**Electronic Supplementary Information**

**For**

# *Pyridil-benzimidazole stator as platform for luminescent turnstiles*

*by*

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## 1. Experimental section

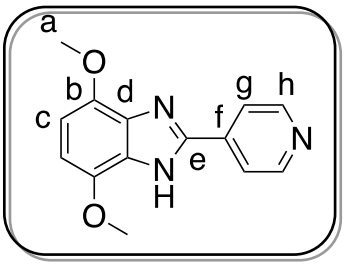
### *1.1 General considerations*

Reagents and solvents were used as received unless differently stated. $^{1}$H- and $^{13}$C-NMR spectra were recorded at 298 K on either Bruker AV300, Bruker AV400 or Bruker AV500 spectrometers in deuterated solvents and the residual solvent peak was used as the internal reference. All the chemical shifts (δ) are reported in ppm. Electron spray ionization Mass Spectrometry (ESI-MS) was performed by the "Service Spectrometrie de Masse" at the Faculty of Chemistry of the University of Strasbourg. Compound **2**[1], **9** and **10**[2] were synthetized as described in literature.

### *1.2 Synthetic procedures*

The synthesis of compounds **3** and **4** were carried out by following the procedure reported elsewhere[3] with some minor modifications: THF was used instead of EtOAc in each reaction.

**Synthesis of 5.**



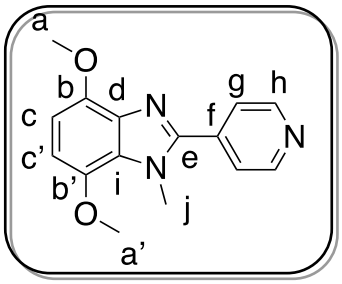

Compound **4** (2.5 g, 15 mmol, 1eq) and $Na_2S_2O_5$ (4.3g, 23 mmol, 1.5 eq) were dissolved in 300 mL of ethanol under argon atmosphere. 4-Pyridinecarboxaldehyde (1.4 mL, 15 mmol, 1 eq) was slowly added under argon. The mixture was refluxed for 15 hours. Ice was then added. A pale-yellow solid was obtained and filtrated over a glass frit and washed with water. Compound **5** was purified by column chromatography ($SiO_2$, $CH_2Cl_2$ to $CH_2Cl_2$/MeOH: 100 to 95/5). (2.7 g, 11 mmol, 70%).

**$^{1}$H NMR** (500 MHz, DMSO): δ = 13.37 (s, 1H, NH), 8.69 (d, J = 6.2 Hz, 2H, Hh), 8.15 (d, J = 6.2 Hz, 2H, Hg), 6.64 (s, 2H, Hc), 3.90 (s, 6H, Ha).

**$^{13}$C NMR** (125 MHz, DMSO) δ = 150.40 (Ch), 150.36;150.33 (Ce,f), 147.41(Cd), 137.19 (Cb), 120.43(Cg), 55.67 (Ca).

**ESI-MS (ESI$^+$):** m/z calculated for $[C_{14}H_{14}N_3O_2]^+$ $[M+H^+]$ = 256.11, found = 256.10.

**Synthesis of 6.**



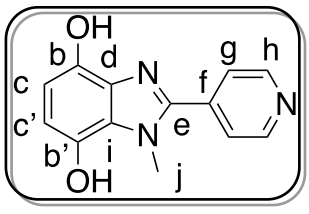

Compound **5** (1.0 g, 3.9 mmol, 1 eq.) was dissolved in degassed DMF (100 mL). Copper iodide (0.12 g, 0.59 mmol, 0.15 eq.), $Cs_2CO_3$ (3.2 g, 9.8 mmol, 2.5 eq.), 1,10-Phenanthroline(0.18 g, 0.98 mmol, 0.25 eq) and iodomethane (0.4 mL, 6.27 mmol, 1.6 eq) were then added under argon. The mixture was heated at 100 °C during 20 hours. The solvent was then removed, and the resulting crude was poured in $CH_2Cl_2$ (100 mL). The organic phase was washed twice with water before being dried with $MgSO_4$ and evaporated to dryness. Column chromatography ($SiO_2$, $CH_2Cl_2$/MeOH 100 to 97/3) afforded **6** as an orange/red solid (0.61 g, 2.3 mmol, 58%).

**$^1$H NMR** (500 MHz, $CDCl_3$): δ = 8.77 (d, J = 6.1 Hz, 2H, Hh), 7.71 (d, J = 6.1 Hz, 2H, Hg), 6.63 (d, J = 8.5 Hz, 1H, Hc'), 6.57 (d, J = 8.5 Hz, 1H, Hc), 4.13 (s, 3H, Hj), 3.99 (s, 3H, Ha'), 3.93 (s, 3H, Ha).

**$^{13}$C NMR** (126 MHz, $CDCl_3$): δ = 150.25 (Ch), 150.13 (Ce), 146.34 (Ci), 141.99 (Cf), 137.91;135.19 (Cb,b'), 127.62 (Cd), 123.92(Cg), 104.15;101.95 (Cc,c'), 56.12 (Ca), 56.01 (Ca'), 34.52 (Cj).

**MS (ESI$^+$):** m/z calculated for $[C_{15}H_{16}N_3O_2]^+$ $[M+H^+]$ = 270.12, found = 270.12.

**Synthesis of 7.**




Compound **6** (190 mg, 0.705 mmol, 1eq) was dissolved in 35 mL of dry $CH_2Cl_2$ under argon. Then 8, 0 mL of $BBr_3$ (1M in $CH_2Cl_2$, 10 eq) were dropwise added at -78 °C. The reaction was then allowed to reach room temperature. After 20 hours ice was added, the precipitate was

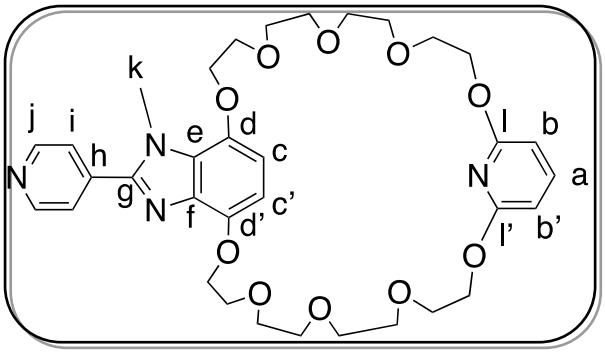
filtrated over a glass frit, washed with cold water and dried under vacuum affording compound **7** as a yellow solid. (0.170g, 82%).

**NMR $^{1}$H** (DMSO, 500 MHz): δ = 10.13 (s, 2H), 8.98 (d, *J* = 6.3 Hz, 2H), 8.02 (d, *J* = 5.3 Hz, 2H), 6.78 – 6.69 (m, 2H), 4.13 (s, 3H).

**RMN $^{13}$C** (DMSO, 125 MHz): δ = 151.94 (Ch), 148.83;148.79 (Ce,f), 146.66 (Cd,i), 138.03 (Cb), 124.80 (Cg), 116.83 (Cb') 111.01;109,87 (Cc,c'), 34.71 (Cj).

**MS (ESI$^{+}$):** m/z calculated for $[C_{13}H_{12}N_3O_2]^+$ $[M+H^+]$ = 242.09, found = 242.09.

**Synthesis of T1.**




Compound **10** (0.36 g, 0.58 mmol, 1 eq.) was dissolved in DMF (400 mL) and the resulting solution degassed by vacuum argon cycles 5 times before addition of $Cs_2CO_3$ (0.76 g, 2.3 mmol, 4 eq.) under argon. The mixture was degassed again before adding compound **7** (0.14 g, 0.58 mmol, 1 eq.) under argon. The mixture was heated to 90 °C for 48 hours. The solvent was evaporated and the residue was dissolved in a mixture of $CH_2Cl_2$ (50 mL) and water (50 mL). The two phases were separated and the aqueous phase was extracted three times with $CH_2Cl_2$. The combined organic phases were washed with water (50 mL) and with a solution of $NH_4Cl$ (10%) (50 mL). The organic layer was dried over $MgSO_4$ and evaporated to dryness. The crude was purified by column chromatography ($SiO_2$, $CH_2Cl_2$/MeOH 100 to 95/5) to give **T1** as a yellow oil (0.13 g, 0.31 mmol, 33%).

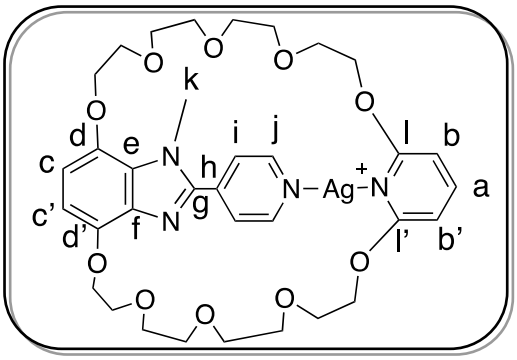
**$^{1}$H NMR** (500 MHz, $CD_3CN$): δ = 8.71 (m, 2H, Hj), 7.73 (d, J = 5.2 Hz, 2H, Hi), 7.45 (t, J = 7.9 Hz, 1H, Ha), 6.67 (d, J = 8.5, 1H, Hc), 6.57 (d, J = 8.5, 1H, Hc'), 6.20 (dd, J = 7.9, 3.7 Hz, 2H, Hb), 4.29 – 4.23 (m, 2H), 4.22 – 4.18 (m, 2H), 4.16 – 4.01 (m, 4H), 4.10 (s, 3H, Hk), 3.92 – 3.76 (m, 4H), 3.68 – 3.61 (m, 6H), 3.61 – 3.49 (m, 14H).

**$^{13}$C NMR** (125 MHz, $CD_3CN$): δ = 163.29;163.27 (Cl,l'), 150.72 (Cg), 150.63 (Cj), 146.08 (Ce), 142.26 (Ca), 142.13 (Ch), 138.92;135.80 (Cd,d'), 129.01 (Cf), 124.65(Ci), 107.32;105.04

(Cc,c'), 102.05;101.95 (Cb,b'), 71.35, 71.28, 71.26, 71.24, 71.22, 71.19, 71.11, 70.31, 70.22, 70.14, 70.02, 69.96, 69.27, 66.12, 66.07, 35.04(Ck).

**HRMS (ESI$^+$):** m/z calculated for $[C_{34}H_{45}N_4O_{10}]^+$ [M+H$^+$] = 669.31, found = 669.31.

**Synthesis of T1-Ag$^+$.**




**T1** (27.1 mg, 40.5 µmol, 1 eq.) was dissolved in degassed $CH_3CN$ (2 mL). To this solution, $AgCF_3SO_3$ (10.4 mg, 40.5 µmol, 1 eq.) dissolved in $CH_3CN$ (696 µL) was added with an eppendorf and the reaction mixture was stirred at room temperature for 2 hours in the dark under argon. After removal of the solvent, **T1-Ag$^+$** was obtained quantitatively as a yellow solid.

**$^1$H NMR** (500 MHz, $CD_3CN$) : δ = 8.73 (d, J = 6.1 Hz, 2H, Hj), 7.70 (d, J = 6.1 Hz, 2H, Hi), 7.41 (t, J = 7.9 Hz, 1H, Ha), 6.76 (d, J = 8.6 Hz, 1H, Hc'), 6.71 (d, J = 8.6 Hz, 1H, hc), 6.18 (dd, J = 7.9, 3.5 Hz, 2H, Hb,b'), 4.27 – 4.19 (m, 4H), 4.16 – 4.10 (m, 2H), 4.10 – 4.05 (m, 2H), 4.08 (s, 3H, Hk), 3.87 – 3.82 (m, 2H), 3.77 – 3.72 (m, 2H), 3.67 – 3.60 (m, 4H), 3.60 – 3.54 (m, 5H), 3.60 – 3.47 (m, 11H).

**$^{13}$C NMR** (125 MHz, $CD_3CN$): δ = 163.28;163.21(Cl,l'), 151.33 (Cg), 151.21 (Cj), 144.44 (Ce), 142.56 (Ca), 142.34 (Ch), 141.57, (Cd,d')128,05 (Cf), 124.83 (Ci), 108.18,106.91(Cc,c'), 102.00;101.84 (Cb,b'), 71.41, 71.25, 71.22, 71.14, 71.10, 71.00, 70.40, 70.19, 70.11, 70.02, 69.99, 69.94, 66.34, 66.17, 35.48 (Ck).

**MS (ESI$^+$):** m/z calculated for $[C_{34}H_{44}N_4O_{10}Ag]^+$ [M]$^+$ = 775.21, found = 775.21.

## 2. Measurement of binding constants

The NMR dosage was conducting as following: In an NMR tube, the turnstile was dissolved in $CD_3CN$ (500 µL, concentration of $1.36\times10^{-3}$ M). Successive additions of a solution of $AgCF_3SO_3$ in $CD_3CN$ (concentration of $4.9.10^{-2}$ M) were done using a 50 µL microsyringe. The data were then compilated in a file and analysed with a titration software, Hypspec (http://www.hyperquad.co.uk/HypSpec.htm) which uses multivariate factor analysis to obtain globally optimized parameters. The mathematical analysis of the titration data was done with a titration software, Hypspec (http://www.hyperquad.co.uk/HypSpec.htm) which uses multivariate factor analysis to obtain globally optimized parameters. The fit of the complete titration data was good with $\sigma_{1:1}$=0.02 and $\sigma_{2:1}$=0.03 (Fig. S3). The simulation for the speciation was done with the software Hyperquad.

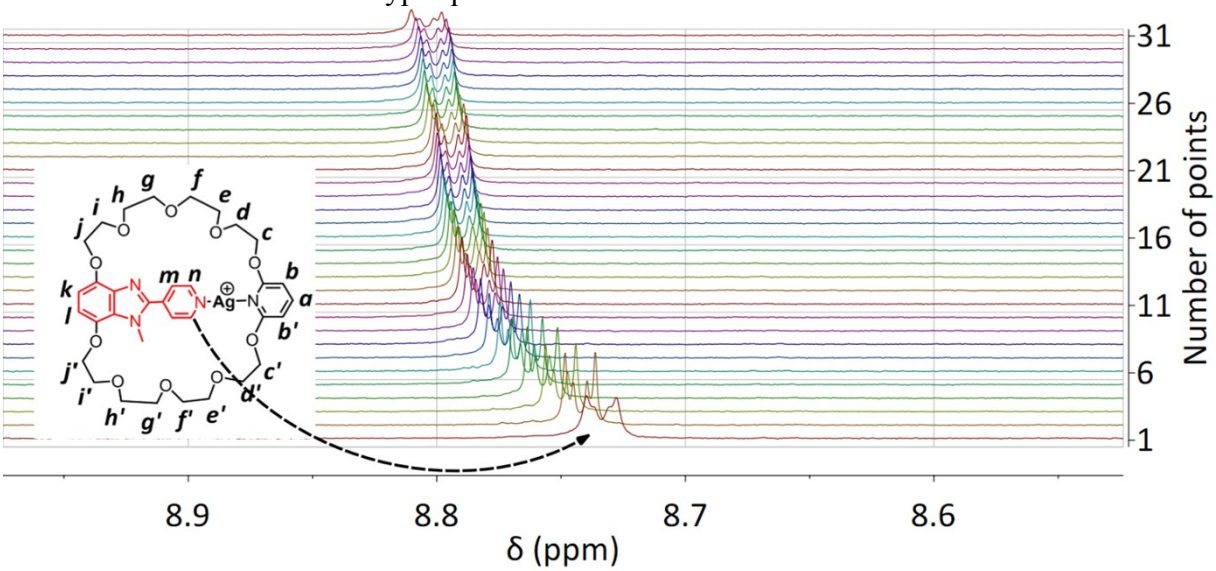



**Figure S1**. $^1H$ NMR ($CD_3CN$, 500 MHz, 298 K) spectra of **T1** after addition of 0 to 25 equivalents of $CF_3SO_3Ag$.

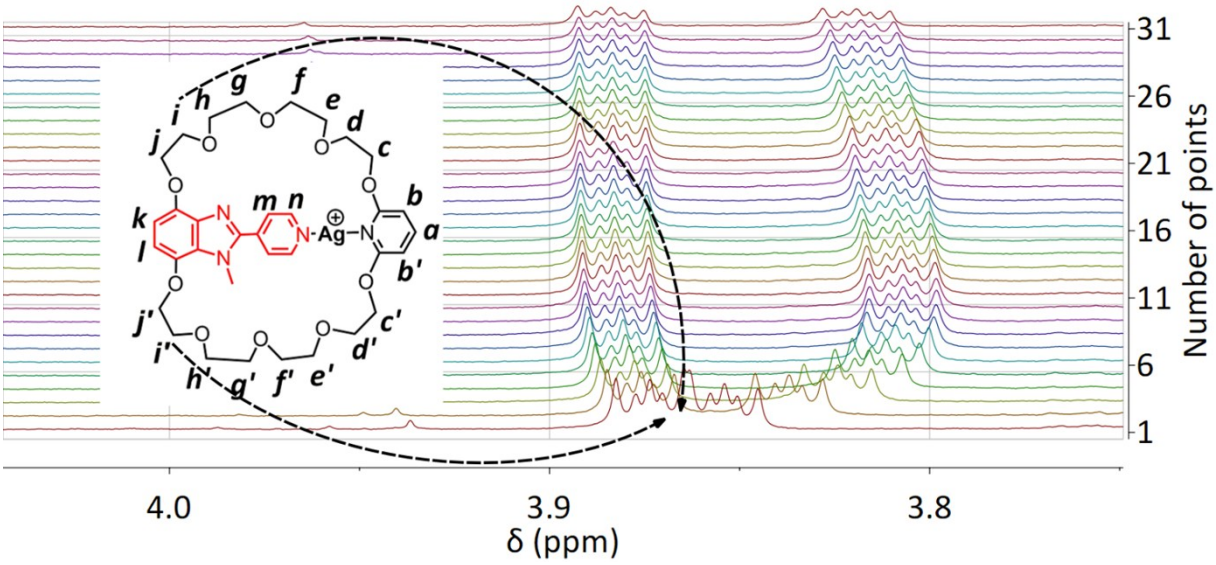
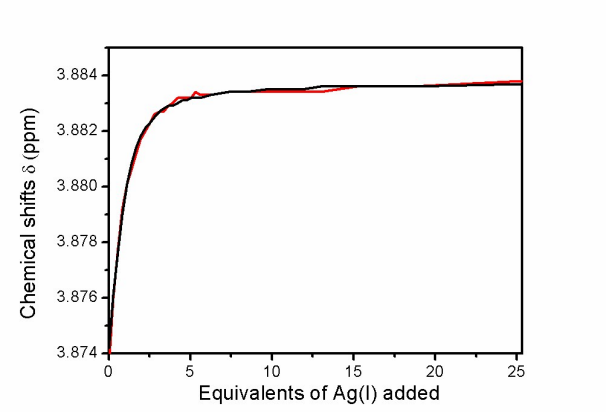
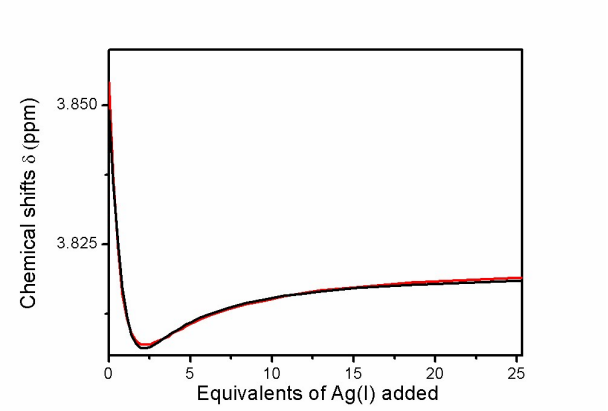



**Figure S2**. $^{1}$H NMR $^{1}$H ($CD_3CN$, 500 MHz, 298 K) spectra of **T1** after addition of 0 to 25 equivalents of $CF_3SO_3Ag$.

**a)**




**b)**




**c)**

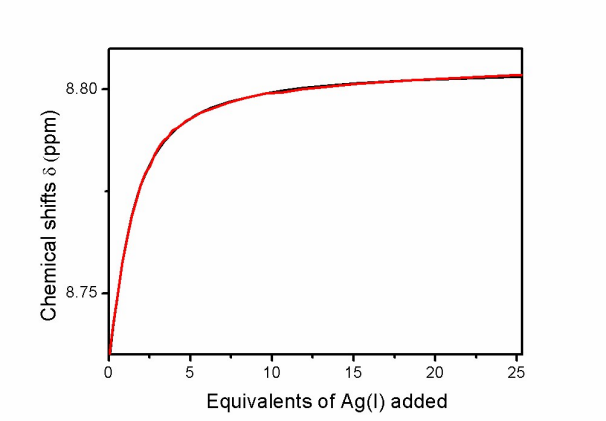
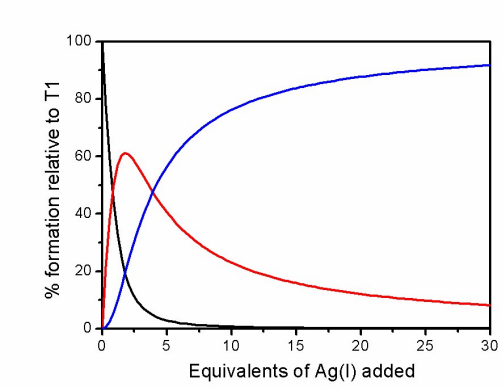
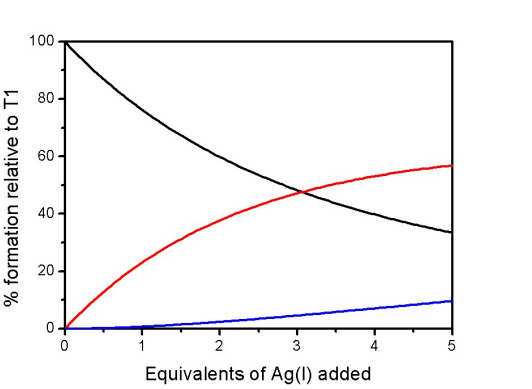



**Figure S3**. Plot of the variation of the experimental (red trace) and calculated (black trace) chemical shift as a function of the number of the $CF_3SO_3Ag$ equivalents added a) hydrogens H*n* b) hydrogens of the polyethylenglycol chain H*i* c) hydrogens of the polyethylenglycol chain H*i'*.

**a)**




**b)**




**c)**

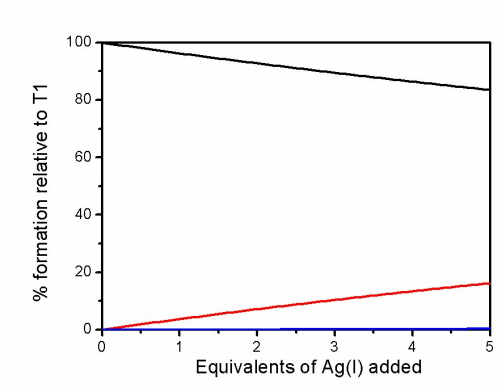


**Figure S4**. Simulated speciation profiles for titrations of **T1** with Ag (I) at different concentrations representing the proportion of **T1** (black trace), the 1:1 $Ag^+$/**T1** complex (red trace) and the 2:1 $Ag^+$/**T1** (blue trace), function of the number of equivalents of $CF_3SO_3Ag$.

a) [T1] = $1.0\times10^{-3}$ M**.**

b) [T1] = $1.0\times10^{-4}$ M**.**

c) [T1] = $1.0\times10^{-5}$ M**.**

## 3. Photophysical measurements

Electronic absorption spectra of samples in solution at room temperature were recorded on a double-beam Perkin-Elmer Lambda 650 S spectrophotometer and baseline corrected. Steady-state emission spectra were recorded on a HORIBA Jobin-Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm $mm^{-1}$; 1200 grooves $mm^{-1}$) and a PPD850 photomultiplier tube. Emission and excitation spectra were corrected for source intensity (lamp and grating) and emission spectral response (detector and grating) by standard correction curves. Time-resolved measurements were performed using the time-correlated single-photon-counting (TCSPC) option on the Fluorolog 3. NanoLEDs ($\lambda_{exc}$ = 340 or 370 nm; FWHM <1 ns) with repetition rates between 10 kHz and 1 MHz used to excite the sample. The excitation source were mounted on the sample chamber at 90° to a double grating emission monochromator (2.1 nm $mm^{-1}$ dispersion; 1200 grooves $mm^{-1}$) and collected by a PPD850 single-photon-counting detector. The photons collected at the detector were correlated by a time-to-amplitude converter (TAC) to the excitation pulse. Signals were collected using an IBH DataStation Hub photon counting module and data analysis was performed using the commercially available DAS6 software (HORIBA Jobin Yvon IBH). The goodness of fit was assessed by minimizing the reduced chi-

square function ($\chi$) and visual inspection of the weighted residuals. Photoluminescence quantum yields (PLQY) were measured in optically dilute solution (optical density <0.1 at the excitation wavelength) and compared to reference emitters by the method of Demas and Crosby[4]. Quinine sulfate in 0.05 M $H_2SO_4$ was used as reference at room temperature (PLQY = 0.53)[5]. All the solvents were spectrophotometric grade.

## 4. Supplementary Figures

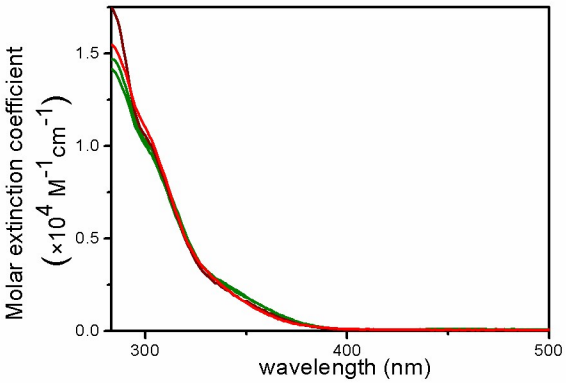
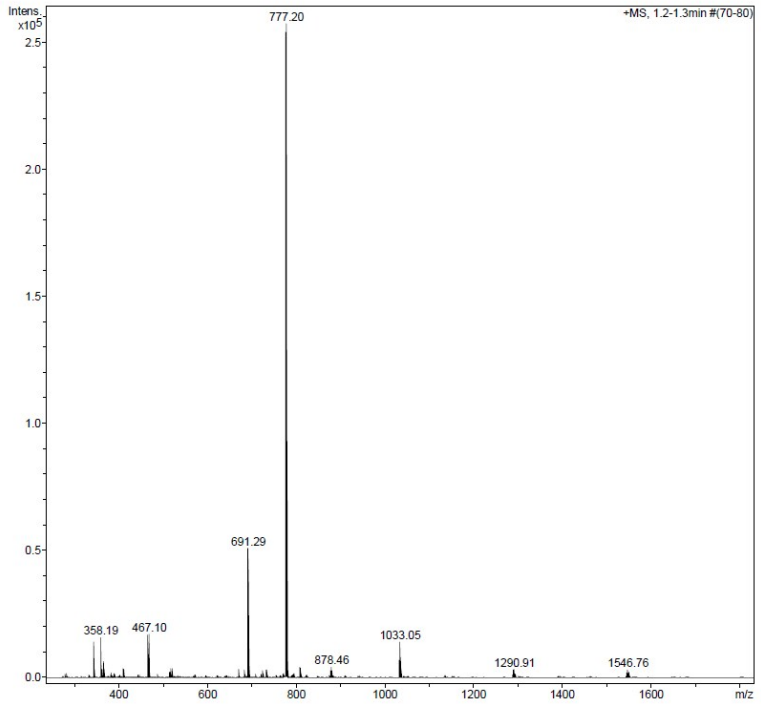



**Figure S5**. Solvent effect for **T1**. Absorption spectra of samples of **T1** in toluene (red wine trace), in $CH_2Cl_2$ (dark trace), $CH_3CN$ (red trace) and DMF (olive trace).

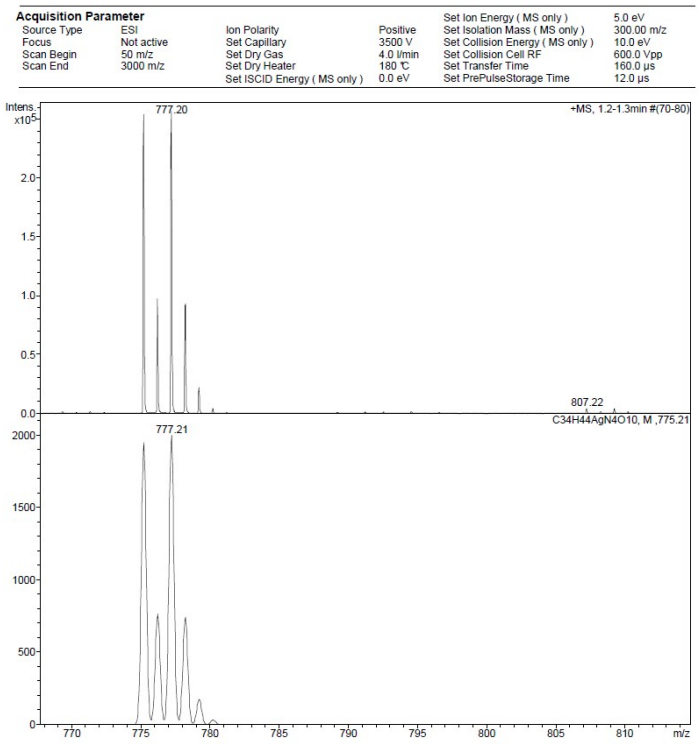
**a)**

**Acquisition Parameter**

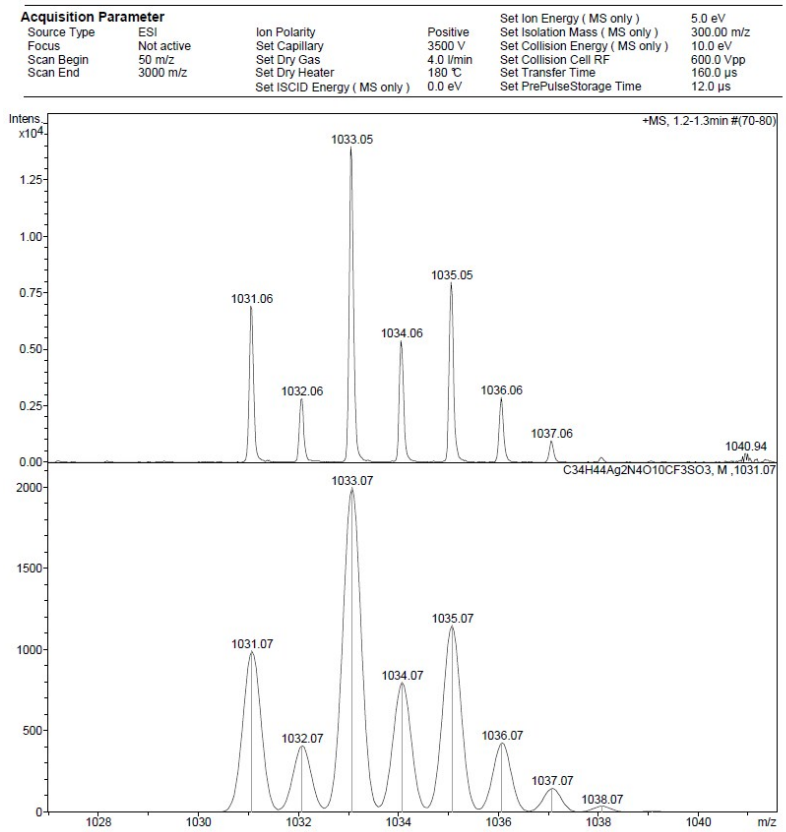
| | | | | | |
|---|---|---|---|---|---|
| Source Type | ESI | Ion Polarity | Positive | Set Ion Energy ( MS only ) | 5.0 eV |
| Focus | Not active | Set Capillary | 3500 V | Set Isolation Mass ( MS only ) | 300.00 m/z |
| Scan Begin | 50 m/z | Set Dry Gas | 4.0 l/min | Set Collision Energy ( MS only ) | 10.0 eV |
| Scan End | 3000 m/z | Set Dry Heater | 180 °C | Set Collision Cell RF | 600.0 Vpp |
| | | Set ISCID Energy ( MS only ) | 0.0 eV | Set Transfer Time | 160.0 µs |
| | | | | Set PrePulseStorage Time | 12.0 µs |




**b)**


Acquisition Parameter
Source Type ESI
Focus Not active
Scan Begin 50 m/z
Scan End 3000 m/z
Ion Polarity Positive
Set Capillary 3500 V
Set Dry Gas 4.0 l/min
Set Dry Heater 180 ℃
Set ISCID Energy ( MS only ) 0.0 eV
Set Ion Energy ( MS only ) 5.0 eV
Set Isolation Mass ( MS only ) 300.00 m/z
Set Collision Energy ( MS only ) 10.0 eV
Set Collision Cell RF 600.0 Vpp
Set Transfer Time 160.0 µs
Set PrePulseStorage Time 12.0 µs
Intens.
x10^5
+MS, 1.2-1.3min #(70-80)
777.20
807.22
C34H44AgN4O10, M ,775.21
777.21
m/z

**c)**


Acquisition Parameter
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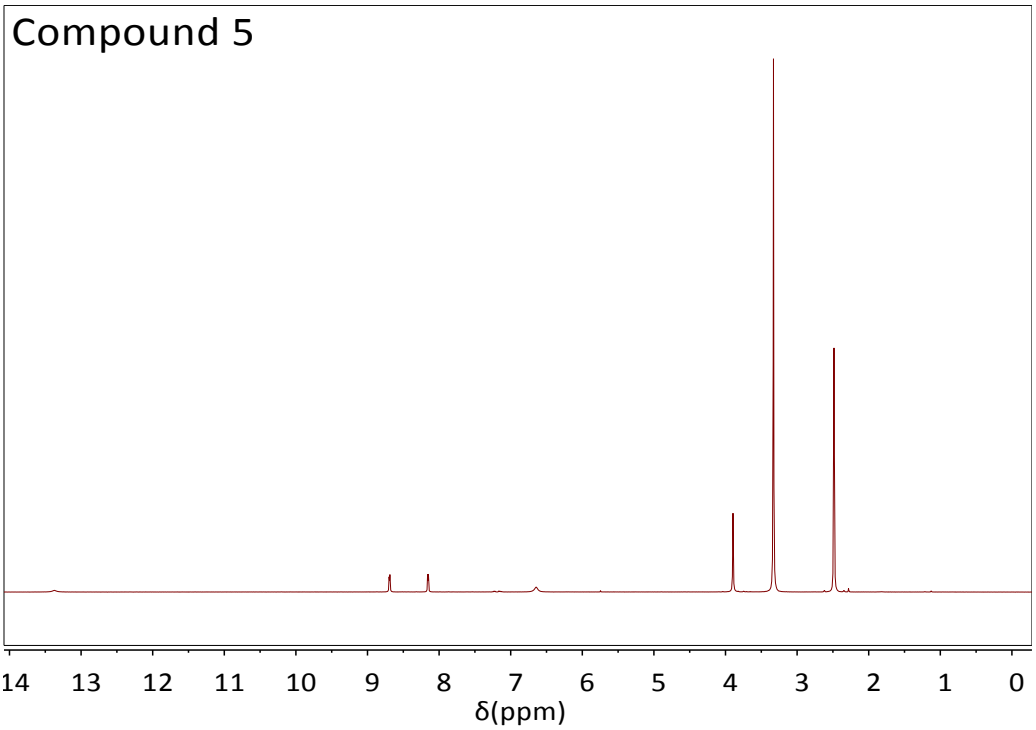
Focus Not active
Scan Begin 50 m/z
Scan End 3000 m/z
Ion Polarity Positive
Set Capillary 3500 V
Set Dry Gas 4.0 l/min
Set Dry Heater 180 ℃
Set ISCID Energy ( MS only ) 0.0 eV
Set Ion Energy ( MS only ) 5.0 eV
Set Isolation Mass ( MS only ) 300.00 m/z
Set Collision Energy ( MS only ) 10.0 eV
Set Collision Cell RF 600.0 Vpp
Set Transfer Time 160.0 µs
Set PrePulseStorage Time 12.0 µs
Intens.
x10^4
+MS, 1.2-1.3min #(70-80)
1033.05
1031.06
1035.05
1034.06
1032.06
1036.06
1037.06
1040.94
C34H44Ag2N4O10CF3SO3, M ,1031.07
1033.07
1031.07
1035.07
1034.07
1032.07
1036.07
1037.07
1038.07
m/z

**Figure S6.** a) ESI MS spectra of the sample **T1** obtained after addition of 25 equivalents of $CF_3SO_3Ag$ to **T1** ($1.10^{-3}$ M) b) Zoom and enlarged image of a) corresponding to the 1:1 (ie $[T+Ag]^+$) c) Zoom and enlarged image of a) corresponding to the 2:1 $Ag^+$/**T1(**ie $[T1+2Ag+CF_3SO_3]^+$) (c).

## 5. Chemical characterization of the compounds: $^1H$-, $^{13}C$-NMR and MS spectra



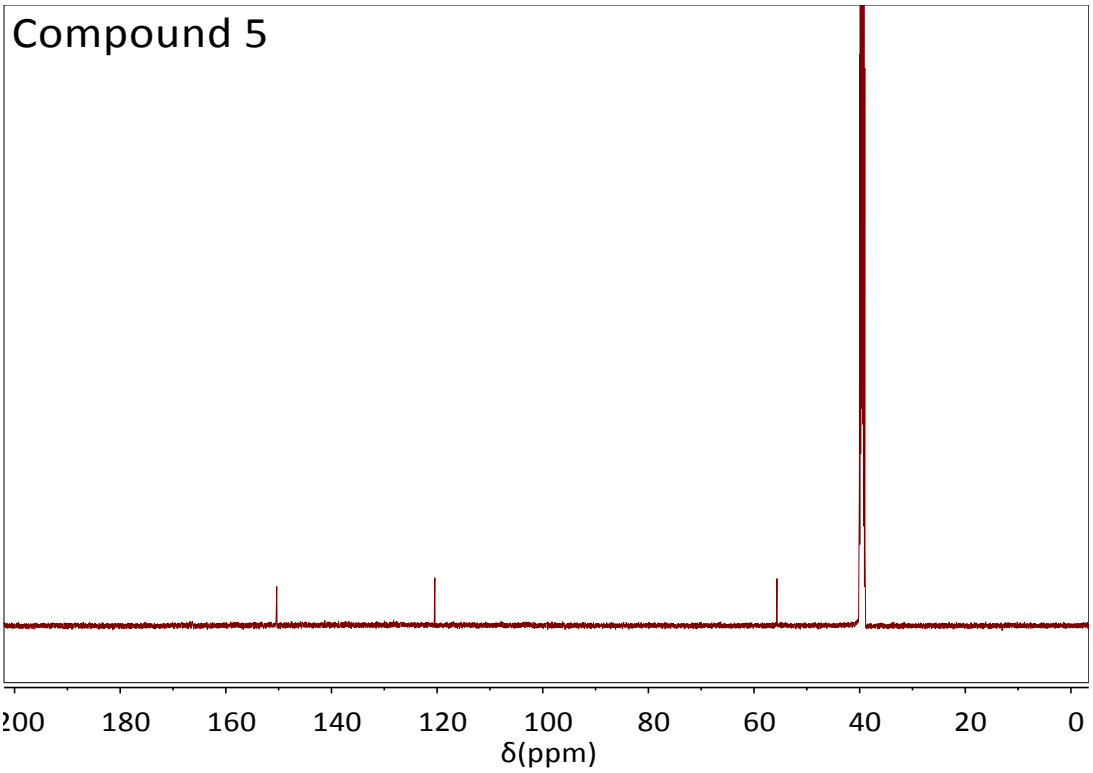
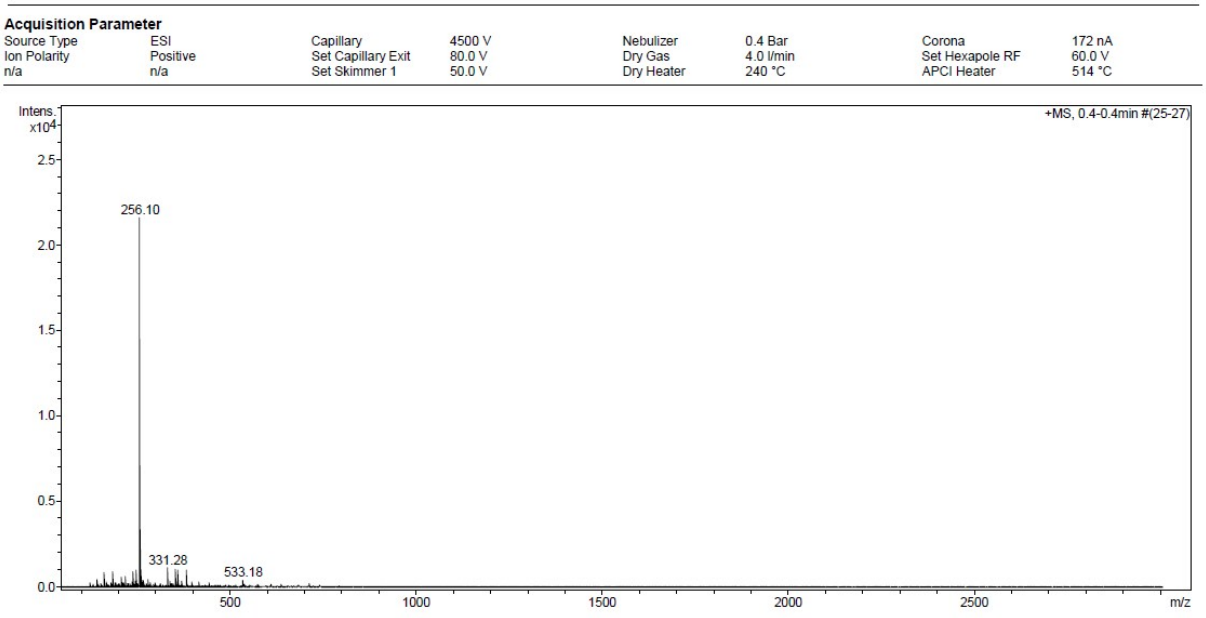



**Figure S7.** $^{1}H$ (500 MHz, top) and $^{13}C$ NMR (125 MHz, bottom) spectra of compound **5** (DMSO, 298K).



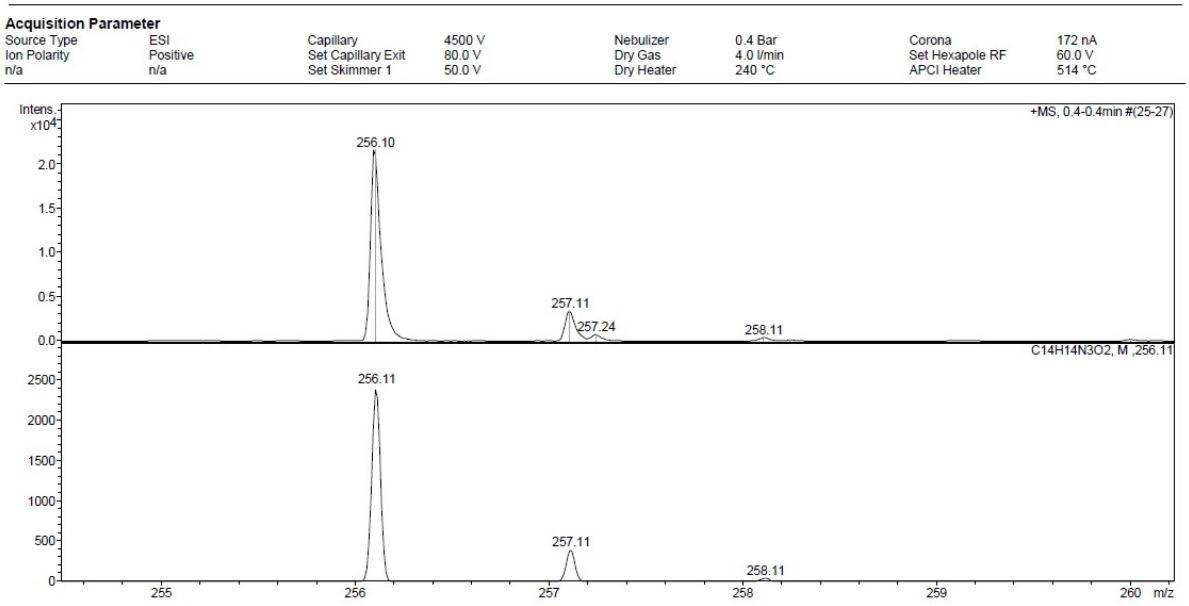



**Figure S8.** ESI-MS spectrum of compound **5** and enlarged image (bottom).

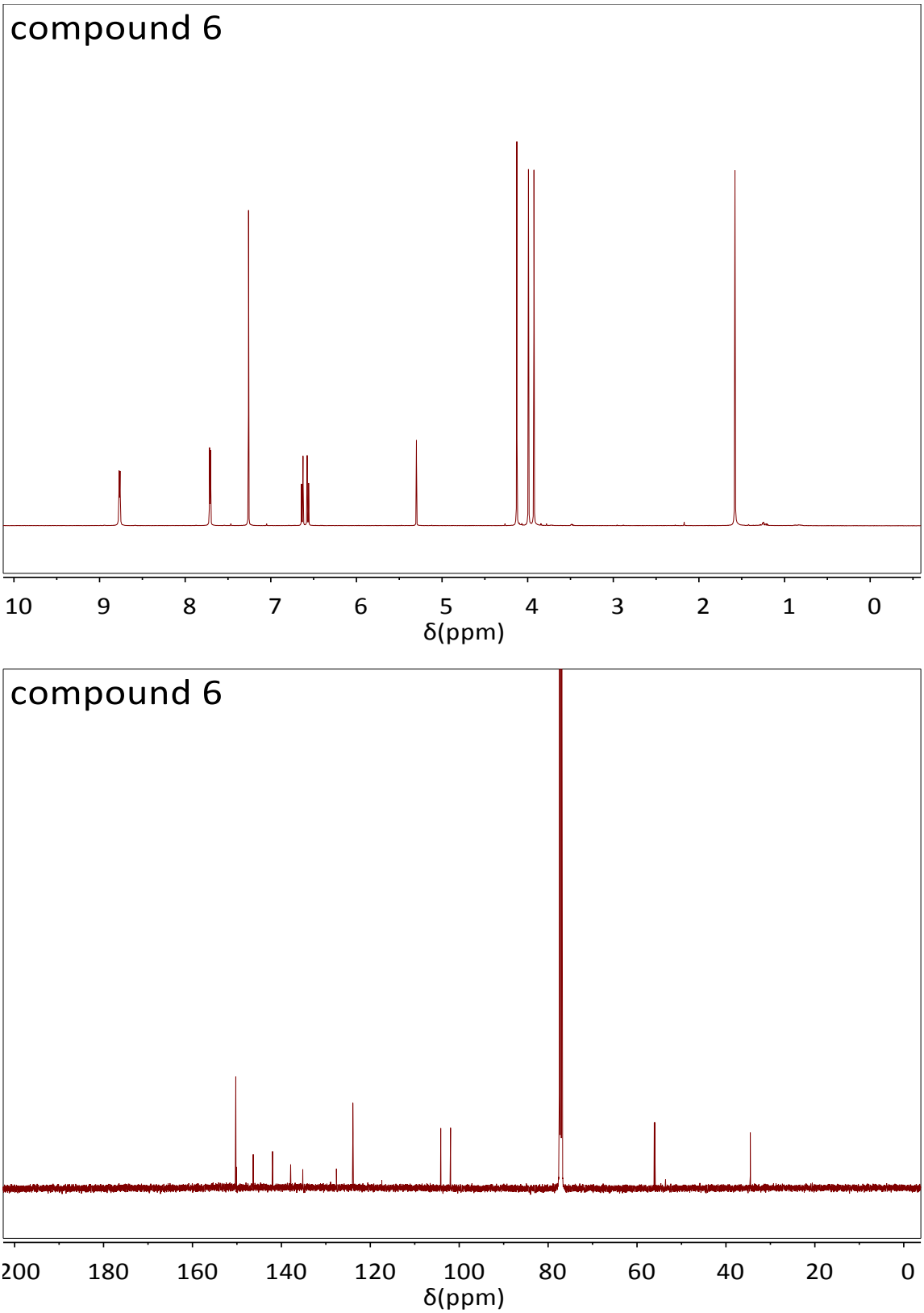



**Figure S9.** $^{1}H$ (500 MHz, top) and $^{13}C$ NMR (125 MHz, bottom) spectra of compound **6** ($CDCl_3$, 298K).

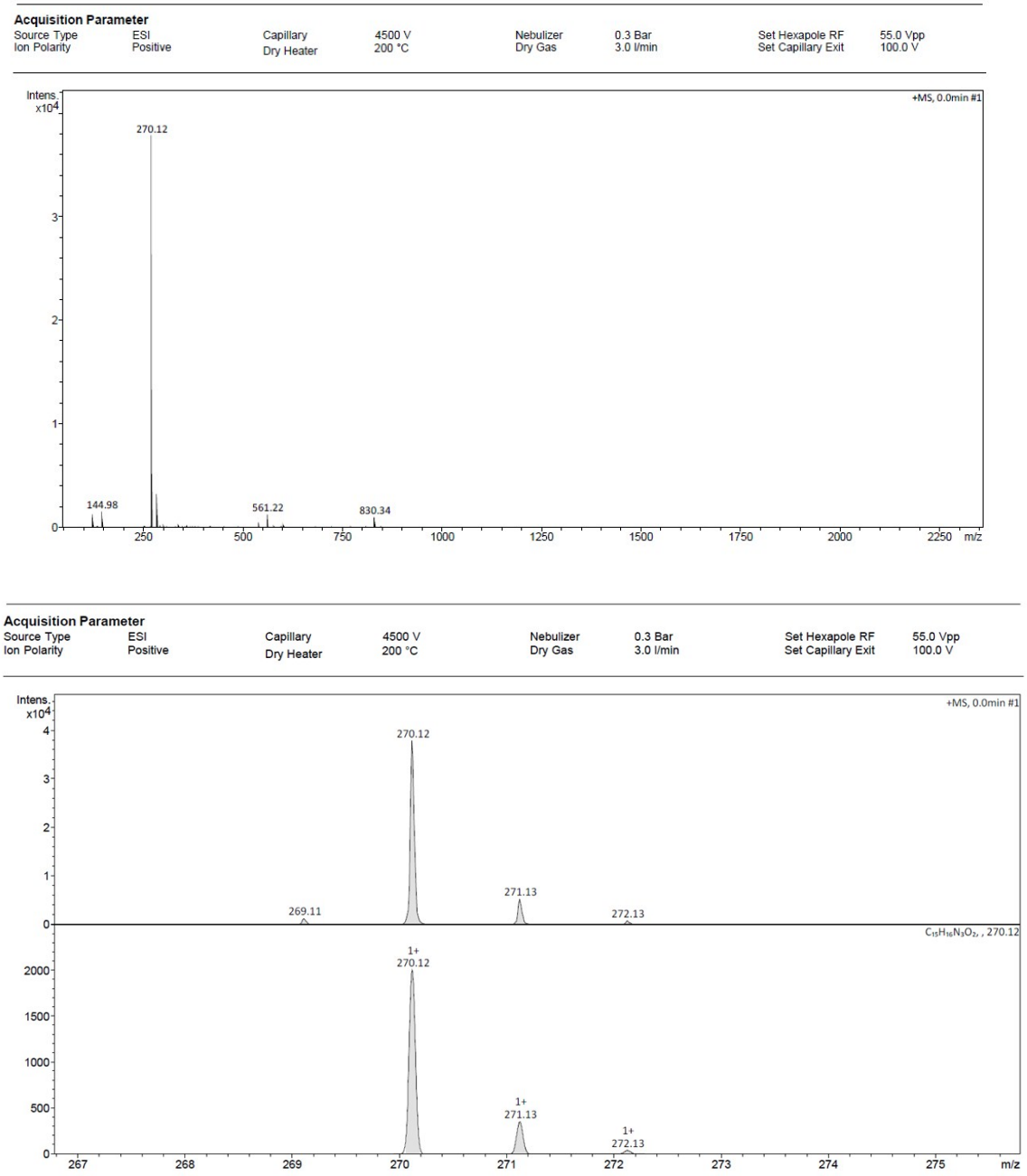
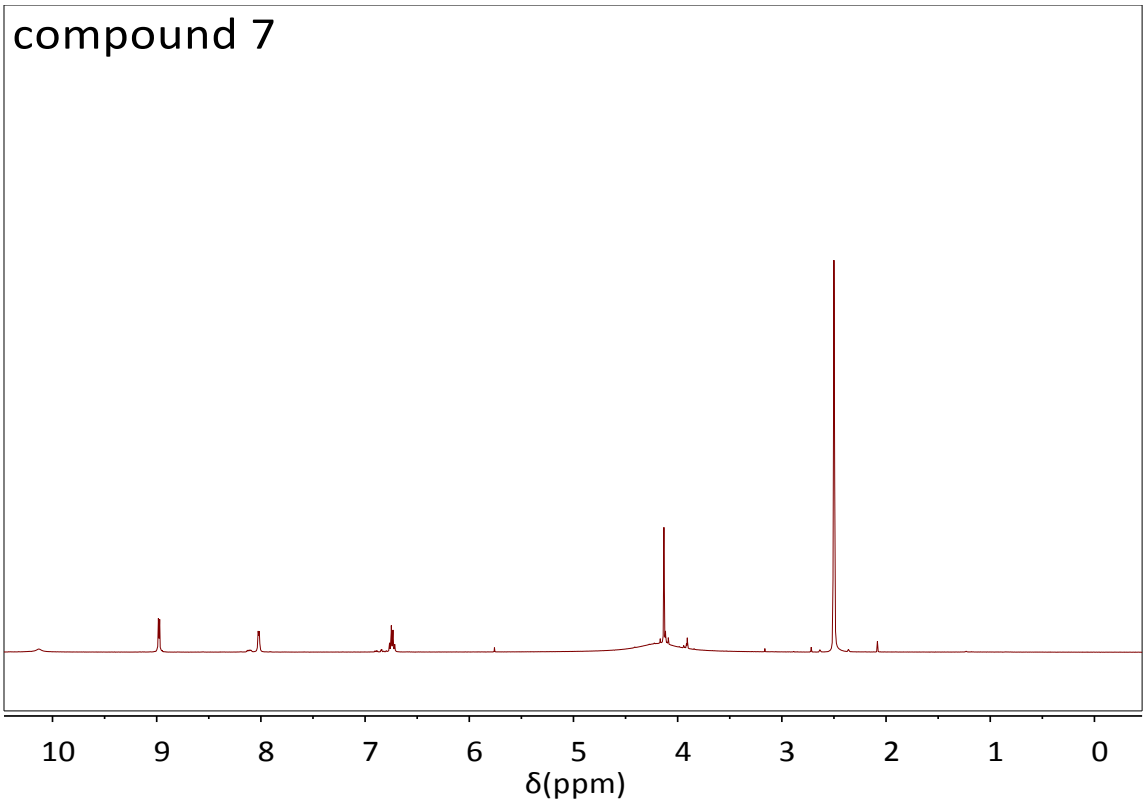



**Figure S10.** ESI-MS spectrum of compound **6** and enlarged image (bottom).



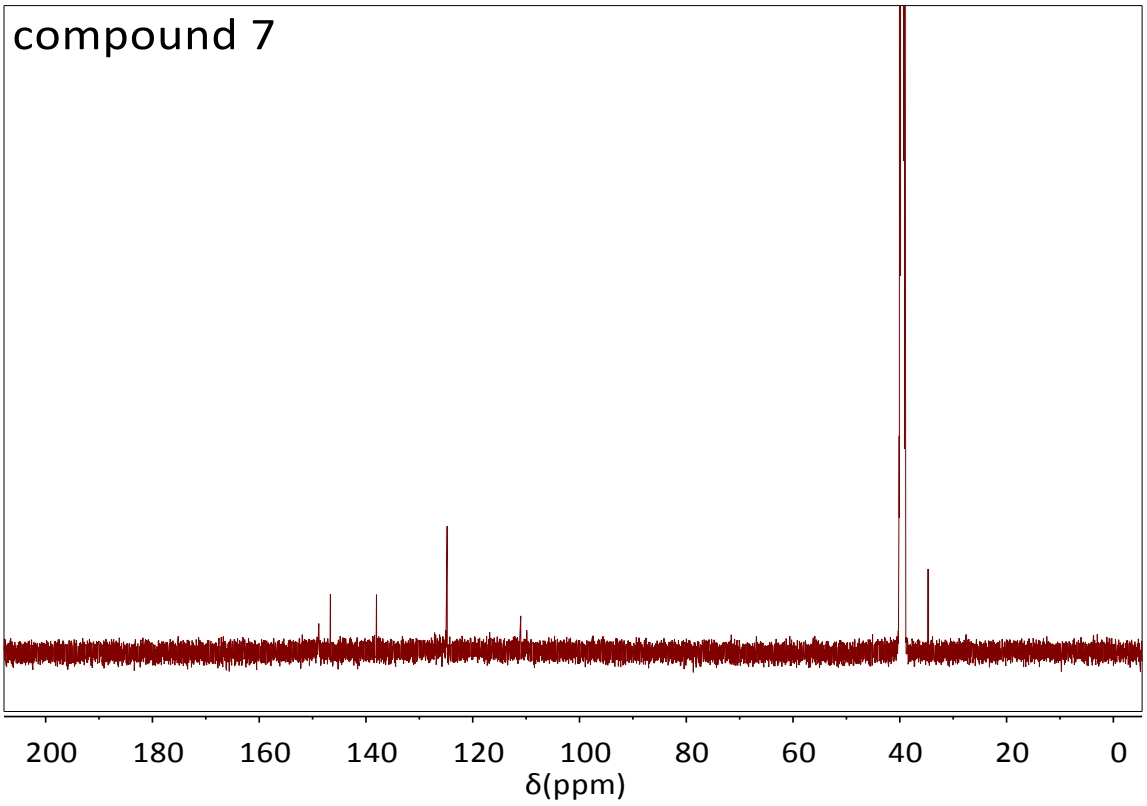




**Figure S11.** $^{1}H$ (500 MHz, top) and $^{13}C$ NMR (125 MHz, bottom) spectra of compound **7** (DMSO, 298K).

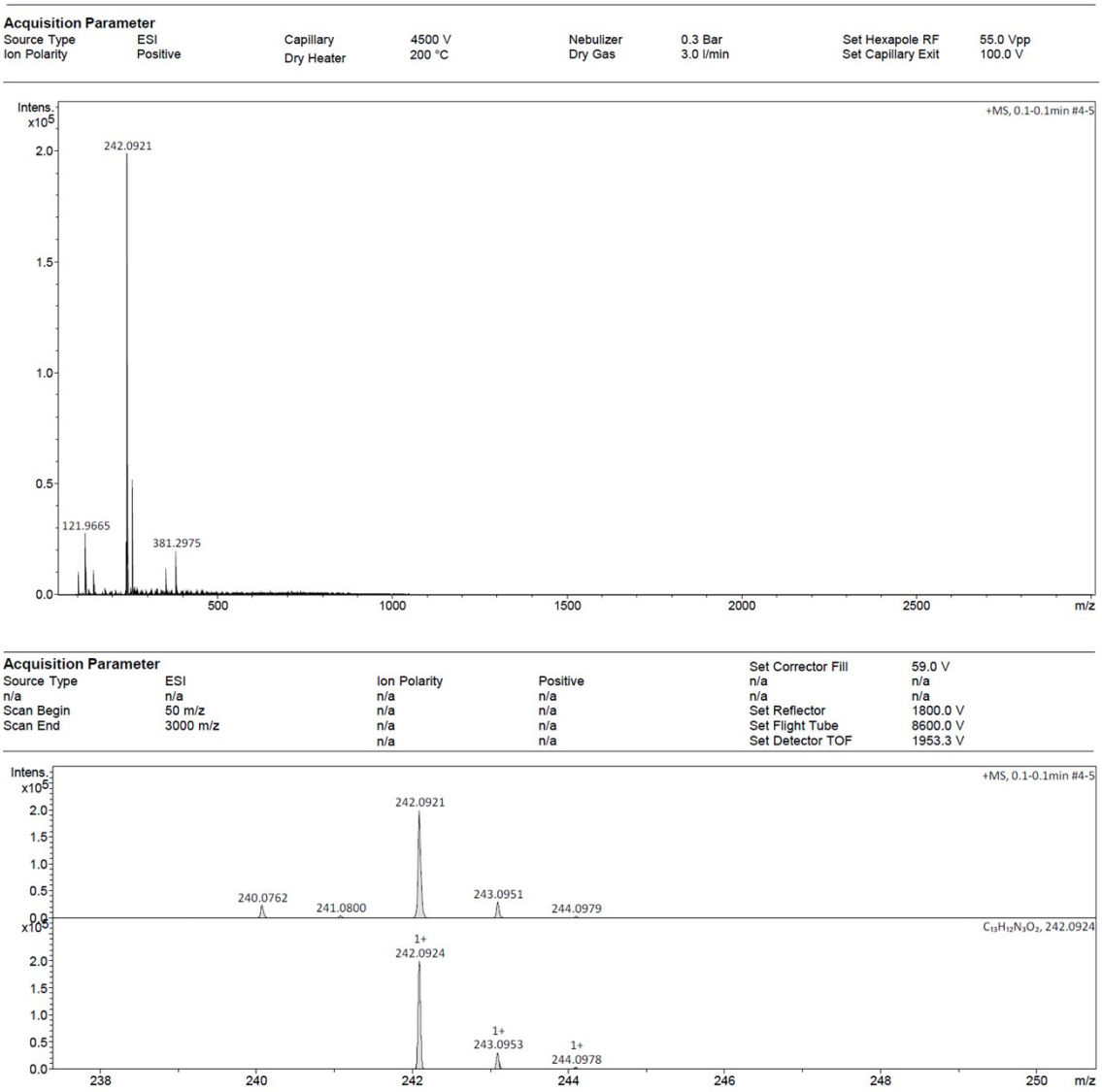



**Figure S12.** ESI-MS spectrum of **7** (top) and enlarged image (bottom).

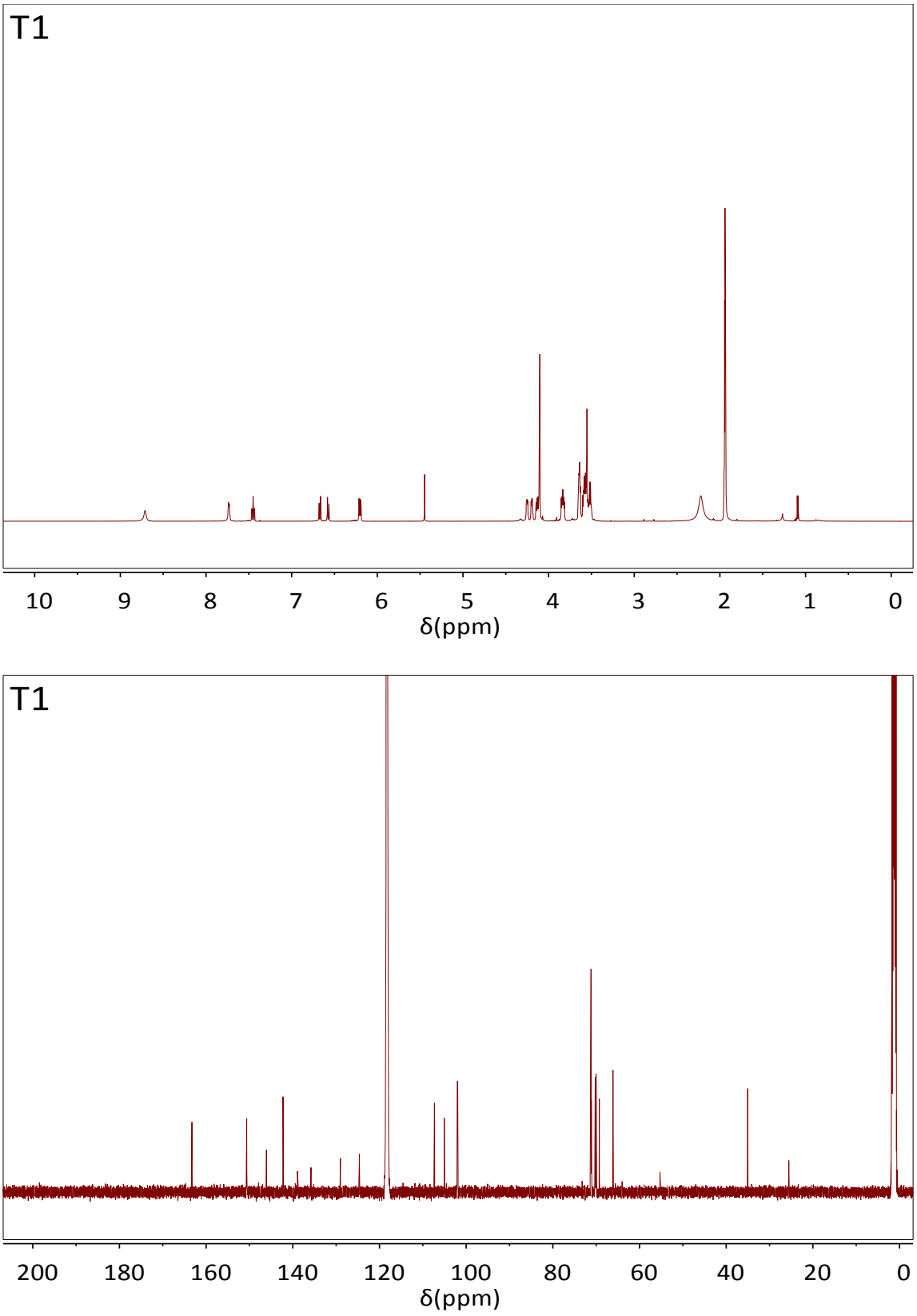



**Figure S13.** $^{1}H$ (500 MHz, top) and $^{13}C$ NMR (125 MHz, bottom) spectra of compound **T1** ($CD_3CN$, 298K).

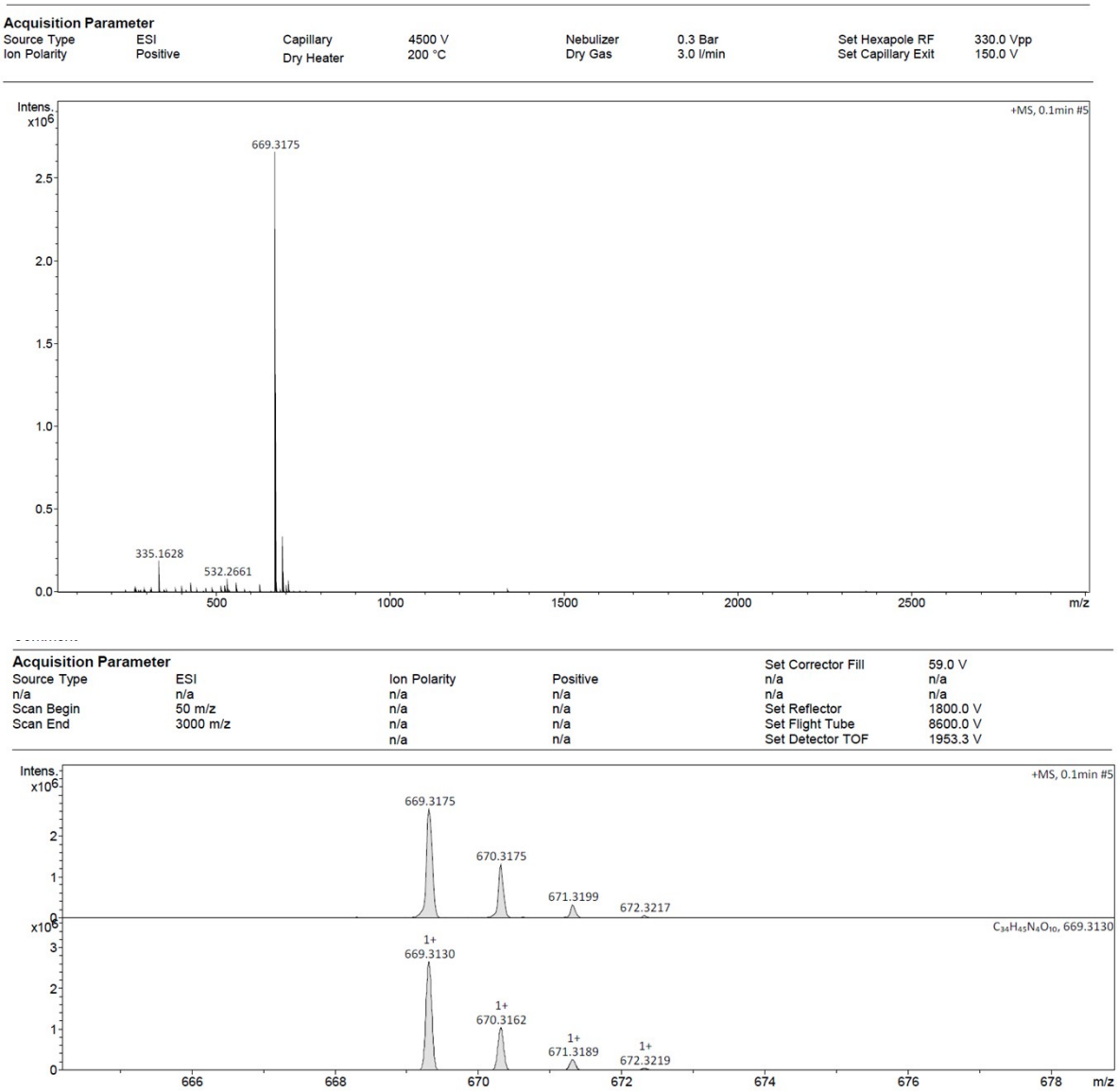



**Figure S14.** HRMS spectrum of **T1** (top) and enlarged image (bottom).

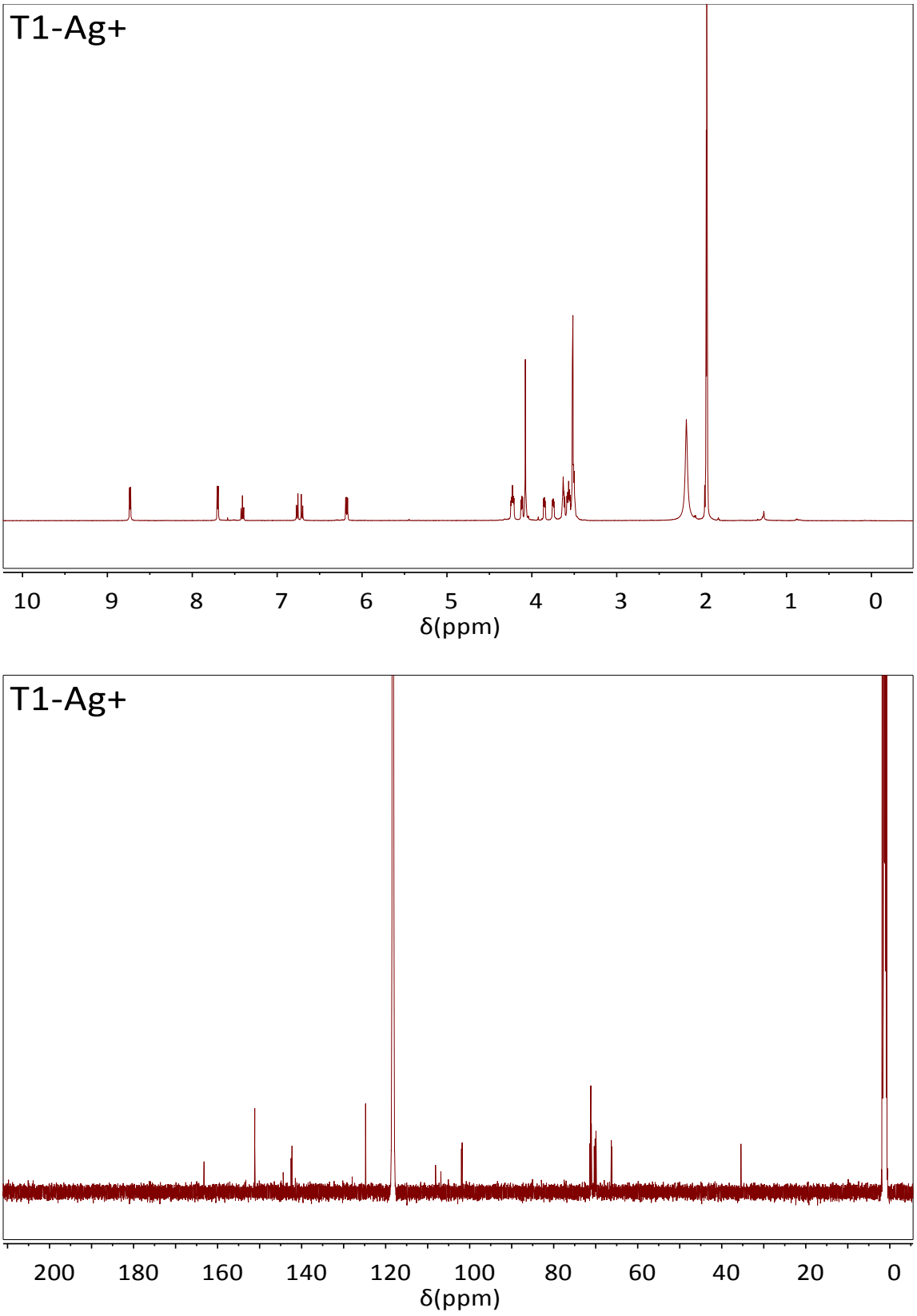



**Figure S15.** $^{1}H$ (500 MHz, top) and $^{13}C$ NMR (125 MHz, bottom) spectra of compound **T1-Ag$^{+}$** ($CD_3CN$, 298K).

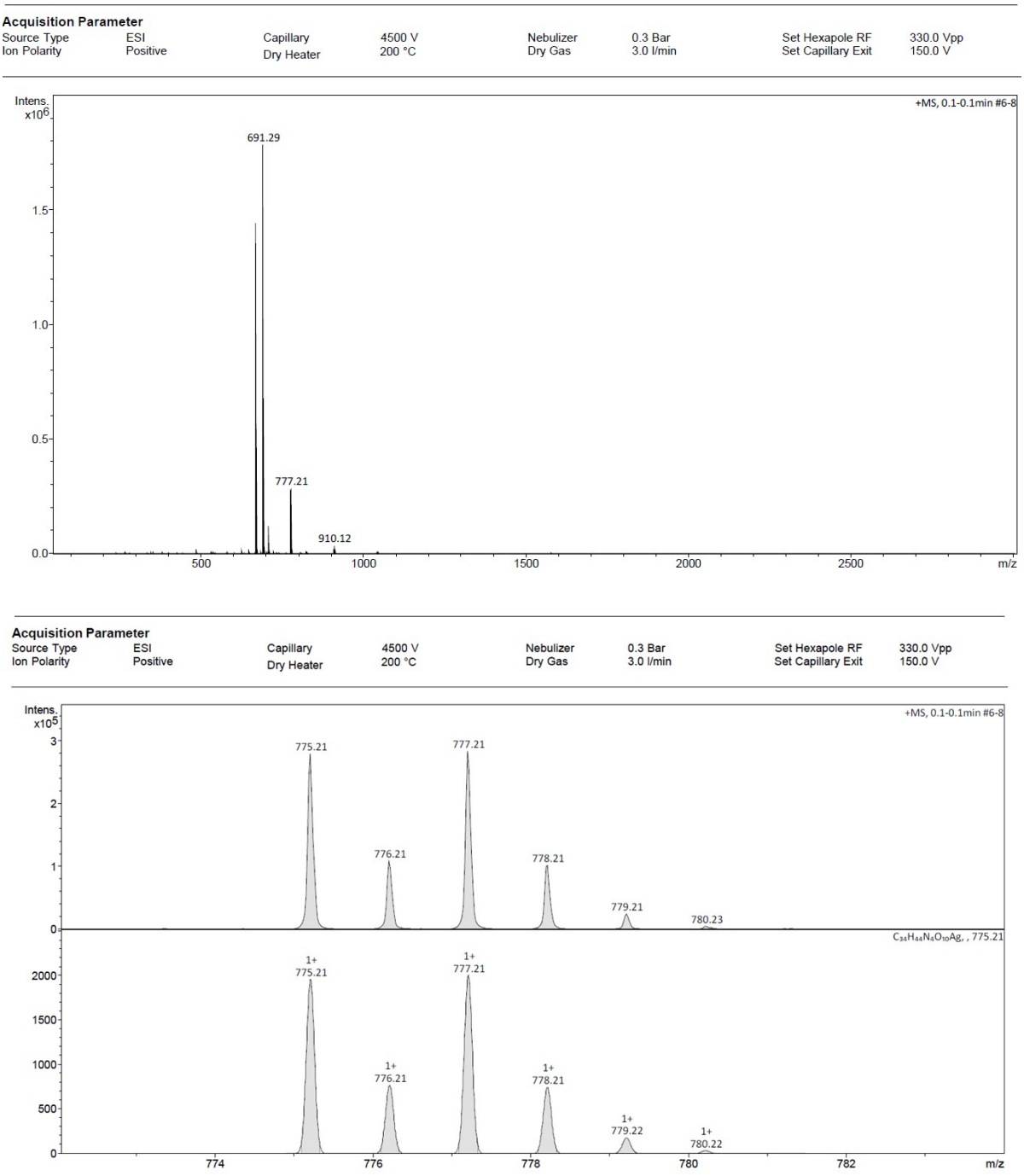



**Figure S16.** ESI-MS spectrum obtained after addition of one equivalent of $CF_3SO_3Ag$ to **T1** (top), enlarged image and simulation of the 1:1 (ie $[T1+Ag]^+$) complex.

## 6. References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