Supporting Information

A PEG bridged tertiary amine functionalized ionic liquid exhibiting thermoregulated reversible biphase behavior with cyclohexane/isopropanol: synthesis and application in Knoevenagel condensation

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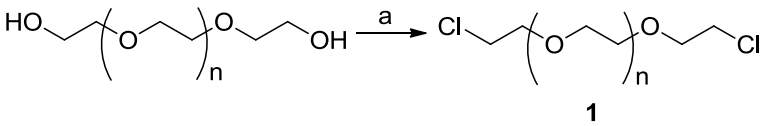
1. General

All of the reagents and solvents are commercially available and were used without further purification.

Melting points were determined on a Perkin – Elmer differential scanning calorimeter and were uncorrected. IR spectra were recorded in KBr disks with a Bomem MB154S FT-IR spectrometer. Mass spectra were taken on an Agilent LC-MS 1100 series instrument in the electrospray ionization (positive ESI) mode. GC analyses were performed on an Agilent 7890A instrument. ^{1}H NMR spectra were recorded on Bruker DRX500 (500 MHz) and ^{13}CNMRspectra on Bruker DRX500 (125 MHz) spectrometer using tetramethylsilane (TMS) as internal standard. Elemental analysis was performed on an Elementar Vario MICRO spectrometer. The thermo gravimetric analysis (TGA) was performed on a TGA/SDTA851e thermal analyzer (Mettler Toledo). Samples were loaded into an alumina crucible and heated at a rate of 20℃·min^{-1} from 50℃ to 600℃ under N_2.

2. Additional preparation experiments and identification data

Preparation of intermediate 1:



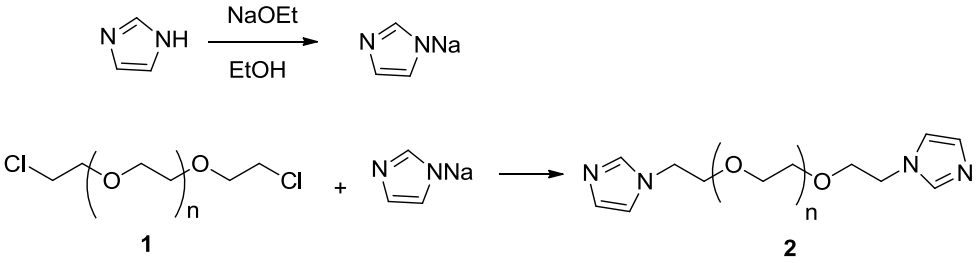
1

7.9 g (100 mmol) dry pyridine was added into a solution of 40.0 g (50 mmol) PEG-800 in 120 mL dry dichloromethane, then 13.1 g (110 mmol) thionyl chloride was added dropwise under nitrogen atmosphere, the mixture was stirred at ambient temperature for 12 h, pyridinium chloride formed was filtered of and then solvent was evaporated. Thereafter, ethyl acetate was added to precipitate remanent pyridinium chloride, the pyridinium chloride precipitated was filtered of. This precipitation-filtration process was repeated several times for sure of complete removal of salt. Cl-PEG_{800}-Cl **1a** was obtained after removing solvent on a rotary evaporator, 39.94 g, 96%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.73-3.75 (t, *J* = 5.0Hz, 4H), 3.60-3.67 (m,

65.0H, $(OCH_2CH_2)_n$) (**Figure S1a**)

Cl-PEG_{1000}-Cl (**1b**) was prepared as the same procedure, 95%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.76-3.78 (t, *J* = 5.0Hz, 4H), 3.63-3.69 (m, 78.3H, $(OCH_2CH_2)_n$). (**Figure S1b**)

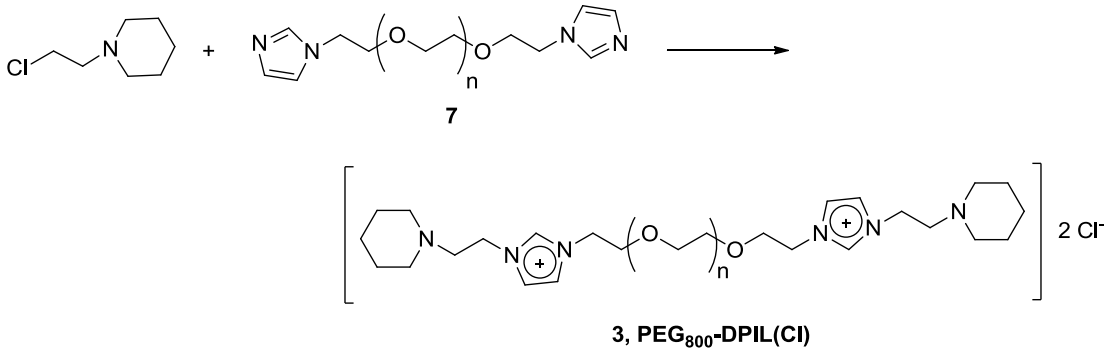
Preparation of intermediate Im-PEG-Im (2):



Sodium (1.13 g, 50 mmol) was added to 100 mL dry ethanol. After melted, imidazole (3.34 g, 50 mmol) was added and the solution was stirred at 70℃ for 10 h. To this yellow solution, compound **1** (20 g, 23.4 mmol) was added, the mixture was heated to reflux and let react for 10 h. Thereafter, the mixture was filtered, the filtrate was concentrated, the yellow oil containing white solid (NaCl) was saturated with 10 mL deionized water and the pH value was adjusted to 9 with concentrate hydrochloric acid, extracted with dichloromethane, combined the extract liquors, dried over anhydrous sodium sulfate, filtered and concentrated to give intermediate Im-PEG_{800}-Im **2a** as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.54 - 3.59 (m, 70.62H), 3.69 - 3.71 (t, *J* = 5.5 Hz, 4.36H), 4.05 - 4.07 (t, *J* = 5.5 Hz, 4.25H), 6.95 (s, 2H), 7.00 (s, 2H), 7.48(s, 2H) (**Figure S2a**).

Im-PEG_{1000}-Im (**2b**) was prepared as the same procedure. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.53-3.58 (m, 87.34H), 3.68-3.70 (t, *J* = 5.5 Hz, 4.42H), 4.04-4.06 (t, *J* = 5.5 Hz, 4.22H), 6.94 (s, 2H), 6.97 (s, 2H), 7.47(s, 2H) (**Figure S2b**).

Synthesis of PEG_{800}-DPIL(Cl) (3) via route one:

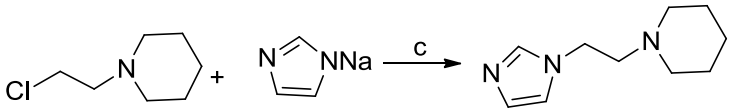


To a solution of Im-PEG_{800}-Im (**2a**, 10.0 g, 11.1 mmol) in 100 mL dry ethanol was added dropwise a solution of 1-(2-chloroethyl) piperidine hydrochloride (4.3 g, 23.3 mmol) in 50 mL dry ethanol within 3 h at 80℃ under nitrogen atmosphere, the mixture was stirred for another 30 h at the same temperature. After concentration，the brown oily residue was dissolved in deionized waster (15 mL), the pH value was adjusted to 9 with aqueous KOH. Ethanol (30 mL) was added to make major inorganic salt precipitate. The inorganic salt precipitated was filtered of, the liquor was concentrated to give an oily residue. The residue was saturated with dichloromethane for further precipitation of remain salt coated by ionic liquid, the inorganic salt was filtered of and the filtrate was concentrated. This process was repeated several times to make sure of complete removal of inorganic salt. The target product PEG_{800}-DPIL(Cl) (**3**) was obtained as a brown oil, 12.9 g, 91%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.29-1.30 (m, 4H), 1.39-1.43 (m, 8H), 2.31 (s, 8H), 2.61-2.63 (t, *J* = 5.60 Hz, 4H), 3.43-3.52 (m, 75H). 3.74-3.76 (t, *J* = 4.50 Hz, 4H), 4.27-4.29 (t, *J* = 5.55 Hz, 4H), 4.46-4.48 (t, *J* = 4.50 Hz, 4H), 7.54 (s, 2H), 7.61 (s, 2H), 10.04 (s, 2H) **(Figure S3)**; ^{13}C NMR (125 MHz, D_2O) δ: 23.22, 24.67, 46.04, 49.20, 53.73, 57.03, 68.37, 69.54, 69.61, 122.37, 122.94 **(Figure S4)**; IR (cm^{-1}) 2863, 1563, 1455, 1349, 1301, 1251, 1095, 1038, 946, 846, 757, 727, 695 **(Figure S5)**; ESI-MS (m/z): 545.35 (M^{2+}/2, n = 16), 567.40 (M^{2+}/2, n = 17), 589.50 (M^{2+}/2, n = 18), 611.55 (M^{2+}/2, n = 19) **(Figure S6)**; Anal. calcd for $C_{55.52}H_{105.04}Cl_2N_6O_{16.76}$: C, 55.88; H, 8.79; N, 7.03; found: C, 56.07; H, 8.95; N, 6.91%.

[PEG_{1000}-DPIL]Cl (**5**) was prepared as the same procedure. ^{1}H NMR (500 MHz,

D_2O) δ: 1.40-1.41 (s, 4H), 1.53-1.55 (m, 8H), 2.56 (s, 8H), 2.91-2.93 (t, *J* = 6.95 Hz, 4H), 3.54-3.63 (m, 89.96H). 3.84-3.86 (t, *J* = 4.90 Hz, 4H), 4.34-4.39 (m, 8H), 7.53 (s, 4H) **(Figure S7)**.

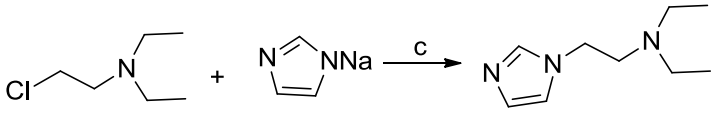
Preparation of 1-(2-(1*H*-imidazol-1-yl)ethyl) piperidine (4)



4

Imidazole (8.9 g, 130 mmol) was melted at 100 ℃ then NaOH (4.8 g, 120 mmol) was added with stirring. After the solid NaOH melted, toluene (50 mL) was added to azeotropic removal of water for 3 h. After which, toluene was removed by rotary evaporation under reduced pressure. Subsequently, 1-(2-chloroethyl) piperidine hydrochloride (11.1 g, 60 mmol) and CH_3CN (80 mL) was added. The mixture was stirred at 80℃ for 12 h and filtered. The filtrate was concentrated under reduced pressure, the yellow residue obtained was dissolved in 100 mL CH_2Cl_2 and extracted by water for several times to remove inorganic salts and excess of imidazole. After removal of solvent, 1-(2-(1*H*-imidazol-1-yl)ethyl) piperidine (**4**) was obtained and used for the next reaction without further purification (9.8 g, 91 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.19-1.22 (m, 2H), 1.30-1.36 (m, 4H), 2.16-2.17 (s, 2H), 2.36-2.40 (t, *J* = 6.65 Hz, 2H), 3.75-3.79 (t, *J* = 6.65 Hz, 2H), 6.74 (s, 1H), 6.78 (s, 1H), 7.29 (s, 1H) (**Figure S8**); ^{13}C NMR (126MHz, $CDCl_3$) δ: 24.01, 25.80, 44.59, 54.46, 59.20, 119.08, 128.76, 137.13 (**Figure S9**); ESI-MS (m/z): 179 (M^+).

Preparation of *N,N*-diethyl-2-(1*H*-imidazol-1-yl)ethanamine (6):

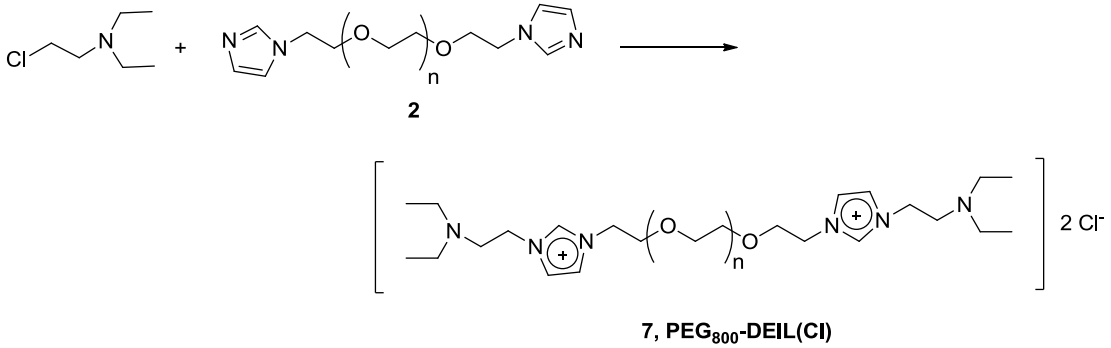


6

Imidazole (8.9 g, 130 mmol) was melted at 100 ℃ and NaOH (4.8 g, 120 mmol) was added with stirring. After the solid NaOH thawed, toluene (50 mL) was added to

azeotropic removal of water for 3 h. Then, the toluene was evaporated under reduced pressure. Subsequently, 2-chloro-*N,N*-diethylethanamine hydrochloride (10.3 g, 60 mmol) and CH_3CN (80 mL) was added. The mixture was stirred at 80℃ for 12 h and then filtered. The filtrate was concentrated under reduced pressure, the yellow residue obtained was dissolved in 100 mL CH_2Cl_2 and extracted by water several times to remove inorganic salts and excess of imidazole. After removal of solvent, *N,N*-diethyl-2-(1*H*-imidazol-1-yl) ethanamine (**6**) was obtained and used for the next reaction without further purification (8.7 g, 87 % yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.91-0.94 (t, *J* = 15 Hz, 6H), 2.45-2.50 (q, *J* = 15 Hz, 4H), 2.66-2.69 (t, *J* = 10 Hz, 2H), 3.90-3.93 (t, *J* = 10 Hz, 2H), 6.91 (s, 1H), 6.98 (s, 1H), 7.46 (s, 1H) (**Figure S10**); ESI-MS: m/z 167.

Synthesis of PEG_{800}-DEIL(Cl) (7) via route one:



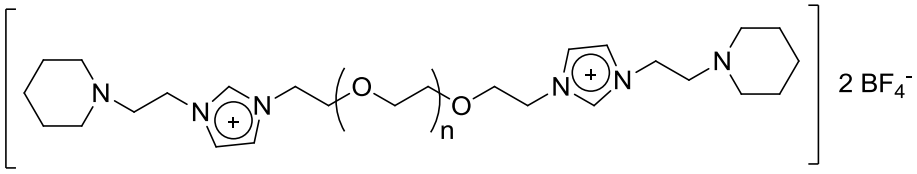
To a solution of Im-PEG_{800}-Im (**2**, 10.0 g, 11.1 mmol) in 100 mL dry ethanol was added dropwise a solution of 2-chloro-*N,N*-diethylethanamine hydrochloride (4.0 g, 23.3 mmol) in 30 mL dry ethanol within 2 h at 80℃ under nitrogen atmosphere, then stirred for another 30 h at the same temperature. The following workup was just the same as described above. The target product PEG_{800}-DEIL(Cl) (**7**) was obtained as a brown oil, 11.9 g, 92%. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 0.80-0.83 (t, *J* = 14.1 Hz, 12.11H), 2.42-2.47 (q, *J* = 14.1 Hz, 8.04H), 2.73-2.75 (t, *J* = 5.1 Hz, 4H), 3.51 (m, 66.32H), 3.75-3.77 (t, *J* = 4.3 Hz, 4.12H). 4.25-4.27 (t, *J* = 5.1 Hz, 3.93H), 4.47-4.49 (t, *J* = 4.3 Hz, 3.98H), 7.52 (s, 2H), 7.60 (s, 2H), 9.95 (s, 2H) (**Figure S11**);^{13}C NMR (126 MHz, $CDCl_3$) δ: 11.55, 46.76, 47.99, 49.48, 52.59, 69.11,70.13, 70.17, 70.26, 70.36, 77.47, 122.33, 122.74, 137.24 ppm (**Figure S12**).

[PEG_{1000}-DEIL]Cl (**8**) was prepared as the same procedure. ^{1}H NMR (500 MHz, D_2O) δ: 0.96-0.98 (t, *J* = 14.4 Hz, 12.06H), 2.56-2.58 (q, *J* = 14.4 Hz, 8.0H), 2.94-2.97 (t, *J* = 6.8 Hz, 3.94H), 3.62-3.70 (m, 88.93H), 3.86-3.88 (t, *J* = 4.7 Hz, 4.07H). 4.31-4.33 (t, *J* = 6.8 Hz, 4.0H), 4.36-4.38 (t, *J* = 4.7 Hz, 3.98H), 7.55 (s, 2H), 7.56 (s, 1.83H) (**Figure S13**); ^{13}C NMR (126MHz, D_2O) δ: 10.20, 46.69, 46.74, 49.21, 51.09, 68.39, 69.55, 69.62, 122.34, 122.97 ppm (**Figure S14**).

Preparation of PEG_{800}-DPIL(Cl) (3) via route two

To the solution of **4** (6.3 g, 37.5 mmol) in 30 mL acetonitrile was added in portions the solution of **1** (9.0 g, 10.0 mmol) in 30 mL acetonitrile at ambient temperature under nitrogen atmosphere. The mixture was stirred for 7 days. Thereafter, the solvent was removed in vacuum, the residue obtained was dissolved in 150 mL deionized water and extracted with CH_2Cl_2 (5×20 mL) to remove unreacted raw materials. After removal of water on a rotary evaporator, the piperidine-functionalized PEG-800 bridged dicationic ionic liquid PEG_{800}-DPIL(Cl) (**3**) was obtained as a brown oil, 12.0 g, 93 % yield.

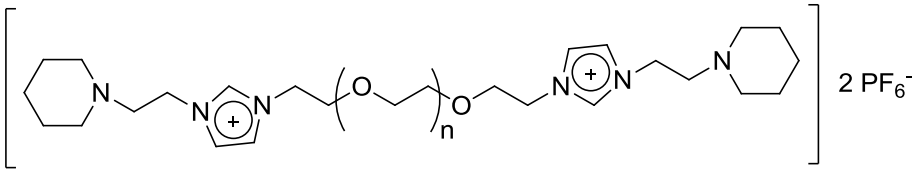
Prepation of PEG_{800}-DPIL(BF_4) (9):



9, PEG_{800}-DPIL(BF_4)

To the solution of **3** (6.0 g, 5 mmol) in CH_2Cl_2 (50 mL) was added $NaBF_4$ (4.4 g, 20 mmol) and stirred at ambient temperature for 36 h, filtered and evaporated to give a pale yellow oil product **9**, 6.2 g, 95% yield.

Prepation of PEG_{800}-DPIL(PF_6) (10):



10, PEG_{800}-DPIL(PF_6)

To the solution of **3** (6.0 g, 5 mmol) in CH_2Cl_2 (50 mL) was added KPF_6 (7.4 g, 20 mmol) and stirred at ambient temperature for 36 h, filtered and evaporated to give a pale yellow oil product **10**, 6.9 g, 98% yield.

3. Solubility test

The solubility of PEG-DPILs and PEG-DEILs in some solvents were tested at different temperatures. The results are listed in **Table S1~S7**.

Table S1 Solubility of ILs at room temperature[a]

Solvents	**3**	**5**	**7**	**8**	**9**	**10**
H_2O	s	s	s	s	s	s
MeOH	s	s	s	s	s	s
EtOH	s	s	s	s	s	ps
Isopropanol	ps	s	s	s	i	i
CH_2Cl_2	s	s	s	s	s	s
AcOEt	i	i	i	i	i	ps
Acetone	ps	s	s	s	s	s
Et_2O	i	i	i	i	i	i
Cyclohexane	i	i	i	i	i	i
heptane	i	i	i	i	i	i
Petroleum Ether	i	i	i	i	i	i
Toluene	i	ps	i	ps	i	i
DMF	s	s	s	s	s	s
DMSO	s	s	s	s	s	s

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S2 Solubility of PEG_{800}-DPIL(Cl) (**3**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	s	s	s	-
AcOEt	i	i	i	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	i	i	i	i

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S3 Solubility of PEG_{1000}-DPIL(Cl) (**5**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	s	s	s	-
AcOEt	i	i	i	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	ps	ps	ps	ps

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S4 Solubility of PEG_{800}-DEIL(Cl) (**7**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	s	s	s	-
AcOEt	i	i	i	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	i	i	i	i

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S5 Solubility of PEG_{1000}-DEIL(Cl) (**8**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	s	s	s	-
AcOEt	i	i	i	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	ps	ps	ps	ps

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S6 Solubility of PEG_{800}-DPIL(BF_4) (**9**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	i	i	ps	-
AcOEt	i	i	i	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	i	i	i	i

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S7 Solubility of PEG_{800}-DPIL(PF_6) (**10**) at different temperature[a]

Solvents	40℃	60℃	80℃	100℃
EtOH	s	s	s	-
Isopropanol	i	ps	ps	-
AcOEt	ps	ps	ps	-
Cyclohexane	i	i	i	i
n-heptane	i	i	i	i
Toluene	i	i	i	i

[a] s: soluble; i: insoluble; ps: partly soluble.

Table S8 The relationship between the critical temperature of PEG_{800}-DPIL(Cl)/CYH/IPA with the volume of mixture solvent

V/mL	Critical temperature/℃
7.0	22
6.0	25
5.5	33
5.1	40
4.7	47
4.2	52
4.0	60
3.8	67
3.6	80
3.4	92
3.2	106
3.0	110

4. Copies of identification spectra of ILs and their intermediates

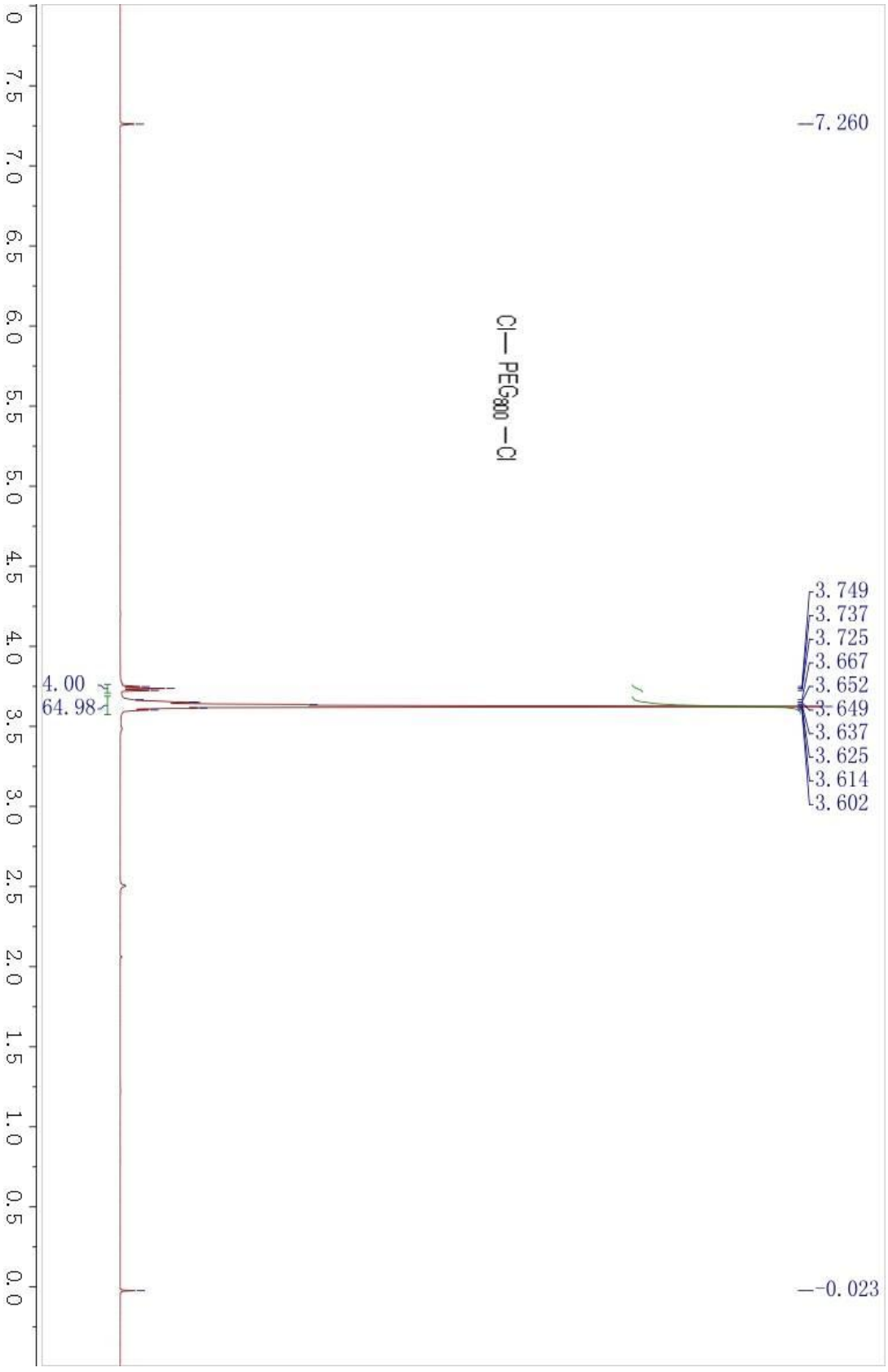


Figure S1a ^{1}H NMR spectrum of PEG-800 dichloride (**1a**)

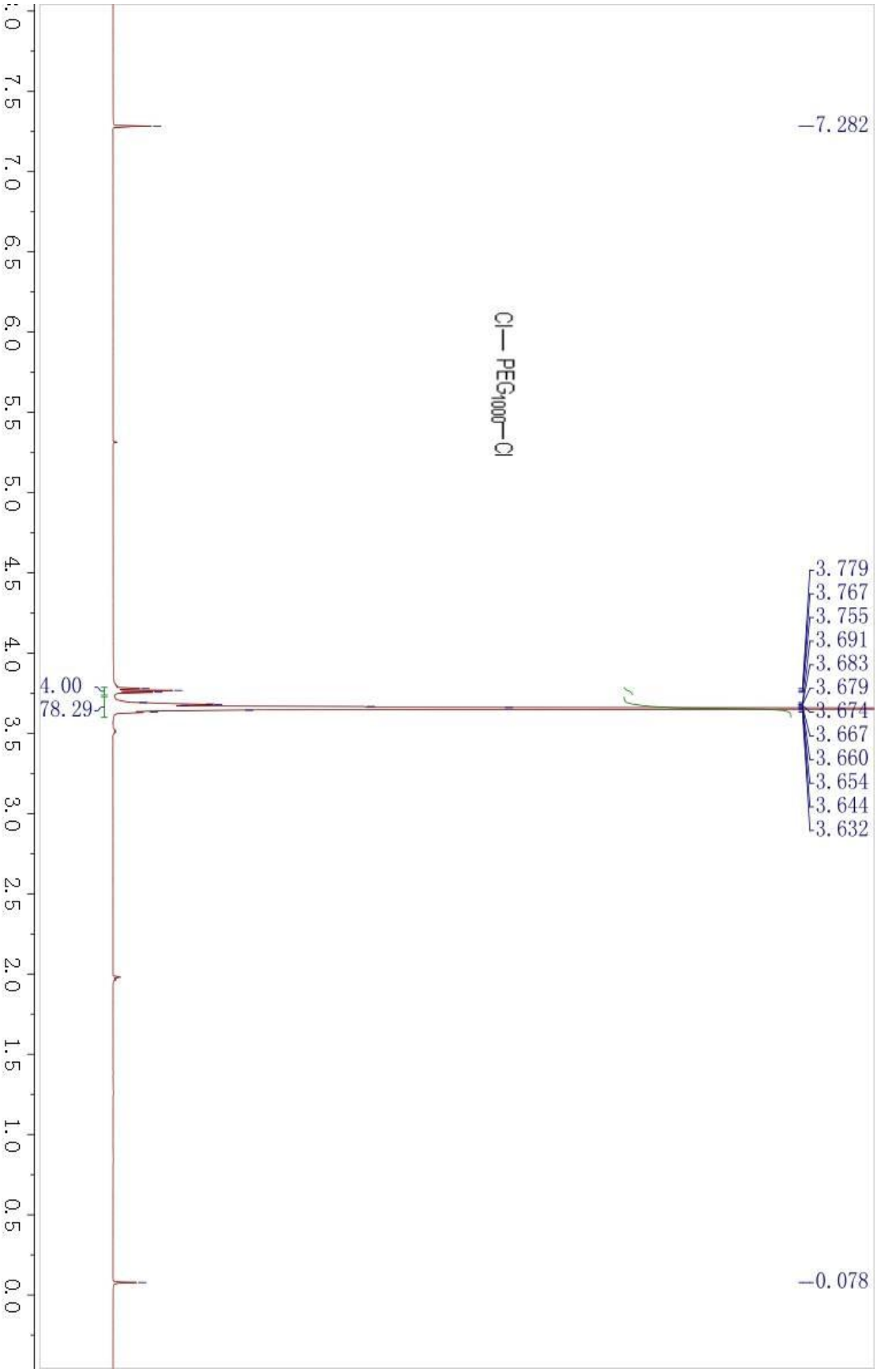


Figure S1b ^{1}H NMR spectrum of PEG-1000 dichloride (**1b**)

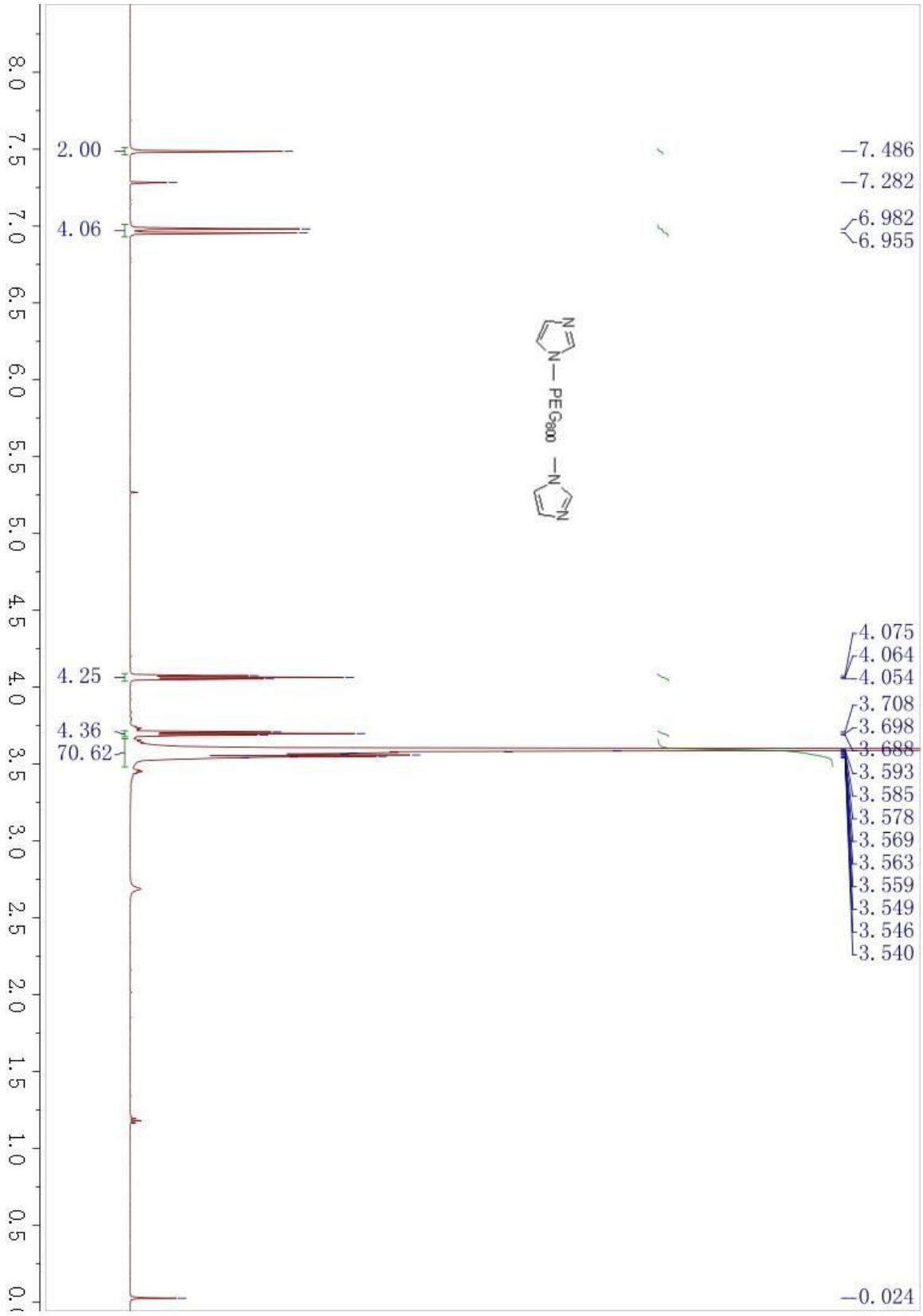


Figure S2a ^{1}H NMR spectrum of Im-PEG$_{800}$-Im (**2a**)

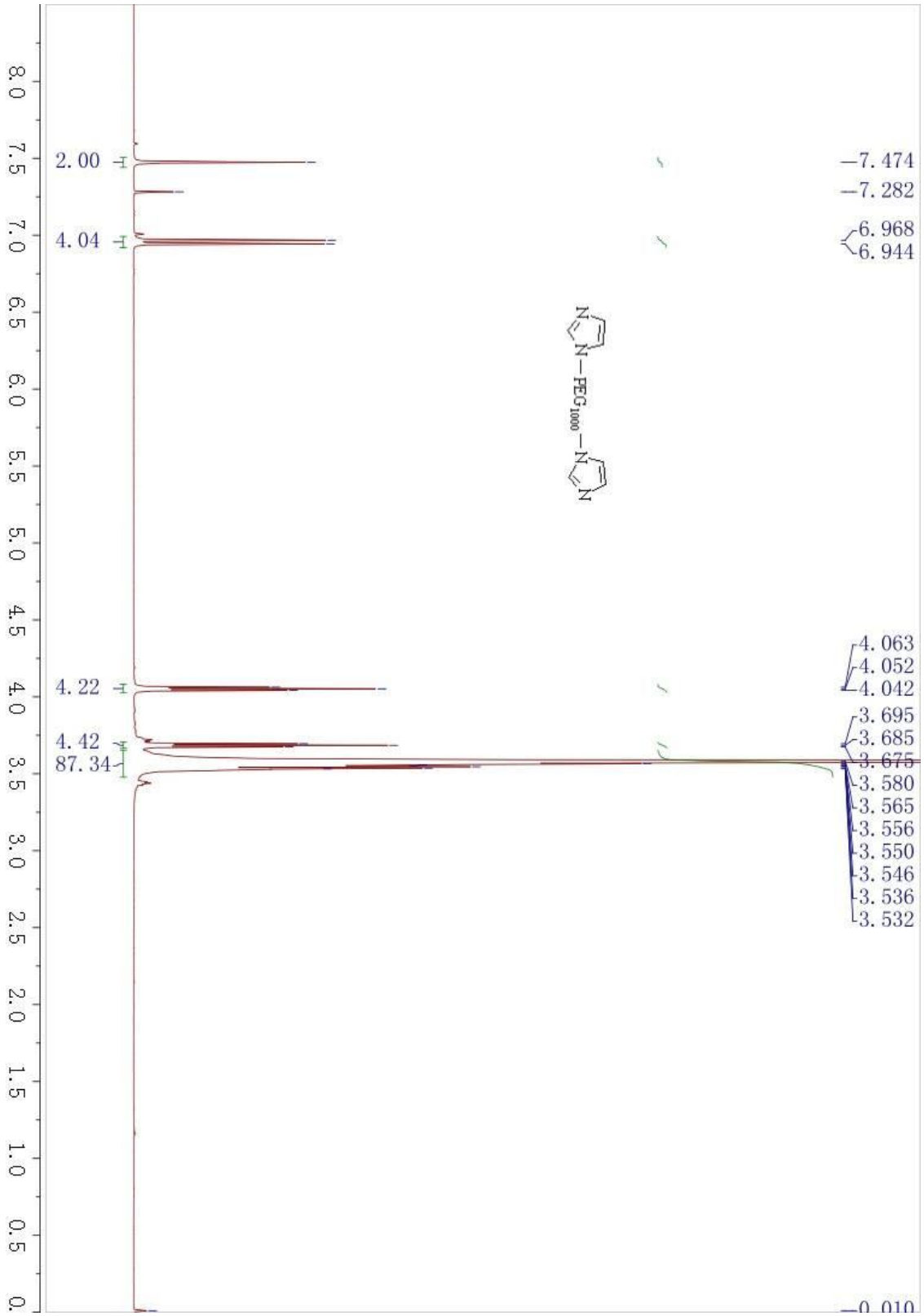


Figure S2b ^{1}H NMR spectrum of Im-PEG$_{1000}$-Im (**2b**)

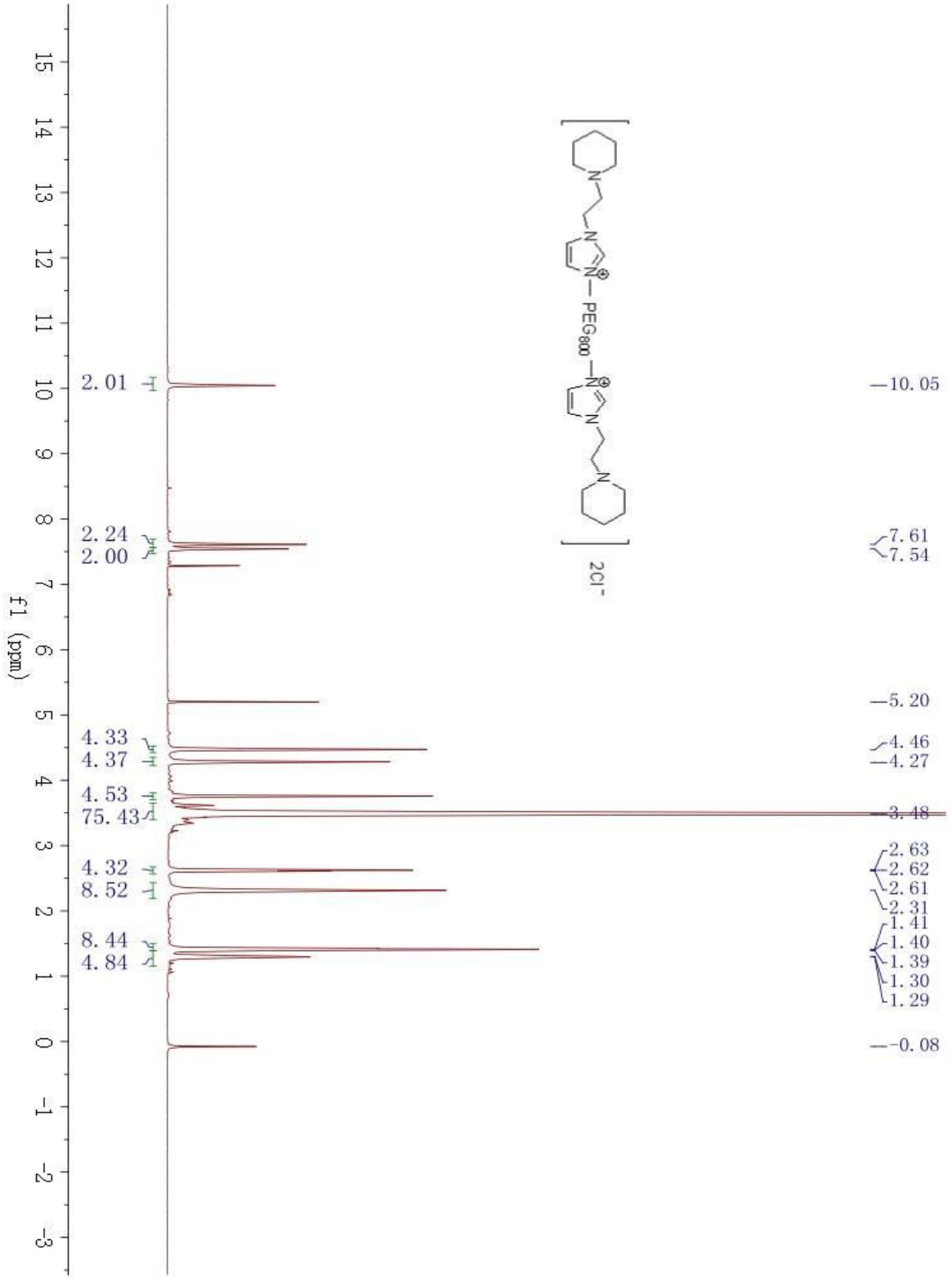


Figure S3 ^{1}H NMR spectrum of PEG_{800}-DPIL(Cl) (**3**)

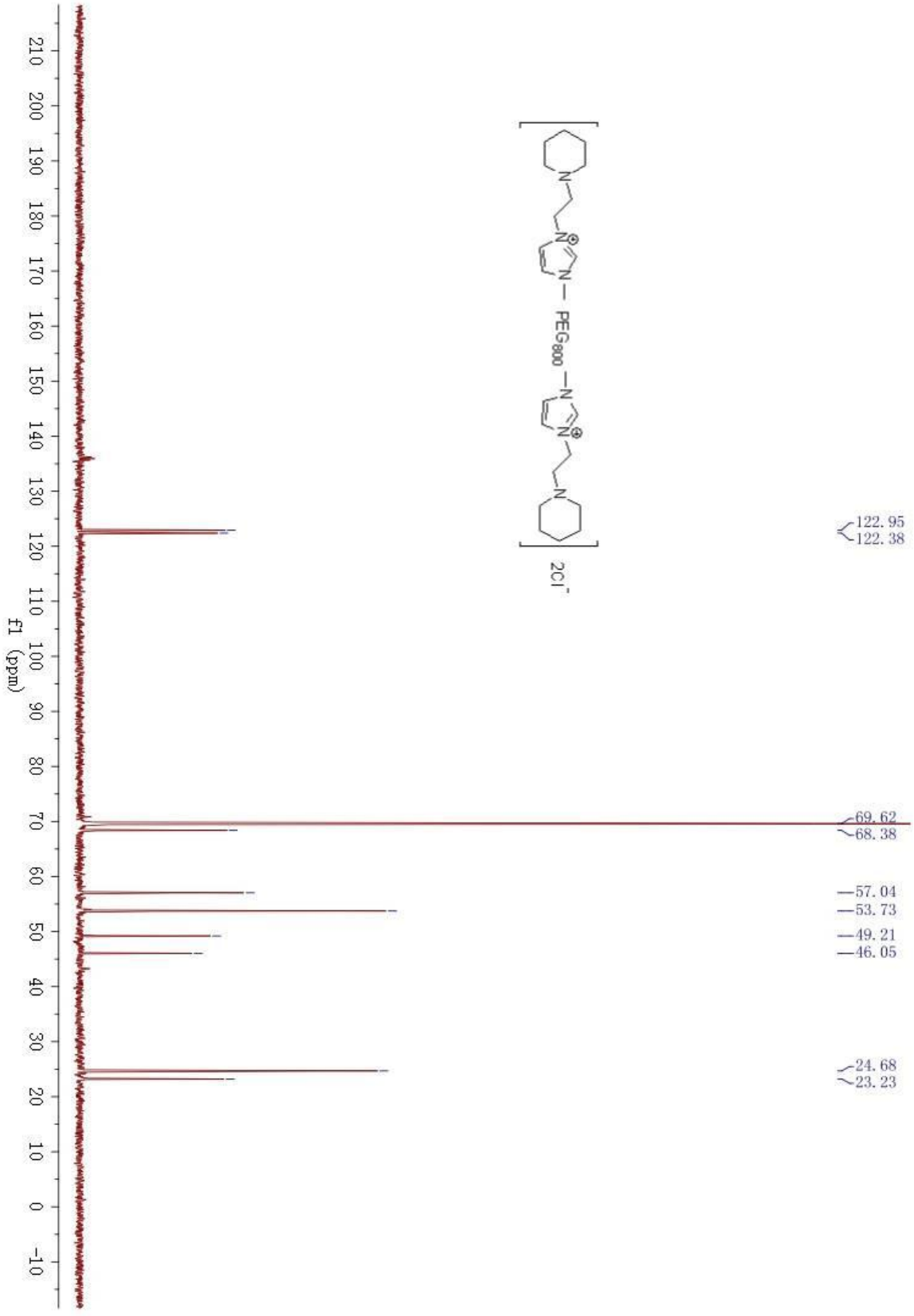


Figure S4 ^{13}C NMR spectrum of PEG_{800}-DPIL(Cl) (**3**)

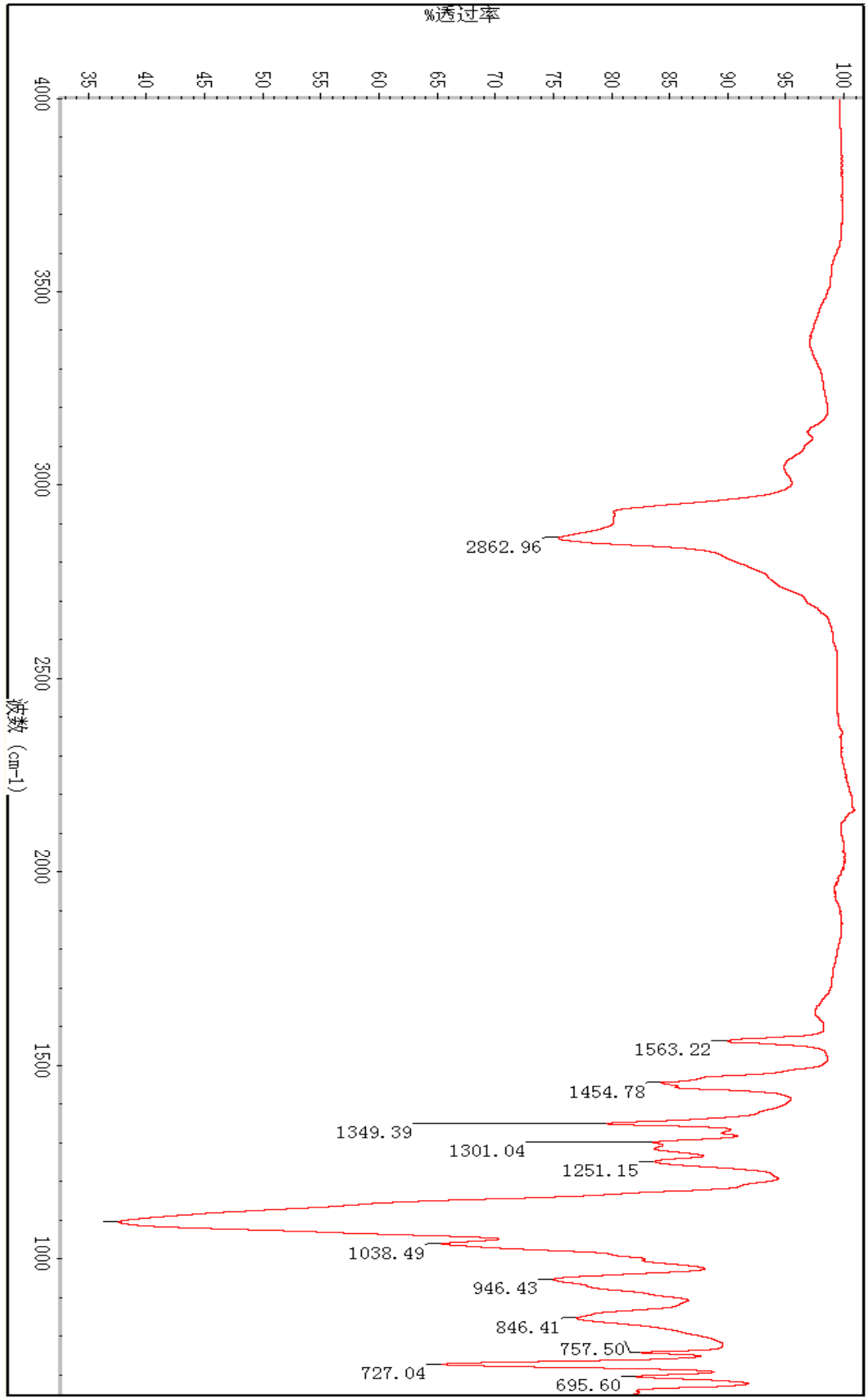


Figure S5 FTIR spectrum of PEG_{800}-DPIL(Cl) (**3**)

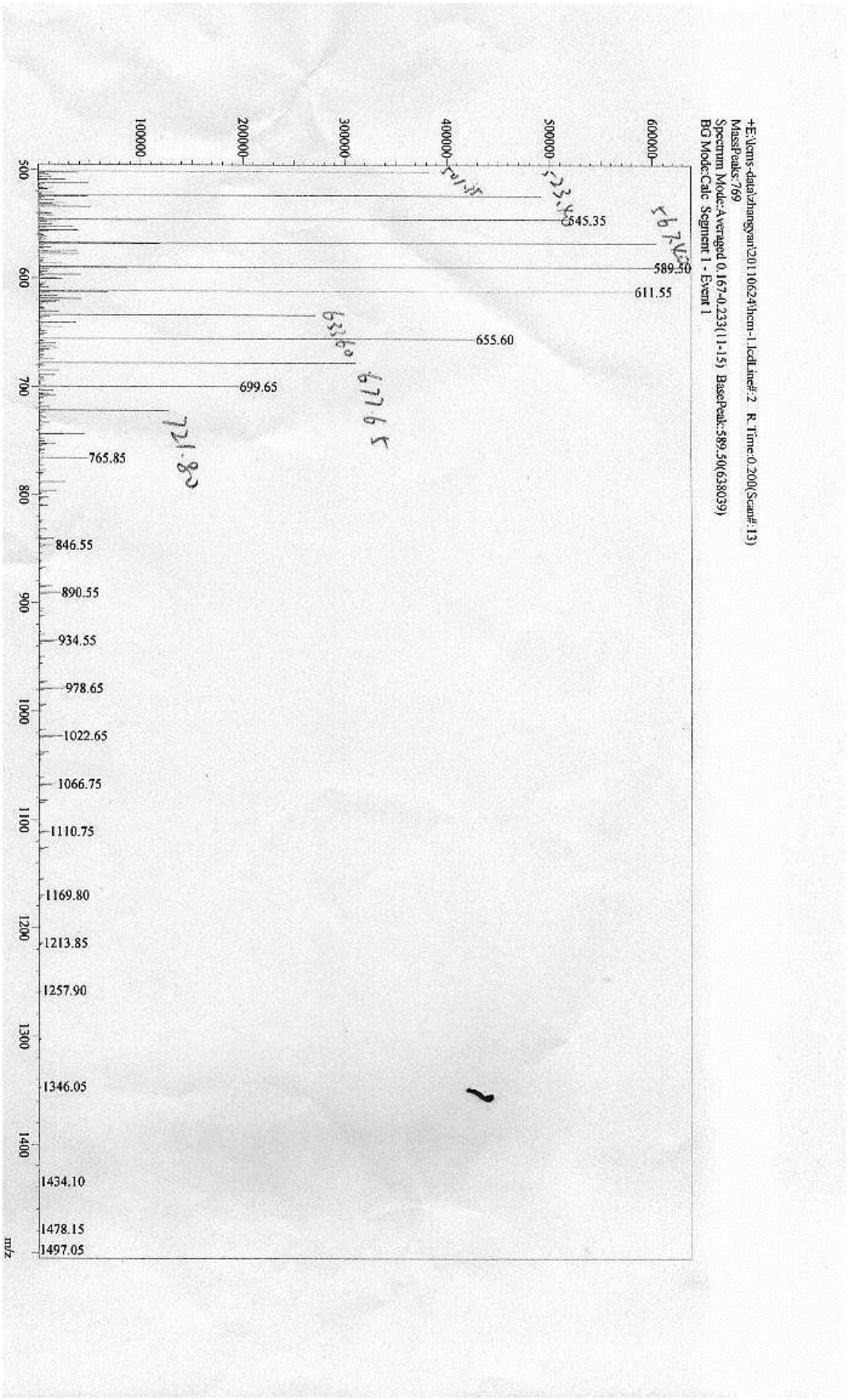


Figure S6 ESI-MS spectrum of PEG_{800}-DPIL(Cl) (**3**)

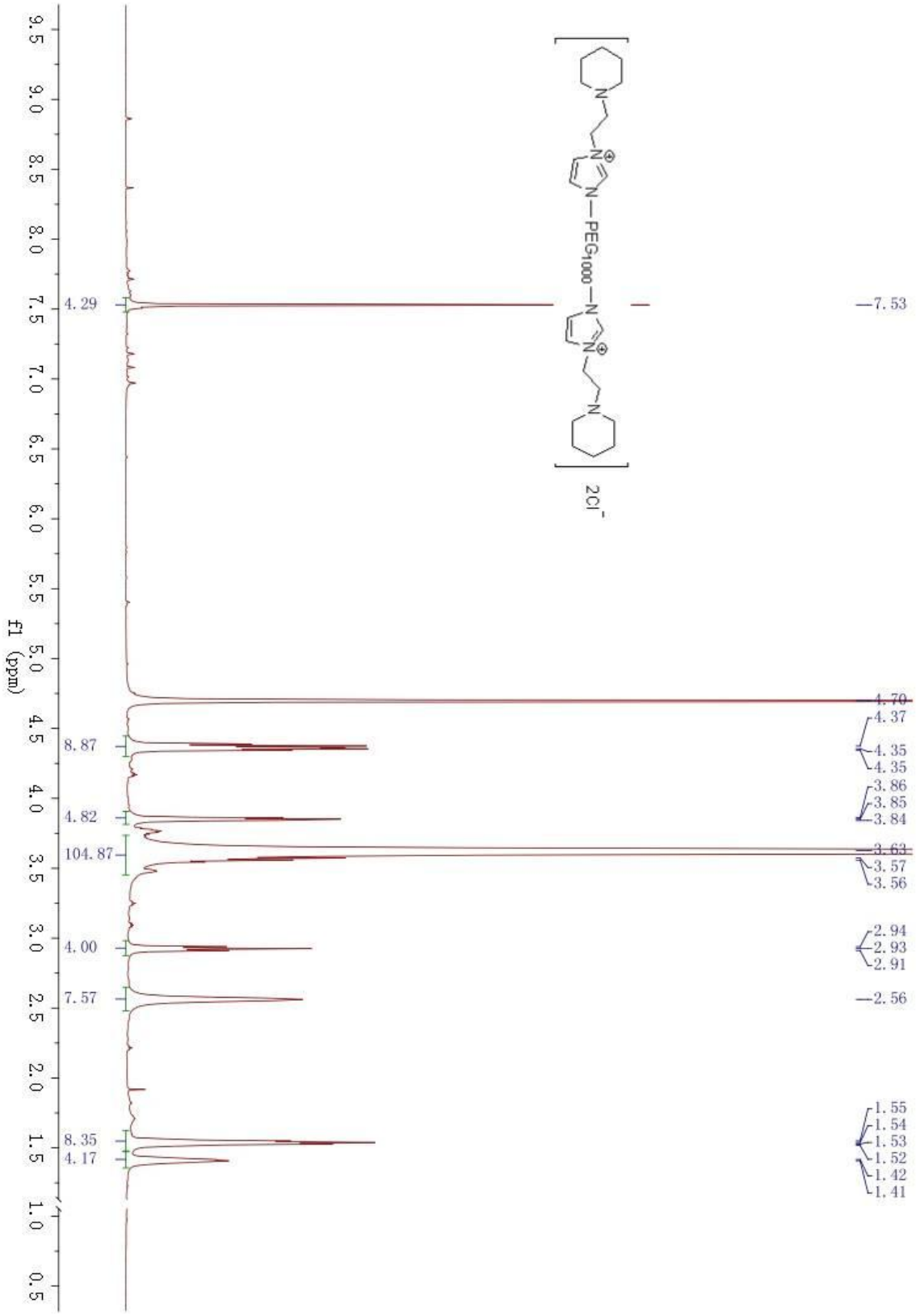


Figure S7 ^{1}H NMR spectrum of PEG_{1000}-DPIL(Cl) (**5**)

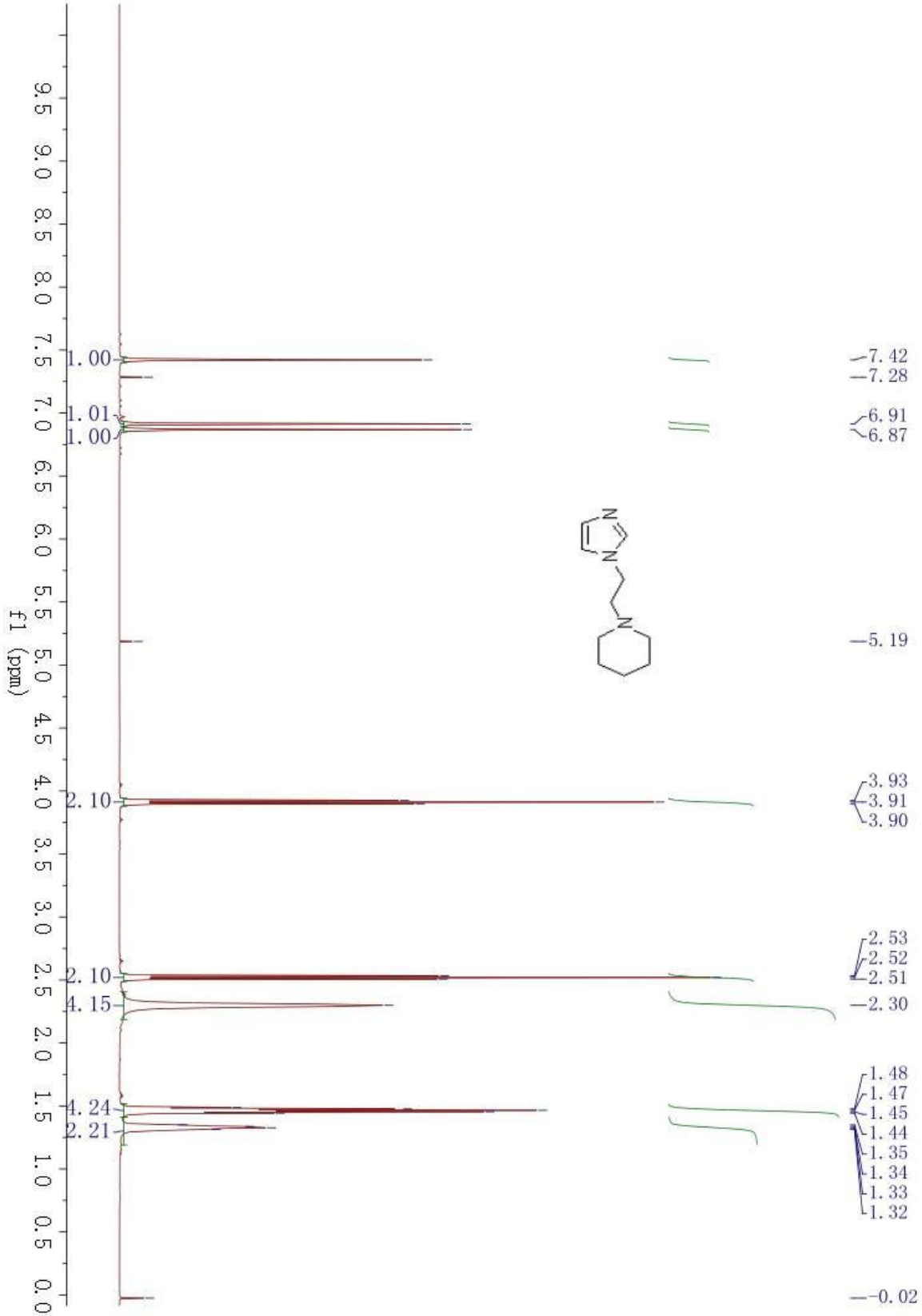


Figure S8 ^{1}H NMR spectrum of 1-(2-(1*H*-imidazol-1-yl)ethyl) piperidine (**4**)

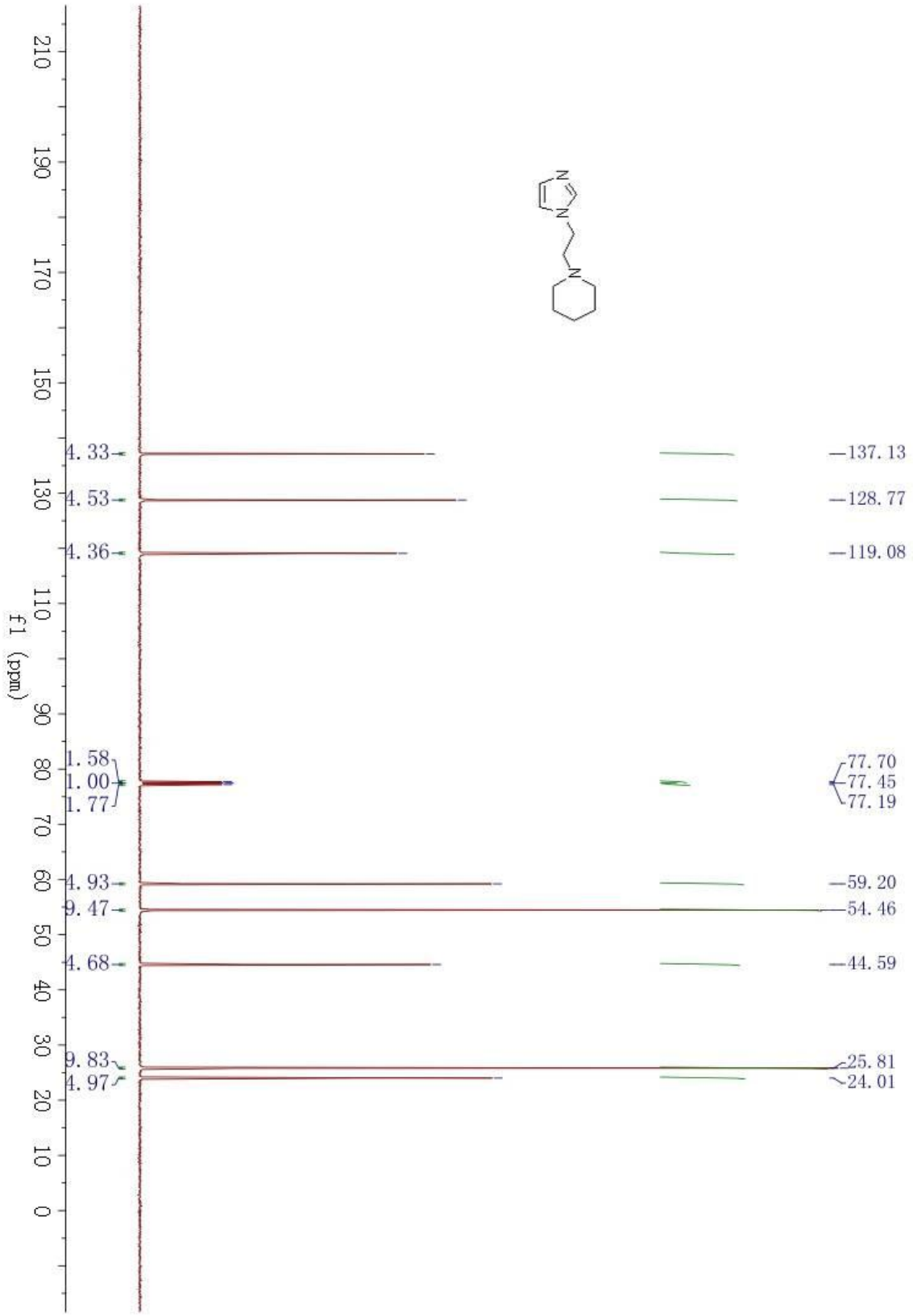


Figure S9 ^{13}C NMR spectrum of 1-(2-(1*H*-imidazol-1-yl)ethyl) piperidine (**4**)

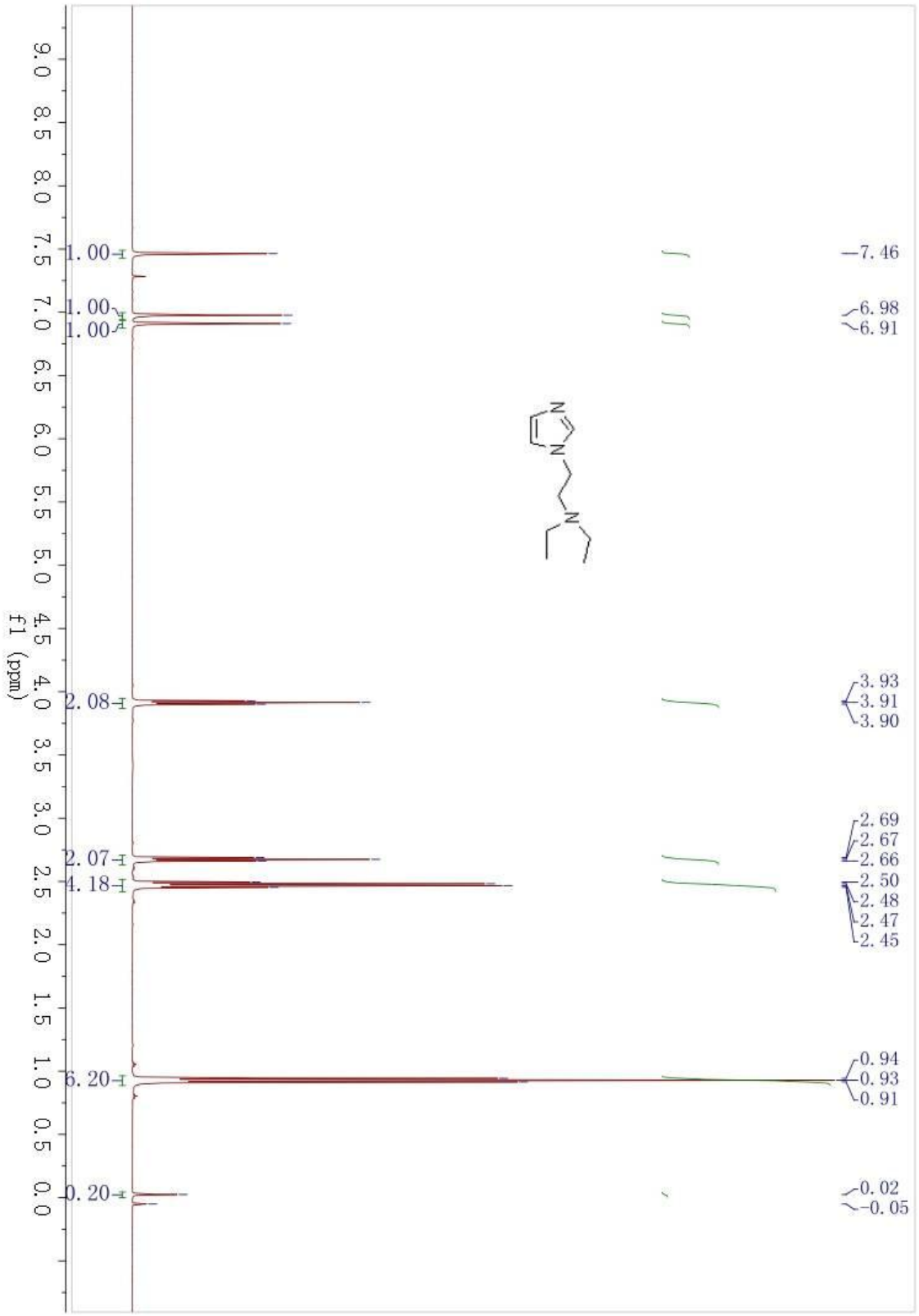


Figure S10 ^{1}H NMR spectrum of *N*,*N*-diethyl-2-(1*H*-imidazol-1-yl)ethanamine (**6**)

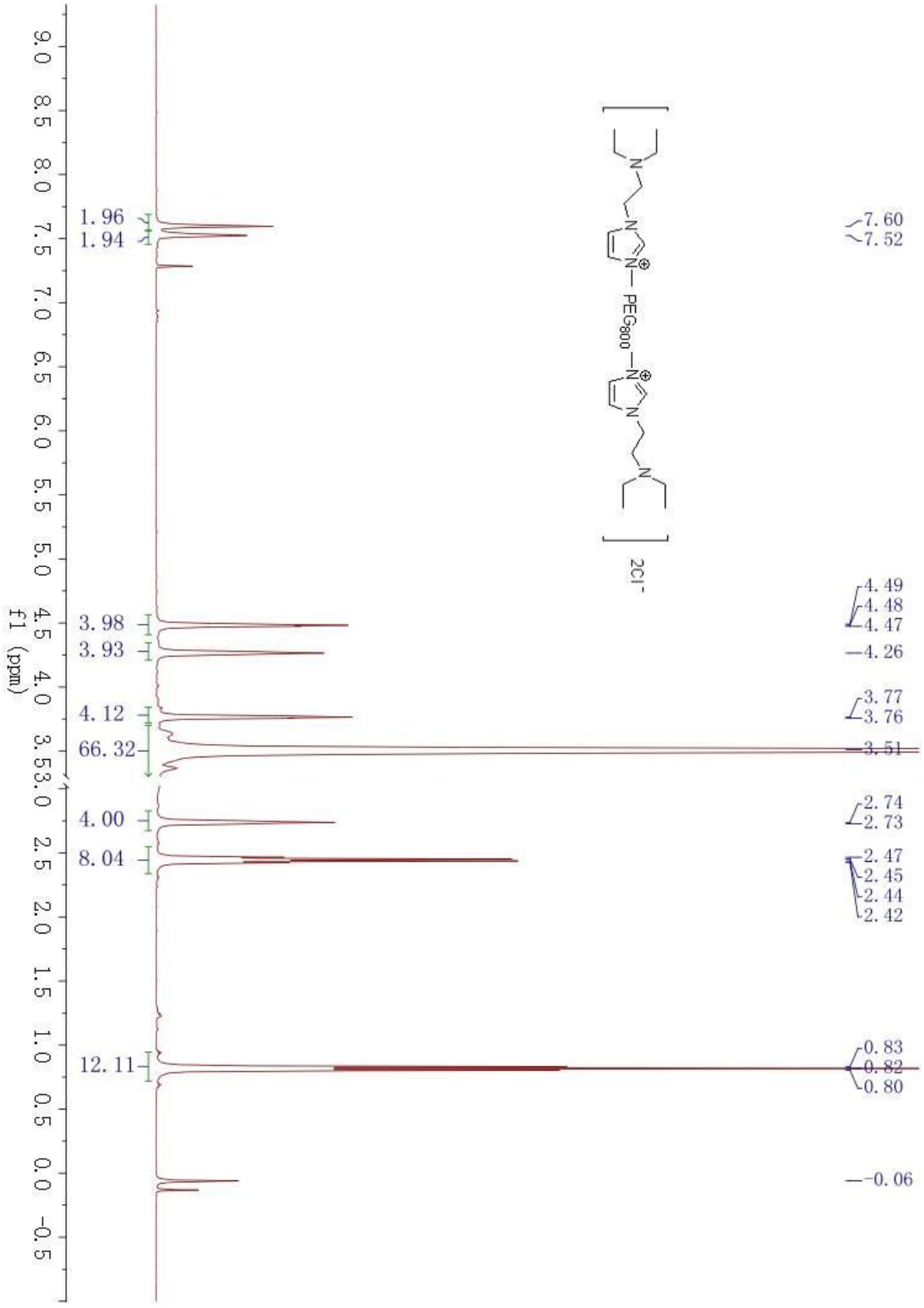


Figure S11 ^{1}H NMR spectrum of PEG_{800}-DEIL(Cl) (**7**)

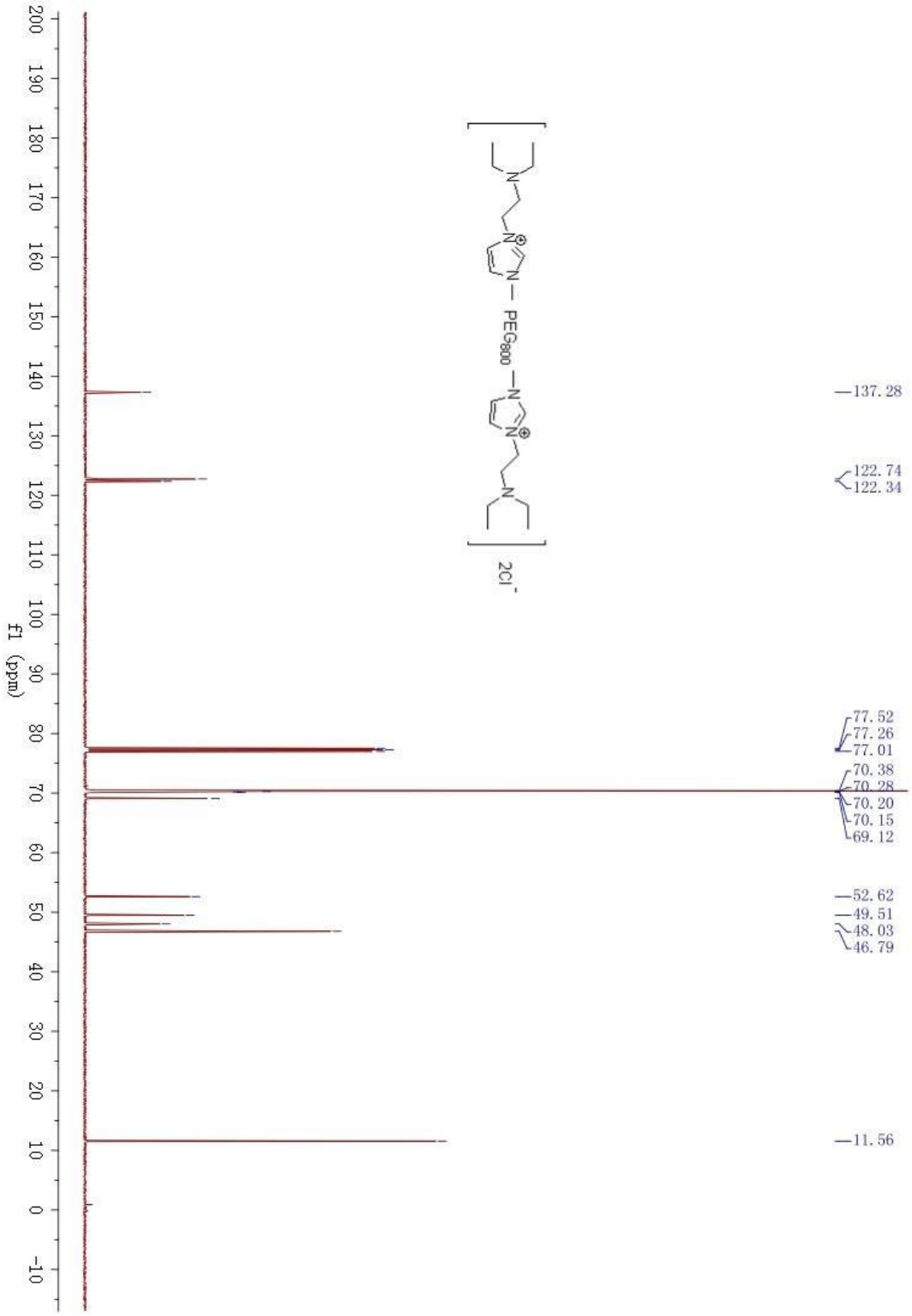


Figure S12 ^{13}C NMR spectrum of PEG_{800}-DEIL(Cl) (**7**)

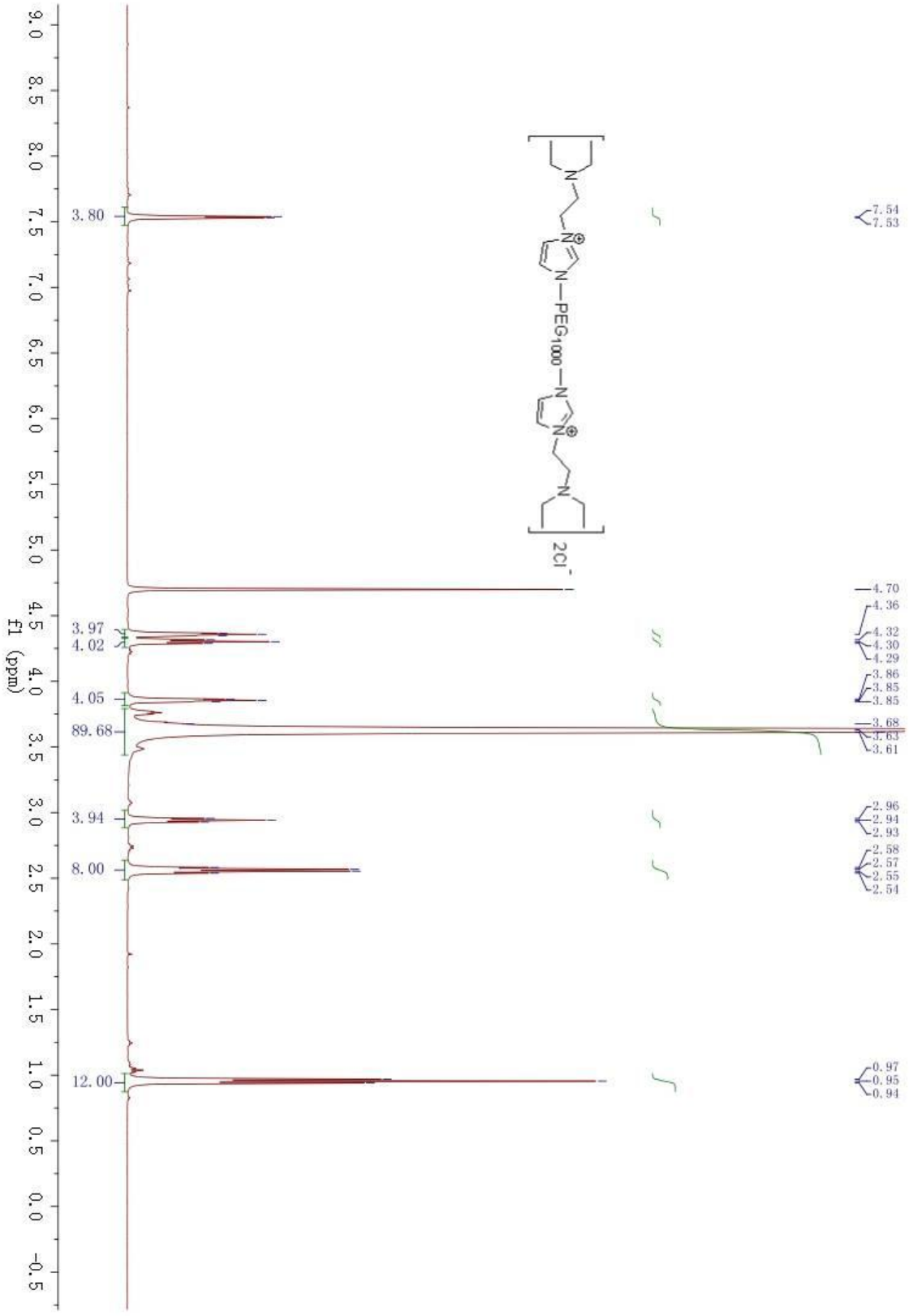


Figure S13 ^{1}H NMR spectrum of PEG_{1000}-DEIL(Cl) (**8**)

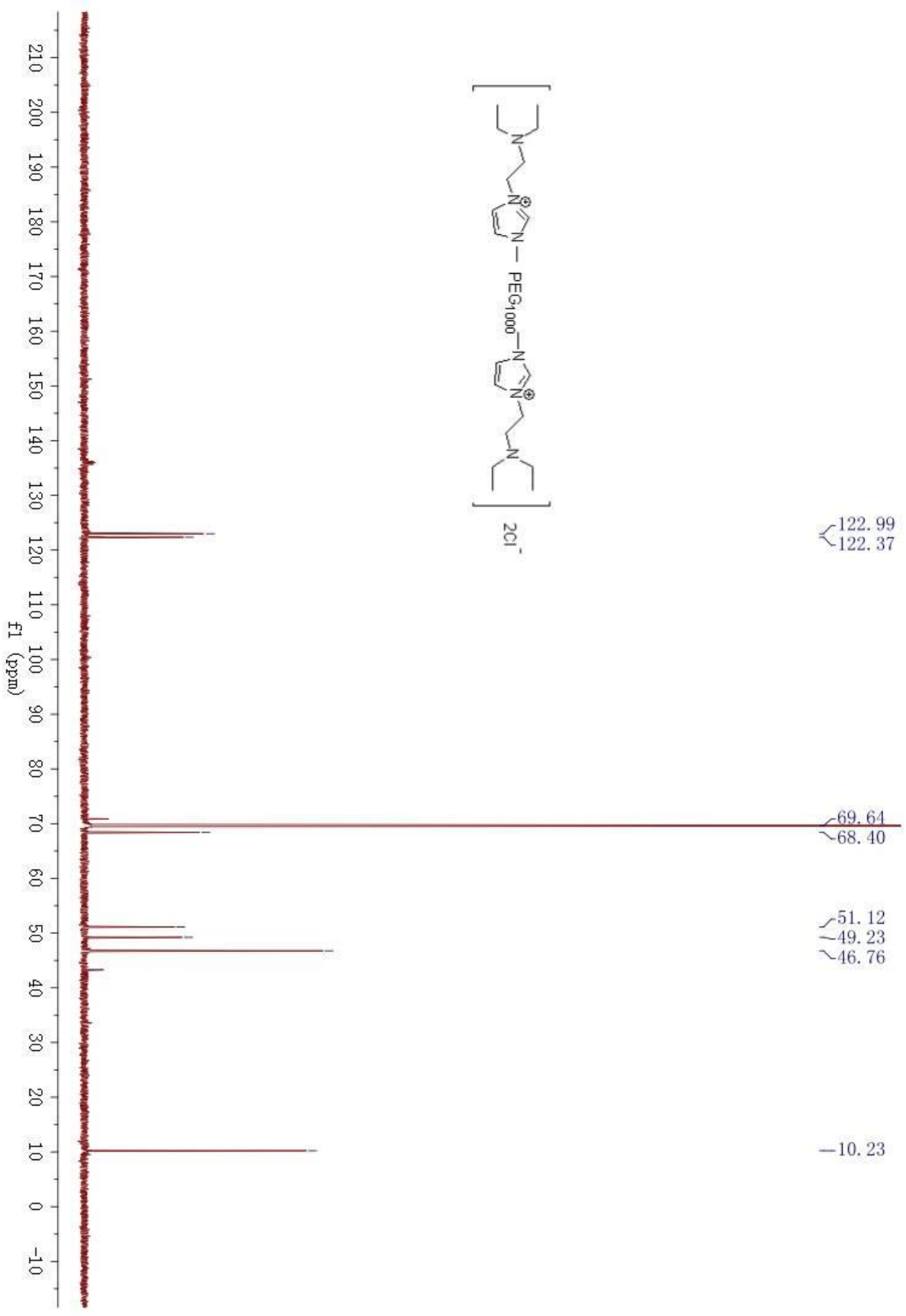


Figure S14 ^{13}C NMR spectrum of PEG$_{800}$-DEIL(Cl) (**8**)