Highly efficient transformation of levulinic acid into pyrrolidinones by iridium catalysed transfer hydrogenation

Yawen Wei,[a] Chao Wang,*[a] Xue Jiang,[a] Dong Xue,[a] Jia Li,[a] and Jianliang Xiao*[a,b]

[a] Key Laboratory of Applied Surface and Colloid Chemistry, Ministry of Education, School of Chemistry & Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, China

[b] Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK

Contents

1. General information ……..…S2

2. Effect of pH on RA of LA …… S2

3. Effect of different catalysts on RA of LA …… S3

4. Spontaneous cyclisation of **3** to **2a** in NMR tube …… S4

5. General procedure for preparation of cyclometalated iridium complexes……S4

6. General procedure for preparation HCOOH/HCOONa aqueous solution ……...S4

7. Typical procedure for reductive amination ……..……S5

8. Analytic data of iridium complexes ……...…… S6-S8

9. Analytic data of products ……..……S8-S17

10. References ……S17

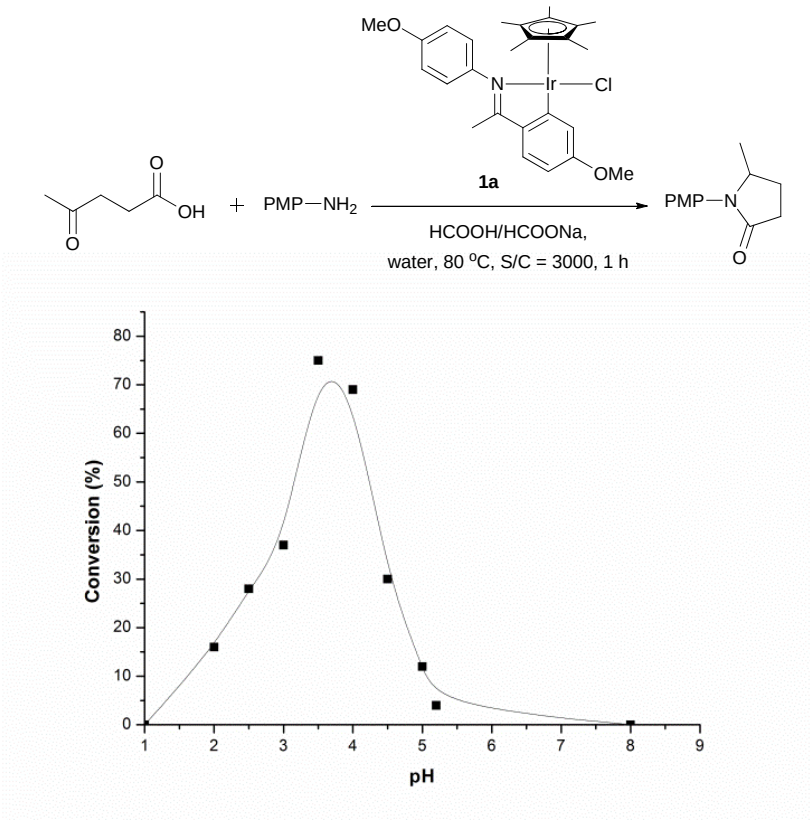
11. Traces of ^{1}H and ^{13}C NMR spectra of catalysts ……S18-S24

12. Traces of ^{1}H and ^{13}C NMR spectra of products ……S25-S47

1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. MeOH was dried over magnesium and distilled prior to use. Dichloromethane (DCM) was dried over CaH_2 and distilled prior to use. Water was distilled water. NMR spectra were recorded on a Bruker 400 Hz NMR spectrometer with TMS as the internal standard. Imines were prepared according to the literature[1]. pH was measured with a Sartorius PB-10 pH meter at 25 ^{o}C. HRMS data were recorded on a Bruker Apex IV FTMS spectrometer using ESI method and Bruker Maxis with EI method.

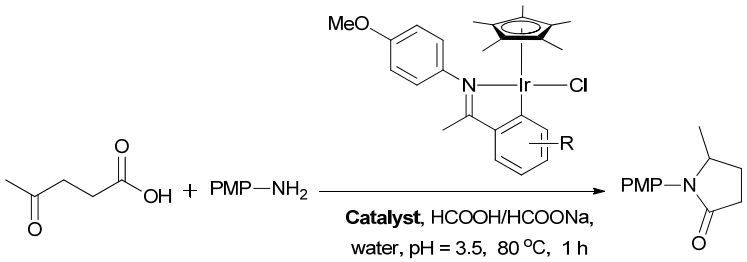
2. Effect of pH on RA of LA



Scheme S1 The effect of pH on RA of LA with *p*-anisidine catalysed by **1a** using HCOOH/HCOONa as hydrogen source. Reaction conditions: LA (7.5 mmol), *p*-anisidine (15 mmol), **1a** (0.0025 mmol), aqueous HCOOH/HCOONa solution (14.5 mol/L, 8 mL), 80 ^{o}C, 1 h. PMP = *para*-methoxyphenyl

3. Effect of different catalysts on RA of LA

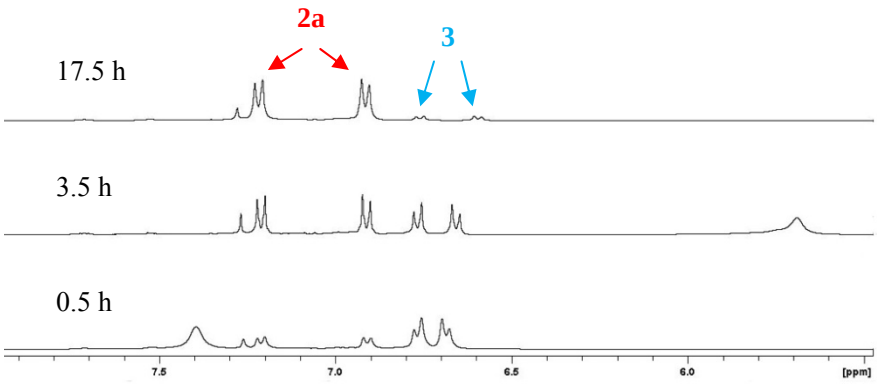
Table S1 Effects of different catalysts on RA of LA[a]



Entry	R	**Catalyst**	Conversion[b] (%)
1	*p*-OMe	**1a**	75
2	*p*-Me	**1b**	41
3	*p*-H	**1c**	44
4	*p*-Cl	**1d**	44
5	*p*-Br	**1e**	34
6	*p*-NO_2	**1f**	35
7	*p*-CN	**1g**	30
8[c]	-	$[Cp^*IrCl_2]_2$	22
9[c]	-	$[Cp^*RhCl_2]_2$	30
10[c,d]	-	$[(p\text{-cymene})RuCl_2]_2$/Ts-DPEN	9
11[c,d]	-	$[Cp^*RhCl_2]_2$/Ts-DPEN	15
12[c]	-	Pd/C	0

[a] Reaction conditions: LA (7.5 mmol), *p*-anisidine (15 mmol), catalyst (0.0025 mmol), aqueous HCOOH/HCOONa solution (14.5 M, 8 mL), 80 °C, 1 h, S/C = 3000. [b] Determined by ^{1}H NMR. [c] 1 mmol LA, S/C = 200. [d] Catalyst was prepared in situ, Ts-DPEN = *N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine.

4. Spontaneous cyclisation of 3 to 2a in NMR tube



Scheme S2 The change of aromatic region for ^{1}H NMR of **3** with time in $CDCl_3$ at r. t.. **3** was prepared by RA of LA via $NaBH(OAc)_3$ reduction in THF with 1 equiv. of HOAc.

5. General procedure for preparation of cyclometalated iridium complexes [2, 3, 4]

To $IrCl_3 \cdot 3H_2O$ (0.5 g, 1.35 mmol) in 13 mL methanol was added excess pentamethylcyclopentadiene (0.4 mL). The mixture was refluxed for 36 h. After the mixture was cooled to room temperature, the product $[Cp^*IrCl_2]_2$ was isolated by filtration and washed with cold methanol and dried in *vacuo*.

$[Cp^*IrCl_2]_2$ (1 equiv.), an imine ligand (2.2 equiv.) and NaOAc (10 equiv.) were placed into a Schlenk tube. The tube was then degassed and recharged with argon three times. DCM was then added and the resulting mixture was stirred at room temperature overnight. The reaction mixture was filtered through celite, and dried over Na_2SO_4. Following removal of the solvent under vacuum the resulting solid was washed with diethyl ether/petroleum ether to afford cyclometalated iridium complexes.

6. General procedure for preparation HCOOH/HCOONa aqueous solution

Aqueous HCOONa solution (c = 0.714 g/mL) and HCOOH (88 w/w %) were mixed in a beaker at 25 °C. After stirring for 5 minutes, the pH of the mixed solution was measured by a pH meter. Different pHs were obtained by varying the volume of the aqueous HCOONa solution and that of

HCOOH. For example, to obtain a solution of pH 2.5, 17 mL of aqueous HCOONa solution was mixed with 25 mL of HCOOH.

7. Typical procedure for reduction amination

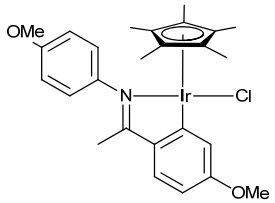
(1) Procedure for screening the reaction conditions

p-Anisidine (15 mmol), catalyst (0.0025mmol), levulinic acid (7.5 mmol; S/C = 3000), and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 8 mL of HCOOH/HCOONa aqueous solution. The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 1 h. After cooling to room temperature, the reaction was basified with saturated NaOH solution, and 1,3,5-trimethoxybenzene (0.5 mmol) was added as internal standard. The resulting mixture was extracted with DCM (10 × 3 mL). The organic layers were washed with brine and dried over Na_2SO_4. After removing DCM in *vacuuo*, the conversion was determined by ^1H NMR using $CDCl_3$ as slovent.

(2) Procedure for expanding the substrate

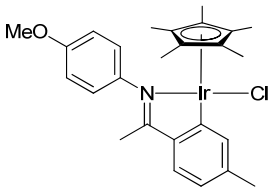
Amine (7.6 mmol), complex **1a** (0.0016 mmol), levulinic acid (3.2 mmol; S/C = 2000), and a magnetic stir bar were placed in a pressure tube. To the mixture was injected 3 mL of pH 3.5 HCOOH/HCOONa aqueous solution. The mixture was bubbled with argon for 15 min, and then stirred at 80 °C for 2-24 h. After cooling to room temperature, the reaction was basified with saturated NaOH solution, and extracted with DCM (10 × 3 mL). The organic layers were washed with brine and dried over Na_2SO_4. After removing DCM in *vacuuo*, the product was purified by flash chromatography using petroleum ether and ethyl acetate with 1% triethylamine as elute. The volume of aqueous HCOOH/HCOONa solution was 4 mL and 2 mL for S/C = 1000 and 500, respectively.

8. Analytic data of iridium complexes



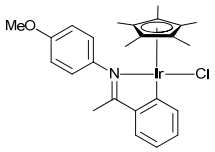
1a

Iridium complex 1a:[4] Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.45 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 2.4 Hz, 1H), 6.93 (d, J = 7.4 Hz, 2H), 6.58 (dd, J = 8.8 Hz, 2.4 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.38 (s, 3H) ,1.44 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.1, 170.4, 162.1, 157.6, 144.3, 141.3, 130.0, 124.7, 119.2, 113.6, 107.8, 89.0, 55.5, 55.0, 16.8, 8.6; HRMS for $C_{26}H_{31}ClIrNO_2$ $[M\text{-}Cl]^+$: m/z calc.: 582.1984. Found: 582.1979.



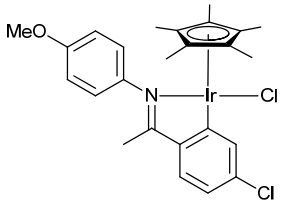
1b

Iridium complex 1b: Orange solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.62 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 6.93 (d, J = 6.0 Hz, 2H), 6.83 (d, J = 7.2 Hz, 1H), 3.85 (s, 3H), 2.44 (s, 3H), 2.40 (s, 3H), 1.43 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 181.1, 168.2, 157.6, 145.4, 144.3, 142.1, 135.8, 128.3, 124.3, 122.5, 113.1, 107.8, 88.9, 55.5, 22.0, 16.8, 8.6; HRMS for $C_{26}H_{31}ClIrNO$ $[M\text{-}Cl]^+$: m/z calc.: 566.2035. Found: 566.2066.



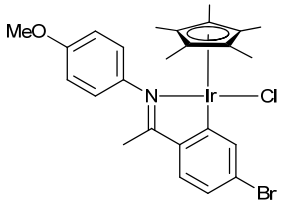
1c

Iridium complex 1c: Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.82 (d, J = 7.4 Hz, 1H), 7.50 (d, J = 7.6 Hz, 1H), 7.27 (t, J = 7.4 Hz, 1H), 7.04-7.00 (m, 1H), 6.95 (d, J = 6.2 Hz, 2H), 3.86 (s, 3H), 2.44 (s, 3H) ,1.44 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 181.6, 168.1, 157.7, 147.8, 144.3, 135.1, 132.0, 128.4, 124.0, 121.4, 113.7, 89.1, 55.5, 16.8, 8.6; HRMS for $C_{25}H_{29}ClIrNO$ $[M\text{-}Cl]^+$: m/z calc.:552.1878. Found: 552.1908



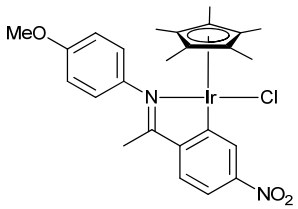
1d

Iridium complex 1d: Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.74 (s, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.96-6.94 (m, 2H), 3.86 (s, 3H), 2.40 (s, 3H), 1.43 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.7, 169.7, 157.9, 146.3, 144.0, 137.8, 134.4, 129.5, 124.3, 121.6, 115.4, 89.4, 55.6, 17.0, 8.56; HRMS for $C_{25}H_{28}Cl_2IrNO$ $[M\text{-}Cl]^+$: m/z calc.: 586.1489. Found: 586.1473.



1e

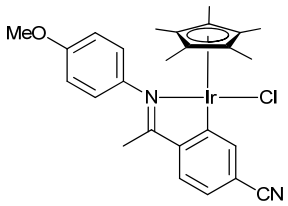
Iridium complex 1e: Yellow solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.91 (d, *J* = 1.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 6.95-6.94 (m, 2H), 3.86 (s, 3H), 2.40 (s, 3H), 1.43 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.9, 170.2, 157.9, 146.6, 144.0, 137.3, 129.8, 127.4, 124.4, 124.2, 122.6, 89.4, 55.6, 17.0, 8.6; HRMS for $C_{25}H_{28}BrClIrNO$ $[M\text{-}Cl]^+$: m/z calc.: 630.0984. Found: 630.0949.



1f

Iridium complex 1f: Black solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.62 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 6.99-6.97 (m, 2H), 3.87 (s, 3H), 2.84 (s, 3H), 1.46 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.4, 168.6, 158.2, 153.4, 149.0, 143.7, 129.2, 128.5, 123.7, 116.8, 113.4, 90.1, 55.6, 17.5, 8.6; HRMS for $C_{25}H_{28}ClIrN_2O_3$ $[M\text{-}Cl]^+$: m/z calc.:

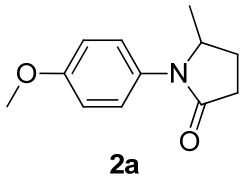
597.1729. Found: 597.1721.



1g

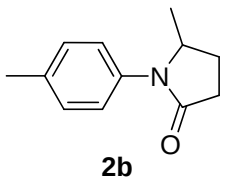
Iridium complex 1g:[4] Red solid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.04 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 6.98-6.97 (m, 2H), 3.86 (s, 3H), 2.45 (s, 3H), 1.44 (s, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 180.9, 167.6, 158.2, 151.7, 143.7, 138.3, 128.0, 125.0, 123.7, 119.8, 114.3, 113.3, 89.9, 55.6, 17.2, 8.6; HRMS for $C_{26}H_{28}ClIrN_2O$ $[M-Cl]^+$: m/z calc.: 577.1831. Found: 577.1818.

9. Analytic data of products.



2a

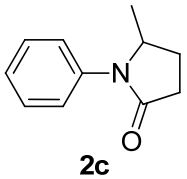
1-(4-Methoxyphenyl)-5-methylpyrrolidin-2-one 2a:[5] 617 mg; 94% yield (S/C=2000); White solid; mp. = 59~60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.17 (sextet, *J* = 6.4 Hz, 1H), 3.79 (s, 3H), 2.64-2.47 (m, 2H), 2.40-2.31 (m, 1H), 1.77-1.72 (m, 1H), 1.17 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 174.3, 157.7, 130.4, 126.1, 114.4, 56.1, 55.4, 31.1, 26.8, 20.3; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}NO_2$ $[M+Na]^+$: calc.: 228.1000. Found: 228.1005.



2b

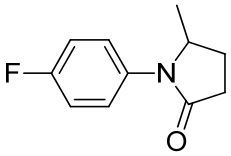
5-Methyl-1-p-tolylpyrrolidin-2-one 2b:[5] 565 mg; 93% yield (S/C=2000); White solid; mp. = 75~76 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.23 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz,

2H), 4.24 (sextet, *J* = 6.0 Hz, 1H), 2.66-2.48 (m, 2H), 2.40-2.34 (m, 4H), 1.78-1.71 (m, 1H), 1.19 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 135.6, 135.0, 129.6, 124.2, 55.8, 31.3, 26.8, 21.0, 20.2; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}NO$ $[M+Na]^+$: calc.: 212.1051. Found: 212.1052.



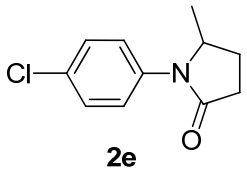
2c

5-Methyl-1-phenylpyrrolidin-2-one 2c:[5] 510 mg; 91% yield (S/C=2000); White solid; mp. = 49~50 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37-7.34 (m, 4H), 7.20-7.18 (m, 1H), 4.28 (sextet, *J* = 6.4 Hz, 1H), 2.67-2.48 (m, 2H), 2.40-2.31 (m, 1H), 1.78-1.72 (m, 1H), 1.19 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 137.6, 129.0, 125.7, 124.0, 55.6, 31.3, 26.8, 20.2; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{11}H_{13}NO$ $[M+Na]^+$: calc.: 198.0895. Found: 198.0894.



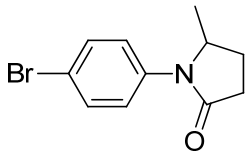
2d

1-(4-Fluorophenyl)-5-methylpyrrolidin-2-one 2d:[5] 544 mg; 88% yield (S/C=2000); White solid; mp. = 74~75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33-7.30 (m, 2H), 7.10-7.06 (m, 2H), 4.23 (sextet, *J* = 6.4 Hz, 1H), 2.67-2.49 (m, 2H), 2.42-2.33 (m, 1H), 1.80-1.73 (m, 1H), 1.19 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 160.4 (d, $^1J_{C\text{-}F}$ = 243.8Hz), 133.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 126.0 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 115. 8 (d, $^2J_{C\text{-}F}$ = 22.4 Hz), 55.8, 31.1, 26.8, 20.1; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{11}H_{12}FNO$ $[M+Na]^+$: calc.: 216.0800. Found: 216.0802.



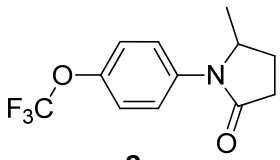
2e

1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one 2e:[6] 489 mg; 73% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.33 (s, 4H), 4.26 (sextet, *J* = 6.4 Hz, 1H), 2.67-2.47 (m, 2H), 2.40-2.31 (m, 1H), 1.79-1.74 (m, 1H), 1.19 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 136.2, 130.9, 129.0, 124.9, 55.4, 31.2, 26.6, 20.0; IR (KBr): 1700 cm^{-1}; HRMS (ESI) for $C_{11}H_{12}ClNO$ $[M+Na]^+$: calc.: 232.0505. Found: 232.0511.



2f

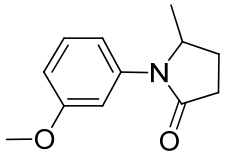
1-(4-Bromophenyl)-5-methylpyrrolidin-2-one 2f: 698 mg; 86% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.49 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 4.27 (sextet, *J* = 6.4 Hz, 1H), 2.67-2.47 (m, 2H), 2.40-2.32 (m, 1H), 1.79-1.74 (m, 1H), 1.20 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.1, 136.7, 132.0, 125.2, 118.6, 55.3, 31.2, 26.6, 20.0; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{11}H_{12}BrNO$ $[M+Na]^+$: calc.: 276.0000. Found: 276.0006.



2g

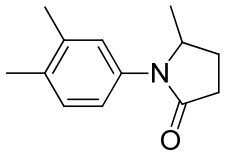
5-Methyl-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-one 2g: 596 mg; 72% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, *J* = 9.2 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 4.28 (sextet, *J* = 6.4 Hz, 1H), 2.68-2.48 (m, 2H), 2.41-2.32 (m, 1H), 1.80-1.75 (m, 1H), 1.21 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 146.3, 136.2, 124.9, 121.5,120.5 (q, J_{C-F} = 255.6 Hz), 55.5, 31.2, 26.6, 20.0; IR (KBr): 1700 cm^{-1}; HRMS (ESI) for

$C_{12}H_{13}F_3NO_2$ $[M+Na]^+$: calc.: 282.0718. Found: 282.0727.



