Electronic Supplementary Material (ESI) for ChemComm.

Thiazolium Carbene Catalysts for the Fixation of CO_2 onto Amines

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Contents:

1 General experimental details:

The carbene precursors and all other reagents were purchased from commercial sources and used without further purification. Purification of the products was conducted with technical grade solvents on silica gel. GC was performed on an Agilent 7890 equipped with a HP-5 column. NMR spectra were recorded at 293 K on a Bruker DMX 400 instrument with TMS as internal standard in $CDCl_3$. High resolution mass spectra were recorded on a Micromass Q-TOF Ultima API (ESI).

2 Catalytic procedures

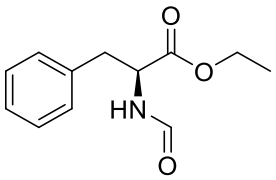
Catalyst preparation: In a glovebox, the catalyst precursor (0.15 mmol) and NaH (0.15 mmol) were placed in a 10 mL Schlenk tube. Using Schlenk techniques, 2 mL of dry DMA was added to and the system was stirred at r.t. for 30 min and the solution kept without stirring until a clear solution appeared. 1 mL of this solution was used for each reaction.

Catalytic N-formlyation reaction: The carbene solution (1 mL) was transferred into a dry three neck flask (after three vacuum and CO_2–purge cycles) already charged with the starting material (0.5 mmol) and connected to a CO_2 balloon. Next, DMA (2.5 mL) and of PMHS (200 µL) were introduced into the flask. The flask was heated to 50°C and the reaction was monitored by TLC and GC-MS. Upon completion the reaction mixture was filtered through celite and washed with ethyl acetate. After aqueous work up excess ethyl acetate was added to afford a clear solution. The combined organic phases were dried with anhydrous sodium sulfate and the product was purified using column chromatography using ethyl acetate-pentane and 1% triethylamine.

Catalytic N-methlyation reaction: The reaction was conducted as described above for the N-formlyation reaction except it was conducted at 100°C.

3. Product characterization

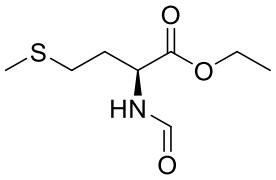
ethyl formyl-L-phenylalaninate



off-white solid

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.11 (s, 1H), 7.28 – 7.18 (m, 4H), 7.09 – 7.02 (m, 2H), 5.98 (s, 1H), 4.88 (dtd, *J* = 8.0, 5.8, 0.9 Hz, 1H), 4.12 (qd, *J* = 7.2, 0.8 Hz, 2H), 3.18 – 3.02 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) 171.0, 160.4, 135.5, 129.4, 129.36, 128.6, 127.2, 77.2, 61.7, 51.8, 37.8, 14.1. HRMS (ESI) for $C_{12}H_{15}NO_3$ [M^+Na^+]: calc.: 244.0944. Found: 244.0950.

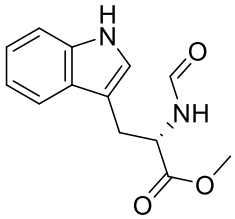
ethyl formyl-L-methioninate:



off-white solid

^{1}H NMR (400 MHz, DMSO-d_6) : 8.40 (s, 1H), 8.03 – 7.90 (s, 1H), 4.32 (tt, *J* = 8.9, 4.5 Hz, 1H), 4.12 – 3.92 (m, 2H), 1.99 – 1.91 (m, 3H), 1.90 – 1.69 (m, 3H), 1.08 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) 171.8, 161.6, 61.1, 50.0, 31.0, 29.8, 15.0, 14.5. HRMS (ESI) for $C_8H_{15}NO_3S$ [M^+Na^+]: calc.: 228.0665. Found: 228.0670.

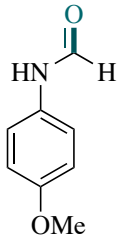
methyl formyl-L-tryptophanate[1]



Colorless liquid

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.35 (s, 1H), 8.14 (s, 1H), 7.56 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.36 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.14 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.24 (d, *J* = 8.0 Hz, 1H), 5.09 – 4.99 (m, 1H), 3.72 (s, 3H), 3.36 (dd, *J* = 5.4, 3.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 170.9, 159.8, 135.0, 126.4, 121.9, 121.3, 118.6, 117.4, 110.3, 108.3, 59.4, 51.4, 50.5, 26.4. HRMS (ESI) for $C_{13}H_{14}N_2O_3$ [M^+Na^+]: calc.: 269.0897. Found: 269.0893.

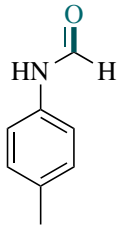
N-(4-methoxyphenyl)formamide[2]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.48 – 8.21 (m, 1H), 7.42 – 7.30 (m, 1H), 7.03 – 6.89 (m, 1H), 6.88 – 6.76 (m, 2H), 3.73 (d, *J* = 4.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 162.8, 158.7, 157.6, 156.7, 121.7, 114.9, 114.2, 77.2, 55.5. MS (EI): *m*/*z* (rel. int.) 152.

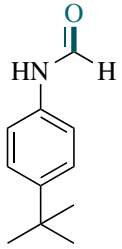
***N*-*p*-tolylformamide**[2]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.61 – 8.22 (m, 1H), 7.42 – 7.30 (m, 1H), 7.07 (dd, *J* = 10.7, 8.1 Hz, 2H), 7.00 – 6.86 (m, 1H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 162.7, 158.9, 130.2, 129.5, 120.0, 119.1, 20.8. MS (EI): *m*/*z* (rel. int.) 136.

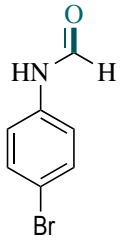
***N*-(4-(*tert*-butyl)phenyl)formamide**[3]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.63 – 8.26 (m, 1H), 7.44 – 7.35 (m, 1H), 7.34 – 7.23 (m, 2H), 6.96 (d, *J* = 8.5 Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 162.8, 159.1, 126.5, 125.8, 119.8, 118.8, 34.4, 31.3. MS (EI): *m*/*z* (rel. int.) 178.1.

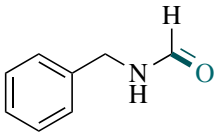
***N*-(4-bromophenyl)formamide**[4]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.60 – 8.31 (m, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.38 (s, 2H), 6.90 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 160.9, 157.7, 131.8, 131.1, 120.4, 119.3. MS (EI): *m*/*z* (rel. int.) 201.

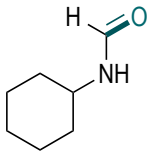
***N*-benzylformamide**[5]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.62 – 8.27 (m, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.26 (m, 2H), 6.95 (d, *J* = 8.6 Hz, 1H), 1.19 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 162.2, 126.6, 125.9, 119.7, 118.9, 31.31. MS (EI): *m*/*z* (rel. int.) 136.

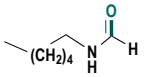
***N*-cyclohexylformamide**[6]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.06 (s, 1H), 5.33 (s, 1H), 1.86 (m, 2H), 1.66 – 1.51 (m, 2H), 1.38 – 1.05 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 159.3, 46.0, 33.7, 32.0, 24.4, 24.0, 23.7. MS (EI): *m*/*z* (rel. int.) 128.

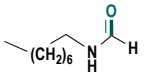
_N_-hexylformamide[7]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.09 (s, 1H), 5.63 (s, 1H), 3.18 (m, 2H), 1.45 (m, 2H), 1.30 – 1.20 (m, 6H), 0.82 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 160.1, 37.1, 30.4, 28.4, 25.4, 21.5, 12.9. MS (EI): *m*/*z* (rel. int.) 130.

