Supporting Information for

Tetra-Armed Cyclen Bearing Two Benzo-15-Crown-5 Ethers in the Side-Arms

Mari Ikeda,†‡ Mikako Matsumoto,§ Shunsuke Kuwahara‡,§, and Yoichi Habata*,‡,§

† Education Center, Faculty of Engineering, Chiba Institute of Technology, Shibazono 2-2-1, Narashino, Chiba 275-0023, Japan

‡ Research Center for Materials with Integrated Properties and §Department of Chemistry, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan

Table of Contents

Title	Figure #	Page
^{1}H NMR and ^{13}C NMR of **1**	**Figures S1a** and **S1b**	S3
FAB-MS of **1**	**Figures S2**	S4
COSY of **1**. Crown ring part	**Figure S3a**	S5
COSY of **1**. Aromatic ring part	**Figure S3b**	S5
COSY of **1**·Ag^{+}. Aromatic ring part	**Figure S3c**	S6
HOHAHA of **1**. Aromatic ring part	**Figure S4a**	S7
HOHAHA of **1**·Ag^{+}. Aromatic ring part	**Figure S4b**	S7
HMQC of **1**. Crown ring part	**Figure S5a**	S8
HMQC of **1**. Aromatic part	**Figure S5b**	S8
Differential NOE of **1**.	**Figure S5c**	S9
Ag^{+}-induced CSI-MS changes	**Figures S6a**–**S6d**	S10
Ag^{+}-induced CSI-MS changes	**Figures S6e**–**S6g**	S11
Electrostatic potential maps	**Figure S7**	S12
Na^{+}-induced ^{1}H NMR spectral changes	**Figure S8a**	S12
K^{+}-induced ^{1}H NMR spectral changes	**Figure S8b**	S13
Detailed data for log*K* values for **1**·Ag^{+} complex		S13
CSI-MS data of NaOTf complex	**Figures S9–S10**	S14
CSI-MS data of KOTf complex	**Figures S11–S12**	S15
CSI-MS of NaOTf and KOTf complex	**Figures S13–S16**	S16–S19

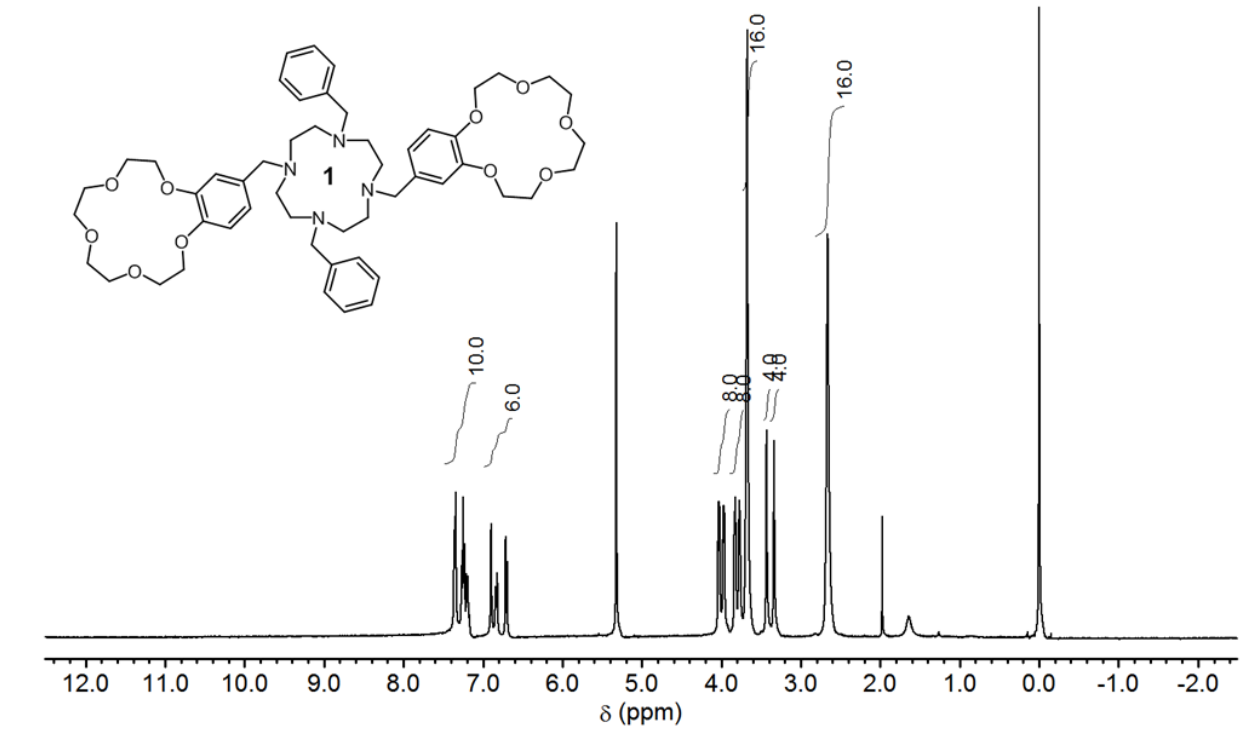

Figure S1a. ^{1}H NMR spectrum of **1** (CD_2Cl_2).

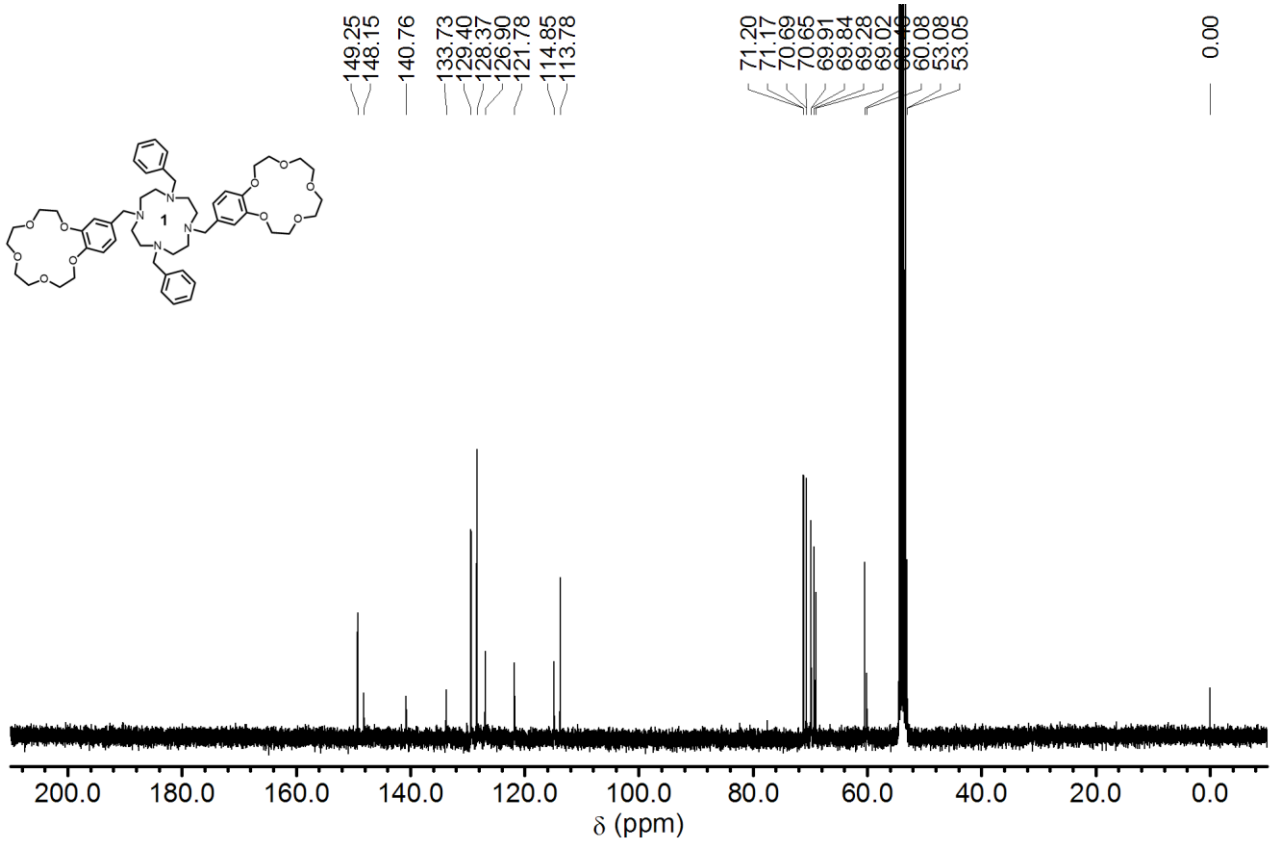

Figure S1b. ^{13}C NMR of **1** (CD_2Cl_2).

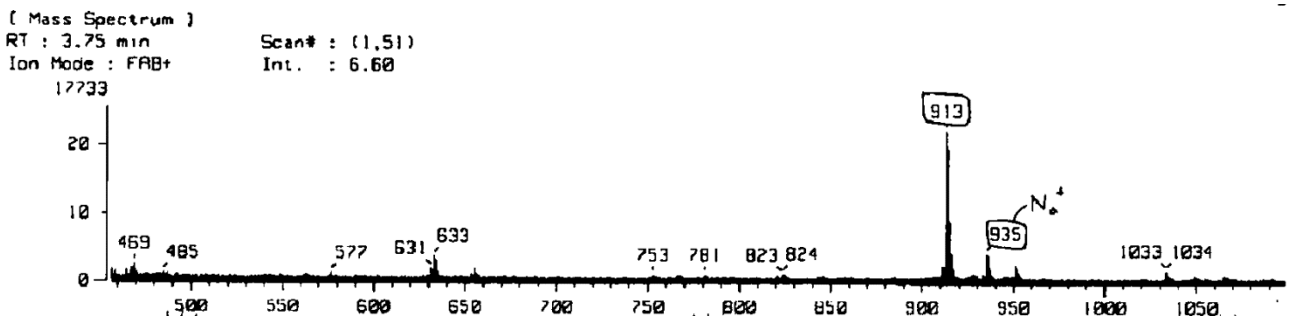

Figure S2. FAB-MS of **1**.

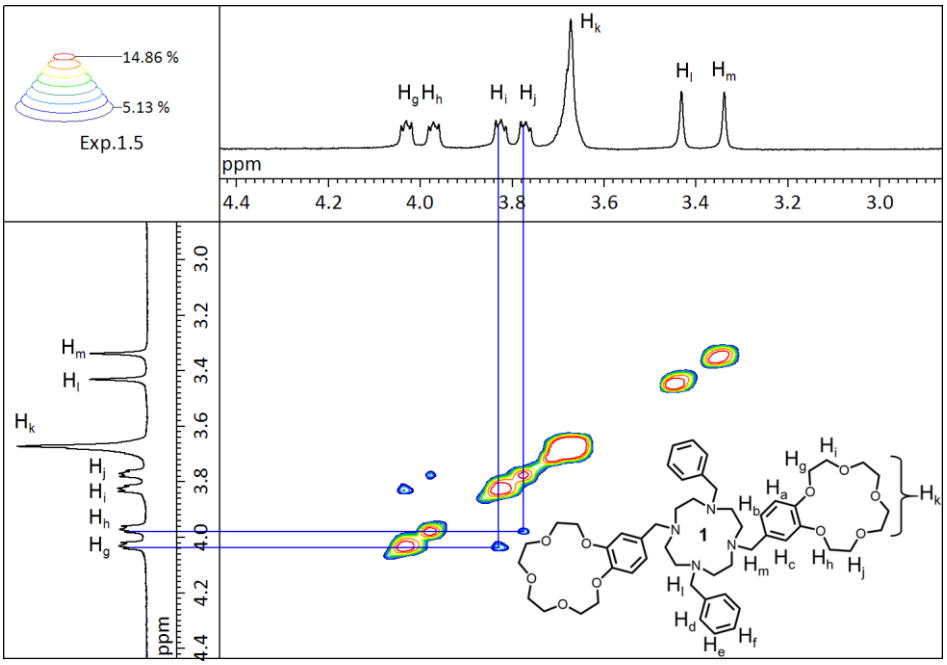

Figure S3a. COSY of **1**. Crown ring part (CD_2Cl_2).

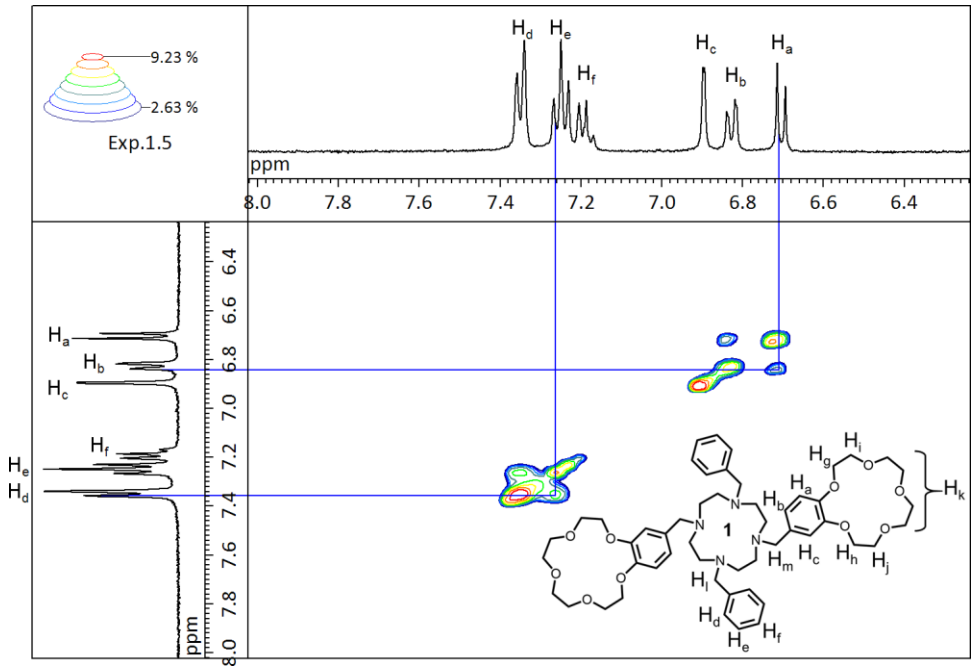

Figure S3b. COSY of **1**. Aromatic ring part (CD_2Cl_2).

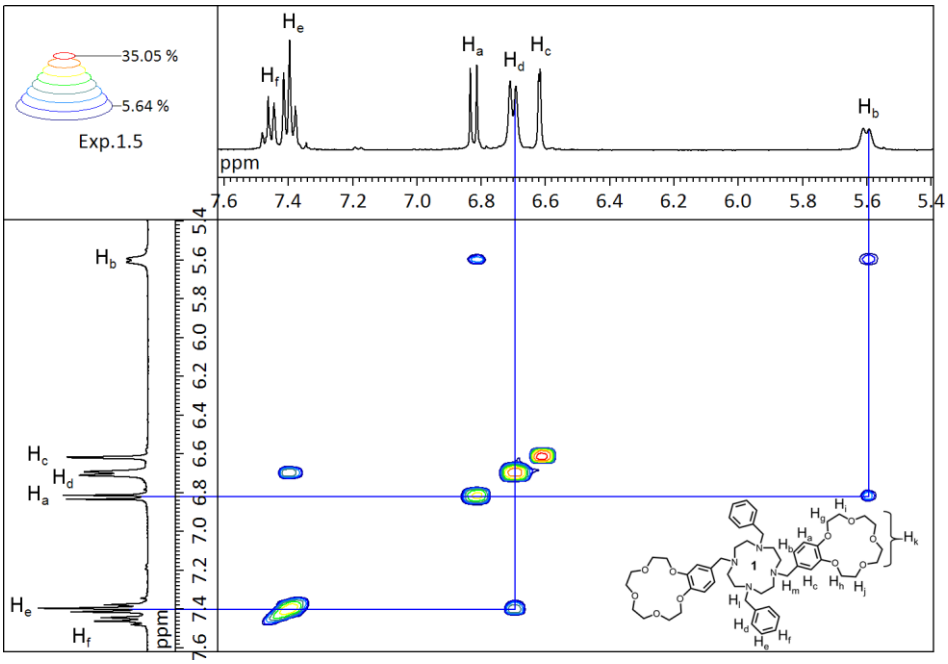

Figure S3c. COSY of **1**·Ag^{+} complex. Aromatic ring part (CD_2Cl_2).

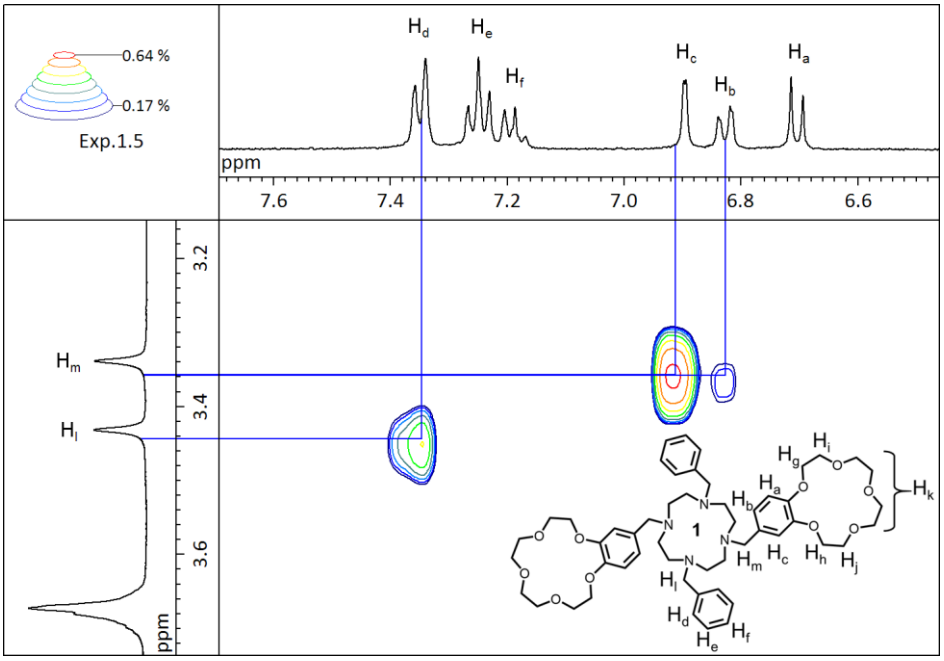

Figure S4a. HOHAHA of **1**. Aromatic ring part (CD_2Cl_2).

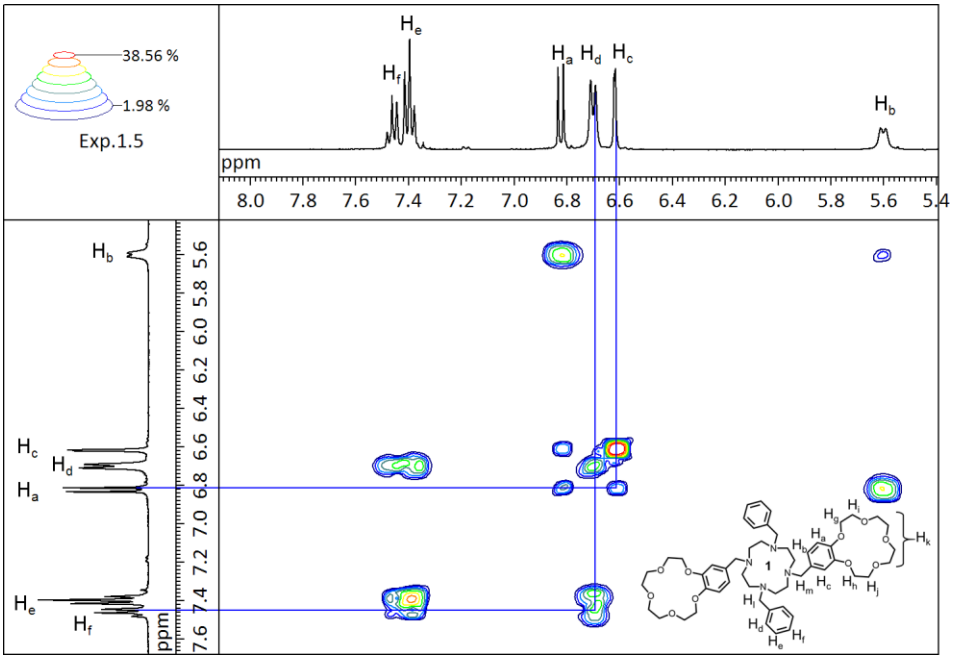

Figure S4b. HOHAHA of **1**·Ag^+ complex. Aromatic ring part (CD_2Cl_2).

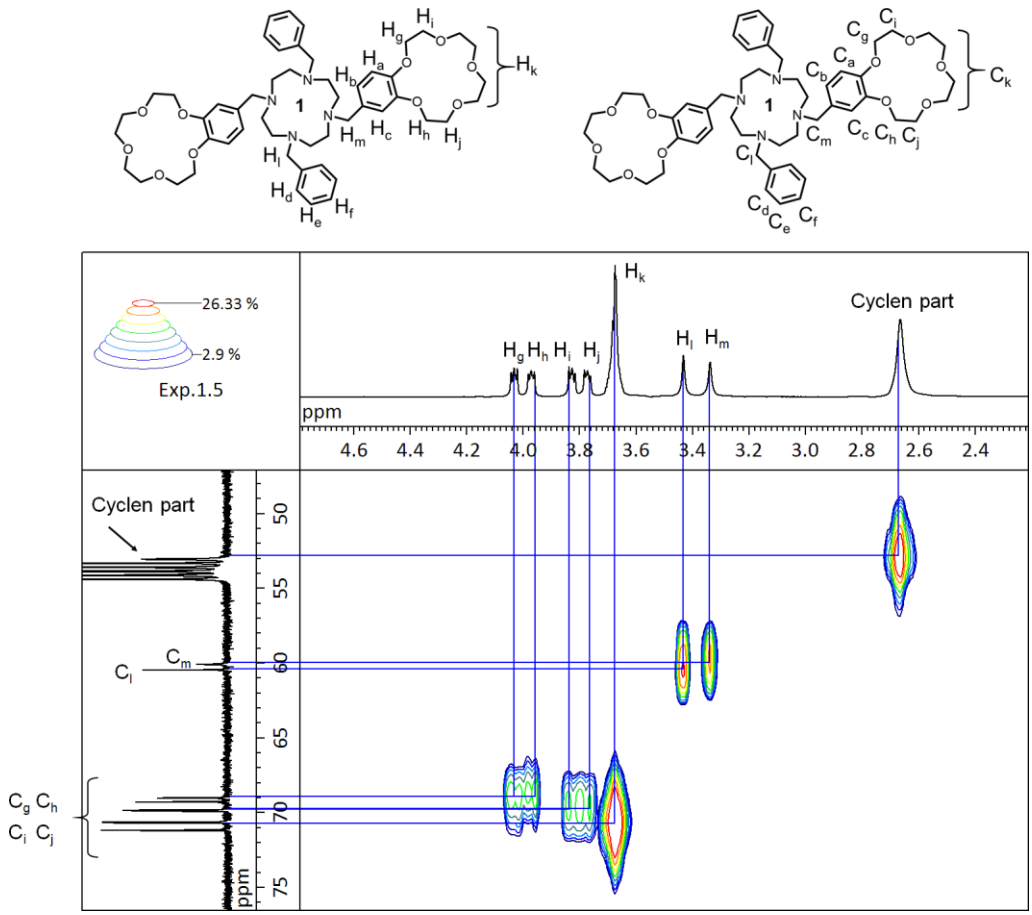

Figure S5a. HMQC of **1**. Crown ether ring part (CD_2Cl_2).

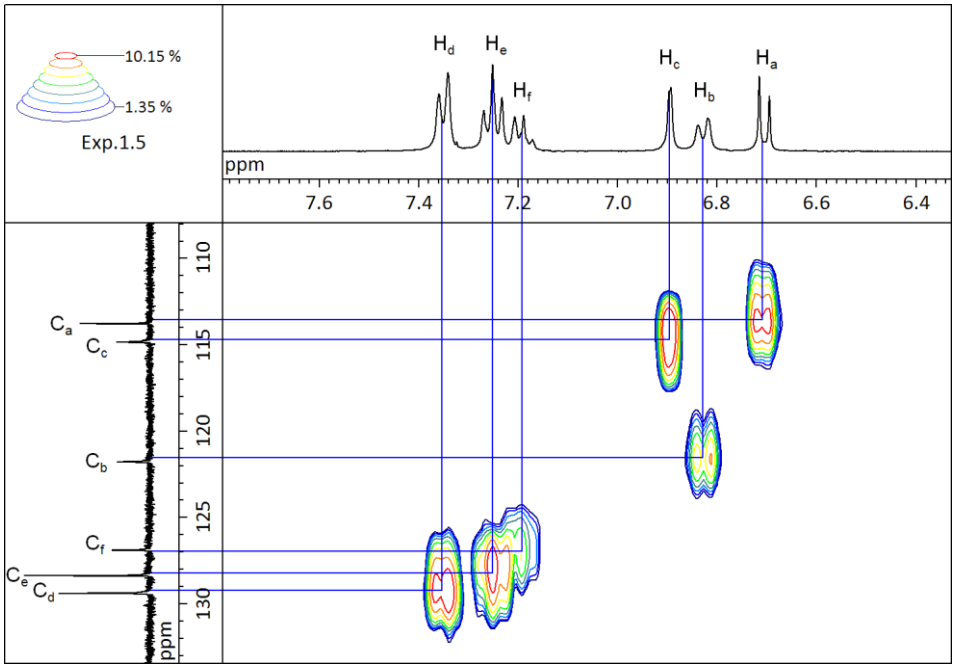

Figure S5b. HMQC of **1**. Aromatic ring part (CD_2Cl_2).

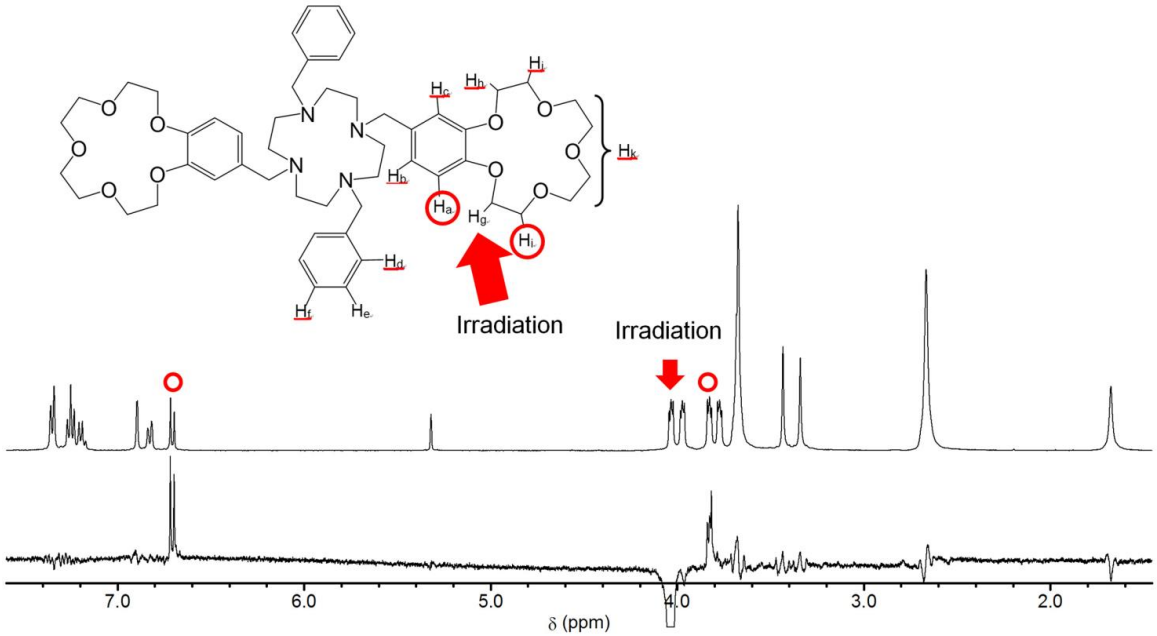

Figure S5c. Differential NOE of **1** (CD_2Cl_2).

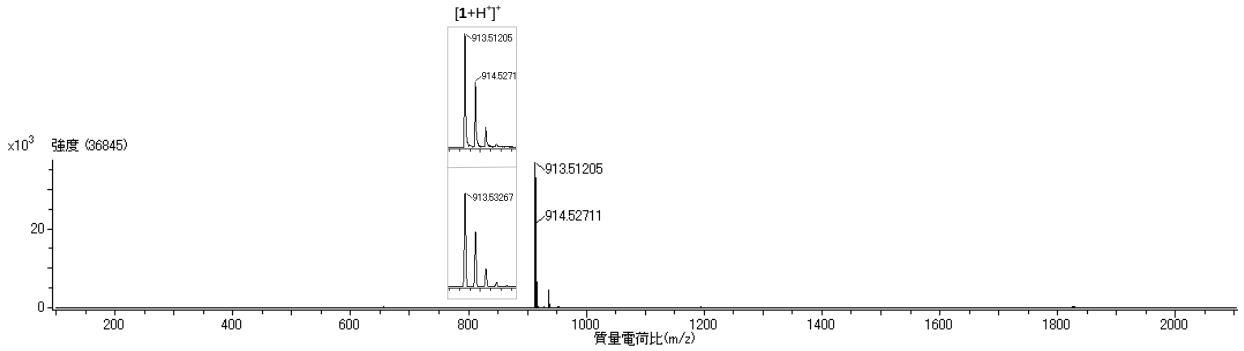

Figure S6a. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 0.0) in methanol.

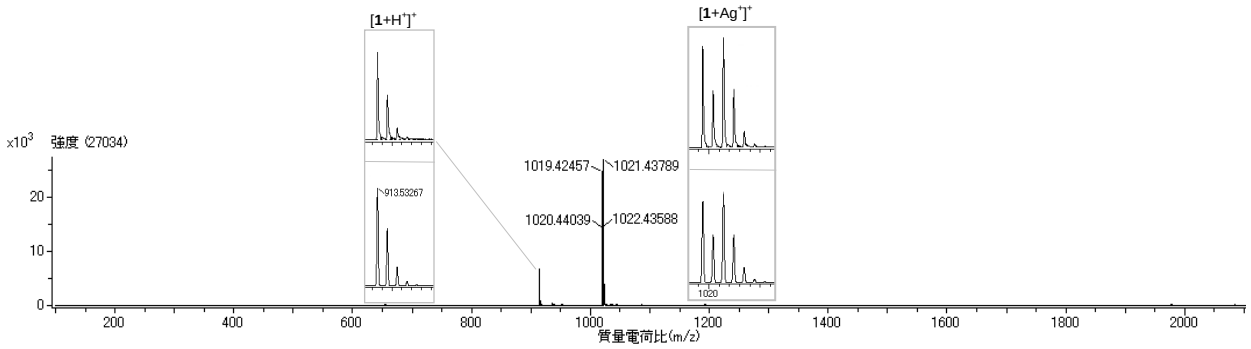

Figure S6b. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 0.5) in methanol.

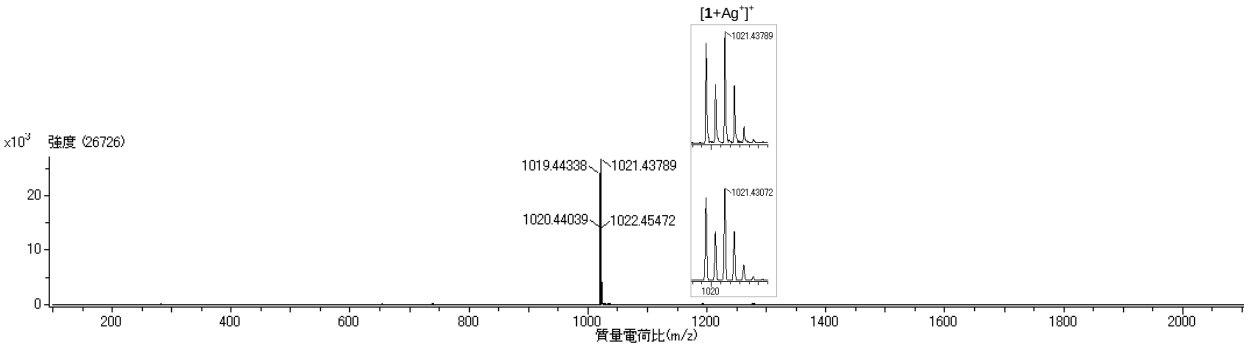

Figure S6c. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 1.0) in methanol.

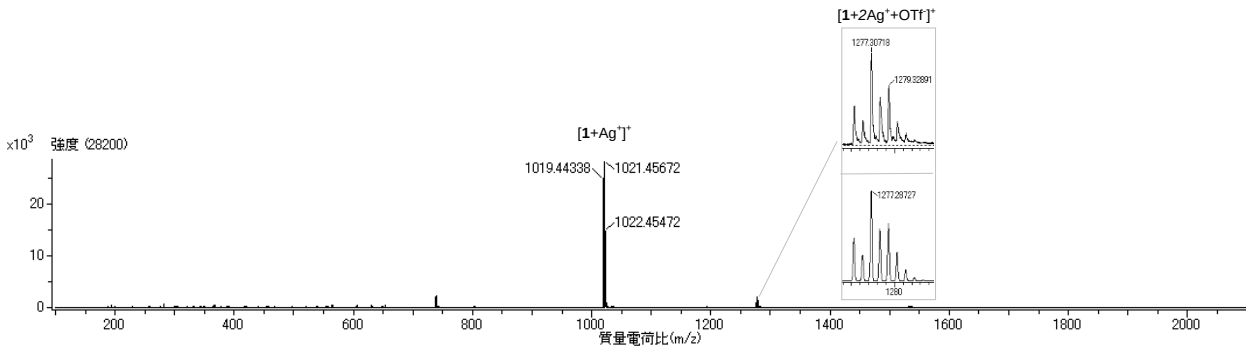

Figure S6d. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 1.5) in methanol.

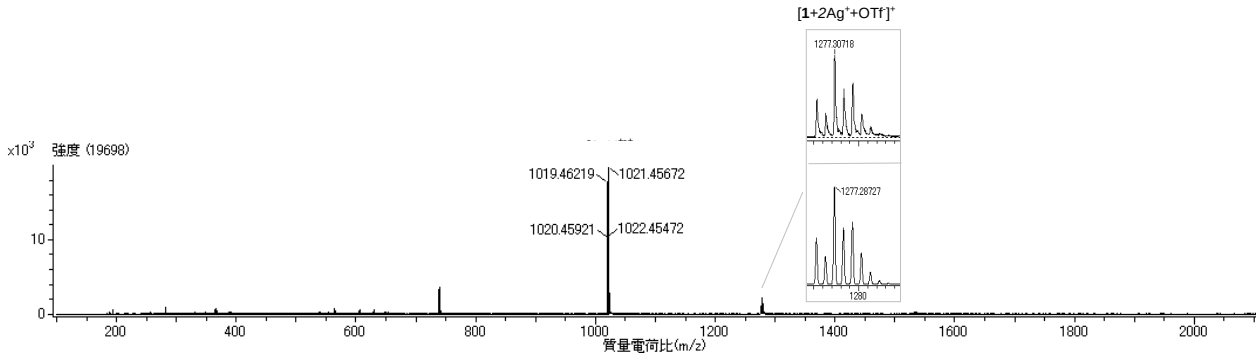

Figure S6e. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 2.0) in methanol.

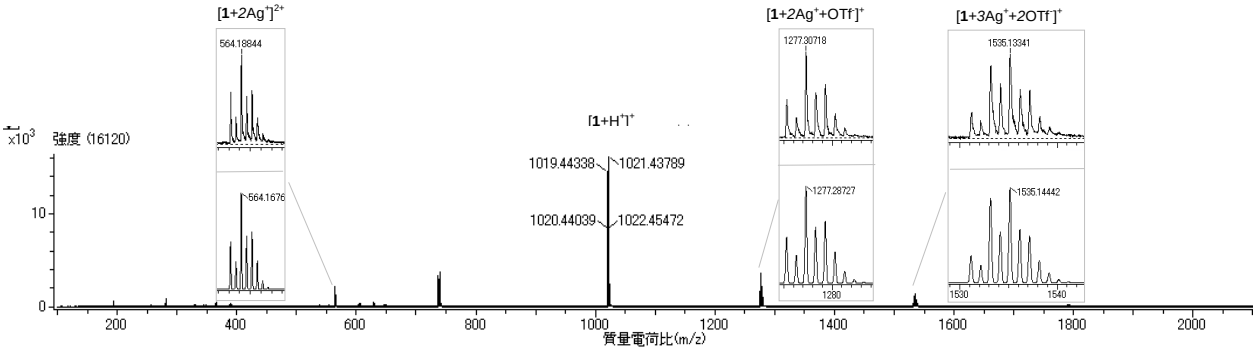

Figure S6f. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 2.5) in methanol.

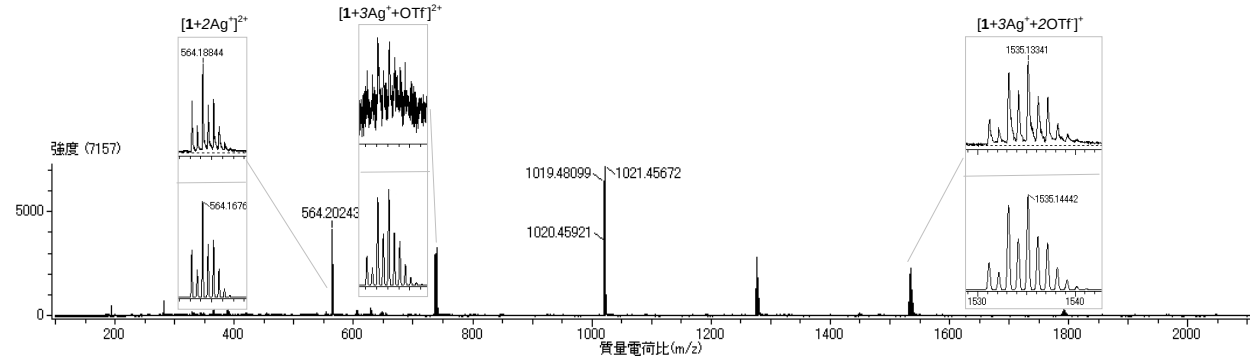

Figure S6g. CSI-MS of a mixture of **1** and AgOTf (= 1.0 : 3.0) in methanol.

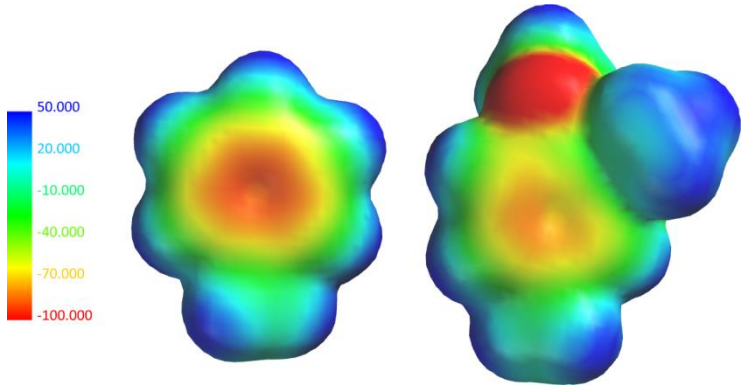

Figure S7. ESI maps of toluene (a) and 3,4-dimethoxytoluene optimized using B3LYP/6-31G*.

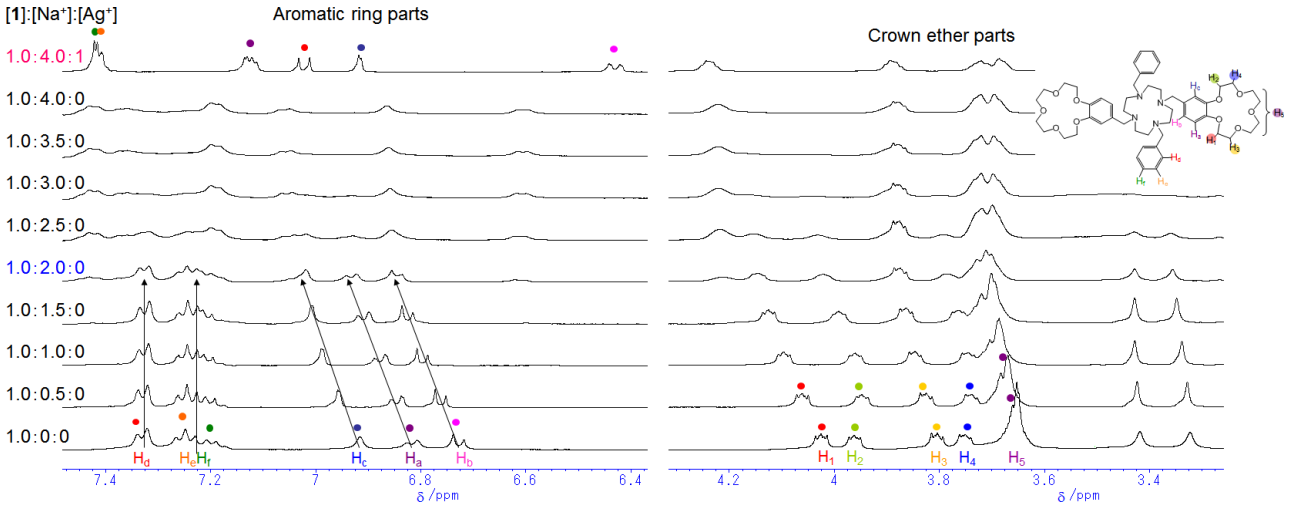

Figure S8a. Na^+-induced-^1H NMR spectral changes in the absence of Ag^+ (CD_3CN/CD_3OD)

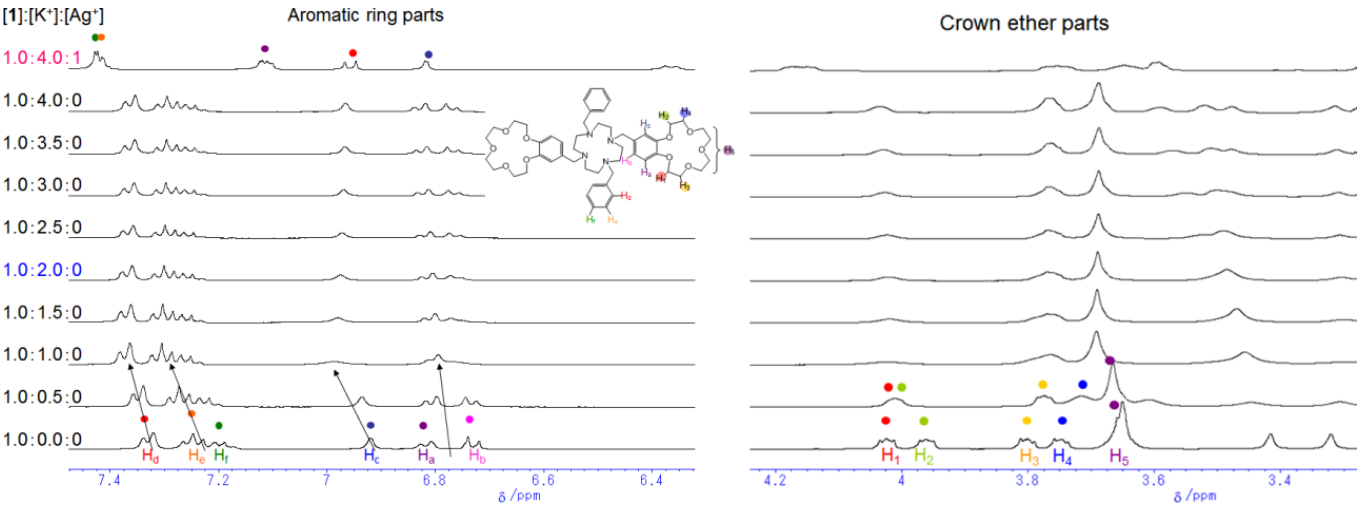

Figure S8b. K^+-induced-^1H NMR spectral changes in the absence of Ag^+ (CD_3CN/CD_3OD)

Detailed data for log*K* values for **1**·Ag^+ complex

Spectral changes and speciation analysis in the UV-vis titration experiments is available as a multimedia file (mikako.avi).

```
Hyperquad refinement output. Version number 1.1.33
</intro>
<iterations>
Initial Sigma =2.3858E-04
Iteration 1
            relative
Parameter     shift     new value
Log beta AB   0.0000    9.3825
Log beta AB2  0.0000    15.2296
Log beta AB3  0.0000    19.2344

New sigma =2.3858E-04
Change =1923.4414%
</iterations>
<results>
HypSpec. Refinement concluded at 2014/08/05 17:04:54
Data from I:¥Dropbox¥0000_HyperSpec¥18_Mameko¥UV_Ag_Ag_Ag¥Mari_Mikako_1.HQD
Project title:
Converged in 1 iterations with sigma = 2.3858E-04

                  standard
Log beta   value     deviation
AB        9.3825    0.021
AB2       15.2296   0.0286
AB3       19.2344   0.0296

Correlation coefficients
  2     0.944
  3     0.935     0.997
       1         2
Parameter numbers
 1 AB
 2 AB2
 3 AB3
</results>
```

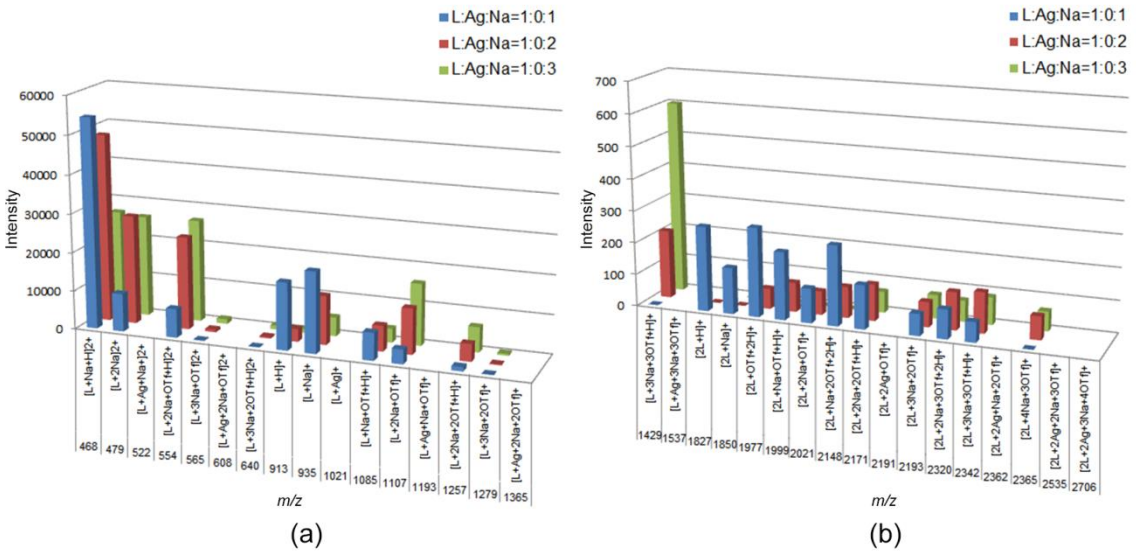

Figure S9. CSI-MS data of mixtures of **1**, AgOTf and NaOTf ([**1**] : [AgOTf] : [NaOTf] = 1:0:1, 1:0:2, and 1:0:3) in methanol. (a) *m/z* =468–1365 and (b) *m/z* = 1429–2706.

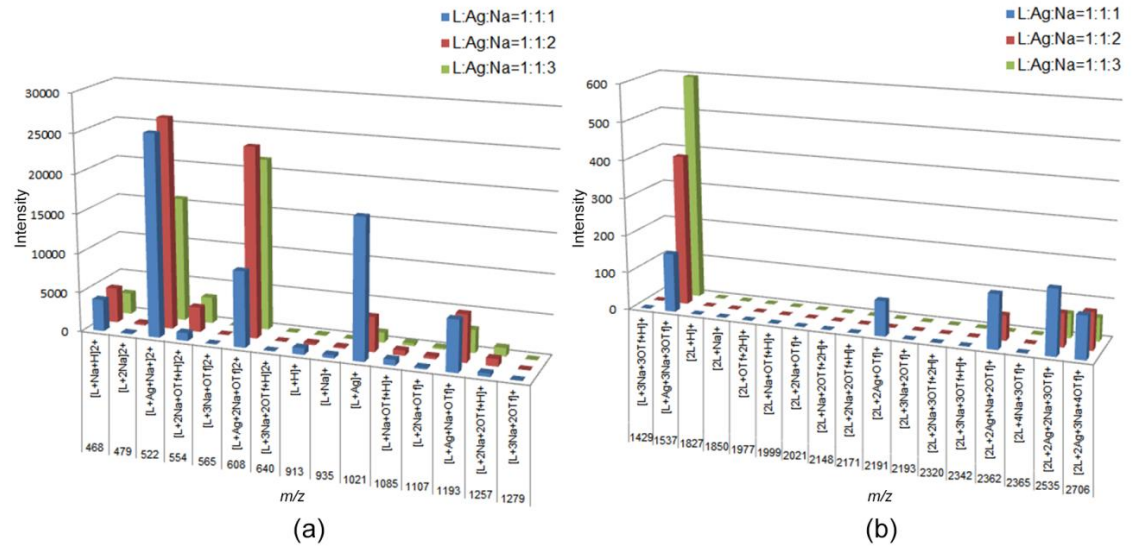

Figure S10. CSI-MS data of mixtures of **1**, AgOTf and NaOTf ([**1**] : [AgOTf] : [NaOTf] = 1:1:1, 1:1:2, and 1:1:3) in methanol. (a) *m/z* =468–1279 and (b) *m/z* = 1429–2706.

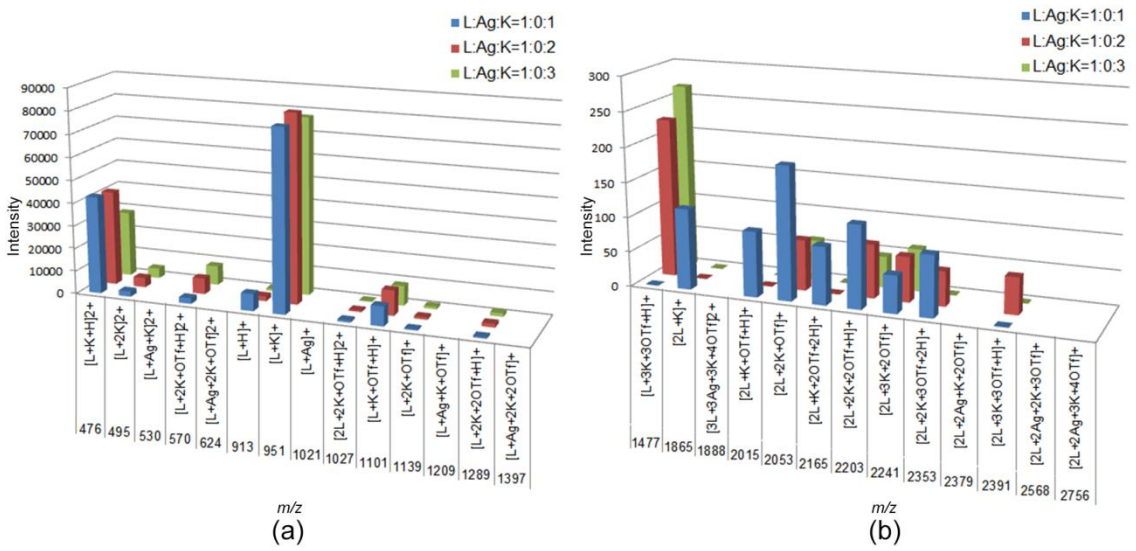

Figure S11. CSI-MS data of mixtures of **1**, AgOTf and KOTf ([**1**] : [AgOTf] : [KOTf] = 1:0:1, 1:0:2, and 1:0:3) in methanol. (a) *m/z* =476–1397 and (b) *m/z* = 1477–2756.

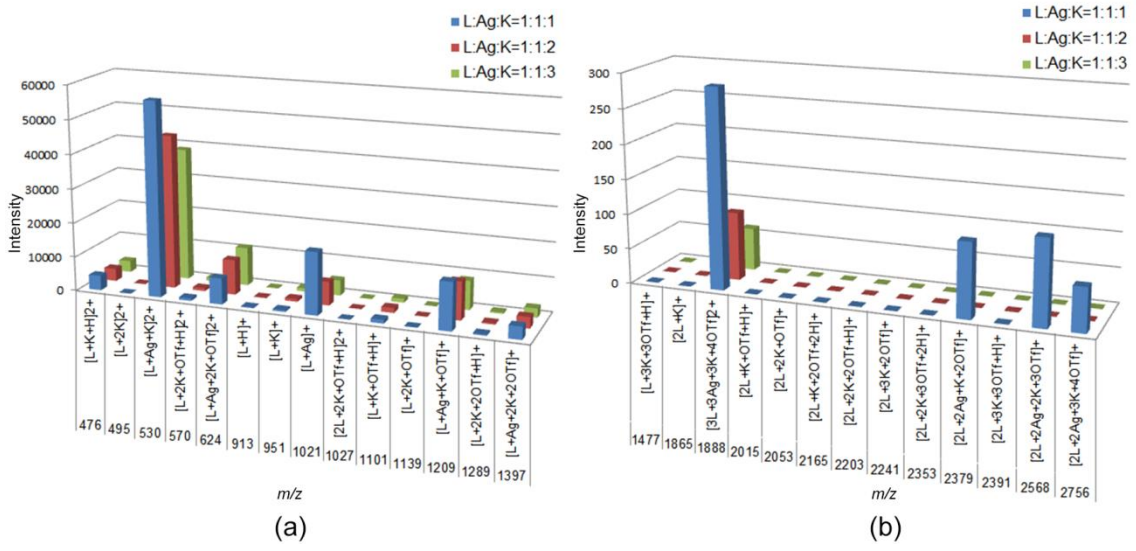

Figure S12. CSI-MS data of mixtures of **1**, AgOTf and KOTf ([**1**] : [AgOTf] : [KOTf] = 1:1:1, 1:1:2, and 1:1:3) in methanol. (a) *m/z* =476–1397 and (b) *m/z* = 1477–2756.

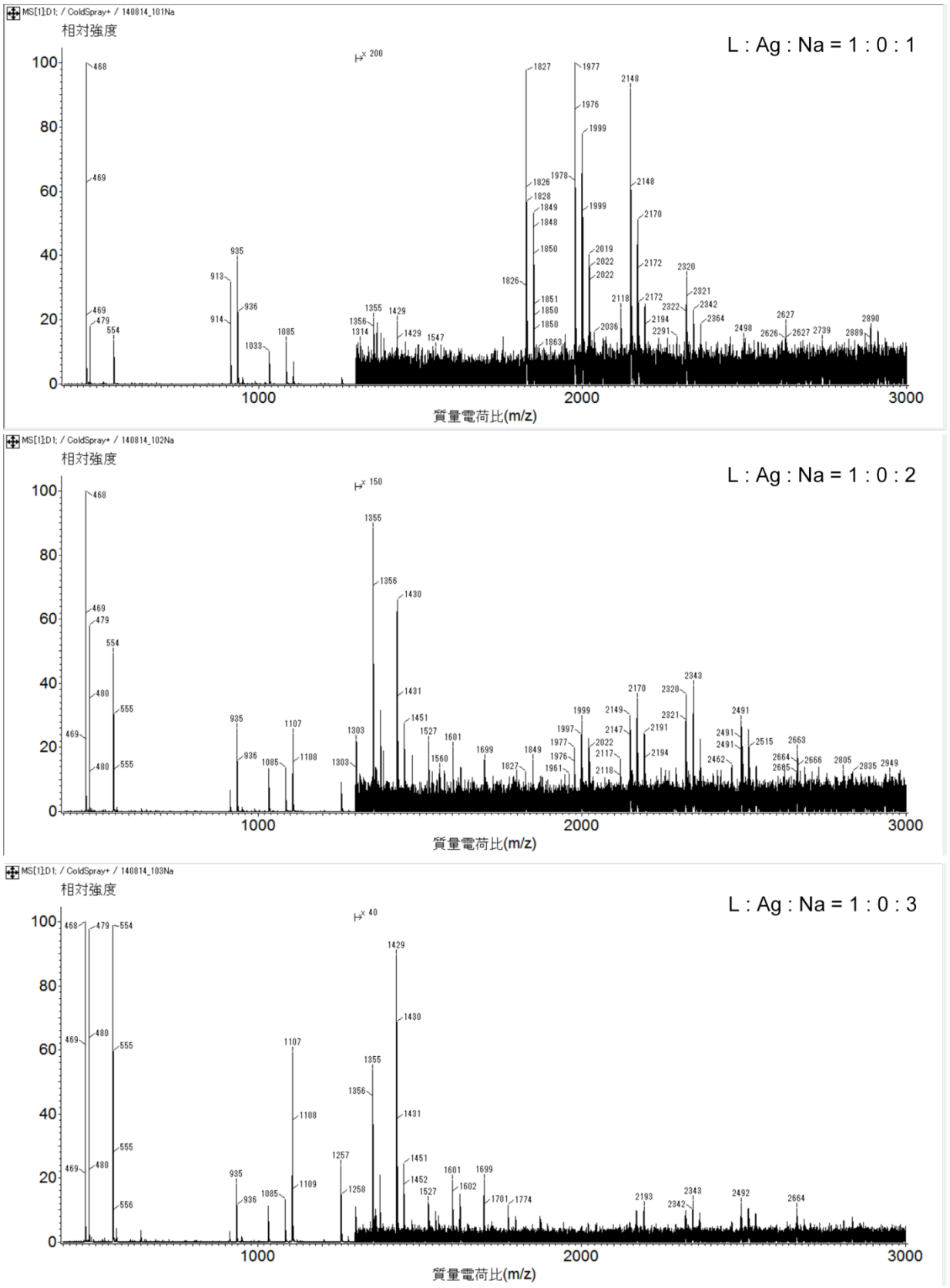

Figure S13. CSI-MS spectra of mixtures of **1**, AgOTf and NaOTf ([**1**] : [AgOTf] : [NaOTf] = 1:0:1, 1:0:2, and 1:0:3) in methanol.

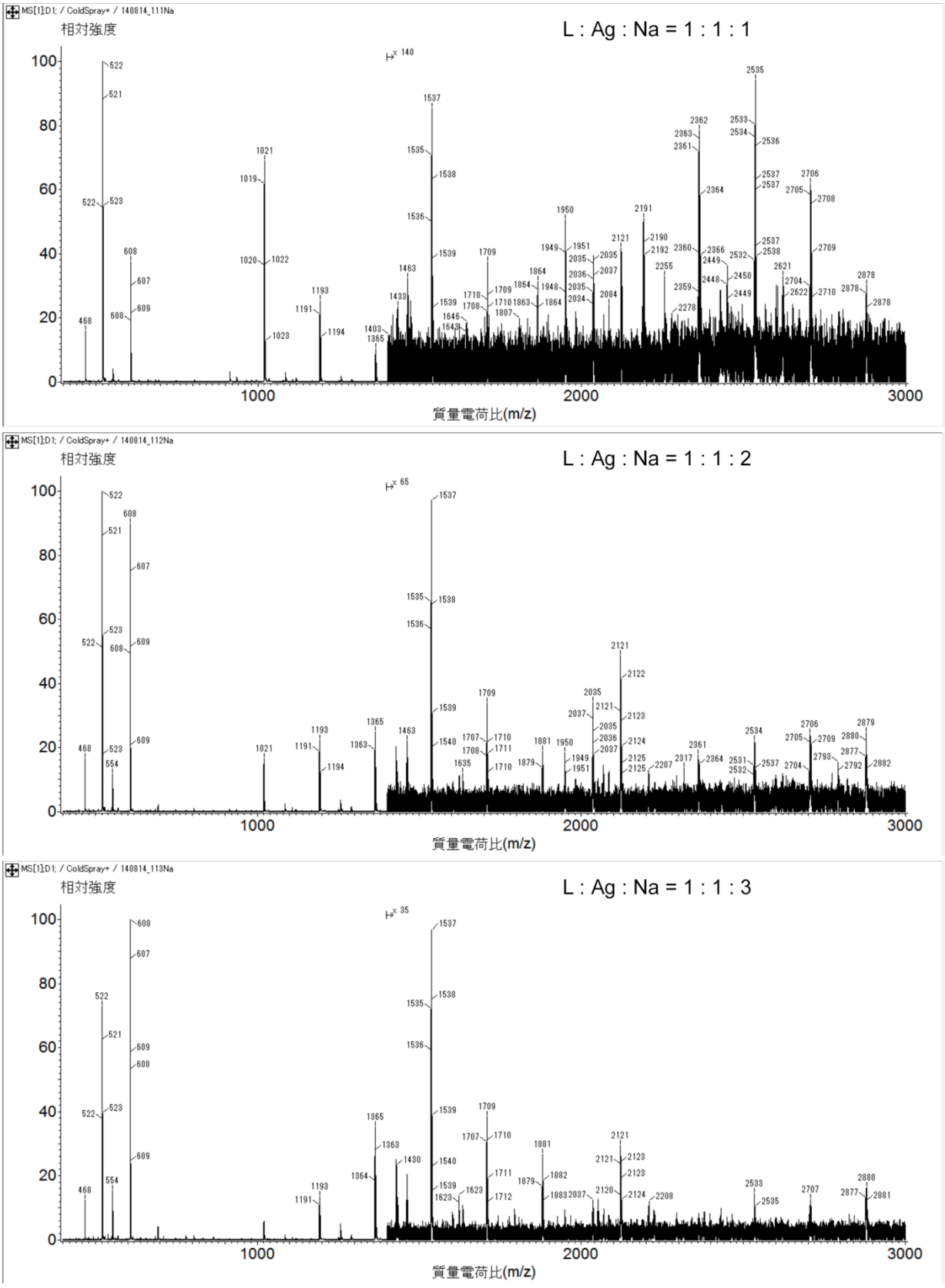

Figure S14. CSI-MS spectra of mixtures of **1**, AgOTf and NaOTf ([**1**] : [AgOTf] : [NaOTf] = 1:1:1, 1:1:2, and 1:1:3) in methanol.

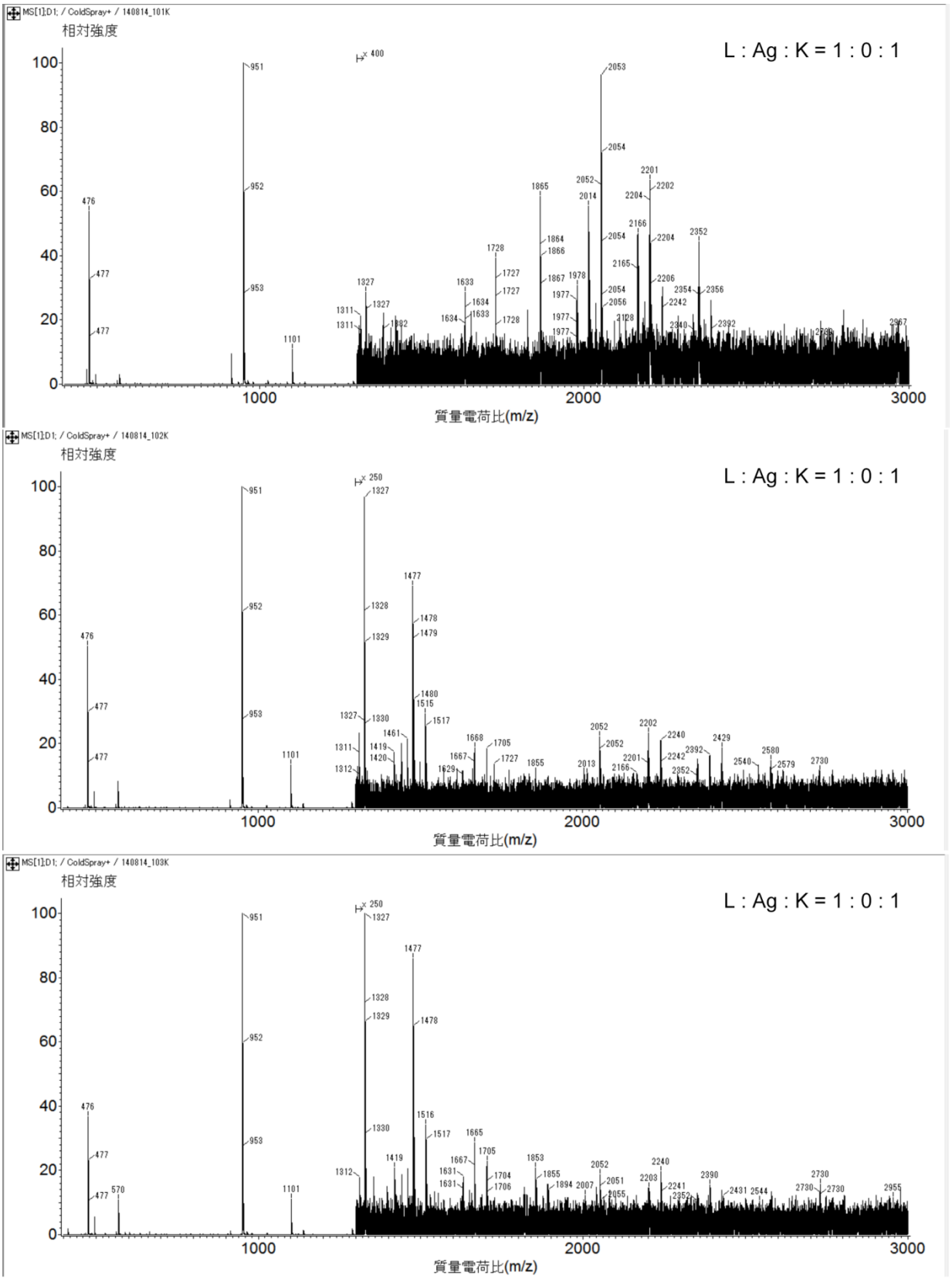

Figure S15. CSI-MS spectra of mixtures of **1**, AgOTf and KOTf ([**1**] : [AgOTf] : [KOTf] = 1:0:1, 1:0:2, and 1:0:3) in methanol.

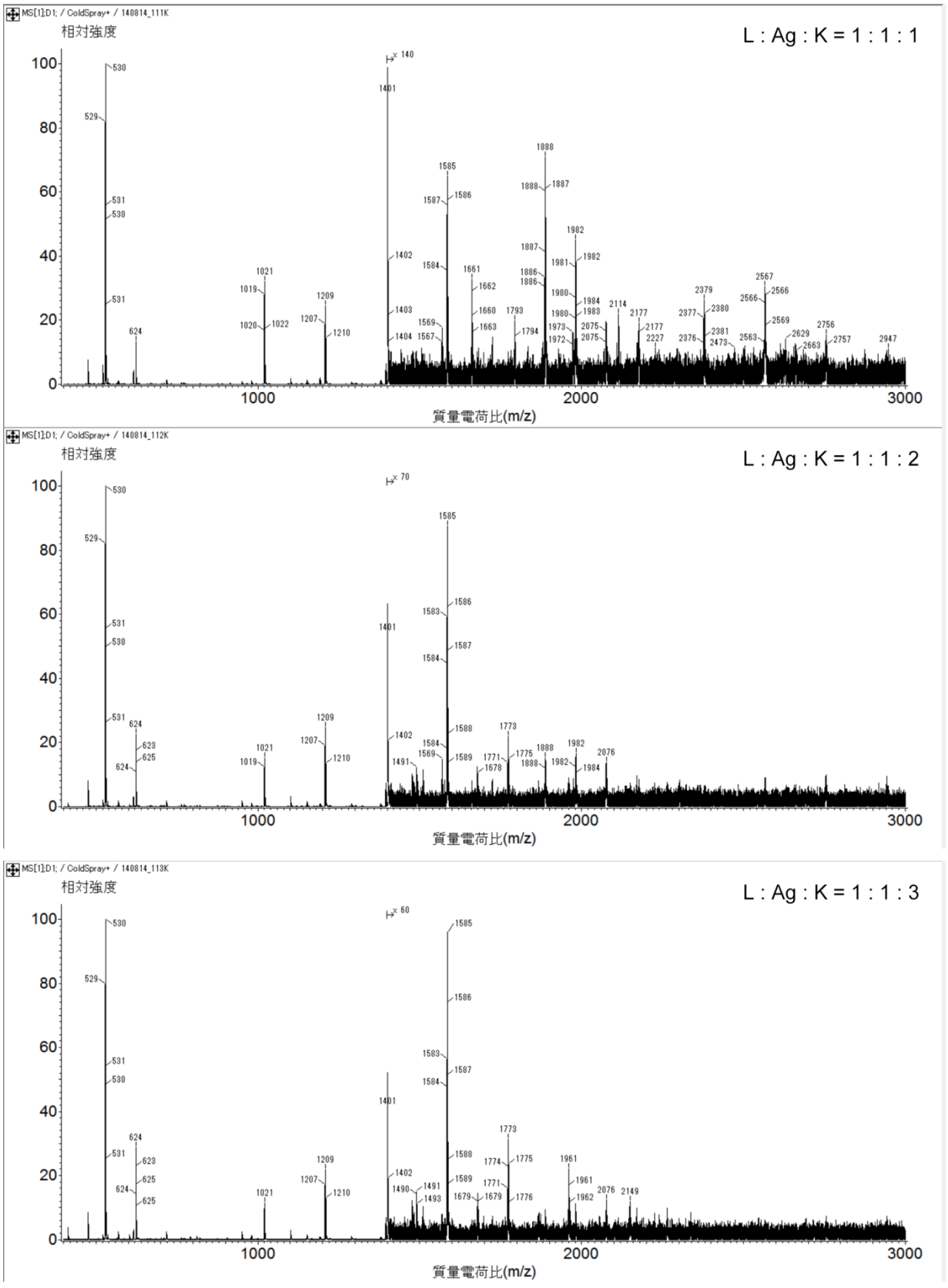

Figure S16. CSI-MS spectra of mixtures of **1**, AgOTf and KOTf ([**1**] : [AgOTf] : [KOTf] = 1:1:1, 1:1:2, and 1:1:3) in methanol.