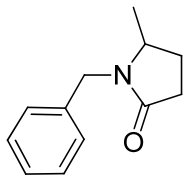
2h

1-(3-Methoxyphenyl)-5-methylpyrrolidin-2-one 2h: 251 mg; 76% yield (S/C=1000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.28 (d, *J* = 8.0 Hz, 1H), 7.03-7.02 (m, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.75 (dd, *J* = 8.2, 2.4 Hz, 1H), 4.27 (sextet, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.67-2.48 (m, 2H), 2.40-2.31 (m, 1H), 1.78-1.70 (m, 1H), 1.21 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 160.1, 138.8, 129.6, 116.0, 111.3, 110.1, 55.7, 55.3, 31.4, 26.7, 20.1; IR (KBr): 1630 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}NO_2$ $[M+Na]^+$: calc.: 228.1000. Found: 228.1005.



2i

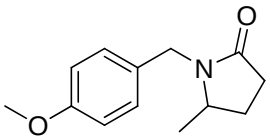
1-(3,4-Dimethylphenyl)-5-methylpyrrolidin-2-one 2i: 530 mg; 82% yield (S/C=2000); White solid; mp. = 85~87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14-7.11 (m, 2H), 7.02 (m, 1H), 4.21 (m, 1H), 2.65-2.47 (m, 2H), 2.39-2.32 (m, 1H), 2.26 (s, 3H), 2.23(s, 3H), 1.77-1.68 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 137.3 135.2, 134.5, 130.1, 125.9, 121.9, 55.9, 31.3, 26.9, 20.3, 19.9, 19.3; IR (KBr): 1670 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NO$ $[M+Na]^+$: calc.: 226.1208. Found: 226.1212.



2j

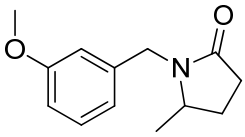
1-Benzyl-5-methylpyrrolidin-2-one 2j: [5] 523 mg; 86% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.32-7.21 (m, 5H), 4.95 (d, *J* = 15.2 Hz, 1H), 3.97 (d, *J* = 15.2 Hz,

1H), 3.51 (sextet, J = 6.2 Hz, 1H), 2.48-2.34 (m, 2H), 2.18-2.11 (m, 1H), 1.61-1.55 (m, 1H), 1.14 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 136.9, 128.6, 127.9, 127.4, 52.8, 43.9, 30.2, 26.7, 19.6; IR (KBr): 1630 cm^{-1}; HRMS (ESI) for $C_{12}H_{15}NO$ $[M+Na]^+$: calc.: 212.1051. Found: 212.1056.



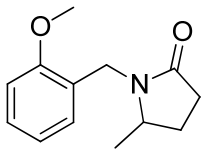
2k

1-(4-Methoxybenzyl)-5-methylpyrrolidin-2-one 2k:[5] 659 mg; 94% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.15 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.90 (d, J = 14.8 Hz, 1H), 3.90 (d, J = 14.8 Hz, 1H), 3.78 (s, 3H), 3.49 (sextet, J = 6.4 Hz, 1H), 2.51-2.32 (m, 2H), 2.16-2.07 (m, 1H), 1.61-1.52 (m, 1H), 1.15 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 159.0, 129.3, 129.0, 114, 55.2, 52.6, 43.3, 30.3, 26.6, 19.6; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1157. Found: 242.1164.



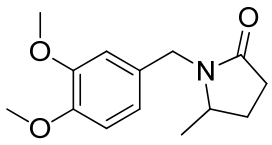
2l

1-(3-Methoxybenzyl)-5-methylpyrrolidin-2-one 2l: 654 mg; 94% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22 (t, J = 7.8 Hz, 1H), 6.81-6.76 (m, 3H), 4.93 (d, J = 15.0 Hz, 1H), 3.95 (d, J = 15.0 Hz, 1H), 3.78 (s, 3H), 3.54 (sextet, J = 6.4 Hz, 1H), 2.54-2.36 (m, 2H), 2.19-2.10 (m, 1H), 1.63-1.54 (m, 1H), 1.16 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 159.9, 138.5, 129.6, 120.3, 113.6, 112.8, 55.2, 52.8, 43.9, 30.2, 26.7, 19.6; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1153. Found: 242.1162.



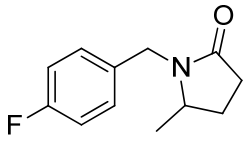
2m

1-(2-Methoxybenzyl)-5-methylpyrrolidin-2-one 2m: 169 mg; 96% yield (S/C=200); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24-7.17 (m, 2H), 6.91-6.83 (m, 2H), 4.80 (d, *J* = 15.2 Hz, 1H), 4.20 (d, *J* = 15.2 Hz, 1H), 3.81 (s, 3H), 3.53 (sextet, *J* = 6.4 Hz, 1H), 2.47-2.31 (m, 2H), 2.16-2.10 (m, 1H), 1.60-1.54 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 157.3, 129.4, 128.5 125.0, 120.6, 110.3, 55.3, 53.2, 38.2, 30.2, 26.7, 19.6; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1157. Found: 242.1161.



2n

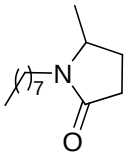
1-(3,4-Dimethoxybenzyl)-5-methylpyrrolidin-2-one 2n: 679 mg; 84% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.78 (m, 3H), 4.90 (d, *J* = 14.8 Hz, 1H), 3.90 (d, *J* = 14.8 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.51 (sextet, *J* =6.4 Hz, 1H), 2.52-2.32 (m, 2H), 2.17-2.08 (m, 1H), 1.58-1.56 (m, 1H), 1.16 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 149.2, 148.5, 129.5, 120.4, 111.4, 111.1, 55.9, 55.8, 52.7, 43.7, 30.3, 26.6, 19.6; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{14}H_{19}NO_3$ $[M+Na]^+$: calc.: 272.1263. Found: 272.1272.



2o

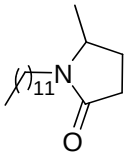
1-(4-Fluorobenzyl)-5-methylpyrrolidin-2-one 2o: 602 mg; 91% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.17 (m, 2H), 6.95 (m, 2H), 4.83 (d, *J* = 15.2 Hz, 1H), 3.96 (d, *J* = 15.2 Hz, 1H), 3.47 (sextet, *J* = 6.4 Hz, 1H), 2.45-2.32 (m, 2H), 2.14-2.09 (m, 1H), 1.59-1.53 (m, 1H), 1.11 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 162.1

(d, $^{1}J_{C\text{-}F}$ = 244.2 Hz), 132.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 129.6 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 115.4 (d, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 52.9, 43.2, 30.2, 26.7, 19.6; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{12}H_{14}FNO$ $[M+Na]^{+}$: calc.: 230.0957. Found: 230.0964.



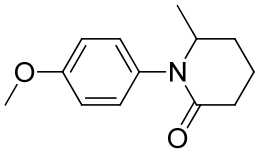
2p

1-Ethyl-5-methylpyrrolidin-2-one 2p: 150 mg; 88% yield (S/C=500); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.64 (sextet, *J* = 6.4 Hz, 1H), 3.57-3.50 (m, 1H), 2.89-2.84 (m, 1H), 2.36-2.28 (m, 2H), 2.16-2.11 (m, 1H), 1.54-1.47 (m, 2H), 1.40-1.37 (m, 2H), 1.25-1.22 (m, 10H), 1.16 (d, *J* = 6.0 Hz, 3H), 0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.6, 53.2, 40.0, 31.7, 30.3, 29.2, 29.1, 27.4, 26.9, 26.8, 22.6, 19.7, 14.0; IR (KBr): 1690 cm^{-1}; HRMS (ESI) for $C_{13}H_{25}NO$ $[M+Na]^{+}$: calc.: 234.1834. Found: 234.1838.



2q

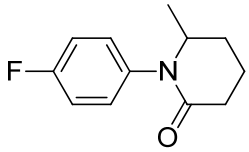
1-Ethyl-5-methylpyrrolidin-2-one 2q: 68 mg; 73% yield (S/C=500); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.66 (sextet, *J* = 6.4Hz, 1H), 3.57-3.50 (m, 1H), 2.90-2.83 (m, 1H), 2.41-2.24 (m, 2H), 2.18-2.09 (m, 1H), 1.55-1.45 (m, 2H), 1.42-1.32 (m, 1H), 1.21 (s, 18H), 1.16 (d, *J* = 6.4 Hz, 3H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 53.4, 40.2, 31.9, 30.3, 29.59, 29.58, 29.54, 29.51, 29.31, 29.29, 27.4, 27.0, 26.9, 22.6, 19.7, 14.0; IR (KBr): 1680 cm^{-1}; HRMS (ESI) for $C_{17}H_{33}NO$ $[M+Na]^{+}$: calc.: 290.2460. Found: 290.2465.



2r

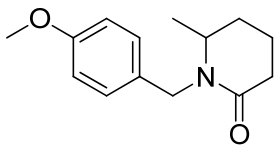
1-(4-Methoxyphenyl)-6-methylpiperidin-2-one 2r: 587 mg; 84% yield (S/C=2000); Yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.06 (d, *J* = 9.2 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.85 (sextet, *J* = 6.4 Hz, 1H), 3.80 (s, 3H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.13-2.05 (m, 1H), 2.02-1.93 (m, 1H), 1.88-1.78 (m, 1H), 1.75-1.67 (m, 1H), 1.07 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 158.3, 134.3, 129.0, 114.4, 55.9, 55.4, 32.8, 30.9, 20.9, 18.4; IR (KBr): 1650 cm^{-1}; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1157. Found: 242.1162.



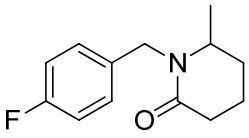
2s

1-(4-Fluorophenyl)-6-methylpiperidin-2-one 2s: 654 mg; 98% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14-7.05 (m, 4H), 3.87 (sextet, *J* = 6.4 Hz, 1H), 2.51 (t, *J* = 6.8 Hz, 2H), 2.14-2.06 (m, 1H), 2.04-1.94 (m, 1H), 1.88-1.79 (m, 1H), 1.76-1.68 (m, 1H), 1.06 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.5, 161.4 (d, $^1J_{C\text{-}F}$ = 247.1 Hz), 137.4(d, $^4J_{C\text{-}F}$ = 3.2 Hz), 129.7 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 22.7 Hz), 55.9, 32.7, 30.9, 20.9, 18.4; IR (KBr): 1640 cm^{-1}; HRMS (ESI) for $C_{12}H_{14}FNO$ $[M+Na]^+$: calc.: 230.0957. Found: 230.0961.



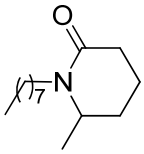
2t

1-(4-Methoxybenzyl)-6-methylpiperidin-2-one 2t: 611 mg; 82% yield (S/C=1000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.16 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.27 (d, *J* = 14.8 Hz, 1H), 3.91 (d, *J* = 14.8 Hz, 1H), 3.78 (s, 3H), 3.44 (sextet, *J* = 6.2 Hz, 1H), 2.46-2.43 (m, 2H), 1.99-1.85 (m, 1H), 1.83-1.75 (m, 1H), 1.73-1.66 (m, 1H), 1.62-1.56 (m, 1H), 1.19 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.1, 158.8, 129.9, 129.1, 113.9, 55.2, 50.6, 46.5, 32.2, 30.2, 19.5, 17.5; IR (KBr): 1630 cm^{-1}; HRMS (ESI) for $C_{14}H_{19}NO_2$ $[M+Na]^+$: calc.: 256.1313. Found: 256.1319.



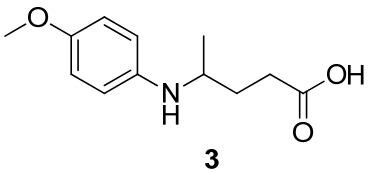
2u

1-(4-Fluorobenzyl)-6-methylpiperidin-2-one 2u: 567 mg; 81% yield (S/C=2000); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.21-7.18 (m, 2H), 6.97 (m, 2H), 5.20 (d, *J* = 14.8 Hz, 1H), 4.00 (d, *J* = 14.8 Hz, 1H), 3.43 (sextet, *J* = 6.4 Hz, 1H), 2.46-2.43 (m, 1H), 1.94-1.77 (m, 2H), 1.75-1.67 (m, 1H), 1.63-1.57 (m, 1H), 1.18 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 170.2, 162.0 (d, $^{1}J_{C\text{-}F}$= 246.0 Hz), 133.7 (d, $^{4}J_{C\text{-}F}$ = 3.2 Hz), 129.3 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.5 Hz), 51.2, 46.6, 32.2, 30.2, 19.6, 17.5; IR (KBr): 1630 cm^{-1}; HRMS (ESI) for $C_{13}H_{16}FNO$ $[M+Na]^+$: calc.: 244.1119. Found: 244.1114.



2v

1-Ethyl-6-methylpiperidin-2-one 2v: 155 mg; 86% yield (S/C=500); Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.77-3.69 (m, 1H), 3.55-3.48 (m, 1H), 2.90-2.83 (m, 1H), 2.35-2.32 (m, 2H), 1.88-1.83 (m, 2H), 1.71-1.66 (1, 1H), 1.64-1.48 (m, 3H), 1.26-1.20 (m, 13H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 169.6, 51.8, 45.1, 32.2, 31.8, 30.2, 29.4, 29.2, 27.7, 27.1, 22.6, 20.0, 17.5, 14.0; IR (KBr): 1640 cm^{-1}; HRMS (ESI) for $C_{14}H_{27}NO$ $[M+Na]^+$: calc.: 248.1990. Found: 248.1993.



3

4-((4-Methoxyphenyl)amino)pentanoic acid 3: Yellow oil; ^{1}H NMR (400 MHz, CD_3SOCD_3) δ (ppm): 6.69 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.62 (s, 3H), 3.32 (sextet, *J* = 6.2 Hz, 1H), 2.31-2.24 (m, 2H), 1.75-1.56 (m, 2H), 1.05 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz,

CD_3SOCD_3) δ (ppm): 174.6, 150.4, 142.4, 114.6, 113.6, 55.3, 47.5, 31.3, 30.5, 20.1; HRMS (ESI) for $C_{12}H_{17}NO_3$ $[M-H]^-$: calc.: 222.1130. Found: 222.1129.

10. References

[1] J. S. M. Samec and J. E. Backvall, *Chem. Eur. J.* **2002**, *8*, 2955-2961.

[2] R. G. Ball, W. A. G. Graham, D. M. Heinekey, J. K. Hoyano, A. D. McMaster, B. M. Mattson, S. T. Michel, *Inorg. Chem.* **1990**, *29*, 2023-2025.

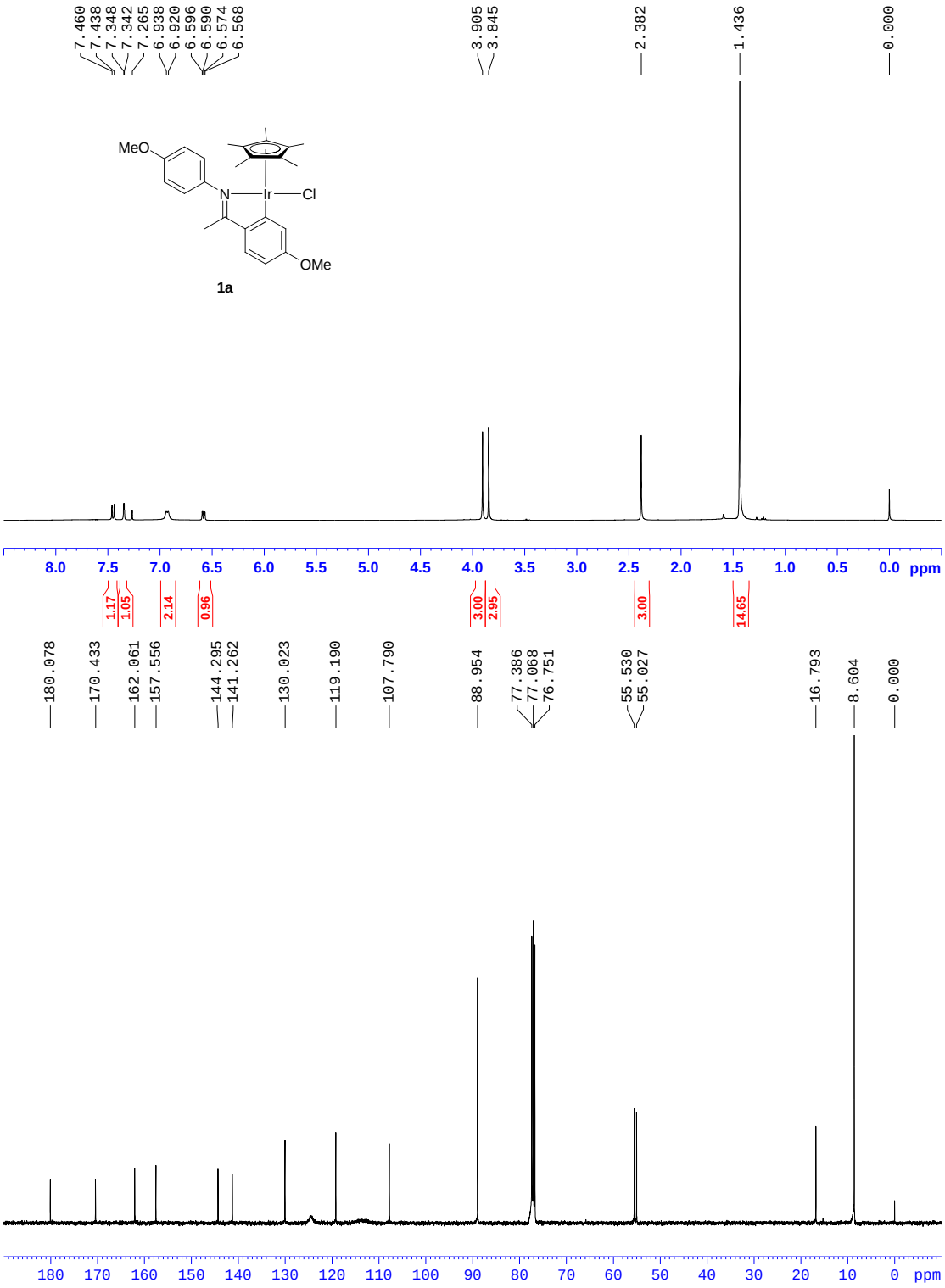
[3] D. L. Davies, O. Al-Duaij, J. Fawcett, M. Giardiello, S. T. Hilton, D. R. Russell, *Dalton Trans.***2003**, 4132-4138.

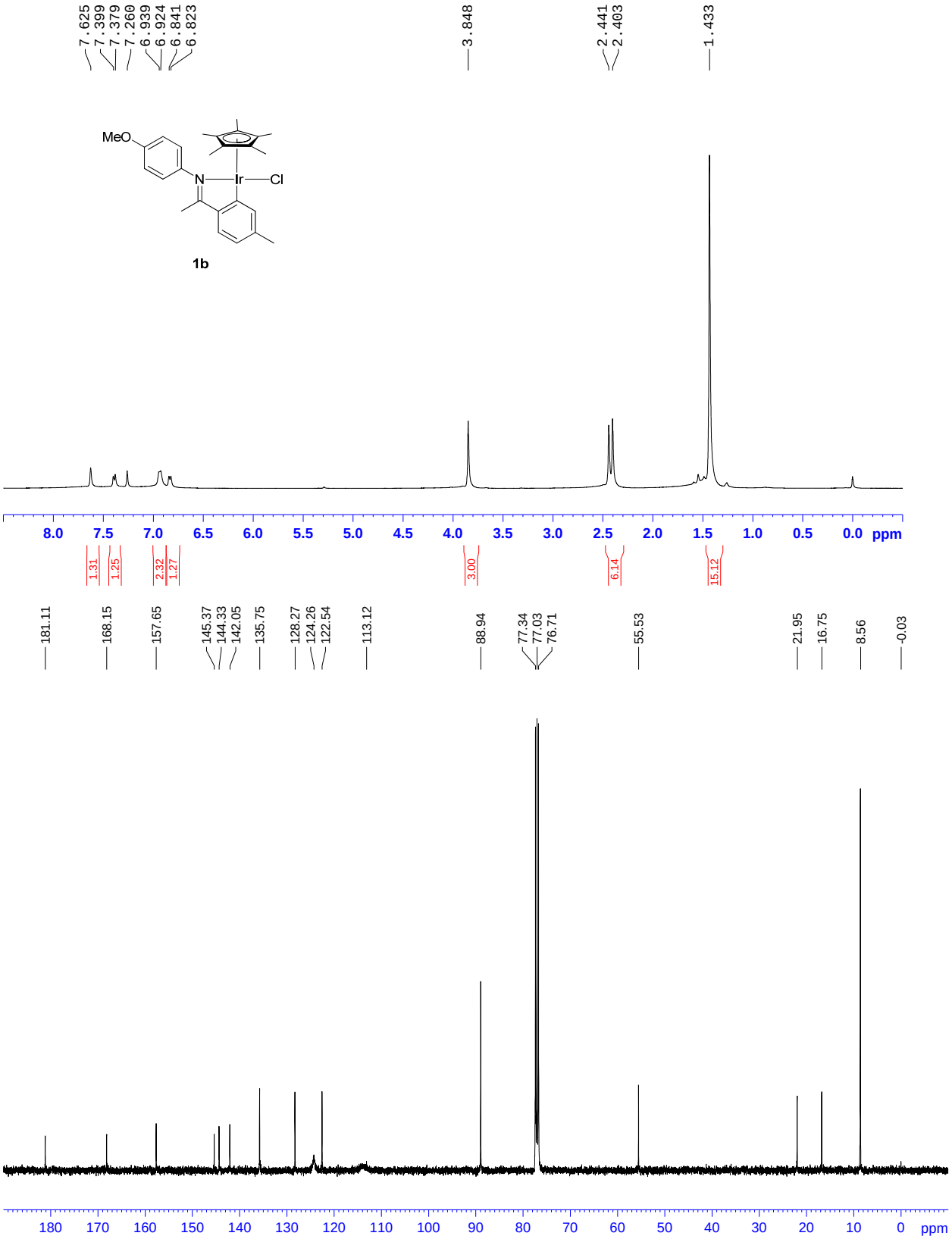
[4] C. Wang, A. Pettman, J. Bacsa and J. L. Xiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 7948-7552.

