Electronic Supplementary Information

Title: Effect of tetrabutyl phosphonium cation on the physico-chemical properties of amino acid ionic liquids

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Experimental

General procedure for [TBP][amino acid] ionic liquid synthesis

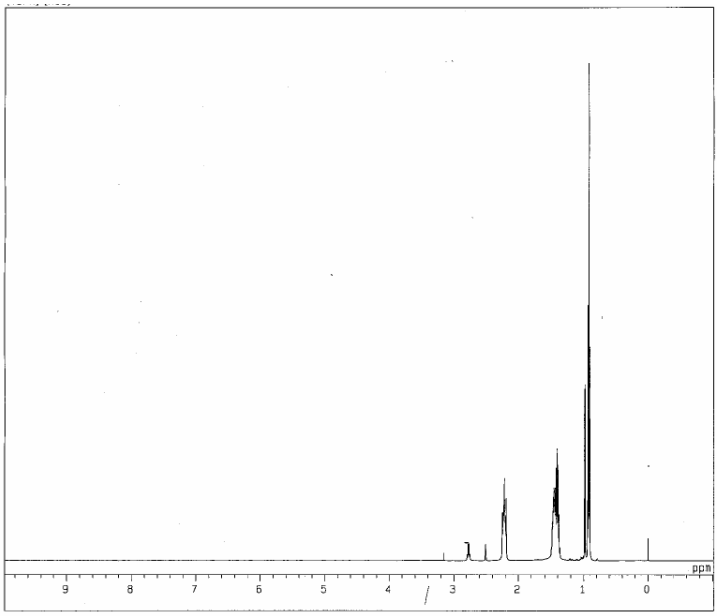
An [TBP][OH] aqueous solution(40 %, from Hokko Chemical Co. Ltd, 26 ml) was added dropwise to a slightly excess amino acid(0.045 mol). After gentle mixing for 10 min, water was gradually evaporated at 50 °C with rotary evaporator. To this reaction mixture were added 60 ml of acetonitrile and 40 ml of methanol. Then the mixture was stirred vigorously for 30-60 min, depending on amino acid species. Free amino acid was insoluble in this mixed solvent. The mixture was then filtered to remove excess amino acid. Filtration was repeated together with washing for a few times. Filtrate was evaporated to remove solvents at room temerature. The product was dried in vacuo for 1 day at 70 °C. Structure of AAILs was confirmed by ^{1}H NMR spectroscopy (JEOL α-500). TMS was used as an inner reference for their ^{1}H-NMR measurements.

The Glass transition temperature (T_g) and melting temperature (T_m) were recorded in the range of -140 to 200 ^{o}C , scan rate of 10 ^{o}C/min, using DSC-120 (SEIKO Instrument Inc.). The decomposition temperature (T_{dec}) was recorded with scan rate of 10 ^{o}C/min using TG/DTA 220 (SEIKO Instrument Inc.) under N_2 atmosphere. The viscosity was measured by Cone/Plate viscometer using LVDV-1+ (BROOKFIELD).

^{1}H—NMR Spectra characterization

[TBP][Ala]

Yield 80 %



(DMSO, δ/ppm)

0.917 (t, 12H, J=14.5Hz)

0.982 (t, 3H, J=7 Hz)

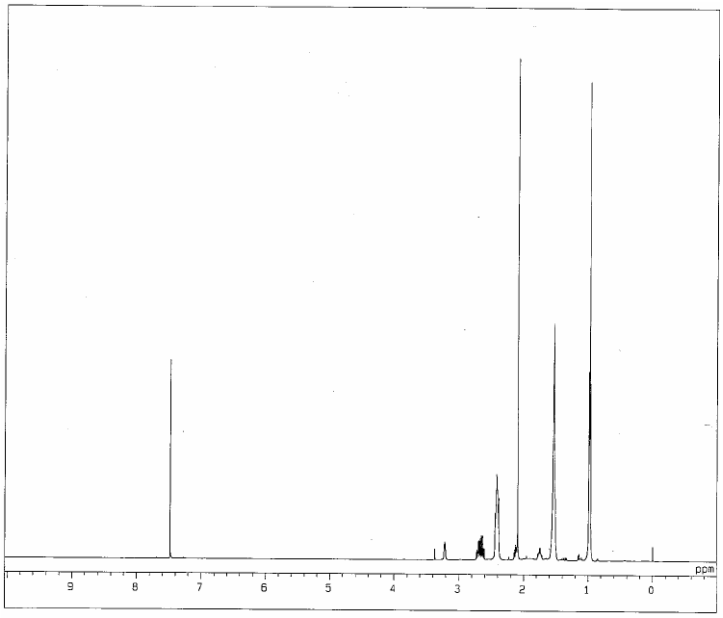
1.369-1.503 (m, 16H)

2.214 (m, 8H, J=30 Hz),

2.769 (q, 1H, J=20 Hz)

[TBP][Met]

Yield 75 %



(CDCl$_3$, δ/ppm)

0.918 (t, 12H, J=14.5 Hz),

1.511-1.549 (m, 16H)

1.721-2.148 (m, 5H)

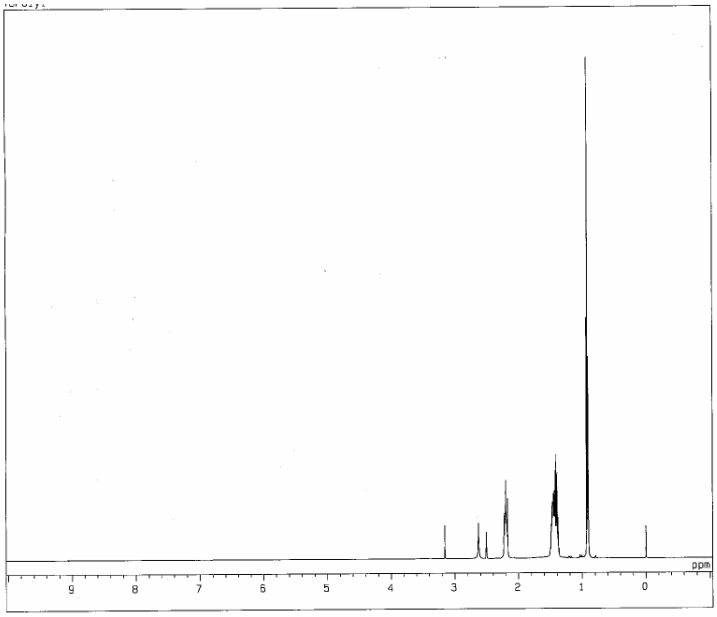
2.413 (m, 8H, J=29.5 Hz)

2.666 (m, 2H, J=29.5 Hz)

3.218 (q, 1H, J=12.5 Hz)

[TBP][Gly]

Yield 83 %



(DMSO, δ/ppm)

0.918 (t, 12H, J=14 Hz)

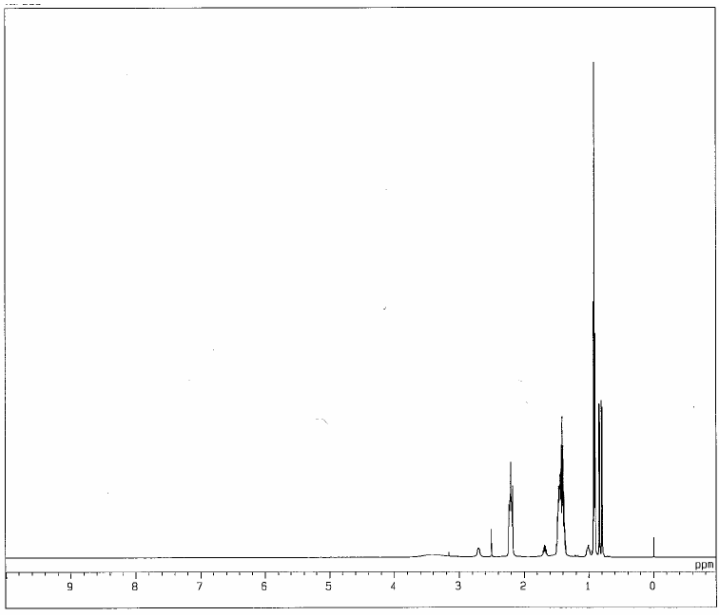
1.368-1.500 (m, 16H)

2.200 (m, 8H, J=30 Hz)

2.630 (q, 2H, J=6.5 Hz)

[TBP][Leu]

Yield 70 %



(DMSO, δ/ppm)

0.819 (q, 6H, J=25 Hz)

0.918 (t, 12H, J=14.5 Hz),

1.359-1.500 (m, 17H),

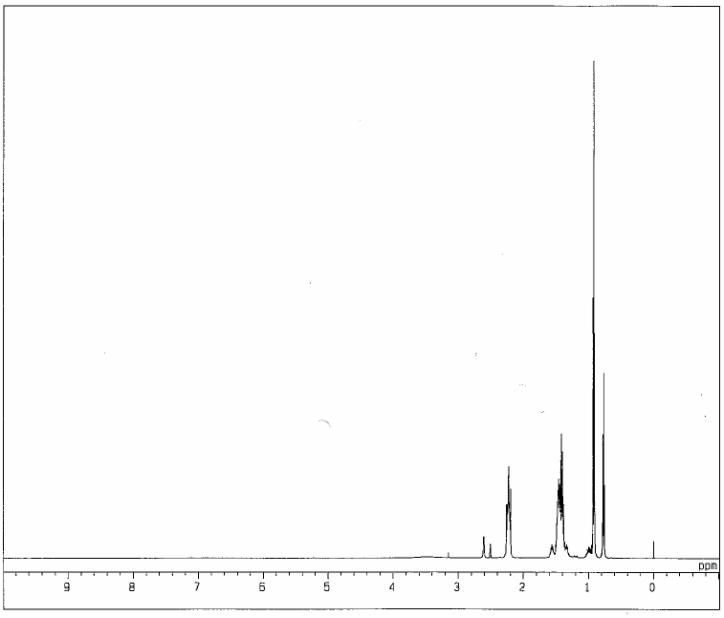
1.343 (m, 2H, J=380.5 Hz)

2.205 (m, 8H, J=29.5 Hz)

2.699 (s, 1H)

[TBP][Ile]

Yield 83 %



(DMSO, δ/ppm)

0.750-0.783 (m, 6H)

0.917 (t, 12H, J=14 Hz)

0.985 (m, 1H, J=30.5 Hz)

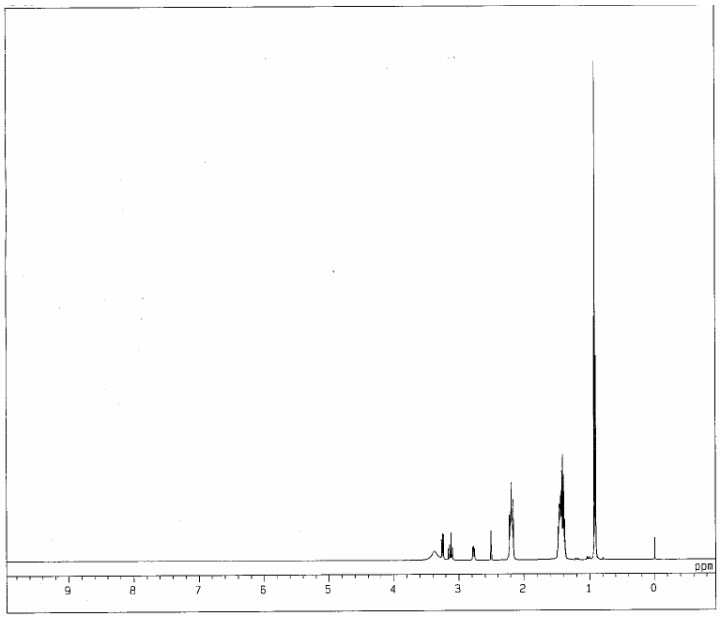
1.309-1.585 (m, 18H)

2.228 (m, 8H, J=30 Hz)

2.612 (d, 1H, J=4.5 Hz)

[TBP][Ser]

Yield 73 %



(DMSO, δ/ppm)

0.917 (t, 12H, J=14 Hz)

1.369-1.500 (m, 16H)

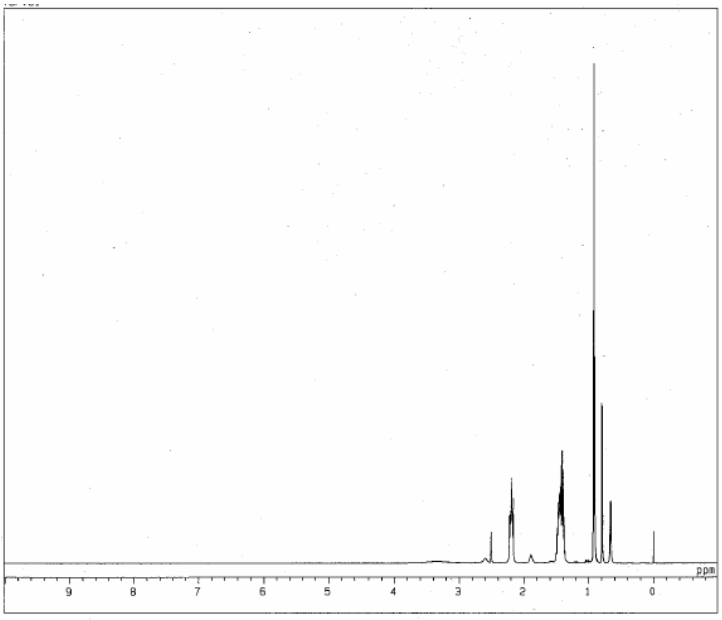
2.191 (m, 8H, J=29.5 Hz)

2.775 (q, 1H, J=15.5 Hz)

3.187 (m, 2H, J=83.5 Hz)

[TBP][Val]

Yield 80 %



(DMSO, δ/ppm)

0.662 (d, 3H, J=7Hz)

0.793 (d, 3H, J=6.5Hz)

0.917 (t, 12H, J=14.5 Hz),

1.370-1.488 (m, 16H)

