Supporting Information

Atom-Economical and Tandem Conversion of Nitriles to N-Methylated Amides using Methanol and Water

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1. General Consideration

Reagent Information. Unless otherwise stated, all the experiments were carried out under argon atmosphere using either argon filled Glove box or standard schlenk line technique. Glass apparatus were oven dried and immediately prior to use. Solvents were dried according to literature methods. Methanol was distilled over sodium under argon atmosphere and deoxygenated prior to use. All the nitriles, cobalt precursor and others commertially available reagents were purchased from Sigma-aldrich, Alfa-acear, SD-fine chemicals, Avra Spectrochem. Silica gel (100-200 mesh) was used for the column chromatography with a gradient elution of hexane/ethyl acetate, based on silica gel coated aluminium TLC plate.

Analytical Information. ^{1}H and ^{13}C spectra were recorded on JEOL 400 MHz and 500 MHz Spectrometer using $CDCl_3$ and DMSO-d_6. All ^{1}H NMR experiments were reported in parts per million (ppm) units, and were measured relative to the signals for residual chloroform (7.25 ppm) in the deuterated solvent, unless otherwise stated and coupling constant (*J*) was reported in hertz (Hz). All ^{1}H decoupled ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.10 ppm). All the GC analysis were performed using Perkein Elmer Clarus 600 Gas Chromatograph and GC-MS were taken using Agilent 7890A Gas Chromatograph equipped with Agilent 5890 triple-quadrupole mass system.

2. General Procedures

Tandem Conversion of Nitrile to N-Methylated Amide using Methanol. An oven dried 9 mL screw cap tube was taken inside the argon filled glove box and charged with a magnetic stir-bar, nitrile (0.5 mmol), $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (PP_3) (7.5 mol %), Cs_2CO_3 (0.5 mmol), KO^tBu (0.25 mmol) and water (5.0 mmol) followed by the addition of methanol/*m*-xylene (2.5 mL, 1:1 v/v). Then, the tube was sealed and placed in a preheated oil bath at 140 $^{\circ}$C (oil bath temperature) for 3-72 h. After completion of the reaction, the tube was allowed to cool at room temperature. Then, 25 μL reaction mixture was syringed out and filtered through a small plug of silica and subjected for GC analysis using mesitylene as internal standard to determine conversion as well as product selectivity. The remaining solvent was evaporated and the crude residue was purified by silica gel column chromatography using hexane-ethyl acetate as eluent which afforded the desired N-methylated amide.

Calculation of Response Factor

All the response factor were calculated following the literature procedure.[1] For this purpose, mesitylene was used as an internal standard and stock solution of the corresponding component at the different concentration was prepared and was analysed by GC.

Let, the response factor is R_f for the analyte with respect to internal standard.

Now, using the response factor formula,

area of analyte signal / concentration of analyte = $R_f \times$ area of internal standard signal / concentration of internal standard.

i.e., $a_x / c_x = R_f \times a_i / c_i$

Hence, $R_f = (a_x \times c_i) / (a_i \times c_x)$……..(1)

where, a_x and a_i are the area of analyte and that of internal standard respectively. c_i and c_x are the concentration of analyte and that of internal standard respectively.

This equation should give a linear response of the detector to both the known analyte and the internal standard. By varying randomly the concentration of known analytes keeping the internal standard's concentration fixed, and recording the chromatogram, we checked the linearity of response factor (R_f). Now, a plot of a_x/a_i versus c_x/c_i for a series of measurements will give a straight line fitting and the slope of the line will be R_f (Table **S1**-**S4**).

Thus, from the equation (1) we can calculate the concentration of each components after getting response factor for all individuals with respect to same internal standard. For a reaction of type,

*% GC yield of **B** = [concentration of **B** / {concentration of **A** + concentration of **B** + concentration of **C** + concentration of **D**}×100.*

Table S1. Response Factor (R_f) for Benzonitrile with respect to Mesitylene

Entry	**Conc. of mesitylene (c_i) (M)**	**Area of mesitylene (a_i)**	**Conc. of Benzonitrile (c_x) (M)**	**Area of Benzonitrile (a_x)**	**$R_f = (a_x/a_i)/(c_x/c_i)$**
1	0.0297	9696390	0.0336	7337882	0.704
2	0.0297	10136723	0.0596	14310329	
3	0.0297	9661782	0.0894	20724655	
4	0.0297	8722501	0.1491	31119466	

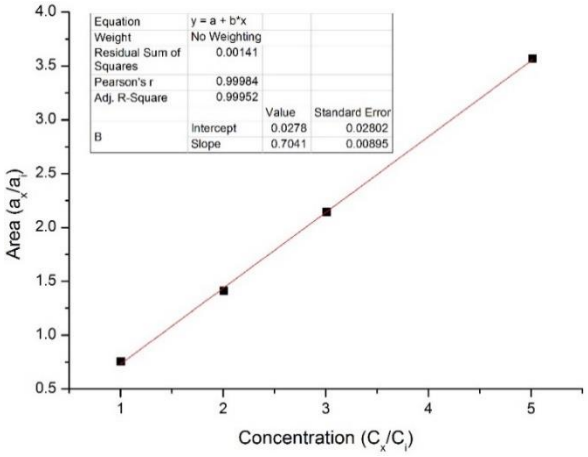


Figure S1. Determination of Response Factor for Benzonitrile with respect to Mesitylene

Table S2. Response Factor (R_f) for N-methylbenzamide with respect to Mesitylene

Entry	Conc. of mesitylene (c_i) (M)	Area of mesitylene (a_i)	Conc. of N-methylbenzamide (c_x) (M)	Area of N-methylbenzamide (a_x)	$R_f = (a_x/ a_i)/(c_x/ c_i)$
1	0.0297	9289093	0.0296	6152627	0.792
2	0.0297	9433136	0.0592	12602188	
3	0.0297	9465346	0.0888	19669744	
4	0.0297	9884933	0.1184	28849406	
5	0.0297	9463042	0.1479	36131064	

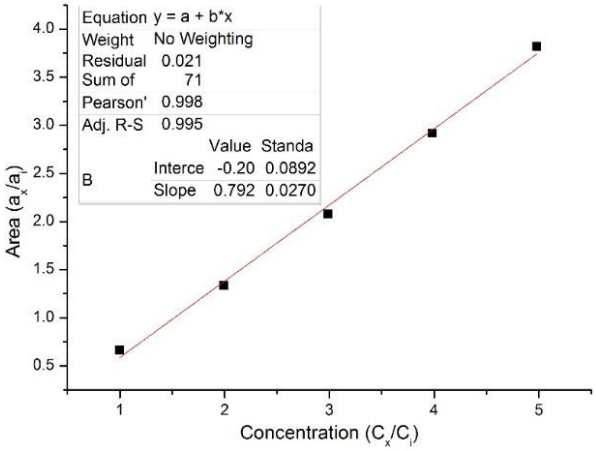


Figure S2. Determination of Response Factor for N-methylbenzamide with respect to Mesitylene.

Table S3. Response Factor (R_f) for Benzamide with respect to Mesitylene

Entry	Conc. of mesitylene (c_i) (M)	Area of mesitylene (a_i)	Conc. of Benzamide (c_x) (M)	Area of Benzamide (a_x)	$R_f = (a_x/ a_i)/(c_x/ c_i)$
1	0.0297	9365133	0.0301	1572929	0.400
2	0.0297	9986458	0.0596	4834728	
3	0.0297	9368027	0.0896	9324003	
4	0.0297	9917047	0.1191	13065864	
5	0.0297	9573103	0.1491	16806895	

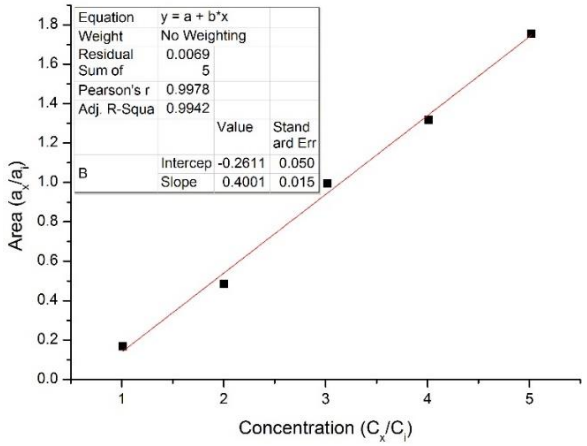


Figure S3. Determination of Response Factor for Benzamide with respect to Mesitylene.

Table S4. Response Factor (R_f) for Benzyl Alcohol with respect to Mesitylene

Entry	Conc. of mesitylene (c_i) (M)	Area of mesitylene (a_i)	Conc. of Benzyl Alcohol (c_x) (M)	Area of Benzyl Alcohol (a_x)	$R_f = (a_x/ a_i)/(c_x/ c_i)$
1	0.0297	9740604	0.0296	4900872	0.520
2	0.0297	10304893	0.0414	9953860	
3	0.0297	10242361	0.0886	14835653	
4	0.0297	10233831	0.1209	20495428	
5	0.0297	10570175	0.1477	27153647	

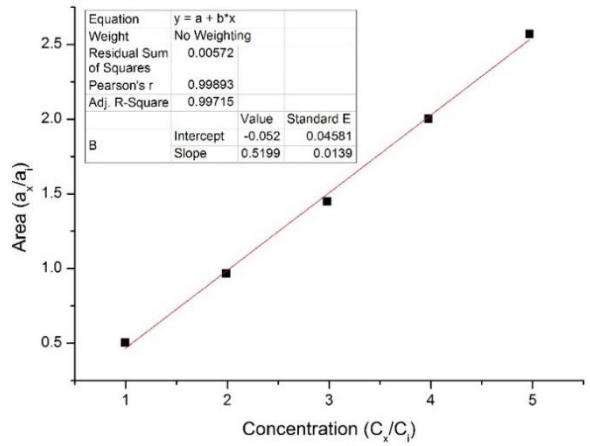
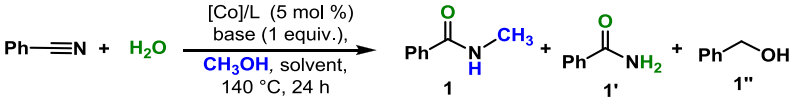


Figure S4. Determination of Response Factor for Benzyl Alcohol with respect to Mesitylene.

A representative Calculation of Yield from Response factor (R_f) as in Table S7, entry 2

After carefully analysing the GC-MS data as well as the ^{1}H-NMR spectra of the crude reaction mixture after the reaction is over, we found only four components such as PhCN, **1, 1′** and **1″**.



As shown above, from eqn. 1, we can write for an analyte **X**,

$c_x = (a_x/ R_{f(X)}) \times (c_i/ a_i)$

where, a_x and a_i are the area of the component **X** and internal standard respectively; c_x and c_i are the concentration of component **X** and internal standard respectively. $R_{f(x)}$ is the response factor of component **X**.

So, % GC yield of **1** = $\{(a_1/ R_{f1}) \times (c_i/ a_i)\} / [\{(a_{PhCN}/ R_{f\text{-}PhCN}) \times (c_i/ a_i)\} + \{(a_1/ R_{f1}) \times (c_i/ a_i)\} + \{(a_{1'} / R_{f1'}) \times (c_i/ a_i)\} + \{(a_{1''} / R_{f1''}) \times (c_i/ a_i)\}] \times 100$

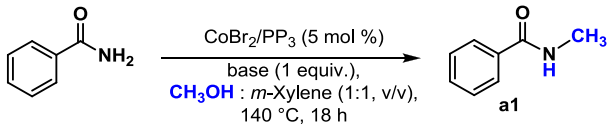
or, % GC yield of **1** = $(a_1/ R_{f1}) / [(a_{PhCN}/ R_{f\text{-}PhCN}) + (a_1/ R_{f1}) + (a_{1'} / R_{f1'}) + (a_{1''} / R_{f1''})] \times 100$

Table S5. Calculation of % GC Yield from Response factor (R_f) as in Table **S7**, entry **2**

Entry	**PhCN**	**1**	**1′**	**1″**
Response Factor ($R_{f(x)}$)	0.704	0.792	0.400	0.520
Area (a_x)	2158115	21330661	21108193	13492602
$a_x/R_{f(X)}$	3065505	26932653	52770482	25947312
Yield (%)	2.82	24.77	48.54	23.87

3. Optimization Details

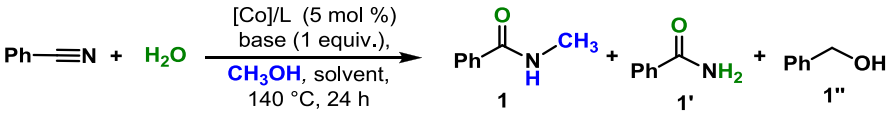
Table S6. Screening of Base for the N-Methylation of Benzamide[a]



Entry	Base (1 equiv.)	Conversion (%)	Yield (%)
1	NaOH	41	36
2	NaOMe	56	50
3	KO^{t}Bu	55	53
4	NaOAc	12	5
5	K_3PO_4	19	13
6	K_2CO_3	61	59
7	**Cs_2CO_3**	**85**	**85**

[a]Reaction conditions: benzamide (0.5 mmol), methanol/*m*-xylene (2.5 mL; 1:1, v/v), conversions and yields were determined by GC using mesitylene as internal standard (PP_3 = tris[2-(diphenylphosphino)ethyl]phosphine).

Table S7. Optimization Details for the Tandem Transformation of Nitrile to N-Methylated Amide[a]



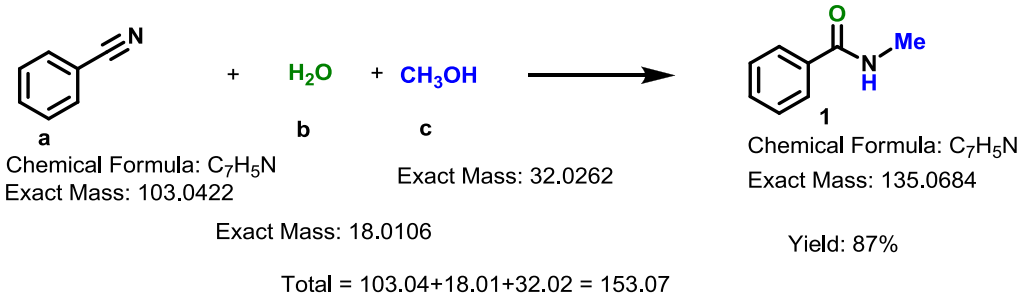
Entry	[co]	Ligand	Base		Additional Base (equiv.)	Yield (**1**) (%)	Yield (**1'**) (%)	Yield (**1''**) (%)
1	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH	-	16	59	23
2	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : Toluene (0.5:1)	-	25	48	24
3	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : Toluene (1:1)	-	36	40	21
4	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : Toluene (2:1)	-	29	46	22
5	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : Benzene (1:1)	-	33	41	22
6	**$CoBr_2$ (5)**	**PP_3 (5)**	**Cs_2CO_3**	**MeOH : *m*-Xylene (1:1)**	**-**	**43**	**30**	**27**
7	$CoBr_2$ (5)	DPPF (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	7	81	10
8	$CoBr_2$ (5)	Xantphos (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	2	84	14
9	$CoBr_2$ (5)	Triphos (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	7	78	12
10	$Co(BF_4)_2.6H_2O$(5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	39	37	21
11	$Co(OAc)_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	37	36	23
12	$Co(acac)_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	41	31	24
13	$CoBr_2$ (5)	PP_3 (5)	K_2CO_3	MeOH : *m*-Xylene (1:1)	-	28	57	13
14	$CoBr_2$ (5)	PP_3 (5)	KO^{t}Bu	MeOH : *m*-Xylene (1:1)	-	25	56	16
15	$CoBr_2$ (5)	PP_3 (5)	NaOH	MeOH : *m*-Xylene (1:1)	-	21	66	11
16[b]	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	-	37	35	24
17	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	NaOH (0.2)	44	29	23
18	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KOH (0.2)	53	28	19
19	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	$CsOH.H_2O$ (0.2)	58	23	18
20	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	LiO^{t}Bu (0.2)	44	47	7
21	$CoBr_2$ (5)	PP_3 (5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (0.2)	68	22	7
22	**$CoBr_2$ (5)**	**PP_3 (5)**	**Cs_2CO_3**	**MeOH : *m*-Xylene (1:1)**	**KO^{t}Bu (0.5)**	**69**	**30**	**0**
23	**$CoBr_2$ (7.5)**	**PP_3 (7.5)**	**Cs_2CO_3**	**MeOH : *m*-Xylene (1:1)**	**KO^{t}Bu (0.5)**	**96**	**2**	**0**
24	$CoBr_2$ (7.5)	PP_3 (7.5)	-	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (1.5)	54	43	0
25	$CoBr_2$ (7.5)	PP_3 (7.5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	Cs_2CO_3 (1.5)	66	5	24
26[c]	$CoBr_2$ (7.5)	PP_3 (7.5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (0.5)	67	5	26
27[d]	$CoBr_2$ (7.5)	PP_3 (7.5)	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (0.5)	85	14	0
28[e]	-	-	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (0.5)	97	2	0
29[f]	-	-	Cs_2CO_3	MeOH : *m*-Xylene (1:1)	KO^{t}Bu (0.5)	N. D.	12	N. D.

[a]Reaction conditions: benzonitrile (0.5 mmol), methanol/*m*-xylene (2.5 mL, 1:1 v/v), water (10 equiv.), GC yield. [b]0.75 equiv. Cs_2CO_3. [c]5 equiv. H_2O. [d]15 equiv. H_2O. [e]With isolated metal complex. [f]3 h (ND = not detected). All the yields were calculated by using mesitylene as internal standard and the numbers were round up to nearest integer.

4. Preparative Scale Reaction for the Determination of Green Chemistry Metrics

An oven dried 30 mL screw cap tube was taken inside the argon filled glove box and charged with a magnetic stir-bar, benzonitrile (10.0 mmol), $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (**PP_3**) ligand (7.5 mol %), Cs_2CO_3 (10.0 mmol), KO^{t}Bu (5.0 mmol) and water (100.0 mmol) followed by the addition of methanol/*m*-xylene (15.0 mL, 1:1 v/v). Then, the tube was sealed and placed in a preheated oil bath at 140 °C (oil bath temperature) for 24 h. After completion of the reaction, the tube was allowed to cool at room temperature. The reaction mixture was used for the determination of green chemistry metrics[2] and the details as mentioned in the Table **S8**.

Table S8. Evaluation of Green Chemistry Metrics



Reactant **a**	Benzonitrile	1.0 g	FW 103.04
Reactant **b**	Water	1.75 g	FW 18.01
Reactant **c**	Methanol	5.94 g	FW 32.02
Base	Cs_2CO_3 + ^{t}BuOK	3.16 g + 0.54 g = 3.7 g	FW 325.82, 112.21
Solvent	*m*-Xylene	6.45 g	FW 106.16
Recycle solvent	-	11.4 g	-
Auxiliary	-	-	-
Product	N-Methylbenzamide	1.14 g	FW 135.06

- ✓ **E factor** = [{(1 g + 1.75 g + 5.94 g + 3.7 g + 6.45 g) - (11.4 g + 1.14 g)}/1.14 g] = [(18.84 g -12.54 g)/1.14 g] = 6.3 g/1.14 g = **5.52 kg waste/1 kg product**
- ✓ **Atom economy** = (135.06/135.06) x 100 = **100%**
- ✓ **Atom efficiency** = 87 x (100/100) = **87%**
- ✓ **Carbon efficiency** = (8/8) x 100 = **100%**
- ✓ **Reaction mass efficiency** = [1.14 g / (1 g + 0.31 g)] x 100 = **87%**

5. Labelling Experiments

A. Using H_2O^{18}

Inside a argon filled glove box, an oven dried 2.5 mL screw cap tube was taken and charged with benzonitrile (0.2 mmol), $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (**PP_3**) ligand (7.5 mol %), Cs_2CO_3 (0.2 mmol), KO^{t}Bu (0.1 mmol) and H_2O^{18} (2.0 mmol) followed by the addition of methanol/*m*-xylene (0.5 mL, 1:1 v/v). Then, the tube was sealed and placed in a preheated oil bath at 140 °C (oil bath temperature) for 3-24 h. The conversion and yield of the reactions were determined by GC analysis using mesitylene as internal standard. The products were confirmed through the ESI-MS analysis.

B. Using Methanol-D_4

i) Parallal Reaction

Inside a argon filled glove box an oven dried 2.5 mL screw cap tube was taken and charged with benzonitrile or benzamide or N-(hydroxymethyl)benzamide (0.2 mmol), $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (**PP_3**) ligand (7.5 mol %), Cs_2CO_3 (0.2 mmol), KO^{t}Bu (0.1 mmol) and H_2O (2.0 mmol) followed by the addition of methanol-d_4/*m*-xylene (0.5 mL, 1:1 v/v). Then, the tube was sealed and placed in a preheated oil bath at 140 °C (oil bath temperature) for 30-40 h. The conversion of the reactions were determined by GC analysis using mesitylene as internal standard. The products were confirmed through ESI-MS analysis.

ii) Competitive Reaction

Inside a argon filled glove box an oven dried 2.5 mL screw cap tube was taken and charged with a magnetic stir-bar, benzonitrile (0.2 mmol), $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (**PP_3**) ligand (7.5 mol %), Cs_2CO_3 (0.2 mmol), KO^{t}Bu (0.1 mmol) and H_2O (2.0 mmol) followed by the addition of methanol, methanol-d_4 and *m*-xylene (0.5 mL, 1:1:2 v/v). Then, the tube was sealed and placed in a preheated oil bath at 140 °C (oil bath temperature) for 36 h. The conversion of the reactions were determined by GC analysis using mesitylene as internal standard. The products were confirmed by ^{1}H NMR and ESI-MS analysis (see Figure **S5** and **S6**).

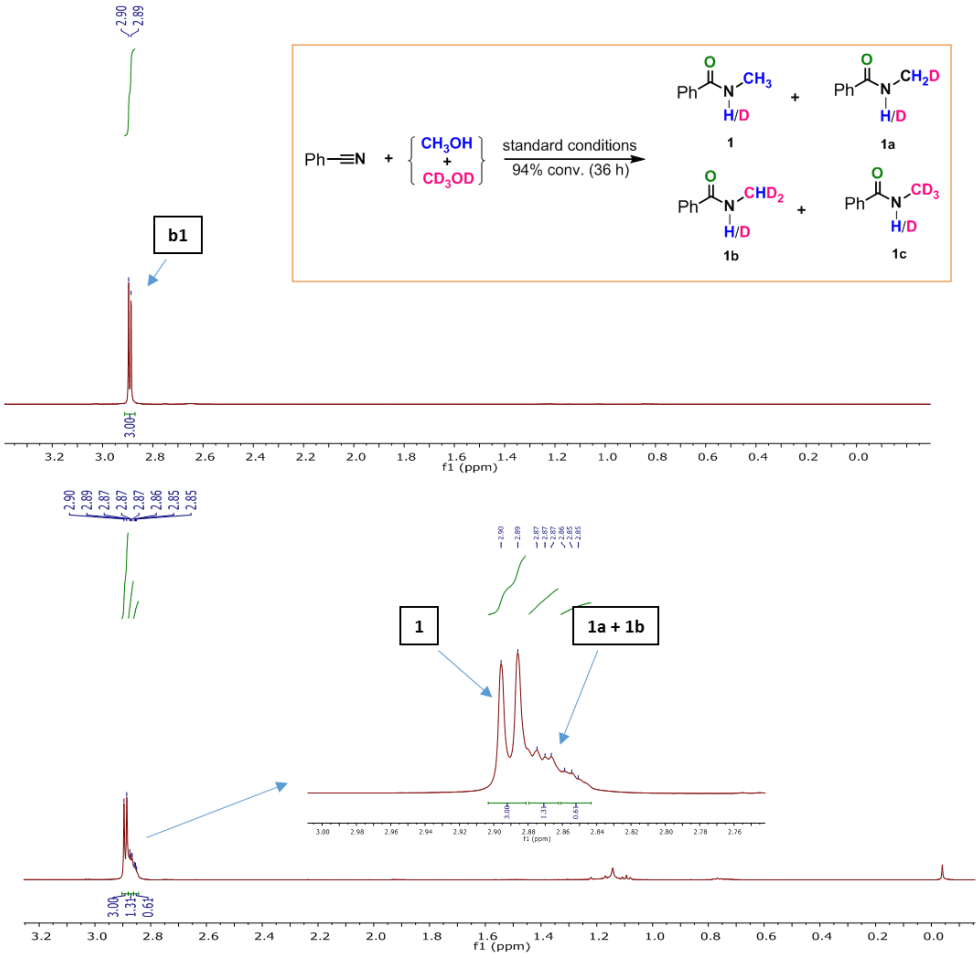


Figure S5. Partial NMR spectra of the methylated products generated from the competitive reaction.

C. ESI-MS Analysis of the Selected Compounds Generated from Labelling Experiments

1: ESI-MS calculated for C_8H_9NO; 136.0762 $(M+H)^+$, found: 136.0775. **1a**: ESI-MS calculated for C_8H_8DNO; 137.0825 $(M+H)^+$, found: 137.0835. **1b**: ESI-MS calculated for $C_8H_7D_2NO$; 138.0888 $(M+H)^+$, found: 138.0898. **1c**: ESI-MS calculated for $C_8H_6D_3NO$; 139.0951 $(M+H)^+$, found: 139.0959. **1d** ESI-MS calculated for $C_7H_7N^{18}O$; 124.0648 $(M+H)^+$, found: 124.0673. **1e**: ESI-MS calculated for $C_8H_9N^{18}O$; 138.0805 $(M+H)^+$, found: 138.0830.

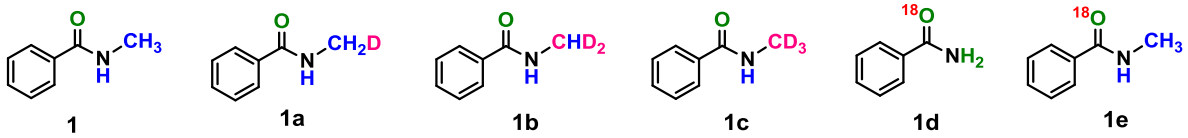


Figure S6. Structure of the selected compounds generated from labelling experiments.

6. Procedure for the Control Experiment with *in-situ* Generated [Co^I-H]

Inside a argon filled globe box an oven dried 4 mL screw cap tube was charged with a magnatic stir-bar, $CoBr_2$ (7.5 mol %), tris[2-(diphenylphosphino)ethyl]phosphine (**PP_3**) ligand (7.5 mol %) followed by the addition of 1.0 mL methanol. The reaction mixture was allowed to stir at room temperature for 0.5 h. To this reaction mixture, $NaBH_4$ (3.0 equiv.) was added and the reaction mixture was allowed to stir for another 1.5 h. After that, benzonitrile (0.4 mmol), Cs_2CO_3 (0.4 mmol), KO^tBu (0.2 mmol), H_2O (4.0 mmol) and *m*-xylene (1.0 mL) were added to the resultant solution. Then, the tube was sealed and placed in a preheated oil bath at 140 °C (oil bath temperature) for 24 h. The conversion and yield of the reactions were determined by GC analysis using mesitylene as internal standard.

7. Time Dependent Experiment

Several experiments for the direct synthesis of N-methylated amide from benzonitrile were conducted following the outlined procedure with varying time. An oven dried screw cap tube was charged with benzonitrile (0.4 mmol), $CoBr_2$ (7.5 mol %), PP_3 (7.5 mol %), Cs_2CO_3 (0.4 mmol), KO^tBu (0.2 mmol), H_2O (4.0 mmol) followed by the addition of methanol/*m*-xylene (2.0 mL, 1:1, v/v) and mesitylene as internal standard. All the tubes were placed in a preheated oil–baths at 140 °C with stirring and the progress of the reaction was analysed by GC. The progress of the reaction was monitored by gas chromatography using mesitylene as internal standard. All the reactions were repeated twice and the average data were plotted as conversion (%) vs time (min).

8. Determination of Reaction Order

Two identical experiments were carried out following the general procedure varying only the amount of benzonitrile. After completion of the reaction, the tube was allowed to cool at room temperature and the mixture was filtered through a small plug of silica gel and directly subjected for GC analysis using mesitylene as internal standard to determine conversion of benzonitrile and the yield of the N-methyl benzamide. Accordingly, the concentration of substrate and the final product were calculated at different time. All the reactions were repeated twice and the average data were plotted as substrate cons. vs time (min) or product cons. vs time (min) in the Figure **S7** and **S8** respectively. Then, the initial rate for the different run was calculated to determine the order with respect to nitrile.

In this transformation, we performed kinetic experiments to determine the order during the nitrile hydration and the N-methylated amide formation process as mentioned bellow.

Table S9. Experimental Details.

Run	Benzonitrile	Cs_2CO_3	KO^tBu	$CoBr_2/PP_3$	H_2O	Methanol/*m*-Xylene (1:1, v/v)
Run 1	**0.2 mmol**	0.2 mmol	0.1 mmol	3.28 mg + 10.1 mg	36 µL	1.0 mL
Run 2	**0.4 mmol**	0.2 mmol	0.1 mmol	3.28 mg + 10.1 mg	36 µL	1.0 mL

A. Determination of Order for the Nitrile Hydration

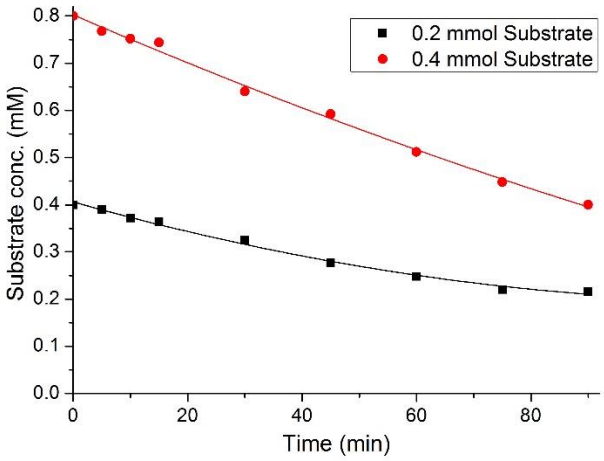


Figure S7. Determination of initial slopes for the benzonitrile hydration.

Initial slope for run 1 at 20 min = 17.88×10^{-3} (mM)/min

Initial slope for run 2 at 20 min = 34.96×10^{-3} (mM)/min

Simplified rate equation for this system (r)= $k[\text{Benzonitrile}]^a[Cs_2CO_3]^b[^t\text{BuOK}]^c[\text{Catalyst}]^d[H_2O]^e\ [\text{Methanol}]^f[m\text{-xylene}]^g$

(all terms have their usual significance)

Now for run 1, $r_1 = 17.88 \times 10^{-3}$ (mM)/min = $k[0.2]^a[Cs_2CO_3]^b[^t\text{BuOK}]^c[\text{Catalyst}]^d[H_2O]^e[\text{Methanol}]^f[m\text{-xylene}]^g$ …… (1)

and run 2, $r_2 = 34.96 \times 10^{-3}$ (mM)/min = $k[0.4]^a[Cs_2CO_3]^b[^t\text{BuOK}]^c[\text{Catalyst}]^d[H_2O]^e[\text{Methanol}]^f[m\text{-xylene}]^g$ ……..(2)

Comparing the initial rate,

$r_1/r_2 = 17.88/34.96 = (0.2/0.4)^a$

or, $0.51 = 0.5^a$; or, log 0.51 = a log 0.5; or, a = log 0.51/ log 0.5

or, a = -0.29/-0.30 = 0.97 ~ 1

so, **Rate = k [benzonitrile]^1**

B. Determination of Order for the Tandem Conversion of Nitrile to the N-Methylated Amide

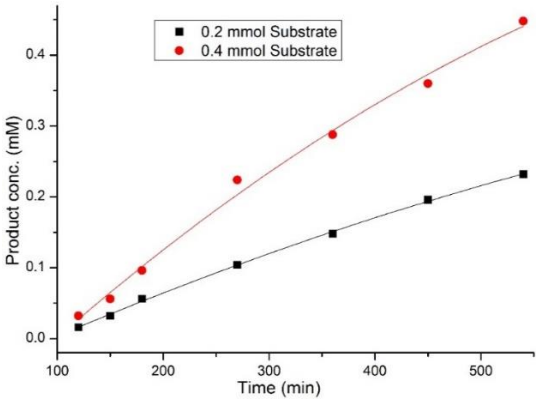


Figure S8. Determination of initial slopes for the tandem transformation of benzonitrile to N-methylbenzamide.

Initial slope for run 1 at 4 h = 3.64×10^{-4} (mM)/min

Initial slope for run 2 at 4 h = 7.16×10^{-4} (mM)/min

Simplified rate equation for this system (r)= k[Benzonitrile]^a[Cs_2CO_3]^b[^{t}BuOK]^c[Catalyst]^d[H_2O]^e [Methanol]^f[*m*-xylene]^g

(all terms have their usual significance)

Now for run 1, $r_1 = 3.64 \times 10^{-4}$ (mM)/min = k[0.2]^a[Cs_2CO_3]^b[^{t}BuOK]^c[Catalyst]^d[H_2O]^e [Methanol]^f[*m*-xylene]^g …… (1)

and run 2, $r_2 = 7.16 \times 10^{-4}$ (mM)/min = k[0.4]^a[Cs_2CO_3]^b[^{t}BuOK]^c[Catalyst]^d[H_2O]^e [Methanol]^f[*m*-xylene]^g ……..(2)

Comparing the initial rate,

$r_1/r_2 = 3.64/7.16 = (0.2/0.4)^a$

or, $0.508 = 0.5^a$; or, log 0.508 = a log 0.5; or, a = log 0.508/ log 0.5

or, a = -0.29/-0.30 = 0.97 ~ 1

so, **Rate = k [benzonitrile]^1**

These experiments stated that nitrile hydration as well as the sequential hydration-methylation process follow a first order kinetics with respect to the nitrile concentration.

9. Kinetic Isotope Effect (KIE) Studies

Parallel reactions for the synthesis of N-methylbenzamide from benzonitrile were carried out using CH_3OH/*m*-xylene (1:1, v/v) and CD_3OD/*m*-xylene (1:1, v/v) under identical conditions following the outlined procedure. All the tubes were placed in a preheated oil–baths at 140 °C with stirring and the progress of the reaction was analysed by GC using mesitylene as internal standard. All the reactions were repeated twice and the average data were plotted as ln(a/a-x) vs time (min) (Figure **S9**).

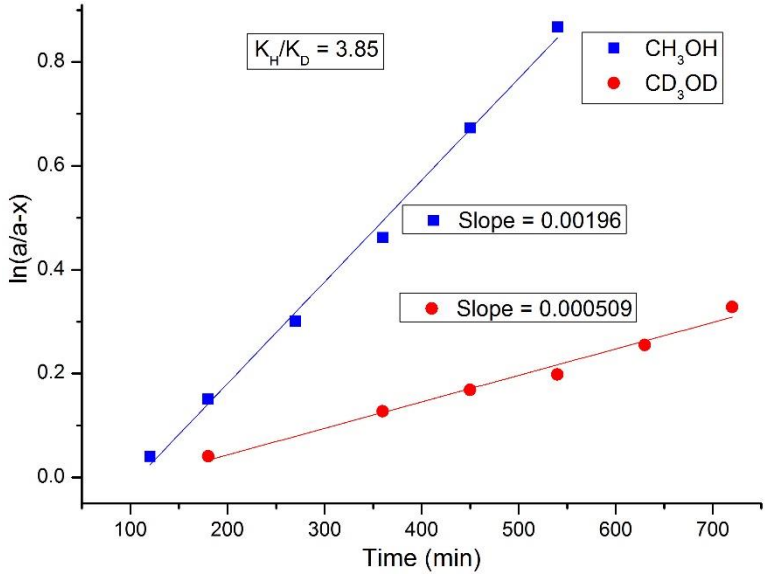
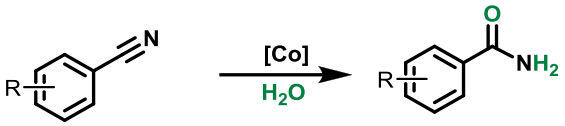


Figure S9. Kinetic isotopic effect analysis during the methylation process using methanol.

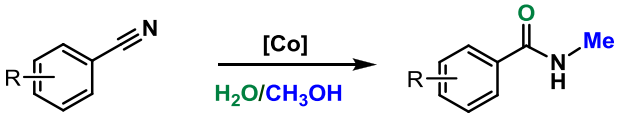
10. Hammett Studies

An oven dried screw cap tube was charged with several electronically disparate benzonitriles (0.4 mmol), $CoBr_2$ (7.5 mol %), PP_3 (7.5 mol %), Cs_2CO_3 (0.4 mmol), KO^tBu (0.2 mmol), H_2O (4.0 mmol) followed by the addition of methanol/*m*-xylene (2 mL; 1:1, v/v). All the tubes were placed in a preheated oil–baths at 140 °C with stirring. The progress of the reaction was analysed by GC using mesitylene as internal standard. Reactivity towards the nitrile hydration and reductive N-methylation of amide from nitrile follows the sequence: *p*-CF_3 >*p*-Cl>*p*-H >*p*-Me >*p*-OMe (Figure **2e** and **2f** (see manuscript); Figure **S10, S11** and **S12**; Table **S10** and **S11**).

Table S10. Hammett Analysis with the Para Substitution Constant (σ_P)

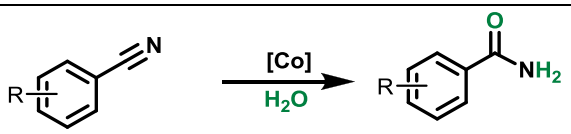


Substrate	k x 10^{-4} (min^{-1})	K_X/k_H	$Log(K_X/k_H)$	σ_P	ρ
4-Methoxy benzonitrile	44.6	0.4775	-0.3207	-0.268	
4-Methyl benzonitrile	55.7	0.5963	-0.2245	-0.170	
Benzonitrile	93.4	1	0	0	**+1.85**
4-Chloro benzonitrile	336.1	3.598	0.556	0.227	
4-Trifluoromethyl benzonitrile	1233.3	13.2	1.1205	0.54	

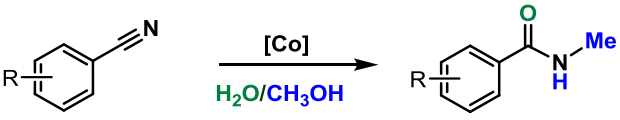


4-Methoxy benzonitrile	10.1	0.5153	-0.2879	-0.268	
4-Methyl benzonitrile	12.1	0.6173	-0.2095	-0.170	
Benzonitrile	19.6	1	0	0	**+1.06**
4-Chloro benzonitrile	33.2	1.6938	0.2288	0.227	
4-Trifluoromethyl benzonitrile	71.6	3.6530	0.5626	0.54	

Table S11. Hammett Analysis with the Substitution Constant σ-.



Substrate	k x 10^{-4} (min^{-1})	K_X/k_H	$Log(K_X/k_H)$	σ-	ρ
4-Methoxy benzonitrile	44.6	0.4775	-0.3207	-0.26	
4-Methyl benzonitrile	55.7	0.5963	-0.2245	-0.17	
Benzonitrile	93.4	1	0	0	**+1.65**
4-Chloro benzonitrile	336.1	3.598	0.556	0.19	
4-Trifluoromethyl benzonitrile	1233.3	13.2	1.1205	0.65	



4-Methoxy benzonitrile	10.1	0.5153	-0.2879	-0.26	
4-Methyl benzonitrile	12.1	0.6173	-0.2095	-0.17	
Benzonitrile	19.6	1	0	0	**+0.95**
4-Chloro benzonitrile	33.2	1.6938	0.2288	0.19	
4-Trifluoromethyl benzonitrile	71.6	3.6530	0.5626	0.65	

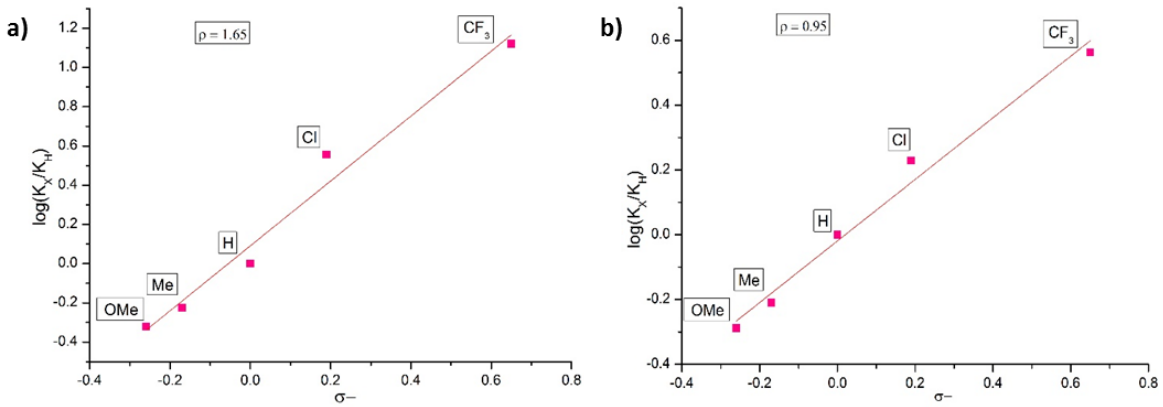


Figure S10. Hammett analysis using substitution constant σ- for a) nitrile hydration; b) N-methylated amide formation from nitrile using methanol.

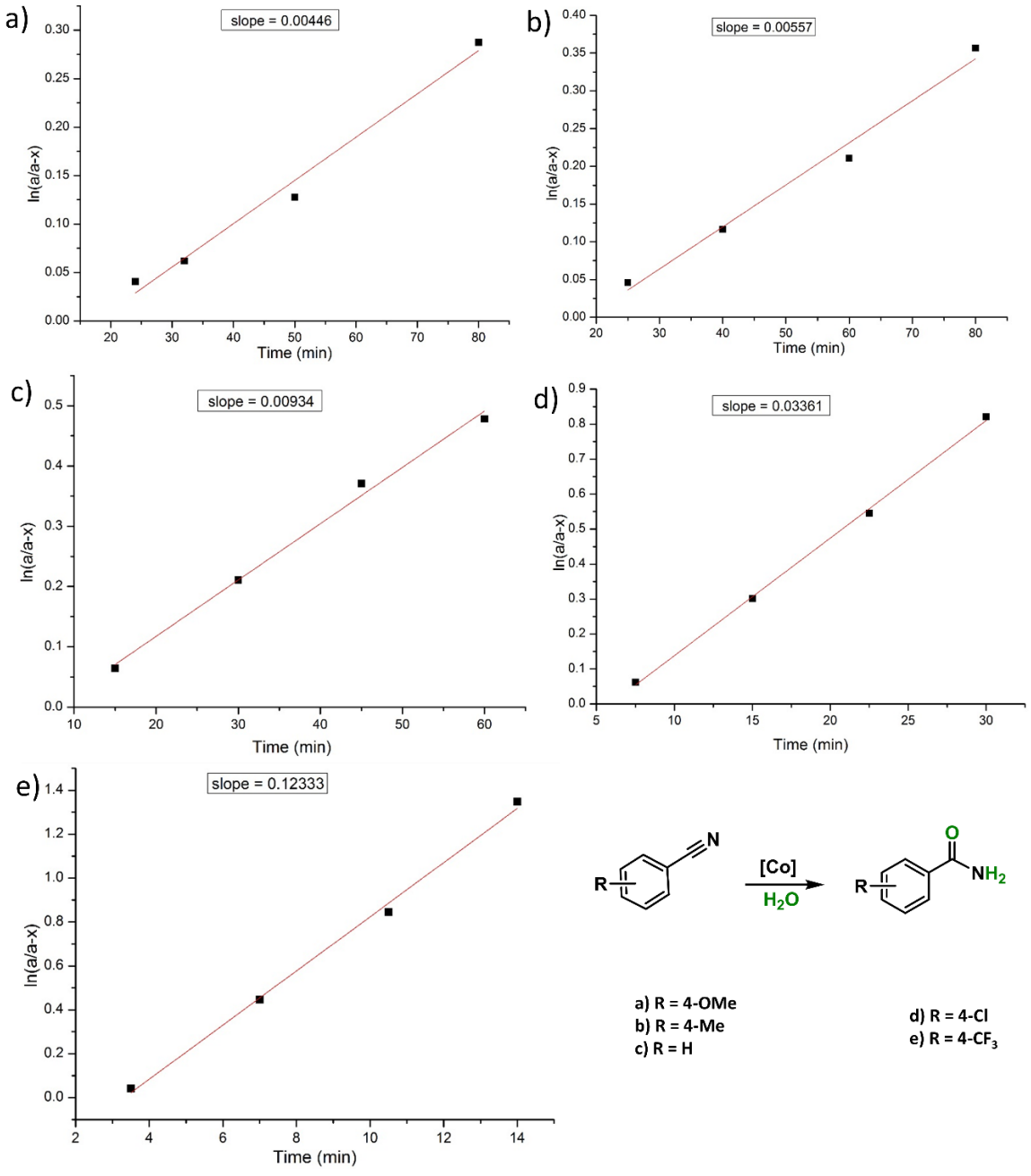


Figure S11. Determination of rate constant for the electronically disparate nitriles during the hydration process.

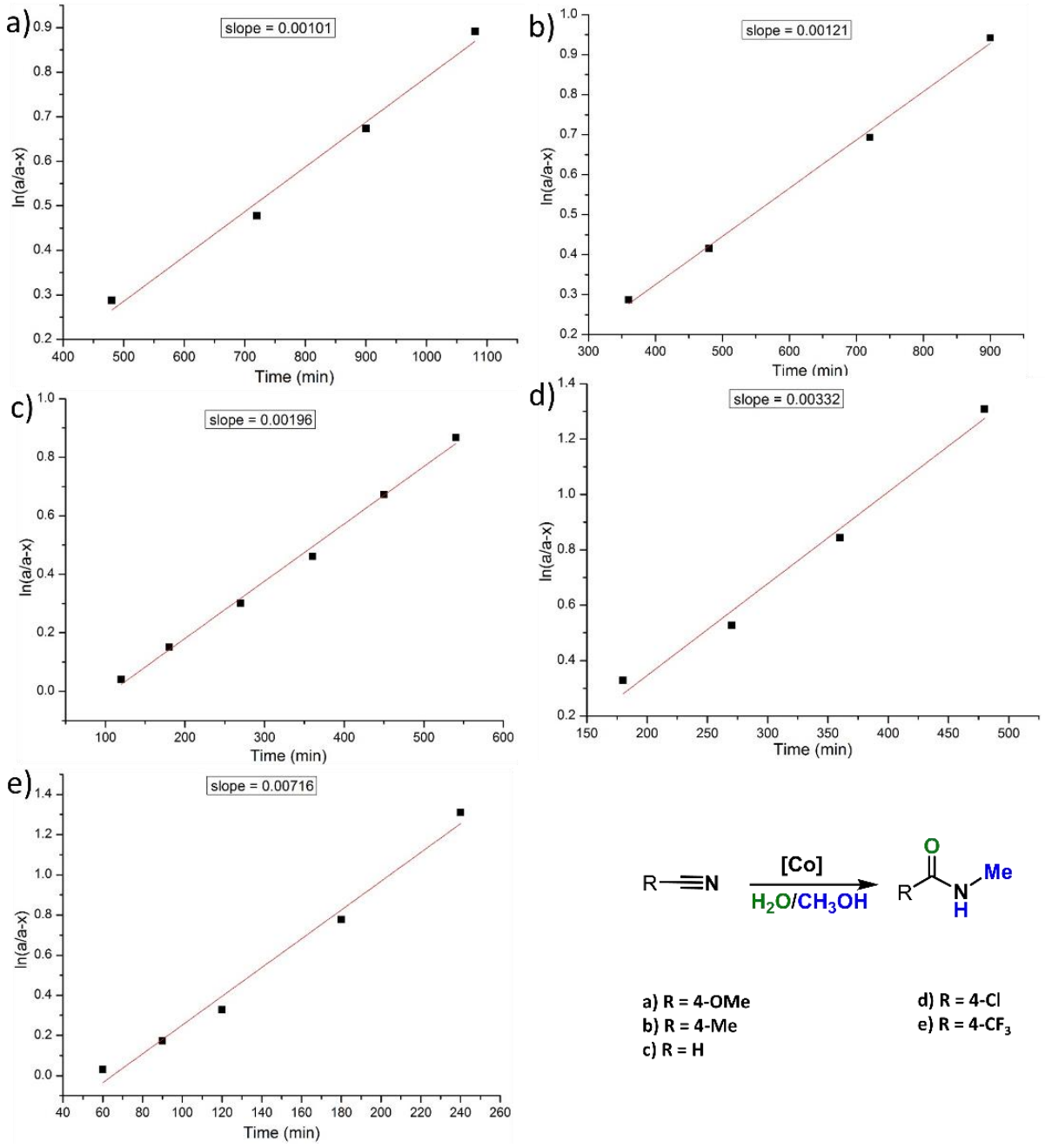


Figure S12. Determination of rate constant for the electronically disparate nitriles during the N-methylation process.

11. Temperature Dependent Kinetic Studies

Several experiments for the direct synthesis of N-methylated amide from benzonitrile were conducted following the outlined procedure with varying time at different temperature

(such as 120 °C, 130 °C, 140 °C, 150 °C and 160 °C). The progress of the reaction was monitored by gas chromatography using mesitylene as internal standard. All the reactions were repeated twice and the average data were plotted as ln(a/a-x) vs time (min) (Figure **S13**).

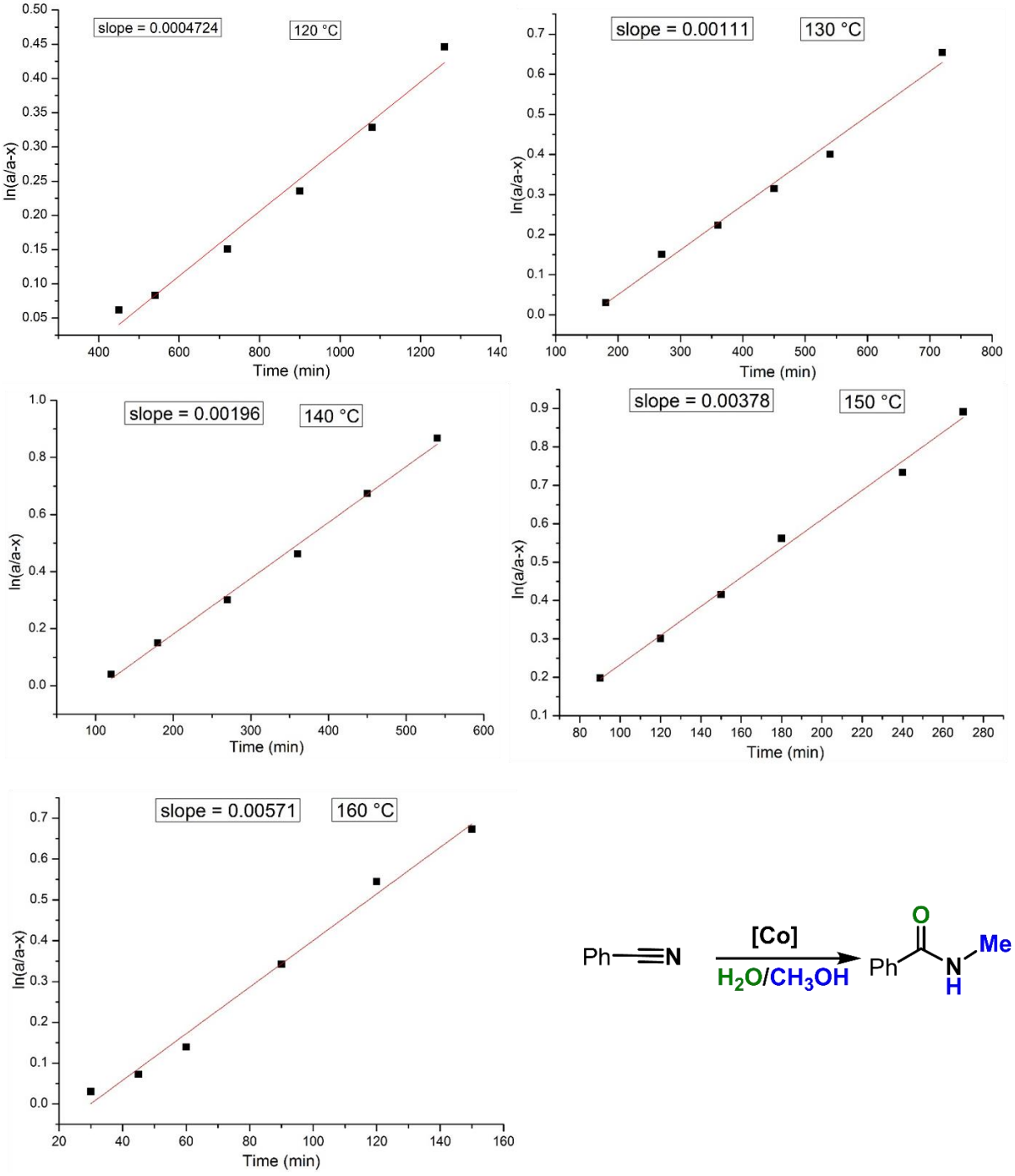


Figure S13. Determination of the rate constant at different temperature.

12. Synthesis of Co (II) Complexes

Synthesis of [CoBr(PP$_3$)]Br (1): In a Schlenk flask tris[2-(diphenylphosphino)ethyl]phosphine (0.2 g; 0.298 mmol), $CoBr_2$ (0.065.g; 0.298 mmol) and 10 mL dry methanol were taken and the mixture was allowed to stirr at room temperature for 3 hour. The solvent was evaporated in vacuum, washed with dry diethyl ether and hexane, finally dried under vacuum to provide the title paramagnatic cobalt (II) compound as a dark purple powder. Yield: 228 mg (86%). **ESI-MS**: Calculated for $C_{42}H_{42}Br_2CoP_4$; 808.0752 $(M-Br)^+$, found: 808.0795. **Anal. Calculated** ($C_{42}H_{42}Br_2P_4Co$) (**Found**): C, 56.72 (56.63); H, 4.76 (4.69). Attempt to get the suitable single crystal was unsuccessful. To get the single crystal the counter anion (bromide) of the complex **1** was exchanged with the larger anion tetraphenylborate.

Synthesis of [CoBr(PP$_3$)]BPh$_4$ (1a): In a Schlenk flask complex **1** (150 mg, 0.168 mmol) was taken in 10 mL dry methanol and sodium tetraphenylborate (86.6 mg, 0.252 mmol) was added to it. Now, the mixture was allowed to stirr at room temperature for 1.5 hour during which a dark red precipitate was emerged. The precipitate was filtered, washed with dry diethyl ether and dried under vacuum to provide the title paramagnatic cobalt (II) compound as a dark-red powder. Yield: 154.2 mg (81%). **ESI-MS**: Calculated for $C_{66}H_{62}BBrP_4Co$; 808.0752 $(M-BPh_4)^+$, found: 808.0797. **Anal. Calculated** ($C_{66}H_{62}BBrP_4Co$) (**Found**): C, 70.23 (70.08); H, 5.54 (5.41). Single crystal was obtained by the slow diffusion of benzene and THF into dichloromethane solution of complex **1a.** For the details, see 'X-Ray Crystallographic Studies' section.

13. X-Ray Crystallographic Studies

Single-crystal X-ray data of the complex **1a** was collected by using a Bruker SMART APEX II CCD diffractometer and Bruker D8 Quest Single Crystal diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å). All these data were collected at 100 K temperature. The frames were indexed, integrated and scaled using SMART and SAINT software package[3] and the data were corrected for absorption using the SADABS program.[4] The structures were solved and refined using WINGX and SHELX programs.[3, 5] The crystallographic figures have been generated using Diamond 3 software 10 (30% probability thermal ellipsoids).[6] (Figure **S14**). In the crystal, one THF molecule was found as highly disorder, hence could not be located. So, 'solvent mask' command of OLEX-2 had been

performed to remove those peaks. The CCDC number of the complexes **1a** is CCDC 1880437 (Table **S12**).

Table S12. Crystal Data and Structure Refinement for Complex **1a**

Identification code	Complex **1a**
Empirical formula	$C_{148}H_{144}B_2Br_2Co_2OP_8$
Formula weight	2485.68
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	22.5631(8)
b/Å	32.8804(10)
c/Å	18.0742(6)
α/°	90
β/°	102.2190(10)
γ/°	90
Volume/Å^3	13105.2(8)
Z	4
ρ_{calc}g/cm^3	1.260
μ/mm^{-1}	1.011
F(000)	5176.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.448 to 50.998
Index ranges	-27 ≤ h ≤ 27, -39 ≤ k ≤ 39, -21 ≤ l ≤ 21
Reflections collected	170663
Independent reflections	24375 [R_{int} = 0.0652, R_{sigma} = 0.0405]
Data/restraints/parameters	24375/0/1468
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0919
Final R indexes [all data]	R_1 = 0.0544, wR_2 = 0.1022
Largest diff. peak/hole / e Å^{-3}	1.24/-0.66

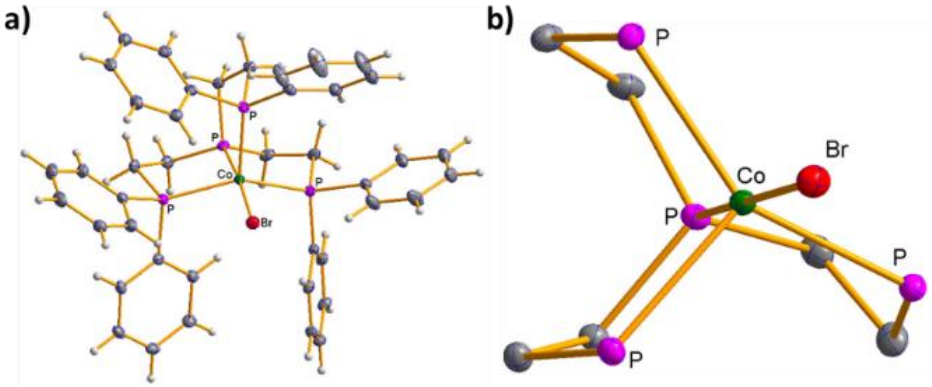


Figure S14. a) Solid state structure of the isolated cobalt complex. **b**) Geometry around the cobalt centre; counter anion was removed.

14. Computational Studies

All the calculations were performed using the Gaussian 09 package.[7] Full geometry optimization followed by frequency calculations on the stationary points were carried out to ascertain the nature of the stationary points as minima or first order saddle point. Hybrid functional, M06-2X was used with the LANL2DZ basis set[8] for Co and 6-31G** basis set[9] for non-metal elements. The transition states (TS) were further confirmed by performing intrinsic reaction coordinate (IRC) calculation using same method. As the mixture of solvents (methanol/*m*-xylene; 1:1, v/v) was used in this transformation, the effect of solvent during the calculation was not incorporated in the manuscript. The calculated resultant dielectric constant for the mixture of methanol/*m*-xylene (1:1, v/v) was closer to isopropanol. Hence, indirectly solvent effect was incorporated using the conductor-like polarizable continuum model (CPCM) with isopropanol, as shown in Figure **S15** and **S16**.[10]

Notes. *Before moving to the DFT calculations, we performed the kinetic experiment to check the involvement of the singlet or triplet species. This suggested that cobalt (I) hydride is the active species in this transformation and this species showed diamagnetic behavior in the NMR spectrum. In addition, diamagnetic NMR signal of similar cobalt (I) hydride species as well as the DFT calculation demonstrated by Shubina et al.[11] also supported our experimental observation. Additionally, as phosphine is a strong field ligand this also favour the low-spin singlet state. Therefore, based on our experimental observation and literature report, in the DFT calculation, we considered the energy of the singlet state.*

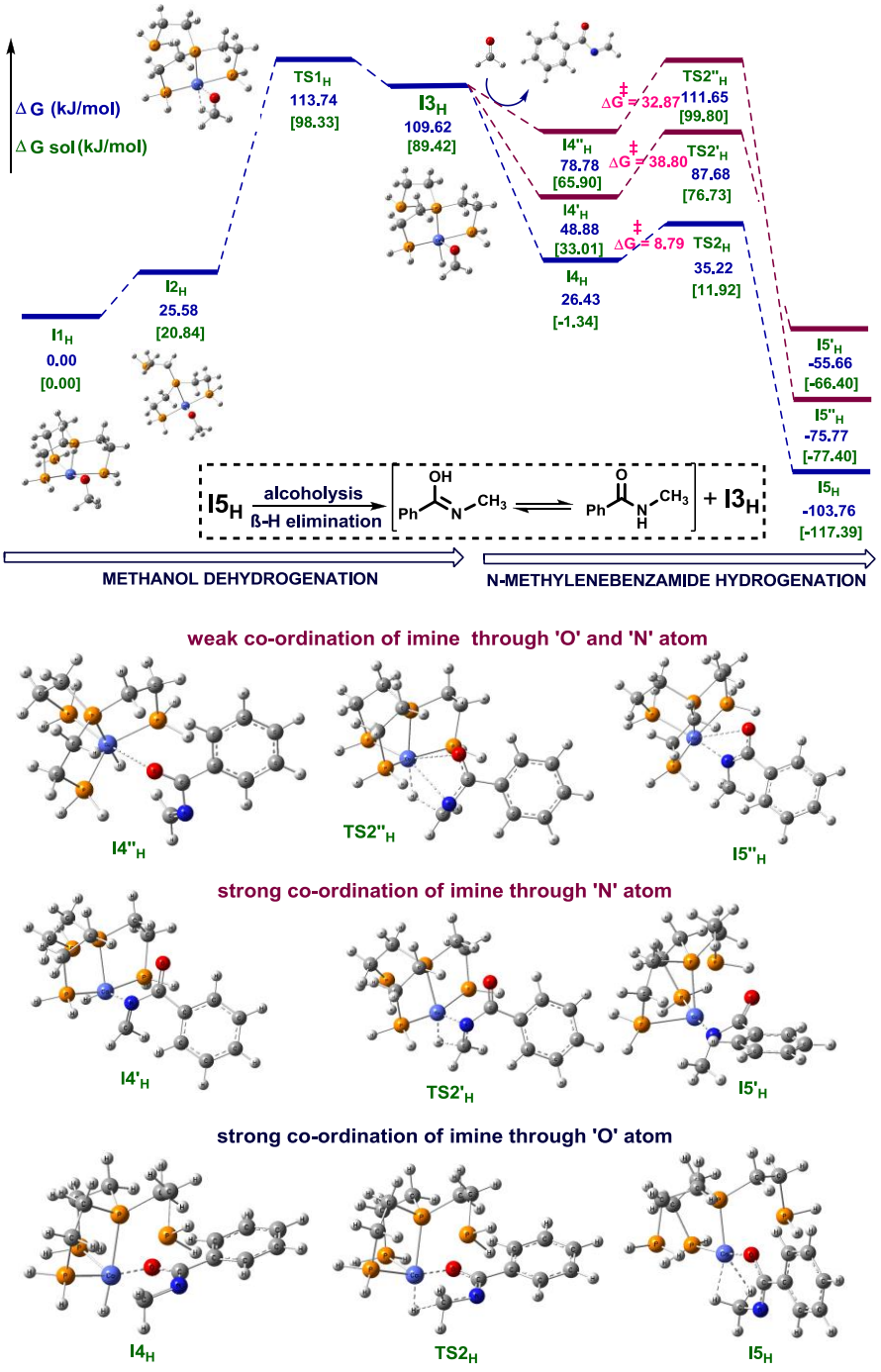


Figure S15. Computed pathway by incorporating solvent correction in the methylation process.

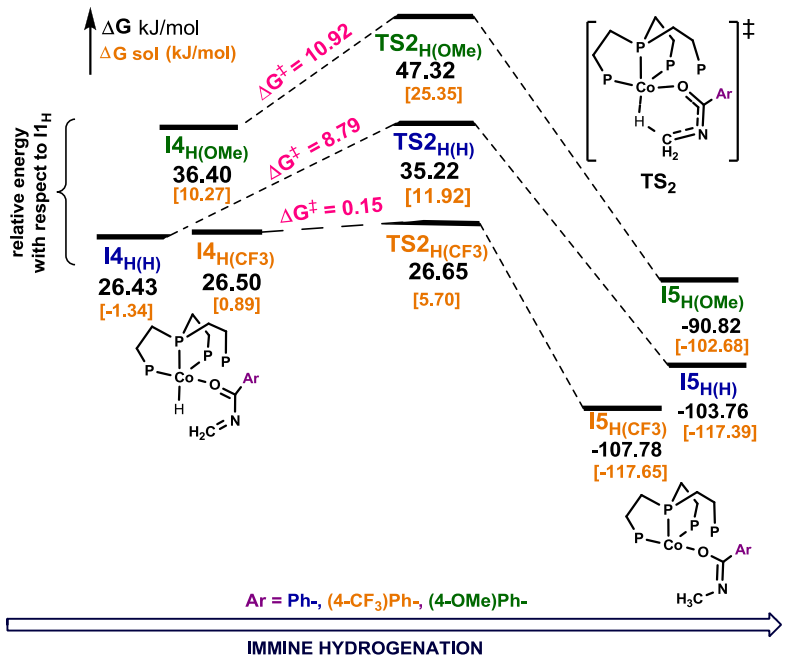
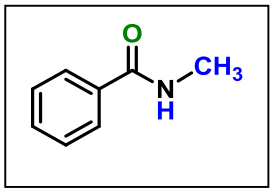
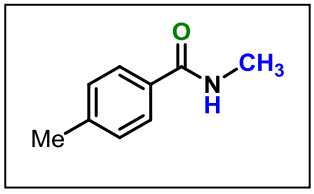


Figure S16. Computed pathway for the electronic effect during the imine hydrogenation by incorporating solvent correction.

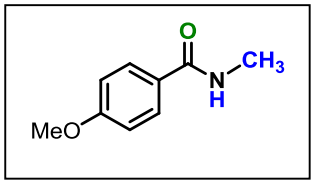
15. Spectral Data for the N-Methylated Amides



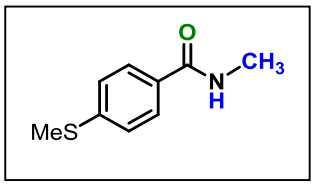
N-Methylbenzamide (1):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.76-7.73 (m, 2H), 7.48-7.45 (m, 1H), 7.41-7.37 (m, 2H), 6.35 (brs, 1H), 2.98 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.36, 134.66, 131.39, 128.59, 126.90, 26.90. **GC-MS** (M^+) = 135.1.



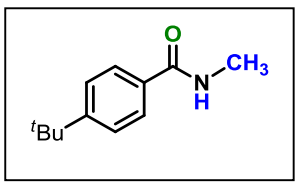
N,4-Dimethylbenzamide (2):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.65 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.16 (d, $J_{H,H}$ = 8 Hz, 2H), 6.56 (brs, 1H), 2.94 (d, $J_{H,H}$ = 4.8 Hz, 3H) 2.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.29, 141.61, 131.74, 129.13, 126.91, 26.77, 21.40. **GC-MS** (M^+) = 149.1.



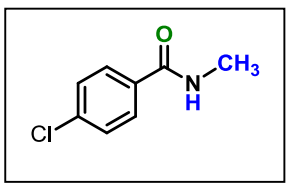
4-Methoxy-N-methylbenzamide (3):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71 (d, $J_{H,H}$ = 8.8 Hz, 2H), 6.90 (d, $J_{H,H}$ = 8.9 Hz, 2H), 6.13 (brs, 1H), 3.83 (s, 3H), 2.98 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.86, 162.13, 128.67, 126.99, 113.80, 55.46, 26.87. **GC-MS** (M^+) = 165.1.



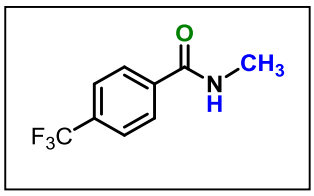
N-Methyl-4-(methylthio)benzamide (4):[13] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.66 (d, $J_{H,H}$ = 8.5 Hz, 2H), 7.24 (d, $J_{H,H}$ = 8.6 Hz, 2H), 6.09 (brs, 1H), 2.99 (d, $J_{H,H}$ = 4.8 Hz, 3H), 2.49 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 167.74, 143.33, 130.86, 127.31, 125.57, 26.91, 15.16. **GC-MS** (M^+) = 181.1.



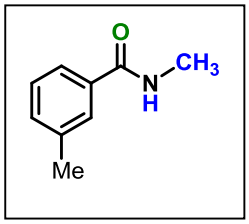
4-Tert-butyl-N-methylbenzamide (5):[12] **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.69 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.42 (d, $J_{H,H}$ = 8.2 Hz, 2H), 6.20 (brs, 1H), 2.99 (d, $J_{H,H}$ = 4.8 Hz, 3H), 1.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ = 168.28, 154.88, 131.84, 126.73, 125.55, 34.97, 31.24, 26.86. **GC-MS** (M^+) = 191.1.



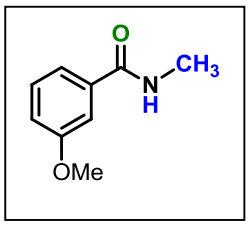
4-Chloro-N-methylbenzamide (6):[14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.71-7.68 (m, 2H), 7.39-7.36 (m, 2H), 6.34 (brs, 1H), 2.98 (d, $J_{H,H}$ = 4.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.28, 137.63, 133.04, 128.85, 128.39, 26.97. **GC-MS** (M^+) = 169.1.



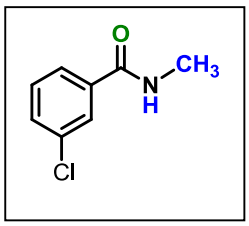
N-Methyl-4-(trifluoromethyl)benzamide (7):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.84 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.55 (d, $J_{H,H}$ = 8.2 Hz, 2H), 7.41 (brs, 1H), 2.87 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.83, 137.92, 132.69, 132.36, 127.52, 125.16 (J = 4 Hz), 122.27, 26.68. **GC-MS** (M^+) = 203.1.



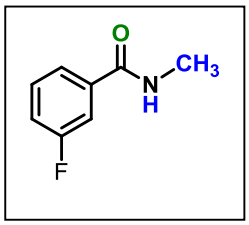
N,3-Dimethylbenzamide (8):[15] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.57 (s, 1H), 7.51 (td, $J_{H,H}$ = 4.4, 1.6 Hz, 1H), 7.26 (d, $J_{H,H}$ = 4.9 Hz, 2H), 6.42 (brs, 1H), 2.96 (d, $J_{H,H}$ = 4.9 Hz, 3H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.58, 138.37, 134.60, 132.08, 128.41, 127.69, 123.83, 26.85, 21.37. **GC-MS** (M^+) = 149.1.



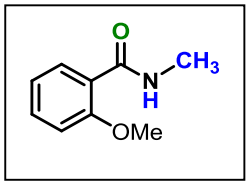
3-Methoxy-N-methylbenzamide (9):[14] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.34-7.27 (m, 2H), 7.25-7.23 (m, 1H), 7.0 (ddd, $J_{H,H}$ = 7.9, 2.4, 1.0 Hz, 1H), 6.24 (brs), 3.82 (s, 3H), 2.98 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.19, 159.85, 136.16, 129.60, 118.62, 117.64, 112.27, 55.47, 26.94. **GC-MS** (M^+) = 165.1.



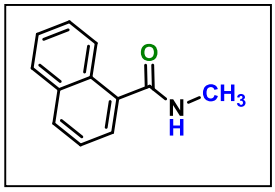
3-Chloro-N-methylbenzamide (10):[16] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.73 (t, $J_{H,H}$ = 1.8 Hz, 1H), 7.62-7.60 (m, 1H), 7.38 (dt, $J_{H,H}$ = 8.0, 1.2 Hz, 1H), 7.28 (d, $J_{H,H}$ = 7.8 Hz, 1H), 7.0 (brs, 1H) 2.93 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.20, 136.28, 134.55, 131.31, 129.77, 127.32, 125.07, 26.92. **GC-MS** (M^+) = 169.1.



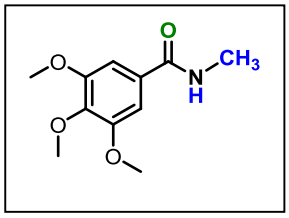
3-Fluoro-N-methylbenzamide (11):[17] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.51-7.46 (m, 2H), 7.38-7.33 (m, 1H), 7.18-7.13 (m, 1H), 6.53 (brs, 1H), 2.97 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.17, 164.0, 161.53, 136.87 (J = 7.0 Hz), 130.24 (J = 8.0 Hz), 122.41 (J = 3.0 Hz), 118.51, 118.30, 114.47, 114.24, 26.97. **GC-MS** (M^+) = 153.1.



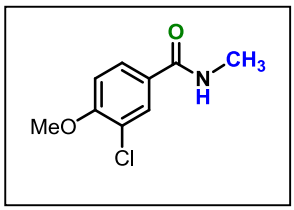
2-Methoxy-N-methylbenzamide (12):[18] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.19 (dd, $J_{H,H}$ = 7.8, 1.8 Hz, 1H), 7.81 (brs, 1H), 7.43-7.39 (m, 1H), 7.07-7.03 (m, 1H), 6.94 (d, $J_{H,H}$ = 8.5 Hz, 1H), 3.93 (s, 3H), 2.99 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.01, 157.43, 132.66, 132.27, 121.50, 121.28, 111.24, 55.91, 26.59. **GC-MS** (M^+) = 165.1.



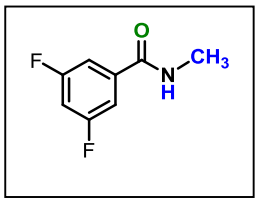
N-Methyl-1-naphthamide (13):[17] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27 (d, $J_{H,H}$ = 7.4 Hz, 1H), 7.89-7.83 (m, 2H), 7.56-7.50 (m, 3H), 7.43-7.39 (m, 1H), 6.05 (brs, 1H), 3.06 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.34, 134.63, 133.71, 130.58, 130.16, 128.34, 127.12, 126.47, 125.48, 124.92, 124.77, 26.91. **GC-MS** (M^+) = 185.1.



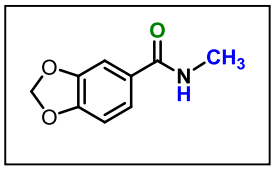
3,4,5-Trimethoxy-N-methylbenzamide (14):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.98 (s, 2H), 6.25 (brs, 1H), 3.86 (s, 6H), 3.85 (s, 3H), 2.98 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.05, 153.21, 140.73, 130.19, 104.25, 60.97, 56.30, 26.99. **GC-MS** (M^+) = 225.1.



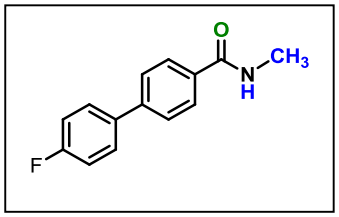
3-Chloro-4-methoxy-N-methylbenzamide (15): ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, $J_{H,H}$ = 2.0 Hz, 1H), 2.66 (dd, $J_{H,H}$ = 8.6, 2.1 Hz, 1H), 6.93 (d, $J_{H,H}$ = 8.6 Hz, 1H), 6.11 (brs, 1H), 3.93 (s, 3H), 2.98 (d, $J_{H,H}$ = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.69, 157.46, 129.06, 127.80, 127.01, 122.67, 111.55, 56.38, 26.96. **ESI-MS**: Calculated for $C_9H_{10}ClNO_2$; 200.0478 $(M+H)^+$, found: 200.0471.



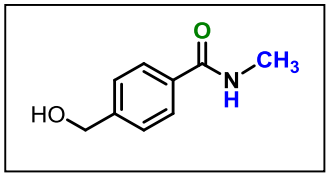
3,5-Difluoro-N-methylbenzamide (16):[19] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 2H), 6.92 (tt, $J_{H,H}$ = 8.6, 2.2 Hz, 1H), 6.37 (brs, 1H), 2.99 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 165.92, 164.29 (J = 12.0 Hz), 161.77 (J = 12.0 Hz), 137.98, 110.24 (J = 26.0 Hz), 106.82 (J = 25.5 Hz), 27.07. **GC-MS** (M^+) = 171.0.



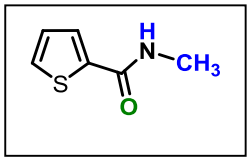
N-Methylbenzo[d][1,3]dioxole-5-carboxamide (17):[20] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.28-7.26 (m, 2H), 6.78 (d, $J_{H,H}$ = 7.9 Hz, 1H), 6.21 (brs, 1H), 5.99 (s, 2H), 2.95 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.62, 150.24, 147.97, 128.89, 121.45, 108.02, 107.63, 101.69, 26.94. **GC-MS** (M^+) = 179.1.



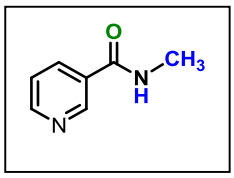
4'-Fluoro-N-methylbiphenyl-4-carboxamide (18):[21] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.81 (d, $J_{H,H}$ = 8.4 Hz, 2H), 7.59-7.53 (m, 4H), 7.13 (t, $J_{H,H}$ = 8.8 Hz, 2H), 6.24 (brs, 1H), 3.03 (d, $J_{H,H}$ = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.93, 164.17, 161.68, 143.24, 136.24, 133.36, 128.89 (J = 8.0 Hz), 127.51, 127.15, 115.92 (J = 22.0 Hz), 26.97. **GC-MS** (M^+) = 229.1.



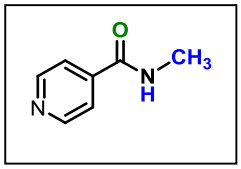
4-(Hydroxymethyl)-N-methylbenzamide (19):[22] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.69 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.36 (d, $J_{H,H}$ = 8.0 Hz, 2H), 6.27 (brs, 1H), 4.71 (s, 2H), 2.98 (d, $J_{H,H}$ = 4.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.21, 144.55, 133.68, 127.11, 126.83, 64.65, 26.93. **GC-MS** (M^+) = 165.1.



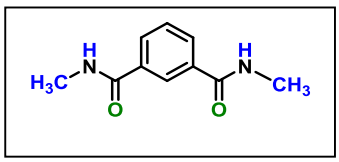
N-Methylthiophene-2-carboxamide (20):[12] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.55 (d, $J_{H,H}$ = 3.5 Hz, 1H), 7.41 (d, $J_{H,H}$ = 4.8 Hz, 1H), 7.02 (t, $J_{H,H}$ = 4.6 Hz, 1H), 6.55 (brs, 1H), 2.95 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 162.80, 139.07, 129.68, 128.10, 127.67, 26.75. **GC-MS** (M^+) = 141.0.



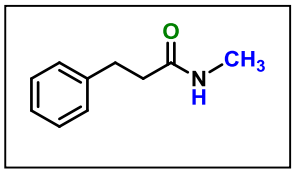
N-Methylnicotinamide (21):[13] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.89 (s, 1H), 8.51 (d, $J_{H,H}$ = 3.9 Hz, 1H), 8.0 (d, $J_{H,H}$ = 8.0 Hz, 1H), 7.74 (brs, 1H), 7.21-7.18 (m, 1H), 2.80 (d, $J_{H,H}$ = 4.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.09, 151.44, 148.19, 134.90, 130.17, 123.02, 26.44. **GC-MS** (M^+) = 136.1.



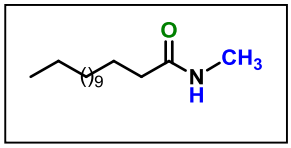
N-Methylisonicotinamide (22):[19] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.68 (d, $J_{H,H}$ = 5.4 Hz, 2H), 7.59 (d, $J_{H,H}$ = 5.6 Hz, 2H), 6.74 (brs, 1H), 2.99 (d, $J_{H,H}$ = 4.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 166.33, 150.49, 141.81, 120.99, 26.97. **GC-MS** (M^+) = 136.1.



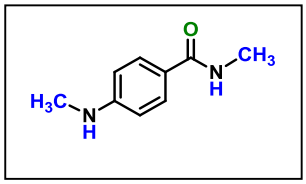
N1,N3-Dimethylisophthalamide (23):[23] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.06 (s, 1H), 7.74 (dd, $J_{H,H}$ = 7.8, 1.7 Hz, 2H), 7.59 (d, $J_{H,H}$ = 3.5 Hz, 2H), 7.22 (t, $J_{H,H}$ = 7.8 Hz, 1H), 2.70 (d, $J_{H,H}$ = 4.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.19, 134.37, 129.77, 128.20, 125.15, 26.36. **GC-MS** (M^+) = 192.1.



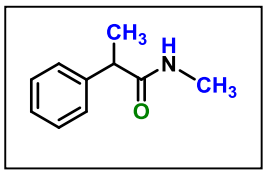
N-Methyl-3-phenylpropanamide (24):[24] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.27-7.23 (m, 2H), 7.18-7.15 (m, 3H), 6.04 (brs, 1H), 2.93 (t, $J_{H,H}$ = 7.5 Hz, 2H), 2.72 (d, $J_{H,H}$ = 4.8 Hz, 3H), 2.45 (t, $J_{H,H}$ = 8.1 Hz, 2H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 172.96, 140.90, 128.44, 128.23, 126.13, 38.21, 31.72, 26.20. **GC-MS** (M^+) = 163.1.



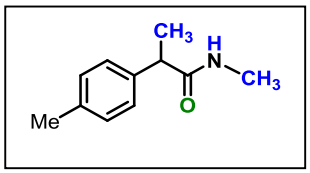
N-Methyltetradecanamide (25):[25] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 5.52 (brs, 1H), 2.78 (d, $J_{H,H}$ = 4.8 Hz, 3H), 2.14 (t, $J_{H,H}$ = 7.5 Hz, 2H), 1.60 (quint, $J_{H,H}$ = 7.4 Hz, 2H), 1.23 (brs, 20H), 0.86 (t, $J_{H,H}$ = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 173.95, 36.83, 31.99, 29.72, 29.57, 29.43, 26.34, 25.88, 22.76, 14.20. **GC-MS** (M^+) = 241.2.



N-Methyl-4-(methylamino)benzamide (26):[26] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.58 (d, $J_{H,H}$ = 8.7 Hz, 2H), 6.50 (d, $J_{H,H}$ = 8.6 Hz, 2H), 6.32 (brs, 1H), 2.89 (d, $J_{H,H}$ = 4.8 Hz, 3H), 2.79 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.30, 151.84, 128.57, 122.70, 111.46, 30.34, 26.77. **GC-MS** (M^+) = 164.1.



