

Contents:

1. Materials
2. Measurements
3. Thermal properties
4. Ionic conductivity
5. Diffusion coefficient
6. Alkali-resistance test
7. Syntheses
8. NMR spectra
9. References

1. Materials

Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Nacalai Tesque, Inc. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), potassium hydroxide (KOH), and chloroform-*d* (CDCl_3) were purchased from FUJIFILM Wako Pure Chemical, Co. 1,3,5-Tri-*tert*-butylbenzene was purchased from Tokyo Chemical Industry Co., Ltd. Methanol-*d*₃ (CD_3OH) was purchased from ISOTECH. Trihexylphosphine^[1] and trihexylarsine^[2] were prepared according to the literature.

2. Measurement

^1H (400 MHz), $^{13}\text{C}\{^1\text{H}\}$ (100 MHz), ^{19}F -NMR (376 MHz) and $^{31}\text{P}\{^1\text{H}\}$ -NMR (162 MHz) NMR spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer or a JEOL ECZ-400S NMR spectrometer using Me_4Si (TMS) as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quintet, m: multiplet.

3. Thermal properties

The sample was placed in an open-type aluminum pan and accurately weighed. Measurements were carried out at 25–500 °C using a thermogravimetric–differential thermal analysis (TG–DTA) 7200 instrument (Hitachi High-Tech). The N_2 gas flow rate was 200 mL min^{-1} and the heating rate was 10 °C min^{-1} . The phase transition behavior was investigated via differential scanning calorimetry (DSC) using a DSC7020 system (Hitachi High-Tech) at a scanning rate of 10 °C min^{-1} . The samples were sealed in aluminum pans in an argon-filled glove box. The reported data were obtained from the second heating scan. The measurement temperature ranged from –150 to 100 °C.

4. Ionic conductivity

Impedance measurements were carried out using a locally designed cell made from two platinum electrodes. The cell constants were calculated with a 0.01 mol L^{-1} KCl aqueous solution. The ionic conductivity values were obtained by measuring the complex impedance between 5 Hz to 1 MHz (applied voltage: 10 mV) using an impedance analyzer, VSP-300 (BioLogic) over the temperature range of –30 to 100 °C. The temperatures of the samples were controlled by placing the measurement cell in a thermostatic chamber (SU-262, ESPEC Corp.).

5. Diffusion coefficient

Pulsed-field gradient NMR (PFG-NMR) diffusion measurements were performed on a Bruker 400 MHz UltraShield spectrometer with an Avance III console utilizing a Diff30 diffusion probe. The various constituents of the samples were measured using the ^1H nuclei for the onium cations and ^{19}F nuclei for the TFSA anion. The experiments were performed using the stimulated spin-echo (STE) pulse sequence by varying the gradient in eight steps up to the maximum gradient strength. This data was fit to the Stejskal-Tanner diffusion Eq. (1) using the nonlinear least-squares method. Samples were packed and sealed in 5 mm NMR tubes in an argon gas atmosphere. The measurement temperature ranged from 30 to 100 °C.

$$A = A_0 \exp[-(\gamma\delta G)^2(\Delta - \delta/3)D] \quad (1)$$

where A_0 is the signal area without a gradient, γ is the gyromagnetic ratio of the nuclei under study, G is the gradient strength, Δ is the delay between the two gradients, δ is the duration of one of the gradient pulses, and D is the diffusion coefficient. For each measurement, the gradient pulse duration and diffusion time was typically 1 ms, respectively, and the gradient strength ($G = 350 - 1700 \text{ G cm}^{-1}$) was optimized according to the diffusion coefficients.

6. Alkali-resistance test

The salt (**1**·TFSA or **2**·TFSA, approximately 15 mg) was dissolved in a 1 M KOH/methanol ($\text{CD}_3\text{OH}/\text{CH}_3\text{OH} = 1/9 \text{ v/v}$) solution (0.6 ml) containing a small amount of 1,3,5-tri-*tert*-butylbenzene as an internal standard and was added to an NMR tube. After the NMR tube was flame-sealed, the initial amount of the cation (**1** or **2**) was determined by the integration of a signal (2.32 ppm for **1** and 2.15 ppm for **2**) relative to that of a signal at 7.17 ppm of 1,3,5-tri-*tert*-butylbenzene in a ^1H -NMR spectrum. In the ^1H NMR measurement, the $-\text{CH}_3$ signal in CH_3OH (3.32 ppm) was suppressed by the presaturation technique with a 5 s presaturation delay. The NMR sample was then heated in an oil bath at 80 °C. The residual amount of the cation was determined by ^1H -NMR spectroscopy over a period of 8 weeks.

7. Syntheses

Synthesis of 1-1

To a THF solution (10 mL) of trihexylarsine (1.240 g, 3.75 mmol) was added *ca.* 2 eq. of MeI (1.099 g, 7.74 mmol). The mixture was stirred at 60 °C overnight. The volatile was removed *in vacuo*. The residue was washed with hexane. The product was obtained as a

yellow viscous liquid in 66% (1.168 g, 2.48 mmol). The methylation was checked by ¹H-NMR. ¹H-NMR (CDCl₃, 400 MHz): δ 2.47–2.32 (m, 6H), 1.63–1.46 (m, 12H), 1.38–1.22 (m, 15H), 0.92–0.86 (m, 9H) ppm.

Synthesis of 2·I

To a THF (5 mL) solution of trihexylphosphine (0.392 g, 1.37 mmol) was added *ca.* 2 eq. of MeI (0.385 g, 2.71 mmol). The mixture was stirred at 25 °C overnight. The volatile was removed *in vacuo*. The residue was washed with hexane. The product was obtained as a yellow viscous liquid in 89% (0.522 g, 1.22 mmol). Methylation was checked by ¹H-NMR. ¹H-NMR (CDCl₃, 400 MHz): δ 2.36–2.31 (m, 6H), 1.62–1.54 (m, 6H), 1.48–1.41 (m, 6H), 1.38–1.25 (m, 15H), 0.91–0.87 (m, 9H) ppm.

Synthesis of 1·TFSA

To a THF solution (10 mL) of 1·I (1.17 g, 2.48 mmol) was added 1.05 eq. of LiTFSA (0.747 g, 2.60 mmol). The mixture was stirred at 25 °C overnight. The volatile was removed *in vacuo*. The residue was washed with water four times to eliminate remaining lithium salts. The viscous liquid was dried *in vacuo* at 100 °C for 5 h and settled in the glovebox for one week to remove water. The product was obtained quantitatively as a yellow viscous liquid. We attempted to remove the yellow coloration several times using sodium thiosulfate, but slight coloration still remained. ¹H-NMR (CDCl₃, 400 MHz): δ 2.40–2.36 (m, 6H), 1.85 (s, 3H), 1.61–1.55 (m, 6H), 1.47–1.43 (m, 6H), 1.34–1.29 (m, 12H), 0.92–0.88 (m, 9H) ppm. ¹³C{¹H}-NMR (CDCl₃, 100 MHz): δ 41.86, 31.84, 30.86, 30.26, 29.89, 26.94, 23.85, 22.85, 22.61, 22.27, 22.02, 14.05, 13.81, 2.84 ppm. ¹⁹F-NMR (CDCl₃, 376 MHz): δ –80.03 ppm.

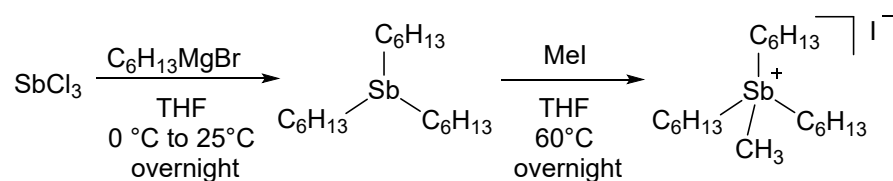
Synthesis of 2·TFSA

To a THF solution (6 mL) of 2·I (0.358 g, 0.838 mmol) was added 1.05 eq. of LiTFSA (0.260 g, 0.905 mmol). The mixture was stirred at 25 °C overnight. The volatile was removed *in vacuo*. The residue was washed with water four times to eliminate remaining lithium salts. The viscous liquid was dried *in vacuo* at 100 °C for 5 h and settled in the glovebox for one week to remove water. The product was obtained quantitatively as a yellow viscous liquid. We attempted to remove the yellow coloration several times using sodium thiosulfate, but slight coloration still remained. ¹H-NMR (CDCl₃, 400 MHz): δ 2.15–2.09 (m, 6H), 1.79–1.77 (d, 3H), 1.52–1.47 (m, 12H), 1.32–1.31 (m, 12H), 0.91–0.88 (m, 9H) ppm. ¹³C{¹H}-NMR (CDCl₃, 100 MHz): δ 30.87, 30.16, 30.04, 22.25, 21.42,

21.39, 20.33, 19.94, 13.81, 4.23, 3.81 ppm. ^{19}F -NMR (CDCl_3 , 376 MHz): δ -78.87 ppm.
 $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3 , 162 MHz): δ 31.33 ppm.

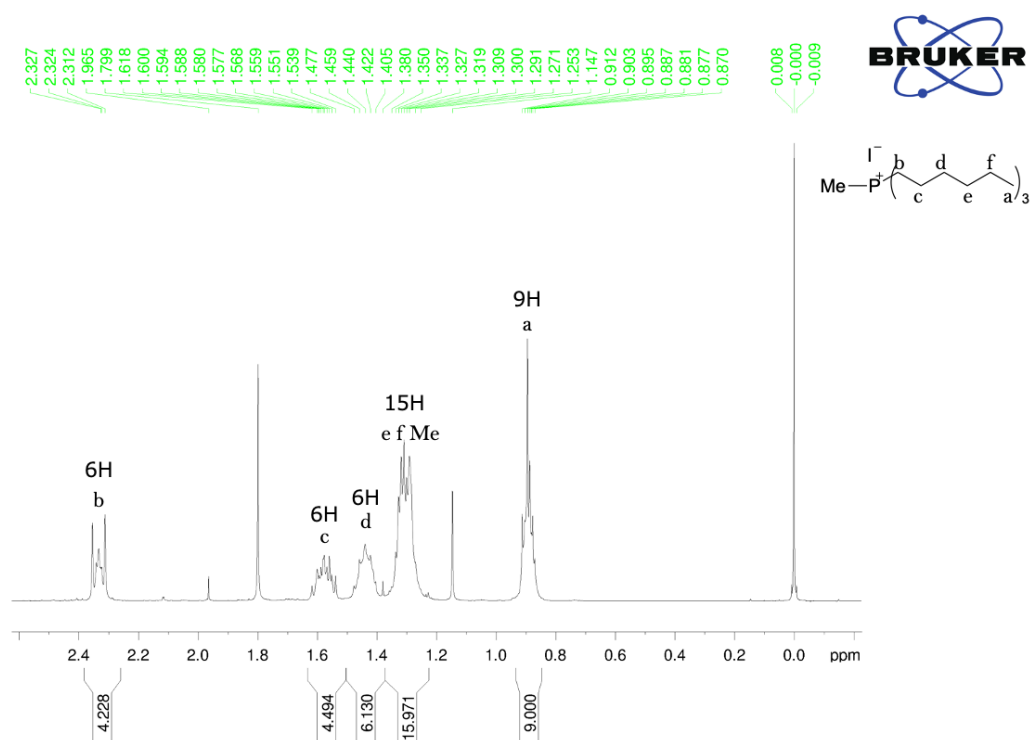
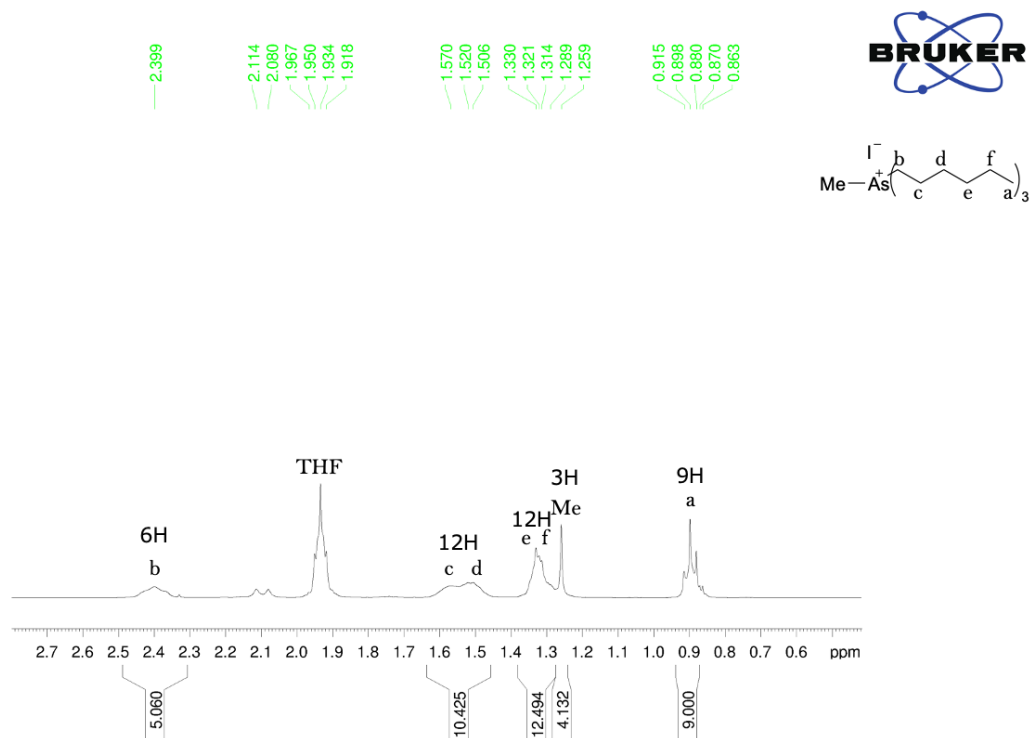
Trials for the synthesis of antimony-containing IL.

SbCl_3 was added dropwise to a THF solution (40 mL) of hexylmagnesium bromide, which was prepared from $\text{C}_6\text{H}_{13}\text{Br}$ (3.97 g, 24 mmol) and magnesium (1.16 g, excess), at $0\text{ }^\circ\text{C}$ under N_2 atmosphere. The reaction mixture was warmed to $25\text{ }^\circ\text{C}$, and stirred overnight. The volatiles were removed *in vacuo*, and the obtained liquid product was filtrated to remove the inorganic components. The synthesis of $\text{Sb}(\text{C}_6\text{H}_{13})_3$ was confirmed by NMR.^[3] The filtrated $\text{Sb}(\text{C}_6\text{H}_{13})_3$ (0.36 g, 0.95 mmol) was dissolved by THF (20 mL) and MeI (0.28 g, 1.95 mmol) was added. The reaction solution was stirred at $60\text{ }^\circ\text{C}$ overnight under N_2 atmosphere. After the reaction, the solution was exposed to air, and then insoluble precipitates generated. Even after filtration, the precipitates further generated again. Thus we concluded that the isolation of $[\text{Sb}(\text{C}_6\text{H}_{13})_3\text{CH}_3]\text{I}$ is difficult due to the instability.



Scheme S1. Synthesis of $[\text{Sb}(\text{C}_6\text{H}_{13})_3\text{CH}_3]\text{I}$.

8. NMR spectra



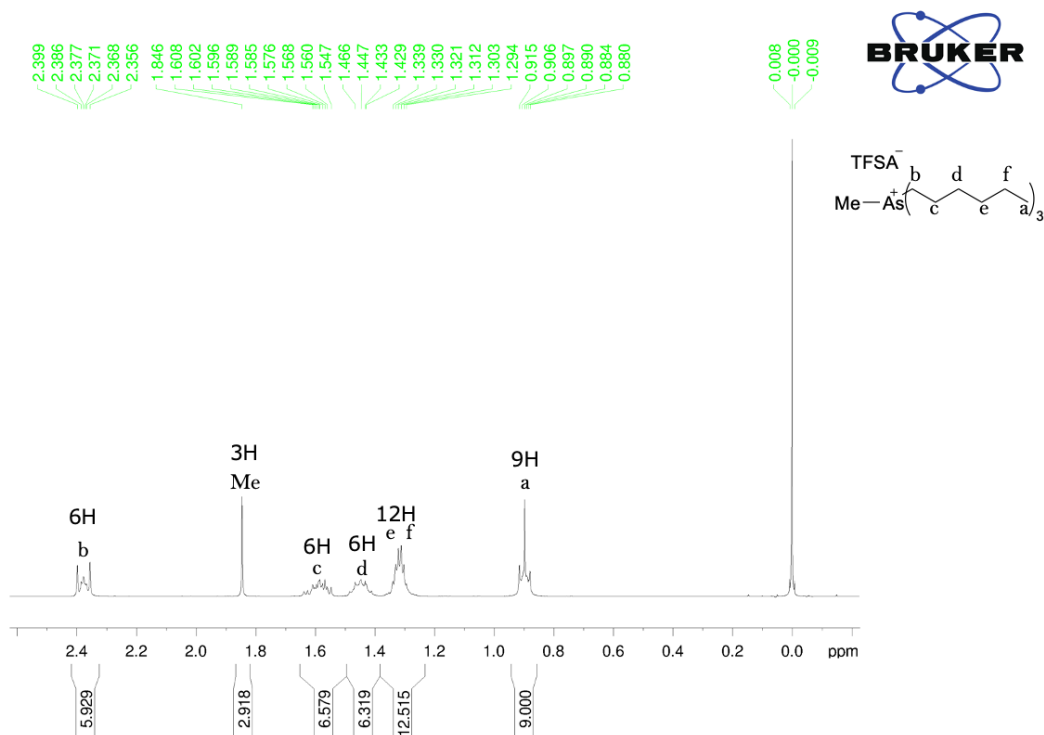


Figure S3. ^1H -NMR spectrum (400 MHz) of **1**·TFSA in CDCl_3 .

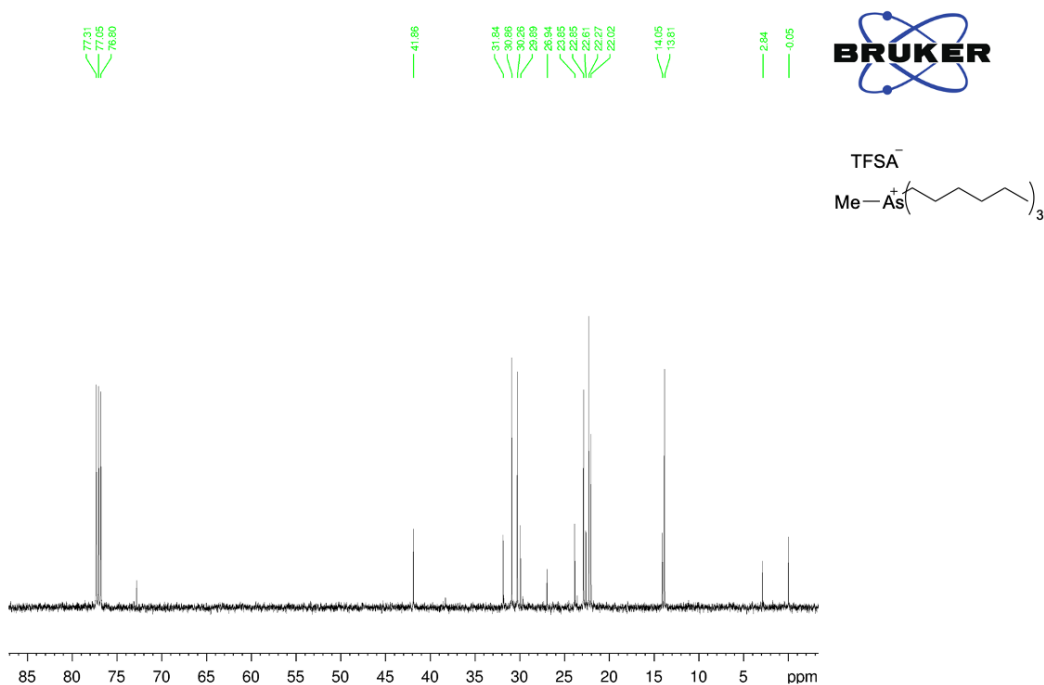


Figure S4. ^{13}C -NMR spectrum (100 MHz) of **1**·TFSA in CDCl_3 .

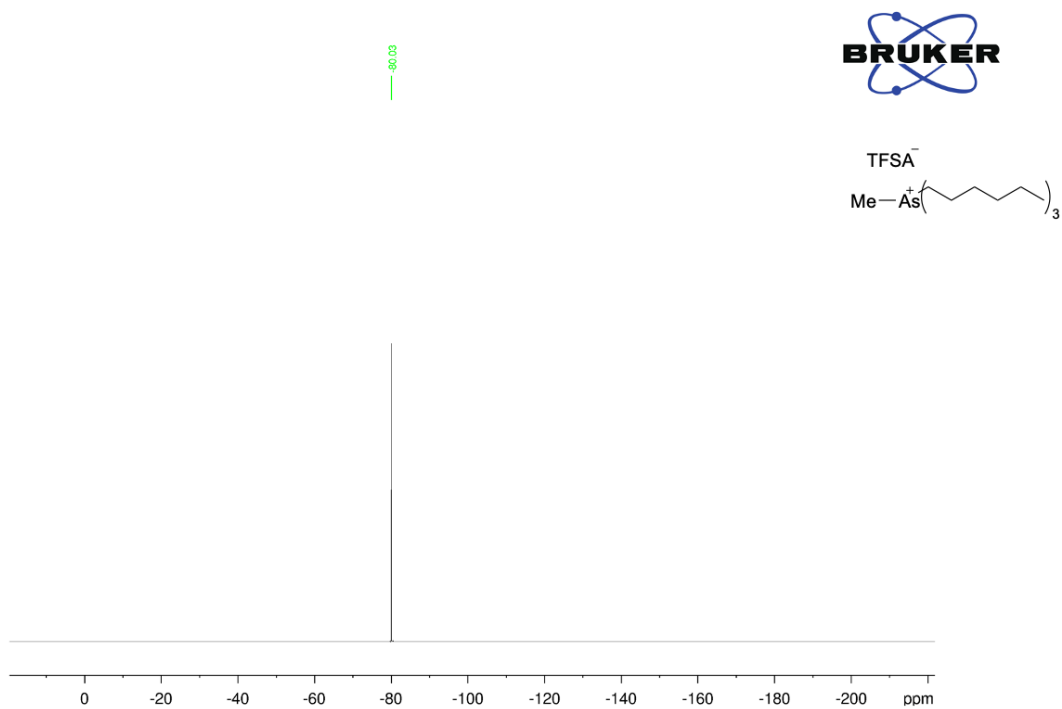


Figure S5. ^{19}F -NMR spectrum (400 MHz) of $1 \cdot \text{TFSA}$ in CDCl_3 .

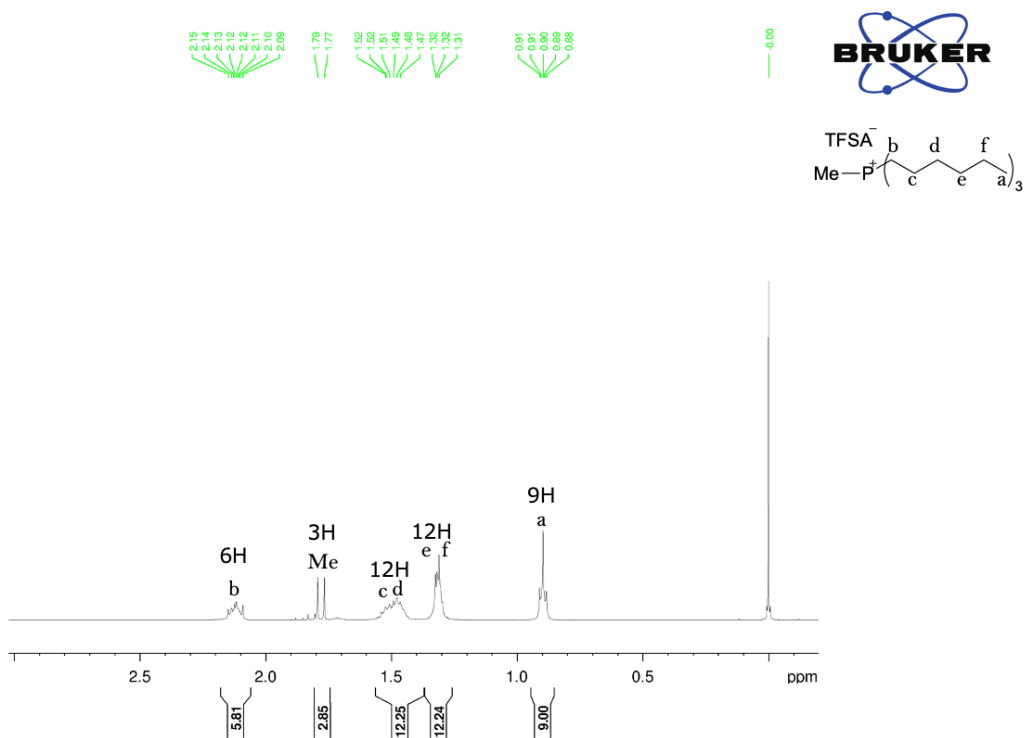


Figure S6. ^1H -NMR spectrum (400 MHz) of $2 \cdot \text{TFSA}$ in CDCl_3 .

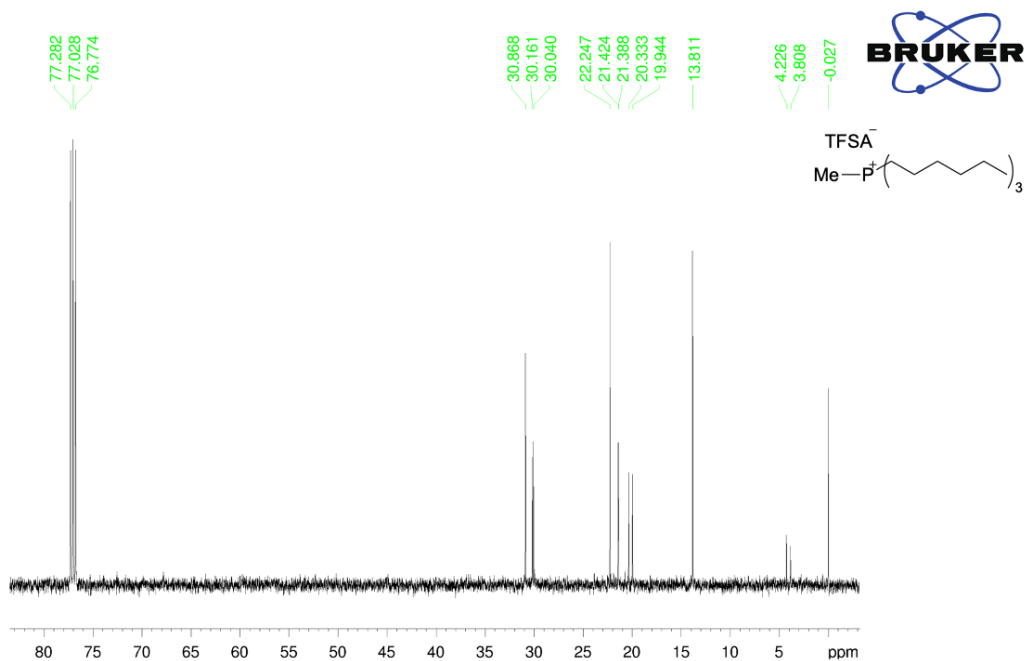


Figure S7. ¹³C-NMR spectrum (100 MHz) of 2·TFSA in CDCl₃.

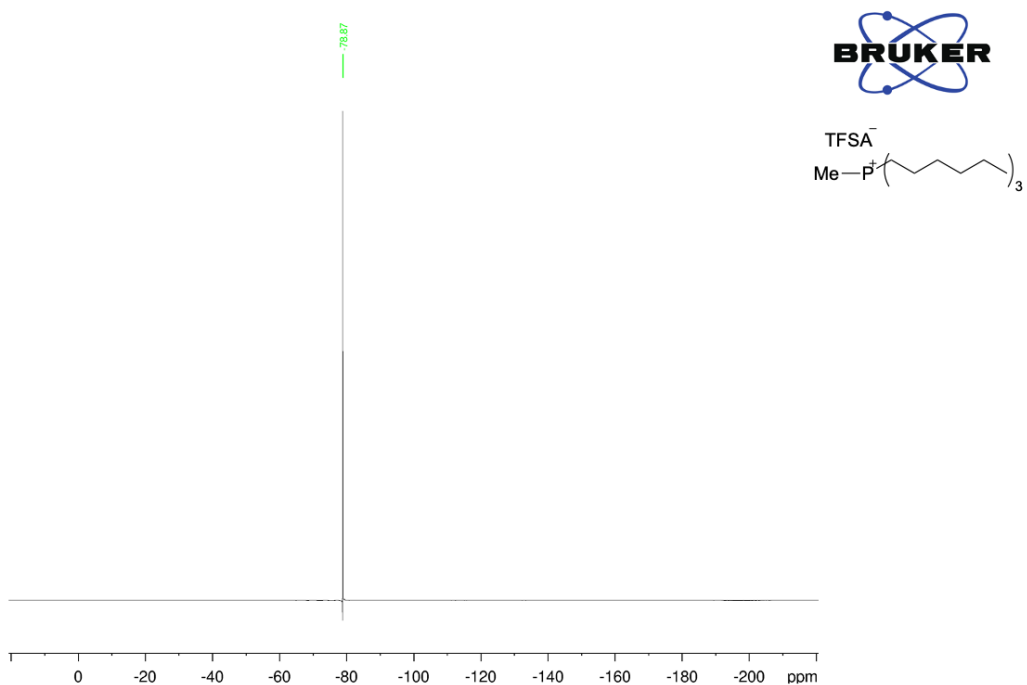


Figure S8. ¹⁹F-NMR spectrum (376 MHz) of 2·TFSA in CDCl₃.

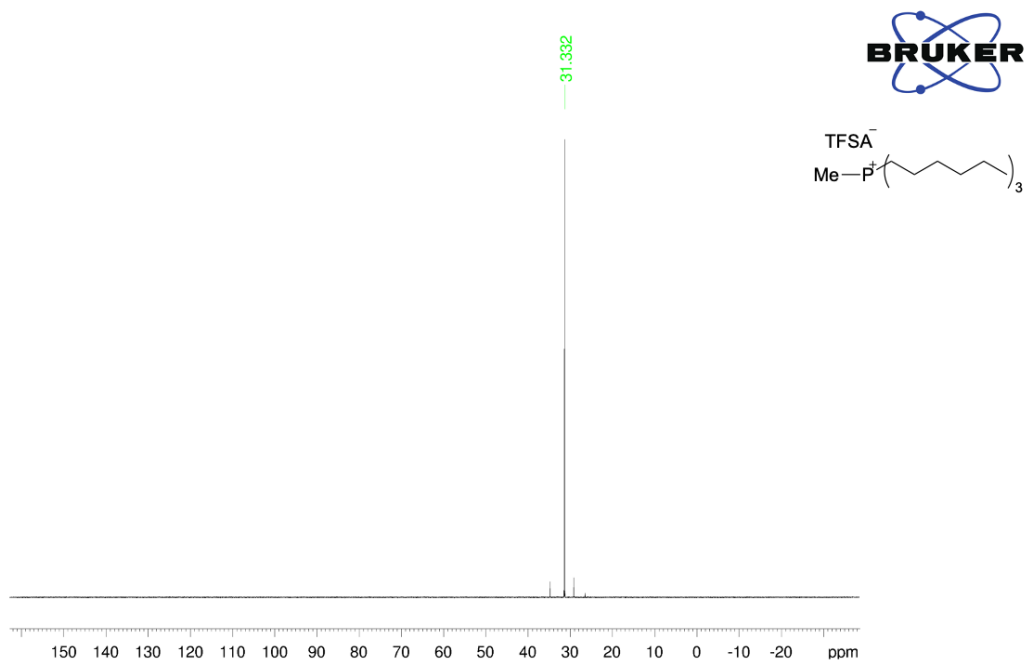


Figure S9. ^{31}P -NMR spectrum (162 MHz) of **2**·TFSA in CDCl_3 .

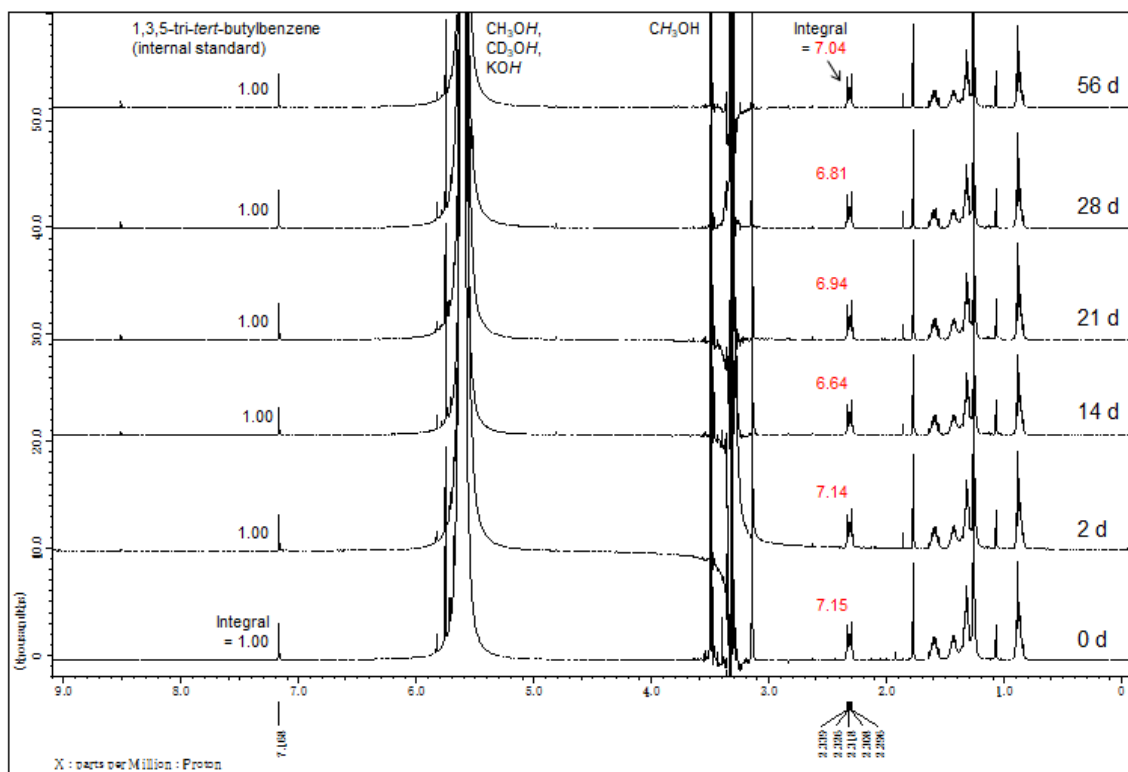


Figure S10. ¹H-NMR spectra of **1**·TFSA in the presence of 1 M KOH in CD₃OH/CH₃OH (9/1). The alkali resistance test was performed at 80 °C.

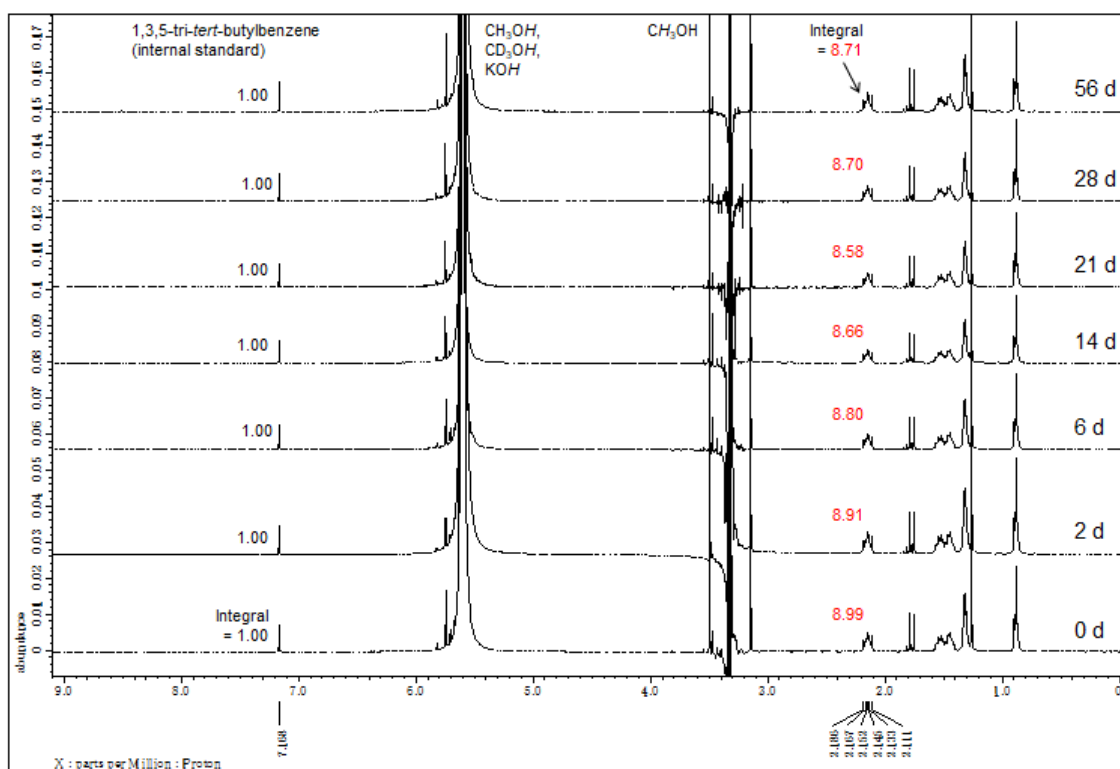


Figure S11. $^1\text{H-NMR}$ spectra of **2**·TFSA in the presence of 1 M KOH in $\text{CD}_3\text{OH}/\text{CH}_3\text{OH}$ (9/1). The alkali resistance test was performed at $80\text{ }^\circ\text{C}$.

9. References

- [1] M. Selva, M. Fabris, V. Lucchini, A. Perosa and M. Noe, *Org. Biomol. Chem.*, 2010, **8**, 5187–5198.
- [2] J. Yukiyasu, R. Inaba, T. Yumura, H. Imoto and K. Naka, *Org. Chem. Front.*, 2022, **9**, 6786–6794.
- [3] W. J. C. Dyke, W. C. Davies and W. J. Jones, *J. Chem. Soc.*, 1930, 463–467.