ELECTRONIC SUPPLEMENTARY INFORMATION

Umpolung reactions in ionic liquid catalyzed by electrogenerated N-heterocyclic carbenes. Synthesis of saturated esters from activated α,β-unsaturated aldehydes.

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Experimental procedure.

Electrolyses under galvanostatic control were carried out with an Amel 552 potentiostat equipped with an Amel 721 integrator. ^{1}H and ^{13}C-NMR spectra were recorded using a Bruker AC 200 spectrometer using $CDCl_3$ as internal standard. All ionic liquids were purchased from IOLITEC and used as received. All other reagents were purchased from Aldrich and used as received.

Constant current electrolyses were carried out using a glass two-compartment home-made cell. Anolyte (ca. 0.5 ml) and catholyte (ca. 1.5 ml) were separated through a glass disk (porosity 4). The electrode apparent surface areas were 1.0 cm^2 for the cathodic Pt spiral (99.9%) and 0.8 cm^2 for the anodic Pt spiral (99.9%). The current density was 20 mA/cm^2. Electrolyses were carried out at 60°C, under nitrogen atmosphere, using BMIM-BF_4 as anolyte and catholyte. After the consumption of 0.7 Faradays per mol of aldehyde (or a different amount, as reported in Table 1), the current was switched off and aldehyde (1 mmol) was added to the catholyte under stirring; when the dissolution was complete, alcohol (3 mmol, or the amount reported in Table 1) was added. The mixture was kept at 60°C for 1 h (or a different time, till disappearance of aldehyde on TLC, up to 4 h). The catholyte was extracted with diethyl ether, the solvent was removed under vacuum and the residue was analyzed by ^{1}H-NMR and purified by flash-chromatography (using *n*-hexane/ethyl acetate 9/1 as eluent), affording the corresponding pure ester. All esters are known compounds and gave spectral data in accordance with the ones reported in the literature.

Recycle of catholyte. After ethereal extraction of the cathodic Bmim-BF_4 and isolation of ester **3aa** (Table 1, entry 8), the catholyte was kept under vacuum under stirring at 60°C for 1h, then the catholyte was used in a new electrolysis for the synthesis of **3aa**. The same ionic liquid was used five times, obtaining (after 1 F/mol of **1a** each time) **3aa** in 85, 76, 70, 72, 73% yields, respectively.

Reaction with trans 2-hexenal. The electrolysis was carried out following the general procedure, but modified in two different ways:

a) 1 mmol of 1,3-dimesitylimidazolium chloride (IMes-Cl) or 1,3-dimethylbenzimidazolium iodide (BI-I) was added to the catholyte before the electrolysis;

b) at the end of the electrolysis 1 mmol of 1,3-dimesitylimidazolium chloride (IMes-Cl) or 1,3-dimethylbenzimidazolium iodide (BI-I) was added to the catholyte 10 minutes before the addition of the aldehyde and alcohol.

The yields of benzyl hexanoate **3da** were the following:

a) 7 % with IMes-Cl and 10 % with BI-I; b) 28 % with IMes-Cl and 13 % with BI-I.

Benzyl 3-phenylpropanoate 3aa.[1] R_f (10% ethyl acetate in *n*-hexane) 0.63; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.70 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 5.13 (s, 2H), 7.19-7.39 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.0, 35.9, 66.3, 126.3, 128.2, 128.3, 128.5, 128.6, 136.0, 140.4, 172.7.

4-Methylbenzyl 3-phenylpropanoate 3ab.[2] R_f (10% ethyl acetate in *n*-hexane) 0.66; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H), 5.01 (s, 2H), 7.16-7.34 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.2, 31.0, 36.0, 66.3, 126.3, 128.2, 128.3, 128.4, 128.5, 129.2, 132.9, 138.1, 140.5, 172.8.

4-Methoxybenzyl 3-phenylpropanoate 3ac.[3] R_f (10% ethyl acetate in *n*-hexane) 0.56; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.66 (t, *J* = 7.5 Hz, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 3.82 (s, 3H), 5.01 (s, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 7.18-7.31 (m, 7H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 31.0, 36.0, 55.3, 66.2, 114.0, 126.3, 128.1, 128.4, 128.5, 130.2, 140.5, 159.7, 172.8.

4-Chlorobenzyl 3-phenylpropanoate 3ad.[2] R_f (10% ethyl acetate in *n*-hexane) 0.49; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.68 (t, *J* = 7.5 Hz, 2H), 2.97 (t, *J* = 7.5 Hz, 2H), 5.06 (s, 2H), 7.17-7.33 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.9, 35.8, 65.4, 126.3, 128.3, 128.5, 128.7, 129.6, 134.1, 134.4, 140.3, 172.6.

4-Nitrobenzyl 3-phenylpropanoate 3ae.[3] R_f (10% ethyl acetate in *n*-hexane) 0.22; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.74 (t, *J* = 7.5 Hz, 2H), 2.99 (t, *J* = 7.5 Hz, 2H), 5.18 (s, 2H), 7.18-7.40 (m, 7H), 8.18 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.9, 35.7, 64.7, 123.8, 126.4, 128.3, 128.3, 128.6, 140.1, 143.2, 147.6, 172.4.

Ethyl 3-phenylpropanoate 3af.[4] R_f (10% ethyl acetate in *n*-hexane) 0.62; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H), 2.62 (t, J = 7.4 Hz, 2H), 2.95 (t, J = 7.4 Hz, 2H), 4.12 (t, J = 7.2 Hz, 2H), 7.19-7.31 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.3, 31.0, 36.0, 60.5, 126.3, 128.4, 140.7, 173.0.

Octyl 3-phenylpropanoate 3ag.[2] R_f (10% ethyl acetate in *n*-hexane) 0.69; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86-0.93 (m, 3H), 1.28 (m, 10H), 1.58-1.63 (m, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 7.20-7.34 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.1, 22.7, 25.9, 28.6, 28.2, 29.2, 31.0, 31.8, 35.9, 64.7, 126.2, 128.3, 128.5, 140.6, 173.0.

Cyclohexyl 3-phenylpropanoate 3ah.[5] R_f (10% ethyl acetate in *n*-hexane) 0.60; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25-1.55 (m, 6H), 1.63-1.82 (m, 4H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 4.71-4.78 (m, 1H), 7.17-7.31 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.8, 25.4, 31.1, 31.6, 36.3, 72.7, 126.2, 128.3, 128.3, 140.6, 172.4.

Benzyl 3-(4-methoxyphenyl)propanoate 3ba.[6] R_f (10% ethyl acetate in *n*-hexane) 0.46; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.66 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 3.80 (s, 3H), 5.12 (s, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.28-7.39 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.1, 36.2, 55.2, 66.2, 113.9, 128.2, 128.5, 129.3, 132.5, 135.9, 158.1, 172.8.

Benzyl 3-(furan-2-yl)propanoate 3ca.[7] R_f (10% ethyl acetate in *n*-hexane) 0.57; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.73 (t, *J* = 7.4 Hz, 2H), 3.01 (t, *J* = 7.4 Hz, 2H), 5.15 (s, 2H), 6.01-6.03 (m, 1H), 6.27-6.30 (m, 1H), 7.27-7.41 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.5, 32.7, 66.4, 105.4, 110.2, 128.2, 128.3, 128.6, 135.9, 141.2, 154.0, 172.3.

Benzyl Hexanoate 3da.[8] R_f (10% ethyl acetate in *n*-hexane) 0.73; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.5 Hz, 3H), 1.28-1.35 (m, 4H), 1.61-1.70 (m, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 5.13 (s, 2H), 7.37 (m, 5H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.9, 22.3, 24.6, 31.3, 34.3, 66.1, 128.2, 128.2, 128.5, 136.1, 173.7.

References

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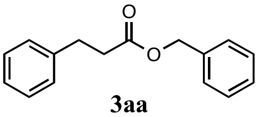
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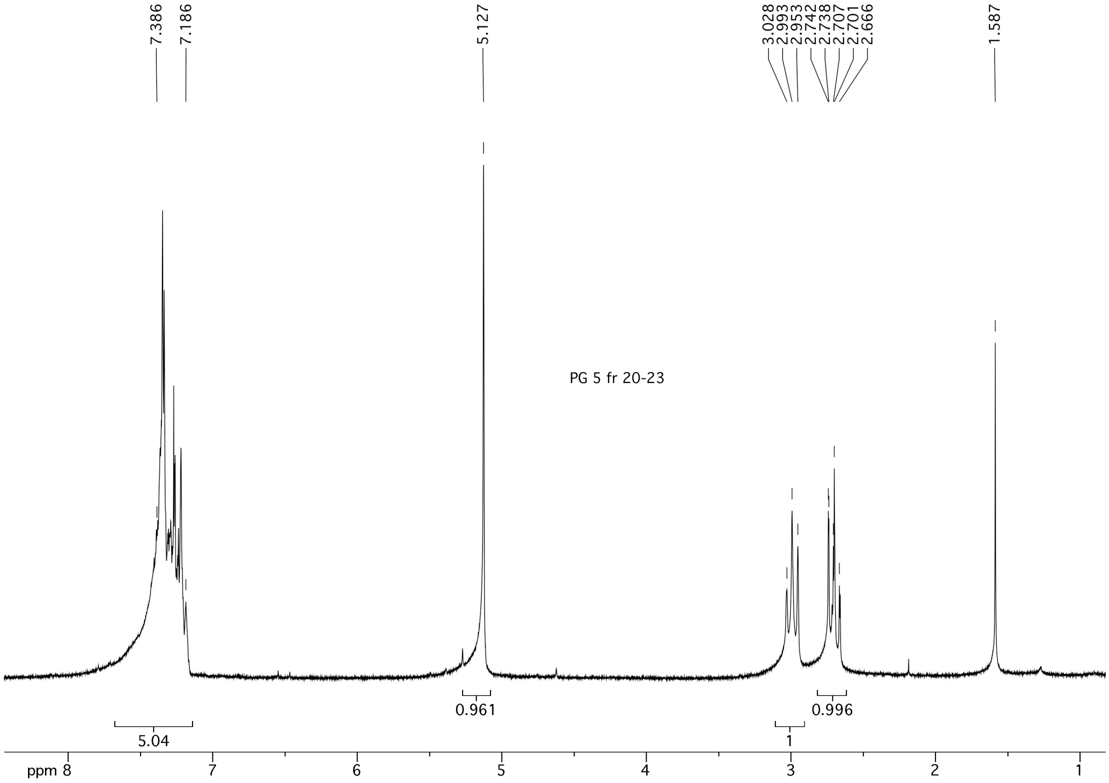
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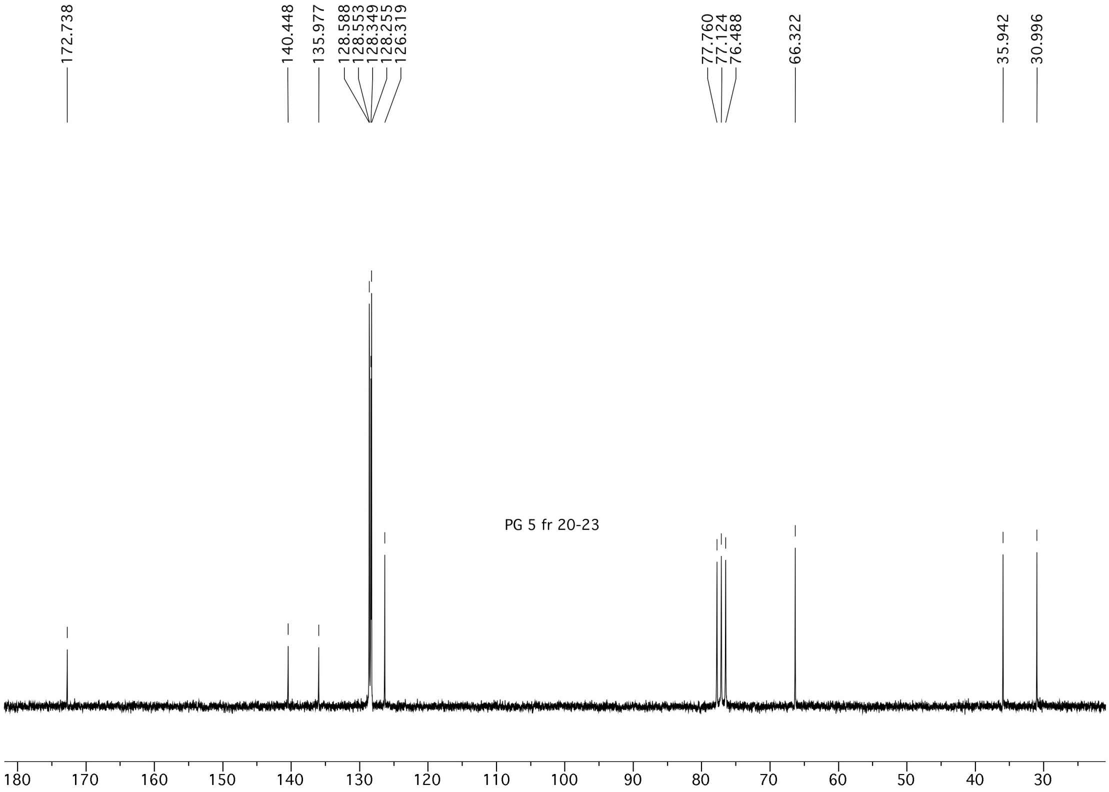
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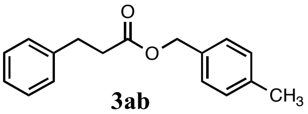
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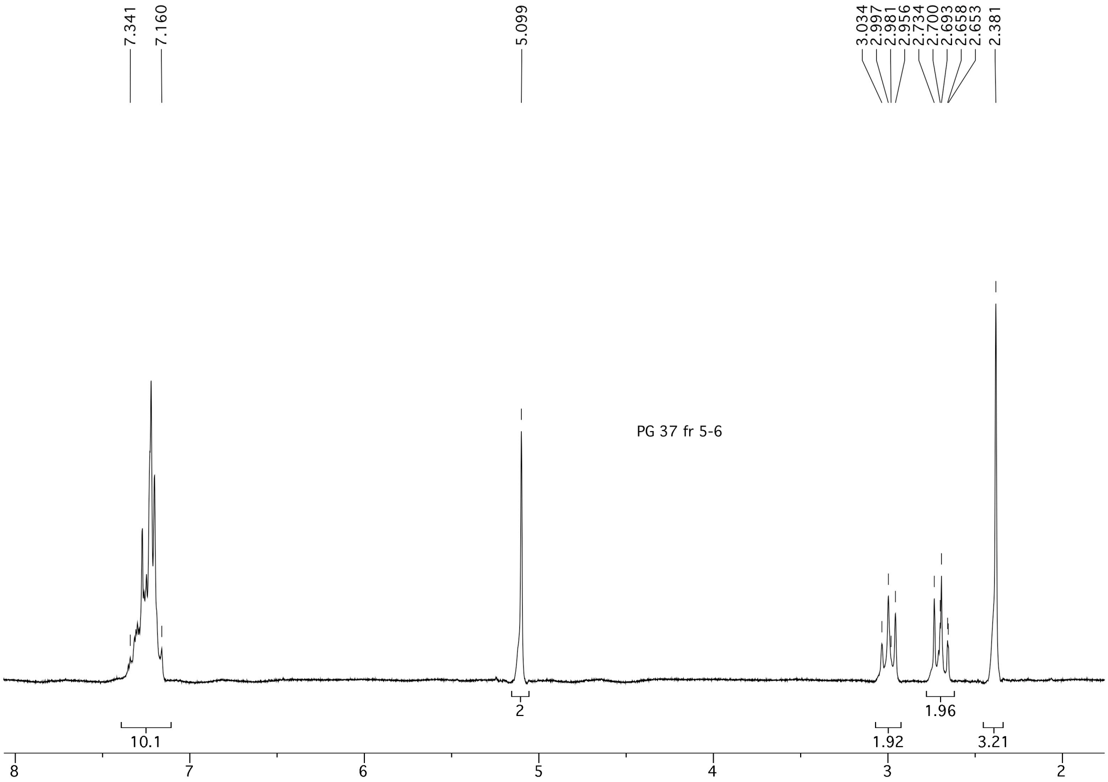
