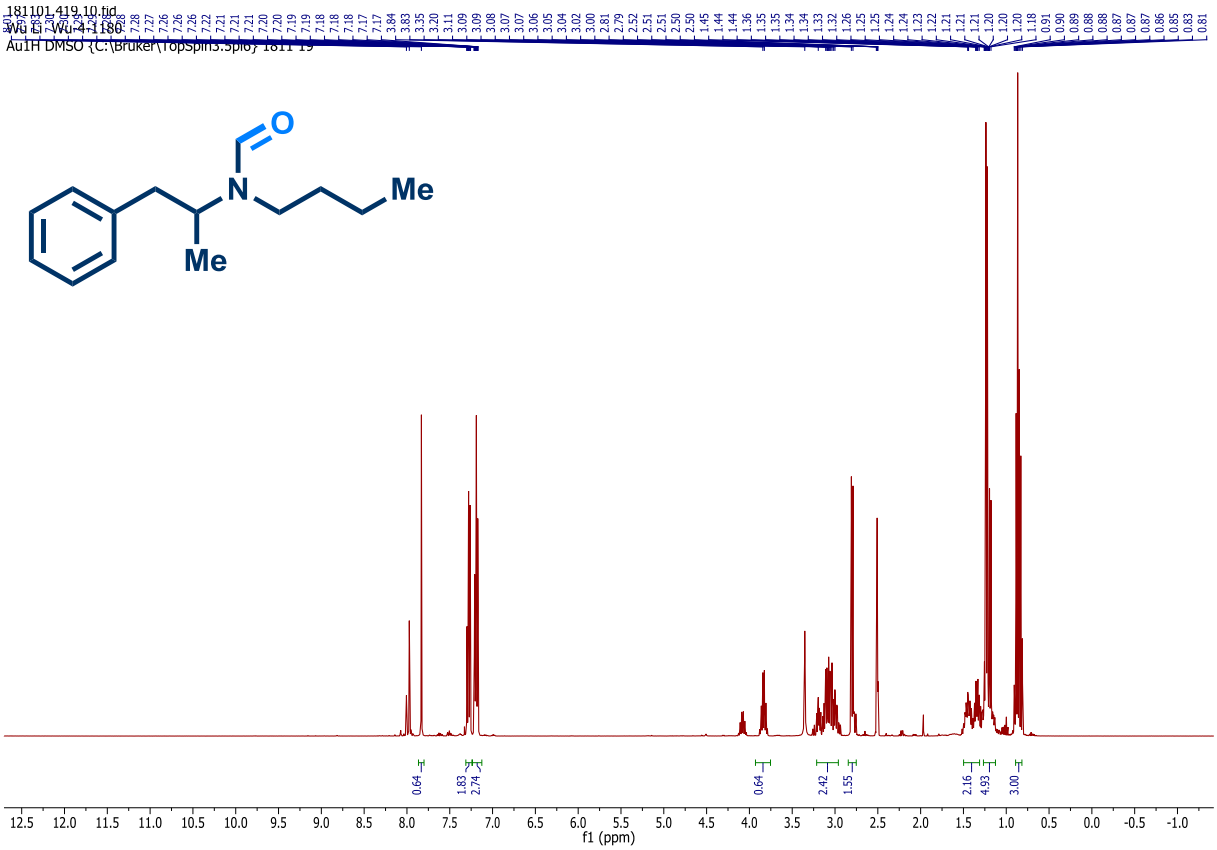


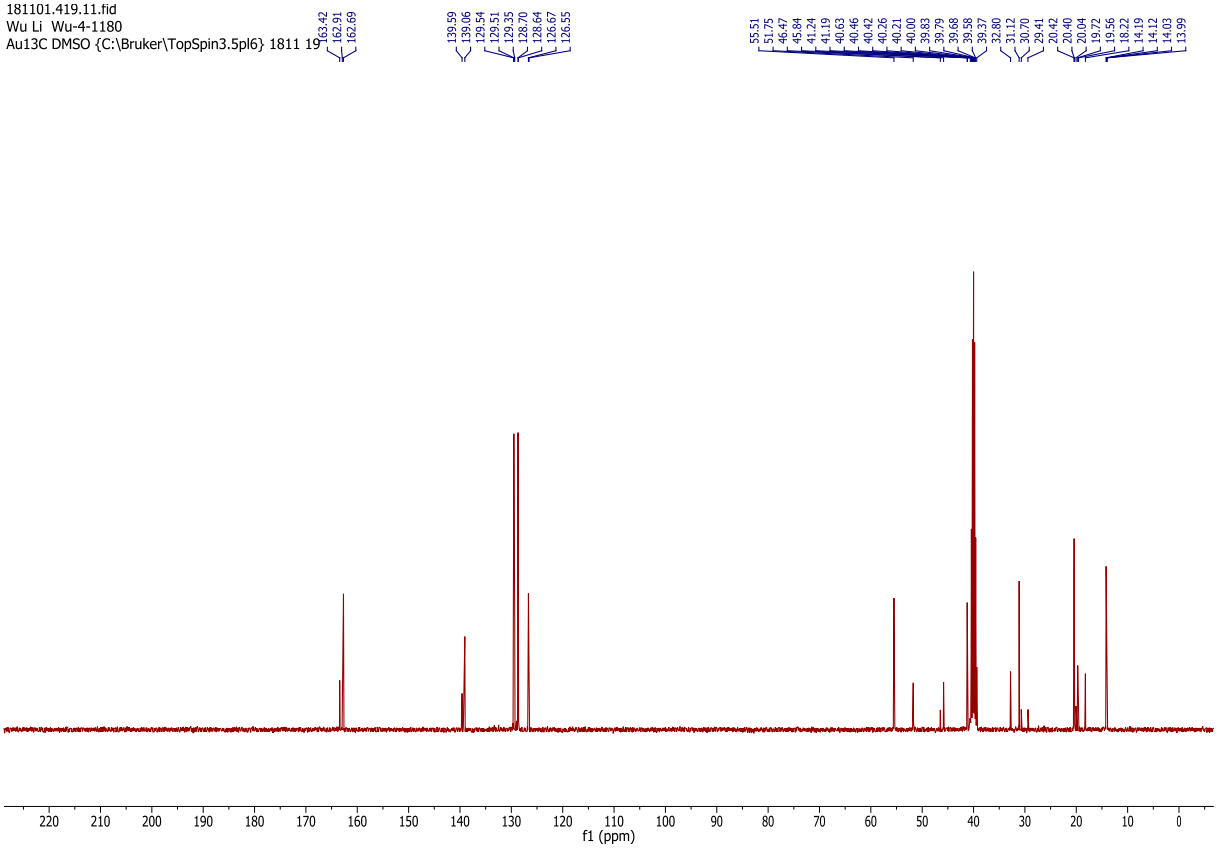
Original spectra for **18b**:





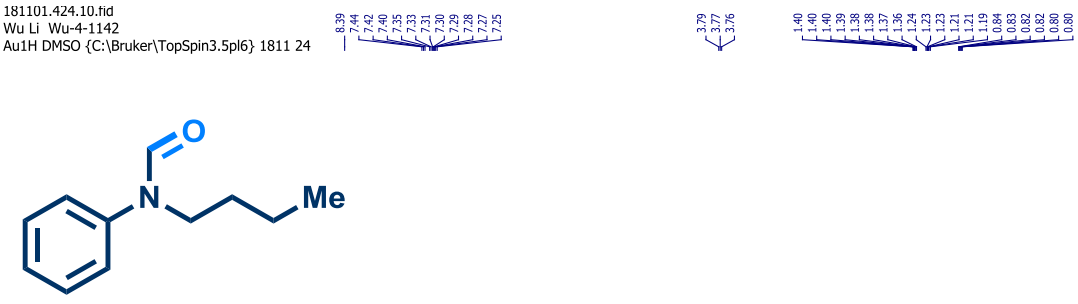
Original spectra for **19b**:

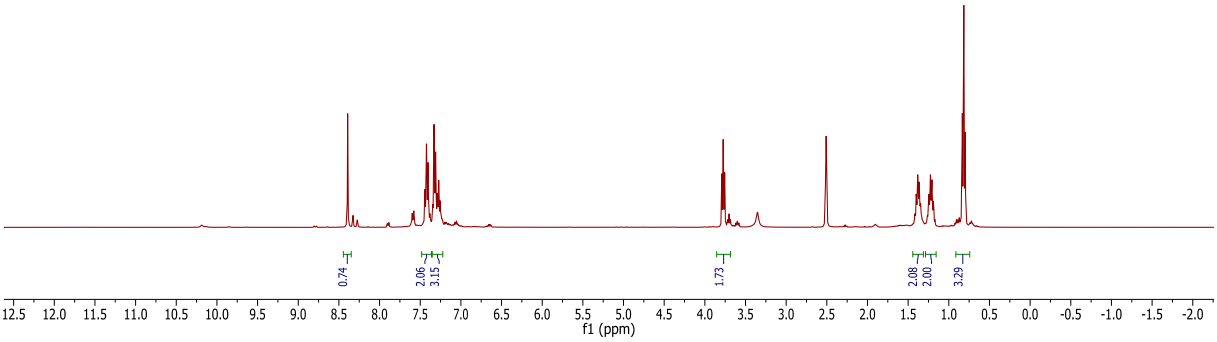




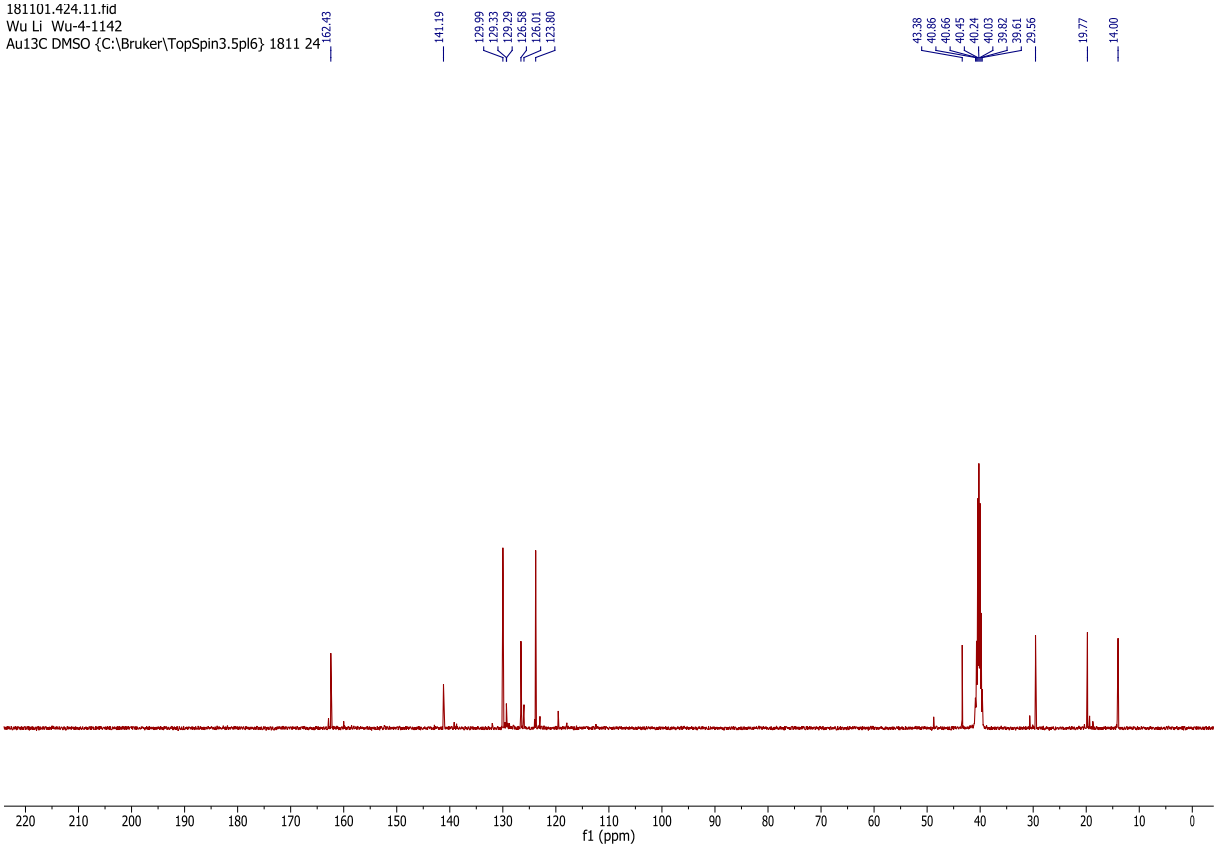
Original spectra for **20b**:

181101.424.10.fid
Wu Li Wu-4-1142
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1811 24



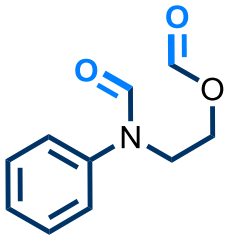


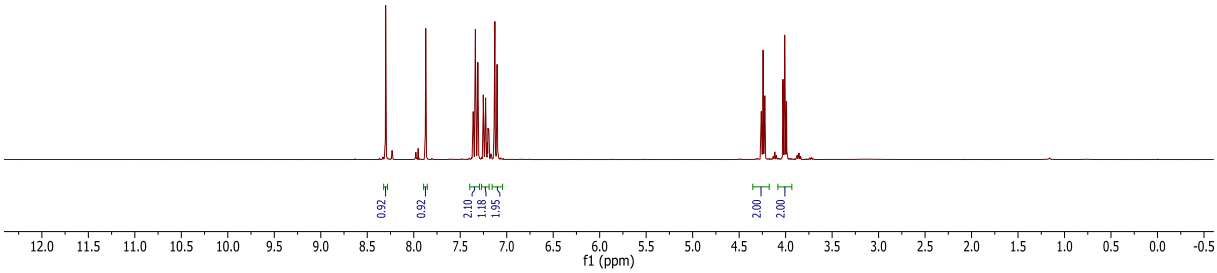
181101.424.11.fid
Wu Li Wu-4-1142
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1811 24



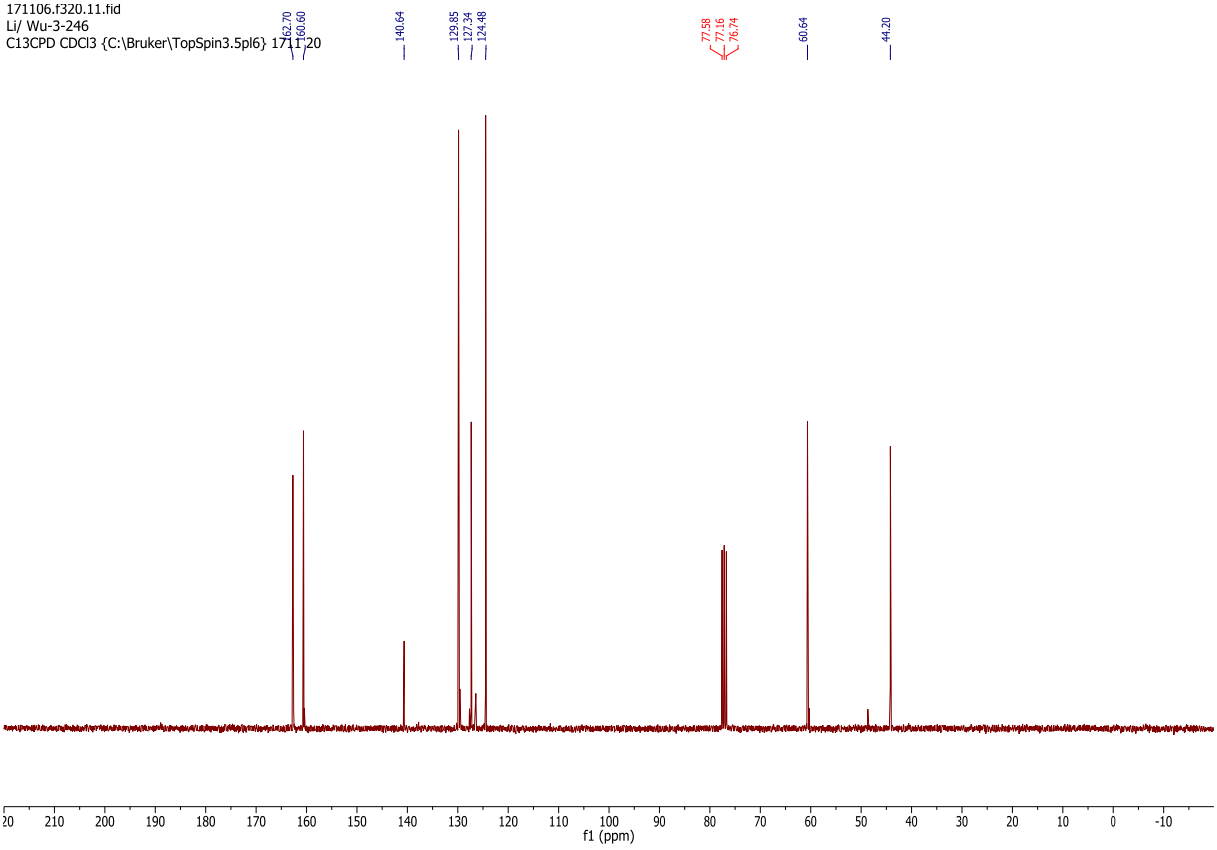
Original spectra for **21b**:

171106.f320.10.fid
Li/ Wu-3-246
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1711 20

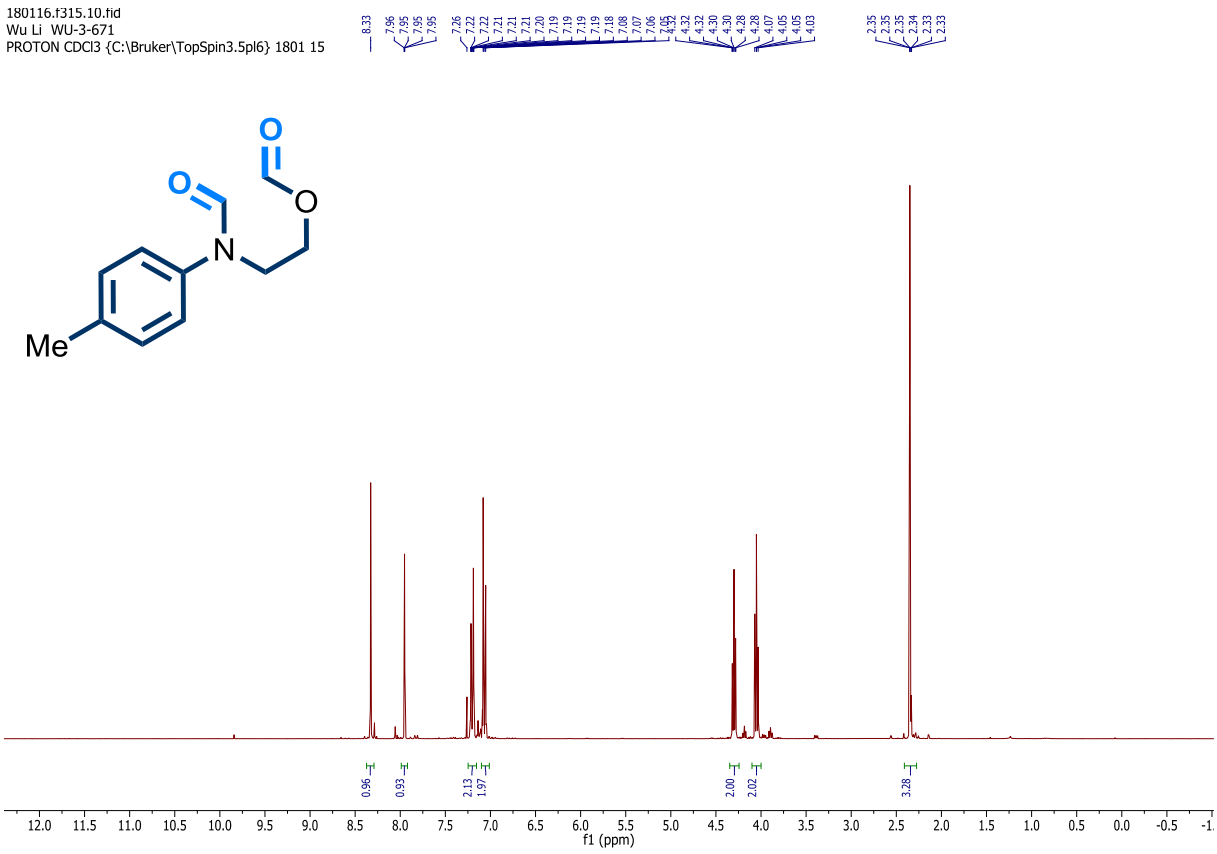


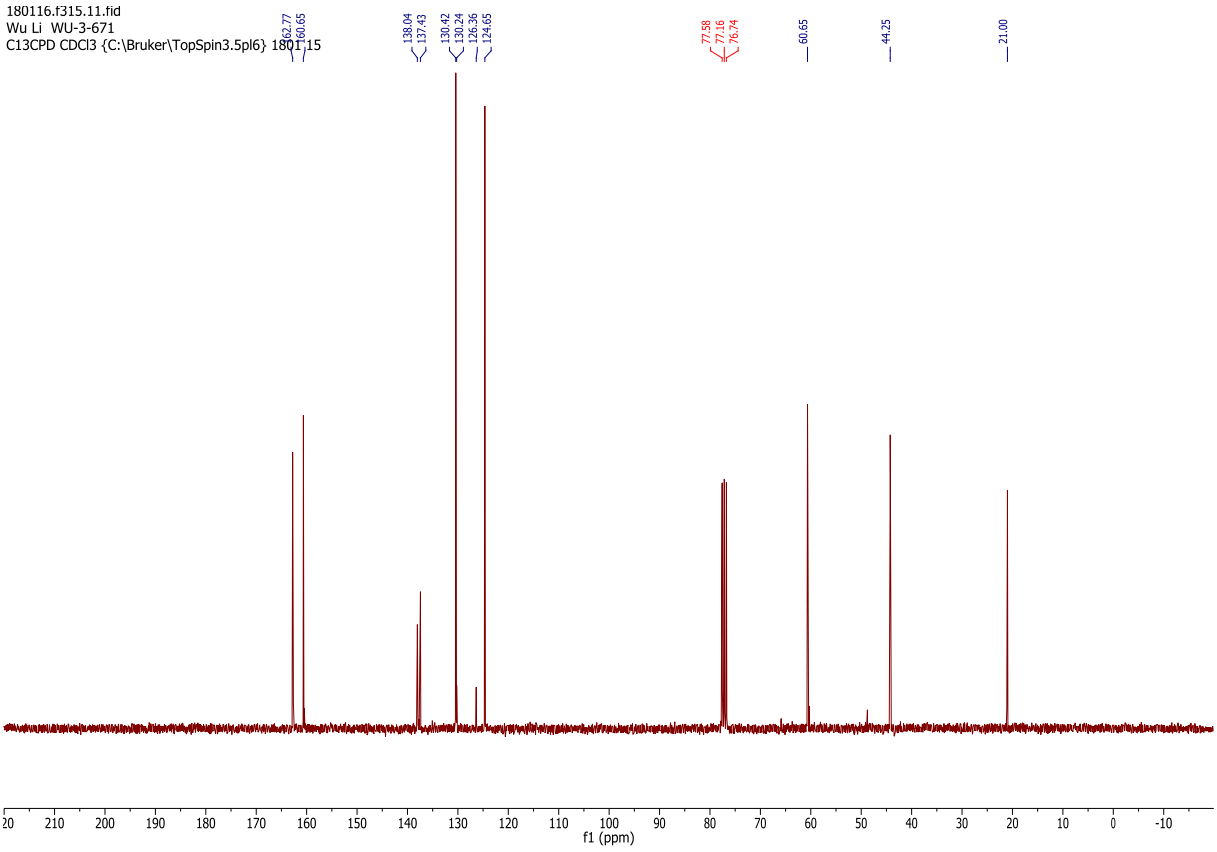


171106.f320.11.fid
Li/ Wu-3-246
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1711 20

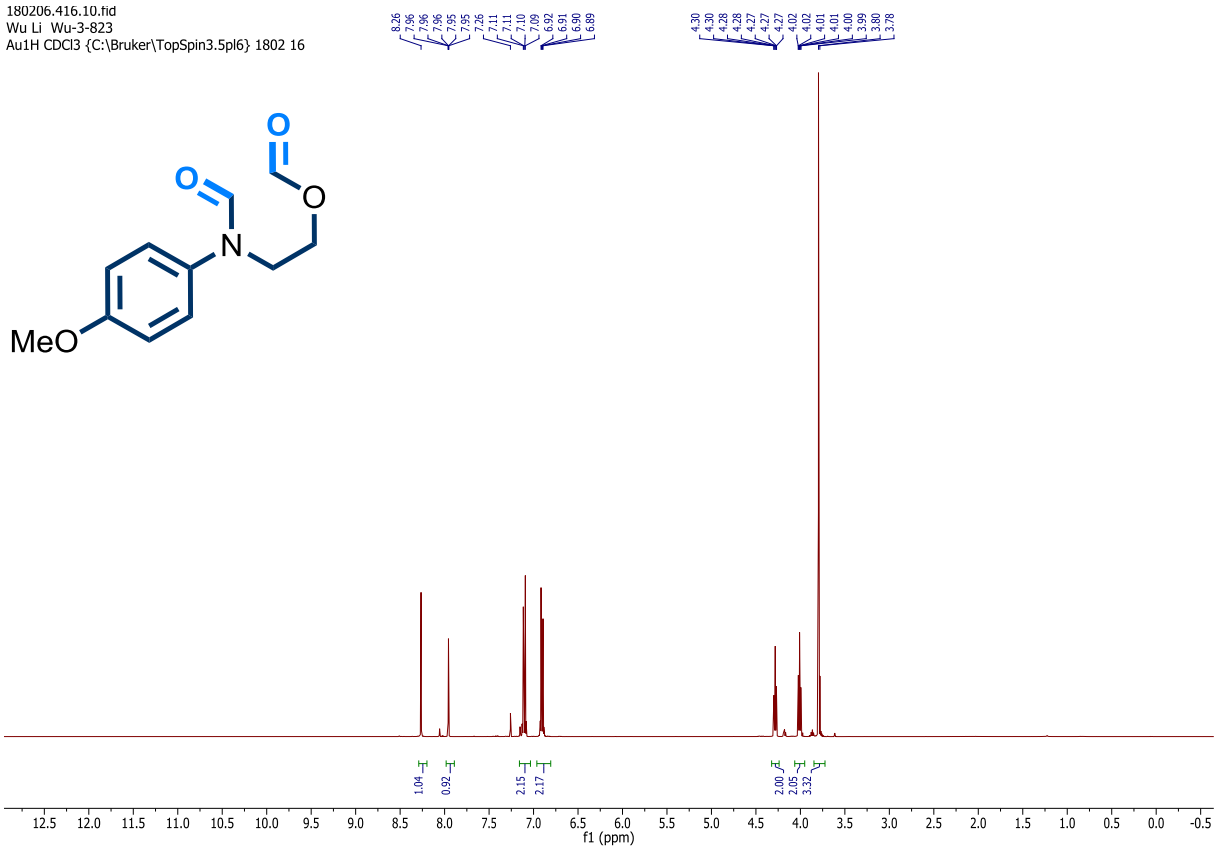


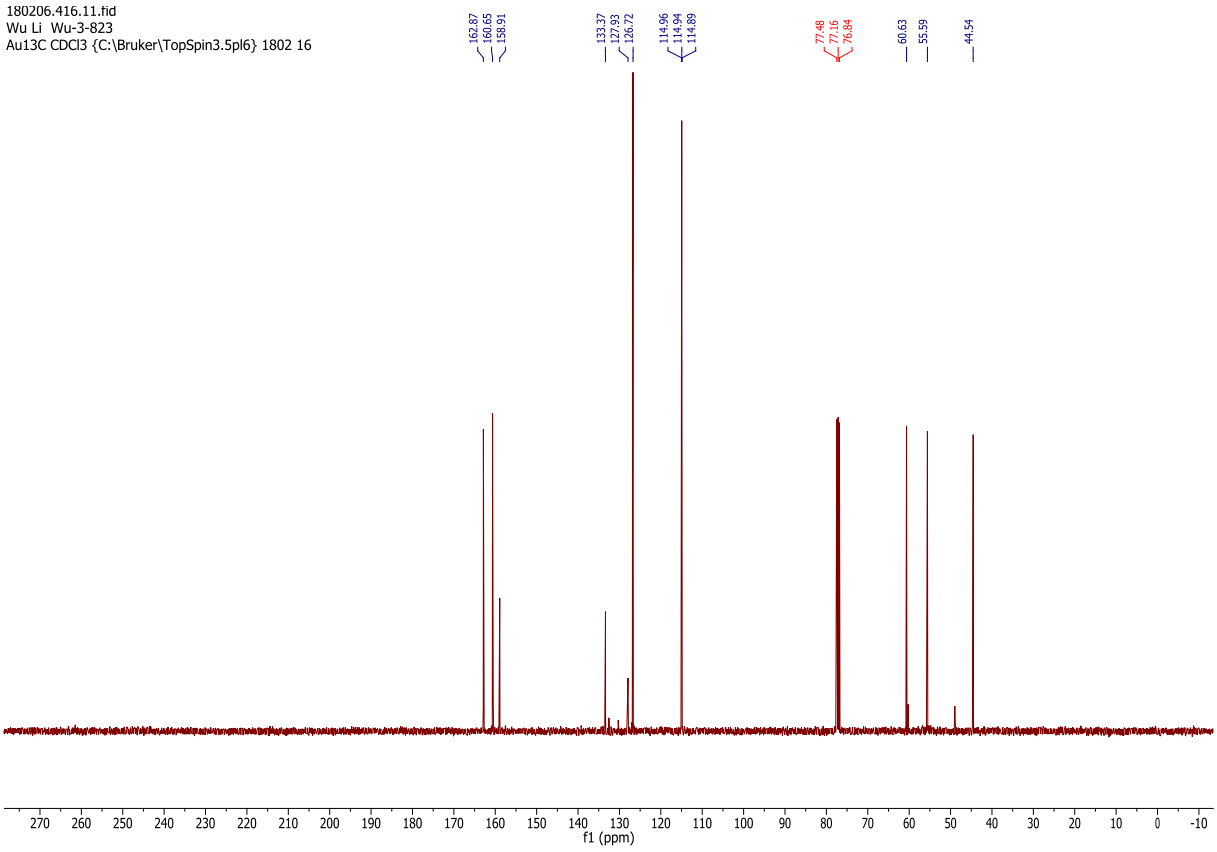
Original spectra for **22b**:





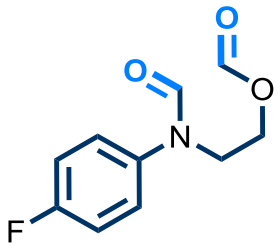
Original spectra for **23b**:

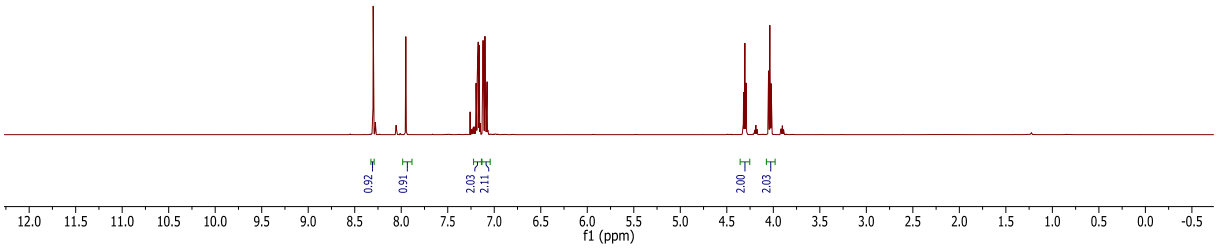




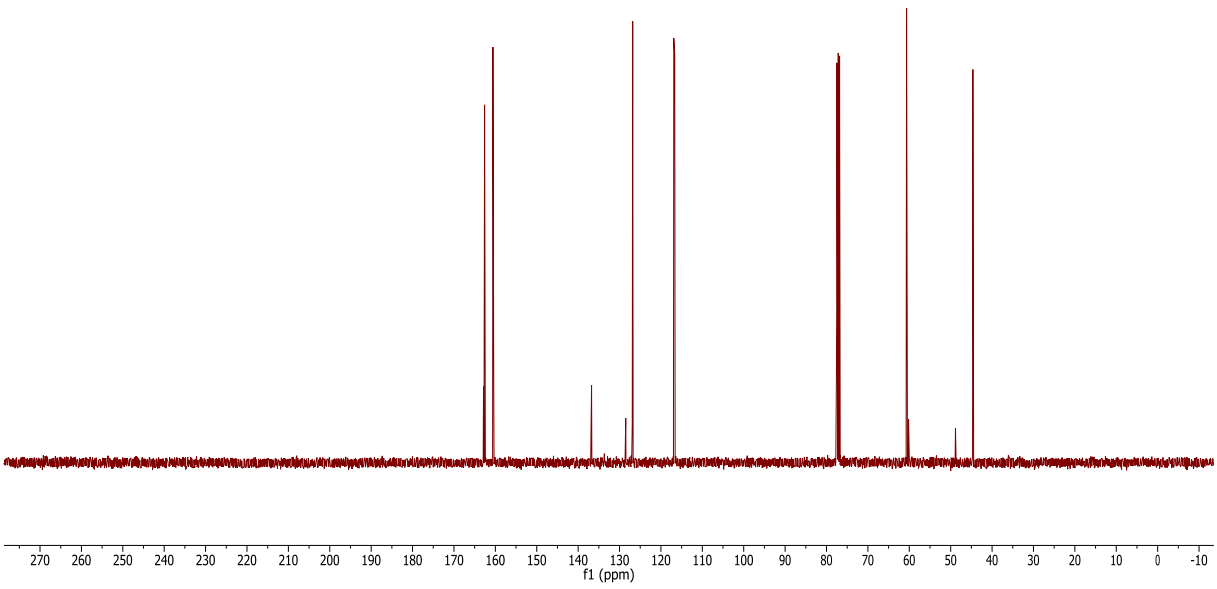
Original spectra for **24b**:

180206.423.10.fid
Wu Li Wu-3-830
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1802 23

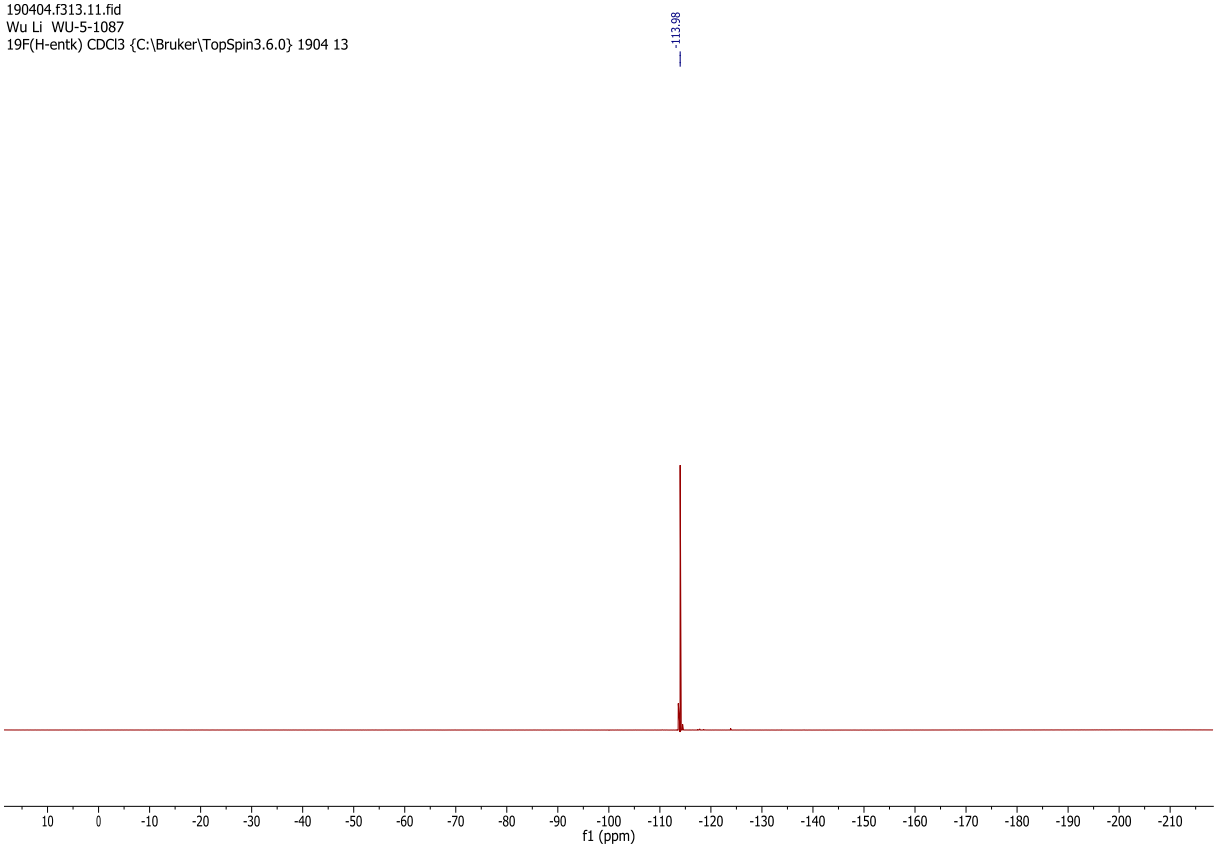




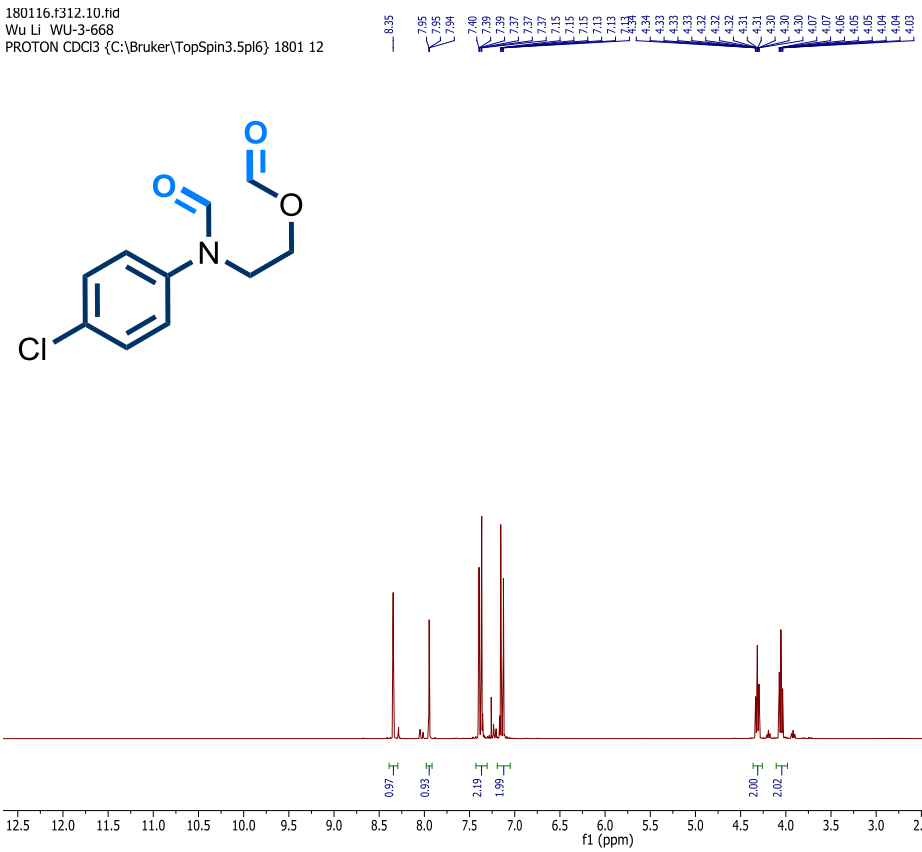
180206.423.11.fid
Wu Li Wu-3-830
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1802 23

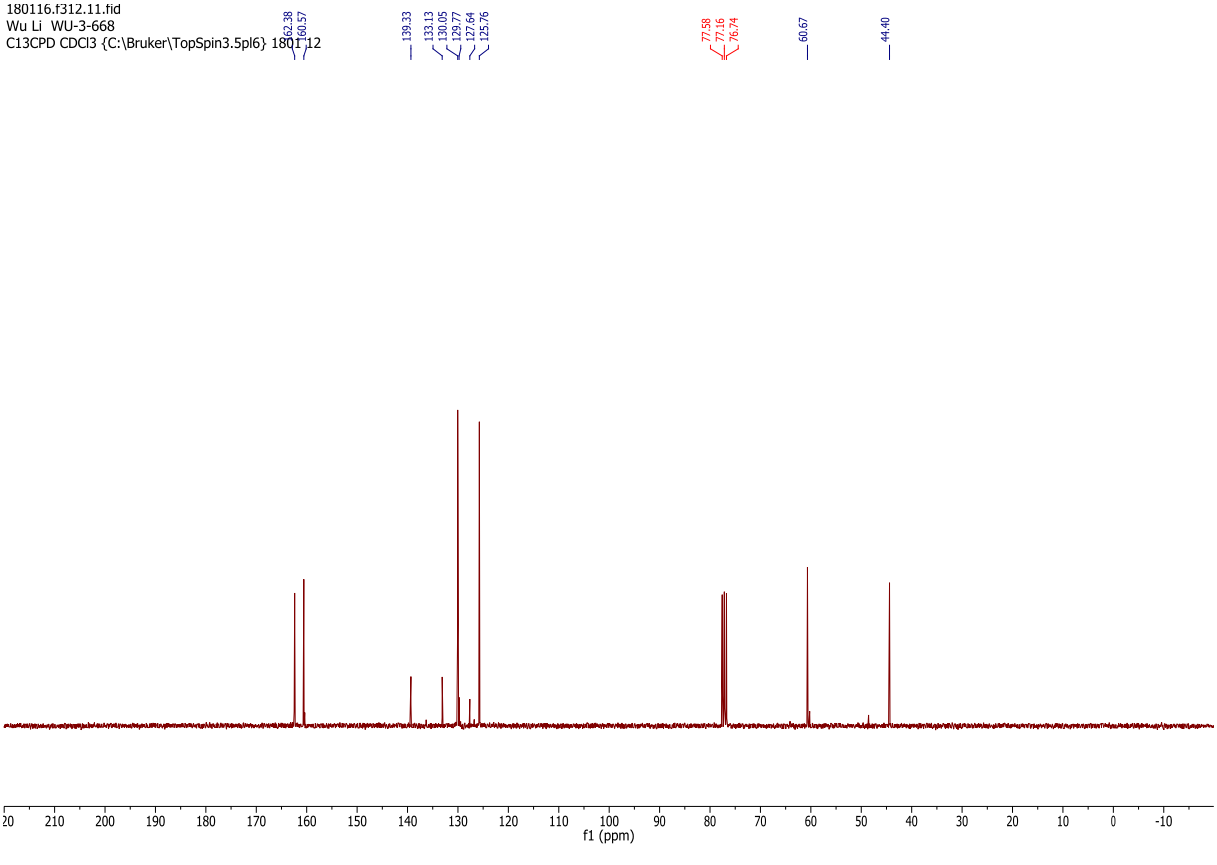


190404.f313.11.fid
Wu Li WU-5-1087
19F(H-entk) CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 13

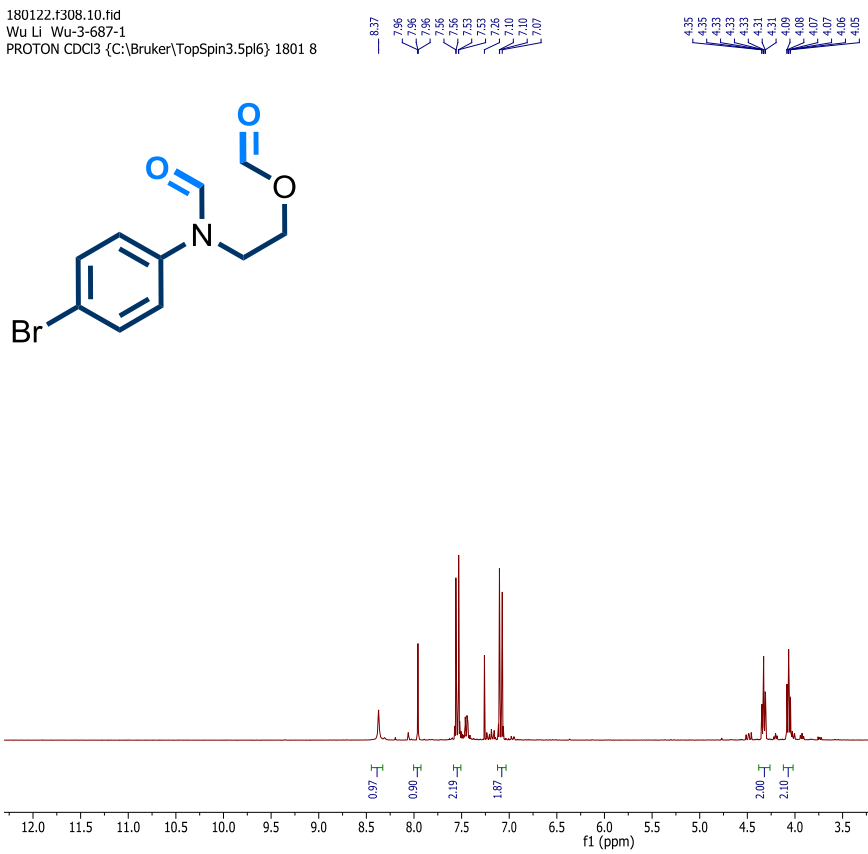


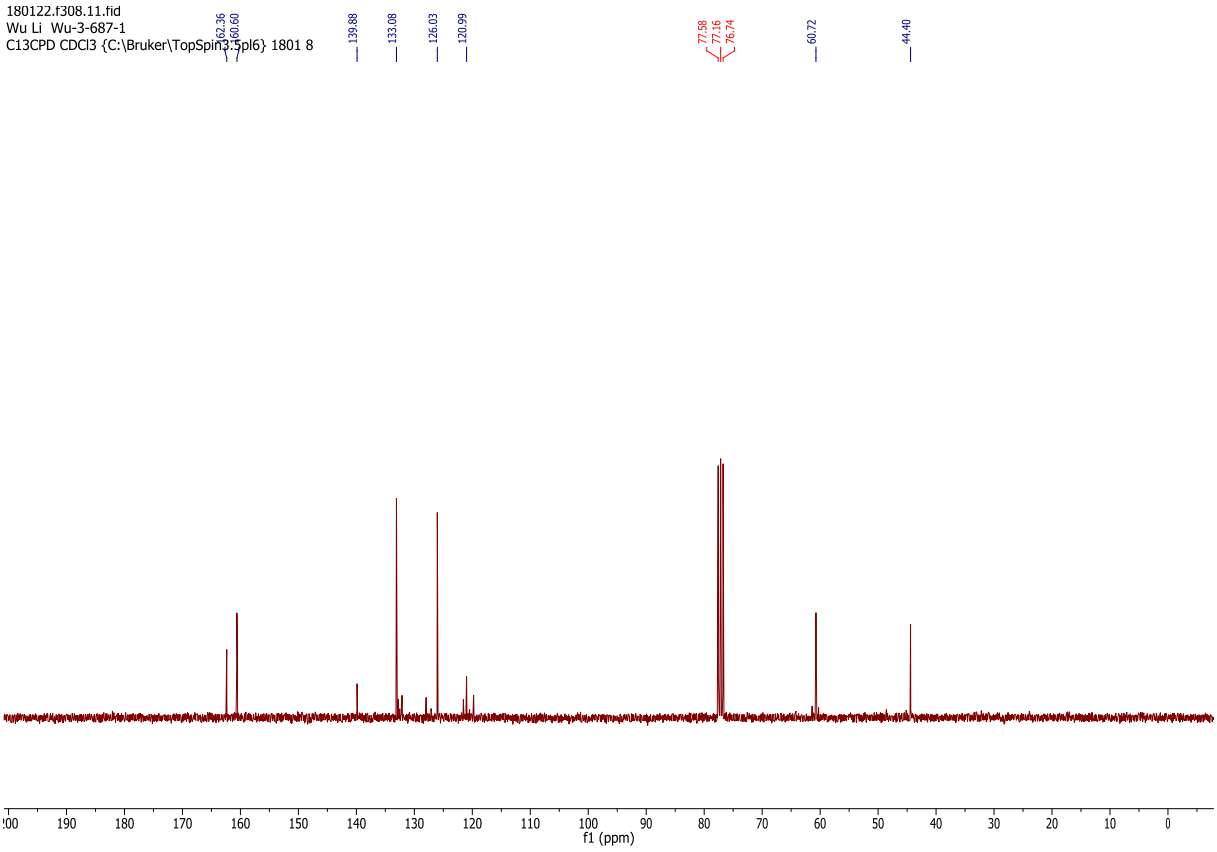
Original spectra for **25b**:



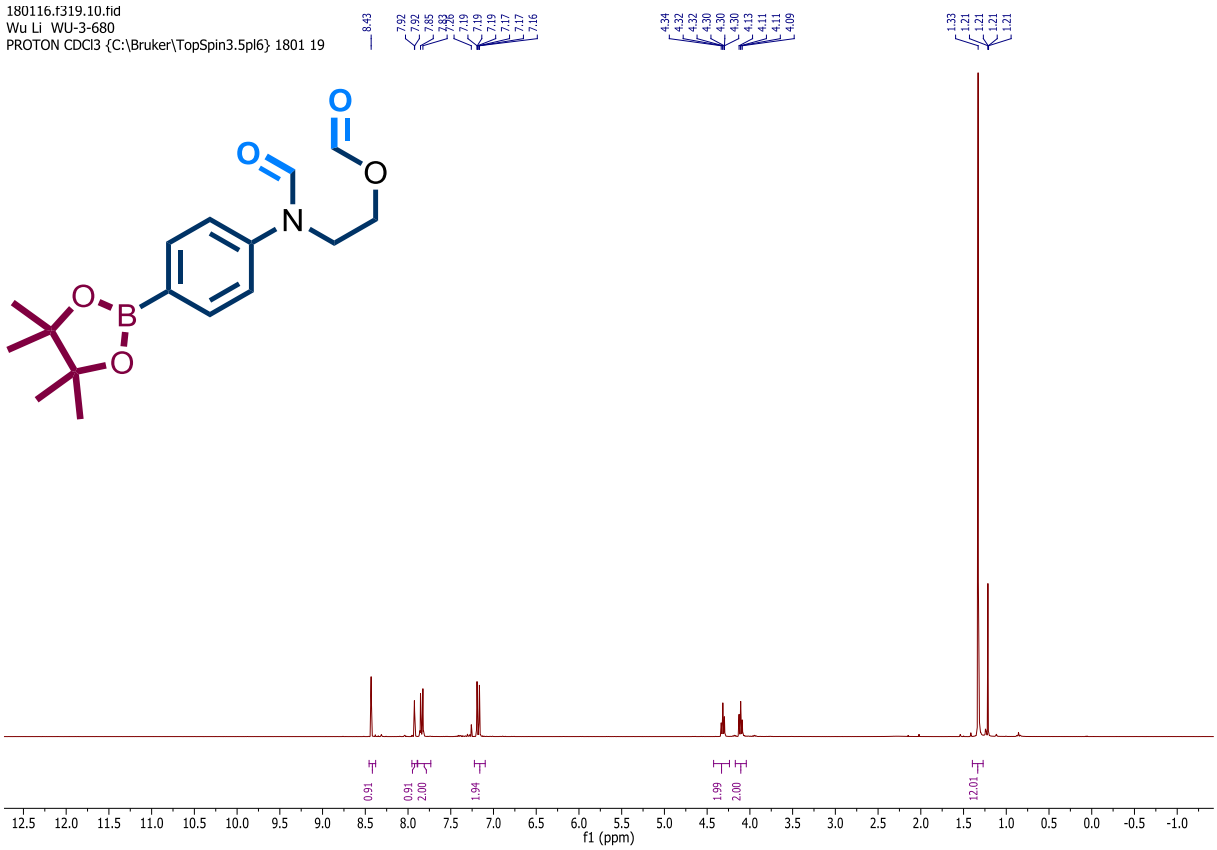


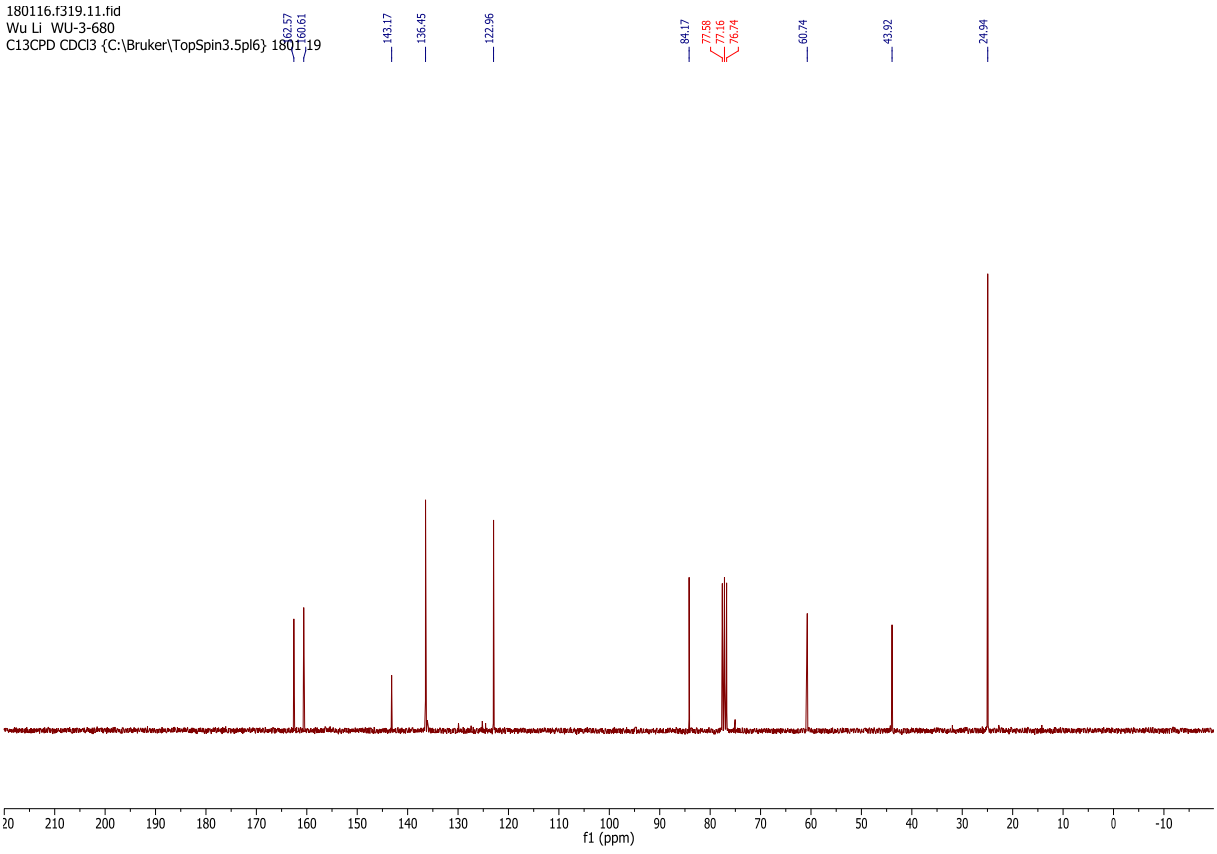
Original spectra for **26b**:



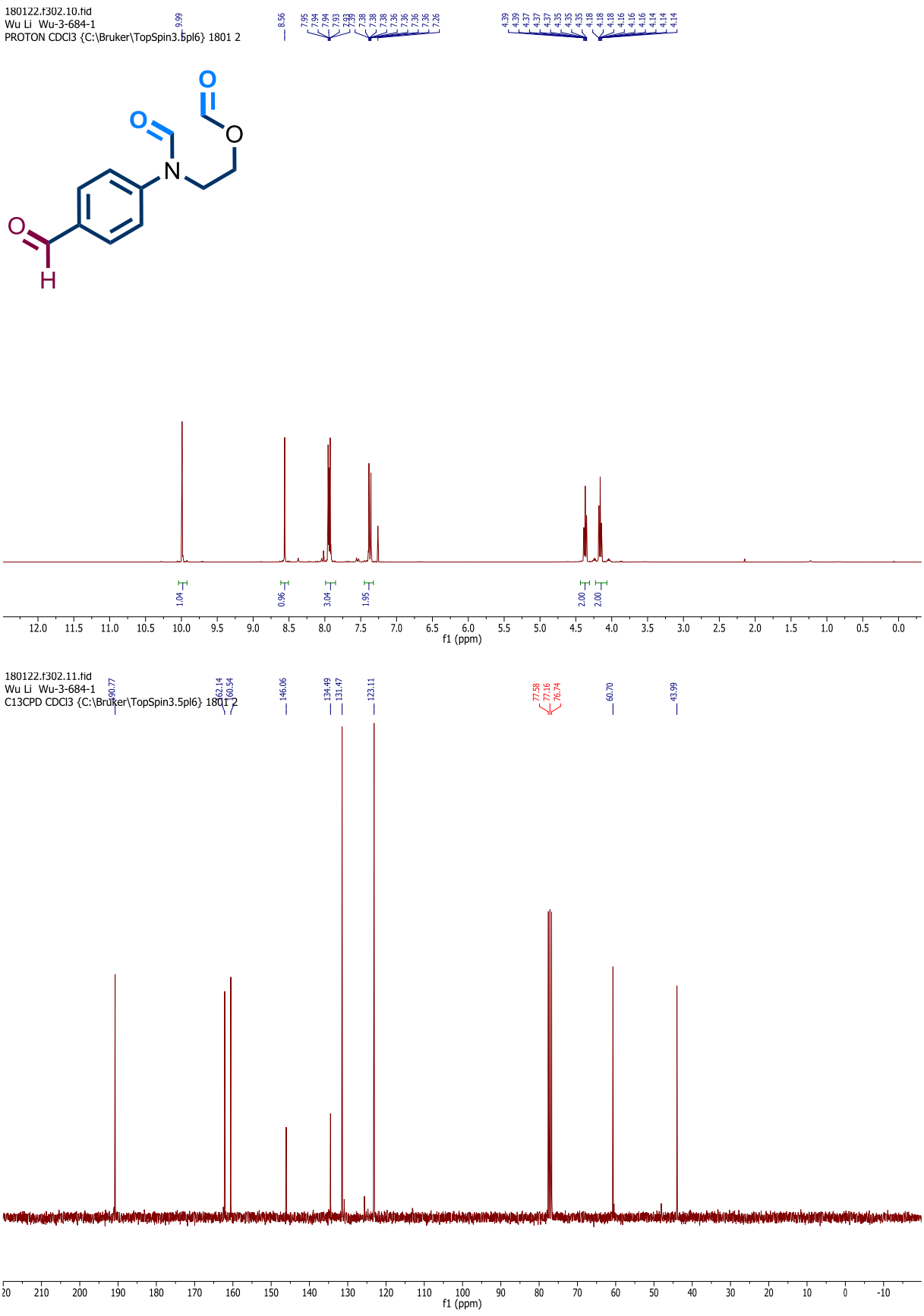


Original spectra for **27b**:

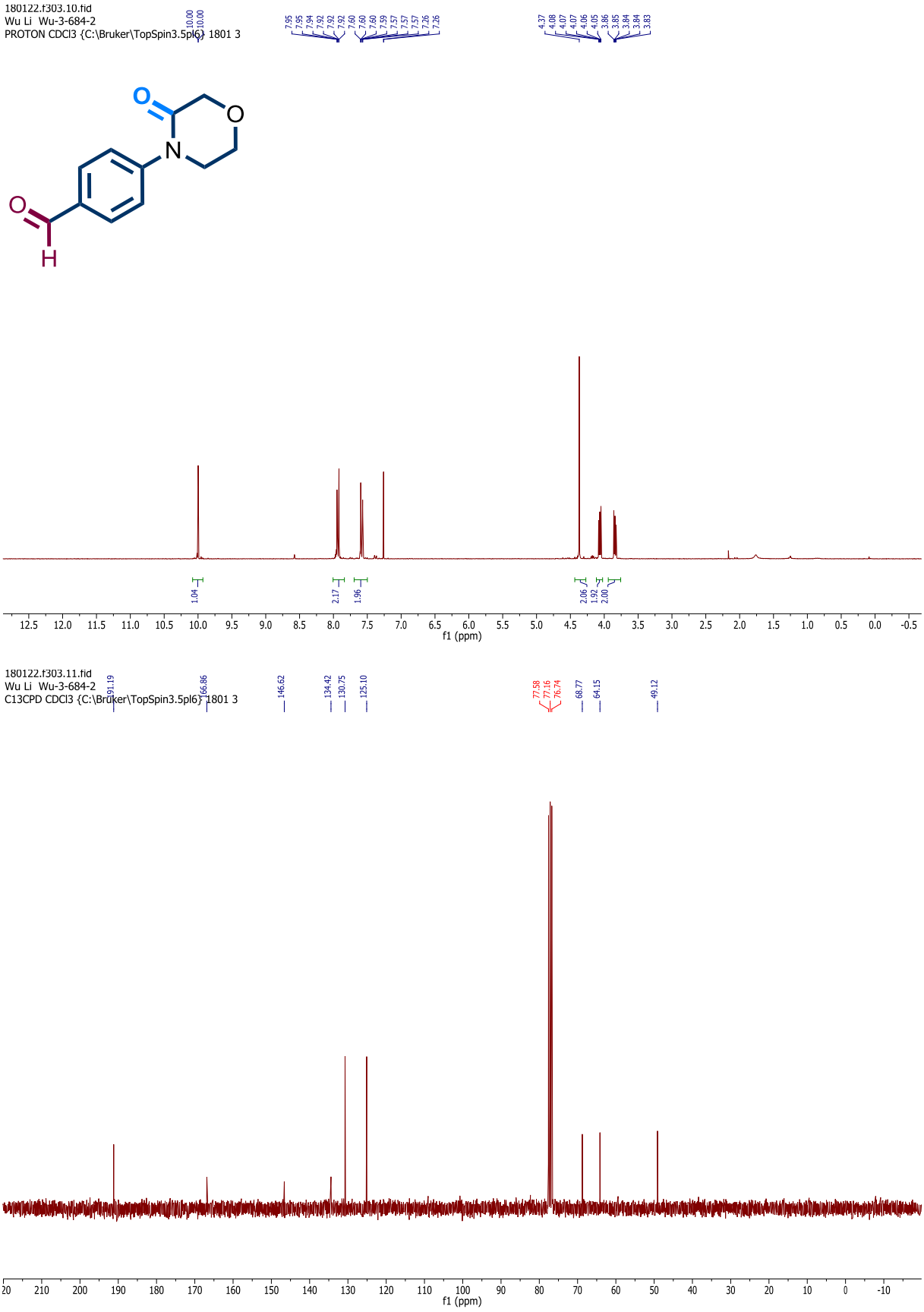




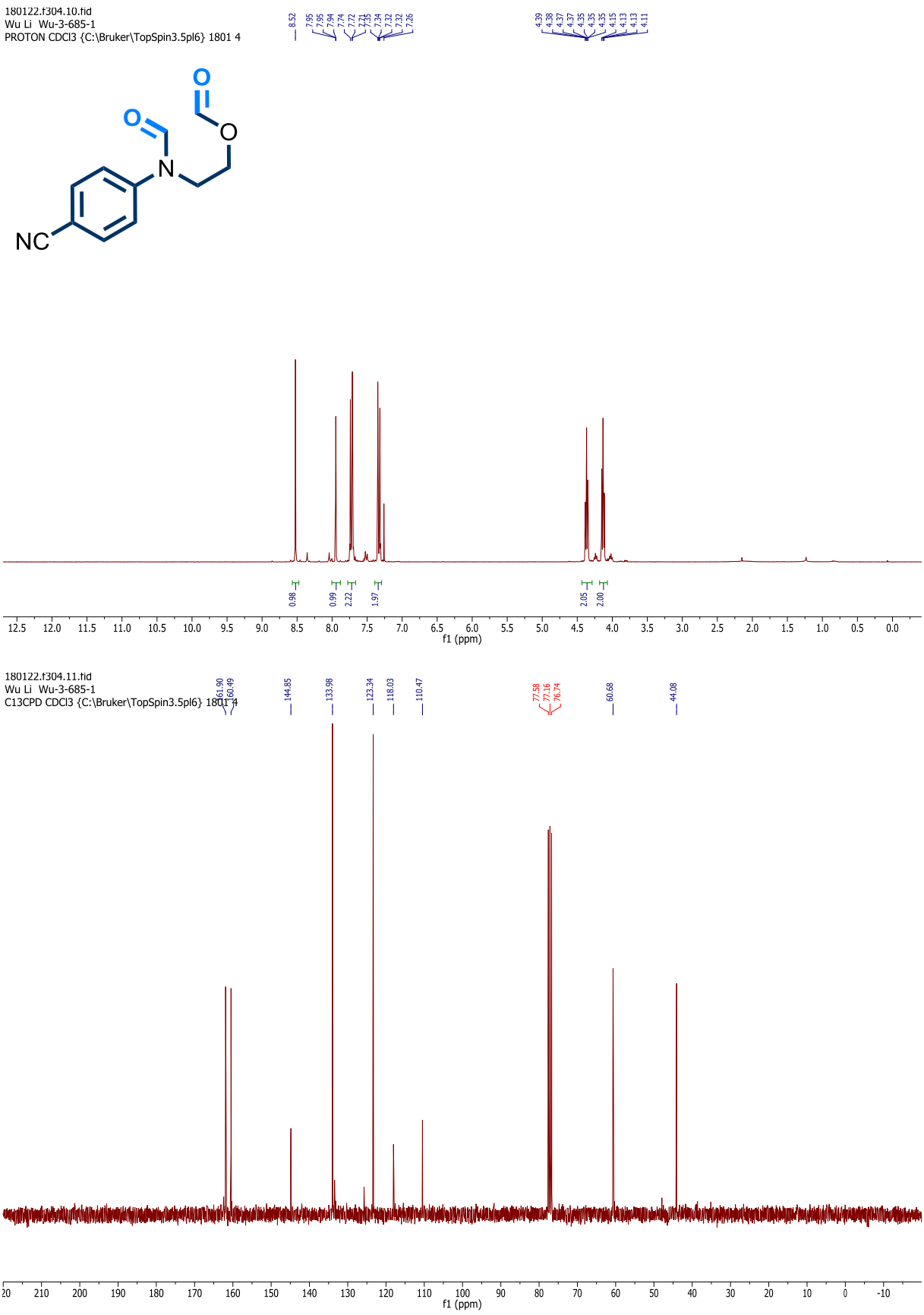
Original spectra for **28b**:



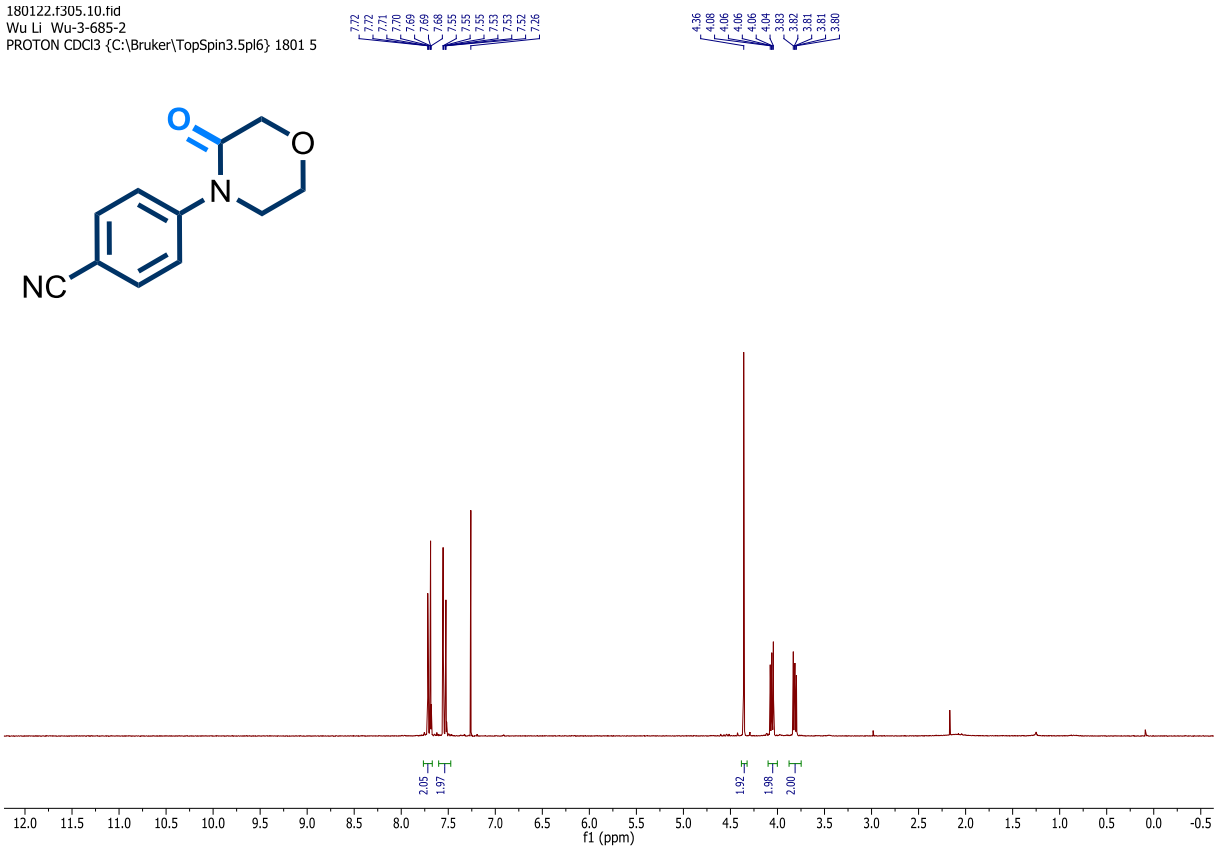
Original spectra for **28c**:

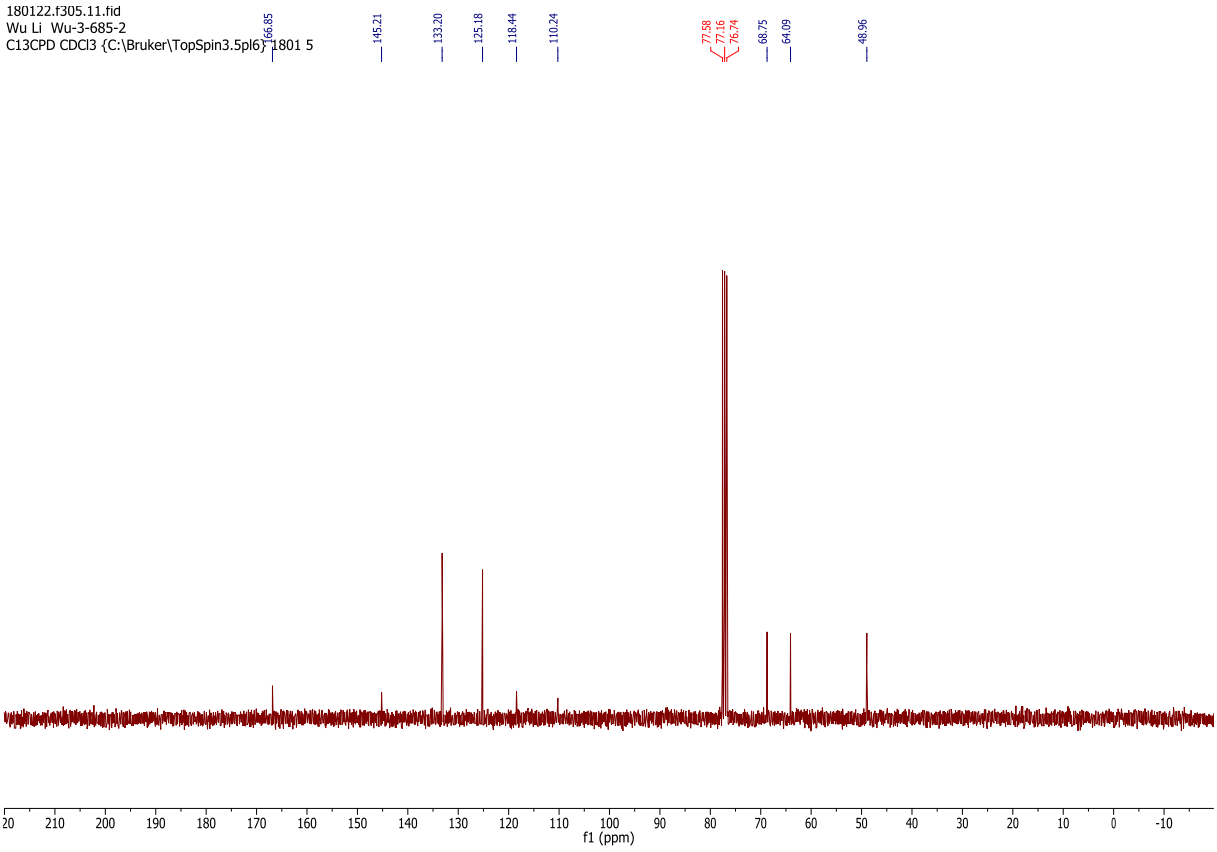


Original spectra for **29b**:

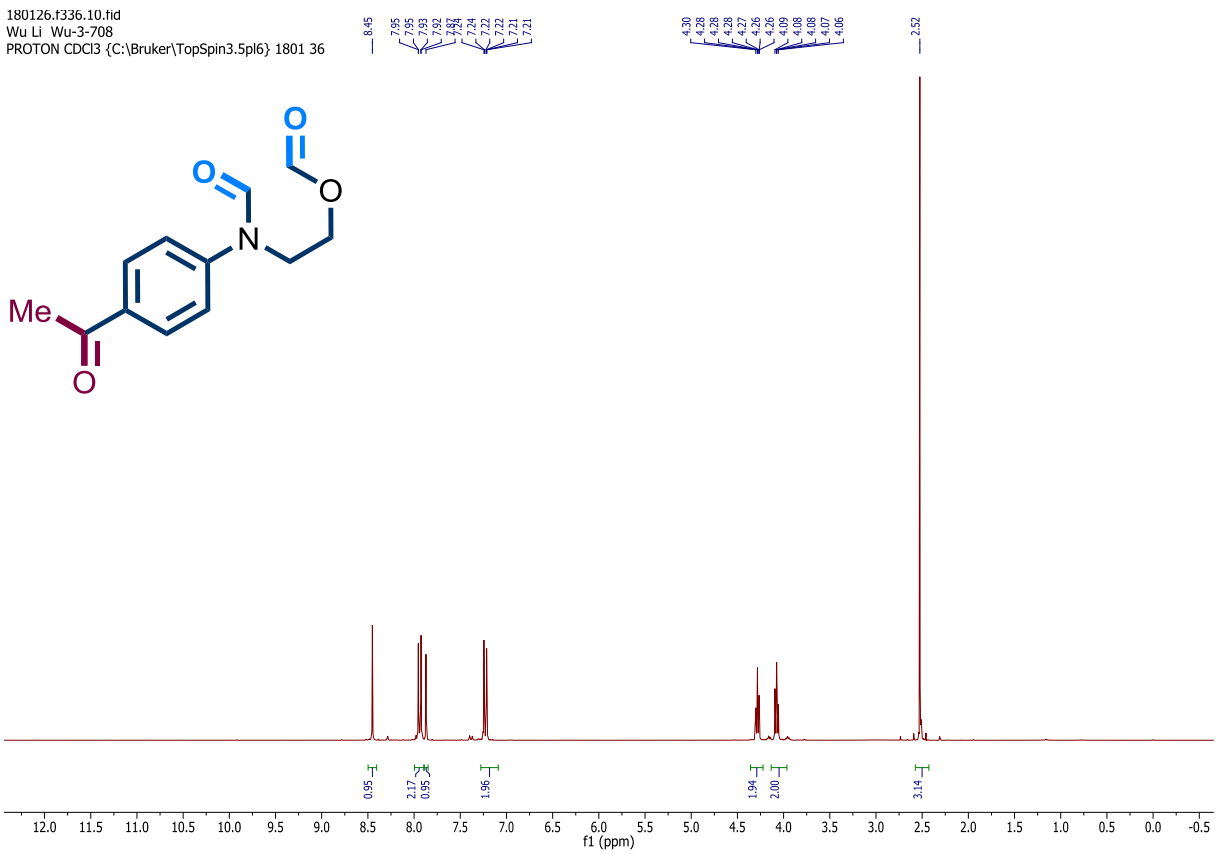


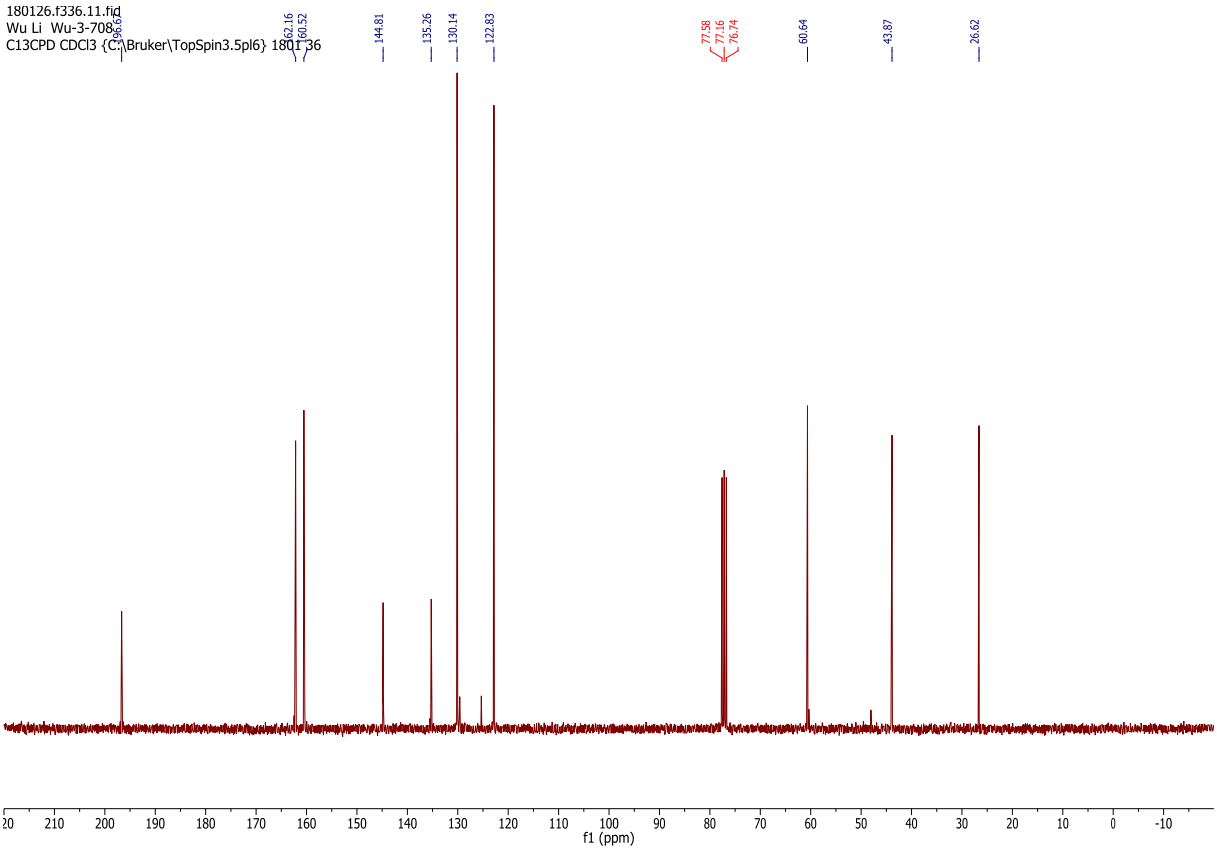
Original spectra for **29c**:



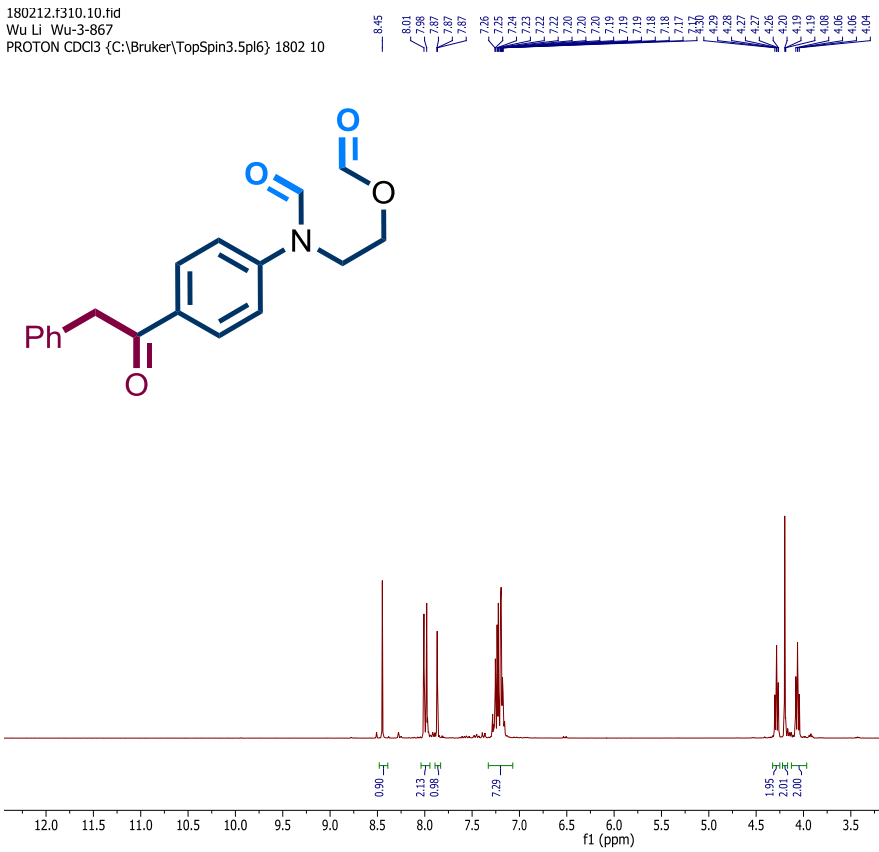


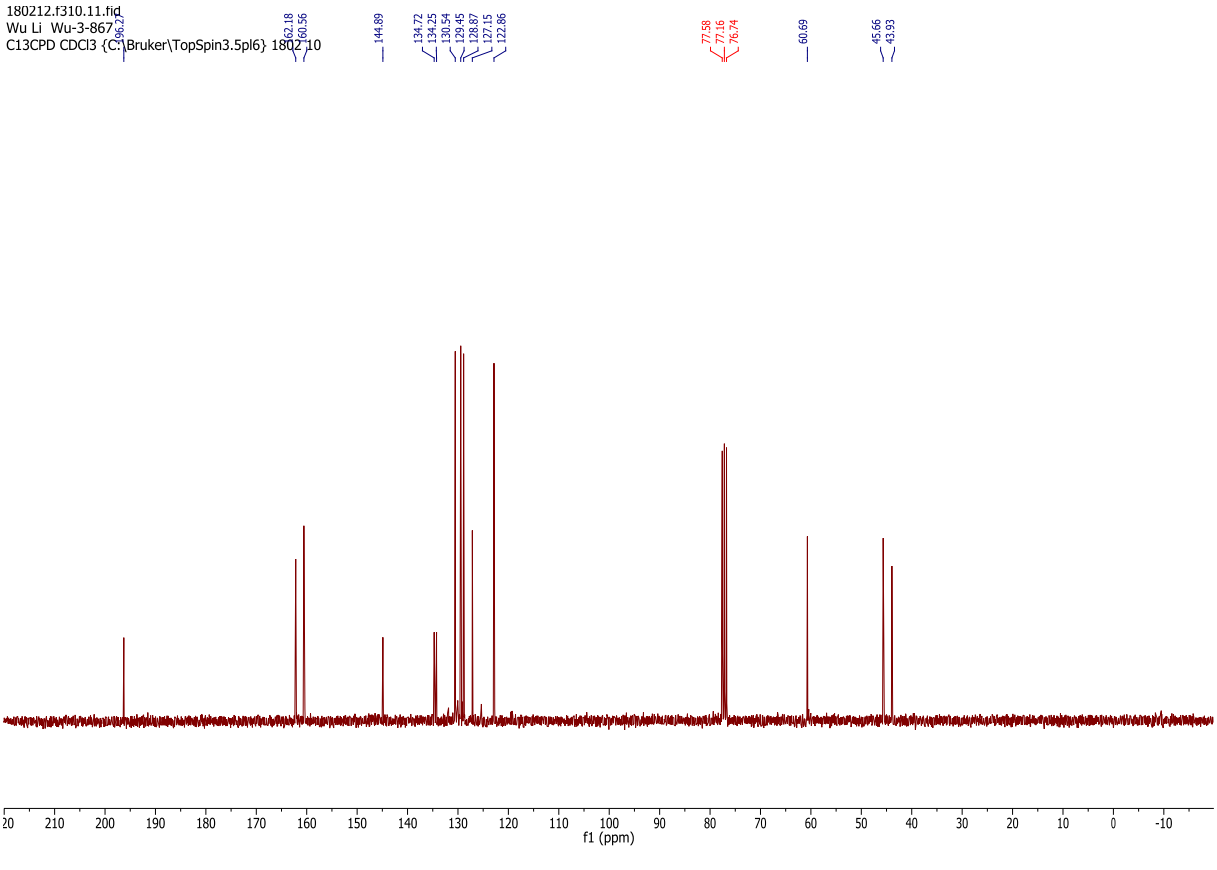
Original spectra for **30b**:



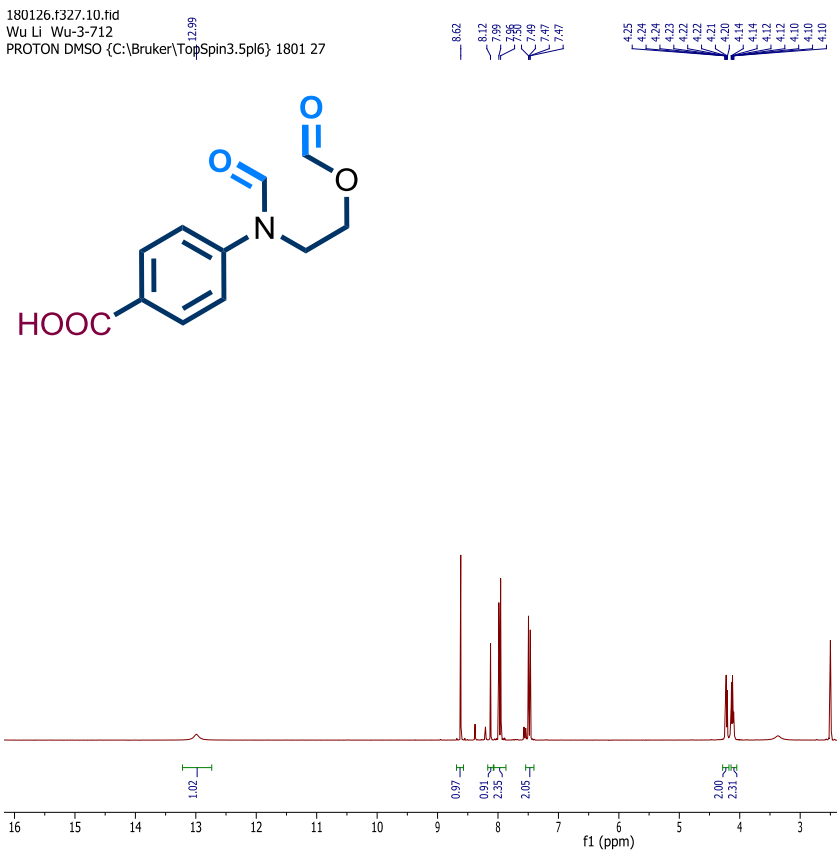


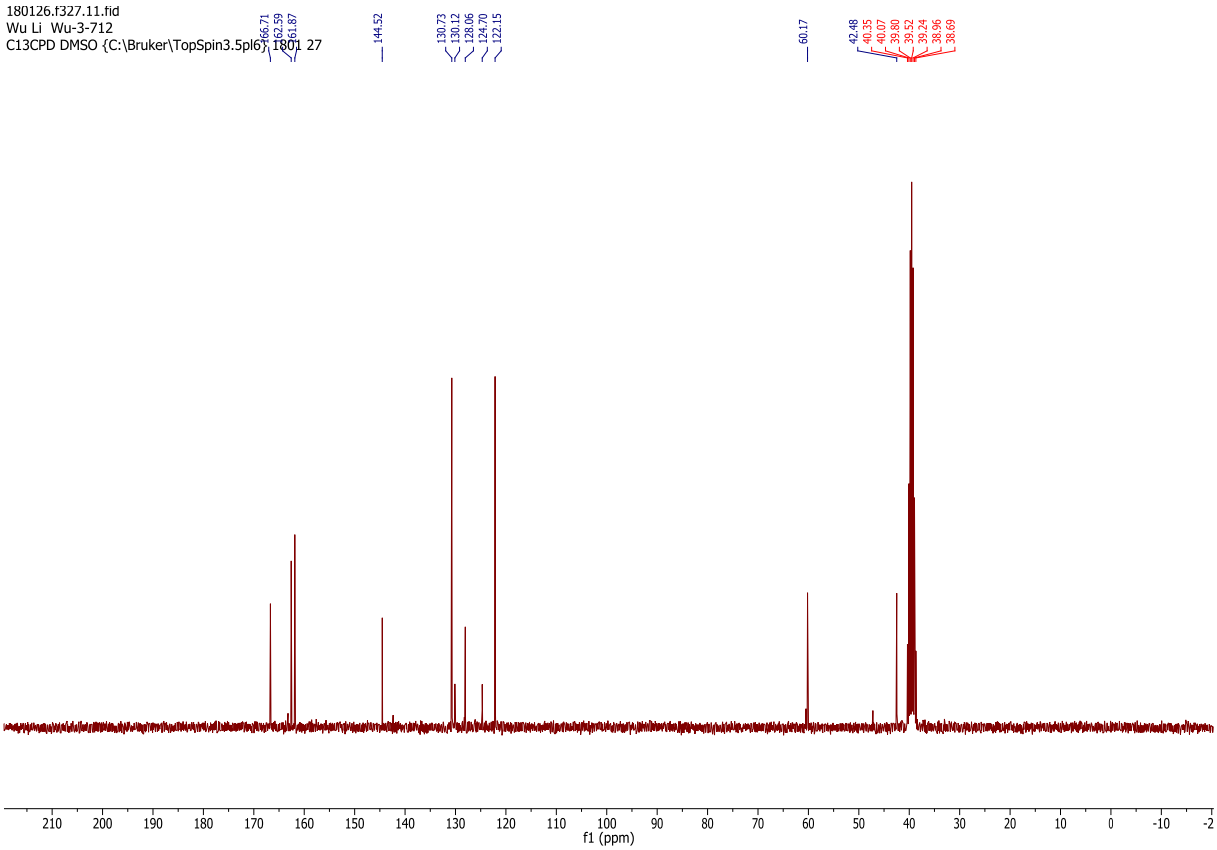
Original spectra for **31b**:



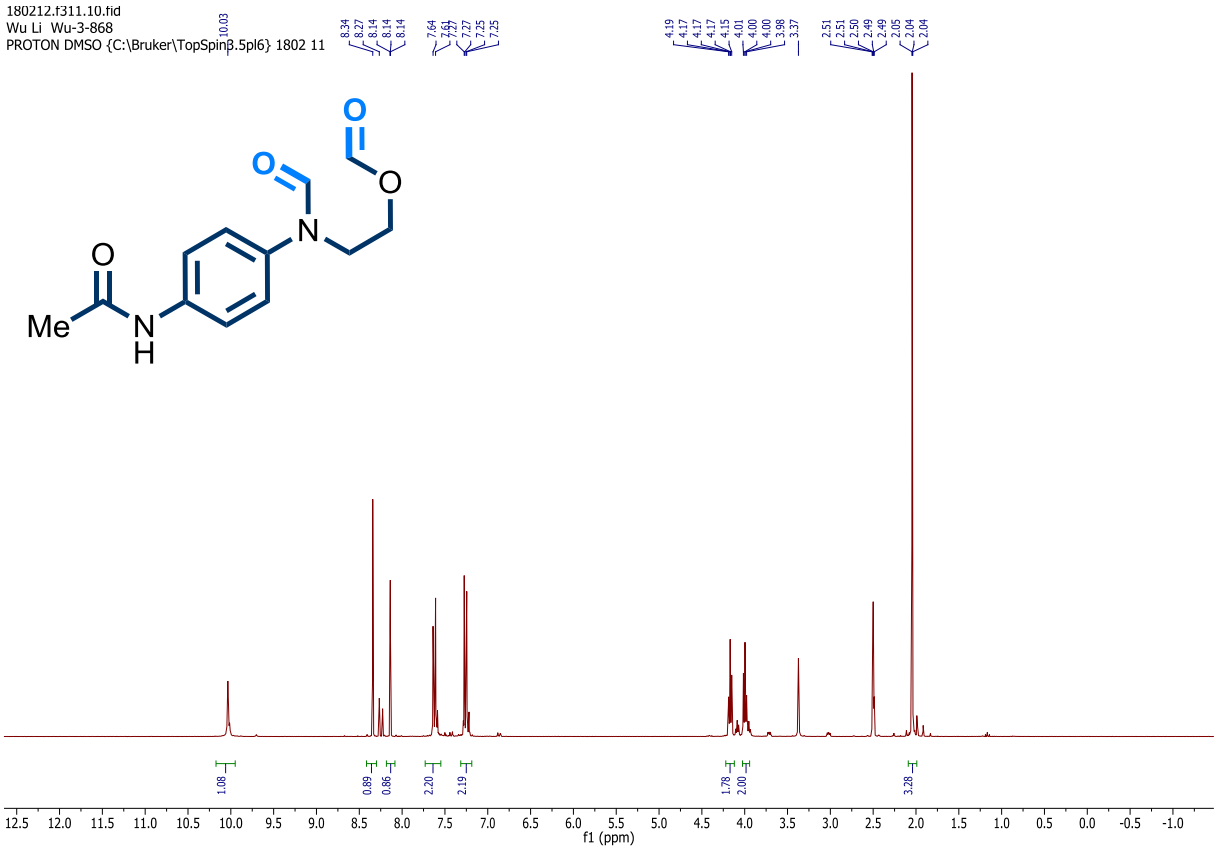


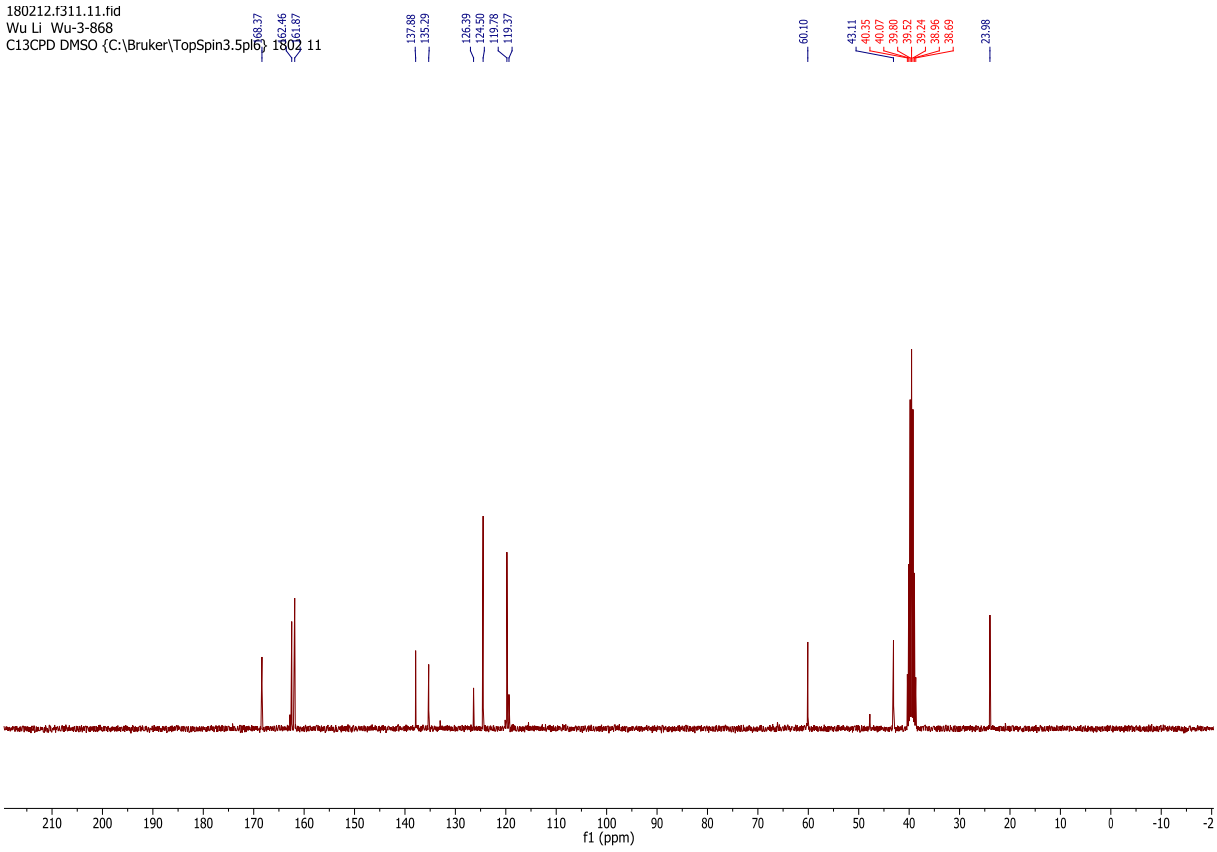
Original spectra for **32b**:



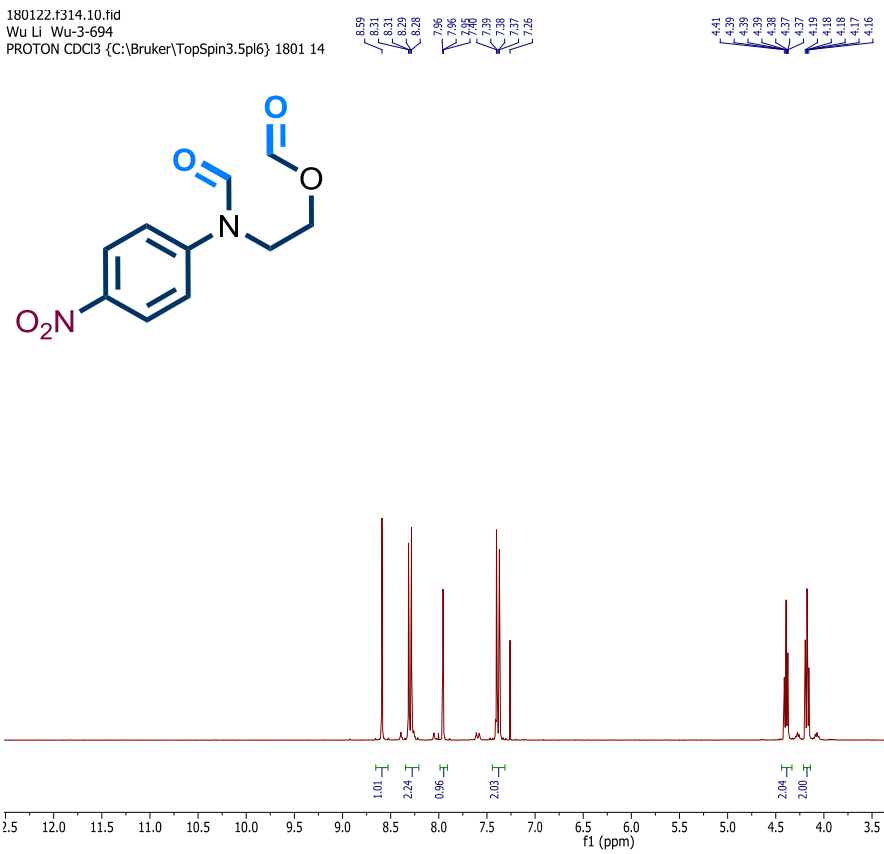


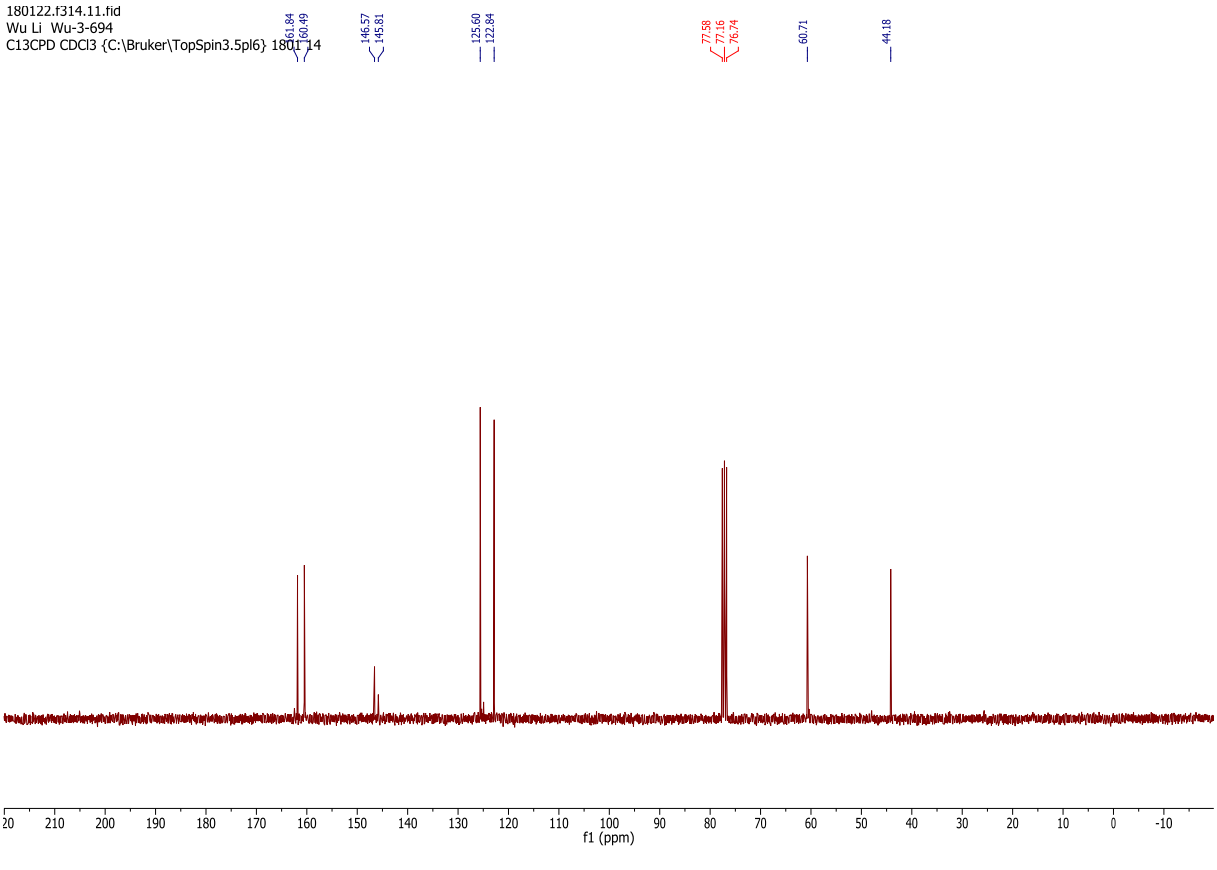
Original spectra for **33b**:



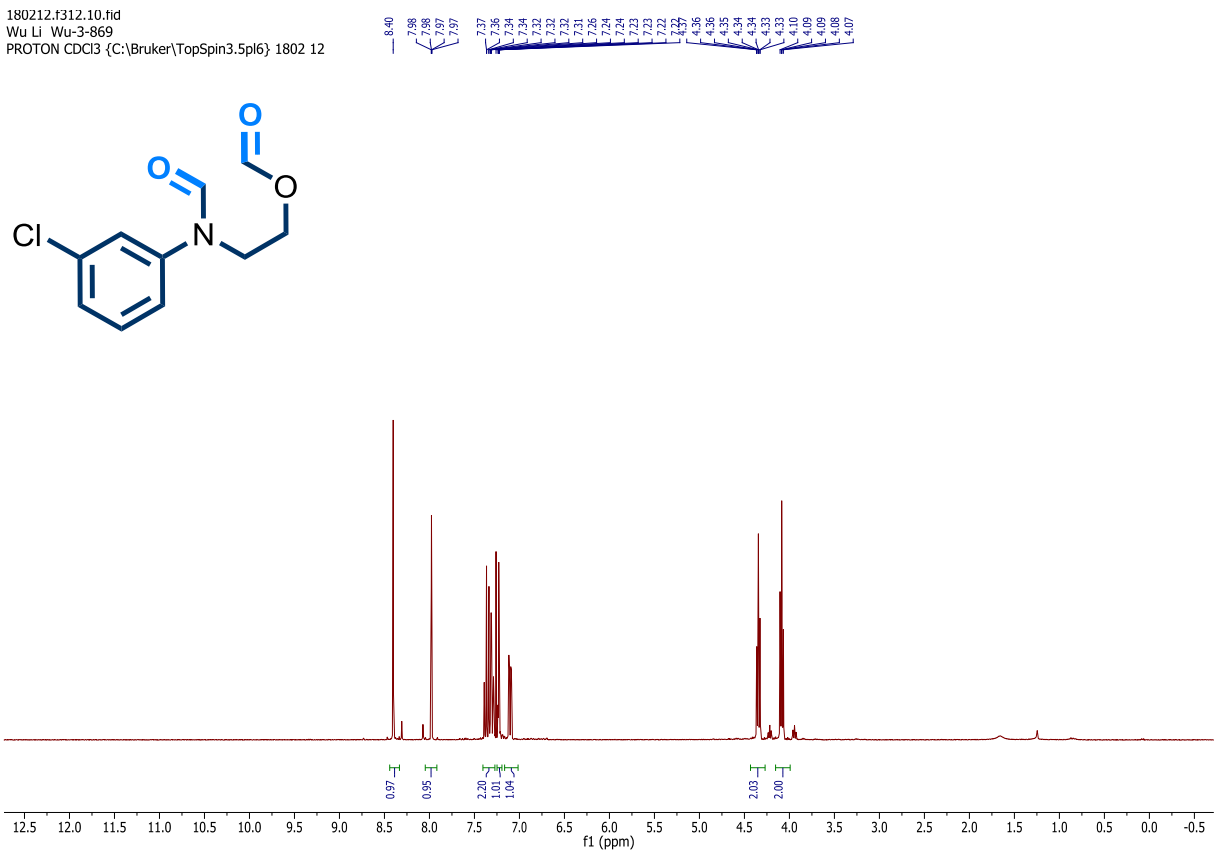


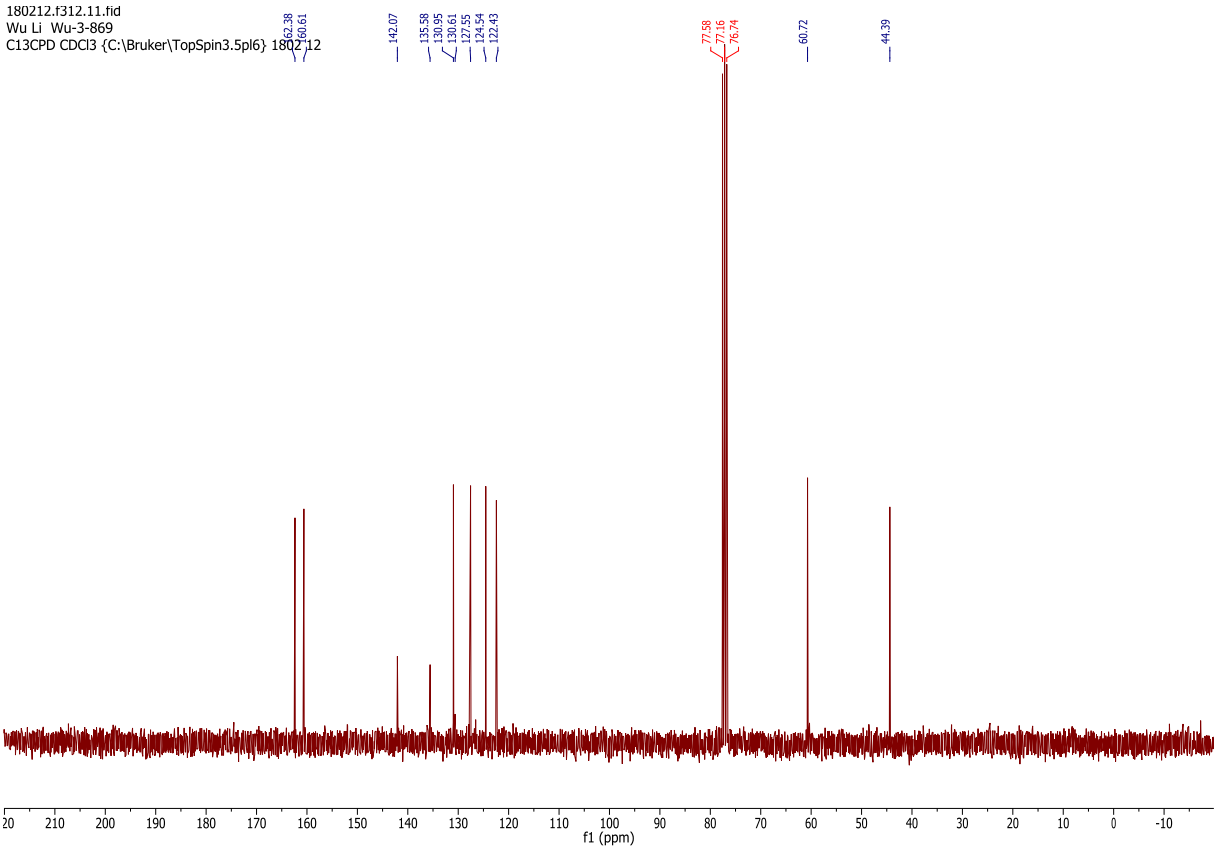
Original spectra for **34b**:



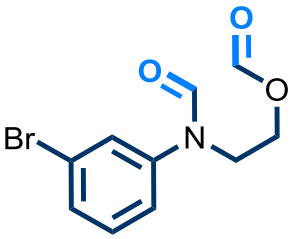


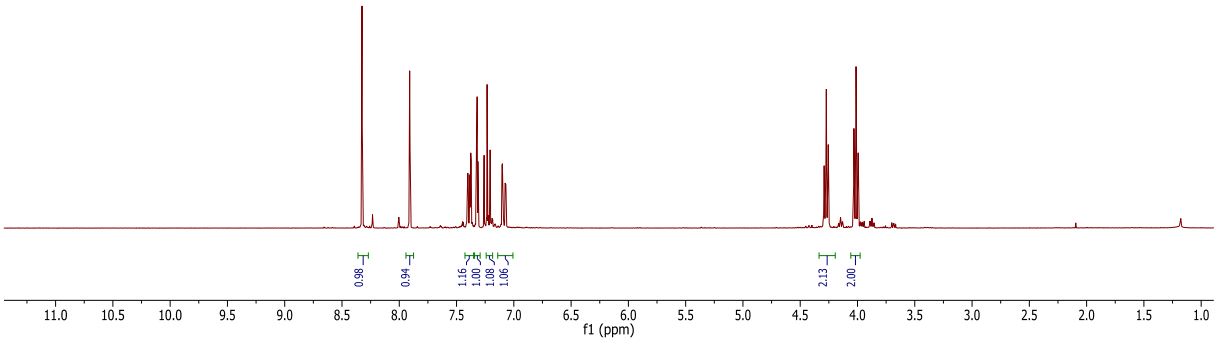
Original spectra for **35b**:

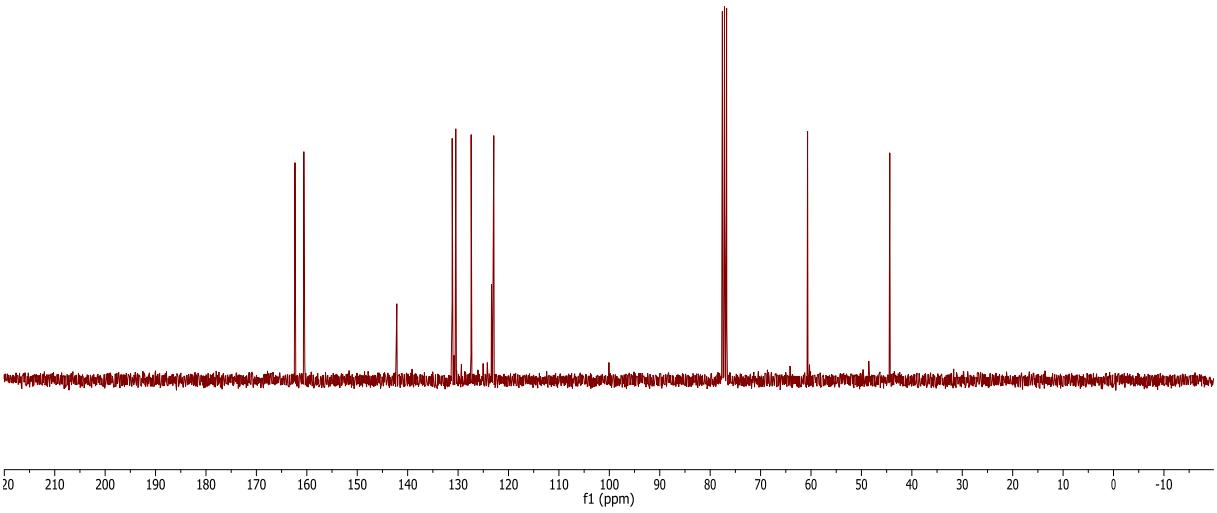




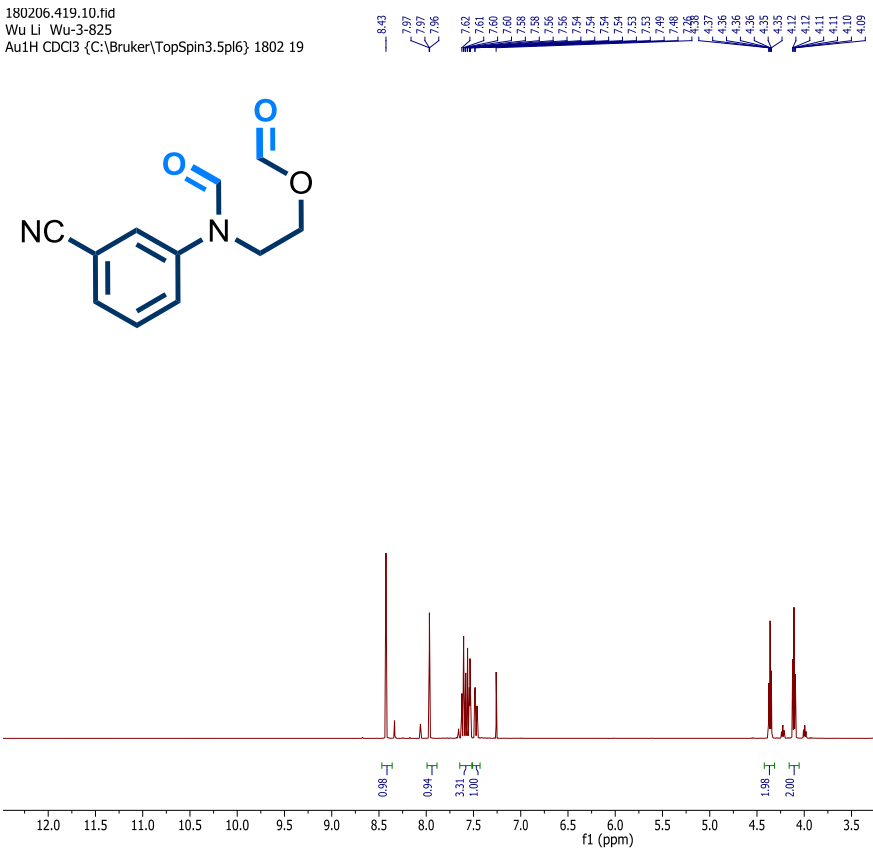
Original spectra for **36b**:

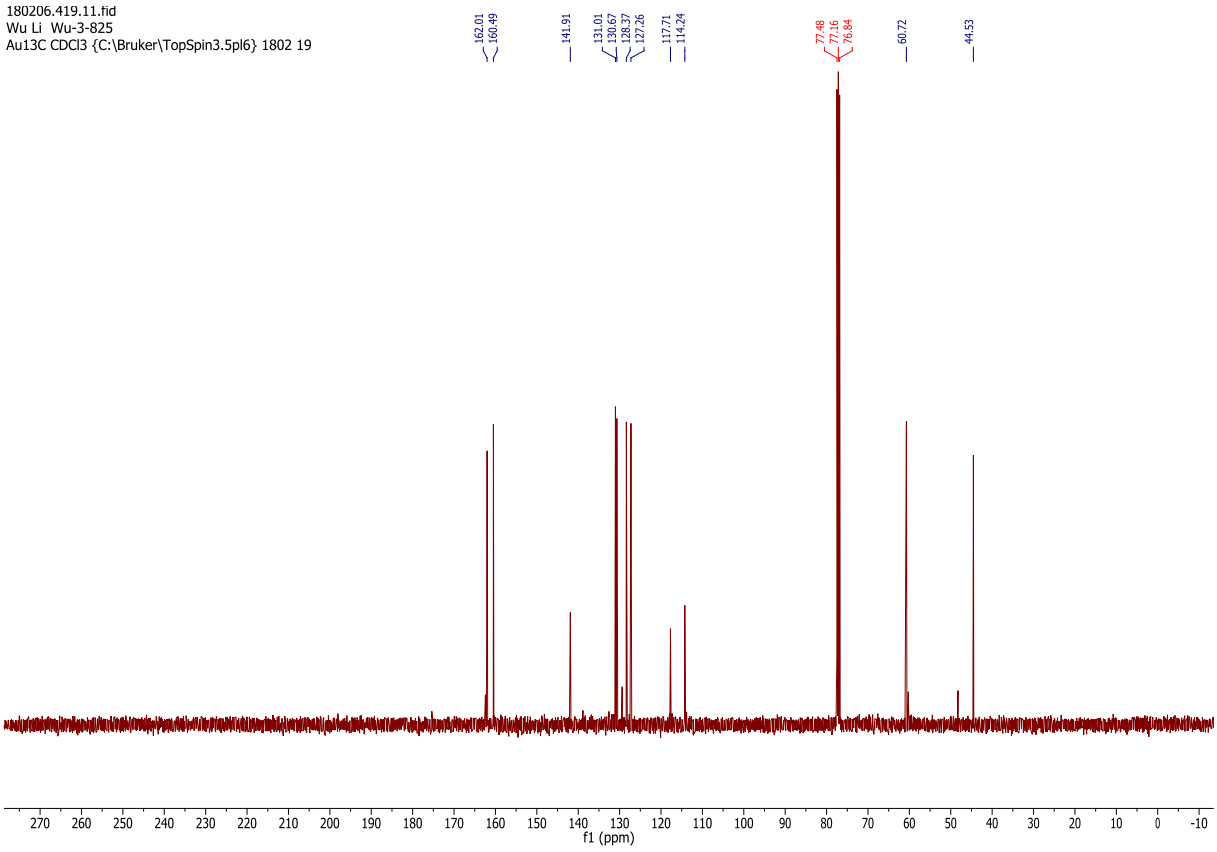




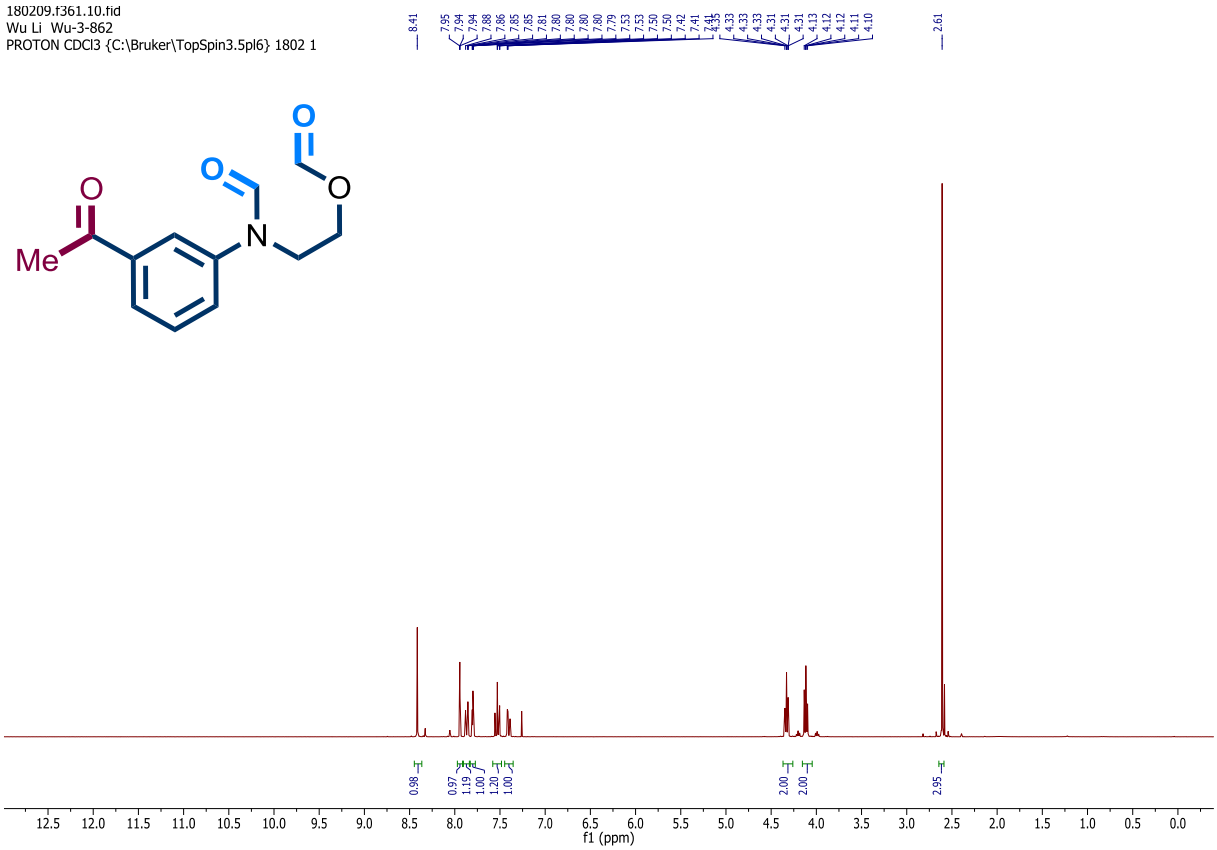


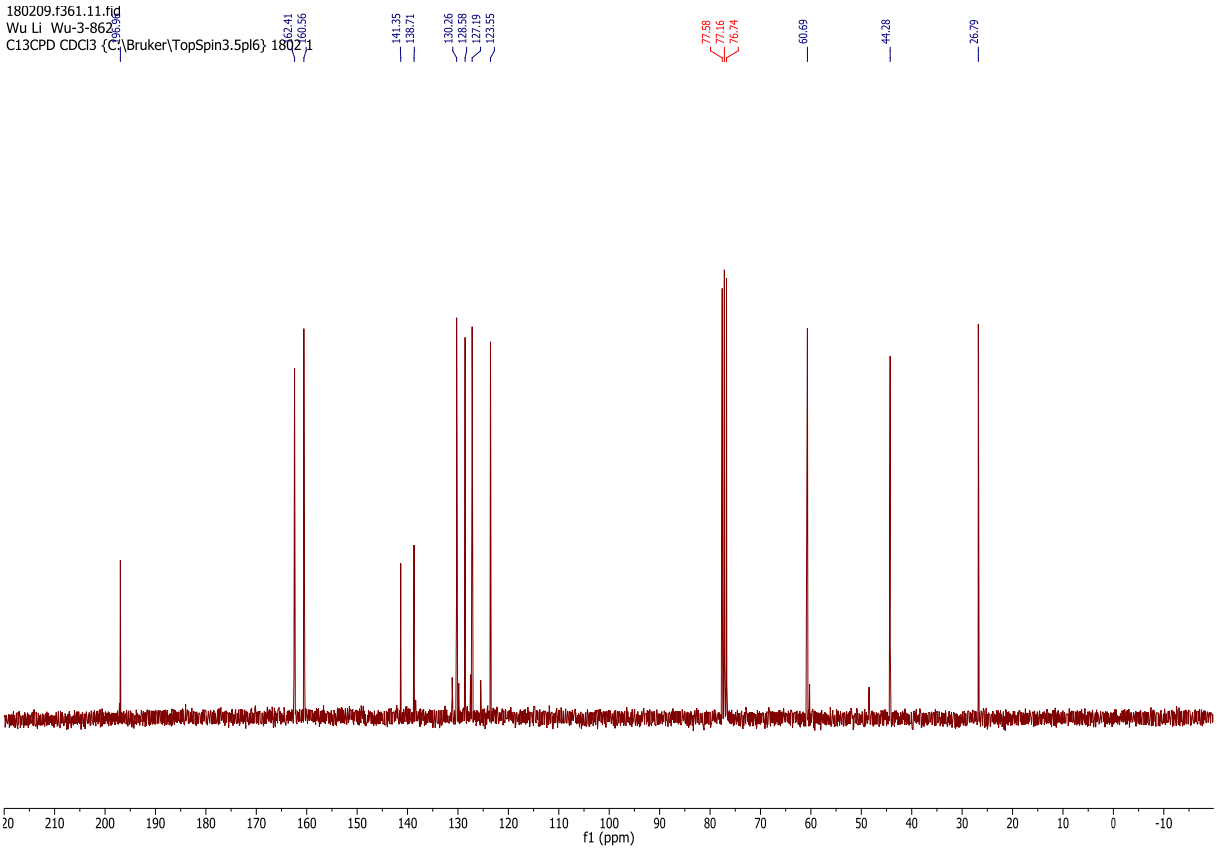
Original spectra for **37b**:



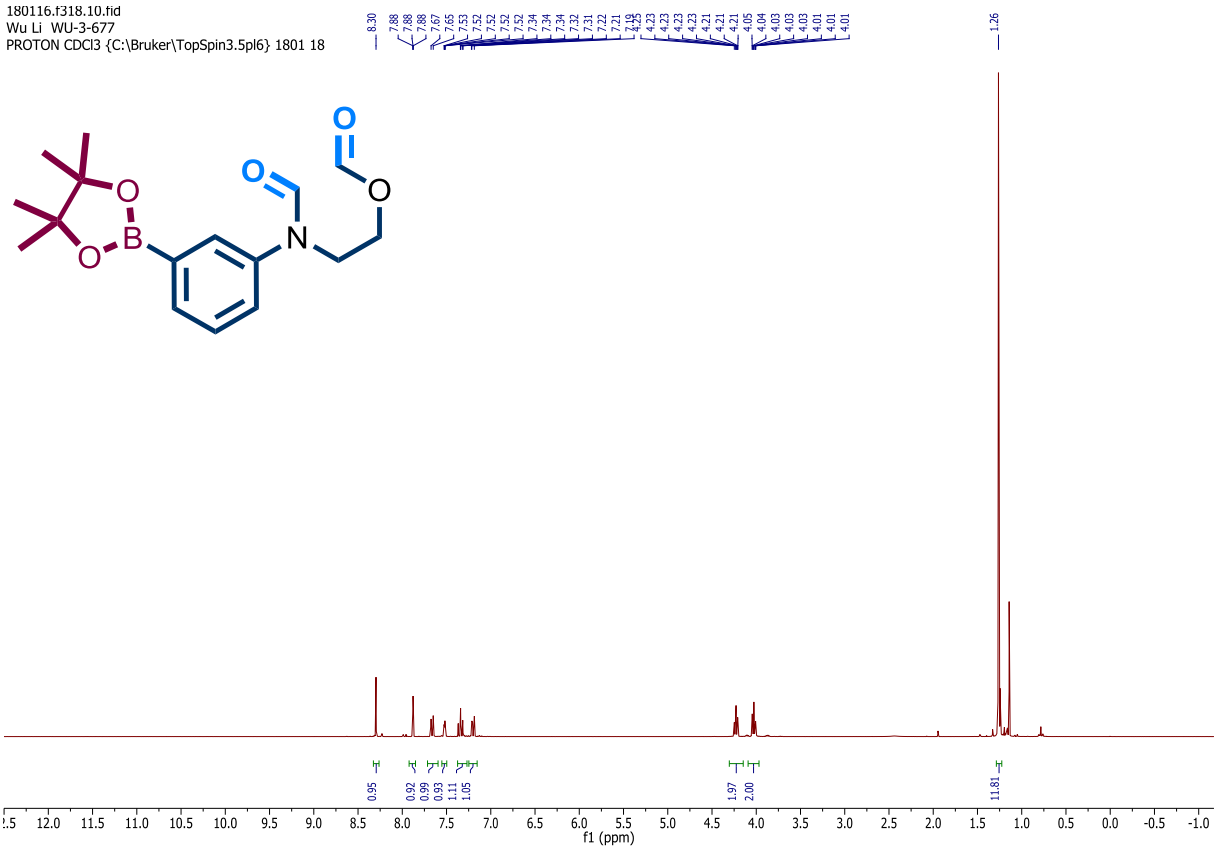


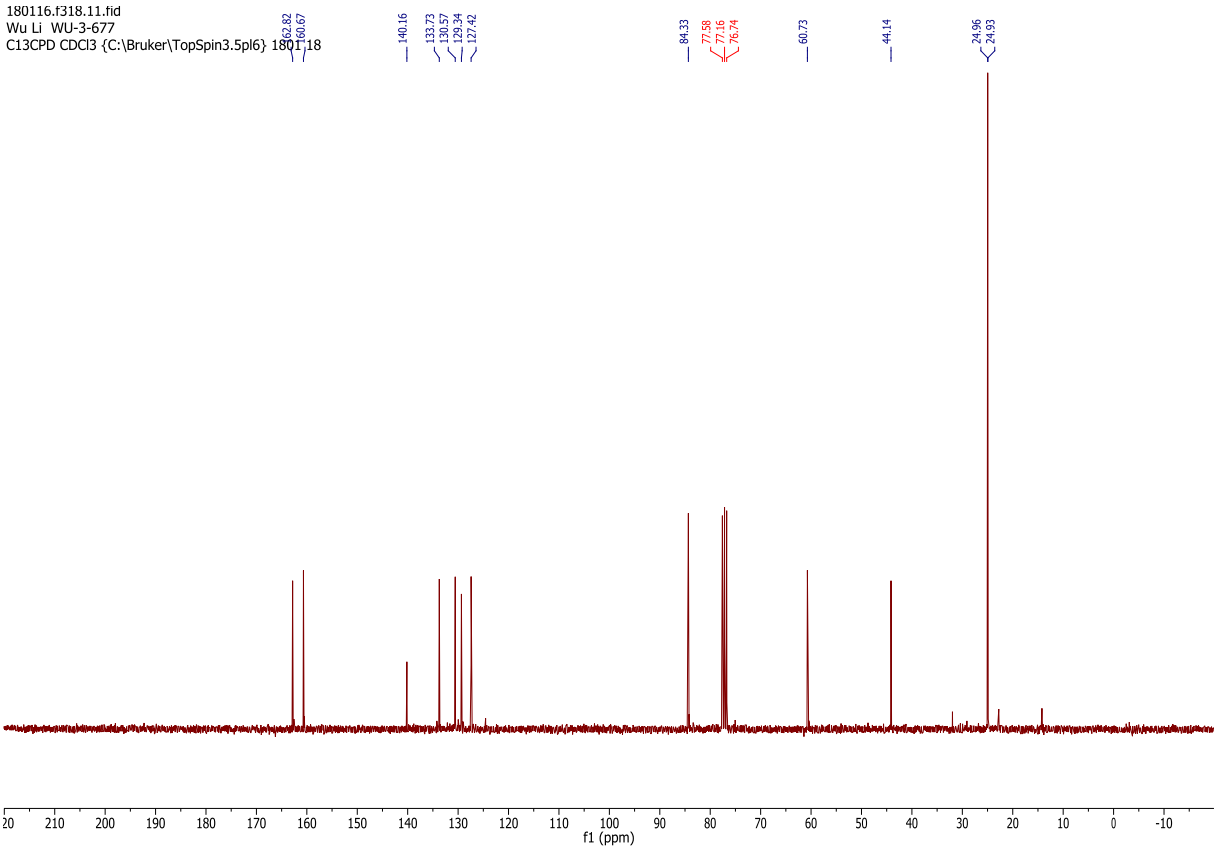
Original spectra for **38b**:



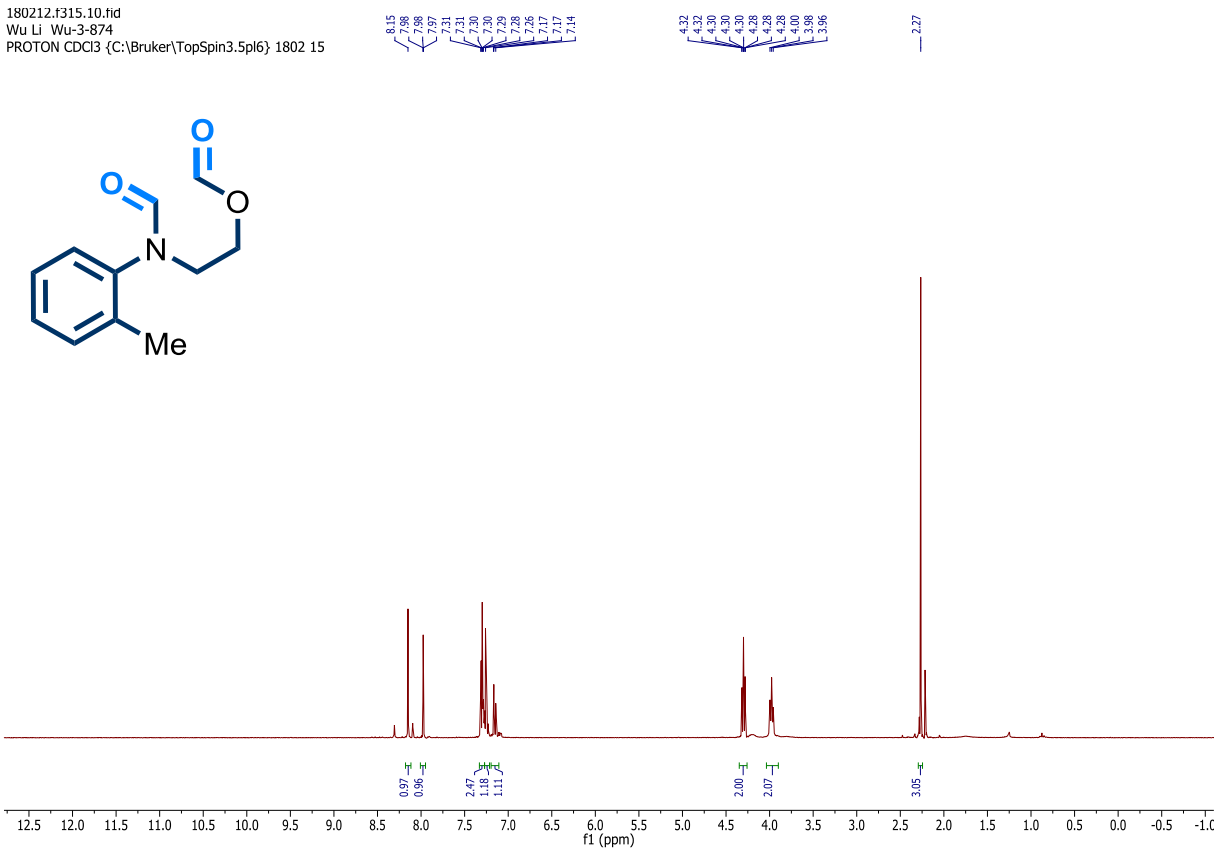


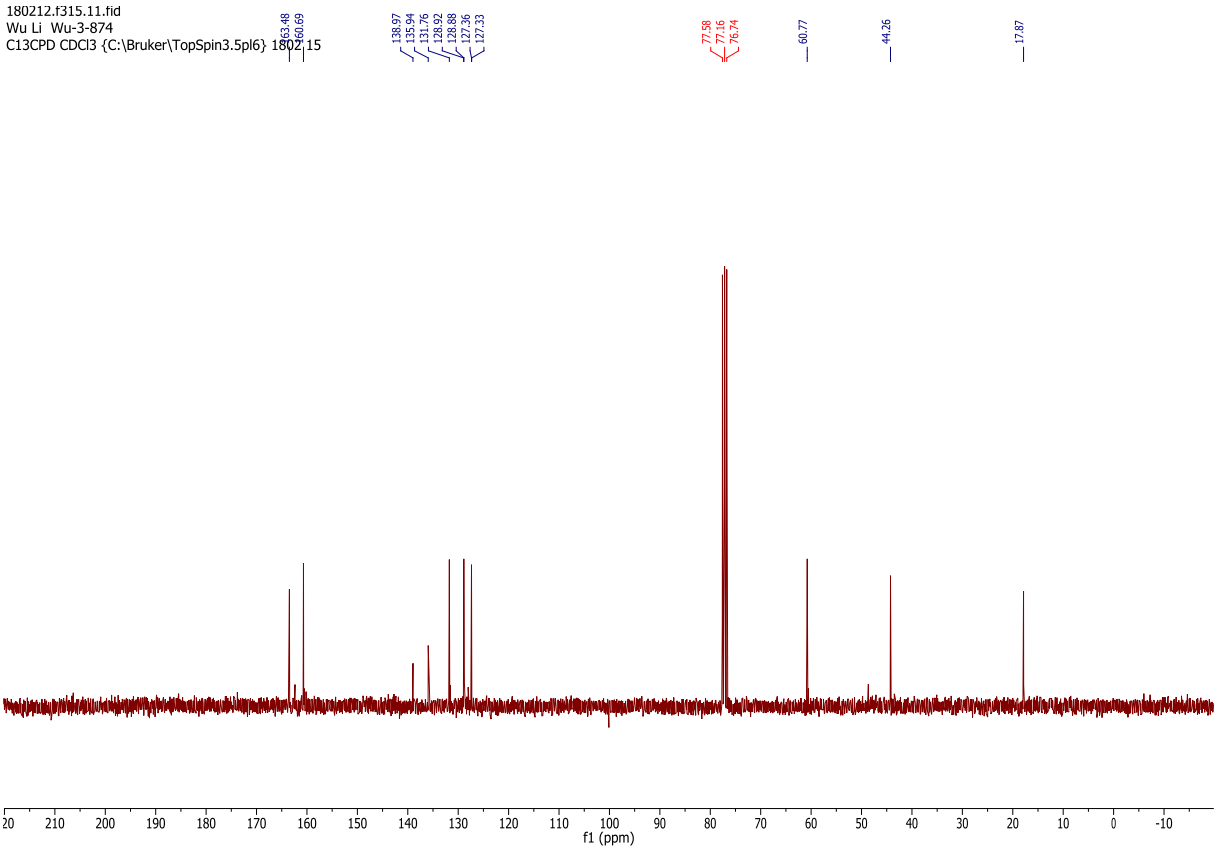
Original spectra for **39b**:



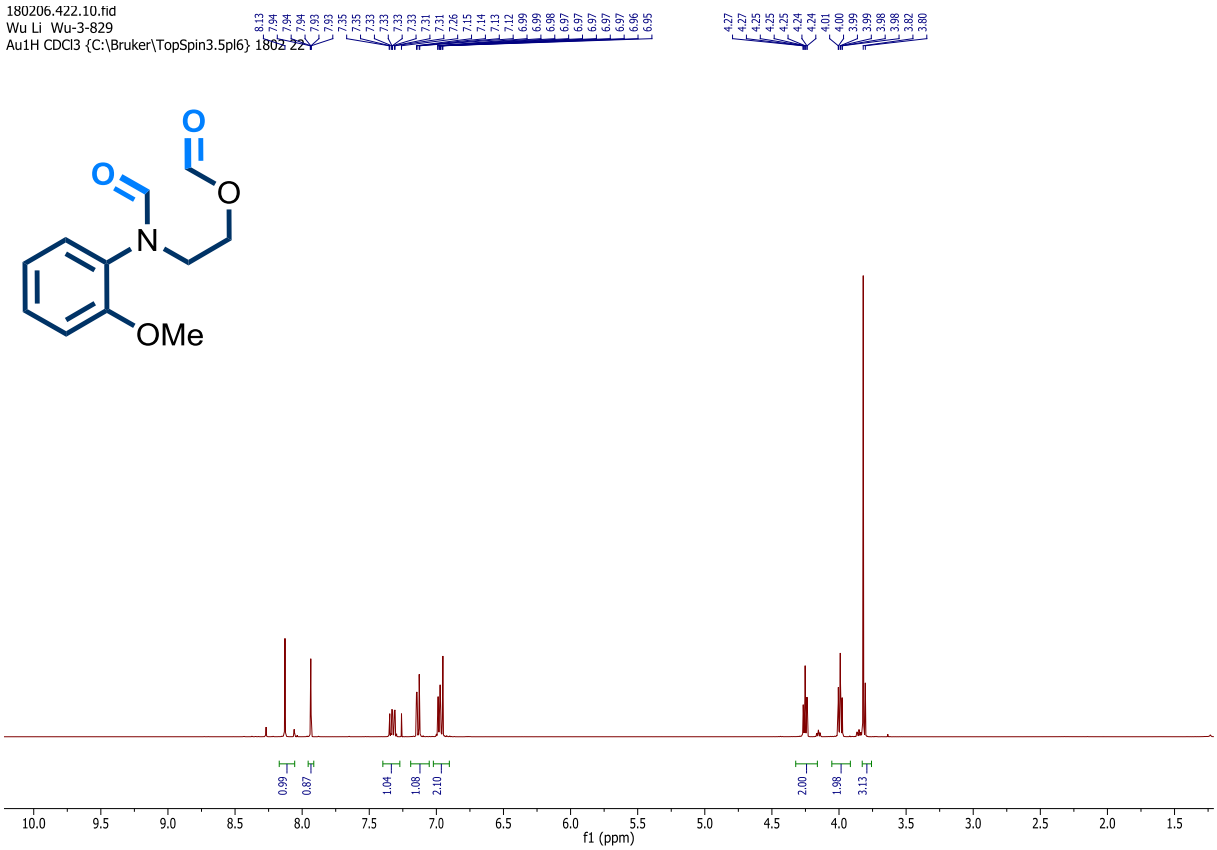


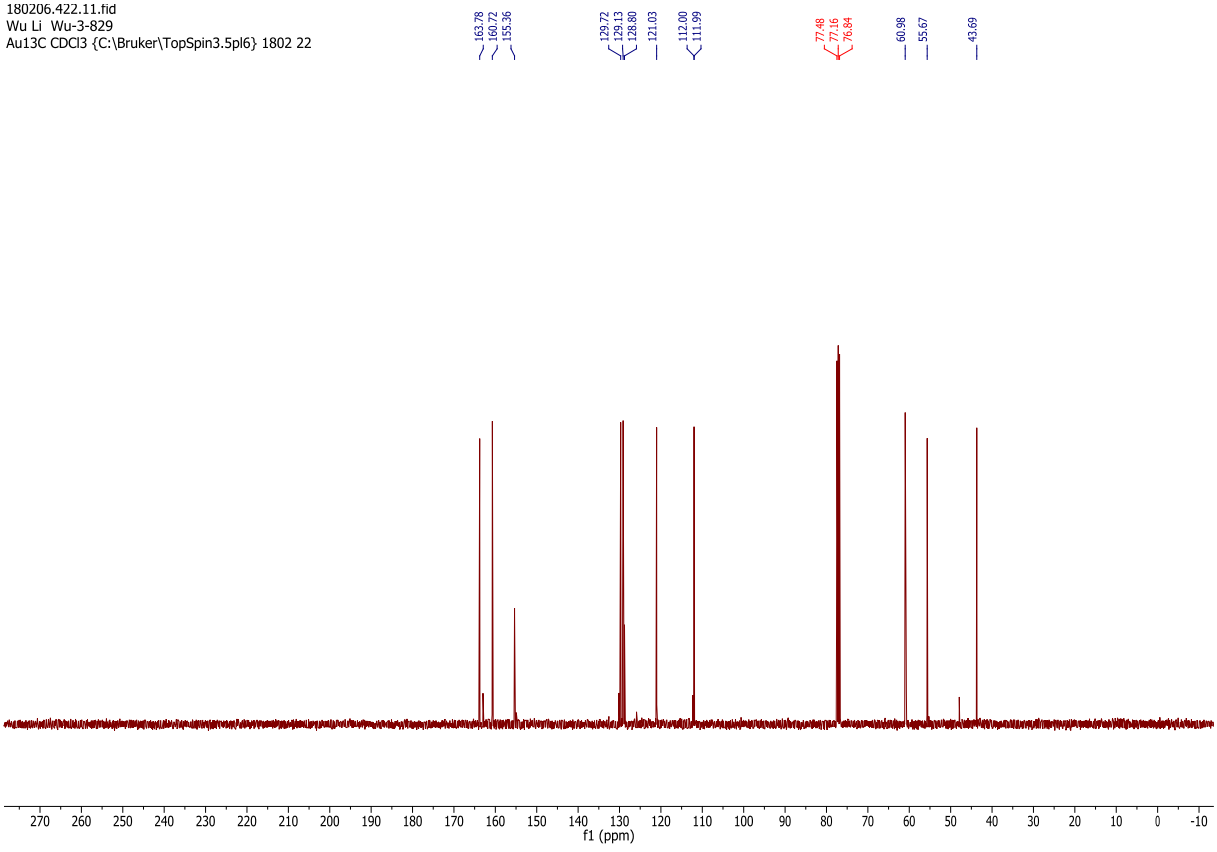
Original spectra for **40b**:



