Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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Supporting Information for:

Biomimetic Rabe amination after a century: direct addition of *N*-heterocycles to carbonyl compounds.

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1. General methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded at 400 MHz or 300 MHz and 100 Mz or 75 Mz. Chemical shifts are reported in ppm relative to the resonance of $CHCl_3$ (δ = 7.26) for ^{1}H-NMR and to the central peak of $CDCl_3$ (δ = 77.0) for ^{13}C-NMR. Flash chromatography (FC) was carried out using Merck silica gel 60 (230-400 mesh) as stationary phase and mixtures of petroleum ether 30-50 °C (PE), dichloromethane, ethyl acetate and methanol. Enantiomeric excesses (ee) of the products were determined by HPLC, using a CHIRALPAK IC column and a LC-20AT Shimadzu pump with a SPD-M-20A Shimadzu diode array detector.

1.1 Materials

Ketones **1a-i**, aldehydes **4a-d**, catalyst **I**, solvents and amines, employed in the synthesis of the *N*-chloroamines **2a-b**, are commercially available and were used as received.

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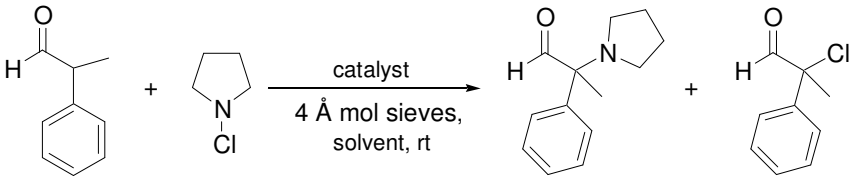
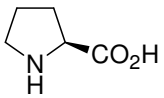
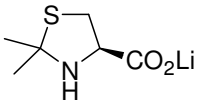
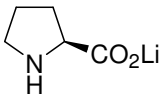
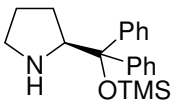
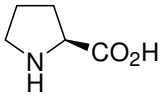
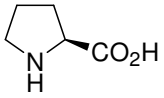
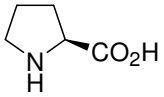
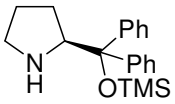
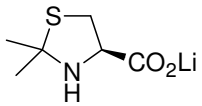
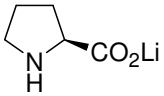
2. Additional screening results

TABLE 3. Organocatalyzed addition of hydratropaldehyde 4a to *N*-chloro pyrrolidine 2b



4a **2b** **5b** **6b**

Entry[a]	Catalyst	Solvent	Yield of **5b** (%)[b]	*Ee* (%)[c]
1[d]	 **I**	Toluene	40	-
2[d]	 **II**	Toluene	22	-
3[d]	 **III**	Toluene	15	-
4[d]	 **IV**	Toluene	10	-
5	 **I**	Toluene	45	12
6	 **I**	DMSO	63	-
7	 **I**	Iodobenzene	47	13

8	 **IV**	Toluene	35	-
9	 **II**	Toluene	-	-
10	 **III**	Toluene	55	-

[a] Reactions are run employing 50 mg of **4a**, 1.5 equiv of **2b**, 1 equiv of the catalyst and 1 mL of the solvent; reaction times: 2-24h. [b] Isolated yield of **5b** determined after purification *via* FC. [c] *Ee* determined by HPLC on a chiral stationary phase: *n*-hexane / *i*-propanol 94:6, IC Chiralpak column, flow 0.9mL/min. FC. [d] Reactions are run employing 0.3 equiv of the catalyst and without molecular sieves.

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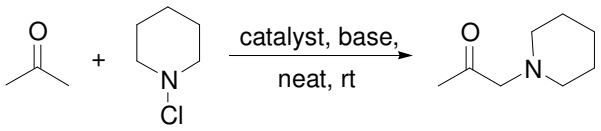
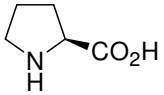
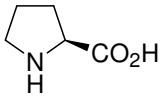
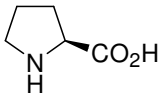
TABLE 4. Addition of acetone 1a to *N*-chloro piperidine 2a employing different bases



1a **2a** **3a**

Entry[a]	Catalyst	Base	Yield of **5b** (%)[b]
1	 **I**	Et_3N	63
2	 **I**	DBU	Complex mixture
3	-	K_2CO_3	No reaction
4	 **I**	K_2CO_3	11
5	-	Na_2CO_3 x H_2O	No reaction
6	-	$KHCO_3$	No reaction

[a] Reactions are run employing 200 mg of **2a**, 1 mL of **1a**, 0.3 equiv of the catalyst (if used) and 2 equiv of the base; reaction times: 18-24h. [b] Isolated yield of **5b** determined after purification *via* FC.

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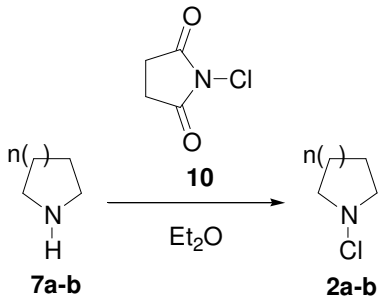
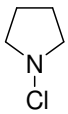
3. General procedure for the preparation of of *N*-chloroamines 2a-b



To a mixture of *N*-chlorosuccinimide **10** (3.782 g, 27.9 mmol, 1.1 eq) in Et_2O (125 mL), the amine **7a-b** (25.2 mmol, 1 eq) is added dropwise at room temperature. The reaction is left under stirring until substrate **7a-b** is totally consumed (TLC, about three hours). The precipitate is then removed by filtration and washed with Et_2O (25 mL); the combined organic phases are washed with water (3 x 25 mL) and dried with anhydrous sodium sulfate. The solvent is removed in vacuo and the chlorinated compound is obtained as a liquid.

Due to the well-known thermal instability of chlorinated amines, the solvent must be removed without heating.

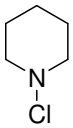


2a

2a.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.1-3.0 (m, 4H), 1.9-1.7 (m, 4H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 62.6, 22.3.



2b

2b.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.7-2.4 (m, 4H), 1.7-1.5 (m, 4H), 1.5-1.1 (m, 2H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 63.6, 27.3, 22.7.

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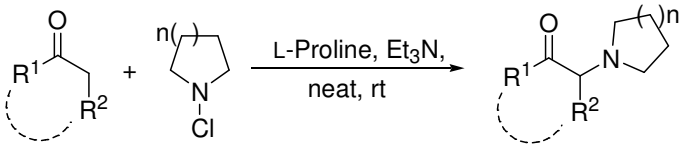
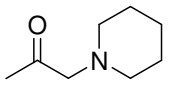
4. General procedure for the preparation of compounds 3a-i



1a-f **2a-b** **3a-i**

To a mixture of L-proline **I** (0.3 eq) in a ketone (1 mL), triethylamine (1 mL) is added. Then the mixture is cooled to 0°C, the *N*-chloroamine **2a-b** (200 mg, 1 eq) is added dropwise and the reaction is left warming up with stirring. The reaction is monitored by TLC (AcOEt/MeOH 5:1) until the substrate is totally converted (TLC traces revealable by $KMnO_4$ stain).

When there is no more *N*-chloroamine left, the reaction is diluted with a saturated water solution of NaCl and a saturated water solution of $NaHCO_3$. The acqueous phase is extracted three times with AcOEt and the combined organic phases are dried with anhydrous sodium sulphate. The solvent is removed in vacuo and the mixture is loaded on a chromatographic column filled with silica gel and packed with a mixture of petroleum ether and AcOEt 10:1 (eluant PE:AcOEt from 10:1 to 1:2 first, then AcOEt and AcOEt/MeOH from 10:1 to 3:1). Removal of the solvent in vacuo provides products **3a-i** as yellowish-reddish oils.



3a

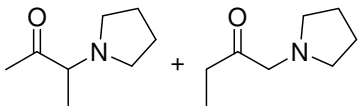
3a. Isolated yield: 45%; reaction time: 18h; Table 1, entry 1.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.07 (s, 2H), 2.4-2.3 (m, 4H), 2.09 (s, 3H), 1.7-1.5 (m, 4H), 1.4-1.3 (m, 2H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 207.4, 69.1, 54.7, 27.5, 25.6, 23.8.

HRMS calculated $C_8H_{16}NO$: 142.1232; found 142.1237.

.



3b **3b'**

3b+3b'. Isolated yield (mixture of the two regioisomers): 58%; reaction time: 12 days; Table 1, entry 2.

^{1}H-NMR (300 MHz) δ ($CDCl_3$) (mixture of **3d** and **3d'**): 3.30 (s, 2H), 2.86 (q, 1H, J = 6.9 Hz), 2.6-2.3 (m, 10H), 2.10 (s, 3H), 1.8-1.6 (m, 8H), 1.18 (d, 3H, J = 6.9 Hz), 0.99 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 209.0, 208.7, 69.9, 64.9, 54.1, 51.4, 33.4, 25.5, 23.5, 23.3, 15.8, 7.6.

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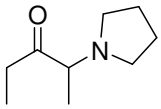
HRMS calculated $C_8H_{16}NO$: 142.1232; found 142.1227.



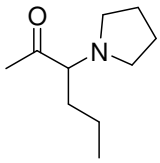
3c

3c. Isolated yield: 35%; reaction time: 14 days Table 1, entry 3.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 2.97 (q, 1H, J = 6.9 Hz), 2.7-2.4 (m, 6H), 1.9-1.7 (m, 4H), 1.22 (d, 3H, J = 6.9 Hz), 1.03 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.6, 69.3, 51.5, 31.6, 23.4, 16.0, 7.8.

HRMS calculated $C_9H_{18}NO$: 156.1388; found 156.1382.



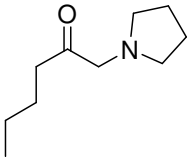
3d

3d. Isolated yield: 23%; reaction time: 20 days Table 1, entry 4.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 2.8-2.7 (m, 1H), 2.6-2.3 (m, 4H), 2.10 (s, 3H), 1.8-1.5 (m, 6H), 1.4-1.1 (m, 2H), 0.86 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 211.0, 75.3, 51.6, 32.7, 26.1, 23.1, 18.8, 14.1.

HRMS calculated $C_{10}H_{20}NO$: 170.1545; found 170.1548.



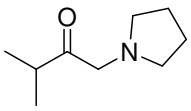
3d'

3d'. Isolated yield: 22%; reaction time: 20 days; Table 1, entry 4.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.25 (s, 2H), 2.6-2.4 (m, 4H), 2.31 (t, 2H, J = 7.5 Hz), 1.8-1.6 (m, 4H), 1.5-1.4 (m, 2H), 1.3-1.1 (m, 2H), 0.79 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.5, 65.3, 54.0, 39.8, 25.7, 23.4, 22.1, 13.6.

HRMS calculated $C_{10}H_{20}NO$: 170.1545; found 170.1548.



3e

3e. Isolated yield: 25%; reaction time: 26 days Table 1, entry 5.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.41 (s, 2H), 2.7-2.5 (m, 5H), 1.8-1.7 (m, 4H), 1.06 (d, 6H, J = 6.9 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 211.9, 63.3, 54.1, 38.3, 23.6, 18.3.

HRMS calculated $C_9H_{18}NO$: 156.1388; found 156.1385.

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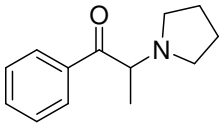


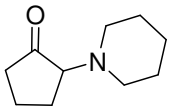
3f

3f. Isolated yield: 22%; reaction time: 23 days; Table 1, entry 6.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 8.2-8.0 (m, 2H), 7.6-7.4 (m, 3H), 4.01 (q, 1H, J = 6.9 Hz), 2.8-2.6 (m, 4H), 1.9-1.7 (m, 4H), 1.38 (d, 3H, J = 6.9 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 200.9, 135.8, 133.0, 128.6, 128.5, 64.3, 51.1, 23.5, 16.5.

HRMS calculated $C_{13}H_{18}NO$: 204.1388; found 204.1390.



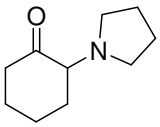
3g

3g. Isolated yield: 38%; reaction time: 10 days; Table 1, entry 7.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.1-3.0 (m, 1H), 2.7-2.6 (m, 2H), 2.5-2.4 (m, 2H), 2.3-2.0 (m, 4H), 1.9-1.5 (m, 6H), 1.5-1.4 (m, 2H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 217.3, 71.9, 51.1, 37.5, 26.0, 24.2, 23.7, 18.3.

HRMS calculated $C_{10}H_{18}NO$: 168.1388; found 168.1388.



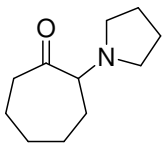
3h

3h. Isolated yield: 36%; reaction time: 20 days; Table 1, entry 8.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.1-2.9 (m, 1H), 2.7-2.4 (m, 4H), 2.3-2.2 (m, 2H), 2.2-2.0 (m, 2H), 2.0-1.5 (m, 8H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 211.2, 72.0, 50.9, 40.8, 33.2, 28.3, 23.4, 22.9.

HRMS calculated $C_{10}H_{18}NO$: 168.1388; found 168.1393.



3i

3i. Isolated yield: 25%; reaction time: 20 days; Table 1, entry 9.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.5-3.3 (m, 1H), 3.00 (dd, 1H, J = 9.6 Hz, J = 4.5 Hz), 2.7-2.3 (m, 6H), 2.0-1.3 (m, 11H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.7, 74.2, 51.5, 41.3, 30.3, 29.1, 26.1, 24.3, 23.3.

HRMS calculated $C_{11}H_{20}NO$: 182.1545; found 182.1548.

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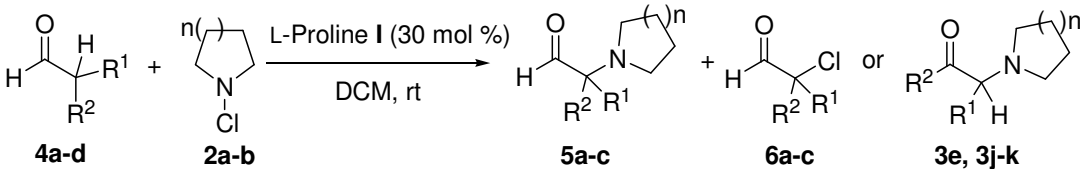
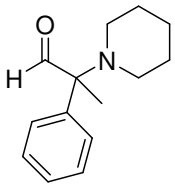
5. General procedure for the preparation of compounds 5a-c or 3e, 3j-k



4a-d **2a-b** **5a-c** **6a-c** **3e, 3j-k**

To a mixture of an aldehyde **4a-d** (50 mg, 1 eq) and L-proline **I** (0.3 eq) in DCM (1ml), cooled to 0°C, the *N*-chloroamine **2a-b** (1.5 eq) is added dropwise. The mixture is left warming up with stirring. The reaction is monitored by TLC (AcOEt/MeOH 5:1) until the substrate is totally converted (TLC traces revealable by $KMnO_4$ stain).

When there is no more *N*-chloroamine left, the reaction is diluted with a saturated water solution of NaCl and a saturated water solution of $NaHCO_3$. The acqueous phase is extracted three times with AcOEt and the combined organic phases are dried with anhydrous sodium sulphate. The solvent is removed in vacuo (due to thermal instability of the products, the solvent must be removed with gentle heating) and the mixture is loaded on a chromatographic column filled with silica gel (eluant PE:AcOEt from 10:1 to 1:2 first, then AcOEt and AcOEt/MeOH from 10:1 to 3:1 for compounds **3e**, **3j-k**; PE:AcOEt from 100:1 to 20:1 for compounds **5a-c**). Removal of the solvent in vacuo provides products **5a-c** or **3e**, **3j-k** as colorless oils.



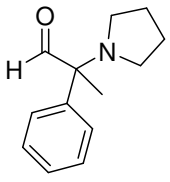
5a

5a. Isolated yield: 43%; reaction time: 2 days; Table 2, entry 1.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 9.35 (s, 1H), 7.5-7.1 (m, 5H), 2.5-2.2 (m, 4H), 1.6-1.5 (m, 4H), 1.5-1.3 (m, 2H), 1.39 (s, 3H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 200.8, 138.9, 128.7, 127.9, 127.7, 72.9, 48.3, 26.7, 24.9, 8.9.

HRMS calculated $C_{14}H_{20}NO$: 218.1545; found 218.1555.



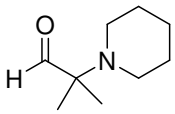
5b

5b. Isolated yield: 87%; reaction time: 2 days; Table 2, entry 2.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 9.53 (s, 1H), 7.6-7.2 (m, 5H), 2.7-2.5 (m, 4H), 1.9-1.7 (m, 4H), 1.50 (s, 3H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 200.8, 128.6, 127.7, 127.6, 70.0, 46.2, 23.9, 11.1.

HRMS calculated $C_{13}H_{18}NO$: 204.1388; found 204.1385.



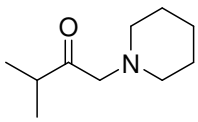
5c

5c. Isolated yield: 25%; reaction time: 16h; Table 2, entry 3.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 9.44 (s, 1H), 2.5-2.4 (m, 4H), 1.7-1.5 (m, 4H), 1.5-1.4 (m, 2H), 1.07 (s, 6H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 205.8, 65.8, 47.9, 26.6, 24.8, 17.1.

HRMS calculated $C_9H_{18}NO$: 156.1388; found 156.1392.



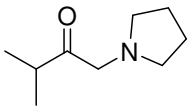
3j

3j. Isolated yield: 46%; reaction time: 26 days; Table 2, entry 4.

^{1}H-NMR (400 MHz) δ ($CDCl_3$): 3.16 (s, 2H), 2.69 (h, 1H, J = 6.8 Hz), 2.4-2.3 (m, 4H), 1.7-1.5 (m, 4H), 1.4-1.3 (m, 2H), 1.04 (d, 6H, J = 6.8 Hz).

^{13}C-NMR (100 MHz) δ ($CDCl_3$): 212.5, 66.5, 54.7, 38.2, 25.7, 23.9, 18.2.

HRMS calculated $C_{10}H_{20}NO$: 170.1545; found 170.1543.



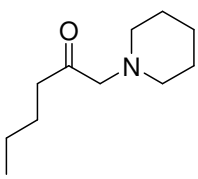
3e

3e. Isolated yield: 17%; reaction time: 1 day; Table 2, entry 5.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 3.41 (s, 2H), 2.7-2.5 (m, 5H), 1.8-1.7 (m, 4H), 1.06 (d, 6H, J = 6.9 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 211.9, 63.3, 54.1, 38.3, 23.6, 18.3.

HRMS calculated $C_9H_{18}NO$: 156.1388; found 156.1385.



3k

3k. Isolated yield: 38%; reaction time: 10 days; Table 2, entry 6.

^{1}H-NMR (400 MHz) δ ($CDCl_3$): 3.13 (s, 2H), 2.5-2.3 (m, 6H), 1.7-1.1 (m, 10H), 0.90 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (100 MHz) δ ($CDCl_3$): 209.4, 68.5, 54.8, 40.1, 25.9, 25.7, 23.9, 22.3, 13.8.

6. Procedure for the conversion of compound 6a into 5a

Compound **6a** (100 mg, 0.60 mmol) was dissolved in 3 mL of toluene and excess piperidine **7a** (3 eq.) was added at once. After 30 min, a check on TLC showed that all starting material had been consumed. Direct purification of the crude mixture by FC afforded compound **5a** in 72% yield..

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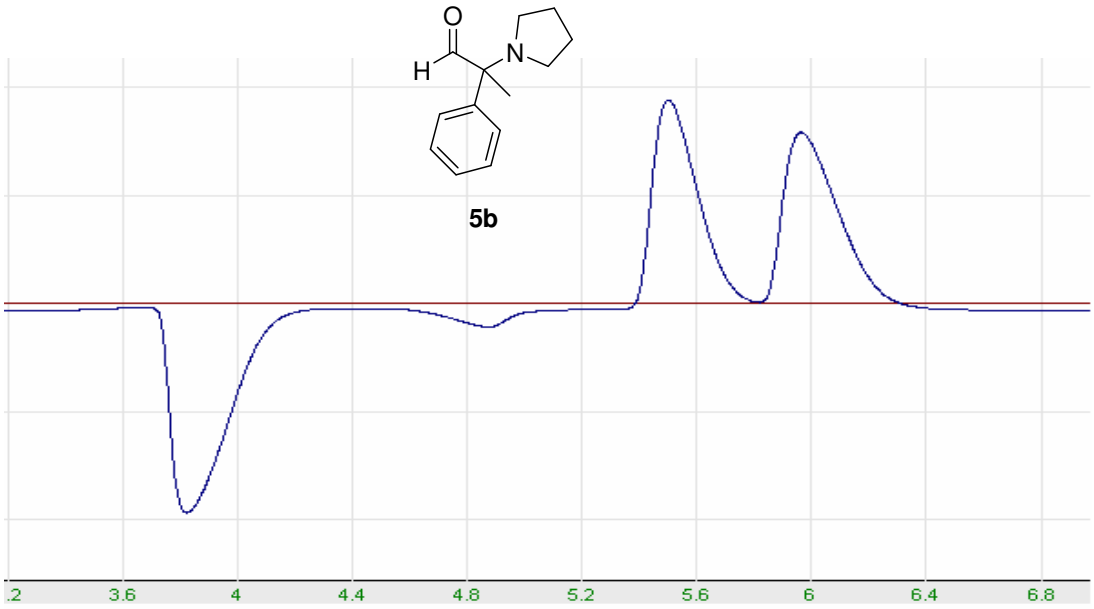
7. Chromatograms

The *ee* of compound **5b** was determined by a CSP-HPLC instrument (IC Chiralpack column; *n*-hexane / *i*-propanol 94:6, flow 0.9mL/min).

Racemic sample



Picco	Tempo	IniT	IniV	TopT	TopV	EndT	EndV	Area
1	5.500	5.356	-4732	5.500	188823	5.805	1372	34766.41
2	5.962	5.815	1070	5.962	158577	6.445	-5131	35225.22

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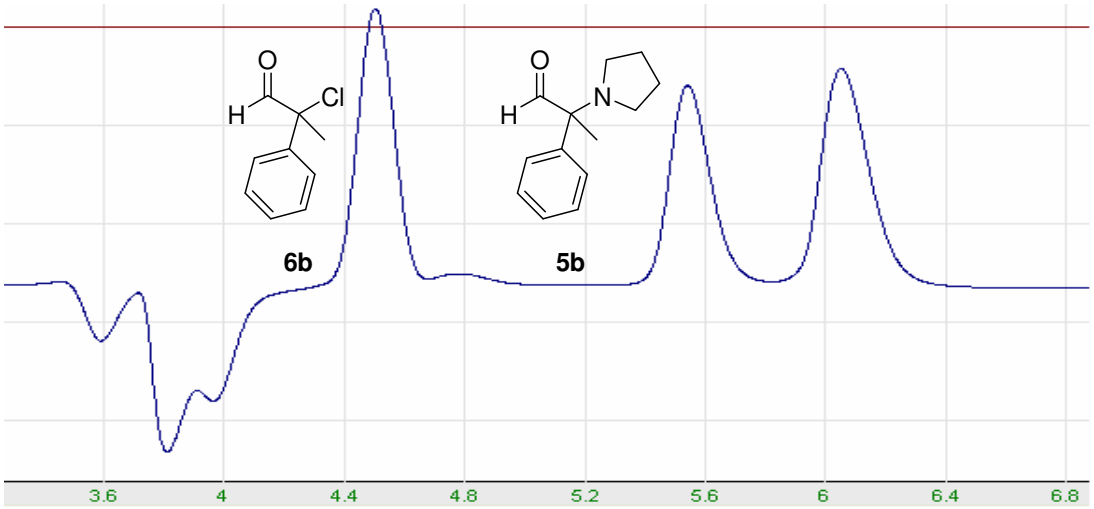
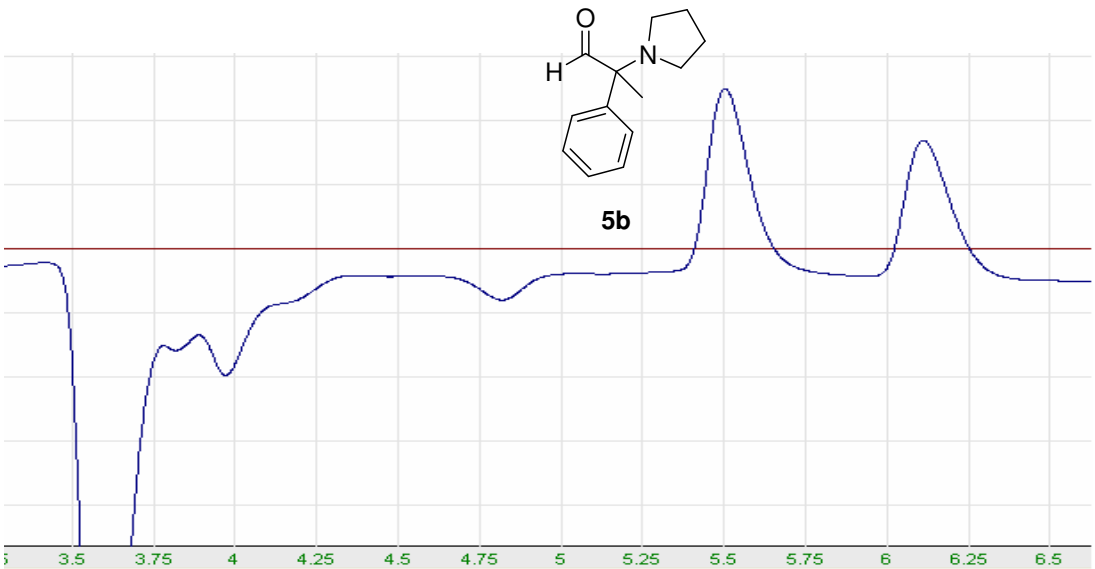
Table 3, entry 5 (L-proline employed as the catalyst)



Picco	Tempo	IniT	IniV	TopT	TopV	EndT	EndV	Area
1	5.540	5.332	-52308	5.540	-11755	5.802	-51665	6285.70
2	6.050	5.829	-51710	6.050	-8327	6.450	-52711	8097.46

Table 3, entry 5 (D-proline employed as the catalyst)



Picco	Tempo	IniT	IniV	TopT	TopV	EndT	EndV	Area
1	5.629	5.436	-3578	5.629	39897	5.923	-2917	6791.79
2	6.212	6.081	-1586	6.212	30103	6.499	-2679	5299.46

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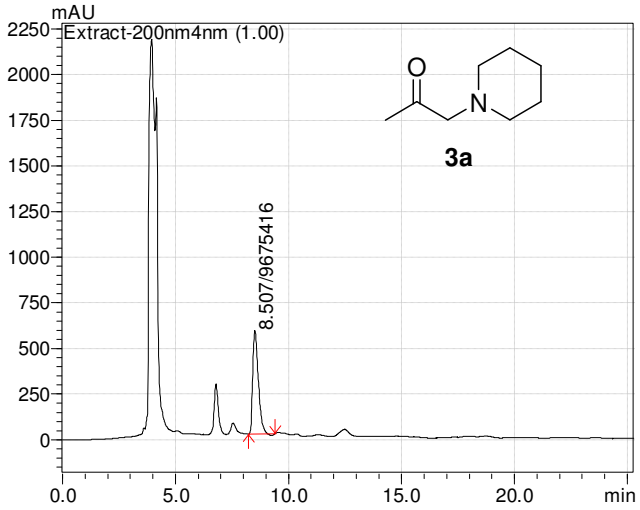

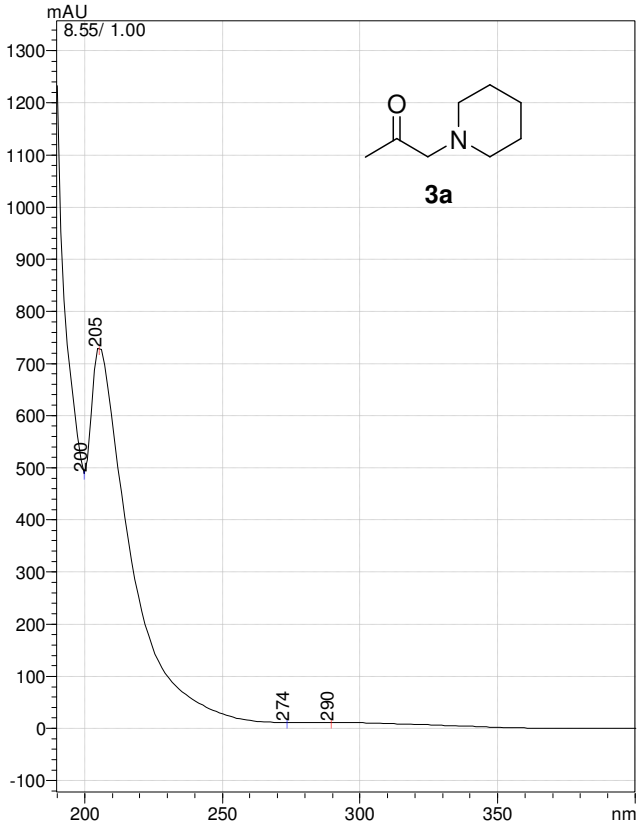

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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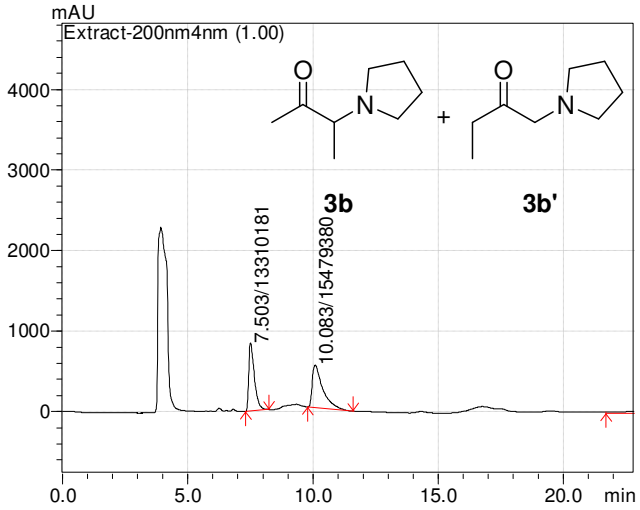

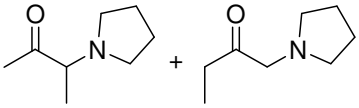

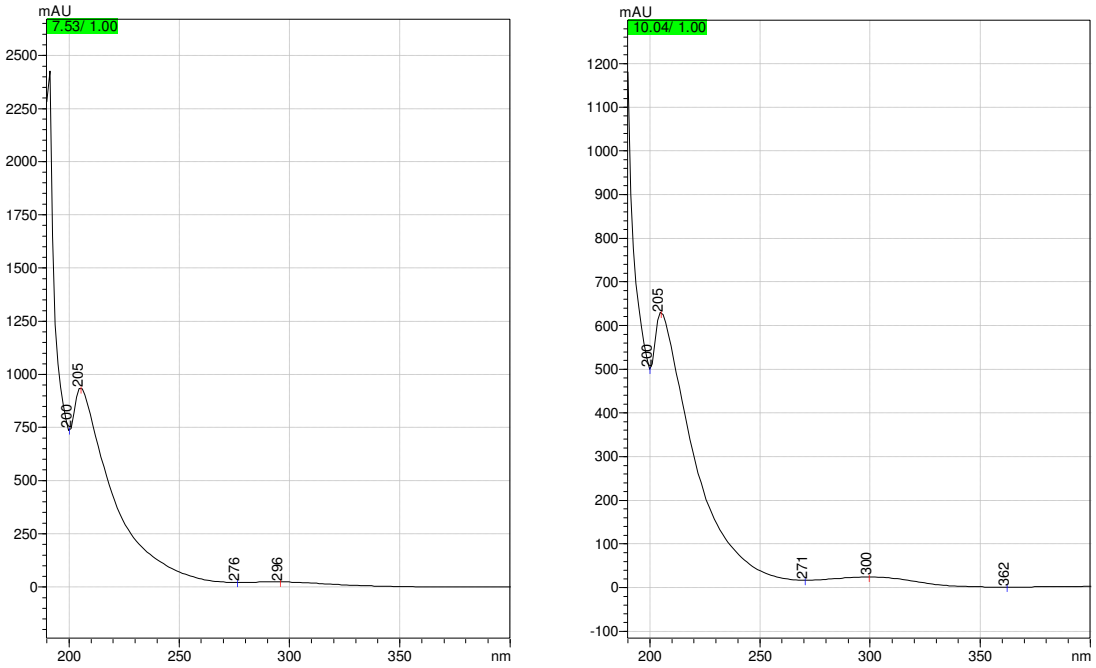

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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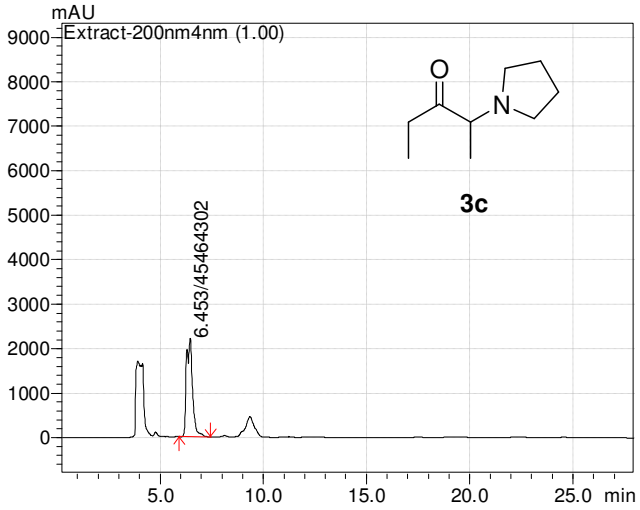

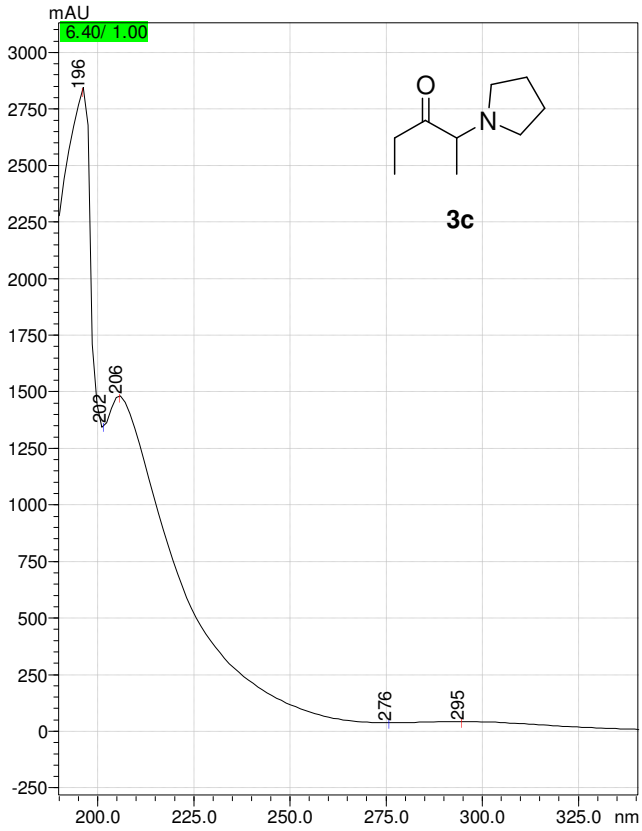

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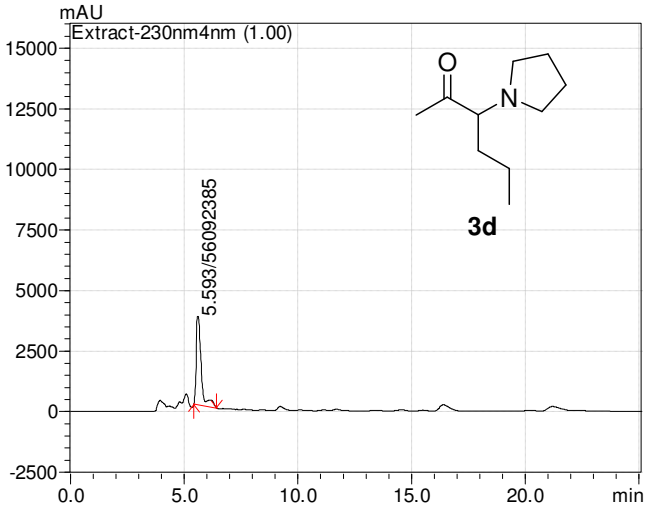

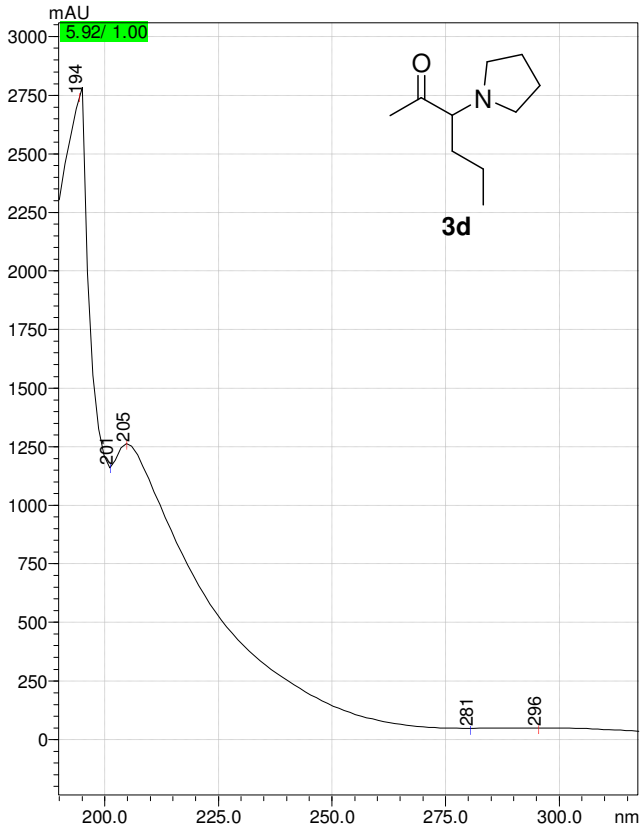

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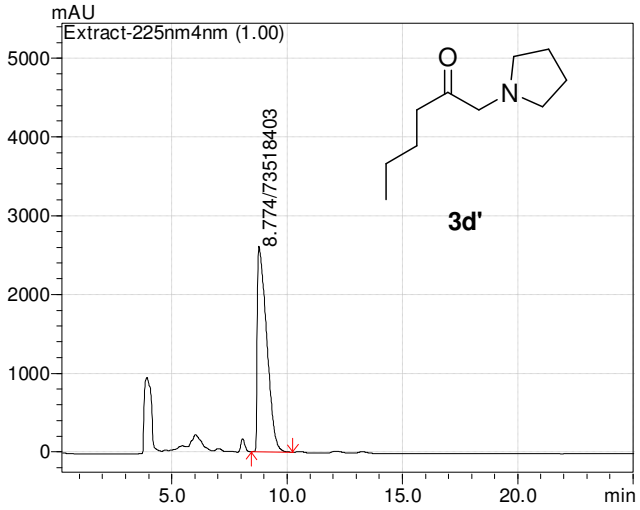

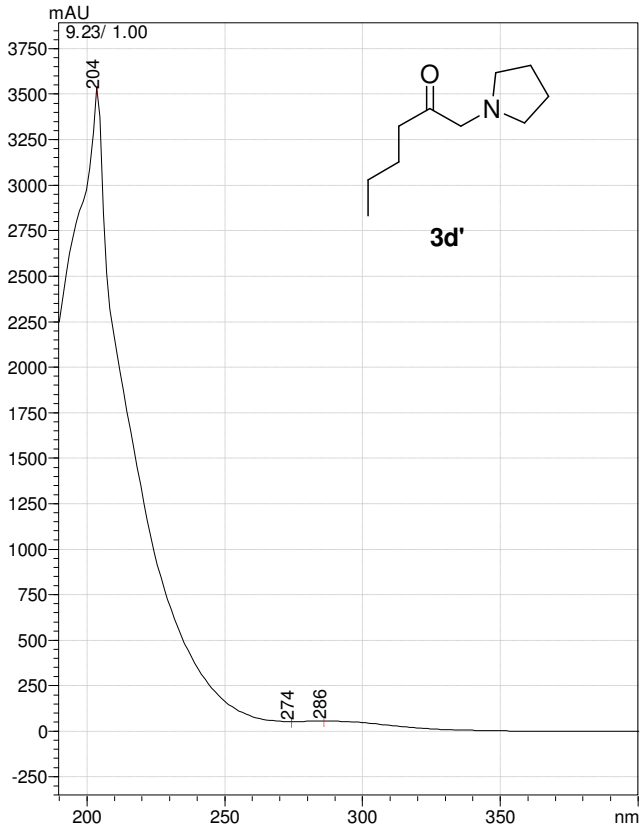

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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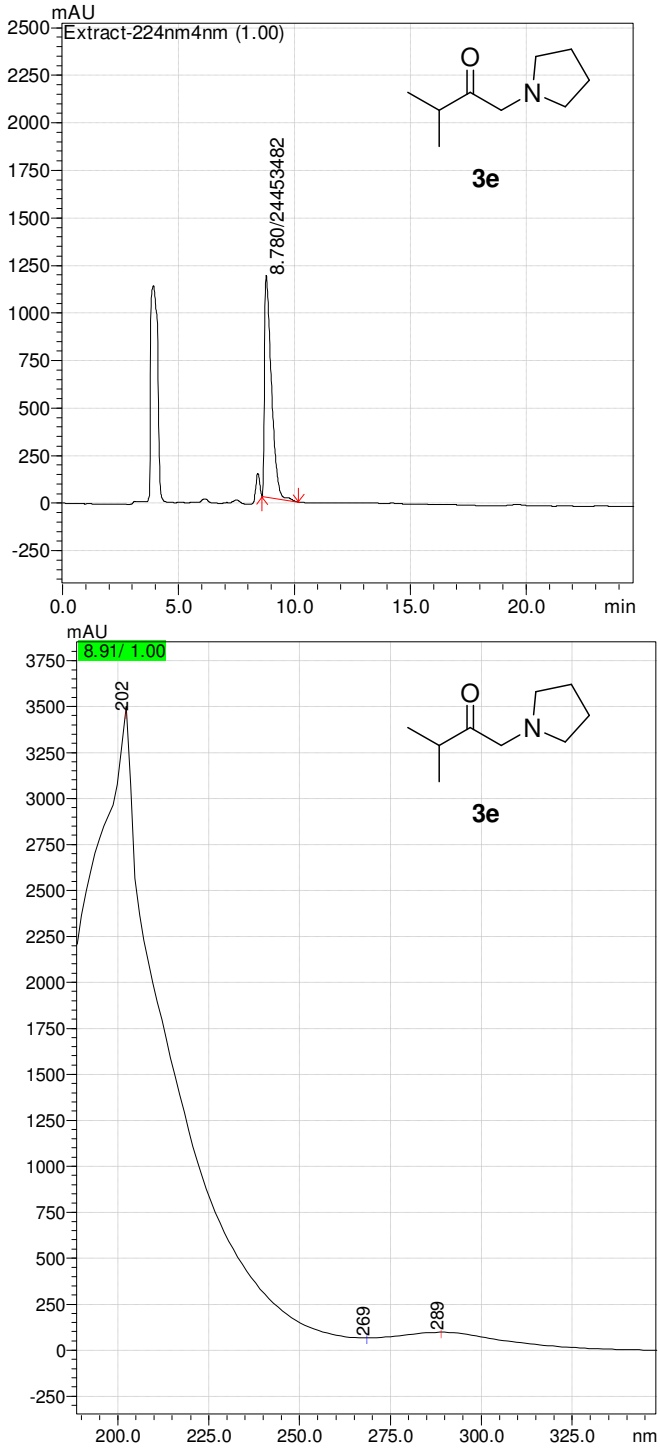

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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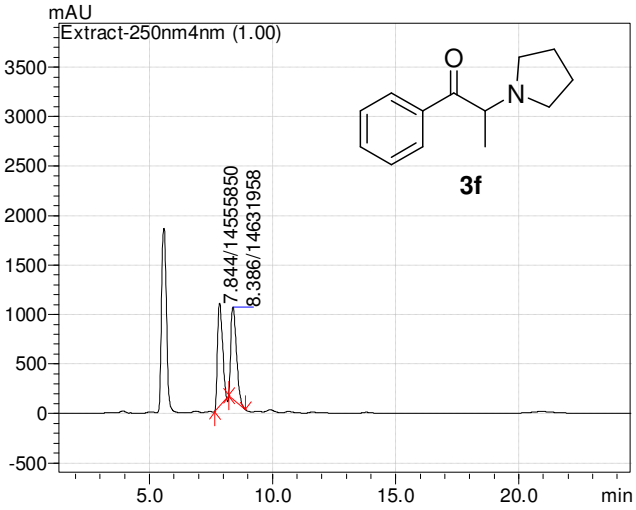

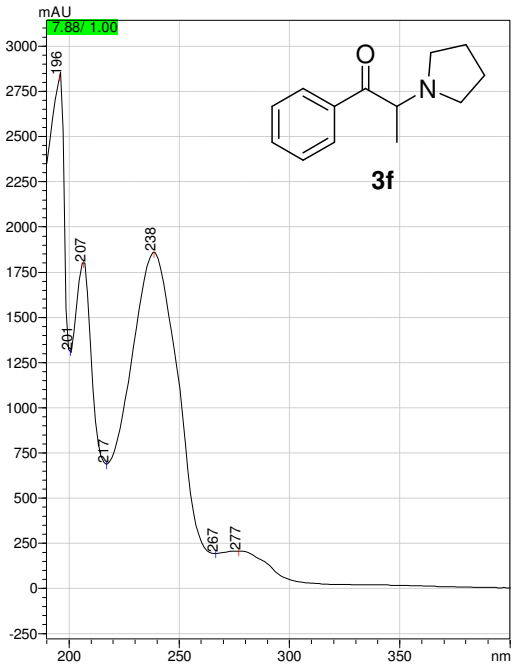

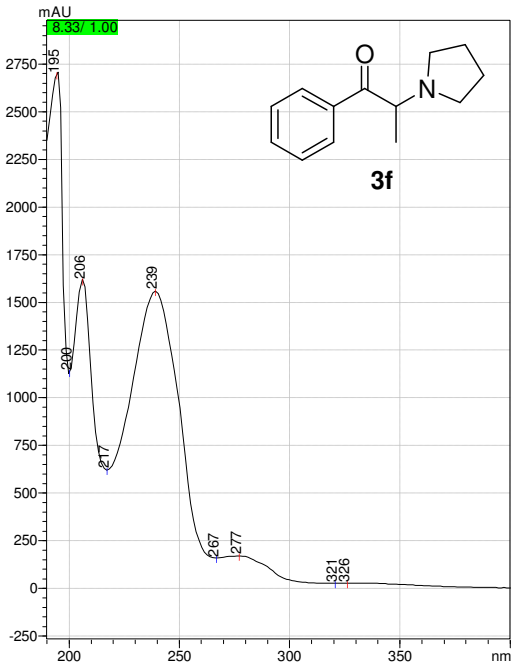

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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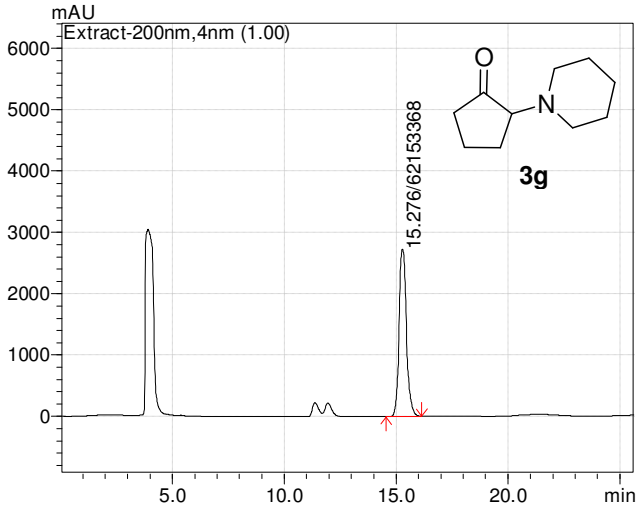

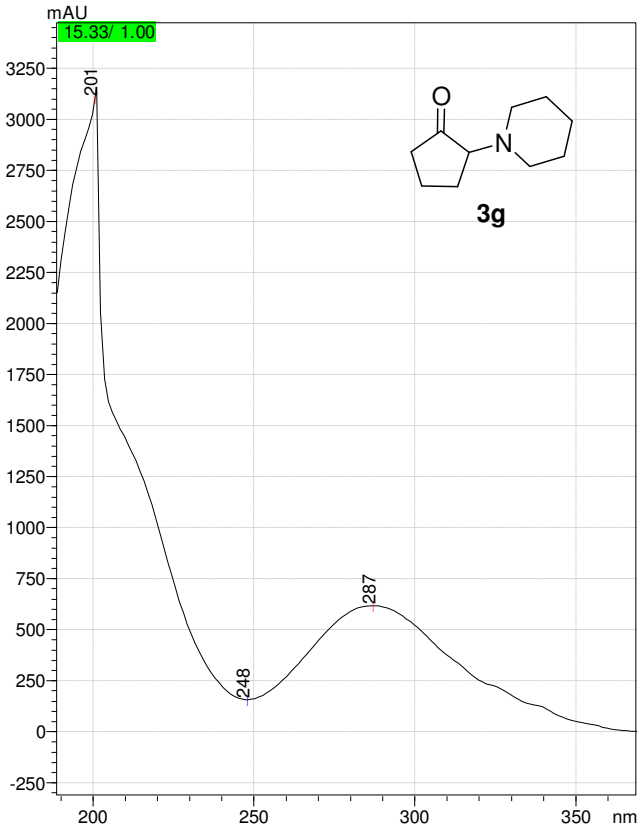

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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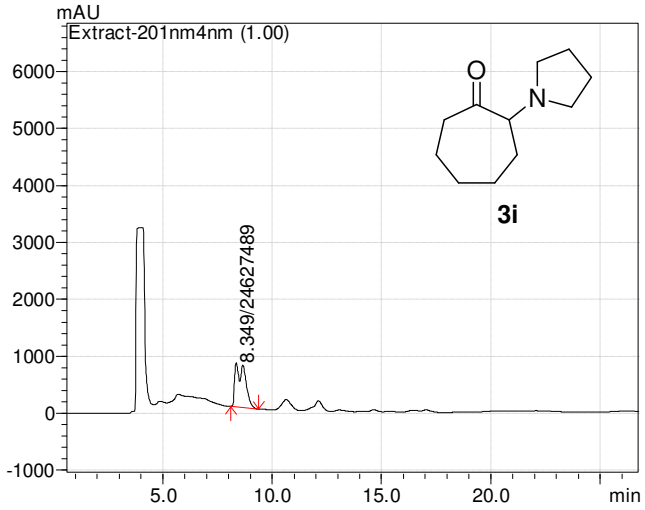

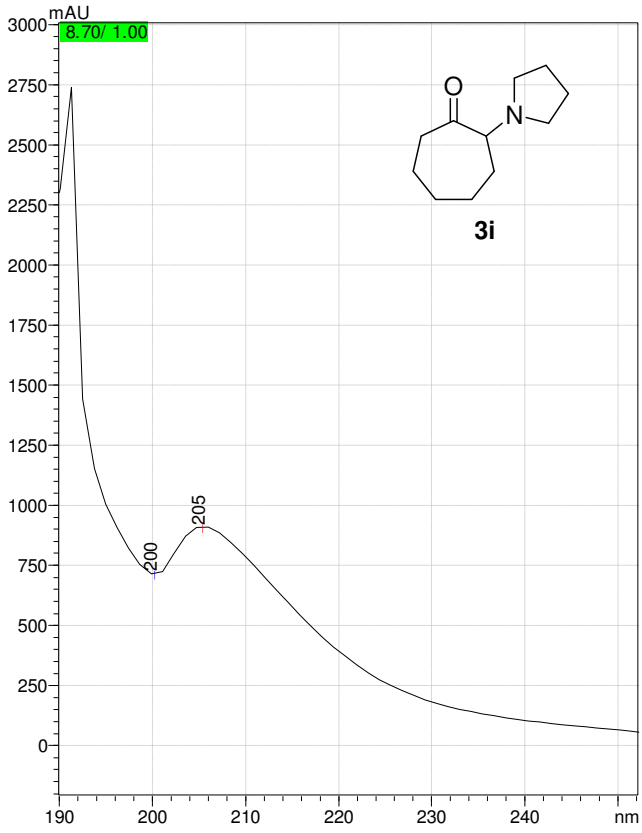

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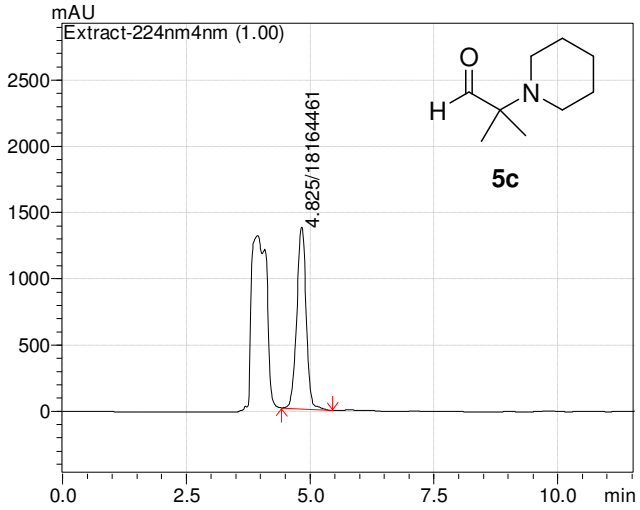

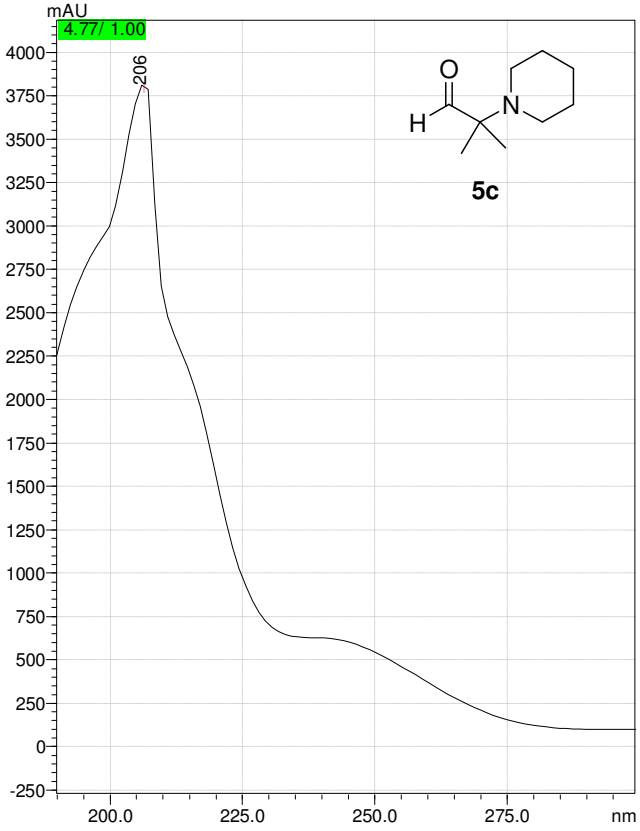

HPLC conditions: (IC Chiralpack column; *n*-hexane / *i*-propanol 89:11, flow 0.9mL/min).

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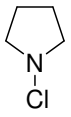
8. Copies of ^{1}H and ^{13}C-NMR spectra



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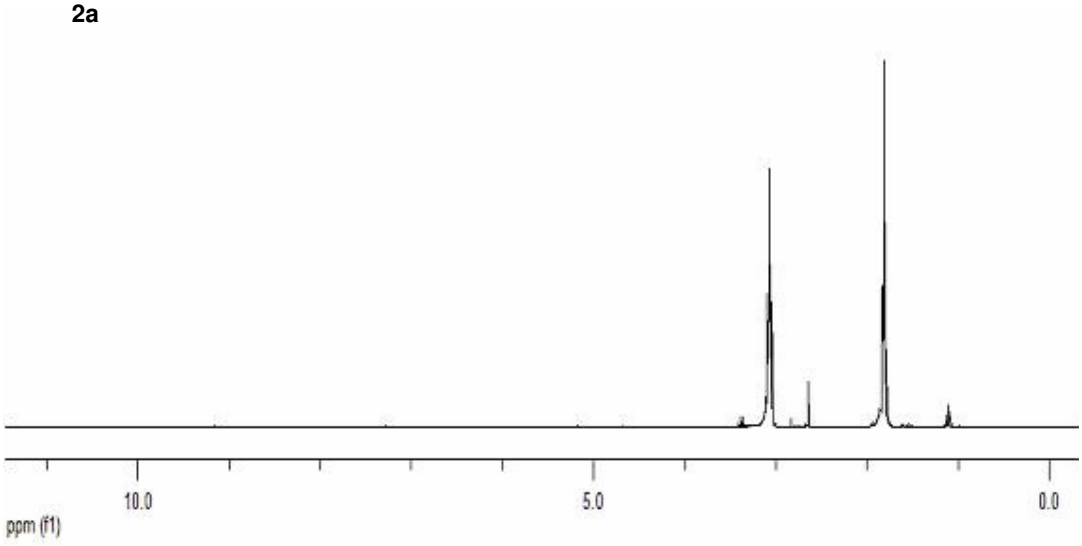

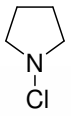

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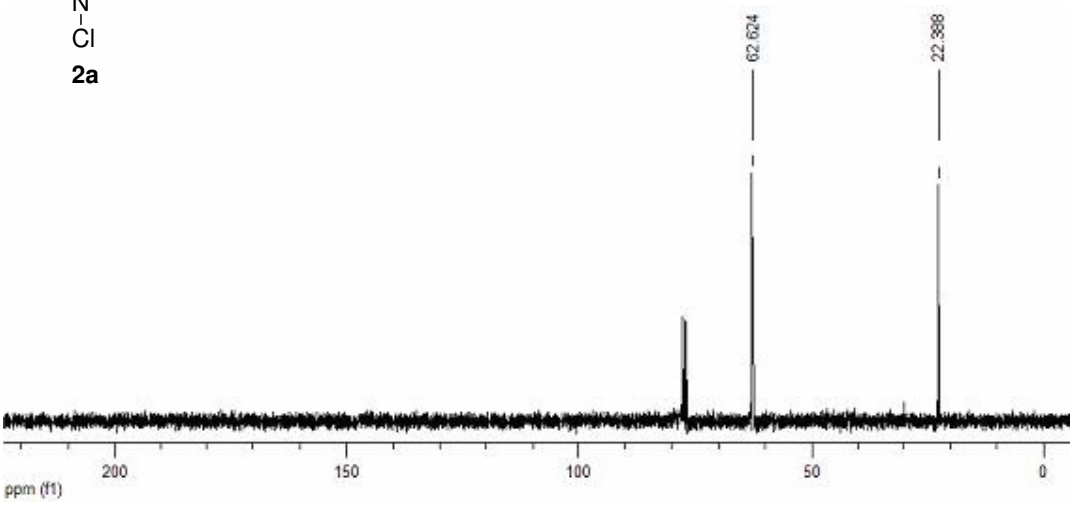

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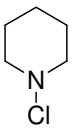

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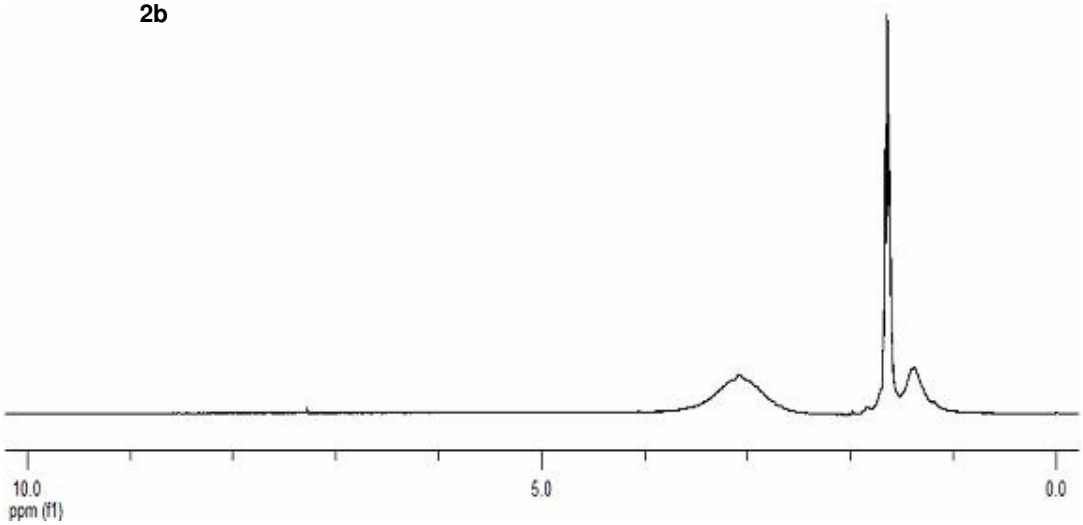

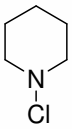

2b

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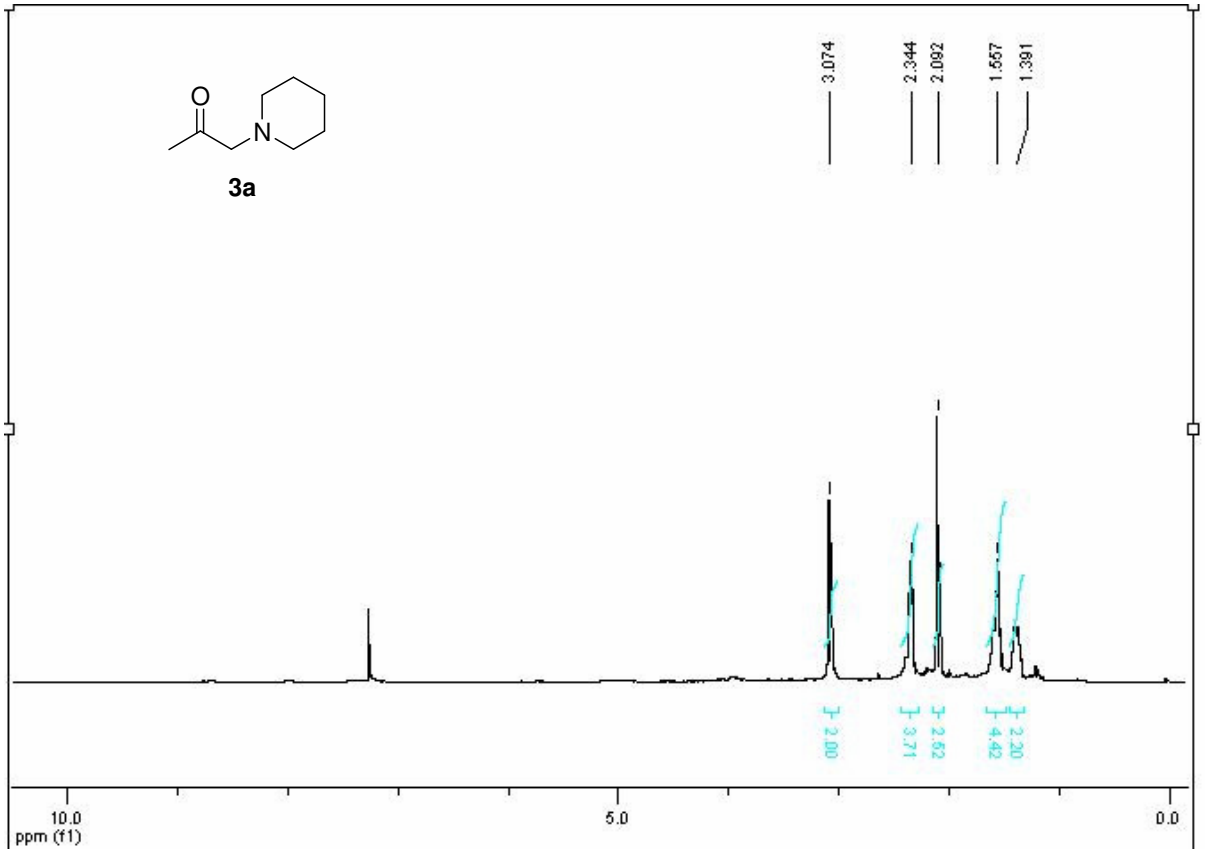

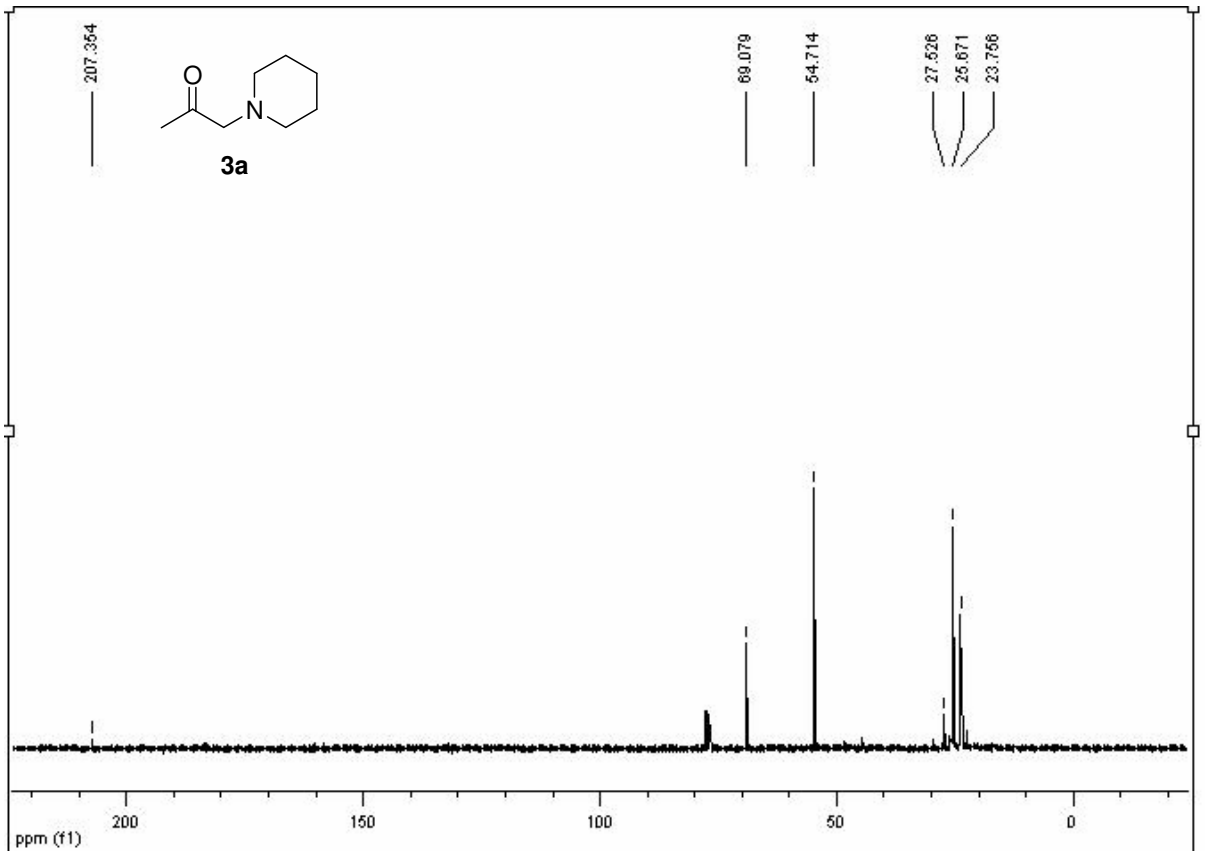

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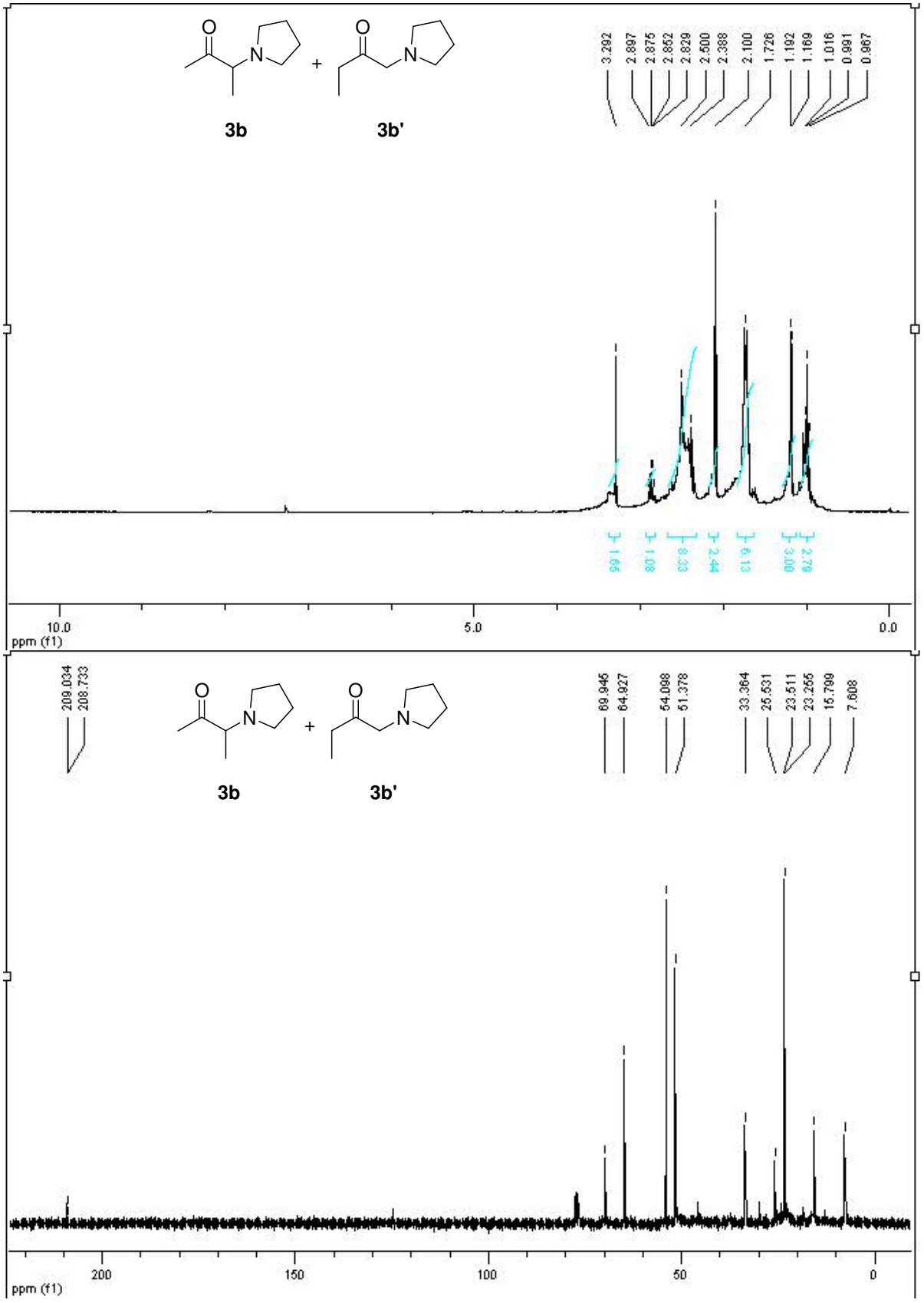

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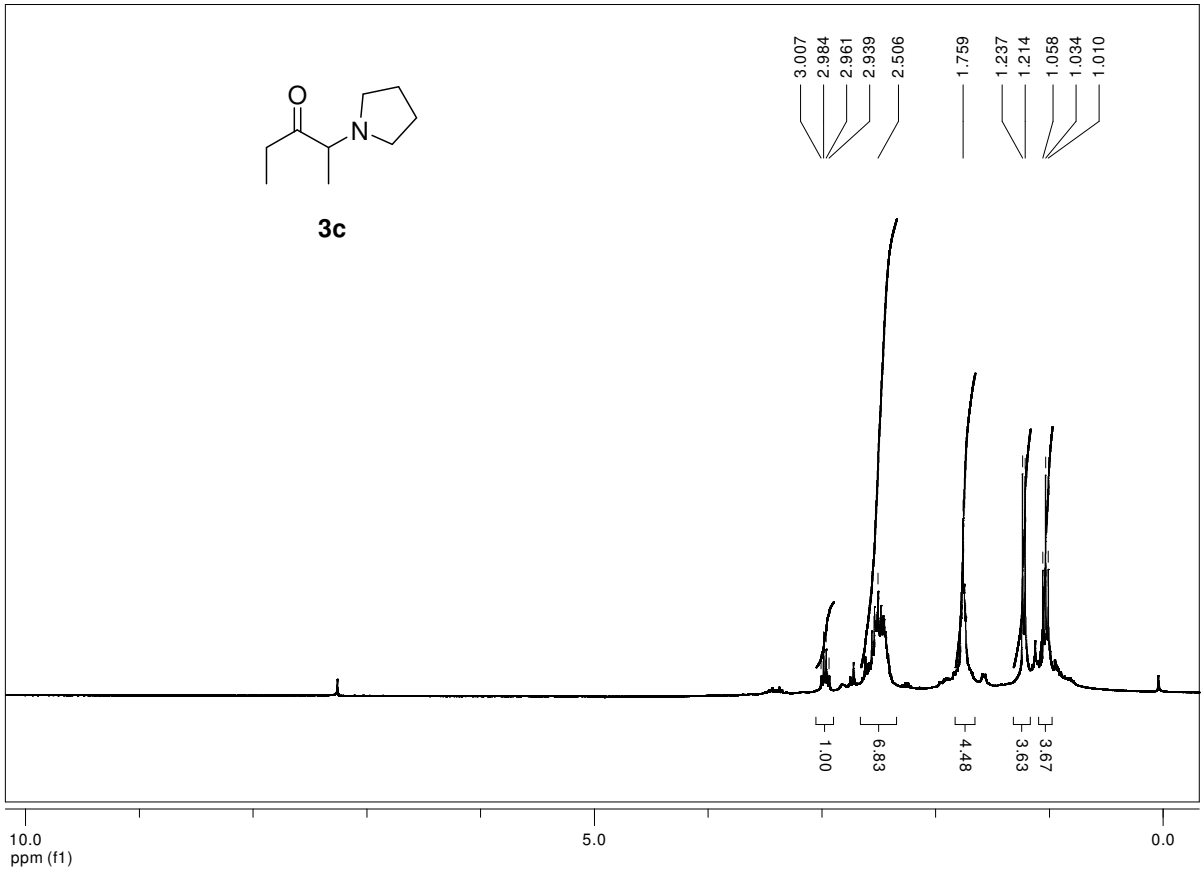

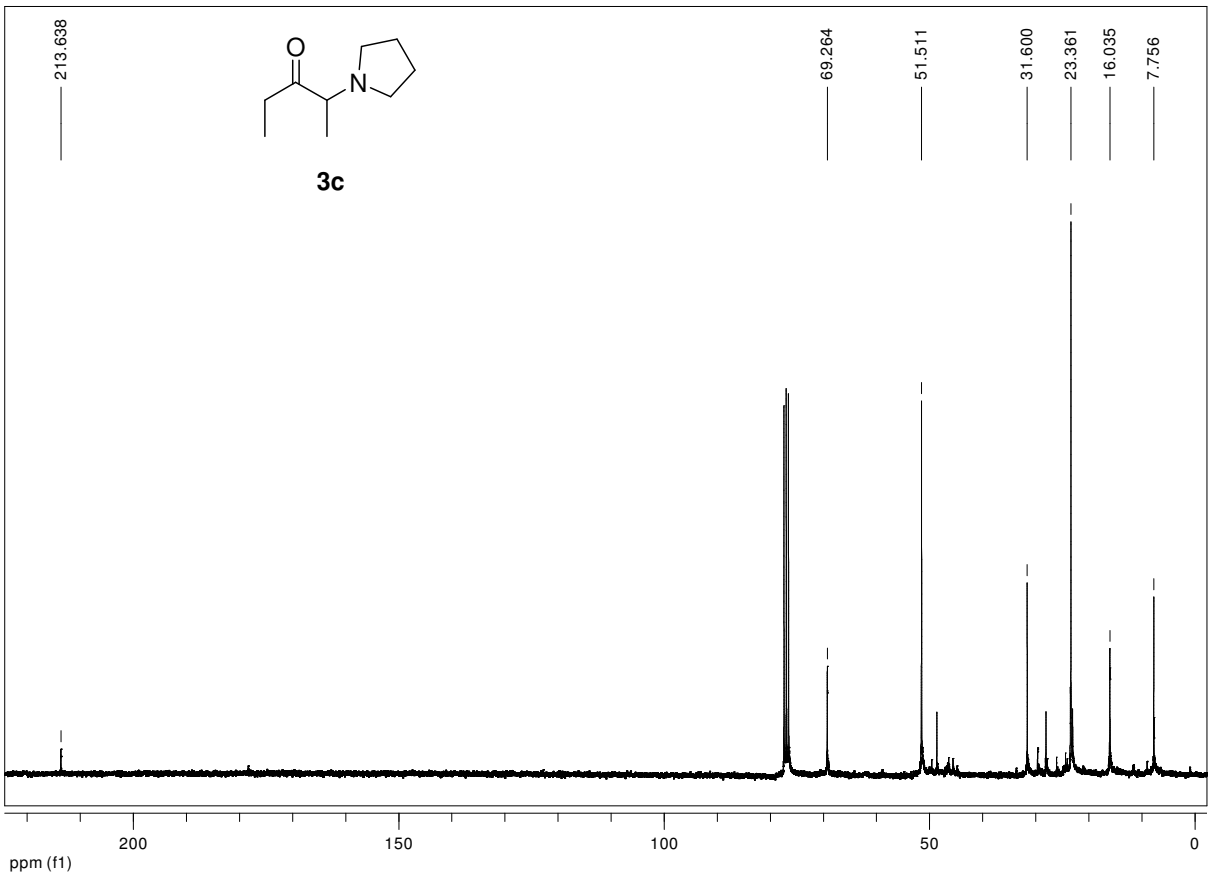

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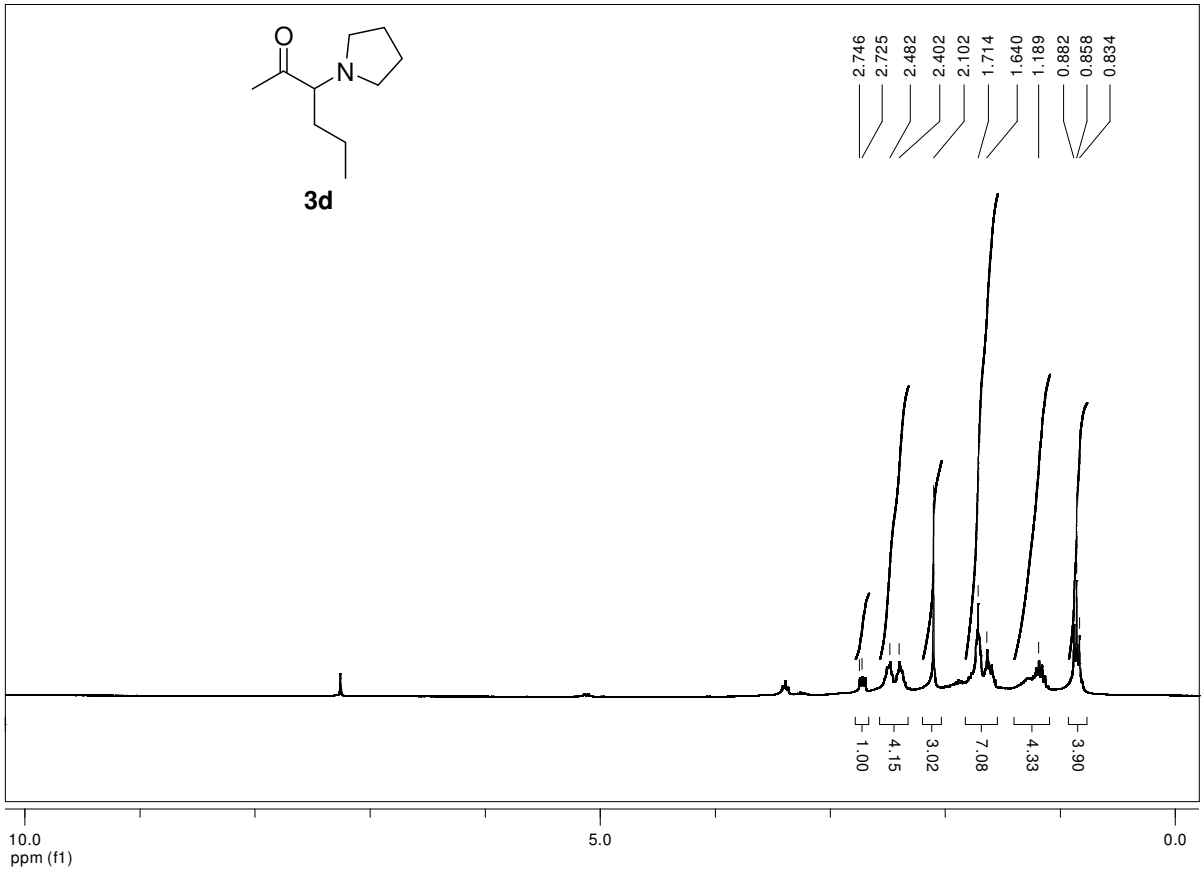

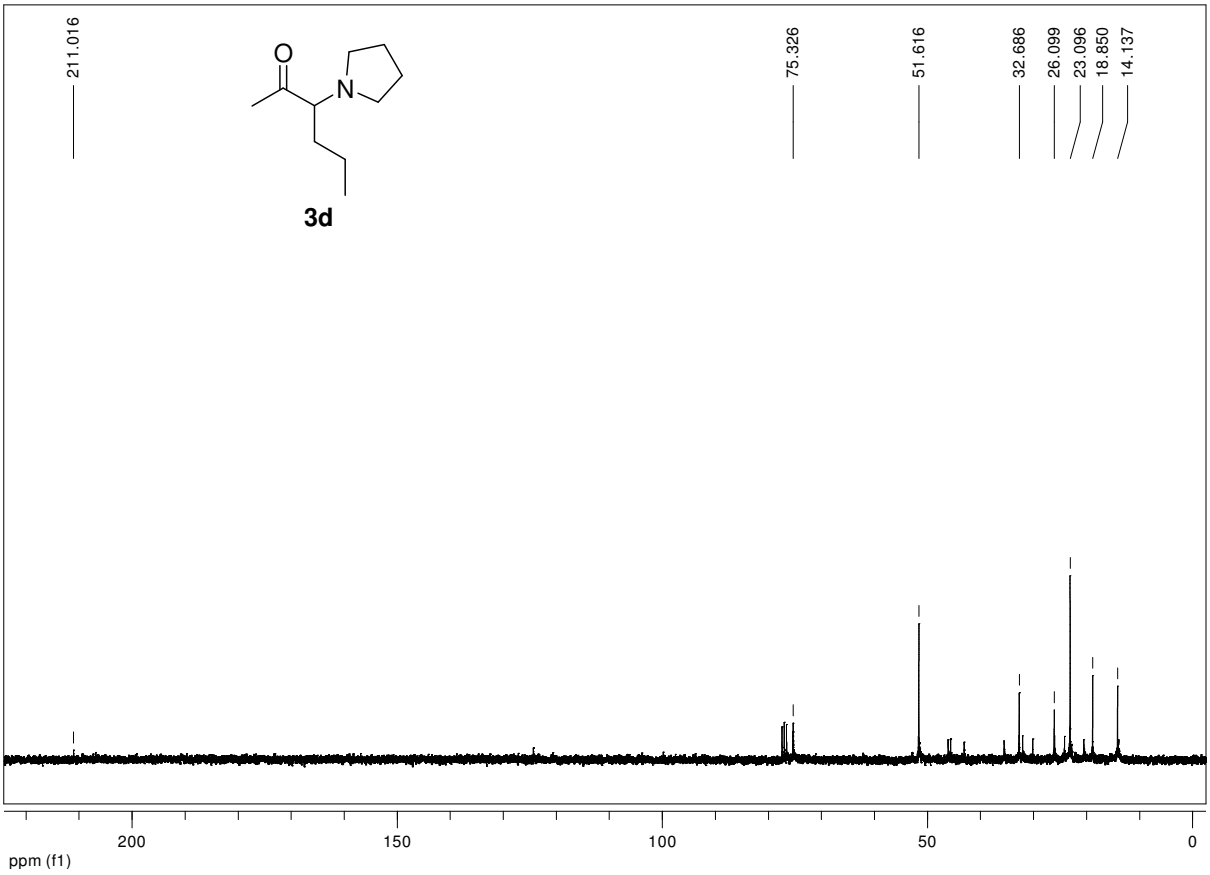

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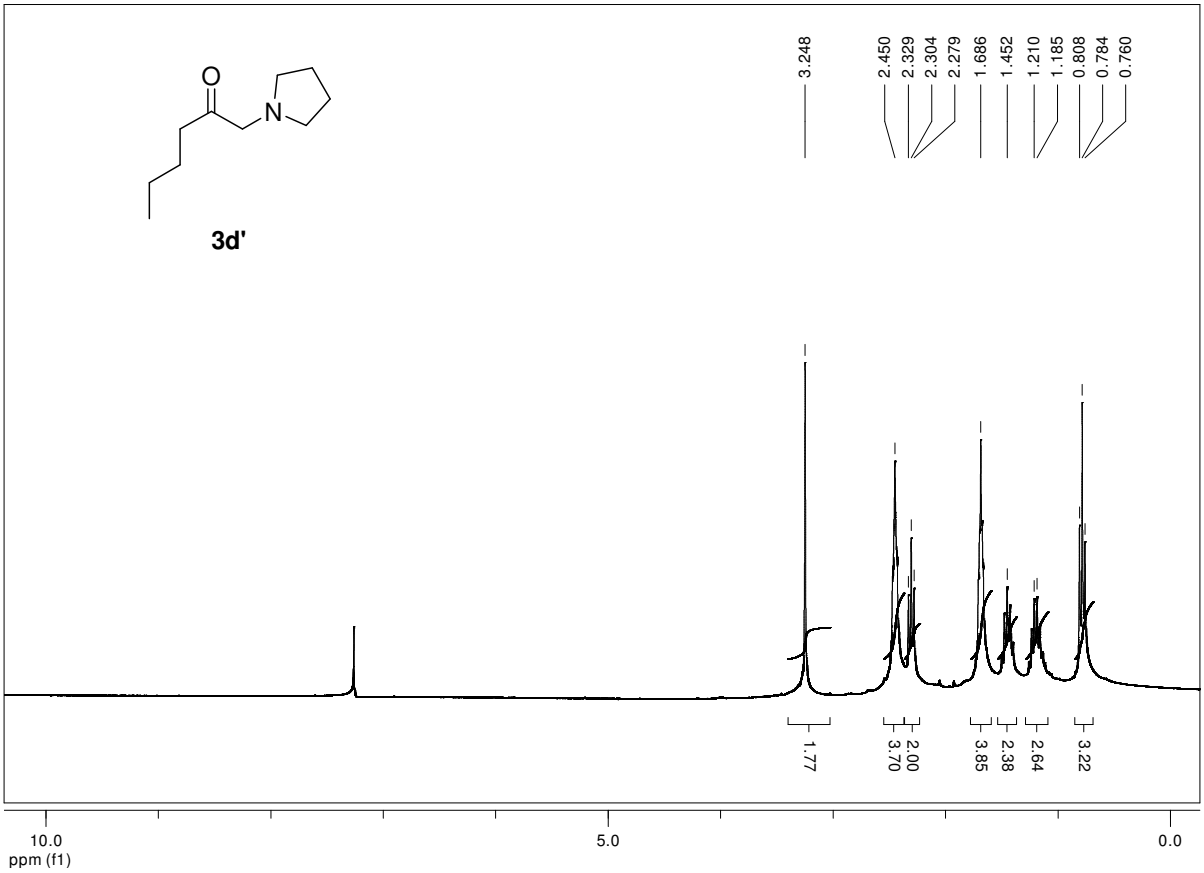

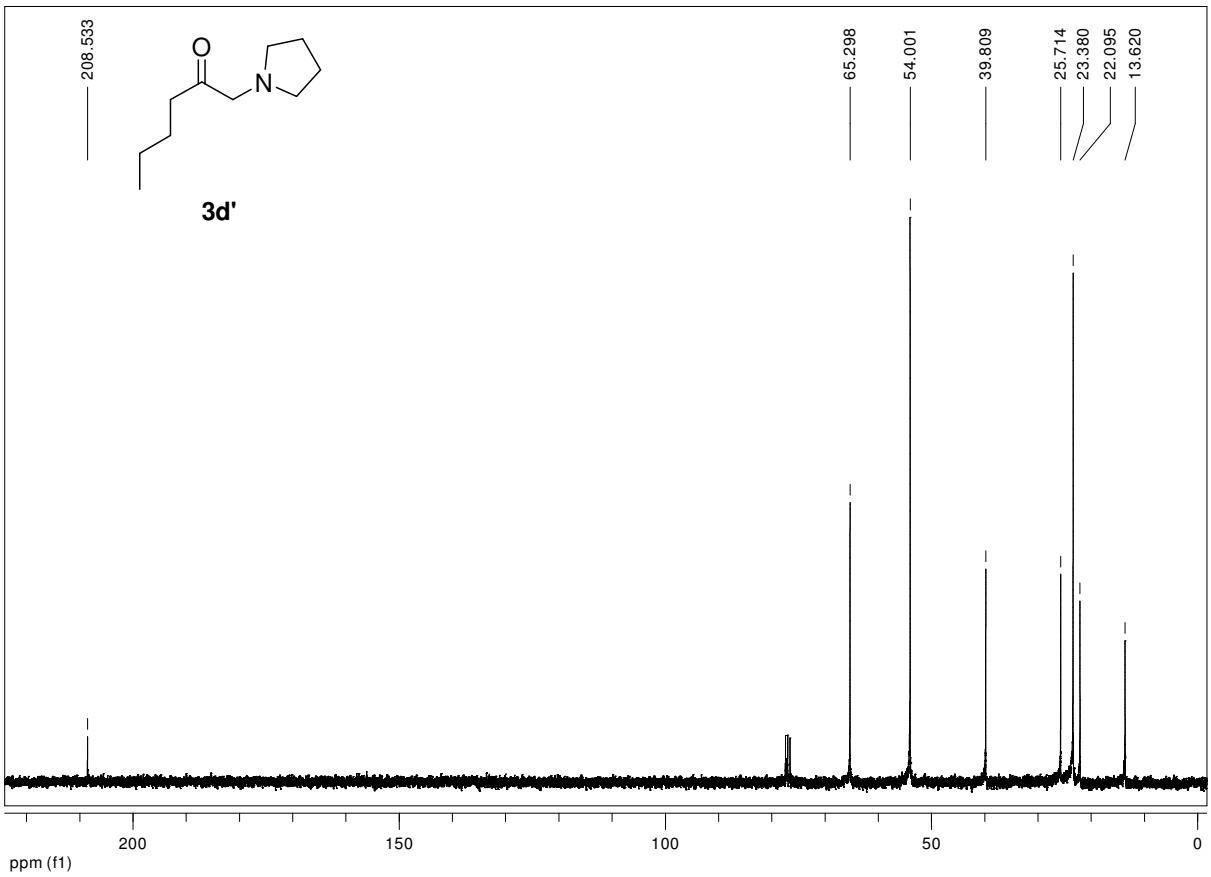

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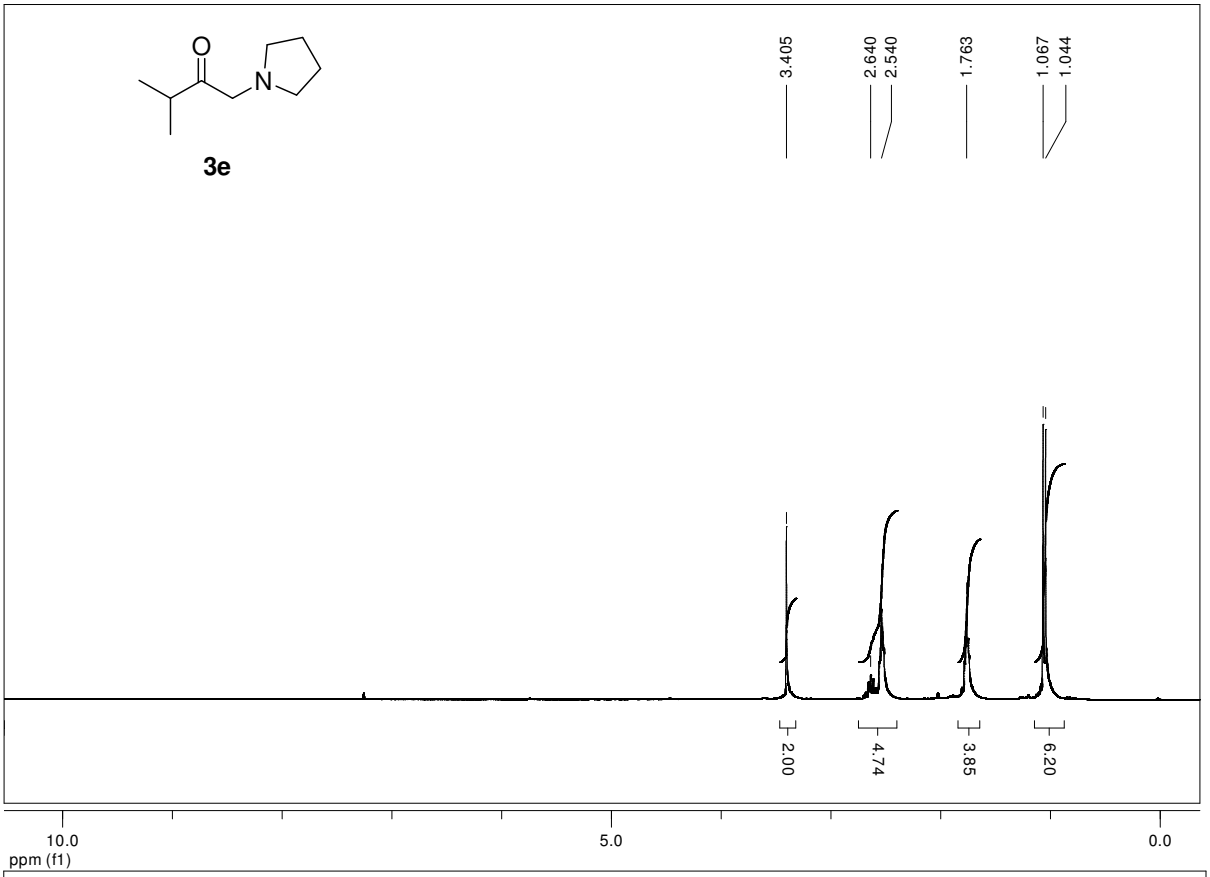

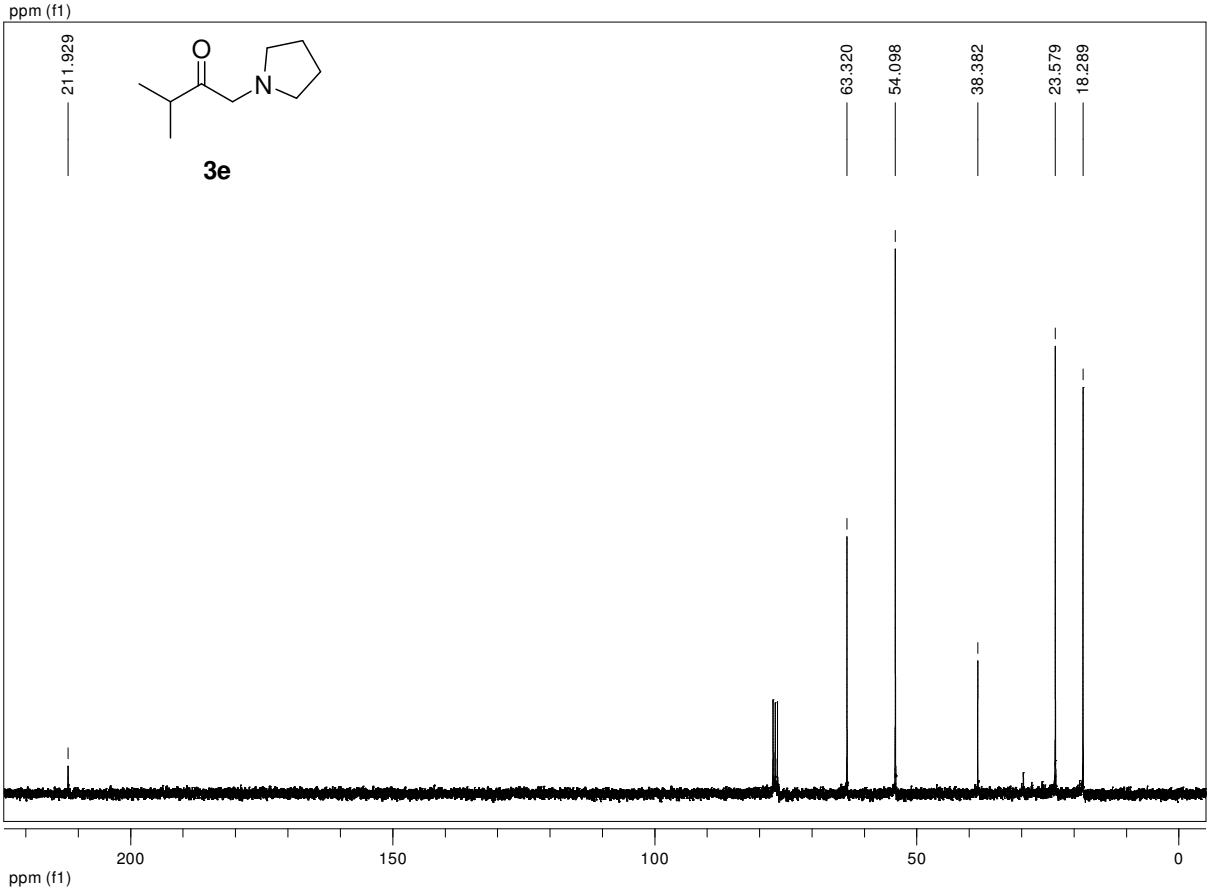

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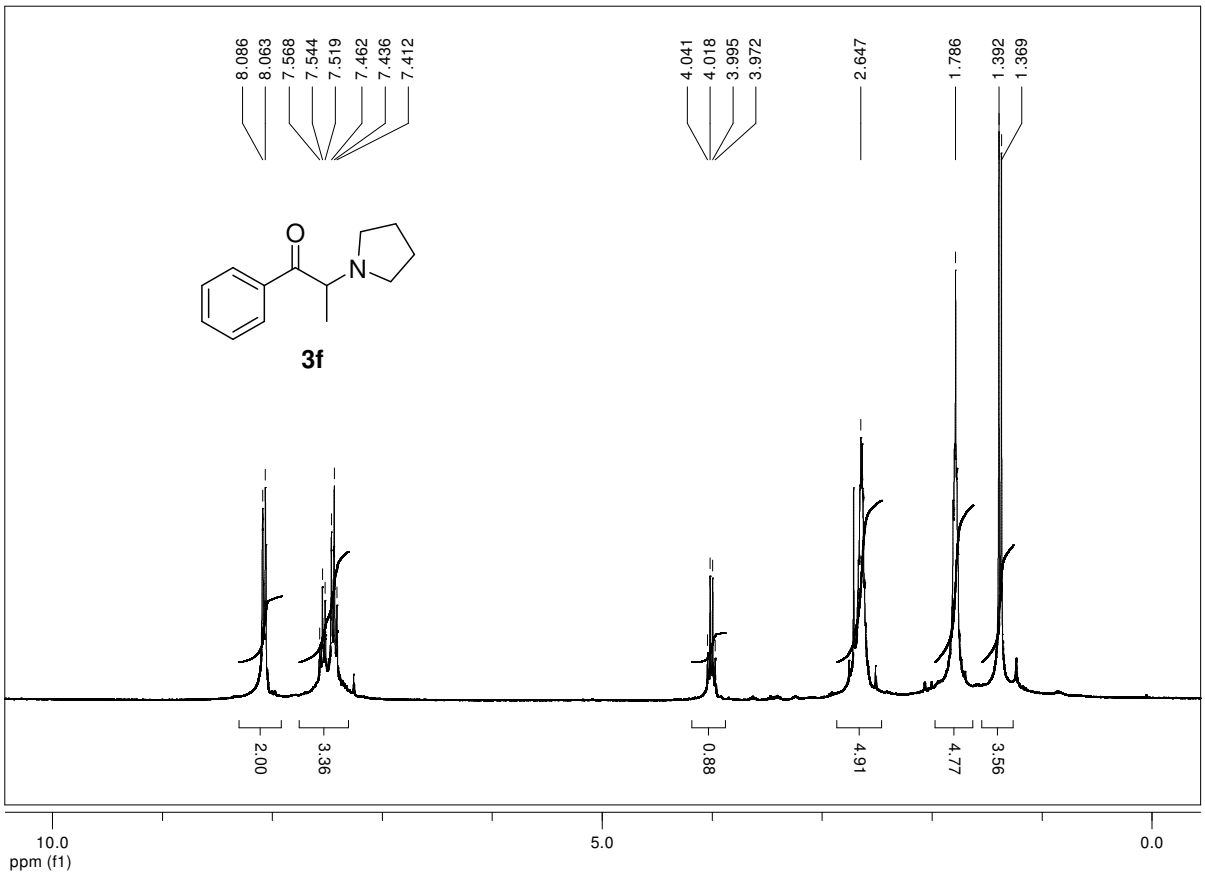

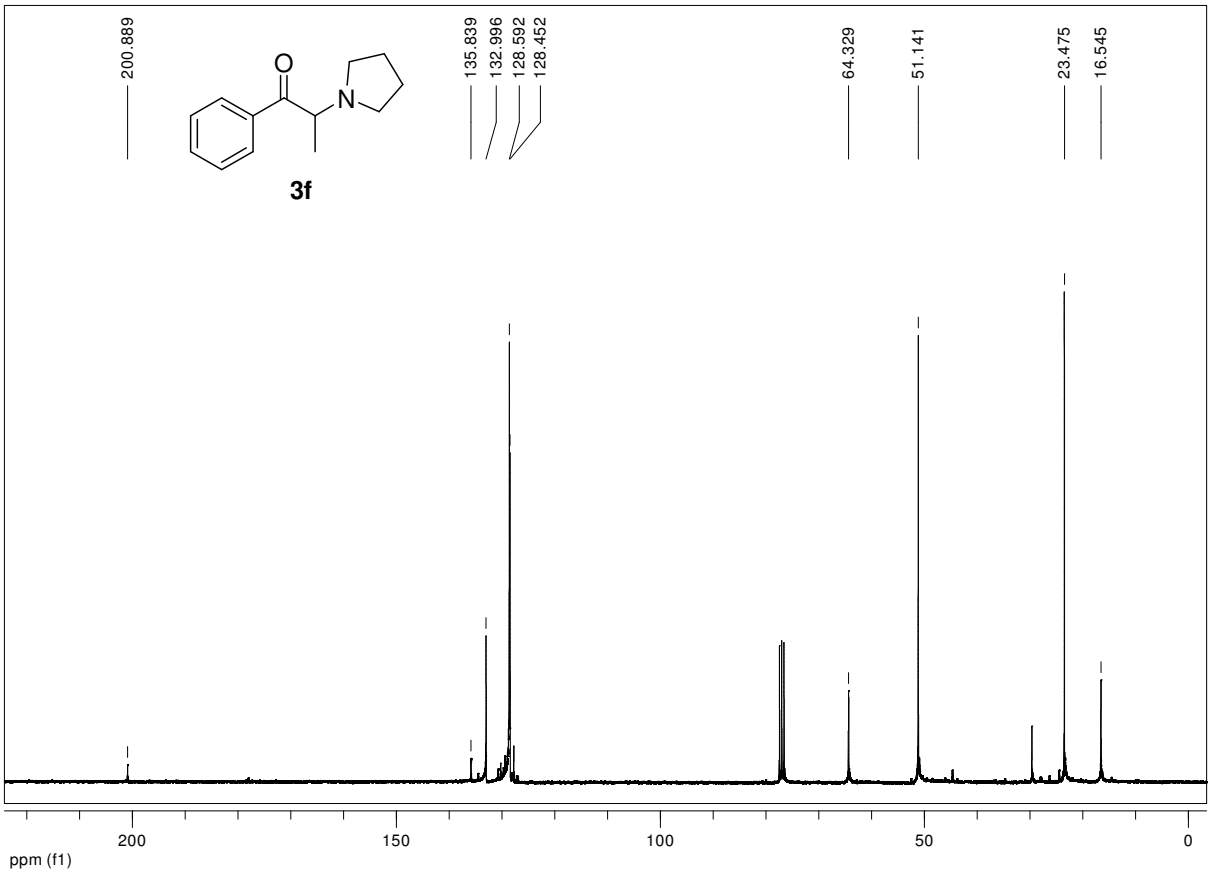

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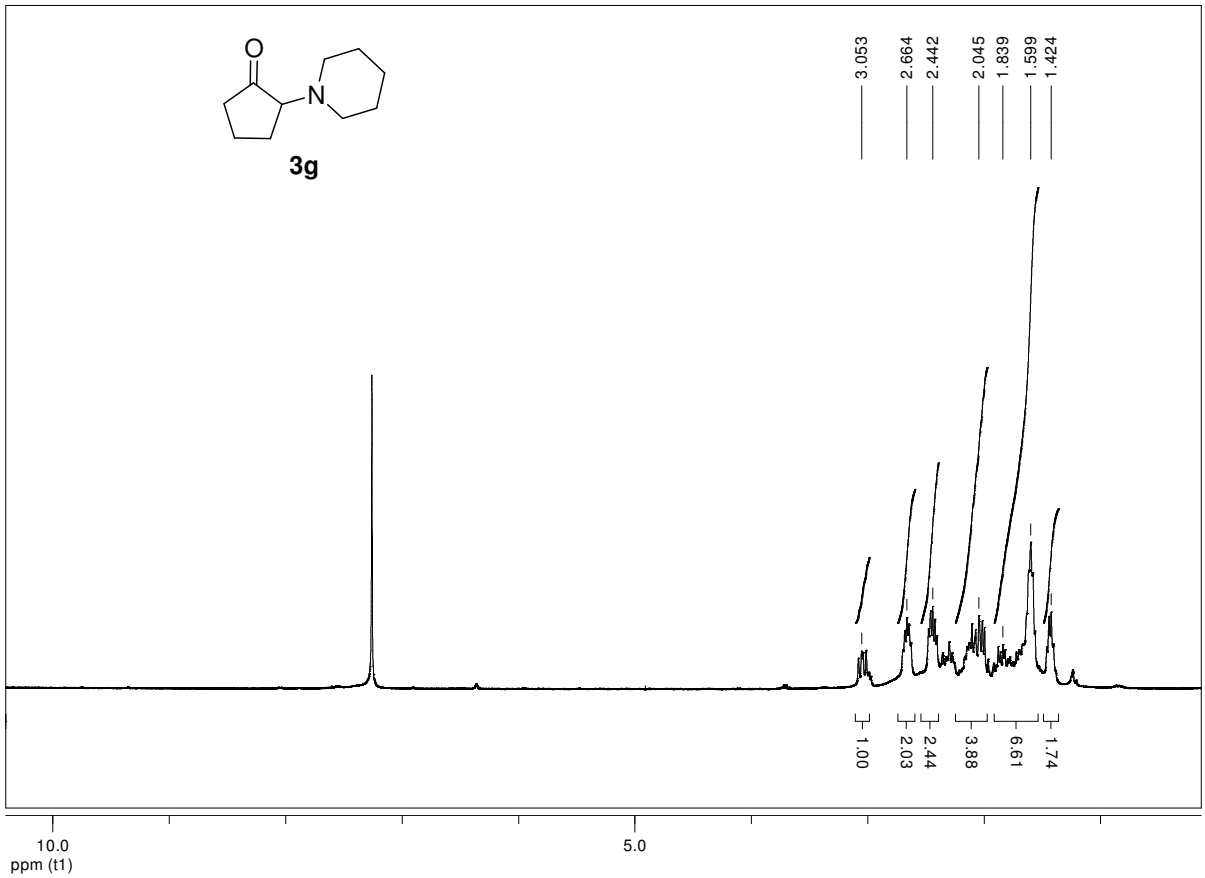

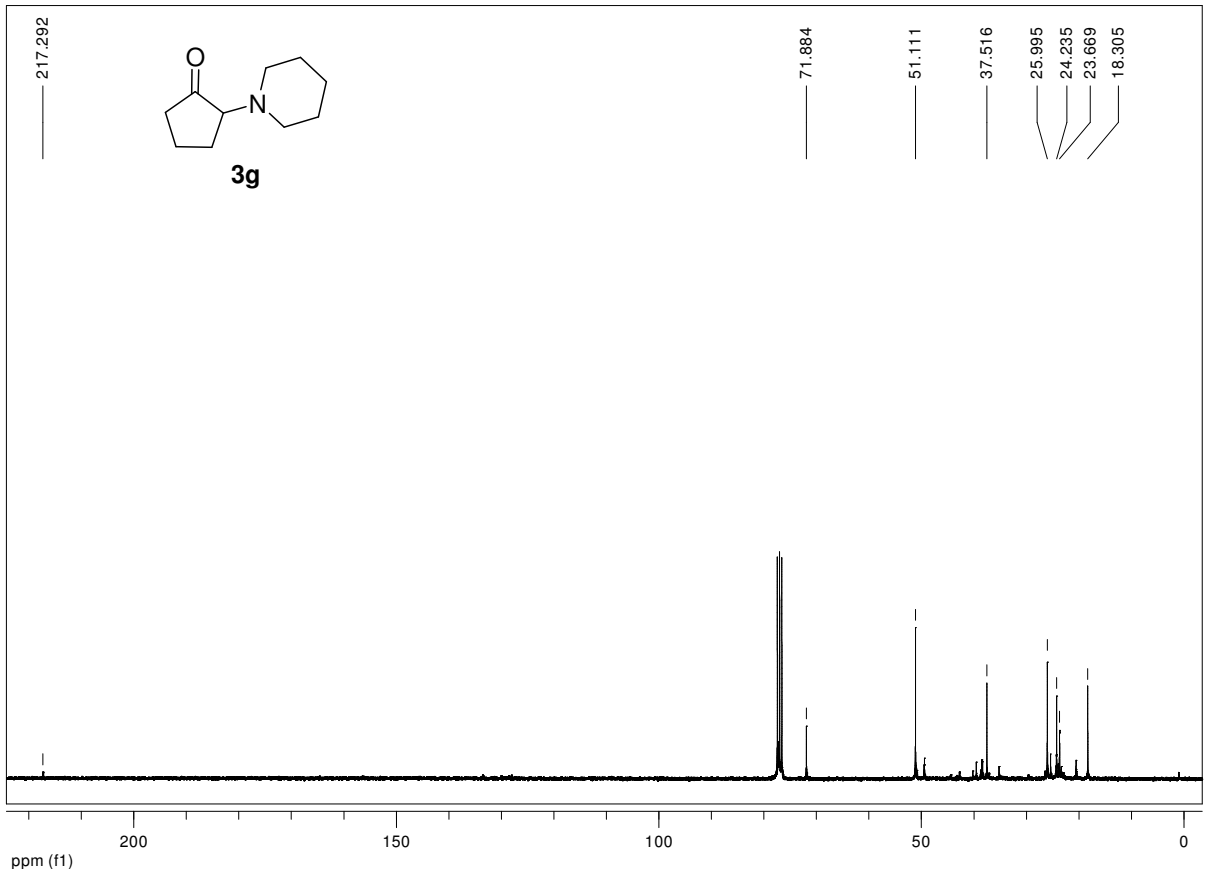

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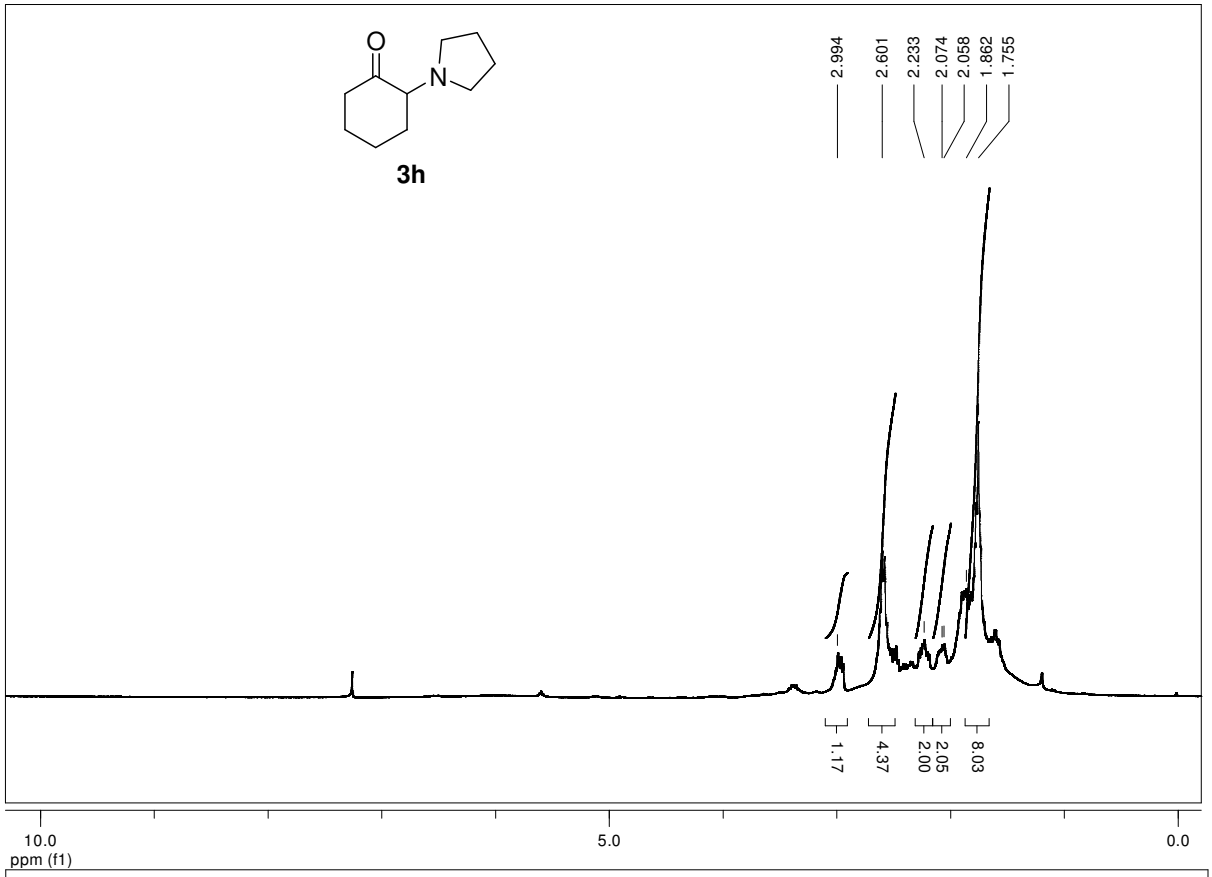

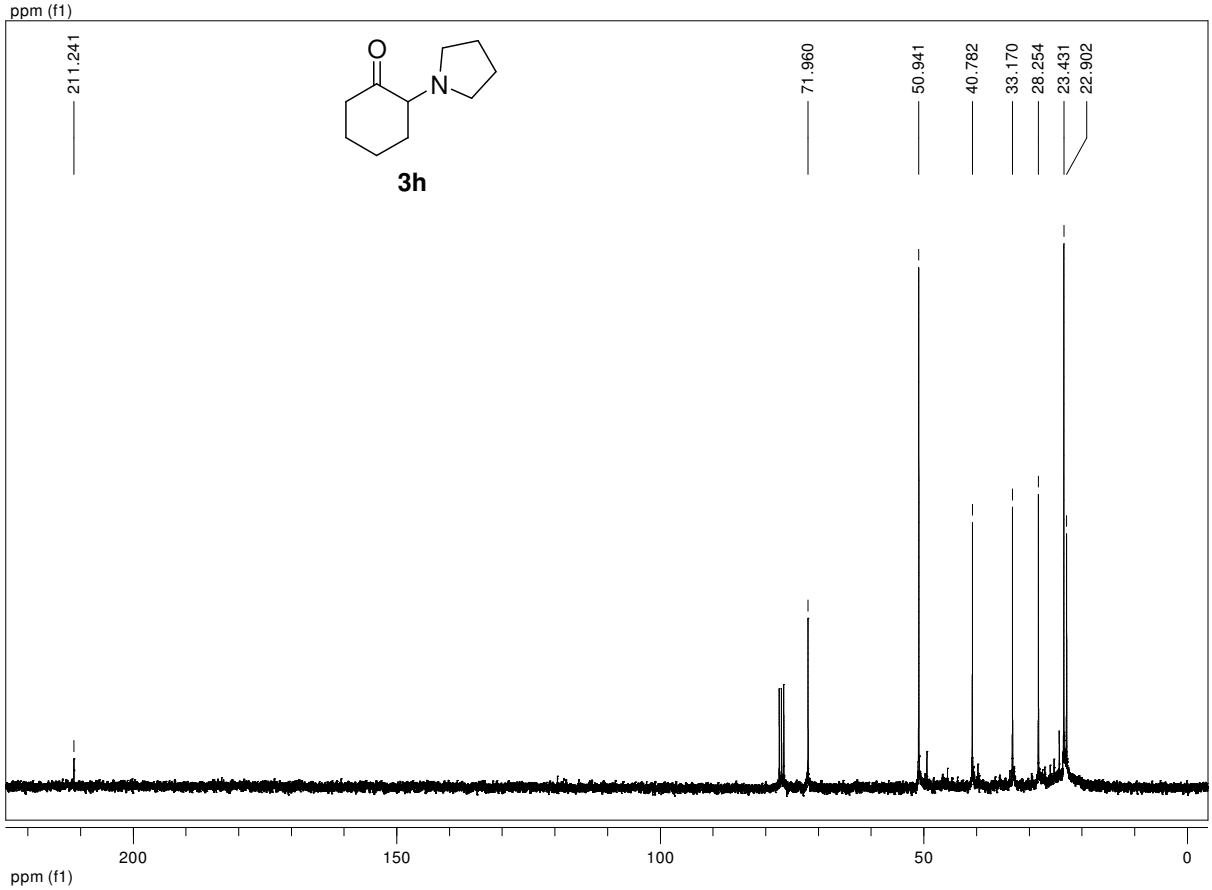

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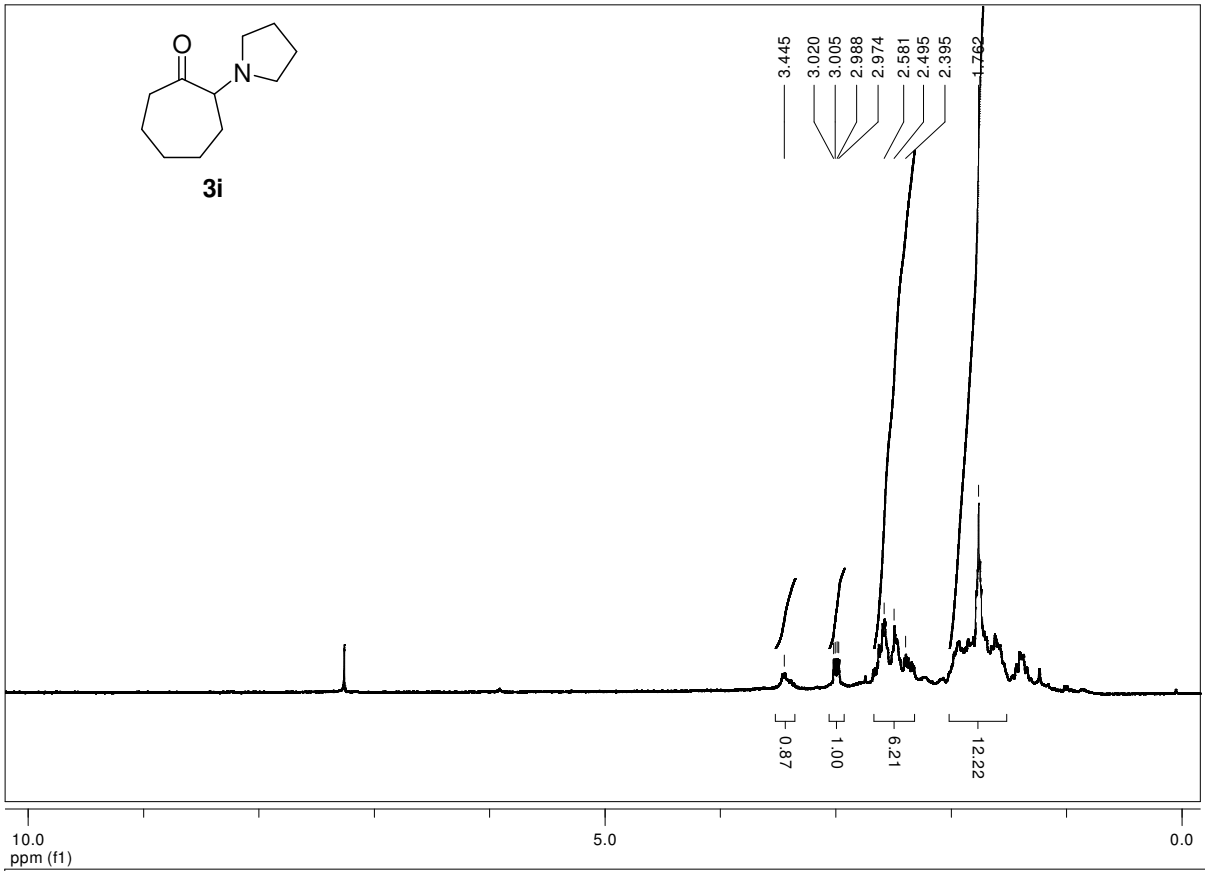

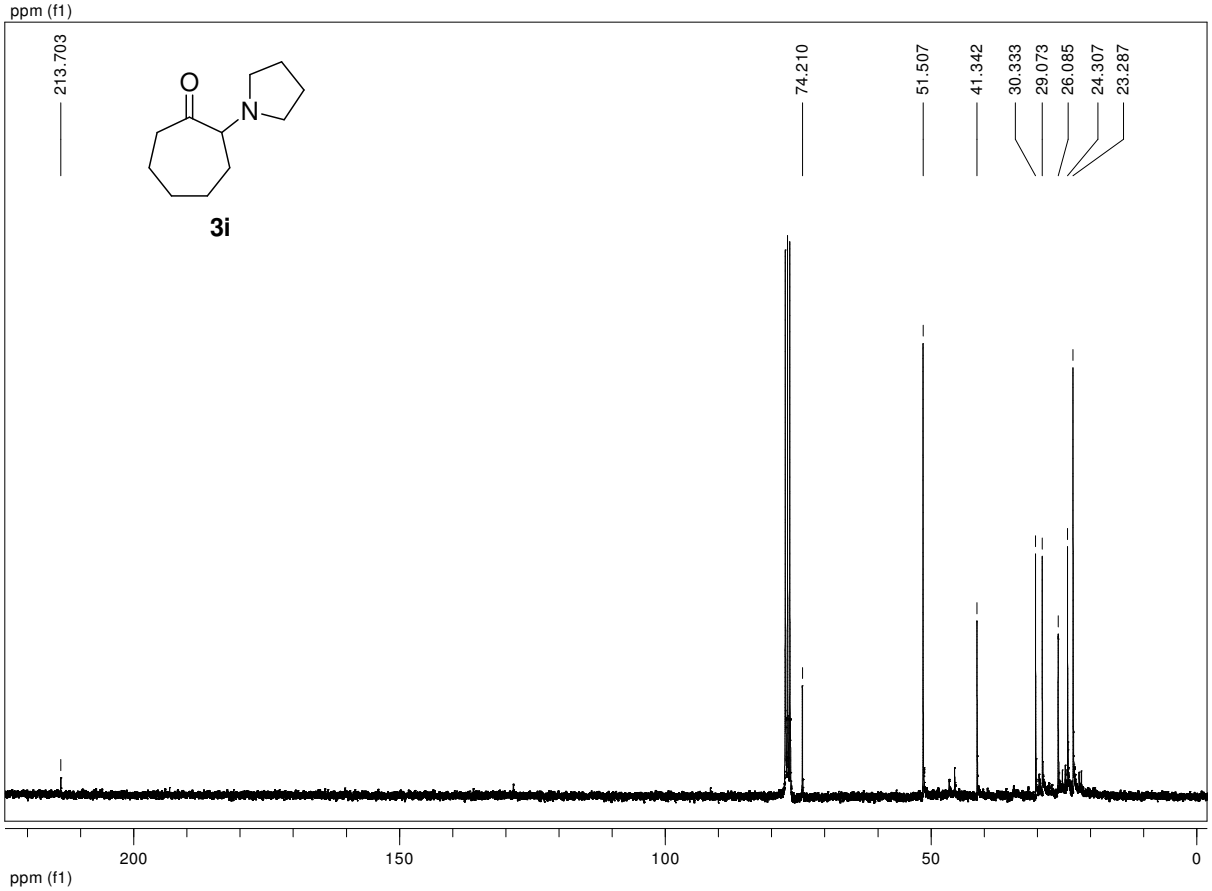

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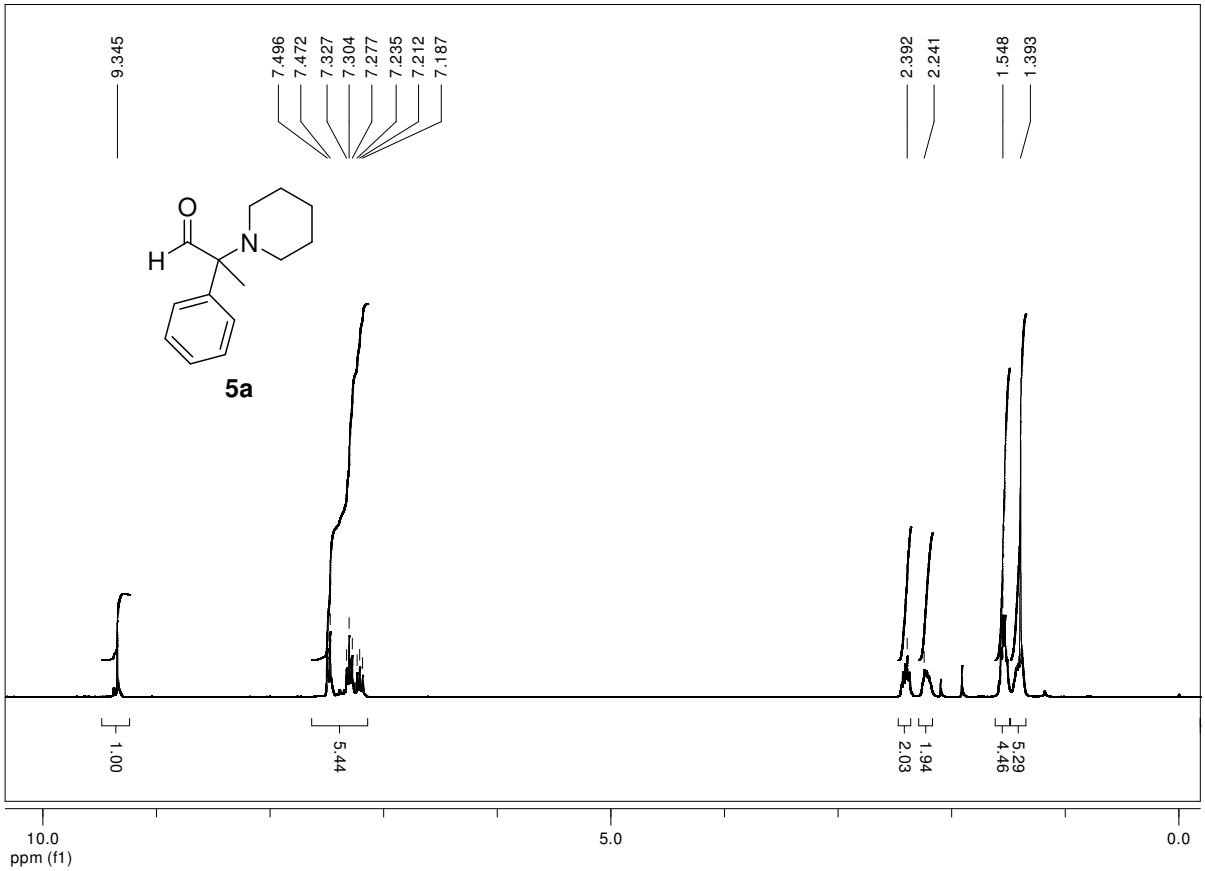

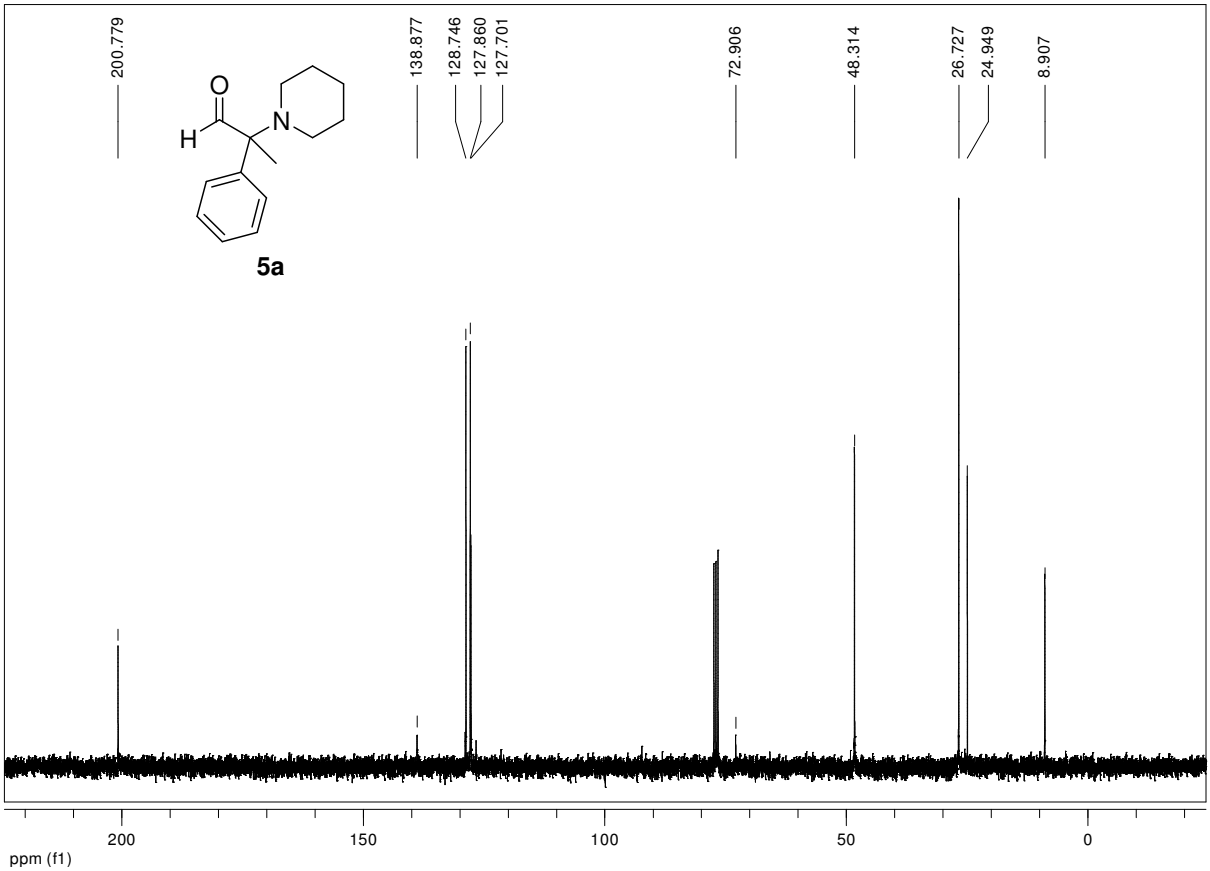

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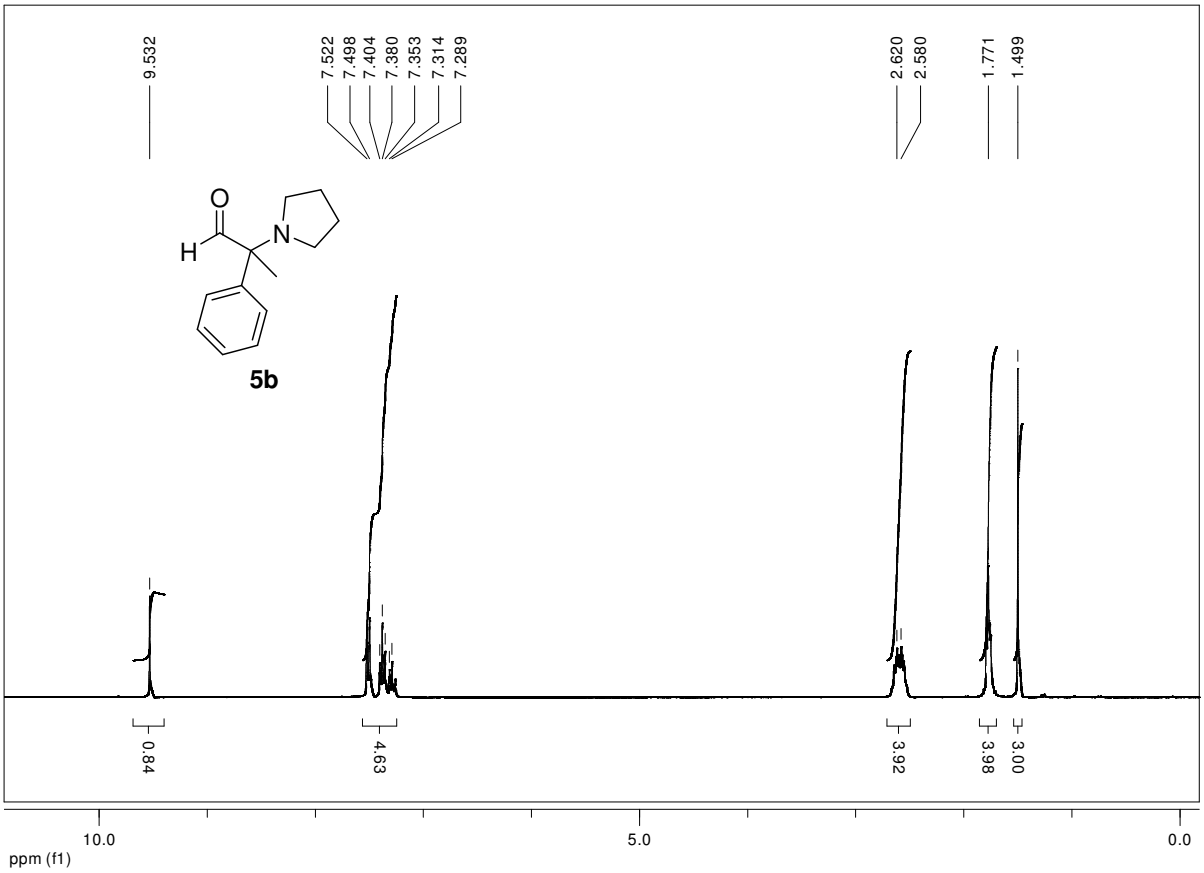

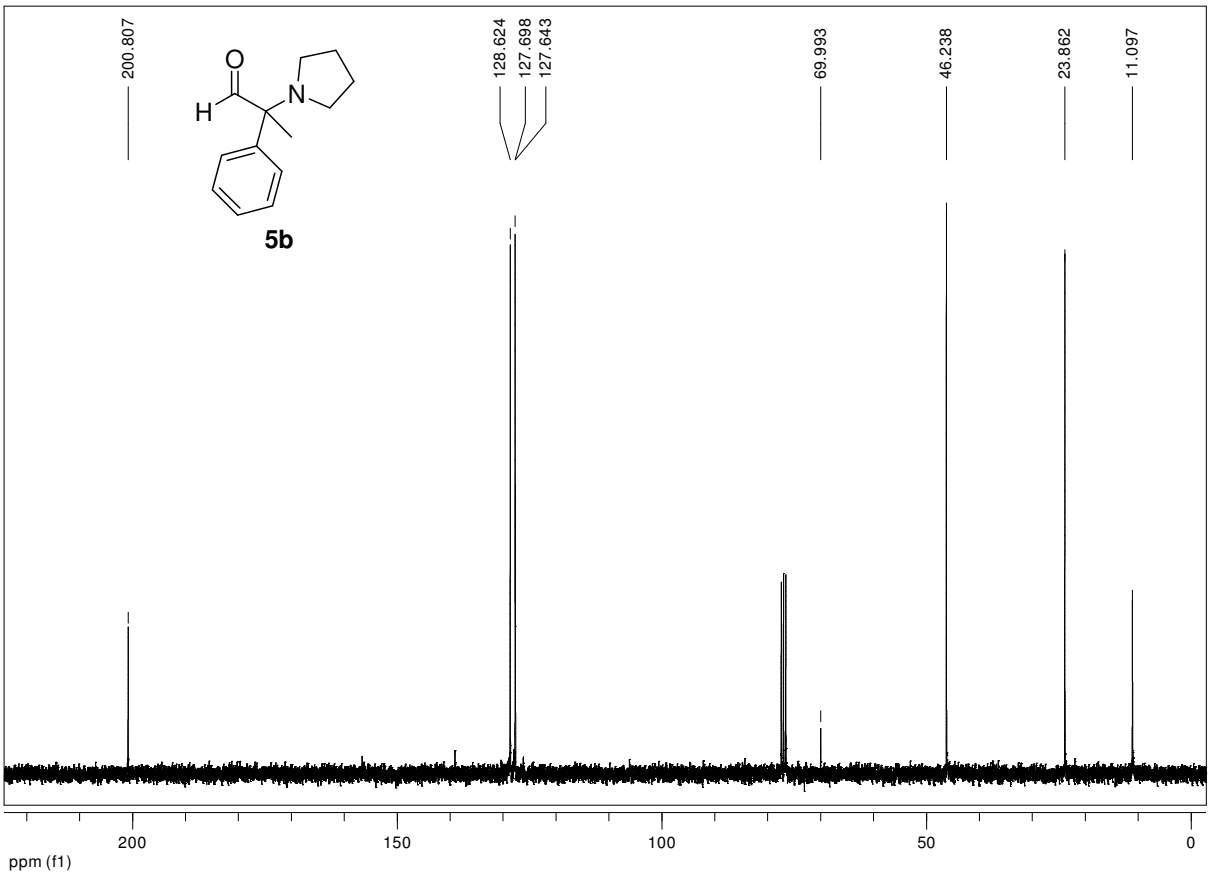

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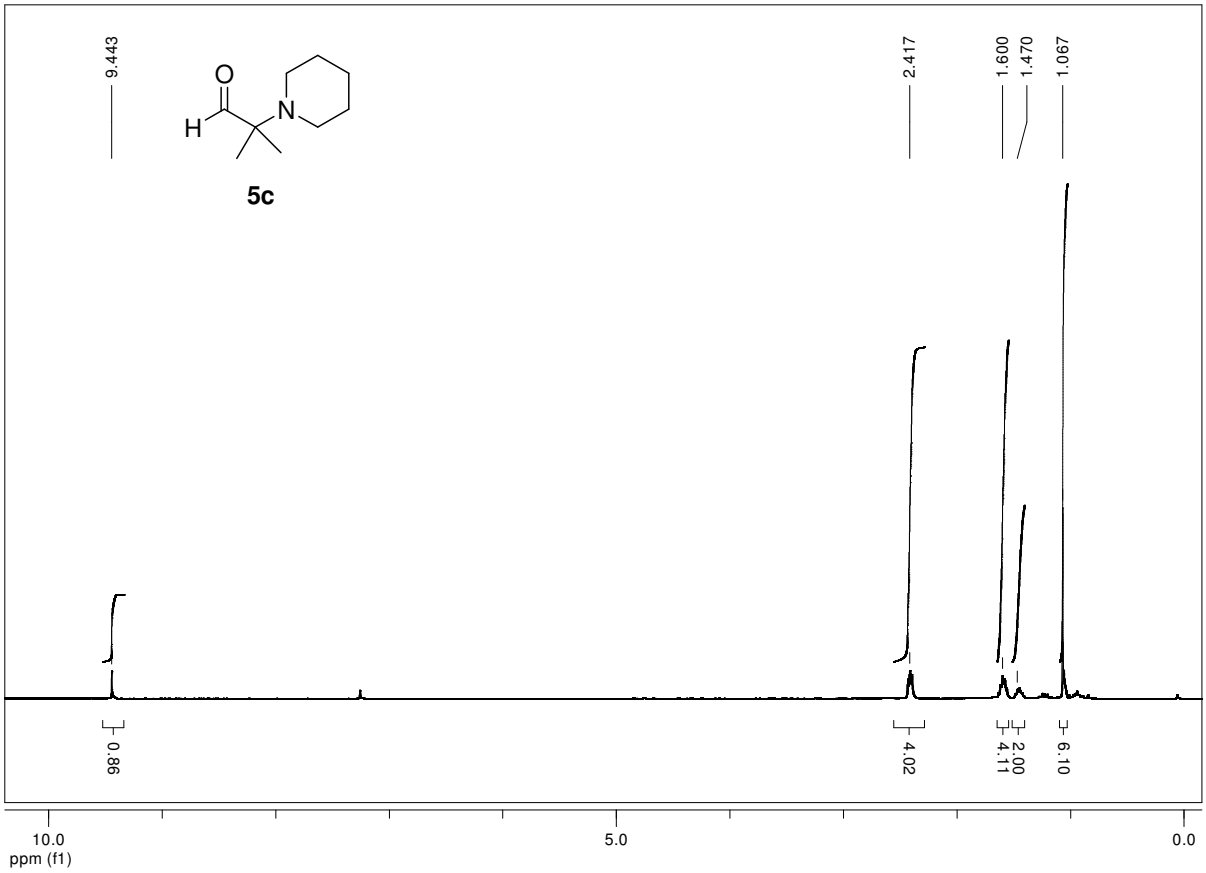

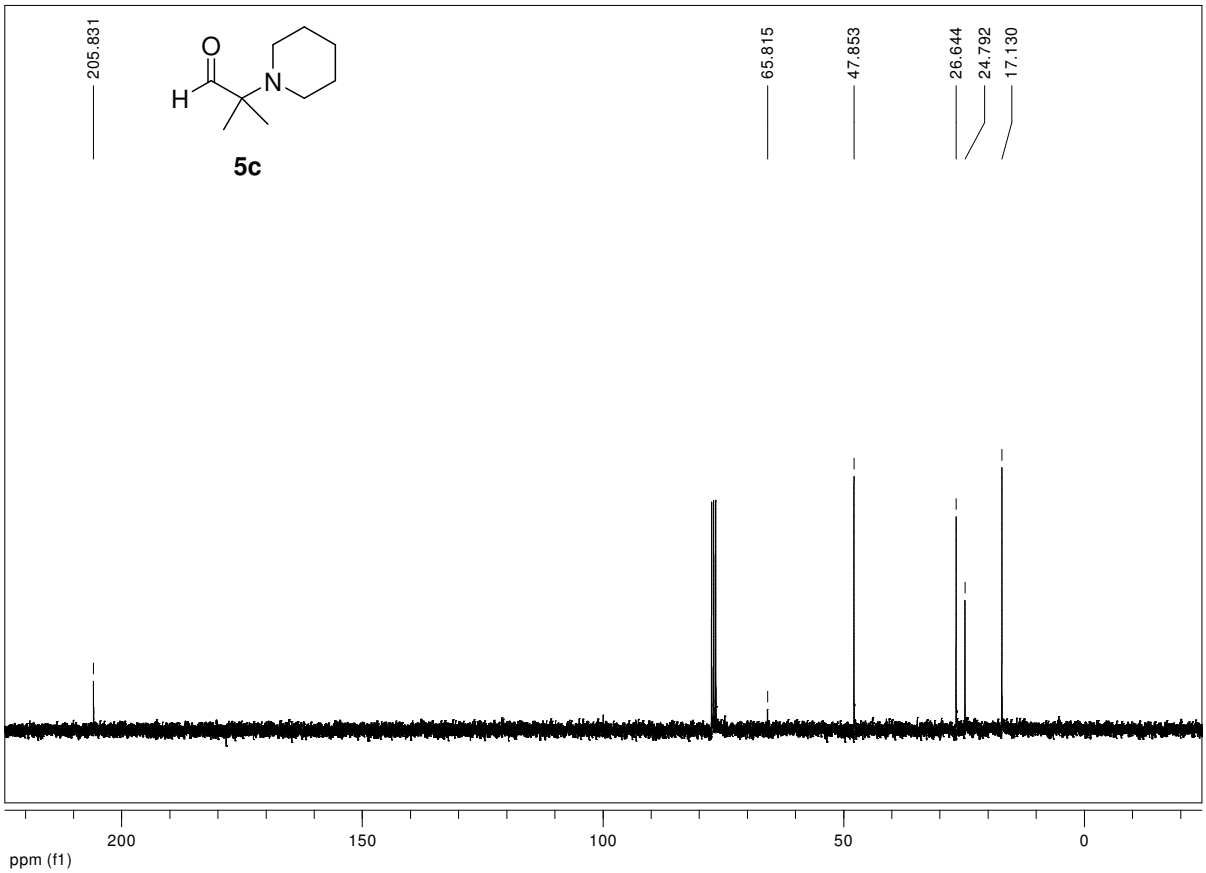

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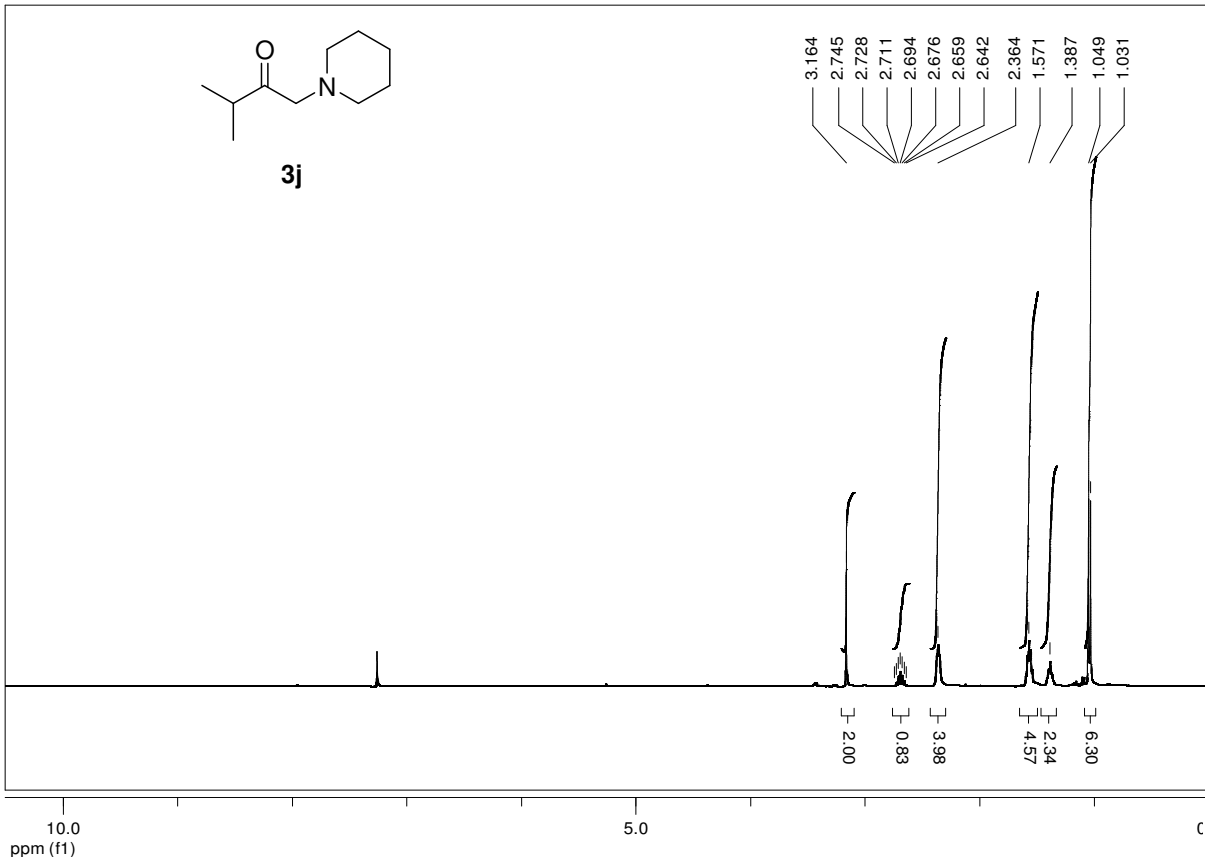

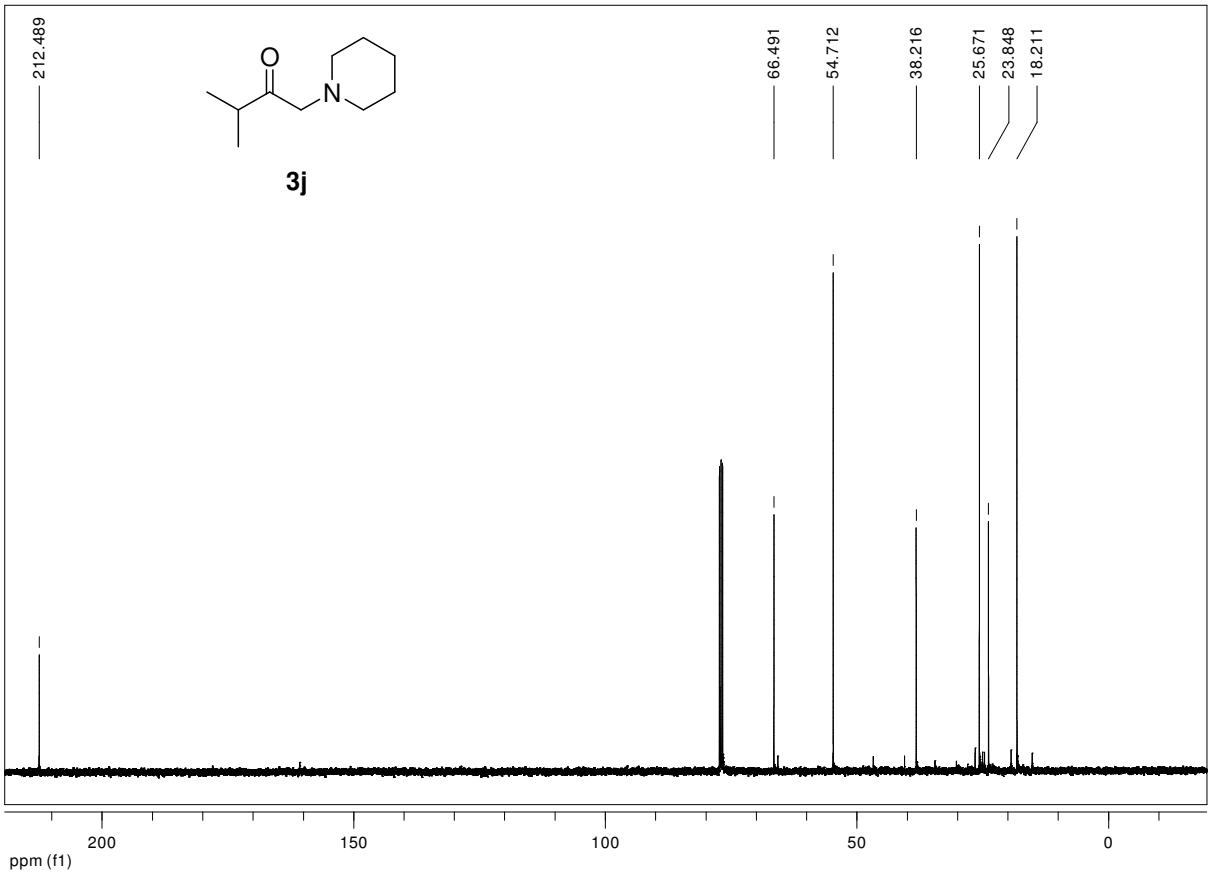

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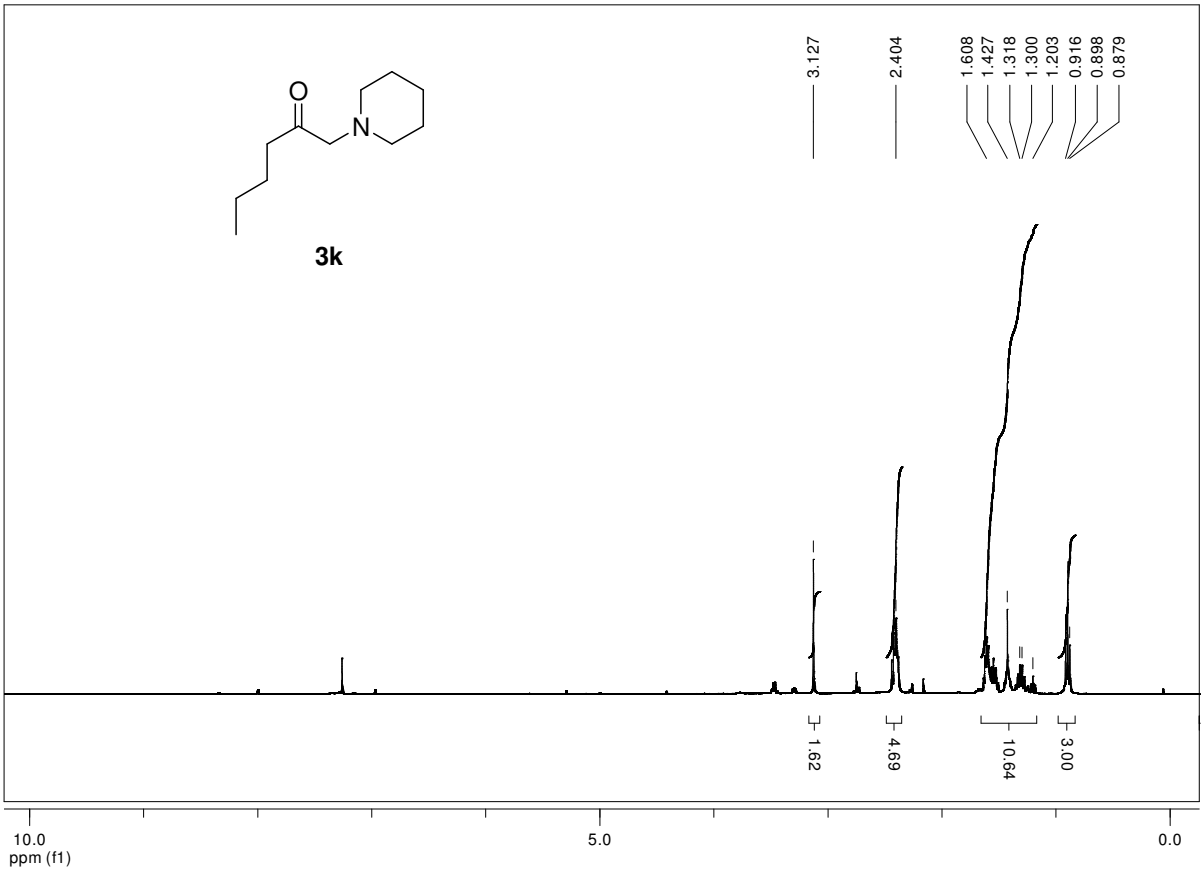

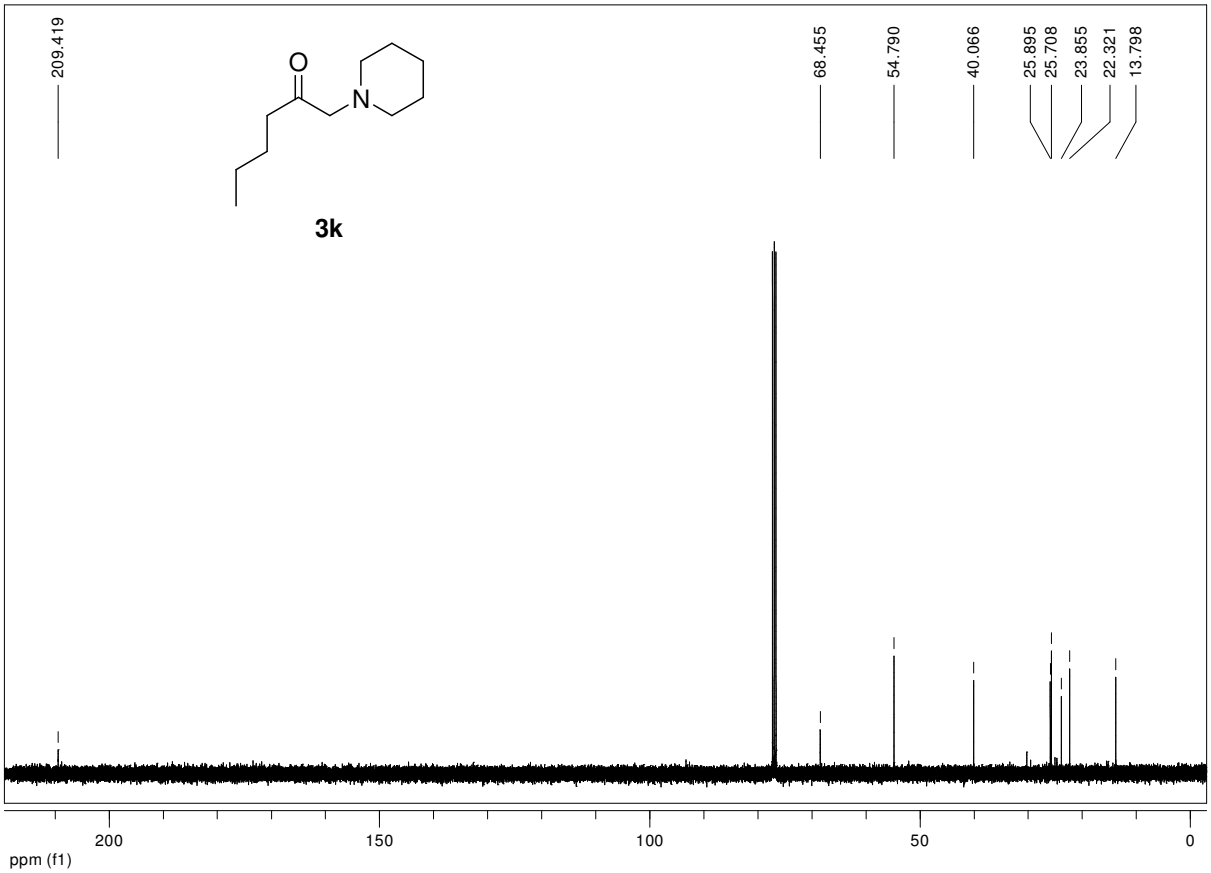

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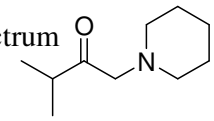
^{1}H-^{1}H COSY spectrum



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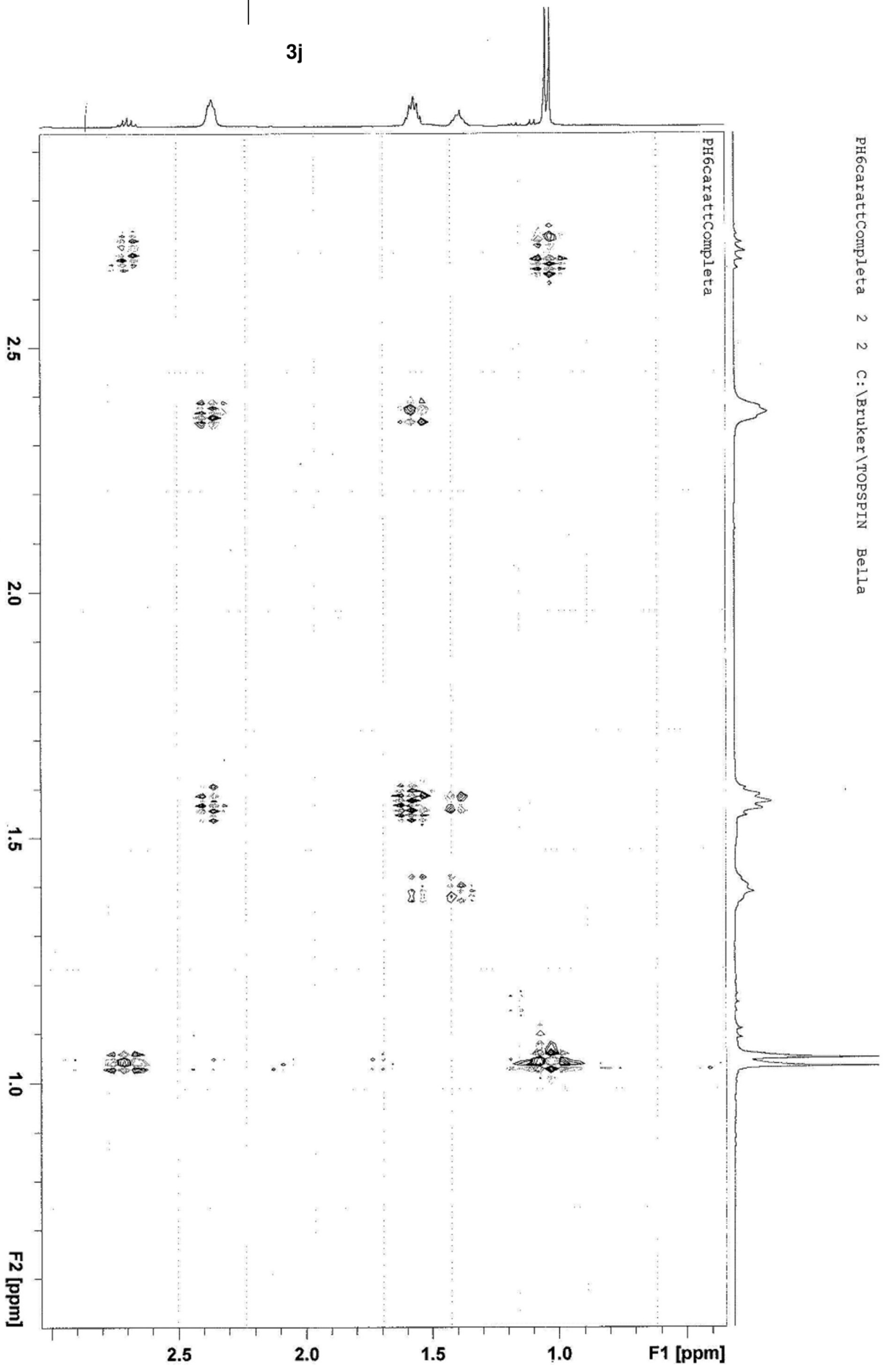

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^{1}H-^{13}C-HSQC spectrum