N-octylformamide[8]

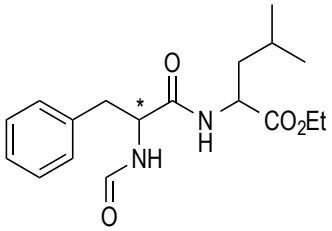


Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 8.10 (s, 1H), 3.19 (m, 2H), 1.45 (m, 2H), 1.21 (m, 11H), 0.81 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 160.0, 37.1, 30.7, 28.5, 28.1, 25.8, 25.3, 21.6, 13.0. MS (EI): *m*/*z* (rel. int.) 158.

Ethyl formylphenylalanylleucinate

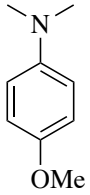
Preparation of peptide: Under N_2, 1,07 g of BOC-L-Phenylalanine was dissolved in 15 mL of $CHCl_3$ and cooled down to -20 °C. 0.44 mL of N-methylmorpholine and 0.61 mL of isobutylchloroformate were added dropwise to the solution. The mixture was stirred for 20 min at -20 °C. L-leucine methyl ester hydrochloride (0.8 g) and 0.44 mL of N-methylmorpholine were added. The mixture was stirred for 1h at -20 °C, then brought to r.t and stirred overnight. After reaction, the $CHCl_3$ was removed under vacuum. Then, the BOC protecting group was removed by stirring the product in a 1:1 ratio of TFA: DCM (total volume: 2 mL) at r.t. for 3h.



The peptide was synthesized under the catalytic formylation conditions with 10 mol% catalyst B. There was no starting material left in the reaction mixture after 48 h heating at 50°C which was confirmed by HRMS and the product peak was found in the HRMS data. Due to purification problems we could not isolate the product.

HRMS (ESI) for $C_{18}H_{26}N_2O_4$ [M^+H^+] & [M^+Na^+]: calc.: 335.1965 & 357.1785. Found: 335.2333 & 357.2032

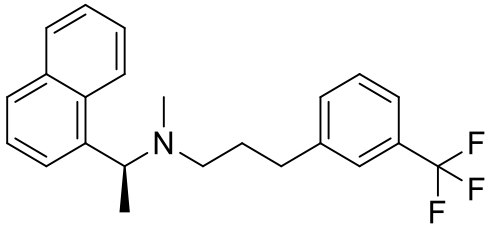
***4-methoxy-N,N-dimethylaniline*:** [9]



Colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) : 6.91 – 6.84 (m, 2H), 6.84 – 6.75 (m, 2H), 3.80 (s, 3H), 2.90 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) : 152.0, 145.7, 114.9, 114.6, 55.7, 41.8. MS (EI): *m*/*z* (rel. int.) 152.

***(R)-N-methyl-N-(1-(naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine*:**[11]



Colorless liquid.

^{11}H NMR (400 MHz, Chloroform-*d*) : 8.44 (d, *J* = 9.5 Hz, 1H), 7.89 (d, *J* = 9.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.58-7.45 (m, 4H), 7.43-7.41 (m, 1H), 7.35-7.28 (m, 2H), 7.22-7.18 (m, 1H), 4,33 (q, *J* = 6.7 Hz, 1H), 2.59-2.43 (m, 4H), 2.32 (s, 3H), 1.83-1.75 (p, *J* = 7.4 Hz, 2H), 1.49 (d, *J* = 6.7 Hz, 3H). NMR (101 MHz, Chloroform-*d*) : 142.4, 139.7, 133.3, 133.0, 130.8, 130.7, 127.6, 127.5, 126.6, 126.3, 124.4, 124.3, 124.3, 123.4, 121.4, 59.5, 52.5, 37.6, 32.1, 28.0, 15.7. HRMS (ESI) for $C_{23}H_{24}F_3N$ [M^+H^+]: calc.: 372.194. Found: 372.1934.

References

[1] S. Rasheed, D. N. Rao, A. S Reddy, R Shankar, P. Das, *RSC Adv.* **2015**, *5*, 10567–10574.
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[4] M. Nasrollahzadeh, A. Zahraei, A. Ehsani, M. Khalaj, *RSC. Adv.* **2014,** 4, 20351.
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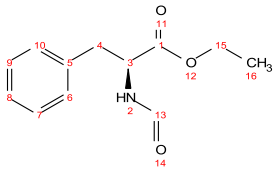
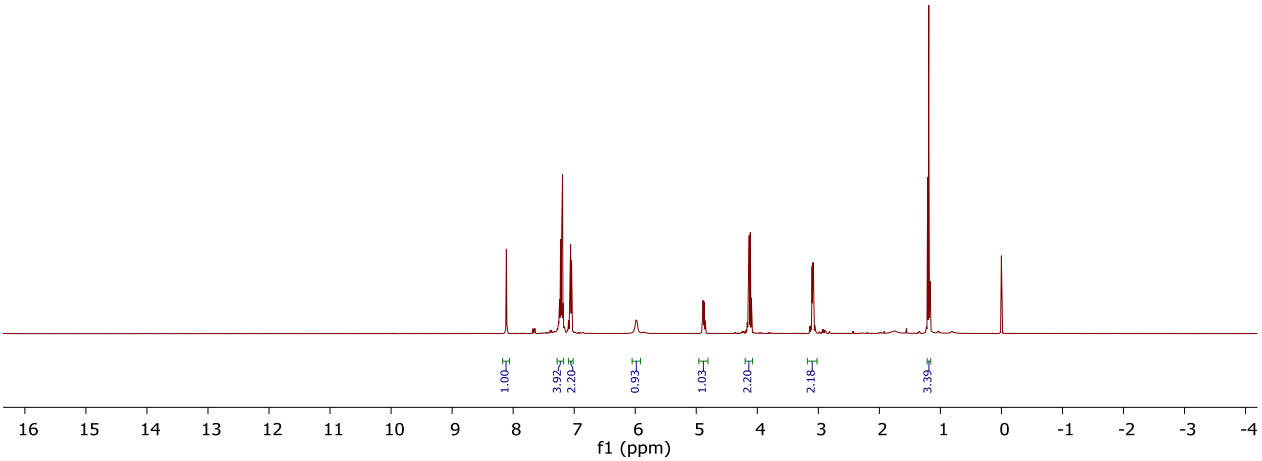
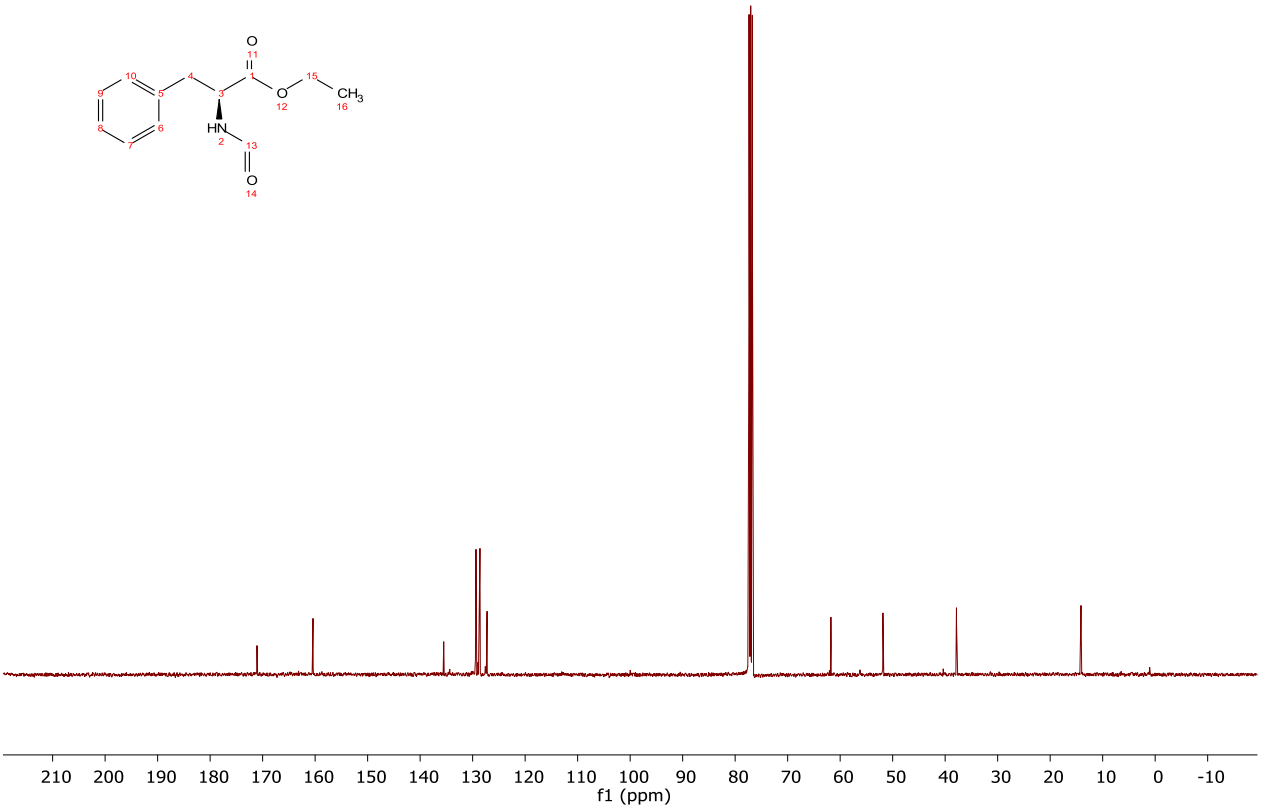
[9] M. O. Ratnikov, M. P. Doyle, *J. Am. Chem. Soc.* **2013**, 135, 1549-1557.



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15
9
5
3
1
O
12
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16
HN
2
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8
6
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O
14
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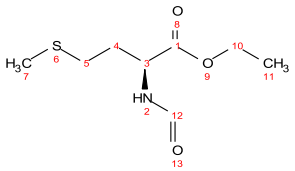
f1 (ppm)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4
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CH_3
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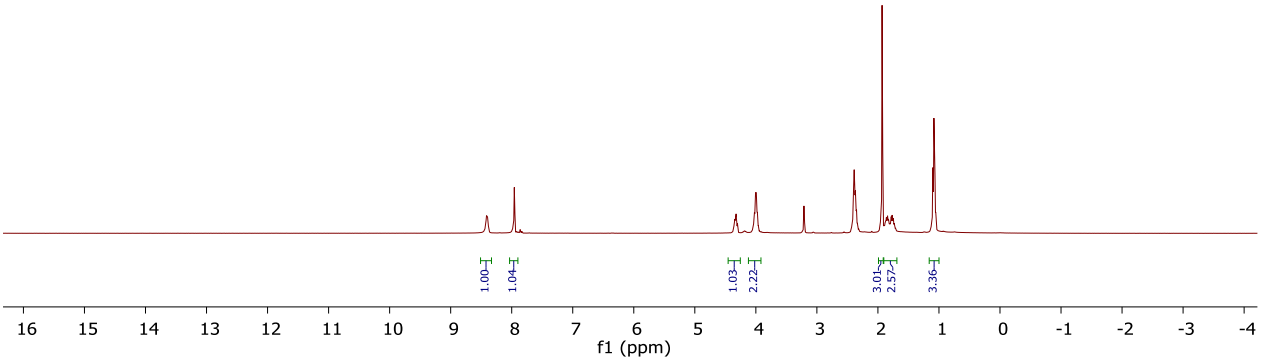
12
O
13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2.57
3.36
16
15
14
13
12
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8
7
6
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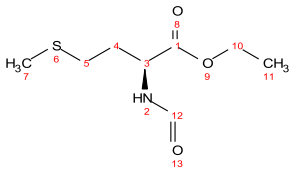
-3
-4
f1 (ppm)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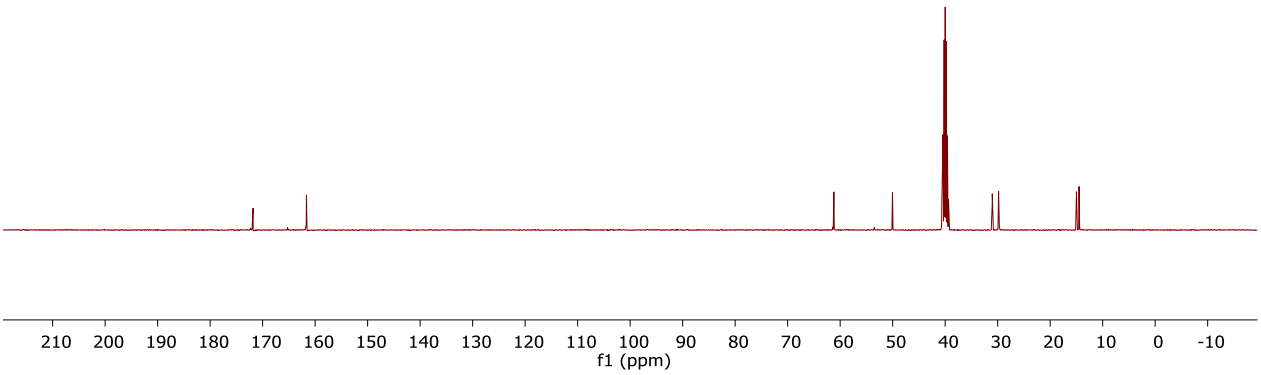
13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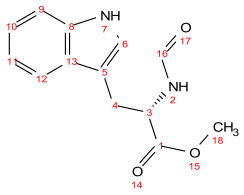
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CH3
O
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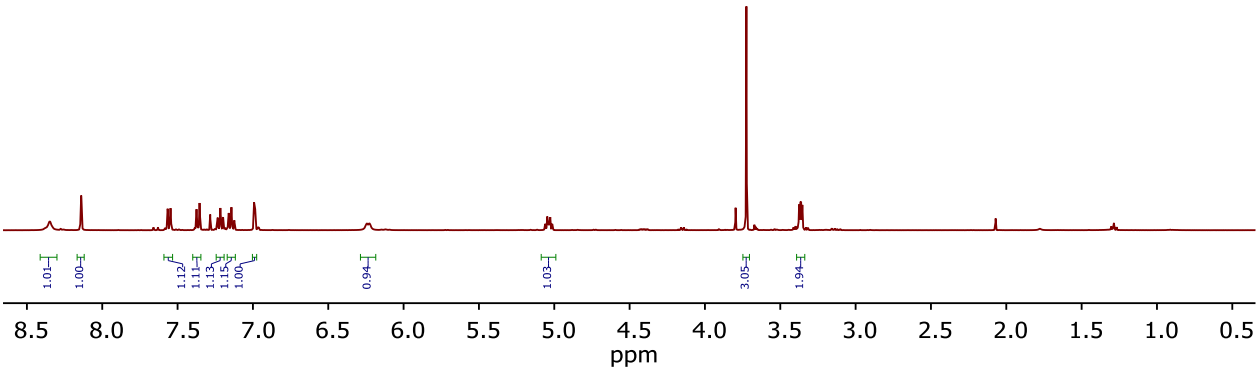
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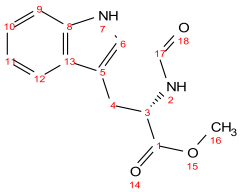
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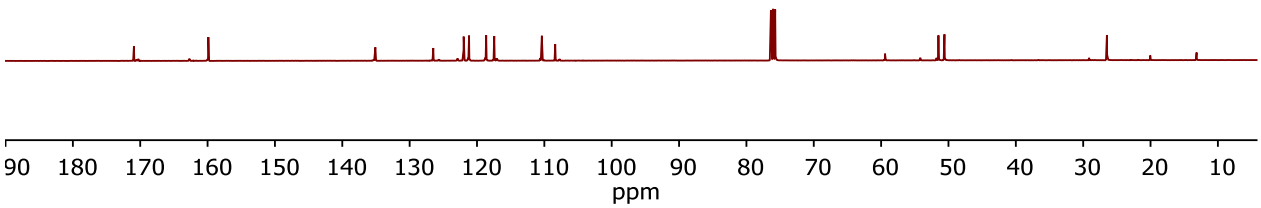
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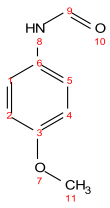
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O
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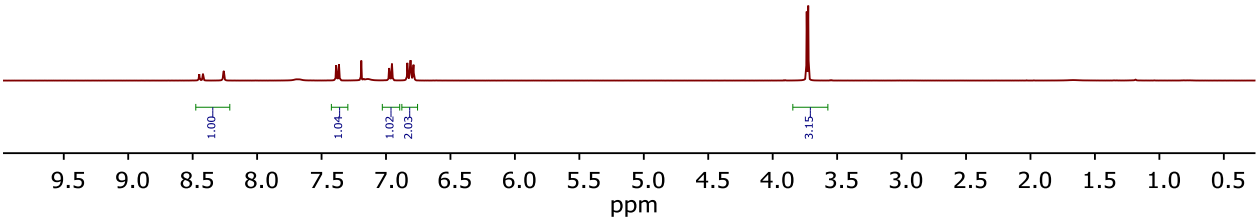
CH3
11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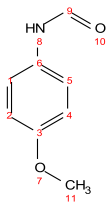
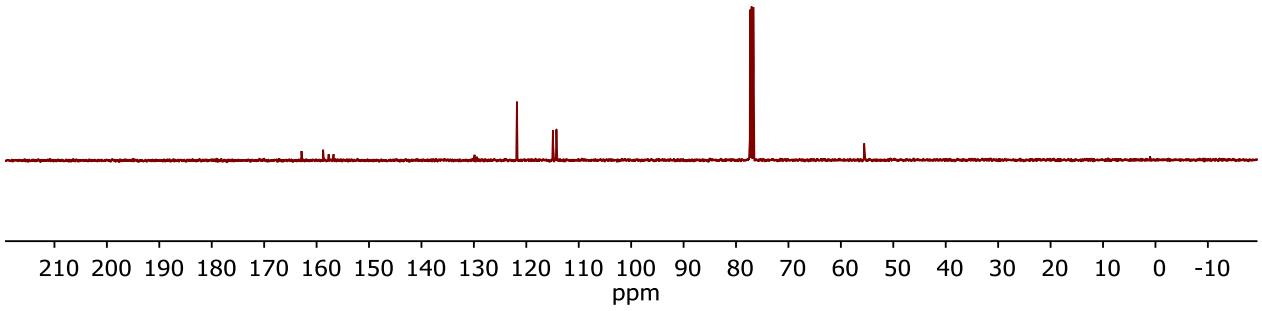
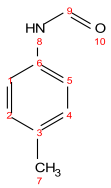
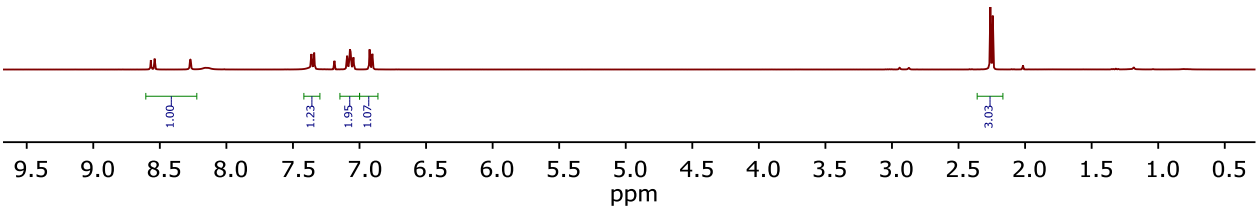
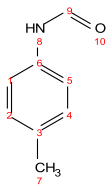
1.04
1.02
2.03
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

