Supporting Information

Identifying Structure-Function Relationships to Modulate Crossover in Nonaqueous Redox Flow Batteries

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I. General Information

a. General Reagent and Materials Information

Acetonitrile (99.8% anhydrous) was obtained from Sigma Aldrich and used as received. Potassium hexafluorophosphate (≥99%) was obtained from Sigma Aldrich and dried under high vacuum at 100 ºC for 16 h. Stock solutions of KPF_6 in MeCN were prepared in a nitrogen-filled glovebox and dried over activated 3Å molecular sieves for at least two days prior to use. Molecular sieves were activated by heating at 200 ºC under vacuum. Reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros Organics, Combi-Blocks, Oakwood Chemicals, Astatech, and TCI America and used as received, unless stated otherwise. Chromatographic purification was carried out using 230-400 mesh silica gel or 50-200 μm, 60 Å basic aluminum oxide. Thin-layer chromatography (TLC) was performed on 250 μm SiliCycle silica gel F_{254} plates or Analytical Chromatography basic aluminum oxide 60 F_{254} plates.

b. General Analytical Information

Unless otherwise noted, all yields refer to chromatographically and spectroscopically (^{1}H NMR) homogenous materials. ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained on a Varian MR400, Varian VnmrS 500, or a Bruker Advance Neo 500 and reported in parts per million (ppm) relative to TMS via internal referencing to residual protio solvent signals. ^{1}H NMR spectroscopic data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, ddd= doublet of doublet of doublets, dtd= doublet of triplet of doublets, b = broad), coupling constant (Hz), and integration. Data for decoupled ^{13}C NMR spectra are reported in terms of chemical shift and multiplicity when applicable. IR spectra were recorded on a Thermo-Nicolet IS-50 and reported in wave numbers of absorbance (cm $^{-1}$). High resolution mass spectra (HRMS) were obtained by a Micromass AutoSpec Ultima Magnetic Sector Mass Spectrometer using electrospray ionization (ESI). Cyclic voltammetry (CV) was performed in a N_2-filled glovebox with a Biologic VSP multichannel potentiostat/galvanostat using a three-electrode electrochemical cell, consisting of a glassy carbon disk working electrode (0.071 cm 2, BASi), a silver wire pseudo reference electrode, and a platinum wire counter electrode. All experiments were conducted in a 0.50 M KPF_6 electrolyte stock solution.

c. Abbreviations

PTFE = polytetrafluoroethylene
DCM = dichloromethane
EtOAc = ethyl acetate
MeCN = acetonitrile
CV = cyclic voltammetry or cyclic voltammogram

II. Rate of Crossover

a. H-cell Assembly

H-cells were obtained from Adams & Chittenden Scientific Glass Co-Op (Part No. 950569). Viton O-Ring No. 107 were used. Stirring in crossover assays was performed with PTFE-coated 10 x 3 mm stir bars. Silver wire reference electrodes were assembled from 0.5 mm 99.9% annealed silver wire (obtained from Strem Chemicals) in a glass tube sealed with epoxy (see Figure S1, panel 7, I.). Platinum wire counter electrodes were assembled by welding platinum and copper together in a vacuum-sealed glass tube, with only the platinum remaining exposed to the assay (see Figure S1, panel 7, J). Glassy carbon working electrodes were 3 mm in diameter and were obtained from CH Instruments (Part No. CHI104P). The membrane used in this study was Fumasep FAP-375-PP (obtained from Fumatech). The membrane was ion exchanged prior to use by soaking pre-cut membranes in a saturated aqueous solution of KPF_6 (three times for 8-16 h per soak). After each soak, the membrane was rinsed with deionized water. The membrane was the stored under ambient atmosphere. Prior to use, the membranes (along with the glass H-cells) were dried in a vacuum oven at 50 ºC overnight. Stir bars were oven-dried at 150 °C for 12 h. The H-cells were then assembled as shown in Figure S1, panels A-F, and immediately cycled into an N_2-atmosphere glovebox.

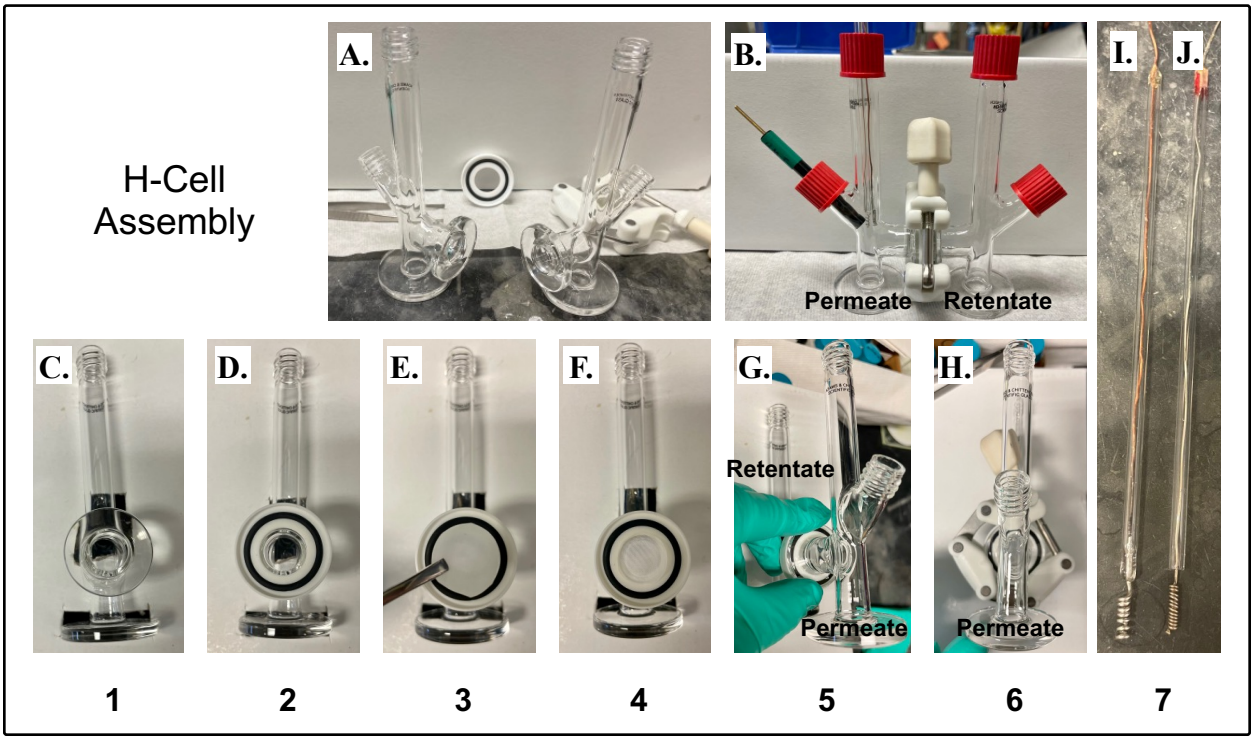


Figure S1. H-cell assembly. **A.** Glass half-cells after drying. **B.** Fully assembled H-cell. **C-H.** Steps of H-cell assembly. **C.** Half-cell placement. **D.** O-ring placement. **E.** Membrane placement. **F.** View of half-cell with correct o-ring and membrane placement. **G.** Placement of other half-cell. **H.** Assembly of H-cell with clamp. **I.** Platinum counter electrode. **J.** Silver wire reference electrode.

b. Initial Rate of Crossover Measurements

General procedure. A 6 mL solution of each electrolyte **1-20** was prepared as a 25 mM solution in 0.5 M KPF_6 in MeCN. This solution (the retentate) was placed in one half of the assembled H-cell. To the other, electrode-containing half of the H-cell, was added 6 mL of a solution of KPF_6 in MeCN (the permeate). The concentration of KPF_6 in the permeate was between 0.5 M-0.575 M, adjusted based on the charge of the electrolyte to maintain an osmotically balanced solution across the H-cell. The H-cell was sealed with a Teflon-lined screw cap, and an initial cyclic voltammogram (CV) was acquired. The permeate and retentate were subsequently allowed to stir vigorously at ambient temperature (which varied from 25-32 °C on the stir plate in the glovebox where the experiment was conducted). Crossover was monitored by CV at time points as indicated. Notably, before data collection, stirring was paused, and the solution was allowed to settle for 1-2 min.

c. Calculation of Concentration from Cyclic Voltammetry

General procedure. Cyclic voltammetry experiments were performed in a nitrogen-filled glove box with a Biologic VSP multichannel potentiostat/galvanostat using a three-electrode setup. A glassy carbon electrode (0.07 cm2, BASi) was used as the working electrode, and a coiled platinum wire was used as the counter electrode. Silver wire was used as a pseudo-reference electrode. All potentials are referenced to Ag/Ag^+. The CVs were performed with a scan rate of 100 mV/s, using 0.5 M KPF_6 in MeCN as supporting electrolyte.

d. Data Analysis Using the Randles-Sevcik Equation

Electrolyte crossover was determined by CV measurements, which were used to calculate the concentration *via* the Randles-Sevcik equation[1] (eq. 1) with i_p being peak current. Derivation of eq. 1 as shown in eq. 2 to eq. 3, and the assumption made in eq. 4, gives eq. 5, which was used to determine concentration (C_x) of electrolyte present in the permeate at a given timepoint. i_{pn} was determined by measuring the peak height (i_{pcn} or i_{pan}, dependent on electrolyte examined) at 1.0 mM (C_n) for each compound **1-20** in triplicate. i_{px} is i_{pcx} or i_{pax}, dependent on electrolyte examined and indicated on each cyclic voltammogram, as listed in section VII.

$$i_p = 0.446nFAC^0\left(\frac{nFvD_0}{RT}\right)^{1/2} \quad \text{[eq. 1]}$$

$$C^0 = \frac{i_p}{0.446nFA\left(\frac{nFvD_0}{RT}\right)^{1/2}} \quad \text{[eq. 2]}$$

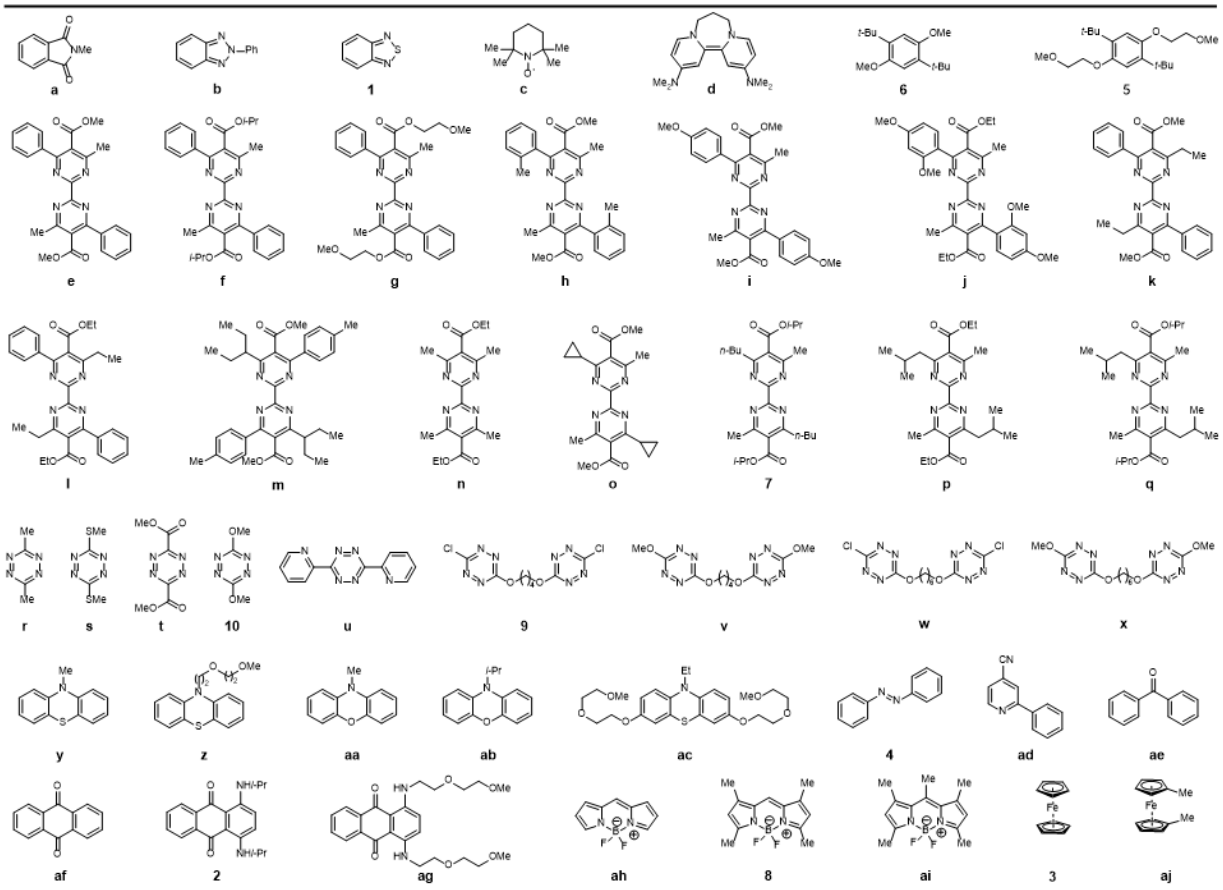
$$\frac{C_n}{C_x} = \frac{i_{pn}}{(D_n)^{1/2}} \cdot \frac{(D_x)^{1/2}}{i_{px}} \quad \text{[eq. 3]}$$

$$(D_x)^{1/2} \approx (D_n)^{1/2} \quad \text{[eq. 4]}$$

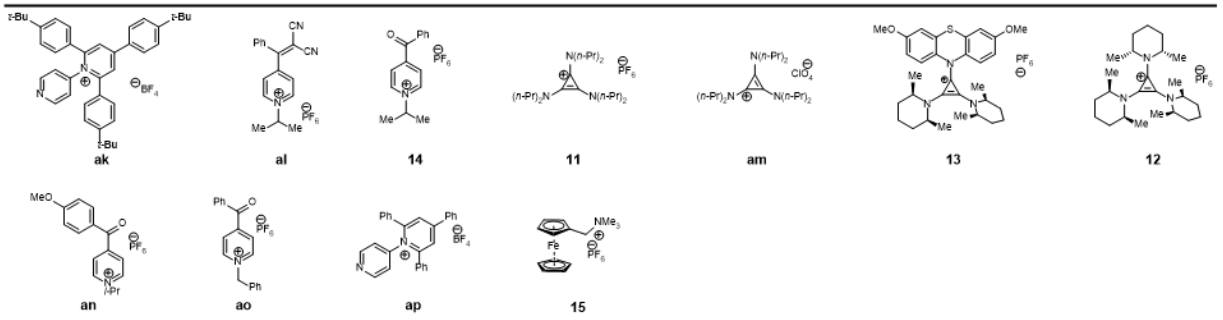
$$\frac{C_n}{C_x} = \frac{i_{pn}}{i_{px}} \quad \text{[eq. 5]}$$

III. Electrolyte Pool

Neutral



Monocationic



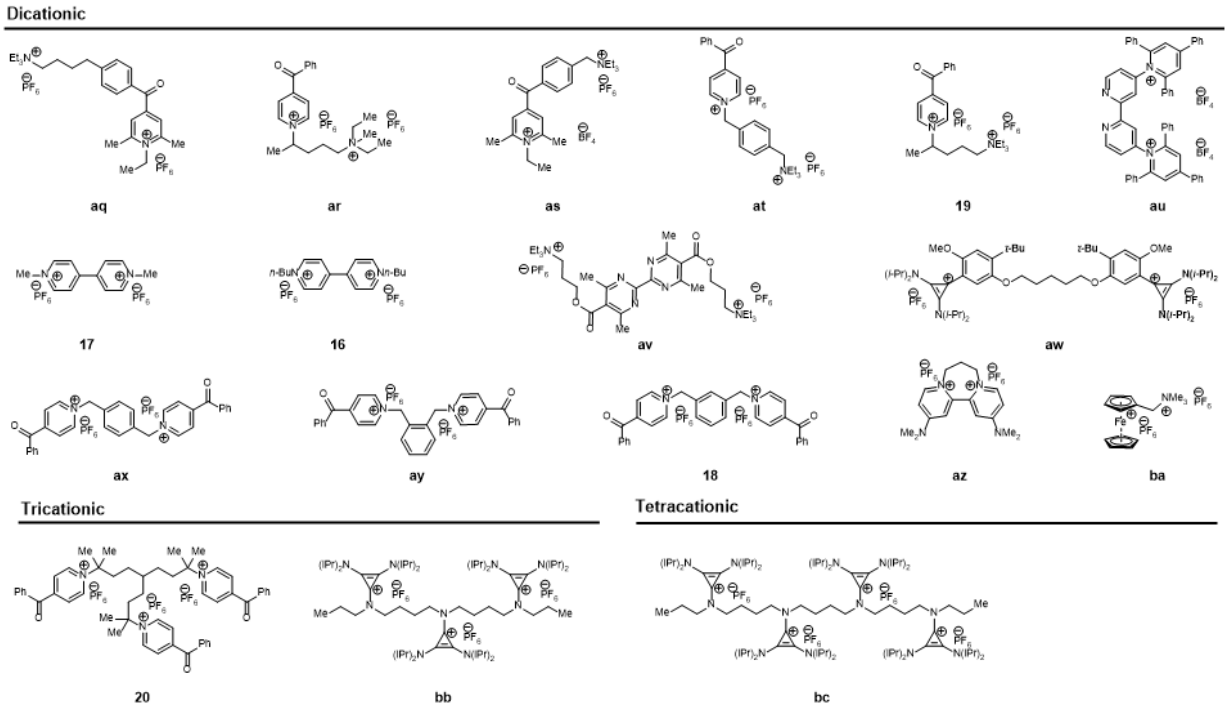


Figure S2. Electrolytes examined.

IV. Diffusion Coefficient Calculations

Diffusion coefficients (*D*) were derived from the Randles-Sevcik equation[1] (eq. 6) by varying the scan rate between 20 and 200 mV/s for CV. Plotting the anodic and cathodic current vs the square root of the scan results in a linear relationship, where the slope of the line can be used to estimate the diffusion coefficient.

In the Randles-Sevcik equation[1], i_p is the peak current (amperes), n is the number of electrons (1 e^-), F is Faraday constant (96,485 C/mol e^-), A is the electrode area (0.071 cm^2), C is the bulk concentration (5×10^{-6} mol/mL), R is the universal gas constant (8.314 J/mol•K), T is the temperature in Kelvin (298.15 K), v is the scan rate (V/s), and D is the diffusion coefficient (cm^2/s). Combining all constants, the equation simplifies to eq. 7, and imputing experimental values results in eq. 8. Finally, rearranging eq. 8 to solve for D, we can input the slope of the linear correlation to estimate the diffusion coefficient values for each compound using eq. 10.

$$i_p = 0.446nFAC^0\left(\frac{nFvD_0}{RT}\right)^{1/2} \qquad \text{[eq. 6]}$$

$$i_p = 268600\, n^{3/2}\, ACv^{1/2}D^{1/2} \qquad \text{[eq. 7]}$$

$$i_p = 0.095\, v^{\frac{1}{2}}D^{\frac{1}{2}} \qquad \text{[eq. 8]}$$

$$\frac{i_p}{v^{1/2}} = 0.095\, D^{1/2} \qquad \text{[eq. 9]}$$

$$D^{1/2} = \frac{i_p/v^{1/2}}{0.095} = \frac{slope}{0.095} \qquad \text{[eq. 10]}$$

Unless otherwise noted, cyclic voltammograms for diffusion coefficients were conducted in 0.55 M KPF_6/MeCN at 1.0 mM concentration of compound, using the scan rates 20, 40, 60, 100, and 200 mV/s. Diffusion coefficients were determined experimentally for all compounds where this value was not reported in the literature (**1**, **3**, **4**, **6**, **10**, **15**, and **17**).

For compounds **2**, **14**, and **16** diffusion coefficients were also derived via DOSY NMR. DOSY diffusion coefficients were derived from higher concentrations of compounds **2**, **14**, and **16** (60 mM, 83 mM, and 57 mM, respectively) in 0.55 M KPF_6/CD_3CN. ^{1}H DOSY spectra were obtained on a Varian VnmrS 500 MHz using a 60 gauss/cm gradient amplifier with the following parameters: 25 °C controlled temperature, course gradient, 2.0 ms diffusion gradient length, 20 ms diffusion delay, 5.0 s relaxation delay, 8-16 scans, and 8 steady state pulses. Spectra were processed via VnmrJ software with correction for non-uniform gradients. Pulsed field gradient strength was calibrated with D_2O at 25 °C (HDO diffusion coefficient = 19.02E-10 m^2/s).[2]

V. Permeability Calculations

Permeability calculations were derived from Fick's First Law via eq. 11.[3]

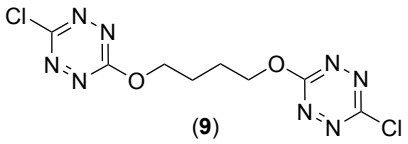
$$P = \frac{\Delta \ln\left[1 - 2\frac{C_r(t)}{C_d(0)}\right]\left(-\frac{VL}{2A}\right)}{\Delta t} \qquad \text{[eq. 11]}$$

In eq. 11 P is permeability (cm^2/s) , V is the electrolyte volume of each side (6.0 mL), L is membrane thickness (estimated 75 μm)[4], A is membrane area (1.32665 cm^2), t is time, $C_r(t)$ is time-dependent concentration of crossed-over molecule, and $C_d(0)$ is the initial concentration of the molecule on the retentate side of the cell (25 mM).

P was calculated for each time point (same as initial rate time points) of the crossover experiments, then the slope of eq. 12 (y-axis) vs Δt of (x-axis) was used to determine P for each molecule.

$$\Delta \ln\left[1 - 2\frac{C_r(t)}{C_d(0)}\right]\left(-\frac{VL}{2A}\right) \qquad \text{[eq. 12]}$$

VI. Synthesis and Characterization of Molecules



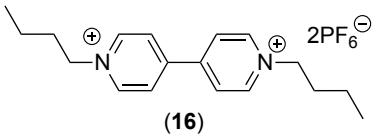
(**9**)

Compound 9. 1,4-butanediol (0.3 mL, 3.3 mmol, 1.0 equiv), 2,4,6-trimethylpyridine (1.0 mL, 7.5 mmol, 2.3 equiv), and anhydrous DCM (150 mL) were added under N_2 to a 1 L oven-dried round bottom flask at ambient temperature. Following this, 3,6-dichlorotetrazine (1.0 g, 6.6 mol, 2.0 equiv) in anhydrous DCM (50 mL) was added. The reaction was stirred for 16 h at ambient temperature. The DCM was removed under vacuum, and the resulting pink solids were redissolved in a 20:80 mixture of ethyl acetate:hexanes (20 mL) and then passed through a plug of silica gel. The plug was washed with hexanes (~200 mL), and the combined eluent was concentrated under vacuum. The product was purified by column chromatography on silica (0-100% EtOAc/hexanes, R_F = 0.8) to afford **9** as a bright pink powder (789 mg, 77% yield).[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.77 (m, 4H), 2.22 (p, *J* = 2.8 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 164.7, 70.2, 25.3.

HRMS (ESI) m/z: $[M - C_2ClN_4O]^-$ calc for $C_6H_8ClN_4O^+$ 187.0382; found 187.0376.



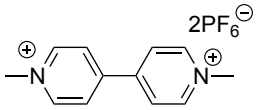
(**16**)

Compound 16. 4,4-Bipyridine (4.69 g, 30.0 mmol, 1.0 equiv) was dissolved in acetonitrile (86 mL, 0.35 M), and then 1-bromobutane (9.7 mL, 90.0 mmol, 3.0 equiv) was added slowly over approximately three minutes at ambient temperature. The reaction was heated to reflux and stirred for 4 d. After cooling to room temperature, the mixture was concentrated under vacuum, filtered, and the precipitate washed with additional acetonitrile (20 mL). The crude residue was dissolved in water (50 mL), and ammonium hexafluorophosphate (19.56 g, 120.0 mmol, 4.0 equiv) was added, resulting in the formation of a white precipitate. The resulting solid was collected by filtration, washed with diethyl ether (3 x 20 mL), and dried at 40 ºC under reduced pressure to yield **16** as a white solid (13.90 g, 83% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 8.90 (d, *J* = 7.0 Hz, 4H), 8.38 (d, *J* = 6.9 Hz, 4H), 4.62 (t, *J* = 7.5 Hz, 4H), 2.00 (p, *J* = 7.6 Hz, 4H), 1.42 (h, *J* = 7.4 Hz, 4H), 0.99 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, CD_3CN) δ 151.0, 146.5 (t, *J* = 8.7 Hz), 128.2, 62.9, 33.8, 19.9, 13.7.

HRMS (ESI) m/z: $[M - C_4H_9F_{12}P_2]^+$ calc for $C_{14}H_{17}N_2^+$ 213.1387; found 213.1385.

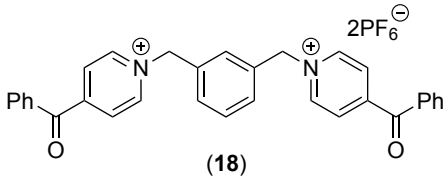


(**17**)

Compound 17. Methyl viologen hydrate (di-chloride salt) (84 mg, 0.33 mmol, 1 equiv) was obtained from Acros Organics and was dissolved in water (5 mL). Ammonium hexafluorophosphate (215 mg, 1.32 mmol, 4.0 equiv) was added, resulting in the precipitation of a white solid. The resulting solid was collected by filtration and then dissolved in acetonitrile (2 mL) and added dropwise to cold diethyl ether (0 °C, 40 mL), immediately forming a white precipitate. The solid was collected by filtration and dried under vacuum in the presence of P_2O_5 to afford compound **17** as a white powder (34 mg, 22% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 8.84 (d, *J* = 7.0 Hz, 4H), 8.37 (d, *J* = 6.8 Hz, 4H), 4.40 (s, 6H).

^{13}C NMR (126 MHz, CD_3CN) δ 150.61, 147.46, 127.78, 49.58.



(**18**)

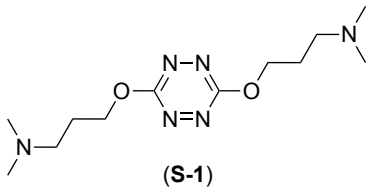
Compound 18. α,α-Dibromo-*m*-xylene (2.03 g, 7.7 mmol, 1.0 equiv) and 4-benzoyl pyridine (4.22 g, 23.0 mmol, 3.0 equiv) were dissolved in acetonitrile (10 mL) in a 40 mL vial. The vial was sealed with a Teflon-lined cap, and the reaction mixture was heated at 60 °C for 3 d, during which time a yellow precipitate formed. This precipitate was collected by filtration, then added to a stirring 1 M aqueous solution of NH_4PF_6 (30 mL). This addition resulted in the immediate formation of a white solid, which was collected by filtration and washed with diethyl ether (100 mL). This material was recrystallized from MeCN/diethyl ether. The resulting white crystalline solid was collected by filtration, washed with diethyl ether (75 mL), and dried under vacuum in the presence of P_2O_5 to afford **18** as a white crystalline solid (4.09 g, 70% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 8.90 (d, *J* = 6.8 Hz, 4H), 8.21 (d, *J* = 6.2 Hz, 4H), 7.83 (d, *J* = 6.8 Hz, 4H), 7.78 (t, *J* = 7.5 Hz, 2H), 7.65-7.55 (multiple peaks, 8H), 5.82 (s, 4H).

^{13}C NMR (126 MHz, CD_3CN) δ 192.6, 153.8, 146.5, 135.9, 135.2, 134.7, 131.9, 131.7, 131.5, 131.2, 130.1, 128.7, 65.1.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_{32}H_{26}F_6N_2O_2P^+$ 615.1631; found 615.1843.

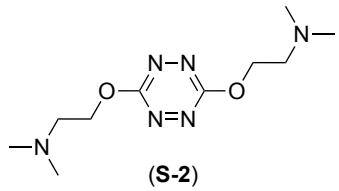
IR (ν/cm^{-1}): 1660 (C=O).



(**S-1**)

Compound S-1. 3,6-Dichloro-1,2,4,5-tetrazine (906 mg, 6.0 mmol, 1.0 equiv) was dissolved in dry DCM (45 mL). 3-(Dimethylamino)propan-1-ol (3.5 mL, 30.0 mmol, 5.0 equiv) was added slowly over approximately 2 min at ambient temperature. (Note: gas evolves during this addition.) The reaction was allowed to stir at ambient temperature for 24 h. The resulting mixture was diluted with 10% aqueous NaOH (20 mL) and extracted with DCM (3 x 35 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography on basic alumina (0-5% EtOAc/hexanes, R_F = 0.1 in 50% EtOAc/hexanes) to afford **S-1** as a dark red oil (536 mg, 31% yield). This oil was carried forward to the N-alkylation step without further purification.

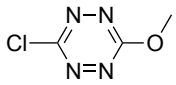
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (t, *J* = 6.4 Hz, 4H), 2.49 (t, *J* = 7.2 Hz, 4H), 2.24 (s, 12H), 2.07 (p, 4H).



(**S-2**)

Compound S-2. 3,6-Dichloro-1,2,4,5-tetrazine (151 mg, 1.0 mmol, 1.0 equiv) was dissolved in dry DCM (8 mL). 2-(Dimethylamino)ethan-1-ol (0.5 mL, 5.0 mmol, 5.0 equiv) was added slowly over approximately 5 min at ambient temperature. (Note: gas evolves during this addition.) The reaction was allowed to stir at ambient temperature for 3 d. The resulting mixture was diluted with 10% aqueous NaOH (10 mL) and extracted with DCM (3 x 20 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography on basic alumina (0-40% EtOAc/hexanes, R_F = 0.2) to afford **S-2** as a dark red oil (46 mg, 18% yield). This oil was carried forward to the N-alkylation step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.65 (t, *J* = 5.7 Hz, 4H), 2.83 (t, *J* = 5.7 Hz, 4H), 2.34 (s, 12H).

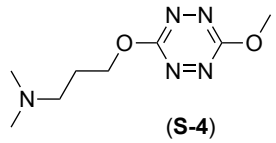


(**S-3**)

Compound S-3. 3,6-Dichloro-1,2,4,5-tetrazine (906 mg, 6.0 mmol, 1.0 equiv) was dissolved in dry DCM (17 mL). Anhydrous methanol (1.3 mL, 30.0 mmol, 5.0 equiv) and collidine (1.0 mL, 7.2 mmol, 1.2 equiv) were added dropwise over approximately 5 min at ambient temperature. (Note: gas evolves during this addition.) The reaction was allowed to stir at ambient temperature for 1 h. The resulting mixture was concentrated under reduced pressure to yield a red solid. This material was purified by column chromatography on silica (0-10% EtOAc/hexanes, R_F = 0.3) to afford **S-3** as a bright red solid (783 mg, 89% yield).[6] This oil was carried forward without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (s, 3H).

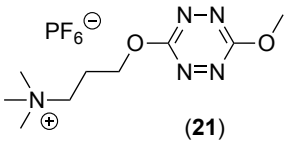
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.08, 164.65, 57.54.



(**S-4**)

Compound S-4. Compound **S-3** (295 mg, 2.0 mmol, 1.0 equiv) was dissolved in dry DCM (17.5 mL). 3-(Dimethylamino)propan-1-ol (0.7 mL, 6.0 mmol, 3.0 equiv) was added slowly over approximately 3 min at ambient temperature. The reaction was allowed to stir at ambient temperature for 9 h. The resulting mixture was diluted with 10% aqueous NaOH (10 mL) and extracted with dichloromethane (3 x 20 mL). The combined organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. The crude residue was purified by column chromatography on basic alumina (15-50% EtOAc/hexanes, R_F = 0.3) to afford **S-4** as a dark red oil (39 mg, 9% yield). This oil was carried forward to the N-alkylation step without further purification.

^{1}H NMR (500 MHz, C_6D_6) δ 4.37 (t, J = 6.5 Hz, 2H), 3.58 (s, 3H), 2.21 (t, J = 6.8 Hz, 2H), 1.99 (s, 6H), 1.74 (p, J = 6.6 Hz, 2H).



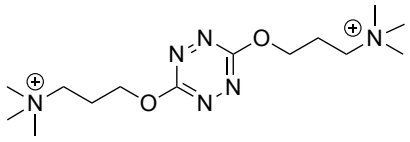
(**21**)

Compound 21. Compound **S-4** (70 mg, 0.33 mmol, 1.0 equiv) was dissolved in acetonitrile (2.6 mL). Methyl iodide (0.2 mL, 3.3 mmol, 10.0 equiv) was added slowly over approximately over 3 min at room temperature. The reaction was heated to 40 ºC and stirred for about 22 h. The resulting mixture was allowed to cool to ambient temperature and then concentrated under reduced pressure. The residue was dissolved in water (3 mL), and NH_4PF_6 (168 mg, 1.0 mmol, 3.0 equiv) was added, resulting in the precipitation of a red-orange solid. This material was collected by filtration, washed with diethyl ether (100 mL), and dried under vacuum in the presence of P_2O_5 to afford **21** as a bright red solid (66 mg, 54% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 4.63 (t, *J* = 5.9 Hz, 1H), 4.20 (s, 2H), 3.50 (m, 1H), 3.07 (s, 5H), 2.35 (dq, *J* = 11.1, 5.4 Hz, 1H).

^{13}C NMR (126 MHz, CD_3CN) δ 167.6, 166.9, 66.9 (t, *J* = 2.1 Hz), 64.6 (t, *J* = 3.4 Hz), 57.3, 54.0 (t, *J* = 4.0 Hz), 23.4.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_9H_{18}N_5O_2^+$ 228.1455; found 228.1476.



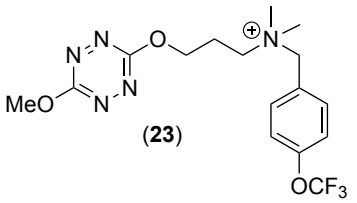
(**22**)

Compound 22. Compound **S-1** (248 mg, 0.9 mmol, 1.0 equiv) was dissolved in dry acetonitrile (7.0 mL). Methyl iodide (0.55 mL, 8.8 mmol, 10 equiv) was added slowly over approximately 3 min at ambient temperature. The reaction was allowed to stir at ambient temperature for 4 h, during which time a red-orange precipitate formed. The resulting mixture was concentrated under reduced pressure to yield a red-orange powder. This material was dissolved in water (4 mL), and NH_4PF_6 (899 mg, 5.5 mmol, 6.3 equiv) was added. The salt addition resulted in the immediate formation of a bright pink precipitate, which was collected by filtration, washed with diethyl ether (100 mL), and dried under vacuum in the presence of P_2O_5 to afford **22** as a pink solid (475 mg, 90% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 4.62 (t, *J* = 5.9 Hz, 4H), 3.50 (m, 4H), 3.08 (s, 18H), 2.36 (m, 4H).

^{13}C NMR (126 MHz, CD_3CN) δ 167.1, 67.1 (t, *J* = 2.0 Hz), 64.6 (t, *J* = 3.3 Hz), 54.1 (t, *J* = 4.2 Hz), 23.5.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_{14}H_{30}F_6N_6O_2P^+$ 459.2067; found 459.2212.



(**23**)

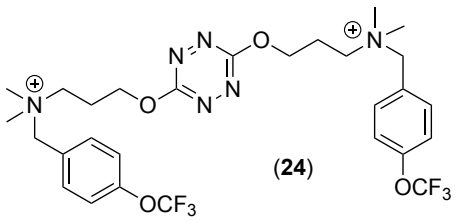
Compound 23. Compound **S-4** (72 mg, 0.3 mmol, 1.0 equiv) was dissolved in acetonitrile (2.7 mL). 1-(Bromomethyl)-4-(trifluoromethoxy)benzene (0.06 mL, 0.4 mmol, 1.1 equiv) was added slowly over approximately 3 min at room temperature. The reaction mixture was allowed to stir at ambient temperature for about 24 h. The resulting reaction mixture was concentrated under reduced pressure. The residue was then dissolved in water (5 mL) and NH_4PF_6 (111 mg, 0.7 mmol, 2.0 equiv) was added, resulting in the precipitation of a red solid. This material was collected by filtration and washed with water (20 mL) followed by diethyl ether (30 mL). The resulting semi-solid was recrystallized from hot ethanol, collected by filtration, washed with diethyl ether (40 mL), and dried under vacuum in the presence of P_2O_5 to afford **23** as a bright pink-red powder (105 mg, 58% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 7.63 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 4.64 (t, J = 5.8 Hz, 2H), 4.46 (s, 2H), 4.20 (s, 3H), 3.50 (m, 2H), 2.98 (s, 6H), 2.44 (dq, J = 11.9, 5.7 Hz, 2H).

^{13}C NMR (126 MHz, CD_3CN) δ 167.7, 167.0, 151.7, 136.1, 127.2, 122.5, 121.4 (d, J = 256.8 Hz), 67.8 (t, J = 3.2, 2.6 Hz), 67.0, 62.6 (t, J = 3.6 Hz), 57.4, 50.7 (t, J = 4.6, 3.9 Hz), 23.3.

^{19}F NMR (376 MHz, CD_3CN) δ -58.57, -71.94, -73.82.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc'd for $C_{16}H_{21}F_3N_5O_3^+$ 388.1591; found 388.1674.



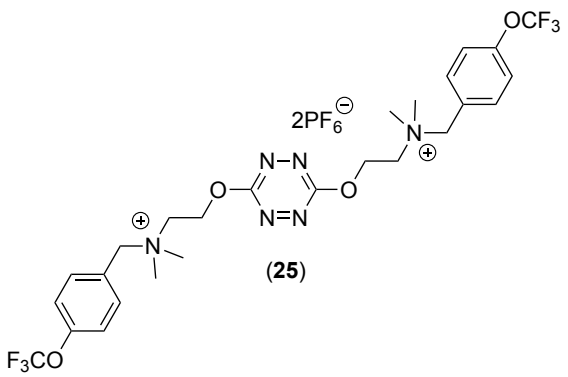
Compound 24. Compound **S-1** (486 mg, 1.7 mmol, 1.0 equiv) was dissolved in dry acetonitrile (14.0 mL, 0.13 M). 1-(Bromomethyl)-4-(trifluoromethoxy)benzene (0.55 mL, 3.4 mmol, 2.0 equiv) was added slowly over approximately two minutes at ambient temperature. The reaction was allowed to stir at ambient temperature for 24 h, during which time a precipitate formed. The mixture was concentrated under reduced pressure. The residue was then dissolved in water (20 mL), and NH_4PF_6 (1.12 g, 6.9 mmol, 4.0 equiv) was added. This addition resulted in formation of a red precipitate, which was collected by filtration, and washed with water (20 mL) and diethyl ether (30 mL). The resulting solid recrystallized from ethanol. This material was collected by filtration, washed with diethyl ether (40 mL) and dried under vacuum in the presence of P_2O_5 to afford **24** as a bright pink powder (1.15 g, 73% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 7.64 (d, J = 8.8 Hz, 4H), 7.44 (d, J = 7.9 Hz, 4H), 4.65 (t, J = 5.8 Hz, 4H), 4.47 (s, 4H), 3.51 (m, 4H), 2.99 (s, 12H), 2.45 (m, 4H).

^{13}C NMR (126 MHz, CD_3CN) δ 167.0, 151.7, 136.0, 127.2, 122.4, 122.3 (t, J = 258.2, 256.5 Hz), 67.7, 67.0, 62.5 (t, J = 3.4 Hz), 50.7 (t, J = 3.8 Hz), 23.2.

^{19}F NMR (376 MHz, CD_3CN) δ -58.56, -71.88, -73.77.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_{28}H_{36}F_{12}N_6O_4P^+$ 779.2339; found 779.2727.



(**25**)

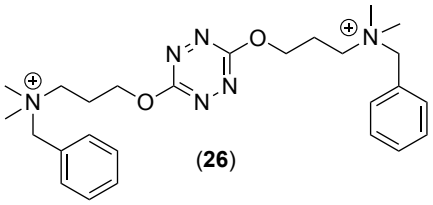
Compound 25. Compound **S-2** (38 mg, 0.1 mmol, 1.0 equiv) was dissolved in dry acetonitrile (1.2 mL). 1-(Bromomethyl)-4-(trifluoromethoxy)benzene (0.05 mL, 0.3 mmol, 2.0 equiv) was added slowly over approximately 5 min at ambient temperature. The reaction was allowed to stir at ambient temperature for 4 d, during which time a red-orange precipitate formed. The resulting mixture was concentrated under reduced pressure to yield a red-orange solid. This material was then dissolved in water (40 mL), and NH_4PF_6 (110 mg, 0.7 mmol, 4.6 equiv) was added. This addition resulted in the precipitation of a pale red powder, which was collected by filtration and washed with water (10 mL) followed by diethyl ether (30 mL). This solid was then recrystallized from MeCN/diethyl ether. The product was collected by filtration, washed with diethyl ether (20 mL), and dried under vacuum in the presence of P_2O_5 to afford **25** as a bright pink powder (50 mg, 38% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 7.67 (d, J = 8.8 Hz, 4H), 7.46 (d, J = 8.1 Hz, 4H), 5.02 (s, 4H), 4.59 (s, 4H), 3.86 (m, 4H), 3.11 (s, 12H).

^{13}C NMR (126 MHz, CD_3CN) δ 166.6, 136.2, 127.0, 122.5, 122.3 (t, J = 257.2 Hz), 68.9, 63.8, 63.7, 51.3.

^{19}F NMR (376 MHz, CD_3CN) δ -58.57, -71.93, -73.81.

HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_{26}H_{32}F_{12}N_6O_4P^+$ 751.2026; found 751.2199.



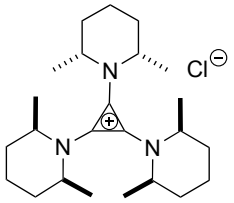
(**26**)

Compound 26. Compound **S-1** (406 mg, 1.4 mmol, 1.0 equiv) was dissolved in dry acetonitrile (11 mL). Benzyl bromide (0.3 mL, 3.0 mmol, 2.1 equiv) was added slowly over approximately 2 min at ambient temperature. The reaction was allowed to stir at ambient temperature for 48 h, during which time a red-orange precipitate formed. The mixture was concentrated under reduced pressure to yield a red-orange solid. This solid was then dissolved in water (40 mL), and NH_4PF_6 (933 mg, 5.7 mmol, 4.0 equiv) was added. The salt addition resulted in the immediate formation of a red precipitate, which was collected by filtration and washed with water (20 mL) followed by diethyl ether (30 mL). This solid was recrystallized four times from MeCN/diethyl ether. The resulting material was collected by filtration, washed with diethyl ether (40 mL), and dried under vacuum in the presence of P_2O_5 to afford **26** as a bright pink powder (643 mg, 59% yield).

^{1}H NMR (500 MHz, CD_3CN) δ 7.61-7.50 (multiple peaks, 10H), 4.65 (t, J = 5.8 Hz, 4H), 4.45 (s, 4H), 3.50 (m, 4H), 2.99 (s, 12H), 2.45 (dq, J = 11.9, 5.6 Hz, 4H).

^{13}C NMR (126 MHz, CD_3CN) δ 167.0, 133.9, 131.7, 130.2, 128.1, 68.9 (t, J = 3.2, 2.5 Hz), 67.1, 62.3 (t, J = 3.3 Hz), 50.7 (t, J = 3.9 Hz), 23.2.

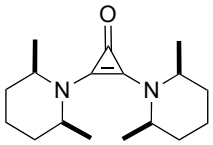
HRMS (ESI) m/z: $[M - PF_6]^+$ calc for $C_{26}H_{38}F_6N_6O_2P^+$ 611.2693; found 611.2776.



(**S-5**)

Compound S-5. Pentachlorocyclopropane (0.77 mL, 6.0 mmol, 1.0 equiv) was dissolved in dry dichloromethane (34 mL). This solution was cooled to 0 ºC, and *cis*-2,6-dimethylpiperidine (5.7 mL, 42.3 mmol, 7.1 equiv) was added slowly over approximately 5 min. The reaction was stirred at 0 ºC for 1 h then allowed to warm to ambient temperature and stirred overnight. The resulting mixture was washed with 2M aqueous HCl (2 x 30 mL), 1 M aqueous HCl (1 x 30 mL), water (1 x 30 mL), and brine (1 x 30 mL). The organic extracts were dried over magnesium sulfate and concentrated under reduced pressure. **S-5** was isolated as a yellow powder (2.30 g, 94% yield) and carried forward without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (p, J = 7.1 Hz, 6H), 1.96-1.85 (multiple peaks, 6H), 1.85-1.74 (multiple peaks, 3H), 1.74-1.65 (multiple peaks, 6H), 1.61 (dt, J = 13.5, 3.6 Hz, 3H), 1.38 (d, J = 7.1 Hz, 18H).

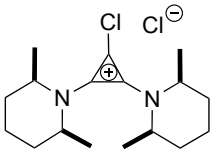


(**S-6**)

Compound S-6. S-5 (2.22 g, 5.5 mmol, 1.0 equiv) was dissolved in water (30 mL). Separately, potassium hydroxide (3.06 g, 54.5 mmol, 10 equiv) was dissolved in water (11 mL). The KOH solution was added slowly to the stirring **S-5** solution over approximately 5 min at room temperature. The reaction was then heated to 65 ºC and allowed to stir for 1.5 h. The resulting mixture was concentrated under reduced pressure to a total volume of approximately 15 mL, resulting in the precipitation of a brown solid. This material was collected by filtration and then dissolved in DCM, and the resulting solution was filtered through a plug of glass wool. The organic solution was dried over magnesium sulfate and then concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (20-100% EtOAc/hexanes) followed by (0-10% MeOH/EtOAc, R_F = 0.25). **S-6** was obtained as a yellow powder (492 mg, 33% yield), which was carried forward without additional purification.

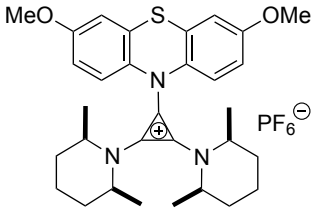
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.76 (m, 4H), 1.78-1.68 (multiple peaks, 6H), 1.56-1.46 (multiple peaks, 6H), 1.29 (d, *J* = 7.0 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.25, 120.71, 52.44, 30.29, 21.83, 14.31.



(**S-7**)

Compound S-7. Under an atmosphere of N_2, **S-6** (347 mg, 1.3 mmol, 1.0 equiv) dissolved in anhydrous dichloromethane (12.5 mL). The solution was cooled to 0 ºC, and oxalyl chloride (1.25 mL, 2.5 mmol, 2.0 equiv) was added slowly over approximately 5 min. The reaction was stirred at 0 ºC for 10 min and then allowed to warm to ambient temperature and stirred for an additional 1 h. The crude mixture was concentrated under reduced pressure to yield **S-7** as a golden brown solid in quantitative yield. This material was used as received.



(**13**)

Compound 13. This compound was synthesized by the reaction of **S-7** with 3,7-dimethoxy-10H-phenothiazine according to reported methods.[7] The characterization data for **13** matched those reported in the literature.

VII. Parameter Acquisition and Modeling

a. Computational Methods

Conformational searches of electrolytes with and without their associated counterion(s) were performed using Macromodel version 11.8 and the OPLS3e forcefield with an energy window of 2.5 kcal/mol. Conformational ensembles of compounds which contained >50 conformers were clustered by RMSD. The number of centroids to export was <50 in each case and identified by Kelley Penalty. Parameters from 2D SMILES notation of each electrolyte were calculated from DataWarrior version 5.5.0.[8] Dynamic parameters of the 3D conformational ensembles were calculated in UCSF's ChimeraX (v1.1) developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco, with support from National Institutes of Health R01-GM129325 and the Office of Cyber Infrastructure and Computational Biology, National Institute of Allergy and Infectious Diseases.[9,10]

b. Collected Parameters for Model Generation

A full set of parameters and their values can be found in the accompanying excel sheet. QSAR-type parameters were collected as a global description for each compound. The specific methods for the calculation of each DataWarrior parameter can be found in the program's supporting documentation at openmolecules.org. The Charge parameter is an integer value of the formal charge of the molecule. Dynamic parameters (dynamic surface area and dynamic volume) for each ligand were formulated by enclosing the conformational ensemble of a ligand in a fictitious surface at 2.8 Å resolution and computing topographical properties of the surface.

c. Model Generation

All model development was performed using in-house Python scripts implemented in a Jupyter Notebook. In brief, the dataset (Figure 1) was partitioned into 70% training set and 30% test set by a y-equidistant algorithm. Normalization of molecular features by scaling (standard scalar) allows the coefficients of each feature in resultant models to be compared so that the relative importance of each feature can be understood. Forward stepwise selection of models was performed, keeping 54 candidates at each step for two steps. Collinearity criteria was 0.4. Resulting models were evaluated and validated by quantitative metrics such as statistics (Training R^2, Test R^2, Leave-One-Out Q^2, 5-Fold R^2) as well as qualitative metrics like interpretability.

d. Descriptor Values

Compound	Glob. Vol	cLogP	DSA	DV
1	0.87889	2.1762	126.3	107.5
2	0.72523	3.8586	320.7	347.3
3	0.92588	1.1064	142.8	125.9
4	0.7686	3.8618	187.3	163.2
5	0.71028	4.4984	410.4	502.9
6	0.7749	4.6834	272.3	274.4
7	0.64058	5.7576	618.8	955.6
8	0.77807	1.9627	239.7	226.3
9	0.70005	0.7938	386.7	458.8
10	0.82349	-0.5238	150.9	131.1
11	0.72411	5.6482	421.3	649
12	0.78567	5.242	356.6	511.5
13	0.70949	6.7968	584.3	866.4
14	0.76527	-1.3915	250	254.4
15	0.87183	-2.2085	222	209.7
16	0.70418	-4.2006	336.9	406.7
17	0.78674	-6.5302	212.9	212.7
18	0.65289	-3.2144	492.6	712
19	0.59472	-2.3596	453.1	639.6
20	0.5861	-2.3596	997.7	1463
21	0.76201	-3.3074	438.2	594.4
22	0.69805	-0.7903	671	1069
23	0.69655	-6.091	771.8	1447
24	0.65281	-3.2548	655.1	1293
25	0.64477	-1.9656	1050	1971
26	0.61786	-1.0568	735.9	1344

Table S1. Predictions vs. experimental log(rate)

e. Predictions vs Experimental log(rate)

The training dataset 1-20 was used to retrain models A-C and predictions for **21-26** were calculated using each model.

	Model A log(rate)	Model B log(rate)	Model C log(rate)	Experimental log(rate)
Model Error (MAE)	0.14	0.11	0.11	--
21	-0.30	-0.35	-0.40	-0.31
22	-0.85	-1.26	-1.17	-0.92
23	-0.42	-0.68	-0.76	-0.65
24	-0.99	-0.95	-0.90	-1.19
25	-0.96	-1.54	-1.52	-1.21
26	-0.93	-0.99	-0.83	-1.11

Table S2. Predictions vs. experimental log(rate)

VIII. References

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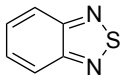
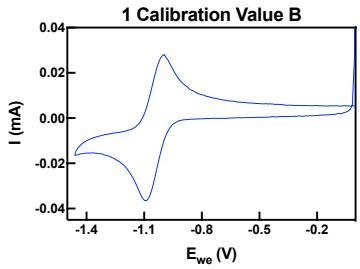
IX. Cyclic Voltammograms



(**1**)

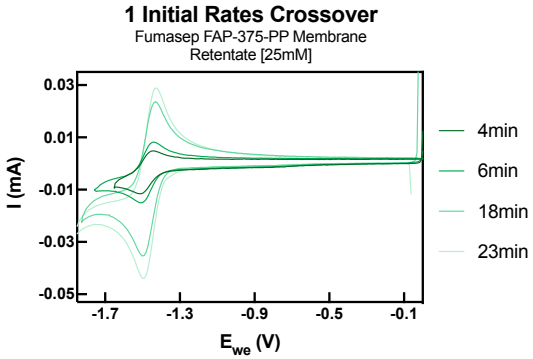
Conditions: General procedure outlined in Section IIb was followed using 25 mM **1** on the retentate side and 0.5 M KPF_6/MeCN on both sides of the cell. Crossover was monitored by CV over 48 h.

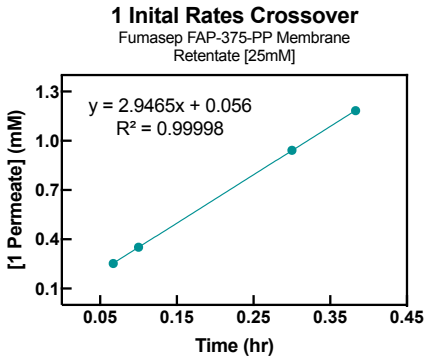
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.0383
B	0.03552
C	0.03288
D	0.03456
Average	0.035315

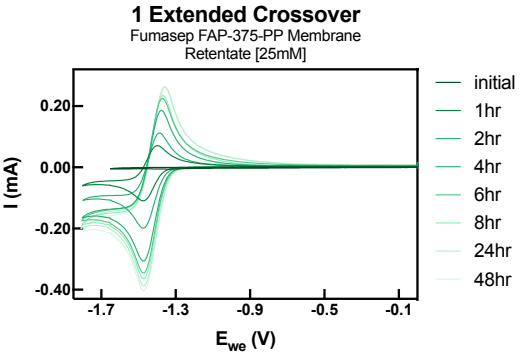
Initial Rates:

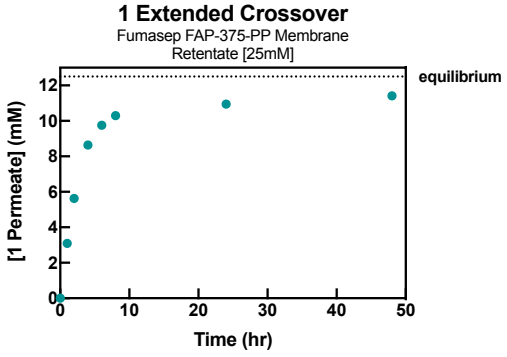


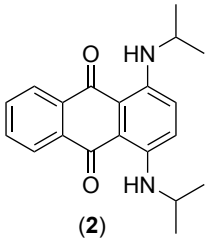


1 Initial Rates	
Time (h)	**[C] (mM)**
0.067	0.252
0.1	0.352
0.3	0.942
0.383	1.183

Extended Crossover:



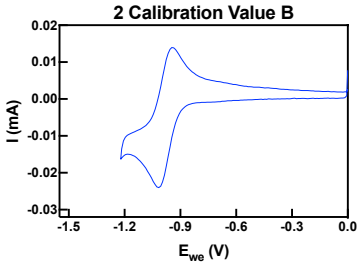




(**2**)

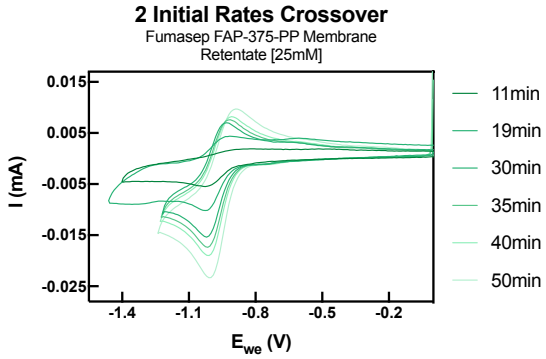
Conditions: General procedure outlined in Section IIb was followed using 25 mM **2** on the retentate side and 0.5 M KPF_6/MeCN on both sides of the cell. Crossover was monitored by CV over 48 h.

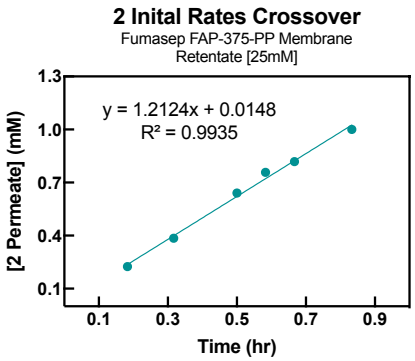
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.02184
B	0.02364
C	0.02231
Average	0.02260

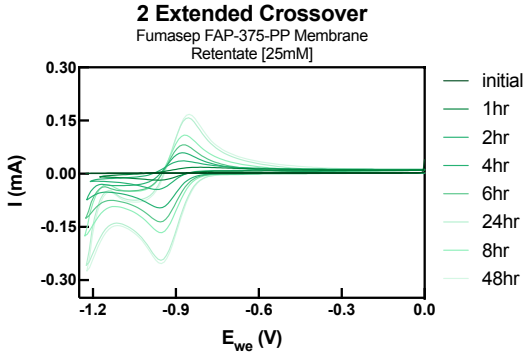
Initial Rates:

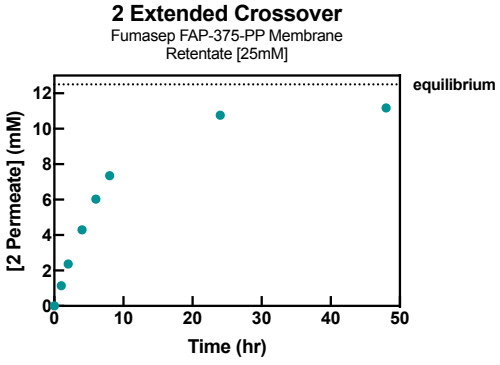


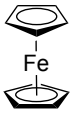


2 Initial Rates	
Time (h)	**[C] (mM)**
0.183	0.225
0.317	0.385
0.5	0.641
0.583	0.758
0.667	0.818
0.833	1.000

Extended Crossover:



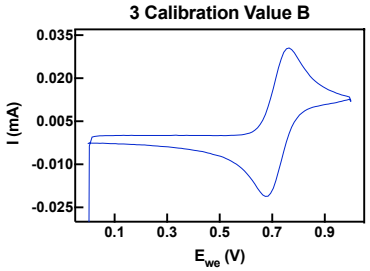




(**3**)

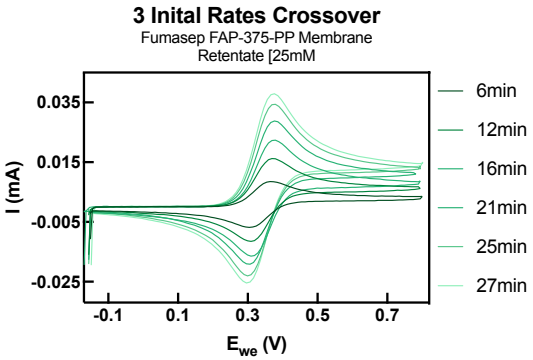
Conditions: General procedure outlined in Section IIb was followed using 25 mM **3** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

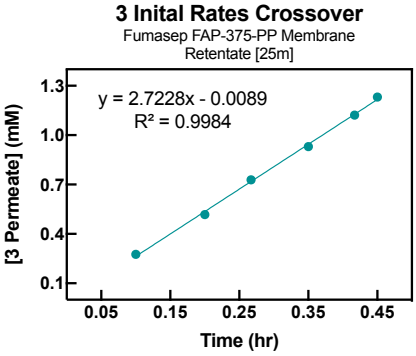
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.02916
B	0.03017
C	0.0326
Average	0.03064

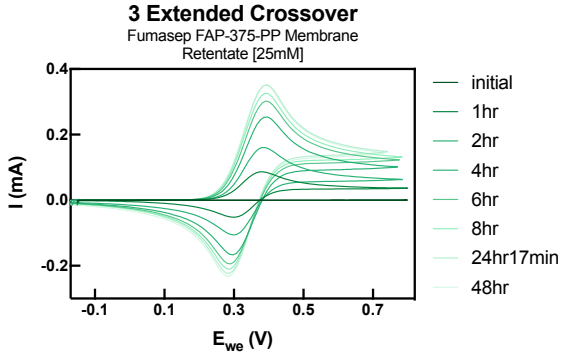
Initial Rates:

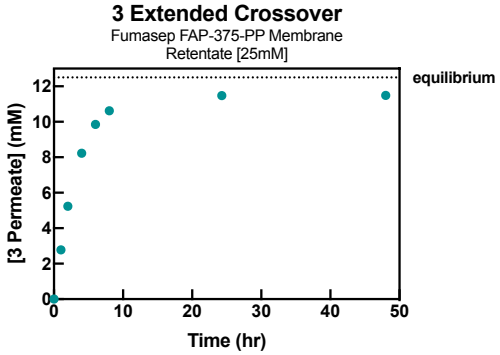


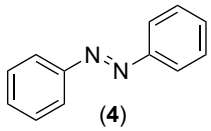


3 Initial Rates	
Time (h)	**[C] (mM)**
0.1	0.276
0.2	0.517
0.267	0.729
0.35	0.930
0.417	1.122
0.45	1.231

Extended Crossover:



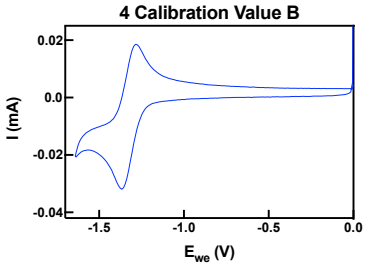




(**4**)

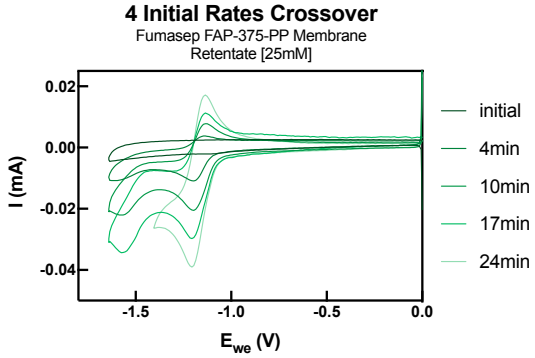
Conditions: General procedure outlined in Section IIb was followed using 25 mM **4** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

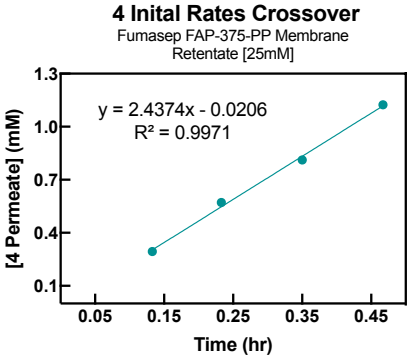
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.03497
B	0.0303
C	0.03096
Average	0.03208

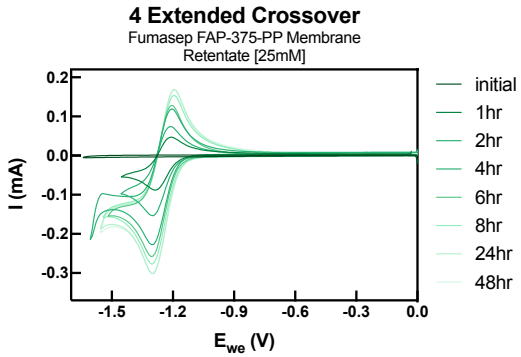
Initial Rates:

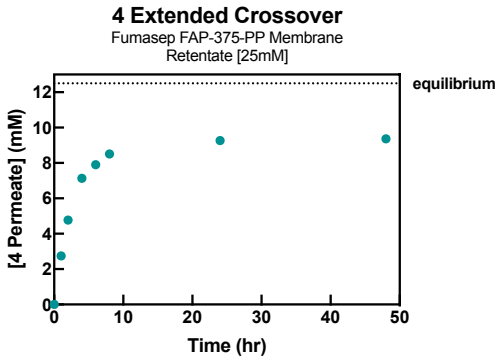


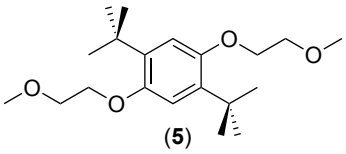


4 Initial Rates	
Time (h)	**[C] (mM)**
0.133	0.294
0.233	0.571
0.35	0.812
0.467	1.124

Extended Crossover:



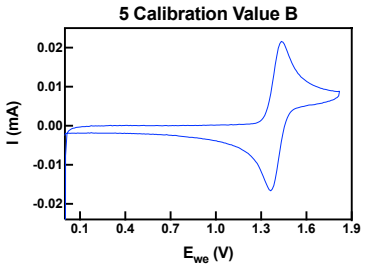




(**5**)

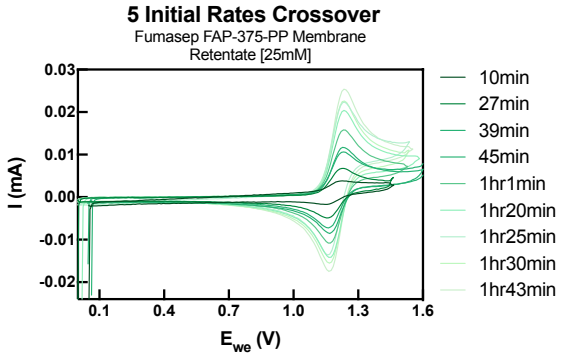
Conditions: General procedure outlined in Section IIb was followed using 25 mM **5** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

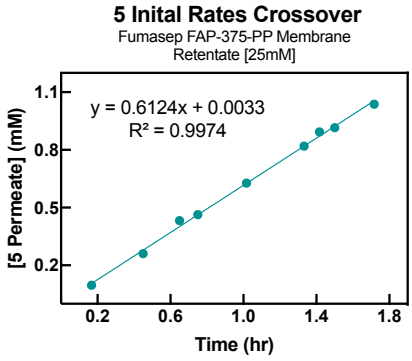
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.02522
B	0.02089
C	0.02526
D	0.02445
Average	0.023955

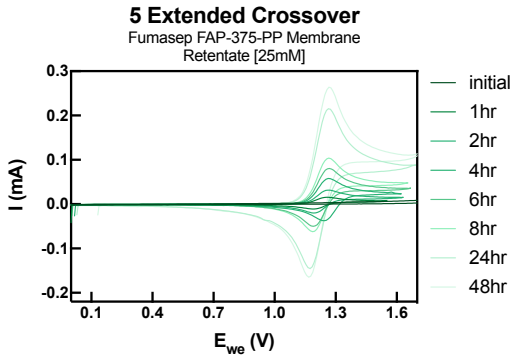
Initial Rates:

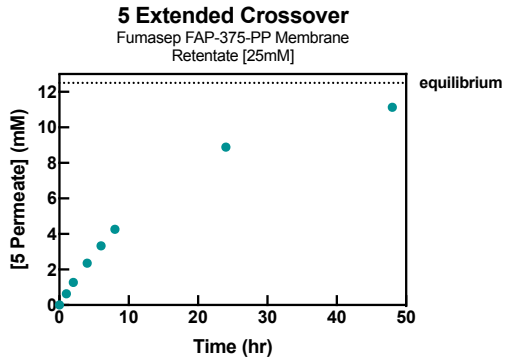


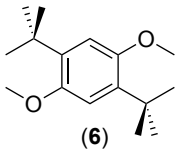


5 Initial Rates	
Time (h)	**[C] (mM)**
0.167	0.096
0.45	0.260
0.65	0.432
0.75	0.463
1.017	0.627
1.333	0.820
1.417	0.893
1.5	0.915
1.717	1.037

Extended Crossover:



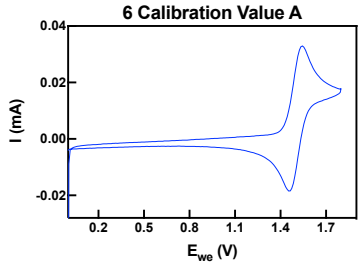




(**6**)

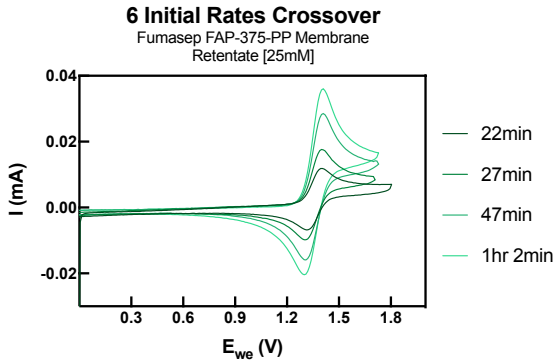
Conditions: General procedure outlined in Section IIb was followed using 25 mM **6** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

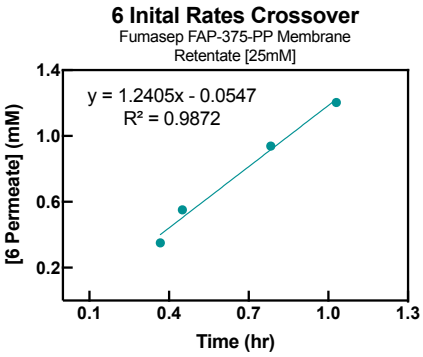
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.02874
B	0.03119
C	0.02864
Average	0.02952

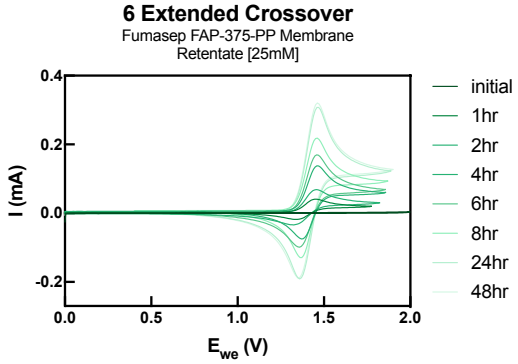
Initial Rates:

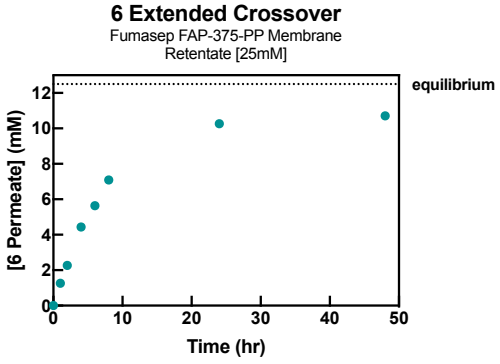


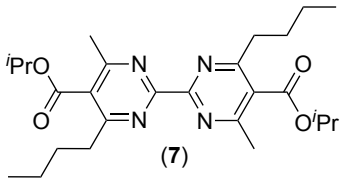


6 Initial Rates	
Time (h)	**[C] (mM)**
0.367	0.351
0.45	0.551
0.783	0.938
1.03	1.203

Extended Crossover:



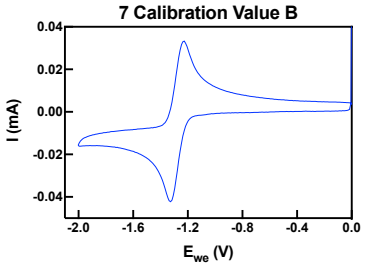




(**7**)

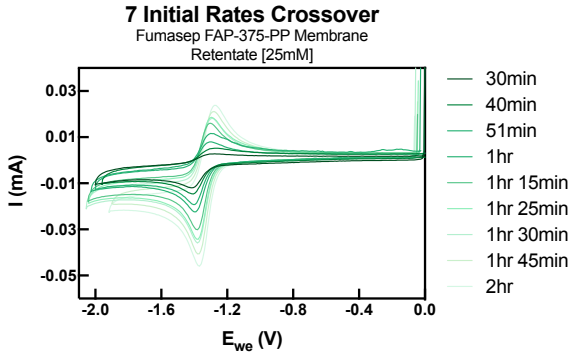
Conditions: General procedure outlined in Section IIb was followed using 25 mM **7** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

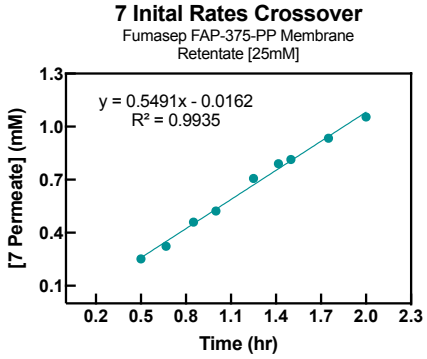
Calibration CVs [1.0 mM]



Trial	i_{pc}
B	0.04198
C	0.04543
D	0.04356
Average	0.04366

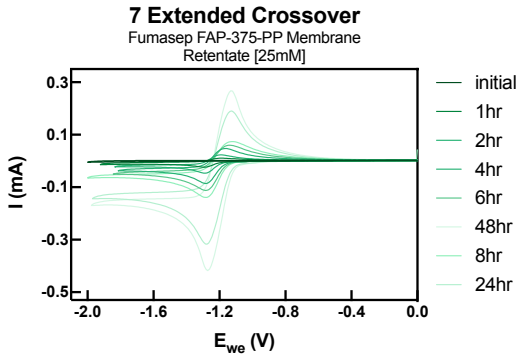
Initial Rates:

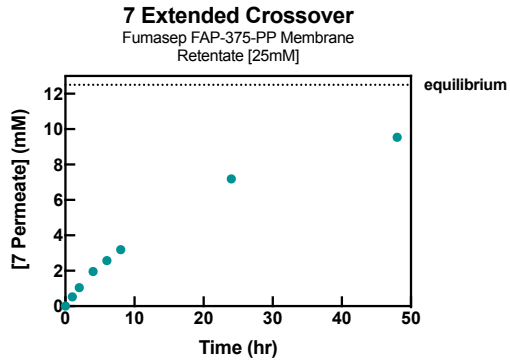


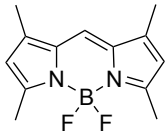


7 Initial Rates	
Time (h)	**[C] (mM)**
0.5	0.252
0.667	0.323
0.85	0.460
1	0.523
1.25	0.707
1.417	0.790
1.5	0.814
1.75	0.934
2	1.055

Extended Crossover:



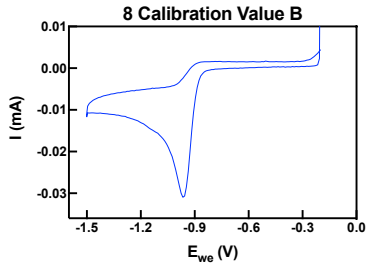




(**8**)

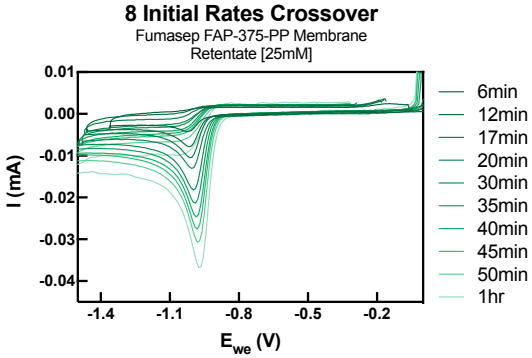
Conditions: General procedure outlined in Section IIb was followed using 25 mM **8** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

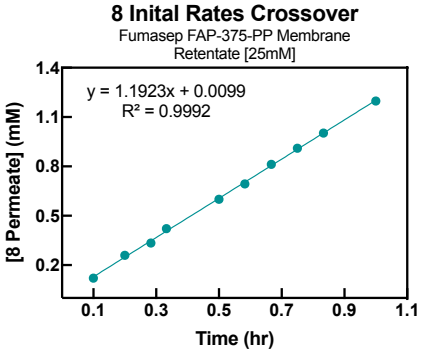
Calibration CVs [1.0 mM]



Trial	i_{pc}
B	0.03093
C	0.03095
E	0.02971
Average	0.03053

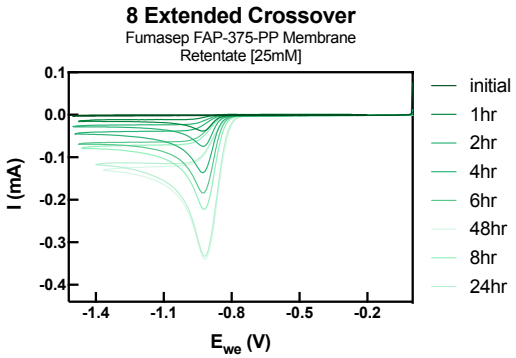
Initial Rates:

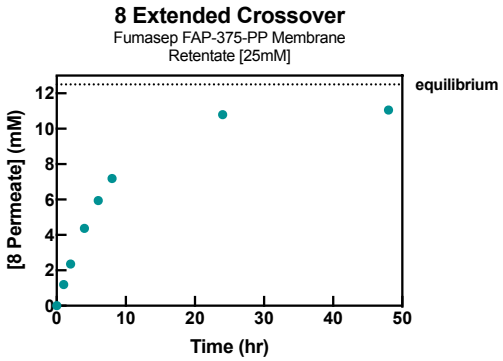


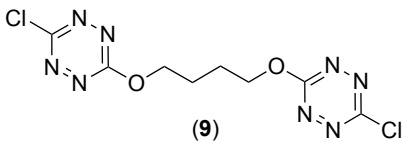


8 Initial Rates	
Time (hr)	**[C] (mM)**
0.1	0.121
0.2	0.260
0.283	0.334
0.333	0.422
0.5	0.600
0.583	0.694
0.667	0.812
0.75	0.911
0.833	1.003
1	1.198

Extended Crossover:



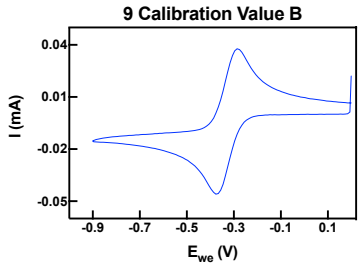




(**9**)

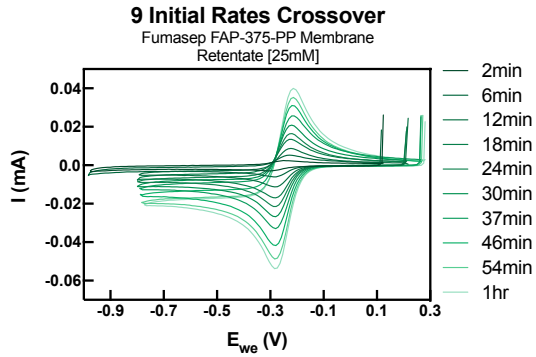
Conditions: General procedure outlined in Section IIb was followed using 25 mM **9** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

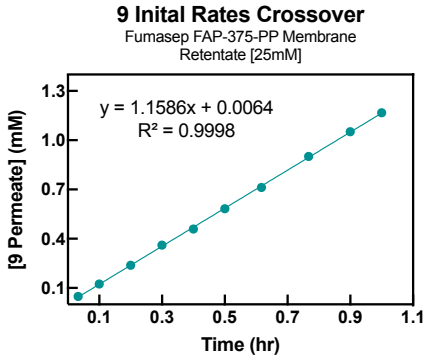
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.04419
B	0.04565
C	0.04679
Average	0.04554

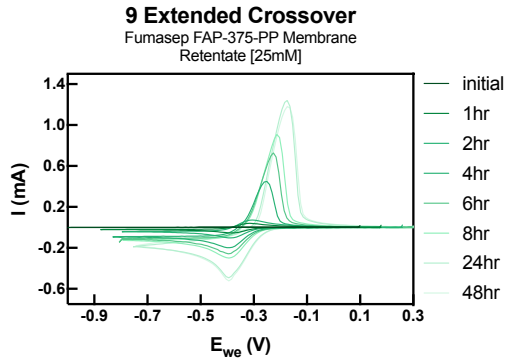
Initial Rates:

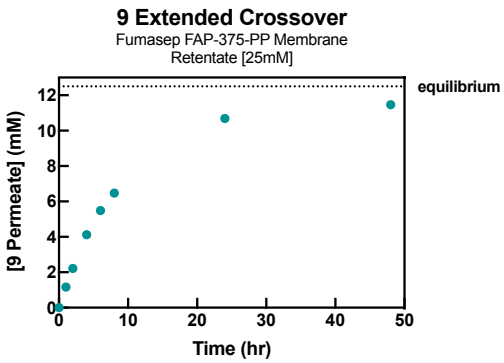


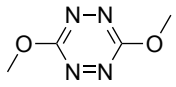


9 Initial Rates	
Time (h)	**[C] (mM)**
0.033	0.048
0.1	0.124
0.2	0.239
0.3	0.361
0.4	0.459
0.5	0.583
0.617	0.712
0.767	0.901
0.9	1.052
1	1.167

Extended Crossover:



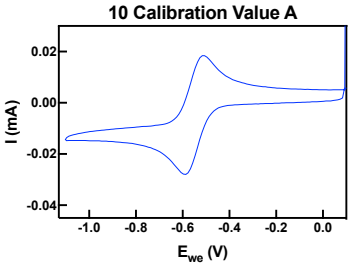




(**10**)

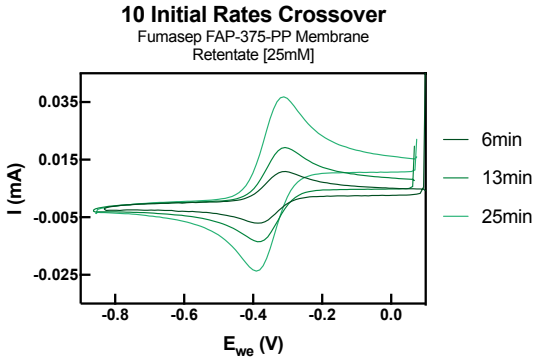
Conditions: General procedure outlined in Section IIb was followed using 25 mM **10** on the retentate side and 0.5 M KPF_6/MeCN solutions on both sides of the cell. Crossover was monitored by CV over 48 h.

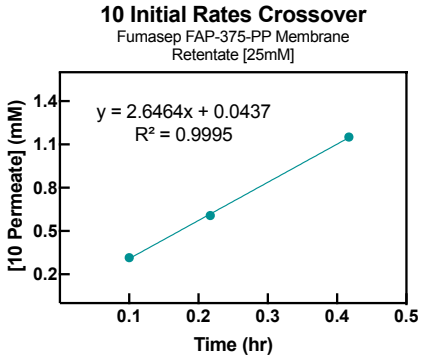
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.02788
B	0.02856
C	0.03154
Average	0.02933

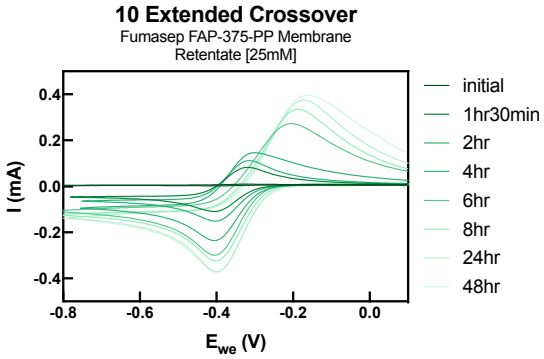
Initial Rates:

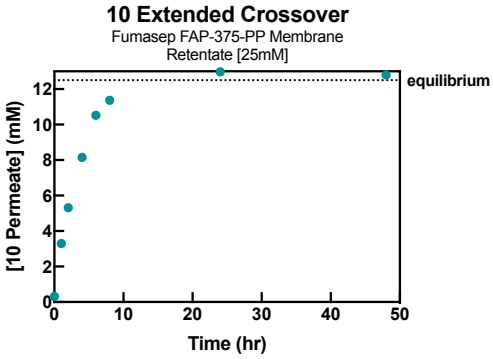


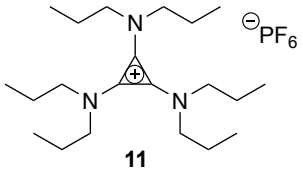


10 Initial Rates	
Time (h)	**[C] (mM)**
0.1	0.315
0.217	0.607
0.417	1.151

Extended Crossover:



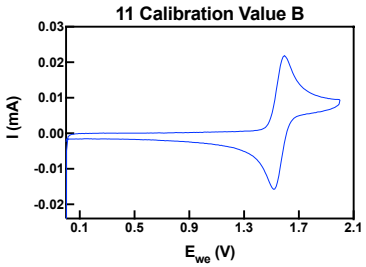




11

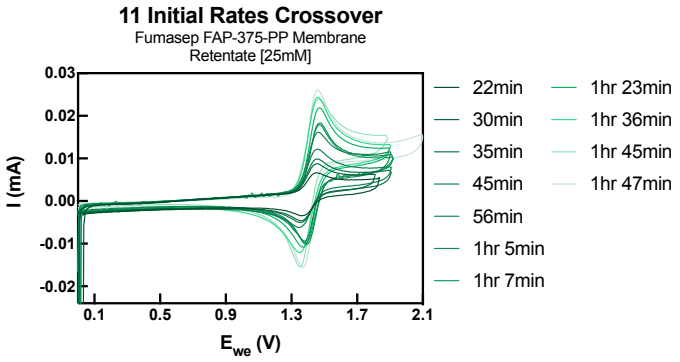
Conditions: General procedure outlined in Section IIb was followed using 25 mM **11** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

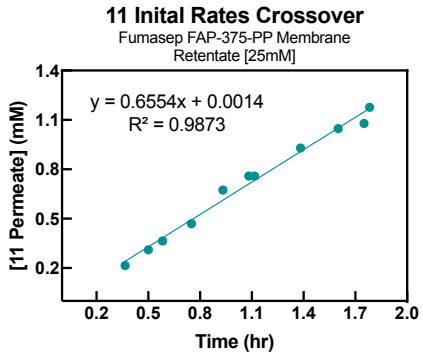
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.0215
B	0.02078
C	0.02091
Average	0.02106

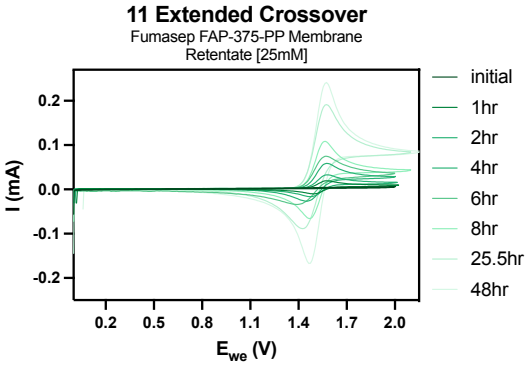
Initial Rates:

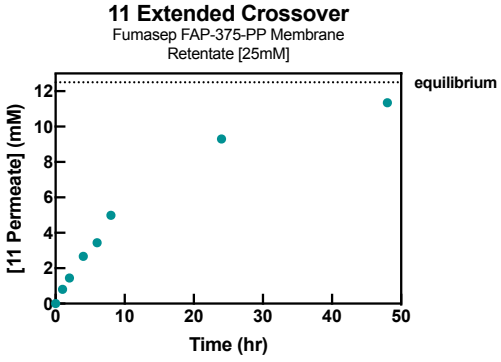


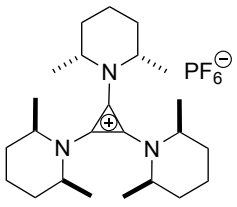


11 Initial Rates	
Time (h)	**[C] (mM)**
0.3663	0.215
0.5003	0.311
0.5833	0.365
0.7503	0.470
0.9333	0.674
1.0833	0.759
1.1163	0.759
1.3833	0.929
1.6003	1.047
1.7503	1.078
1.7833	1.176

Extended Crossover:



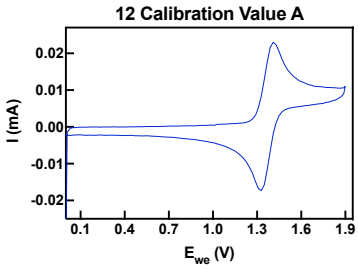




(**12**)

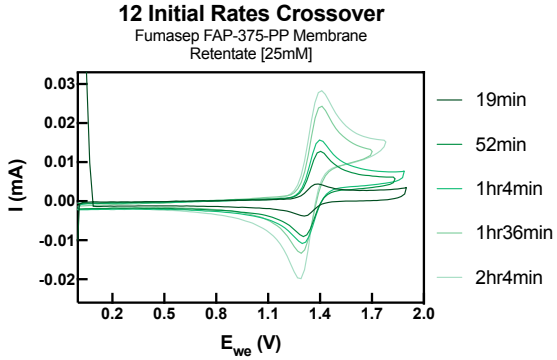
Experiment Conditions: General procedure outlined in Section IIb was followed using 25 mM **12** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

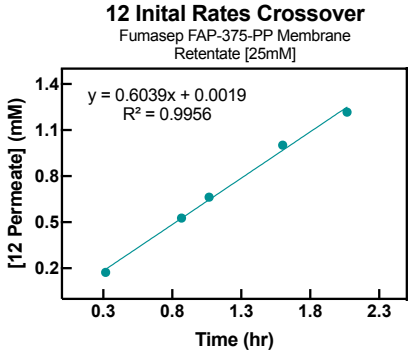
Calibration CVs [1.0 mM]:



Trial	i_{pa}
A	0.0232
B	0.02179
C	0.02221
Average	0.0224

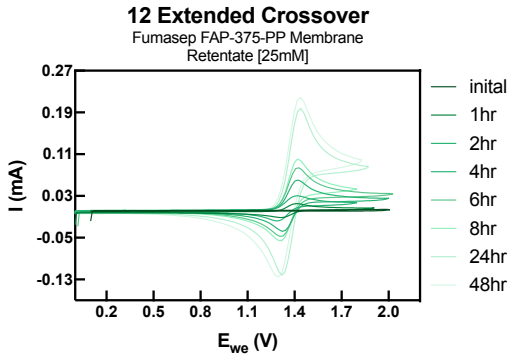
Initial Rates:

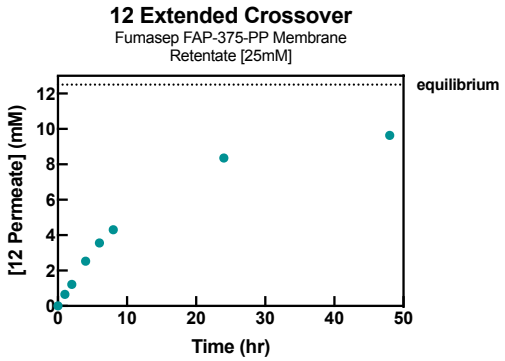


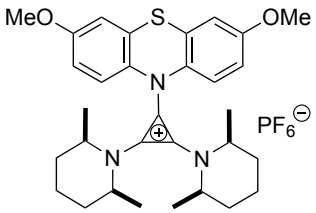


12 Initial Rates	
Time (h)	**[C] (mM)**
0.317	0.173
0.867	0.527
1.067	0.663
1.6	1.002
2.067	1.217

Extended Crossover:



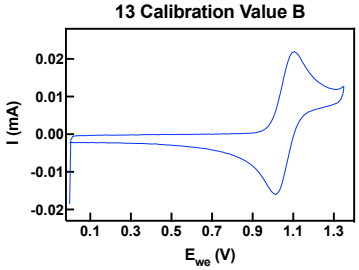




(**13**)

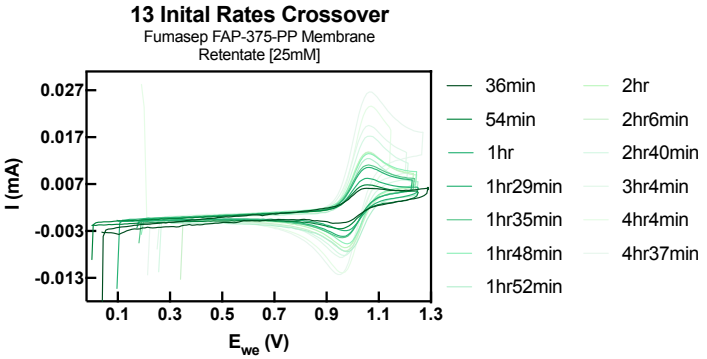
Conditions: General procedure outlined in Section IIb was followed using 25 mM **13** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

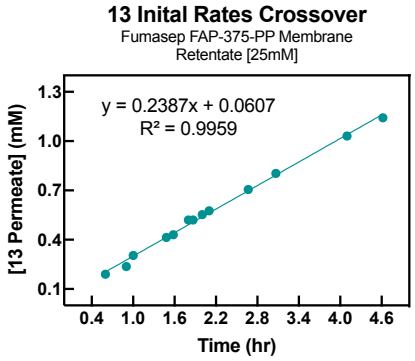
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.02139
B	0.02168
C	0.0221
Average	0.02172

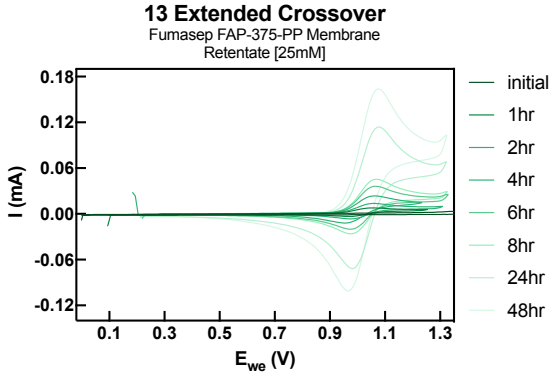
Initial Rates:

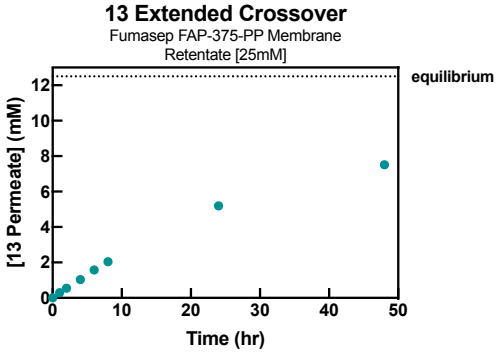


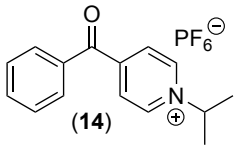


13 Initial Rates	
Time (h)	**[C] (mM)**
0.6	0.1896
0.9	0.2358
1	0.3041
1.483	0.4137
1.583	0.4294
1.8	0.5197
1.867	0.5202
2	0.5529
2.1	0.5759
2.667	0.7048
3.067	0.8028
4.1	1.0311
4.617	1.1416

Extended Crossover:

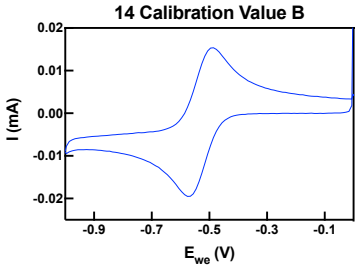






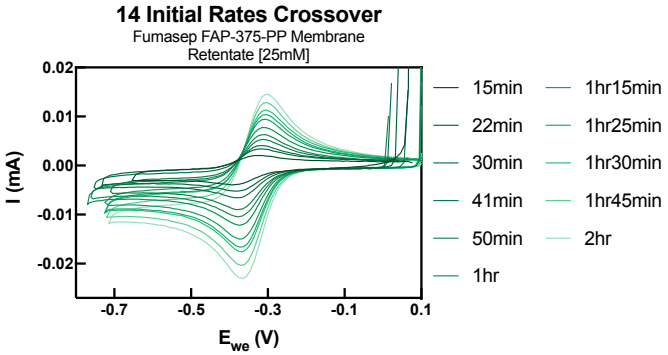
Conditions: General procedure outlined in Section IIb was followed using 25 mM **14** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

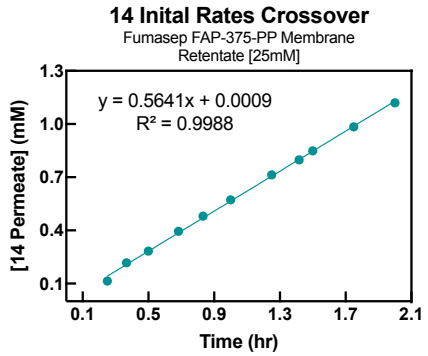
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.01915
B	0.01921
C	0.02105
Average	0.01980

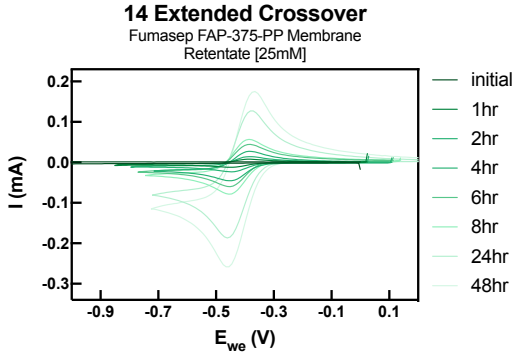
Initial Rates:

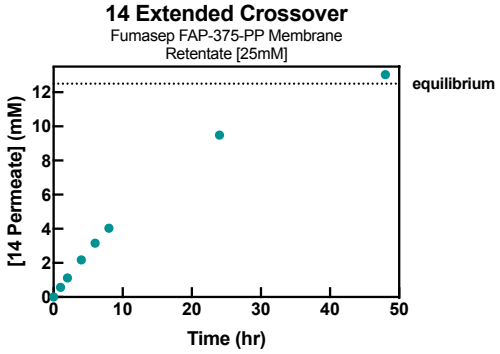


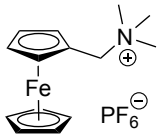


14 Initial Rates	
Time (h)	**[C] (mM)**
0.25	0.114
0.367	0.217
0.5	0.283
0.683	0.395
0.833	0.480
1	0.573
1.25	0.713
1.417	0.798
1.5	0.849
1.75	0.984
2	1.120

Extended Crossover:



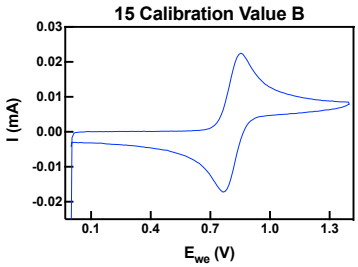




(**15**)

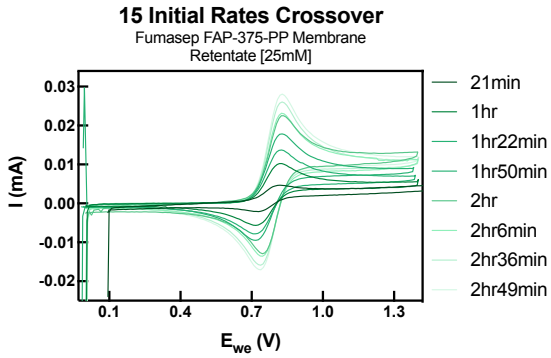
Conditions: General procedure outlined in Section IIb was followed using 25 mM **15** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

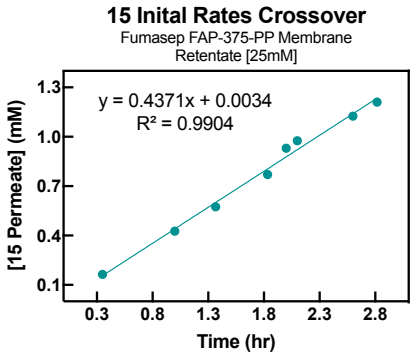
Calibration CVs [1.0 mM]



Trial	i_{pa}
A	0.02463
B	0.02211
C	0.02278
Average	0.023173

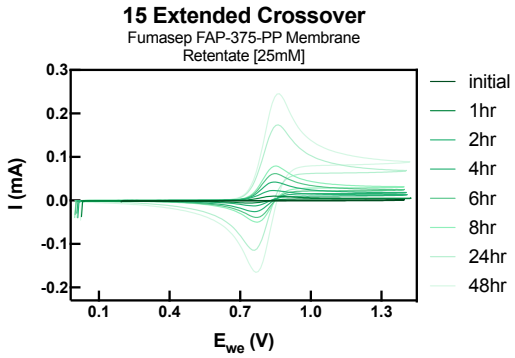
Initial Rates:

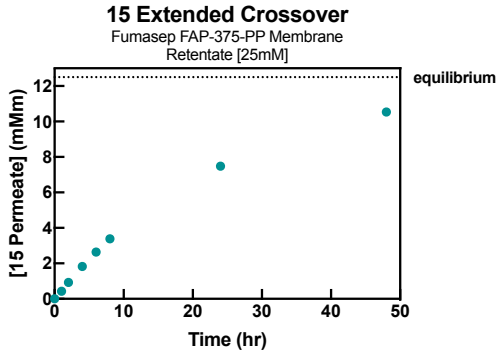


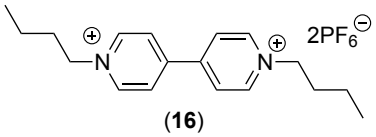


15 Initial Rates	
Time (h)	**[C] (mM)**
0.35	0.164
1	0.426
1.367	0.575
1.833	0.770
2	0.930
2.1	0.976
2.6	1.125
2.817	1.210

Extended Crossover:



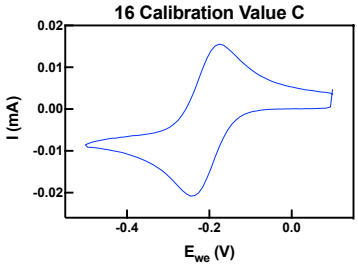




(**16**)

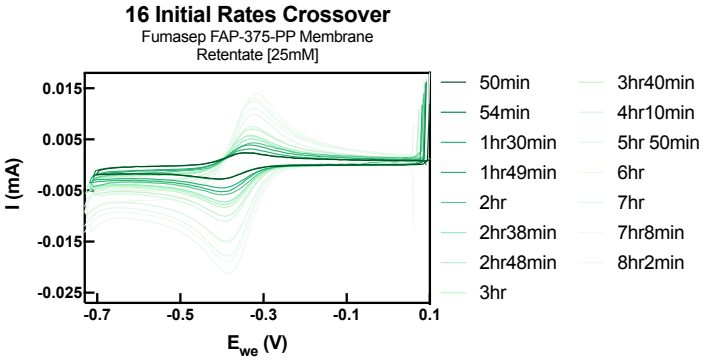
Conditions: General procedure outlined in Section IIb was followed using 25 mM **16** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

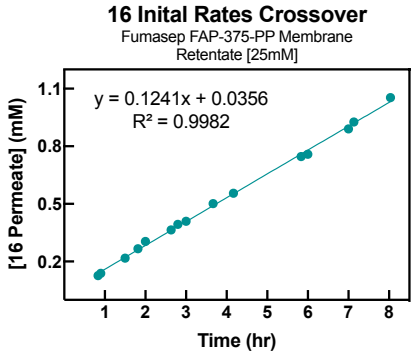
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.01923
B	0.01953
C	0.02056
D	0.02007
Average	0.01985

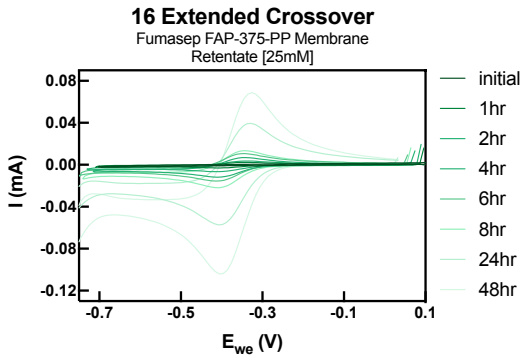
Initial Rates:

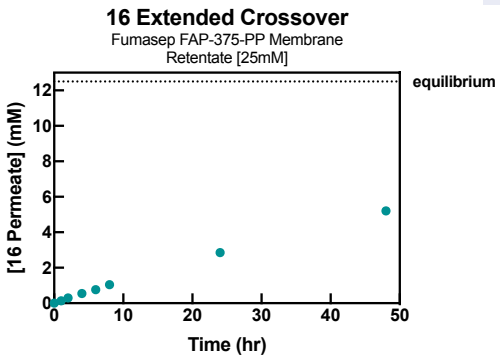


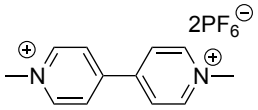


16 Initial Rates	
Time (h)	**[C] (mM)**
0.833	0.126
0.9	0.138
1.5	0.217
1.817	0.266
2	0.304
2.633	0.364
2.8	0.393
3	0.410
3.667	0.501
4.167	0.555
5.833	0.746
6	0.758
7	0.890
7.133	0.926
8.033	1.053

Extended Crossover:



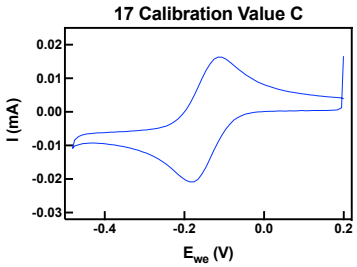




(**17**)

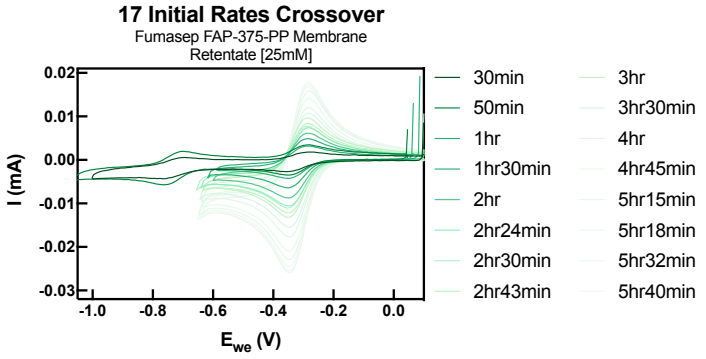
Experiment Conditions: General procedure outlined in Section IIb was followed using 25 mM **17** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

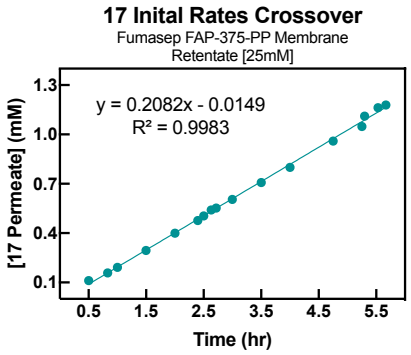
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.0214
B	0.02301
C	0.0208
Average	0.02174

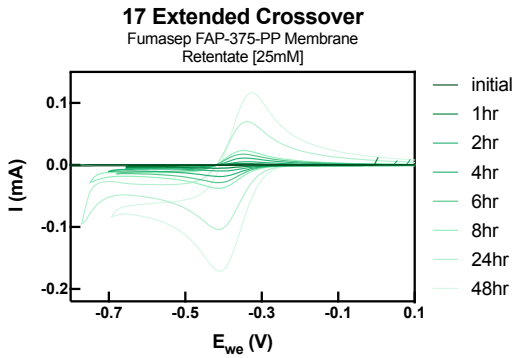
Initial Rates:

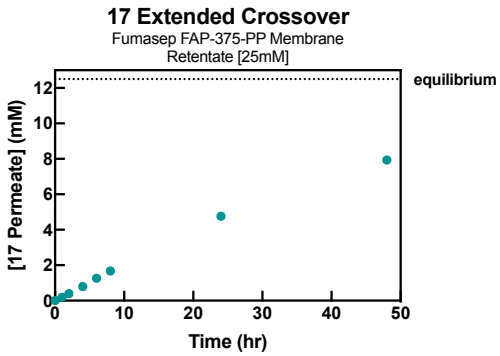


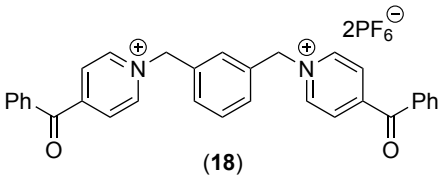


17 Initial Rates	
Time (h)	**[C] (mM)**
0.5	0.111
0.833	0.158
1	0.192
1.5	0.294
2	0.400
2.4	0.476
2.5	0.504
2.633	0.541
2.717	0.552
3	0.605
3.5	0.707
4	0.800
4.75	0.959
5.25	1.048
5.3	1.111
5.533	1.163
5.667	1.179

Extended Crossover:



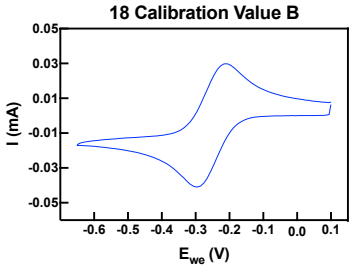




(**18**)

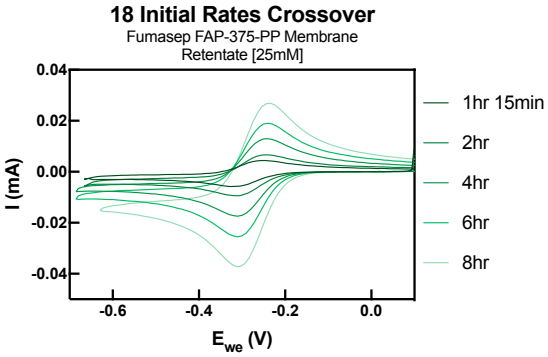
Conditions: General procedure outlined in Section IIb was followed using 25 mM **18** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

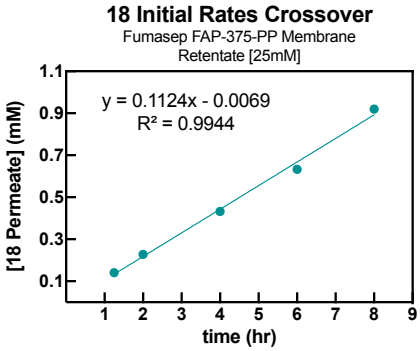
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.04074
B	0.04047
C	0.03918
Average	0.04013

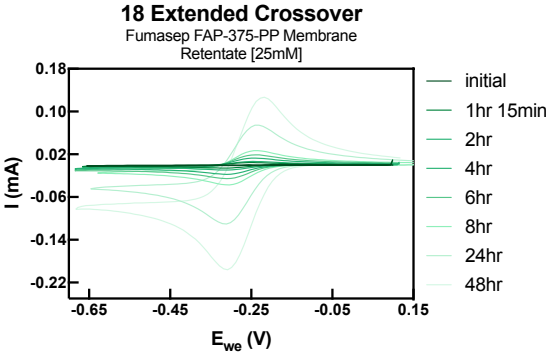
Initial Rates:

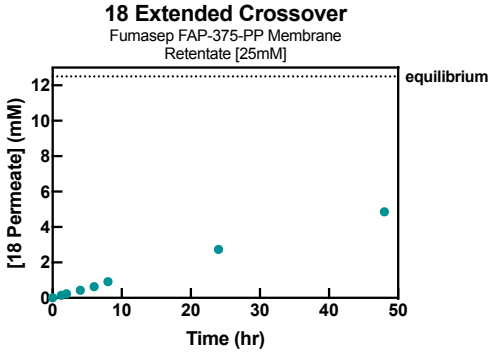


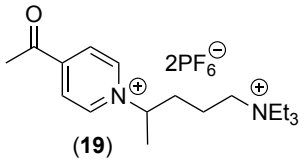


18 Initial Rates	
Time (h)	**[C] (mM)**
1.25	0.141
2	0.228
4	0.432
6	0.633
8	0.920

Extended Crossover:



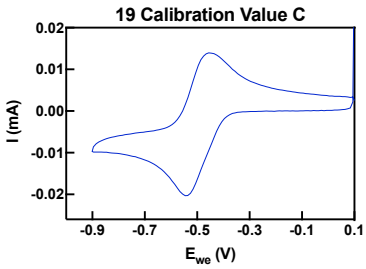




(**19**)

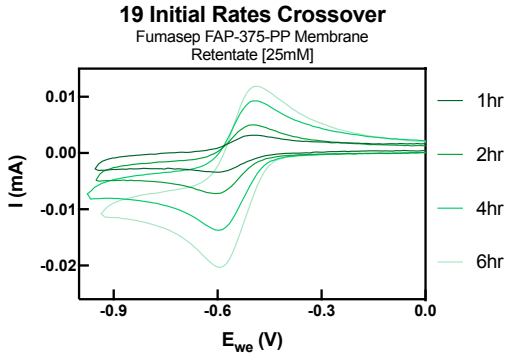
Conditions: General procedure outlined in Section IIb was followed using 25 mM **19** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

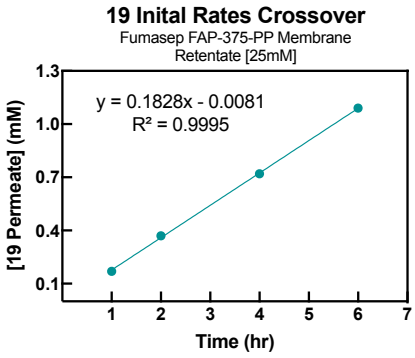
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.01515
B	0.01951
C	0.0199
Average	0.018187

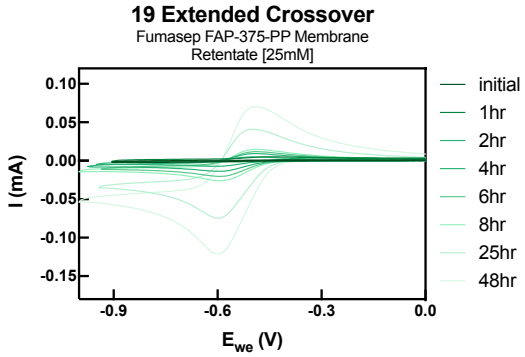
Initial Rates:

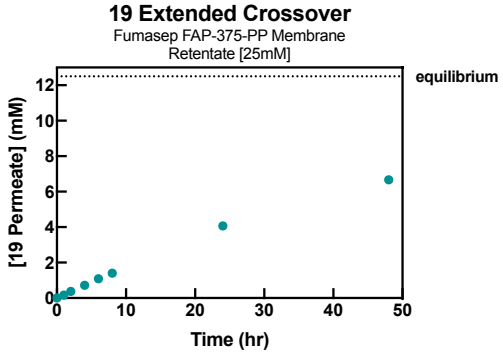


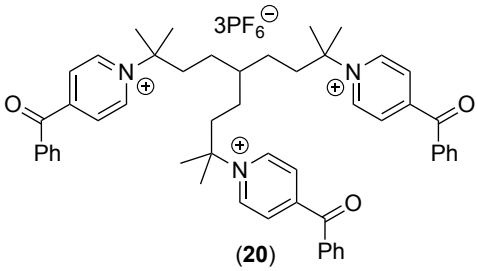


19 Initial Rates	
Time (h)	**[C] (mM)**
1	0.17
2	0.37
4	0.72
6	1.09

Extended Crossover:

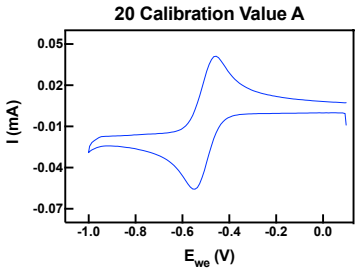






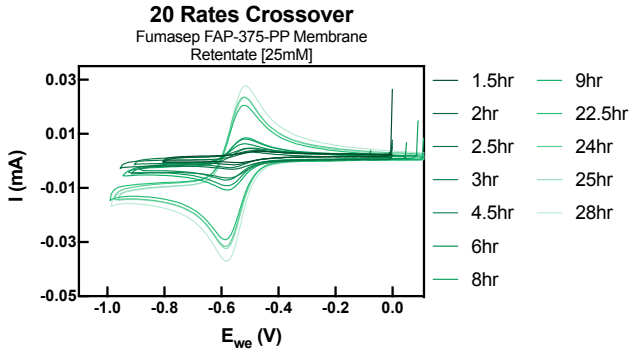
Conditions: General procedure outlined in Section IIb was followed using 25 mM **20** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.575 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

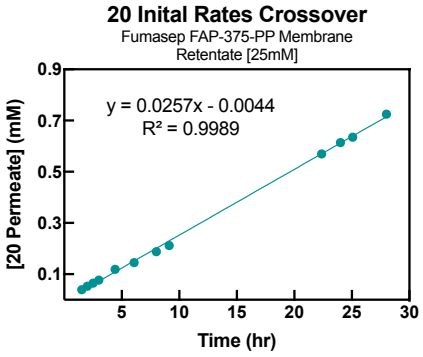
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.05454
B	0.04741
C	0.04827
D	0.05422
Average	0.05111

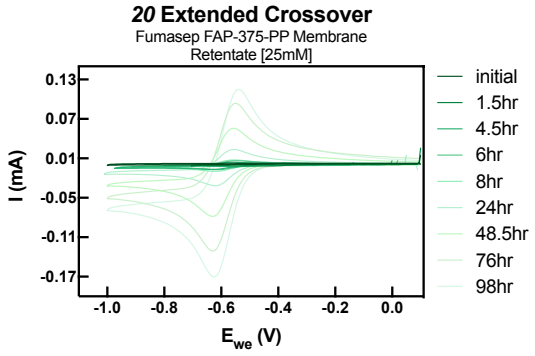
Initial Rates:

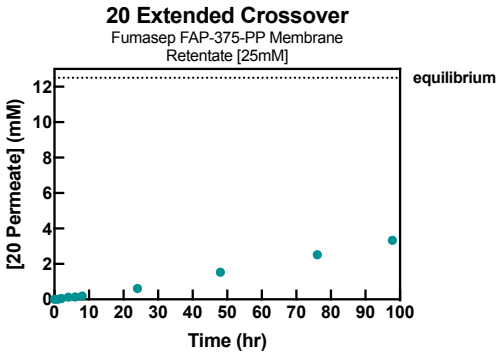


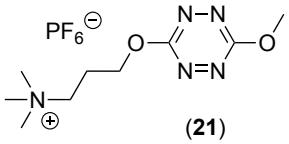


20 Initial Rates	
Time (h)	**[C] (mM)**
1.517	0.039
2	0.053
2.5	0.065
3	0.077
4.417	0.119
6.083	0.145
8	0.188
9.133	0.212
22.367	0.570
24	0.614
25.067	0.635
28	0.725

Extended Crossover:



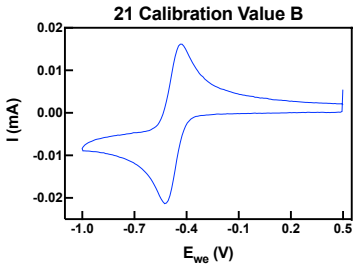




(**21**)

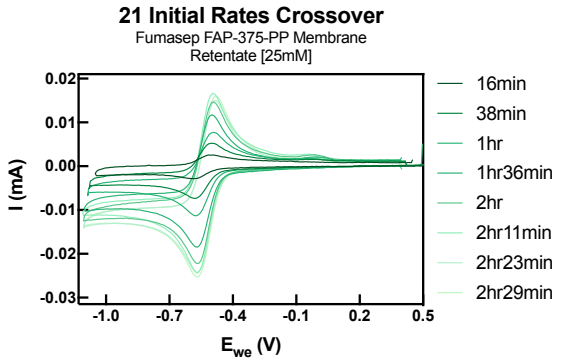
Conditions: General procedure outlined in Section IIb was followed using 25 mM **21** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

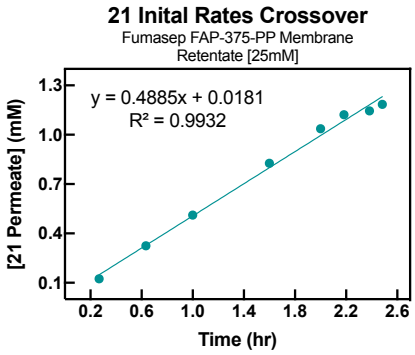
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.02032
B	0.02085
C	0.0205
Average	0.02056

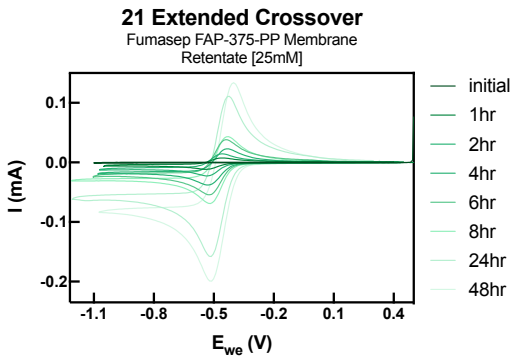
Initial Rates:

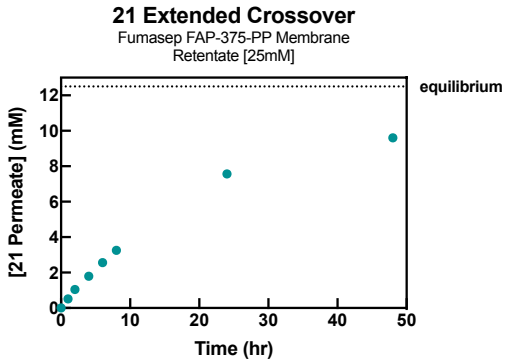


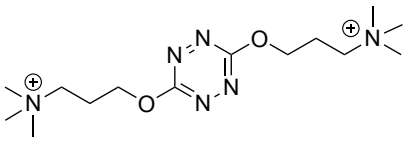


21 Initial Rates	
Time (h)	**[C] (mM)**
0.267	0.124
0.633	0.325
1	0.511
1.6	0.827
2	1.036
2.183	1.122
2.383	1.145
2.483	1.185

Extended Crossover:



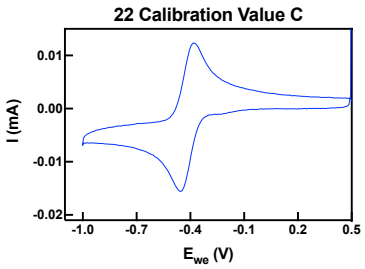




(**22**)

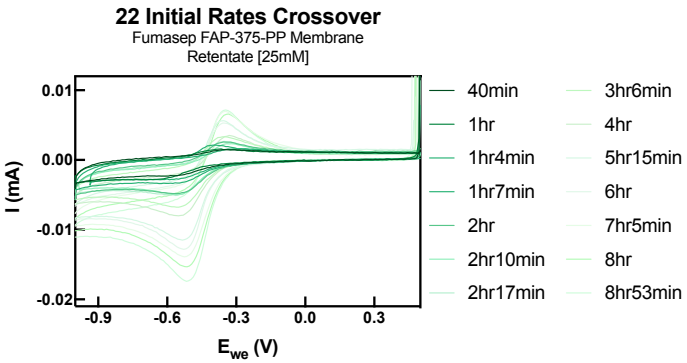
Conditions: General procedure outlined in Section IIb was followed using 25 mM **22** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

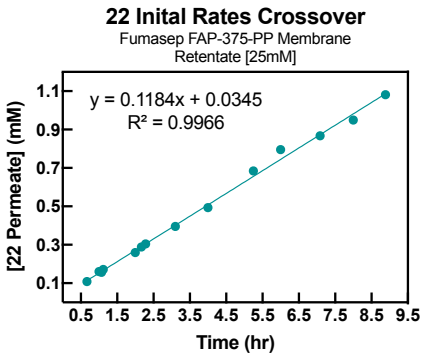
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.0154
B	0.01676
C	0.01537
Average	0.01584

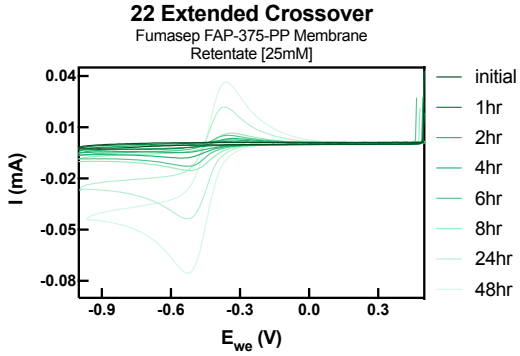
Initial Rates:

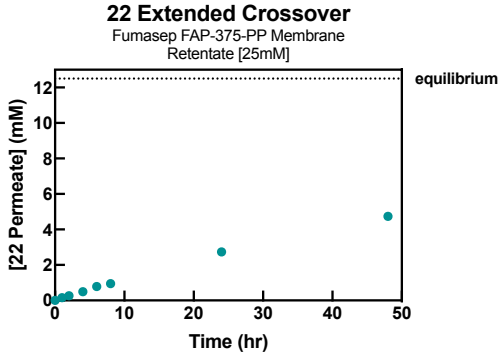


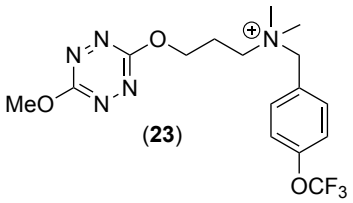


22 Initial Rates	
Time (h)	**[C] (mM)**
0.667	0.108
1	0.160
1.067	0.156
1.117	0.171
2	0.259
2.167	0.288
2.283	0.304
3.1	0.395
4	0.493
5.25	0.684
6	0.795
7.083	0.867
8	0.950
8.883	1.081

Extended Crossover:



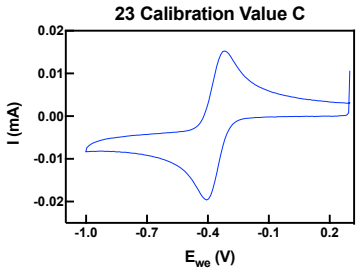




(**23**)

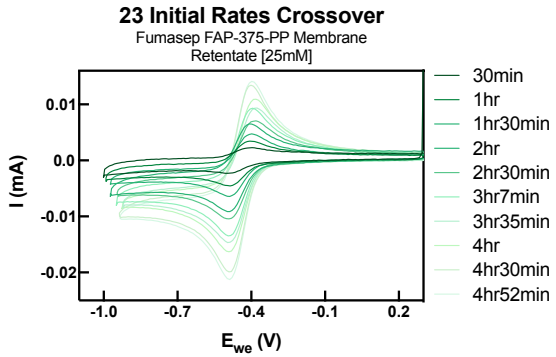
Conditions: General procedure outlined in Section IIb was followed using 25 mM **23** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.525 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

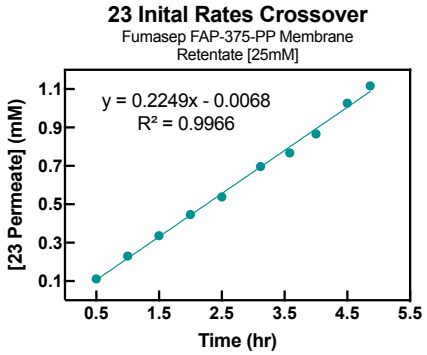
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.018
B	0.01891
C	0.01853
D	0.01933
Average	0.01869

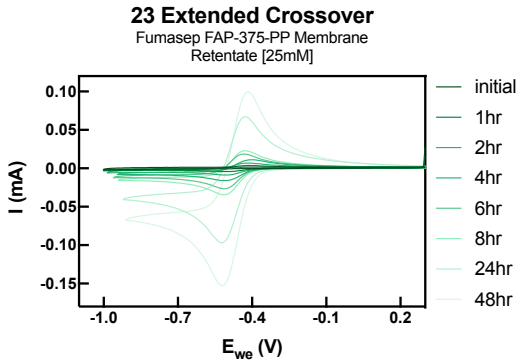
Initial Rates:

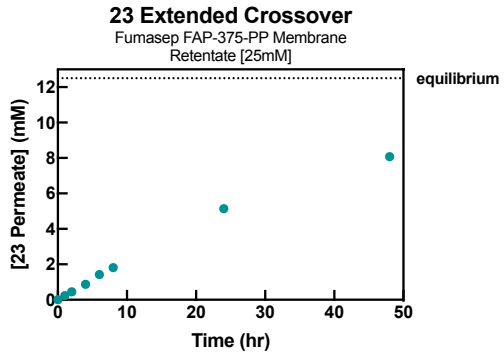


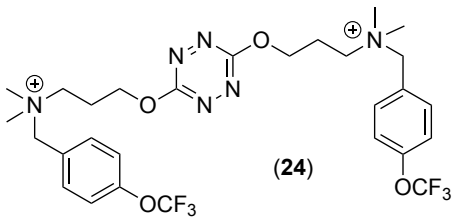


23 Initial Rates	
Time (h)	**[C] (mM)**
0.5	0.111
1	0.230
1.5	0.336
2	0.446
2.5	0.538
3.117	0.697
3.583	0.767
4	0.866
4.5	1.026
4.867	1.116

Extended Crossover:

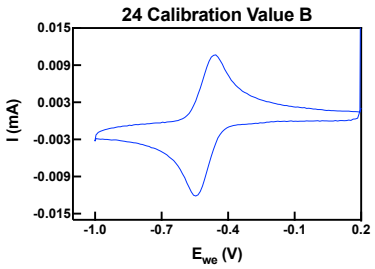






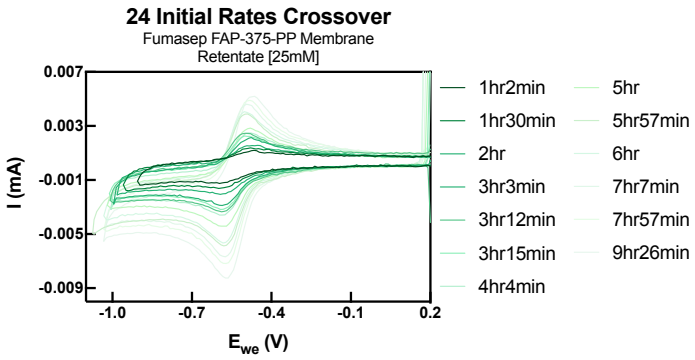
Conditions: General procedure outlined in Section IIb was followed using 25 mM **24** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

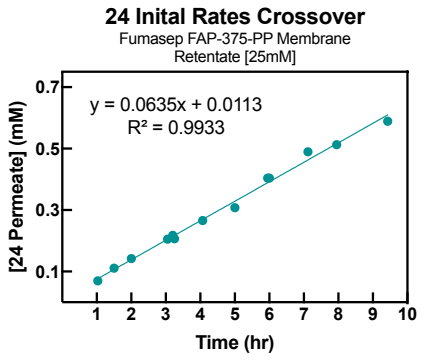
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.01376
B	0.01336
C	0.01376
Average	0.01363

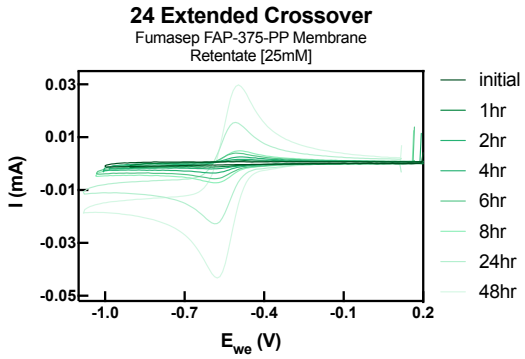
Initial Rates:

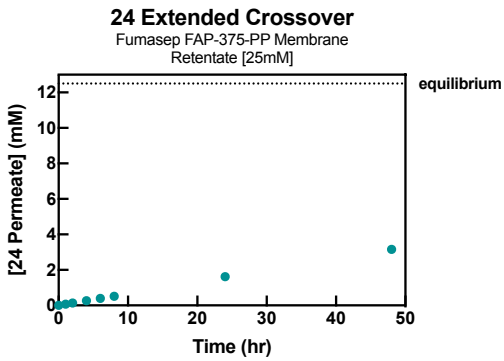


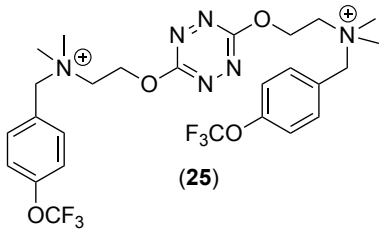


24 Initial Rates	
Time (h)	**[C] (mM)**
1.033	0.0694
1.5	0.1107
2	0.1425
3.05	0.2053
3.2	0.2179
3.25	0.2068
4.067	0.2658
5	0.3076
5.95	0.4038
6	0.4040
7.117	0.4898
7.95	0.5127
9.433	0.5893

Extended Crossover:



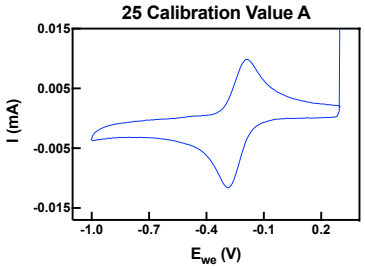




(**25**)

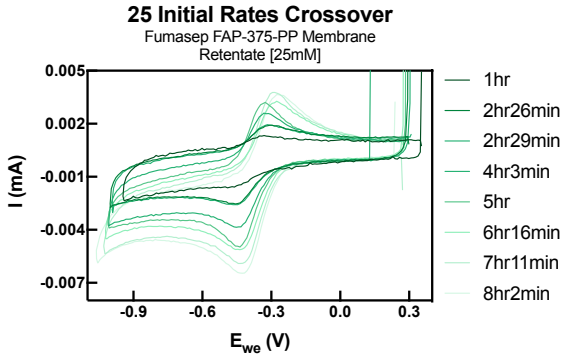
Conditions: General procedure outlined in Section IIb was followed using 25 mM **25** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

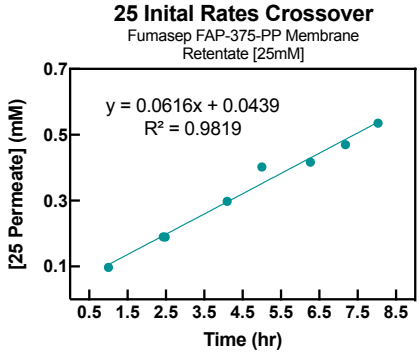
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.0115
B	0.01129
C	0.01283
Average	0.01187

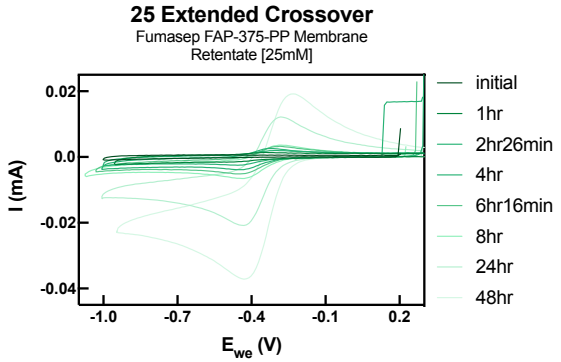
Initial Rates:

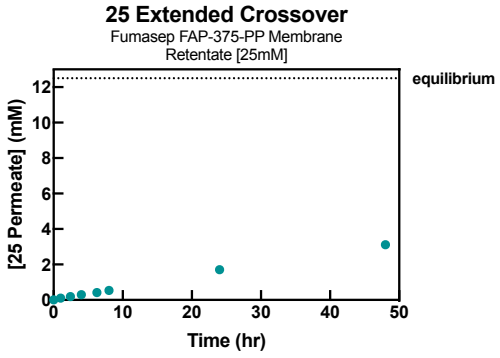


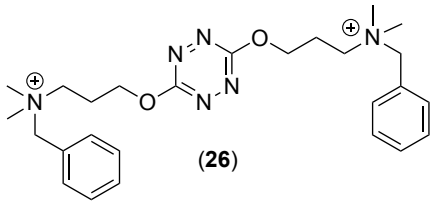


25 Initial Rates	
Time (h)	**[C] (mM)**
1	0.097
2.433	0.190
2.483	0.189
4.1	0.298
5	0.402
6.267	0.417
7.183	0.470
8.033	0.535

Extended Crossover:



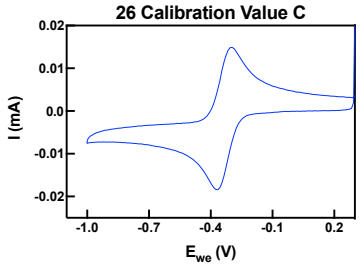




(**26**)

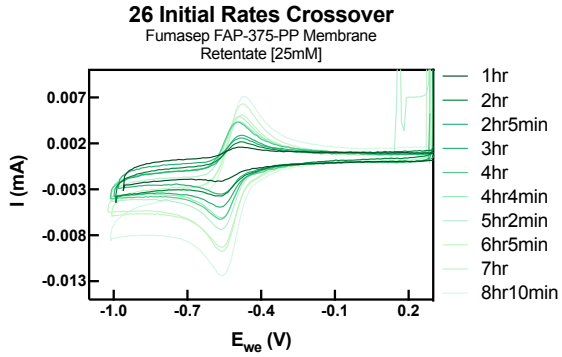
Conditions: General procedure outlined in Section IIb was followed using 25 mM **26** in 0.5 M KPF_6/MeCN solution on the retentate side and 0.55 M KPF_6/MeCN on the permeate side of the cell. Crossover was monitored by CV over 48 h.

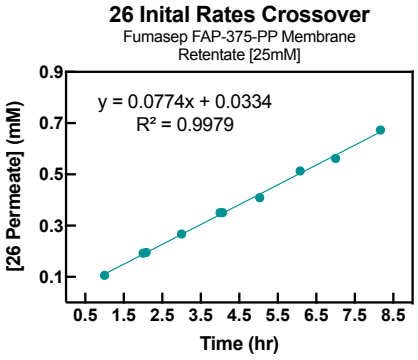
Calibration CVs [1.0 mM]



Trial	i_{pc}
A	0.01706
B	0.01654
C	0.01743
D	0.01674
E	0.01798
Average	0.01715

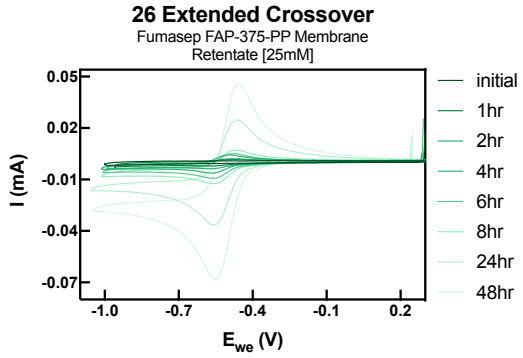
Initial Rates:

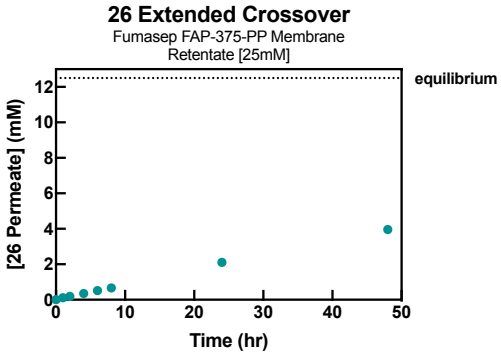




26 Initial Rates	
Time (h)	**[C] (mM)**
1	0.106
2	0.192
2.083	0.195
3	0.267
4	0.351
4.067	0.351
5.033	0.409
6.083	0.513
7	0.562
8.167	0.673

Extended Crossover:





X. Diffusion Coefficient Data

Compound	Diffusion Coefficient (cm^2/s); CV	Diffusion Coefficient (cm^2/s); DOSY
1[a]	1.950E-05	N/A
2	1.374E-05	1.077E-05
3[b]	2.110E-05	N/A
4[c]	2.850E-05	N/A
5	1.209E-05	N/A
6[d]	1.020E-05	N/A
7[i]	3.794E-05	N/A
8	2.208E-05	N/A
9[i]	4.439E-05	N/A
10[e]	1.650E-05	N/A
11	1.100E-05	N/A
12[ii]	1.256E-05	N/A
13	1.508E-05	N/A
14	1.586E-05	1.093E-05
15[f]	9.590E-06	N/A
16	9.697E-06	8.396E-06
17[f]	8.490E-06	N/A
18[i]	3.424E-05	N/A
19	9.486E-06	N/A
20	1.983E-05	N/A
21[iii]	1.088E-05	N/A
22	8.498E-06	N/A
23	3.765E-06	N/A
24	3.438E-06	N/A
25[iv]	3.081E-06	N/A
26	6.375E-06	N/A

[a] *J. Power Sources* **2019**, *443*, 227283. [b] *Anal. Chem.* **2002**, *74*, 149. [c] *Nature Commun*. **2020** 11:3843. [d] *RSC Adv.* **2019**, *9*, 13128. [e] *J. Mat. Chem. A* **2022**, *10*, 18745. [f] *ACS Energy Lett.* **2022**, 7, 4118.

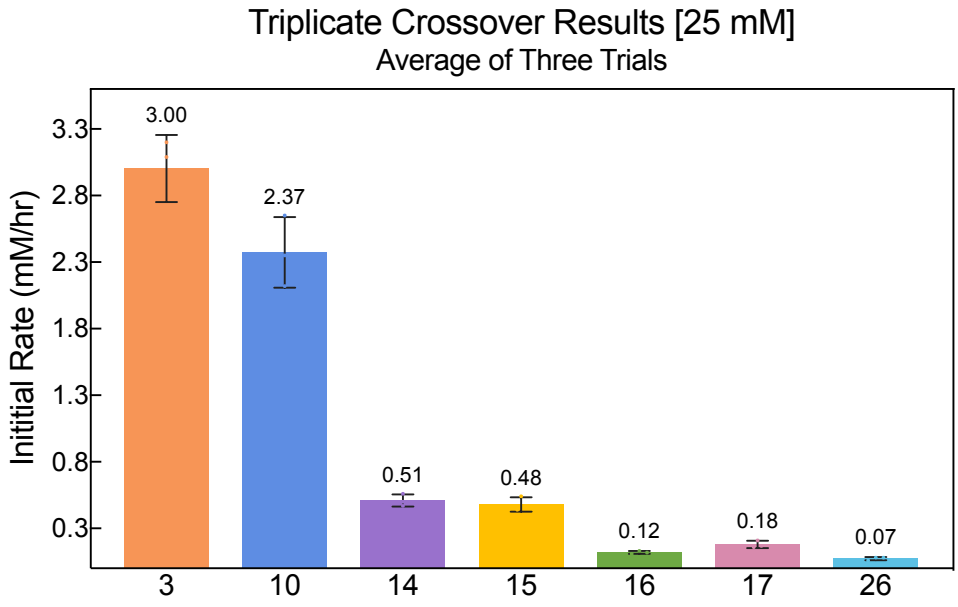
[i] Average of triplicate values. [ii] 0.7 mM used in experiment. [iii] 0.3 mM used in experiment. [iv] 1.2 mM used in experiment.

XI. Initial Rate and Permeability Values

Compound	Initial Rate (mM/h)	Permeability (cm^2/s)
1	2.95	1.18E-06
2	1.21	4.81E-07
3	2.72	1.09E-06
4	2.44	9.75E-07
5	0.61	2.42E-07
6	1.24	4.99E-07
7	0.55	2.18E-07
8	1.19	4.74E-07
9	1.16	4.59E-07
10	2.65	1.06E-06
11	0.66	2.62E-07
12	0.60	2.41E-07
13	0.24	9.51E-08
14	0.56	2.24E-07
15	0.44	1.75E-07
16	0.12	4.90E-08
17	0.21	8.29E-08
18	0.11	4.42E-08
19	0.18	7.25E-08
20	0.03	9.98E-09
21	0.49	1.95E-07
22	0.12	4.68E-08
23	0.22	8.91E-08
24	0.065	2.46E-08
25	0.062	2.38E-08
26	0.078	3.01E-08

XII. Triplicate Initial Rate Values

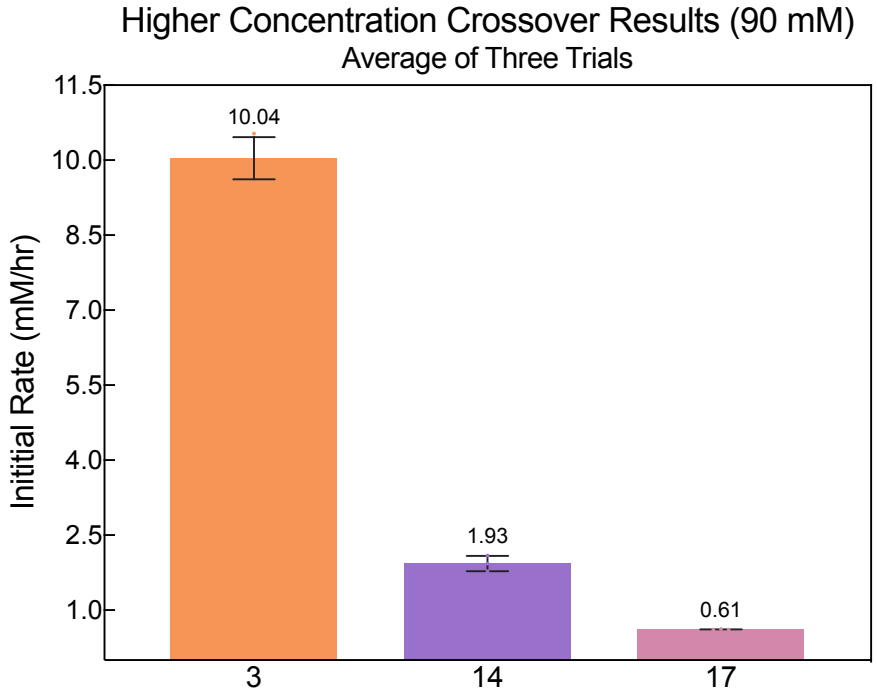
	Initial Rate (mM/h)				Averages	
Compound	**Trial 1**	**Trial 2**	**Trial 3**	**Standard Deviation**	**Initial Rate (mM/h)**	**Permeability (cm^2/s)**
3	3.20	3.09	2.72	0.25	3.00	1.21E-06
10	2.65	2.12	2.35	0.27	2.37	9.52E-07
14	0.56	0.47	0.50	0.05	0.51	2.04E-07
15	0.54	0.44	0.46	0.05	0.48	1.91E-07
16	0.11	0.12	0.13	0.01	0.12	4.87E-08
17	0.17	0.21	0.16	0.03	0.18	7.09E-08
26	0.08	0.06	0.08	0.01	0.07	2.82E-08



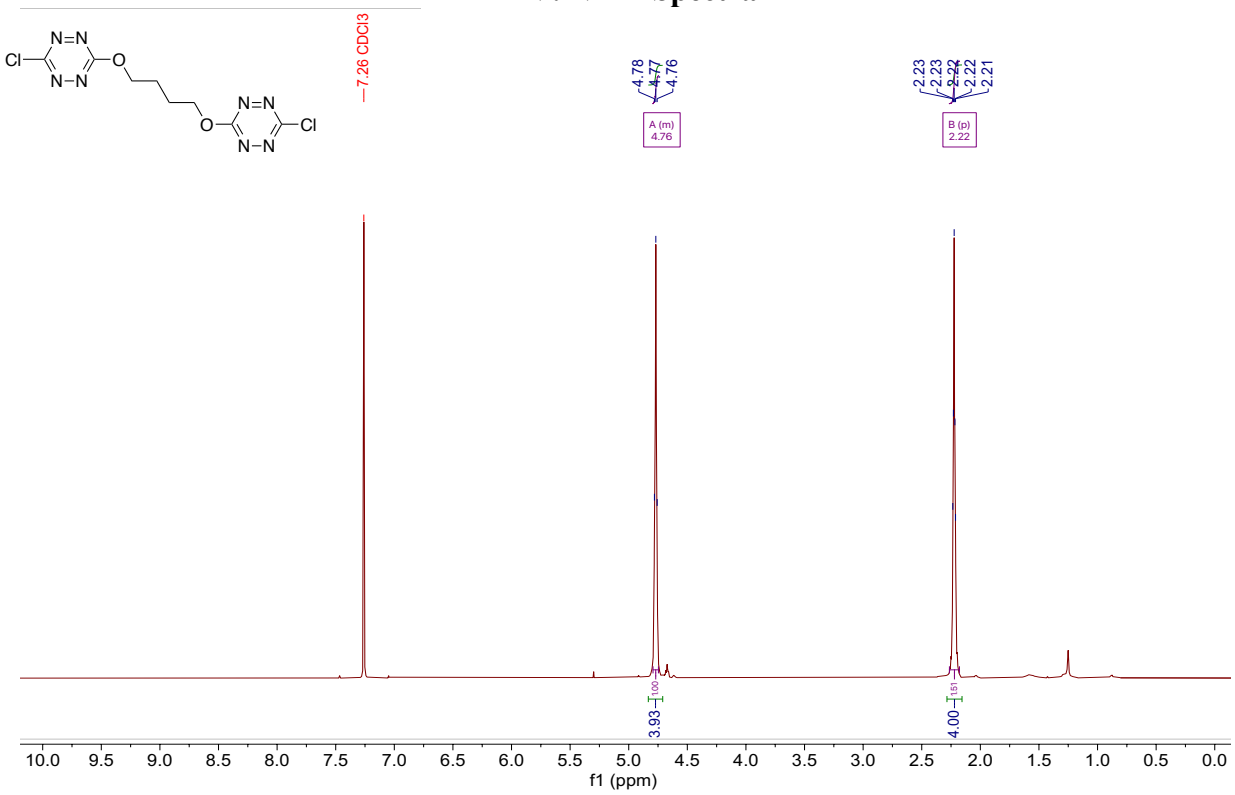
XIII. Higher Concentration Crossover Experiments

Three representative molecules were chosen to run at a higher concentration (90 mM, 3.6 times the concentration of the original experiments): neutral ferrocene (**3**), mono-cation pyridinium (**14**), and di-cation methyl viologen (**17**). Each compound was run in triplicate. Each compound was in solution of 0.5 M KPF_6/MeCN on the retentate side, while the permeate side contained 0.5 M, 0.58 M, and 0.68 M KPF_6/MeCN, in respect to each compound.

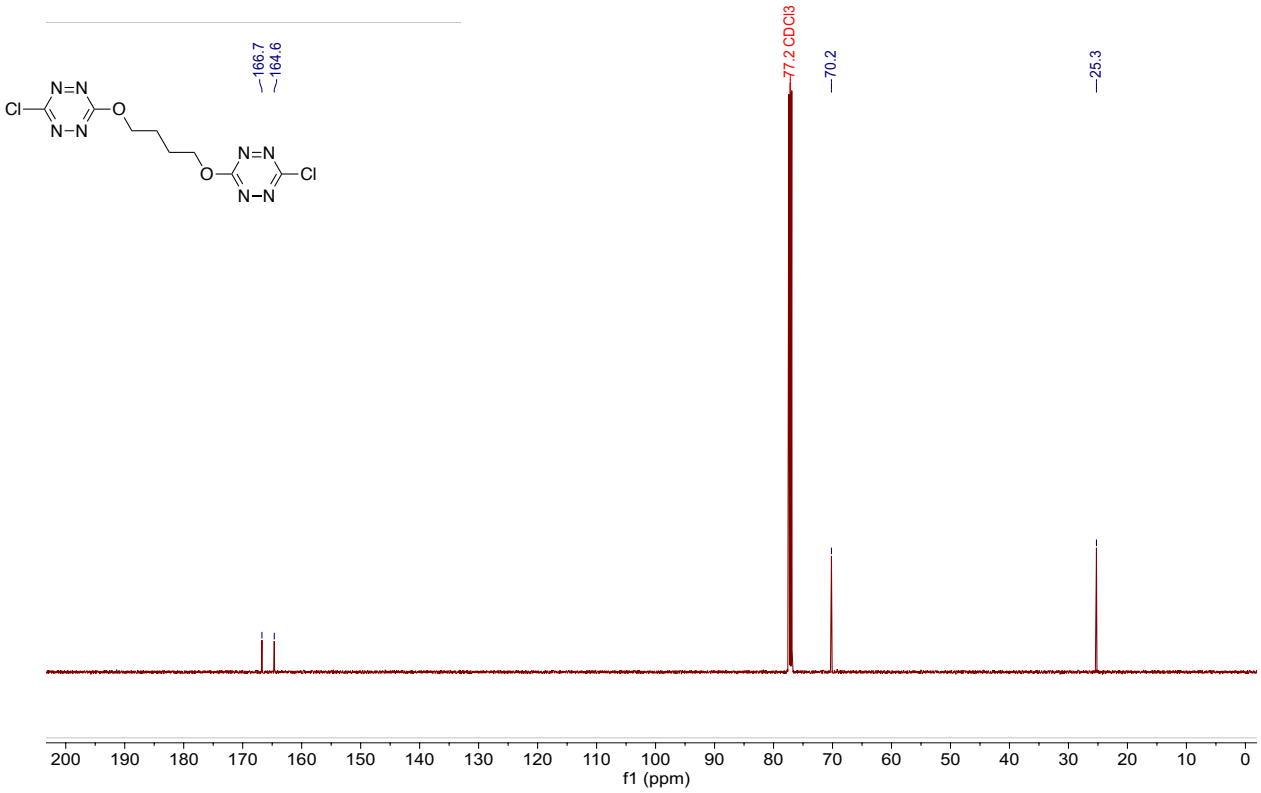
	Initial Rate (mM/h)				Averages	
Compound	**Trial 1**	**Trial 2**	**Trial 3**	**Standard Deviation**	**Initial Rate (mM/h)**	**Permeability (cm^2/s)**
3	9.78	9.81	10.53	0.425	10.040	1.120E-06
14	1.93	2.09	1.78	0.155	1.933	2.150E-07
17	0.61	0.62	0.61	0.006	0.613	6.813E-08



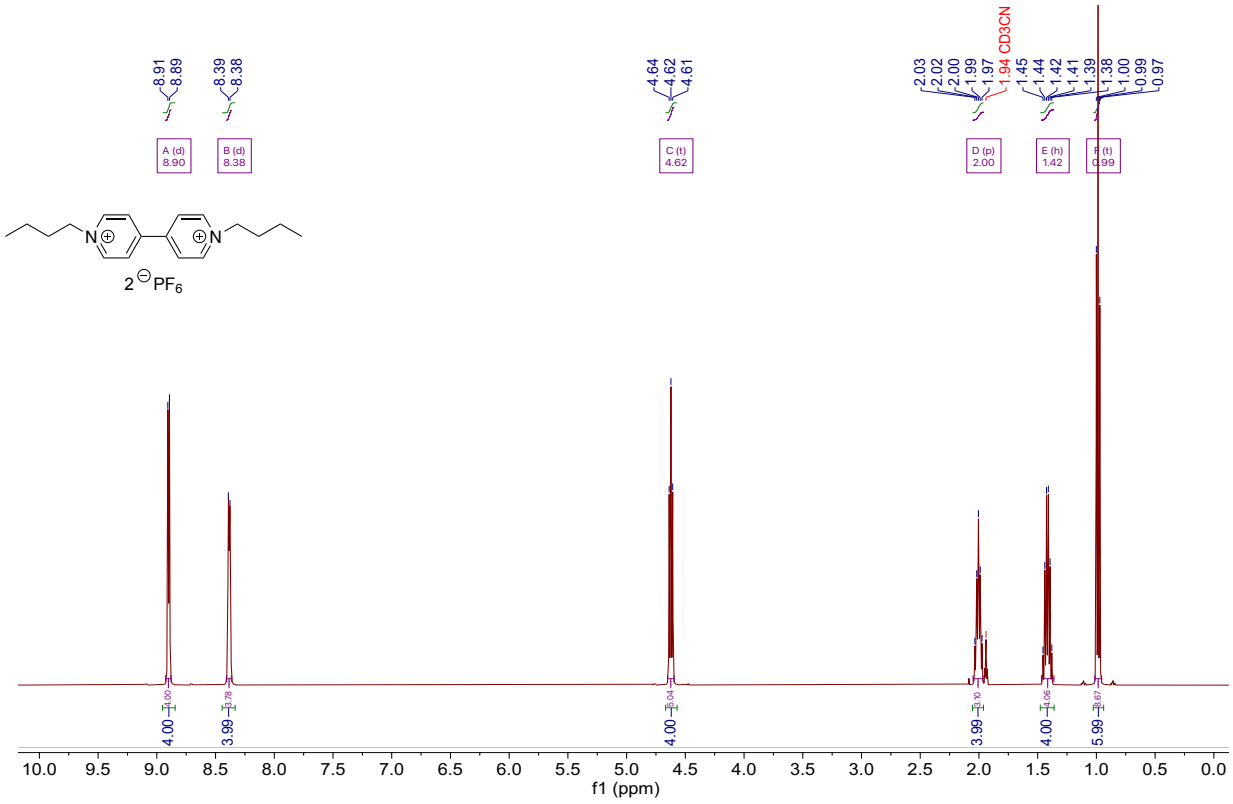
XIV. NMR Spectra



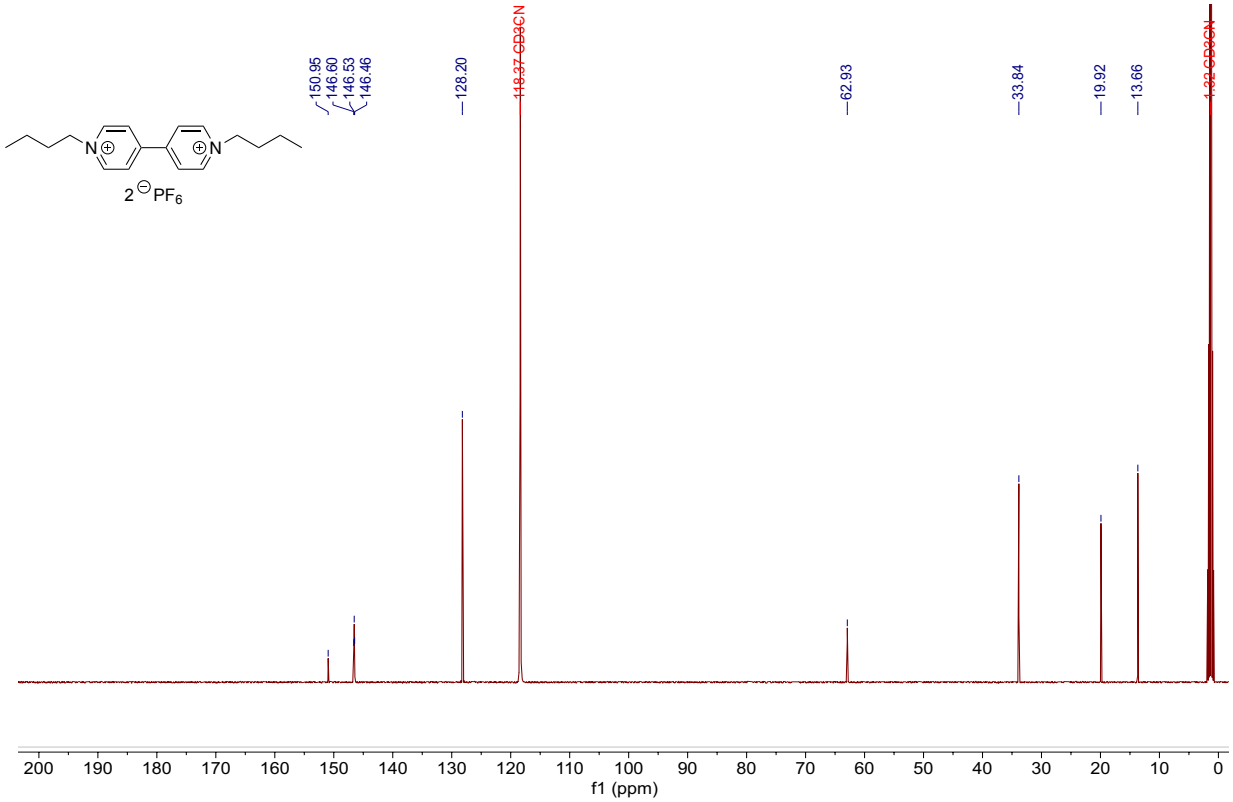
^{1}H NMR spectrum of **9** in $CDCl_3$



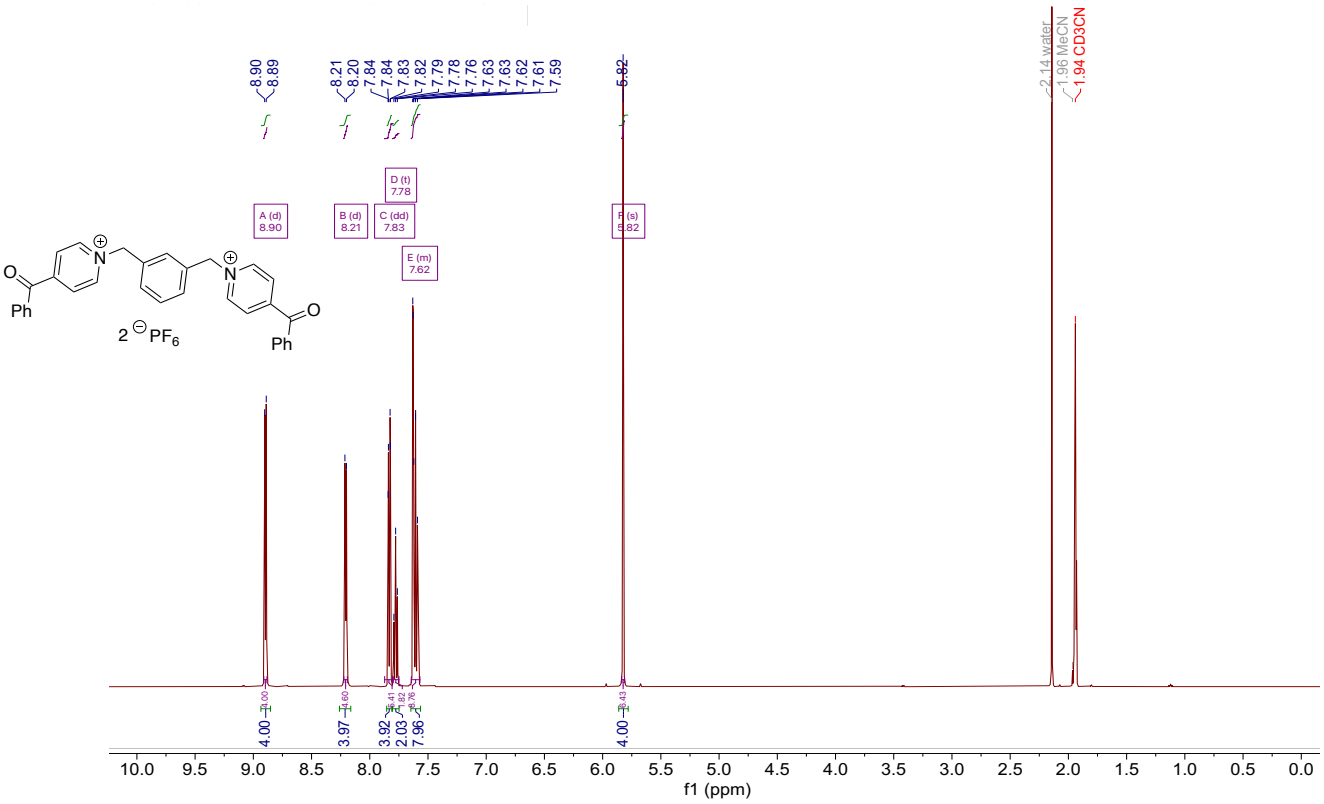
^{13}C NMR spectrum of **9** in $CDCl_3$



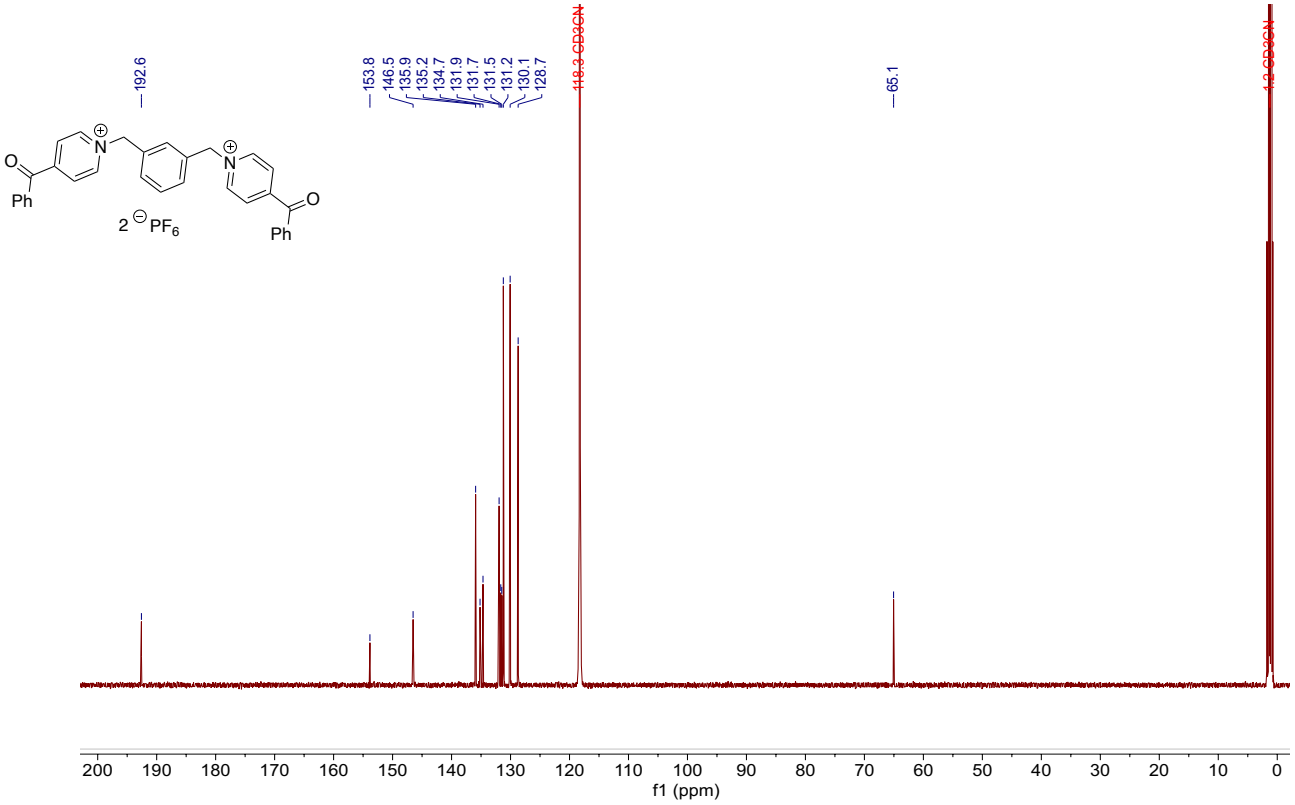
^{1}H NMR spectrum of **16** in CD_3CN



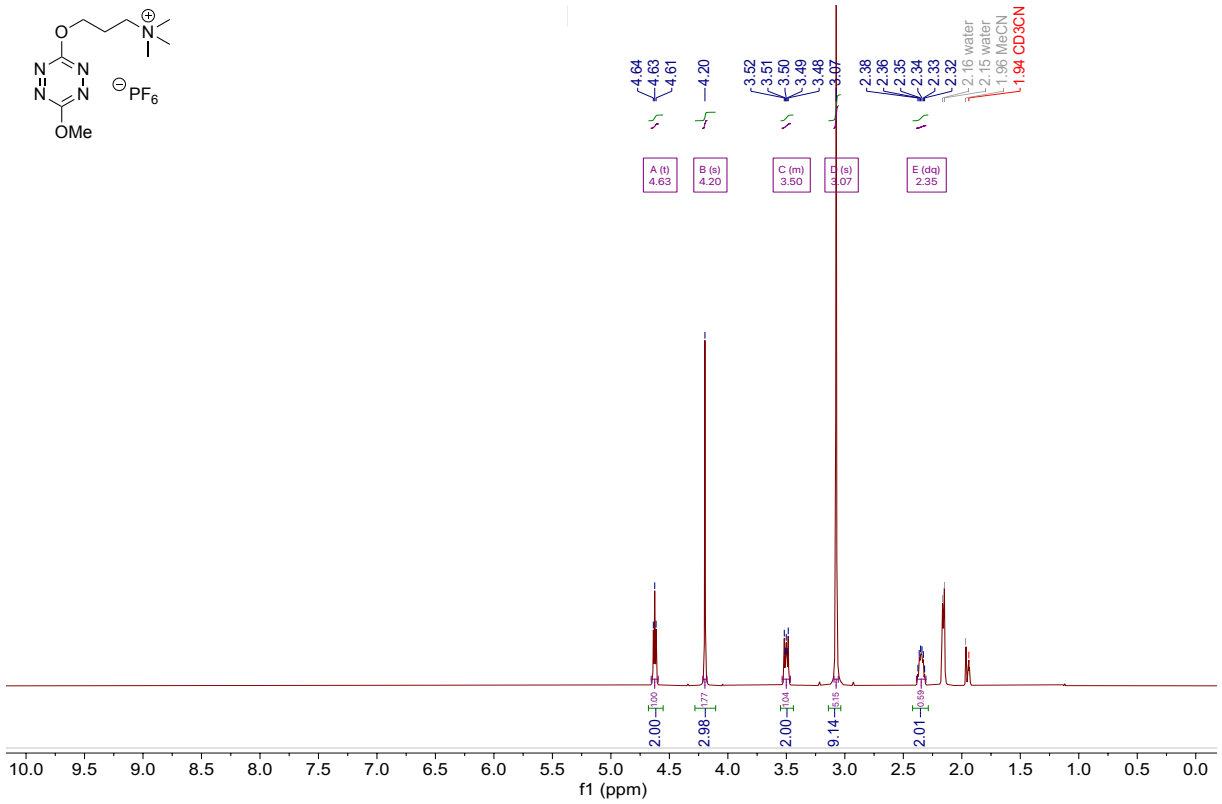
^{13}C NMR spectrum of **16** in CD_3CN



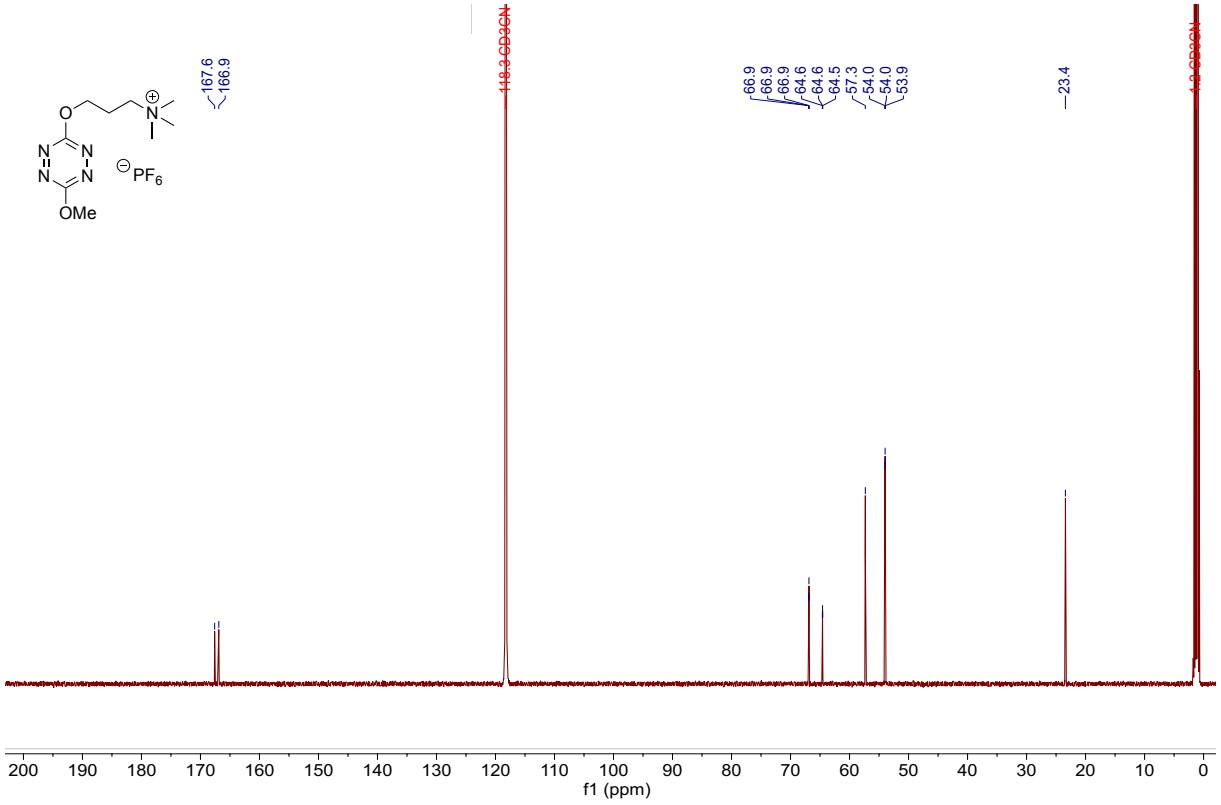
^{1}H NMR spectrum of **18** in CD_3CN



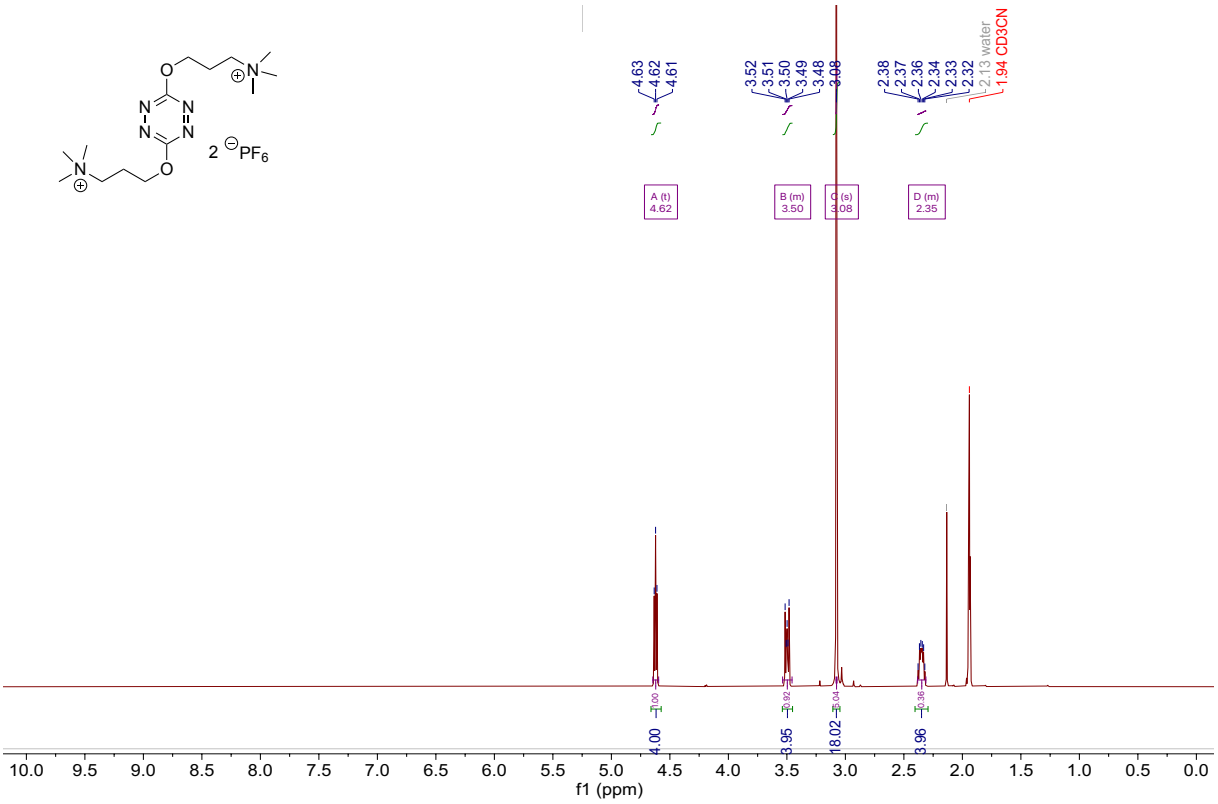
^{13}C NMR spectrum of **18** in CD_3CN



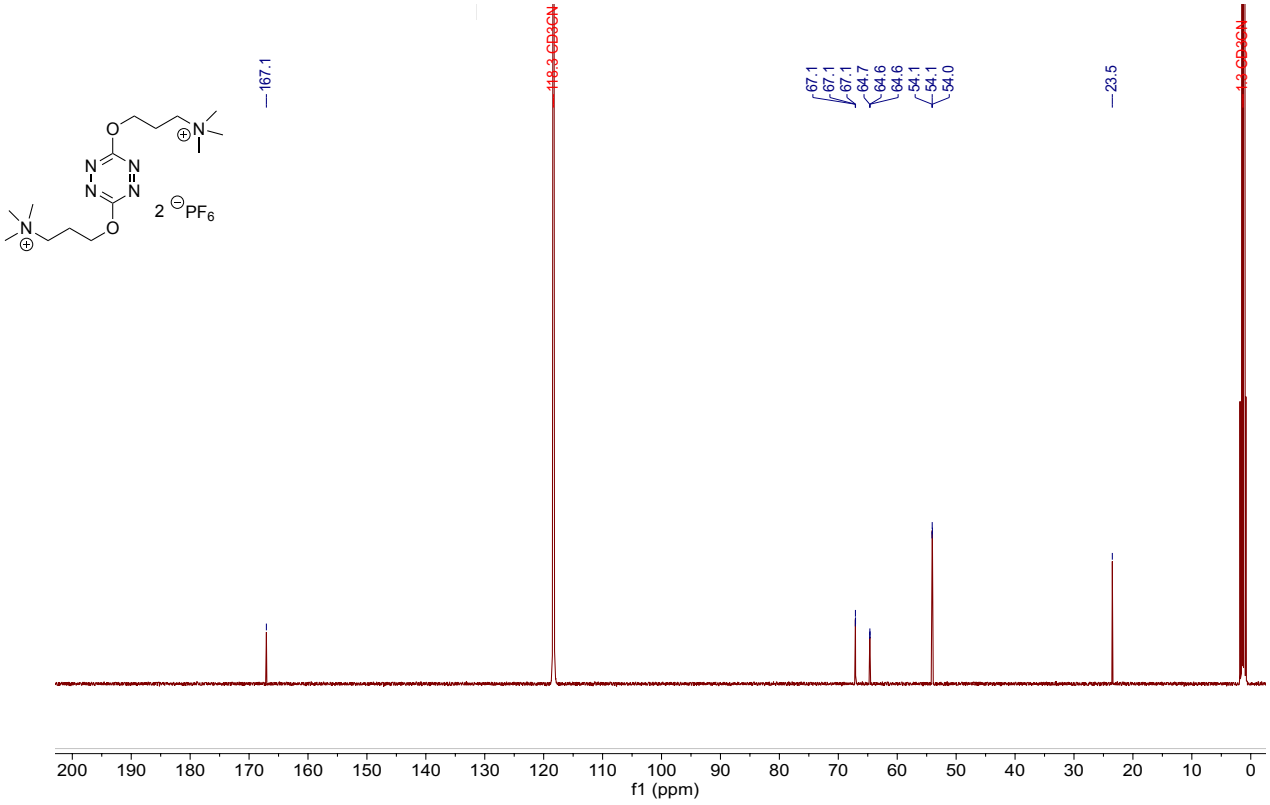
^{1}H NMR spectrum of **21** in CD_3CN



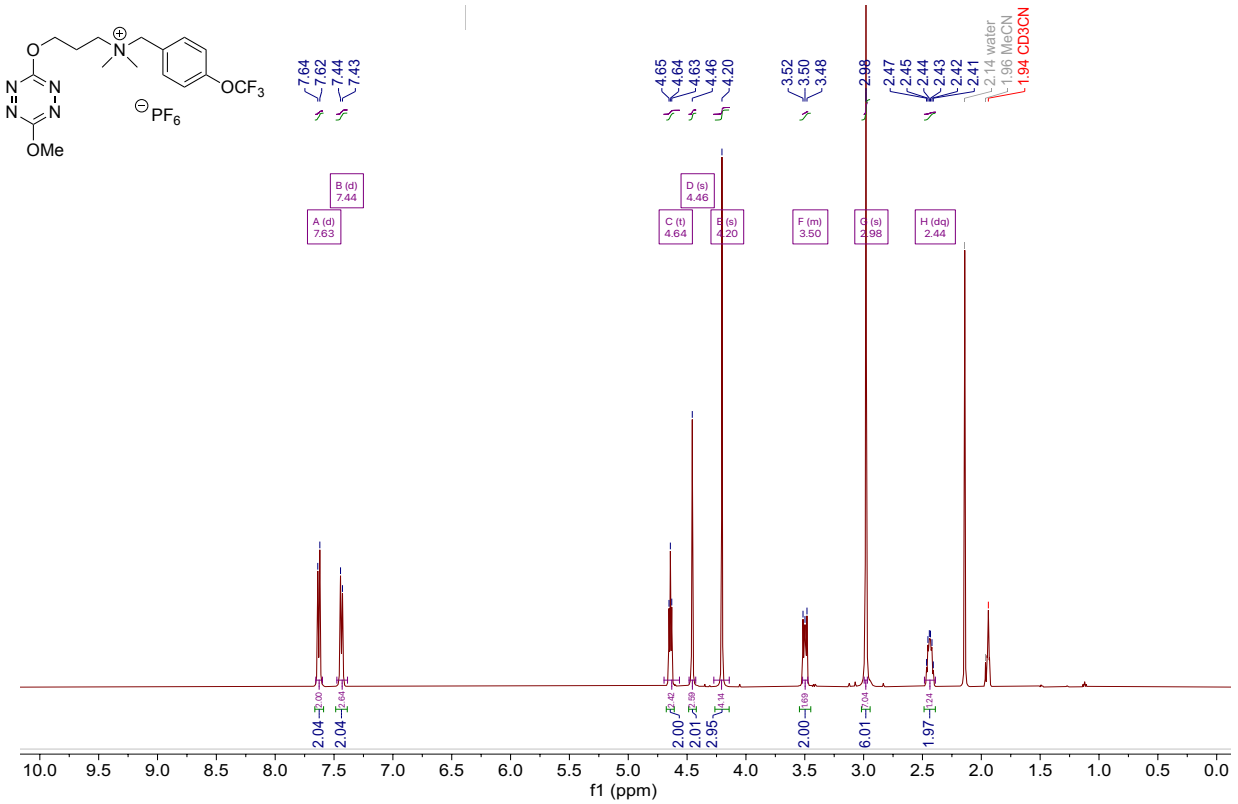
^{13}C NMR spectrum of **21** in CD_3CN



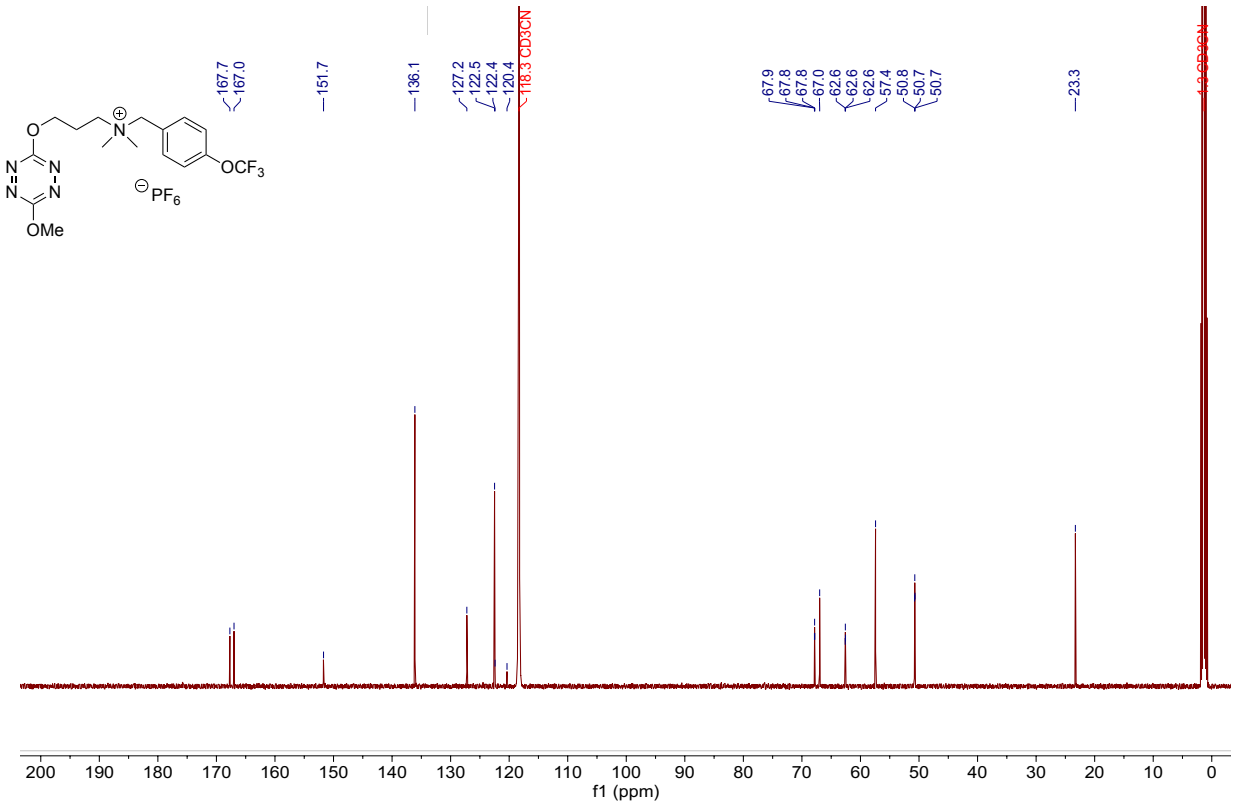
^{1}H NMR spectrum of **22** in CD_3CN



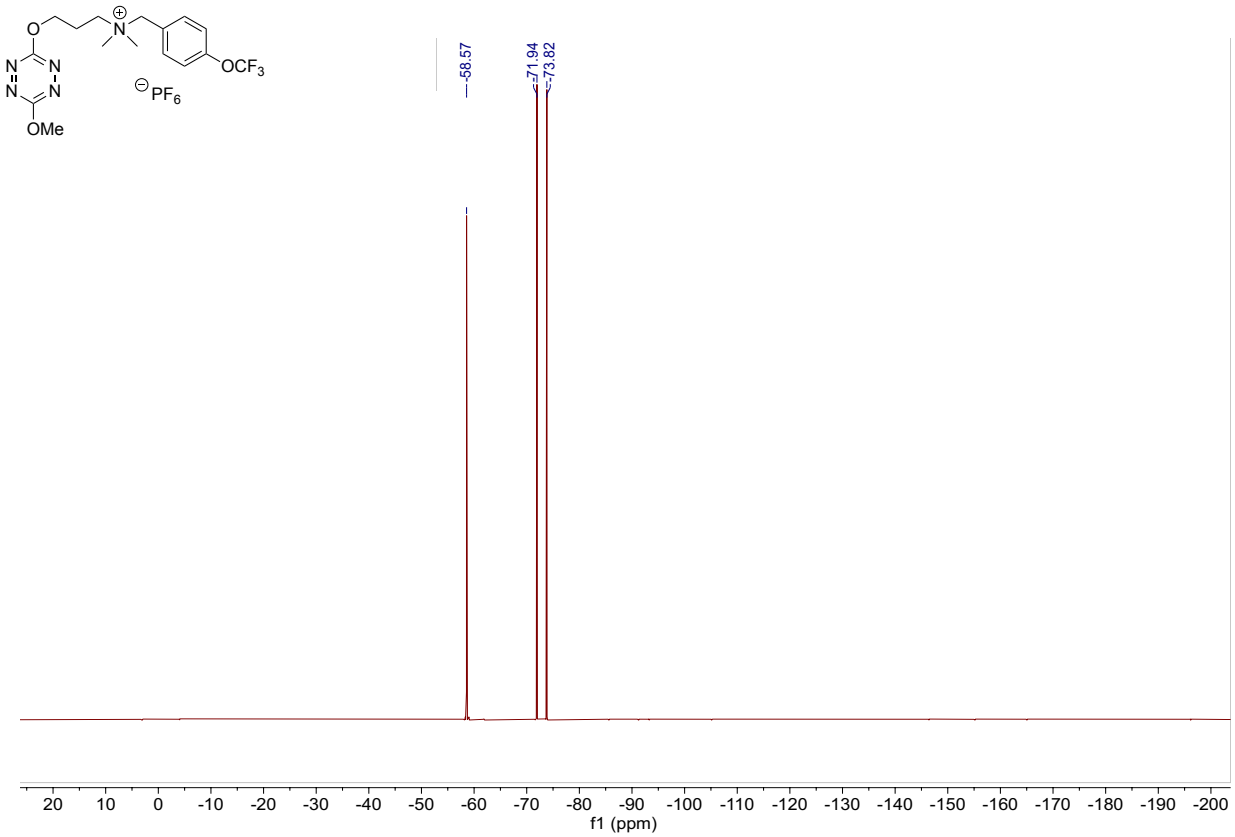
^{13}C NMR spectrum of **22** in CD_3CN



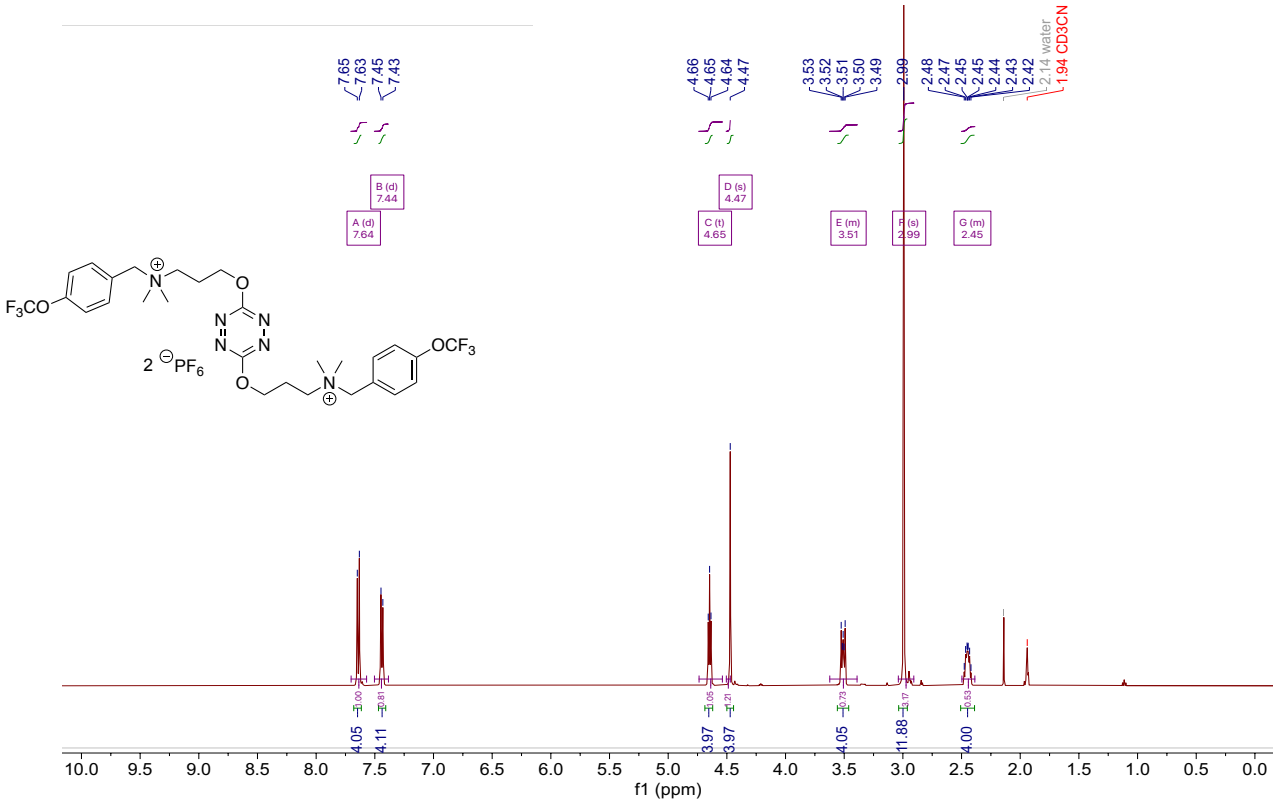
^{1}H NMR spectrum of **23** in CD_3CN



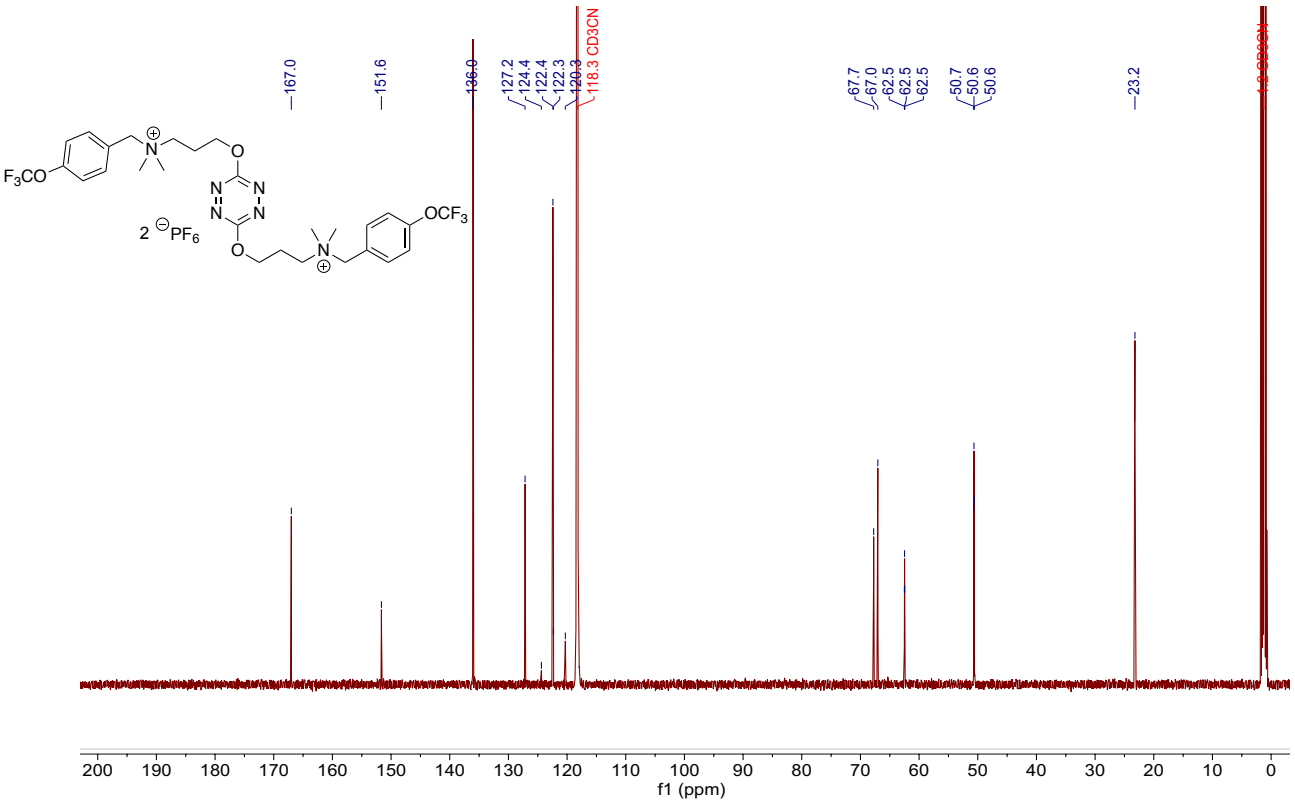
^{13}C NMR spectrum of **23** in CD_3CN



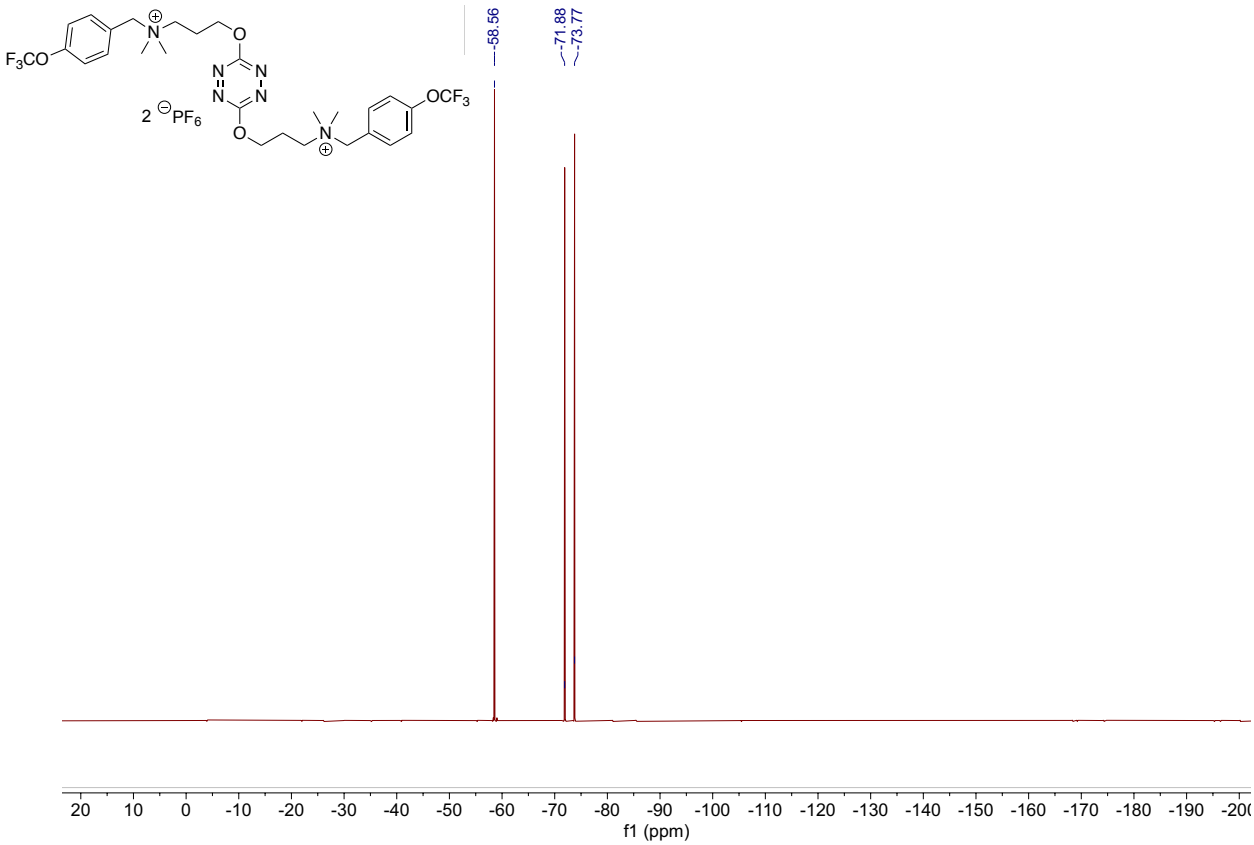
^{19}F NMR spectrum of **23** in CD_3CN



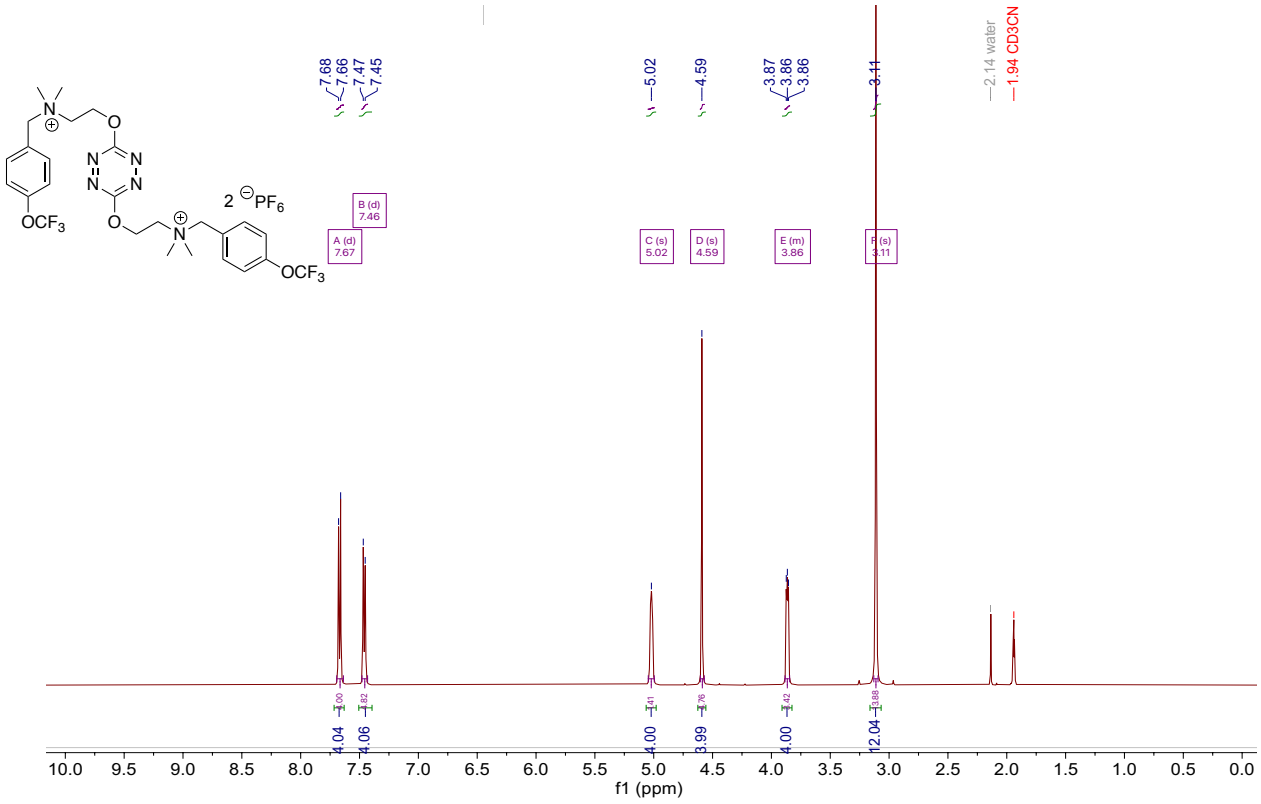
^{1}H NMR spectrum of **24** in CD_3CN



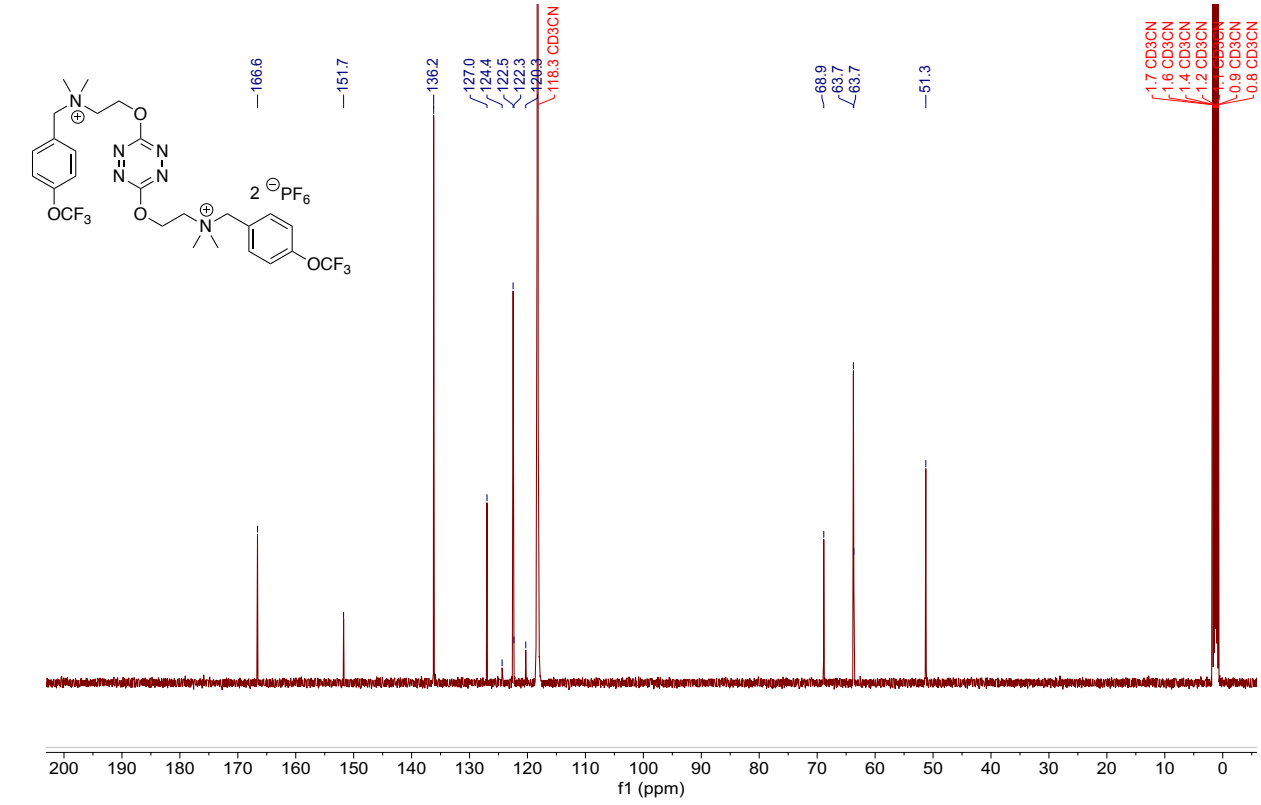
^{13}C NMR spectrum of **24** in CD_3CN



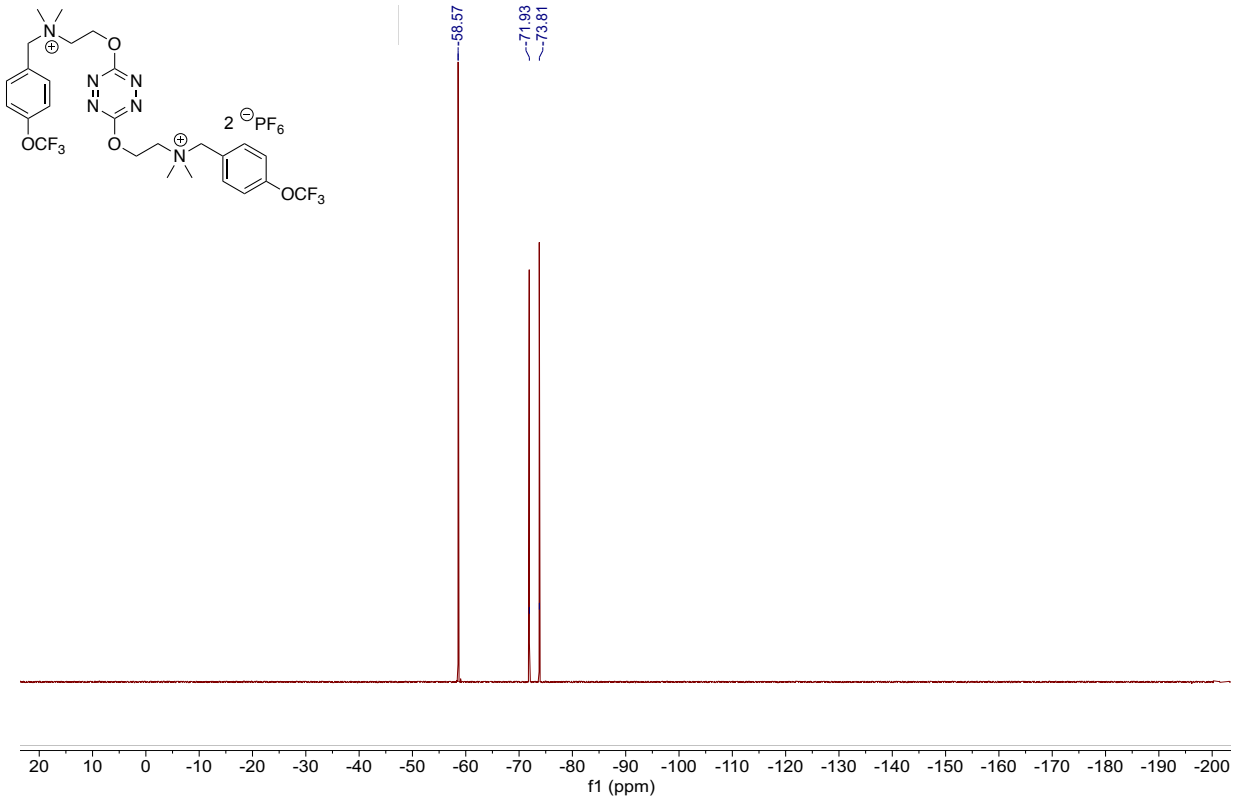
^{19}F NMR spectrum of **24** in CD_3CN



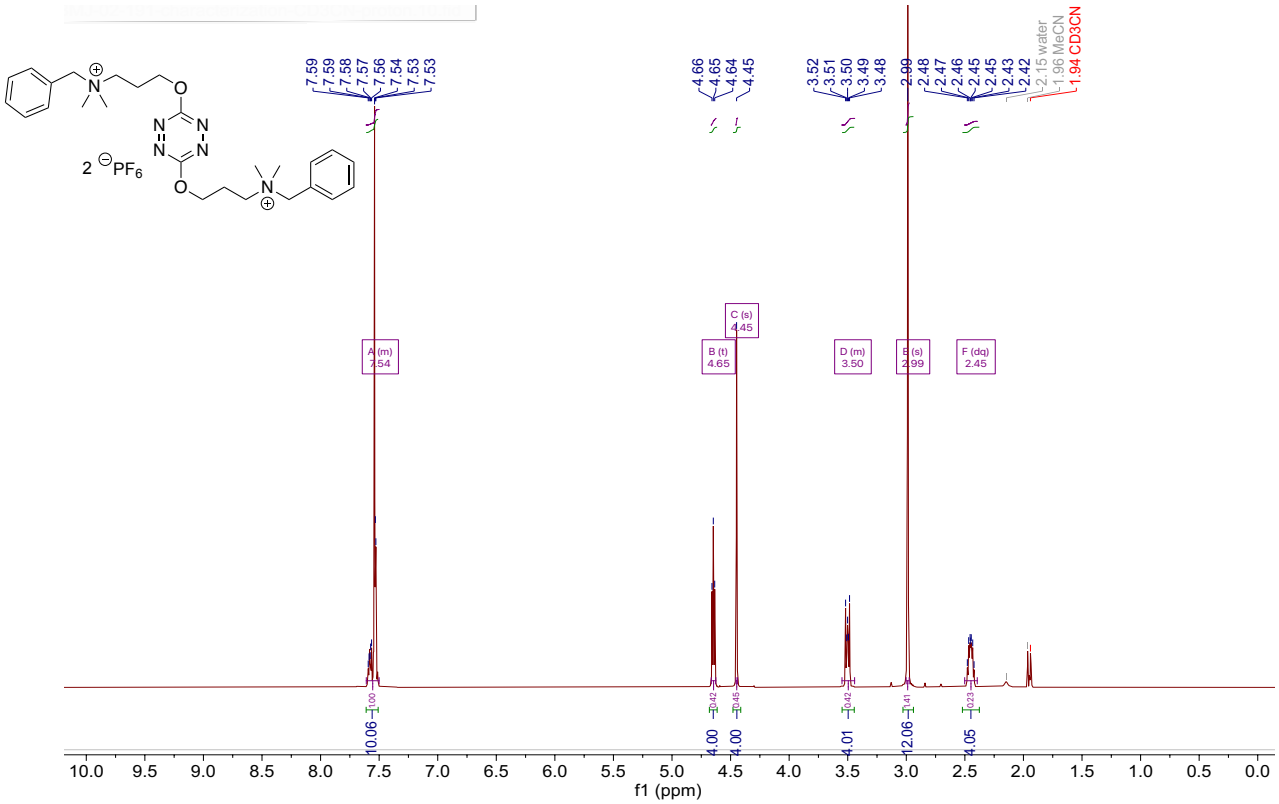
[1]HNMR spectrum of **25** in CD_3CN



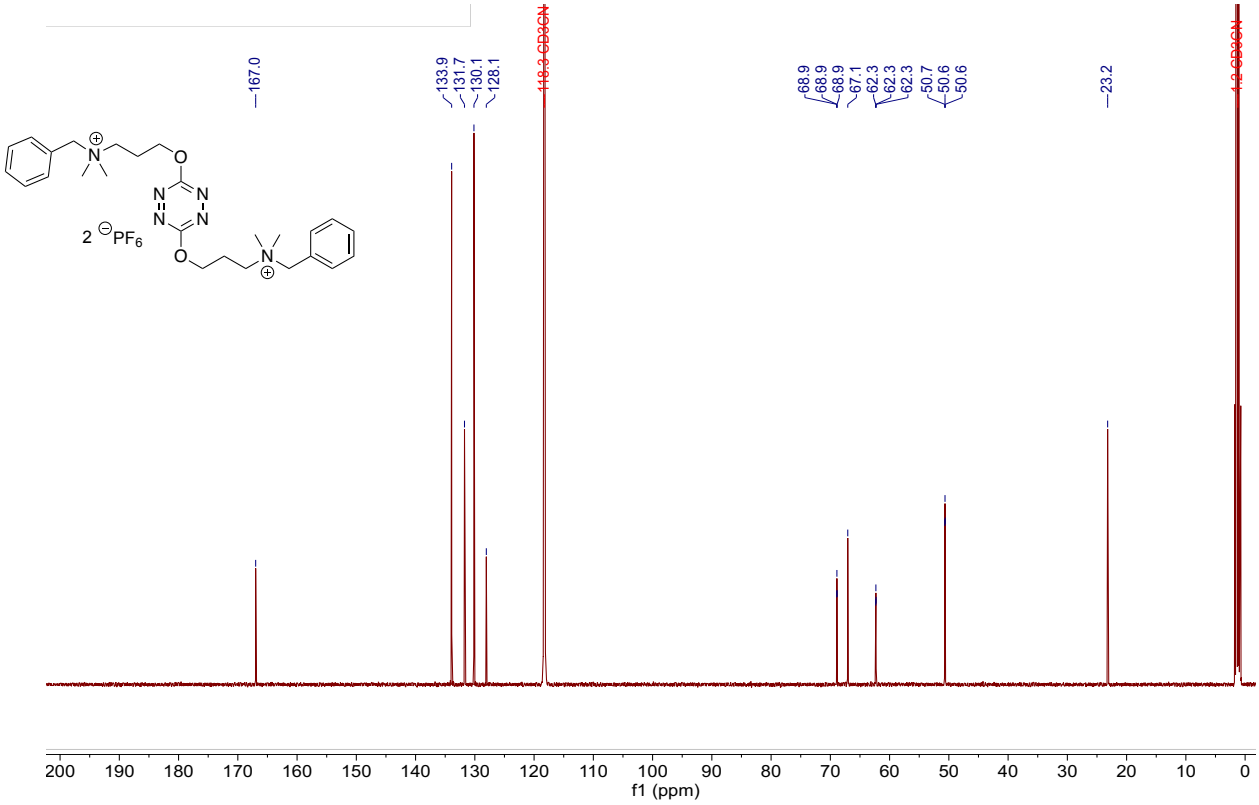
[13]CNMR spectrum of **25** in CD_3CN



^{19}F NMR spectrum of **25** in CD_3CN



^{1}H NMR spectrum of **26** in CD_3CN



^{13}C NMR spectrum of **26** in CD_3CN