SUPPORTING INFORMATION

1. Synthesis

1.1 General details about synthesis and basic characterizations.

All the reactions involving sensitive compounds were carried out under dry Ar, in flame-dried glassware. If not noted otherwise, reactants and reagents were commercially available and used as received from Fluorochem, TCI-Chemicals and Sigma-Aldrich.

TLC analyses were carried out with Merk 60 F254 plates (0.2mm).

^{1}H NMR spectra were recorded in Chloroform-d, Acetone-d_6, Methanol-d_4 DMSO-d_6 on a Bruker 400 MHz NMR or on a JEOL ECZ400S spectrometer. The following abbreviations are used: s=singlet, d=doublet, dd=double doublet, ddd=double double doublet, dddd=double double double doublet, dt=double triplet, t=triplet, tdd= triple double doublet, tt=triple triplet, q=quartet, m=multiplet. ^{13}C NMR spectra were recorded at 101 MHz and ^{19}F spectra were recorded at 376 MHz. ^{1}H and ^{13}C NMR chemical shifts (ppm) are referred to TMS as external standard.

Elemental analyses were obtained using an Elementar Vario MICRO cube equipment.

1.2 Synthetic protocols and NMR spectra

Sodium 6-ethoxy-2-naphthtoic carboxylate **12-Na**

To a clear solution of NaOH (14.60 g, 0.37 mol) and NaI (5.55 g, 0.037 mol) in water (360 cm^3), 6-hydroxy-2-naftoic acid (22.65 g, 0.12 mol) was added. After dissolving of the carboxylic acid, 2-bromoethanol (13.0 cm^3, 0.18 mol) was added to the yellow solution. The solution was stirred at 60 °C for 24 h. After 4 h the precipitation of a white solid was observed. The mixture was cooled at 0 °C, filtered and the solid was washed with cold water. The white solid was dried under reduced pressure to give 28,52 g (0.11 mmol, 94%) of sodium carboxylate **12-Na**. **^{1}H NMR** (401 MHz, DMSO-d_6) δ 8.36 (s, 1H), 8.02 (dd, J = 8.4, 1.6 Hz, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 2.5 Hz, 1H), 7.13 (dd, J = 8.9, 2.5 Hz, 1H), 5.12 (s, 1H), 4.10 (t, J = 5.0 Hz, 2H), 3.79 (t, J = 5.0 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 170.7, 157.0, 135.3, 135.0, 130.2, 128.5, 127.9, 125.4, 118.5, 106.5, 69.6, 59.6.

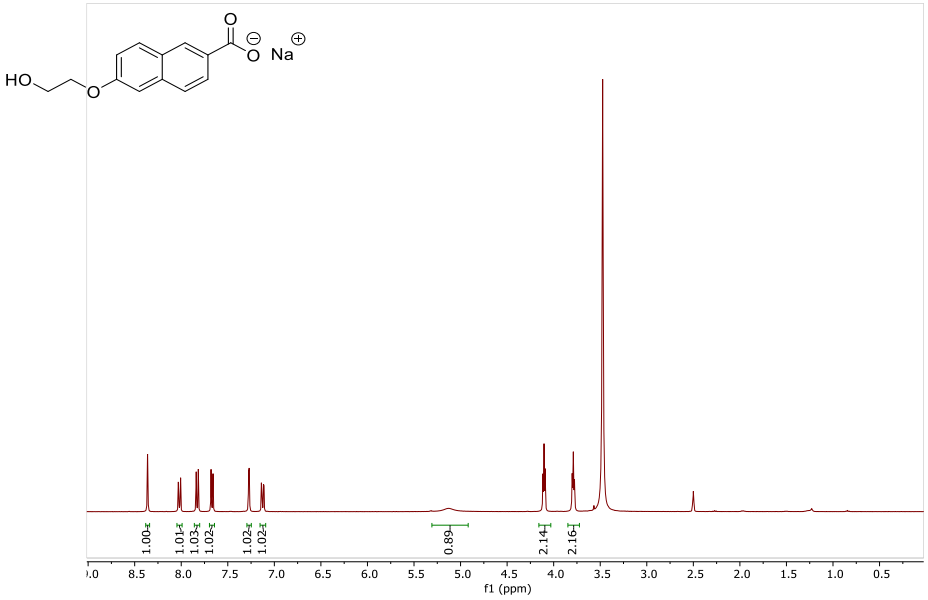


Figure S1.1 ^{1}H NMR (401 MHz, DMSO-d_6) spectrum of compound **12-Na**

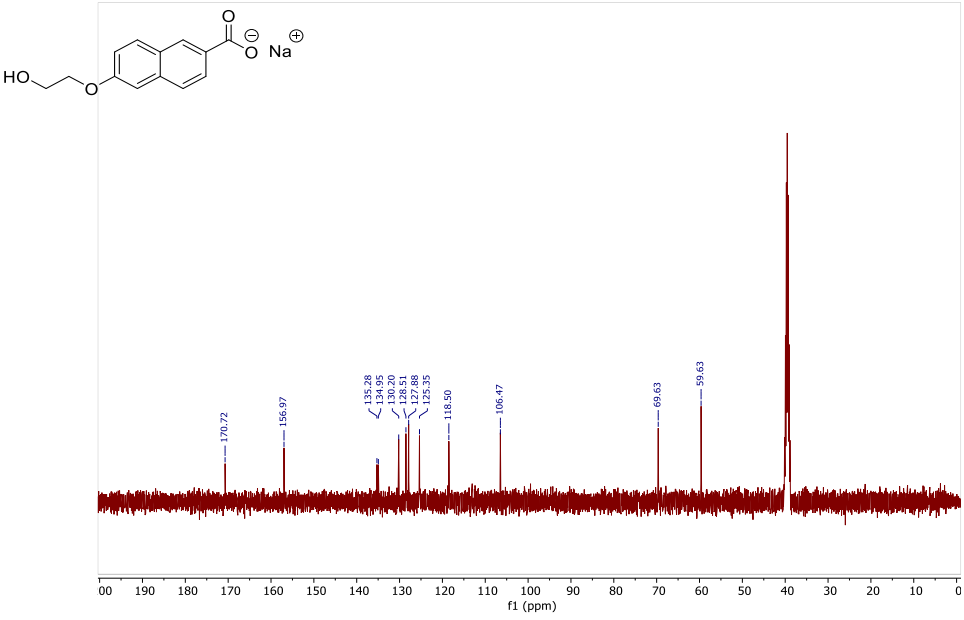


Figure S1.2 ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound **12-Na**

6-(2-hydroxy)ethoxy-2-naphthoic acid **12**

Carboxylate 12-Na was dispersed in H_2O (150 cm^3), acidified with $HCl_{(aq)}$ 5% until pH ≈1 and stirred for 1 h. The solid was filtered and dried at 70 °C overnight to give the pure product **12** as a white solid (20.69 g, 0.09 mol, 74%). **^{1}H NMR** (401 MHz, DMSO-d_6) δ 12.89 (s, 1H), 8.53 (s, 1H), 8.01 (d, J = 9.0 Hz, 1H), 7.93 (dd, J = 8.6, 1.7 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.39 (d, J = 2.5 Hz, 1H), 7.25 (dd, J = 9.0, 2.5 Hz, 1H), 4.95 (s, 1H), 4.14 (t, J = 4.9 Hz, 2H), 3.80 (t, J = 4.9 Hz, 2H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 167.6, 158.6, 136.8, 130.9, 130.4, 127.5, 126.9, 125.8, 125.7, 119.7, 106.6, 69.8, 59.5. **m.p.** 214-218 °C

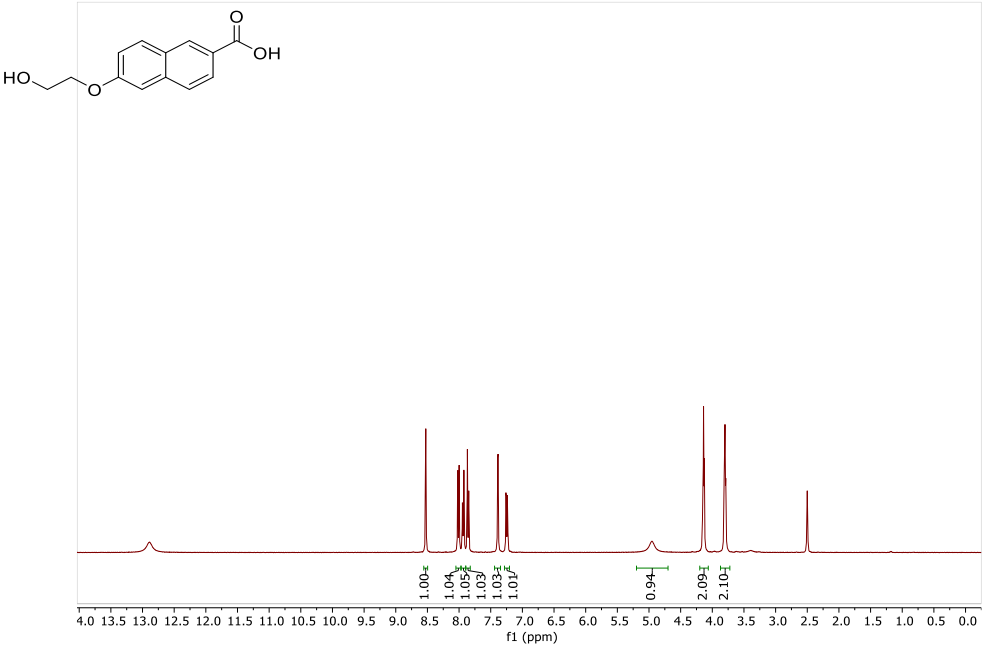


Figure S1.3 ^{1}H NMR (401 MHz, DMSO-d_6) spectrum of compound **12**

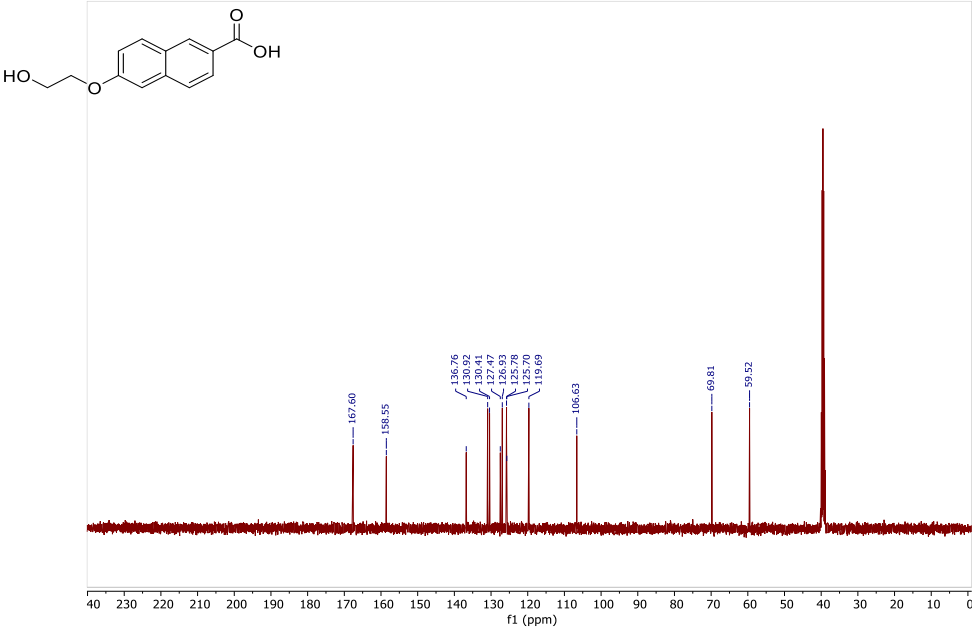


Figure S1.4 ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound **12**

6-(2-methanesulfonyloxy)ethoxy-2-naphthoic acid **13**

1.31g (5.6 mmol) of **12** were dissolved in the minimum amount of hot 1,4-dioxane. To the cooled colourless solution, Et_3N (2.6 cm^3, 18.7 mmol) was added. Then methane sulfonyl chloride (1.6 cm^3, 20.6 mmol) was slowly added to the colourless solution and the mixture was stirred at room-temperature. The reaction was followed by TLC analysis ($CHCl_3$: MeOH 9 : 1). After 3h, saturated $NaHCO_{3(aq)}$ was added until pH≈9 and then the mixture was acidified until pH ≈ 1 with 10% $HCl_{(aq)}$. The solids were filtered off, and the filtrate was extracted with CH_2Cl_2 (3x100 cm^3). The organic phases were reunited, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give 1.79g of crude as a white solid. NMR analysis showed the presence of the desired carboxylic acid (**13**) and its anhydride (**13-Anh**) in a 95 : 5 ratio, together with some Et_3N (or its ammonium salt). The crude was used without any further purification.

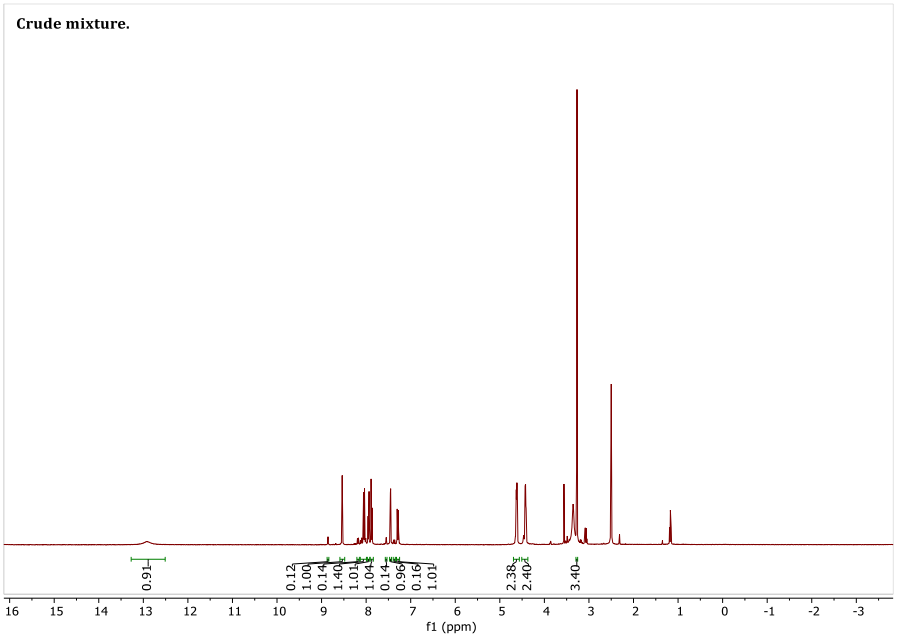


Figure S1.5 ^1H NMR (401 MHz, DMSO-d_6) spectrum of crude **13** containing **13** and **13-Anh** with a ratio of 95:5.

Eventually, to obtain some reference material, some crude was purified by flash chromatography on silica gel ($CHCl_3$:MeOH) to give the chemically pure product and its anhydride.

13: **^{1}H NMR** (401 MHz, DMSO-d_6) δ 8.55 (s, 1H), 8.06 (d, J = 9.1 Hz, 1H), 7.98 – 7.84 (m, 2H), 7.46 (d, J = 2.6 Hz, 1H), 7.30 (dd, J = 9.0, 2.5 Hz, 1H), 4.65 – 4.59 (m, 2H), 4.46 – 4.39 (m, 2H), 3.27 (s, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 168.0, 158.2, 137.0, 131.6, 130.9, 128.2, 127.5, 126.5, 126.3, 119.9, 107.5, 69.1, 66.5, 37.4. **m.p.** 188-195 °C (decomposition).

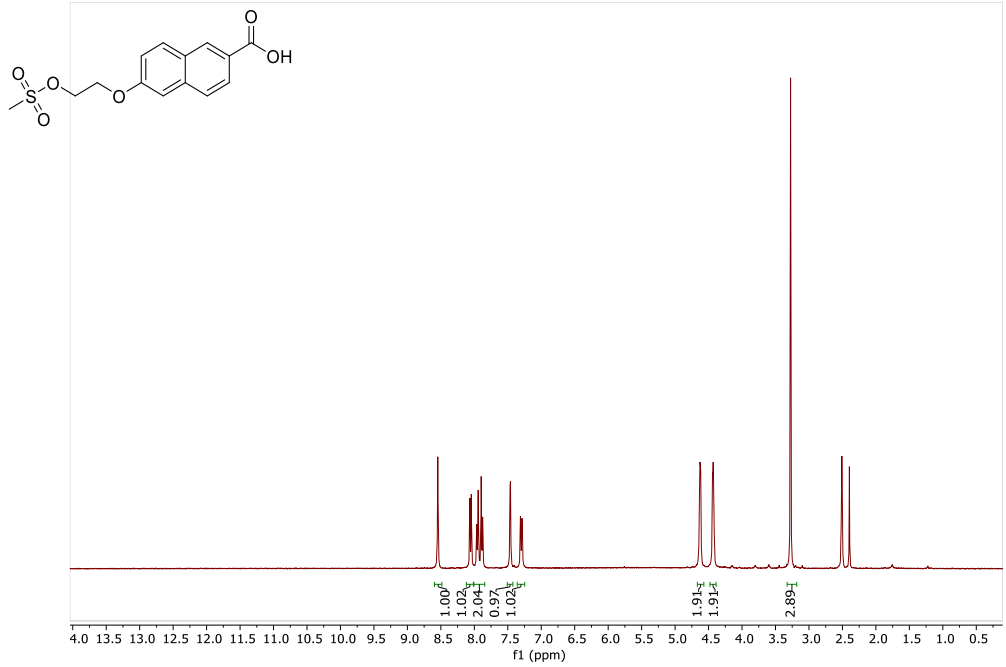


Figure S1.6 ^{1}H NMR (401 MHz, DMSO-d_6) spectrum of **13**.

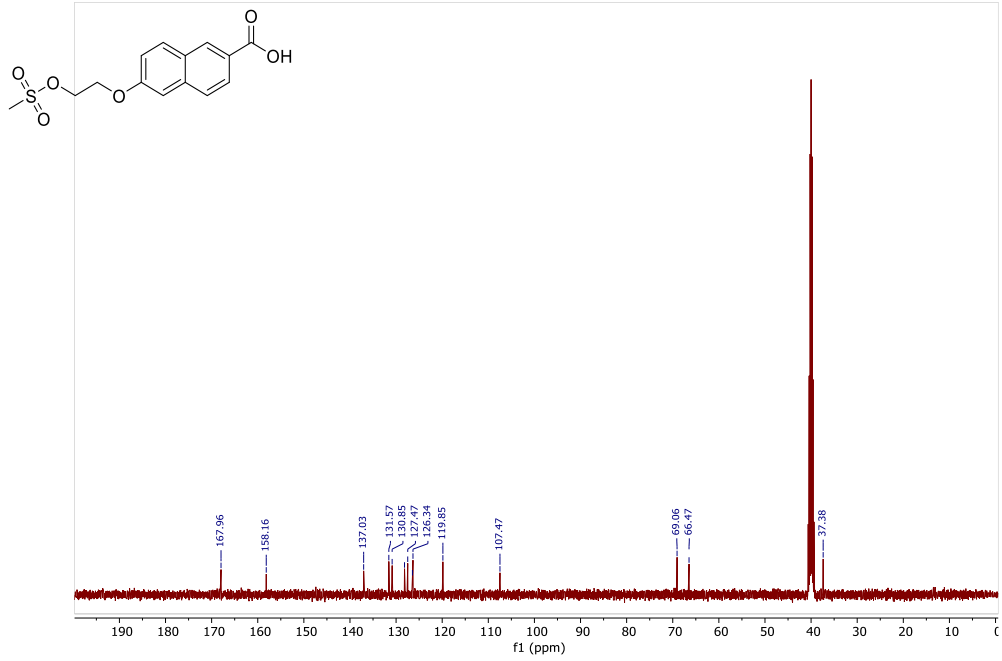


Figure S1.7 ^{13}C NMR (101 MHz, DMSO-d_6) spectrum of compound **13**.

13-Anh: **^{1}H NMR** (401 MHz, DMSO-d_6) δ 8.86 (s, 1H), 8.18 (d, J = 9.1 Hz, 1H), 8.11 (dd, J = 8.6, 1.9 Hz, 1H), 8.02 (d, J = 8.8 Hz, 1H), 7.55 (d, J = 2.6 Hz, 1H), 7.37 (dd, J = 9.0, 2.5 Hz, 1H), 4.66 – 4.60 (m, 2H), 4.49 – 4.44 (m, 2H), 3.27 (s, 2H).

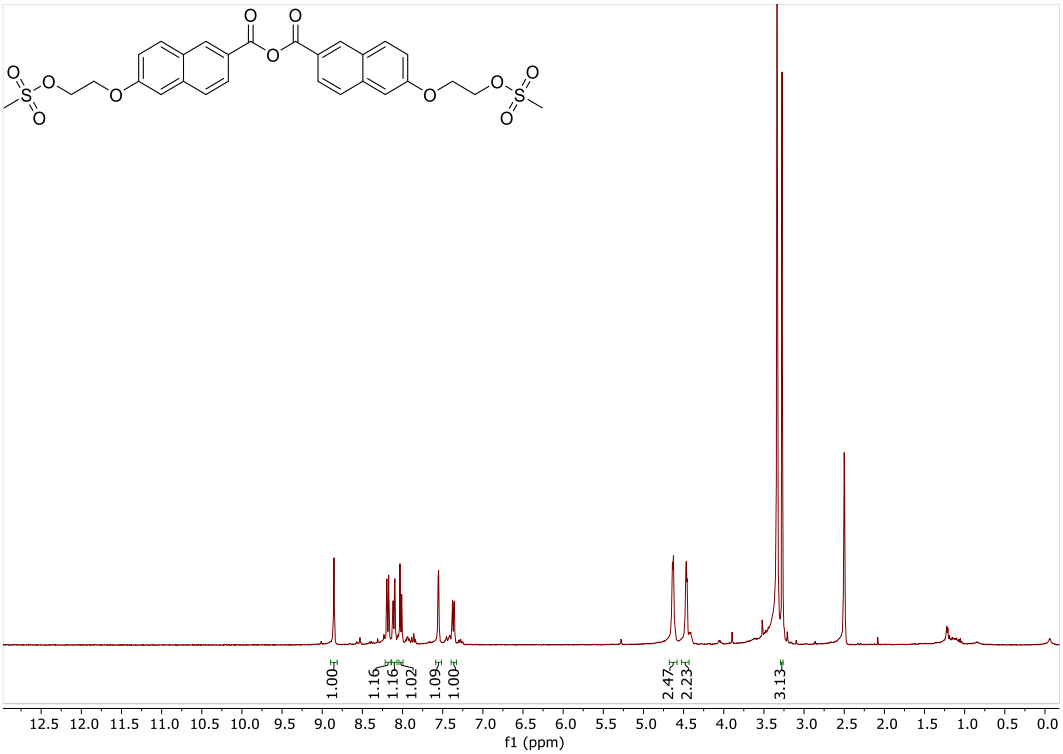


Figure S1.8 ^{1}H NMR (401 MHz, DMSO-d_6) spectrum of compound **13-Anh**.

Diesters **6m and 6s**

Under an Ar atmosphere, to a mixture of isohexide (4.0 mmol) and crude **13** (≈10.4 mmol assuming that the crude contains only acid) in CH_2Cl_2 (30 cm^3), EDC·HCl (12.8 mmol) and DMAP (2.3 mmol) were added at 0 °C. The mixture was stirred at RT and the reaction was followed by TLC ($CHCl_3$: MeOH 9:1). After 18 h the heterogeneous white mixture was diluted with CH_2Cl_2 (80 cm^3) and washed with water (50 cm^3). The aqueous phase was extracted with CH_2Cl_2 (50 cm^3), then the organic phases were reunited and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by recrystallization (CH_2Cl_2/MeOH) to give the pure product as a white solid.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-methanesulfonyloxy)ethoxy-2-naphthoate ***6m***

6m: White solid, 2.13g (73%). **^{1}H NMR** (401 MHz, Chloroform-*d*) δ 8.60 (s, 2H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 7.21 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.16 (d, *J* = 2.5 Hz, 2H), 5.41 (tdd, *J* = 6.3, 3.9, 1.5 Hz, 2H), 4.98 – 4.92 (m, 2H), 4.68 – 4.62 (m, 4H), 4.44 – 4.36 (m, 4H), 4.20 (dd, *J* = 9.4, 6.3 Hz, 2H), 4.11 (dd, *J* = 9.4, 6.6 Hz, 2H), 3.11 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 158.1, 137.2, 131.5, 131.3, 128.3, 127.2, 126.4, 125.1, 119.6, 106.9, 81.0, 74.5, 70.9, 67.7, 66.0, 38.0. **m.p.** 164 °C.

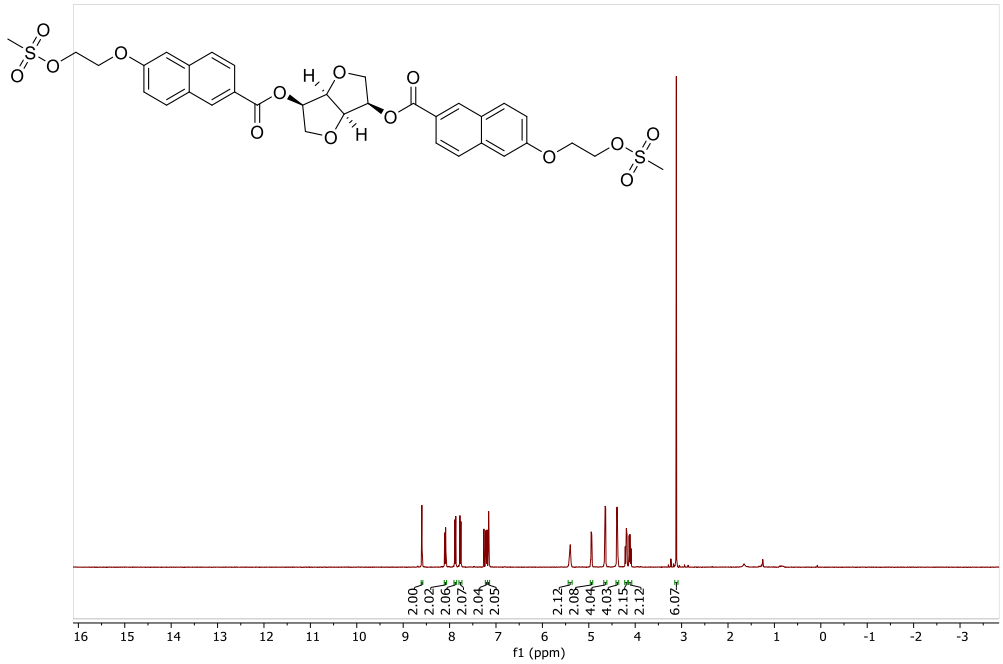


Figure S1.9 ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **6m**.

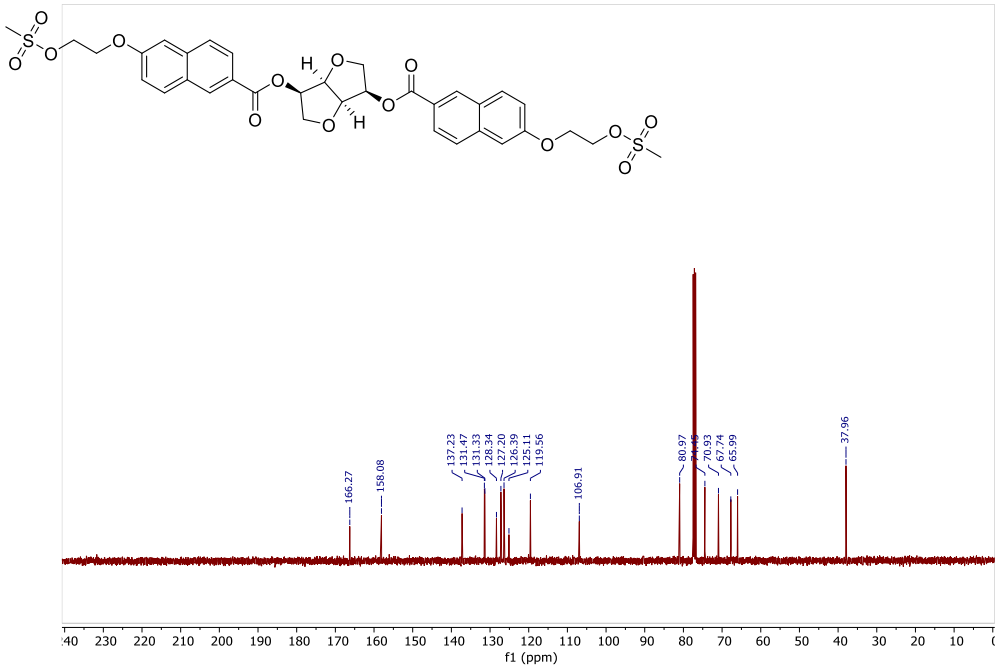


Figure S1.10 ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **6m**.

(3R,3aR,6S,6aR)- hexahydrofuro[3,2-b]furan-3,6-di-6-(2-methanesulfonyloxy)ethoxy-2-naphthoate ***6s***

6s: White solid, 1.82g (69%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.59 (s, 1H), 8.51 (s, 1H), 8.08 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.01 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.88 (dd, *J* = 13.4, 9.0 Hz, 2H), 7.76 (dd, *J* = 11.3, 8.6 Hz, 2H), 7.22 (ddd, *J* = 9.0, 3.8, 2.5 Hz, 2H), 7.16 (dd, *J* = 6.5, 2.5 Hz, 2H), 5.57 (d, *J* = 3.1 Hz, 1H), 5.50 (q, *J* = 5.3 Hz, 1H), 5.15 (t, *J* = 5.0 Hz, 1H), 4.76 (d, *J* = 4.4 Hz, 1H), 4.69 – 4.62 (m, 4H), 4.42 – 4.37 (m, 4H), 4.24 – 4.08 (m, 4H), 3.12 (d, *J* = 2.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 165.9, 158.1, 158.1, 137.3, 131.5, 131.5, 131.3, 128.4, 128.3, 127.2, 127.2, 126.4, 126.2, 125.2, 125.1, 119.7, 119.6, 106.9, 86.4, 81.4, 78.6, 77.4, 74.8, 73.8, 70.9, 67.7, 66.0, 38.0. **m.p.** 115-120 °C.

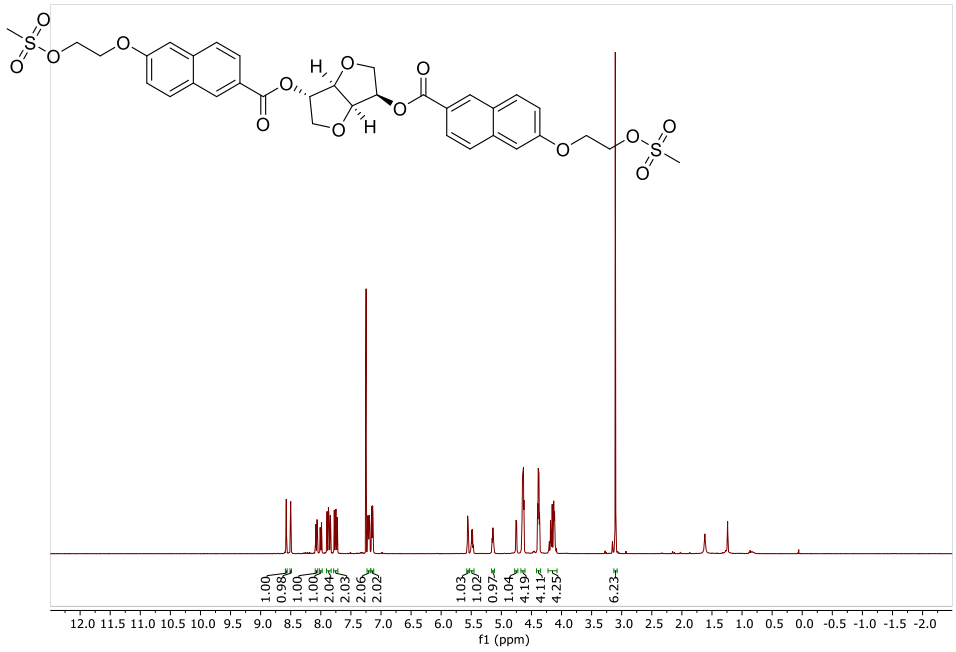


Figure S1.11 ^{1}H NMR (400 MHz, Chloroform-*d*) spectrum of compound **6m**.

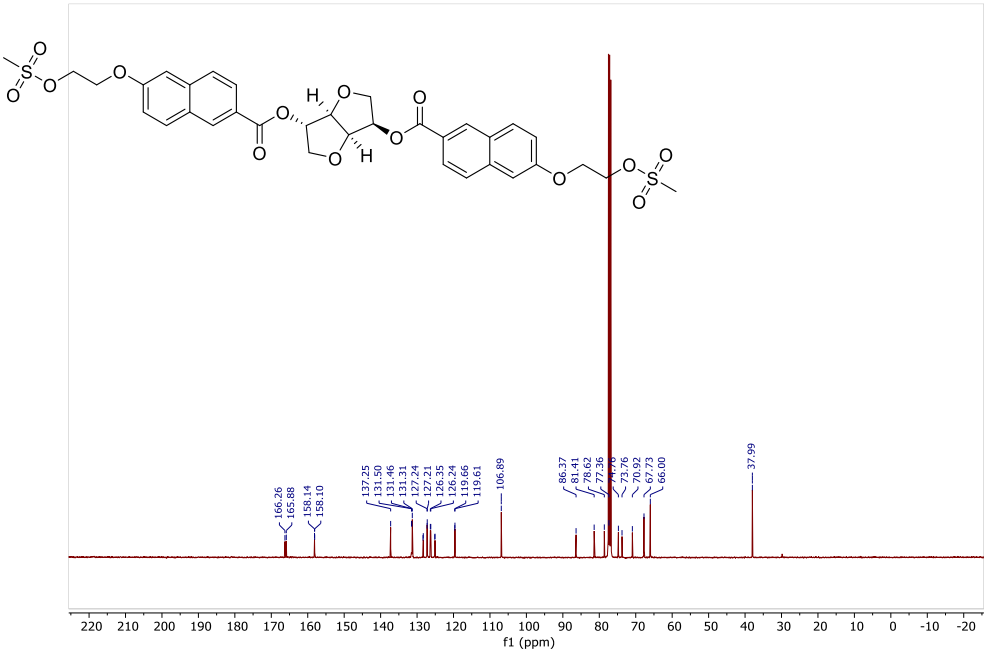


Figure S1.12 ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **6s**.

*Quaternization of diesters with N-methyl imidazole (***3mM** *and* **3sM***)*

1-methylimidazole (20.0 mmol) was added to a solution of **6m** (3.2 mmol) in 20 cm^3 of CH_3CN. The solution was heated under reflux and the reaction was monitored by TLC analysis ($CHCl_3$: MeOH 9:1). After 24 h the solvent was removed under reduced pressure and the crude product was washed overnight with 30 cm^3 of an acetone-diethyl ether 1:1 mixture and then with acetone (2x30 cm^3) to yield the chemically pure desired product.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3mM***

3mM: White solid, 864.3 mg (75%). **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.54 (s, 2H), 7.99 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.60 (d, *J* = 2.0 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 7.24 (dd, *J* = 8.9, 2.5 Hz, 1H), 5.40 – 5.31 (m, 1H), 4.93 – 4.89 (m, 1H), 4.73 (t, *J* = 5.0 Hz, 2H), 4.52 (t, *J* = 5.0 Hz, 2H), 4.13 (dd, *J* = 9.4, 6.2 Hz, 1H), 4.05 (dd, *J* = 9.4, 6.4 Hz, 1H), 3.95 (s, 3H), 2.70 (s, 3H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 167.5, 159.3, 138.6, 132.3, 132.0, 129.6, 128.4, 126.9, 126.2, 124.9, 124.3, 120.6, 108.1, 82.2, 75.8, 71.8, 67.3, 50.3, 39.6, 36.6.

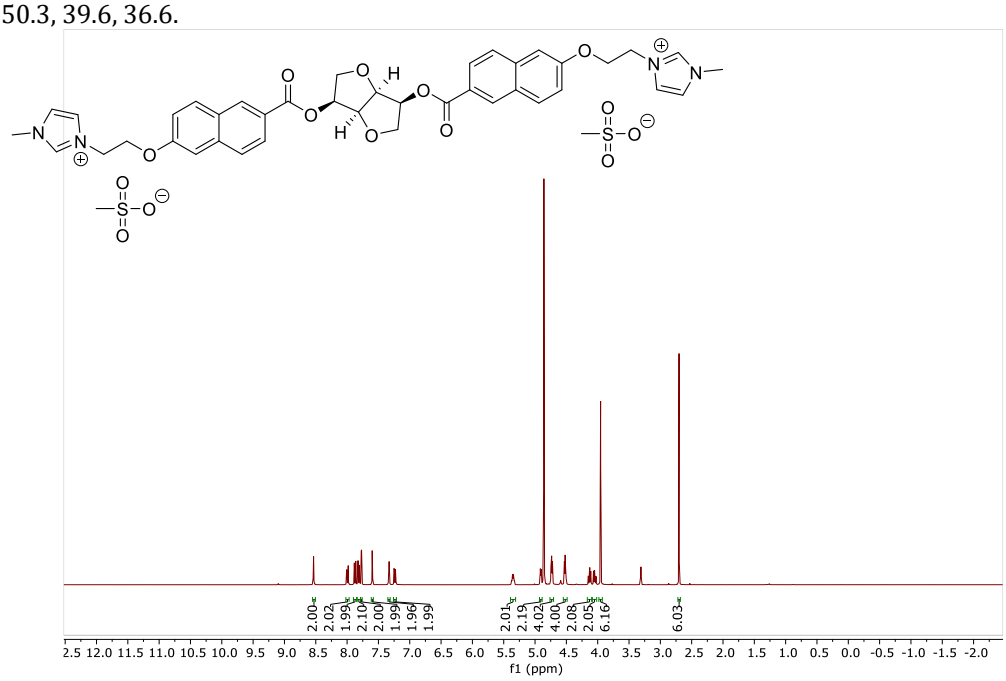


Figure S1.13 ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound **3mM**.

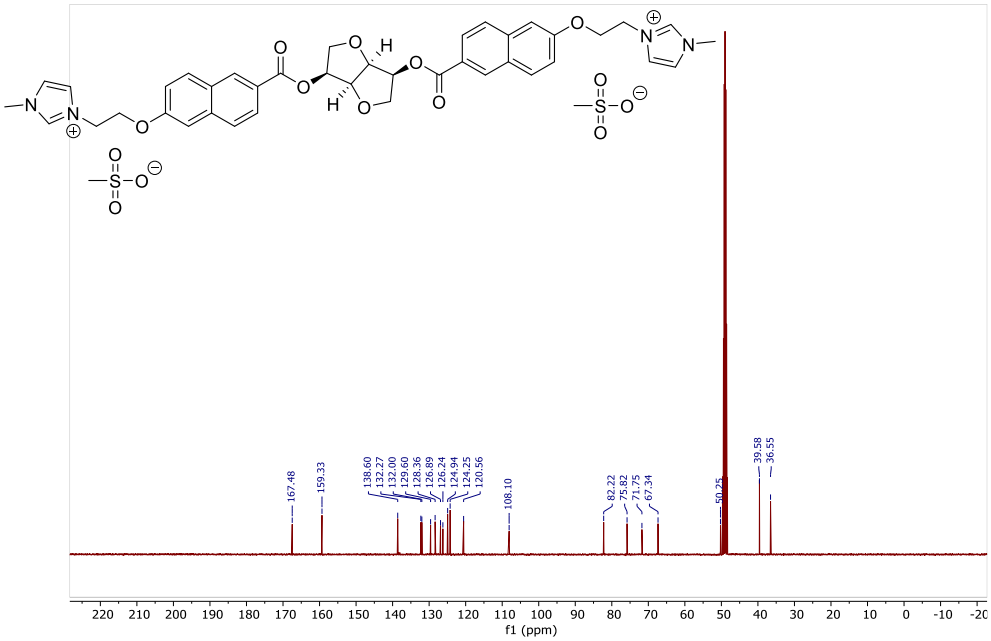


Figure S1.14 ^{13}C NMR (101MHz, Methanol-d_4) spectrum of compound **3mM**.

*(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate **3sM***

3b: Off-white solid, 947.4 mg (88%) **^{1}H NMR** (400 MHz, Methanol-d_4) δ 8.59 (d, J = 1.7 Hz, 1H), 8.53 (d, J = 1.7 Hz, 1H), 8.04 (dd, J = 8.7, 1.7 Hz, 1H), 8.01 – 7.91 (m, 3H), 7.86 (dd, J = 12.5, 8.7 Hz, 2H), 7.78 (dd, J = 3.4, 2.0 Hz, 2H), 7.61 (t, J = 2.3 Hz, 2H), 7.38 (dd, J = 7.5, 2.5 Hz, 2H), 7.28 (ddd, J = 9.0, 6.4, 2.5 Hz, 2H), 5.55 – 5.50 (m, 1H), 5.49 (d, J = 3.0 Hz, 1H), 5.13 (t, J = 5.3 Hz, 1H), 4.76 – 4.71 (m, 5H), 4.54 (q, J = 4.6 Hz, 4H), 4.18 – 4.04 (m, 4H), 3.96 (d, J = 2.4 Hz, 6H), 2.70 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 167.4, 167.2, 159.4, 159.3, 138.6, 138.6, 132.3, 132.3, 132.0, 131.9, 129.6, 129.6, 128.4, 128.3, 126.9, 126.8, 126.2, 124.9, 124.3, 120.6, 108.1, 87.5, 82.8, 79.9, 76.2, 74.2, 72.2, 67.4, 50.3, 39.6, 36.5.

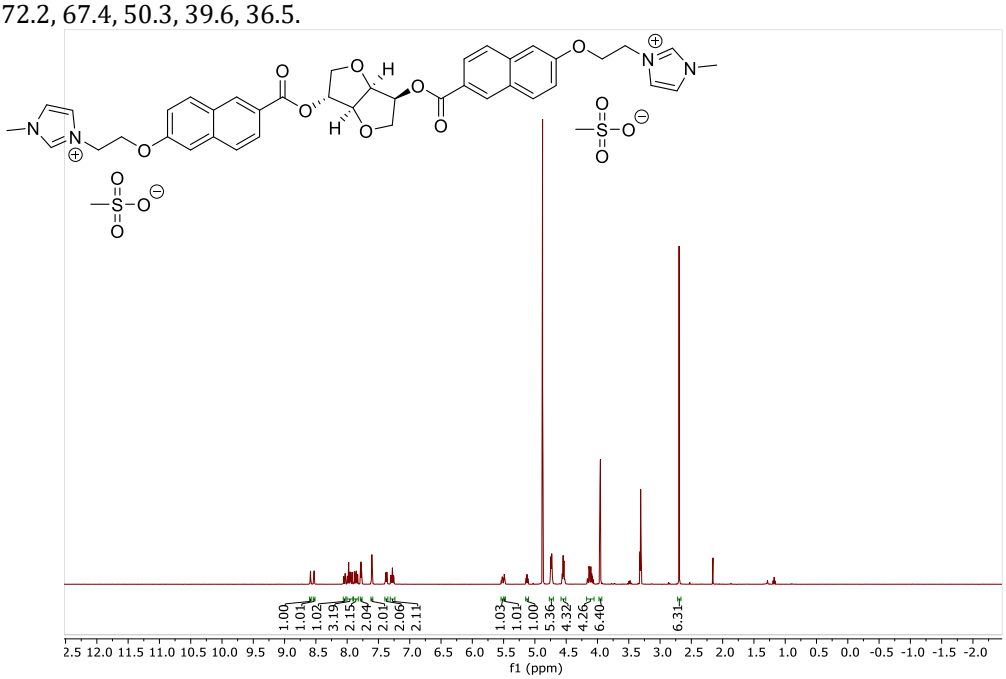


Figure S1.15 ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound **3sM**.

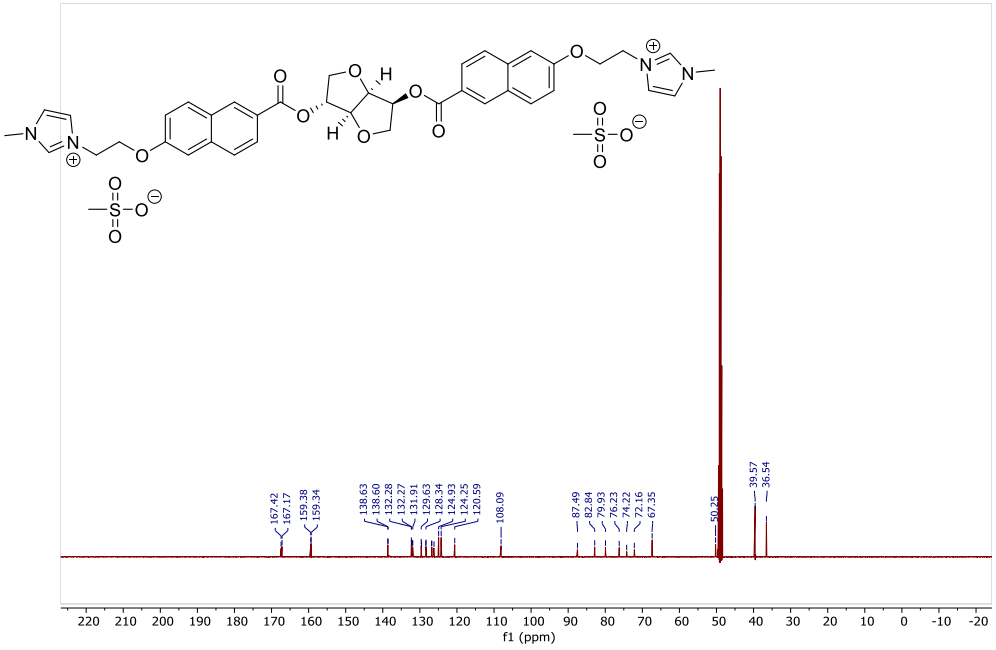


Figure S1.16 ^{13}C NMR (101 MHz, Methanol-d_4) spectrum of compound **3b 3sM**..

Quaternization of diesters with Pyridine (**4mM** and **4sM**)

Pyridine (2.5 mmol) was added to a yellow solution of **3** (1.2 mmol) in 8 cm^3 of CH_3CN. The solution was heated under reflux and the reaction was monitored by TLC analysis ($CHCl_3$: MeOH 9:1). To drive the reaction to completion, further pyridine (3.7 mmol) was added after 15 h, 39 h, 65 h). After 90 h the solvent was removed under reduced pressure and the crude product was stripped with toluene (3x 20 cm^3) and washed overnight with diethyl ether (20 cm^3) to yield the chemically pure product.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4mM***

4mM : White solid, 885.4 mg (84%) **^{1}H NMR** (400 MHz, Methanol-d_4) δ 9.24 – 9.10 (m, 4H), 8.65 (tt, *J* = 7.8, 1.4 Hz, 2H), 8.57 (d, *J* = 1.8 Hz, 2H), 8.21 – 8.14 (m, 4H), 8.03 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.88 (dd, *J* = 23.7, 8.9 Hz, 4H), 7.37 (d, *J* = 2.5 Hz, 2H), 7.21 (dd, *J* = 9.0, 2.5 Hz, 2H), 5.44 – 5.33 (m, 2H), 5.18 (t, *J* = 4.6 Hz, 4H), 4.96 – 4.90 (m, 2H), 4.71 (t, *J* = 4.8 Hz, 4H), 4.14 (dd, *J* = 9.4, 6.2 Hz, 2H), 4.05 (dd, *J* = 9.3, 6.5 Hz, 2H), 2.70 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 167.4, 159.0, 147.5, 146.8, 138.5, 132.3, 132.0, 129.7, 129.4, 128.4, 126.9, 126.4, 120.4, 108.2, 82.2, 75.8, 71.7, 67.6, 62.1, 39.6.

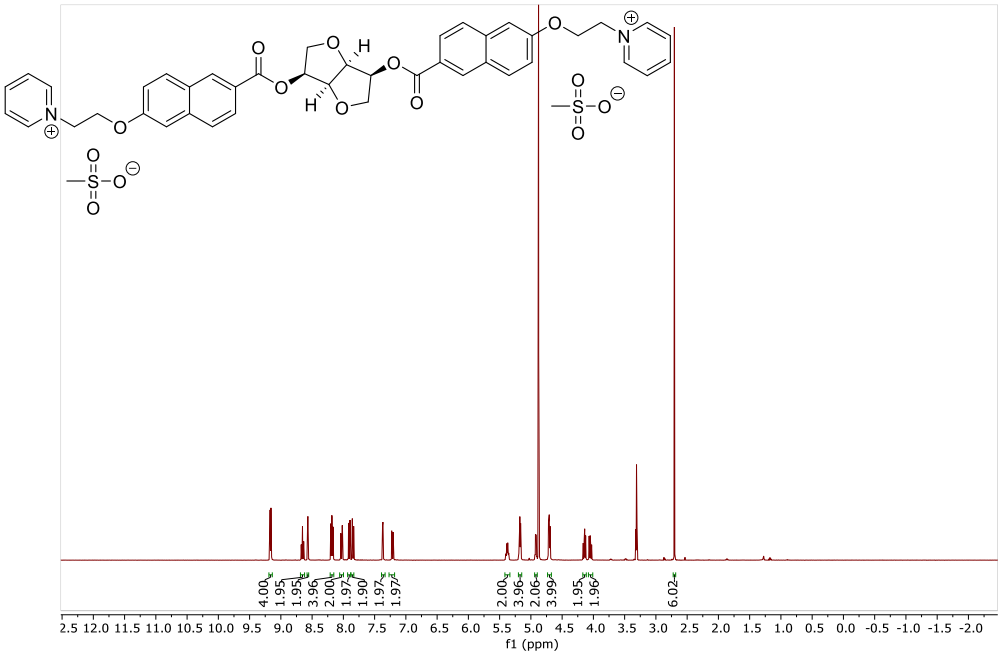


Figure 1.17 ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound **4mM**.

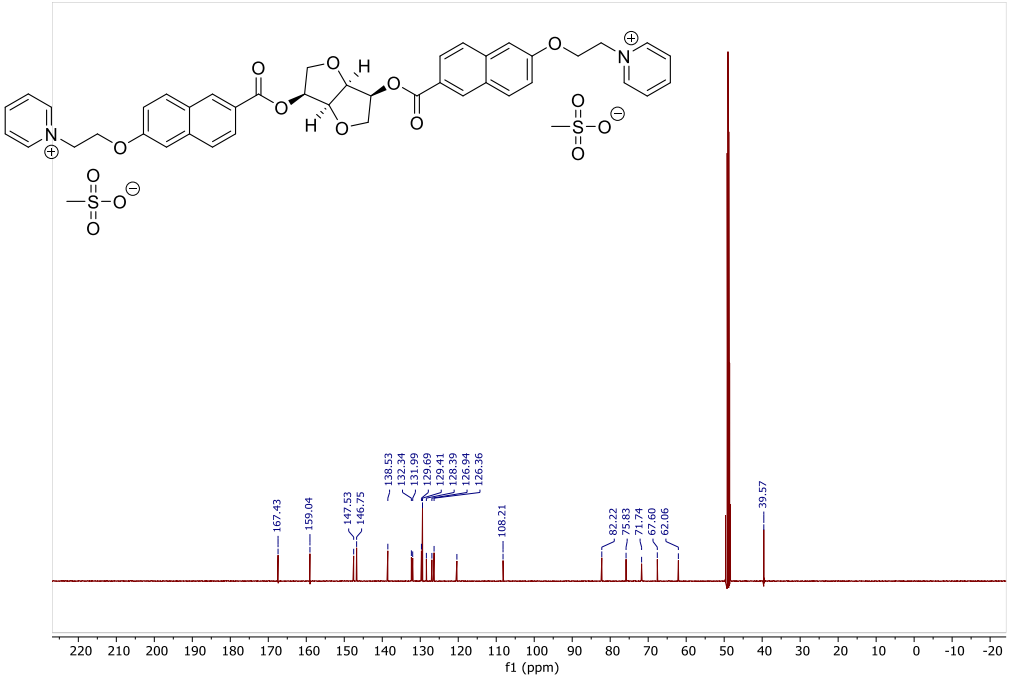


Figure 1.18 ^{13}C NMR (101 MHz, Methanol-d_4) spectrum of compound **4mM.**

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4sM***

4b: Off-white solid, 907.1 mg (86%) **^{1}H NMR** (400 MHz, Methanol-d_4) δ 9.16 (ddd, *J* = 6.7, 3.0, 1.4 Hz, 4H), 8.64 (tdt, *J* = 7.8, 2.5, 1.4 Hz, 2H), 8.52 – 8.49 (m, 1H), 8.44 – 8.41 (m, 1H), 8.21 – 8.13 (m, 4H), 7.97 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.92 – 7.74 (m, 5H), 7.33 (dd, *J* = 8.1, 2.5 Hz, 2H), 7.19 (ddd, *J* = 9.0, 7.6, 2.5 Hz, 2H), 5.47 (td, *J* = 5.5, 3.9 Hz, 1H), 5.43 (d, *J* = 2.9 Hz, 1H), 5.21 – 5.14 (m, 4H), 5.09 (t, *J* = 5.3 Hz, 1H), 4.72 – 4.65 (m, 5H), 4.13 – 4.01 (m, 4H), 2.71 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 167.4, 167.1, 159.1, 159.0, 147.5, 146.7, 138.5, 132.3, 132.3, 132.0, 131.9, 129.7, 129.6, 129.4, 128.4, 128.4, 126.9, 126.8, 126.4, 126.3, 120.4, 108.2, 87.5, 82.8, 79.9, 76.2, 74.2, 72.1, 67.6, 62.1, 39.6.

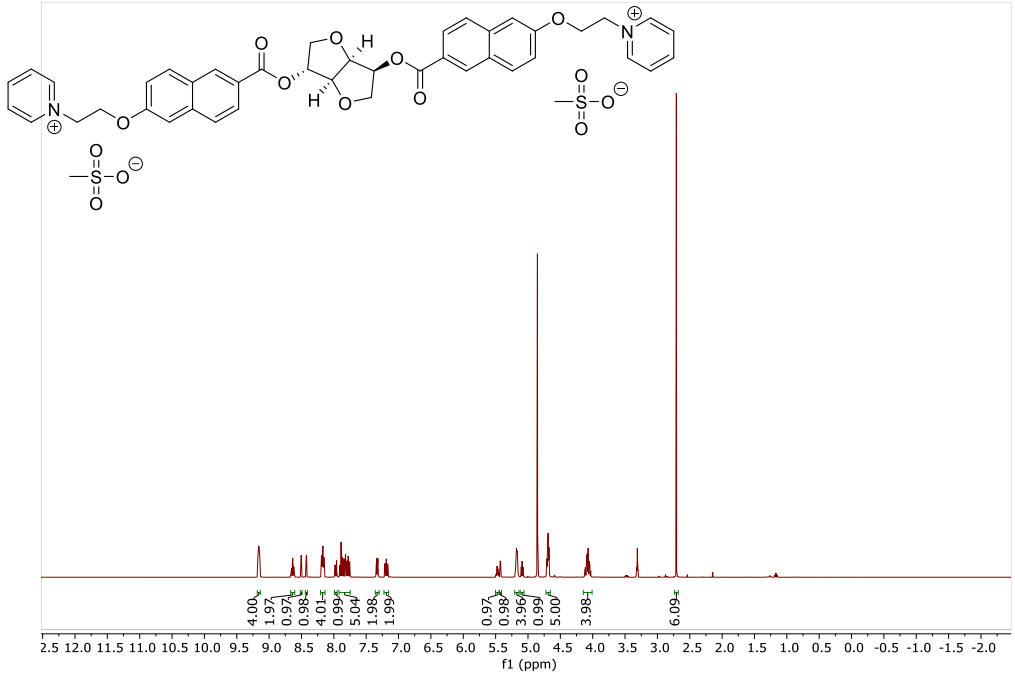


Figure S1.19 ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound 4sM.

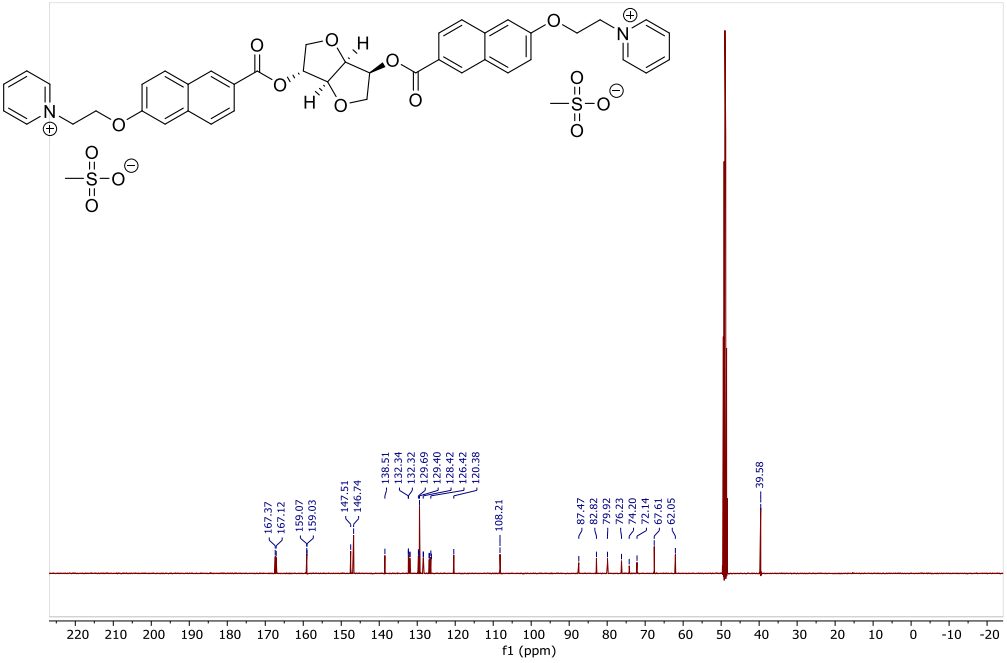


Figure S1.20 ^{13}C NMR (101 MHz, Methanol-d_4) spectrum of compound 4sM.

*Quaternization of diesters with Quinoline (***5mM***)*

Quinoline (120 μL, 1.0 mmol) was added to a yellow solution of **8a** (361.2 mg, 0.49 mmol) in 3 cm^3 of CH_3CN. The solution was heated under reflux and the reaction was monitored by TLC analysis ($CHCl_3$: MeOH 9 : 1). To drive towards complete conversion of the starting material, further quinoline (3.0 mmol) was added after 48 h and 76 h. After 4 days the reaction was stopped: the solvent was removed under reduced pressure from the purple solution obtained to give a purple glue. The crude was purified through a recrystallization from MeOH/Et_2O (20 cm^3/100 cm^3) to give the pure product as a slightly yellow solid (**5mM**, 180.0 mg, 36%). **m.p.** 120-122 °C.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-quinoliniumethoxy)-2-naphthoate methanesulfonate ***5mM***

5mM: ^{1}H NMR (400 MHz, Methanol-d_4) δ 9.53 (d, *J* = 5.8 Hz, 2H), 9.18 (d, *J* = 8.3 Hz, 2H), 8.72 (d, *J* = 9.0 Hz, 2H), 8.40 – 8.33 (m, 4H), 8.34 – 8.26 (m, 2H), 8.12 (dd, *J* = 8.4, 5.8 Hz, 2H), 8.00 (t, *J* = 7.6 Hz, 2H), 7.84 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.66 (dd, *J* = 11.1, 8.9 Hz, 4H), 7.20 (d, *J* = 2.5 Hz, 2H), 7.01 (dd, *J* = 9.0, 2.5 Hz, 2H), 5.60 (t, *J* = 4.8 Hz, 4H), 5.32 – 5.21 (m, 2H), 4.85 – 4.83 (m, 2H), 4.75 (t, *J* = 4.8 Hz, 4H), 4.01 (ddd, *J* = 34.3, 9.4, 6.2 Hz, 4H), 2.72 (s, 6H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 167.3, 158.9, 151.6, 149.7, 139.7, 138.3, 137.4, 132.2, 132.2, 131.8, 131.6, 131.4, 129.4, 128.3, 126.8, 126.2, 122.9, 120.3, 119.9, 108.0, 82.2, 75.7, 71.7, 66.8, 58.1, 39.7.

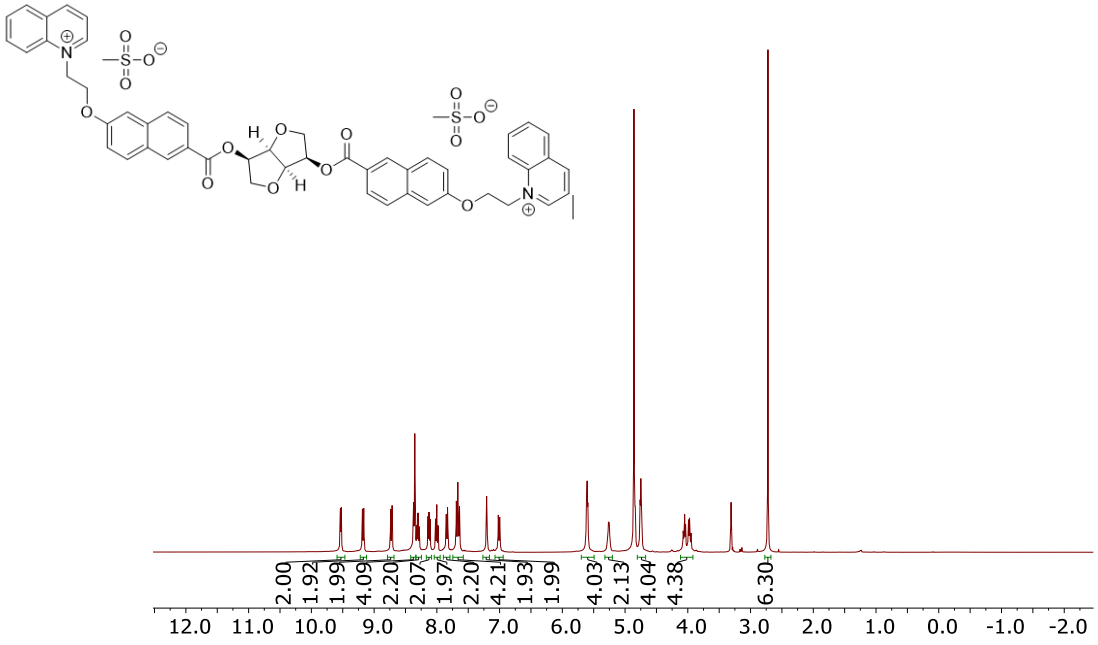


Figure S1.21 ^{1}H NMR (400 MHz, Methanol-d_4) spectrum of compound **5sM**.

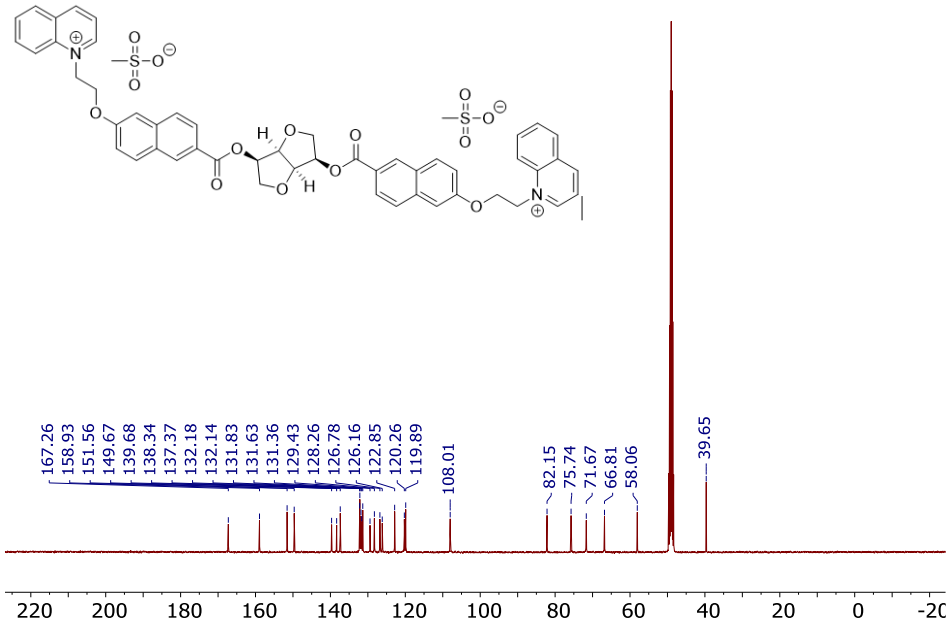


Figure S1.22 ^{13}C NMR (101 MHz, Methanol-d_4) spectrum of compound **5sM**.

Anion metathesis with bis[(trifluoromethyl)sulfonyl]imide anion* (3mT,3sT,4mT,4sT,5mT*)

To a clear solution of **3mM, 3sM, 4mM, 4sM, 5mM** (0.3 mmol) in methanol (6 cm^3), lithium bistriflimide (1.0 mmol) was added. The mixture was stirred at RT for 24h. In some cases (**3c** and **4c**) a white precipitate was observed; the solid was filtered, washed with a small amount of methanol and dried under vacuum to give the pure product as a white solid. The solution was dried under reduced pressure and the crude was dissolved in a 5:1 mixture of CH_2Cl_2:acetone (20 cm^3 : 5 cm^3) and washed with water (3x20 cm^3). The organic phase was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give the pure product as a white solid.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6 di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide 3c ***3mT***

3c 3mT: White solid, 337.6 mg, (86%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.26 (s, 1H), 8.63 (s, 1H), 8.10 – 8.01 (m, 2H), 7.96 – 7.88 (m, 2H), 7.77 (t, *J* = 1.8 Hz, 1H), 7.46 (d, *J* = 2.5 Hz, 1H), 7.31 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.46 – 5.36 (m, 1H), 4.99 – 4.92 (m, 3H), 4.72 – 4.66 (m, 2H), 4.17 (dd, *J* = 9.2, 6.4 Hz, 1H), 4.11 (s, 3H), 4.05 (dd, *J* = 9.2, 6.7 Hz, 1H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -79.81. **^{13}C NMR** (101 MHz, Acetone-d_6) δ 166.4, 158.9, 138.1, 138.1, 132.1, 131.6, 129.2, 129.2, 128.1, 126.8, 126.3, 124.8, 124.2, 121.0 (-CF_3, q, *J* = 321.3 Hz), 120.5, 108.0, 81.6, 75.4, 71.2, 67.1, 50.0, 36.8.

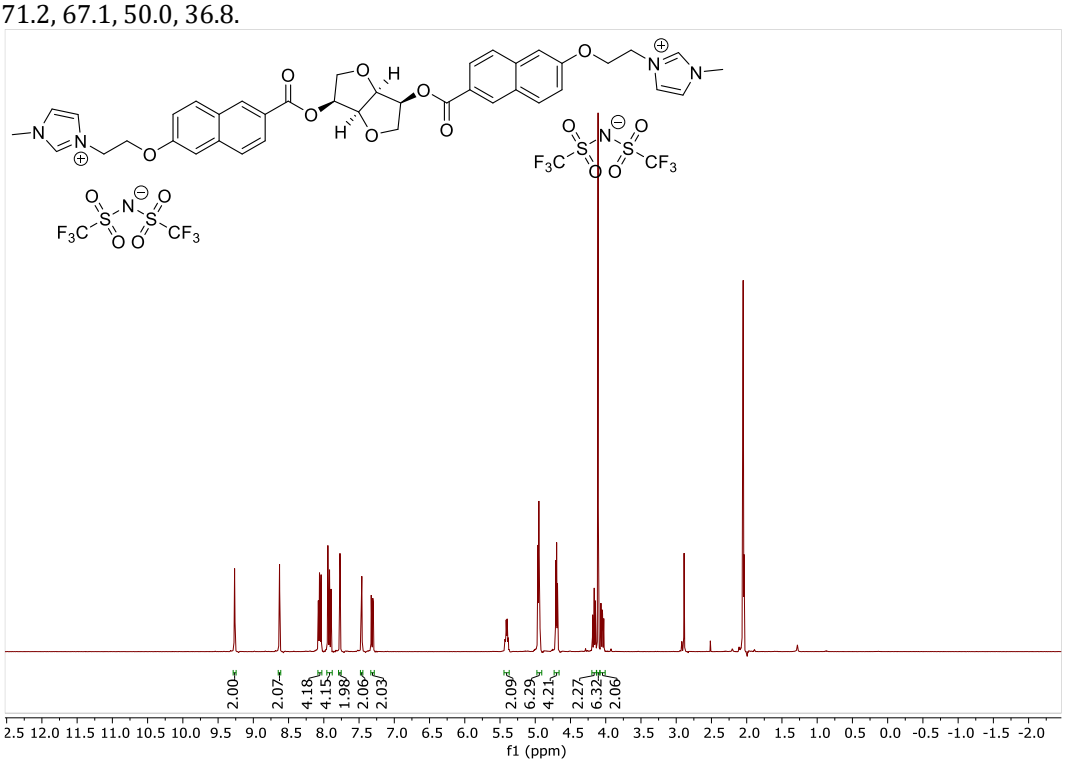


Figure S1.23 ^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound **3mT**.

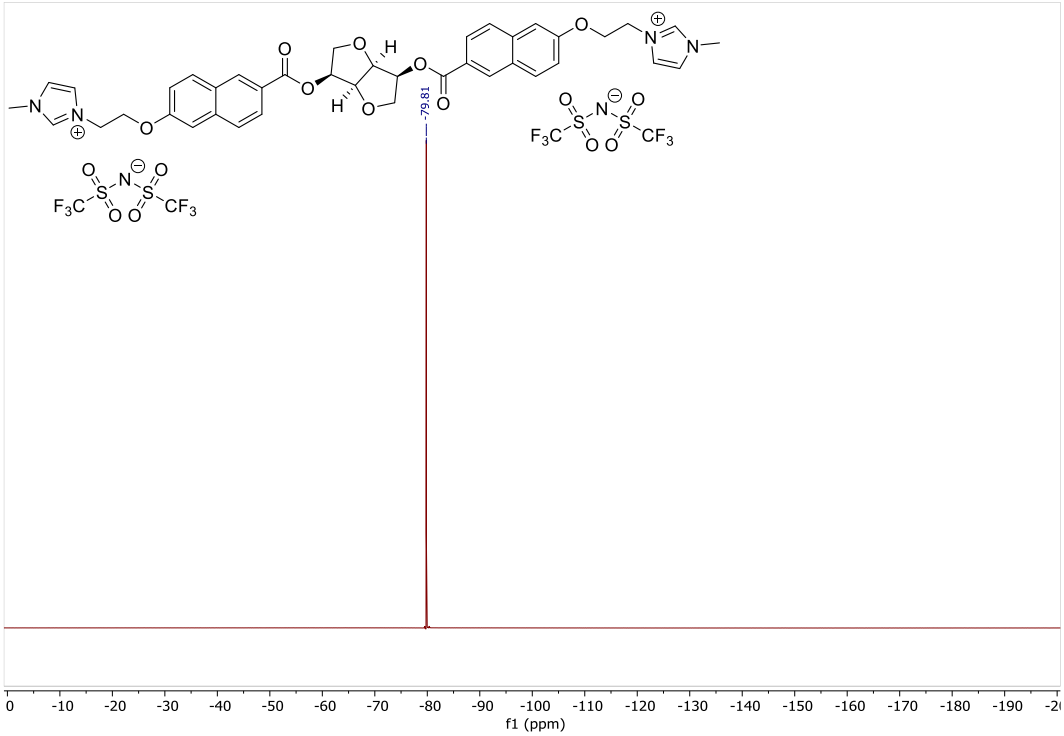


Figure S1.24 - ^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound **3c 3mT**.

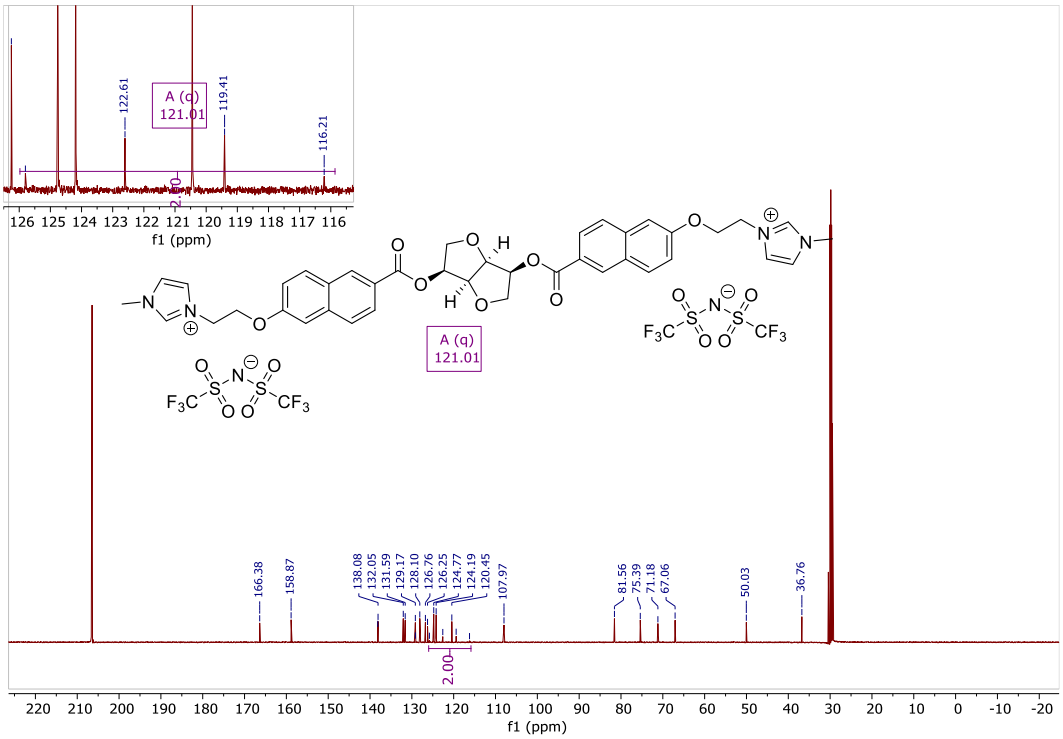


Figure S1.25- ^{13}C NMR (101 MHz, Acetone-d_6) spectrum of compound **3mT**.

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6 di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide **3sT**

3sT: Beige solid, 258.8 mg, (82%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.29 – 9.25 (m, 2H), 8.64 (d, *J* = 1.7 Hz, 1H), 8.58 (d, *J* = 1.7 Hz, 1H), 8.10 – 7.97 (m, 4H), 7.94 (dt, *J* = 3.4, 1.8 Hz, 2H), 7.92 – 7.86 (m, 2H), 7.77 (q, *J* = 2.0 Hz, 2H), 7.46 (dd, *J* = 7.4, 2.6 Hz, 2H), 7.31 (ddd, *J* = 9.0, 5.3, 2.5 Hz, 2H), 5.57 – 5.51 (m, 1H), 5.47 (d, *J* = 2.9 Hz, 1H), 5.14 (t, *J* = 5.3 Hz, 1H), 4.97 – 4.92 (m, 4H), 4.77 (d, *J* = 4.8 Hz, 1H), 4.69 (q, *J* = 5.1 Hz, 4H), 4.22 – 4.04 (m, 9H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -79.83. **^{13}C NMR** (101 MHz, Acetone-d_6) δ 166.2, 158.9, 138.2, 138.1, 132.0, 132.0, 131.7, 131.5, 129.2, 129.1, 128.1, 128.1, 128.1, 126.7, 126.6, 126.1, 124.7, 124.2, 122.1 (-CF_3, q, *J* = 321.2 Hz), 120.5, 120.4, 108.0, 107.9, 87.0, 82.2, 79.5, 75.7, 73.8, 71.6, 67.1, 50.0, 36.7.

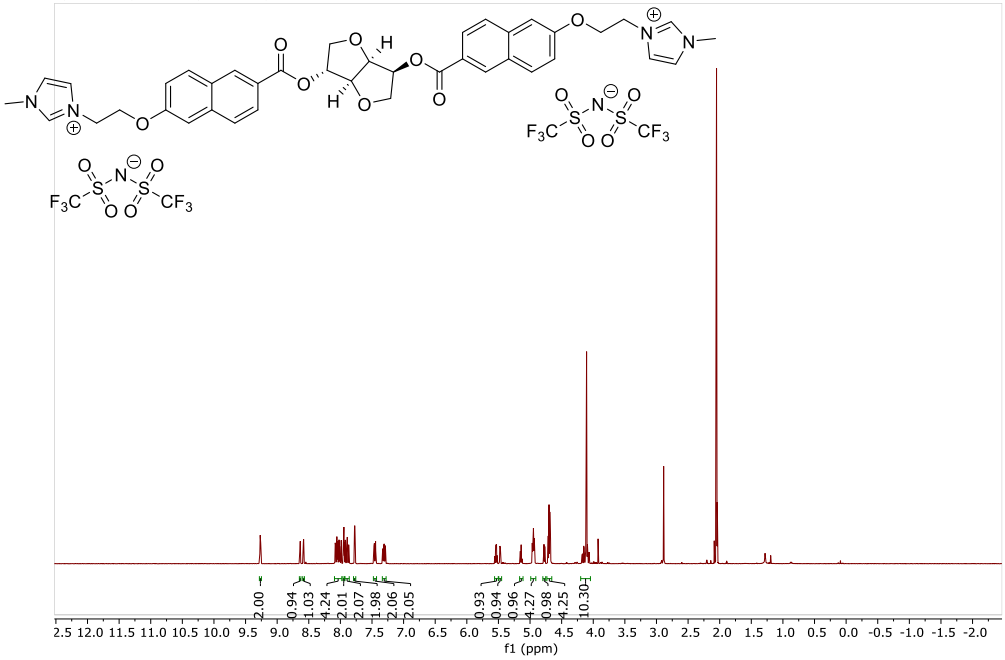


Figure S1.26 ^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound **3sT**.

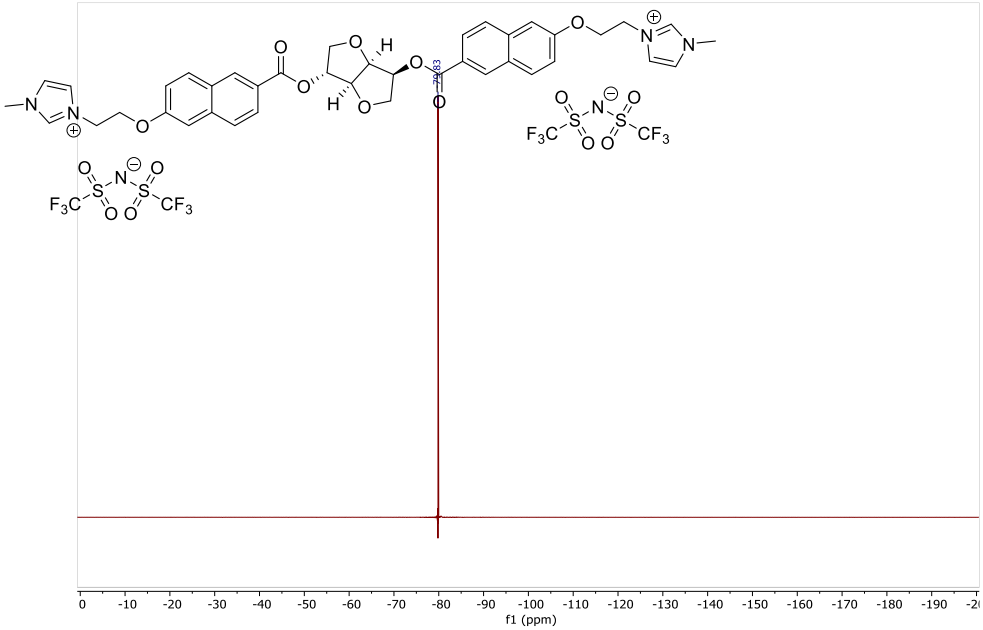


Figure S1.27 ^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound **3sT**.

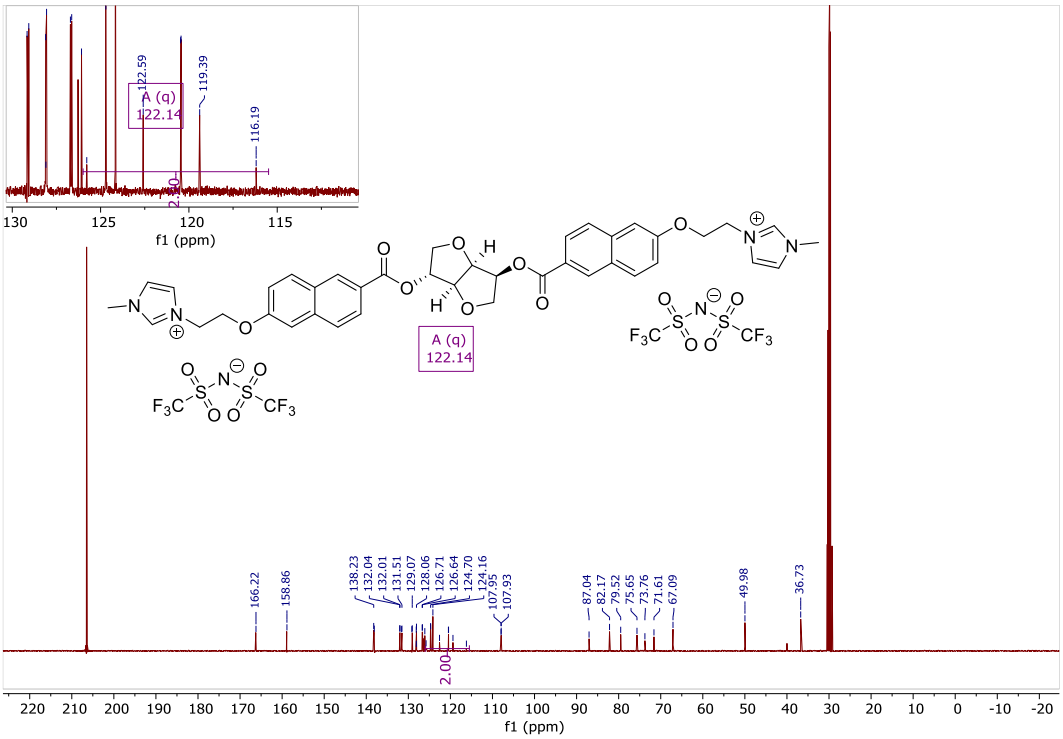


Figure S1.28 ^{13}C NMR (101 MHz, Acetone-d_6) spectrum of compound **3sT**.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide 4c **4mT**

4mT: White solid, 316.2 mg, (83%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.40 – 9.36 (m, 4H), 8.82 (tt, *J* = 7.8, 1.4 Hz, 2H), 8.62 (d, *J* = 1.7 Hz, 2H), 8.40 – 8.33 (m, 4H), 8.04 (td, *J* = 8.6, 1.2 Hz, 4H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 2.5 Hz, 2H), 7.28 (dd, *J* = 9.0, 2.5 Hz, 2H), 5.43 (t, *J* = 4.6 Hz, 4H), 5.41 – 5.36 (m, 1H), 4.97 – 4.93 (m, 2H), 4.90 (t, *J* = 5.0 Hz, 4H), 4.16 (dd, *J* = 9.2, 6.4 Hz, 2H), 4.03 (dd, *J* = 9.2, 6.8 Hz, 2H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -79.80. **^{13}C NMR** (101 MHz, Acetone-d_6) δ 166.3, 158.6, 147.4, 146.6, 138.0, 132.1, 131.6, 129.3, 128.1, 128.1, 126.8, 121.0 (-CF_3, q, *J* = 321.3 Hz), 120.3, 108.1, 81.6, 75.4, 71.2, 67.3, 61.9.

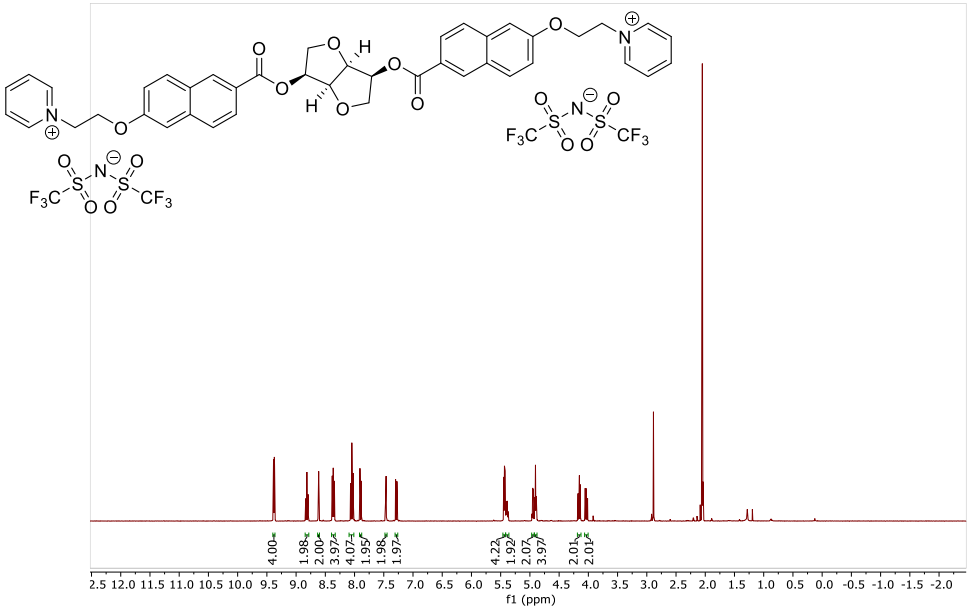


Figure S1.29 ^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound **4mT**.

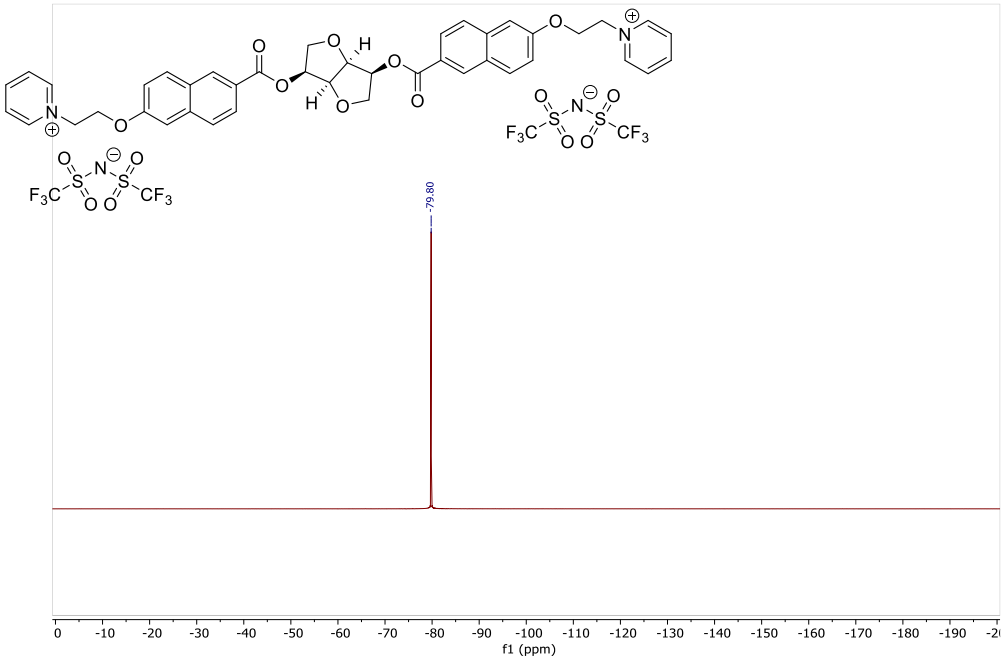


Figure S1.30 ^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound **4mT**

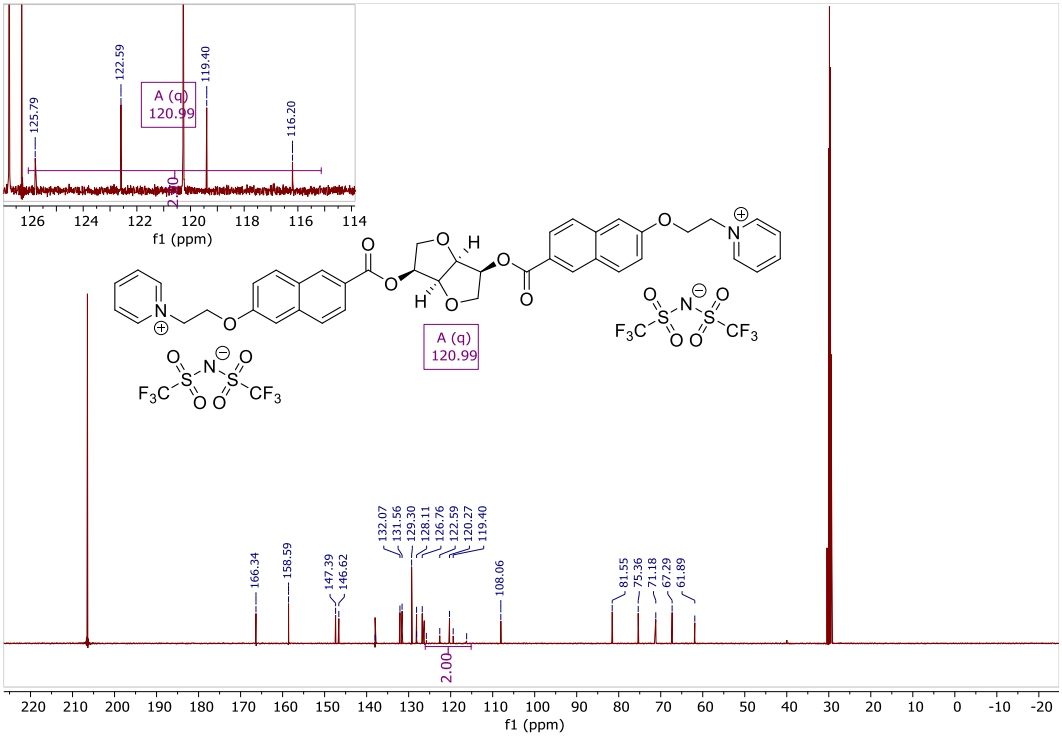


Figure S1.31 ^{13}C NMR (101 MHz, Acetone-d_6) spectrum of compound **4mT**.

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide **4sT**

4sT: Glassy solid, 330.1 mg, (89%). **^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.40 – 9.35 (m, 4H), 8.81 (dddd, *J* = 7.8, 6.5, 2.3, 1.2 Hz, 2H), 8.62 (d, *J* = 1.7 Hz, 1H), 8.57 (d, *J* = 1.7 Hz, 1H), 8.39 – 8.33 (m, 4H), 8.08 – 7.97 (m, 4H), 7.92 – 7.85 (m, 2H), 7.46 (dd, *J* = 7.7, 2.6 Hz, 2H), 7.28 (ddd, *J* = 9.0, 5.1, 2.5 Hz, 2H), 5.58 – 5.49 (m, 1H), 5.48 – 5.40 (m, 5H), 5.13 (t, *J* = 5.2 Hz, 1H), 4.95 – 4.85 (m, 4H), 4.76 (d, *J* = 4.9 Hz, 1H), 4.19 – 4.03 (m, 4H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -79.81. **^{13}C NMR** (101 MHz, Acetone-d_6) δ 166.2, 158.6, 147.4, 146.6, 138.0, 132.1, 132.0, 131.7, 131.5, 129.3, 129.1, 128.1, 128.1, 126.7, 126.7, 126.4, 126.2, 121.0 (-CF_3, q, J = 321.5 Hz), 120.3, 120.3, 108.1, 108.1, 87.0, 82.2, 79.5, 75.7, 73.8, 71.6, 67.3, 67.3, 61.9.

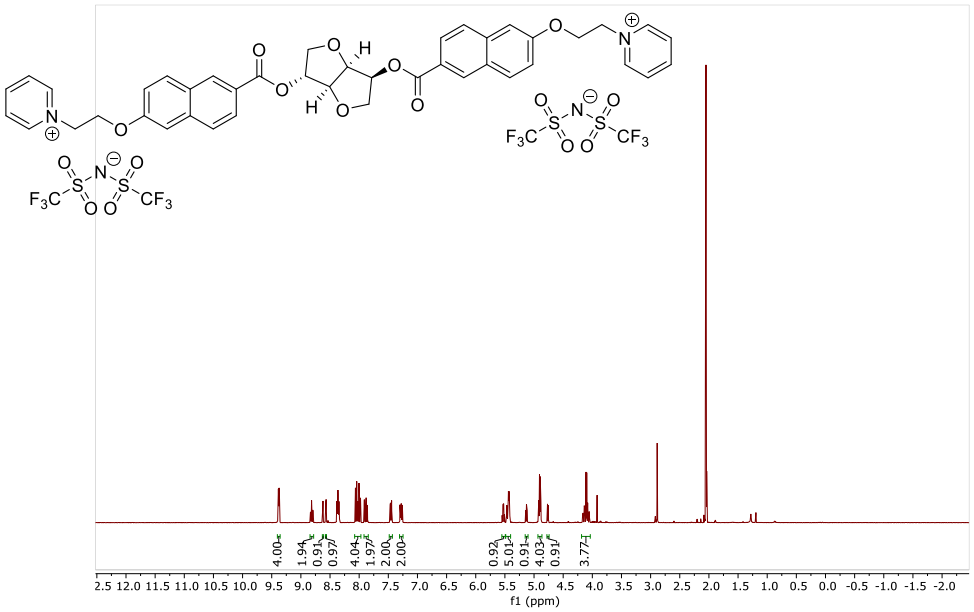


Figure S1.32 ^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound **4sT**

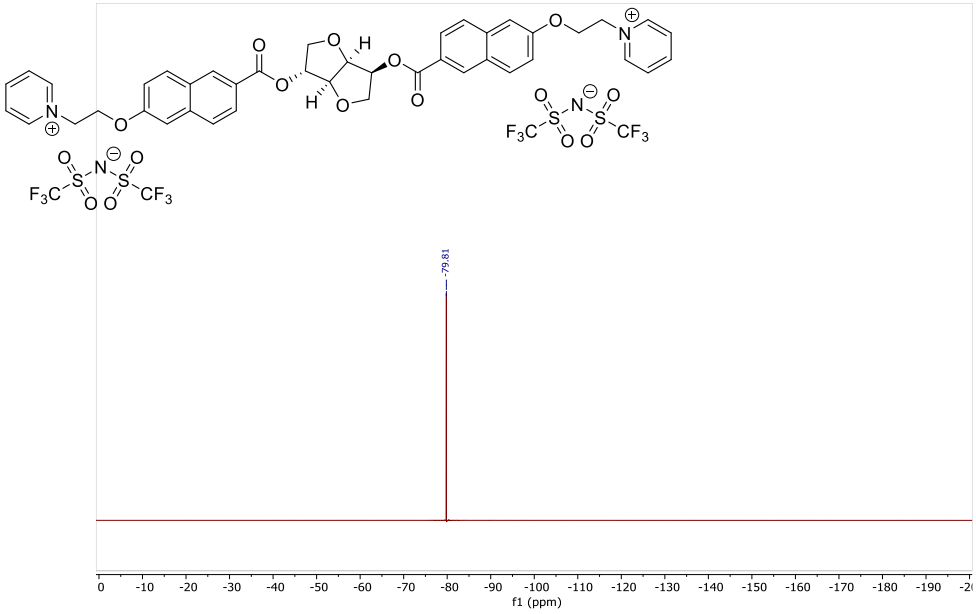


Figure S1.32 ^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound **4sT**.

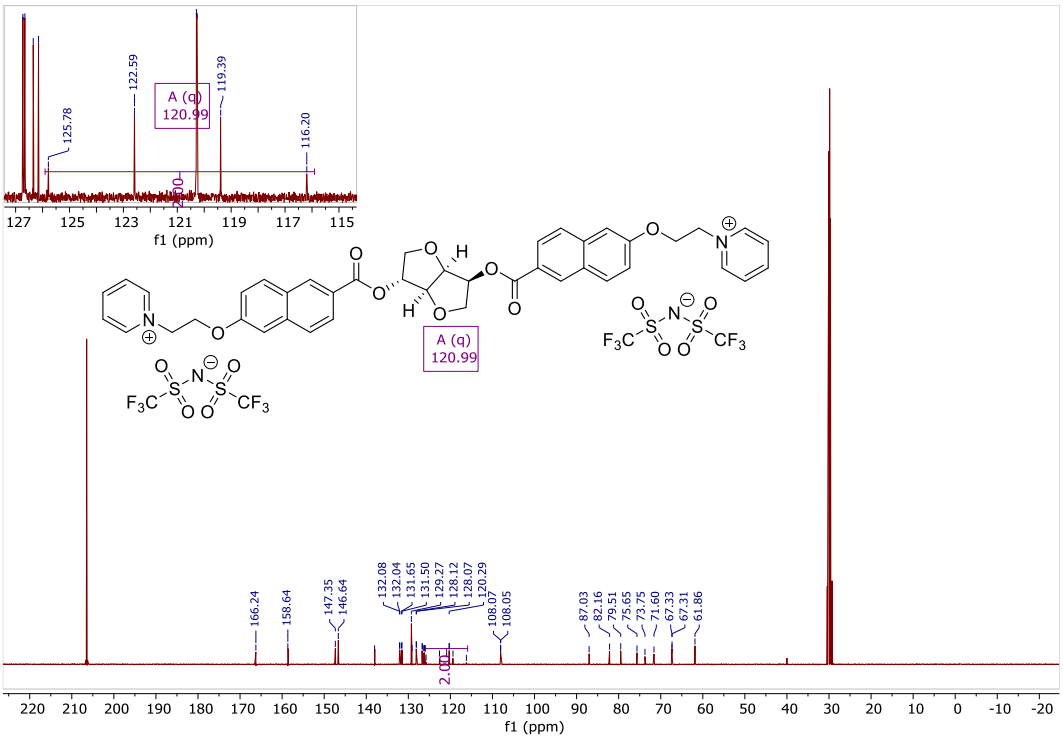
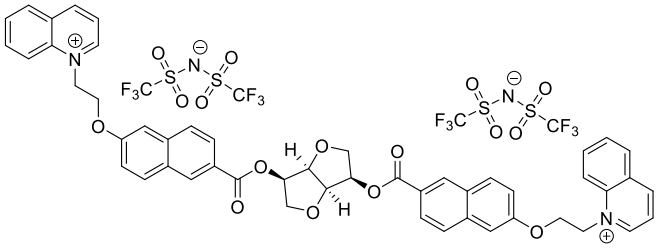


Figure S1.33- ^{13}C NMR (101 MHz, Acetone-d_6) spectrum of compound **4sT**.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-quinoliniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***5mT***



5mT: Off-white solid, 1.31 g (96%).**^{1}H NMR** (400 MHz, Acetone-d_6) δ 9.81 (dd, *J* = 5.8, 1.5 Hz, 2H), 9.43 (d, *J* = 8.3 Hz, 2H), 8.95 (d, *J* = 9.0 Hz, 2H), 8.60 – 8.55 (m, 4H), 8.44 (ddd, *J* = 8.8, 7.0, 1.5 Hz, 2H), 8.37 (dd, *J* = 8.4, 5.9 Hz, 2H), 8.18 – 8.13 (m, 2H), 8.04 – 7.95 (m, 4H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.40 (d, *J* = 2.5 Hz, 2H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 2H), 5.90 (t, *J* = 4.8 Hz, 4H), 5.43 – 5.33 (m, 2H), 5.00 (t, *J* = 4.8 Hz, 4H), 4.96 – 4.90 (m, 2H), 4.14 (dd, *J* = 9.2, 6.4 Hz, 2H), 4.00 (dd, *J* = 9.2, 6.8 Hz, 2H). **^{19}F NMR** (376 MHz, Acetone-d_6) δ -79.80. **^{13}C NMR** (101 MHz, Acetone-d_6) δ 166.3, 158.6, 151.4, 149.5, 139.5, 137.9, 137.0, 132.0, 131.9, 131.5, 131.3, 131.1, 129.1, 128.0, 126.7, 126.2, 125.8, 122.9, 122.6, 121.0 (q, *J* = 321.4 Hz), 120.2, 119.8, 119.4, 116.2, 107.9, 81.5, 75.3, 71.1, 66.5, 58.0.

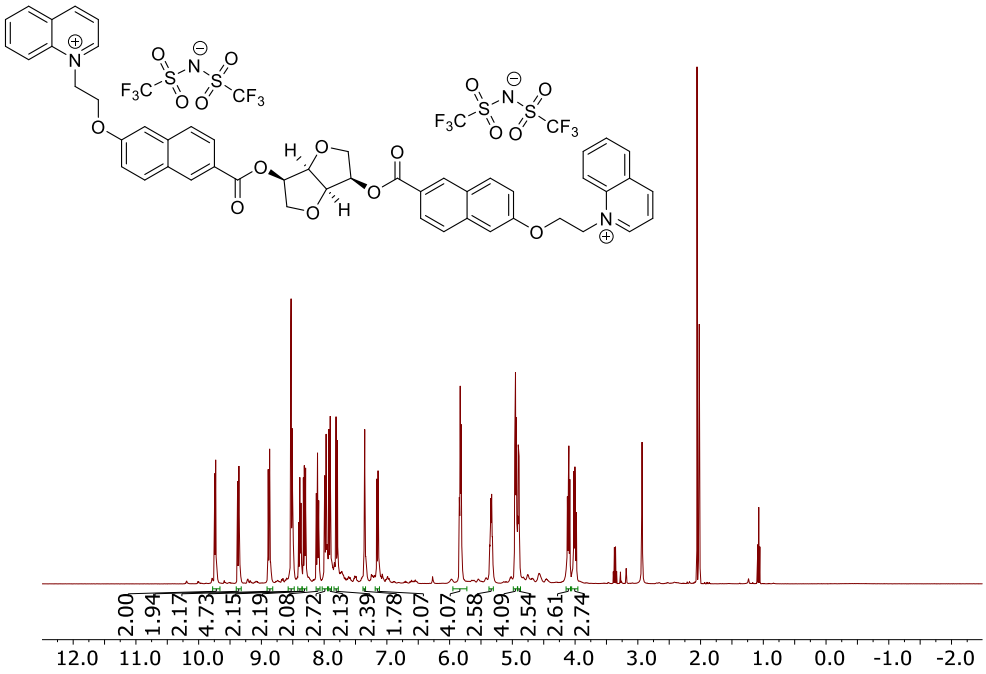


Figure S1.- ^{1}H NMR (400 MHz, Acetone-d_6) spectrum of compound **5mT**.

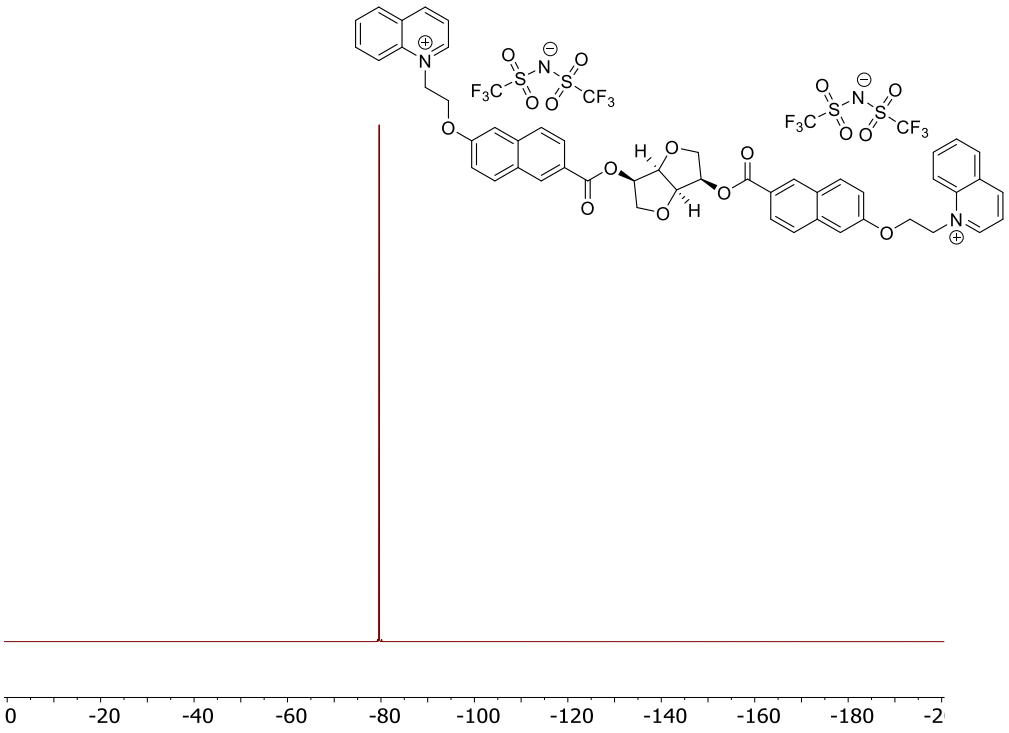


Figure S1. ^{19}F NMR (376 MHz, Acetone-d_6) spectrum of compound **5mT**.

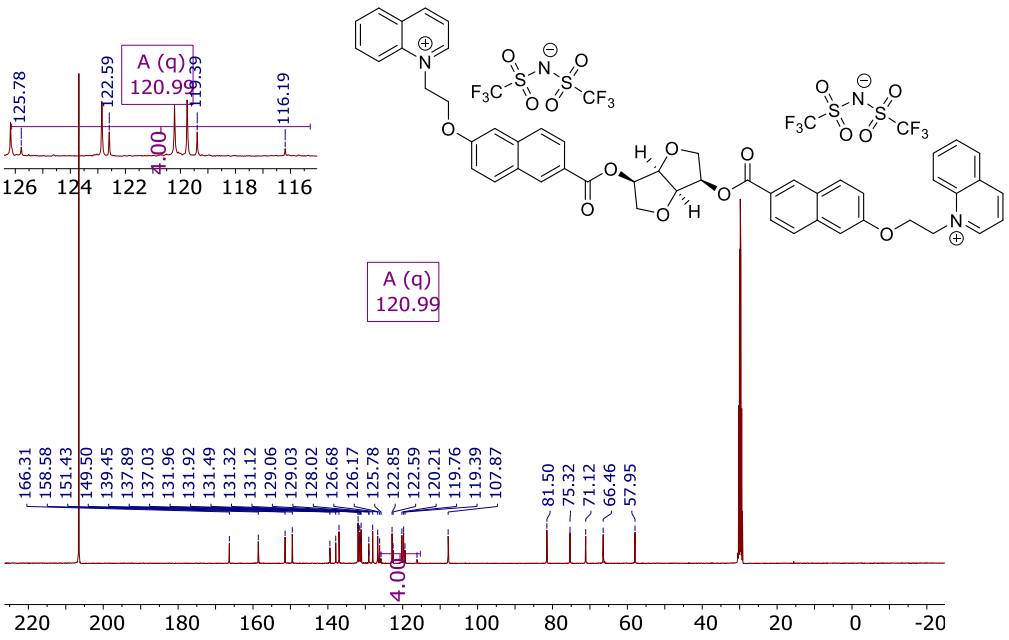
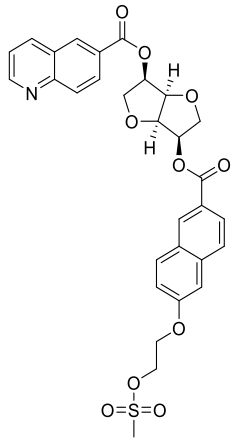


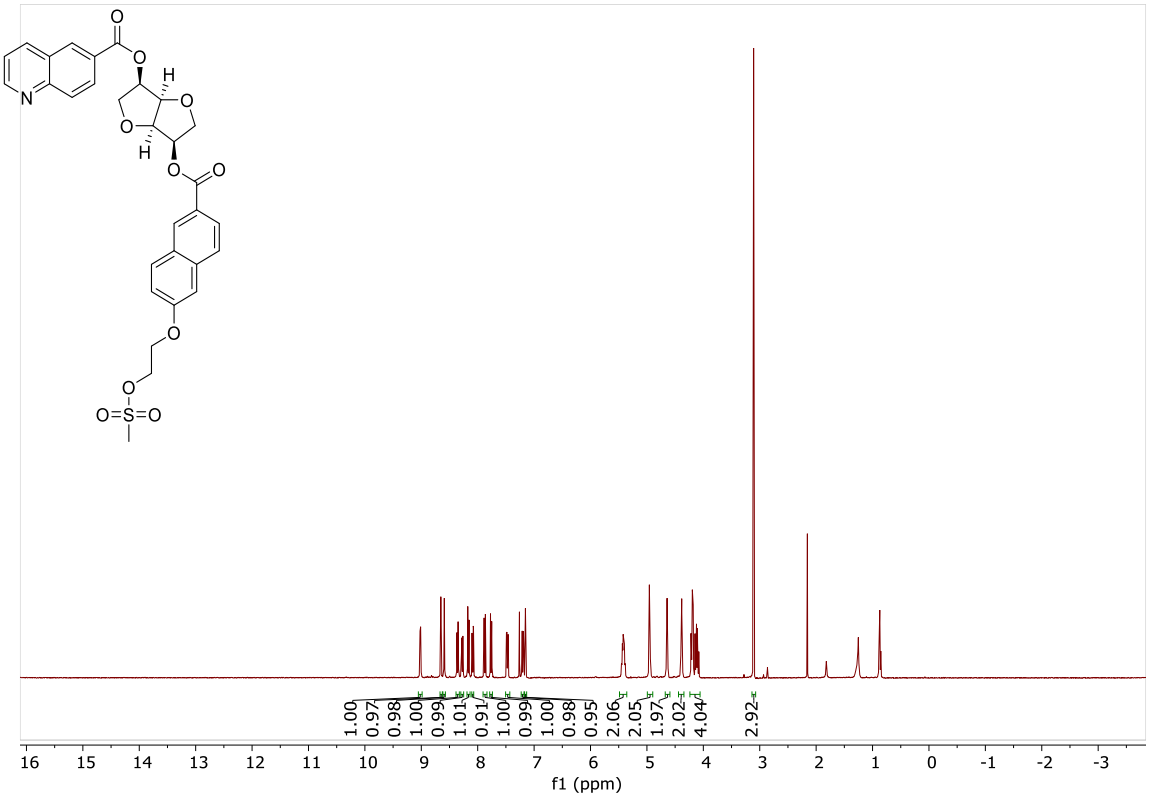
Figure S1.- ^{13}C NMR (101 MHz, Acetone-d_6) spectrum of compound **5mT**.



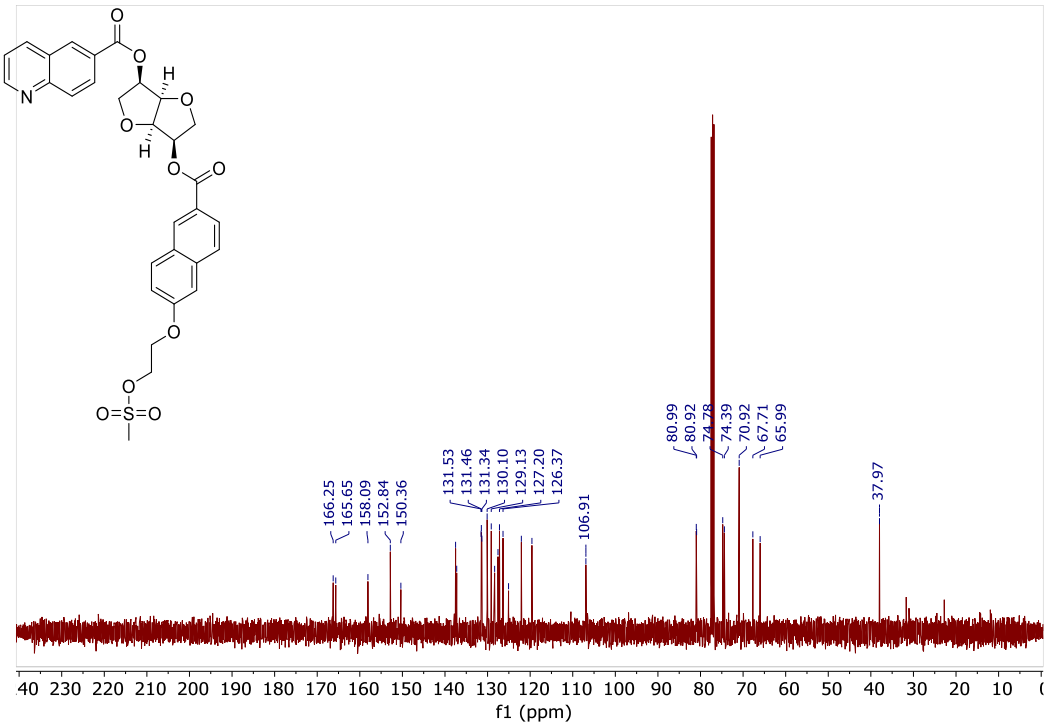
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3-[6-(2-methanesulfonyloxy)ethoxy]-2-naphthoate-6-[6-quinolin(carboxilate)] ***7m***

Under an Ar atmosphere, to a solution of *DVZ 62* (147.2 mg, 1.0 mmol) in CH_2Cl_2 (5 cm^3), DCC (247.8 mg, 1.2 mmol) and DMAP (14.3 mg, 0.12 mmol) were added. The mixture was stirred at RT and the reaction was followed by TLC ($CHCl_3$:MeOH 9:1). After 24h, the solids were filtered off and the solvent was removed under reduced pressure. The crude was dissolved in CH_2Cl_2 (30 cm^3) and the organic phase was washed with water (3x10 cm^3) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by recrystallization from acetone/hexane to give the pure product as a yellowish solid (423.6 mg; 72%).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 9.02 (dd, J = 4.2, 1.8 Hz, 1H), 8.66 (d, J = 1.9 Hz, 1H), 8.59 (s, 1H), 8.36 (dd, J = 8.8, 1.9 Hz, 1H), 8.27 (dd, J = 8.6, 1.0 Hz, 1H), 8.17 (d, J = 8.8 Hz, 1H), 8.09 (dd, J = 8.6, 1.7 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.6 Hz, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 7.20 (dd, J = 9.0, 2.5 Hz, 1H), 7.15 (d, J = 2.5 Hz, 1H), 5.42 (dq, J = 9.1, 6.1 Hz, 2H), 4.98 – 4.92 (m, 2H), 4.69 – 4.59 (m, 2H), 4.42 – 4.35 (m, 2H), 4.24 – 4.06 (m, 4H), 3.11 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 165.7, 158.1, 152.8, 150.4, 137.5, 137.3, 131.5, 131.5, 131.4, 130.1, 129.1, 128.3, 127.8, 127.2, 126.4, 125.1, 122.1, 119.6, 106.9, 81.0, 80.9, 74.8, 74.4, 70.9, 67.7, 66.0, 38.0.



SI 1.34. ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **7m**.

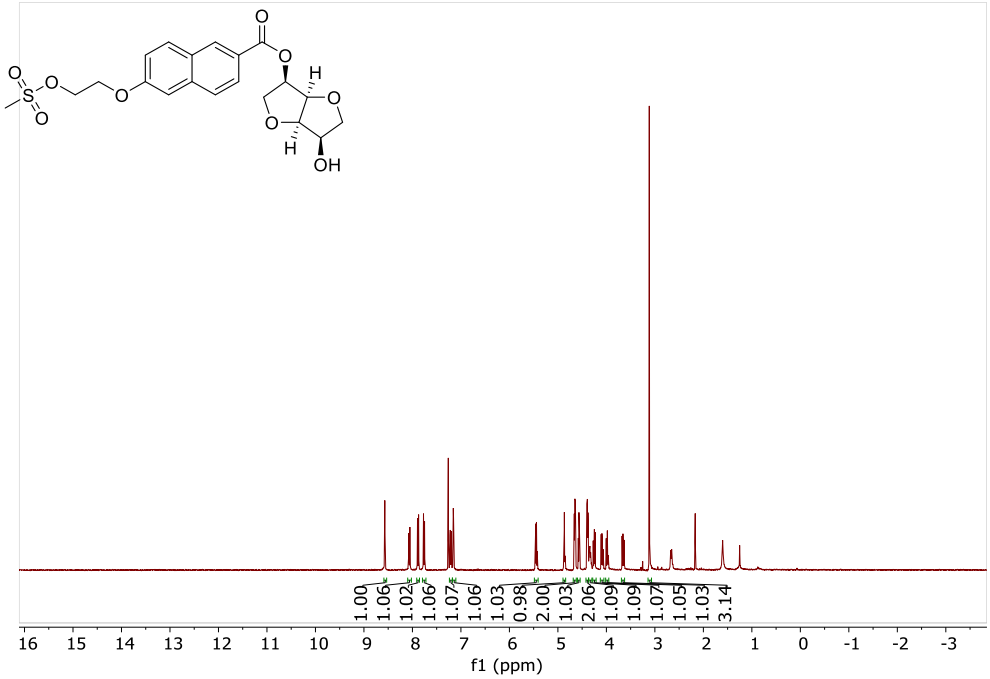


S1.35 ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **7m**

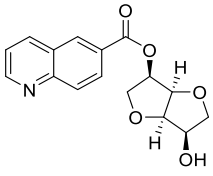
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3-[6-(2-methanesulfonyloxy)ethoxy]-2-naphthoate-6-ol ***8m***

Under an Ar atmosphere, to a solution of isomannide **1** (599.5 mg, 4.1 mmol) and crude **10** (≈1 mmol assuming that the crude contains only acid) in CH_3CN (10 cm^3), EDC·HCl (221.4 mg, 1.2 mmol) and DMAP (41.5 mg, 0.3 mmol) were added. The mixture was stirred at RT and the reaction was followed by TLC (CH_2Cl_2:Acetone 95:5). After 24h, the solids were filtered off and the solvent was removed under reduced pressure. The crude was dissolved in CH_2Cl_2 (30 cm^3) and the organic phase was washed with water (3x10 cm^3) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by Biotage® Isolera chromatograph (CH_2Cl_2:Acetone) to give the pure product as a white solid (218.1 mg; 55%).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.06 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 1H), 7.21 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 5.45 (q, *J* = 5.9 Hz, 1H), 4.87 (t, *J* = 5.3 Hz, 1H), 4.69 – 4.62 (m, 2H), 4.57 (t, *J* = 5.3 Hz, 1H), 4.43 – 4.37 (m, 2H), 4.36 – 4.29 (m, 1H), 4.25 (dd, *J* = 9.6, 6.2 Hz, 1H), 4.09 (dd, *J* = 9.6, 6.1 Hz, 1H), 3.98 (dd, *J* = 9.2, 6.3 Hz, 1H), 3.66 (dd, *J* = 9.2, 7.1 Hz, 1H), 3.12 (s, 3H). **m.p.** 110 °C.



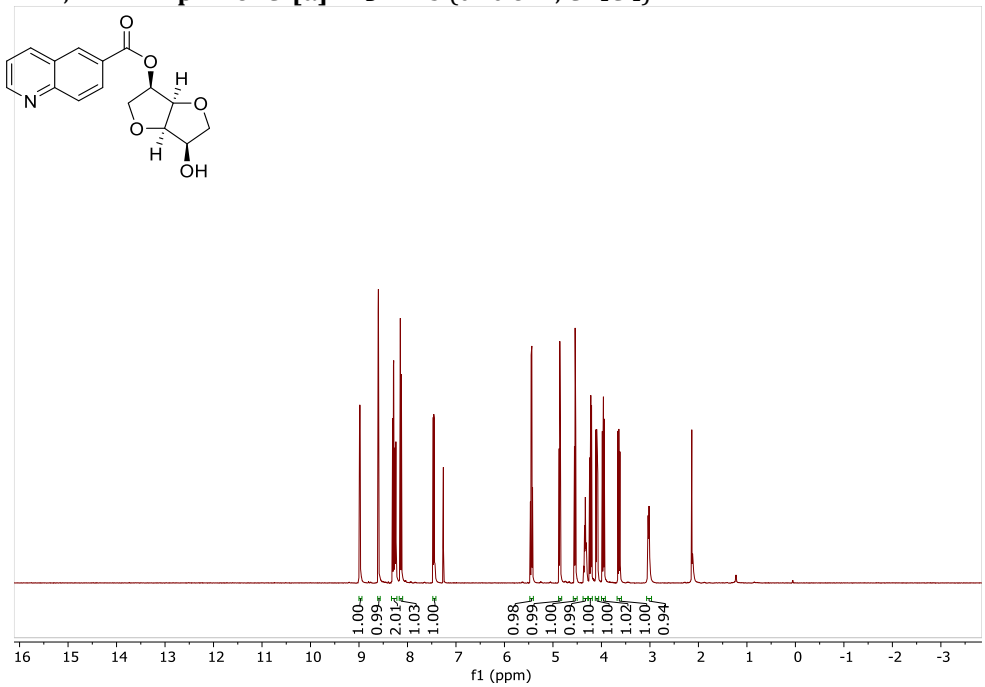
SI 1.36 ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **8m.**



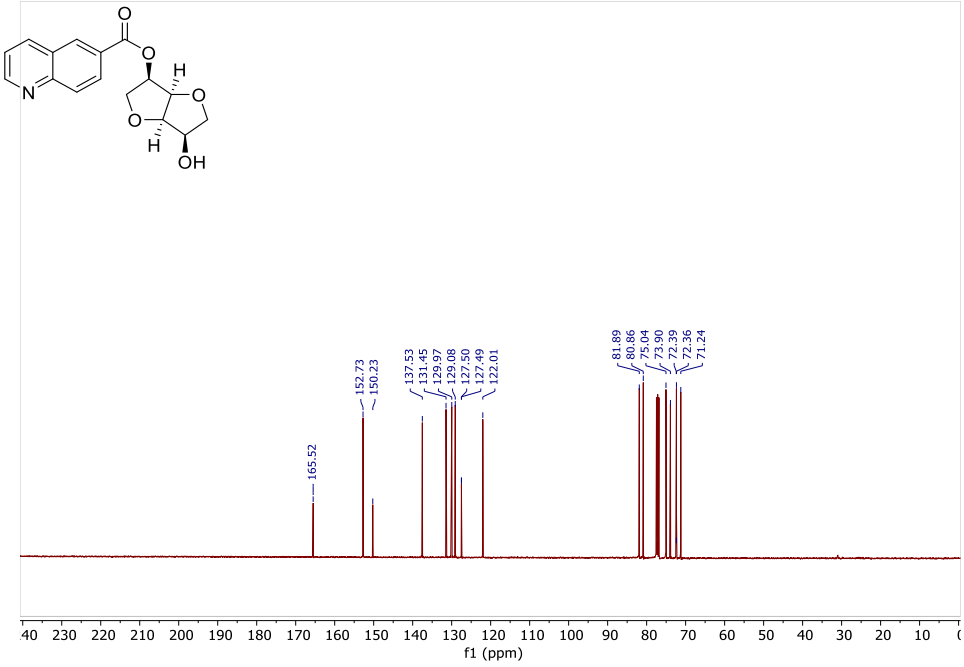
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3-(6-quinolin)carboxylate-6-ol ***10m***

Under an Ar atmosphere, to a solution of isomannide **1** (2.95 g, 20.2 mmol) and 6-quinolyne carboxylic acid (875.9 mg, 5.0 mmol) in CH_3CN (30 cm^3), DCC (1.15 g, 5.6 mmol) and DMAP (130.8 mg, 1.1 mmol) were added. The mixture was stirred at RT and the reaction was followed by TLC ($CHCl_3$:MeOH 9:1). After 24h, the solids were filtered off and the solvent was removed under reduced pressure. The crude was dissolved in CH_2Cl_2 (30 cm^3) and the organic phase was washed with water (3x10 cm^3) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude was purified by Biotage® Isolera chromatograph (Ethyl acetate) to give the pure product as a white solid (784.9 mg, 52%).

^{1}H NMR (401 MHz, Chloroform-*d*) δ 8.98 (dd, J = 4.2, 1.8 Hz, 1H), 8.60 (d, J = 1.9 Hz, 1H), 8.30 (dd, J = 8.8, 1.9 Hz, 1H), 8.27 – 8.23 (m, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.45 (dd, J = 8.3, 4.2 Hz, 1H), 5.44 (q, J = 5.9 Hz, 1H), 4.86 (t, J = 5.3 Hz, 1H), 4.54 (t, J = 5.2 Hz, 1H), 4.33 (p, J = 6.7 Hz, 1H), 4.22 (dd, J = 9.7, 6.1 Hz, 1H), 4.09 (dd, J = 9.7, 5.9 Hz, 1H), 3.96 (dd, J = 9.1, 6.3 Hz, 1H), 3.64 (dd, J = 9.1, 7.3 Hz, 1H), 3.03 (d, J = 7.8 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ:165.5, 152.7, 150.2, 137.5, 131.5, 130.0, 129.1, 127.5, 127.5, 122.0, 81.9, 80.9, 75.0, 73.9, 72.4, 72.4, 71.2. . **m.p.** 148 °C. **$[\alpha]^{25°C}_{D}$**= +75 (c= 0.827, CH_2Cl_2)

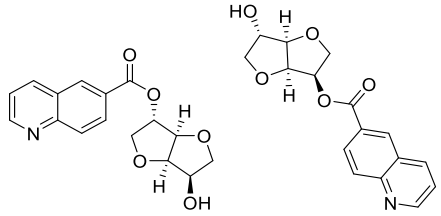


SI 1.37. ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **10m**



SI 1.37 ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **10m.**

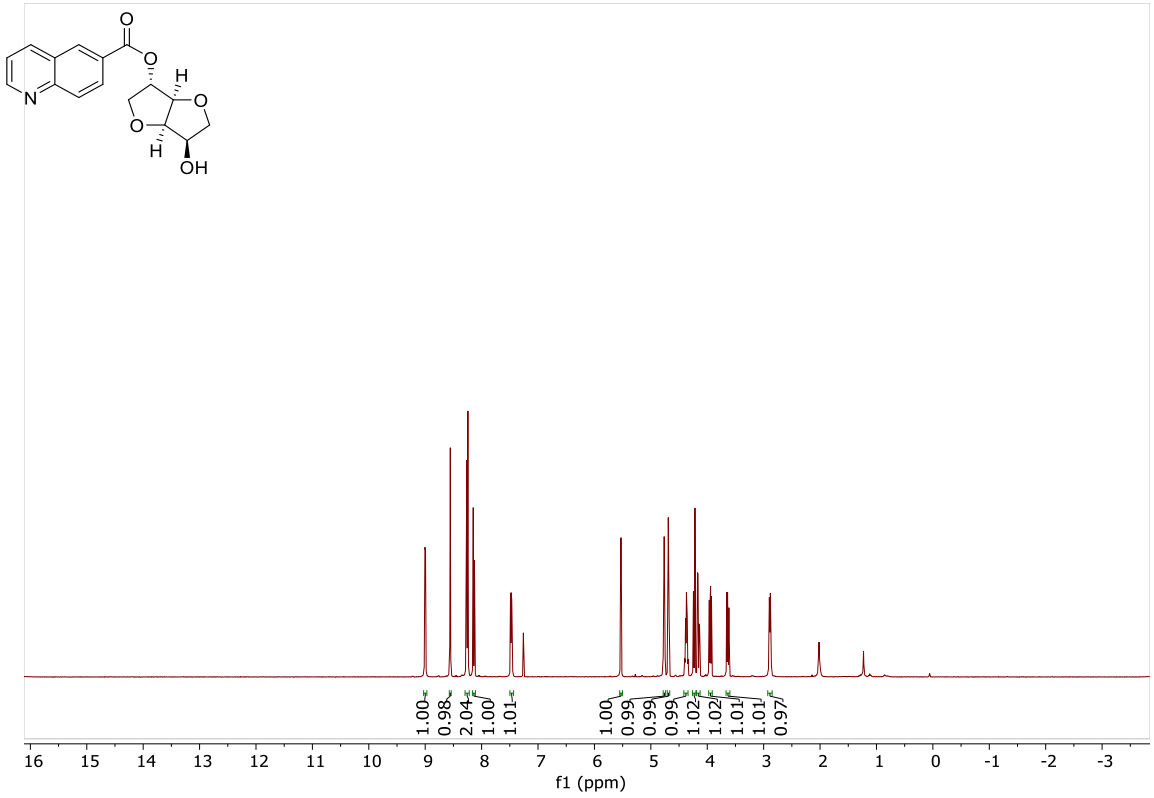
(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-6-(6-quinolin)carboxylate-6-ol ***10s*** *and (3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3-(6-quinolin)carboxylate-6-ol* ***11s***



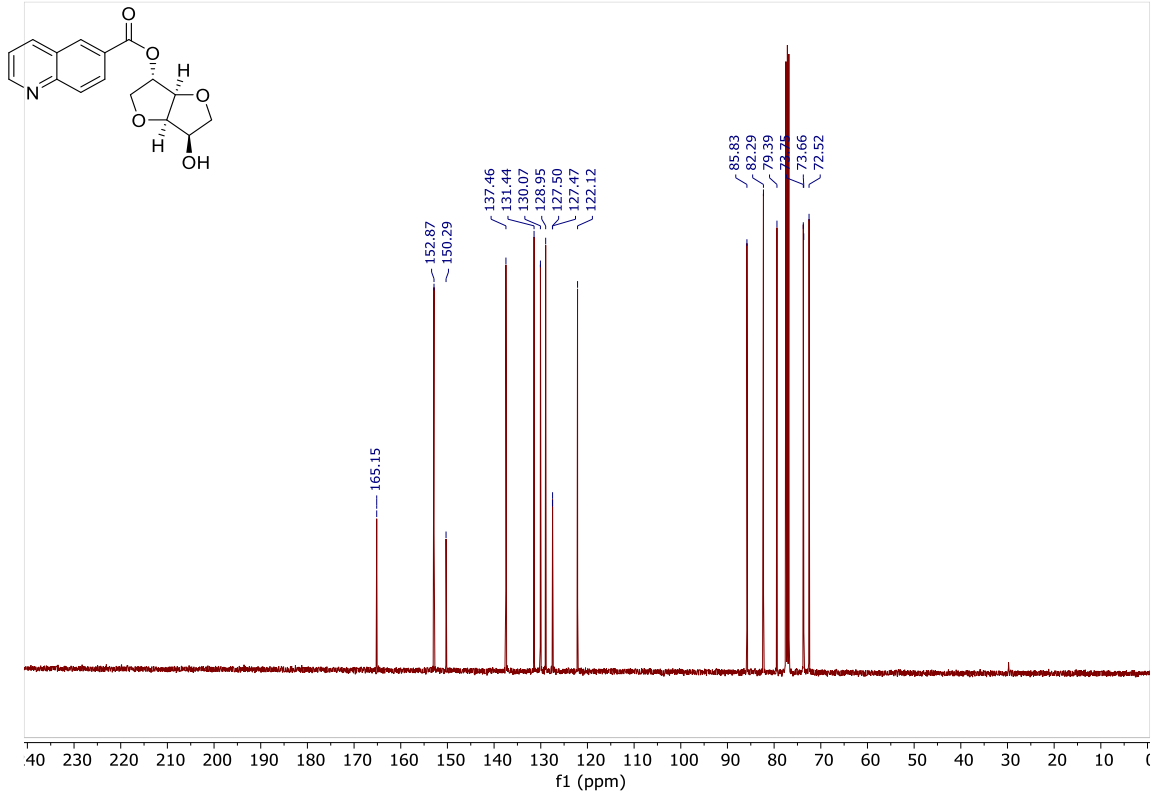
Under an Ar atmosphere, to a solution of isosorbide **2** (733.2 mg, 5.0 mmol) and 6-quinolyne carboxylic acid (172.0 mg, 1.0 mmol) in CH_3CN (8 cm^3), DCC (229.7 mg, 1.1 mmol) and DMAP (35.0 mg, 0.29 mmol) were added. The mixture was stirred at RT and the reaction was followed by TLC ($CHCl_3$:MeOH 9:1). After 24h, the solids were filtered off and the solvent was removed under reduced pressure. The crude was dissolved in CH_2Cl_2 (30 cm^3) and the organic phase was washed with water (3x10 cm^3) and dried over anhydrous Na_2SO_4. The solvent was removed under the reduced pressure and the crude was purified by Biotage® Isolera chromatograph (CH_2Cl_2:Acetone) to give **10s** as a white solid (114.6 mg, 38%) and **11s** as a white solid (45.8 mg, 15%).

EXO: **^{1}H NMR** (401 MHz, Chloroform-*d*) δ 9.04 – 8.97 (m, 1H), 8.56 (s, 1H), 8.25 (d, J = 8.9 Hz, 2H), 8.14 (d, J = 8.9 Hz, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 5.53 (d, J = 3.5 Hz, 1H), 4.76 (t, J = 5.0 Hz, 1H), 4.69 (d, J = 4.5 Hz, 1H), 4.37 (p, J = 6.1 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H), 4.15 (dd, J = 10.8, 3.6 Hz, 1H), 3.94 (dd, J = 9.5, 6.1 Hz, 1H), 3.63 (dd, J = 9.5, 6.1 Hz, 1H), 2.89 (d, J = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.2, 152.9, 150.3, 137.5, 131.4, 130.1, 129.0, 127.5, 127.5, 122.1, 85.8, 82.3, 79.4, 73.8, 73.7, 72.5. **m.p.** 137 °C.

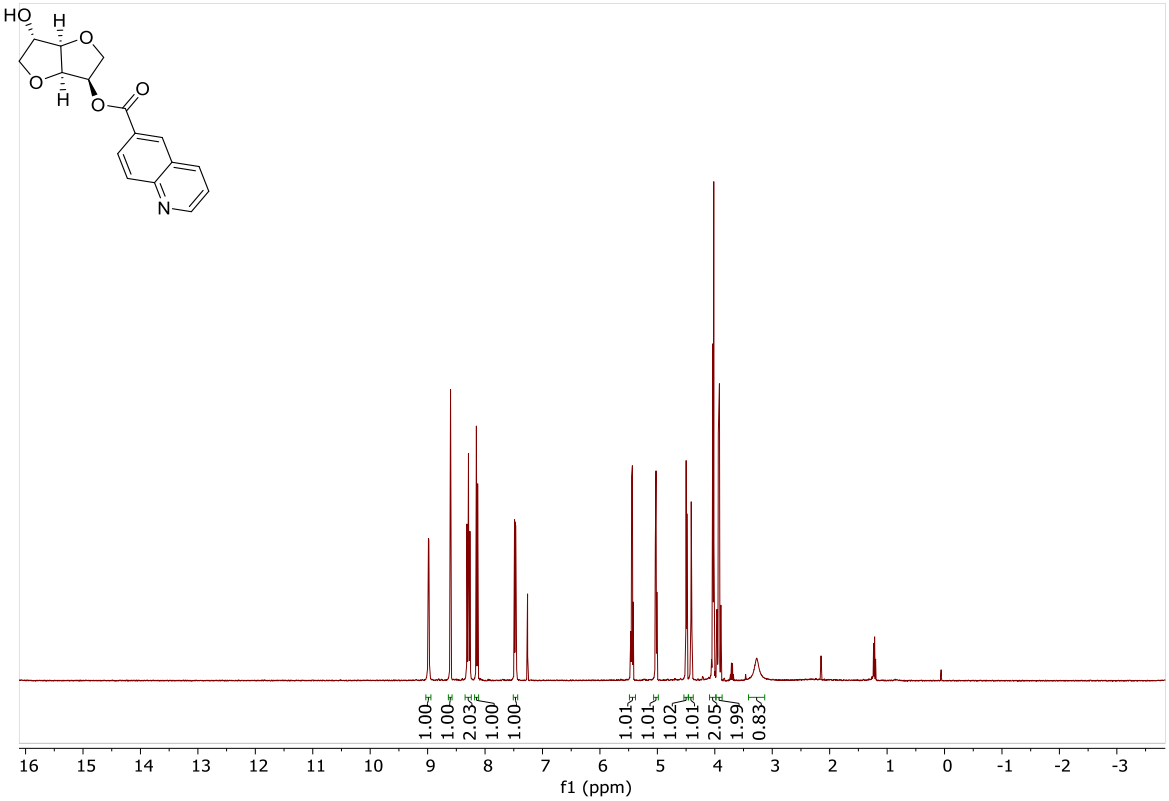
ENDO: **^{1}H NMR** (401 MHz, Chloroform-*d*) δ 8.98 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.60 (d, *J* = 1.9 Hz, 1H), 8.29 (ddd, *J* = 11.6, 8.6, 1.9 Hz, 2H), 8.14 (d, *J* = 8.9 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 5.44 (q, *J* = 5.3 Hz, 1H), 5.02 (t, *J* = 5.1 Hz, 1H), 4.49 (d, *J* = 4.6 Hz, 1H), 4.41 (d, *J* = 2.9 Hz, 1H), 4.02 (d, *J* = 5.2 Hz, 2H), 3.99 – 3.88 (m, 2H), 3.27 (s, 1H).



SI 1.38 ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **10s**



SI 1.39 ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of compound **10s**



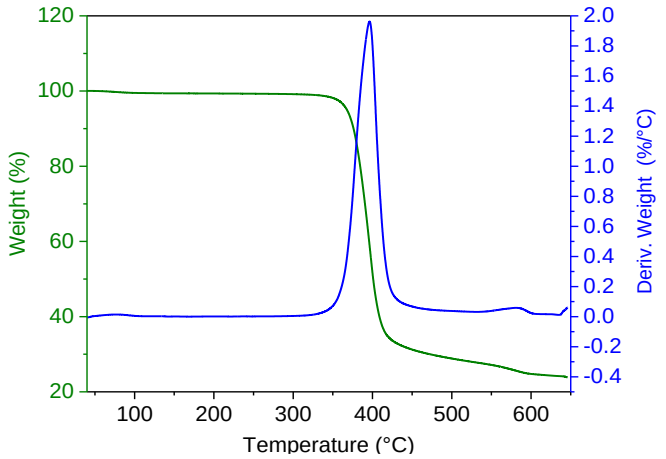
SI 1.40 ^{1}H NMR (401 MHz, Chloroform-*d*) spectrum of compound **11s**

2. Thermal analyses

2.1 Thermogravimetric Analysis TGA

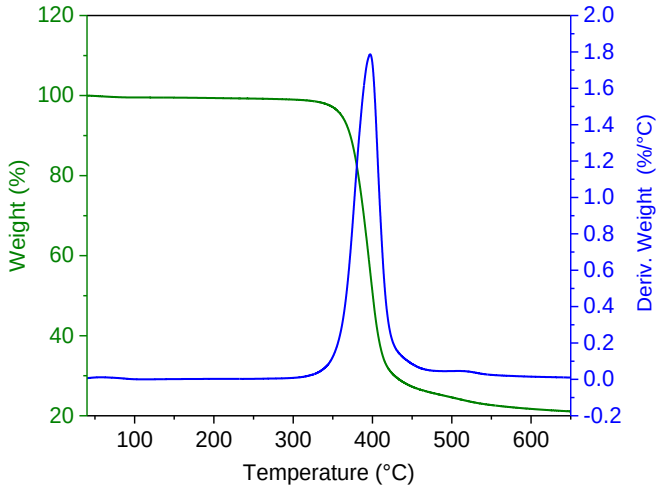
Decomposition temperatures were measured by a TGA Q500 V20.13 Build 39 thermogravimetric analyser (TA Instruments). The samples were measured in a platinum pan (100 μL), at a heating rate of 10 °C/min starting from 40 °C to 900 °C under a nitrogen atmosphere. Every sample was dried in the furnace at 60 °C for 10 minutes under a nitrogen atmosphere prior to measurement. The onset of the weight loss, the temperature at 5% weight loss and 10% weight loss were used as a measure of the decomposition temperatures.

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3mM***



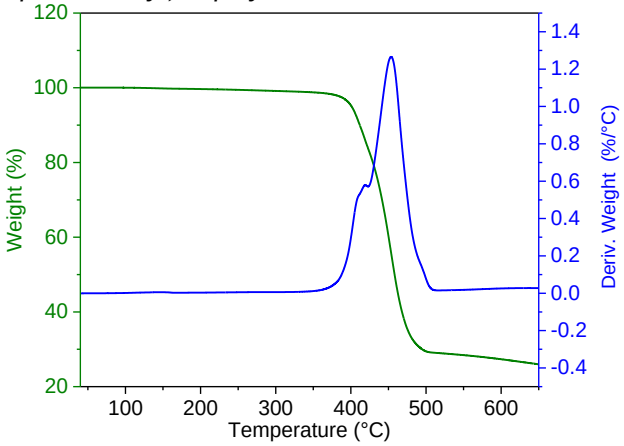
TG (green line) and DTG (blue line) curves of compound **3mM**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3sM***



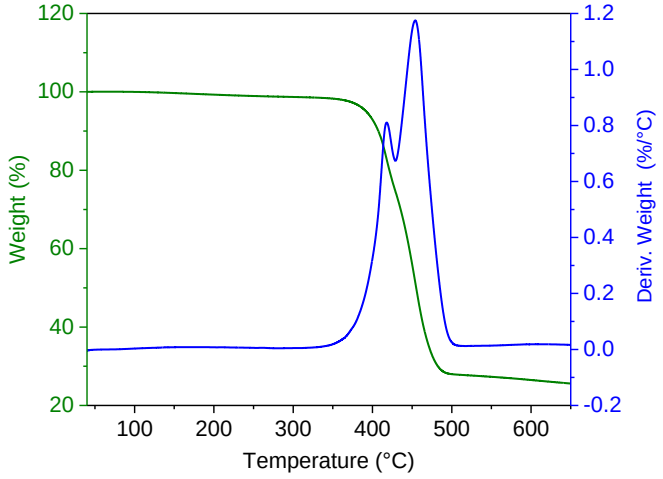
TG (green line) and DTG (blue line) curves of compound **3sM**. (10 °C/min; 40 °C to 650 °C)

3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3mT***



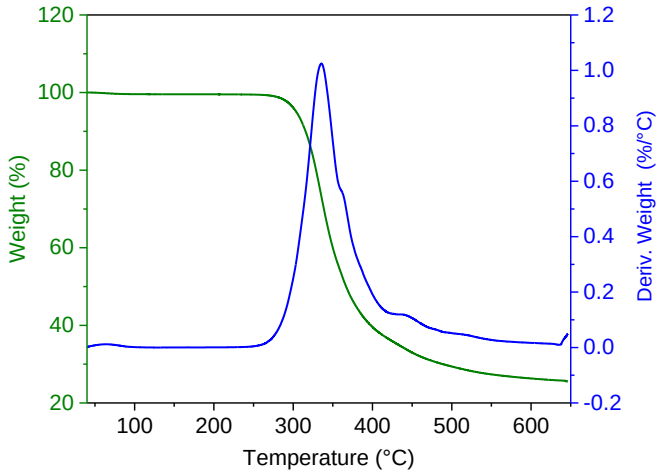
TG (green line) and DTG (blue line) curves of compound **3mT**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3sT***



TG (green line) and DTG (blue line) curves of compound **3sT**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4mM***



TG (green line) and DTG (blue line) curves of compound **4mM**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4sM***

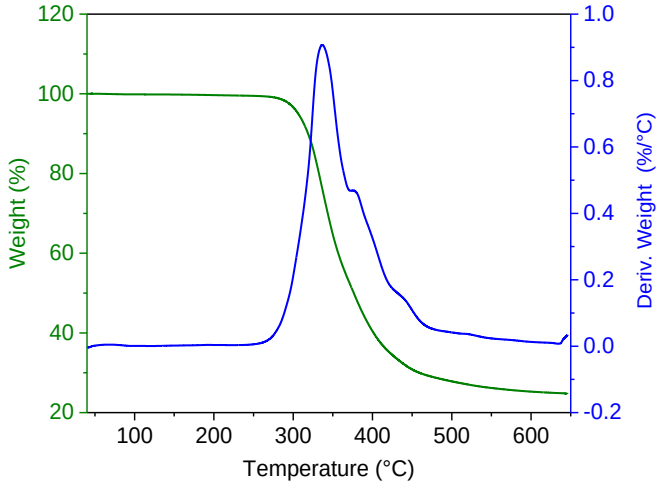
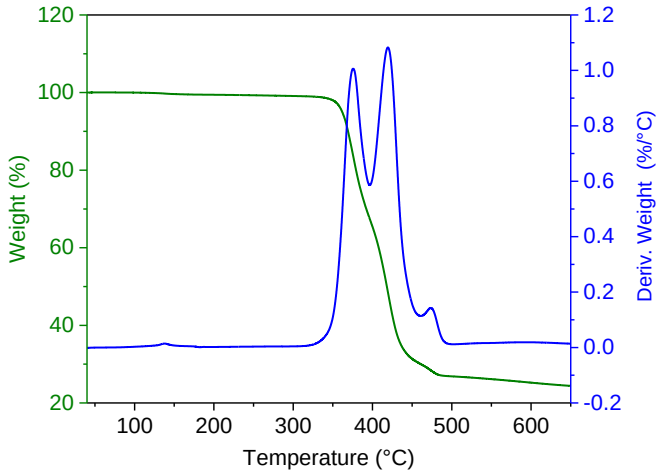


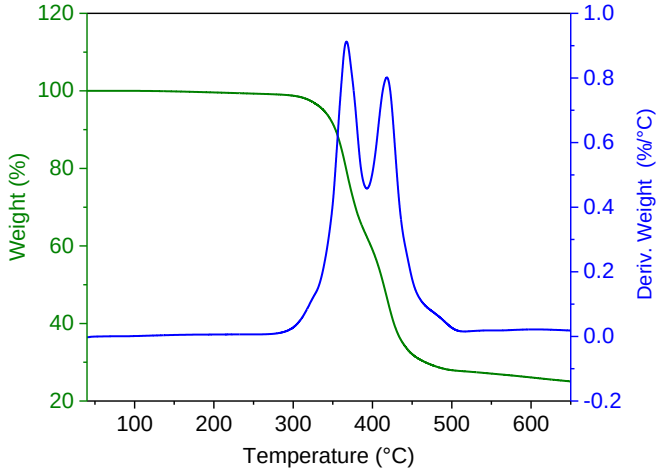
Figure E **Errore. Nel documento non esiste testo dello stile specificato.**.14. TG (green line) and DTG (blue line) curves of compound **4sM**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4mT***



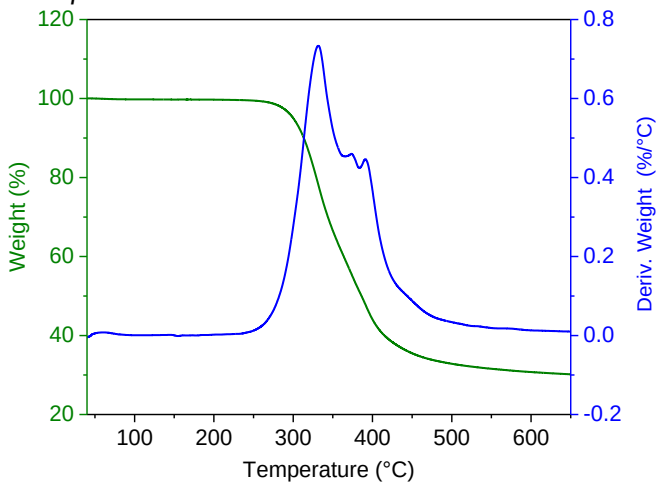
TG (green line) and DTG (blue line) curves of compound **4mT**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4sT***



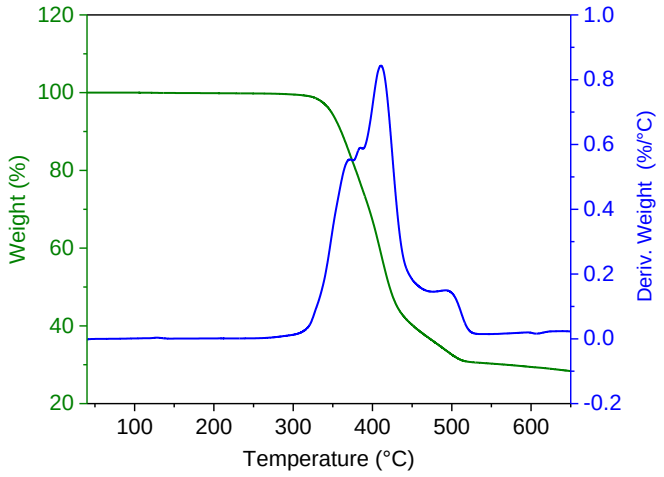
TG (green line) and DTG (blue line) curves of compound **4sT**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-quinoliniumethoxy)-2-naphthoate methanesulfonate ***5mM***



TG (green line) and DTG (blue line) curves of compound **5mM**. (10 °C/min; 40 °C to 650 °C)

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-quinoliniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***5mT***

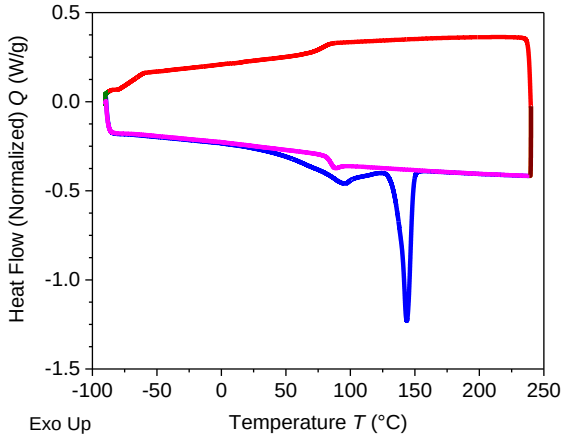


TG (green line) and DTG (blue line) curves of compound **5mT**. (10 °C/min; 40 °C to 650 °C)

2.2 Differential Scanning Calorimetry DSC

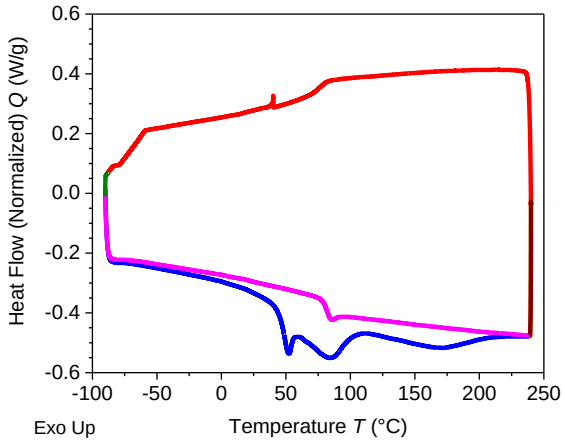
The melting points, crystallization temperatures and glass transitions were measured by a DSC250 (TA Instruments) equipped with a RSC90 refrigerated cooling system. Dry nitrogen gas was purged through the DSC cell at a flow rate of 30 cm^3/min. Each sample (1.44-7.21 mg) was sealed in an aluminium pan (Tzero, TA instruments) with a pinhole on the cap. The samples were heated to the maximal temperature (10 °C/min) to remove thermal history, then cooled to -90 °C (5 °C/min) and heated from -90 °C to the maximal temperature (10 °C/min). .

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3mM***



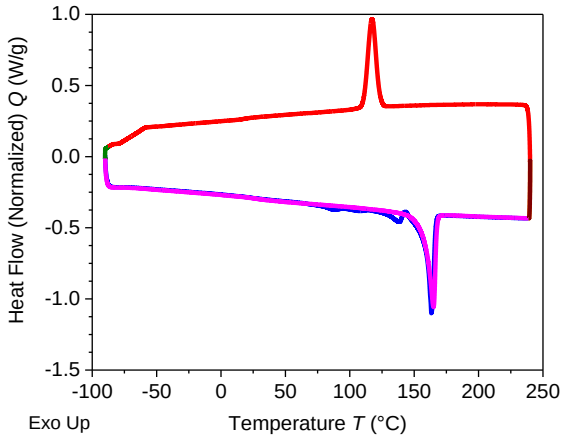
DSC of compound **3mM** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3sM***



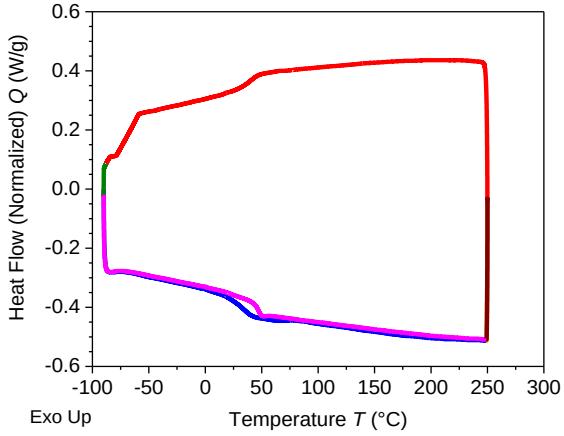
DSC of compound **3sM** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3mT***



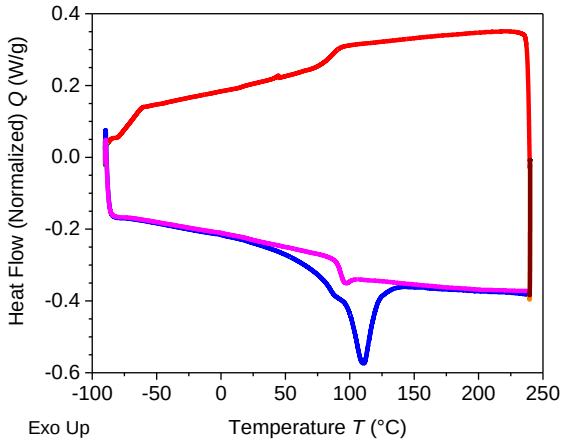
DSC of compound **3mT** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3sT***



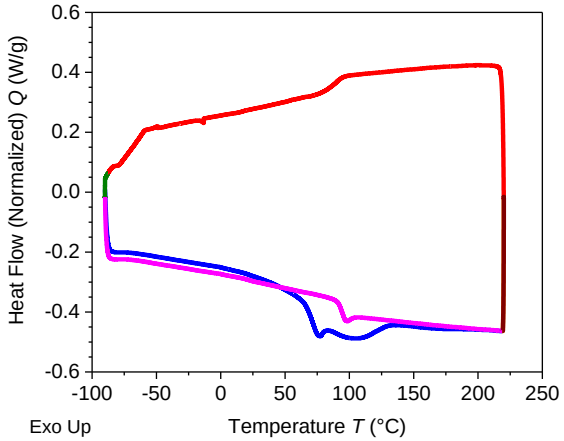
DSC of compound **3sT** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4mM***



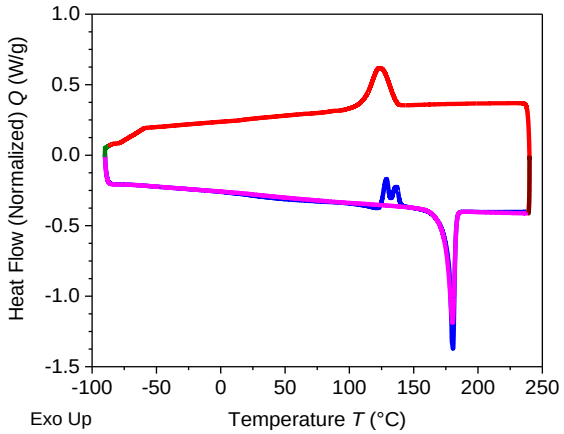
DSC of compound **4mM** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4sM***



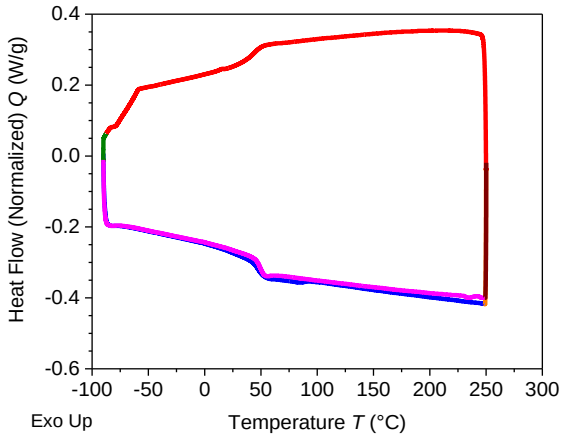
DSC of compound **4sM** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4mT***



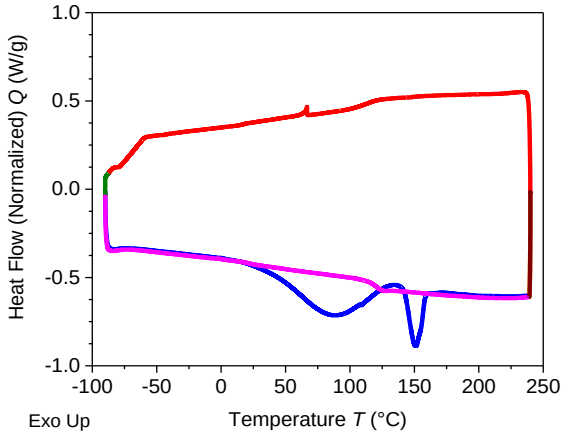
DSC of compound **4mT** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4sT***



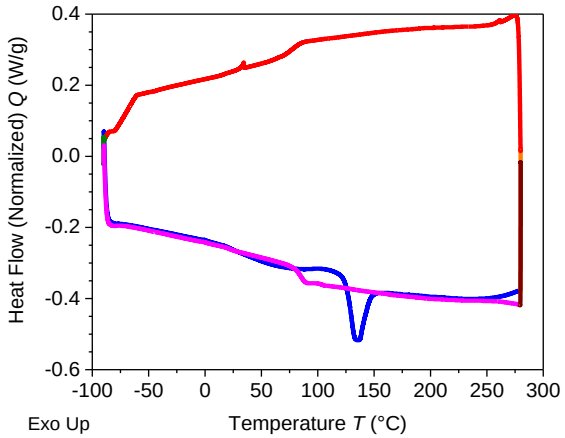
DSC of compound **4sT** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-quinoliniumethoxy)-2-naphthoate methanesulfonate ***5mM***



DSC of compound 5mM (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-quinoliniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***5mT***

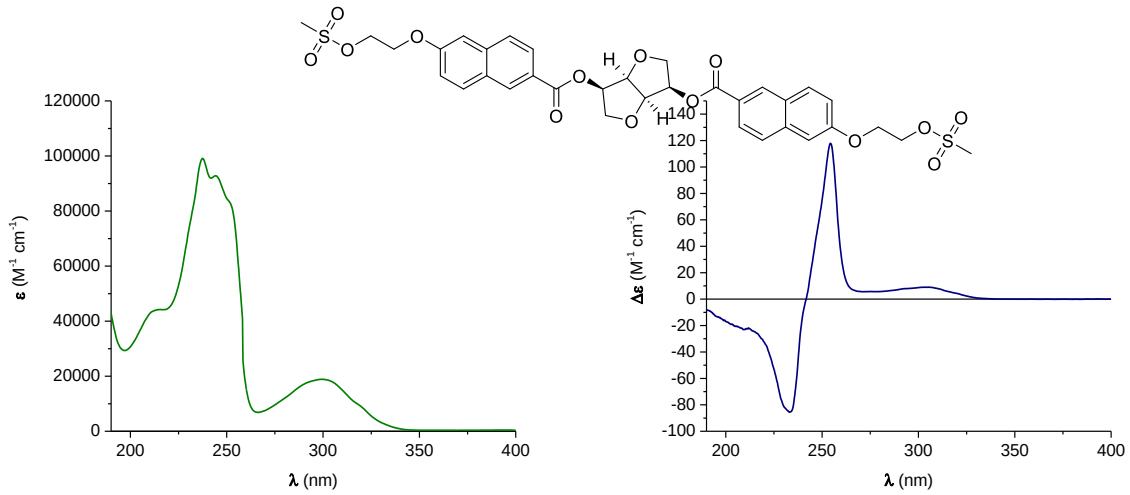


DSC of compound **5mT** (Heating ramp at 10 °C/min (blue line); Cooling ramp at 10 °C/min (red line); Heating ramp at 10 °C/min (magenta line)).

3. Electronic Absorption and Circular Dichroism Spectroscopy

ECD/UV spectra were recorded using a J-815 spectrometer (Jasco, Tokyo, Japan) at room temperature in spectroscopic grade solvents. Solutions with suitable concentrations (details are given in the legend of each figure) were measured in quartz cells with a path length of 0.01, 0.02, 0.05, 0.1 cm. All spectra were recorded using a scanning speed of 100 nm/min, a step size of 0.2 nm, a bandwidth of 1 nm, a response time of 0.5 s, and an accumulation of 8 scans. The spectra were background-corrected using the respective solvent spectra recorded under the same conditions.

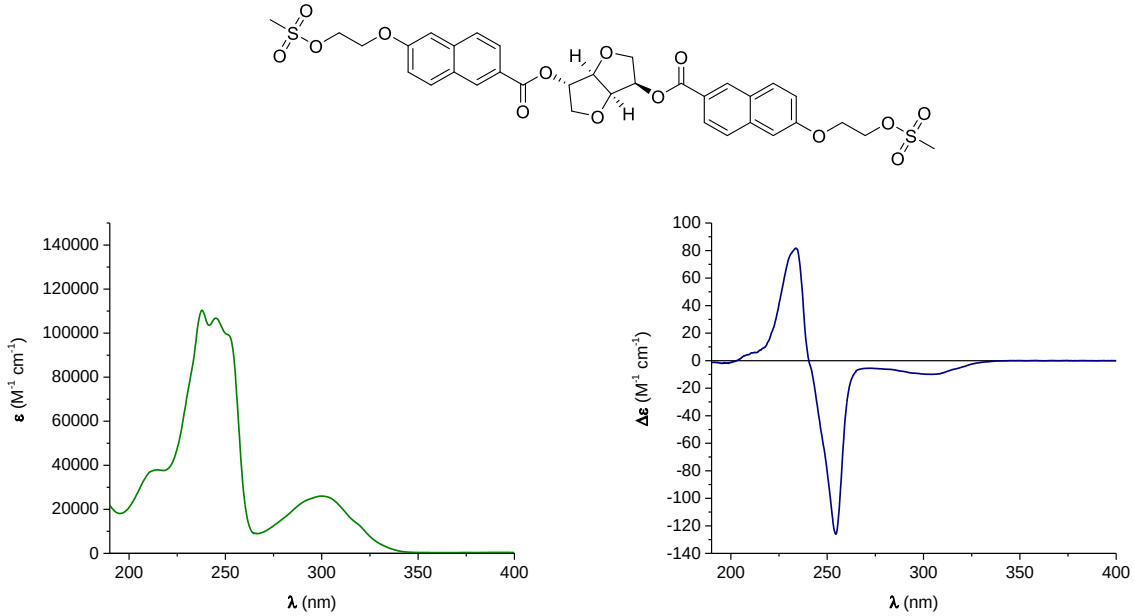
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-methanesulfonyloxy)ethoxy-2-naphthoate ***6m***



Absorption (left side) and ECD (right side) spectra of compound **6m**

(c = 3.2·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

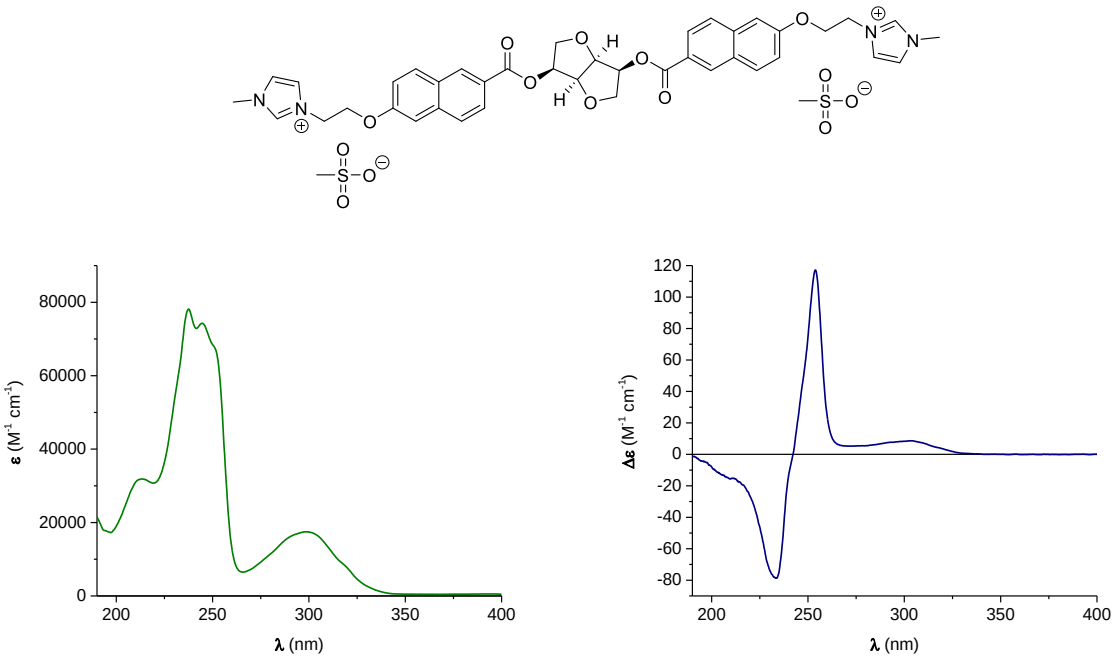
(3R,3aR,6S,6aR)- hexahydrofuro[3,2-b]furan-3,6-di-6-(2-methanesulfonyloxy)ethoxy-2-naphthoate ***6s***



Absorption (left side) and ECD (right side) spectra of compound 6s

(c = 3.4·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3mM***



Absorption (left side) and ECD (right side) spectra of compound **3mM**

(c=2.8·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate methanesulfonate ***3sM***

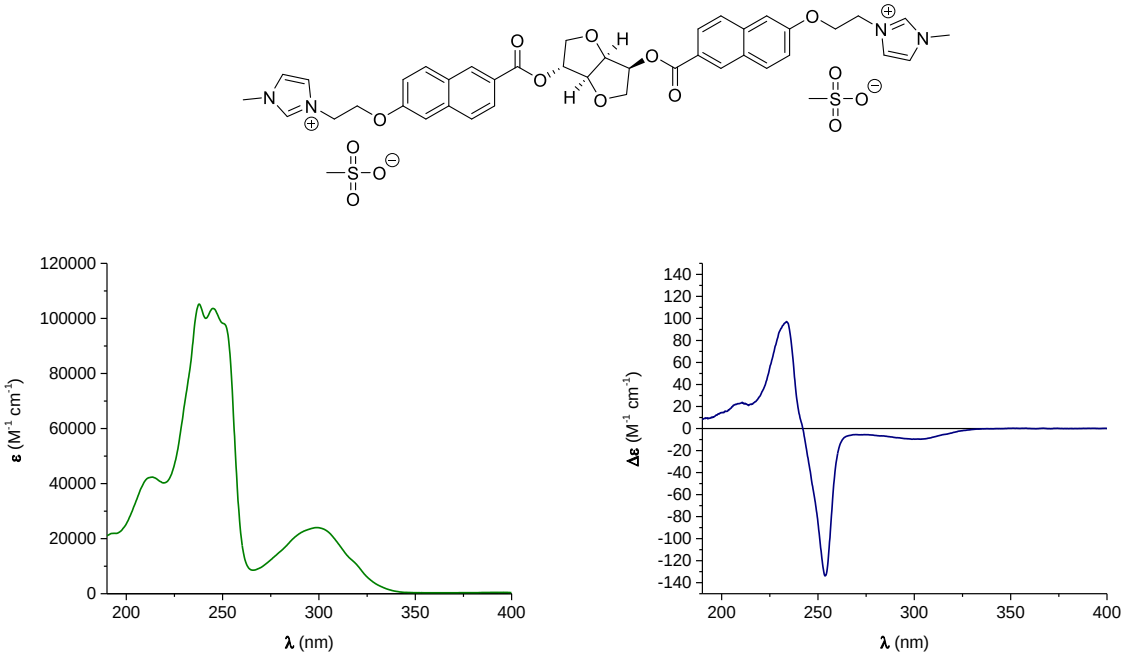
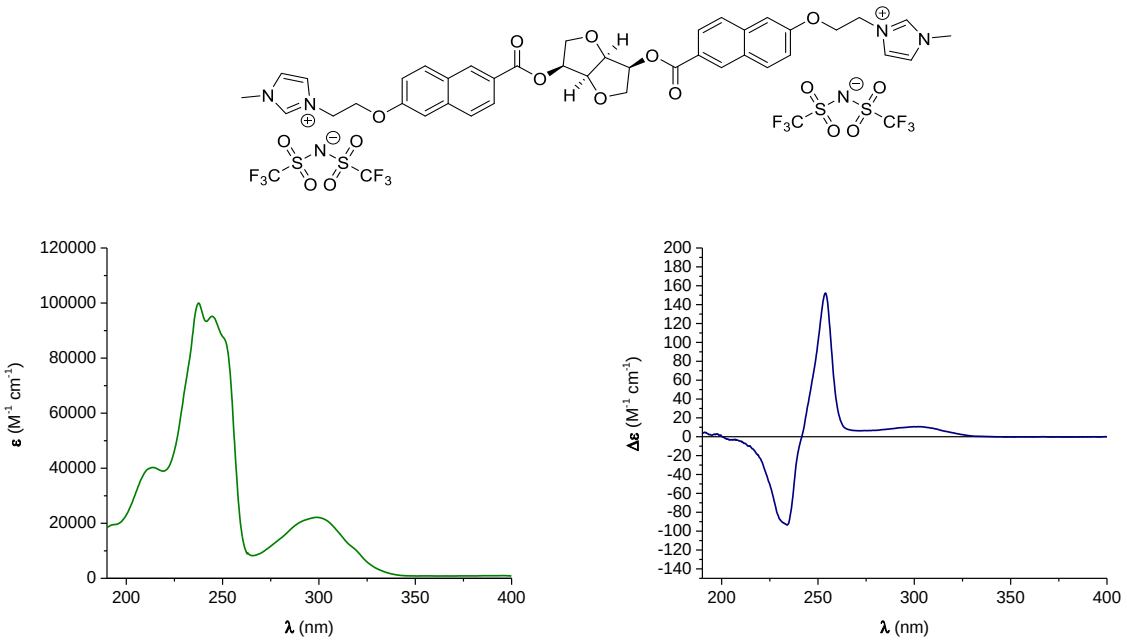


Figure S- Absorption (left side) and ECD (right side) spectra of compound **3sM**

(c=1.8·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

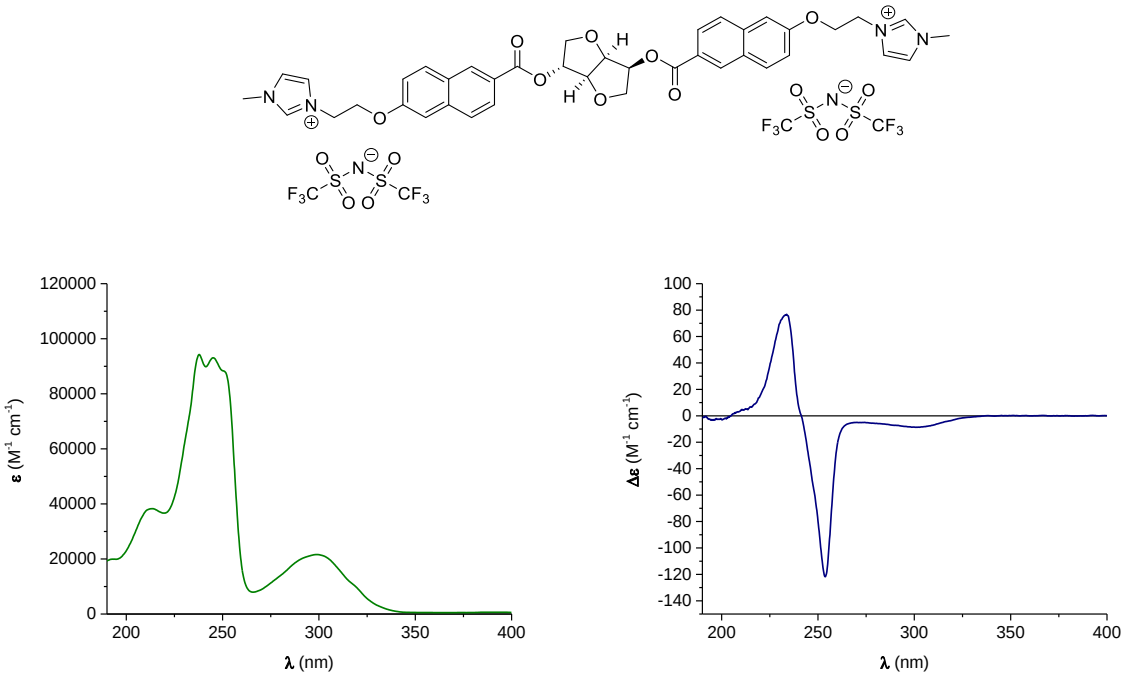
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6 di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3mT***



Absorption (left side) and ECD (right side) spectra of compound **3mT**

(c = 1.9·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

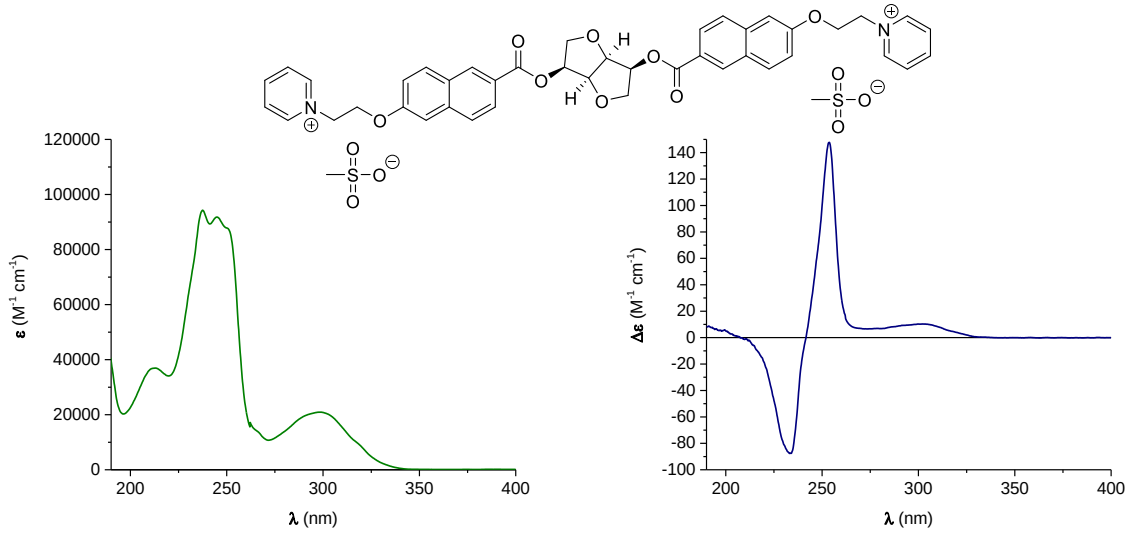
(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6 di-6-(2-N-methylimidazolium-ethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***3sT***



Absorption (left side) and ECD (right side) spectra of compound **3sT**

(c = 1.9·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

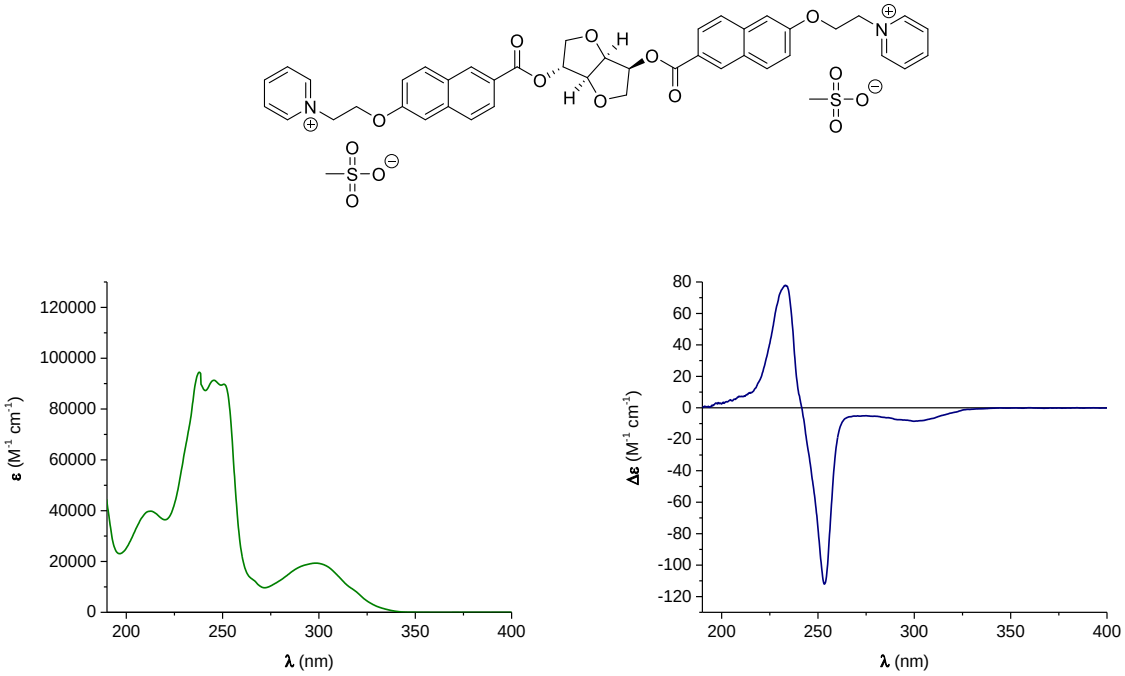
(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4mM***



Absorption (left side) and ECD (right side) spectra of compound **4mM**

(c = 2.1·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

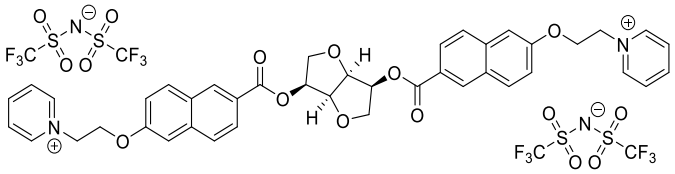
(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate methanesulfonate ***4sM***

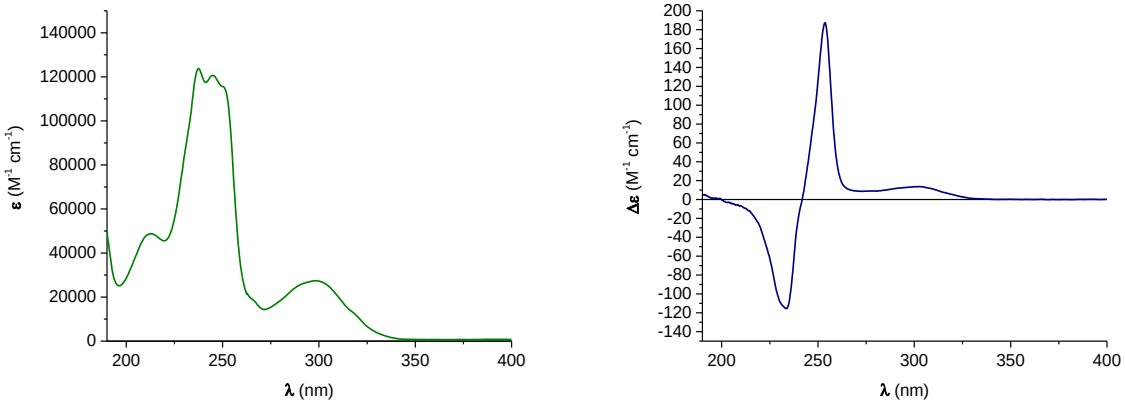


Absorption (left side) and ECD (right side) spectra of compound **4sM**

(c = 4.6·10^{-4} M in Acetonitrile, 0.01 and 0.05 cm path length).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4mT***

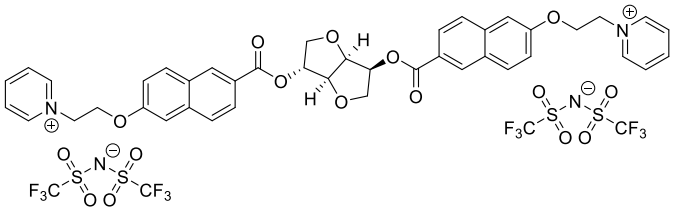


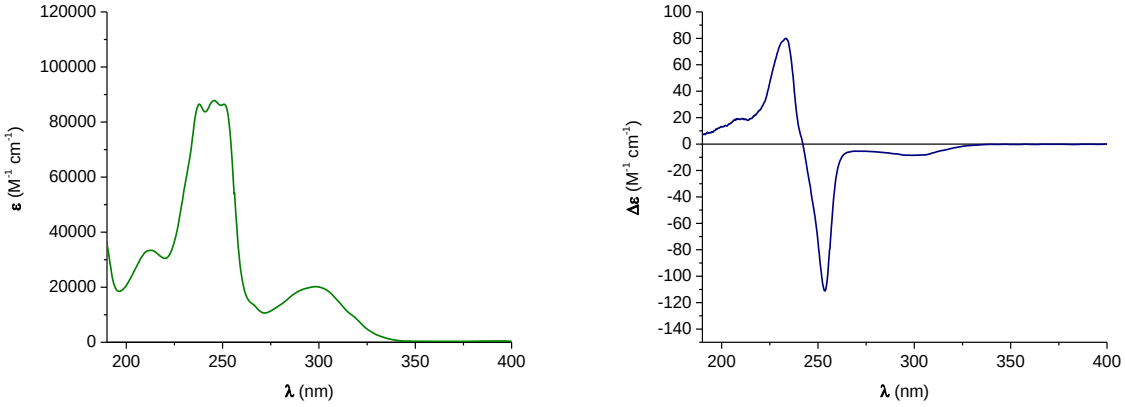


Absorption (left side) and ECD (right side) spectra of compound **4mT**

(c = 2.0·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

(3R,3aR,6S,6aR)-hexahydrofuro[3,2-b]furan-3,6-di-6-(2-pyridiniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***4sT***

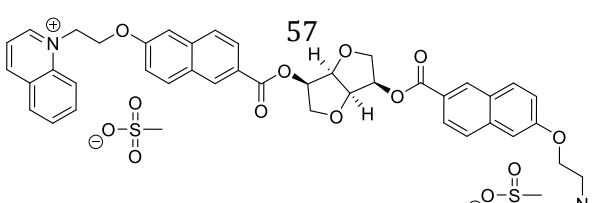


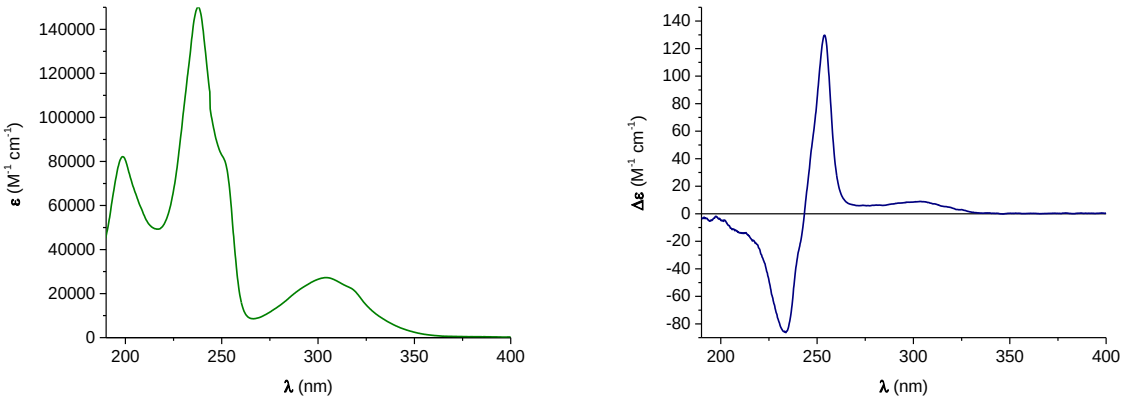


Absorption (left side) and ECD (right side) spectra of compound **4sT**

(c = 2.0·10^{-4} M in Acetonitrile, 0.02 and 0.1 cm path length).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-quinoliniumethoxy)-2-naphthoate methanesulfonate ***5mM***

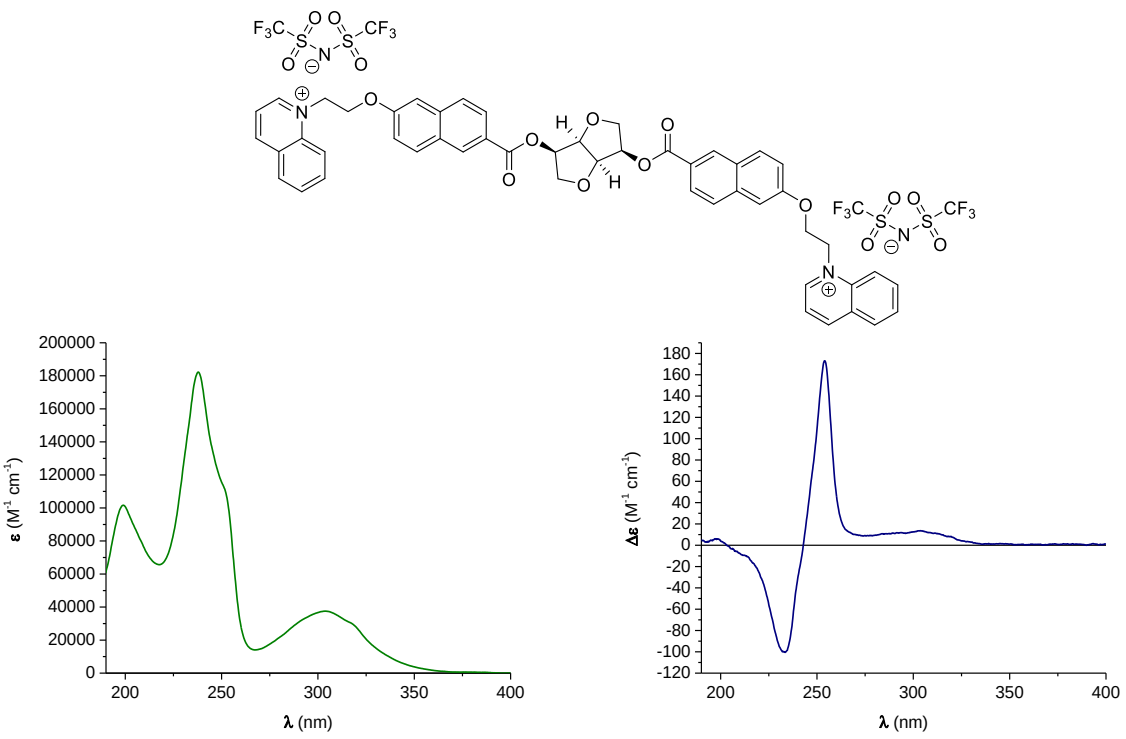




Absorption (left side) and ECD (right side) spectra of compound **5mM**

(c =2.9·10^{-4} M in Acetonitrile, 0.01 and 0.05 cm path length).

(3R,3aR,6R,6aR)-hexahydrofuro[3,2-b]furan-3,6- di-6-(2-quinoliniumethoxy)-2-naphthoate bis[(trifluoromethyl)sulfonyl]imide ***5mT***



Absorption (left side) and ECD (right side) spectra of compound **5mT**

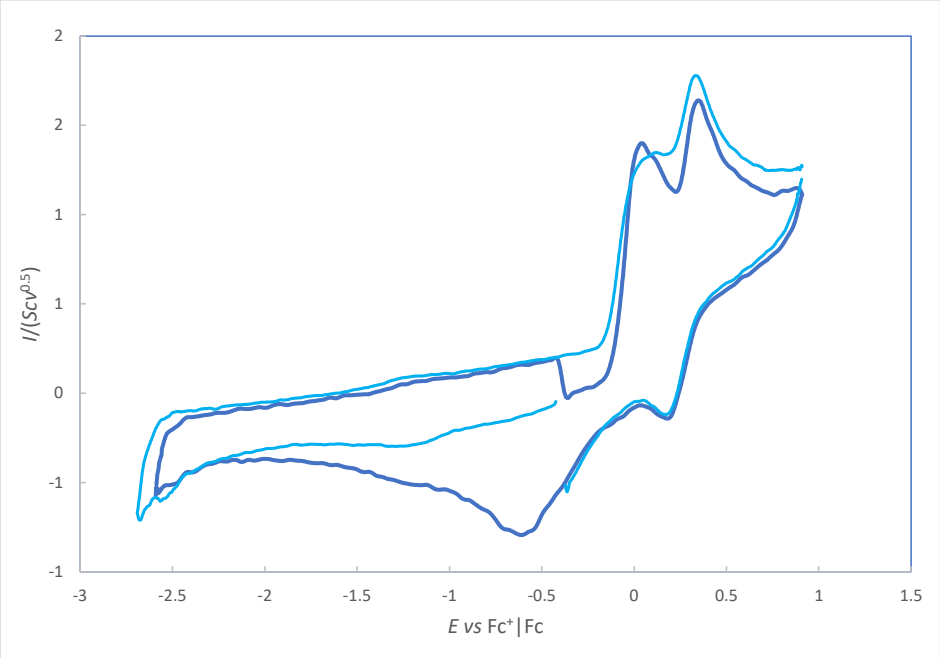
(c = 4.6·10^{-4} M in Acetonitrile, 0.01 and 0.05 cm path length).

4 Electrochemical characterization protocol and CV pattern of TMAI in $CH_3CN+TBAPF_6$

The study has been carried out by cyclic voltammetry CV at different potential scan rates (and in some cases also by differential pulse voltammetry DPV) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate $TBAPF_6$ as supporting electrolyte (while the tweezers were usually at ~0.0007-0.001 M concentration), using an Autolab PGStat potentiostat (managed by a PC with GPES software) also enabling to correct ohmic drop by the positive feedback technique. The 3-electrode glass minicell (working solution volume: 3 cm^3) included an AMEL glassy carbon working electrode (diameter 1.5 mm, mechanically polished when necessary with Aldrich synthetic diamond powder on a wet Struers DP-nap cloth), a Pt wire counter electrode, as well as a saturated calomel electrode (SCE) as reference electrode; to avoid water and KCl contamination of the working solution, the reference electrode was inserted in a compartment filled with the solvent + supporting electrolyte medium, communicating with the working compartment through a porous frit. The potentials of the recorded voltammograms were afterwards referred to the formal potential of the ferricinium|ferrocene $Fc^+|Fc$ intersolvental reference redox couple, measured in the same conditions.

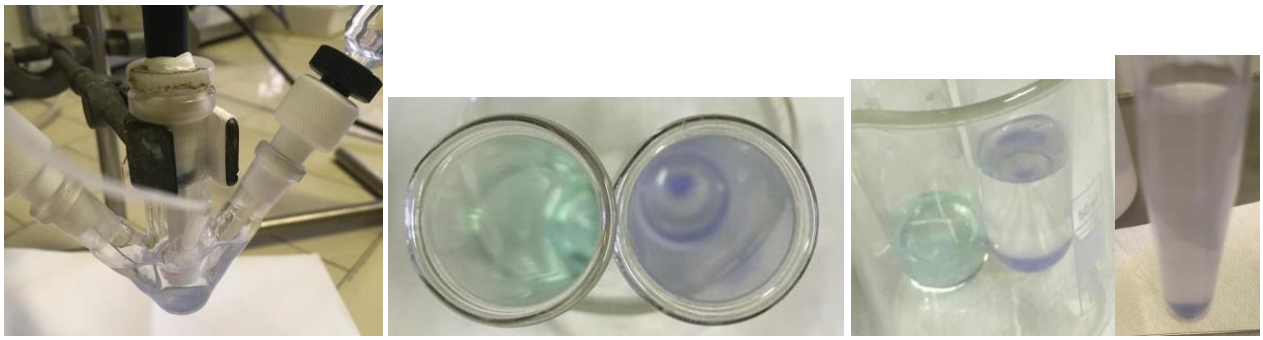
CV pattern of TMAI in $CH_3CN+TBAPF_6$

(for comparison, when discussing the CV patterns of iodide tweezers)

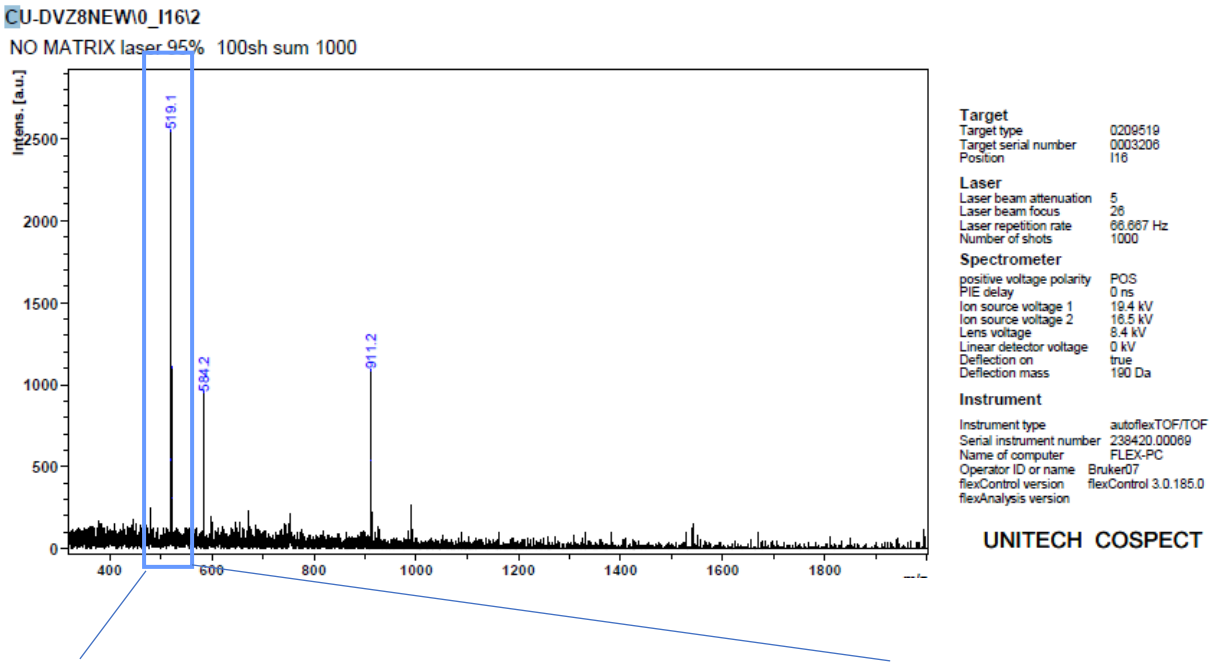


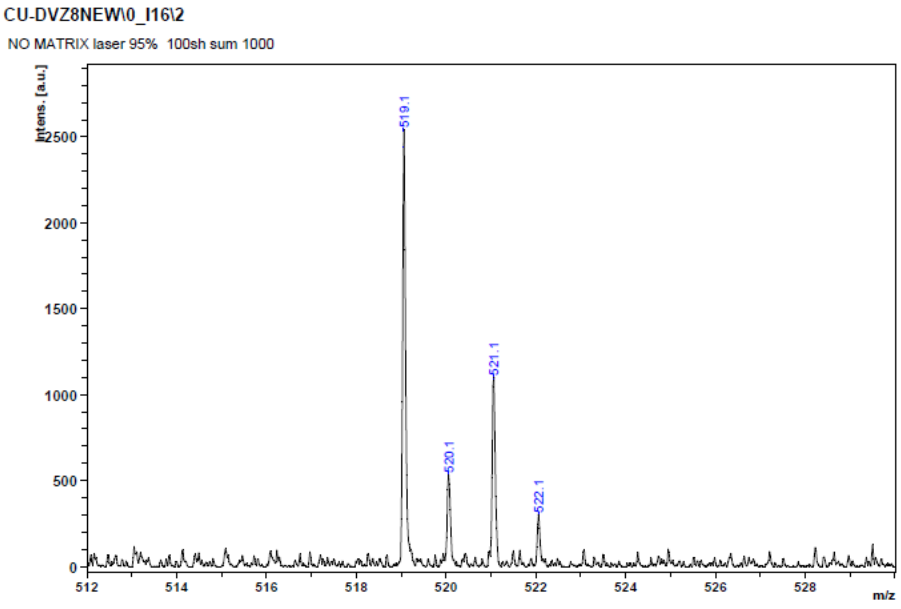
5. Solid chiral coordination compound of tweezer 9m with $Cu(NO_3)_2$

a) Images of the wisteria-coloured solid obtained by combination of neutral tweezer **9m** with $Cu(NO_3)_2$ in acetonitrile. For sake of comparison the light blue salt solution without tweezer is also reported.



b) HR LDI of the precipitate including the wisteria coordination compound and a tweezer dimer.

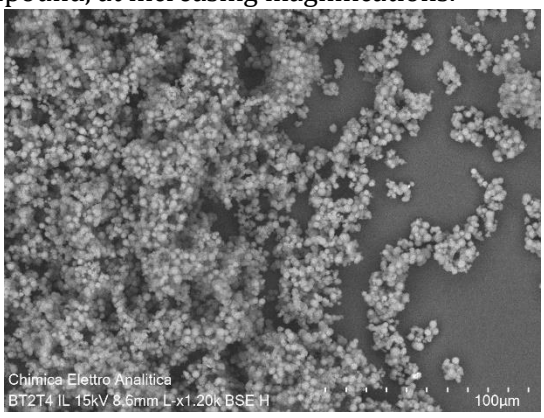




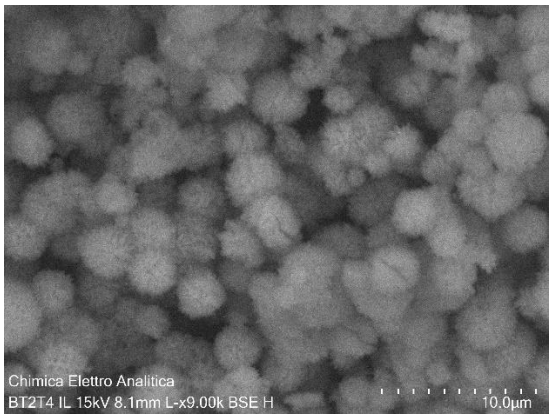
Predicted for 1:1

m/z	Intens.	Area
519.0569	2542	204
520.057	534	53
521.0572	1101	92
522.0597	304	25
584.1773	944	74
911.1889	1081	132
912.2051	531	68

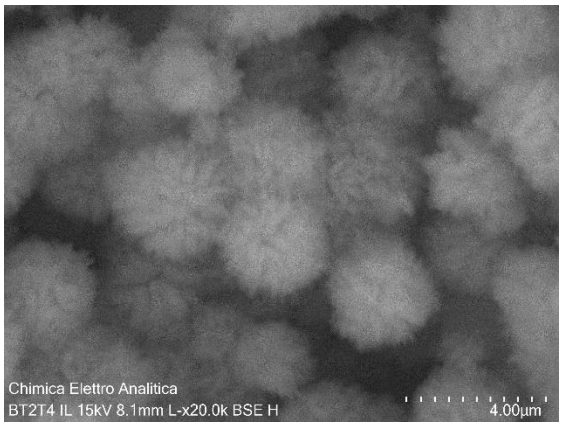
c) SEM photographs (Hitachi TM4000 II (Oxford – AztecOne)) of the precipitate including the wisteria-coloured coordination compound, at increasing magnifications.

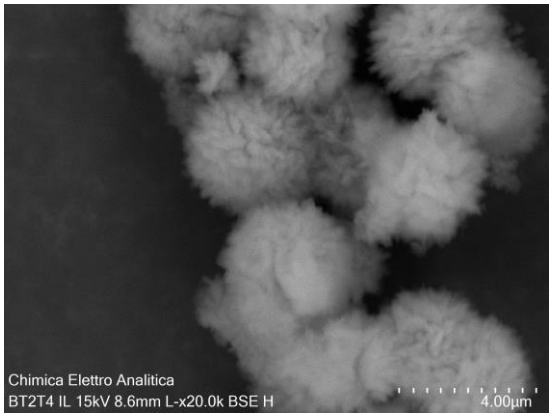


x1200

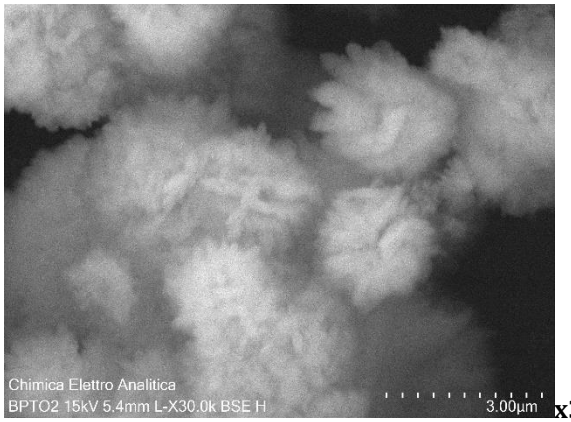


x9000



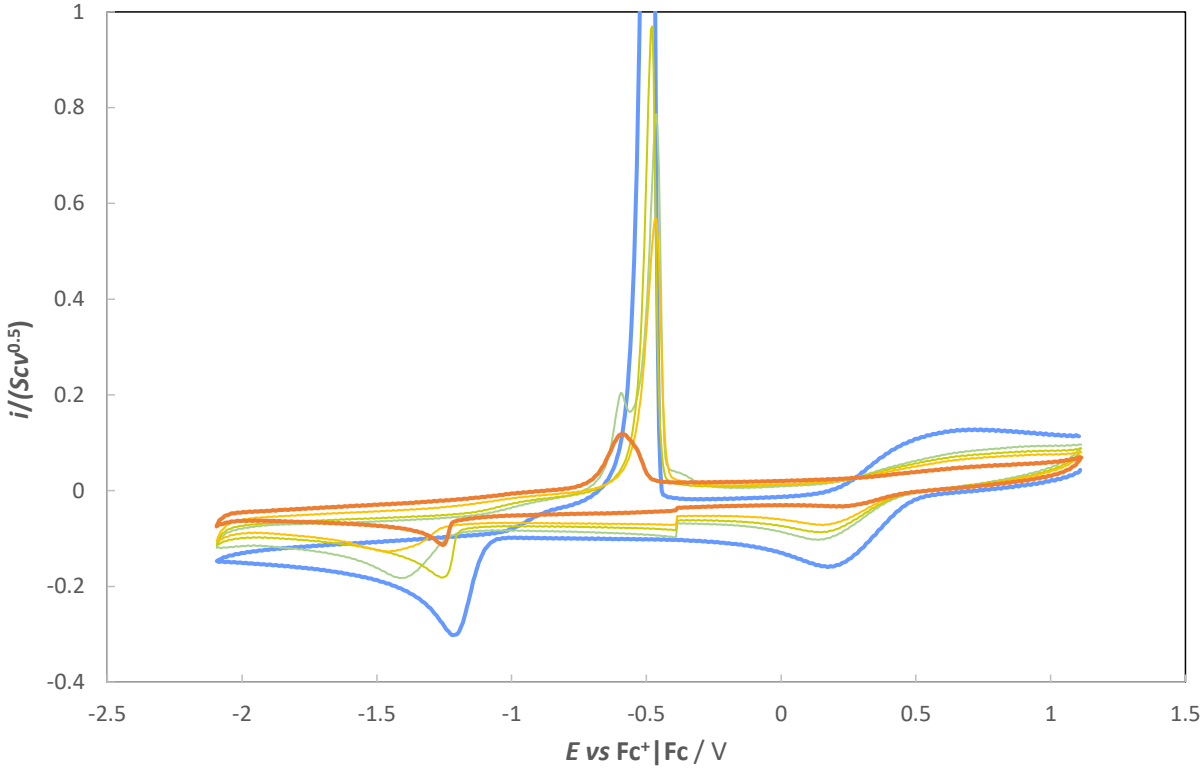


x20000

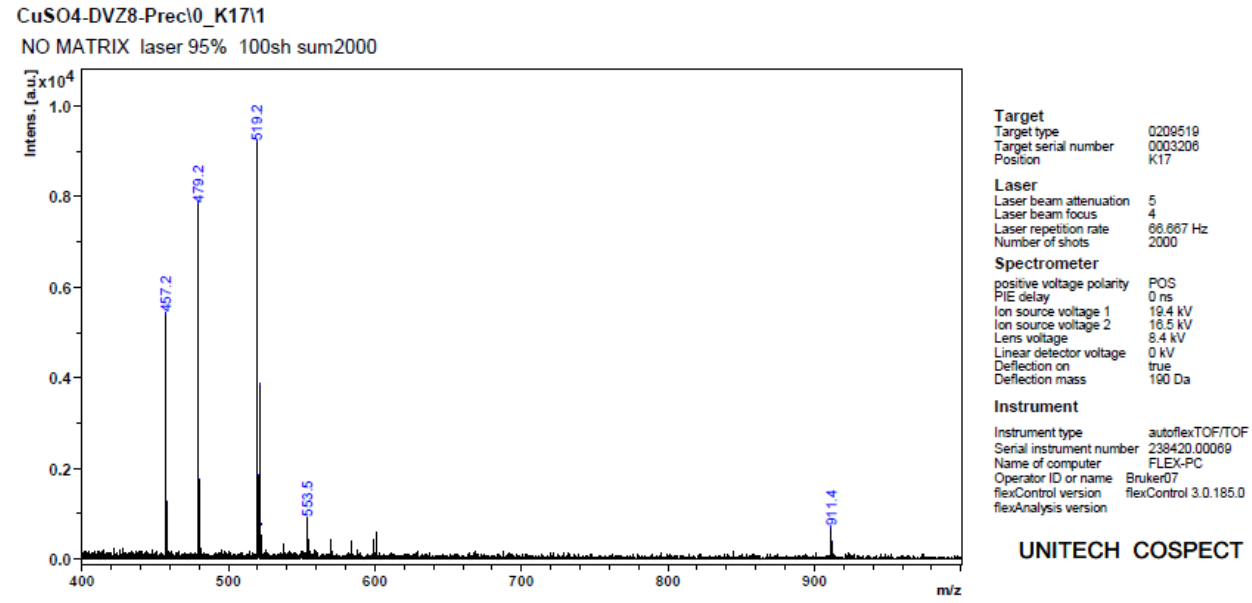


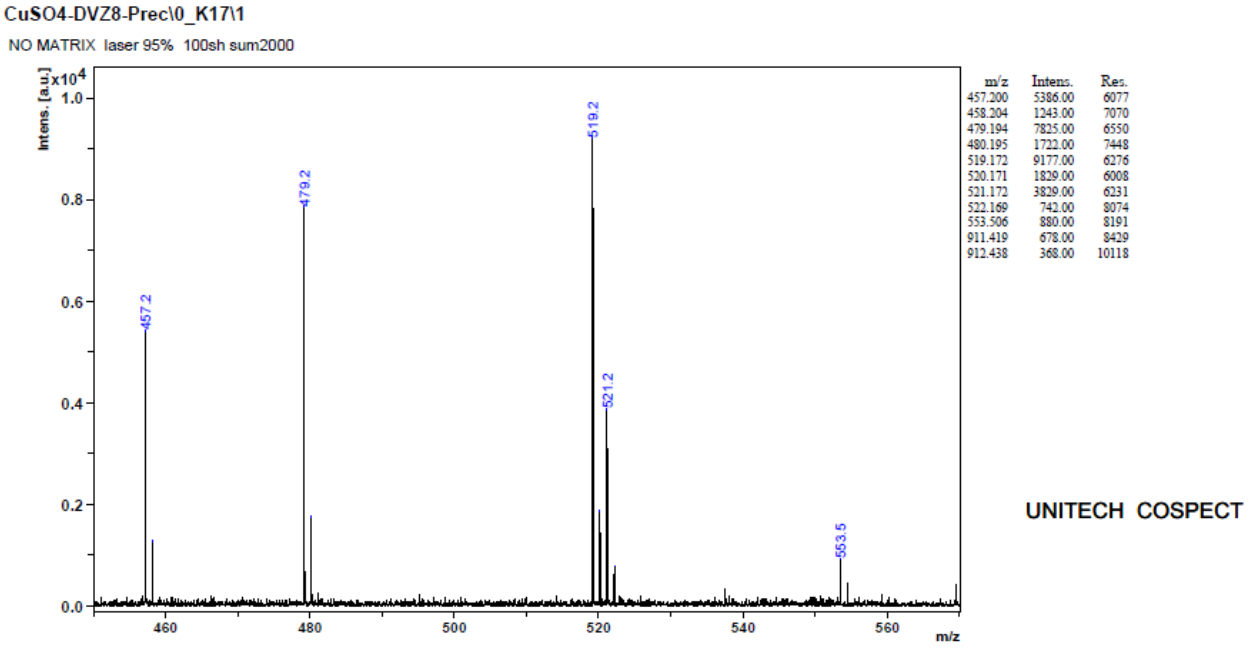
x30000

d) Selected patterns from CV monitoring of the coordination experiment (blue: $Cu(NO_3)_2$ in CH_3CN + $TBAPF_6$; green/olive/orange/sienna: subsequent changes after addition of **9m** tweezer



d) HR LDI of the spare precipitate obtained in the same conditions employing $CuSO_4$ instead of $Cu(NO_3)_2$





6. Enantiodiscrimination test protocols

Discrimination tests discussed in the main paper have been carried out working in a drop of BMIMTFSI achiral ionic liquid (Aldrich), deposited on minicells with C working and counter electrodes and Ag pseudoreference electrodes, screen printed on flexible plastic supports, employing as probes:

- (*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol (TFAE), 0.005 M in the presence of diastereomeric, quasi enantiomeric 0.1 M tweezers 2mT or 2sT;
- (+)-DNB or (–)–DNB, 0.005 M in the presence of tweezers 3mT, 5mT and 1 mT

7. Ancillary CV patterns of single compounds in conditions similar to ~~the~~ enantiodiscrimination ~~protocol~~ test ones (for sake of comparison)