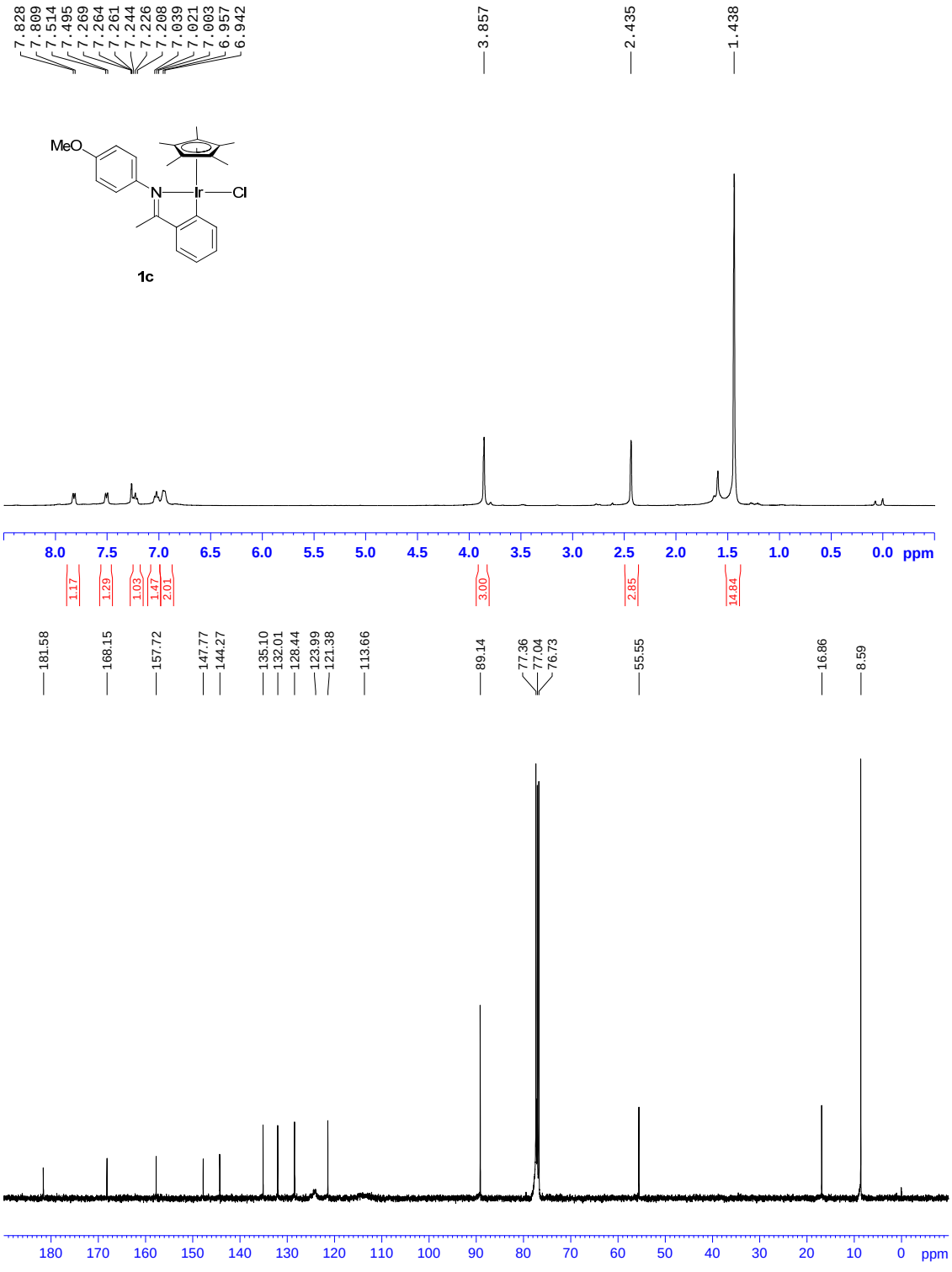
[5] Y. B. Huang, J. J. Dai, X. J. Deng, Y. C. Qu, Q. X. Guo, Y.Fu. *Chemsuschem,* **2011**, *4*, 1578-1581.

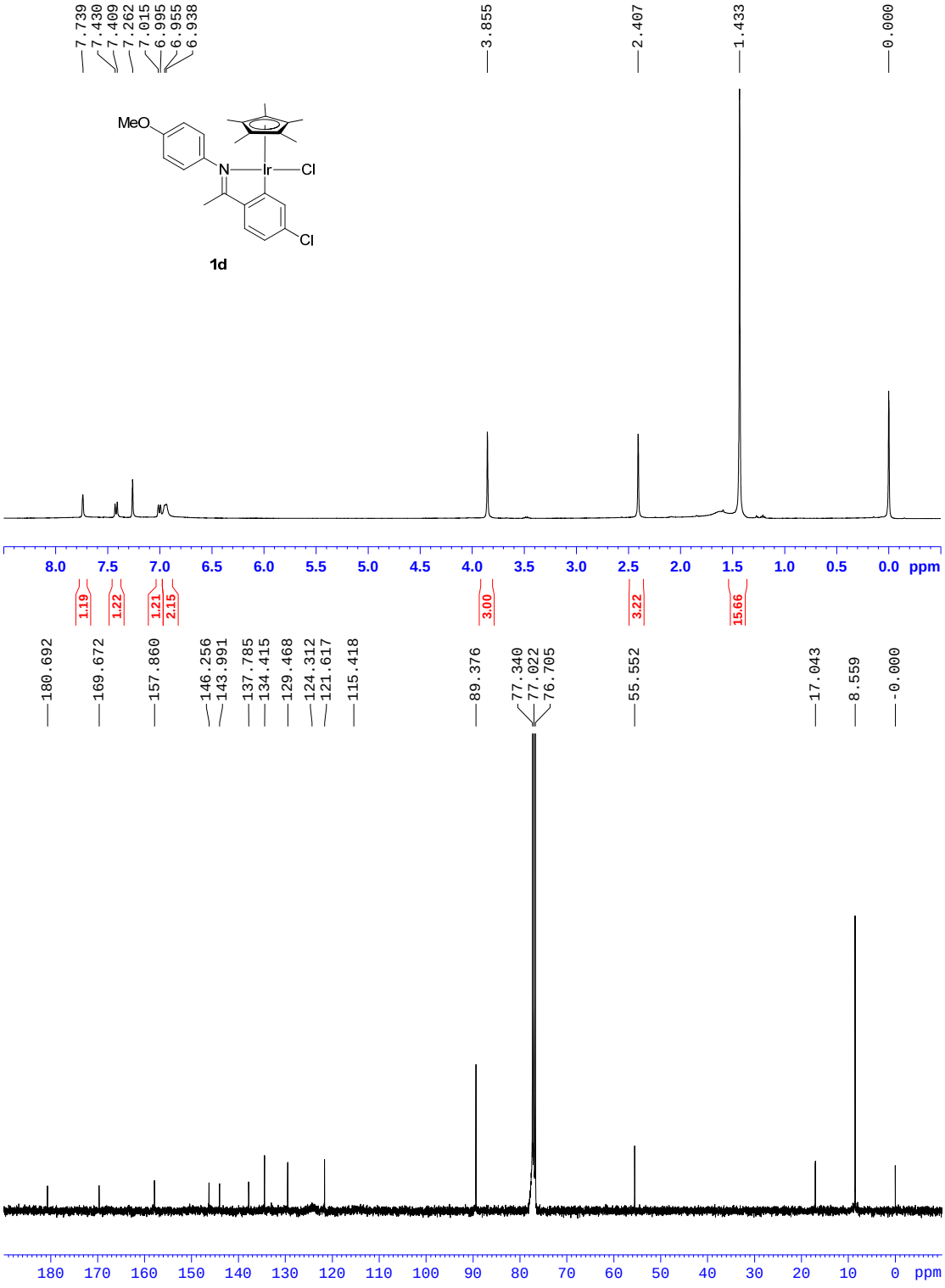
[6] X. L. Du, L. He, Sh. Zhao, Y. M. Liu, Y. Cao, H. Y. He, K. N. Fan. *Angew. Chem. Int. Ed.* **2011**, *50*, 7815-7818.

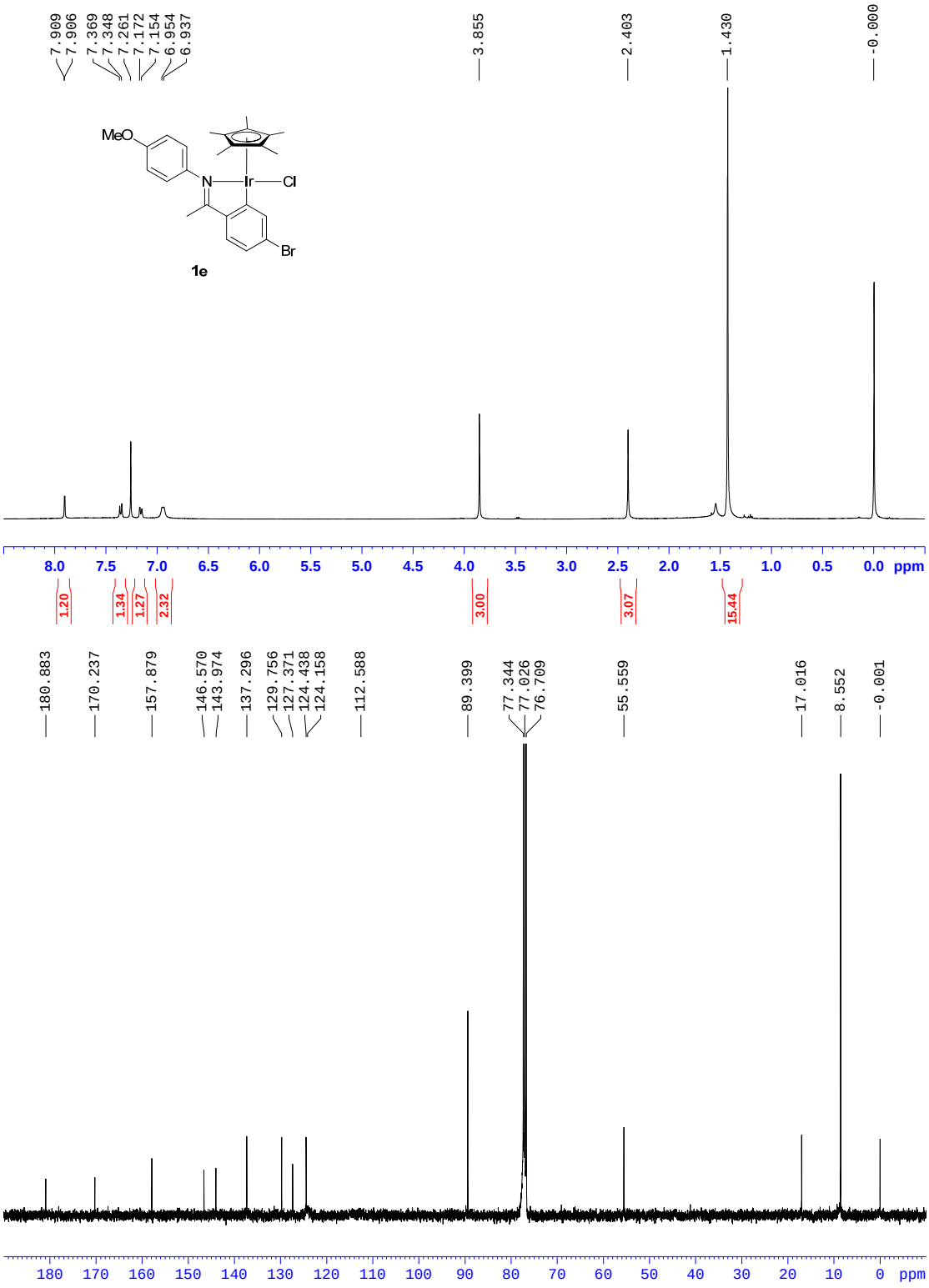
11. Traces of ^{1}H and ^{13}C NMR spectra of catalysts

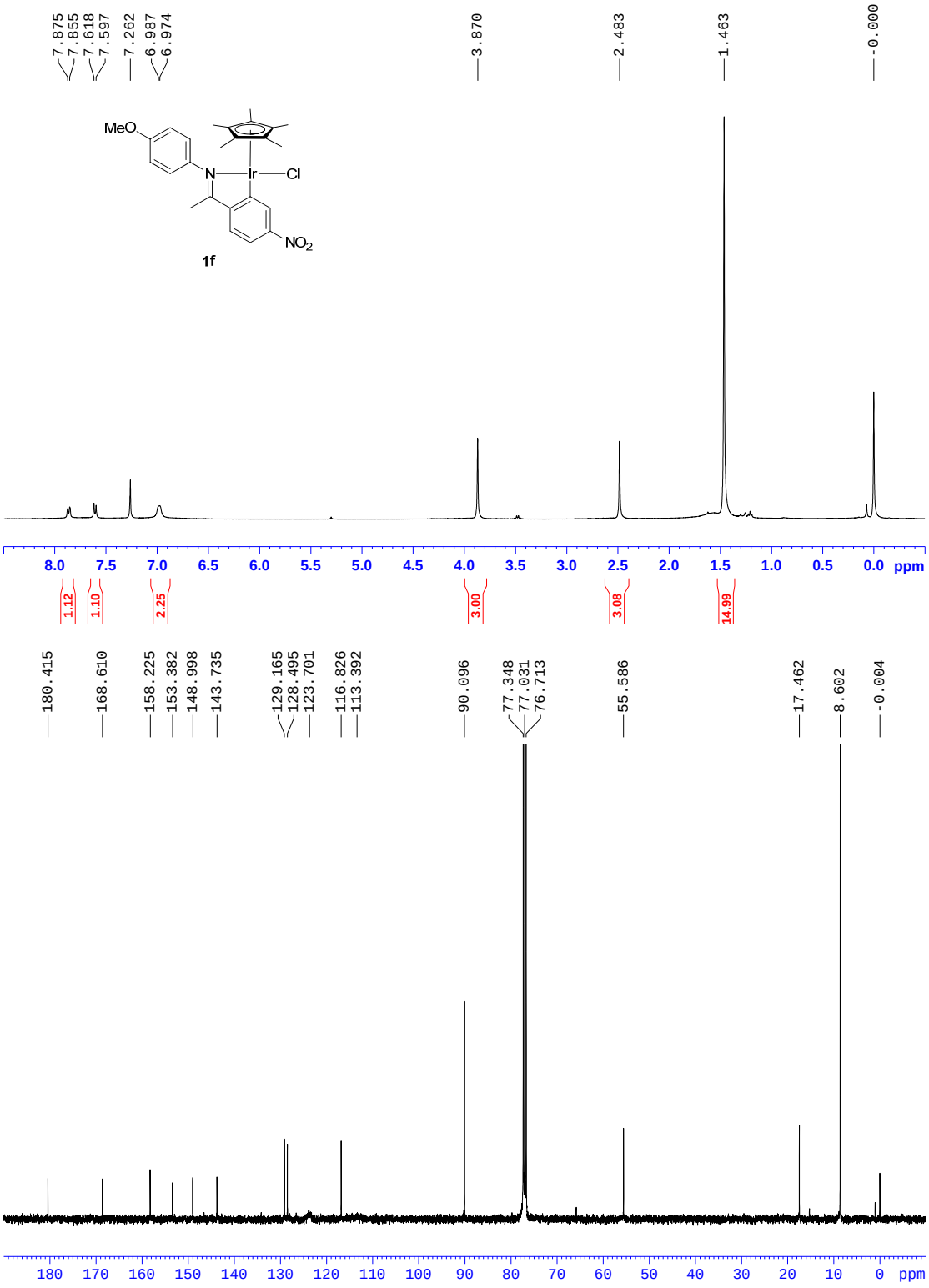


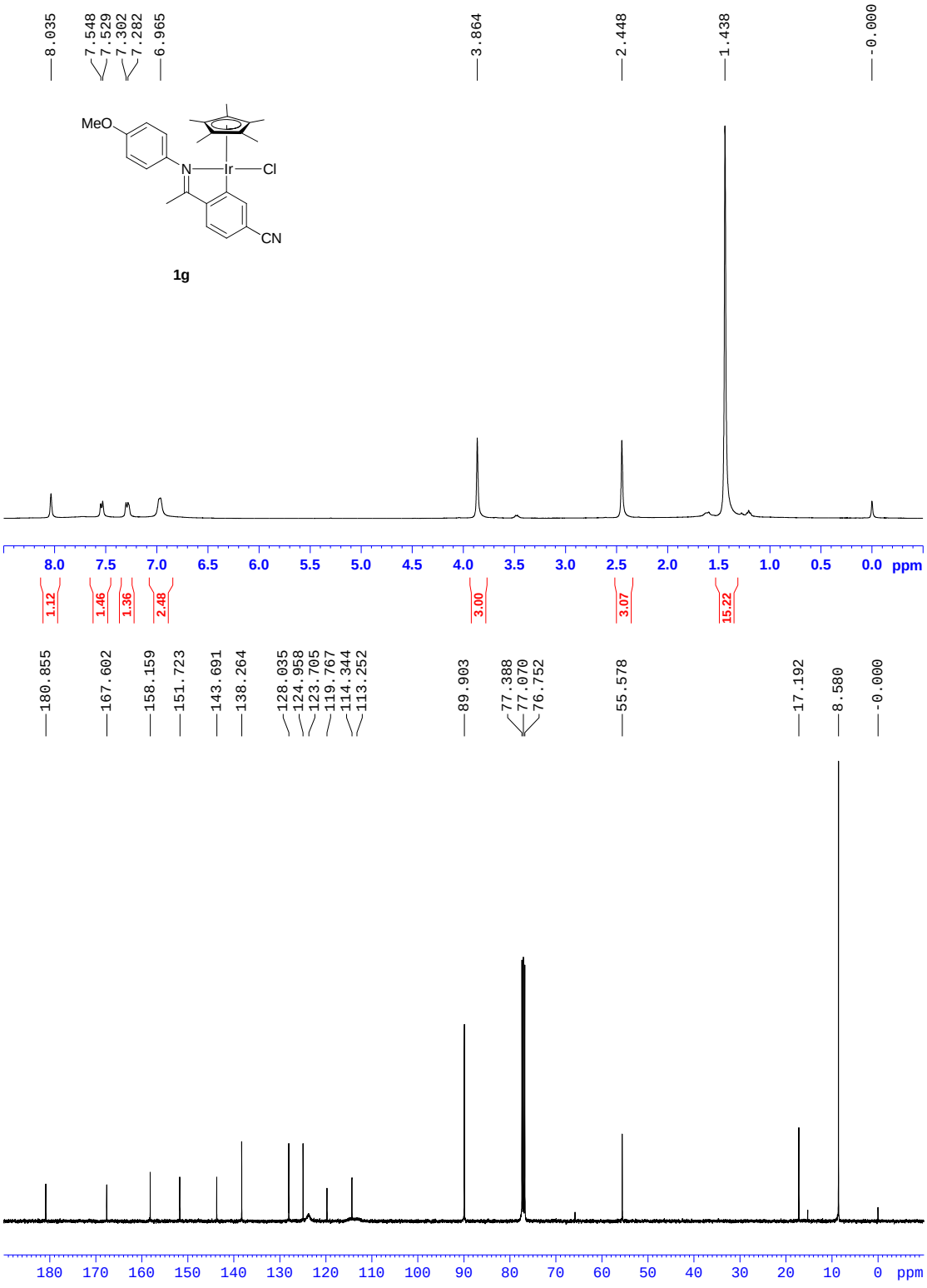

7.625
7.399
7.379
7.260
6.939
6.924
6.841
6.823
3.848
2.441
2.403
1.433
MeO
N
Ir
Cl
1b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.31
1.25
2.32
1.27
3.00
6.14
15.12
181.11
168.15
157.65
145.37
144.33
142.05
135.75
128.27
124.26
122.54
113.12
88.94
77.34
77.03
76.71
55.53
21.95
16.75
8.56
-0.03
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.828
7.809
7.514
7.495
7.269
7.264
7.261
7.244
7.226
7.208
7.039
7.021
7.003
6.957
6.942
3.857
2.435
1.438
MeO
N
Ir
Cl
1c
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
ppm
1.17
1.29
1.03
1.47
2.01
3.00
2.85
14.84
181.58
168.15
157.72
147.77
144.27
135.10
132.01
128.44
123.99
121.38
113.66
89.14
77.36
77.04
76.73
55.55
16.86
8.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

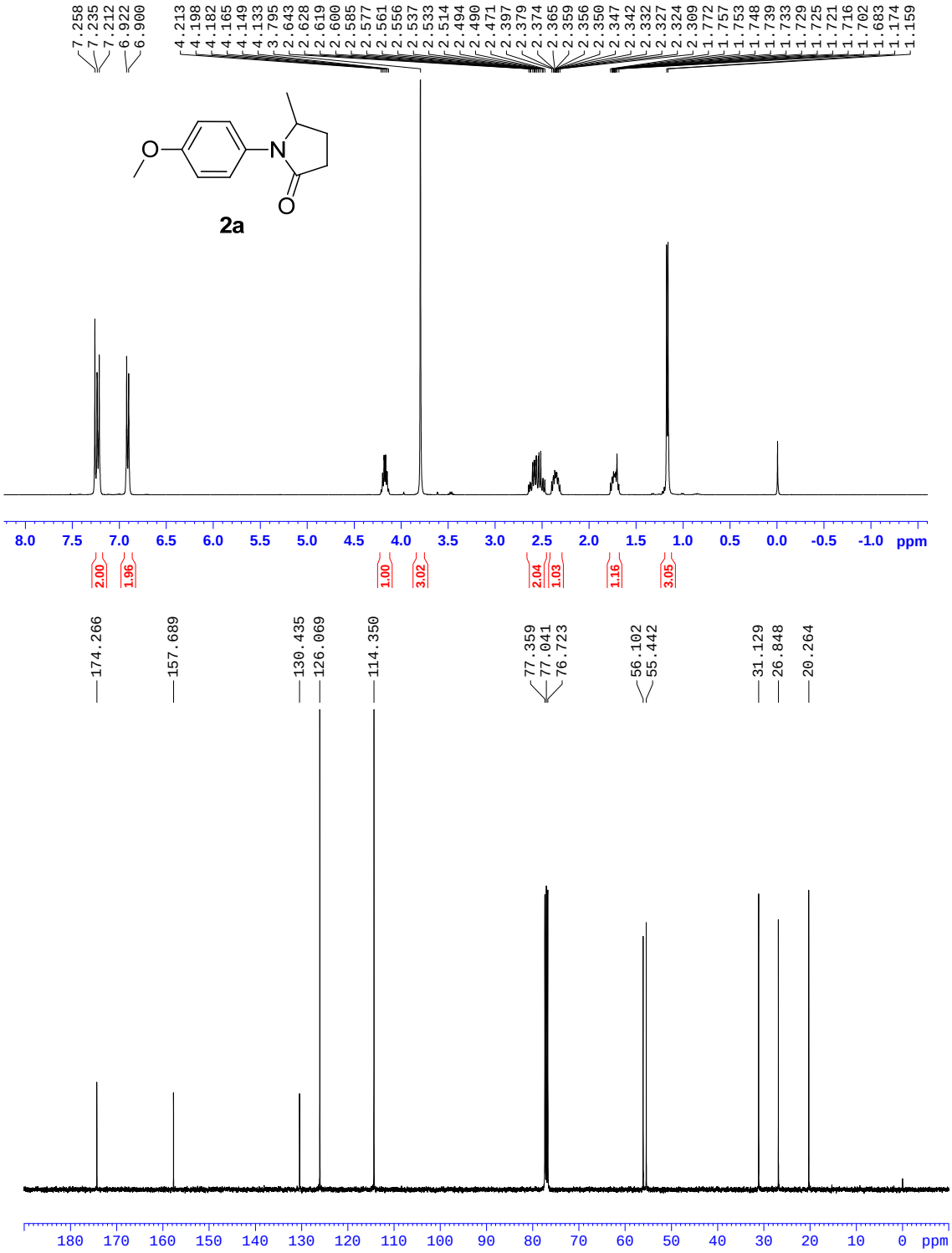

7.739
7.430
7.409
7.262
7.015
6.995
6.955
6.938
3.855
2.407
1.433
0.000
MeO
N
Ir
Cl
Cl
1d
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.19
1.22
1.21
2.15
3.00
3.22
15.66
180.692
169.672
157.860
146.256
143.991
137.785
134.415
129.468
124.312
121.617
115.418
89.376
77.340
77.022
76.705
55.552
17.043
8.559
-0.000
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

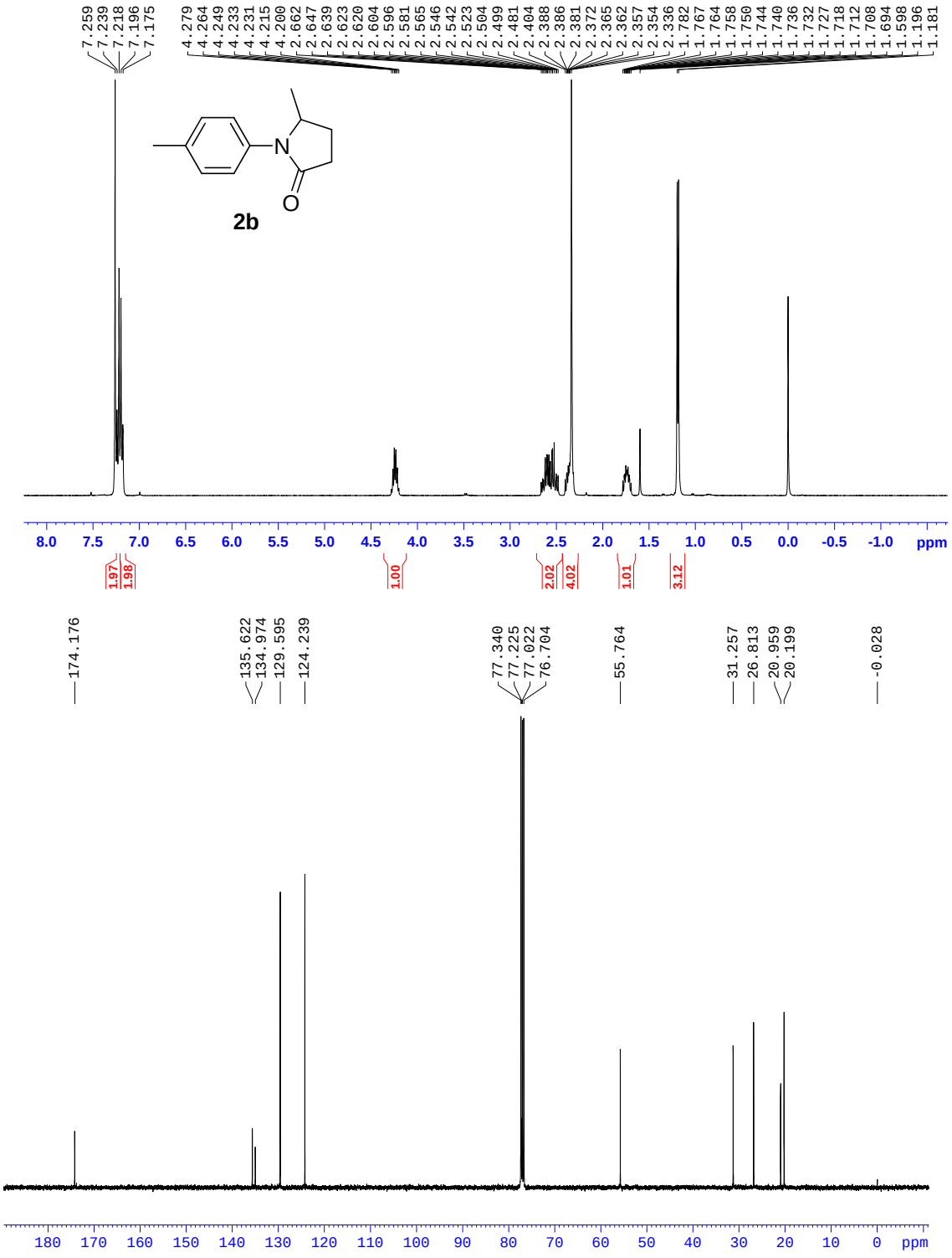

7.909
7.906
7.369
7.348
7.261
7.172
7.154
6.954
6.937
3.855
2.403
1.430
-0.000
MeO
N
Ir
Cl
Br
1e
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.20
1.34
1.27
2.32
3.00
3.07
15.44
180.883
170.237
157.879
146.570
143.974
137.296
129.756
127.371
124.438
124.158
112.588
89.399
77.344
77.026
76.709
55.559
17.016
8.552
-0.001
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

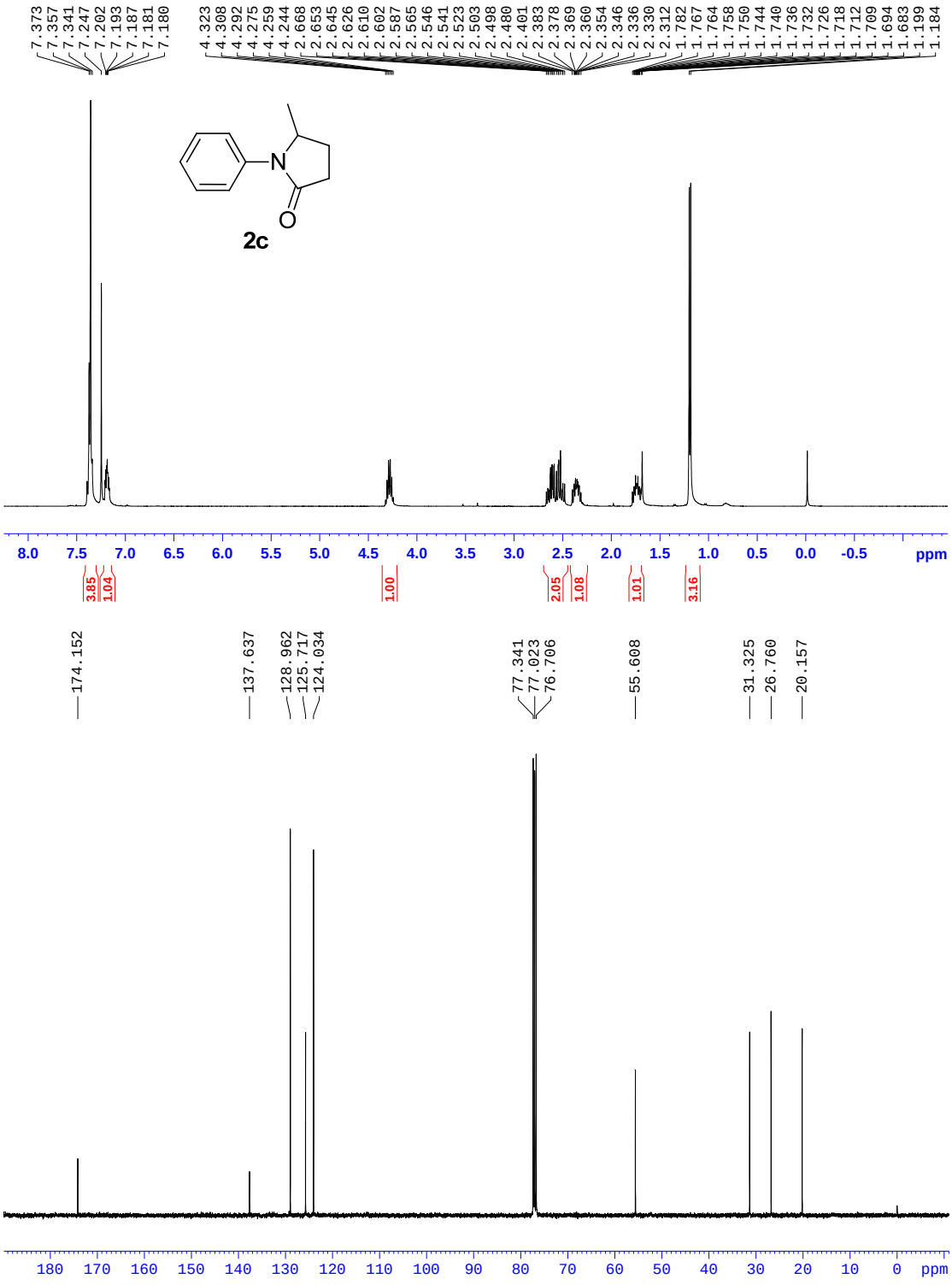

7.875
7.855
7.618
7.597
7.262
6.987
6.974
3.870
2.483
1.463
-0.000
MeO
N
Ir
Cl
NO2
1f
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.12
1.10
2.25
3.00
3.08
14.99
180.415
168.610
158.225
153.382
148.998
143.735
129.165
128.495
123.701
116.826
113.392
90.096
77.348
77.031
76.713
55.586
17.462
8.602
-0.004
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

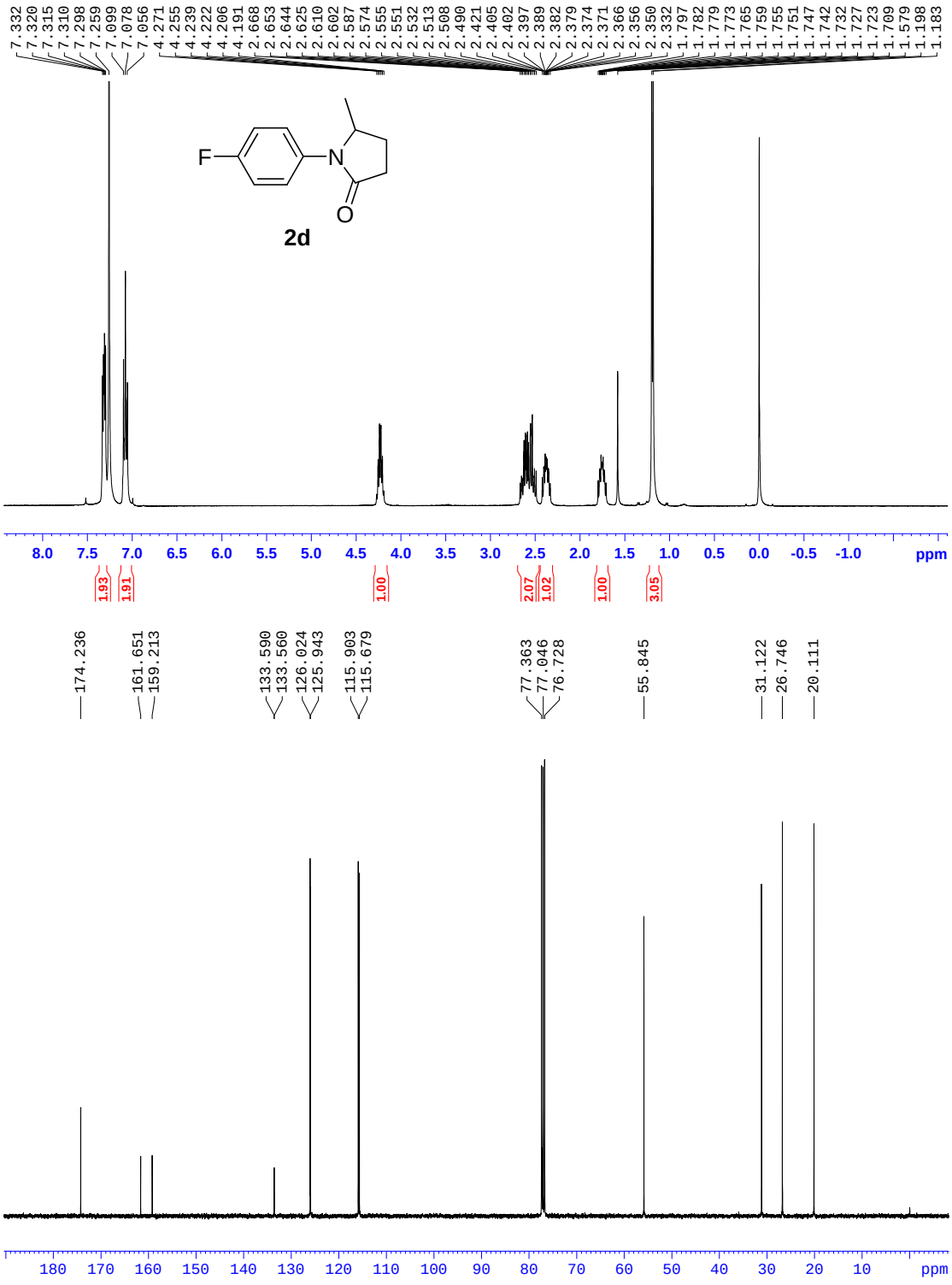

8.035
7.548
7.529
7.302
7.282
6.965
3.864
2.448
1.438
-0.000
MeO
N
Ir
Cl
CN
1g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.12
1.46
1.36
2.48
3.00
3.07
15.22
180.855
167.602
158.159
151.723
143.691
138.264
128.035
124.958
123.705
119.767
114.344
113.252
89.903
77.388
77.070
76.752
55.578
17.192
8.580
-0.000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

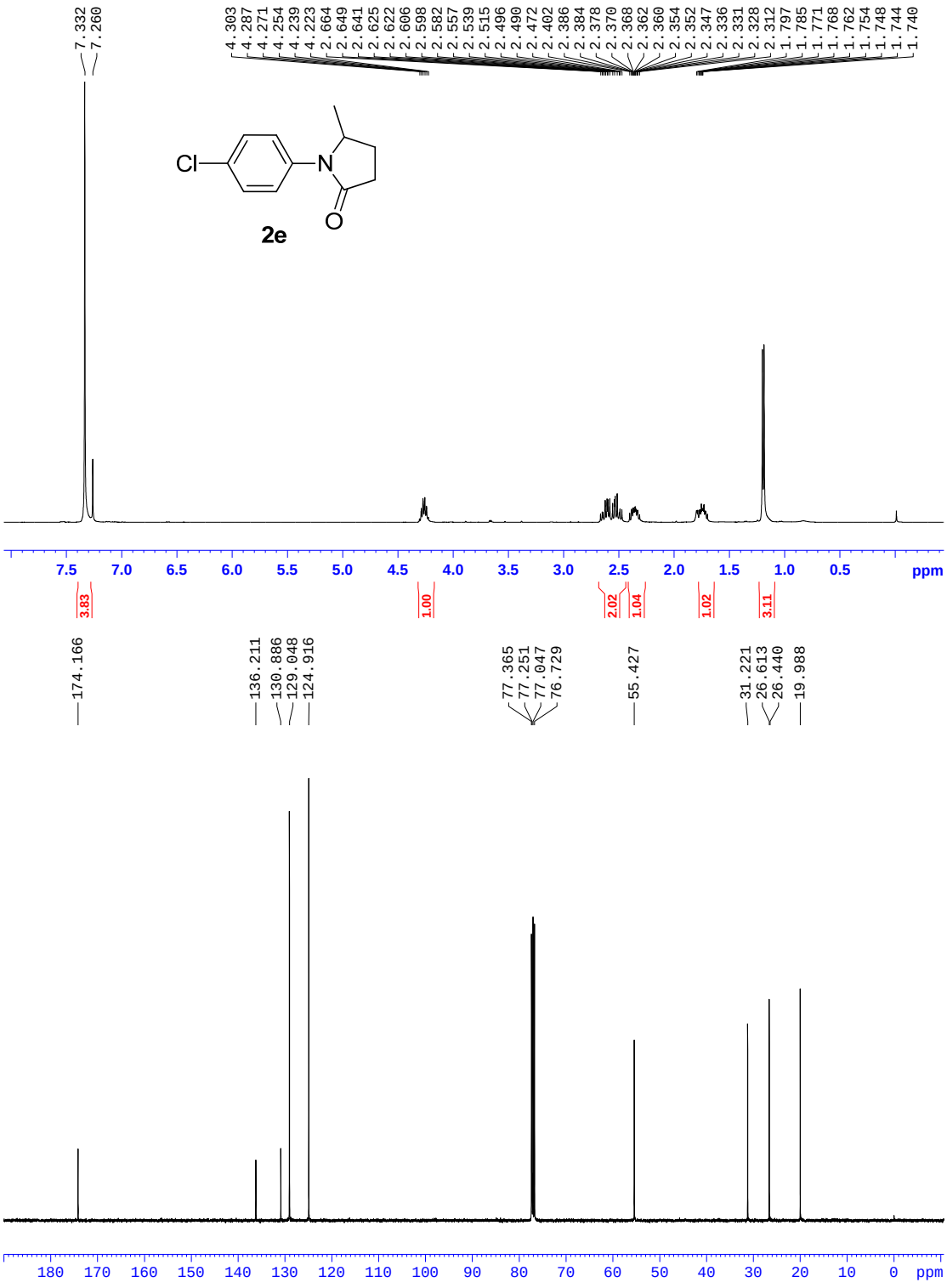
12. Traces of ^{1}H and ^{13}C NMR spectra of products

