Electronic Supplementary Material (ESI) for Dalton Transactions.

# Supporting Information

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## Contents

# 1 NMR Spectra

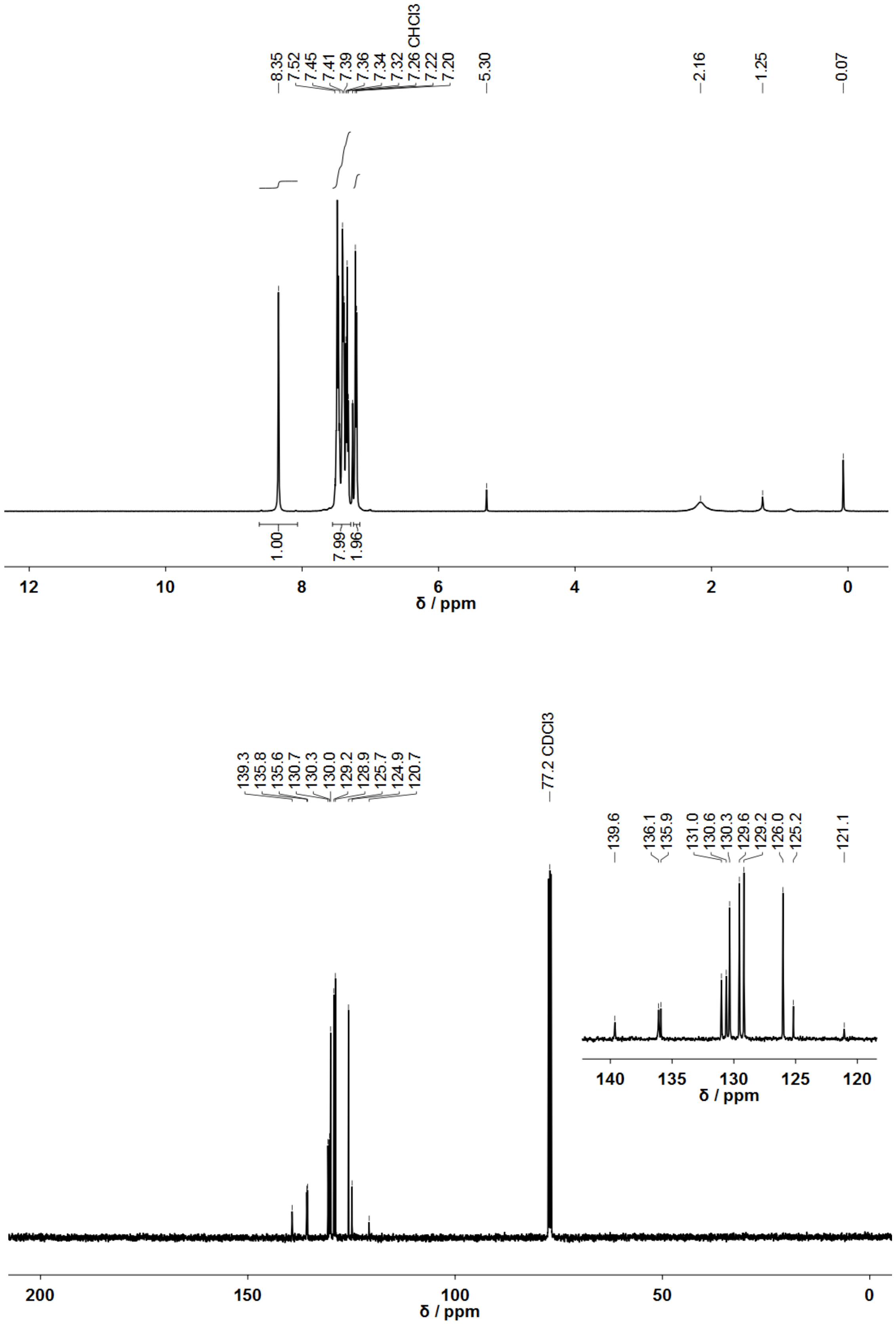
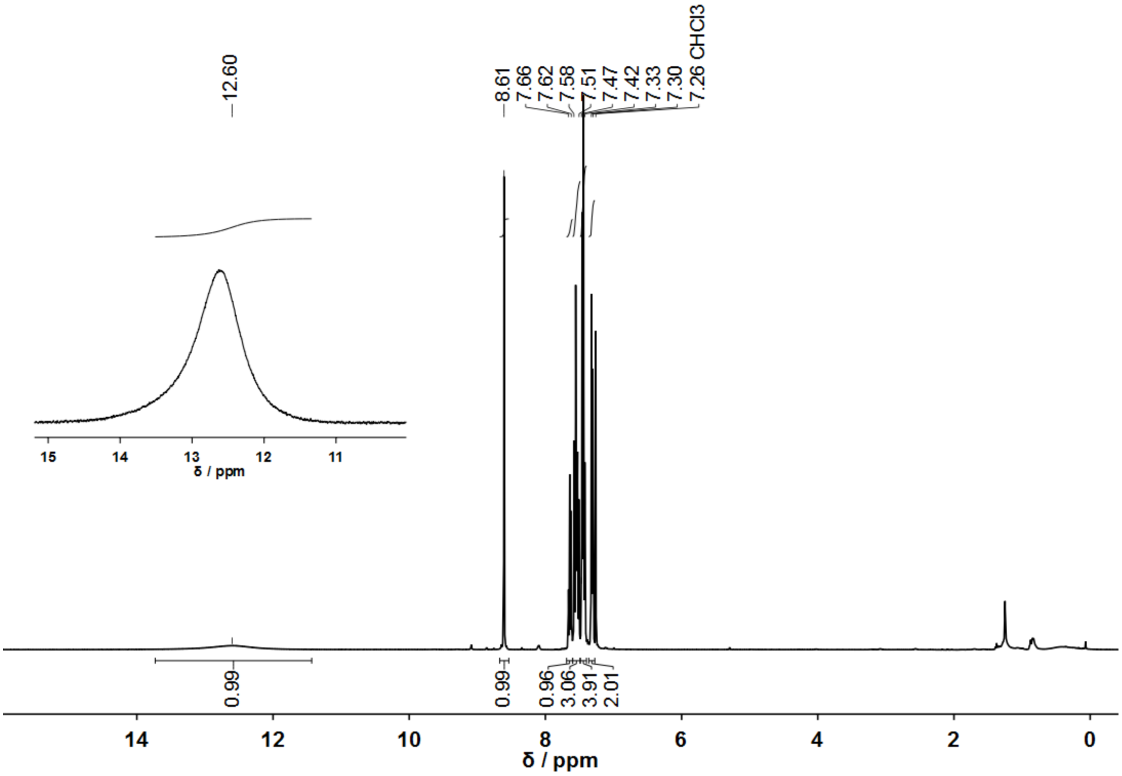


**Figure S1.** $^{1}H$ and $^{13}C\{^{1}H\}$ NMR of **4** (measured in $CDCl_3$).



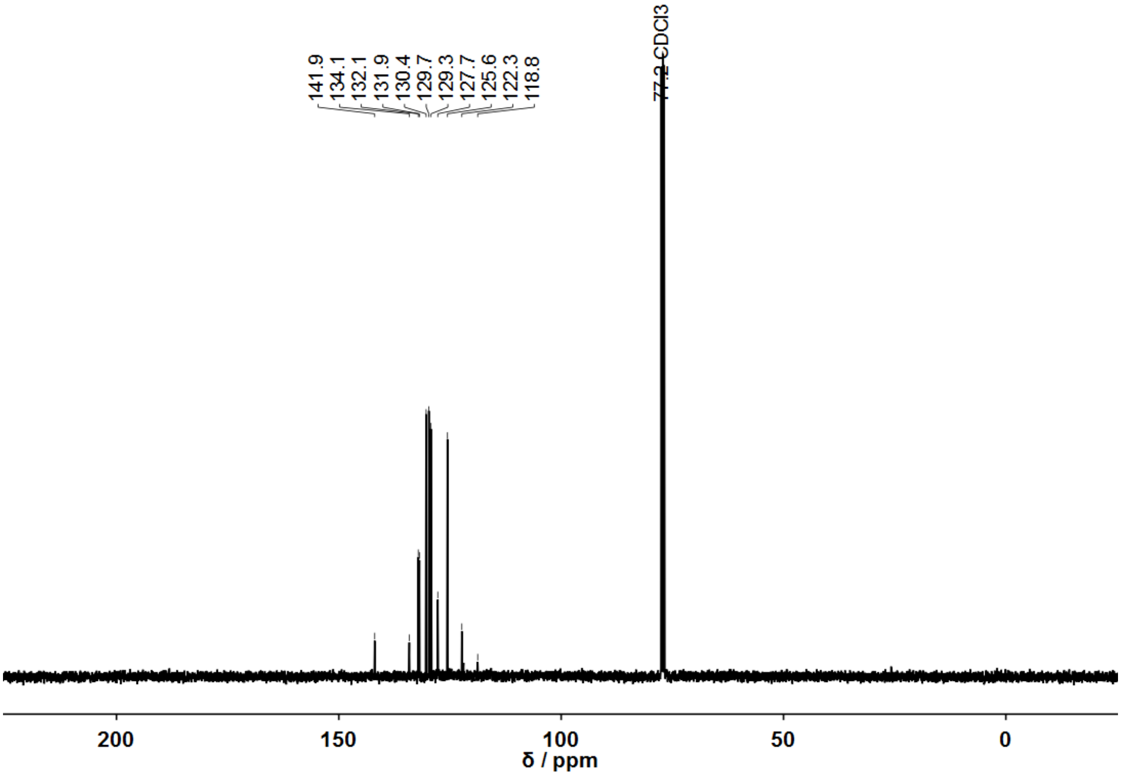


**Figure S2.** $^{1}H$ and $^{13}C\{^{1}H\}$ NMR of **8** (measured in $CDCl_3$).

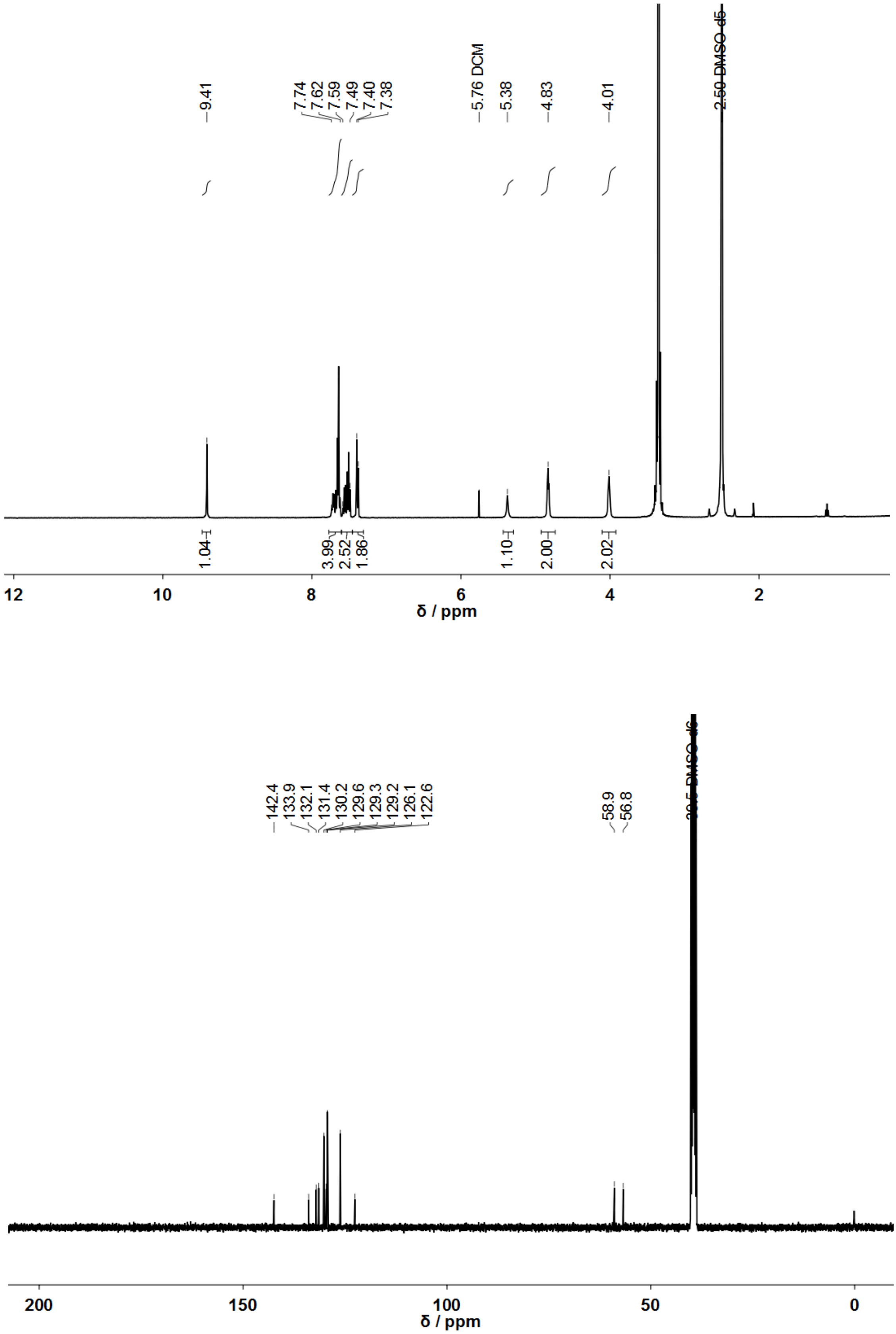


**Figure S3.** $^1$H and $^{13}$C{$^1$H} NMR of new triazolium salt **15** (measured in DMSO−d$_6$).

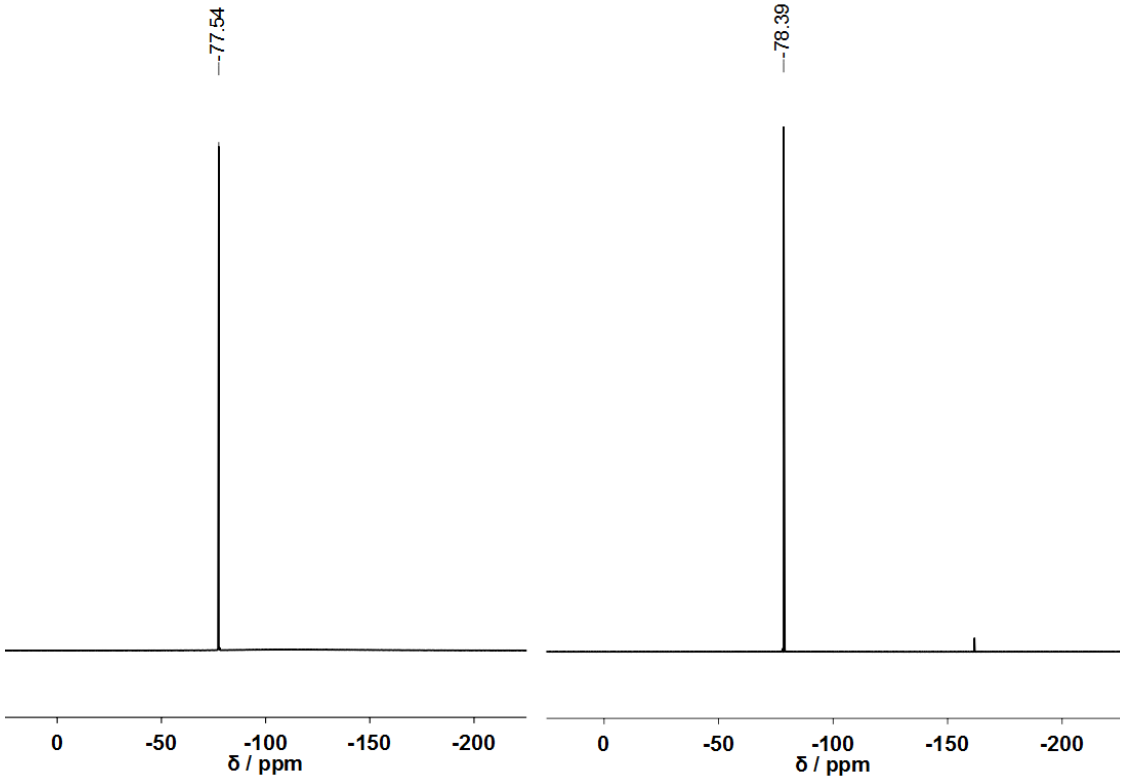


**Figure S4.** $^{19}$F NMR of **4** (left) and **8** (right) (measured in $CDCl_3$).

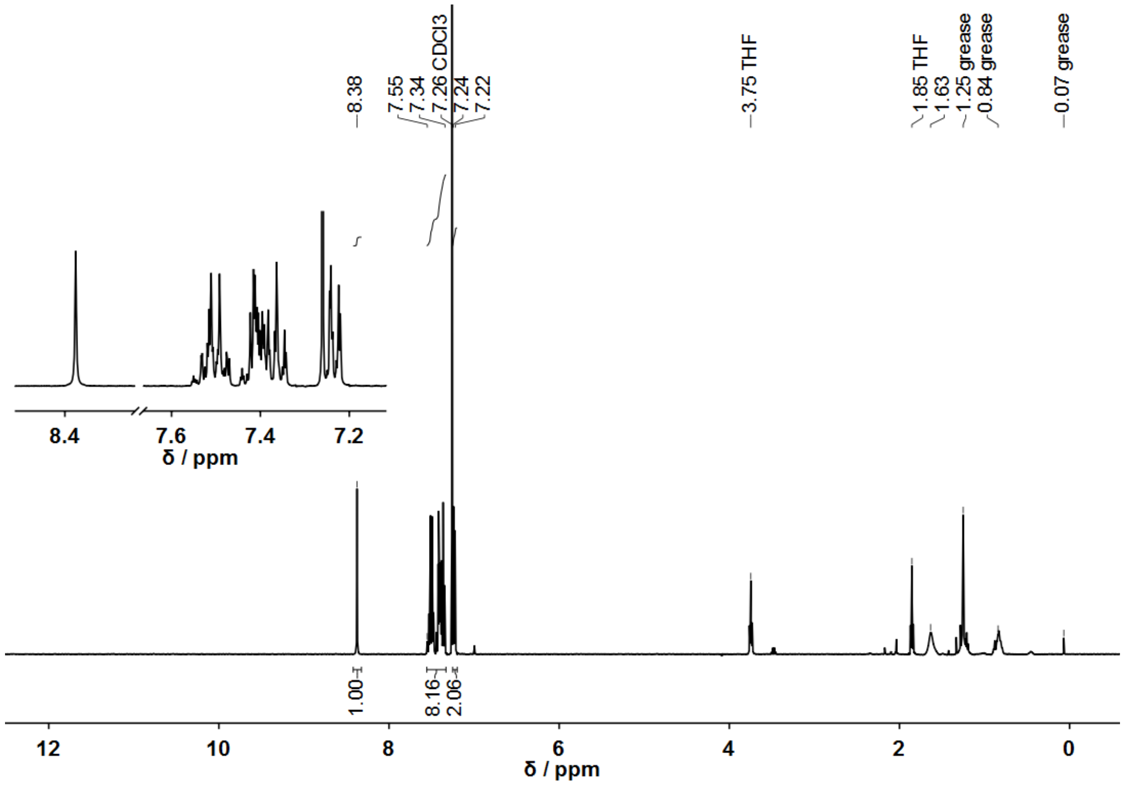


**Figure S5.** $^1$H NMR of single crystals of **4b** – crystallization from THF/$Et_2O$ (measured in $CDCl_3$).

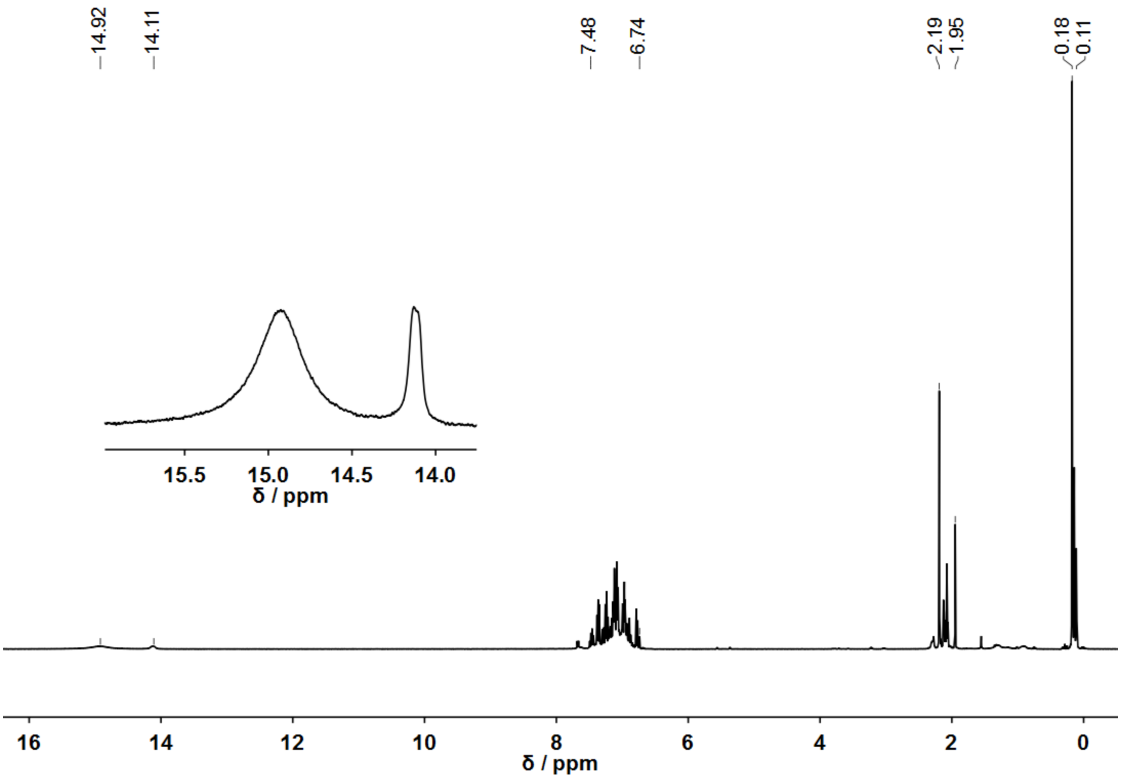


**Figure S6.** $^1$H NMR of green residue, possibly containing **6** (measured in toluene−d$_8$), free triflic acid at 14.92 ppm.

## 2 Crystallograhic Details & Molecular Structures

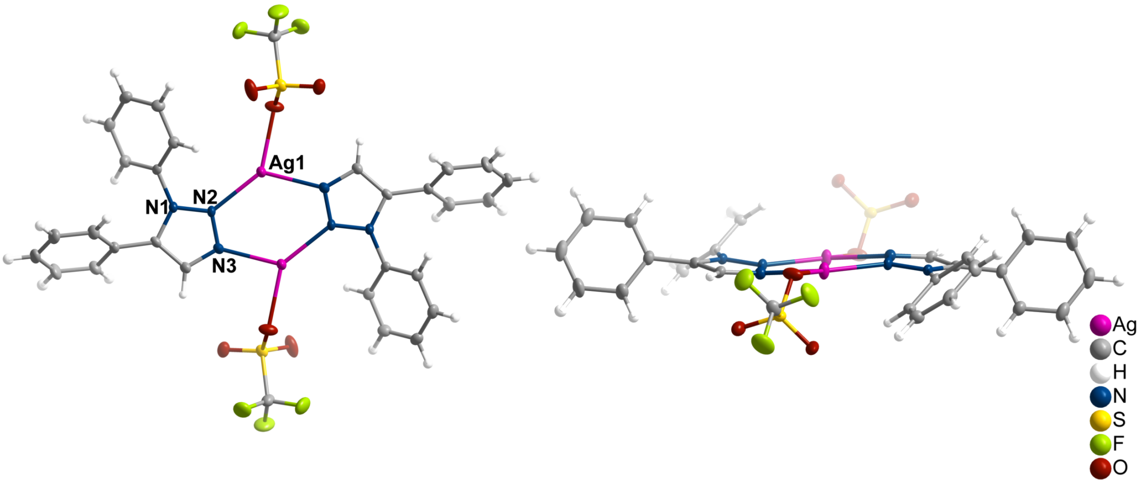


**Figure S7.** ORTEP view of **4a**, top and side view. Ellipsoids shown at 50% probabbility level.

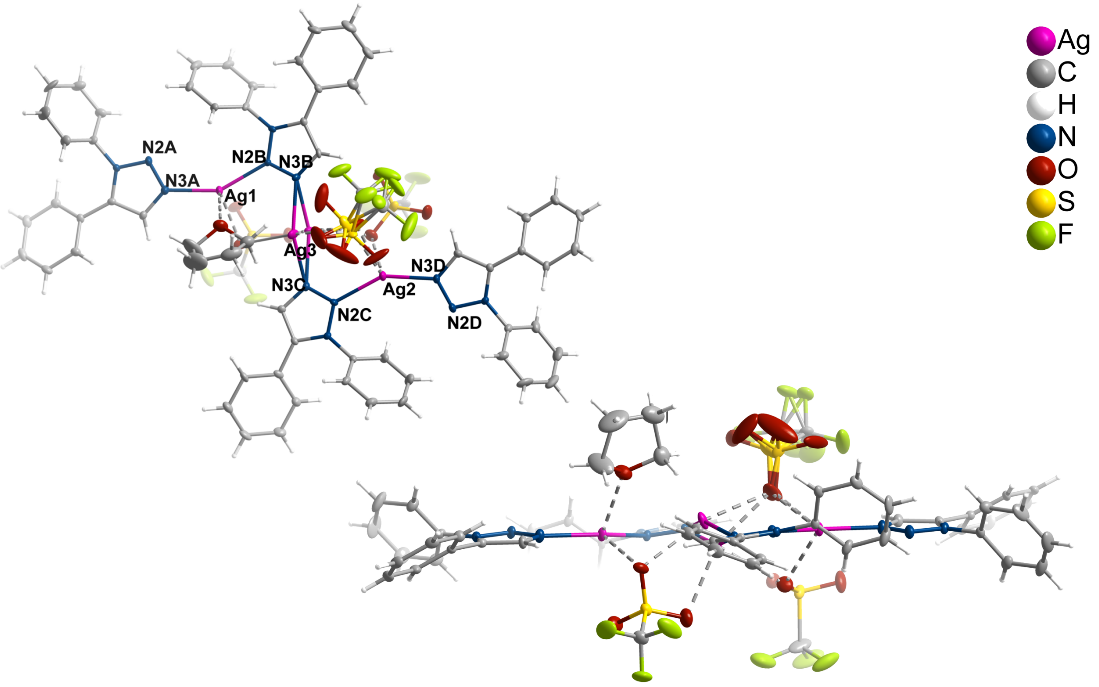


**Figure S8.** ORTEP view of **4b**, top and side view. Ellipsoids shown at 50% probabbility level.

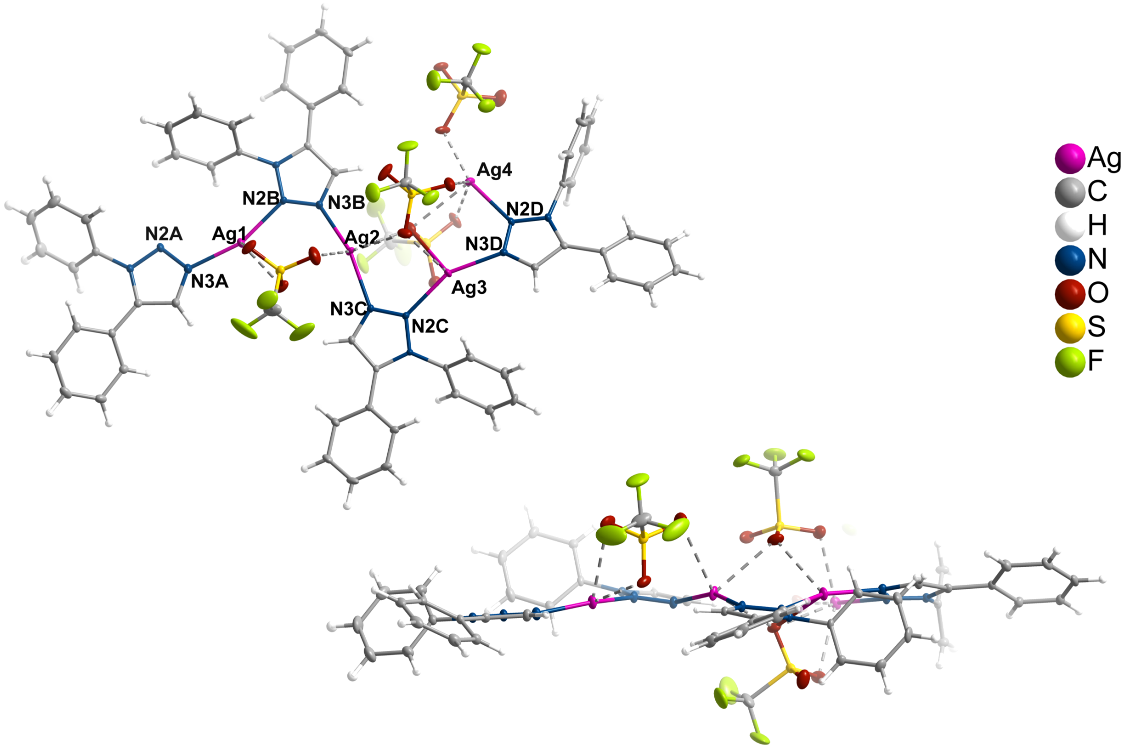


**Figure S9.** ORTEP view of **4c**, top and side view. Ellipsoids shown at 50% probabbility level.

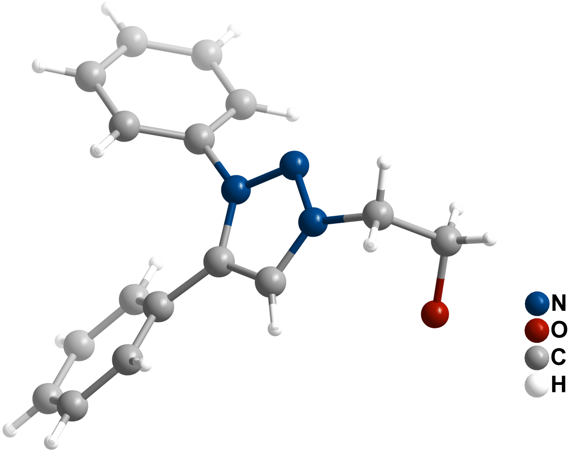


**Figure S10.** Ball-and-stick representation of **15** obtained from X-ray analysis, anion omitted for clarity. Connectivity of the glycol substitutent at the N3-atom confirmed.

**Table S1.** Crystallographic data.

| | **4a** | **4b** | **4c** | **8** |
|---|---|---|---|---|
| Chemical formula | $C_{30}H_{22}Ag_2F_6N_6O_6S_2$ | $C_{63}H_{52}Ag_3F_9N_{12}O_{10}S_3$ | $C_{60}H_{44}Ag_4F_{12}N_{12}O_{12}S_4$ | $C_{15}H_{12}F_3N_3O_3S$ |
| $M_r$ | 956.39 | 1727.95 | 1912.79 | 371.34 |
| Crystal System | triclinic | triclinic | triclinic | monoclinic |
| Space group | $P\bar{1}$ | $P1$ | $P\bar{1}$ | $P2_1/c$ |
| a (Å) | 6.3470(4) | 11.3183(12) | 11.6056(11) | 5.7679(5) |
| b (Å) | 10.9429(7) | 12.0408(12) | 11.9727(12) | 20.4230(16) |
| c (Å) | 13.4498(9) | 13.8230(13) | 25.294(2) | 13.8248(10) |
| $\alpha$ (°) | 68.090(2) | 65.850(4) | 99.526(4) | 90 |
| $\beta$ (°) | 84.194(2)) | 89.910(4) | 92.150(3) | 93.623(3) |
| $\gamma$ (°) | 79.220(2) | 75.722(4) | 105.030(3) | 90 |
| V (Å$^3$) | 850.88(10) | 1655.3(3) | 3335.6(6)) | 1625.3(2) |
| Z | 1 | 1 | 2 | 4 |
| Density (g·cm$^{-3}$) | 1.866 | 1.733 | 1.904 | 1.518 |
| F(000) | 472 | 864 | 1888 | 760 |
| Radiation Type | $MoK_\alpha$ | $MoK_\alpha$ | $MoK_\alpha$ | $MoK_\alpha$ |
| µ(mm$^{-1}$) | 1.359 | 1.067 | 1.387 | 0.252 |
| Crystal size | 0.5 x 0.4 x 0.2 | 0.2 x 0.1 x 0.1 | 0.55 x 0.4 x 0.35 | 0.45 x 0.25 x 0.09 |
| Meas. Refl. | 17787 | 39132 | 91800 | 15491 |
| Indep. Refl. | 4218 | 21828 | 23595 | 4704 |
| Observ. $[I > 2\sigma(I)]$ relf. | 3766 | 18554 | 19598 | 3522 |
| $R_{int}$ | 0.0589 | 0.0347 | 0.0363 | 0.0547 |
| R $[F^2 > \sigma(F^2)]$, $wR(F^2)$, S | 0.0331, 0.0830, 1.071 | 0.0431, 0.0879, 1.056 | 0.0378, 0.0847, 1.031 | 0.0551, 0.1221, 1.026 |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (eÅ$^{-3}$) | 0.553, -1.296 | 1.427, -0.732 | 2.166, -1.176 | 0.376, -0.498 |

# 3 Additional Information

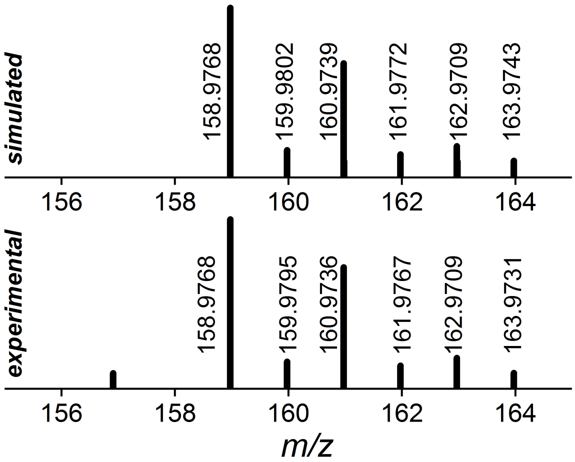
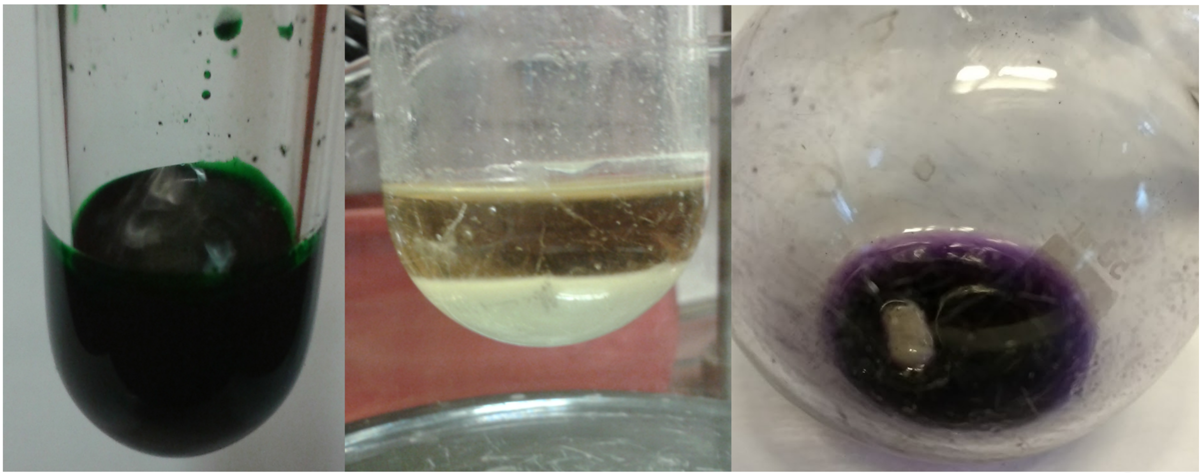


**Figure S11.** Simulated and experimental HR-ESI mass spectra of $[\mathbf{10}]^+$.



**6** in toluene

**8** (precipitate) in toluene

Purple solution of **5** and AgOTf in *n*-hexane

**Figure S12.** Pictures of solutions referenced in the manuskript.

# 4 Synthesis Attempts towards Tris-Triazolium Salts

## 4.1 From Iodoform

**1** In a Schlenk tube, iodoform (0.12 mmol, 50.8 mg, 1.0 equiv.), **1** (0.40 mmol, 100 mg, 3.3 equiv.) and silver triflate (0.40 mmol, 103 mg, 3.3 equiv.) were suspended in *n*-hexane/toluene (12 mL, *v*/*v* 1:2), capped and heated to 90 °C under exclusion of light overnight. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **4**.

**2** In a Schlenk tube, iodoform (0.07 mmol, 27.6 mg, 1.0 equiv.) and **1** (0.23 mmol, 50.0 mg, 3.1 equiv.) were suspended in toluene (4 mL), capped and heated to 90 °C under exclusion of light overnight to form a dark reddish-brown solution. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**3** In a Schlenk tube, iodoform (0.07 mmol, 27.6 mg, 1.0 equiv.), **1** (0.23 mmol, 50.0 mg, 3.1 equiv.), and potassium hexafluorophosphate (0.23 mmol, 50.0 mg, 3.1 equiv.) were suspended in toluene (4 mL), capped and heated to 90 °C under exclusion of light overnight to form a dark reddish-brown solution. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**4** To evaluate the substitution of only one iodide, iodoform (0.10 mmol, 42.3 mg, 1.0 equiv.), **1** (0.23 mmol, 50.0 mg, 3.3 equiv.), and silver triflate (0.10 mmol, 25.8 mg, 1.0 equiv.) were suspended in toluene (3 mL), capped and heated to 110 °C under exclusion of light overnight to form a dark reddish-brown solution. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**5** In a Schlenk tube, iodoform (0.10 mmol, 39.4 mg, 1.0 equiv.) and **1** (0.30 mmol, 66.3 mg, 3.0 equiv.) were capped and heated to 130 °C and reaction occurred in the melt of the triazole for 4 days. After cooling to room temperature, the mixture was dissolved in acetone, treated with aqueous potassium hexafluorophosphate, and the resulting prescipitate was dissolved in DCM, dried with $Na_2SO_4$. The solvent was evaporated and the resulting crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**7** In a Schlenk tube, iodoform (0.15 mmol, 59 mg, 1.0 equiv.), **1** (0.40 mmol, 100 mg, 3.3 equiv.) and silver triflate (0.40 mmol, 103 mg, 3.3 equiv.) were suspended in MeCN (5 mL), capped and heated to 80 °C under exclusion of light overnight. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**8** In a Schlenk tube, iodoform (0.10 mmol, 39.1 mg, 1.0 equiv.), **1** (0.30 mmol, 66.3 mg, 3.0 equiv.) and silver triflate (0.3 mmol, 77.1 mg, 3.0 equiv.) were suspended in THF/$Et_2O$ (6 mL, *v/v* 1:1), capped and heated to 50 °C under exclusion of light overnight. After cooling to room temperature, the mixture was filtered over celite and the solvent removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **4**.

## 4.2 From Benzotrichloride

**1** In a Schlenk flask, benzotrichloride (0.10 mmol, 15 µL, 1.0 equiv.) and **1** (0.31 mmol, 68.5 mg, 3.1 equiv.) were suspended in toluene (2 mL) and heated to 80 °C. As soon as all components were dissolved, silver triflate (0.10 mmol, 25.6 mg, 1.0 equiv.) was added and the mixture again heated to 80 °C for 1 hour. This was repeated two more times. After cooling to room temperature, the solvent was evaporated. The crude NMR in $CDCl_3$ was coincident with the one obtained for **4**.

**2** In a Schlenk tube, benzotrichloride (0.07 mmol, 10 µL, 1.0 equiv.), silver triflate (0.2 mmol, 159 mg, 3.0 equiv.) and **1** (0.20 mmol, 44.2 mg, 3.0 equiv.) were suspended in hexafluorobenzene (2 mL) and heated to 100 °C. After cooling to room temperature, the solvent was evaporated. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**3** In a Schlenk flask, benzotrichloride (0.20 mmol, 30 µL, 1.0 equiv.) and silver triflate (0.62 mmol, 159 mg, 3.1 equiv.) were suspended in hexafluorobenzene (3 mL) and heated to 80 °C. The solution turned a brownish color under formation of a precipitate. The solution was decanted and added to a new flask containing **1** (0.62 mmol, 137 mg, 3.1 equiv.) and the mixture again heated to 80 °C overnight. After cooling to room temperature, the solvent was evaporated. The crude NMR in $CDCl_3$ was coincident with the one obtained for **8**.

**4** In a Schlenk flask, benzotrichloride (0.20 mmol, 30 µL, 1.0 equiv.) and silver triflate (0.62 mmol, 159 mg, 3.1 equiv.) were suspended in *n*-hexane (2 mL) under instant color change to deep purple. This solution was transferred to a Schlenk flask containing **1** (0.62 mmol, 137 mg, 3.1 equiv.) in hexafluorobenzene (5 mL). The formation of a colorless suspension could be observed within seconds. This mixture was heated to 80 °C for 3 hours before the solvent was removed. The crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**5** In a Schlenk tube, benzotrichloride (0.35 mmol, 50 µL, 1.0 equiv.), **1** (1.20 mmol, 265 mg, 3.5 equiv.) and TMSOTf (1.40 mmol, 0.25 mL, 4.0 equiv.) were suspended in toluene (3 mL) and heated to 80 °C overnight. After cooling to room temperature, the mixture was poured into $Et_2O$ and the beige precipitate was collected by filtration. The crude NMR in $CDCl_3$ was coincident with the one obtained for **8**.

**6** In a Schlenk tube, benzotrichloride (0.35 mmol, 50 µL, 1.0 equiv.), **1** (1.20 mmol, 265 mg, 3.5 equiv.) were suspended in THF (8 mL) and heated to 80 °C overnight. After cooling to room temperature, TMSOTf (1.40 mmol, 0.25 mL, 4.0 equiv.) was added, heated again for 2 hours and the mixture then was poured into $Et_2O$ and the beige precipitate was collected by filtration. The crude NMR in $CDCl_3$ was coincident with the one obtained for **8**.

**7** In a Schlenk tube, benzotrichloride (0.35 mmol, 50 µL, 1.0 equiv.) and **1** (1.20 mmol, 265 mg, 3.5 equiv.) were heated to 130 °C for 2 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**8** In a Schlenk tube, benzotrichloride (0.35 mmol, 50 µL, 1.0 equiv.) and **1** (1.20 mmol, 265 mg, 3.0 equiv.) were dissolved in 1,4-doxane (3 mL) and heated to 120 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**9** In a Schlenk tube, benzotrichloride (0.35 mmol, 50 µL, 1.0 equiv.) and **1** (1.20 mmol, 265 mg, 3.5 equiv.) were dissolved in THF and heated to 80 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

## 4.3 From 2,2,2-Tribromoacetic Acid

**1** In a Schlenk tube, 2,2,2-tribromoacetic acid (0.1 mmol, 30.0 mg, 1.0 equiv.) and **1** (0.3 mmol, 66.0 mg, 3.5 equiv.) were dissolved in toluene (1.5 mL) and heated to 110 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**2** In a Schlenk tube, 2,2,2-tribromoacetic acid (0.1 mmol, 30.0 mg, 1.0 equiv.) and **1** (0.3 mmol, 66.0 mg, 3.5 equiv.) were dissolved in THF (1.5 mL) and heated to 80 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**3** In a Schlenk tube, 2,2,2-tribromoacetic acid (0.1 mmol, 30.0 mg, 1.0 equiv.) and **1** (0.3 mmol, 66.0 mg, 3.5 equiv.) were dissolved in 1,4-dioxane (1.5 mL) and heated to 80 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

## 4.4 From Methyl 2,2,2-Tribromoacetate

**1** In a Schlenk tube, metyhl 2,2,2-tribromoacetate (1.0 mmol, 310 mg, 1.0 equiv.) and **1** (4.0 mmol, 888 mg, 4.0 equiv.) were dissolved in toluene (5 mL) and heated to 110 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**2** In a Schlenk tube, metyhl 2,2,2-tribromoacetate (1.0 mmol, 310 mg, 1.0 equiv.) and **1** (4.0 mmol, 888 mg, 4.0 equiv.) were dissolved in THF (5 mL) and heated to 110 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.

**3** In a Schlenk tube, metyhl 2,2,2-tribromoacetate (1.0 mmol, 310 mg, 1.0 equiv.) and **1** (4.0 mmol, 888 mg, 4.0 equiv.) were dissolved in 1,4-dioxane (5 mL) and heated to 110 °C for 3 days. After cooling to room temperature, the crude NMR in $CDCl_3$ was coincident with the one obtained for **1**.