

Supporting information

Biocompatible ionic liquid [Betaine][H₂PO₄] as reusable catalyst for substitution of xanthen-9-ol under solvent-free condition

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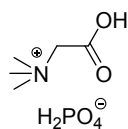
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1. General information

All of the reagents were purchased with AR grade and used without further purifications. ¹H-NMR and ¹³C-NMR spectra were recorded on Bruker AV-400 and AV-600 instrument using D₂O or CDCl₃ as solvent. Fourier Transform Infrared (FT-IR) spectra were measured using from KBr pellets using Perkin Elmer 400 FTIR spectrometer over the 4000-400 cm⁻¹ range at the resolution of 1 cm⁻¹. Melting Points were detected using melting point measurer (Sichuan University instrument factory) without correction.

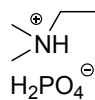
2. Selected spectra data for the utilized ionic liquids and substitution products

[Betaine][H₂PO₄]



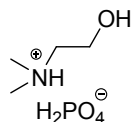
¹H NMR (400 MHz, D₂O) δ 4.03 (s, 2H), 3.25 (s, 9H) ppm; ¹³C NMR (100 MHz, D₂O) δ 168.1, 64.8, 53.5 ppm.

[DMEA][H₂PO₄]



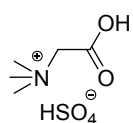
^1H NMR (400 MHz, D_2O) δ 3.01 (q, $J = 7.2$ Hz, 2H), 2.69 (s, 6H), 1.14 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 52.8, 41.9, 8.9 ppm.

[DMEOA][H_2PO_4]



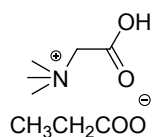
^1H NMR (400 MHz, D_2O) δ 3.67 - 3.65 (m, 2H), 3.06 - 3.03 (m, 2H), 2.68 (s, 6H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 58.5, 55.1, 42.6 ppm.

[Betaine][HSO_4]



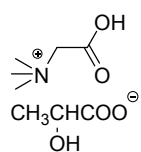
^1H NMR (400 MHz, D_2O) δ 4.19 (s, 2H), 3.25 (s, 9H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 166.9, 63.4, 53.8 ppm.

[Betaine][Pro]



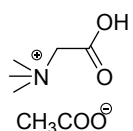
^1H NMR (400 MHz, D_2O) δ 3.82 (s, 2H), 3.18 (s, 9H), 2.30 (q, $J = 7.5$ Hz, 2H), 1.00 (t, $J = 7.6$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 179.6, 168.8, 66.1, 53.3, 27.3, 8.5 ppm.

[Betaine][Lac]



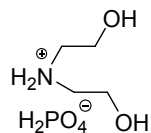
^1H NMR (400 MHz, D_2O) δ 4.23 (q, $J = 7.0$ Hz, 1H), 3.82 (s, 2H), 3.15 (s, 9H), 1.28 (d, $J = 7.0$ Hz, 3H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 178.7, 168.6, 66.5, 65.7, 53.3, 19.4 ppm.

[Betaine][Ac]



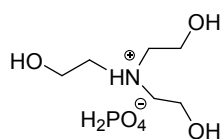
^1H NMR (400 MHz, D_2O) δ 3.82 (s, 2H), 3.18 (s, 9H), 2.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 176.7, 169.0, 66.1, 53.3, 20.5 ppm.

[DEA][H_2PO_4]



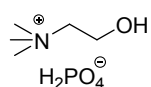
^1H NMR (400 MHz, D_2O) δ 3.53 - 3.33 (m, 4H), 2.89 - 2.69 (m, 4H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 56.2, 48.5 ppm.

[TEOA][H_2PO_4]



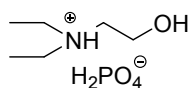
^1H NMR (400 MHz, D_2O) δ 3.91 (t, $J = 4.0$ Hz, 6H), 3.44 (t, $J = 4.0$ Hz, 6H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 55.2, 54.9 ppm.

[Choline][H_2PO_4]



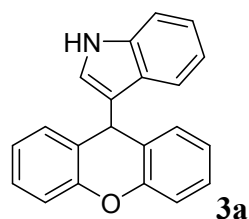
^1H NMR (400 MHz, D_2O) δ 4.00 - 3.96 (m, 2H), 3.45 - 3.43 (m, 2H), 3.12 (s, 9H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 67.3, 55.5, 53.8 ppm.

[DEEOA][H_2PO_4]



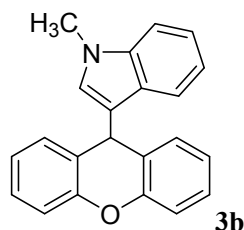
^1H NMR (400 MHz, D_2O) δ 3.88 - 3.85 (m, 2H), 3.28 - 3.20 (m, 6H), 1.27 (t, $J = 4.0$ Hz, 6H) ppm; ^{13}C NMR (150 MHz, D_2O) δ 55.2, 53.1, 47.5, 7.9 ppm.

3-(9H-Xanthen-9-yl)-1H-indole



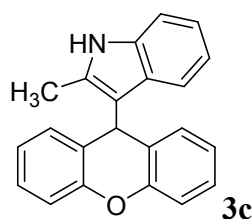
^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.21 - 6.88 (m, 11H), 5.55 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.4, 136.8, 129.5, 127.7, 125.9, 124.5, 123.1, 122.8, 122.2, 120.5, 119.7, 119.7, 116.3, 111.2, 35.5 ppm.

1-Methyl-3-(9H-xanthen-9-yl)-1H-indole



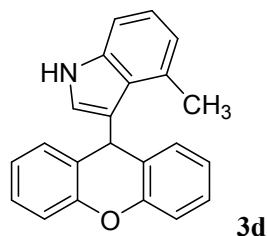
^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, 1H), 7.28 - 6.87 (m, 12H), 5.53 (s, 1H), 3.74 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 137.4, 129.5, 129.5, 127.6, 127.6, 127.5, 126.4, 124.8, 123.1, 123.1, 121.7, 119.7, 119.2, 119.1, 116.3, 109.3, 35.4, 32.7 ppm.

2-Methyl-3-(9H-xanthen-9-yl)-1H-indole



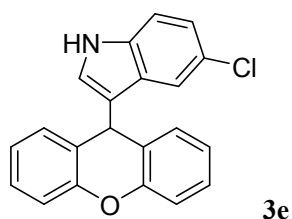
^1H NMR (400 MHz, CDCl_3) δ 7.83 (s, 1H), 7.28 - 6.80 (m, 12H), 5.61 (s, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 135.4, 132.3, 129.4, 127.6, 124.1, 123.1, 121.2, 119.5, 118.9, 116.2, 115.3, 110.3, 33.7, 12.0 ppm.

4-Methyl-3-(9H-xanthen-9-yl)-1H-indole



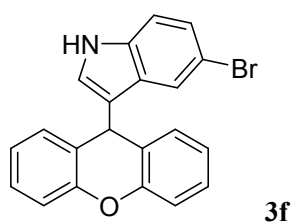
^1H NMR (600 MHz, CDCl_3) δ 8.16 (s, 1H), 7.24 - 6.67 (m, 12H), 5.74 (s, 1H), 2.01 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 150.9, 131.1, 129.2, 127.7, 126.2, 125.6, 123.1, 122.4, 121.7, 116.2, 109.1, 36.1, 29.8, 21.3 ppm.

5-Chloro-3-(9H-xanthen-9-yl)-1H-indole



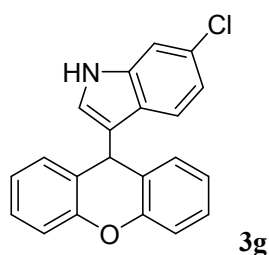
^1H NMR (600 MHz, CDCl_3) δ 8.06 (s, 1H), 7.32 - 6.89 (m, 12H), 5.51 (s, 1H) ppm;
 ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 135.1, 129.3, 127.9, 126.9, 125.4, 124.3, 124.1, 123.2, 122.6, 120.2, 119.1, 116.5, 112.3, 35.4 ppm.

5-Bromo-3-(9H-xanthen-9-yl)-1H-indole



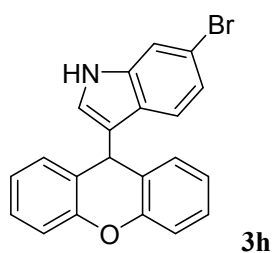
^1H NMR (600 MHz, CDCl_3) δ 8.05 (s, 1H), 7.50 (s, 1H), 7.25 - 6.95 (m, 12H), 5.51 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 135.3, 129.2, 127.9, 127.6, 125.2, 124.1, 123.2, 122.1, 120.2, 116.5, 113.0, 112.7, 35.4 ppm.

6-Chloro-3-(9H-xanthen-9-yl)-1H-indole



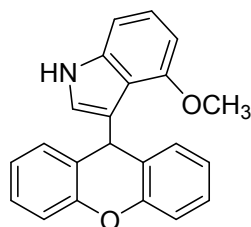
^1H NMR (600 MHz, CDCl_3) δ 7.99 (s, 1H), 7.32 (d, 1H), 7.24 - 7.05 (m, 8H), 6.96 - 6.89 (m, 3H), 5.51 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 137.2, 129.3, 128.2, 127.9, 124.4, 124.0, 123.3, 123.2, 120.6, 120.5, 120.5, 116.4, 111.2, 35.5 ppm.

6-Bromo-3-(9H-xanthen-9-yl)-1H-indole



^1H NMR (600 MHz, CDCl_3) δ 7.98 (s, 1H), 7.47 (s, 1H), 7.18 (m, 5H), 7.12 - 7.02 (m, 4H), 6.93 (m, 2H), 5.51 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 137.6, 129.3, 127.9, 124.7, 123.9, 123.3, 123.2, 123.0, 120.9, 120.5, 116.4, 115.9, 114.12, 35.5 ppm.