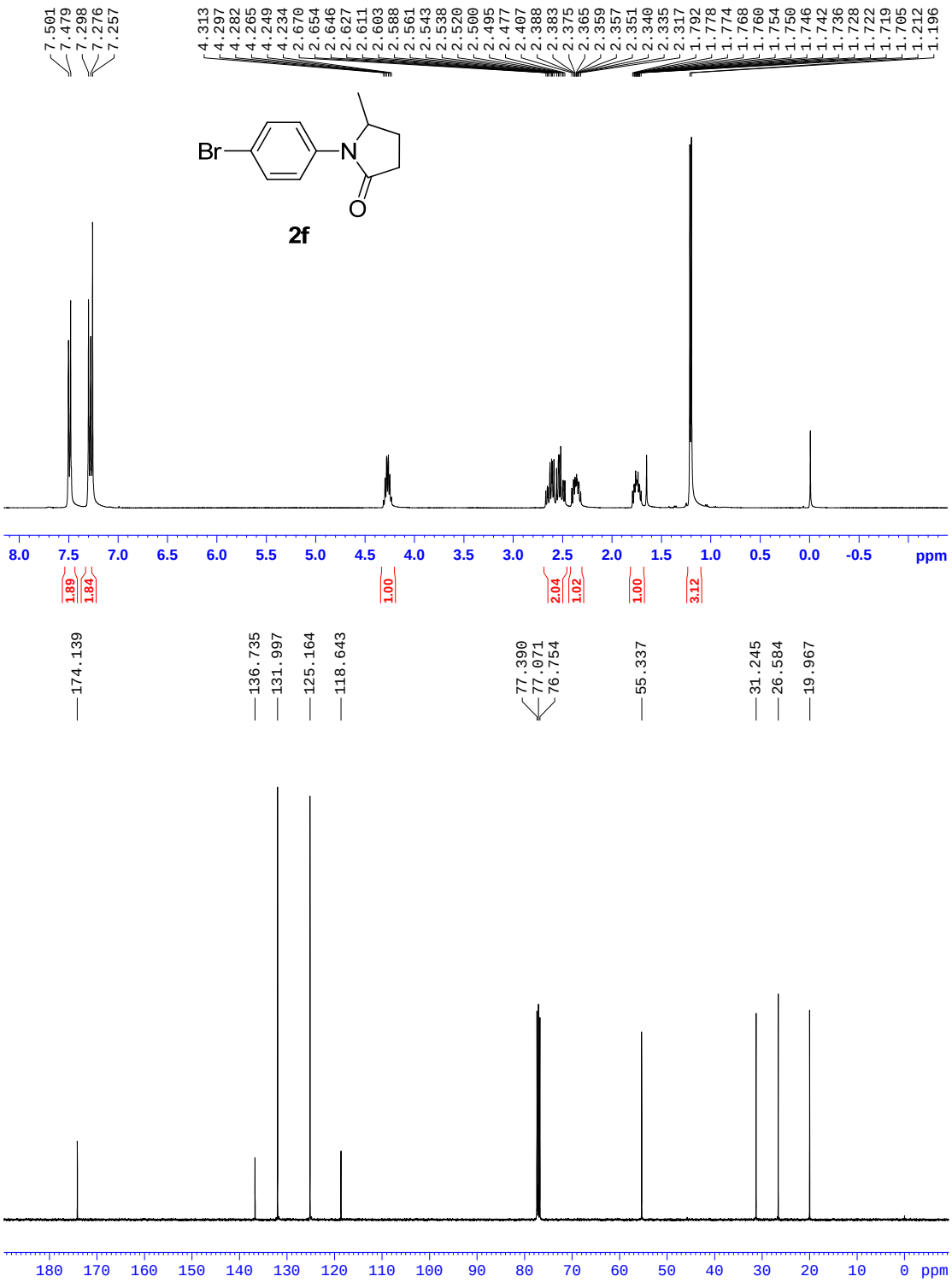


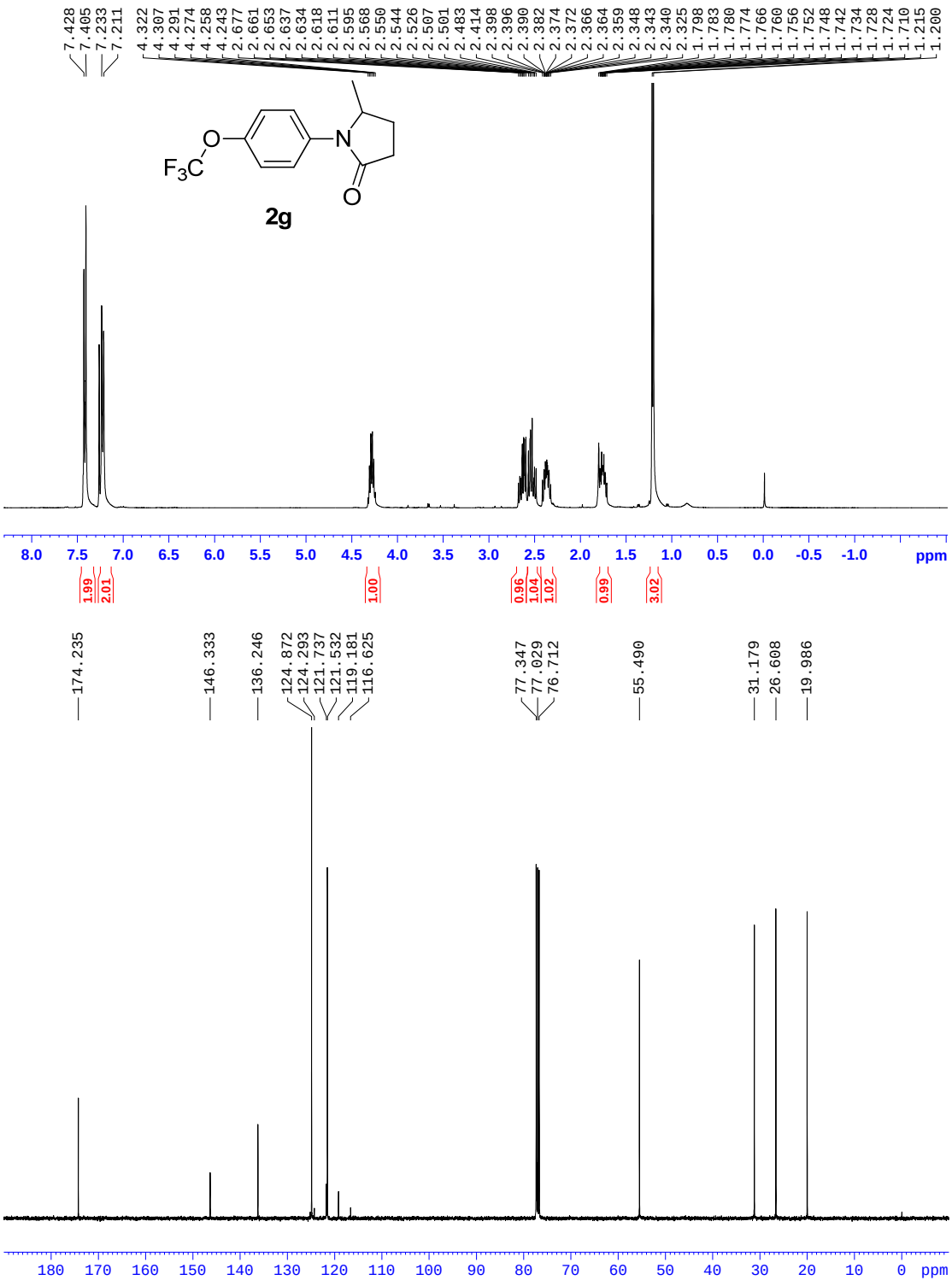

7.259
7.239
7.218
7.196
7.175
4.279
4.264
4.249
4.233
4.231
4.215
4.200
2.662
2.647
2.639
2.623
2.620
2.604
2.596
2.581
2.565
2.546
2.542
2.523
2.504
2.499
2.481
2.404
2.388
2.386
2.381
2.372
2.365
2.362
2.357
2.354
2.336
1.782
1.767
1.764
1.758
1.750
1.744
1.740
1.736
1.732
1.727
1.718
1.712
1.708
1.694
1.598
1.196
1.181
N
O
2b
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 ppm
1.97
1.98
1.00
2.02
4.02
1.01
3.12
174.176
135.622
134.974
129.595
124.239
77.340
77.225
77.022
76.704
55.764
31.257
26.813
20.959
20.199
-0.028
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

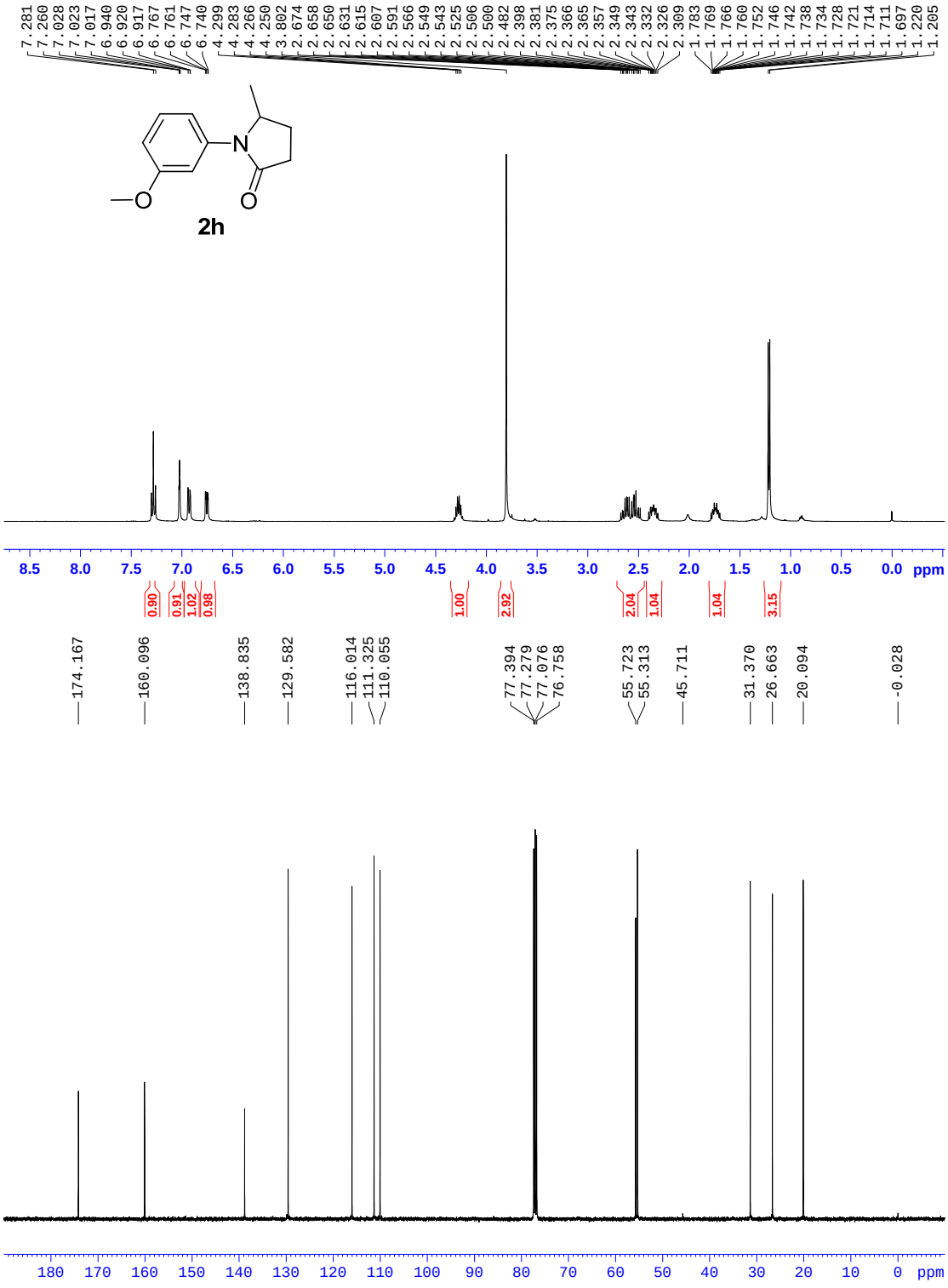

7.373
7.357
7.341
7.247
7.202
7.193
7.187
7.181
7.180
4.323
4.308
4.292
4.275
4.259
4.244
2.668
2.653
2.645
2.626
2.610
2.602
2.587
2.565
2.546
2.541
2.523
2.503
2.498
2.480
2.401
2.383
2.378
2.369
2.360
2.354
2.346
2.336
2.330
2.312
1.782
1.767
1.764
1.758
1.750
1.744
1.740
1.736
1.732
1.726
1.718
1.712
1.709
1.694
1.683
1.199
1.184
N
O
2c
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 ppm
3.85
1.04
1.00
2.05
1.08
1.01
3.16
174.152
137.637
128.962
125.717
124.034
77.341
77.023
76.706
55.608
31.325
26.760
20.157
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

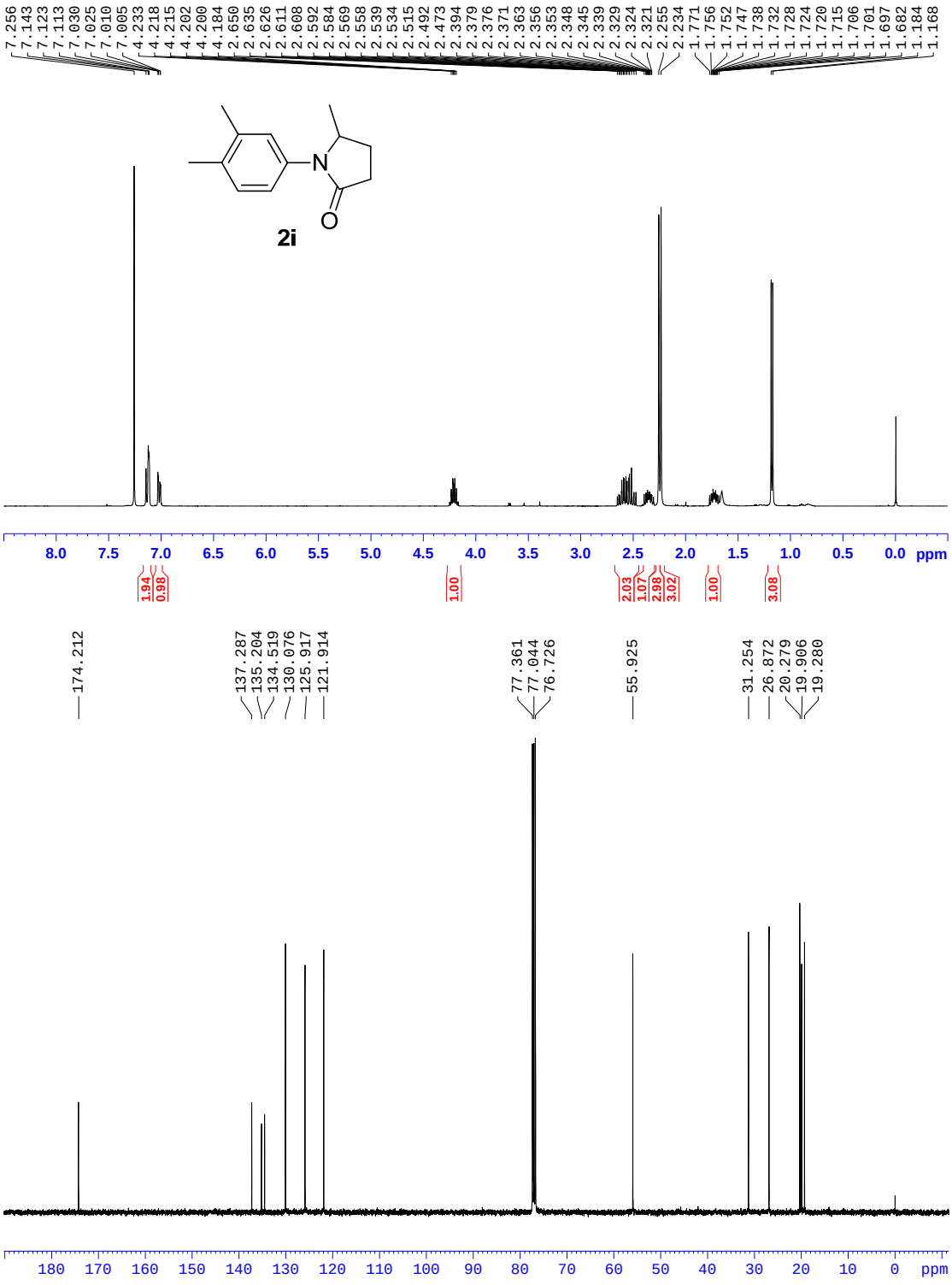

7.332
7.320
7.315
7.310
7.298
7.259
7.099
7.078
7.056
4.271
4.255
4.239
4.222
4.206
4.191
2.668
2.653
2.644
2.625
2.610
2.602
2.587
2.574
2.555
2.551
2.532
2.513
2.508
2.490
2.421
2.405
2.402
2.397
2.389
2.382
2.379
2.374
2.371
2.366
2.356
2.350
2.332
1.797
1.782
1.779
1.773
1.765
1.759
1.755
1.751
1.747
1.742
1.732
1.727
1.723
1.709
1.579
1.198
1.183
F
N
O
2d
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 ppm
1.93
1.91
1.00
2.07
1.02
1.00
3.05
174.236
161.651
159.213
133.590
133.560
126.024
125.943
115.903
115.679
77.363
77.046
76.728
55.845
31.122
26.746
20.111
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

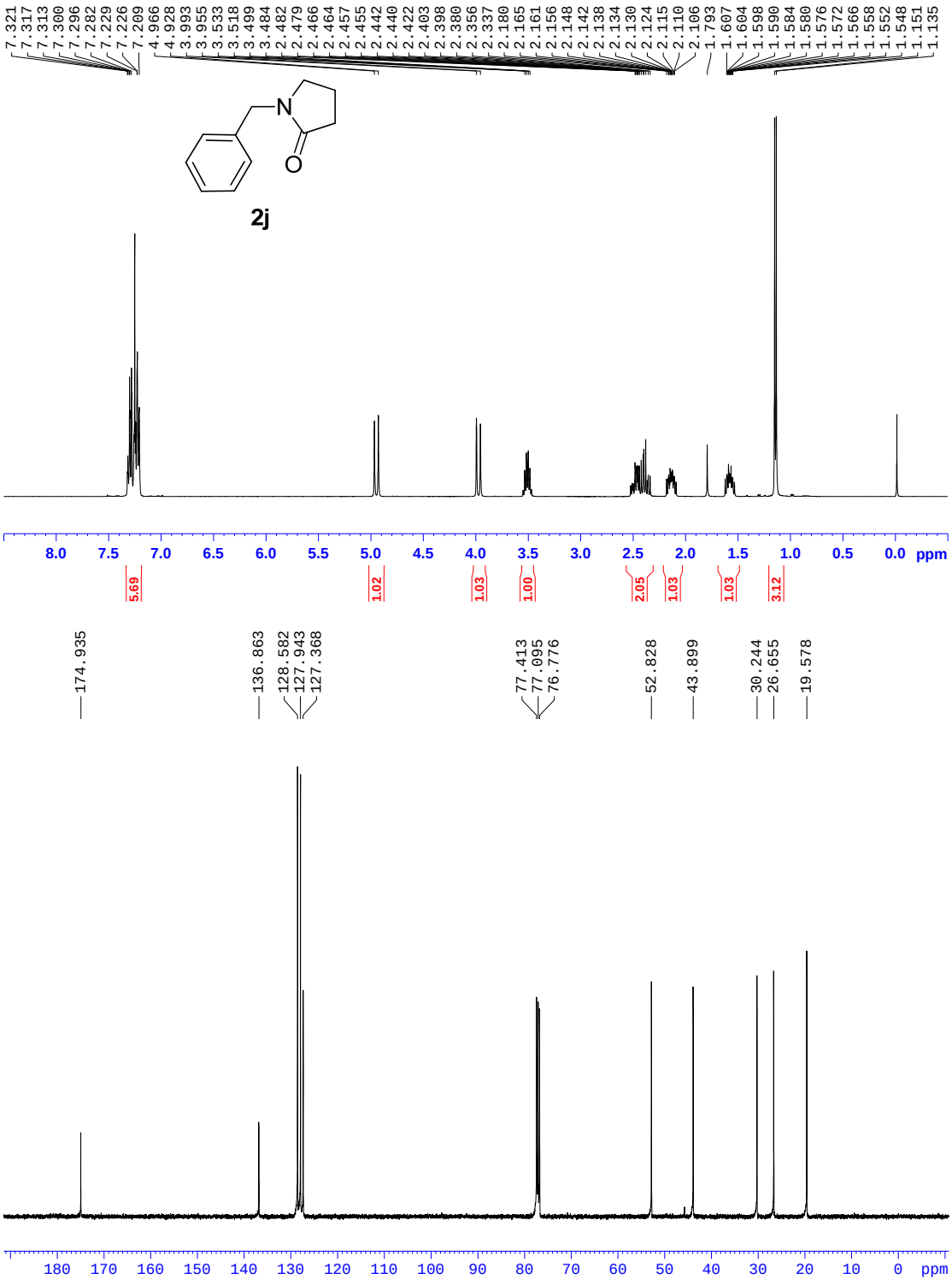

7.332
7.260
4.303
4.287
4.271
4.254
4.239
4.223
2.664
2.649
2.641
2.625
2.622
2.606
2.598
2.582
2.557
2.539
2.515
2.496
2.490
2.472
2.402
2.386
2.384
2.378
2.370
2.368
2.362
2.360
2.354
2.352
2.347
2.336
2.331
2.328
2.312
1.797
1.785
1.771
1.768
1.762
1.754
1.748
1.744
1.740
Cl
N
O
2e
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
3.83
1.00
2.02
1.04
1.02
3.11
174.166
136.211
130.886
129.048
124.916
77.365
77.251
77.047
76.729
55.427
31.221
26.613
26.440
19.988
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

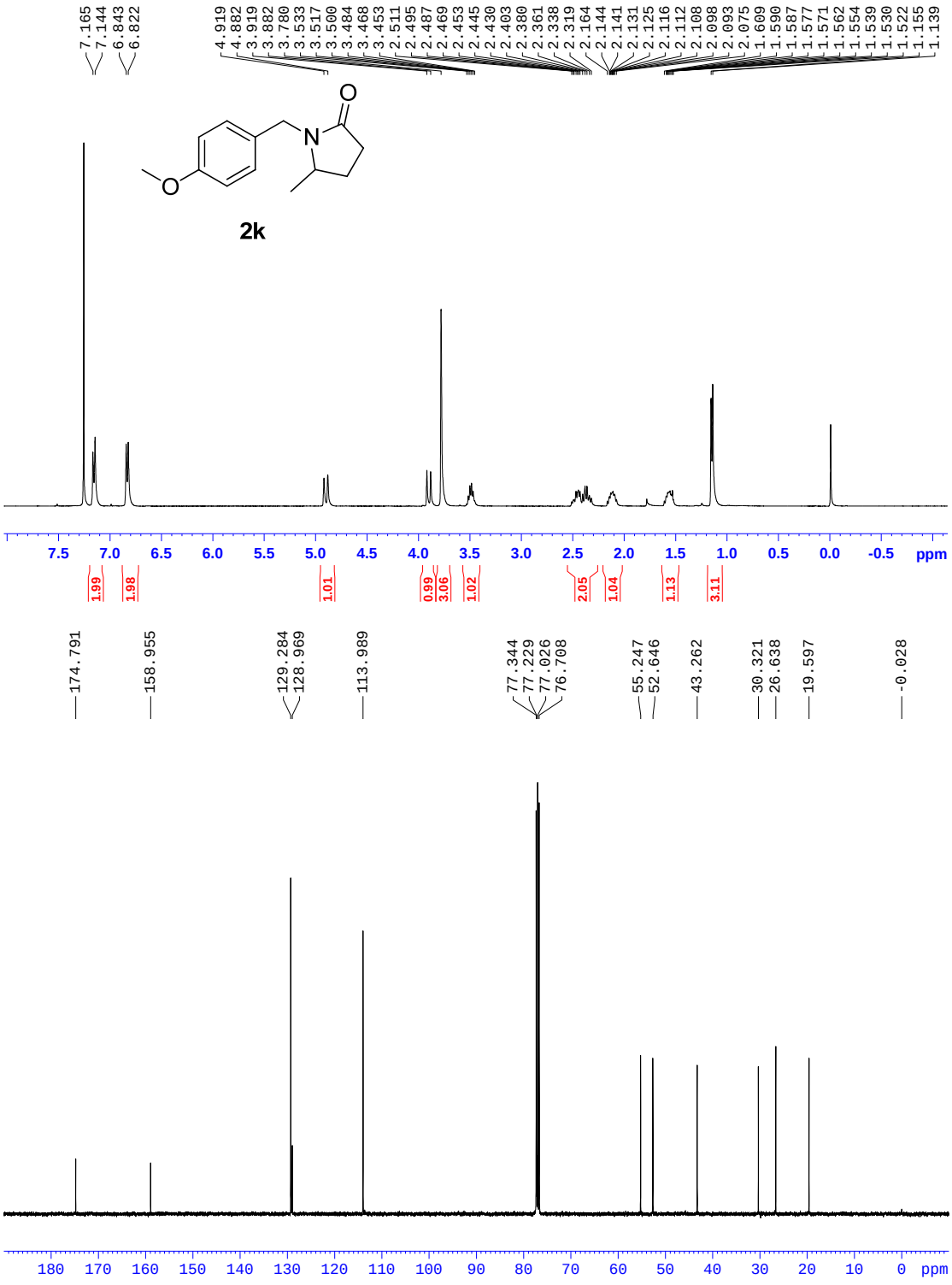

7.501
7.479
7.298
7.276
7.257
4.313
4.297
4.282
4.265
4.249
4.234
2.670
2.654
2.646
2.627
2.611
2.603
2.588
2.561
2.543
2.538
2.520
2.500
2.495
2.477
2.407
2.388
2.383
2.375
2.365
2.359
2.357
2.351
2.340
2.335
2.317
1.792
1.778
1.774
1.768
1.760
1.754
1.750
1.746
1.742
1.736
1.728
1.722
1.719
1.705
1.212
1.196
Br
N
O
2f
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
ppm
1.89
1.84
1.00
2.04
1.02
1.00
3.12
174.139
136.735
131.997
125.164
118.643
77.390
77.071
76.754
55.337
31.245
26.584
19.967
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

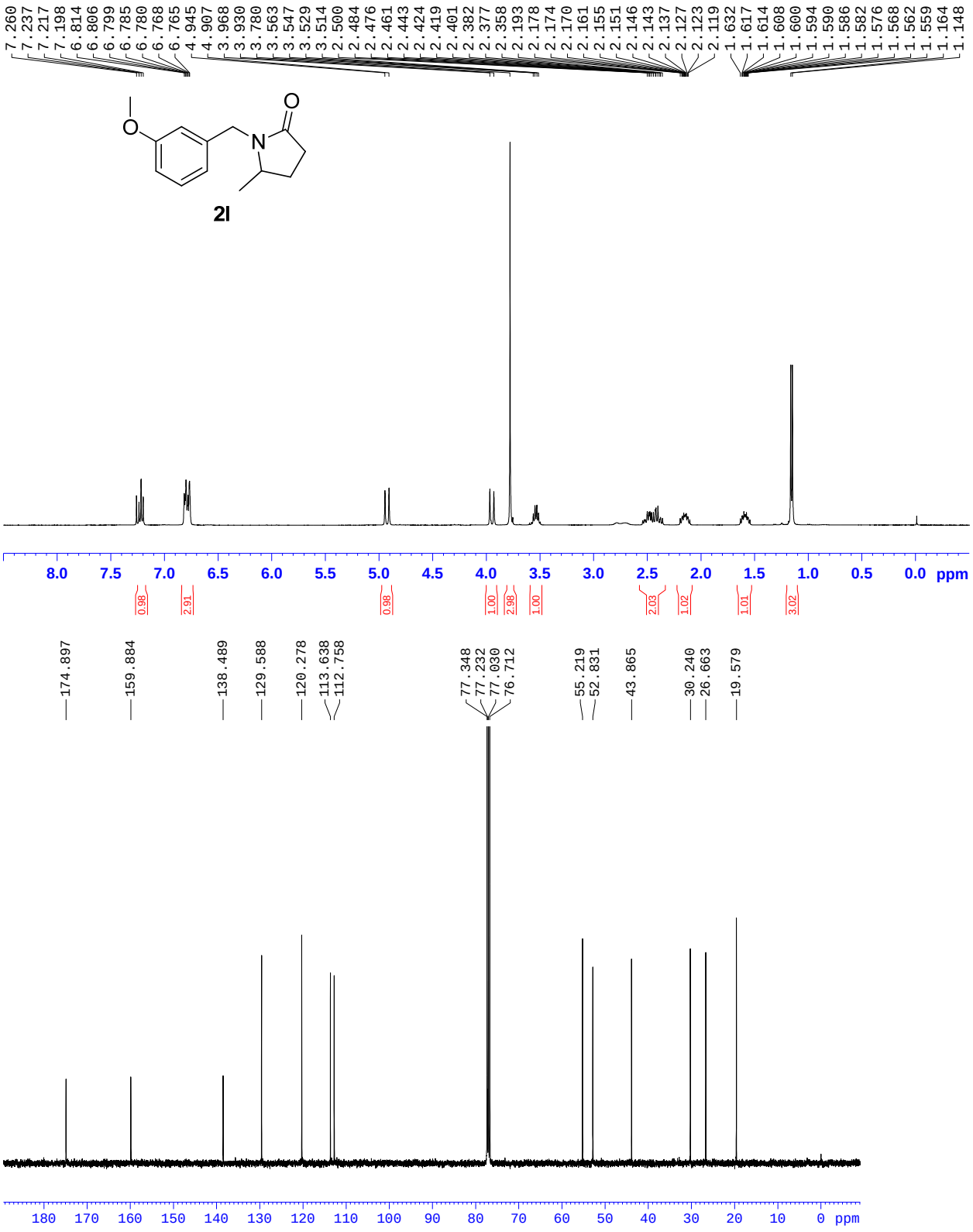

7.428
7.405
7.233
7.211
4.322
4.307
4.291
4.274
4.258
4.243
2.677
2.661
2.653
2.637
2.634
2.618
2.611
2.595
2.568
2.550
2.544
2.526
2.507
2.501
2.483
2.414
2.398
2.396
2.390
2.382
2.374
2.372
2.366
2.364
2.359
2.348
2.343
2.340
2.325
1.798
1.783
1.780
1.774
1.766
1.760
1.756
1.752
1.748
1.742
1.734
1.728
1.724
1.710
1.215
1.200
O
F3C
N
O
2g
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 ppm
1.99
2.01
1.00
0.96
1.04
1.02
0.99
3.02
174.235
146.333
136.246
124.872
124.293
121.737
121.532
119.181
116.625
77.347
77.029
76.712
55.490
31.179
26.608
19.986
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

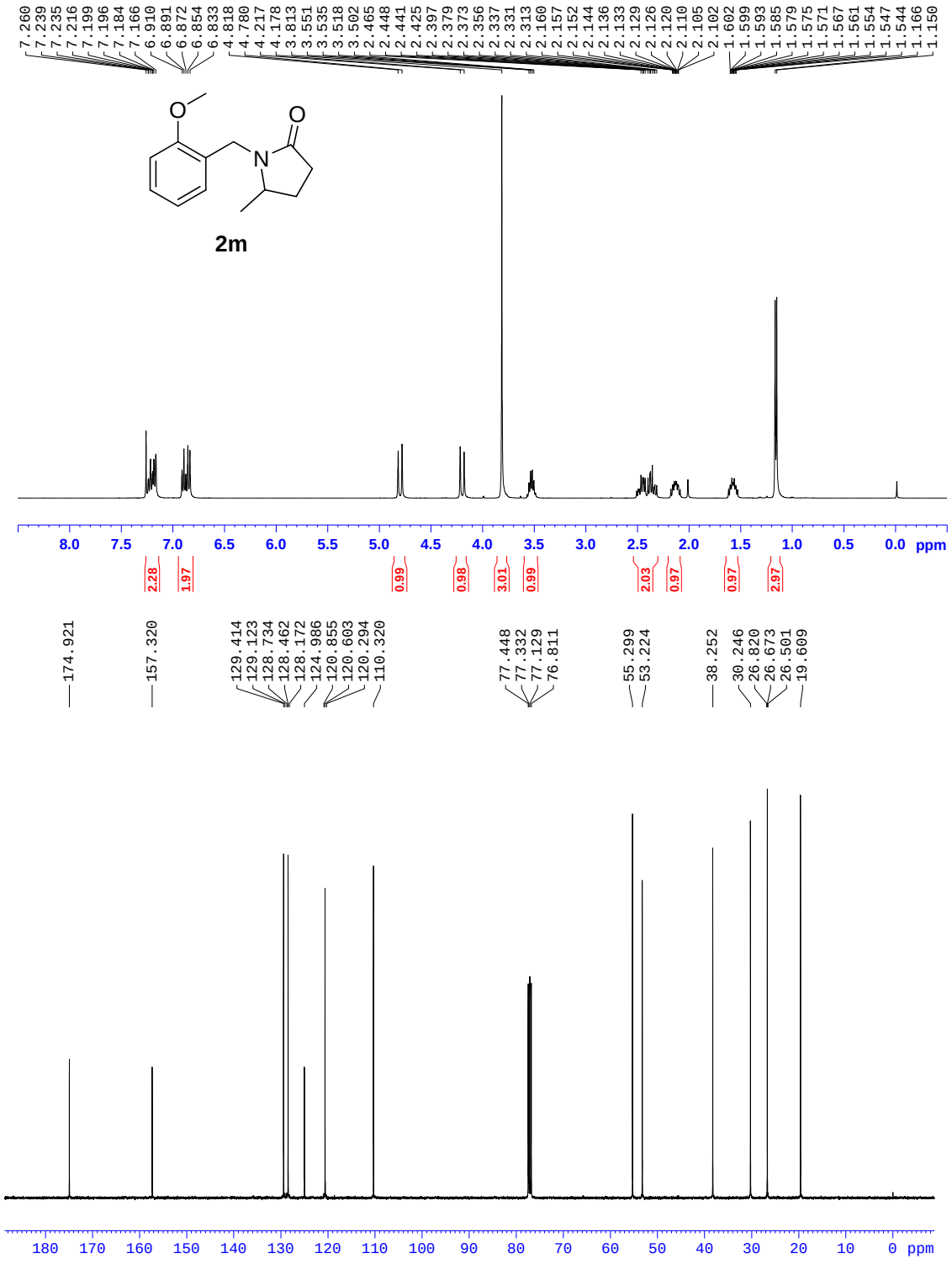

7.281
7.260
7.028
7.023
7.017
6.940
6.920
6.917
6.767
6.761
6.747
6.740
4.299
4.283
4.266
4.250
3.802
2.674
2.658
2.650
2.631
2.615
2.607
2.591
2.566
2.549
2.543
2.525
2.506
2.500
2.482
2.398
2.381
2.375
2.366
2.365
2.357
2.349
2.343
2.332
2.326
2.309
1.783
1.769
1.766
1.760
1.752
1.746
1.742
1.738
1.734
1.728
1.721
1.714
1.711
1.697
1.220
1.205
N
O
O
2h
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 ppm
0.90
0.91
1.02
0.98
1.00
2.92
2.04
1.04
1.04
3.15
174.167
160.096
138.835
129.582
116.014
111.325
110.055
77.394
77.279
77.076
76.758
55.723
55.313
45.711
31.370
26.663
20.094
-0.028
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

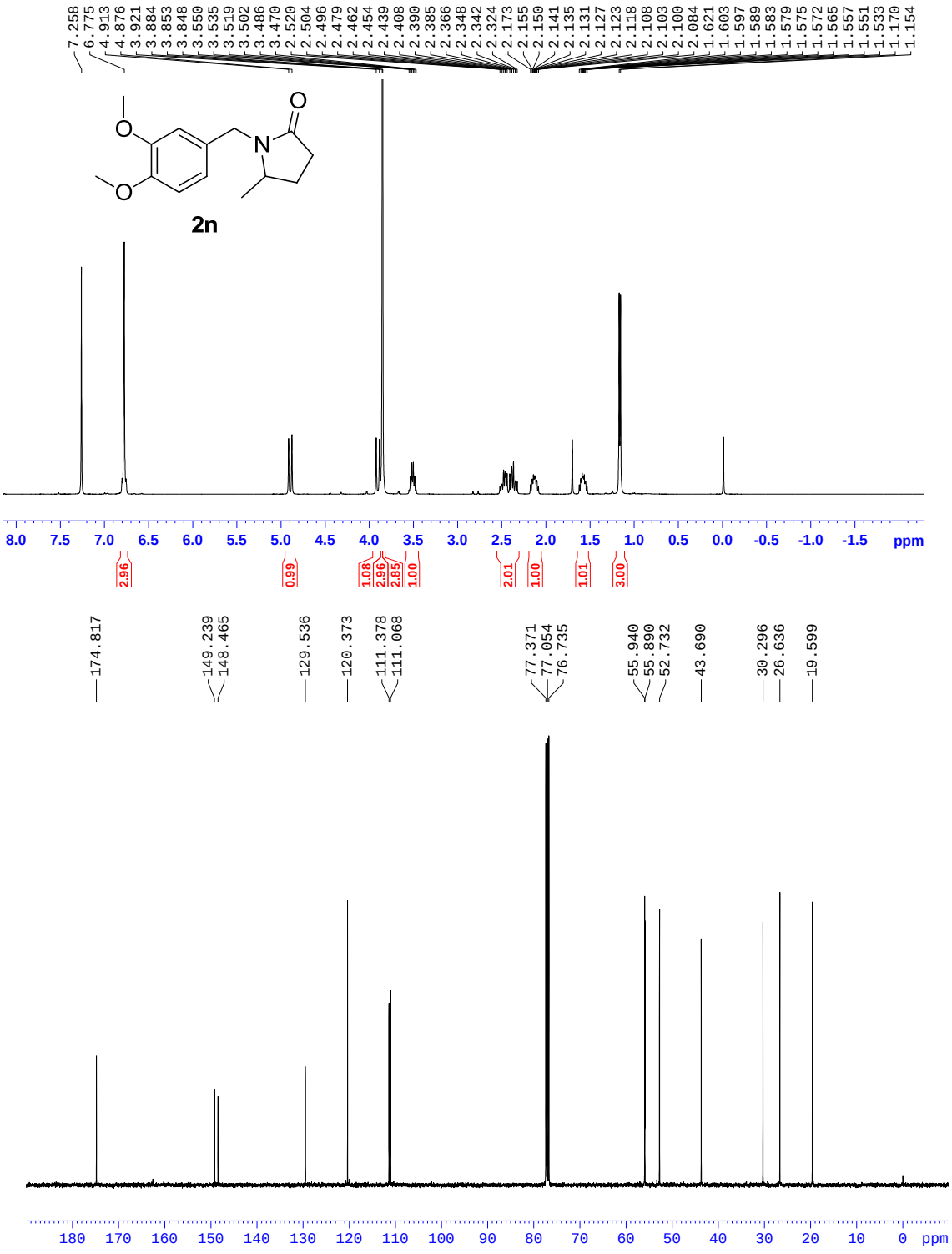

7.256
7.143
7.123
7.113
7.030
7.025
7.010
7.005
4.233
4.218
4.215
4.202
4.200
4.184
2.650
2.635
2.626
2.611
2.608
2.592
2.584
2.569
2.558
2.539
2.534
2.515
2.492
2.473
2.394
2.379
2.376
2.371
2.363
2.356
2.353
2.348
2.345
2.339
2.329
2.324
2.321
2.255
2.234
1.771
1.756
1.752
1.747
1.738
1.732
1.728
1.724
1.720
1.715
1.706
1.701
1.697
1.682
1.184
1.168
N
O
2i
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 ppm
1.94
0.98
1.00
2.03
1.07
2.98
3.02
1.00
3.08
174.212
137.287
135.204
134.519
130.076
125.917
121.914
77.361
77.044
76.726
55.925
31.254
26.872
20.279
19.906
19.280
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

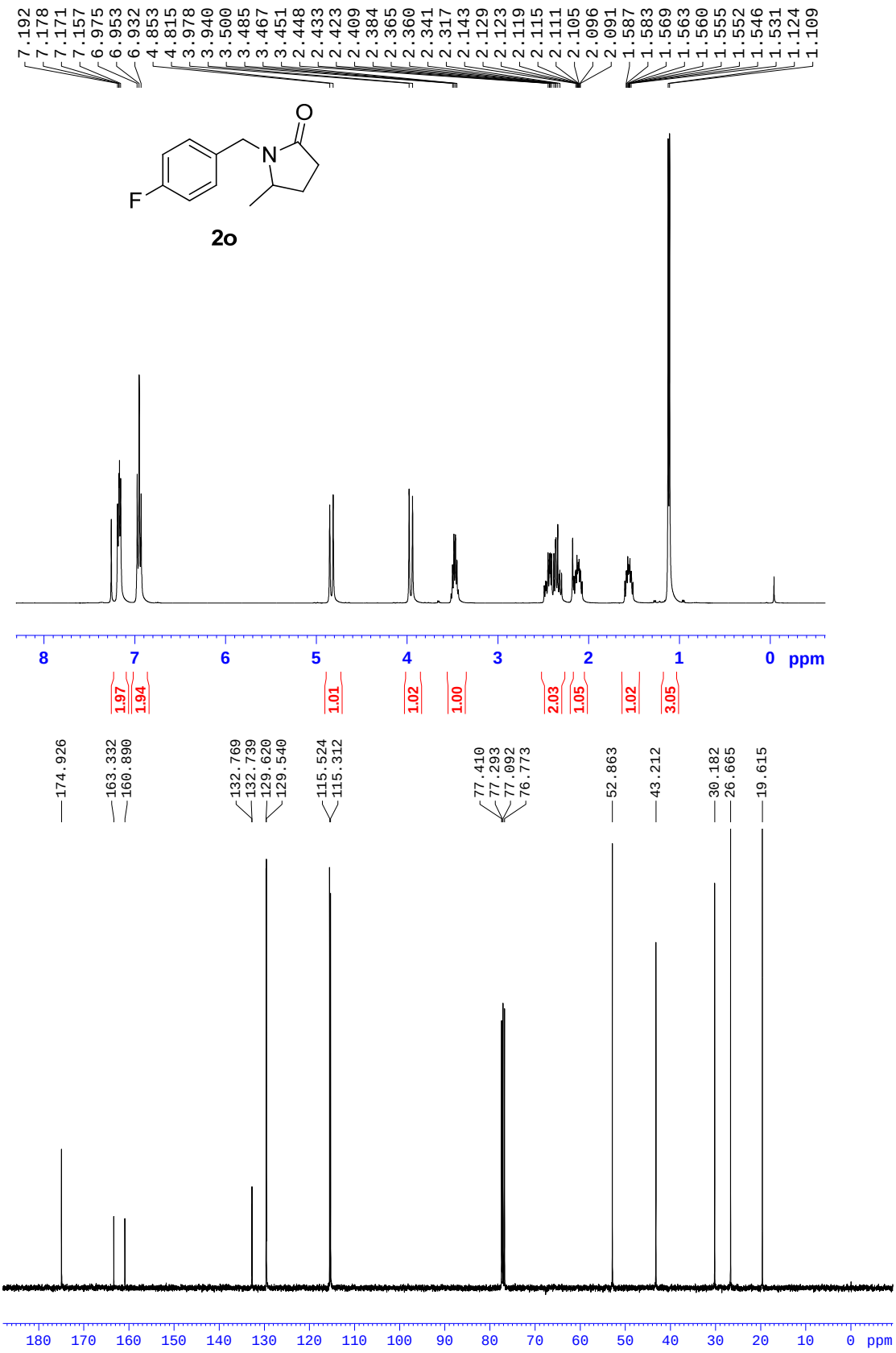

7.321
7.317
7.313
7.300
7.296
7.282
7.229
7.226
7.209
4.966
4.928
3.993
3.955
3.533
3.518
3.499
3.484
2.482
2.479
2.466
2.464
2.457
2.455
2.442
2.440
2.422
2.403
2.398
2.380
2.356
2.337
2.180
2.165
2.161
2.156
2.148
2.142
2.138
2.134
2.130
2.124
2.115
2.110
2.106
1.793
1.607
1.604
1.598
1.590
1.584
1.580
1.576
1.572
1.566
1.558
1.552
1.548
1.151
1.135
N
O
2j
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 ppm
5.69
1.02
1.03
1.00
2.05
1.03
1.03
3.12
174.935
136.863
128.582
127.943
127.368
77.413
77.095
76.776
52.828
43.899
30.244
26.655
19.578
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

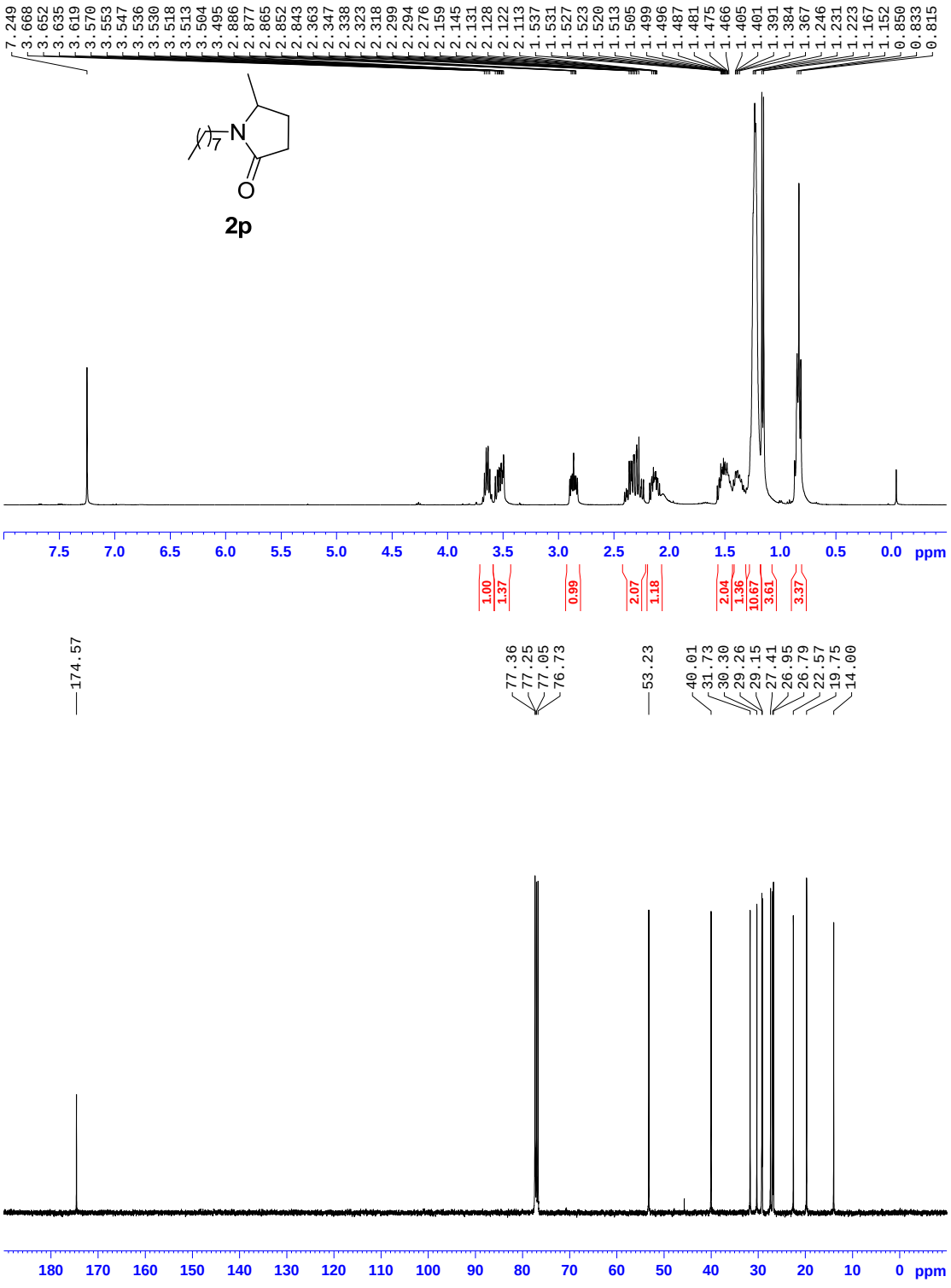

7.165
7.144
6.843
6.822
4.919
4.882
3.919
3.882
3.780
3.533
3.517
3.500
3.484
3.468
3.453
2.511
2.495
2.487
2.469
2.453
2.445
2.430
2.403
2.380
2.361
2.338
2.319
2.164
2.144
2.141
2.131
2.125
2.116
2.112
2.108
2.098
2.093
2.075
1.609
1.590
1.587
1.577
1.571
1.562
1.554
1.539
1.530
1.522
1.155
1.139
O
N
O
2k
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 ppm
1.99
1.98
1.01
0.99
3.06
1.02
2.05
1.04
1.13
3.11
174.791
158.955
129.284
128.969
113.989
77.344
77.229
77.026
76.708
55.247
52.646
43.262
30.321
26.638
19.597
-0.028
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

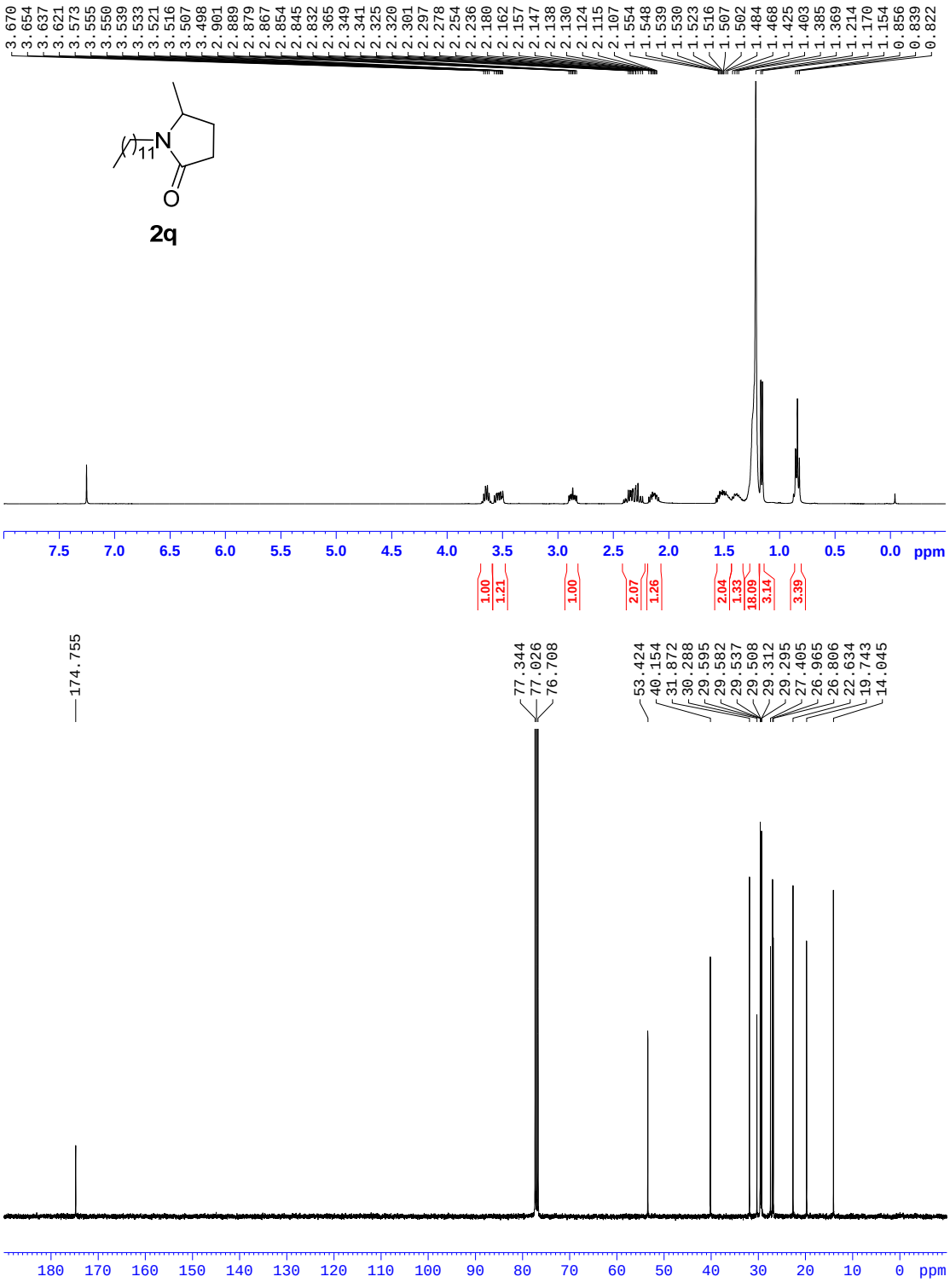

7.260
7.237
7.217
7.198
6.814
6.806
6.799
6.785
6.780
6.768
6.765
4.945
4.907
3.968
3.930
3.780
3.563
3.547
3.529
3.514
2.500
2.484
2.476
2.461
2.443
2.424
2.419
2.401
2.382
2.377
2.358
2.193
2.178
2.174
2.170
2.161
2.155
2.151
2.146
2.143
2.137
2.127
2.123
2.119
1.632
1.617
1.614
1.608
1.600
1.594
1.590
1.586
1.582
1.576
1.568
1.562
1.559
1.164
1.148
O
O
N
2l
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 ppm
0.98
2.91
0.98
1.00
2.98
1.00
2.03
1.02
1.01
3.02
174.897
159.884
138.489
129.588
120.278
113.638
112.758
77.348
77.232
77.030
76.712
55.219
52.831
43.865
30.240
26.663
19.579
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

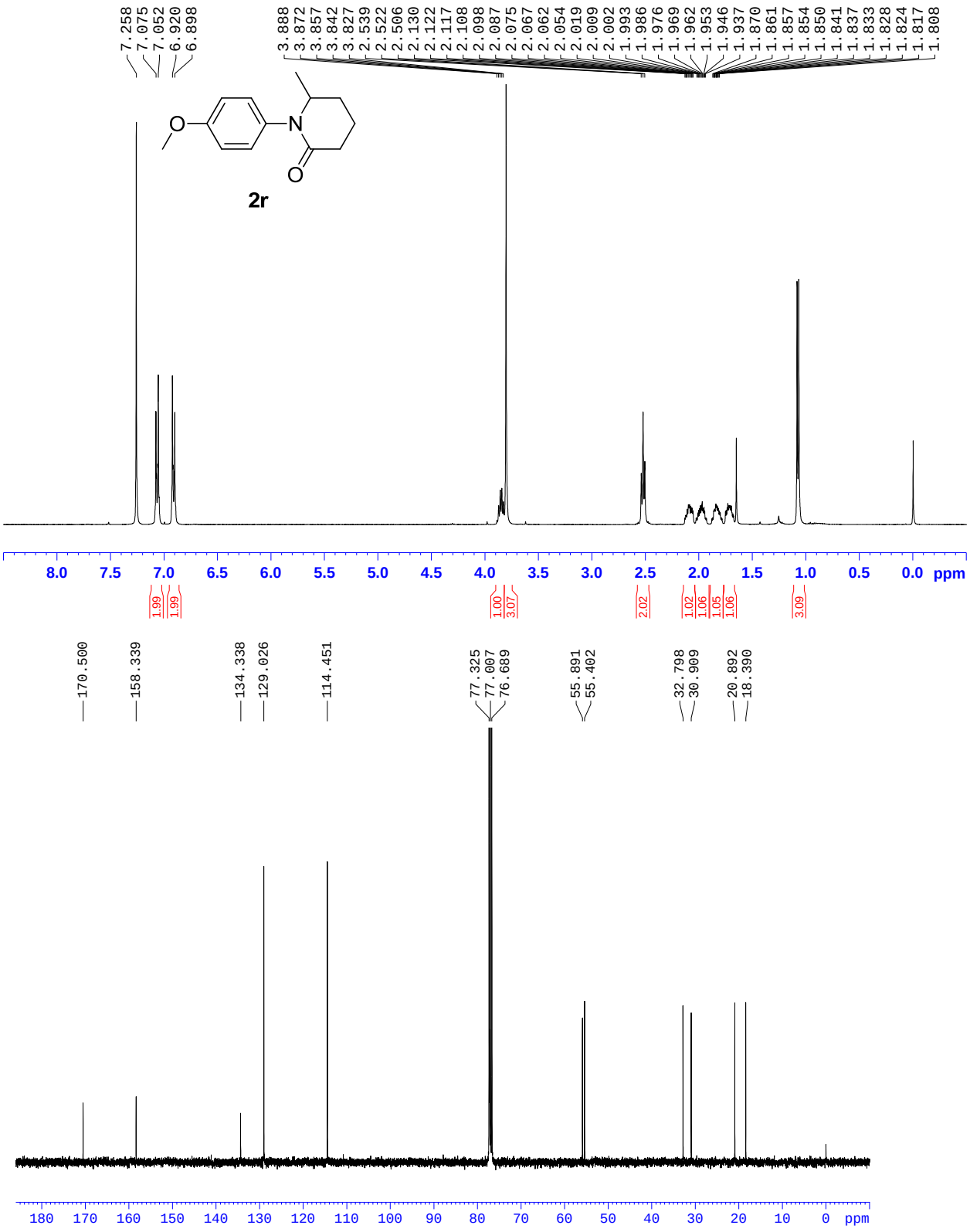

7.260
7.239
7.235
7.216
7.199
7.196
7.184
7.166
6.910
6.891
6.872
6.854
6.833
4.818
4.780
4.217
4.178
3.813
3.551
3.535
3.518
3.502
2.465
2.448
2.441
2.425
2.397
2.379
2.373
2.356
2.337
2.331
2.313
2.160
2.157
2.152
2.144
2.136
2.133
2.129
2.126
2.120
2.110
2.105
2.102
1.602
1.599
1.593
1.585
1.579
1.575
1.571
1.567
1.561
1.554
1.547
1.544
1.166
1.150
O
O
N
2m
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 ppm
2.28
1.97
0.99
0.98
3.01
0.99
2.03
0.97
0.97
2.97
174.921
157.320
129.414
129.123
128.734
128.462
128.172
124.986
120.855
120.603
120.294
110.320
77.448
77.332
77.129
76.811
55.299
53.224
38.252
30.246
26.820
26.673
26.501
19.609
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

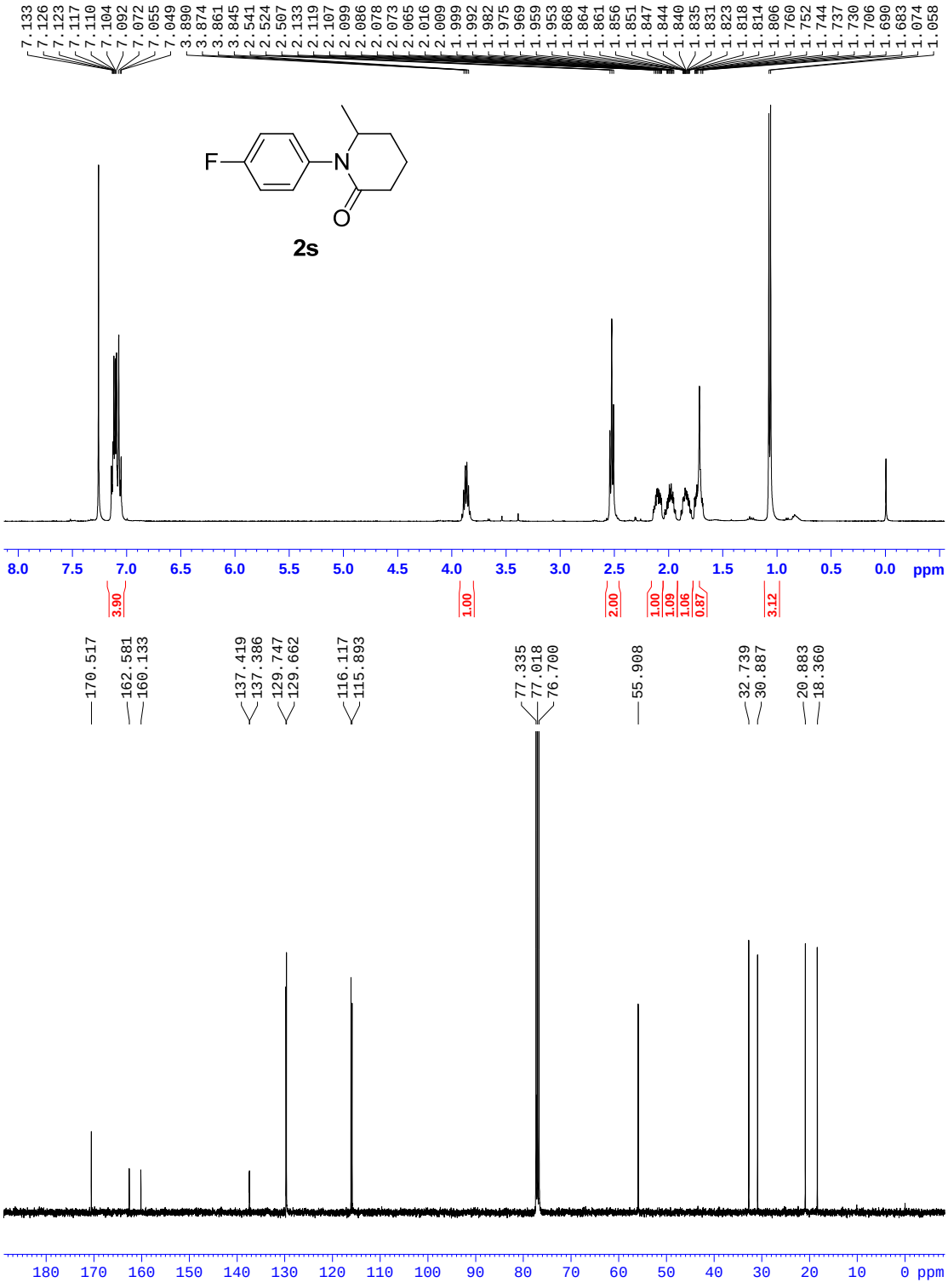

7.258
6.775
4.913
4.876
3.921
3.884
3.853
3.848
3.550
3.535
3.519
3.502
3.486
3.470
2.520
2.504
2.496
2.479
2.462
2.454
2.439
2.408
2.390
2.385
2.366
2.348
2.342
2.324
2.173
2.155
2.150
2.141
2.135
2.131
2.127
2.123
2.118
2.108
2.103
2.100
2.084
1.621
1.603
1.597
1.589
1.583
1.579
1.575
1.572
1.565
1.557
1.551
1.533
1.170
1.154
O
O
N
O
2n
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 -1.5 ppm
2.96
0.99
1.08
2.96
2.85
1.00
2.01
1.00
1.01
3.00
174.817
149.239
148.465
129.536
120.373
111.378
111.068
77.371
77.054
76.735
55.940
55.890
52.732
43.690
30.296
26.636
19.599
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

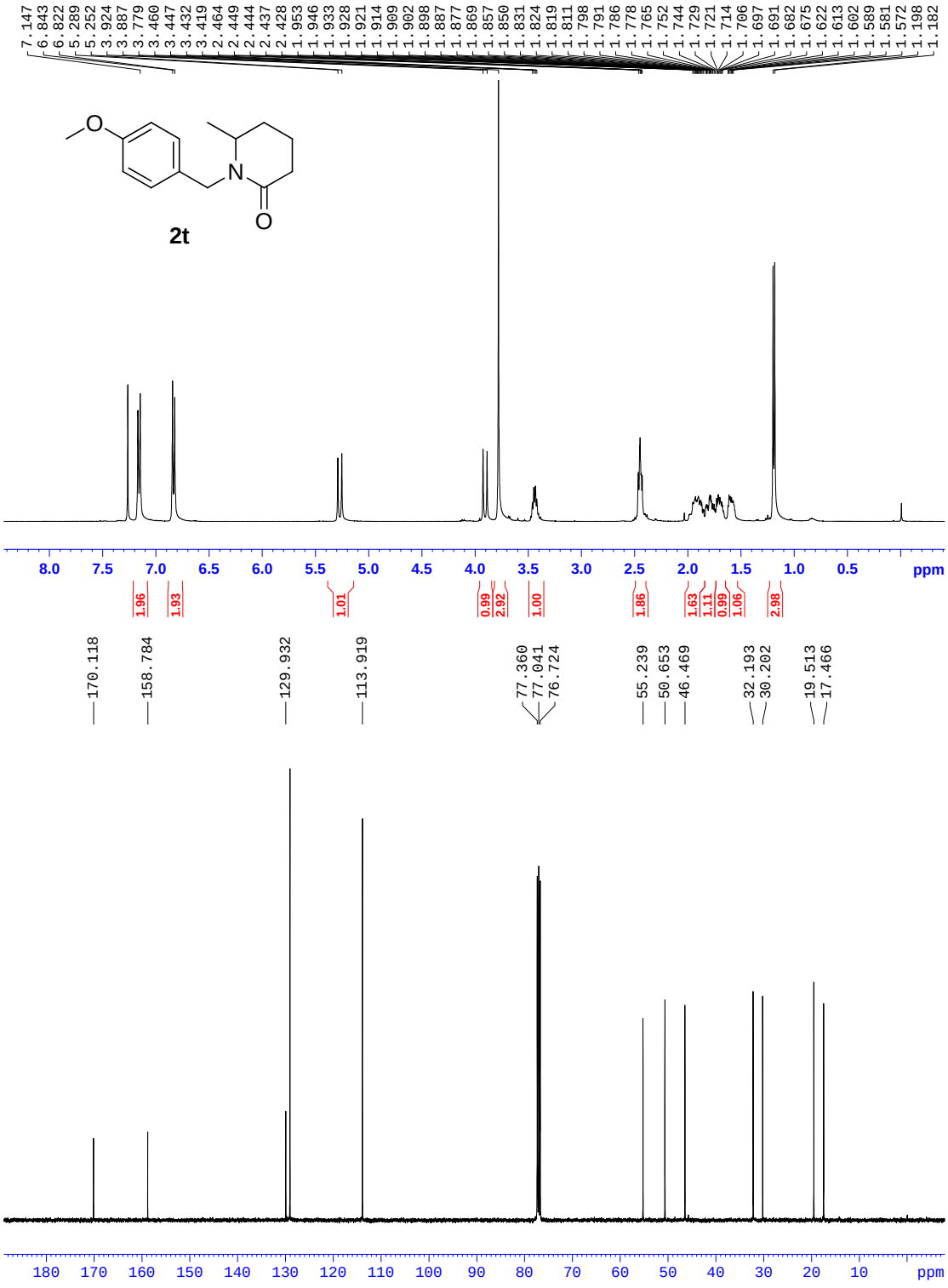

7.192
7.178
7.171
7.157
6.975
6.953
6.932
4.853
4.815
3.978
3.940
3.500
3.485
3.467
3.451
2.448
2.433
2.423
2.409
2.384
2.365
2.360
2.341
2.317
2.143
2.129
2.123
2.119
2.115
2.111
2.105
2.096
2.091
1.587
1.583
1.569
1.563
1.560
1.555
1.552
1.546
1.531
1.124
1.109
O
N
F
2o
8
7
6
5
4
3
2
1
0 ppm
1.97
1.94
1.01
1.02
1.00
2.03
1.05
1.02
3.05
174.926
163.332
160.890
132.769
132.739
129.620
129.540
115.524
115.312
77.410
77.293
77.092
76.773
52.863
43.212
30.182
26.665
19.615
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

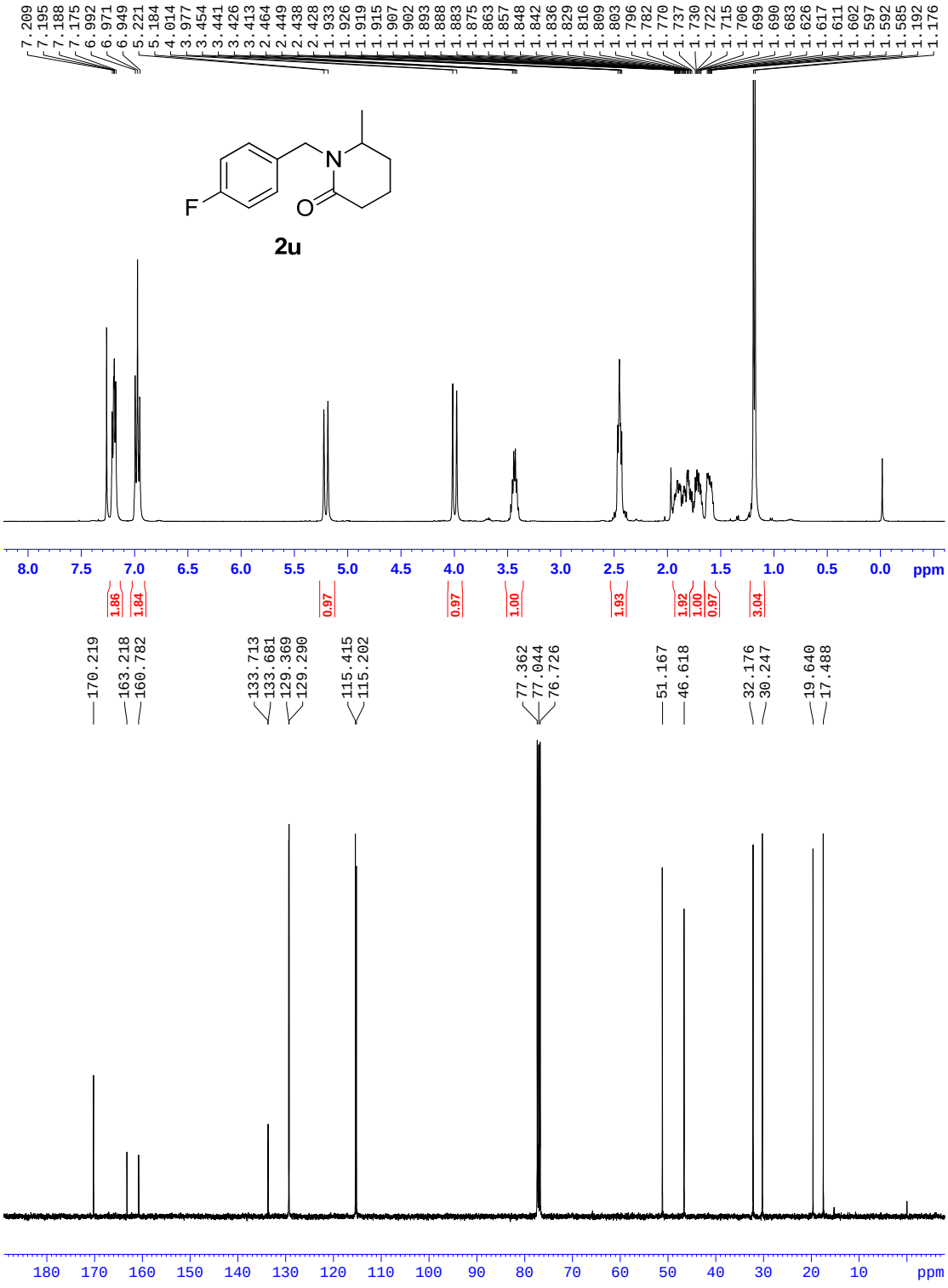

7.249
3.668
3.652
3.635
3.619
3.570
3.553
3.547
3.536
3.530
3.518
3.513
3.504
3.495
2.886
2.877
2.865
2.852
2.843
2.363
2.347
2.338
2.323
2.318
2.299
2.294
2.276
2.159
2.145
2.131
2.128
2.122
2.113
1.537
1.531
1.527
1.523
1.520
1.513
1.505
1.499
1.496
1.487
1.481
1.475
1.466
1.405
1.401
1.391
1.384
1.367
1.246
1.231
1.223
1.167
1.152
0.850
0.833
0.815
N
7
O
2p
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 ppm
1.00
1.37
0.99
2.07
1.18
2.04
1.36
10.67
3.61
3.37
174.57
77.36
77.25
77.05
76.73
53.23
40.01
31.73
30.30
29.26
29.15
27.41
26.95
26.79
22.57
19.75
14.00
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

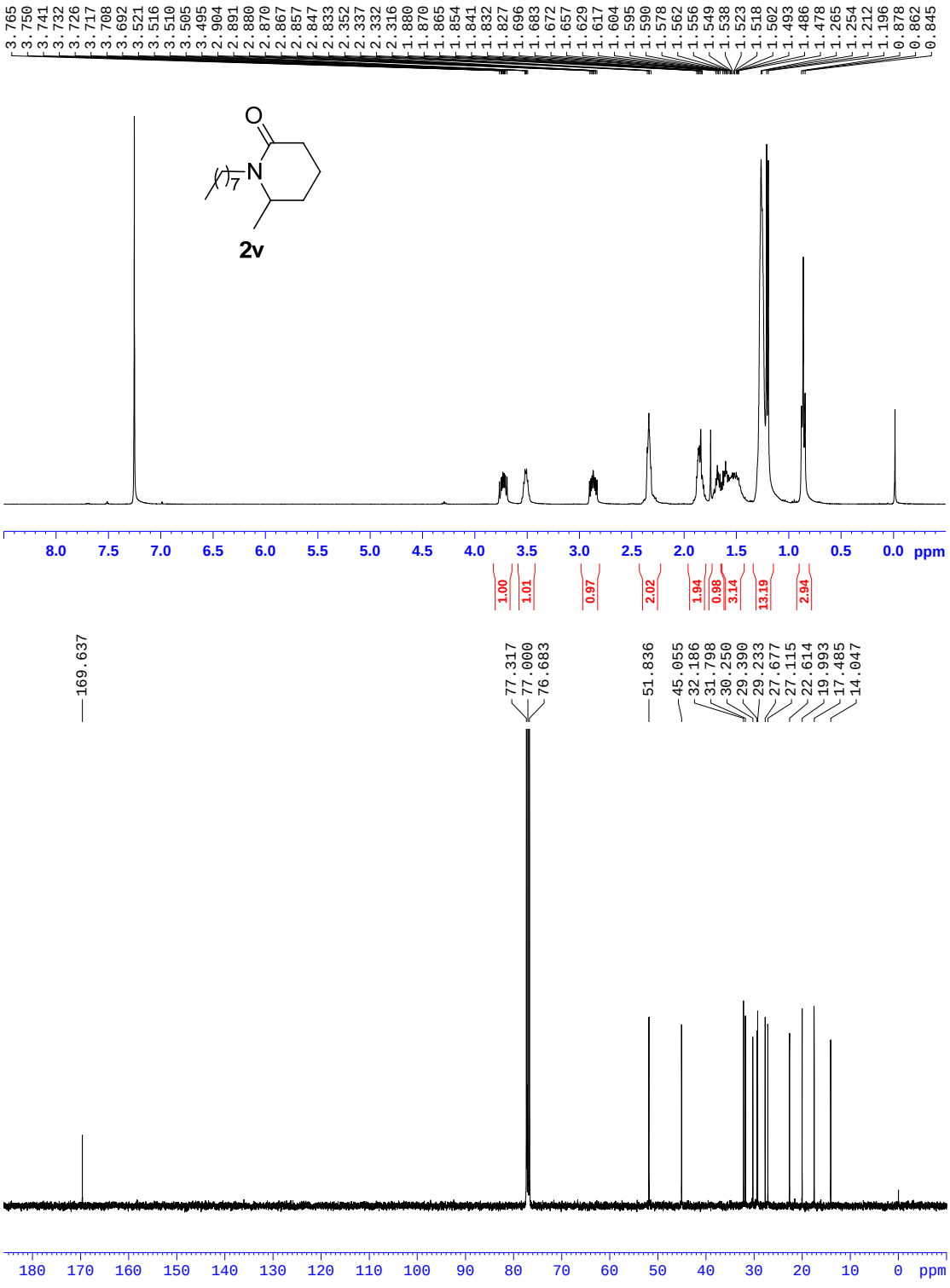

3.670
3.654
3.637
3.621
3.573
3.555
3.550
3.539
3.533
3.521
3.516
3.507
3.498
2.901
2.889
2.879
2.867
2.854
2.845
2.832
2.365
2.349
2.341
2.325
2.320
2.301
2.297
2.278
2.254
2.236
2.180
2.162
2.157
2.147
2.138
2.130
2.124
2.115
2.107
1.554
1.548
1.539
1.530
1.523
1.516
1.507
1.502
1.484
1.468
1.425
1.403
1.385
1.369
1.214
1.170
1.154
0.856
0.839
0.822
N
11
O
2q
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 ppm
1.00
1.21
1.00
2.07
1.26
2.04
1.33
18.09
3.14
3.39
174.755
77.344
77.026
76.708
53.424
40.154
31.872
30.288
29.595
29.582
29.537
29.508
29.312
29.295
27.405
26.965
26.806
22.634
19.743
14.045
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

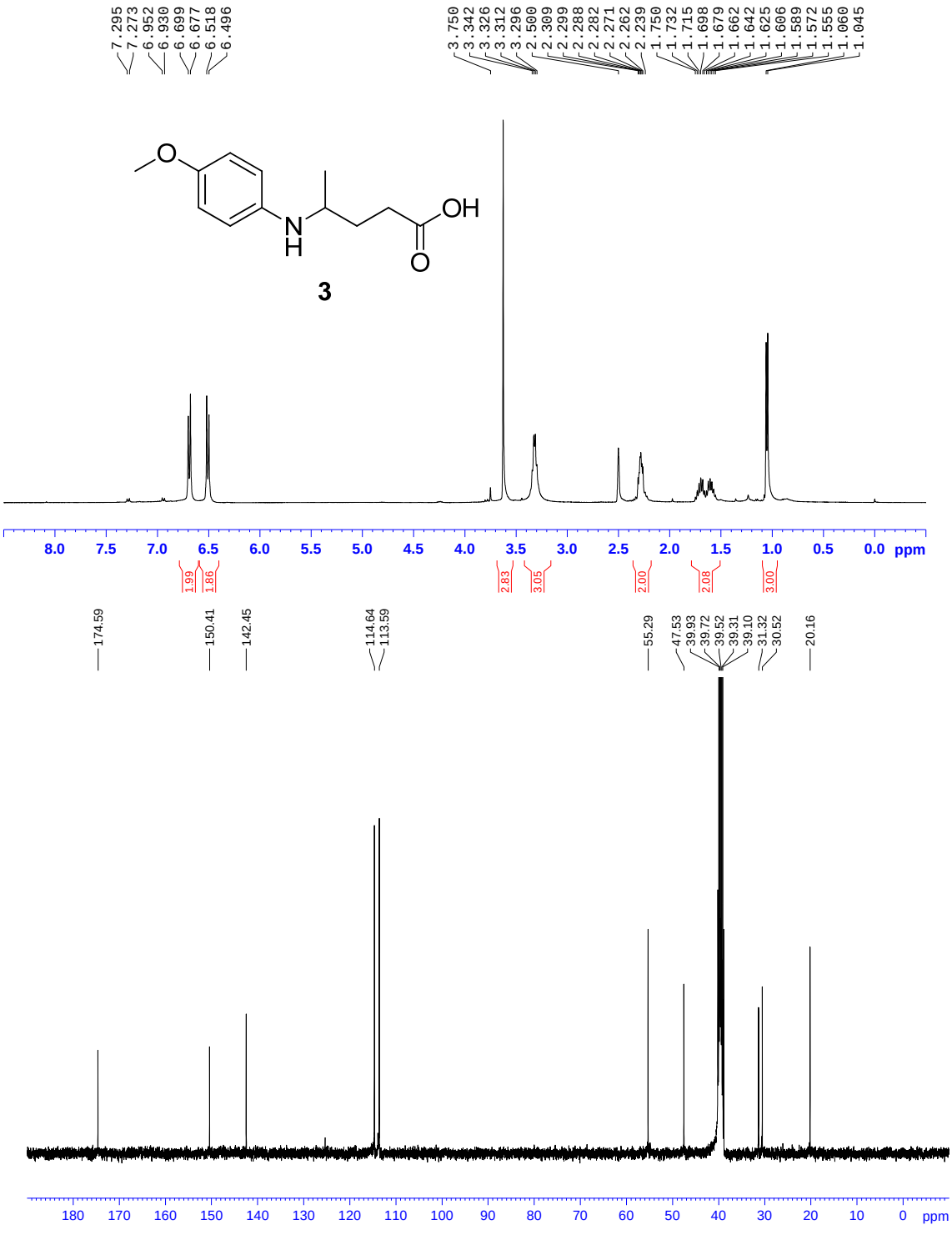

7.258
7.075
7.052
6.920
6.898
3.888
3.872
3.857
3.842
3.827
2.539
2.522
2.506
2.130
2.122
2.117
2.108
2.098
2.087
2.075
2.067
2.062
2.054
2.019
2.009
2.002
1.993
1.986
1.976
1.969
1.962
1.953
1.946
1.937
1.870
1.861
1.857
1.854
1.850
1.841
1.837
1.833
1.828
1.824
1.817
1.808
O
N
O
2r
8.0 7.5 7.0 6.5 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 ppm
1.99
1.99
1.00
3.07
2.02
1.02
1.06
1.05
1.06
3.09
170.500
158.339
134.338
129.026
114.451
77.325
77.007
76.689
55.891
55.402
32.798
30.909
20.892
18.390
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.133
7.126
7.123
7.117
7.110
7.104
7.092
7.072
7.055
7.049
3.890
3.874
3.861
3.845
2.541
2.524
2.507
2.133
2.119
2.107
2.099
2.086
2.078
2.073
2.065
2.016
2.009
1.999
1.992
1.982
1.975
1.969
1.959
1.953
1.868
1.864
1.861
1.856
1.851
1.847
1.844
1.840
1.835
1.831
1.823
1.818
1.814
1.806
1.760
1.752
1.744
1.737
1.730
1.706
1.690
1.683
1.074
1.058
F
N
O
2s
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
ppm
3.90
1.00
2.00
1.00
1.09
1.06
0.87
3.12
170.517
162.581
160.133
137.419
137.386
129.747
129.662
116.117
115.893
77.335
77.018
76.700
55.908
32.739
30.887
20.883
18.360
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.147
6.843
6.822
5.289
5.252
3.924
3.887
3.779
3.460
3.447
3.432
3.419
2.464
2.449
2.444
2.437
2.428
1.953
1.946
1.933
1.928
1.921
1.914
1.909
1.902
1.898
1.887
1.877
1.869
1.857
1.850
1.831
1.824
1.819
1.811
1.798
1.791
1.786
1.778
1.765
1.752
1.744
1.729
1.721
1.714
1.706
1.697
1.691
1.682
1.675
1.622
1.613
1.602
1.589
1.581
1.572
1.198
1.182
O
N
O
2t
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
1.96
1.93
1.01
0.99
2.92
1.00
1.86
1.63
1.11
0.99
1.06
2.98
170.118
158.784
129.932
113.919
77.360
77.041
76.724
55.239
50.653
46.469
32.193
30.202
19.513
17.466
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.209
7.195
7.188
7.175
6.992
6.971
6.949
5.221
5.184
4.014
3.977
3.454
3.441
3.426
3.413
2.464
2.449
2.438
2.428
1.933
1.926
1.919
1.915
1.907
1.902
1.893
1.888
1.883
1.875
1.863
1.857
1.848
1.842
1.836
1.829
1.816
1.809
1.803
1.796
1.782
1.770
1.737
1.730
1.722
1.715
1.706
1.699
1.690
1.683
1.626
1.617
1.611
1.602
1.597
1.592
1.585
1.192
1.176
F
N
O
2u
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 ppm
1.86
1.84
0.97
0.97
1.00
1.93
1.92
1.00
0.97
3.04
170.219
163.218
160.782
133.713
133.681
129.369
129.290
115.415
115.202
77.362
77.044
76.726
51.167
46.618
32.176
30.247
19.640
17.488
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


3.765
3.750
3.741
3.732
3.726
3.717
3.708
3.692
3.521
3.516
3.510
3.505
3.495
2.904
2.891
2.880
2.870
2.867
2.857
2.847
2.833
2.352
2.337
2.332
2.316
1.880
1.870
1.865
1.854
1.841
1.832
1.827
1.696
1.683
1.672
1.657
1.629
1.617
1.604
1.595
1.590
1.578
1.562
1.556
1.549
1.538
1.523
1.518
1.502
1.493
1.486
1.478
1.265
1.254
1.212
1.196
0.878
0.862
0.845
O
N
7
2v
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 ppm
1.00
1.01
0.97
2.02
1.94
0.98
3.14
13.19
2.94
169.637
77.317
77.000
76.683
51.836
45.055
32.186
31.798
30.250
29.390
29.233
27.677
27.115
22.614
19.993
17.485
14.047
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.295
7.273
6.952
6.930
6.699
6.677
6.518
6.496
3.750
3.342
3.326
3.312
3.296
2.500
2.309
2.299
2.288
2.282
2.271
2.262
2.239
1.750
1.732
1.715
1.698
1.679
1.662
1.642
1.625
1.606
1.589
1.572
1.555
1.060
1.045
O
N
H
OH
O
3
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 ppm
1.99
1.86
2.83
3.05
2.00
2.08
3.00
174.59
150.41
142.45
114.64
113.59
55.29
47.53
39.93
39.72
39.52
39.31
39.10
31.32
30.52
20.16
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm