

Pd/C-Catalyzed Synthesis of Oxamates by Oxidative Cross Double Carbonylation of Alcohols and Tertiary Amines through C-N Bond Cleavage

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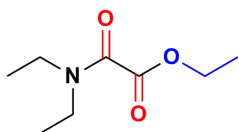
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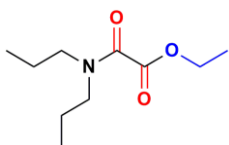
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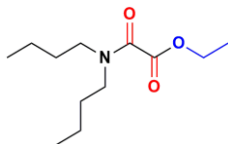
1) Analytical data of oxamate product:



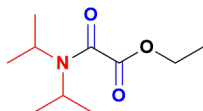
Ethyl 2-(diethyl amino)-2-oxoacetate (3a): ^1H NMR (500 MHz, CDCl_3) δ 4.31 (d, J = 7.1 Hz, 2H), 3.40 (d, J = 7.2 Hz, 2H), 3.27 (d, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.23, 161.44, 61.85, 42.45, 39.00, 14.15, 13.97, 12.50.



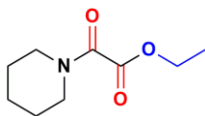
Ethyl 2-(dipropyl amino)-2-oxoacetate (3b): ^1H NMR (400 MHz, CDCl_3) δ 4.28 (d, J = 7.2 Hz, 2H), 3.31 – 3.10 (m, 4H), 1.58 (dt, J = 14.9, 7.3 Hz, 4H), 1.31 (t, J = 7.1 Hz, 3H), 0.86 (dt, J = 14.6, 7.4 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.25, 161.96, 61.70, 49.59, 45.98, 21.82, 20.36, 13.93, 11.18, 10.89.



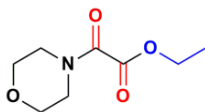
Ethyl 2-(dibutyl amino)-2-oxoacetate (3c): ^1H NMR (400 MHz, CDCl_3) δ 4.26 (q, J = 7.1 Hz, 2H), 3.34 – 3.24 (m, 2H), 3.18 – 3.09 (m, 2H), 1.51 (dd, J = 15.2, 6.4 Hz, 4H), 1.27 (m, 7H), 0.86 (dd, J = 13.2, 7.3 Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.23, 161.80, 61.65, 47.69, 44.12, 30.65, 29.17, 20.00, 19.73, 13.89, 13.60.



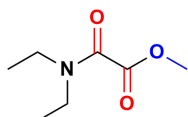
Ethyl 2-(diisopropyl amino)-2-oxoacetate (3d): ^1H NMR (500 MHz, cdcl_3) δ 4.30 (q, J = 7.2 Hz, 2H), 3.72 – 3.65 (m, 1H), 3.52 – 3.44 (m, 1H), 1.44 (d, J = 6.8 Hz, 6H), 1.34 (t, J = 7.1 Hz, 3H), 1.23 (d, J = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, cdcl_3) δ 163.44, 161.62, 61.55, 50.56, 45.87, 20.63, 19.99, 13.97.



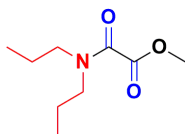
Ethyl 2-Oxo-2-(piperidine-1-yl) acetate (3e): ^1H NMR (500 MHz, CDCl_3) δ 4.24 (t, J = 7.1 Hz, 2H), 3.52 – 3.46 (m, 2H), 3.30 – 3.22 (m, 2H), 1.66 – 1.49 (m, 6H), 1.28 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.20, 160.21, 61.81, 47.16, 42.05, 26.10, 25.03, 24.24, 13.92.



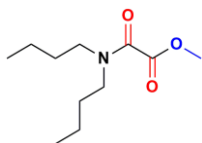
Ethyl 2-(morpholino amino)-2-oxoacetate (3f): ^1H NMR (400 MHz, CDCl_3) δ 4.31 (q, J =7.1 Hz, 2H), 3.72-3.60 (m, 6H), 3.48-3.41 (m, 2H), 1.34 (t, J =7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.29, 160.09, 66.58, 66.33, 62.21, 46.35, 41.71, 13.93.



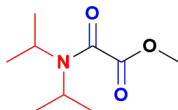
Methyl 2-(diethyl amino)-2-oxoacetate (3g): ^1H NMR (400 MHz, CDCl_3) δ 4.31 (q, J = 7.1 Hz, 2H), 3.72 – 3.60 (m, 6H), 3.48 – 3.41 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.29, 160.09, 66.58, 66.33, 62.21, 46.35, 41.71, 13.93.



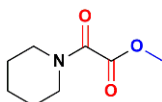
Methyl 2-(dipropyl amino)-2-oxoacetate (3h): ^1H NMR (400 MHz, CDCl_3) δ 3.81 (d, J = 6.1 Hz, 3H), 3.32 – 3.06 (m, 4H), 1.64 – 1.47 (m, 4H), 0.95 – 0.76 (m, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.54, 161.64, 52.29, 49.61, 46.02, 21.80, 20.31, 11.16, 10.89.



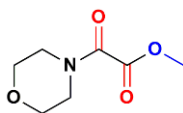
Methyl 2-(dibutyl amino)-2-oxoacetate (3i): ^1H NMR (500 MHz, CDCl_3) δ 3.83 (s, 3H), 3.36 – 3.31 (t, 2H), 3.24 – 3.15 (t, 2H), 1.53 (dt, J = 15.6, 7.7 Hz, 4H), 1.35 – 1.25 (m, 4H), 0.90 (t, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.55, 161.52, 52.25, 47.72, 44.21, 30.65, 29.16, 20.07, 19.70, 13.77, 13.61.



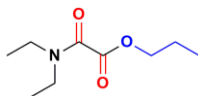
Methyl 2-(diisopropyl amino)-2-oxoacetate (3j): ^1H NMR (500 MHz, cdcl_3) δ 3.80 – 3.76 (m, 3H), 3.65 – 3.40 (m, 2H), 1.41 – 1.36 (m, 6H), 1.19 – 1.16 (m, 6H). ^{13}C NMR (126 MHz, cdcl_3) δ 163.74, 161.34, 52.15, 50.60, 45.84, 20.58, 19.88.



Methyl 2-Oxo-2-(piperidine-1-yl) acetate (3k): ^1H NMR (500 MHz, CDCl_3) δ 3.83 (s, 3H), 3.56 – 3.51 (m, 2H), 3.32 – 3.28 (m, 2H), 1.65 (d, J = 4.4 Hz, 2H), 1.59 (dd, J = 10.7, 5.5 Hz, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 163.55, 159.98, 52.46, 47.25, 42.21, 26.18, 25.08, 24.28.



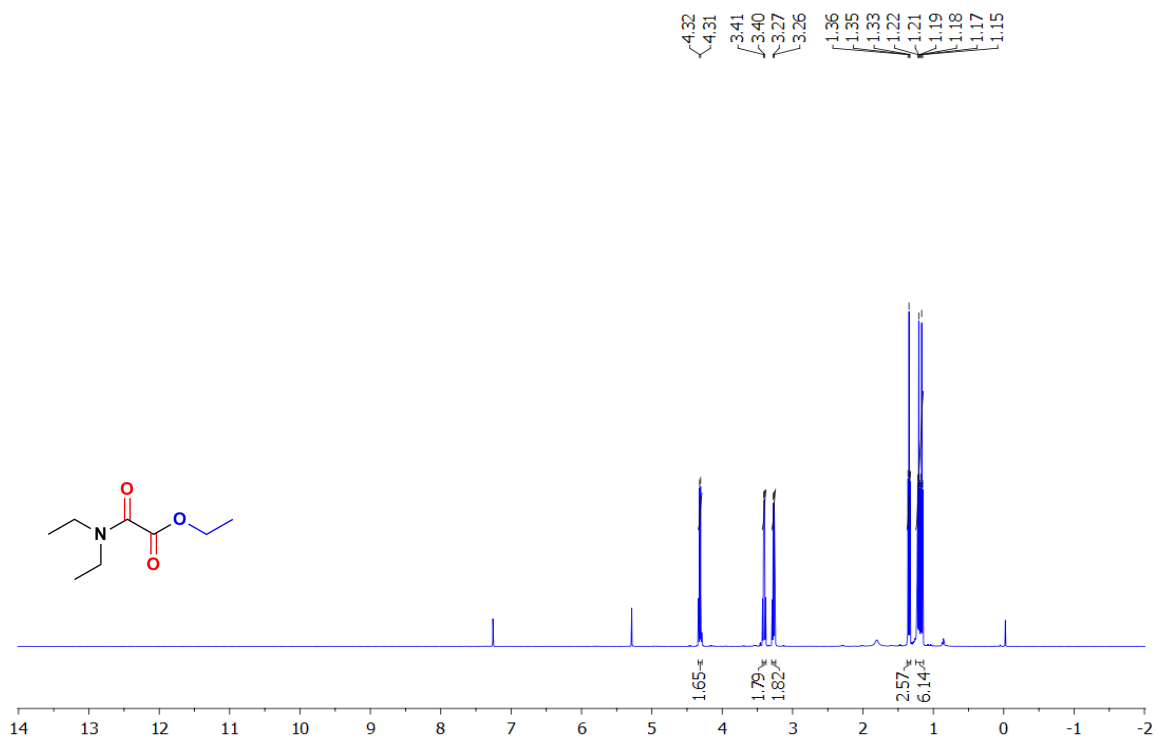
Methyl 2-(morpholino amino)-2-oxoacetate (3m): ^1H NMR (400 MHz, CDCl_3) δ 3.85 (d, J = 4.4 Hz, 3H), 3.73 – 3.57 (m, 6H), 3.44 (d, J = 4.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 162.58, 159.77, 66.59, 66.31, 52.67, 46.38, 41.79.