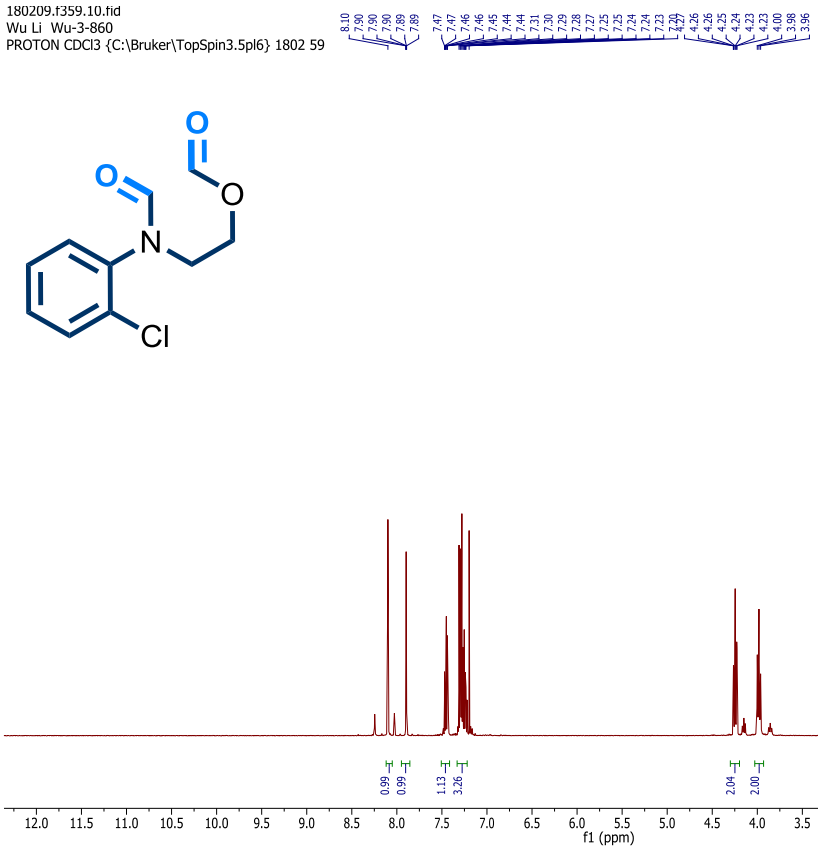


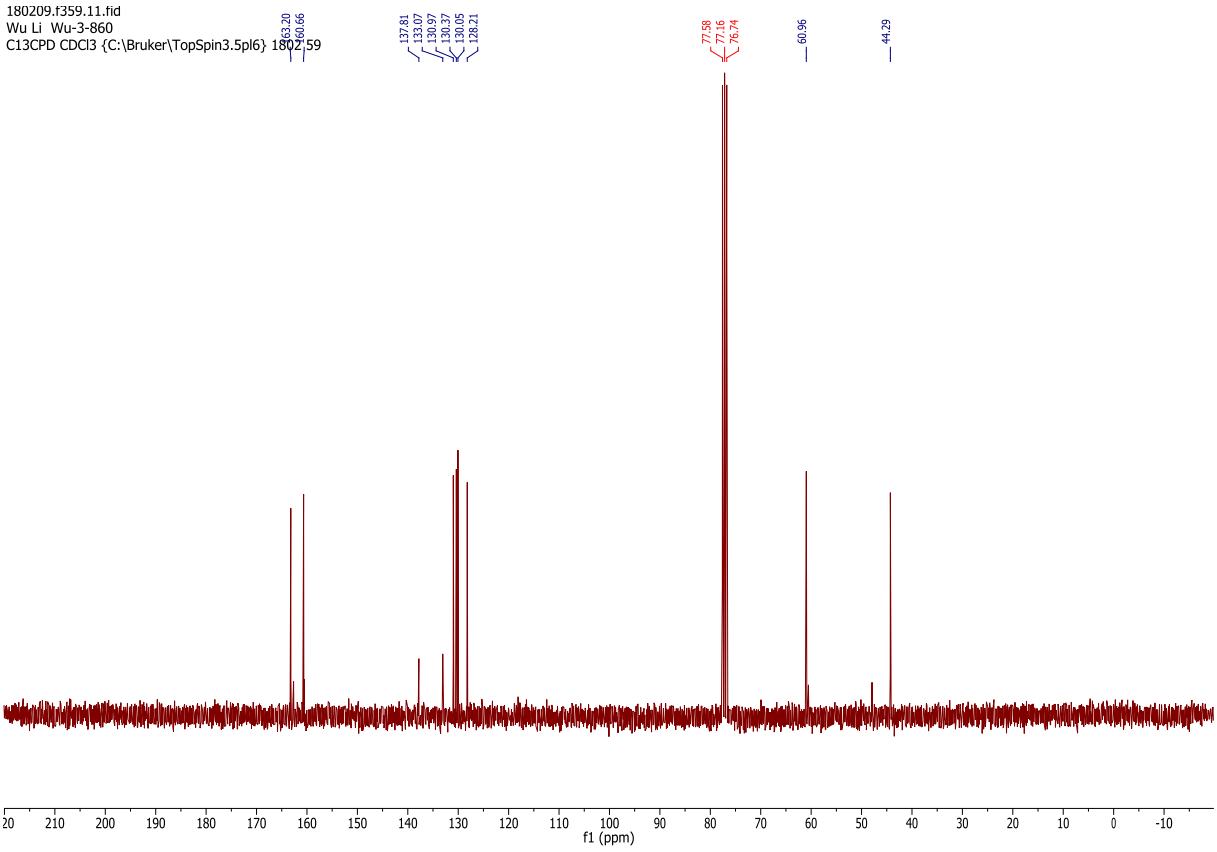
Original spectra for **41b**:



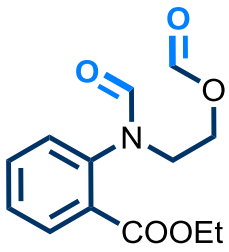


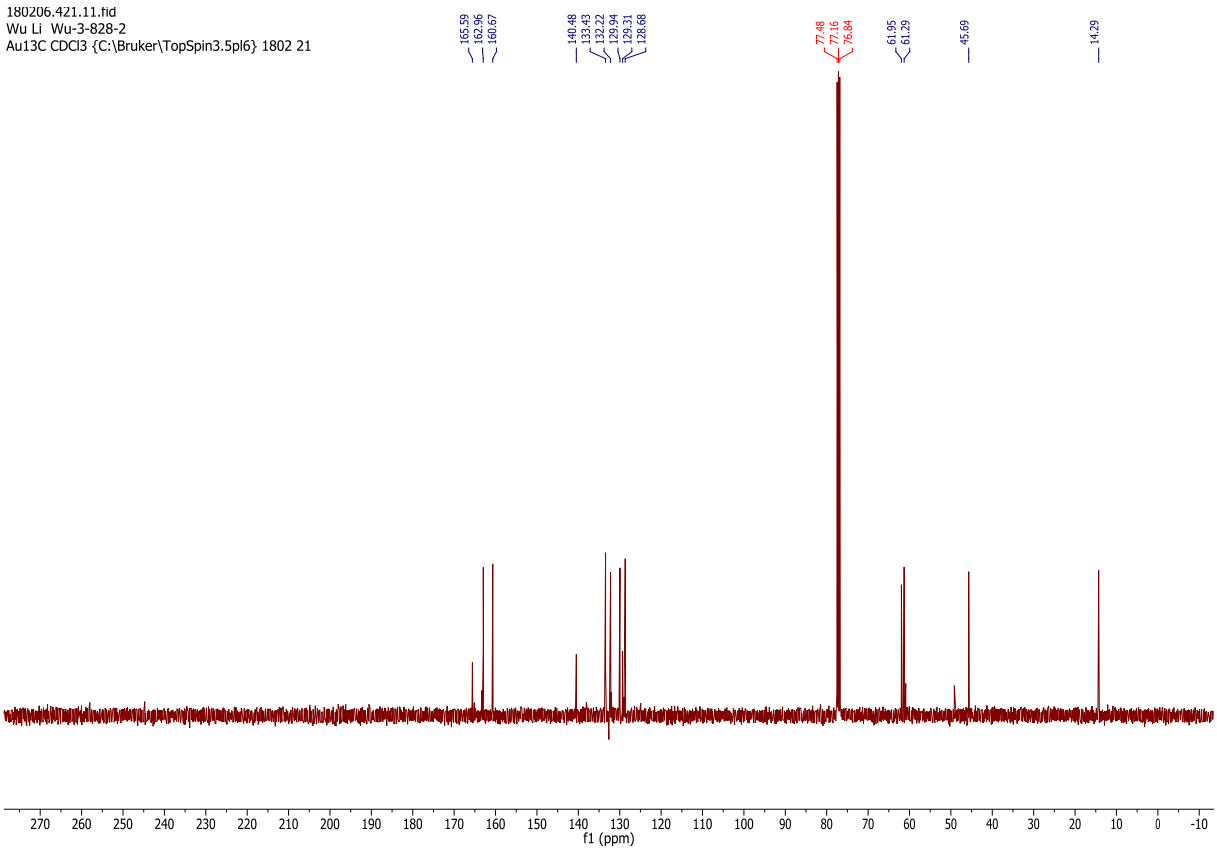
Original spectra for **42b**:



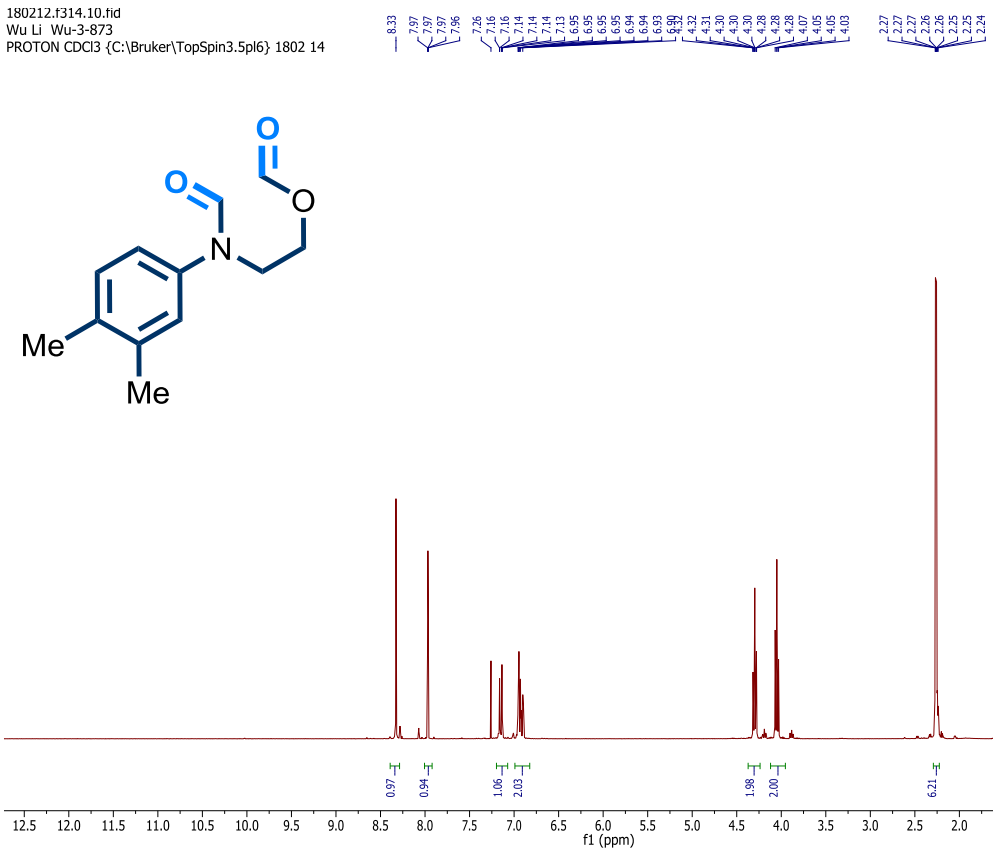


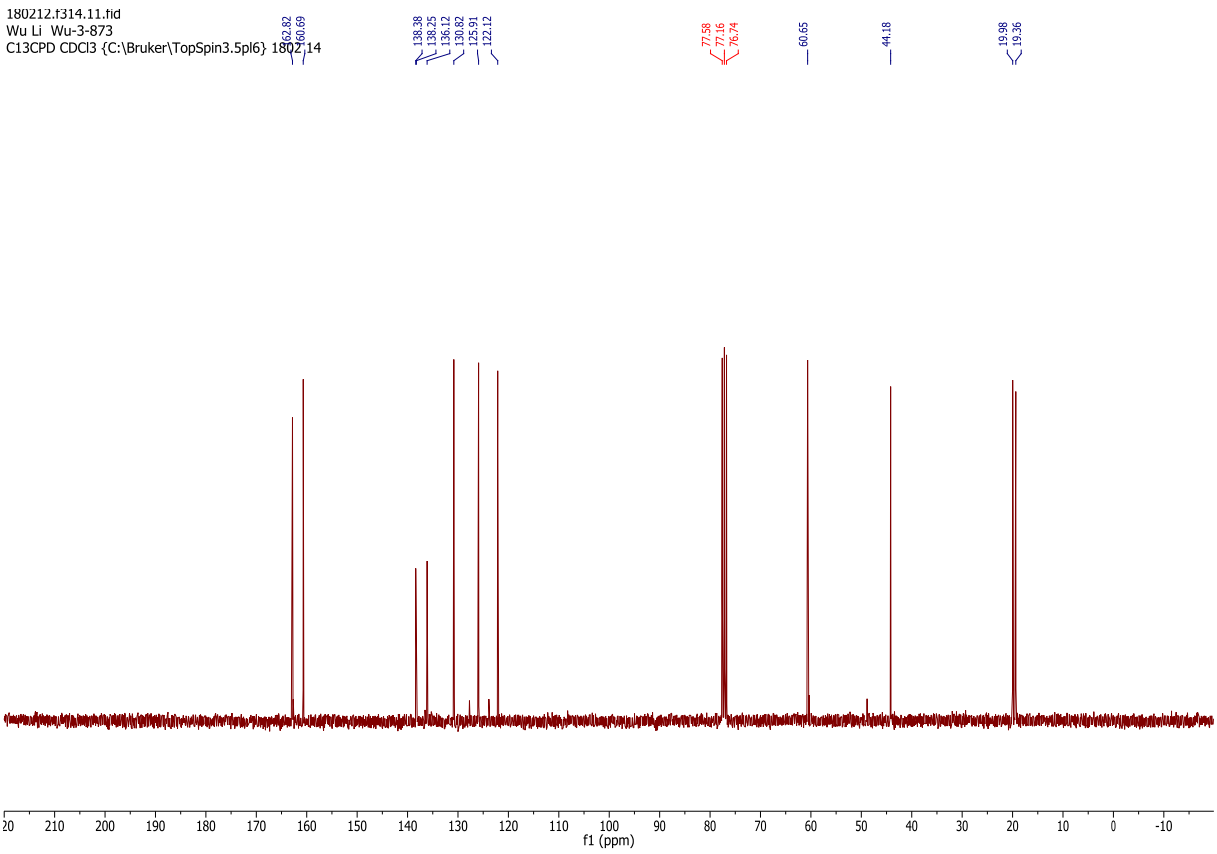
Original spectra for **43b**:



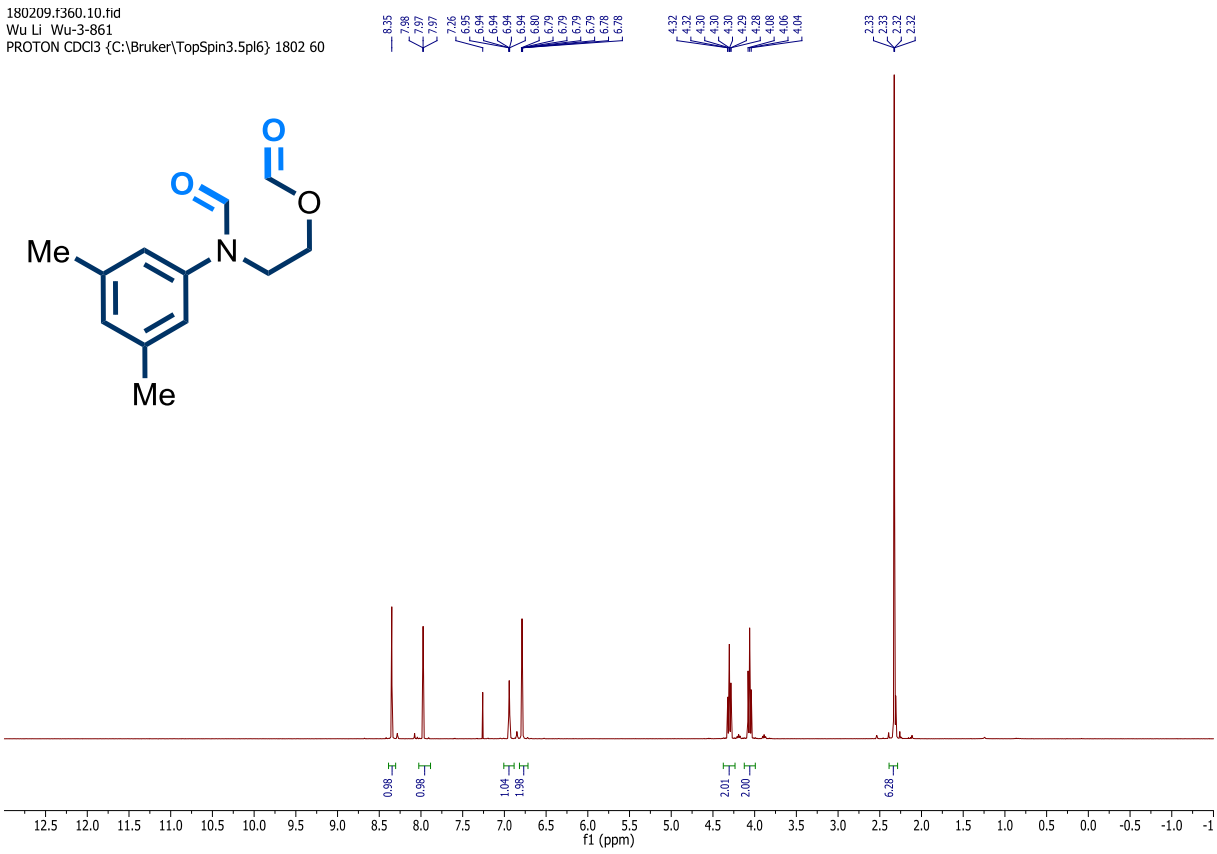


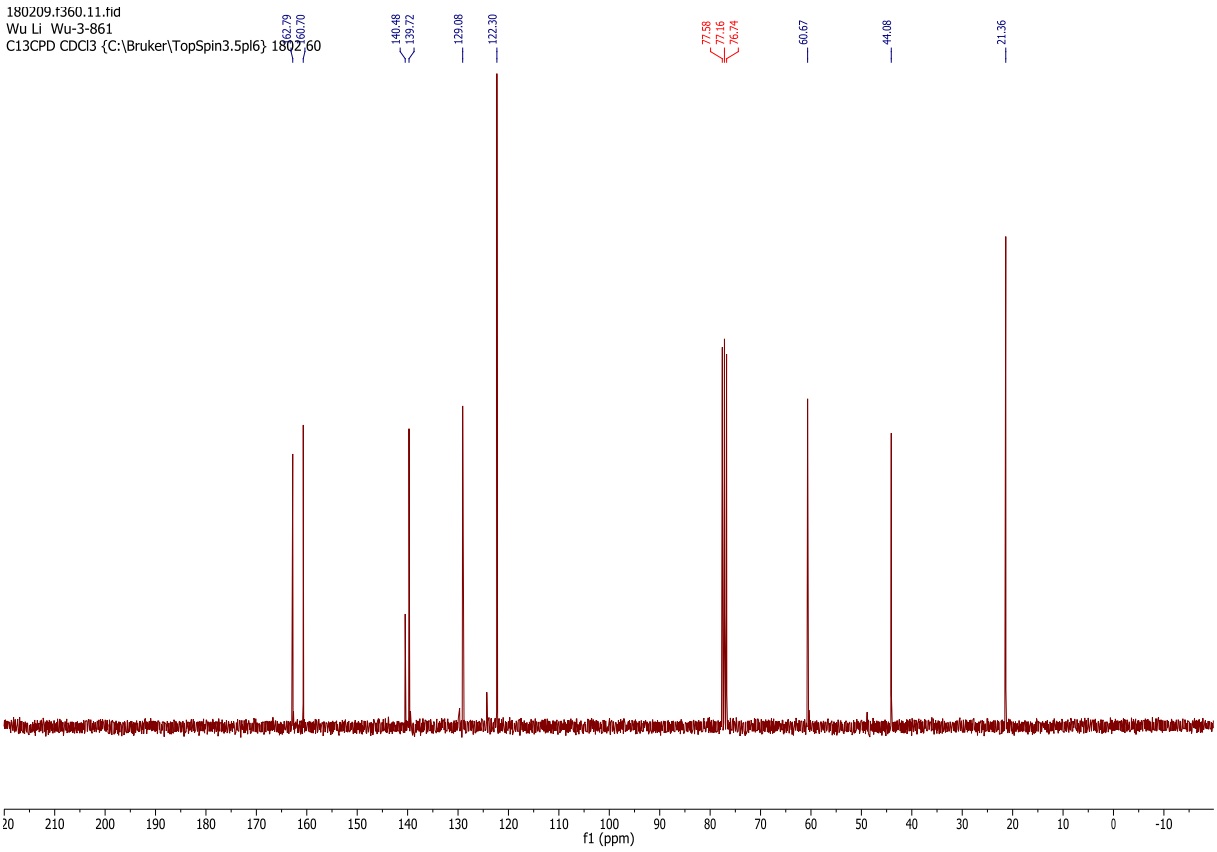
Original spectra for **44b**:



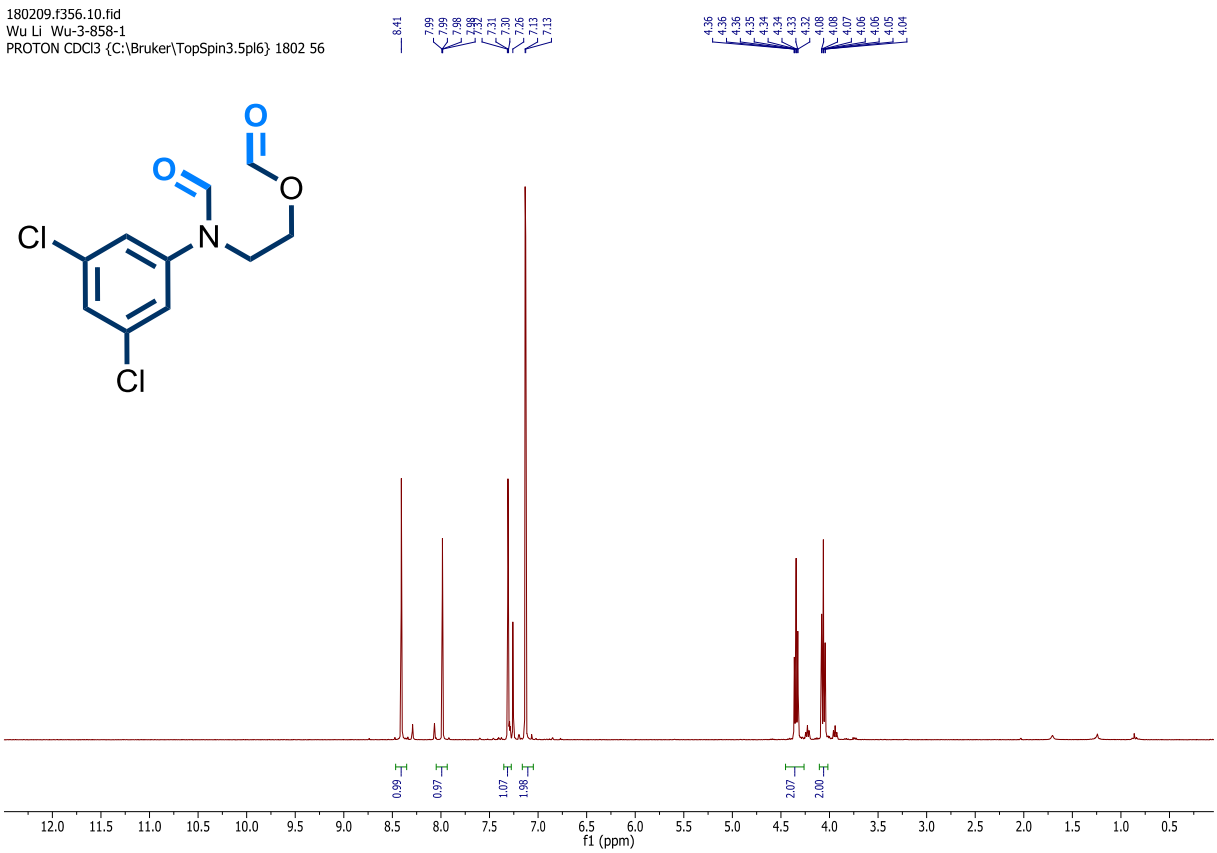


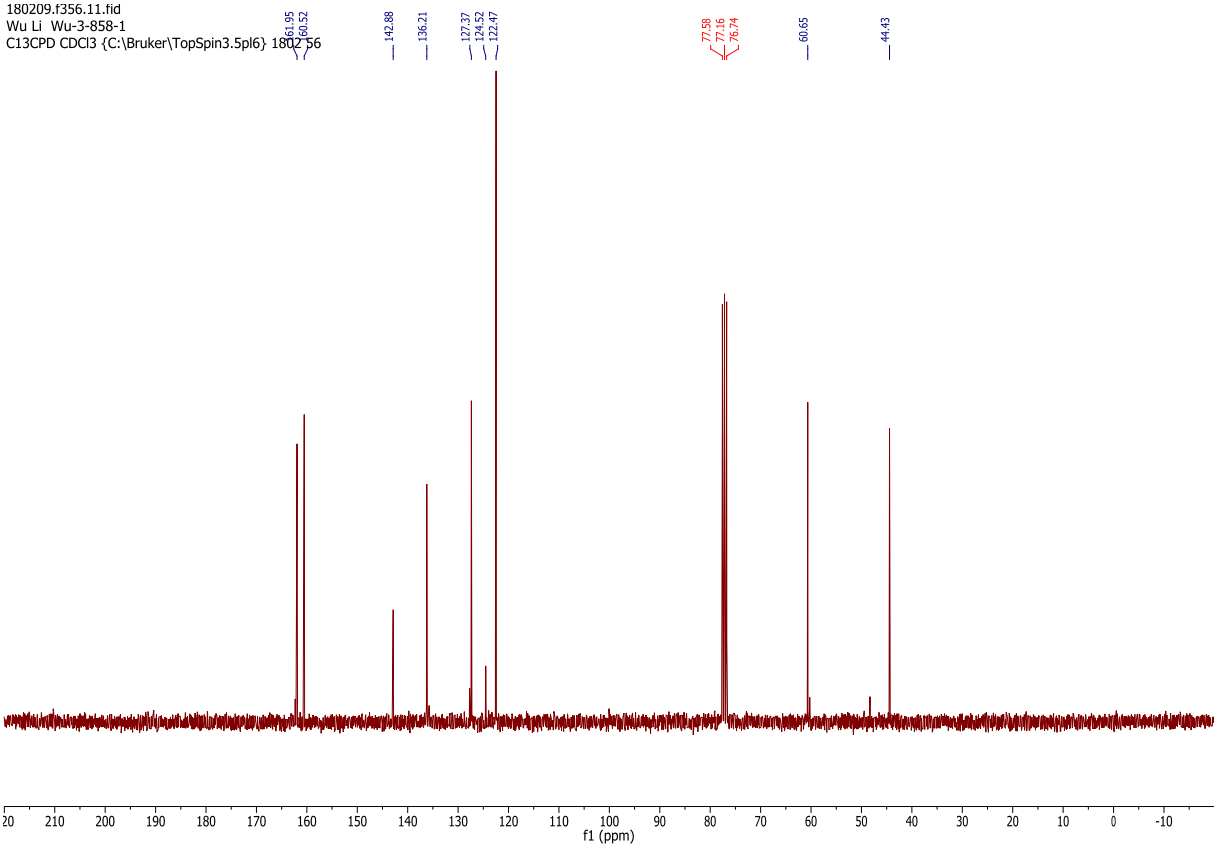
Original spectra for **45b**:



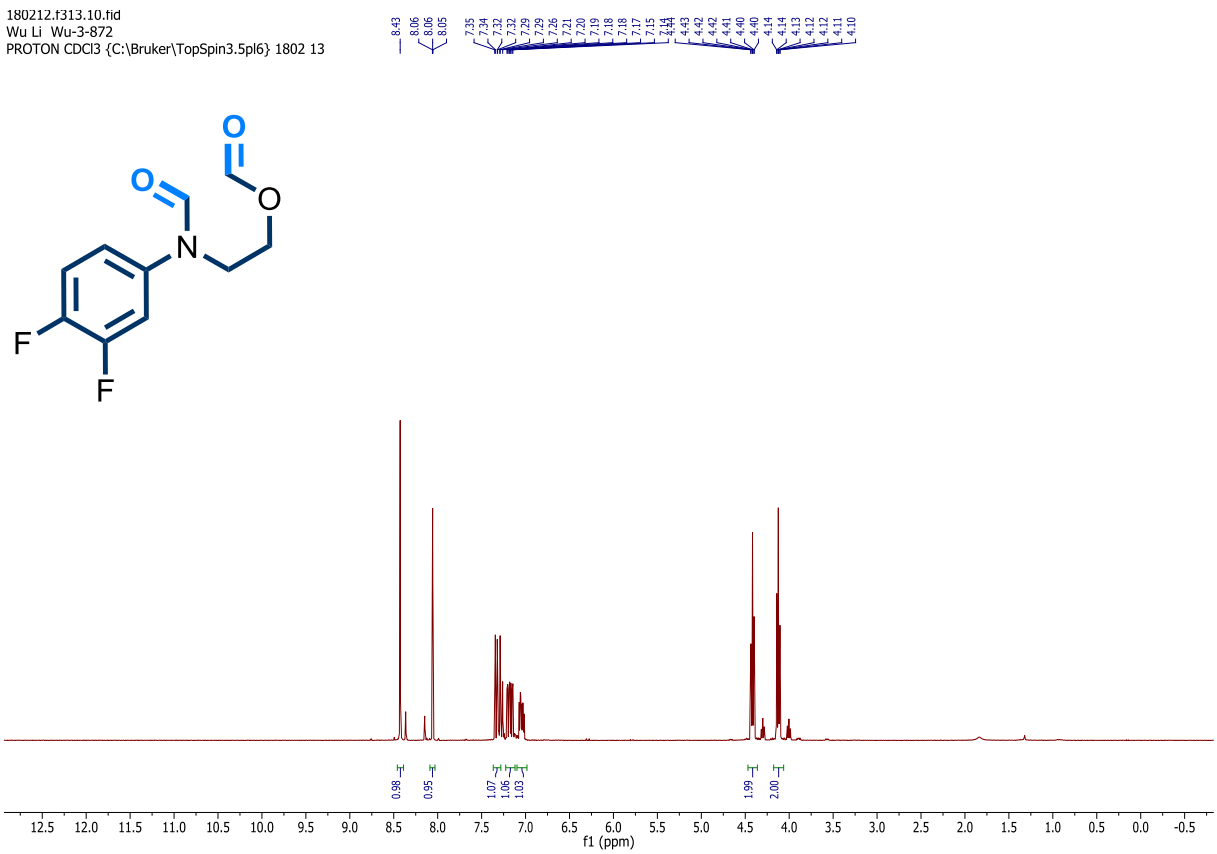


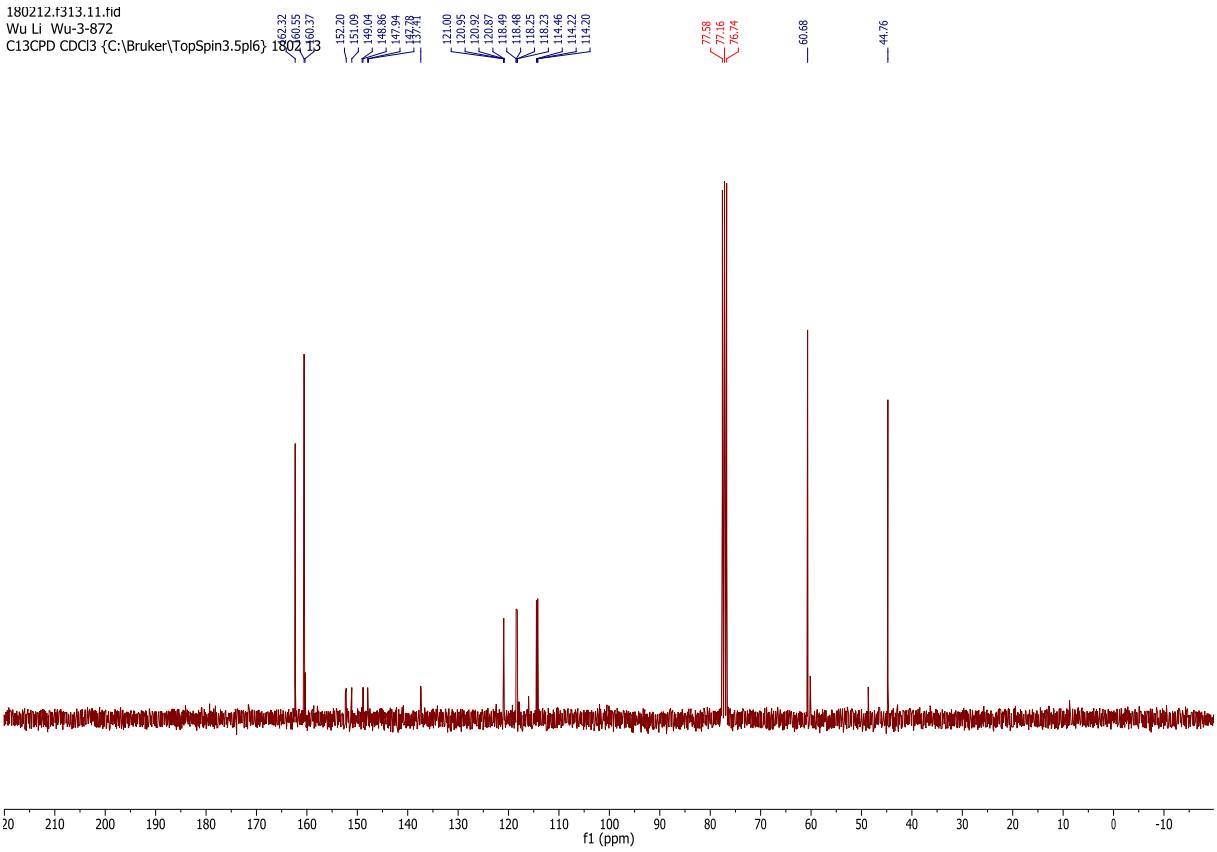
Original spectra for **46b**:





Original spectra for **47b**:





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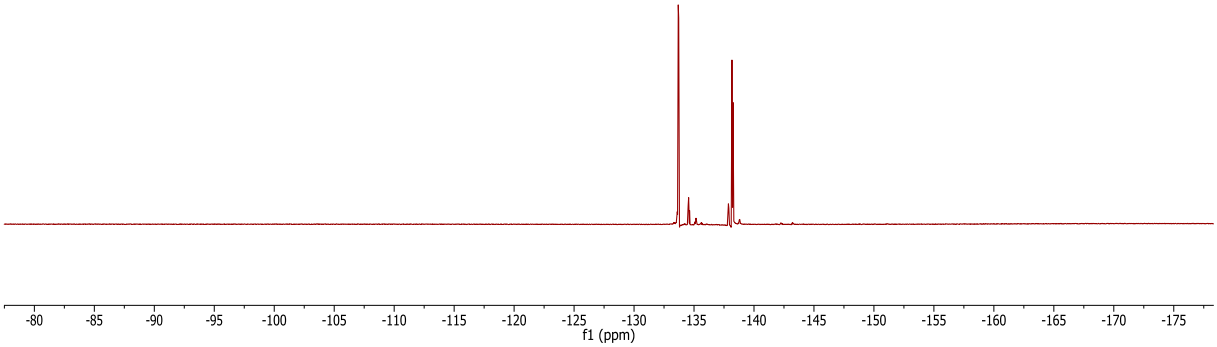
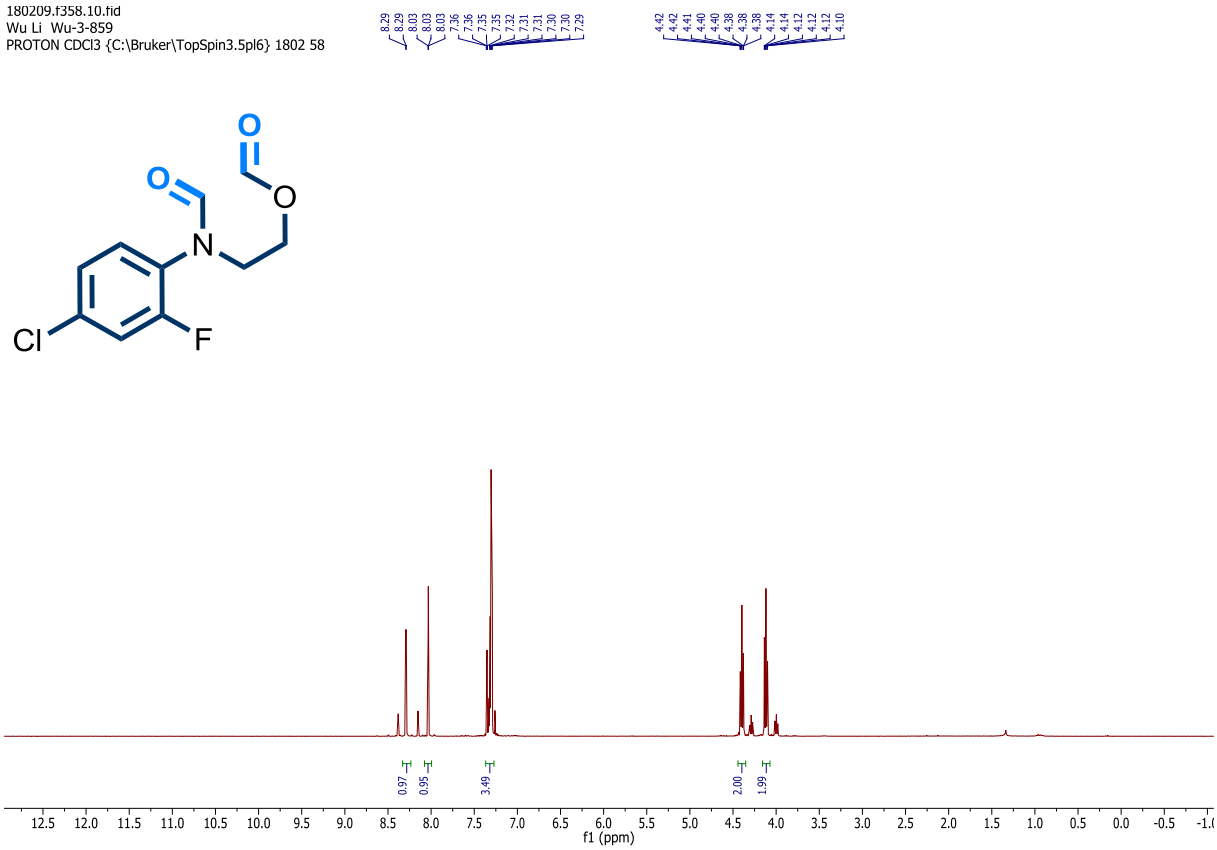
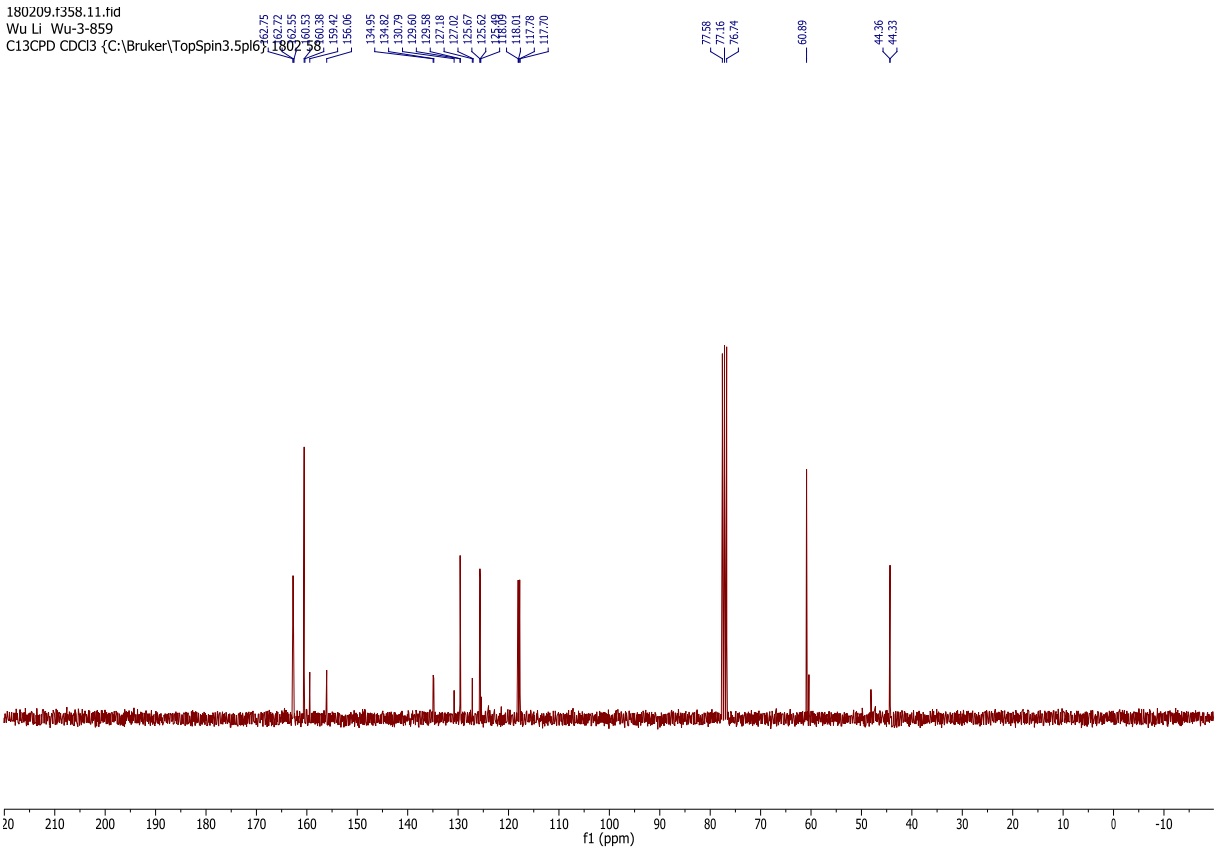
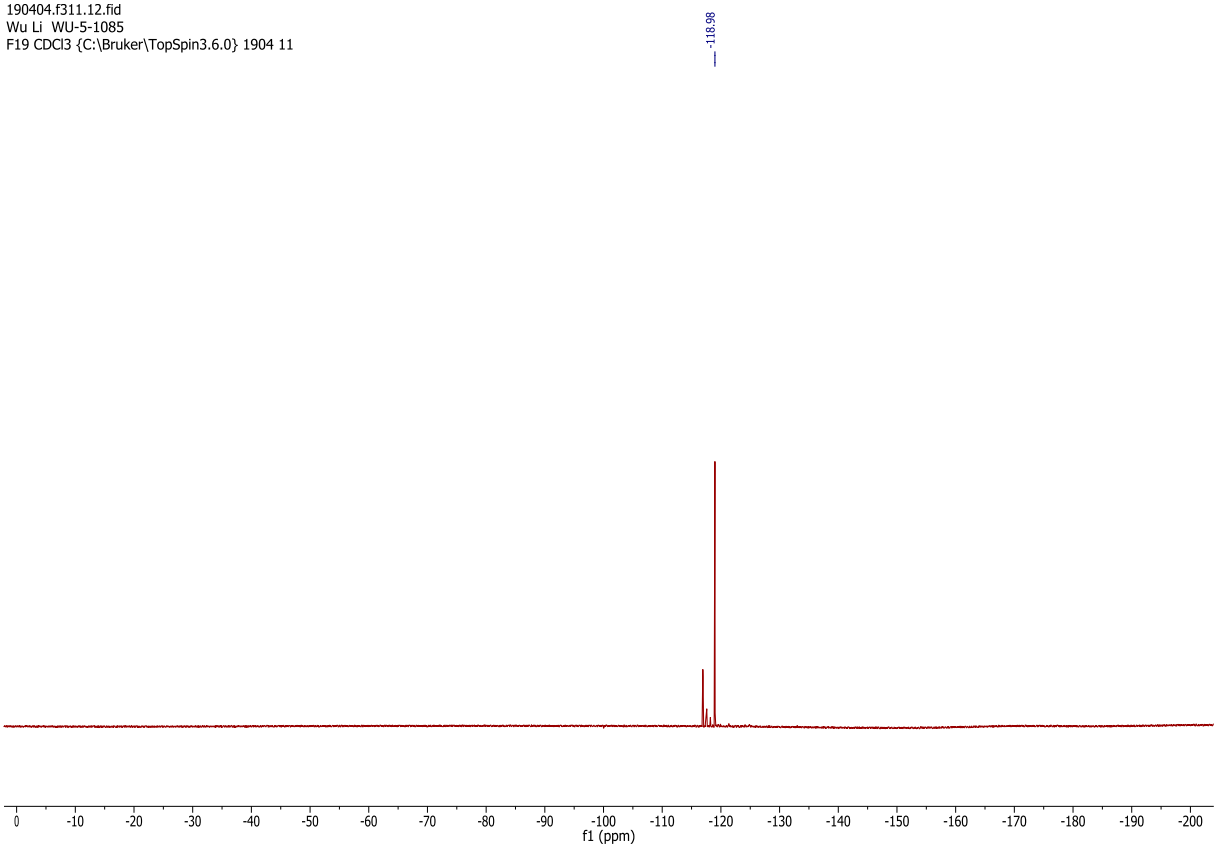
Wu Li WU-5-1086
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 12



Original spectra for **48b**:



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Wu Li WU-5-1085
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 11
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-80
-90
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-180
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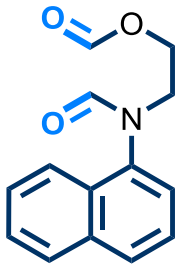
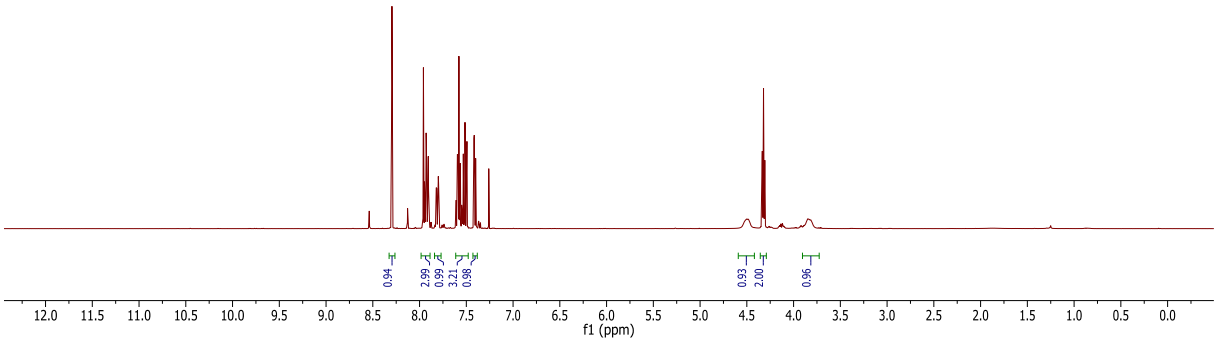
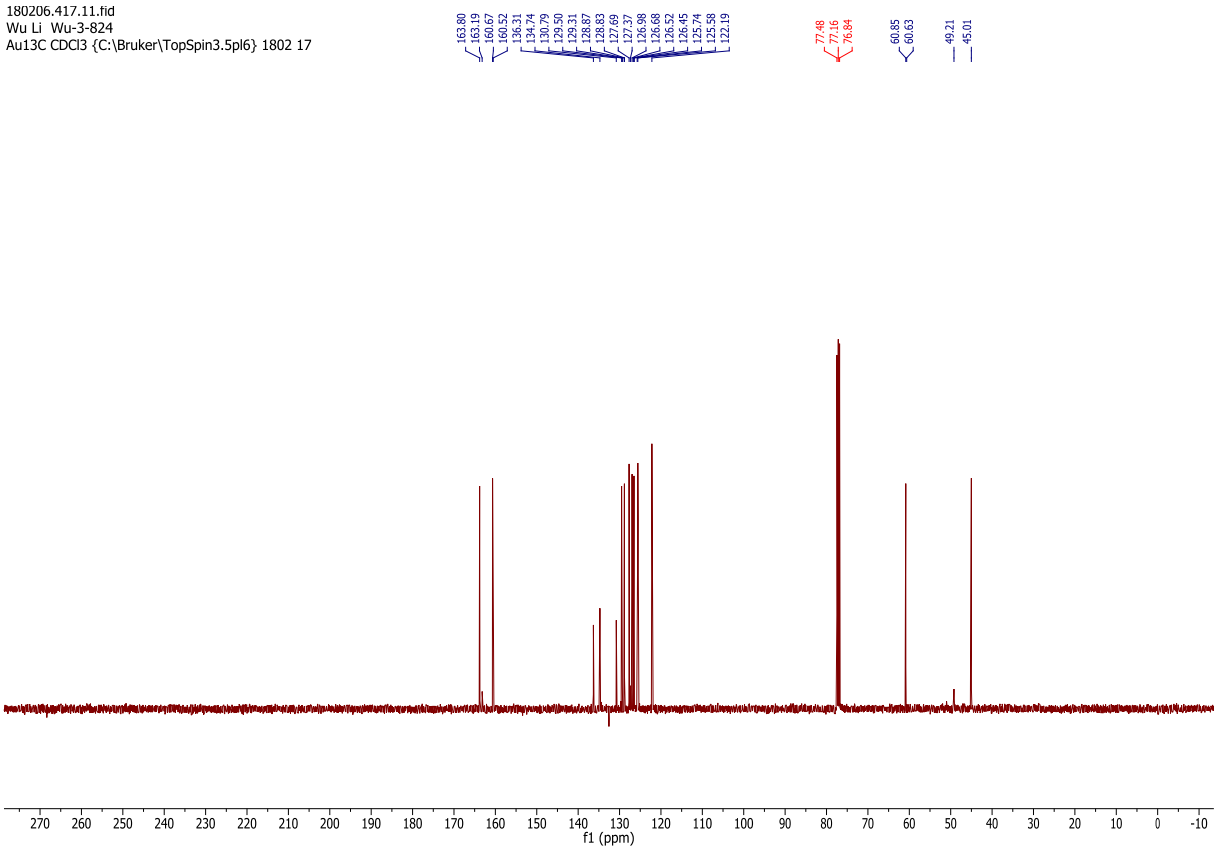
-200
f1 (ppm)

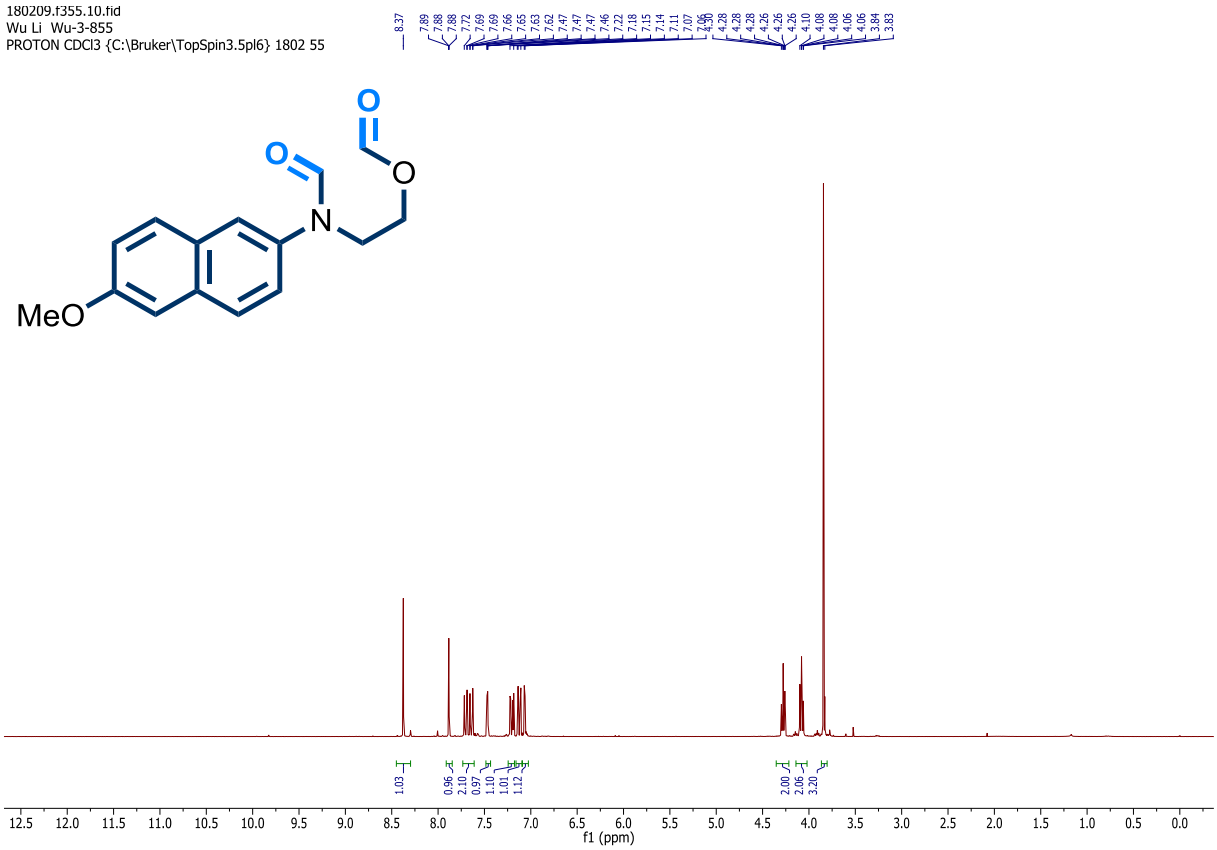
Original spectra for **49b**:

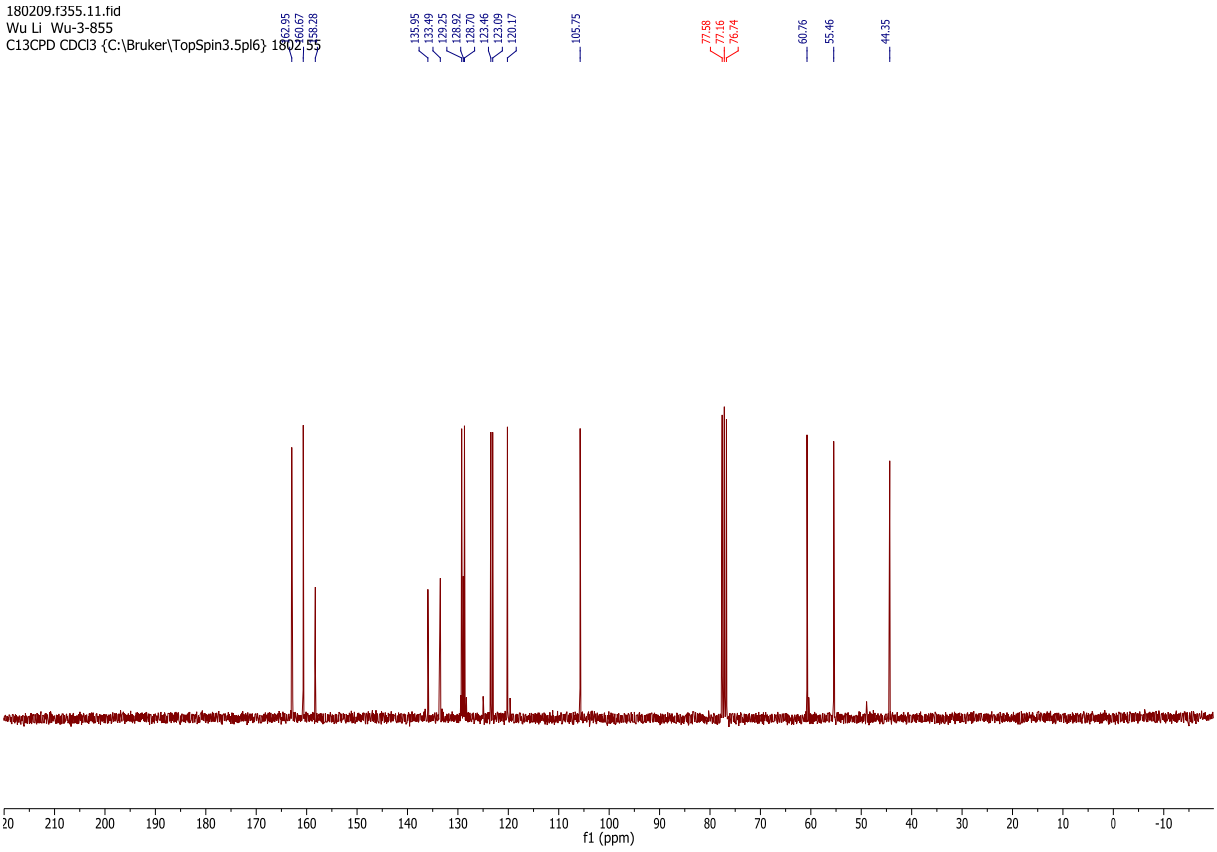




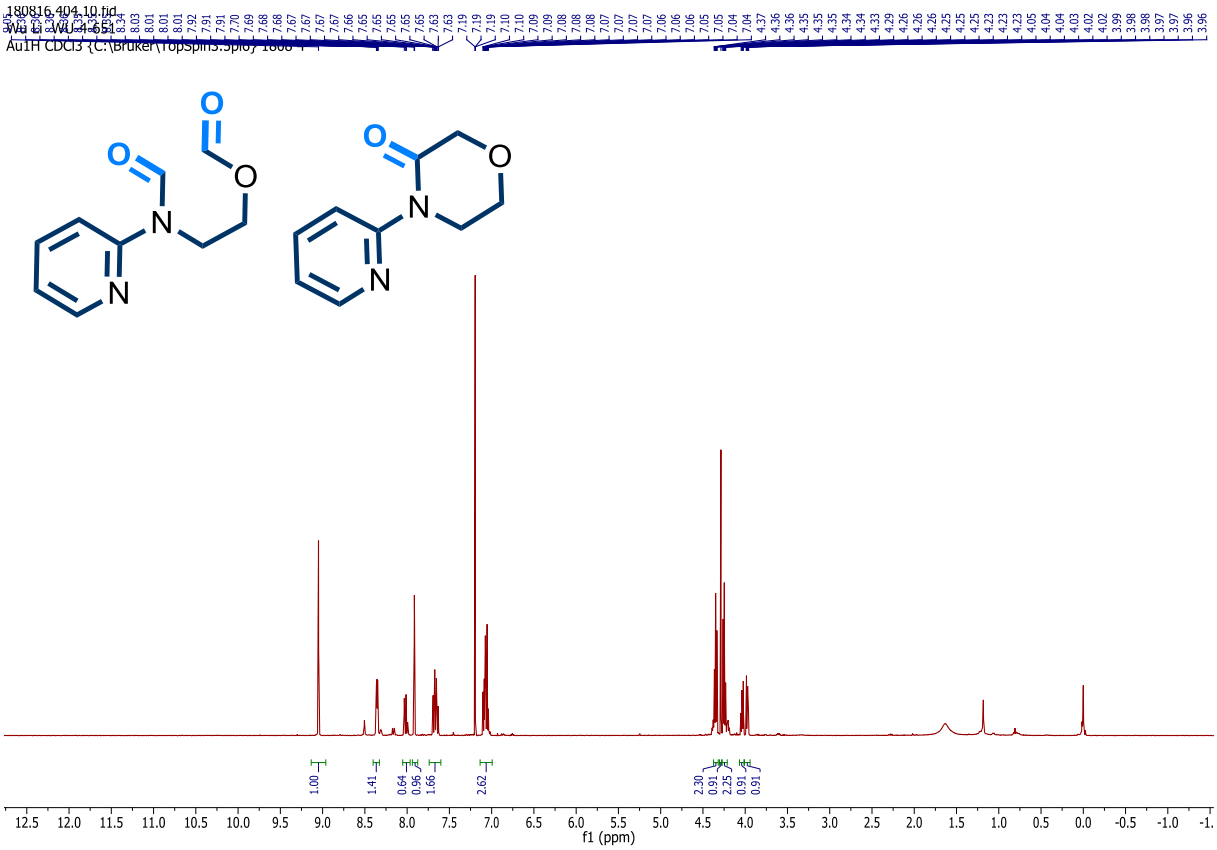


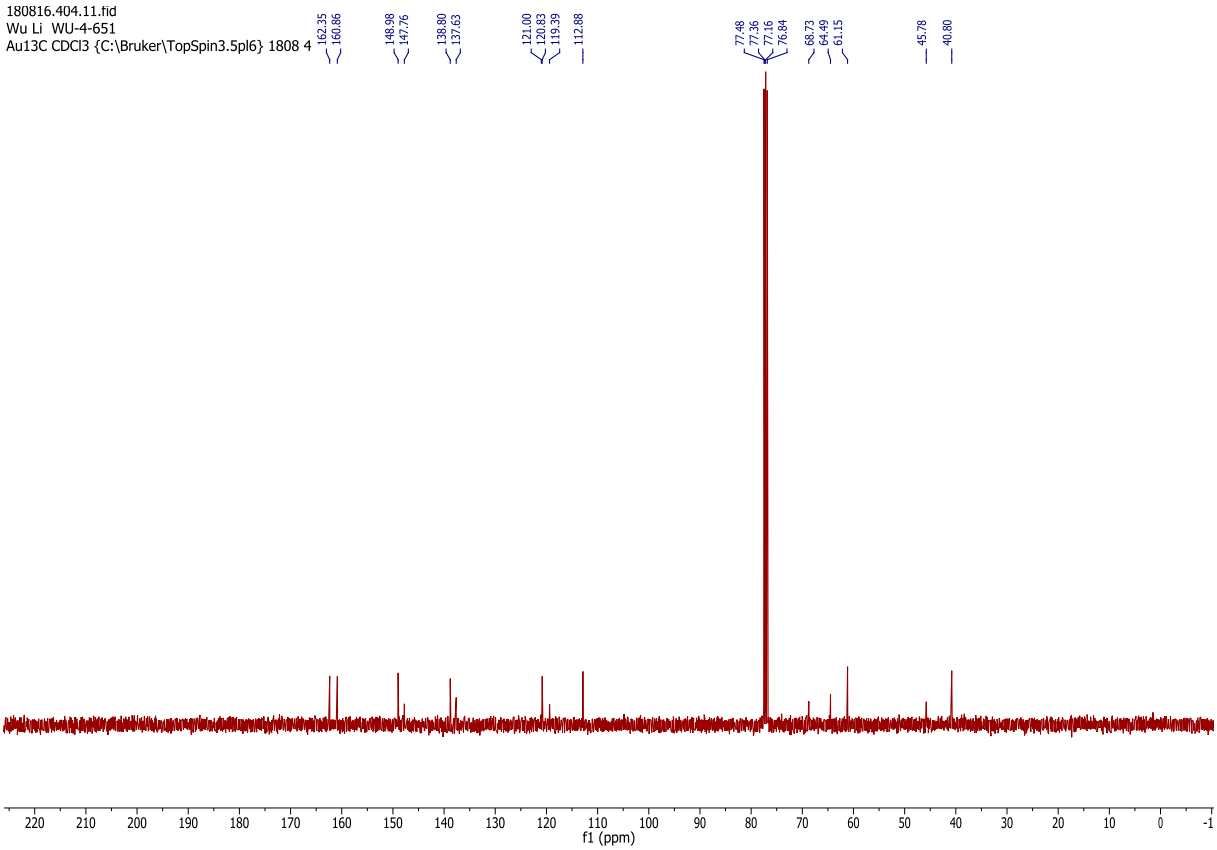
Original spectra for **50b**:



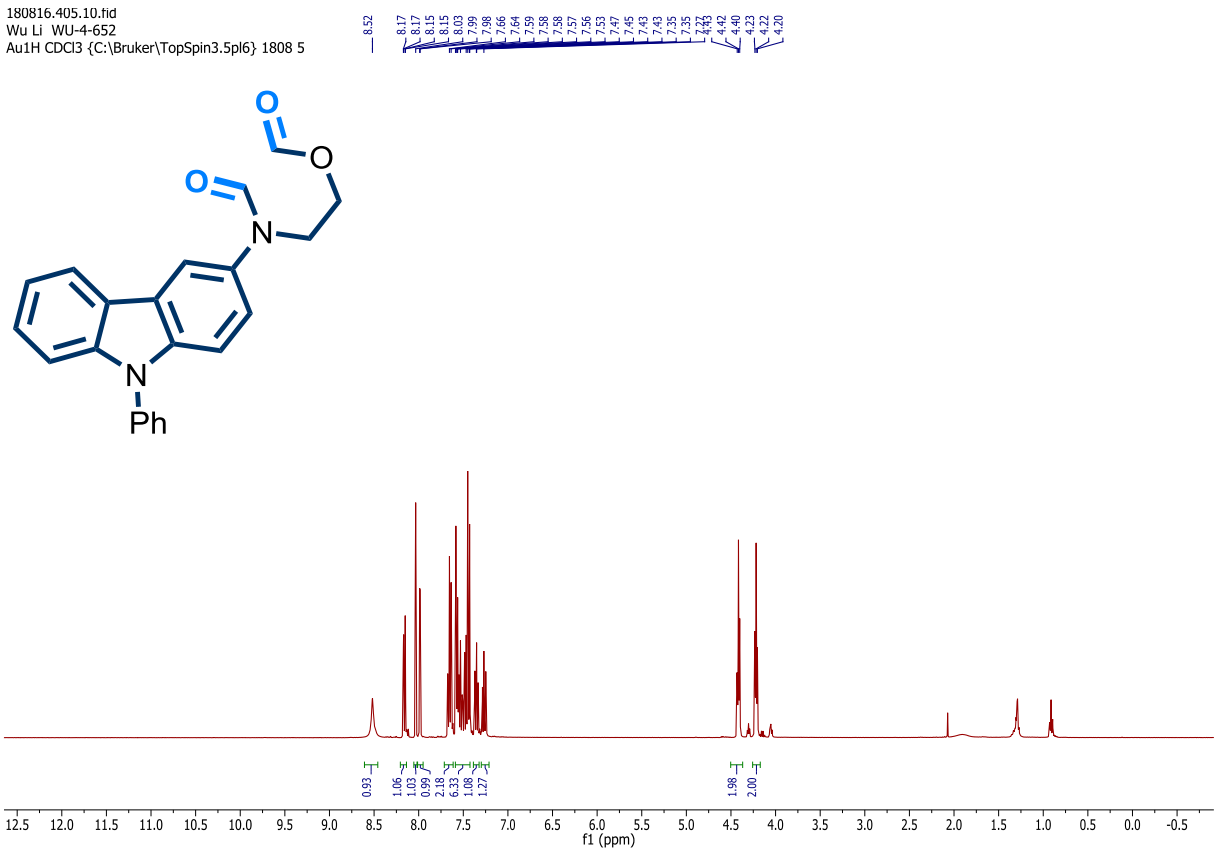


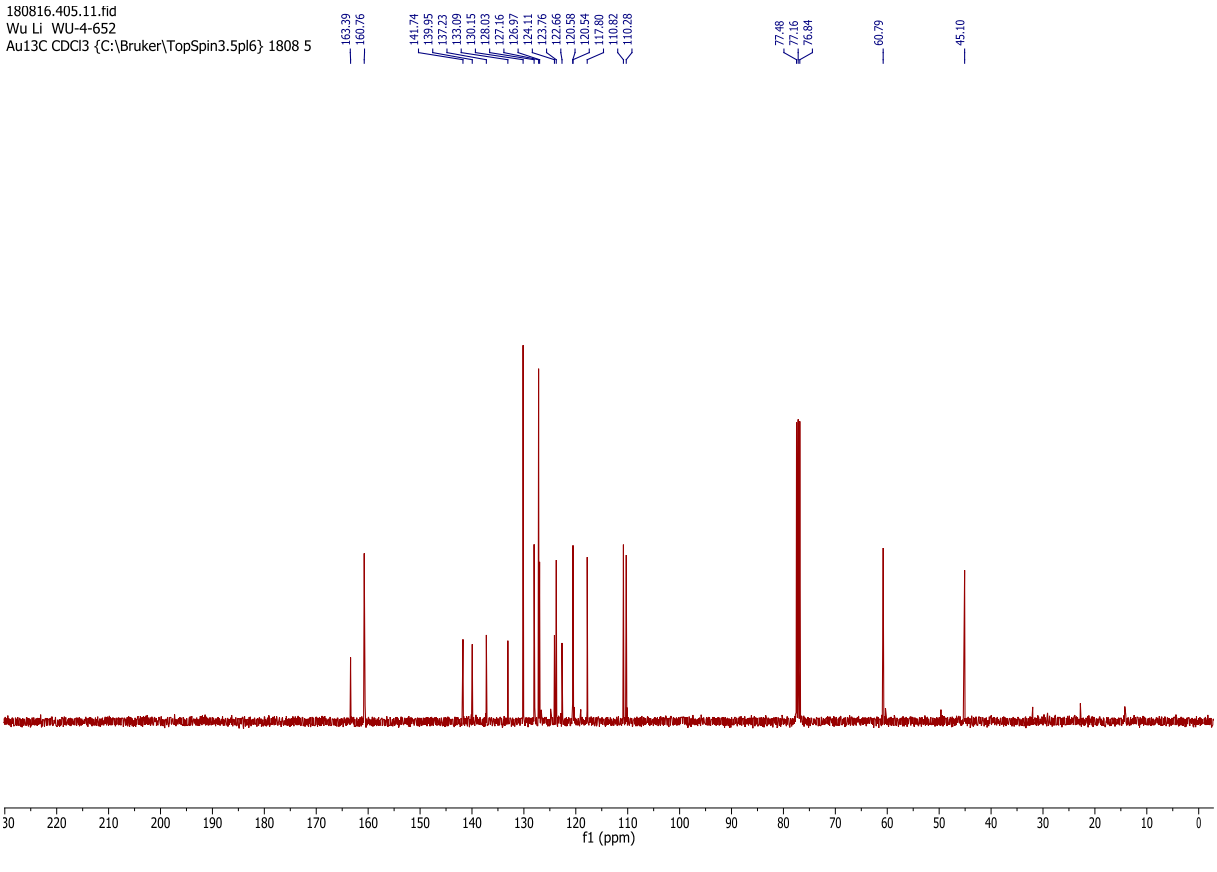
Original spectra for **51b** and **51c**:



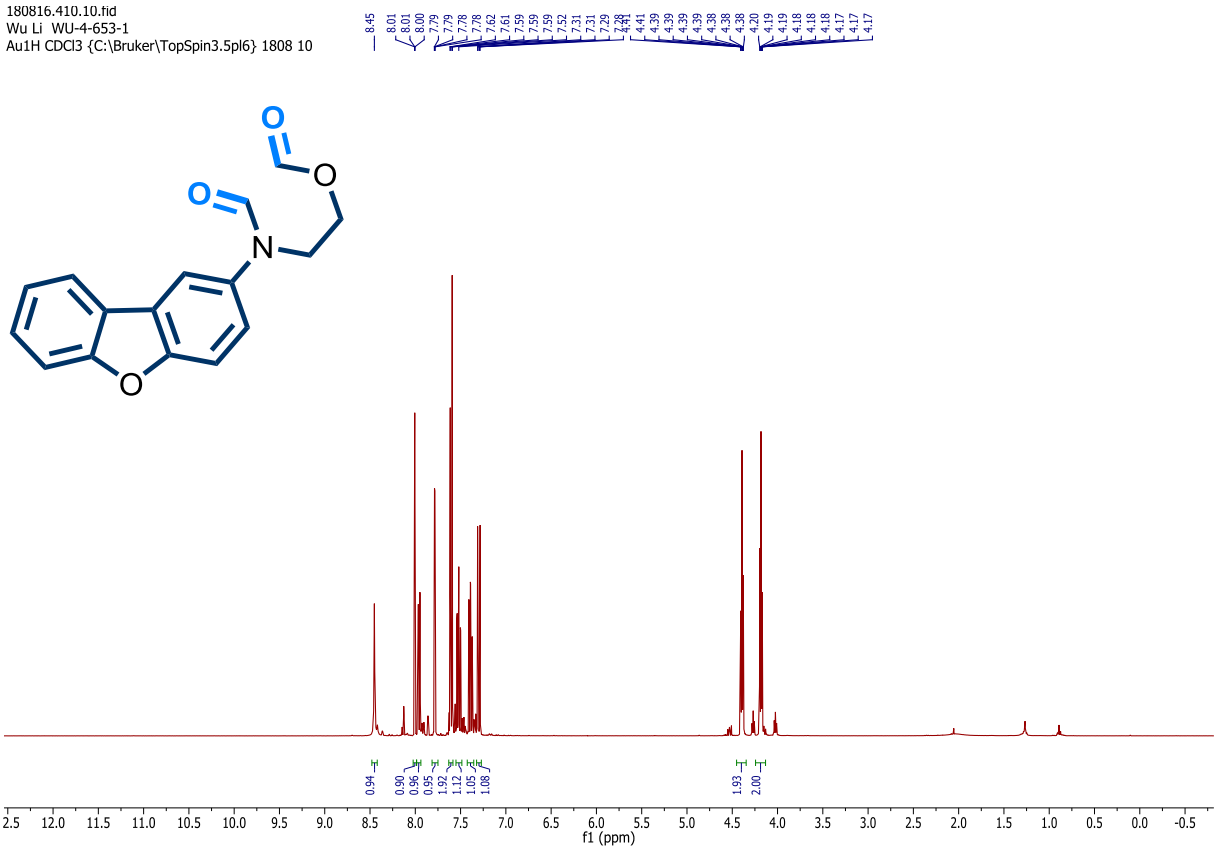


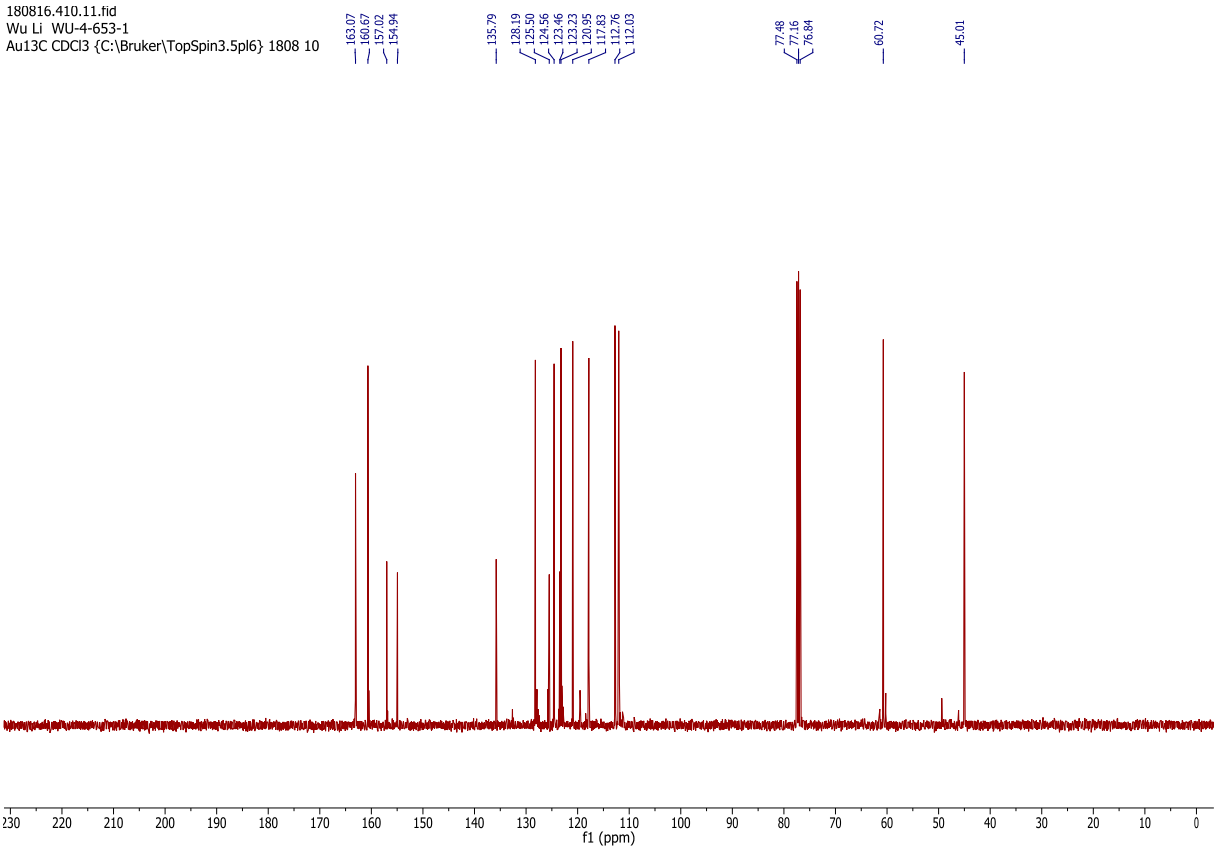
Original spectra for **52b**:



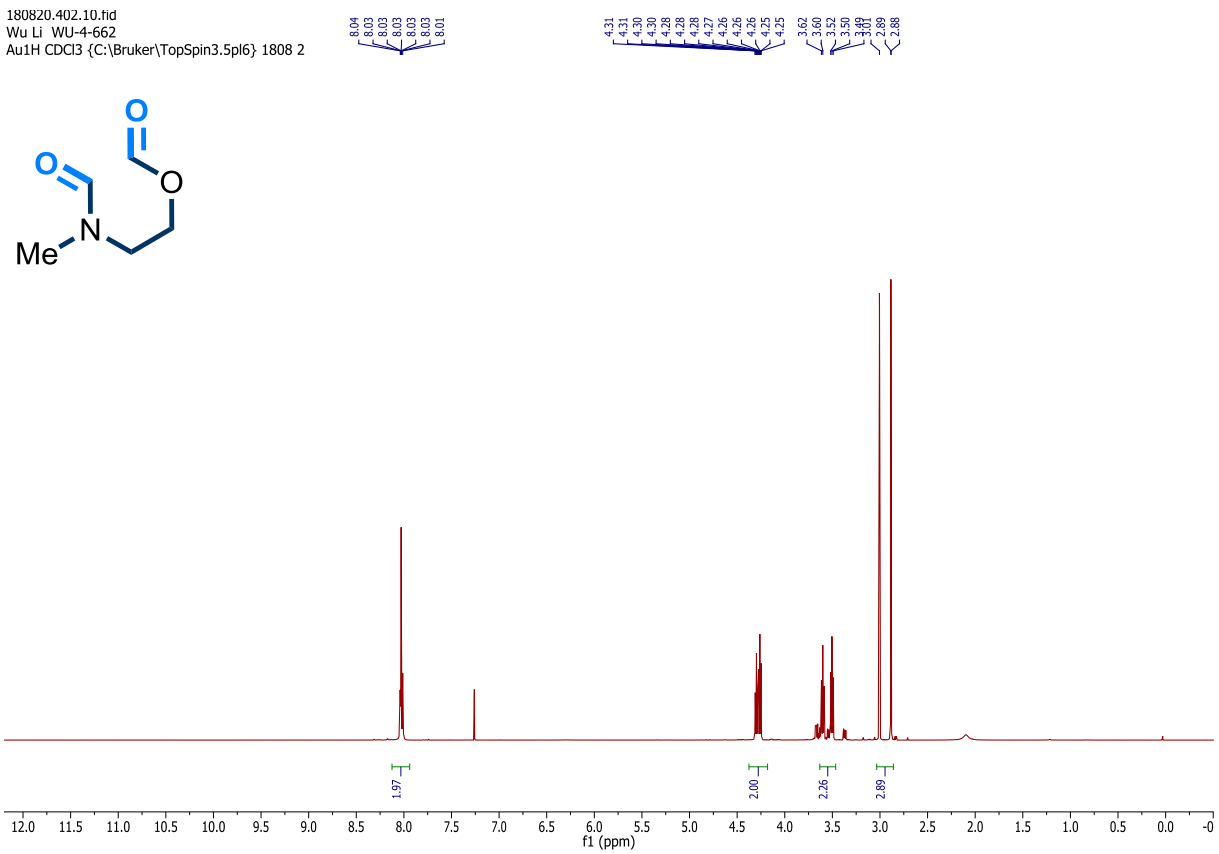


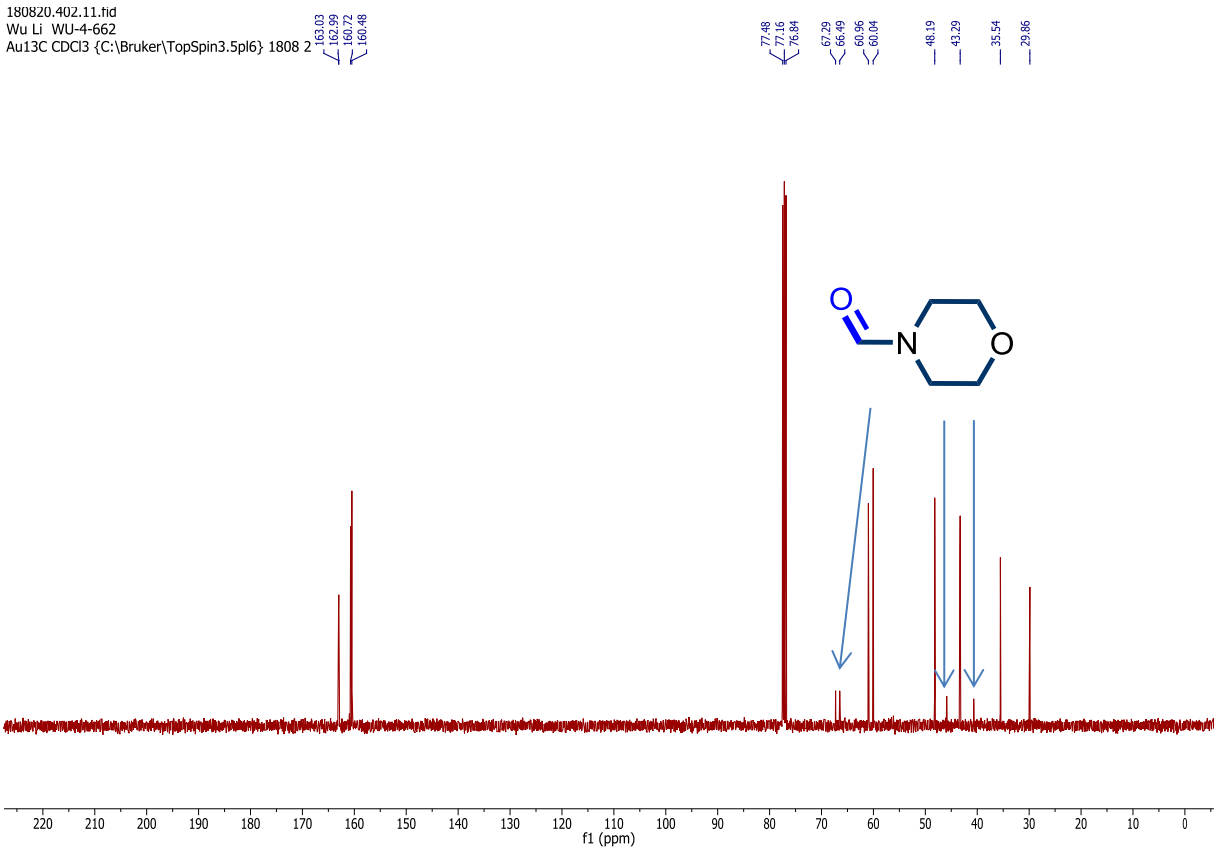
Original spectra for **53b**:



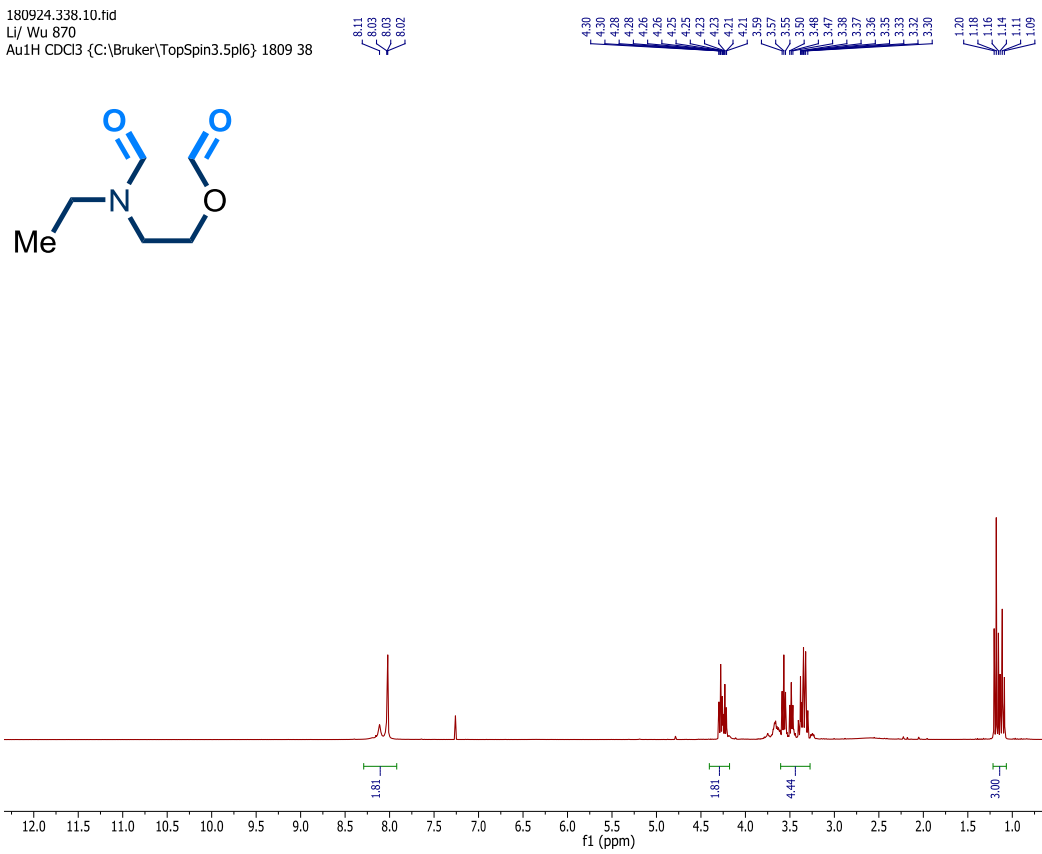


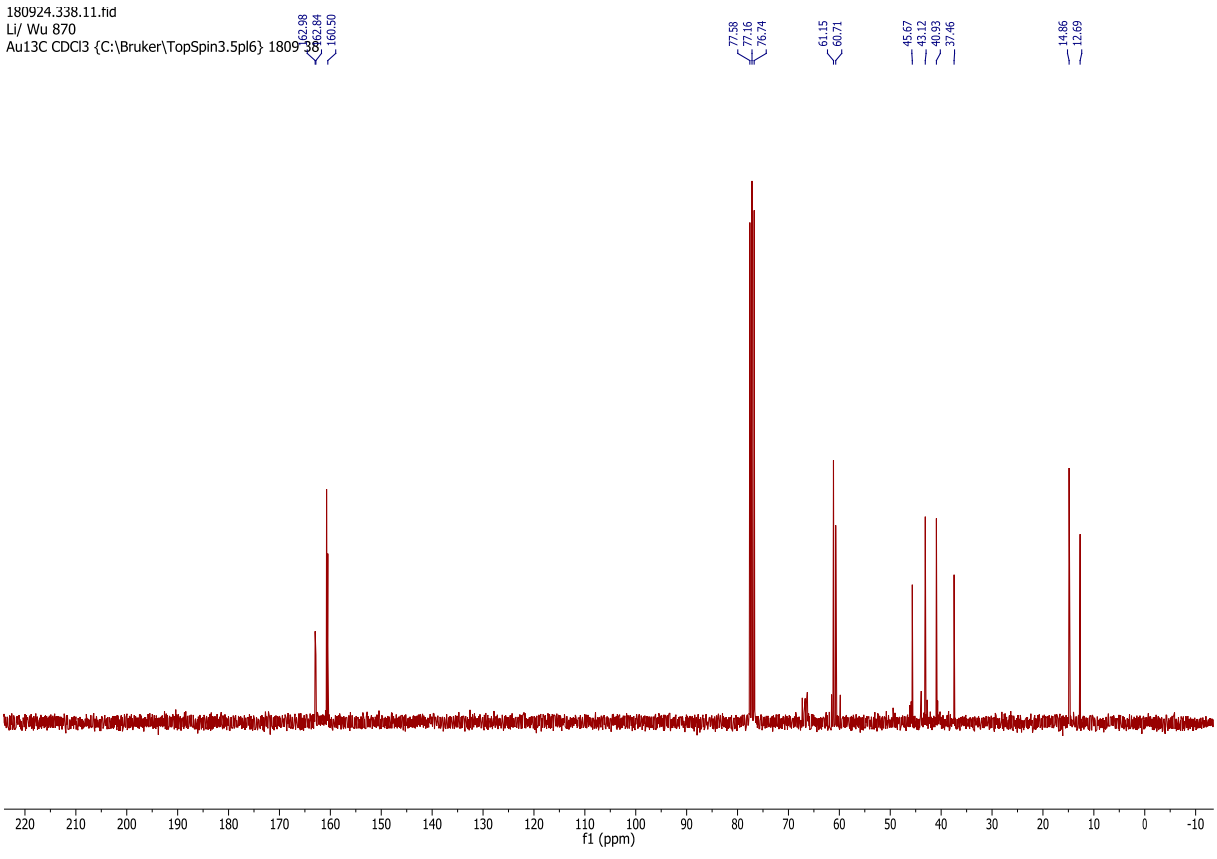
Original spectra for **54b**:



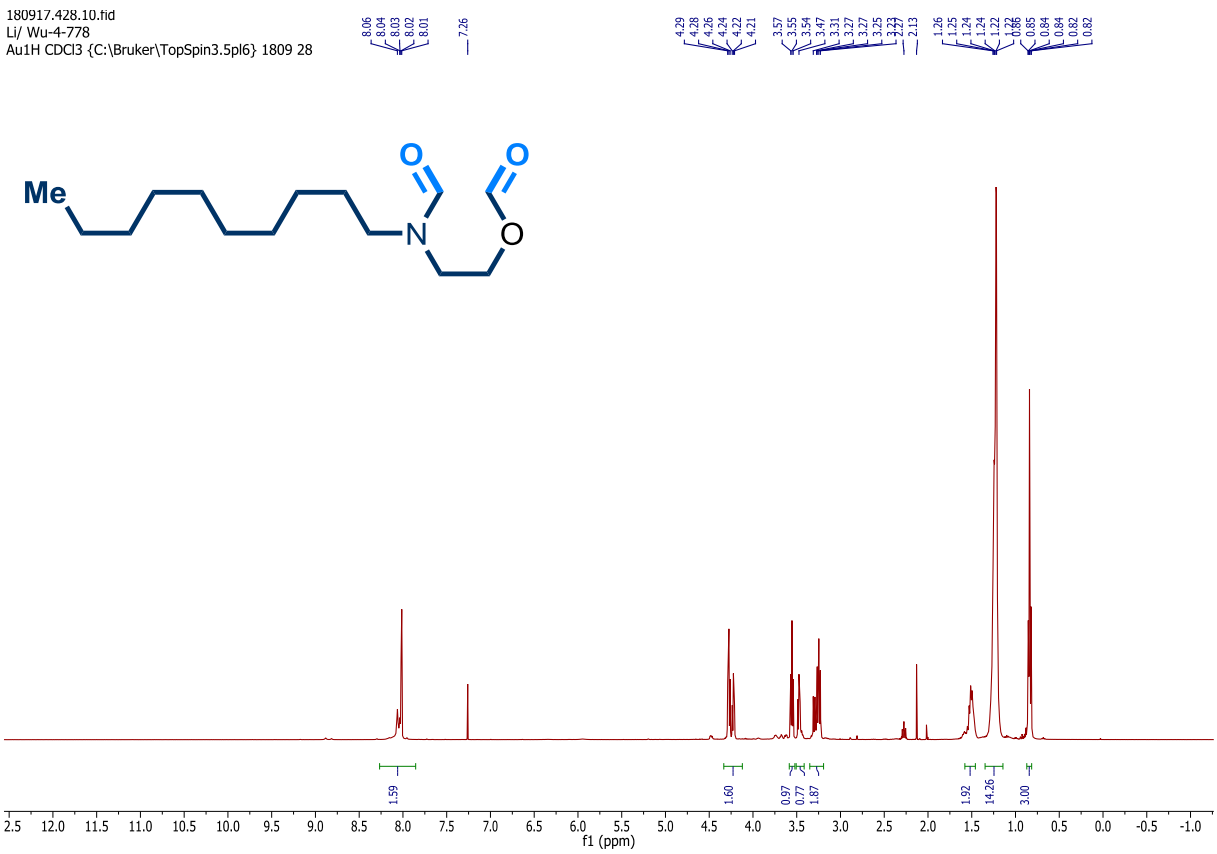


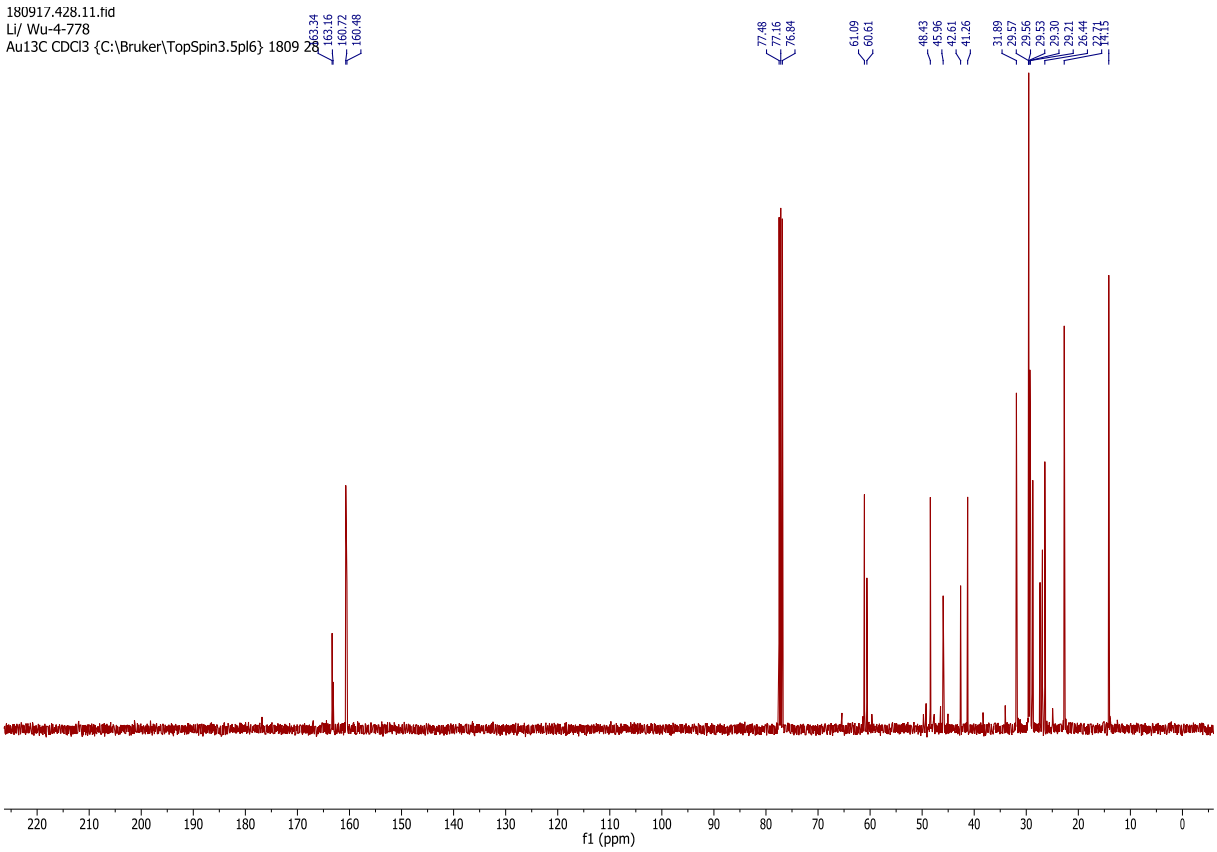
Original spectra for **55b**:



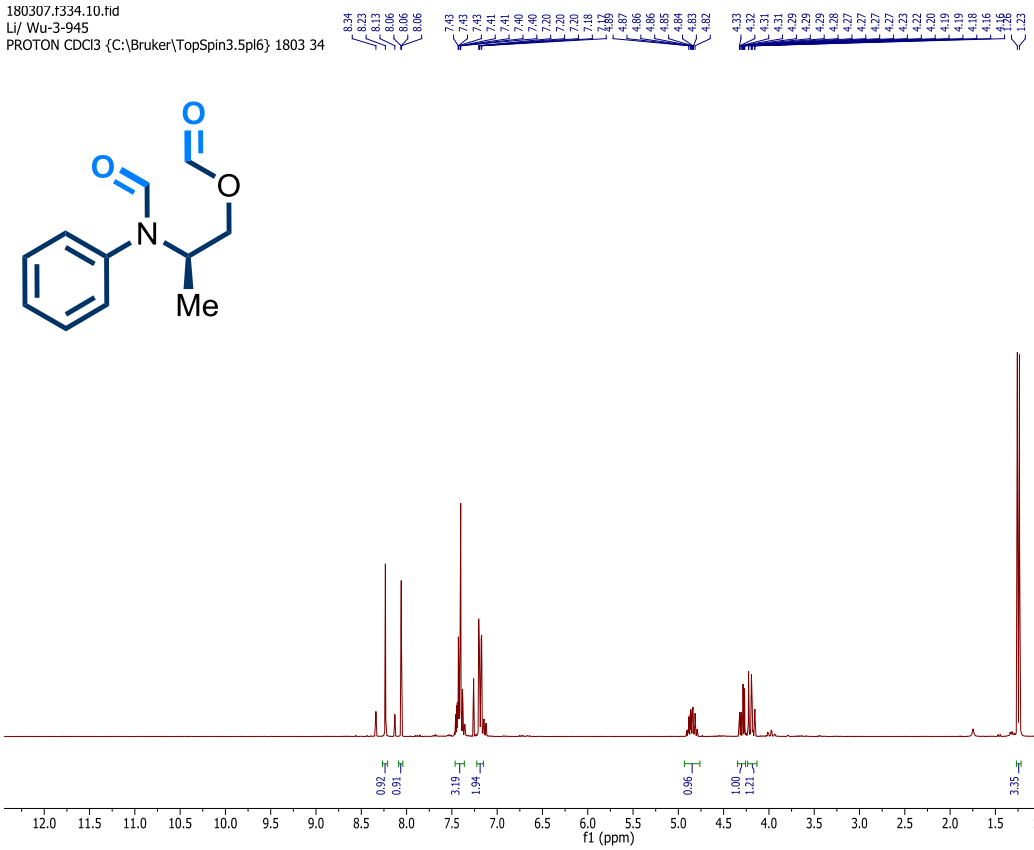


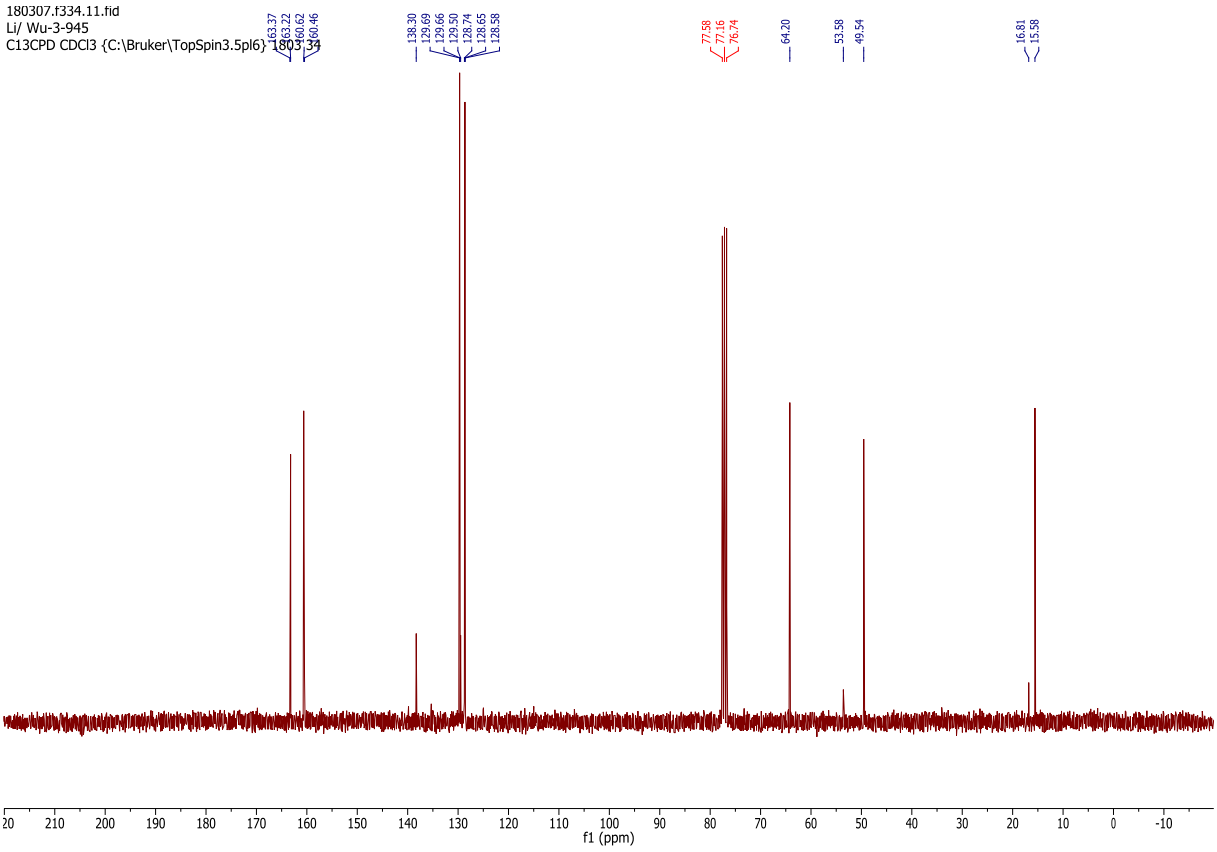
Original spectra for **56b**:



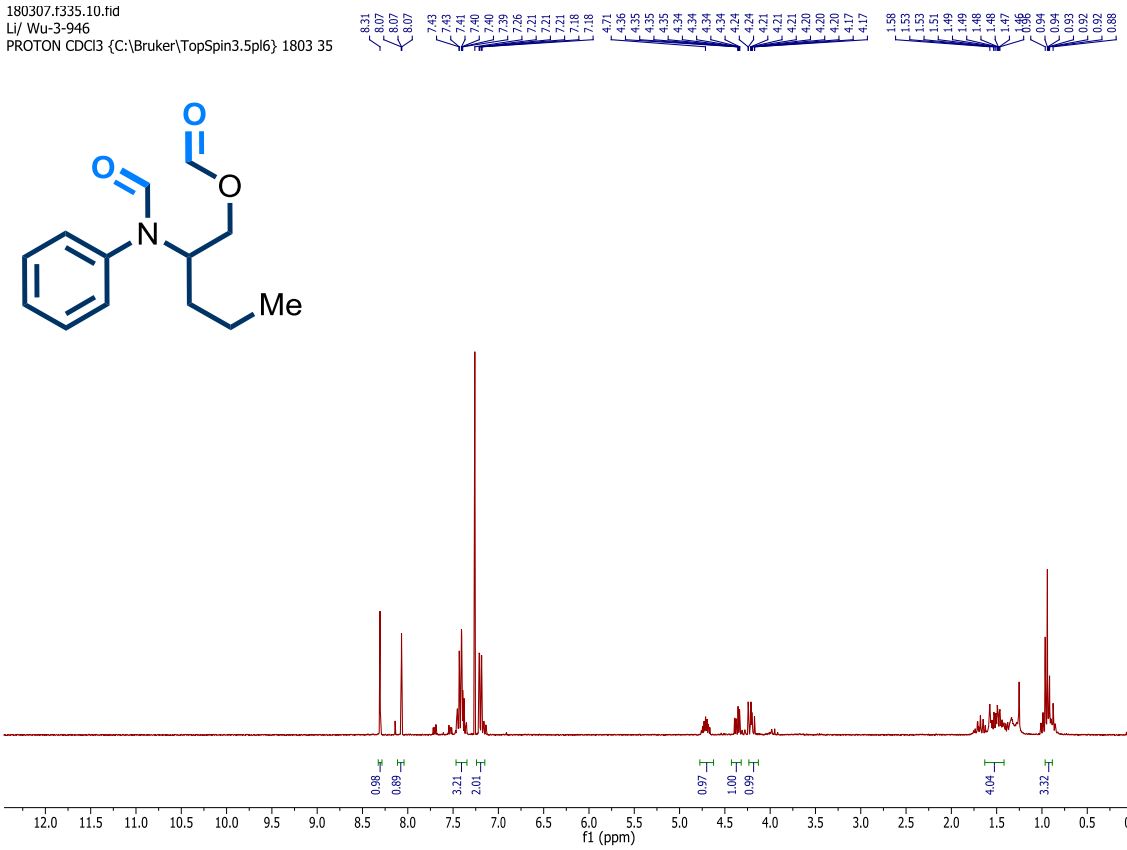


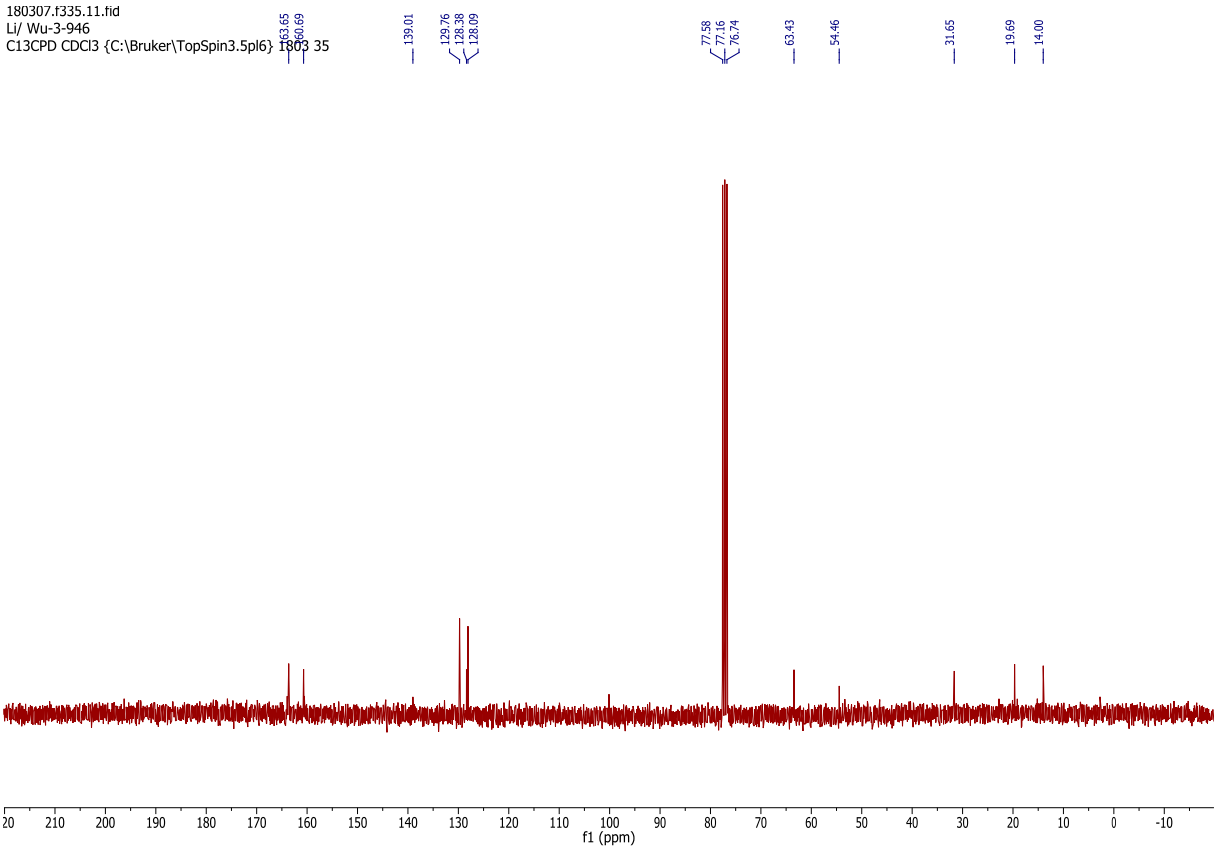
Original spectra for **57b**:



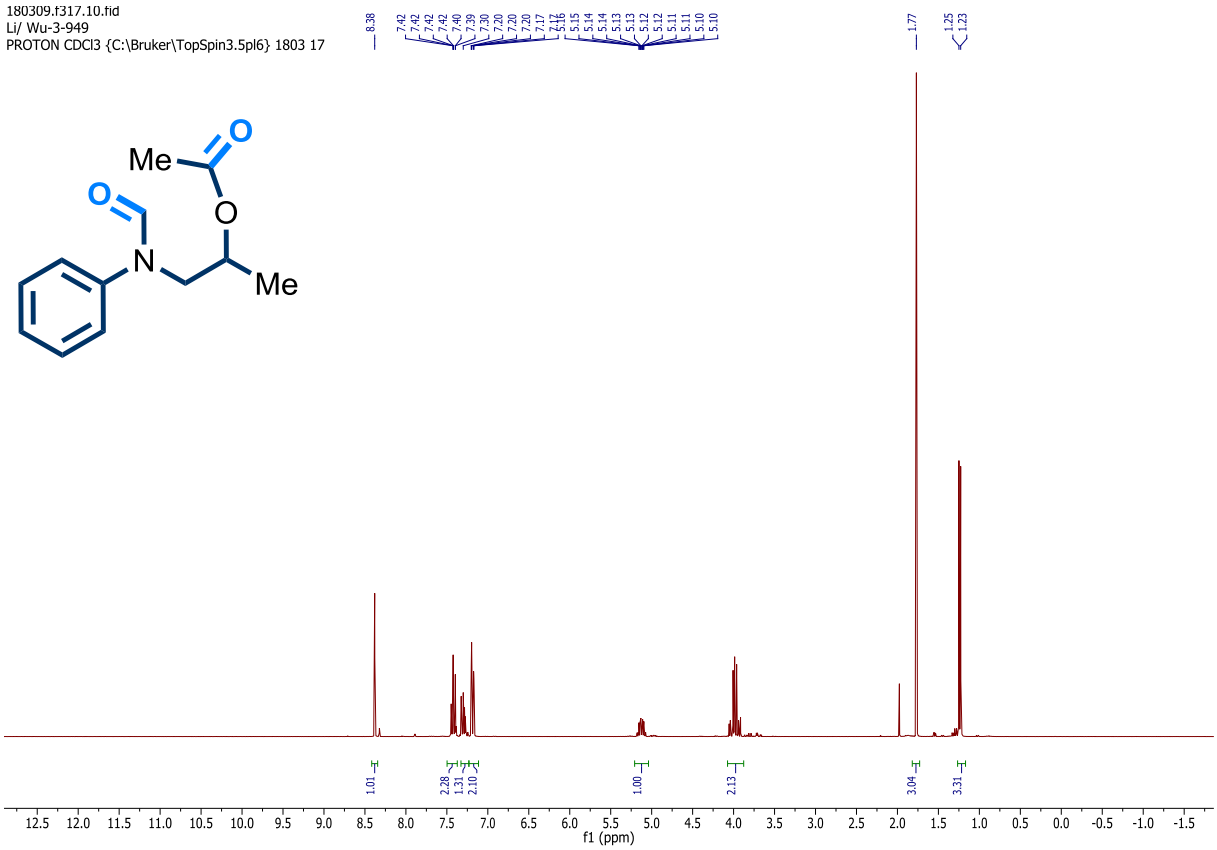


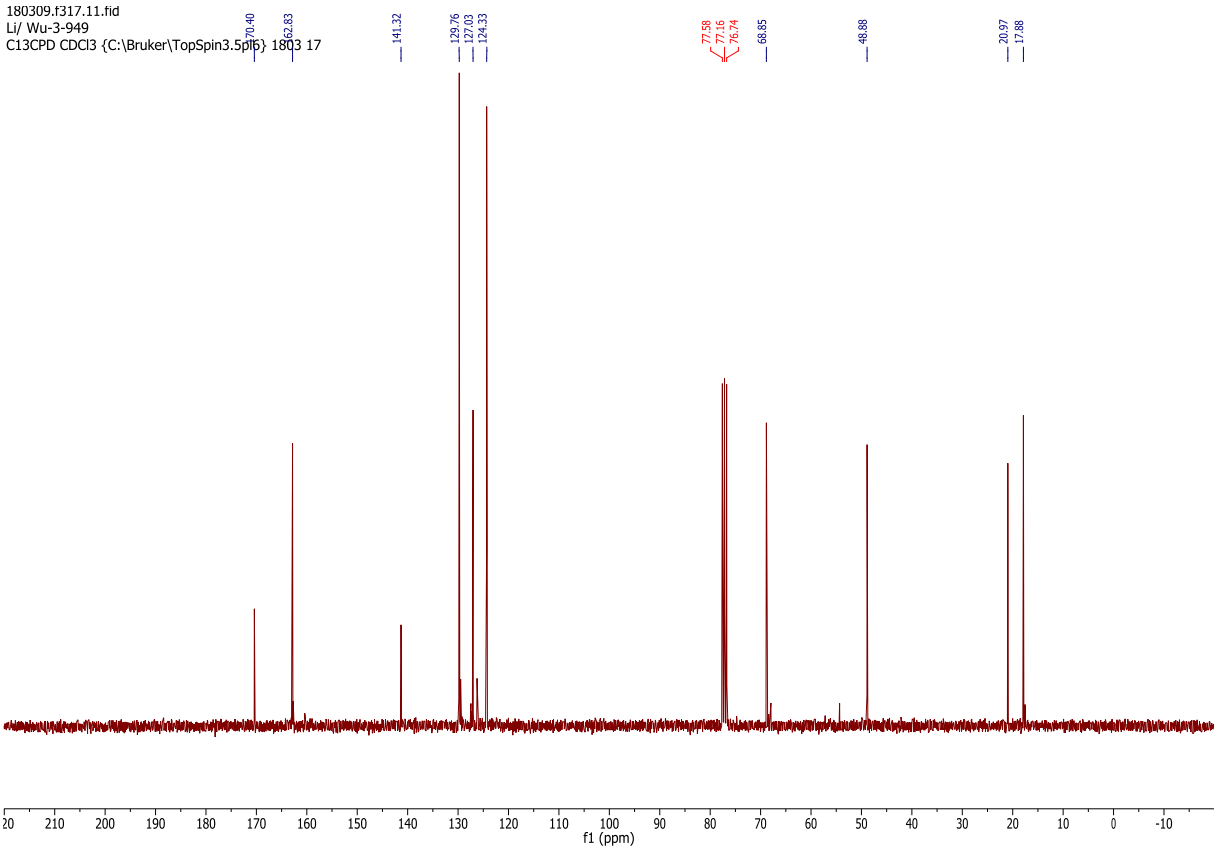
Original spectra for **58b**:



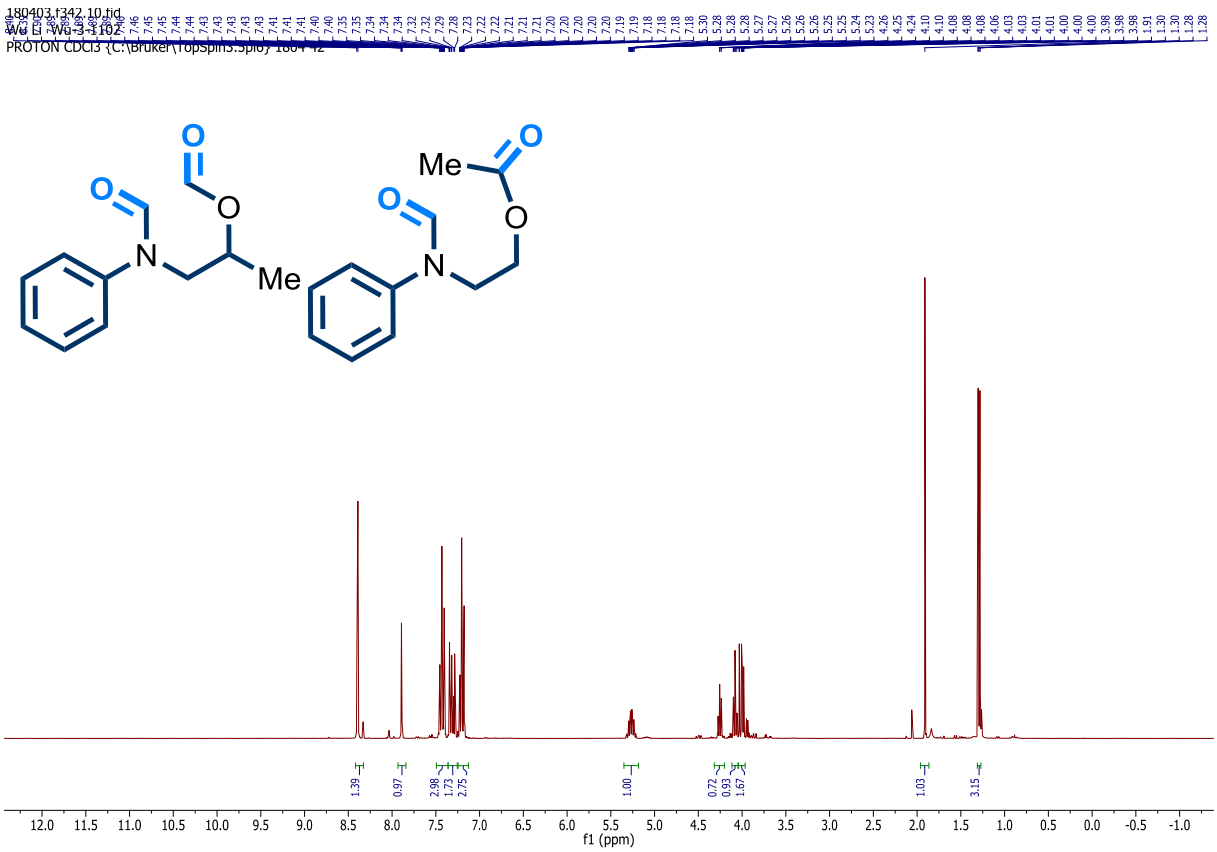


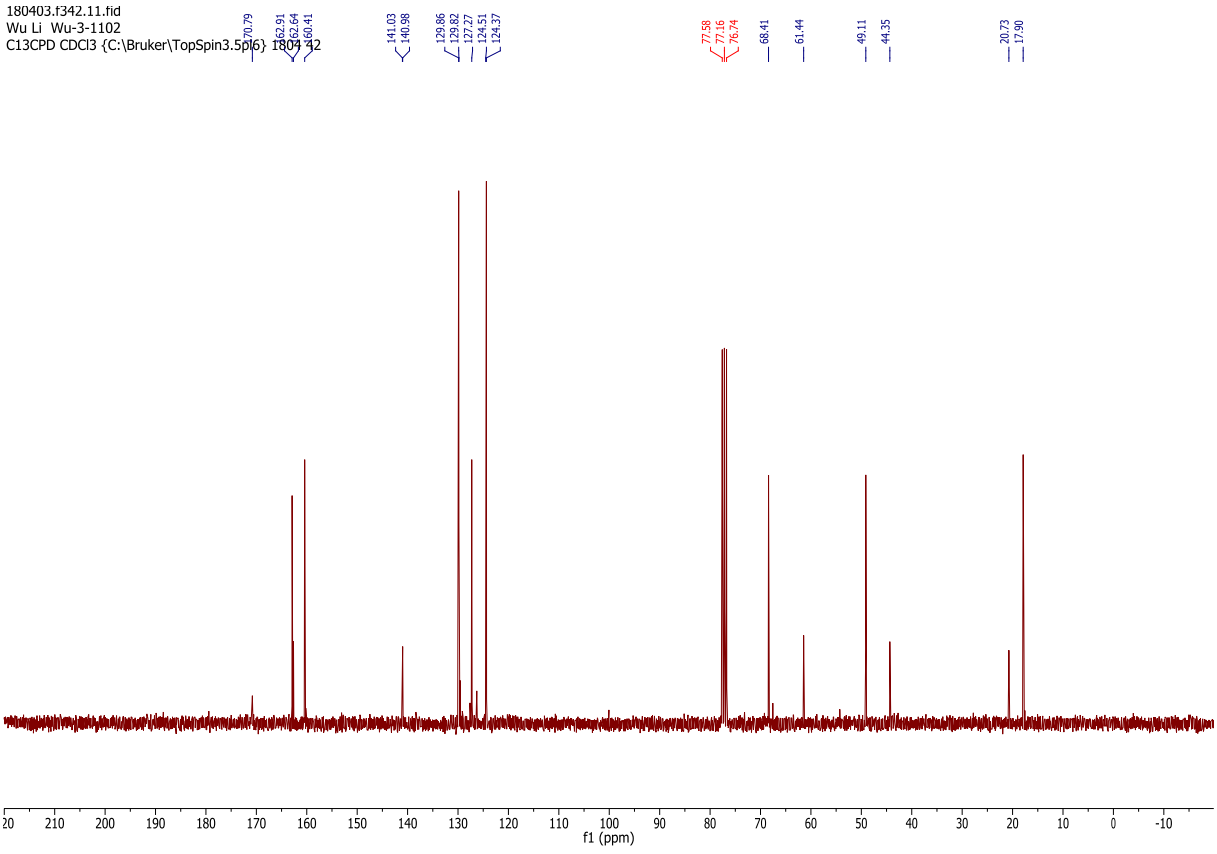
Original spectra for **59b**:



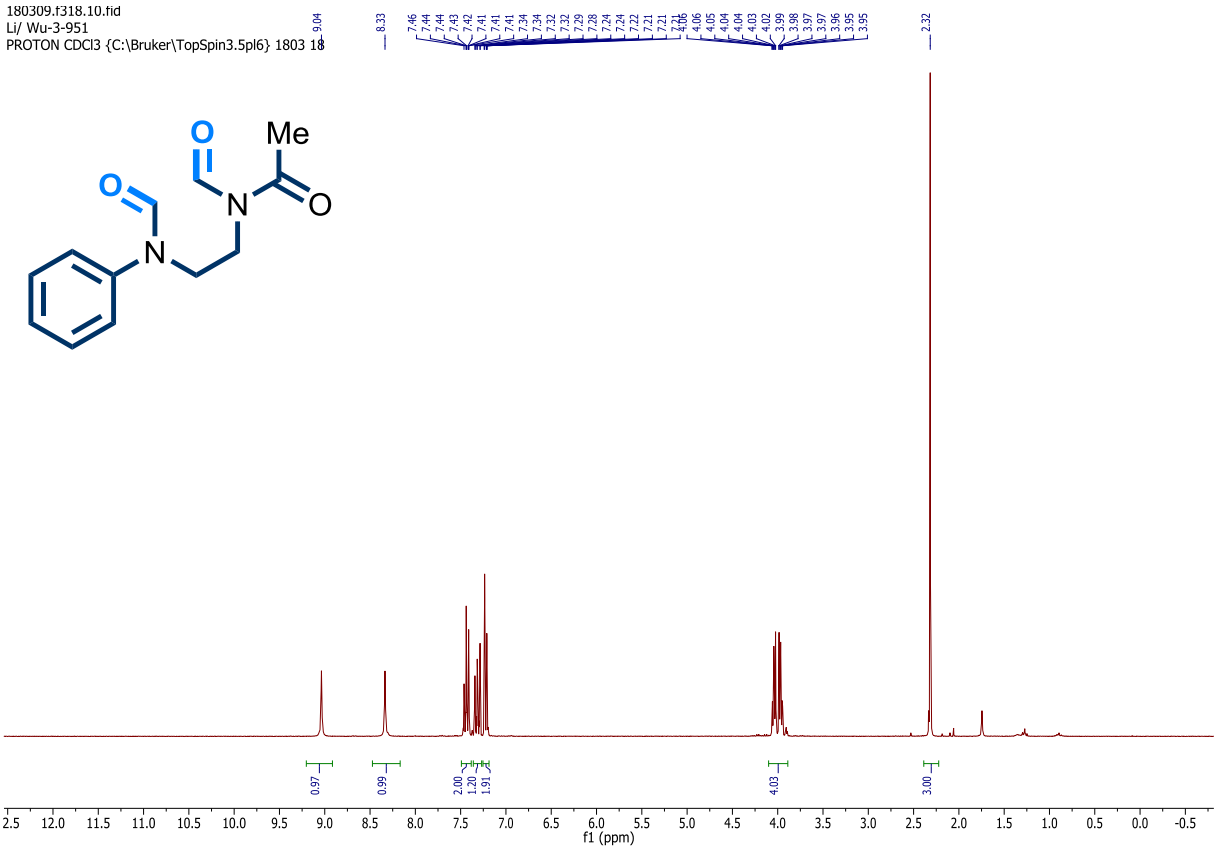


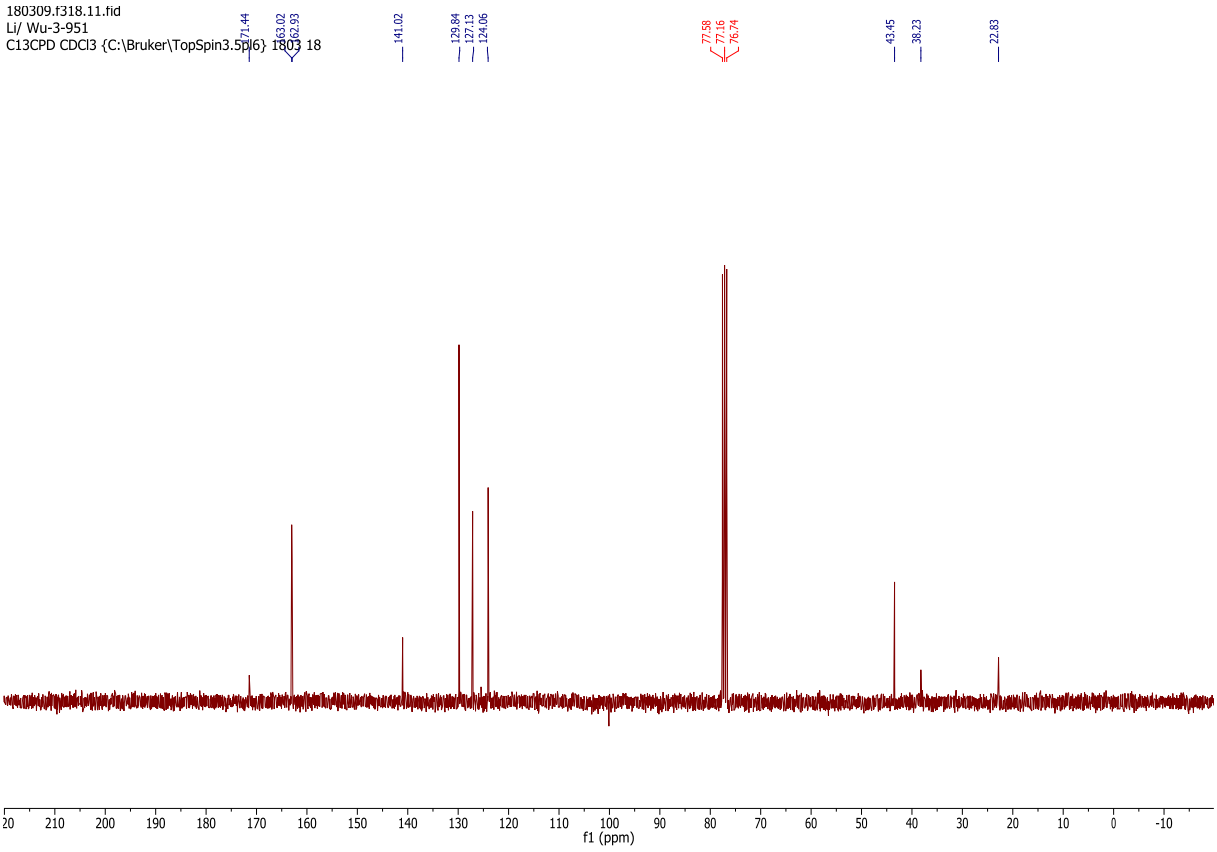
Original spectra for **60b** and **60c**:



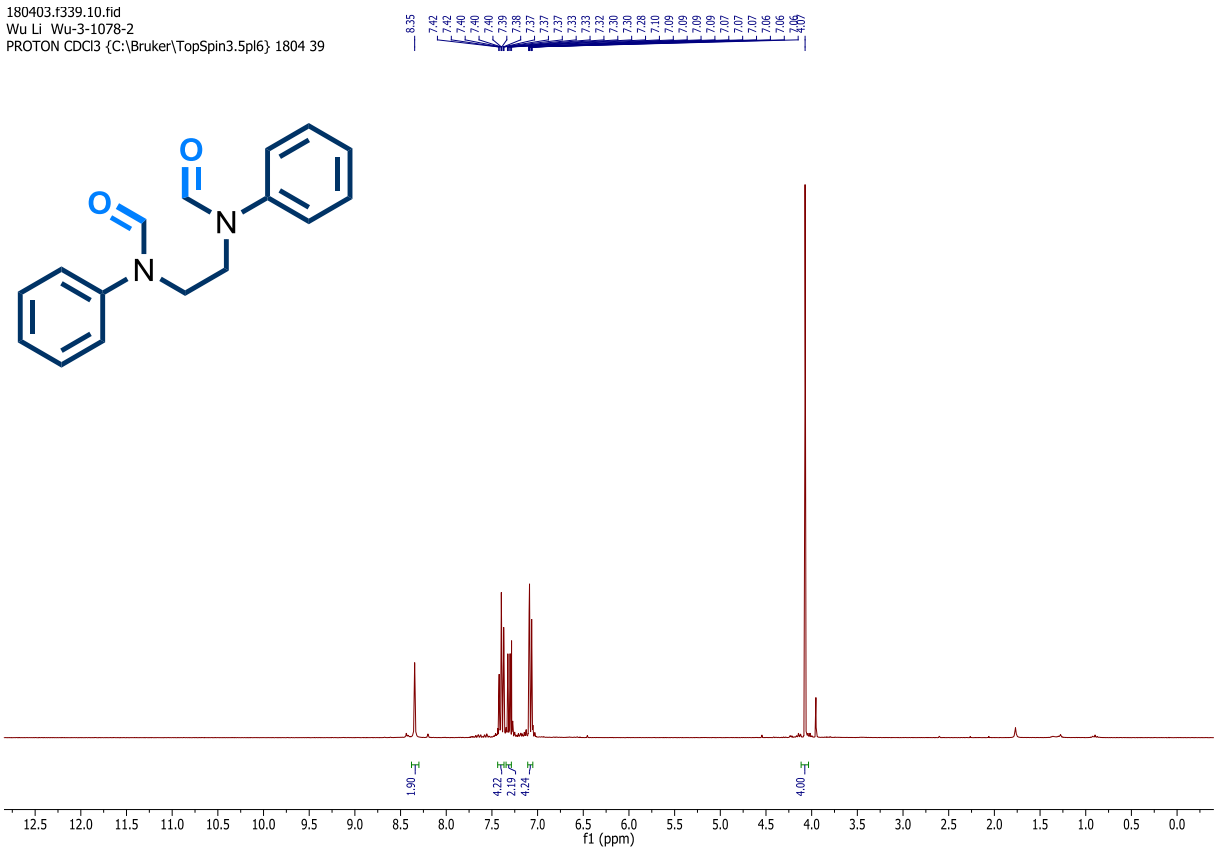


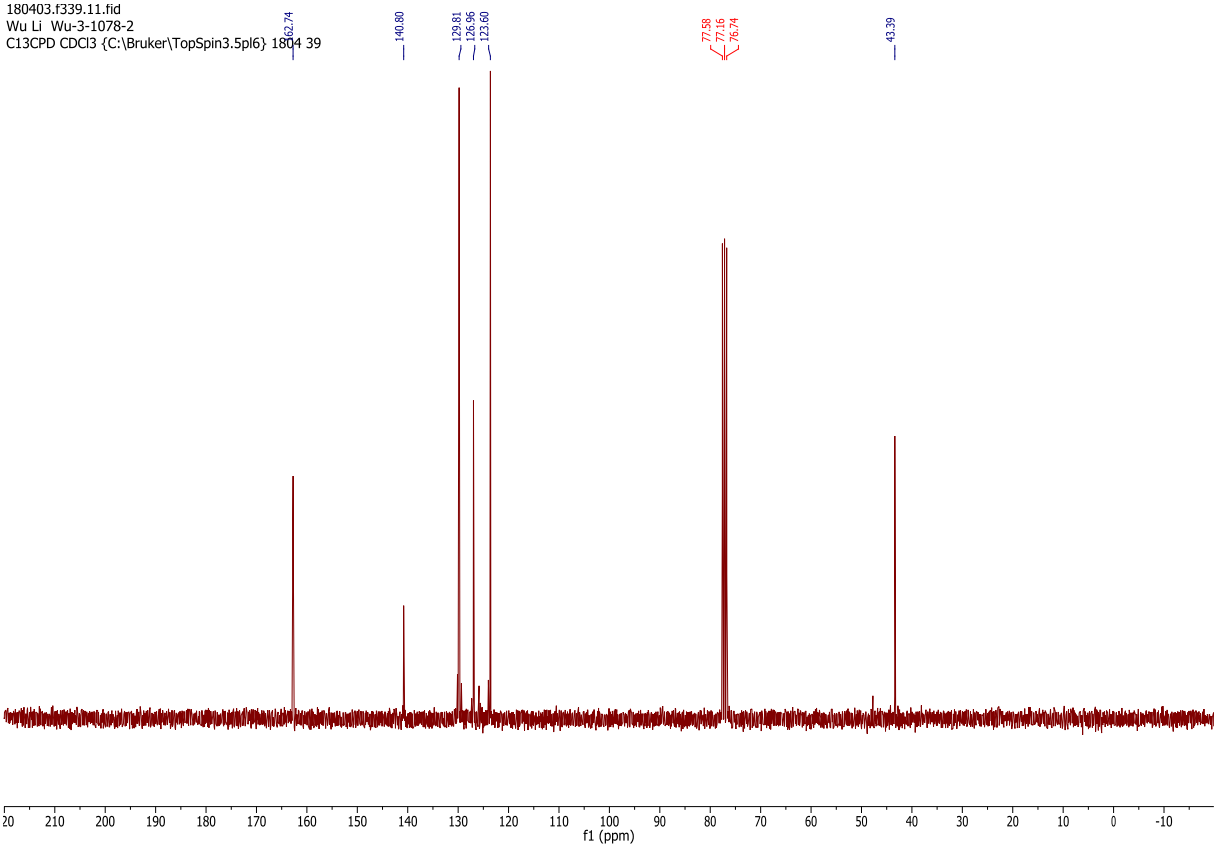
Original spectra for **61b**:



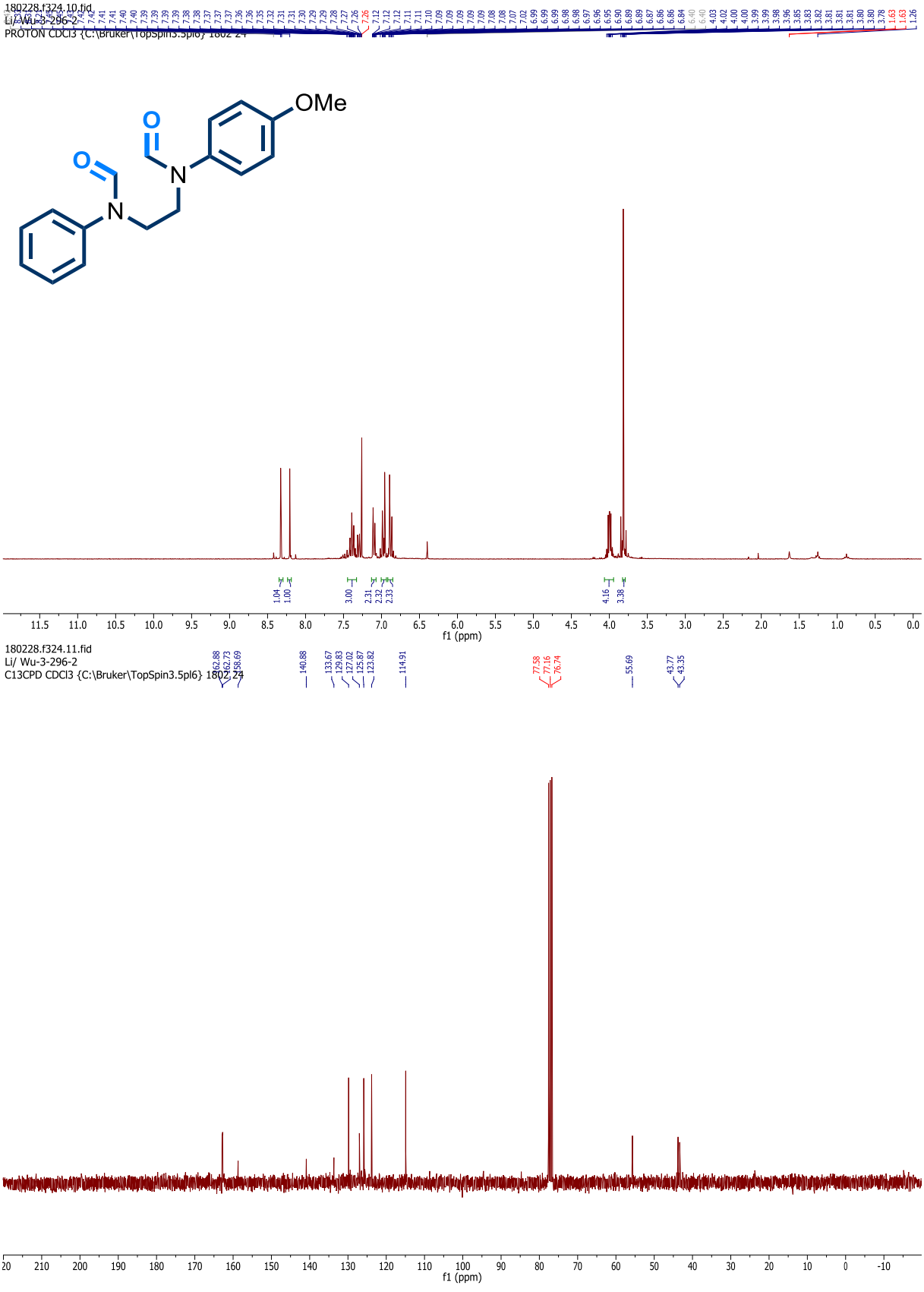


Original spectra for **62b**:

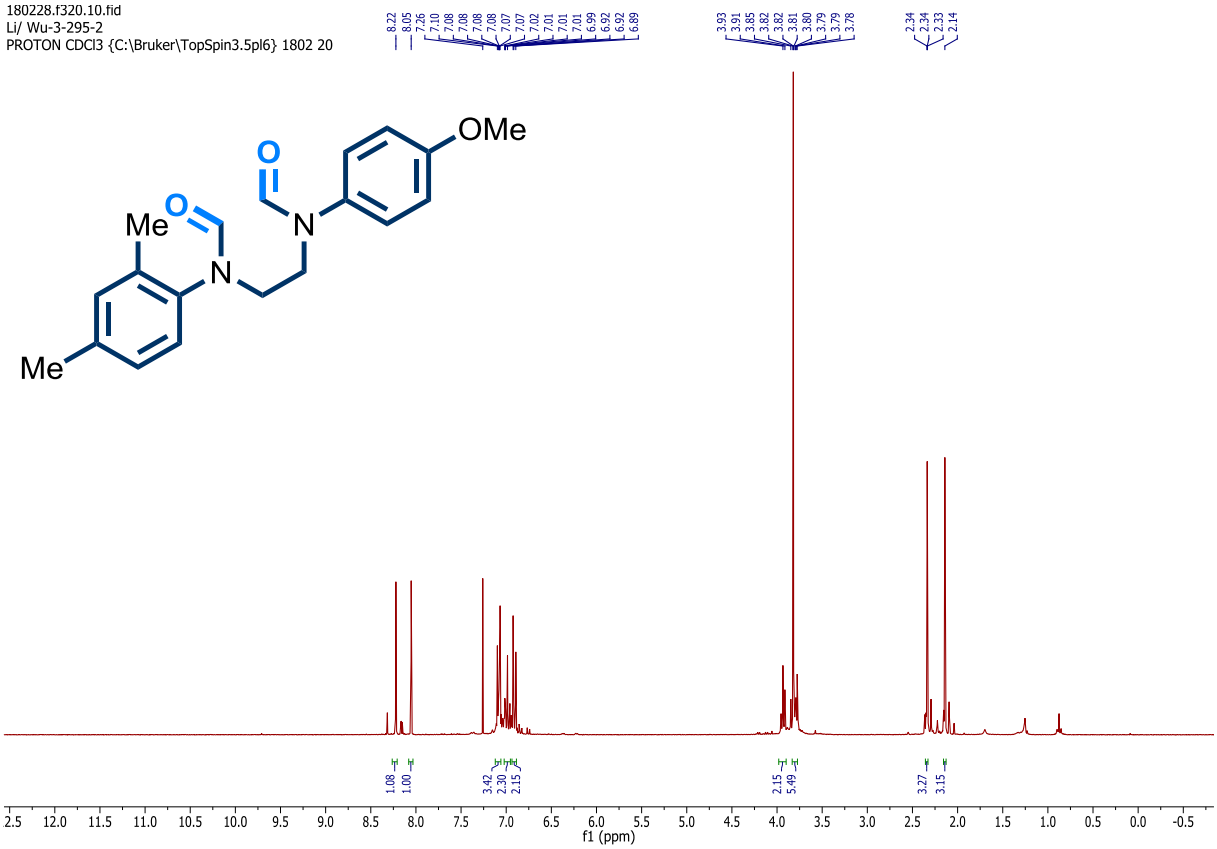


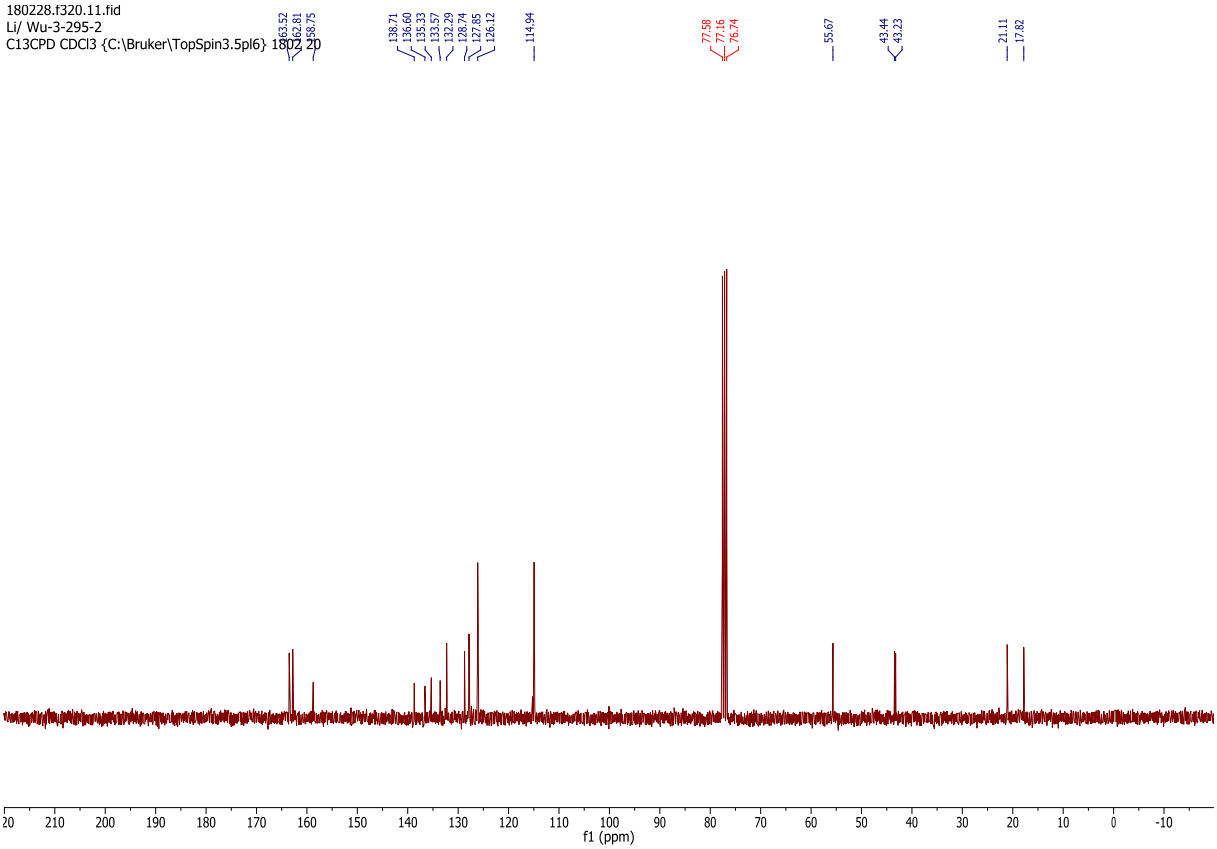


Original spectra for **63b**:

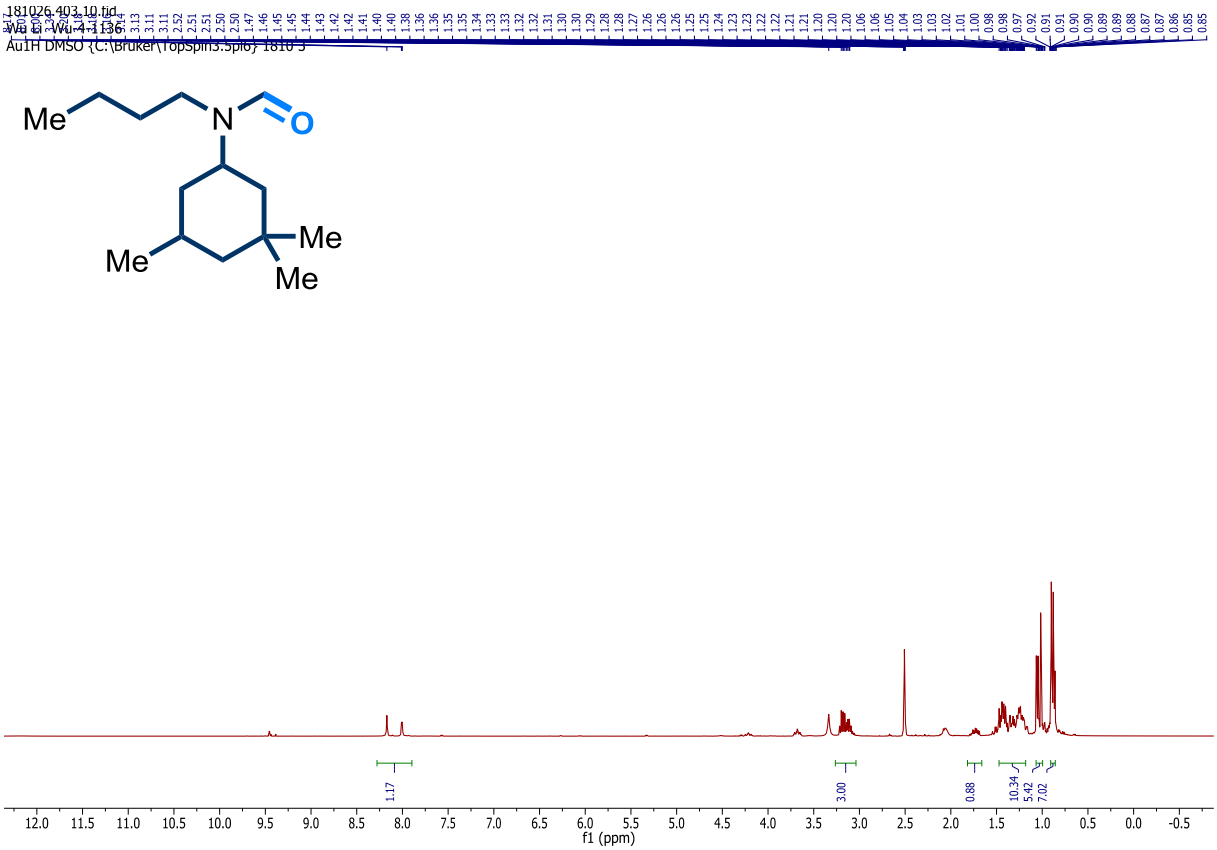


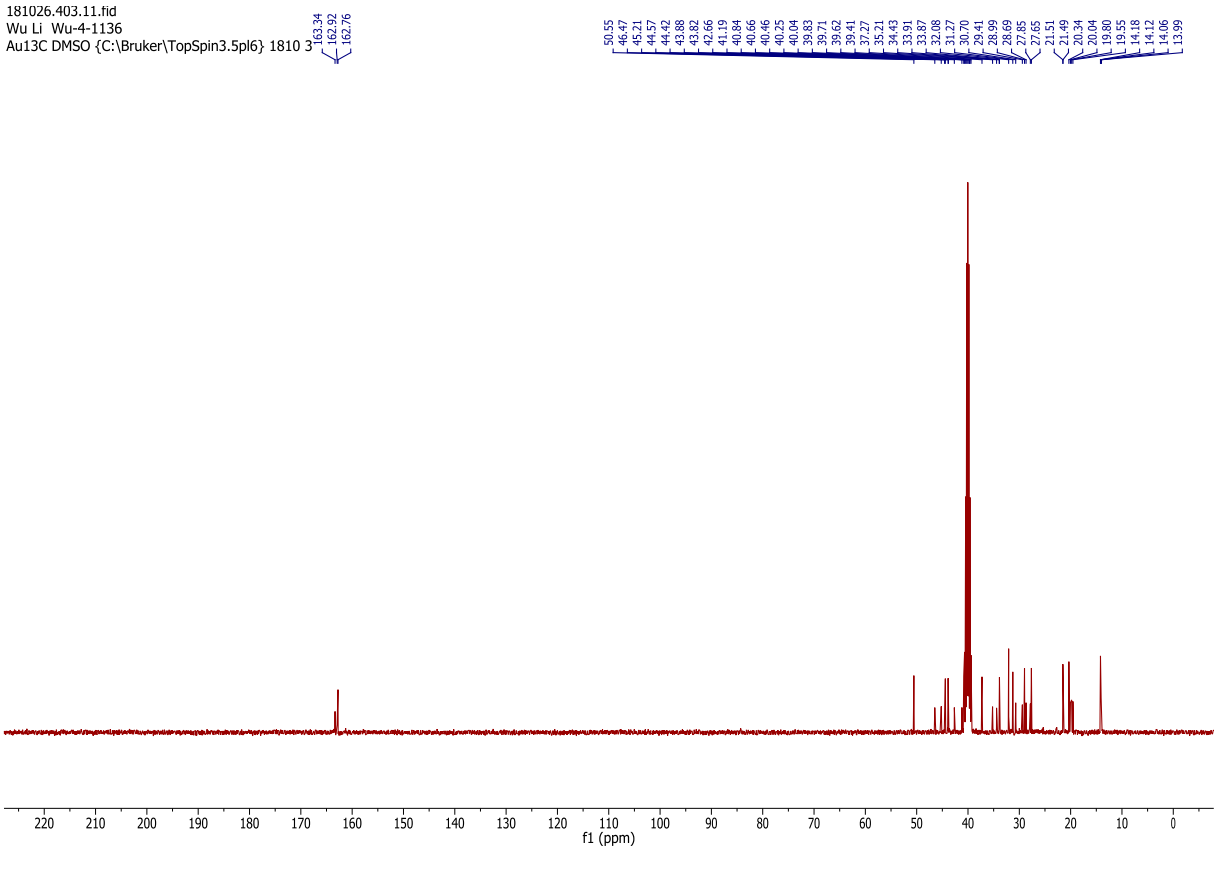
Original spectra for **64b**:



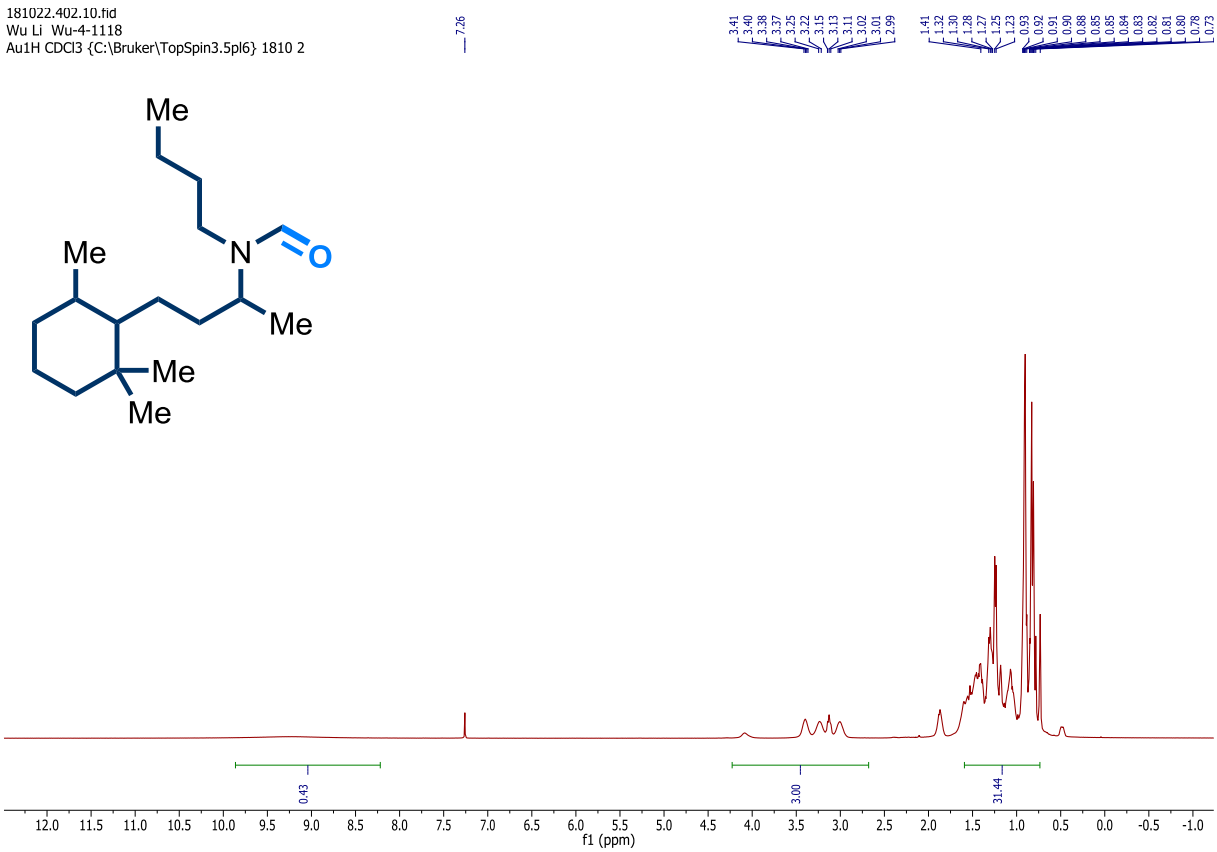


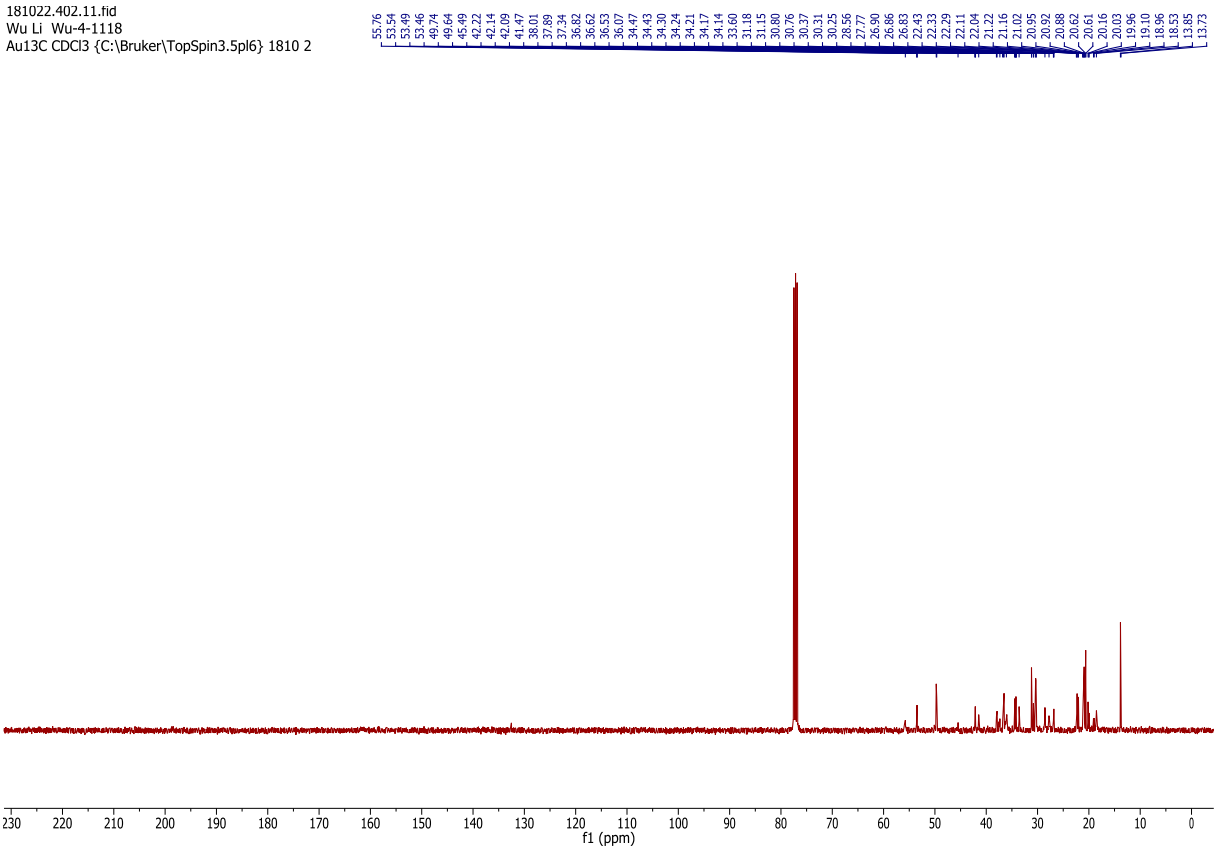
Original spectra for **65b**:



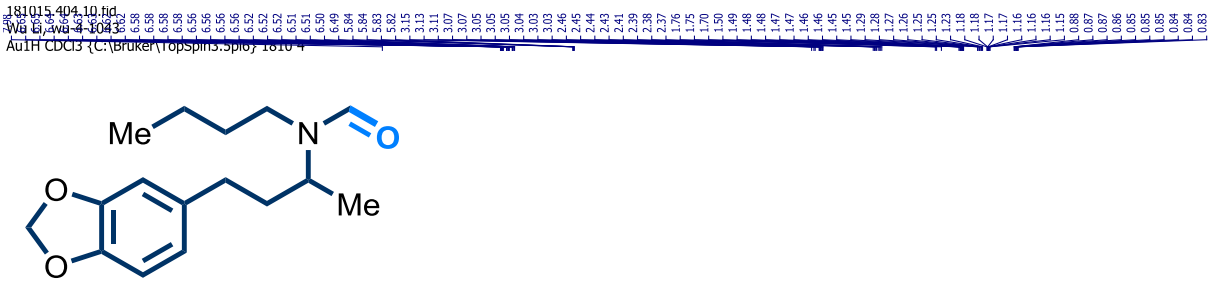


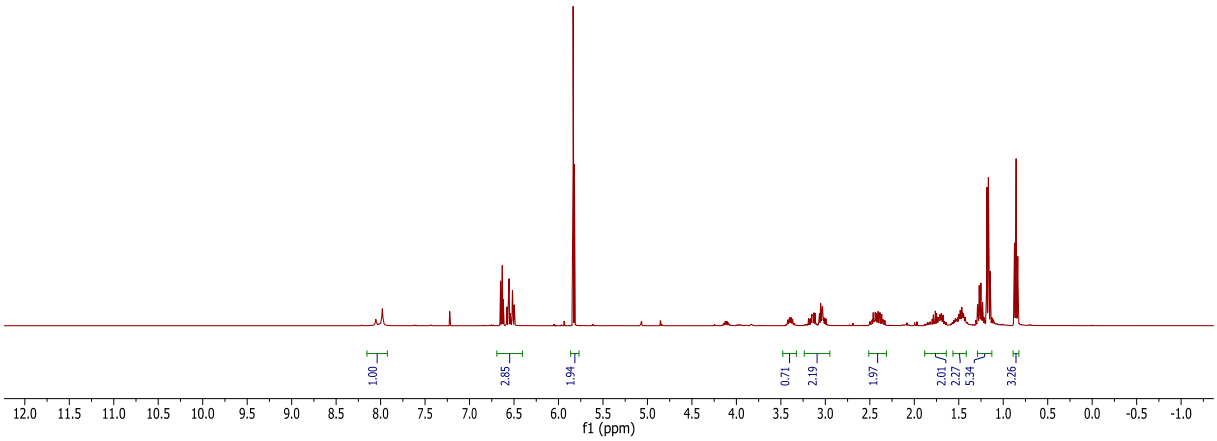
Original spectra for **66b**:

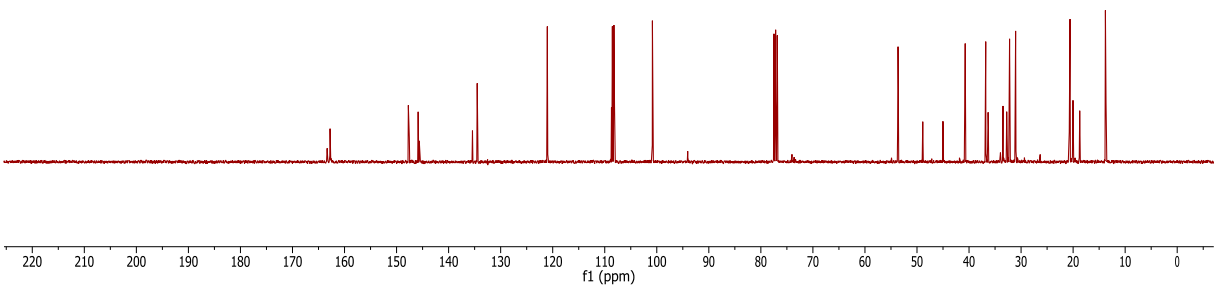




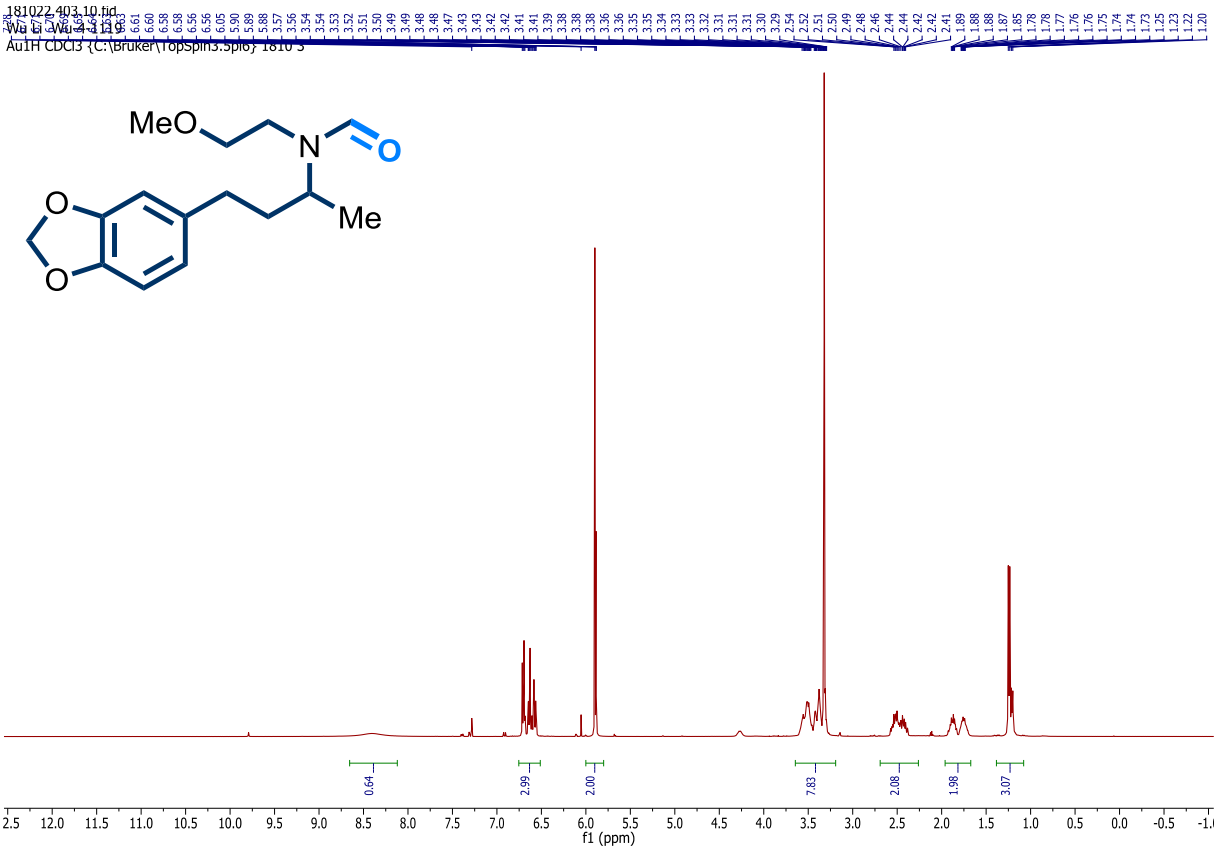
Original spectra for **67b**:

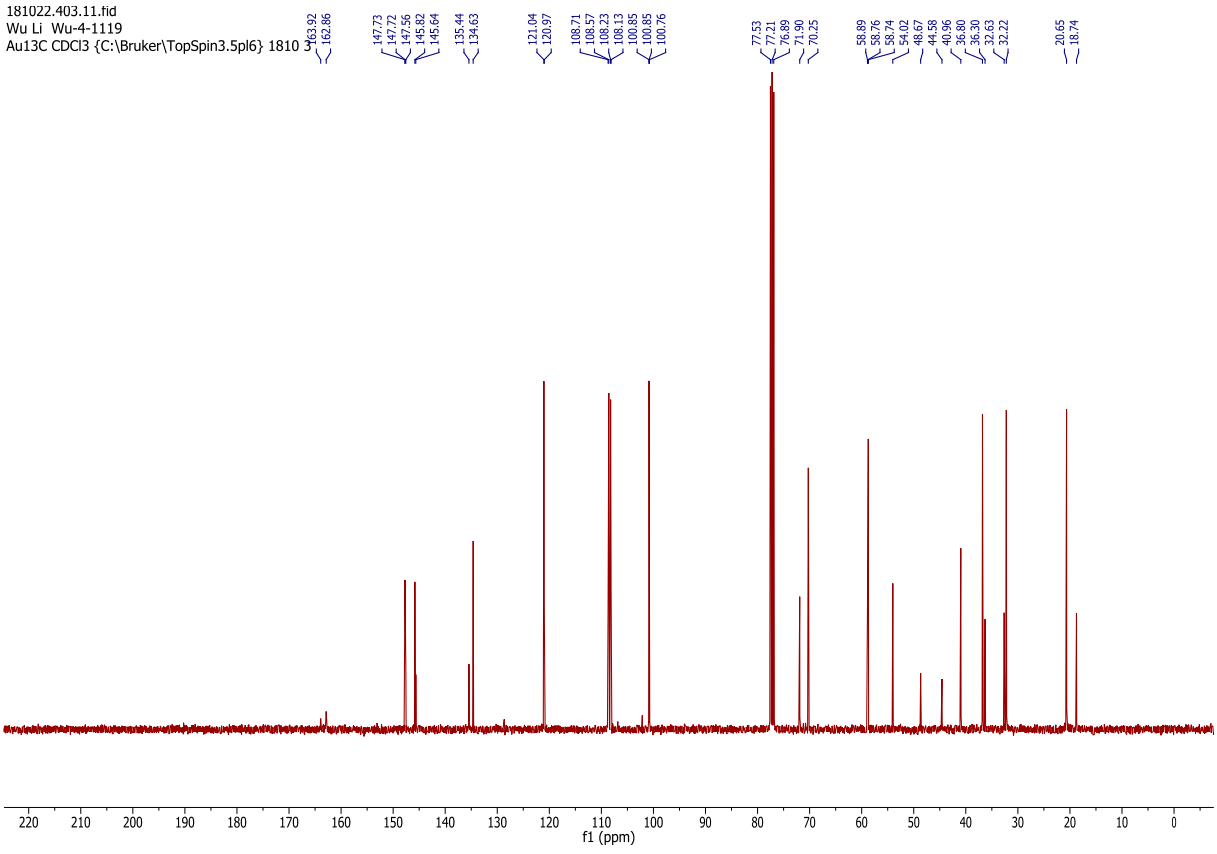




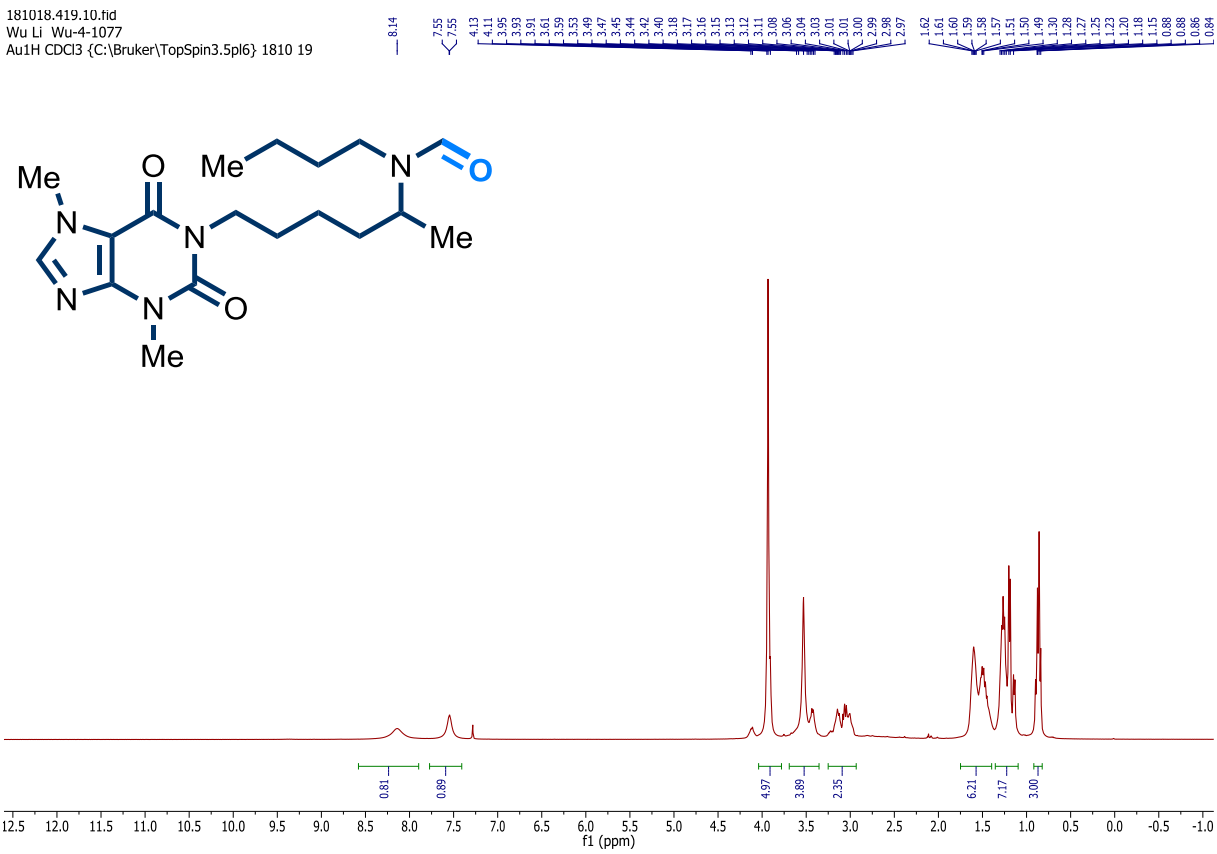


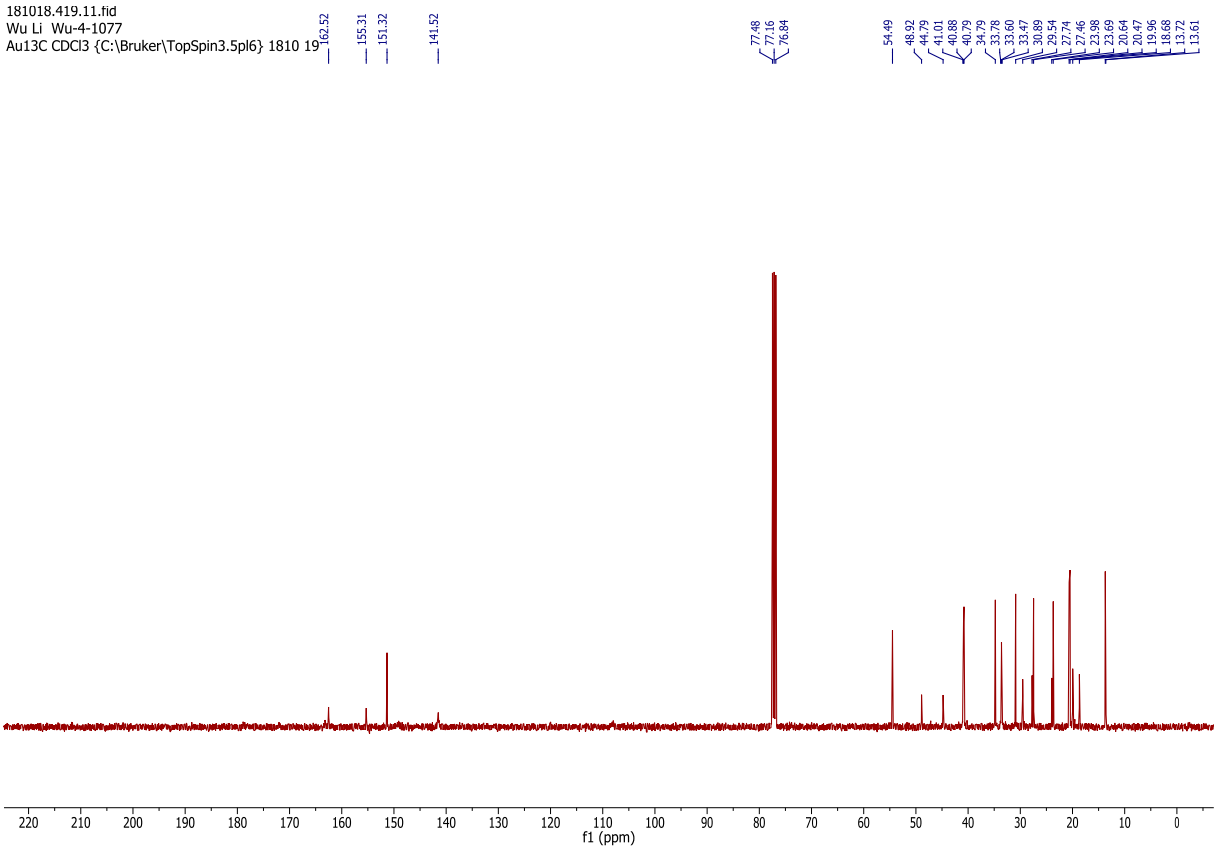
Original spectra for **68b**:



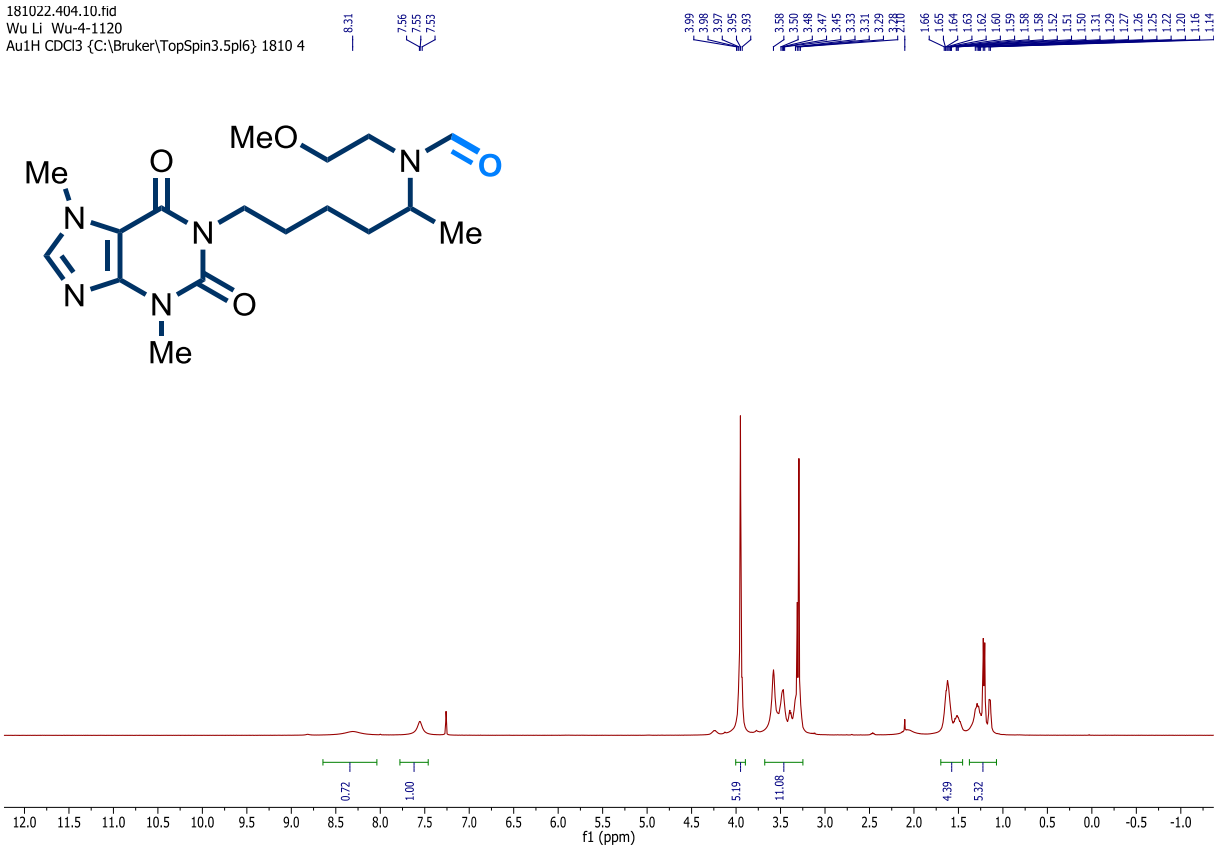


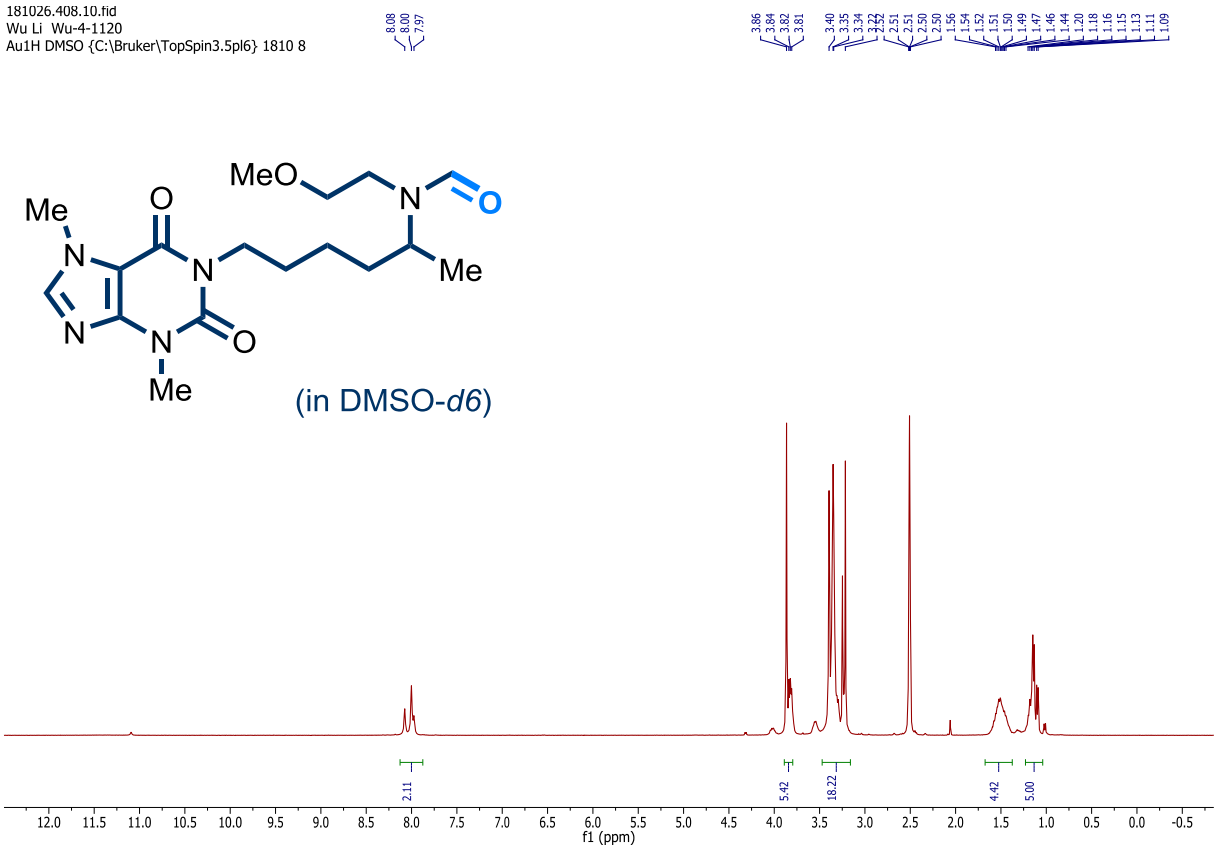
Original spectra for **69b**:

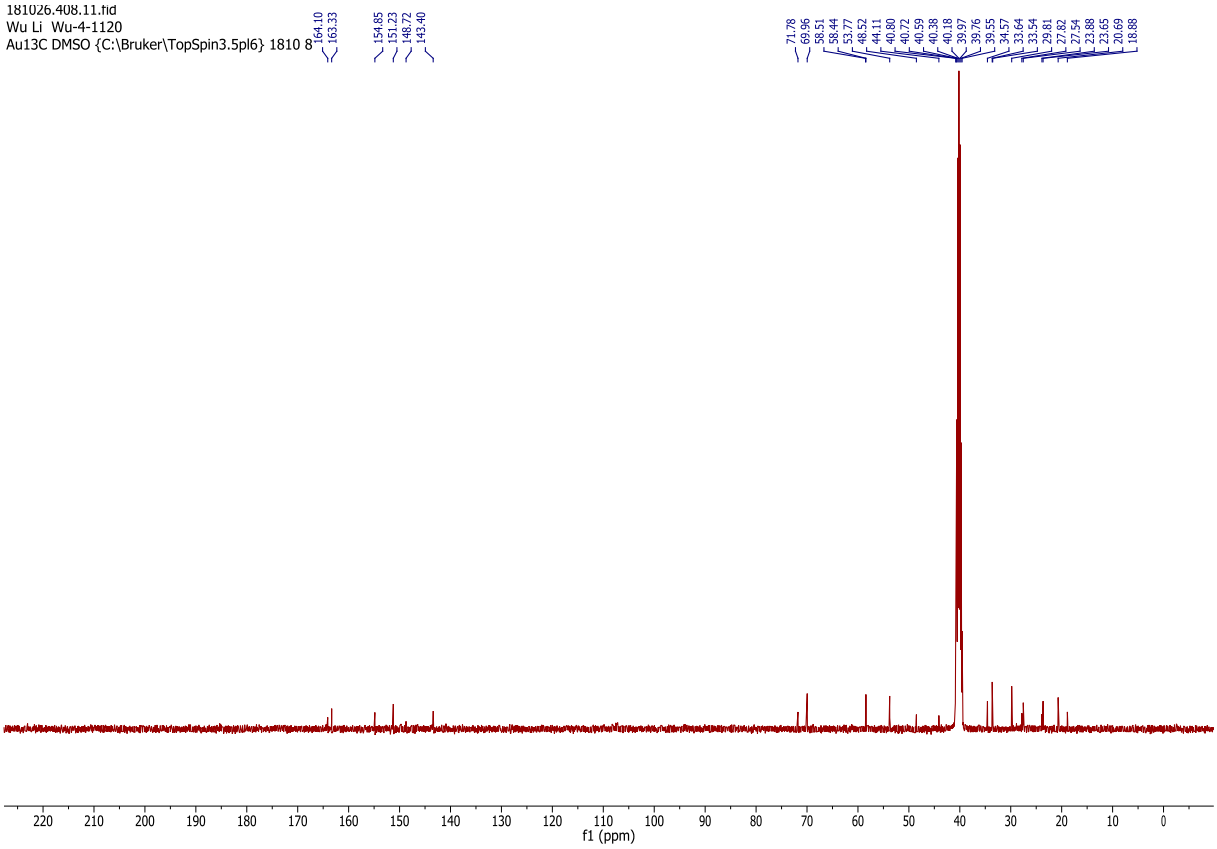




Original spectra for **70b** (in $CDCl_3$):

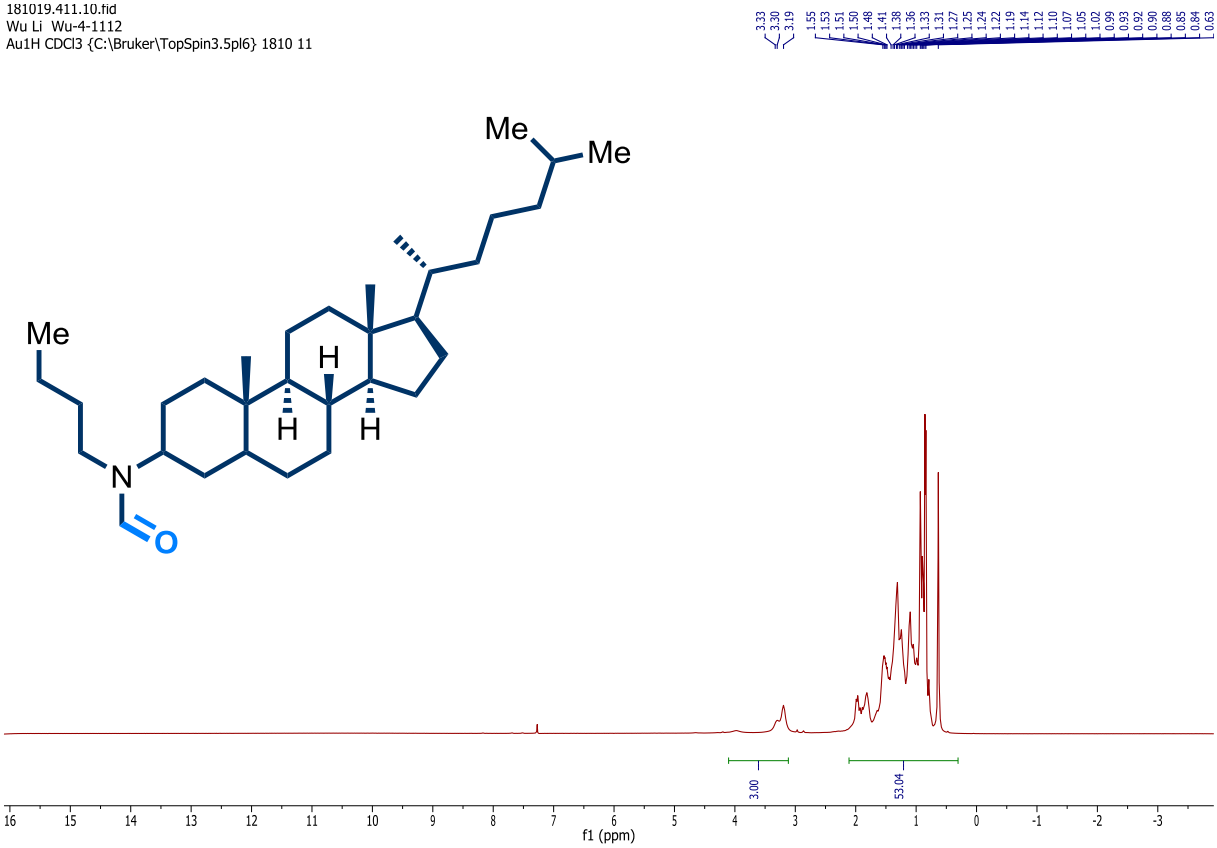




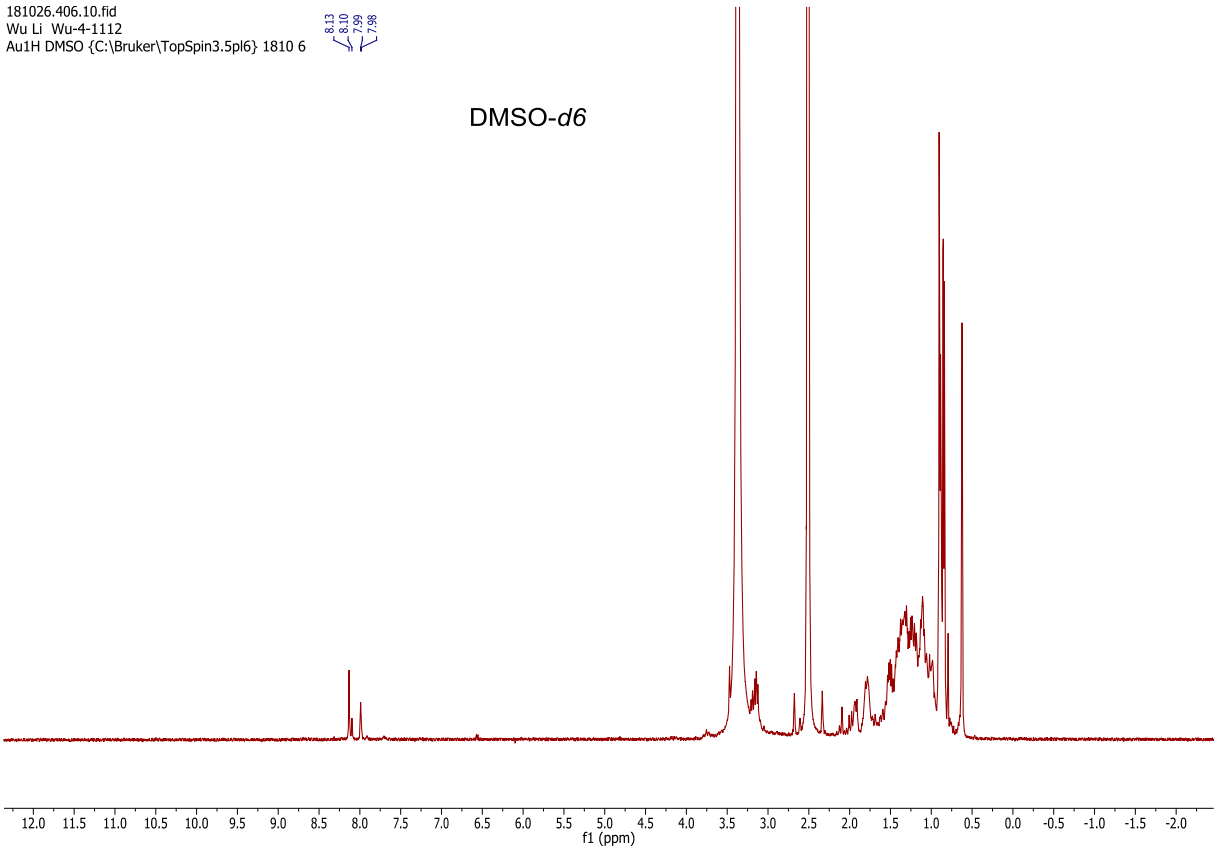

181026.408.11.fid
Wu Li Wu-4-1120
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1810 8
164.10
163.33
154.85
151.23
148.72
143.40
71.78
69.96
58.51
58.44
53.77
46.52
44.11
40.80
40.72
40.59
40.38
40.18
39.97
39.76
39.55
34.57
33.64
33.54
29.81
27.82
27.54
23.88
23.65
20.69
18.88
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

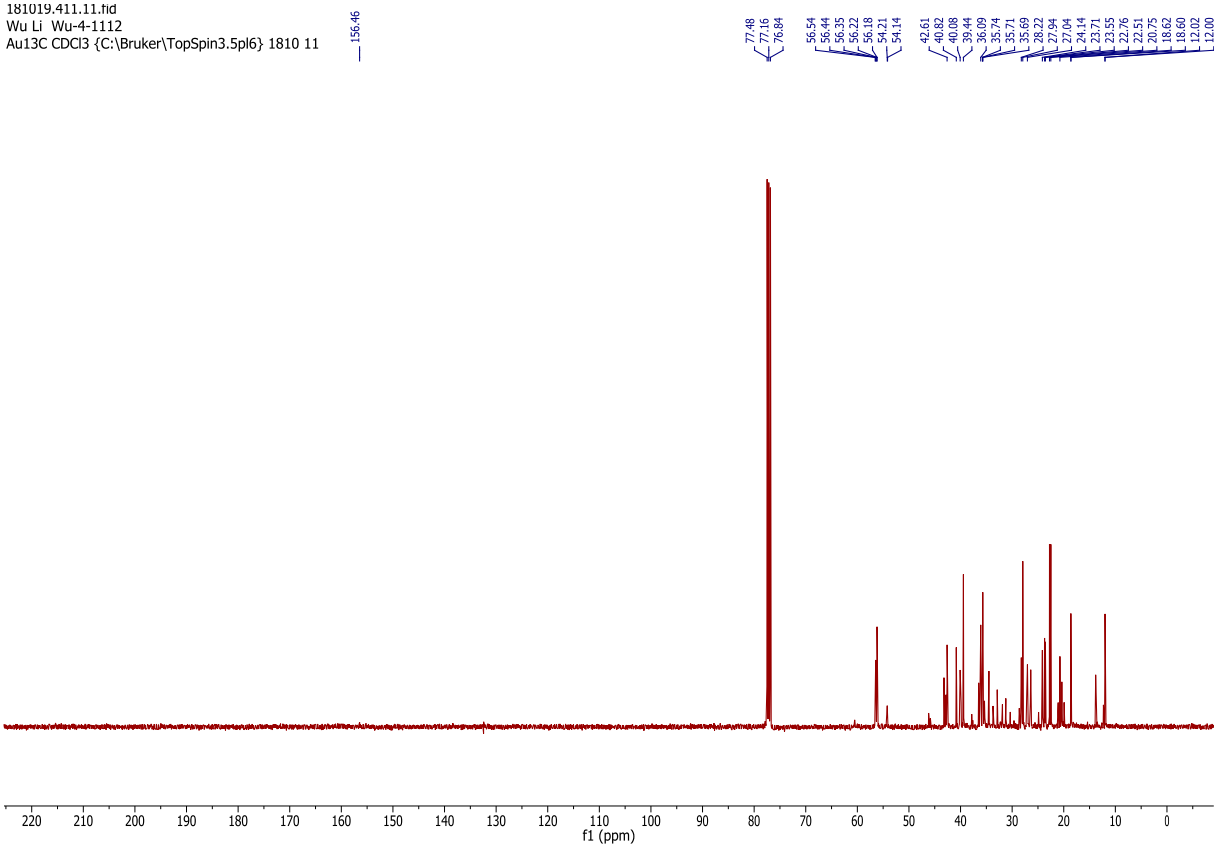
Original spectra for **71b**:

181019.411.10.fid
Wu Li Wu-4-1112
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 11

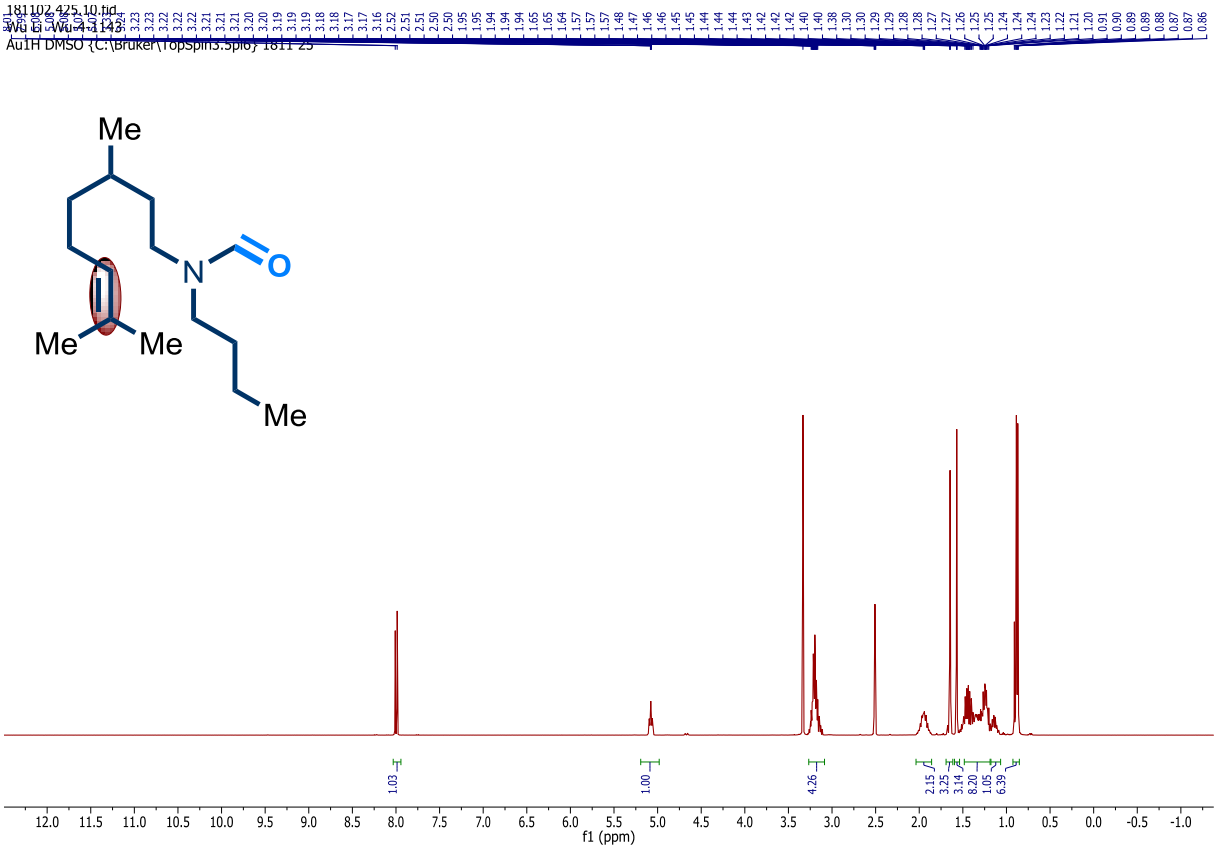


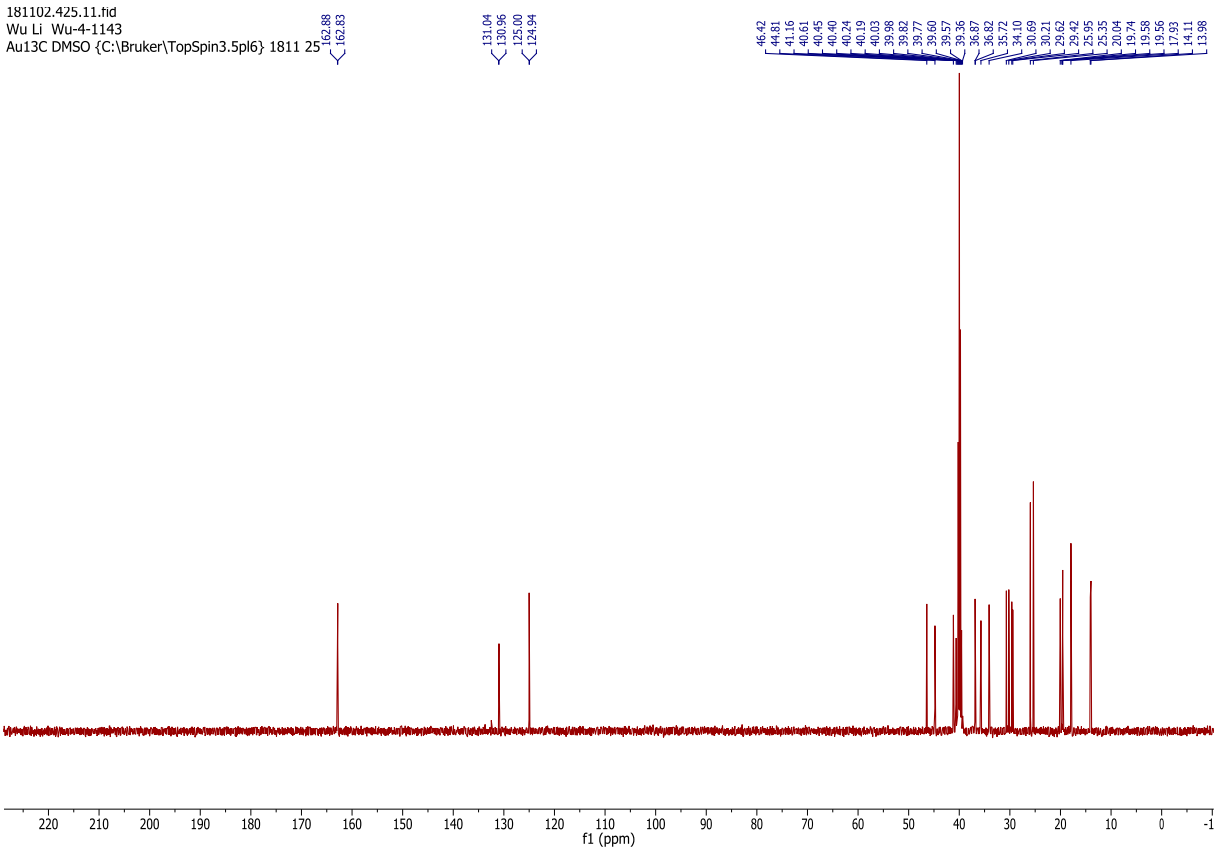
181026.406.10.fid
Wu Li Wu-4-1112
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1810 6



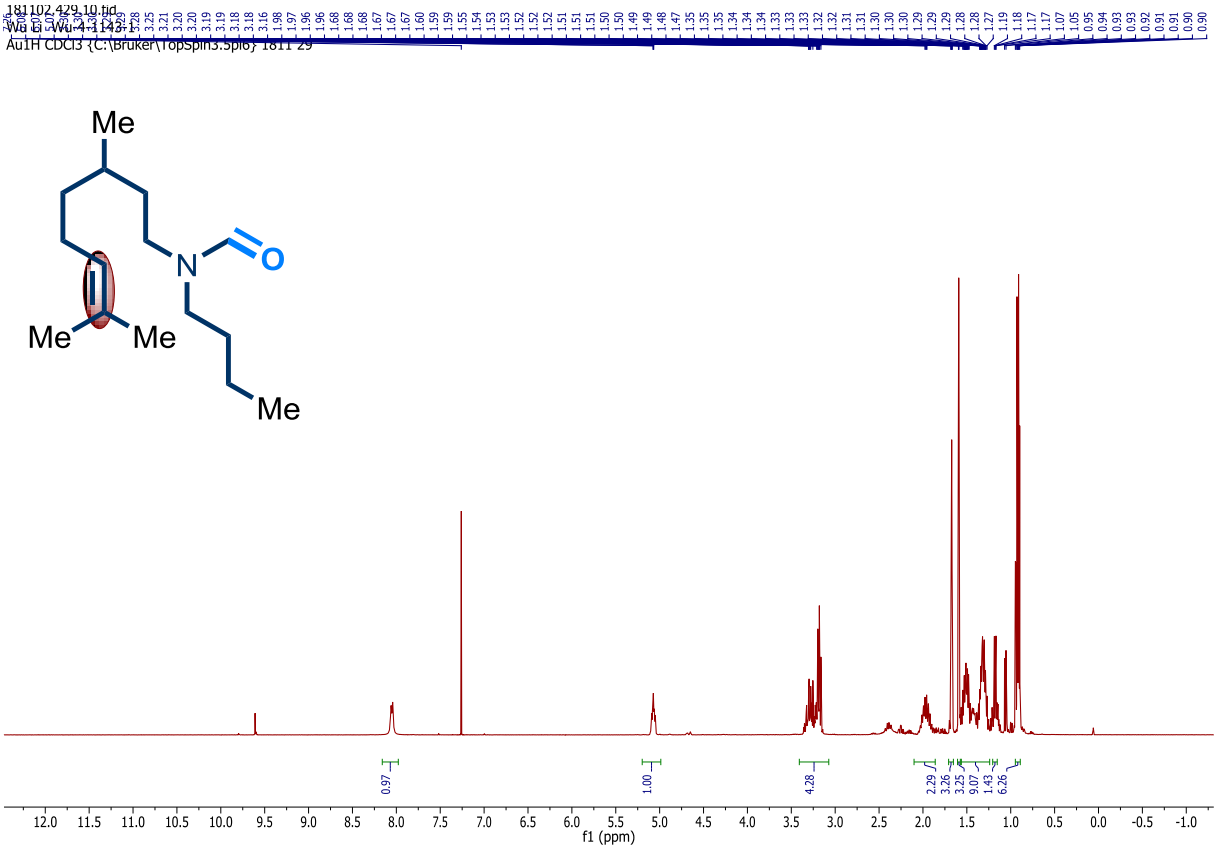

181019.411.11.fid
Wu Li Wu-4-1112
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1810 11
156.46
77.48
77.16
76.84
56.54
56.44
56.35
56.22
56.18
54.21
54.14
42.61
40.82
40.08
39.44
36.09
35.74
35.71
35.69
28.22
27.94
27.04
24.14
23.71
23.55
22.76
22.51
20.75
18.62
18.60
12.02
12.00
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

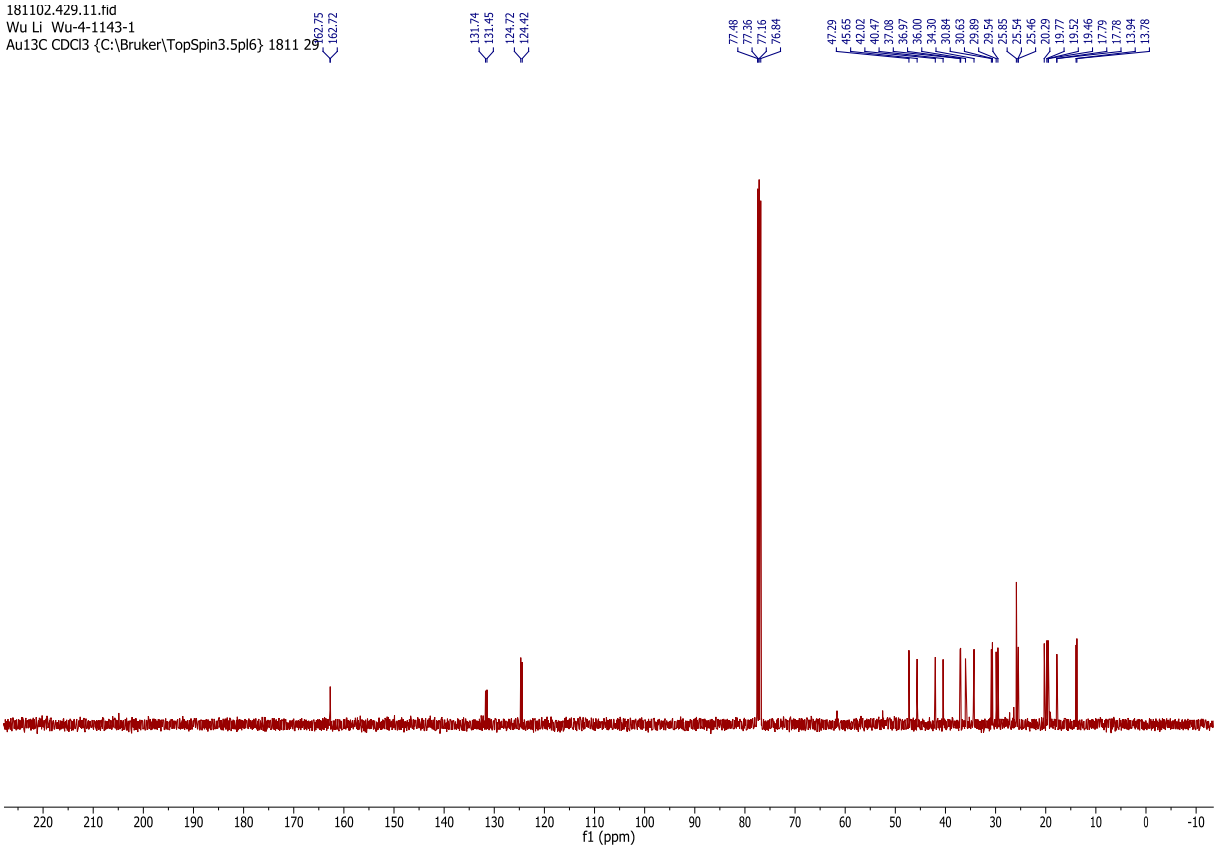
Original spectra for **72b** (in DMSO-*d6*):



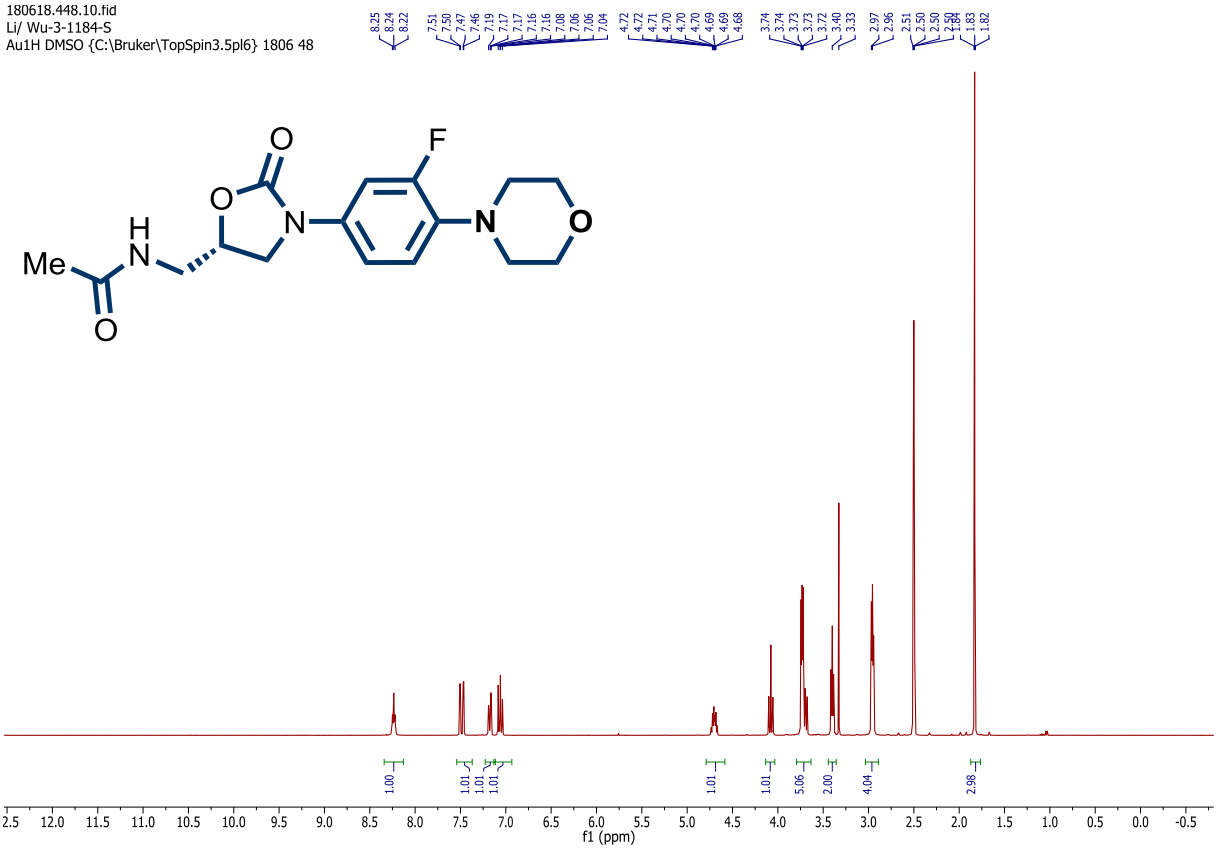


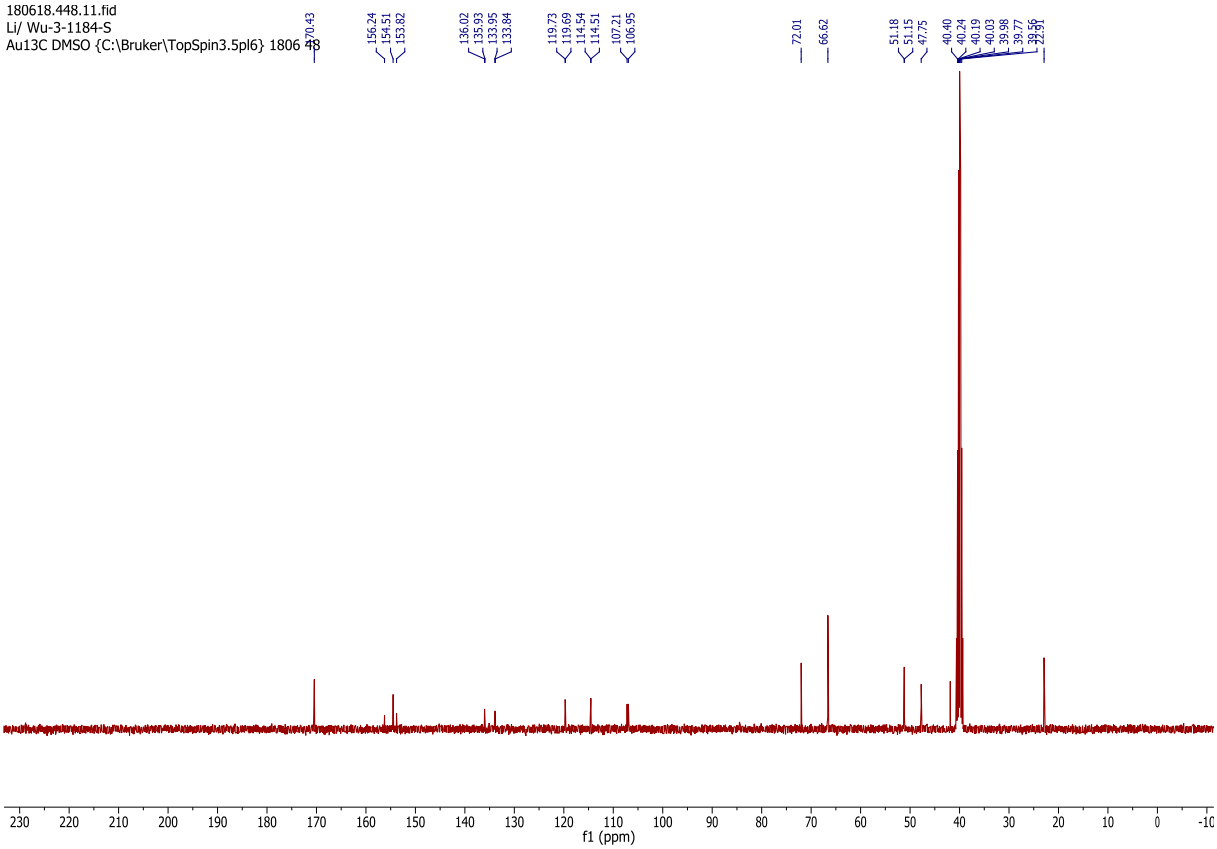
Original spectra for **72b** (in $CDCl_3$):



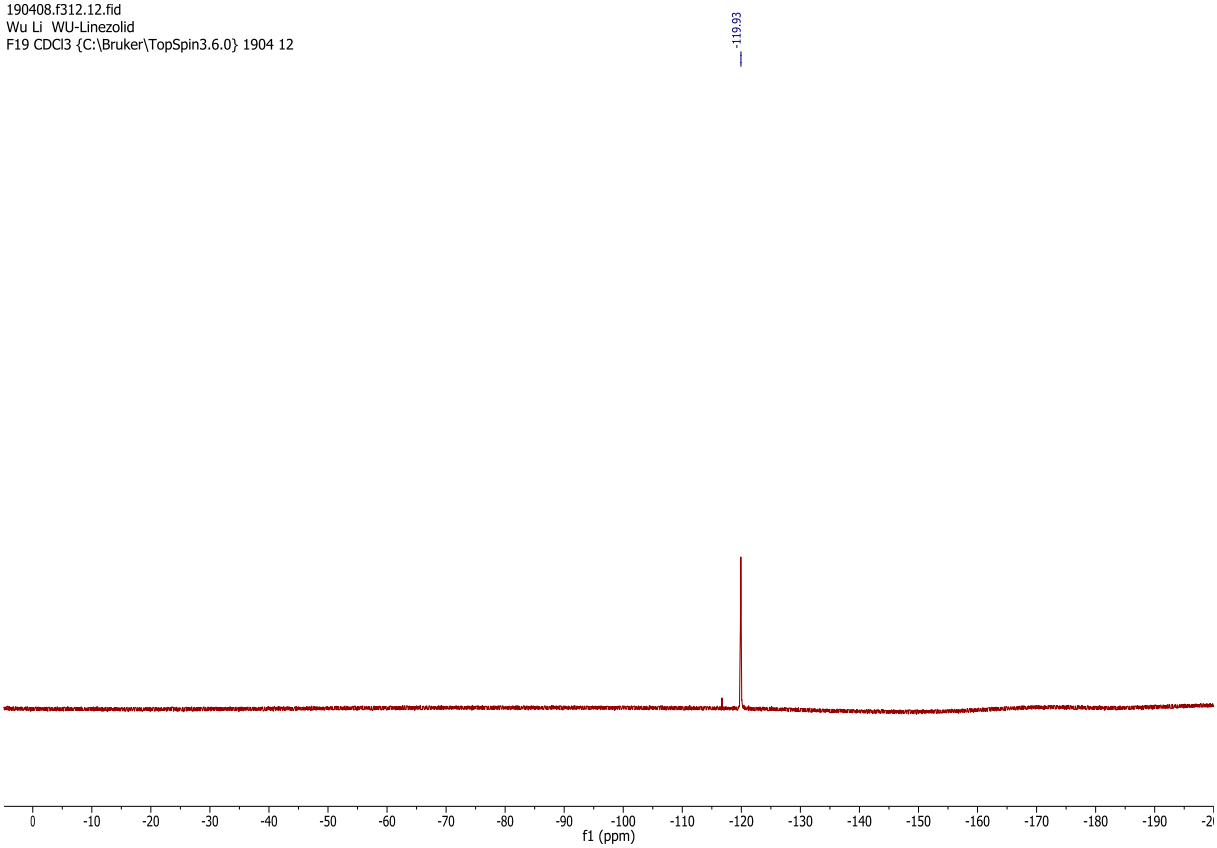


Original spectra for **73a**:

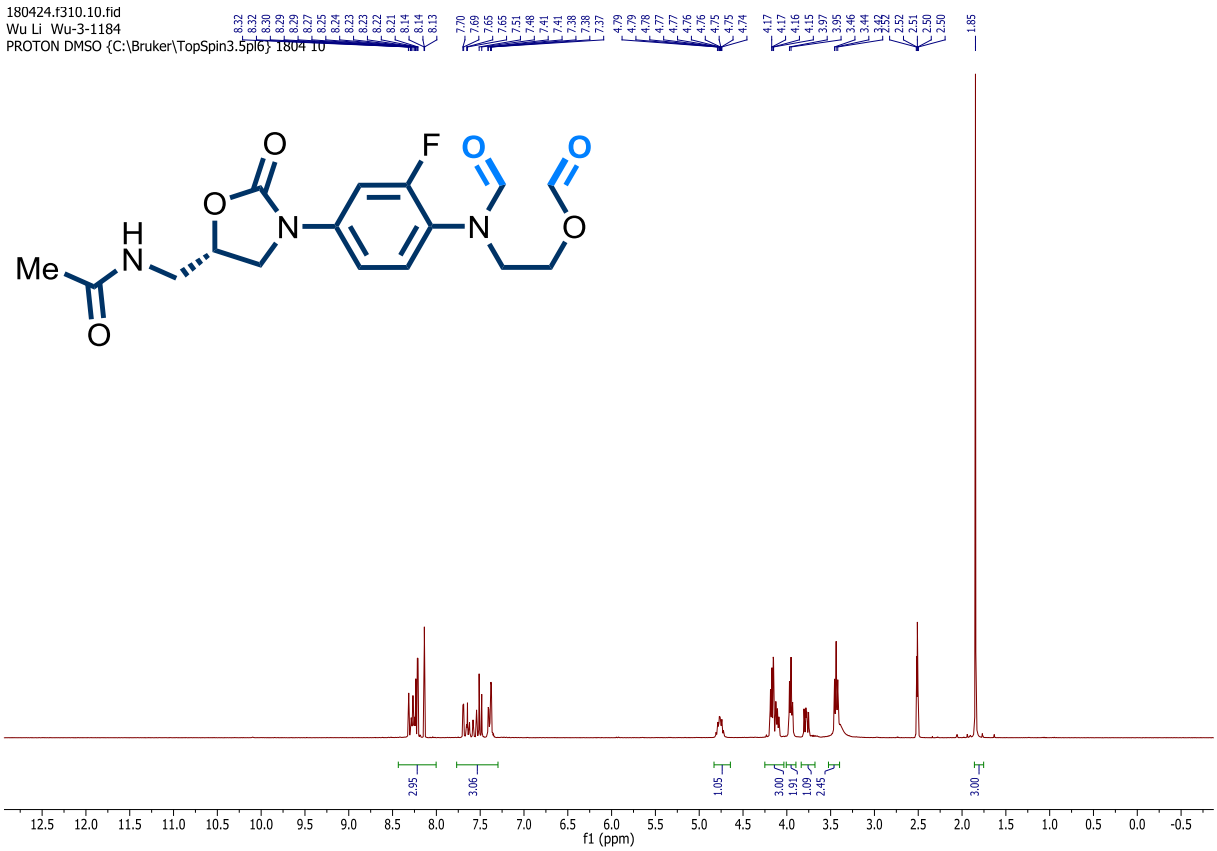


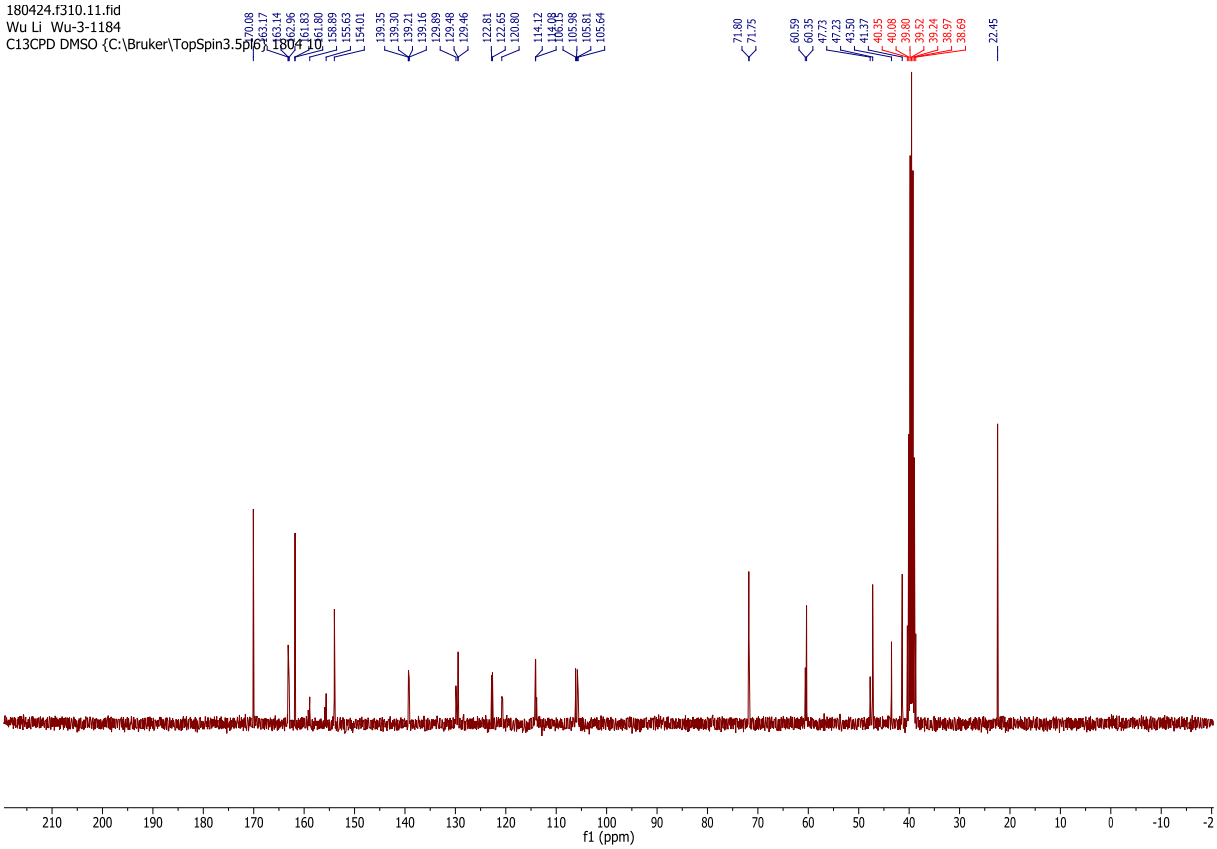


190408.f312.12.fid
Wu Li WU-Linezolid
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1904 12

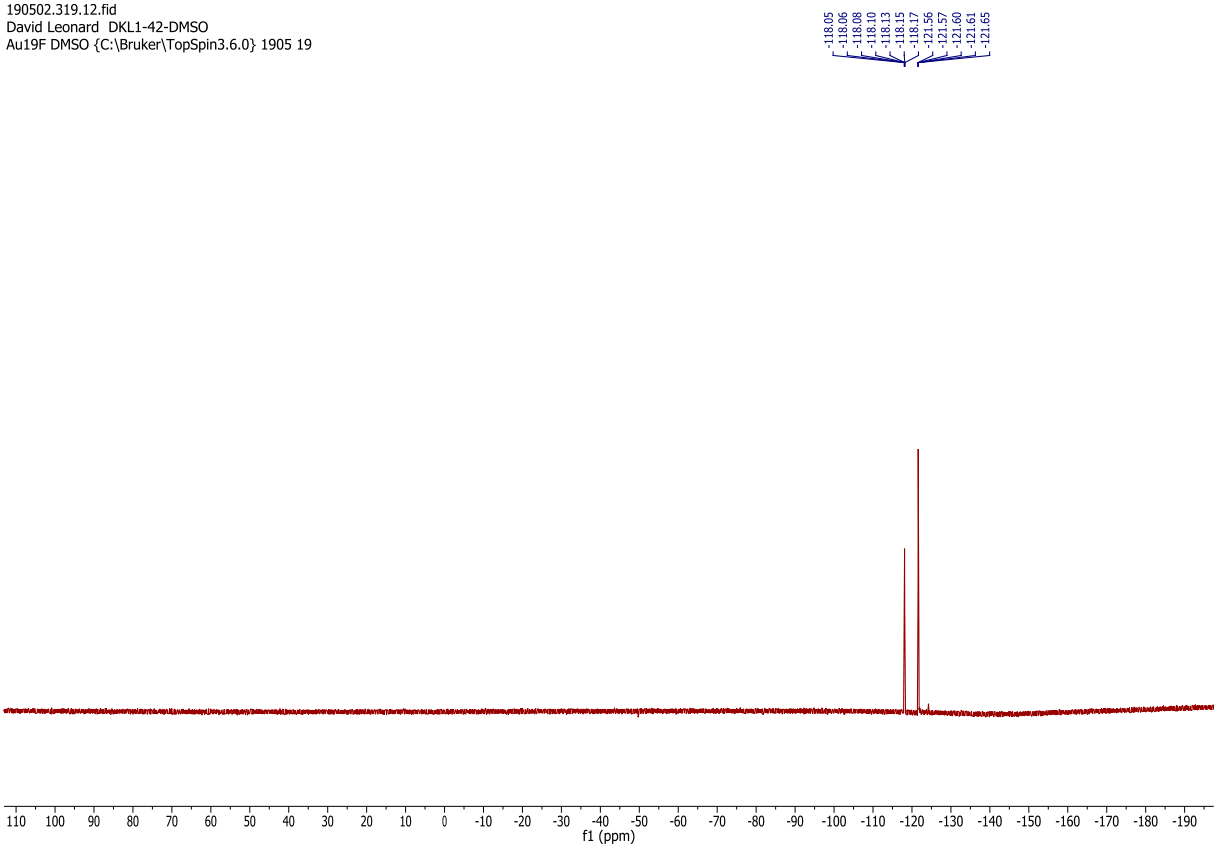


Original spectra for **73b**:

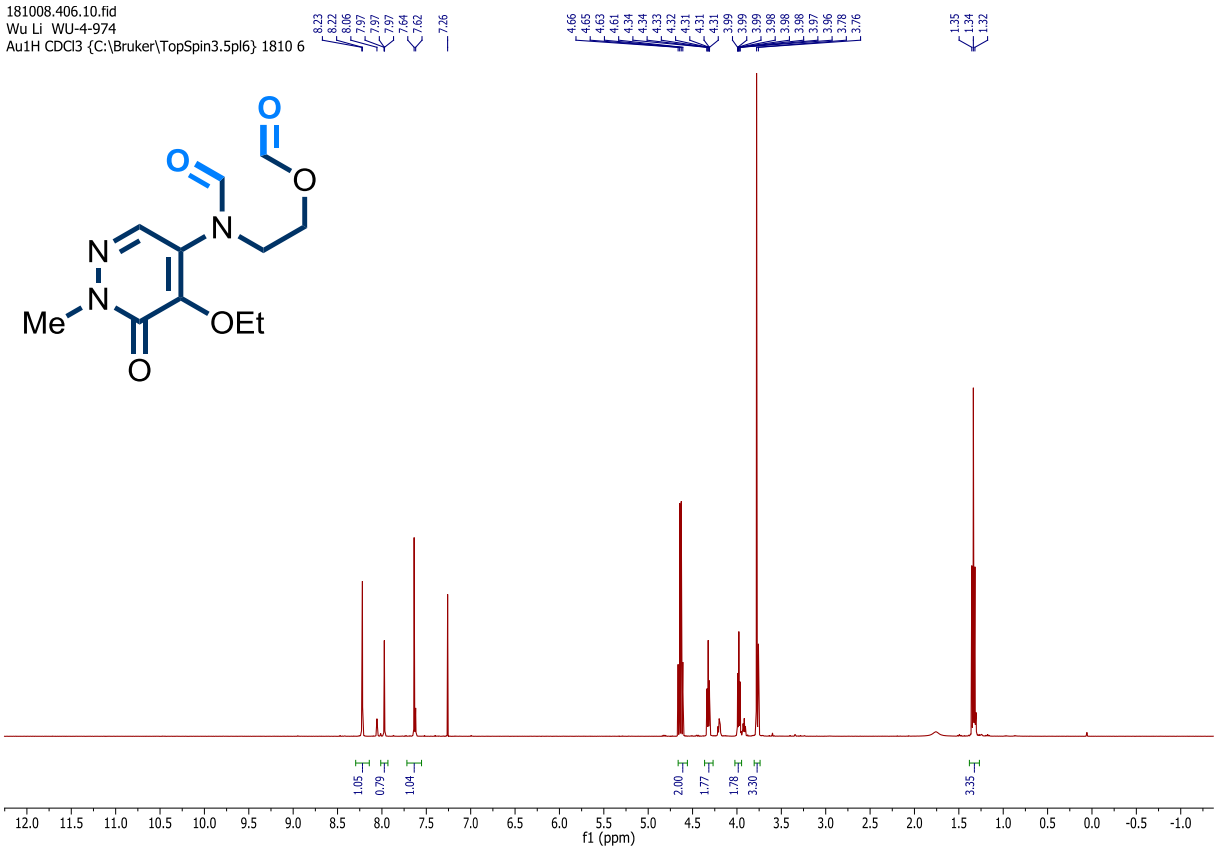


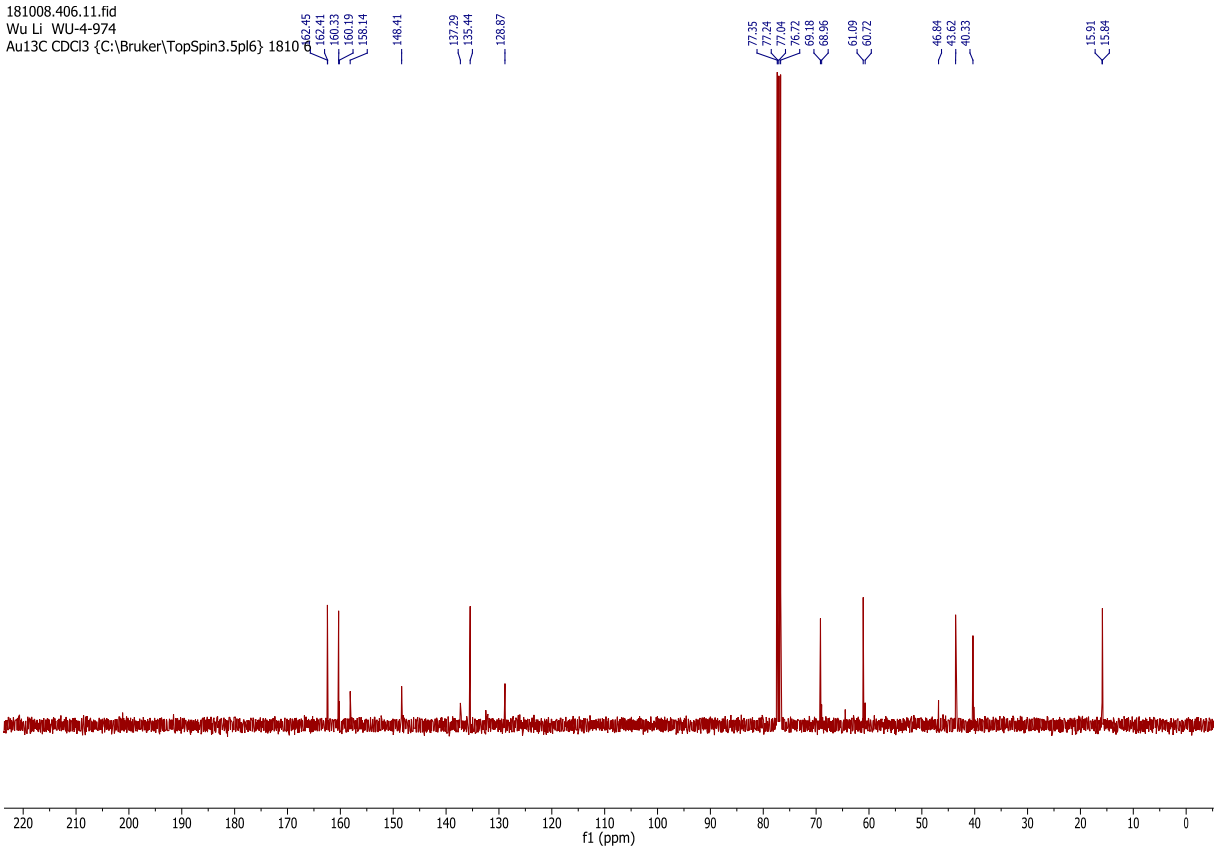


190502.319.12.fid
David Leonard DKL1-42-DMSO
Au19F DMSO {C:\Bruker\TopSpin3.6.0} 1905 19



Original spectra for **74b**:





11. References

[1] D. Wang, A. B. Weinstein, P. B. White, S. S. Stahl, *Chem. Rev.* **2018**, *118*, 2636-2679.

[2] R. Stößer, G. Scholz, K. Möckel, E. Backhaus, *J. Mol. Struct.* **1994**, *319*, 203-210.

[3] R. Suarez-Bertoa, F. Saliu, M. Bruschi, B. Rindone, *Tetrahedron* **2012**, *68*, 8267-8275.

[4] F. Saliu, M. Orlandi, M. Bruschi, *ISRN Org. Chem.* **2012**, *2012*, 281642.