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Supporting Information

Iron(III) corroles and porphyrins as superior catalysts for the reactions of diazoacetates with nucleophilic substrates (containing nitrogen or sulfur): synthetic utilizations and mechanistic insights

Iris Aviv and Zeev Gross*[a]

[a] Dr. I. Aviv, Prof. Dr. Z. Gross
Schulich Faculty of Chemistry
Technion – Israel Institute of Technology
Haifa 32,000, Israel
Fax: (+)972-4829-5703
E-mail: chr10zg@tx.technion.ac.il

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Iron(III) corroles and porphyrins as superior catalysts for the reactions of diazoacetates with nucleophilic substrates (containing nitrogen or sulfur): synthetic utilizations and mechanistic insights

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Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 32000, Israel

Physical methods

The ^{1}H NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer (AV300) equipped with a QNP $^{1}H/^{19}F/^{31}P/^{13}C$-2H 5 mm probe head (operating at 300 MHz for ^{1}H and 282 MHz for ^{19}F). Chemical shifts are reported in ppm relative to residual hydrogen atoms in deuterated chloroform (δ_H = 7.24) or relative to $CFCl_3$ (δ_F = 0.00). An HP 8453 diode array spectrophotometer was used to record the electronic spectra. Gas chromatographic analysis was performed on a HP-5890 GC equipped with a HP-5 capillary column and FID detector: initial (3 min) and final temperatures of 80 and 200 $^{\circ}C$ respectively, heating rate of 10 $^{\circ}C$ min^{-1}, at 7 psi. HPLC analysis was performed on Merck-Hitachi Lachrom system equipped with a L-7100 pump, L-7400 Uv-Vis detector, D-7000 system manager and a chiral column (OD, Daicel, 0.46ϕ cm x 25nm). All the products were eluted with 90% hexane and 10% isopropyl alcohol at a flow rate of 0.5 mL/min by monitoring at 250 nm. Circular Dichroism (CD) spectroscopy analysis was performed on a J-810 JASCO spectropolarimeter.

NMR data and GC retention times for the products obtained from insertion of EDA into:

4-Cl-aniline, white solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.12 (d, 2H), 6.51 (d, 2H), 4.23 (q, 2H, *J*=7.2 Hz), 3.85 (s, 2H), 1.28 (t, 3H, *J*=7.2 Hz). GC retention time: 16.5 min.

Aniline, white solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.17 (t, 2H), 6.72 (t, 1H), 6.57 (d, 2H), 4.20 (q, 2H, *J*=7.2 Hz), 3.86 (s, 2H), 1.26 (t, 3H, *J*=7.2 Hz)**.** GC retention time: 13.7 min.

3-CN-aniline, brownish solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.24 (t, 2H), 7.00 (d, 1H), 6.79 (d, 1H), 4.21 (q, 2H, *J*=7.2 Hz), 3.88 (s, 2H), 1.31 (t, 3H, *J*=7.2 Hz).GC retention time: 19.1 min.

4-CN-aniline, brownish solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.45 (d, 2H), 6.56 (d, 2H), 4.26 (q, 2H, *J*=7.2 Hz), 3.91 (s, 2H), 1.30 (t, 3H, *J*=7.2 Hz).GC retention time: 21.6 min.

4-OMe-aniline, brownish solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.78 (d, 2H), 6.57 (d, 2H), 4.22 (q, 2H, *J*=7.2 Hz), 3.86 (s, 2H), 3.73 (s, 3H), 1.30 (t, 3H, *J*=7.2 Hz). GC retention time: 17.53 min.

4-Me-aniline, brownish solid, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.00 (d, 2H), 6.54 (d, 2H), 4.23 (q, 2H, *J*=7.2 Hz), 3.88 (s, 2H), 2.25 (s, 3H), 1.29 (t, 3H, *J*=7.2 Hz). GC retention time: 15.38 min.

***N*-Methylaniline**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.24 (t, 2H), 6.75 (t, 1H), 6.69 (d, 2H), 4.18 (q, 2H, *J*=7.2 Hz), 4.06 (s, 2H), 3.07 (s, 3H), 1.24 (t, 3H, *J*=7.2 Hz). GC retention time: 14. 69 min.

Morpholine, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.17 (q, 2H, *J*=7.2 Hz), 3.74 (m, 4H), 3.18 (s, 2H), 2.56 (m, 4H), 1.25 (t, 3H, *J*=7.2 Hz). GC retention time: 10.25.

Propylamine, colorless oil, GC retention time: 6.35 min, bis-substituted product: colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.13 (q, 4H, *J*=7.2 Hz), 3.50 (s, 4H), 2.62 (t, 2H), 1.46 (m, 2H), 1.23 (t, 6H, *J*=7.2 Hz), 0.85 (t, 3H). GC retention time: 13.15 min.

Piperidine, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.13 (q, 2H, *J*=7.2 Hz), 3.12 (s, 2H), 2.45 (t, 4H), 1.52 (m, 4H), 1.39 (m, 2H), 1.24 (t, 3H, *J*=7.2 Hz).GC retention time: 10.30 min.

2-methyl piperidine, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.14 (q, 2H, *J*=7.2 Hz), 3.35 (s, 2H), 2.82 (m, 1H), 2.51 (m, 2H), 1.66 (m, 1H), 1.55 (m, 3H), 1.30 (m, 2H), 1.24 (t, 3H, *J*=7.2 Hz), 1.05 (d, 3H). GC retention time: 10.60 min.

2-methyl indoline, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.02 (t, 2H), 6.65 (t, 1H, *J*=7.2 Hz), 6.32 (d, 1H, *J*=7.8 Hz), 4.17 (q, 2H, *J*=7.2 Hz), 3.86 (m, 3H), 3.17

(dd, 1H), 2.64 (dd, 1H), 1.3 (d, 3H, *J*=6.3 Hz), 1.23 (t, 3H, *J*=7.2 Hz). GC retention time: 15.83 min.

Alanine ethyl ester, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.16 (q, 4H), 3.42 (d AB pattern, 1H, *J*=17.1 Hz), 3.32 (d AB pattern, 1H, *J*=17.1 Hz), 3.35 (q, 1H, *J*=6.9 Hz), 2.1 (s, 1H), 1.3 (d, 3H, *J*=6.9 Hz), 1.24 (t, 3H, *J*=7.2 Hz), 1.23 (t, 3H, *J*=7.2 Hz). GC retntion time: 11.43 min.

NMR and GC retention times for the products obtained from insertion of EDP (ethyl diazopropionate) into:

4-Cl-aniline, colorless oil, δ = 7.10 (d, 2H), 6.47 (d, 2H), 4.13 (q, 2H, *J*=7.2 Hz), 4.02 (q, 1H, *J*=6.9 Hz), 1.40 (d, 3H, *J*=6.9 Hz), 1.20 (t, 3H, *J*=7.2 Hz). GC retention time: 16.5 min.

Aniline, colorless oil, δ = 7.16 (t, 2H), 6.73 (t, 1H), 6.59 (d, 2H), 4.17 (q, 2H, *J*=7.2 Hz), 4.09 (q, 1H, *J*=6.9 Hz), 1.45 (d, 3H, *J*=6.9 Hz), 1.23 (t, 3H, *J*=7.2 Hz). HPLC retention times: 13.5, 22.0 min.

4-OMe-aniline, colorless oil, δ = 6.73 (d, 2H), 6.59 (d, 2H), 4.15 (q, 2H, *J*=7.2 Hz), 4.03 (q, 1H, *J*=6.9 Hz), 3.72 (s, 3H), 1.43 (d, 3H, *J*=6.9 Hz), 1.19 (t, 3H, *J*=7.2 Hz). HPLC retention times: 16.4, 17.9 min.

Physical data of the 2,3-sigmatropic rearrangement products obtained from quantitative reactions of EDA with the following amines and sulfides:

***N,N*-dimethylallylamine**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.72 (m, 1H), 5.04 (m, 2H), 4.14 (q, 2H, *J* = 7.2 Hz), 3.14 (dd, 1H, *J* = 8.3, 6.6 Hz), 2.41 (m, 2H), 2.35 (s, 6H), 1.24 (t, 3H, *J* = 7.2 Hz).

***N,N*-dimethylpropargyl amine**, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.21 (dt, 1H, *J* = 8.7, 6.6 Hz), 4.79 (dd, 2H, *J* = 6.6, 1.5 Hz), 4.17 (q, 2H, *J* = 7.2 Hz), 3.58 (dt, 1H, *J* = 8.7, 1.5 Hz), 2.29 (s, 6H), 1.23 (t, 3H, *J* = 7.2 Hz).

***N*-allyl-*N*-methylaniline,** colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21 (m, 2H), 6.77 (m, 2H), 5.74 (m, 1H), 5.09 (m, 2H), 4.41 (dd, 1H, *J* = 8.9, 6.4 Hz), 4.15 (m, 2H), 2.89 (s, 3H), 2.7 (m, 1H), 2.61 (m, 1H), 1.21 (t, 3H, *J* = 6.9 Hz).

allyl methyl sulfide, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.74 (m, 1H), 5.06 (dd, 2H), 4.15 (q, 2H, *J* = 7.2 Hz), 3.21 (m, 1H), 2.57 (dd, 1H), 2.38 (dd, 1H), 2.12 (s, 3H), 1.24 (t, 3H, *J* = 7.2 Hz).

GC: 8.89 min, chiral 15.11, 15.23 min.

allyl methyl sulfide + ethyldiazopropionate (EDP), colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.74 (m, 1H), 5.11 (dd, 2H), 4.16 (q, 2H, *J* = 7.2 Hz), 2.66 (dd, 1H), 2.41 (dd, 1H), 2.08 (s, 3H), 1.40 (s, 3H), 1.26 (t, 3H, *J* = 7.2 Hz).

pneylpropargyl sulfide, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ =7.46 (m, 2H), 7.30 (m, 3H), 5.35 (dt, 1H, *J* = 9.0, 6.6 Hz), 4.77 (m, 2H), 4.29 (dt, 1H, *J* = 9.0, 1.5 Hz), 4.13 (q, 2H, *J* = 6.9 Hz), 1.19 (t, 3H, *J* = 6.9 Hz).

Physical data of products obtained from the reactions of EDA with the following thiols:

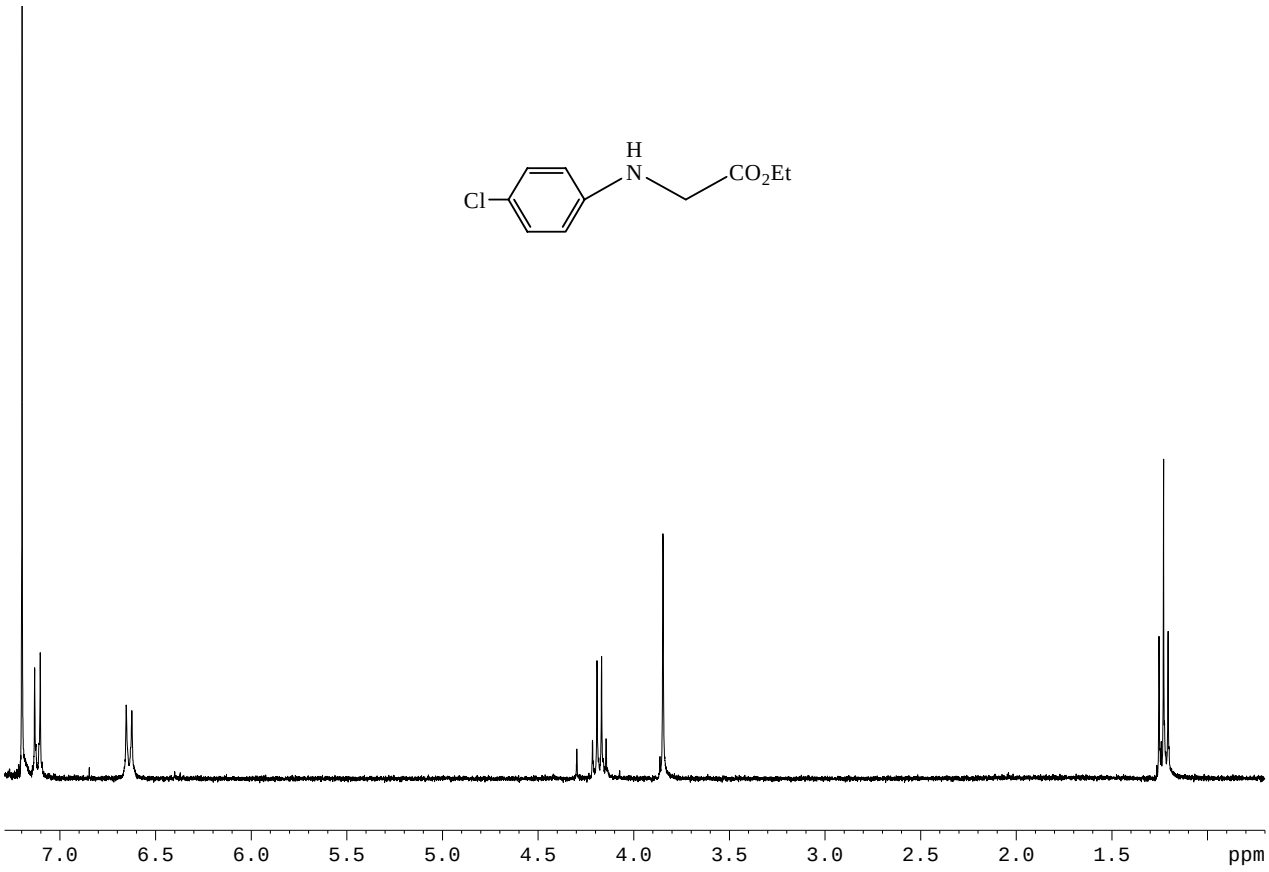
Thiophenol, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.39 (m, 2H), 7.26 (m, 3H), 4.15 (q, 2H, *J* = 7.2 Hz), 3.61 (s, 2H), 1.20 (t, 3H, *J* = 7.2 Hz). GC retention time: 13.998 min.

4-methyl benzenthiol, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.31 (d, 2H), 7.09 (d, 2H), 4.13 (q, 2H, *J* = 7.2 Hz), 3.56 (s, 2H), 2.30 (s, 3H), 1.20 (t, 3H, *J* = 7.2 Hz). GC retention time: 15.46 min.

2-methyl-2-propanethiol, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.16 (q, 2H, *J* = 7.2 Hz), 3.26 (s, 2H), 1.30 (s, 9H), 1.26 (t, 3H, *J* = 7.2 Hz). GC retention time: 8.78 min.

Ethanethiol, colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.16 (q, 2H, *J* = 7.2 Hz), 3.19 (s, 2H), 2.63 (q, 2H, *J* = 7.5 Hz), 1.26 (t, 3H, *J* = 7.2 Hz), 1.24 (t, 3H, *J* = 7.5 Hz). GC retention time: 7.33 min.

Thiophenol + ethyldiazopropionate (EDP), colorless oil, ^{1}H NMR (300 MHz, CDCl3): δ = 7.46 (m, 2H), 7.35 (m, 3H), 4.09 (q, 2H, *J*=7.2 Hz), 3.78 (q, 1H, *J*=7.2 Hz), 1.47 (d, 3H, *J*=7.2 Hz), 1.16 (t, 3H, *J*=7.2 Hz). GC retention time: 14.14 min.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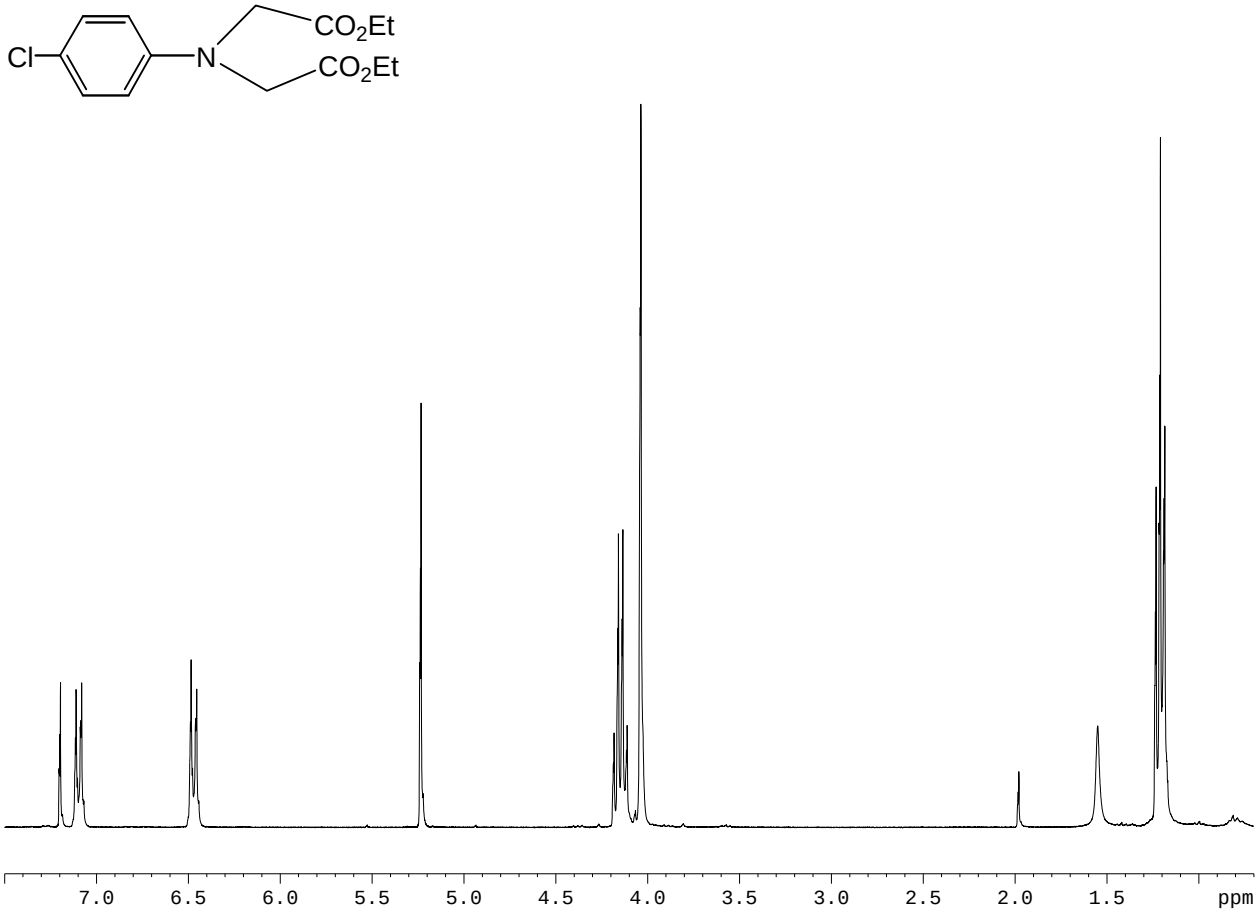
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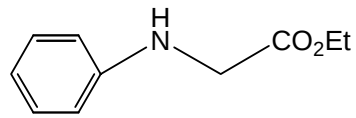
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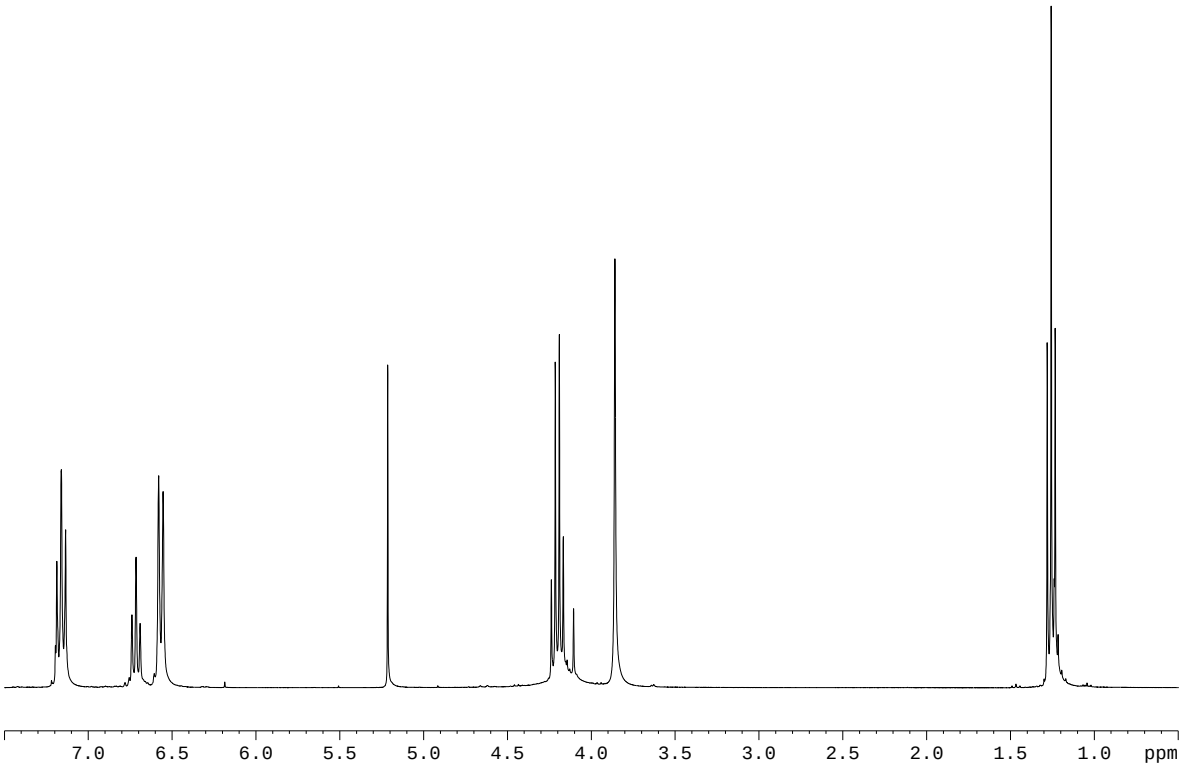
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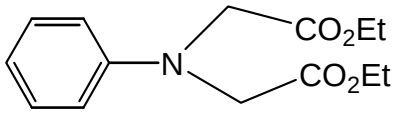
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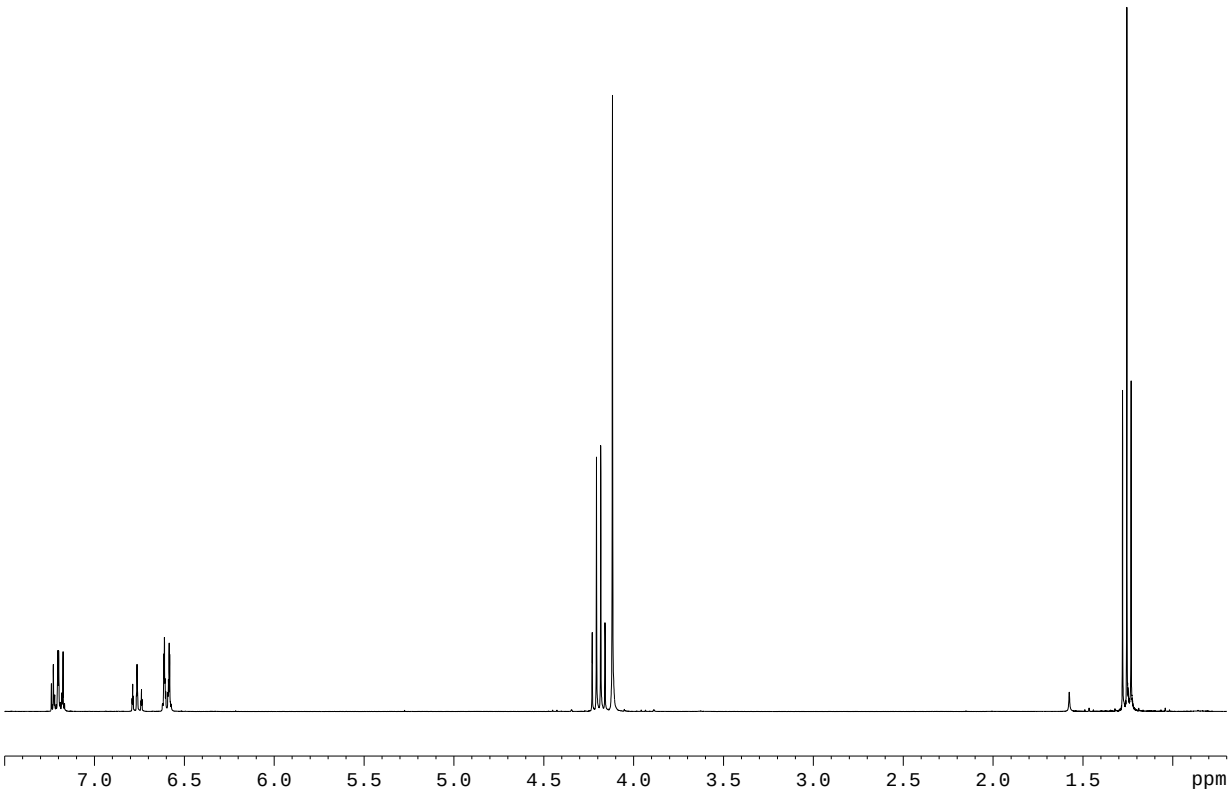
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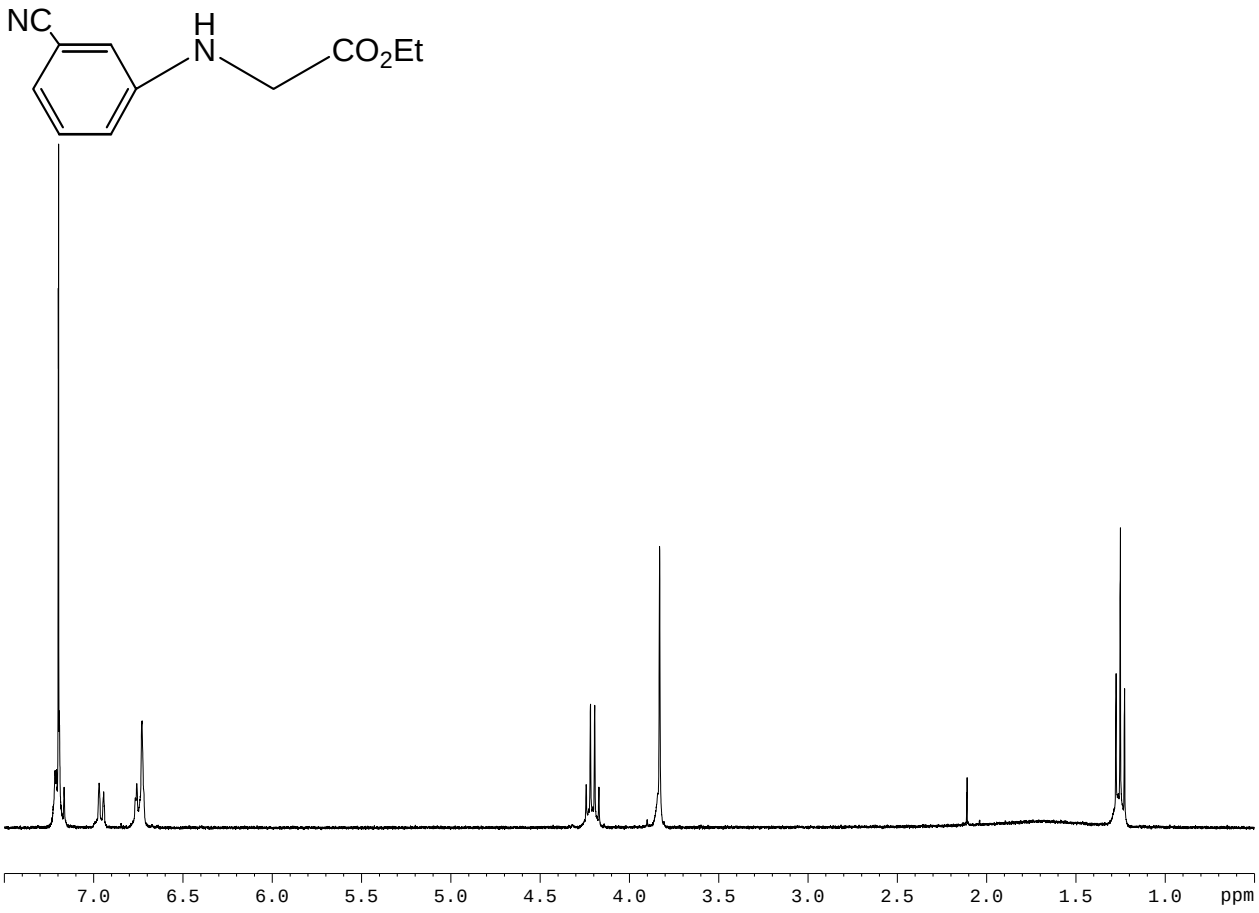
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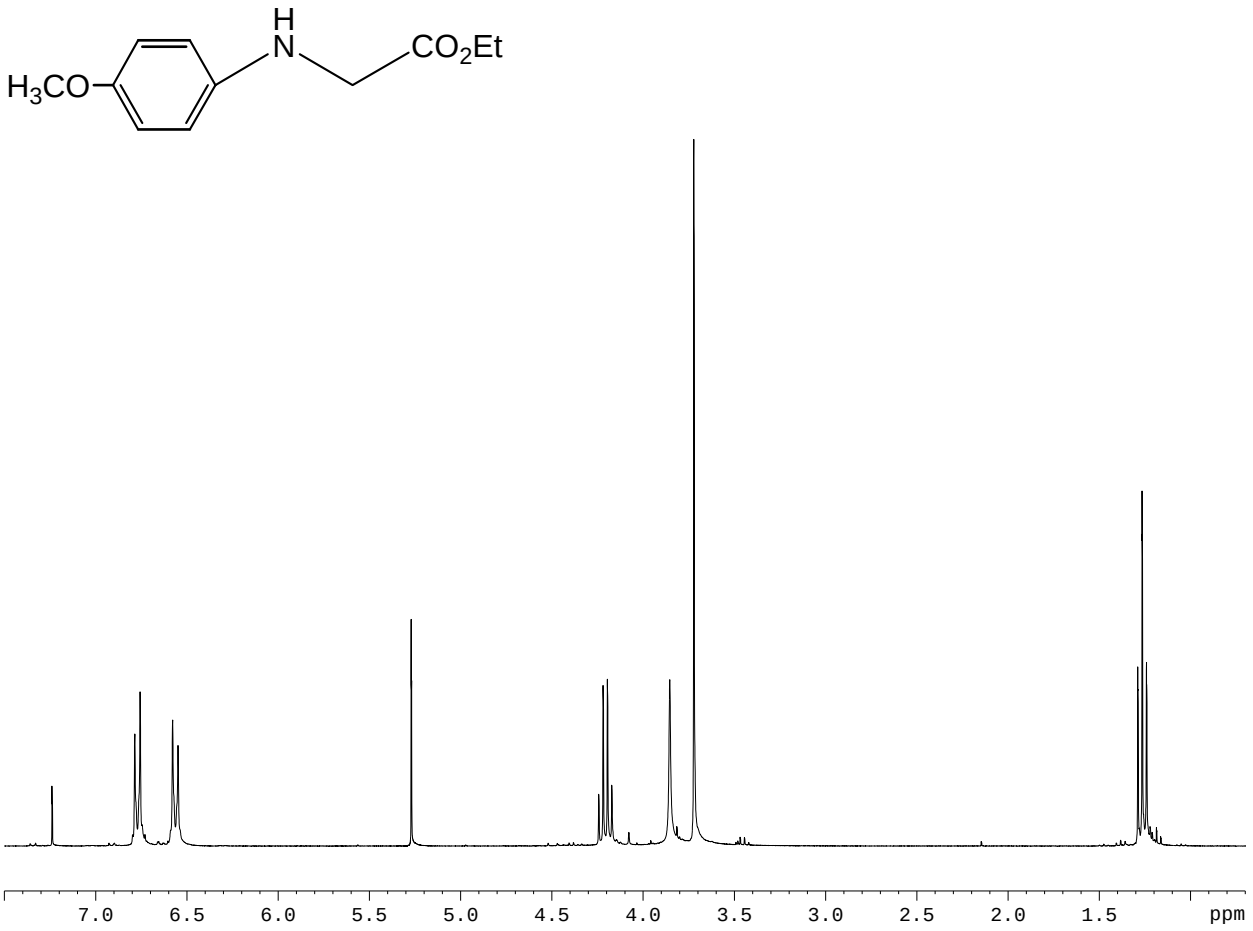
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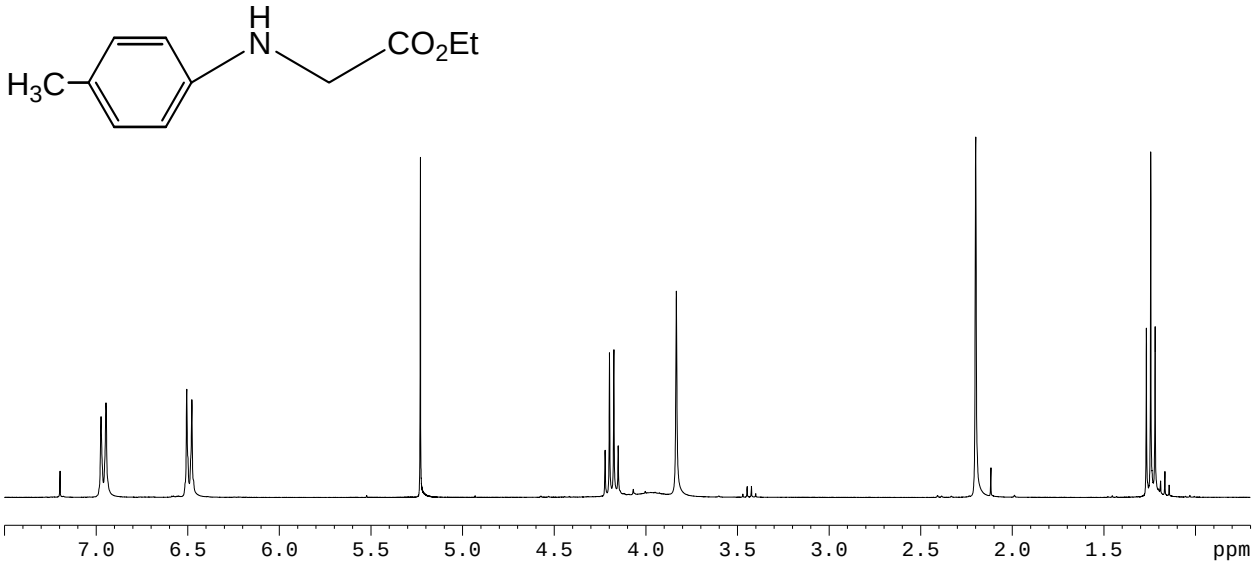
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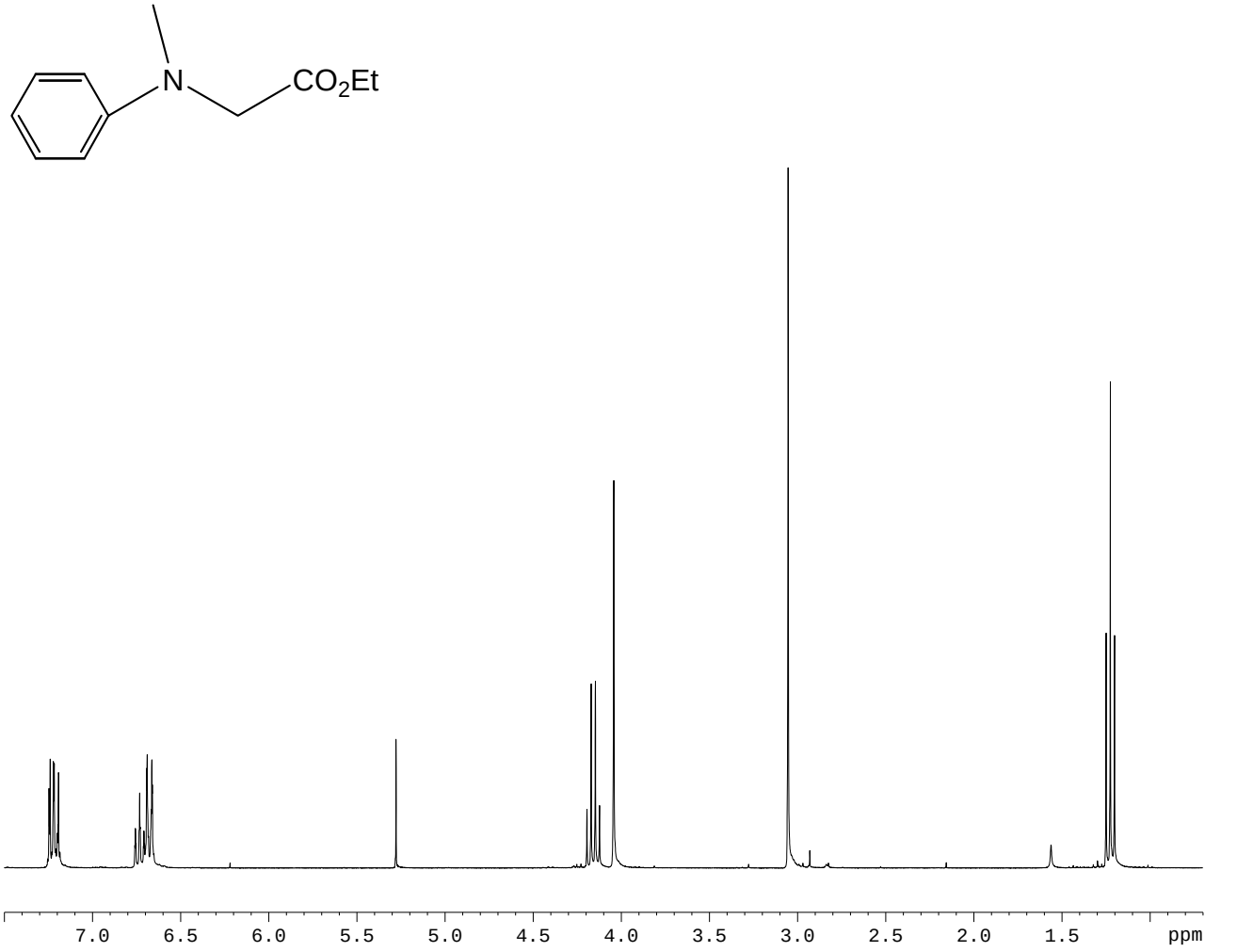
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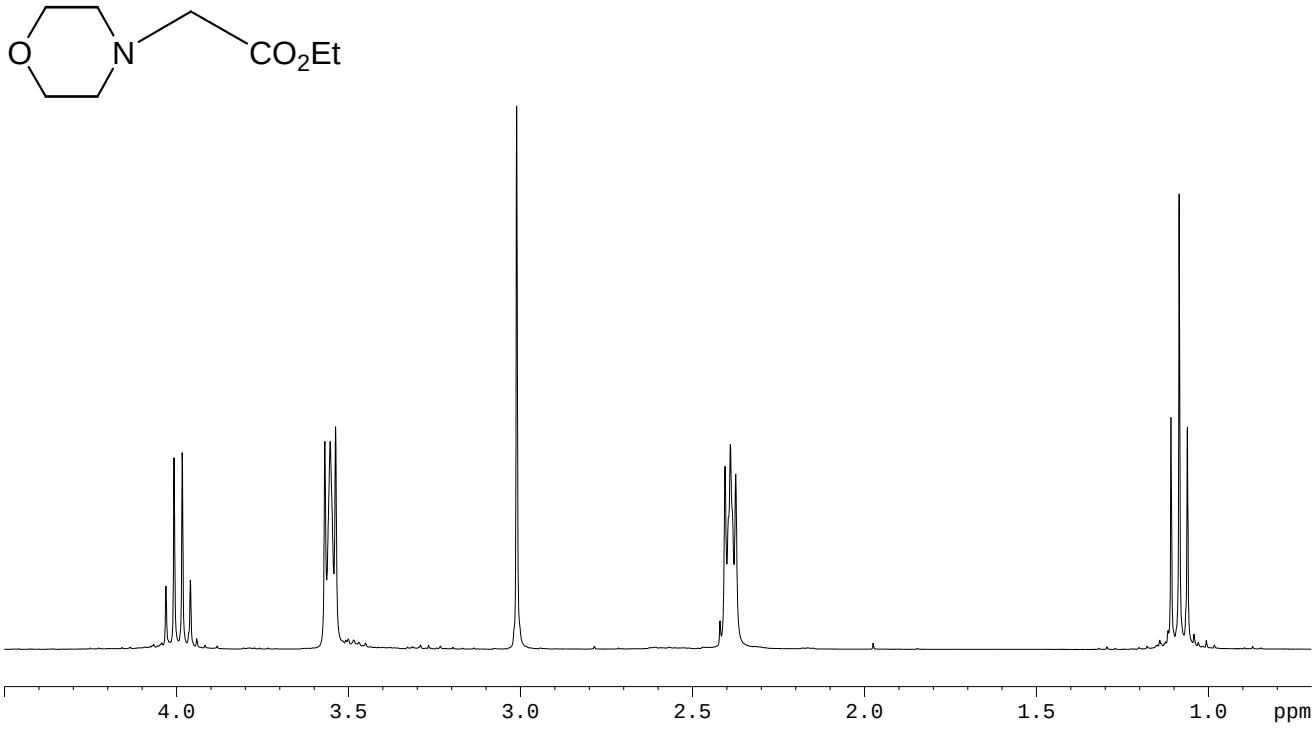
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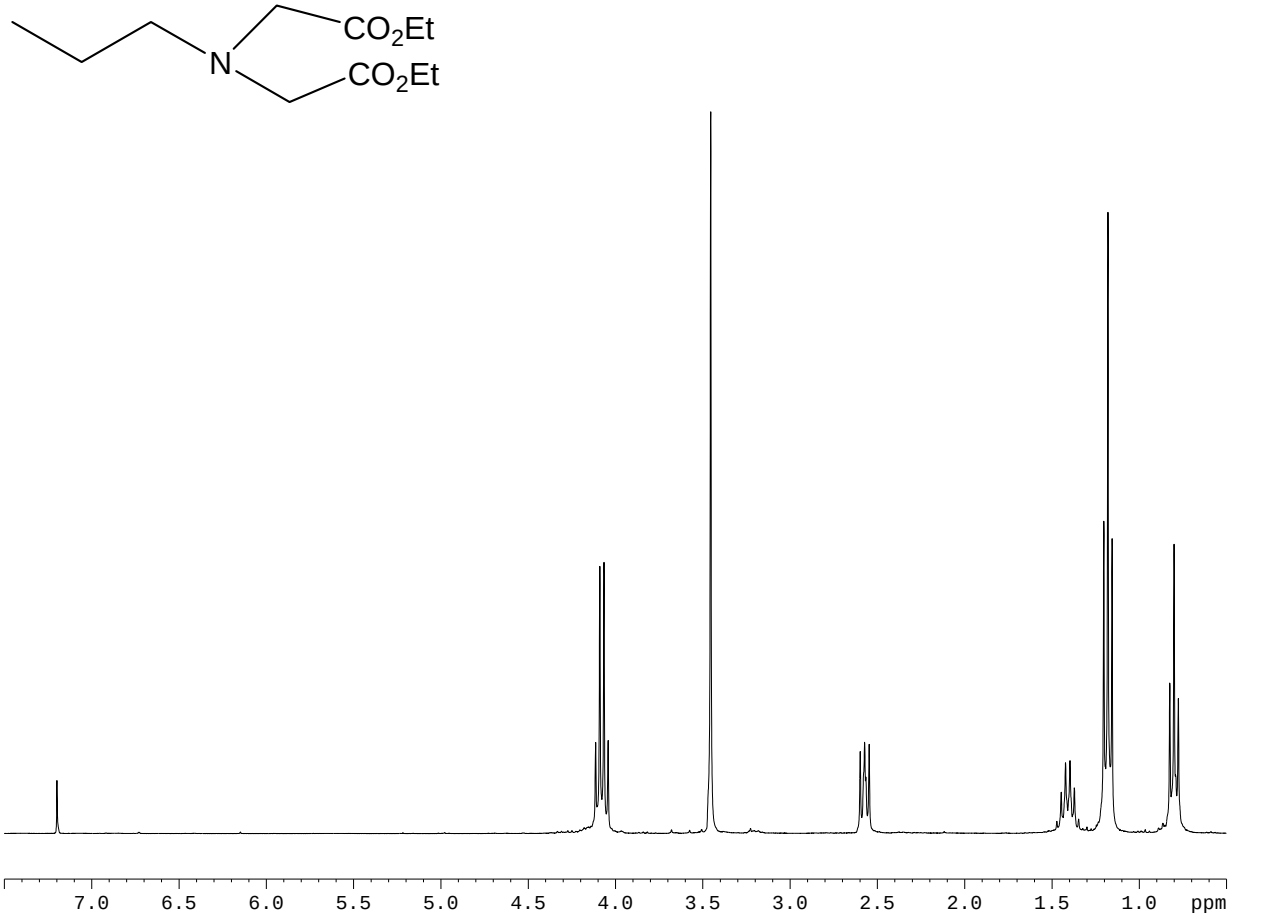
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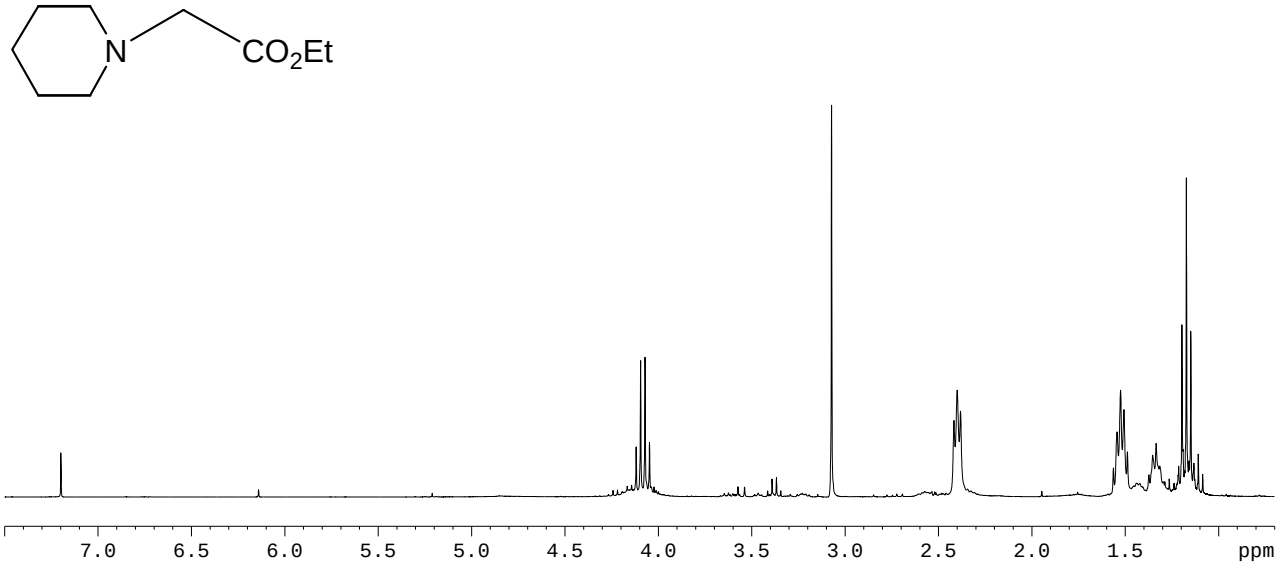
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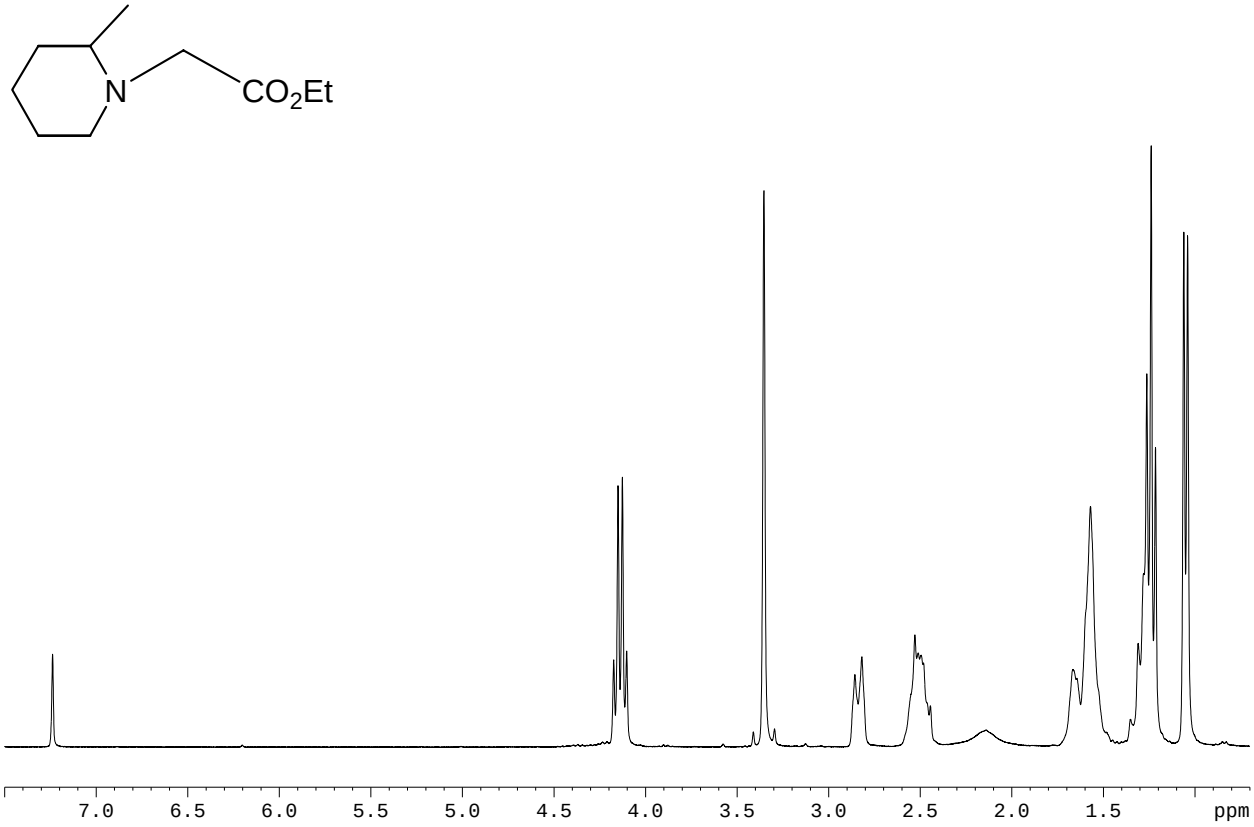
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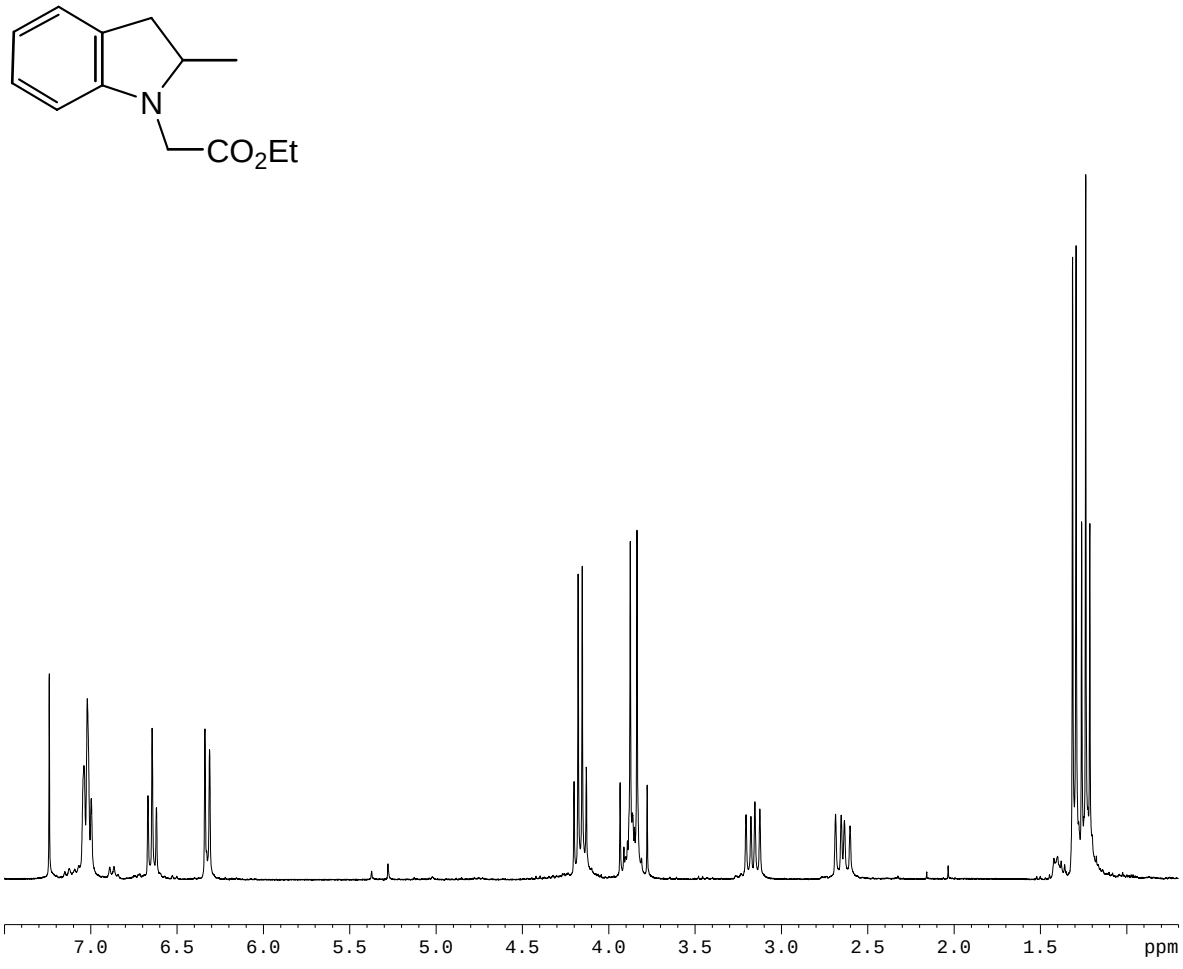
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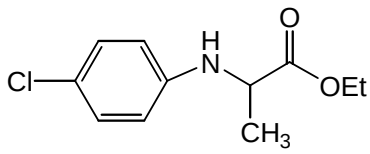
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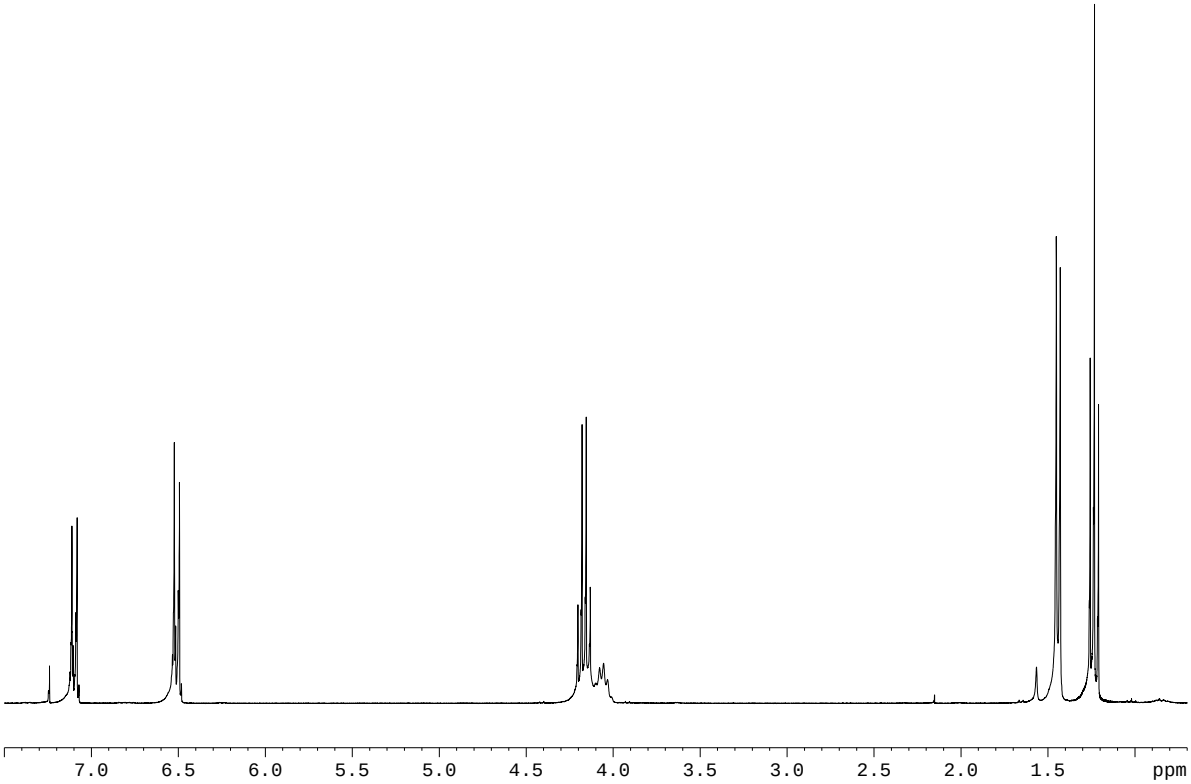
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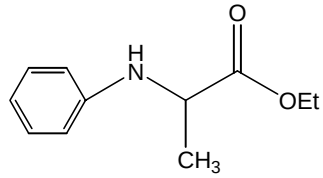
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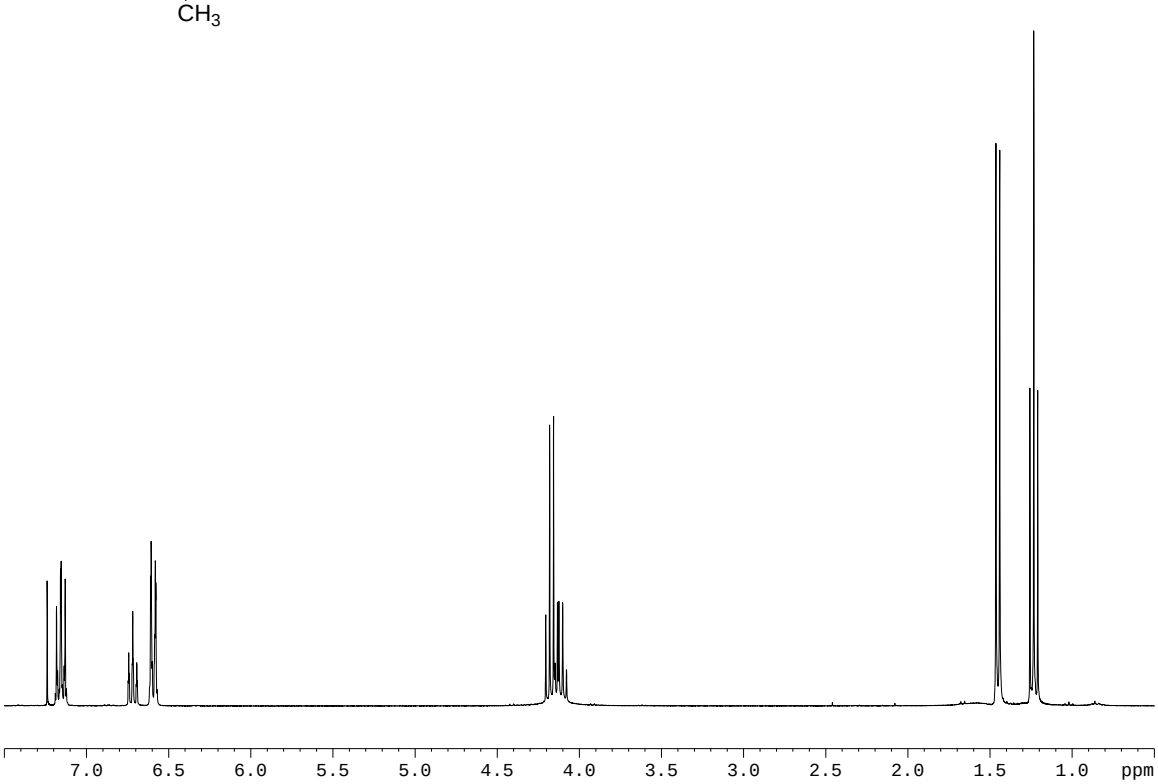
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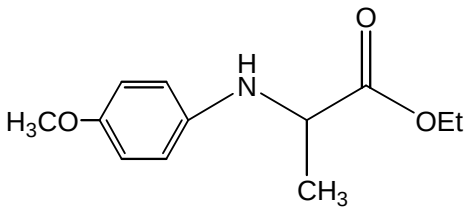
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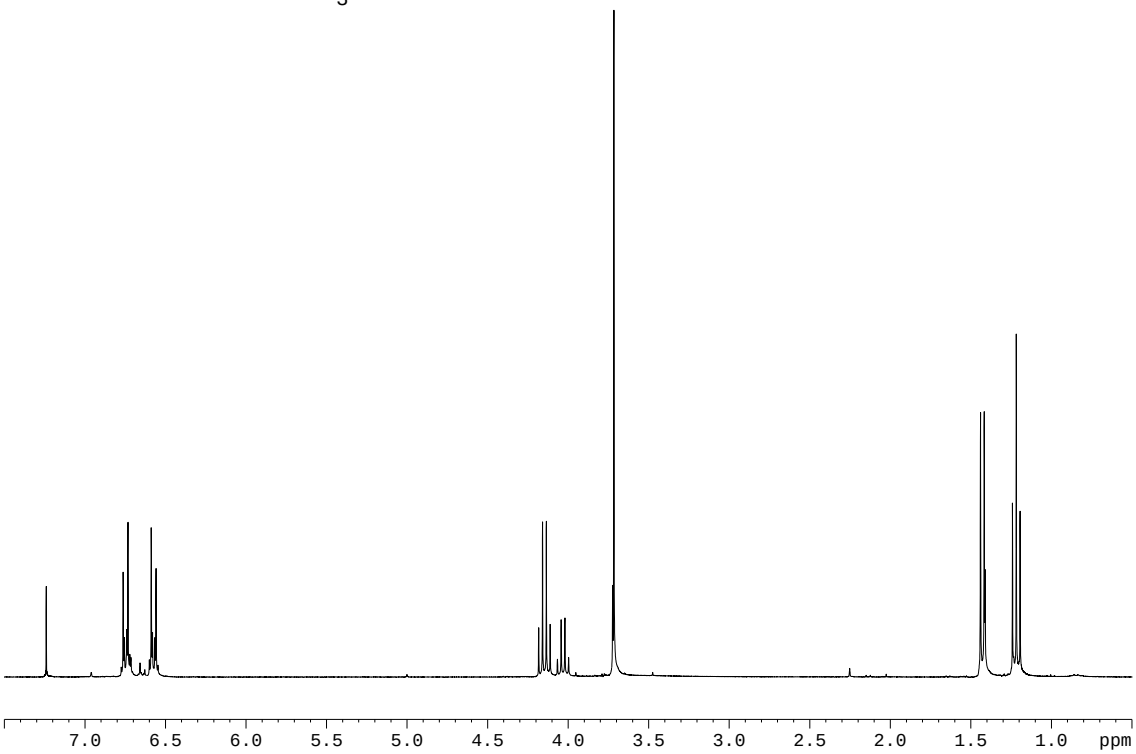
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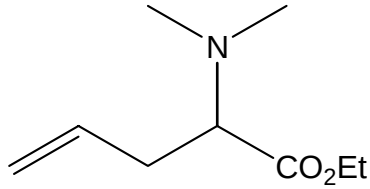
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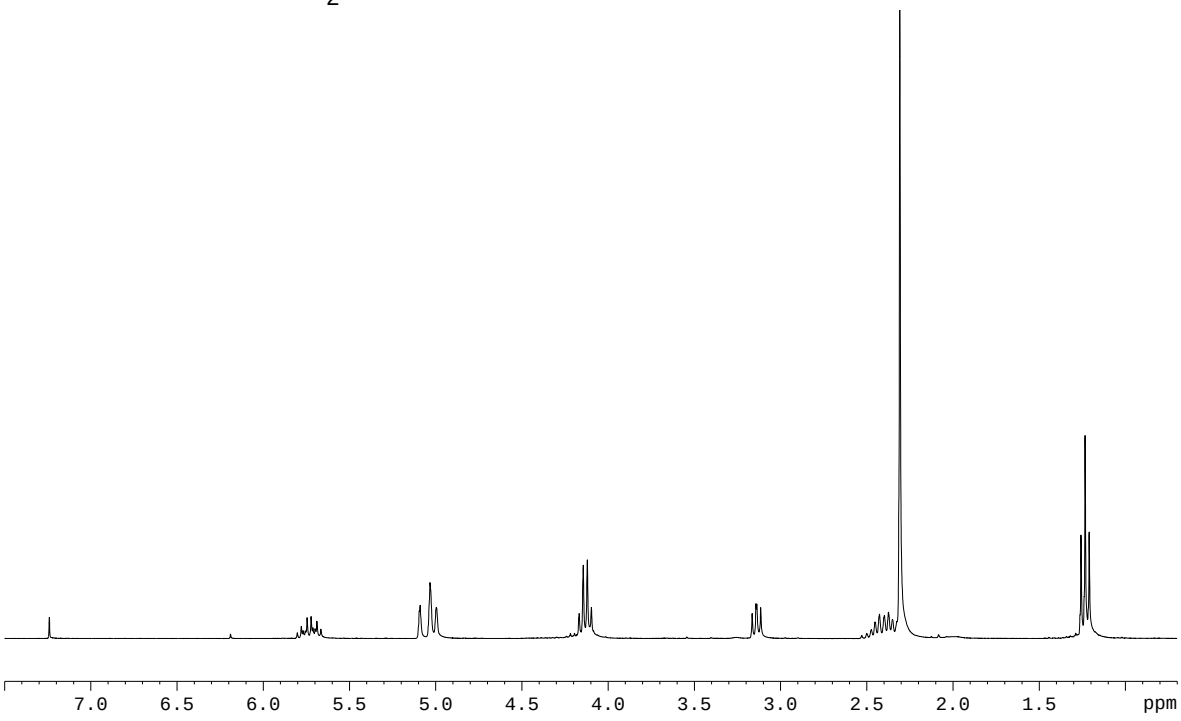
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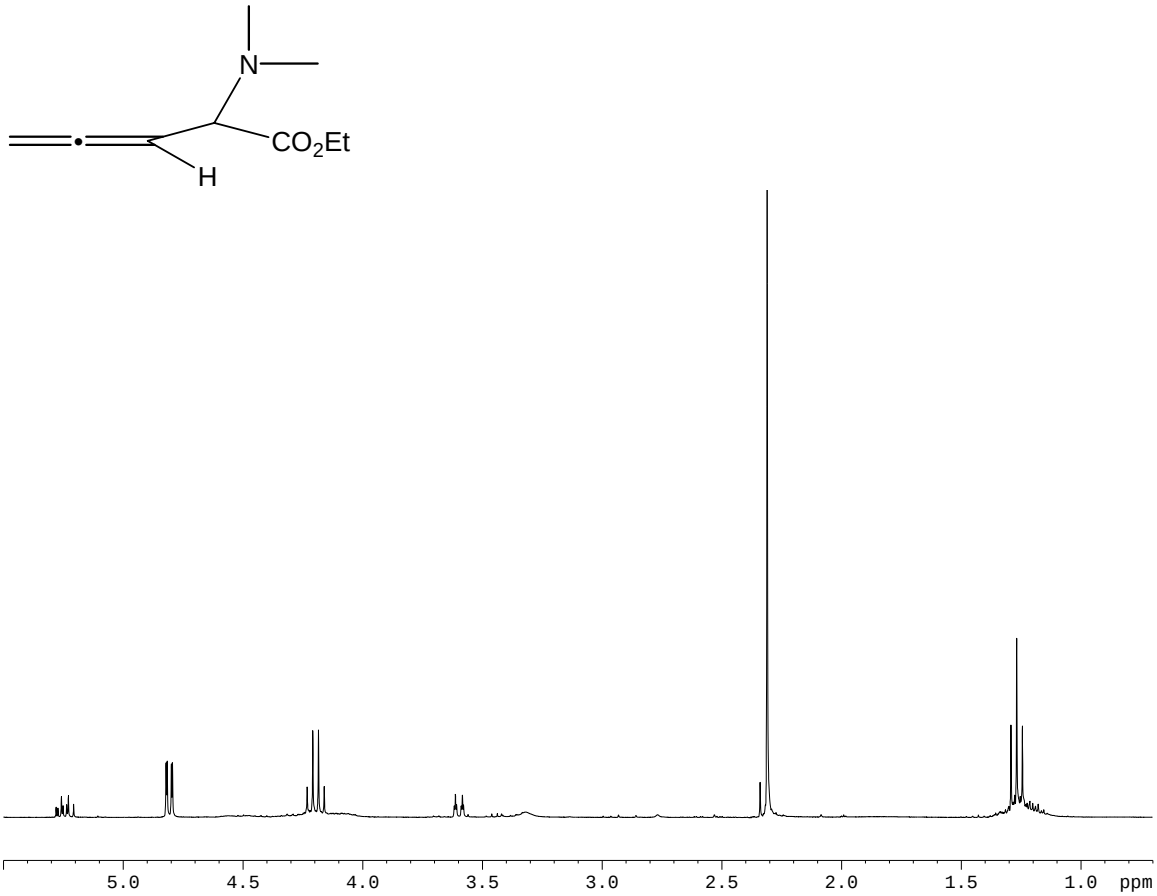
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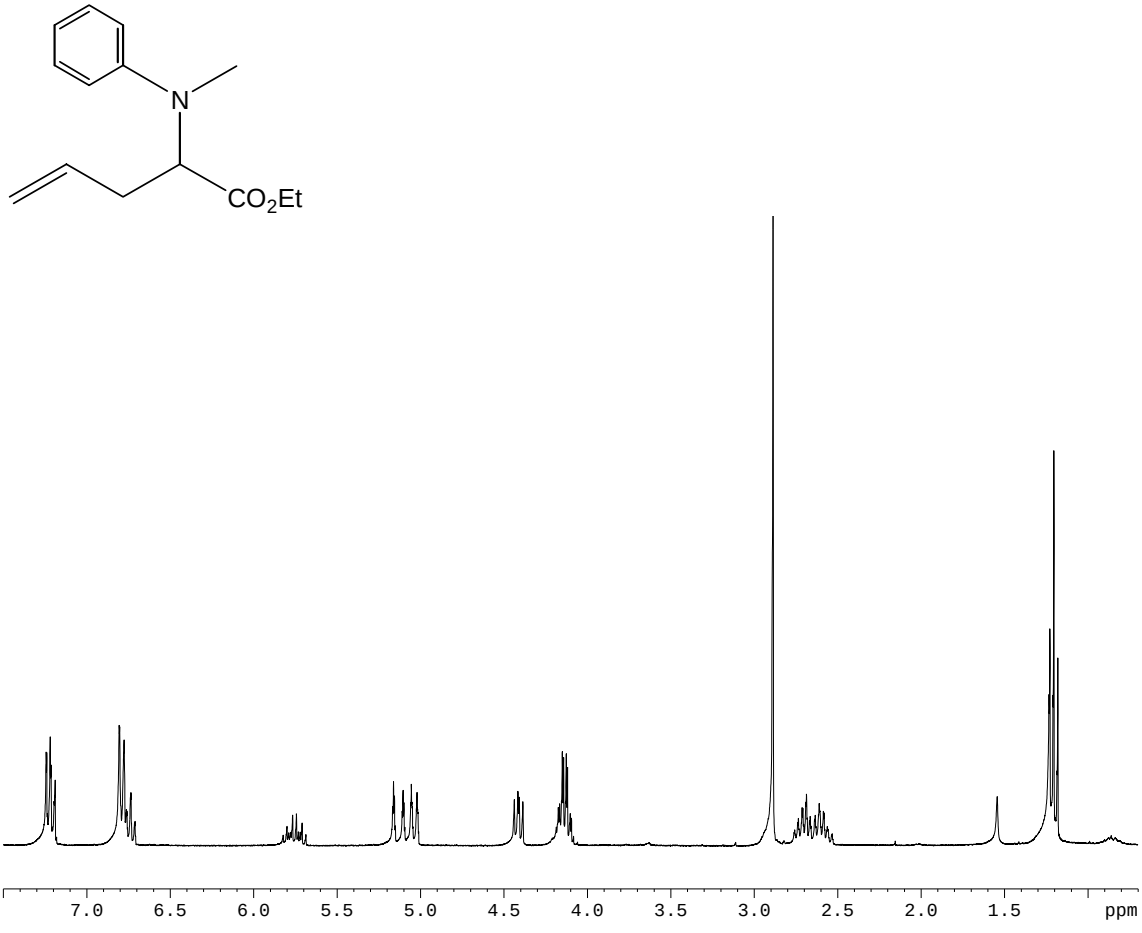
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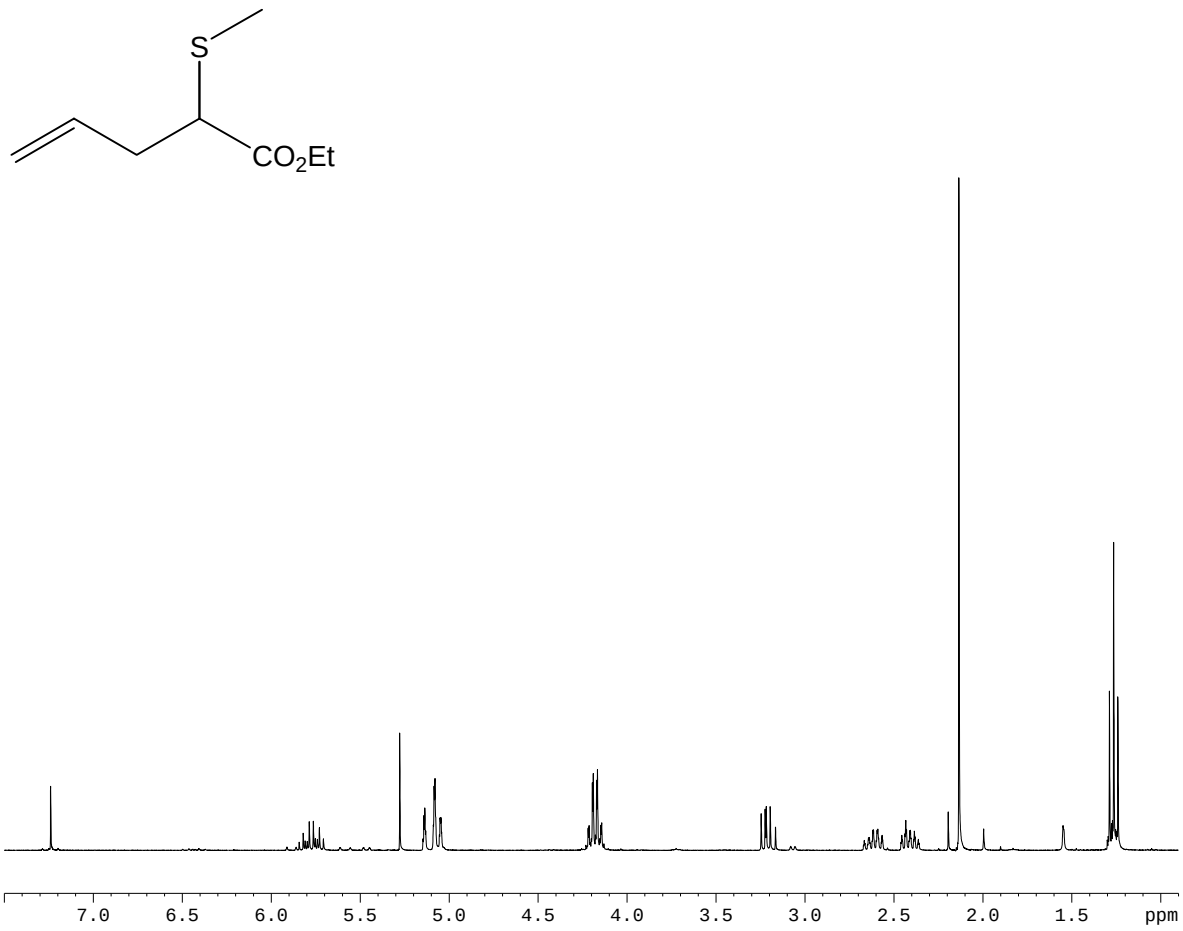
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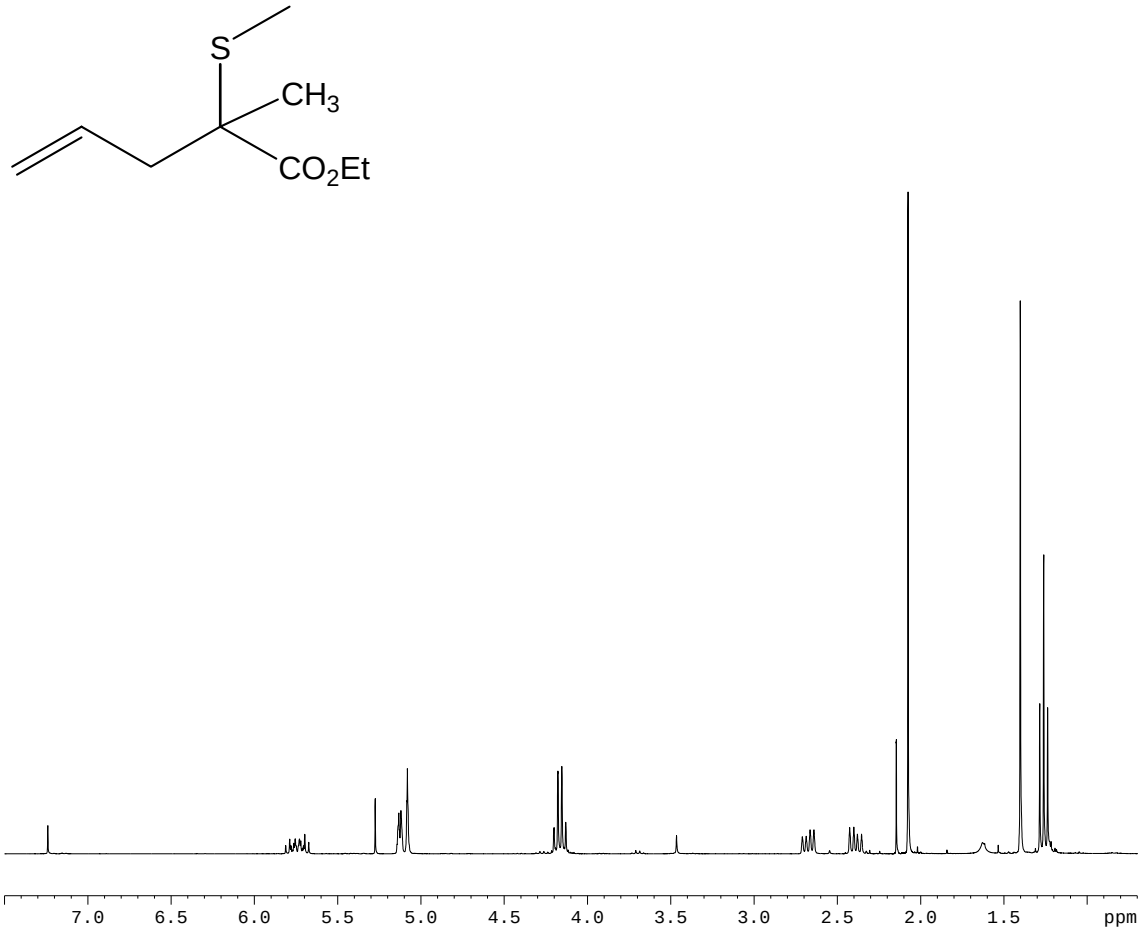
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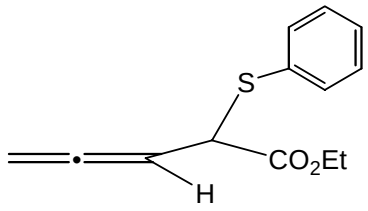
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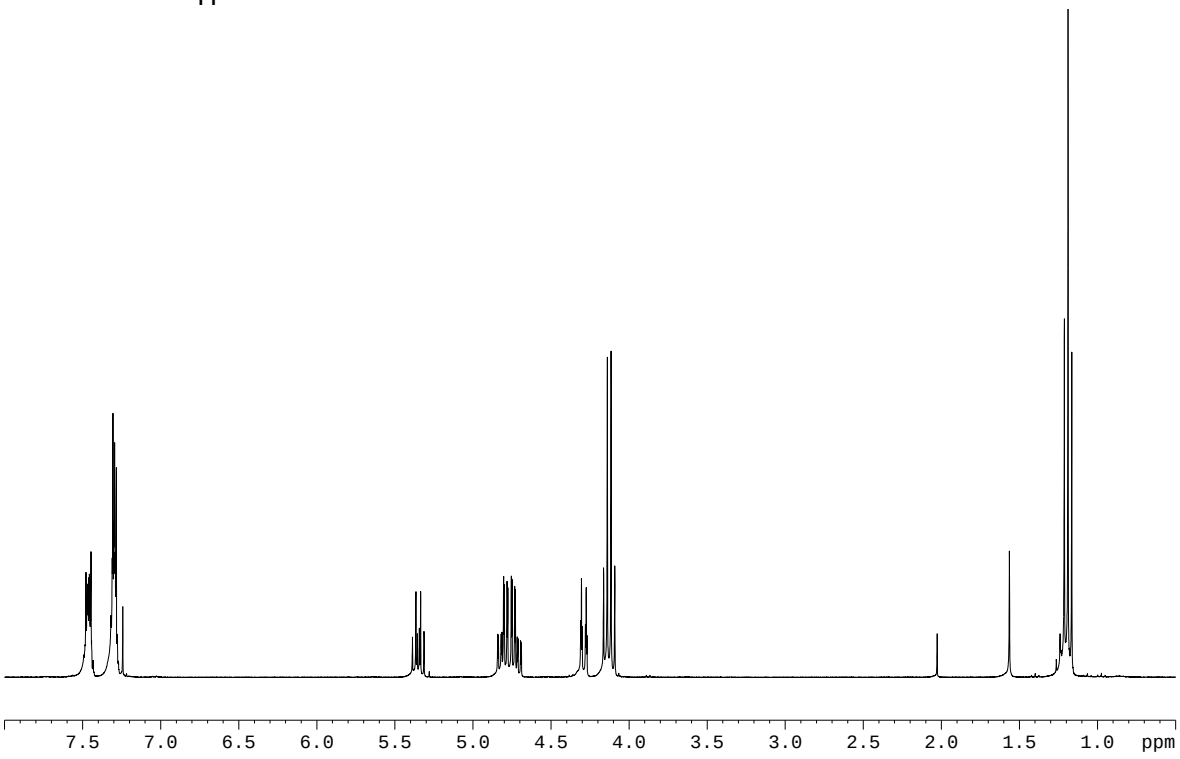
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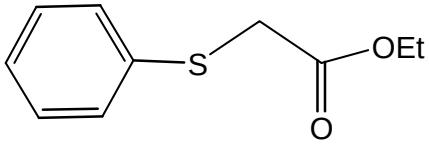
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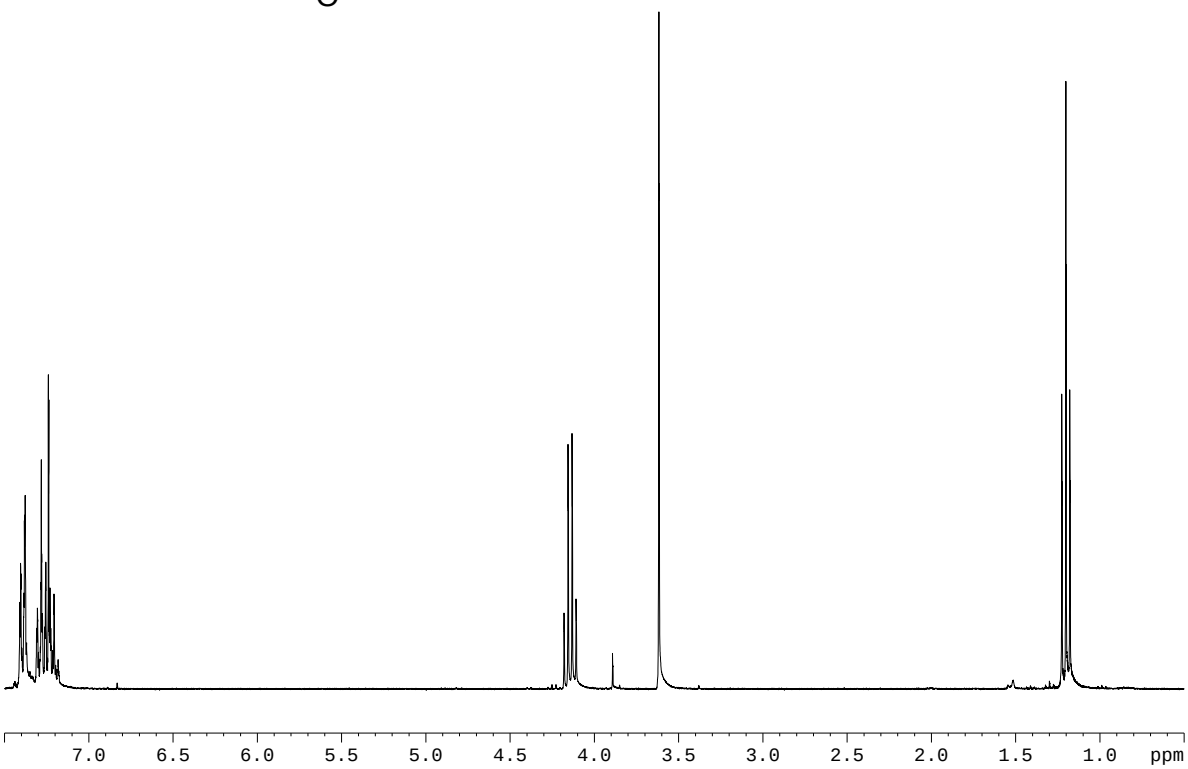
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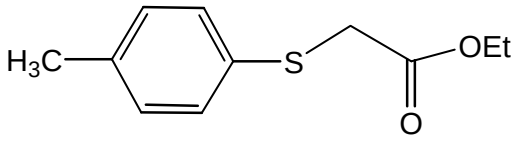
H3C
S
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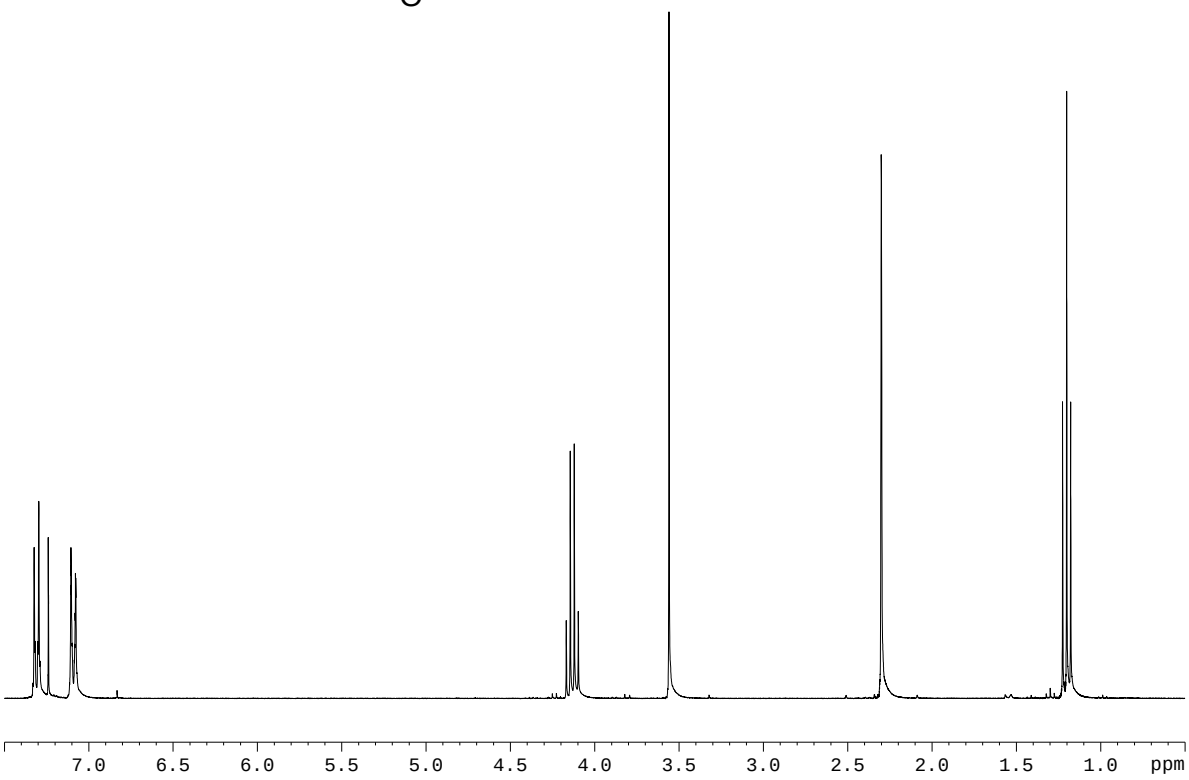
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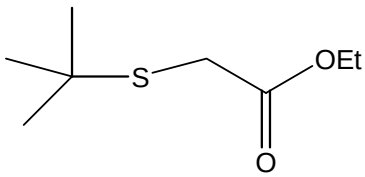
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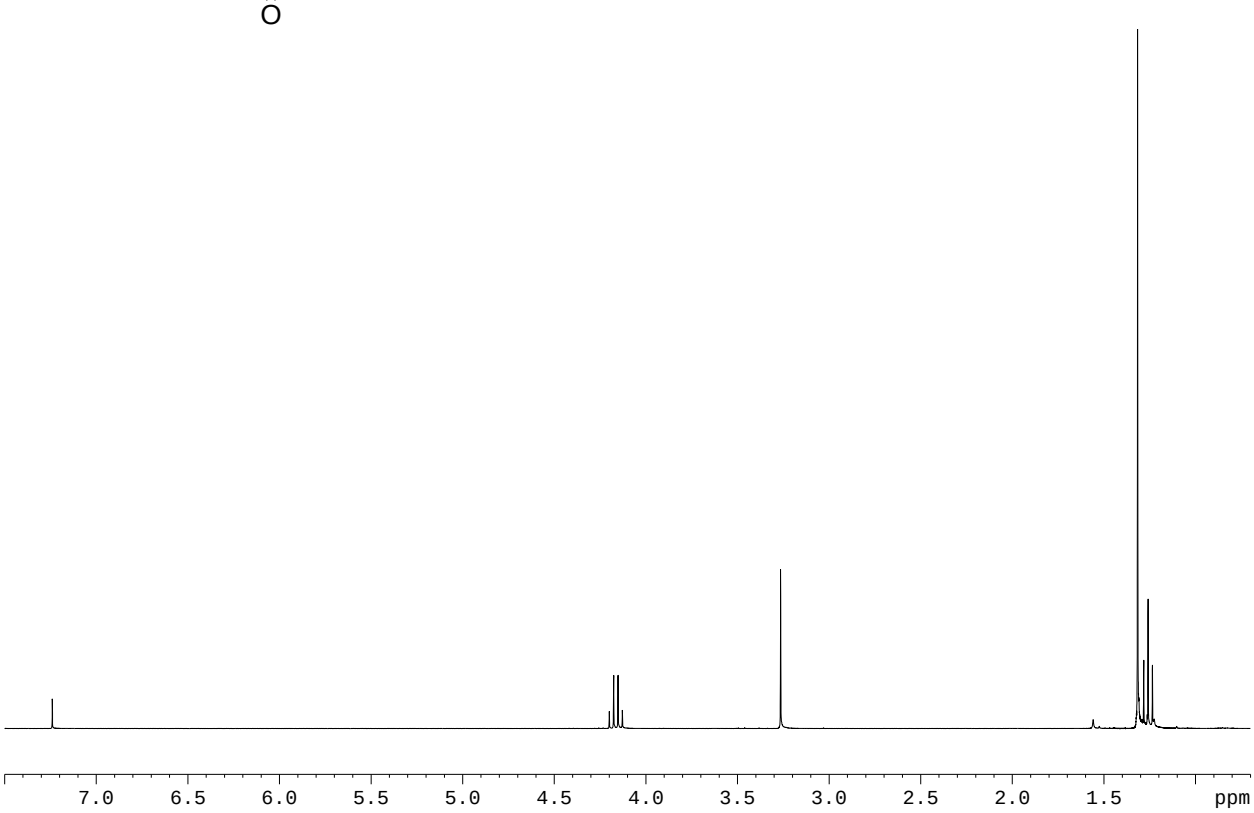
O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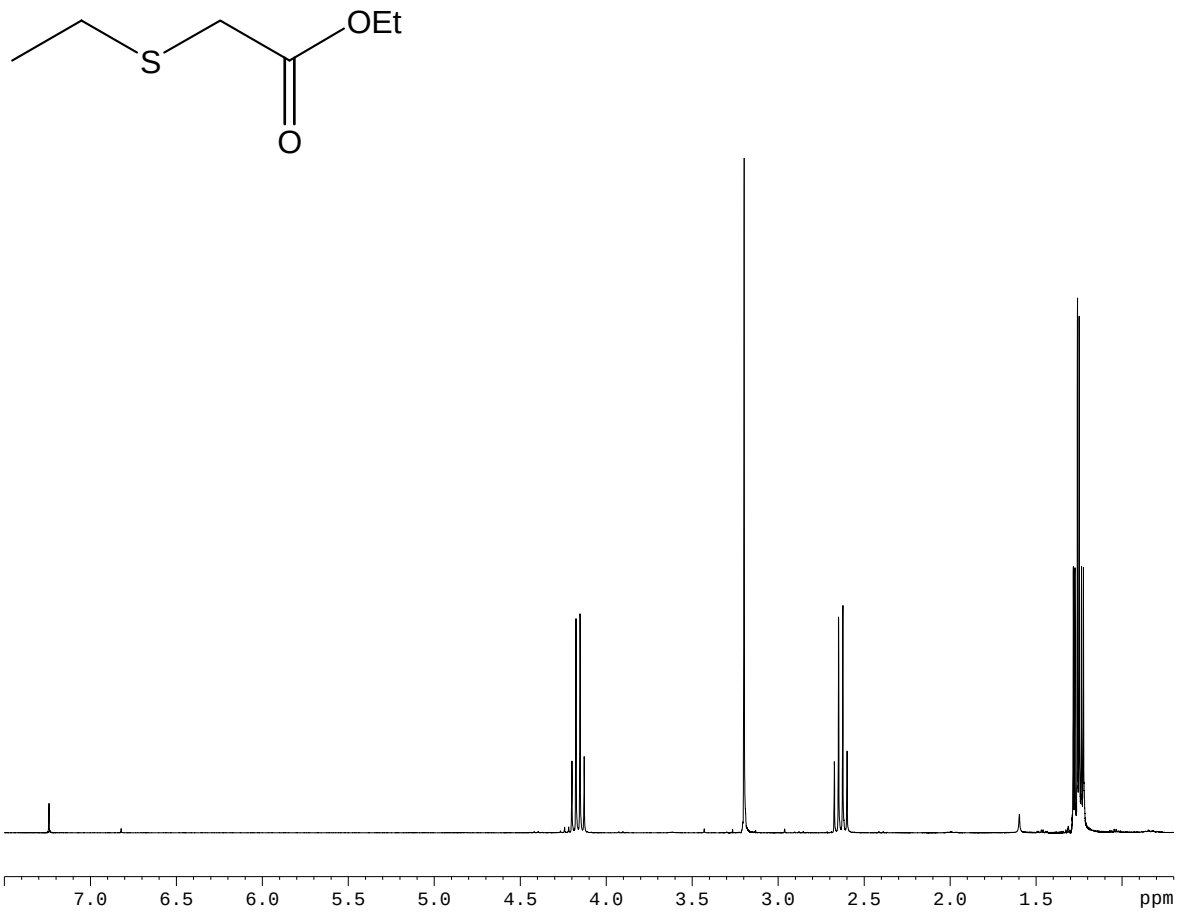
ppm


OEt
S
O
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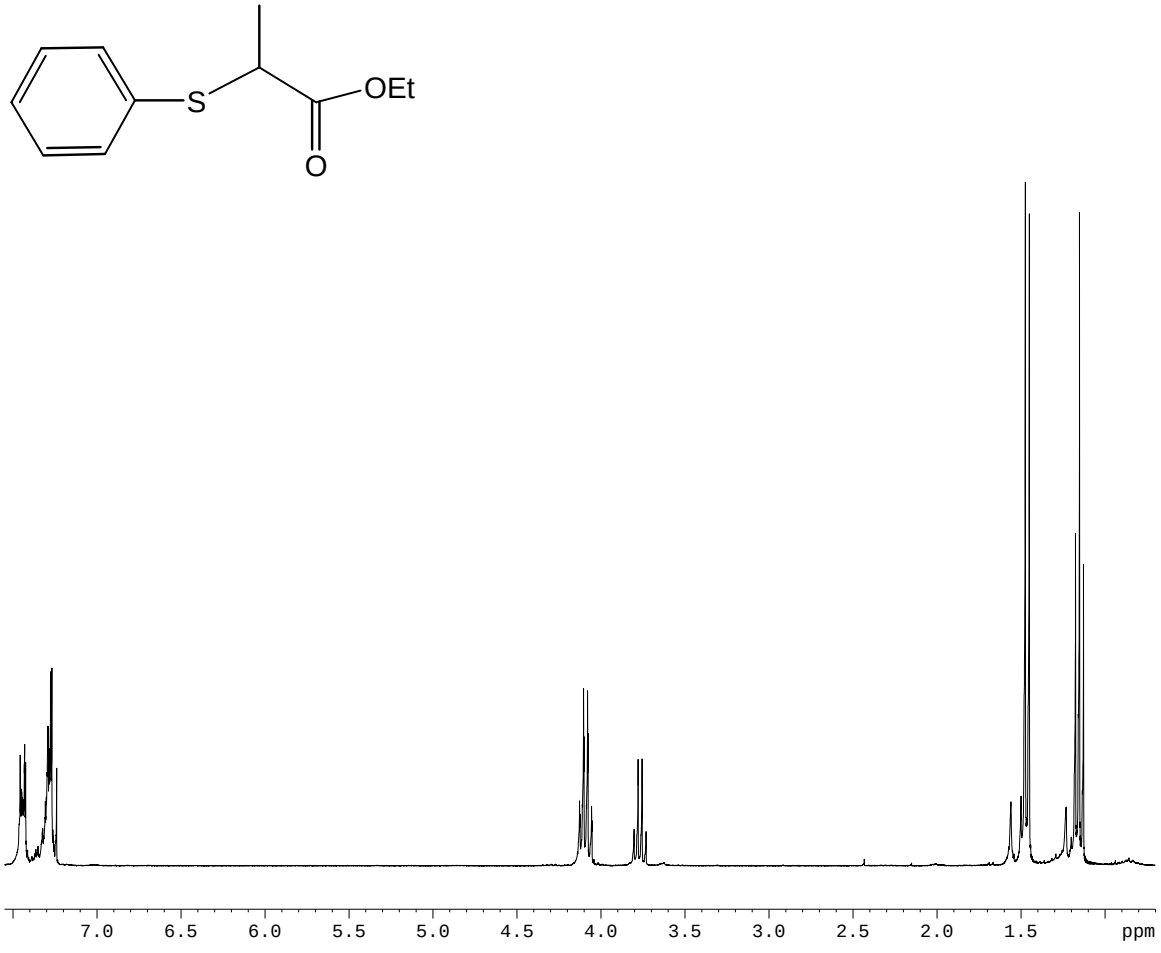
S
OEt
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2.0
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ppm