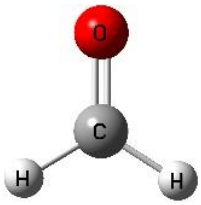
N-Methyl-2-phenylpropanamide (27):[27] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.31-7.26 (m, 4H), 7.24-7.20 (m, 1H), 5.91 (brs, 1H), 3.53 (q, $J_{H,H}$ = 7.2 Hz, 1H), 2.68 (d, $J_{H,H}$ = 4.8 Hz, 3H), 1.48 (d, $J_{H,H}$ = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 174.93, 141.44, 128.72, 127.56, 127.08, 46.80, 26.37, 18.47. **ESI-MS:** Calculated for $C_{10}H_{13}NO$; 164.1075 $(M+H)^+$, found: 164.1071.



N-Methyl-2-p-tolylpropanamide (28):[28] **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.17 (d, $J_{H,H}$ = 8.1 Hz, 2H), 7.11 (d, $J_{H,H}$ = 8.1 Hz, 2H), 5.81 (brs, 1H), 3.51 (q, $J_{H,H}$ = 7.2 Hz, 1H), 2.68 (d, $J_{H,H}$ = 4.8 Hz, 3H), 2.30 (s, 3H), 1.47 (d, $J_{H,H}$ = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 175.12, 138.40, 136.73, 129.43, 127.46, 46.42, 26.37, 20.96, 18.47. **ESI-MS:** Calculated for $C_{11}H_{15}NO$; 178.1232 $(M+H)^+$, found: 178.1236.

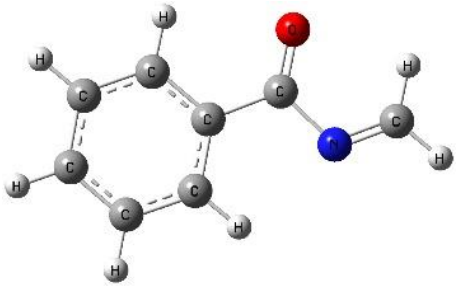
16. Cartesian Coordinates and Statistical Thermodynamic Analysis

(Energy in Hartree Unit)



SCF done	-114.44715561
SCF done for solvent	-114.45163938
Zero-point correction	0.027267
Thermal correction to Gibbs free energy	0.005613

C	0.52714800	-0.00000100	-0.00003800
O	-0.67404600	-0.00002200	0.00000900
H	1.11490500	-0.93812200	0.00007700
H	1.11456900	0.93830200	0.00007700

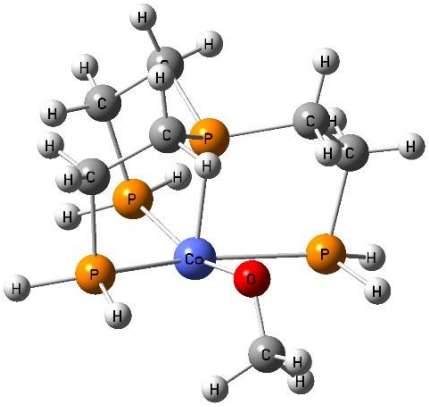


SCF done	-438.83519701
SCF done for solvent	-438.84111698
Zero-point correction	0.133164
Thermal correction to Gibbs free energy	0.100451

C	0.15023900	0.11559400	-0.00010300
C	0.66660900	-1.18274800	-0.00016100
C	2.04488800	-1.37533500	-0.00004100
C	2.90308100	-0.27873400	0.00014300
C	2.38769300	1.01810900	0.00020500
C	1.01425300	1.21564400	0.00008100
H	-0.01827300	-2.02228000	-0.00030800

H	2.44966300	-2.38205700	-0.00009000
H	3.97763100	-0.43335800	0.00023600
H	3.05923600	1.87025000	0.00035000
H	0.58487200	2.21206900	0.00012300
O	-1.77864300	1.49295200	-0.00030700
C	-1.31278100	0.37587200	-0.00022400
C	-3.37386000	-0.61220800	0.00037600
H	-3.79828000	0.39679600	0.00146900
H	-4.05004000	-1.46648700	0.00081400
N	-2.12234300	-0.82510300	-0.00025700

$I1_H$

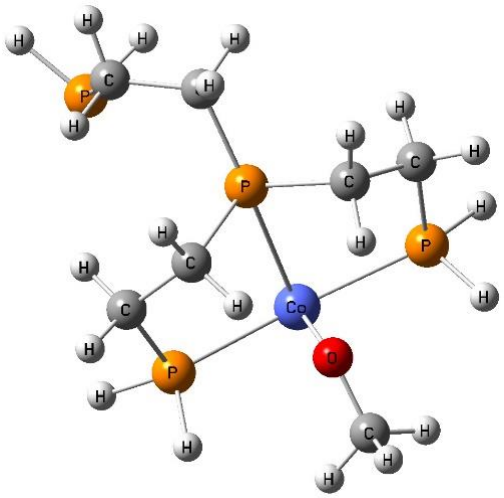


SCF done	-1864.68467526
SCF done for solvent	-1864.69451269
Zero-point correction	0.272006
Thermal correction to Gibbs free energy	0.226811

C	2.50346800	0.93873000	1.07710300
C	1.39694400	0.44188800	2.02429300
C	1.61361800	-2.46022600	-0.44131600
C	0.94396100	-2.34446900	0.94413800
C	-1.36874300	-0.71917900	2.01430500
C	-2.48408700	-1.13619900	1.03939200
Co	-0.18244900	0.41866800	-0.85848300
H	3.14879700	1.65337200	1.59494200
H	3.14107900	0.09705200	0.77795500
H	1.82895400	-0.03846700	2.90860900
H	0.78125100	1.29055800	2.33776300
H	2.57216300	-1.92846600	-0.43532500
H	1.65062200	-2.59764700	1.74136100
H	1.82248500	-3.50160900	-0.70058500
H	-1.53767200	0.31075400	2.34415800
H	-1.34871800	-1.37758700	2.88883500

H	0.10747200	-3.05133400	1.00971800
H	-2.31555600	-2.16826800	0.70362100
H	-3.45264600	-1.12376400	1.54644200
P	1.86572700	1.69096400	-0.53360500
P	0.22633400	-0.63893600	1.09778900
P	0.58527300	-1.62118900	-1.77258400
P	-2.56278600	-0.10766400	-0.54291400
C	-1.23246600	2.97480100	-0.25726300
H	-0.47933300	3.44925600	-0.91916900
O	-0.76434100	1.82820200	0.35907200
H	-1.52943500	3.73440900	0.48461000
H	-2.11743400	2.79097700	-0.89999200
H	1.38584500	-1.95249500	-2.89163200
H	-0.38392800	-2.63235700	-1.98151800
H	-3.32876900	0.98069100	-0.07749200
H	-3.66117100	-0.83048800	-1.08719800
H	1.64014700	3.01367400	-0.10408400
H	3.16230600	1.93237400	-1.06875700

$I2_H$

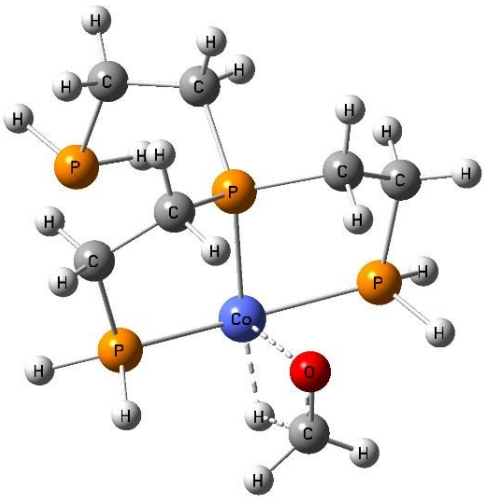


SCF Done	-1864.67212211
SCF done for solvent	-1864.68376428
Zero-point correction	0.272016
Thermal correction to Gibbs free energy	0.224003

C	0.97204500	2.14977100	0.90207900
C	0.76136100	0.81523200	1.63251900

C	3.64983700	-0.46429300	0.51012200
C	2.47171400	-1.36619700	0.88802700
C	-0.32354000	-1.87365500	1.26878800
C	-1.02717800	-2.75711800	0.22877900
Co	-1.26825200	0.40252900	-0.93562900
H	1.06312200	2.97395700	1.61469800
H	1.89012600	2.12486900	0.30389300
H	1.51950300	0.69030300	2.41484100
H	-0.23255200	0.80507800	2.08820100
H	3.64063100	0.43629900	1.13544800
H	2.50763000	-1.59105800	1.96149600
H	4.59092100	-0.98203200	0.70971400
H	-1.06985700	-1.29393900	1.81897400
H	0.24049800	-2.49869900	1.97003000
H	2.54962900	-2.31985500	0.35157900
H	-0.29334800	-3.21640700	-0.44469700
H	-1.57618300	-3.56921000	0.71295400
P	-0.40967700	2.50017700	-0.30265200
P	0.80762900	-0.63152300	0.45102900
P	3.59026400	0.12023000	-1.27675500
P	-2.17729700	-1.76519400	-0.85640000
C	-3.36763200	1.04057400	0.78904800
H	-3.41280900	2.06872800	0.37531900
O	-2.08840900	0.51193500	0.80038500
H	-3.78597900	1.09180300	1.80758700
H	-4.08239700	0.44611700	0.18323400
H	4.99417200	0.17483600	-1.47603400
H	3.46279500	-1.16534100	-1.86383900
H	-3.37090800	-1.80640900	-0.11069300
H	-2.50807900	-2.77698000	-1.78815000
H	-1.31678300	3.20639800	0.50932600
H	0.15653100	3.61654100	-0.95946800

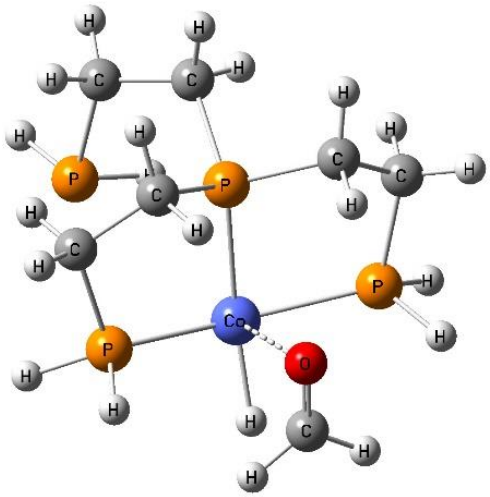
$TS1_H$



SCF done	-1864.63358649
SCF done for solvent	-1864.64929421
Zero-point correction	0.265755
Thermal correction to Gibbs free energy	0.219045

C	1.35724700	1.89939200	1.32430900
C	0.76876900	0.65124700	2.00389800
C	3.19493400	-1.02776400	0.20638600
C	1.93016500	-1.71885900	0.72516200
C	-0.83782200	-1.78366100	1.49885800
C	-1.49136300	-2.61817900	0.38499000
Co	-0.76602500	0.43191700	-0.91500800
H	1.42642800	2.73256900	2.02762000
H	2.36735800	1.69696100	0.95572100
H	1.42425900	0.28143800	2.80049900
H	-0.20496800	0.90063800	2.44017700
H	3.54679600	-0.29803700	0.94445100
H	2.10281100	-2.11099800	1.73491000
H	3.98837800	-1.76953200	0.09069200
H	-1.58791200	-1.13021500	1.95789400
H	-0.40091400	-2.42191400	2.27459600
H	1.69414900	-2.57444100	0.08038700
H	-0.75324300	-3.28714100	-0.07282200
H	-2.29727400	-3.24347100	0.77626800
P	0.32219300	2.34314600	-0.17388400
P	0.41246400	-0.65076400	0.73324800
P	2.93161500	-0.08946900	-1.40719800
P	-2.08973400	-1.45957600	-0.96101400
C	-2.91076200	1.61179400	0.02715600
H	-1.87317500	1.29816900	-1.73811100
O	-2.43393000	1.10291800	1.04172500
H	-2.72969100	2.66653900	-0.23129000
H	-3.72190300	1.12618700	-0.53745100
H	4.22640000	-0.32954500	-1.93730200
H	2.32697800	-1.15210400	-2.12406500
H	-3.42291900	-1.26319700	-0.53937800
H	-2.38182900	-2.39819800	-1.97563600
H	-0.50357300	3.34292500	0.38727100
H	1.21288900	3.21440100	-0.83483300

$I3_H$

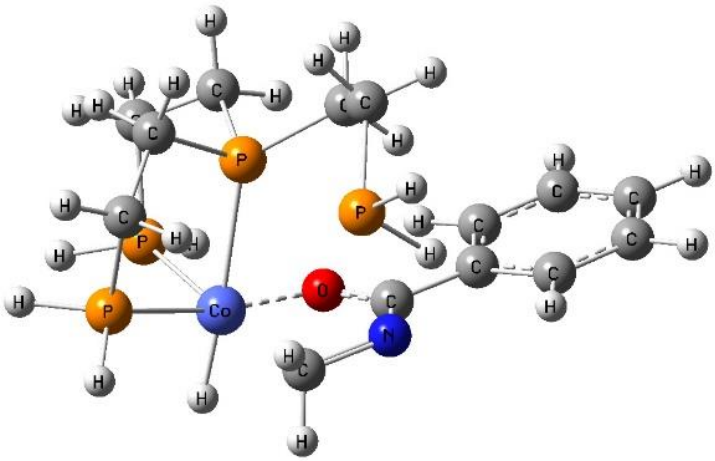


SCF done	-1864.63426980
SCF done for solvent	-1864.65180129
Zero-point correction	0.265925
Thermal correction to Gibbs free energy	0.218158

C	1.28797100	1.97966800	1.29867300
C	0.70925800	0.75329400	2.02583100
C	3.17090100	-0.97166800	0.27690500
C	1.91891700	-1.64706700	0.84501900
C	-0.86521000	-1.72777900	1.55709800
C	-1.45422800	-2.61267000	0.44527900
Co	-0.66372200	0.36294400	-0.99251800
H	1.32850200	2.84743500	1.96128100
H	2.30933600	1.77704000	0.96061400
H	1.36171500	0.42402700	2.84223200
H	-0.27071300	1.00663700	2.44663900
H	3.52845300	-0.20820600	0.97711100
H	2.10204000	-1.98118100	1.87368800
H	3.96788600	-1.71247100	0.18127200
H	-1.64631600	-1.07771400	1.96676100
H	-0.44587700	-2.33020900	2.37025300
H	1.68742100	-2.53874600	0.24938800
H	-0.69229500	-3.30497800	0.06871600
H	-2.28614500	-3.21676800	0.81504700
P	0.27445900	2.32563100	-0.24253900
P	0.38998300	-0.59719000	0.79574300
P	2.87803800	-0.10422100	-1.37169400
P	-1.95809700	-1.52003400	-0.99530100

C	-3.01361600	1.57013700	0.03035800
H	-1.63052800	1.11341600	-2.03130300
O	-2.57896900	1.13429300	1.07811200
H	-2.77577400	2.58446400	-0.32818700
H	-3.71867900	1.00002400	-0.59617700
H	4.15748100	-0.38309100	-1.92031600
H	2.24154800	-1.18790000	-2.02744200
H	-3.32391800	-1.32965000	-0.68514400
H	-2.17072800	-2.50876900	-1.98361100
H	-0.60267000	3.30926900	0.27200000
H	1.14182400	3.21727300	-0.90786100

$I4_{H\ (H)}$

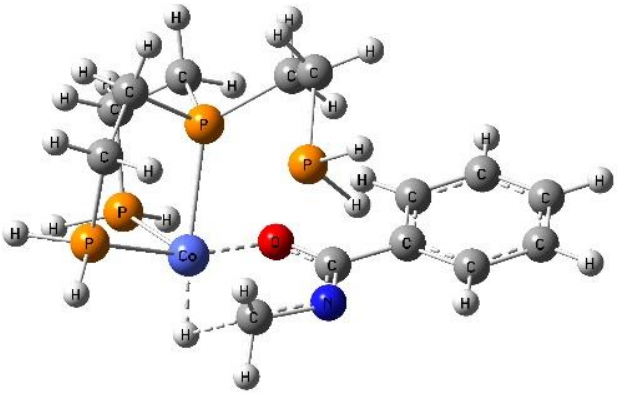


SCF done	-2189.05886903
SCF done for solvent	-2189.08071541
Zero-point correction	0.373013
Thermal correction to Gibbs free energy	0.317867

C	-0.20145200	2.85689800	1.66935500
C	-0.36426900	1.34143000	1.78785300
C	3.30356400	1.48015300	0.11535100
C	2.63569500	1.04908200	1.43394400
C	0.87254400	-1.14274500	2.29874500
C	1.81565200	-2.30176400	1.96478400
Co	1.09025000	-0.81767100	-1.10002000
H	-1.10533400	3.32809400	2.06296900
H	0.63284100	3.19694800	2.29265900
H	-0.48427400	1.07703800	2.84490600
H	-1.27382300	1.02177100	1.26490900

H	2.75471600	2.33016400	-0.30278100
H	2.54596600	1.90653600	2.10849500
H	4.33929600	1.79065900	0.27571800
H	-0.16966200	-1.47947700	2.23107400
H	1.04223300	-0.78360000	3.32028200
H	3.25423900	0.30355800	1.94878100
H	2.85916900	-1.99476500	2.10368400
H	1.63939200	-3.15174900	2.62825600
P	0.14573900	3.45525600	-0.07248400
P	0.97834700	0.26252400	1.08490400
P	3.19482700	0.14772400	-1.18618900
P	1.64617100	-2.77324100	0.16808500
C	-1.49742500	-0.33786300	-1.05347800
H	1.23703200	-1.47835000	-2.37134600
O	-0.73934100	-1.36915500	-0.76270400
H	3.62628400	0.84761200	-2.32758800
H	4.38142000	-0.58097500	-0.94895100
H	0.55480800	-3.65883500	0.20794700
H	2.67981800	-3.72849800	0.06822200
H	-1.06168800	3.03954700	-0.67604900
H	-0.23562400	4.80187300	0.14823600
C	-2.90144300	-0.39461600	-0.53891000
C	-3.78870900	0.66190500	-0.76591900
C	-3.32515200	-1.49761900	0.20511600
C	-5.08042200	0.61231900	-0.25480400
H	-3.44121400	1.50550200	-1.35343600
C	-4.62053900	-1.54758500	0.71293000
H	-2.62390400	-2.30980700	0.36415100
C	-5.50016700	-0.49250400	0.48609500
H	-5.76628600	1.43421500	-0.43715400
H	-4.94462300	-2.41168000	1.28532700
H	-6.51078300	-0.53111800	0.88118800
N	-1.09471000	0.71111300	-1.68280900
C	0.26504100	0.59437000	-2.17131100
H	0.26380700	0.35355700	-3.23929200
H	0.79337900	1.55163700	-2.05163500

$TS2_{H\ (H)}$

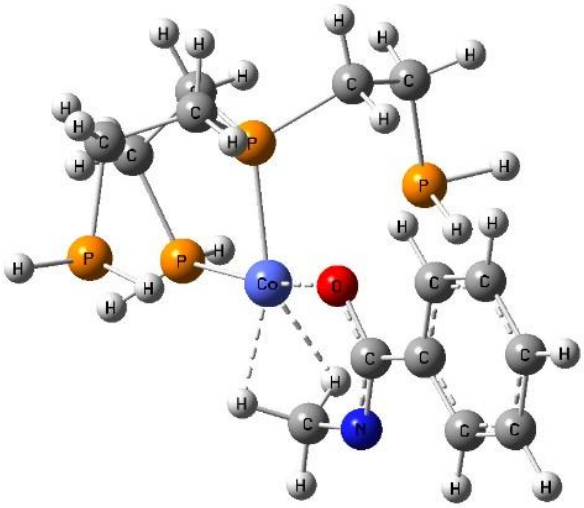


SCF done	-2189.05597265
SCF done for solvent	-2189.07612331
Zero-point correction	0.372238
Thermal correction to Gibbs free energy	0.318321

C	-0.21737200	2.72131400	1.80520200
C	-0.20333200	1.20654200	2.01096200
C	3.31235400	1.61045000	0.07697000
C	2.76812500	1.08951400	1.42038000
C	1.17600300	-1.23188400	2.26652800
C	2.11425900	-2.33312100	1.76505300
Co	1.03929300	-0.68305100	-1.10328600
H	-1.13536900	3.12351000	2.23979000
H	0.62054600	3.18087900	2.34065500
H	-0.15743300	0.98124300	3.08285300
H	-1.13194400	0.76516600	1.62385500
H	2.69416500	2.44942600	-0.25956800
H	2.69141400	1.90951200	2.14185000
H	4.34321900	1.96143900	0.17057500
H	0.14290400	-1.60082200	2.28206000
H	1.43792000	-0.92996300	3.28722000
H	3.45679500	0.35096200	1.84905700
H	3.15534300	-1.98923000	1.80123400
H	2.04802700	-3.22075200	2.39858600
P	-0.05691900	3.22986500	0.00702300
P	1.12530100	0.24736200	1.14193600
P	3.16034000	0.33186300	-1.27606200
P	1.75387800	-2.72381100	-0.02404100
C	-1.58579100	-0.38144600	-1.05741700
H	0.89452600	-1.07316600	-2.48111700
O	-0.73276400	-1.24703800	-0.56827300
H	3.56761400	1.08893000	-2.39272900
H	4.36262900	-0.38985000	-1.10193500
H	0.68529200	-3.62961900	0.10909600
H	2.77736200	-3.66796300	-0.26010500
H	-1.19772800	2.55994300	-0.49750100
H	-0.66818300	4.50137800	0.13728900
C	-2.97201500	-0.43678400	-0.49477600
C	-3.96993900	0.41753700	-0.97272200
C	-3.26715000	-1.32022800	0.54512800
C	-5.24369100	0.38431400	-0.41827700
H	-3.71762700	1.09531800	-1.78137100
C	-4.54307200	-1.34983100	1.10267700
H	-2.48226800	-1.98143500	0.89728600
C	-5.53390400	-0.49814400	0.62235800
H	-6.01502800	1.04811000	-0.79701900
H	-4.76538600	-2.04031300	1.91092400
H	-6.52967500	-0.52238900	1.05469300

N	-1.30513800	0.51770400	-1.93595400
C	0.07308800	0.54843700	-2.35155400
H	0.13902800	0.47359700	-3.44063000
H	0.53665900	1.51163500	-2.08438400

$I5_{H\ (H)}$

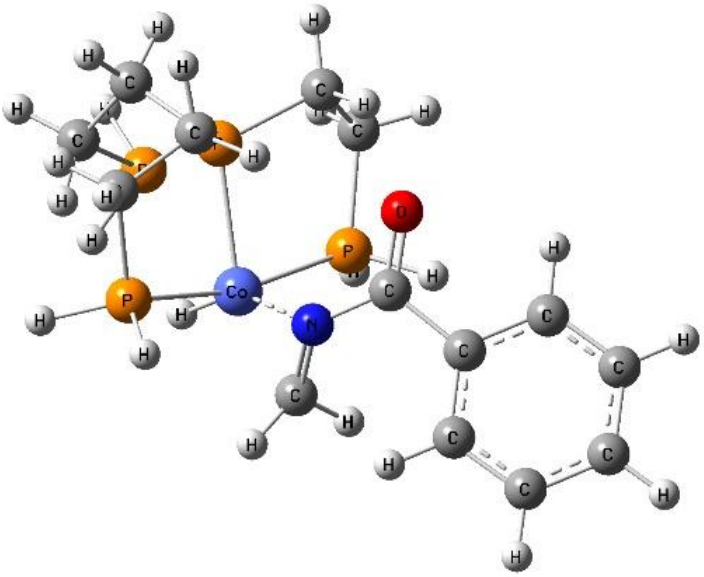


SCF done	-2189.10742325
SCF done for solvent	-2189.12388572
Zero-point correction	0.375856
Thermal correction to Gibbs free energy	0.316832

C	1.97159000	-2.45648300	-1.92621800
C	1.32510600	-1.12253700	-2.30820100
C	3.98619000	-0.25528800	0.18559000
C	3.40271600	0.52949900	-1.00238200
C	0.85675300	1.66122500	-2.03181300
C	1.13153300	3.04470600	-1.43556600
Co	0.69903800	-0.08763900	0.97334200
H	1.67748000	-3.21254700	-2.65758300
H	3.06375200	-2.37292100	-1.97790400
H	1.67674300	-0.80435300	-3.29737300
H	0.23584800	-1.24214000	-2.36145000
H	3.97570000	-1.32917900	-0.02640700
H	3.91292800	0.27054200	-1.93659100
H	5.02083800	0.03390500	0.38445100
H	-0.22136700	1.45944400	-2.00746900
H	1.18515200	1.62817900	-3.07739300
H	3.54794700	1.60366100	-0.83570100

H	2.17578900	3.32894700	-1.60424600
H	0.51534600	3.77955700	-1.95804500
P	1.54331900	-3.04863300	-0.18843600
P	1.57118700	0.24338900	-1.09087900
P	2.92445800	-0.04129100	1.70978500
P	0.82764500	3.15059400	0.42023800
C	-2.07879600	-0.20594800	0.91030100
H	-0.20399800	0.60561300	2.61278000
O	-1.03330500	-0.07557800	0.13945300
H	3.57776900	-0.93856100	2.57947100
H	3.47380000	1.14872300	2.23558800
H	-0.52825000	2.74312600	0.39666200
H	0.54180500	4.54096400	0.43691300
H	0.13568400	-2.96351200	-0.31273100
H	1.60616600	-4.43509000	-0.48686600
C	-3.40810900	-0.17974600	0.21923300
C	-4.59245900	-0.27618600	0.95453500
C	-3.47445500	-0.05719400	-1.16913400
C	-5.82241400	-0.24859500	0.30846700
H	-4.51900100	-0.37183300	2.03219700
C	-4.70678200	-0.03059300	-1.81641100
H	-2.54682100	0.01187800	-1.72730800
C	-5.88381500	-0.12531200	-1.07921800
H	-6.73848200	-0.32225900	0.88682100
H	-4.74949800	0.06427700	-2.89746700
H	-6.84557100	-0.10316200	-1.58284400
N	-2.06460200	-0.35300600	2.19533100
C	-0.74585900	-0.36468300	2.76247500
H	-0.77203200	-0.50315500	3.84455400
H	-0.11943200	-1.21624600	2.38420600

I4'$_{H\ (H)}$

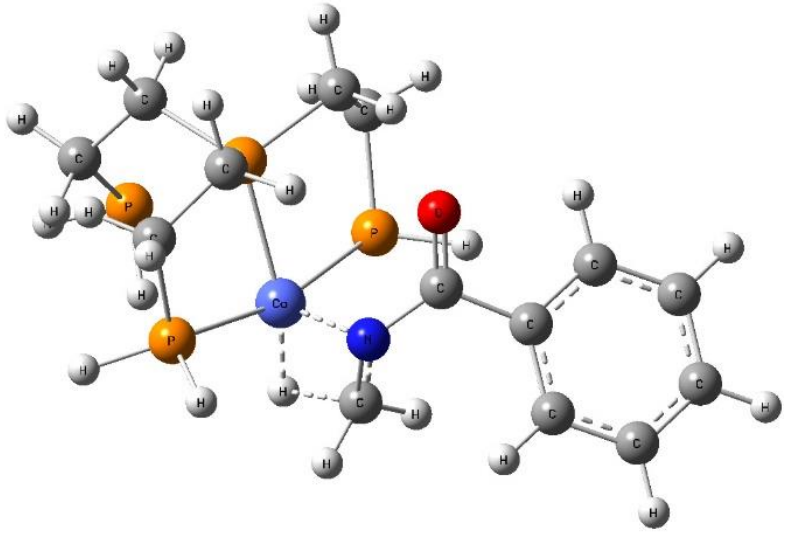


SCF done	-2189.05188111
SCF done for solvent	-2189.06919684
Zero-point correction	0.373518
Thermal correction to Gibbs free energy	0.319430

C	1.73538900	2.72142700	1.24410800
C	1.38322200	1.47102000	2.07077600
C	4.26203900	0.02021500	-0.33253400
C	3.67178100	-0.07182200	1.08090500
C	1.18088300	-1.53741700	1.85586900
C	1.00541600	-2.61786700	0.77349900
Co	0.58755700	0.35819000	-0.89211700
H	1.34215000	3.62811600	1.70901400
H	2.82398800	2.83745000	1.18805300
H	1.89599000	1.49288600	3.03820800
H	0.30251800	1.39177300	2.23195200
H	3.77541300	0.82842400	-0.88693400
H	4.02885000	0.75879700	1.70158500
H	5.33379500	0.22797400	-0.29337300
H	0.20712900	-1.25773800	2.26758000
H	1.83665800	-1.88753200	2.65904000
H	3.99072200	-0.99417700	1.58073500
H	1.98016300	-2.98630000	0.43919900
H	0.43465500	-3.46790300	1.15476700
P	1.13533000	2.57012700	-0.53235500
P	1.81093000	-0.00353700	1.04705300
P	3.92637000	-1.55313600	-1.29870600
P	0.19107600	-1.90443700	-0.75487700
C	-1.17116300	0.80713400	-1.64347400
H	1.59375100	0.13578200	-2.00143400
H	4.20432700	-1.05581800	-2.59088300
H	5.21426800	-2.13119500	-1.12606300
H	-1.15311800	-2.30100600	-0.58438700
H	0.56589600	-2.84715000	-1.72783900
H	0.06039700	3.47699200	-0.57619100
H	2.10046400	3.36793500	-1.18124500
C	-1.98637700	0.24219100	0.60846100
N	-1.19246300	0.90495200	-0.25804200
O	-1.58979100	-0.16517200	1.70914700
C	-3.43854700	0.03617600	0.24957300
C	-4.10504500	0.79446300	-0.71559900
C	-4.14016900	-0.94857300	0.94977900
C	-5.45073600	0.56003700	-0.98401700
H	-3.57332400	1.57869300	-1.24373100
C	-5.48009600	-1.19231400	0.67195900
H	-3.61005700	-1.50354800	1.71647400
C	-6.13806000	-0.43792500	-0.29729200
H	-5.96444000	1.15880700	-1.72957700

H	-6.01456100	-1.96626900	1.21396600
H	-7.18570900	-0.62352300	-0.51331200
H	-1.18810900	1.73923800	-2.21000900
H	-1.72711100	-0.00086500	-2.12412100

TS2'$_{H\ (H)}$

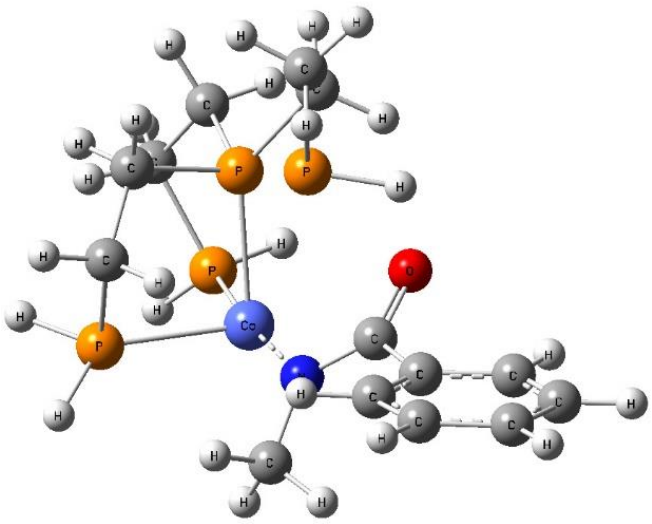


SCF done	-2189.03507987
SCF done for solvent	-2189.05052418
Zero-point correction	0.372013
Thermal correction to Gibbs free energy	0.317407

C	2.21392600	2.47913200	1.20254800
C	1.58714800	1.35335000	2.04506500
C	4.24585500	-0.45093700	-0.16259600
C	3.48728200	-0.69714600	1.14698700
C	0.77652700	-1.57112800	1.86595000
C	0.55257500	-2.65279500	0.79368600
Co	0.57214300	0.32574200	-0.88650100
H	2.00856500	3.45789200	1.64116600
H	3.30372300	2.36282000	1.17621100
H	2.08479200	1.27374700	3.01723800
H	0.51332200	1.51072700	2.19205500
H	4.22264700	0.60825500	-0.43763300
H	3.96293400	-0.16391900	1.97889600
H	5.29688500	-0.72434300	-0.02769000
H	-0.17496400	-1.13743400	2.19300700
H	1.30553200	-1.97649100	2.73426100
H	3.51841500	-1.76553400	1.39071100
H	1.50839600	-3.10042200	0.49574300

H	-0.08853700	-3.45586700	1.16456900
P	1.63595500	2.41990000	-0.58689400
P	1.69821300	-0.19619400	1.05773600
P	3.57759700	-1.51496400	-1.56402900
P	-0.15290000	-1.88072000	-0.75962300
C	-1.14973100	1.21706200	-1.47163100
H	0.22292900	0.47742400	-2.35059200
H	2.88686300	-0.52669200	-2.30038200
H	4.74864200	-1.48290700	-2.36429800
H	-1.53718300	-2.09441900	-0.56468100
H	0.06436900	-2.92099300	-1.68540500
H	0.75706500	3.51688100	-0.65355400
H	2.75107000	3.04756500	-1.19105500
C	-1.90769000	0.72991200	0.75124400
N	-1.11711600	1.42313700	-0.10873200
O	-1.58722700	0.49365300	1.92377900
C	-3.28458200	0.28368500	0.30527500
C	-4.05718300	1.01076300	-0.60300400
C	-3.81667400	-0.87542100	0.87612600
C	-5.33213700	0.57383900	-0.95107200
H	-3.66151500	1.93150500	-1.02088900
C	-5.08116500	-1.32551300	0.51294400
H	-3.22199800	-1.40461900	1.61483500
C	-5.84129600	-0.60089900	-0.40333400
H	-5.92982500	1.15224200	-1.64855000
H	-5.48036300	-2.23528900	0.95055500
H	-6.83189100	-0.94589600	-0.68273400
H	-1.02848600	2.11232600	-2.08131000
H	-1.87175600	0.51345200	-1.89104600

I5'$_{H\ (H)}$

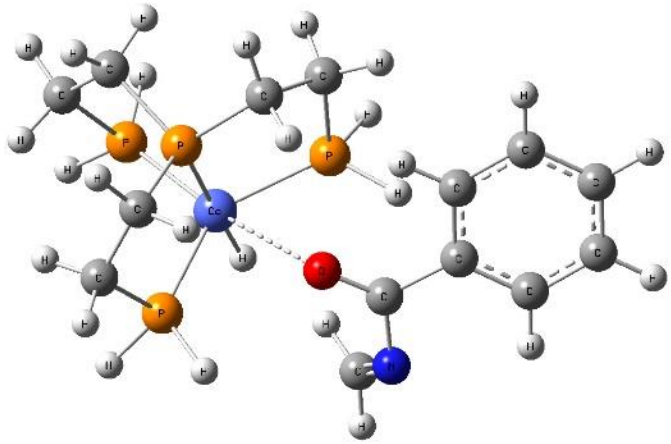


SCF done	-2189.09431510
SCF done for solvent	-2189.10967557
Zero-point correction	0.377016
Thermal correction to Gibbs free energy	0.322048

C	0.15865900	3.39404700	0.08952900
C	-0.74831100	2.63499000	-0.87960200
C	-1.21958200	0.16934900	2.40009400
C	-1.86162200	1.31379200	1.60041100
C	-3.35311100	1.47823300	-0.85689700
C	-4.27234000	0.26570300	-0.68239100
Co	-1.25241700	-1.25645400	-0.43944400
H	0.61909200	4.22993000	-0.44360500
H	-0.42754700	3.82857800	0.90654800
H	-1.50908100	3.32171500	-1.26824700
H	-0.15217300	2.25895600	-1.71590100
H	-0.14157100	0.15207900	2.20096600
H	-1.44497800	2.26757000	1.93815200
H	-1.37585700	0.31915700	3.47176400
H	-3.26266800	1.71915400	-1.92313000
H	-3.77195800	2.36014800	-0.35808200
H	-2.94057200	1.35253300	1.80162600
H	-4.45292900	0.07527900	0.38273300
H	-5.24400500	0.42133900	-1.15714600
P	1.47764100	2.31782200	0.87275500
P	-1.62379800	1.10693400	-0.25094400
P	-1.86000500	-1.49842200	1.86144500
P	-3.42430900	-1.25737300	-1.33883600
C	1.17275700	-2.45110400	0.78074600
H	0.51539600	-3.32162000	0.67767800
H	-1.34017800	-2.29062800	2.91150200
H	-3.17067100	-1.40784100	2.40020400
H	-3.60443600	-1.06737100	-2.72672500
H	-4.44627600	-2.21565300	-1.16211200
H	2.35454200	2.23459600	-0.22901500
H	2.16697500	3.38072700	1.51588300
C	1.49060000	-0.55708400	-0.71831600
N	0.66801100	-1.37031000	-0.04853800
O	1.09106000	0.27732200	-1.55656600
C	2.98845200	-0.57463600	-0.47665400
C	3.55258500	-0.57066100	0.80136300
C	3.82651200	-0.45058000	-1.58652600
C	4.93164700	-0.46323200	0.96511000
H	2.90501200	-0.62692500	1.67176900
C	5.20551100	-0.36946400	-1.42697100
H	3.37177300	-0.40193400	-2.57059700
C	5.76181600	-0.37425200	-0.14918900
H	5.35747400	-0.44779000	1.96379400

H	5.84822200	-0.28954300	-2.29847600
H	6.83747000	-0.29956700	-0.02199200
H	1.19170300	-2.19180100	1.85266100
H	2.18358900	-2.76828300	0.50649500

I4"$_{H\ (H)}$

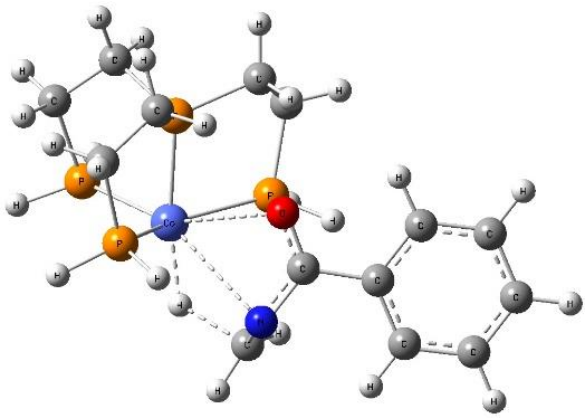


SCF done	-2189.03737535
SCF done for solvent	-2189.05355743
Zero-point correction	0.372562
Thermal correction to Gibbs free energy	0.316315

C	2.34138400	1.56877800	2.08440900
C	1.67212600	0.22887000	2.42431900
C	4.25996300	-1.22461700	0.10345800
C	3.13555600	-1.91082800	0.89368900
C	0.16807100	-1.94262400	1.05317900
C	-0.32756400	-2.30918900	-0.35549400
Co	1.55669800	0.40541600	-0.95206900
H	2.17423200	2.30640100	2.87327100
H	3.42410000	1.43215200	1.98342400
H	2.16419500	-0.27313300	3.26362300
H	0.62351100	0.40096500	2.68992500
H	4.67245100	-0.39701500	0.69213000
H	3.45257500	-2.18487600	1.90553000
H	5.07793700	-1.91938400	-0.10448500
H	-0.58783000	-1.34654700	1.57230700
H	0.38459600	-2.83311000	1.65238900
H	2.83507600	-2.83409200	0.38181800
H	0.32126500	-3.07935400	-0.78841300
H	-1.34298400	-2.71558900	-0.32508800
P	1.74494300	2.17217600	0.40557300
P	1.62984700	-0.81704200	0.89274500

P	3.56308300	-0.44021700	-1.46151100
P	-0.19394400	-0.82890800	-1.51610900
C	-1.47633700	2.71726300	-0.98259800
H	1.42405500	1.27377500	-2.22396000
H	4.72685100	0.25898900	-1.86521400
H	3.77708500	-1.52304300	-2.35502800
H	-1.55076800	-0.39911700	-1.51153500
H	-0.31433700	-1.52398400	-2.74239400
H	0.66129500	2.98828100	0.82464900
H	2.65333600	3.24471000	0.24013900
C	-2.34198100	1.18795500	0.50084900
N	-2.39483300	2.43005700	-0.15395100
O	-1.40619700	0.86048500	1.20804400
C	-3.54934700	0.32901000	0.31148200
C	-4.63339300	0.75444200	-0.46000100
C	-3.56408100	-0.94079700	0.89423000
C	-5.71962300	-0.09306700	-0.65413800
H	-4.61918600	1.74734300	-0.89575300
C	-4.64883900	-1.78504900	0.69722100
H	-2.71812600	-1.24790800	1.50001800
C	-5.72675900	-1.36138600	-0.07982100
H	-6.56211100	0.23682800	-1.25298200
H	-4.65864100	-2.77173000	1.14887200
H	-6.57466700	-2.02125100	-0.23460100
H	-1.49764100	3.70145400	-1.45376100
H	-0.65770900	2.03602100	-1.25090000

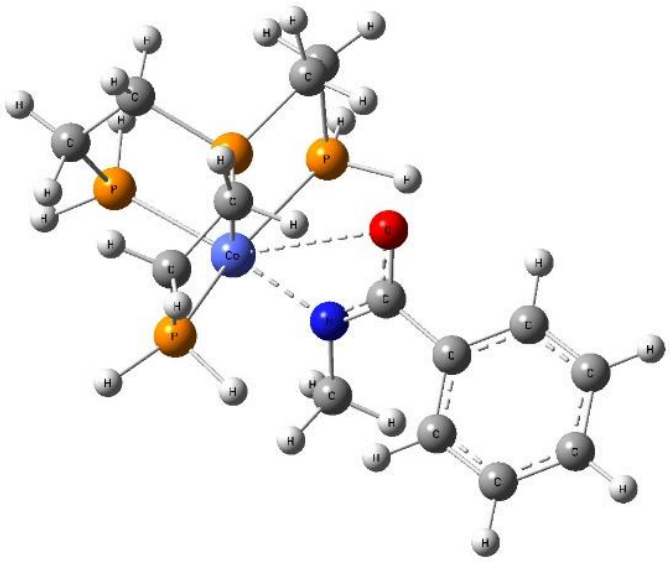
TS2"$_{H\ (H)}$



SCF done	-2189.02403058
SCF done for solvent	-2189.03981904
Zero-point correction	0.370740
Thermal correction to Gibbs free energy	0.315490

C	-2.19876100	-1.56983300	2.22511000
C	-1.72459300	-0.13264500	2.48735400
C	-4.31470700	0.57725200	-0.18295300
C	-3.46891700	1.51388200	0.69486000
C	-0.63163100	2.25822500	1.11749300
C	-0.25330000	2.78040800	-0.27661800
Co	-1.16555700	-0.47536200	-0.86730700
H	-1.98052300	-2.21666600	3.07817300
H	-3.28394200	-1.58691900	2.07171700
H	-2.30639500	0.35361400	3.27719400
H	-0.66957400	-0.14554000	2.77930500
H	-4.55032900	-0.33868200	0.37112300
H	-3.95276500	1.70706800	1.65833000
H	-5.26364300	1.04880700	-0.45063500
H	0.25609300	1.85375700	1.61640800
H	-1.06233700	3.04532500	1.74492400
H	-3.34968300	2.48128100	0.18992000
H	-1.11473400	3.27365900	-0.74252200
H	0.55346500	3.51525100	-0.22249000
P	-1.42291500	-2.21294800	0.64103400
P	-1.75929900	0.81105900	0.89986700
P	-3.35901800	0.02142200	-1.70928400
P	0.18664200	1.33585700	-1.38980300
C	1.34259700	-1.90534500	-1.51770000
H	-0.36172400	-1.52222100	-1.88237700
H	-4.39097000	-0.76937400	-2.27451100
H	-3.65282200	1.15036100	-2.52231500
H	1.58748200	1.28321300	-1.17689800
H	0.26510000	2.03065200	-2.61963500
H	-0.26301000	-2.84355300	1.12689400
H	-2.21616300	-3.37372000	0.48307600
C	2.01323600	-0.91543700	0.48963000
N	1.65990500	-2.00507600	-0.26158300
O	1.27617400	-0.43035900	1.34707900
C	3.39747700	-0.34753200	0.29865300
C	4.32122500	-0.92249400	-0.57607300
C	3.74858600	0.80032100	1.01534100
C	5.57860000	-0.34699900	-0.74086200
H	4.05299700	-1.82710600	-1.11081200
C	5.00245200	1.37426700	0.85031500
H	3.01965300	1.21970500	1.70120900
C	5.91912100	0.80124300	-0.03127100
H	6.29469300	-0.79778000	-1.42052900
H	5.27031100	2.26546500	1.40906800
H	6.90021400	1.24784000	-0.16016000
H	1.17538100	-2.82549300	-2.07326100
H	1.61508400	-1.03852700	-2.12635100

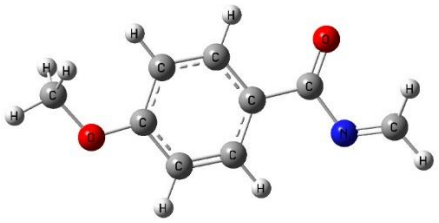
I5"$_{H\ (H)}$



SCF done	-2189.10138854
SCF done for solvent	-2189.11328009
Zero-point correction	0.376203
Thermal correction to Gibbs free energy	0.321458

C	-0.99391200	-2.31617800	1.74760000
C	-0.81780800	-0.90374400	2.33645600
C	-4.04945300	-0.87022900	0.33857600
C	-3.46735200	0.00819800	1.46010400
C	-1.37990300	2.04922700	1.69378700
C	-1.66705500	2.91371200	0.44926100
Co	-0.99389700	-0.18991500	-1.06601100
H	-0.38398500	-3.03908500	2.29492700
H	-2.03721300	-2.63612300	1.86156900
H	-1.21072900	-0.87252800	3.35845900
H	0.23521700	-0.60727700	2.34361200
H	-3.75341500	-1.91681900	0.47710800
H	-3.68036400	-0.42782400	2.44304000
H	-5.14211700	-0.84006900	0.32670500
H	-0.33168700	2.13896000	1.97946100
H	-2.02173500	2.35465300	2.52683500
H	-3.95189700	0.99226400	1.43263100
H	-2.74559600	2.91518500	0.23897600
H	-1.37972300	3.95257400	0.63038200
P	-0.61948500	-2.44842700	-0.10077200
P	-1.63369000	0.29179000	1.19858500
P	-3.33402900	-0.35391200	-1.30953500
P	-0.85970600	2.28162900	-1.13313600

C	1.60714600	-0.70531100	-2.24110600
H	1.03137800	-0.35544800	-3.10597800
H	-4.11701400	-1.15725100	-2.16977300
H	-4.06337200	0.84219500	-1.50866500
H	0.45661800	2.74183700	-0.94068400
H	-1.28798200	3.36082500	-1.95083900
H	0.77052800	-2.68367400	-0.04173000
H	-0.99769300	-3.81336200	-0.21322500
C	1.72478400	0.32888300	-0.03617900
N	1.01000700	-0.16331800	-1.03740000
O	1.20353500	0.95453700	0.92189600
C	3.22689300	0.15281900	0.03482900
C	3.85482300	-1.06772300	-0.22050000
C	3.99515800	1.22743400	0.48699700
C	5.22958200	-1.20661000	-0.04651200
H	3.26216400	-1.91814200	-0.54718500
C	5.37098200	1.09926600	0.63866300
H	3.48729500	2.15539000	0.72910900
C	5.99192600	-0.12009400	0.37269400
H	5.70502300	-2.16386200	-0.23735100
H	5.96066600	1.94629200	0.97576000
H	7.06493800	-0.22525300	0.50034600
H	1.56634600	-1.80722300	-2.26350100
H	2.65000700	-0.40569000	-2.38620400

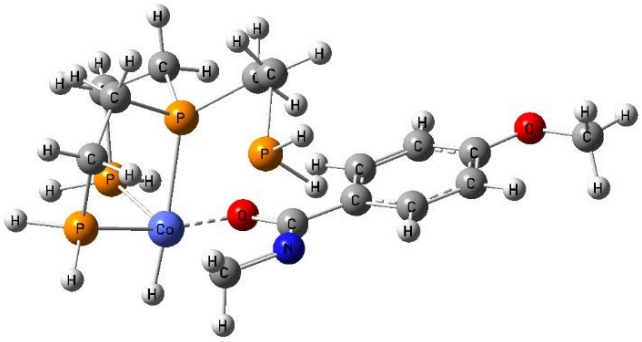


SCF done	-553.31742641
SCF done for solvent	-553.32576419
Zero-point correction	0.166522
Thermal correction to Gibbs free energy	0.129280

C	0.75889400	0.12744900	-0.10021600
C	0.25658400	-1.18027700	-0.14842000
C	-1.10639900	-1.40420300	-0.09376000
C	-1.99228800	-0.32298300	0.00546300
C	-1.50098100	0.98680400	0.05153800
C	-0.12936800	1.19831800	-0.00118000
H	0.94869100	-2.00984500	-0.23849900

H	-1.52216600	-2.40475200	-0.13331100
H	-2.17167400	1.83363900	0.12656000
H	0.27640100	2.20427900	0.03313900
O	2.66636700	1.54085700	-0.17267100
C	2.21007100	0.41766400	-0.14272900
C	4.15638400	-0.62760000	0.41832600
H	4.44407600	0.28850600	0.94523300
H	4.85930800	-1.46037100	0.40302600
N	3.04470400	-0.74732700	-0.17884200
O	-3.30496600	-0.64582100	0.04772300
C	-4.24247600	0.40748900	0.12449700
H	-4.16917500	1.07066100	-0.74528800
H	-5.22521400	-0.06251100	0.13969600
H	-4.10691200	0.99544300	1.03981500

$I4_{H\ (OMe)}$

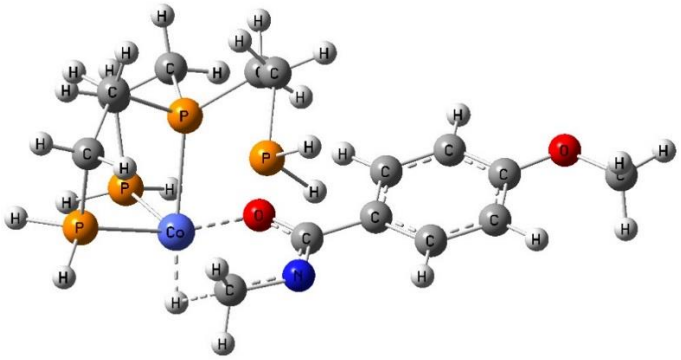


SCF done	-2303.53817220
SCF done for solvent	-2303.56181425
Zero-point correction	0.406177
Thermal correction to Gibbs free energy	0.347568

C	0.20497200	2.83449500	1.65324300
C	0.06425300	1.31524400	1.74827600
C	3.80929800	1.49899000	0.21279000
C	3.08899900	1.08119700	1.50791600
C	1.33464600	-1.14019300	2.31378900
C	2.29856400	-2.28902400	2.00542600
Co	1.65748000	-0.81070400	-1.07521300
H	-0.73200500	3.28529900	1.98933000
H	0.98893000	3.18484100	2.33353200
H	-0.10440600	1.03682700	2.79495600

H	-0.81192400	0.98574100	1.17652000
H	3.27280500	2.33986800	-0.23798000
H	2.95800300	1.94969800	2.16126000
H	4.83523800	1.81878900	0.41297300
H	0.29854400	-1.48896900	2.21898700
H	1.47268800	-0.77846500	3.33914900
H	3.69363800	0.35388700	2.06375300
H	3.33527400	-1.96889200	2.16483700
H	2.11827400	-3.13890200	2.66796700
P	0.65597200	3.45208000	-0.05750100
P	1.45776800	0.26527000	1.10154600
P	3.76378300	0.15191800	-1.07690200
P	2.17167400	-2.76552000	0.20690800
C	-0.93129000	-0.33056900	-1.14795100
H	1.85479400	-1.47142900	-2.34052000
O	-0.18535800	-1.35785200	-0.81283400
H	4.24923700	0.83959700	-2.20333600
H	4.93853000	-0.57364600	-0.77418900
H	1.08137100	-3.65354900	0.22464800
H	3.20896100	-3.71862300	0.13255000
H	-0.50189600	3.02105500	-0.74331900
H	0.23969900	4.79089200	0.14506000
C	-2.35815600	-0.39270700	-0.71119900
C	-3.24606600	0.63913800	-1.01048200
C	-2.82124700	-1.48290700	0.03410100
C	-4.57094200	0.59637500	-0.58364000
H	-2.87909800	1.47706300	-1.59454600
C	-4.13696500	-1.54067400	0.46410500
H	-2.12731600	-2.28654500	0.25645100
C	-5.01925500	-0.50022500	0.15686800
H	-5.23824300	1.41181900	-0.83600800
H	-4.51454300	-2.38155400	1.03634400
N	-0.49921600	0.71724000	-1.76073500
C	0.88291400	0.60563900	-2.17993900
H	0.93859000	0.37090500	-3.24793800
H	1.40232700	1.56396900	-2.02888500
O	-6.29137900	-0.64570900	0.62099300
C	-7.22050200	0.35970000	0.29124000
H	-8.17144600	0.05245300	0.72679700
H	-6.92803200	1.33110100	0.70929400
H	-7.33483800	0.46049400	-0.79506400

$TS2_{H\ (OMe)}$

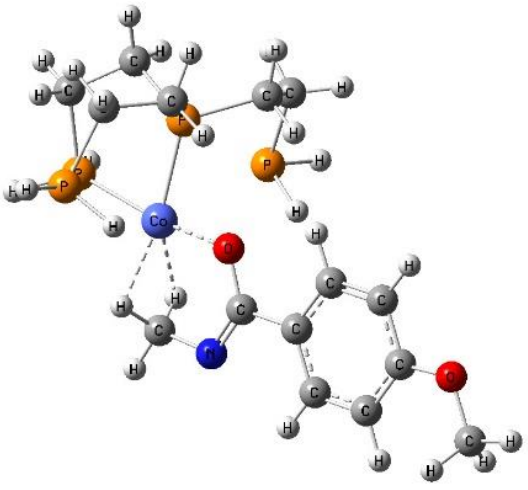


SCF done	-2303.53546662
SCF done for solvent	-2303.55752650
Zero-point correction	0.405738
Thermal correction to Gibbs free energy	0.349021

C	0.24400000	2.70897800	1.79859000
C	0.25221400	1.19256300	1.99095700
C	3.84805600	1.59440100	0.17922300
C	3.24721900	1.08859700	1.50411700
C	1.63488600	-1.23832900	2.29166800
C	2.58116700	-2.34216700	1.81160100
Co	1.60157100	-0.68121000	-1.08025100
H	-0.69426000	3.10563300	2.19314700
H	1.05485500	3.16521100	2.37681500
H	0.25392800	0.95710900	3.06158500
H	-0.65838000	0.75311500	1.56086100
H	3.24951500	2.43468200	-0.18888300
H	3.13889400	1.91753900	2.21109200
H	4.87637800	1.94022100	0.31220000
H	0.60089700	-1.60510600	2.28248100
H	1.87248500	-0.93762100	3.31868800
H	3.91721400	0.35637100	1.97162500
H	3.62203800	-1.99985900	1.86663600
H	2.50078000	-3.22829700	2.44563200
P	0.48931900	3.23135700	0.01412200
P	1.61634200	0.24238800	1.16746800
P	3.74399100	0.30357100	-1.16673200
P	2.25303800	-2.73341700	0.01645900
C	-1.02058800	-0.34719000	-1.16549300
H	1.50794400	-1.06918600	-2.46281300
O	-0.19991000	-1.21534500	-0.62702300
H	4.21221200	1.04270200	-2.27042700
H	4.92862400	-0.42973200	-0.92795600

H	1.17222900	-3.62710000	0.13149600
H	3.27022600	-3.69015200	-0.19701000
H	-0.62059200	2.55734400	-0.55142100
H	-0.13577500	4.49804400	0.12177400
C	-2.43435300	-0.40054400	-0.68590000
C	-3.40674400	0.43800700	-1.22746700
C	-2.79908300	-1.27434100	0.34403000
C	-4.71887300	0.41448600	-0.76285000
H	-3.11293400	1.11071800	-2.02647200
C	-4.09993300	-1.30542700	0.82134300
H	-2.04082900	-1.93240100	0.75548200
C	-5.06720600	-0.46056600	0.26904900
H	-5.45339000	1.07592000	-1.20671300
H	-4.40064900	-1.97661400	1.61888500
N	-0.68555600	0.54865000	-2.02937900
C	0.71302700	0.56990100	-2.36683400
H	0.84174500	0.50288700	-3.45095200
H	1.17161100	1.52552600	-2.06526300
O	-6.31637200	-0.56166600	0.80246900
C	-7.32639800	0.24636000	0.24554400
H	-8.24100600	0.01166500	0.79010200
H	-7.09919600	1.31333300	0.36283300
H	-7.47253200	0.02939300	-0.81980600

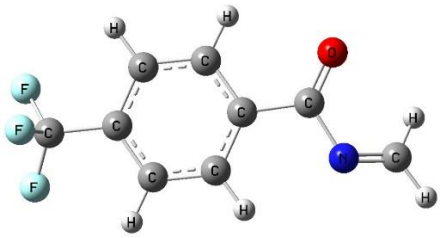
$I5_{H\ (OMe)}$



SCF done	-2303.58680665
SCF done for solvent	-2303.60501191
Zero-point correction	0.409222
Thermal correction to Gibbs free energy	0.347745

C	2.35655600	-2.43496600	-2.05350400
C	1.70067200	-1.08774400	-2.36664900
C	4.54829900	-0.26547400	-0.05842900
C	3.87911700	0.53735100	-1.18752000
C	1.27950000	1.69222700	-2.01755700
C	1.59585600	3.06375900	-1.41456300
Co	1.32583400	-0.10834600	0.96655100
H	2.00092900	-3.17445400	-2.77426600
H	3.44298300	-2.36246800	-2.18327800
H	1.98488200	-0.75705800	-3.37321400
H	0.60906300	-1.19546000	-2.34507900
H	4.52688700	-1.33583700	-0.28583700
H	4.31985000	0.29703100	-2.16127200
H	5.59371000	0.02492000	0.07024600
H	0.20351900	1.49565600	-1.93314000
H	1.54448800	1.67651800	-3.08148700
H	4.03482500	1.60872500	-1.01142200
H	2.63016200	3.34661900	-1.63871000
H	0.95410300	3.80994300	-1.88799300
P	2.04663700	-3.05413900	-0.29992500
P	2.04522400	0.25567300	-1.14807600
P	3.59795700	-0.07825200	1.54062100
P	1.39787400	3.13851500	0.45720400
C	-1.44857900	-0.21262900	1.11808300
H	0.56150500	0.55332700	2.68990800
O	-0.46419200	-0.07957000	0.26960400
H	4.31252400	-0.98663300	2.34800200
H	4.18140500	1.10512200	2.04447100
H	0.04492700	2.72400200	0.50294100
H	1.10715000	4.52707400	0.51116600
H	0.63695900	-2.92866700	-0.31431100
H	2.04918400	-4.43523800	-0.63110600
C	-2.82341400	-0.15887300	0.53302000
C	-3.95038300	-0.28453300	1.34201800
C	-3.00273200	0.02325000	-0.84153600
C	-5.23366100	-0.23060100	0.80472600
H	-3.80109300	-0.42522400	2.40716600
C	-4.27283700	0.08018000	-1.39224000
H	-2.12387700	0.11438400	-1.47082600
C	-5.39627100	-0.04573100	-0.57006700
H	-6.09005000	-0.33061900	1.46090600
H	-4.42946000	0.22045100	-2.45659200
N	-1.33554700	-0.38174600	2.39587400
C	0.02280000	-0.41585500	2.85824300
H	0.07984500	-0.57830100	3.93594400
H	0.61113300	-1.26321800	2.41468800
O	-6.60296500	0.02386500	-1.19883600
C	-7.75554400	-0.11880900	-0.40284600
H	-7.82271500	0.67222200	0.35439700

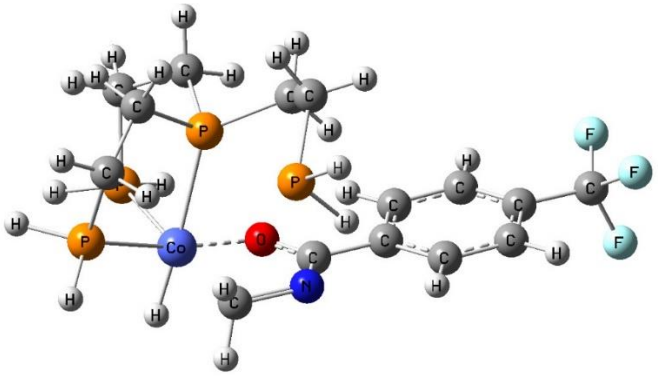
H	-8.60667700	-0.04206700	-1.07955600
H	-7.77924800	-1.09382000	0.09967100



SCF done	-775.77107260
SCF done for solvent	-775.77761071
Zero-point correction	0.138728
Thermal correction to Gibbs free energy	0.098493

C	1.38412800	0.19668000	0.11469200
C	0.77187200	-1.05548500	0.19714800
C	-0.61318800	-1.15066500	0.12878300
C	-1.37481300	0.00469700	-0.02047700
C	-0.76972400	1.25813000	-0.09929400
C	0.61253900	1.35215500	-0.03101000
H	1.38478400	-1.94100900	0.31890700
H	-1.10447000	-2.11595300	0.18518200
H	-1.38078300	2.14561600	-0.22246500
H	1.11763900	2.31010700	-0.09367700
O	3.41631800	1.42579100	0.19266900
C	2.86714700	0.34770100	0.15935400
C	4.67859500	-0.88879500	-0.45193100
H	5.02787800	-0.02093300	-1.02139700
H	5.29955200	-1.78374400	-0.43718300
N	3.58679700	-0.88387200	0.19282400
C	-2.87441100	-0.09893800	-0.04564600
F	-3.39079000	-0.04898300	1.19094000
F	-3.42707800	0.90145200	-0.74469300
F	-3.27942000	-1.25315700	-0.59404800

$I4_{H\ (CF3)}$

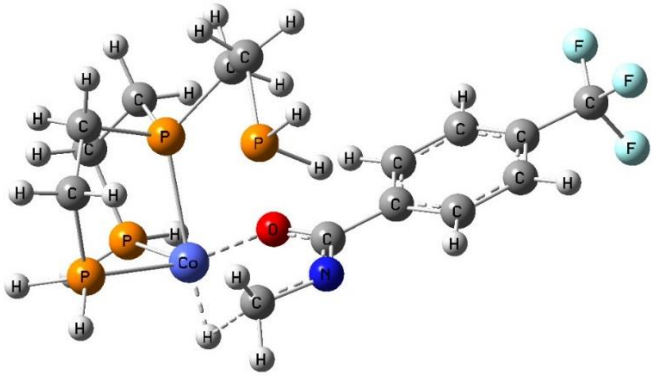


SCF done	-2525.99734604
SCF done for solvent	-2526.01899410
Zero-point correction	0.378677
Thermal correction to Gibbs free energy	0.318540

C	0.72079300	2.81868600	1.69869600
C	0.55260900	1.30069000	1.76460800
C	4.30721200	1.40215100	0.18788100
C	3.57857600	1.04415300	1.49583600
C	1.82967000	-1.15537600	2.34913200
C	2.75525000	-2.32625500	2.00667600
Co	2.08391000	-0.84896500	-1.05676400
H	-0.21336400	3.28080700	2.02696700
H	1.49950600	3.14312900	2.39743000
H	0.36214200	1.00603700	2.80285500
H	-0.32026500	0.99711900	1.17387600
H	3.78912100	2.23995500	-0.28922100
H	3.45559300	1.94079100	2.11154300
H	5.33990600	1.70576000	0.37792300
H	0.78392400	-1.48450600	2.30692000
H	2.02067200	-0.78745900	3.36381600
H	4.17285800	0.33361500	2.08352800
H	3.80473100	-2.02270300	2.10464800
H	2.59629300	-3.16455300	2.68901000
P	1.21122700	3.45305300	0.00514900
P	1.93670300	0.23642000	1.11904900
P	4.23191900	0.01568600	-1.05595100
P	2.52100500	-2.81779200	0.22305800
C	-0.47319600	-0.23849200	-1.21043900
H	2.24961800	-1.51176800	-2.32294900
O	0.20826200	-1.28988500	-0.82638000
H	4.75476400	0.64337900	-2.20017200
H	5.37427000	-0.74303500	-0.71056700
H	1.39799400	-3.66092100	0.30664400

H	3.51394400	-3.81289700	0.10509200
H	0.04805000	3.06946400	-0.70102900
H	0.83061800	4.79954400	0.22444300
C	-1.92399200	-0.22791800	-0.83905100
C	-2.74211700	0.84768700	-1.20035500
C	-2.45933500	-1.28069600	-0.09539300
C	-4.07695700	0.86876800	-0.82257300
H	-2.30300400	1.65250300	-1.77992800
C	-3.79780400	-1.26515300	0.28293800
H	-1.80950000	-2.10623700	0.17225500
C	-4.60160700	-0.18883400	-0.07955800
H	-4.71499800	1.70377100	-1.09341000
H	-4.21966800	-2.07898000	0.86328800
N	0.02023900	0.78115200	-1.82128600
C	1.41838700	0.62018200	-2.16827700
H	1.51835100	0.41386800	-3.23880700
H	1.96159300	1.55592800	-1.96653700
C	-6.05619400	-0.18302600	0.28259600
F	-6.49988700	1.05829500	0.54029300
F	-6.30665600	-0.93244400	1.36802800
F	-6.82313000	-0.66690200	-0.70841400

$TS2_{H\ (CF3)}$

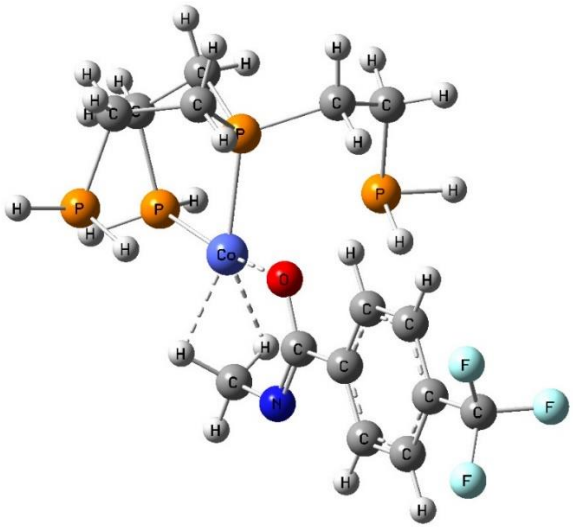


SCF done	-2525.99468298
SCF done for solvent	-2526.01455147
Zero-point correction	0.377380
Thermal correction to Gibbs free energy	0.315932

C	0.85265600	2.74142100	1.84022500
C	0.78671500	1.22647900	2.03525200
C	4.40229800	1.42613400	0.20361000

C	3.76503600	0.96983400	1.52898000
C	2.04934600	-1.27351200	2.32026700
C	2.93162300	-2.42330500	1.82573100
Co	2.03076600	-0.71072400	-1.06337500
H	-0.06331900	3.18587200	2.23623100
H	1.68676800	3.15749500	2.41551700
H	0.78807200	0.99192700	3.10594900
H	-0.14922300	0.83337100	1.61613600
H	3.85655300	2.29591700	-0.17693700
H	3.69386800	1.81379500	2.22272200
H	5.44797000	1.71304700	0.34092500
H	0.99872900	-1.58968600	2.32932300
H	2.31762500	-0.98597700	3.34344300
H	4.39307600	0.21195000	2.01345400
H	3.98926400	-2.13399300	1.86322000
H	2.81699900	-3.30421000	2.46175400
P	1.12379900	3.24487700	0.05503400
P	2.09260500	0.20764300	1.19642000
P	4.23266400	0.13269100	-1.13125600
P	2.55256800	-2.79755400	0.03741900
C	-0.56231400	-0.22357000	-1.24305300
H	1.92823300	-1.07672900	-2.45024100
O	0.18564900	-1.12441100	-0.65990300
H	4.74931600	0.83111600	-2.23890200
H	5.36780100	-0.67113900	-0.87783900
H	1.41963100	-3.62153100	0.17379200
H	3.50372300	-3.81568000	-0.19138900
H	-0.04012700	2.66247500	-0.50210800
H	0.59812200	4.55484000	0.16580900
C	-2.00558200	-0.21438900	-0.84304700
C	-2.89533800	0.70409900	-1.40919900
C	-2.46216200	-1.10708700	0.12773400
C	-4.22419300	0.72503700	-1.01166200
H	-2.51471200	1.39025500	-2.15763300
C	-3.79368000	-1.08885900	0.53060800
H	-1.75596500	-1.81186300	0.55238300
C	-4.67004100	-0.17171700	-0.04021400
H	-4.91975800	1.43826000	-1.44202500
H	-4.15438800	-1.77721800	1.28751800
N	-0.15156900	0.65105400	-2.09396900
C	1.26228200	0.60585500	-2.36261800
H	1.43898300	0.55926800	-3.44081300
H	1.75154800	1.52964500	-2.01437000
C	-6.11911700	-0.17790700	0.34267300
F	-6.85847900	-0.90861500	-0.50865000
F	-6.31439400	-0.69284100	1.56734900
F	-6.64194800	1.05926700	0.33866100

$I5_{H\ (CF3)}$

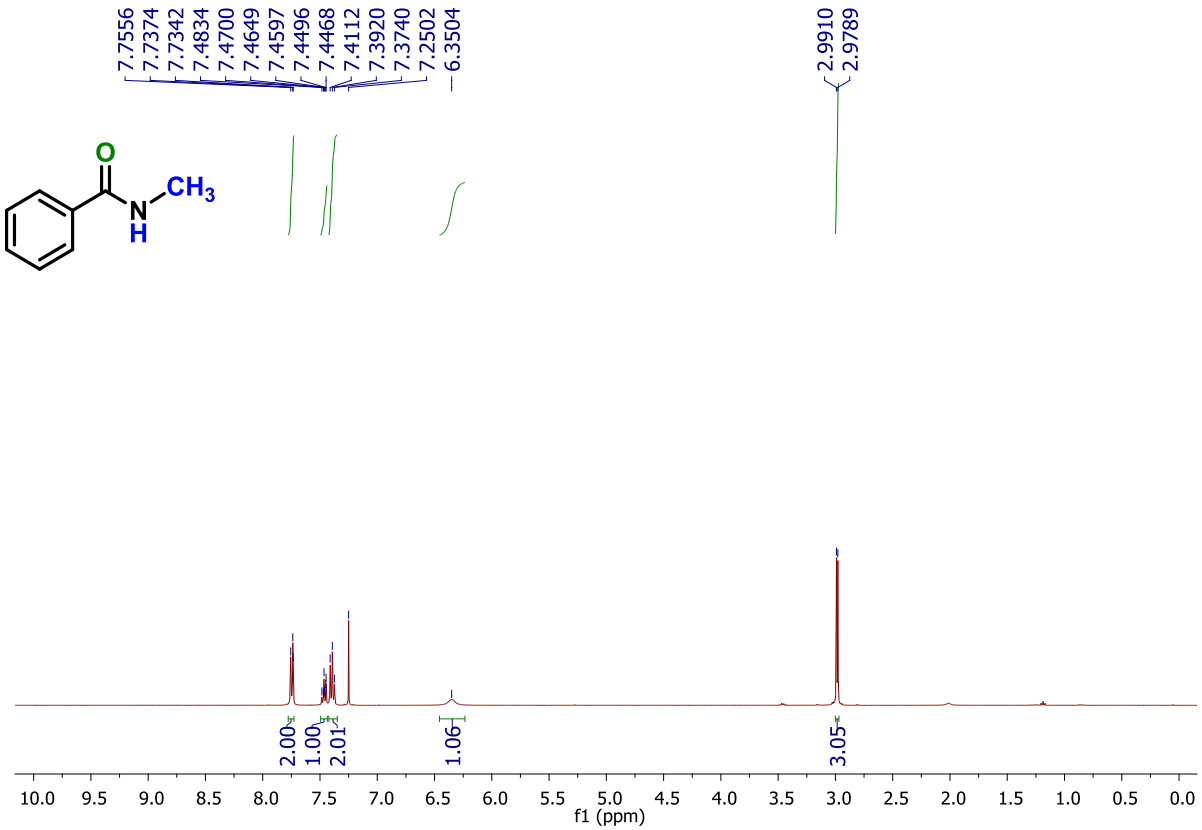


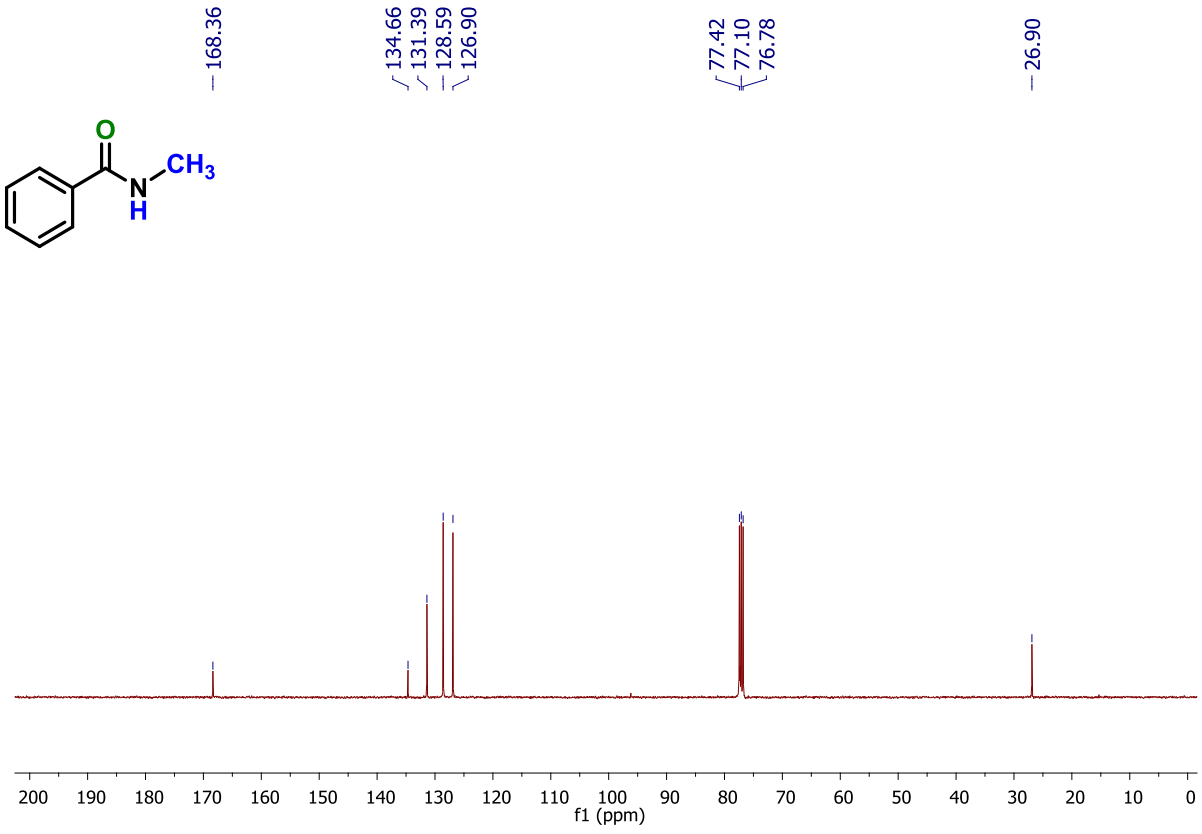
SCF done	-2526.04582771
SCF done for solvent	-2526.06147750
Zero-point correction	0.380930
Thermal correction to Gibbs free energy	0.315877

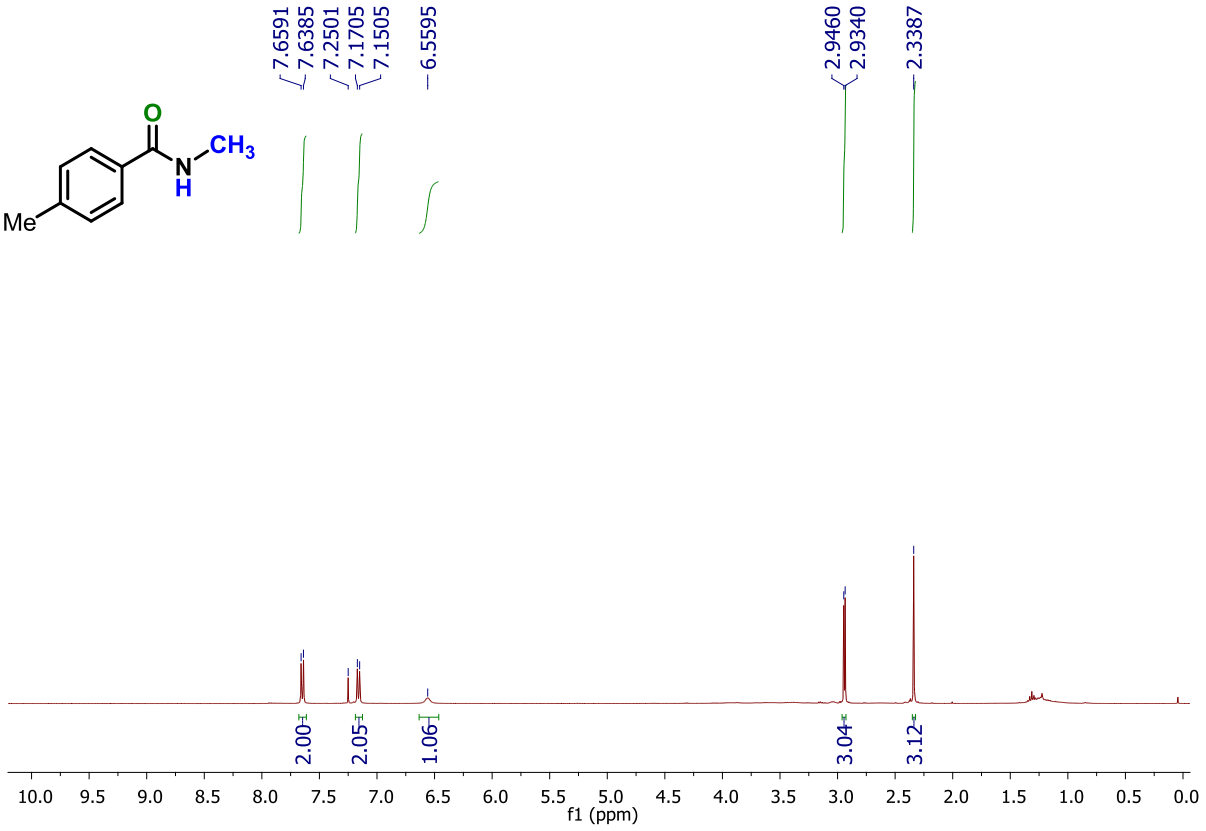
C	2.68348400	-2.46699200	-2.08632100
C	2.01440900	-1.12308300	-2.38541900
C	5.00084000	-0.26911300	-0.26762700
C	4.26200000	0.51026500	-1.36911700
C	1.62197300	1.66507700	-2.05164800
C	1.98070700	3.04407300	-1.49047200
Co	1.85382600	-0.09145700	0.96094500
H	2.28951900	-3.21683200	-2.77566200
H	3.76136500	-2.39827000	-2.27535900
H	2.24680900	-0.80850000	-3.41033400
H	0.92513100	-1.22675600	-2.30701100
H	4.96134200	-1.34429300	-0.46823400
H	4.63730500	0.24326200	-2.36309300
H	6.05316400	0.01957500	-0.21420200
H	0.55192700	1.47711000	-1.89997500
H	1.82138500	1.63164000	-3.12927500
H	4.43306900	1.58470100	-1.23079200
H	3.00053600	3.31839800	-1.78143500
H	1.31452300	3.78622300	-1.93543200
P	2.46742300	-3.05577900	-0.30878500
P	2.43269300	0.23723200	-1.20891600
P	4.15616600	-0.04235200	1.38264300

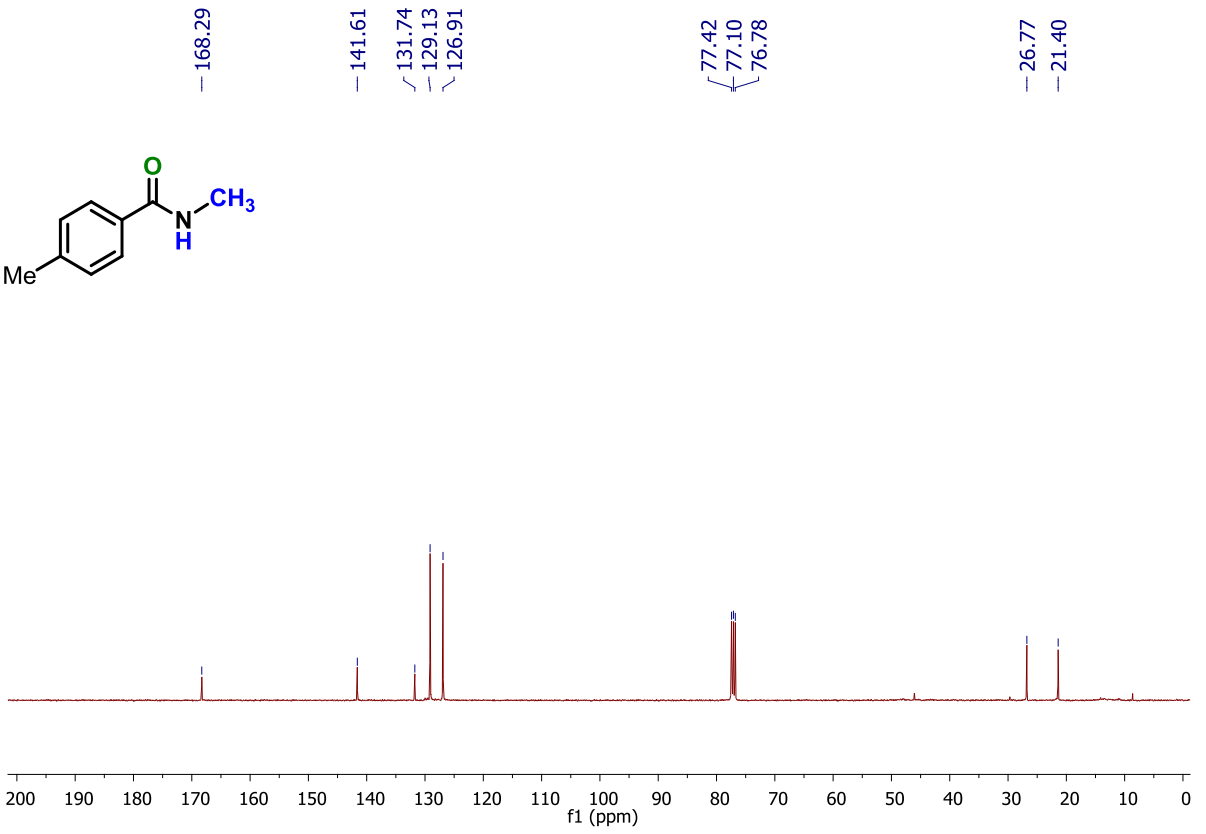
P	1.89735300	3.14817800	0.38830300
C	-0.90049800	-0.20584100	1.31374400
H	1.20465400	0.60651400	2.71467200
O	0.01376000	-0.08568900	0.39217200
H	4.91800600	-0.93322200	2.16635900
H	4.76681300	1.15178900	1.82263500
H	0.54777200	2.74352800	0.52136100
H	1.61766900	4.53848300	0.44031900
H	1.05730900	-2.94254100	-0.25680300
H	2.46608000	-4.44236000	-0.61271500
C	-2.32013800	-0.17437300	0.83170100
C	-3.37979200	-0.26017400	1.73844900
C	-2.59137400	-0.06017400	-0.53244300
C	-4.69222500	-0.22843900	1.28733600
H	-3.14592500	-0.35395100	2.79278700
C	-3.90342400	-0.03004800	-0.99015700
H	-1.75761300	-0.00220200	-1.22293800
C	-4.95100500	-0.11353100	-0.07759500
H	-5.51874500	-0.30098700	1.98639000
H	-4.11924500	0.04956600	-2.05062300
N	-0.69916900	-0.34601700	2.58283500
C	0.68988600	-0.36131700	2.94866600
H	0.82359700	-0.49538700	4.02312800
H	1.24839600	-1.21642000	2.48372800
C	-6.36462700	-0.02226000	-0.56712000
F	-7.22204100	-0.65416000	0.24870400
F	-6.78212200	1.25250900	-0.65575300
F	-6.50470800	-0.55676200	-1.79192300

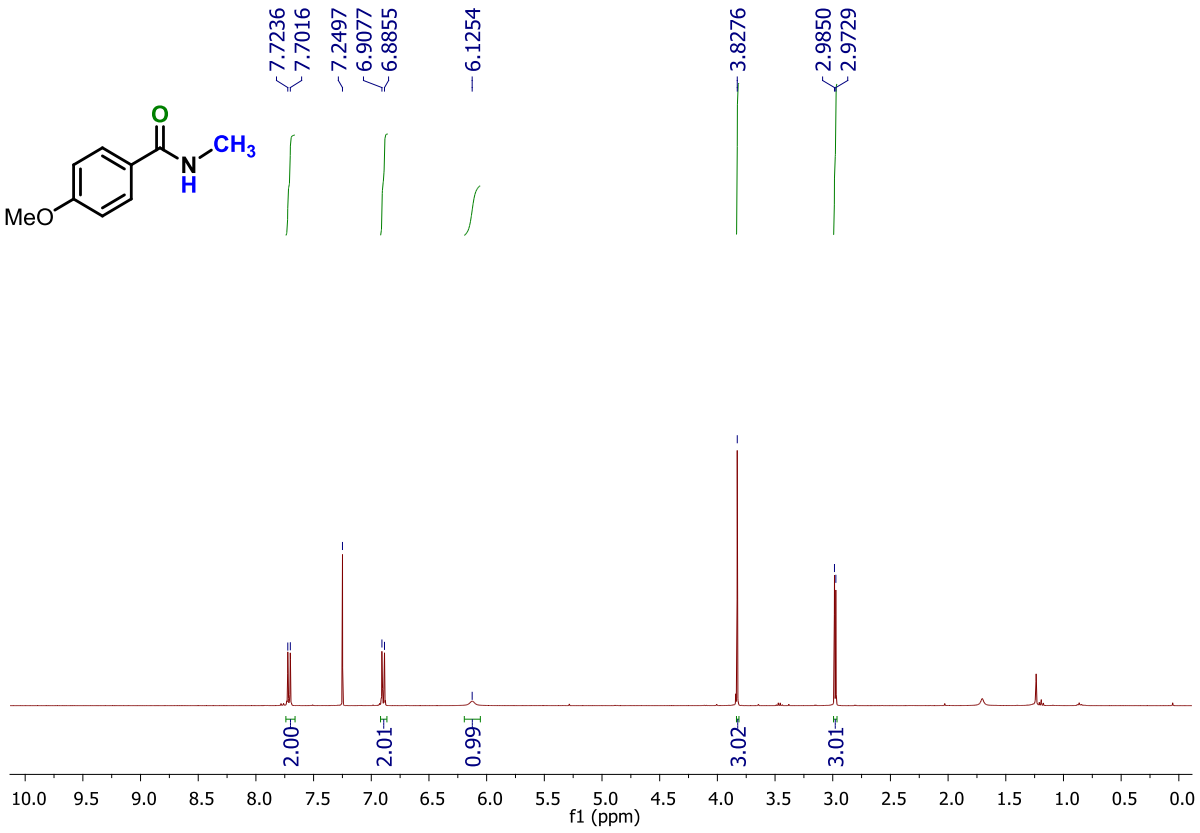
17. Copies of ^{1}H and ^{13}C NMR of the N-Methylated Amides

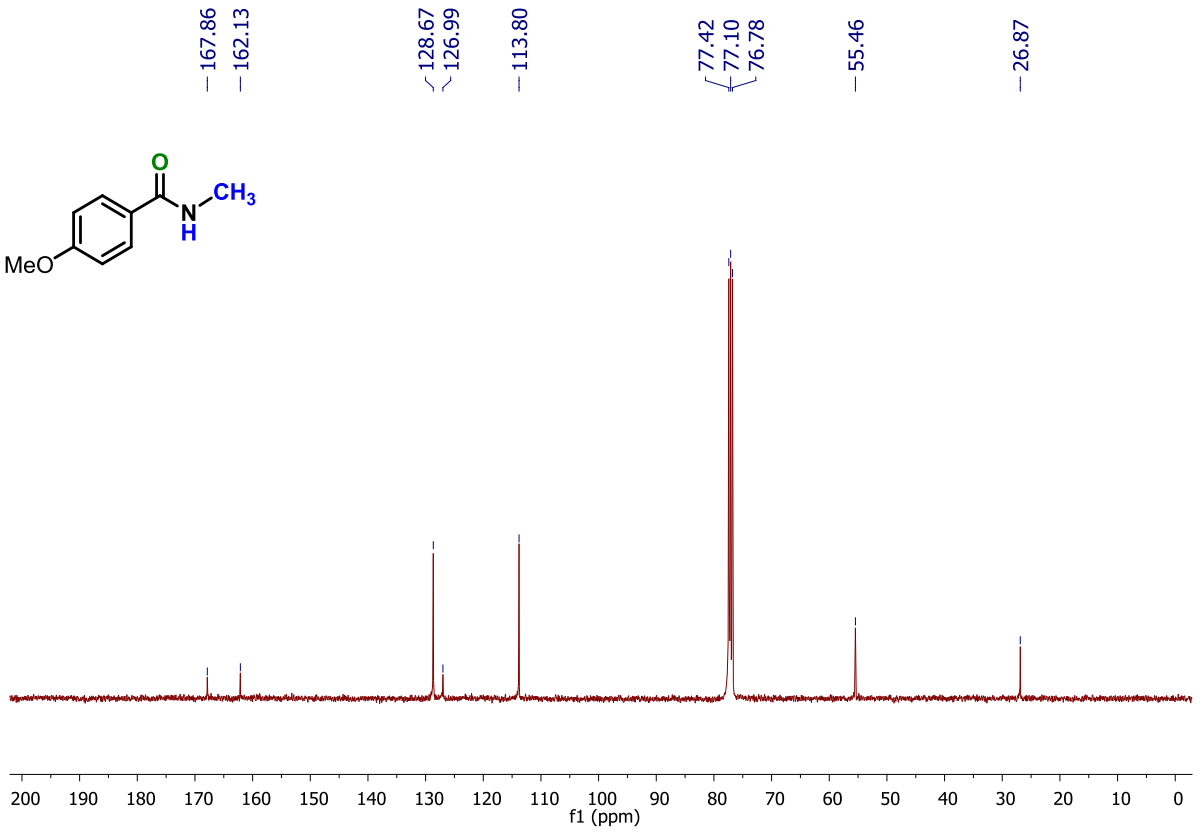


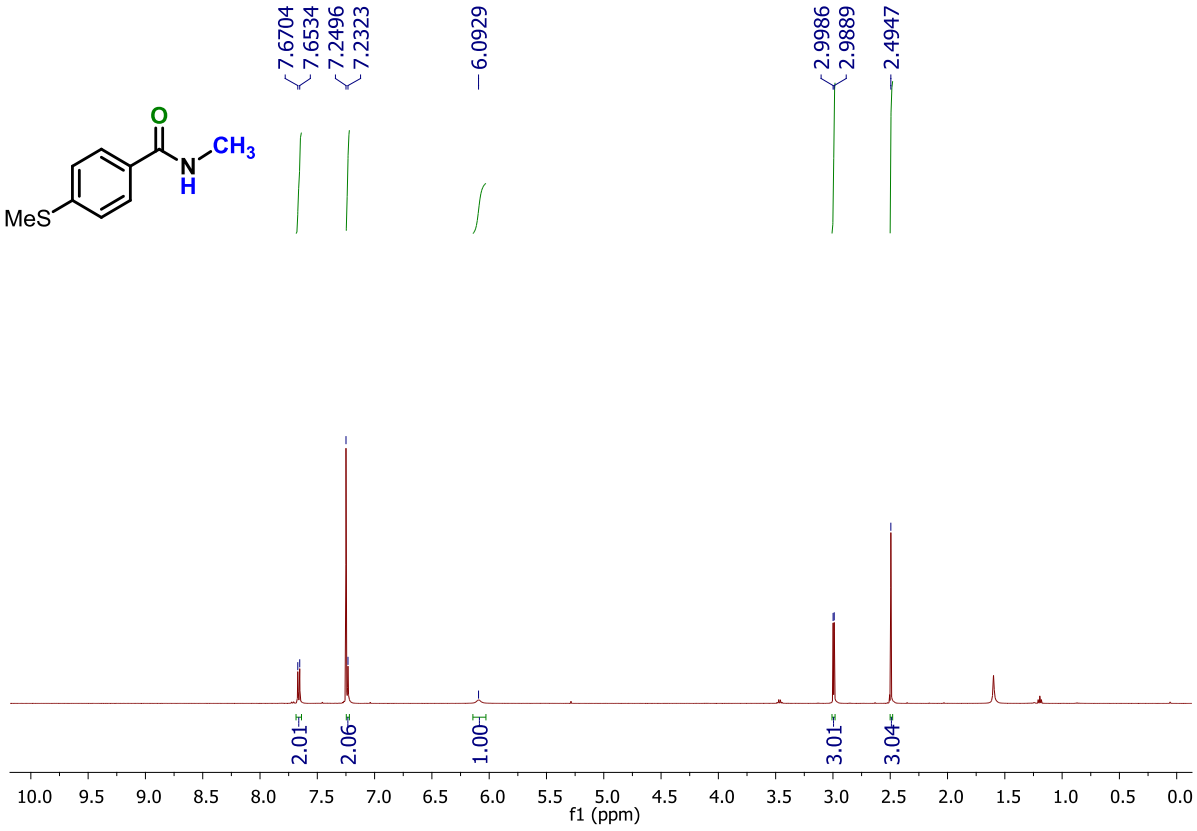


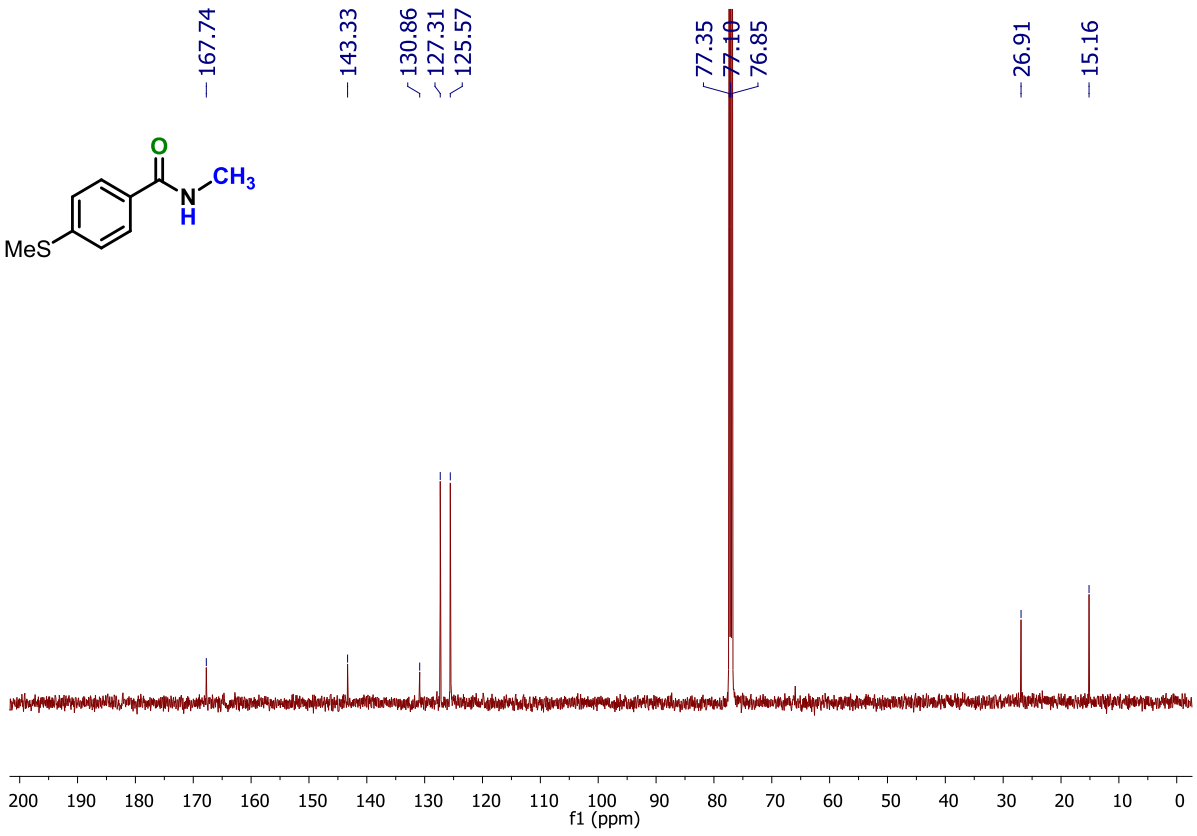

7.6591
7.6385
7.2501
7.1705
7.1505
6.5595
2.9460
2.9340
2.3387
O
N
H
CH3
Me
2.00
2.05
1.06
3.04
3.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

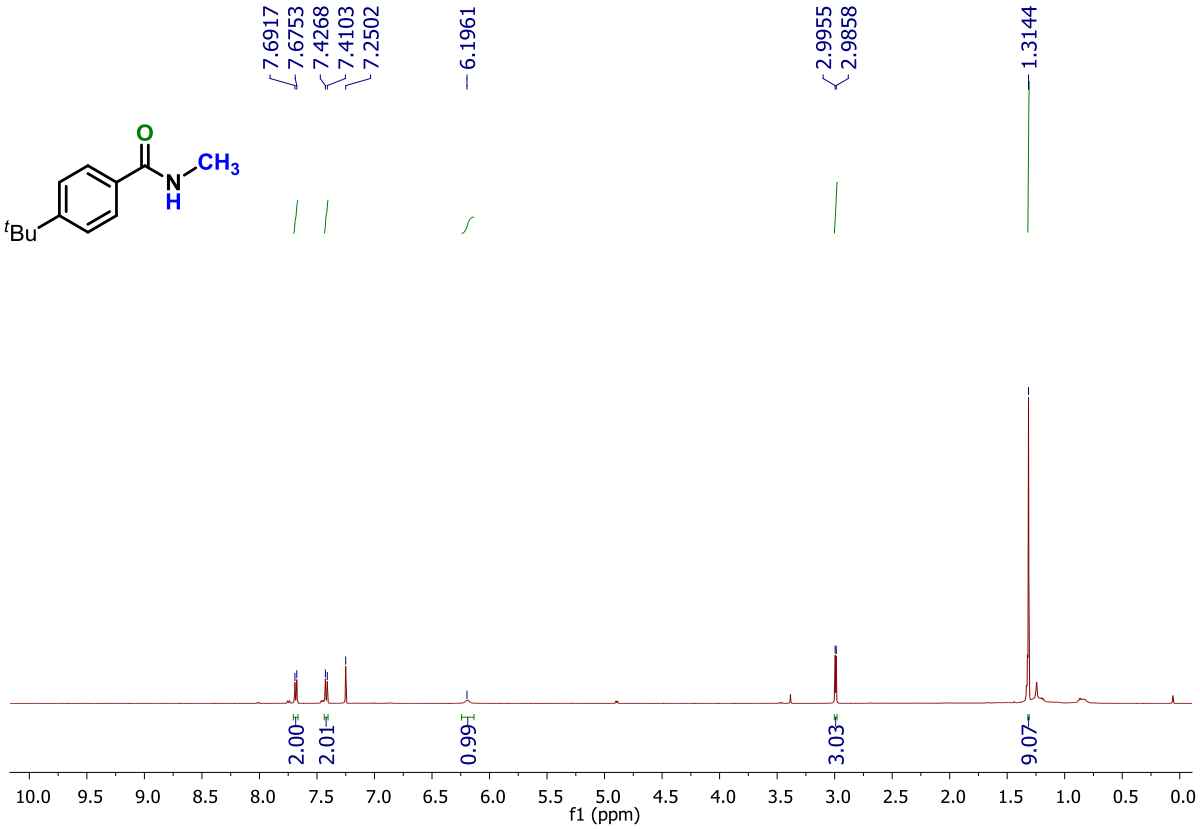

168.29
141.61
131.74
129.13
126.91
77.42
77.10
76.78
26.77
21.40
O
N
H
CH3
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

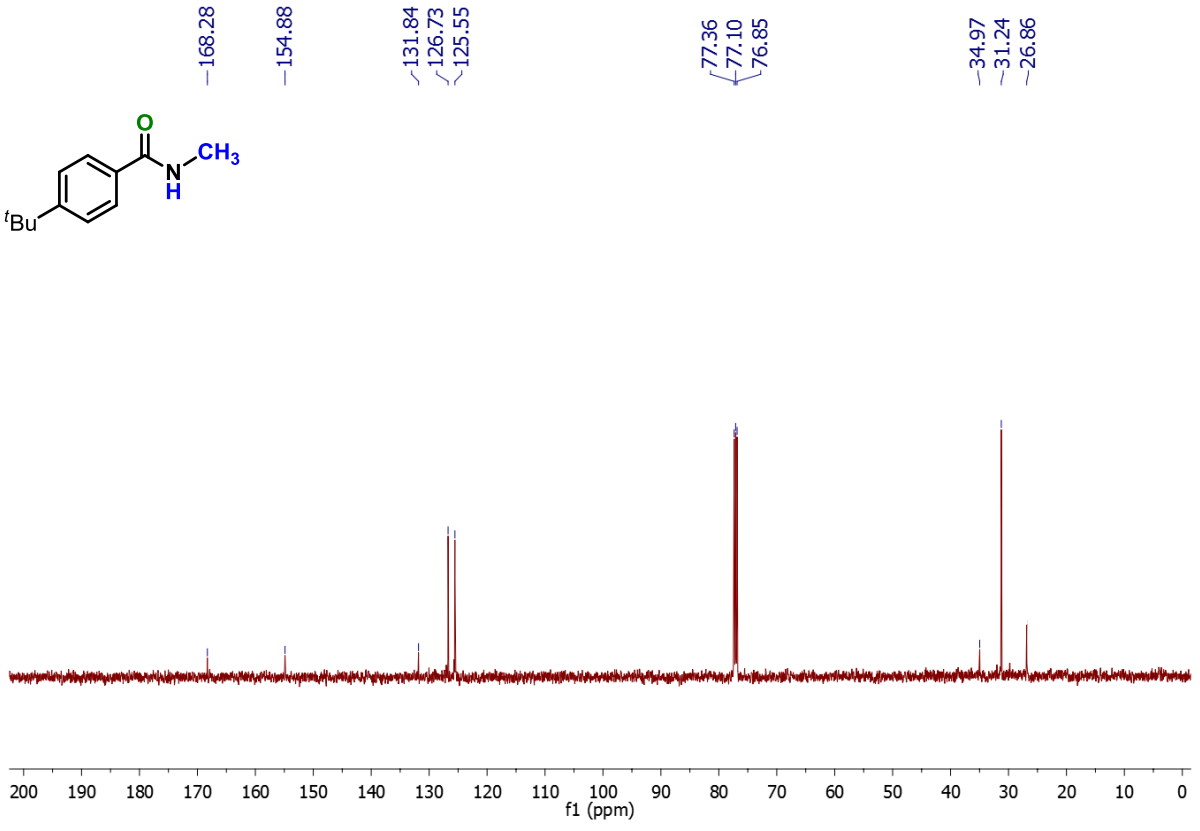

7.7236
7.7016
7.2497
6.9077
6.8855
6.1254
3.8276
2.9850
2.9729
O
N
H
CH3
MeO
2.00
2.01
0.99
3.02
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

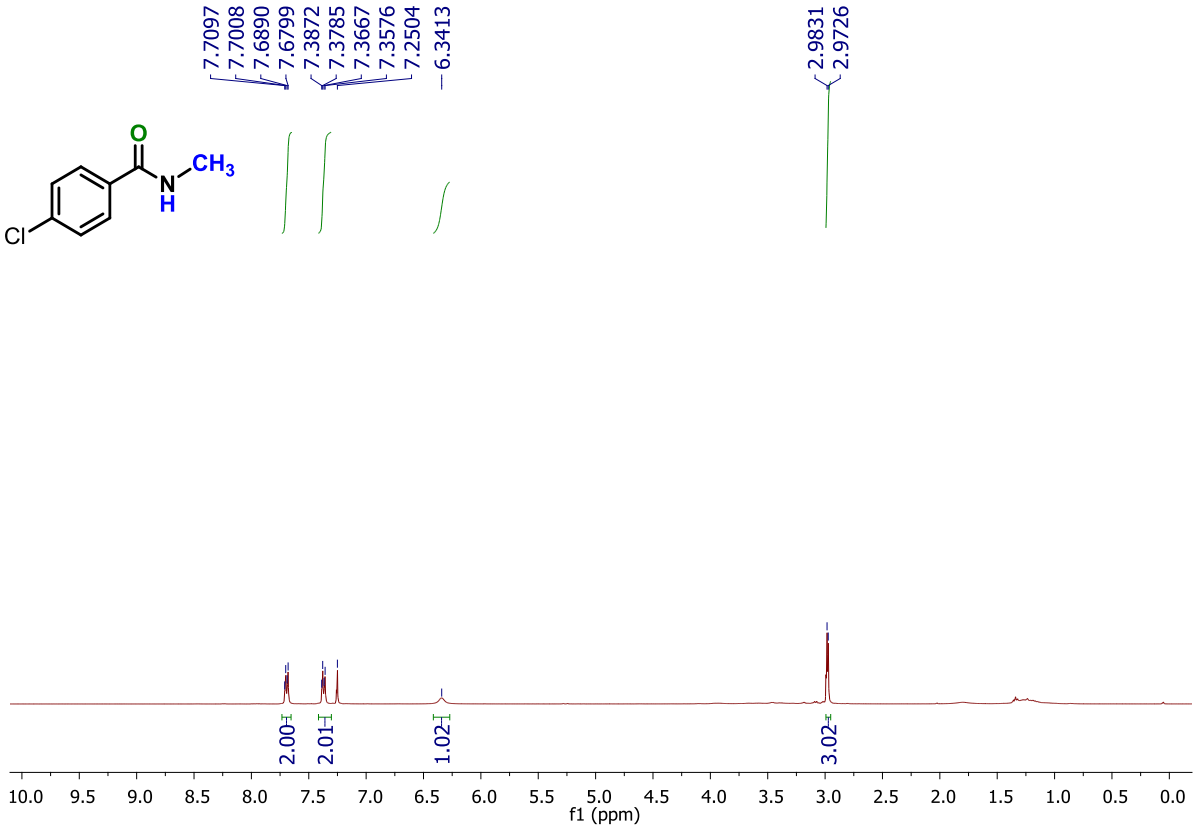

167.86
162.13
128.67
126.99
113.80
77.42
77.10
76.78
55.46
26.87
O
N
H
CH3
MeO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

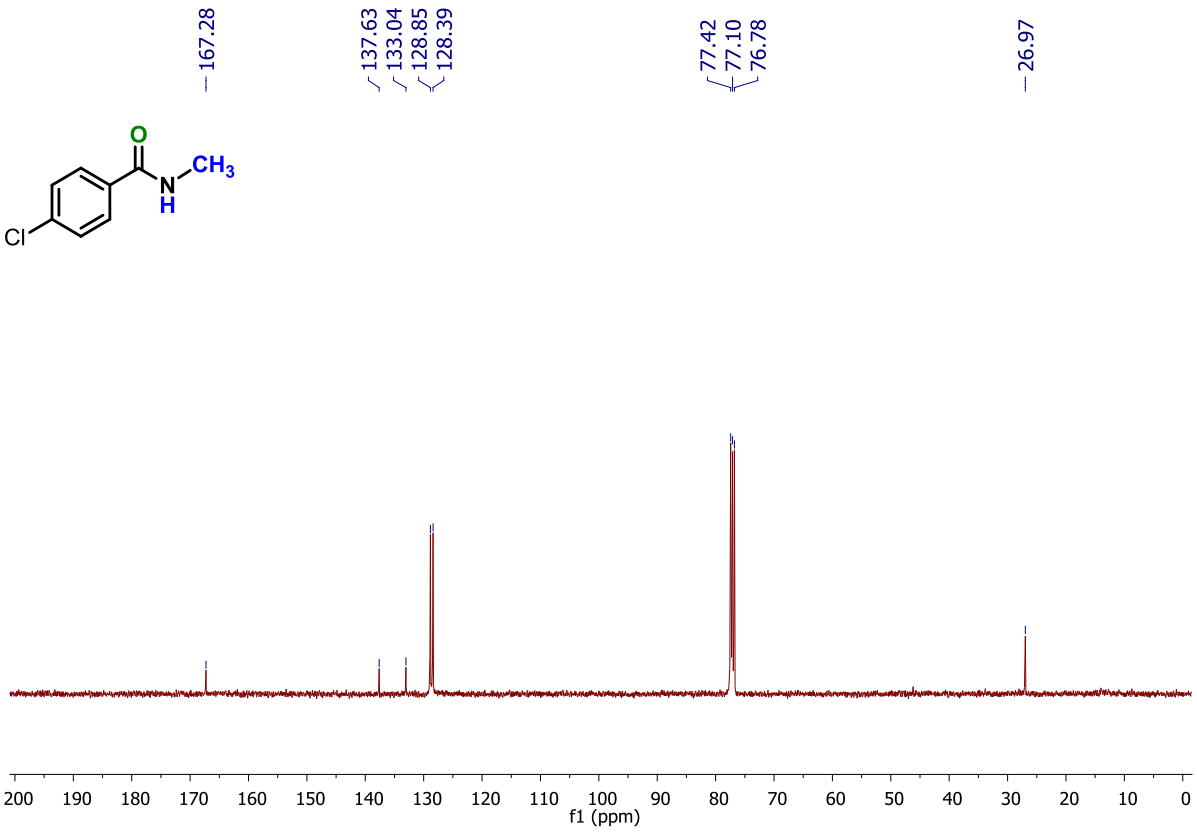

7.6704
7.6534
7.2496
7.2323
6.0929
2.9986
2.9889
2.4947
O
N
H
CH3
MeS
2.01
2.06
1.00
3.01
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

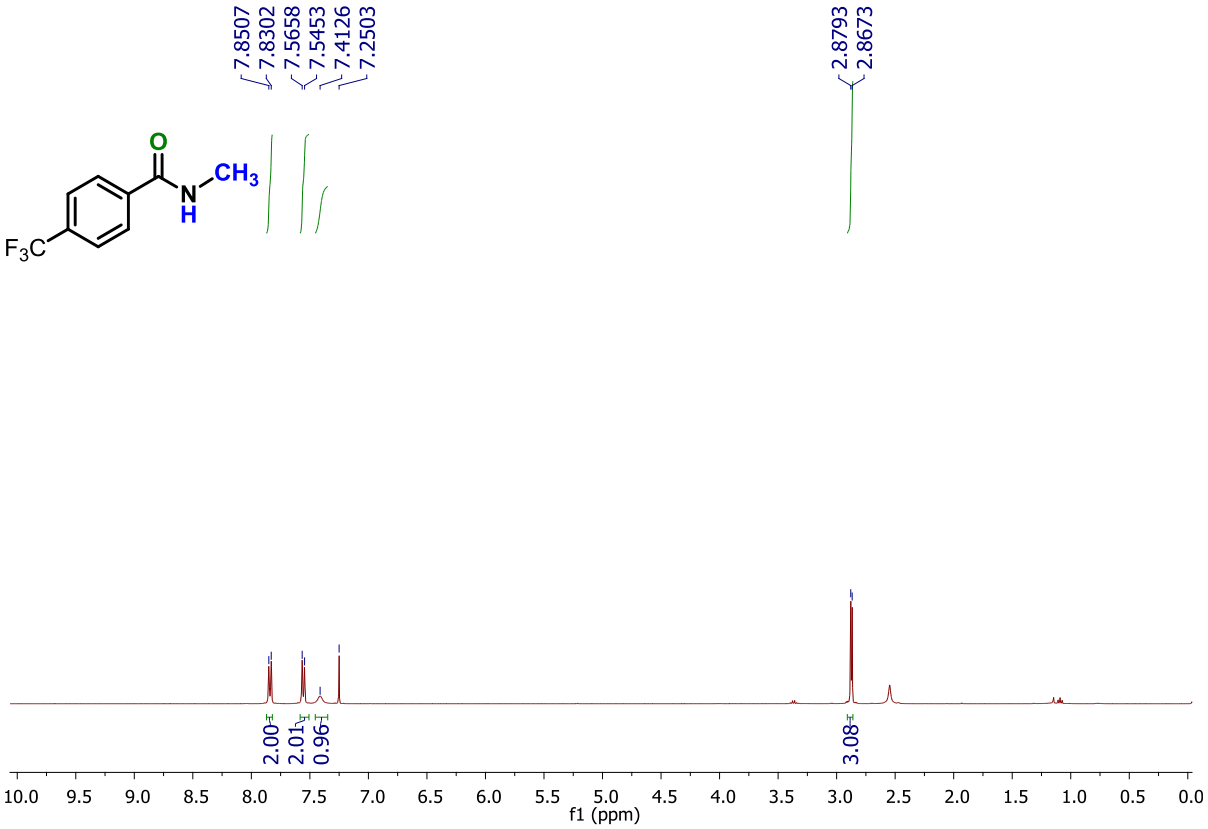

167.74
143.33
130.86
127.31
125.57
77.35
77.10
76.85
26.91
15.16
O
N
H
CH3
MeS
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

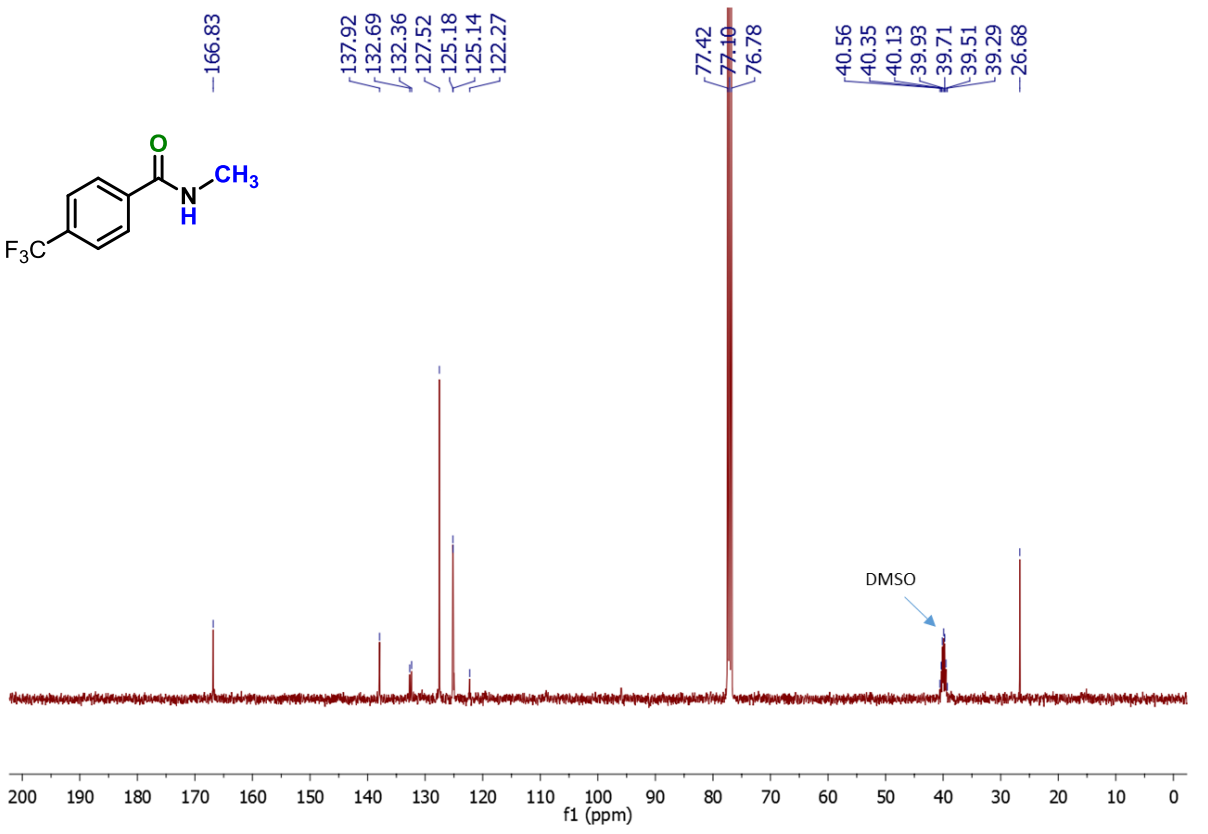

7.6917
7.6753
7.4268
7.4103
7.2502
6.1961
2.9955
2.9858
1.3144
O
N
H
CH3
tBu
2.00
2.01
0.99
3.03
9.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

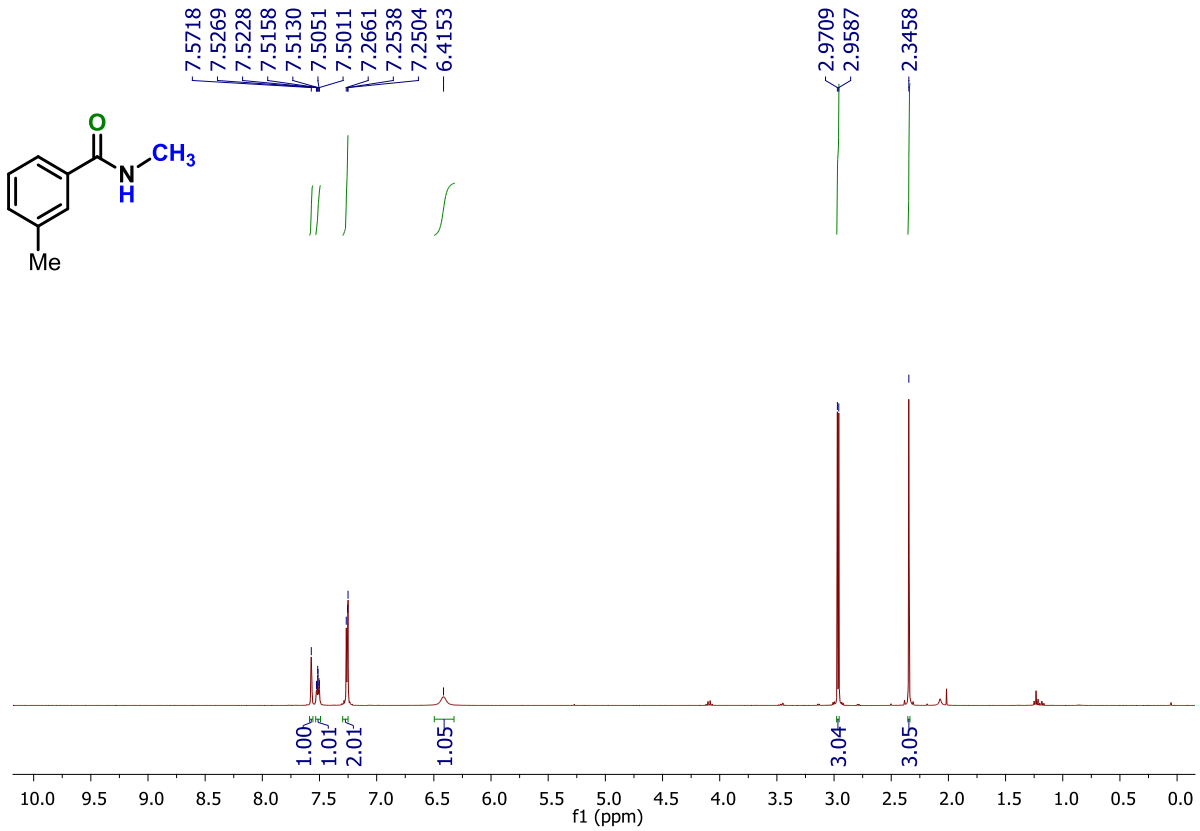

168.28
154.88
131.84
126.73
125.55
77.36
77.10
76.85
34.97
31.24
26.86
O
N
H
CH3
tBu
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

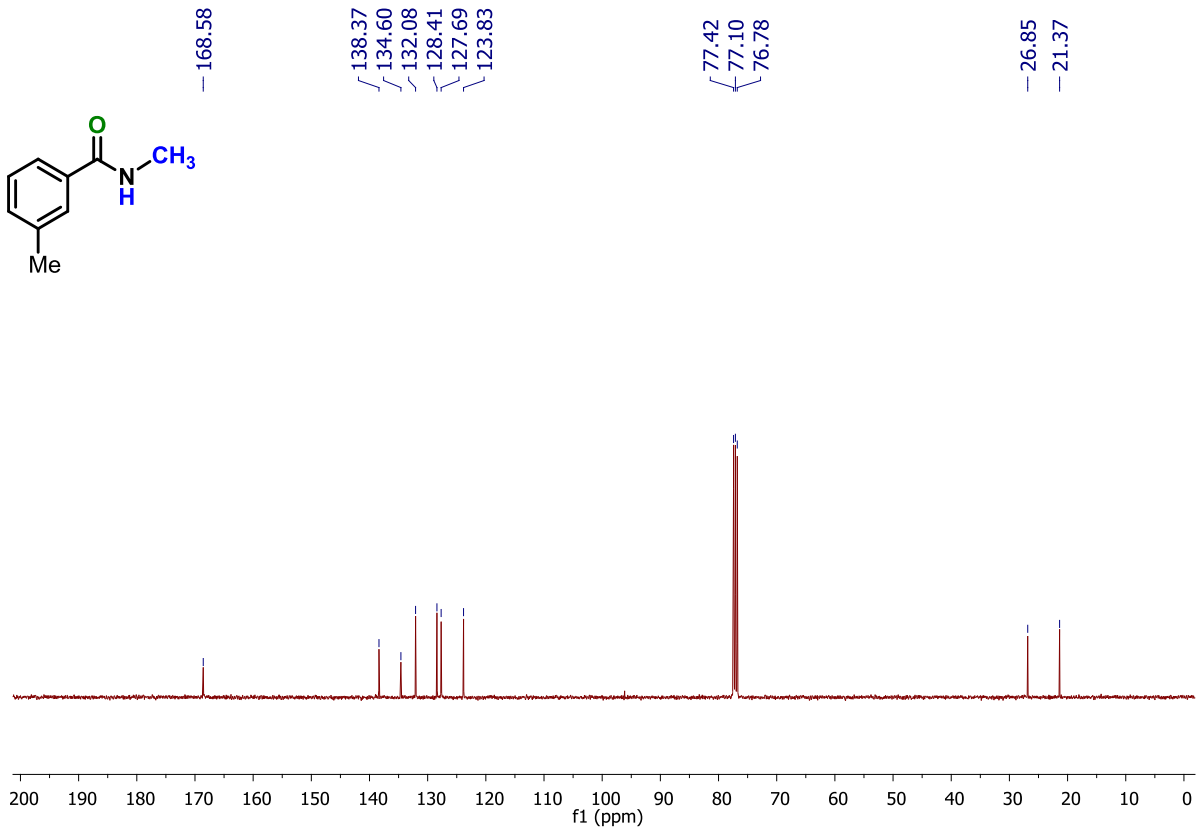

7.7097
7.7008
7.6890
7.6799
7.3872
7.3785
7.3667
7.3576
7.2504
6.3413
2.9831
2.9726
O
N
H
CH3
Cl
2.00
2.01
1.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

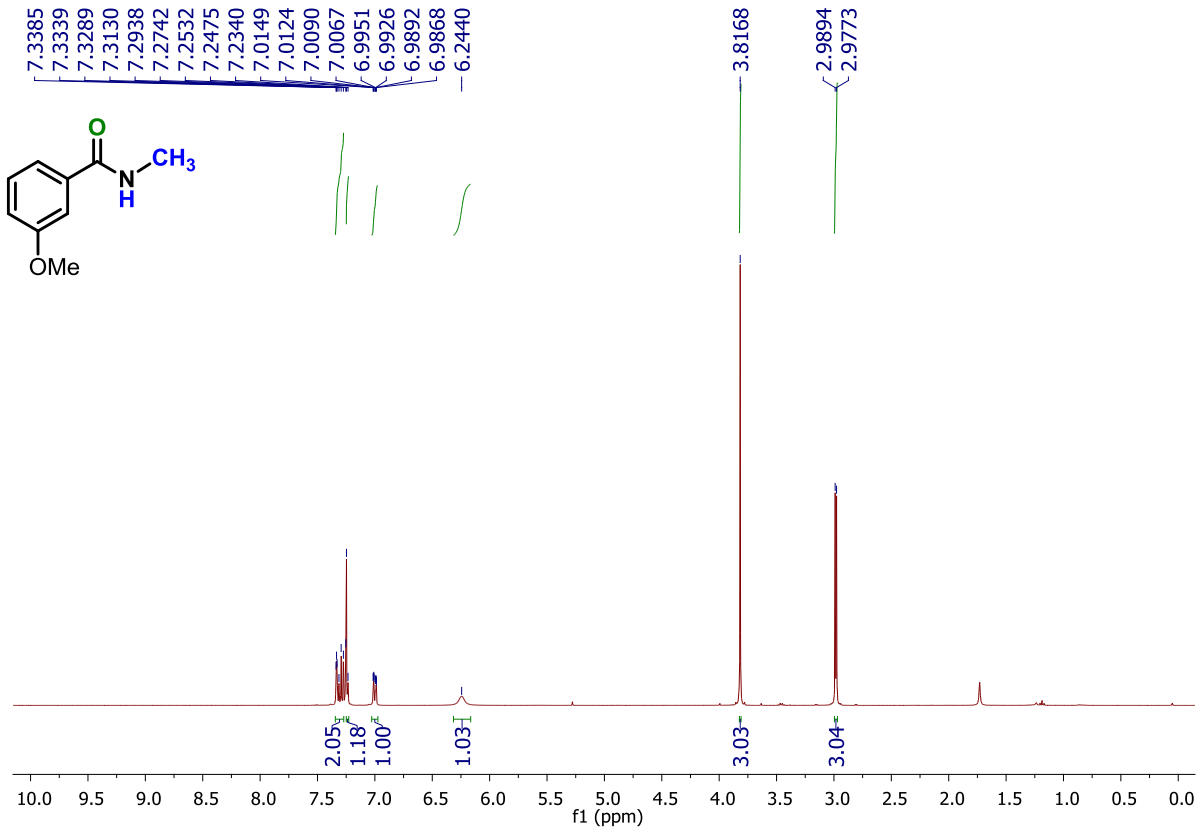

167.28
137.63
133.04
128.85
128.39
77.42
77.10
76.78
26.97
O
N
H
CH3
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

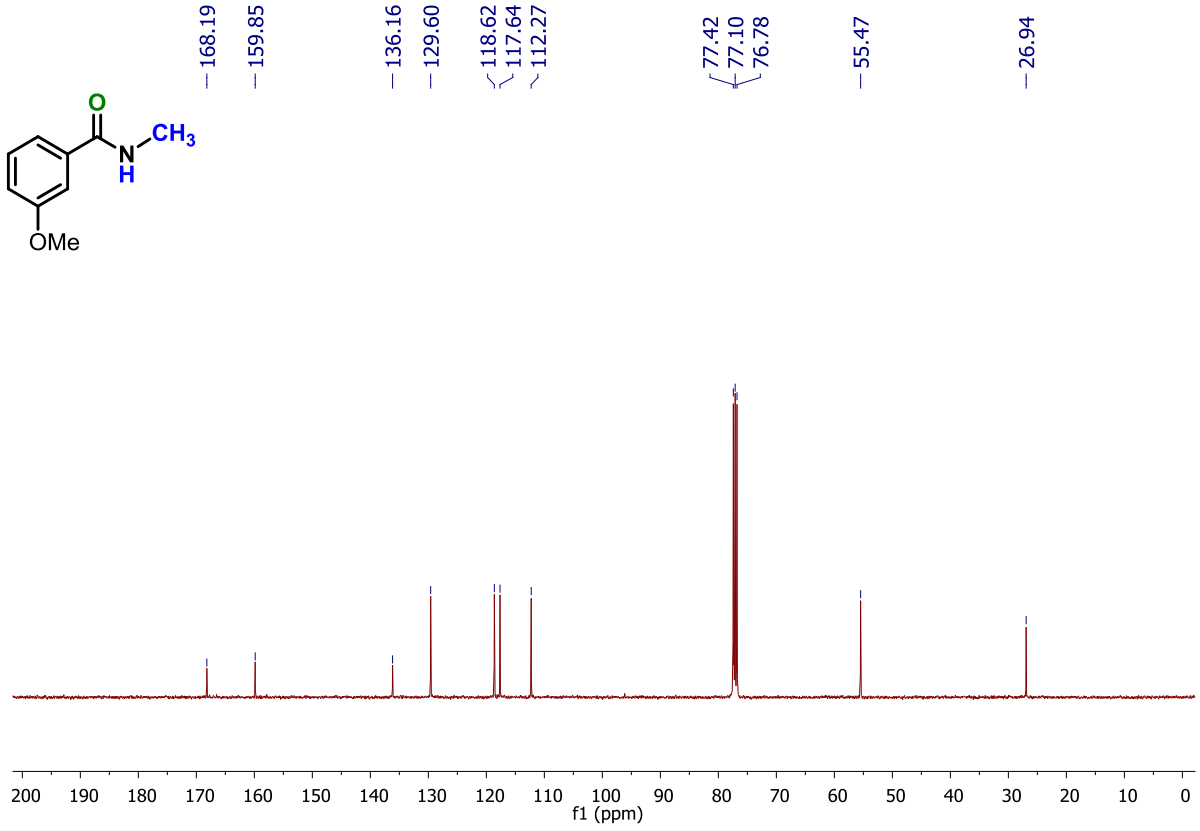

7.8507
7.8302
7.5658
7.5453
7.4126
7.2503
2.8793
2.8673
O
N
H
CH3
F3C
2.00
2.01
0.96
3.08
f1 (ppm)

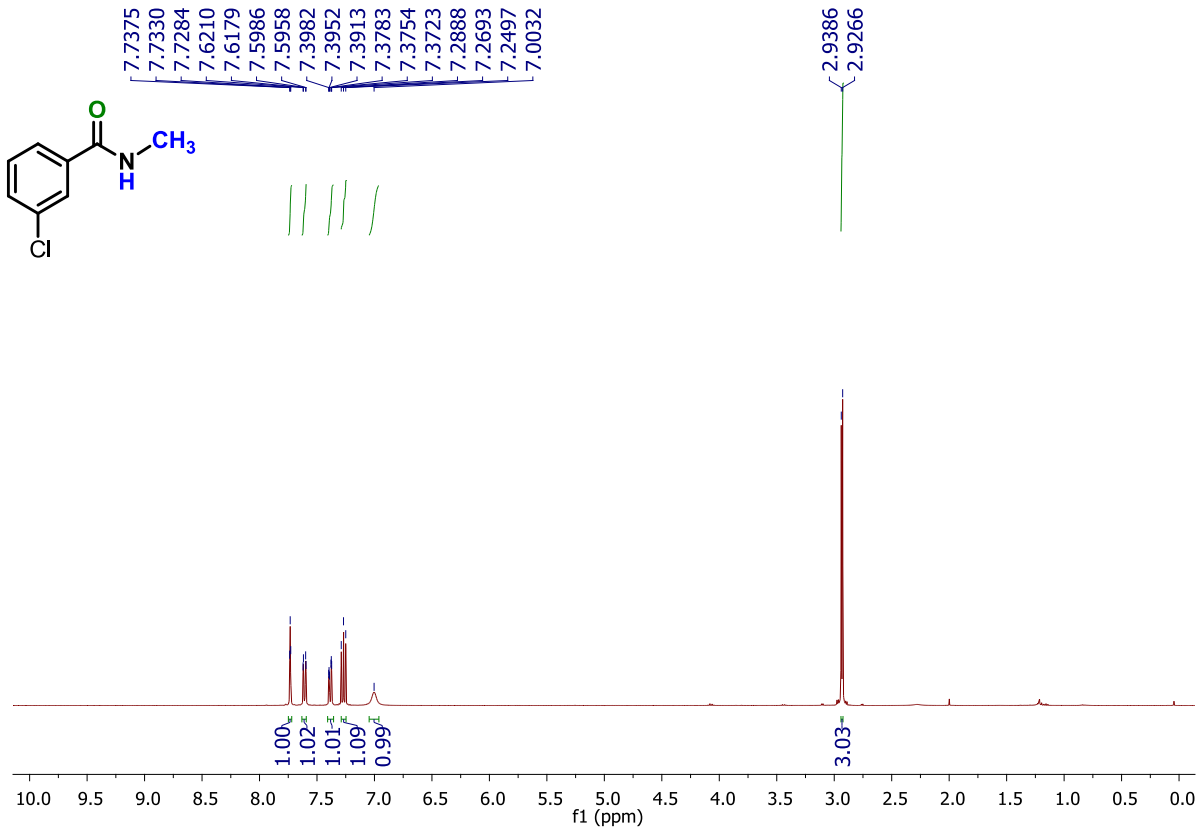

166.83
137.92
132.69
132.36
127.52
125.18
125.14
122.27
77.42
77.10
76.78
40.56
40.35
40.13
39.93
39.71
39.51
39.29
26.68
DMSO
O
N
H
CH3
F3C
f1 (ppm)

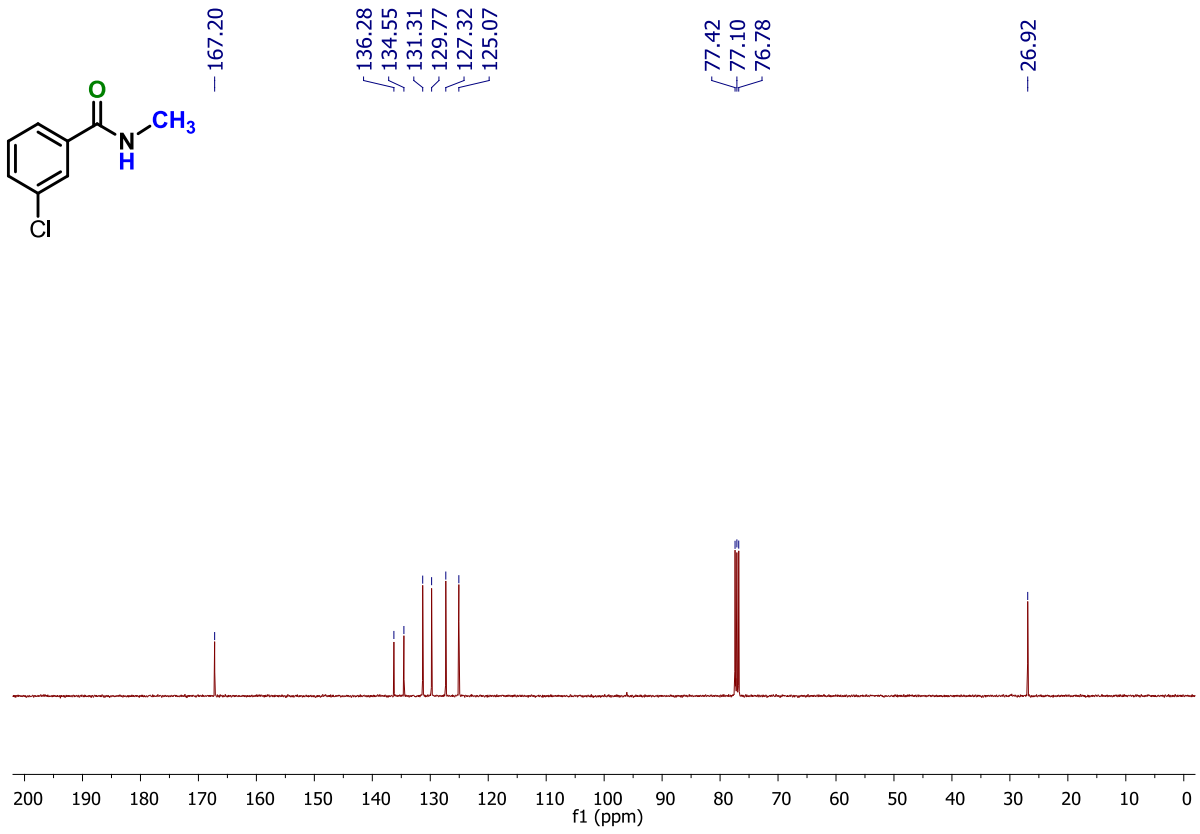

7.5718
7.5269
7.5228
7.5158
7.5130
7.5051
7.5011
7.2661
7.2538
7.2504
6.4153
2.9709
2.9587
2.3458
O
N
H
CH3
Me
1.00
1.01
2.01
1.05
3.04
3.05
f1 (ppm)

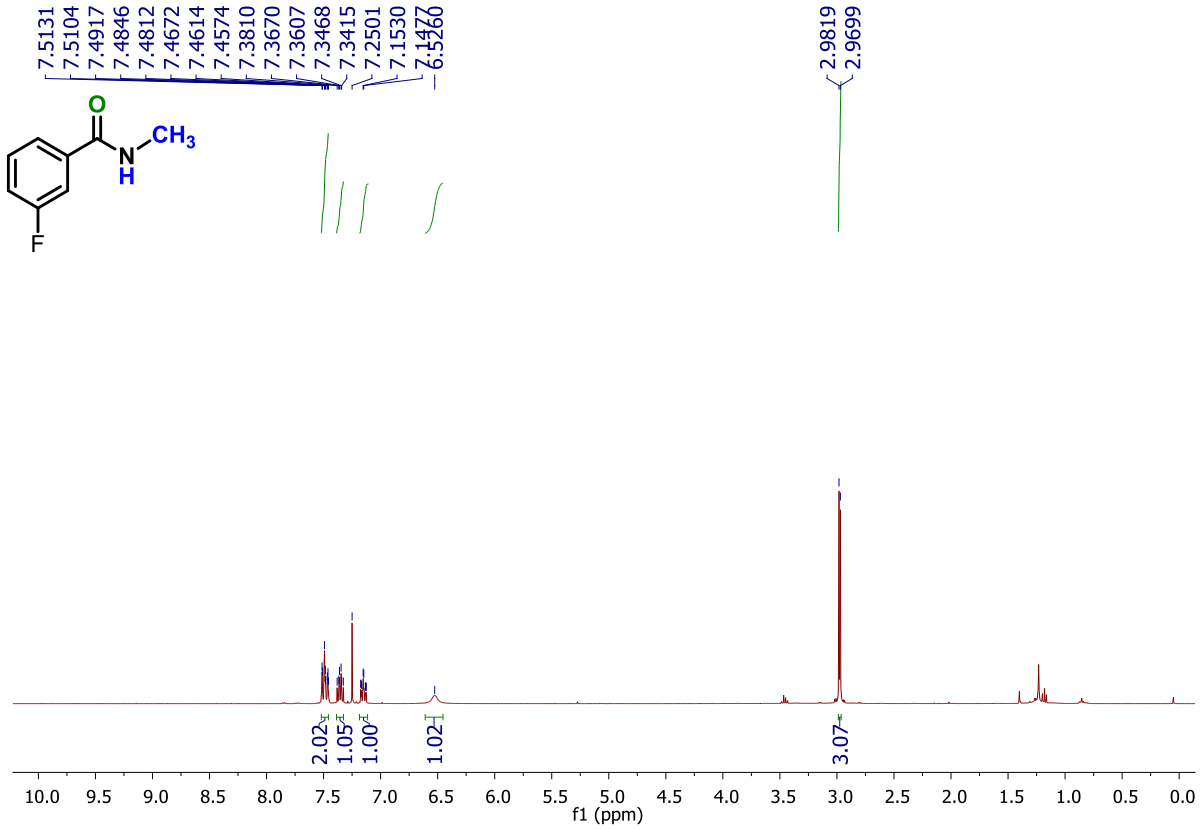

168.58
138.37
134.60
132.08
128.41
127.69
123.83
77.42
77.10
76.78
26.85
21.37
O
N
H
CH3
Me
f1 (ppm)

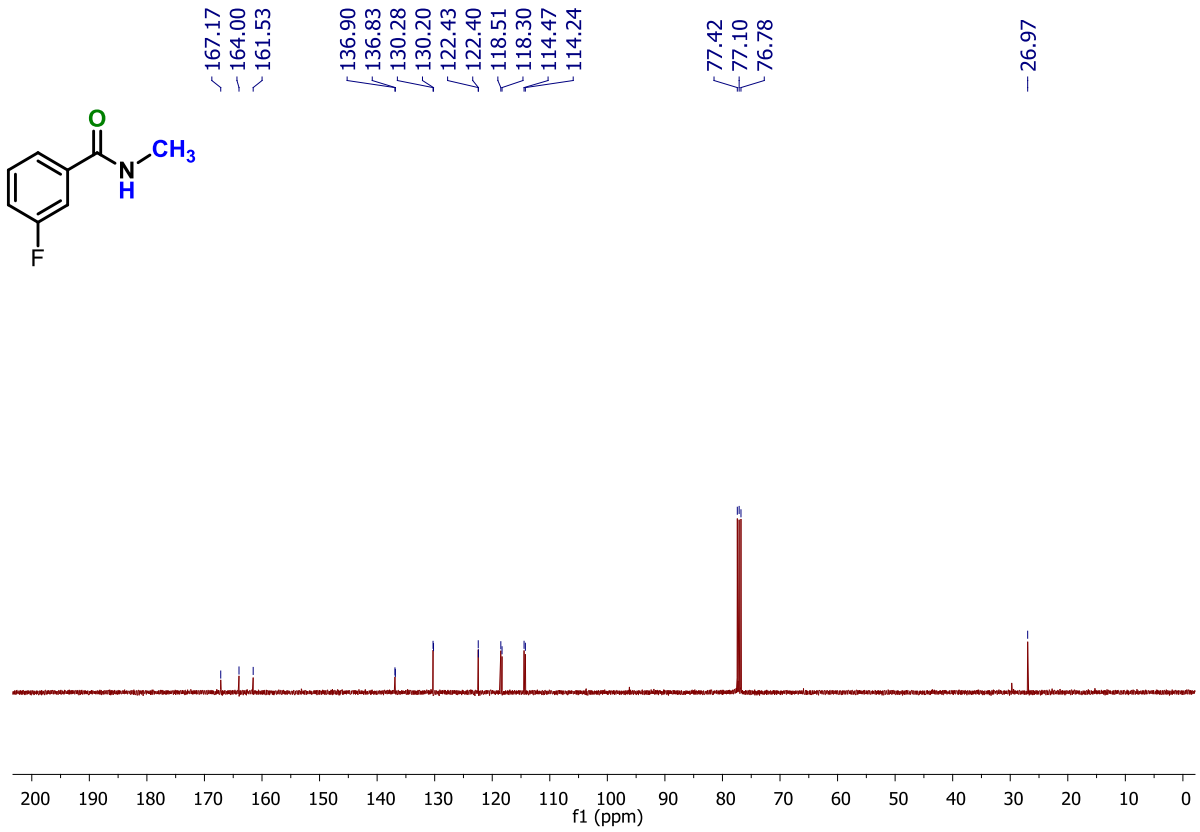

7.3385
7.3339
7.3289
7.3130
7.2938
7.2742
7.2532
7.2475
7.2340
7.0149
7.0124
7.0090
7.0067
6.9951
6.9926
6.9892
6.9868
6.2440
3.8168
2.9894
2.9773
O
N
H
CH3
OMe
2.05
1.18
1.00
1.03
3.03
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

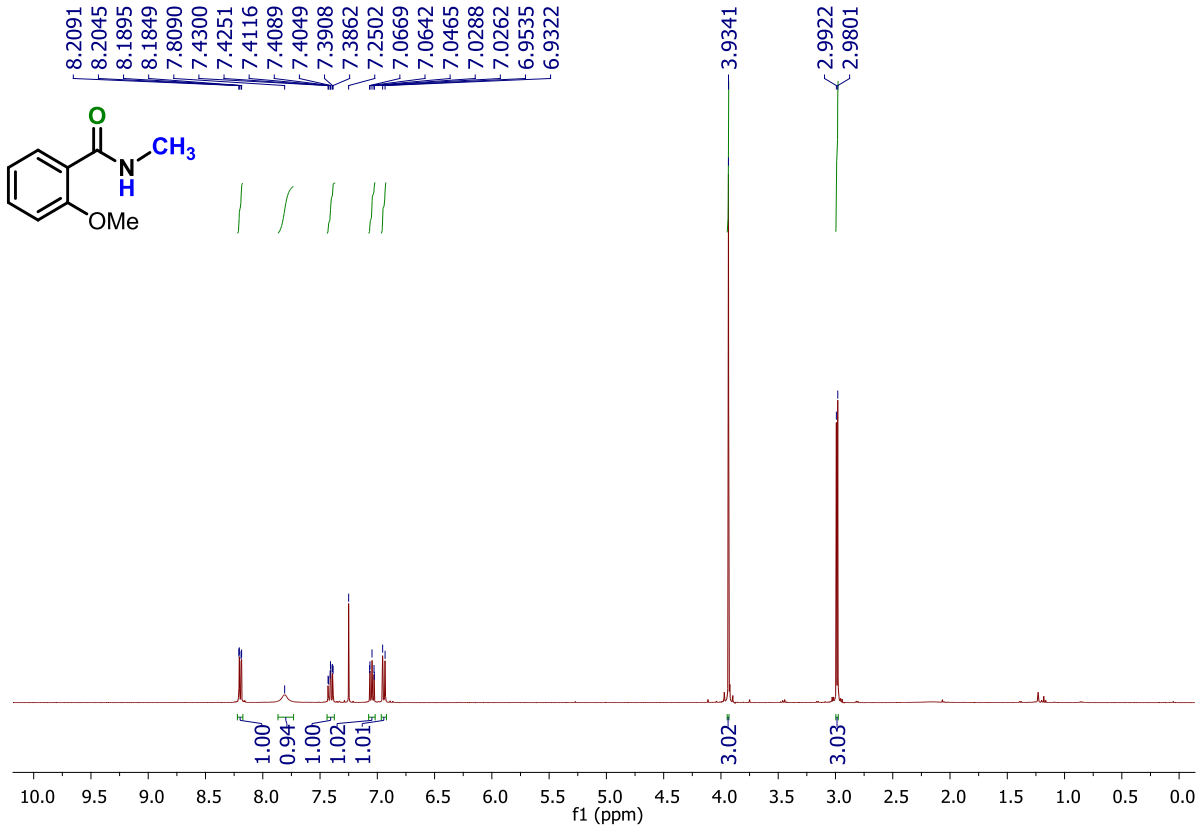

168.19
159.85
136.16
129.60
118.62
117.64
112.27
77.42
77.10
76.78
55.47
26.94
O
N
H
CH3
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

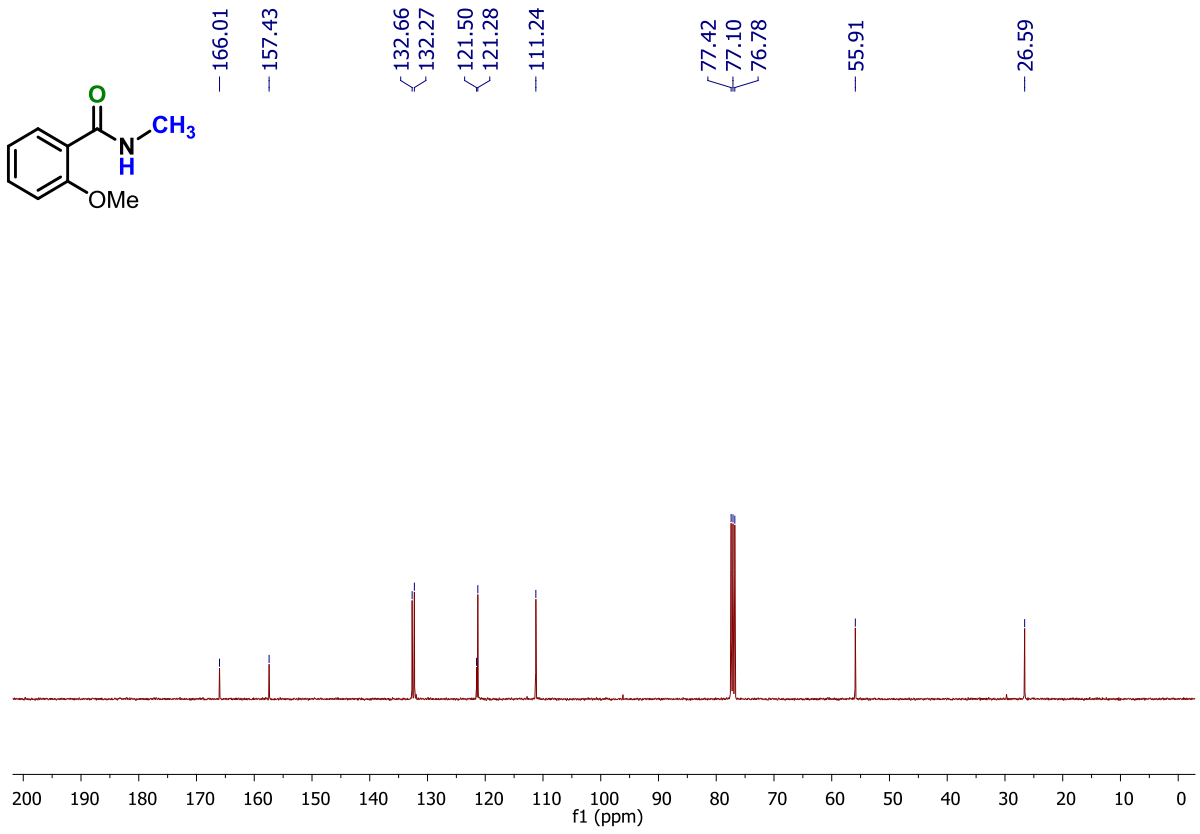

7.7375
7.7330
7.7284
7.6210
7.6179
7.5986
7.5958
7.3982
7.3952
7.3913
7.3783
7.3754
7.3723
7.2888
7.2693
7.2497
7.0032
2.9386
2.9266
O
N
H
CH3
Cl
1.00
1.02
1.01
1.09
0.99
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

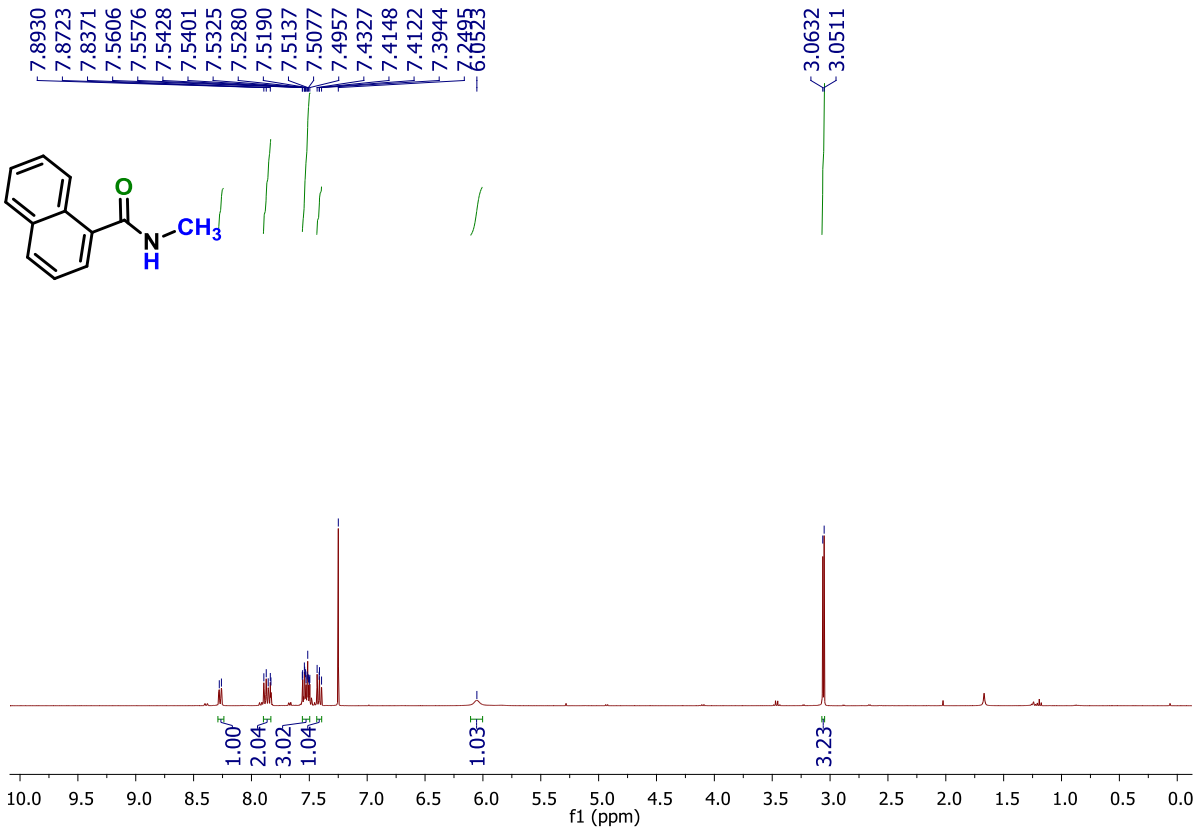

167.20
136.28
134.55
131.31
129.77
127.32
125.07
77.42
77.10
76.78
26.92
O
N
H
CH3
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

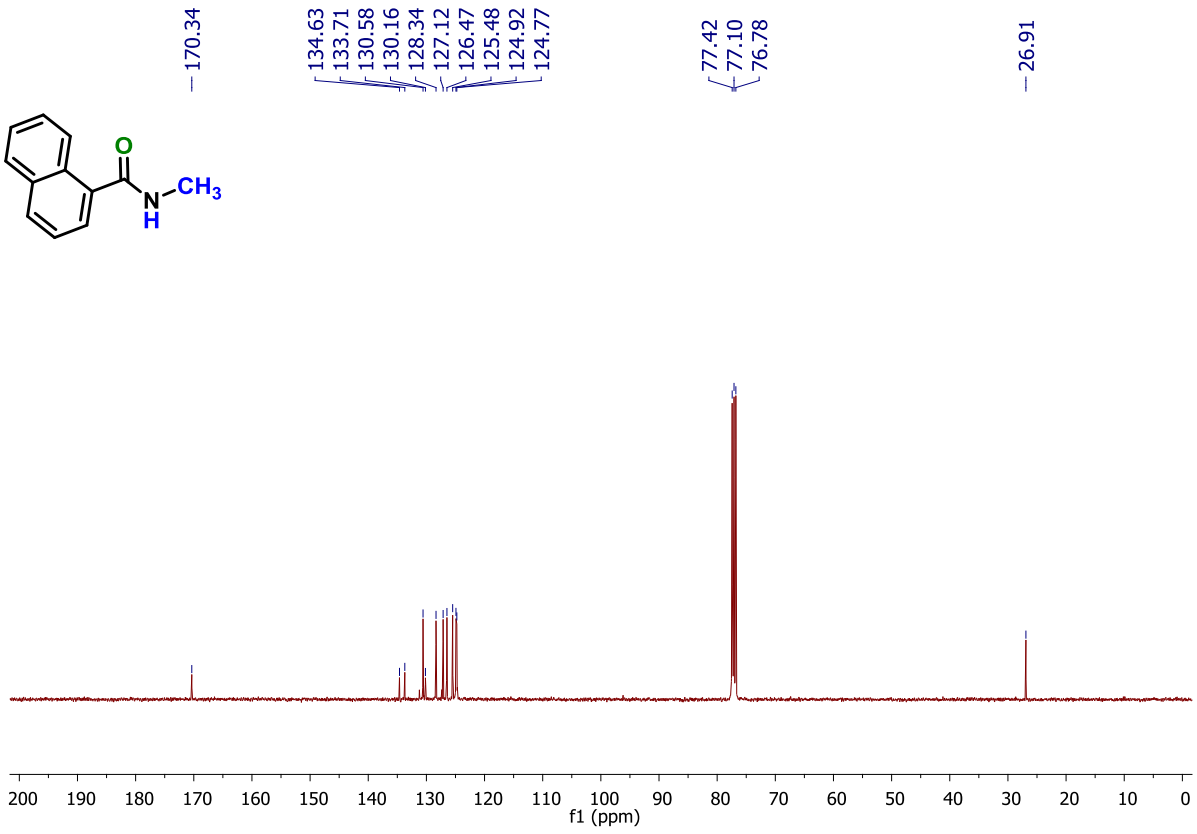

7.5131
7.5104
7.4917
7.4846
7.4812
7.4672
7.4614
7.4574
7.3810
7.3670
7.3607
7.3468
7.3415
7.2501
7.1530
2.9819
2.9699
O
N
H
CH3
F
2.02
1.05
1.00
1.02
3.07
f1 (ppm)

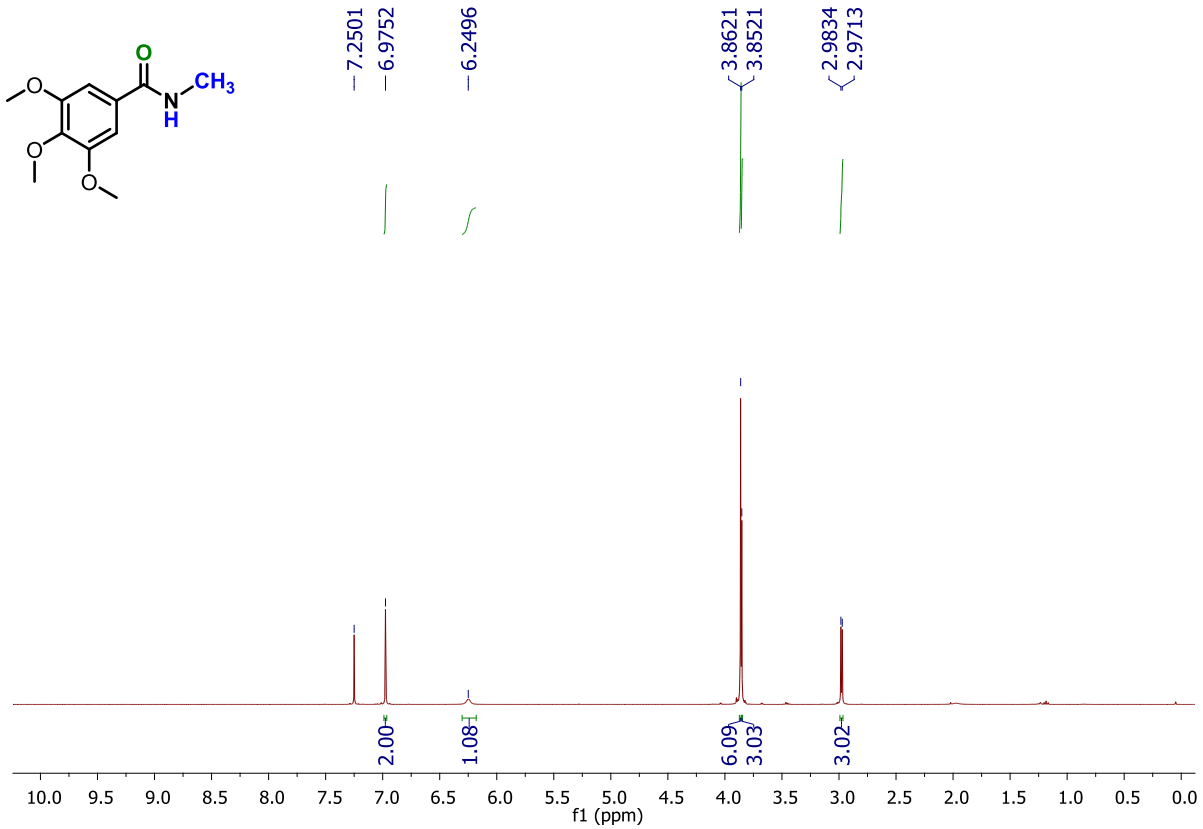

167.17
164.00
161.53
136.90
136.83
130.28
130.20
122.43
122.40
118.51
118.30
114.47
114.24
77.42
77.10
76.78
26.97
O
N
H
CH3
F
f1 (ppm)

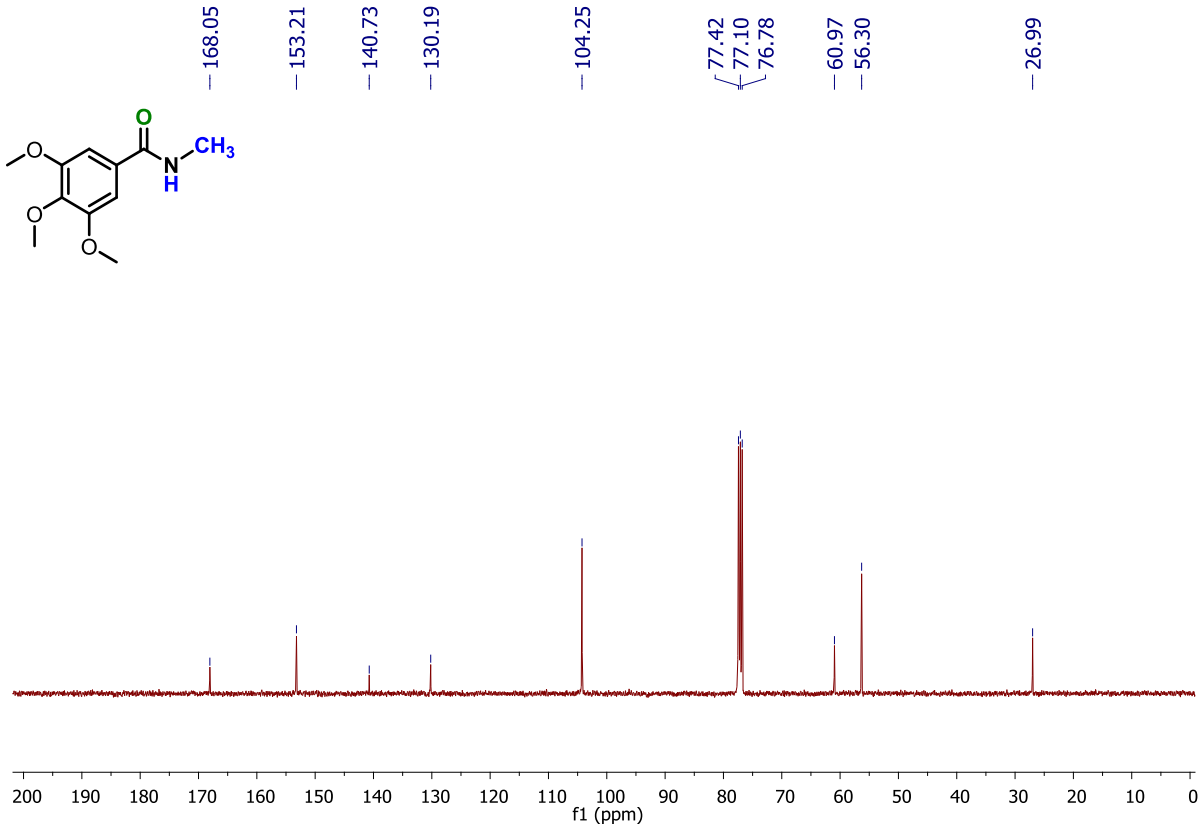

8.2091
8.2045
8.1895
8.1849
7.8090
7.4300
7.4251
7.4116
7.4089
7.4049
7.3908
7.3862
7.2502
7.0669
7.0642
7.0465
7.0288
7.0262
6.9535
6.9322
3.9341
2.9922
2.9801
O
CH3
N
H
OMe
1.00
0.94
1.00
1.02
1.01
3.02
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

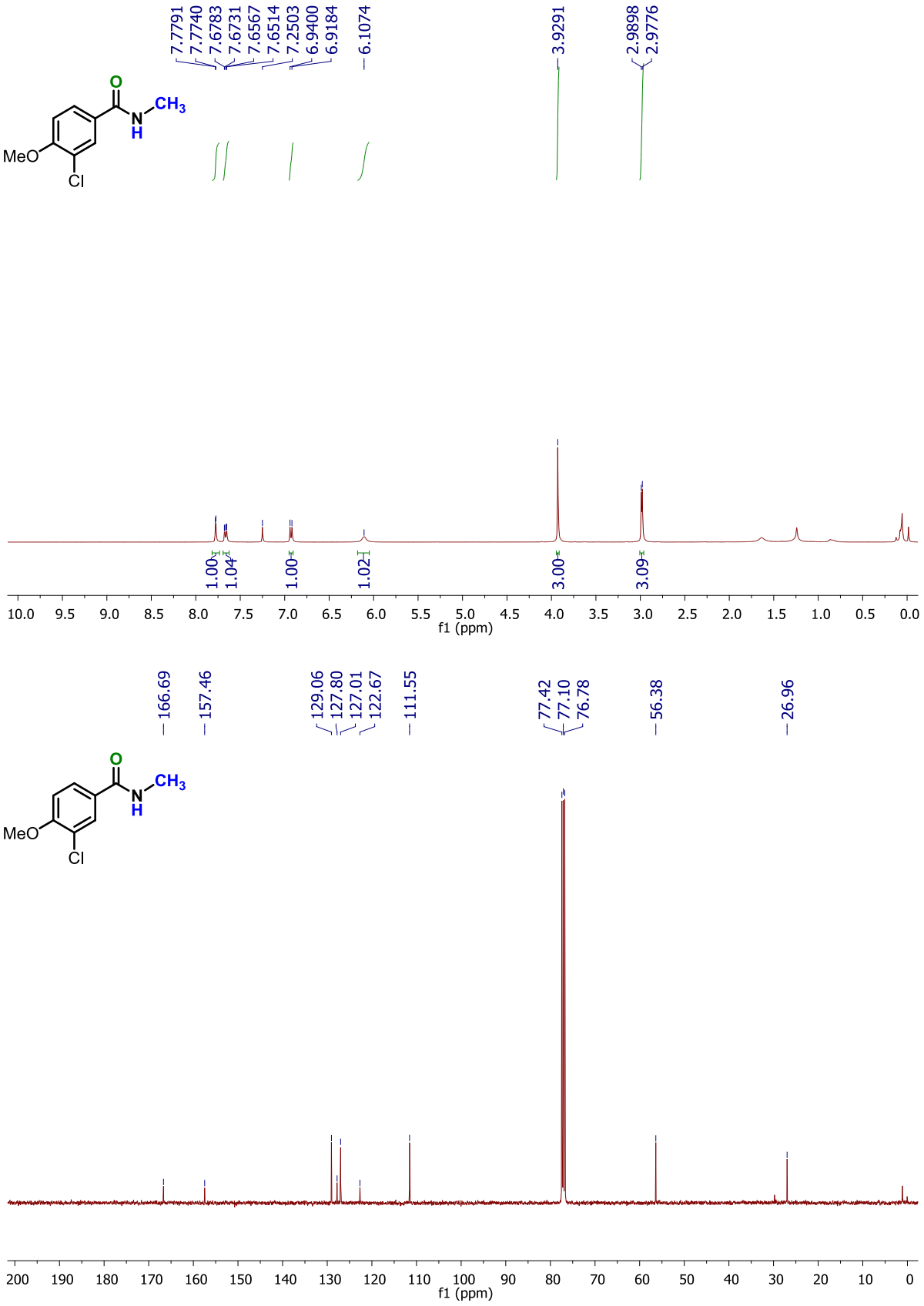

166.01
157.43
132.66
132.27
121.50
121.28
111.24
77.42
77.10
76.78
55.91
26.59
O
CH3
N
H
OMe
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

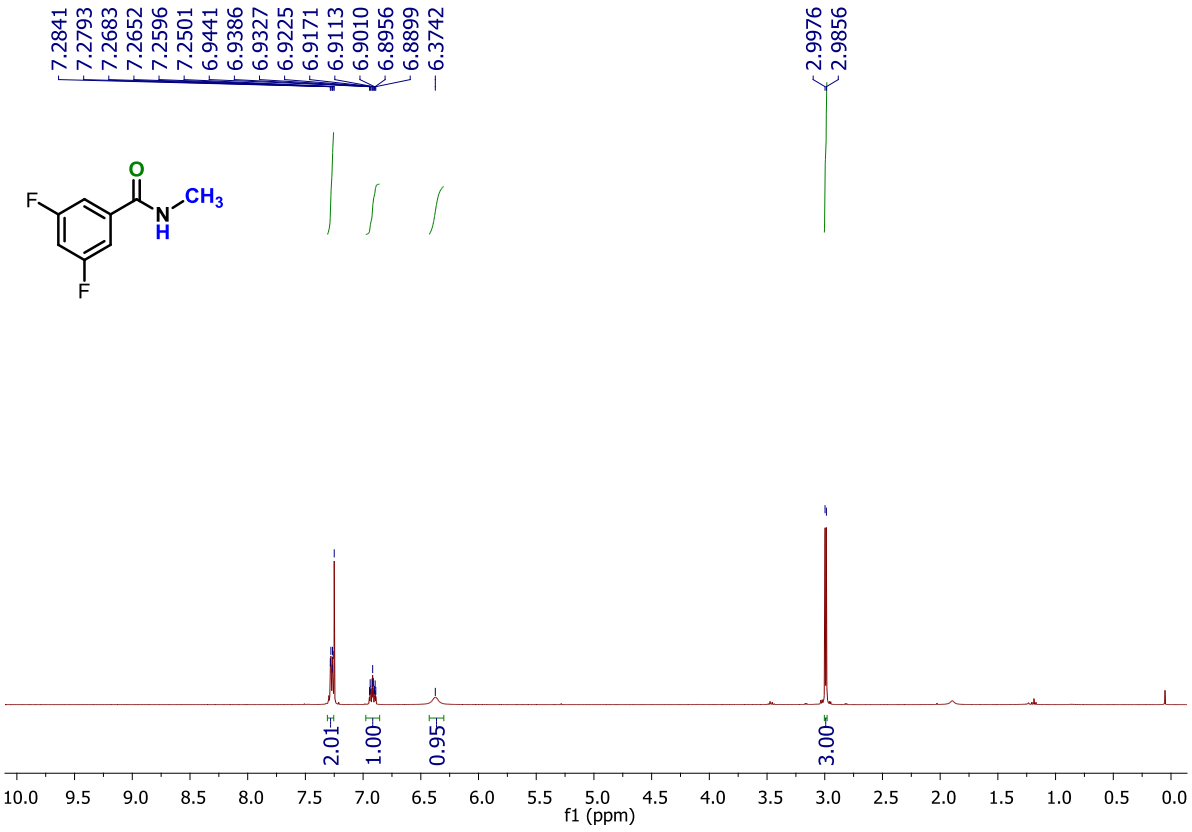

7.8930
7.8723
7.8371
7.5606
7.5576
7.5428
7.5401
7.5325
7.5280
7.5190
7.5137
7.5077
7.4957
7.4327
7.4148
7.4122
7.3944
7.2495
6.0523
3.0632
3.0511
O
N
H
CH3
1.00
2.04
3.02
1.04
1.03
3.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

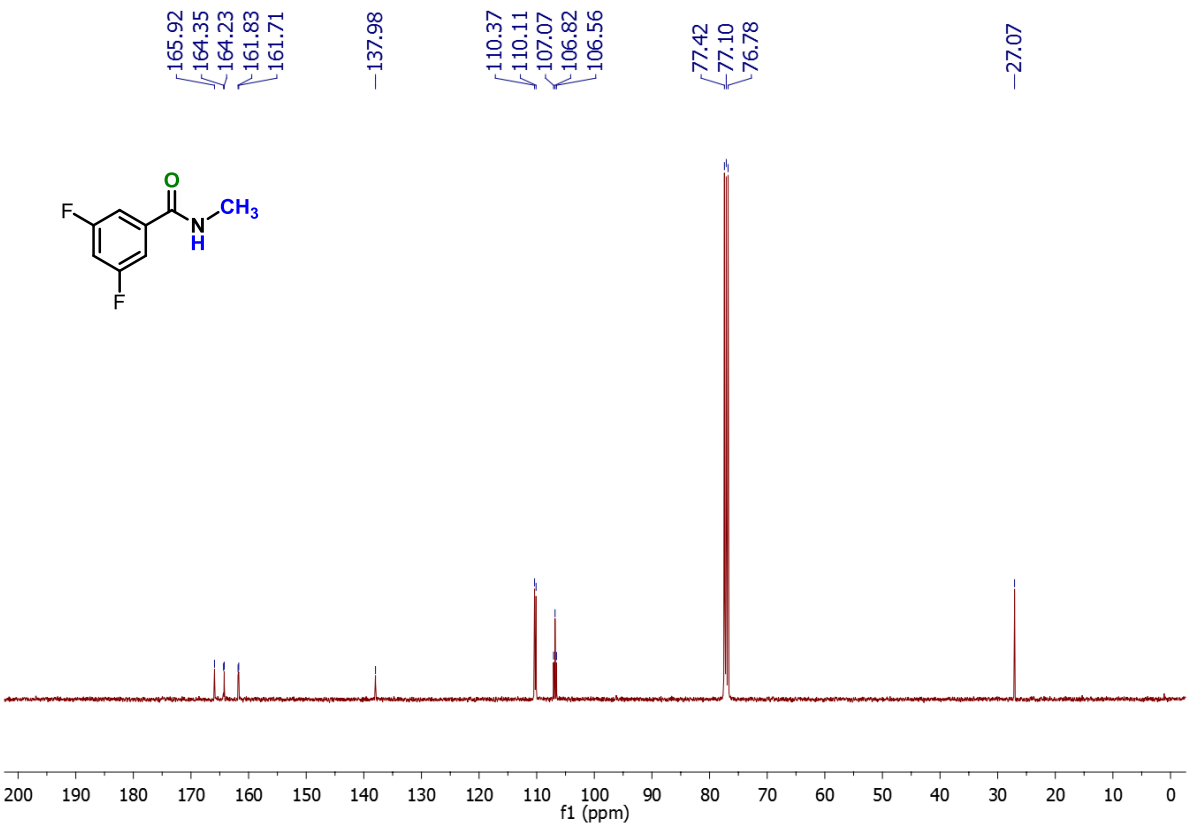

170.34
134.63
133.71
130.58
130.16
128.34
127.12
126.47
125.48
124.92
124.77
77.42
77.10
76.78
26.91
O
N
H
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

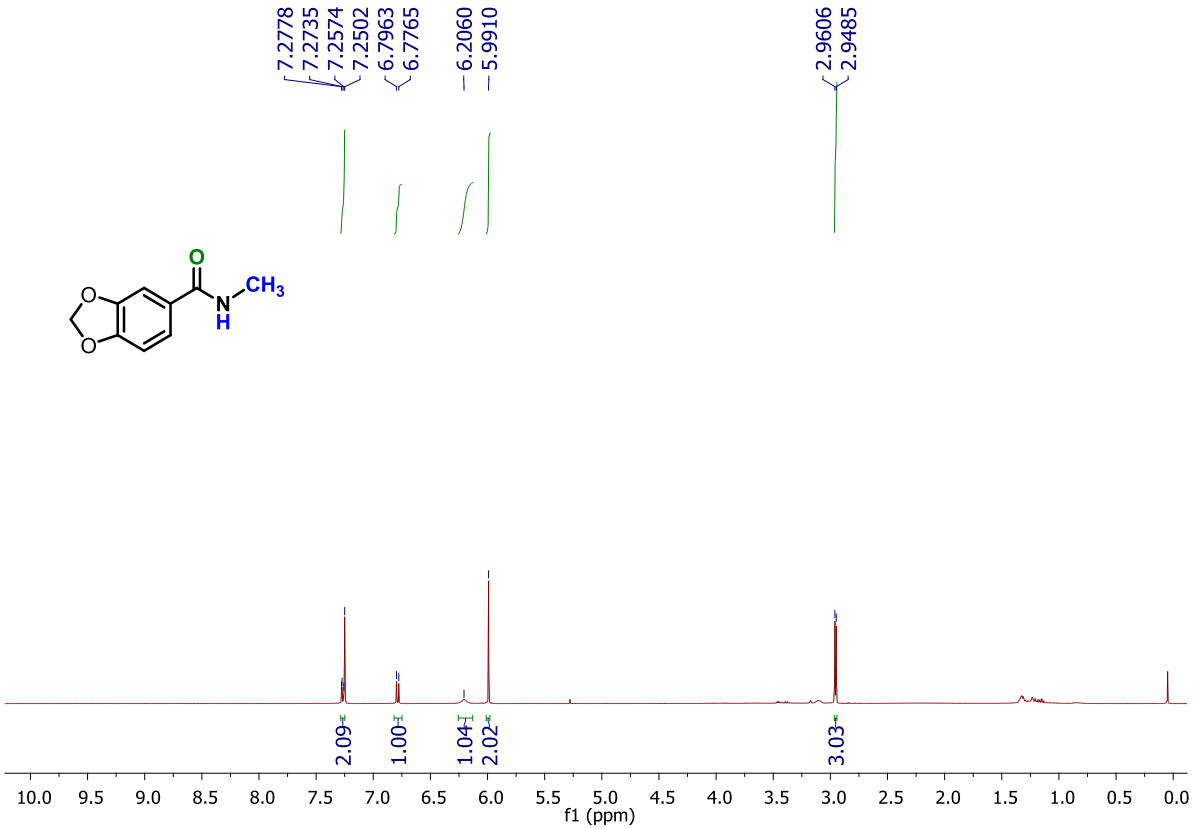

7.2501
6.9752
6.2496
3.8621
3.8521
2.9834
2.9713
2.00
1.08
6.09
3.03
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

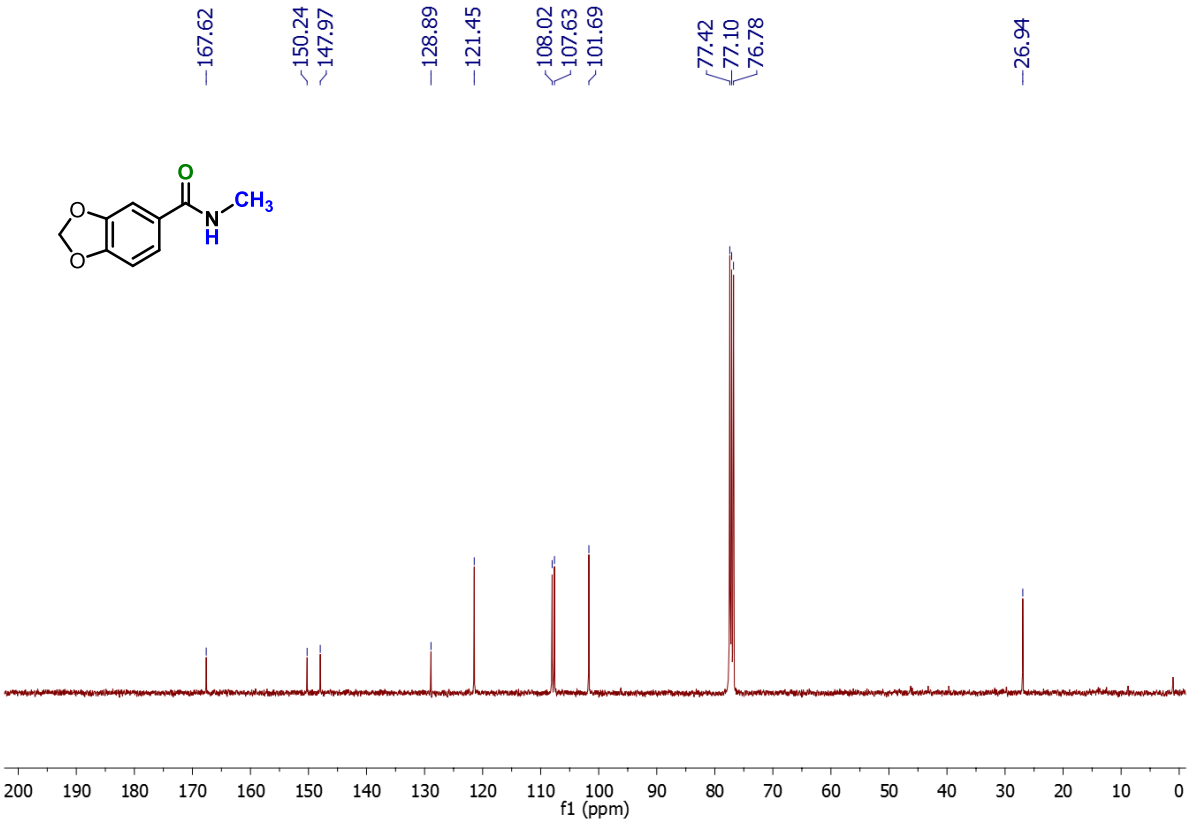

168.05
153.21
140.73
130.19
104.25
77.42
77.10
76.78
60.97
56.30
26.99
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

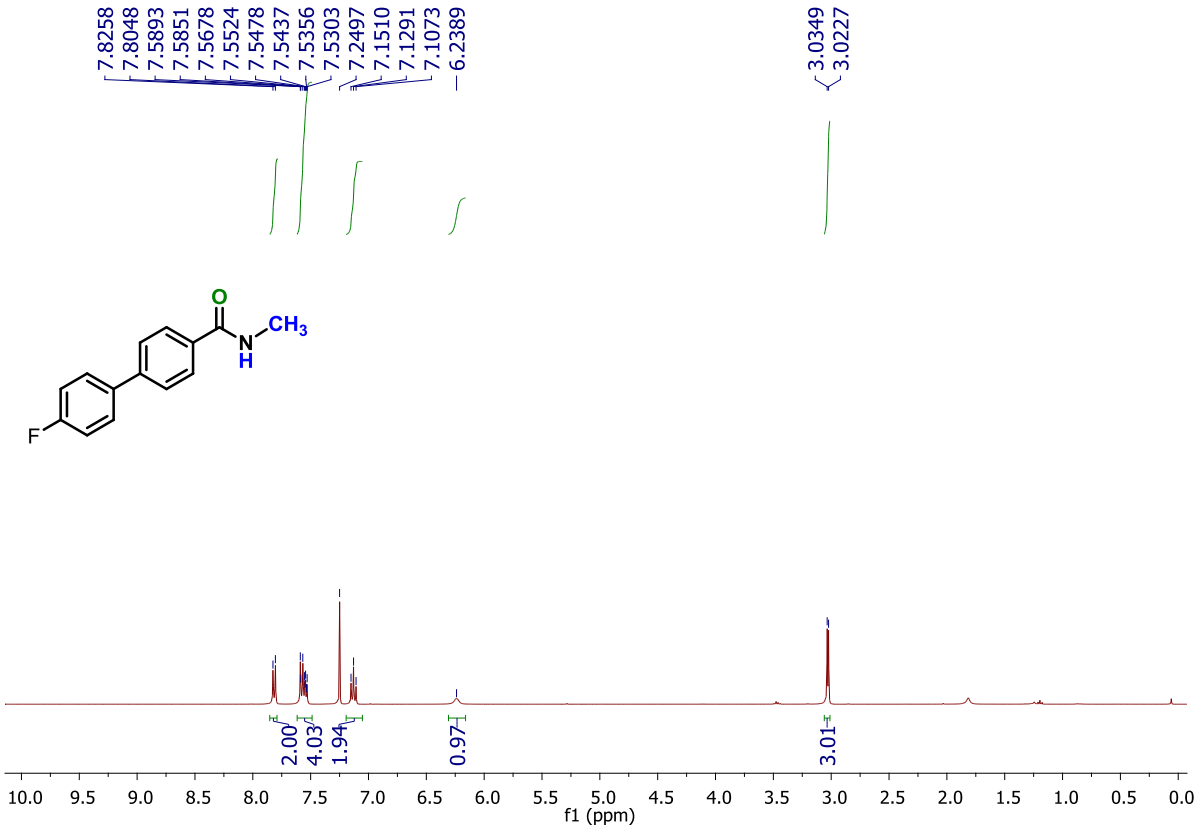

7.7791
7.7740
7.6783
7.6731
7.6567
7.6514
7.2503
6.9400
6.9184
6.1074
3.9291
2.9898
2.9776
O
N
H
CH3
MeO
Cl
1.00
1.04
1.00
1.02
3.00
3.09
f1 (ppm)
166.69
157.46
129.06
127.80
127.01
122.67
111.55
77.42
77.10
76.78
56.38
26.96
f1 (ppm)

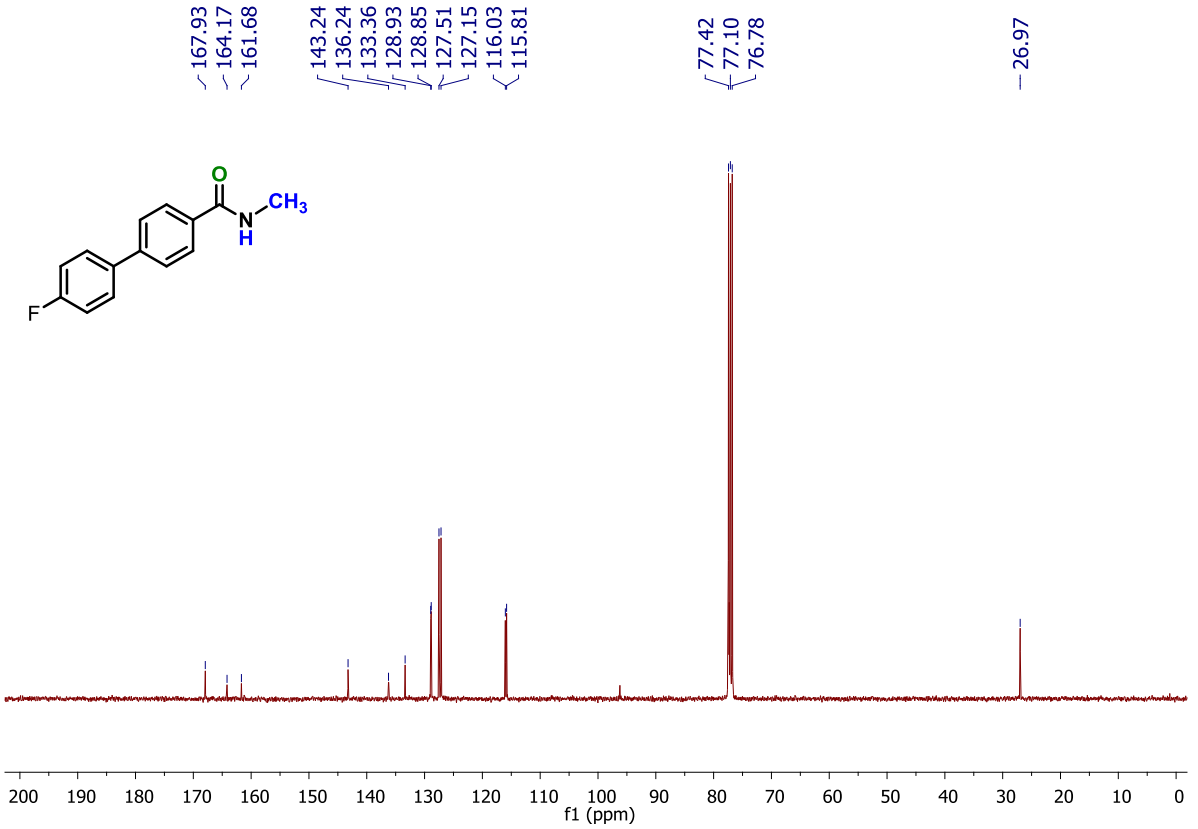

7.2841
7.2793
7.2683
7.2652
7.2596
7.2501
6.9441
6.9386
6.9327
6.9225
6.9171
6.9113
6.9010
6.8956
6.8899
6.3742
2.9976
2.9856
O
N
H
CH3
F
F
2.01
1.00
0.95
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

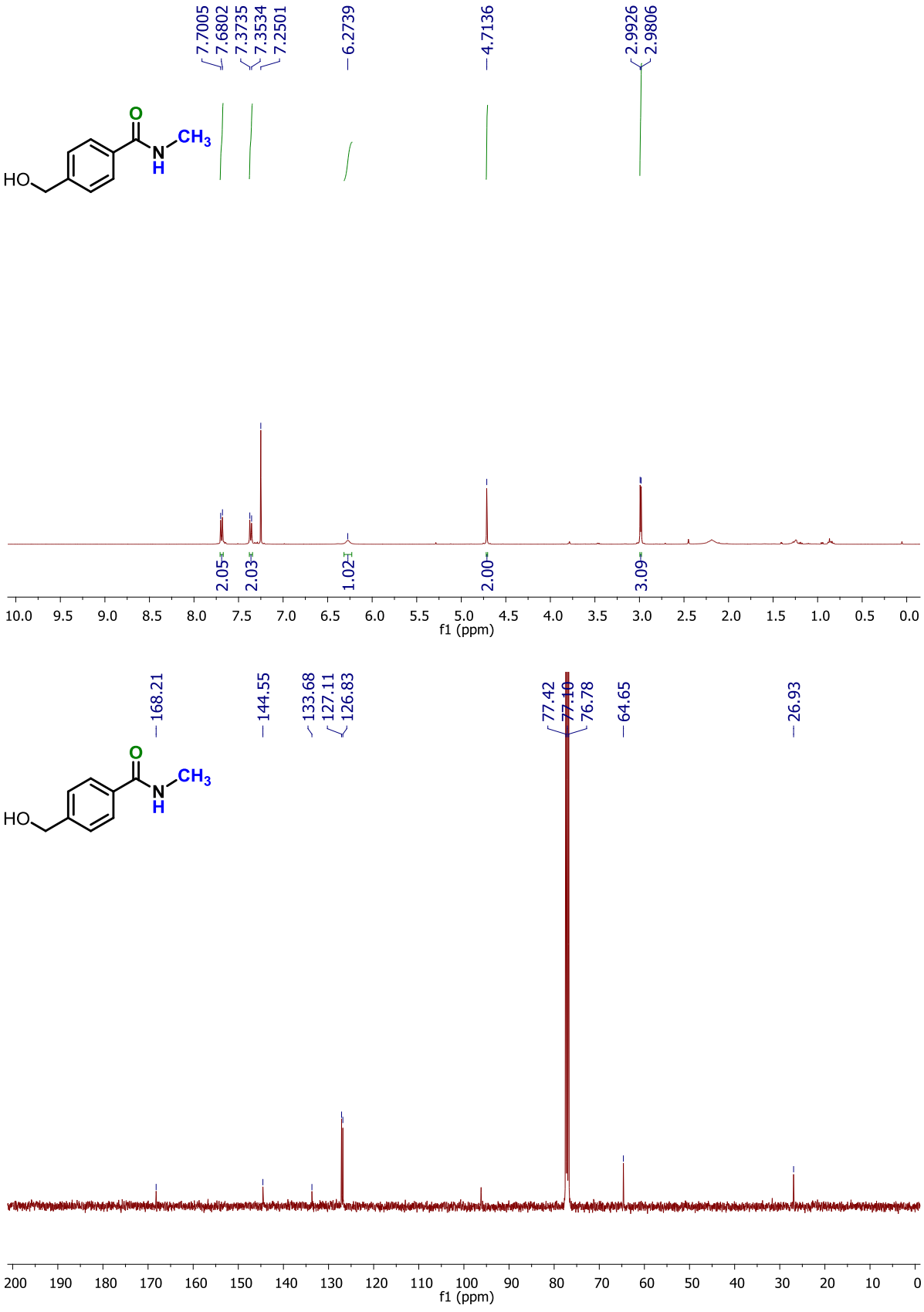

165.92
164.35
164.23
161.83
161.71
137.98
110.37
110.11
107.07
106.82
106.56
77.42
77.10
76.78
27.07
O
N
H
CH3
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

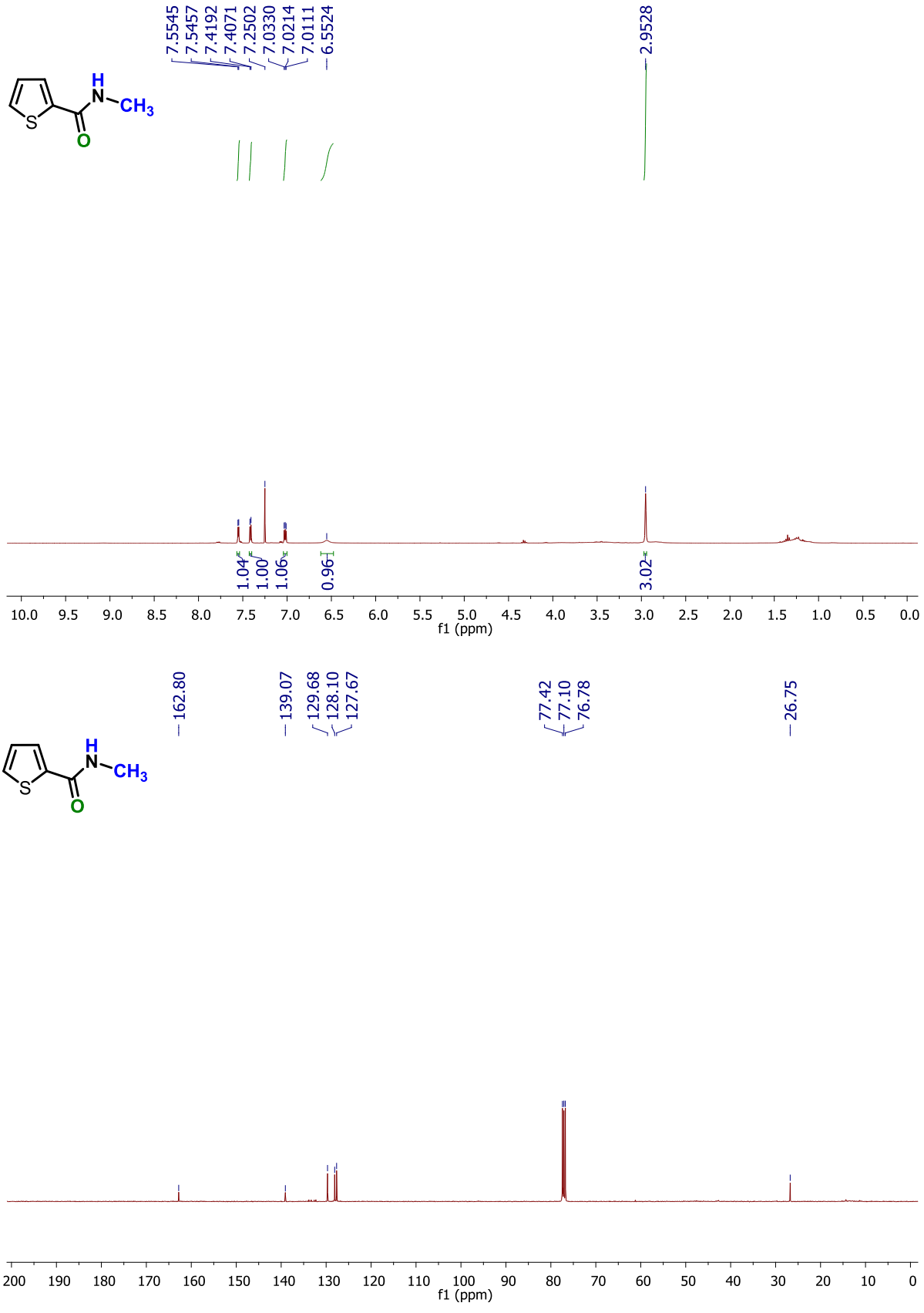

7.2778
7.2735
7.2574
7.2502
6.7963
6.7765
6.2060
5.9910
2.9606
2.9485
O
N
H
CH3
2.09
1.00
1.04
2.02
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

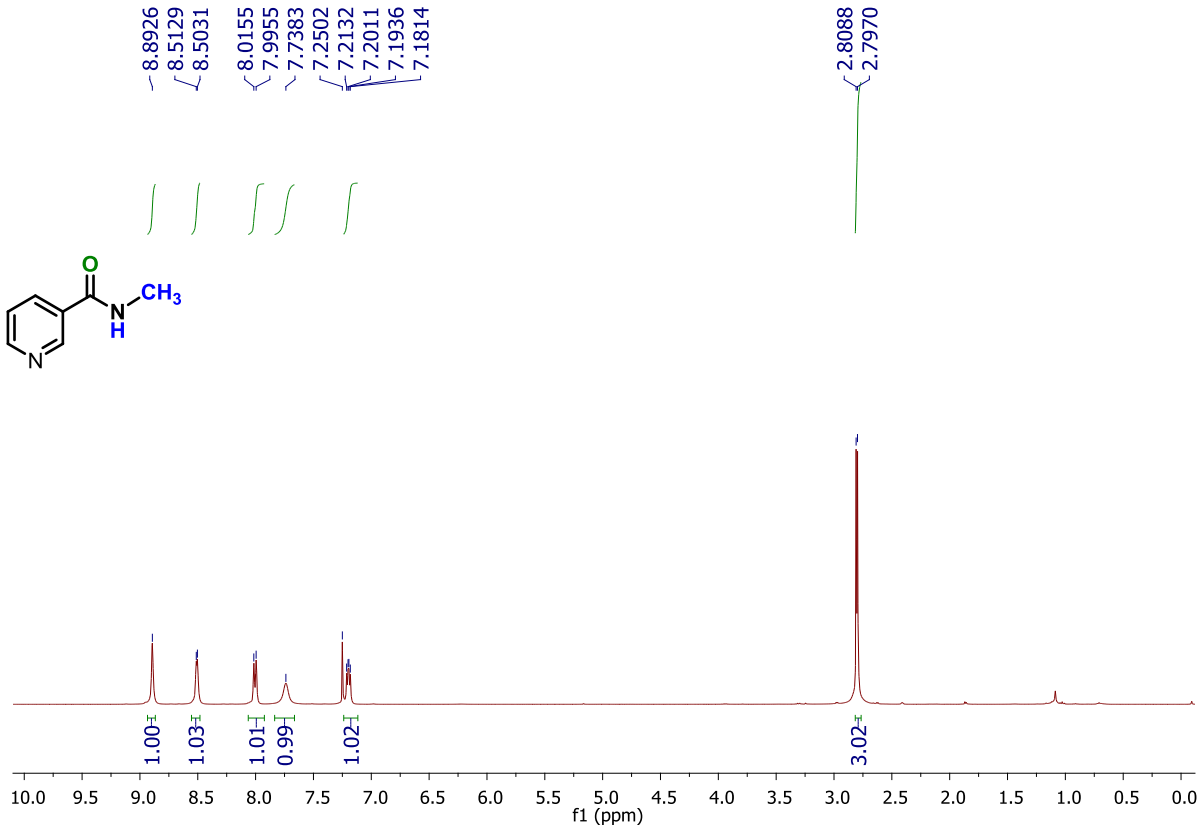

167.62
150.24
147.97
128.89
121.45
108.02
107.63
101.69
77.42
77.10
76.78
26.94
O
N
H
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

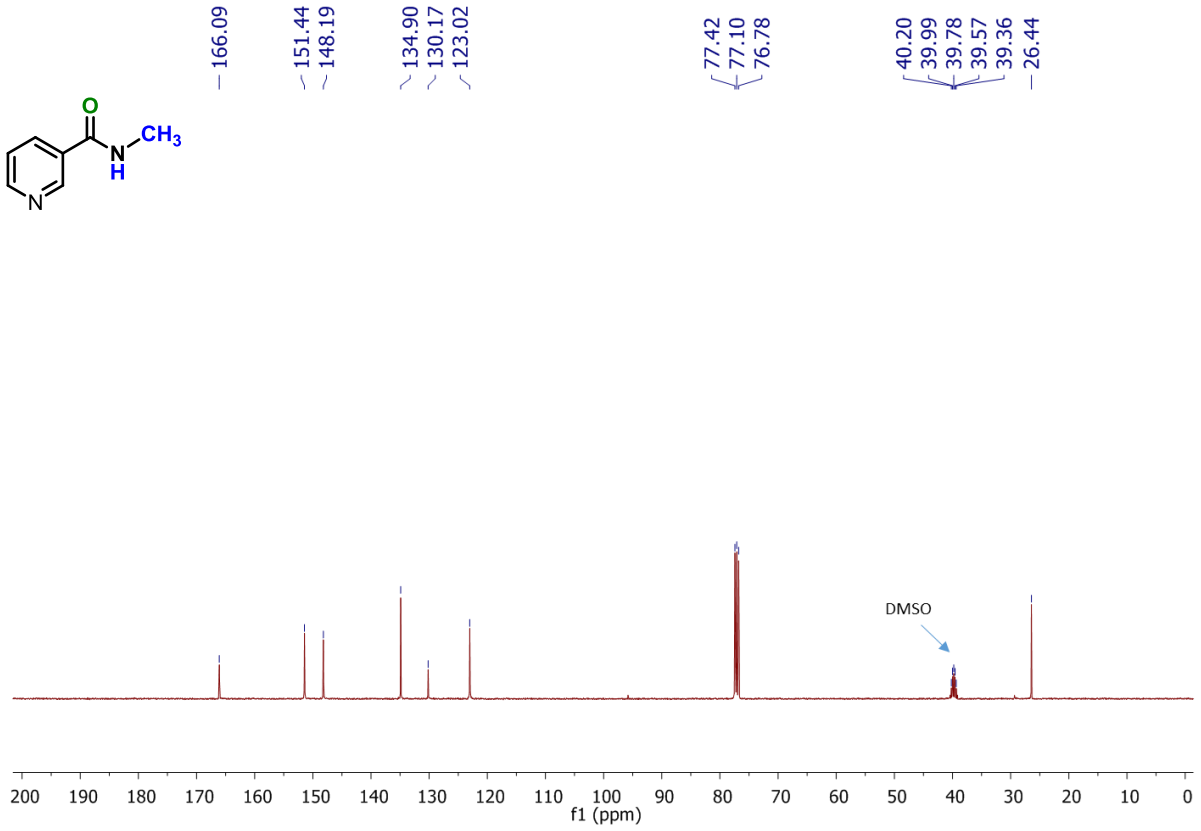

7.8258
7.8048
7.5893
7.5851
7.5678
7.5524
7.5478
7.5437
7.5356
7.5303
7.2497
7.1510
7.1291
7.1073
6.2389
3.0349
3.0227
O
N
H
CH3
F
2.00
4.03
1.94
0.97
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

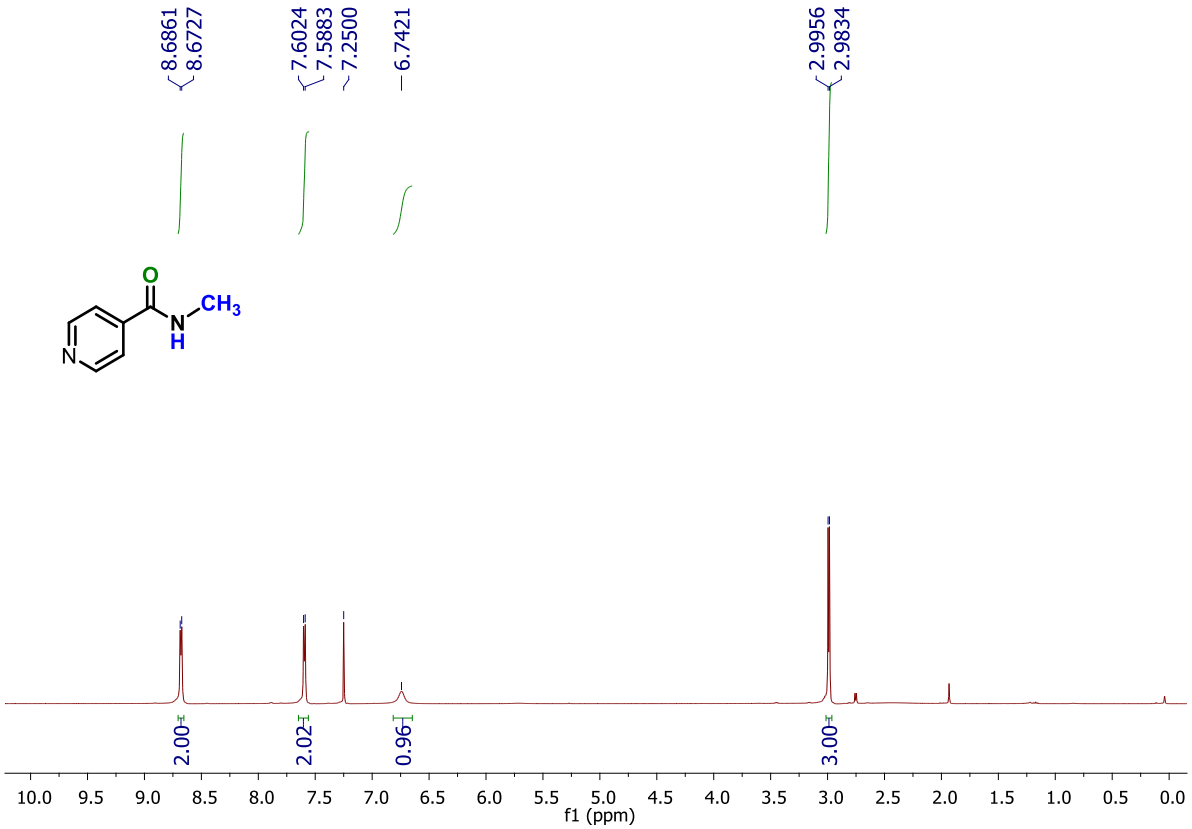

167.93
164.17
161.68
143.24
136.24
133.36
128.93
128.85
127.51
127.15
116.03
115.81
77.42
77.10
76.78
26.97
O
N
H
CH3
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

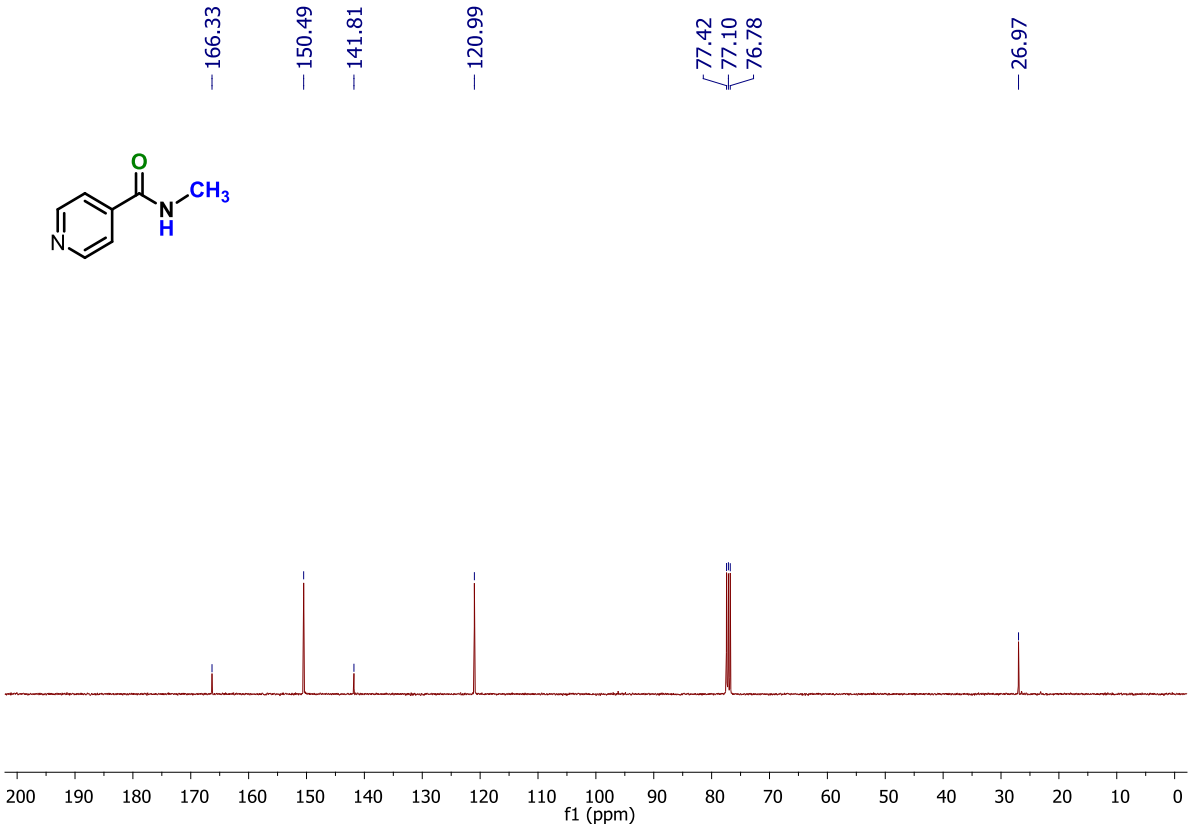

7.7005
7.6802
7.3735
7.3534
7.2501
6.2739
4.7136
2.9926
2.9806
O
N
H
CH3
HO
2.05
2.03
1.02
2.00
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
168.21
144.55
133.68
127.11
126.83
77.42
77.10
76.78
64.65
26.93
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

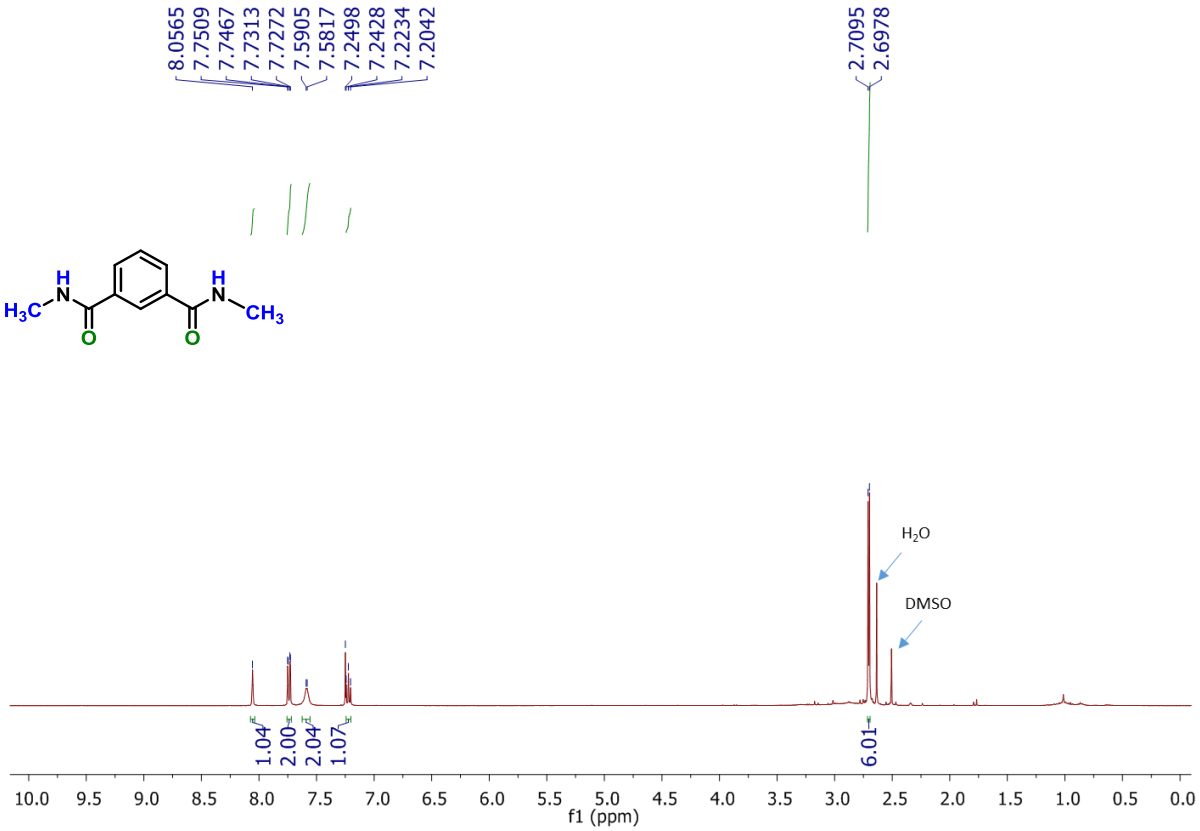

7.5545
7.5457
7.4192
7.4071
7.2502
7.0330
7.0214
7.0111
6.5524
2.9528
1.04
1.00
1.06
0.96
3.02
f1 (ppm)
162.80
139.07
129.68
128.10
127.67
77.42
77.10
76.78
26.75
f1 (ppm)

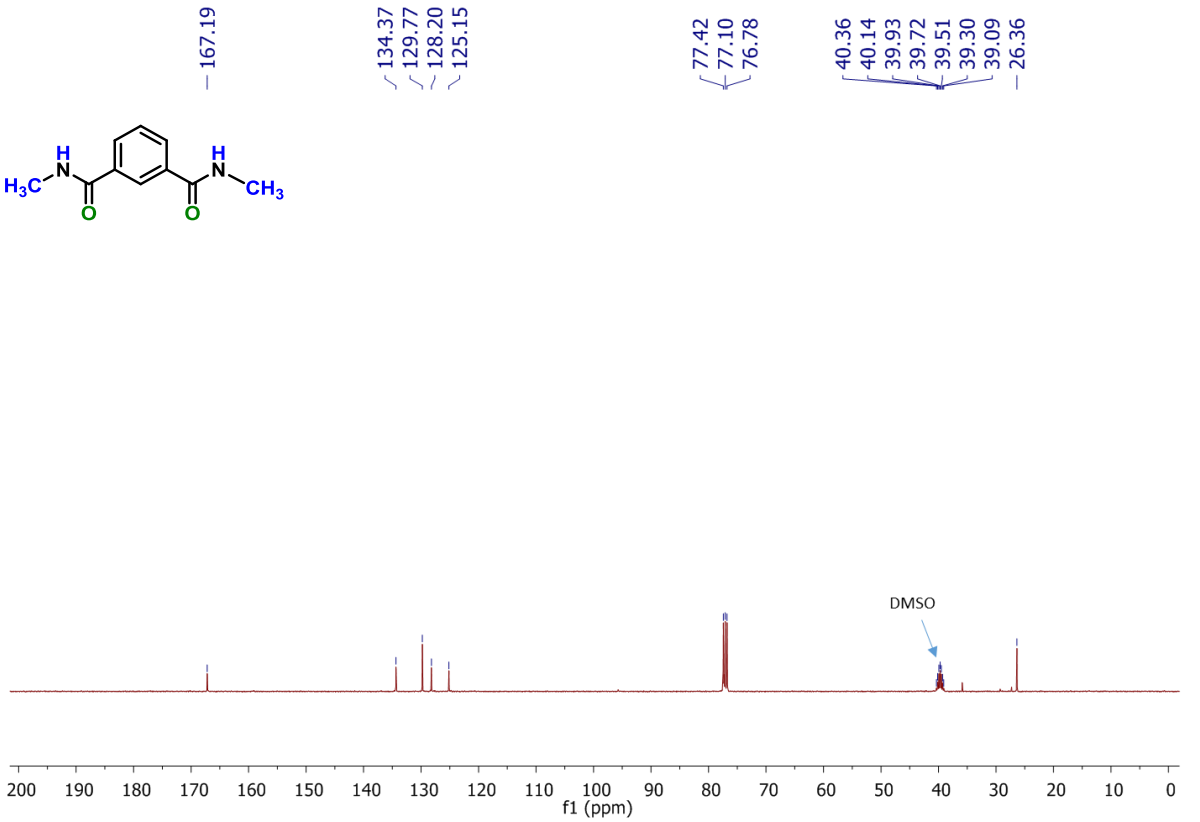

8.8926
8.5129
8.5031
8.0155
7.9955
7.7383
7.2502
7.2132
7.2011
7.1936
7.1814
2.8088
2.7970
O
N
H
CH3
N
1.00
1.03
1.01
0.99
1.02
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

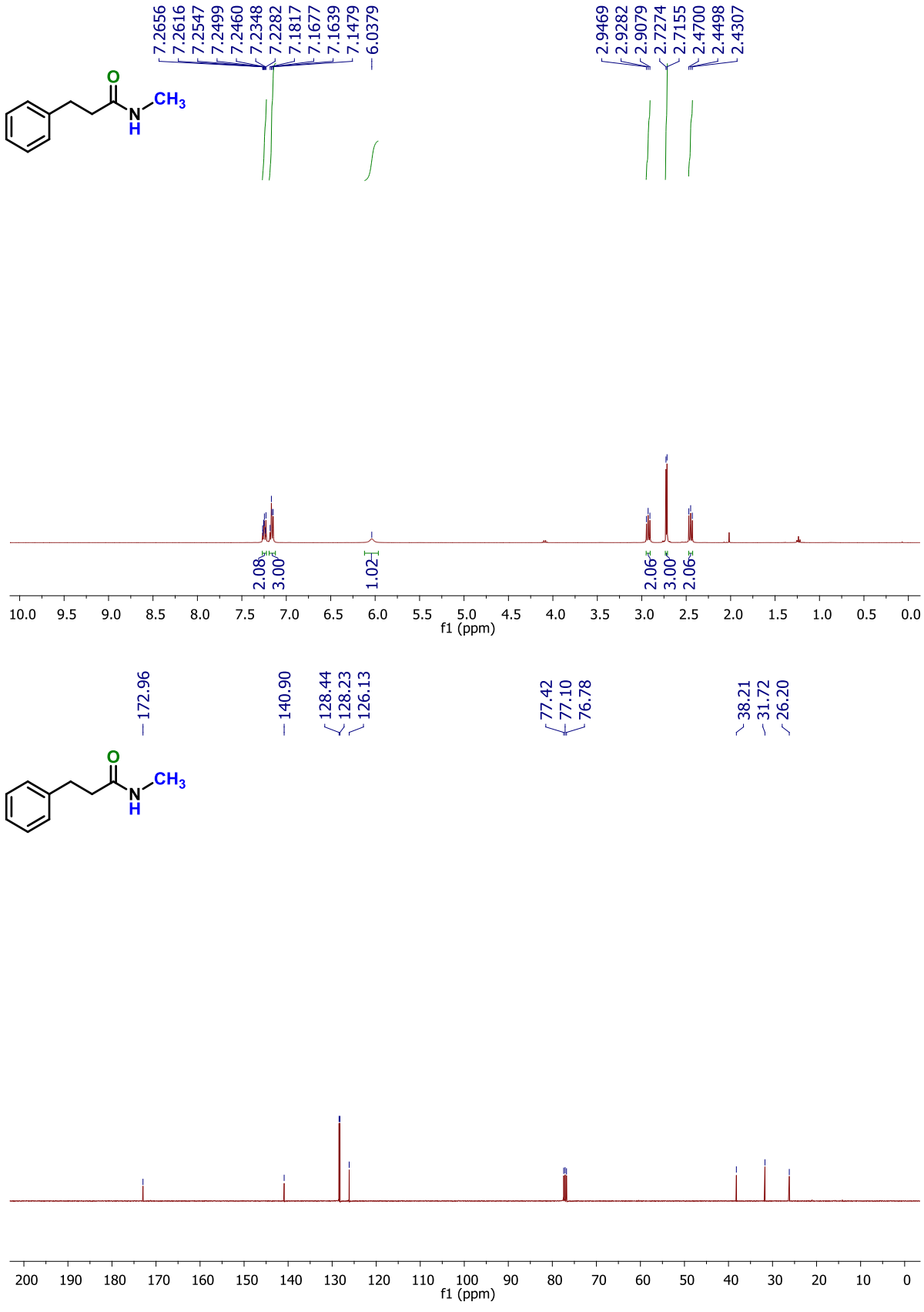

166.09
151.44
148.19
134.90
130.17
123.02
77.42
77.10
76.78
40.20
39.99
39.78
39.57
39.36
26.44
O
N
H
CH3
N
DMSO
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

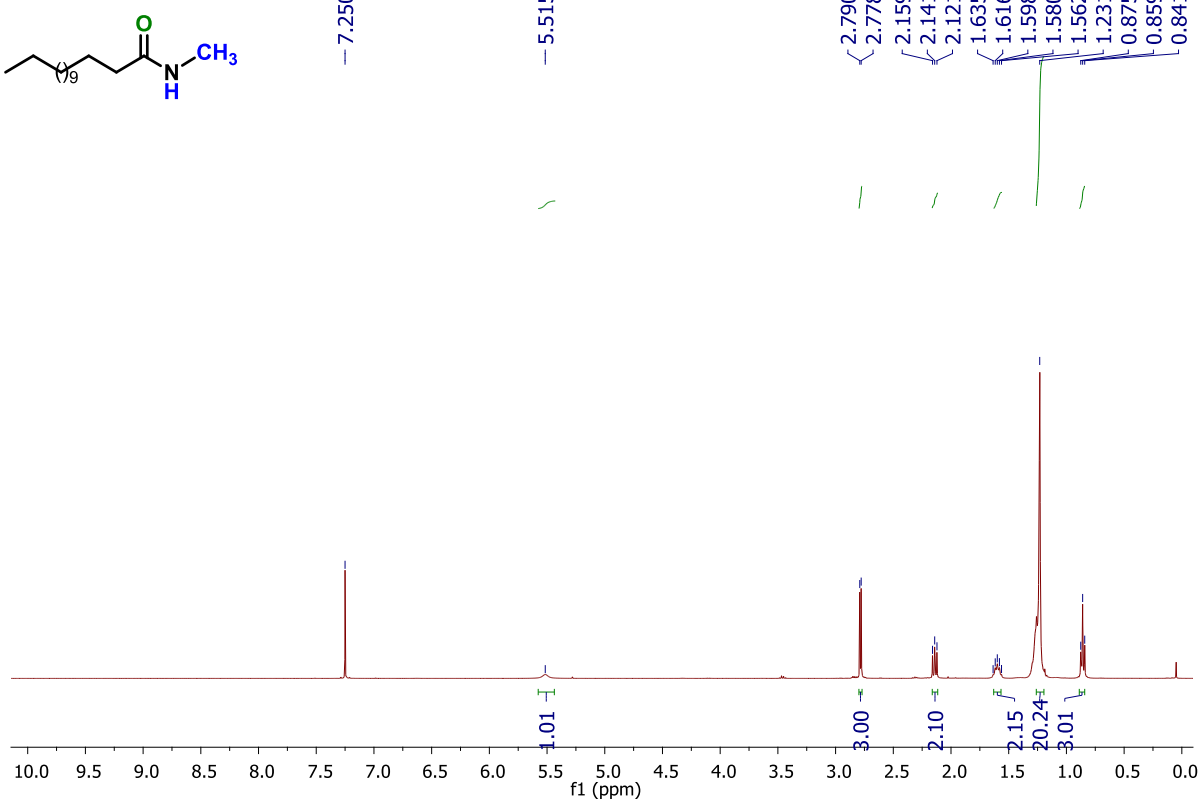

8.6861
8.6727
7.6024
7.5883
7.2500
6.7421
2.9956
2.9834
O
N
H
CH3
2.00
2.02
0.96
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

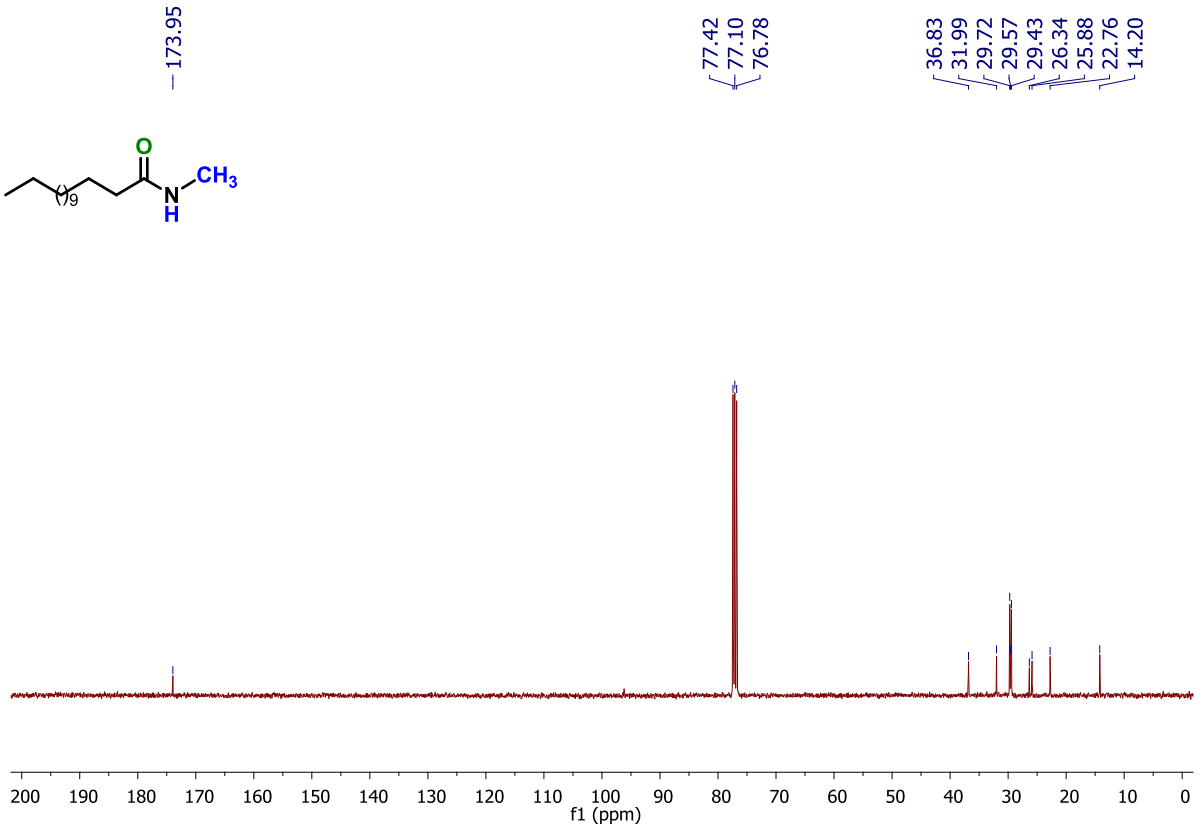

166.33
150.49
141.81
120.99
77.42
77.10
76.78
26.97
O
N
H
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

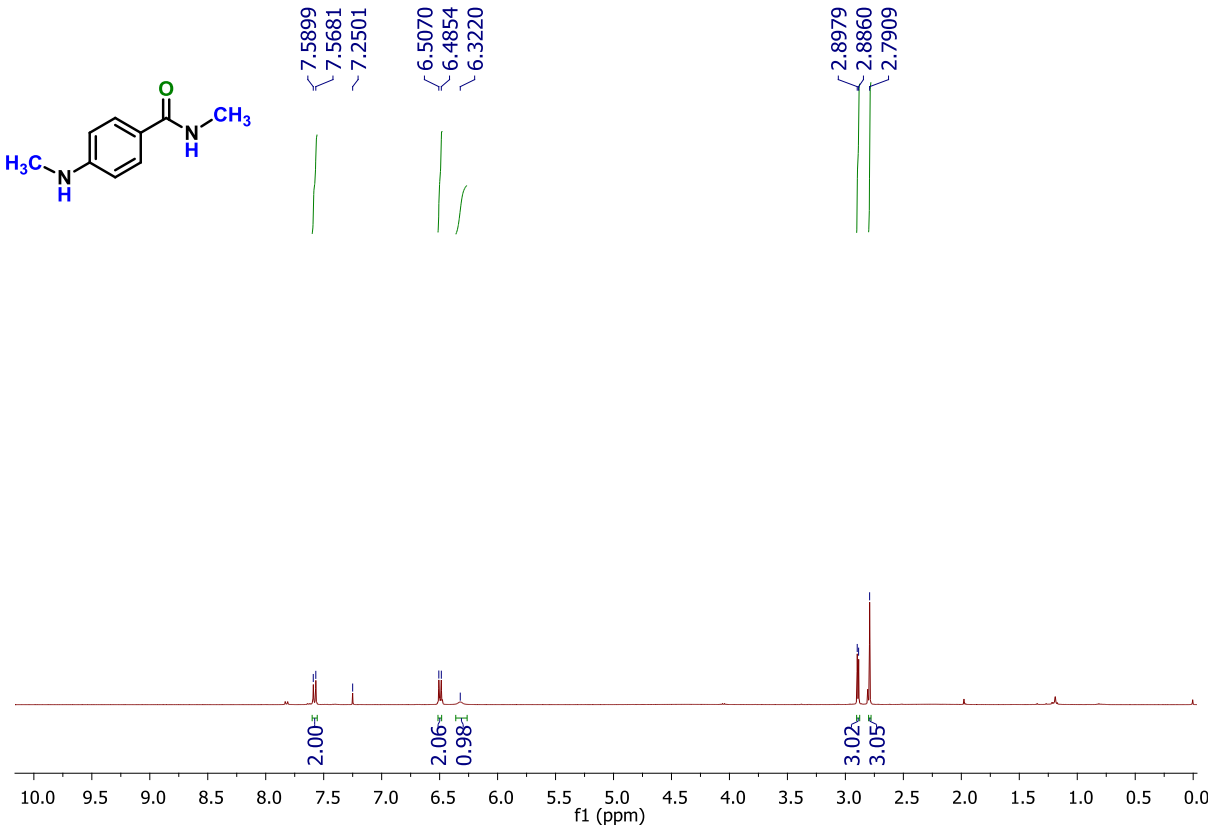

8.0565
7.7509
7.7467
7.7313
7.7272
7.5905
7.5817
7.2498
7.2428
7.2234
7.2042
2.7095
2.6978
H2O
DMSO
1.04
2.00
2.04
1.07
6.01
f1 (ppm)

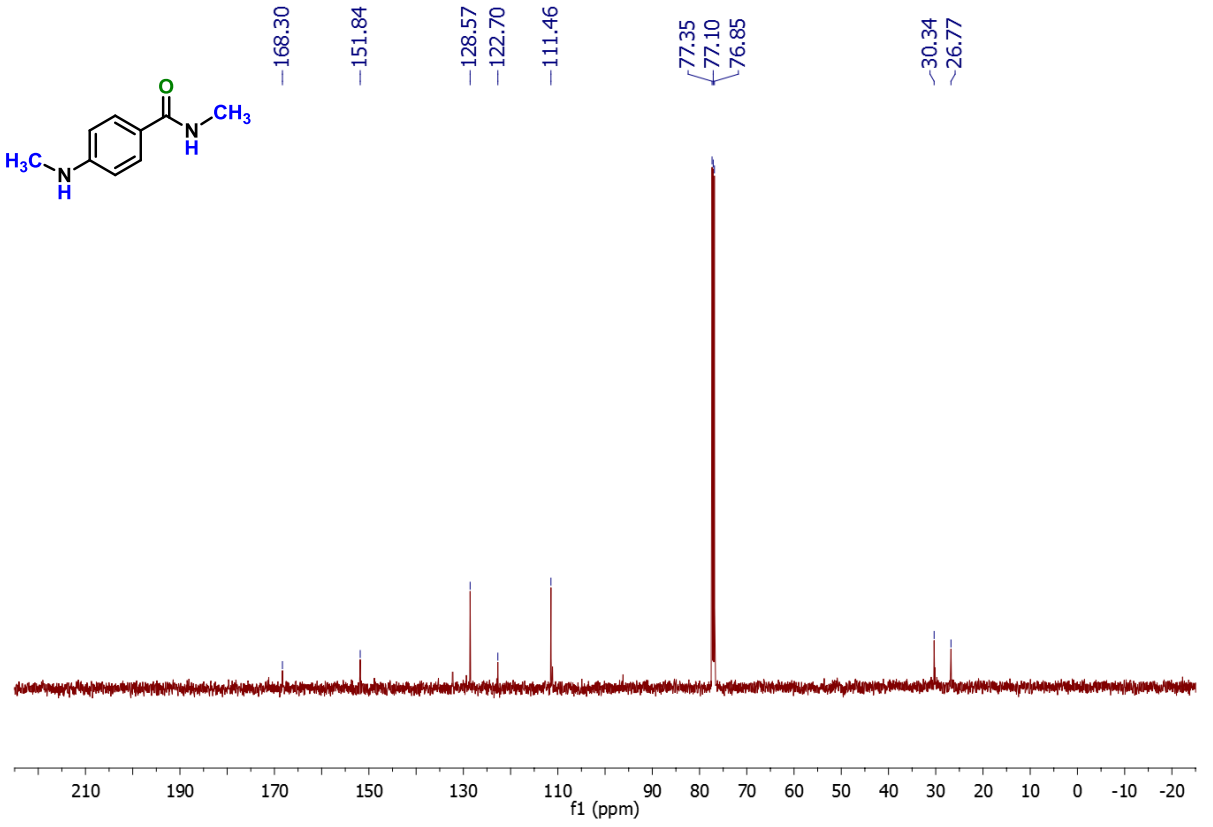

167.19
134.37
129.77
128.20
125.15
77.42
77.10
76.78
40.36
40.14
39.93
39.72
39.51
39.30
39.09
26.36
DMSO
f1 (ppm)

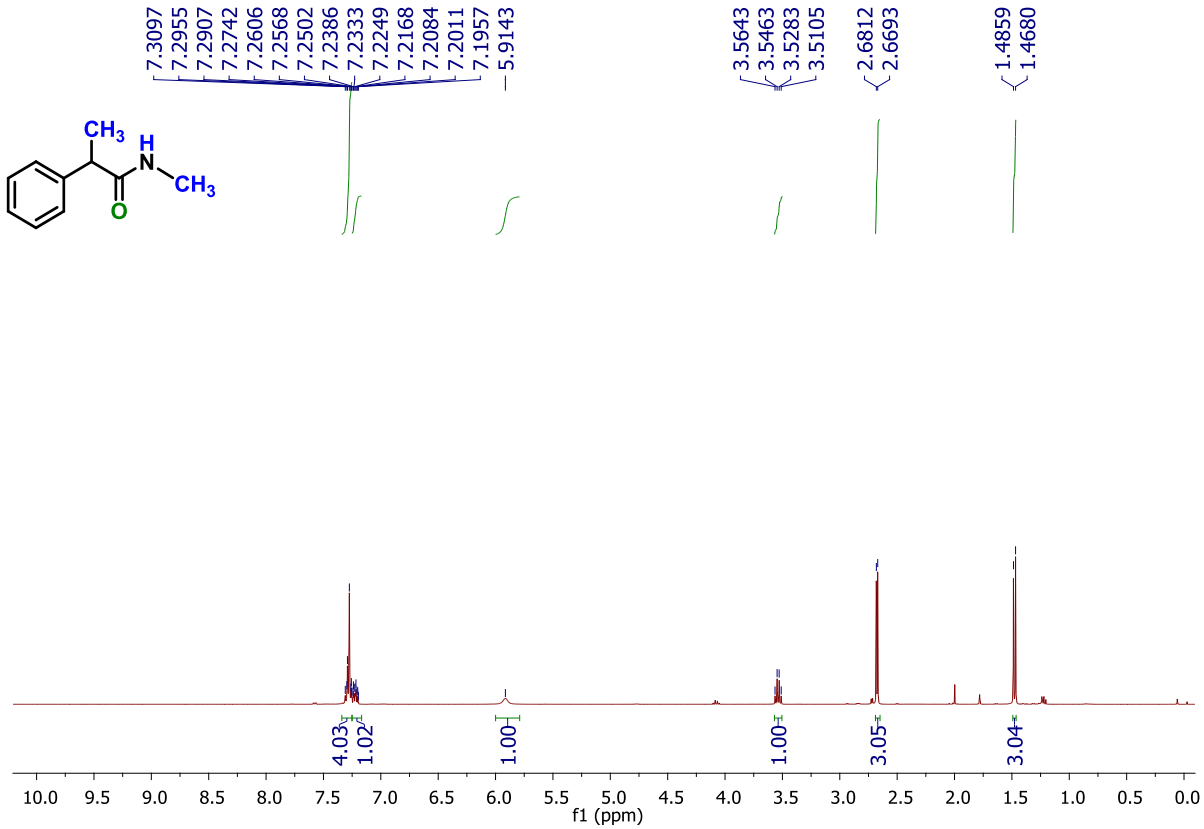

7.2656
7.2616
7.2547
7.2499
7.2460
7.2348
7.2282
7.1817
7.1677
7.1639
7.1479
6.0379
2.9469
2.9282
2.9079
2.7274
2.7155
2.4700
2.4498
2.4307
O
N
H
CH3
2.08
3.00
1.02
2.06
3.00
2.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
172.96
140.90
128.44
128.23
126.13
77.42
77.10
76.78
38.21
31.72
26.20
O
N
H
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

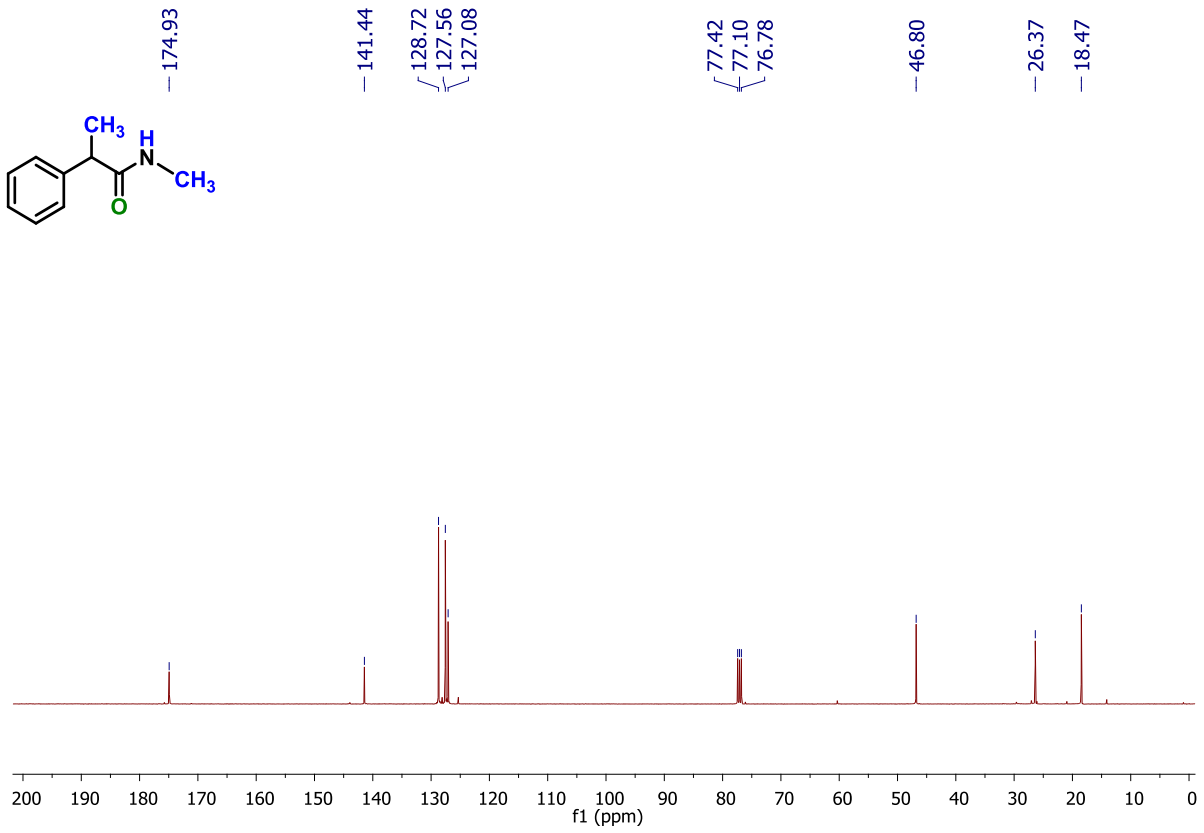

7.2503
5.5156
2.7904
2.7783
2.1599
2.1412
2.1216
1.6353
1.6167
1.5988
1.5804
1.5623
1.2312
0.8758
0.8593
0.8414
1.01
3.00
2.10
2.15
20.24
3.01
f1 (ppm)

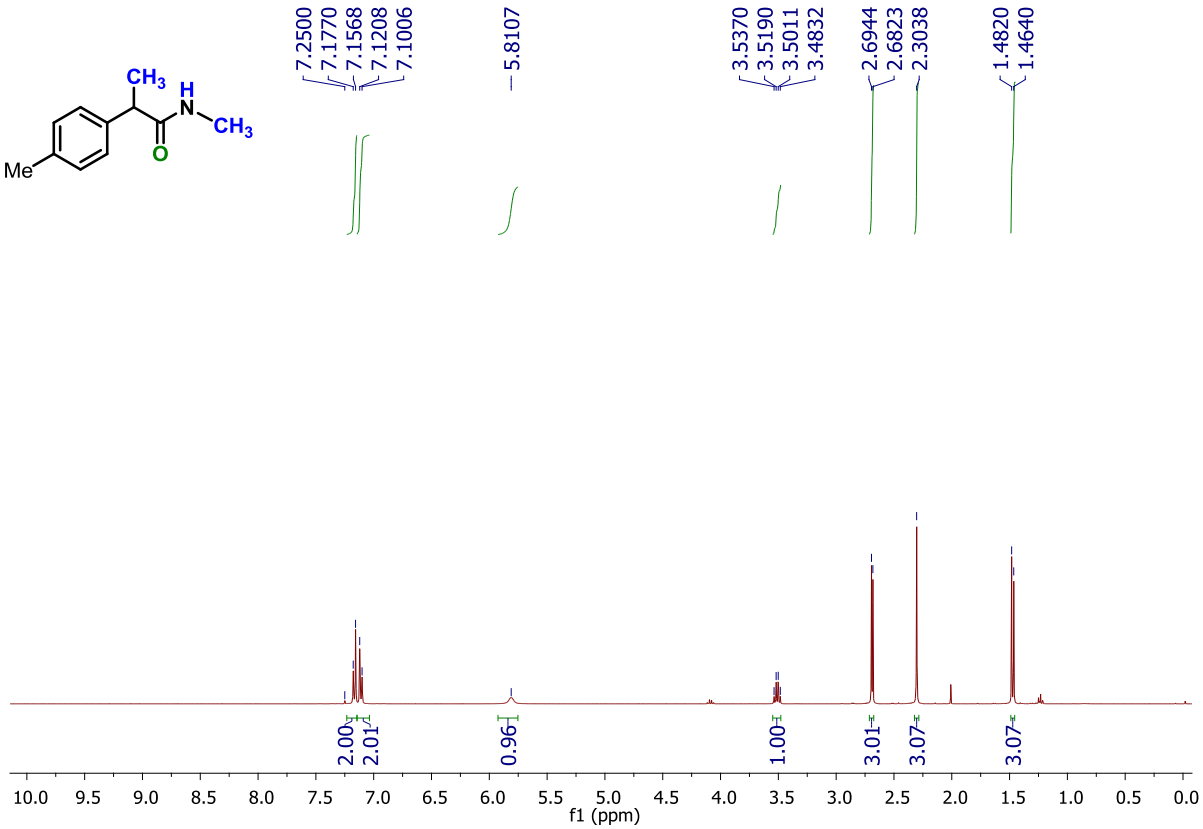

173.95
77.42
77.10
76.78
36.83
31.99
29.72
29.57
29.43
26.34
25.88
22.76
14.20
f1 (ppm)

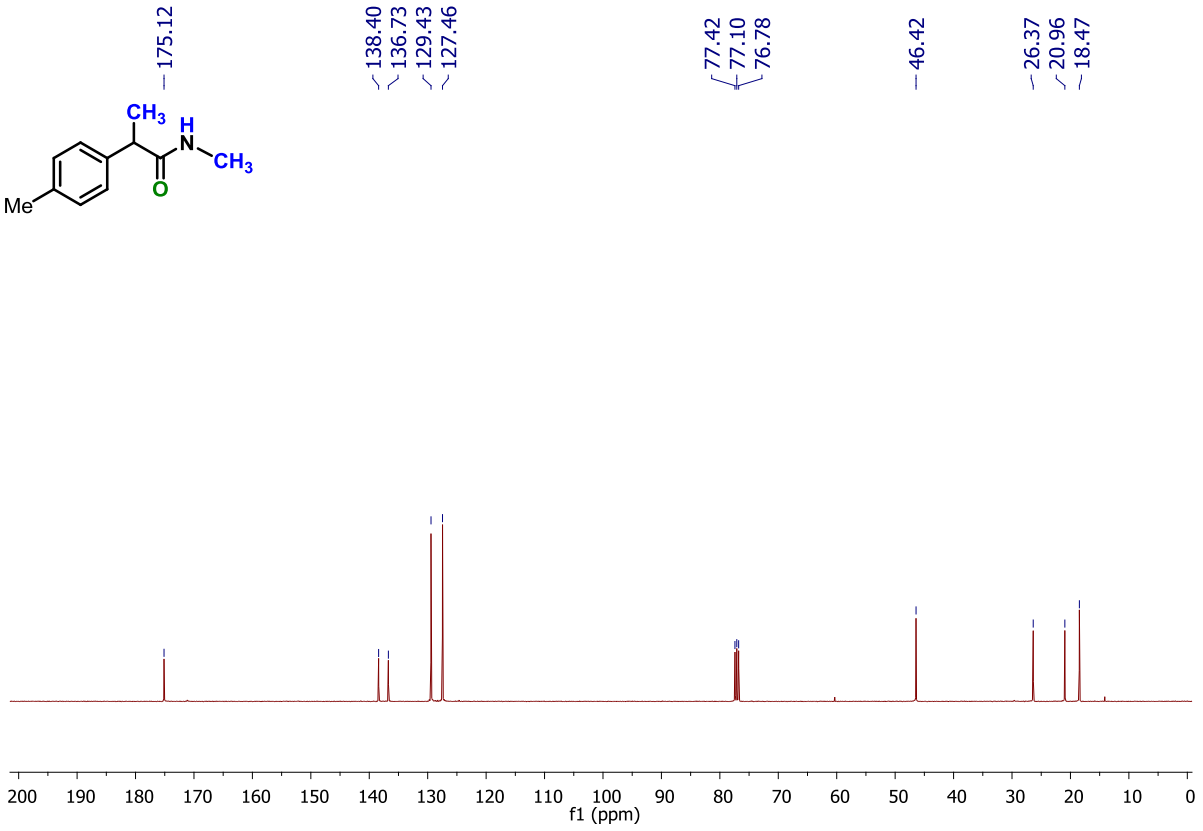

7.5899
7.5681
7.2501
6.5070
6.4854
6.3220
2.8979
2.8860
2.7909
O
CH3
N
H
H3C
N
H
2.00
2.06
0.98
3.02
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.30
151.84
128.57
122.70
111.46
77.35
77.10
76.85
30.34
26.77
O
CH3
N
H
H3C
N
H
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.3097
7.2955
7.2907
7.2742
7.2606
7.2568
7.2502
7.2386
7.2333
7.2249
7.2168
7.2084
7.2011
7.1957
5.9143
3.5643
3.5463
3.5283
3.5105
2.6812
2.6693
1.4859
1.4680
CH3
H
N
CH3
O
4.03
1.02
1.00
1.00
3.05
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.93
141.44
128.72
127.56
127.08
77.42
77.10
76.78
46.80
26.37
18.47
CH3
H
N
CH3
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.2500
7.1770
7.1568
7.1208
7.1006
5.8107
3.5370
3.5190
3.5011
3.4832
2.6944
2.6823
2.3038
1.4820
1.4640
CH3
H
N
CH3
O
Me
2.00
2.01
0.96
1.00
3.01
3.07
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


175.12
138.40
136.73
129.43
127.46
77.42
77.10
76.78
46.42
26.37
20.96
18.47
CH3
H
N
CH3
O
Me
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

18. References

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