Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Lewis Acidity Quantification and Catalytic Activity of Ti, Zr and Al-Supported Mesoporous Silica

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Materials. ACS grade organic solvents were used for the synthesis of metalated mesoporous SBA-15 materials without further purification. Titanium *iso*-propoxide, zirconium butoxide and aluminum *iso*-propoxide were purchased from Sigma-Aldrich and used as received. For the study of the Lewis acidity and for the amidation reaction, solvents were pre-treated and distilled under a N_2 atmosphere over sodium/benzophenone before use. Aniline (≥99.0%, Sigma-Aldrich) was distilled prior to use, and undecanoic acid (98%, Sigma-Aldrich) and morpholine (≥99.0%, Sigma-Aldrich) were used as received. Pyridine (99.8%) was purchased from Sigma-Aldrich and distilled under an N_2 atmosphere. Hammet indicators butter yellow (analytical grade), phenylazodiphenylamine (97%) and dicinnamalacetone (98%) were purchased from Sigma-Aldrich and used without further purification.

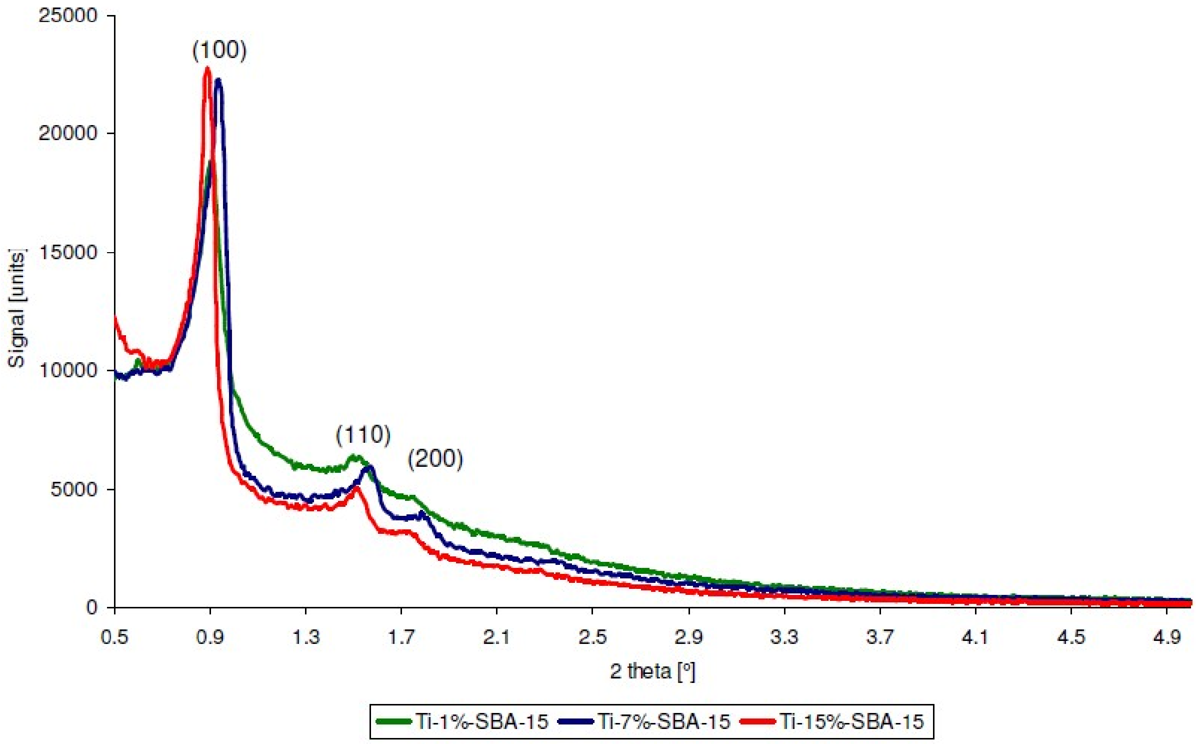
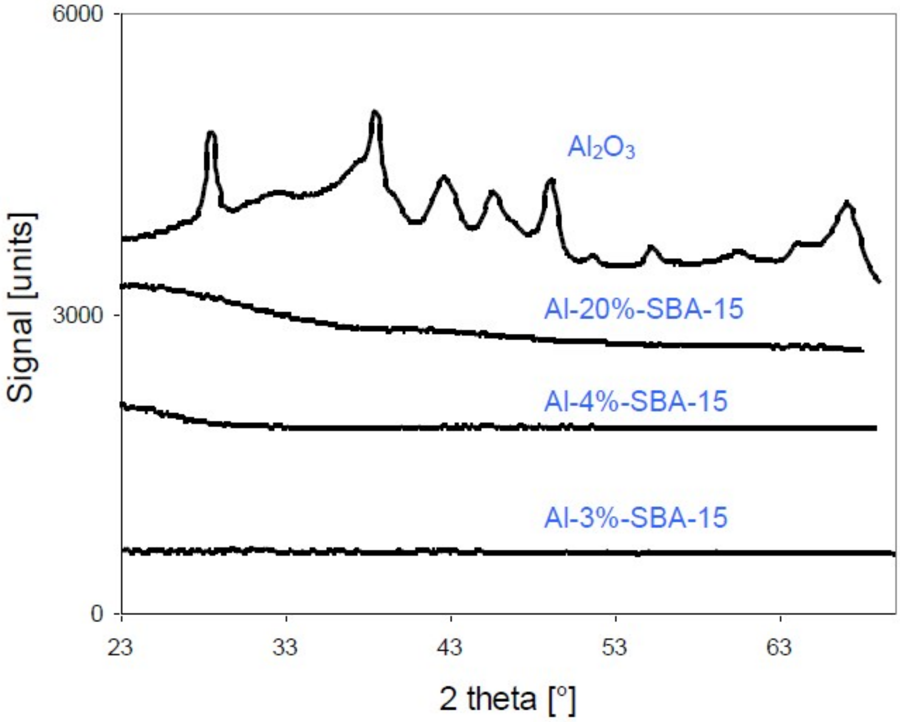
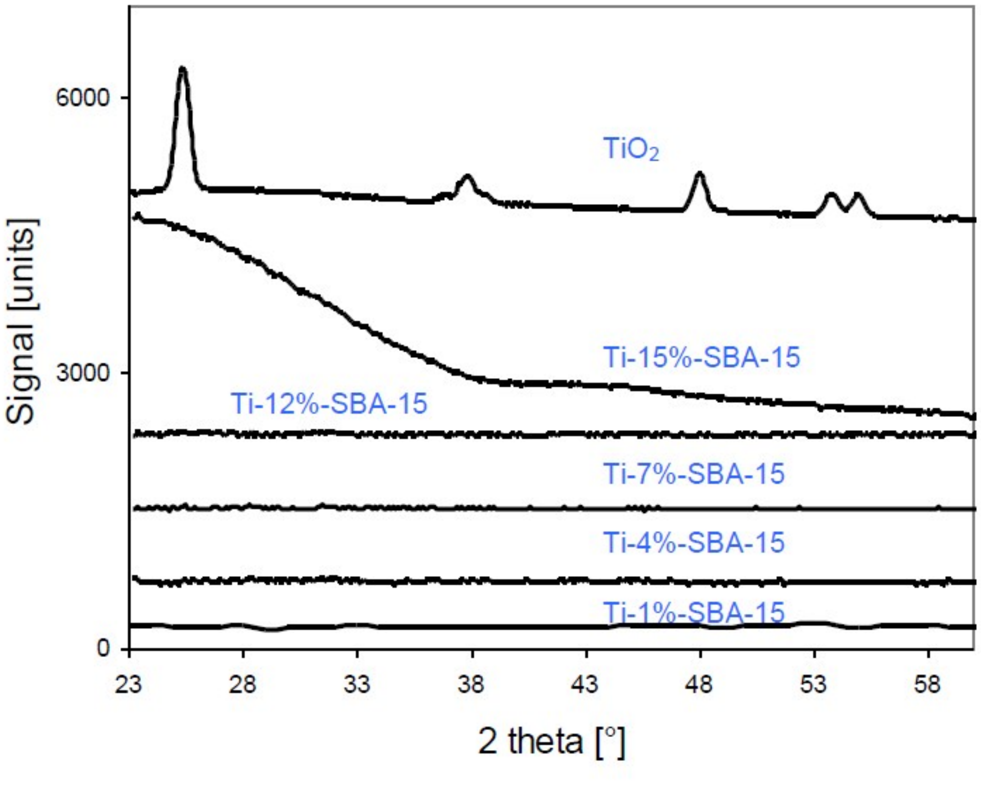


Figure S1. Low-angle X-ray diffractograms of Ti-SBA-15 samples with different Ti loadings.


6000
3000
0
Signal [units]
23
33
43
53
63
2 theta [°]
Al_2O_3
Al-20%-SBA-15
Al-4%-SBA-15
Al-3%-SBA-15


6000
3000
0
Signal [units]
23
28
33
38
43
48
53
58
2 theta [°]
TiO_2
Ti-15%-SBA-15
Ti-12%-SBA-15
Ti-7%-SBA-15
Ti-4%-SBA-15
Ti-1%-SBA-15

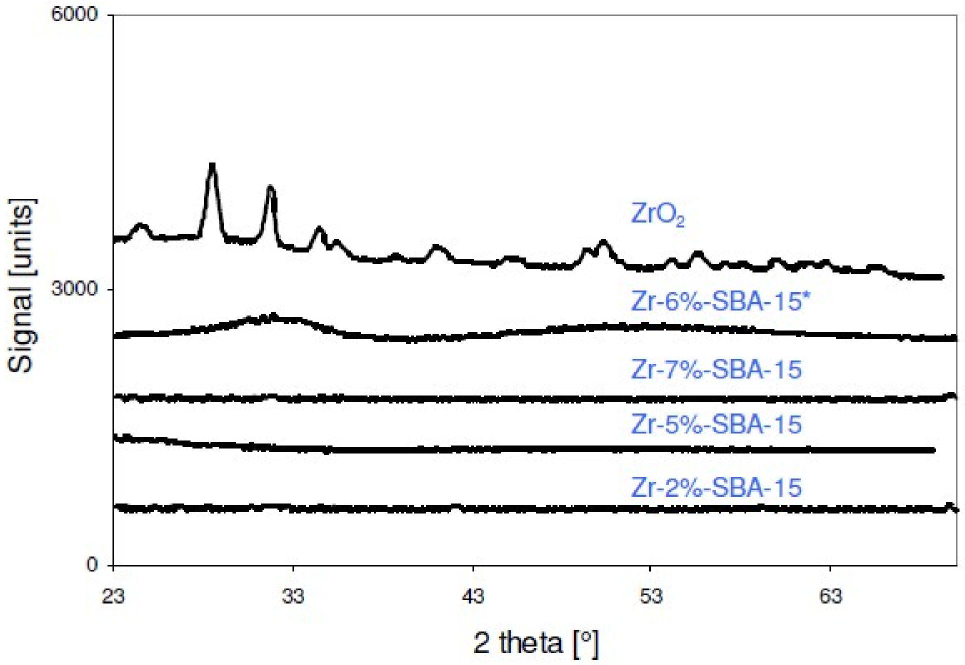


Figure S2. Wide-angle X-ray powder diffractograms of Ti-SBA-15, Al-SBA-15 and Zr-SBA-15 silica materials, as well as reference crystalline metal oxides as references.

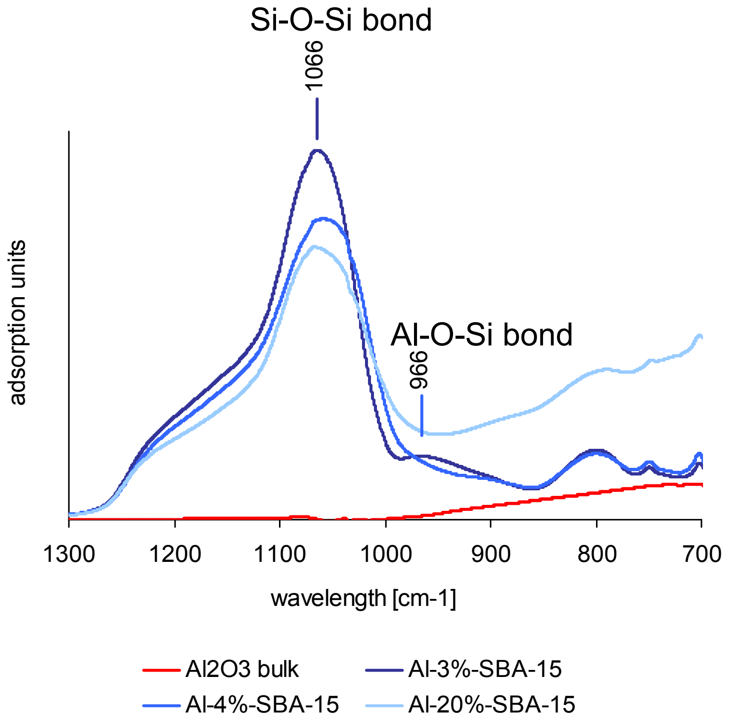


Figure S3. FT-IR spectra of Al_2O_3 and Al-SBA15 materials with different Al concentrations.

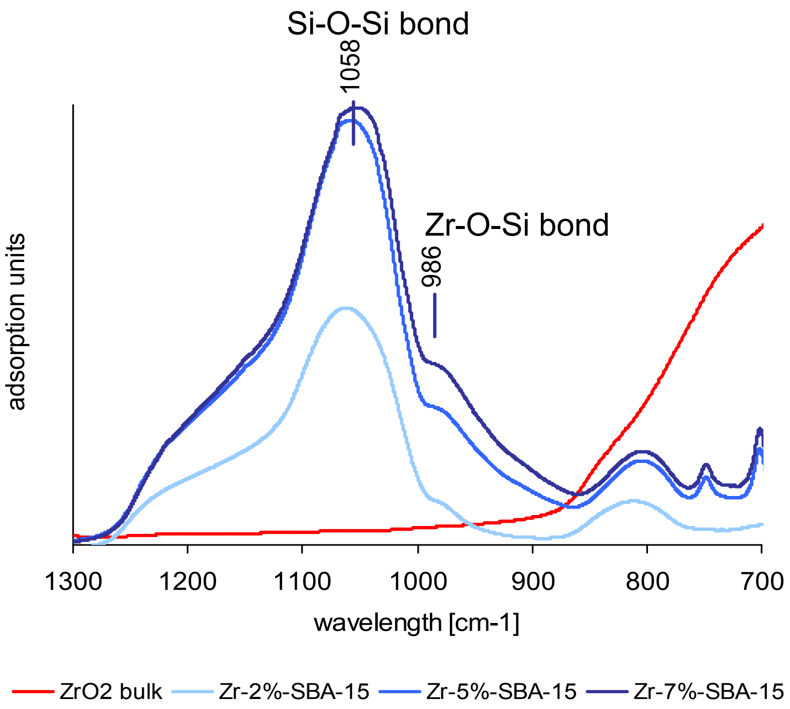


Figure S4. FT-IR spectra of ZrO_2 and Zr-SBA15 materials with different Zr concentrations.

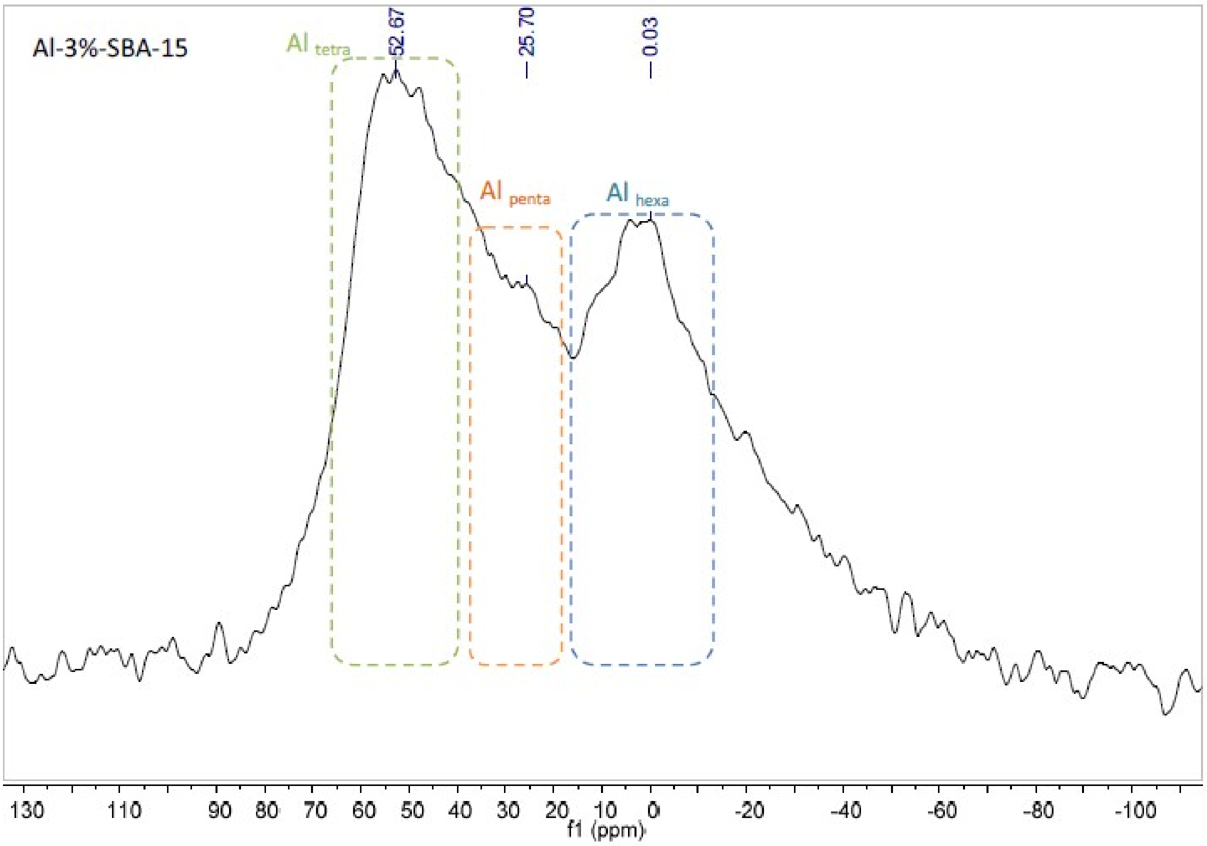


Figure S5. ^{27}Al MAS NMR spectrum of Al-3%-SBA-15 material.

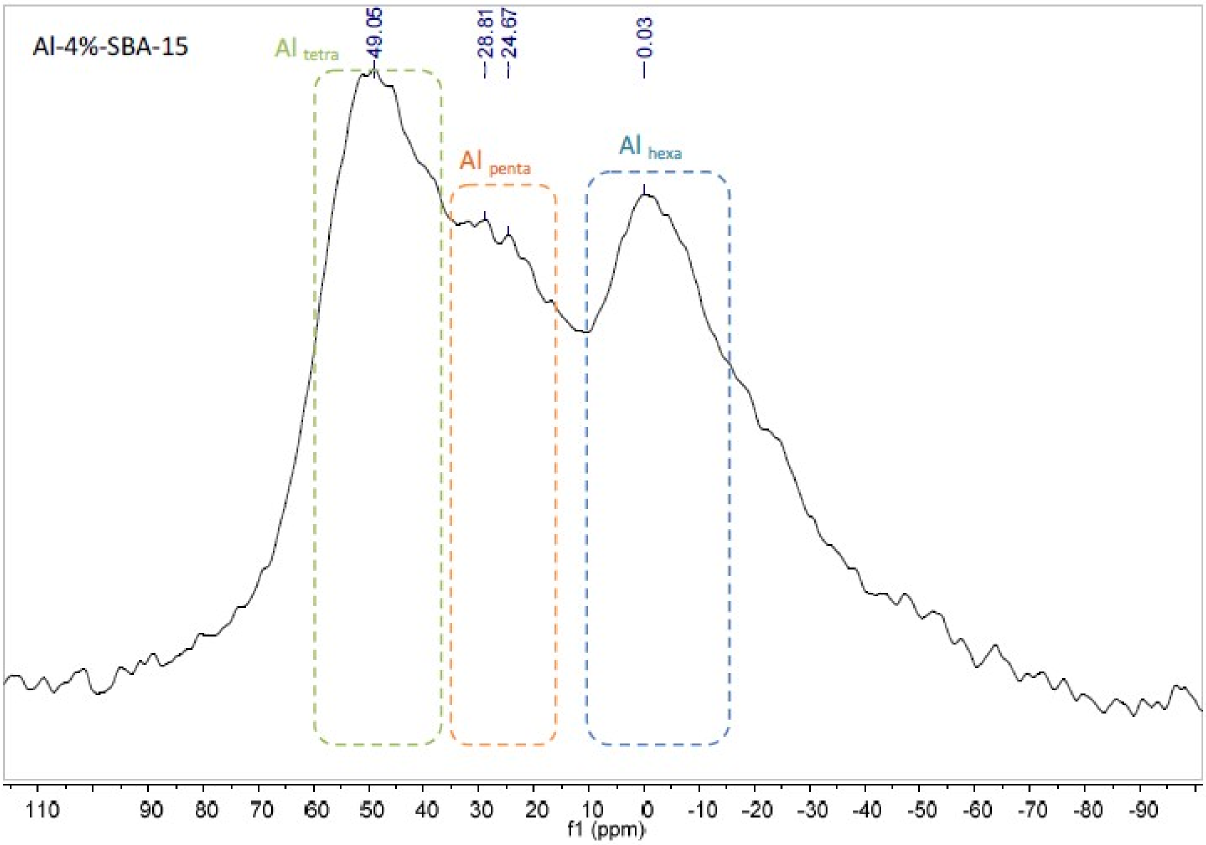


Figure S6. ^{27}Al MAS NMR spectrum of Al-4%-SBA-15 material.

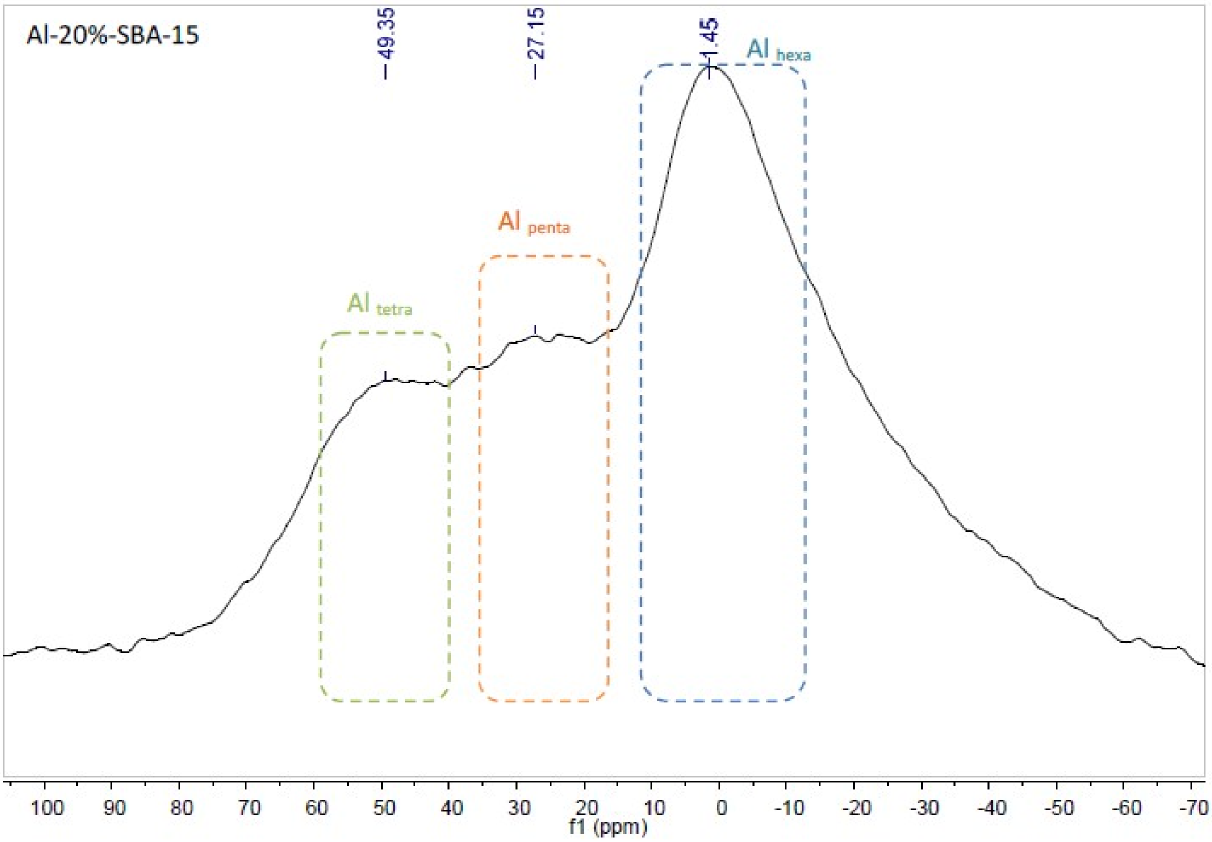


Figure S7. ^{27}Al MAS NMR spectrum of Al-20%-SBA-15 material.

Lewis acidity tests

When the indicator (B) reacts with a Bronsted acid (AH) to form the corresponding conjugated acid (HB^+) and base (A^-), the acid strength is expressed by the Hammett acidity function in the following way:

$$H_0 = \mathrm{p}K_\mathrm{a} + \log [\mathrm{B}]/[\mathrm{BH}^+]$$

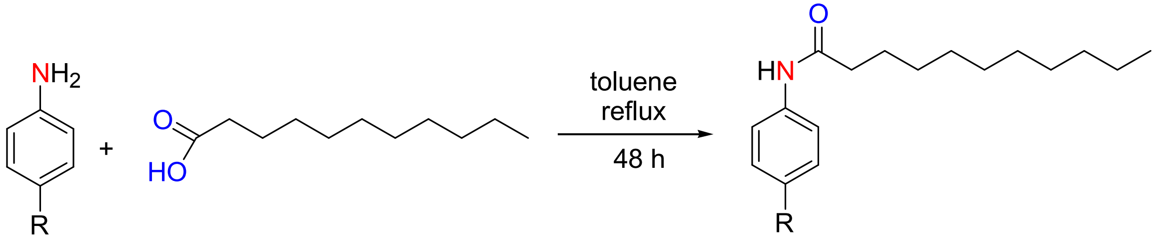
In the case of the interaction with a Lewis acid site, H_O is expressed by

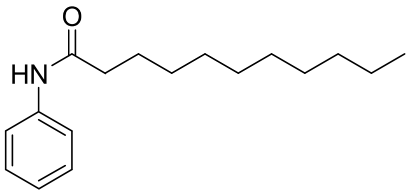
$$H_0 = \mathrm{p}K_\mathrm{a} + \log [\mathrm{B}]/[\mathrm{AB}]$$

where [B] is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor, A. At this point, the acid strength (for both Bronsted + Lewis acidity) of a solid catalyst can be estimated by noting which members of a series of Hammett indicators are present in the acidic form. An indicator is chosen so the color of the conjugated acid is intense enough to mask the color of the basic form. The determination was carried out in the following way: Hammett indicators were diluted in benzene and added to separate samples of the dried solid and the resulting colors were noted. In the case where the color of the conjugate acid was observed, it was considered that H_O value of the surface was similar or lower than the pK_a of the conjugate acid of the indicator.[i]

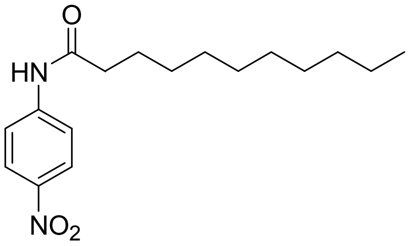
Catalytic tests

Passivated metalated and non-metalated solid catalysts were degassed at 70 °C under reduced pressure in a vacuum oven for 24 h prior to the catalytic tests. In a typical experiment, the carboxylic acid (1 mmol), the amine (1 mmol) in toluene (2.5 ml) and the metalated SBA-15 (50 mg) were added to a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The reaction mixture was heated at reflux under an N_2 atmosphere and stirred for 48 h. After completion of the reaction, dichloromethane (25 ml) was added to the mixture, and the solid catalyst was separated by centrifugation followed by one cycle of washing with 25 ml of dichloromethane after which the centrifugation was repeated. After a second centrifugation, the organic fractions were combined and acidified with 5 % aqueous HCl. The final product was extracted from the dichloromethane organic phase, dried over $MgSO_4$ and concentrated under a rotary evaporator. The yield of the product was determined by ^1H NMR spectroscopy using dry 1,3,5-trimethoxybenzene as an internal standard (signals marked in blue on the first spectrum).

