

PhD Student Position: Precision Polymer Group (UW-Madison)

Led by Assistant Professor Dylan M. Barber

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Madison, Wisconsin, USA

About the Opportunity

The Precision Polymer Group is looking for a driven, ambitious PhD student excited to push the boundaries of polymer chemistry and soft-matter physics. We design and synthesize molecules that unlock properties conventional materials cannot reach. Then we characterize them to understand their fundamental physics and deploy them in real devices.

If you're energized by big questions about how molecular design shapes macroscopic function, this is the place to build new materials and do cutting-edge science.

What You'll Do

As a PhD student, you will:

- Lead original research in polymer synthesis (sequence-controlled polymers, novel architectures, polyelectrolytes) and polymer physics (dielectric spectroscopy, rheology, scattering, structure-property theory).
- Design and implement new synthetic routes to novel monomers and polymers.
- Characterize materials across multiple scales:
 - **Molecular structure:** multinuclear NMR, MS, MALDI-TOF, GPC, FTIR
 - **Thermal:** TGA, DSC
 - **Mechanical:** rheology, DMA
 - **Dielectric & transport:** broadband dielectric spectroscopy
 - **Nanoscale:** light, neutron, and x-ray scattering
- Collaborate across chemistry, physics, and engineering to translate polymers into technologies such as dielectric actuators, batteries, and bioelectronic devices.
- Contribute to the full research cycle: idea generation, experimentation, data analysis, manuscript preparation, assistance with proposal writing, presenting your work at conferences, and mentoring junior researchers.

Who We're Looking For

You will thrive here if you have:

- Strong training in synthetic organic chemistry, polymer chemistry, and/or polymer physics (air- and moisture-free techniques preferred).
- Independent drive, intellectual curiosity, and enthusiasm for ambitious, high-impact research.
- A record of research experience and clear, effective scientific communication.
- A desire to work across disciplines and think deeply about structure–property relationships.
- A willingness to tackle difficult problems, iterate quickly, and collaborate with a team from a broad range of technical backgrounds.
- Intellectual humility and the ability to update your mental models when presented with new data.

Qualifications

- B.S. or M.S. in Chemistry, Chemical Engineering, Materials Science, Polymer Science, or a related field.
- Prior experience in organic synthesis and/or polymer materials.
- Prior experience characterizing polymer dynamics by rheology or broadband dielectric spectroscopy.
- Interest in learning advanced characterization techniques.
- Readiness to join a full-time 4–6-year PhD program at UW–Madison.
- English proficiency suitable for independent research.

Why UW–Madison?

- A top-tier Materials Science & Engineering program with exceptional facilities and a strong polymer, synthesis, and soft matter research community.
- Opportunities to pursue high-impact problems in energy storage, dielectric materials, and molecular engineering.
- Close mentorship from a faculty member with expertise spanning synthesis, mesoscale assembly, high-throughput methods, and device translation.
- Freedom to build your research identity, publish in leading journals, and help shape next-generation polymer technologies.



**Department of Materials
Science & Engineering**
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How to Apply

Email the following materials (PDF preferred) to dmbarber@wisc.edu:

- Cover letter describing your research interests and motivation.
- Curriculum vitae, including any publications or presentations.
- Short research statement (1–2 pages) describing what next steps you would take to build on the research in the publication attached to the bottom of this document (DOI 10.1016/j.matt.2025.102049).
- Contact information for two or more references and a description of your relationship to each.

Start Date & Funding

Preferred start: Summer-Fall 2026, contingent on acceptance to UW–Materials Science and Engineering PhD program: deadline December 15th (<https://guide.wisc.edu/graduate/materials-science-engineering/materials-science-engineering-phd/#admissionstext>).

Includes competitive stipend, full tuition remission, health insurance, and research support.

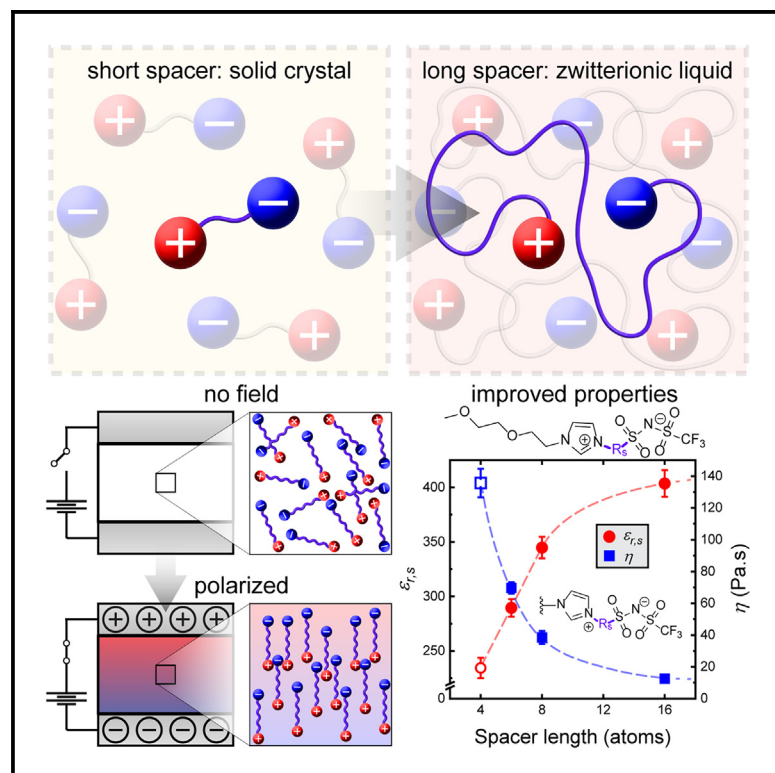
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Rational design and synthesis of zwitterionic liquid dielectrics

Graphical abstract



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In brief

Stable zwitterionic liquids offer routes to polarizable soft matter, but known zwitterions are limited by high melting points and viscosities. We demonstrate that long, flexible inter-charge spacers suppress crystallization in small-molecule zwitterions, decrease viscosity up to 500-fold compared to an established benchmark, and achieve dielectric constants up to, and even exceeding, 400. These high-permittivity liquids provide a roadmap to polarizable soft matter, unlocking opportunities for high-sensitivity and tissue-compatible bioelectronics, all-soft transistors, and high-conductivity battery electrolytes.

Highlights

- Entropy answers the decades-old problem of high melting points in zwitterions
- Our zwitterionic liquids are up to 500-fold less viscous than benchmark molecules
- They feature static dielectric constants up to 400



Understanding

Dependency and conditional studies on material behavior

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Article

Rational design and synthesis of zwitterionic liquid dielectrics

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PROGRESS AND POTENTIAL Next-generation soft electronics, robotics, and bioelectronics demand materials that combine high dielectric permittivity with mechanical softness. Zwitterionic liquids offer a potential solution by endowing extraordinary dipole moments with the freedom to bias in an electric field. Yet, the vast majority of zwitterions either melt above 150°C or are prohibitively viscous. In this work, we outline a strategy that increases the entropy of fusion to suppress the melting point in imidazolium-derived zwitterions, affording zwitterionic liquids. The resulting liquids are up to 500-fold less viscous than an established benchmark and feature dielectric constants up to, or even exceeding, 400 at room temperature, the largest reported to date for organic molecules. Downstream applications include soft, high-gain field-effect transistors, bioelectronic sensors, and high-conductivity liquid- or gel-state electrolytes for next-generation batteries.

SUMMARY

Zwitterions (ZIs) are emerging candidates for soft dielectrics but are limited by high melting points (T_m), glass transition temperatures (T_g), and viscosities (η) dramatically exceeding those of ionic liquids. To overcome these limitations, we synthesized 18 imidazolium-derived zwitterions with systematically varied composition at the (1) imidazolium tail (R_1), (2) imidazolium 2 position (R_2), (3) inter-charge spacer (R_s), and (4) anion (R_a). We found that long, flexible spacers yield stable zwitterionic liquids (ZILs), which we attribute to amplified entropy of fusion. Remarkably, stable ZILs with an elongated (6–16 atom length) inter-charge spacer, flexible tail, and a CF_3 -sulfonimide anion are 100- to 500-fold less viscous at room temperature than a benchmark supercooled ZI with a 4-atom spacer and a sulfonate anion. Moreover, these previously unreported ZILs exhibit high permittivities ranging from $\epsilon_{r,s} = 290$ (6-atom spacers) to $\epsilon_{r,s} = 404$ (16-atom spacers), highlighting the promise of this class of polarizable soft matter.

INTRODUCTION

Soft functional materials are under development with potential applications spanning ion conduction,^{1–5} ionoelastomer logic elements,⁶ low-voltage electroadhesion,⁷ wearable and implantable devices,^{8–13} actuators,^{14–22} and grippers.^{23,24} Among these, soft dielectrics that exhibit strong polarization in an applied electric field, play a crucial role.^{8,13,22,24–26} While their property requirements vary by application, they are unified by the need for mechanical compliance and high dielectric properties. Presently, few materials offer both high compliance and polarizability, necessitating compromises in device design. For example, implantable bioelectronic sensors are often mechanically mismatched with the surrounding tissue,^{10–12} while the low static dielectric constant ($\epsilon_{r,s} \sim 2$ –10) of most elastomers limits their practical utility.^{14–21}

Embedding permanent dipoles in a soft medium enables both mechanical compliance and high permittivity. Both polar small molecules and tethered dipoles exhibit bulk polarization in an electric field.²⁷ Below their polarization volume overlap, static dielectric permittivity scales as $\epsilon_{r,s} \sim \rho_d \mu^2$, where ρ_d is the number density of dipoles, and μ is dipole moment.^{28–31} At higher concentrations, $\epsilon_{r,s}$ undershoots this prediction yet still increases with μ .³⁰ Hence, μ represents the most effective route to achieve high permittivity in a dipolar system. This has been demonstrated using sulfonyl,³² nitrile,³³ and amide³⁴ groups ($\mu \sim 3.7$ –4.5 Debye).^{35–38} Even stronger dipoles have been reported recently by Mei et al., who prepared liquid, solvated, and supercooled zwitterions (ZIs) with dipole moments above 50 Debye and $\epsilon_{r,s}$ up to 350, offering the first proof of concept of high permittivity in such materials.^{30,31,39} ZIs, which consist of oppositely charged ions separated by a covalent spacer, exhibit superlative

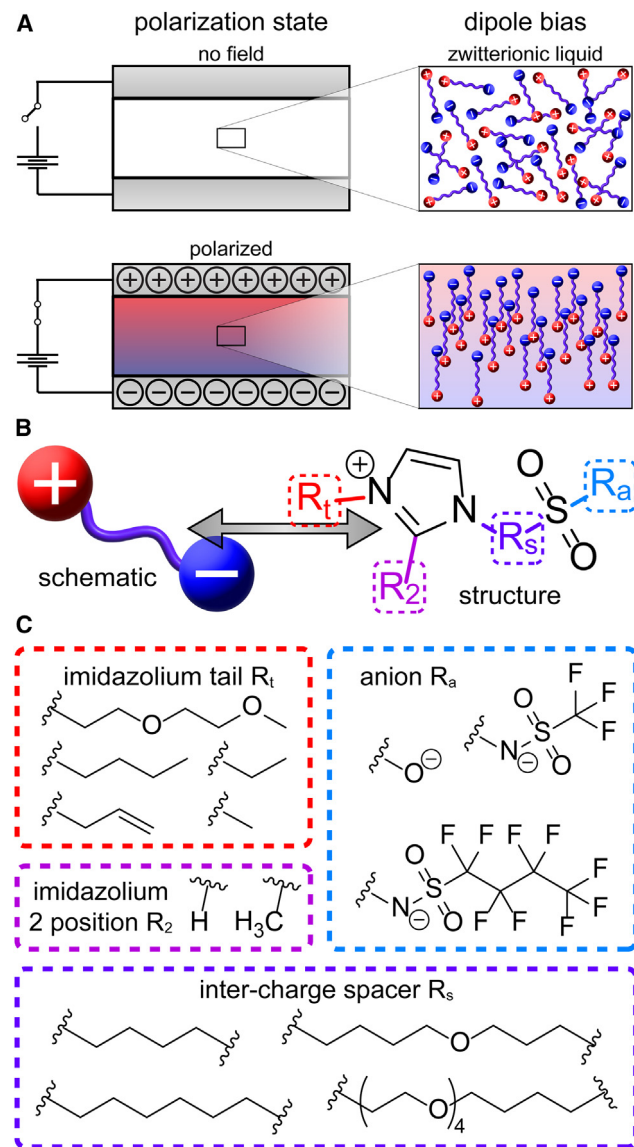


Figure 1. Soft polarizable materials composed of ZILs

(A) Schematic of a bulk material (left) composed of a ZIL (inset, right) in the absence (top) or presence (bottom) of an applied electric field.
(B) Schematics representing imidazolium sulfonyl ZILs synthesized to explore effects of R_1 , 2-position R_2 , inter-charge spacer (R_s), and anion R_a on thermal phase behavior, viscosity, and dielectric properties.
(C) Molecular structures of R_1 , R_2 , R_s , and R_a used to synthesize 18 ZILs.

dipole moments for two reasons. First, each pole carries a full charge (cation and anion), enabling a larger polarization amplitude compared to electronegativity- and delocalization-mediated dipoles. Second, they can be prepared with inter-charge spacers of arbitrary length to enable longer dipoles and, thus, higher μ .

Despite these promising attributes, most ZILs suffer from key limitations. First, they possess high melting points (T_m), with the vast majority melting above 150°C.⁴⁰ This poses a challenge, as arrested phases (i.e., crystal and glass) are stiff under ambient

conditions, undermining their mechanical compliance. These arrested states also inhibit field-mediated dipole bias and bulk polarization and, hence, do not result in high permittivity. Second, zwitterionic liquids (ZILs) reported to date are extremely viscous. For example, Yoshizawa-Fujita et al. reported a supercooled imidazolium sulfonate with a viscosity that was too high to measure under ambient conditions.⁴¹ Others acknowledged, without quantifying, the exceptional viscosity of their imidazolium carboxylate ZILs⁴² or reported a viscosity of 1.5 Pa s at 70°C,⁴³ limiting practical use at room temperature.

Here, we report the rational design and synthesis of ZILs (Figures 1, 2, and 3) that exhibit excellent stability, low viscosity, and high permittivity under ambient conditions. Specifically, we create a library of 18 small-molecule ZILs (structures are shown in Figure 2, and synthesis pathways are shown in Figure 3) that include three previously reported ZILs (control molecules 1–3) and another 15 as-yet unreported ZILs (molecules 4–18). Next, their melting behavior, shear rate-dependent viscosity, and frequency-dependent dielectric behavior are characterized to reveal the distinct contributions of the (1) imidazolium tail (R_1), (2) imidazolium 2 position (R_2), (3) inter-charge spacer (R_s), and (4) anion (R_a) (Figure 1B) to determine compositional effects (Figure 1C) on these properties. First, the effects of each moiety on the enthalpy (ΔH_m) and entropy (ΔS_m) of fusion are quantified to understand their melting behavior. Next, by strategically employing functional groups designed to increase the entropy of fusion, including long, flexible spacers, six ZILs (molecules 13–18) are synthesized that reside in the liquid state under ambient conditions. By replacing the sulfonate anion with sulfonimide, increasing R_s length, and using a long, ether-rich tail, these ZILs exhibit a 500-fold reduction in apparent viscosity ($\eta = 13$ Pa s) at room temperature compared to a supercooled ZIL 3 ($\eta = 6490$ Pa s), which has been reported previously.^{30,31,39} Last, we show that these ZILs exhibit static dielectric constants ranging from $\epsilon_{r,s} = 290$ for a 6-atom (ZIL 13) to 404 for a 16-atom (ZIL 18) R_s , approaching a 2-fold higher value than benchmark ZIL 3. Given their stability in the liquid state, low viscosity, and high permittivity under ambient conditions, these ZILs offer a route to polarizable soft matter for applications ranging from soft electronics to liquid electrolytes.

RESULTS

ZI synthesis

To create this zwitterionic library, we first prepare multi-gram quantities of the sulfonimide anion^{5,31,44–47} with a functional handle to enable ZI synthesis. We achieve this goal by building around our target 4-, 6-, 8-, and 16-atom spacers. Specifically, we design and synthesize intermediate molecules **A**, **D**, **G**, and **J** (Figure 3), which all consist of a spacer terminated at one end by a strongly electrophilic sulfonyl chloride and at the other by a modestly electrophilic primary chloroalkane. These groups are advantageous because they can be installed simultaneously in a single step, shortening the pathway to the zwitterionic targets. Next, these α -chloro- ω -sulfonyl chlorides are combined with a CF_3 - or C_4F_9 -sulfonamide in the presence of a weak base (K_2CO_3) to generate the sulfonimide potassium salt (intermediates **B**, **E**, **H**, and **K**). Finally, the primary chloroalkyl groups are reacted with functional imidazoles to yield ZILs 4–18. Their purity is confirmed

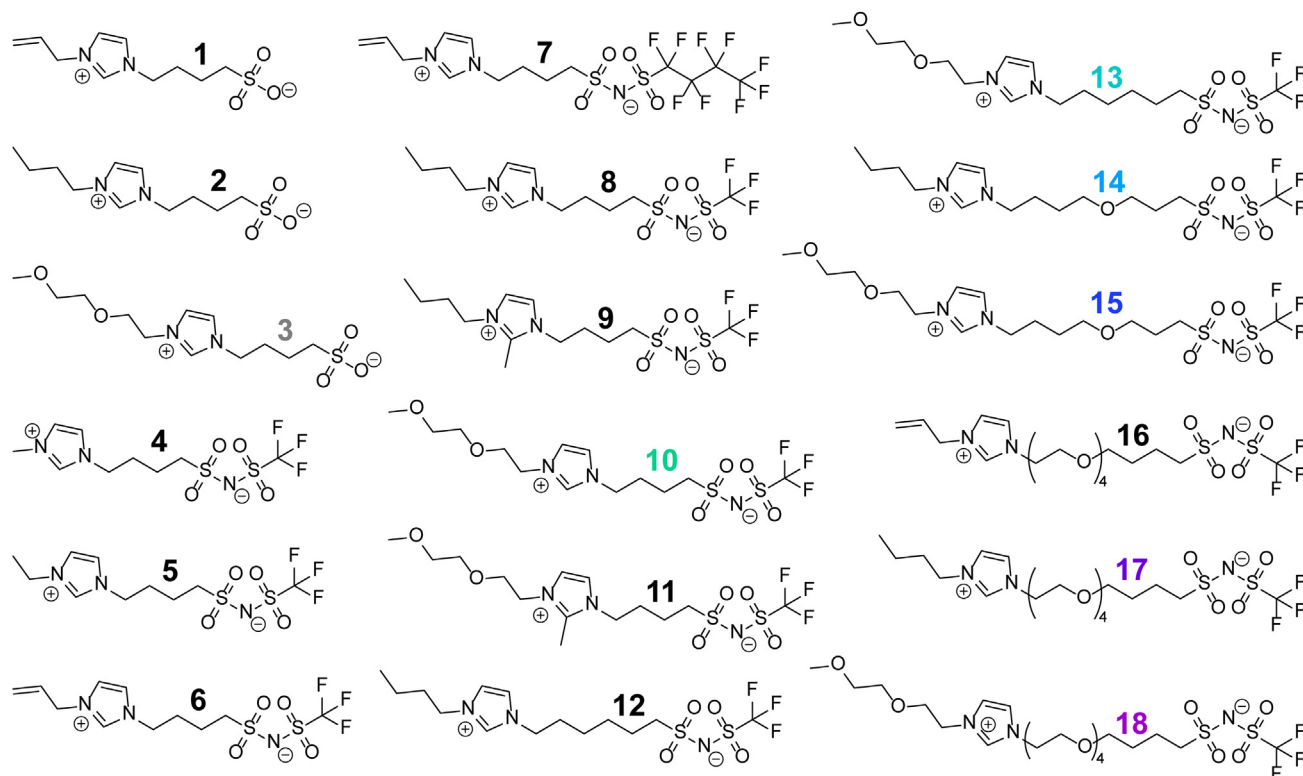


Figure 2. ZI library

ZIs 1–3 have been reported previously, while 4–18 have not.

by ^1H , ^{13}C , and ^{19}F NMR and by high-resolution mass spectrometry (see [supplemental information](#) or download our source data).

While the route from α -chloro- ω -sulfonyl chlorides to target ZIs is straightforward, the pathway to these intermediates varies by spacer length and composition. Of these, intermediate **A** (4-carbon spacer) is the most scalable. It is prepared by refluxing 1,4-butanedisulfone in neat thionyl chloride, which ring opens the sulfone and chlorinates both the sulfonyl and alkyl termini in a single step. For longer spacers (6–16 atoms), the α -chloro- ω -sulfonyl chloride is prepared in two steps. First, α -hydroxy- ω -sulfonates are created by reacting 6-chlorohexanol with sodium sulfite (6-atom-spacer intermediate **D**), ring-opening 1,3-butanedisulfone with excess 1,4-butanediol in the presence of tert-butoxide (8-atom-spacer intermediate **G**), and ring-opening 1,4-butanedisulfone with excess tetraethylene glycol in the presence of hydroxide (16-atom-spacer intermediate **J**). Asymmetric syntheses (diol and sulfone in the presence of base) required careful column chromatography to separate the mono-functional target from inevitable difunctional side products and excess starting diol ([methods](#)). The α -hydroxy- ω -sulfonates are then converted into α -chloro- ω -sulfonyl chlorides by refluxing in excess thionyl chloride in the presence of catalytic dimethylformamide.

ZI phase behavior

ZIs melt at higher temperatures than untethered salts composed of the same ion pair.^{5,31,40,47,48} We hypothesize that this arises

from an entropic penalty incurred by the zwitterionic linker R_s (Figures 4A–4C). To examine this hypothesis, we first consider the thermodynamics of melting in conventional ionic liquids.^{46,49–55} Consider sodium chloride (NaCl), which melts at 800°C,^{46,56} and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BT), which melts at –3°C (Figures 4D and 4E).^{46,57} This extraordinary difference in T_m is driven almost exclusively by the entropy of fusion ($\Delta S_m(\text{BT}) = 3.4 \times \Delta S_m(\text{NaCl})$) combined with a small contribution from the enthalpy of fusion ($\Delta H_m(\text{BT}) = 0.85 \times \Delta H_m(\text{NaCl})$) (Figure 4F). To understand how this changes in the presence of a zwitterionic tether, we synthesize ZI **8**, which serves as a zwitterionic analog to BT (Figure 4D) with a 4-carbon spacer. ZI **8** melts at 73°C, which is far higher than BT. This difference is driven exclusively by a decrease in ΔS_m from 88.0 to 69.2 J mol^{–1} K^{–1} upon installing the inter-charge tether (Figures 4E and 4F). Next, ZI **12**, which features a 6-carbon spacer, is synthesized to interrogate the impact of spacer length on ΔH_m and ΔS_m . Interestingly, T_m increases to 103°C because, although ΔS_m increases to 89.8 J mol^{–1} K^{–1}, ΔH_m increases by a larger margin to 33.8 kJ mol^{–1}. Hence, although a longer spacer increases entropy of fusion, it only serves the goal of T_m suppression if a simultaneous increase in ΔH_m can be avoided. We therefore hypothesize that greater spacer flexibility might more selectively increase ΔS_m . We further note that polyethers, such as poly(ethylene oxide) (PEO), have shorter Kuhn lengths ($b_{\text{PEO}} = 1.1$ nm) than straight-chain alkanes, such as polyethylene (PE, $b_{\text{PE}} = 1.4$ nm), suggesting greater chain

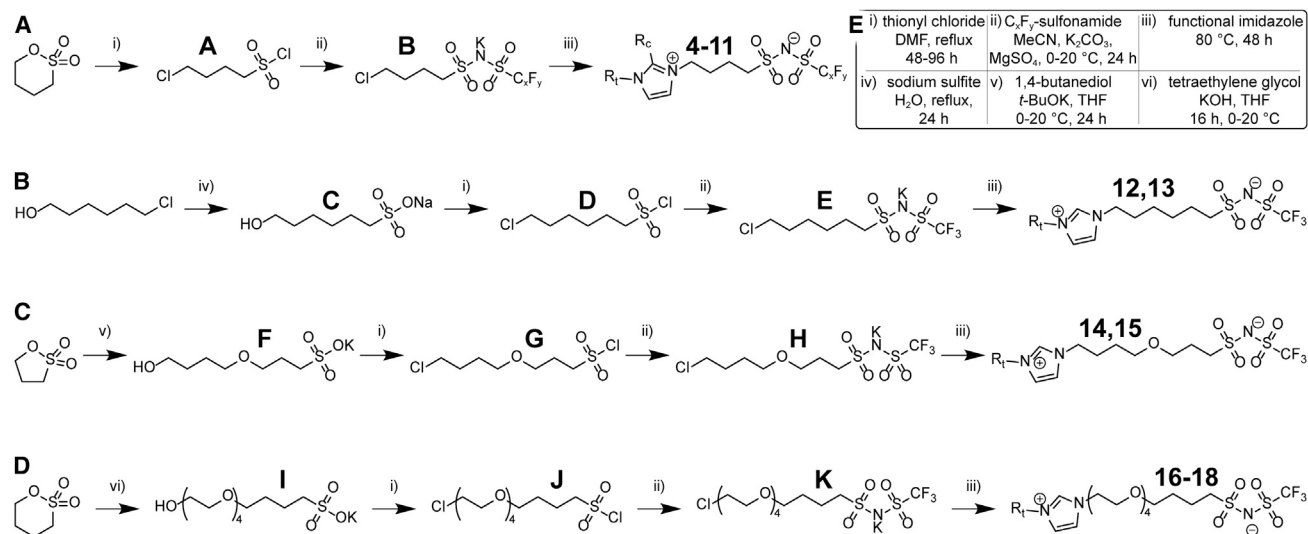


Figure 3. The synthetic pathway depends on spacer length

(A) The 4-atom spacer is synthesized by directly ring-opening 1,4-butanedisulfone in refluxing thionyl chloride to produce **A**.

(B) The 6-atom spacer is synthesized by reacting 6-chlorohexanol with sodium sulfite in aqueous solution to yield **C** and then chlorinated in refluxing thionyl chloride to produce **D**.

(C) The 8-atom spacer is synthesized by ring-opening 1,3-propanedisulfone with 1,4-butanediol in the presence of *tert*-butoxide, isolating **F**, then refluxing in thionyl chloride to yield **G**.

(D) The 16-atom spacer is synthesized by ring-opening 1,4-butanedisulfone with tetraethylene glycol in the presence of hydroxide, isolating **I**, then refluxing in thionyl chloride to yield **J**.

In all cases, the sulfonate intermediate is reacted with triflamide in the presence of K₂CO₃ to yield sulfonimides **B**, **E**, **H**, and **K** and then reacted with R_t-imidazole to generate ZILs **4-18**.

flexibility.⁵⁸ To enhance chain length and flexibility, we prepared ZIL **14** and ZIL **17**, which are composed of 8- and 16-atom spacers with 1 and 4 ether groups, respectively. Both are isolated as liquids at room temperature and remain stable under prolonged storage (>6 months at 22 °C in a vacuum desiccator), suggesting good stability under ambient temperatures.

R_t is dominated by enthalpic contributions for tail lengths of 1–4 carbon atoms and by entropy for a longer, 7-atom tail, as determined by ZILs **4**, **5**, **6**, **8**, and **10** (Figure S1A). ZIL **4**, with a methyl tail, is the highest-melting of the five, with $T_m = 150^\circ\text{C}$ (Figure S1B), arising from a large $\Delta H_m = 43.3 \text{ kJ mol}^{-1}$ and $\Delta S_m = 102 \text{ J mol}^{-1} \text{ K}^{-1}$ (Figure S1C). Replacing the methyl tail with ethyl yields ZIL **5**, whose lower T_m (126 °C; Figure S1B) arises from a decrease in ΔH_m to 27.7 kJ mol^{−1} (Figure S1C). Incorporating an allyl tail produces ZIL **6**, the lowest-melting species ($T_m = 57^\circ\text{C}$) of this set of five, driven by a drop in ΔH_m to 18.5 J mol^{−1} K^{−1}. Incorporating a butyl tail leads to ZIL **8**, which melts at 73 °C (Figure S1B) with $\Delta H_m = 23.9 \text{ kJ mol}^{-1}$ (Figure S1C). Finally, using a 2-(2-methoxyethoxy)ethyl (MEE) tail leads to ZIL **10**, with $T_m = 69^\circ\text{C}$ (Figure S1B), accompanied by a striking increase in both ΔH_m (to 41.9 kJ mol^{−1}) and ΔS_m (to 122 J mol^{−1} K^{−1}). Next, the effects of the 2-position R₂ are elucidated by replacing the 2-proton in ZILs **8** and **10** with methyl groups to yield ZILs **9** and **11** (Figure S2A). This change primarily impacts ΔS_m . Compared to **8** ($T_m = 73^\circ\text{C}$; Figure S2B), 2-methylated ZIL **9** melts at 132 °C, driven by a drop in ΔS_m from 69.2 to 45.1 J mol^{−1} K^{−1} and attenuated by a drop in ΔH_m from 23.9 to 18.2 kJ mol^{−1} (Figure S2C). A similar result is observed when comparing 2-H ZIL **10** to 2-Me ZIL **11**;

2-methyl substitution decreases ΔH_m from 41.9 to 28.6 kJ mol^{−1} and ΔS_m from 122 to 82.4 J mol^{−1} K^{−1} (Figure S2C) to raise T_m from 69 °C to 74 °C. Finally, we characterize R_a across three anions (Figure S3), including sulfonate (ZIL **1**, R_a = O, $T_m = 112^\circ\text{C}$), CF₃-sulfonimide (ZIL **6**, R_a = NTf, $T_m = 57^\circ\text{C}$), and C₄F₉-sulfonimide (ZIL **7**, R_a = NNf, $T_m = 114^\circ\text{C}$). The dramatic decrease of 55 °C–57 °C in T_m (**6**) compared to **1** and **7** is driven by a relatively lower ΔH_m (by ~9 kJ mol^{−1}) and attenuated by a decrease in ΔS_m (by ~15 J mol^{−1} K^{−1}). T_g , T_m , ΔH_m , and ΔS_m for all 18 ZILs are provided in Figure S4, while triplicate differential scanning calorimetry (DSC) traces are shown in the supplemental information.

Rheological properties

Shear-rate-dependent viscosity is measured for seven ZILs, including five of our six stable ZILs (**13**, **14**, **15**, **17**, and **18**) and two crystalline ZILs (**3** and **10**) that are first melted and super-cooled prior to each measurement. ZIL **3** serves as a control, as it is one of the most frequently reported ZILs.^{30,31,39} Each ZIL exhibits a low-shear plateau viscosity η at shear rates, $\dot{\gamma}$, below 10¹ s^{−1}, followed by a shear-thinning response at higher shear rates (Figure 5A). This effect is most pronounced for ZILs with higher viscosity, especially the ZIL **3** control. Their η at $\dot{\gamma} = 1 \text{ s}^{-1}$ is shown as a function of spacer length in Figure 5B, which reveals a more than 10-fold viscosity decrease as spacer length increases from four (ZIL **10**) to 16 (ZIL **18**) atoms. Figure 5B also highlights the roles of tail R_t and anion R_a. For example, liquids **14** ($\eta = 98 \text{ Pa s}$) and **17** ($\eta = 25 \text{ Pa s}$) feature a butyl tail with 8- and 16-atom spacers, respectively. ZILs **15** ($\eta = 38 \text{ Pa s}$) and

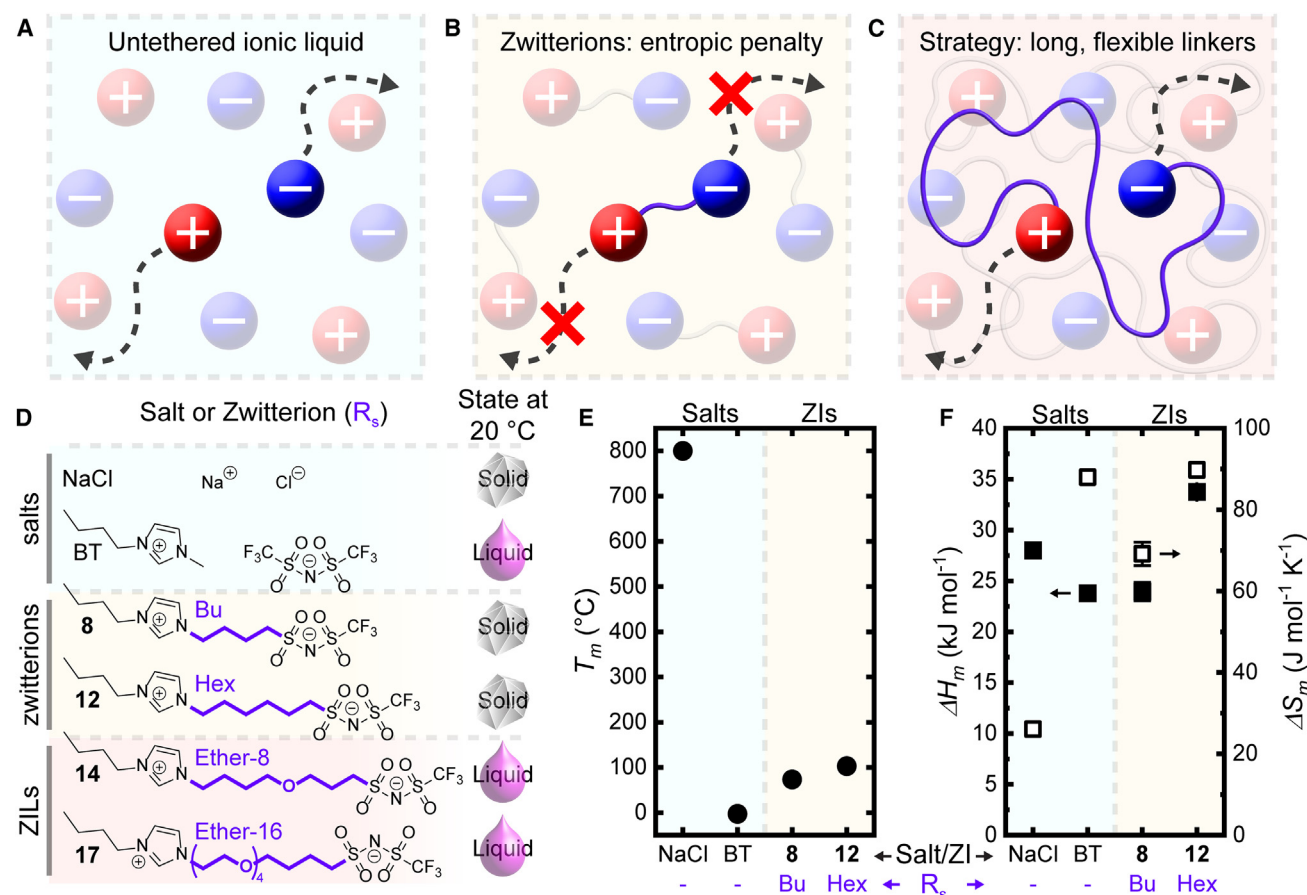


Figure 4. Zwitterionic spacer R_s governs melting behavior

(A) Schematic of a conventional ionic liquid in which dissociated ions can diffuse independently.

(B) Schematic of a ZIL in which individual ions are unable to diffuse independently, incurring an entropic penalty.

(C) We employ long, flexible R_s to depress T_m .

(D) Comparison of salts NaCl and BT with ZILs **8** and **12** and ZILs **14** and **17**.

(E and F) T_m (E) and enthalpy (ΔH_m) and entropy (ΔS_m) of fusion (F) of NaCl, BT, **8** and **12**. Data for NaCl and BT were taken from previous studies.^{45,55,56} Data for **8** and **12** are represented as mean \pm SD; $n = 3$.

18 ($\eta = 13$ Pa s) are identical to **14** and **17** but feature MEE tails, which decrease liquid viscosity by 2.5-fold (**15** versus **14**) or 2-fold (**18** versus **17**). The effect of R_a is even more pronounced. Supercooled benchmark **3** ($\eta = 6490$ Pa s) contains a sulfonate anion and is 48-fold more viscous than supercooled **10** ($\eta = 136$ Pa s), whose only difference is a CF_3 -sulfonimide anion.

Dielectric spectroscopy

Dielectric relaxation spectroscopy measurements are conducted on the same set of seven ZILs and on silicone oil, an additional control, to understand how R_s , R_t , and R_a impact dielectric properties. The real (ϵ' ; Figure 6A) and imaginary (ϵ'' ; Figure 6B) parts of the unitless complex permittivity are measured as a function of angular frequency $\omega = 2\pi\nu$ rad s^{-1} , where dielectric frequency $\nu = 20$ Hz to 2 MHz. In this range, all seven ZILs exhibit a fast relaxation event that is attributed to electric field-mediated dipole bias, yielding the static dielectric constant $\epsilon_{r,s}$ as a plateau in ϵ' and the dielectric relaxation timescale τ_{dr} at the local maximum in ϵ'' .^{30,39}

At longer timescales, a larger polarization event is observed in ϵ' due to macroscopic electrode charging, and the onset of direct current conductivity is observed in ϵ'' . The corresponding real (σ' ; Figure S5A) and imaginary (σ'' ; Figure S5B) parts of conductivity are given by $\sigma^* = i\omega\epsilon_0\epsilon^*$ and are discussed alongside the dielectric loss tangent ($\tan\delta$; Figure S5C) in the supplemental information.⁵⁹

The incorporation of longer spacers R_s leads to a monotonic increase in the polarization magnitude ($\epsilon_{r,s}$; Figure 6C) and decrease in characteristic relaxation times τ_{dr} . For example, the MEE series of ZI **10**, ZIL **13**, ZIL **15**, and ZIL **18** possesses static dielectric constants of 234, 290, 345, and 404 and relaxation timescales of 10, 10, 4, and 2.5 μs , respectively. The R_t has a modest influence on relaxation timescales τ_{dr} , with a ~ 2.5 -fold decrease upon replacing a butyl tail ($\tau_{dr}(\mathbf{14}) = 10$ μs and $\tau_{dr}(\mathbf{17}) = 6.3$ μs) with MEE ($\tau_{dr}(\mathbf{15}) = 4$ μs and $\tau_{dr}(\mathbf{18}) = 2.5$ μs), consistent with the apparent viscosity data for the same ZILs. Next, we characterize the effect of R_a by comparing ZILs **3**

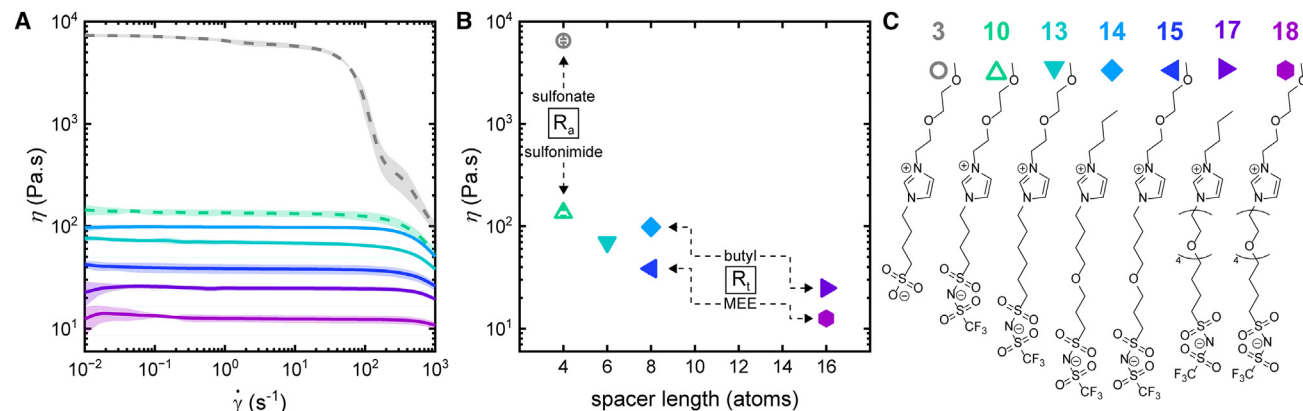


Figure 5. Apparent viscosity of ZILs

(A) Log-log plot of apparent viscosity as a function of shear rate.

(B and C) Semi-log plot (B) of apparent viscosity at a shear rate of 1 s⁻¹ as a function of spacer length for (C) supercooled ZIs 3 and 10 and zwitterionic liquids (ZILs) 13-15, 17, and 18.

Dashed lines and open data points denote supercooled liquids; solid lines and filled points denote ZILs. Data are shown as mean \pm SD; $n = 3$.

(R_a = sulfonate) and 10 (R_a = CF₃-sulfonimide). Consistent with the 48-fold difference in viscosity, $\tau_{dr}(3) = 400 \mu s$, while $\tau_{dr}(10) = 10 \mu s$, confirming the importance of the anion in determining ZIL dynamics. Interestingly, this change in anion has a negligible impact on the static dielectric constant, $\epsilon_{r,s}(3) = 231$ and $\epsilon_{r,s}(10) = 234$ (Figure 6C), whose values are nearly the same as those reported previously for ZI 3 ($\epsilon_{r,s} = 250$).³⁰

DISCUSSION

Spacer R_s: Length and flexibility enable stable ZILs, faster dynamics, and higher permittivity

It is well known that ZIs melt at higher temperatures than untethered ionic liquids (ILs) using the same ion pairs.^{5,31,40,47,48} This phenomenon motivates the experiment shown in Figure 4, which presents the melting thermodynamics of NaCl,⁵⁶ ionic liquid

BT,⁵⁷ ZI 8, and ZI 12. First, there is an extraordinary ΔT_m of 803°C between NaCl and BT. Strikingly, this melting point difference is dominated by entropy (Figures 4E and 4F), consistent with other ionic liquids and alkali halides.⁴⁶ ZIs 8 and 12 were designed to replicate the structure of BT as closely as possible to elucidate why ZIs melt at higher temperatures than their untethered IL counterparts. Importantly, ΔH_m for ZI 8 is identical to that of BT. Yet, the T_m of 8 is 76°C higher than that of BT due to a decrease in entropy of fusion. This result validates our hypothesis that ZIs melt at higher temperatures than ILs because their tethers incur an entropic penalty. To recover the lost entropy of fusion, we prepared ZI 12, which is identical to 8 but replaces its 4-carbon spacer with a 6-carbon spacer whose two additional rotatable bonds should increase the molar entropy in the liquid state. Strikingly, 12 increases ΔS_m by 20 J mol⁻¹ K⁻¹ compared to 8, roughly matching BT. Yet, 12 also melts 30°C higher than 8

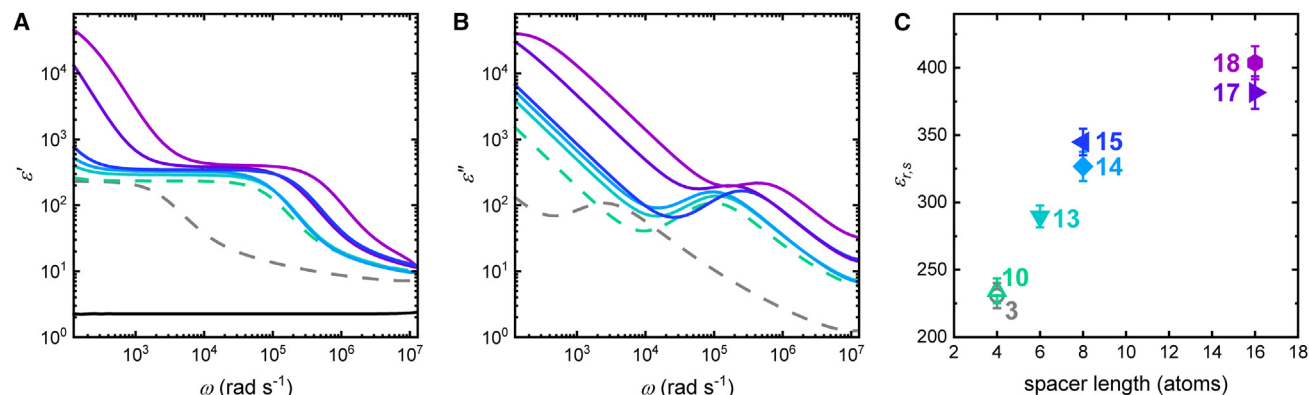


Figure 6. Dielectric properties of neat ZILs

(A and B) Relative (A) storage (ϵ') and (B) loss (ϵ'') permittivity as a function of angular frequency ω at 25°C for supercooled ZIs 3 and 10 and ZILs 13-15, 17, and 18.

(C) Static dielectric constant $\epsilon_{r,s}$ of these ZILs as a function of spacer length.

Dashed lines and open data points denote supercooled liquids; solid lines and filled points denote stable liquids. Data in (C) are shown as the flattest portion (3) or mean (10, 13-15, 17, 18) \pm SD of the plateau regions in (A).

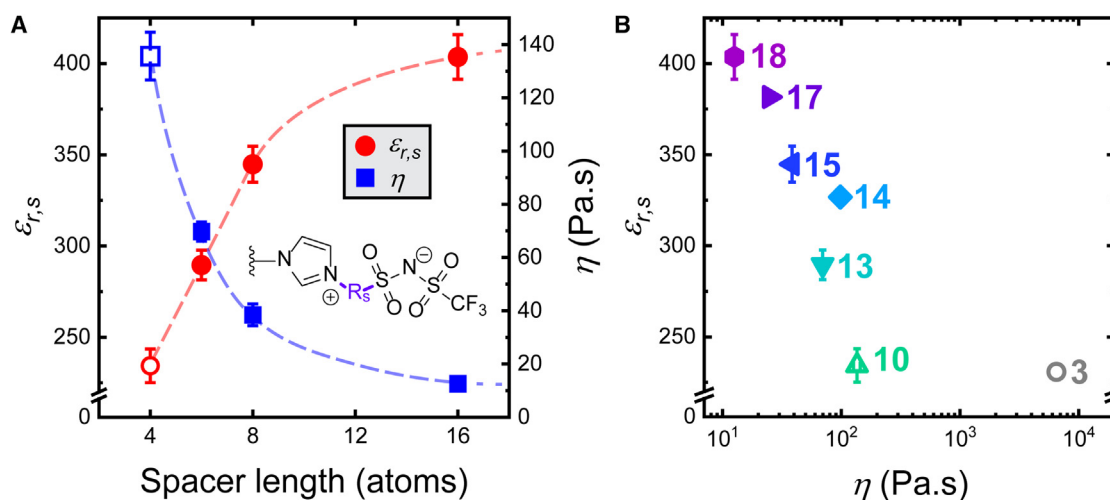


Figure 7. Comparison of ZIL static dielectric constant $\epsilon_{r,s}$ and apparent viscosity η

(A) Orthogonal scaling of $\epsilon_{r,s}$ (circles) and η (squares) as a function of spacer length for the MEE series of supercooled ZI 10 and ZILs 13, 15, and 18.

(B) Semi-log plot of $\epsilon_{r,s}$ as a function of η for supercooled ZIs 3 and 10 and ZILs 13–15, 17, and 18.

Open data points denote supercooled liquids; filled points denote ZILs. Viscosity data are represented as mean \pm SD; $n = 3$. Dielectric data are represented as the flattest portion (3) or mean (10, 13–15, 17, 18) \pm SD of the plateau regions in (Figure 6A).

due to a proportionally larger increase in ΔH_m . This suggests that, while a longer spacer increases ΔS_m , this alone is insufficient to suppress T_m . Rather, the entropy lost by introducing a zwitterionic tether must be recaptured without a concomitant increase in ΔH_m . This observation led us to introduce long and flexible linkers composed of ethers that offer greater flexibility than straight-chain alkanes.⁵⁸ The resulting ZILs 14 and 17 feature 8- and 16-atom spacers containing one and four ether groups, respectively. Both ZILs are stable liquids after drying and purification (>6 months dry storage at ambient temperatures). Moreover, synthesis of ZILs 15, 16, and 18, featuring the same 8- and 16-atom ether-containing spacers, and ZIL 13, whose hexyl spacer is combined with an ether-rich MEE tail, yielded four more stable ZILs. We verified that all six ZILs are pure and water free by ^1H , ^{13}C , and ^{19}F NMR (supplemental information), high-resolution mass spectrometry (supplemental information), thermogravimetric analysis (TGA; Figure S6; supplemental methods), and Fourier transform infrared (FTIR) spectroscopy (Figure S7; supplemental methods). Moreover, their viscosity does not change with prolonged storage (Figure S8), suggesting stable liquid structure over periods of at least 6–9 months. Additional η , T_g , spacer length, and molecular weight correlations are shown in Figures S9 and S10 and discussed in the supplemental methods.

To complement these thermodynamic effects, R_s greatly influences liquid viscosity and dielectric properties. Remarkably, dynamics grow faster as spacer length increases from 4 to 16 atoms. This is particularly pronounced for apparent viscosity, which decreases by more than 10-fold from a 4-carbon (ZI 10) to a 16-atom (ZIL 18) spacer. This trend is attributed to dilution of charge-charge interactions that likely dominate in these materials. However, τ_{dr} shows only a 4-fold decrease over the same interval. To understand this discrepancy, we note that timescale τ_{dr} describes dipole bias, which depends on displacement of

charged end groups and should therefore correlate positively with spacer length. In other words, longer spacers simultaneously decrease the viscosity and increase the diffusion path length of charged end groups in an electric field.

The static dielectric constant $\epsilon_{r,s}$ strongly correlates with spacer length. Interestingly, spacer length-dependent scaling of $\epsilon_{r,s}$ is consistent across the 4-, 6-, and 8-atom spacers and then deviates upon elongation to a 16-atom spacer. Based on their structure, we estimate that the Kuhn lengths b_s of the two ether-containing spacers lie within the range of $b_{PEO} < b_s < b_{PE}$, where $b_{PEO} = 1.1$ nm and $b_{PE} = 1.4$ nm.⁵⁸ Thus, assuming C-C and C-O bond lengths of 1.54 and 1.42 Å, respectively,⁶⁰ we estimate that the 8-atom-spacer is roughly one Kuhn length, suggesting that scaling transitions for longer spacers coincide with a loss in bond-bond correlation. The spacer length dependence of both η and $\epsilon_{r,s}$ for the MEE series of 10, 13, 15, and 18 highlights the critical importance of R_s in determining ZIL properties (Figure 7A), which leads to a synergistic improvement in both η and $\epsilon_{r,s}$ compared to benchmark 3 (Figure 7B).

Tail R_t : A long, flexible tail increases entropy of fusion and decreases viscosity

ZIs 4, 5, and 6 carry R_t = methyl, ethyl, and allyl, respectively, the shortest tail groups. Across this series, their decreasing T_m ($T_m = 150^\circ\text{C}$, 126°C , and 57°C) are driven by decreasing enthalpy of fusion (43.3, 27.7, and 18.5 kJ mol $^{-1}$) that support the hypothesis that, in the limit of short tails, increasing steric hindrance around the cation disrupts intimate charge-charge packing. Finally, an MEE tail (ZI 10) yields $T_m = 69^\circ\text{C}$ with strikingly large values for both ΔH_m and ΔS_m . Thus, MEE subverts the trend that larger tails decrease ΔH_m , possibly due to a different crystalline packing structure than observed for ZIs 4, 5, 6, or 8, or to a strong enthalpic contribution from the MEE tail itself. The large entropy of fusion is more intuitive. MEE adds three more rotatable

bonds than a butyl group, including two flexible ethers. This result supports our earlier argument that long and ether-rich moieties should increase the entropy of fusion compared to straight-chain alkanes, decreasing T_m . R_t also plays a meaningful role in determining viscosity, offering a roughly 2-fold decrease upon exchanging a butyl tail for MEE. The greater tail length of MEE is hypothesized to increase steric hindrance around the imidazolium cation relative to the butyl tail. Moreover, the ether groups, which coordinate cations,^{41–43} may competitively interact with the imidazolium to decrease the strength and duration of charge-charge interactions and decrease bulk viscosity.

R_2 : Methyl substitution decreases entropy of fusion

Exchanging the imidazolium 2-proton for a methyl group is instructive because imidazolium cations concentrate charge density at the 2 position.^{61–63} As a result, the strongest Coulombic interactions occur at this position. Thus, increasing local steric bulk should weaken charge-charge interactions.^{49–51} We replace the 2 proton in ZIs **8** and **10** with methyl groups to produce **9** and **11**. Although we observe the predicted decrease in ΔH_m , 2-methylation still increases T_m because ΔS_m decreases by an even larger margin. However, this effect varies dramatically: 2-methyl ZI **9** melts 49°C higher than 2-H ZI **8**, yet 2-methyl ZI **11** melts only 5°C above 2-H ZI **10**, suggesting that 2-position thermodynamic effects depend strongly on tail composition. Specifically, the MEE tail attenuates the effects of 2-substitution, possibly by increasing the entropy of the liquid with additional rotatable bonds.

R_3 : CF_3 -sulfonimide decreases enthalpy of fusion and viscosity compared to sulfonate

CF_3 -sulfonimide ZI **10** melts 55°C–57°C lower than sulfonate ZI **1** or C_4F_9 -sulfonimide ZI **7** because its enthalpy of fusion is 9 kJ mol^{−1} lower. Anion volume offers a potential explanation. Compared to sulfonate (71 Å³),³¹ structural analogs to CF_3 -sulfonimide, including *N*-carboxytriflamide (173 Å³)³¹ and bis-triflimide (264 Å³),⁶⁴ occupy larger volumes, suggesting a more diffuse charge that may diminish ΔH_m . By contrast, the structures of CF_3 - and C_4F_9 -sulfonimide are quite similar and only distinguished by the length of the perfluoroalkyl chain. The difference in ΔH_m cannot be explained in terms of electron-withdrawing strength, since the acid dissociation constants (pK_a) for the corresponding sulfonic acids are both ~0.7 in acetonitrile.^{65,66} However, prior reports have described strong interactions between fluorine atoms in C_4F_9 -sulfonimide and 1-ethyl-3-methylimidazolium cations, offering a potential explanation for the difference in ΔH_m observed here.⁴⁵ Finally, the viscosity η and dielectric relaxation time τ_{dr} for sulfonate **3** are 48- and 40-fold larger than for CF_3 -sulfonimide **10**. Again, anion volume offers a possible explanation, as the higher charge density of **3** may create a deeper energy well for intimate ion pairs, slowing ion pair dynamics.

Conclusions

We synthesized a library of 18 ZIs, including three known and 15 previously unreported ZIs, to map their melting behavior, apparent viscosity, and dielectric properties across four func-

tional positions. We find that the spacer R_s is the most important given the resulting liquid stability, faster dynamics, and increased permittivity. While a longer spacer increases the entropy of fusion, T_m suppression also demands avoiding a concomitant increase in enthalpy of fusion. We achieved this goal via ether-mediated chain flexibility, yet we anticipate that many alternative strategies may exist. In parallel, we showed that a long, flexible tail and a bulky, diffuse CF_3 -sulfonimide anion decrease T_m and offer faster dynamics than shorter tails and a sulfonate anion. These insights guided the design and synthesis of six room temperature ZILs, which feature static dielectric constants as large as 404 and apparent viscosities 500-fold smaller than supercooled benchmark ZI **3** at room temperature. Together, our results provide the foundation for an emergent class of liquid dielectrics with potential applications in soft electronics and energy storage.

METHODS

Detailed methods can be found in the [supplemental information](#).

RESOURCE AVAILABILITY

Lead contact

Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Dylan M. Barber (dbarber@seas.harvard.edu).

Materials availability

There are restrictions to the availability of the ZIs and precursors reported in this work because of the lack of an external centralized repository for its distribution and our need to maintain the stock. Specific molecules may be made available upon negotiation of possible collaboration and a completed materials transfer agreement.

Data and code availability

Source data, including dielectric spectroscopy, differential scanning calorimetry, fourier transform infrared spectroscopy, nuclear magnetic resonance, mass spectrometry, rheology, and thermogravimetric analysis have been deposited at Zenodo and are publicly available as of the date of publication at Zenodo: <https://doi.org/10.5281/zenodo.14510696> under the title: Source Data for “Rational Design and Synthesis of Zwitterionic Liquid Dielectrics.” No new code was generated by this work.

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AUTHOR CONTRIBUTIONS

Conceptualization, D.M.B.; methodology, D.M.B., M.D.N., and J.A.L.; validation, D.M.B. and M.D.N.; formal analysis, D.M.B. and J.A.L.; investigation, D.M.B. and M.D.N.; resources, J.A.L.; data curation, D.M.B. and J.A.L.;

writing – original draft, D.M.B.; writing – review and editing, D.M.B. and J.A.L.; visualization, D.M.B.; supervision, J.A.L.; project administration, D.M.B. and J.A.L.; funding acquisition, J.A.L.

DECLARATION OF INTERESTS

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Matter, Volume 8

Supplemental information

**Rational design and synthesis
of zwitterionic liquid dielectrics**

Dylan M. Barber, Michael D. Nelwood, and Jennifer A. Lewis

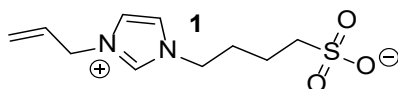
Supplemental Methods

Materials. Dichloromethane (99.9 %) (Avantor Performance Material LLC), 1-methylimidazole (99.0 %), 1-ethylimidazole (98.0 %) (TCI America), toluene (anhydrous, 99.5 %), 2,2,2-trifluoroethanol (99%) (BeanTown Chemical), Tetrahydrofuran (THF, 99%, stabilized ACS), Hexane (98.5 %, mixture of isomers, ACS), Acetonitrile (99.9%, anhydrous, Hi PerSolv CHROMANORM® super gradient grade for HPLC), Acetone (99.5 %), Diethyl ether (Et₂O, 98%, stabilized), Ethyl acetate (EtOAc, 99.5% ACS), Glacial acetic acid (AcOH, 99.7-100.5 % ACS), Methanol (MeOH, 99.8 % ACS, used for workups) (VWR Chemicals BDH®), KOH (85%, Reagent Grade), Sodium sulfite (anhydrous ACS) (VWR), HPLC-grade methanol (99.9%, used for mass spectrometry), 1,4-butanediol (98%), 1,3-propanediol (98%), 1-Butylimidazole (98%), Imidazole (99%, ReagentPlus®), 2-methylimidazole (99%), Magnesium sulfate (MgSO₄, anhydrous, ReagentPlus®, 99.5%), Sodium sulfate (99.0 %, anhydrous, granular), Potassium carbonate (K₂CO₃, anhydrous, free-flowing, Redi-Dri™, ACS reagent, 99%), Silica gel (technical grade, pore size 60 Å, 40-63 µm particle size), 1-Bromobutane (99%, ReagentPlus®), Thionyl chloride (99%, ReagentPlus®), N,N-Dimethylformamide (DMF, 99.8%, Anhydrous), 1,4-butanediol (99% ReagentPlus®), Potassium *tert*-butoxide (*t*-BuOK, 1.0 M in THF), Lithium bis(trimethylsilyl)amide solution (Li-HMDS, 1.0 M in THF), Tetraethylene glycol (TetrEG, 99 %), Butylated hydroxytoluene (BHT, 99 %) (Millipore Sigma), DMSO-*d*₆ (99.9 % D, AcroSeal™), 6-chloro-1-hexanol (97 %), Celite® 535 (Thermo Scientific Chemicals), High purity argon (AR HP300) (Airgas), 1-Bromo-2-(2-methoxyethoxy)ethane (MEE-Br, 97 %) (Combi-Blocks), 1-allylimidazole (97%), Activated charcoal (DARCO® 4-12 mesh) (Avantor), Trifluoromethanesulfonamide (triflamide, 98%), and Perfluorobutanesulfonyl fluoride (95%) (Oakwood Chemical) were used as received without further purification unless otherwise noted.

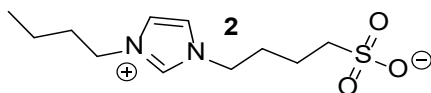
Instrumentation. ¹H NMR (400.2 MHz), ¹³C NMR (100.6 MHz), and ¹⁹F NMR (376.5 MHz) were collected using a 400 MHz Bruker AVANCE NEO NMR spectrometer equipped with a 5 mm RT double resonance broad banded iProbe. Products were dissolved (20 µM) in HPLC-grade MeOH and measured via positive ion (zwitterions, **L**, **N**) and negative ion (sulfonate, sulfonimide, and C₄F₉-sulfonamide intermediates) electrospray ionization on a Bruker Impact II q-TOF mass spectrometer equipped with an Agilent 1260 HPLC system using flow injection analysis. The samples were introduced into the mass spectrometer using 60% acetonitrile with 0.1% formic acid through the HPLC system. The mass scale was internally calibrated using sodium formate clusters which were introduced at the end of each run to achieve high mass accuracy. Differential scanning calorimetry (DSC) was conducted on a TA instruments Discovery 250 calorimeter. All zwitterions were dried for 24 h at 115 °C in a vacuum oven, stored under high purity argon, and quickly transferred to aluminum pans and hermetically sealed for characterization. Room-temperature solids were subjected to heat-cool-heat cycles, and liquids to cool-heat cycles (all ramp rates 10 °C min⁻¹, with equilibration and 5-minute isotherms at each maximum and minimum) followed by a ramp to 25 °C at 20 °C min⁻¹. *T_m* was defined as the onset of the melting endotherm to limit variability with scanning rate and sample mass. ΔS_m was calculated by $\Delta S_m = \Delta H_m / T_m$. *T_g* was determined by taking the mean from the cooling and subsequent heating cycles. ΔC_g was determined as the difference between extrapolated liquid and glass heat capacities at *T_g* during heating. Rheology was conducted on a TA Instruments Discovery Hybrid HR20 rheometer with an 8 mm parallel plate geometry and a 400 µm gap. All liquids were dried for 24 h at 115 °C in a vacuum oven, then immediately transferred to the rheometer for measurement. Dielectric spectroscopy was conducted on a TA Instruments Discovery Hybrid HR20 rheometer with 25 mm custom dielectric parallel plate geometries equipped with a Keysight E4980A LCR meter and operating with 100 mV oscillation amplitude and a 100 µm gap. All molecules were dried for 24 h at 115 °C in a vacuum oven, then stored under high purity argon and transferred to the rheometer for measurement. Molecules **3** and **10** were placed on the bottom electrode as dry powders and heated to 150 °C for 5 minutes. Then, the top electrode was lowered into place and the apparatus quenched to 25 °C before measuring. Thermogravimetric analysis (TGA) was run on a TA Instruments Discovery TGA 550; samples were heated to 600 °C with a ramp rate of 20 °C min⁻¹ under a pure N₂ atmosphere and mass change recorded as a function of time and temperature. FTIR measurements were conducted on a Nicolet iS50 FTIR spectrometer. A background spectrum was collected in the absence of any sample, then samples were

placed on the ATR crystal, and, in the case of crystalline **10**, compressed under the attached metal piston before measuring. FTIR data was processed by applying an Asymmetric Least Squares (AsLS) baseline correction with AsLS Log(λ) = 6 and AsLS asymmetry = 0.000001, then normalized. Water uptake was characterized by drying ZI **10** and ZILs **15** and **18** in a vacuum oven at 115 °C for 24 h before TGA and FTIR measurements. 500 mg samples of each were then sealed in a container with an open cup of deionized water (100% relative humidity) for 1 week before repeating FTIR, TGA, viscosity, and dielectric spectroscopy measurements.

An important note regarding safety with refluxing thionyl chloride. All reactions using refluxing thionyl chloride should be run and quenched with care as thionyl chloride reacts violently with water to produce concentrated hydrochloric acid and sulfur dioxide vapor. This vapor is caustic, toxic, and can damage infrastructure, including the downstream ductwork of a fume hood. To prevent large-scale release of concentrated acid and sulfur dioxide vapor during reaction and quenching, evolved gas should be routed through a vacuum trap to prevent back-suck, followed by a gas scrubber composed of a glass sparger and concentrated aqueous base; we used a stirring, 5 L bath of 5 M KOH. While quenching with ice pellets, it is important to maintain a high stirring rate because liquid water is immiscible with the crude product mixture. A low stirring rate enables formation of a reservoir of liquid water, which can lead to a violent runaway reaction. To avoid this, we maintain a high stirring rate and incremental addition of ice pellets while keeping the reaction vessel at 0 °C. This note applies to the synthesis of sulfonyl chloride intermediates **A**, **D**, **G**, and **J**.

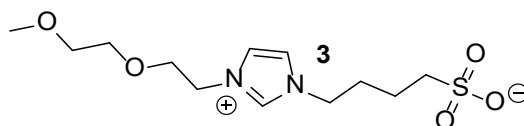


Synthesis of 1. 4.411 g (40.8 mmol) 1-allylimidazole was combined with 5.138 g (37.7 mmol) 1,4-butanedisulfonate and 41 mg (0.19 mmol) in a 20 mL scintillation vial and heated to 80 °C with stirring for 43.5 hours, then stopped by removing from heat. The solid pellet of product was collected by breaking the vial, separating glass fragments, grinding the product in a mortar and pestle, washing with 3x40 mL of acetone, and drying under reduced pressure to afford **1** as a white powder in 7.531 g (82 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.41-9.29 (s, 1H), 7.92-7.85 (s, 1H), 7.82-7.75 (s, 1H), 6.15-5.98 (m, 1H), 5.41-5.24 (m, 2H), 4.94-4.81 (d, 2H), 4.31-4.14 (t, 2H), 2.58-2.42 (t, 2H), 2.00-1.81 (m, 2H), 1.66-1.46 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 136.30 (s, 1C), 131.85 (s, 1C), 122.68 (s, 1C), 122.50 (s, 1C), 120.23 (s, 1C), 50.79 (s, 1C), 50.55 (s, 1C), 48.63 (s, 1C), 28.64 (s, 1C), 21.82 (s, 1C). ESI (m/z): 245.0965 (C₁₀H₁₇N₂O₃S⁺, calculated 245.0954).

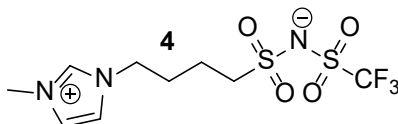


Synthesis of 2. 118.2 g (952 mmol) 1-butylimidazole was combined with 121.0 g (889 mmol) 1,4-butanedisulfonate in a 500 mL round-bottom flask, then heated to 80 °C with stirring for 24 h to afford a white, solid hemisphere in the bottom of the flask. The flask was broken, glass fragments removed, and the solids ground in a mortar and pestle under acetone, then isolated and washed with 3 x 500 mL acetone to afford **2** as a white powder in 230.95 (99.8 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.41-9.34 (s, 1H), 7.90-7.83 (m, 2H), 4.28-4.14 (m, 4H), 2.55-2.45 (t, 2H), 1.97-1.84 (m, 2H), 1.84-1.72 (m, 2H), 1.64-1.49 (m, 2H), 1.34-1.17 (m, 2H), 0.97-0.83 (t, 3H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 136.19 (s, 1C), 122.52 (s, 1C),

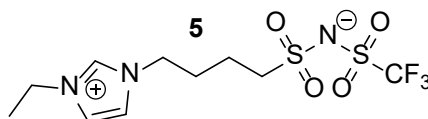
122.43 (s, 1C), 50.53 (s, 1C), 48.54 (s, 1C), 48.50 (s, 1C), 31.31 (s, 1C), 28.64 (s, 1C), 21.81 (s, 1C), 18.78 (s, 1C), 13.26 (s, 1C). ESI (m/z): 261.1268 ($C_{11}H_{21}N_2O_3S^+$, calculated 261.1267).