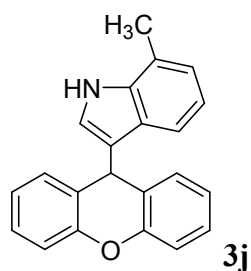
4-Methoxy-3-(9H-xanthen-9-yl)-1H-indole



3i

^1H NMR (600 MHz, CDCl_3) δ 7.92 (s, 1H), 7.25 - 7.05 (m, 7H), 6.96 - 6.89 (m, 3H), 6.73 (s, 1H), 6.49 (d, $J = 7.8$ Hz, 1H), 5.99 (s, 1H), 3.83 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 154.6, 151.0, 137.9, 129.8, 127.1, 126.2, 122.9, 122.8, 122.1, 116.4, 116.0, 104.4, 99.9, 54.8, 35.3 ppm.

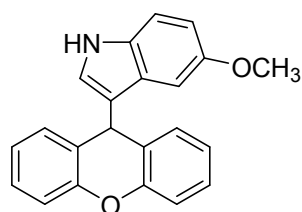
7-Methyl-3-(9H-xanthen-9-yl)-1H-indole



3j

^1H NMR (600 MHz, CDCl_3) δ 7.92 (s, 1H), 7.25 - 6.89 (m, 12H), 5.56 (s, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 136.3, 129.5, 127.7, 125.4, 124.5, 123.1, 122.7, 122.5, 121.0, 120.3, 119.9, 117.5, 116.3, 35.6, 16.6 ppm.

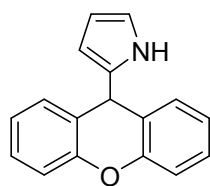
5-Methoxy-3-(9H-xanthen-9-yl)-1H-indole



3l

^1H NMR (600 MHz, CDCl_3) δ 7.89 (s, 1H), 7.24 - 6.76 (m, 12H), 5.52 (s, 1H), 3.69 (s, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 153.9, 151.4, 131.9, 129.5, 127.7, 126.4, 124.4, 123.3, 123.1, 120.4, 116.3, 112.2, 111.8, 101.5, 55.7, 35.6 ppm.

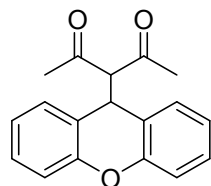
2-(9H-xanthen-9-yl)-1H-pyrrole



3m

^1H NMR (600 MHz, CDCl_3) δ 7.68 (s, 1H), 7.23 (dd, $J = 14.4, 6.6$ Hz, 3H), 7.13 (dd, $J = 22.8, 7.8$ Hz, 4H), 7.02 (t, $J = 7.2$ Hz, 2H), 6.62 (s, 1H), 6.19 - 6.09 (m, 2H), 5.36 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 151.3, 134.2, 129.4, 128.2, 123.4, 122.9, 118.1, 116.7, 108.0, 107.3, 37.3 ppm.

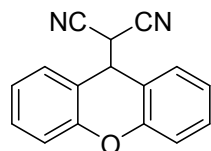
3-(9H-xanthen-9-yl)pentane-2,4-dione



3n

^1H NMR (400 MHz, CDCl_3): δ 1.87 (s, 6H), 4.08 - 4.11 (d, 1H, CH), 4.83 - 4.86 (d, 1H, CH), 7.02 - 7.27 (m, 8H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 201.7, 153.3, 129.1, 128.4, 123.7, 123.4, 116.8, 73.8, 40.2, 31.8 ppm.

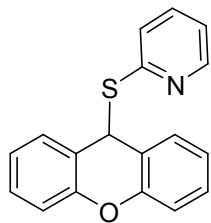
2-(9H-xanthen-9-yl)malononitrile



3o

^1H NMR (600 MHz, CDCl_3) δ 7.46 (d, $J = 7.8$ Hz, 2H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.26 - 7.19 (m, 4H), 4.67 (d, $J = 6.0$ Hz, 1H), 3.84 (d, $J = 6.0$ Hz, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 152.6, 130.5, 129.1, 124.3, 117.5, 117.3, 111.3, 41.6, 32.9 ppm.

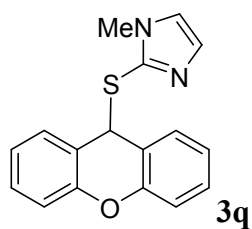
2-(9H-xanthen-9-ylthio)pyridine



3p

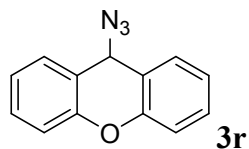
^1H NMR (400 MHz, CDCl_3) δ 8.58 (d, $J = 4.5$ Hz, 1H), 7.50 - 7.47 (m, 3H), 7.24 - 7.21 (m, 2H), 7.11 - 7.01 (m, 6H), 6.78 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 152.2, 149.3, 136.4, 129.4, 128.7, 123.4, 123.3, 122.3, 120.6, 116.6, 41.3 ppm.

1-Methyl-2-(9H-xanthen-9-ylsulfanyl)-1H-imidazole

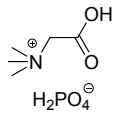


^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.18 (d, $J = 8.3$ Hz, 2H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.53 (d, $J = 2.2$ Hz, 1H), 6.28 (d, $J = 2.2$ Hz, 1H), 3.66 (s, 3H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 162.9, 151.2, 129.9, 129.8, 123.9, 119.3, 118.8, 116.8, 114.9, 51.6, 35.1 ppm.

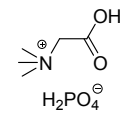
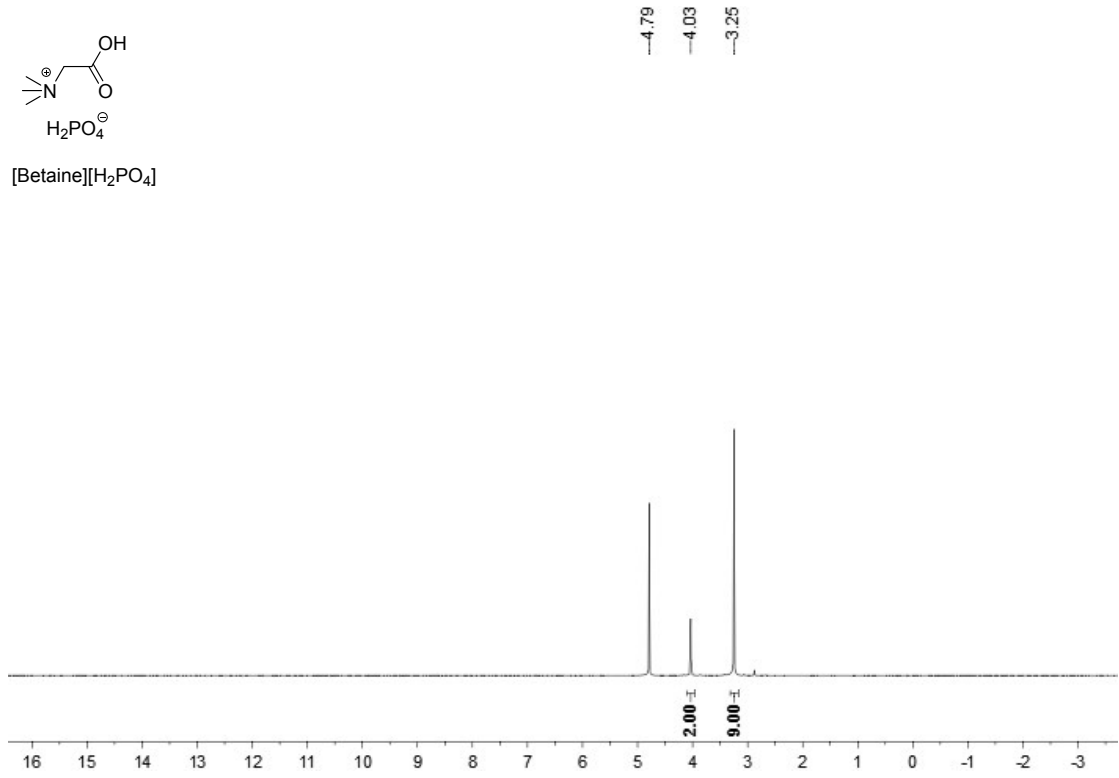
9-Azido-9H-xanthene



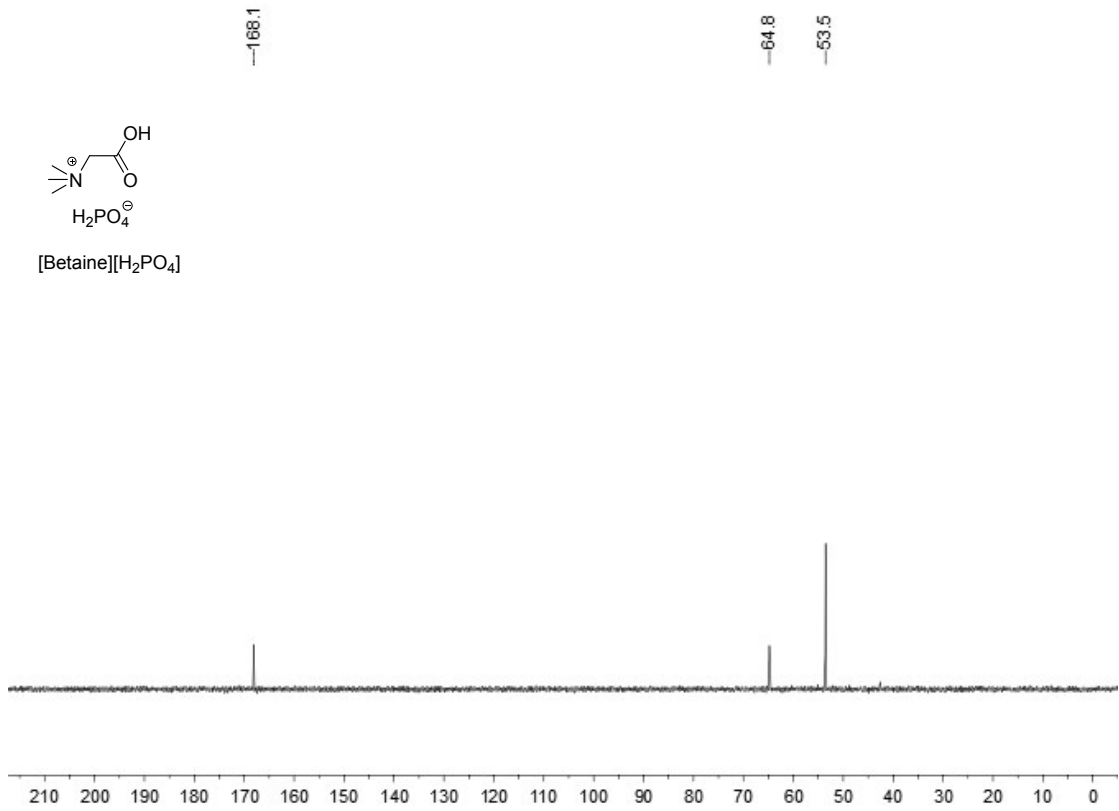
^1H NMR (400 MHz, CDCl_3) δ 7.51 - 7.37 (m, 4H), 7.23 - 7.19 (m, 4H), 5.58 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 133.3, 131.4, 129.1, 128.5, 127.0, 126.7, 65.2 ppm.

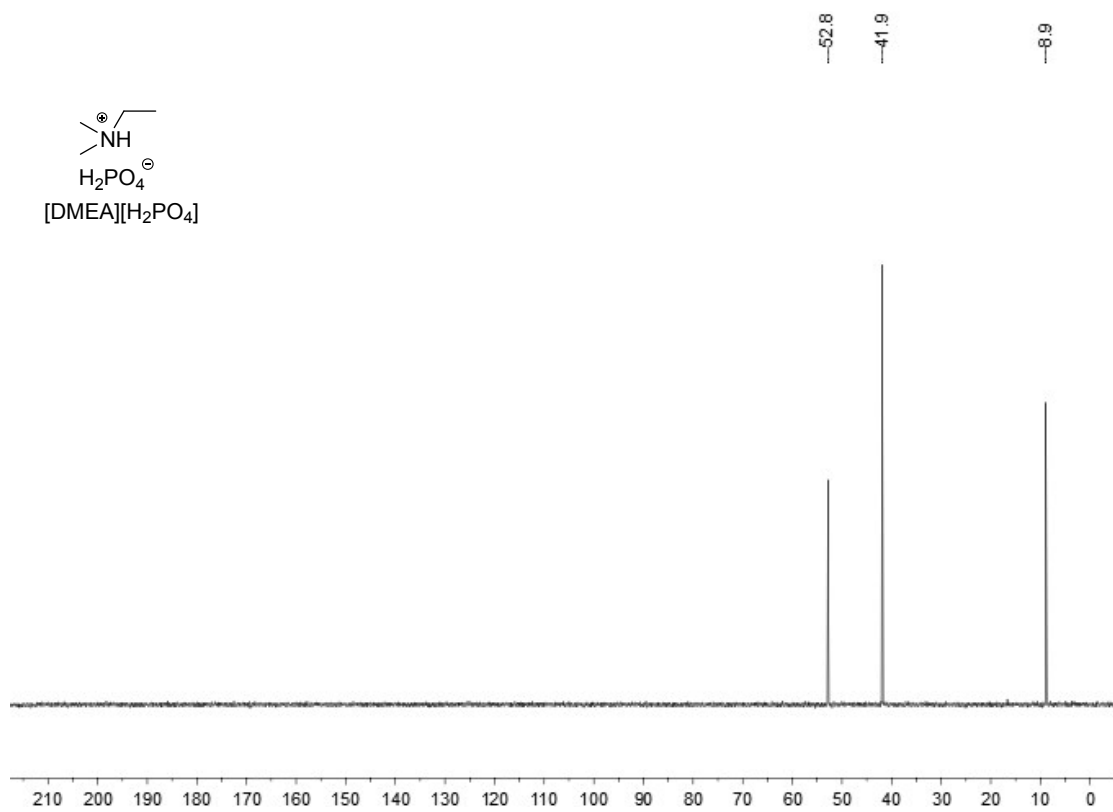
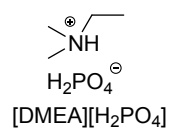
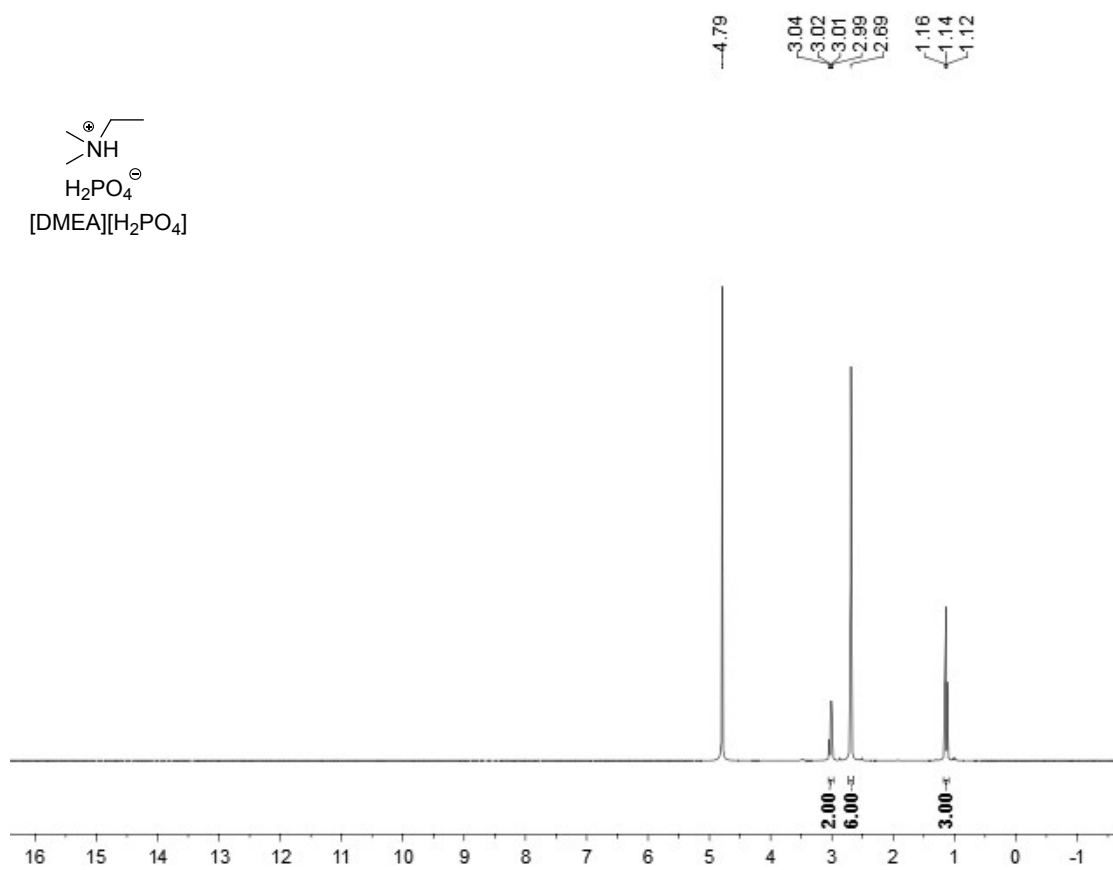
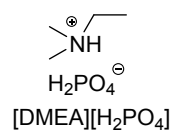


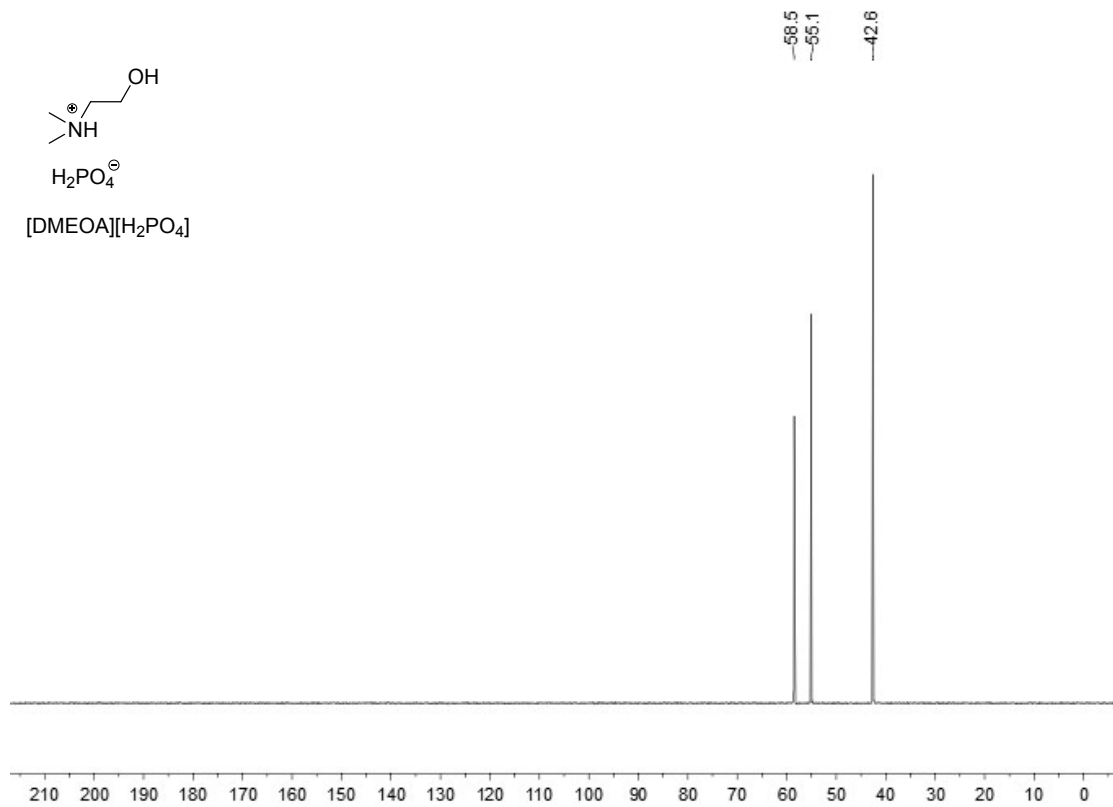
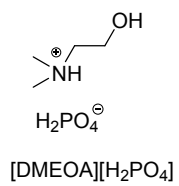
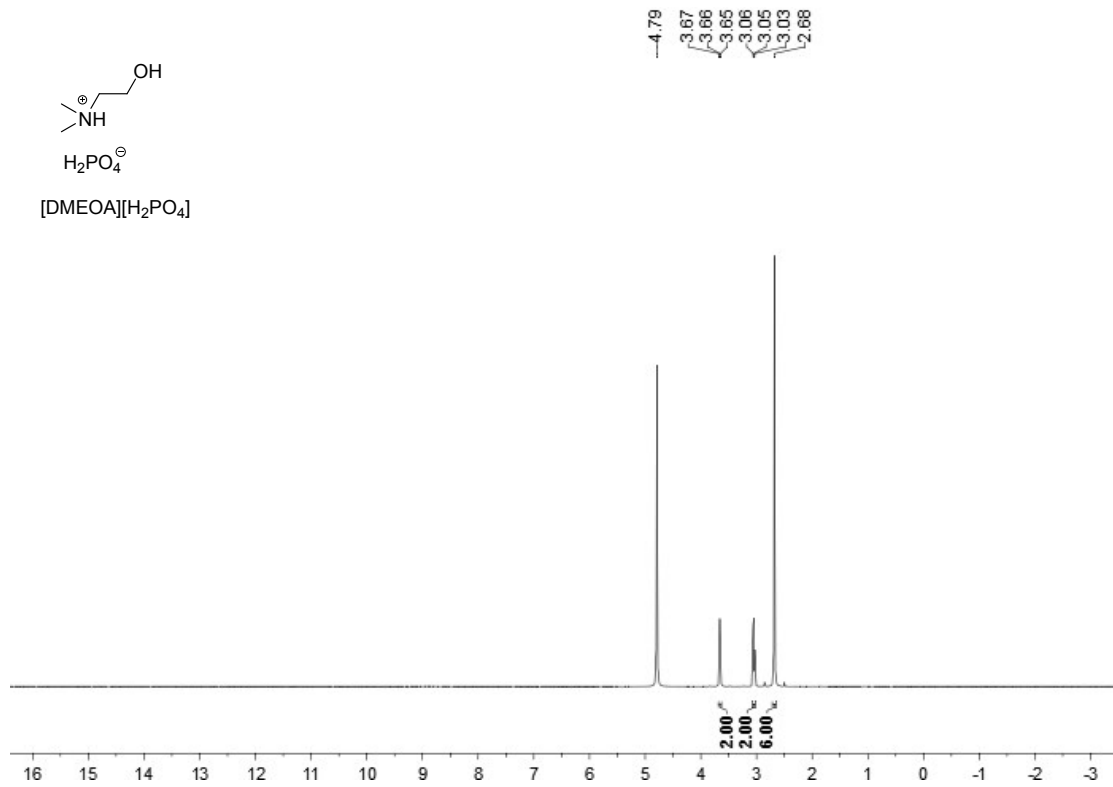
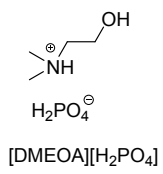
[Betaine][H₂PO₄]

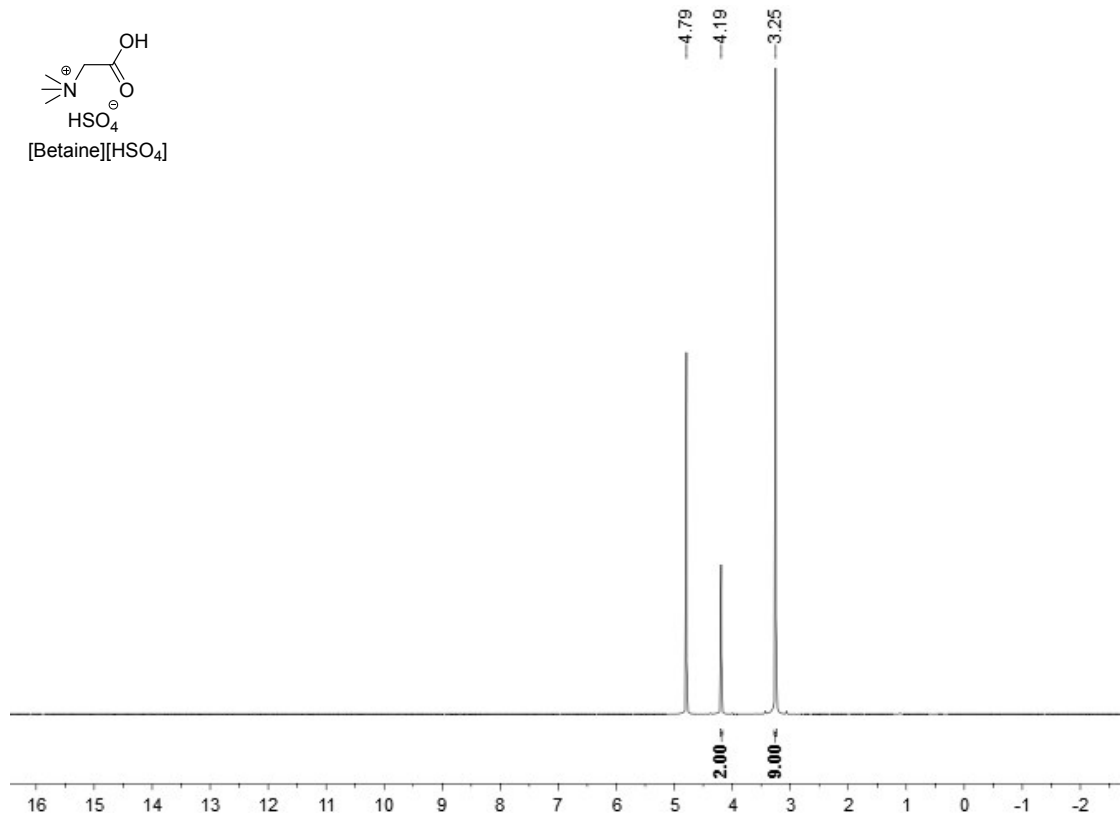
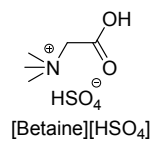


[Betaine][H₂PO₄]





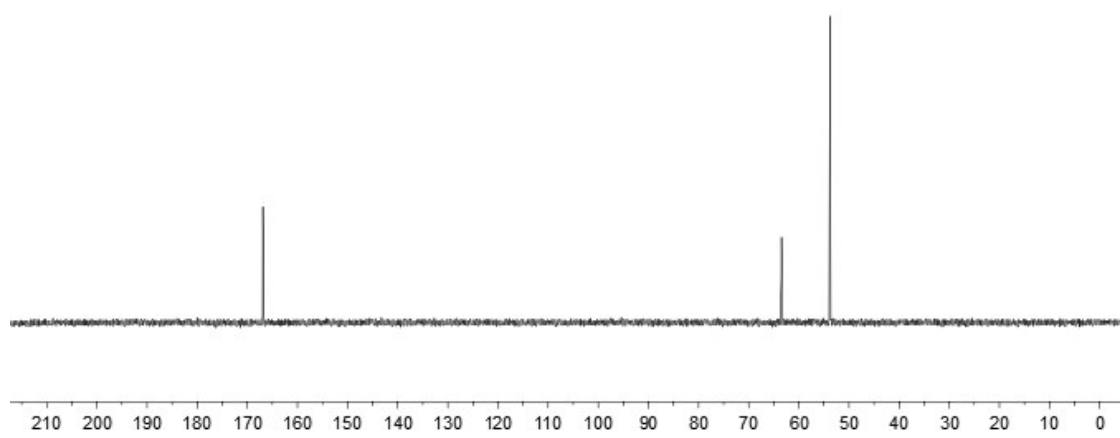
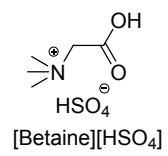


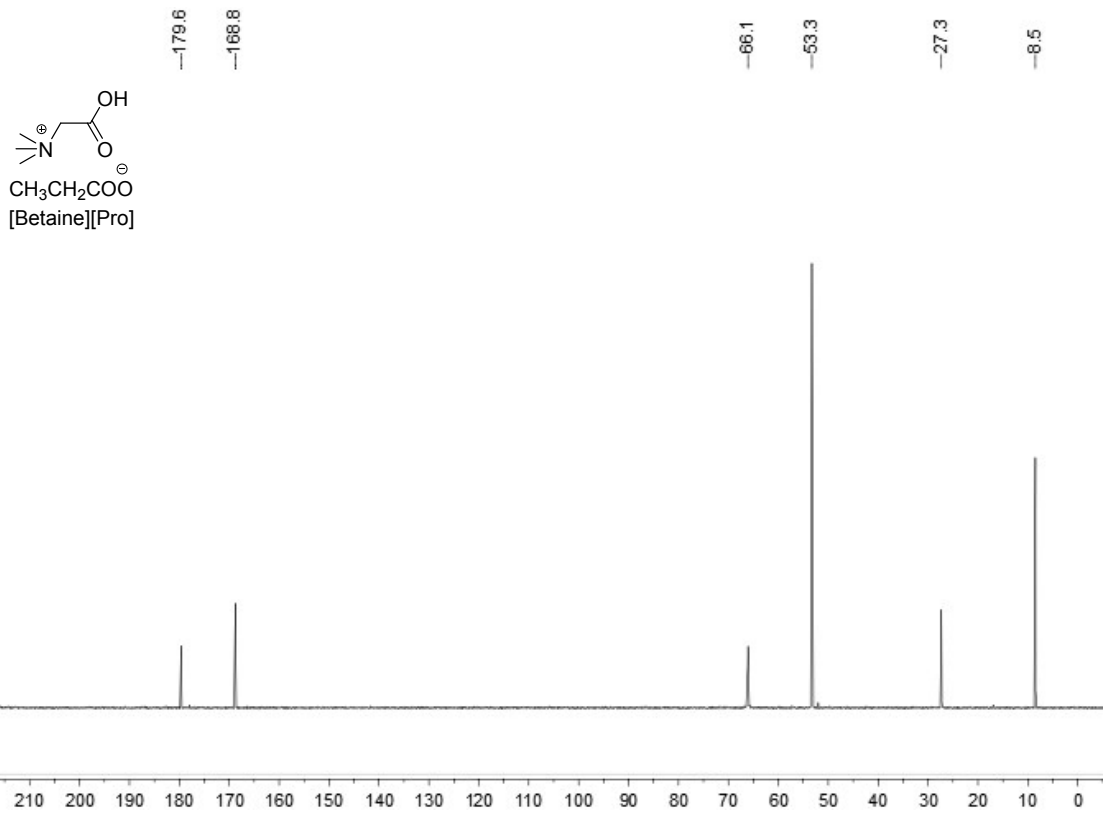
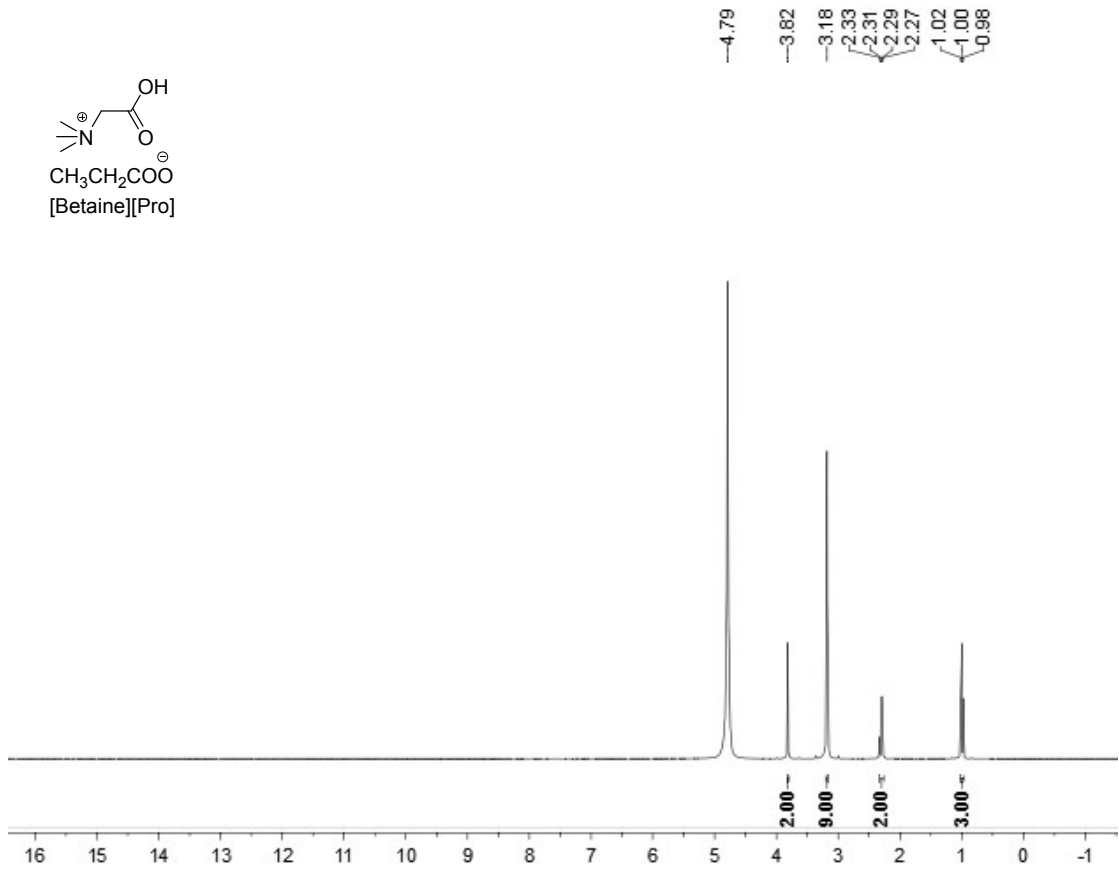
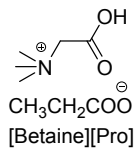


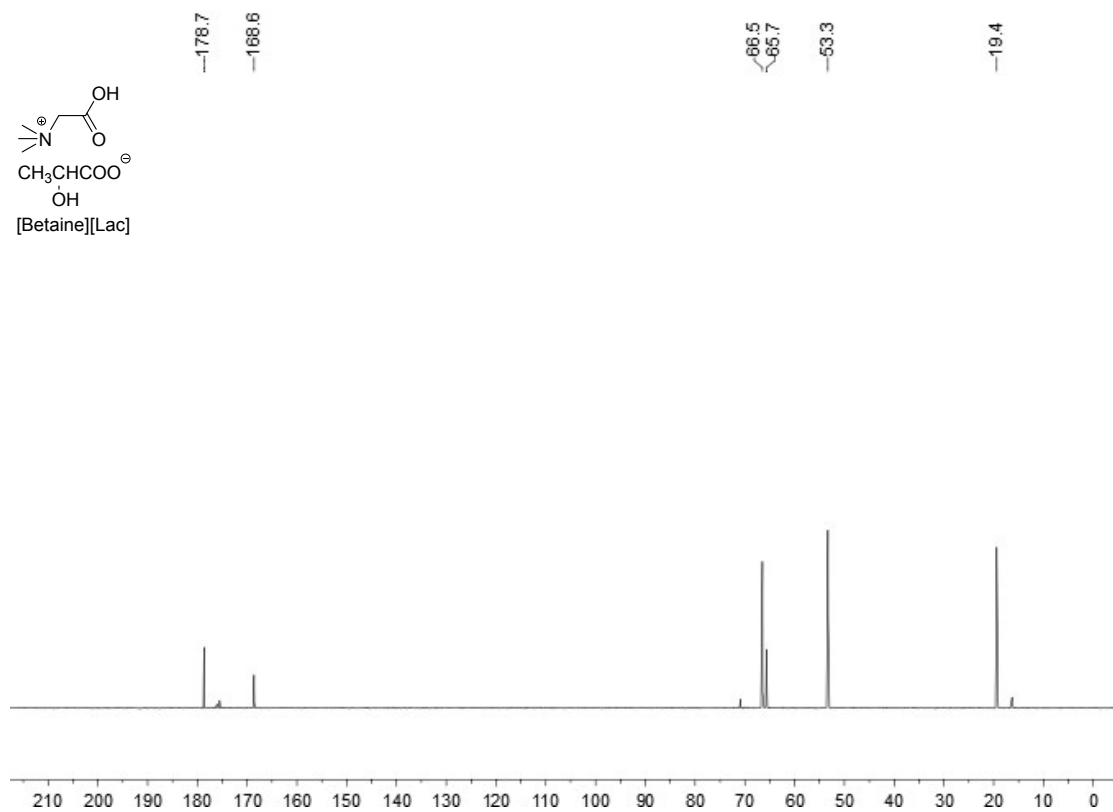
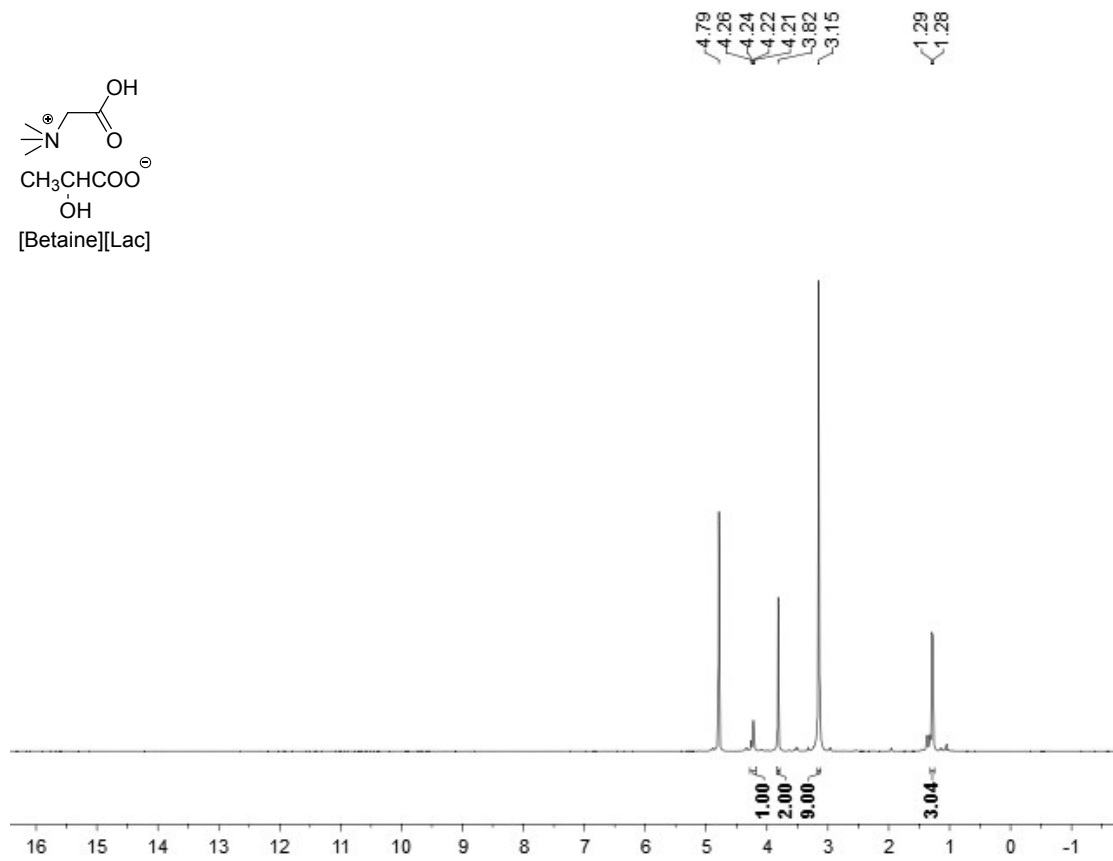
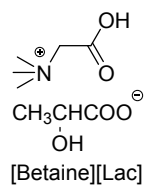
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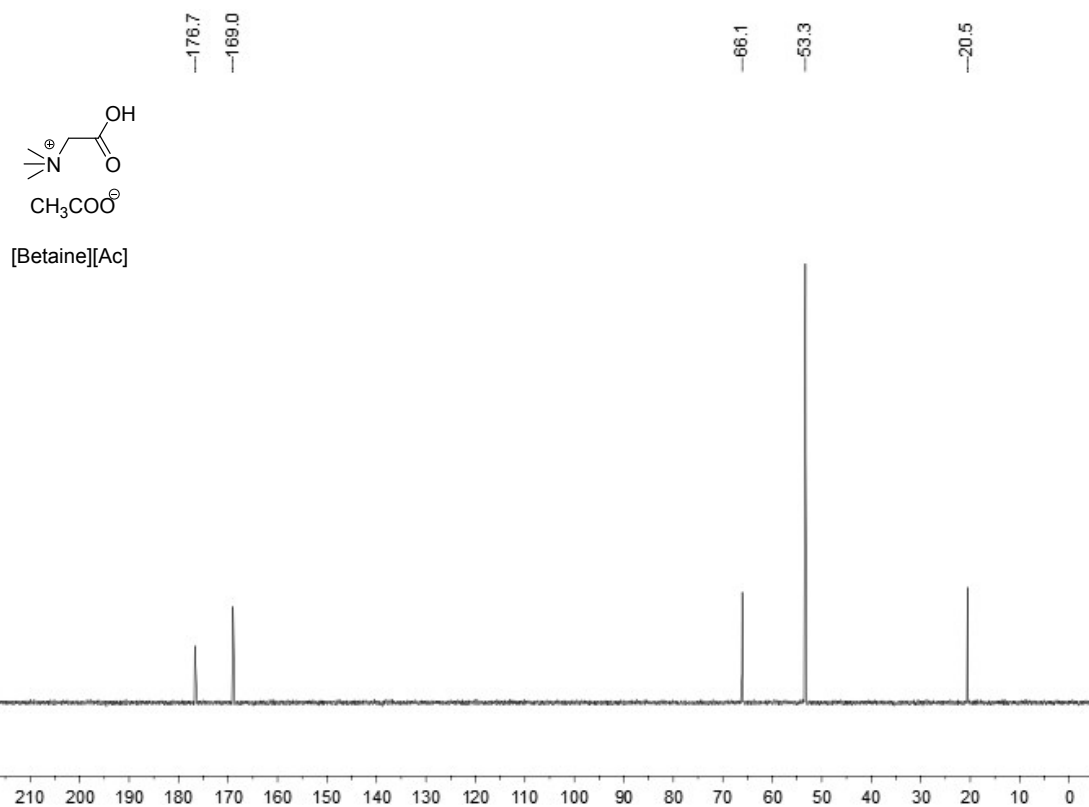
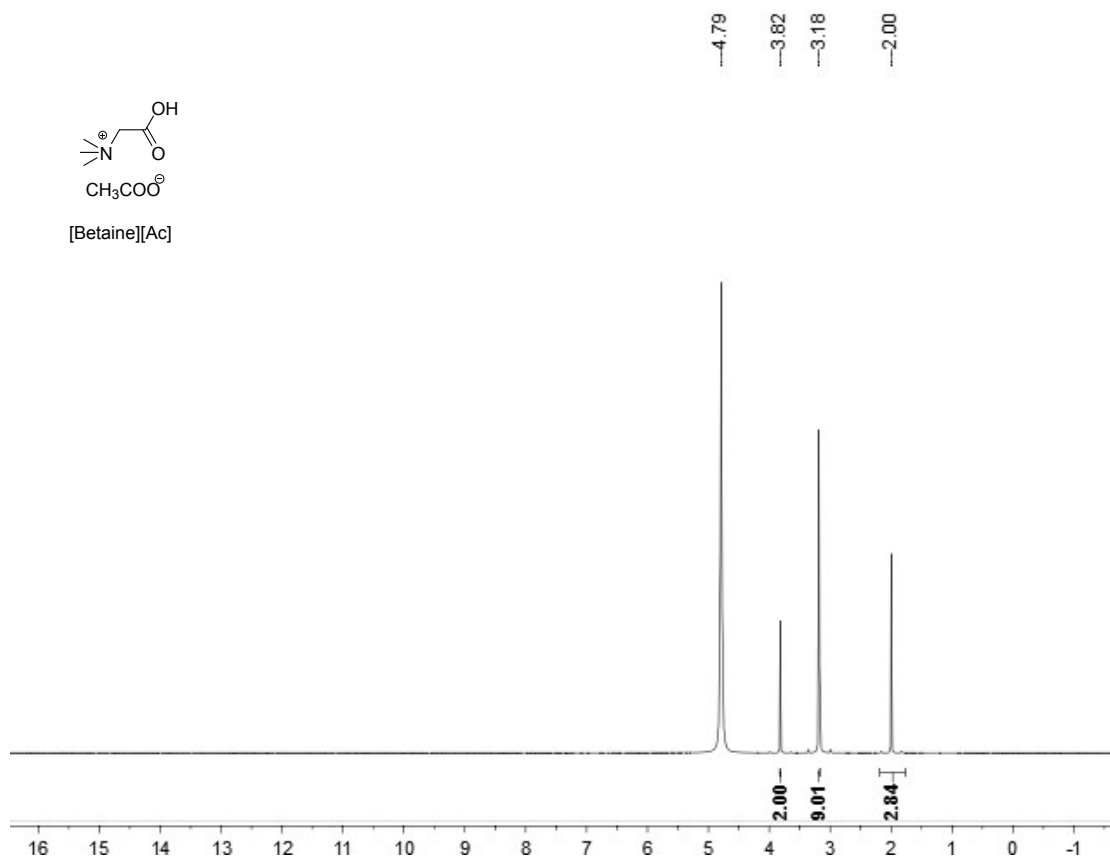
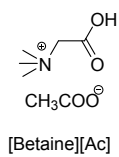
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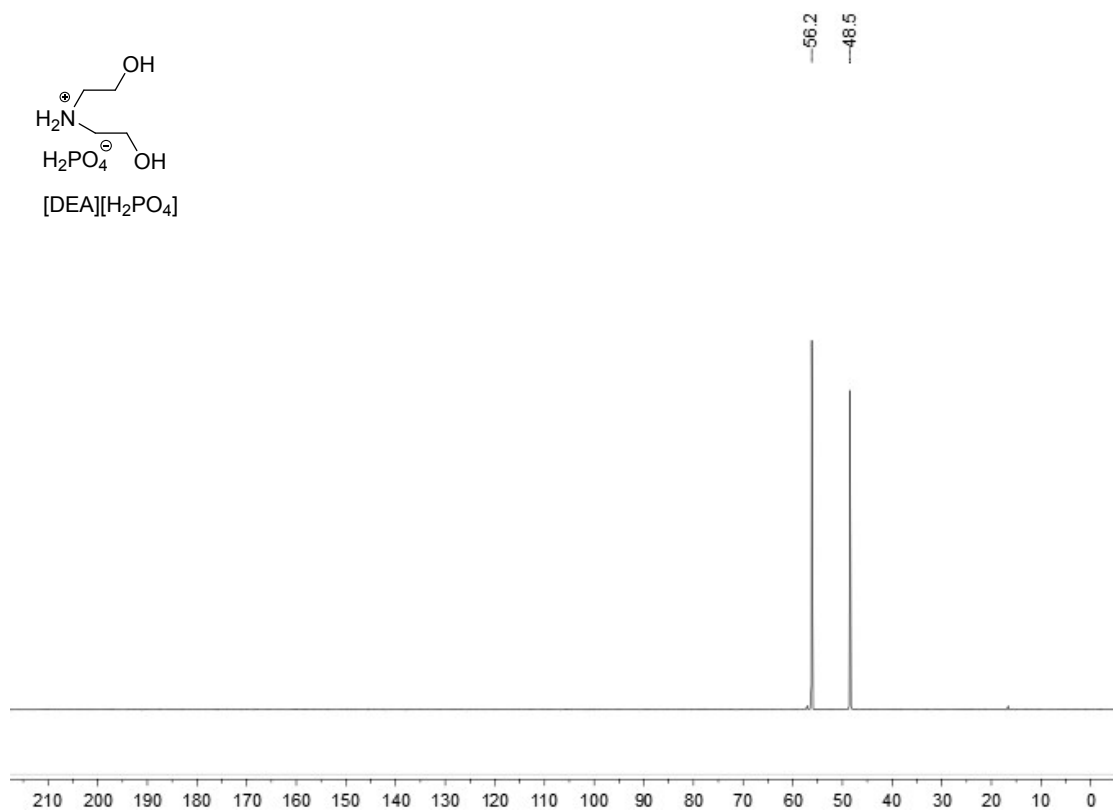
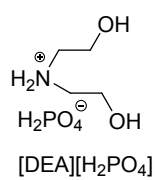
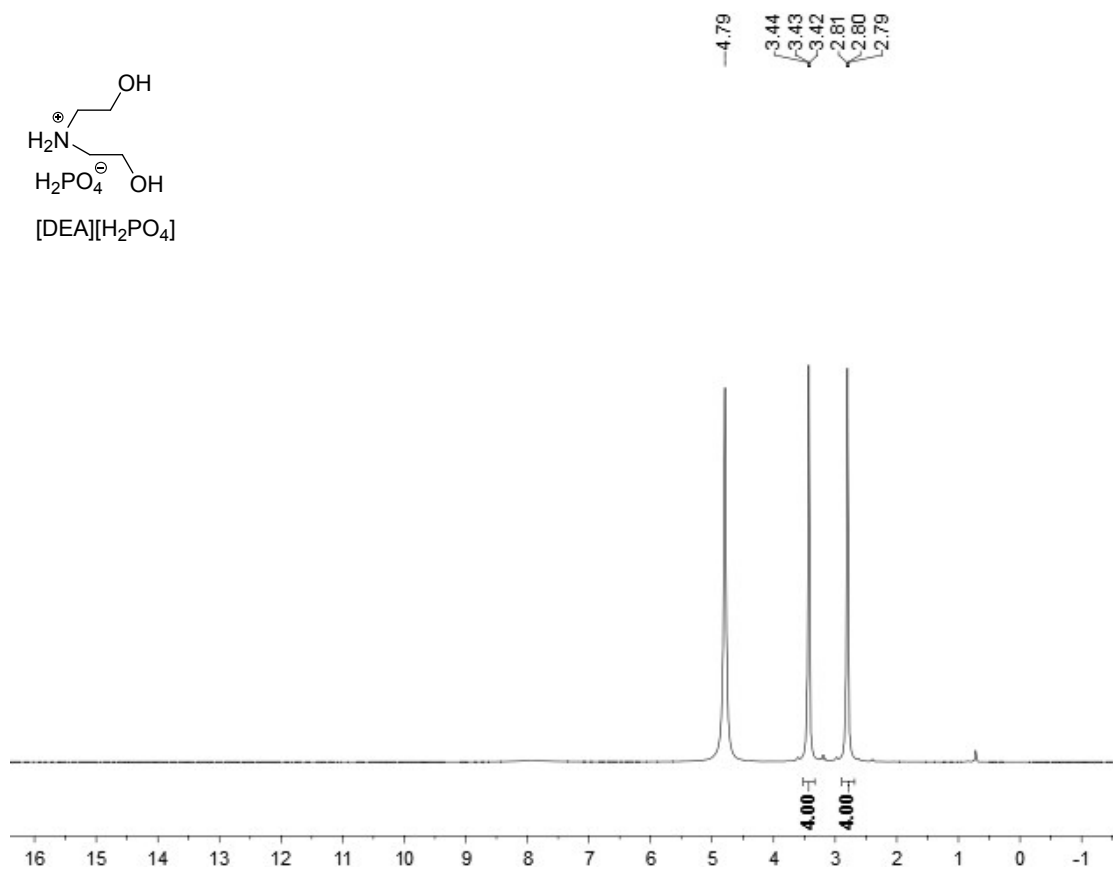
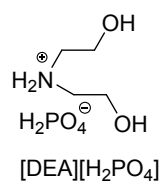
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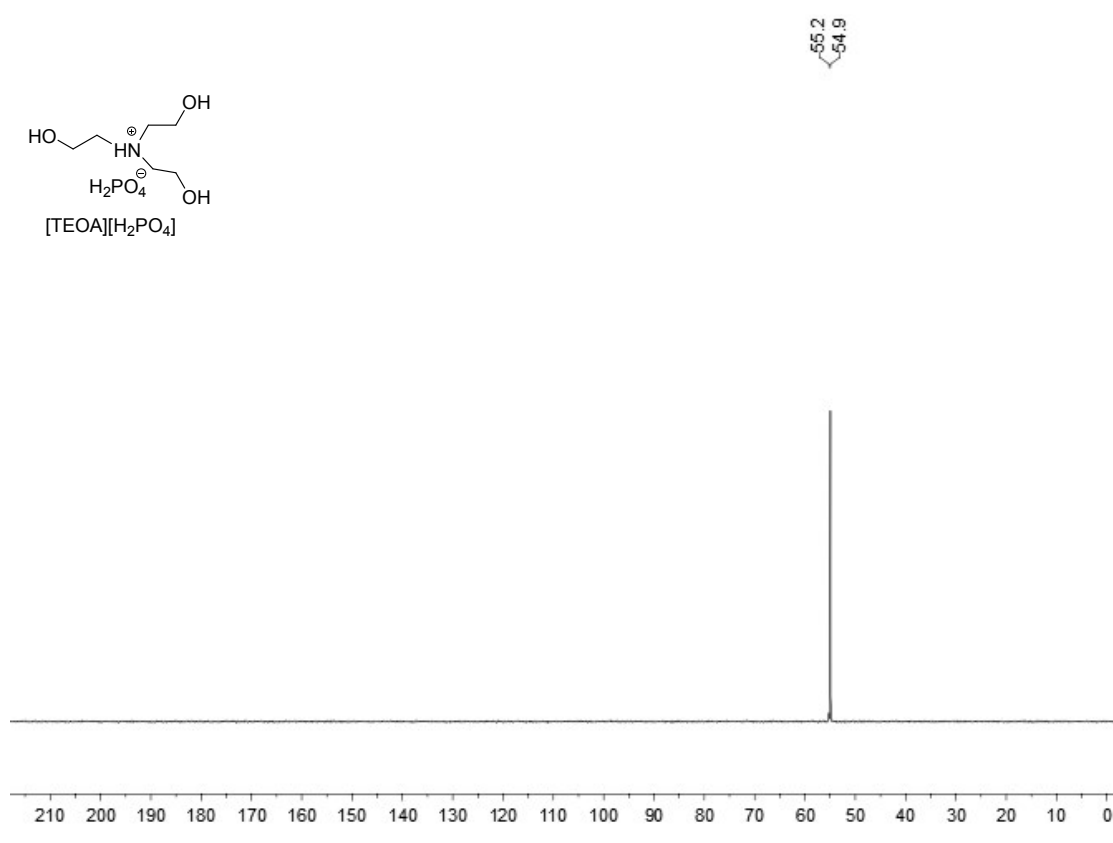
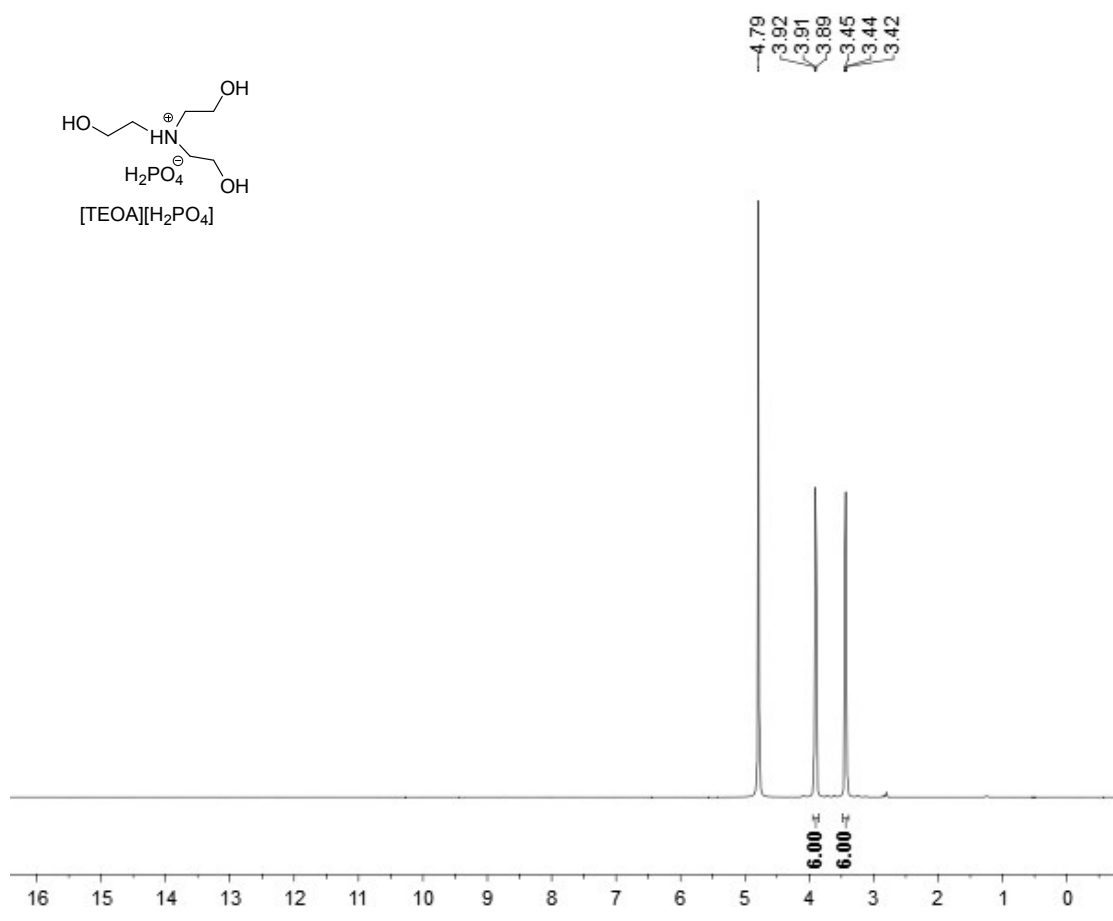


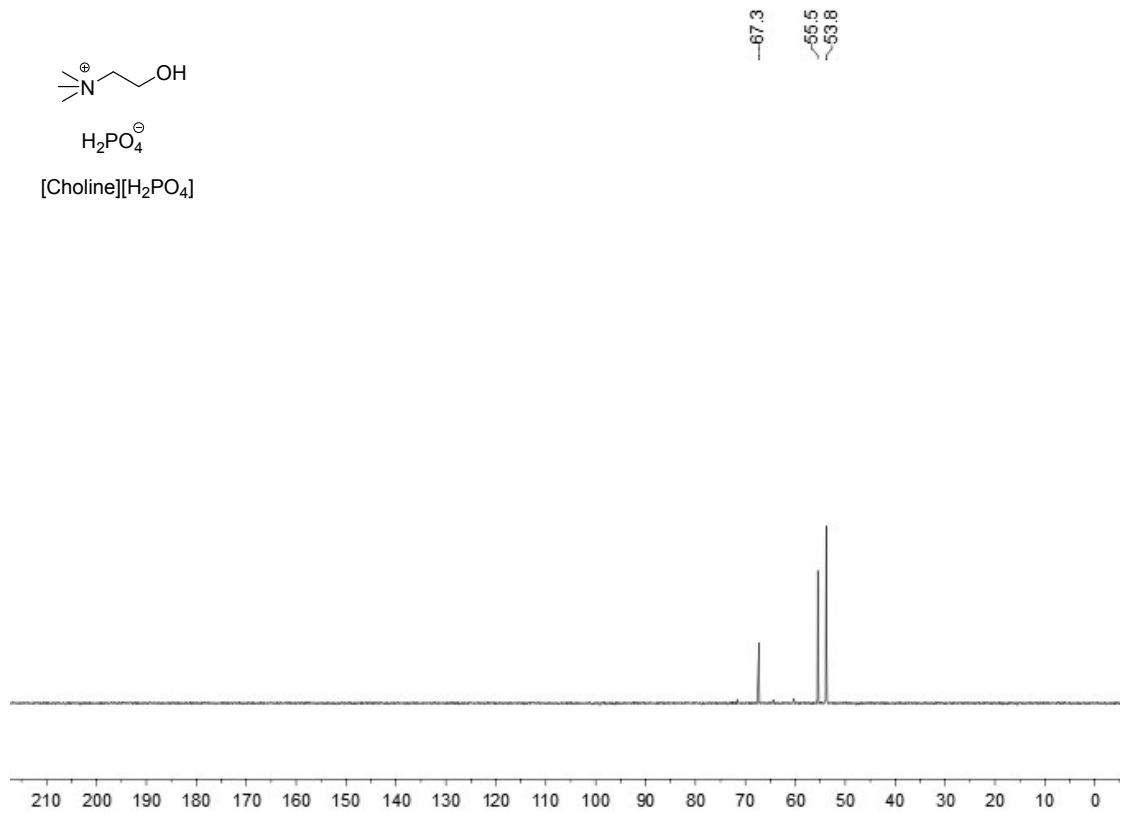
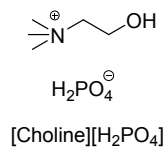
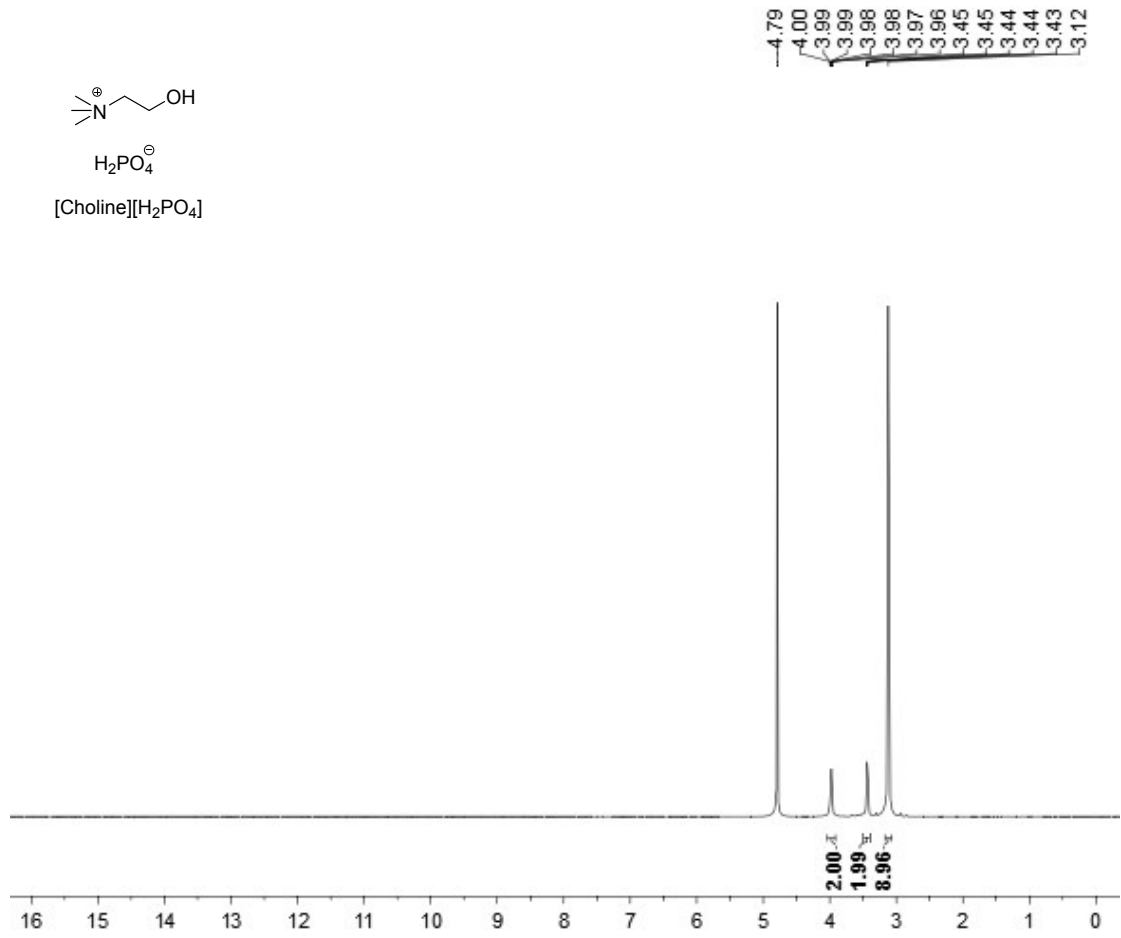
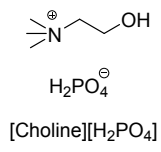


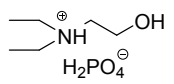




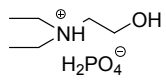
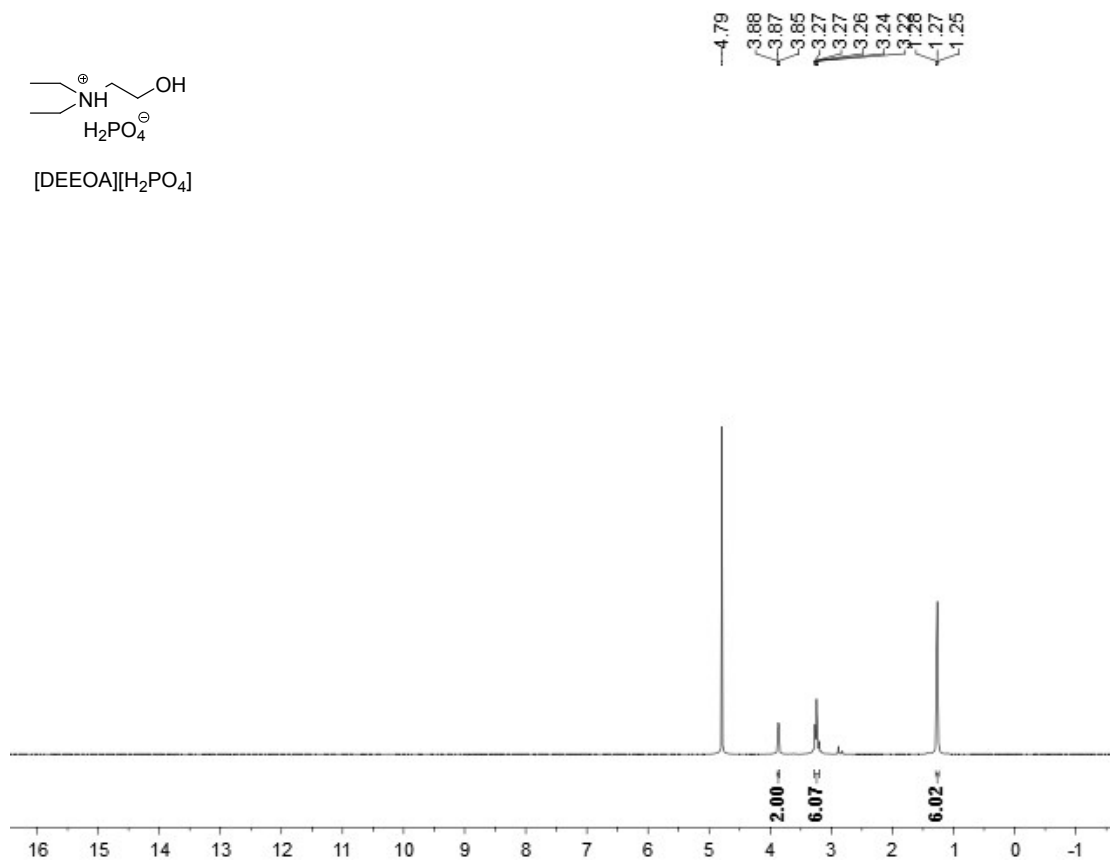




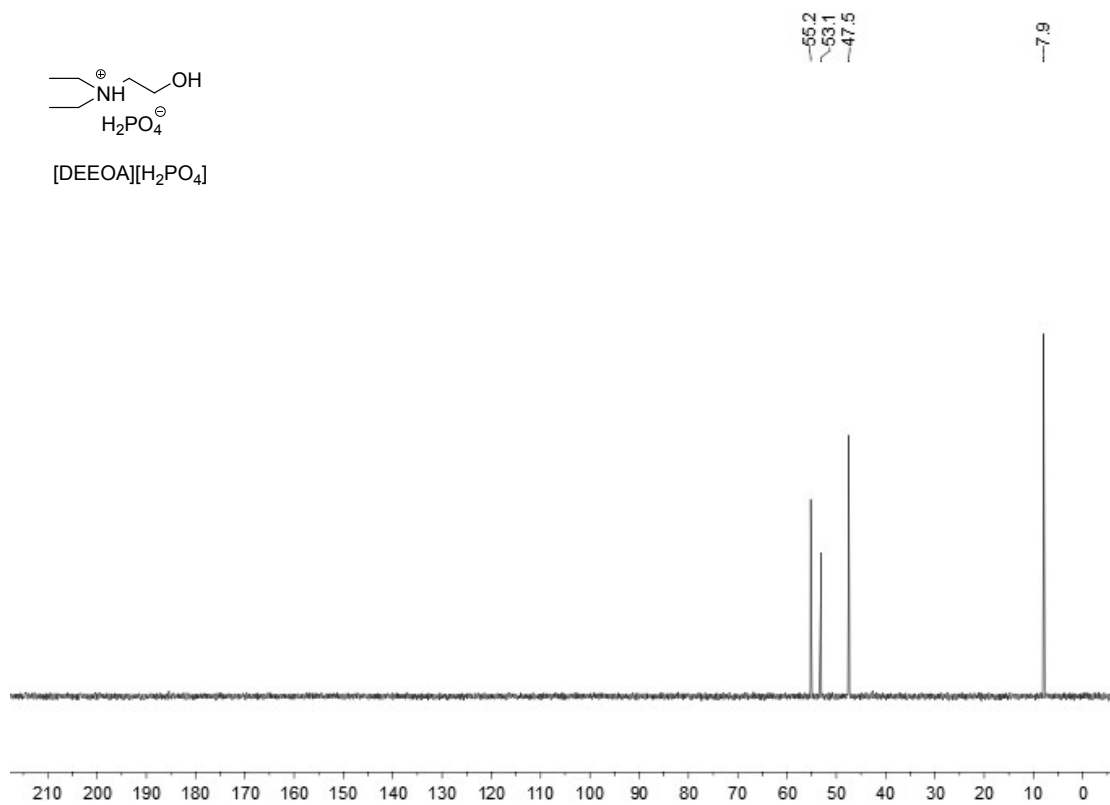




[DEEOA][H₂PO₄]



[DEEOA][H₂PO₄]



[Betaine][H₂PO₄]

