Electronic Supplementary Material (ESI) for Green Chemistry

Catalyst-free transformation of levulinic acid into pyrrolidinones with formic acid

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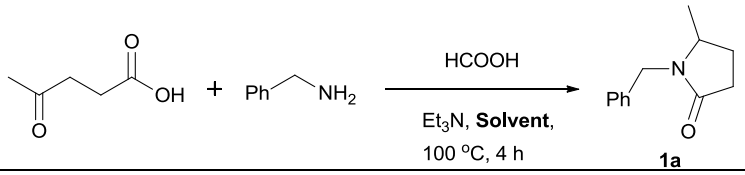
Contents

1. General information

Unless otherwise specified, the chemicals were obtained commercially and used without further purification. NMR spectra were recorded on a Bruker 400 Hz NMR spectrometer with TMS as the internal standard. HRMS data were recorded on a Bruker Apex IV FTMS spectrometer using ESI method and Bruker Maxis with EI method.

2. Effect of different solvents

Table S1 Effect of different solvents on RA of LA with benzylamine[a]



1a

Entry	Solvent	Conversion (%)[b]
1	DMSO	89
2	MeOH	NR
3	H_2O	NR
4	EtOH	NR
5	*i*-PrOH	NR
6	*n*-BuOH	NR
7	DCM	NR
8	DMF	<5
9	THF	9
10	Toluene	NR
11	1,4-dioxane	NR
12	acetone	NR
13	CH_3CN	12
14	Sulfolane	24
15	Tetramethylene sulfoxide	63

[a] Reaction conditions: LA (1 mmol), amine (2 mmol), HCOOH (5 mmol), Et_3N (1 mmol), Solvent (3 mL), 100 °C. [b] Determined by ^1H NMR with 1,3,5-trimethoxylbenzene as internal standard.

3. Effect of formic acid/triethylamine ratio on RA of LA in DMSO

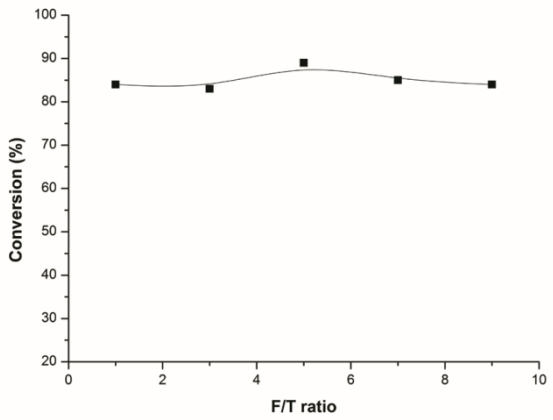
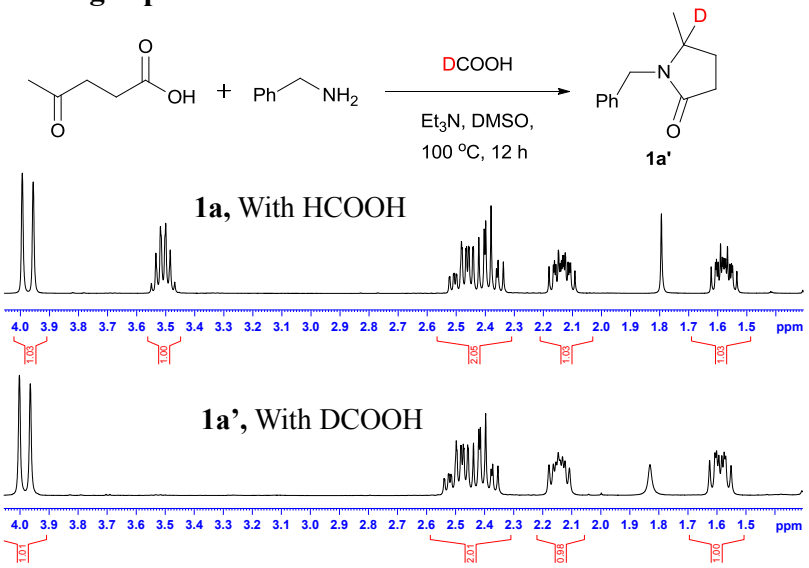


Figure S1 The effect of formic acid/triethylamine (F/T) ratio on RA of LA in DMSO. Reaction conditions: LA (1 mmol), benzylamine (2 mmol), DMSO (3 mL), HCOOH (5 mmol), 100 ^{o}C, 4 h. Conversions were determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

4. Deuterium labelling experiments



Scheme S1 Deuterium labelling experiments for RA of LA with benzylamine. Reaction conditions: LA (1 mmol), benzylamine (2 mmol), DCOOH (5 mmol), Et_3N (1 mmol), DMSO (3 mL), 100 ^{o}C, 12 h.

5. Procedures for RA of LA

5.1 Typical procedure for screening reaction conditions

Benzylamine (2 mmol), levulinic acid (1 mmol), and a magnetic stir bar were placed in a pressure tube. To the mixture was injected solvent (3 ml), HCOOH (5 mmol), and NEt_3 (1

mmol). The mixture was bubbled with argon for 15 min, and then stirred at 100 °C for 4 h. After cooling to room temperature, the reaction mixture was basified with saturated NaOH solution and 1,3,5-trimethoxybenzene (0.1 mmol) was added as internal standard. The resulting mixture was extracted with DCM (5 x 3 mL) and the organic layers were washed with brine, and dried over Na_2SO_4. The organic solvent was removed under reduced pressure. The conversion was determined by ^1H NMR of the crude mixture.

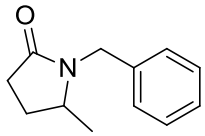
5.2 General procedure for RA of LA with aliphatic amines

Amine (2 mmol), levulinic acid (1 mmol), and a magnetic stir bar were placed in a pressure tube. To the mixture was injected DMSO (3 ml), HCOOH (5 mmol), and NEt_3 (1 mmol). The mixture was bubbled with argon for 15 min, and then stirred at 100 °C for 4 h. After cooling to room temperature, the reaction was basified with saturated NaOH solution and extracted with DCM (5 x 3 mL). The organic layers were washed with brine, and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the product was purified by flash chromatography using petroleum ether and ethyl acetate with 1% triethylamine as elute. Similar yield was obtained with freshly distilled DMSO and newly purchased reaction tube and stir bar.

5.3 General procedure for RA of LA with aromatic amines

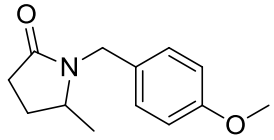
Amine (1.5 mmol), levulinic acid (1 mmol), and a magnetic stir bar were placed in a pressure tube. To the mixture was injected DMSO (3 ml), HCOOH (2.5 mmol), and NEt_3 (0.5 mmol). The mixture was bubbled with argon for 15 min, and then stirred at 100 °C for 3 h. After cooling to 0 ^oC, a portion of amine (0.5 mmol), HCOOH (0.8 mmol), and NEt_3 (0.17 mmol) were added and the resulting mixture was stirred at 100 °C for 3 h, which was repeated twice. After cooling to room temperature, the reaction was basified with saturated NaOH solution and extracted with DCM (5 x 3 mL). The organic layers were washed with brine, and dried over Na_2SO_4. The organic solvent was removed under reduced pressure and the product was purified by flash chromatography using petroleum ether and ethyl acetate with 1% triethylamine as elute.

6. Analytic data of products



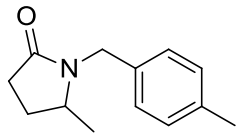
1a

1-Benzyl-5-methylpyrrolidin-2-one 1a:[1] 161 mg, 87% yield; 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): 175.0, 136.8, 128.6, 128.0, 127.4, 52.9, 44.0, 30.3, 26.7, 19.6; HRMS (ESI) for $C_{12}H_{15}NO$ $[M+Na]^+$: calc.: 212.1051. Found: 212.1056.



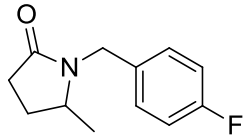
1b

1-(4-Methoxybenzyl)-5-methylpyrrolidin-2-one 1b:[1] 194 mg, 89% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.13 (d, J = 8.4 Hz, 2H), 6.81 (d, J = 8.8 Hz, 2H), 4.87 (d, J = 14.8 Hz, 1H), 3.99 (d, J = 14.8 Hz, 1H), 3.75 (s, 3H), 3.48 (sextet, J = 6.2 Hz, 1H), 2.50-2.31 (m, 2H), 2.15-2.06 (m, 1H), 1.59-1.50 (m, 1H), 1.13 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 159.0, 129.3, 128.8, 114.0, 55.2, 52.7, 43.3, 30.2, 26.6, 19.6; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1157. Found: 242.1164.



1c

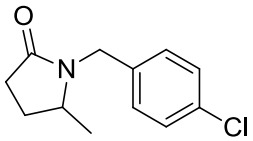
5-Methyl-1-(4-methylbenzyl)pyrrolidin-2-one 1c: 184 mg, 91% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.11 (s, 4H), 4.92 (d, J = 14.8 Hz, 1H), 3.92 (d, J = 14.8 Hz, 1H), 3.50 (sextet, J = 6.4 Hz, 1H), 2.52-2.36 (m, 2H), 2.31 (s, 3H), 2.17-2.08 (m, 1H), 1.61-1.52 (m, 1H), 1.14 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 137.0, 133.8, 129.2, 128.0, 52.7, 43.6, 30.3, 26.6, 21.1, 19.6; HRMS (ESI) for $C_{13}H_{17}NO$ $[M+Na]^+$: calc.: 226.1208. Found: 226.1207.



1d

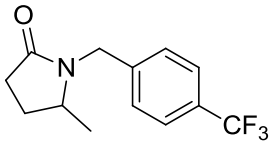
1-(4-Fluorobenzyl)-5-methylpyrrolidin-2-one 1d:[3] 185 mg, 89% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.22-7.19 (m, 2H), 6.99 (t, J = 8.6 Hz, 2H), 4.87 (d, J = 15.0 Hz, 1H), 3.98 (d, J = 15.0 Hz, 1H), 3.51 (sextet, J = 6.2 Hz, 1H), 2.53-2.34 (m, 2H),

2.19-2.10 (m, 1H), 1.64-1.55 (m, 1H), 1.15 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.0, 162.2 (d, $^1J_{C\text{-}F}$ = 244.1 Hz), 132.7 (d, $^4J_{C\text{-}F}$ = 3.7 Hz), 129.6 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 115.5 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 53.0, 43.3, 30.2, 26.7, 19.6; HRMS (ESI) for $C_{12}H_{14}FNO$ $[M+Na]^+$: calc.: 230.0957. Found: 230.0964.



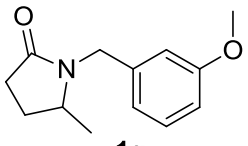
1e

1-(4-Chlorobenzyl)-5-methylpyrrolidin-2-one 1e: 198 mg, 88% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.26 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 4.84(d, J = 15.2 Hz, 1H), 3.99 (d, J = 15.2 Hz, 1H), 3.50 (sextet, J = 6.4 Hz, 1H), 2.52-2.33 (m, 2H), 2.19-2.10 (m, 1H), 1.63-1.54 (m, 1H), 1.13 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.1, 135.4, 135.3, 129.3, 128.8, 53.0, 43.4, 30.2, 26.7, 19.6; HRMS (ESI) for $C_{12}H_{14}ClNO$ $[M+Na]^+$: calc.: 246.0662. Found: 246.0659.



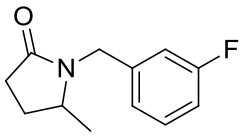
1f

5-Methyl-1-(4-(trifluoromethyl)benzyl)pyrrolidin-2-one 1f: 196 mg, 76% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.57 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.91 (d, J = 15.2 Hz, 1H), 4.11 (d, J = 15.2 Hz, 1H), 3.52 (sextet, J = 6.4 Hz, 1H), 2.54-2.36 (m, 2H), 2.22-2.14 (m, 1H), 1.66-1.57 (m, 1H), 1.15 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.2, 141.1, 129.8 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 128.2, 125.6 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 270.4 Hz), 53.2, 43.7, 30.1, 26.7, 19.7; HRMS (ESI) for $C_{13}H_{14}F_3NO$ $[M+Na]^+$: calc.: 280.0925. Found: 280.0924.



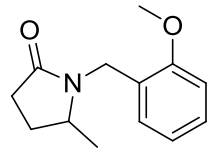
1g

1-(3-Methoxybenzyl)-5-methylpyrrolidin-2-one 1g:[3] 194 mg, 89% yield; 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 = 15.2 Hz, 1H), 3.95 (d, J = 15.2 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): 175.1, 159.9, 138.3, 129.6, 120.3, 113.7, 112.8, 55.2, 53.0, 43.9, 30.2, 26.6, 19.6; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1153. Found: 242.1162.



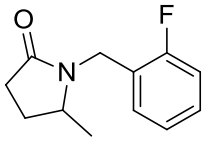
1h

1-(3-Fluorobenzyl)-5-methylpyrrolidin-2-one 1h: 153 mg, 74% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29-7.24 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.96-6.92 (m, 1H), 4.88 (d, J = 15.2 Hz, 1H), 4. 02 (d, J = 15.2 Hz, 1H), 3.54 (sextet, J = 6.4 Hz, 1H), 2.54-2.37 (m, 2H), 2.22-2.13 (m, 1H), 1.65-1.56 (m, 1H), 1.15 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.1, 163.0 (d, $^{1}J_{C\text{-}F}$ = 245.0 Hz), 139.6 (d, $^{3}J_{C\text{-}F}$ = 7.0 Hz), 130.1 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 123.4 (d, $^{4}J_{C\text{-}F}$ = 2.8 Hz), 114.7 (d, $^{2}J_{C\text{-}F}$ = 21.4 Hz), 114.4 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 53.1, 43.6 (d, $^{4}J_{C\text{-}F}$ = 4.3 Hz), 30.1, 26.7, 19.6; HRMS (ESI) for $C_{12}H_{14}FNO$ $[M+Na]^+$: calc.: 230.0957. Found: 230.0957.



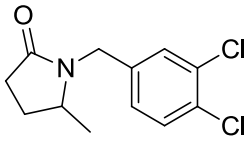
1i

1-(2-Methoxybenzyl)-5-methylpyrrolidin-2-one 1i:[3] 199 mg, 91% yield; 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): 175.0, 157.3, 129.5, 128.5 124.9, 120.6, 110.3, 55.3, 53.4, 38.4, 30.3, 26.7, 19.6; HRMS (ESI) for $C_{13}H_{17}NO_2$ $[M+Na]^+$: calc.: 242.1157. Found: 242.1161.



1j

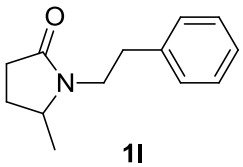
1-(2-Fluorobenzyl)-5-methylpyrrolidin-2-one 1j: 168 mg, 81% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.29 (d, J = 7.6 Hz, 1H), 7.25-7.21 (m, 1H), 7.08 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 9.2 Hz, 1H), 4.85 (d, J = 15.2 Hz, 1H), 4.20 (d, J = 15.2 Hz, 1H), 3.54 (sextet, J = 6.6 Hz, 1H), 2.52-2.32 (m, 2H), 2.20-2.11 (m, 1H), 1.64-1.55 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.2, 160.8 (d, $^{1}J_{C\text{-}F}$ = 244.4 Hz), 130.5 (d, $^{6}J_{C\text{-}F}$ = 4.2 Hz), 129.2 (d, $^{4}J_{C\text{-}F}$ = 8.1 Hz), 124.4 (d, $^{7}J_{C\text{-}F}$ = 3.4 Hz), 123.8 (d, $^{3}J_{C\text{-}F}$ = 14.7 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 21.7 Hz), 53.2, 37.2 (d, $^{5}J_{C\text{-}F}$ = 4.3 Hz), 30.1, 26.7, 19.6; HRMS (ESI) for $C_{12}H_{14}FNO$ $[M+Na]^+$: calc.: 230.0957. Found: 230.0958.



1k

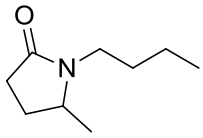
1-(3,4-Dichlorobenzyl)-5-methylpyrrolidin-2-one 1k: 185 mg, 72% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.37 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 2.0 Hz, 1H), 7.07 (dd, J = 8.0, 2.0 Hz, 1H), 4.79 (d, J = 15.6 Hz, 1H), 4.00 (d, J = 15.2 Hz, 1H), 3.52 (sextet, J = 6.2 Hz, 1H), 2.53-2.35 (m, 2H), 2.22-2.13 (m, 1H), 1.65-1.56 (m, 1H), 1.15 (d, J = 6.2 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.2, 137.3, 132.7, 131.6, 130.6, 129.8, 127.3, 53.2, 43.1, 30.0, 26.7, 19.7; HRMS (ESI) for $C_{12}H_{13}Cl_2NO$ $[M+Na]^+$: calc.: 280.0272. Found: 280.0268.



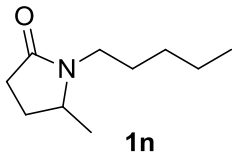
1l

5-Methyl-1-phenethylpyrrolidin-2-one 1l: 175 mg, 86% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.30-7.27 (m, 2H), 7.22-7.18 (m, 3H), 3.82 (ddd, J = 13.8, 9.2, 6.2 Hz, 1H), 3.52 (sextet, J = 6.2 Hz, 1H), 3.14 (ddd, J = 14.2, 8.8, 6.2 Hz, 1H), 2.91-2.73 (m, 2H), 2.43-2.24 (m, 1H), 2.16-2.07 (m, 1H), 1.57-1.49 (m, 1H), 1.15 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 138.9, 128.7, 128.5, 126.4, 53.9, 41.8, 33.9, 30.2, 26.8, 19.7; HRMS (ESI) for $C_{13}H_{17}NO$ $[M+Na]^+$: calc.: 226.1208. Found: 226.1204.



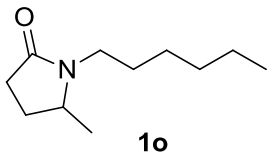
1m

1-Butyl-5-methylpyrrolidin-2-one 1m: 134 mg, 86% yield; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.64 (sextet, J = 6.2 Hz, 1H), 3.53 (ddd, J = 13.8, 9.0, 7.0 Hz, 1H), 2.86 (ddd, J = 13.8, 8.6, 5.2 Hz, 1H), 2.40-2.23 (m, 2H), 2.17-2.08 (m, 1H), 1.56-1.34 (m, 3H), 1.30-1.20 (m, 2H), 1.15 (d, J = 6.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.9, 53.6, 40.0, 30.2, 29.5, 26.8, 20.2, 19.7, 13.7; HRMS (ESI) for $C_9H_{17}NO$ $[M+Na]^+$: calc.: 178.1208. Found: 178.1203.



1n

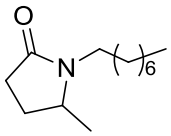
5-Methyl-1-pentylpyrrolidin-2-one 1n: 152 mg, 90% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.68 (sextet, J = 6.2 Hz, 1H), 3.56 (ddd, J = 13.8, 9.0, 7.0 Hz, 1H), 2.90 (ddd, J = 13.8, 8.8, 5.2 Hz, 1H), 2.46-2.29 (m, 2H), 2.21-2.12 (m, 1H), 1.60-1.38 (m, 3H), 1.34-1.21 (m,4H), 1.18 (d, J = 6.4 Hz, 3H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 53.4, 40.1, 30.3, 29.1, 27.0, 26.8, 22.3, 19.7, 13.9; HRMS (ESI) for $C_{10}H_{19}NO$ $[M+Na]^+$: calc.: 192.1364. Found: 192.1361.



1o

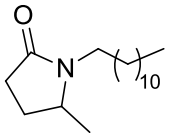
1-Hexyl-5-methylpyrrolidin-2-one 1o:[3] 170 mg, 93% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.65 (sextet, J = 6.4 Hz, 1H), 3.55 (ddd, J = 13.8, 9.0, 7.0 Hz, 1H), 2.88 (ddd, J = 13.8, 9.0, 5.0 Hz, 1H), 2.41-2.24 (m, 2H), 2.19-2.10 (m, 1H), 1.58-1.37 (m,

3H), 1.25 (s, 6H), 1.17 (d, J = 6.4 Hz, 3H), 0.84 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 53.5, 40.2, 31.5, 30.3, 27.4, 26.8, 26.6, 22.5, 19.7, 13.9; HRMS (ESI) for $C_{11}H_{21}NO$ [M+N a]$^+$: calc.: 206.1521. Found: 206.1517.



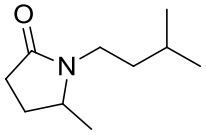
1p

1-Octyl-5-methylpyrrolidin-2-one 1p:[3] 197 mg, 93% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.66 (sextet, J = 6.2 Hz, 1H), 3.55 (ddd, J = 13.8, 9.0, 7.0 Hz, 1H), 2.88 (ddd, J = 13.8, 9.0, 5.0 Hz, 1H), 2.44-2.27 (m, 2H), 2.20-2.11 (m, 1H), 1.59-1.46 (m, 2H), 1.44-1.36 (m, 1H), 1.26-1.24 (m, 10H), 1.18 (d, J = 6.2 Hz, 3H), 0.86-0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.6, 53.2, 40.0, 31.7, 30.3, 29.3, 29.1, 27.4, 27.0, 26.8, 22.6, 19.7, 14.0; HRMS (ESI) for $C_{13}H_{25}NO$ [M+Na]$^+$: calc.: 234.1834. Found: 234.1838.



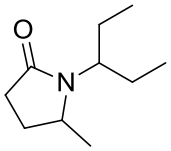
1q

1-Dodecyl-5-methylpyrrolidin-2-one 1q:[3] 234 mg; 88% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.67 (sextet, J = 6.4Hz, 1H), 3.56 (ddd, J = 13.8, 9.2, 7.0 Hz, 1H), 2.89 (ddd, J = 13.8, 9.0, 5.0 Hz, 1H), 2.43-2.26 (m, 2H), 2.20-2.11 (m, 1H), 1.59-1.48 (m, 2H), 1.45-1.39 (m, 1H), 1.21 (s, 18H), 1.18 (d, J = 6.2 Hz, 3H), 0.88-0.84 (m, 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; HRMS (ESI) for $C_{17}H_{33}NO$ [M+Na]$^+$: calc.: 290.2460. Found: 290.2465.



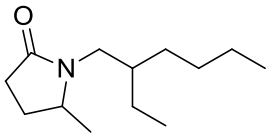
1r

1-Isopentyl-5-methylpyrrolidin-2-one 1r: 137 mg, 77% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.70-3.56 (m, 2H), 2.89 (ddd, J = 14.2, 9.2, 5.2 Hz, 1H), 2.43-2.25 (m, 2H), 2.19-2.10 (m, 1H), 1.59-1.48 (m, 2H), 1.42-1.27 (m, 1H), 1.18 (d, J = 6.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.6, 53.2, 38.4, 36.1, 30.3, 26.8, 26.1, 22.6, 22.2, 19.7; HRMS (ESI) for $C_{10}H_{19}NO$ [M+Na]$^+$: calc.: 192.1364. Found: 192.1356.



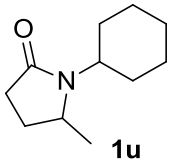
1s

5-Methyl-1-(pentan-3-yl)pyrrolidin-2-one 1s: 148 mg, 87% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.72-3.57 (m, 2H), 2.51-2.42 (m, 1H), 2.33-2.25 (m, 1H), 2.19-2.10 (m, 1H), 1.69-1.48 (m, 5H), 1.22 (d, J = 6.4 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H), 0.82 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.6, 56.6, 53.3, 30.4, 27.7, 27.2, 24.6, 21.8, 11.42, 11.37; HRMS (ESI) for $C_{10}H_{19}NO$ $[M+Na]^+$: calc.: 192.1364. Found: 192.1360.



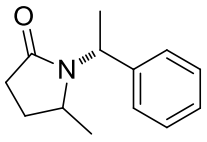
1t

1-(2-Ethylhexyl)-5-methylpyrrolidin-2-one 1t: mixture of isomers; 193 mg, 91% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.59 (sextet, J = 6.4Hz, 1H), 3.52-3.43 (m, 1H), 2.77-2.70 (m, 1H), 2.39-2.23 (m, 2H), 2.16-2.07 (m, 1H), 1.56-1.47 (m, 2H), 1.32-1.16 (m, 6H), 1.13 (d, J = 6.2 Hz, 3H), 0.86-0.77 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.8, 174.7, 52.2, 51.9, 43.4, 43.2, 36.9, 36.6, 30.7, 30.4, 30.2, 28.9, 28.4, 26.71, 26.68, 24.2, 23.5, 23.0, 19.41, 19.36, 13.9, 10.9, 10.2; HRMS (ESI) for $C_{13}H_{25}NO$ $[M+Na]^+$: calc.: 234.1834. Found: 234.1830.



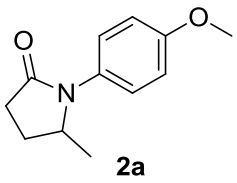
1u

1-Cyclohexyl-5-methylpyrrolidin-2-one 1u: 162 mg, 85% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.80-3.65 (m, 2H), 2.49-2.41 (m, 1H), 2.30-2.22 (m, 1H), 2.16-2.06 (m, 1H), 1.82-1.69 (m, 3H), 1.67-1.42 (m, 5H), 1.39-1.25 (m, 2H), 1.22 (d, J = 6.2 Hz, 3H), 1.16-1.04 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.5, 53.0, 52.6, 31.8, 30.3, 30.1, 27.5, 26.0, 25.9, 25.6, 22.3; HRMS (ESI) for $C_{11}H_{19}NO$ $[M+Na]^+$: calc.: 204.1364. Found: 204.1359.



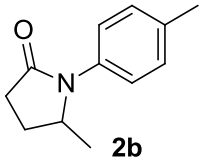
1v

5-Methyl-1-phenylethyl)pyrrolidin-2-one 1v: mixture of isomers; 178 mg, 88% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.38-7.22 (m, 12.5H), 5.47-5.38 (m, 2.5H), 3.85-3.78 (m, 1H), 3.41-3.33 (m, 1.5H), 2.55-2.46 (m, 2.6H), 2.38-2.29 (m, 3H), 2.19-2.10 (m, 1H), 2.08-1.98 (m, 1.5H), 1.64-1.60 (m, 8H), 1.57-1.49 (m, 2.5H), 1.14 (d, J = 6.2 Hz, 4.5H), 0.76 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 175.0, 174.9, 142.2, 139.8, 128.4, 128.2, 127.4, 127.1, 127.0, 52.8, 52.6, 50.2, 49.1, 30.3, 30.2, 27.5, 27.4, 22.2, 21.4, 18.3, 16.1; HRMS (ESI) for $C_{13}H_{17}NO$ $[M+Na]^+$: calc.: 226.1208. Found: 226.1205.



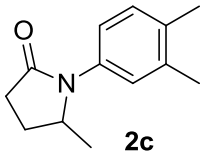
2a

1-(4-Methoxyphenyl)-5-methylpyrrolidin-2-one 2a:[1] 143 mg, 70% yield; 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; HRMS (ESI) for $C_{12}H_{15}NO_2$ $[M+Na]^+$: calc.: 228.1000. Found: 228.1005.



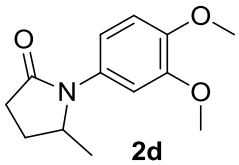
2b

5-methyl-1-p-tolylpyrrolidin-2-one 2b:[1] 83 mg, 44% yield; 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; HRMS (ESI) for $C_{12}H_{15}NO$ $[M+Na]^+$: calc.: 212.1051. Found: 212.1052.



2c

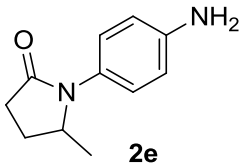
1-(3, 4-Dimethylphenyl)-5-methylpyrrolidin-2-one 2c: 153 mg, 75% yield; white solid; mp. = 85~87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.14-7.11 (m, 2H), 7.02 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.21 (td, *J* = 7.2, 6.0 Hz, 1H), 2.65-2.47 (m, 2H), 2.39-2.32 (m, 1H), 2.26 (s, 3H), 2.23(s, 3H), 1.77-1.68 (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; HRMS (ESI) for $C_{13}H_{17}NO$ $[M+Na]^+$: calc.: 226.1208. Found: 226.1212.



2d

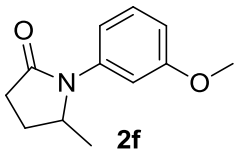
1-(3,4-Dimethoxyphenyl)-5-methylpyrrolidin-2-one 2d: 167 mg, 71% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.97 (d, *J* = 2.2 Hz, 1H), 6.86 (d, *J* = 8.6 Hz , 1H), 6.77 (dd, *J* = 8.6, 2.4 Hz, 1H), 4.18 (sextet, *J* = 6.2 Hz , 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.65-2.48 (m, 2H), 2.40-2.31 (m, 1H), 1.78-1.69 (m, 1H), 1.18 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ (ppm): 174.3, 149.2, 147.3, 130.8, 116.7, 111.2, 109.0, 56.2, 56.0, 55.9, 31.2, 26.8, 20.3; HRMS (ESI) for $C_{13}H_{17}NO_3$ $[M+Na]^+$: calc.: 258.1106. Found: 258.1102.



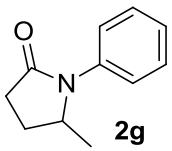
2e

1-(4-Aminophenyl)-5-methylpyrrolidin-2-one 2e: 104 mg, 55% yield; grayish purple solid; mp. = 112~113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.04 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 4.10 (sextet, J = 6.2 Hz, 1H), 3.69 (brs, 2H), 2.61-2.44 (m, 2H), 2.36-2.28 (m, 1H), 1.74-1.65 (m, 1H), 1.14 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.3, 144.9, 128.5, 126.3, 115.5, 56.3, 31.1, 26.9, 20.3; HRMS (ESI) for $C_{11}H_{14}N_2O$ $[M+Na]^+$: calc.: 213.1004. Found: 213.0999.



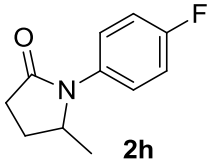
2f

1-(3-Methoxyphenyl)-5-methylpyrrolidin-2-one 2f: 53 mg, 26% yield; 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; HRMS (ESI) for $C_{12}H_{15}NO_2$ $[M+Na]^+$: calc.: 228.1000. Found: 228.1005.



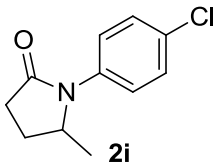
2g

5-Methyl-1-phenylpyrrolidin-2-one 2g:[1] 59 mg, 34% yield; 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; HRMS (ESI) for $C_{11}H_{13}NO$ $[M+Na]^+$: calc.: 198.0895. Found: 198.0894.



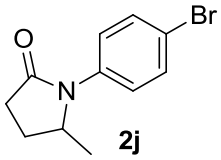
2h

1-(4-Fluorophenyl)-5-methylpyrrolidin-2-one 2h:[1] 54 mg, 28% yield; 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, $^1J_{C\text{-}F}$ = 243.8 Hz), 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; HRMS (ESI) for $C_{11}H_{12}FNO$ $[M+Na]^+$: calc.: 216.0800. Found: 216.0802.



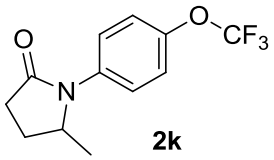
2i

1-(4-Chlorophenyl)-5-methylpyrrolidin-2-one 2i:[2] 27 mg, 13% yield; 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; HRMS (ESI) for $C_{11}H_{12}ClNO$ $[M+Na]^+$: calc.: 232.0505. Found: 232.0511.



2j

1-(4-Bromophenyl)-5-methylpyrrolidin-2-one 2j: 21 mg, 8% yield; 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; HRMS (ESI) for $C_{11}H_{12}BrNO$ $[M+Na]^+$: calc.: 276.0000. Found: 276.0006.



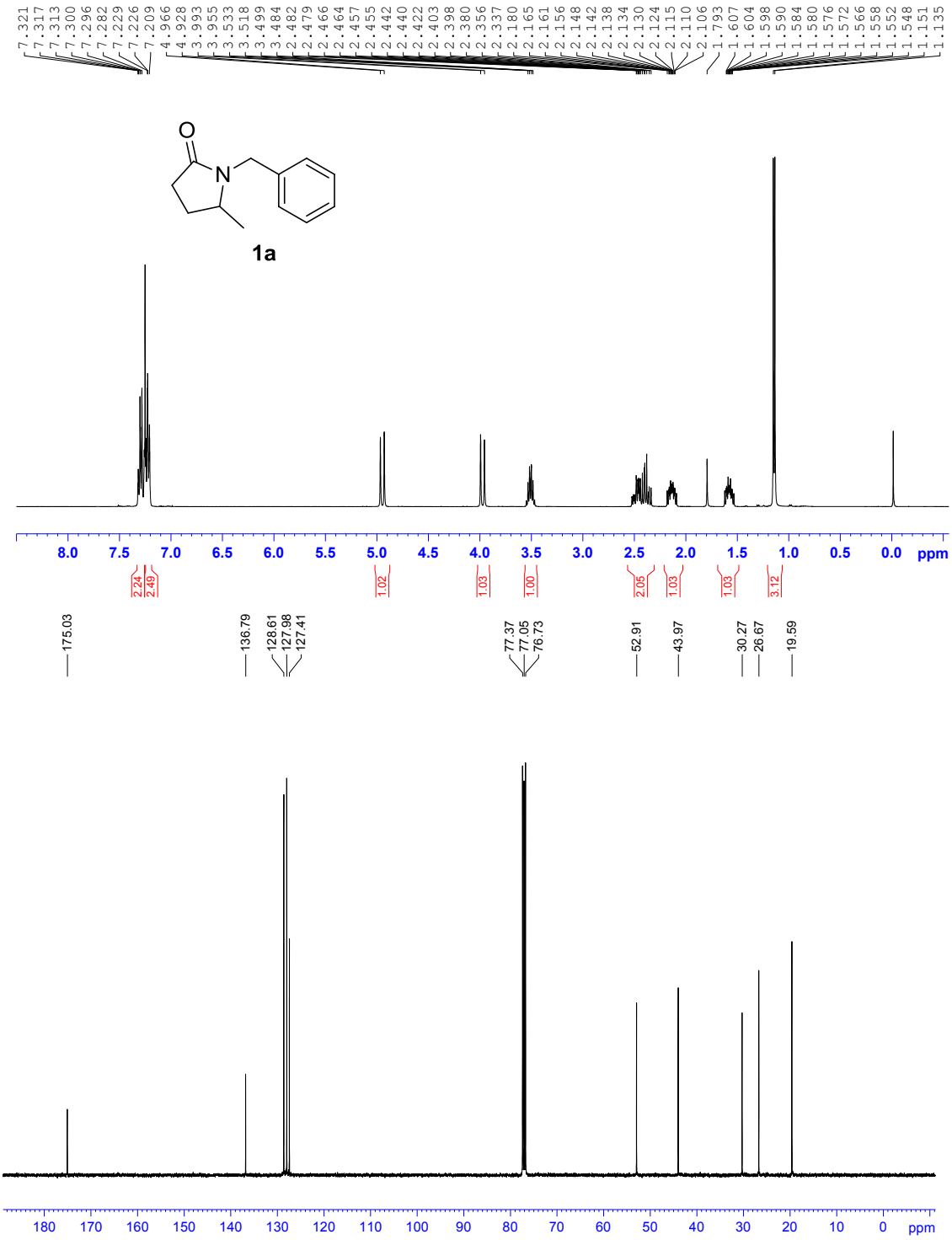
2k

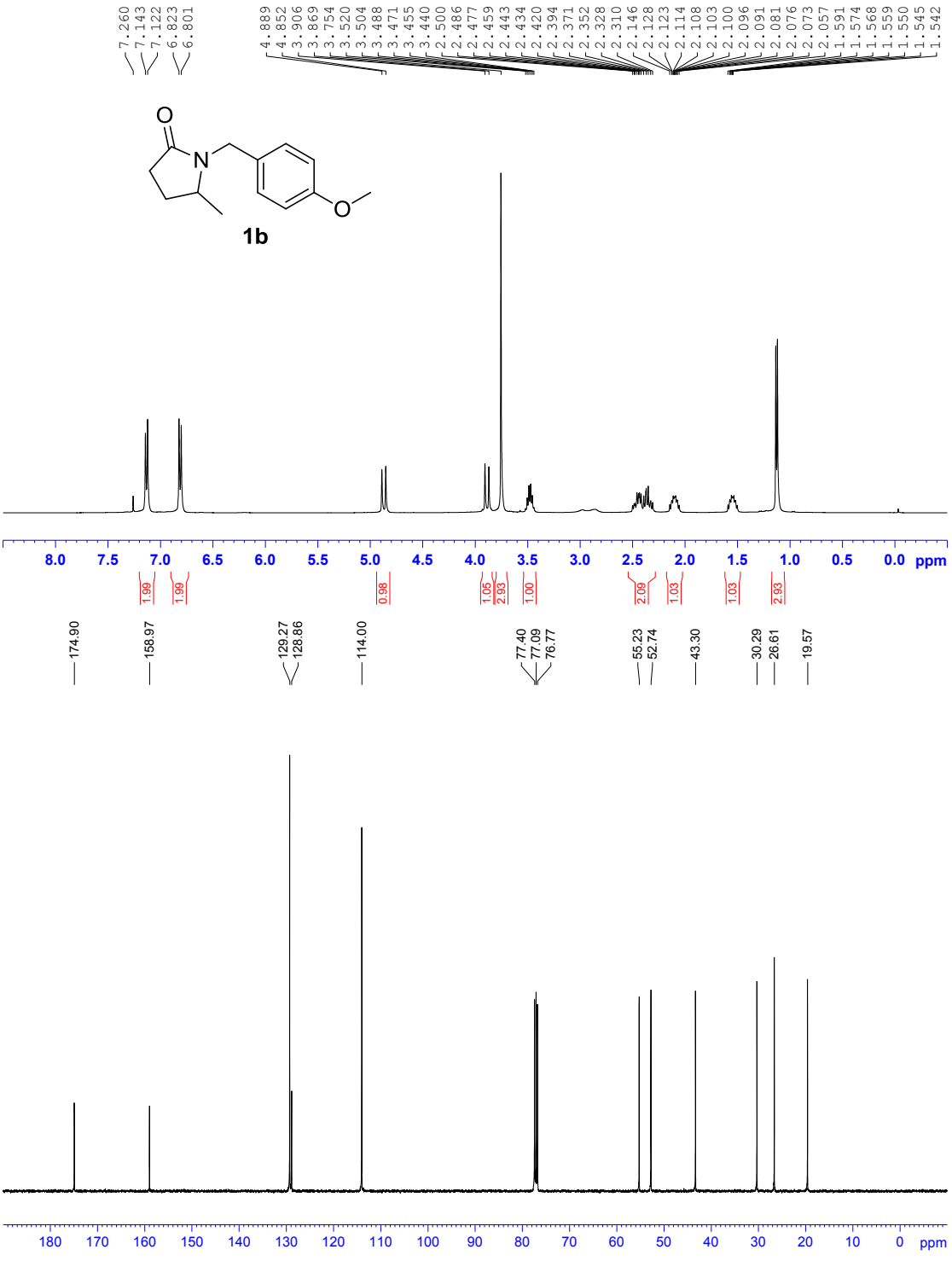
5-Methyl-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-one 2k: 67 mg, 23% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.42 (d, J = 9.2 Hz, 2H), 7.22 (d, J = 8.8 Hz, 2H), 4.28 (sextet, J = 6.4 Hz, 1H), 2.68-2.48 (m, 2H), 2.41-2.32 (m, 1H), 1.80-1.75 (m, 1H), 1.21 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 174.2, 146.3, 136.2, 124.9, 121.5, 120.4 (q, J_{C-F} = 255.6 Hz), 55.5, 31.2, 26.6, 20.0; HRMS (ESI) for $C_{12}H_{13}F_3NO_2$ $[M+Na]^+$: calc.: 282.0718. Found: 282.0727.

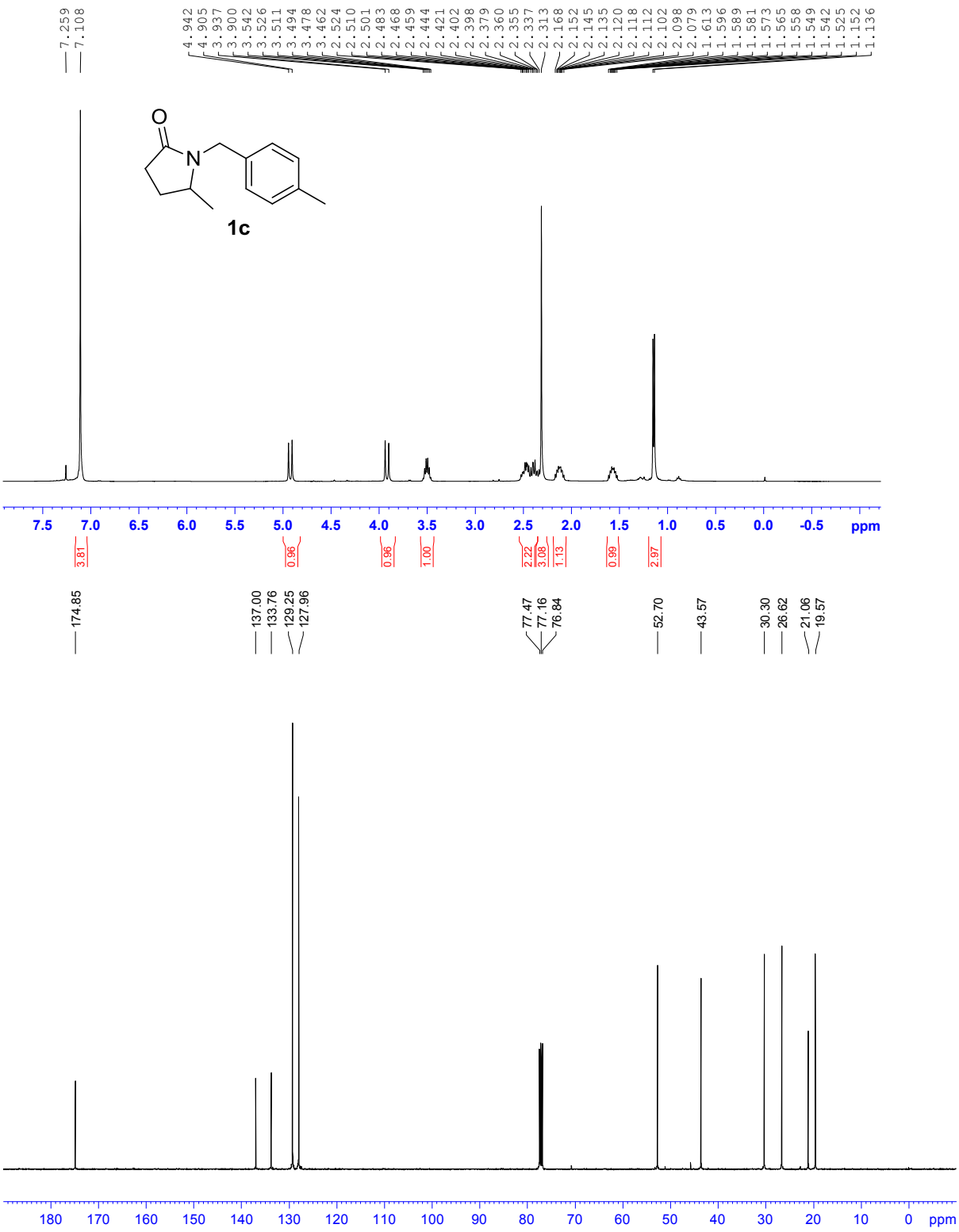
7. References

1. Yao-Bing Huang, Jian-Jun Dai, Xiao-Jian Deng, Yan-Chao Qu, Qing-Xiang Guo, and Yao Fu, *Chemsuschem* **2011**, *4*, 1578-1581.
2. Xian-Long Du, Lin He, She Zhao, Yong-Mei Liu, Yong Cao, He-Yong He, and Kang-Nian Fan, *Angew. Chem. Int. Ed.* **2011**, *50*, 7815-7818.
3. Ya-Wen Wei, Chao Wang, Xue Jiang, Jia Li, Dong Xue, and Jian-Liang Xiao, *Chem. Commun.* **2013**, *49,* 5408-5410.

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



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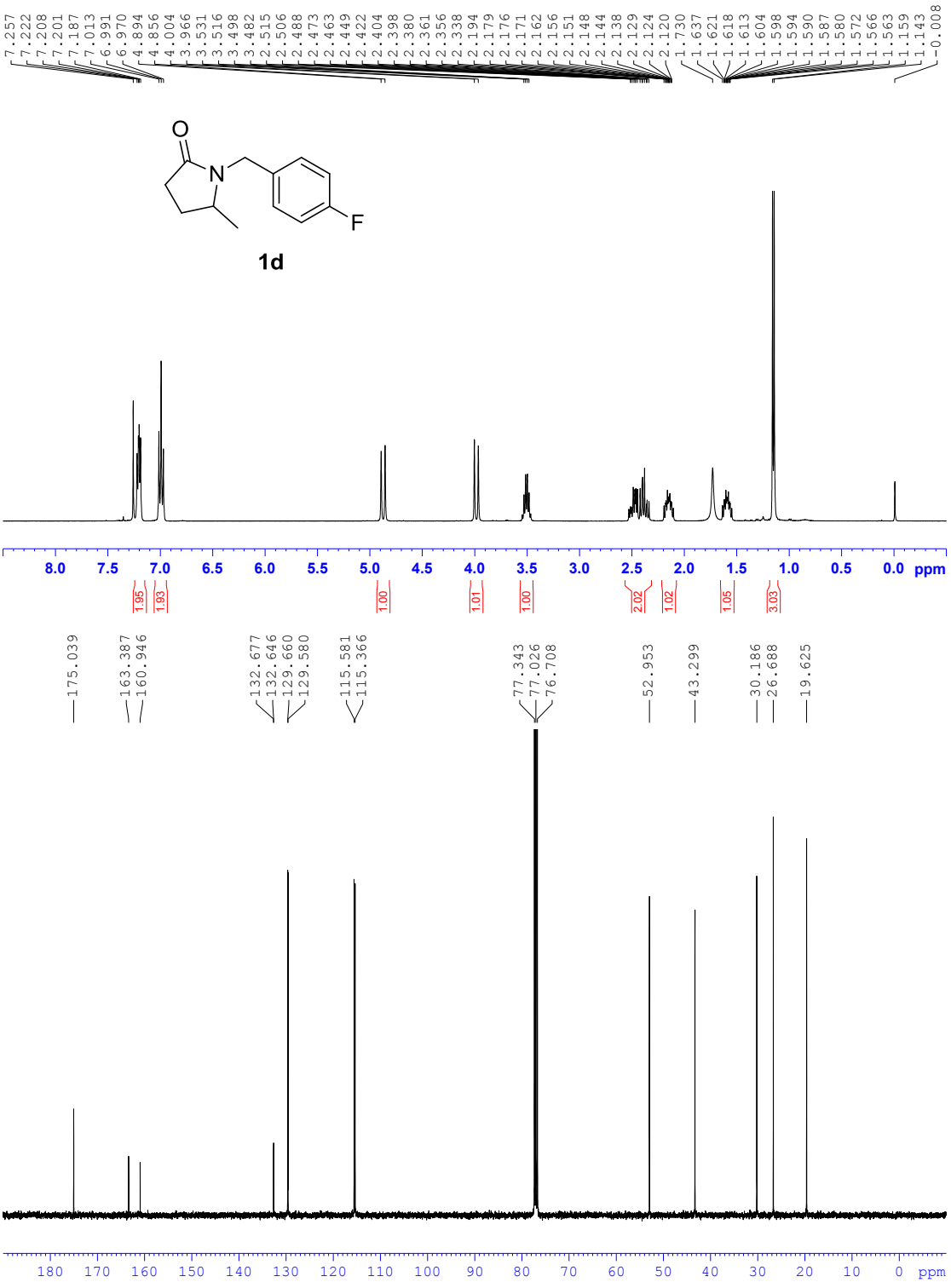
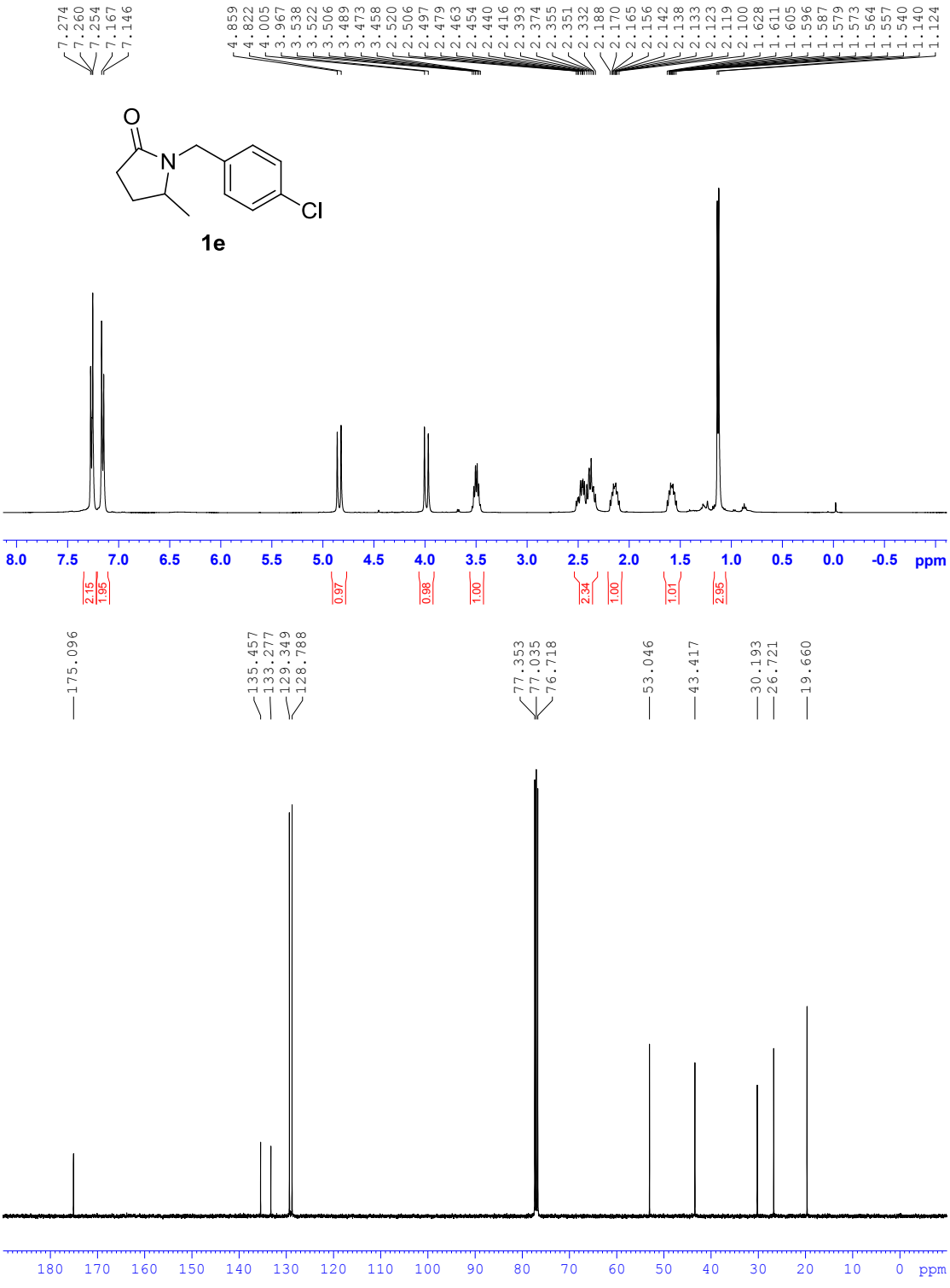
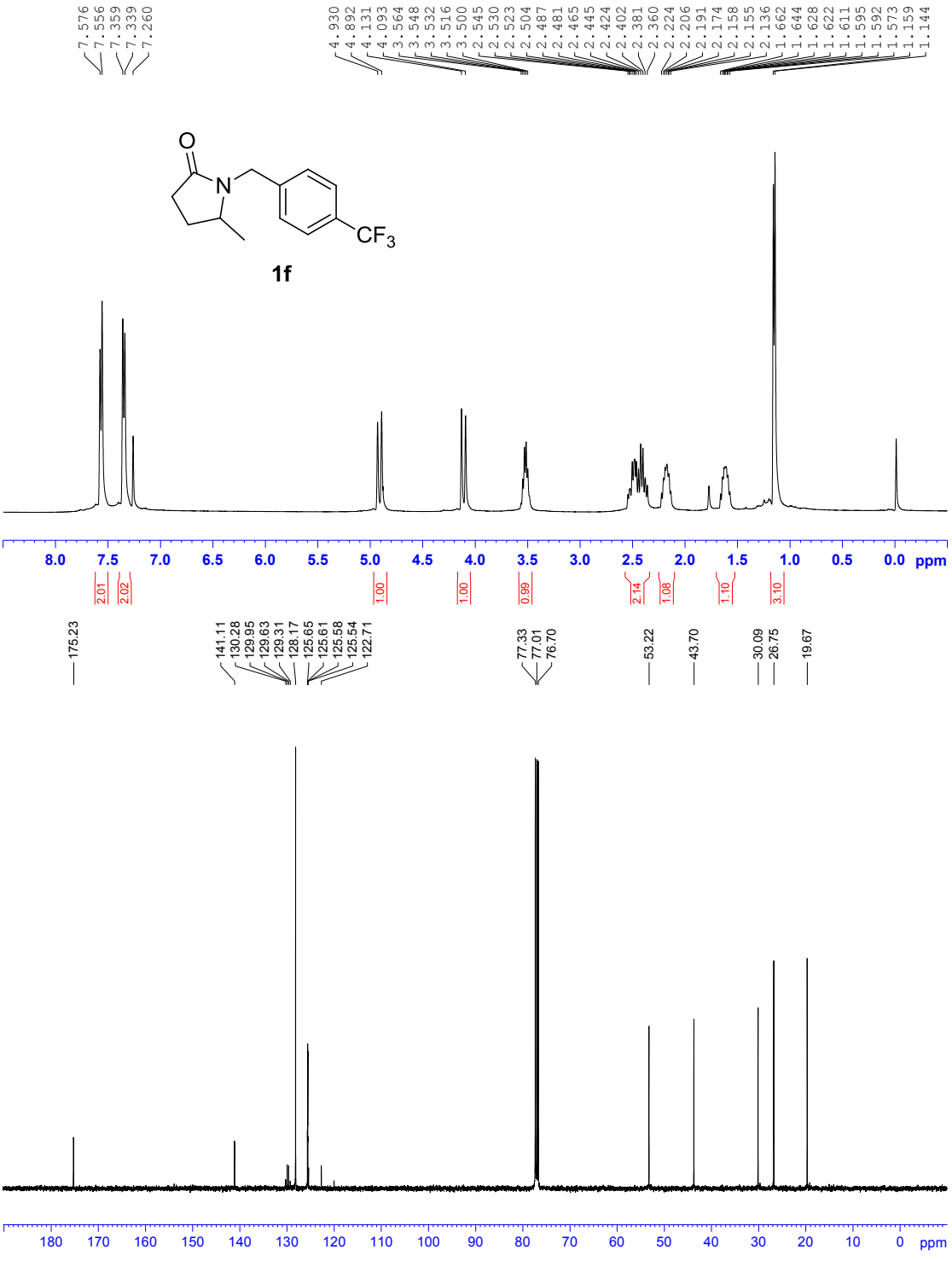
3.462
2.524
2.510
2.501
2.483
2.468
2.459
2.444
2.421
2.402
2.398
2.379
2.360
2.355
2.337
2.313
2.168
2.152
2.145
2.135
2.120
2.118
2.112
2.102
2.098
2.079
1.613
1.596
1.589
1.581
1.573
1.565
1.558
1.549
1.542
1.525
1.152
1.136
O
N
1c
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
3.81
0.96
0.96
1.00
2.22
3.08
1.13
0.99
2.97
174.85
137.00
133.76
129.25
127.96
77.47
77.16
76.84
52.70
43.57
30.30
26.62
21.06
19.57
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



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4.930
4.892
4.131
4.093
3.564
3.548
3.532
3.516
3.500
2.545
2.530
2.523
2.504
2.487
2.481
2.465
2.445
2.424
2.402
2.381
2.360
2.224
2.206
2.191
2.174
2.158
2.155
2.136
1.662
1.644
1.628
1.622
1.611
1.595
1.592
1.573
1.159
1.144
O
N
CF3
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
2.01
2.02
1.00
1.00
0.99
2.14
1.08
1.10
3.10
175.23
141.11
130.28
129.95
129.63
129.31
128.17
125.65
125.61
125.58
125.54
122.71
77.33
77.01
76.70
53.22
43.70
30.09
26.75
19.67
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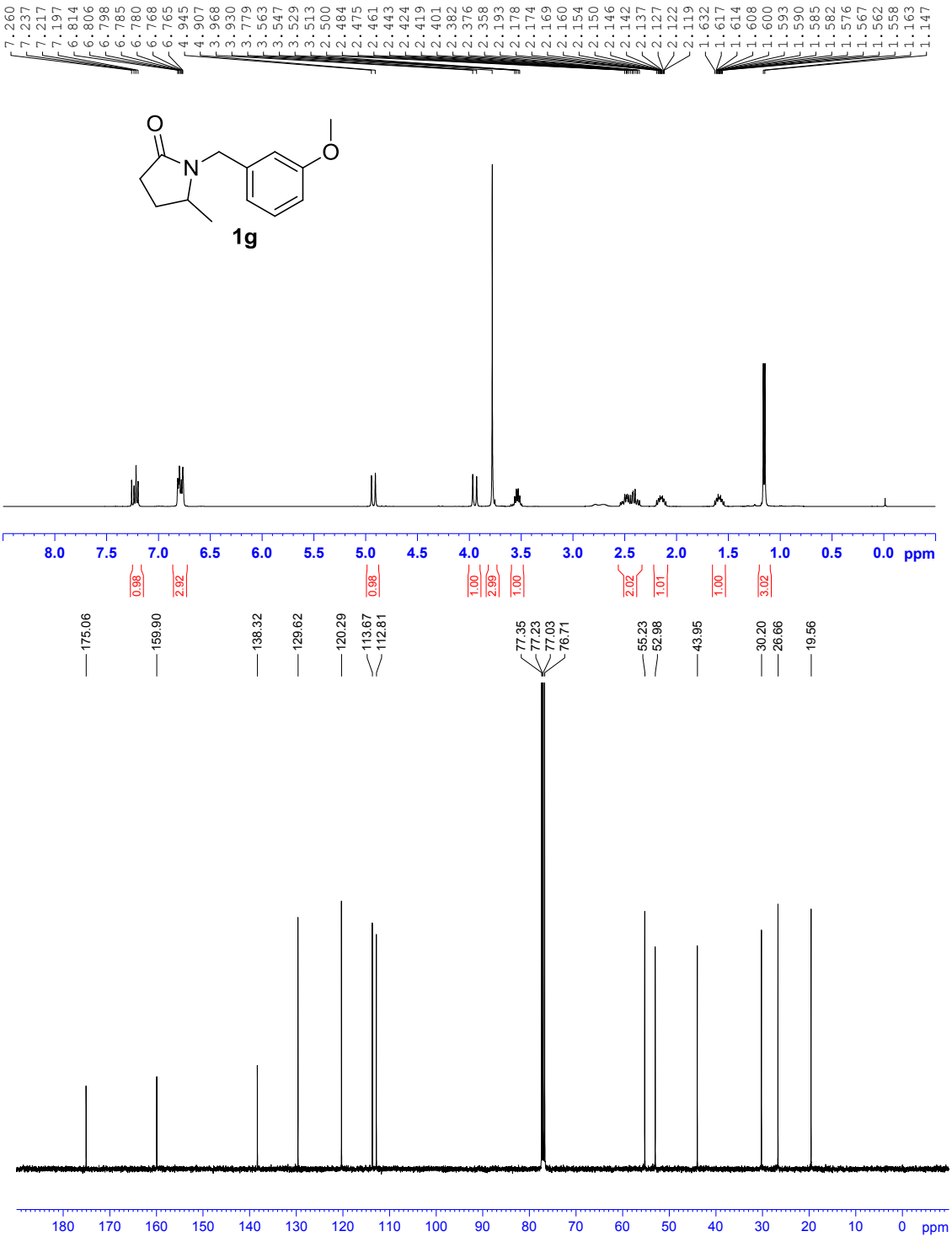

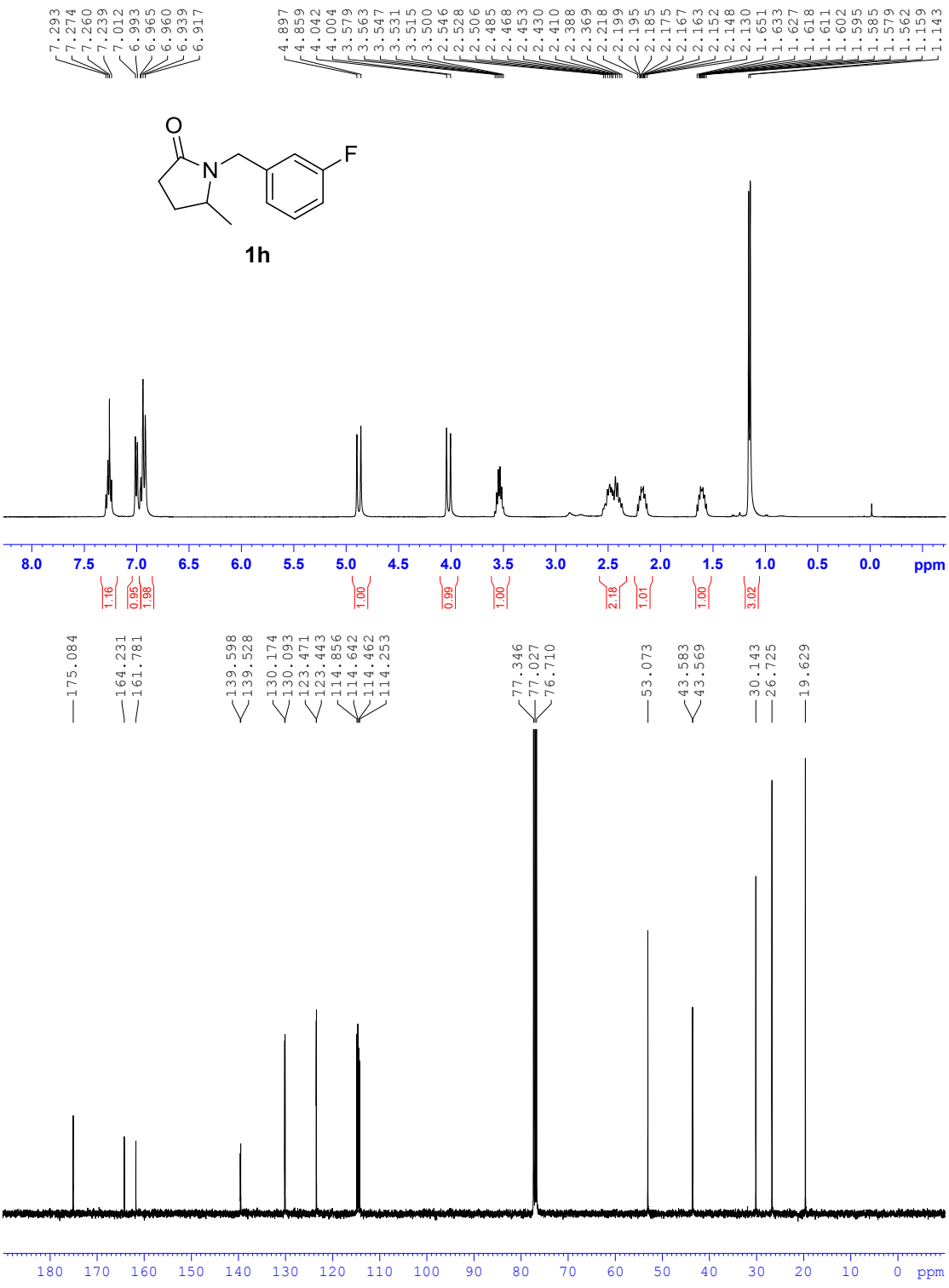
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7.260
7.239
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6.917
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4.859
4.042
4.004
3.579
3.563
3.547
3.531
3.515
3.500
2.546
2.528
2.506
2.485
2.468
2.453
2.430
2.410
2.388
2.369
2.218
2.199
2.195
2.185
2.175
2.167
2.163
2.152
2.148
2.130
1.651
1.633
1.627
1.618
1.611
1.602
1.595
1.585
1.579
1.562
1.159
1.143
O
N
F
1h
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0.95
1.98
1.00
0.99
1.00
2.18
1.01
1.00
3.02
175.084
164.231
161.781
139.598
139.528
130.174
130.093
123.471
123.443
114.856
114.642
114.462
114.253
77.346
77.027
76.710
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43.583
43.569
30.143
26.725
19.629
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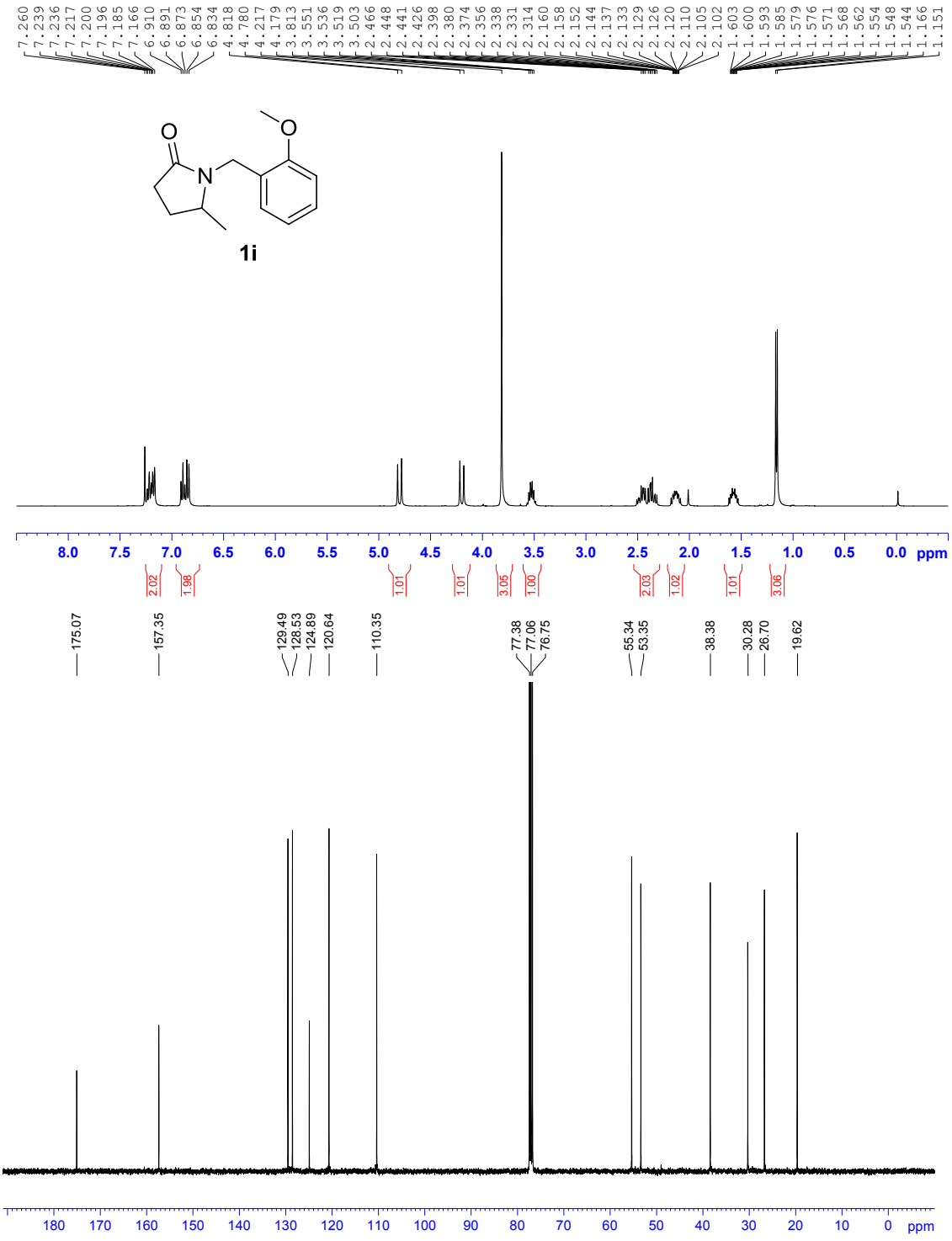
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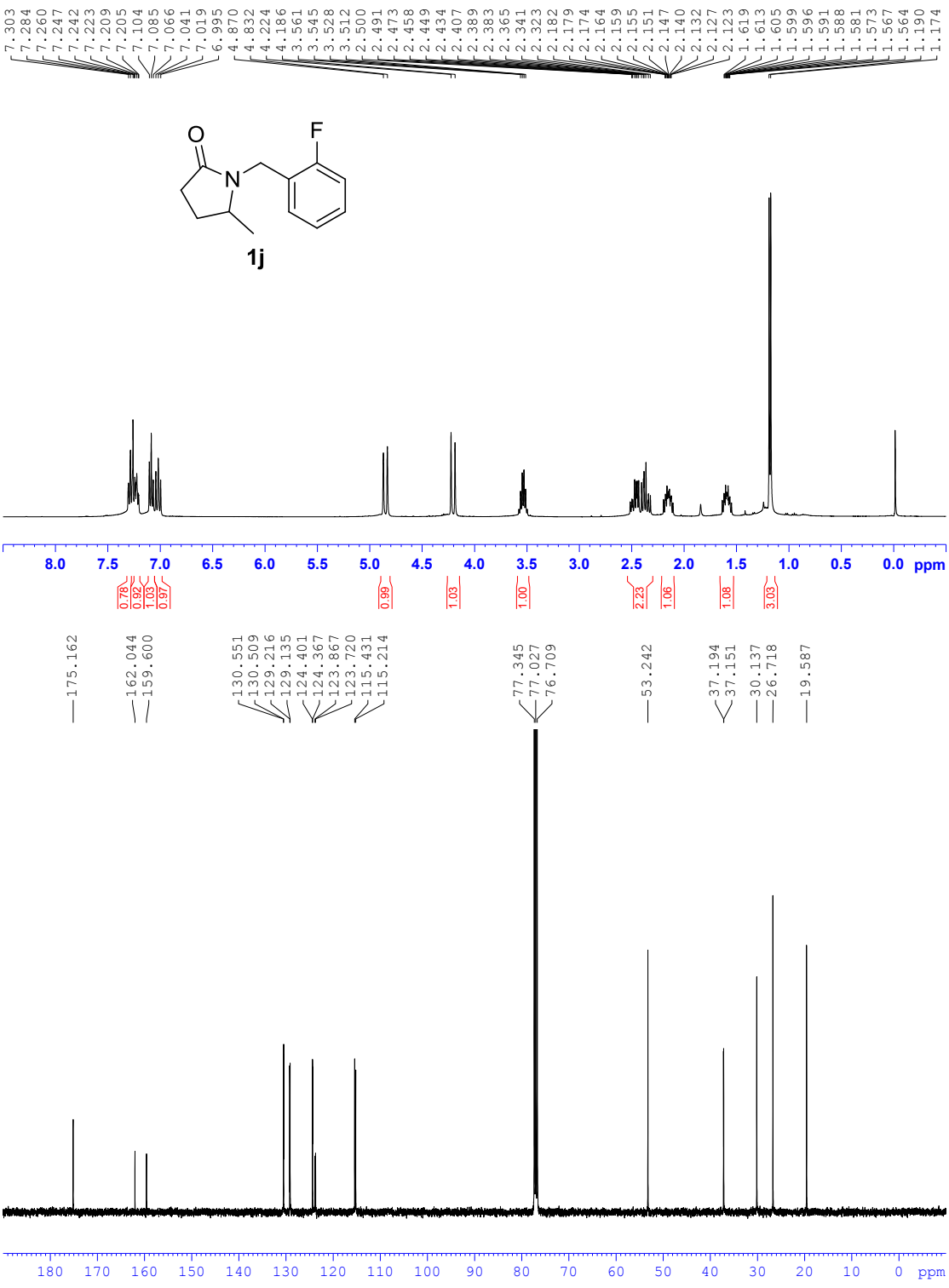
6.834
4.818
4.780
4.217
4.179
3.813
3.551
3.536
3.519
3.503
2.466
2.448
2.441
2.426
2.398
2.380
2.374
2.356
2.338
2.331
2.314
2.160
2.158
2.152
2.144
2.137
2.133
2.129
2.126
2.120
2.110
2.105
2.102
1.603
1.600
1.593
1.585
1.579
1.576
1.571
1.568
1.562
1.554
1.548
1.544
1.166
1.151
O
O
N
1i
8.0 7.5 7.0 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
2.02
1.98
1.01
1.01
3.05
1.00
2.03
1.02
1.01
3.06
175.07
157.35
129.49
128.53
124.89
120.64
110.35
77.38
77.06
76.75
55.34
53.35
38.38
30.28
26.70
19.62
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.205
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7.019
6.995
4.870
4.832
4.224
4.186
3.561
3.545
3.528
3.512
2.500
2.491
2.473
2.458
2.449
2.434
2.407
2.389
2.383
2.365
2.341
2.323
2.182
2.179
2.174
2.164
2.159
2.155
2.151
2.147
2.140
2.132
2.127
2.123
1.619
1.613
1.605
1.599
1.596
1.591
1.588
1.581
1.573
1.567
1.564
1.190
1.174
O
N
F
1j
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
0.78 0.92 1.03 0.97 0.99 1.03 1.00 2.23 1.06 1.08 3.03
175.162
162.044
159.600
130.551
130.509
129.216
129.135
124.401
124.367
123.867
123.720
115.431
115.214
77.345
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37.194
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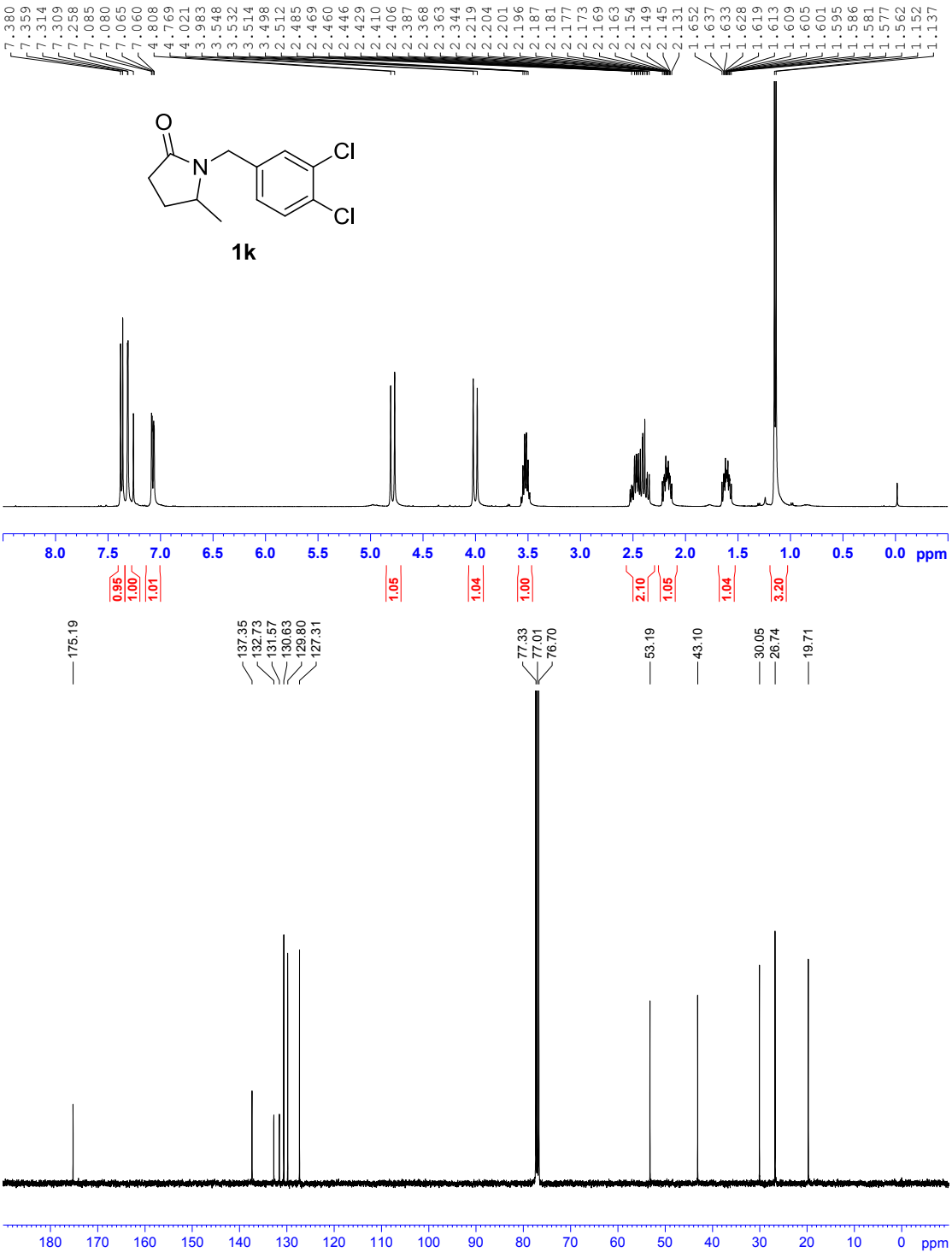
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7.065
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3.983
3.548
3.532
3.514
3.498
2.512
2.485
2.469
2.460
2.446
2.429
2.410
2.406
2.387
2.368
2.363
2.344
2.219
2.204
2.201
2.196
2.187
2.181
2.177
2.173
2.169
2.163
2.154
2.149
2.145
2.131
1.652
1.637
1.633
1.628
1.619
1.613
1.609
1.605
1.601
1.595
1.586
1.581
1.577
1.562
1.152
1.137
O
N
Cl
Cl
1k
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
0.95
1.00
1.01
1.05
1.04
1.00
2.10
1.05
1.04
3.20
175.19
137.35
132.73
131.57
130.63
129.80
127.31
77.33
77.01
76.70
53.19
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30.05
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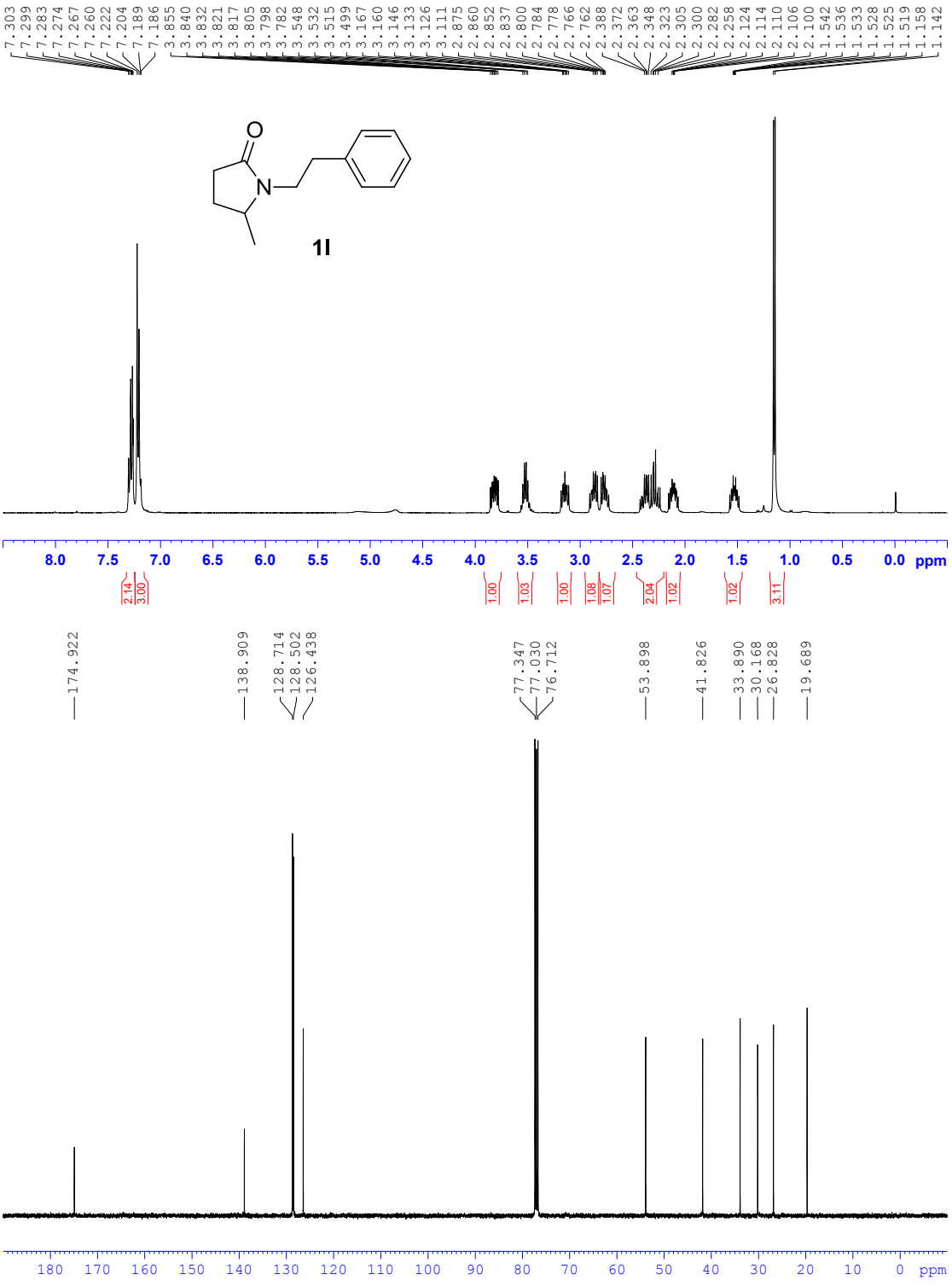
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3.832
3.821
3.817
3.805
3.798
3.782
3.548
3.532
3.515
3.499
3.167
3.160
3.146
3.133
3.126
3.111
2.875
2.860
2.852
2.837
2.800
2.784
2.778
2.766
2.762
2.388
2.372
2.363
2.348
2.323
2.305
2.300
2.282
2.258
2.124
2.114
2.110
2.106
2.100
1.542
1.536
1.533
1.528
1.525
1.519
1.158
1.142
O
N
1l
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
2.14
3.00
1.00
1.03
1.00
1.08
1.07
2.04
1.02
1.02
3.11
174.922
138.909
128.714
128.502
126.438
77.347
77.030
76.712
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41.826
33.890
30.168
26.828
19.689
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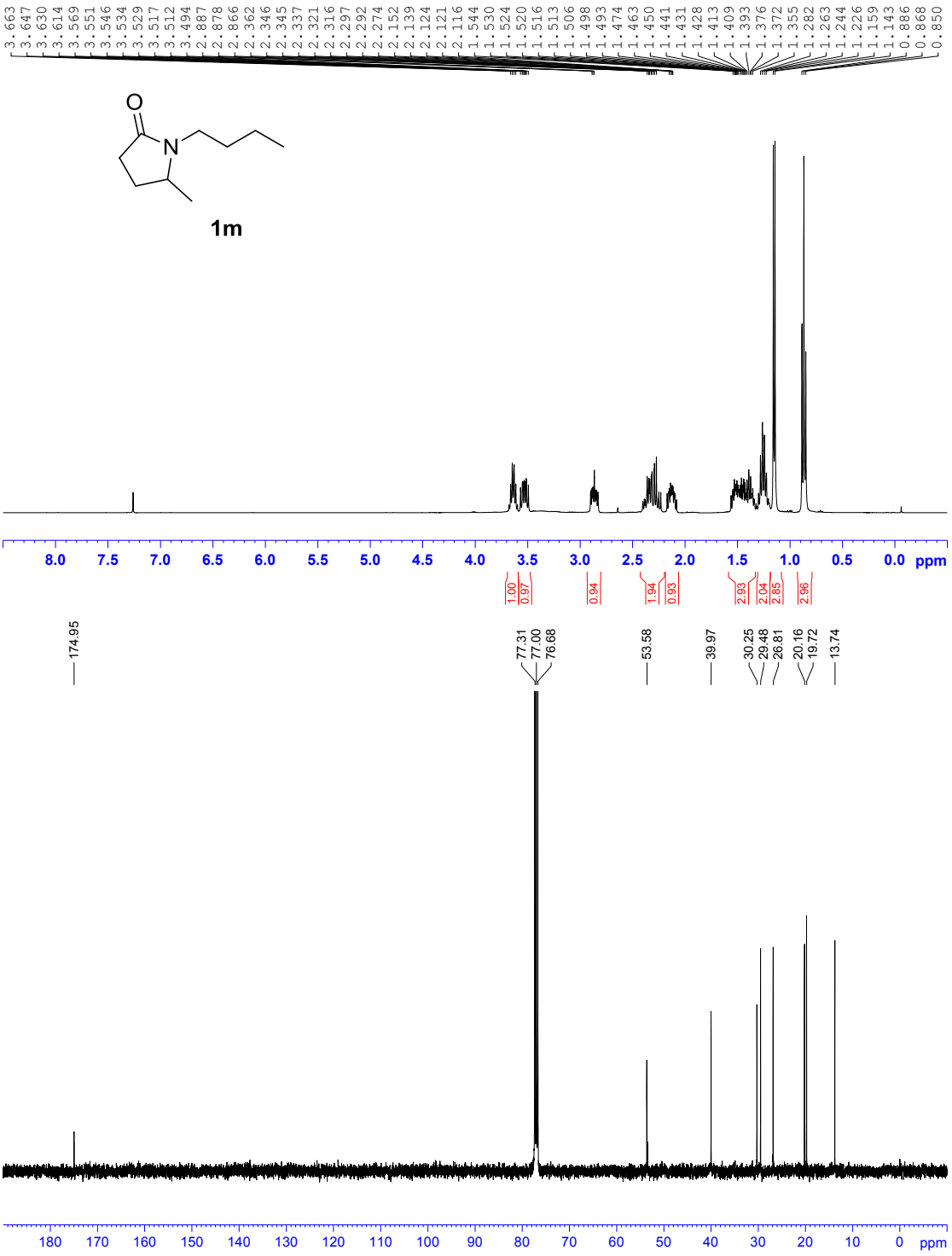
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3.534
3.529
3.517
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3.494
2.887
2.878
2.866
2.362
2.346
2.345
2.337
2.321
2.316
2.297
2.292
2.274
2.152
2.139
2.124
2.121
2.116
1.544
1.530
1.524
1.520
1.516
1.513
1.506
1.498
1.493
1.474
1.463
1.450
1.441
1.431
1.428
1.413
1.409
1.393
1.376
1.372
1.355
1.282
1.263
1.244
1.226
1.159
1.143
0.886
0.868
0.850
O
N
1m
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 0.97 0.94 1.94 0.93 2.93 2.04 2.85 2.96
174.95
77.31
77.00
76.68
53.58
39.97
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29.48
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20.16
19.72
13.74
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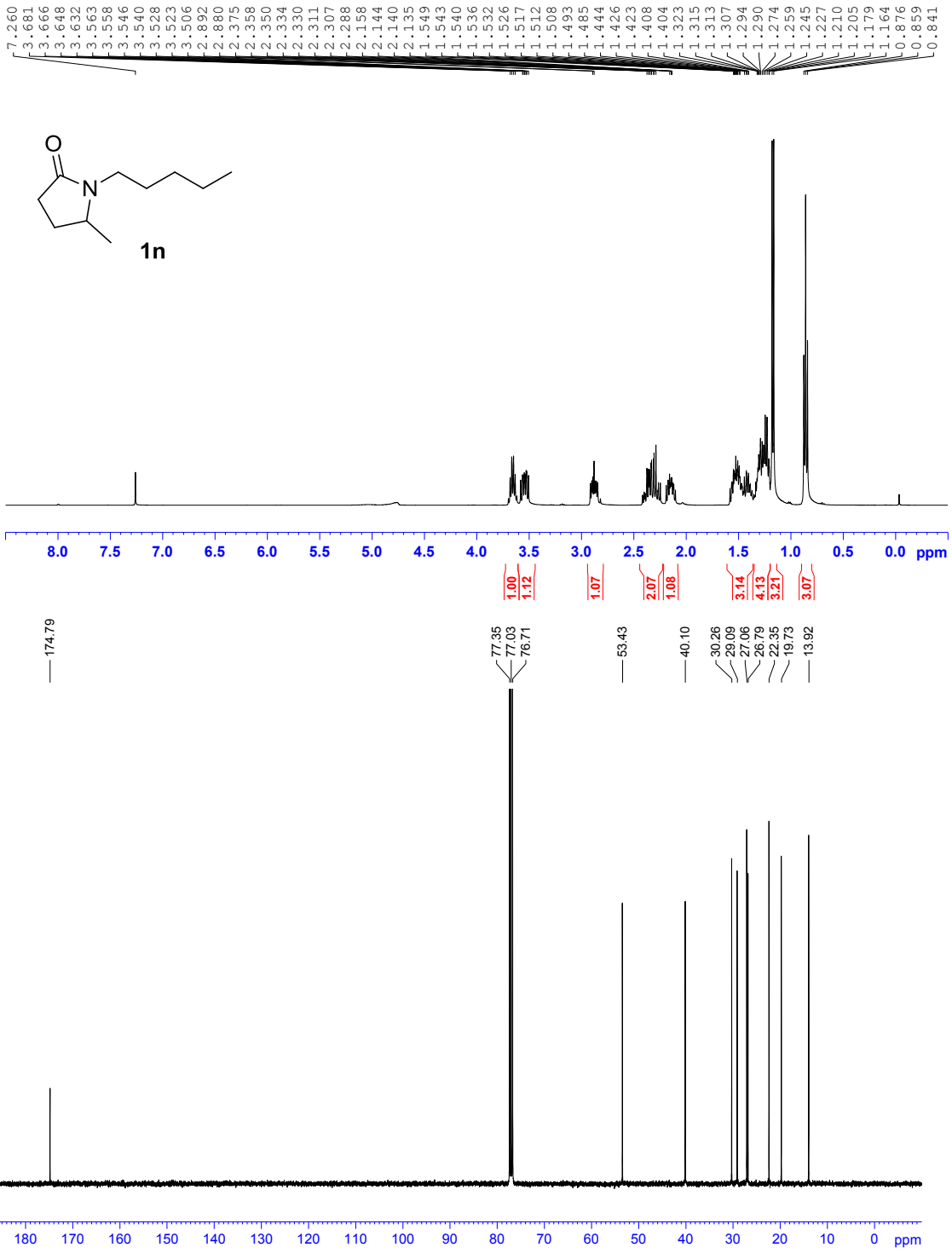
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3.546
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3.528
3.523
3.506
2.892
2.880
2.375
2.358
2.350
2.334
2.330
2.311
2.307
2.288
2.158
2.144
2.140
2.135
1.549
1.543
1.540
1.536
1.532
1.526
1.517
1.512
1.508
1.493
1.485
1.444
1.426
1.423
1.408
1.404
1.323
1.315
1.313
1.307
1.294
1.290
1.274
1.259
1.245
1.227
1.210
1.205
1.179
1.164
0.876
0.859
0.841
O
N
1n
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
1.12
1.07
2.07
1.08
3.14
4.13
3.21
3.07
174.79
77.35
77.03
76.71
53.43
40.10
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27.06
26.79
22.35
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13.92
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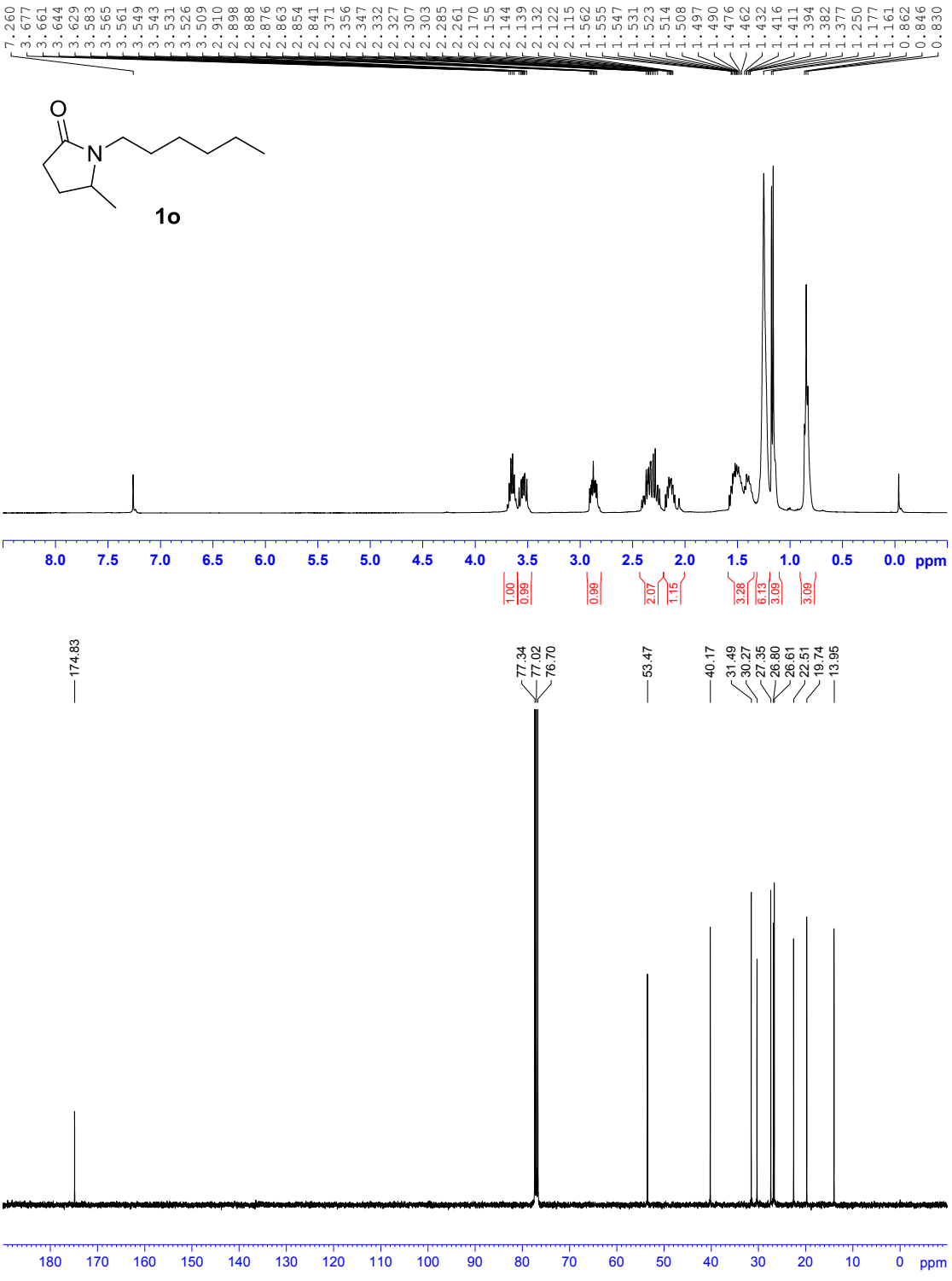
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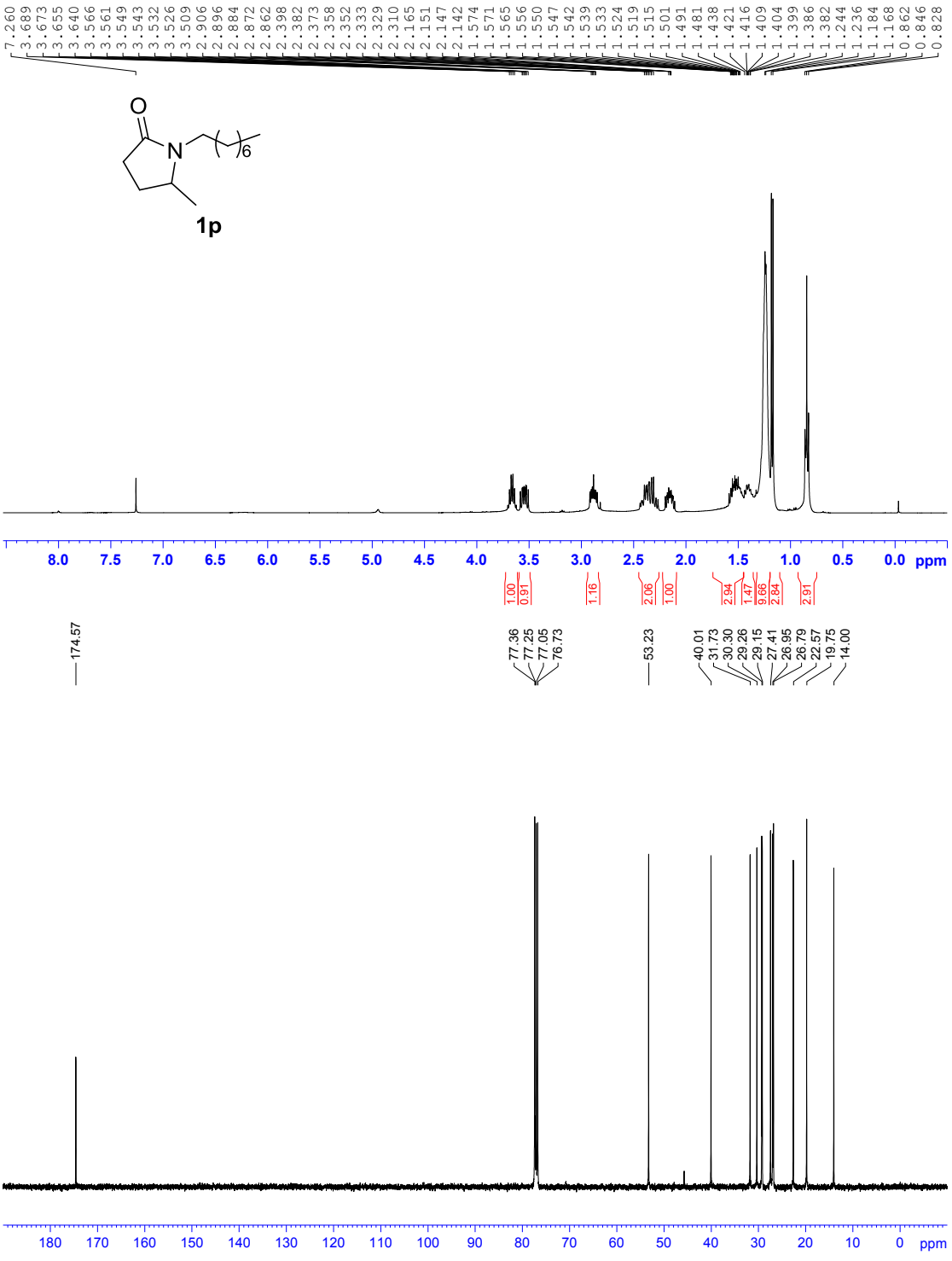
3.583
3.565
3.561
3.549
3.543
3.531
3.526
3.509
2.910
2.898
2.888
2.876
2.863
2.854
2.841
2.371
2.356
2.347
2.332
2.327
2.307
2.303
2.285
2.261
2.170
2.155
2.144
2.139
2.132
2.122
2.115
1.562
1.555
1.547
1.531
1.523
1.514
1.508
1.497
1.490
1.476
1.462
1.432
1.416
1.411
1.394
1.382
1.377
1.250
1.177
1.161
0.862
0.846
0.830
O
N
1o
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 0.99 0.99 2.07 1.15 3.28 6.13 3.09 3.09
174.83
77.34
77.02
76.70
53.47
40.17
31.49
30.27
27.35
26.80
26.61
22.51
19.74
13.95
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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3.566
3.561
3.549
3.543
3.532
3.526
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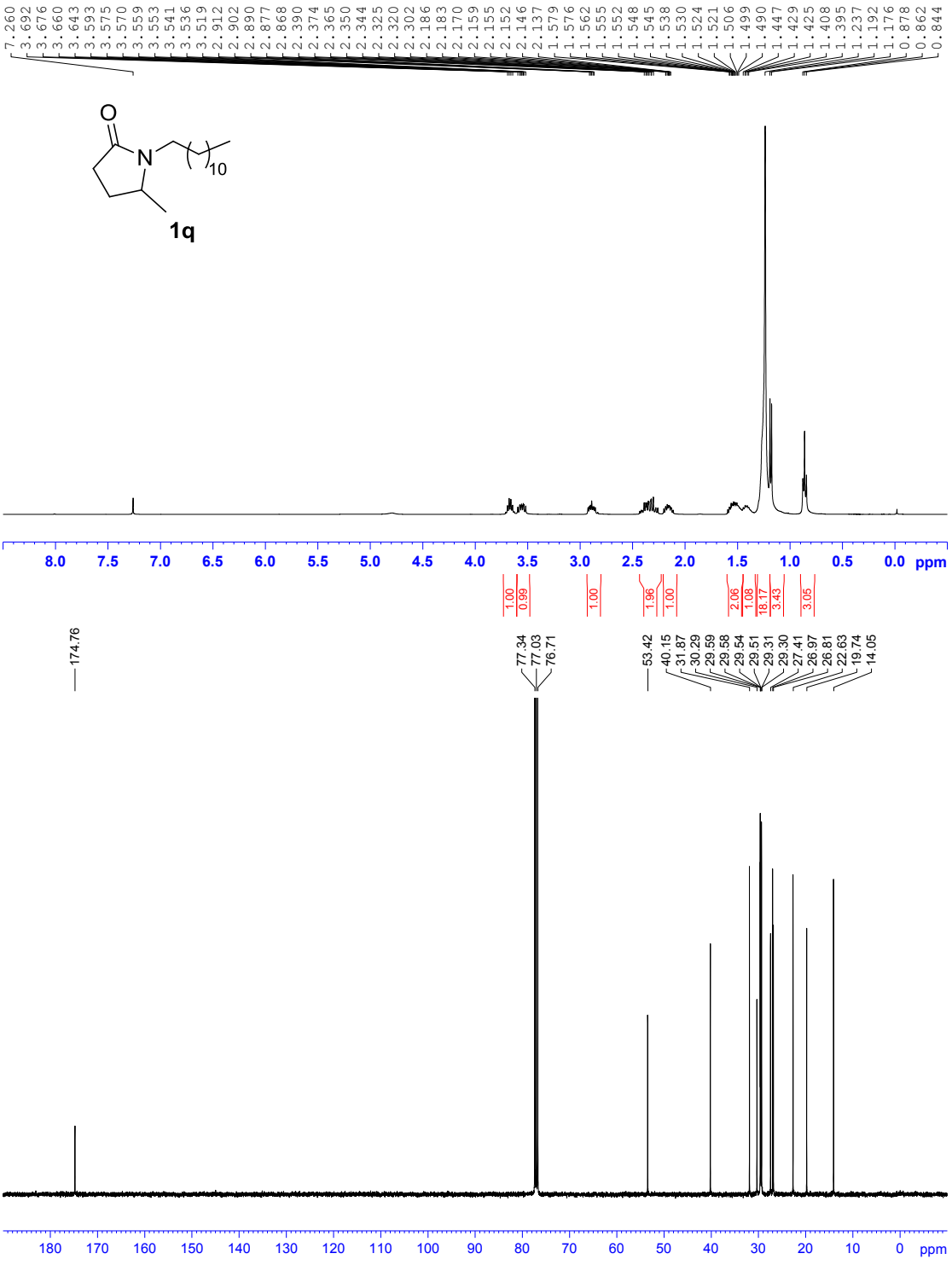
2.906
2.896
2.884
2.872
2.862
2.398
2.382
2.373
2.358
2.352
2.333
2.329
2.310
2.165
2.151
2.147
2.142
1.574
1.571
1.565
1.556
1.550
1.547
1.542
1.539
1.533
1.524
1.519
1.515
1.501
1.491
1.481
1.438
1.421
1.416
1.409
1.404
1.399
1.386
1.382
1.244
1.236
1.184
1.168
0.862
0.846
0.828
O
N
6
1p
8.0 7.5 7.0 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
0.91
1.16
2.06
1.00
2.94
1.47
9.66
2.84
2.91
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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3.570
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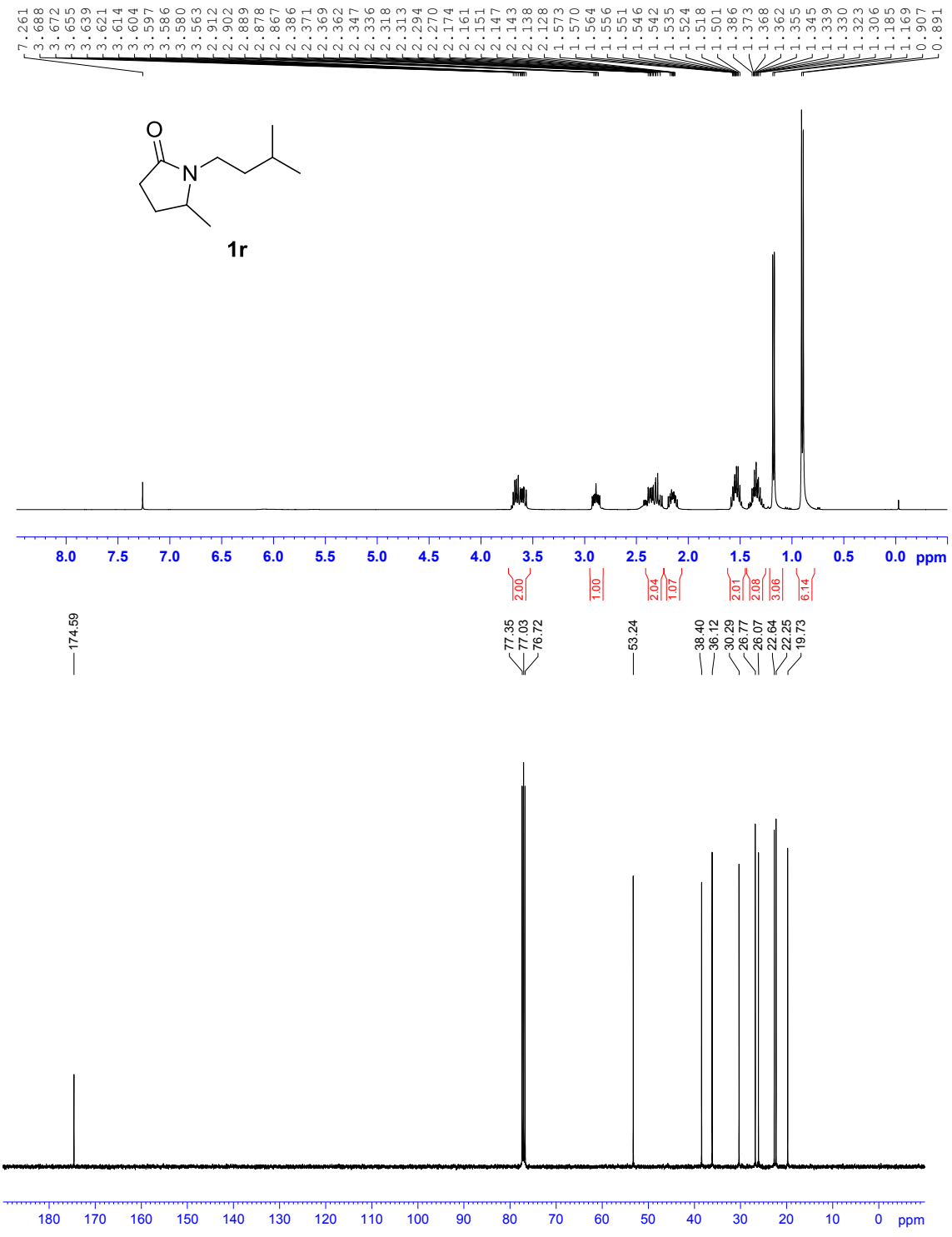
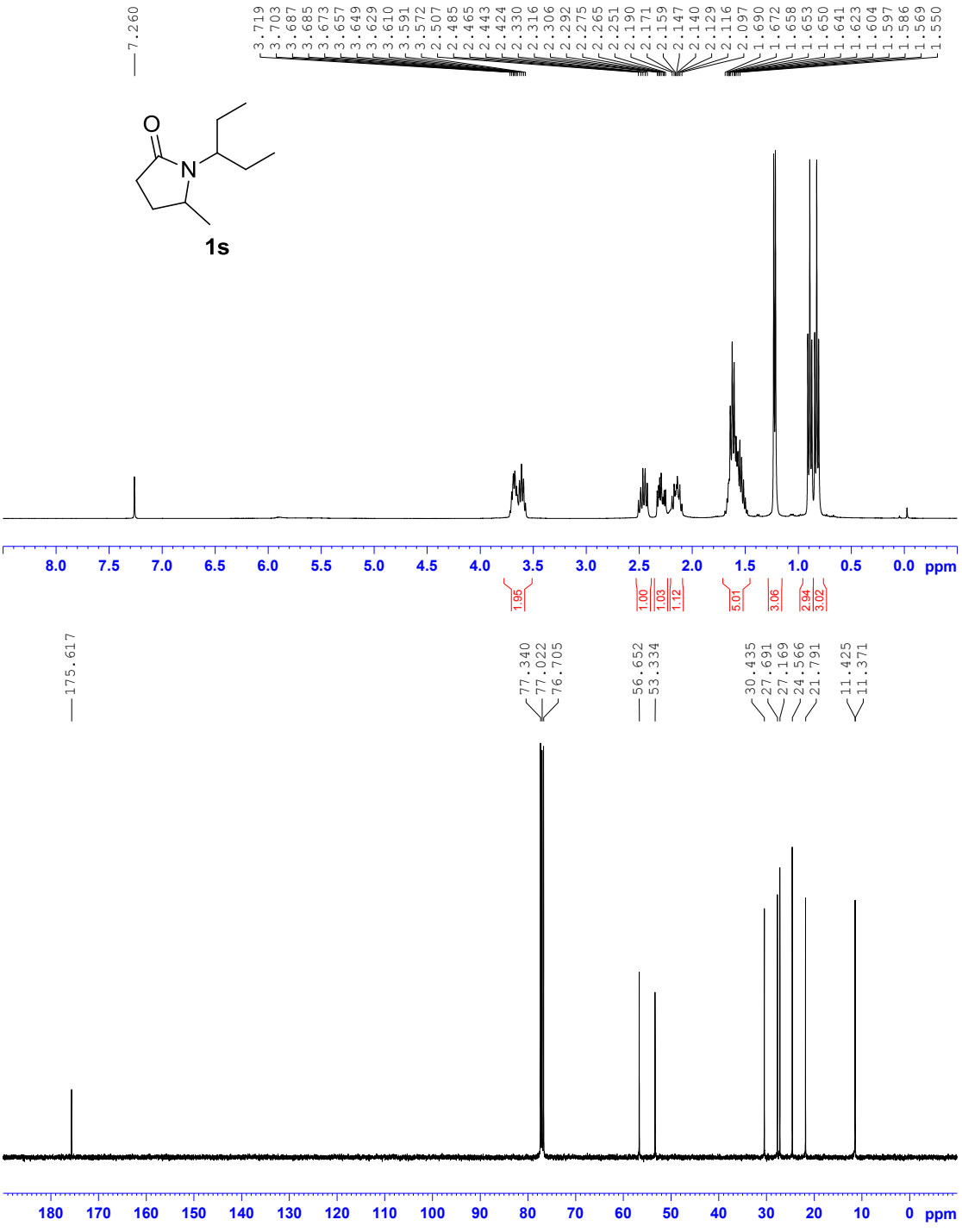
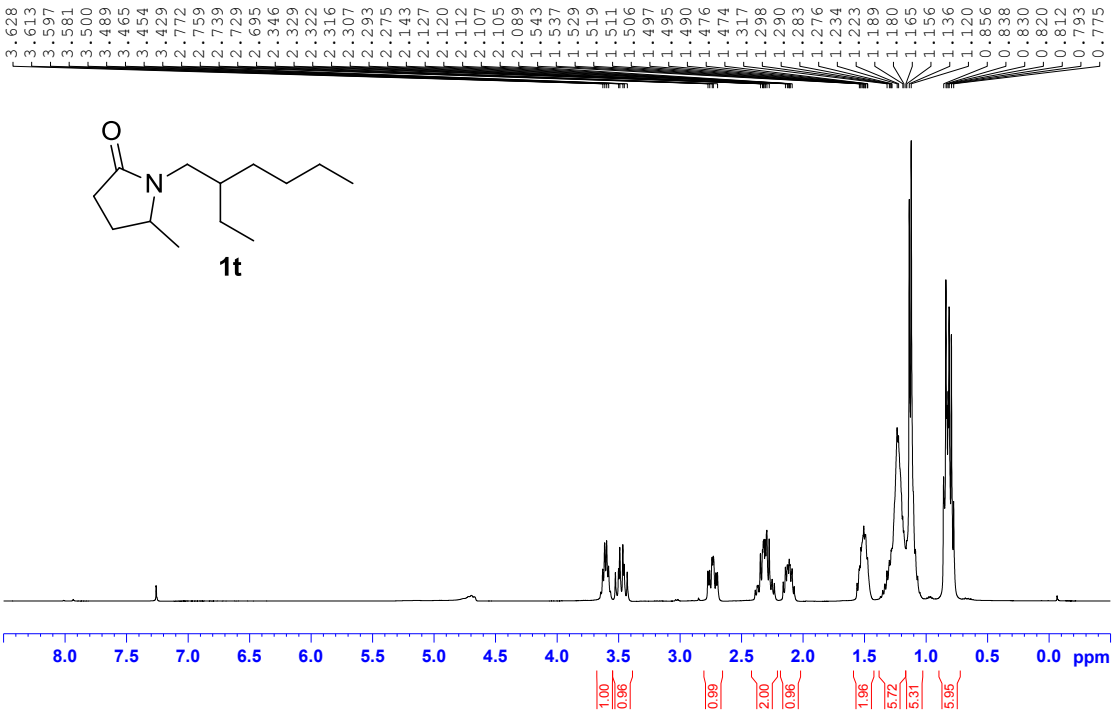
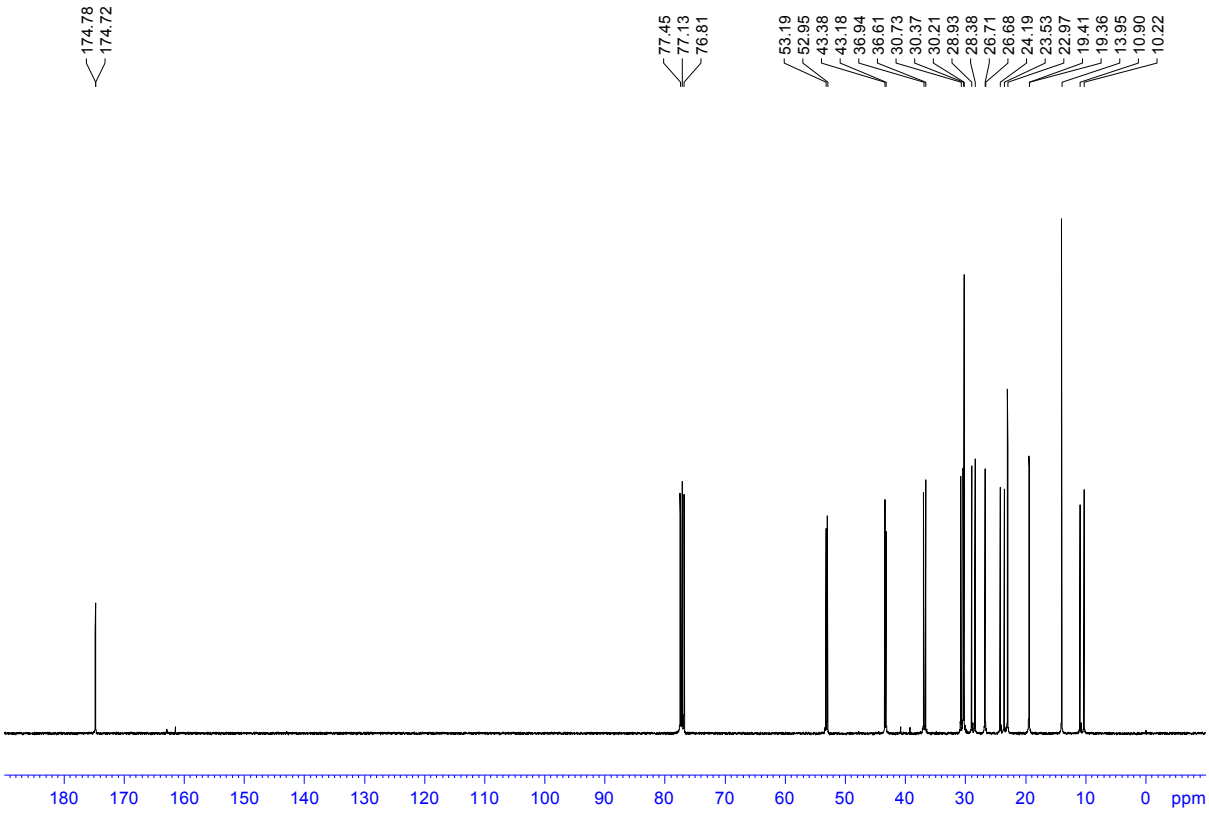
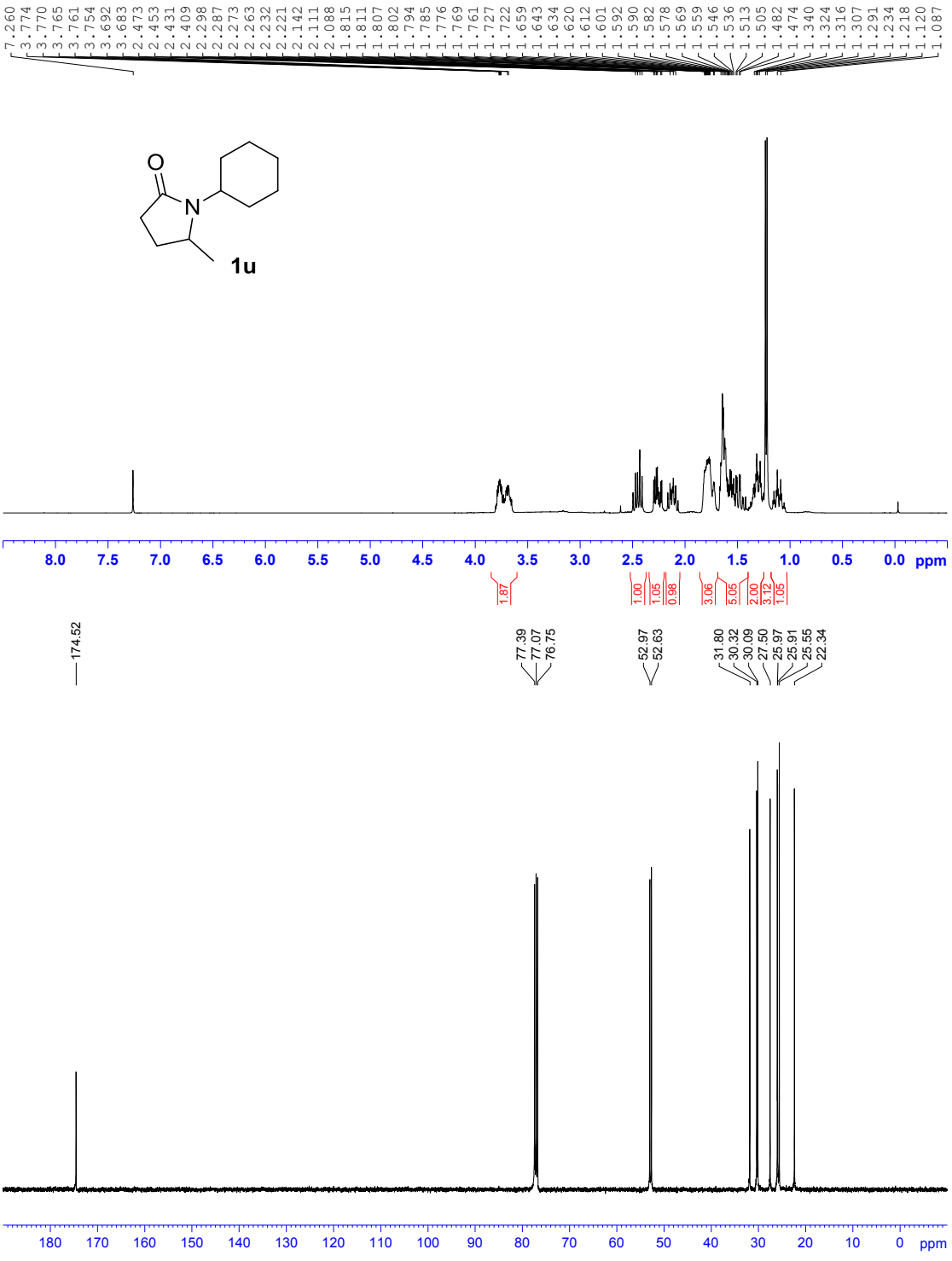
3.536
3.519
2.912
2.902
2.890
2.877
2.868
2.390
2.374
2.365
2.350
2.344
2.325
2.320
2.302
2.186
2.183
2.170
2.159
2.155
2.152
2.146
2.137
1.579
1.576
1.562
1.555
1.552
1.548
1.545
1.538
1.530
1.524
1.521
1.506
1.499
1.490
1.447
1.429
1.425
1.408
1.395
1.237
1.192
1.176
0.878
0.862
0.844
O
N
10
1q
8.0 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
0.99
1.00
1.96
1.00
2.06
1.08
18.17
3.43
3.05
174.76
77.34
77.03
76.71
53.42
40.15
31.87
30.29
29.59
29.58
29.54
29.51
29.31
29.30
27.41
26.97
26.81
22.63
19.74
14.05
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

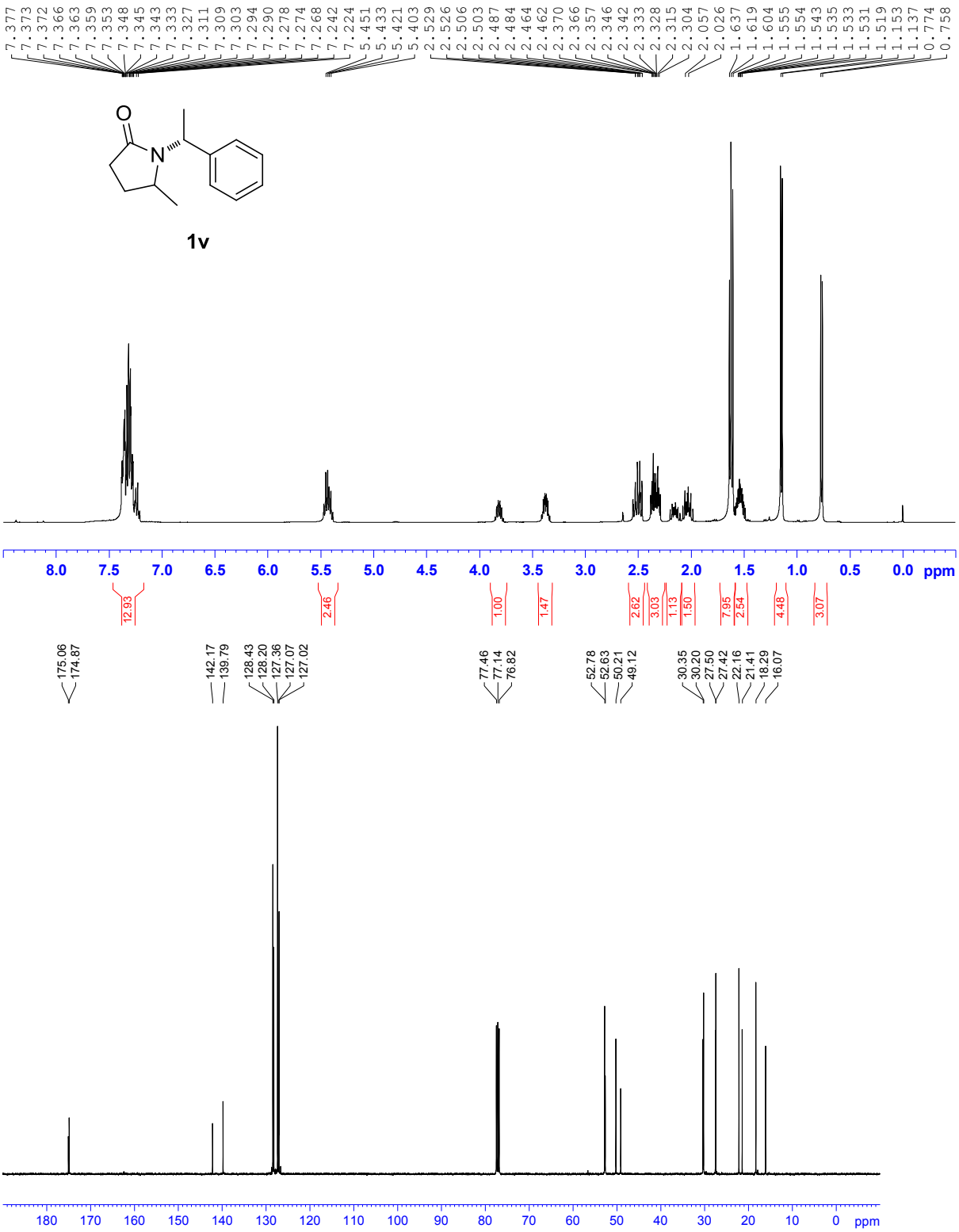


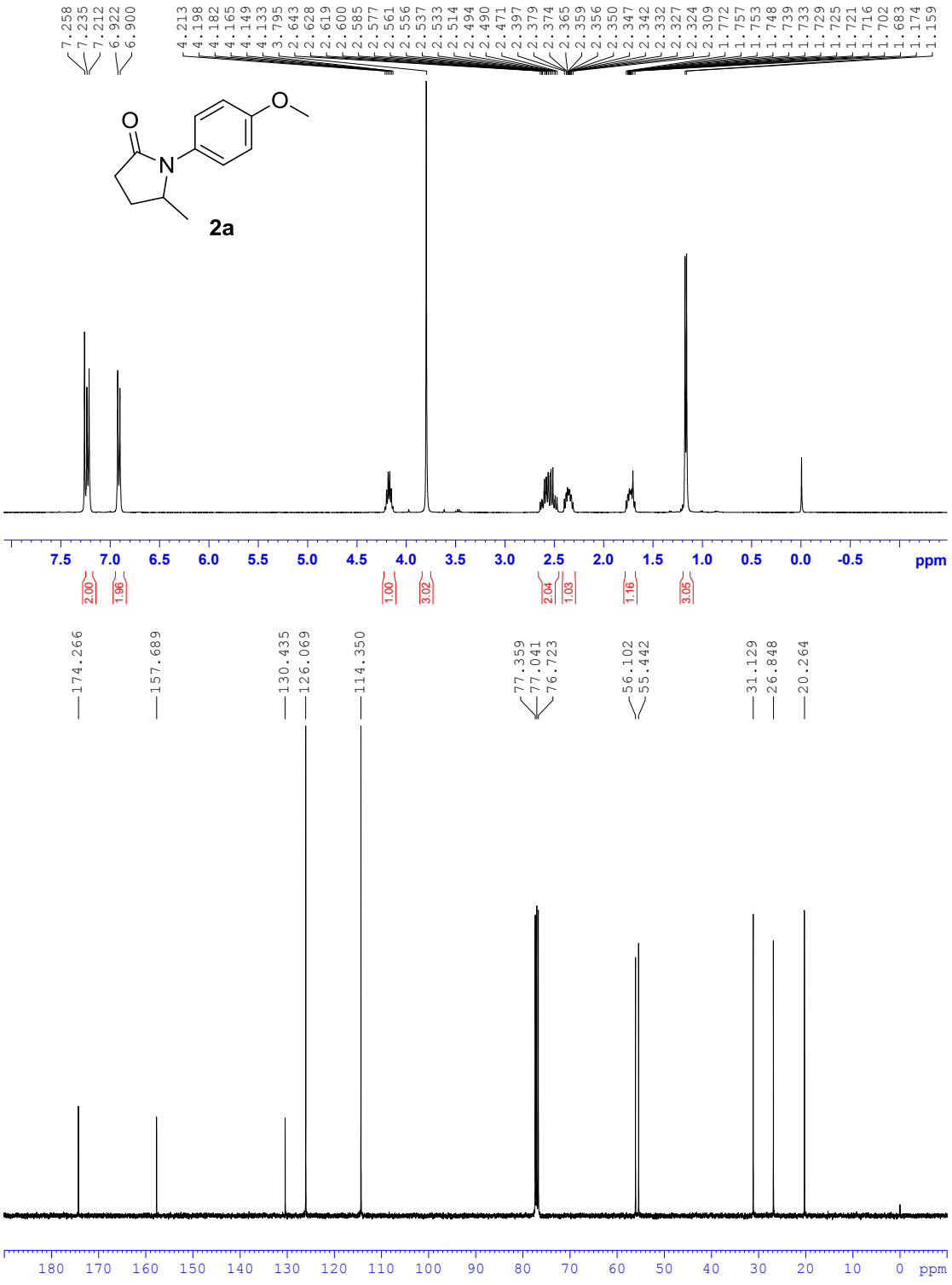








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6.900
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4.182
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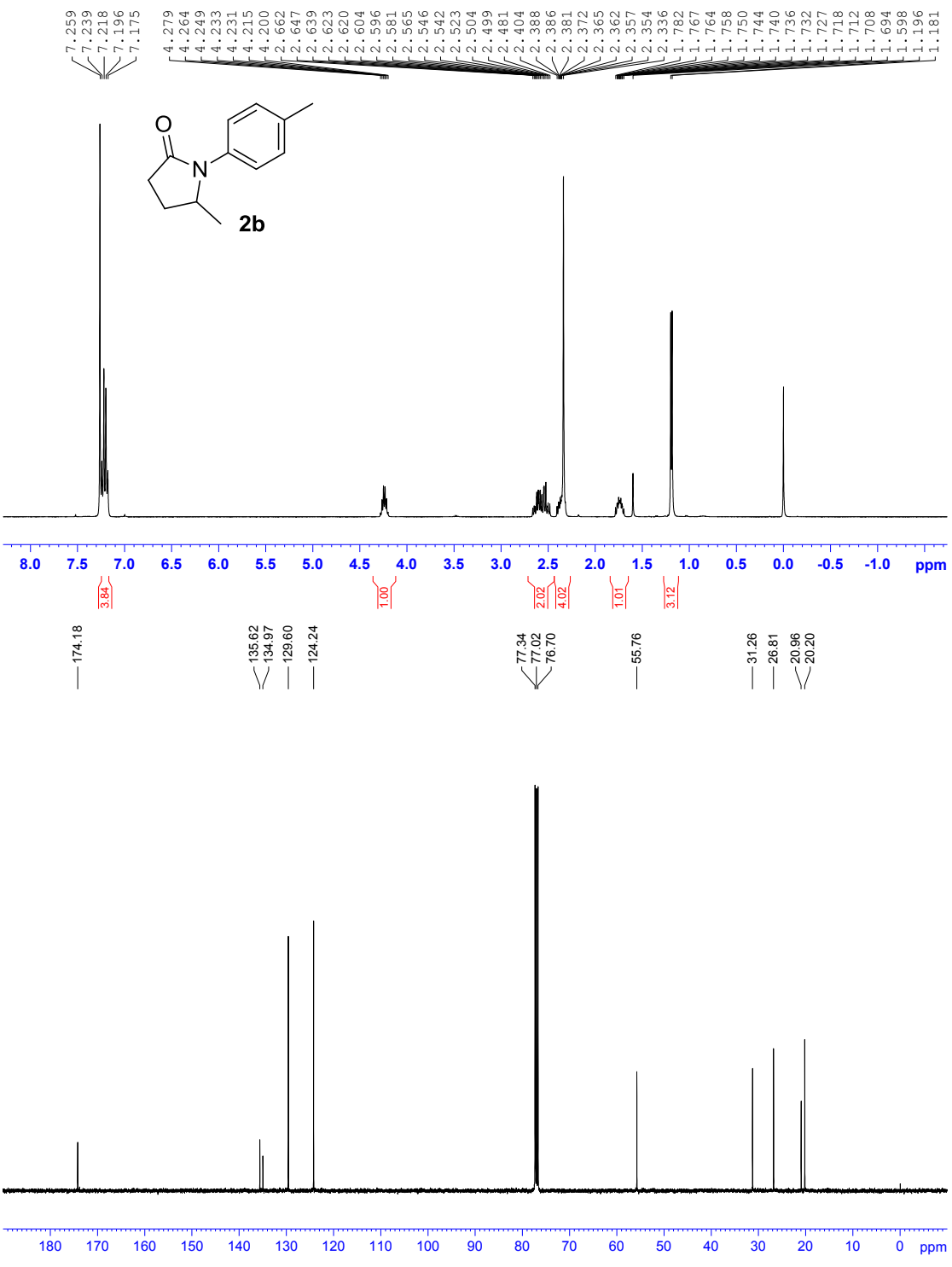
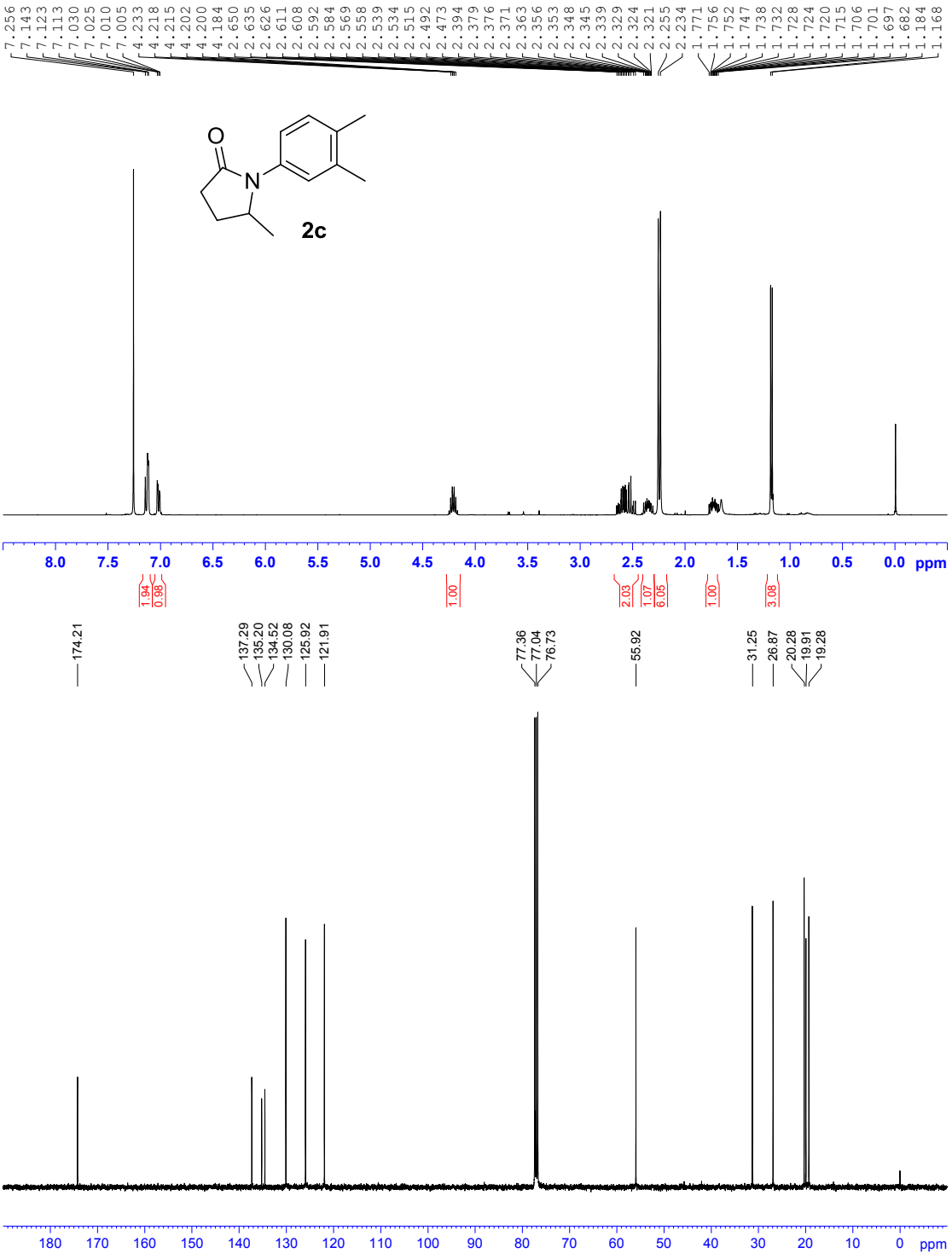
3.795
2.643
2.628
2.619
2.600
2.585
2.577
2.561
2.556
2.537
2.533
2.514
2.494
2.490
2.471
2.397
2.379
2.374
2.365
2.359
2.356
2.350
2.347
2.342
2.332
2.327
2.324
2.309
1.772
1.757
1.753
1.748
1.739
1.733
1.729
1.725
1.721
1.716
1.702
1.683
1.174
1.159
O
O
N
2a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.00
1.96
1.00
3.02
2.04
1.03
1.16
3.05
174.266
157.689
130.435
126.069
114.350
77.359
77.041
76.723
56.102
55.442
31.129
26.848
20.264
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

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7.123
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7.025
7.010
7.005
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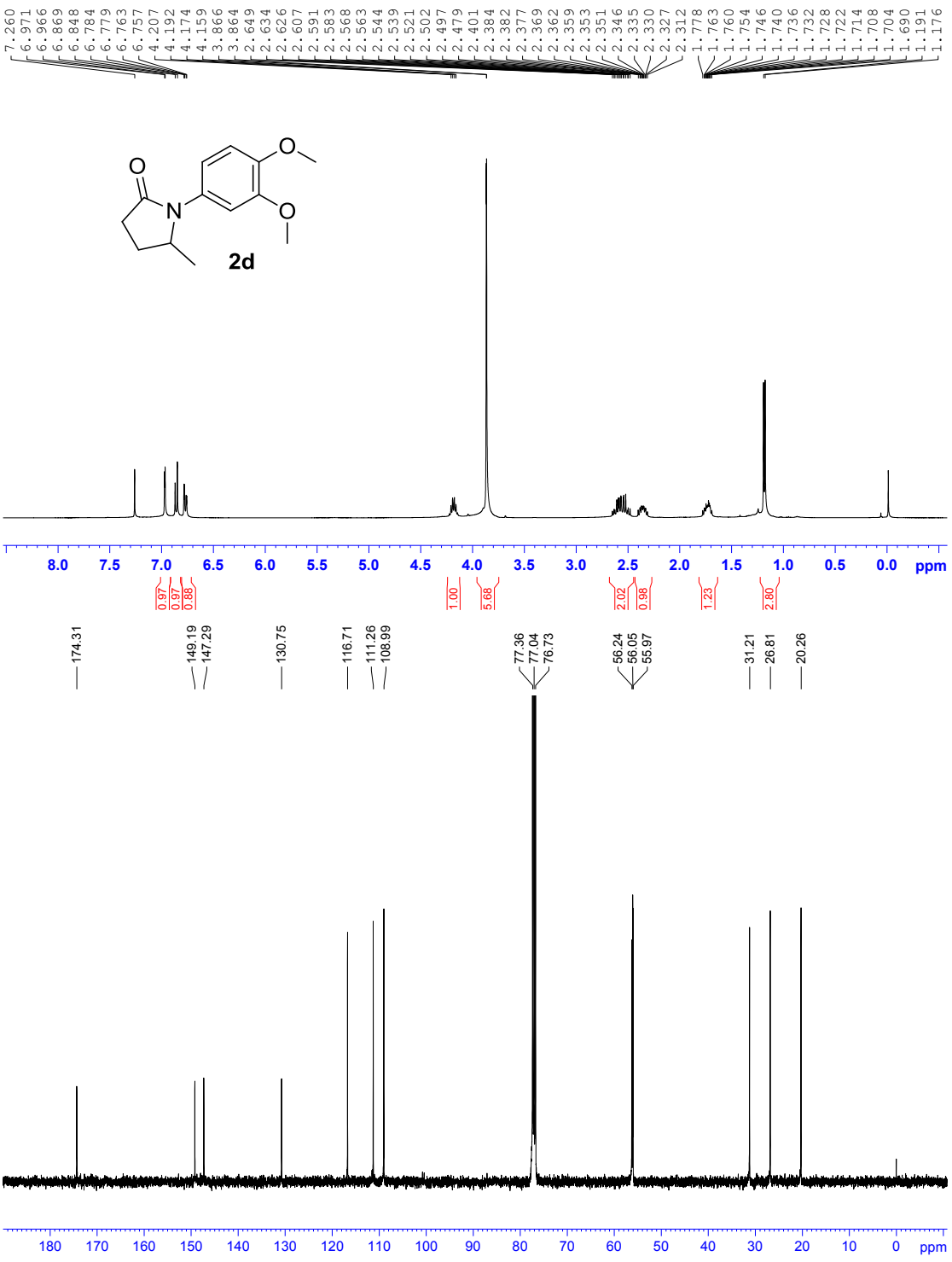
4.218
4.215
4.202
4.200
4.184
2.650
2.635
2.626
2.611
2.608
2.592
2.584
2.569
2.558
2.539
2.534
2.515
2.492
2.473
2.394
2.379
2.376
2.371
2.363
2.356
2.353
2.348
2.345
2.339
2.329
2.324
2.321
2.255
2.234
1.771
1.756
1.752
1.747
1.738
1.732
1.728
1.724
1.720
1.715
1.706
1.701
1.697
1.682
1.184
1.168
O
N
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 ppm
1.94
0.98
1.00
2.03
1.07
6.05
1.00
3.08
174.21
137.29
135.20
134.52
130.08
125.92
121.91
77.36
77.04
76.73
55.92
31.25
26.87
20.28
19.91
19.28
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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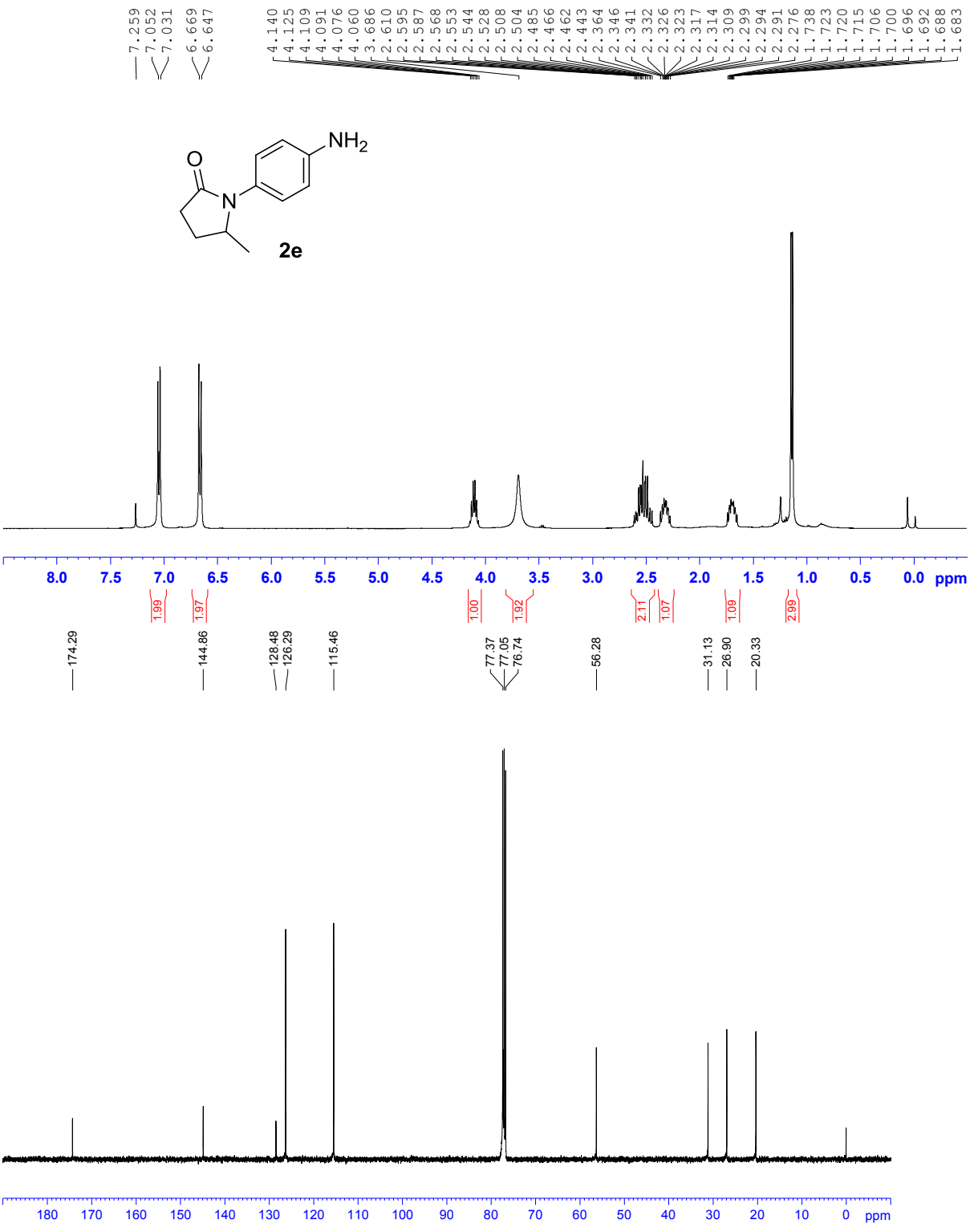
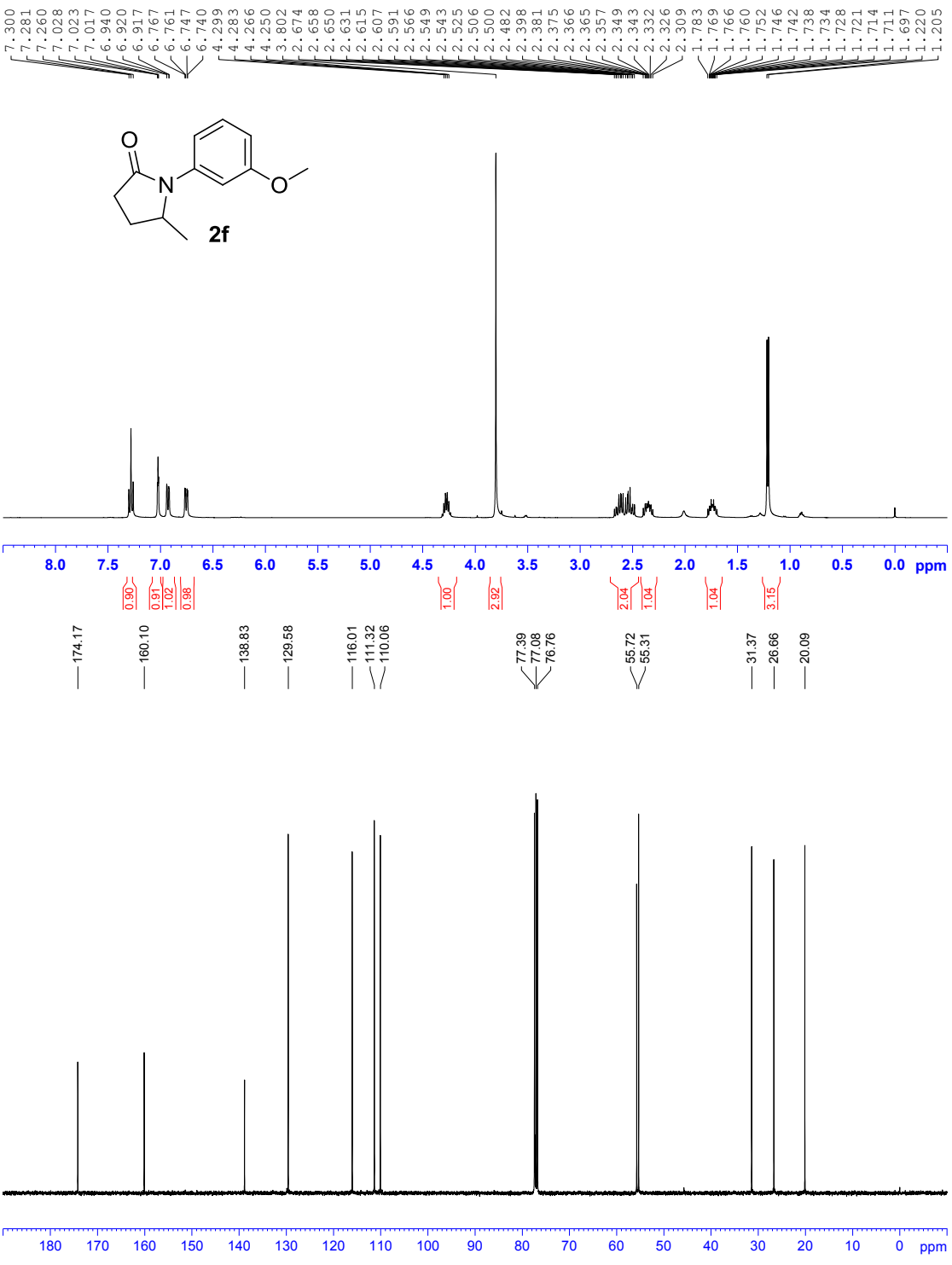
6.763
6.757
4.207
4.192
4.174
4.159
3.866
3.864
2.649
2.634
2.626
2.607
2.591
2.583
2.568
2.563
2.544
2.539
2.521
2.502
2.497
2.479
2.401
2.384
2.382
2.377
2.369
2.362
2.359
2.353
2.351
2.346
2.335
2.330
2.327
2.312
1.778
1.763
1.760
1.754
1.746
1.740
1.736
1.732
1.728
1.722
1.714
1.708
1.704
1.690
1.191
1.176
O
O
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
ppm
0.97
0.97
0.88
1.00
5.68
2.02
0.98
1.23
2.80
174.31
149.19
147.29
130.75
116.71
111.26
108.99
77.36
77.04
76.73
56.24
56.05
55.97
31.21
26.81
20.26
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

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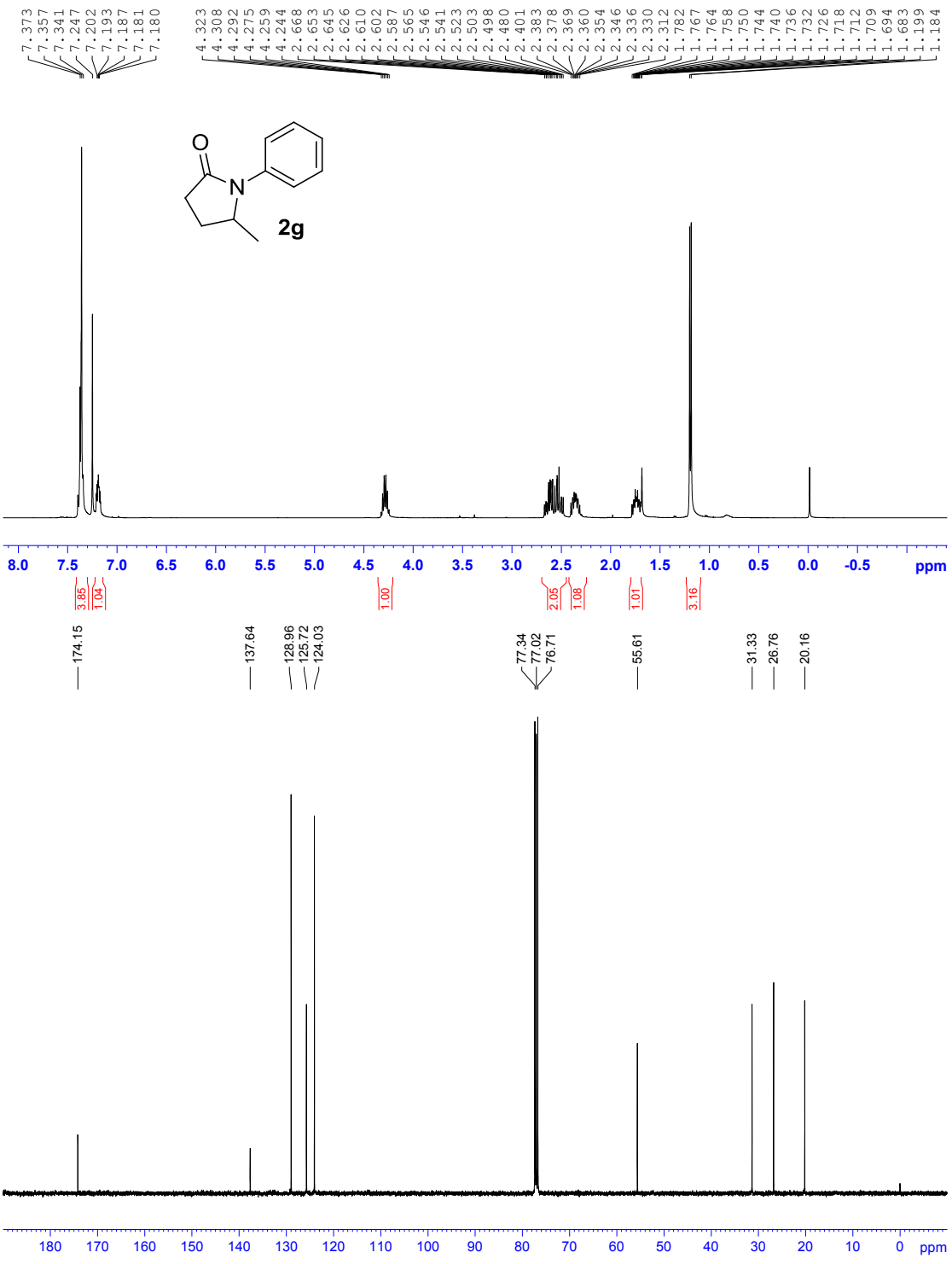
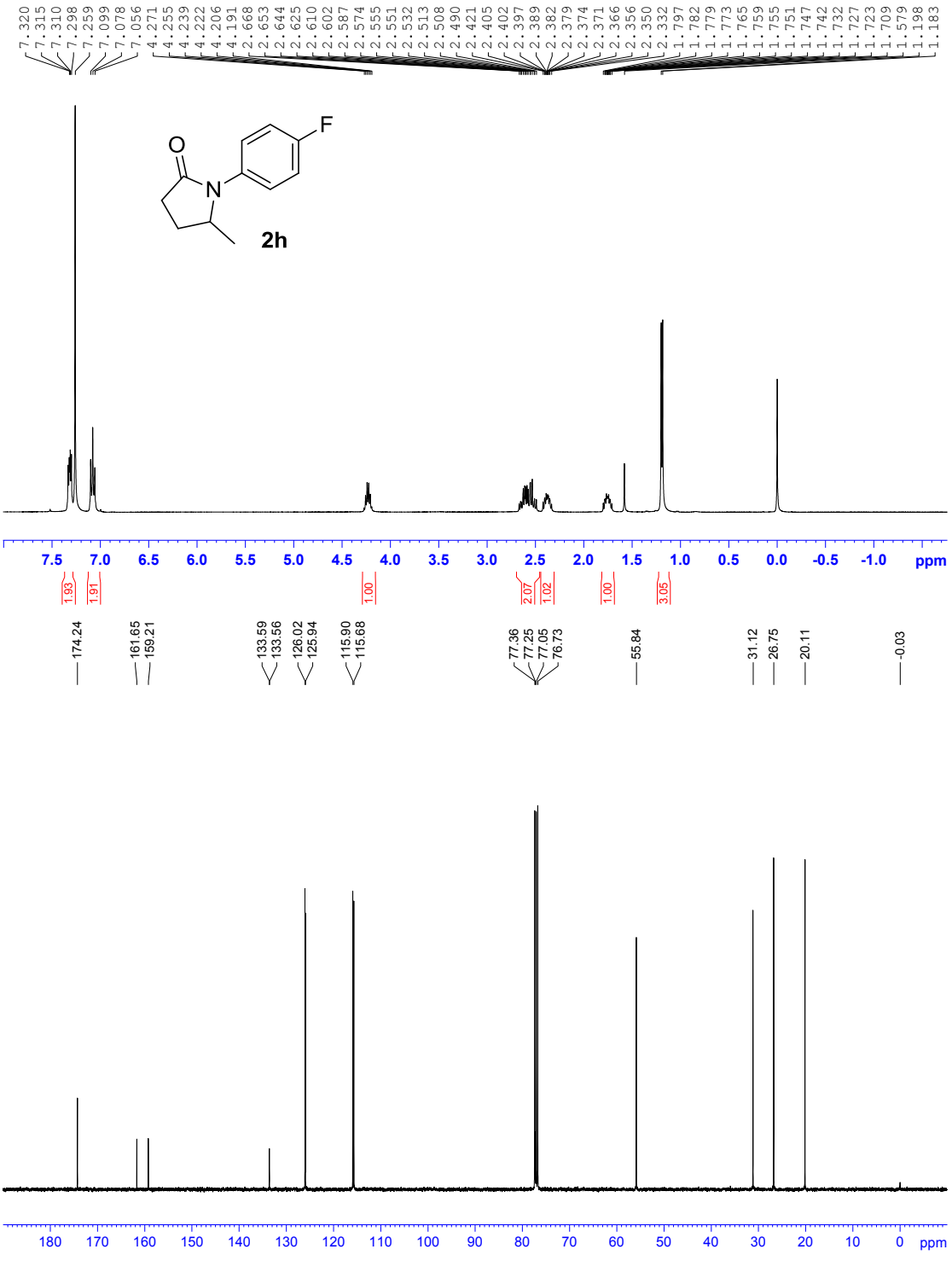
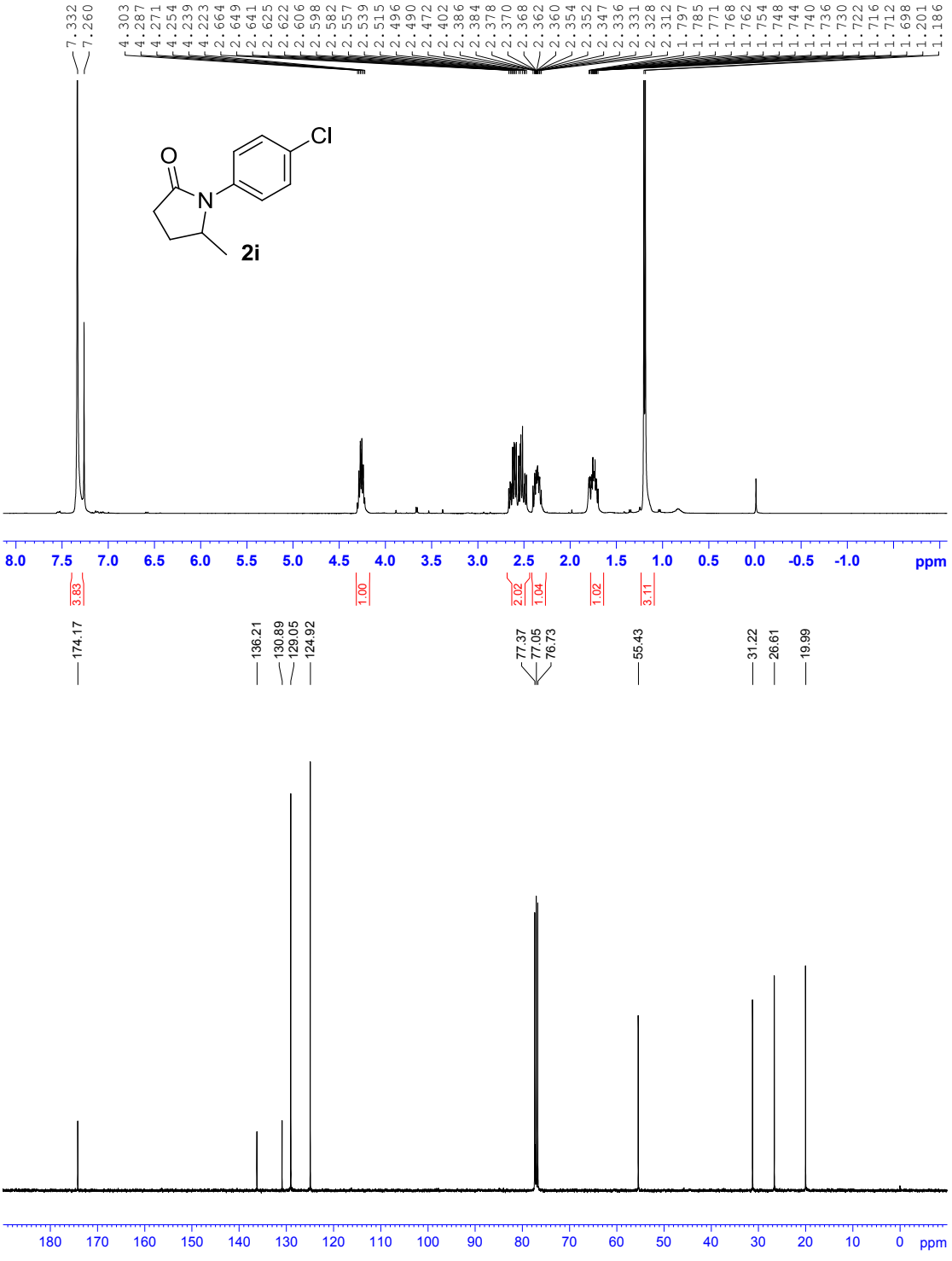
7.017
6.940
6.920
6.917
6.767
6.761
6.747
6.740
4.299
4.283
4.266
4.250
3.802
2.674
2.658
2.650
2.631
2.615
2.607
2.591
2.566
2.549
2.543
2.525
2.506
2.500
2.482
2.398
2.381
2.375
2.366
2.365
2.357
2.349
2.343
2.332
2.326
2.309
1.783
1.769
1.766
1.760
1.752
1.746
1.742
1.738
1.734
1.728
1.721
1.714
1.711
1.697
1.220
1.205
O
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 ppm
0.90
0.91
1.02
0.98
1.00
2.92
2.04
1.04
1.04
3.15
174.17
160.10
138.83
129.58
116.01
111.32
110.06
77.39
77.08
76.76
55.72
55.31
31.37
26.66
20.09
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



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4.223
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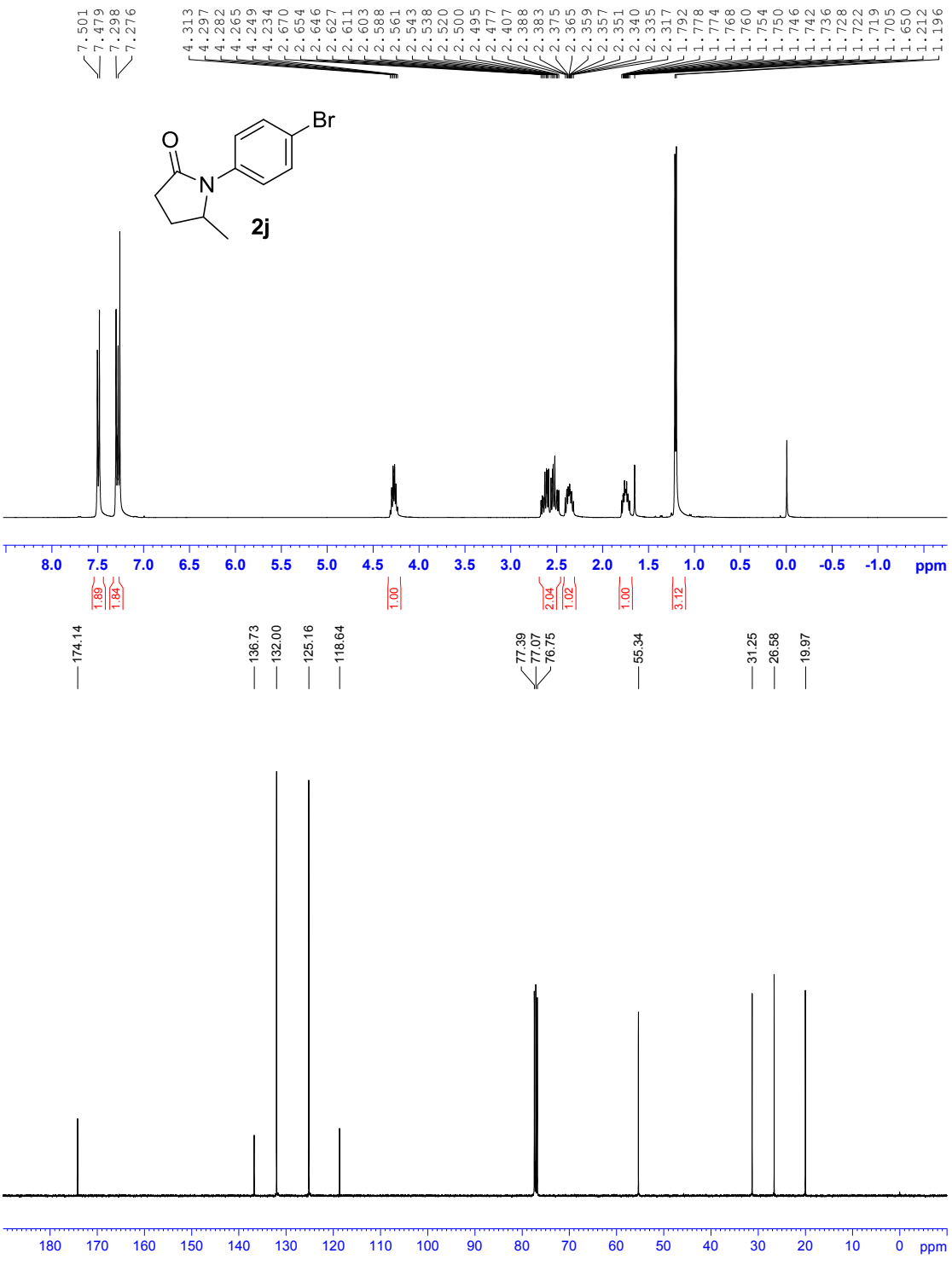
2.622
2.606
2.598
2.582
2.557
2.539
2.515
2.496
2.490
2.472
2.402
2.386
2.384
2.378
2.370
2.368
2.362
2.360
2.354
2.352
2.347
2.336
2.331
2.328
2.312
1.797
1.785
1.771
1.768
1.762
1.754
1.748
1.744
1.740
1.736
1.730
1.722
1.716
1.712
1.698
1.201
1.186
Cl
O
N
2i
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
ppm
3.83
1.00
2.02
1.04
1.02
3.11
174.17
136.21
130.89
129.05
124.92
77.37
77.05
76.73
55.43
31.22
26.61
19.99
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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4.234
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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
1.650
1.212
1.196
Br
O
N
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 -0.5 -1.0 ppm
1.89
1.84
1.00
2.04
1.02
1.00
3.12
174.14
136.73
132.00
125.16
118.64
77.39
77.07
76.75
55.34
31.25
26.58
19.97
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm