

## Supplementary materials for

# Novel ionic liquids from renewable biomaterials: synthesis, characterization and application in the pretreatment of biomass

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## Materials and method

**Materials:** Choline hydroxide ([Ch][OH]), cellulase from *Trichoderma reesei*, Kraft lignin and xylan from beechwood were purchased from Sigma–Aldrich (USA). L-Amino acids were obtained from Juyuan Biotechnological Co. (Shanghai, China), which were used as received. Microcrystalline cellulose was purchased from FMC (USA). Triple-distilled water was used for the preparation of the aqueous solutions in the synthesis of ILs. Methanol and acetonitrile were purified by standard procedures.<sup>1</sup> All other chemicals were of the highest purity commercially available.

## General procedure for preparation of [Ch][AA] ILs

[Ch][OH] aqueous solution was added dropwise to amino acid aqueous solution of

slightly excess, with cooling. The mixture was stirred at about 3 °C for 48 h in the dark. Water was then removed under reduced pressure at 55 °C. To this reaction mixture were added acetonitrile/methanol (9:1, v/v) with stirring vigorously. The excessive amino acid was filtered off. Filtrate was evaporated to remove solvents at 40 °C. The product was dried *in vacuo* for 48 h at 70 °C. The yields of all the desired products were more than 95%.

### Solubility of lignin, xylan and cellulose

To determine lignin, xylan and cellulose solubility, 1 mg sample was added to a glass vial containing 0.5 g IL at room temperature or 90 °C under N<sub>2</sub> with stirring, and visually checked whether it was soluble. If the solution was clear, 2.5 or 5 mg sample was added. The solubility was calculated when the solution remained heterogeneous within 24 h.

Table S1. Solubilities of lignin in representative ILs at room temperature

| Entry <sup>a</sup> | IL        | Lignin (mg/g) |
|--------------------|-----------|---------------|
| 1                  | [Ch][Gly] | 115           |
| 2                  | [Ch][Ala] | 100           |
| 3                  | [Ch][Ser] | 35            |
| 4                  | [Ch][Thr] | 20            |
| 7                  | [Ch][Ile] | 15            |
| 8                  | [Ch][Met] | 65            |
| 9                  | [Ch][Phe] | 25            |
| 11                 | [Ch][Pro] | 55            |
| 16                 | [Ch][Lys] | 20            |

<sup>a</sup> Entry number as in Table 1.

### Rheological studies of the ILs

Rheological studies were carried out on a controlled-stress rheometer (HAAKE RheoStress 600, Germany) equipped with a temperature controller (Amersham Biosciences, Multi Temp III, Germany). To study the effect of shear rate on the viscosity, linear increase of shear rate from 1-1000 s<sup>-1</sup> in 5 min at 25 °C was used to determine the apparent viscosity. The temperature effect on the viscosity was studied in the range of 20-95 °C with a heating rate of 5 °C/min keeping the shear rate of 10 s<sup>-1</sup>.

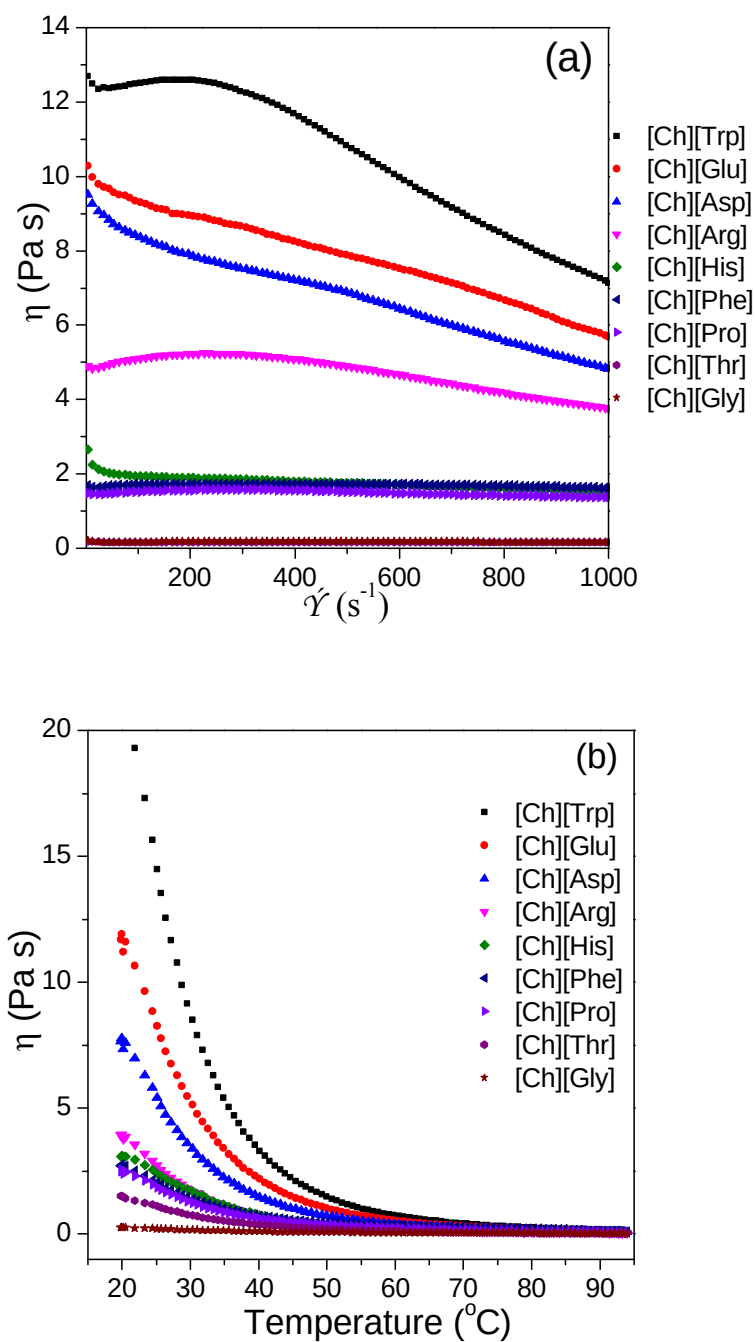


Figure 1S. Shear rate (a) and temperature (b) dependence of the viscosity

### Pretreatment of microcrystalline cellulose and rice straw

Rice straw or microcrystalline cellulose (150 mg) was incubated in 3 g [Ch][Gly] under  $\text{N}_2$  with magnetic stirring at  $90^{\circ}\text{C}$  for 24 h. After incubation, the suspension was diluted by 0.1 mol/L NaOH solution for rice straw or by distilled water for

microcrystalline cellulose and centrifuged (12000 rpm, 20 min). The supernatant was decanted, and the residue was washed by distilled water. Then, the residue was dried by lyophilization and then kept in a sealed bag under -20 °C before use.

### Enzymatic Hydrolysis

To 7 mL citrate buffer (50 mM, pH 4.8) containing cellulase of 35 U/mL, 20 mg biomass was added. The enzymatic hydrolysis was carried out at 200 rpm and 50 °C. Aliquots (200  $\mu$ L) were withdrawn at specified time intervals, and treated at 100 °C for 5 min to stop the enzymatic reaction. Glucose concentrations were measured by HPLC (Waters 996, USA) equipped with a Bio-Rad Aminex HPX-87H column and a refractive index detector. The column temperature was 65 °C. The mobile phase consisted of 5 mM sulfuric acid solution with a flow rate of 0.5 mL/min. All reactions were carried out induplicate.

### Charaterization

$^1\text{H}$  NMR spectra of these ILs were recorded in  $\text{D}_2\text{O}$  or DMSO at 400 MHz by a NMR spectrometer at 400 MHz (Bruker AVANCE Digital 400 MHz NMR, Germany). Elemental analysis of the ILs were carried out on an elemental analyzer (Elementar Vario El III, Germany). IR spectra of the ILs were recorded on a FTIR spectrometer (Bruker Vector 33, Germany) without KBr. The water contents of ionic liquids were determined with a Karl Fischer moisture titrator (Metrohm 787 KF Titrino, Switzerland). The specific rotations of the ILs were obtained in  $\text{CH}_3\text{OH}$  solution ( $c = 2$ ) with an automatic indication polarimeter (Atago-AP300, Japan). The decomposition temperatures ( $T_d$ ) were measured with a thermal gravimetric analyzer (TGA Q500, TA Instruments, UAS), with a heating rate of 5 °C/min under nitrogen. The  $T_d$  is calculated from the intersection of the baseline weight (after the drying step) and the tangent line derived from the decomposition curve, as described previously.<sup>2</sup> The glass transition temperatures ( $T_g$ ) were determined with a differential thermal analyzer (DSC Q200, TA Instruments, UAS) with a heating rate of 10 °C/min, after cooling samples to -70 °C under nitrogen. The viscosity was measured with a viscometer at 25 °C (Brookfield DV- II +Pro, USA).

**[Ch][Gly].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 3.22 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.26 (s, 2H,

CH<sub>2</sub>-N), 3.52 – 3.55 (m, 2H, CH<sub>2</sub>), 4.06 – 4.10 (m, 2H, CH<sub>2</sub>),. Elemental analysis: calc. for C 47.168, N 15.717, H 10.180, found C 47.135, N 15.708, H 10.101. IR:  $\bar{\nu}$  = 3418, 2970, 1581, 1482, 1401, 1086, 1056, 956, 655  $\text{cm}^{-1}$ .

**[Ch][Ala].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 1.24 (d,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>), 3.20 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.33 (q,  $J$  = 6.8, 14.0 Hz, 1H, CH-N), 3.51 – 3.53 (m, 2H, CH<sub>2</sub>), 4.04 – 4.08 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 49.975, N 14.571, H 10.486, found C 49.900, N 14.612, H 10.467. IR:  $\bar{\nu}$  = 3387, 2973, 1575, 1479, 1363, 1406, 1086, 1056, 956, 658  $\text{cm}^{-1}$ .

**[Ch][Ser].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 3.20(s, 9H,CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.41 (t,  $J$  = 5.0 Hz, 1H, CH-N), 3.52 (apparent t, 2H, CH<sub>2</sub>), 3.76 (dd,  $J$  = 4.0, 13.2 Hz, 2H, CH<sub>2</sub>), 4.04 – 4.07 (m, 2H, CH<sub>2</sub>),. Elemental analysis: calc. for C 45.136, N 13.452, H 9.680, found C 46.104, N 13.443, H 9.667. IR:  $\bar{\nu}$  = 3359, 2949, 1577, 1479, 1409, 1347, 1087, 1050, 955  $\text{cm}^{-1}$ .

**[Ch][Thr].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 1.23 (d,  $J$  = 6.4 Hz, 3H, CH<sub>3</sub>), 3.14 (d,  $J$  = 5.2 Hz, 1H, CH-N), 3.22 (s, 9H,CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.52 – 3.55 (m, 2H, CH<sub>2</sub>), 3.96 – 3.99 (m, 1H, CH<sub>2</sub>O), 4.06 – 4.10 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 48.627, N 12.603, H 9.976, found C 48.593, N 12.595, H 9.977. IR:  $\bar{\nu}$  = 3366, 2973, 2933, 1577, 1481, 1402, 1086, 1056, 956  $\text{cm}^{-1}$ .

**[Ch][Val].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 0.89 (d,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>), 0.96 (d,  $J$  = 6.8 Hz, 3H, CH<sub>3</sub>), 1.91 – 1.99 (m, 1H, CH), 3.08 (d,  $J$  = 5.2 Hz, 1H, CH-N), 3.23 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.54 (apparent t, 2H, CH<sub>2</sub>), 4.07 – 4.11 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 54.513, N 12.715, H 10.981, found C 54.475, N 12.708, H 10.981. IR:  $\bar{\nu}$  = 3362, 2961, 2874, 1571, 1475, 1399, 1370, 1087, 955, 670  $\text{cm}^{-1}$ .

**[Ch][Leu].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 0.92 (t,  $J$  = 6.6 Hz, 6H, CH<sub>3</sub>, CH<sub>3</sub>), 1.37 – 1.53 (m, 2H, CH<sub>2</sub>), 1.62 – 1.71 (m, 1H, CH), 3.21 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.29 (q,  $J$  = 6.0, 8.0 Hz, 1H, CH-N), 3.53 (apparent t, 2H, CH<sub>2</sub>), 4.05 – 4.09 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 56.377, N 11.954, H 11.184, found C 56.337, N 11.947,

H 11.196. IR:  $\bar{\nu}$  = 3377, 2956, 2871, 1578, 1474, 1401, 1366, 1087, 1059, 955  $\text{cm}^{-1}$ .

**[Ch][Ile].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 0.86 – 0.92 (t, 3H,  $\text{CH}_3$ ; d, 3H,  $\text{CH}_3$ , overlap), 1.09 – 1.18 (m, 1H,  $\text{CH}_2$ ), 1.38 – 1.44 (m, 1H,  $\text{CH}_2$ ), 1.64 – 1.70 (m, 1H, CH), 3.10 (d,  $J$  = 5.2 Hz, 1H, CH-N), 3.20 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.51 (apparent t, 2H,  $\text{CH}_2$ ), 4.03 – 4.07 (m, 2H,  $\text{CH}_2$ ). Elemental analysis: calc. for C 56.377, N 11.954, H 11.184, found C 56.431, N 11.929, H 11.178. IR:  $\bar{\nu}$  = 3378, 2963, 2935, 2876, 1575, 1478, 1402, 1087, 1060, 956  $\text{cm}^{-1}$ .

**[Ch][Met].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.77 – 1.86 (m, 1H,  $\text{CH}_2$ ), 1.91 – 2.00 (m, 1H,  $\text{CH}_2$ ), 2.15 (s, 3H,  $\text{CH}_3$ ), 2.59 (t,  $J$  = 7.8 Hz, 2H,  $\text{CH}_2$ ), 3.23 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.34 (t,  $J$  = 6.4 Hz, 1H, CH-N), 3.54 (apparent t, 2H,  $\text{CH}_2$ ), 4.05 – 4.10 (m, 2H,  $\text{CH}_2$ ). Elemental analysis: calc. for C 47.588, N 11.100, H 9.586, S 12.681, found C 47.555, N 11.093, H 9.570, S 12.750. IR:  $\bar{\nu}$  = 3366, 2970, 2919, 2840, 1579, 1481, 1443, 1404, 1356, 1087, 1058, 955  $\text{cm}^{-1}$ .

**[Ch][Phe].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.87 – 2.92 (m, 1H,  $\text{CH}_2$ ), 3.02 – 3.07 (m, 1H,  $\text{CH}_2$ ), 3.21 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.51–3.53 (m, 2H,  $\text{CH}_2$ ), 3.55 (q,  $J$  = 5.6, 7.2 Hz; 1H, CH-N), 4.05 – 4.09 (m, 2H,  $\text{CH}_2$ ), 7.32 – 7.45 (m, 5H,  $\text{C}_6\text{H}_5$ ). Elemental analysis: calc. for C 62.656, N 10.439, H 9.015, found C 62.602, N 10.483, H 9.017. IR:  $\bar{\nu}$  = 3363, 3062, 3027, 2950, 1580, 1489, 1453, 1406, 1085, 955  $\text{cm}^{-1}$ .

**[Ch][Trp].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.99 – 3.04 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ; q, 1H,  $\text{CH}_2$ , overlap), 3.18 (q,  $J$  = 5.2, 14.4 Hz, 1H,  $\text{CH}_2$ ), 3.31 (apparent t, 2H,  $\text{CH}_2$ ), 3.57 (q, 1H,  $J$  = 5.6, 7.2 Hz, CH-N), 3.90 – 3.94 (m, 2H,  $\text{CH}_2$ ), 7.13 – 7.24 (m, 2H,  $\text{C}_6\text{H}_4$ ; 1H,  $\text{C}_4\text{H}$ ), 7.48 (d,  $J$  = 8.0 Hz, 1H,  $\text{C}_6\text{H}_4$ ), 7.71 (d,  $J$  = 8.0 Hz, 1H,  $\text{C}_6\text{H}_4$ ). Elemental analysis: calc. for C 62.512, N 13.670, H 8.198, found C 62.469, N 13.562, H 8.250.  $\bar{\nu}$  = 3252, 2921, 2874, 1573, 1483, 1458, 1404, 1233, 1090, 1063, 955  $\text{cm}^{-1}$ .

**[Ch][Pro].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.65 – 1.75 (m, 3H,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 2.06 – 2.14 (m, 1H,  $\text{CH}_2$ ), 2.70 – 2.76 (m, 1H,  $\text{CH}_2$ -N), 3.00 – 3.06 (m, 1H,  $\text{CH}_2$ -N), 3.19 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.43 – 4.47 (m, 1H, CH-N), 3.50 (apparent t, 2H,  $\text{CH}_2$ ), 4.03 – 4.06

(m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 55.017, N 12.833, H 10.159, found C 54.979, N 12.825, H 10.112. IR:  $\bar{\nu}$  = 3389, 2966, 2876, 1584, 1482, 1411, 1349, 1088, 1057, 956  $\text{cm}^{-1}$ .

**[Ch][Glu].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 2.00 – 2.17 (m, 2H, CH<sub>2</sub>), 2.35 (apparent q, 2H, CH<sub>2</sub>), 3.20 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.51 (apparent t, 2H, CH<sub>2</sub>), 3.75 (q,  $J$  = 4.8, 7.2 Hz, 1H, CH-N), 4.04 – 4.08 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 47.983, N 11.192, H 8.860, found C 47.950, N 11.185, H 8.882. IR:  $\bar{\nu}$  = 3390, 2960, 1571, 1486, 1449, 1087, 955, 927  $\text{cm}^{-1}$ .

**[Ch][Asp].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 2.64 – 2.71 (m, 1H, CH<sub>2</sub>), 2.79 – 2.84 (m, 1H, CH<sub>2</sub>), 3.21 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.51 – 3.54 (m, 2H, CH<sub>2</sub>), 3.89 (q,  $J$  = 4.0, 8.8 Hz, 1H, CH-N), 4.05 – 4.09 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 45.750, N 11.857, H 8.533, found C 45.718, N 11.850, H 8.549. IR:  $\bar{\nu}$  = 3385, 2960, 1611, 1560, 1484, 1390, 1087, 1062, 956, 927  $\text{cm}^{-1}$ .

**[Ch][Asn].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 2.41 – 2.47 (m, 1H, CH<sub>2</sub>), 2.66 – 2.71 (m, 1H, CH<sub>2</sub>), 3.22 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.53 (apparent t, 2H, CH<sub>2</sub>), 3.59 (q,  $J$  = 4.8, 9.2 Hz, 1H, CH-N), 4.06 – 4.10 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 45.938, N 17.859, H 8.996, found C 45.826, N 17.848, H 8.991. IR:  $\bar{\nu}$  = 3364, 2966, 1671, 1585, 1481, 1087, 1057, 956  $\text{cm}^{-1}$ .

**[Ch][Gln].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 2.01 – 2.09 (m, 1H, CH<sub>2</sub>), 2.41 (t,  $J$  = 8.0 Hz, 2H, CH<sub>2</sub>), 2.48 – 2.57 (m, 1H, CH<sub>2</sub>), 3.22 (s, 9H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>), 3.53 (apparent t, 2H, CH<sub>2</sub>), 4.06 – 4.10 (m, 2H, CH<sub>2</sub>), 4.17 – 4.20 (q,  $J$  = 5.6, 8.8 Hz, 1H, CH-N). Elemental analysis: calc. for C 48.276, N 16.756, H 9.300, found C 48.192, N 16.845, H 9.356. IR:  $\bar{\nu}$  = 3382, 2965, 1675, 1594, 1482, 1403, 1087, 1057, 956  $\text{cm}^{-1}$ .

**[Ch][Lys].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)  $\delta$ : 1.29 – 1.37 (m, 2H, CH<sub>2</sub>), 1.42 – 1.49 (m, 2H, CH<sub>2</sub>), 1.51 – 1.64 (m, 2H, CH<sub>2</sub>), 2.62 (t,  $J$  = 7.0 Hz, 2H, CH<sub>2</sub>), 3.20 (s, 10H, CH<sub>3</sub>, CH<sub>3</sub>, CH<sub>3</sub>, CH-N), 3.51 (apparent t, 2H, CH<sub>2</sub>), 4.03 – 4.05 (m, 2H, CH<sub>2</sub>). Elemental analysis: calc. for C 52.981, N 16.852, H 10.915, found C 52.944, N 16.841, H 10.815.

IR:  $\bar{\nu}$  = 3358, 2937, 2863, 1570, 1482, 1404, 1807, 1059, 956  $\text{cm}^{-1}$ .

**[Ch][Arg].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 1.52 (br t, 4H,  $\text{CH}_2$ ,  $\text{CH}_2$ ), 3.08 – 3.18 (m, 11H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_2$ ), 3.17 (br d, 1H, CH-N), 3.36 – 3.39 (apparent q, 2H,  $\text{CH}_2$ ), 3.95 (br s, 2H,  $\text{CH}_2$ ). Elemental analysis: calc. for C 47.630, N 25.250, H 9.812, found C 47.597, N 25.335, H 9.875. IR:  $\bar{\nu}$  = 3300, 2947, 2868, 1637, 1570, 1480, 1406, 1088, 956, 687  $\text{cm}^{-1}$ .

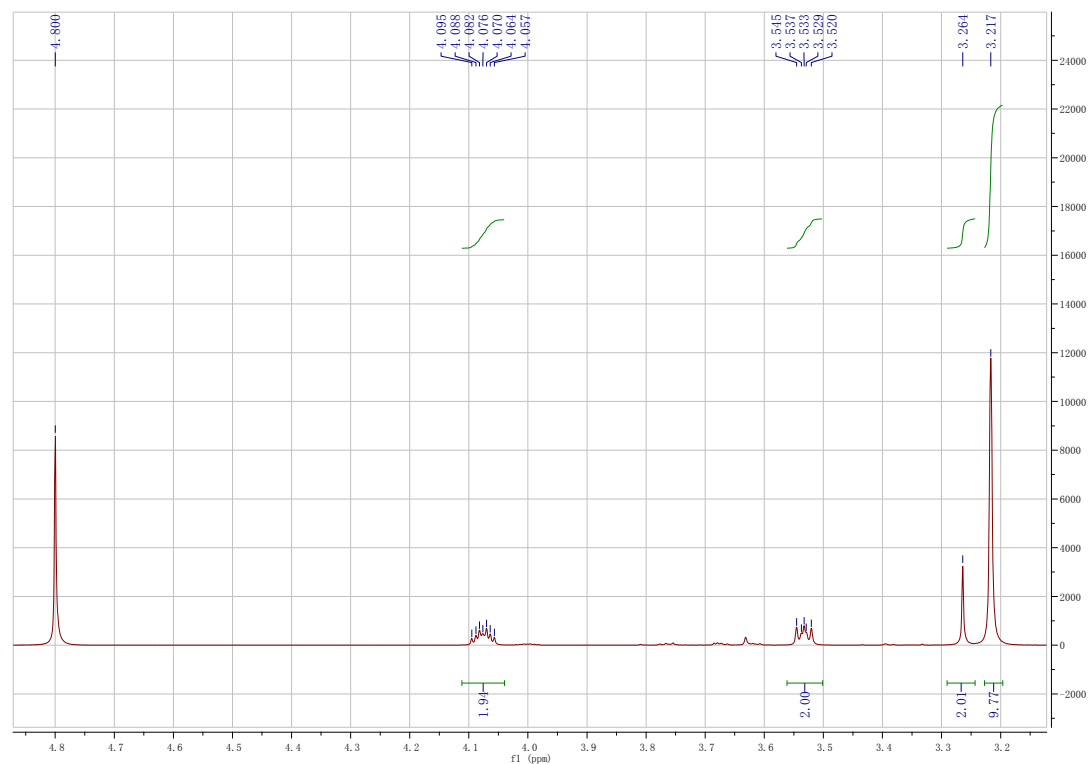
**[Ch][His].**  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 2.79– 2.84 (m, 1H,  $\text{CH}_2$ ), 2.94– 2.99 (m, 1H,  $\text{CH}_2$ ), 3.18 (s, 9H,  $\text{CH}_3$ ,  $\text{CH}_3$ ,  $\text{CH}_3$ ), 3.48– 3.52 (apparent q, 3H,  $\text{CH}_2$ , CH-N), 4.02– 4.06 (m, 2H,  $\text{CH}_2$ ), 6.92 (s, 1H, =CH), 7.67 (s, 1H, =CH). Elemental analysis: calc. for C 51.141, N 21.689, H 8.585, found C 51.105, N 21.676, H 8.627. IR:  $\bar{\nu}$  = 3363, 2971, 1576, 1479, 1408, 1087, 1058, 956, 667  $\text{cm}^{-1}$ .

## References

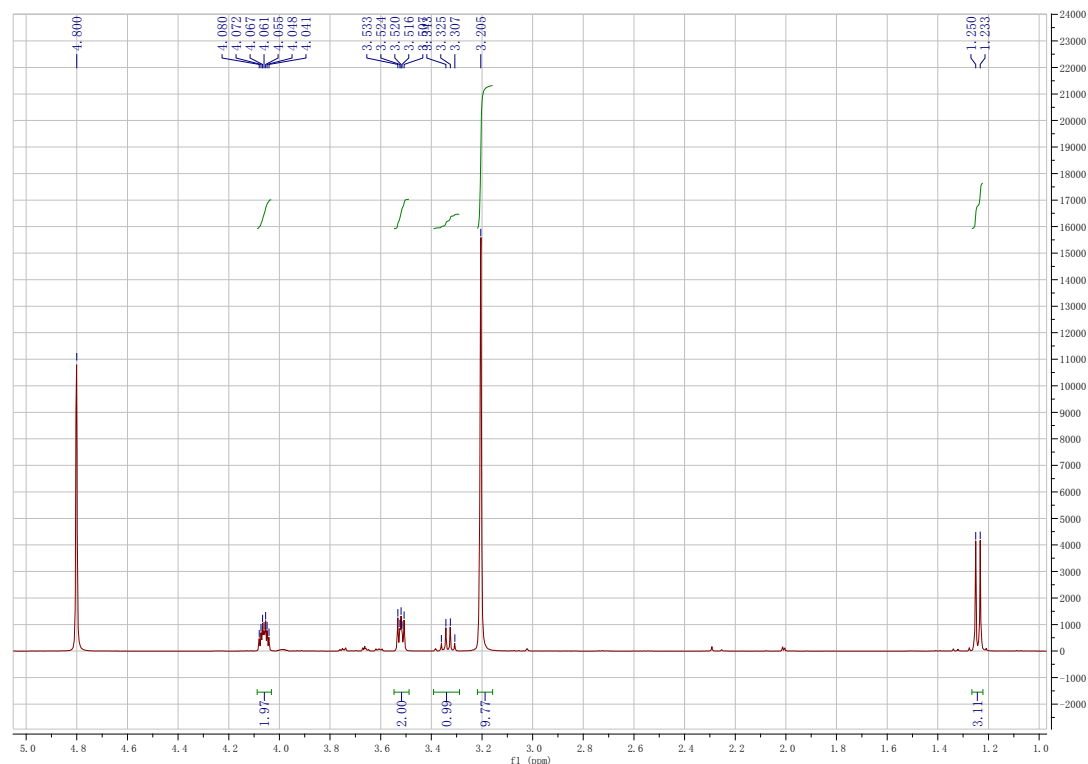
1. W. L. F. Armarego and C. L. L. Chai, *Purification of laboratory chemicals*, Butterworth Heinemann, 2009.
2. C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki and J. F. Brennecke, *J. Chem. Eng. Data*, 2004, **49**, 954-964.



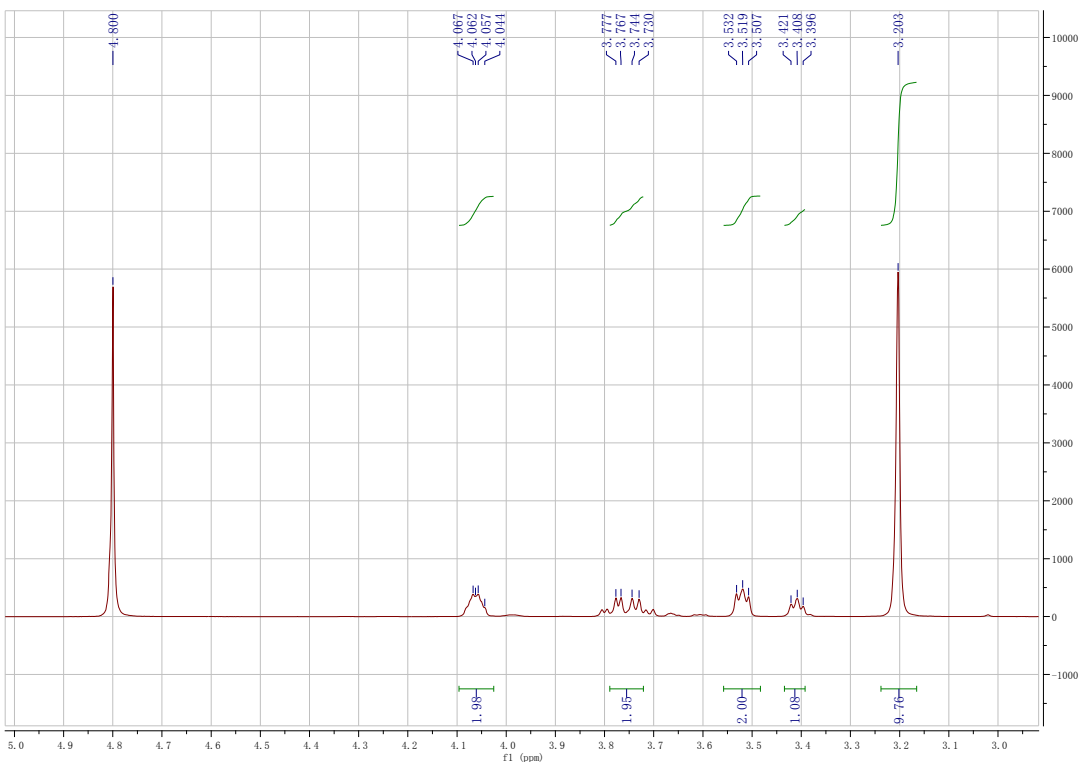
NMR spectra of ILs



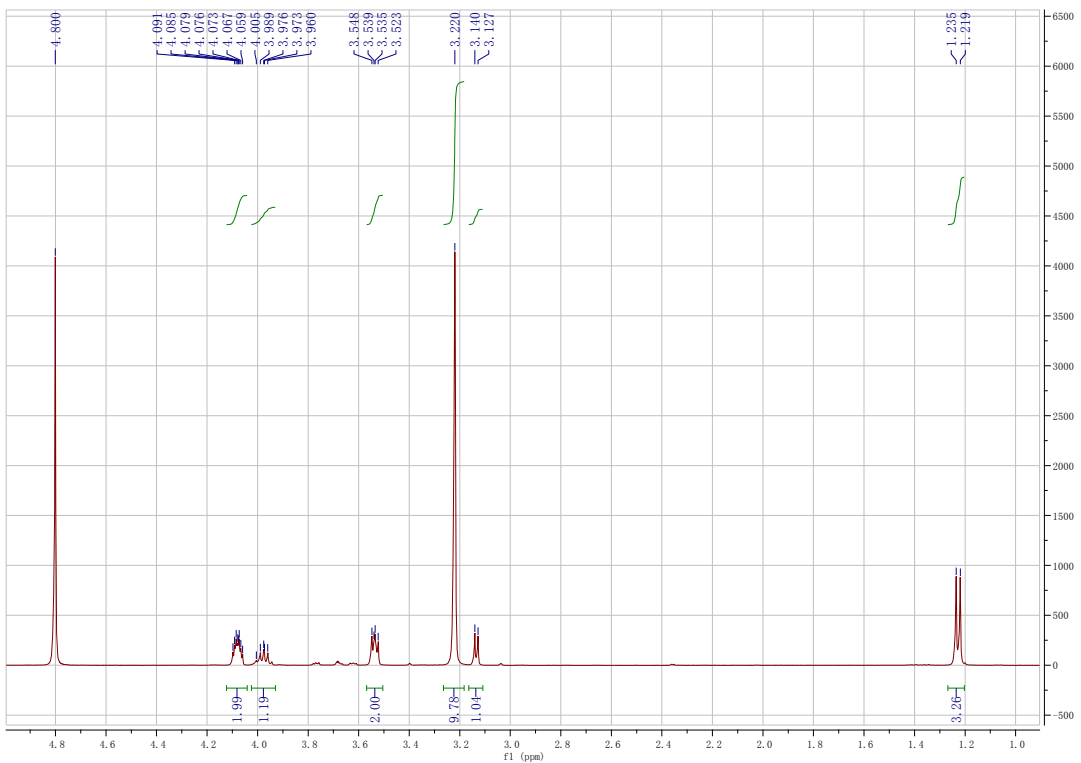
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Gly}]$  in  $\text{D}_2\text{O}$ )



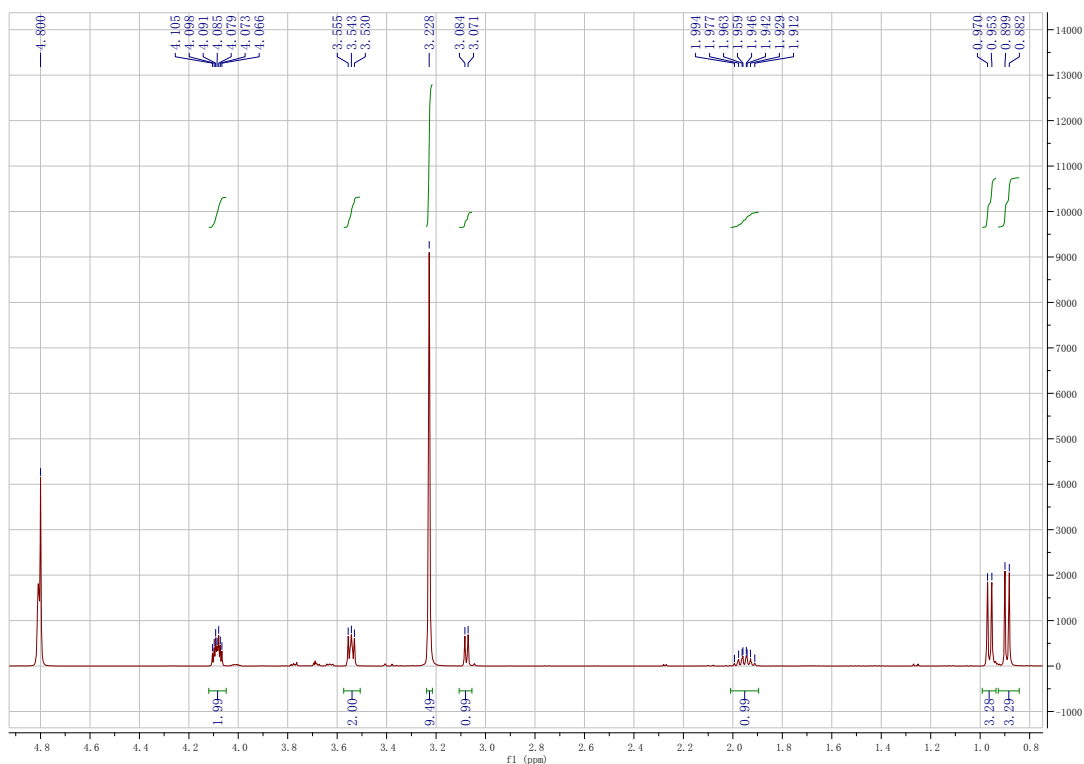
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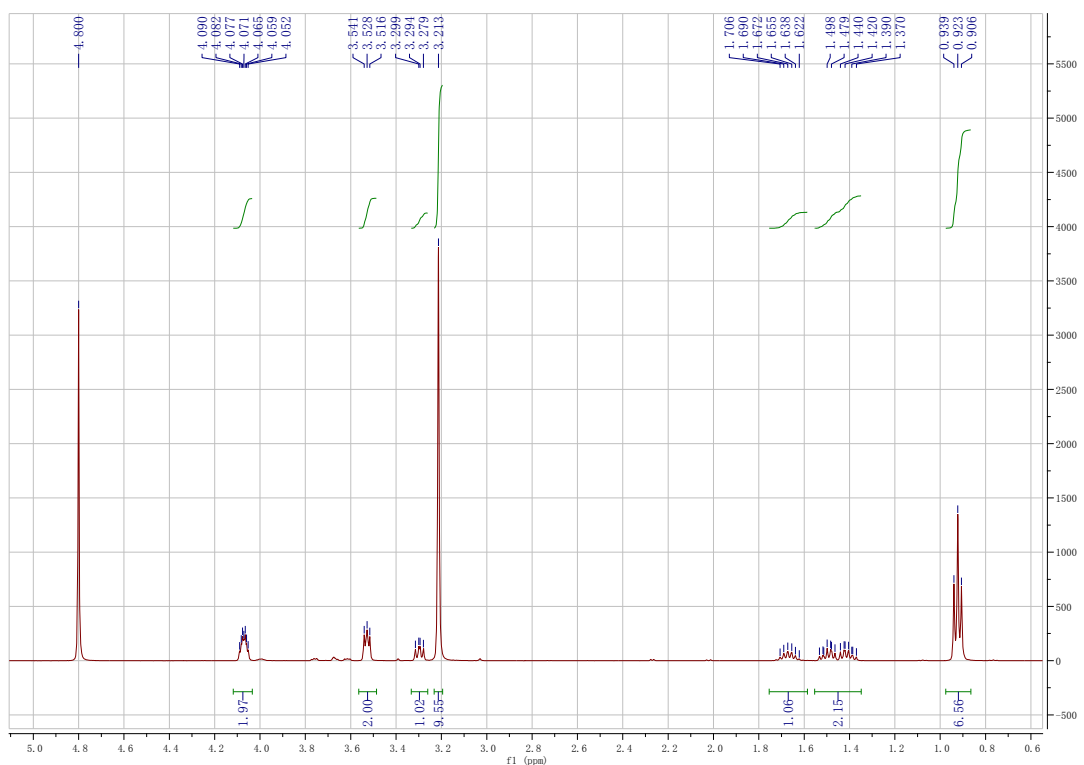
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Ser}]$  in  $\text{D}_2\text{O}$ )



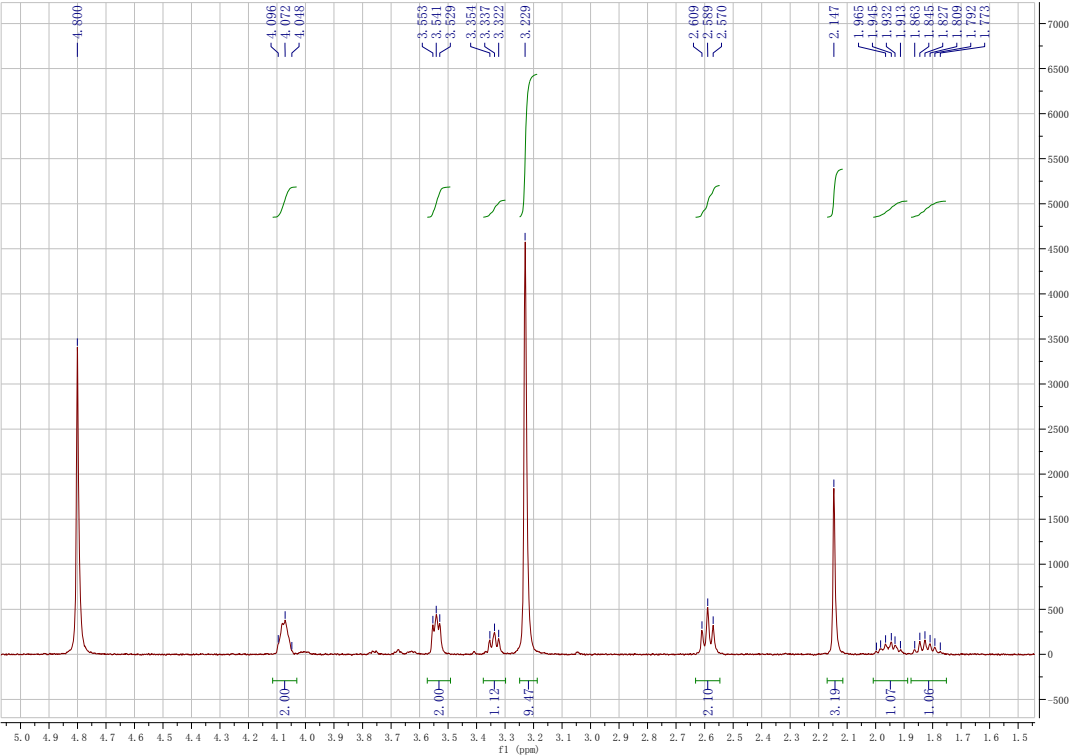
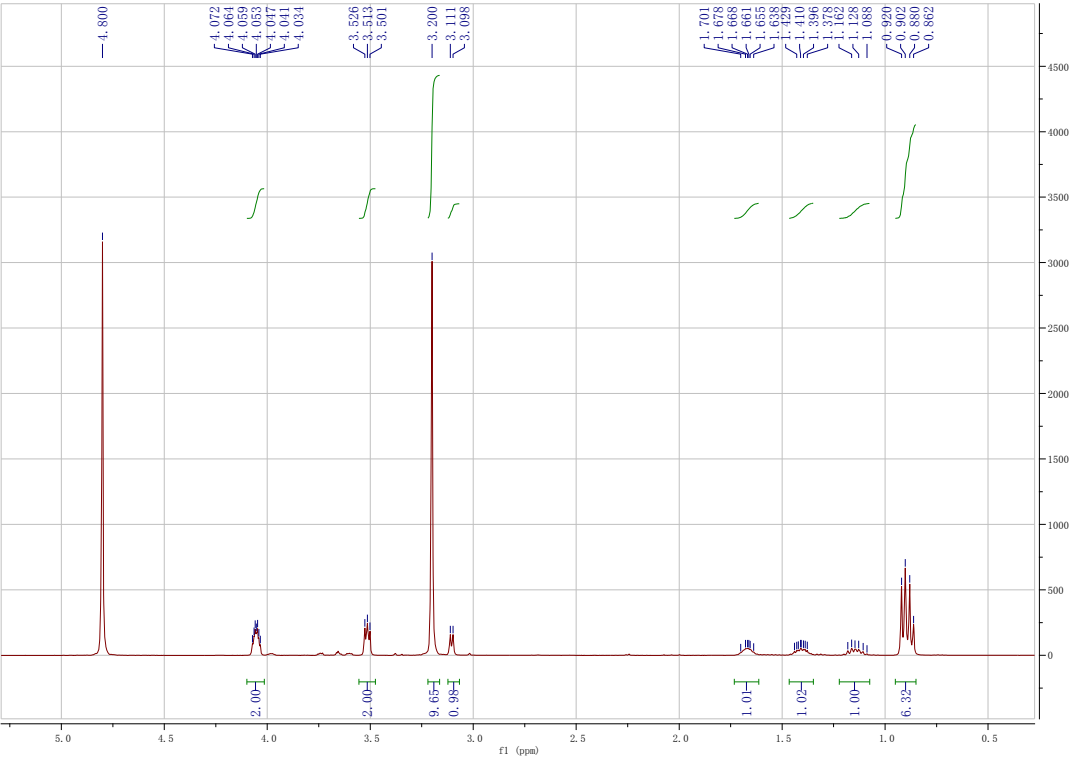
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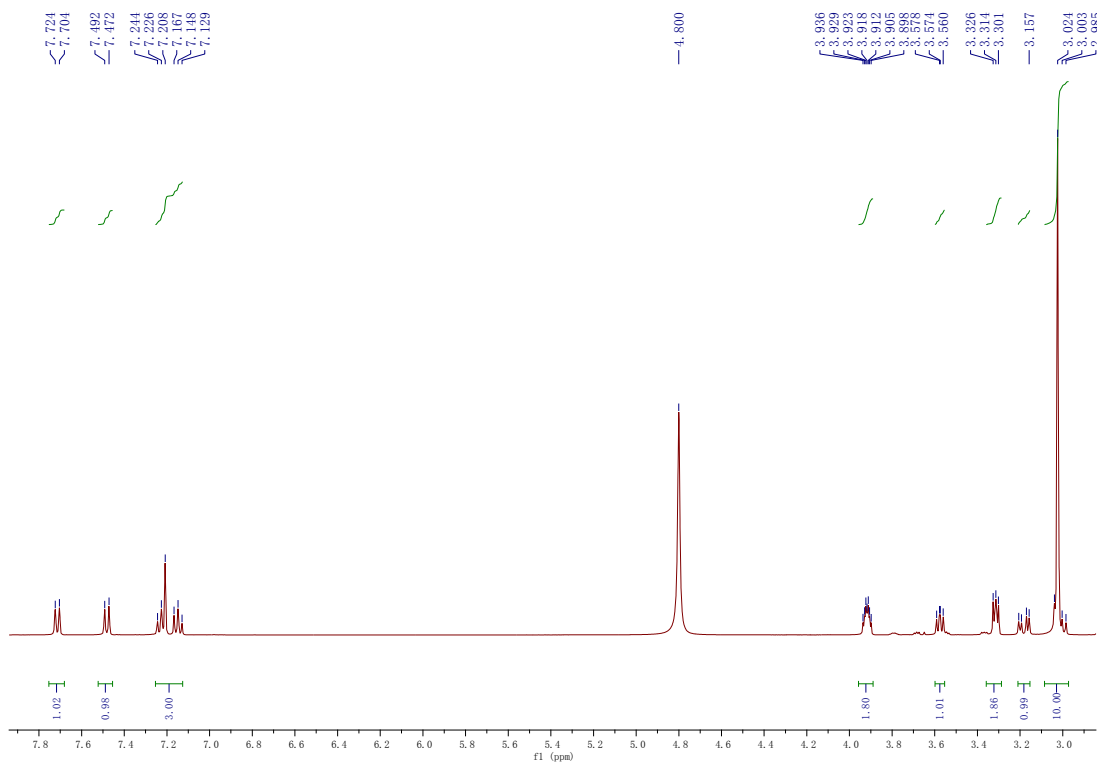
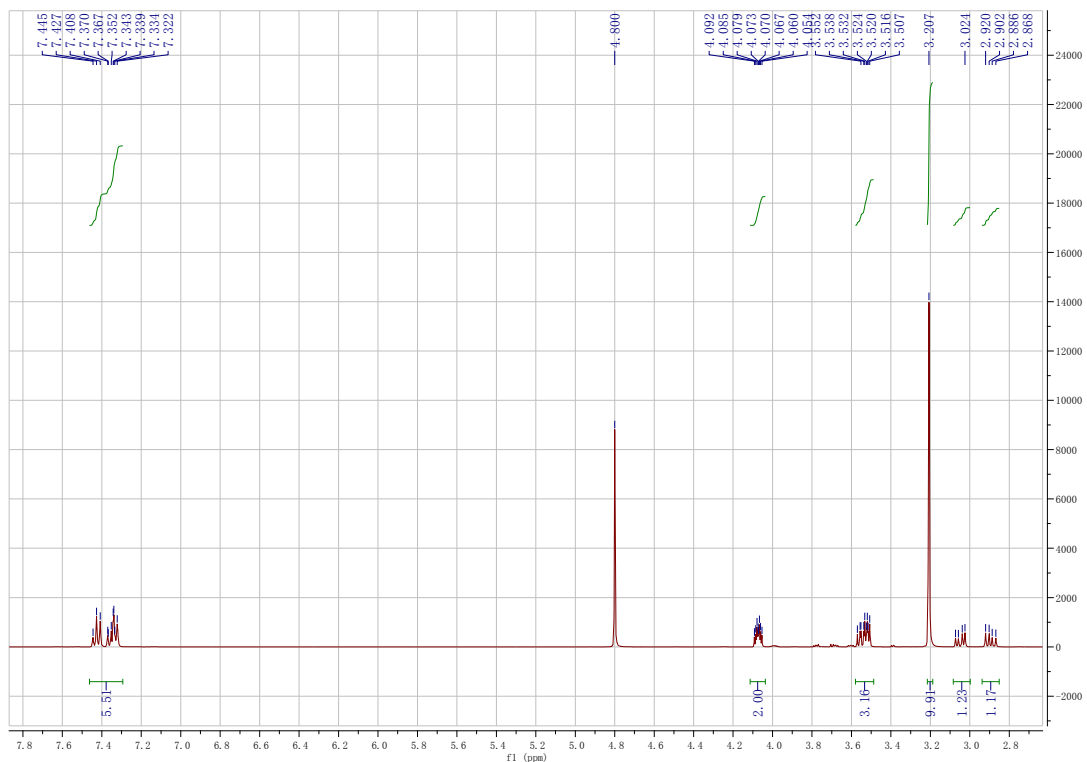


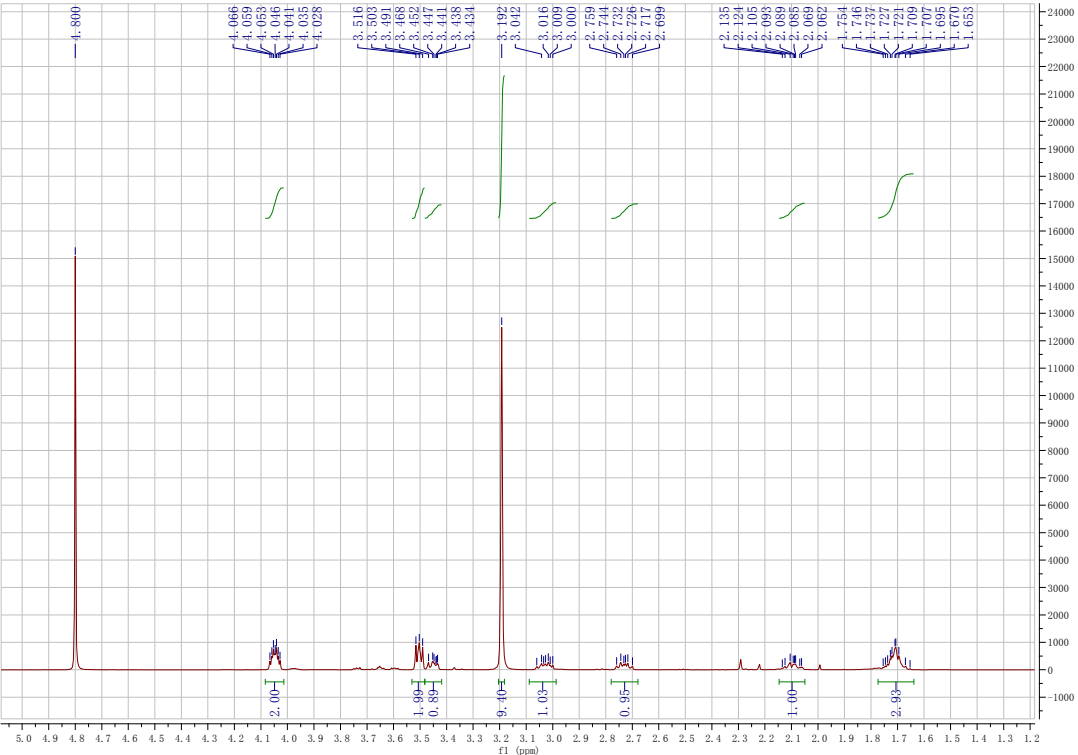
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Val}]$  in  $\text{D}_2\text{O}$ )



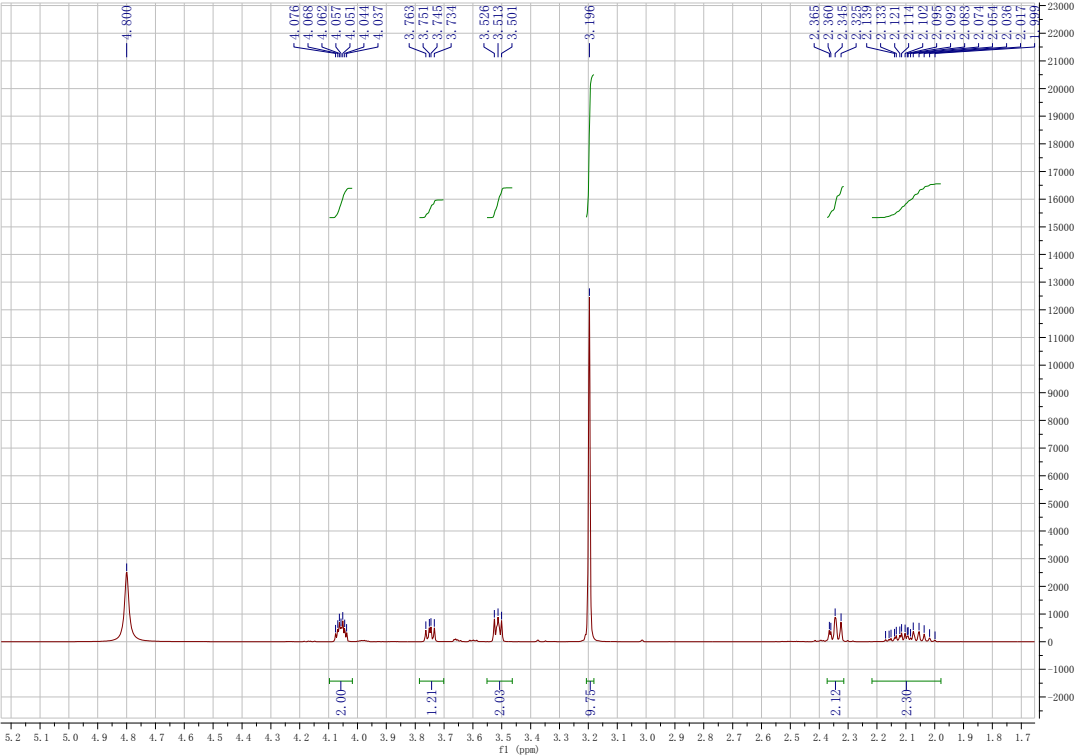
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Leu}]$  in  $\text{D}_2\text{O}$ )



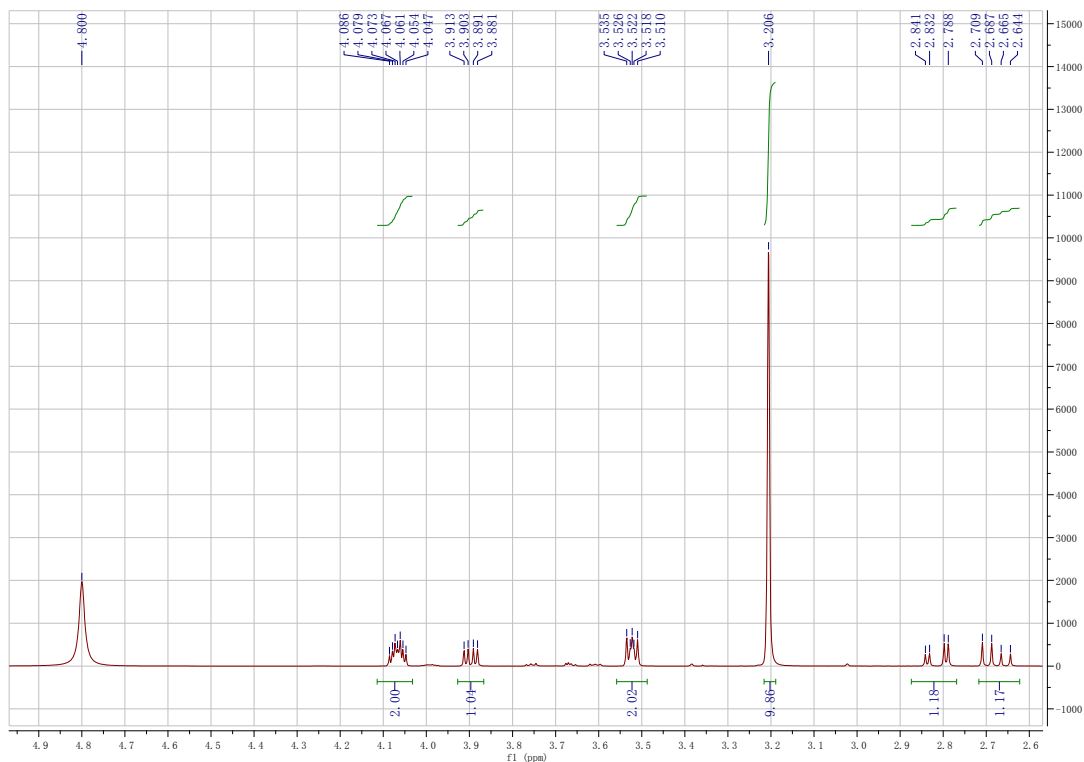




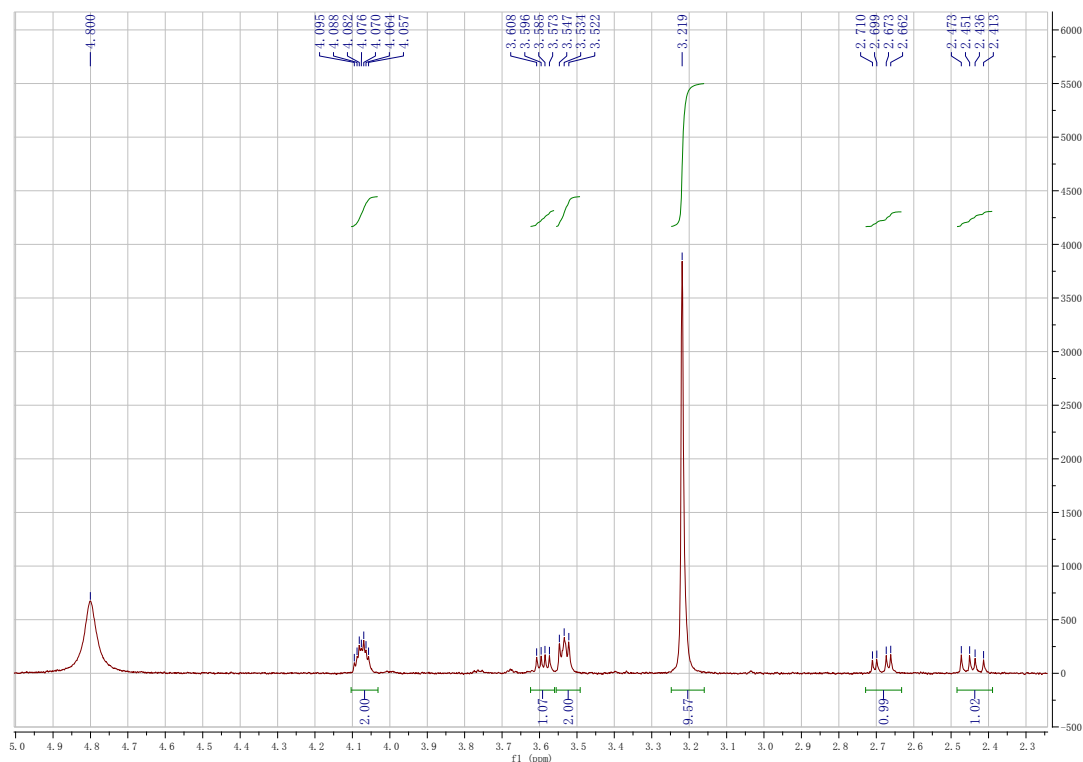
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Pro}]$  in  $\text{D}_2\text{O}$ )



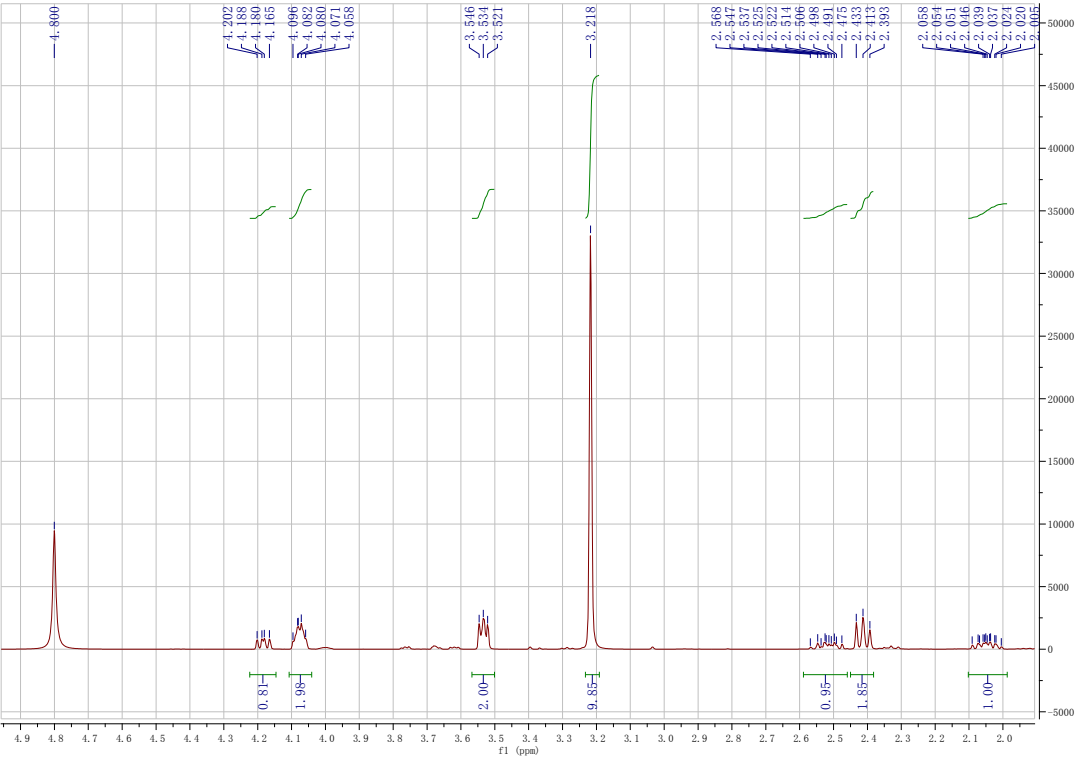
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Glu}]$  in  $\text{D}_2\text{O}$ )



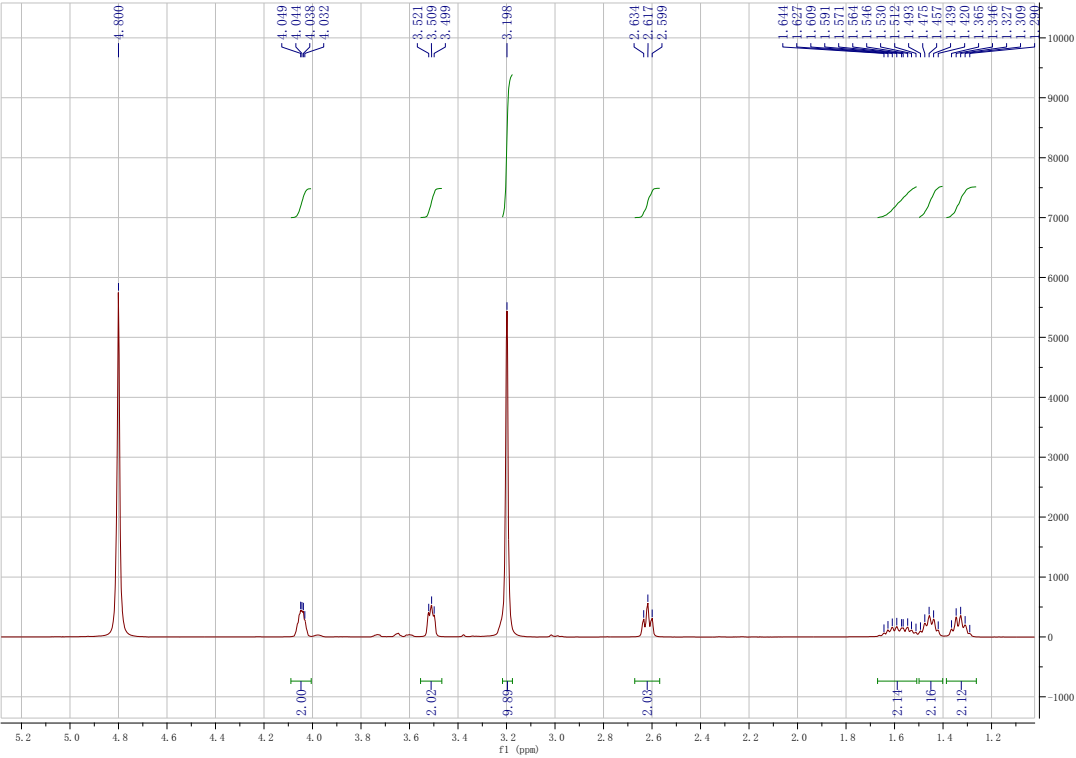
$^1\text{H}$  NMR ( $[\text{Ch}][\text{Asp}]$  in  $\text{D}_2\text{O}$ )



$^1\text{H}$  NMR ( $[\text{Ch}][\text{Asn}]$  in  $\text{D}_2\text{O}$ )

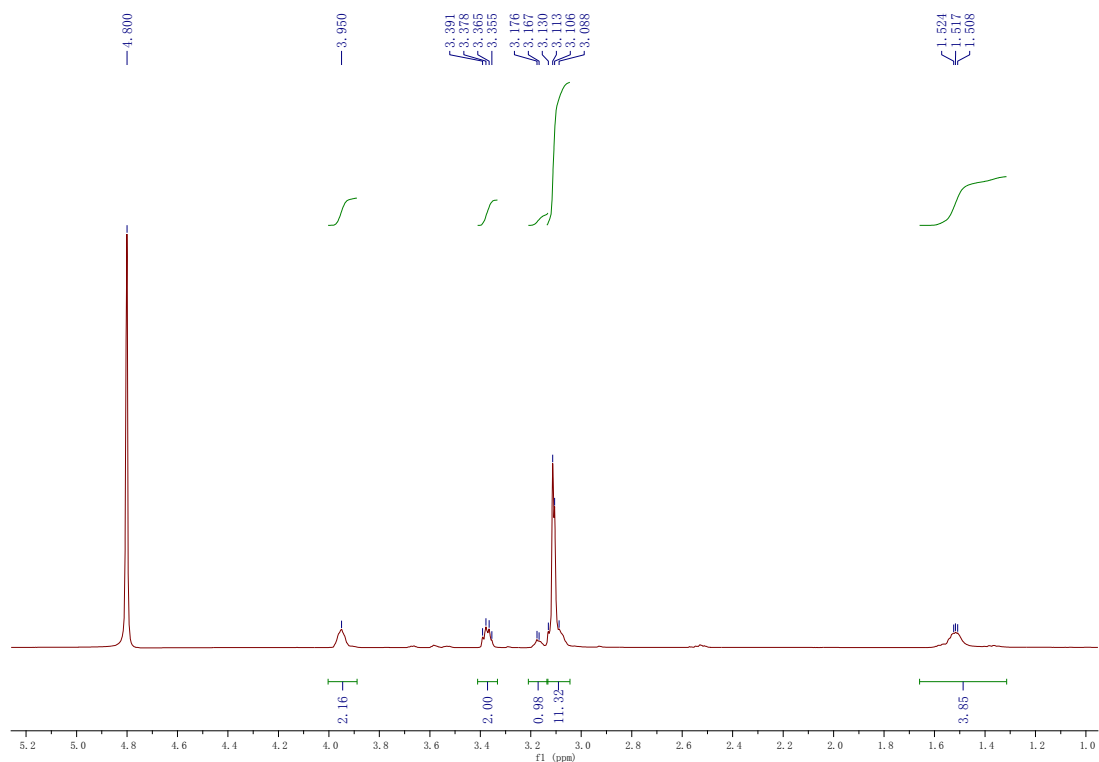


$^1\text{H}$  NMR ( $[\text{Ch}][\text{Gln}]$  in  $\text{D}_2\text{O}$ )

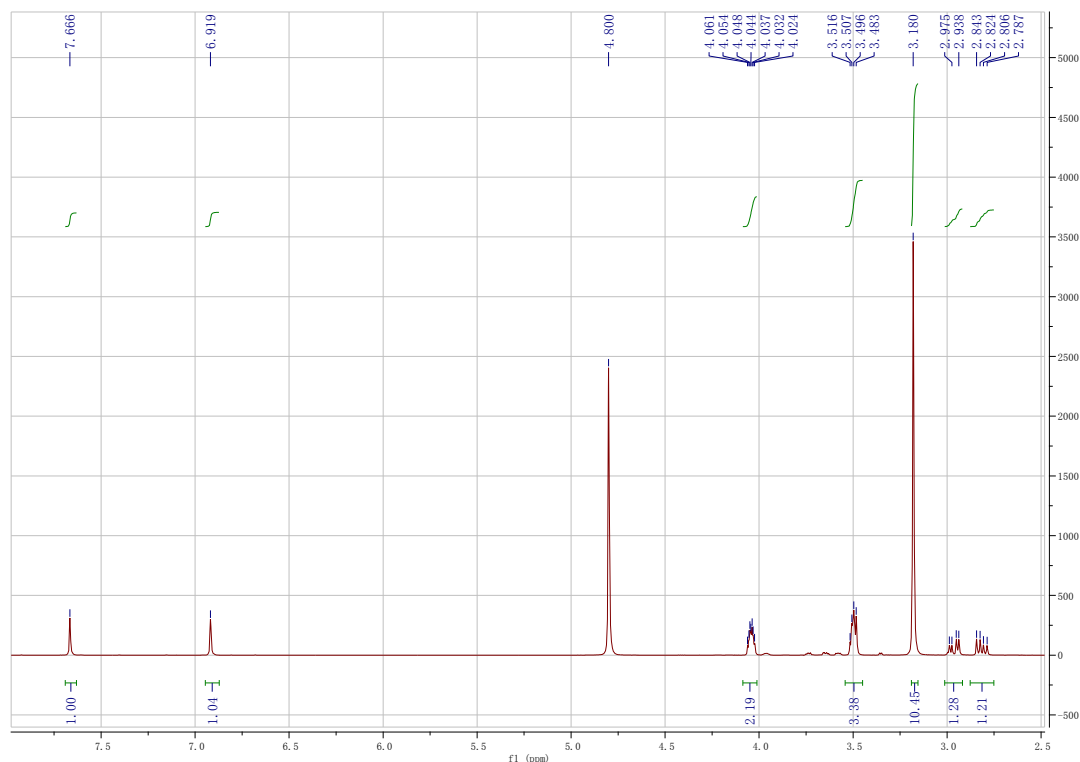


$^1\text{H}$  NMR ( $[\text{Ch}][\text{Lys}]$  in  $\text{D}_2\text{O}$ )





$^1\text{H}$  NMR ( $[\text{Ch}][\text{Arg}]$  in  $\text{D}_2\text{O}$ )



$^1\text{H}$  NMR ( $[\text{Ch}][\text{His}]$  in  $\text{D}_2\text{O}$ )