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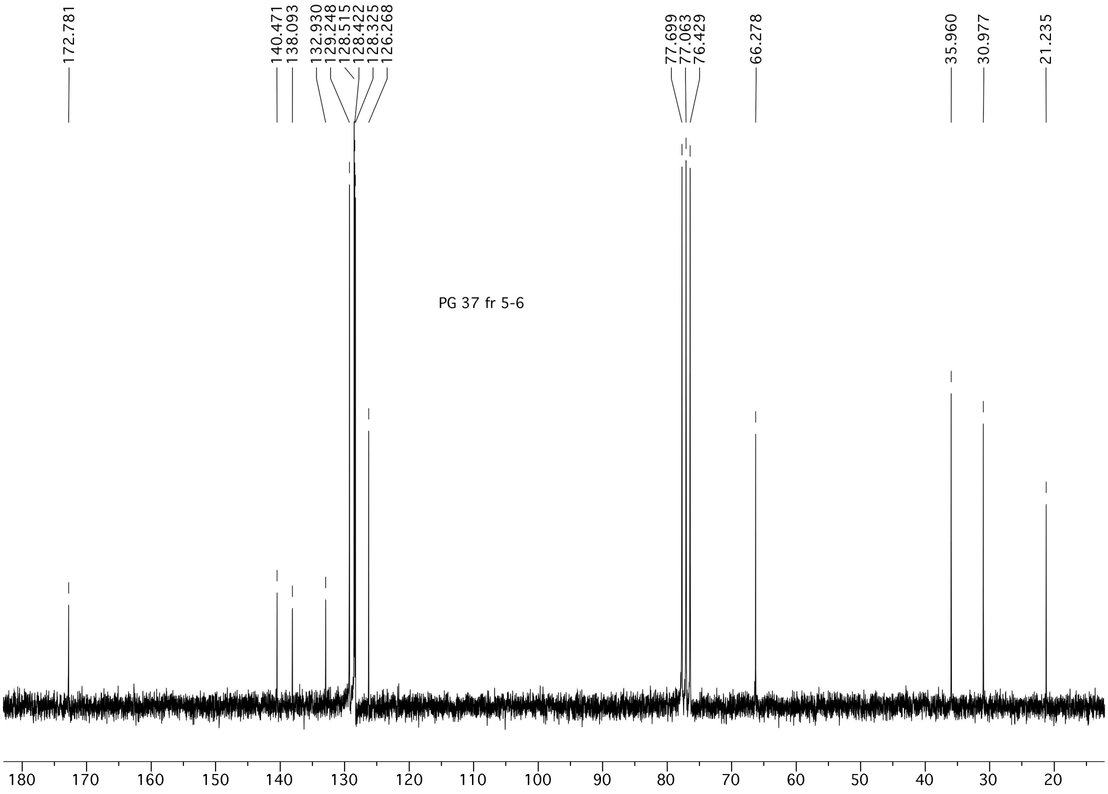
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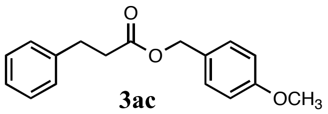
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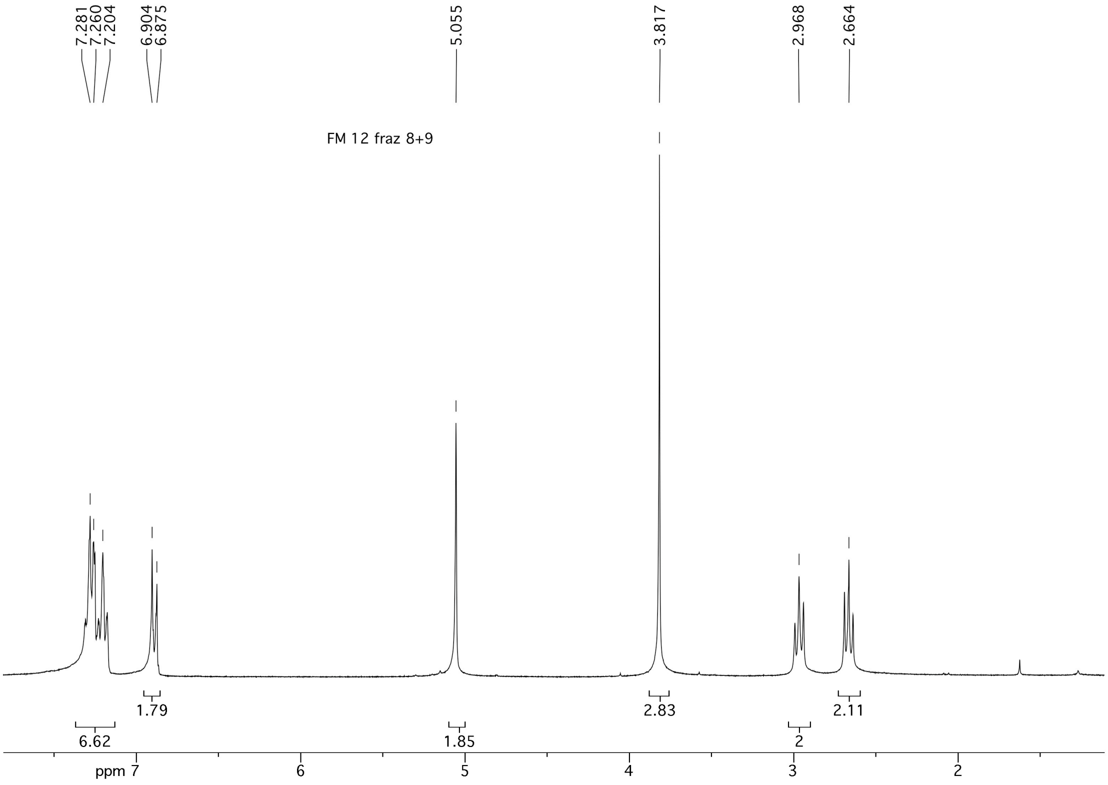
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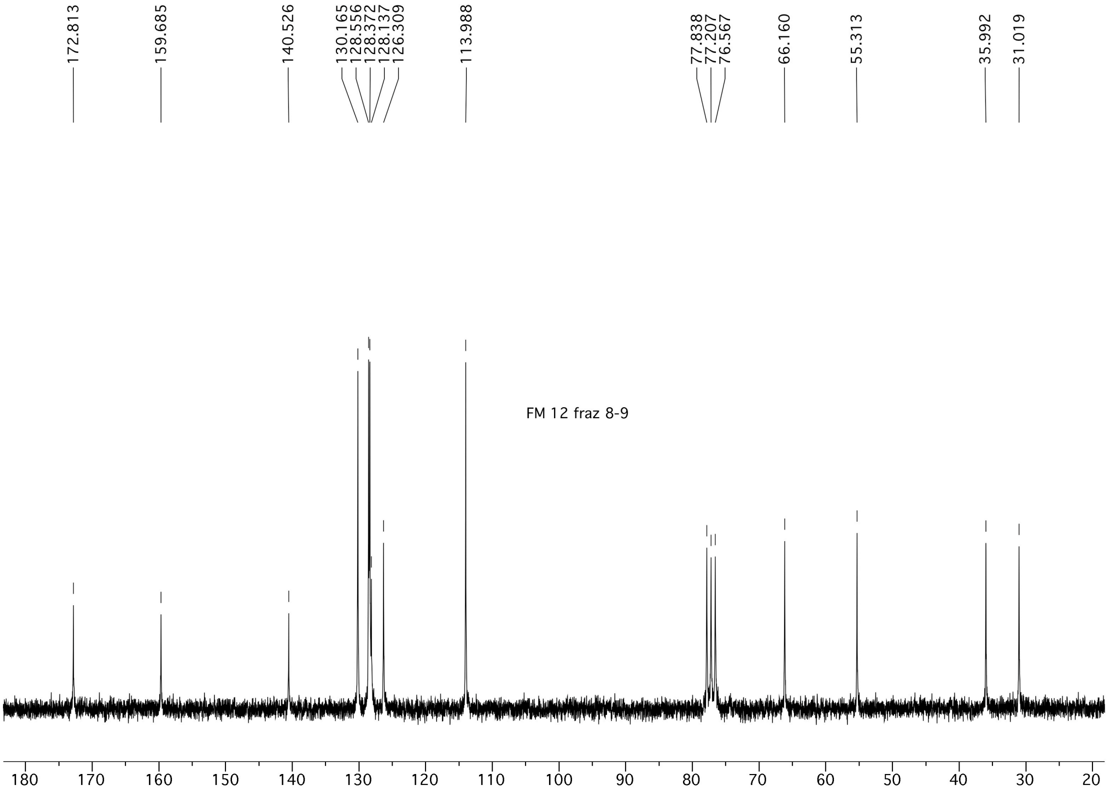
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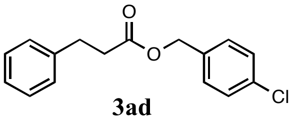
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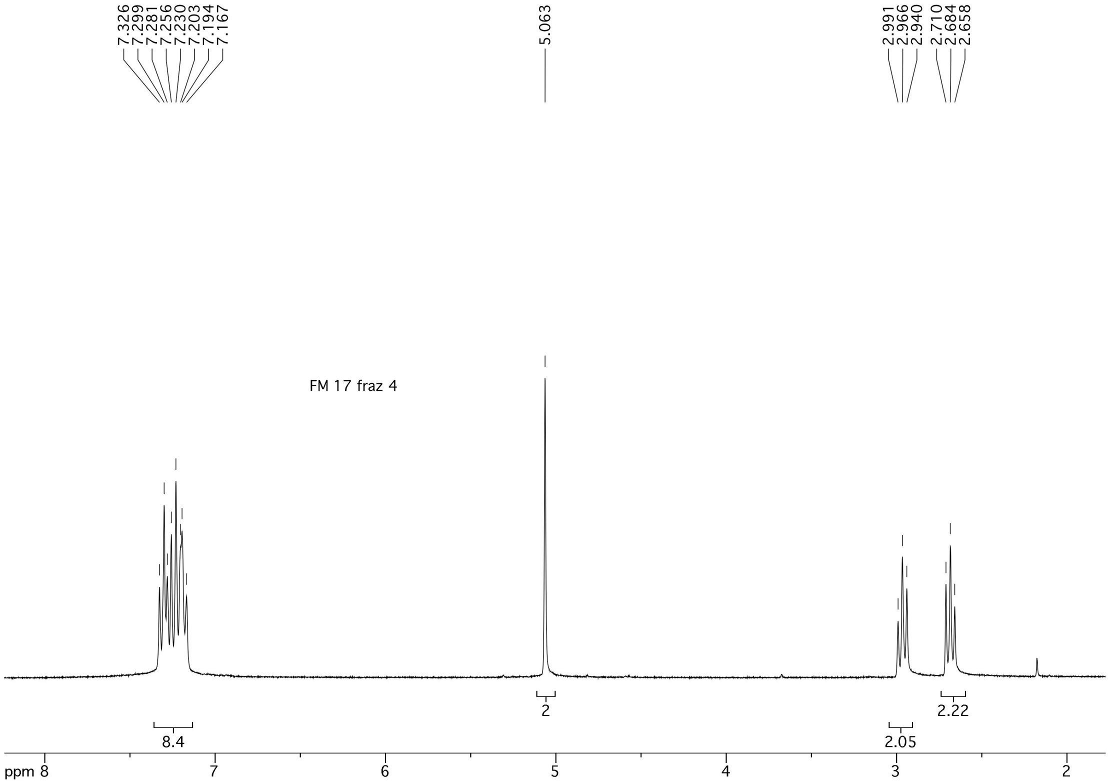
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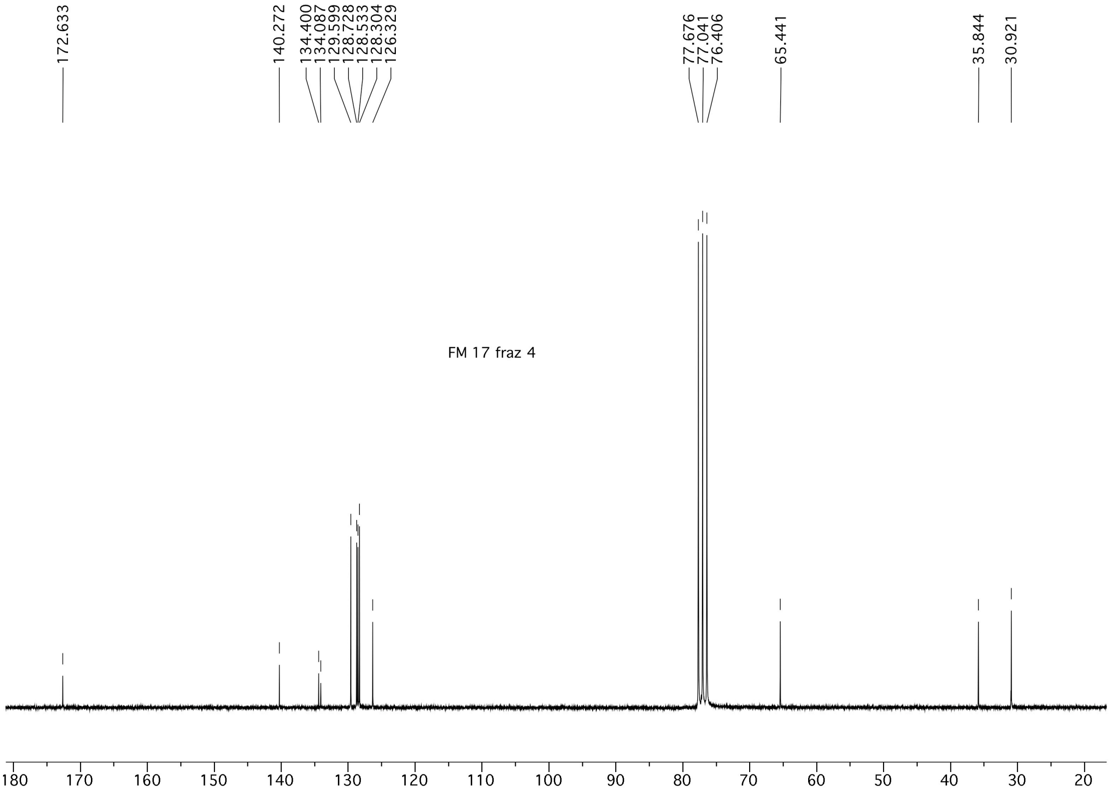
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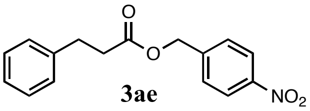
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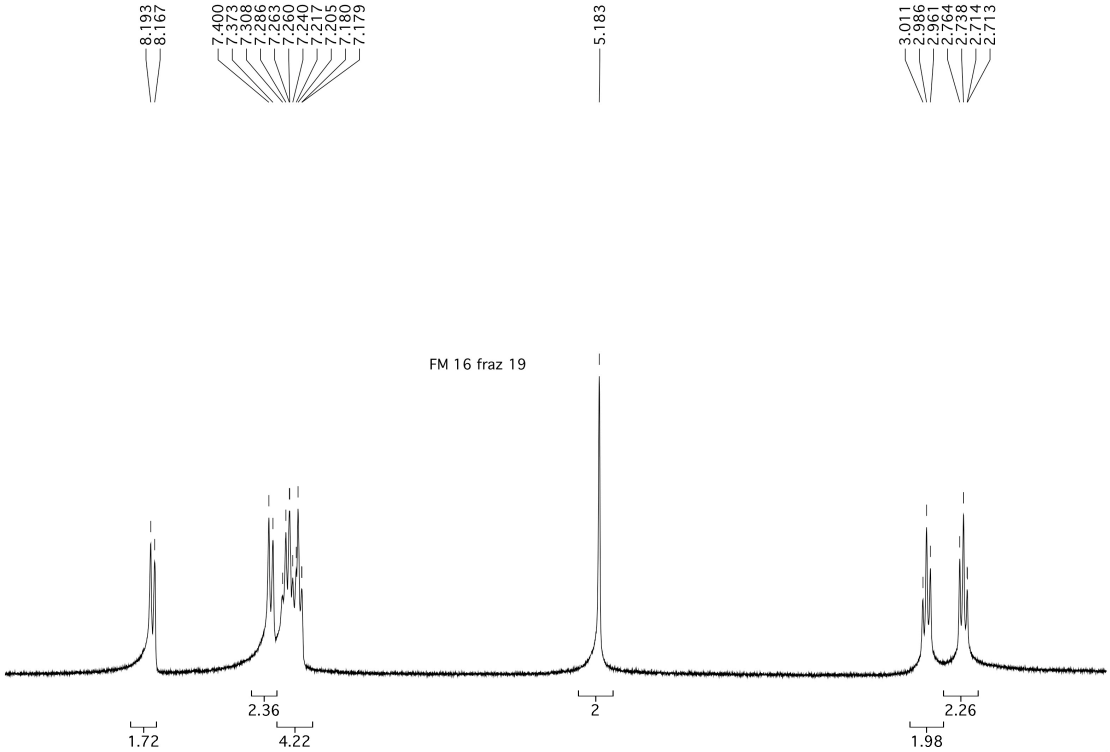
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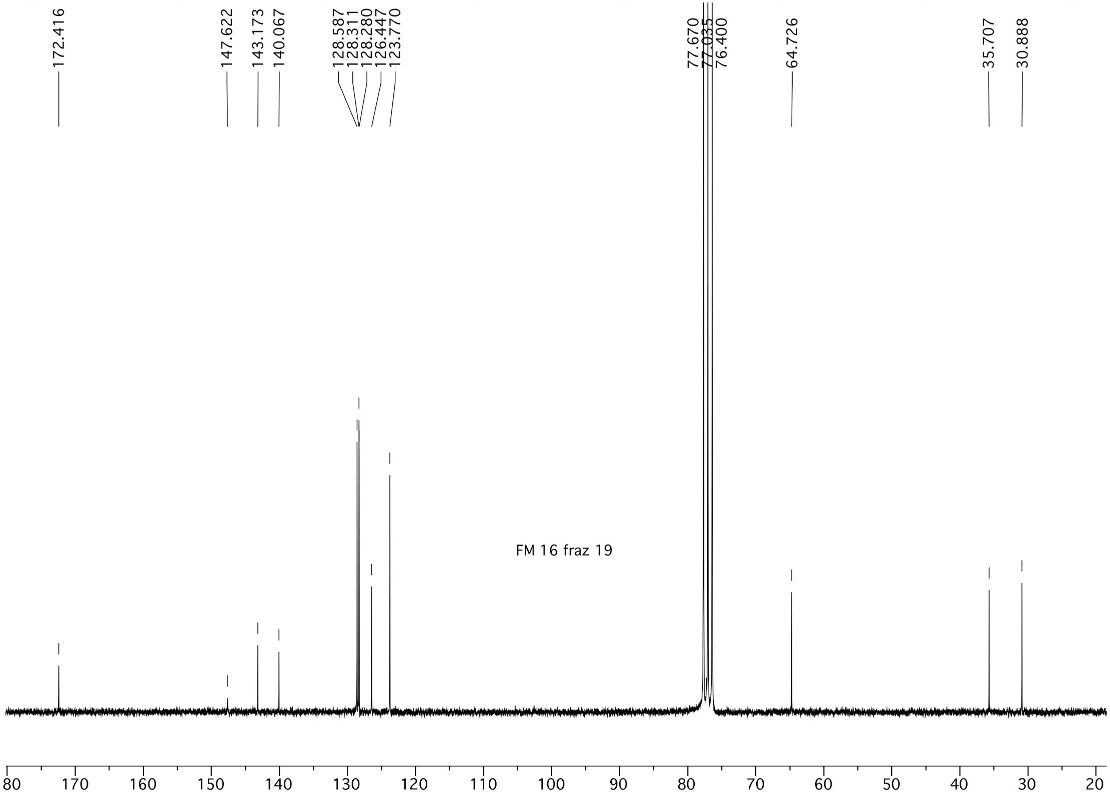
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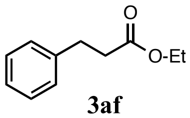
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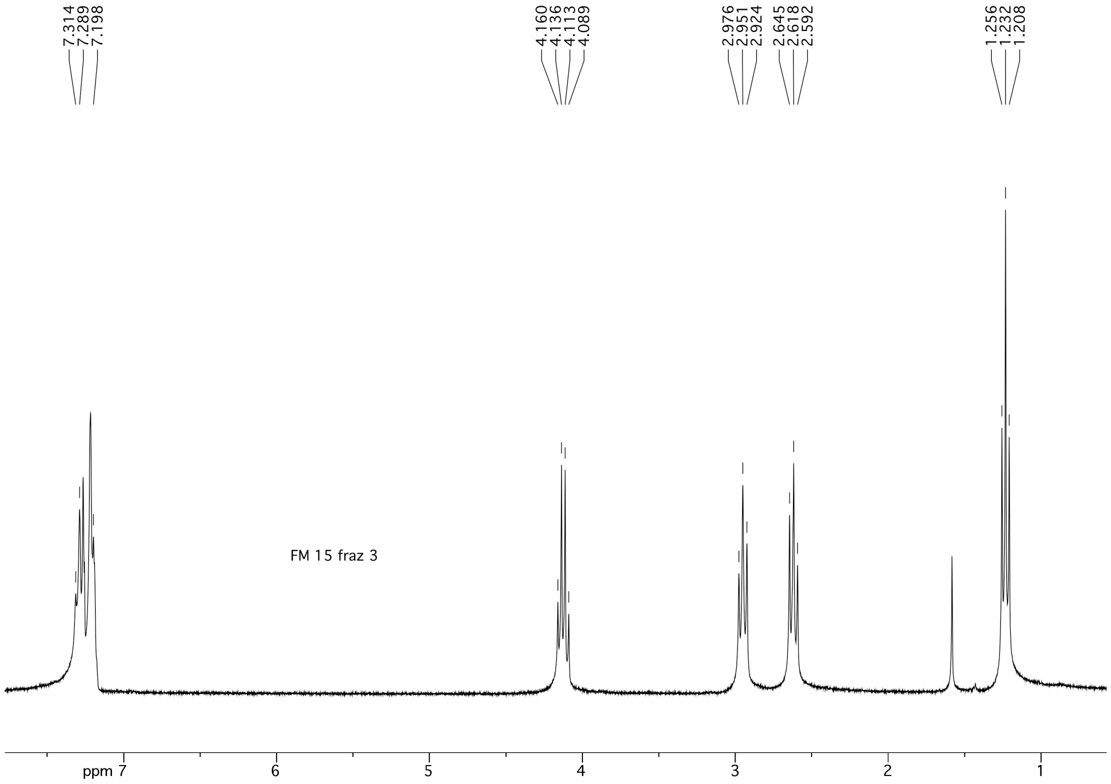
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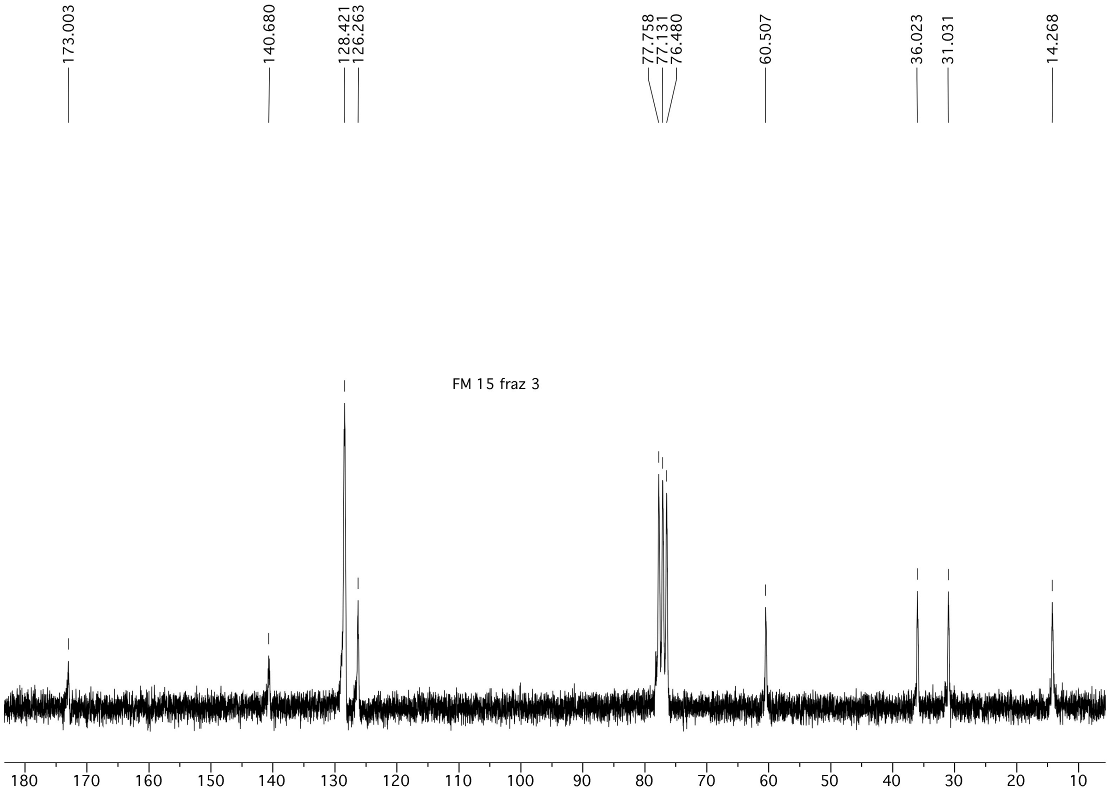
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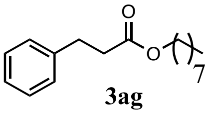
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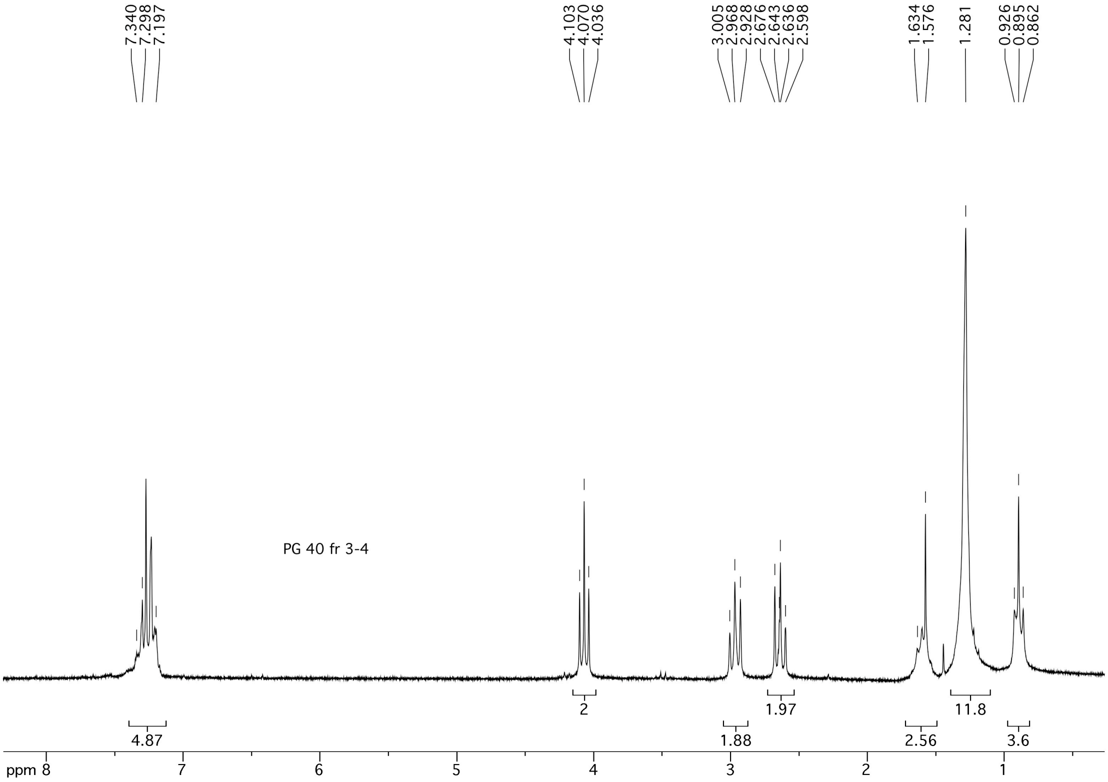
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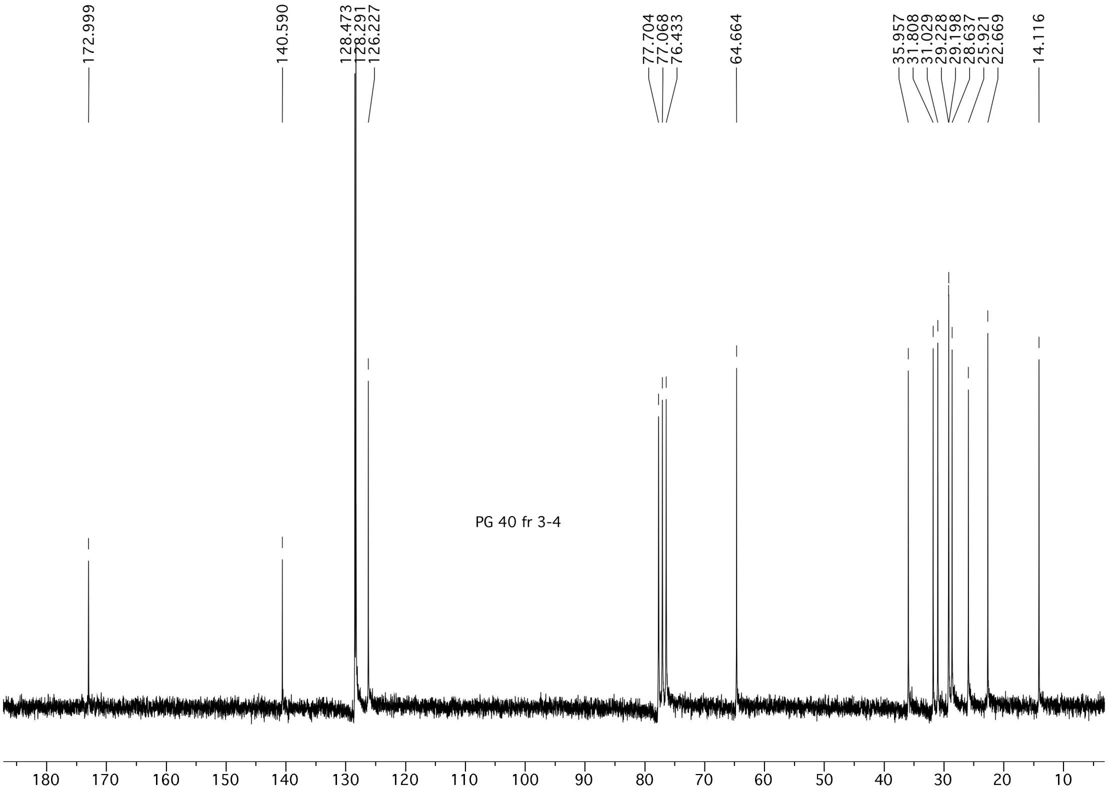
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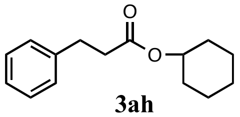

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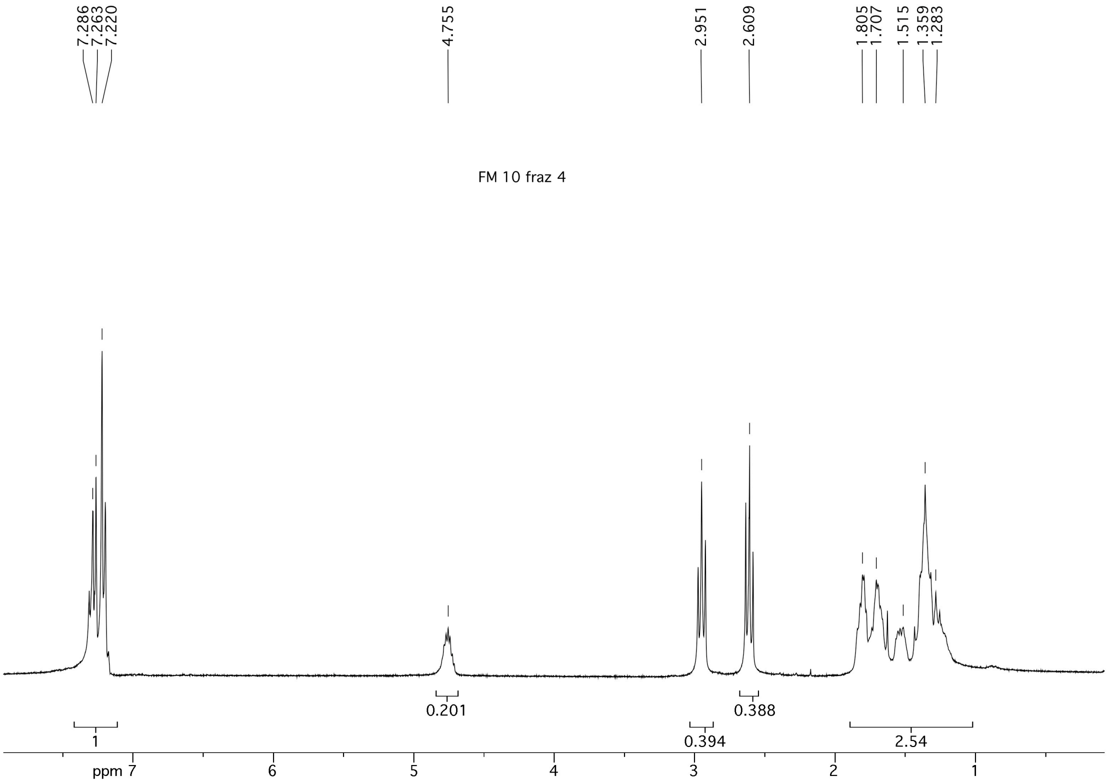
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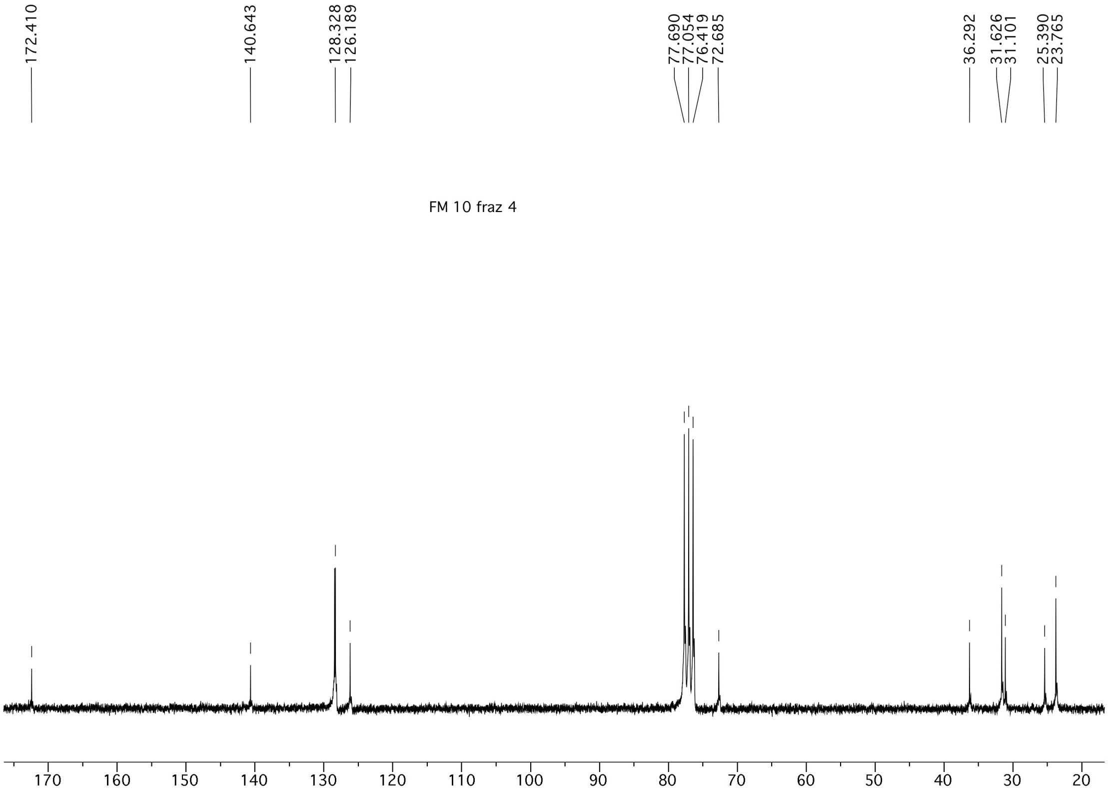
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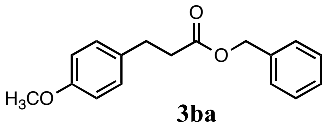
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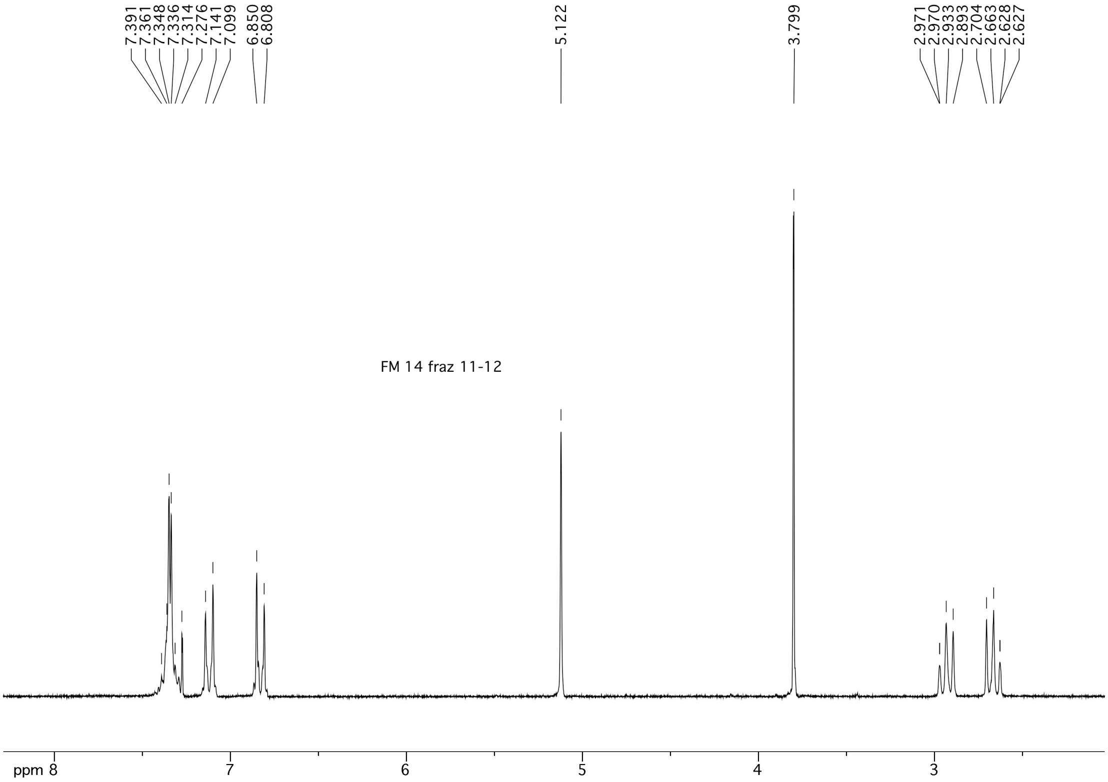
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2.970
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2.663
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2.627
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ppm 8
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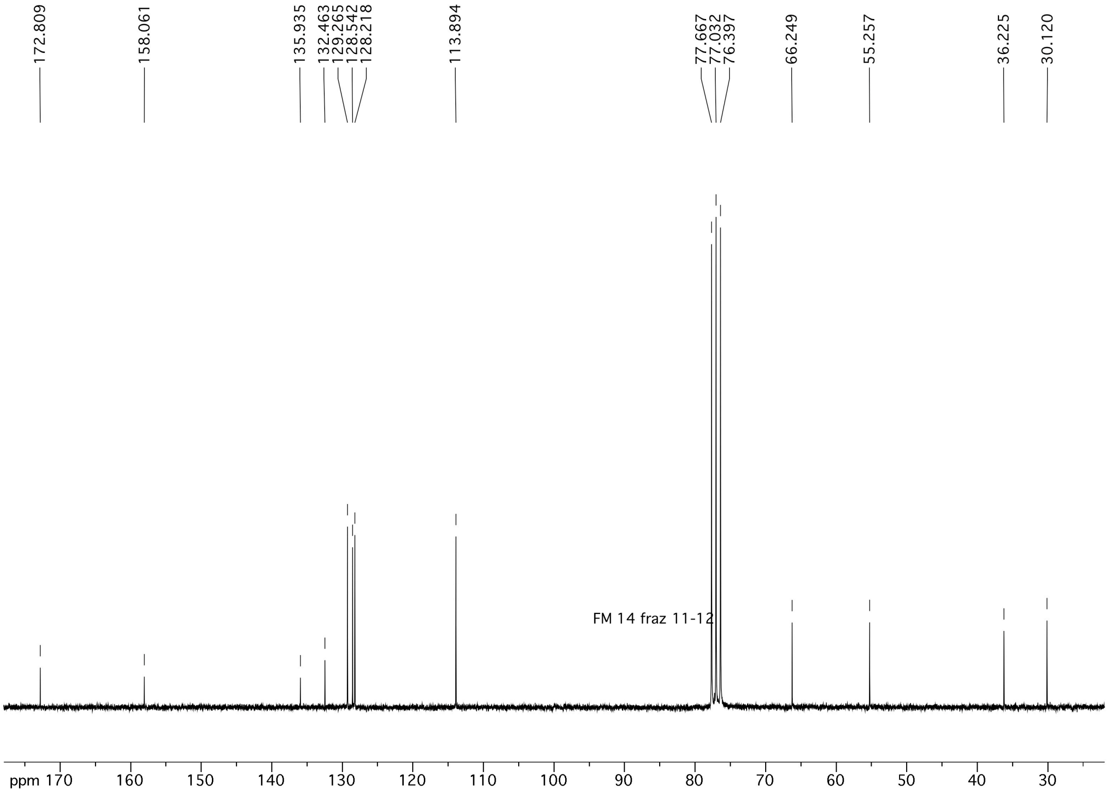
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36.225
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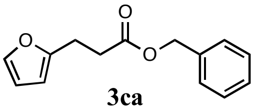

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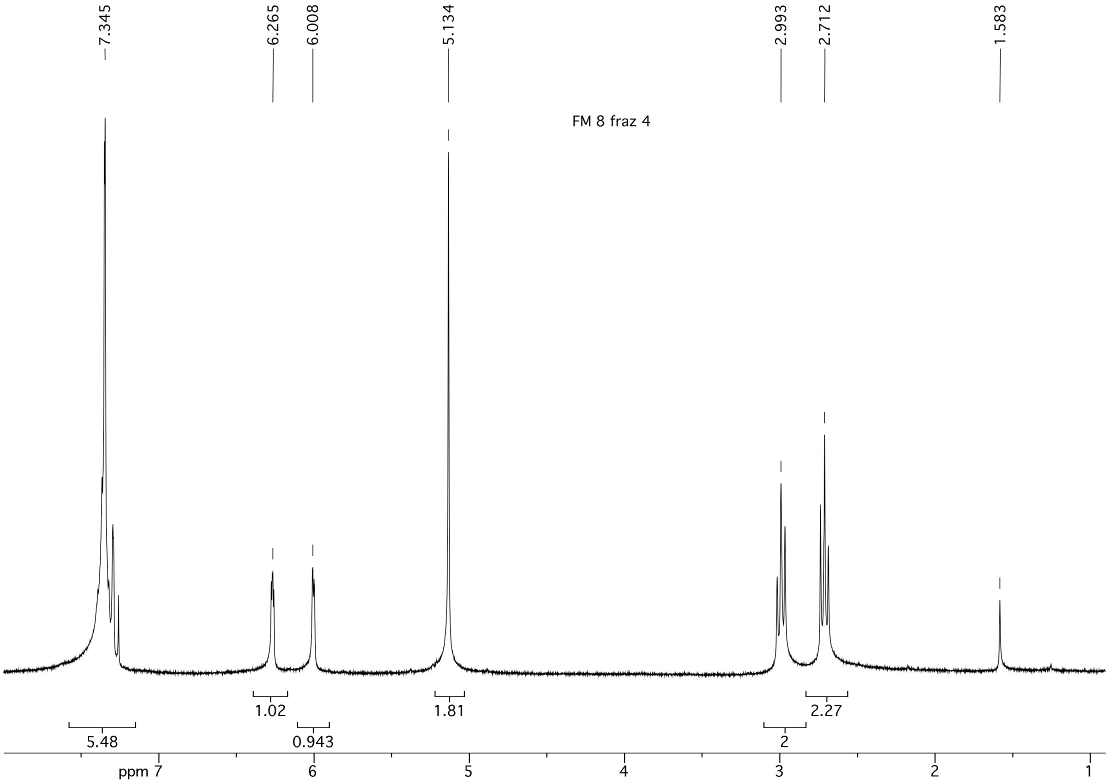
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2
ppm 7
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4
3
2
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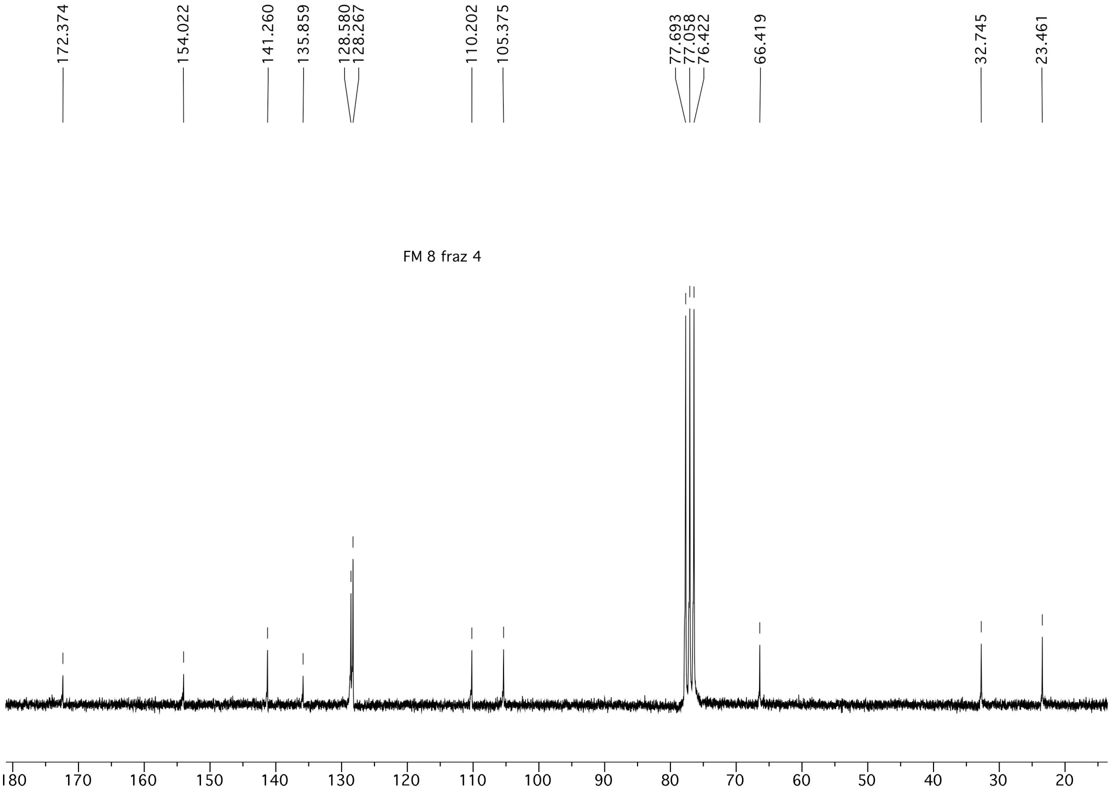
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50
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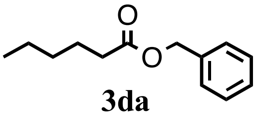

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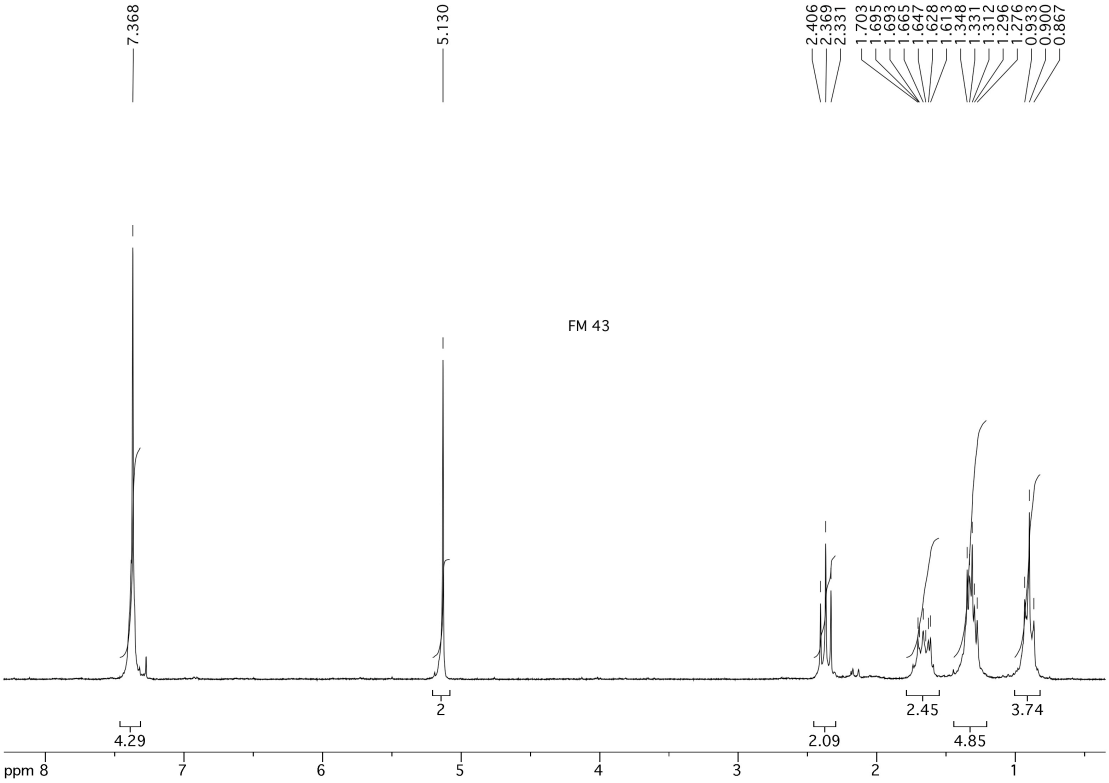
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1.331
1.312
1.296
1.276
0.933
0.900
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2
2.09
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3.74
ppm 8
7
6
5
4
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2
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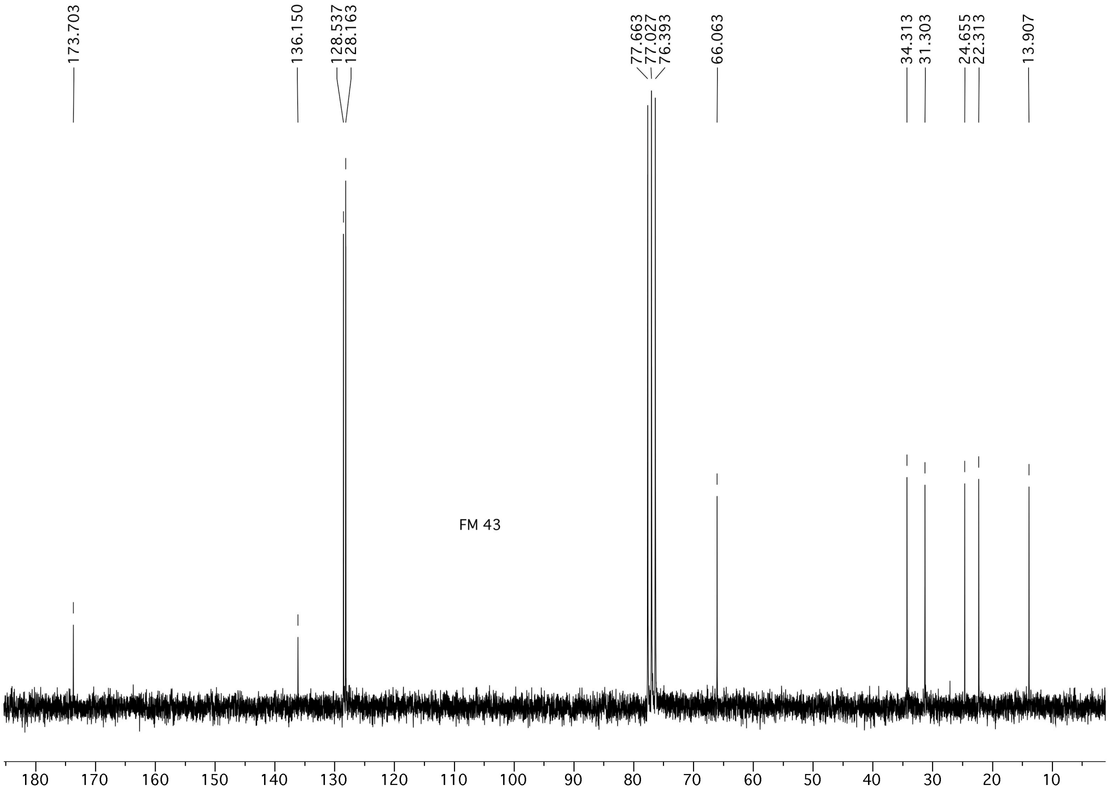
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FM 43
180
170
160
150
140
130
120
110
100
90
80
70
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50
40
30
20
10