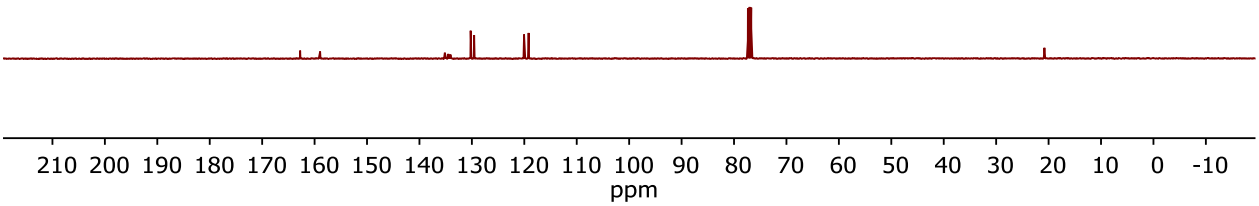

HN
9
O
10
8
6
1
5
2
4
3
O
7
CH3
11

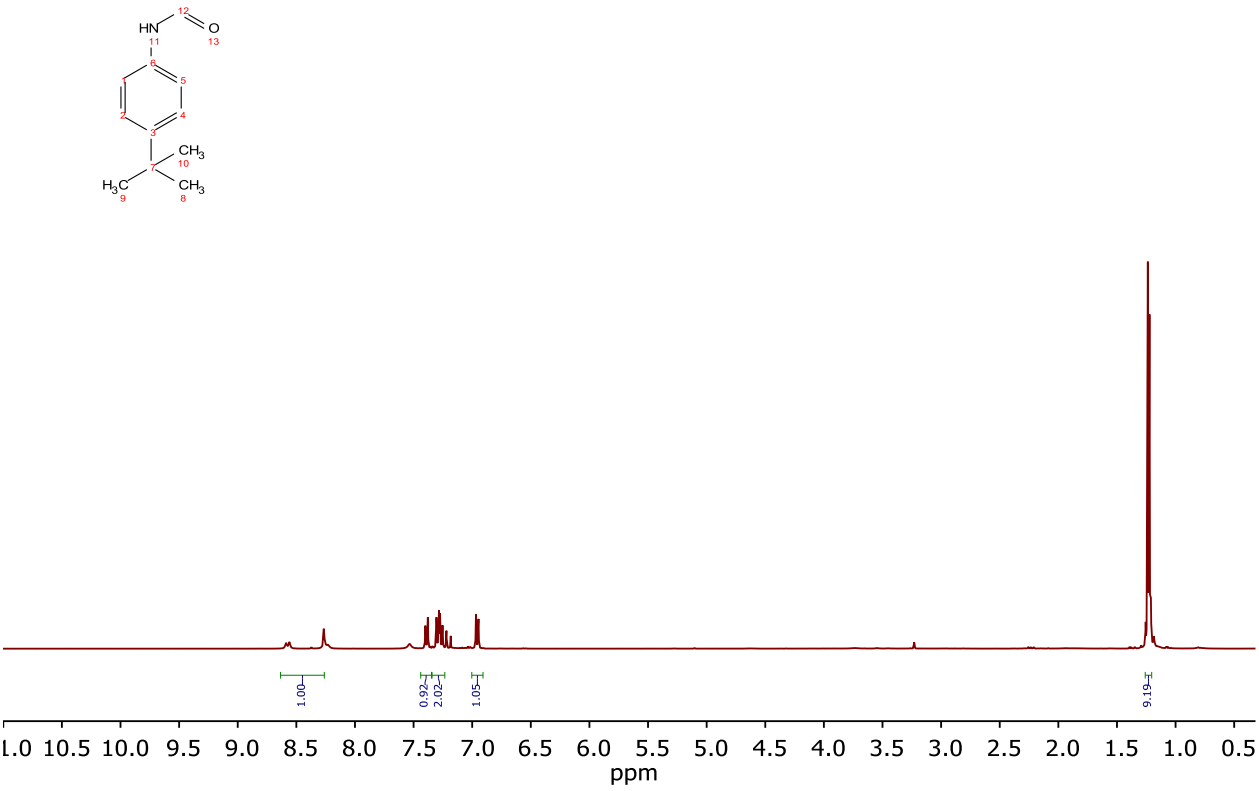

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

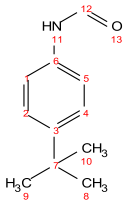

HN
O
CH3

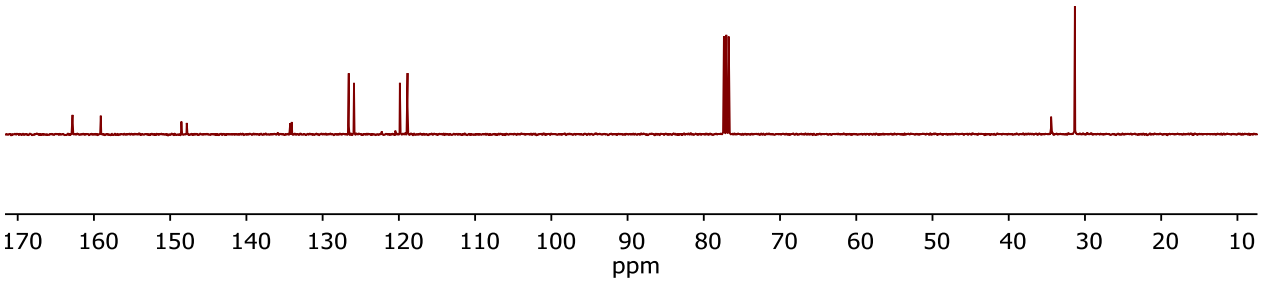

1.00
1.23
1.95
1.07
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

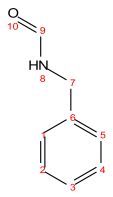

HN
O
CH3

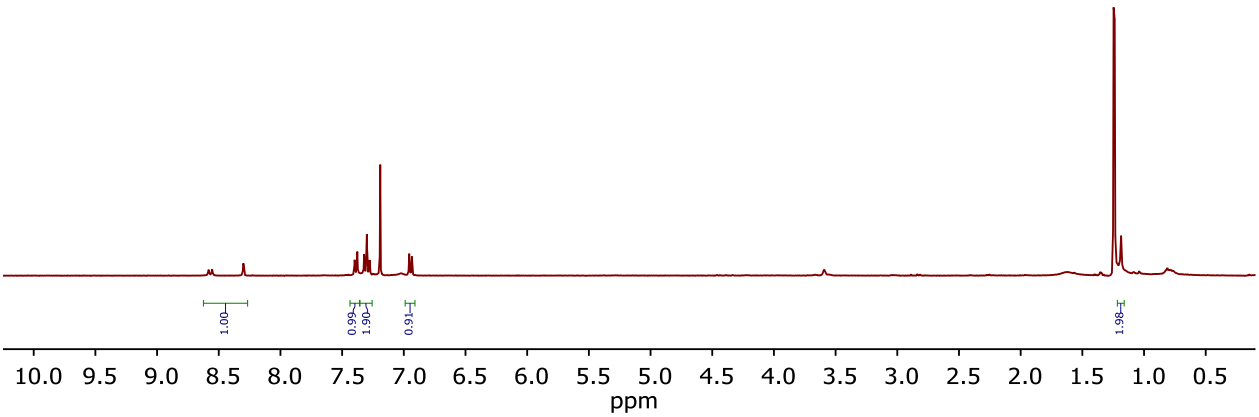

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

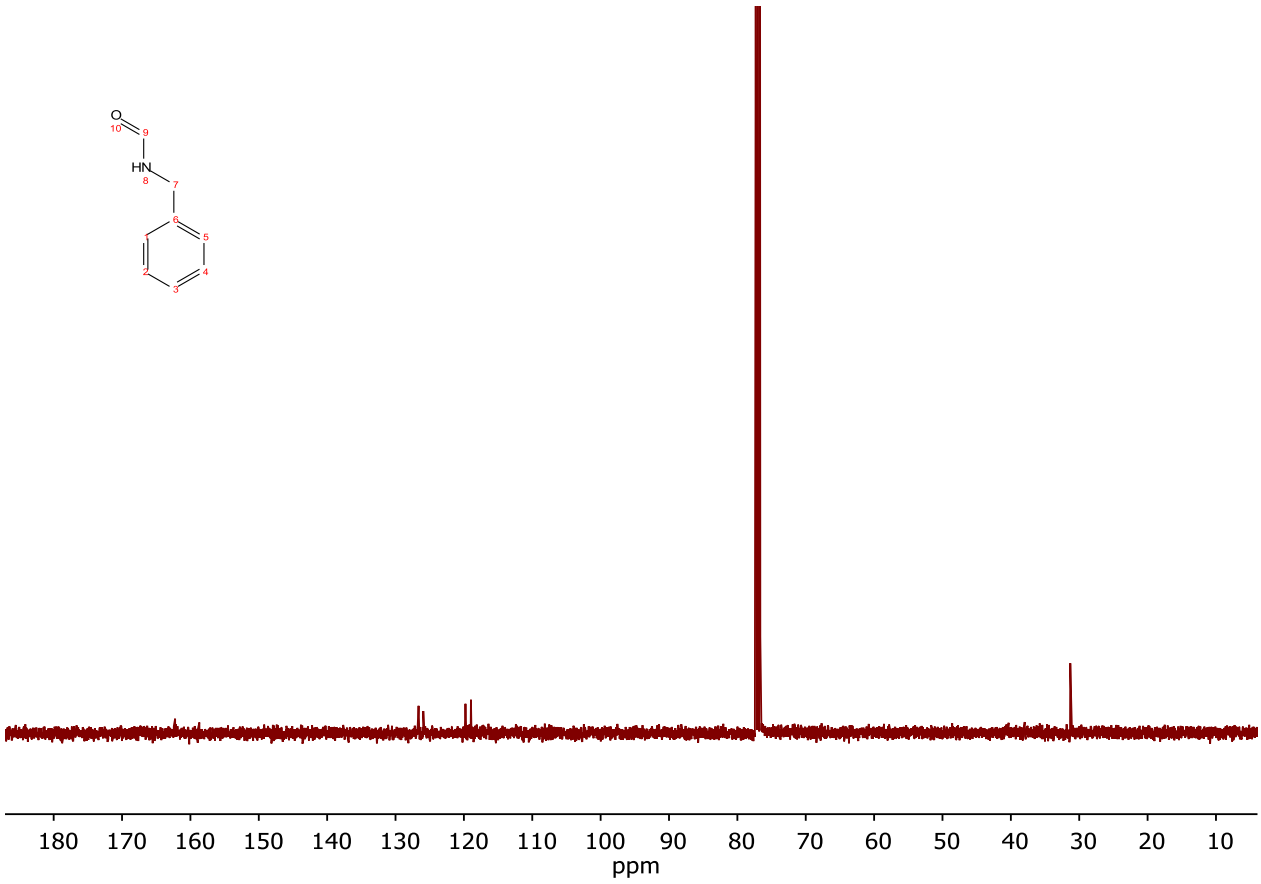

HN
O
CH3
H3C
CH3
1.00
0.92
2.02
1.05
9.19
ppm

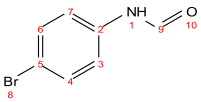

HN
11
12
O
13
1
2
3
4
5
6
7
CH3
10
H3C
9
CH3
8

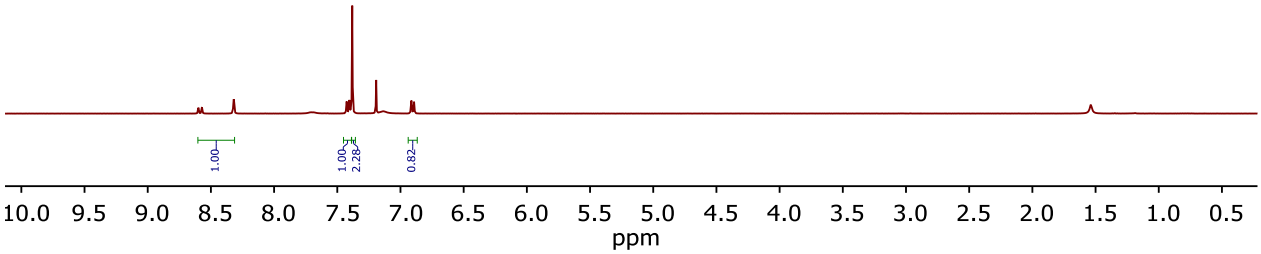

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

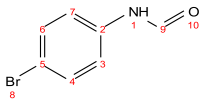

O
10
9
HN
8
7
6
5
1
2
4
3

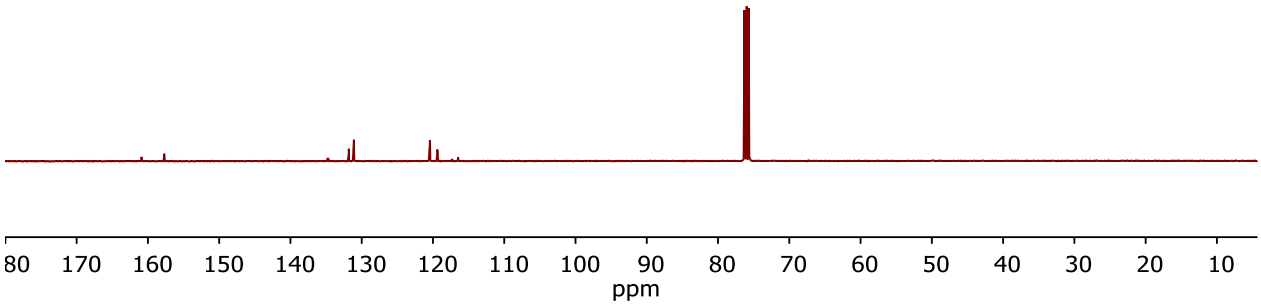

1.00
0.99
1.90
0.91
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

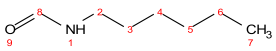

O
10
9
HN
8
7
6
5
1
2
4