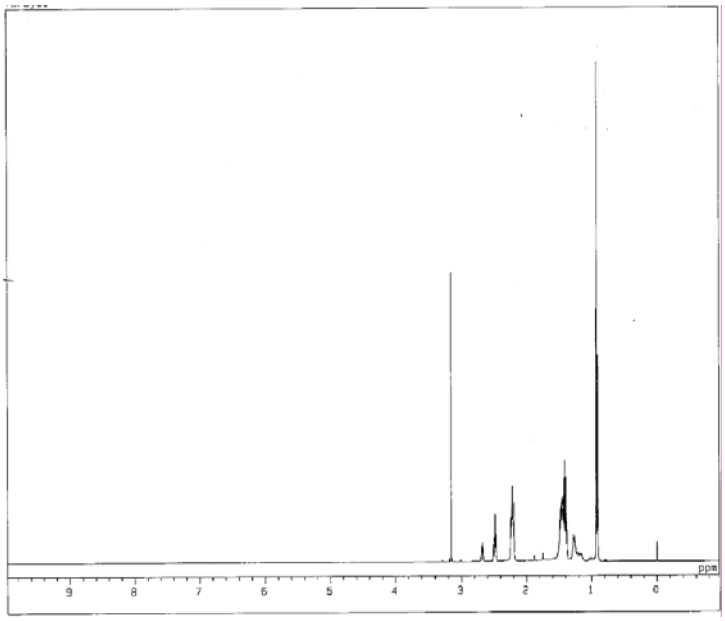
1.891 (m, 1H, J=31.5 Hz)

2.194 (m, 8H, J=30 Hz)

2.503 (t, 1H, J=3.5 Hz)

[TBP][Lys]

Yield 78 %



(DMSO, δ/ppm)

0.917 (t, 12H, J=14.5 Hz),

1.245-1.878 (m, 22H)

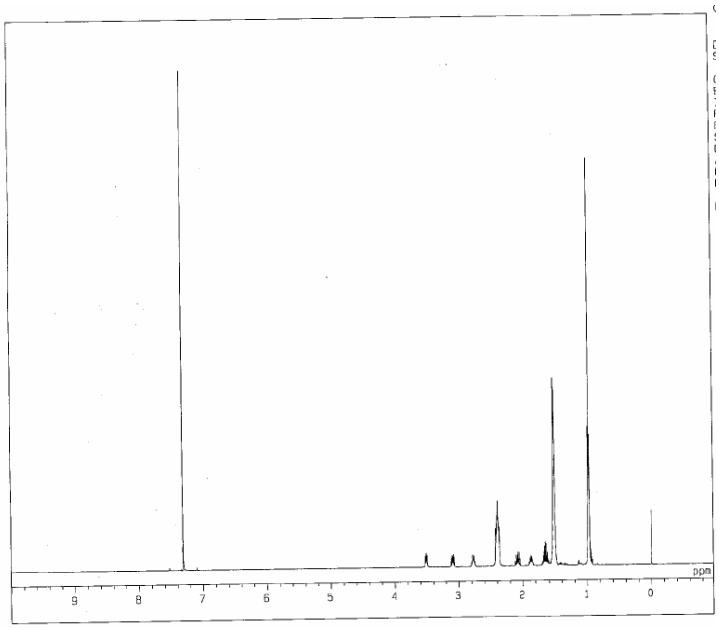
2.216 (m, 8H, J=30 Hz)

2.479 (t, 2H, J=13Hz)

2.679 (q, 1H, J=12 Hz)

[TBP][Pro]

Yield 77 %



(CDCl3, δ/ppm)

0.976 (t, 12H, J=14 Hz)

1.527 (m, 16H, J=19 Hz)

1.657 (m, 2H, J=51 Hz)

1.870 (m, 1H, J=32.5 Hz)

2.082 (m, 1H, J=36 Hz)

2.395 (m, 8H, J=29 Hz)

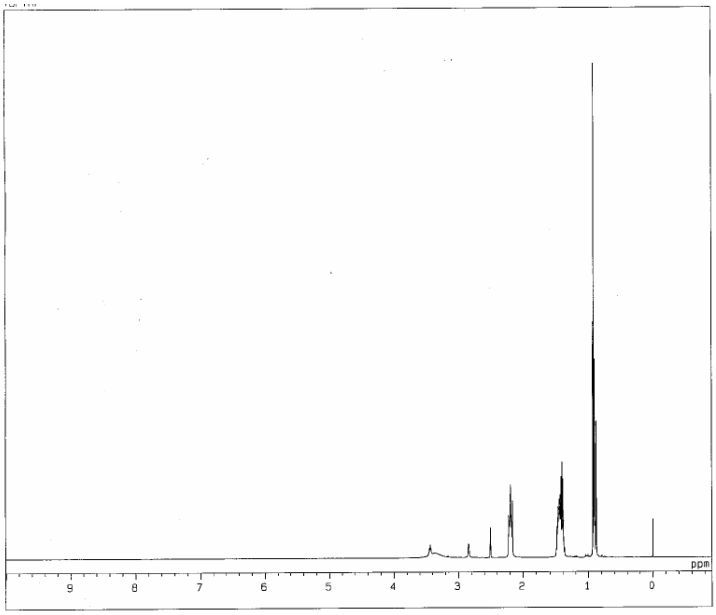
2.784 (m, 1H, J=17.5 Hz)

3.097 (m, 1H, J=23 Hz)

3.511 (m, 1H, J=14.5 Hz)

[TBP][Thr]

Yield 70 %



(DMSO, δ/ppm)

0.880 (d, 3H, J=6 Hz)

0.918 (t, 12H, J=14 Hz)

1.383-1.488 (m, 16H)

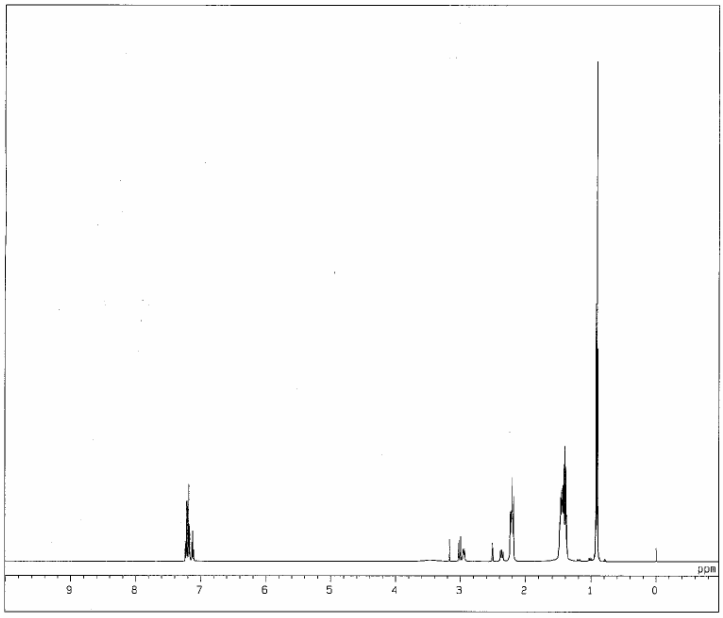
2.193 (m, 8H, J=30.5 Hz)

2.842 (d, 1H, J=4 Hz)

3.443 (m, 1H, J=11 Hz)

[TBP][Phe]

Yield 75 %



(DMSO, δ/ppm)

0.916 (t, 12H, J=14.5 Hz)

1.367-1.487 (m, 16H)

2.208 (m, 8H, J=29.5 Hz)

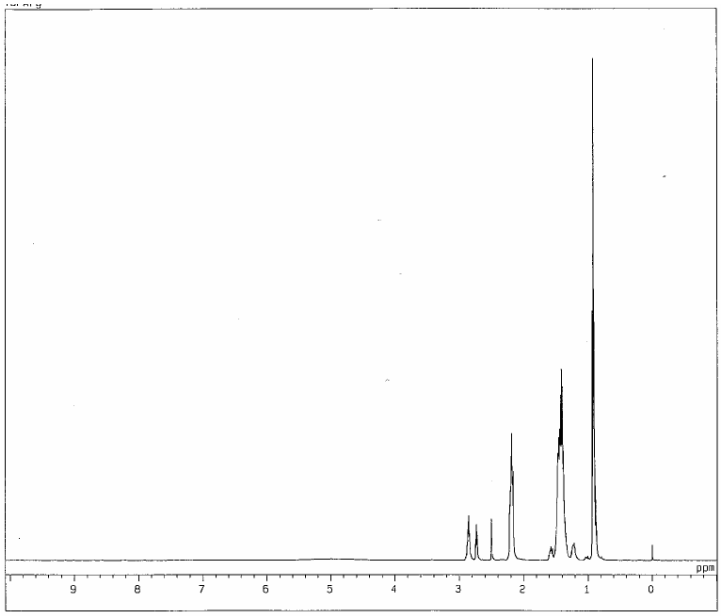
2.365 (q, 1H, J=22.5 Hz)

2.983 (m, 2H, J=45.5 Hz)

7.107-7.236 (m, 5H)

[TBP][Arg]

Yield 65 %



(DMSO, δ/ppm)

0.917 (t, 12H, J=14 Hz)

1.216-1.575 (m, 20H)

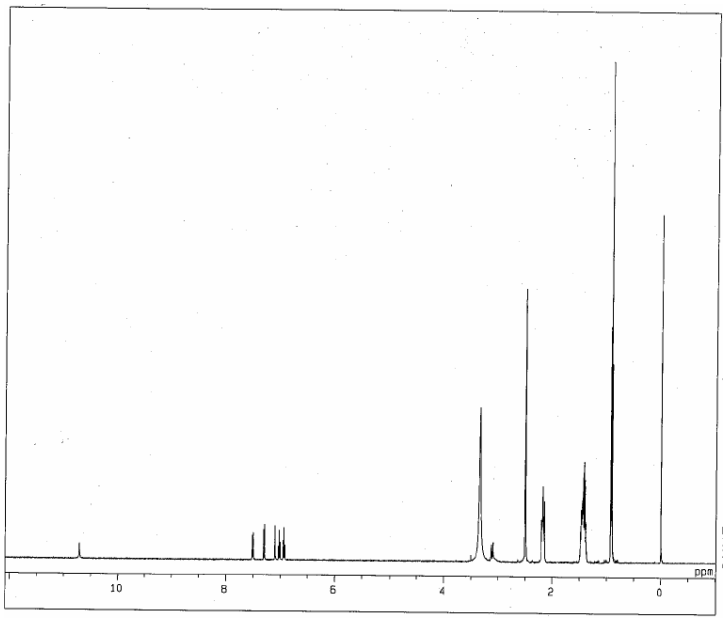
2.192 (m, 8H, J=29 Hz)

2.738 (t, 1H, J=12.5 Hz)

2.862 (m, 2H, J=5.5 Hz)

[TBP][Trp]

Yield 65 %



(DMSO, δ/ppm)

0.918 (t, 12H, J=14 Hz)

1.369-1.485 (m, 16H)

2.175 (m, 8H, J=29.5 Hz)

2.502 (m, 2H, J=75 Hz)

3.108 (q, 1H, J=17 Hz)

6.931 (t, 1H, J=14.5 Hz)

7.021 (t, 1H, J=14 Hz)

7.099 (d, 1H, J=2 Hz)

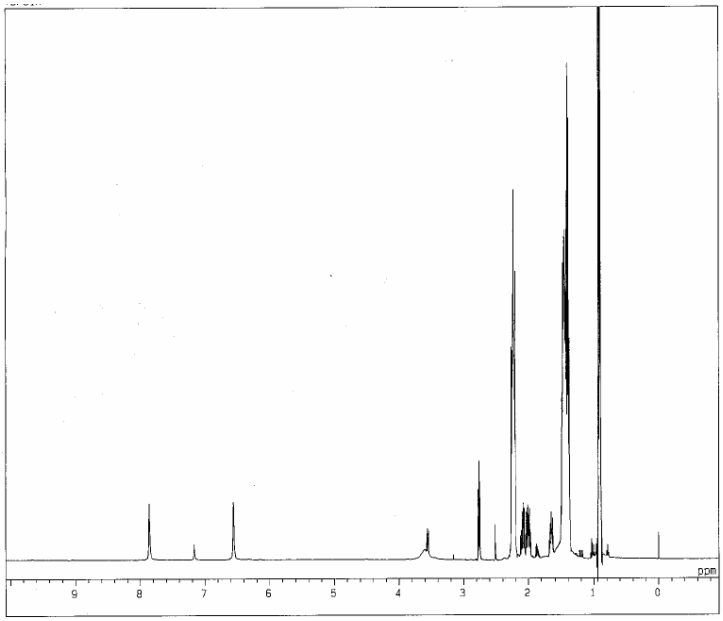
7.298 (d, 1H, J=8 Hz)

7.504 (d, 1H, J=8 Hz)

10.712 (s, 1H)

[TBP][Gln]

Yield 72 %



(DMSO, δ/ppm)

0.915 (t, 12H, J=20 Hz)

1.369-1.685 (m, 18H)

2.042 (m, 2H, J=80 Hz)

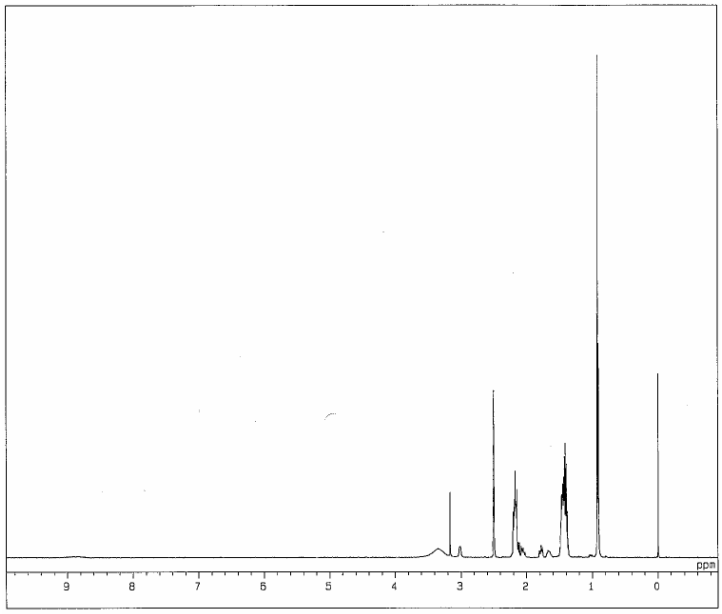
2.236 (m, 8H, J=30 Hz)

2.764 (q, 1H, J=12.5 Hz)

7.213 (d, 2H, J=651 Hz)

[TBP][Glu]

Yield 65 %



(DMSO, δ/ppm)

0.918 (t, 12H, J=14 Hz)

1.368-1.498 (m, 16H)

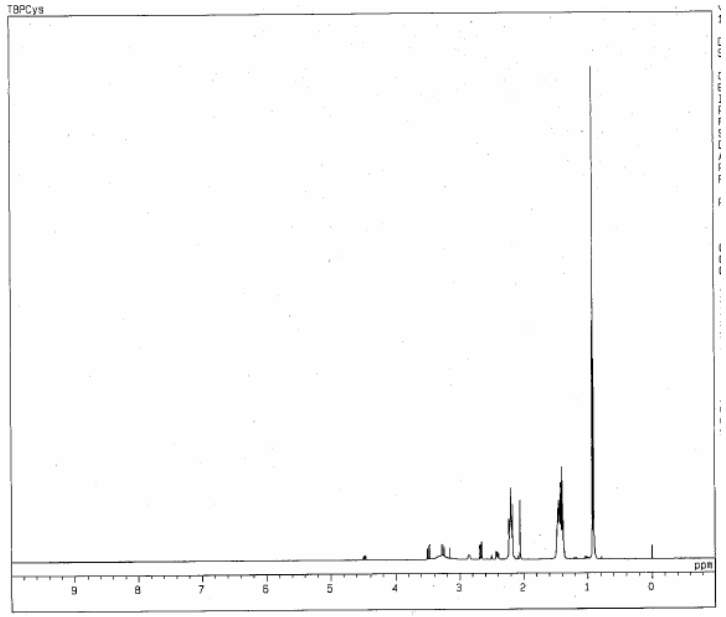
1.764-2.131 (m, 4H)

2.179 (m, 8H, J=30 Hz)

3.012 (s, 1H)

[TBP][Cys]

Yield 74 %



(DMSO, δ/ppm)

0.918 (t, 12H, J=14.5 Hz)

1.370-1.503 (m, 16 H)

2.061 (d, 1H, 2 Hz)

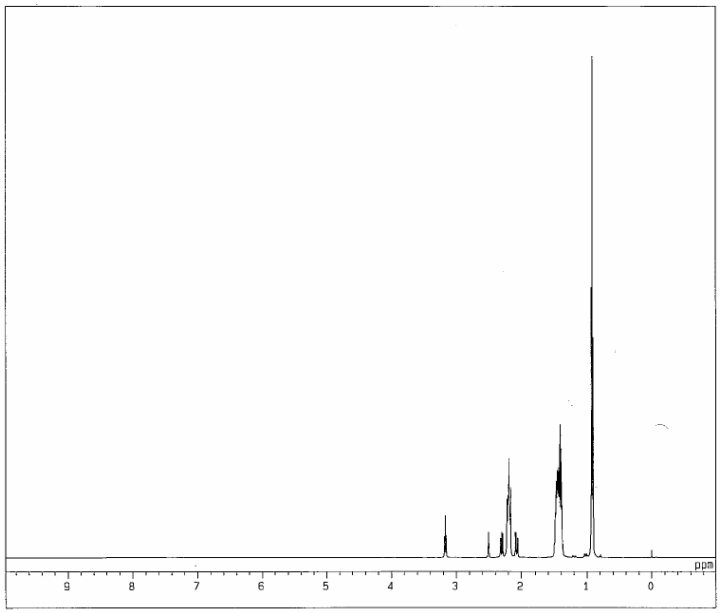
2.204 (m, 8H, J=30 Hz)

2.524 (m, 1H, 156.5 Hz)

3.378 (m, 2H, 130.5 Hz)

[TBP][Asp]

Yield 65 %



(DMSO, δ/ppm)

0.917 (t, 12H, J=14.5 Hz)

1.369-1.502 (m, 16H)

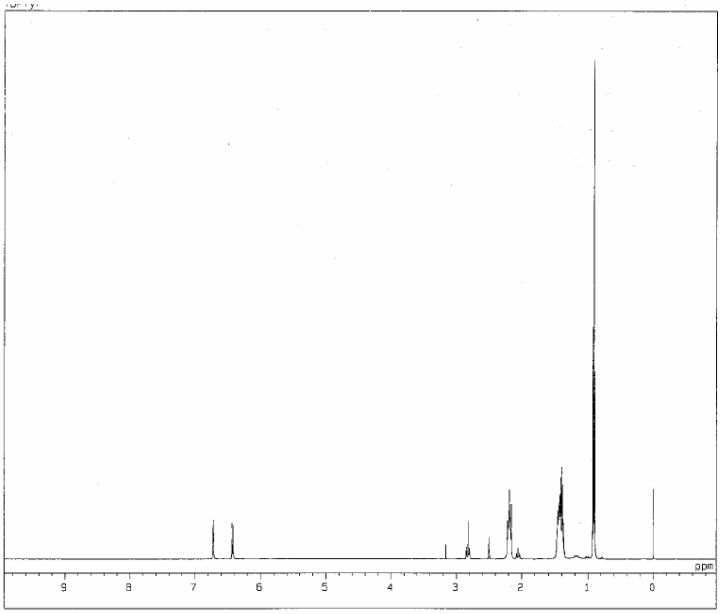
2.191 (m, 8H, J=29.5 Hz)

2.188 (m, 2H, J=139 Hz)

3.170 (t, 1H, J=14 Hz)

[TBP][Tyr]

Yield 76 %



(DMSO, δ/ppm)

0.910 (t, 12H, J=14.5 Hz)

1.403-1.491 (m, 16H)

1.619 (m, 2H, J=456.5 Hz)

2.191 (m, 8H, J=29.5 Hz)

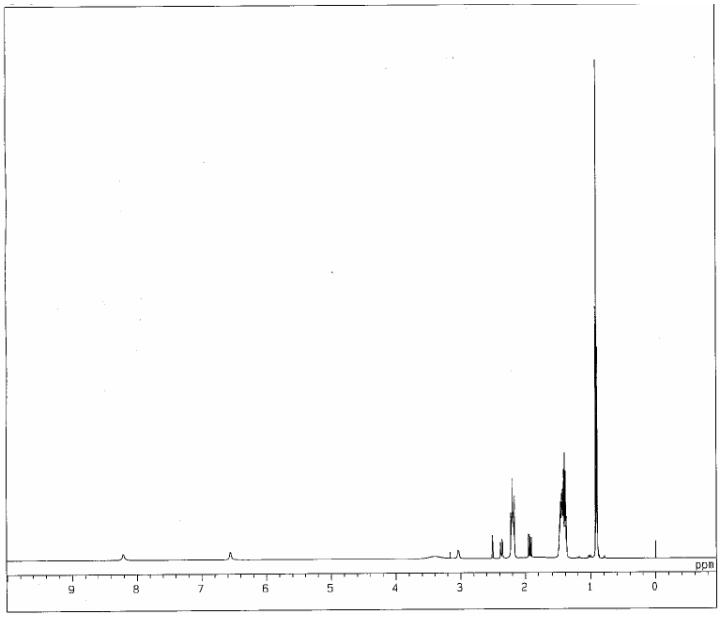
2.826 (m, 1H, J=27.5 Hz)

6.427 (t, 2H, J=8.5Hz)

6.720 (t, 2H, J=8Hz)

[TBP][Asn]

Yield 70%



(DMSO, δ/ppm)

0.917 (t, 12H, J=14.5 Hz)

1.369-1.501 (m, 16H)

2.198 (m, 8H, J=23 Hz)

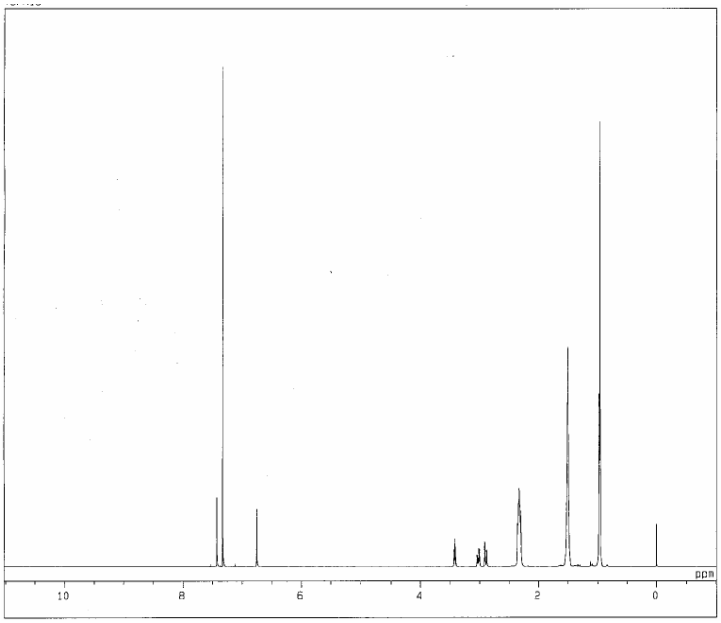
2.150 (m, 2H, 239.5 Hz)

3.037 (s, 1H)

7.385 (d, 2H, J=828 Hz)

[TBP][His]

Yield 80%



(CDCl3, δ/ppm)

0.968 (t, 12H, J=14 Hz)

1.500 (m, 16H, J =15 Hz)

2.331 (m, 8H, J=29.5 Hz)

2.958 (m, 2H, J=335 Hz),

3.417 (q, 1H, J=17 Hz)

6.754 (s, 1H),

7.430 (s, 1H)