

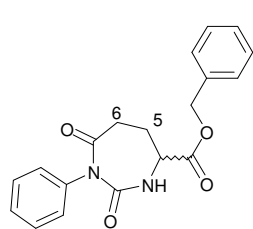
Straightforward Ring Expansion of Pyroglutamates to Perhydro-1,3-Diazepine-2,4-Diones

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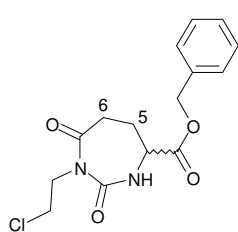
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Table 1 entry 1. 1-phenyl-2,7-dioxo-[1,3]diazepane-4-carboxylic acid benzyl ester.



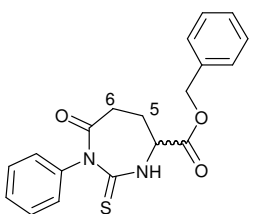
¹H-NMR (300 MHz, CDCl₃) δ: 2.10-2.22 (m, 1H); 2.27-2.38 (m, 1H); 2.59 (t, *J* = 7.1 Hz, 2H); 4.25 (br t, *J* = 5.6 Hz, 1H); 5.13 (s, 2H); 6.36 (br s, 1H); 7.33-7.48 (m, 10H). **¹³C-NMR (75 MHz, CDCl₃)** δ: 27.43 (CH₂, C₅); 30.18 (CH₂, C₆); 56.68 (CH, C₄); 67.34 (OCH₂); 126.59, 128.79, 128.85, 128.93, 129.11 and 129.57 (C_{ar}); 131.75 en 135.86 (C_q, C_{ar}); 156.69 (C=O, urea); 172.83 (C=O); 172.99 (C=O). **MS (ES, Neg) m/z (%)**: 337.2 (M-H⁺, 100). **IR (cm⁻¹, KBr)** *v*_{max}: 1699 (C=O), 1715 (C=O); 1781 (C=O); 3256 (br NH). **Mp**: 144.5-145.4°C. **Purity**: 99%

Table 1 entry 2. 1-(2-chloroethyl)-2,7-dioxo-[1,3]diazepane-4-carboxylic acid benzyl ester.



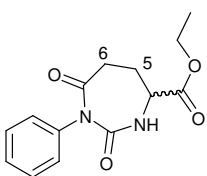
¹H-NMR (300 MHz, CDCl₃) δ: 1.99-2.11 (m, 1H); 2.14-2.28 (m, 1H); 2.52 (t, *J* = 7.4 Hz, 2H); 3.68 (t, *J* = 5.9 Hz, 2H); 3.77-3.82 (m, 2H); 4.13 (br t, *J* = 6.1 Hz, 1H); 5.10 (s, 2H); 7.12 (br s, 1H); 7.27-7.38 (m, 5H). **¹³C-NMR (75 MHz, CDCl₃)** δ: 26.92 (CH₂, C₅); 29.54 (CH₂, C₆); 40.13 (CH₂N of CH₂Cl); 40.74 (CH₂N of CH₂Cl); 56.44 (CH, C₄); 66.90 (OCH₂); 128.44, 128.59 en 128.83 (C_{ar}); 135.77 (C_q, C_{ar}); 157.44 (C=O, urea); 172.67 en 173.80 (C=O, ester en lactam). **MS (ES, Neg) m/z (%)**: 323.3 (M-H⁺, 75), 325.2 (M-H⁺, 25). **IR (cm⁻¹, KBr)** *v*_{max}: 1714 (br, C=O), 1777 (C=O), 3320 (NH). **Purity**: 99%

Table 1 entry 3. 7-oxo-1-phenyl-2-thioxo-[1,3]diazepane-4-carboxylic acid benzyl ester.



¹H-NMR (300 MHz, CDCl₃) δ: 2.13-2.26 (m, 1H); 2.33-2.44 (m, 1H); 2.58-2.65 (m, 2H); 4.35 (dd, *J* = 5.1 Hz and *J* = 6.5 Hz, 1H); 5.16 (s, 2H); 7.28-7.53 (m, 10H); 7.66 (br s, 1H). **¹³C-NMR (75 MHz, CDCl₃)** δ: 26.61 (CH₂, C₅); 29.85 (CH₂, C₆); 59.00 (CH, C₄); 67.10 (OCH₂); 126.31, 128.46, en 129.24 (C_{ar}); 131.45 en (C_q, C_{ar}); 172.69 (C=O) 173.20 (C=O), 183.71 (C=S). **MS (ES, Neg) m/z(%)**: 353.2 (M-H⁺, 100). **IR (cm⁻¹, KBr)** *v*_{max}: 1697 (C=S), 1719 (C=O); 1750 (C=O); 3233 (NH). **Mp**: 167°C. **Purity**: 98%

Table 1 entry 4. 1-phenyl-2,7-dioxo-[1,3]diazepane-4-carboxylic acid ethyl ester.



¹H-NMR (300 MHz, CDCl₃) δ: 1.26 (t, *J* = 7.2 Hz, 3H); 2.08-2.20 (m, 1H); 2.26-2.37 (m, 1H); 2.53 (t, *J* = 6.9 Hz, 2H); 4.16 (q, *J* = 7.2 Hz, 2H); 4.26 (dt, *J* = 1.3 Hz and *J* = 5.7 Hz, 1H); 6.31 (br s, 1H); 7.31-7.50 (m, 5H). **¹³C-NMR (75 MHz, CDCl₃)** δ: 14.14 (CH₃); 26.96 (CH₂, C₅); 29.53 (CH₂, C₆); 56.20 (CH, C₄); 60.95 (OCH₂); 126.21 (CH, C_{ar,meta}); 128.33 (CH, C_{ar,para}); 129.12 (CH, C_{ar,ortho}); 131.38 (C_q, C_{ar}); 156.62 (C=O, ureide); 172.62 (C=O), 172.67 (C=O). **MS (70 eV) (ES, Neg) m/z (%)**: 275.3 (M-H⁺, 100). **IR (cm⁻¹, KBr)** *v*_{max}: 1713 (C=O), 1728 (C=O); 1774 (C=O); 3272 (NH). **Mp**: 84-85°C. **Purity**: 99%

Table 1 entry 5. 1-benzyl-2,7-dioxo-[1,3]diazepane-4-carboxylic acid ethyl ester.

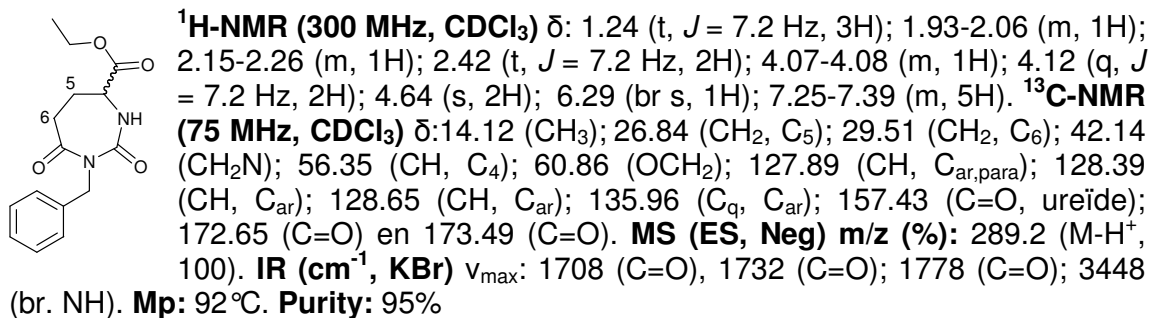


Table 1 entry 6. 1-(2-chloroethyl)-2,7-dioxo-[1,3]diazepane-4-carboxylic acid ethyl ester.

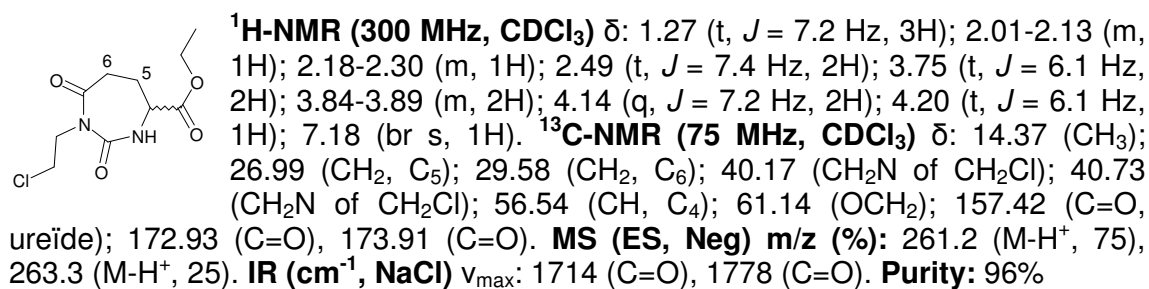


Table 1 entry 7. 1-allyl-2,7-dioxo-[1,3]diazepane-4-carboxylic acid ethyl ester.

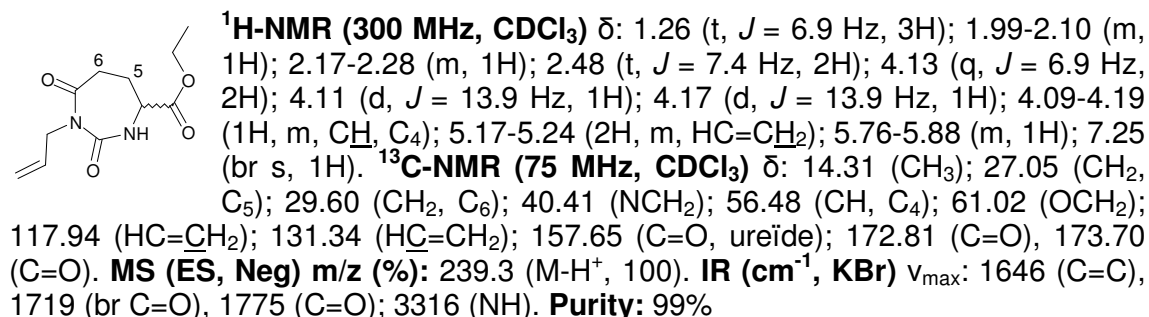
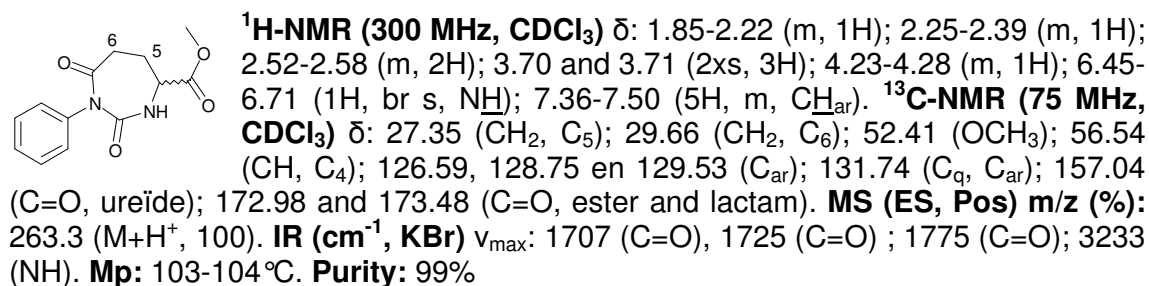
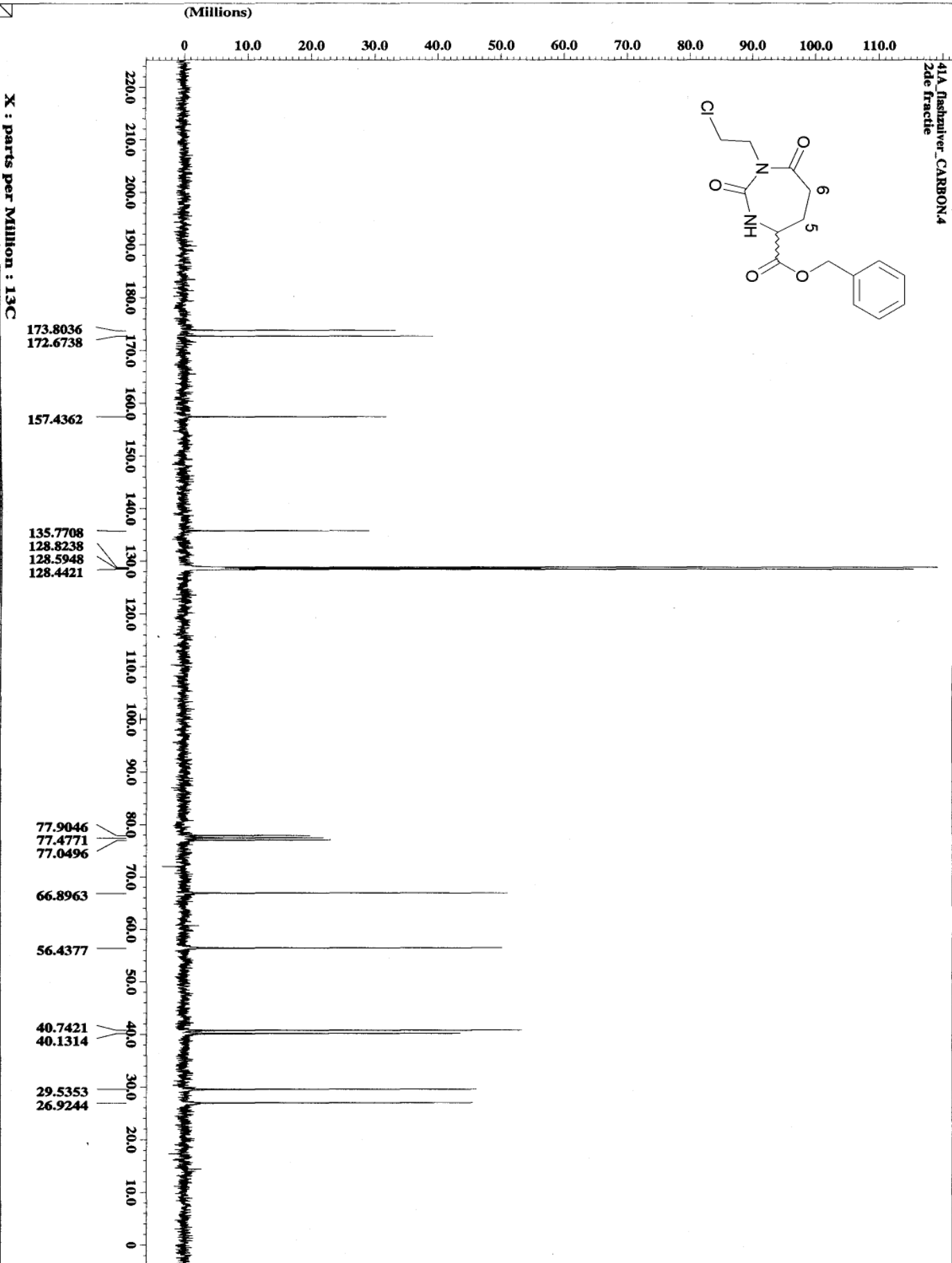


Table 1 entry 8. 1-phenyl-2,7-dioxo-[1,3]diazepane-4-carboxylic acid methyl ester.

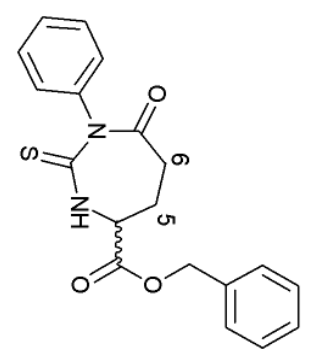




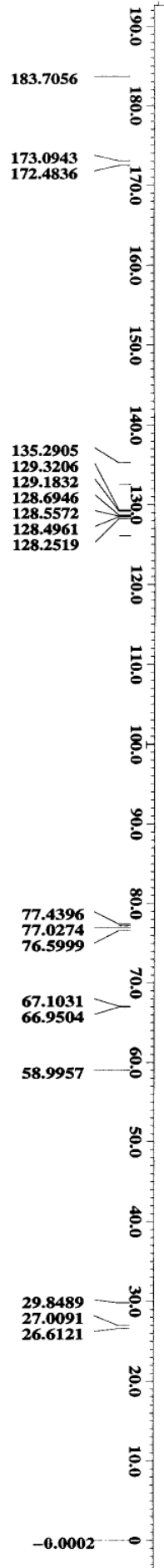
(Billions)

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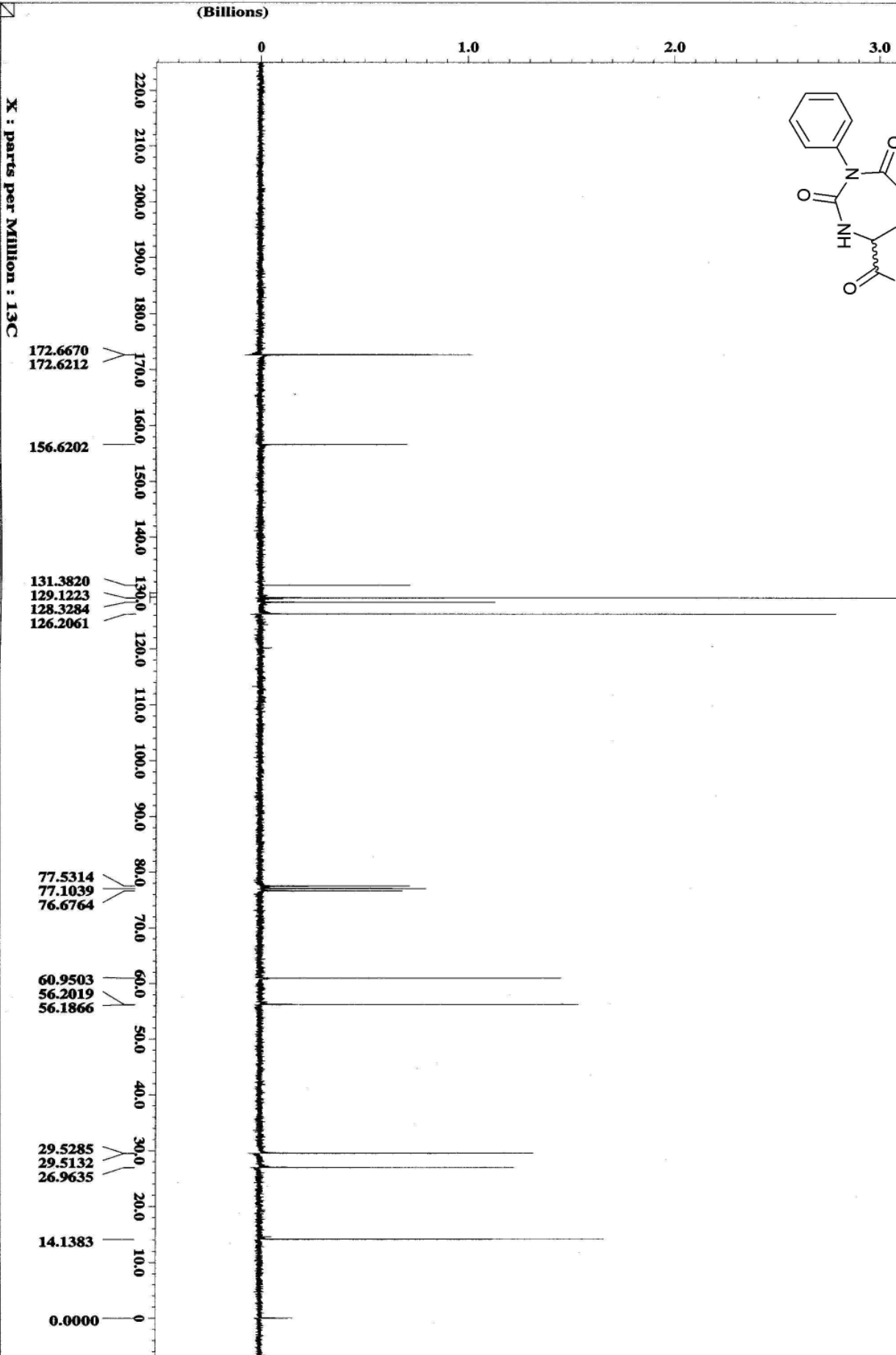
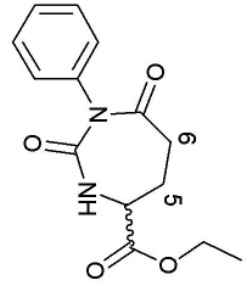
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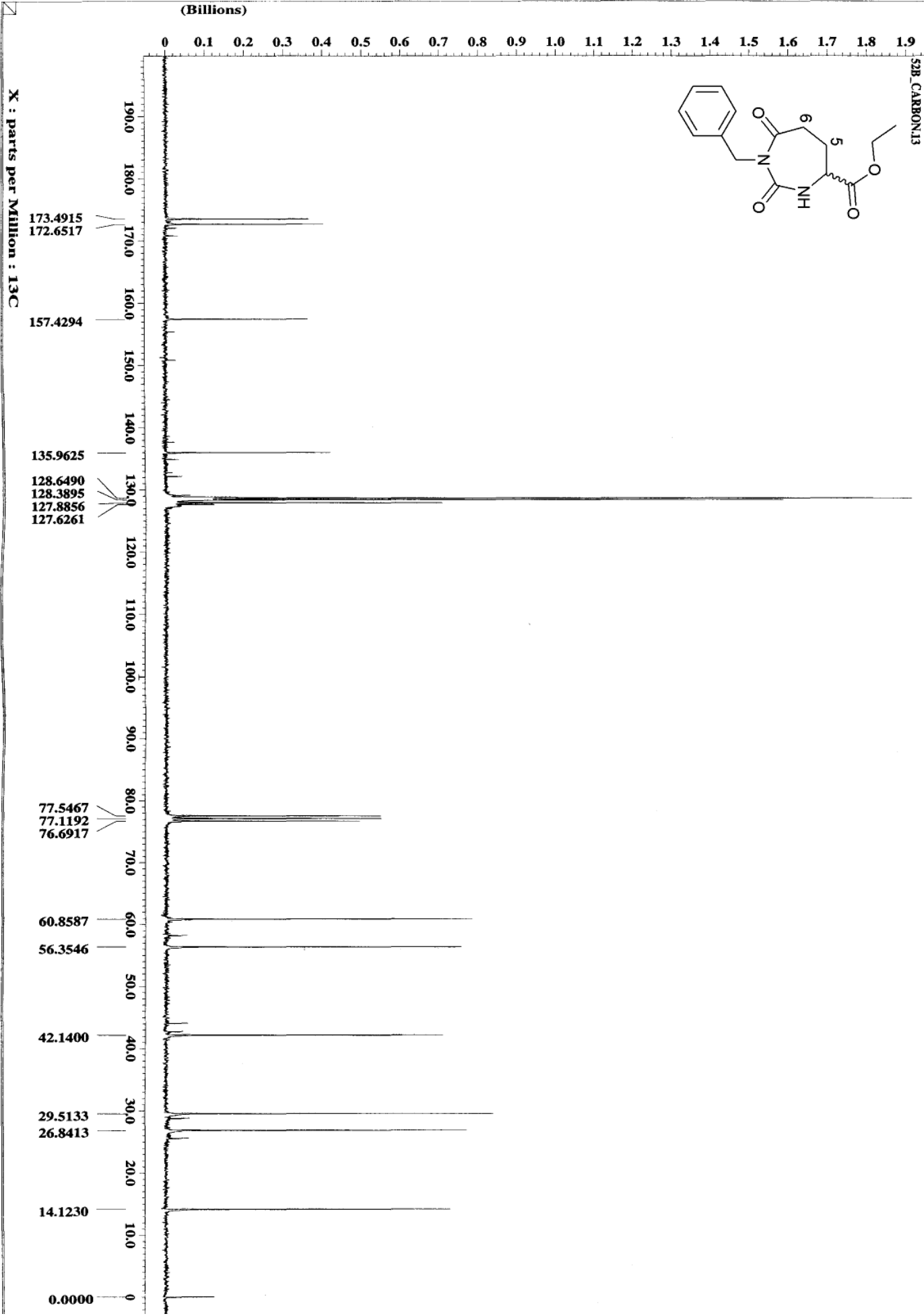


X : parts per Million : 13C



32c.9
Single Pulse with Broadband Decoupling





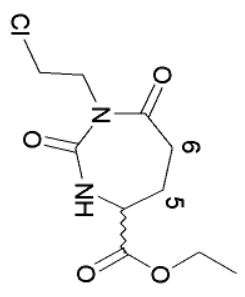
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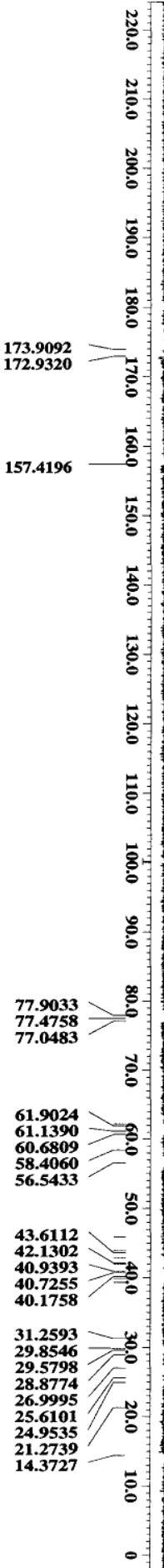
2.0

3.0

42C_CARBON4
3 daigen



X : parts per Million : 13C



(Billions)

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X : parts per Million : 13C

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117.9365

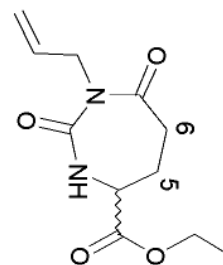
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27.0454

14.3118



75A_allylpyroglutamate_flashzuiver_CARBON7
allylpyroglutamate en ethylpyroglutamate