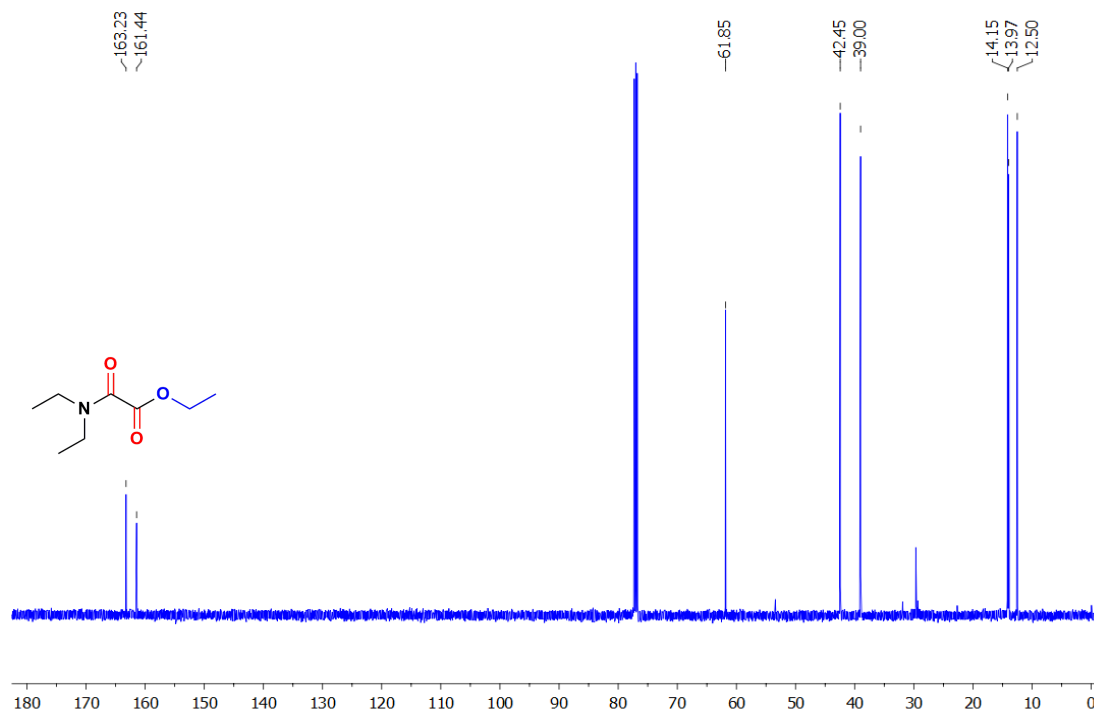
Propyl 2-(diethyl amino)-2-oxoacetate (3n): ^1H NMR (400 MHz, CDCl_3) δ 4.18 (t, J = 6.7 Hz, 2H), 3.38 (q, J = 7.2 Hz, 2H), 3.24 (q, J = 7.1 Hz, 2H), 1.70 (dd, J = 14.3, 7.2 Hz, 2H), 1.20 – 1.11 (m, 6H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.35, 161.46, 67.26, 42.37, 38.90, 21.72, 14.12, 12.45, 10.20.

2. Copies of ^1H and ^{13}C NMR Spectra of the products:

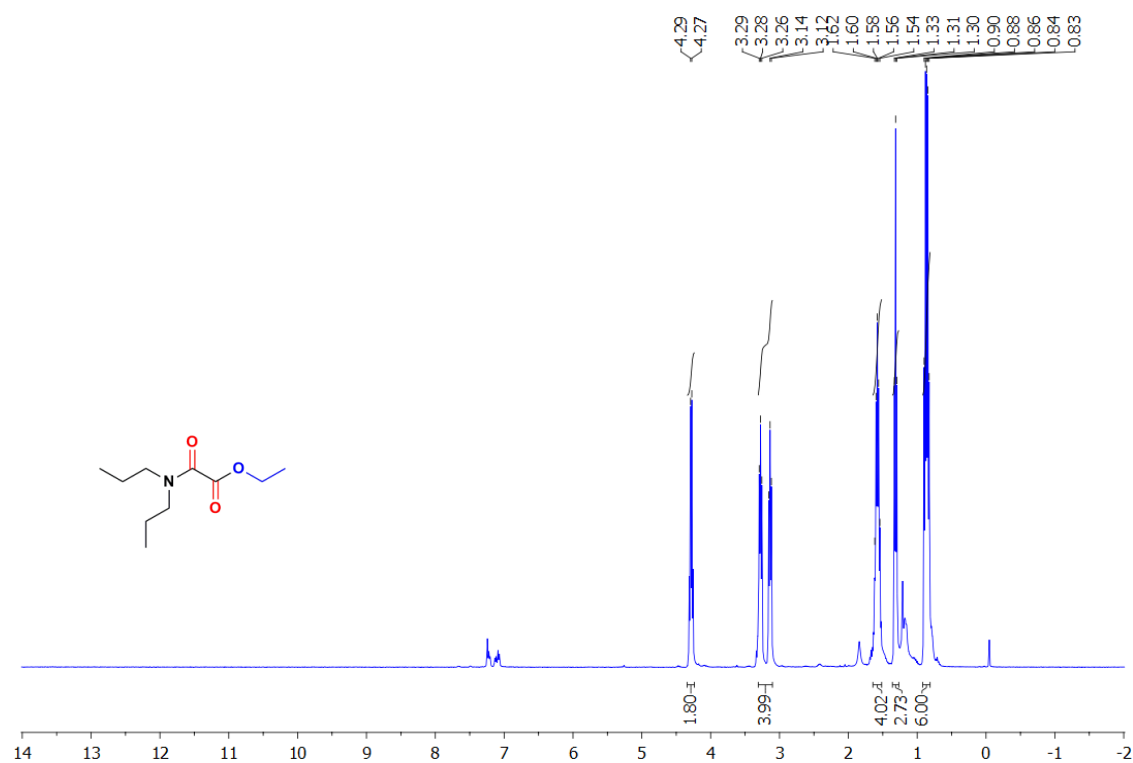
^1H NMR of Ethyl 2-(diethyl amino)-2-oxoacetate (3a)



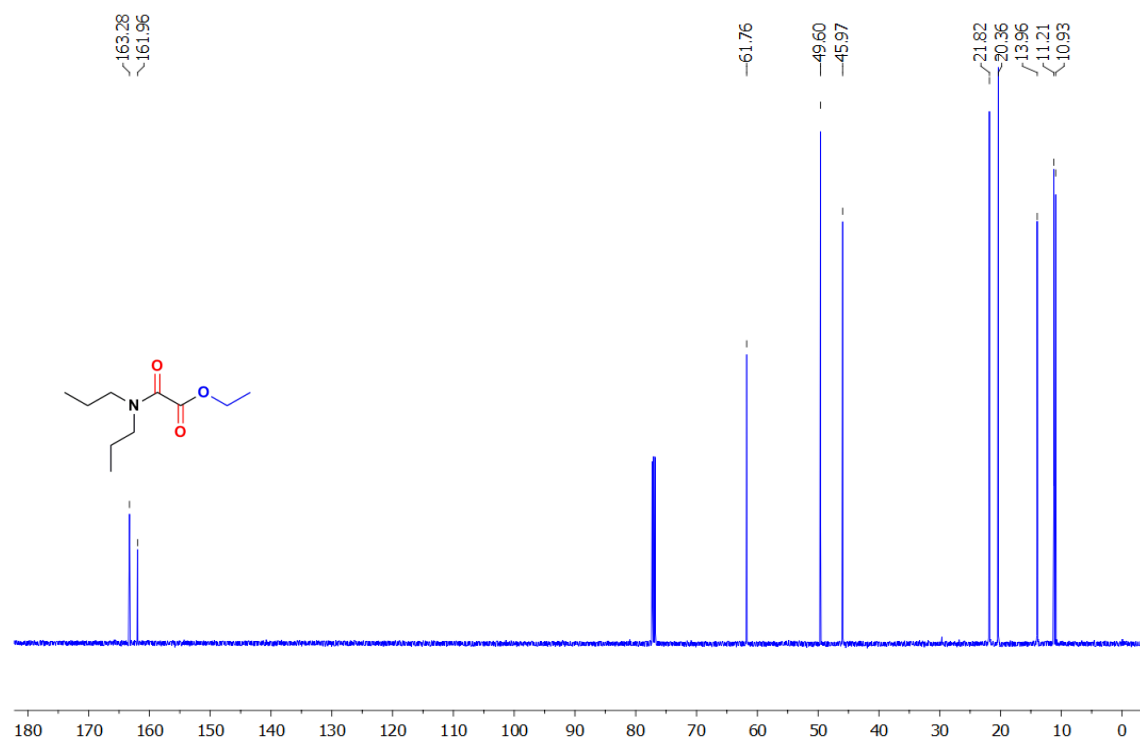
^{13}C NMR of Ethyl 2-(diethyl amino)-2-oxoacetate (3a)



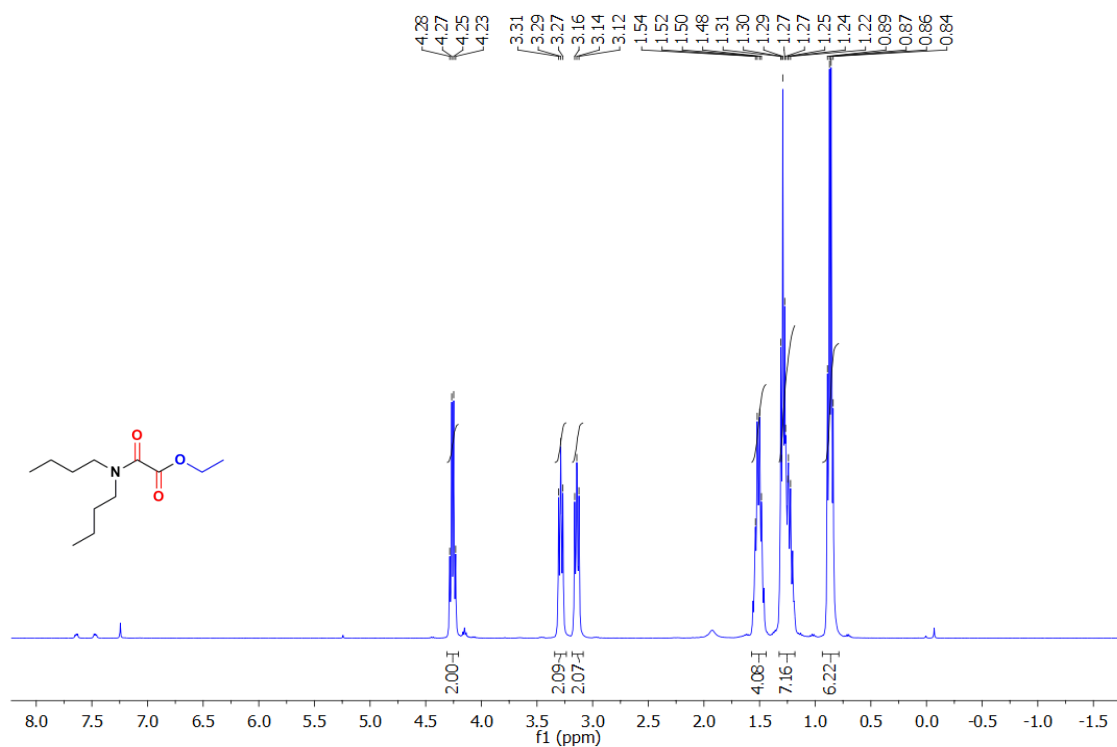
¹H NMR of Ethyl 2-(dipropyl amino)-2-oxoacetate (3b)



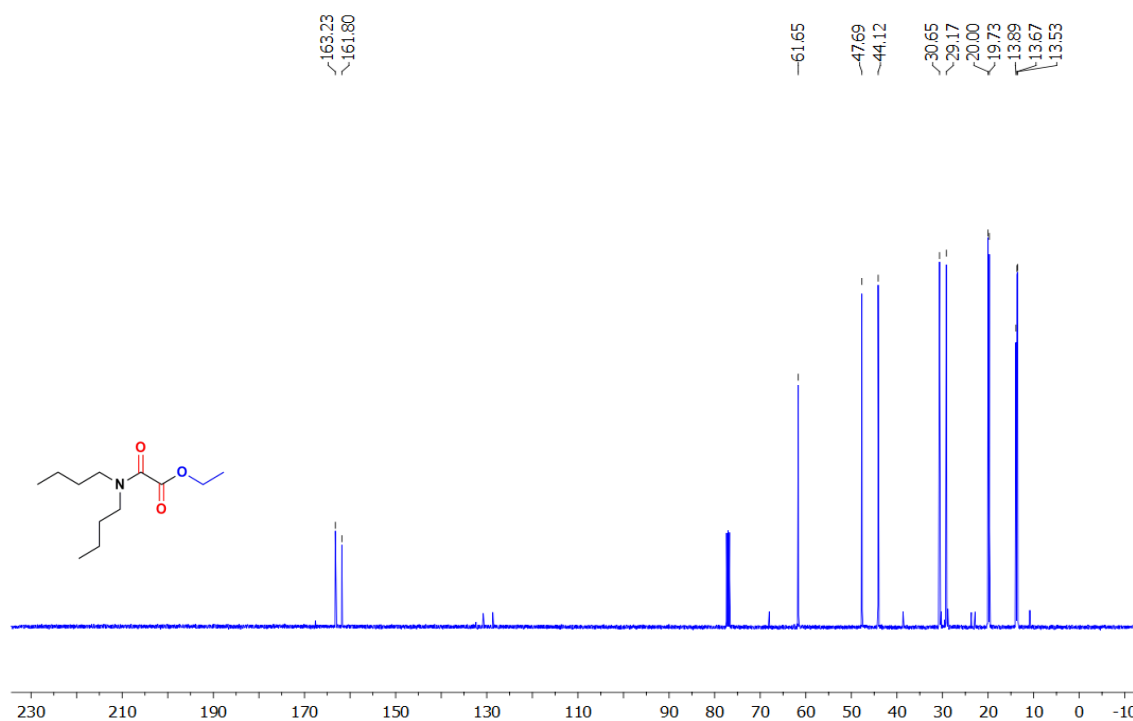
¹³C NMR of Ethyl 2-(dipropyl amino)-2-oxoacetate (3b)



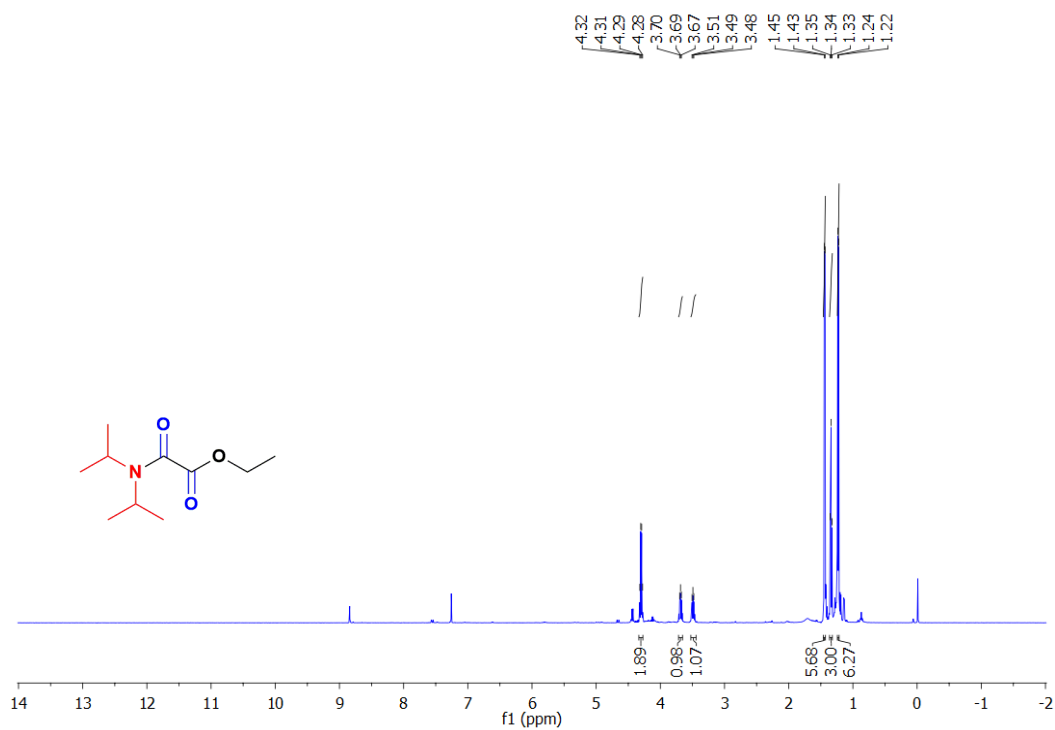
¹H NMR of Ethyl 2-(dibutyl amino)-2-oxoacetate (3c)



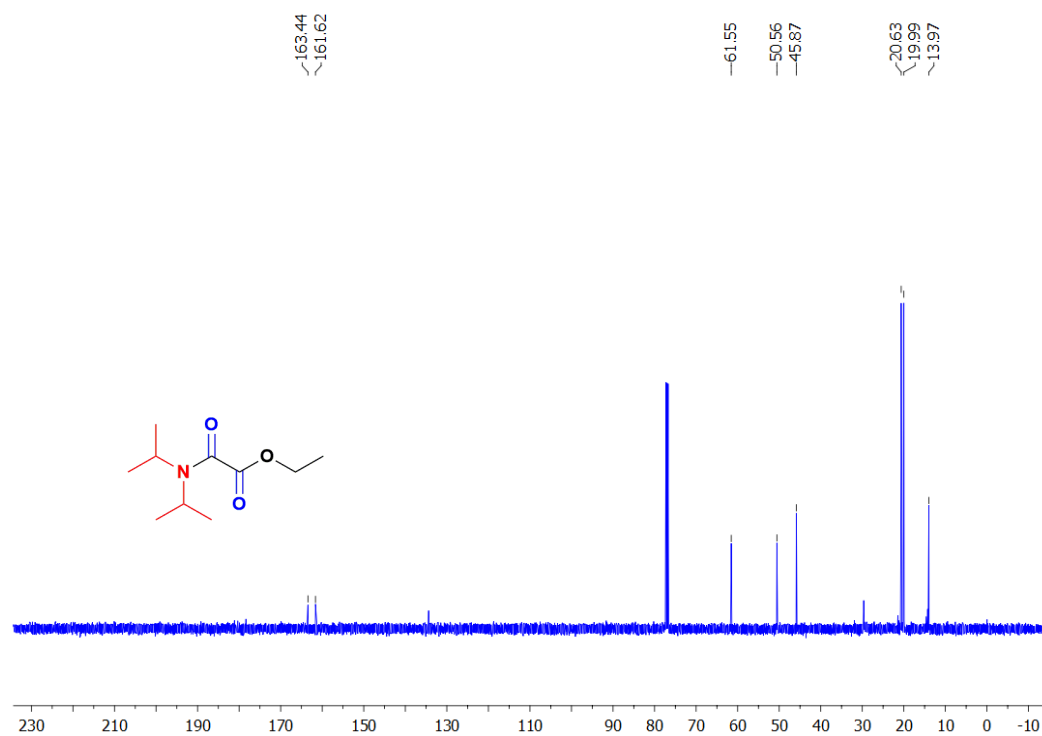
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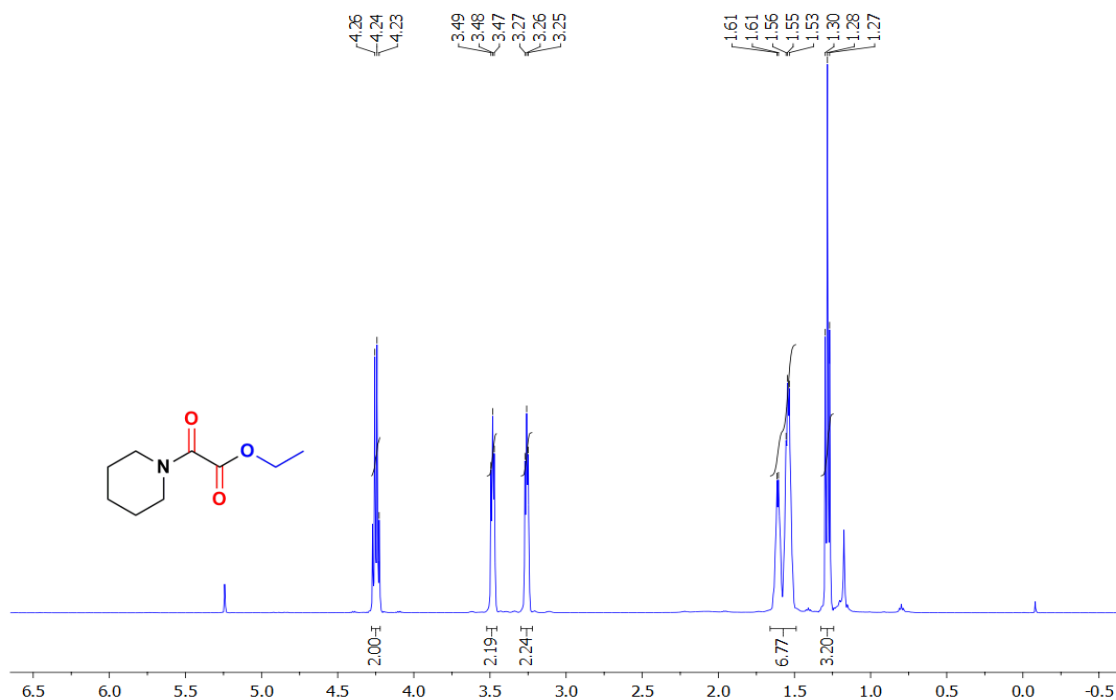
^1H NMR of Ethyl 2-(diisopropyl amino)-2-oxoacetate (3d)



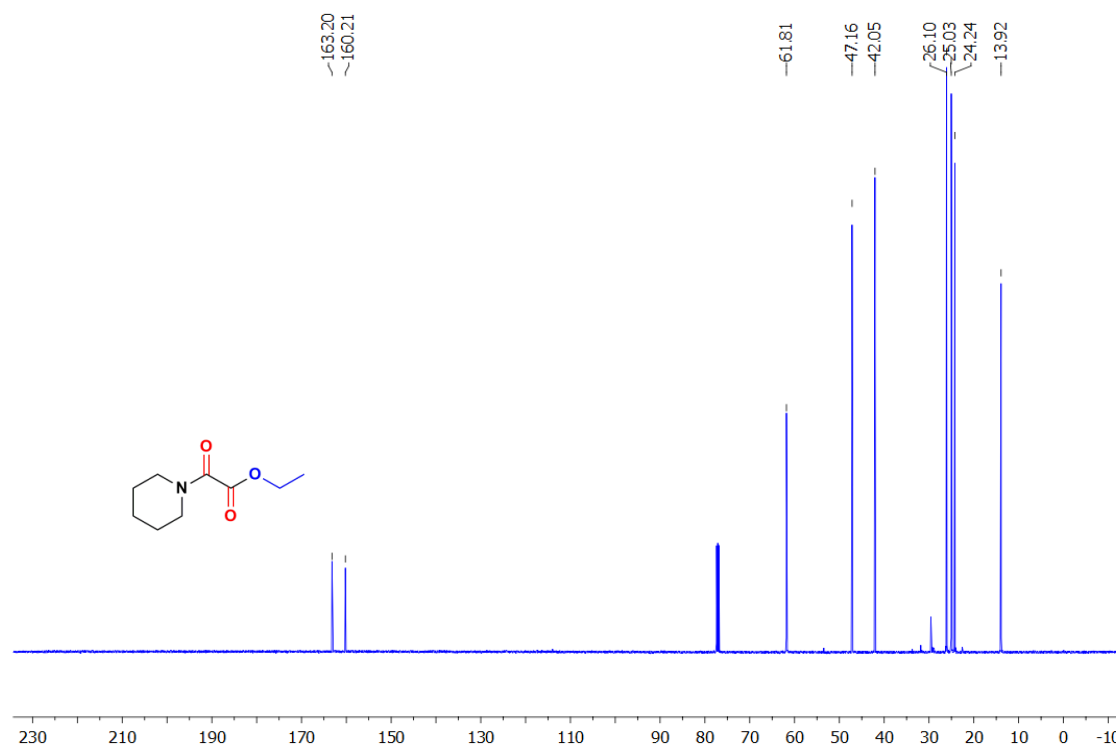
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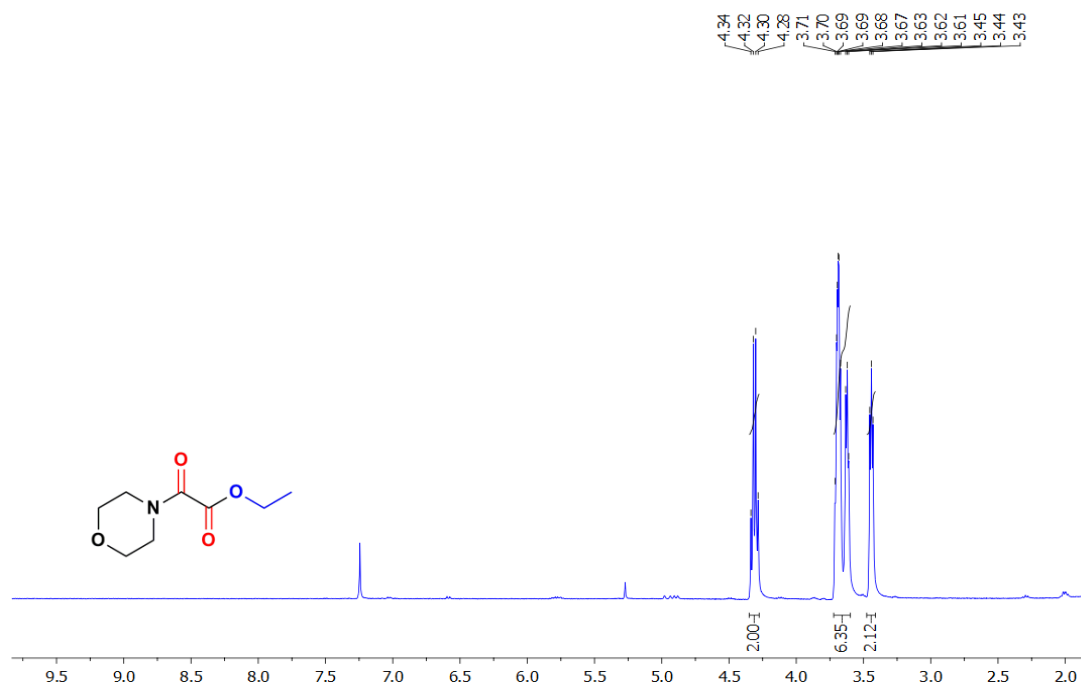
¹H NMR of Ethyl 2-Oxo-2-(piperidine-1-yl) acetate (3e)



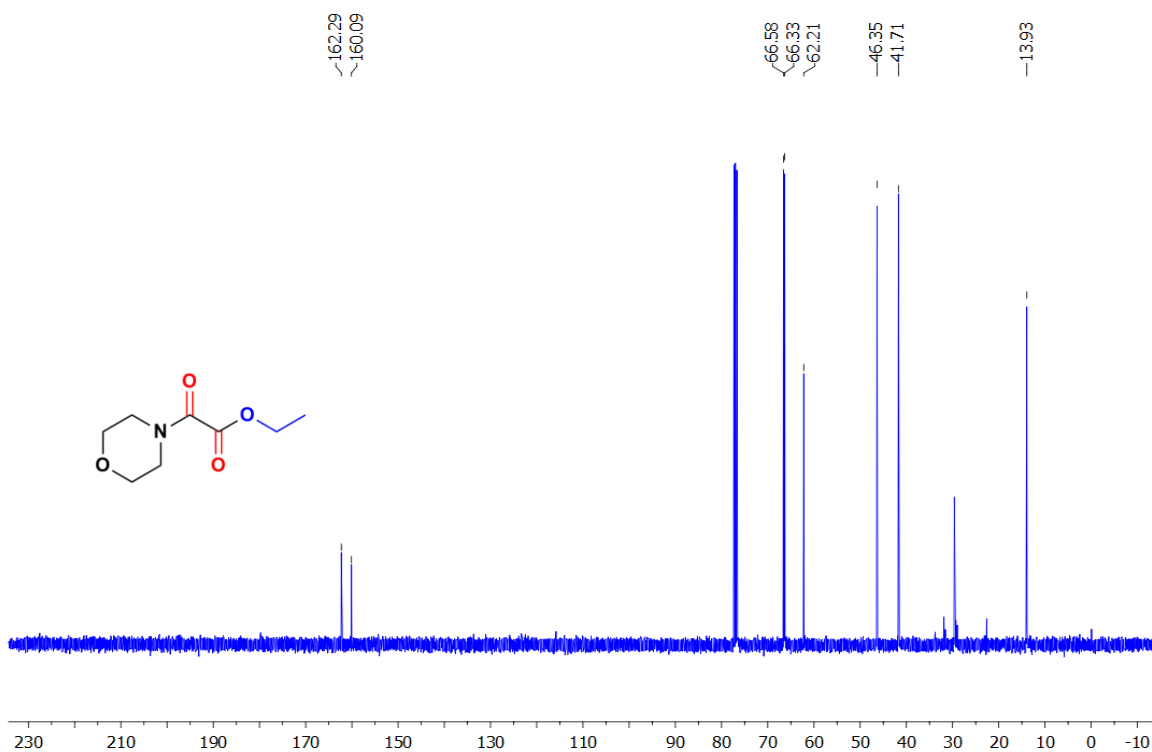
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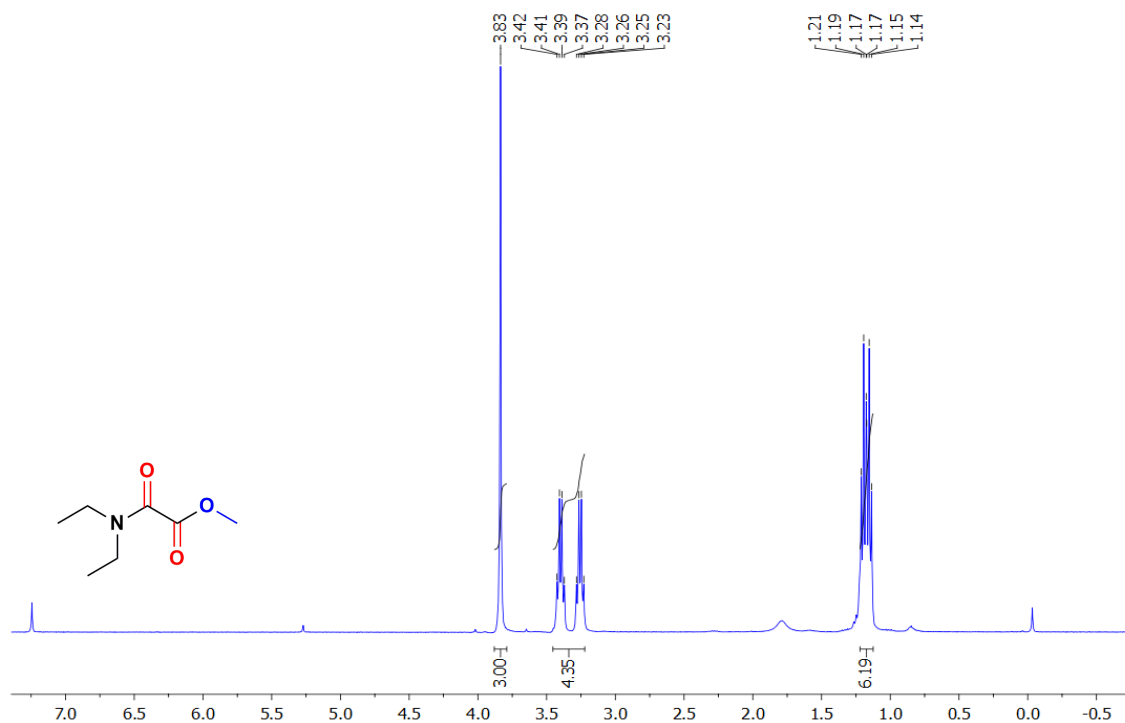
^1H NMR of Ethyl 2-(morpholino amino)-2-oxoacetate (3f)



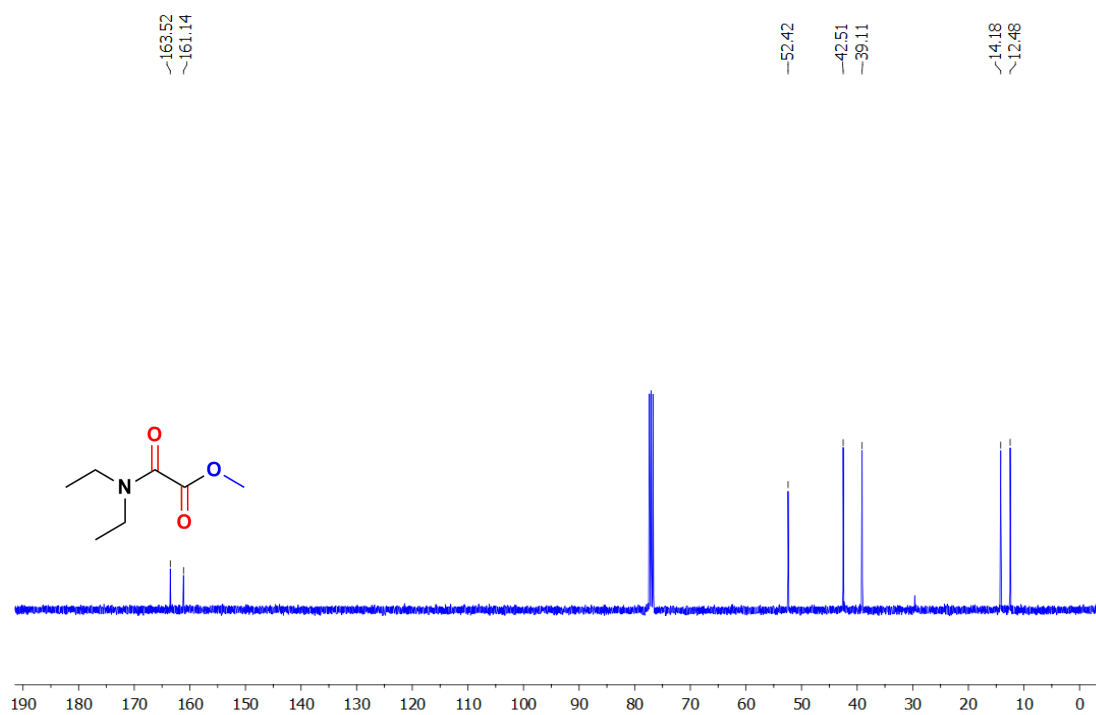
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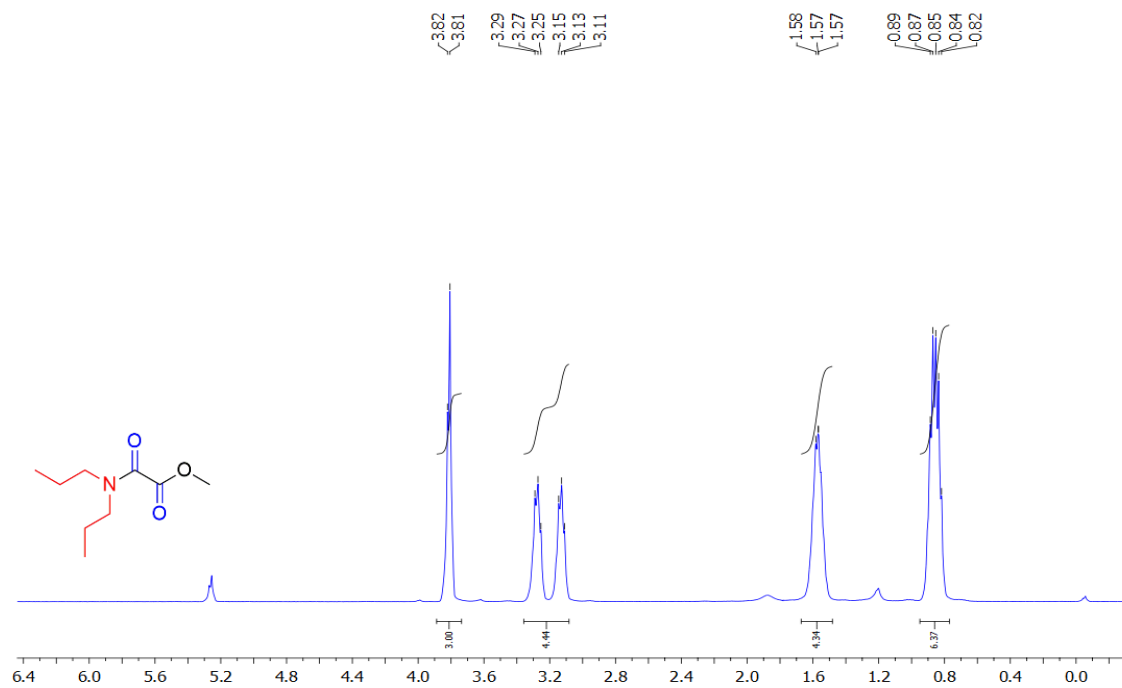
^1H NMR of Methyl 2-(diethyl amino)-2-oxoacetate (3g)



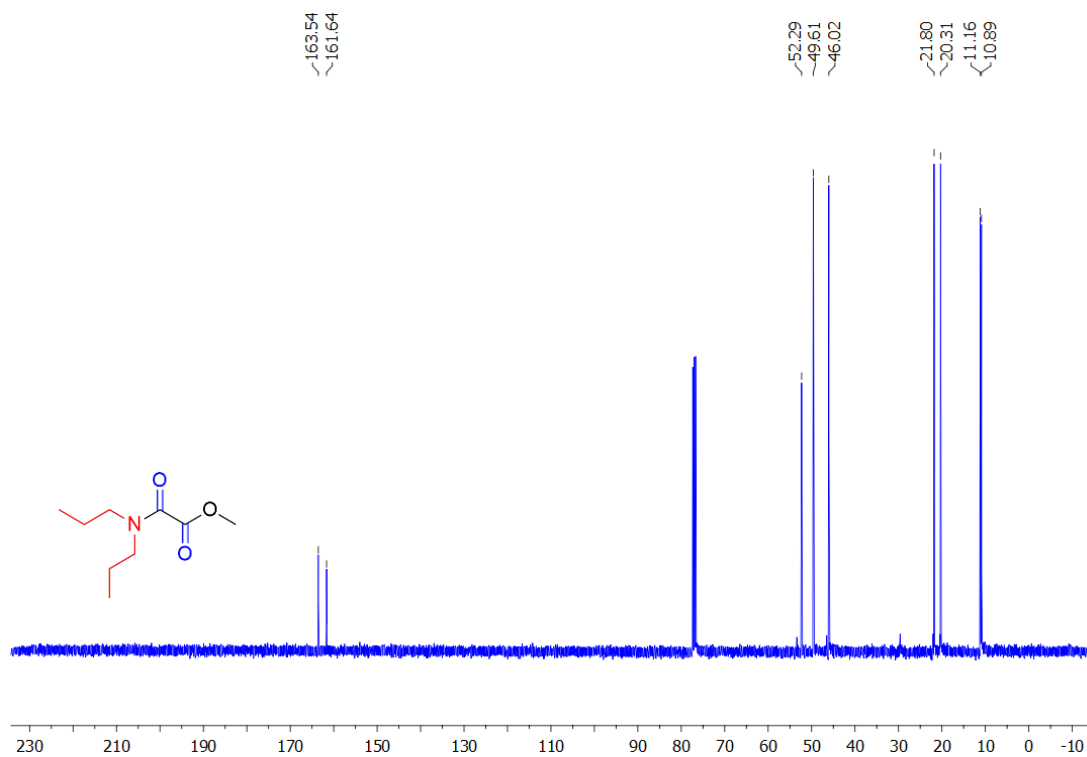
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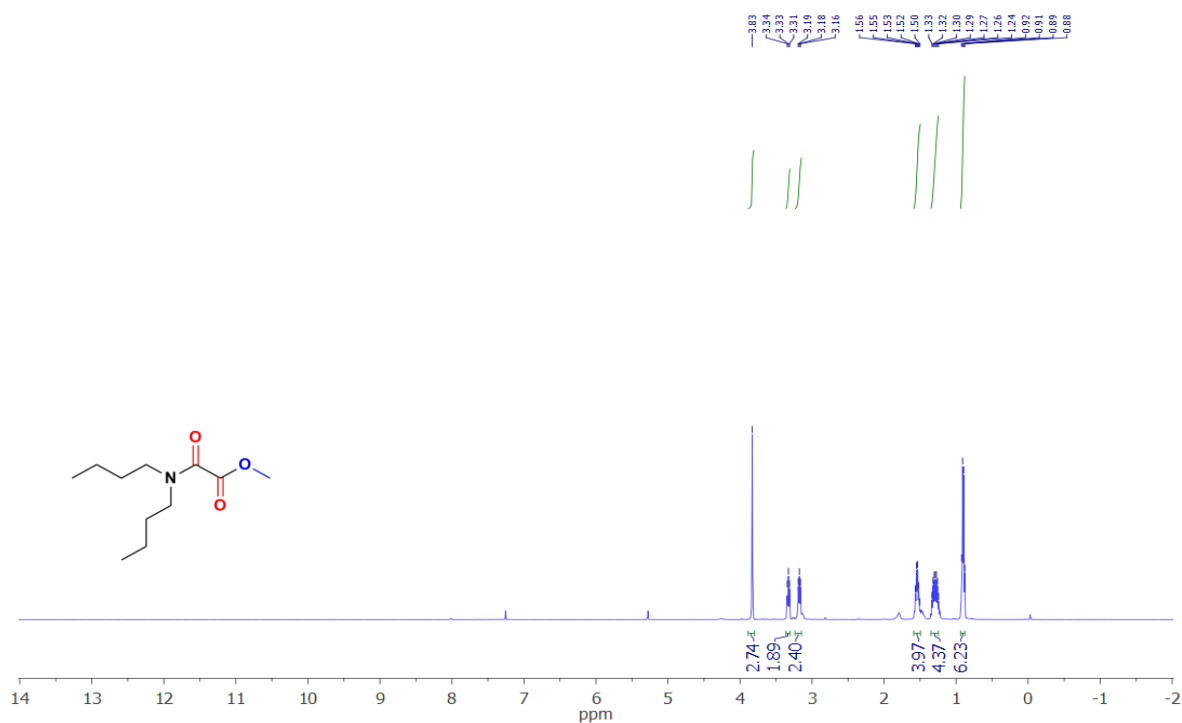
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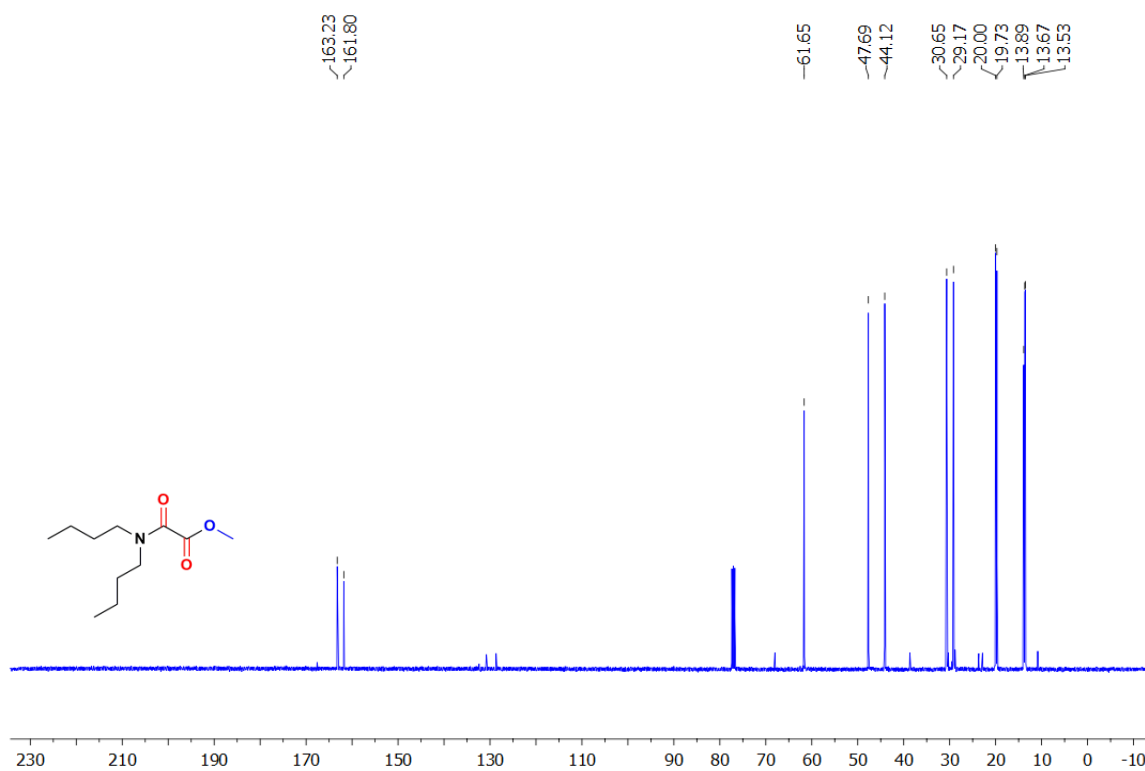
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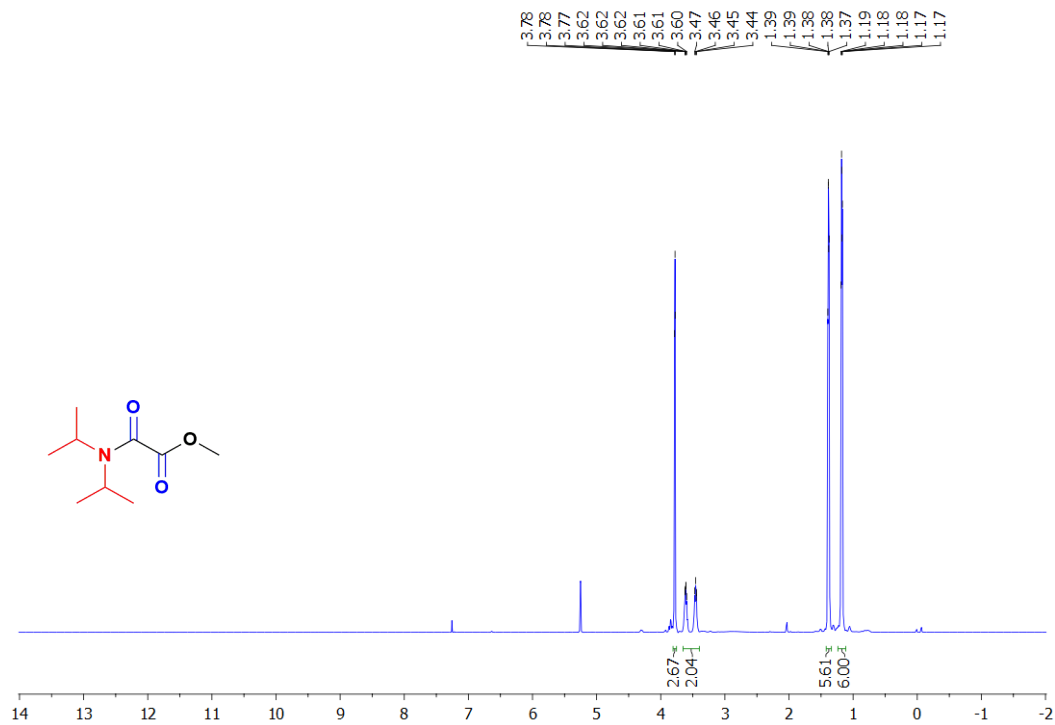
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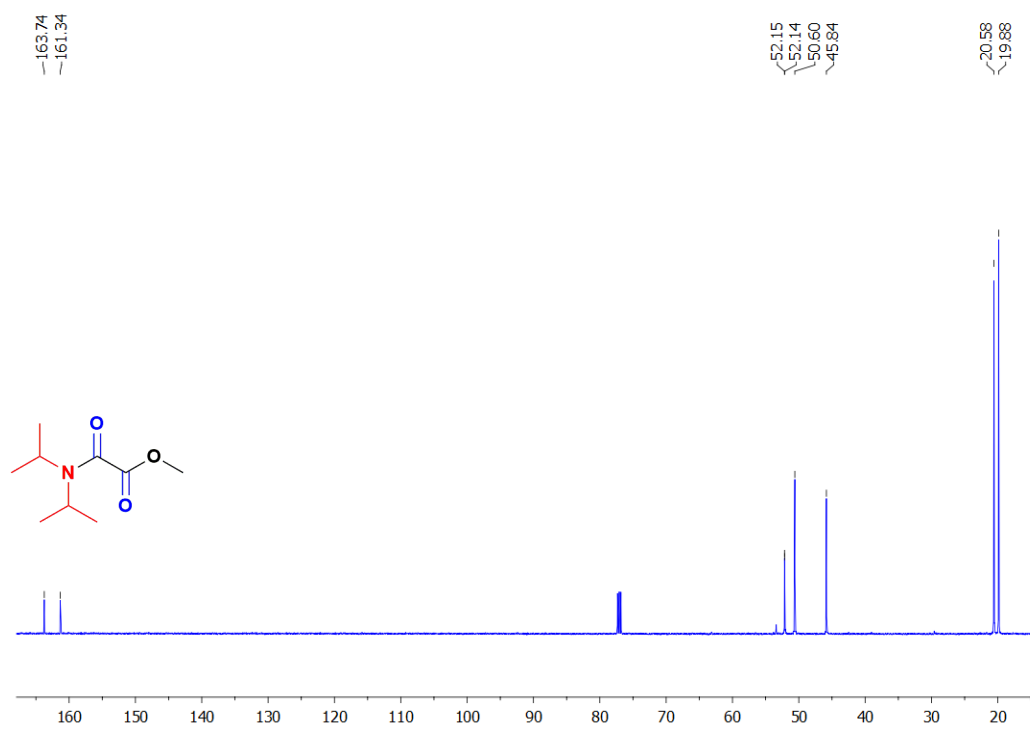
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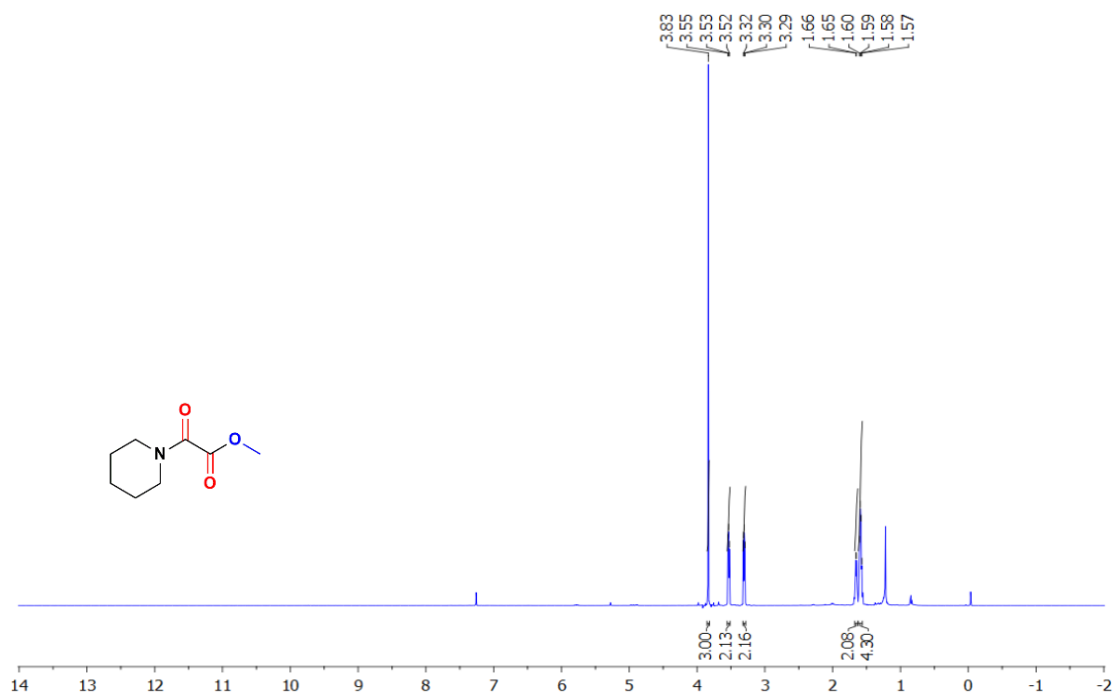
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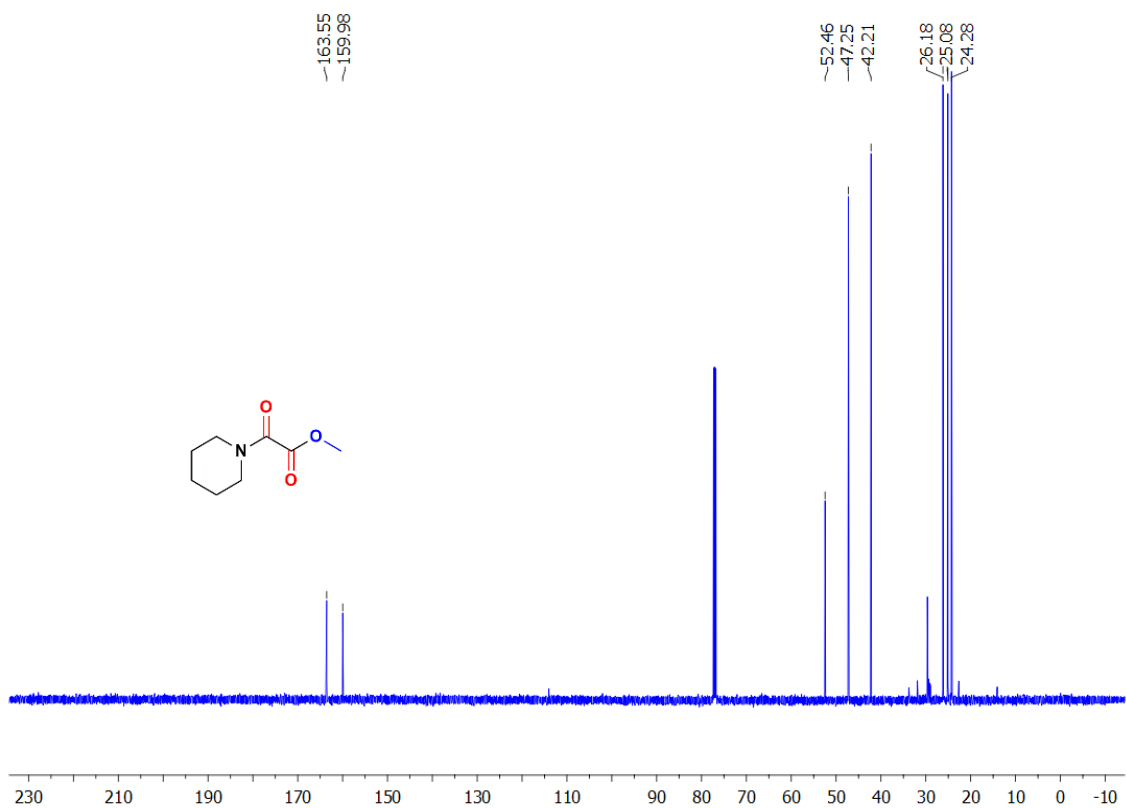
¹³C NMR Methyl 2-(diisopropyl amino)-2-oxoacetate (3j)



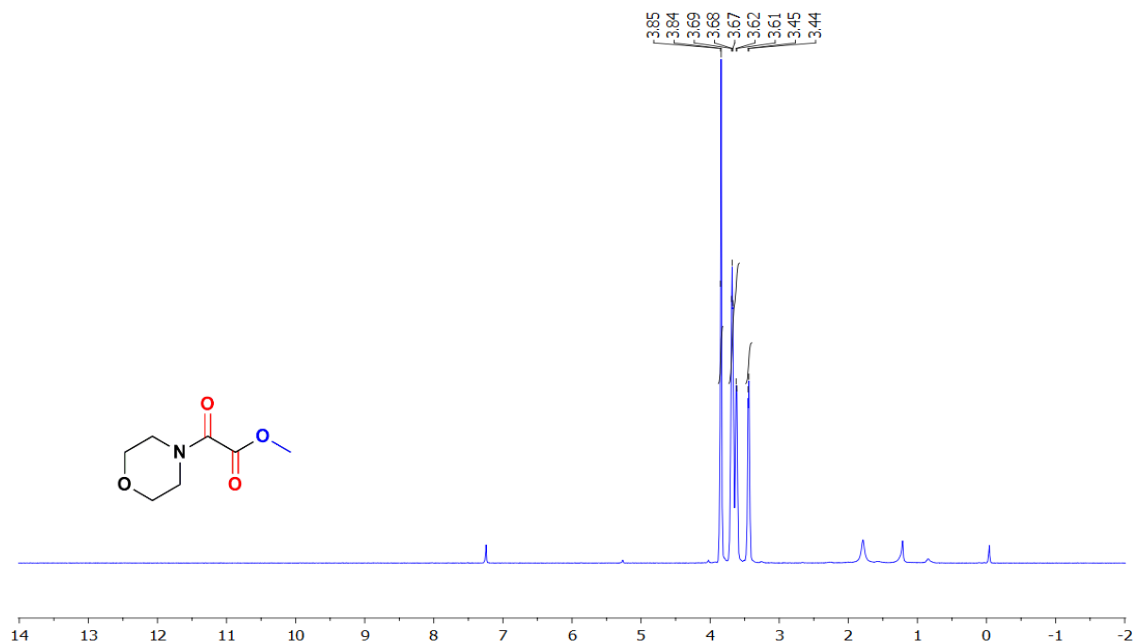
^1H NMR of Methyl 2-Oxo-2-(piperidine-1-yl) acetate (3k)



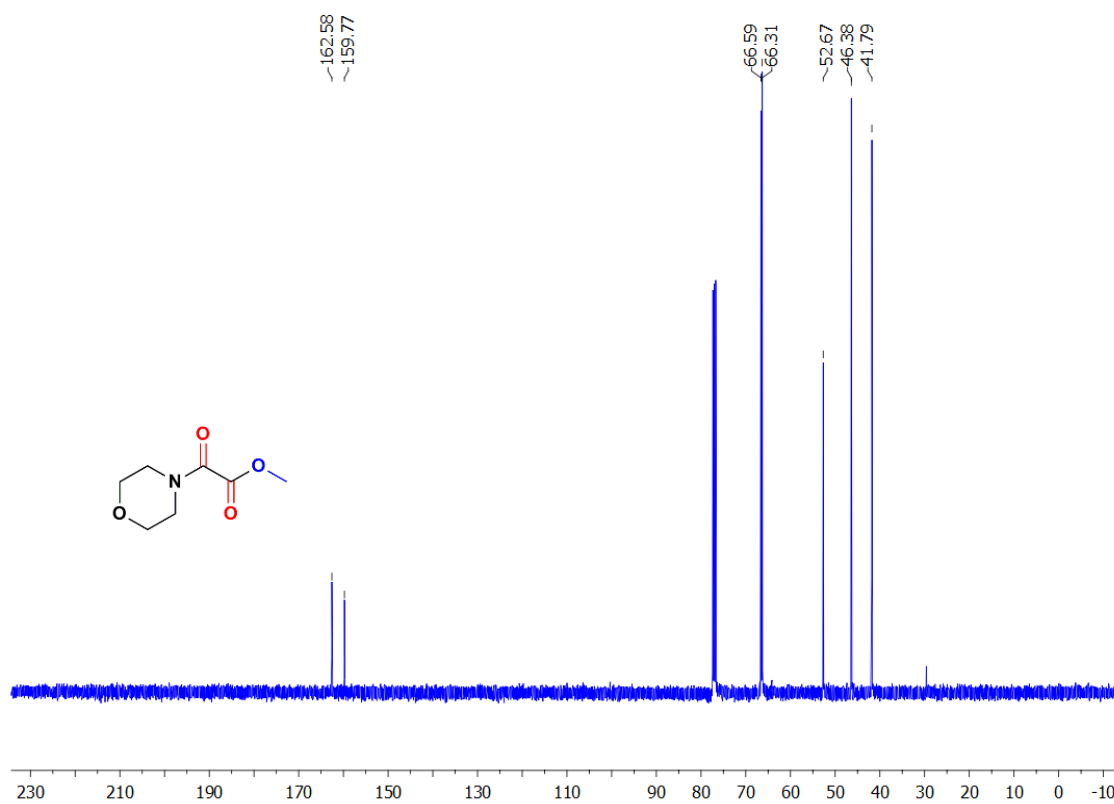
^{13}C NMR of Methyl 2-Oxo-2-(piperidine-1-yl) acetate (3k)



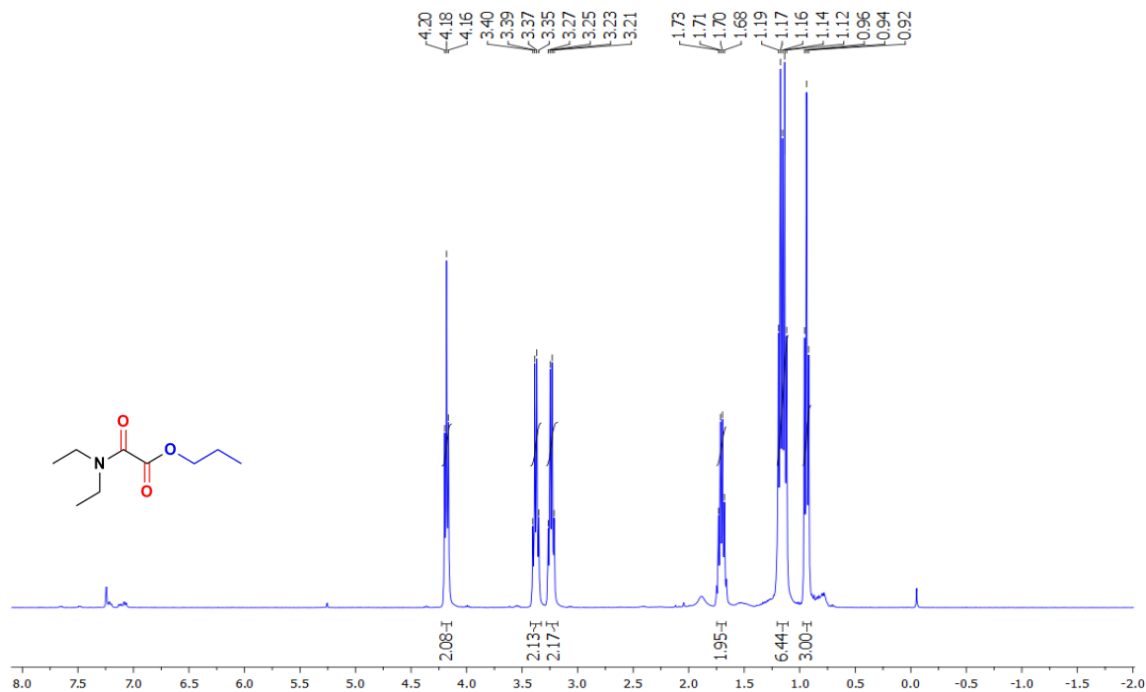
¹H NMR of Methyl 2-(morpholino amino)-2-oxoacetate (3m)



¹³C NMR of Methyl 2-(morpholino amino)-2-oxoacetate (3m)



¹H NMR of Propyl 2-(diethyl amino)-2-oxoacetate (3n)



¹³C NMR of Propyl 2-(diethyl amino)-2-oxoacetate (3n)

