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Highly modular assembly of cationic helical scaffolds: rapid synthesis of diverse helquats via differential quaternization

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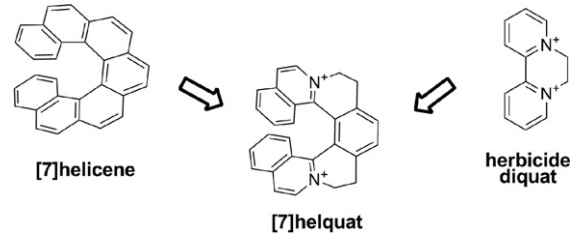
ABSTRACT

A protocol for rapid and highly modular assembly of a diverse set of helquats is described. From a common bis-isoquinoline precursor, two successive distinct pyridine-type nitrogen quaternizations followed by rhodium-catalyzed [2+2+2] cycloaddition afford non-symmetric [7]helquats. This route allows for straightforward molecular editing of cationic helical skeletons as exemplified by the synthesis of 15 different [5]-, [6]-, and [7]helquats.

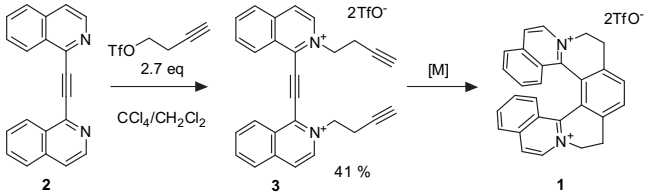
1. Introduction

The family of *N*-heteroaromatic cations[1] features important fluorescent dyes for bio-imaging[2] and non-linear optics,[2c,3] sensitizers for photography,[4] a variety of biologically active species,[5] molecular machine prototypes,[6] ionic liquids,[7] and organocatalysts.[8]

Inspired by the wealth of applications of this class of compounds, we recently introduced helquats,[9] helical dications that represent a missing structural link between helicenes[10,11] and viologens.[12] Specifically, basic [7]helquat[13] is a structural hybrid between [7]helicene and a well known herbicide diquat[12d,k] (Scheme 1). Synthesis of [7]helquat **1** starts with bisquaternization of bis-isoquinoline precursor **2** with an excess of 3-butynyltriflate followed by the key metal-catalyzed [2+2+2] cycloisomerization[9a,14] of the resulting triyne **3** (Scheme 2). Due to the wide variety of alkynyltriflates that can be



Scheme 1. Structural relation of [7]helquat to [7]helicene and herbicide diquat.



Scheme 2. Synthesis of basic [7]helquat via one-pot bis-quaternization.[9a]

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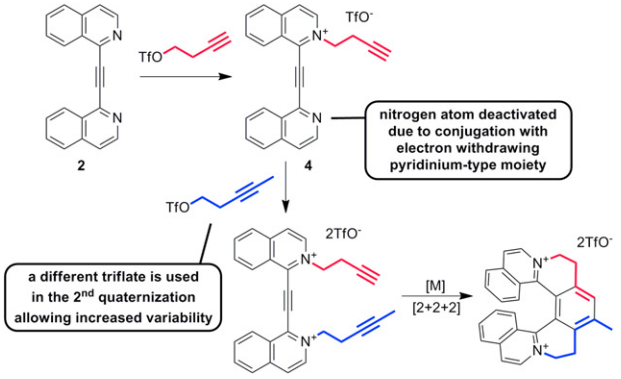
used, the route allows the synthesis of many symmetric helquats for each bis-pyridine type precursor.[9a]

We were intrigued by the possibility of sequentially attaching two different pendent alkyne moieties, thus dramatically increasing the versatility of the route. We believed we could stop the reaction at the monocation stage (Scheme 3) by using 1 equiv of quaternization agent in a low polarity solvent. Such scenario should lead to selective precipitation of monocationic product. In case the precipitation should not take place, tendency toward mono-quaternization will be governed by the likely non-equal reactivity of the pyridine-type nitrogen centers before and after the first quaternization step. Specifically, after the first quaternization, the nucleophilicity of the remaining free pyridine-type nitrogen atom will be decreased due to its conjugation with the newly formed electron poor pyridinium-type moiety, which will suppress formation of bisquaternization product. A second quaternization with a different triflate would provide non-symmetric triynes, and consequently more structurally complex helquats. This would considerably expand the scope of the synthesis of helquats allowing adjustments to the shape and substitution of the helix in a most straightforward manner.



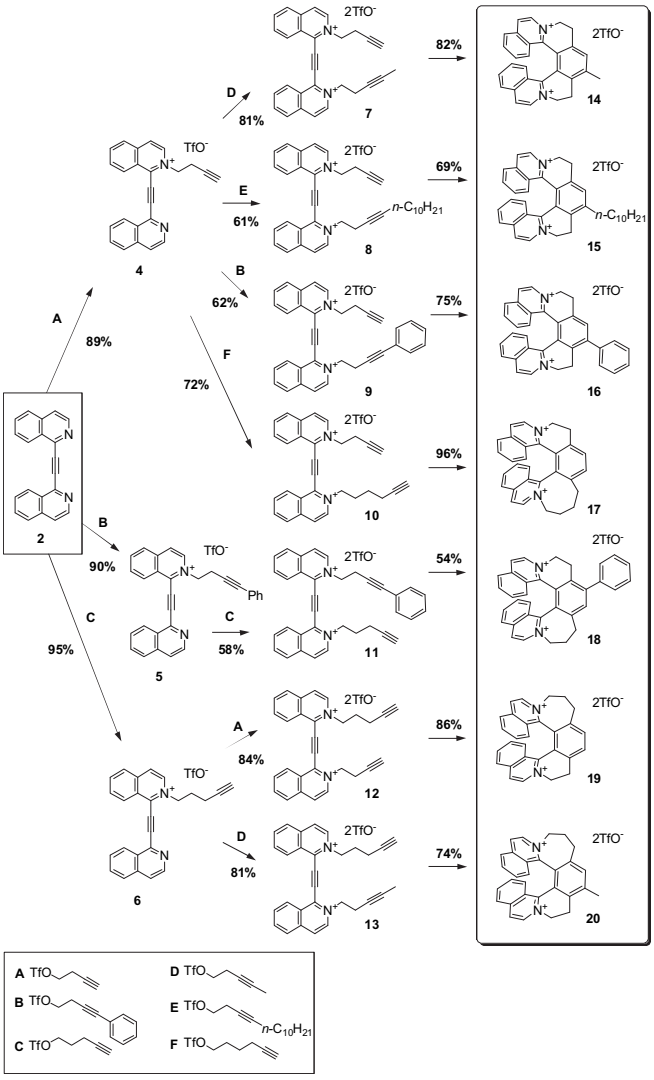
Scheme 3. Rationale for two-step differential quaternization leading to non-symmetric helquats.

2. Results and discussion

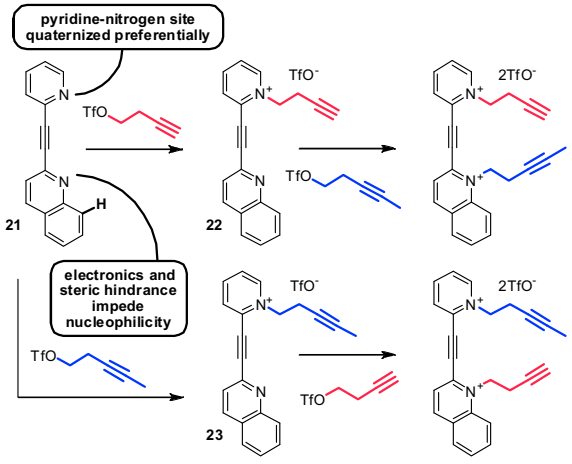
We found that clean formation of monocationic product **4** takes place employing just 1.1 equiv of 3-butynyltriflate in toluene as a solvent (Scheme 4, **2**→**4**). Gratifyingly, the formation of the dication **3** is completely blocked under these conditions and only clean monocation **4** spontaneously precipitates from the reaction mixture in high yield. Analogous monocations **5** and **6** can be prepared equally well using this protocol. With these three monocations in hand we set out to prepare a series of non-symmetric dications **7**–**13** (Scheme 4). The second *N*-quaternization proceeds smoothly in CH_2Cl_2 with an excess of the triflate reagent and the non-symmetric dications **7**–**13** are isolated typically in good yields and purities. The final intramolecular [2+2+2] cycloadditions of the triynes **7**–**13** are facile and open access to a series of non-symmetric [7]helquats **14**–**20**.[15]

The diversification made possible by the presented route deserves special attention. Thus, by combining one symmetric bis-isoquinoline precursor **2** and six distinct triflates (**A**–**F**, see inset in Scheme 4) as many as 15 non-symmetric helquats can be targeted[17] from which seven selected examples are shown in Scheme 4.

To extend this differential quaternization protocol, we decided to explore substrates containing two non-equivalent pyridine-type nitrogen atoms. Notably, if regioselective mono-quaternization of the non-symmetric precursor **21** (Scheme 5), having two different nitrogen sites, is feasible, then the differential quaternization using the same six triflates mentioned above (**A**–**F**) would now open

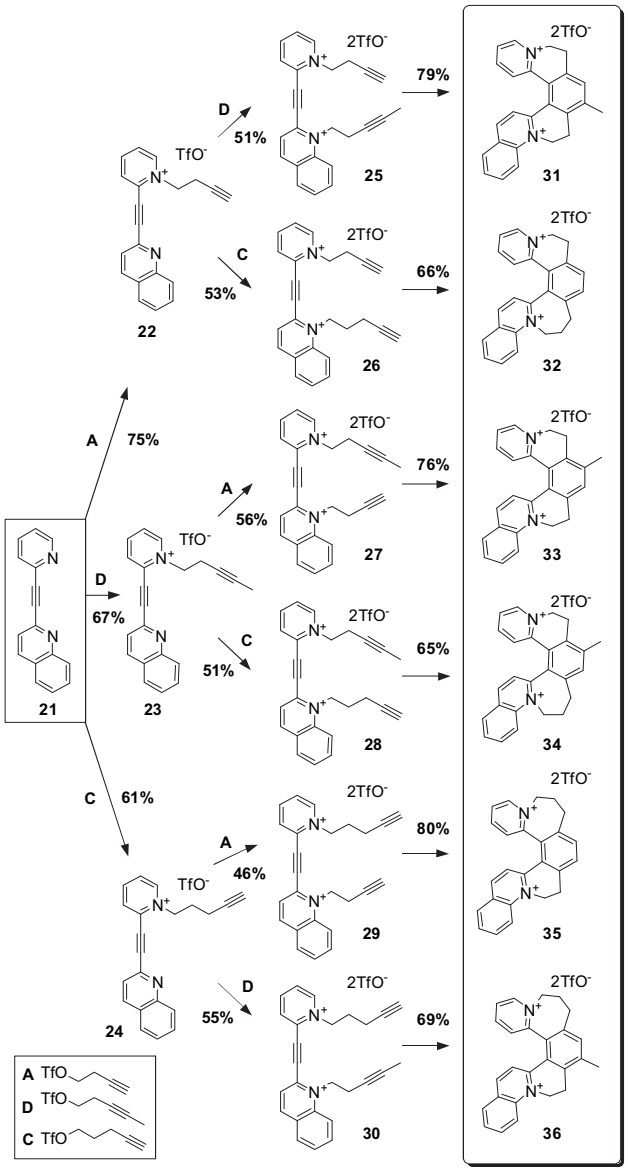


Scheme 4. Diversification of substrate **2** into seven selected non-symmetric [7]helquats. Reagents and conditions: first quaternization: triflate (1.1 equiv), toluene, 25 °C, 24–25 h; second quaternization: triflate (4–4.6 equiv), CH_2Cl_2, 25–35 °C, 46–95 h; [2+2+2] cycloaddition: $[Rh(PPh_3)_3Cl]$ (10–14 mol %), DMF, 110–130 °C, 1-2 h.[16]



Scheme 5. Differential quaternization of a substrate with non-equivalent nitrogen sites.

access to a set of 30 distinct [5]helquats.[18] To demonstrate the preparative power of this strategy we set out to synthesize all six possible non-symmetric [5]helquats starting from **21** and three selected triflates (**A**, **C**, **D**, Scheme 6).



Scheme 6. A single unsymmetric precursor **21** and three alkynyltriflates **A**, **D**, **C** lead to six distinct [5]helquats[13] in total. Reagents and conditions: first quaternization: triflate (1.1 equiv), toluene, 25 °C, 15 h; second quaternization: triflate (2–2.2 equiv), CH_2Cl_2, 50 °C, 48 h; [2+2+2] cycloaddition: $[Rh(PPh_3)_3Cl]$ (10–14 mol %), DMF, 90 °C, 30 min.[16]

The nitrogen atom in the quinoline moiety of **21** is expected to be not only less basic[19] but also less accessible due to the presence of the hydrogen atom in the *peri*-position[20] (Scheme 5). Taking advantage of this, three distinct monocations **22**, **23**, and **24** were prepared via regioselective mono-quaternization of **21** at the pyridine moiety. Subsequently, the monocations **22**–**24** were diversified into six distinct dications **25**–**30** (two dications from each monocation).[15] The six triynes prepared in this manner smoothly underwent the key intramolecular [2+2+2] cycloaddition giving the corresponding helquats **31**–**36**. See Figure 1 for X-ray of triyne **29** and helquat **35**.[15]

Next we turned to a more challenging substrate **37**, where the annulated benzene ring imparts no significant steric bias to the two reactive nitrogen sites (Scheme 7). In this respect, substrate **37** is markedly different from substrate **21** in that its two nucleophilic sites differ only electronically (cf. **37**→**38** and **21**→**22**).

Fortunately, under carefully controlled conditions preferential mono-quaternization of the isoquinoline moiety can be achieved (**37**→**38**). Although the other regioisomer of **38** is also formed

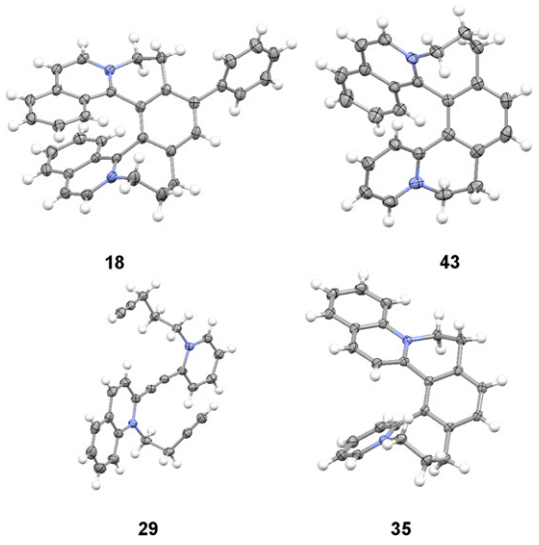
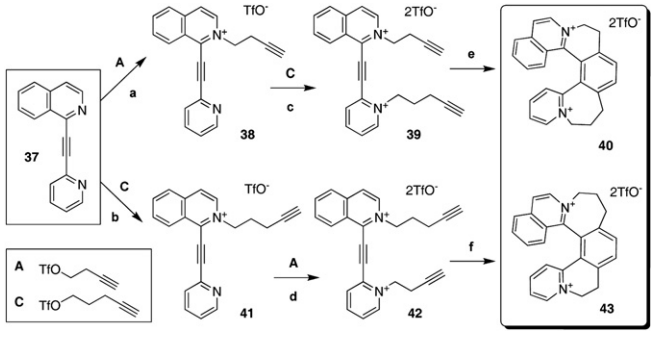


Figure 1. X-ray single crystal structure of compounds **18**, **29**, **35**, and **43**. Triflate counterions are omitted for clarity.



Scheme 7. Diversification of precursor **37** into isomeric [6]helquats **40** and **43**[15] by changing the quaternization order. Reagents and conditions: (a) **A** (1.1 equiv), toluene, −10 °C, 17 h, 49%; (b) **C** (1.1 equiv), toluene, −10 °C, 17 h, 58%; (c) **C** (4 equiv), CH_2Cl_2, 25 °C, 36 h, 82%; (d) **A** (4 equiv), CH_2Cl_2, 25 °C, 36 h, 71%; (e) $[Rh(PPh_3)_3Cl]$ (6 mol %), DMF, 100 °C, 1 h, 84%; (f) $[Rh(PPh_3)_3Cl]$ (8 mol %), DMF, 100 °C, 1 h, 99%.[16]

(ratio 6:1), sufficiently pure material[21] is obtained by means of a single recrystallization. The second quaternization and the subsequent cyclization both proceeded without difficulty to give the desired helquat **40**. Correspondingly, the isomeric helquat **43** was produced by simply switching the order of quaternization steps (see Fig. 1 for X-ray of **43**).[15]

3. Conclusion

In summary, by taking advantage of two successive distinct pyridine-type nitrogen quaternizations we demonstrate that a wide range of dicationic helical scaffolds can be rapidly accessed. The use of pyridine-type nitrogen as a functionalization handle[22] makes the route exclusively skeleton-building and therefore markedly step economic.[23] This allows the preparation of 15 helquats in only 38 steps in total[24] starting from three precursors (**2**, **21**, and **37**) and a set of six triflates **A**–**F**. Noteworthy is also the outstanding modularity inherent to this approach. The same three substrates and six triflates would give rise to a possible 75 non-symmetric helquats in total.[25] All in all, the outlined synthetic protocol considerably expands the utility of the synthesis of helquats and allows for straightforward molecular editing of cationic scaffolds. This will enable the tailoring of cationic species toward the targeted molecular properties in the pursuit of specific applications.

4. Experimental

4.1. General information

Materials, see the Supplementary data section for details. Liquids and solutions were added via needle and syringe unless otherwise stated. Melting points were determined on a Wagner & Munz PolyTherm A micro melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) analysis was performed on silica gel plates (Silica gel 60 F_{254}-coated aluminum sheets, Merck, cat. no. 1.05554.0001) and visualized by UV (UV lamp 254/365 nm, Spectroline® Model ENF—240C/FE) and/or chemical staining with $KMnO_4$ [$KMnO_4$ (1% aq), Na_2CO_3 (2% aq)]. Thin-layer chromatography (TLC) analysis of organic cation salts was achieved using Stoddart's magic mixture[26] (MeOH/NH_4Cl_{aq}(2 M)/$MeNO_2$ 70:20:10) as eluent on silica gel plates. Flash chromatography was performed on silica gel 60 (Fluka, cat. no. 60741) with the indicated eluent. Distillations of triflates were carried out bulb to bulb in a Büchi B-585 Kugelrohr Apparatus. Reactions using microwave irradiation were performed in a CEM DISCOVERY microwave system, using CEM 'snap on' caps. Sonication was conducted with a BANDELIN SONOREX sonicator. NMR spectra were measured on a Bruker Avance 600 (600 MHz for ^1H, 151 MHz for ^{13}C), or Bruker Avance 400 (400 MHz for ^1H, 100.6 MHz for ^{13}C) NMR spectrometer in $CDCl_3$ (δ_C=77.00 ppm) with TMS as internal standard (δ_H=0 ppm), acetone referenced to the CHD_2COCD_3 peak (δ_H=2.09 ppm), (CD_3)$_2$CO (δ_C=29.80 ppm). Chemical shifts are given in δ-scale as parts per million (ppm); coupling constants (J) are given in Hertz. Where indicated, the signal assignments in the NMR spectra are unambiguous; the numbering scheme is arbitrary and is shown in the inserts. Where assigned, all ^1H and ^{13}C resonance assignments are based on analysis of H,H-COSY; H,H-ROESY; H,C-HSQC and H,C-HMBC spectra. IR spectra were recorded on a Bruker EQUINOX55 (IFS55) spectrometer in $CHCl_3$, or CCl_4 (cuvette width 0.1 mm), or as KBr pellets. Abbreviation for intensities of IR bands are as follows: s for strong, vs for very strong, m for medium, w for weak. Mass spectral data were obtained at the Mass Spectrometry Facility operated by the Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic. EIMS spectra were measured at an electron energy of 70 eV; m/z values are given along with their relative intensities (%). FABMS spectra were measured using a thioglycerol–glycerol 3:1 matrix; m/z values are given. In the case of APCI MS spectra measurements, the samples were dissolved in acetone and directly infused into an APCI source (probe temperature 300 °C, source block temperature 120 °C, corona current 3.0 μA, cone voltage 25 V). ESI mass spectra were recorded using a Thermo Scientific LCQ Fleet mass spectrometer equipped with an electrospray ion source and controlled by Xcalibur software. The mobile phase consisted of methanol/water (9:1), flow rate of 200 μl/min. The sample was dissolved, diluted with the mobile phase and injected using a 5 μl loop. Spray voltage, capillary voltage, tube lens voltage and capillary temperature were 5.5 kV, 5 V, 80 V and 275 °C, respectively. HRMS spectra were obtained with the EI or APCI instruments.

Water content in organic cations: often the samples of the organic cations contained varying amounts of water (usually 0.5–2 molecules of water per monocation or dication) as evidenced by respective NMR as well as elemental analyses. Water content in the individual samples can vary slightly between different preparations of the compounds.

Coloration of some compound samples (e.g., brown compound samples **31**–**36** in Scheme 6): From viologen chemistry it is known that trace amounts of pyridine-type starting materials sometimes remain in products after *N*-quaternization reaction steps. They can be difficult to remove and are typically cause of color in viologen samples due to the formation of strongly colored charge-transfer species (discussion in Ref. 12d, page 33). Such species are very probably the cause of the color of some compound samples in this report (e.g., in compounds **31**–**36**). However, we note that only trace amounts of these impurities can be present as suggested both by elemental analyses and NMR spectra (see Supplementary data section for NMR scans). Consequently, according to the elemental analyses and NMR spectra, we regard all the compounds reported herein to be of sufficient purity for all practical purposes and demands of organic synthesis, e.g., as starting materials, reagents, or catalysts. Nevertheless, we note that samples described as 'brown' in this report, most probably will not be suitable for 'photonic' research (e.g., fluorescence studies) unless higher purity will be achieved by additional purification. In this context, we also note that attempted decolorizing by using charcoal does not appear effective in cases tested.

4.2. Synthesis of triflates A–F, general

Recently Quagliotto et al. published paper detailing a facile method for producing triflates.[27] We have found this procedure particularly convenient. Once prepared, the triflates can be stored for months in the freezer, showing no signs of significant decomposition (as seen by ^1H NMR and coloration of the material). The triflates are generally obtained as brown liquids, and can be distilled to give colorless liquids. Bulb to bulb distillation using a Kugelrohr apparatus proved to be especially practical. With or without distillation the triflates gave good results in the transformations described in this paper. It should be noted that the densities of the triflates varied slightly between different runs.

Procedure: A solution of the desired alcohol (1 equiv) and dry pyridine (1 equiv) in dry DCM is added dropwise via syringe to a stirring solution of trifluoromethanesulfonic anhydride (1 equiv) in dry DCM at 0 °C under Ar. Upon addition a white precipitate of pyridinium triflate forms. The reaction mixture stirs at 0 °C for 0.5 h, and is then diluted with water. The organic layer is separated and washed with water (1×), dried over Na_2SO_4, filtered and concentrated in vacuo (300 mbar at 25 °C) to give a light rose colored liquid.

*4.2.1. But-3-ynyl trifluoromethanesulfonate (**A**).* Following the general procedure for triflate formation, a solution of 3-butyn-1-ol (1.38 mL, 18.3 mmol, 1 equiv), and pyridine (1.48 mL, 18.3 mmol, 1 equiv) in DCM (7 mL), and a solution of trifluoromethanesulfonic anhydride (3.0 mL, 18.3 mmol, 1 equiv) in DCM (10 mL) gave but-3-ynyl trifluoromethanesulfonate (**A**) as a colorless liquid after distillation in 52% yield (1.921 g, 9.5 mmol). The spectroscopic characterization data is in agreement with the literature.[27]

d=1.33. Bp 55 °C at 2 mbar. ^1H NMR (400 MHz, $CDCl_3$): δ=2.11 (t, J=2.7 Hz, 1H); 2.73 (td, J=6.7, 2.7 Hz, 2H); 4.57 (t, J=6.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=19.89; 71.77; 73.50; 76.86; 118.61 (q, J=319.6 Hz). Elem. Anal. Calcd for $C_5H_5F_3O_3S$: C, 29.71; H, 2.49; S, 15.86. Found: C, 29.65; H, 2.45; S, 15.67.

*4.2.2. 4-Phenylbut-3-ynyl trifluoromethanesulfonate (**B**).* Following the general procedure for triflate formation, a solution of 4-phenylbut-3-yn-1-ol[28] (66.0 mg, 0.45 mmol, 1 equiv) and pyridine (36.0 μL, 0.45 mmol, 1 equiv) in DCM (2 mL) and a solution of trifluoromethanesulfonic anhydride (77 μL, 0.45 mmol, 1 equiv) in DCM (2 mL) gave pure 4-phenylbut-3-ynyl trifluoromethanesulfonate (**B**) as a brown liquid in 93% yield (117 mg, 0.42 mmol). The spectroscopic characterization data is in agreement with the literature.[29]

d=1.34. ^1H NMR (400 MHz, $CDCl_3$): δ=2.97 (t, J=6.8 Hz, 2H); 4.66 (t, J=6.8 Hz, 2H); 7.27–7.36 (m, 2H); 7.38–7.45 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=20.85; 73.84; 82.04; 83.69; 118.64 (q, J=319.8 Hz); 122.56; 128.31; 128.41; 131.68.

*4.2.3. Pent-4-ynyl trifluoromethanesulfonate (**C**)*[30]. Following the general procedure for triflate formation, a solution of 4-pentyn-1-ol (1.0 mL, 10.7 mmol, 1 equiv) and pyridine (0.84 mL, 10.4 mmol, 0.97 equiv) in DCM (6 mL) and a solution of trifluoromethanesulfonic anhydride (1.85 mL, 11.3 mmol, 1.06 equiv) in DCM (6 mL) gave pure pent-4-ynyl trifluoromethanesulfonate (**C**) as a colorless liquid after distillation in 84% yield (1.950 g, 9.03 mmol).

d=1.42. Bp 55 °C at 2 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.99–2.09 (m, 2H); 2.03 (t, J=2.7 Hz, 1H); 2.39 (td, J=6.8, 2.7 Hz, 2H); 4.68 (t, J=6.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=14.49; 28.01; 70.22; 75.43; 81.13; 118.64 (q, J=319.6 Hz). Elem. Anal. Calcd for $C_6H_7F_3O_3S$: C, 33.34; H, 3.26; S, 14.83. Found: C, 33.15; H, 3.26; S, 14.68.

*4.2.4. Pent-3-ynyl trifluoromethanesulfonate (**D**).* Following the general procedure for triflate formation, a solution of pent-3-yn-1-ol (0.28 mL, 3.05 mmol, 1 equiv) and pyridine (0.25 mL, 3.05 mmol, 1 equiv) in DCM (1.2 mL) and a solution of trifluoromethanesulfonic anhydride (0.5 mL, 3.05 mmol, 1 equiv) in DCM (1.7 mL) gave pure pent-3-ynyl trifluoromethanesulfonate (**D**) as a colorless liquid after distillation in 53% yield (0.350 g, 1.62 mmol). The spectroscopic characterization data is in agreement with the literature.[31]

d=1.28. Bp 65 °C at 2 mbar. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.78 (t, J=2.5, 3H); 2.67 (tq, J=6.9, 2.5 Hz, 2H); 4.53 (t, J=6.9 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=3.28; 20.19; 71.67; 74.41; 79.41; 118.62 (q, J=319.6 Hz). Elem. Anal. Calcd for $C_6H_7F_3O_3S$: C, 33.39; H, 3.26; S, 14.83. Found: C, 32.97; H, 3.27; S, 14.67.

*4.2.5. Tetradec-3-ynyl trifluoromethanesulfonate (**E**).* Following the general procedure for triflate formation, a solution of tetradec-3-yn-1-ol (143.4 mg, 0.68 mmol, 1 equiv) and pyridine (55 μL, 0.68 mmol, 1 equiv) in DCM (2 mL) and a solution of trifluoromethanesulfonic anhydride (117 μL, 0.70 mmol, 1.03 equiv) in DCM (2 mL) gave tetradec-3-ynyl trifluoromethanesulfonate (**E**) as a yellow liquid in 96% yield (0.2254 g, 0.66 mmol).

d=1.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, J=6.8 Hz, 3H); 1.17–1.40 (m, 14H); 1.42–1.53 (m, 2H); 2.14 (tt, J=7.1, 2.3 Hz, 2H); 2.69 (tt, J=6.9, 2.3 Hz, 2H); 4.53 (t, J=6.9 Hz, 2H). ^{13}C NMR (151 MHz, acetone-d_6): δ=14.31; 18.94; 20.51; 23.28; 29.42; 29.45; 29.83; 30.01; 30.22; 30.25; 32.57; 74.54; 77.28; 83.67; 118.92 (q, J=319.6 Hz).

*4.2.6. Hex-5-ynyl trifluoromethanesulfonate (**F**).* Following the general procedure for triflate formation, a solution of hex-5-yn-1-ol (0.50 mL, 4.61 mmol, 1 equiv) and pyridine (0.37 mL, 4.57 mmol, 0.99 equiv) in DCM (5 mL) and a solution of trifluoromethanesulfonic anhydride (0.78 mL, 4.70 mmol, 1.02 equiv) in DCM (5 mL) gave hex-5-ynyl trifluoromethanesulfonate (**F**) as a brown liquid in 79% yield (0.8348 g, 3.63 mmol). The spectroscopic characterization data is in agreement with the literature.[32]

d=1.33. ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.62–1.72 (m, 2H); 1.93–2.02 (m, 2H); 1.99 (t, J=2.7 Hz, 1H); 2.28 (td, J=6.8, 2.7 Hz, 2H); 4.58 (t, J=6.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=17.71; 23.91; 28.17; 69.43; 76.90; 82.83; 118.66 (q, J=319.6 Hz).

4.3. Synthesis of organic monocations

Organic monocations were synthesized by a general procedure, which was followed by one of three workup procedures. The desired alkynyltriflate (**A**–**F**) (1.1 equiv) was added dropwise, either as a solution in toluene or neat, to a stirred solution of Sonogashira coupling product (**2**, **21**, **37**) (1 equiv) in dry toluene at −10 °C or 25 °C under Ar. The flask was protected from light with Al-foil and the reaction stirred at the previously noted temperature for 25 h during which time the product precipitated out of solution as a fine suspension.

4.4. Workup procedure I (4, 5, 6)

The supernatant solution was separated from the fine powder via centrifuge and then removed via decantation. Reagent grade toluene was added to the powder, now contained in a centrifuge tube, and the suspension was sonicated to ensure good mixing of the solid and supernatant solution. The supernatant solution was once again separated from the solid via centrifugation and decantation. The toluene washing procedure was repeated. The product was transferred to a vial and dried under vacuum (2 mbar) to give pure organic monocation salt.

4.5. Workup procedure II (22, 23, 24)

The precipitate was isolated via filtration and the filter cake was washed with cold diethyl ether. Diethyl ether/tetrahydrofuran 1:1 (8 mL) was added to the powder and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min. The supernatant solution was separated from the solid via centrifugation and decantation. The diethyl ether/tetrahydrofuran washing procedure was repeated (2×). The fine solid was isolated via filtration, transferred to a vial and dried under vacuum (2 mbar) to give pure organic monocation salt.

4.6. Workup procedure III (38, 41)

The precipitate was isolated via filtration and the filter cake was washed with toluene, followed by hexane. The crude product was dissolved in a 1:1 mixture of toluene and 2-propanol aided by gentle warming with a heat gun (maximum temperature 50 °C). The solution was closed with a glass stopper and cooled to −20 °C. After two days the desired product had crystallized and was isolated by filtration. The crystals were washed first with a cold 2:1 mixture of toluene and 2-propanol, and then with hexane. The crystals were collected and dried to give the organic monocation salt.

*4.6.1. 2-(But-3-ynyl)-1-(isoquinolin-1-ylethynyl)isoquinolinium trifluoromethanesulfonate (**4**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure I, a solution of but-3-ynyl trifluoromethanesulfonate (**A**) (110 μl, 0.8017 mmol, 1.1 equiv) in toluene (4 mL) and a solution of 1,2-di(isoquinolin-1-yl)ethyne (**2**)[33] (204.3 mg, 0.7288 mmol, 1 equiv) in toluene (16 mL) gave pure organic monocation salt **4** as a yellow powder in 89% yield (315.9 mg, 0.6547 mmol).

Mp 145–147 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ=2.81 (t, J=2.7 Hz, 1H); 3.46 (td, J=6.8, 2.7 Hz, 2H); 5.62 (t, J=6.8 Hz, 2H); 7.96–8.05 (m, 2H); 8.23 (dd, J=5.6, 1.0 Hz, 1H); 8.24–8.28 (m, 1H); 8.38 (ddd, J=8.4, 7.0, 1.2 Hz, 1H); 8.47 (ddd, J=8.3, 7.0, 1.2 Hz, 1H); 8.59 (dt, J=8.2, 1.0 Hz, 1H); 8.70 (m, 1H); 8.86 (m, 1H); 8.88 (d, J=5.6 Hz, 1H); 9.10 (ddt, J=8.5, 1.1, 0.9 Hz, 1H); 9.19 (d, J=6.9 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=20.81; 60.05; 74.75; 79.28; 80.90; 109.72; 124.77; 126.50; 127.13; 128.63; 129.23; 130.01; 130.64; 130.67; 130.69; 132.49; 133.96; 136.88; 137.85; 138.23; 138.55; 141.10; 141.32; 144.76. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1160m, 1224m, 1263vs, 1278vs, 3085w. MS (ESI) m/z: 333 [$(M-OTf)^+$] (100). HRMS (ESI) m/z: [$(M-OTf)^+$] ($C_{24}H_{17}N_2$) calcd: 333.1386, found: 333.1386. Elem. Anal. Calcd for $C_{25}H_{17}F_3N_2O_3S$: C, 62.23; H, 3.55; N, 5.81. Found: C, 62.05; H, 3.71; N, 5.48.

*4.6.2. 1-(Isoquinolin-1-ylethynyl)-2-(4-phenylbut-3-ynyl)isoquinolinium trifluoromethanesulfonate (**5**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure I, a solution of 4-phenylbut-3-ynyl trifluoromethanesulfonate (**B**) (71 μl, 0.3396 mmol, 1.1 equiv) in toluene (4 mL) and a solution of 1,2-

di(isoquinolin-1-yl)ethyne (**2**)[33] (86.5 mg, 0.3086 mmol, 1 equiv) in toluene (7 mL) gave pure organic monocation salt **5** as a yellow powder in 90% yield (156.4 mg, 0.2800 mmol).

Mp 186–188 °C. ^{1}H NMR (400 MHz, acetone-d_6): δ=3.69 (t, J=6.6 Hz, 2H); 5.72 (t, J=6.6 Hz, 2H); 7.25–7.45 (m, 5H); 7.92 (ddd, J=8.2, 6.9, 1.3, 1H); 8.00 (ddd, J=8.3, 6.9, 1.3, 1H); 8.22 (dd, J=5.6, 0.9 Hz, 1H); 8.23–8.26 (m, 1H); 8.38 (ddd, J=8.4, 7.0, 1.2 Hz, 1H); 8.47 (ddd, J=8.3, 6.9, 1.2 Hz, 1H); 8.59 (dt, J=8.5, 0.9 Hz, 1H); 8.69 (dq, J=8.4, 1.0 Hz, 1H); 8.87 (d, J=5.7 Hz, 1H); 8.90 (dd, J=6.8, 0.7 Hz, 1H); 9.12 (dq, J=8.5, 0.9 Hz, 1H); 9.27 (d, J=6.9 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=21.97; 60.30; 81.01; 84.94; 85.48; 109.67; 123.32; 124.75; 126.46; 127.14; 128.63; 129.286; 129.287; 129.34; 130.05; 130.62; 130.64; 130.66; 132.10; 132.45; 134.01; 136.88; 137.82; 138.25; 138.57; 141.19; 141.34; 144.76. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1029s, 1162s, 1258vs, 1273vs, 3057w. MS (ESI) m/z: 464 (30), 409 [(M−OTf)$^+$] (100), 279 (15). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{30}H_{21}N_2$) calcd: 409.1699, found: 409.1706.

*4.6.3. 1-(Isoquinolin-1-ylethynyl)-2-(pent-4-ynyl)isoquinolinium trifluoromethanesulfonate (**6**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure I, a solution of pent-4-ynyl trifluoromethanesulfonate (**C**) (80 μl, 0.5121 mmol, 1.1 equiv) in toluene (6 mL) and a solution of 1,2-di(isoquinolin-1-yl)ethyne (**2**)[33] (130.5 mg, 0.4655 mmol, 1 equiv) in toluene (10 mL) gave pure organic monocation salt **6** as a yellow powder in 95% yield (219.8 mg, 0.4427 mmol).

Mp 152–154 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.39 (t, J=2.6 Hz, 1H); 2.63–2.71 (m, 4H); 5.52 (t, J=6.5 Hz, 2H); 7.99 (ddd, J=8.2, 6.9, 1.4 Hz, 1H); 8.02 (ddd, J=8.5, 6.9, 1.5 Hz, 1H); 8.22 (dd, J=5.6, 1.2 Hz, 1H); 8.25 (m, 1H); 8.35 (ddd, J=8.5, 6.9, 1.2 Hz, 1H); 8.44 (ddd, J=8.3, 6.9, 1.1 Hz, 1H); 8.56 (dt, J=8.3, 1.1 Hz, 1H); 8.69 (ddt, J=8.2, 1.5, 0.9 Hz, 1H); 8.82 (dd, J=6.8, 0.9 Hz, 1H); 8.86 (d, J=5.6 Hz, 1H); 9.08 (ddt, J=8.5, 1.1, 0.9 Hz, 1H); 9.15 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=16.13; 30.02; 61.30; 71.65; 81.01; 82.74; 109.33; 124.68; 126.48; 127.40; 128.62; 129.16; 129.90; 130.55; 130.64; 130.88; 132.48; 133.82; 136.88; 137.80; 137.94; 138.45; 141.08; 141.39; 144.73. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1156m, 1266vs, 1276vs, 2206m, 3084w. MS (ESI) m/z: 379 (30), 347 [(M−OTf)$^+$] (100), 316 (15), 288 (30). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{25}H_{19}N_2$) calcd: 347.1543, found: 347.1543. Elem. Anal. Calcd for $C_{26}H_{19}F_3N_2O_3S$: C, 62.90; H, 3.86; N, 5.64. Found: C, 62.74; H, 3.95; N, 5.42.

*4.6.4. 1-(But-3-ynyl)-2-(quinolin-2-ylethynyl)pyridinium trifluoromethanesulfonate (**22**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure II, neat but-3-ynyl trifluoromethanesulfonate (**A**) (130 μl, 181.5 mg, 0.89 mmol, 1.1 equiv) and a solution of 2-(pyridin-2-ylethynyl)quinoline (**21**)[33] (188.0 mg, 0.82 mmol, 1 equiv) in toluene (5 mL) gave organic monocation salt **22** as a light gray powder in 75% yield (264.5 mg, 0.61 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.73. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.78 (t, J=2.8 Hz, 1H), 3.33 (td, J=2.7, 6.6 Hz, 2H), 5.37 (t, J=6.6 Hz, 2H), 7.81 (ddd, J=8.1, 6.9, 1.2 Hz, 1H), 7.96 (ddd, J=8.5, 6.9, 1.5 Hz, 1H), 8.06 (d, J=8.5 Hz, 1H), 8.13 (ddt, J=8.1, 1.5, 0.7 Hz, 1H), 8.18 (ddt, J=8.5, 1.2, 0.9 Hz, 1H), 8.42 (ddd, J=7.8, 6.2, 1.5 Hz, 1H), 8.61 (dd, J=8.5, 1.2 Hz, 1H), 8.72 (ddd, J=8.0, 1.5, 0.6 Hz, 1H), 8.92 (td, J=7.9, 1.5 Hz, 1H), 9.43 (ddd, J=6.2, 1.5, 0.6 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=20.54, 59.57, 74.89, 78.27, 78.93, 105.04, 125.59, 128.78, 129.00, 129.05, 129.67, 130.21, 131.78, 134.07, 137.69, 138.06, 140.99, 147.08, 148.36, 149.21. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s; 1168s; 1275s; 1618m; 3082w. MS (ESI) m/z: 283 [(M−OTf)$^+$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{20}H_{15}N_2$) calcd: 283.1230, found: 283.1231. Elem. Anal. Calcd for $C_{21}H_{15}F_3N_2O_3S$: C, 50.00; H, 3.42; N, 4.32. Found: C, 49.87; H, 3.35; N, 4.14.

*4.6.5. 1-(Pent-3-ynyl)-2-(quinolin-2-ylethynyl)pyridinium trifluoromethanesulfonate (**23**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure II, neat pent-3-ynyl trifluoromethanesulfonate (**D**) (150 μl, 215.0 mg, 0.99 mmol, 1.1 equiv) and a solution of 2-(pyridin-2-ylethynyl)quinoline (**21**)[33] (208.2 mg, 0.90 mmol, 1 equiv) in toluene (6 mL) gave organic monocation salt **23** as a light gray powder in 67% yield (273.0 mg, 0.60 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.73. Mp 119–121 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.76 (t, J=2.5 Hz, 3H), 3.21 (tq, J=6.5, 2.5 Hz, 2H), 5.30 (t, J=6.5 Hz, 2H), 7.81 (ddd, J=8.1, 6.9, 1.2 Hz, 1H), 7.96 (ddd, J=8.5, 6.9, 1.2 Hz, 1H), 8.05 (d, J=8.4 Hz, 1H), 8.14 (ddt, J=8.1, 1.5, 0.7 Hz, 1H), 8.18 (ddd, J=8.5, 1.2, 0.8 Hz, 1H), 8.42 (ddd, J=7.7, 6.2, 1.5 Hz, 1H), 8.62 (dd, J=8.4, 1.2 Hz, 1H), 8.71 (ddd, J=8.0, 1.5, 0.6, 1H), 8.91 (td, J=7.9, 1.5 Hz, 1H), 9.40 (ddd, J=6.2, 1.5, 0.6 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.09, 21.06, 60.20, 73.83, 78.29, 81.78, 104.77, 125.55, 128.65, 129.00, 129.04, 129.67, 130.21, 131.79, 133.98, 137.55, 138.02, 141.03, 146.94, 148.28, 149.22. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030vs; 1167s; 1272s; 1617m; 3082w. MS (ESI) m/z: 297 [(M−OTf)$^+$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{21}H_{17}N_2$) calcd: 297.1386, found: 297.1387. Elem. Anal. Calcd for $C_{22}H_{17}F_3N_2O_3S\cdot(H_2O)_{0.5}$ C, 58.02; H, 3.98; F, 12.51; N, 6.15; S, 7.04. Found: C, 58.30; H, 3.78; F, 12.19; N, 5.89; S, 7.33.

*4.6.6. 1-(Pent-4-ynyl)-2-(quinolin-2-ylethynyl)pyridinium trifluoromethanesulfonate (**24**).* Following the general procedure for organic monocation formation with a reaction temperature of 25 °C, and general workup procedure II, neat pent-4-ynyl trifluoromethanesulfonate (**C**) (147 μl, 208.1 mg, 0.96 mmol, 1.1 equiv) and a solution of 2-(pyridin-2-ylethynyl)quinoline (**21**)[33] (201.5 mg, 0.87 mmol, 1 equiv) in toluene (5 mL) gave organic monocation salt **24** as a light gray powder in 61% yield (240.9 mg, 0.53 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.73. Mp 109–110 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.53 (t, J=2.6, 1H); 2.54–2.58 (m, 2H); 2.60–2.64 (m, 2H); 5.30 (m, 2H); 7.81 (ddd, J=8.2, 6.8, 1.2, 1H); 7.96 (ddd, J=8.5, 6.8, 1.4, 1H); 8.06 (d, J=8.4, 1H); 8.13 (ddt, J=8.2, 1.4, 0.6, 1H); 8.18 (ddt, J=8.5, 1.2, 0.9, 1H); 8.39 (ddd, J=7.7, 6.2, 1.5, 1H); 8.62 (dd, J=8.4, 1.2, 1H); 8.69 (ddd, J=8.0, 1.5, 0.6, 1H); 8.87 (td, J=7.9, 1.5, 1H); 9.43 (ddd, J=6.2, 1.5, 0.6, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=15.99; 29.78; 60.88; 71.78; 78.37; 82.71; 104.72; 125.51; 129.00; 129.05; 129.12; 129.67; 130.23; 131.79; 134.19; 137.74; 138.10; 140.01, 148.17; 148.66; 149.24. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030vs; 1168s; 1275s; 1617m; 3079w. MS (ESI) m/z: 297 [(M−OTf)$^+$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{21}H_{17}N_2$) calcd: 297.1386, found: 297.1388. Elem. Anal. Calcd for $C_{22}H_{17}F_3N_2O_3S\cdot(H_2O)_{0.5}$ C, 58.02; H, 3.98; F, 12.51; N, 6.15; S, 7.04. Found: C, 58.37; H, 3.79; F, 12.56; N, 5.98; S, 6.95.

*4.6.7. 2-(But-3-ynyl)-1-(pyridin-2-ylethynyl)isoquinolinium trifluoromethanesulfonate (**38**).* Following the general procedure for organic monocation formation with a reaction temperature of −10 °C, and general workup procedure III, neat but-3-ynyl trifluoromethanesulfonate (**A**) (21.0 μL, 30.8 mg, 153 μmol, 1.1 equiv) and a solution of 1-(pyridin-2-ylethynyl)isoquinoline (**37**)[33] (31.8 mg, 138 μmol, 1 equiv) in toluene (1.5 mL) gave organic monocation salt **38** (>20:1 mixture of regioisomers favoring the desired product as judged by ^{1}H NMR) in a 49% yield (29.3 mg, 67.8 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.70. Mp 124–126 °C. ^{1}H NMR (400 MHz, acetone-d_6): 2.71 (t, J=2.7 Hz, 1H); 3.35 (td, J=6.7, 2.7 Hz, 2H); 5.47 (t, J=6.6 Hz, 2H); 7.72 (ddd, J=7.7, 4.8, 1.3 Hz, 1H); 8.11 (td, J=7.7, 1.7 Hz, 1H); 8.21 (dt, J=7.8, 1.1 Hz, 1H); 8.31 (ddd, J=8.3, 6.9, 1.3 Hz, 1H); 8.42 (ddd, J=8.2, 7.0, 1.3 Hz, 1H); 8.53 (broad d, J=8.2 Hz, 1H); 8.78 (broad d, J=6.7 Hz, 1H); 8.89 (ddd, J=4.8, 1.7, 1.0 Hz, 1H); 8.98 (dq, J=8.4, 0.9 Hz, 1H); 9.09 (d, J=6.8 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6): 21.36; 60.57; 75.23; 77.79; 79.88; 100.62; 127.52; 127.88; 129.83; 130.74; 131.15; 134.48; 138.50; 138.69; 138.87; 139.21; 141.40; 141.86; 151.88; 152.83. IR (thin

film): $\tilde{\nu}$(cm^{-1}) 1027s; 1156s; 1221s; 1259s; 1438m; 1510w; 1562m; 1620m; 2212m; 3251m. MS (ESI) *m/z*: 283.2 [$(M-OTf)^+$] (100). HRMS (ESI) *m/z*: [$(M-OTf)^+$] ($C_{20}H_{15}N_2$) calcd: 283.1230, found: 283.1235. Elem. Anal. Calcd for $C_{21}H_{15}F_3N_2O_3S$: C, 58.33; H, 3.50; N, 6.48. Found C, 58.10; H, 3.52; N, 6.20.

*4.6.8. 2-(Pent-4-ynyl)-1-(pyridin-2-ylethynyl)isoquinolinium trifluoromethanesulfonate (**41**).* Following the general procedure for organic monocation formation with a reaction temperature of −10 °C, and general workup procedure III, neat pent-4-ynyl trifluoromethanesulfonate (**C**) (46 μL, 59.1 mg, 0.27 mmol, 1.1 equiv) and a solution of 1-(pyridin-2-ylethynyl)isoquinoline (**37**)[33] (57.2 mg, 0.25 mmol, 1 equiv) in dry toluene (2.75 mL) gave organic monocation salt **41** (>20:1 mixture of regioisomers favoring the desired product as judged by ^{1}H NMR) in a 58% yield (65.5 mg, 144 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.71. Mp 117–119 °C. ^{1}H NMR (400 MHz, acetone-d_6): 2.47 (t, *J*=2.6 Hz, 1H); 2.52–2.64 (m, 4H); 5.38 (t, *J*=7.3 Hz, 2H); 7.70 (ddd, *J*=7.7, 4.8, 1.3 Hz, 1H); 8.09 (td, *J*=7.7, 1.7 Hz, 1H); 8.21 (dt, *J*=7.8, 1.1 Hz, 1H); 8.31 (ddd, *J*=8.3, 6.9, 1.3 Hz, 1H); 8.42 (ddd, *J*=8.2, 7.0, 1.3 Hz, 1H); 8.53 (broad d, *J*=8.2 Hz, 1H); 8.78 (broad d, *J*=6.7 Hz, 1H); 8.89 (ddd, *J*=4.8, 1.7, 1.0 Hz, 1H); 8.98 (dq, *J*=8.4, 0.9 Hz, 1H); 9.09 (d, *J*=6.8 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6): 16.85; 61.80; 72.35; 77.83; 83.54; 103.25; 127.85; 129.79; 130.61; 131.06; 131.41; 134.37; 138.36; 138.61; 138.71; 139.10; 140.92; 141.43; 150.35; 152.86; one carbon peak likely obscured by (CD_3)$_2$CO peak. IR (thin film): $\tilde{\nu}$(cm^{-1}) 1027s; 1151s; 1224s; 1260s; 1438m; 1562m; 1575m; 1603m; 1618m; 2217m; 3237m. MS (ESI) *m/z*: 297.2 [$(M-OTf)^+$] (100). HRMS (ESI) *m/z*: [$(M-OTf)^+$] ($C_{21}H_{17}N_2$) calcd: 297.1386, found: 297.1387. Elem. Anal. Calcd for $C_{22}H_{17}F_3N_2O_3S\cdot(H_2O)_{0.5}$ C, 58.02; H, 3.98; N, 6.15. Found: C, 58.40; H, 3.69; N, 6.13.

4.7. Synthesis of organic dications

Organic dications were synthesized by one of two general procedures which was followed by one of four workup procedures.

4.8. Organic dication formation, general procedure I (7–13, 39, 42)

The desired alkynyltriflate (**A**–**F**) (4–4.5 equiv) was added to a stirred solution of organic monocation salt (1 equiv) in dry DCM at 25 °C under Ar. The flask was protected from light with Al-foil and the reaction stirred at 25 °C for 1–4 days.

4.9. Organic dication formation, general procedure II (25–30)

The desired alkynyltriflate (**A**–**F**) (1–1.1 equiv) was added to a solution of organic monocation salt (1 equiv) in dry DCM contained in a sealable Carius tube stirred under Ar. The reaction vessel was sealed and the reaction mixture stirred 24 h at 50 °C. The reaction was cooled to 25 °C, a second portion of the same alkynyltriflate (**A**–**F**) (1–1.1 equiv) was added and the reaction stirred a further 24 h at 50 °C.

4.10. Organic dication formation, general workup procedure I (7, 8, 10–13)

All volatiles were removed in vacuo from the reaction mixture to give a brown residue. Ethyl acetate was added to the residue and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min giving a fine suspension. The supernatant solution was separated from the fine powder via centrifuge and then removed via decantation. The sonication treatment with ethyl acetate was repeated (2×), the product was transferred to a vial and dried under vacuum (2 mbar) to give the organic dication salt.

4.11. Organic dication formation, general workup procedure II (9)

The reaction mixture was diluted with water and stirred vigorously until all precipitate had dissolved. The aqueous layer was separated and all volatiles were removed in vacuo. Ethyl acetate was added to the resultant residue and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min giving a fine suspension. The supernatant solution was separated from the fine powder via centrifuge and then removed via decantation. The sonication treatment with ethyl acetate was repeated (1×), the product was transferred to a vial and dried under vacuum (2 mbar) to give the organic dication salt.

4.12. Organic dication formation, general workup procedure III (25–30)

The reaction mixture was cooled to rt and concentrated in vacuo to give a brown residue. Diethyl ether was added to the residue and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min. The supernatant solution was separated via decantation. DCM and water were added to the remaining residue and the mixture was stirred vigorously until all material dissolved. The aqueous layer was separated, washed with DCM (3×) and concentrated in vacuo to give a red glass. Diethyl ether/tetrahydrofuran 1:1 was added to the residue and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min. The supernatant solution was separated from the precipitate via centrifuge and then removed via decantation. This washing procedure was repeated (2×) and the product was then dried under vacuum (2 mbar) to give the organic dication salt.

4.13. Organic dication formation, general workup procedure IV (39, 42)

The reaction mixture was diluted with water and stirred vigorously until all the precipitate had dissolved. The aqueous layer was separated, washed with DCM (3×) and concentrated in vacuo to give the organic dication salt.

*4.13.1. 2-(But-3-ynyl)-1-((2-(pent-3-ynyl)isoquinolinium-1-yl)ethynyl)isoquinolinium trifluoromethanesulfonate (**7**).* Following the general procedure for organic dication formation I with a reaction time of four days, and general workup procedure I, neat pent-3-ynyl trifluoromethanesulfonate (**D**) (176 μl, 237.1 mg, 1.097 mmol, 4 equiv) and a solution of organic monocation salt **4** (132.3 mg, 0.274 mmol, 1 equiv) in DCM (8 mL) gave organic dication salt **7** as a light yellow powder in 81% yield (155.2 mg, 0.222 mmol).

Mp 223–225 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.75 (t, *J*=2.5 Hz, 3H), 2.83 (t, *J*=2.7 Hz, 1H); 3.30 (tq, *J*=6.5, 2.5 Hz, 2H); 3.41 (td, *J*=6.5, 2.7 Hz, 2H); 5.57 (t, *J*=6.5 Hz, 2H); 5.65 (t, *J*=6.5 Hz, 2H); 8.31 (ddd, *J*=8.6, 7.1, 1.2 Hz, 1H); 8.33 (ddd, *J*=8.6, 7.1, 1.2 Hz, 1H); 8.47 (ddd, *J*=8.3, 7.1, 1.1 Hz, 1H); 8.48 (ddd, *J*=8.3, 7.1, 1.1 Hz, 1H); 8.63 (dt, *J*=8.3, 1.0 Hz, 1H); 8.65 (dt, *J*=8.3, 1.0 Hz, 1H); 9.00 (broad d, *J*=6.8 Hz, 1H); 9.02 (broad d, *J*=6.9 Hz, 1H); 9.17 (dq, *J*=8.6, 1.0 Hz, 1H); 9.19 (dq, *J*=8.6, 1.0 Hz, 1H); 9.27 (d, *J*=6.8 Hz, 1H); 9.29 (d, *J*=6.9 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.19; 21.35; 21.78; 60.58; 61.26; 74.39; 75.28; 79.48; 82.04; 96.10; 96.38; 128.70; 128.93; 129.23; 129.27; 130.03; 130.05; 131.09; 131.10; 134.33; 134.36; 138.42; 138.48; 138.55; 138.60; 138.83; 138.87; 138.91; 139.10. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1262vs, 1276s, 1623m, 3082w. MS (ESI) *m/z*: 549 [$(M-OTf)^+$] (13), 446 (72), 417 (100), 400 (34), 333 (19), 200 [$(M-2OTf)^{2+}$] (16). HRMS (ESI) *m/z*: [$(M-OTf)^+$] ($C_{30}H_{24}F_3N_2O_3S$) calcd: 549.1454, found: 549.1464. Elem. Anal. Calcd for $C_{31}H_{24}F_6N_2O_6S_2$: C, 53.29; H, 3.46; N, 4.01. Found: C, 53.05; H, 3.51; N, 3.81.

*4.13.2. 2-(But-3-ynyl)-1-((2-(tetradec-3-ynyl)isoquinolinium-1-yl) ethynyl)isoquinolinium trifluoromethanesulfonate (**8**).* Following the general procedure for organic dication formation I with a reaction time of 63 h, and general workup procedure I, neat tetradec-3-ynyl trifluoromethanesulfonate (**E**) (150 μl, 164.0 mg, 0.479 mmol, 4.6 equiv) and a solution of organic monocation salt **4** (49.8 mg, 0.103 mmol, 1 equiv) in DCM (8 mL) gave organic dication salt **8** as a light brown powder in 61% yield (51.8 mg, 0.063 mmol).

Mp 154–156 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=0.91 (t, J=7.2 Hz, 3H); 1.13–1.29 (m, 14H); 1.30–1.35 (m, 2H), 2.16 (tt, J=7.1, 2.4 Hz, 2H); 2.84 (t, J=2.6 Hz, 1H); 3.36 (tt, J=6.5, 2.4 Hz, 2H); 3.41 (td, J=6.6, 2.6 Hz, 2H); 5.60 (t, J=6.5 Hz, 2H); 5.65 (t, J=6.6 Hz, 2H); 8.31–8.35 (m, 2H); 8.47–8.51 (m, 2H); 8.63–8.66 (m, 2H); 9.01–9.03 (m, 2H); 9.18 (dq, J=8.6, 1.0 Hz, 1H); 9.19 (dq, J=8.6, 1.0 Hz, 1H); 9.28 (d, J=6.8 Hz, 1H); 9.29 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=14.31; 18.99; 21.38; 21.85; 23.27; 29.28; 29.45; 29.73; 29.98; 30.24; 30.31; 60.60; 61.20; 75.32; 79.47; 86.64; 96.20; 96.38; 128.71; 128.95; 129.25; 129.30; 130.02; 130.05; 131.06; 131.09; 134.37; 134.41; 138.45; 138.54; 138.61; 138.86; 138.92; 139.06; one carbon peak likely obscured by (CHD_2)(CD_3)CO peak, the three peaks at 75.32, 138.54, and 138.61 each represent two overlapping carbon signals. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1032s, 1159s, 1261vs, 1277vs, 1625m, 3083w. MS (ESI) m/z: 675 [(M−OTf)$^+$] (22), 572 (100), 526 (33), 263 [(M-2OTf)$^{2+}$] (72). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{39}H_{42}F_3N_2O_3S$) calcd: 675.2863, found: 675.2866.

*4.13.3. 2-(But-3-ynyl)-1-((2-(4-phenylbut-3-ynyl)isoquinolinium-1-yl)ethynyl)isoquinolinium trifluoromethanesulfonate (**9**).* Following the general procedure for organic dication formation I with a reaction time of 92 h, and general workup procedure II, neat 4-phenylbut-3-ynyl trifluoromethanesulfonate (**B**) (99 μl, 130.5 mg, 0.469 mmol, 4.5 equiv) and a solution of organic monocation salt **4** (50.3 mg, 0.104 mmol, 1 equiv) in DCM (8 mL) gave organic dication salt **9** as a light orange powder in 62% yield (49.1 mg, 0.065 mmol).

Mp 96–98 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.84 (t, J=2.7 Hz, 1H); 3.37 (td, J=6.5, 2.7 Hz, 2H); 3.65 (t, J=6.3 Hz, 2H); 5.63 (t, J=6.5 Hz, 2H); 5.75 (t, J=6.3 Hz, 2H); 7.30–7.36 (m, 4H); 7.37–7.41 (m, 1H); 8.21 (ddd, J=8.6, 6.9, 1.1 Hz, 1H); 8.33 (ddd, J=8.6, 7.0, 1.2 Hz, 1H); 8.46 (ddd, J=8.3, 6.9, 1.1 Hz, 1H); 8.48 (ddd, J=8.3, 7.0, 1.1 Hz, 1H); 8.63 (dt, J=8.3, 1.0 Hz, 1H); 8.65 (dt, J=8.3, 1.0 Hz, 1H); 9.01 (dd, J=6.8, 0.8 Hz, 1H); 9.06 (dd, J=6.8, 0.8 Hz, 1H); 9.13 (dq, J=8.6, 1.0 Hz, 1H); 9.19 (dq, J=8.6, 1.0 Hz, 1H); 9.28 (d, J=6.8 Hz, 1H); 9.40 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=21.34; 22.39; 60.57; 60.95; 75.34; 79.48; 85.21; 85.83; 96.24; 96.37; 123.22; 128.86; 128.92; 129.25; 129.33; 129.43; 129.51; 130.00; 130.02; 131.04; 131.17; 132.17; 134.33; 134.44; 138.41; 138.60; 138.61; 138.96; 139.03; 139.06; the two peaks at 138.96, and 138.61 each represent two overlapping carbon signals. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1262vs, 1273vs, 3084w. MS (ESI) m/z: 611 [(M−OTf)$^+$] (14), 525 (100), 462 (42), 231 [(M-2OTf)$^{2+}$] (18). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{35}H_{26}F_3N_2O_3S$) calcd: 611.1611, found: 611.1618.

*4.13.4. 2-(But-3-ynyl)-1-((2-(hex-5-ynyl)isoquinolinium-1-yl)ethynyl)isoquinolinium trifluoromethanesulfonate (**10**).* Following the general procedure for organic dication formation I with a reaction time of one day and a reaction temperature of 35 °C and general workup procedure I, neat hex-5-ynyl trifluoromethanesulfonate (**F**) (83 μl, 110.6 mg, 0.480 mmol, 4.5 equiv) and a solution of organic monocation salt **4** (51.5 mg, 0.107 mmol, 1 equiv) in DCM (8 mL) gave organic dication salt **10** as a light brown powder in 72% yield (54.5 mg, 0.077 mmol).

^{1}H NMR (400 MHz, acetone-d_6): δ=1.84 (m, 2H), 2.32 (td, J=7.0, 2.7 Hz, 2H); 2.39 (t, J=2.7 Hz, 1H); 2.56 (m, 2H); 2.83 (t, J=2.7 Hz, 1H); 3.41 (td, J=6.6, 2.7 Hz, 2H); 5.51 (t, J=7.5 Hz, 2H); 5.64 (t, J=6.6 Hz, 2H); 8.29 (ddd, J=8.6, 7.0, 1.2 Hz, 1H); 8.33 (ddd, J=8.5, 7.0, 1.2 Hz, 1H); 8.45 (ddd, J=8.3, 7.0, 1.2 Hz, 1H); 8.48 (ddd, J=8.3, 7.0, 1.2 Hz, 1H); 8.61 (dt, J=8.4, 1.0 Hz, 1H); 8.64 (dt, J=8.4, 1.0 Hz, 1H); 8.98 (dd, J=6.9, 0.8 Hz, 1H); 9.01 (dd, J=6.9, 0.8 Hz, 1H); 9.16 (dq, J=8.6, 0.9 Hz, 1H); 9.17 (dq, J=8.6, 0.9 Hz, 1H); 9.27 (d, J=6.8 Hz, 1H); 9.29 (d, J=6.8 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6): δ=18.54; 21.48; 26.15; 31.20; 60.78; 62.79; 70.77; 75.35; 79.62; 84.18; 96.04; 96.88; 129.05; 129.08; 129.29; 129.32; 129.39; 130.17; 131.30; 131.61; 134.39; 134.59; 138.36; 138.43; 138.57; 138.59; 138.75; 138.88; 138.97; 139.13. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1262vs, 1607m, 3086w. MS (ESI) m/z: 563 [(M−OTf)$^+$] (75), 414 (100), 333 (10), 207 [(M-2OTf)$^{2+}$] (3). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{31}H_{26}F_3N_2O_3S$) calcd: 563.1611, found: 563.1607.

*4.13.5. 2-(Pent-4-ynyl)-1-((2-(4-phenylbut-3-ynyl)isoquinolinium-1-yl)ethynyl)isoquinolinium trifluoromethanesulfonate (**11**).* Following the general procedure for organic dication formation I with a reaction time of 67 h and general workup procedure I, neat pent-4-ynyl trifluoromethanesulfonate (**C**) (63 μl, 87.4 mg, 0.405 mmol, 4.5 equiv) and a solution of monocation **5** (50.2 mg, 0.090 mmol, 1 equiv) in DCM (10 mL) gave organic dication salt **11** as a yellow powder in 58% yield (40.9 mg, 0.053 mmol).

Mp 85–87 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.37 (t, J=2.7 Hz, 1H); 2.54–2.57 (m, 2H); 2.63–2.69 (m, 2H); 3.65 (t, J=6.5 Hz, 2H); 5.53–5.57 (m, 2H); 5.75 (t, J=6.5 Hz, 2H); 7.31–7.35 (m, 4H); 7.37–7.40 (m, 1H); 8.19 (ddd, J=8.6, 7.0, 1.1 Hz, 1H); 8.33 (ddd, J=8.6, 6.9, 1.1 Hz, 1H); 8.43 (ddd, J=8.4, 7.0, 1.1 Hz, 1H); 8.49 (ddd, J=8.4, 6.9, 1.1 Hz, 1H); 8.60 (dt, J=8.4, 1.0 Hz, 1H); 8.65 (dt, J=8.4, 1.0 Hz, 1H); 8.97 (dd, J=6.8, 0.9 Hz, 1H); 9.06 (dd, J=6.8, 0.9 Hz, 1H); 9.11 (dq, J=8.6, 1.0 Hz, 1H); 9.18 (dq, J=8.6, 0.9 Hz, 1H); 9.24 (d, J=6.8 Hz, 1H); 9.39 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=16.03; 22.37; 30.41; 60.94; 61.87; 71.75; 82.94; 85.13; 85.80; 95.96; 96.58; 123.21; 128.90; 129.18; 129.24; 129.37; 129.41; 129.49; 129.88; 129.92; 131.16; 131.34; 132.18; 134.20; 134.45; 138.30; 138.62; 138.66; 138.74; 138.91; 139.02; 139.08; the peak at 138.30 represents two overlapping carbon signals. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1262vs, 1275vs, 1275vs, 3084w. MS (ESI) m/z: 625 [(M−OTf)$^+$] (75), 476 (84), 409 (100), 238 [(M-2OTf)$^{2+}$] (90). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{36}H_{28}F_3N_2O_3S$) calcd: 625.1767, found: 625.1768.

*4.13.6. 2-(But-3-ynyl)-1-((2-(pent-4-ynyl)isoquinolinium-1-yl)ethynyl)isoquinolinium trifluoromethanesulfonate (**12**).* Following the general procedure for organic dication formation I with a reaction time of 54 h and general workup procedure I, neat but-3-ynyl trifluoromethanesulfonate (**A**) (86 μl, 125.6 mg, 0.621 mmol, 4 equiv) and a solution of organic monocation salt **6** (77.1 mg, 0.155 mmol, 1 equiv) in DCM (9 mL) gave organic dication salt **12** as a light yellow powder in 84% yield (91.1 mg, 0.130 mmol).

Mp 176–178 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.36 (t, J=2.7 Hz, 1H); 2.56–2.58 (m, 2H); 2.65–2.71 (m, 2H); 2.83 (t, J=2.7, 1H); 3.40 (td, J=6.6, 2.7 Hz, 2H); 5.56 (t, J=6.7 Hz, 2H); 5.65 (t, J=6.6 Hz, 2H); 8.29 (ddd, J=8.6, 6.9, 1.0 Hz, 1H); 8.32 (ddd, J=8.7, 7.0, 1.1 Hz, 1H); 8.45 (broad t, J=7.5 Hz, 1H); 8.48 (broad t, J=7.6 Hz, 1H); 8.61 (dt, J=8.4, 1.0 Hz, 1H); 8.64 (dt, J=8.3, 1.0 Hz, 1H); 8.98 (broad d, J=6.8 Hz, 1H); 9.02 (broad d, J=6.8 Hz, 1H); 9.15 (broad d, J=8.7 Hz, 1H); 9.17 (broad d, J=8.7 Hz, 1H); 9.25 (d, J=6.8 Hz, 1H); 9.29 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=16.04; 21.32; 30.40; 60.63; 61.89; 71.75; 75.25; 79.42; 82.96; 95.90; 96.60; 128.93; 129.18; 129.22; 129.29; 129.98; 130.03; 131.09; 131.39; 134.26; 134.40; 138.33; 138.49; 138.62; 138.75; 138.96; 139.12; the two peaks at 138.33 and 138.75 each represent two overlapping carbon signals. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1159s, 1266vs, 1623m, 3083w. MS (ESI) m/z: 549 [(M−OTf)$^+$] (100), 400 (56), 200 [(M-2OTf)$^{2+}$] (33). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{30}H_{24}F_3N_2O_3S$) calcd: 549.1454, found: 549.1446. Elem. Anal. Calcd for $C_{31}H_{24}F_6N_2O_6S_2$: C, 53.29; H, 3.46; N, 4.01. Found: C, 53.02; H, 3.46; N, 3.78.

*4.13.7. 2-(Pent-3-ynyl)-1-((2-(pent-4-ynyl)isoquinolinium-1-yl)-ethynyl)isoquinolinium trifluoromethanesulfonate (**13**).* Following the

general procedure for organic dication formation I with a reaction time of 54 h and general workup procedure I, neat pent-3-ynyl trifluoromethanesulfonate (**D**) (100 μl, 134.5 mg, 0.6222 mmol, 4 equiv) and a solution of organic monocation salt **6** (77.2 mg, 0.156 mmol, 1 equiv) in DCM (9 mL) gave organic dication salt **13** as a light yellow powder in 81% yield (89.8 mg, 0.126 mmol).

Mp 178–180 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.75 (t, J=2.6, 3H), 2.36 (t, J=2.6 Hz, 1H); 2.56–2.60 (m, 2H); 2.65–2.71 (m, 2H); 3.31 (tq, J=6.6, 2.6 Hz, 2H); 5.55–5.58 (m, 4H); 8.30 (ddd, J=8.6, 6.9, 1.2 Hz, 1H); 8.32 (ddd, J=8.6, 7.0, 1.2 Hz, 1H); 8.46 (ddd, J=8.3, 6.9, 1.2 Hz, 1H); 8.48 (ddd, J=8.2, 7.0, 1.2 Hz, 1H); 8.62 (dt, J=8.3, 1.0 Hz, 1H); 8.64 (dt, J=8.2, 1.0 Hz, 1H); 8.98 (dd, J=6.8, 0.9 Hz, 1H); 9.01 (dd, J=6.8, 0.9 Hz, 1H); 9.16 (m, 2H); 9.25 (d, J=6.8 Hz, 1H); 9.27 (d, J=6.8 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.21; 16.04; 21.77; 30.43; 61.28; 61.87; 71.72; 74.31; 82.02; 82.95; 95.98; 96.40; 128.73; 129.20; 129.23; 129.28; 129.89; 129.94; 131.10; 131.39; 134.24; 134.35; 138.32; 138.51; 138.62; 138.73; 138.93; 139.11; the peak at 138.32 represents three overlapping carbon signals. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s, 1262vs, 3083w. MS (ESI) m/z: 563 [(M−OTf)$^+$] (5), 414 (8), 347 (100), 207 [(M-2OTf)$^{2+}$] (28). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{31}H_{26}F_3N_2O_3S$) calcd: 563.1616, found: 563.1604. Elem. Anal. Calcd for $C_{32}H_{26}F_6N_2O_6S_2$: C, 53.93; H, 3.68; N, 3.93. Found: C, 53.61; H, 3.73; N, 3.73.

*4.13.8. 2-((1-(But-3-ynyl)pyridinium-2-yl)ethynyl)-1-(pent-3-ynyl)-quinolinium trifluoromethanesulfonate (**25**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat pent-3-ynyl trifluoromethanesulfonate (**D**) (each portion: 41 μL, 53.9 mg, 0.25 mmol, 1.1 equiv) and a solution of organic monocation salt **22** (108.8 mg, 0.22 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **25** as a light red powder in 51% yield (74.4 mg, 0.11 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. Mp 104–108 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.67 (t, J=2.6 Hz, 3H); 2.83 (t, J=2.7 Hz, 1H); 3.31 (tq, J=6.7, 2.6 Hz, 2H); 3.37 (td, J=6.5, 2.7 Hz, 2H); 5.46 (t, J=6.5 Hz, 2H); 5.86 (t, J=6.7 Hz, 2H); 8.26 (ddd, J=8.1, 7.0, 0.9 Hz, 1H); 8.52 (ddd, J=9.1, 7.0, 1.5 Hz, 1H); 8.58 (ddd, J=7.8, 6.1, 1.8 Hz, 1H); 8.68 (ddt, J=8.1, 1.5, 0.5 Hz, 1H); 8.89 (d, J=8.5 Hz, 1H); 8.95 (dq, J=9.1, 0.9 Hz, 1H); 8.99 (ddd, J=8.0, 1.8, 0.6 Hz, 1H); 9.02 (td, J=7.9, 1.4 Hz, 1H); 9.55 (ddd, J=6.1, 1.4, 0.6 Hz, 1H); 9.57 (dd, J=8.5, 0.9 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.15; 20.50; 21.08; 60.18; 55.77; 74.58; 75.45; 79.04; 82.47; 94.19; 94.34; 120.36; 128.11; 130.76; 131.53; 132.09; 132.33; 135.58; 135.61; 138.40; 139.33; 140.43; 147.52; 148.62; 149.21. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s; 1261vs; 1620m; 3070w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (91). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1297. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)_{0.5}$: C, 49.32; H, 3.53; N, 4.26. Found: C, 49.26; H, 3.31; N, 4.13.

*4.13.9. 2-((1-(But-3-ynyl)pyridinium-2-yl)ethynyl)-1-(pent-4-ynyl)-quinolinium trifluoromethanesulfonate (**26**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat pent-4-ynyl trifluoromethanesulfonate (**C**) (each portion: 31 μL, 43.5 mg, 0.20 mmol, 1 equiv) and a solution of monocation **22** (87.0 mg, 0.20 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **26** as a brown oil in 53% yield (69.6 mg, 0.11 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.57 (t, J=2.7 Hz, 1H); 2.58–2.63 (m, 2H); 2.72 (td, J=6.6, 2.7 Hz, 2H); 2.81 (t, J=2.7 Hz, 1H); 3.35 (td, J=6.5, 2.7 Hz, 2H); 5.45 (t, J=6.5 Hz, 2H); 5.77 (m, 2H); 8.24 (ddd, J=8.2, 7.0, 0.8 Hz, 1H); 8.52 (ddd, J=9.1, 7.0, 1.5 Hz, 1H); 8.58 (ddd, J=7.3, 6.2, 1.9 Hz, 1H); 8.67 (ddt, J=8.2, 1.5, 0.5 Hz, 1H); 8.85 (d, J=8.6 Hz, 1H); 8.90 (dq, J=9.1, 0.9 Hz, 1H); 9.00 (ddd, J=7.7, 1.9, 0.8 Hz, 1H); 9.02 (td, J=7.5, 1.4 Hz, 1H); 9.53 (dd, J=8.6, 1.1 Hz, 1H), 9.54 (ddd, J=6.2, 1.4, 0.6 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=16.28; 21.02; 28.95; 56.51; 60.24; 71.80; 75.44; 79.05; 83.31; 93.90; 94.41; 120.07; 128.51; 130.79; 131.73; 132.12; 132.20; 139.16; 135.46; 135.55; 138.52; 140.61; 147.54; 148.33; 149.28. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s; 1161s, 1261vs; 1619m; 3091w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (95). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1293.

*4.13.10. 1-(But-3-ynyl)-2-((1-(pent-3-ynyl)pyridinium-2-yl)ethynyl)quinolinium trifluoromethanesulfonate (**27**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat but-3-ynyl trifluoromethanesulfonate (**A**) (each portion: 35 μL, 48.5 mg, 0.24 mmol, 1.1 equiv) and a solution of organic monocation salt **23** (97.5 mg, 0.21 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **27** as a light red solid in 56% yield (79.5 mg, 0.12 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. Mp 99–103 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=δ 1.78 (t, J=2.5, 3H); 2.80 (t, J=2.7, 1H); 3.24 (tq, J=6.4, 2.5, 2H); 3.41 (td, J=6.8, 2.7, 2H); 5.38 (t, J=6.4, 2H); 5.92 (t, J=6.8, 2H); 8.27 (ddd, J=8.2, 7.0, 0.9, 1H); 8.53 (ddd, J=9.1, 7.0, 1.5, 1H); 8.57 (ddd, J=7.7, 6.2, 1.8, 1H); 8.69 (ddt, J=8.2, 1.5, 0.5, 1H); 8.88 (d, J=8.5, 1H); 8.96 (dq, J=9.1, 0.9, 1H); 8.98 (ddd, J=7.9, 1.8, 0.6, 1H); 9.01 (td, J=7.8, 1.4, 1H); 9.53 (ddd, J=6.2, 1.4, 0.6, 1H); 9.59 (dd, J=8.5, 1.2, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.15; 20.00; 21.60; 55.23; 60.84; 73.97; 75.55; 79.46; 82.40; 93.89; 94.83; 120.33; 128.15; 130.64; 131.56; 132.18; 132.36; 135.42; 135.50; 138.62; 139.54; 140.41; 147.36; 148.52; 149.12. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1031s; 1261vs; 1616m; 3088w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (55). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1297. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2$: C, 50.00; H, 3.42; N, 4.32. Found: C, 49.87; H, 3.35; N, 4.14.

*4.13.11. 2-((1-(Pent-3-ynyl)pyridinium-2-yl)ethynyl)-1-(pent-4-ynyl)quinolinium trifluoromethanesulfonate (**28**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat pent-4-ynyl trifluoromethanesulfonate (**C**) (each portion: 39 μL, 55.2 mg, 0.25 mmol, 1 equiv) and a solution of organic monocation salt **23** (114.0 mg, 0.25 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **28** as a brown oil in 51% yield (87.0 mg, 0.11 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.77 (t, J=2.5 Hz, 3H); 2.58 (t, J=2.7 Hz, 1H); 2.59–2.63 (m, 2H); 2.74 (td, J=6.7, 2.7 Hz, 2H); 3.24 (tq, J=6.5, 2.5 Hz, 2H); 5.38 (t, J=6.5 Hz, 2H); 5.77 (m, 2H); 8.24 (ddd, J=8.2, 7.0, 0.9 Hz, 1H); 8.51 (ddd, J=9.1, 7.0, 1.5 Hz, 1H); 8.56 (ddd, J=7.6, 6.2, 1.8 Hz, 1H); 8.66 (ddt, J=8.2, 1.5, 0.5 Hz, 1H); 8.84 (d, J=8.6 Hz, 1H); 8.90 (dq, J=9.1, 0.8 Hz, 1H); 8.99 (ddd, J=8.0, 1.8, 0.8 Hz, 1H); 9.01 (td, J=7.9, 1.4 Hz, 1H); 9.52 (dt, J=6.2, 1.0 Hz, 1H); 9.53 (dd, J=8.6, 1.0 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.15; 16.26; 21.51; 28.95; 56.49; 60.83; 71.80; 73.94; 82.37; 83.31; 93.64; 94.50; 120.08; 128.49; 130.66; 131.72; 132.11; 132.17; 135.31; 135.47; 138.50; 139.16; 140.61; 147.39; 148.34; 149.20. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1159s, 1261vs; 1617m; 3089w. MS (ESI) m/z: 513 [(M−OTf)$^+$] (71). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{27}H_{24}F_3N_2O_3S$) calcd: 513.1354, found: 513.1450.

*4.13.12. 1-(But-3-ynyl)-2-((1-(pent-4-ynyl)pyridinium-2-yl)ethynyl)-quinolinium trifluoromethanesulfonate (**29**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat but-3-ynyl trifluoromethanesulfonate (**A**) (each portion: 36 μL, 49.3 mg, 0.24 mmol, 1 equiv) and a solution of organic monocation salt **24** (98.1 mg, 0.24 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **29** as a light brown solid in 46% yield (72.4 mg, 0.11 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. Mp 113–116 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.56 (t, J=2.7 Hz, 1H); 2.58–2.61 (m, 4H); 2.74 (t, J=2.8 Hz, 1H); 3.40 (td, J=6.7, 2.8 Hz, 2H); 5.38 (m, 2H); 5.92 (t, J=6.7 Hz, 2H); 8.26 (ddd, J=8.2, 7.0, 0.9 Hz, 1H); 8.52–8.55 (m, 1H); 8.53 (ddd, J=9.0, 7.0, 1.5 Hz, 1H); 8.69 (ddt, J=8.2, 1.5, 0.5 Hz, 1H); 8.89

(d, J=8.6 Hz, 1H); 8.95–8.98 (m, 2H); 8.96 (dq, J=9.0, 0.9 Hz, 1H); 9.54 (dt, J=6.2, 1.1 Hz, 1H); 9.59 (dd, J=8.6, 1.1 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=15.93; 19.99; 30.00; 55.26; 61.50; 72.00; 75.50; 79.46; 82.84; 93.92; 94.89; 120.34; 128.14; 131.09; 131.58; 132.19; 132.36; 135.55; 135.85; 138.63; 139.49; 140.45; 147.05; 148.87; 149.09. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1032s, 1159s, 1255vs; 1617m; 3085w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (76). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1294. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2$: C, 50.00; H, 3.42; N, 4.32. Found: C, 49.58; H, 3.38; N, 4.06.

*4.13.13. 1-(Pent-3-ynyl)-2-((1-(pent-4-ynyl)pyridinium-2-yl)ethynyl)quinolinium trifluoromethanesulfonate (**30**).* Following the general procedure for organic dication formation II and general workup procedure III, two portions of neat pent-3-ynyl trifluoromethanesulfonate (**D**) (each portion: 43 μL, 56.5 mg, 0.26 mmol, 1 equiv) and a solution of organic monocation salt **24** (116.6 mg, 0.26 mmol, 1 equiv) in DCM (2 mL) gave pure organic dication salt **30** as a light brown oil in 55% yield (95.0 mg, 0.14 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.41. ^{1}H NMR (600 MHz, acetone-d_6): δ=1.66 (t, J=2.6 Hz, 3H); 2.57 (t, J=2.7 Hz, 1H); 2.58–2.62 (m, 4H); 3.30 (tq, J=6.7, 2.6 Hz, 2H); 5.37 (m, 2H); 5.85 (t, J=6.7 Hz, 2H); 8.25 (ddd, J=8.2, 7.0, 0.9 Hz, 1H); 8.51 (ddd, J=9.1, 7.0, 1.5 Hz, 1H); 8.51–8.53 (m, 1H); 8.67 (ddt, J=8.2, 1.5, 0.5 Hz, 1H); 8.89 (d, J=8.7, 1H); 8.95 (dq, J=9.1, 0.9 Hz, 1H); 8.95–8.98 (m, 2H); 9.53 (dt, J=6.2, 1.0 Hz, 1H); 9.57 (dd, J=8.7, 0.9 Hz, 1H). ^{13}C NMR (151 MHz, acetone-d_6): δ=3.17; 15.92; 20.48; 29.98; 55.77; 61.46; 71.97; 74.53; 82.44; 82.85; 93.93; 94.48; 120.37; 129.07; 131.05; 131.51; 132.08; 132.28; 135.50; 135.88; 138.39; 139.30; 140.41; 147.05; 148.66; 149.10. IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1157s, 1261vs; 1618m; 3089w. MS (ESI) m/z: 513 [(M−OTf)$^+$] (81). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{27}H_{24}F_3N_2O_3S$) calcd: 513.1454, found: 513.1451.

*4.13.14. 2-(But-3-ynyl)-1-((1-(pent-4-ynyl)pyridinium-2-yl)ethynyl)-isoquinolinium trifluoromethanesulfonate (**39**).* Following the general procedure for organic dication formation I with a reaction time of 36 h and general workup procedure IV, neat pent-4-ynyl trifluoromethanesulfonate (**C**) (21.3 μL, 27.2 mg, 0.126 mmol, 4 equiv) and a solution of organic monocation salt **38** (13.6 mg, 31.5 μmol, 1 equiv) in DCM (1 mL) gave organic dication salt **39** as a light yellow glass in 82% yield (16.8 mg, 25.9 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.42. ^{1}H NMR (400 MHz, acetone-d_6): 2.39 (t, J=2.6 Hz, 1H); 2.48–2.63 (m, 4H); 2.74 (t, J=2.7, 1H); 3.35 (td, J=6.6, 2.7 Hz, 2H); 5.38 (t, J=7.2 Hz, 2H); 5.54 (t, J=6.5 Hz 2H); 8.30 (ddd, J=8.4, 7.0, 1.2 Hz, 1H); 8.43 (ddd, J=8.3, 6.9, 1.1 Hz, 1H); 8.52 (ddd, J=7.5, 6.2, 2.0 Hz, 1H); 8.57 (broad d, J=8.4 Hz, 1H); 8.91–9.01 (m, 3H); 9.06 (dq, J=8.6, 0.9 Hz, 1H); 9.20 (d, J=6.8 Hz, 1H); 9.51 (ddd, J=6.1, 1.4, 0.6 Hz, 1H). ^{13}C NMR (100 MHz, acetone-d_6): 16.62; 21.86; 61.23; 62.35; 72.53; 75.82; 80.00; 83.37; 91.17; 99.23; 129.47; 129.82; 130.65; 131.59; 131.76; 135.09; 136.62; 136.64; 139.22; 139.28; 139.55; 139.60; 147.72; 149.54; 1 carbon peak likely obscured by (CD_3)$_2$CO peak. IR (thin film): $\tilde{\nu}$(cm^{-1}) 1030s; 1053m; 1157m; 1225s; 1258s; 1692m; 2231m; 3489m. MS (ESI) m/z: 499.0 [(M−OTf)$^+$] (100); 396.0 (30); 350.2 [(M-2OTf)$^{2+}$] (20); 283.2 (40); 175.3 (45). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1294.

*4.13.15. 1-((1-(But-3-ynyl)pyridinium-2-yl)ethynyl)-2-(pent-4-ynyl)-isoquinolinium trifluoromethanesulfonate (**42**).* Following the general procedure for organic dication formation I with a reaction time of 36 h and general workup procedure IV, neat but-3-ynyl trifluoromethanesulfonate (**A**) (31 μL, 41.3 mg, 0.204 mmol, 4 equiv) and a solution of organic monocation salt **41** (22.5 mg, 50.4 μmol, 1 equiv) in DCM (1.5 mL) gave organic dication salt **42** as a light yellow glass in 71% yield (23.2 mg, 35.8 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.45. ^{1}H NMR (400 MHz, acetone-d_6): 2.46 (t, J=2.6 Hz, 1H); 2.52–2.65 (m, 4H); 2.80 (t, J=2.7, 1H); 3.33 (td, J=6.6, 2.7, 2H); 5.45 (t, J=6.6, 2H); 5.46 (t, J=7.2 Hz 2H); 8.28 (ddd, J=8.4, 7.0, 1.2 Hz, 1H); 8.41 (ddd, J=8.3, 6.9, 1.2 Hz, 1H); 8.52–8.60 (m, 2H); 8.90 (broad d, J=6.8 Hz, 1H); 8.98–9.06 (m, 3H); 9.17 (d, J=6.8 Hz, 1H); 9.52–9.56 (m, 1H). ^{13}C NMR (100 MHz, acetone-d_6): 16.75; 21.82; 30.92; 61.07; 62.44; 72.49; 76.11; 79.73; 83.69; 91.58; 98.64; 129.82; 129.86; 130.55; 131.54; 131.93; 134.98; 136.41; 136.47; 138.98; 139.00; 139.10; 139.47; 148.23; 149.76. IR (thin film): $\tilde{\nu}$(cm^{-1}) 1030s; 1051m; 1157m; 1226s; 1253s; 1688m; 2229m; 3453m. MS (ESI) m/z: 499.0 [(M−OTf)$^+$] (100); 350.2 [(M-2OTf)$^{2+}$]. HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1288.

4.14. Synthesis of helquats

Helquats were synthesized by one of two general procedures which was followed by one of three workup procedures.

4.15. Helquat formation, general procedure I (14–20, 31–36)

Degassed DMF was added to a mixture of [Rh(PPh$_3$)$_3$Cl] (10–12 mol %) and organic dication salt (1 equiv) under Ar. The solution stirred between 30 min and 2 h at 90–130 °C, and was cooled to 25 °C.

4.16. Helquat formation, general procedure II (40, 43)

A solution of organic dication salt in DMF was added to a Schlenk flask containing [Rh(PPh$_3$)$_3$Cl] (6–8 mol %) prepared under Ar. The reaction was stirred for 1 h at 100 °C and cooled to 25 °C.

4.17. Helquat formation, general workup procedure I (14, 15, 18, 19, 20, 40)

All volatiles were removed in vacuo from the reaction mixture. A mixture of solvents (one of the following three mixtures was used: ethyl acetate/acetone 2:1, ethyl acetate/diethyl ether 1:1, or pure ethyl acetate) was added to the residue and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min giving a fine suspension. The supernatant solution was separated from the fine powder via centrifuge and then removed via pipette. The wash was repeated (2×) and the product was transferred to a vial and dried under vacuum (2 mbar) to give pure helquat.

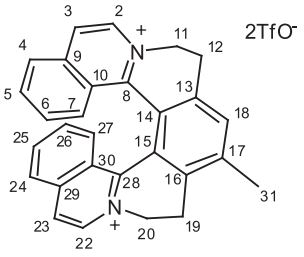
4.18. Helquat formation, general workup procedure II (16, 17, 43)

All volatiles were removed in vacuo from the reaction mixture. Water and DCM were added to the resultant residue, and the mixture was stirred vigorously until all material dissolved. The aqueous layer was separated, washed with DCM (2×) and concentrated in vacuo to give pure helquat.

4.19. Helquat formation, general workup procedure III (31–36)

All volatiles were removed in vacuo from the reaction mixture. Water and DCM were added to the resultant residue, and the mixture was stirred vigorously until all material dissolved. The aqueous layer was separated, washed with DCM (3×) and concentrated in vacuo. Diethyl ether (8 mL) was added to the oil and this mixture, contained in a RBF, was immersed in an ultrasonic bath and sonicated for 1 min giving a fine suspension. The supernatant solution was separated from the fine powder via centrifuge and then removed via decantation. This diethyl ether wash was repeated (2×) and the product was transferred to a vial and dried under vacuum (2 mbar) to give pure helquat.

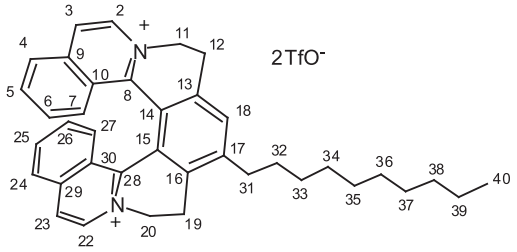
*4.19.1. Helquat **14**.*



Following general procedure for helquat formation I with a reaction time of 1 h and a reaction temperature of 110 °C, and general workup procedure I using ethyl acetate/acetone 2:1, [Rh(PPh$_3$)$_3$Cl] (6.4 mg, 6.92 μmol, 10 mol %), organic dication salt **7** (46.2 mg, 0.066 mmol, 1 equiv), and DMF (7 mL) gave pure helquat **14** as a white solid in 82% yield (38.0 mg, 0.054 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.32. Mp 322–324 °C. R_f [SiO$_2$, Stoddart's magic mixture]: 0.32. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.80 (broad t, J=0.6 Hz, 3H, H-31); 3.53 (dt, J=16.5, 9.5 Hz, 1H, H-12a); 3.68–3.71 (m, 2H, H-19); 3.86 (ddd, J=16.5, 3.1, 2.1 Hz, 1H, H-12b); 5.44–5.55 (m, 4H, H-11 & H-20); 7.65 (ddd, J=8.7, 6.9, 1.3 Hz, 1H, H-6); 7.66 (ddd, J=8.6, 7.0, 1.2 Hz, 1H, H-26); 7.78 (dq, J=8.7, 1.0 Hz, 1H, H-7); 7.78–7.82 (m, 2H, H-5 & H-25); 7.81 (dq, J=8.6, 1.0 Hz, 1H, H-27); 7.90–7.94 (m, 2H, H-4 & H-24); 8.13 (q, J=0.9 Hz, 1H, H-18); 8.26 (dd, J=6.7, 0.7 Hz, 1H, H-23); 8.29 (dd, J=6.7, 0.8, 1H, H-3); 9.02 (d, J=6.7 Hz, 1H, H-22); 9.06 (d, J=6.7 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.87 (C-31); 25.49 (C-19); 28.31 (C-12); 55.71 (C-20); 55.97 (C-11); 125.39 (C-23); 125.64 (C-3); 126.11 (C-14); 126.56 (C-7); 126.60 (C-27); 126.96 (C-10); 127.06 (C-30); 128.07 (C-15); 128.45 (C-4); 128.49 (C-24); 132.15 (C-26 & C-6); 135.19 (C-18); 136.06 (C-5 & C-25); 137.69 (C-22); 137.76 (C-2); 138.87 (C-9 & C-29); 141.42 (C-13); 141.97 (C-16); 143.80 (C-17); 150.87 (C-8); 150.96 (C-28). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1155s, 1261vs, 1625w, 3080w. MS (ESI) m/z: 549 [(M−OTf)$^+$] (100), 400 (59), 200 [(M-2OTf)$^{2+}$] (95). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{30}H_{24}F_3N_2O_3S$) calcd: 549.1454, found: 549.1450. Elem. Anal. Calcd for $C_{31}H_{24}F_6N_2O_6S_2$: C, 53.29; H, 3.46; N, 4.01. Found: C, 53.02; H, 3.53; N, 3.82.

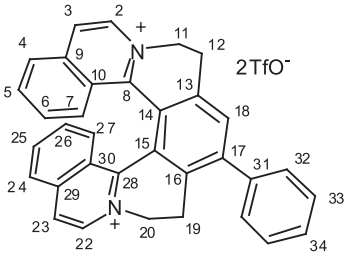
*4.19.2. Helquat **15**.*



Following general procedure for helquat formation I with a reaction time of 2 h and a reaction temperature of 110 °C, and general workup procedure I using ethyl acetate/diethyl ether 2:1, [Rh(PPh$_3$)$_3$Cl] (2.5 mg, 2.70 μmol, 10 mol %), organic dication salt **8** (21.1 mg, 0.026 mmol, 1 equiv), and DMF (4 mL) gave pure helquat **15** as a light brown sticky solid in 69% yield (14.5 mg, 0.018 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.67. ^{1}H NMR (600 MHz, acetone-d_6): δ=0.91 (t, J=7.2 Hz, 3H, H-40); 1.30–1.42 (m, 10H, H-35, H-36, H-37, H-38 & H-39); 1.44–1.50 (m, 2H, H-34); 1.57–1.63 (m, 2H, H-33); 1.83–1.91 (m, 2H, H-32); 3.08–3.20 (m, 2H, H-31); 3.56 (ddd, J=16.9, 11.8, 7.9 Hz, 1H, H-19a); 3.70–3.74 (m, 2H, H-12); 3.92 (dt, J=16.9, 2.6 Hz, 1H, H-19b); 5.43–5.55 (m, 4H, H-11 & H-20); 7.655 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 7.66 (ddd, J=8.5, 7.1, 1.2 Hz, 1H, H-26); 7.77 (dq, J=8.7, 0.9 Hz, 1H, H-7); 7.78–7.81 (m, 2H, H-5 & H-25); 7.81 (dq, J=8.5, 0.9 Hz, 1H, H-27); 7.91 (ddt, J=8.2, 1.2, 0.6 Hz, 1H, H-24); 7.92 (ddt, J=8.2, 1.2, 0.6 Hz, 1H, H-4); 8.16 (s, 1H, H-18); 8.25 (dd, J=6.7, 0.7 Hz, 1H, H-23); 8.29 (dd, J=6.6, 0.8 Hz, 1H, H-3); 9.02 (d, J=6.7 Hz, 1H, H-22); 9.07 (d, J=6.6 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6,): δ=14.31 (C-40); 23.27 (C-39); 25.29 (C-19); 28.37 (C-12); 30.02, 30.05, 30.28, 30.29, 30.32 (C-33, C-34, C-35, C-36 and C-37 not necessarily in that order); 30.96 (C-32); 32.58 (C-38); 33.95 (C-31); 55.80 (C-20); 55.99 (C-11); 125.34 (C-23); 125.63 (C-3); 126.23 (C-14); 126.55 (C-24); 126.62 (C-4); 126.97 (C-30); 127.10 (C-10); 128.29 (C-15); 128.43 (C-27); 128.47 (C-7); 132.15 (C-6); 132.18 (C-26); 134.48 (C-18); 136.03 (C-5); 136.04 (C-25); 137.68 (C-2); 137.78 (C-22); 138.04 (C-9); 138.84 (C-29); 141.12 (C-16); 141.43 (C-13); 148.11 (C-17); 150.89 (C-28); 151.05 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1153s, 1261vs, 1277vs, 1626w, 3084w. MS (ESI) m/z: 675 [(M−OTf)$^+$] (32), 526 (15), 263 [(M-2OTf)$^{2+}$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{39}H_{42}F_3N_2O_3S$) calcd: 675.2863, found: 675.2855.

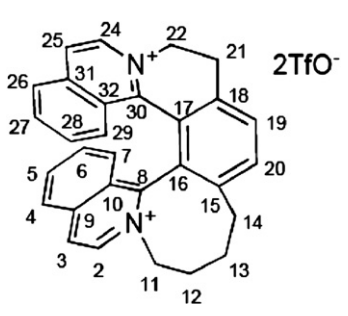
*4.19.3. Helquat **16**.*



Following general procedure for helquat formation I with a reaction time of 2 h and a reaction temperature of 130 °C, and general workup procedure II, [Rh(PPh$_3$)$_3$Cl] (1.2 mg, 1.30 μmol, 13.5 mol %), organic dication salt **9** (7.3 mg, 9.60 μmol, 1 equiv), and DMF (1.5 mL) gave helquat **16** as a yellow oil in 75% yield (5.5 mg, 7.23 μmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0. 51. ^{1}H NMR (600 MHz, acetone-d_6): δ=3.59 (ddd, J=16.8, 3.2, 1.9 Hz, 1H, H-19a); 3.76–3.83 (m, 3H, H-12 & H-19b); 5.40–5.52 (m, 2H, H-11); 5.46 (td, J=13.9, 3.2 Hz, 1H, H-20a); 5.57–5.62 (m, 1H, H-20b); 7.63–7.75 (m, 7H, H-6, H-26, H-32, H-33 & H-34); 7.82 (ddd, J=8.2, 6.8, 1.1 Hz, 1H, H-25); 7.83–7.85 (m, 1H, H-5); 7.86 (dq, J=8.7, 0.8 Hz, 1H, H-27); 7.88 (dq, J=8.7, 0.8 Hz, 1H, H-7); 7.93–7.97 (m, 2H, H-4 & H-24); 8.25 (t, J=0.8, 1H, H-18); 8.30 (dd, J=6.9, 0.8 Hz, 1H, H-23); 8.33 (dd, J=6.7, 0.7 Hz, 1H, H-3); 9.07 (d, J=6.9 Hz, 1H, H-22); 9.08 (d, J=6.7 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=27.49 (C-19); 28.52 (C-12); 56.10 (C-20); 56.16 (C-11); 125.65 (C-23); 126.43 (C-24); 126.64 (C-4); 127.13 (C-14); 127.18 (C-30); 127.56 (C-10); 128.49 (C-27); 128.56 (C-7); 129.03 (C-15); 129.85 (C-33); 129.91 (C-3); 130.01 (C-34); 130.22 (C-32); 132.22 (C-26); 132.38 (C-6); 134.68 (C-18); 136.14 (C-25); 136.15 (C-5); 137.71 (C-22); 137.94 (C-2); 138.63 (C-31); 138.89 (C-29); 138.90 (C-9); 140.30 (C-16); 141.85 (C-13); 146.88 (C-17); 150.79 (C-28); 151.11 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1155s, 1262vs, 1275vs, 1626w, 3085w. MS (ESI) m/z: 611 [(M−OTf)$^+$] (8), 461 (21), 231 [(M-2OTf)$^{2+}$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{35}H_{26}F_3N_2O_3S$) calcd: 611.1616, found: 611.1620.

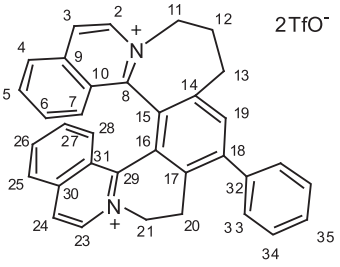
*4.19.4. Helquat **17**.*



Following general procedure for helquat formation I with a reaction time of 1 h and a reaction temperature of 110 °C, and general workup procedure II, [Rh(PPh$_3$)$_3$Cl] (2.2 mg, 2.39 μmol, 10 mol %), organic dication salt **10** (17 mg, 23.85 μmol, 1 equiv), and DMF (3 mL) gave helquat **17** as a yellow glass in 96% yield (16.4 mg, 23.01 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.34. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.09–2.12 (m, 1H, H-13a); 2.23 (ddd, J=14.5, 12.5, 7.6, 1H, H-14a); 2.32–2.40 (m, 2H, H-13b & H-12a); 2.72–2.80 (m, 1H, H-12b); 3.26 (dd, J=14.5, 7.6 Hz, 1H, H-14b); 3.69 (ddd, J=15.9, 3.4, 2.1 Hz, 1H, H-21a); 3.77 (ddd, J=15.9, 13.8, 5.2 Hz, 1H, H-21b); 5.30 (td, J=14.1, 3.4 Hz, 1H, H-22a); 5.35 (ddd, J=14.4, 5.2, 2.1, 1H, H-22b); 5.54 (broad dd, J=13.5, 9.5 Hz, 1H, H-11a); 5.65 (broad dd, J=13.5, 6.1, 1H, H-11b); 7.40 (dq, J=8.7, 0.9 Hz, 1H, H-7); 7.74 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 7.87–7.94 (m, 4H, H-26, H-27, H-28 & H-29); 7.97 (ddd, J=8.2, 6.9, 1.1 Hz, 1H, H-5); 8.08 (dt, J=8.2, 0.9 Hz, 1H, H-4); 8.20 (d, J=6.7 Hz, 1H, H-25); 8.27 (d, J=8.0 Hz, 1H, H-20); 8.29 (dd, J=8.0, 0.6 Hz, 1H, H-19); 8.46 (dd, J=6.8, 0.6 Hz, 1H, H-3); 8.92 (broad d, J=6.6 Hz, 1H, H-24); 9.15 (d, J=6.8 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=26.64 (C-13); 28.68 (C-12); 28.95 (C-21); 32.77 (C-14); 55.80 (C-22); 60.33 (C-11); 125.41 (C-25); 126.77 (C-29); 127.08 (C-32); 127.64 (C-10); 128.04 (C-26); 128.24 (C-3); 128.44 (C-7); 128.73 (C-4); 129.25 (C-17); 129.28 (C-16); 131.23 (C-28); 133.51 (C-6); 133.99 (C-19); 136.52 (C-27); 137.25 (C-5); 137.58 (C-24); 137.82 (C-20); 137.88 (C-2); 138.03 (C-31); 138.51 (C-9); 140.96 (C-18); 146.90 (C-15); 151.54 (C-30); 156.44 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1262vs, 1274vs, 1627w, 3080w. MS (ESI) m/z: 563 [(M−OTf)$^+$] (49), 413 (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{31}H_{26}F_3N_2O_3S$) calcd: 563.1611, found: 563.1621.

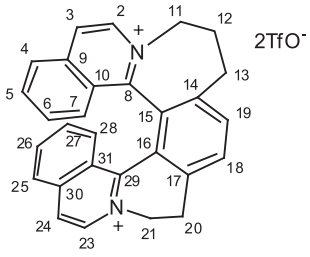
*4.19.5. Helquat **18**.*



Following general procedure for helquat formation I with a reaction time of 1.5 h and a reaction temperature of 110 °C, and general workup procedure I using ethyl acetate/acetone 2:1, [Rh(PPh$_3$)$_3$Cl] (2.9 mg, 3.13 μmol, 10 mol %), organic dication salt **11** (24.8 mg, 0.0320 mmol, 1 equiv), and DMF (4 mL) gave pure helquat **18** as a white solid in 54% yield (13.3 mg, 0.017 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.56. Mp 242–243 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.84–2.92 (m, 2H, H-13a & H-12a); 3.03–3.10 (m, 1H, H-12b); 3.37–3.42 (m, 1H, H-13b); 3.54 (ddd, J=16.2, 13.2, 1.9 Hz, 1H, H-20a); 3.82 (ddd, J=16.2, 13.7, 5.4 Hz, 1H, H-20b); 5.27 (td, J=14.0, 3.2 Hz, 1H, H-21a); 5.32 (broad ddd, J=14.6, 5.4, 1.9 Hz, 1H, H-21b); 5.54–5.56 (m, 2H, H-11); 7.61 (dq, J=8.7, 0.9 Hz, 1H, H-7); 7.63–7.66 (m, 1H, H-35); 7.68–7.72 (m, 2H, H-34); 7.72 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 7.76–7.78 (m, 2H, H-33); 7.80 (ddd, J=8.5, 6.9, 1.3 Hz, 1H, H-27); 7.87 (ddd, J=8.1, 6.9, 1.2 Hz, 1H, H-5); 7.91–7.96 (m, 2H, H-4 & H-26); 7.98 (dq, J=8.5, 0.9 Hz, 1H, H-28); 8.05 (dt, J=8.2, 1.0 Hz, 1H, H-25); 8.25 (dd, J=6.7, 0.7 Hz, 1H, H-24); 8.27 (s, 1H, H-19); 8.42 (dd, J=6.8, 0.9 Hz, 1H, H-3); 8.98 (broad d, J=6.8 Hz, 1H, H-23); 9.12 (d, J=6.8 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=27.62 (C-20); 29.88 (C-13); 33.14 (C-12); 55.82 (C-21); 59.51 (C-11); 125.72 (C-24); 126.11 (C-28); 127.41 (C-31); 127.57 (C-3 & C-7); 128.11 (C-10); 128.20 (C-4); 128.72 (C-25); 128.83 (C-15); 129.85 (C-34); 129.92 (C-35); 130.16 (C-16); 130.34 (C-33); 131.83 (C-27); 133.08 (C-6); 136.33 (C-5); 136.74 (C-19); 136.80 (C-26); 137.51 (C-23); 138.19 (C-2); 138.45 (C-30); 138.64 (C-9); 138.67 (C-32); 139.17 (C-17); 141.51 (C-14); 146.70 (C-18); 151.36 (C-29); 155.69 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1261vs, 1277vs, 1625w, 3083w. MS (ESI) m/z: 625 [(M−OTf)$^+$] (22), 475 (12), 238 [(M-2OTf)$^{2+}$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{36}H_{28}F_3N_2O_3S$) calcd: 625.1767, found: 625.1777.

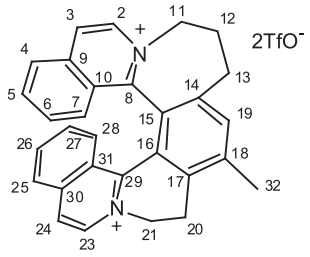
*4.19.6. Helquat **19**.*



Following general procedure for helquat formation I with a reaction time of 1 h and a reaction temperature of 110 °C, and general workup procedure I using ethyl acetate/acetone 2:1, [Rh(PPh$_3$)$_3$Cl] (6.3 mg, 6.81 μmol, 10 mol %), organic dication salt **12** (46.4 mg, 0.066 mmol, 1 equiv), and DMF (7 mL) gave pure helquat **19** as a white solid in 86% yield (39.7 mg, 0.057 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.33. Mp 272–274 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.79 (ddd, J=13.8, 12.5, 7.9 Hz, 1H, H-13a); 2.84–2.91 (m, 1H, H-12a); 3.01–3.09 (m, 1H, H-12b); 3.30 (ddd, J=13.8, 4.5, 1.0 Hz, 1H, H-13b); 3.72 (ddd, J=16.1, 3.9, 2.2 Hz, 1H, H-20a); 3.78 (dddt, J=16.1, 12.5, 6.1, 1.0 Hz, 1H, H-20b); 5.37 (broad ddd, J=14.5, 12.5, 3.9 Hz, 1H, H-21a); 5.40 (dddd, J=14.5, 6.1, 2.2, 0.7 Hz, 1H, H-21b); 5.51 (ddd, J=13.7, 12.4, 5.2 Hz, 1H, H-11a); 5.54 (ddd, J=13.7, 7.3, 1.5 Hz, 1H, H-11b); 7.50 (dq, J=8.7, 0.9 Hz, 1H, H-7); 7.69 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 7.76 (ddd, J=8.6, 6.9, 1.3 Hz, 1H, H-27); 7.84 (ddd, J=8.0, 6.9, 1.2 Hz, 1H, H-26); 7.89–7.93 (m, 3H, H-5, H-25 & H-28); 8.03 (ddt, J=8.2, 1.2, 0.5 Hz, 1H, H-4); 8.20 (d, J=7.8 Hz, 1H, H-19); 8.24 (broad dd, J=6.6, 0.7 Hz, 1H, H-24); 8.26 (dd, J=7.8, 1.1 Hz, 1H, H-18); 8.43 (dd, J=6.7, 1.0 Hz, 1H, H-3); 8.98 (dt, J=6.6, 0.8 Hz, 1H, H-23); 9.13 (d, J=6.7 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=28.81 (C-20); 30.30 (C-13); 33.19 (C-12); 55.90 (C-21); 59.43 (C-11); 125.62 (C-24); 125.82 (C-28); 127.28 (C-31); 127.50 (C-7); 127.63 (C-3); 127.90 (C-10); 128.13 (C-25); 128.71 (C-4); 129.22 (C-15); 129.62 (C-16); 131.68 (C-27); 133.07 (C-6); 133.99 (C-18); 136.22 (C-19); 136.29 (C-26); 136.79 (C-5); 137.77 (C-23); 138.23 (C-2); 138.52 (C-30); 138.69 (C-9); 141.32 (C-17); 141.79 (C-14); 150.93 (C-29); 155.55 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1154s, 1263vs, 1625m, 3076w. MS (ESI) m/z: 549 [(M−OTf)$^+$] (100), 491 (24), 400 (11), 200 [(M-2OTf)$^{2+}$] (47). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{30}H_{24}F_3N_2O_3S$) calcd: 549.1454, found: 549.1449. Elem. Anal. Calcd for $C_{31}H_{26}F_6N_2O_6S_2$: C, 53.29; H, 3.46; N, 4.01. Found: C, 53.10; H, 3.59; N, 3.77.

*4.19.7. Helquat **20**.*

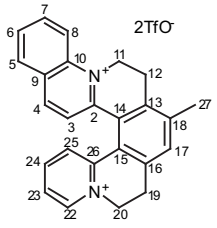


Following general procedure for helquat formation I with a reaction time of 1 h and a reaction temperature of 110 °C, and general workup procedure I using ethyl acetate/acetone 2:1, [Rh(PPh$_3$)$_3$Cl] (5.9 mg, 6.38 μmol, 10 mol %), organic dication **13** (44.0 mg,

0.062 mmol, 1 equiv), and DMF (7 mL) gave pure helquat **20** as a white solid in 74% yield (32.4 mg, 0.046 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.39. Mp 251–253 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.77 (ddd, J=13.9, 12.4, 8.0 Hz, 1H, H-13a); 2.81 (s, 3H, H-32); 2.83–2.92 (m, 1H, H-12a); 3.00–3.08 (m, 1H, H-12b); 3.24 (dd, J=13.9, 6.6 Hz, 1H, H-13b); 3.56 (ddd, J=16.3, 14.1, 4.9 Hz, 1H, H-20a); 3.85 (ddd, J=16.3, 3.2, 1.8 Hz, 1H, H-20b); 5.32 (td, J=14.3, 3.2 Hz, 1H, H-21a); 5.38 (ddd, J=14.5, 4.9, 1.8 Hz, 1H, H-21b); 5.49–5.52 (m, 2H, H-11); 7.52 (dq, J=8.7, 0.9 Hz, 1H, H-7); 7.70 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 7.75 (ddd, J=8.5, 6.9, 1.3 Hz, 1H, H-27); 7.83 (ddd, J=8.2, 6.9, 1.1 Hz, 1H, H-26); 7.88–7.91 (m, 2H, H-25 & H-28); 7.90 (ddd, J=8.2, 6.9, 1.1 Hz, 1H, H-5); 8.02 (ddt, J=8.2, 1.2, 0.5 Hz, 1H, H-4); 8.09 (s, 1H, H-19); 8.21 (d, J=6.6 Hz, 1H, H-24); 8.38 (broad d, J=6.8 Hz, 1H, H-3); 8.97 (broad d, J=6.6 Hz, 1H, H-23); 9.09 (d, J=6.8 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.82 (C-32); 25.44 (C-20); 30.31 (C-13); 33.25 (C-12); 55.45 (C-21); 59.43 (C-11); 125.46 (C-24); 126.04 (C-28); 127.34 (C-3 & C-15); 127.36 (C-31); 127.65 (C-7); 128.05 (C-10); 128.11 (C-25); 128.65 (C-4); 129.17 (C-16); 131.60 (C-27); 132.99 (C-6); 136.21 (C-26); 136.70 (C-5); 137.52 (C-23); 137.61 (C-19); 138.10 (C-2); 138.42 (C-30); 138.62 (C-9); 140.38 (C-17); 141.13 (C-14); 142.96 (C-18); 151.29 (C-29); 155.86 (C-8). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1262vs, 1275vs, 1626m, 3085w. MS (ESI) m/z: 563 [(M−OTf)$^+$] (87), 413 (53), 288 (14), 207 [(M-2OTf)$^{2+}$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{31}H_{26}F_3N_2O_3S$) calcd: 563.1611, found: 563.1608. Elem. Anal. Calcd for $C_{32}H_{26}F_6N_2O_6S_2$: C, 53.93; H, 3.68; N, 3.93. Found: C, 53.67; H, 3.88; N, 3.72.

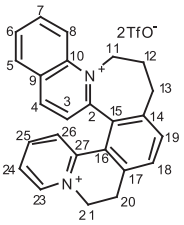
*4.19.8. Helquat **31**.*



Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (5.3 mg, 5.72 μmol, 10 mol %), organic dication salt **25** (37.5 mg, 0.057 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **31** as a brown powder in 79% yield (29.7 mg, 0.045 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.32. Mp 138–141 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.66 (d, J=0.9 Hz, 3H, H-27); 3.41 (ddd, J=17.8, 13.7, 4.9 Hz, 1H, H-12a); 3.56–3.62 (m, 2H, H-19); 3.78 (ddd, J=17.8, 3.8, 1.7 Hz, 1H, H-12b); 5.02 (ddd, J=15.0, 13.7, 3.8 Hz, 1H, H-11a); 5.22 (ddd, J=13.4, 11.0, 8.1 Hz, 1H, H-20a); 5.31 (ddd, J=13.4, 4.2, 2.4 Hz, 1H, H-20b), 6.18 (ddd, J=15.0, 4.9, 1.7 Hz, 1H, H-11b); 7.90 (q, J=0.9 Hz, 1H, H-17); 8.09 (m, 1H, H-23); 8.10 (ddd, J=8.1, 7.0, 1.0 Hz, 1H, H-6); 8.28–8.30 (m, 2H, H-24 & H-25); 8.39 (ddd, J=8.9, 7.0, 1.7 Hz, 1H, H-7); 8.42 (d, J=8.8 Hz, 1H, H-3); 8.47 (dd, J=8.1, 1.7 Hz, 1H, H-5); 8.90–8.93 (m, 2H, H-4 & H-8); 9.25 (ddd, J=6.2, 1.5, 0.7 Hz, 1H, H-22). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.43 (C-27); 25.49 (C-12); 28.00 (C-19); 48.45 (C-11); 56.03 (C-20); 119.93 (C-8); 126.75 (C-3); 127.21 (C-23); 128.10 (C-15); 128.77 (C-14); 130.03 (C-9); 130.76 (C-6); 131.29 (C-25); 131.36 (C-5); 135.11 (C-17); 136.57 (C-7); 140.94 (C-10); 141.24 (C-16); 141.72 (C-13); 142.59 (C-18); 145.67 (C-24); 145.89 (C-4); 147.18 (C-22); 147.82 (C-26); 151.55 (C-2). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1154s, 1260vs; 1602m; 3085w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1294. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)$: C, 48.65; H, 3.63; N, 4.20. Found: C, 48.31; H, 3.49; N, 4.14.

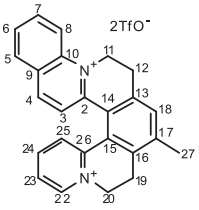
*4.19.9. Helquat **32**.*



Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (6.5 mg, 7.02 μmol, 10 mol %), organic dication salt **26** (45.8 mg, 0.071 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **32** as a brown powder in 66% yield (31.7 mg, 0.047 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.32. Mp 118–122 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.63 (td, J=14.2, 6.5 Hz, 1H, H-13a), 2.72–2.79 (m, 1H, H-12a); 3.04–3.11 (m, 1H, H-12b); 3.20 (dd, J=14.4, 5.9 Hz, 1H, H-13b); 3.62–3.70 (m, 2H, H-20); 5.14 (ddd, J=14.7, 13.6, 5.5 Hz, 1H, H-11a); 5.19 (td, J=13.1, 6.3 Hz, 1H, H-21a); 5.31 (ddd, J=13.2, 4.4, 2.2 Hz, 1H, H-21b); 6.00 (dd, J=14.7, 5.9 Hz, 1H, H-11b); 7.93 (dd, J=8.2, 1.4 Hz, 1H, H-26); 7.94 (d, J=7.7 Hz, 1H, H-18); 8.02 (broad d, J=7.7 Hz, 1H, H-19); 8.08 (ddd, J=7.7, 6.1, 0.6 Hz, 1H, H-24); 8.17 (ddd, J=8.1, 7.0, 0.8 Hz, 1H, H-6); 8.23 (dddd, J=8.2, 7.7, 1.6, 0.7 Hz, 1H, H-25); 8.25 (d, J=8.7 Hz, 1H, H-3); 8.45 (ddd, J=9.0, 7.0, 1.5 Hz, H, H-7); 8.57 (dd, J=8.1, 1.5 Hz, 1H, H-5); 8.99 (broad d, J=9.0 Hz, 1H, H-8); 9.12 (dd, J=8.7, 1.0 Hz, 1H, H-4); 9.28 (ddd, J=6.1, 1.6, 0.6 Hz, 1H, H-23). ^{13}C NMR (151 MHz, acetone-d_6): δ=28.15 (C-20); 30.31 (C-13); 31.88 (C-12); 53.42 (C-11); 56.24 (C-21); 120.01 (C-8); 127.12 (C-3); 127.42 (C-16 & C-24); 127.64 (C-15); 130.75 (C-9); 131.20 (C-26); 131.25 (C-6); 131.81 (C-5); 133.69 (C-18); 135.00 (C-19); 137.30 (C-7); 140.37 (C-14); 140.51 (C-10); 140.68 (C-17); 145.91 (C-25); 147.30 (C-27); 147.59 (C-4); 147.66 (C-23); 157.54 (C-2). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1152s, 1261vs; 3086w. MS (ESI) m/z: 499 [(M−OTf)$^+$] (100). HRMS (ESI) m/z: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1294. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)_{1.5}$: C, 48.00; H, 3.73; N, 4.15. Found: C, 47.57; H, 3.52; N, 4.15.

*4.19.10. Helquat **33**.*

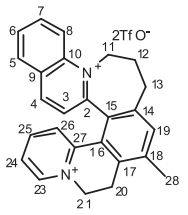


Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (6.1 mg, 6.59 μmol, 10 mol %), organic dication salt **27** (42.9 mg, 0.066 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **33** as a brown powder in 76% yield (33.1 mg, 0.050 mmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.32. Mp 135–139 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.66 (d, J=0.8 Hz, 3H, H-27); 3.40 (ddd, J=17.5, 13.3, 4.8 Hz, 1H, H-19a); 3.60 (ddd, J=17.5, 15.3, 4.8 Hz, 1H, H-12a); 3.67 (ddd, J=17.5, 4.2, 1.8 Hz, 1H, H-12b); 3.70 (ddd, J=17.5, 3.8, 1.6 Hz, 1H, H-19b); 5.03 (td, J=14.3, 4.2 Hz, 1H, H-11a); 5.20 (td, J=13.3, 3.8 Hz, 1H, H-20a); 5.36 (ddd, J=13.3, 4.8, 1.6 Hz, 1H, H-20b); 6.14 (ddd, J=13.5, 4.8, 1.8 Hz, 1H, H-11b); 7.90 (q, J=0.8 Hz, 1H, H-18); 8.08 (ddd, J=8.1, 7.0, 0.8 Hz, 1H, H-6); 8.13 (ddd, J=7.2, 6.1, 1.8 Hz, 1H, H-23); 8.29 (ddd, J=8.3, 1.8, 0.8 Hz, 1H, H-25); 8.32 (ddd, J=8.3, 7.2, 1.4 Hz, 1H, H-24); 8.37 (ddd, J=9.0, 7.0, 1.6 Hz,

1H, H-7); 8.40 (d, *J*=8.8 Hz, 1H, H-3); 8.47 (ddt, *J*=8.1, 1.6, 0.6 Hz, 1H, H-5); 8.89 (dq, *J*=9.0, 0.8 Hz, 1H, H-8); 8.91 (dd, *J*=8.8, 0.9 Hz, 1H, H-4); 9.29 (ddq, *J*=7.2, 1.4, 0.7 Hz, 1H, H-22). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.73 (C-27); 25.52 (C-19); 27.78 (C-12); 48.68 (C-11); 55.60 (C-20); 119.82 (C-8); 126.55 (C-3); 126.57 (C-14); 127.53 (C-23); 128.32 (C-15); 129.90 (C-9); 130.64 (C-6); 131.39 (C-5); 131.63 (C-25); 133.89 (C-18); 136.52 (C-7); 140.61 (C-10); 141.36 (C-13); 141.66 (C-16); 143.97 (C-17); 145.69 (C-24); 145.82 (C-4); 147.03 (C-22); 147.92 (C-26); 151.41 (C-2). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1154s, 1260vs; 1600m; 3090w. MS (ESI) *m*/*z*: 499 [(M−OTf)$^+$] (62). HRMS (ESI) *m*/*z*: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1298. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)$: C, 48.65; H, 3.63; N, 4.20. Found: C, 48.70; H, 3.58; N, 4.16.

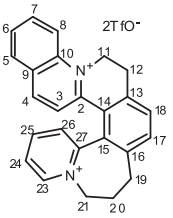
*4.19.11. Helquat **34**.*



Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (7.7 mg, 8.32 μmol, 10 mol %), organic dication salt **28** (55.4 mg, 0.083 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **34** as a brown powder in 65% yield (37.0 mg, 0.054 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.32. Mp 131–134 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.61–2.67 (m, 1H, H-13a); 2.66 (t, *J*=0.6 Hz, 3H, H-28); 2.71–2.79 (m, 1H, H-12a); 3.05–3.12 (m, 1H, H-12b); 3.15 (dd, *J*=14.7, 5.9 Hz, 1H, H-13b); 3.44 (ddd, *J*=17.2, 15.2, 4.8 Hz, 1H, H-20a); 3.72 (ddd, *J*=17.2, 3.8, 1.8 Hz, 1H, H-20b); 5.13 (ddd, *J*=14.7, 13.6, 5.5 Hz, 1H, H-11a); 5.15 (dddt, *J*=15.2, 13.3, 3.8, 0.9 Hz, 1H, H-21a); 5.32 (ddd, *J*=13.3, 4.8, 1.8 Hz, 1H, H-21b); 5.98 (dd, *J*=14.7, 5.8 Hz, 1H, H-11b); 7.84 (q, *J*=0.6 Hz, 1H, H-19); 7.89 (dd, *J*=8.2, 1.3 Hz, 1H, H-26); 8.07 (ddd, *J*=7.6, 6.1, 1.3 Hz, 1H, H-24); 8.16 (ddd, *J*=8.0, 7.0, 0.9 Hz, 1H, H-6); 8.21 (dddd, *J*=8.2, 7.6, 1.5, 0.6 Hz, 1H, H-25); 8.22 (d, *J*=8.6 Hz, 1H, H-3); 8.43 (ddd, *J*=8.9, 7.0, 1.5 Hz, 1H, H-7); 8.55 (dd, *J*=8.0, 1.5 Hz, 1H, H-5); 8.96 (m, 1H, H-8); 9.08 (dd, *J*=8.6, 0.9 Hz, 1H, H-4); 9.27 (ddd, *J*=6.1, 1.5, 0.6 Hz, 1H, H-23). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.55 (C-28); 25.27 (C-20); 30.31 (C-13); 31.97 (C-12); 53.52 (C-11); 55.74 (C-21); 119.98 (C-8); 127.25 (C-24); 127.40 (C-3); 127.69 (C-16); 129.61 (C-15); 130.57 (C-9); 131.13 (C-6); 131.35 (C-26); 131.77 (C-5); 136.32 (C-19); 137.19 (C-7); 139.48 (C-17); 140.22 (C-14); 140.49 (C-10); 142.86 (C-18); 145.75 (C-25); 147.31 (C-4); 147.35 (C-23); 147.64 (C-27); 157.87 (C-2). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1152s, 1261vs; 1599m; 3086w. MS (ESI) *m*/*z*: 513 [(M−OTf)$^+$] (68). HRMS (ESI) *m*/*z*: [(M−OTf)$^+$] ($C_{27}H_{24}F_3N_2O_3S$) calcd: 513.1454, found: 513.1450. Elem. Anal. Calcd for $C_{28}H_{24}F_6N_2O_6S_2\cdot(H_2O)_{1.5}$: C, 48.77; H, 3.95; N, 4.06. Found: C, 48.41; H, 3.69; N, 4.06.

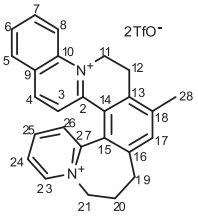
*4.19.12. Helquat **35**.*



Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (6.3 mg, 6.81 μmol, 10 mol %), organic dication salt **29** (44.2 mg, 0.068 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **35** as a brown powder in 80% yield (35.4 mg, 0.054 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.32. Mp 256–262 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.59–2.71 (m, 2H, H-19a & H-20a); 3.18–3.22 (m, 1H, H-19b); 2.93–3.00 (m, 1H, H-20b); 3.65 (broad ddd, *J*=14.7, 13.5, 4.2 Hz, 1H, H-12a); 3.72 (ddd, *J*=17.0, 4.2, 2.1 Hz, 1H, H-12b); 5.01 (dddd, *J*=14.7, 13.5, 4.2, 0.7 Hz, 1H, H-11a); 5.09 (td, *J*=13.6, 5.7 Hz, 1H, H-21a); 5.27 (dd, *J*=13.8, 6.6 Hz, 1H, H-21b); 6.08 (dddt, *J*=13.5, 4.8, 2.1, 0.7, 1H, H-11b); 7.77 (d, *J*=8.8 Hz, 1H, H-3); 7.97 (d, *J*=7.7 Hz, 1H, H-17); 8.04 (dd, *J*=7.0, 1.0 Hz, 1H, H-18); 8.07 (ddd, *J*=8.1, 7.0, 0.8 Hz, 1H, H-6); 8.15 (dd, *J*=8.0, 1.8 Hz, 1H, H-26); 8.31 (ddd, *J*=7.7, 6.2, 1.8 Hz, 1H, H-24); 8.37 (ddd, *J*=9.0, 7.0, 1.5 Hz, 1H, H-7); 8.41 (dd, *J*=8.1, 1.5 Hz, 1H, H-5); 8.48 (td, *J*=8.7, 1.5 Hz, 1H, H-25); 8.85 (broad d, *J*=8.8 Hz, 1H, H-4); 8.87 (m, 1H, H-8); 9.49 (ddd, *J*=6.2, 1.5, 0.6 Hz, 1H, H-23). ^{13}C NMR (151 MHz, acetone-d_6): δ=27.92 (C-12); 30.31 (C-19); 32.27 (C-20); 49.04 (C-11); 59.41 (C-21); 119.80 (C-8); 126.06 (C-3); 129.06 (C-24); 129.17 (C-14); 129.76 (C-9); 130.81 (C-6); 131.19 (C-15), 131.38 (C-5); 132.74 (C-18); 132.84 (C-26); 135.62 (C-17); 136.75 (C-7); 140.52 (C-13); 140.80 (C-10); 140.81 (C-16); 146.03 (C-4); 146.74 (C-25); 148.18 (C-23); 150.86 (C-2); 153.32 (C-27). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1030s, 1162s, 1266vs; 1602m; 3081w. MS (ESI) *m*/*z*: 499 [(M−OTf)$^+$] (100). HRMS (ESI) *m*/*z*: [(M−OTf)$^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298, found: 499.1294. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)_{0.5}$: C, 49.32; H, 3.53; N, 4.26. Found: C, 49.07; H, 3.37; N, 4.12.

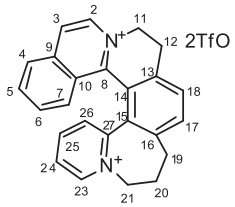
*4.19.13. Helquat **36**.*



Following general procedure for helquat formation I with a reaction time of 30 min and a reaction temperature of 90 °C, and general workup procedure III, [Rh(PPh$_3$)$_3$Cl] (7.8 mg, 8.43 μmol, 10 mol %), organic dication salt **30** (56.1 mg, 0.084 mmol, 1 equiv), and DMF (2 mL) gave pure helquat **36** as a brown powder in 69% yield (39.2 mg, 0.058 mmol).

R_f [SiO$_2$, Stoddart's magic mixture]: 0.32. Mp 230–234 °C. ^{1}H NMR (600 MHz, acetone-d_6): δ=2.60–2.71 (m, 3H, H-19a & H-20); 2.67 (t, *J*=0.7 Hz, 3H, H-28); 3.13–3.17 (m, 1H, H-19b); 3.46 (ddd, *J*=17.4, 15.1, 5.1 Hz, 1H, H-12a); 3.79 (ddd, *J*=17.4, 3.8, 1.9 Hz, 1H, H-12b); 4.98 (dddd, *J*=15.1, 13.7, 3.8, 0.8, 1H, H-11a); 5.08 (td, *J*=13.6, 5.9 Hz, 1H, H-21a); 5.26 (dd, *J*=13.7, 6.5 Hz, 1H, H-21b); 6.10 (ddd, *J*=13.7, 5.1, 1.9 Hz, 1H, H-11b); 7.86 (q, *J*=0.7 Hz, 1H, H-17); 7.74 (d, J=8.8 Hz, 1H, H-3); 8.07 (ddd, *J*=8.1, 7.0, 0.8 Hz, 1H, H-6); 8.13 (dd, *J*=8.0, 1.7 Hz, 1H, H-26); 8.28 (ddd, *J*=7.8, 6.2, 1.7 Hz, 1H, H-24); 8.37 (ddd, *J*=9.0, 7.0, 1.5 Hz, 1H, H-7); 8.40 (dd, *J*=8.1, 1.5 Hz, 1H, H-5); 8.45 (td, *J*=7.9, 1.5 Hz, 1H, H-25); 8.82 (broad d, *J*=8.8 Hz, 1H, H-4); 8.88 (m, 1H, H-8); 9.46 (ddd, *J*=6.2, 1.5, 0.6 Hz, 1H, H-23). ^{13}C NMR (151 MHz, acetone-d_6): δ=19.30 (C-28); 25.23 (C-19); 29.34 (C-12); 32.35 (C-20); 48.65 (C-11); 59.45 (C-21); 119.80 (C-8); 126.23 (C-3); 128.75 (C-24); 128.94 (C-14); 129.21 (C-15); 129.65 (C-9); 130.76 (C-6); 131.34 (C-5); 132.99 (C-26); 136.67 (C-7); 136.89 (C-17); 139.61 (C-13); 140.30 (C-16); 140.64 (C-10); 141.84 (C-18); 145.82 (C-4); 146.61 (C-25); 148.07 (C-23); 151.24 (C-2); 153.65 (C-27). IR (KBr): $\tilde{\nu}$(cm^{-1}) 1029s, 1167s, 1262vs; 1623m; 3083w. MS (ESI) *m*/*z*: 513 [(M−OTf)$^+$] (78). HRMS (ESI) *m*/*z*: [(M−OTf)$^+$] ($C_{27}H_{24}F_3N_2O_3S$) calcd: 513.1454, found: 513.1454. Elem. Anal. Calcd for $C_{28}H_{24}F_6N_2O_6S_2\cdot(H_2O)_{0.5}$ C, 50.07; H, 3.75; N, 4.17. Found: C, 49.81; H, 3.64; N, 4.14.

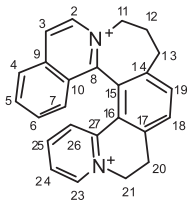
*4.19.14. Helquat **40**.*



Following general procedure for helquat formation II and general workup procedure I using pure ethyl acetate, $[Rh(PPh_3)_3Cl]$ (1.0 mg, 1.08 μmol, 6 mol %) and a solution of organic dication salt **39** (12.2 mg, 18.8 μmol, 1 equiv) in DMF (1.2 mL) gave helquat **40** as a white solid in 84% yield (10.4 mg, 15.8 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.37. Mp 297–299 °C. ^{1}H NMR (600 MHz, acetone-d_6): 2.59 (broad td, J=14.0, 7.5 Hz, 1H, H-19a); 2.80–2.86 (m, 1H, H-20a); 2.99–3.06 (m, 1H, H-20b); 3.24 (ddd, J=14.6, 7.0, 1.2 Hz, 1H, H-19b); 3.64 (ddd, J=16.4, 3.5, 1.8 Hz, 1H, H-12a); 3.74 (dddt, J=16.4, 15.0, 4.6, 1.2 Hz, 1H, H-12b); 5.12 (broad td, J=14.4, 3.5 Hz, 1H, H-11a); 5.36 (dddd, J=13.8, 4.6, 1.8, 0.6 Hz, 1H, H-11b); 5.48 (ddd, J=13.4, 7.0, 1.3 Hz, 1H, H-21a); 5.52 (td, J=13.5, 5.6 Hz, 1H, H-21b); 7.63 (broad dd, J=8.0, 1.5 Hz, 1H, H-26); 7.85 (ddd, J=8.7, 6.9, 1.2 Hz, 1H, H-6); 8.00 (ddd, J=7.7, 6.1, 1.5 Hz, 1H, H-24); 8.01 (ddd, J=8.1, 6.9, 1.0 Hz, 1H, H-5); 8.05 (broad d, J=7.8 Hz, 1H, H-17); 8.08 (td, J=7.8, 1.6 Hz, 1H, H-25); 8.11 (dq, J=8.7, 0.9 Hz, 1H, H-7); 8.14 (broad d, J=7.8 Hz, 1H, H-18); 8.30 (ddt, J=8.1, 1.2, 0.7 Hz, 1H, H-4); 8.60 (dd, J=6.6, 0.7 Hz, 1H, H-3); 9.08 (broad d, J=6.7 Hz, 1H, H-2); 9.38 (ddd, J=6.1, 1.6, 0.5 Hz, 1H, H-23). ^{13}C NMR (151 MHz, acetone-d_6): 29.02 (C-12); 29.71 (C-19); 32.74 (C-20); 56.30 (C-11); 59.01 (C-21); 126.16 (C-3); 127.27 (C-7); 127.45 (C-10 & C-14); 128.70 (C-24); 128.96 (C-4); 132.11 (C-6); 132.55 (C-15); 132.70 (C-26); 133.24 (C-18); 135.95 (C-17); 136.36 (C-5); 138.11 (C-2); 139.69 (C-9); 140.79 (C-16); 142.49 (C-13); 146.34 (C-25); 147.69 (C-23); 150.74 (C-8); 153.35 (C-27). IR (thin film): $\tilde{\nu}$(cm^{-1}) 1029s; 1155s; 1225s; 1259s; 1509m; 1559m; 1625m; 3580m. MS (ESI) m/z: 499.1 [$(M-OTf)^+$] (100); 350.3 [$(M\text{-}2OTf)^{2+}$] (10); 349.2 (20). HRMS (ESI) m/z: [$(M-OTf)^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298; found: 499.1301. Elem. Anal. Calcd for $C_{27}H_{22}F_6N_2O_6S_2\cdot(H_2O)_{0.5}$: C, 49.32; H, 3.53; N, 4.26. Found: C, 49.37; H, 3.44; N, 3.93.

*4.19.15. Helquat **43**.*



Following general procedure for helquat formation II and general workup procedure II, $[Rh(PPh_3)_3Cl]$ (2.5 mg, 2.7 μmol, 8 mol %), and a solution of organic dication salt **42** (23.2 mg, 35.8 μmol, 1 equiv) in DMF (2.3 mL) gave helquat **43** as a yellow glass, which solidified to a yellow solid after one week, in 99% yield (23.0 mg, 35.5 μmol).

R_f [SiO_2, Stoddart's magic mixture]: 0.32. Mp 240–243 °C. ^{1}H NMR (600 MHz, acetone-d_6): 2.60–2.72 (m, 2H, H-12a & H-13a); 2.93–2.98 (m, 1H, H-12b); 3.20–3.25 (m, 1H, H-13b); 3.66–3.74 (m, 2H, H-20); 5.10 (td, J=13.8, 5.8 Hz, 1H, H-21a); 5.33–5.42 (m, 2H, H-11); 5.34 (dd, J=13.9, 6.2 Hz, 1H, H-21b); 7.46 (broad dd, J=8.3, 1.4 Hz, 1H, H-26); 7.83 (ddd, J=8.8, 6.9, 1.2 Hz, 1H, H-6); 7.91 (ddd, J=7.7, 6.1, 1.4 Hz, 1H, H-24); 7.97 (dq, J=8.8, 1.0 Hz, 1H, H-7); 8.04 (td, J=8.0, 1.6 Hz, 1H, H-25); 8.05 (d, J=7.7 Hz, 1H, H-18); 8.12 (dt, J=7.7, 0.8 Hz, 1H, H-19); 8.14 (ddd, J=8.3, 6.9, 1.1 Hz, 1H, H-5); 8.43 (dt, J=8.3, 1.0 Hz, 1H, H-4); 8.83 (dd, J=6.8, 0.9 Hz, 1H, H-3); 9.22 (ddt, J=6.1, 1.6, 0.8 Hz, 1H, H-23); 9.23 (d, J=6.8 Hz, 1H, H-2). ^{13}C NMR (151 MHz, acetone-d_6): 28.08 (C-20); 29.38 (C-13); 32.40 (C-12); 56.45 (C-11); 59.74 (C-21); 127.32 (C-24); 127.41 (C-15); 127.53 (C-16); 128.04 (C-3); 128.25 (C-4); 128.73 (C-7); 129.07 (C-10); 129.29 (C-26); 133.58 (C-6); 133.92 (C-19); 135.21 (C-18); 137.23 (C-5); 138.24 (C-2); 139.69 (C-14); 139.85 (C-9); 141.33 (C-17); 146.36 (C-25); 147.06 (C-27); 147.75 (C-23); 155.78 (C-8). IR (thin film): $\tilde{\nu}$(cm^{-1}) 1030s; 1161s; 1226s; 1258s; 1510m; 1567m; 1625m; 3546m. MS (ESI) m/z: 499.1 [$(M-OTf)^+$] (100); 350.3 [$(M\text{-}2OTf)^{2+}$] (5); 349.2 (10); 321.3 (5). HRMS (ESI) m/z: [$(M-OTf)^+$] ($C_{26}H_{22}F_3N_2O_3S$) calcd: 499.1298; found: 499.1300.

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Supplementary data

Supplementary data (scans of NMR spectra of all compounds, experimental procedures for compounds **2**, **21**, **37**, and X-ray crystallographic data of compounds **18**, **29**, **35**, and **43**) can be found. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.03.007.

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15. The crystallographic data of structures **18**, **29**, **35**, and **43** in Fig. 1 can be found at Cambridge Crystallographic Data Centre (CCDC). Deposition numbers: 733,193, 733,194, 733,195, 734,276 respectively. See also Supplementary data for further details.
16. See Experimental section and Supplementary data section for full experimental details.
17. Combination count is enumerated using a formula for combination without repetition: $N=[n(n-1)\ldots(n-k+1)]/(k!)$, where $n=6$, $k=2$; $N=15$.
18. This number is enumerated using a formula for variation without repetition: $N=n(n-1)\ldots(n-k+1)$, where $n=6$, $k=2$; $N=30$.
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24. Out of the total of 38 steps, 23 are *N*-quaternizations and 15 are [2+2+2] cycloadditions.
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