3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

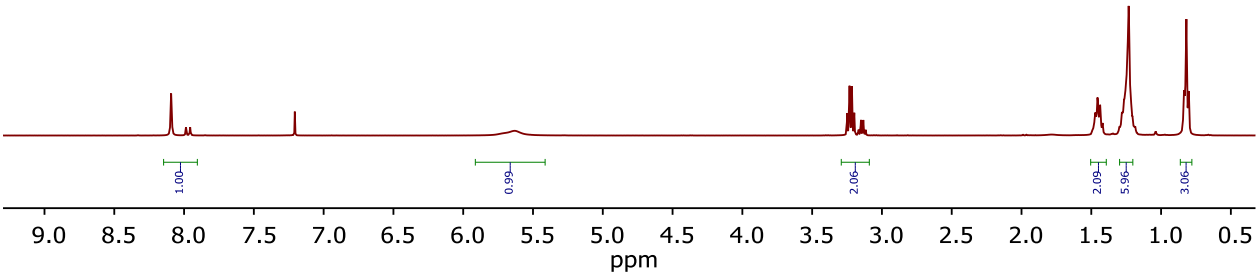

NH
1
O
10
Br
8

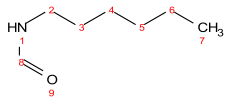

1.00
1.00
2.26
0.82
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

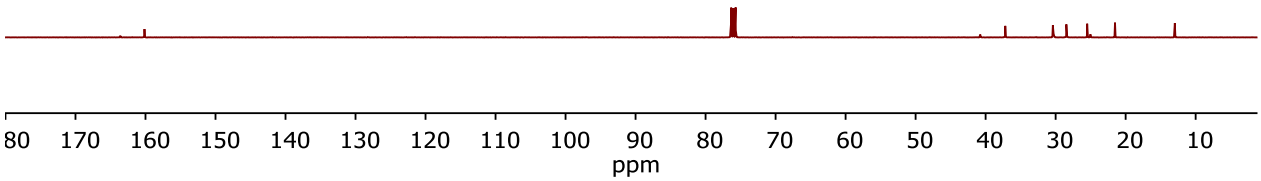

NH
1
O
10
Br
8

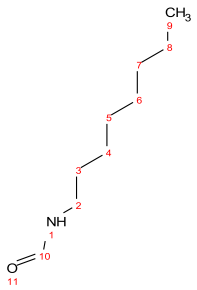

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

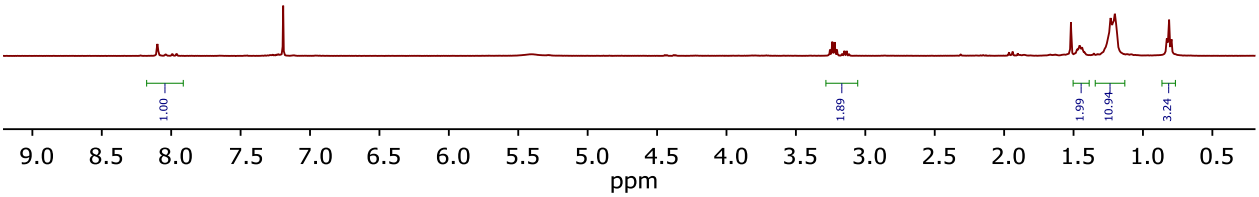

O
NH
CH3
1
2
3
4
5
6
7
8
9

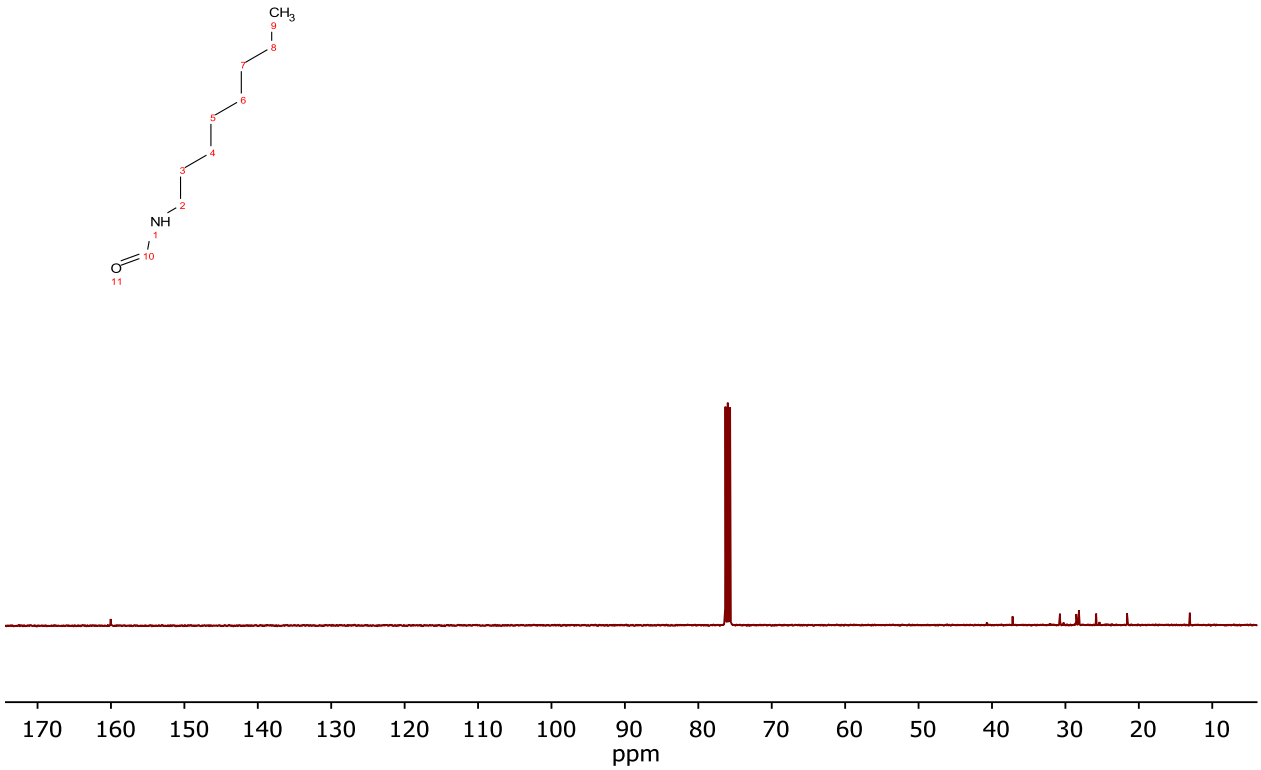

1.00
0.99
2.06
2.09
5.96