Synthesis of 3. 1.254 g (7.37 mmoles) **L** was combined with 1.010 g (7.42 mmoles) 1,4-butanedisulfone and 7 mL acetone in a 20 mL scintillation vial and heated to 50 °C with stirring for 120 hours, then returned to room temperature and precipitated in 12 mL Et₂O. The dense phase was 5x (diluted to 2 mL in MeOH and precipitated in 12 mL EtOAc) followed by 3x (dilute to 2 mL in MeOH and precipitate in 12 mL Et₂O). The viscous liquid was then sonicated in 15 mL Et₂O to induce crystallization, Et₂O was decanted, the solid pellet broken into a powder, and sonicated in 15 mL additional Et₂O before centrifuging, decanting, and leaving at reduced pressure for 24 h to remove residual Et₂O to afford **3** as a white powder in 1.26 g (56 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.26-9.19 (s, 1H), 7.86-7.80 (m, 1H), 7.80-7.74 (m, 1H), 4.43-4.28 (m, 2H), 4.28-4.15 (m, 2H), 3.83-3.72 (m, 2H), 3.60-3.49 (m, 2H), 3.46-3.37 (m, 2H), 3.27-3.16 (s, 3H), 2.49-2.43 (m, 2H), 1.96-1.82 (m, 2H), 1.62-1.48 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 136.46 (s, 1C), 122.75 (s, 1C), 122.29 (s, 1C), 71.07 (s, 1C), 69.35 (s, 1C), 68.08 (s, 1C), 58.08 (s, 1C), 50.46 (s, 1C), 48.78 (s, 1C), 48.58 (s, 1C), 28.70 (s, 1C), 21.78 (s, 1C). ESI (m/z): 307.1337 ($C_{12}H_{23}N_2O_5S^+$, calculated 307.1322).

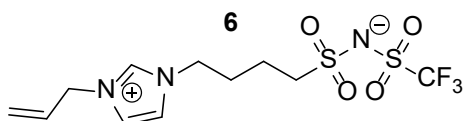


Synthesis of 4. 1.019 g (3.36 mmoles) **B-CF₃** (as conjugate acid), 2.709 g (33.0 mmoles) 1-methylimidazole, 1.053 g (7.62 mmoles) K₂CO₃, and 415 mg (3.45 mmoles) MgSO₄ were combined in a 20 mL scintillation vial and heated to 80 °C for 48 h, returned to room temperature, centrifuged to remove solids, then precipitated into acetone. Then, the resulting solids were 3x (diluted into 10 mL trifluoroethanol and precipitated into 150 mL Et₂O) afford **4** as a white, crystalline solid in 1.07 g (91 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.15-9.09 (s, 1H), 7.79-7.74 (m, 1H), 7.73-7.68 (m, 1H), 4.26-4.15 (m, 2H), 3.90-3.80 (s, 3H), 3.06-2.98 (m, 2H), 1.98-1.85 (m, 2H), 1.71-1.58 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 136.61 (s, 1C), 124.93-115.26 (q, 1C), 123.68 (s, 1C), 122.25 (s, 1C), 53.60 (s, 1C), 48.24 (s, 1C), 35.75 (s, 1C), 28.02 (s, 1C), 20.46 (s, 1C). ¹⁹F NMR (376.5 MHz, DMSO-*d*₆, δ): -77.51 (s, 3F). ESI (m/z): 350.0454 ($C_9H_{15}F_3N_3O_4S_2^+$, calculated 350.0451).

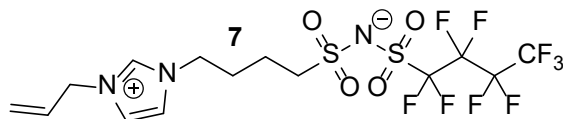


Synthesis of 5. 1.031 g (3.39 mmoles) **B-CF₃** (as conjugate acid), 3.184 g (33.1 mmoles) 1-ethylimidazole, 1.017 g (7.36 mmoles) K₂CO₃, and 415 mg (3.45 mmoles) MgSO₄ were combined in a 20 mL scintillation vial and heated to 80 °C for 48 h, returned to room temperature, centrifuged to remove solids, then precipitated into acetone. Then, the resulting solids were 3x (diluted into 10 mL trifluoroethanol and precipitated into 150 mL Et₂O) to afford **5** as a white, crystalline solid in 960 mg (78 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.22-9.15 (s, 1H), 7.84-7.75 (m, 2H), 4.27-4.12 (m, 4H), 3.09-2.97 (m, 2H), 2.00-1.85

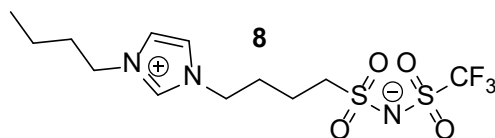
(m, 2H), 1.73-1.58 (m, 2H), 1.48-1.37 (t, 3H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 135.73 (s, 1C), 124.93-115.26 (q, 1C), 122.39 (s, 1C), 122.21 (s, 1C), 53.57 (s, 1C), 48.30 (s, 1C), 44.25 (s, 1C), 27.96 (s, 1C), 20.49 (s, 1C), 14.91 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.52 (s, 3F) ESI (m/z): 364.0610 ($\text{C}_{10}\text{H}_{17}\text{F}_3\text{N}_3\text{O}_4\text{S}_2^+$, calculated 364.0607)



Synthesis of 6. 1.082 g (3.56 mmoles) **B-CF₃** (as conjugate acid), 1.857 g (17.2 mmoles) 1-allylimidazole, 969 mg (7.01 mmoles) K_2CO_3 , and 414 mg (3.44 mmoles) MgSO_4 were combined in a 20 mL scintillation vial and heated to 80 °C for 24 h, then returned to 20 °C, diluted to 20 mL in acetone, and centrifuged to remove solids before precipitating into 100 mL of Et_2O . The resulting viscous brown oil was 2x (dissolved to 20 mL in acetone and precipitated in 100 mL of Et_2O) and placed under low vac to afford **6** as a tan, crystalline solid (1.1 g, 82 %). ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 9.25-9.11 (s, 1H), 7.89-7.68 (m, 2H), 6.15-5.95 (m, 1H), 5.45-5.23 (m, 2H), 4.92-4.77 (m, 2H), 4.33-4.14 (t, 2H), 3.08-2.98 (t, 2H), 2.03-1.85 (m, 2H), 1.74-1.58 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 136.15 (s, 1C), 131.61 (s, 1C), 124.94-115.26 (q, 1C), 122.62 (s, 1C), 122.59 (s, 1C), 120.32 (s, 1C), 53.60 (s, 1C), 50.94 (s, 1C), 48.41 (s, 1C), 28.00 (s, 1C), 20.49 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.53 (s, 3F). ESI (m/z): 376.0614 ($\text{C}_{11}\text{H}_{17}\text{F}_3\text{N}_3\text{O}_4\text{S}_2^+$, calculated 376.0607).

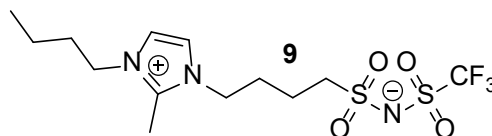


Synthesis of 7. 5.007 g (10.2 mmoles) **B-C₄F₉** was combined with 1.107 g (10.2 mmoles) allylimidazole, 26 mg (0.12 mmoles) BHT, and 2 mL acetonitrile in a 20 mL scintillation vial, then heated to 80 °C with stirring for 24 h. Solids were removed by centrifugation, then the supernatant was combined with an equal volume of reverse osmosis water to induce crystallization and solvent was removed via air stream at 50 °C to afford a yellow solid. This was washed 2x with reverse osmosis water and the resulting solid dried via vacuum oven to afford **7** as a white, crystalline solid (3.54 g, 77%). ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 9.22-9.15 (s, 1H), 7.86-7.77 (m, 1H), 7.77-7.70 (m, 1H), 6.16-5.94 (m, 1H), 5.45-5.21 (m, 2H), 4.94-4.76 (m, 2H), 4.35-4.13 (t, 2H), 3.10-2.99 (t, 2H), 2.07-1.83 (m, 2H), 1.79-1.57 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 136.19 (s, 1C), 131.62 (s, 1C), 122.62 (s, 1C), 122.59 (s, 1C), 121.34-108.25 (br m, 4C, fluorinated), 120.26 (s, 1C), 53.86 (s, 1C), 50.95 (s, 1C), 48.41 (s, 1C), 28.00 (s, 1C), 20.48 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -80.52 (m, 3F), -112.88 (m, 2F), -121.02 (m, 2F), -125.74 (m, 2F). ESI (m/z): 526.0491 ($\text{C}_{14}\text{H}_{17}\text{F}_9\text{N}_3\text{O}_4\text{S}_2^+$, calculated 526.0511).

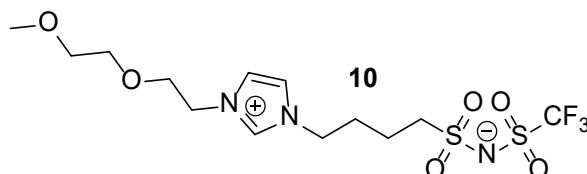


Synthesis of 8. 1.044 g (3.44 mmoles) **B-CF₃** (as conjugate acid), 2.131 g (17.2 mmoles) 1-butyylimidazole, 963 mg (6.97 mmoles) K_2CO_3 , and 412 mg (3.42 mmoles) MgSO_4 were combined in a 20 mL scintillation vial and heated to 80 °C for 24 h, then returned to 20 °C, diluted to 20 mL in acetone, and centrifuged to remove solids before precipitating into 100 mL of Et_2O . The resulting viscous brown oil was 2x (dissolved to 20 mL in acetone and precipitated in 100 mL of Et_2O) and placed under low vac to afford **8** as a tan,

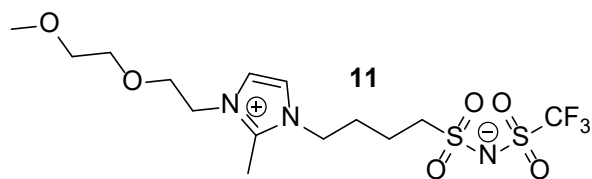
crystalline solid (1.1 g, 82 %). ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 9.27-9.11 (s, 1H), 7.87-7.72 (m, 2H), 4.33-4.05 (m, 4H), 3.08-2.98 (t, 2H), 2.00-1.87 (m, 2H), 1.84-1.72 (m, 2H), 1.72-1.59 (m, 2H), 1.33-1.19 (m, 2H), 0.95-0.84 (t, 3H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 136.00 (s, 1C), 124.94-115.27 (q, 1C), 122.52 (s, 1C), 122.43 (s, 1C), 53.60 (s, 1C), 48.65 (s, 1C), 48.35 (s, 1C), 31.25 (s, 1C), 27.97 (s, 1C), 20.48 (s, 1C), 18.80 (s, 1C), 13.20 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -77.60 (s, 3F). ESI (m/z): 392.0924 ($\text{C}_{12}\text{H}_{21}\text{F}_3\text{N}_3\text{O}_4\text{S}_2^+$, calculated 392.0920).



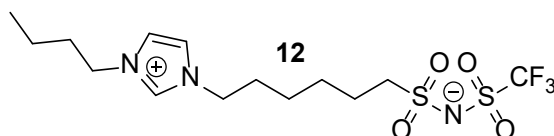
Synthesis of 9. 1.007 g (3.32 mmoles) **B-CF₃** (as conjugate acid), 2.301 g (16.6 mmoles) **N**, 927 mg (6.71 mmoles) K_2CO_3 , and 398 mg (3.31 mmoles) MgSO_4 were combined in a 20 mL scintillation vial and heated to 80 °C for 48 h, then returned to 20 °C, diluted to 15 mL in acetone, and centrifuged to remove solids before precipitating into 120 mL of Et_2O . The resulting tan solid was washed with 3x 40 mL Et_2O before placing under low vac to afford **9** as a tan powder in 716 mg (53 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 7.74-7.64 (m, 2H), 4.23-4.01 (m, 4H), 3.08-2.97 (t, 2H), 2.70-2.56 (s, 3H), 1.96-1.79 (m, 2H), 1.79-1.62 (m, 4H), 1.39-1.20 (m, 2H), 1.01-0.83 (t, 3H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 143.76 (s, 1C), 124.94-115.27 (q, 1C), 121.28 (s, 2C), 53.68 (s, 1C), 47.31 (s, 1C), 46.99 (s, 1C), 31.03 (s, 1C), 27.54 (s, 1C), 20.55 (s, 1C), 18.92 (s, 1C), 13.37 (s, 1C), 9.09 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -7.51 (s, 3F). ESI (m/z): 406.1081 ($\text{C}_{13}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_4\text{S}_2^+$, calculated 406.1077).



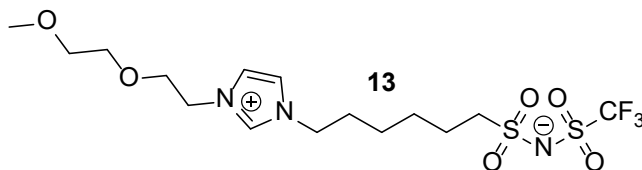
Synthesis of 10. 5.009 g (14.7 mmoles) **B-CF₃** was combined with 17.494 g (103 mmoles) **L**, and 410 mg (2.97 mmoles) K_2CO_3 , and 884 mg (7.34 mmoles) MgSO_4 under an argon atmosphere, sealed, and heated to 80 °C for 48 hours. The mixture was returned to 20 °C, centrifuged (5 minutes, 4500 RPM) to remove solids, then the solids were washed with 3x10 mL acetone. The crude product and acetone washes were combined and left under reduced pressure for 24 h to remove acetone. Then, the crude product mixture was washed with 10 x 20 mL Et_2O and purified by flash column chromatography (silica gel stationary phase, gradient eluent $\text{EtOAc} \rightarrow 2:1 \text{ EtOAc:acetone}$) and concentrated under reduced pressure to afford **10** as an amber crystalline solid in 4.895 g (76 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 9.15-9.10 (s, 1H), 7.81-7.72 (m, 2H), 4.39-4.31 (t, 2H), 4.28-4.19 (t, 2H), 3.81-3.73 (m, 2H), 3.59-3.50 (m, 2H), 3.45-3.38 (m, 2H), 3.26-3.18 (s, 3H), 3.09-2.99 (t, 2H), 2.00-1.87 (m, 2H), 1.73-1.61 (m, 2H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 136.42 (s, 1C), 124.97-115.30 (q, 1C), 122.86 (s, 1C), 122.20 (s, 1C), 71.09 (s, 1C), 69.41 (s, 1C), 68.06 (s, 1C), 58.05 (s, 1C), 53.63 (s, 1C), 48.91 (s, 1C), 48.35 (s, 1C), 28.11 (s, 1C), 20.49 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -77.57 (s, 3F). ESI (m/z): 438.0978 ($\text{C}_{13}\text{H}_{23}\text{F}_3\text{N}_3\text{O}_6\text{S}_2^+$, calculated 438.0975).



Synthesis of 11. 349 mg (1.15 mmol) **B-CF₃** (as conjugate acid) was combined with 1.02 g (5.54 mmol) **O**, 319 mg (2.31 mmol) K₂CO₃, and 141 mg (1.17 mmol) MgSO₄ in a 20 mL scintillation vial and heated to 80 °C for 48 h with stirring before returning to room temperature, removing solids by centrifugation, and washing the resulting brown oil with 3 x 12 mL Et₂O to afford **11** as a tan solid (392 mg, 76 %). ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 7.77-7.57 (m, 2H), 4.38-4.24 (t, 2H), 4.24-4.10 (t, 2H), 3.79-3.67 (m, 2H), 3.56-3.46 (m, 2H), 3.44-3.35 (m, 2H), 3.25-3.16 (s, 3H), 3.09-2.97 (m, 2H), 2.69-2.58 (s, 3H), 1.93-1.78 (m, 2H), 1.77-1.63 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 144.53 (s, 1C), 124.96-115.28 (q, 1C), 121.61 (s, 1C), 121.19 (s, 1C), 71.12 (s, 1C), 69.55 (s, 1C), 68.42 (s, 1C), 58.05 (s, 1C), 53.69 (s, 1C), 47.62 (s, 1C), 47.03 (s, 1C), 27.67 (s, 1C), 20.55 (s, 1C), 9.33 (s, 1C). ¹⁹F NMR (376.5 MHz, DMSO-*d*₆, δ): -77.50 (s, 3F). ESI (m/z): 452.1140 (C₁₄H₂₅F₃N₃O₆S₂⁺, calculated 452.1131).

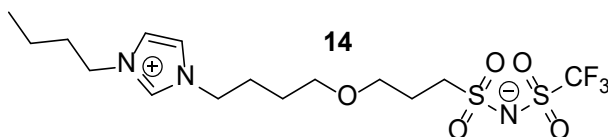


Synthesis of 12. 613 mg (1.66 mmol) **E** was combined with 1.23 g (9.91 mmol) 1-butylimidazole, 246 mg (1.78 mmol) K₂CO₃, and 126 mg (1.04 mmol) MgSO₄, in a 20 mL scintillation vial, then heated to 80 °C with stirring for 48 h. Solids were removed by centrifugation, then the product was washed with 5 x 12 mL Et₂O to afford **12** as a tan powder (625 mg, 90 %). ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.23-9.13 (s, 1H), 7.85-7.73 (m, 2H), 4.23-4.09 (m, 4H), 3.01-2.89 (t, 2H), 1.87-1.72 (m, 4H), 1.72-1.60 (m, 2H), 1.45-1.32 (m, 2H), 1.32-1.18 (m, 4H), 0.96-0.85 (t, 3H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 135.93 (s, 1C), 124.97-115.30 (q, 1C), 122.47 (s, 1C), 122.44 (s, 1C), 54.25 (s, 1C), 48.75 (s, 1C), 48.60 (s, 1C), 31.23 (s, 1C), 29.01 (s, 1C), 26.88 (s, 1C), 25.03 (s, 1C), 23.44 (s, 1C), 18.78 (s, 1C), 13.21 (s, 1C). ¹⁹F NMR (376.5 MHz, DMSO-*d*₆, δ): -77.52 (s, 3F). ESI (m/z): 420.1238 (C₁₄H₂₅F₃N₃O₄S₂⁺, calculated 420.1233).

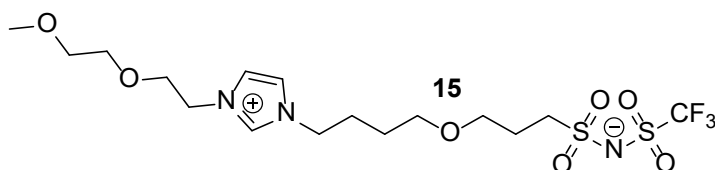


Synthesis of 13. 1.02 g (2.76 mmol) **E**, 2.98 g (17.5 mmol) **L**, 387 mg (2.80 mmol) K₂CO₃, and 178 mg (1.48 mmol) MgSO₄ were combined in a 20 mL scintillation vial and stirred at 80 °C for 50 h. The crude reaction mixture was cooled to 20 °C, then washed with 3 x 12 mL Et₂O and purified by flash column chromatography (29.8 g silica, acetone eluent) to afford **13** as a viscous brown oil (817 mg, 64 %). ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.21-9.05 (s, 1H), 7.87-7.67 (m, 2H), 4.41-4.29 (t, 2H), 4.25-4.13 (t, 2H), 3.85-3.71 (m, 2H), 3.61-3.49 (m, 2H), 3.47-3.36 (m, 2H), 3.24-3.18 (s, 3H), 3.01-2.91 (t, 2H), 1.88-1.73 (m, 2H), 1.73-1.61 (m, 2H), 1.47-1.32 (m, 2H), 1.32-1.17 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 136.35 (s, 1C), 124.99-115.32 (q, 1C), 122.78 (s, 1C), 122.20 (s, 1C), 71.08 (s, 1C), 69.37 (s, 1C), 68.04 (s, 1C), 58.06 (s, 1C), 54.30 (s, 1C), 48.86 (s, 1C), 48.76 (s, 1C), 29.14 (s, 1C), 26.95 (s, 1C), 25.05 (s, 1C), 23.47 (s,

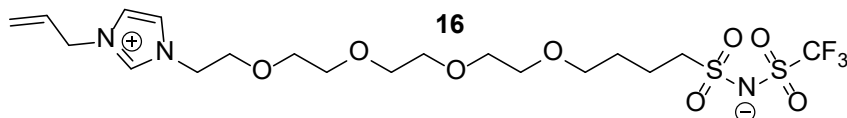
1C). ^{19}F NMR (376.5 MHz, $\text{DMSO}-d_6$, δ): -77.55 (s, 3F). ESI (m/z): 488.1115 ($\text{C}_{15}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_6\text{S}_2^+$, calculated 488.1107).



Synthesis of 14. 5.67 g (14.2 mmol) **H** was combined with 17.13 g (138 mmol) 1-butylimidazole, 2.29 g, (16.6 mmol) K_2CO_3 , and 2.13 g (17.7 mmol) MgSO_4 and heated to 80 °C with stirring for 48 h, then returned to room temperature and washed with 3x40 mL hexanes before purifying by flash column chromatography (135 g silica, mixed eluent starting with EtOAc, then switching to a gradient 1:1 acetone:hexanes \rightarrow pure acetone) and concentrated under reduced pressure to afford **14** as a viscous brown oil in 5.79 g (91 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO}-d_6$, δ): 9.24-9.07 (s, 1H), 7.88-7.69 (m, 2H), 4.29-4.08 (m, 4H), 3.53-3.28 (m, 4H), 3.13-2.92 (t, 2H), 2.02-1.68 (m, 6H), 1.61-1.39 (m, 2H), 1.38-1.15 (m, 2H), 1.01-0.80 (t, 3H). ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$, δ): 135.90 (s, 1C), 124.96-115.29 (q, 1C), 122.44 (s, 1C), 122.42 (s, 1C), 69.07 (s, 1C), 68.12 (s, 1C), 51.79 (s, 1C), 48.76 (s, 1C), 48.63 (s, 1C), 31.27 (s, 1C), 26.57 (s, 1C), 25.75 (s, 1C), 24.26 (s, 1C), 18.78 (s, 1C), 13.17 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO}-d_6$, δ): -77.65 (s, 3F). ESI (m/z): 472.1174 ($\text{C}_{15}\text{H}_{27}\text{F}_3\text{N}_3\text{O}_5\text{S}_2^+$, calculated 472.1158).

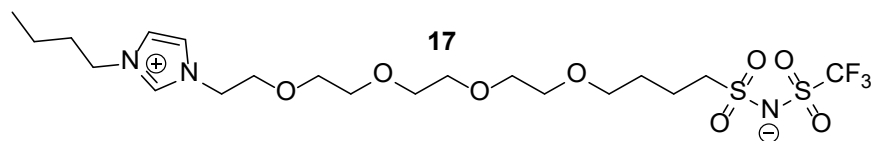


Synthesis of 15. 1 g (2.5 mmol) **H** was combined with 3.02 g (17.7 mmol) **L**, 361 mg (2.6 mmol) K_2CO_3 , and 162 mg (1.3 mmol) MgSO_4 and heated to 80 °C for 48 h, returned to room temperature, and washed with 3x40 mL Et_2O and concentrated under reduced pressure to afford **15** as a viscous brown oil in 1.27 g (100 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO}-d_6$, δ): 9.15-9.07 (s, 1H), 7.82-7.70 (m, 2H), 4.40-4.29 (t, 2H), 4.27-4.17 (t, 2H), 3.83-3.72 (m, 2H), 3.59-3.50 (m, 2H), 3.49-3.35 (m, 6H), 3.24-3.19 (s, 3H), 3.06-2.99 (t, 2H), 1.96-1.79 (m, 4H), 1.55-1.42 (m, 2H). ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$, δ): 136.36 (s, 1C), 124.98-115.30 (q, 1C), 122.78 (s, 1C), 122.19 (s, 1C), 71.08 (s, 1C), 69.37 (s, 1C), 69.07 (s, 1C), 68.16 (s, 1C), 68.03 (s, 1C), 58.04 (s, 1C), 51.79 (s, 1C), 48.85 (s, 1C), 48.74 (s, 1C), 26.62 (s, 1C), 25.74 (s, 1C), 24.27 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO}-d_6$, δ): -77.59 (s, 3F). ESI (m/z): 518.1238 ($\text{C}_{16}\text{H}_{29}\text{F}_3\text{N}_3\text{O}_7\text{S}_2^+$, calculated 518.1213).

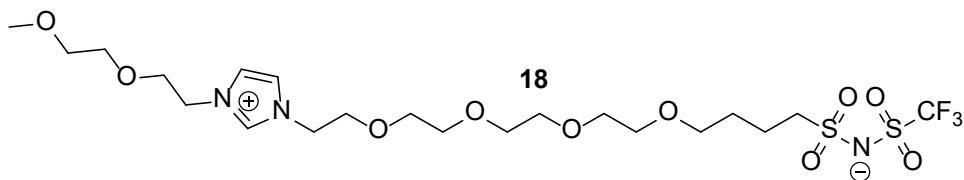


Synthesis of 16. 7.089 g (13.7 mmol) of **K** was combined with 1.487 g (13.8 mmol) of 1-allylimidazole and a stir bar under an argon atmosphere in a 20 mL scintillation vial, then stirred at 80 °C for 72 h. The reaction was stopped by removing from heat, then ran 3x (diluted to 12.5 mL in acetone, precipitated into 35 mL of Et_2O , shaken vigorously, centrifuged 4500 RPM for 120 s, decanted the buoyant phase). The product was

purified by silica gel column chromatography using a gradient eluent (EtOAc \rightarrow 3:1 EtOAc:acetone), concentrated under reduced pressure, dried over MgSO_4 , then transferred to a vacuum oven for 24 h at 115 °C to afford **16** as an amber oil (5.6 g, 74 %). ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 9.15-9.05 (s, 1H), 7.81-7.74 (s, 1H), 7.74-7.66 (s, 1H), 6.13-5.98 (m, 1H), 5.41-5.33 (dd, 1H), 5.33-5.24 (dd, 1H), 4.92-4.82 (d, 2H), 4.43-4.32 (t, 2H), 3.85, 3.75 (t, 2H), 3.62-3.43 (br m, 12 H), 3.43-3.34 (t, 2H), 3.04-2.93 (t, 2H), 1.77-1.65, (m, 2H), 1.62-1.51, (m, 2H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 136.44 (s, 1C), 131.69 (s, 2C overlapping), 125.01-115.33 (q, 1C, CF_3), 123.02 (s, 1C), 122.25 (s, 1C), 120.12 (s, 1C), 69.82 (s, 2C overlapping), 69.79 (s, 1C), 69.72 (s, 1C), 69.61 (s, 1C), 69.56 (s, 1C), 69.51 (s, 1C), 68.06 (s, 1C), 54.39 (s, 1C), 50.87 (s, 1C), 48.93 (s, 1C), 27.87 (s, 1C), 20.81 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -77.59 (s, 3F). ESI (m/z): 552.1666 ($\text{C}_{19}\text{H}_{33}\text{F}_3\text{N}_3\text{O}_8\text{S}_2^+$, calculated 552.1656).

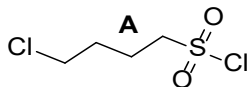


Synthesis of 17. **K** (334 mg, 0.645 mmoles) was combined with 1-butylimidazole (1.22 g, 9.83 mmoles) K_2CO_3 (111 mg, 0.803 mmoles), and MgSO_4 (22 mg, 0.183 mmoles) under argon in a 20 mL scintillation vial. The mixture was sealed and heated to 80 °C while stirring for 48 h. Solids were removed by centrifugation and washed with acetone. Then, the crude liquid phase and acetone washes were combined, solvent was removed *in vacuo*, then the mixture washed with 3x10 mL hexanes. Then, the crude product was purified by flash column chromatography (10 g silica, gradient eluent EtOAc \rightarrow acetone) and concentrated under vacuum to afford 380 mg **17** (100 %) as an amber oil. ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 9.15-9.08 (s, 1H), 7.82-7.72 (s+s, 2H overlapping), 4.40-4.29 (t, 2H), 4.25-4.14 (t, 2H), 3.84-3.73 (t, 2H), 3.62-3.43 (br m, 12H), 3.43-3.34 (t, 2H), 3.01-2.94 (t, 2H), 1.84-1.64 (br m, 4H), 1.63-1.50 (m, 2H), 1.33-1.19 (m, 2H), 0.96-0.84 (t, 3H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 136.30 (s, 1C), 124.99-115.31 (q, 1C, CF_3), 122.83 (s, 1C), 122.16 (s, 1C), 69.81 (s, 2C overlapping), 69.78 (s, 1C), 69.71 (s, 1C), 69.61 (s, 1C), 69.54 (s, 1C), 69.51 (s, 1C), 68.06 (s, 1C), 54.36 (s, 1C), 48.85 (s, 1C), 48.57 (s, 1C), 31.36 (s, 1C), 27.87 (s, 1C), 20.79 (s, 1C), 18.75 (s, 1C), 13.21 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -77.54 (s 3F). ESI (m/z): 568.1989 ($\text{C}_{20}\text{H}_{37}\text{F}_3\text{N}_3\text{O}_8\text{S}_2^+$, calculated 568.1969).

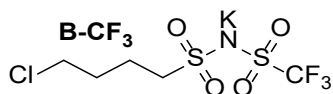


Synthesis of 18. 6.898 g (13.3 mmol) **K** was combined with 2.304 g (13.5 mmol) **L** in a 20 mL scintillation vial under argon, then sealed and stirred at 80 °C for 88 h, then removed from heat and ran 8x (dilute to 10 mL in acetone, precipitate in 35 mL Et_2O , centrifuge, decant buoyant phase). Then, added 12.5 g silica gel, stirred for 12 h in EtOAc to encourage adsorption, added the crude product-silica slurry to a column packed in EtOAc, and purified by silica gel column chromatography using a gradient EtOAc \rightarrow 3:1 EtOAc:acetone eluent, removed most solvent via rotary evaporator, dried over MgSO_4 , then removed remaining solvent via vacuum oven (115 °C) to afford **18** as an amber oil in 3.48 g (42 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 9.11-9.02 (m, 1H), 7.79-7.69 (m, 2H), 4.43-4.32 (t, 4H), 3.83-3.74 (q, 4H), 3.59-3.44 (br m, 14H), 3.44-3.35 (br m, 4H), 3.25-3.19 (s, 3H), 3.02-2.94 (m, 2H), 1.77-1.65 (m, 2H), 1.63-1.51 (m, 2H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 136.66 (s, 1C, aromatic), 125.01-115.33 (q, 1C, CF_3), 122.63 (s, 1C, aromatic), 122.49 (s, 1C, aromatic), 71.09 (s, 1C), 69.83 (s, 2C overlapping), 69.79 (s, 1C), 69.73 (s, 1C), 69.63 (s, 1C), 69.57

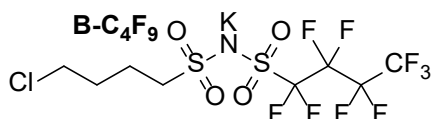
(s, 1C), 69.52 (s, 1C), 69.40 (s, 1C), 68.14 (s, 2C overlapping), 58.05 (s, 1C), 54.38 (s, 1C), 48.87 (s, 1C), 48.85 (s, 1C), 27.88 (s, 1C), 20.81 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.55 (s, 3F). ESI (m/z): 614.2044 ($\text{C}_{21}\text{H}_{39}\text{F}_3\text{N}_3\text{O}_{10}\text{S}_2^+$, calculated 614.2023)



Synthesis of A. 197.6 g (1.45 moles) 1,4-butanediol was combined with 15 mL (194 mmoles) DMF, and 500 mL (6.85 moles) thionyl chloride in a 3 L round-bottom flask fitted with a reflux condenser, a vacuum trap, and a gas scrubber to neutralize the evolved acidic vapor. and heated to reflux for 1 week. Then, the reaction was cooled to 0 °C and quenched by incrementally adding ice while stirring vigorously. When gas stopped evolving, the mixture was returned to 20 °C and washed with 4 x 750 mL reverse osmosis water, dried over MgSO_4 , and concentrated under reduced pressure to afford **A** (218.9, 69 %) as a yellow oil. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.63-3.52 (t, 2H), 2.71-2.61 (t, 2H), 1.82-1.62 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ) 50.89 (s, 1C), 45.56 (s, 1C), 31.38 (s, 1C), 22.50 (s, 1C).

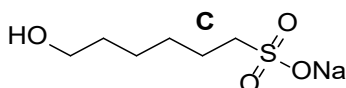


Synthesis of B-CF₃. 218.7 g (1.14 moles) **A** was combined with 206.7 g (1.39 moles) triflamide, 1 L acetonitrile and 36.4 g (302 mmoles) magnesium sulfate, and stirred until triflamide was fully solvated, then cooled to 0 °C while stirring. Then, 675.8 g (4.89 moles) K_2CO_3 was added incrementally over 2.5 h while maintaining a temperature of 0 °C. The mixture was allowed return to room temperature while stirring for 64 h, then stopped by filtering out solids and blowing off solvent via air stream. The resulting brown paste was washed with 3 x 500 mL Et_2O , then acidified with 800 mL (14 moles) acetic acid and diluted with an additional 800 mL of acetone. The mixture was stirred until all visible solid pieces dissolved, then concentrated under air stream to afford a tan paste. This was washed with 3 x 1.5 L Et_2O , then taken up in 1.5 L acetone, basified with 569 g (4.12 moles) K_2CO_3 , and stirred vigorously for 19 hours before filtering out solids and concentrating the filtrate via air stream. The resulting solid was washed with 1 L Et_2O and placed under reduced pressure to afford **B-CF₃** as a white, crystalline powder (257.5 g, 66 %). ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.71-3.59 (t, 2H), 3.06-2.94 (t, 2H), 1.88-1.73 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 124.97-115.30 (q, 1C), 53.69 (s, 1C), 44.97 (s, 1C), 30.63 (s, 1C), 21.31 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.49 (s, 3F). ESI (m/z): 301.9545 ($\text{C}_5\text{H}_8\text{ClF}_3\text{NO}_4\text{S}_2^-$, calculated 301.9530).

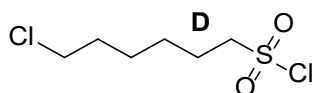


Synthesis of B-C₄F₉. **A** (40 g of 86 wt % solution in acetonitrile, 180 mmoles) was combined with 30.374 g (102 mmoles) **M** and 100 mL acetonitrile, then stirred until **M** was solvated. Then, the reaction was cooled to 0 °C under argon and 60.8 g (440 mmoles) K_2CO_3 was added. The reaction was allowed to return to room temperature while stirring for 96 h, then the solids were removed by filtration. The filtrate was concentrated under air stream, washed with 4x100 mL of dichloromethane, and placed under vacuum to afford **B-C₄F₉** as a tan powder (40.6 g, 88 %). ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.70-3.60 (t, 2H), 3.06-

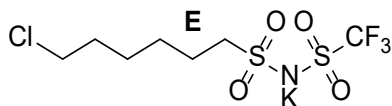
2.95 (t, 2H), 1.89-1.75 (m, 4H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 120-105 (br m, 4C, fluorinated), 53.97 (s, 1C), 44.95 (s, 1C), 30.65 (s, 1C), 21.32 (s, 1C). ^{19}F NMR (376.5 MHz, $\text{DMSO-}d_6$, δ): -80.49 (m, 3F), -112.90 (m, 2F), -120.99 (m, 2F), -125.72 (m, 2F). ESI (m/z): 451.9455 ($\text{C}_8\text{H}_8\text{ClF}_9\text{NO}_4\text{S}_2^-$, calculated 451.9434).



Synthesis of C. 10.00 g (73.2 mmol) 6-chloro-1-hexanol was combined with 10.45 g (82.9 mmol) sodium sulfite and deionized water (56.35 g) and refluxed at 120 °C for 24 h before removing water via air stream at 90 °C and washing the resulting white powder with 4 x 40 mL MeOH. MeOH was removed from the combined washes via air stream, then the resulting white solid was crushed and placed under reduced pressure to afford **C** as a white powder in 11.3 g (76 %) yield. ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 3.40-3.32 (t, 2H), 2.47-2.39 (m, 2H), 1.62-1.49 (m, 2H), 1.45-1.34 (m, 2H), 1.34-1.19 (m, 4H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 60.77 (s, 1C), 51.49 (s, 1C), 32.47 (s, 1C), 28.38 (s, 1C), 25.43 (s, 1C), 25.11 (s, 1C). ESI (m/z): 181.0541 ($\text{C}_6\text{H}_{13}\text{O}_4\text{S}^-$, calculated 181.0529).

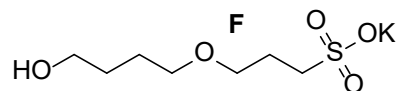


Synthesis of D. 16.9 g (82.8 mmol) **C** was dried via azeotropic distillation of toluene (100 mL), then combined with dry DMF (8.5 mL, 110 mmol) and thionyl chloride (60 mL, 823 mmol) under argon in a 500 mL round-bottom flask fitted with a reflux condenser, a vacuum trap, and a gas scrubber to neutralize the evolved acidic vapor. Then, the mixture was stirred at 20 °C for 15 minutes before heating to reflux. After 27 h, an additional 60 mL (823 mmol) of thionyl chloride was added and the reflux continued for another 21 h before returning to room temperature, cooling to 0 °C, and quenching excess thionyl chloride by incremental addition of ice with vigorous stirring. The mixture was returned to 20 °C and extracted into 3 x 100 mL of Et_2O , then the combined organic washes were dried over MgSO_4 and concentrated under vacuum to afford crude **D** as a yellow oil (22.4 g, exceeding theoretical yield due to impurities). ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 3.60-3.50 (t, 2H), 2.70-2.60 (m, 2H), 1.72-1.50 (m, 4H), 1.42-1.24 (m, 4H). ^{13}C NMR (100.6 MHz, $\text{DMSO-}d_6$, δ): 51.57 (s, 1C), 45.63 (s, 1C), 32.29 (s, 1C), 27.60 (s, 1C), 26.35 (s, 1C), 24.63 (s, 1C).

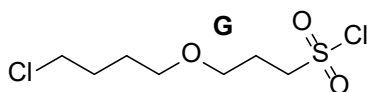


Synthesis of E. 22.4 g (102 mmol) crude **D** was combined with triflamide (18.3 g, 123 mmol), 4.02 g (33.3 mmol) MgSO_4 , and 100 mL acetonitrile in a 500 mL round-bottom flask. Then, the reaction was started by adding 59.3 (429 mmol) of K_2CO_3 . After stirring at 20 °C for 24 h, the solids were removed by filtration and solvent evaporated via air stream. Then, the mixture was washed with 3 x 100 mL of Et_2O , re-diluted to 200 mL in acetone, and acidified by adding 17.5 mL (306 mmol) glacial acetic acid. The solvent was then evaporated via air stream and the crude mixture washed with another 3 x 100 mL Et_2O , re-dissolved in acetone, filtered to remove solid precipitate, and basified with 34.6 g (250 mmol) of K_2CO_3 . The mixture was stirred vigorously for 18 h, then solids were removed by filtration and concentrated via air stream to afford **E** as a tan powder (20.82 g, 55 %). ^1H NMR (400.2 MHz, $\text{DMSO-}d_6$, δ): 3.67-3.58 (t, 2H),

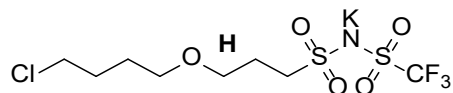
3.00-2.90 (m, 2H), 1.77-1.59 (m, 4H), 1.44-1.31 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 124.99-115.32 (q, 1C), 54.38 (s, 1C), 45.28 (s, 1C), 31.82 (s, 1C), 26.91 (s, 1C), 25.89 (s, 1C), 23.54 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.53 (s, 3F). ESI (m/z): 329.9856 ($\text{C}_7\text{H}_{12}\text{ClF}_3\text{NO}_4\text{S}_2^-$, calculated 329.9843).



Synthesis of F. 22.6 g (251 mmoles) 1,4-butanediol was added to a dry, 250 mL round-bottom flask under argon atmosphere and dried by azeotropic distillation with toluene. Then, 50 mL (50 mmoles) 1M *t*-BuOK in THF was added dropwise over 20 minutes, followed by 1,3-butanedisulfone (7.10 g, 58.1 mmoles). The reaction was allowed to stir for 2 h at room temperature before diluting in 150 mL acetone and filtering to collect solids. These were washed with 2x100 mL acetone, then placed under vacuum to remove trace solvent to afford 11.4 g (91 %) of **F** as a powdery white solid. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 4.43-4.38 (t, 1H), 3.42-3.29 (m, 6H), 2.59-2.43 (m, 2H), 1.88-1.71 (m, 2H), 1.60-1.34 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 69.93 (s, 1C), 69.23 (s, 1C), 60.68 (s, 1C), 48.50 (s, 1C), 29.36 (s, 1C), 26.00 (s, 1C), 25.69 (s, 1C). ESI (m/z): 211.0647 ($\text{C}_7\text{H}_{15}\text{O}_5\text{S}^-$, calculated 211.0635).

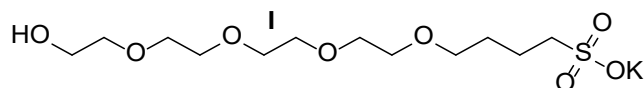


Synthesis of G. 11.1 g (44.3 mmoles) **F** was azeotropically distilled with toluene in a 250 mL round-bottom flask fitted with a reflux condenser, a vacuum trap, and a gas scrubber to neutralize acidic vapor. Then, thionyl chloride (64 mL, 877 mmoles) and DMF (4.5 mL, 58.1 mmoles) were added and the solution refluxed at 80 °C for 48 h before cooling to 0 °C and quenching by gradual addition of ice pellets. Crude product was extracted into 3x50 mL of diethyl ether, and the combined organic washes were dried over MgSO_4 and concentrated under vacuum to afford crude **G** as a yellow oil in 12.6 g (100%) crude yield. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.65-3.57 (t, 2H), 3.44-3.29 (m, 4H), 2.69-2.60 (m, 2H), 1.86-1.67 (m, 4H), 1.62-1.52 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 69.34 (s, 1C), 68.83 (s, 1C), 48.63 (s, 1C), 45.54 (s, 1C), 29.40 (s, 1C), 26.82 (s, 1C), 25.35 (s, 1C).

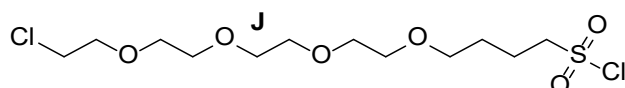


Synthesis of H. 12.6 g (50.6 mmoles) crude **G** was combined with 53 mL acetonitrile, 3.255 g (27.0 mmoles) MgSO_4 , and 9.45 g (63.4 mmoles) triflamide in a 250 mL round-bottom flask and stirred until a homogeneous white dispersion. Then, K_2CO_3 was incrementally added and then the mixture was allowed to stir for 24 h at 20 °C. The solids were removed by filtration and washed with acetone. The filtrate and acetone washes were combined, and solvent was removed via air stream. The resulting tan solid was washed with hexanes and passed over a plug of silica (40 g silica, acetone eluent), then combined with 7.4 mL (129 mmoles) acetic acid, concentrated via air stream, and washed with 3x50 mL Et_2O . The product was purified by flash column chromatography (silica gel stationary phase, EtOAc eluent) and concentrated under reduced pressure to afford **H** (8.5 g, 42 %) as a soft brown solid. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.68-3.61 (t, 2H), 3.47-3.40 (t, 2H), 3.40-2.94 (t, 2H), 3.03-2.94 (m, 2H), 1.93-1.82 (m, 2H), 1.82-1.71 (m, 2H), 1.66-1.55 (m, 2H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 124.97-115.29 (q, 1C), 69.04 (s, 1C), 68.14 (s,

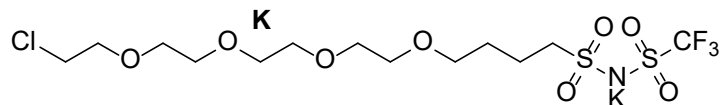
1C), 51.78 (s, 1C), 45.31 (s, 1C), 29.10 (s, 1C), 26.53 (s, 1C), 24.29 (s, 1C). ^{19}F NMR (376.5 MHz, DMSO- d_6 , δ): -77.53 (s, 3F). ESI (m/z): 359.9980 ($\text{C}_8\text{H}_{14}\text{ClF}_3\text{NO}_5\text{S}_2^-$, calculated 359.9949).



Synthesis of I. 430.6 g (2.22 moles) TetrEG, 60.2 g (442 mmoles) 1,4-butanedisulfone, and 440 mL THF were combined in a 3 L round-bottom flask and stirred until homogeneous. The mixture was cooled to 0 °C under argon and the reaction was started by adding 75.3 g (1.34 moles) KOH. The reaction was allowed to return to 20 °C over 24 h, then cooled again to 0 °C and quenched by adding 83.2 g (1.39 moles) glacial acetic acid. The crude product mixture was washed with 2x1 L hexanes and 3x1 L EtOAc before purifying via flash column chromatography (gradient eluent THF \rightarrow 2:1 EtOAc:acetone) and concentrating via rotovap and then vacuum oven (100 °C) to afford **I** as a faintly amber solid in 133.5g (82 %) yield. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.63-3.30 (m, 18H), 2.62-2.52 (m, 2H), 1.68-1.48 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 72.37 (s, 1C), 70.09-69.52 (m, 7C), 60.25 (s, 1C), 51.20 (s, 1C), 28.34 (s, 1C), 21.70 (s, 1C). ESI (m/z): 329.1281 ($\text{C}_{12}\text{H}_{25}\text{O}_8\text{S}$, calculated 329.1265).

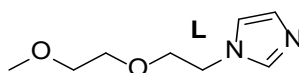


Synthesis of J. 133.5 g (362 mmoles) **I** was combined with 22 mL (284 mmoles) DMF in a 3 L round-bottom flask under argon. The flask was fitted with a reflux condenser with a gas outlet routed through a vacuum trap and a gas scrubber composed of a glass sparger submerged in 5 L of 5M KOH to prevent release of concentrated acid vapor. Then, 500 mL (5.5 moles) thionyl chloride was added. After the reaction finished bubbling, it was heated to reflux for 72 h before returning to room temperature and quenching by incremental addition of ice pellets with vigorous stirring. After complete quenching of residual thionyl chloride, another 100 mL of water was added and the mixture was stirred vigorously for 20 minutes before extracting with 3x 500 mL Et₂O. The extracted organic phase was transferred to a 3L round-bottom flask with 51 g (42.4 mmoles) MgSO₄ and concentrated under reduced pressure before purifying via silica gel column chromatography (silica gel stationary phase, gradient eluent hexanes \rightarrow 4:1 Et₂O:hexanes) and concentrating under reduced pressure to afford **J** in 64.2 g (48 %) yield. ^1H NMR (400.2 MHz, DMSO- d_6 , δ): 3.74-3.61 (m, 4H), 3.61-3.41 (m, 12H), 3.41-3.31 (m, 2H), 2.68-2.57 (m, 2H), 1.69-1.49 (m, 4H). ^{13}C NMR (100.6 MHz, DMSO- d_6 , δ): 70.61 (s, 1C), 70.05-69.55 (q, 7C), 51.20 (s, 1C), 43.65 (s, 1C), 28.27 (s, 1C), 21.58 (s, 1C).

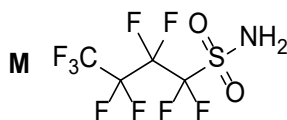


Synthesis of K. 64.2 g (175 mmoles) **J** was combined with 31.35 g (210 mmoles) triflamide, 30.8 g (256 mmoles) MgSO₄, and 174 mL acetonitrile under argon. The mixture was stirred until triflamide was solvated, then cooled to 0 °C and 101.5 g (735 mmoles) K₂CO₃ was added to start the reaction. The mixture was allowed to return to room temperature over 24 hours, then stirring stopped to allow the mixture to settle. Then, the liquid phase was decanted through a vacuum filtration apparatus and the solids washed with acetone until the wash solution came away colorless. The combined liquid phase and acetone washes were acidified with 36 mL (630 mmoles) AcOH and concentrated under reduced pressure. Then the mixture was

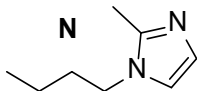
washed with 3x300 mL hexanes and 5x300 mL Et₂O. Due to product precipitation during the Et₂O washes, we ran them by stirring vigorously in a round-bottom flask (rather than shaking in a separatory funnel), then stopping the stir bar to allow phase separation, and decanting the buoyant phase. The crude product was then dissolved in EtOAc, then 164 g silica gel was added and the mixture stirred for 12 h before adding the slurry to the top of a silica gel column and purifying with a gradient eluent (EtOAc → acetone). The product fractions were concentrated under reduced pressure and basified by adding 25.3 g (183 mmol) K₂CO₃ and 2.23 g (19 mmol) MgSO₄ and stirring vigorously for 12 hours before filtering out solids, washing solids with acetone, combining product solution and acetone washes, concentrating under reduced pressure, and precipitating in Et₂O to afford **K** as a tan powder in 42.8 g (47 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 3.75-3.63 (m, 4H), 3.61-3.43 (m, 12H), 3.43-3.34 (t, 2H), 3.02-2.91 (m, 2H), 1.77-1.63 (m, 2H), 1.63-1.52 (m, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 125.46-115.78 (q, 1C), 70.99-69.95 (m, 8C), 54.81 (s, 1C), 44.03 (s, 1C), 28.35 (s, 1C), 21.21 (s, 1C). ¹⁹F NMR (376.5 MHz, DMSO-*d*₆, δ): -77.50 (s, 3F). ESI (m/z): 478.0601 (C₁₃H₂₄ClF₃NO₈S₂⁻, calculated 478.0578).



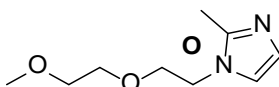
Synthesis of L. 10.059 g (148 mmol) imidazole was stirred in 125 mL acetonitrile until fully dissolved, affording a clear, colorless solution. Then, 41.289 g (736 mmol) KOH was added and allowed to stir for 25 minutes, affording a colorless, opaque mixture., followed by 30.832 g (168 mmol) MEE-Br was added dropwise over 5 minutes to start the reaction. The mixture was allowed to stir for 24 h at 20 °C before decanting the yellow product solution, concentrating via air stream while stirring over MgSO₄, and then purified by flash column chromatography (silica gel stationary phase, gradient EtOAc → 6:1 EtOAc:MeOH eluent) and concentrated under reduced pressure to afford **L** as an amber oil in 23.232 g (92 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 7.62-7.56 (s, 1H), 7.18-7.13 (m, 1H), 6.89-6.84 (m, 1H), 4.13-4.07 (t, 2H), 3.69-3.63 (t, 2H), 3.53-3.48 (m, 2H), 3.44-3.38 (m, 2H), 3.25-3.20 (s, 3H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 137.47 (s, 1C), 128.12 (s, 1C), 119.60 (s, 1C), 71.19 (s, 1C), 69.81 (s, 1C), 69.44 (s, 1C), 58.08 (s, 1C), 45.95 (s, 1C). ESI (m/z): 171.1147 (C₈H₁₅N₂O₂⁺, calculated 171.1128).



Synthesis of M. 254.55 g (843 mmol) perfluorobutanesulfonyl fluoride was added to a 3 L round-bottom flask. Then, 1 L of 1 M Li-HMDS in THF was added by cannula transfer with vigorous stirring over 6 h and allowed to stir for 24 h before reducing the volume to ~500 mL via air stream. Then, 700 mL of 6 N HCl was added over the course of 1 day. The organic phase was collected, then the aqueous phase washed with 4x 75 mL of Et₂O; the organic phase and Et₂O washes were combined and stirred over anhydrous sodium sulfate and activated charcoal, stirred for 24 h, and passed over a plug of celite and concentrated by stirring under reduced pressure to afford **M** as a tacky brown-orange powder in 233 g (92 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 9.26-8.99 (s, 2H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 121.6-104.6 (br m, 4C). ¹⁹F NMR (376.5 MHz, DMSO-*d*₆, δ): -80.56 (m, 3F), -114.18 (m, 2F), -121.28 (m, 2F), -125.89 (m, 2F). ESI (m/z): 297.9594 (C₄HF₉NO₂S⁻, calculated 297.9579).



Synthesis of **N.** 13.075 g (159 mmol) 2-methylimidazole, 23.958 g (175 mmol) 1-bromobutane, and 80 mL THF were combined in a 250 mL round-bottom flask and stirred until homogeneous. 22.632 g (403 mmol) KOH was added to start the reaction, the mixture was stirred for 17 h at 20 °C, and the solvent removed via forced air stream over 3 h. The resulting red oil was decanted and the remaining solids washed with 4 x 30 mL Et₂O. The decanted oil and Et₂O washes were combined and dried over MgSO₄, then centrifuged, decanted, and concentrated under reduced pressure. The resulting brown oil was extracted into 4x70 mL hexanes and concentrated under reduced pressure to afford **N** as a brown oil in 18.541 g (37 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 7.04-6.97 (d, 1H), 6.75-6.67 (d, 1H), 3.89-3.78 (t, 2H), 2.30-2.21 (s, 3H), 1.67-1.55 (m, 2H), 1.32-1.19 (m, 2H), 0.94-0.83 (t, 3H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 143.90 (s, 1C), 126.57 (s, 1C), 119.89 (s, 1C), 45.32 (s, 1C), 32.80 (s, 1C), 19.68 (s, 1C), 13.91 (s, 1C), 13.02 (s, 1C). ESI (m/z): 139.1236 (C₈H₁₅N₂⁺, calculated 139.1230).



Synthesis of **O.** 1.012 g (12.3 mmol) 2-methylimidazole was combined with 2.488 g (13.6 mmol) MEE-Br and 12.2 mL acetonitrile and stirred until homogeneous. The reaction was started by adding 1.860 g (33.1 mmol) KOH and allowed to stir at 20 °C for 18 h before centrifuging to remove solids, concentrating under reduced pressure, washing with 3x2 mL hexanes, and extracting into 5x3 mL Et₂O to afford **O** as a brown oil in 1.1 g (48 %) yield. ¹H NMR (400.2 MHz, DMSO-*d*₆, δ): 7.05-7.01 (d, 1H), 6.73-6.68 (d, 1H), 4.05-3.97 (t, 2H), 3.68-3.60 (t, 2H), 3.51-3.46 (m, 2H), 3.44-3.37 (m, 2H), 3.24-3.19 (s, 3H), 2.29-2.25 (s, 3H). ¹³C NMR (100.6 MHz, DMSO-*d*₆, δ): 144.07 (s, 1C), 126.02 (s, 1C), 119.78 (s, 1C), 71.24 (s, 1C), 69.86 (s, 1C), 69.61 (s, 1C), 58.10 (s, 1C), 45.23 (s, 1C), 12.66 (s, 1C). ESI (m/z): 185.1288 (C₉H₁₇N₂O₂⁺, calculated 185.1285).

Supplemental Notes

DC conductivity, electrode polarization, and $\tan(\delta)$. Complex conductivity was calculated according to $\sigma^* = i\omega\epsilon_0\epsilon^*$ and is shown in **Fig S5**.¹ The lower frequency range captures the onset of apparent DC conductivity (σ_{DC}), shown in **Fig 6b** as a straight, negative-sloping line and in **Fig S5a** as a low-frequency plateau. The exception is control ZI **3**, which does not fully plateau before the lowest frequency ($\nu = 20$ Hz, $\omega = 126$ rad s⁻¹) accessible to our instrument. Molecules **17** and **18** have sufficiently fast dynamics that we fully visualize the entire plateau before electrode charging begins to dominate, shown by a positive slope in **Fig S5a** for $\omega(\mathbf{18}) < 1000$ rad s⁻¹ and $\omega(\mathbf{17}) < 300$ rad s⁻¹. For ZI **10** and ZILs **13**, **14**, and **15**, the accessible frequency range captured enough of the plateau region to confidently estimate σ_{DC} but did not capture the transition from conductivity-dominated to electrode charging-dominated behavior. Among the six molecules for which this plateau is visible, σ_{DC} varied dramatically from 1.7 (ZI **10**) to 120 $\mu\text{S m}^{-1}$ (ZIL **18**). However, we emphasize, in agreement with a previous report on solvated and supercooled imidazolium sulfonate zwitterions, that this does not imply long-range ion transport in these systems.² Rather, because the molecules are net-charge-neutral, this value captures the aggregate contribution of a series of enormous dipoles, which, when driven to align in an electric field, afford a large *apparent* conductivity on the timescales of dipole alignment. For completeness, the imaginary part of $\sigma^*(\omega)$ is shown in **Fig S5b**.

The dielectric loss tangent $\tan(\delta)$ is shown in **Fig S5c**. For all molecules but control ZI **3**, it shows two maxima that we attribute to bulk polarization by dipole alignment (high frequency) and the onset of apparent DC conductivity (low frequency). The low-frequency peak is not fully resolved for molecules **10**, **13**, **14**, and **15**, and only a tail is visible for control ZI **3** due to its slow dynamics. At the high-frequency range, **18** shows the shoulder of an additional peak that is not fully resolved in the accessible frequency range but suggests an additional relaxation event that is also partially visible in the real permittivity of **Fig 6a**. Such complex behavior is unsurprising given the length and flexibility of the dipole in **18**, which likely samples a wide distribution of conformational modes and dipole lengths, in addition to carrying smaller local dipoles throughout the molecule, including within each charged end-group.^{3,4}

Water uptake from ambient humidity. To quantify water uptake in a humid environment, samples of crystalline ZI **10** and ZILs **15** and **18** were first dried in a vacuum oven at 115 °C, then characterized by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). Then, 500 mg of each molecule was equilibrated at 100% relative humidity for 1 week before repeating FTIR, TGA, and (for liquids **15** and **18**) dielectric relaxation spectroscopy and viscosity measurements. To maximize the surface area of solid **10**, the sample was ground to a fine powder in a mortar and pestle before humidifying.

Water uptake was quantified by TGA (**Fig S6**). Thermograms of samples dried in a vacuum oven showed negligible weight change below 300 °C (**Fig S6a**). By contrast, the humidified samples (**Fig S6b**) showed large variability in behavior. Humidified powder **10** afforded a nearly identical thermogram to the dried sample (*i.e.*, negligible mass loss below 300 °C), suggesting no water uptake. By contrast, humidified ZILs **15** and **18** showed considerable mass loss below 150 °C that we attribute to absorbed water. This difference in behavior between crystalline and liquid materials suggests that crystallinity of **10** stabilizes the material against water uptake, while the liquids are far more susceptible to environmental humidity. **Fig S6c** tabulates the remaining weight percent of each material at 100, 200, and 300 °C in the “dried” and “humidified” states. By 200 °C, dried molecules **10**, **15**, and **18** have lost 0.6, 0.5, and 0.5 weight percent of their original mass, respectively. This suggests a quite small amount of residual volatiles, including water, after drying in the vacuum oven. At the same temperature, the humidified samples have lost 0.5, 16.3, and 22.1 weight percent of their initial mass, respectively, supporting the idea that the liquids adsorb water in humid environments.

FTIR spectroscopically confirms negligible water content in all three molecules after 24 h at 115 °C, and that **15** and **18** readily adsorb atmospheric moisture, while crystalline **10** does not (**Fig S7**). For all three molecules, the dried “as synthesized” samples show a negligible O-H stretch at ~3400 wavenumbers. For **10**, this remains unchanged after 1 week at 100% relative humidity, but strong O-H stretches emerge for both **15** and **18**.

Fig S8 shows shear-rate-dependent viscosity of ZILs **15** and **18** i) “as synthesized,” immediately after their original synthesis and purification, ii) after 9 (ZIL **15**) and 6 (ZIL **18**) months of storage in a vacuum desiccator, and iii) after 1 week in 100% relative humidity. After humidification, both samples exhibit a viscosity decrease of ~2 orders of magnitude compared to the “as synthesized” and “storage” samples, suggesting considerable water uptake.

NMR further supports negligible water content after drying in the vacuum oven. Our NMR spectra were all run in DMSO-*d*₆. Even dry DMSO kept in a desiccator and used under argon inevitably contributes a small amount of water, increasing the apparent water content. Despite this, the water peaks at ~3.3 ppm in the ¹H NMR spectra of all 18 zwitterions, particularly ZILs **13-18**, are negligible compared to the product peaks. This suggests, consistent with our TGA and FTIR results, that the water content after drying in a vacuum oven is negligible.

Finally, we replicated dielectric spectroscopy experiments with humidified **15** and **18**. The low-frequency end of the spectrum was dominated by electrode charging as characterized by $\epsilon' > 10,000$, while at high frequencies, ϵ' and ϵ'' were both negative. This suggests sufficiently low impedance that inductive effects from the coaxial cables dominated the measurement.^{1,5} As a result, these measurements reflect

artifacts of the measurement apparatus rather than material properties. Hence, we have not prepared a supplemental figure with this data.

Correlations in Viscosity, T_g , heat capacity, spacer length, and molecular weight. Several thermal and dynamic parameters showed interdependent behaviors and spacer-length-dependent trends. These are shown in **Figs S9-10** and discussed in this section.

Fig S9a shows that T_g correlates negatively with spacer length, decreasing by 11-21 °C as the spacer grows from four to sixteen atoms. To better understand this and the ZIL energy landscape, we quantified the change in heat capacity (ΔC_g) at T_g .⁶⁻⁸ For each DSC scan, we estimated the liquid ($C_{g,liq}$) and glass ($C_{g,gl}$) heat capacities at T_g by extrapolating the linear regions of the thermogram on either side of the transition. We then calculated $\Delta C_g = C_{g,liq} - C_{g,gl}$ on both specific ($\Delta C_{g,s}$, **Fig S9b**) and molar ($\Delta C_{g,m}$, **Fig S9c**) bases and found that ΔC_g shows a strong positive relationship with length and flexibility for both the *spacer* R_s and the *tail* R_t . This is intuitive on a molar basis, because a molecule with more rotatable bonds can access a broader range of structural and vibrational modes.⁹ However, it is striking that this trend holds on a specific basis, since it implies a net gain in available states despite fewer molecules per unit mass. This observation supports the hypothesis that, when transitioning from arrested to melt states, the magnitude of entropy gain *increases* with spacer length. **Fig S9d** shows a negative correlation between $\Delta C_{g,m}$ and T_g , as predicted by spacer length and an MEE tail. This trend suggests that T_g might be suppressed further by designing zwitterions with more rotatable bonds that unlock additional conformational entropy in the liquid state. Finally, viscosity at 22 °C correlates positively with T_g (**Fig S9e**) and negatively with $\Delta C_{g,m}$ (**Fig S9f**).

Fig S10 shows T_g (**Fig S10a**), $\Delta C_{g,m}$ (**Fig S10b**), and η (**Fig S10c**) as a function of zwitterion molecular weight. **Figs S10a-b** show data for sixteen of our eighteen zwitterions; we were unable to determine T_g for ZIs **4** and **9** because they recrystallized too quickly during the cooling cycle to trap them in the amorphous state (see DSC data at the end of this document or download our source data). The general trends are that T_g correlates negatively with molecular weight, while $\Delta C_{g,m}$ correlates positively. ZI **7** is an outlier in both data sets, with a larger T_g and a smaller $\Delta C_{g,m}$ than predicted by the trend of the other fifteen molecules. This outlier is instructive. Most of the molecular weight distribution across these 16 molecules can be attributed to changes in the tail or spacer length, which add a rotatable bond for every additional 14 (-CH₂-) or 16 (-O-) g mol⁻¹. By contrast, increasing the size of the perfluoroalkyl tail on the sulfonimide anion adds another 50 g mol⁻¹ (-CF₂-) for every rotatable bond. Moreover, we expect that the larger steric bulk of -CF₂- compared to -O- or -CH₂- will afford larger barriers to bond rotation, suggesting a smaller contribution to the conformational entropy and liquid heat capacity than methylene or ether groups. Finally, liquid viscosity correlates negatively with molecular weight for supercooled **3** and **10**, and ZILs **13**, **14**, **15**, **17**, and **18** (**Fig S10c**), supporting the idea that, in the context of ZILs, increasing molecular size via long, flexible tails and spacers can decrease viscosity.

Supplemental references

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Supplemental Figures

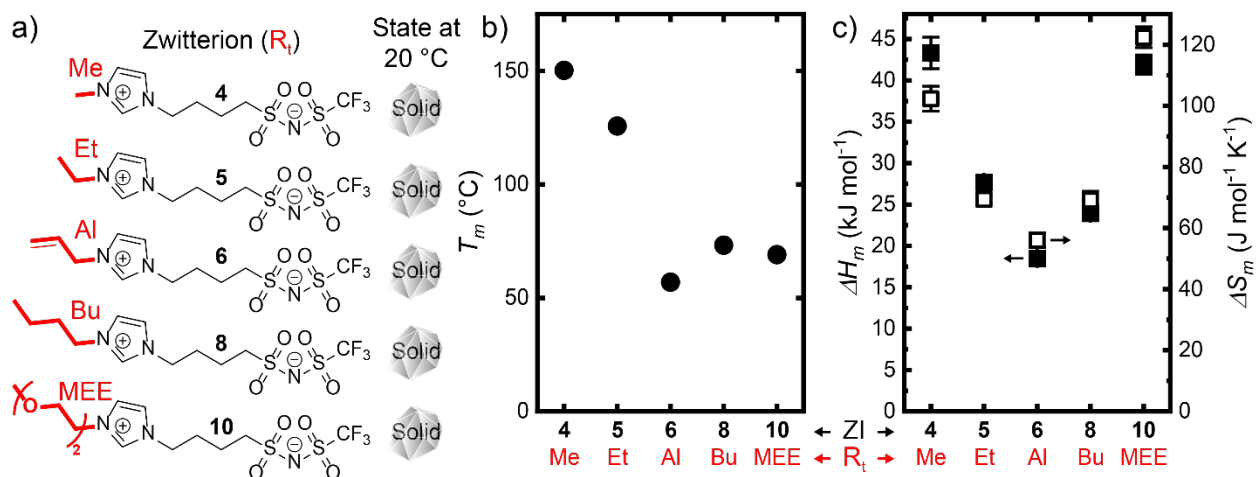


Figure S1. Imidazolium tail R_t impacts melting behavior of zwitterions. a) zwitterions **4**, **5**, **6**, **8**, and **10** were used to compare methyl (Me), ethyl (Et), allyl (Al), *n*-butyl (Bu) and (2-(2-methoxy)-ethoxy)-ethyl (MEE) tail groups to highlight their impact on (b) T_m , and (c) ΔH_m and ΔS_m . Data are represented as mean \pm SD, N = 3.

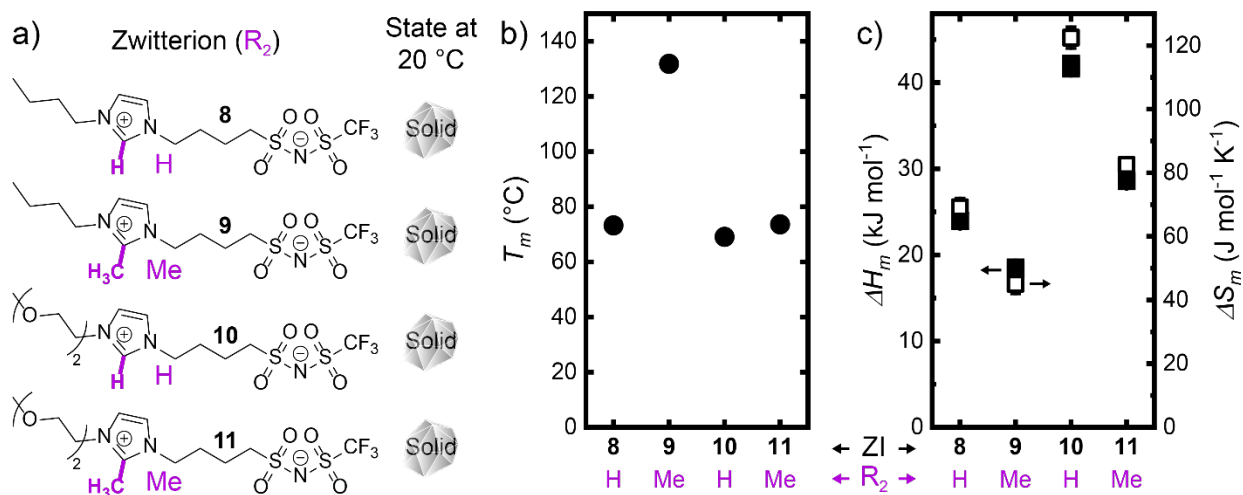


Figure S2. Imidazolium 2 position R_2 impacts melting behavior of zwitterions. a) zwitterions **8**, **9**, **10**, and **11** were used to compare proton (H) versus methyl (Me) at the 2 position on the imidazolium cation to highlight their impact on (b) T_m , and (c) ΔH_m and ΔS_m . Data are represented as mean \pm SD, N = 3.

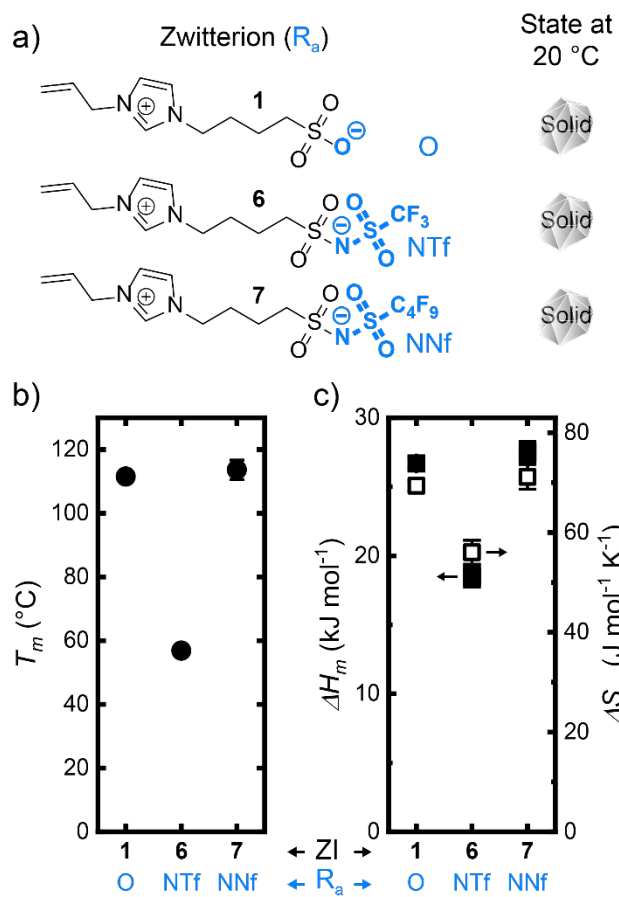


Figure S3. Anion R_a impacts melting behavior of zwitterions. a) zwitterions **1**, **6**, and **7** were used to compare sulfonate (O) triflimide (NTf), and nonaflimide (NNf), anions to highlight their impact on (b) T_m , and (c) ΔH_m and ΔS_m . Data are represented as mean \pm SD, N = 3.

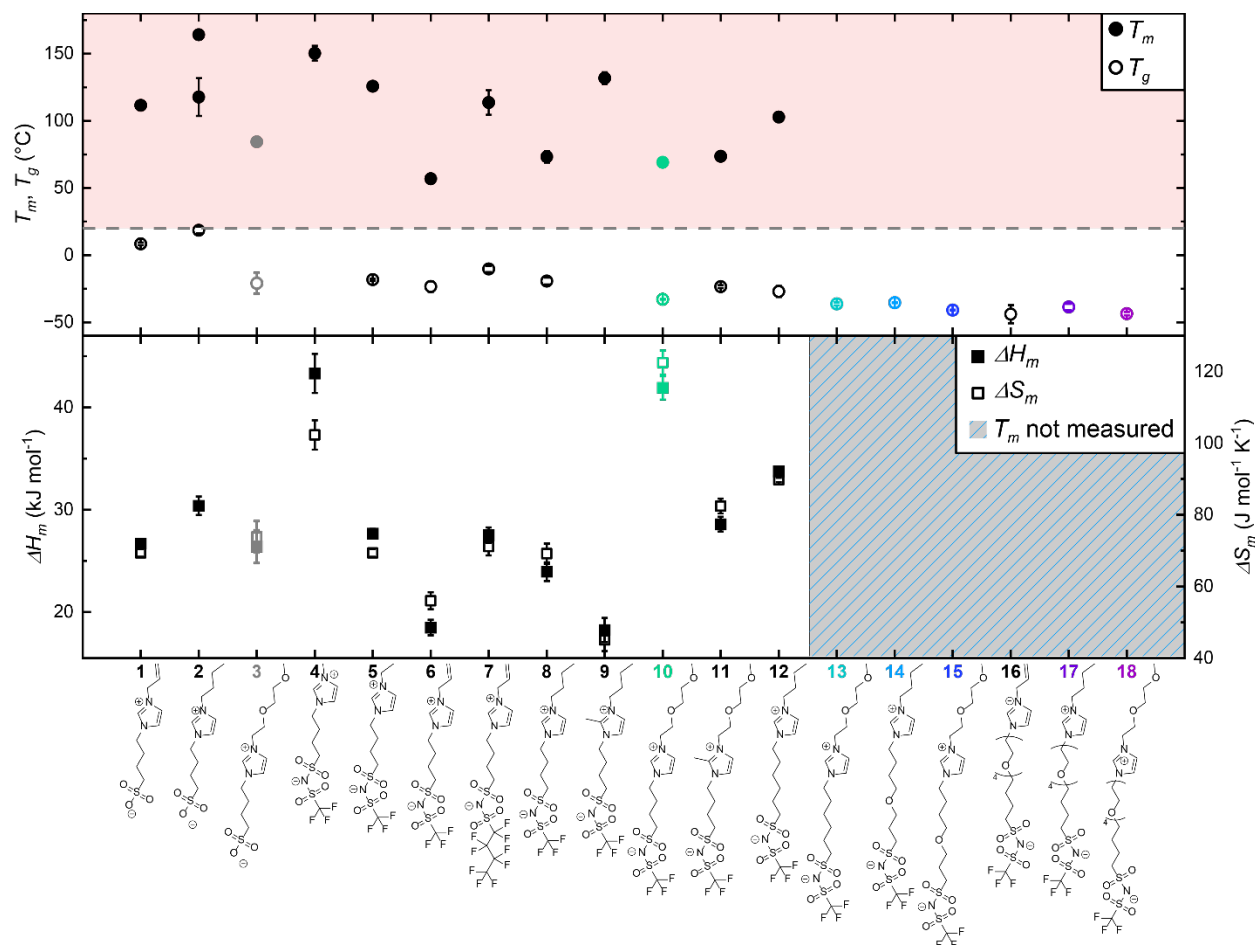


Figure S4. Thermal characterization of synthetic library of zwitterions. T_m , T_g (top) and ΔH_m , ΔS_m (bottom) of the eighteen molecules studied in this work. The dashed line represents 20 °C; molecules 1-12 exhibit $T_m > 20$ °C and reach thermodynamic minima as crystalline solids at room temperature. Molecules 13-18 were isolated as liquids and exhibited no crystallization when cycled to -90 °C at 10 °C min⁻¹ or when stored at 22 °C in a vacuum desiccator for at least 4 months. Data are represented as mean \pm SD, N = 3. Color-coding of molecules 3, 10, 13, 14, 15, 17, and 18 corresponds to Figs 5-6.

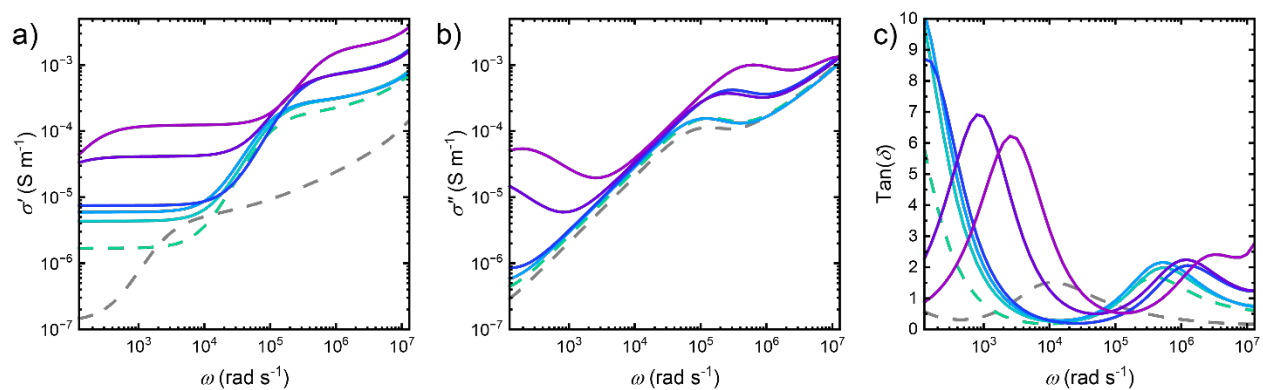


Figure S5. Additional electrical properties of neat zwitterions. (a) real σ' and (b) imaginary σ'' parts of conductivity at 25 °C for supercooled zwitterions: **3** and **10** and ZILs: **13-15**, **17**, and **18**; (c) dielectric loss tangent $\text{tan}(\delta)$ as a function of angular frequency ω . Dashed lines denote supercooled liquids; solid lines denote stable liquids. Color-coding is consistent with **Figs 5-6**.

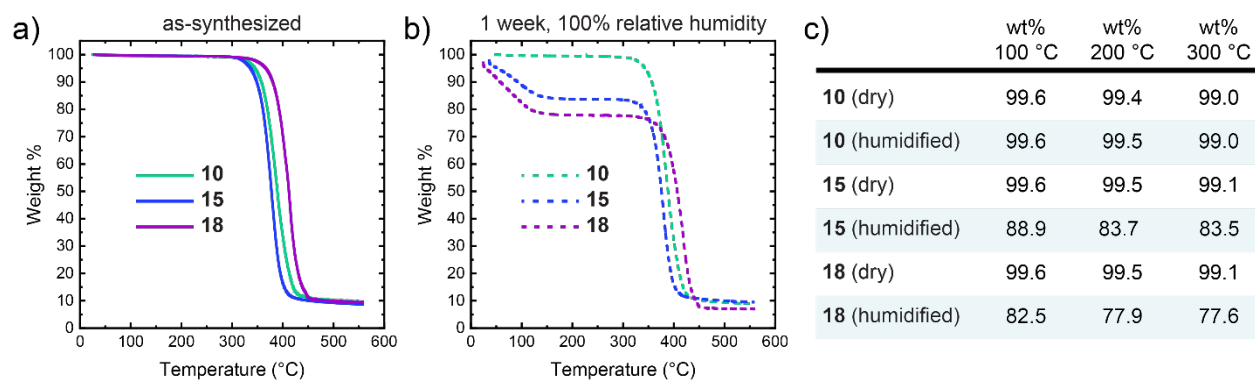


Figure S6. Thermogravimetric analysis of ZI **10** and ZILs **15** and **18**. a) as-synthesized after 24 h at 115 °C in a vacuum oven; b) after equilibrating for 1 week in 100% relative humidity; c) tabulated data for all 3 molecules in the dry and humidified state at 100, 200, and 300 °C.

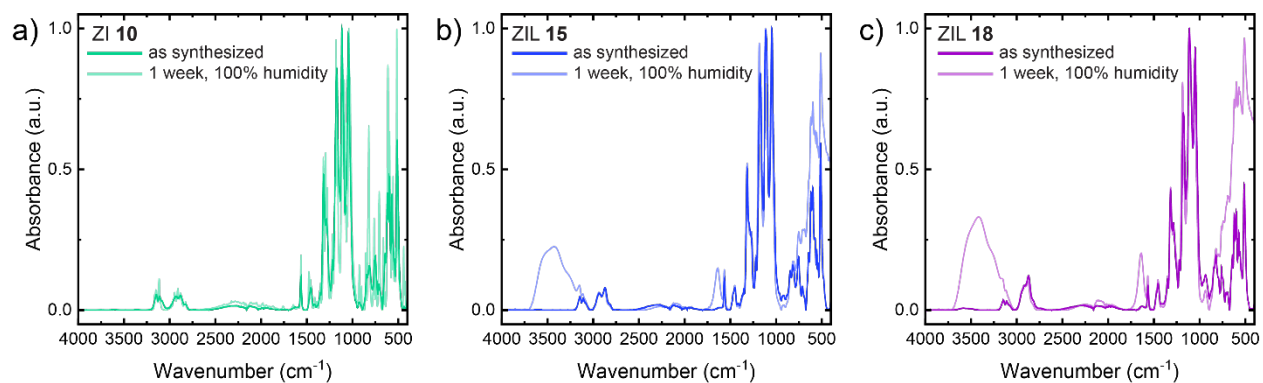


Figure S7. FTIR spectra of (a) ZI **10** and ZILs (b) **15** and (c) **18** as synthesized after 24 h at 115 °C in a vacuum oven (dark lines) and after 1 week in 100% relative humidity (light lines).

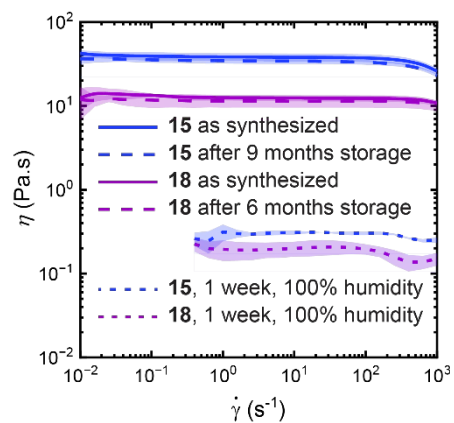


Figure S8. Apparent viscosity of **15** and **18** immediately after synthesis and purification (solid lines), after 9 (ZIL **15**) and 6 (ZIL **18**) months of storage (dashed line), and after equilibrating for 1 week in 100% relative humidity (dotted line). Data are shown as mean \pm SD, N = 3.

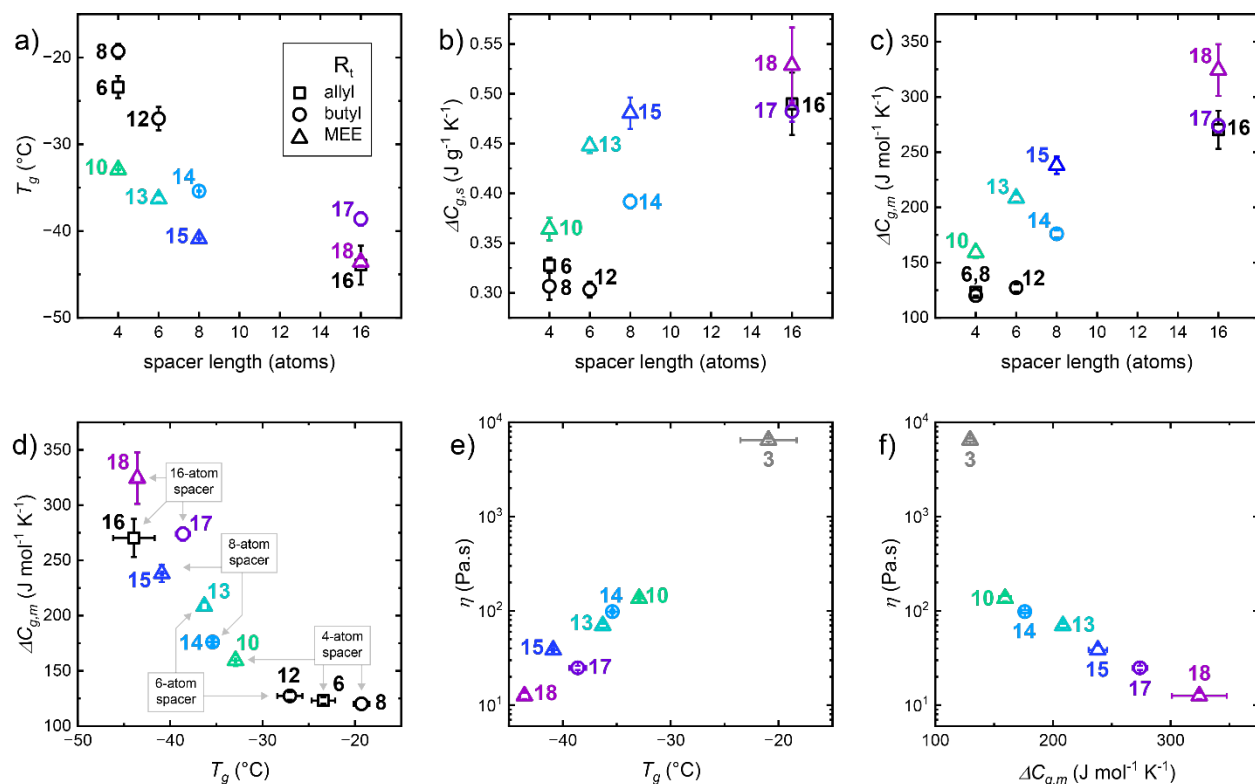


Figure S9. Viscosity, T_g , and spacer length correlations in reported zwitterions. a) T_g as a function of spacer length for zwitterions with R_t = allyl, butyl, and MEE; b) specific ($\Delta C_{g,s}$) and c) molar ($\Delta C_{g,m}$) heat capacity jump at T_g as a function of spacer length. d) $\Delta C_{g,m}$ as a function of T_g . Semilog plots of apparent viscosity at a shear rate of 1 s⁻¹ as a function of e) T_g , and f) $\Delta C_{g,m}$. Data are shown as mean \pm SD, $n = 3$. Color-coding of molecules **3**, **10**, **13**, **14**, **15**, **17**, and **18** corresponds to **Figs 5-6**.

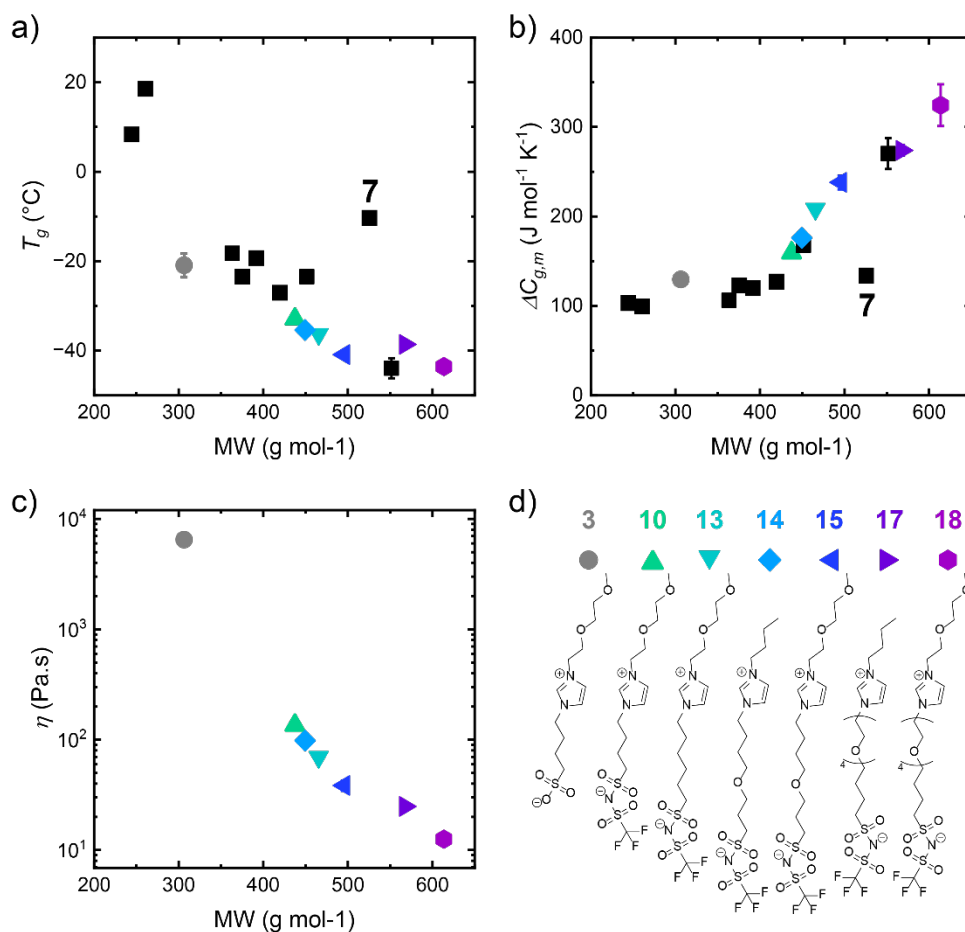
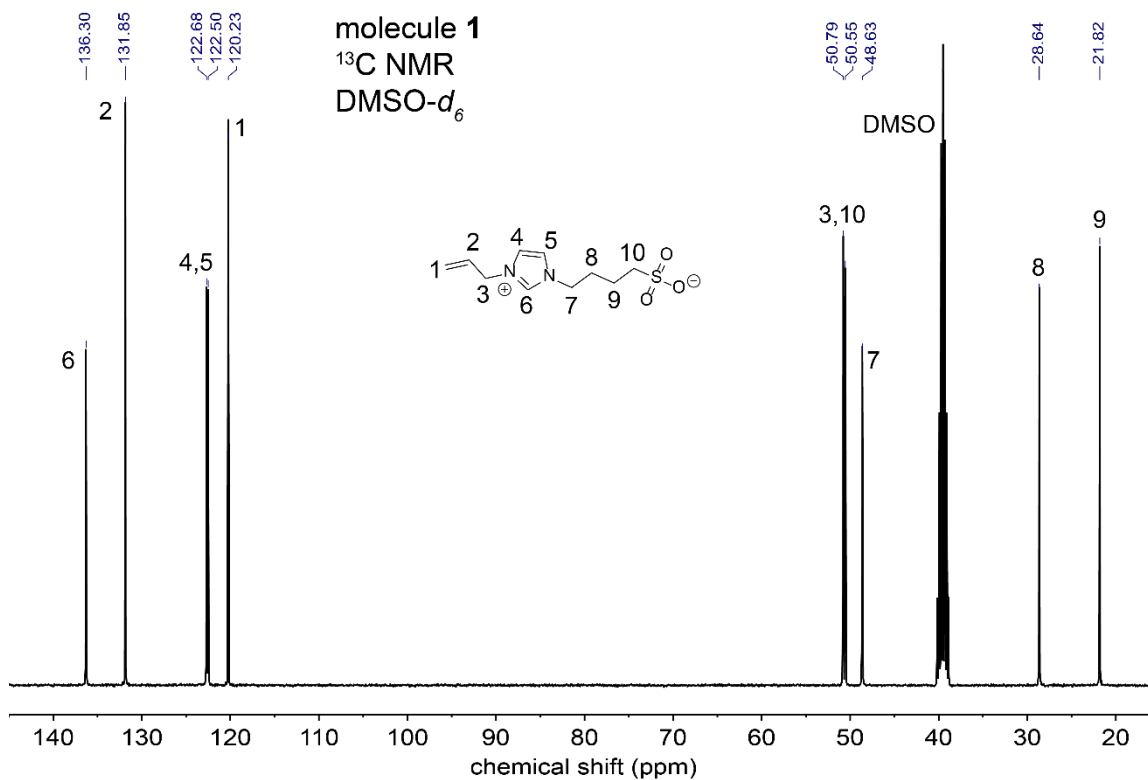
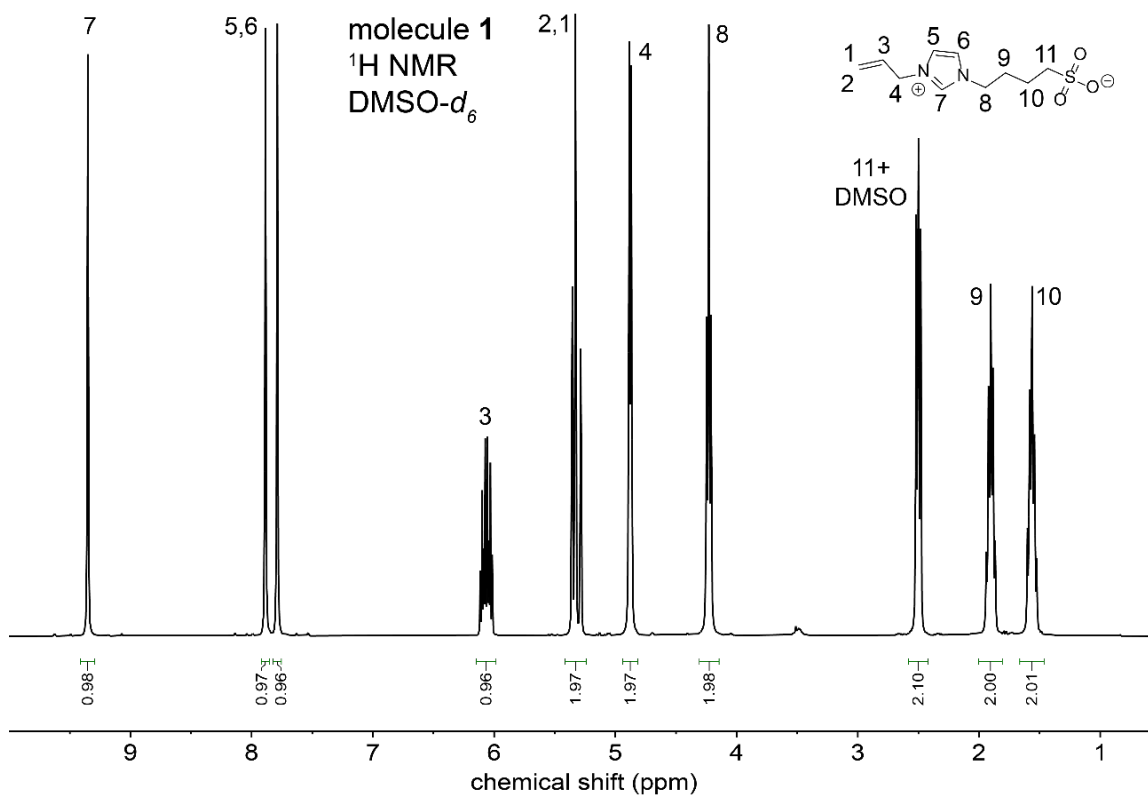


Figure S10. Molecular weight-dependence of thermal and kinetic behavior. a) T_g , b) $\Delta C_{g,m}$, and c) η as a function of molecular weight. d) supercooled zwitterions: **3** and **10** and zwitterionic liquids (ZILs): **13-15**, **17**, and **18**. Data are represented as mean \pm SD, N = 3. Molecule **7** is highlighted as an outlier in a) and b). Color-coding of molecules **3**, **10**, **13**, **14**, **15**, **17**, and **18** corresponds to **Figs 5-6**.

Data S1: Nuclear magnetic resonance of zwitterions and intermediates

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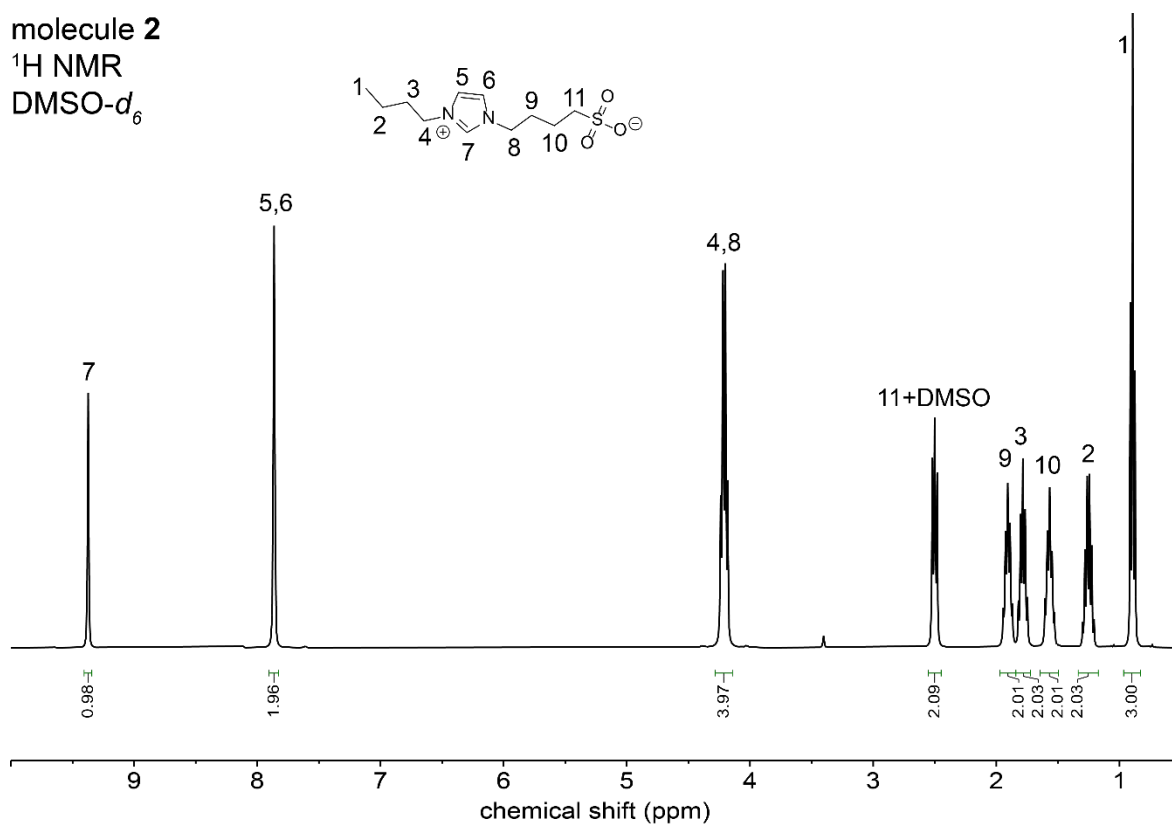


Molecule 2

molecule 2

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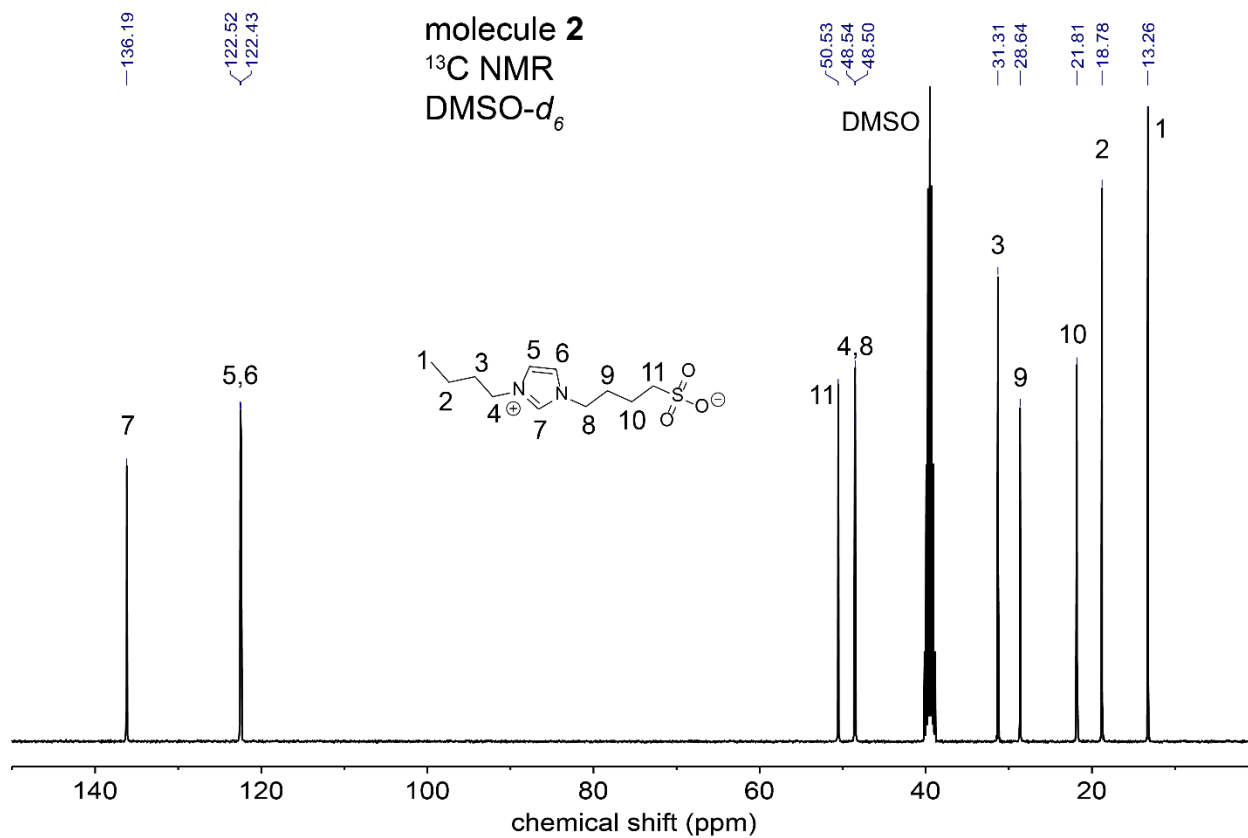
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molecule 2

¹³C NMR

DMSO-*d*₆

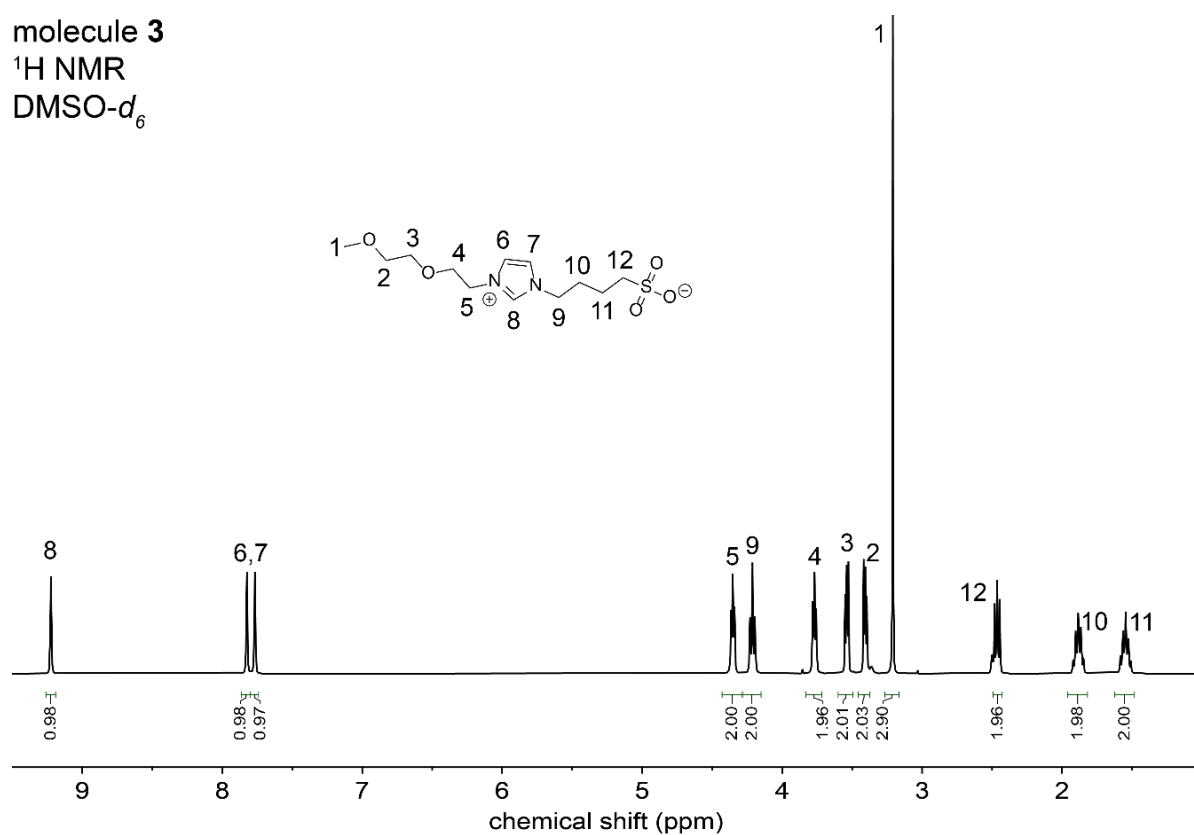


Molecule 3

molecule 3

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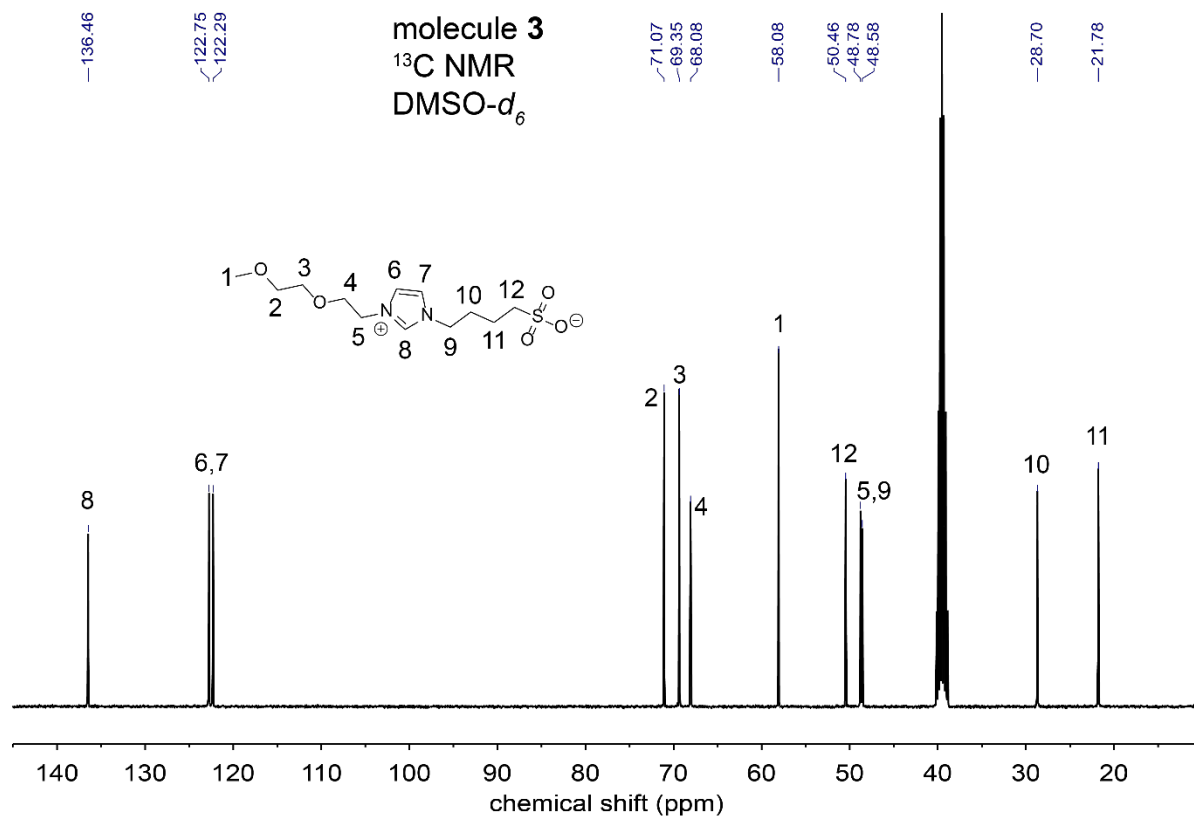
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molecule 3

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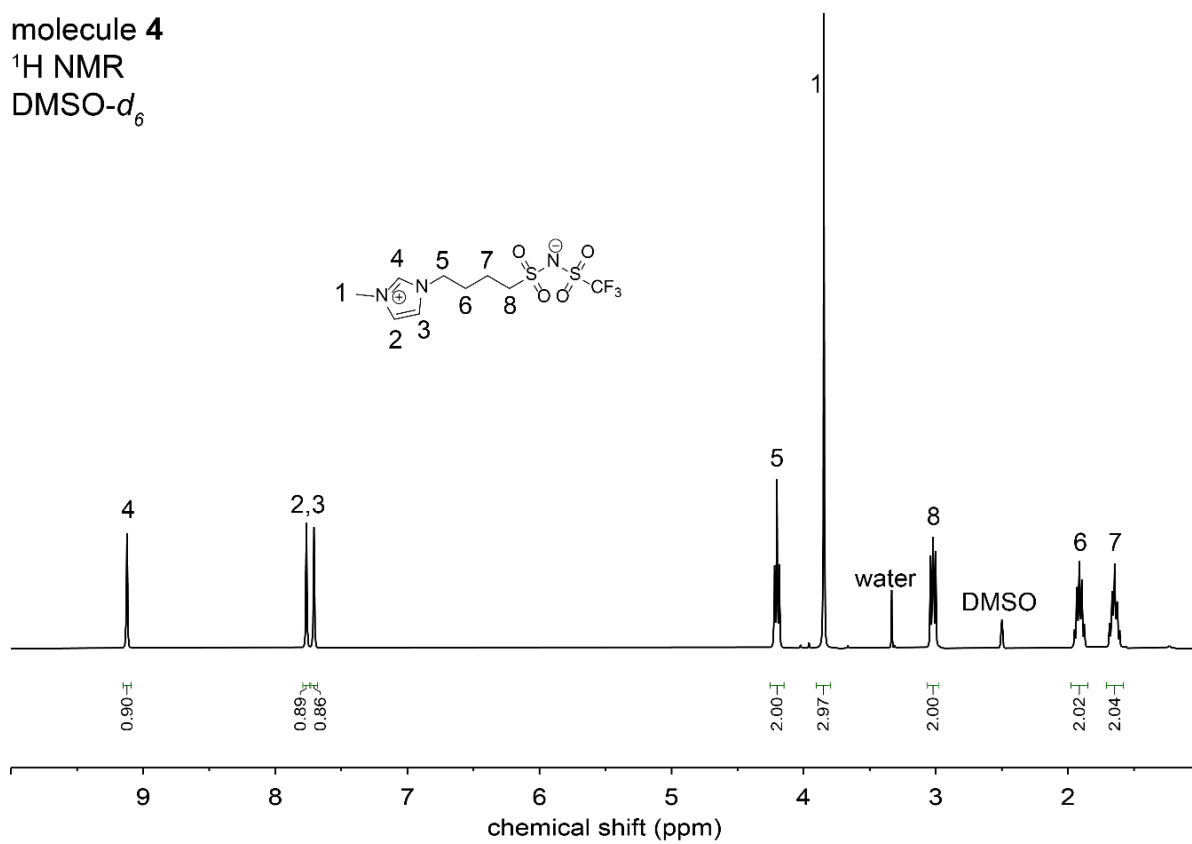


Molecule 4

molecule 4

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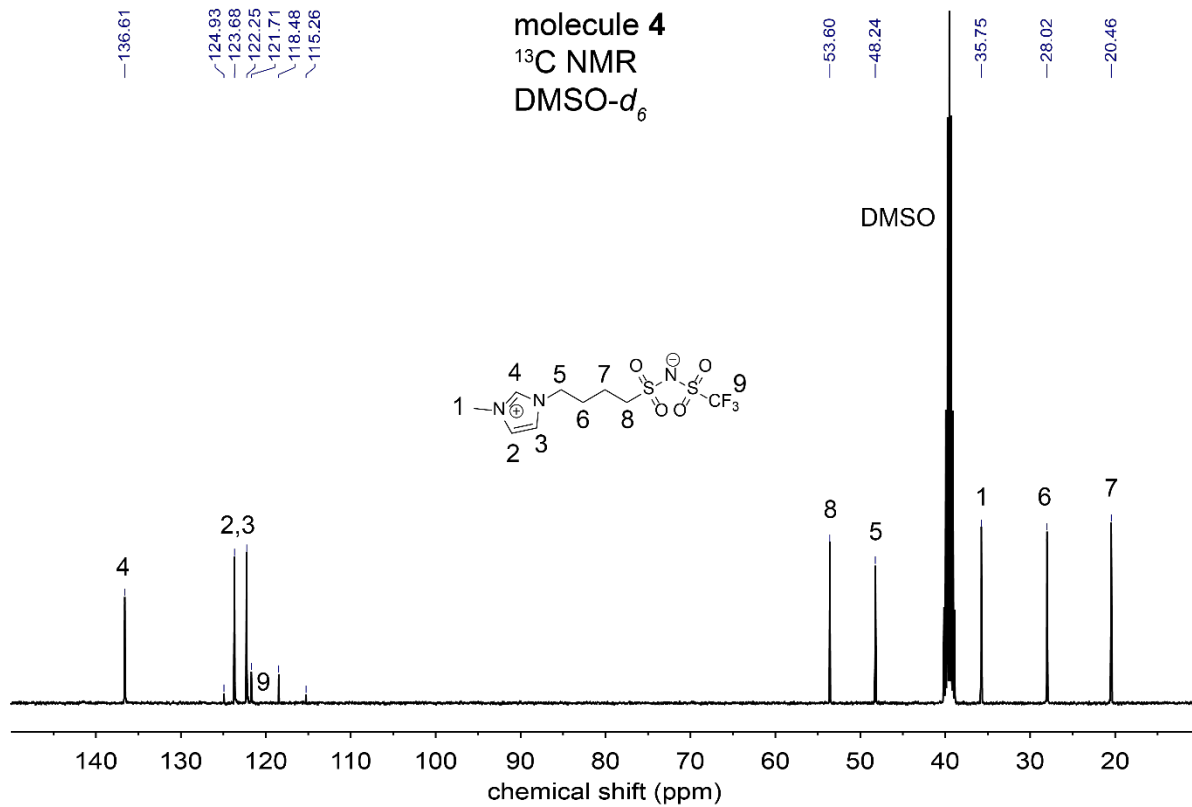
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molecule 4

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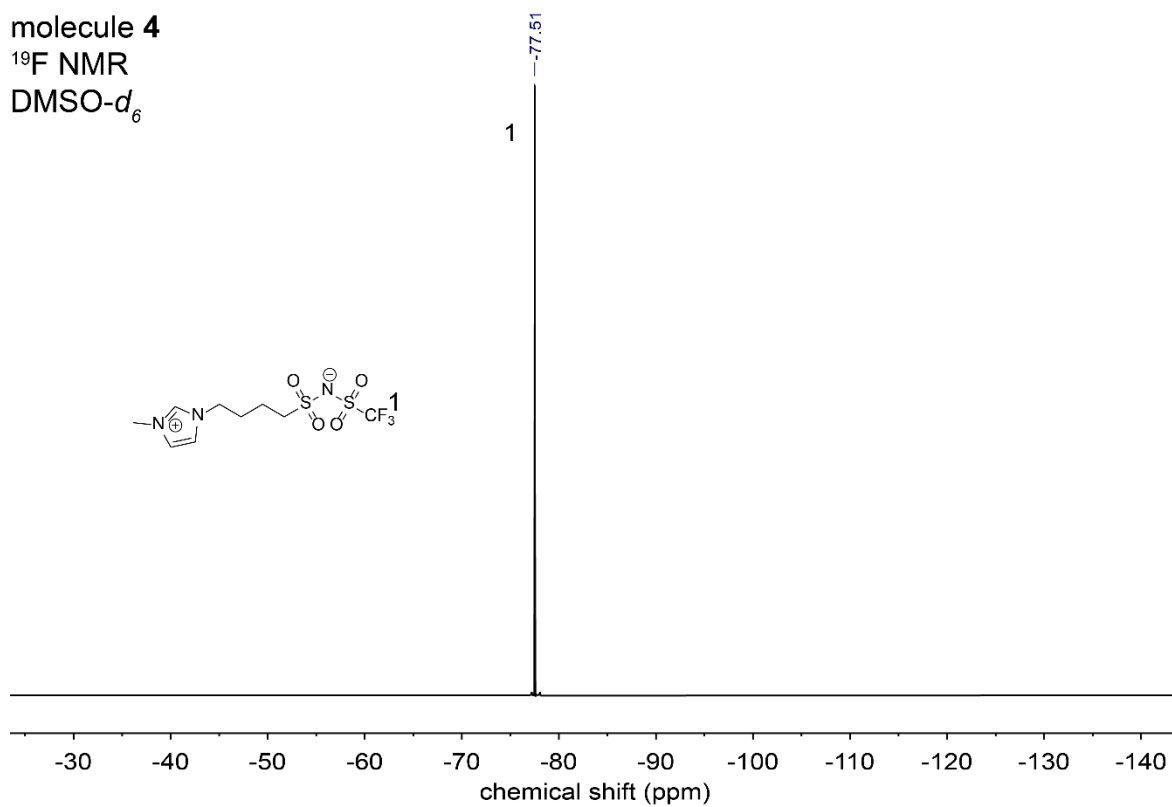
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molecule 4

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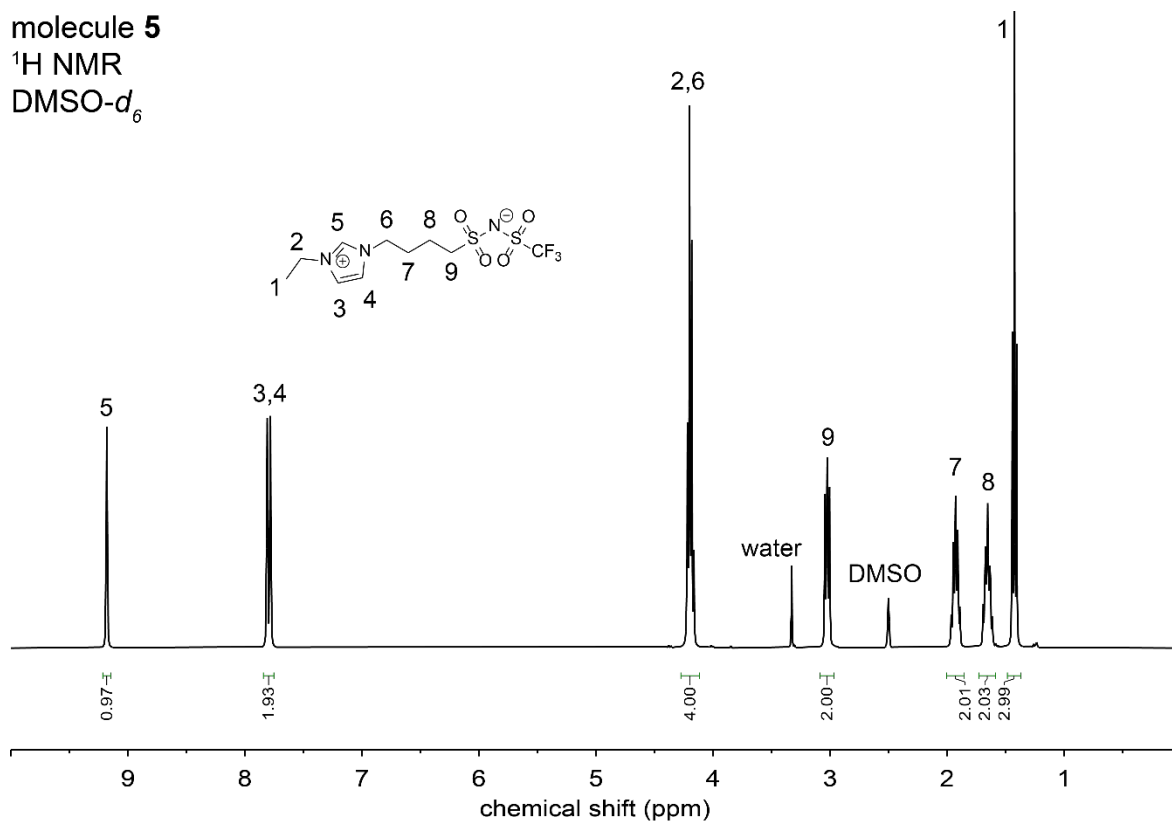


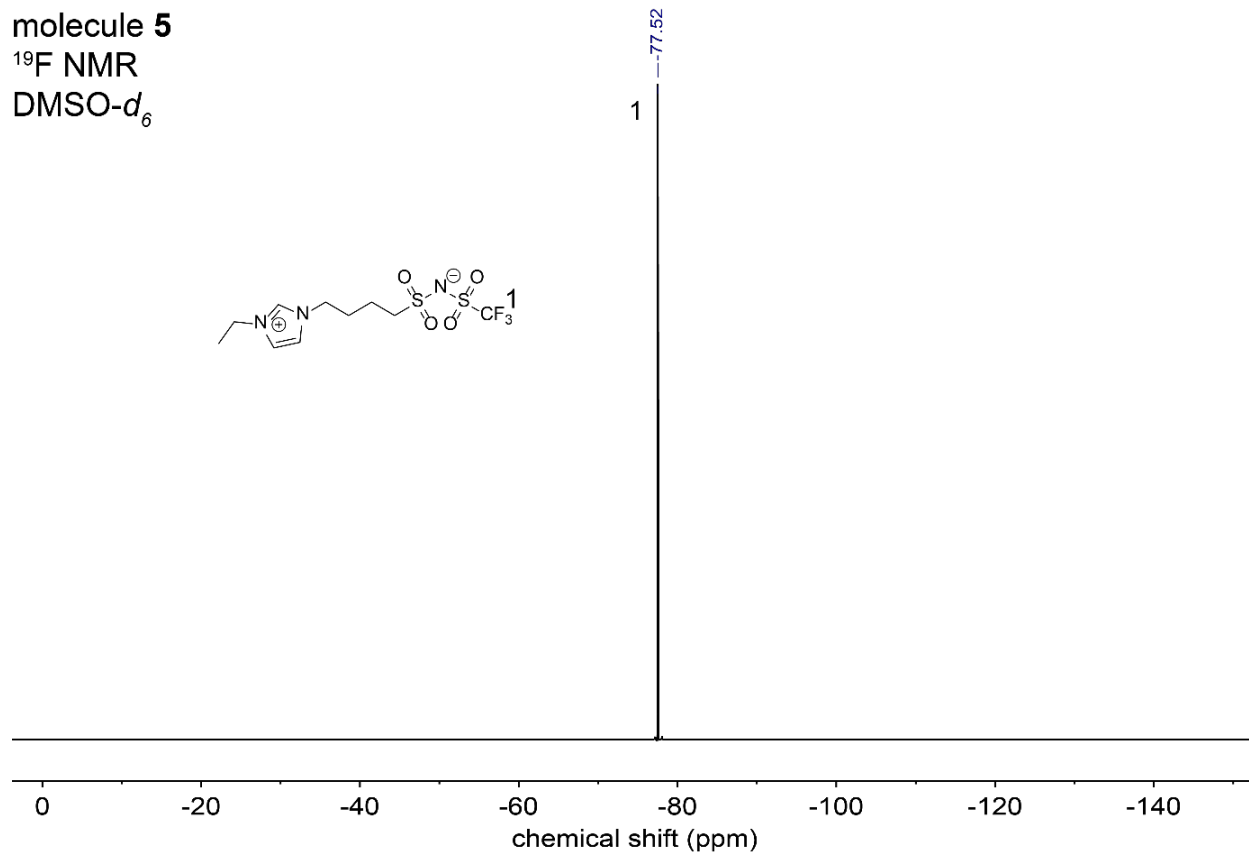
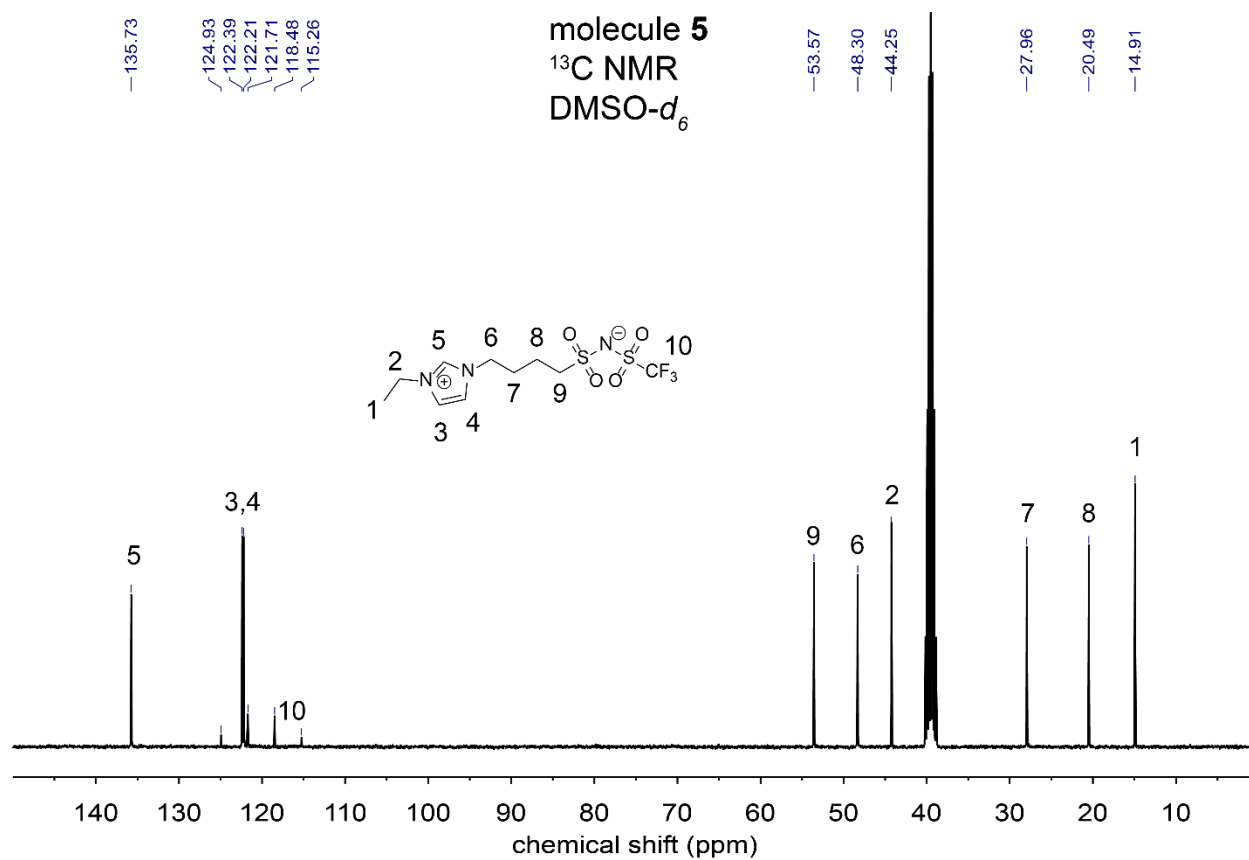
Molecule 5

molecule 5

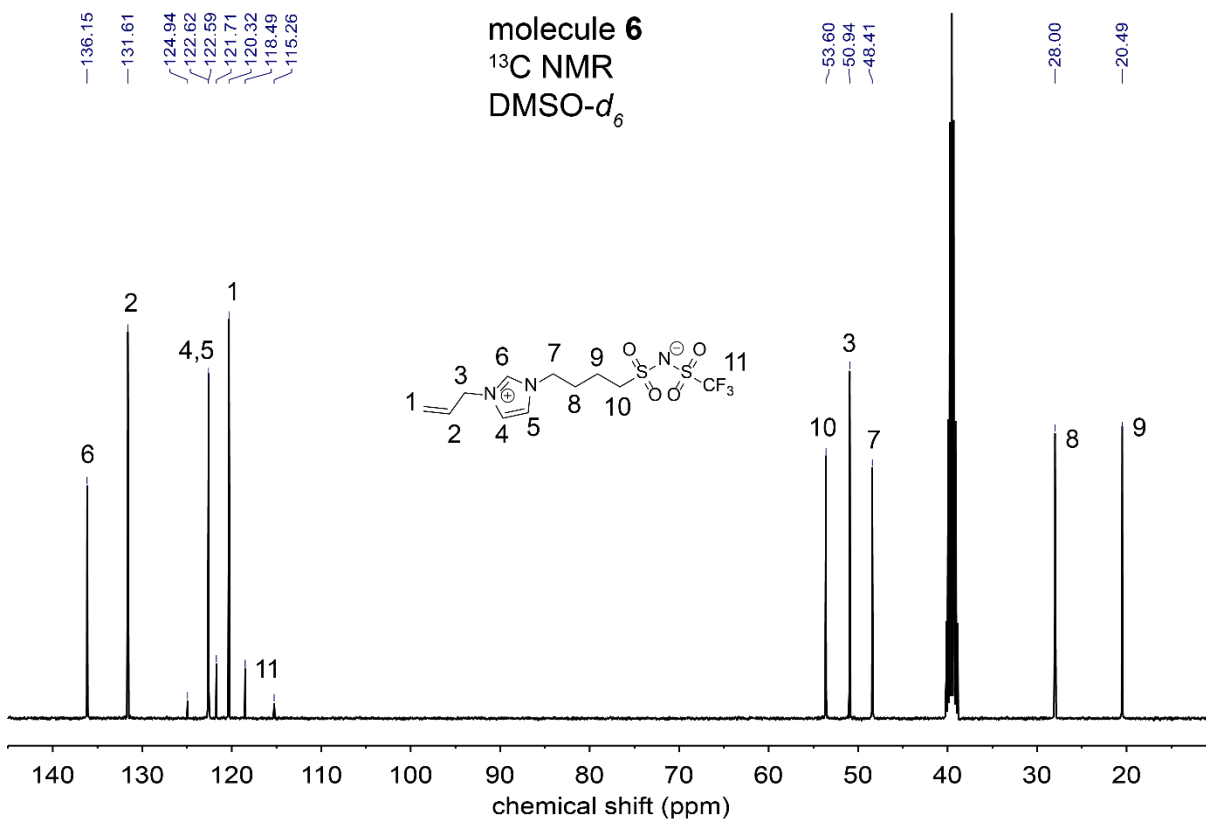
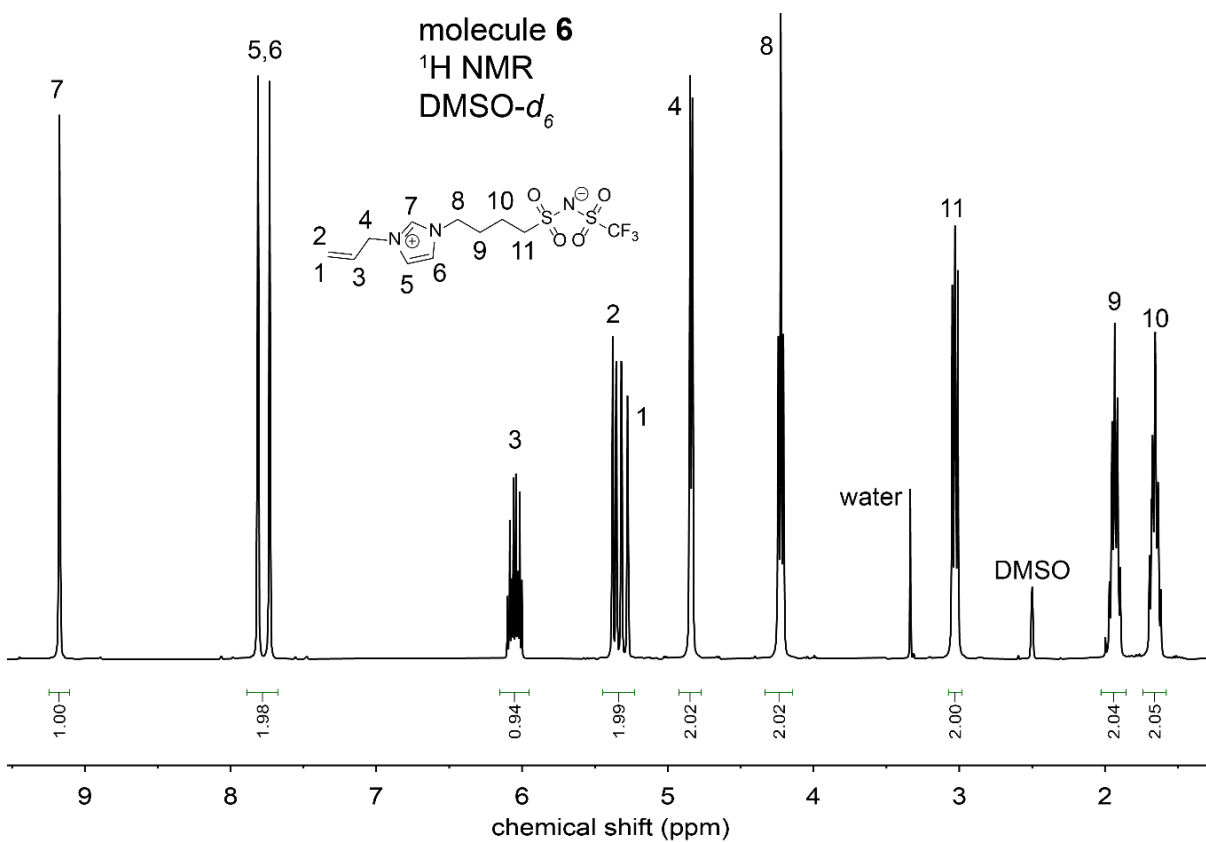
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$\text{DMSO-}d_6$

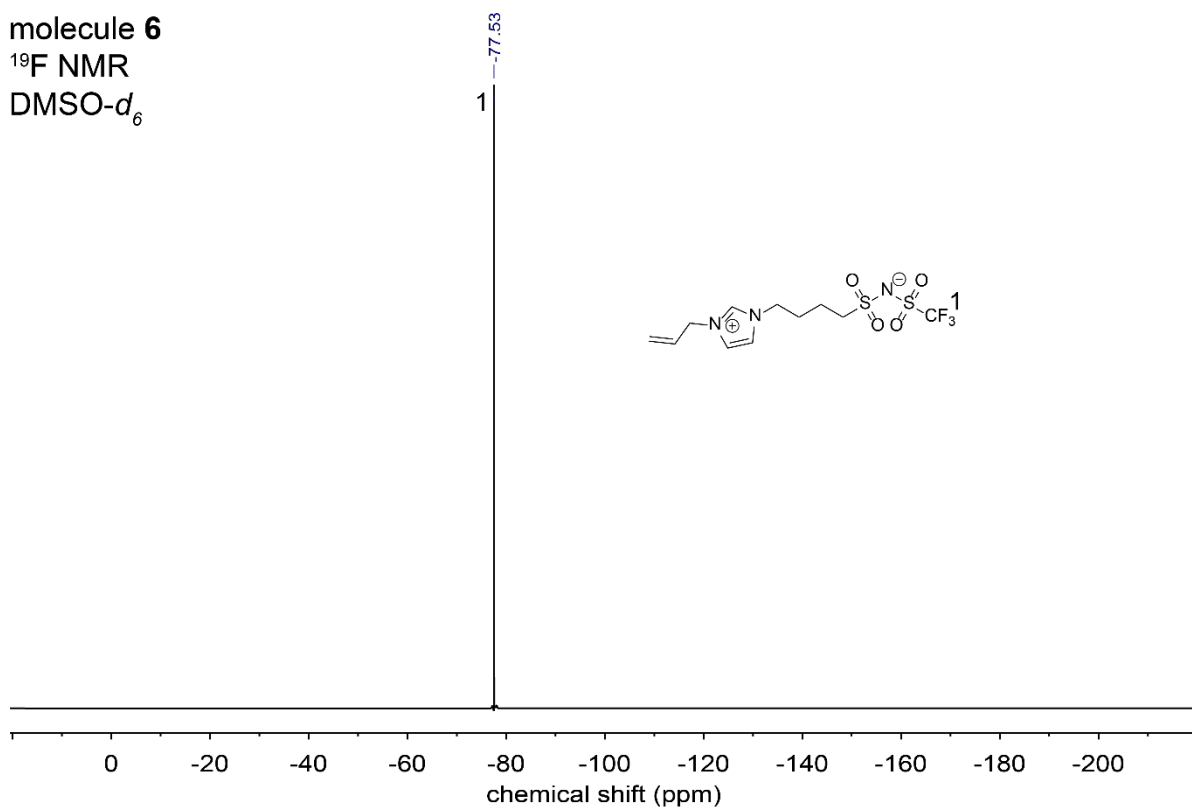




Molecule 6

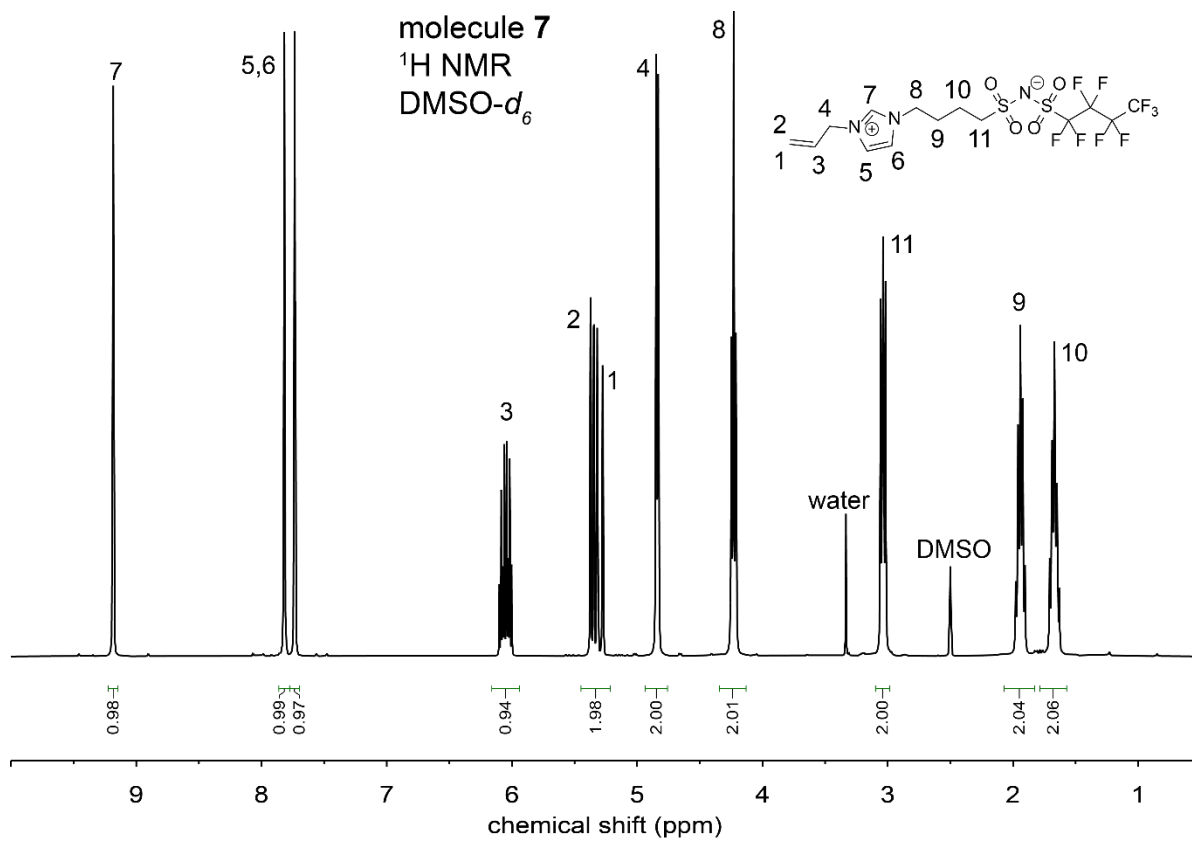


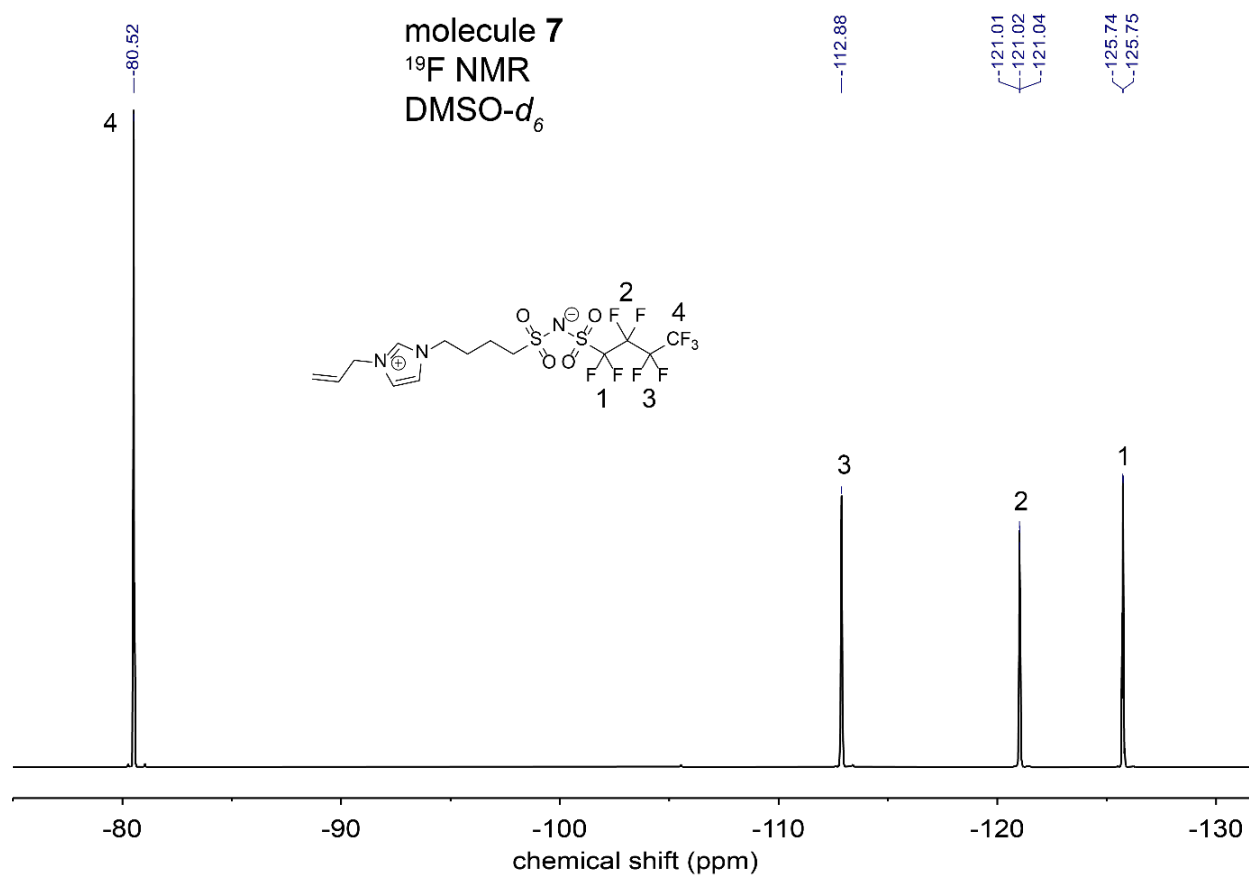
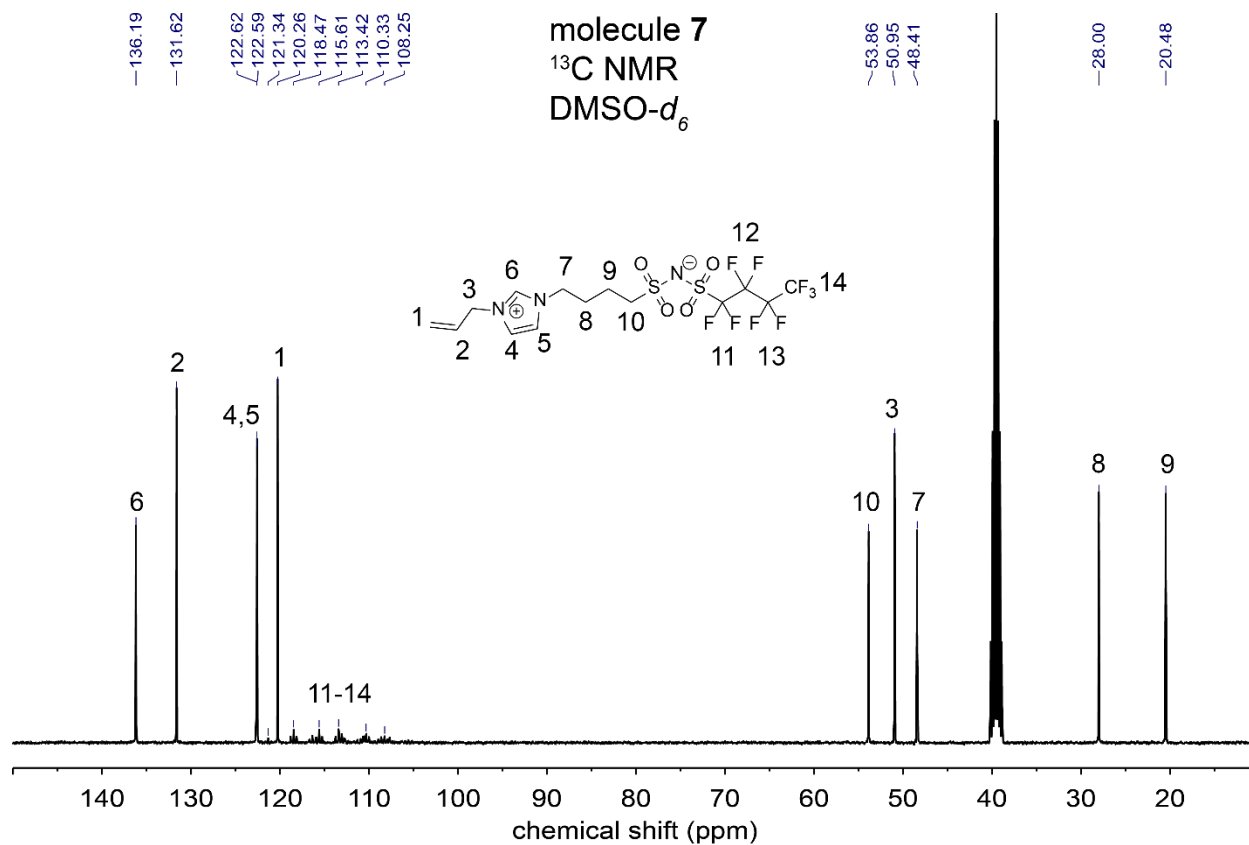
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 DMSO- d_6



Molecule 7

molecule 7
 ^1H NMR
 DMSO- d_6



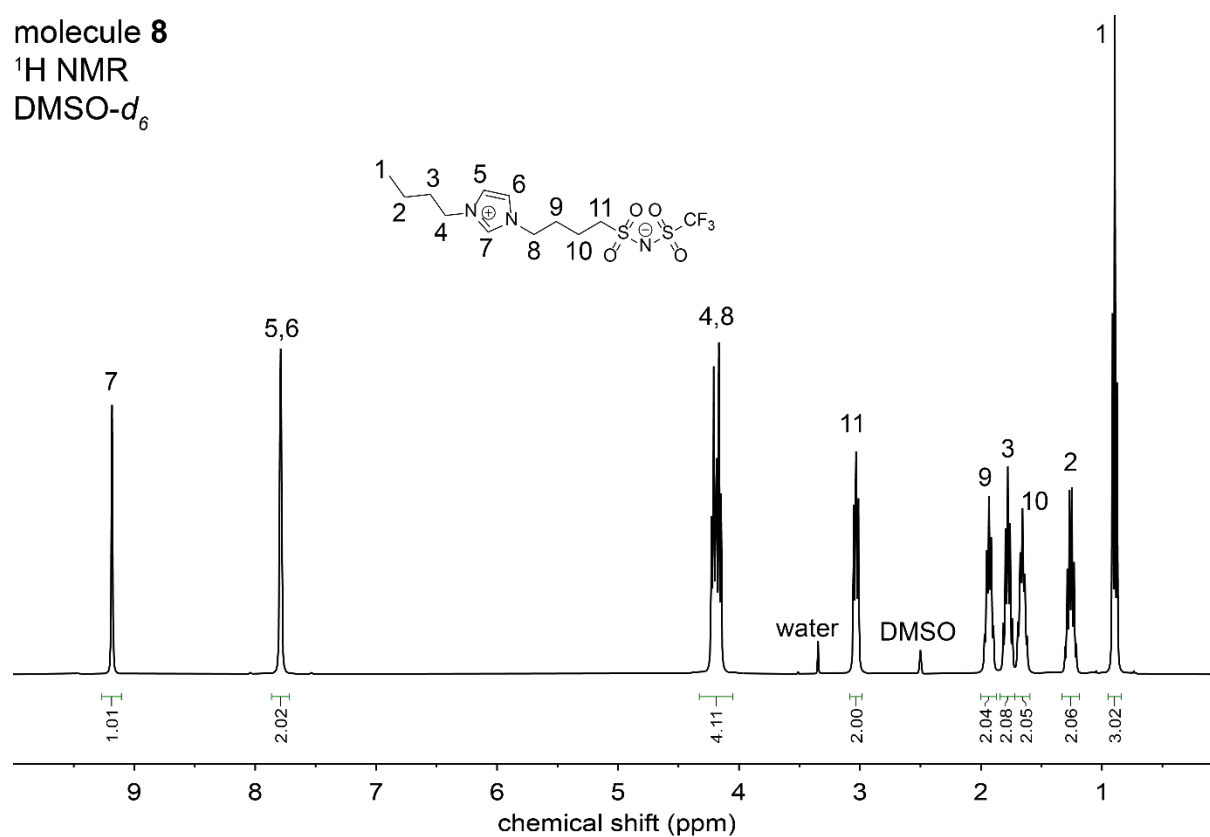


Molecule 8

molecule 8

^1H NMR

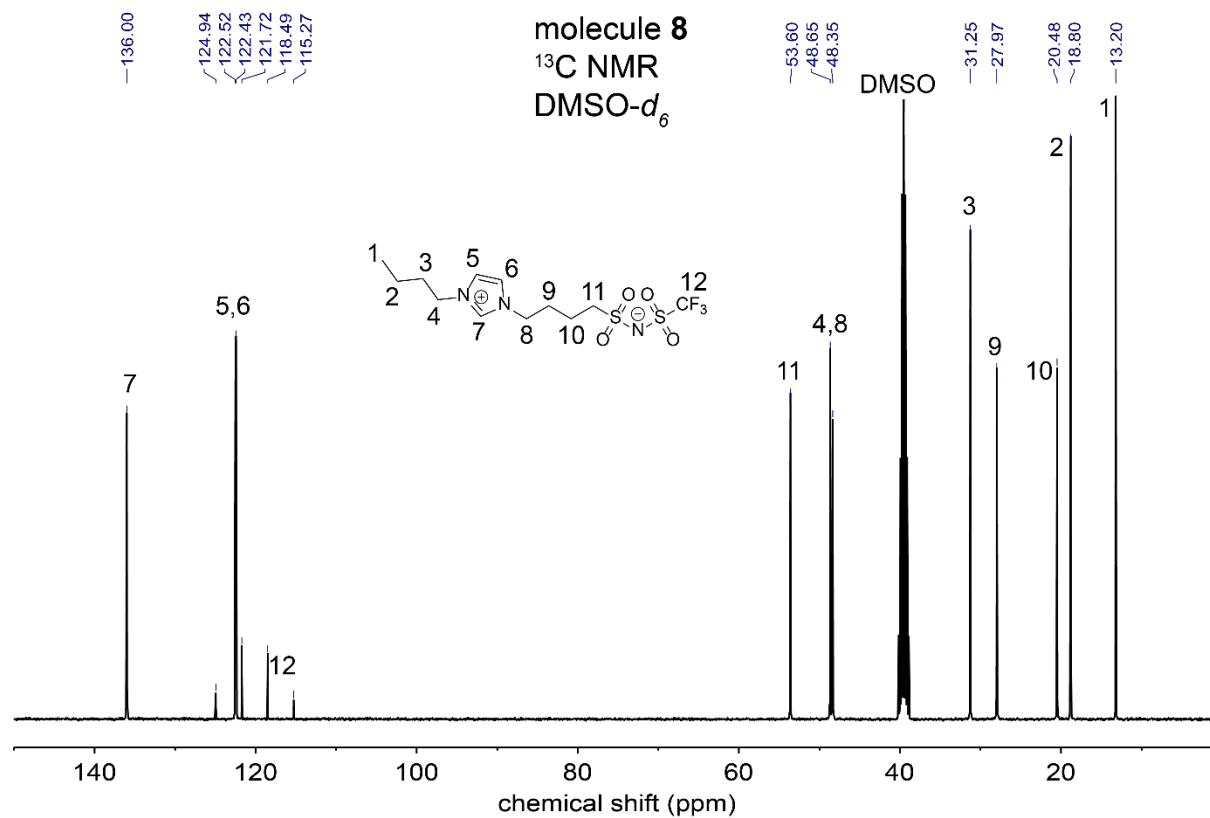
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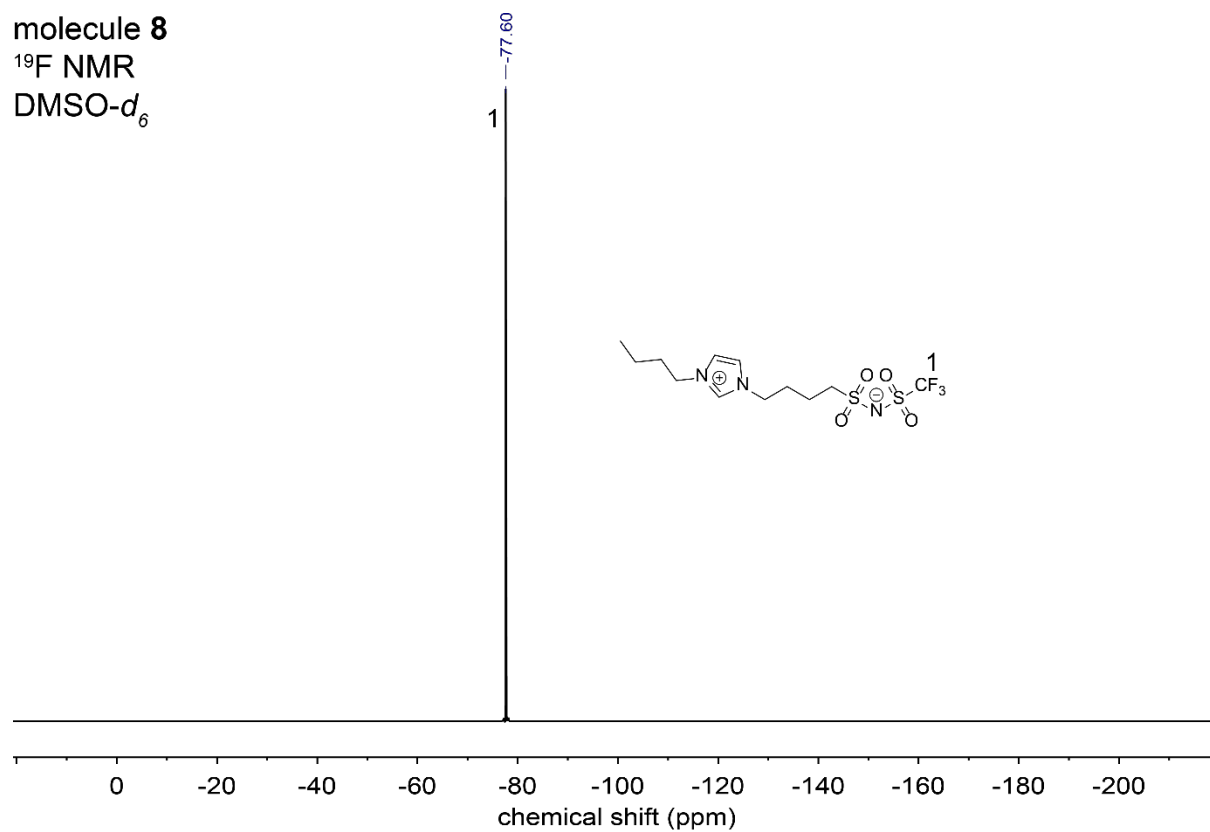
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molecule 8

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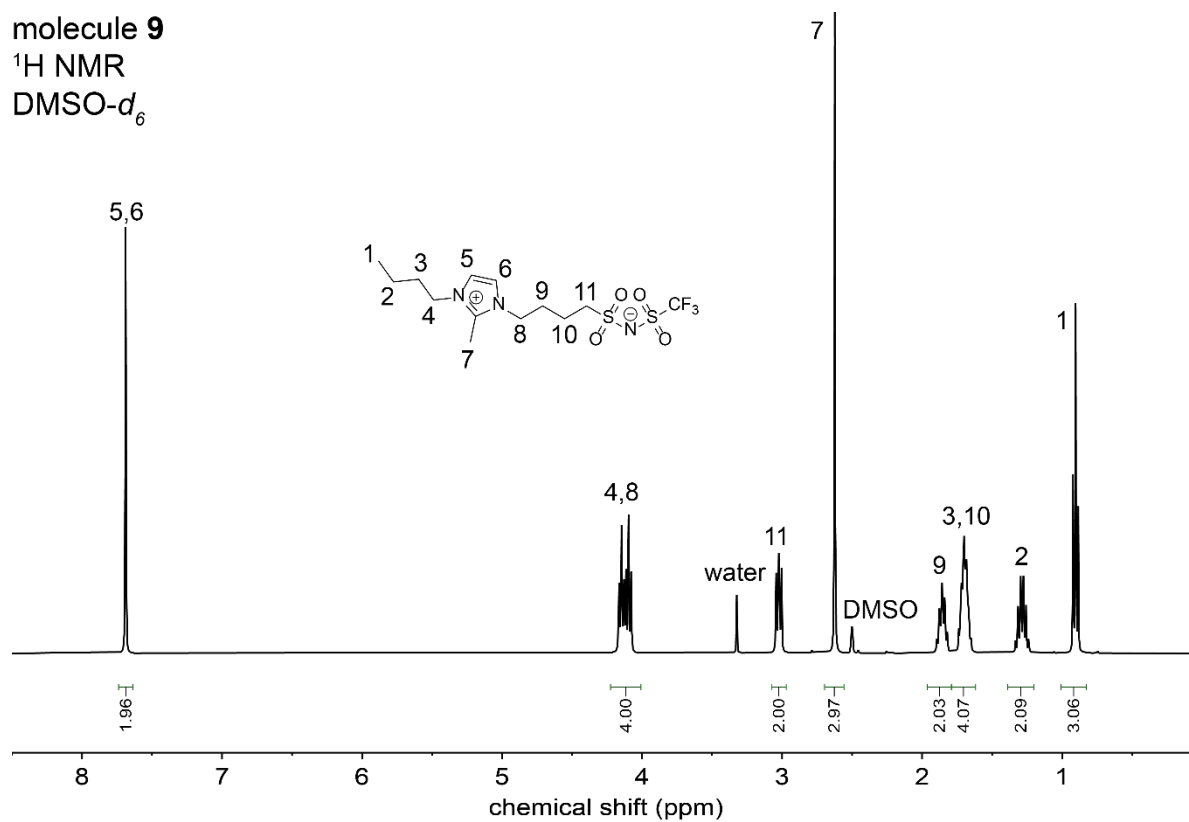


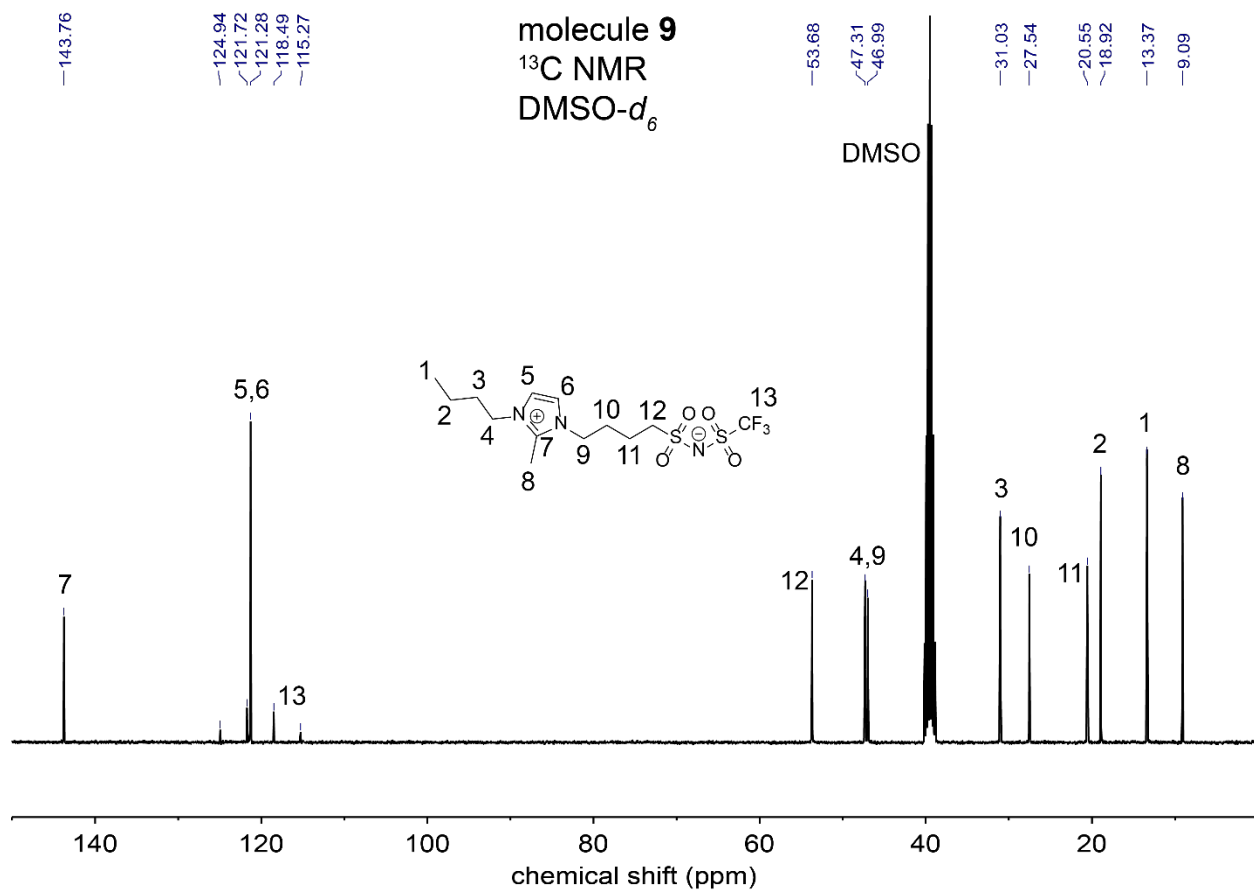
Molecule 9

molecule 9

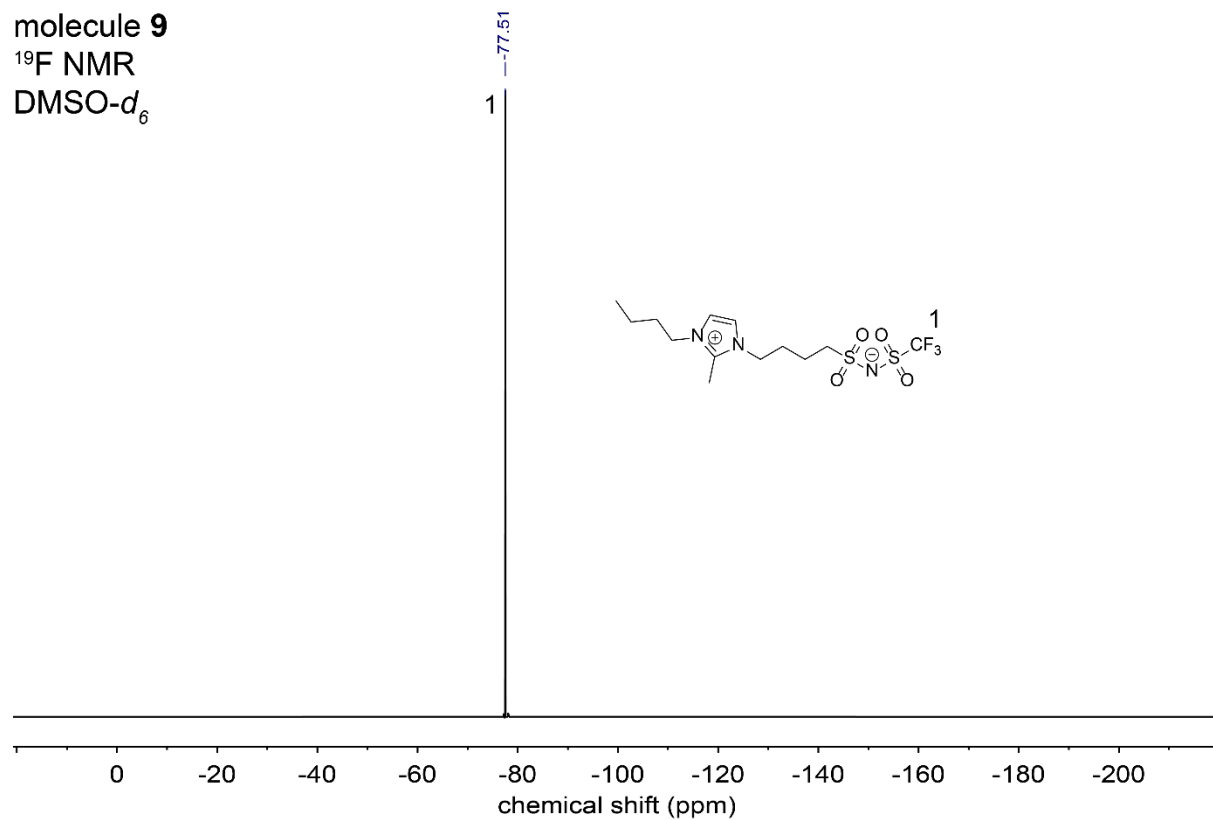
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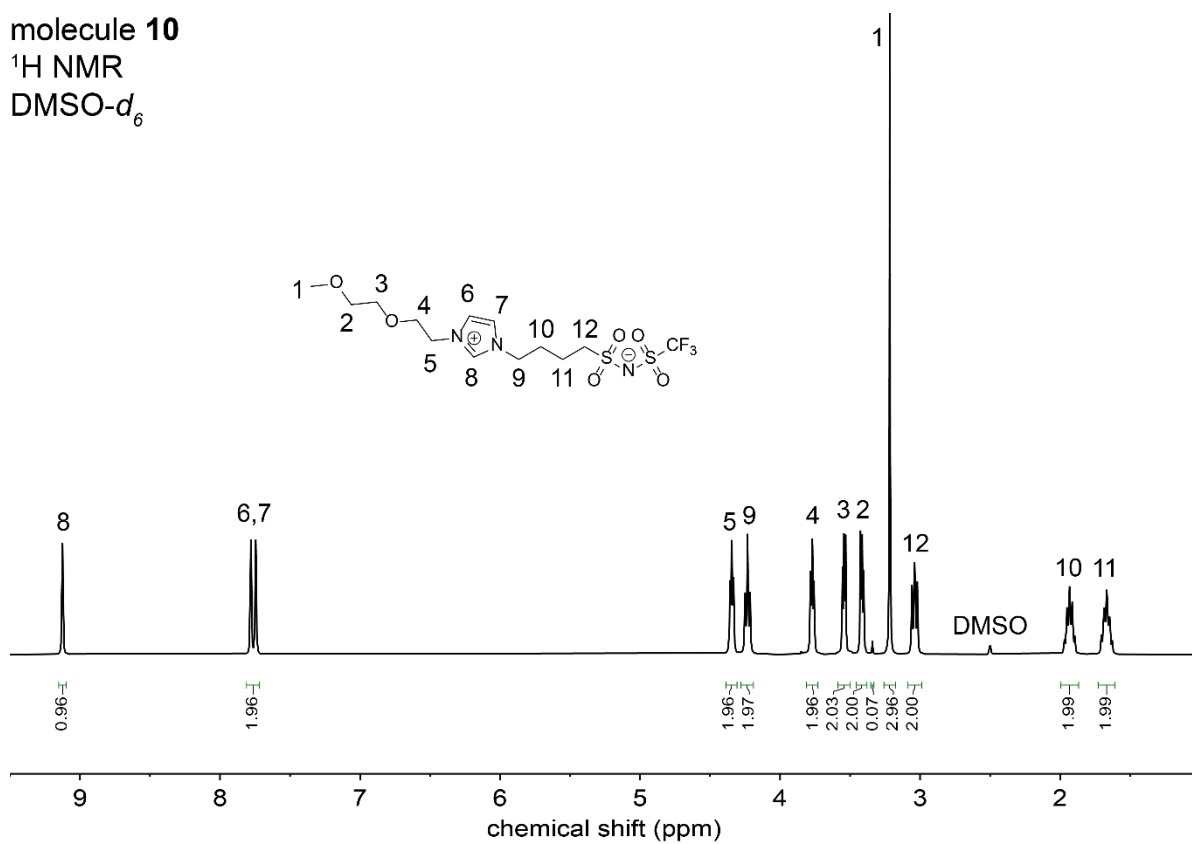
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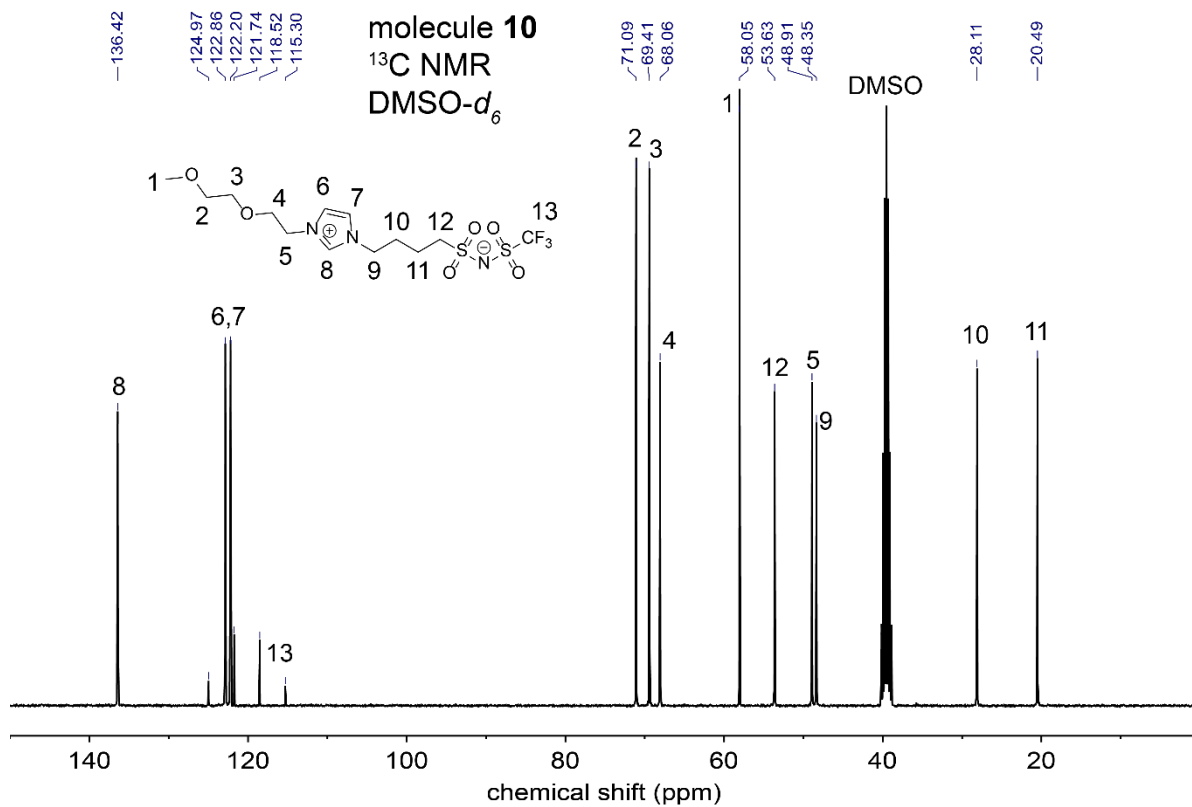


molecule 9
¹⁹F NMR
DMSO-*d*₆



molecule **10**¹H NMRDMSO- d_6 

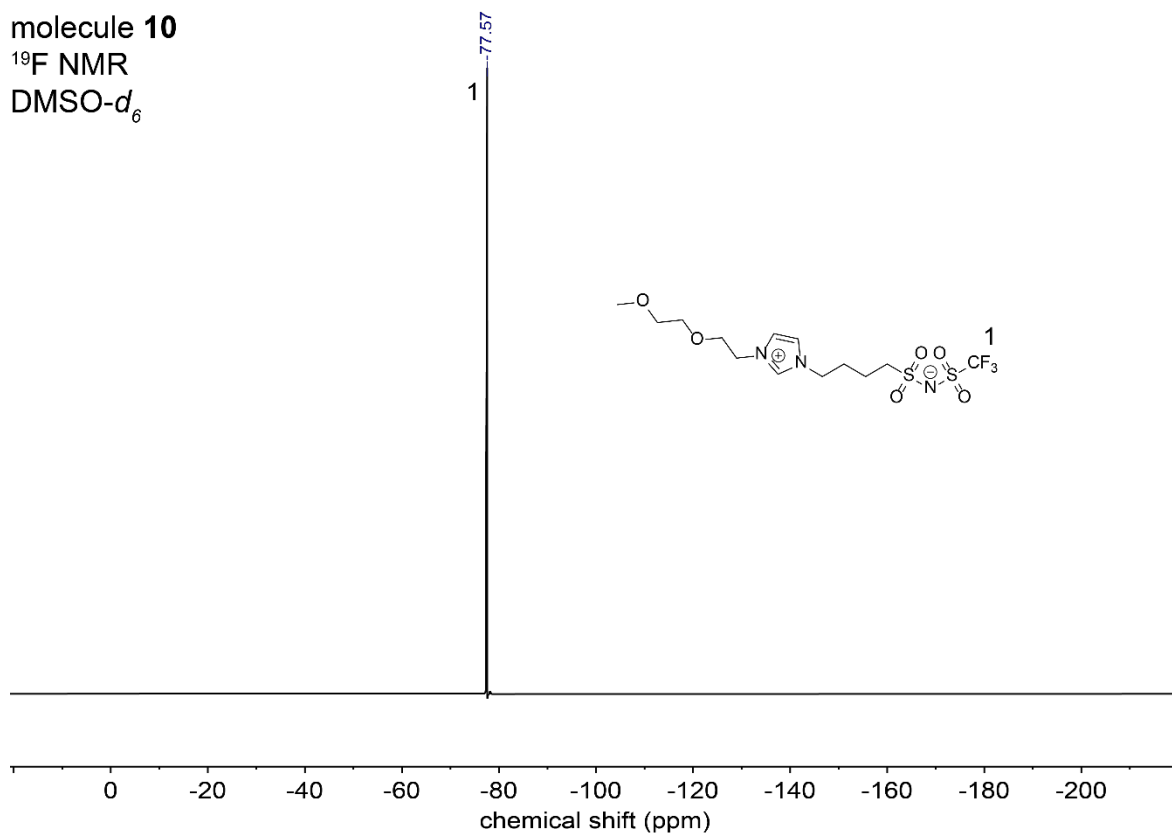
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molecule **10**

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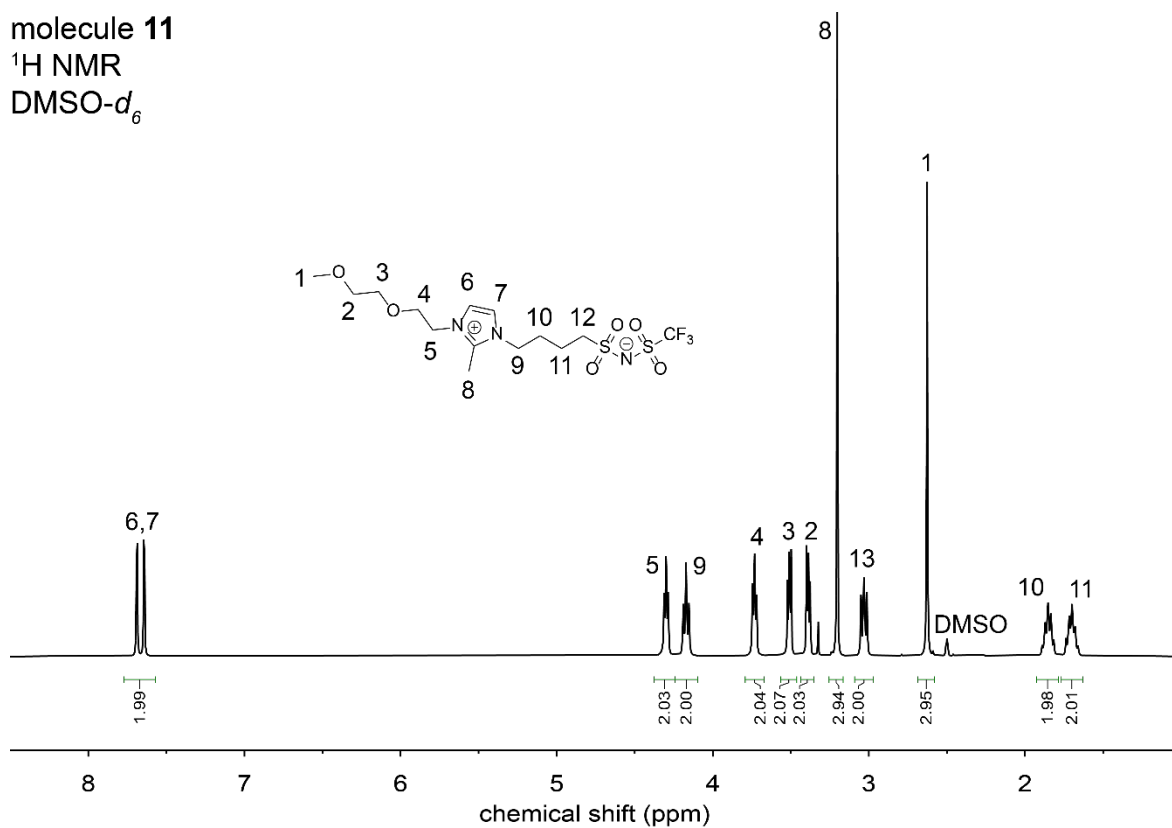


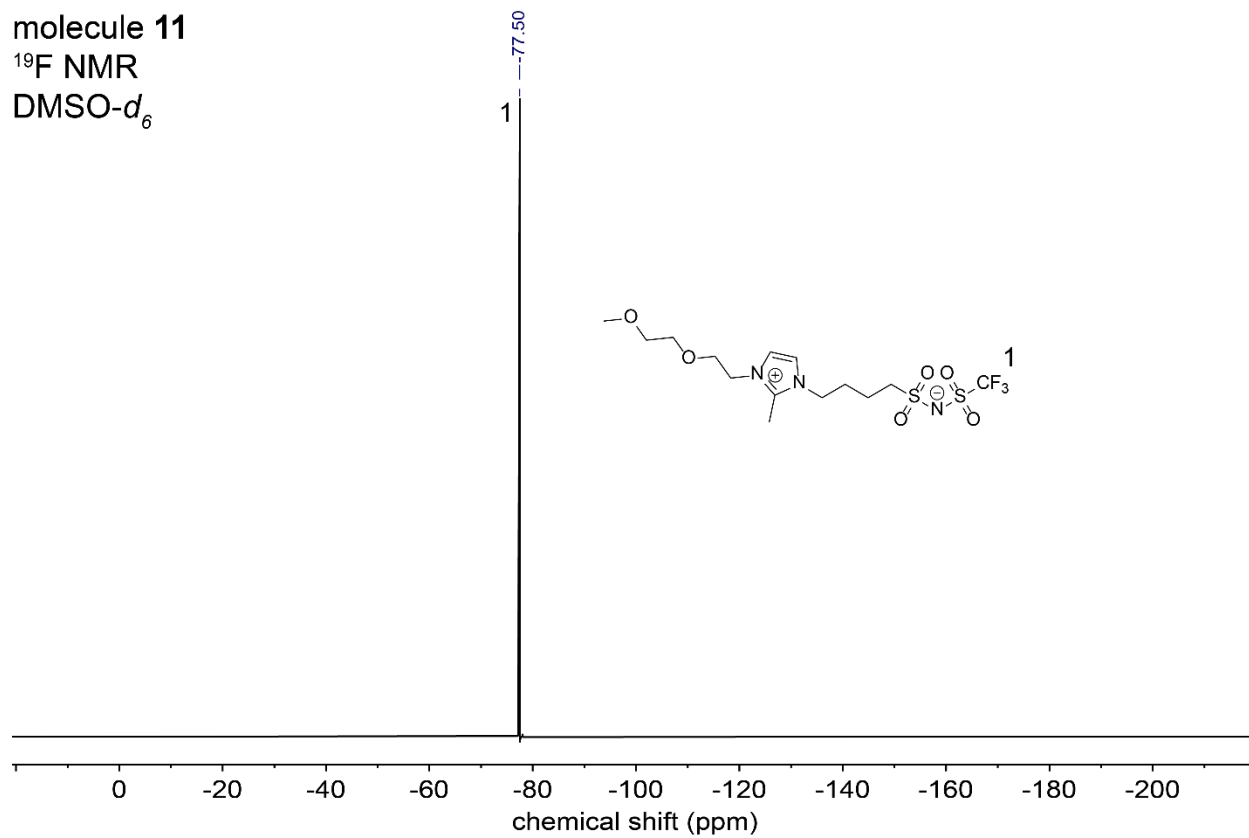
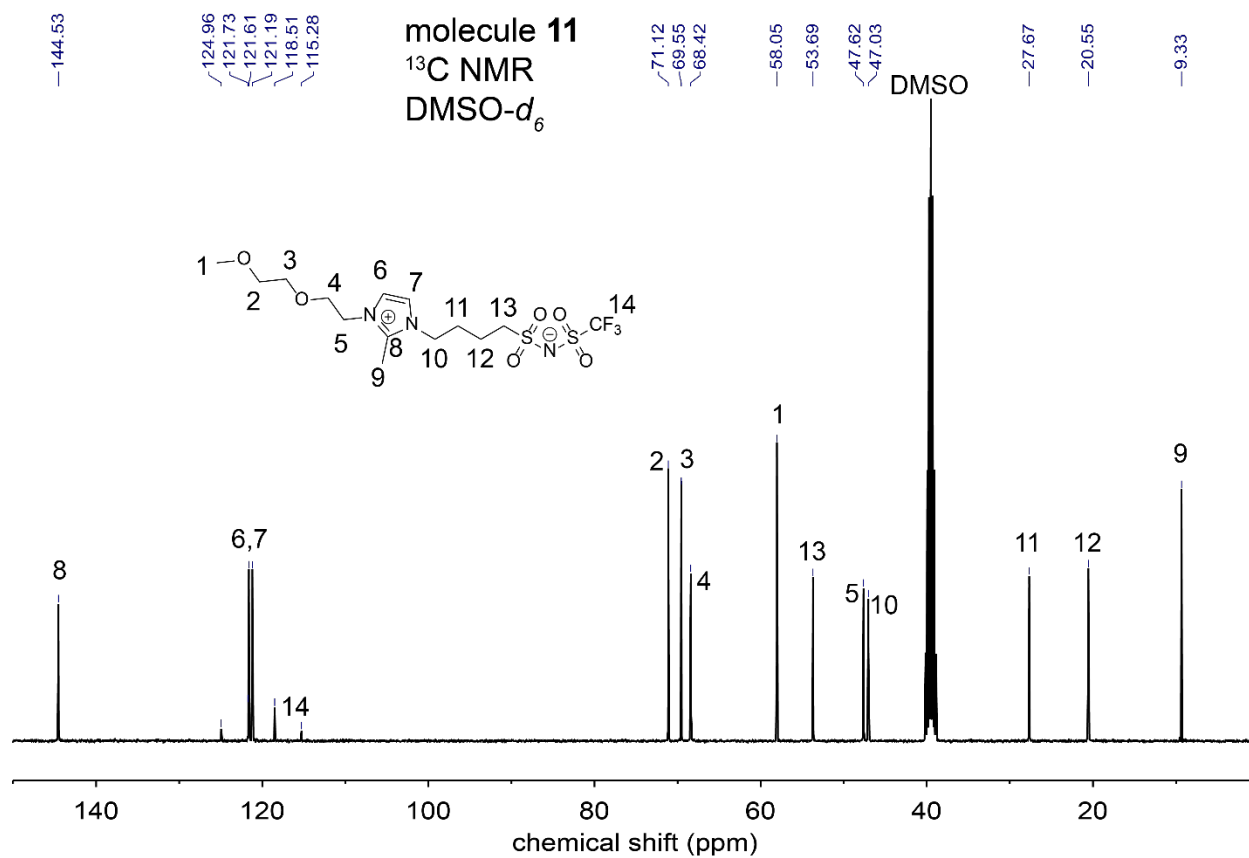
Molecule **11**

molecule **11**

^1H NMR

$\text{DMSO}-d_6$



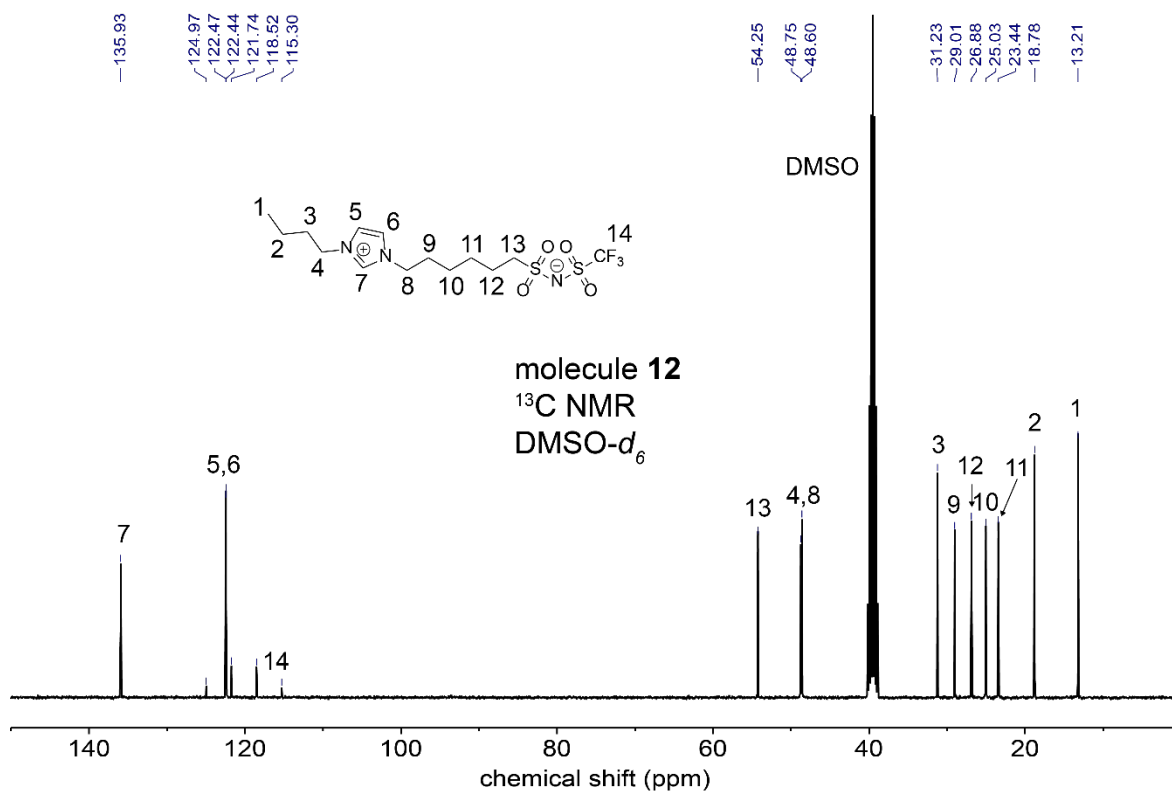
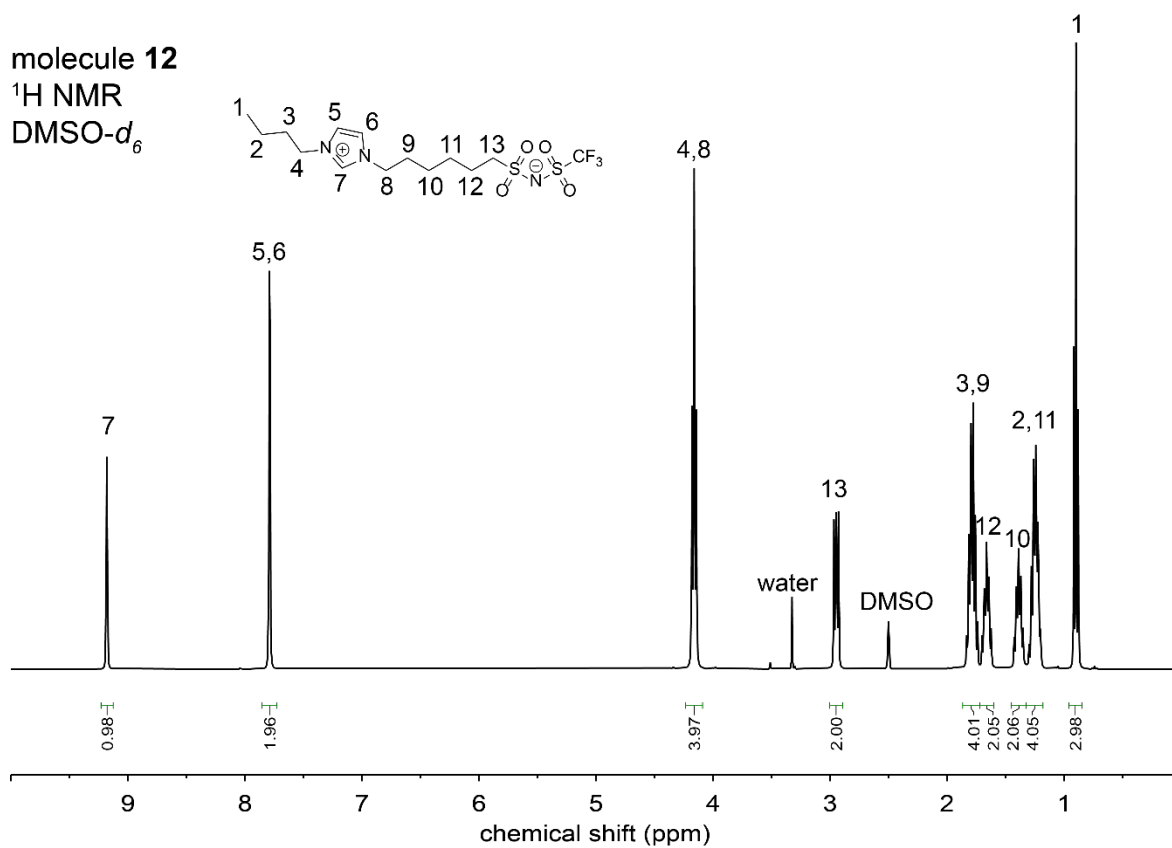


Molecule 12

molecule 12

¹H NMR

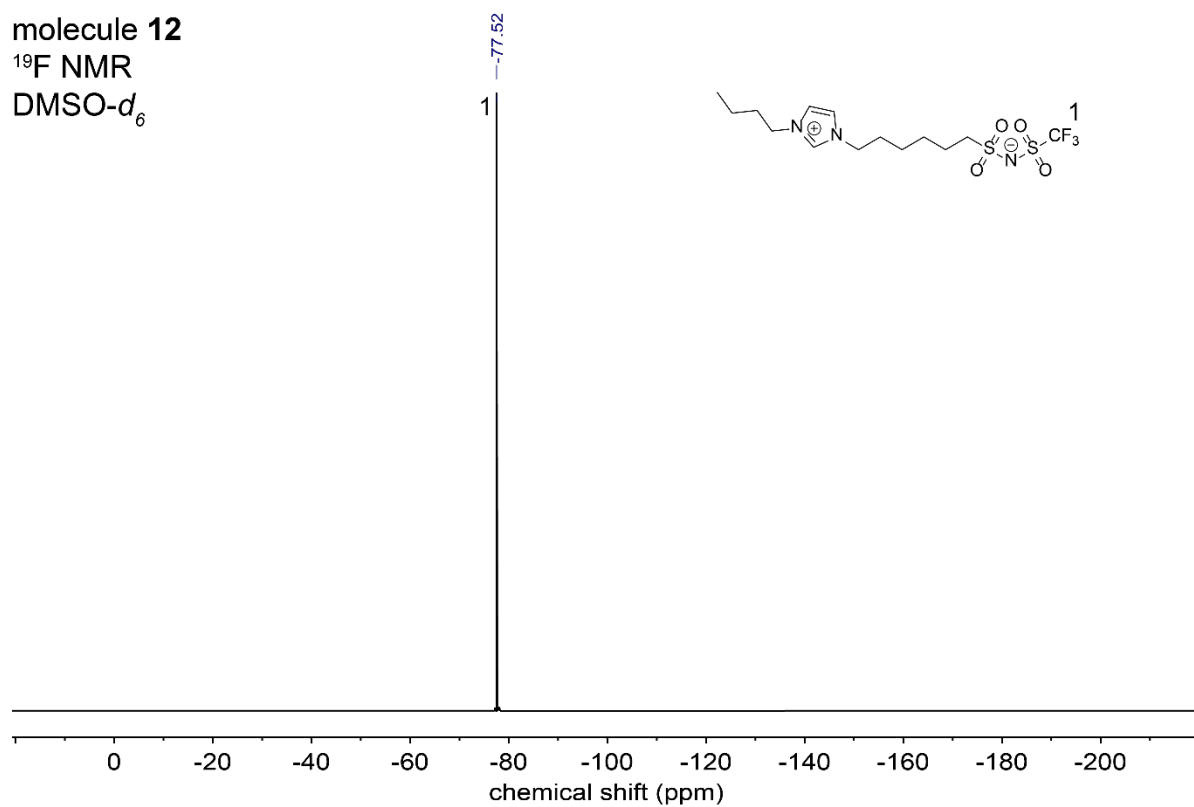
DMSO-*d*₆



molecule 12

^{19}F NMR

$\text{DMSO}-d_6$

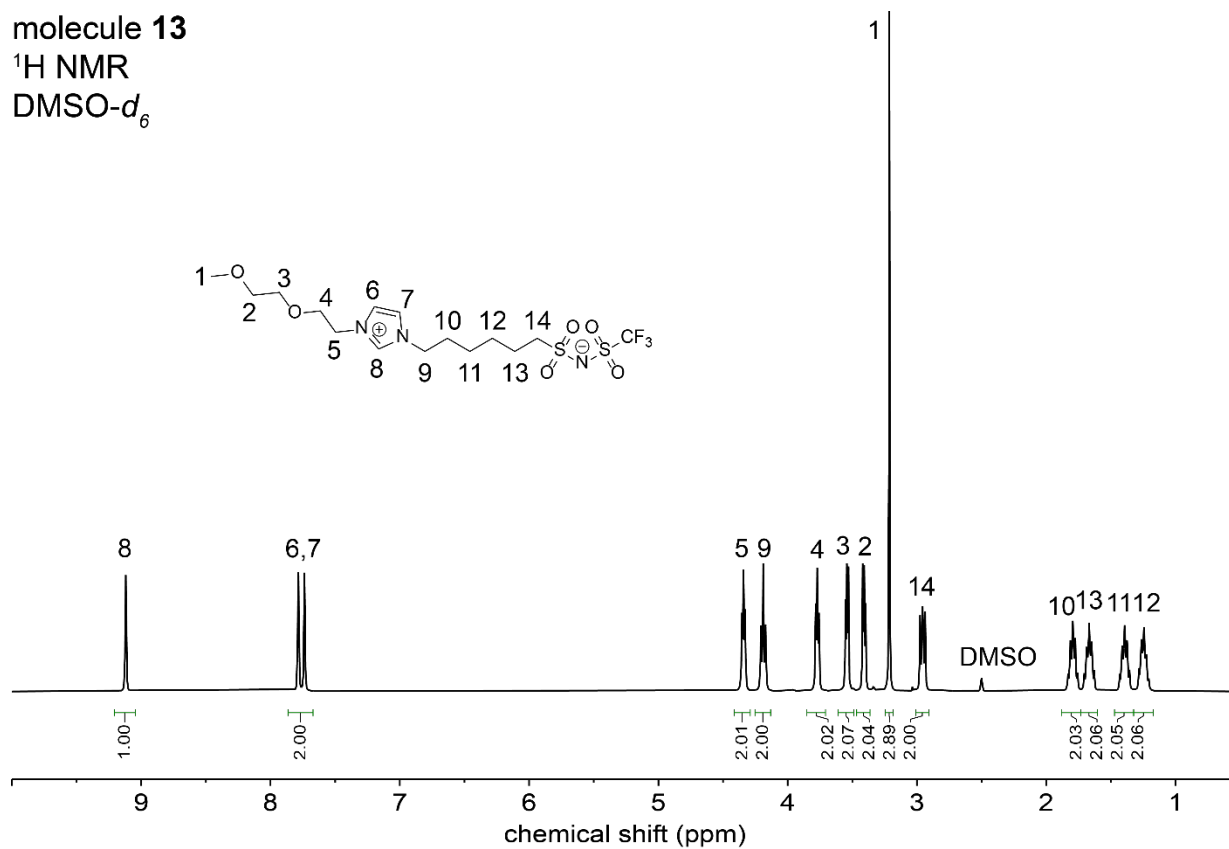


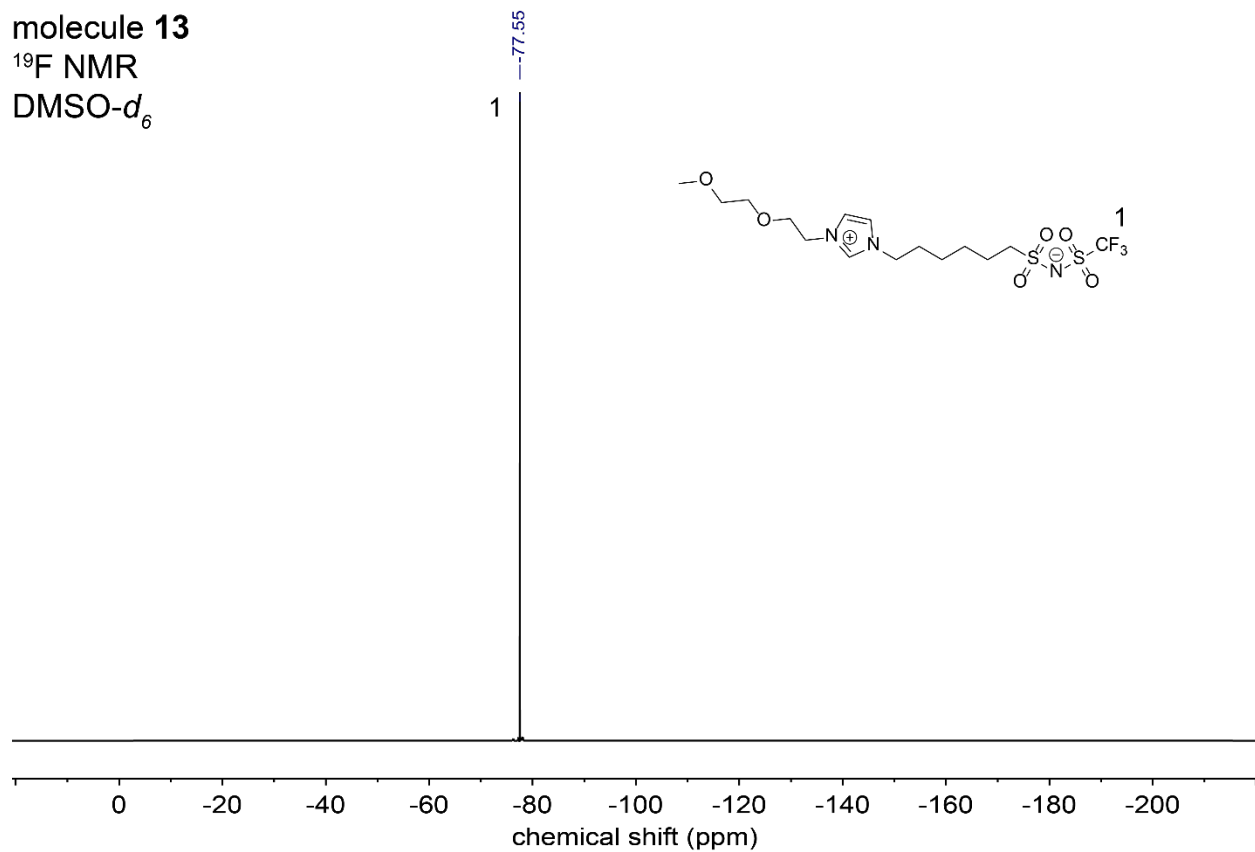
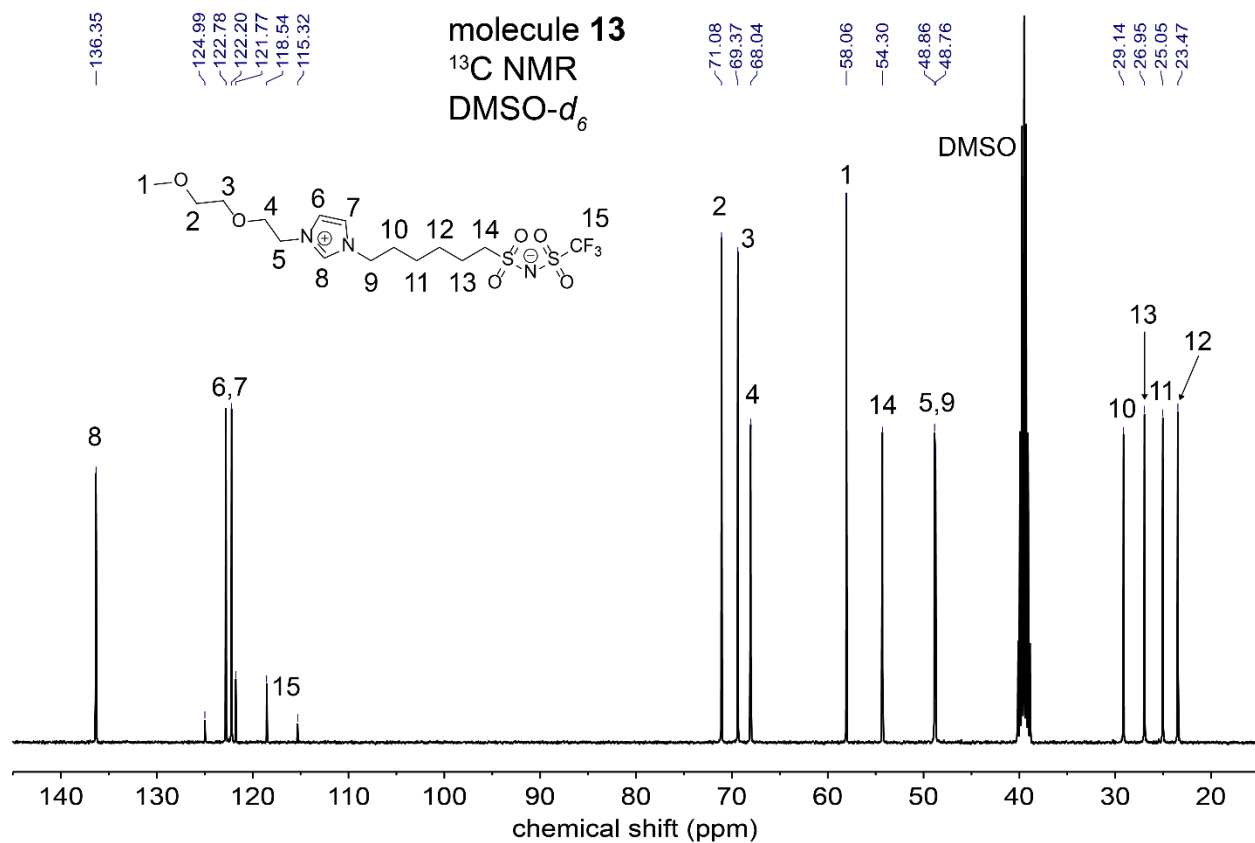
Molecule 13

molecule 13

^1H NMR

$\text{DMSO}-d_6$



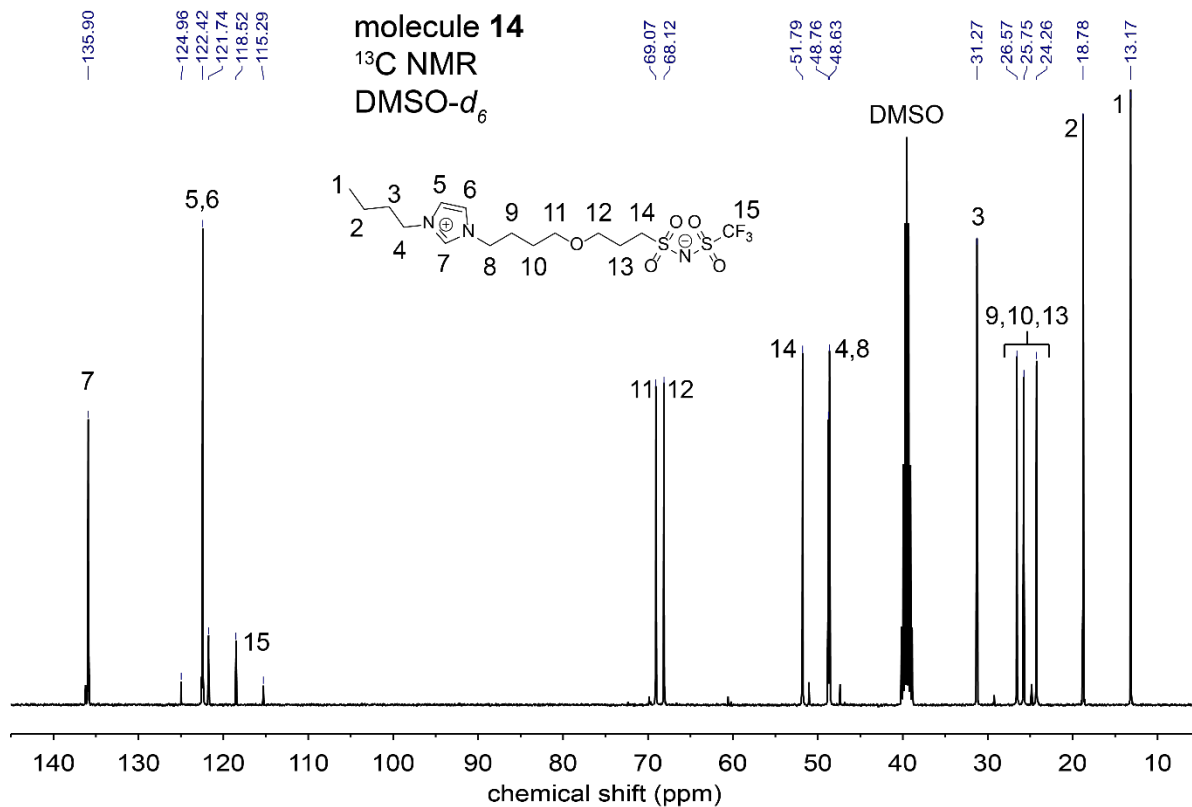
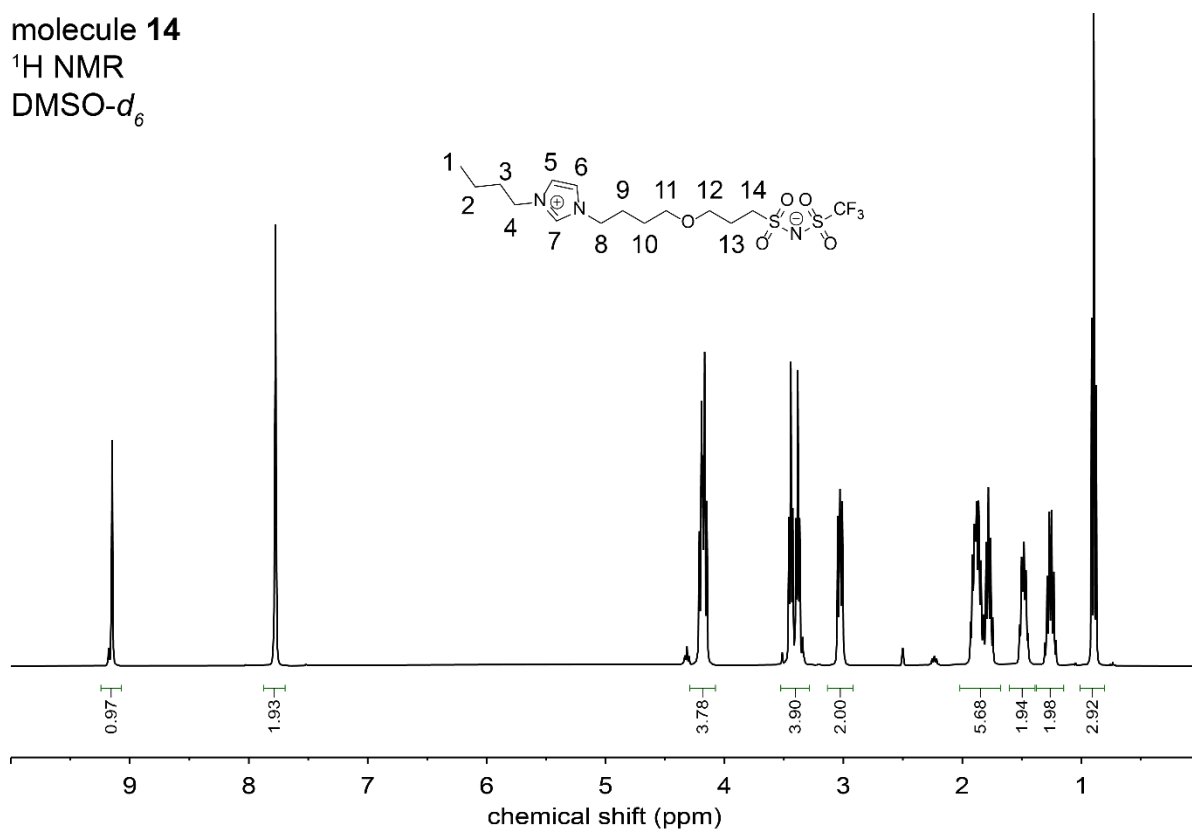