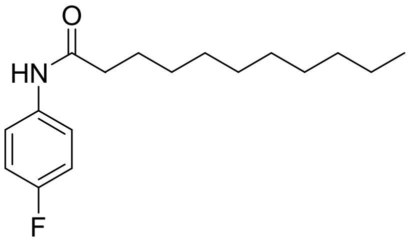




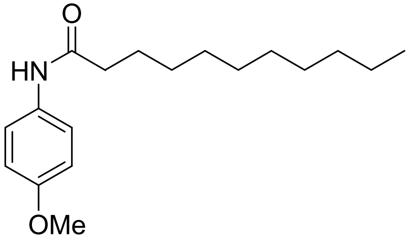
^{1}H (400 MHz, chloroform-*d*): δ 7.51 (d, 2H, J=7.9 Hz), 7.32 (t, 2H, J=7.9 Hz), 7.12 (br, 1H), 7.10 (t, 1H, J=7.4 Hz), 2.35 (t, 2H, J=7.6 Hz), 1.72 (quint, 2H, J=7.5 Hz), 1.43-1.19 (m, 14H), 0.88 (t, 3H, J=6.9 Hz). ^{13}C NMR (101 MHz, chloroform-*d*): δ 171.5, 138.1, 129.1, 124.3, 119.9, 38.0, 32.0, 29.7, 29.6, 29.5, 29.5, 29.4, 25.8, 22.8, 14.3. IR cm^{-1}: (neat) 1653, 2849, 2917, 3299. HRMS (ESI, m/z): Calcd for $C_{17}H_{27}NO$ $[M+H]^+$: 262.21709, found: 262.2176 (100%). M.p.= 65.3-67.3 °C.



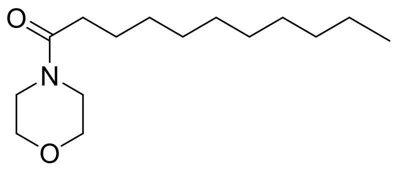
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.22 – 8.19(m, 2H), 7.73 – 7.51 (m, 2H), 7.54 (s, 1 H), 2.41 (t, *J* = 7.5 Hz, 2H), 1.72 (quint, *J* = 7.5 Hz, 2H), 1.33 – 1.25 (m, 14H), 0.73 (t, 1H, J=7.2 Hz); ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.1, 144.0, 143.5, 125.2, 119.1, 38.0, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 25.5, 22.8, 14.3. IR cm^{-1}: (neat) 1507, 2815, 2919, 3341. HRMS (ESI, m/z): Calcd for $C_{17}H_{26}N_2O_3$ $[M+H]^+$: 307.20219, found: 307.2030 (100%). M.p.=73.3-75.4 °C.



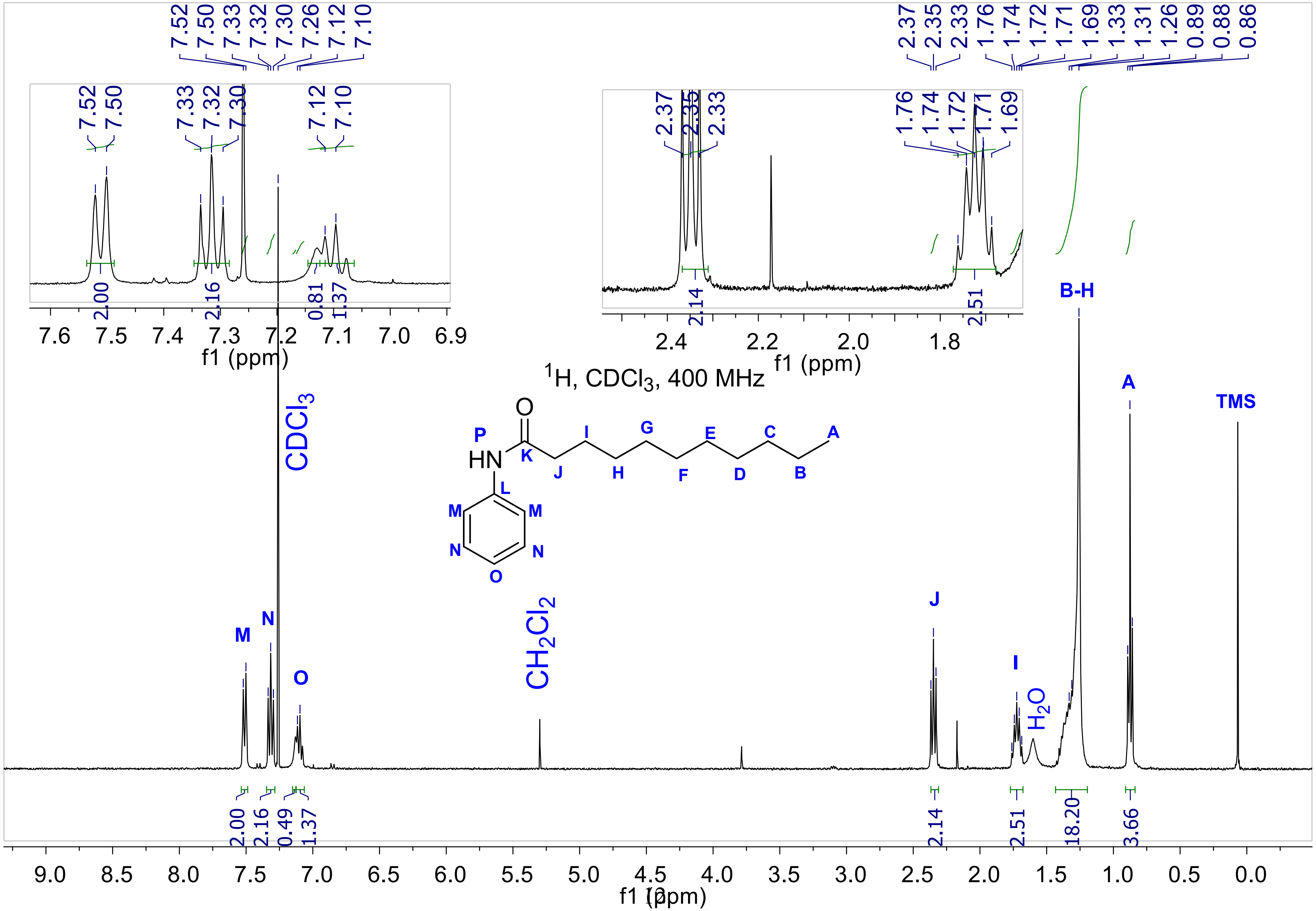
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 8.9, 4.7 Hz, 2H), 7.24 (br, 1H), 7.00 (t, *J* = 8.6 Hz, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.72 (q, *J* = 7.3 Hz, 2H), 1.27 (d, *J* = 10.5 Hz, 14H), 0.91 – 0.84 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ171.7, 160.61, 158.2, 134.1, 121.9, 115.8, 37.8, 32.0, 29.7, 29.6, 29.5, 29.4, 29.4, 25.8, 22.8, 14.3. IR cm^{-1}: (neat) 1646, 2849, 2916, 3293. HRMS (ESI, m/z): Calcd for $C_{17}H_{26}FNO$ [M+H]$^+$: 280.20767, found: 280.2085 (100%). M.p.=68.2-69.9 °C.



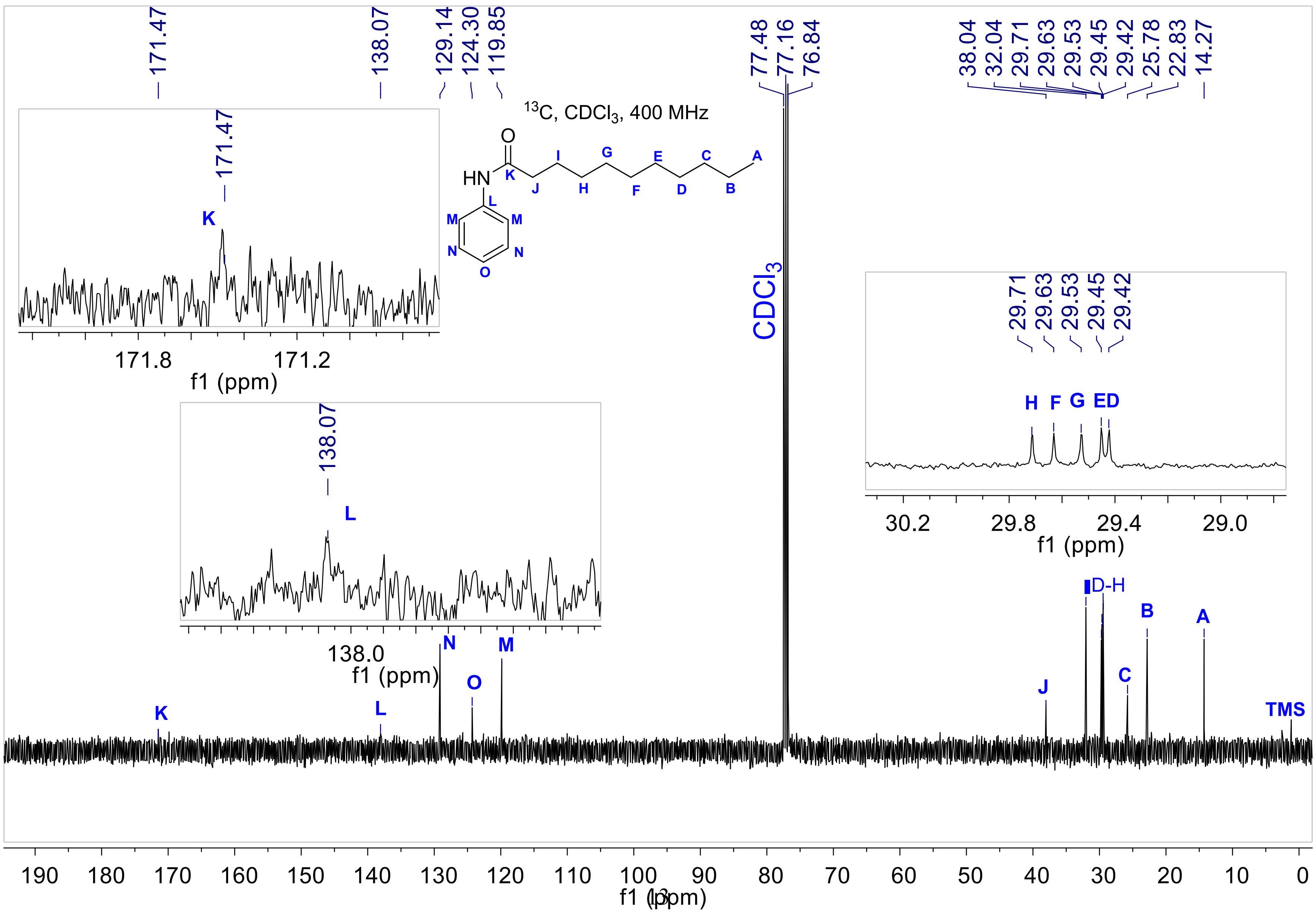
^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.48 – 7.34 (m, 2H), 7.12 (s, 1H), 6.92 – 6.79 (m, 2H), 3.78 (s, 3H), 2.32 (t, 2H, J=7.7 Hz), 1.71 (quint, *J* = 7.6 Hz, 2H), 1.44 – 1.13 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, Chloroform-*d*): δ 171.6, 156.6, 131.1, 122.1, 114.1, 55.6, 37.8, 32.0, 29.7, 29.6, 29.5 (x3), 25.9, 22.8, 14.3. IR cm^{-1}: (neat) 1653, 2849, 2918, 3298. HRMS (ESI, m/z): Calcd for $C_{18}H_{29}NO_2$ [M+H]$^+$: 292.22766, found: 292.2278 (100%). M.p.=95.6- 99.9 °C.

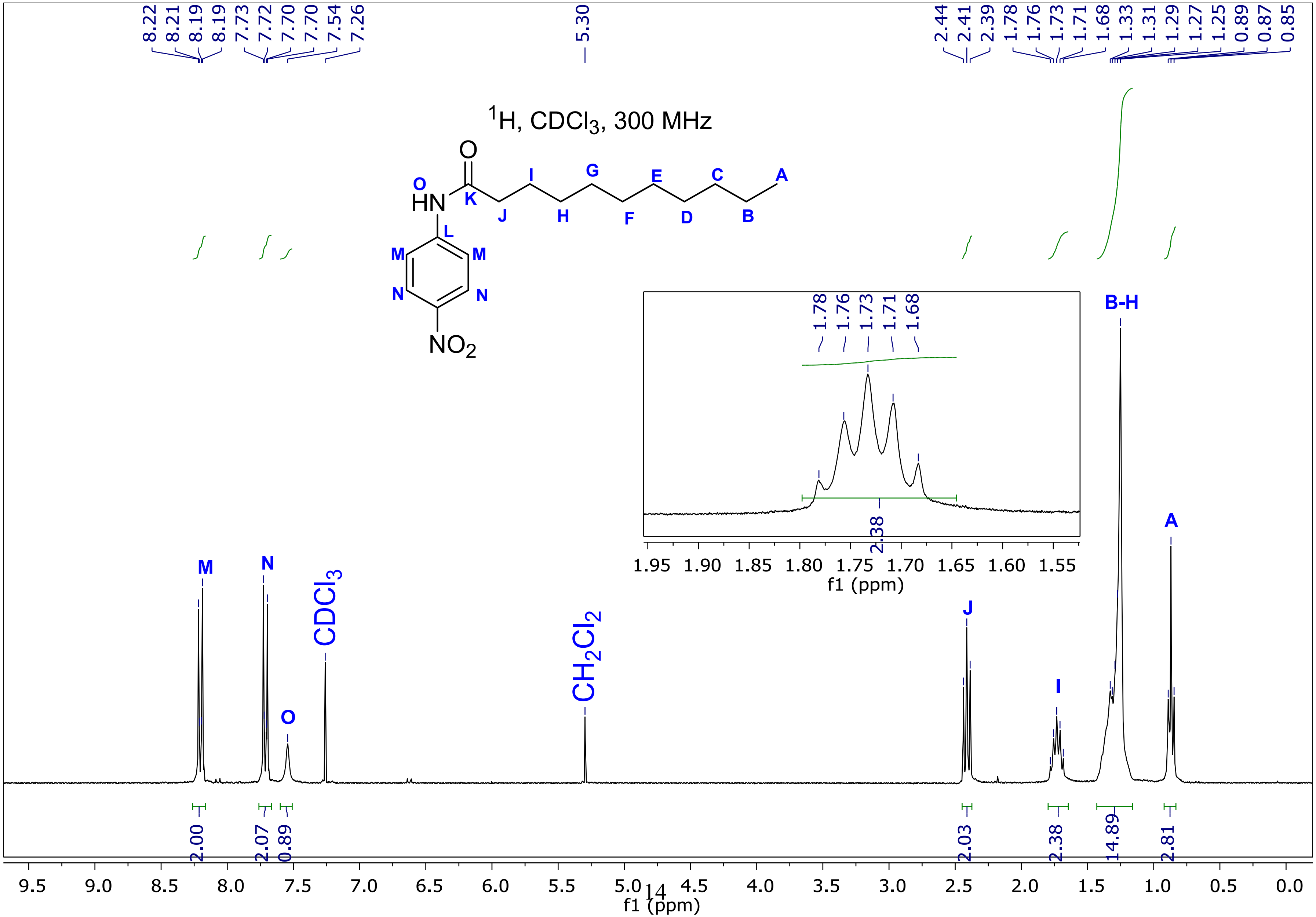


^{1}H NMR (400 MHz, Chloroform-*d*): δ 3.67 – 3.59 (m, 4H), 3.59 (d, *J* = 5.0 Hz, 2H), 3.49 – 3.40 (m, 2H), 2.3 – 2.26 (m, 2H), 1.59 (p, *J* = 7.3 Hz, 2H), 1.36 – 1.16 (m, 14H), 0.87 – 0.80 (m, 3H). ^{13}C NMR (75 MHz, Chloroform-*d*): δ 172.1, 67.0, 46.1, 42.0, 32.0, 29.6, 29.6, 29.5, 29.5, 29.4, 25.3, 22.7, 14.2. IR cm^{-1}: (neat) 1652, 2854, 2924. HRMS (ESI, m/z): Calcd for $C_{15}H_{29}NO_2$ $[M+H]^+$: 256.22766, found: 256.22829 (100%).