3.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

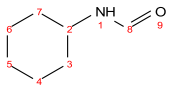

HN
1
2
3
4
5
6
CH3
7
8
O
9

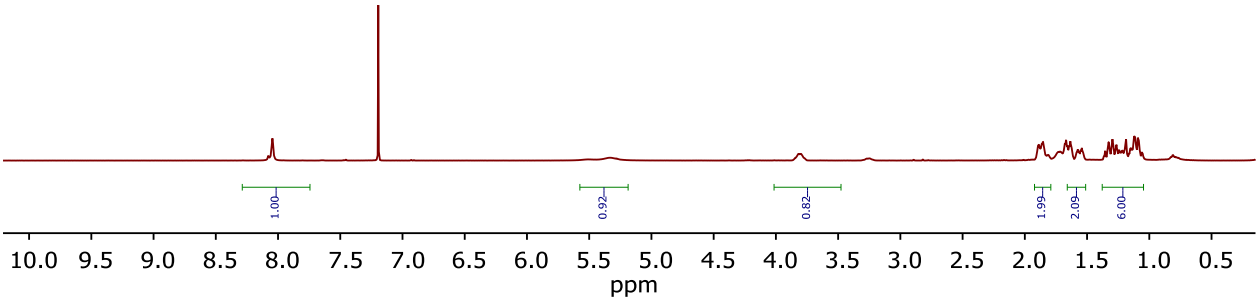

80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

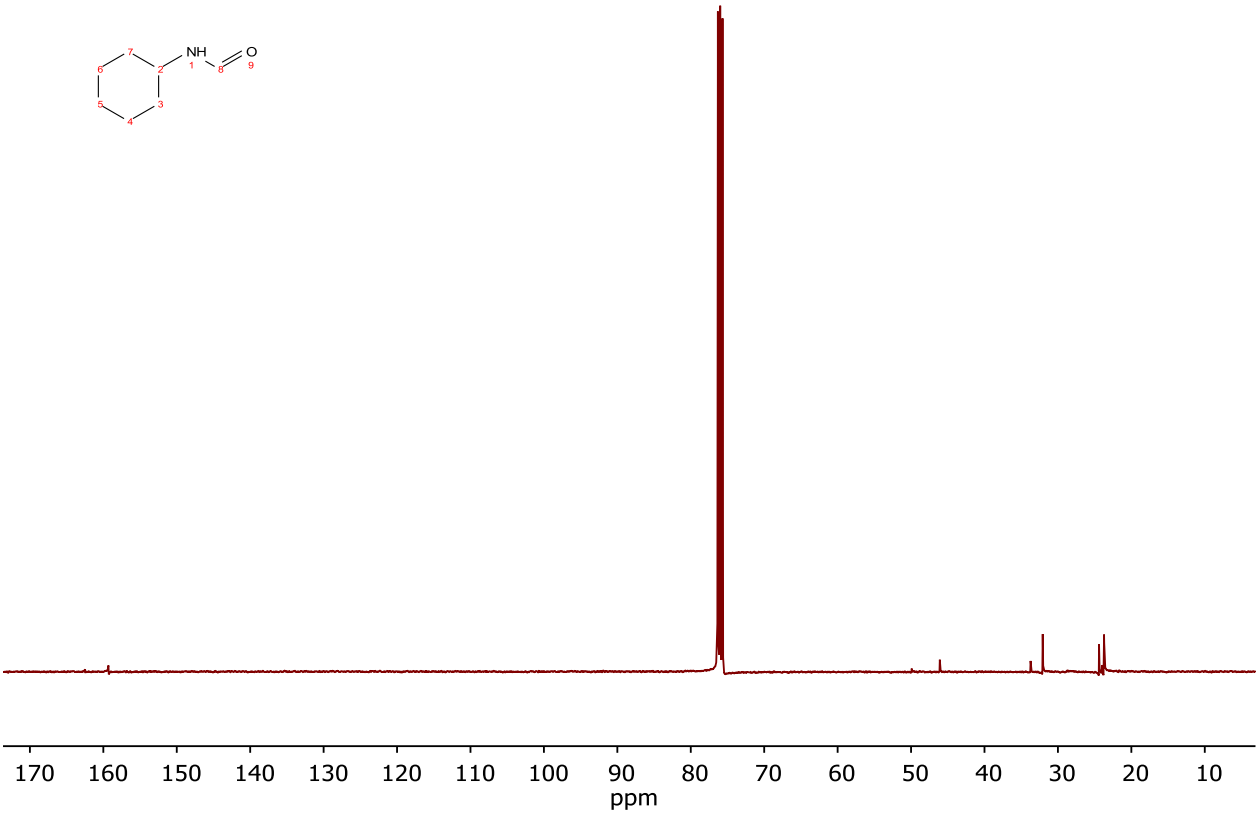

CH3
9
8
7
6
5
4
3
2
NH
1
10
O
11

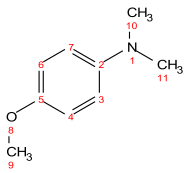

1.00
1.89
1.99
10.94
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

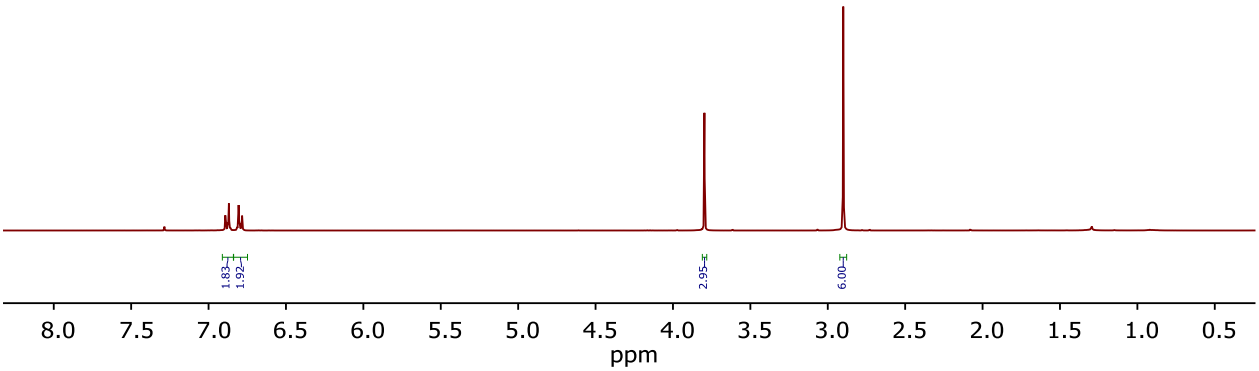

CH3
9
8
7
6
5
4
3
2
NH
1
10
O
11
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

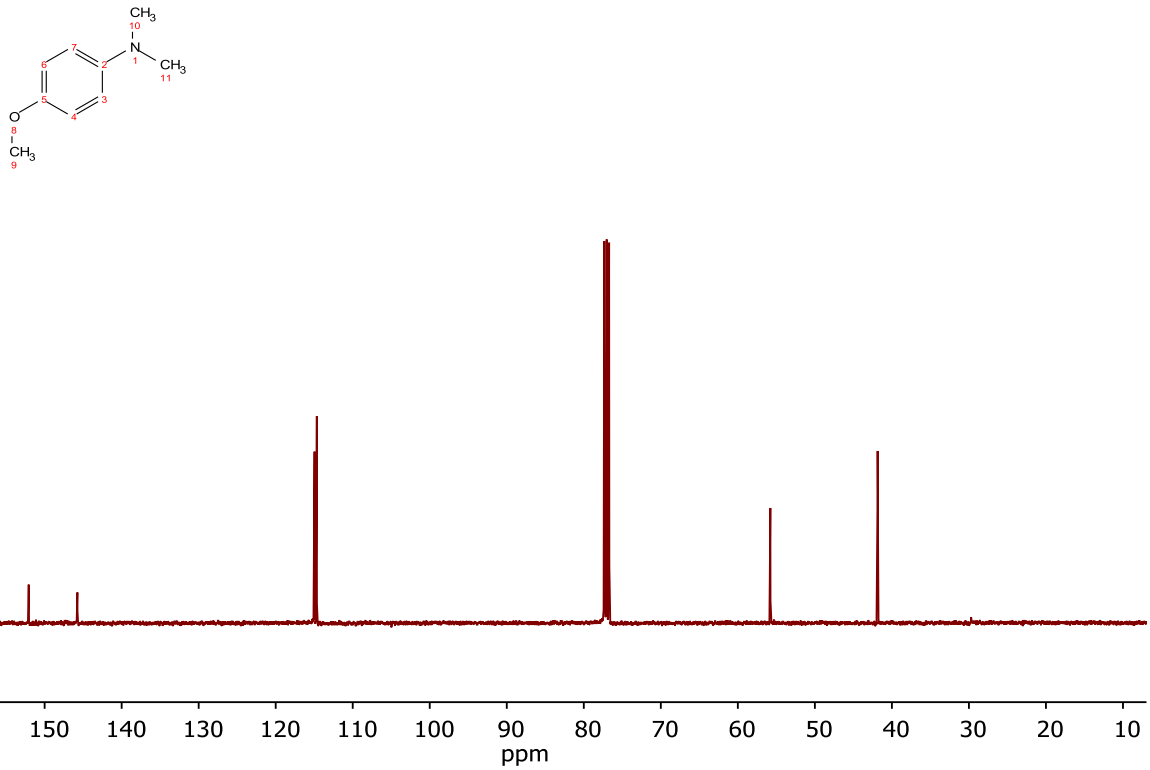

NH
O
1
2
3
4
5
6
7
8
9

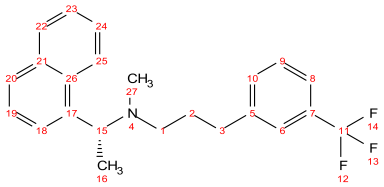

1.00
0.92
0.82
1.99
2.09
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

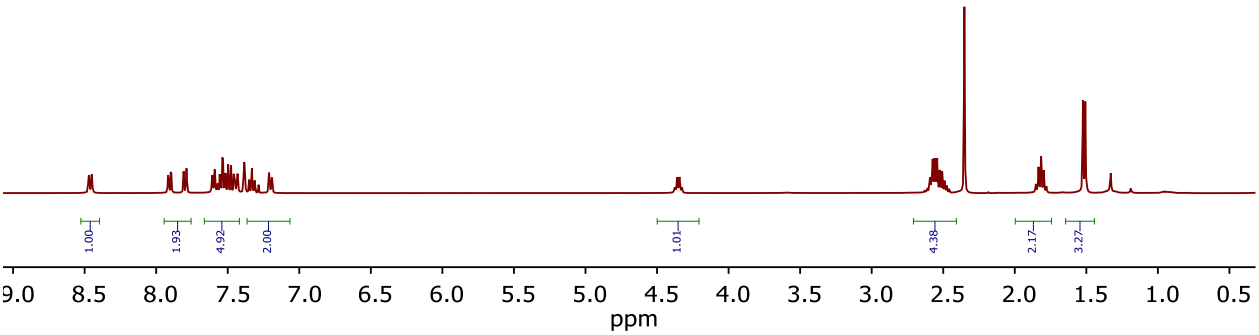

NH
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

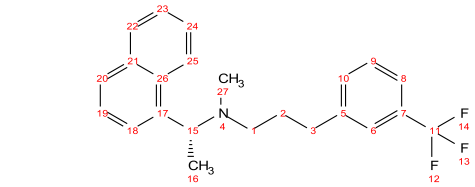

CH3
10
N
1
CH3
11
O
8
CH3
9

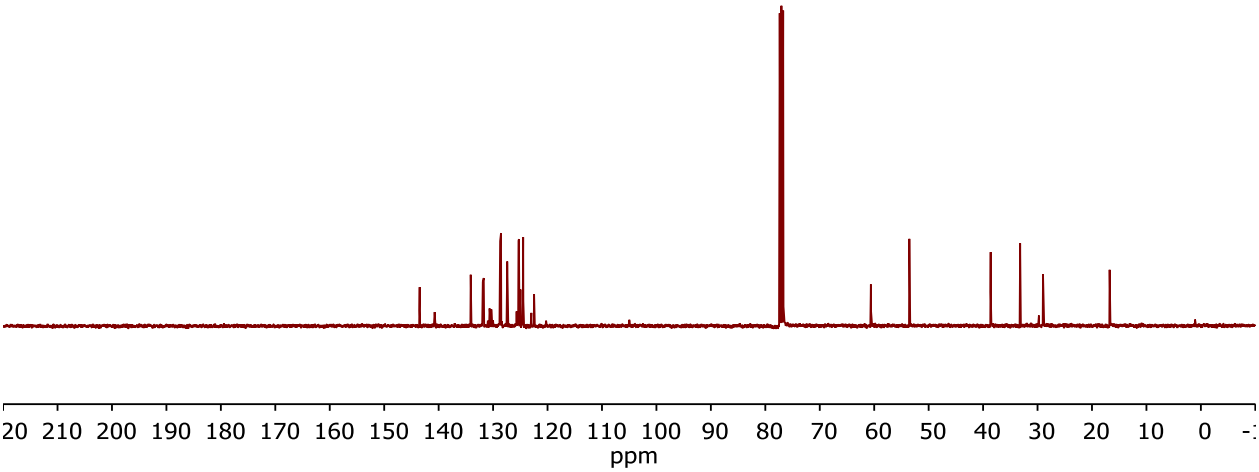

1.83
1.92
2.95
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


CH3
10
N
1
CH3
11
O
8
CH3
9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CH3
27
N
4
CH3
16
F
14
F
13
F
12


1.00
1.93
4.92
2.00
1.01
4.38
2.17
3.27
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
ppm


23
22
24
21
25
20
26
CH3
27
19
17
N
4
10
9
8
18
15
1
2
3
5
6
7
11
F
14
F
13
CH3
16
F
12


20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm