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Electronic Supplementary Information (ESI)

Fixation and recycling of nitrogen monoxide through carbonitrosation reactions

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Contents

1 General remarks

Solvents and reagents were used as received. ^{1}H-NMR spectra were recorded on 360 and 600 MHz spectrometers using $CDCl_3$ as solvents referenced to TMS (0 ppm) and $CHCl_3$ (7.26 ppm). Chemical shifts are reported in parts per million (ppm). The following abbreviations are used for the description of signals: bs (broad singlet), s (singlet), d (doublet), t (triplet), spt (sept), m (multiplet). ^{13}C-NMR spectra were recorded at 90.5 and 150 MHz in $CDCl_3$, using $CDCl_3$ (77.0 ppm) as standard. Chemical shifts are given in parts per million (ppm). Infrared spectra were recorded on Jasco FT/IR-410 using a sodium chloride crystal as carrier. Wavenumbers $\tilde{\nu}$ are given in cm^{-1}, the intensity of absorption is characterised as broad (b), s (strong), m (medium) and weak (w). Mass spectra were recorded using electron impact (EI) or electrospray ionisation (ESI). Analytical TLC was carried out on Merck silica gel plates using short wave (254 nm) UV light to visualise components. Silica gel (Kieselgel 60, 40-63 mm, Merck) was used for flash column chromatography.

Arenediazoniumsalts were prepared according to literature.[1]

2 Syntheses

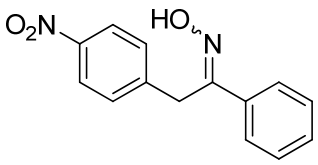
2.1 Synthesis of oximes under nitrogen with iron (II)-sulfate, 100% nitrogen monoxide (General Procedure 1, GP1)

To a mixture of DMSO and H_2O (10:1, *v*/*v*) (50 mL) containing NaOAc (2.00 mmol, 164 mg) and AcOH (2.00 mmol, 0.16 mL) $FeSO_4 \times 7\ H_2O$ (3.00 mmol, 834 mg) was added. The resulting solution was flushed with nitrogen (ca. 2 min) and afterwards nitrogen monoxide was bubbled through the solution for 15 seconds. The alkene (10.0 mmol) was added and a solution of the aryldiazonium tetrafluoroborate (1.00 mmol) in DMSO (3 mL) was added dropwise over 3 minutes. The resulting mixture was stirred for 2 minutes, remaining nitrogen monoxide was removed through a stream of nitrogen and ascorbic acid (5.00 mmol, 881 mg) was added. After additional stirring for 30 minutes, the solution was diluted with water (50 mL) and subsequently extracted with ethyl acetate (4 × 50 ml). The combined organic phases were washed with saturated aqueous NaCl and dried over Na_2SO_4. Removal of the

solvents under reduced pressure and purification by column chromatography on silica gel gave the desired product.

2.2 Characterisation of oximes 3a-3u

2.2.1 Ethanone 2-(4-nitrophenyl)-1-phenyloxime (3a)



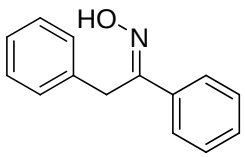
$C_{14}H_{12}N_2O_3$
256.26 g/mol

Compound **3a** was prepared from 4-nitrophenyldiazonium tetrafluoroborate (1.00 mmol, 237 mg) and styrene (30.0 mmol, 3.40 mL) according to the general procedure GP1. Ethanone 2-(4-nitrophenyl)-1-phenyloxime (**3a**) was obtained as brown oil (*E*:*Z* =10:1) in 60% (0.60 mmol, 156 mg) yield.

^{1}H-NMR (360 MHz, $CDCl_3$, major isomer): δ (ppm) = 4.30 (s, 2 H), 7.34-7.38 (m, 3 H), 7.41 (d, *J* = 8.5 Hz, 2 H), 7.56-7.60 (m, 2 H), 8.1 (d, *J* = 8.6 Hz, 2 H).

Analytical data for **3a** in agreement with those reported in literature.[2]

2.2.2 (*E*)-Benzyl phenyl ketoxime (3b)



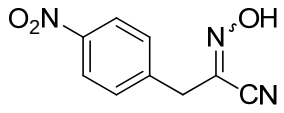
$C_{14}H_{13}NO$
211.26 g/mol

Compound **3b** was prepared from phenyldiazonium tetrafluoroborate (1.00 mmol, 237 mg) and styrene (30.0 mmol, 3.4 mL) according to the general procedure GP1. Benzyl phenyl ketoxime (**3b**) was obtained as brown oil in 50% (0.50 mmol, 106 mg) yield.

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 4.22 (s, 2 H), 7.16-7.20 (m, 1 H), 7.23-7.27 (m, 2 H), 7.27-7.36 (m, 5 H), 7.60-7.63 (m, 2 H).

Analytical data for **3b** in agreement with those reported in literature.[2]

2.2.3 2-(Hydroxyimino)-3-(4-nitrophenyl)propanenitrile (3c)



$C_9H_7N_3O_3$
205.17 g/mol

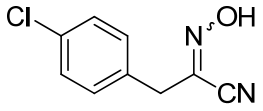
Compound **3c** was prepared from 4-nitrophenyldiazonium tetrafluoroborate (1.00 mmol, 237 mg) and acrylonitrile (30.0 mmol, 2.00 mL) according to the general procedure GP1. 2-(Hydroxyimino)-3-(4-nitrophenyl)propanenitrile (**3c**) was obtained as a brown oil (ca. 1:1 mixture of *E:Z* isomers) in 78% (0.78 mmol, 160 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$, *E* isomer): δ (ppm) = 3.96 (s, 2 H), 7.43-7.48 (m, 2 H), 8.19-8.24 (m, 2 H).

^{1}H-NMR (600 MHz, $CDCl_3$, *Z* isomer): δ (ppm) = 3.88 (s, 2 H), 7.43-7.48 (m, 2 H), 8.19-8.24 (m, 2 H).

Analytical data for **3c** in agreement with those reported in literature.[2]

2.2.4 3-(4-Chlorophenyl)-2-(hydroxyimino)propanenitrile (3d)



$C_9H_7ClN_2O$
194.62 g/mol

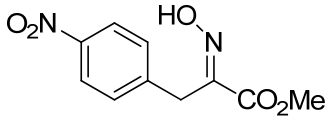
Compound **3d** was prepared from 4-chlorophenyldiazonium tetrafluoroborate (1.00 mmol, 226 mg) and acrylonitrile (30.0 mmol, 2.00 mL) according to the general procedure GP1. 3-(4-Chlorophenyl)-2-(hydroxyimino)propanenitrile (**3d**) was obtained as brown solid (ca. 1:1 mixture of *E*:*Z* isomers) in 71% (0.71 mmol, 138 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$, *E* isomer): δ (ppm) = 3.83 (s, 2 H), 7.16-7.20 (m, 2 H), 7.30-7.34 (m, 2 H).

^{1}H-NMR (600 MHz, $CDCl_3$, *Z* isomer): δ (ppm) = 3.73 (s, 2 H), 7.16-7.20 (m, 2 H), 7.30-7.34 (m, 2 H).

Analytical data for **3d** in agreement with those reported in literature.[2]

2.2.5 (*E*)-Methyl 2-(hydroxyimino)-3-(4-nitrophenyl)propanoate (3e)



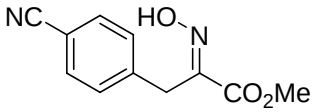
$C_{10}H_{10}N_2O_5$
238.20 g/mol

Compound **3e** was prepared from 4-nitrophenyldiazonium tetrafluoroborate (1.00 mmol, 237 mg) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 2-(hydroxyimino)-3-(4-nitrophenyl)propanoate (**3e**) was obtained as a yellow solid 84% (0.84 mmol, 200 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3 H), 4.06 (s, 2 H), 7.43 (d, *J* = 8.5 Hz, 2 H), 8.13 (d, *J* = 8.5 Hz, 2 H).

Analytical data for **3e** in agreement with those reported in literature.[2]

2.2.6 (*E*)-Methyl 3-(4-cyanophenyl)-2-(hydroxyimino)propanoate (3f)



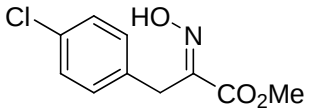
$C_{11}H_{10}N_2O_3$
218.21 g/mol

Compound **3f** was prepared from 4-cyanophenyldiazonium tetrafluoroborate (1.00 mmol, 217 mg) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 3-(4-cyanophenyl)-2-(hydroxyimino)propanoate (**3f**) was obtained as a yellow solid in 82% (0.82 mmol, 178 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.85 (s, 3 H), 4.04 (s, 2 H), 7.43 (d, *J* = 8.1 Hz, 2 H), 7.57 (d, *J* = 8.1 Hz, 2 H).

Analytical data for **3f** in agreement with those reported in literature.[2]

2.2.7 (*E*)-Methyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (3g)



$C_{10}H_{10}ClNO_3$
227.64 g/mol

Compound **3g** was prepared from 4-chlorophenyldiazonium tetrafluoroborate (1.00 mmol, 226 mg) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (**3g**) was obtained as a yellow solid in 70% (0.70 mmol, 159 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.83 (s, 3 H), 3.91 (s, 2 H), 7.22-7.26 (m, 4 H).

Analytical data for **3g** in agreement with those reported in literature.[2]

Compound **3g** was also prepared according to the following procedures:

a) Synthesis of **3g** under air with iron (II)-sulfate, ca. 10% nitrogen monoxide:
To a mixture of DMSO and H_2O (10:1, *v*/*v*) (100 mL) containing NaOAc (2.00 mmol, 164 mg) and AcOH (2.00 mmol, 0.16 mL) $FeSO_4 \times 7\ H_2O$ (5.00 mmol, 1.39 g) was added. The resulting solution was flushed with a simulated stream of waste gas containing ca. 10% of nitrogen monoxide in air. For the generation of the stream, nitrogen monoxide (100 mL/min) was mixed with compressed air (1 L/min). The resulting gas stream was then passed through the absorption solution over 1 minute. Methylacrylate (5.00 mmol. 0.45 mL) was added and a solution of *p*-chlorodiazonium tetrafluoroborate (1.00 mmol, 226 mg) in DMSO (3 mL) was added dropwise over 3 minutes. The resulting mixture was stirred for 2 minutes, remaining nitrogen monoxide was removed through a stream of nitrogen and ascorbic acid (5.00 mmol, 881 mg) was added. After additional stirring for 30 minutes, the solution was diluted with water (50 mL) and subsequently extracted with ethyl acetate (4 × 50 ml). The combined organic phases were washed with saturated aqueous NaCl and dried over

Na_2SO_4. Removal of the solvents under reduced pressure and purification by column chromatography on silica gel gave the desired product. Compound **3g** was obtained in 43% yield.

b) Synthesis of **3g** under air with iron (II)-sulfate, ca. 5% nitrogen monoxide:

To a mixture of DMSO and H_2O (10:1, *v*/*v*) (100 mL) containing NaOAc (2.00 mmol, 164 mg) and AcOH (2.00 mmol, 0.16 mL) $FeSO_4 \times 7\ H_2O$ (2.50 mmol, 695 mg) was added. The resulting solution was flushed with a simulated stream of waste gas containing ca. 5% of nitrogen monoxide in air. For the generation of the stream, nitrogen monoxide (50 mL/min) was mixed with compressed air (1 L/min). The resulting gas stream was then passed through the absorption solution over 1 minute. Methylacrylate (2.50 mmol. 0.23 mL) was added and a solution of *p*-chlorodiazonium tetrafluoroborate (0.50 mmol, 113 mg) in DMSO (3 mL) was added dropwise over 3 minutes. The resulting mixture was stirred for 2 minutes, remaining nitrogen monoxide was removed through a stream of nitrogen and ascorbic acid (5.00 mmol, 881 mg) was added. After additional stirring for 30 minutes, the solution was diluted with water (50 mL) and subsequently extracted with ethyl acetate (4 × 50 ml). The combined organic phases were washed with saturated aqueous NaCl and dried over Na_2SO_4. Removal of the solvents under reduced pressure and purification by column chromatography on silica gel gave the desired product. Compound **3g** was obtained in 20% yield.

c) Synthesis of **3g** under air with iron (II)-sulfate, 100% nitrogen monoxide and ca. 2% sulphur dioxide:

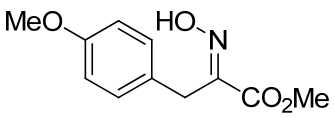
To a mixture of DMSO and H_2O (10:1, *v*/*v*) (100 mL) containing NaOAc (2.00 mmol, 164 mg) and AcOH (2.00 mmol, 0.16 mL) $FeSO_4 \times 7\ H_2O$ (5.00 mmol, 1.39 g) was added. The resulting solution was flushed with a stream of pure nitrogen monoxide with ca. 2% SO_2. For the generation of SO_2 (ca. 10 mL) a solution of HCl (5 mL, 5 N) was slowly added to $NaHSO_3$ (0.45 mmol, 46.7 mg) and was allowed to react over 1 minute. A stream of nitrogen monoxide was passed through the reaction vessel and subsequently passed through the absorption solution over1 minute. Methylacrylate (30.0 mmol, 2.70 mL) was added and a solution of *p*-chlorodiazonium tetrafluoroborate (1.00 mmol, 226 mg) in DMSO (3 mL) was added dropwise over 3 minutes. The

resulting mixture was stirred for 2 minutes, remaining nitrogen monoxide was removed through a stream of nitrogen and ascorbic acid (5.00 mmol, 881 mg) was added. After additional stirring for 30 minutes, the solution was diluted with water (50 mL) and subsequently extracted with ethyl acetate (4 × 50 ml). The combined organic phases were washed with saturated aqueous NaCl and dried over Na_2SO_4. Removal of the solvents under reduced pressure and purification by column chromatography on silica gel gave the desired product. Compound **3g** was obtained in 67% yield.

d) Synthesis of **3g** under air with iron (II)-sulfate, ca. 10% nitrogen monoxide and ca. 2% sulphur dioxide in air:

To a mixture of DMSO and H_2O (10:1, *v*/*v*) (100 mL) containing NaOAc (2.00 mmol, 164 mg) and AcOH (2.00 mmol, 0.16 mL) $FeSO_4 \times 7\ H_2O$ (5.00 mmol, 1.39 g) was added. The resulting solution was flushed with a simulated waste gas stream containing ca. 10% NO and ca. 2% SO_2. For the generation of SO_2 (ca. 20 mL) a solution of HCl (10 mL, 5 N) was slowly added to $NaHSO_3$ (0.90 mmol, 93.4 mg) and was allowed to react over 1 minute. A stream of nitrogen monoxide (50 mL/min) and air (1 L/min) (ca. 10% NO in air) was passed through the reaction vessel and subsequently passed through the absorption solution over 1 minute. Methylacrylate (5.00 mmol, 0.45 mL) was added and a solution of *p*-chlorodiazonium tetrafluoroborate (1.00 mmol, 226 mg) in DMSO (3 mL) was added dropwise over 3 minutes. The resulting mixture was stirred for 2 minutes, remaining nitrogen monoxide was removed through a stream of nitrogen and ascorbic acid (5.00 mmol, 881 mg) was added. After additional stirring for 30 minutes, the solution was diluted with water (50 mL) and subsequently extracted with ethyl acetate (4 × 50 ml). The combined organic phases were washed with saturated aqueous NaCl and dried over Na_2SO_4. Removal of the solvents under reduced pressure and purification by column chromatography on silica gel gave the desired product. Compound **3g** was obtained in 31% yield.

2.2.8 (*E*)-Methyl 2-(hydroxyimino)-3-(4-methoxyphenyl)propanoate (3h)



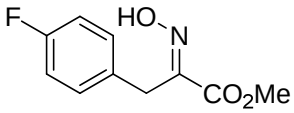
$C_{11}H_{13}NO_4$
223.23 g/mol

Compound **3h** was prepared from 4-methoxyphenyldiazonium tetrafluoroborate (1.00 mmol, 221 mg) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 2-(hydroxyimino)-3-(4-methoxyphenyl)propanoate (**3h**) was obtained as a yellow solid in 55% (0.55 mmol, 122 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.77 (s, 3 H), 3.83 (s, 3 H), 3.92 (s, 2 H), 6.81 (d, *J* = 8.6 Hz, 2 H), 7.24 (d, *J* = 8.6 Hz, 2 H).

Analytical data for **3h** in agreement with those reported in literature.[2]

2.2.9 (*E*)-Methyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (3i)



$C_{10}H_{10}FNO_3$
211.19 g/mol

Compound **3i** was prepared from 4-fluorophenyldiazonium tetrafluoroborate (10.0 mmol, 2.10 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (**3i**) was obtained as brown oil in 62% (6.20 mmol, 1.30 g) yield.

***R*$_f$** 0.5 (EtOAc / hexane = 1:2) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3 H), 3.95 (s, 2 H), 6.94-6.98 (m, 2 H), 7.27-7.31 (m, 2 H).

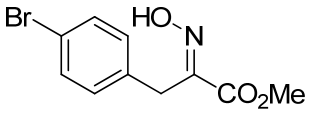
^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 29.7 (CH_2), 52.8 (CH_3), 115.3 (d, J_{CF} = 21.4 Hz, 2 × CH), 130.7 (d, J_{CF} = 8.0 Hz, 2 × CH), 131.2 (d,

J_{CF} = 3.3 Hz, C_q), 150.9 (d, J_{CF} = 0.9 Hz, C_q), 161.7 (d, J_{CF} = 245.1 Hz, C_q), 163.6 (C_q).

MS (EI) *m/z* (%): 211 (26) [M^+], 149 (26), 135 (42), 134 (100), 109 (85), 108 (22), 107 (15), 83 (17), 59 (31).

HRMS (EI) calculated for $C_{10}H_{10}FNO_3$ [M^+]: 211.0645, found: 211.0645.

2.2.10 (*E*)-Methyl 3-(4-bromophenyl)-2-(hydroxyimino)propanoate (3j)



$C_{10}H_{10}BrNO_3$
270.98 g/mol

Compound **3j** was prepared from 4-bromophenyldiazonium tetrafluoroborate (10.0 mmol, 2.71 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(4-bromophenyl)-2-(hydroxyimino)propanoate (**3j**) was obtained as brown oil in 69% (6.20 mmol, 1.88 g) yield.

***R*f** 0.3 (EtOAc / hexane = 1:2) [UV].

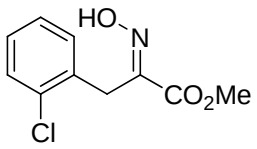
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3 H), 3.93 (s, 2 H), 7.19 (d, *J* = 8.2 Hz, 2 H), 7.40 (d, *J* = 8.3 Hz, 2 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 29.9 (CH_2), 52.9 (CH_3), 120.7 (C_q), 130.9 (2 × CH), 131.6 (2 × CH), 134.5 (C_q), 150.3 (C_q), 163.5 (C_q).

MS (EI) *m/z* (%):271 (50) [M^+], 273 (30), 271 (32), 257 (16), 255 (17), 211 (25), 209 (20), 197 (35), 196 (100), 195 (36), 194 (94), 171 (52), 169 (52), 143 (13), 131 (10), 117 (12), 116 (69), 115 (17), 90 (42), 89 (61), 59 (45).

HRMS (EI) calculated for $C_{10}H_{10}BrNO_3$ [M^+]: 270.9844, found: 270.9843.

2.2.11 (*E*)-Methyl 3-(2-chlorophenyl)-2-(hydroxyimino)propanoate (3k)

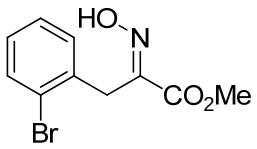


$C_{10}H_{10}ClNO_3$
227.64 g/mol

Compound **3k** was prepared from 2-chlorophenyldiazonium tetrafluoroborate (10.0 mmol, 2.26 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(2-chlorophenyl)-2-(hydroxyimino)propanoate (**3k**) was obtained as brown oil in 59% (5.90 mmol, 1.34 g) yield.

R_f	0.5 (EtOAc / hexane = 1:2) [UV].
^{1}H-NMR	(600 MHz, $CDCl_3$): δ (ppm) = 3.79 (s, 3 H), 4.10 (s, 2 H), 7.10-7.13 (m, 1 H), 7.13-7.16 (m, 2 H), 7.33-7.36 (m, 1 H).
^{13}C-NMR	(90.5 MHz, $CDCl_3$): δ (ppm) = 28.5 (CH_2), 52.8 (CH_3), 126.8 (CH), 127.9 (CH), 129.4 (CH) 129.5 (CH), 133.3 (C_q), 133.9 (C_q), 150.0 (C_q), 163.6 (C_q).
MS (EI)	*m/z* (%): 227 (48) [M^+], 229 (17), 192 (23), 176 (17), 167 (24), 165 (33), 160 (22), 153 (11), 152 (44), 151 (31), 150 (100), 127 (29), 126 (10), 125 (91), 116 (43), 115 (14), 90 (12), 89 (49), 75 (10), 63 (14), 59 (38).
HRMS (EI)	calculated for $C_{10}H_{10}ClNO_3$ [M^+]: 227.0349, found: 227.0349.

2.2.12 (*E*)-Methyl 3-(2-bromophenyl)-2-(hydroxyimino)propanoate (3l)



$C_{10}H_{10}BrNO_3$
270,98 g/mol

Compound **3l** was prepared from 2-bromophenyldiazonium tetrafluoroborate (9.10 mmol, 2.48 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general

procedure GP1. (*E*)-Methyl 3-(2-bromophenyl)-2-(hydroxyimino)propanoate (**3l**) was obtained as brown oil in 70% (6.37 mmol, 1.73 g) yield.

***R*f** 0.5 (EtOAc / hexane = 1:2) [UV].

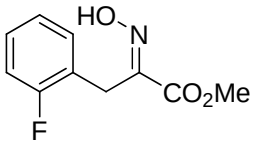
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.82 (s, 3 H), 4.11 (s, 2 H), 7.07-7.11 (m, 2 H), 7.21 (t, *J* = 7.4 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 1 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 31.3 (CH_2), 52.9 (CH_3), 124.5 (C_q), 127.5 (CH), 128.2 (C_q), 129.3 (C_q), 132.9 (C_q), 135.1 (C_q), 150.5 (C_q), 163.6 (C_q).

MS (EI) *m/z* (%): 270 (4) [M^+], 197 (14), 196 (36), 195 (13), 194 (34), 193 (12), 192 (100), 176 (10), 169 (31), 160 (16), 143 (17), 116 (40), 115 (23), 90 (26), 85 (45), 63 (15), 59 (24).

HRMS (EI) calculated for $C_{10}H_{10}BrNO_3$ [M^+]: 270.9844, found: 270.9845.

2.2.13 (*E*)-Methyl 3-(2-fluorophenyl)-2-(hydroxyimino)propanoate (3m)



$C_{10}H_{10}FNO_3$
211.19 g/mol

Compound **3m** was prepared from 2-fluorophenyldiazonium tetrafluoroborate (10.0 mmol, 2.10 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(2-fluorophenyl)-2-(hydroxyimino)propanoate (**3m**) was obtained as brown oil in 59% (5.90 mmol, 1.25 g) yield.

***R*f** 0.3 (EtOAc / hexane = 1:3) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.87 (s, 3 H), 4.07 (s, 2 H), 7.03 (dd, J_{HF} = 7.9 Hz, *J* = 15.0 Hz, 2 H), 7.21-7.26 (m, 2 H).

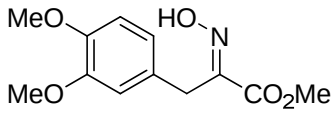
^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 23.7 (d, J_{CF} = 3.8 Hz, CH_2), 52.7 (CH_3), 115.3 (d, J_{CF} = 21.9 Hz, CH), 122.5 (d, J_{CF} = 15.7 Hz, C_q), 124.0 (d,

J_{CF} = 3.5 Hz, CH), 128.3 (d, J_{CF} = 8.0 Hz, CH), 130.4 (d, J_{CF} = 3.9 Hz, CH), 149.8 (C_q), 160.7 (d, J_{CF} = 246.5 Hz, C_q), 163.5 (C_q).

MS (EI) *m/z* (%): 211 (26) [M^+], 195 (22), 149 (26), 136 (23), 135 (39), 134 (78), 115 (10), 109 (100), 108 (22), 107 (18), 83 (18), 59 (23).

HRMS (EI) calculated for $C_{10}H_{10}FNO_3$ [M^+]: 211.0645, found: 211.0645.

2.2.14 (*E*)-Methyl 3-(3,4-dimethoxyphenyl)-2-(hydroxyimino)propanoate (3n)



$C_{12}H_{15}NO_5$
253.25 g/mol

Compound **3n** was prepared from 3,4-dimethoxyphenyldiazonium tetrafluoroborate (10.0 mmol, 2.52 g) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(3,4-dimethoxyphenyl)-2-(hydroxyimino)propanoate (**3n**) was obtained as brown oil in 63% (6.30 mmol, 1.59 g) yield.

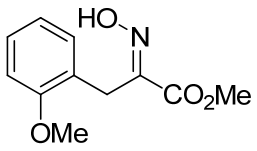
***R*$_f$** 0.2 (EtOAc / hexane = 1:2) [UV].

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.87 (s, 3 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 3.96 (s, 2 H), 6.8 (d, *J* = 8.1 Hz, 1 H), 6.88-6.92 (m, 2 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 29.9 (CH_2), 52.6 (CH_3), 55.7 (CH_3), 55.8 (CH_3), 111.2 (CH), 112.5 (CH), 121.2 (CH), 128.0 (C_q), 147.7 (C_q), 148.7 (C_q), 150.9 (C_q) 163.8 (C_q).

HRMS (ESI) calculated for $C_{12}H_{15}NO_5Na$ [M^+ + Na]: 276.0842, found: 276.0846.

2.2.15 (*E*)-Methyl 3-(2-methoxyphenyl)-2-(hydroxyimino)propanoate (3o)

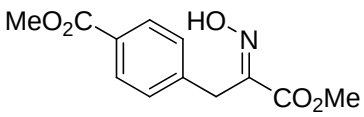


$C_{11}H_{13}NO_4$
223.22 g/mol

Compound **3o** was prepared from 2-methoxyphenyldiazonium tetrafluoroborate (4.27 mmol, 947 mg) and methyl acrylate (100 mmol, 9.00 mL) according to the general procedure GP1. (*E*)-Methyl 3-(2-methoxyphenyl)-2-(hydroxyimino)propanoate (**3o**) was obtained as brown oil in 79% (3.40 mmol, 752 mg) yield.

R_f	0.4 (EtOAc / hexane = 1:2) [UV].
^{1}H-NMR	(600 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3 H), 3.86 (s, 3 H), 4.00 (s, 2 H), 6.86-6.92 (m, 2 H), 7.14 (d, *J* = 7.3 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H).
^{13}C-NMR	(90.5 MHz, $CDCl_3$): δ (ppm) = 25.8 (CH_2), 52.7 (CH_3), 55.4 (CH_3), 110.4 (CH), 120.5 (CH), 124.1 (CH), 127.8 (C_q), 129.6 (CH), 151.7 (C_q), 157.2 (C_q), 164.0 (C_q).
MS (EI)	*m/z* (%): 223 (53) [M^+], 207 (23), 192 (11), 176 (14), 175 (10), 174 (43), 173 (12), 148 (22), 147 (46), 146 (100), 133 (11), 132 (28), 131 (12), 121 (49), 120 (14), 119 (13), 118 (19), 116 (23), 111 (11), 108 (13), 107 (26), 105 (11), 104 (15), 97 (14), 93 (11), 92 (13), 91 (82), 89 (18), 85 (84), 83 (92), 78 (12), 77 (32), 65 (16), 57 (10), 55 (14).
HRMS (EI)	calculated for $C_{11}H_{13}NO_4$ [M^+]: 223.0845, found: 223.0842.

2.2.16 (*E*)-Methyl 4-(2-(hydroxyimino)-3-methoxy-3-oxopropyl)benzoate (3p)



$C_{12}H_{13}NO_5$
251.24 g/mol

Compound **3p** was prepared from 4-methoxycarbonylphenyldiazonium tetrafluoroborate (1.00 mmol, 250 mg) and methyl acrylate (30.0 mmol, 2.70 mL)

according to the general procedure GP1. (*E*)-Methyl 4-(2-(hydroxyimino)-3-methoxy-3-oxopropyl)benzoate (**3p**) was obtained as brown oil in 55% (0.55 mmol, 138 mg) yield.

***R*f** 0.3 (EtOAc / hexane = 1:2) [UV].

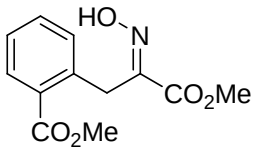
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.84 (s, 3 H), 3.90 (s, 3 H), 4.04 (s, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.95 (d, *J* = 8.1 Hz, 2 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 30.6 (CH_2), 52.1 (CH_3), 52.9 (CH_3), 128.6 (C_q), 129.1 (2 × CH), 129.9 (2 × CH), 140.9 (C_q), 150.3 (C_q), 163.6 (C_q), 167.0 (C_q).

MS (EI) *m/z* (%): 251 (48) [M^+], 235 (28), 220 (22), 202 (11), 189 (61), 176 (24), 175 (52), 174 (100), 158 (32), 149 (46), 146 (27), 145 (10), 144 (86), 143 (23), 133 (10), 131 (10), 130 (15), 121 (27), 118 (16), 116 (35), 115 (12), 91 (13), 90 (27), 89 (41), 77 (10), 59 (50).

HRMS (EI) calculated for $C_{12}H_{13}NO_5$ [M^+]: 251.0794, found: 251.0792.

2.2.17 (*E*)-Methyl 2-(2-(hydroxyimino)-3-methoxy-3-oxopropyl)benzoate (3q)



$C_{12}H_{13}NO_5$
251.24 g/mol

Compound **3q** was prepared from 2-methoxycarbonylphenyldiazonium tetrafluoroborate (1.00 mmol, 250 mg) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 2-(2-(hydroxyimino)-3-methoxy-3-oxopropyl)benzoate (**3q**) was obtained as brown oil in 68% (0.68 mmol, 170 mg) yield.

***R*f** 0.1 (EtOAc / hexane = 1:3) [UV].

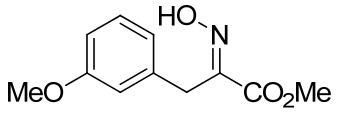
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 3.81 (s, 3 H), 3.92 (s, 3 H), 4.42 (s, 2 H), 7.22 (ddd, *J* = 0.5 Hz, *J* = 1.2 Hz, *J* = 7.8 Hz, 1 H), 7.28 (ddd, *J* = 1.3 Hz, *J* = 7.6 Hz, *J* = 7.8 Hz, 1 H), 7.41 (dt, *J* = 1.5 Hz, *J* = 7.6 Hz, 1 H), 7.90 (dd, *J* = 1.3 Hz, *J* = 7.8 Hz, 1 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 29.1 (CH_2), 52.1 (CH_3), 52.8 (CH_3), 126.6 (CH), 129.8 (CH), 130.0 (C_q), 130.7 (CH), 132.1 (CH), 136.8 (C_q), 151.7 (C_q), 163.8 (C_q), 168.1 (C_q).

MS (EI) *m/z* (%): 251 (48) [M^+], 234 (33), 219 (70), 204 (17), 203 (36), 189 (37), 174 (17), 157 (10), 149 (28), 145 (84), 143 (45), 117 (12), 116 (22), 105 (30), 91 (36), 89 (62), 83 (37), 71 (55), 69 (41), 58 (100), 57 (52).

HRMS (ESI) calculated for $C_{12}H_{13}NO_5Na$ [M^+ + Na]: 274.0686 , found: 274.0694.

2.2.18 (*E*)-Methyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (3r)



$C_{11}H_{13}NO_4$
223.08 g/mol

Compound **3r** was prepared from 3-methoxyphenyldiazonium tetrafluoroborate (10.0 mmol, 2.20 g) and methyl acrylate (30.0 mmol, 2.70 mL) according to the general procedure GP1. (*E*)-Methyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (**3r**) was obtained as brown oil in 48% (4.80 mmol, 1.07 g) yield.

***R*$_f$** 0.3 (EtOAc / hexane = 1:2) [UV].

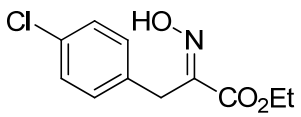
^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 3.78 (s, 3H), 3.83 (s, 3 H), 3.97 (s, 2 H), 6.76 (ddd, *J* = 0.9 Hz, *J* = 2.6 Hz, *J* = 8.3 Hz, 1 H), 6.86-6.91 (m, 2 H), 7.16-7.21 (m, 1H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 30.6 (CH_2), 52.8 (CH_3), 55.2 (CH_3), 112.1 (CH), 114.9 (CH), 121.5 (CH), 129.5 (CH), 137.0 (C_q), 159.7 (C_q), 163.7 (C_q), one C_q-signal missing due to overlap.

MS (EI) *m/z* (%): 223 (92) [M^+], 208 (13), 207 (99), 206 (27), 192 (10), 174 (47), 173 (28), 161 (10), 148 (54), 147 (95), 146 (100), 133 (11), 132 (14), 122 (22), 121 (98), 117 (11), 116 (19), 104 (15), 91 (31), 90 (12), 89 (13), 85 (15), 83 (20), 78 (21), 77 (25), 65 (10), 63 (10), 59 (15), 51 (12), 44 (12).

HRMS (EI) calculated for $C_{11}H_{13}NO_4$ [M^+]: 223.0845, found: 223.0845.

2.2.19 (*E*)-Ethyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (3s)



$C_{11}H_{12}ClNO_3$
241.67 g/mol

Compound **3s** was prepared from 4-chlorophenyldiazonium tetrafluoroborate (10.0 mmol, 2.26 g) and ethyl acrylate (30.0 mmol, 8.34 g) according to the general procedure GP1. (*E*)-Ethyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (**3s**) was obtained as brown oil in 61% (6.10 mmol, 1.47 g) yield.

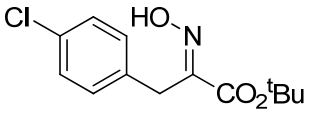
***R*f** 0.4 (EtOAc / hexane = 1:2) [UV].

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.30 (t, *J* = 7.1 Hz, 3 H), 3.91 (s, 2 H), 4.28 (*J* = 7.1 Hz, 2 H), 7.19 (d, *J* = 8.6 Hz, 2 H), 7.37 (d, *J* = 8.5 Hz, 2 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 14.0 (CH_3), 29.9 (CH_2), 62.0 (CH_2), 120.6 (C_q), 130.9 (2 × CH), 131.6 (2 × CH), 134.6 (C_q), 150.3 (C_q), 163.0 (C_q).

MS (ESI) *m/z* (%): 241 (4) [M^+], 198 (12), 197 (66), 196 (38), 195 (68), 194 (33), 171 (28), 169 (31), 117 (20), 116 (100), 115 (10), 97 (12), 90 (22), 89 (43), 71 (12), 69 (15), 57 (20).

2.2.20 (*E*)-*tert*-Butyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (3t)



$C_{13}H_{16}ClNO_3$
269.72 g/mol

Compound **3t** was prepared from 4-chlorophenyldiazonium tetrafluoroborate (1.00 mmol, 226 mg) and *tert*-butyl acrylate (10.0 mmol, 1.40 mL) according to the general procedure GP1. (*E*)-*tert*-Butyl 3-(4-chlorophenyl)-2-hydroxyimino)propanoate (**3t**) was obtained as brown oil in 60% (0.60 mmol, 161 mg) yield.

***R*f** 0.5 (EtOAc / hexane = 1:3) [UV].

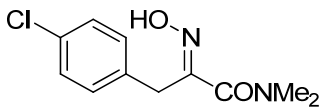
^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 1.49 (s, 9 H), 3.89 (s, 2 H), 7.23 (m, 4 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 28.0 (3 × CH_3), 29.8 (CH_2), 83.0 (C_q), 128.6 (2 × CH), 130.5 (2 × CH), 132.4 (C_q), 134.4 (C_q), 151.5 (C_q), 162.0 (C_q).

MS (EI) *m/z* (%): 269 (5) [M^+], 215 (22), 213 (64), 196 (13), 153 (21), 152 (15), 151 (63), 150 (19), 125 (26), 117 (14), 116 (100), 89 (20), 57 (81), 56 (40), 55 (16).

HRMS (EI) calculated for $C_{13}H_{16}ClNO_3$ [M^+]: 269.0819, found: 269.0818.

2.2.21 (*E*)-3-(4-Chlorophenyl)-2-(hydroxyimino)-*N*,*N*-dimethylpropanamide (3u)



$C_{11}H_{13}ClN_2O_2$
240.69 g/mol

Compound **3u** was prepared from 4-chlorophenyldiazonium tetrafluoroborate (1.00 mmol, 226 mg) and acrylamide (10.0 mmol, 991 mg) according to the general procedure GP1. (*E*)-3-(4-Chlorophenyl)-2-(hydroxyimino)-*N*,*N*-dimethyl-propanamide (**3u**) was obtained as brown oil in 44% (0.44 mmol, 105 mg) yield.

***R*f** 0.1 (EtOAc / hexane = 1:2) [UV].

^{1}H-NMR (360 MHz, $CDCl_3$): δ (ppm) = 2.85 (s, 3 H), 2.95 (s, 3 H), 3.99 (s, 2 H), 7.25-7.27 (m, 4 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 31.2 (CH_2), 35.3 (CH_3), 38.4 (CH_3), 128.6 (2 × CH), 130.6 (2 × CH), 132.5 (C_q), 133.9 (C_q), 152.9 (C_q), 165.9 (C_q).

MS (EI) *m/z* (%): 240 (57) [M^+], 242 (19), 224 (10), 153 (14), 152 (19), 151 (33), 150 (37), 127 (15), 125 (48), 117 (11), 116 (90), 89 (40), 75 (10), 73 (18), 72 (100), 63 (14).

HRMS (EI) calculated for $C_{11}H_{13}ClN_2O_2$ [M^+]: 240.0666, found: 240.0666.

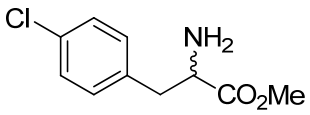
2.3 General procedure for the reduction of oximes to amines (GP2)[3]

A solution of oxime **3** (1 equiv) in formic acid (25 mL) was heated to 50 °C in the presence of catalytic amount of iron dust (ca. 20 mg). Under vigorous stirring, zinc dust (10 equiv) was added in small amounts, at such rate that the temperature was maintained at 50–55 °C. After the addition was completed, stirring was continued for two hours at a temperature of 60–65 °C. The precipitate was filtered off at RT and washed with formic acid (20 mL). The filtrate was neutralized with a saturated aqueous Na_2CO_3 solution. Afterwards, the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were dried over Na_2SO_4. The racemic product was obtained by removing the solvent in vacuum.

During characterisation, slight deviations of the ^{1}H-NMR data compared to literature reported values were observed for some compounds, which is likely to be due to the presence of traces of moisture or acid in previously measured samples.

2.4 Characterisation of amines 5g,i-o,s

2.4.1 Methyl 2-amino-3-(4-chlorophenyl)propanoate (5g)



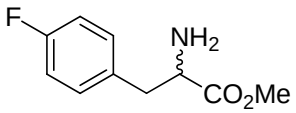
$C_{10}H_{12}ClNO_2$
213.66 g/mol

Compound **5g** was obtained by reduction of **3g** (1.57 mmol, 357 mg) with formic acid (25 mL), Fe dust (0.36 mmol, 20.0 mg) and Zn dust (15.3 mmol, 1.00 g) following the general procedure GP2. Methyl 2-amino-3-(4-chlorophenyl)propanoate (**5g**) was obtained as yellow oil in 96% (1.51 mmol, 322 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.52 (bs, 2 H), 2.84 (dd, *J* = 7.8 Hz, *J* = 13.6 Hz, 1 H), 3.05 (dd, *J* = 5.2 Hz, *J* = 13.6 Hz, 1 H), 3.71 (bs, 4H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.27 (d, *J* = 8.3 Hz, 2 H).

Analytical data of **5g** is in agreement with those reported in literature.[4]

2.4.2 Methyl 2-amino-3-(4-fluorophenyl)propanoate (5i)



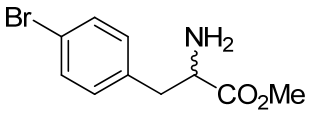
$C_{10}H_{12}FNO_2$
197.21 g/mol

Compound **5i** was obtained by reduction of **3i** (1.50 mmol, 317 mg) with formic acid (25 mL), Fe dust (0.36 mmol, 20.0 mg) and Zn dust (15.3 mmol, 1.00 g) following the general procedure GP2. Methyl 2-amino-3-(4-fluorophenyl)propanoate (**5i**) was obtained as yellow oil in 75% (1.13 mmol, 221.8 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.51 (bs, 2 H), 2.85 (dd, J = 7.7 Hz, J = 13.7 Hz, 1 H), 3.05 (dd, J = 5.3 Hz, J =13.7 Hz, 1 H), 3.71 (s, 4H), 6.99 (t, J_{HF} = 8.6 Hz, 2 H), 7.15 (dd, J_{HF} = 5.6 Hz, J = 8.1 Hz, 2 H).

Analytical data of **5i** in agreement with those reported in literature.[5]

2.4.3 Methyl 2-amino-3-(4-bromophenyl)propanoate (5j)



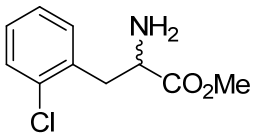
$C_{10}H_{12}BrNO_2$
258.11 g/mol

Compound **5j** was obtained by reduction of **3j** (1.44 mmol, 393 mg) with formic acid (25 mL), Fe dust (0.36 mmol, 20.0 mg) and Zn dust (15.3 mmol, 1.00 g) following the general procedure GP2. Methyl 2-amino-3-(4-bromophenyl)propanoate (**5j**) was obtained as yellow oil in 92% (1.33 mmol, 342 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.49 (bs, 2 H), 2.83 (dd, J = 7.8 Hz, J = 13.6 Hz, 1 H), 3.03 (dd, J = 5.2 Hz, J = 13.6 Hz, 1 H), 3.71 (s, 4H), 7.07 (d, J = 8.2 Hz, 2 H), 7.43 (d, J = 8.2 Hz, 2 H).

Analytical data of **5j** in agreement with those reported in literature.[6]

2.4.4 Methyl 2-amino-3-(2-chlorophenyl)propanoate (5k)



$C_{10}H_{12}ClNO_2$
213.66 g/mol

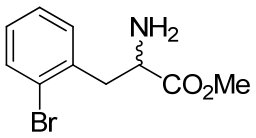
Compound **5k** was obtained by reduction of **3k** (2.20 mmol, 500 mg) with formic acid (25 mL), Fe dust (0.36 mmol, 20.0 mg) and Zn dust (15.3 mmol, 1.00 g) following the general procedure GP2. Methyl 2-amino-3-(2-chlorophenyl)propanoate (**5k**) was obtained as yellow oil in 68% (1.50 mmol, 320 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.55 (s, 2 H), 2.93 (dd, *J* = 8.6 Hz, *J* = 13.6 Hz, 1 H), 3.25 (dd, *J* = 5.6 Hz, *J* = 13.6 Hz, 1 H), 3.71 (s, 3 H), 3.84 (dd, *J* = 5.9 Hz, *J* = 8.1 Hz, 1 H), 7.16-7.25 (m, 3 H), 7.34-7.39 (m, 1 H).

^{13}C-NMR (90.5 MHz, $CDCl_3$): δ (ppm) = 39.1 (CH_2), 52.0 (CH_3), 54.3 (CH_2), 126.6 (CH), 128.3 (CH), 129.7 (CH), 131.6 (CH), 134.4 (C_q), 135.3 (C_q), 175.4 (C_q).

HRMS (ESI) calculated for $C_{10}H_{13}ClNO_2$ [M^+ + H]: 214.0629, found: 214.0636.

2.4.4 Methyl 2-amino-3-(2-bromophenyl)propanoate (5l)



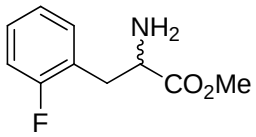
$C_{10}H_{12}BrNO_2$
258.11 g/mol

Compound **5l** was obtained by reduction of **3l** (1.84 mmol, 500 mg) with formic acid (25 mL), Fe dust (0.36 mmol, 20.0 mg) and Zn dust (15.3 mmol, 1.00 g) following the general procedure GP2. Methyl 2-amino-3-(2-bromophenyl)propanoate (**5l**) was obtained as yellow oil in 95% (1.74 mmol, 450 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.55 (s, 2 H), 2.93 (dd, *J* = 8.6 Hz, *J* = 13.6 Hz, 1 H), 3.25 (dd, *J* = 5.6 Hz, *J* = 13.6 Hz, 1 H), 3.71 (s, 3 H), 3.84 (dd, *J* = 5.9 Hz, *J* = 8.1 Hz, 1 H), 7.16-7.25 (m, 3 H), 7.34-7.39 (m, 1 H).

Analytical data of **5l** in agreement with those reported in literature.[7]

2.4.5 Methyl 2-amino-3-(2-fluorophenyl)propanoate (5m)



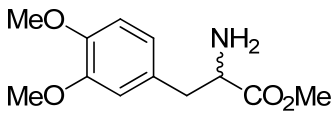
$C_{10}H_{12}FNO_2$
197.21 g/mol

Compound **5m** was obtained by reduction of **3m** (2.30 mmol, 486 mg) with formic acid (25 mL), Fe dust (0.18 mmol, 10.0 mg) and Zn dust (9.18 mmol, 600 mg) following the general procedure GP2. Methyl 2-amino-3-(2-fluorophenyl)propanoate (**5m**) was obtained as yellow oil in 93% (2.14 mmol, 421 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.56 (bs, 2 H), 2.91 (dd, *J* = 8.0 Hz, *J* = 13.6 Hz, 1 H), 3.11 (dd, *J* = 5.5 Hz, *J* = 13.7 Hz, 1 H), 3.71 (s, 3H), 3.77 (m, 1 H), 7.06 (td, J_{HF} = 8.2 Hz, *J* = 8.6 Hz, 2 H), 7.22 (td, J_{HF} = 6.9 Hz, *J* = 15.7 Hz, 2 H).

Analytical data of **5m** in agreement with those reported in literature.[8]

2.4.6 Methyl 2-amino-3-(3,4-dimethoxyphenyl)propanoate (5n)



$C_{12}H_{17}NO_4$
239.27 g/mol

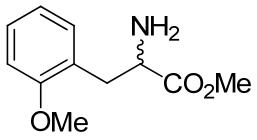
Compound **5n** was obtained by reduction of **3n** (2.11 mmol, 535 mg) with formic acid (25 mL), Fe dust (0.18 mmol, 10.0 mg) and Zn dust (9.18 mmol, 600 mg) following the

general procedure GP2. Methyl 2-amino-3-(3,4-dimethoxyphenyl)propanoate (**5n**) was obtained as yellow oil in 67% (1.41 mmol, 338 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.58 (bs, 2 H), 2.80 (dd, *J* = 7.8 Hz, *J* = 13.6 Hz, 1 H), 3.02 (dd, *J* = 5.1 Hz, *J* = 13.6 Hz, 1 H), 3.71 (s, 4 H), 3.83 (s, 3 H), 3.84 (s, 3 H), 6.69-6.70 (m, 1H), 6.72 (d, *J* = 2.0 Hz ,1H), 6.79 (d, *J* = 8.0 Hz, 1 H).

Analytical data from **5n** in agreement with those reported in literature.[9]

2.4.7 Methyl 2-amino-3-(2-methoxyphenyl)propanoate (5o)



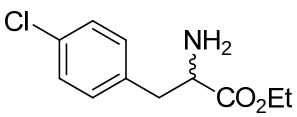
$C_{11}H_{15}NO_3$
209.24 g/mol

Compound **5o** was obtained by reduction of **3o** (2.61 mmol, 583 mg) with formic acid (25 mL), Fe dust (0.18 mmol, 10.0 mg) and Zn dust (9.18 mmol, 600 mg) following the general procedure GP2. Methyl 2-amino-3-(2-methoxyphenyl)propanoate (**5o**) was obtained as yellow oil in 68% (1.77 mmol, 371 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.54 (bs, 2 H), 2.85 (dd, *J* = 8.2 Hz, *J* = 13.2 Hz, 1 H), 3.12 (dd, *J* = 5.5 Hz, *J* = 13.3 Hz, 1 H), 3.70 (s, 3 H), 3.82 (s, 4 H), 6.88 (dd, *J* = 7.7 Hz, *J* = 14.6 Hz, 2 H), 7.12 (d, *J* = 7.1 Hz, 1 H), 7.23 (t, *J* = 7.9 Hz, 1 H).

Analytical data of **5o** in agreement with those reported in literature.[10]

2.4.8 Ethyl 2-amino-3-(4-chlorophenyl)propanoate (5s)



$C_{11}H_{14}ClNO_2$
227.69 g/mol

Compound **5s** was obtained by reduction of **3s** (3.49 mmol, 841 mg) with formic acid (60 mL), Fe dust (0.90 mmol, 50.0 mg) and Zn dust (32.2 mmol, 2.5 g) following the general procedure GP2. Ethyl 2-amino-3-(4-chlorophenyl)propanoate (**5s**) was obtained as yellow oil in 89% (3.10 mmol, 700 mg) yield.

^{1}H-NMR (600 MHz, $CDCl_3$): δ (ppm) = 1.24 (t, *J* = 7.1 Hz, 3 H), 1.50 (bs, 2 H), 2.82 (dd, *J* = 7.7 Hz, *J* = 13.6 Hz, 1 H), 3.02 (dd, *J* = 5.5 Hz, *J* = 13.6 Hz, 1 H), 3.67 (dd, *J* = 5.8 Hz, *J* = 7.2 Hz, 1 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 7.08 (d, *J* = 8.4 Hz, 2 H), 7.42 (d, *J* = 8.4 Hz, 2 H).

Analytical data of **5s** in agreement with those reported in literature.[11]

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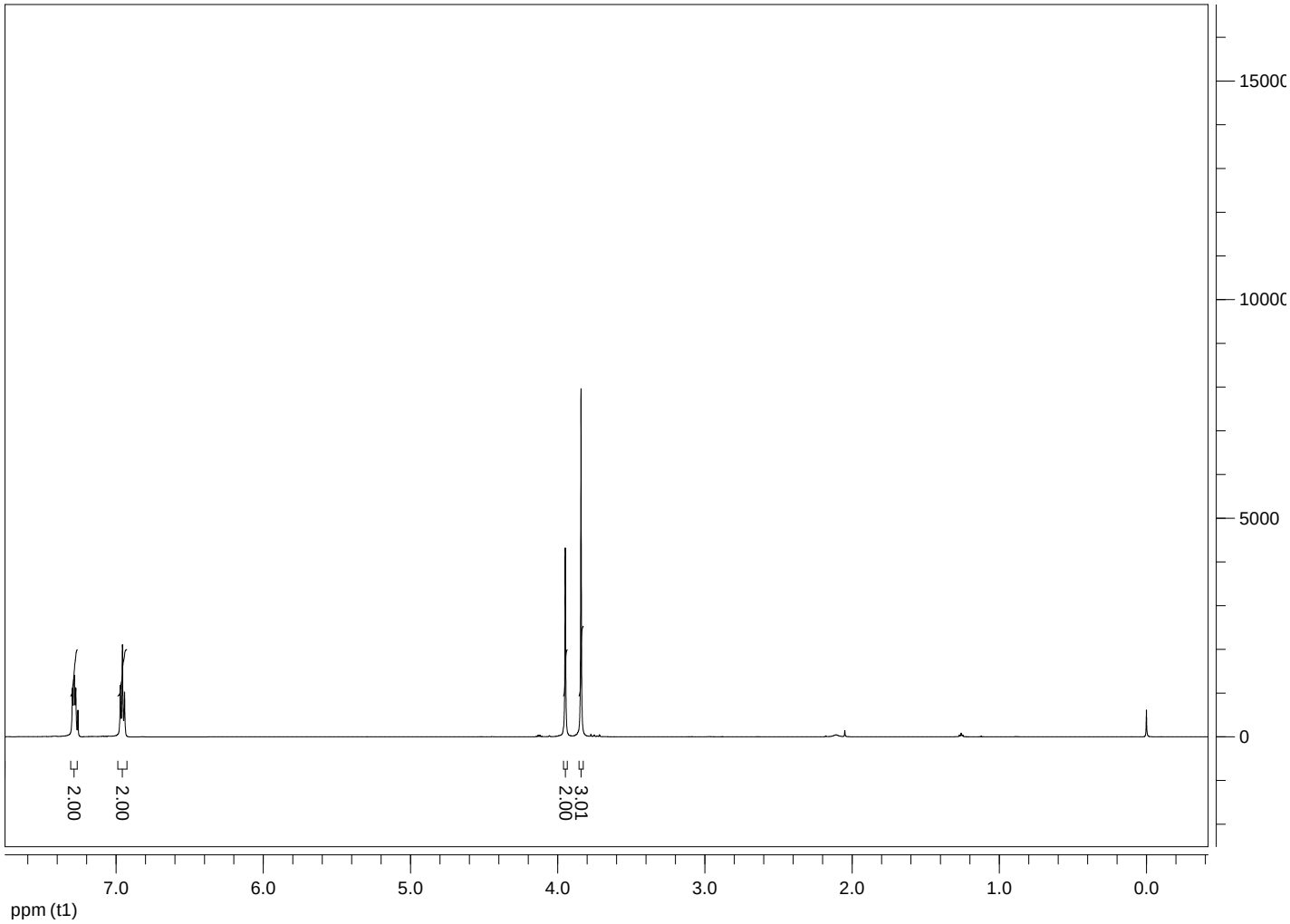
(*E*)-Methyl 3-(4-fluorophenyl)-2-(hydroxyimino)propanoate (3i)



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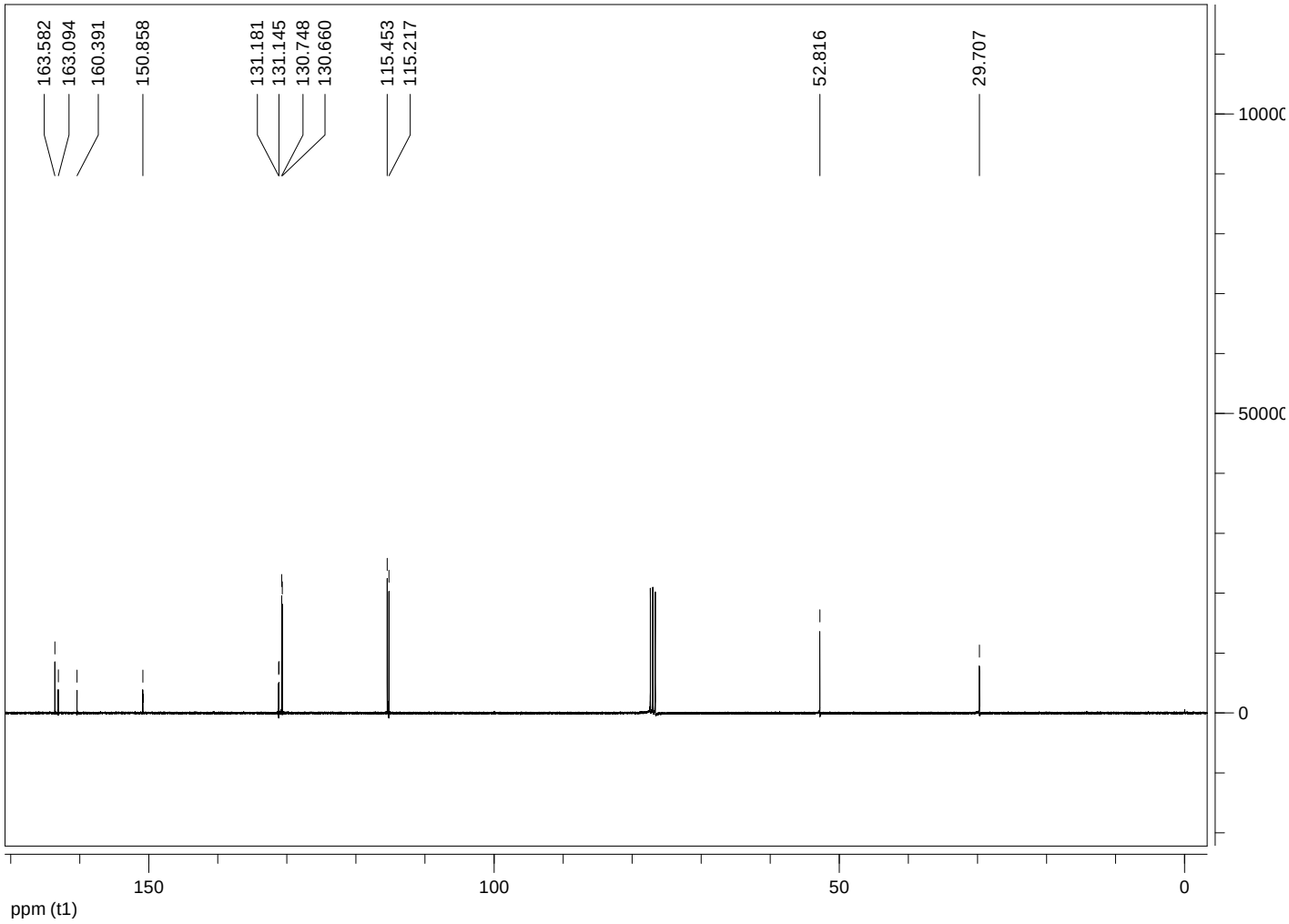

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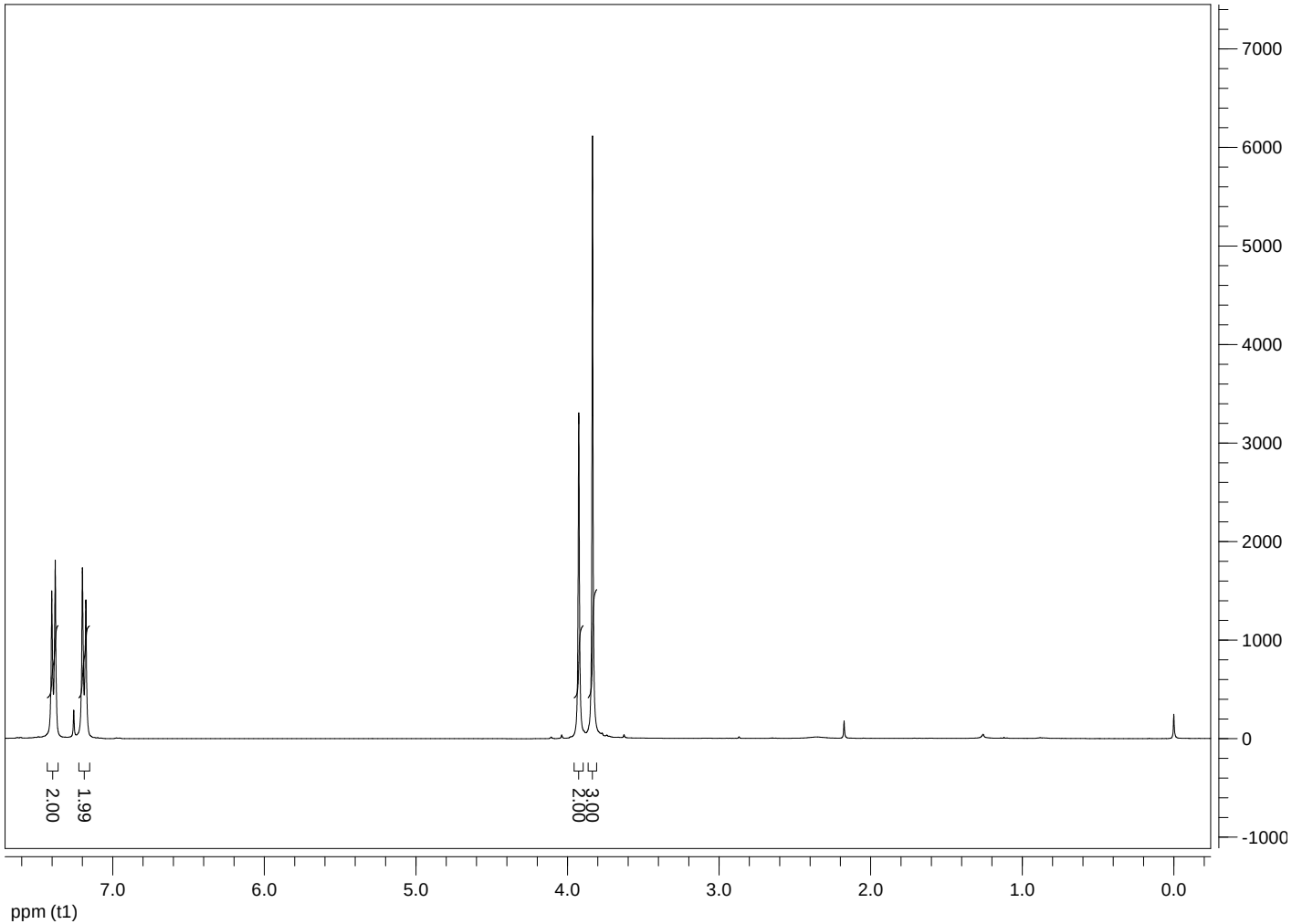

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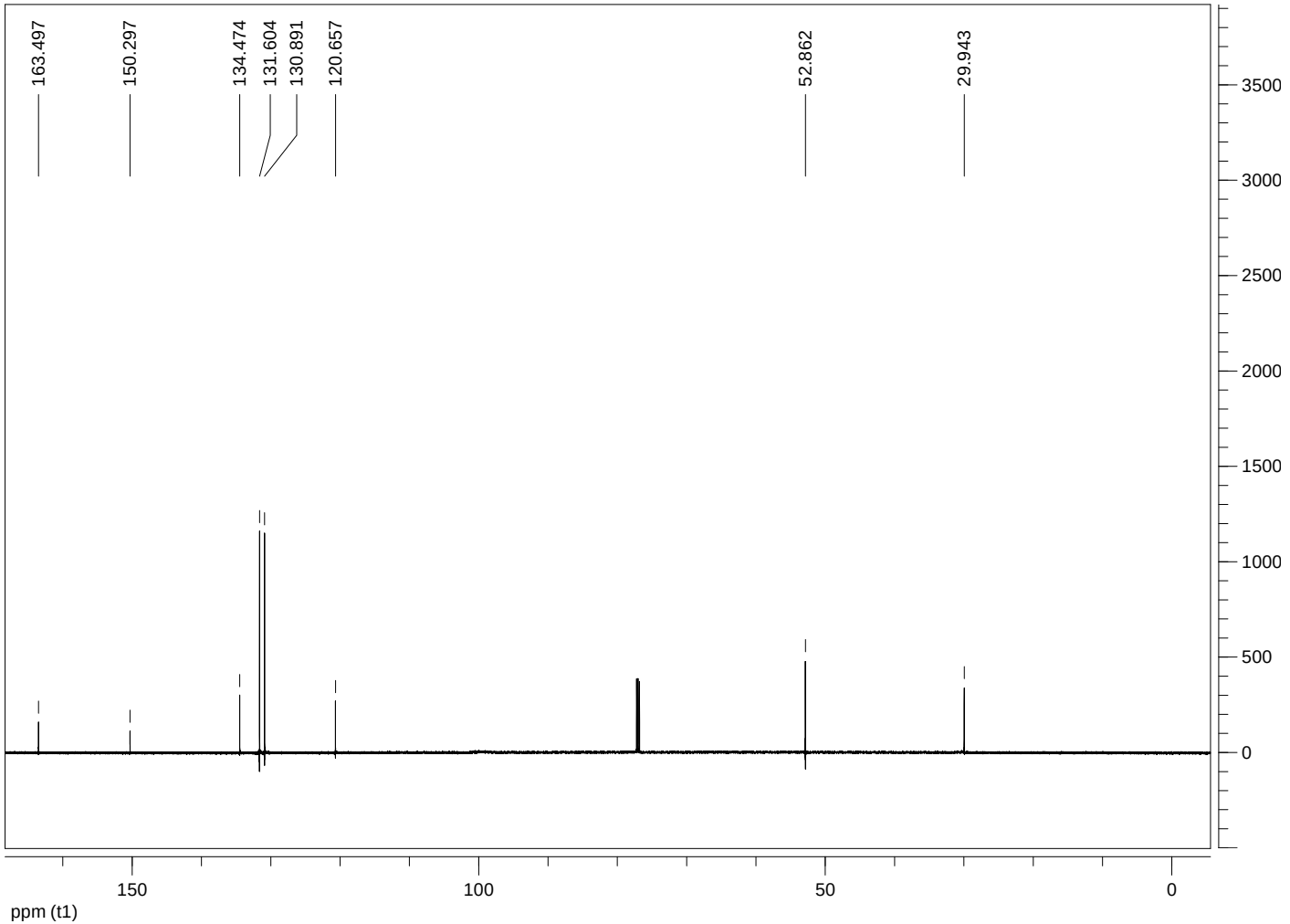

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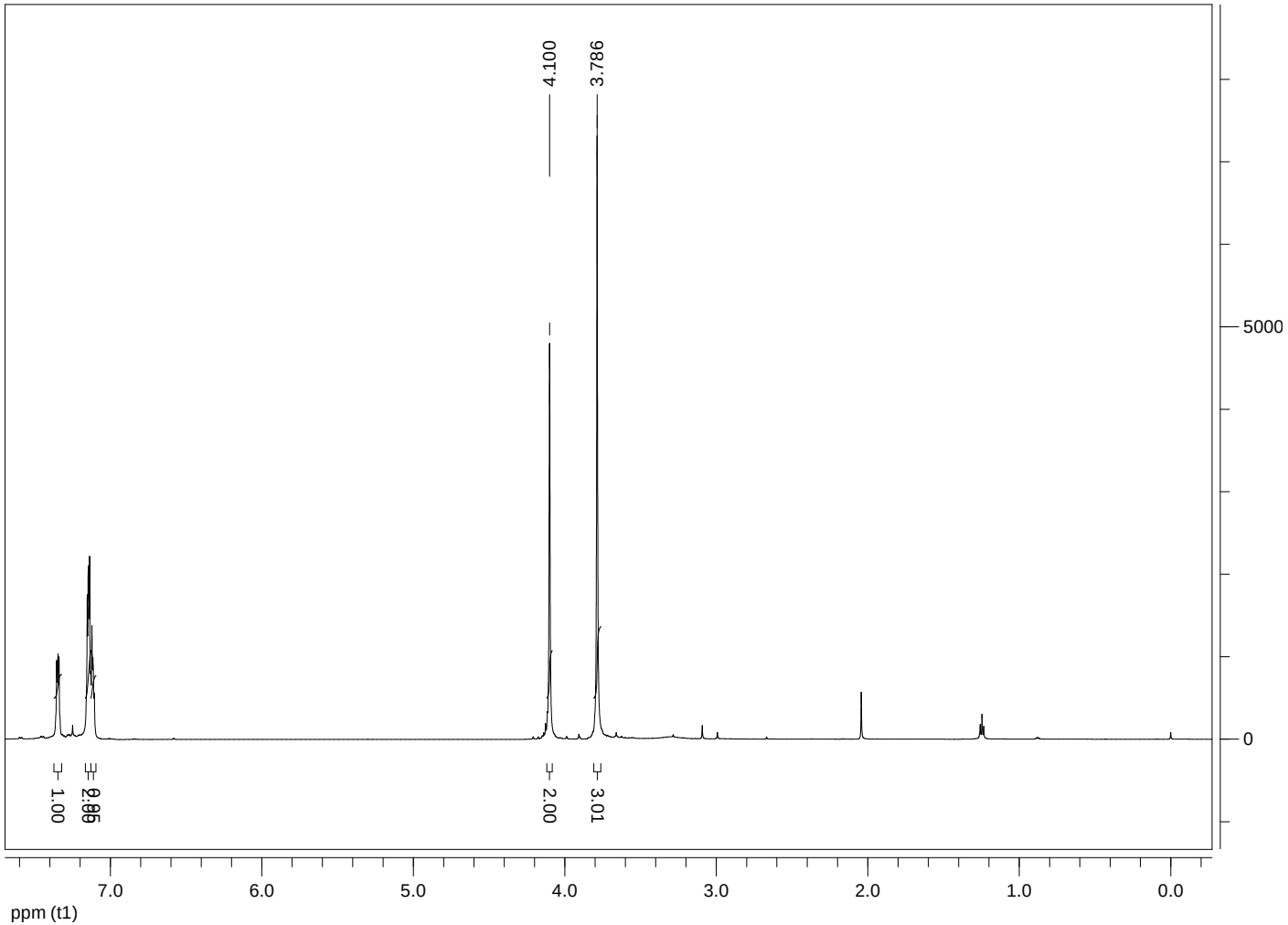

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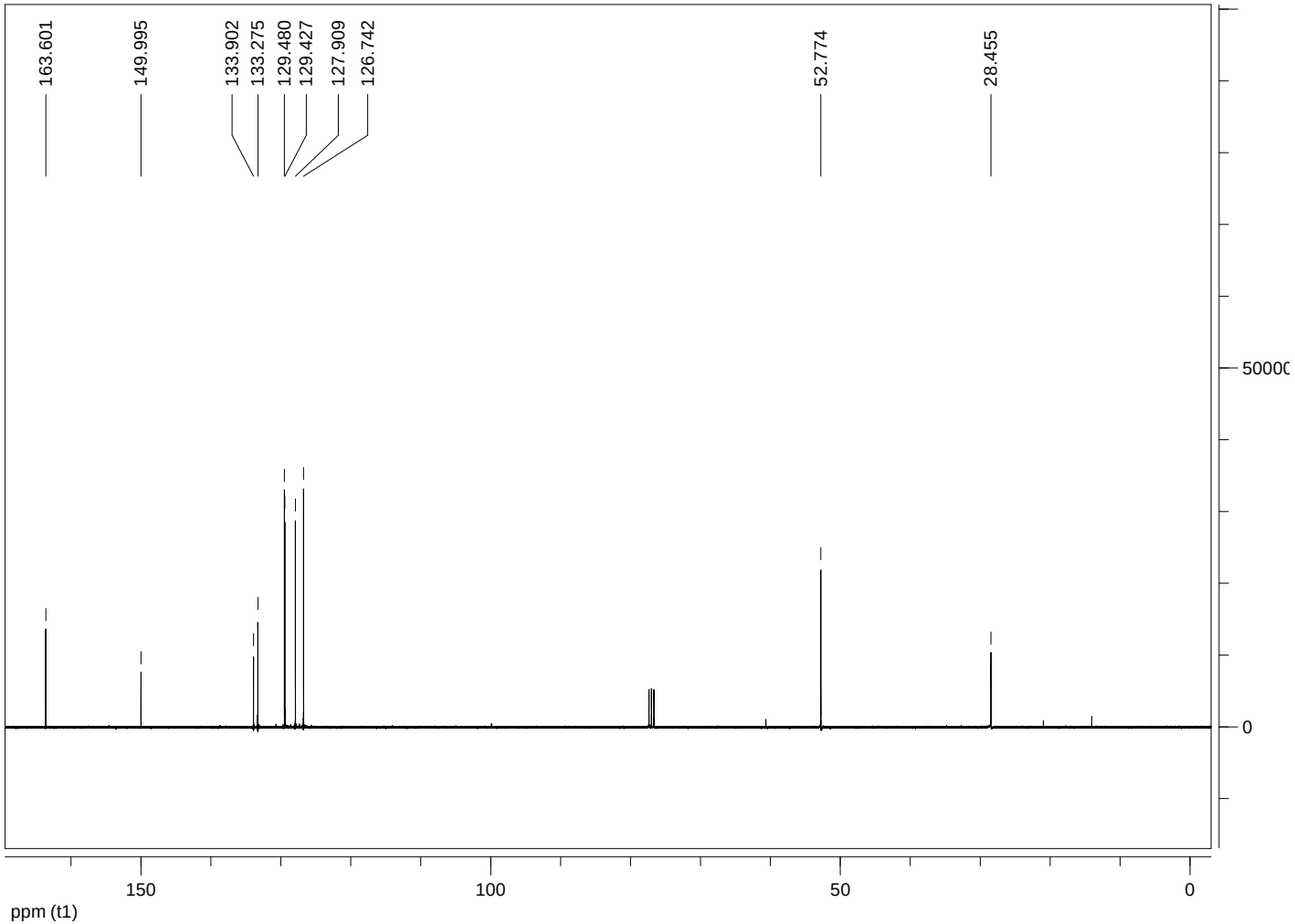

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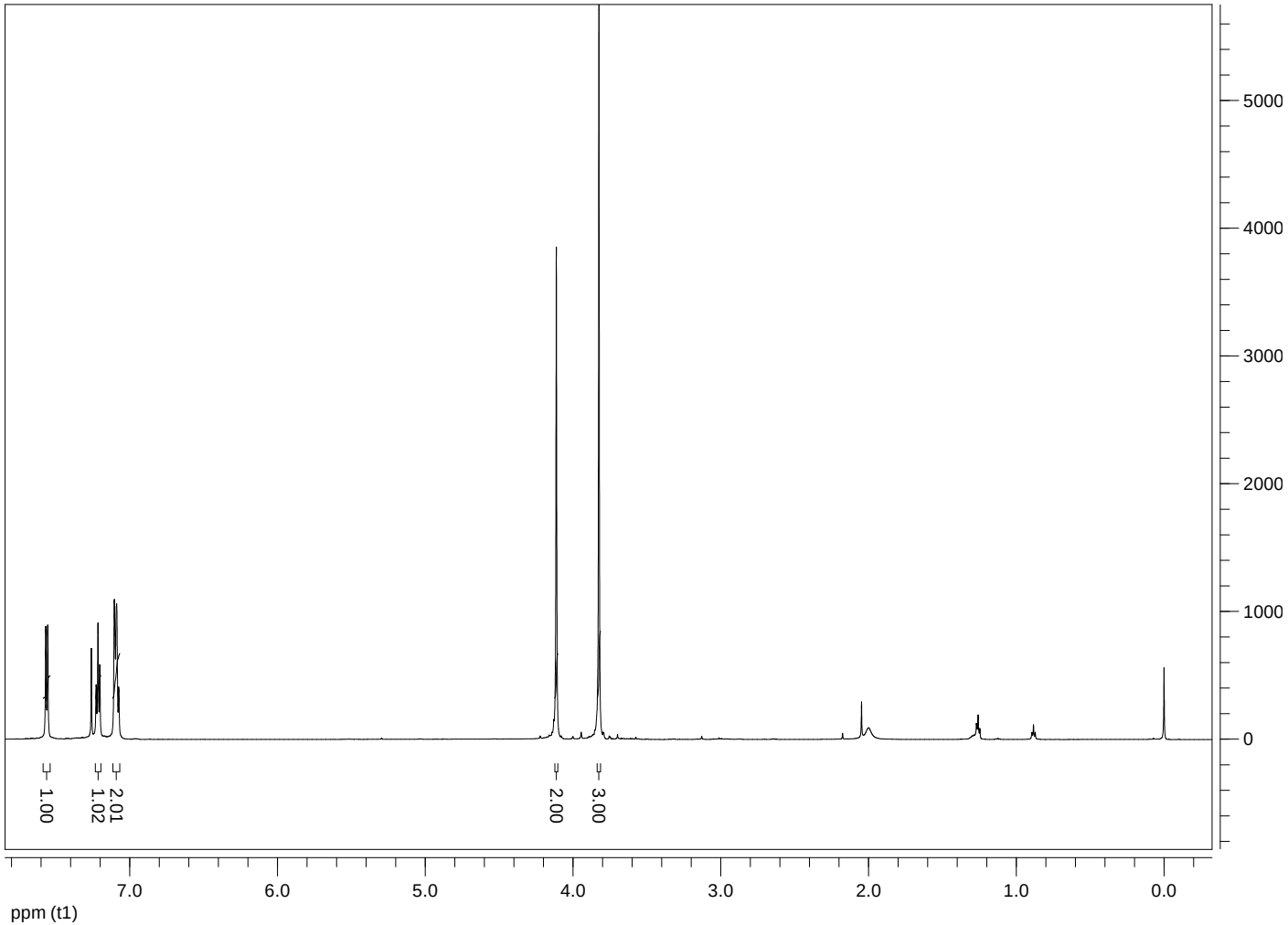

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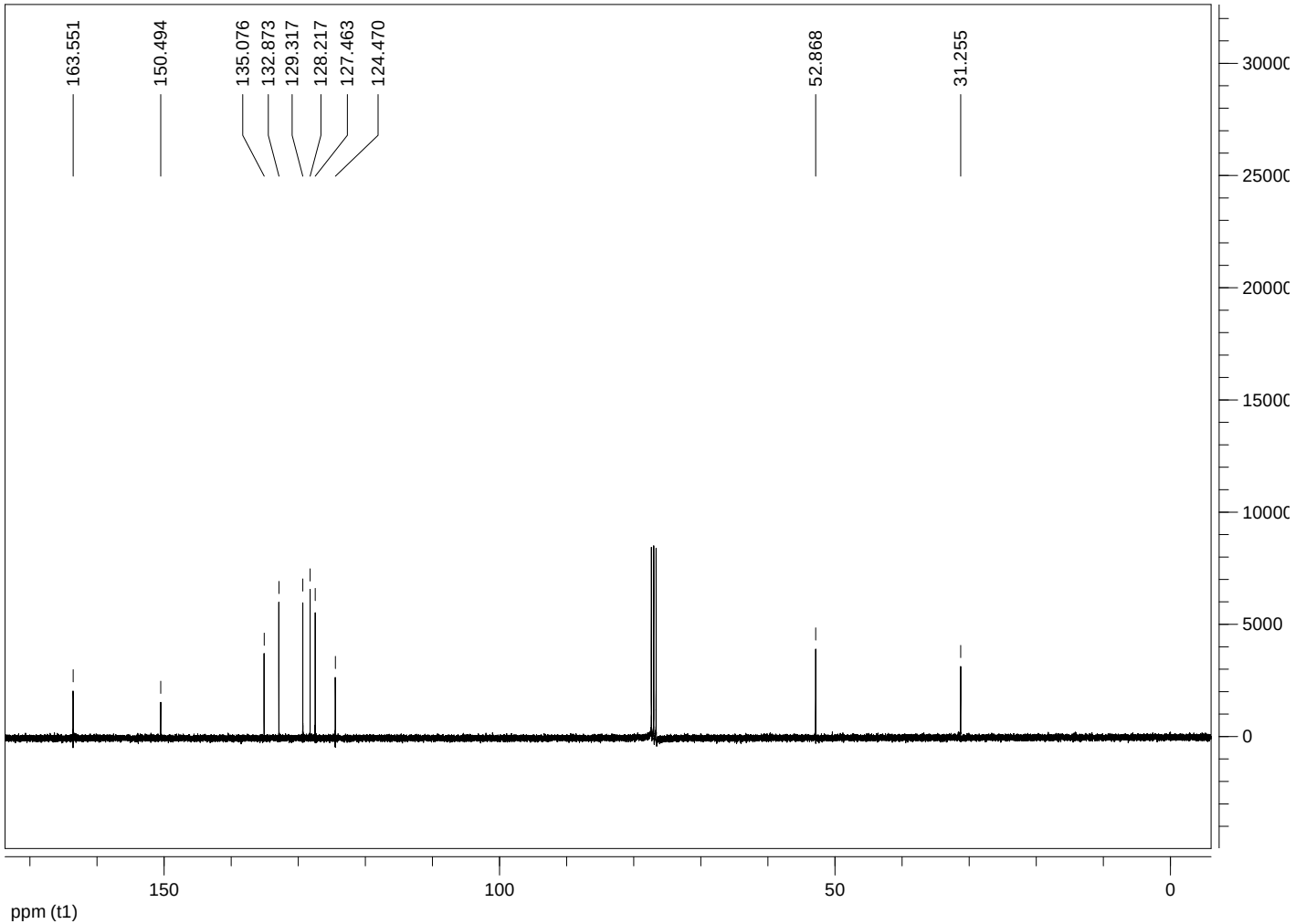

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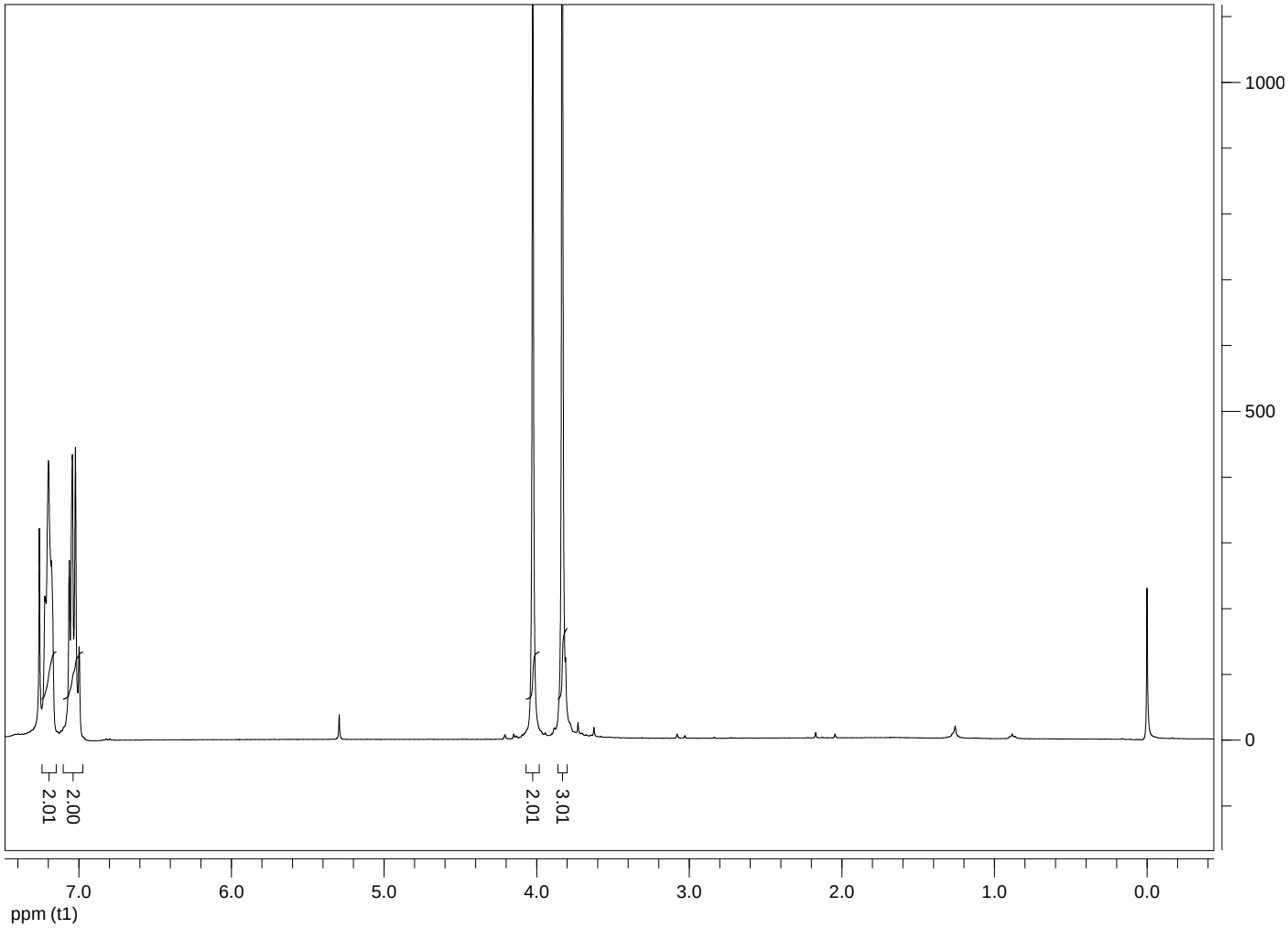

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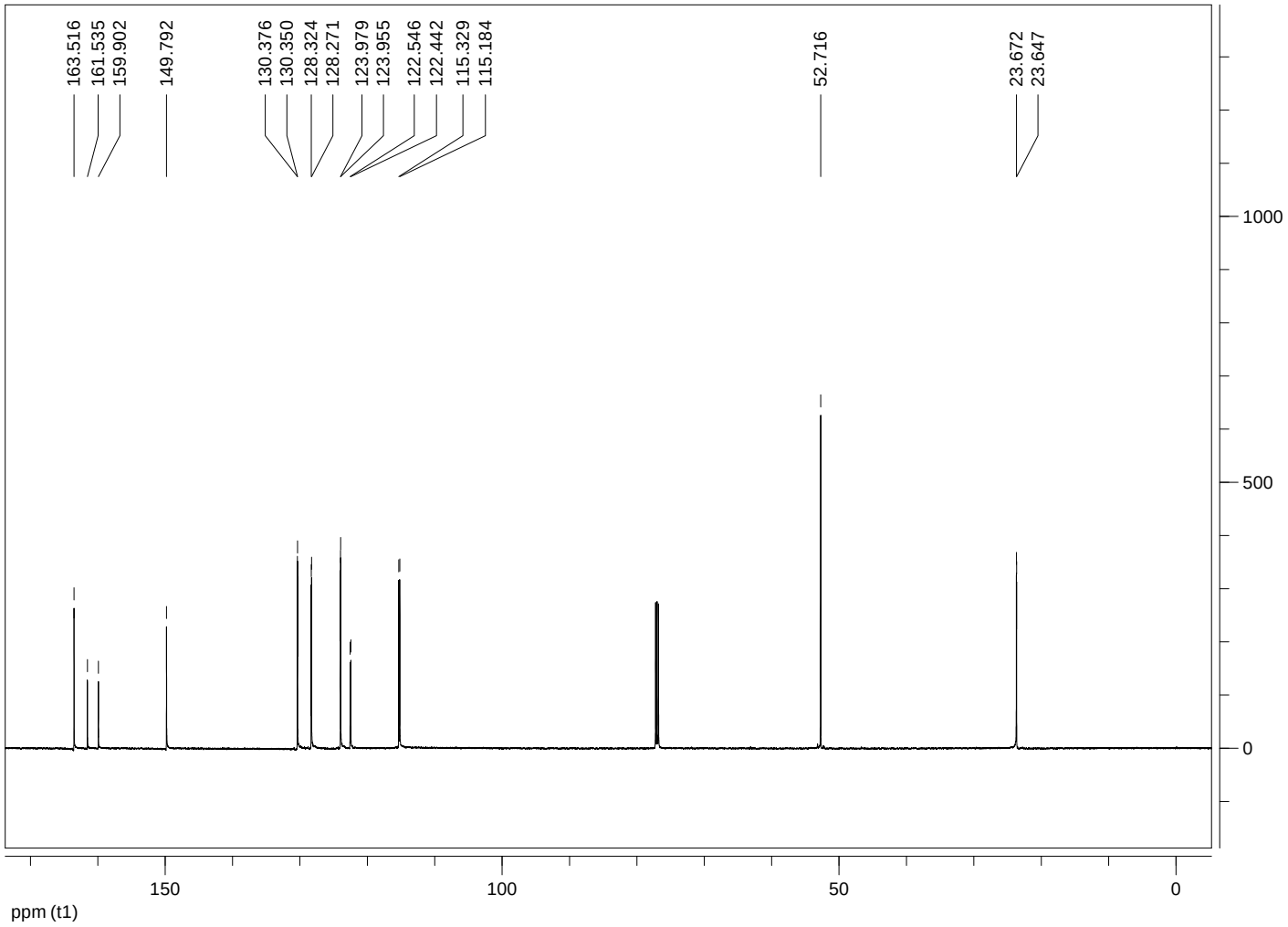

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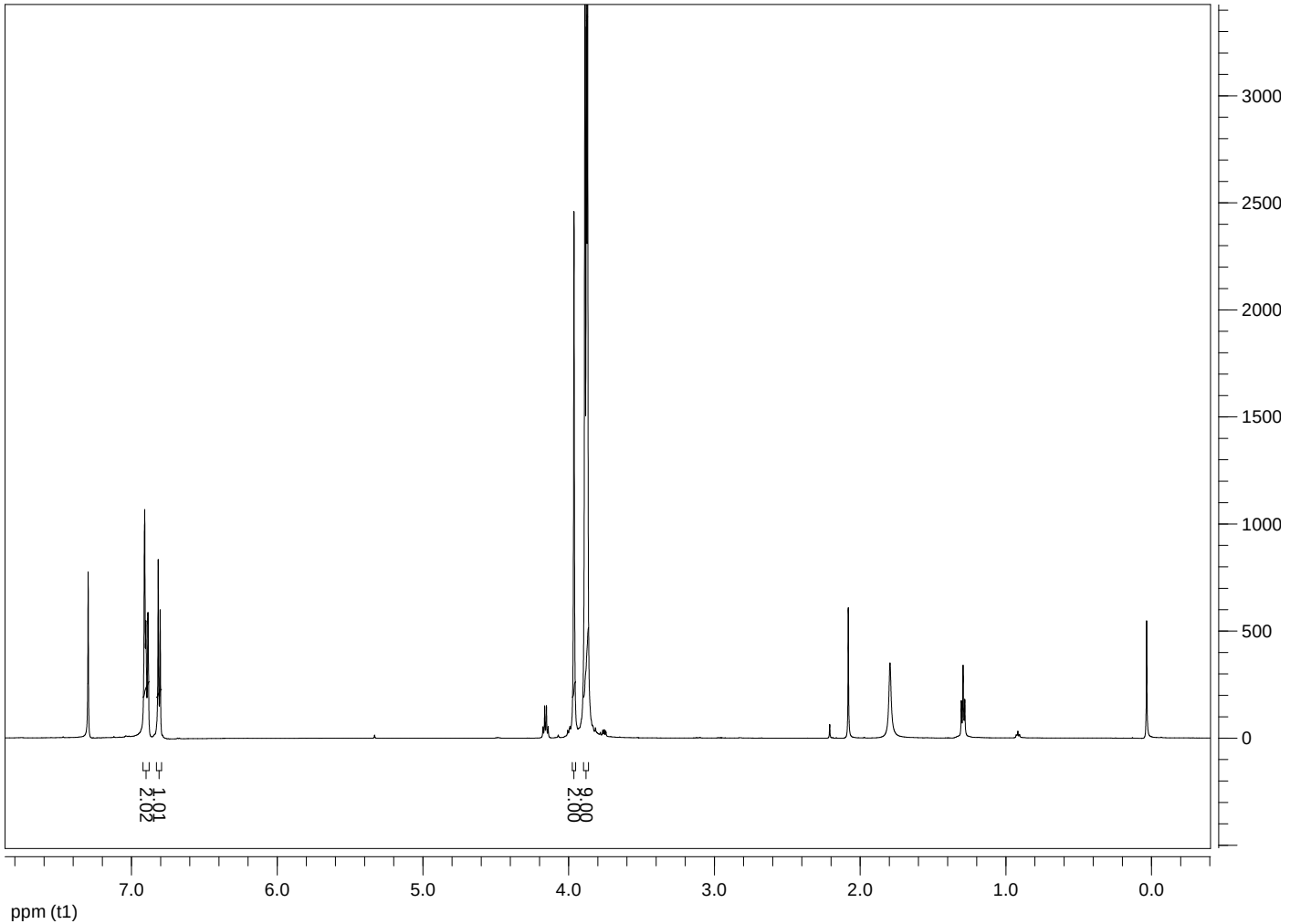

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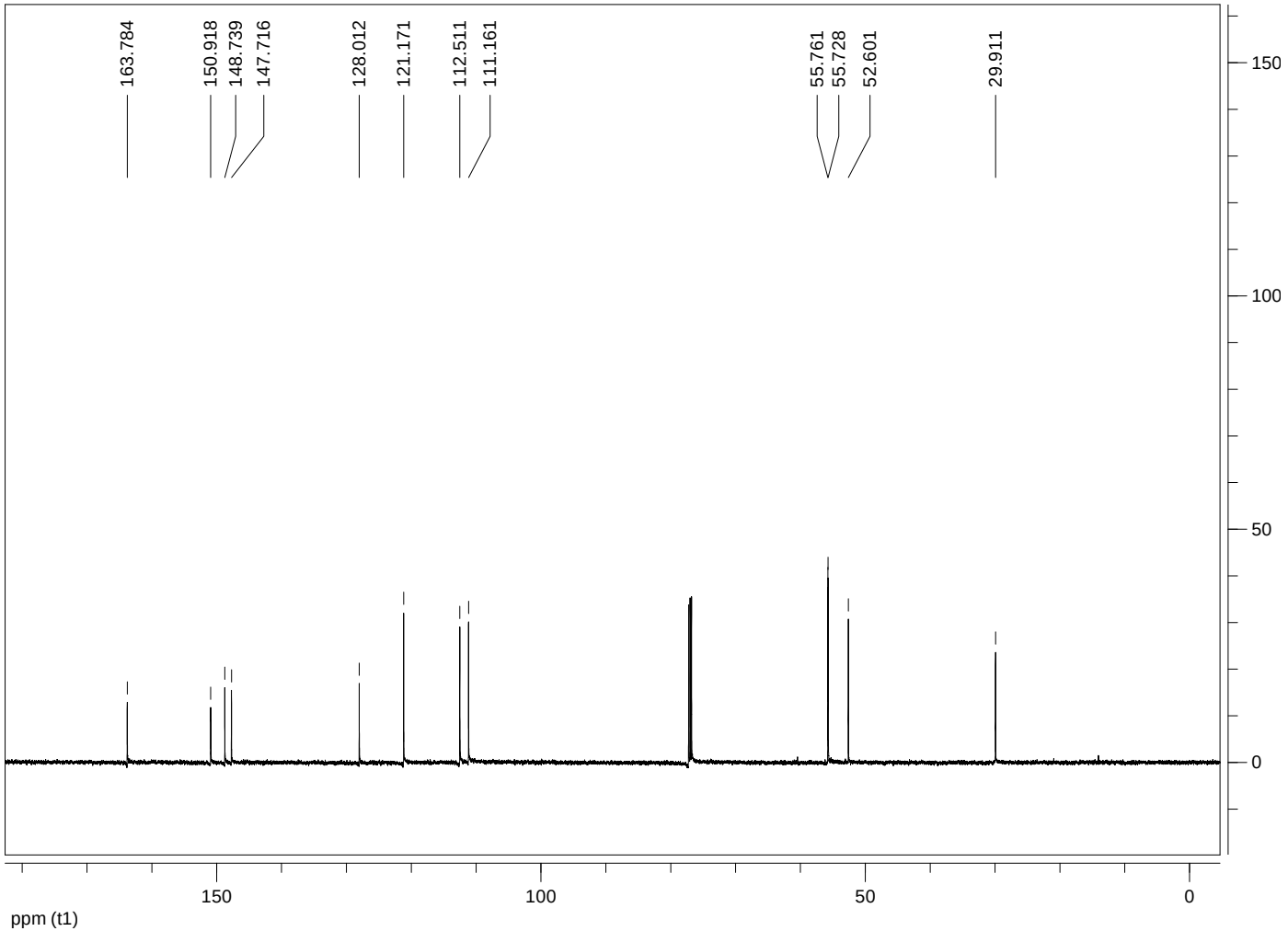

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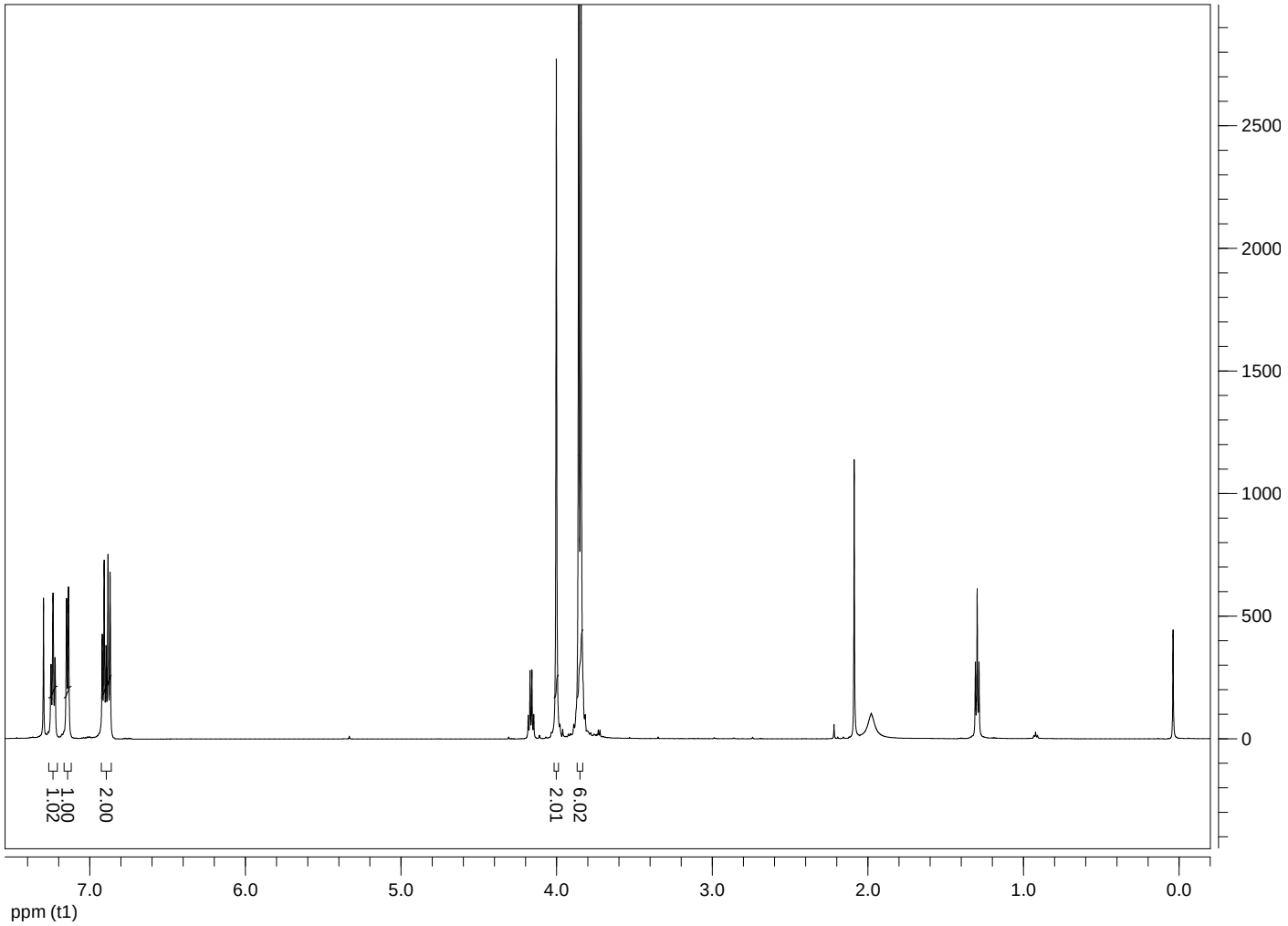

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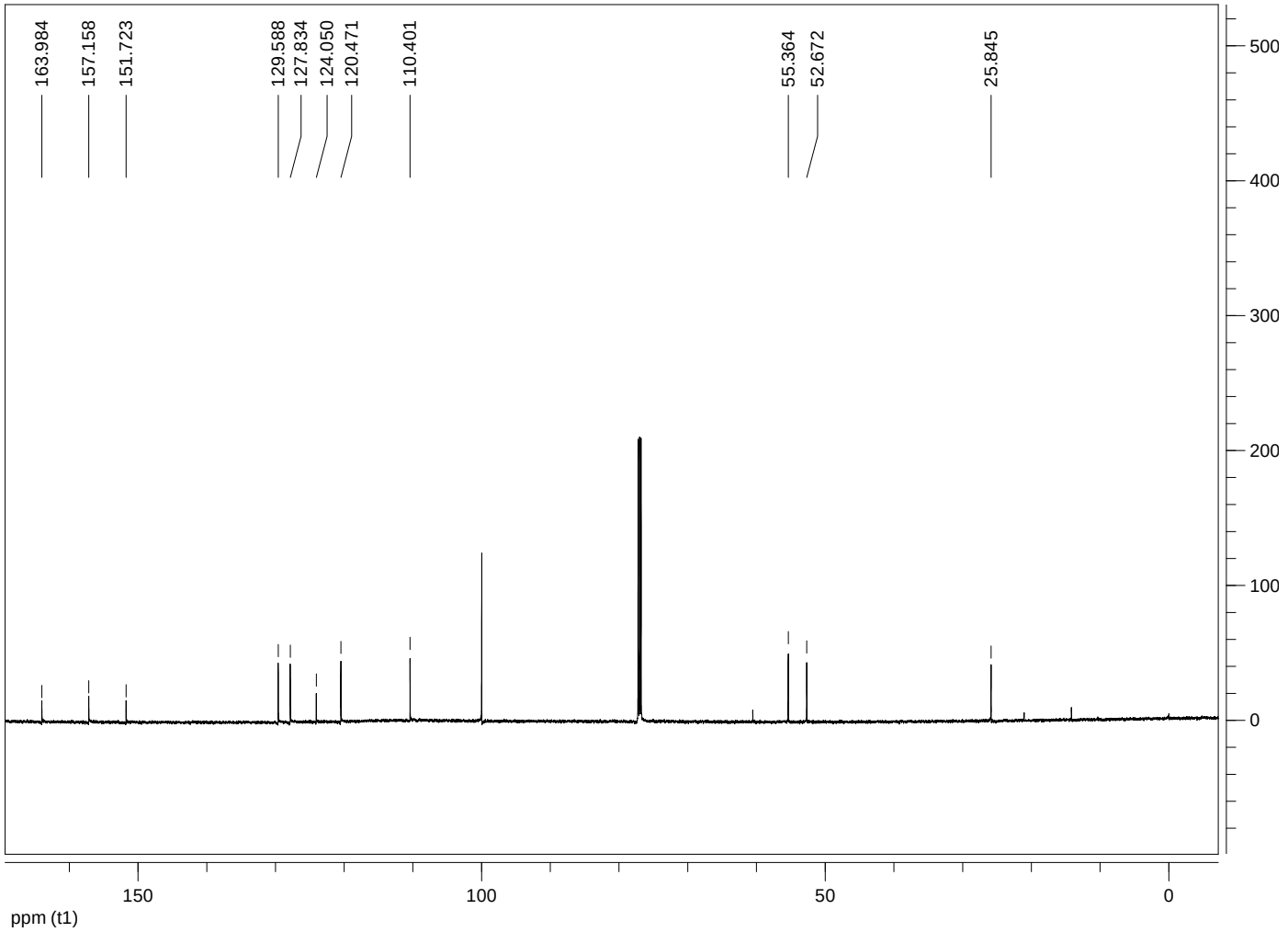
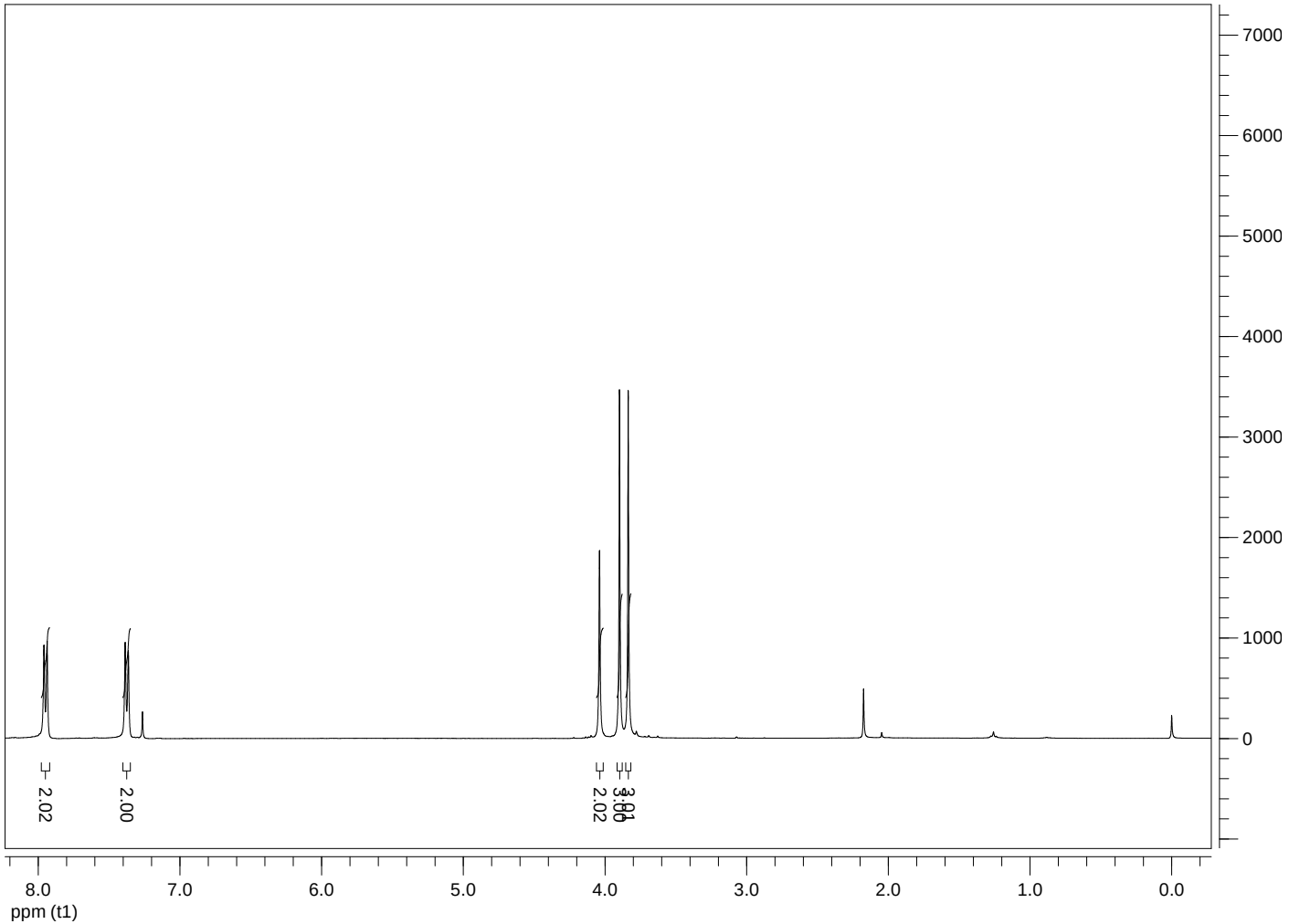


(*E*)-Methyl 4-(2-(hydroxyimino)-3-methoxy-3-oxopropyl)benzoate (3p)



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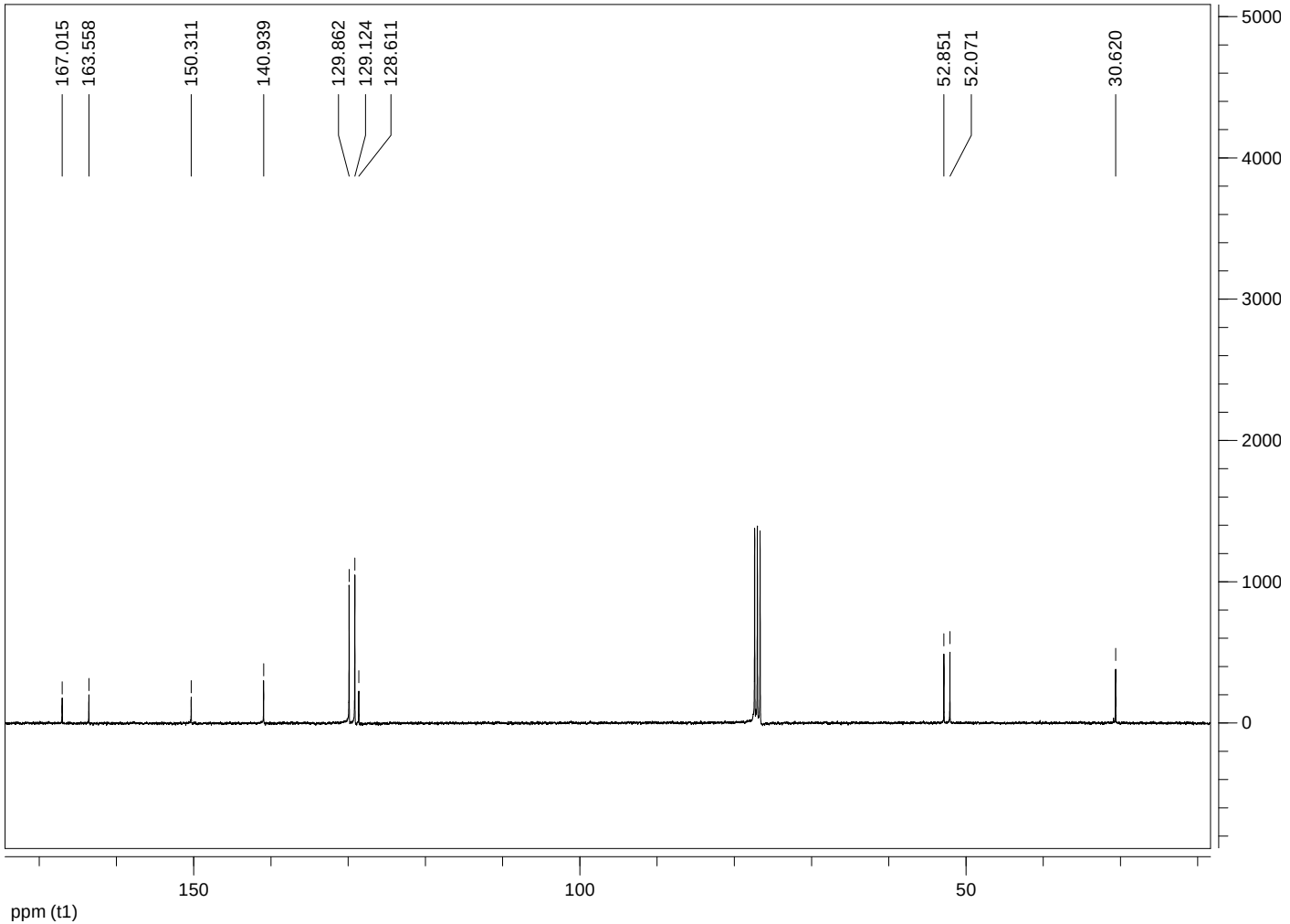

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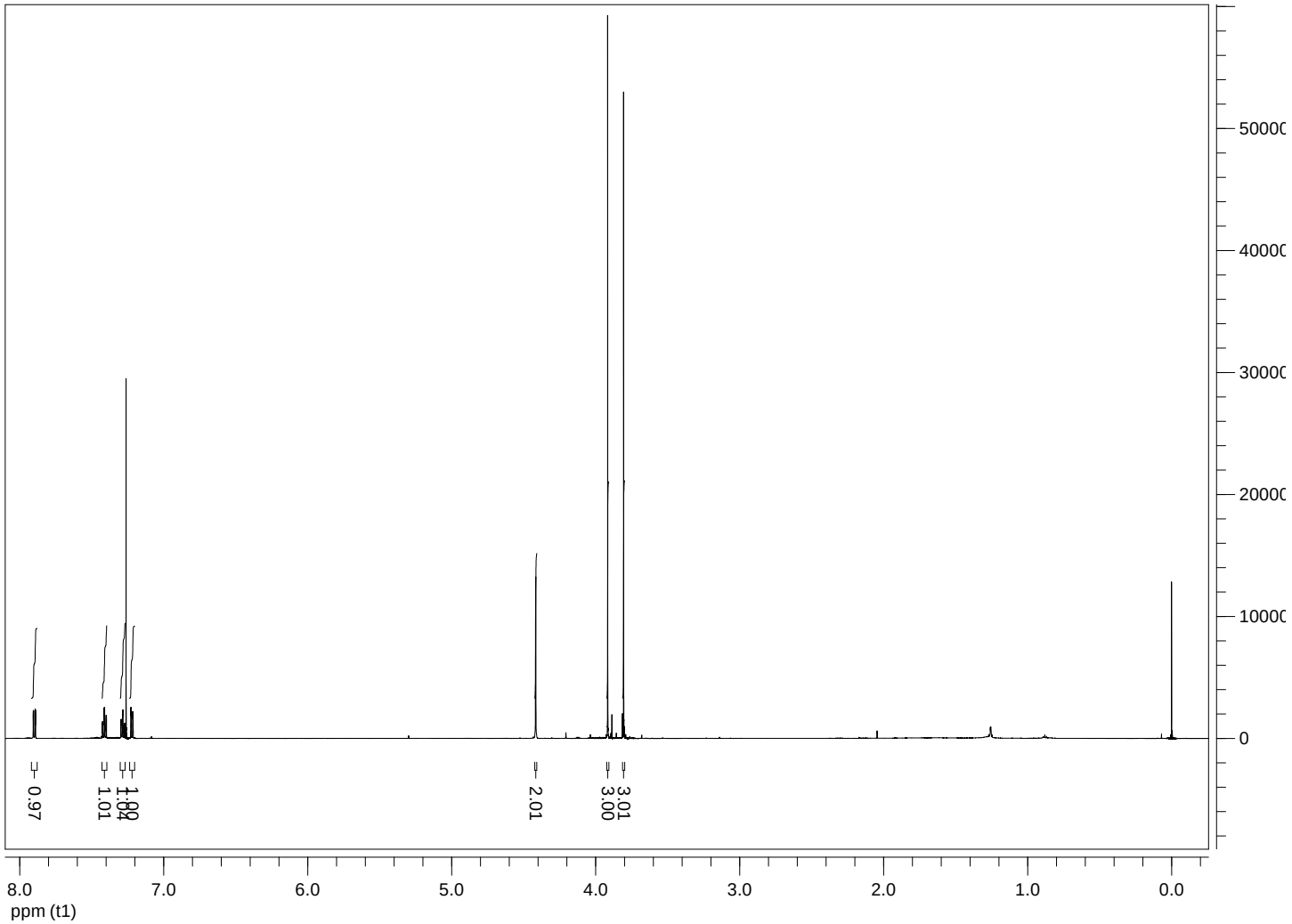

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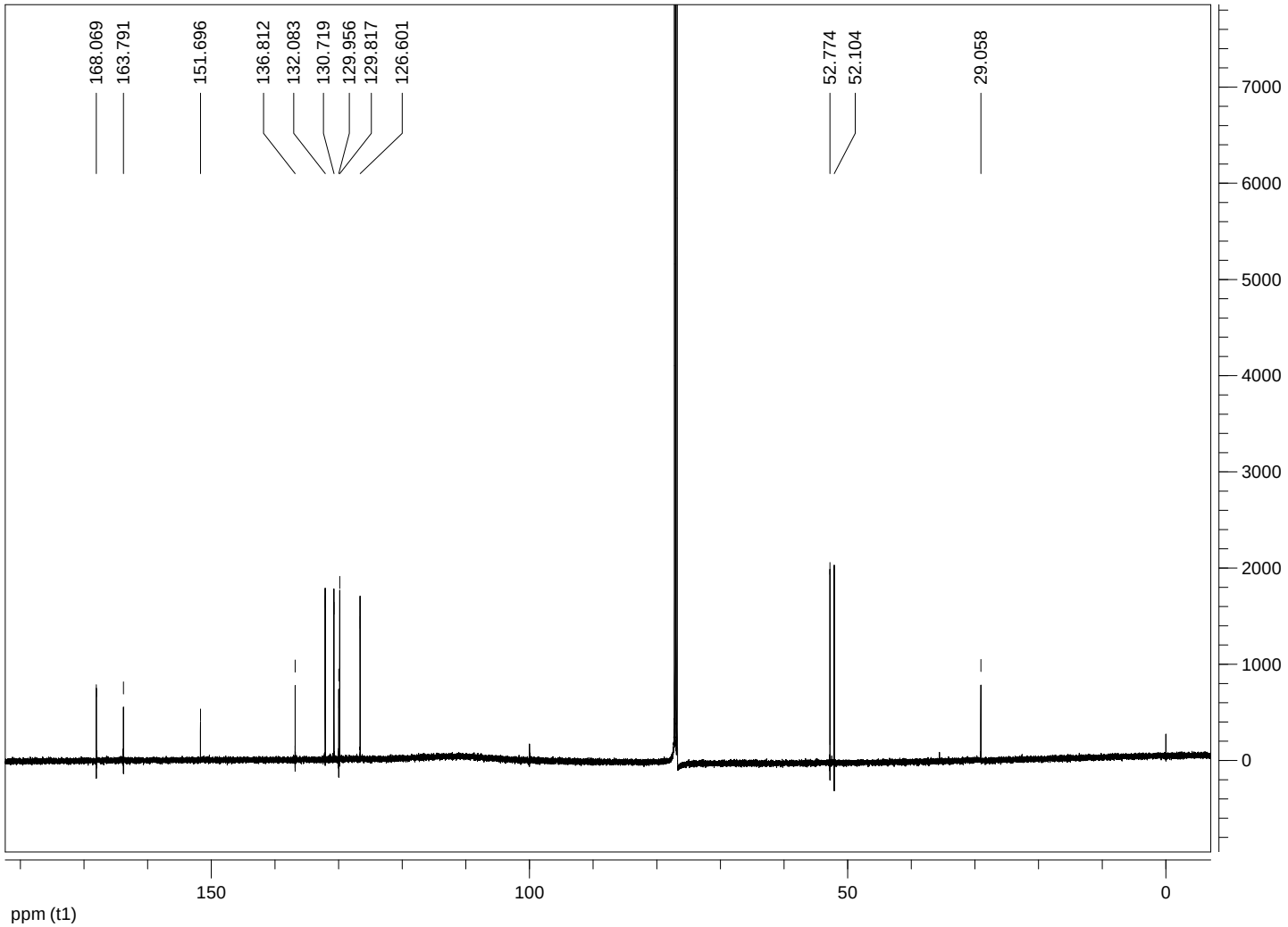
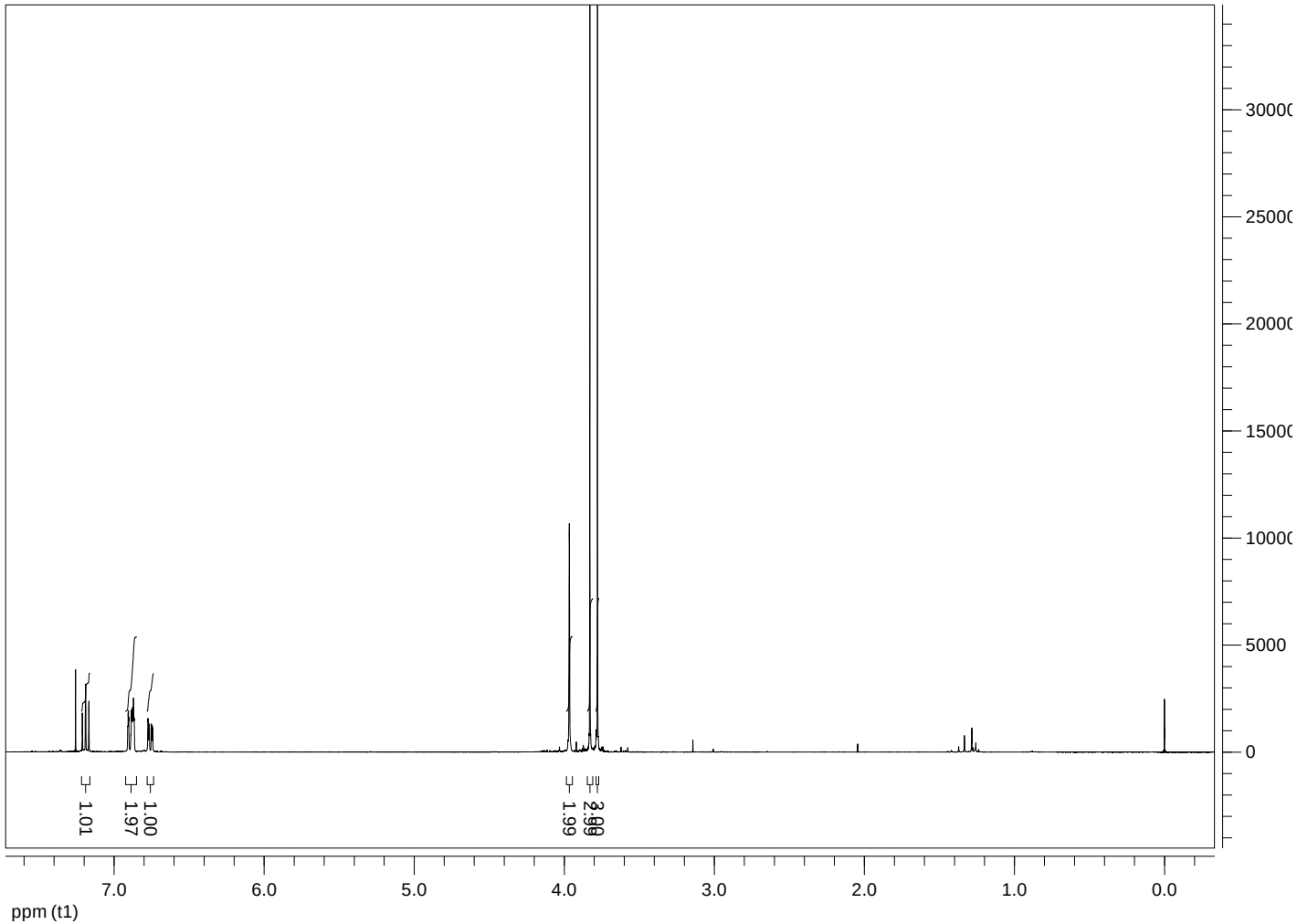


(*E*)-Methyl 2-(hydroxyimino)-3-(3-methoxyphenyl)propanoate (3r)



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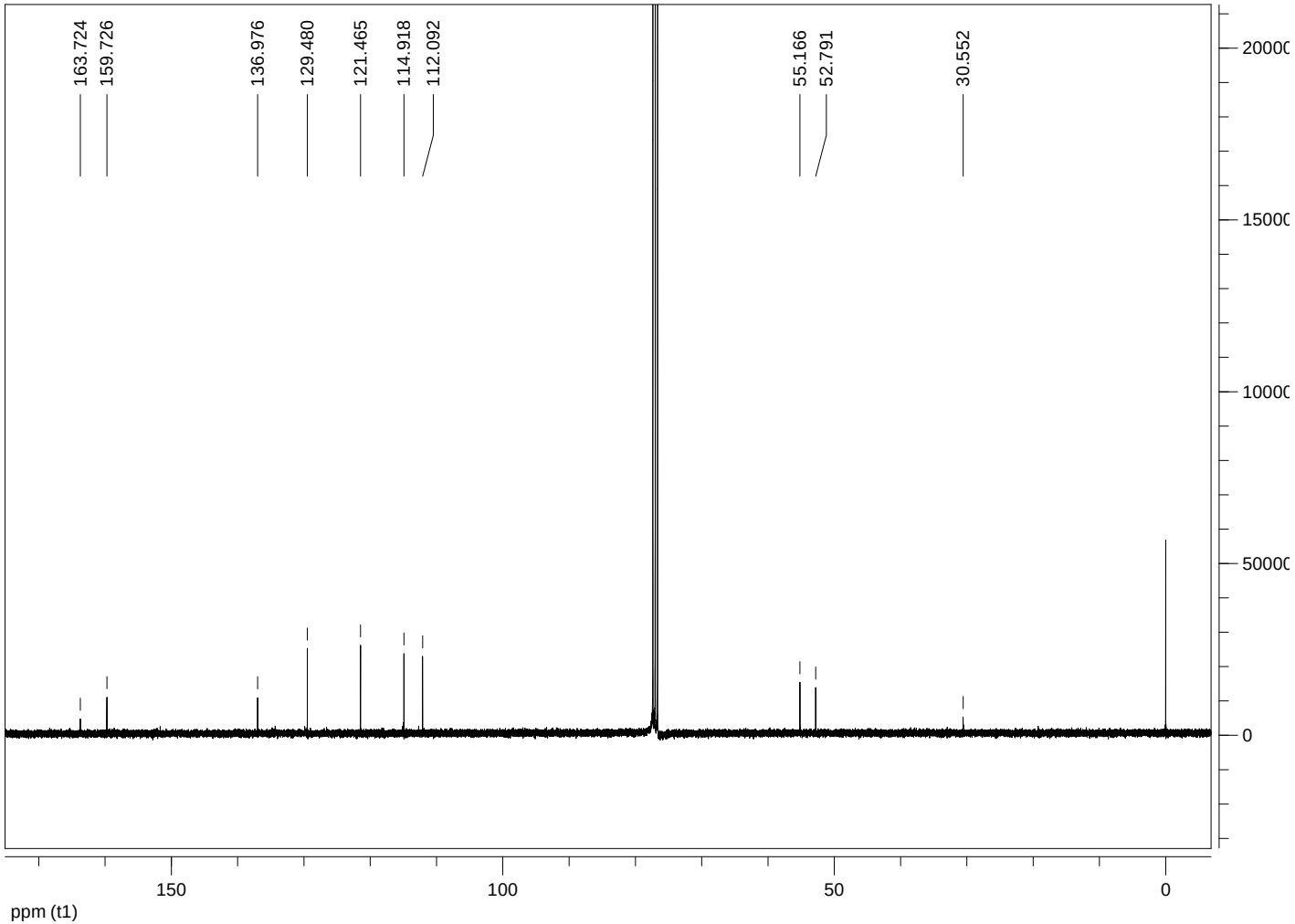
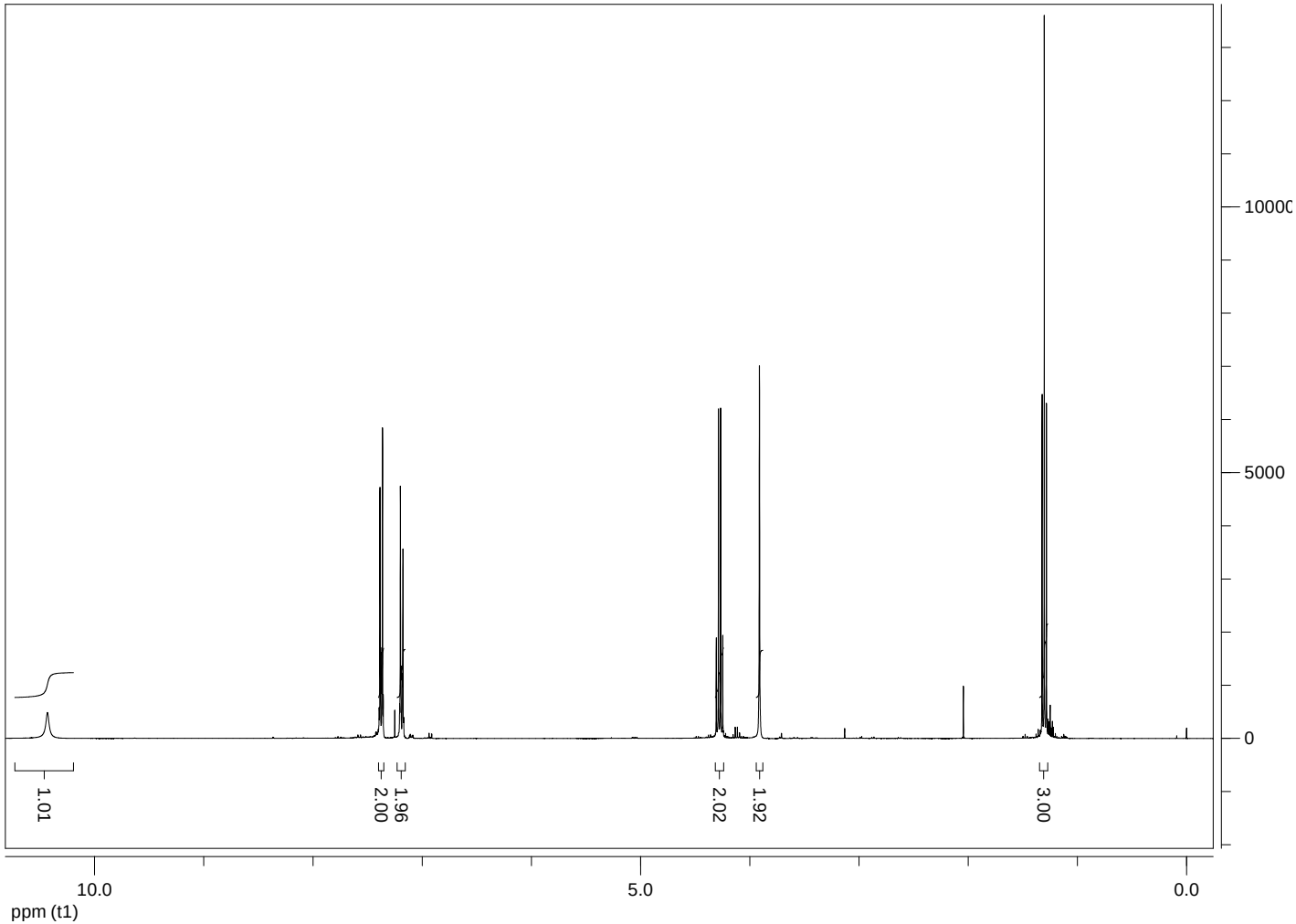


(*E*)-Ethyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (3s)



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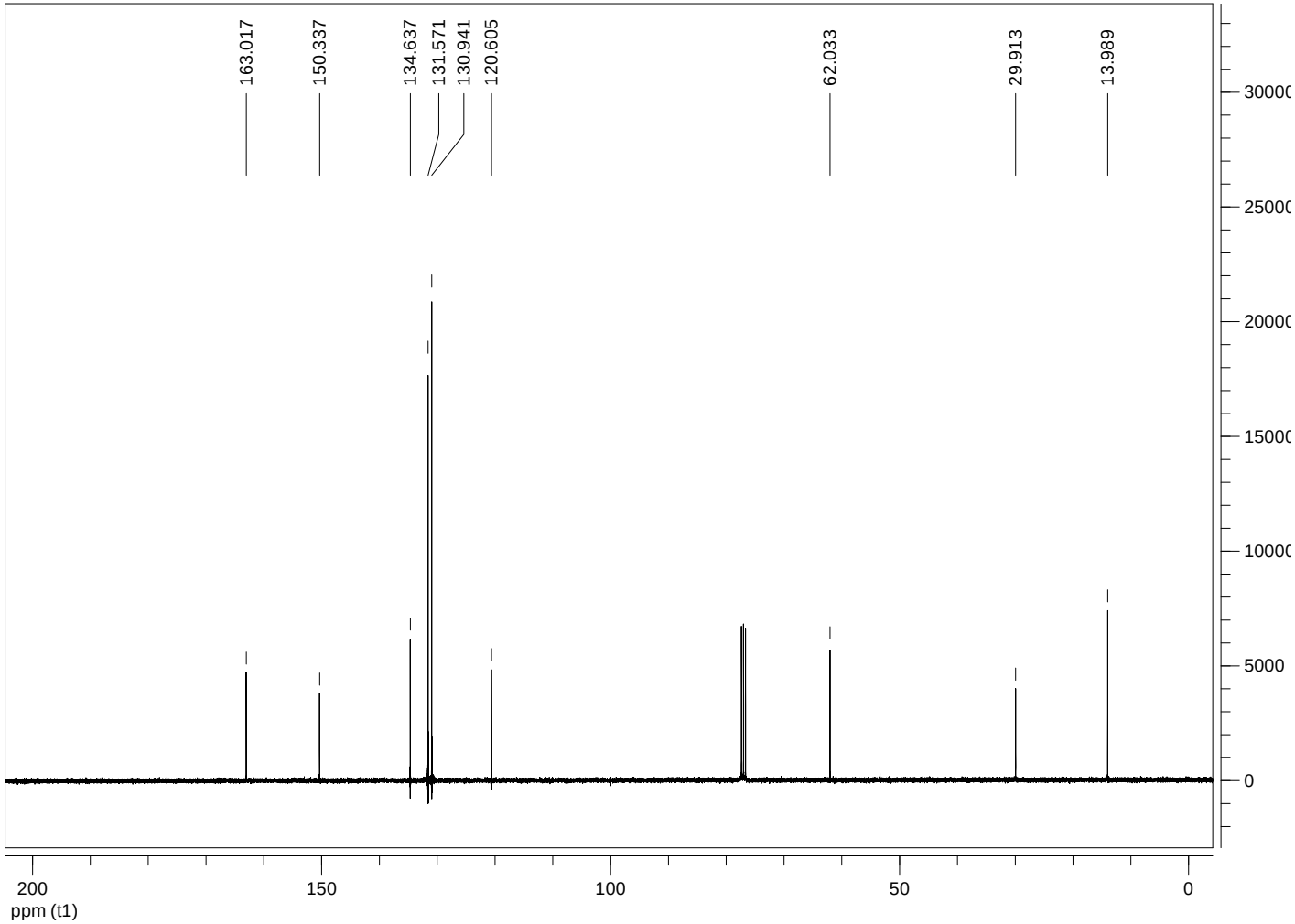
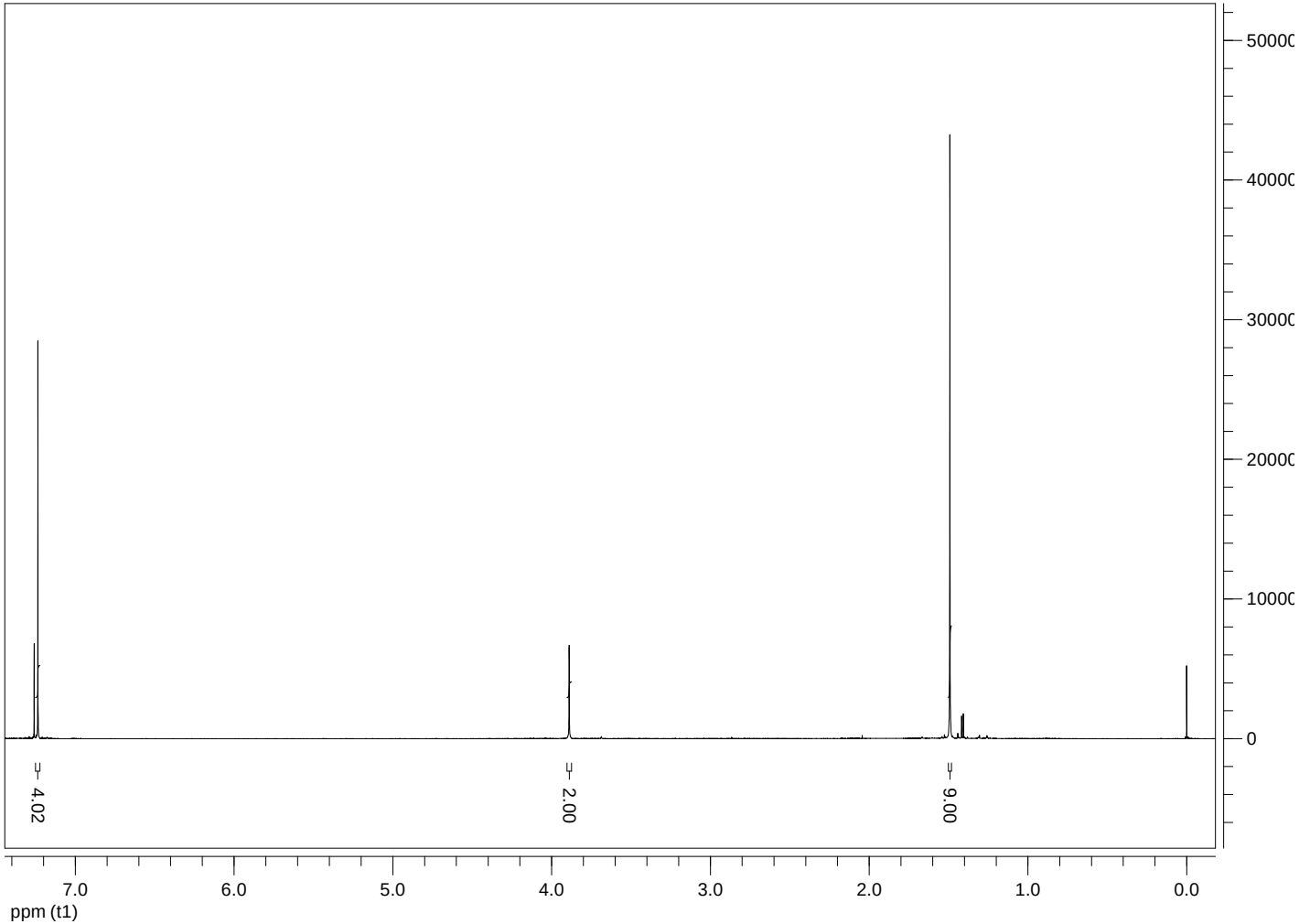


(*E*)-*tert*-Butyl 3-(4-chlorophenyl)-2-(hydroxyimino)propanoate (3t)



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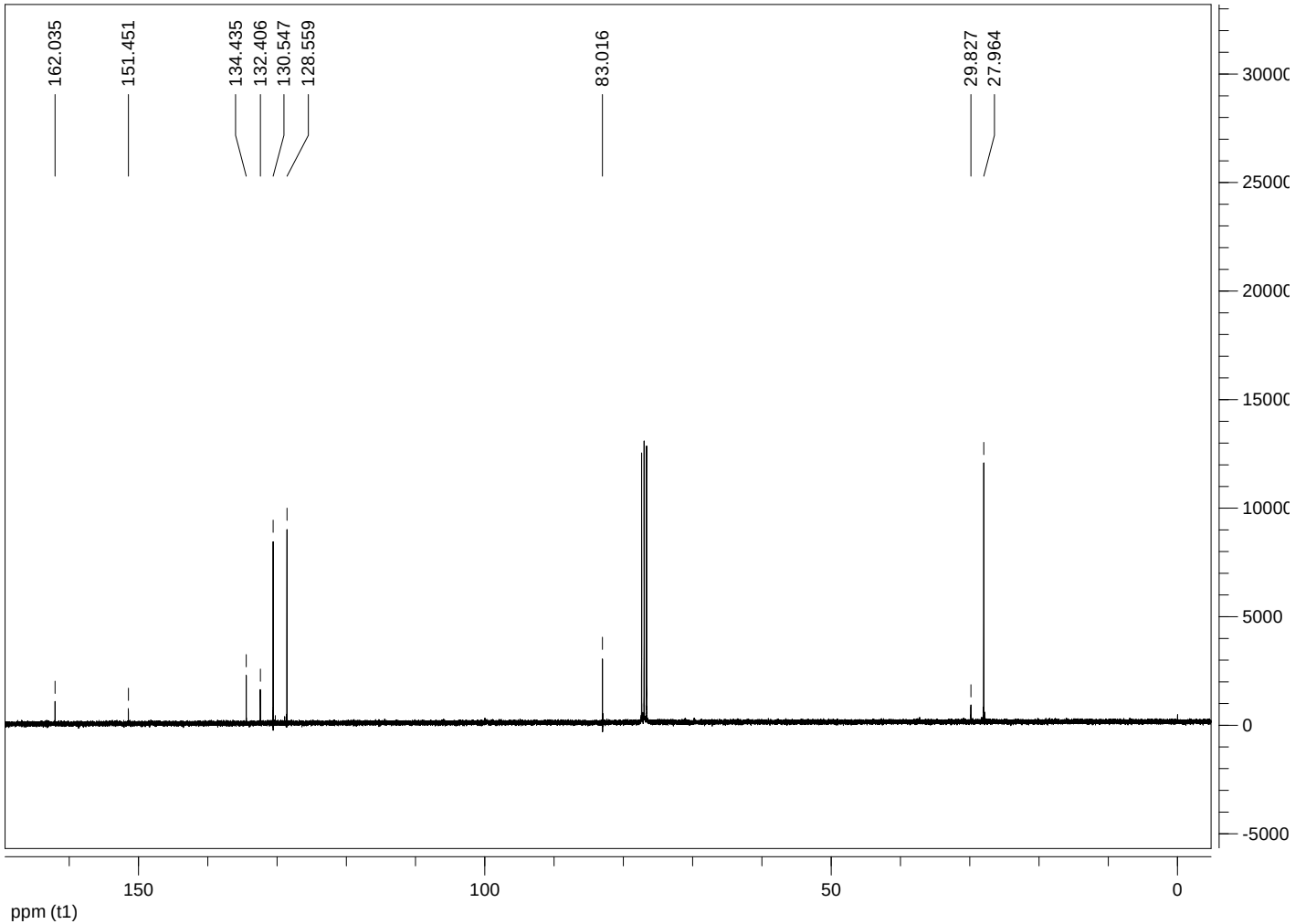
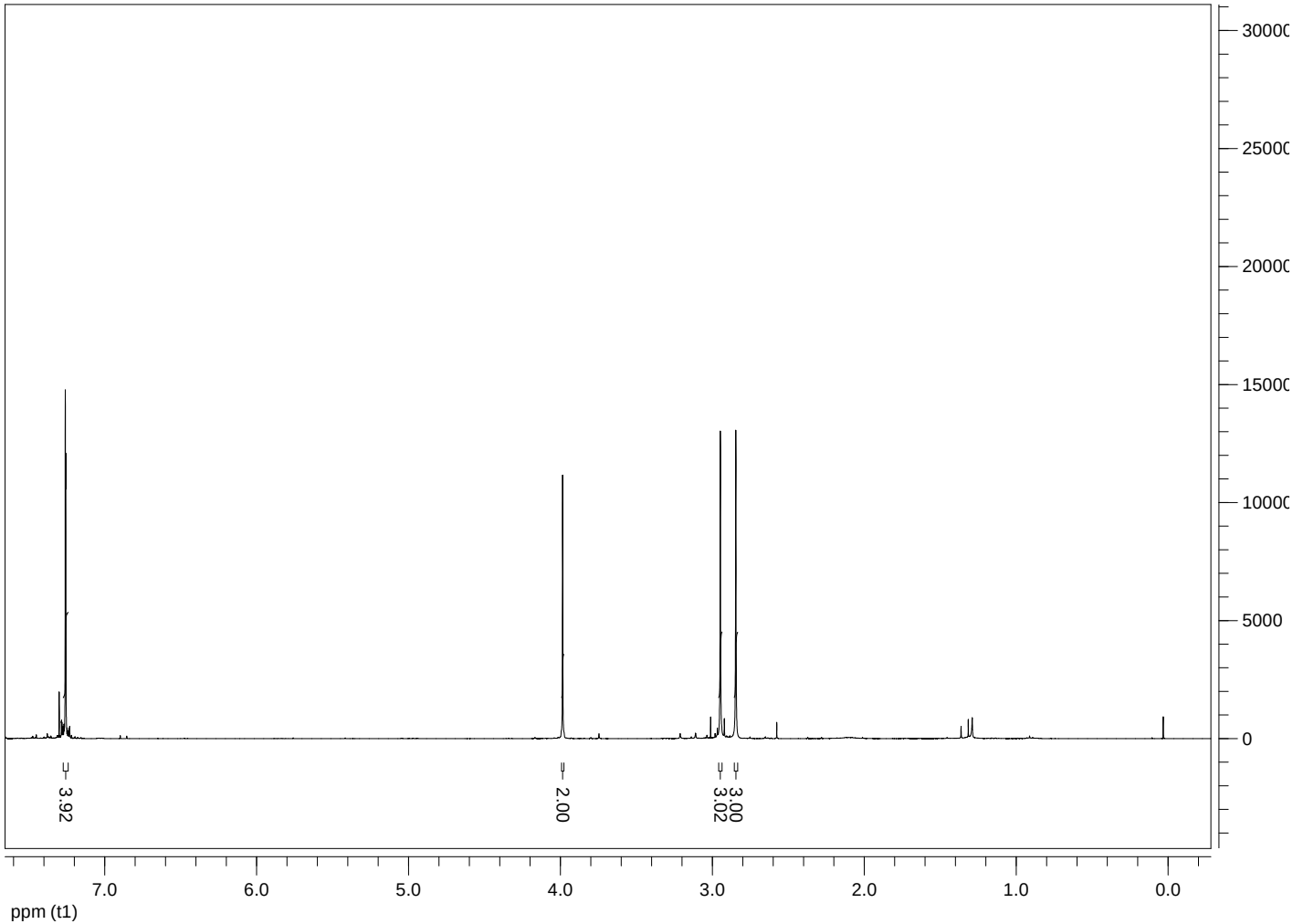
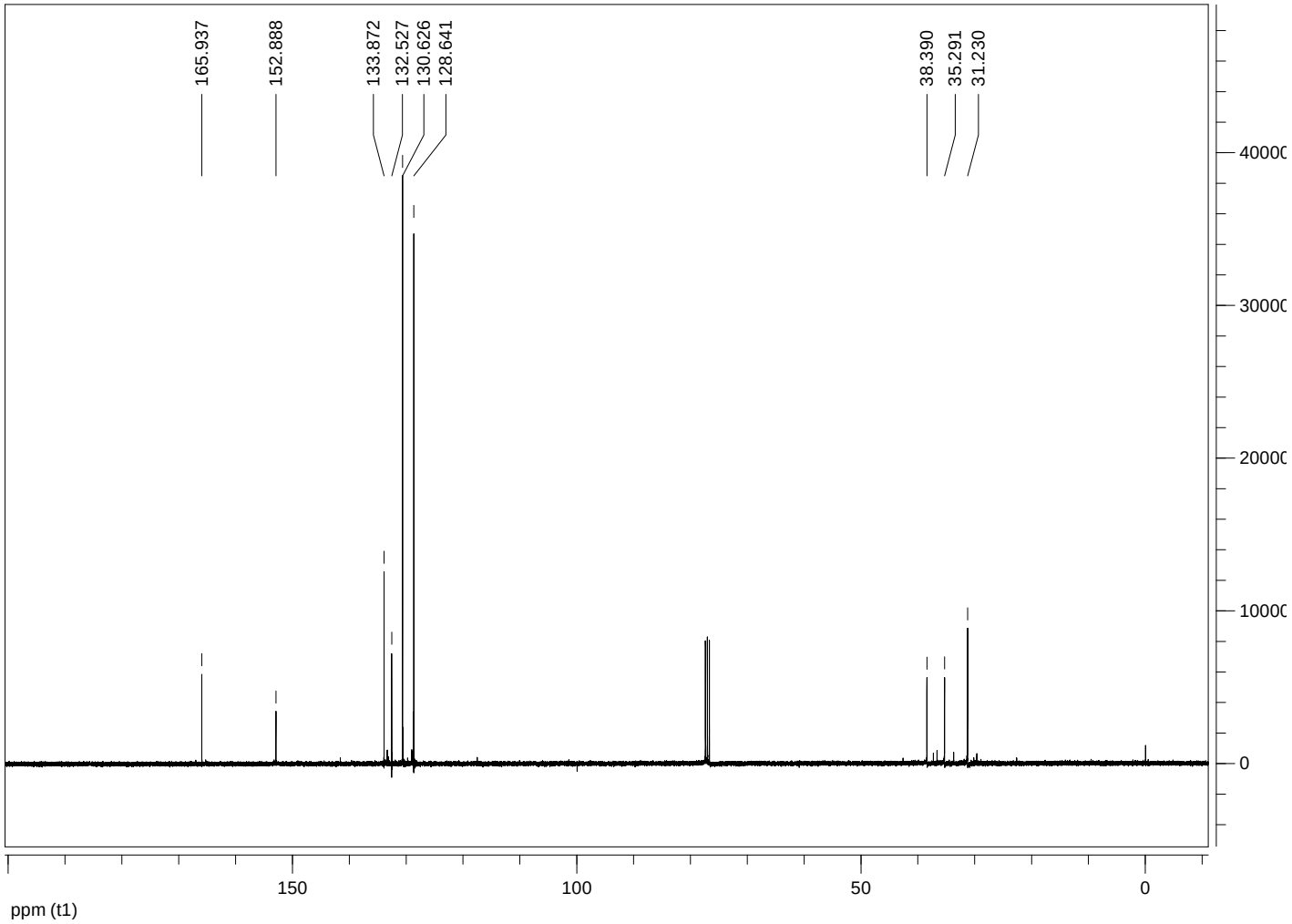


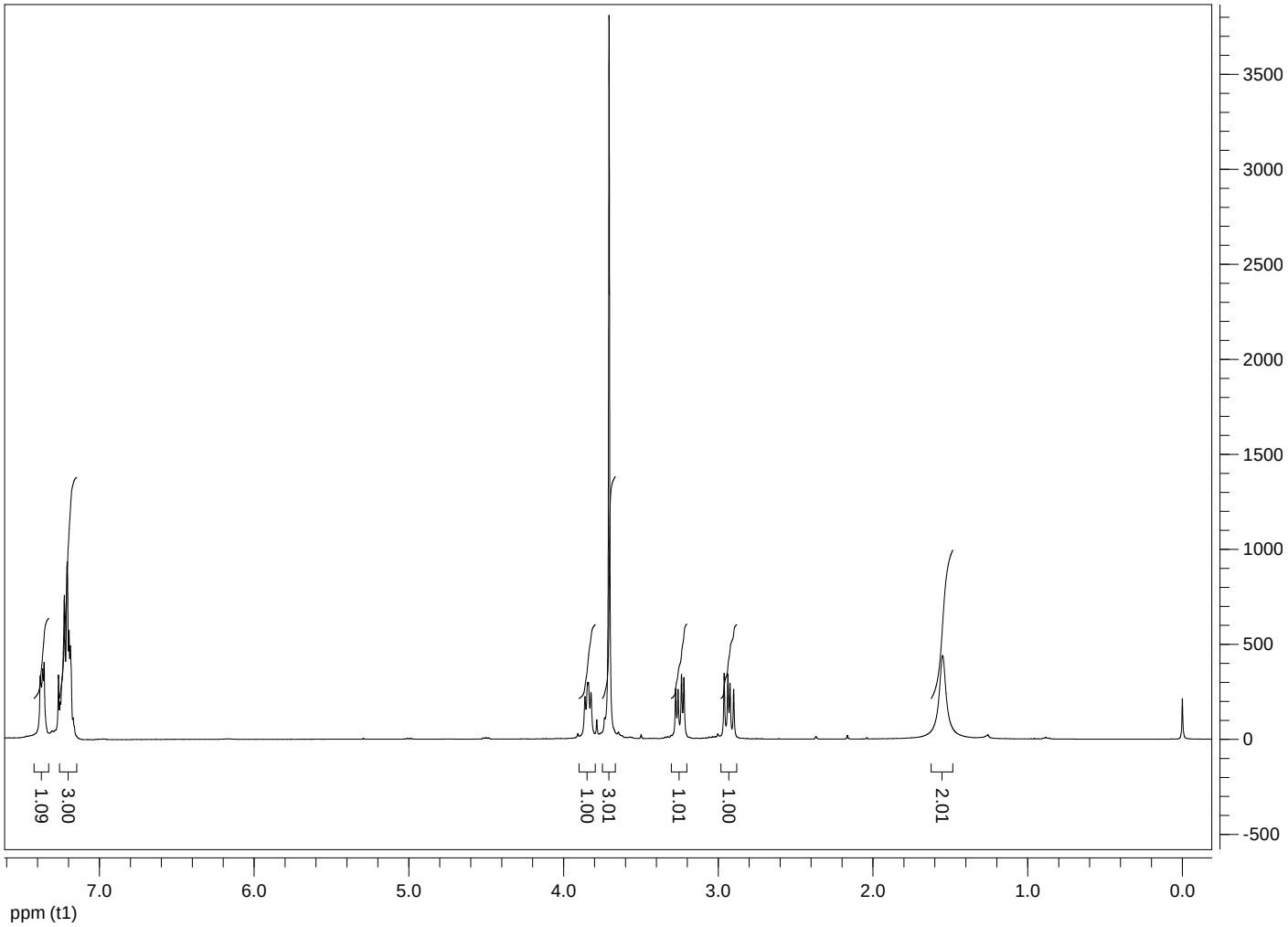
(*E*)-3-(4-Chlorophenyl)-2-(hydroxyimino)-*N*,*N*-dimethylpropanamide (3u)



(*E*)-3-(4-Chlorophenyl)-2-(hydroxyimino)-*N*,*N*-dimethylpropanamide (3u)



Methyl 2-amino-3-(2-chlorophenyl)propanoate (5k)



Methyl 2-amino-3-(2-chlorophenyl)propanoate (5k)