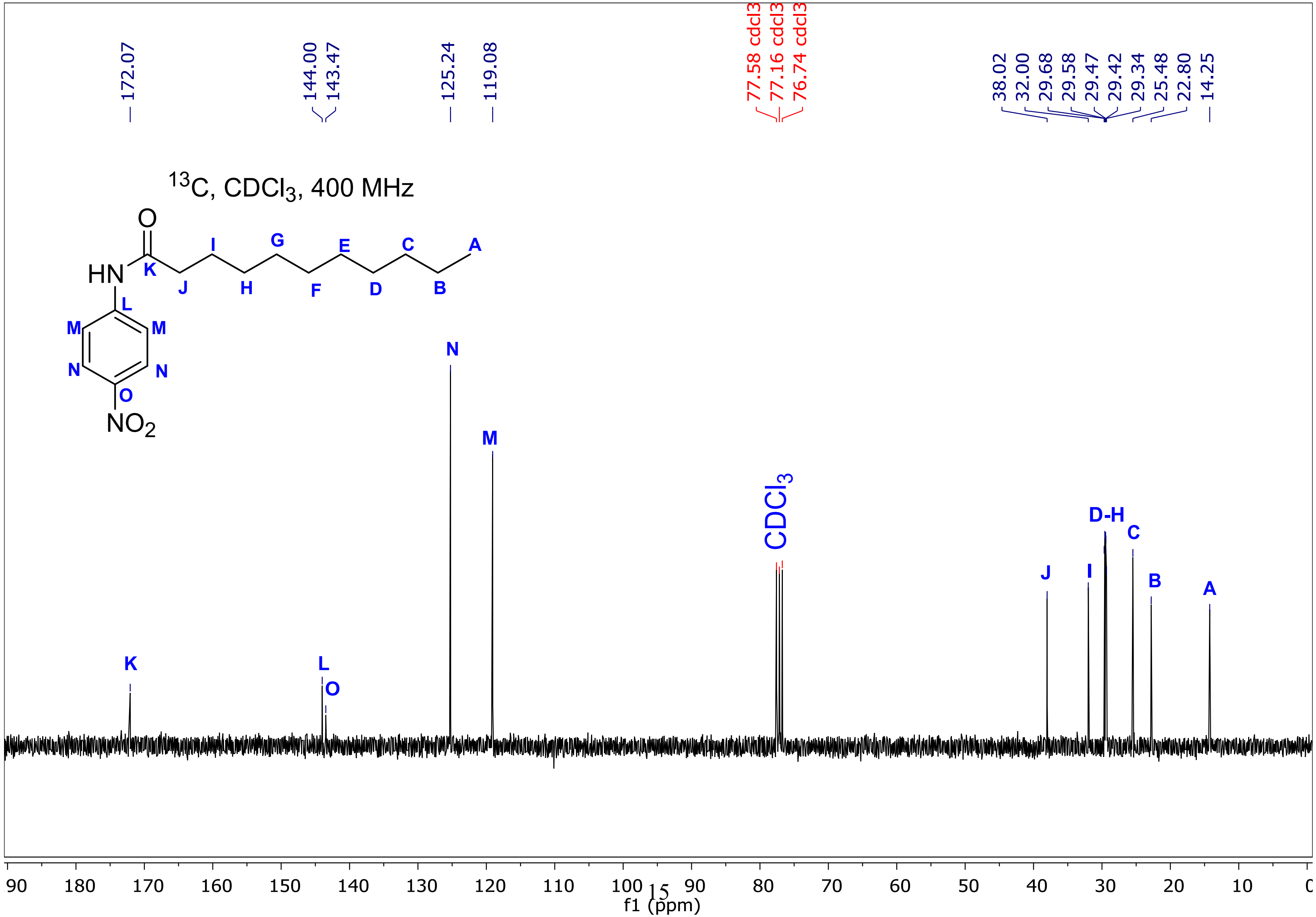


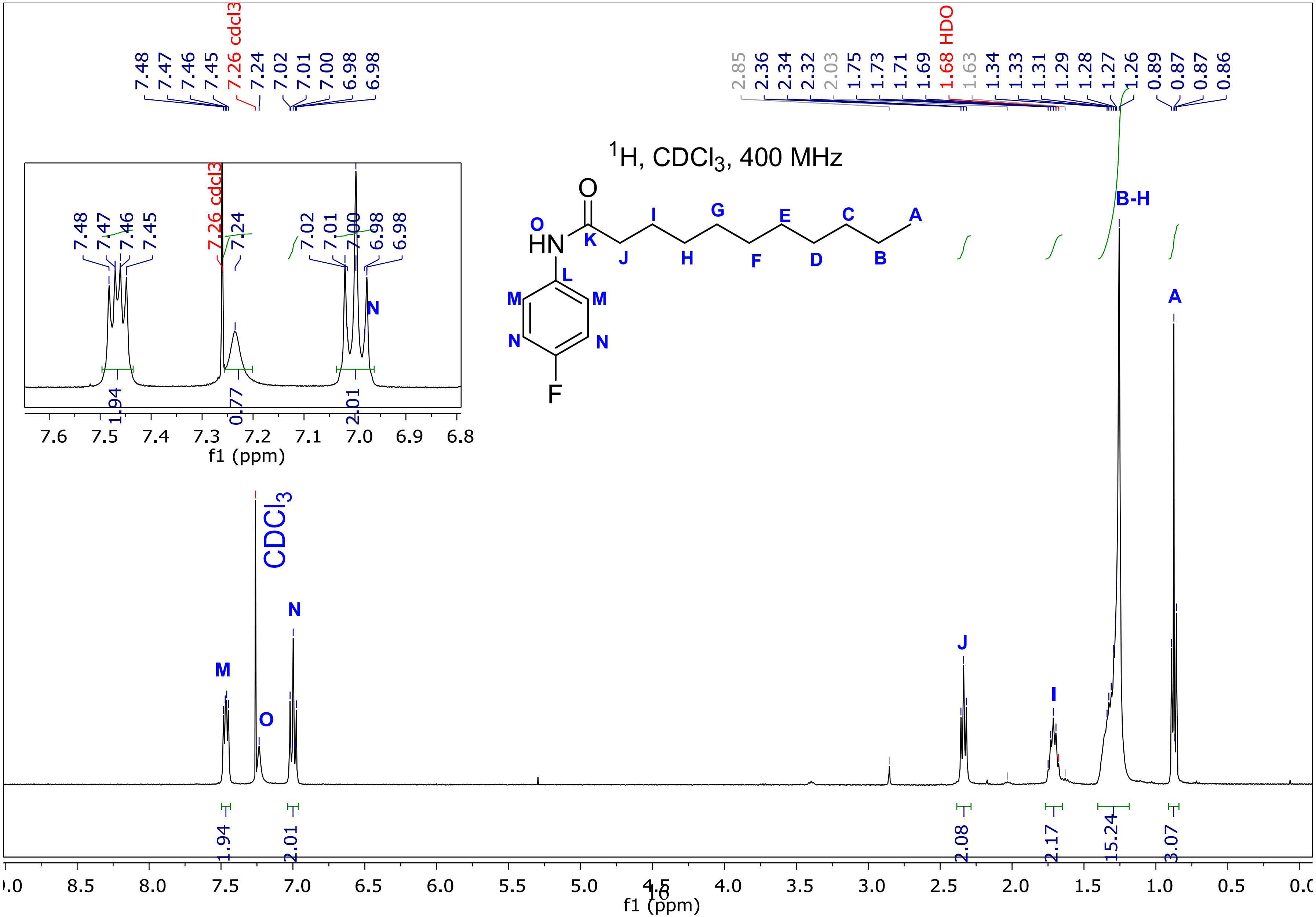
7.52 7.50 7.33 7.32 7.30 7.26 7.12 7.10
2.37 2.35 2.33 1.76 1.74 1.72 1.71 1.69 1.33 1.31 1.26 0.89 0.88 0.86
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
2.00 2.16 0.81 1.37
2.4 2.2 2.0 1.8
f1 (ppm)
2.14 2.51
^{1}H, $CDCl_3$, 400 MHz
$CDCl_3$
CH_2Cl_2
H_2O
TMS
M
N
O
J
I
B-H
A
P
HN
K
L
B
C
D
E
F
G
H
2.00 2.16 0.49 1.37 2.14 2.51 18.20 3.66
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)


171.47
138.07
129.14
124.30
119.85
77.48
77.16
76.84
38.04
32.04
29.71
29.63
29.53
29.45
29.42
25.78
22.83
14.27
^{13}C, CDCl$_3$, 400 MHz
O
HN
K
L
I
G
E
C
A
J
H
F
D
B
M
M
N
N
O
171.47
K
171.8
171.2
f1 (ppm)
138.07
L
138.0
f1 (ppm)
CDCl$_3$
29.71
29.63
29.53
29.45
29.42
H
F
G
ED
30.2
29.8
29.4
29.0
f1 (ppm)
D-H
B
A
C
J
TMS
N
M
O
K
L
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