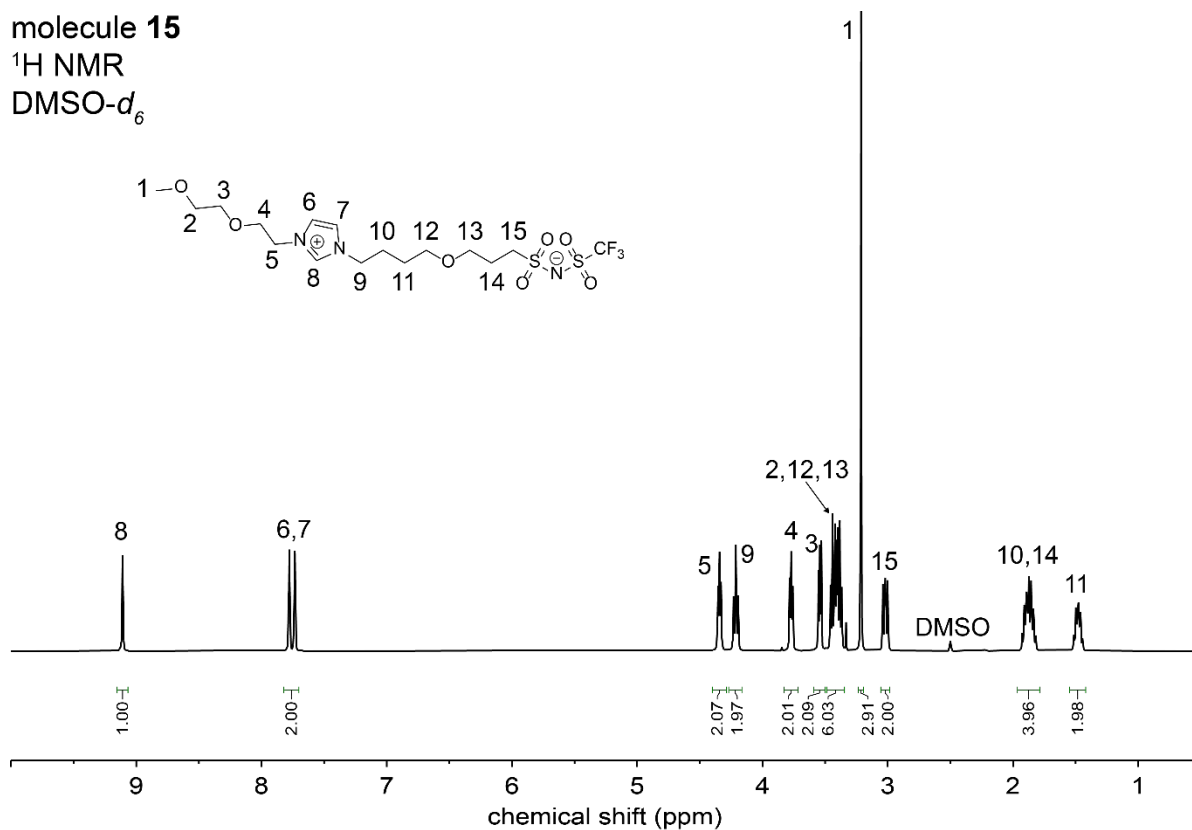
Molecule 14

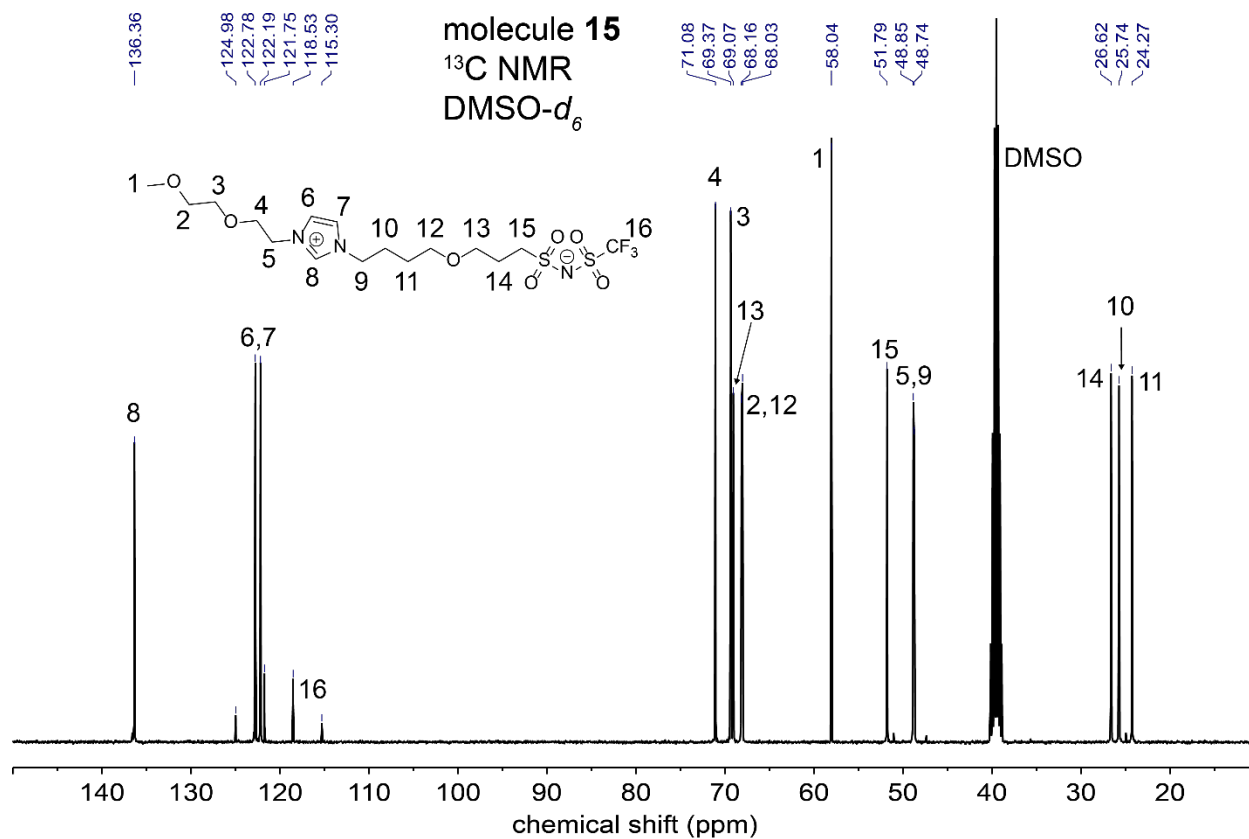
molecule 14

^1H NMR

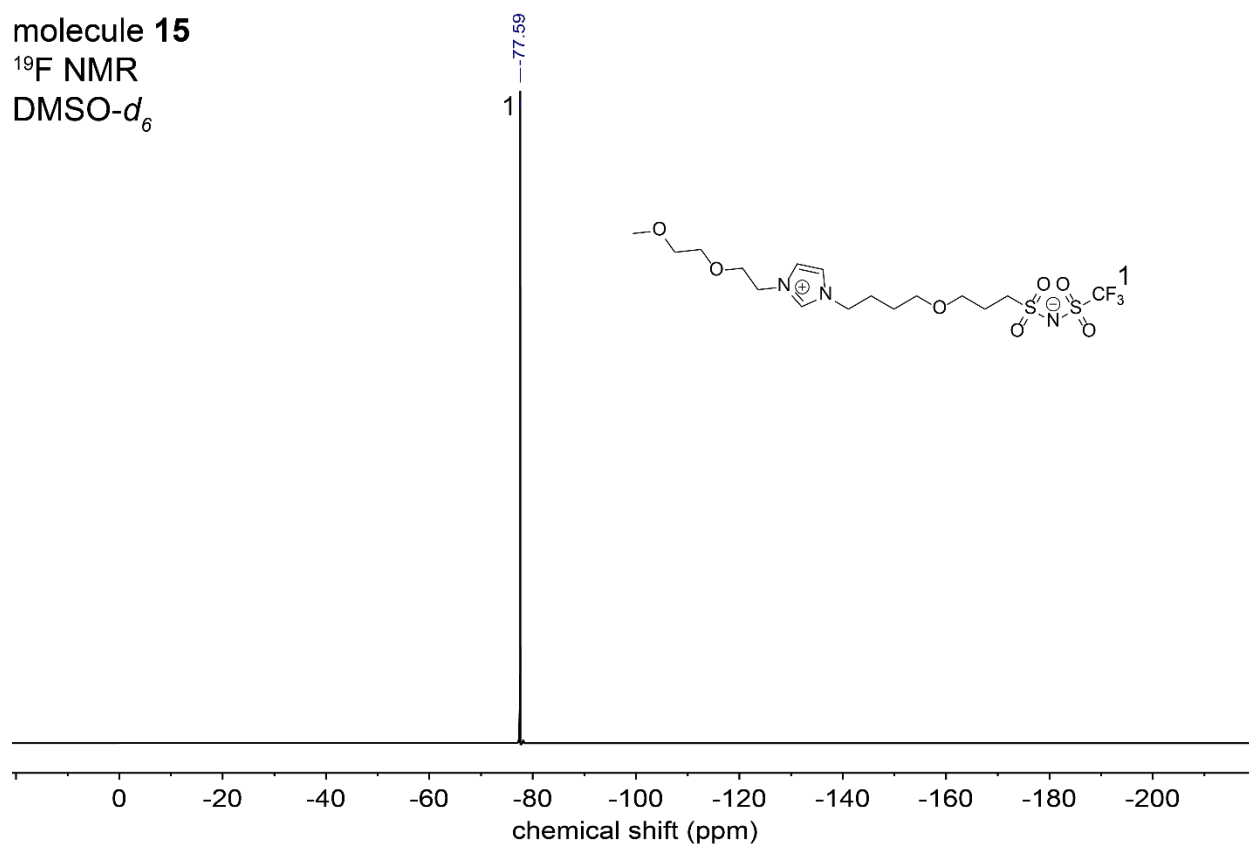
$\text{DMSO}-d_6$



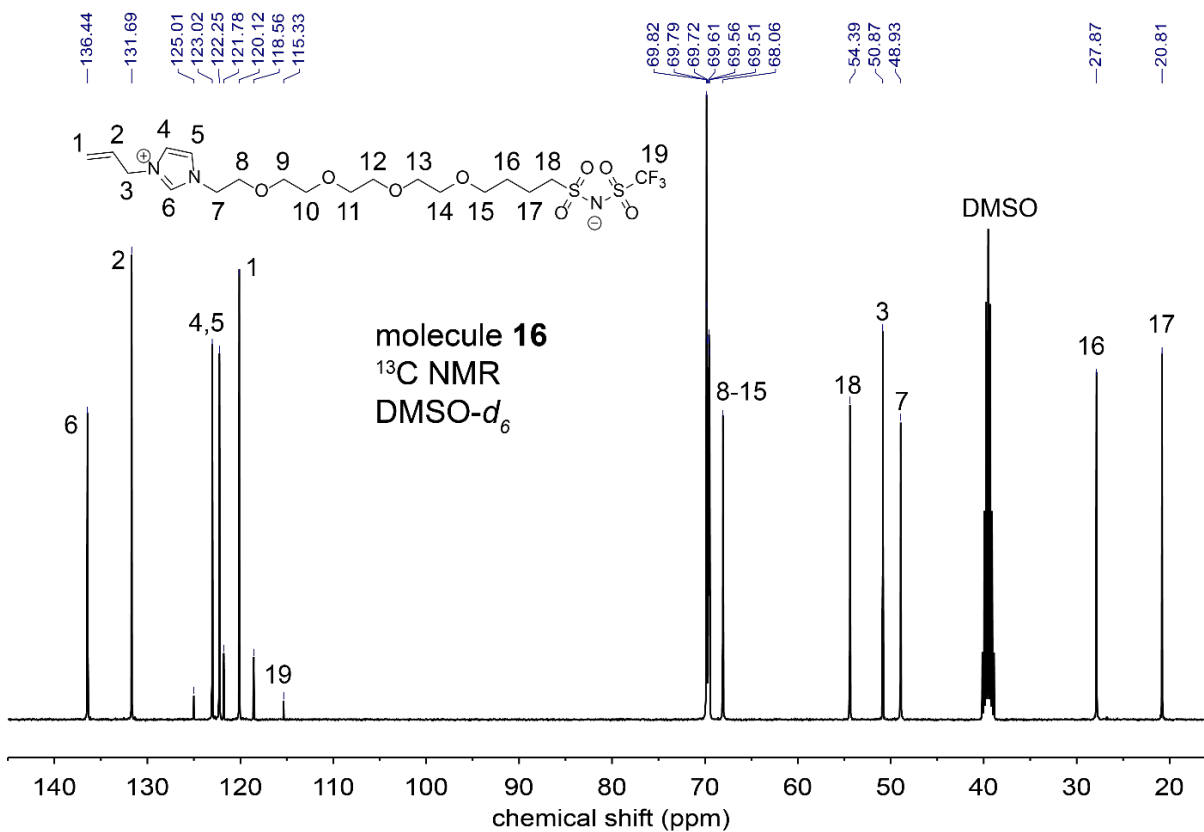
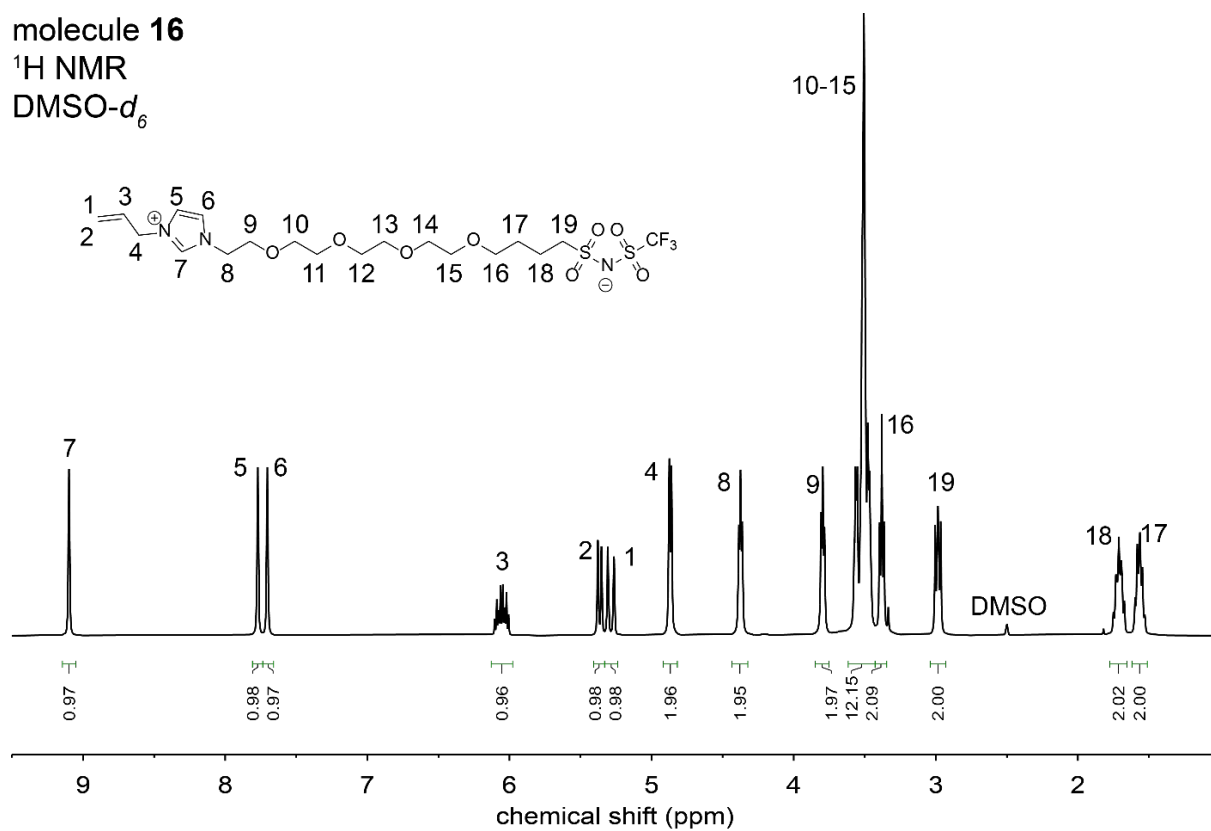
DMSO- d_6 DMSO- d_6 



molecule 15
¹⁹F NMR
DMSO-*d*₆



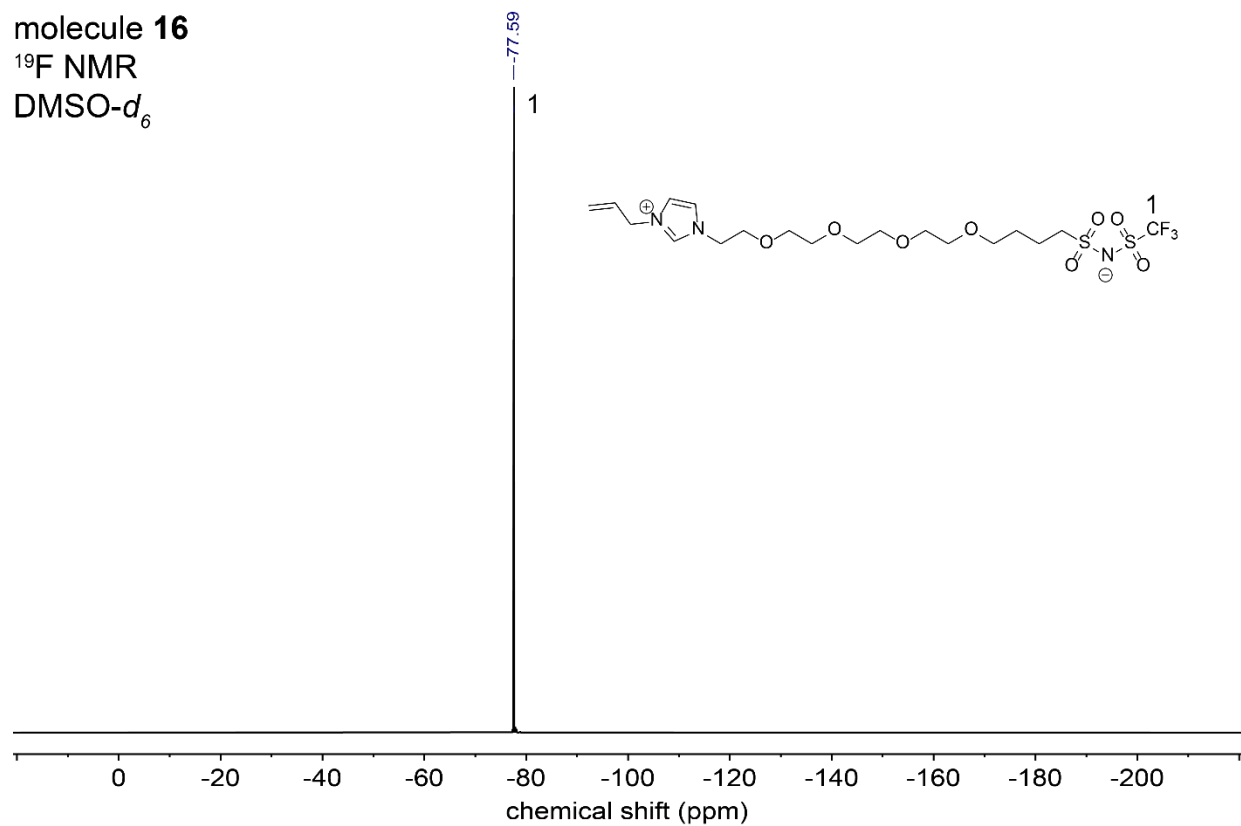
molecule 16

¹H NMRDMSO- d_6 DMSO- d_6 

molecule **16**

^{19}F NMR

$\text{DMSO}-d_6$

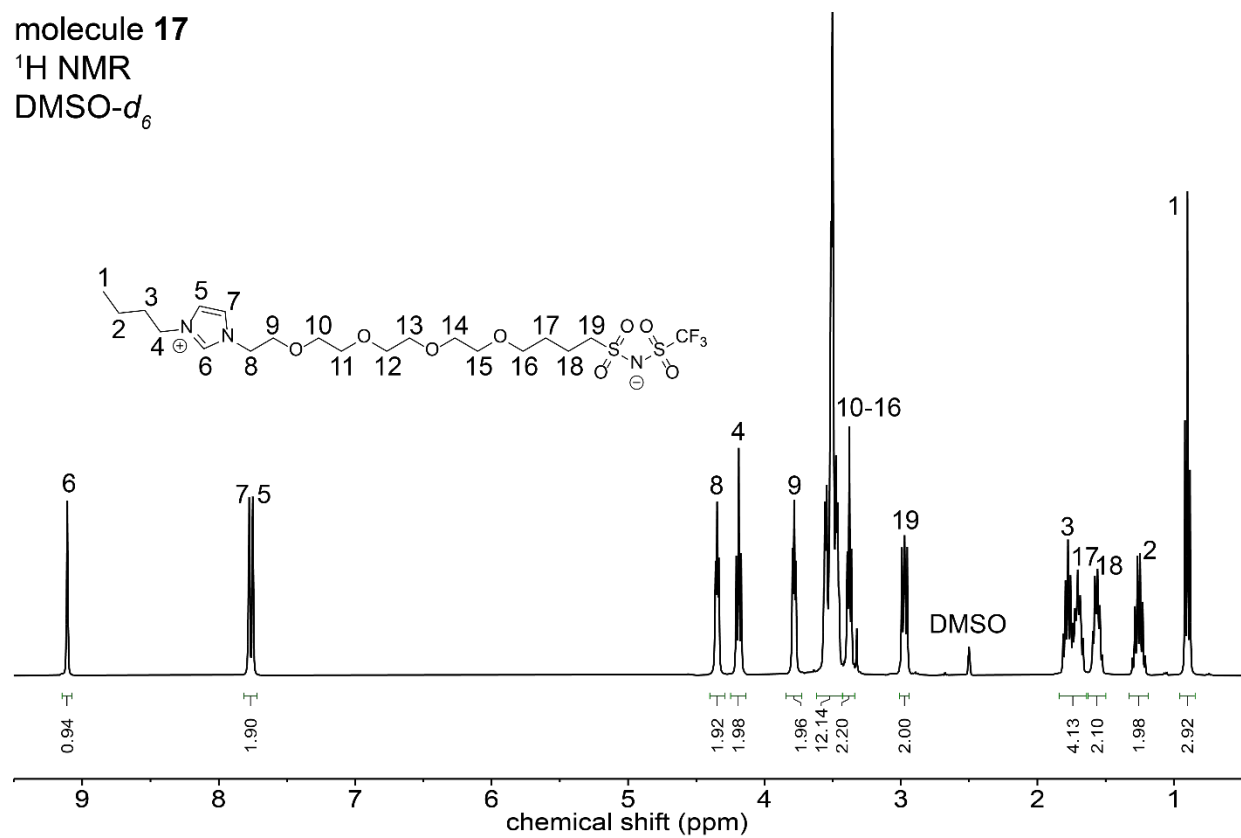


Molecule **17**

molecule **17**

^1H NMR

$\text{DMSO}-d_6$

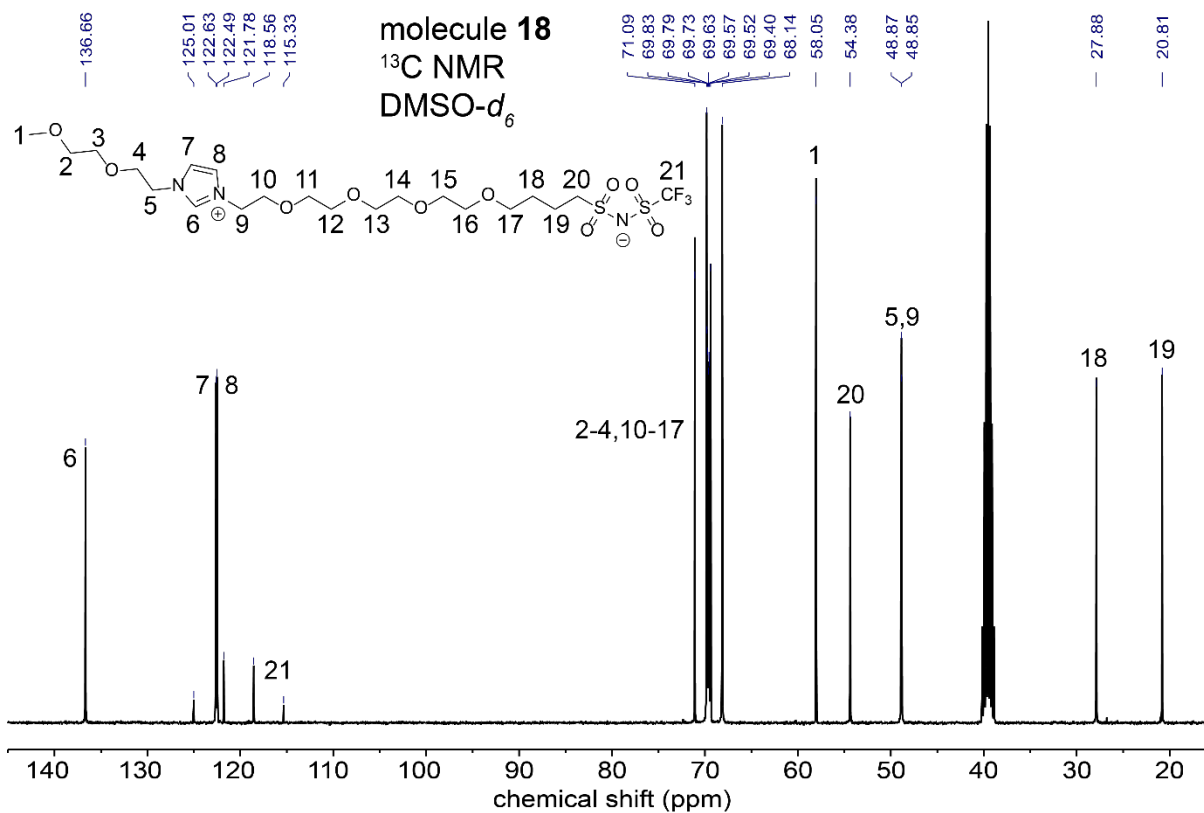
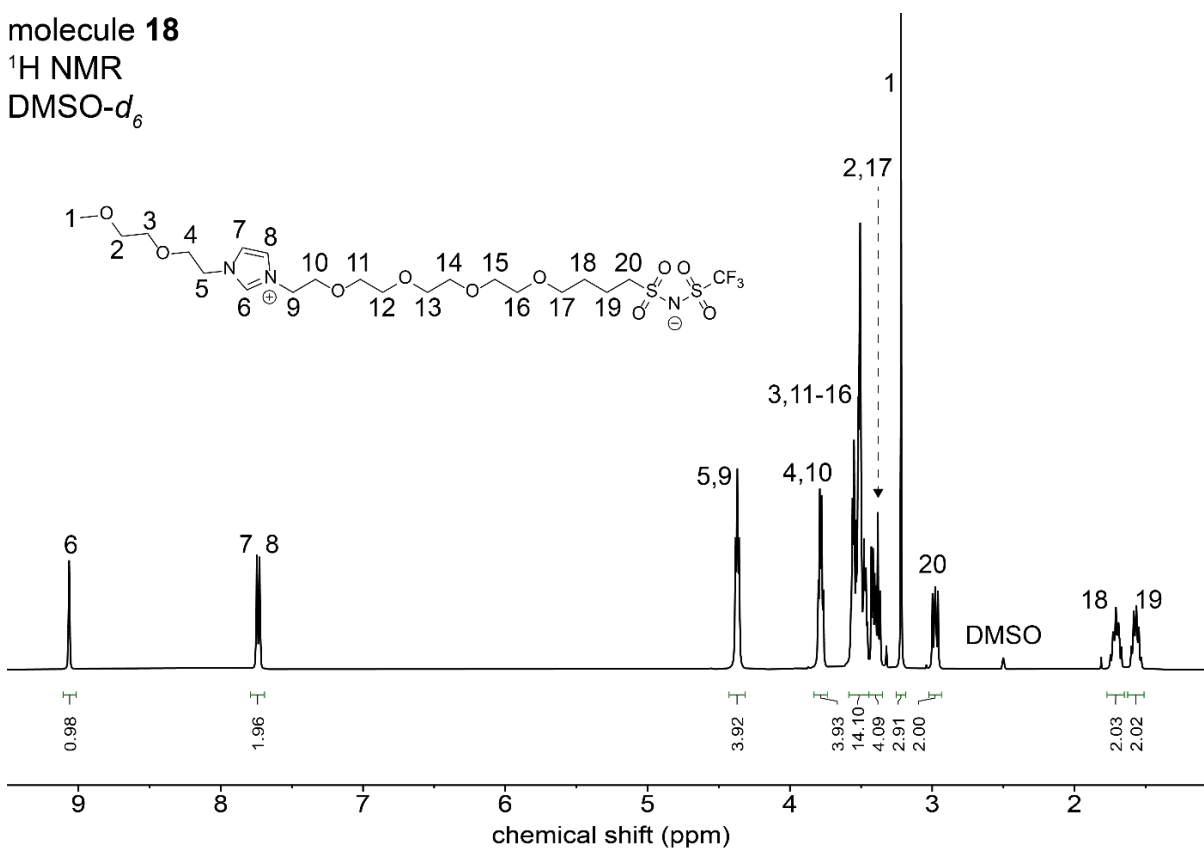


Molecule 18

molecule 18

^1H NMR

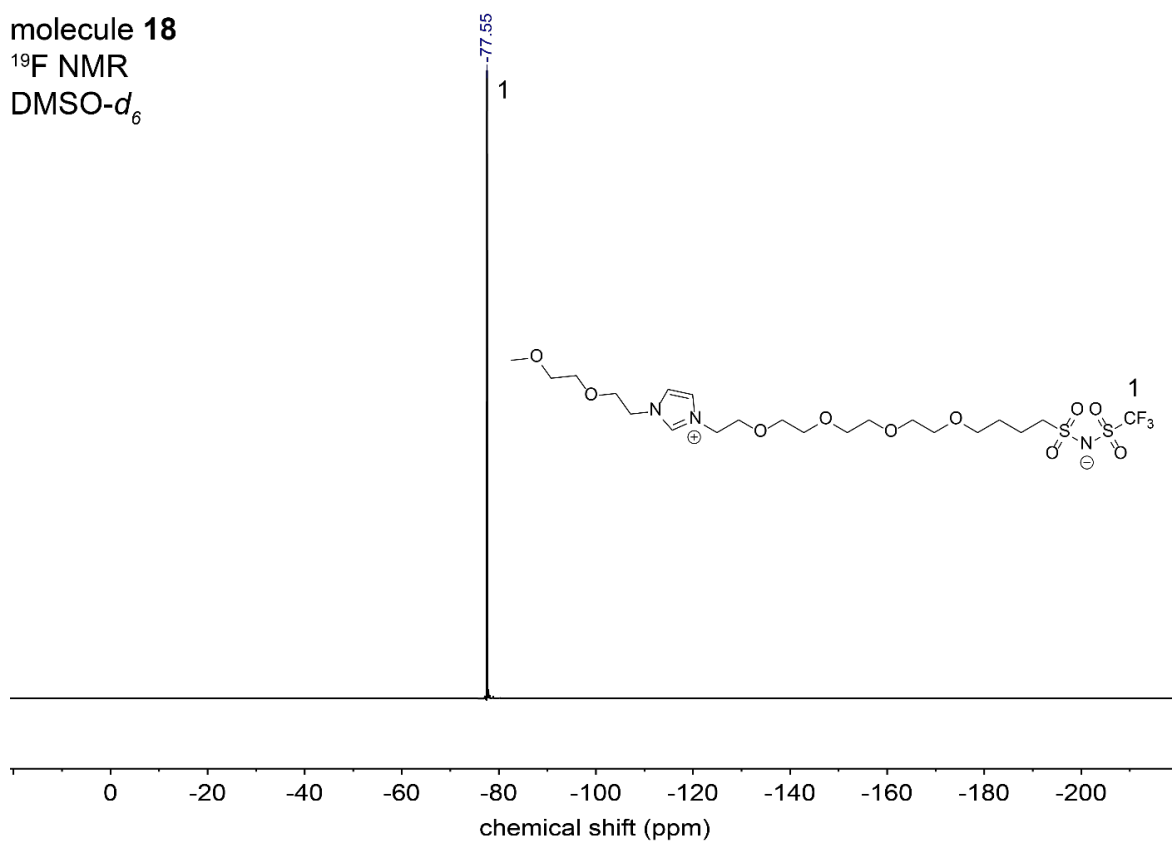
$\text{DMSO-}d_6$



molecule **18**

^{19}F NMR

$\text{DMSO}-d_6$

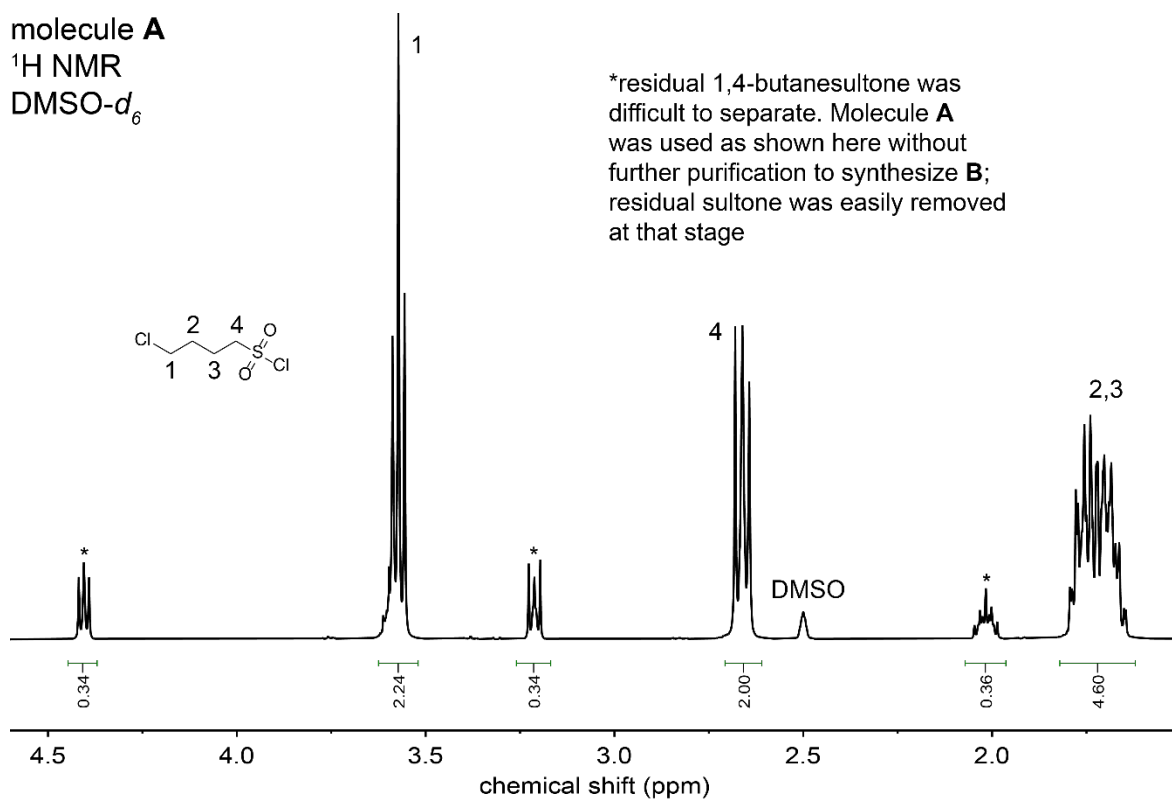


Molecule **A**

molecule **A**

^1H NMR

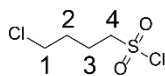
$\text{DMSO}-d_6$



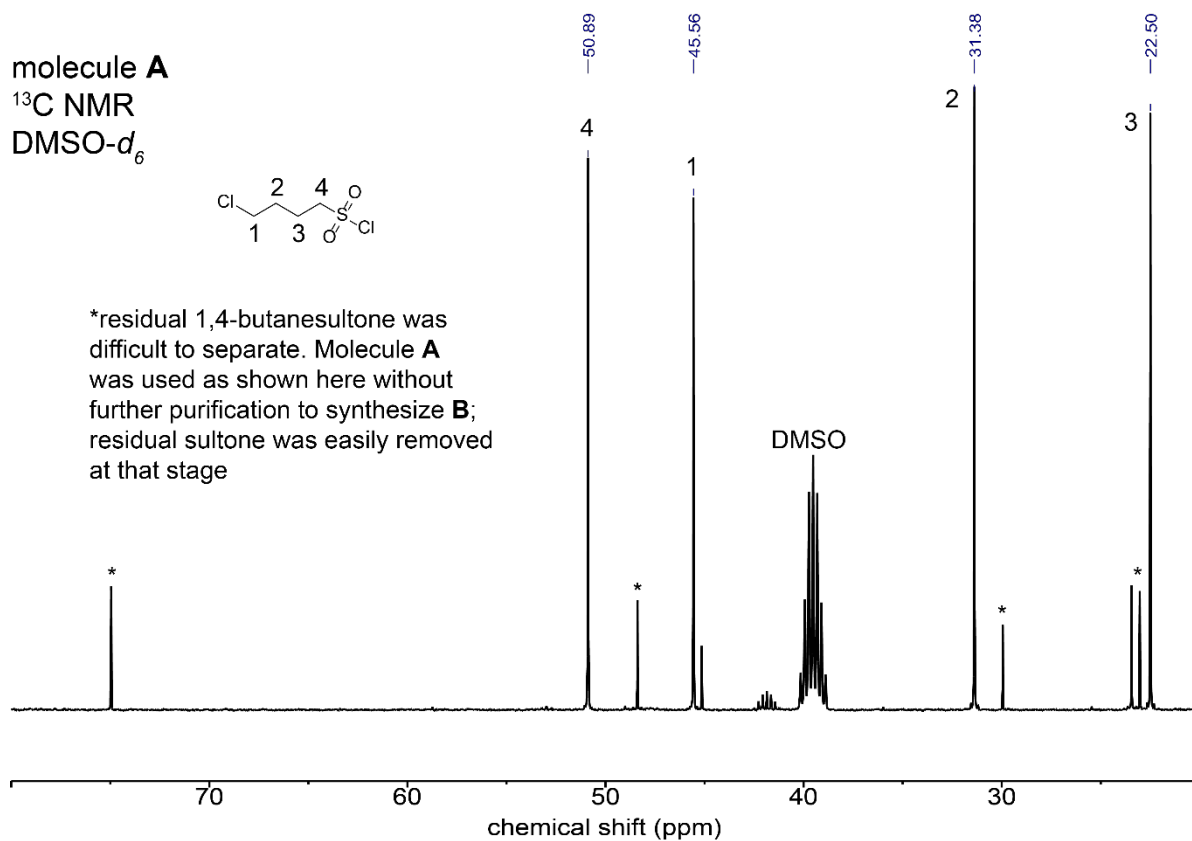
molecule **A**

^{13}C NMR

$\text{DMSO}-d_6$



*residual 1,4-butanedisulfone was difficult to separate. Molecule **A** was used as shown here without further purification to synthesize **B**; residual sulfone was easily removed at that stage

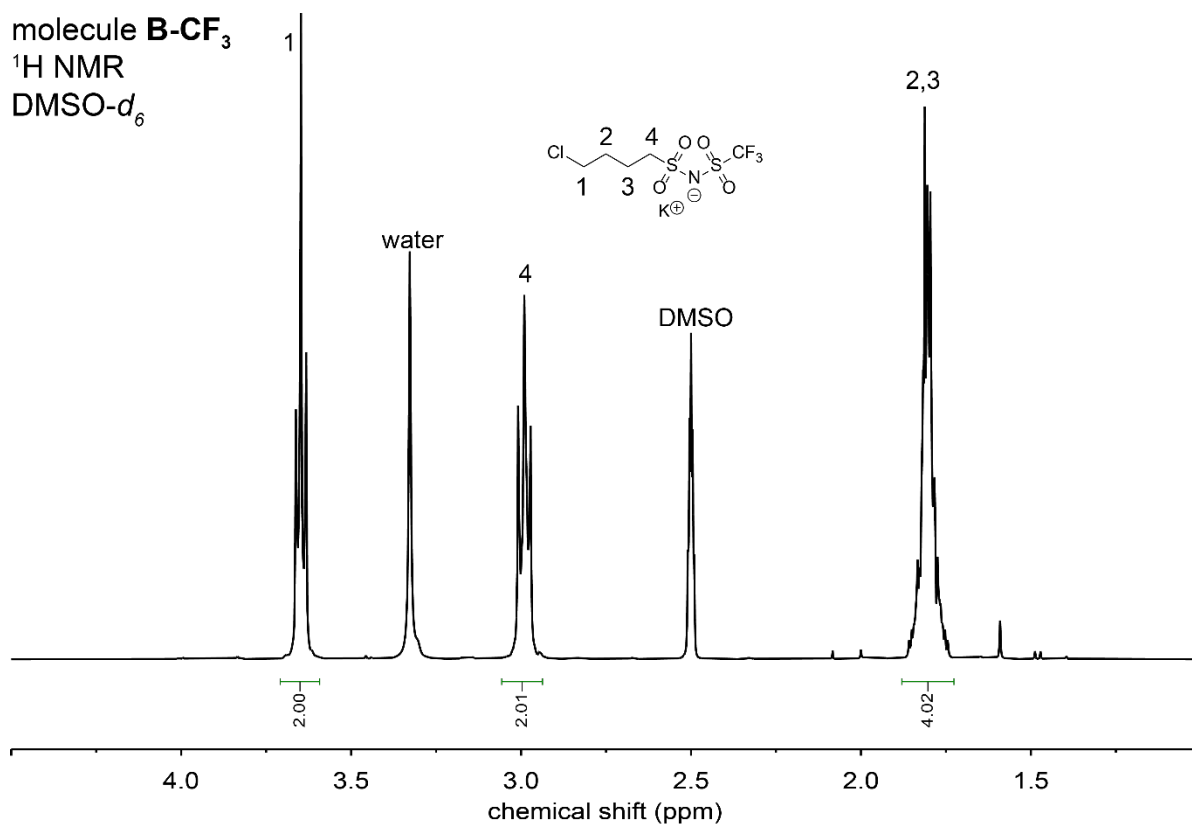
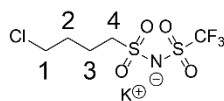


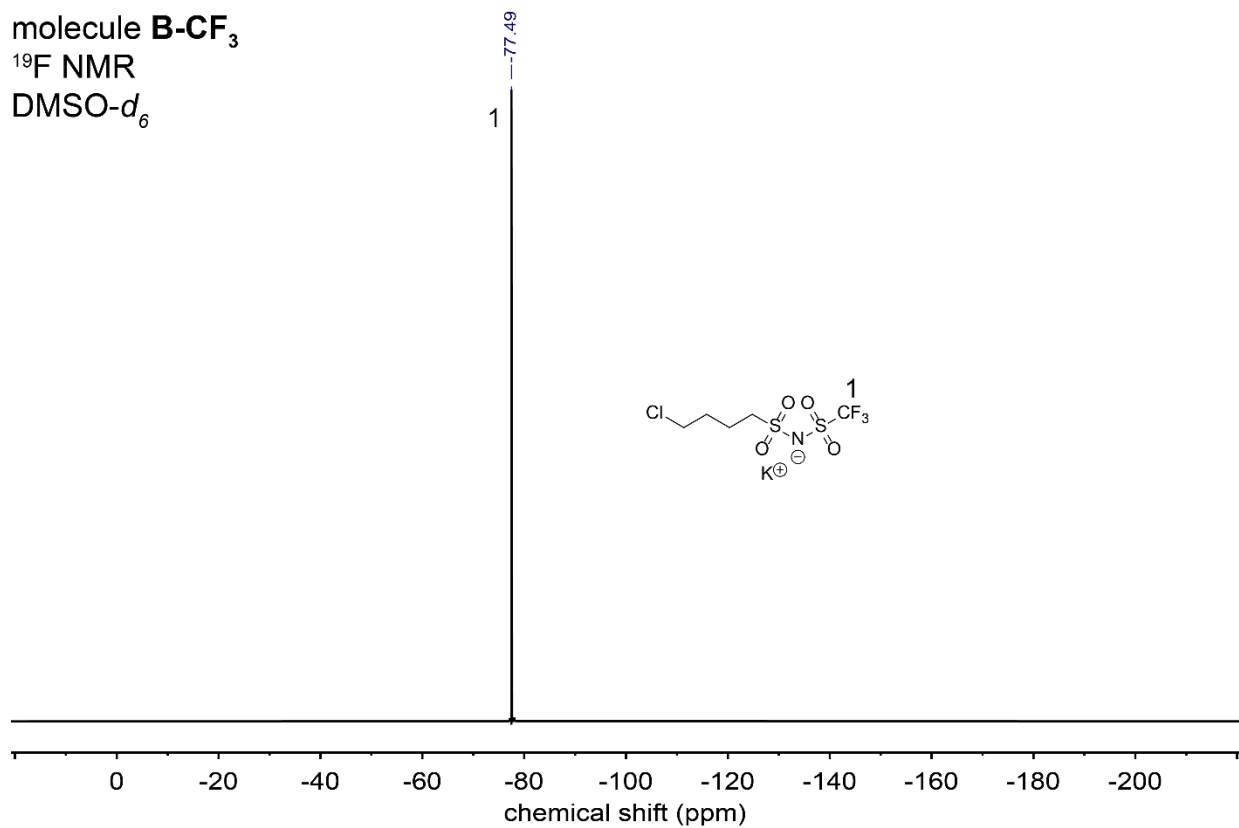
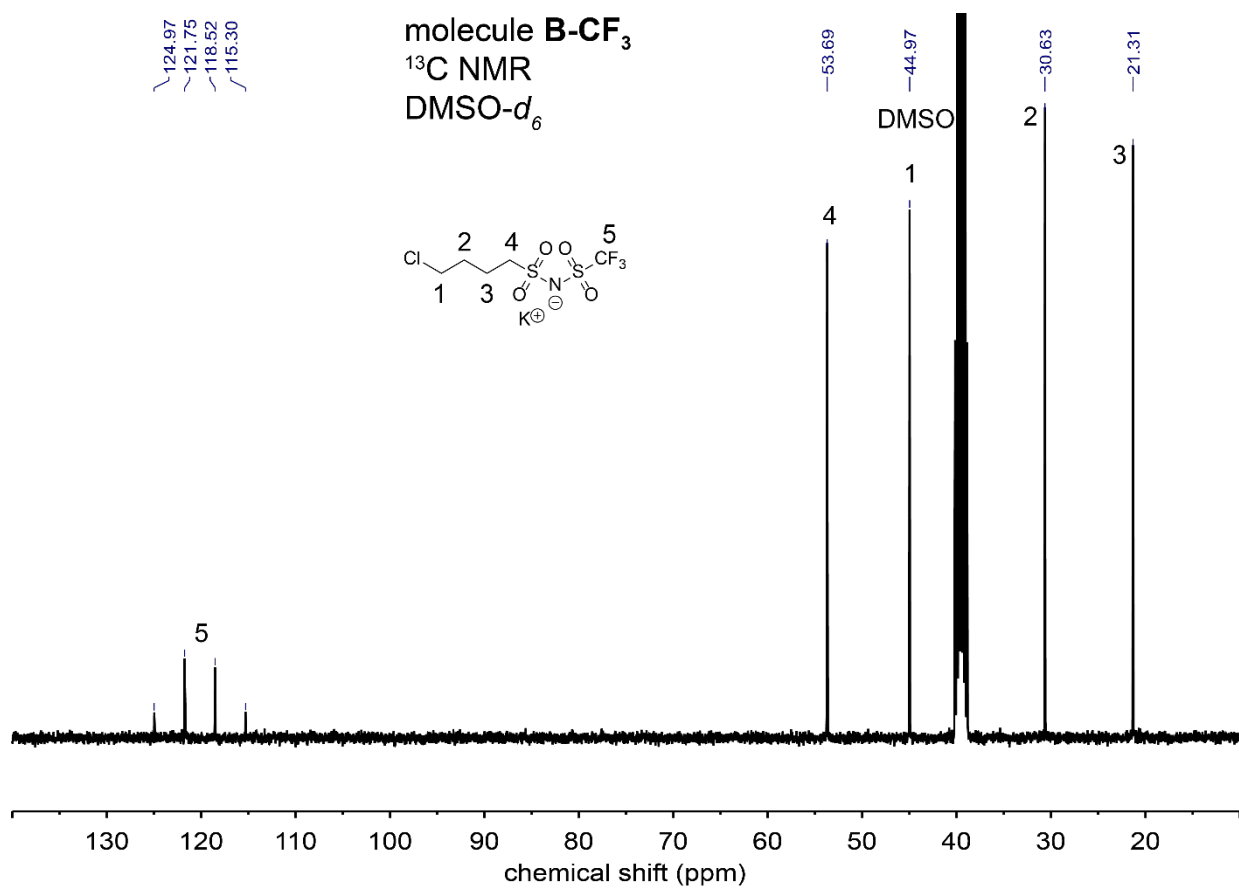
Molecule **B-CF₃**

molecule **B-CF₃**

^1H NMR

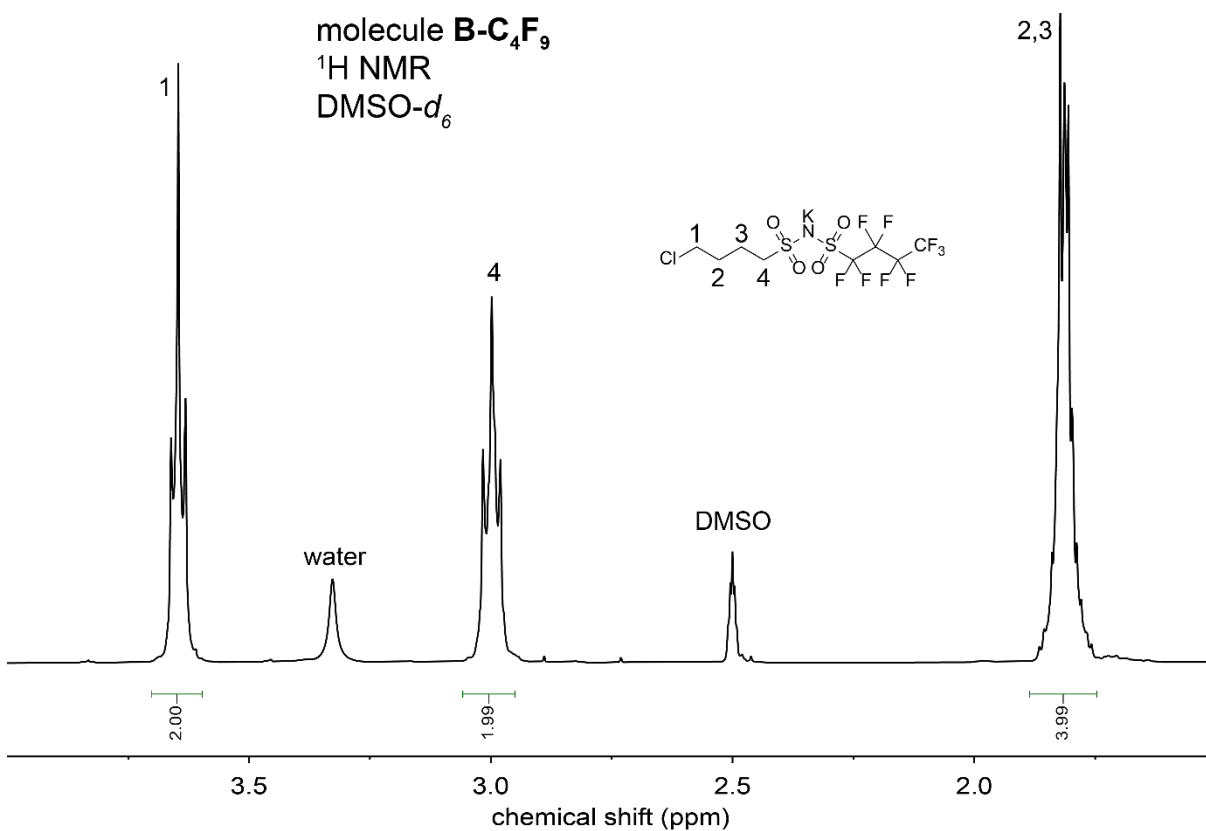
$\text{DMSO}-d_6$



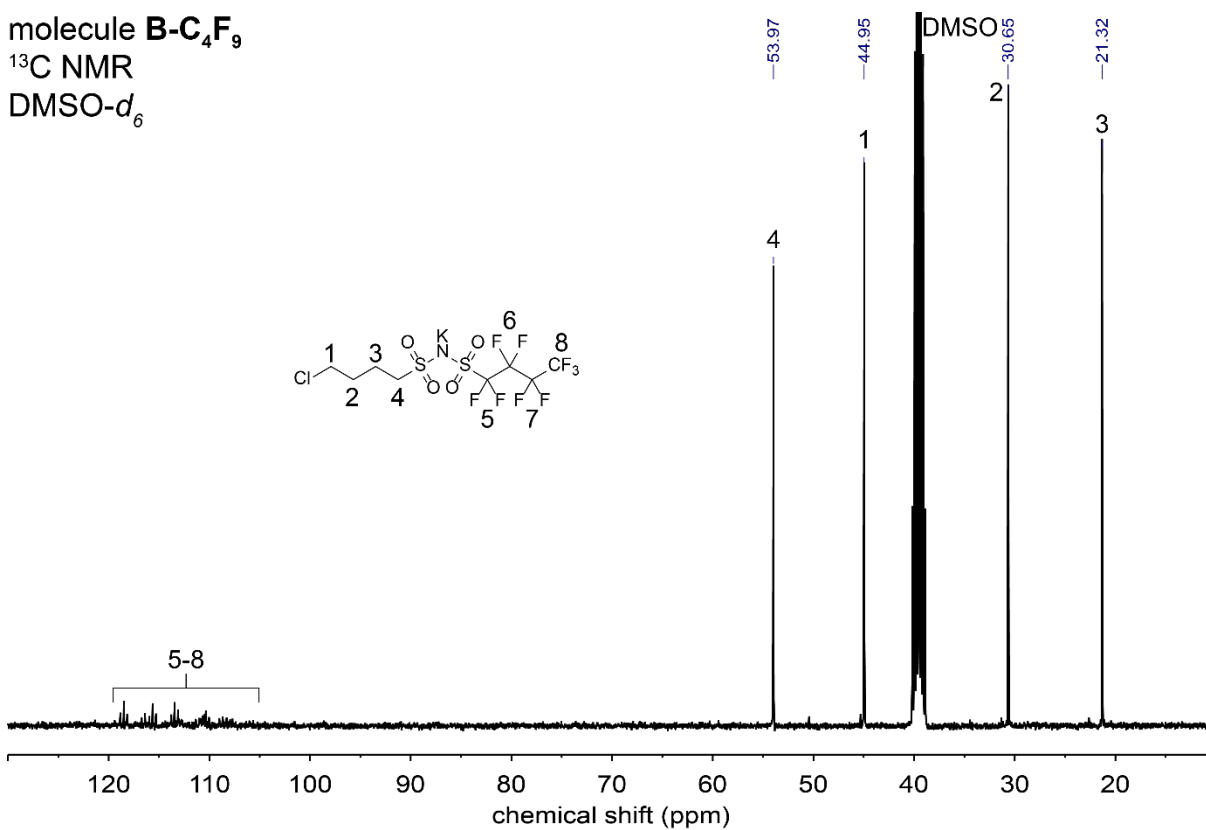


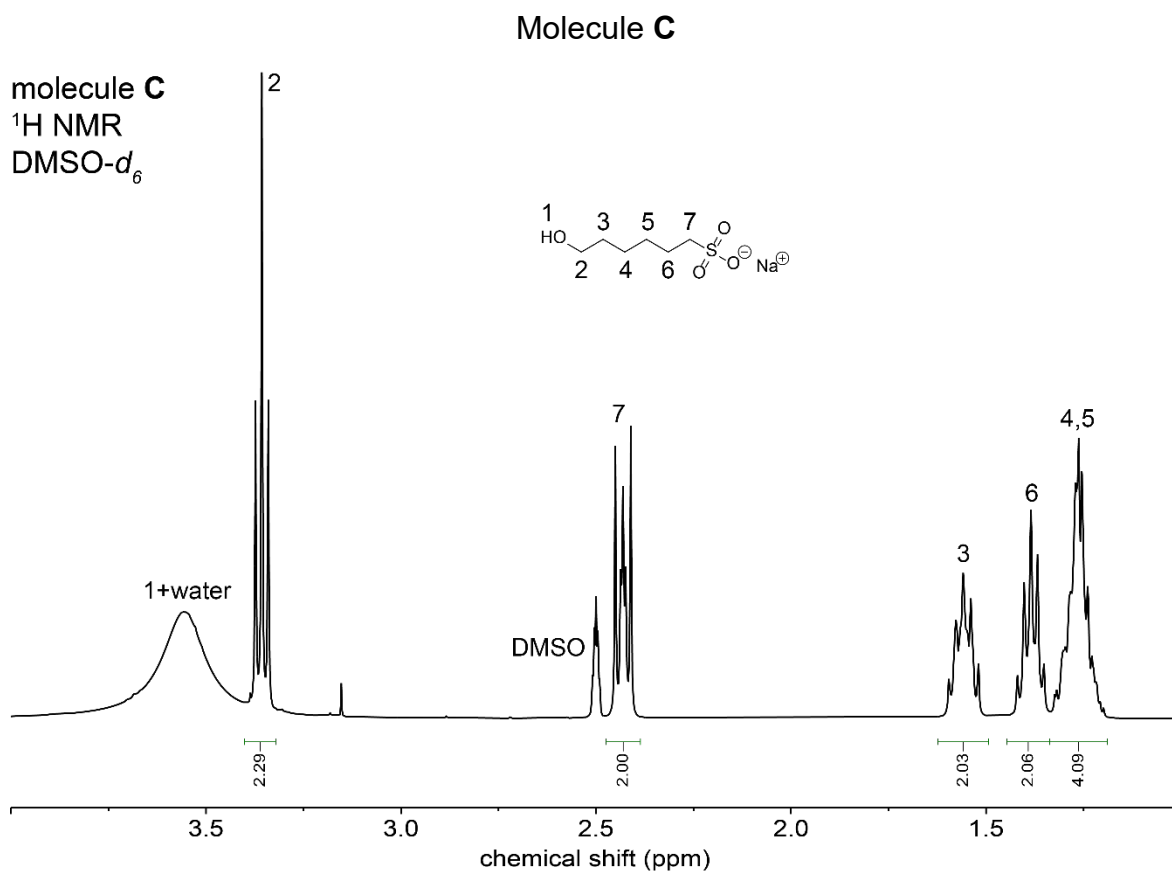
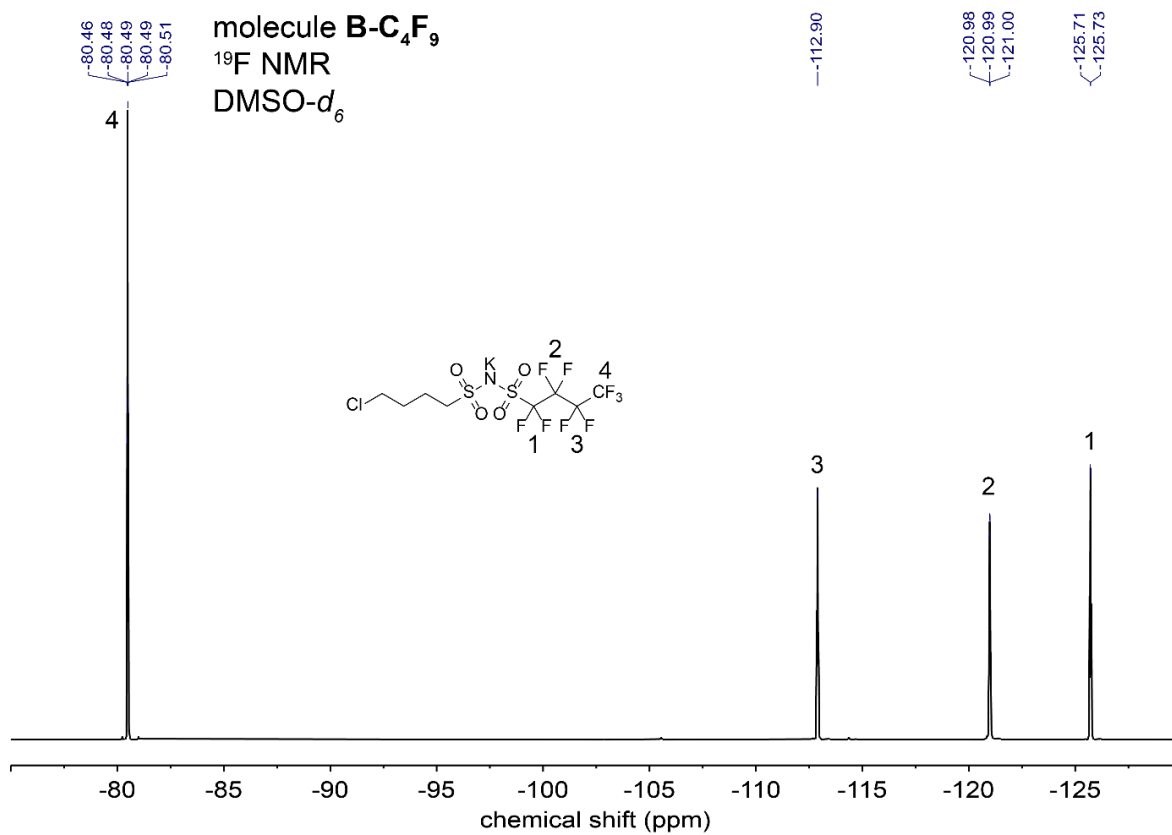
Molecule **B-C₄F₉**

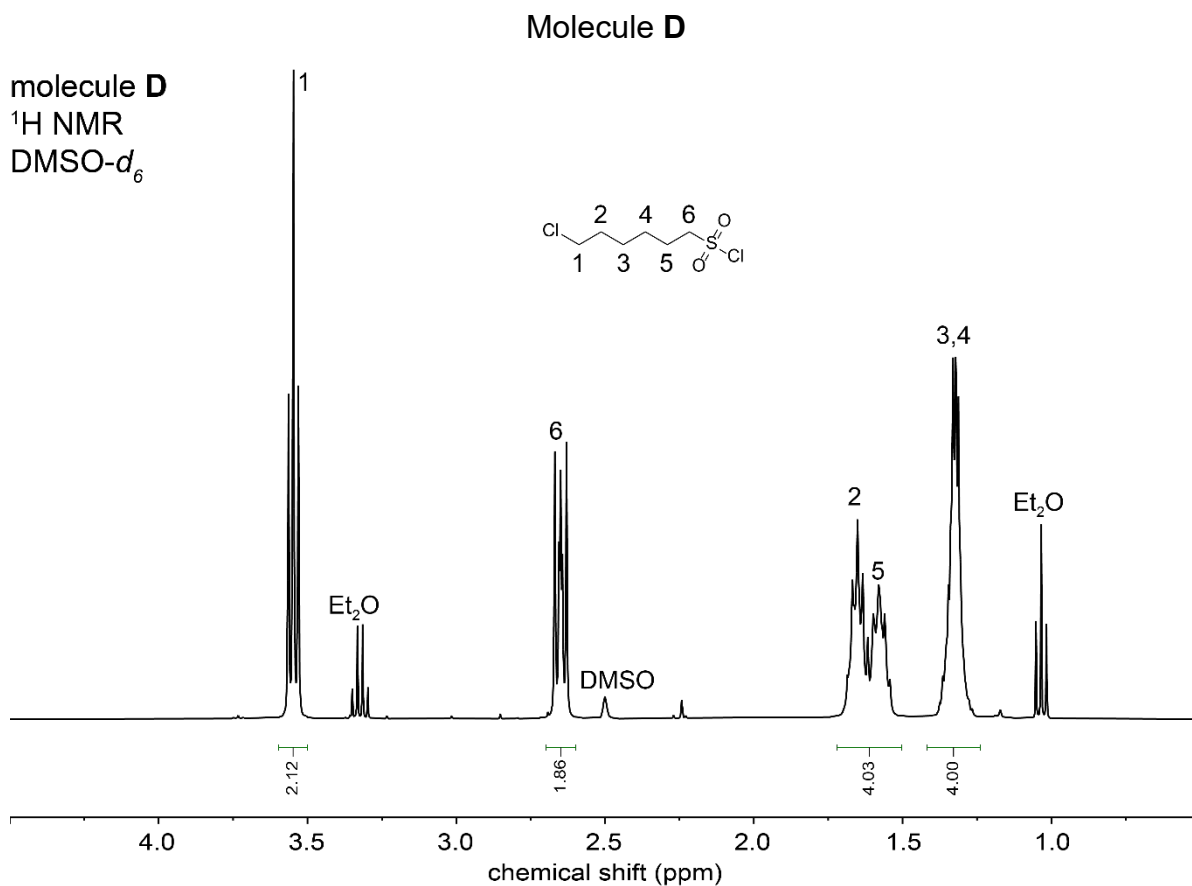
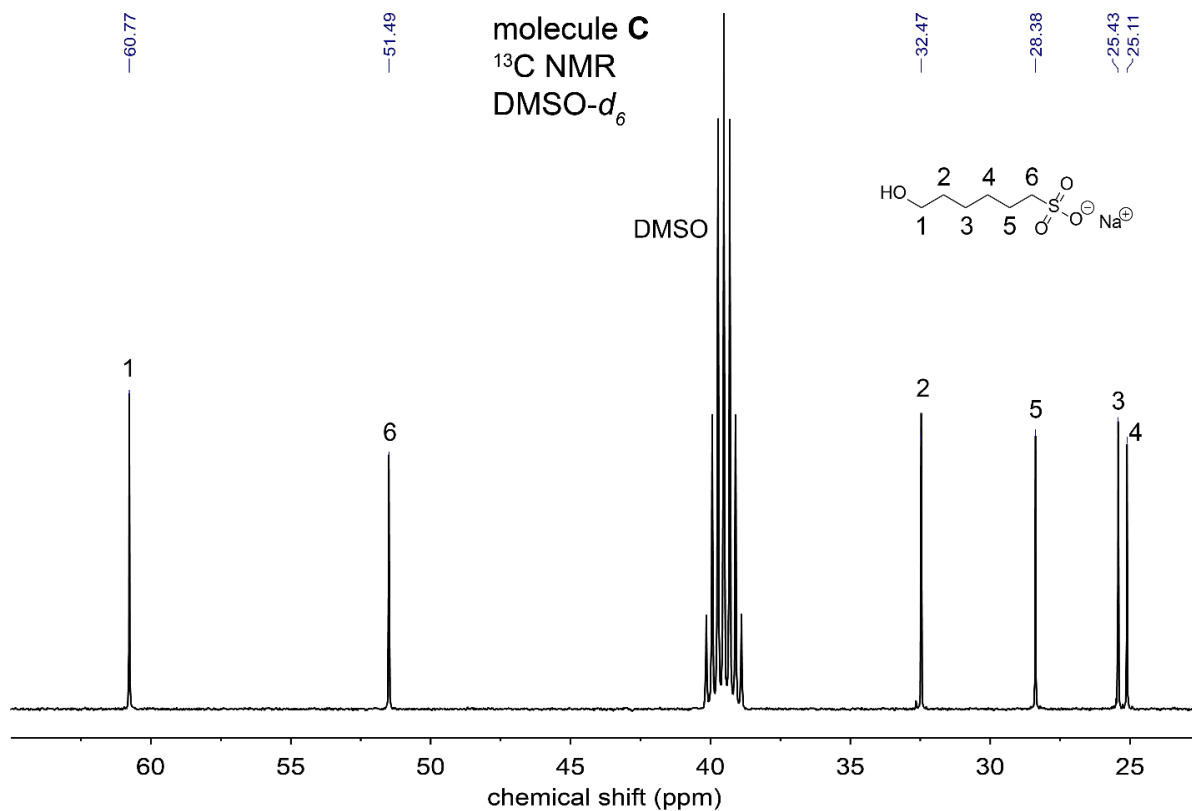
molecule **B-C₄F₉**
¹H NMR
 DMSO-*d*₆



molecule **B-C₄F₉**
¹³C NMR
 DMSO-*d*₆



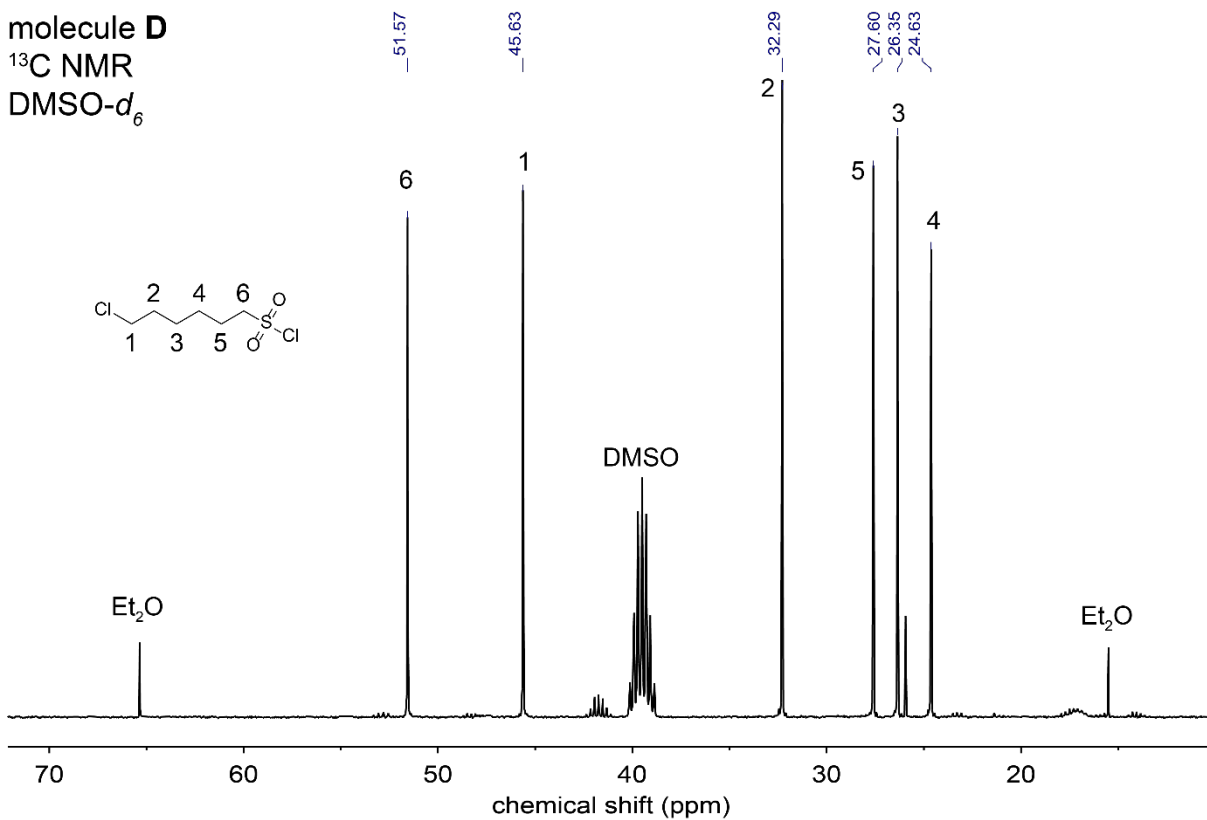




molecule **D**

^{13}C NMR

$\text{DMSO}-d_6$

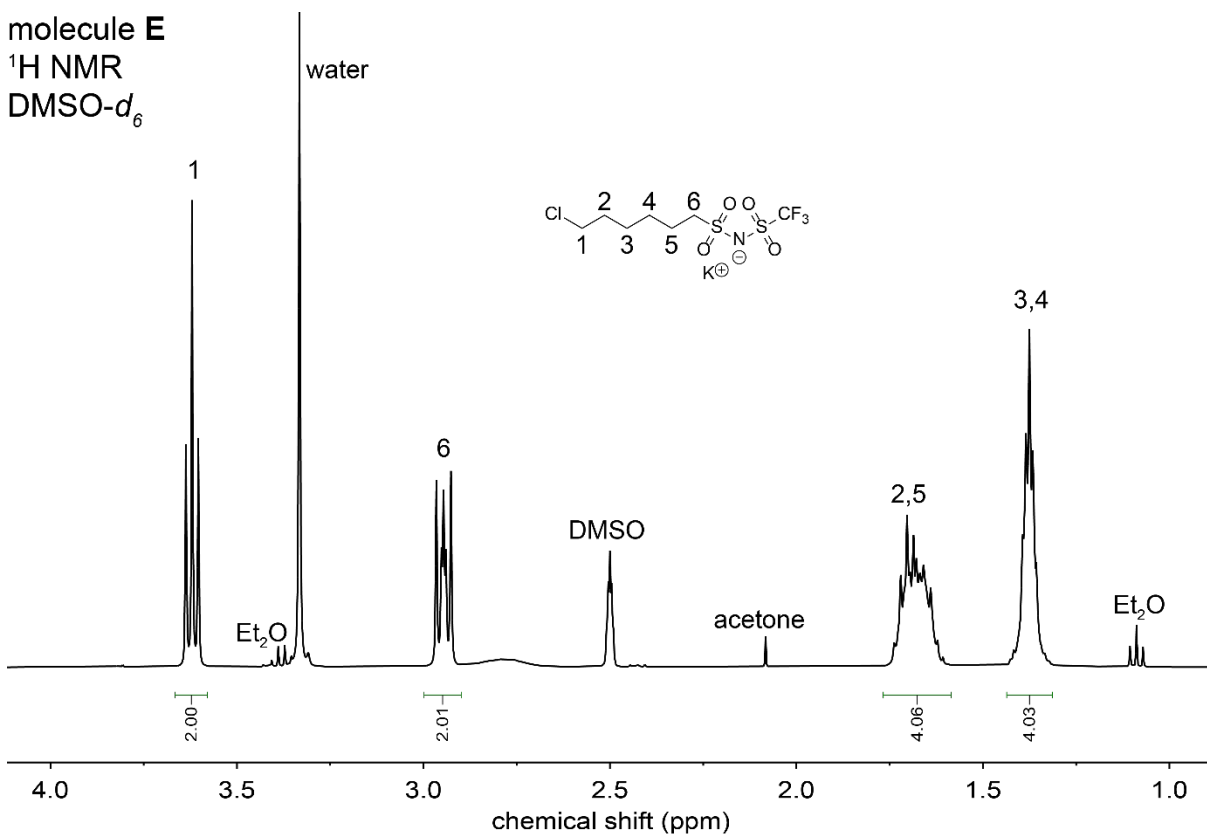


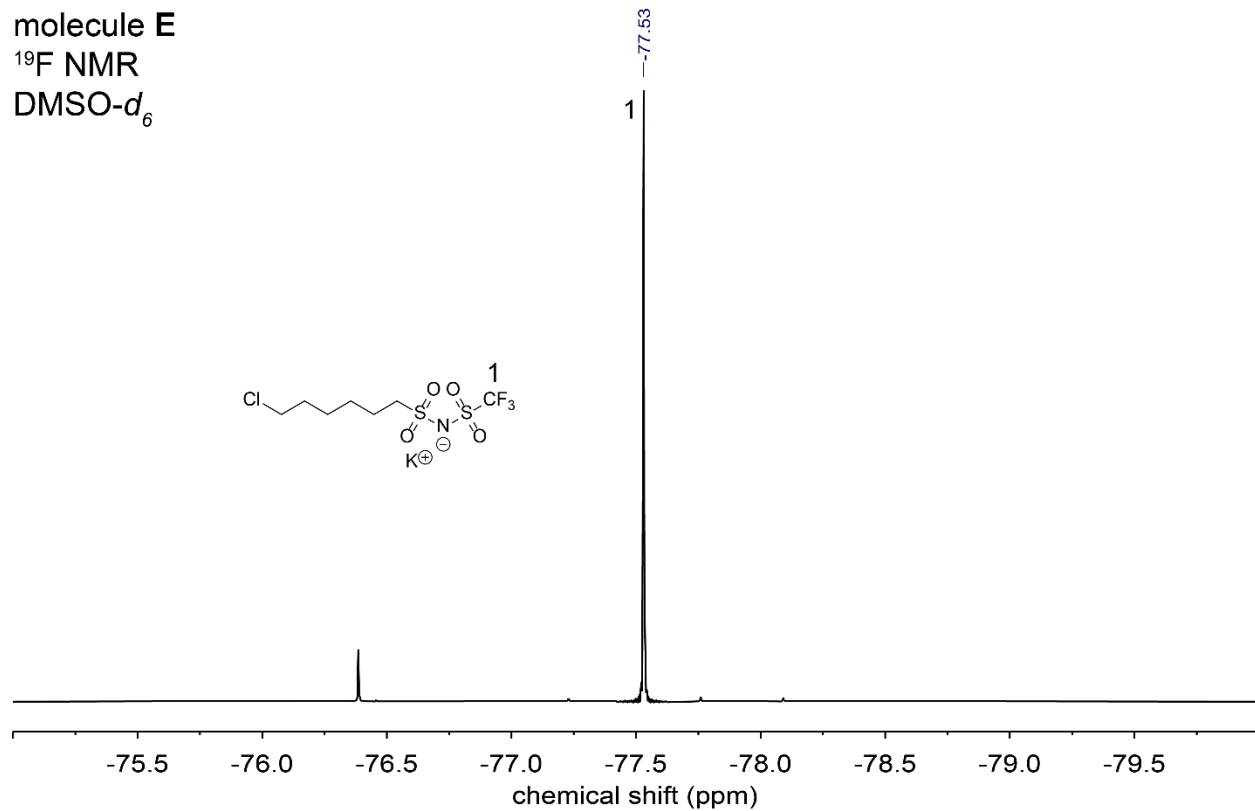
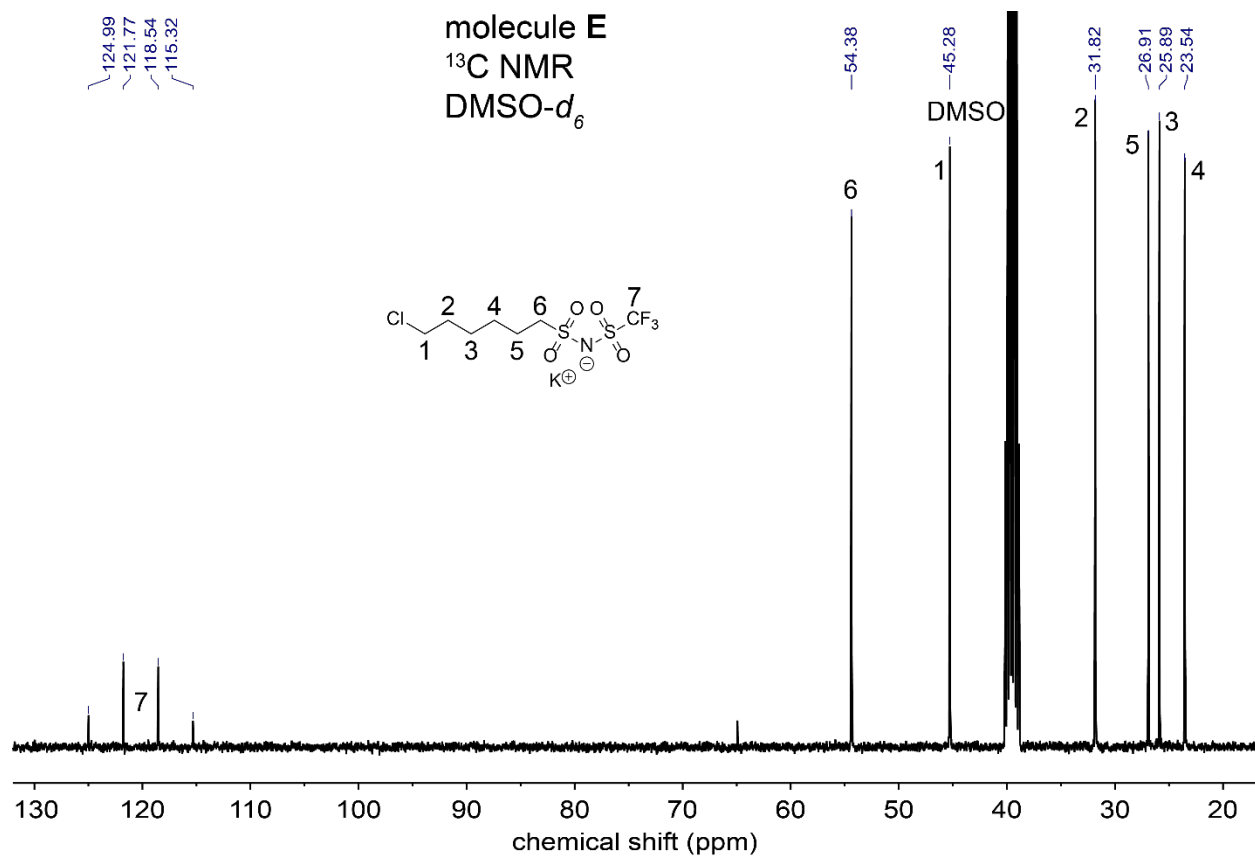
Molecule **E**

molecule **E**

^1H NMR

$\text{DMSO}-d_6$



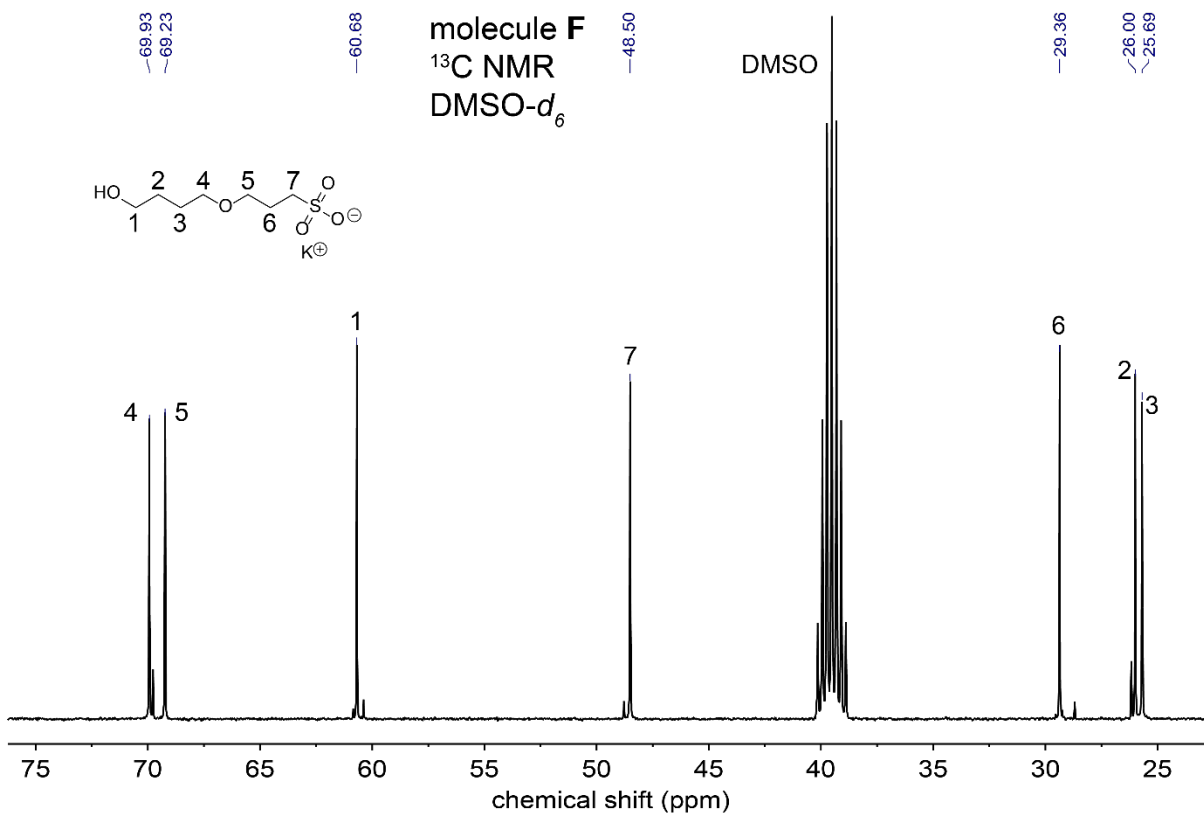
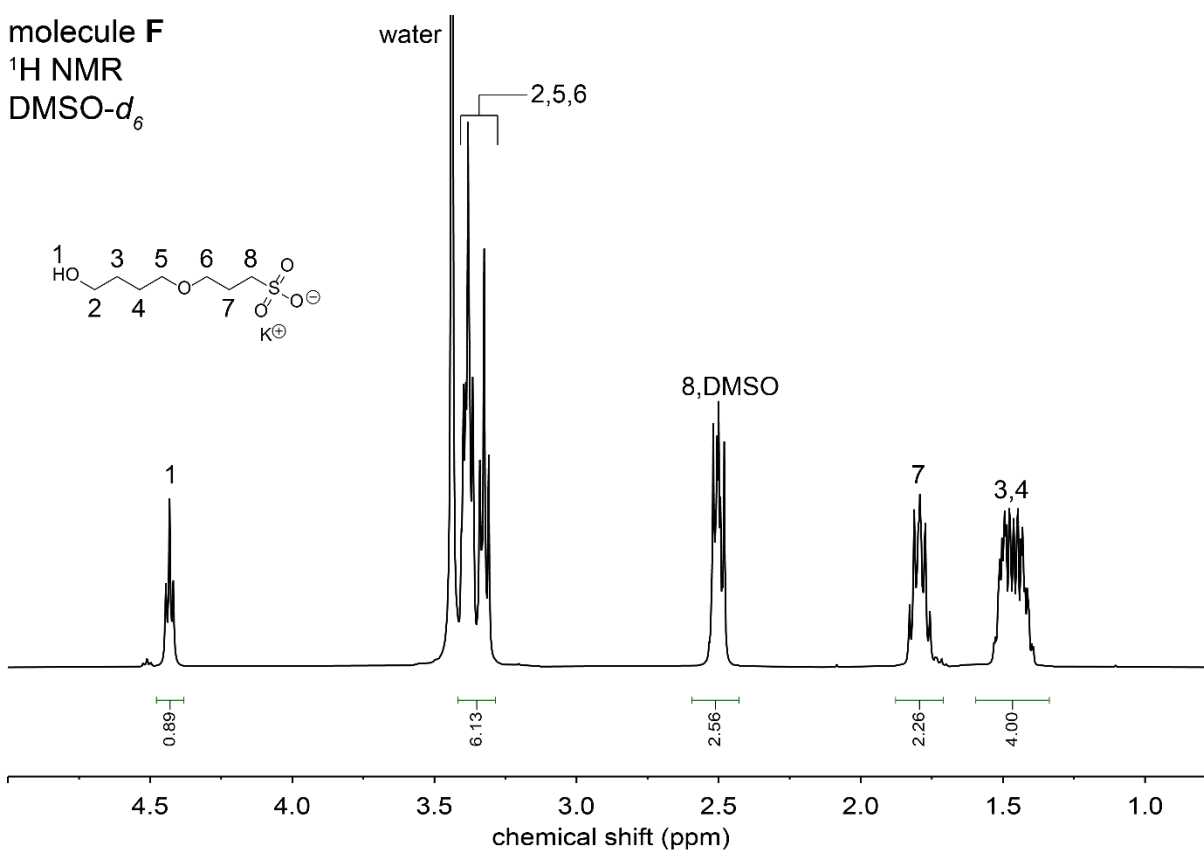


Molecule F

molecule F

^1H NMR

$\text{DMSO-}d_6$

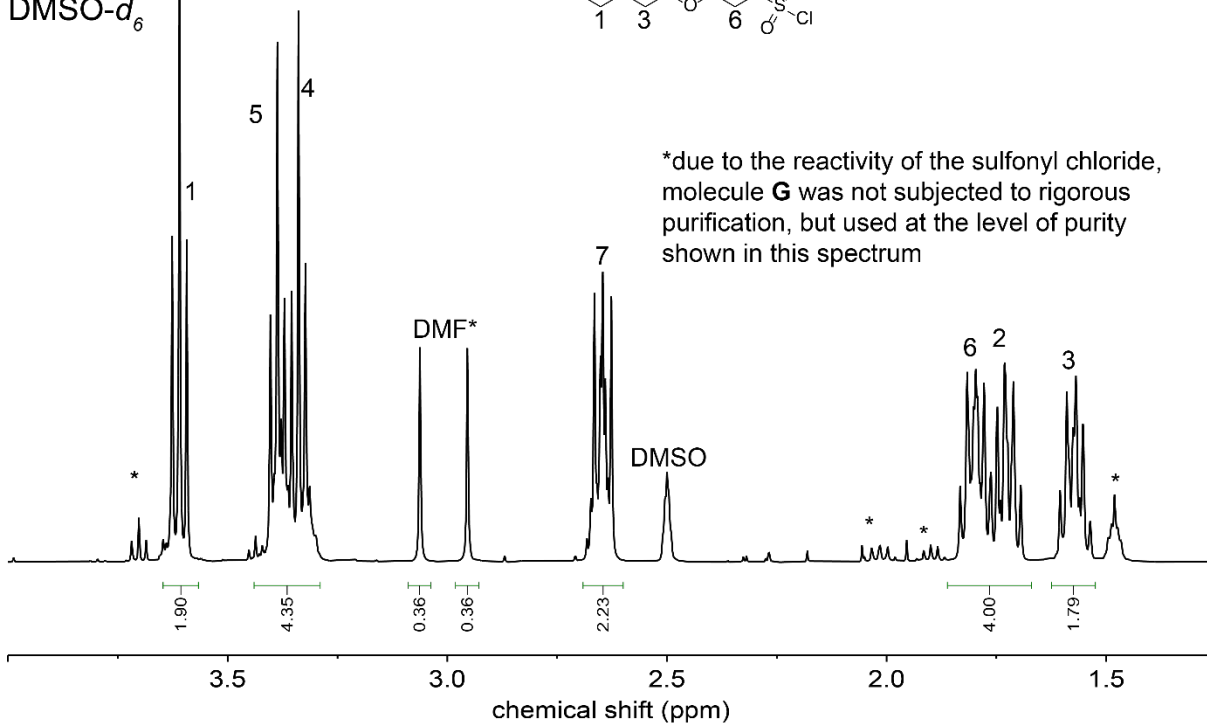
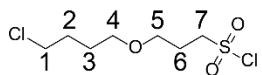


Molecule G

molecule G

¹H NMR

DMSO-*d*₆



69.34
68.83

molecule G

¹³C NMR

DMSO-*d*₆

48.63

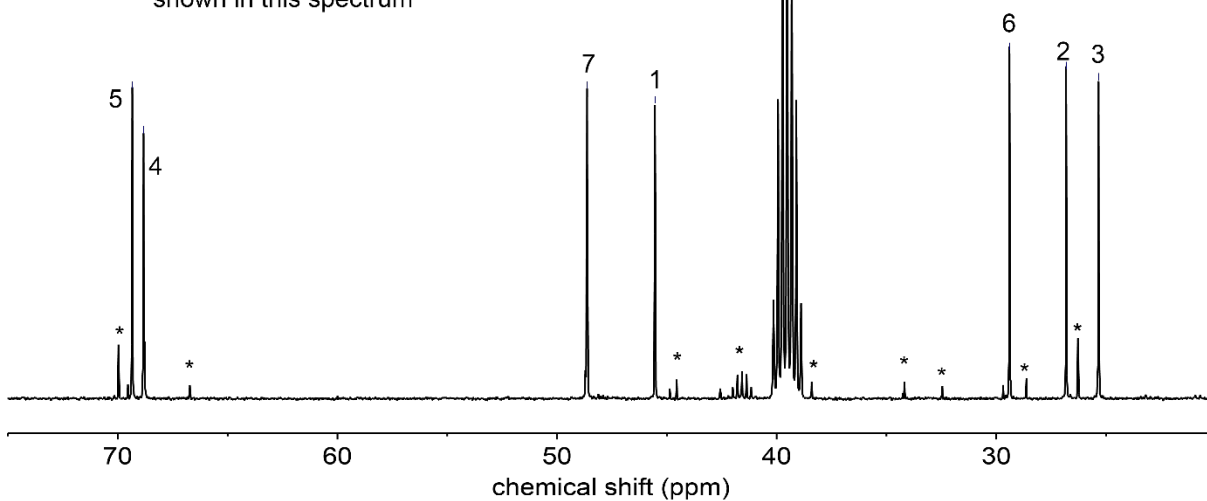
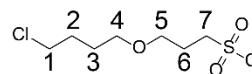
45.54

29.40

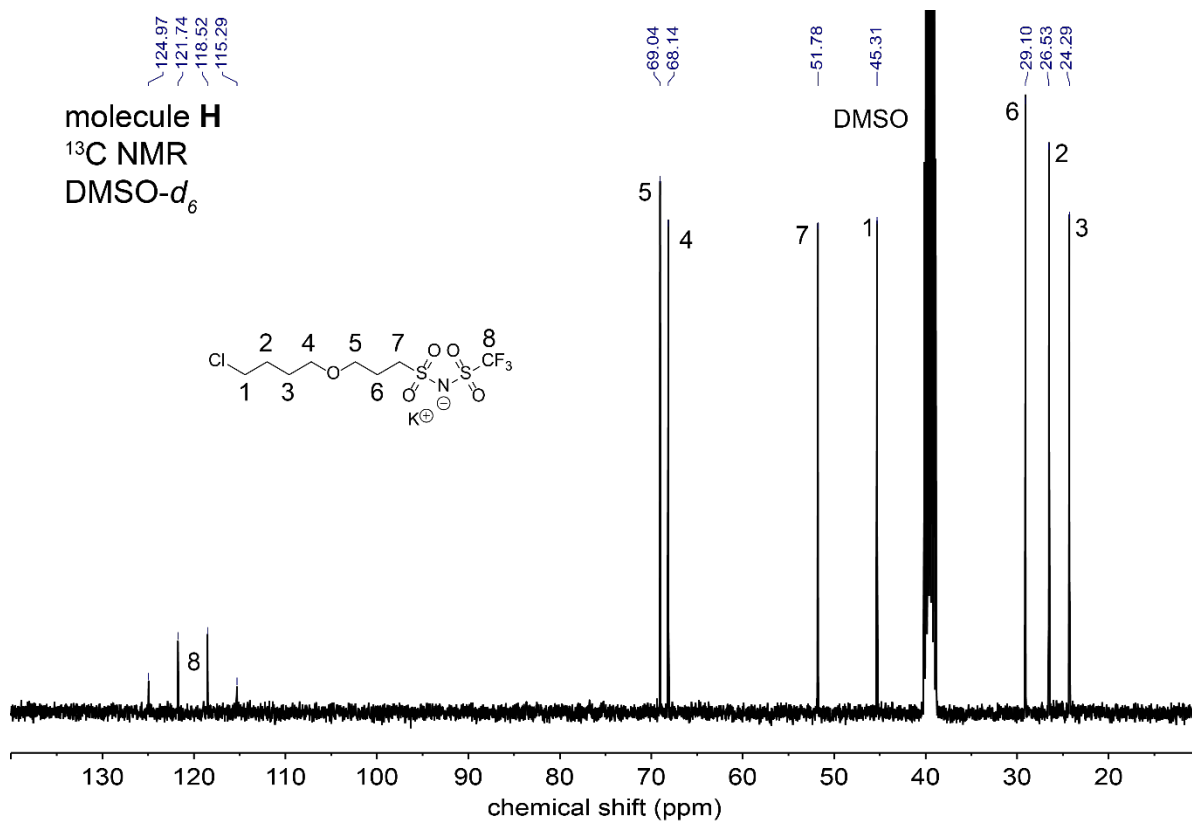
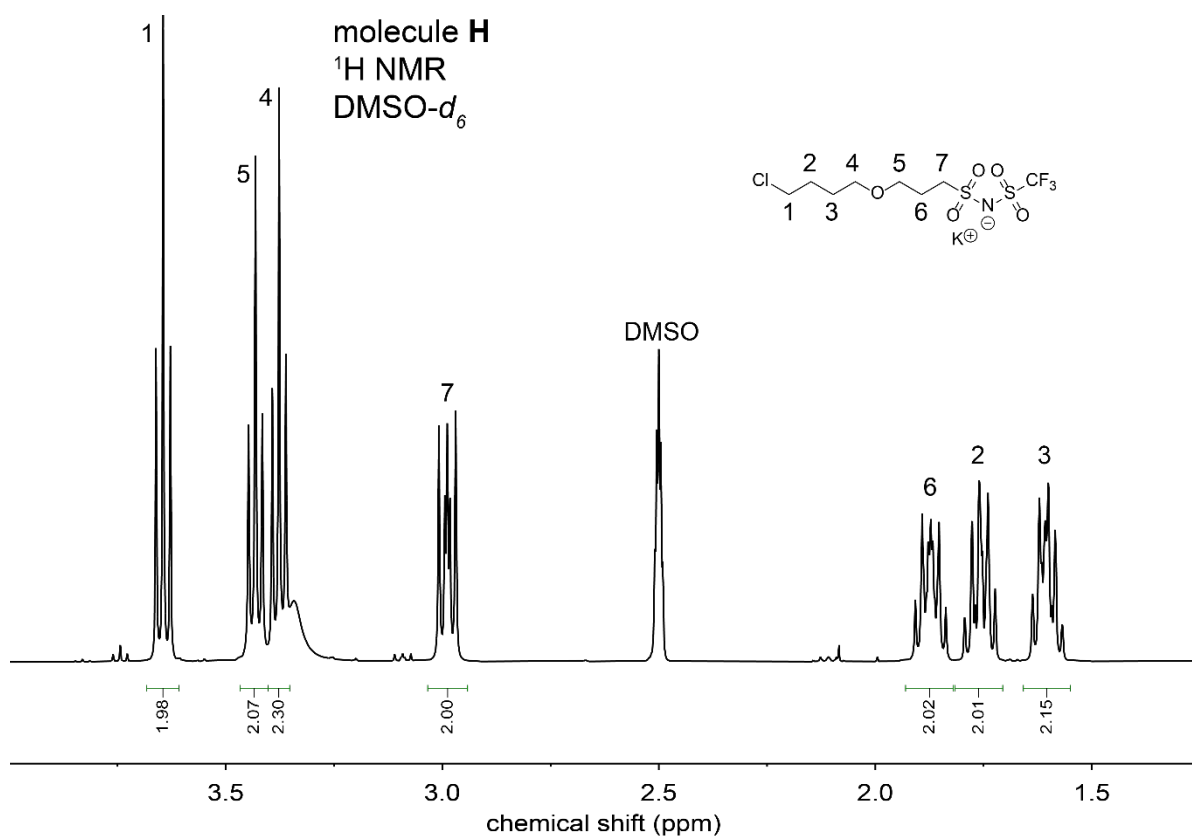
26.82

25.35

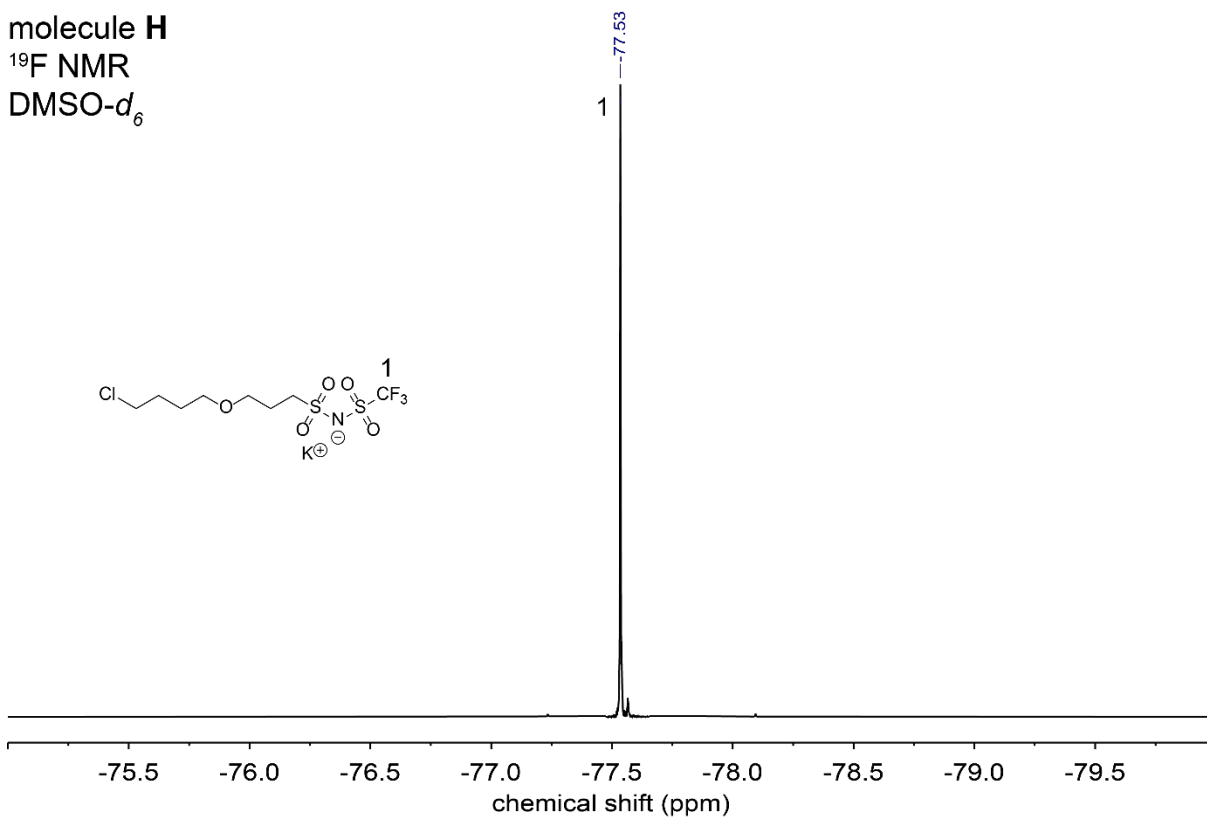
*due to the reactivity of the sulfonyl chloride, molecule G was not subjected to rigorous purification, but used at the level of purity shown in this spectrum



Molecule H

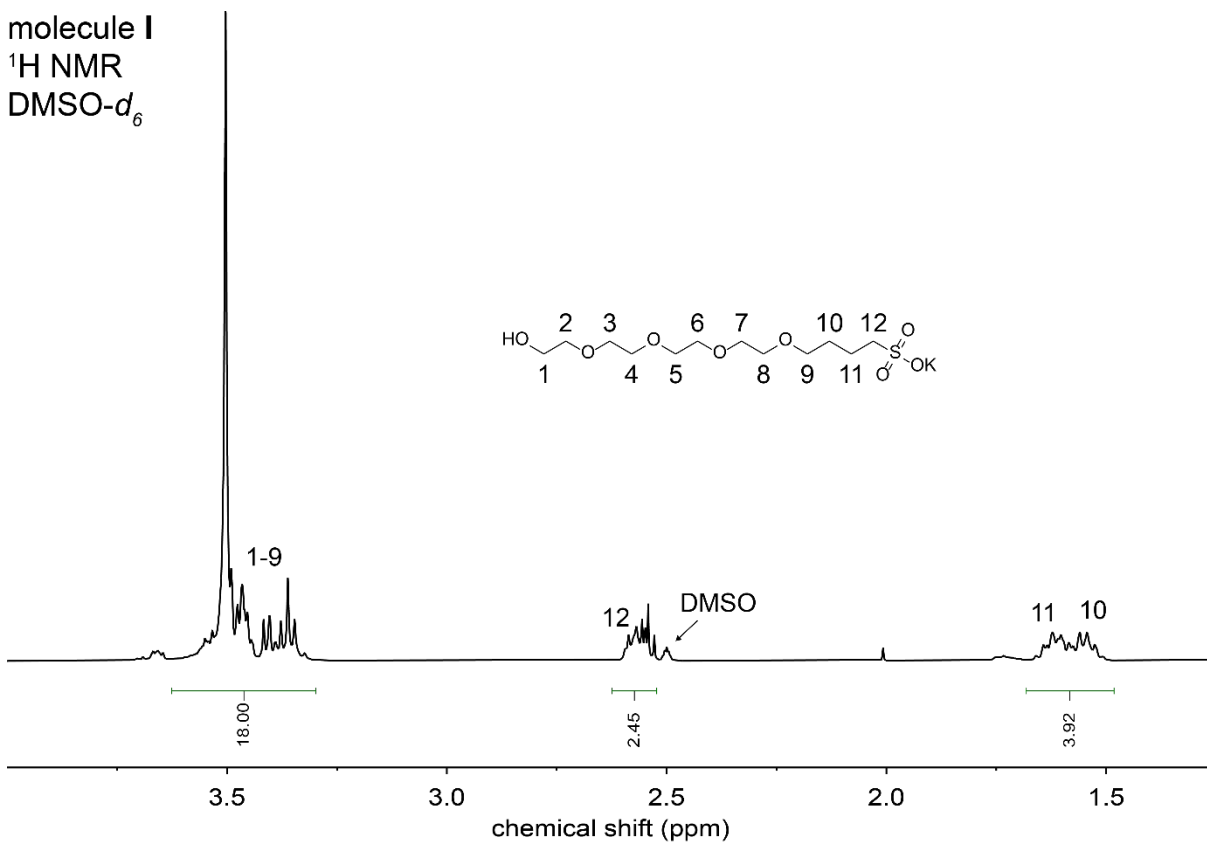


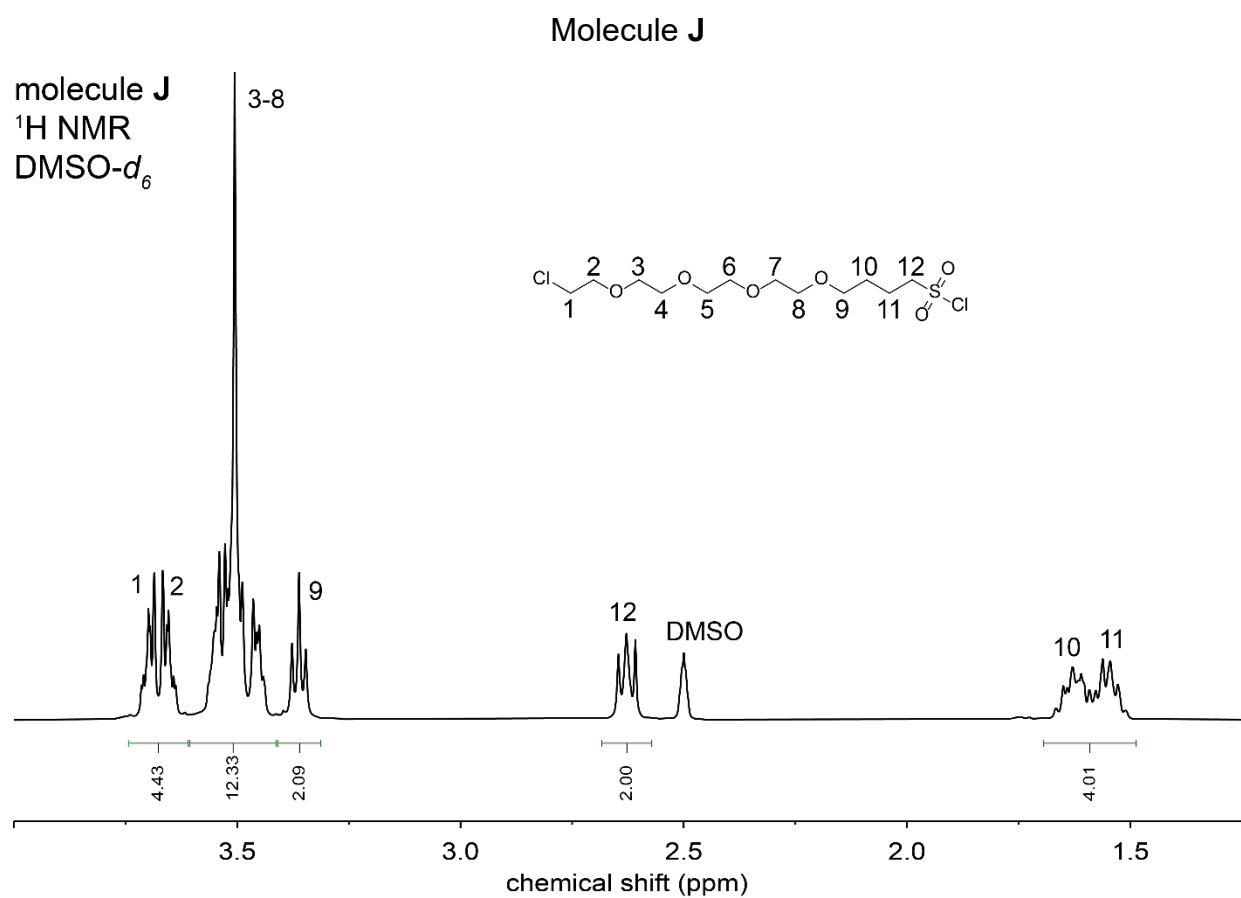
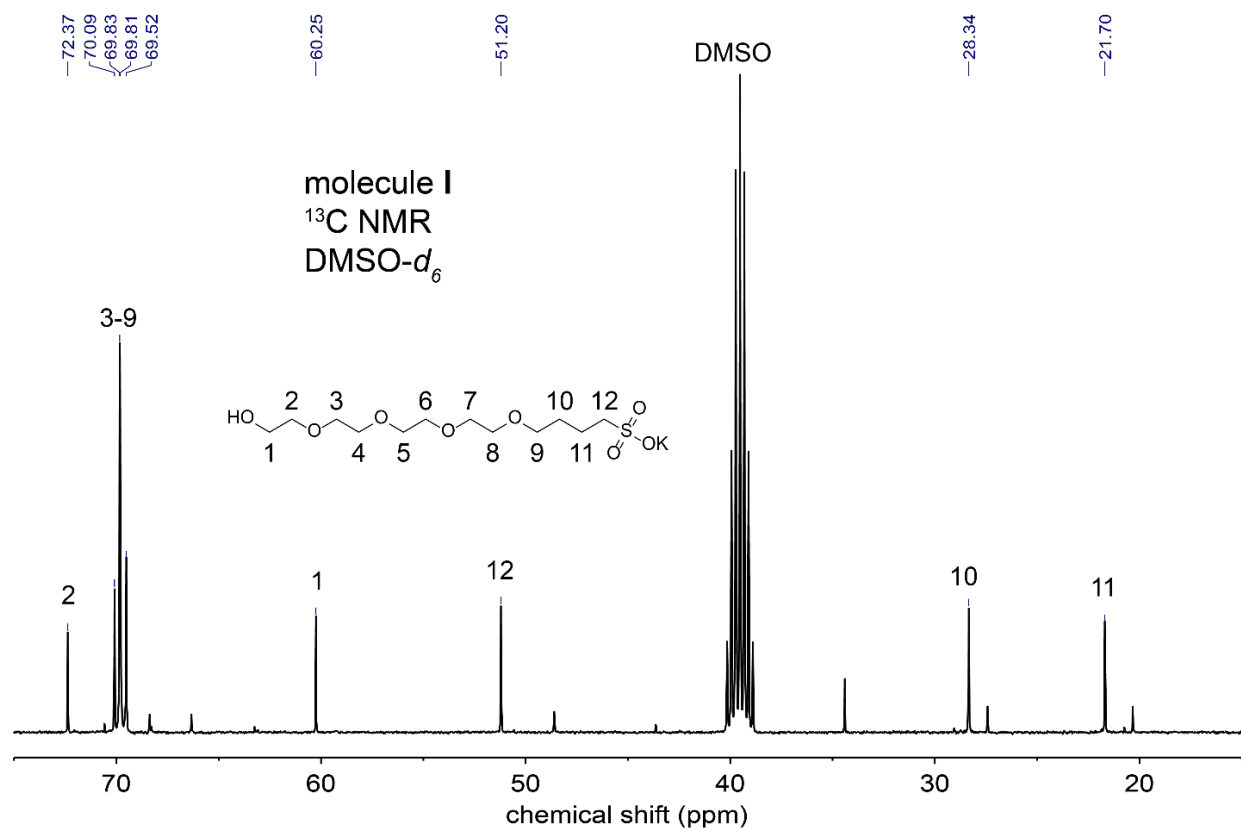
molecule **H**
 ^{19}F NMR
 DMSO- d_6

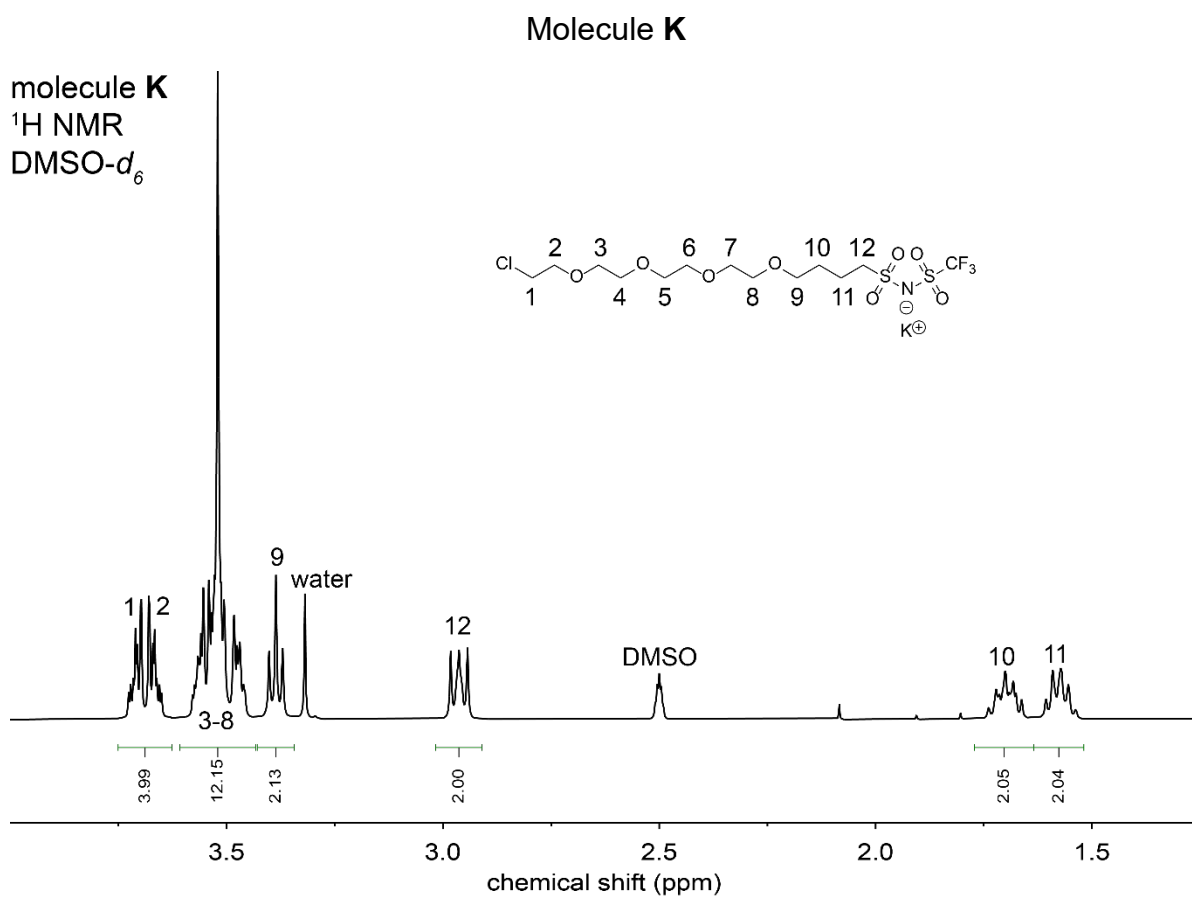
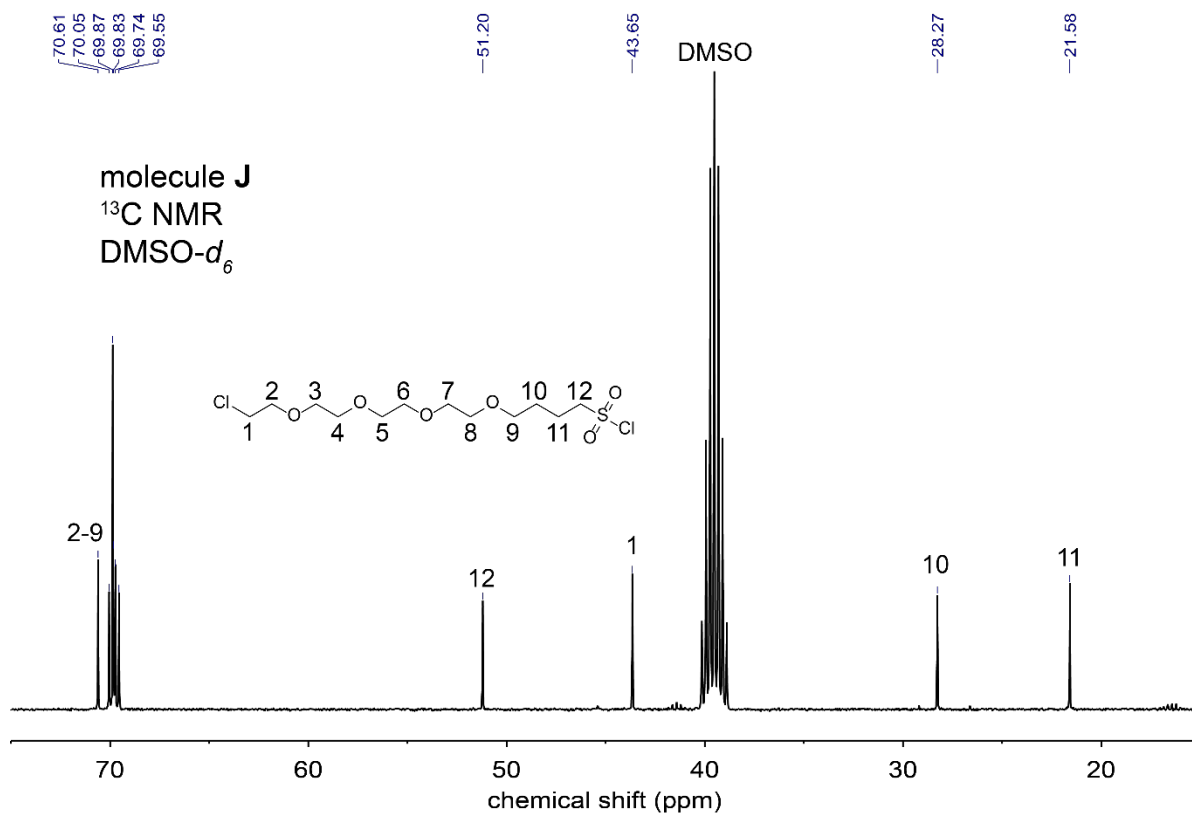


Molecule **I**

molecule **I**
 ^1H NMR
 DMSO- d_6

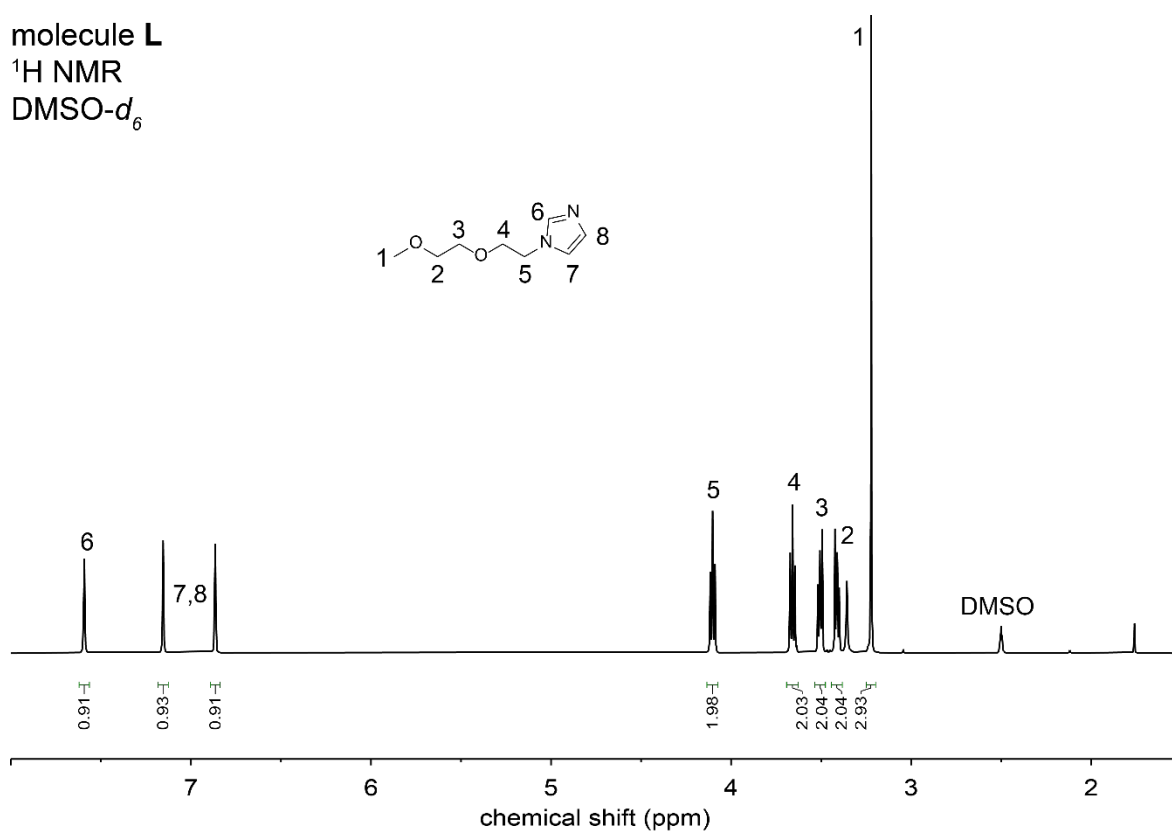




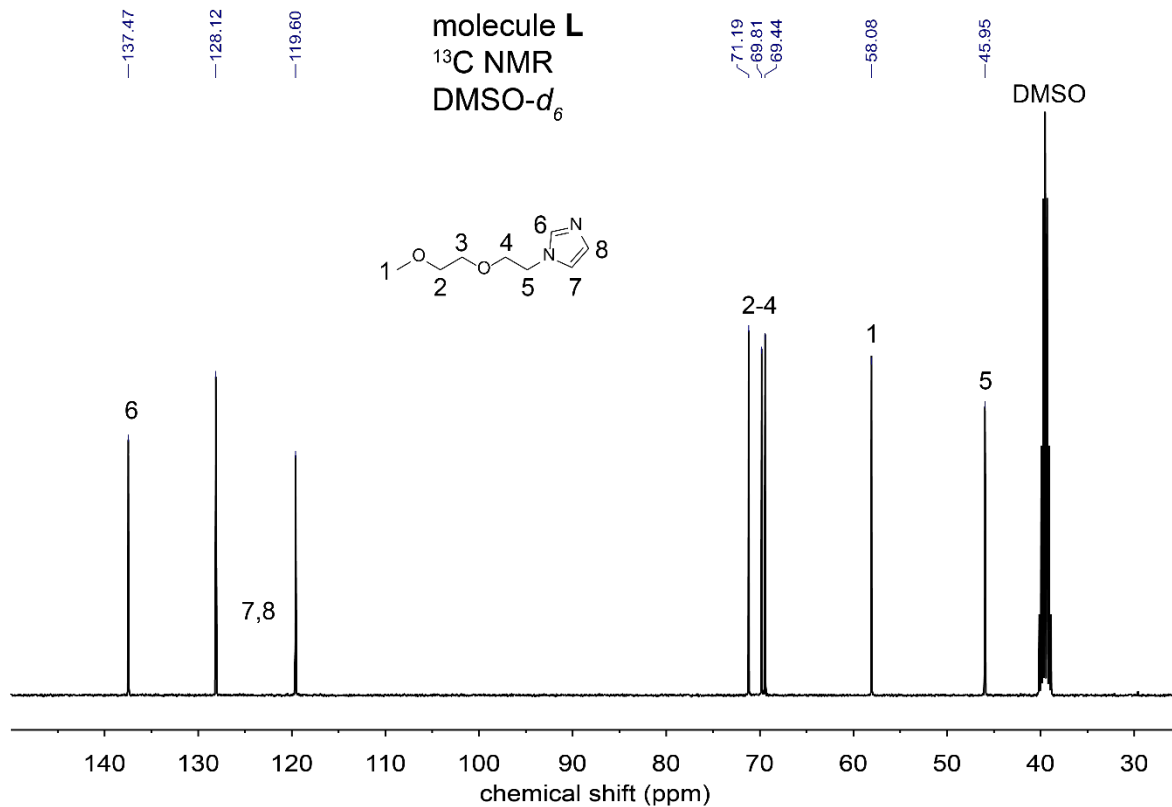


Molecule L

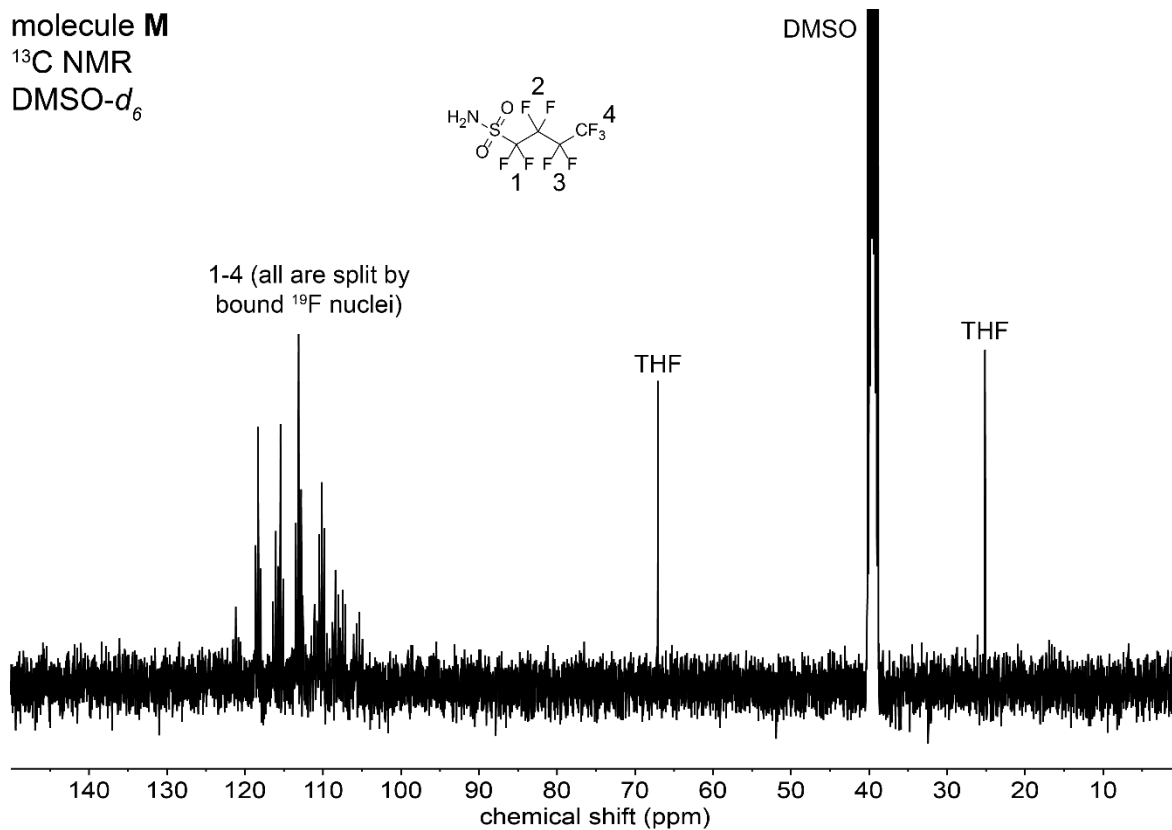
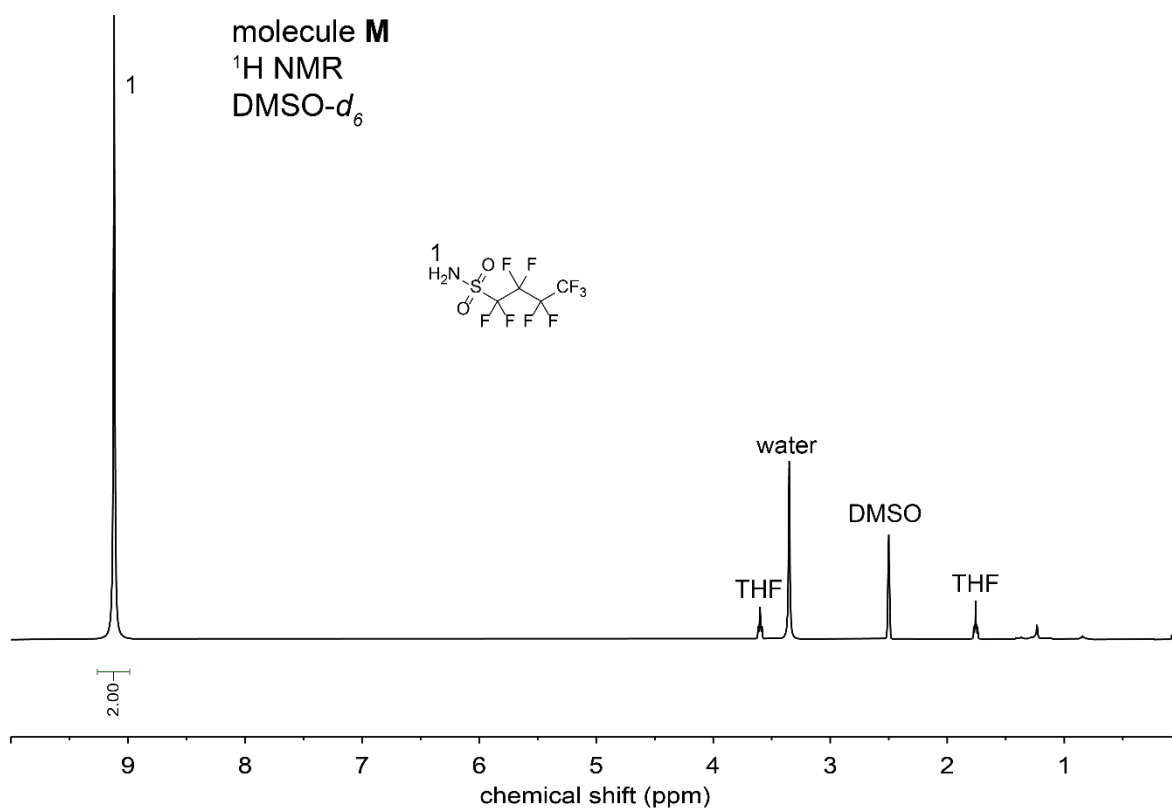
molecule L
¹H NMR
 DMSO-*d*₆

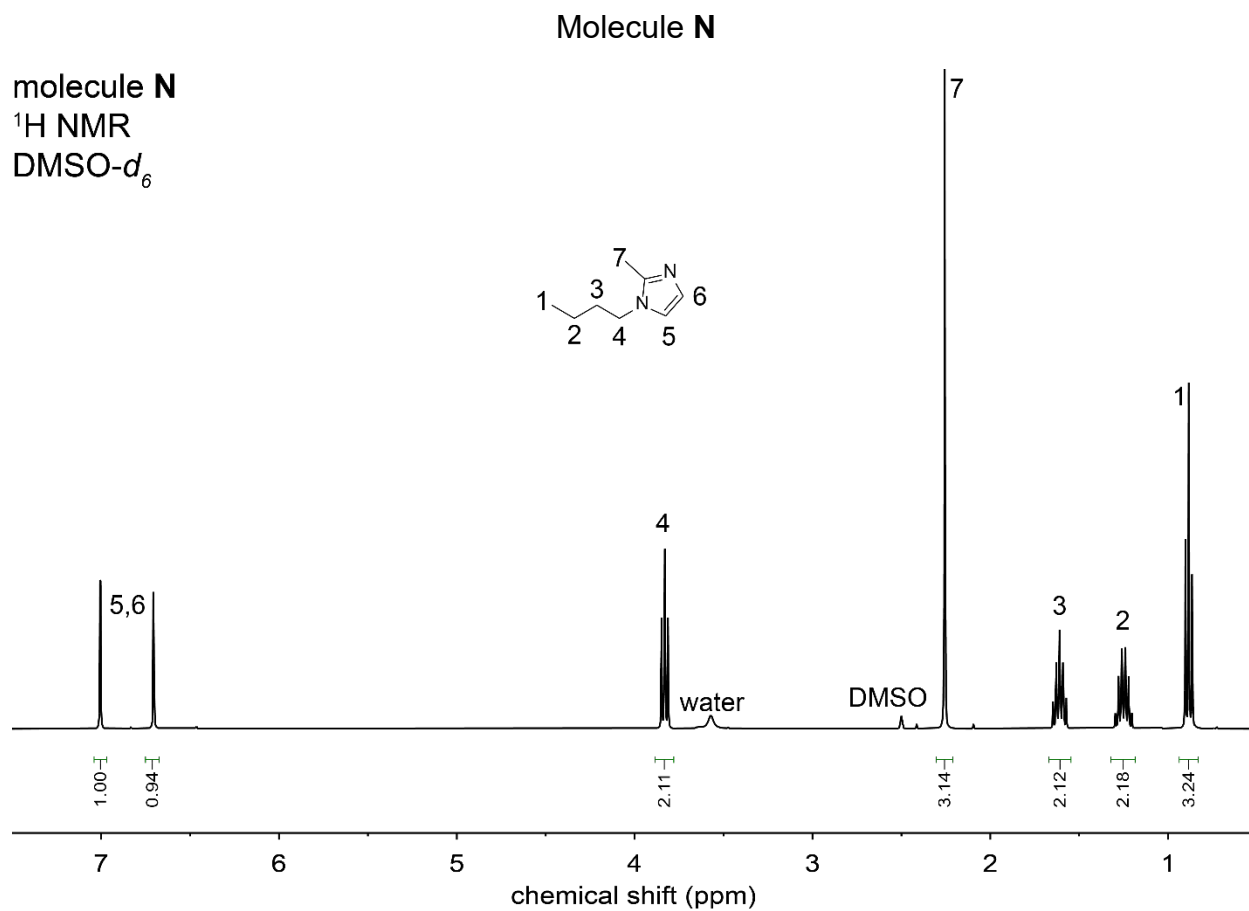
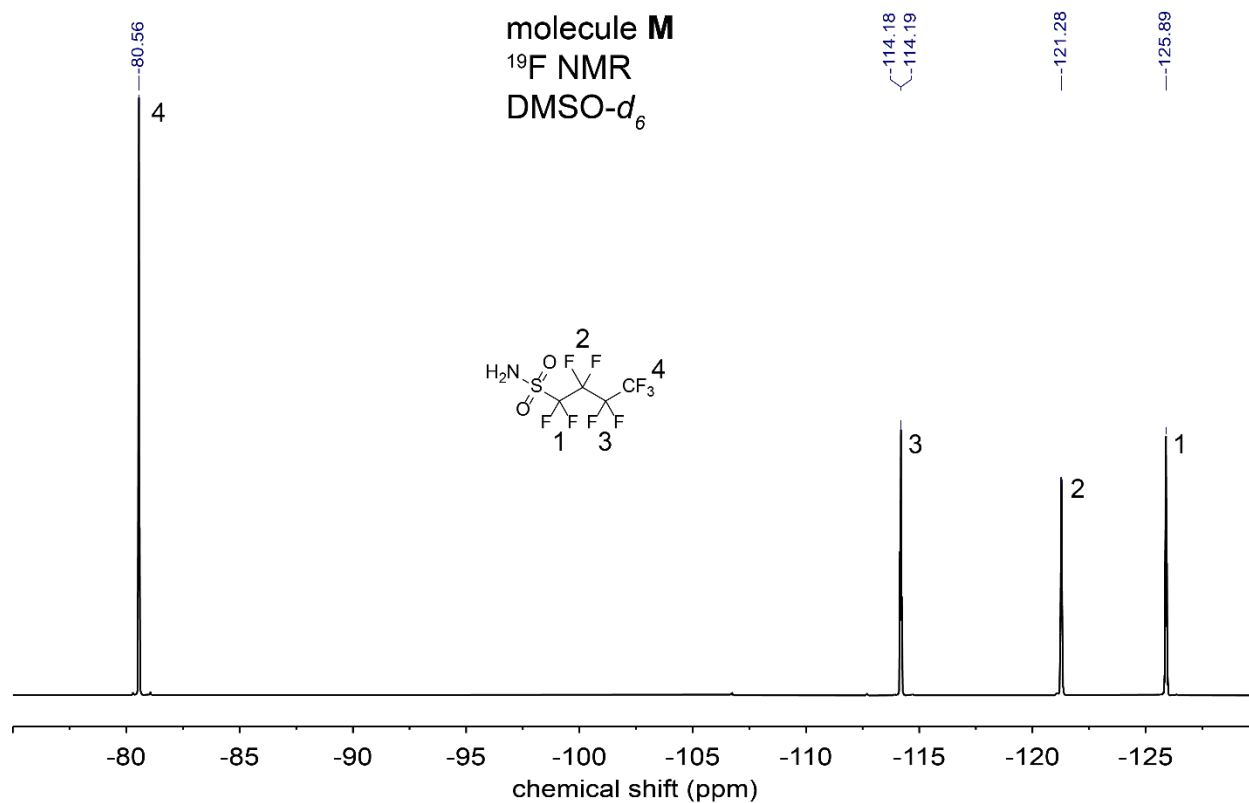


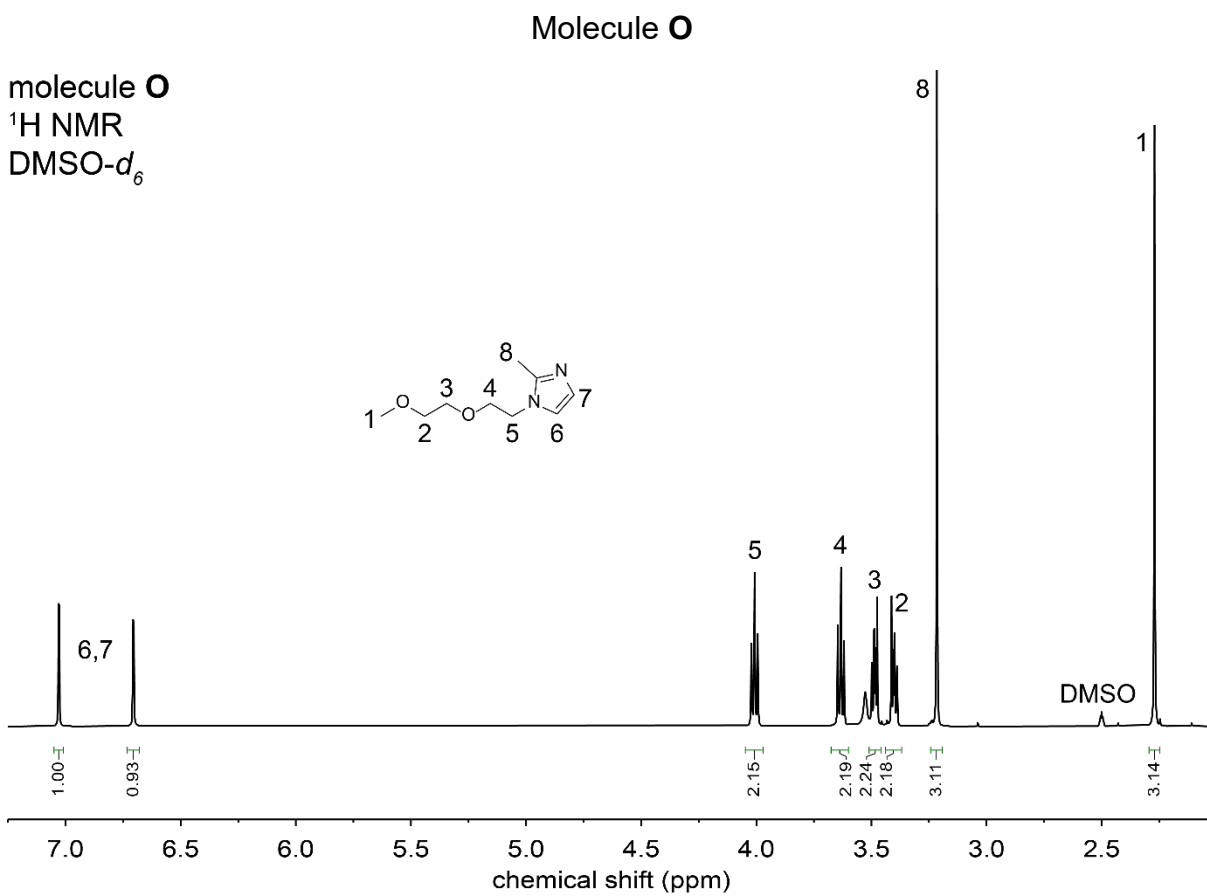
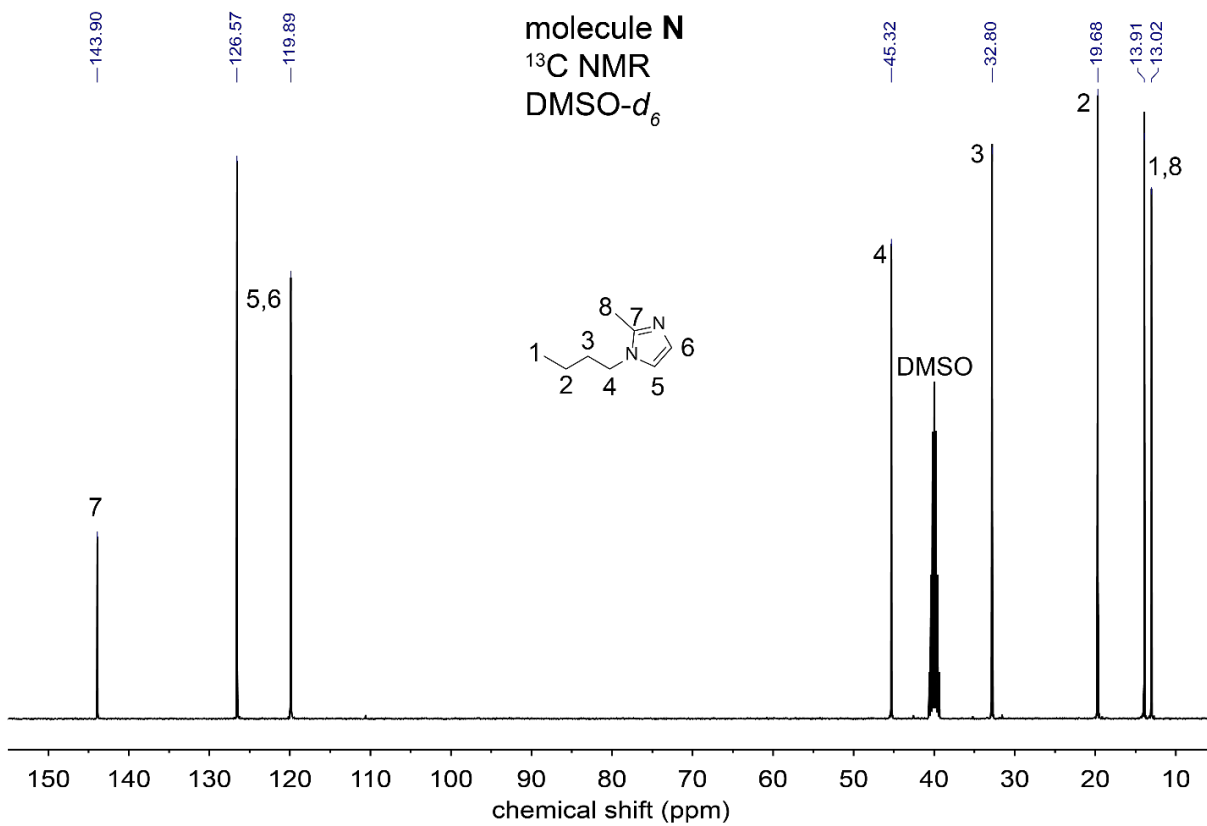
molecule L
¹³C NMR
 DMSO-*d*₆

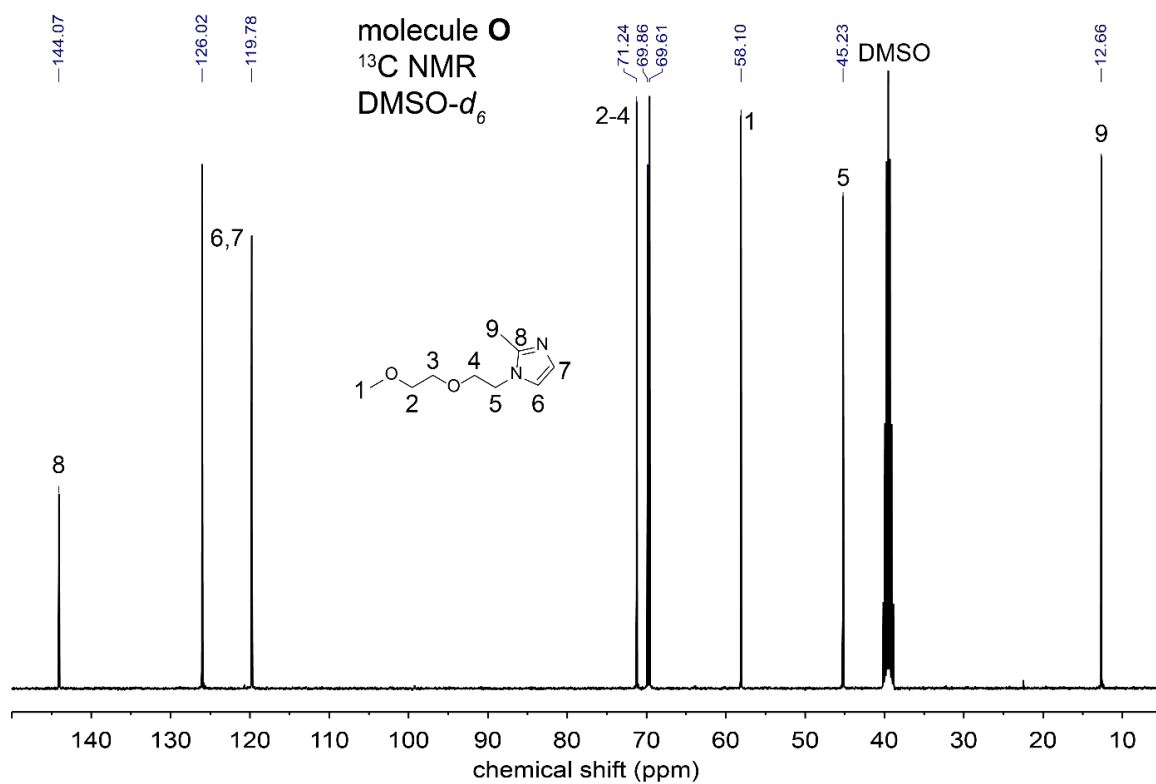


Molecule **M**



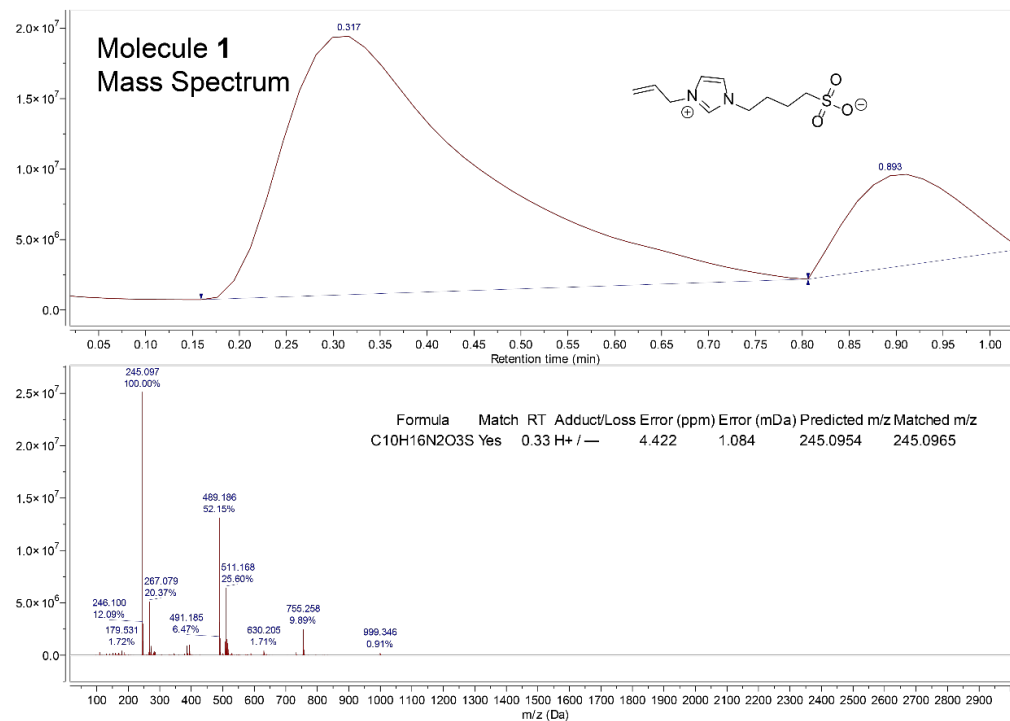




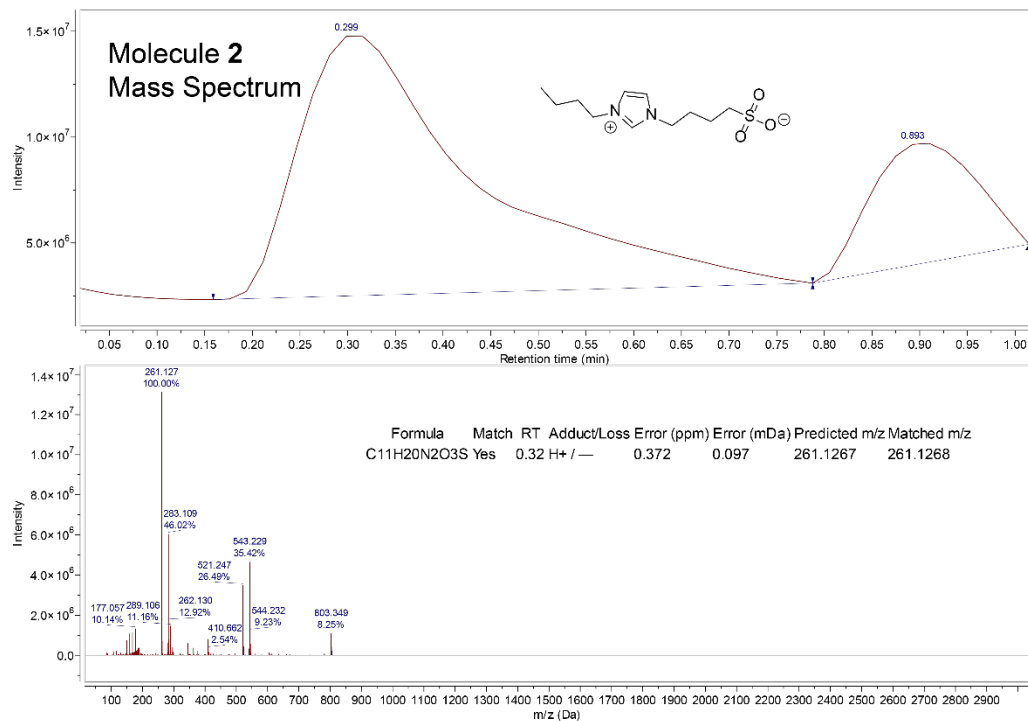


Data S2: Mass spectrometry of zwitterions and intermediates

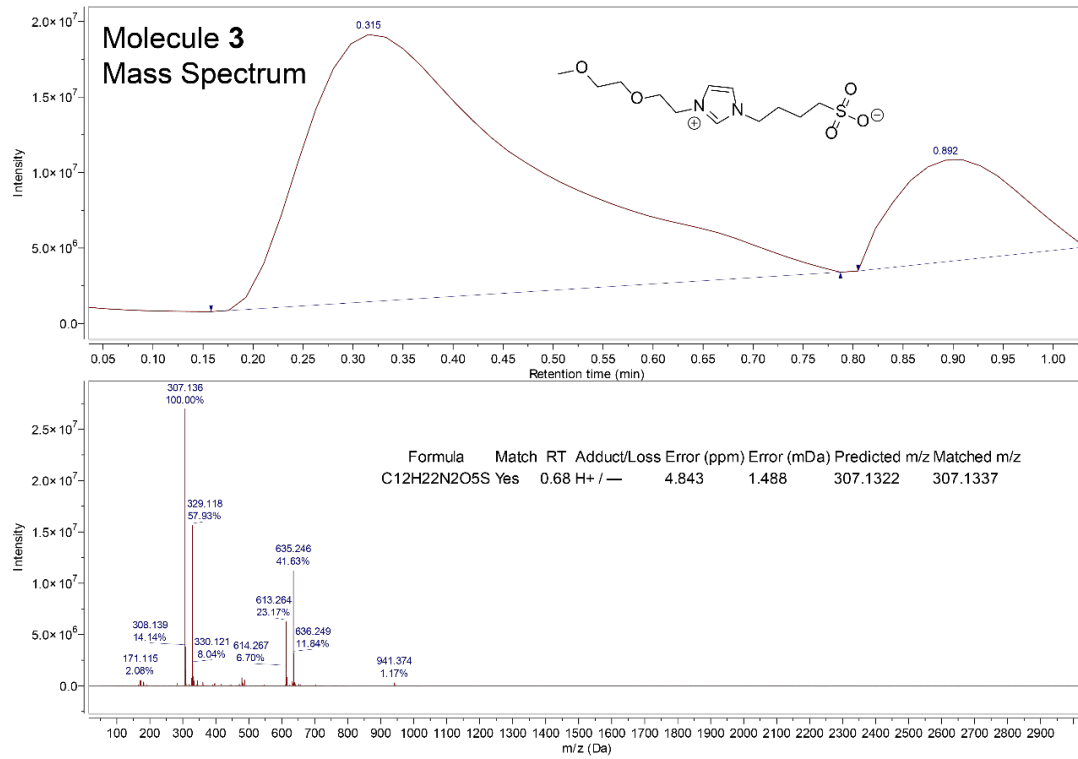
Molecule 1



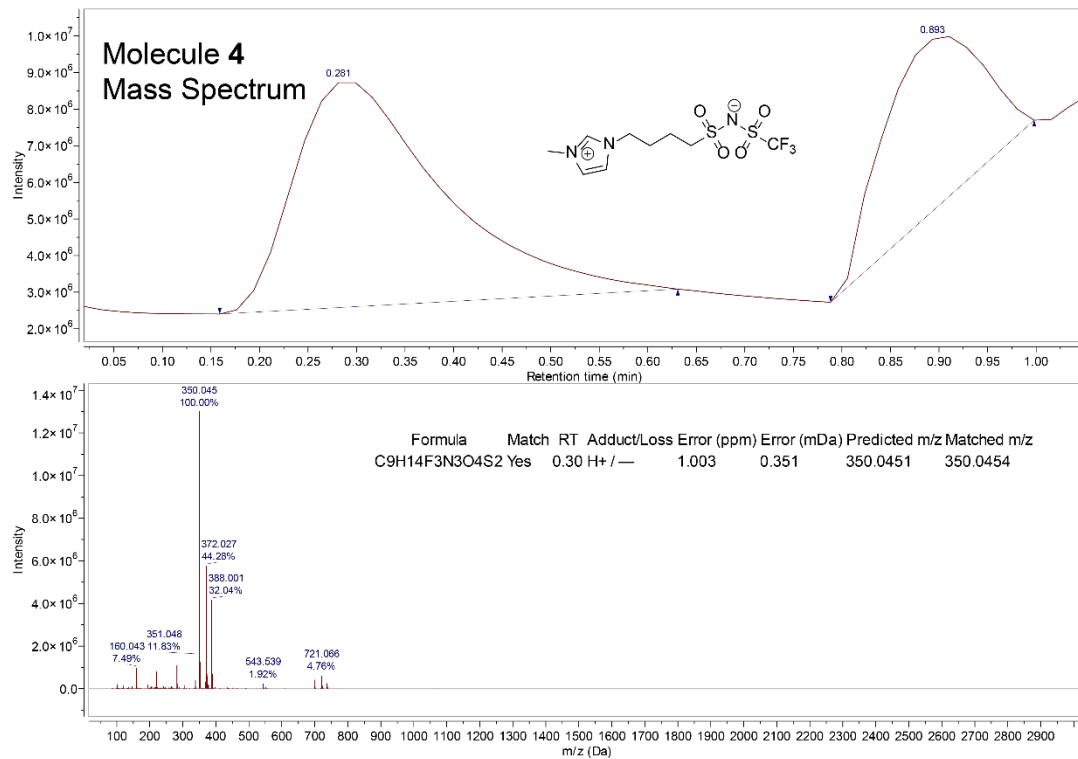
Molecule 2



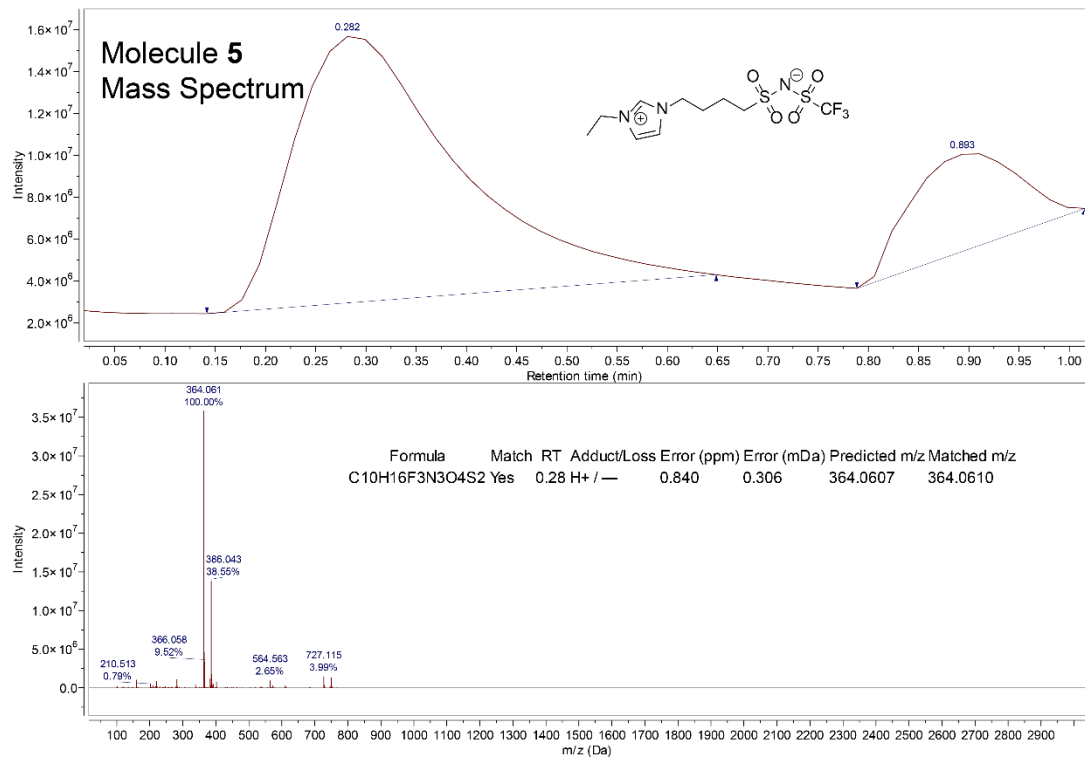
Molecule 3



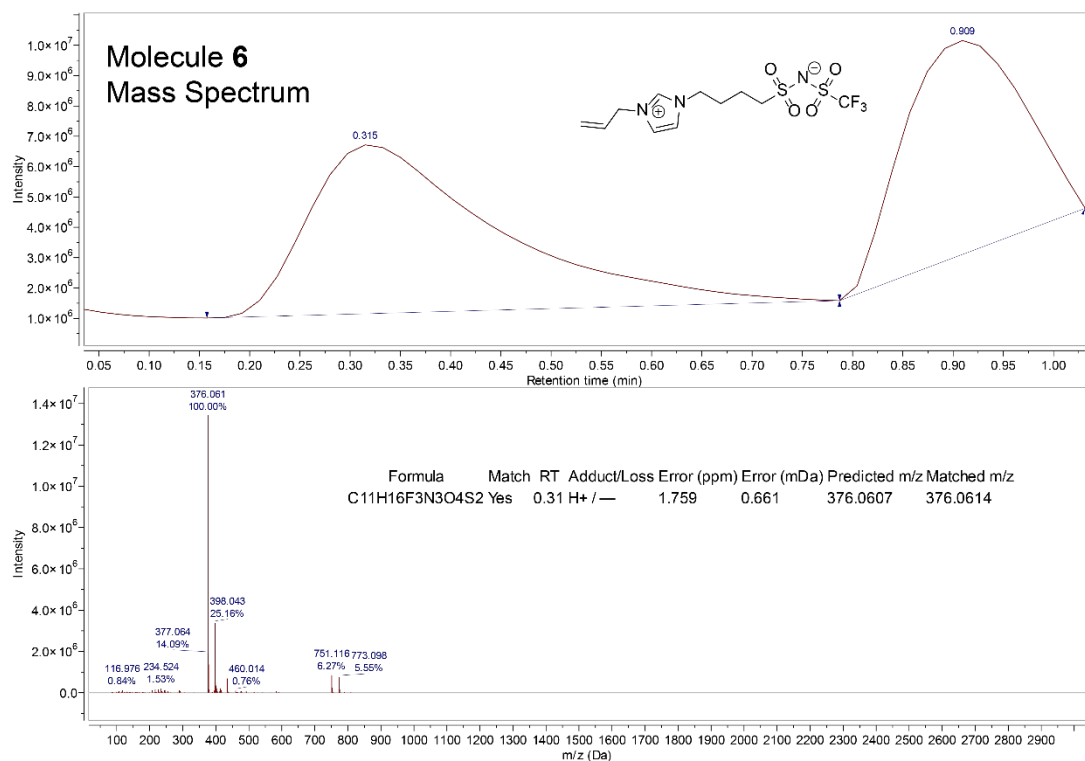
Molecule 4



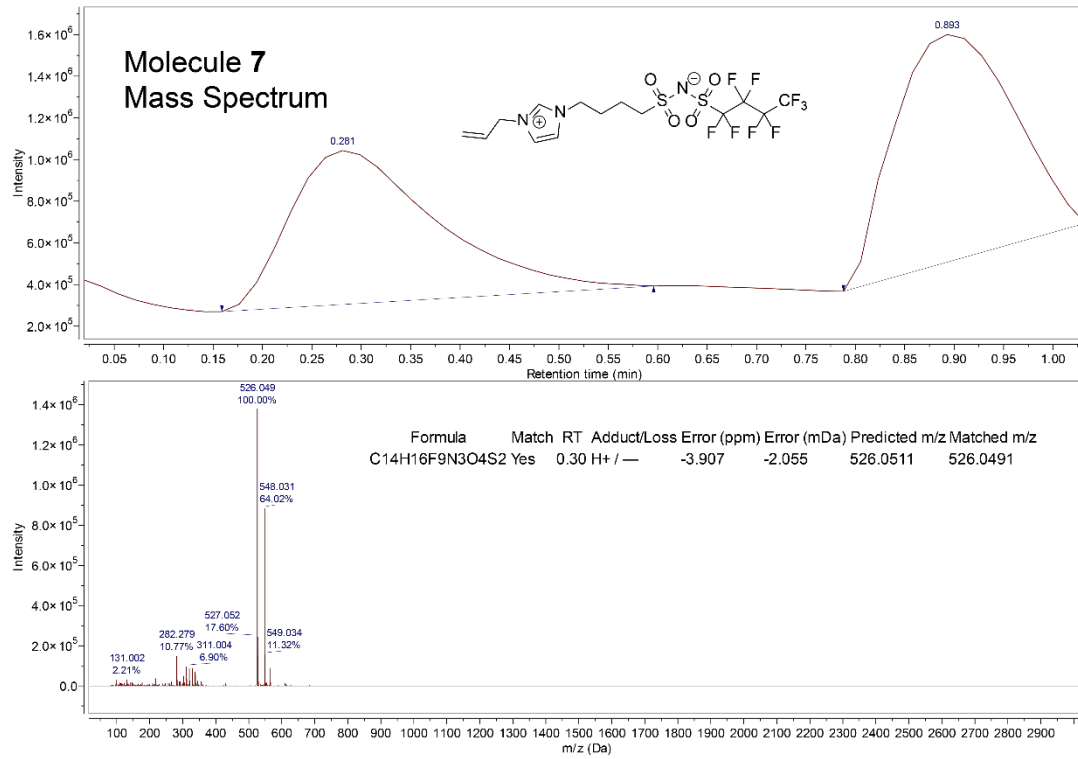
Molecule 5



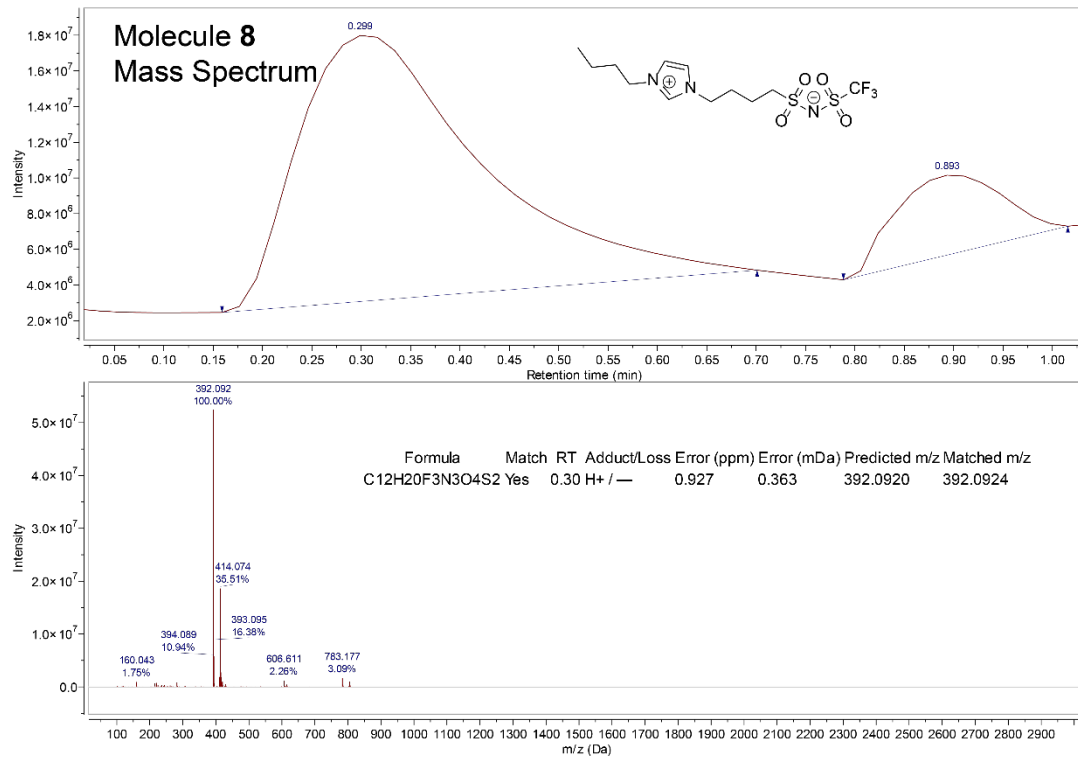
Molecule 6



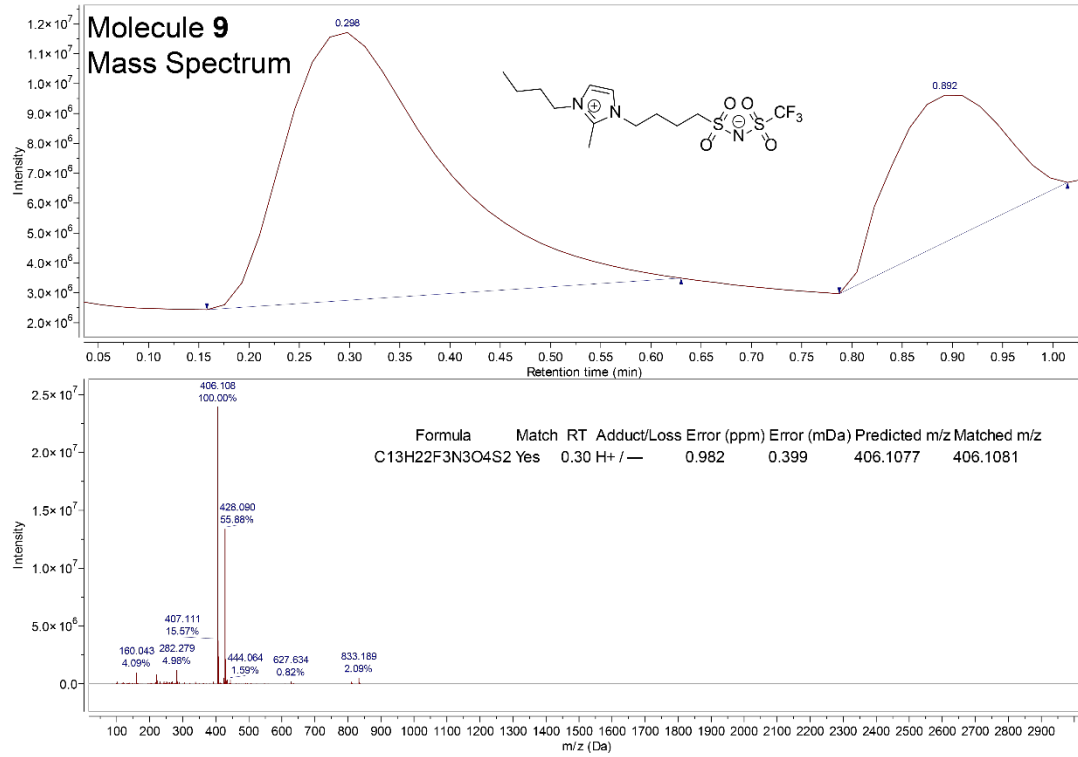
Molecule 7



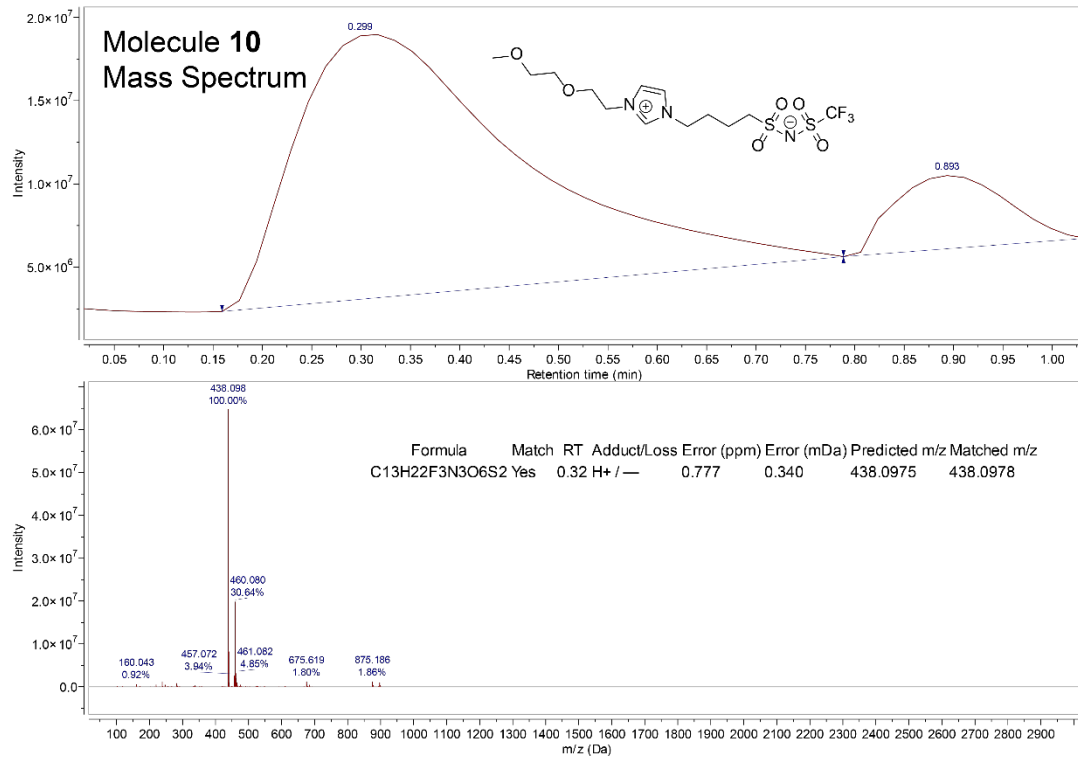
Molecule 8



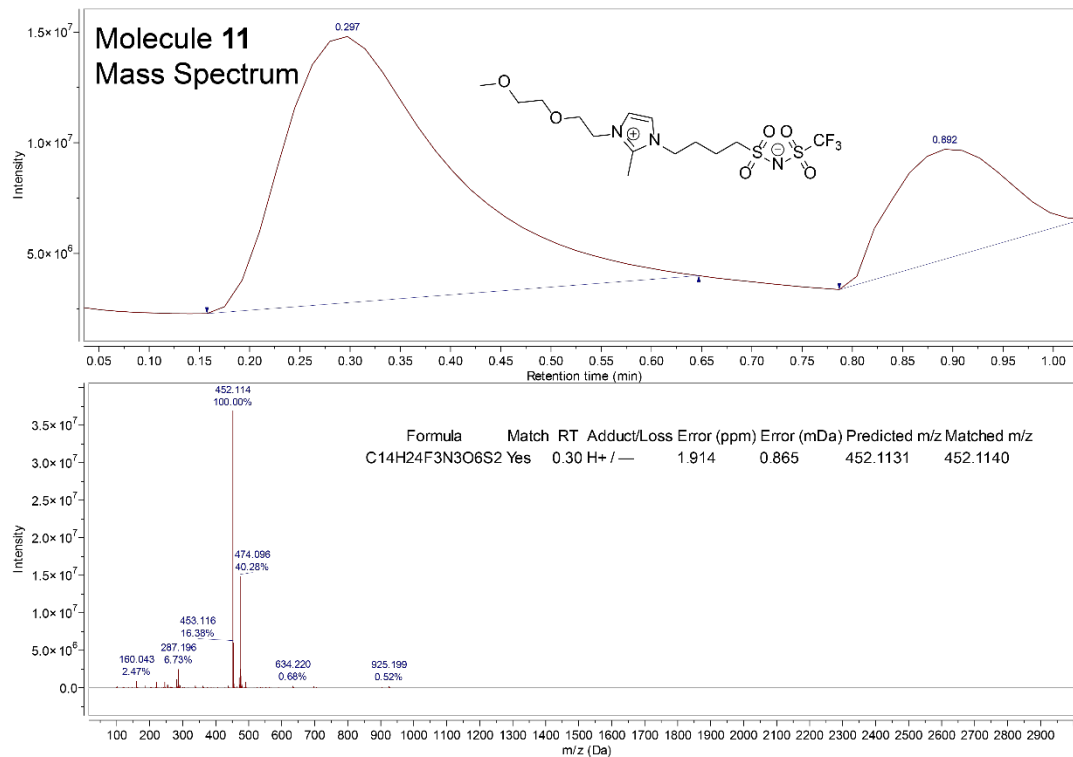
Molecule 9



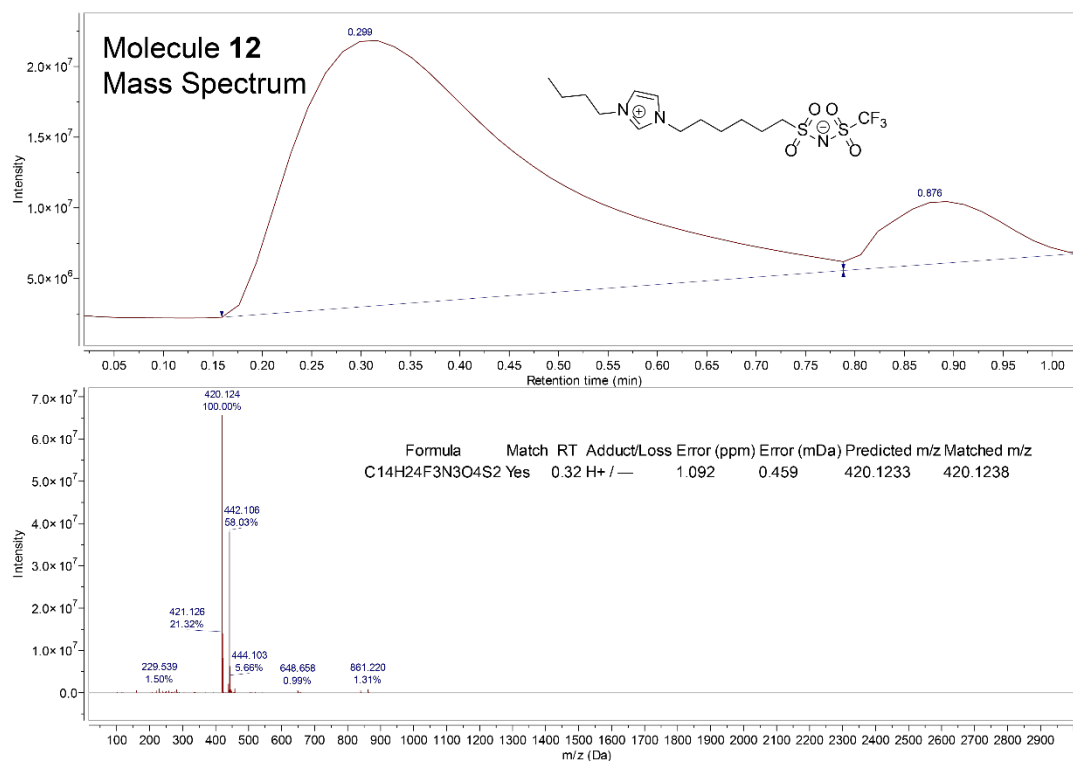
Molecule 10



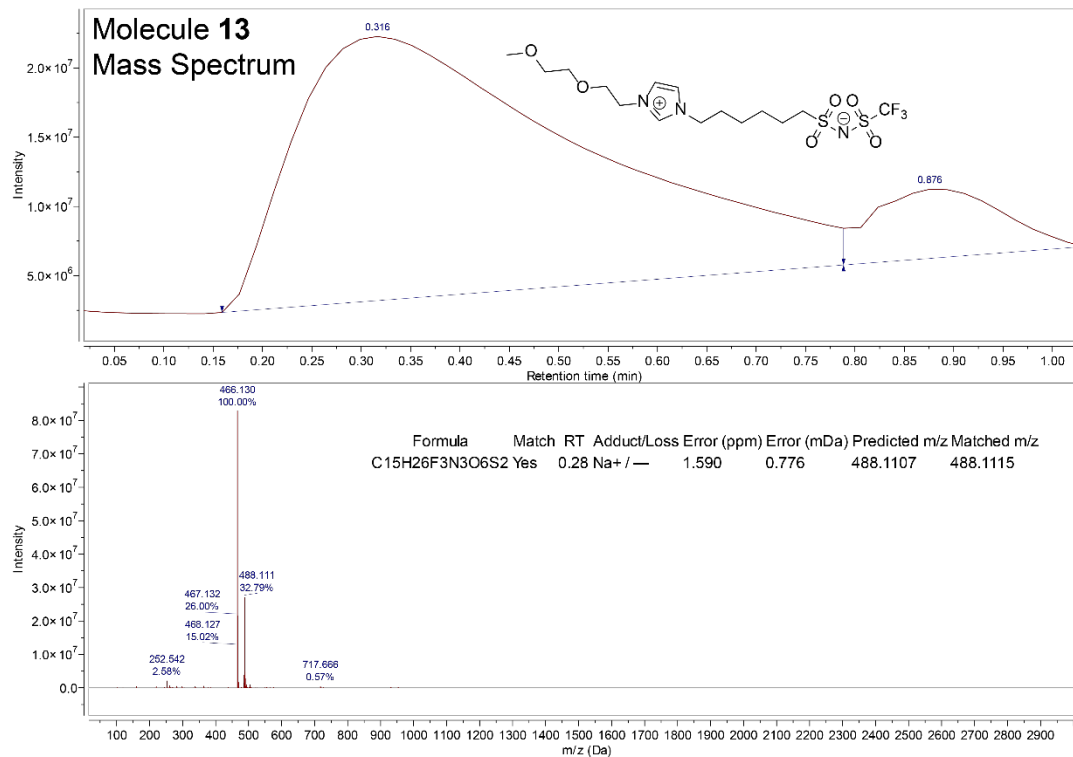
Molecule 11



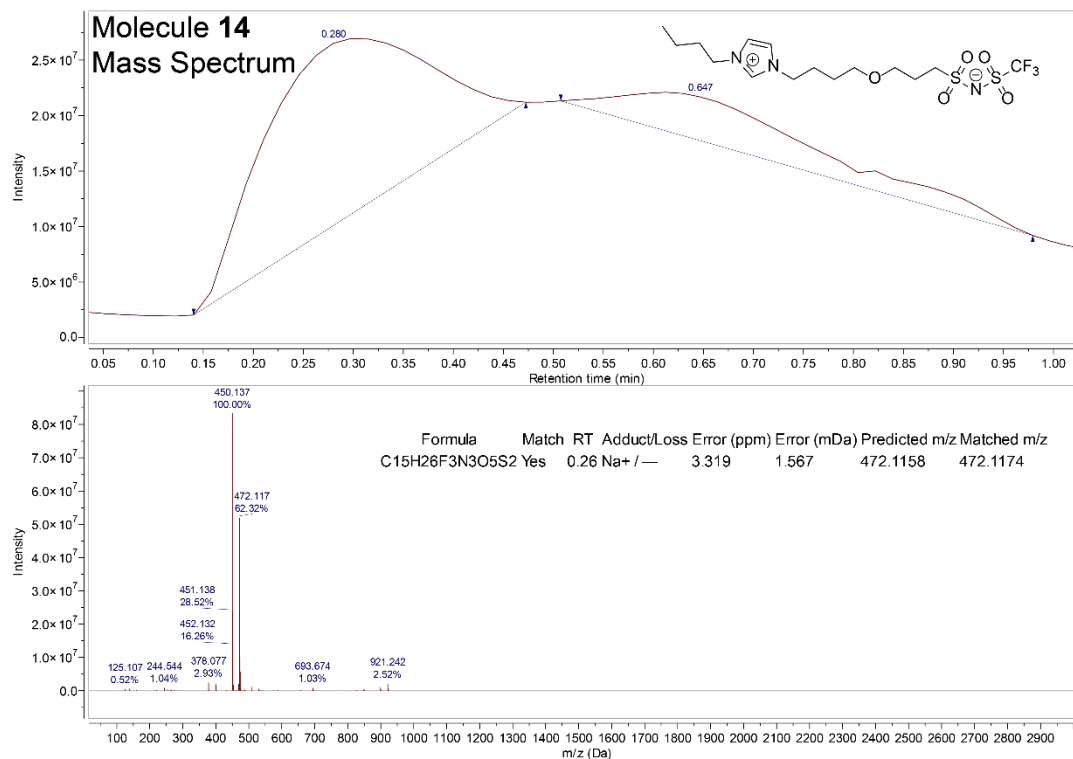
Molecule 12



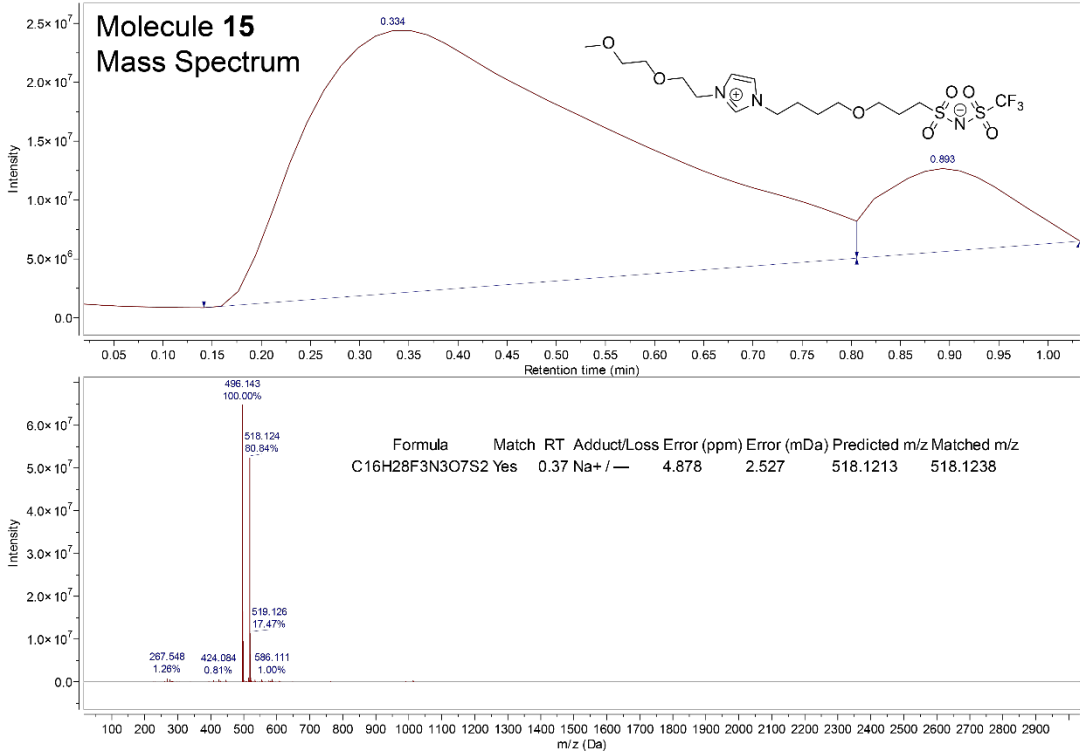
Molecule 13



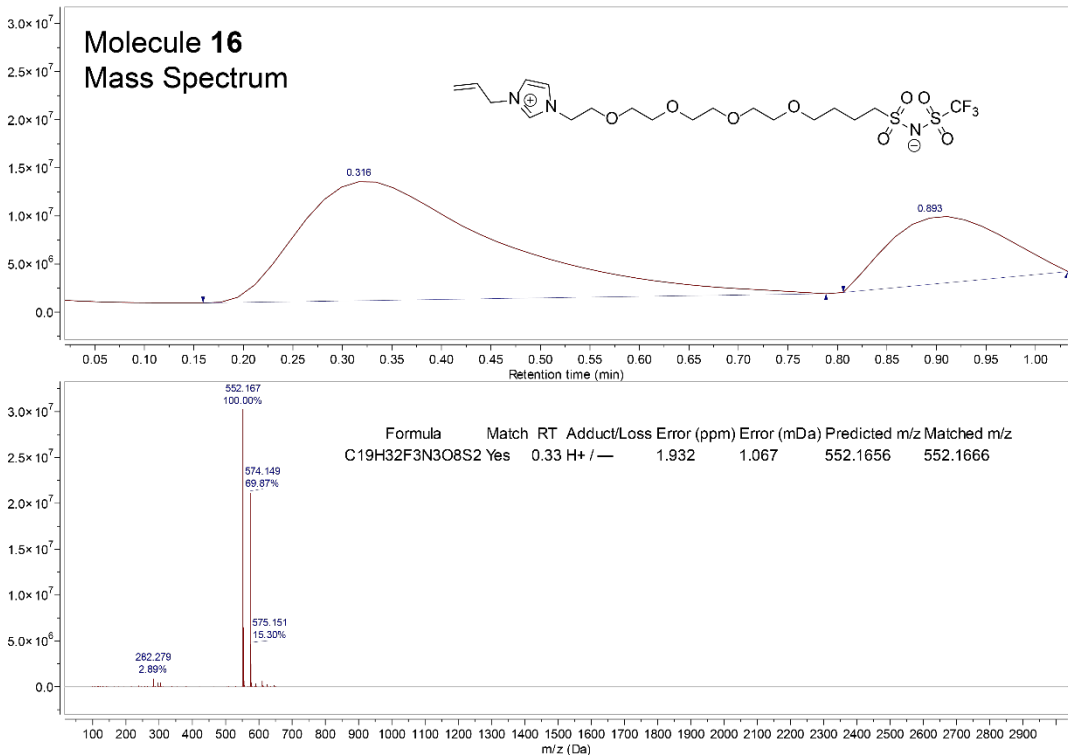
Molecule 14



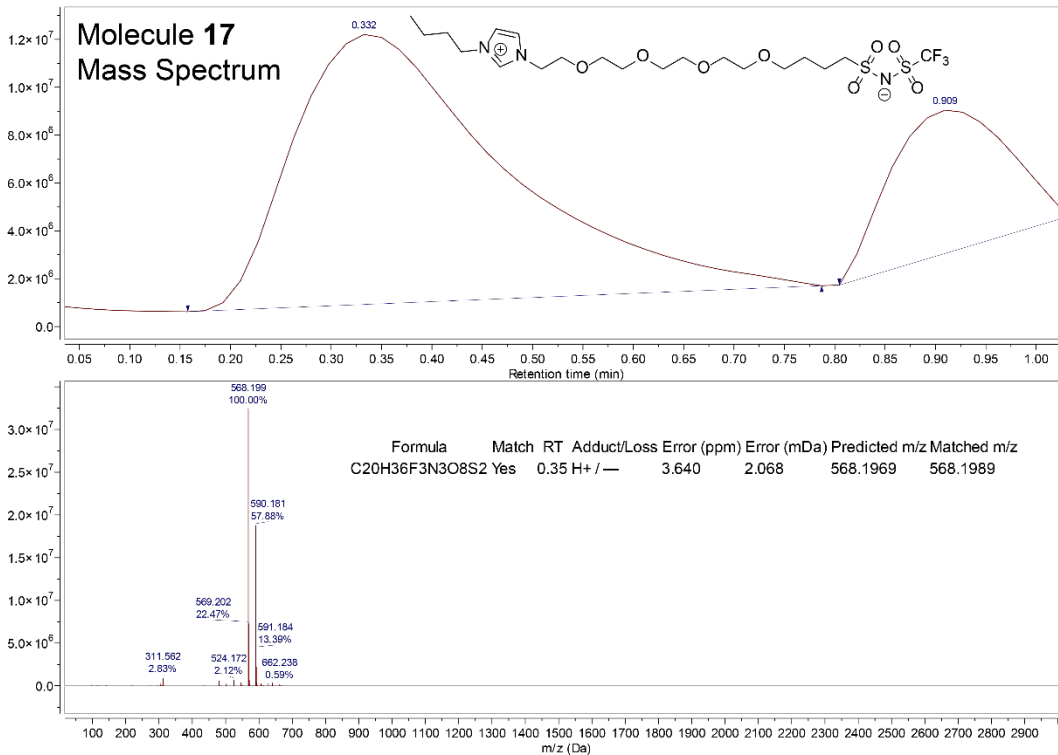
Molecule 15



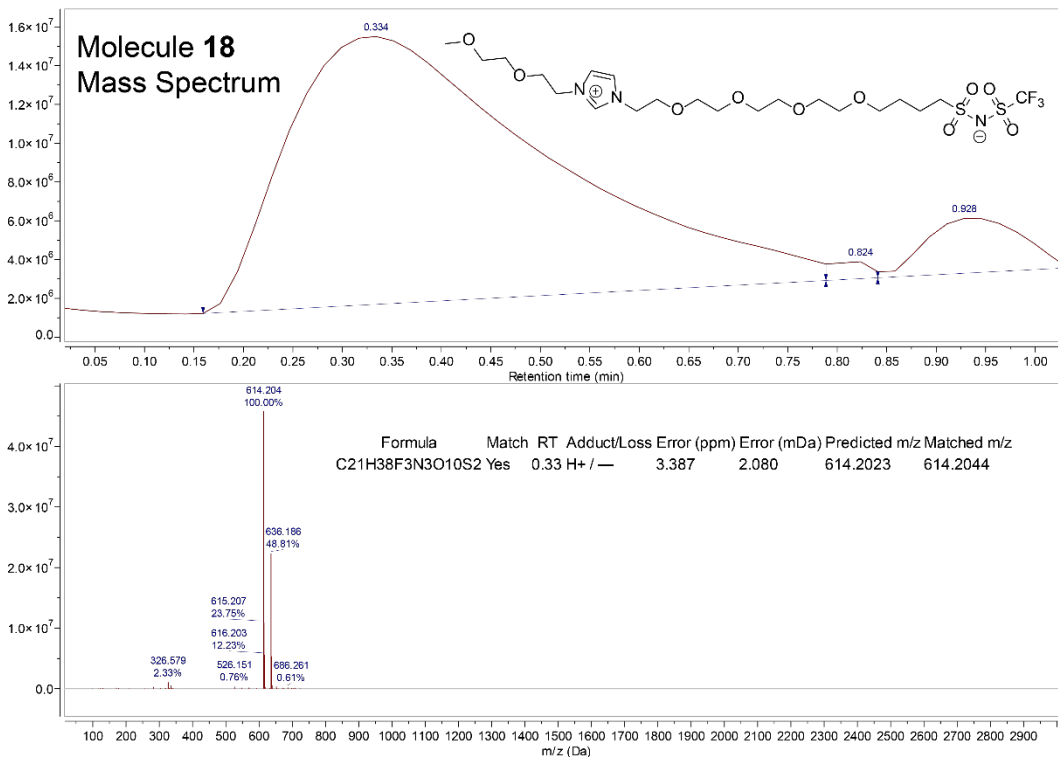
Molecule 16



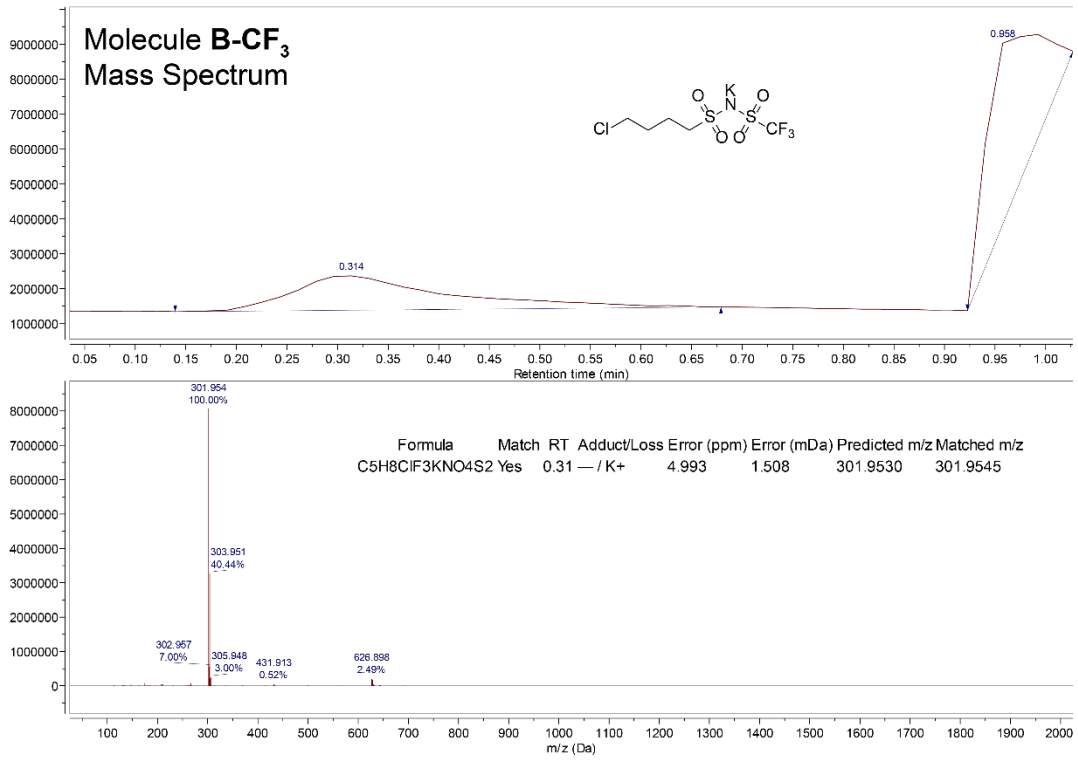
Molecule 17



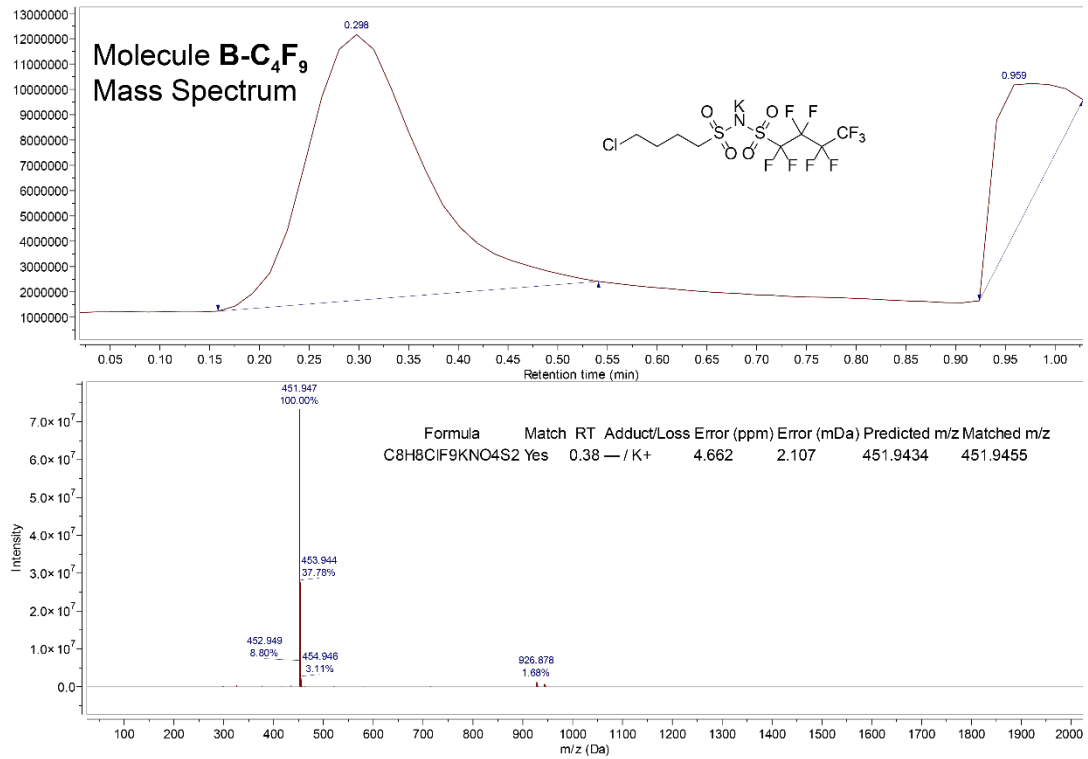
Molecule 18



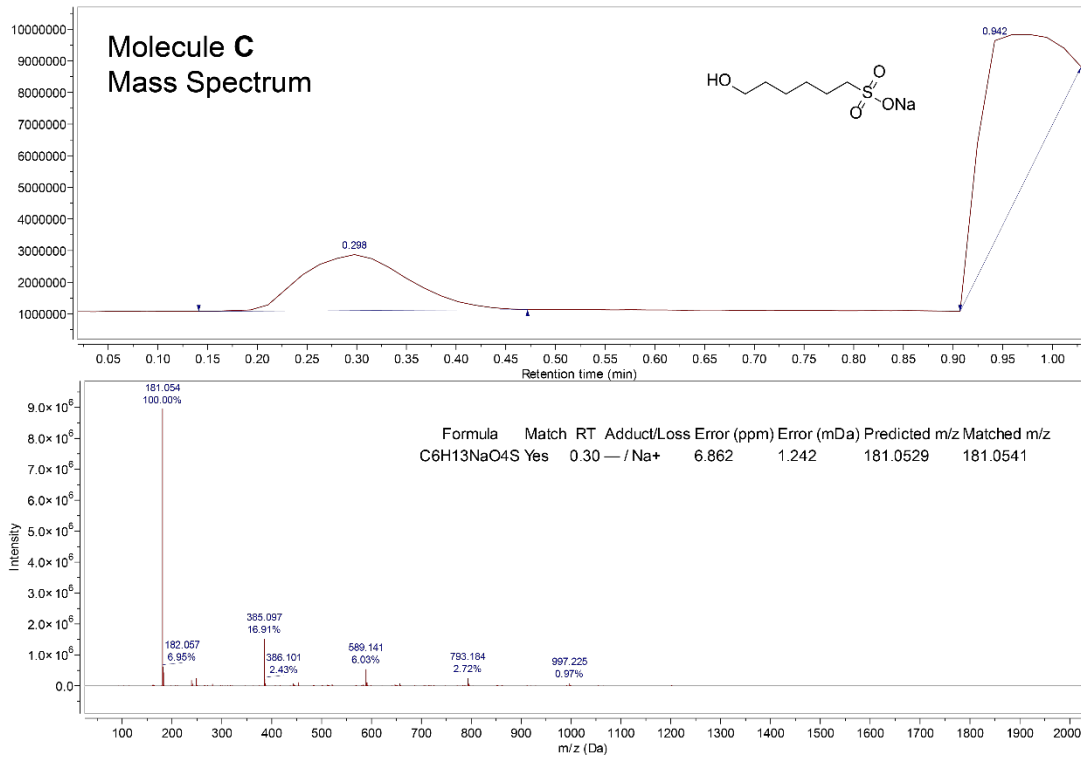
Molecule B-CF₃



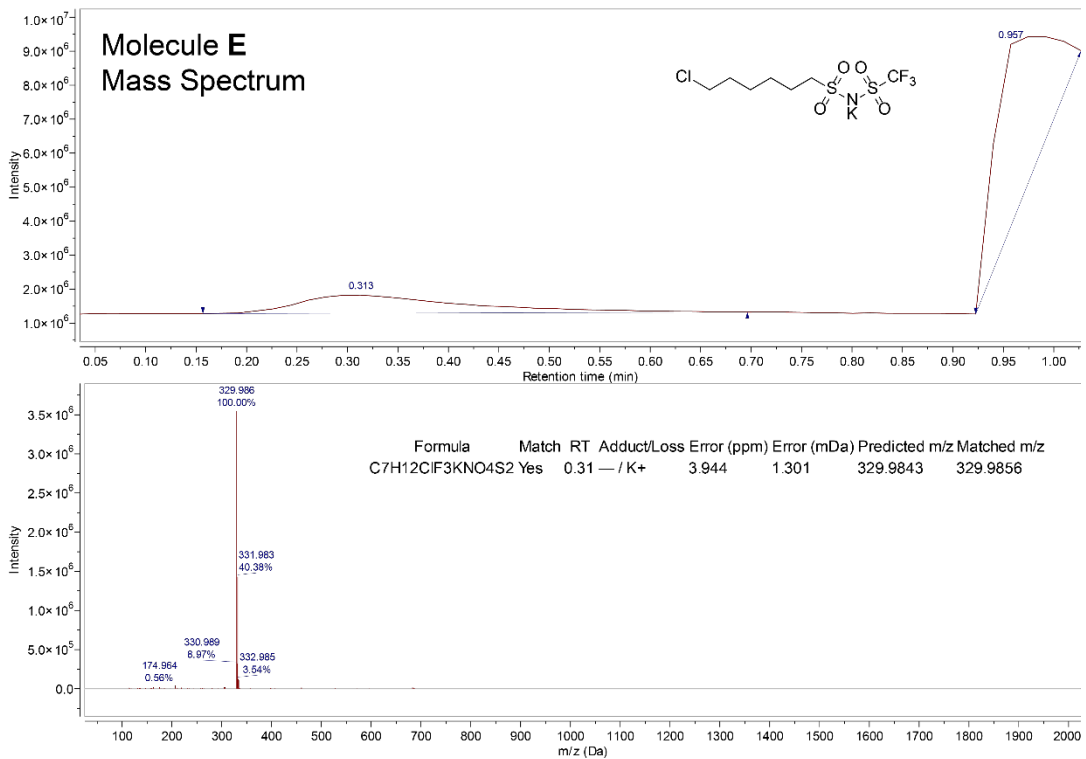
Molecule B-C₄F₉



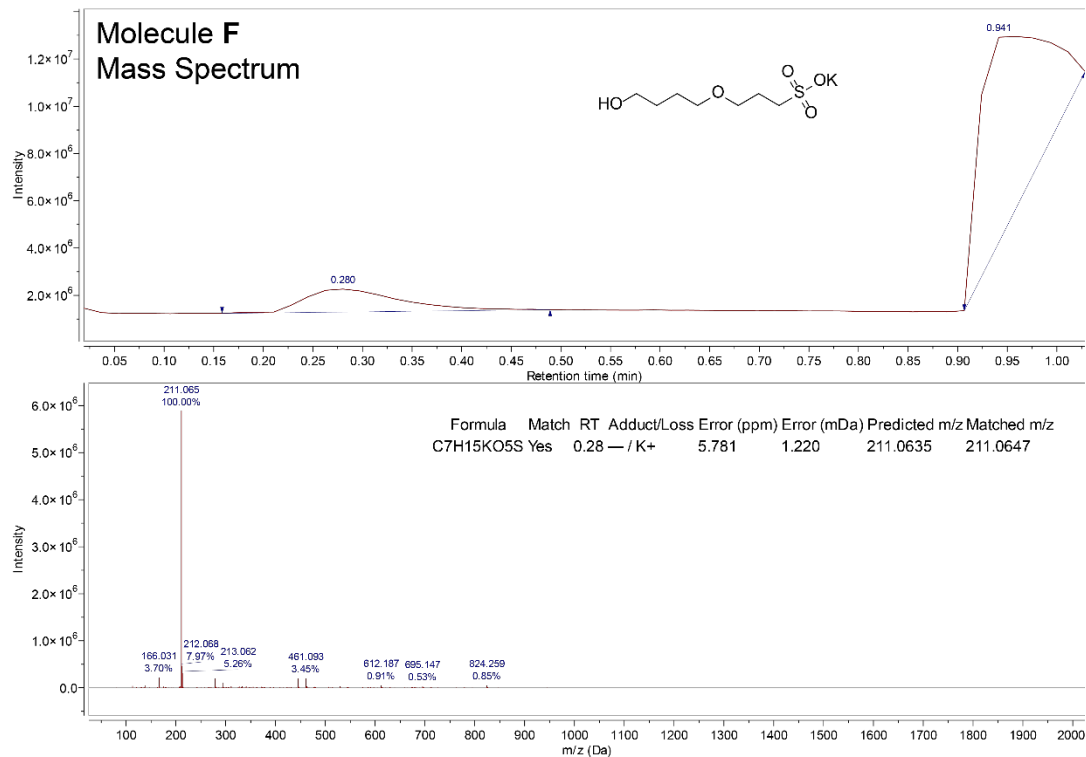
Molecule C



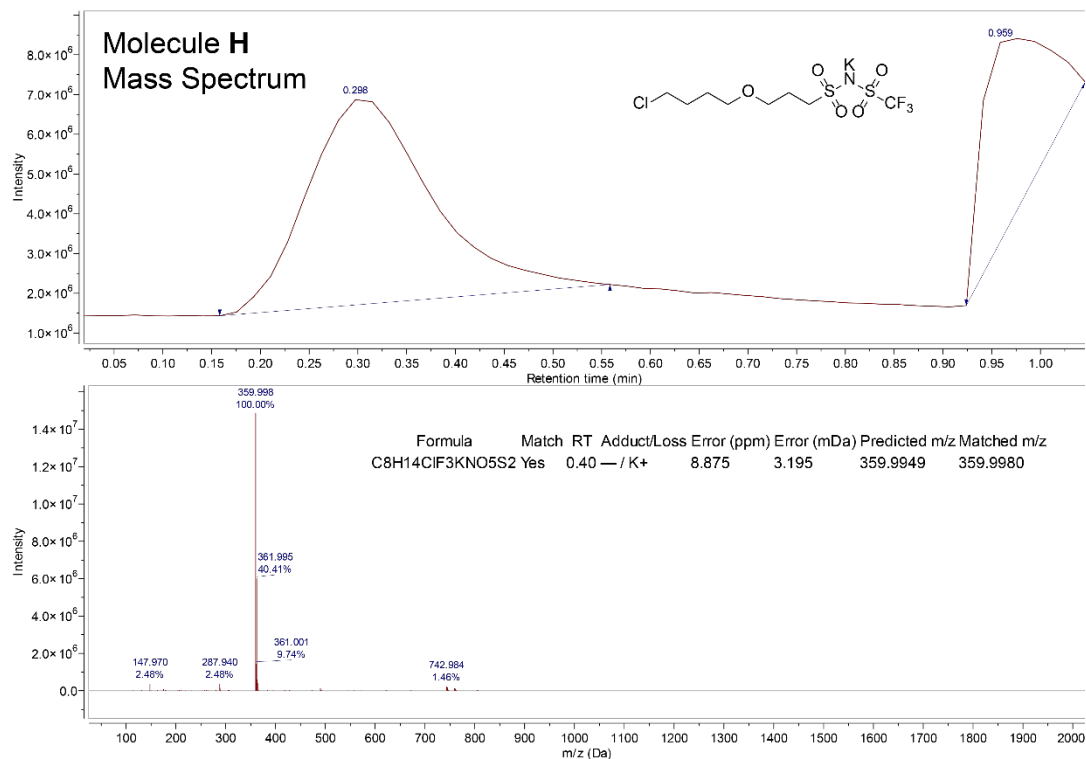
Molecule E



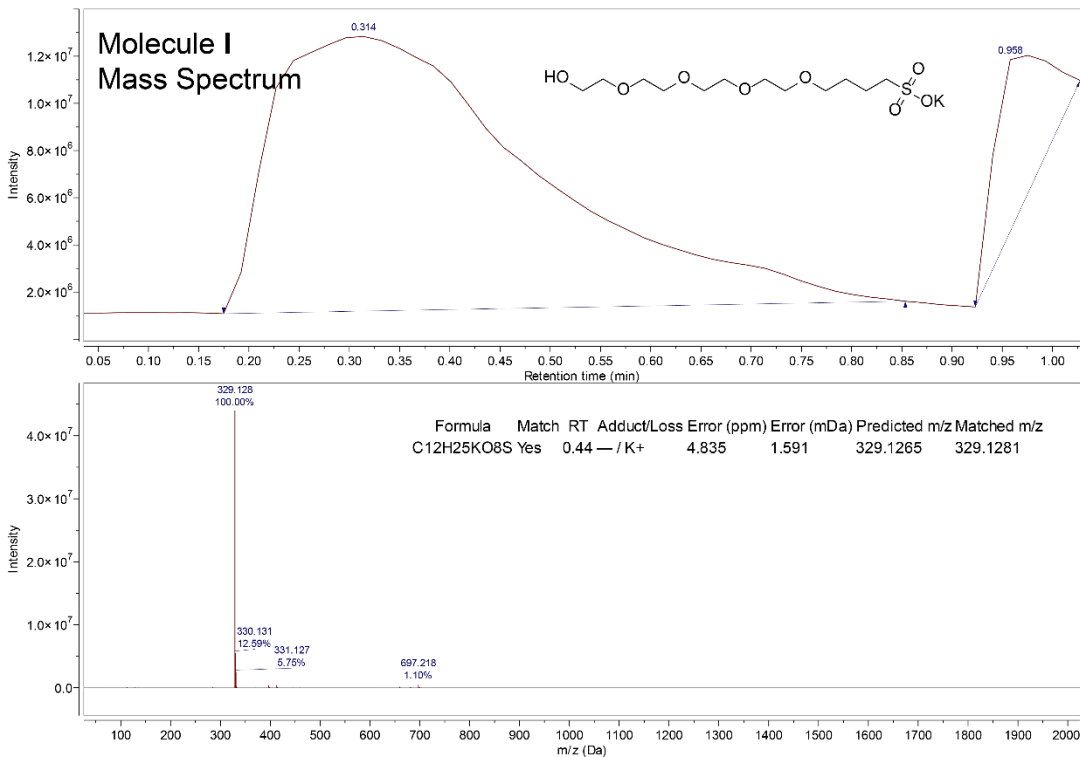
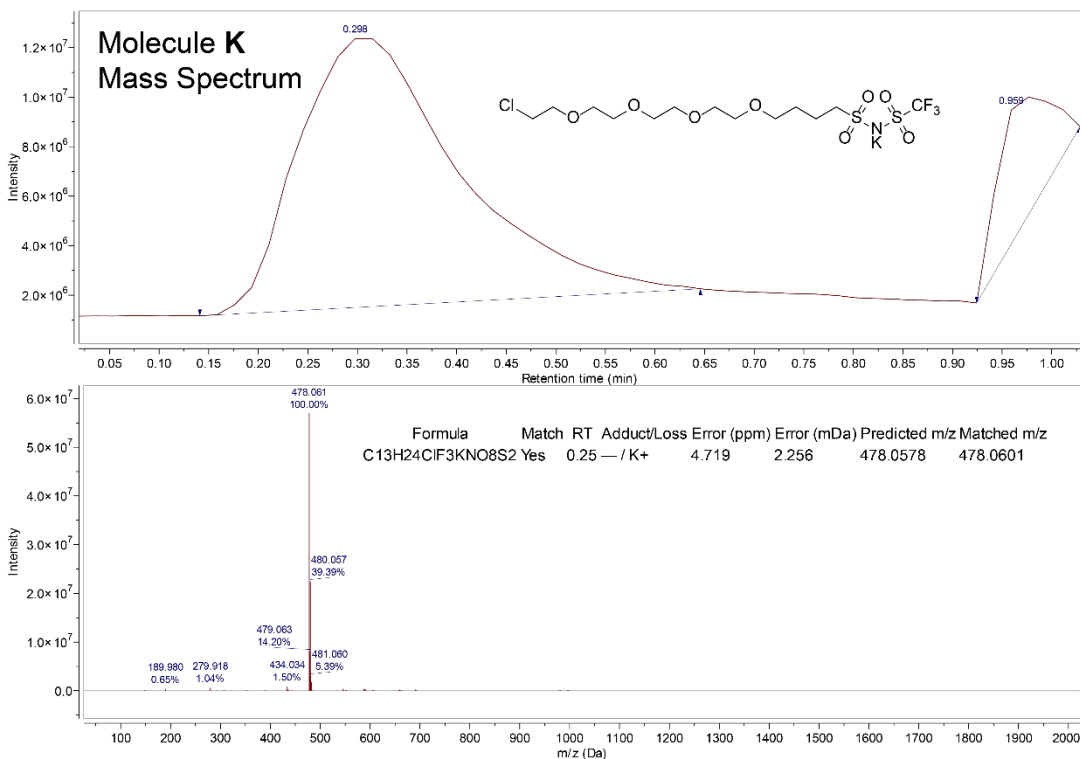
Molecule F



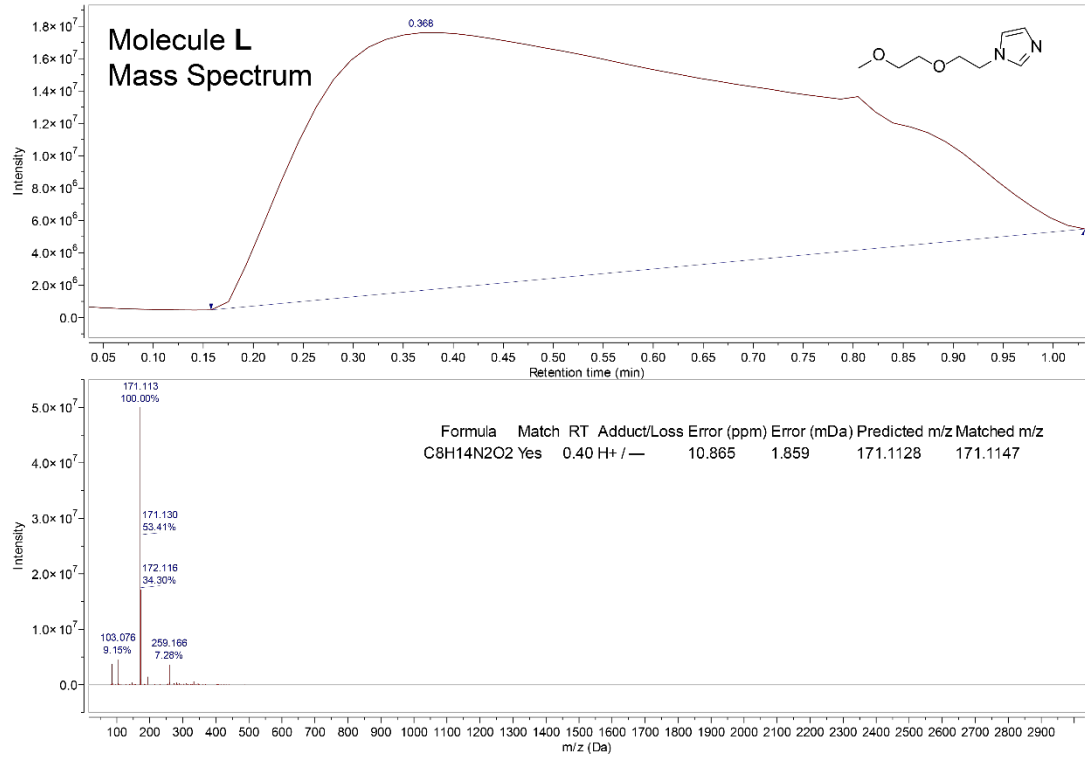
Molecule H



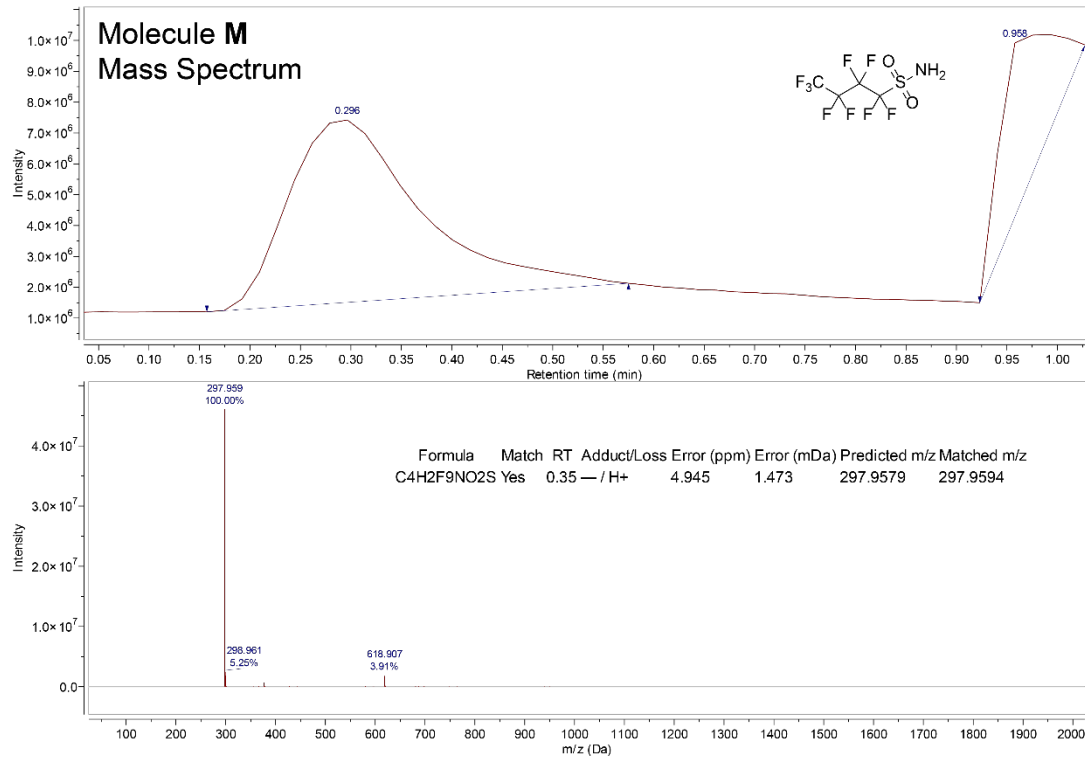
Molecule 1

Molecule **K**

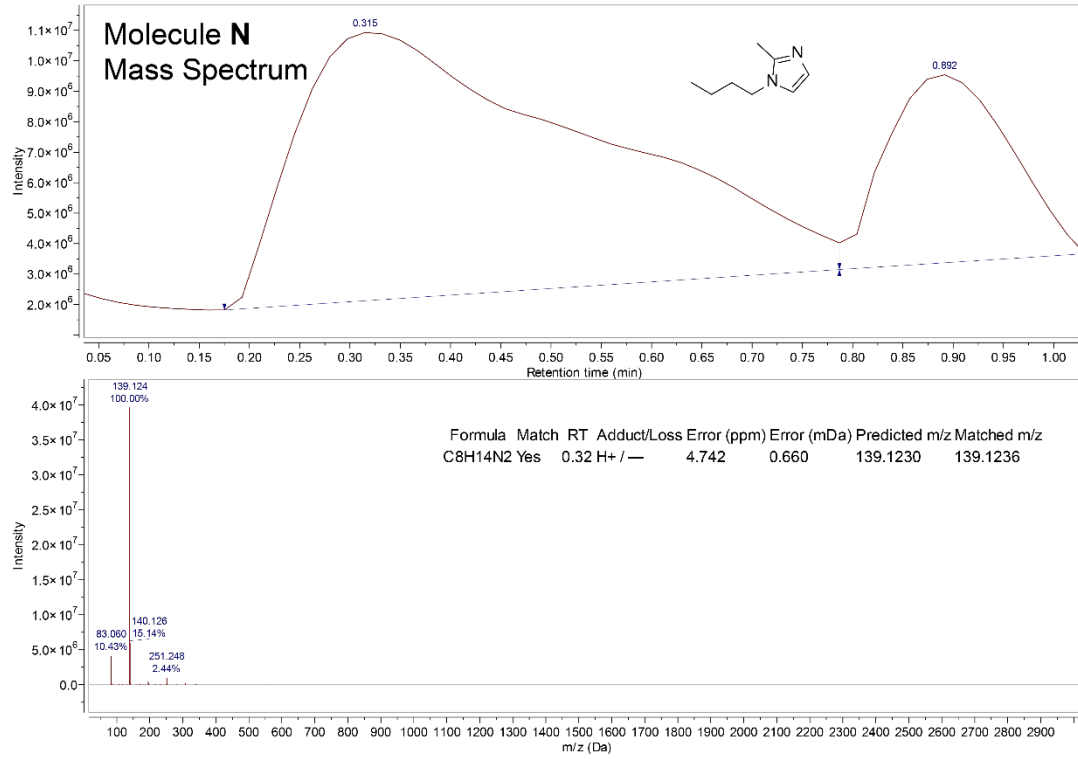
Molecule L



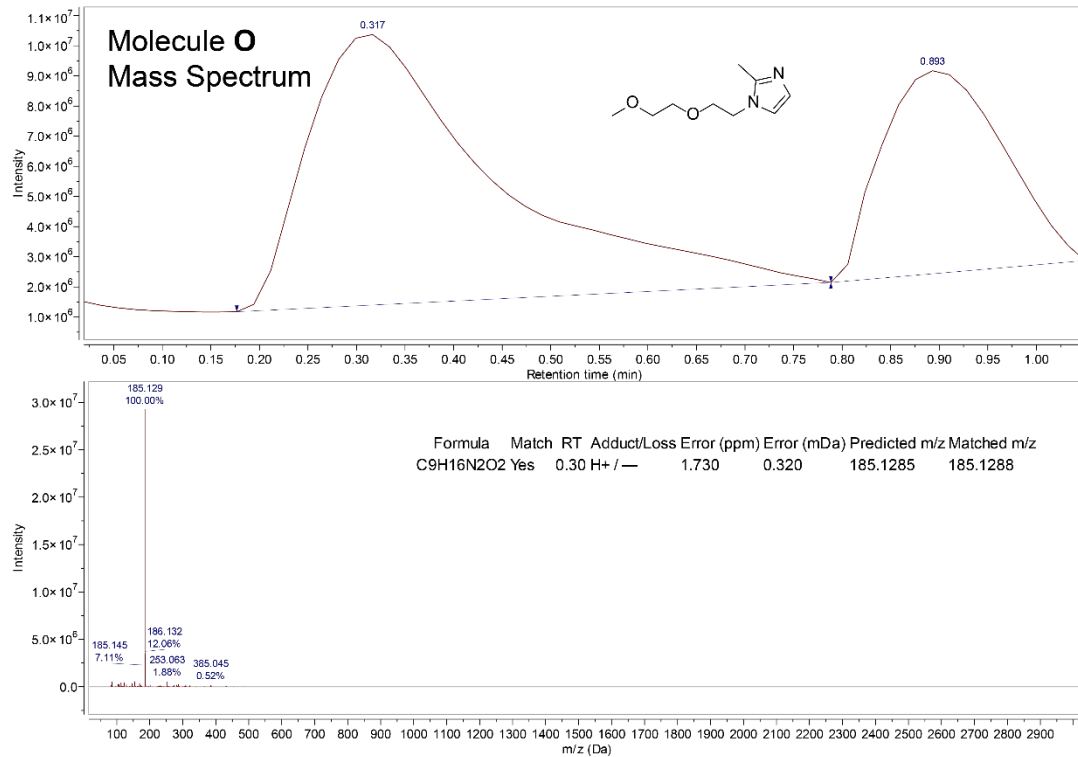
Molecule M



Molecule N

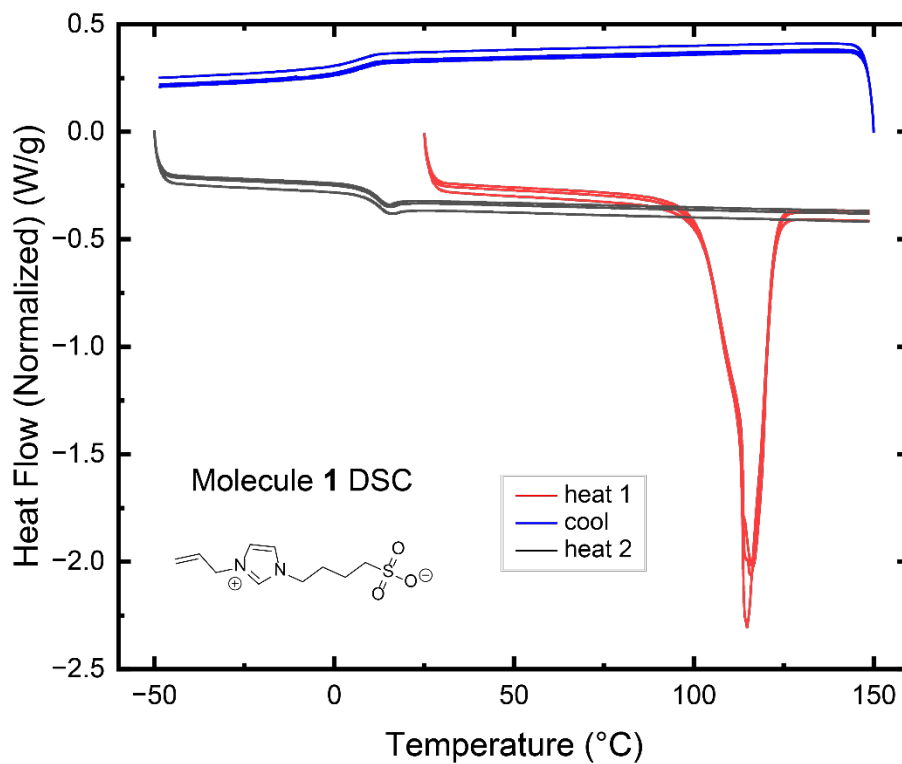


Molecule O

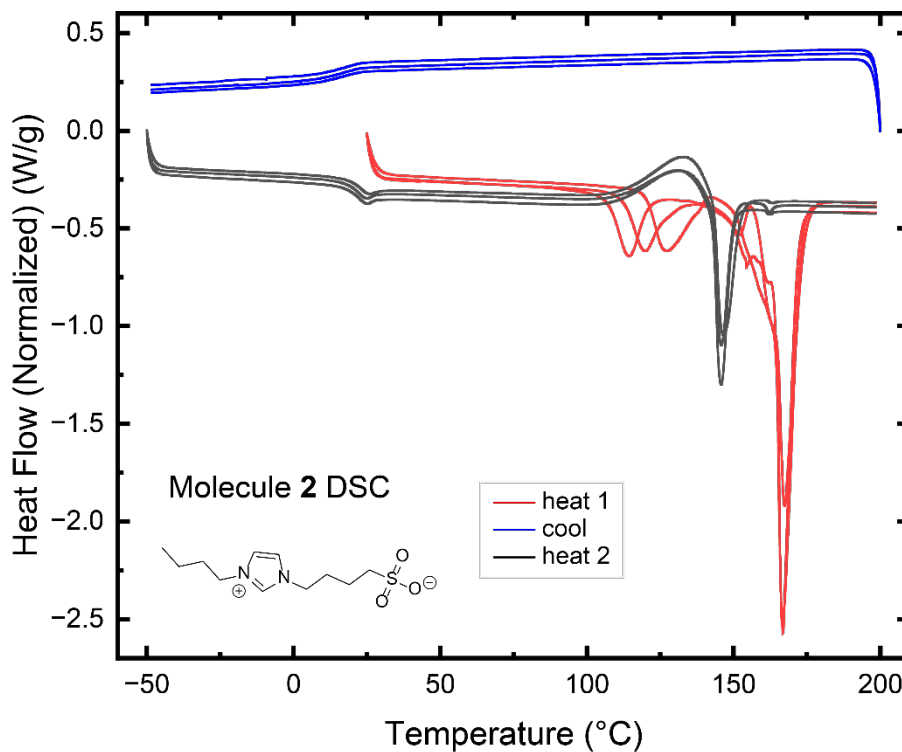


Data S3: Differential scanning calorimetry (exo up) of zwitterions

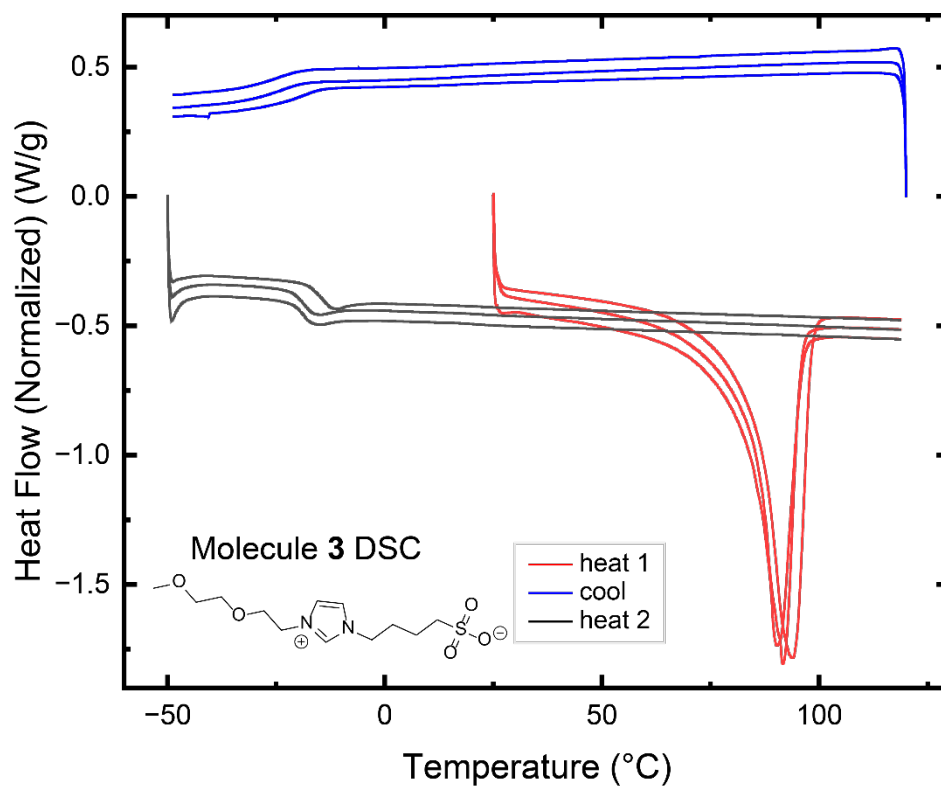
Molecule 1



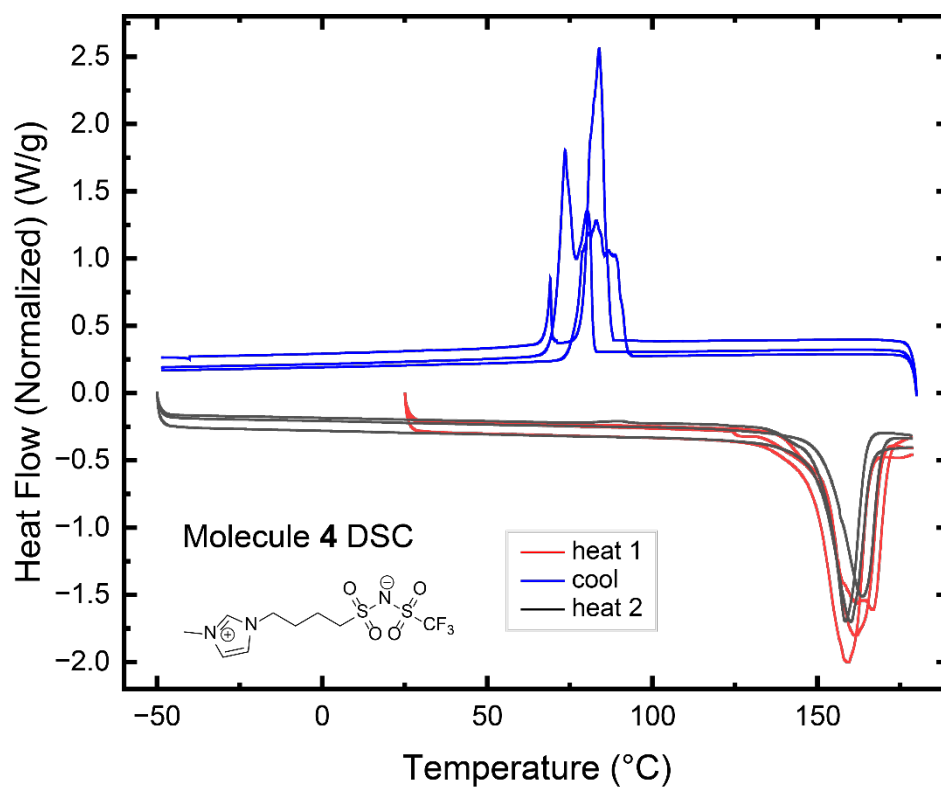
Molecule 2



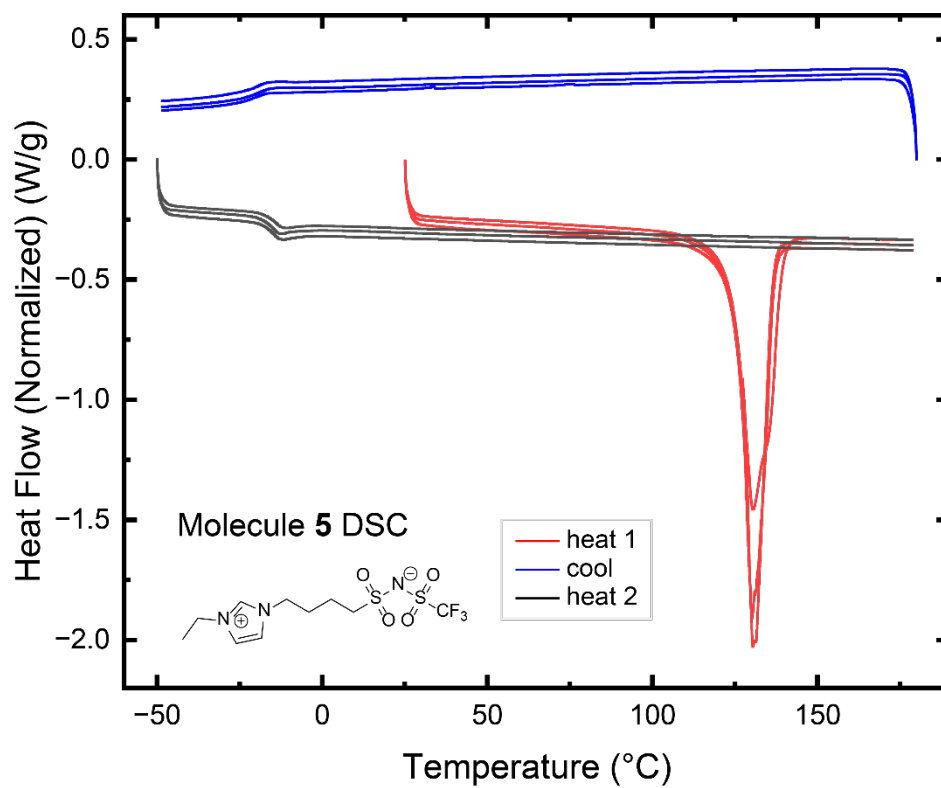
Molecule 3



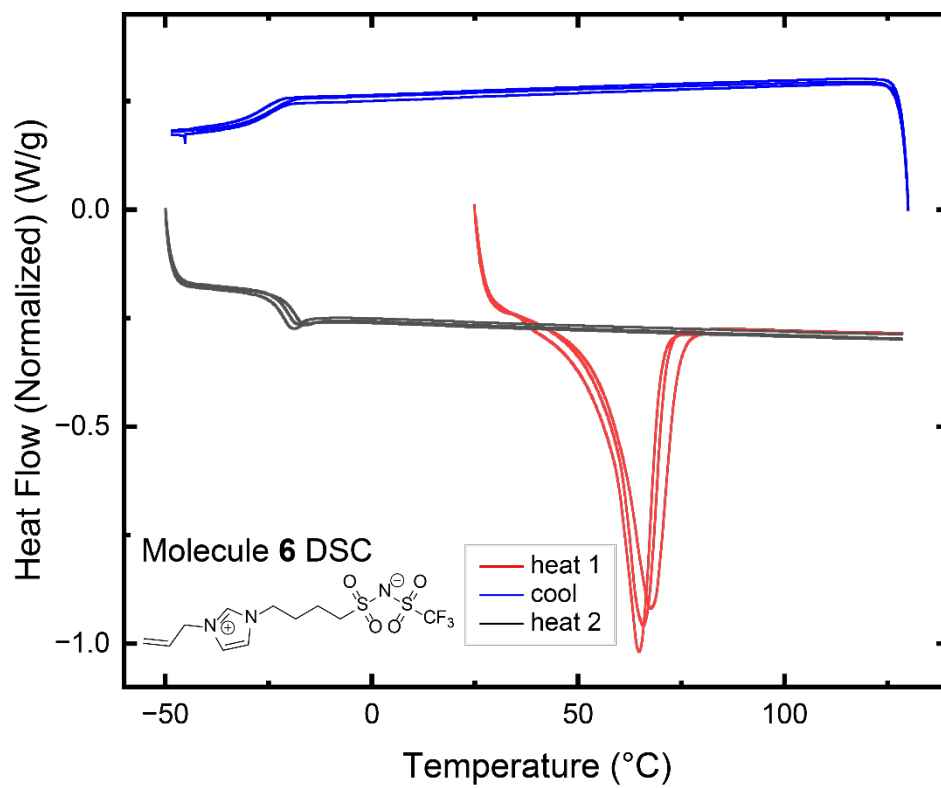
Molecule 4



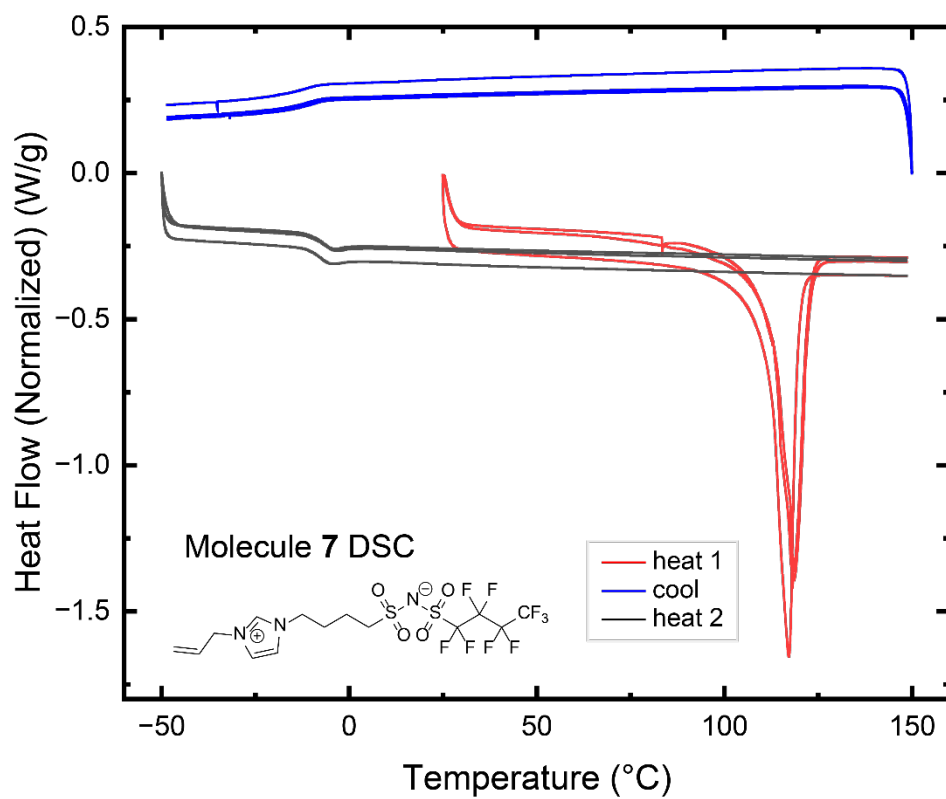
Molecule 5



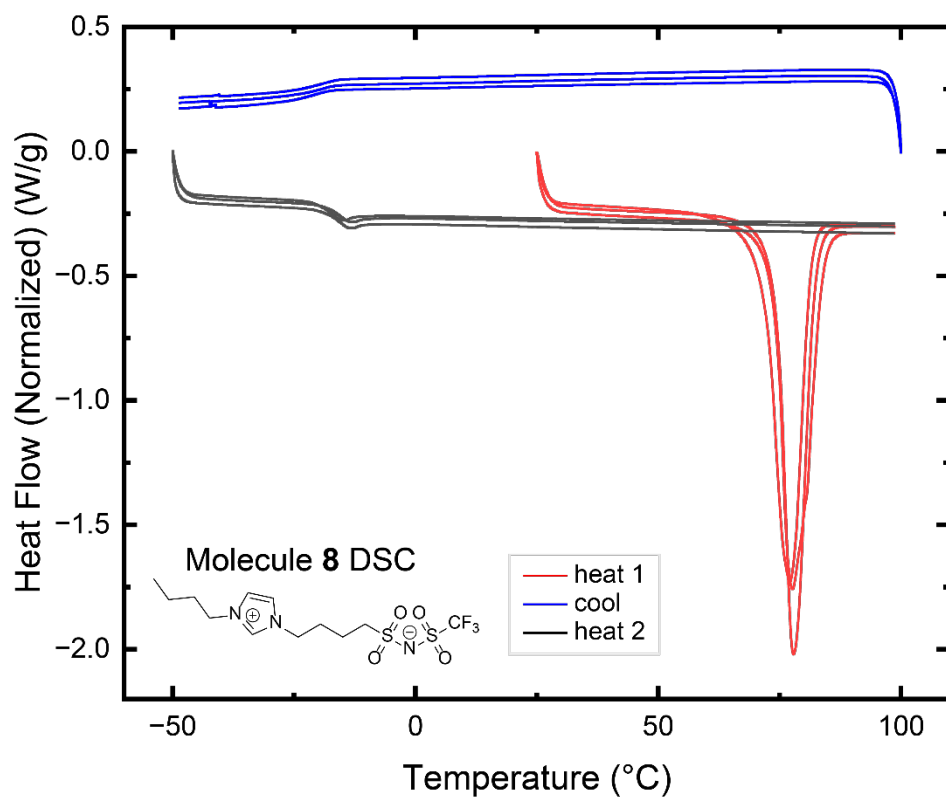
Molecule 6



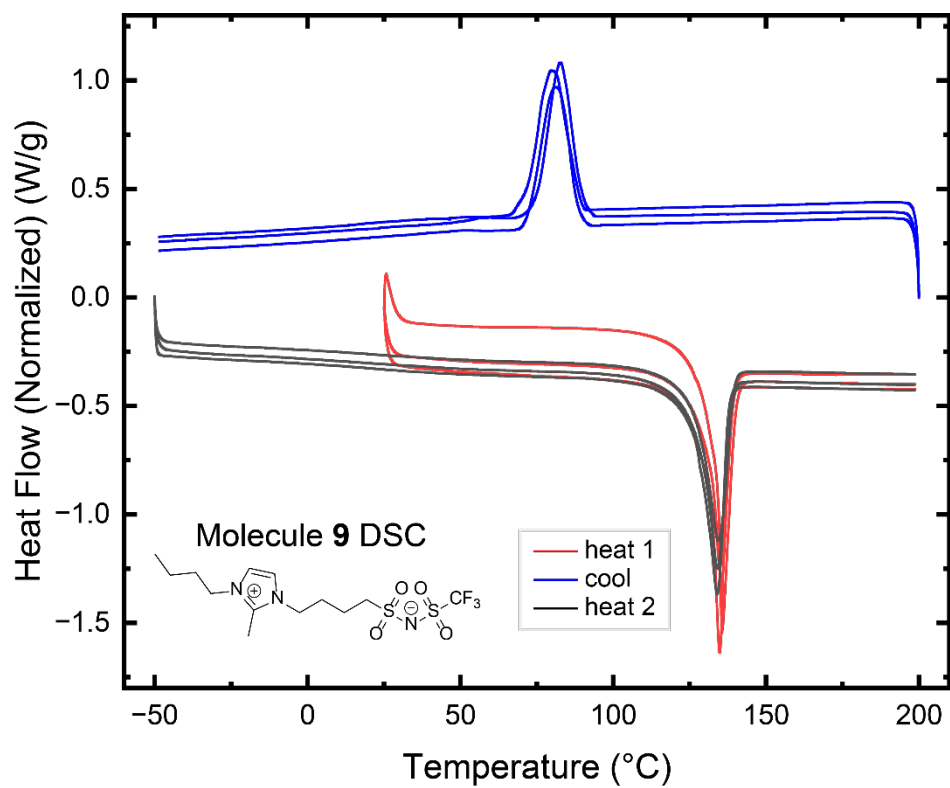
Molecule 7



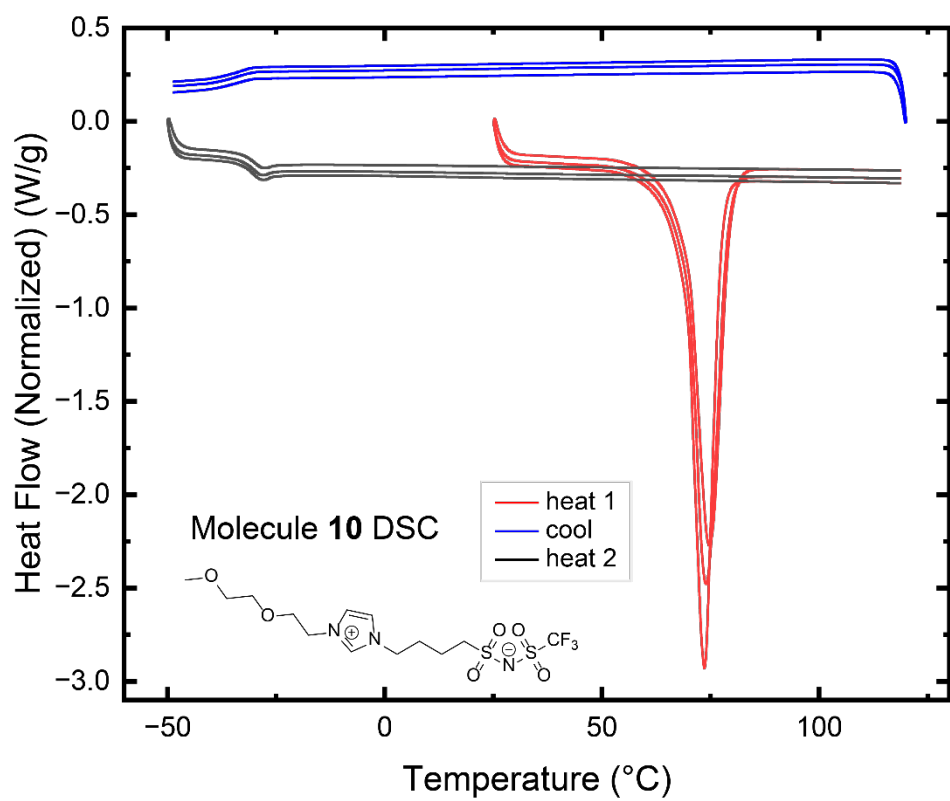
Molecule 8



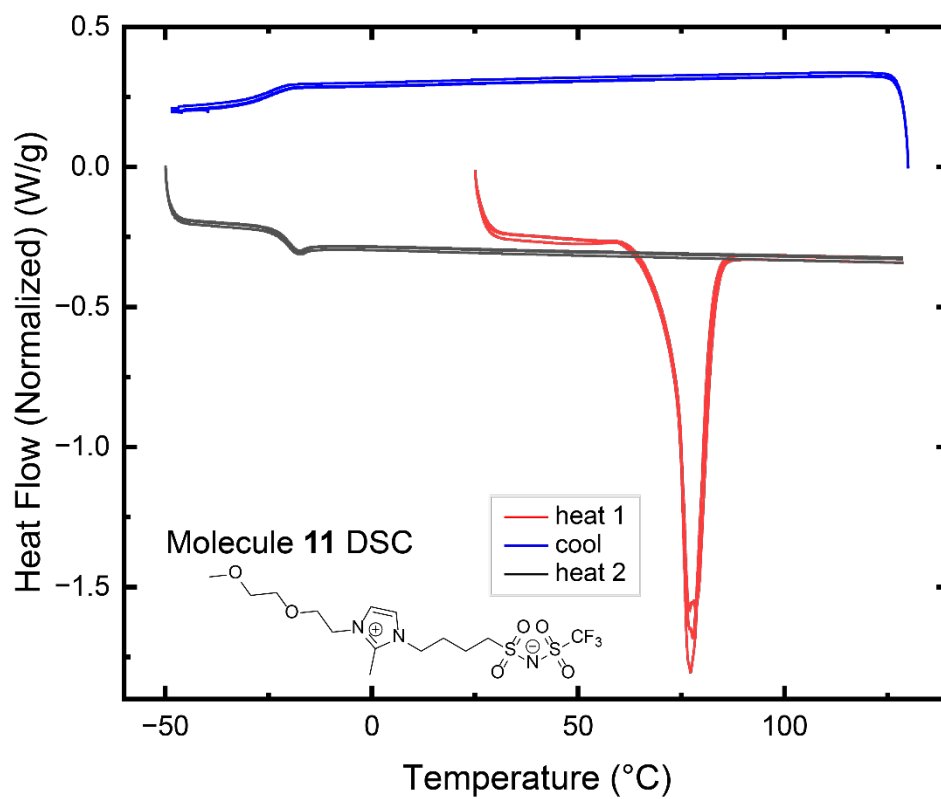
Molecule 9



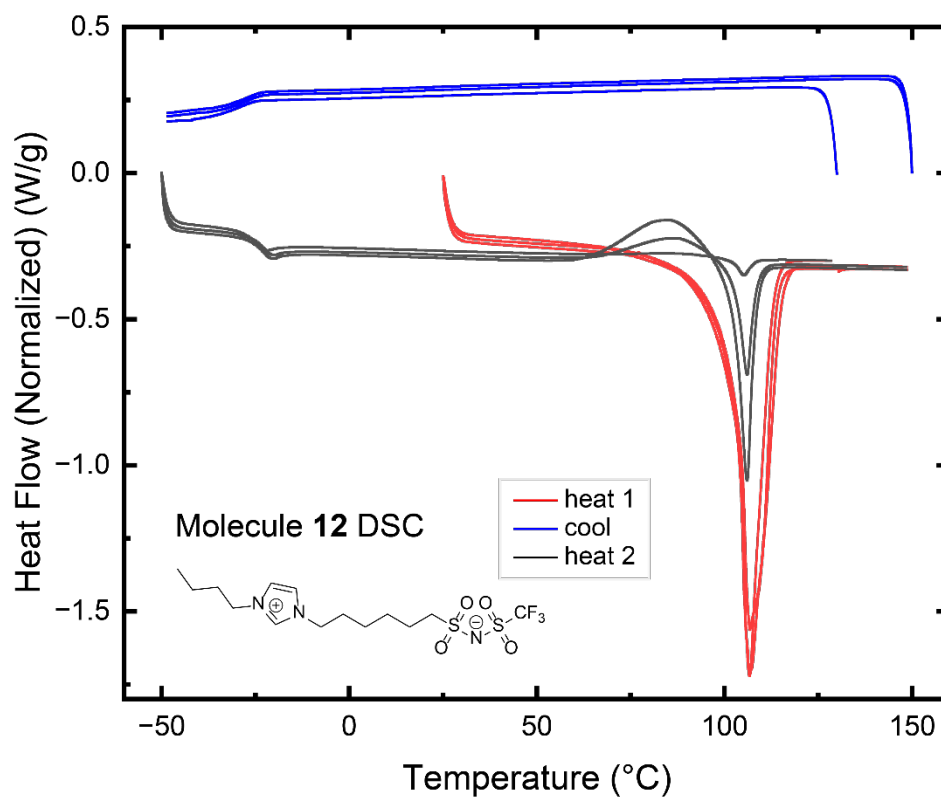
Molecule 10



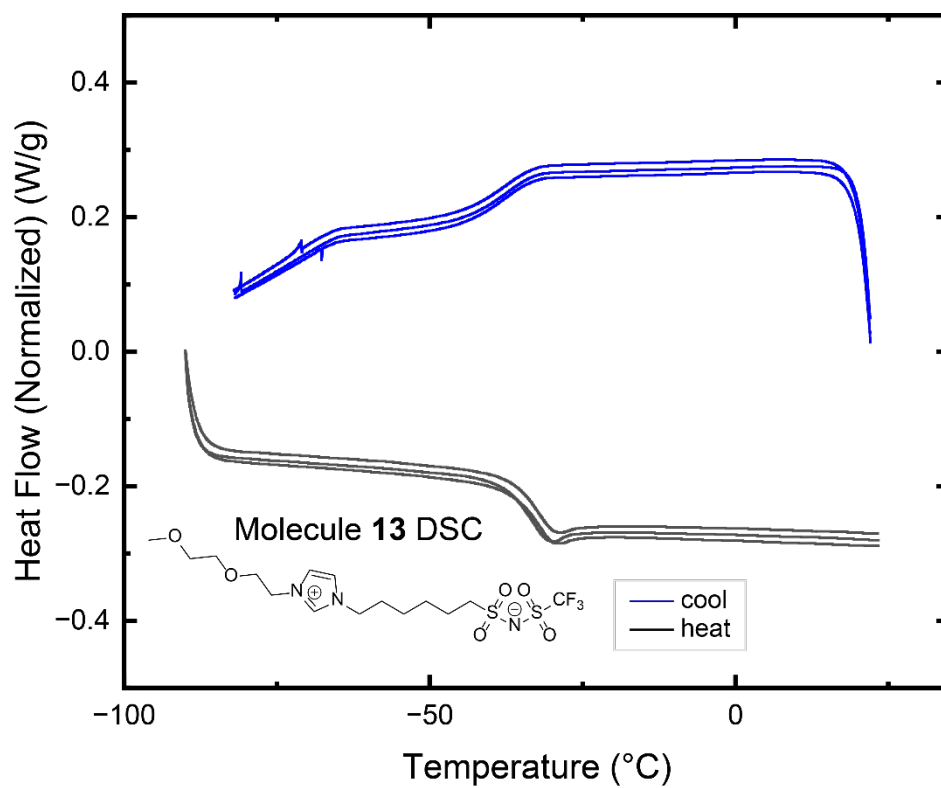
Molecule 11



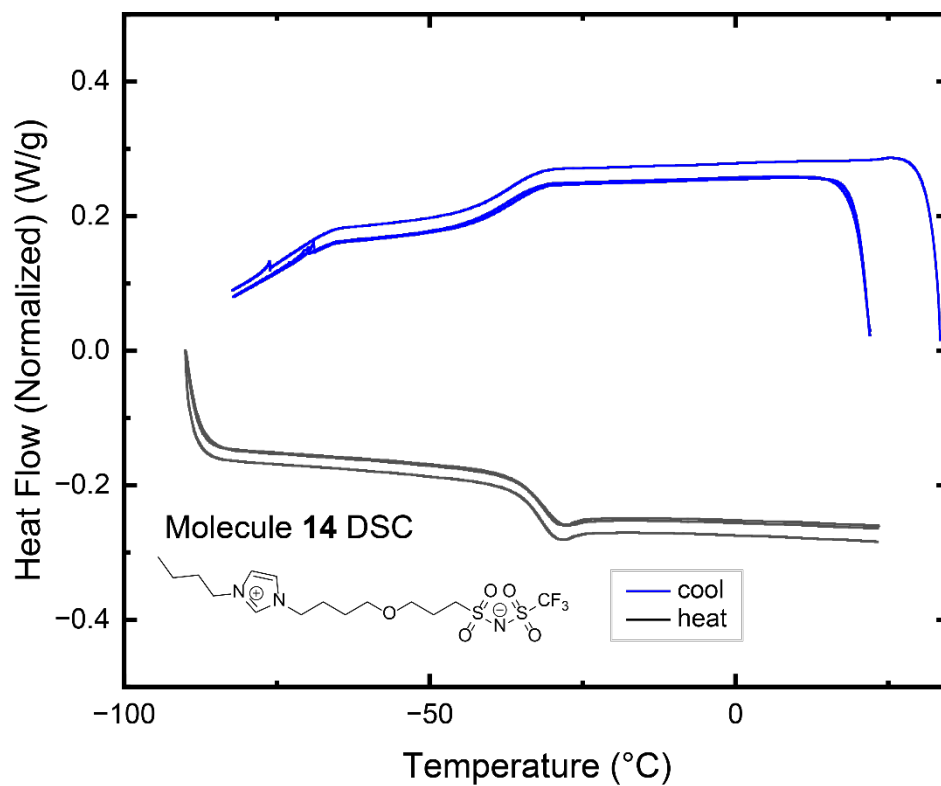
Molecule 12



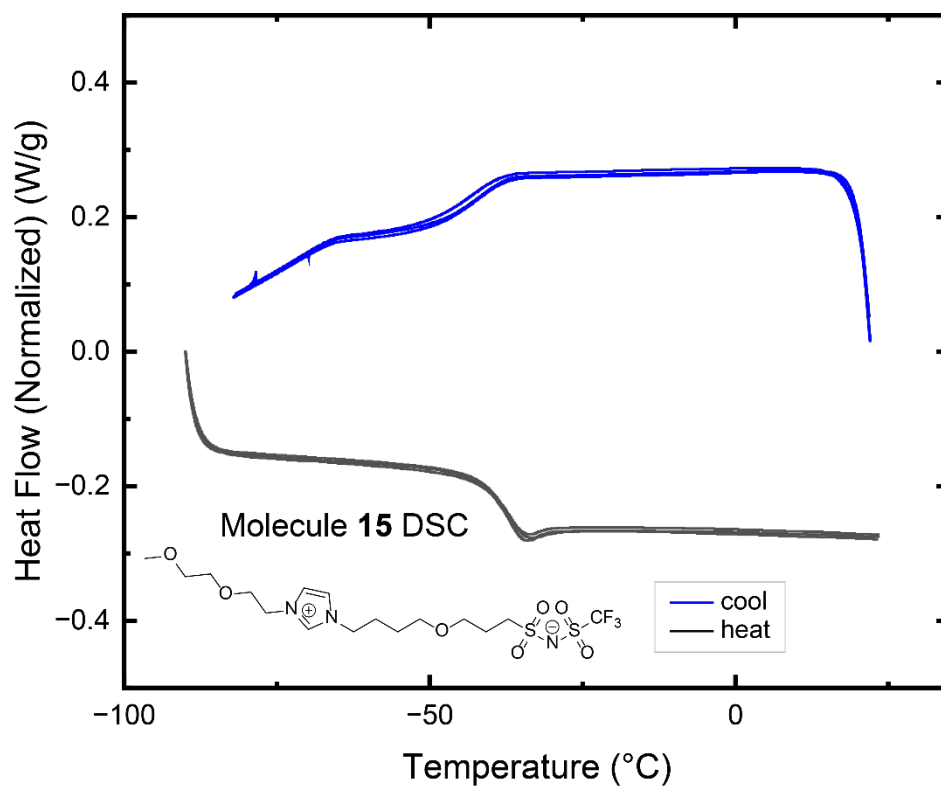
Molecule 13



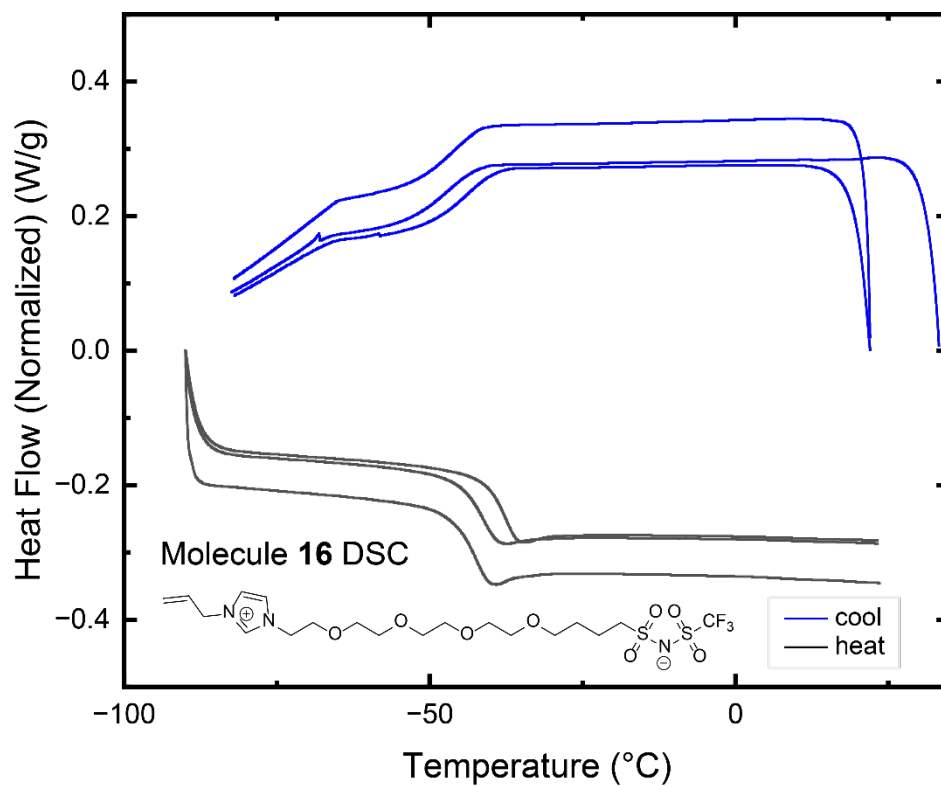
Molecule 14



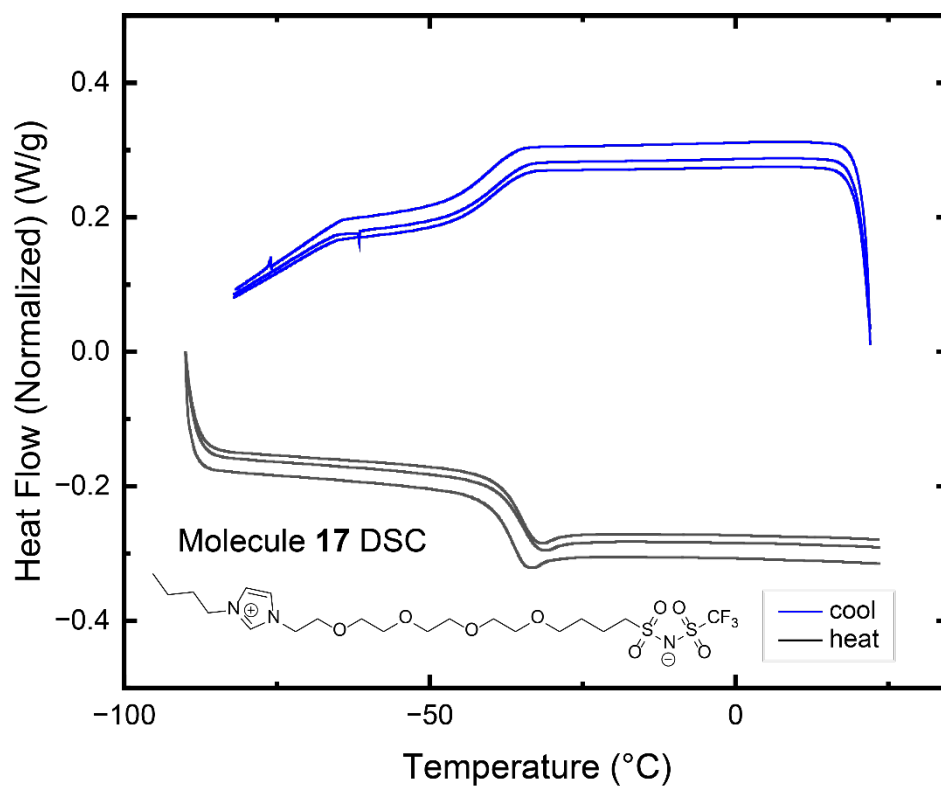
Molecule 15



Molecule 16



Molecule 17



Molecule 18