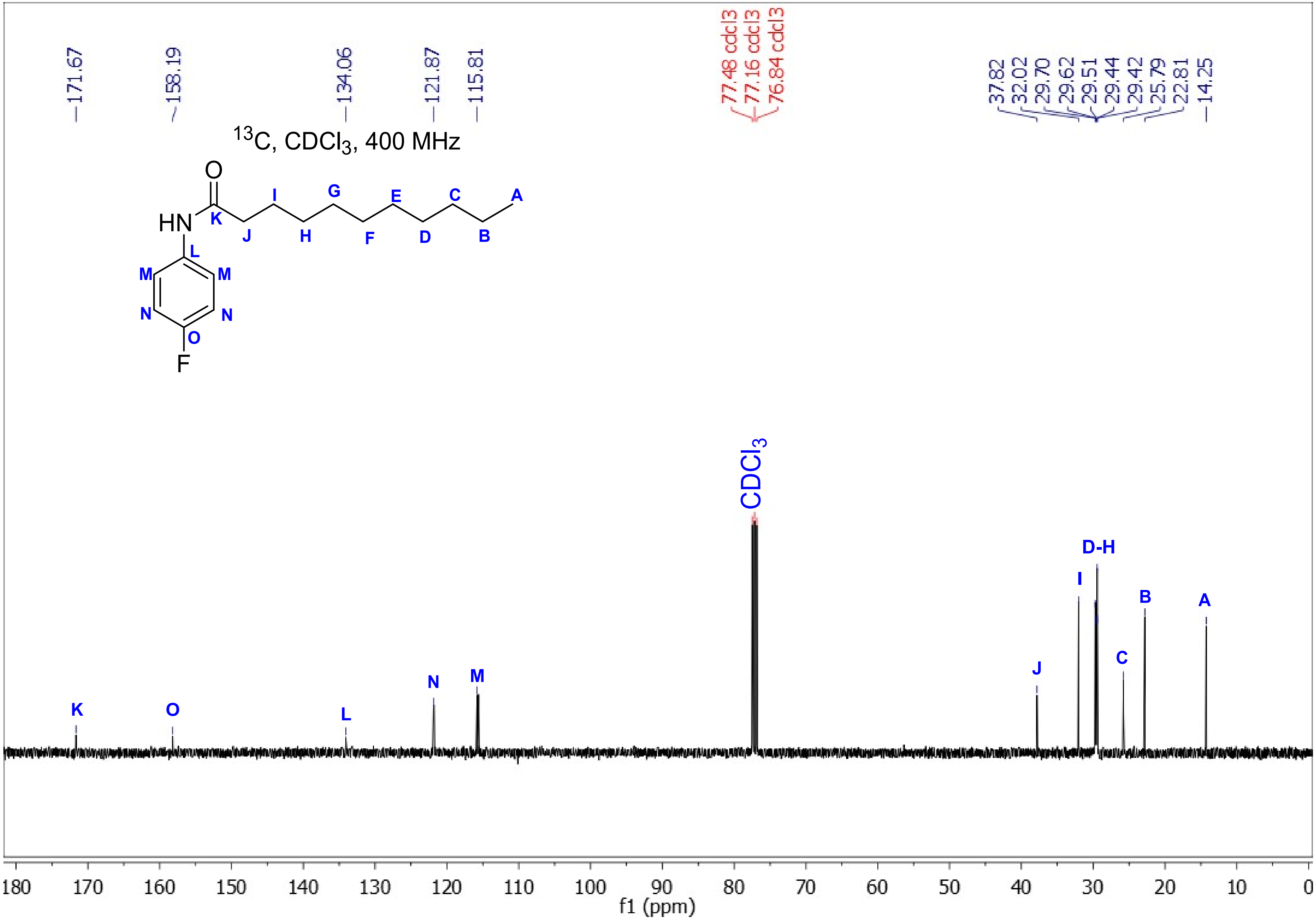


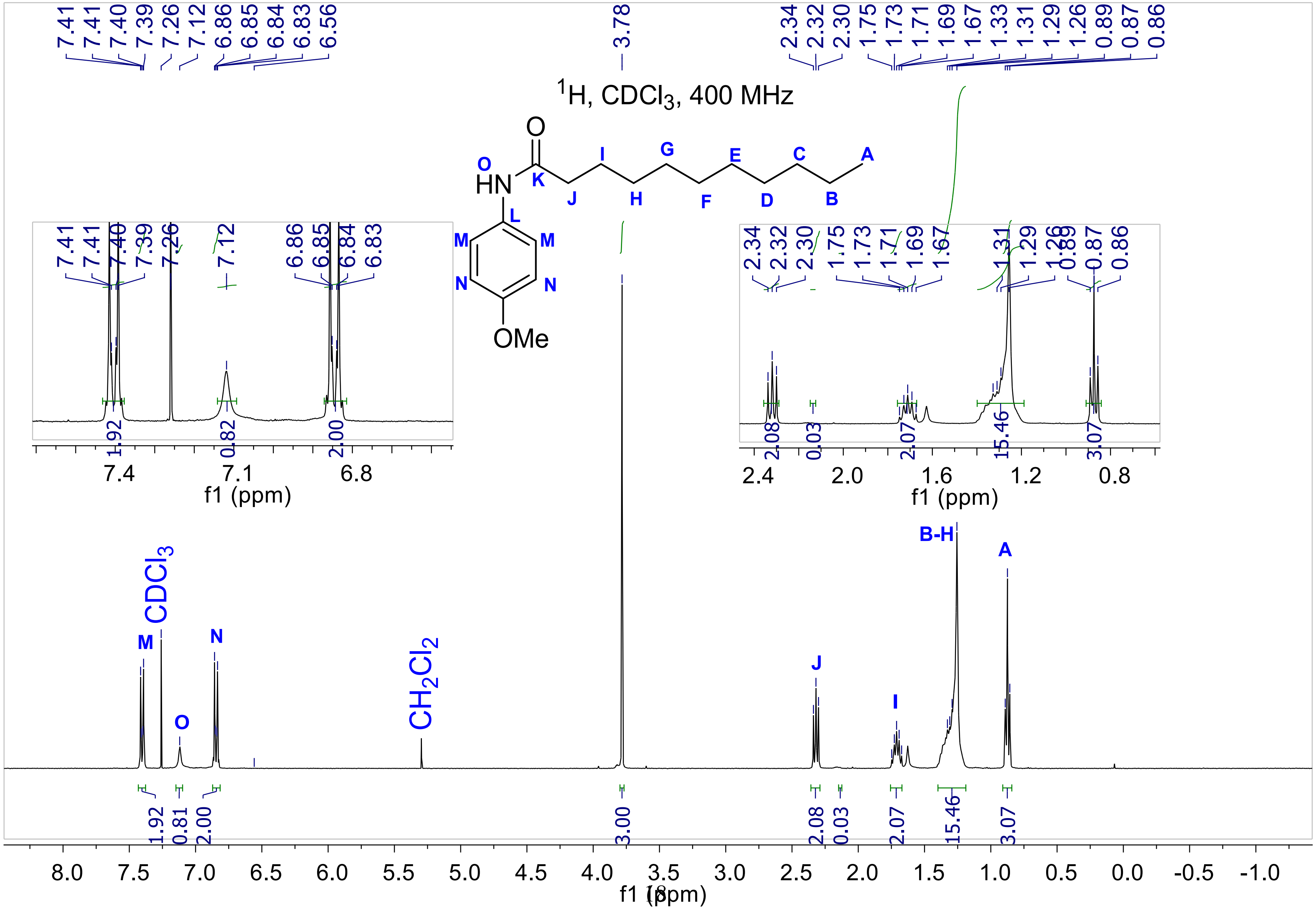
1H, CDCl3, 300 MHz
8.22
8.21
8.19
8.19
7.73
7.72
7.70
7.70
7.54
7.26
5.30
2.44
2.41
2.39
1.78
1.76
1.73
1.71
1.68
1.33
1.31
1.29
1.27
1.25
0.89
0.87
0.85
O
HN
O
K
I
G
E
C
A
J
H
F
D
B
L
M
M
N
N
NO2
B-H
A
M
N
O
CDCl3
CH2Cl2
J
I
2.38
1.95
1.90
1.85
1.80
1.75
1.70
1.65
1.60
1.55
f1 (ppm)
2.00
2.07
0.89
2.03
2.38
14.89
2.81
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)

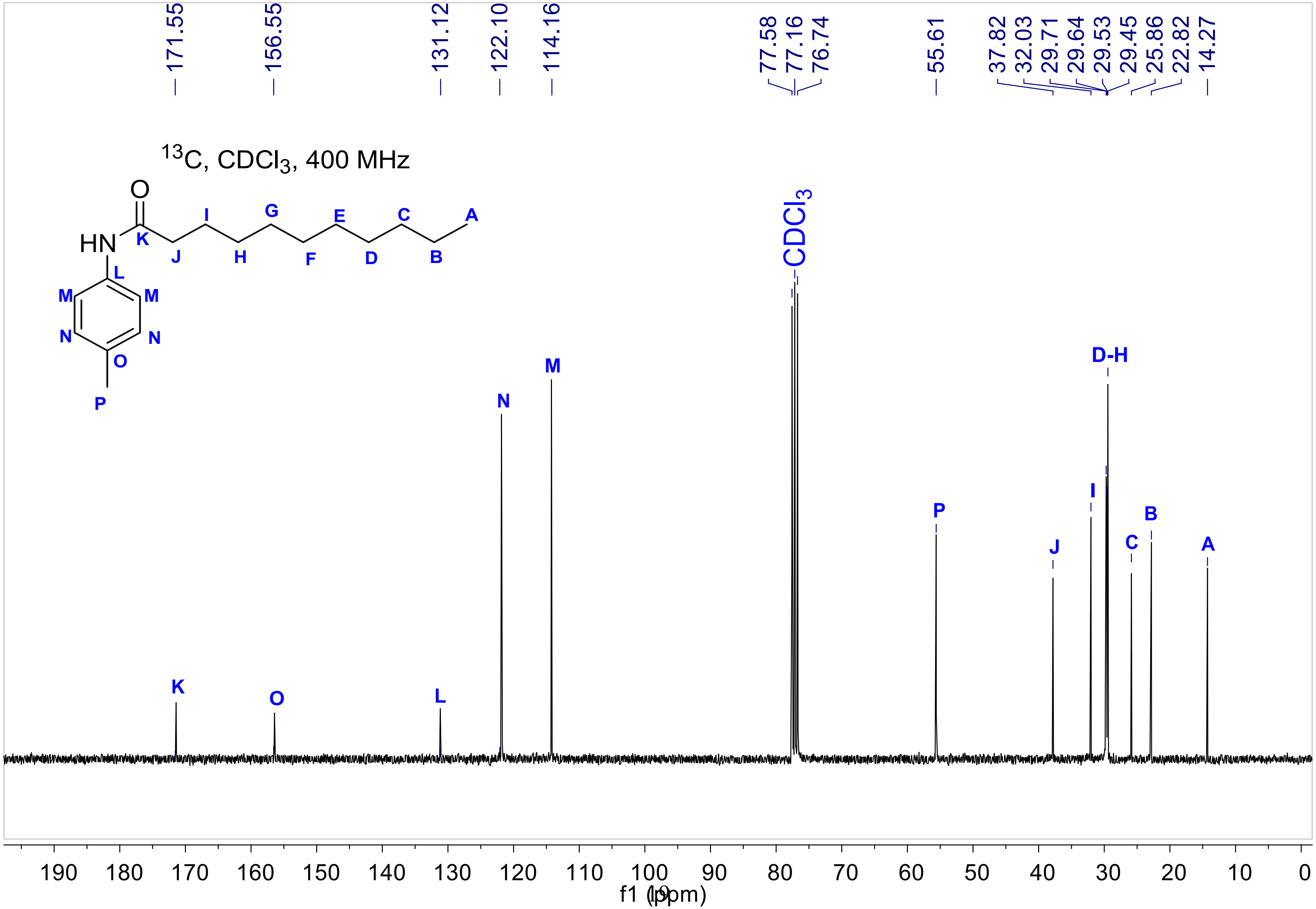

172.07
144.00
143.47
125.24
119.08
77.58 cdcl3
77.16 cdcl3
76.74 cdcl3
38.02
32.00
29.68
29.58
29.47
29.42
29.34
25.48
22.80
14.25
^{13}C, CDCl$_3$, 400 MHz
O
HN
NO$_2$
A
B
C
D
E
F
G
H
I
J
K
L
M
N
O
CDCl$_3$
D-H
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

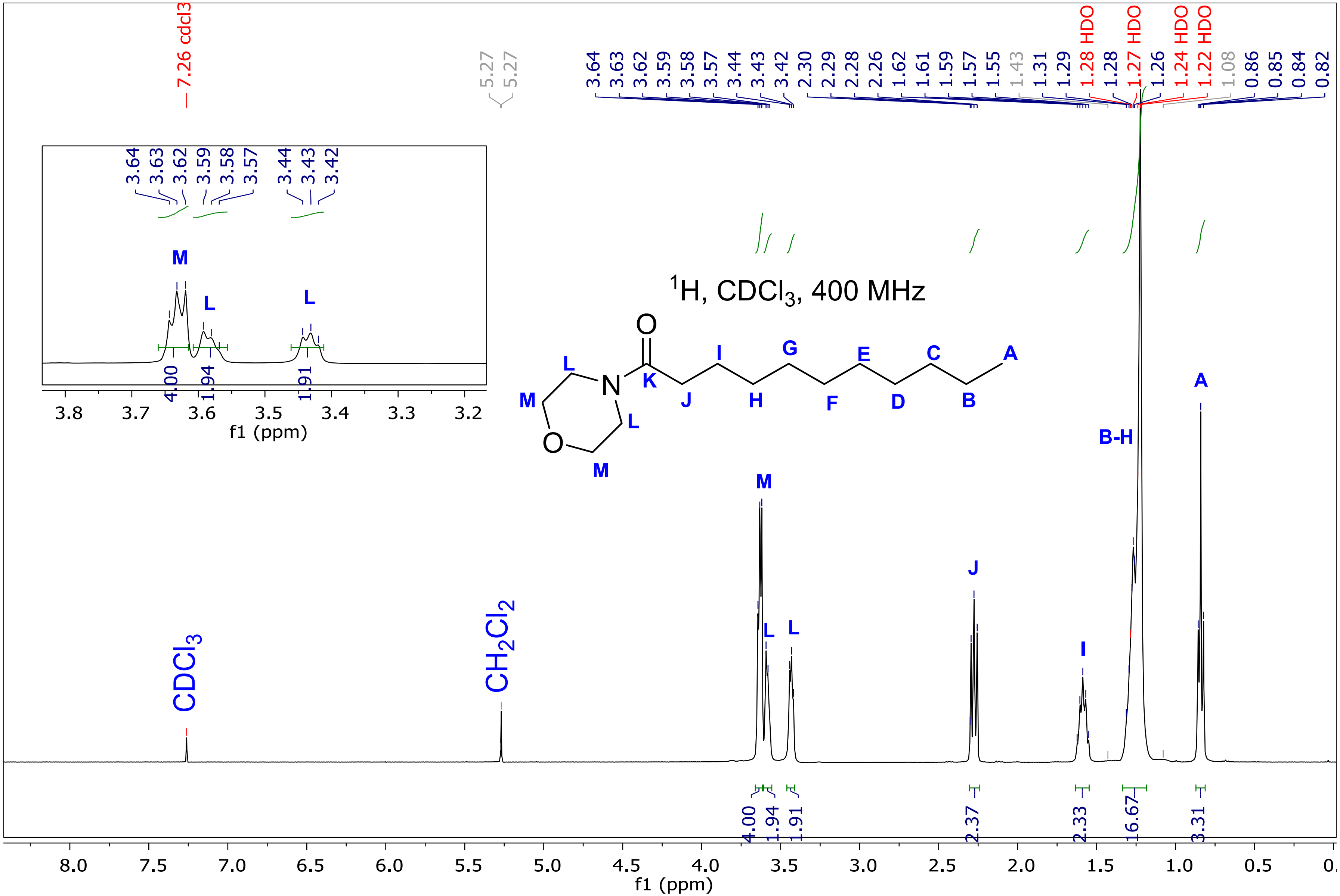


^{1}H, CDCl$_3$, 400 MHz
7.48
7.47
7.46
7.45
7.26 cdcl3
7.24
7.02
7.01
7.00
6.98
6.98
2.85
2.36
2.34
2.32
2.03
1.75
1.73
1.71
1.69
1.68 HDO
1.63
1.34
1.33
1.31
1.29
1.28
1.27
1.26
0.89
0.87
0.87
0.86
O
HN
K
J
I
H
G
F
E
D
C
B
A
L
M
M
N
N
F
B-H
A
J
I
M
O
N
CDCl$_3$
1.94
0.77
2.01
2.08
2.17
15.24
3.07
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f1 (ppm)
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)

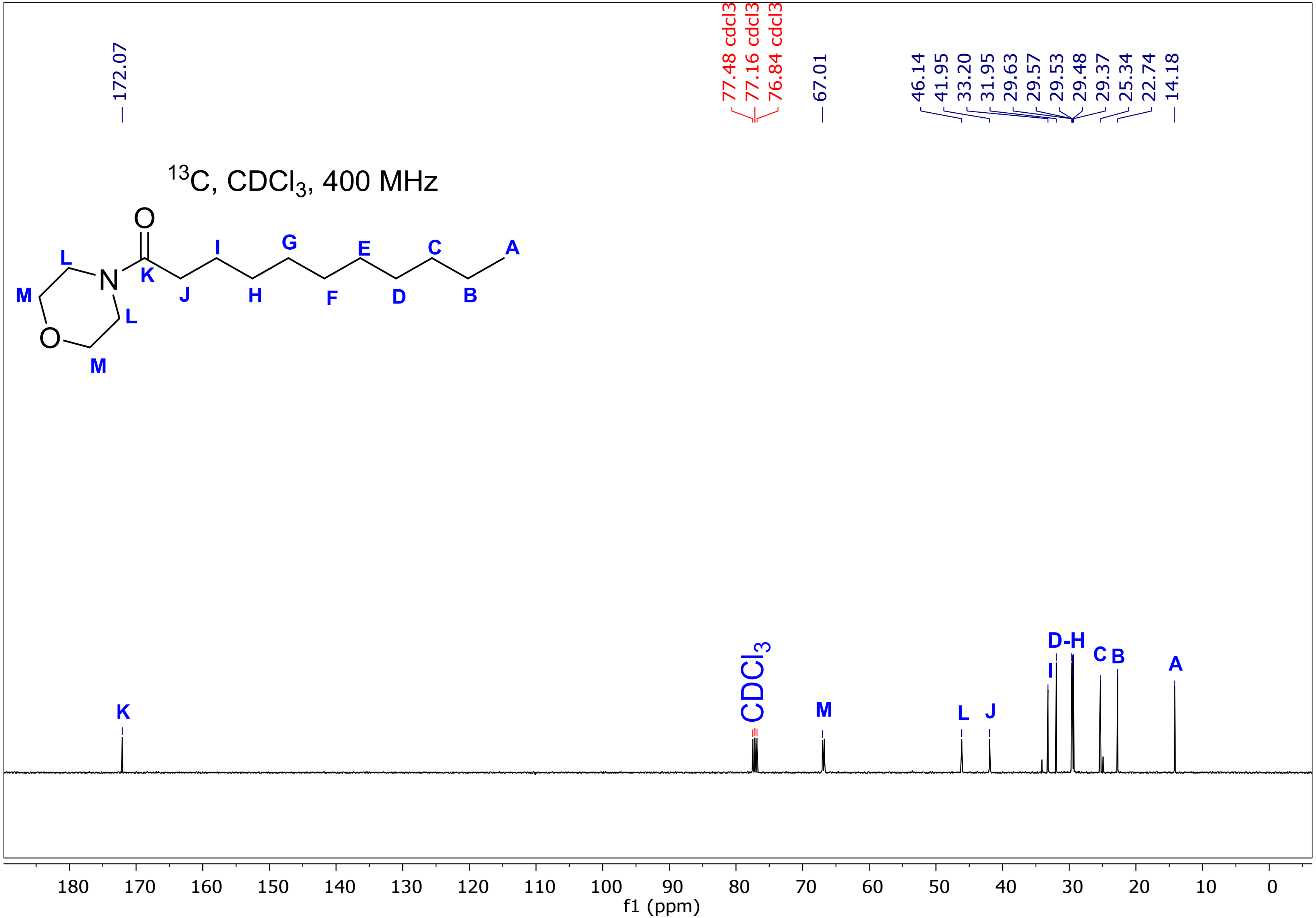

171.67
158.19
134.06
121.87
115.81
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
37.82
32.02
29.70
29.62
29.51
29.44
29.42
25.79
22.81
14.25
^{13}C, $CDCl_3$, 400 MHz
O
HN
F
A B C D E F G H I J K L M M N N O
$CDCl_3$
K
O
L
N
M
J
I
D-H
C
B
A
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


1H, CDCl3, 400 MHz
7.41 7.41 7.40 7.39 7.26 7.12 6.86 6.85 6.84 6.83 6.56
3.78
2.34 2.32 2.30 1.75 1.73 1.71 1.69 1.67 1.33 1.31 1.29 1.26 0.89 0.87 0.86
O
HN
K
J
I
H
G
F
E
D
C
B
A
L
M
N
OMe
CDCl3
CH2Cl2
B-H
1.92
0.81
2.00
3.00
2.08
0.03
2.07
15.46
3.07
0.82
f1 (ppm)
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 -0.5 -1.0
7.4 7.1 6.8
2.4 2.0 1.6 1.2 0.8


171.55
156.55
131.12
122.10
114.16
77.58
77.16
76.74
55.61
37.82
32.03
29.71
29.64
29.53
29.45
25.86
22.82
14.27
13C, CDCl3, 400 MHz
O
HN
K
J
I
H
G
F
E
D
C
B
A
L
M
M
N
N
O
P
CDCl3
K
O
L
N
M
P
J
I
D-H
C
B
A
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



1H, CDCl3, 400 MHz
7.26 cdcl3
5.27
5.27
3.64
3.63
3.62
3.59
3.58
3.57
3.44
3.43
3.42
2.30
2.29
2.28
2.26
1.62
1.61
1.59
1.57
1.55
1.43
1.31
1.29
1.28 HDO
1.28
1.27 HDO
1.26
1.24 HDO
1.22 HDO
1.08
0.86
0.85
0.84
0.82
O
N
O
A
B
C
D
E
F
G
H
I
J
K
L
L
M
M
CDCl3
CH2Cl2
M
L
L
J
I
B-H
A
4.00
1.94
1.91
2.37
2.33
16.67
3.31
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.
f1 (ppm)
3.8
3.7
3.6
3.5
3.4
3.3
3.2
f1 (ppm)


172.07
77.48 cdcl3
77.16 cdcl3
76.84 cdcl3
67.01
46.14
41.95
33.20
31.95
29.63
29.57
29.53
29.48
29.37
25.34
22.74
14.18
13C, CDCl3, 400 MHz
O
N
O
A
B
C
D
E
F
G
H
I
J
K
L
L
M
M
K
CDCl3
M
L
J
I
D-H
C
B
A
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

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[i] H. A. Benesi, *J. Phys. Chem*., 1957, **61**, 970.