Supporting Information for

Design and Synthesis of Asymmetric Anhydrous Quaternary Ammonium Fluoride Electrolytes for Fluoride Ion Batteries

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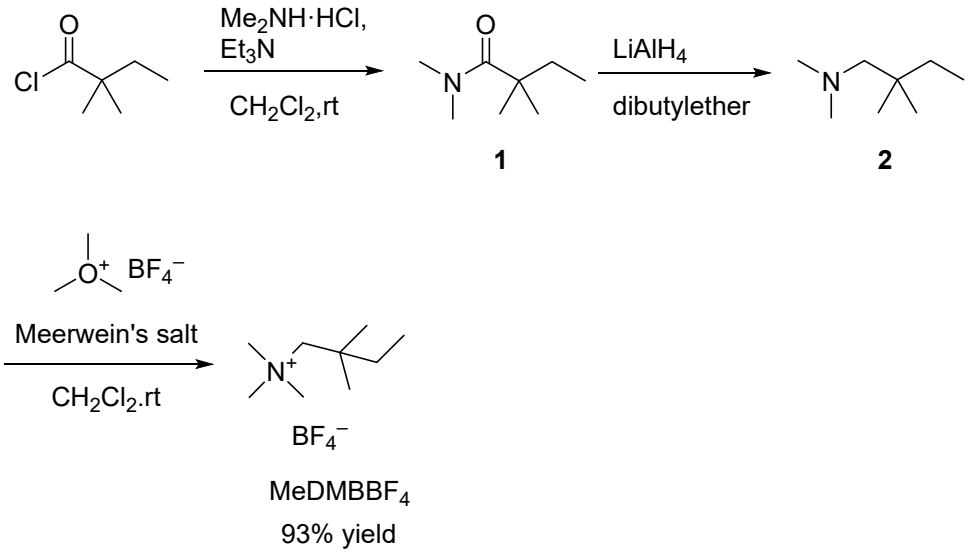
Synthesis of MeDMBBF$_4$

Scheme S1

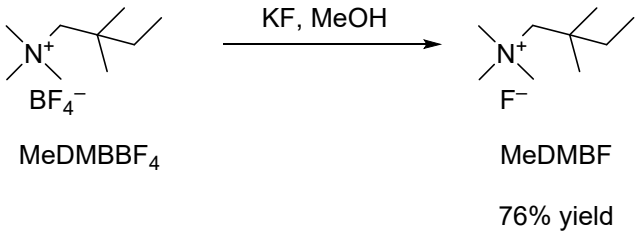


2,2-Dimethylbutanoyl chloride (20.4 mL, 18.0 g, 0.149 mol) was slowly added to a room temperature solution of dimethylamine hydrochloride (14.5g, 0.177 mol) and triethylamine (48.6 mL, 35.3 g, 0.349 mol) in dichloromethane (300 mL) and stirred at room temperature for 16 hours. Following the reaction, the mixture was washed with water. The organic layer was dried over anhydrous magnesium sulfate, and filtered, followed by low vacuum evaporation to remove the solvent. The resulting *N, N*, 2, 2-tetramethylbutanamide (**1**) (15.0 g, 0.106 mol) was added into the suspension of lithium aluminium hydride (5.0 g, 0.14 mol) in dibutyl ether at 0 °C. The mixture stirred at 80 °C for 6 hours. The solution was cooled to room temperature and treated with NaOH aqueous solution then filtered. The resulting solution was treated with concentrated hydrochloric acid until pH = 1. Most of the solvent was removed in vacuo, after which the mixture was moved to a water bath (< 22 °C), treated with concentrated sodium hydroxide solution until pH = 14, and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and filtered, followed by low vacuum evaporation to partially remove residual solvent. The resulting *N*,*N*,2,2-tetramethylbutan-1-amine (**2**) (10.6 g, 77.8 mmol in diethyl ether, 52 wt%) was slowly added to a suspension of Meerwein's salt (trimethyloxonium tetrafluoroborate, 13.3 g, 89.9 mmol) in 200 mL dry dichloromethane. The suspension was stirred at room temperature for 12 hours, and most of the solvent was removed by evaporation to obtain a white solid. The crude product was further purified by recrystallization from methanol/diethyl ether to obtain MeDMBBF$_4$ and then dried under vacuum at 80 °C for 14 hours to obtain anhydrous MeDMBBF$_4$ (17.1 g, 74.0 mmol) in 93% yield.

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.25 (s, 2H), 3.14 (s, 9H), 1.40 (q, 2H, J=7.6 Hz), 1.09 (s, 6H), 0.85 (t, 3H, J=7.6 Hz); ^{13}C NMR (101 MHz, DMSO-d_6): δ 74.25, 54.76, 35.56, 34.51, 26.14, 8.01; ^{19}F NMR (376 MHz, DMSO-d_6): δ –150.

Synthesis of MeDMBF

Scheme S2

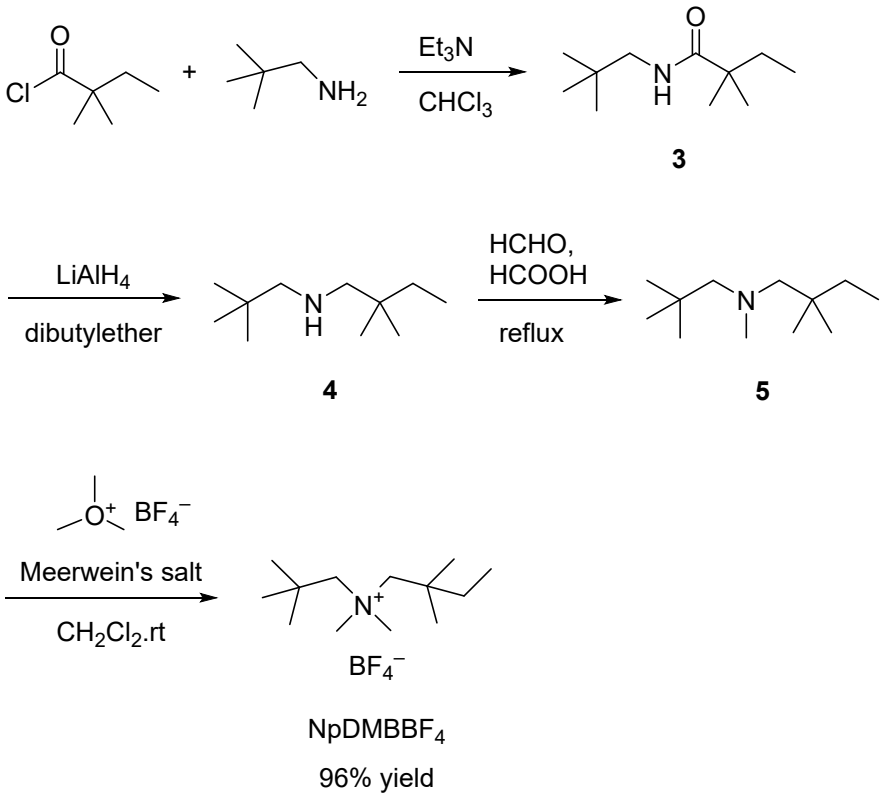


Anhydrous $MeDMBBF_4$ (3.0 g, 13 mmol) was dissolved into 20 mL methanol (water content < 30 ppm). After the addition of KF (1.0 g, 17 mmol, dried at 250 °C for 8 hours) a precipitate of KBF_4 was formed instantly and filtered. The conversion rate of BF_4^- ion to fluoride was monitored by ^{19}F NMR: If BF_4^- ions were detected, more KF was added to the solution until the BF_4^- ion impurity was no longer observed in the product. Methanol in the resulting solution was subsequently removed by vacuum evaporation. The excess KF was removed by precipitation from methanol/diethyl ether (water content < 30 ppm) to obtain a colorless solution which was further dried under vacuum at 90 °C for 19 hours. White solid product (1.7 g, 10 mmol) was retrieved with a purification yield of 76%.

^1H NMR (400 MHz, MeCN-d_3): δ 3.42 (s, 2H), 3.35 (s, 9H), 1.43 (q, 2H, J=7.6 Hz), 1.09 (s, 6H), 0.87 (t, 3H, J=7.6 Hz); ^{13}C NMR (101 MHz, MeCN-d_3): δ 75.51, 55.67, 36.59, 35.72, 26.90, 8.35; ^{19}F NMR (376 MHz, MeCN-d_3): δ –74, –147.

Synthesis of NpDMBBF$_4$

Scheme S3



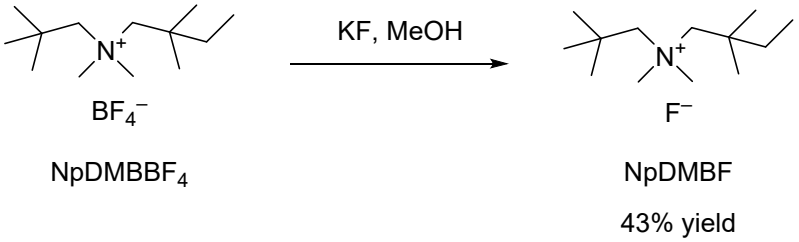
2,2-Dimethylbutanoyl chloride (15.4 mL, 14.4 g, 0.107 mol) was slowly added to a solution of triethylamine (15.4 mL, 11.2 g, 0.107 mol) and neopentylamine (8.1 g, 0.093 mol) in chloroform (80 mL) and refluxed for 18 hours. The mixture was washed with water and the organic layer was dried over anhydrous magnesium sulfate, and filtered, followed by low vacuum evaporation to obtain 2,2-dimethyl-*N*-neopentylbutanamide quantitatively. Lithium aluminium hydride (5.4 g, 0.14 mol) was suspended in to dibutyl ether at 0 °C and *N, N*, 2, 2-tetramethylbutanamide (**3**) (17.5 g, 94.6 mmol) was added. The mixture stirred at 80 °C for 6 hours. The solution was cooled to room temperature and treated with NaOH aqueous solution then filtered. The resulting solution was treated with concentrated hydrochloric acid until pH = 1. Most of the solvent was removed in vacuo, after which the mixture was moved to a water bath (< 22 °C), treated with concentrated sodium hydroxide solution until pH = 14, and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and filtered, followed by low vacuum evaporation to partially remove most of residual solvent to give 2,2-dimethyl-*N*-neopentylbutan-1-amine (**4**) in 88% yield (14.2 g, 83.0 mmol in ether, 57 wt%). The resulting colorless solution was moved to an ice bath, formic acid (10.3 g, 0.223 mol) was added followed by formaldehyde (aq. 37 wt%, 10.2 g, 0.126 mol). The mixture was refluxed for 3 hours. The solution was cooled to room temperature and treated with concentrated hydrochloric acid until pH = 1. The solvent was partially removed in vacuo at 45 °C until a white solid appeared, after which the mixture was moved to a water bath (< 22 °C), treated with concentrated sodium hydroxide solution until pH = 14, and extracted with diethyl ether. The organic layer was dried over anhydrous magnesium sulfate and filtered, followed by low vacuum evaporation to partially remove residual solvent. The resulting *N*,2,2-trimethyl-*N*-neopentylbutan-1-amine (**5**) (10.7 g, 57.8 mmol in diethyl ether, 53 wt%) was slowly added to a suspension of Meerwein's salt (trimethyloxonium tetrafluoroborate, 9.3 g, 63 mmol) in 100 mL dry dichloromethane. The suspension was stirred at room temperature for 12 hours, and most of the solvent was removed by evaporation to obtain a white solid. The crude product was

further purified by recrystallization from methanol/diethyl ether to obtain $NpDMBBF_4$ and then dried under vacuum at 80 °C for 14 hours to obtain anhydrous $NpDMBBF_4$ (16.0 g, 55.7 mmol) in 96% yield.

^{1}H NMR (400 MHz, MeCN-d_3): δ 3.28 (s, 2H), 3.26 (s, 2H), 3.17 (s, 6H), 1.47 (q, 2H, J=7.6 Hz), 1.19 (m, 15H), 0.90 (t, 3H, J=7.6 Hz); ^{13}C NMR (101 MHz, MeCN-d_3): δ 77.53, 76.13, 52.55, 35.03, 34.14, 32.30, 27.94, 24.71, 5.85; ^{19}F NMR (376 MHz, MeCN-d_3): δ –153.

Synthesis of NpDMBF

Scheme S4

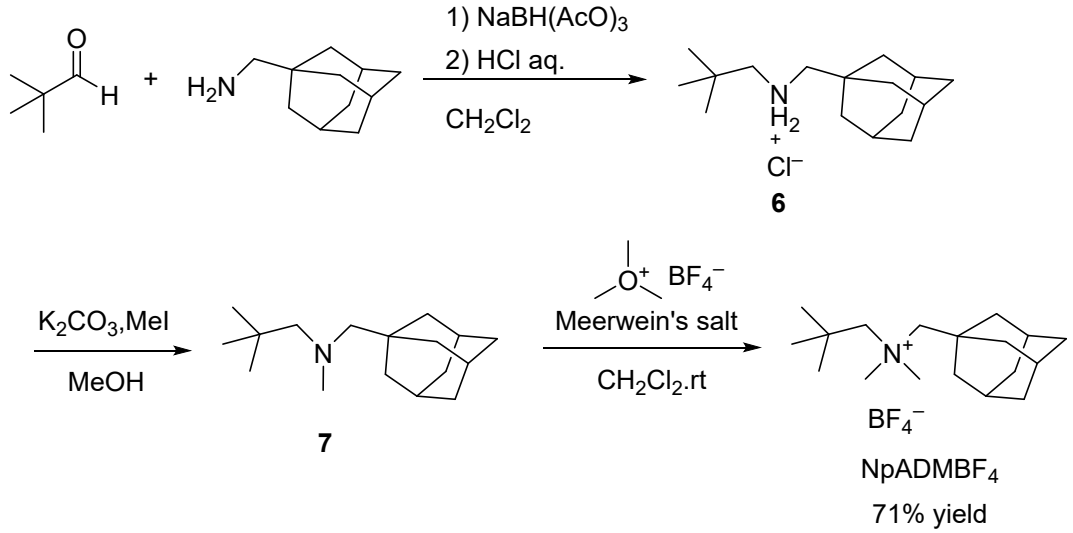


Anhydrous $NpDMBBF_4$ (3.0 g, 10 mmol) was dissolved into 20 mL methanol (water content < 30 ppm). After the addition of KF (0.80 g, 14 mmol, dried at 250 °C for 8 hours) a precipitate of KBF_4 was formed instantly and filtered. The conversion rate of BF_4^- ion to fluoride was monitored by ^{19}F NMR: If BF_4^- ions were detected, more KF was added to the solution until the BF_4^- ion impurity was no longer observed in the product. Methanol in the resulting solution was subsequently removed by vacuum evaporation. The excess KF was removed by precipitation from methanol/diethyl ether (water content < 30 ppm) to obtain a colorless solution which was further dried under vacuum at 90 °C for 19 hours. White solid (0.95 g, 4.3 mmol) product was retrieved with a purification yield of 43%.

^{1}H NMR (400 MHz, MeCN-d_3): δ 3.36 (s, 2H), 3.34 (s, 2H), 3.23 (s, 6H), 1.48 (q, 2H, J=7.6 Hz), 1.18 (s, 9H), 1.16 (s, 6H), 0.90 (t, 3H, J=7.6 Hz); ^{13}C NMR (101 MHz, MeCN-d_3): δ 78.75, 77.33, 54.38, 37.22, 36.50, 34.52, 30.47, 27.26, 8.57; ^{19}F NMR (376 MHz, MeCN-d_3): δ –73, –147.

Synthesis of $NpADMBF_4$

Scheme S5

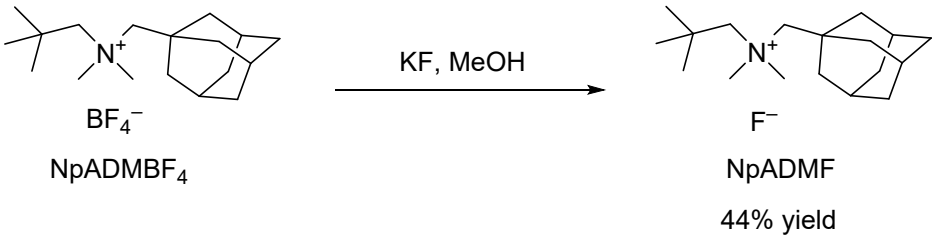


1-(Adamantan-1-yl)methanamine (5.0 g, 30 mmol) was added to a room temperature solution of pivalaldehyde (3.3 mL, 2.6 g, 30 mmol) in dichloromethane (50 mL) and stirred for 0.5 hour. The solution was then moved to a water bath (< 22 °C), sodium triacetoxyborohydride (9.1 g, 43 mmol) was added and the mixture was stirred for 16 hours. Following the reaction, the mixture was quenched with $NaHCO_3$ aqueous solution, and extracted with diethyl ether. The organic layer was treated with concentrated hydrochloric acid to obtain corresponding hydrochloride salt (**6**) quantitatively. Compound **6** and K_2CO_3 (12 g, 87 mmol) was added in 50 mL MeOH, then MeI (5.00 mL, 11.4 g, 80.9 mmol) was added into this mixture then heated at 40 °C for 26 hours. The mixture was filtered and the solvent was removed by low vacuum evaporation to obtain colorless liquid of *N*-(adamantan-1-ylmethyl)-*N*,2,2-trimethylpropan-1-amine (**7**) (5.1 g, 21 mmol) in 70% yield. This resulting amine was slowly added to a suspension of Meerwein's salt (trimethyloxonium tetrafluoroborate, 4.0 g, 21 mmol) in 20 mL dry dichloromethane. The suspension was stirred at room temperature for 16 hours, and most of the solvent was removed by evaporation to obtain a white solid. The crude product was further purified by recrystallization from methanol/diethyl ether to obtain $NpADMBF_4$ and then dried under vacuum at 80 °C for 14 hours to obtain anhydrous $NpADMBF_4$ (6.4 g, 15 mmol) in 71% yield.

^{1}H NMR (400 MHz, MeCN-d_3): δ 3.26 (s, 2H), 3.16 (s, 6H), 3.09 (s, 2H), 2.02 (m, 3H), 1.81 (m, 6H), 1.72 (m, 6H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, MeCN-d_3): δ 80.34, 79.16, 55.01, 42.37, 37.17, 36.90, 34.64, 30.34, 29.34; ^{19}F NMR (376 MHz, MeCN-d_3): δ –153.

Synthesis of NpADMF

Scheme S6



Anhydrous $NpADMBF_4$ (2.0 g, 5.7 mmol) was dissolved into 20 mL methanol (water content < 30 ppm). After the addition of KF (0.40 g, 6.9 mmol, dried at 250 °C for 8 hours) a precipitate of KBF_4 was formed instantly and filtered. The conversion rate of BF_4^- ion to fluoride was monitored by ^{19}F NMR: If BF_4^- ions were detected, more KF was added to the solution until the BF_4^- ion impurity was no longer observed in the product. Methanol in the resulting solution was subsequently removed by vacuum evaporation. The excess KF was removed by precipitation from methanol/diethyl ether (water content < 30 ppm) to obtain a colorless solution which was further dried under vacuum at 90 °C after 19 hours. White solid product (0.7 g, 2.5 mmol) was retrieved with a purification yield of 44%.

^{1}H NMR (400 MHz, MeCN-d_3): δ 3.49 (s, 2H), 3.33 (m, 8H), 1.96 (m, 3H), 1.78 (m, 6H), 1.68 (m, 6H), 1.15 (s, 9H); ^{13}C NMR (101 MHz, MeCN-d_3): δ 79.56, 78.33, 54.66, 42.53, 37.01, 34.49, 30.54, 29.39; ^{19}F NMR (376 MHz, MeCN-d_3): δ –73, –147.

Solubility and Water Content of Various Organic Solvents

Table S1 shows the solubility of MeDMBF, Np_2F, NpDMBF and NPADMF fluoride salts in methanol (MeOH), 1,3-dimethylimidazolidin-2-one (DMI), diethyl carbonate (DEC), dimethylsulfoxide (DMSO), 1-methylpyrrolidin-2-one (NMP), N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), γ-butyrolactone (GBL), ethyl acetate (EtOAc), acetonitrile (MeCN), propionitrile (PN), tetrahydrofuran (THF), diethyl ether (Et_2O), 1,2-dimethoxyethane (DME), tetraethylene glycol dimethyl ether (TEGDME), dicholomethane (DCM), bis(2,2,2-trifluoroethyl) ether (BTFE).

Table S1. Solubility these Anhydrous Fluoride electrolytes in Dry Organic Solvents

Solvent	Solubility (M)			
	MeDMBF	Np_2F	NpDMBF	NPADMF
MeOH	> 11	> 16	> 16	> 2.0
DMI	< 0.1	< 0.1	< 0.3	< 0.1
DEC	< 0.1	< 0.1	< 0.1	< 0.1
DMSO	< 1.0	< 1.1[a]	> 2.0	< 0.1
NMP	< 0.1	< 0.1	< 0.3	< 0.1
DMA	< 0.1	< 0.1	< 0.1	< 0.1
DMF	< 0.1	< 0.2 [a]	< 0.3	< 0.1
GBL	> 1.0	> 1.0	> 1.0	< 0.1
EtOAc	< 0.1	< 0.1	< 0.1	< 0.1
MeCN	> 1.0	> 1.0[a]	> 1.0	< 0.2
PN	< 0.2	> 1.0	> 1.0	< 0.1
THF	< 0.1	< 0.1	< 0.1	< 0.1
Et_2O	< 0.1	< 0.1	< 0.1	< 0.1
DME	< 0.1	< 0.1	< 0.1	< 0.1
TEGDME	< 0.1	< 0.1	< 0.1	< 0.1
DCM	> 1.0	> 1.0	> 1.0	< 0.5
BTFE	> 2.0	> 2.0[a]	> 2.0	< 0.1

[a]Results from Reference 1.[1]

Table S2. Measured Water Content of Various Organic Solvents Used in the Work

Solvent	Water Content (ppm)
MeOH	29
DMI	53
DEC	13
DMSO	2
NMP	29
DMA	24
DMF	9
GBL	18
EtOAc	47
MeCN	2
PN	20
THF	7
Et_2O	18
DME	24
TEGDME	41
DCM	14
BTFE	3

Deuterated solvents were purchased from Eurisotop or Cambridge Isotope Laboratories, Inc. Solvents were purchased from FUJIFILM Wako chemicals. All solvents with super dehydrated grade (< 10 ppm) were used as received, others were dried over 3 Å molecular sieves. Water content was measured by Karl Fischer Moisture Titrator (MKH-710M KYOTO ELECTRONICS MANUFACTURING CO., LTD.).

Cyclic Voltammetry Measurements

Cyclic voltammetry (CV) was performed on an HZ-Pro, Hokuto Denko Corp.analyzer in the glove box ($H_2O < 0.1$ ppm, $O_2 < 0.1$ ppm). A three-electrode cell using Pt as the working electrode and the counter electrode, A silver wire immersed in 1-methyl-1-propylpyrrolidinium bis(fluorosulfonyl)imide (MPPy-FSI) containing 0.1 M silver trifluoromethanesulfonate then placed in a compartment that was filled with MPPy-FSI and immersed in 0.9M electrolyte as the reference electrode (vs. ref.). The potential of Fc/Fc^+ in a 0.2 M LiTFSI/DMSO solution was determined to be –0.42 V vs. ref. This value was subsequently converted to Li^+/Li based on the literature report.[2]

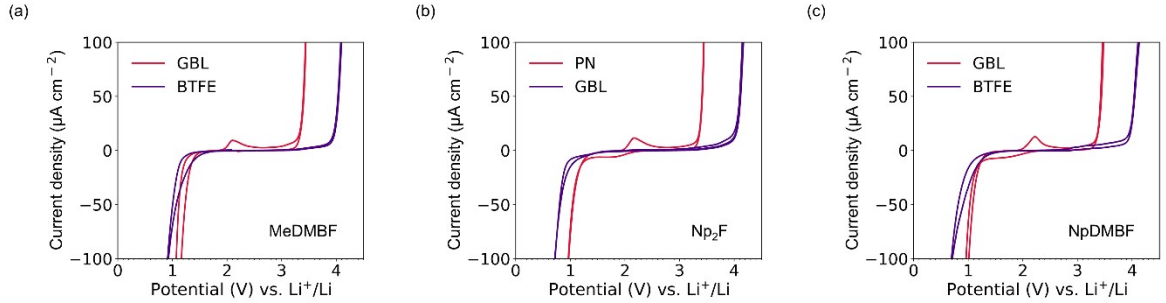


Figure S1. Electrochemical window of the 0.1 M electrolytes in GBL and BTFE with 1 mV/s scan rate. (a) MeDMBF, (b) Np_2F, and (c) NpDMBF.

Conductivity Measurements

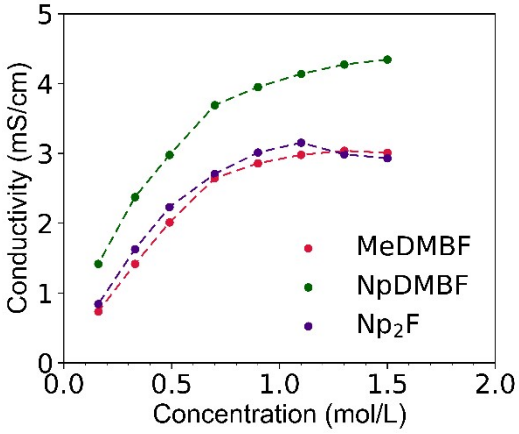


Figure S2. Relationship between the concentration and ionic conductivity at room temperature.

DOSY, HOESY NMR Measurements

DOSY was recorded with a Bruker Advance III, 600 MHz spectrometer equipped with a BBFO probe for samples in BTFE solution. The diffusion time was 0.05 s for both ^{1}H and ^{19}F DOSY measurement. The samples in CD_3OD was recorded with a Bruker Advance III, 400 MHz spectrometer with BBFO probe. The diffusion time was 0.03 s for both ^{1}H and ^{19}F DOSY measurement.

Diffusion coefficient ($m^2\ s^{-1}$) was obtained using the following equation.

$$I = I_0 exp[-D\gamma^2 g^2 \delta^2 \left(\Delta - \frac{\delta}{3}\right)]$$

I is the observed intensity, I_0 is the reference intensity (unattenuated signal intensity), γ is the gyromagnetic ratio of the observed nucleus, g is the gradient strength, δ is the length of the gradient, Δ is the diffusion time.

^{19}F, ^{1}H HOESY was recorded with a Bruker Advance III, 600 MHz spectrometer equipped with a BBFO probe with 0.5 s mixing time for the samples in BTFE. The samples in CD_3OD was recorded with a Bruker Advance III, 400 MHz spectrometer with BBFO probe with 0.7 s mixing time.

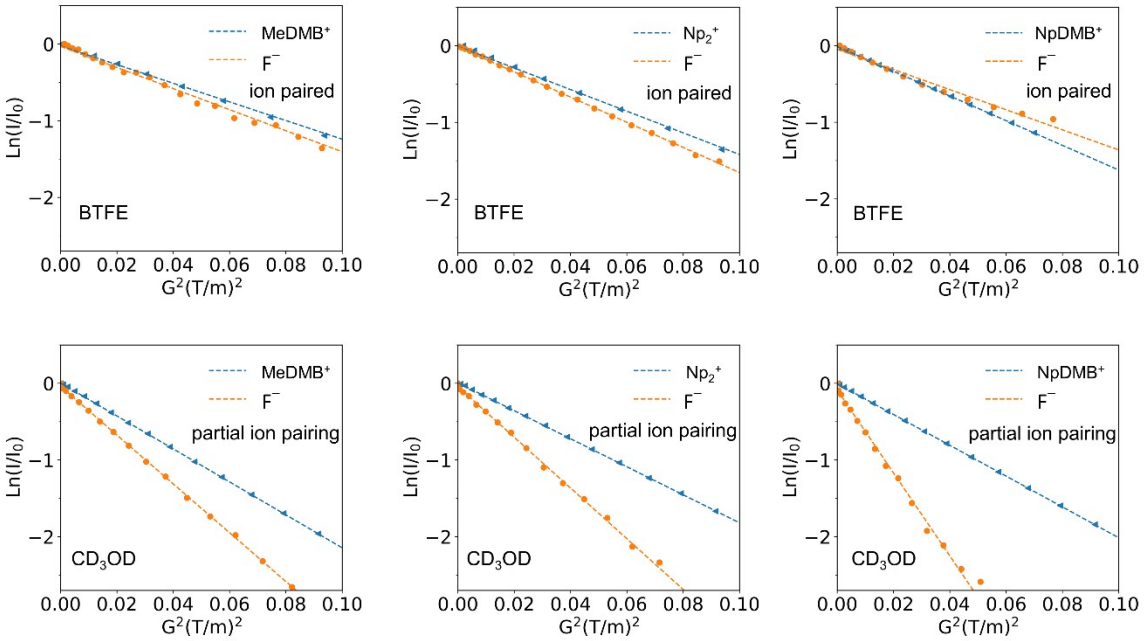


Figure S3. Plots of $Ln(I/I_0)$ against the square of the gradient amplitude (G^2) for DOSY measurements in 0.9M solutions.

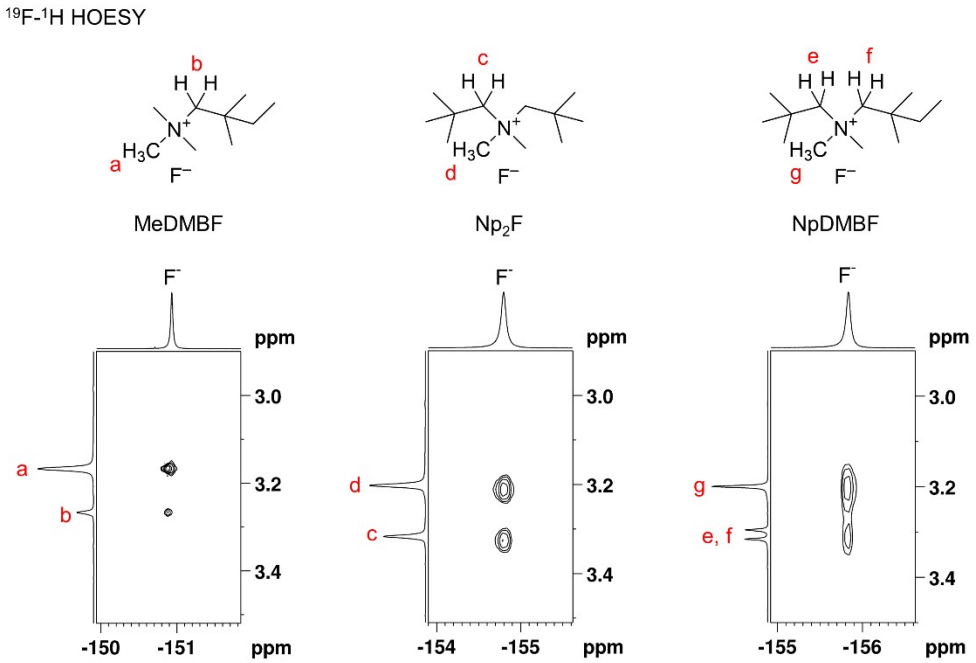


Figure S4. (a) ^{19}F, ^{1}H HOESY spectra of 0.9 M MeDMBF, Np_2F and NpDMBF in CD_3OD.

Thermogravimetric Analysis

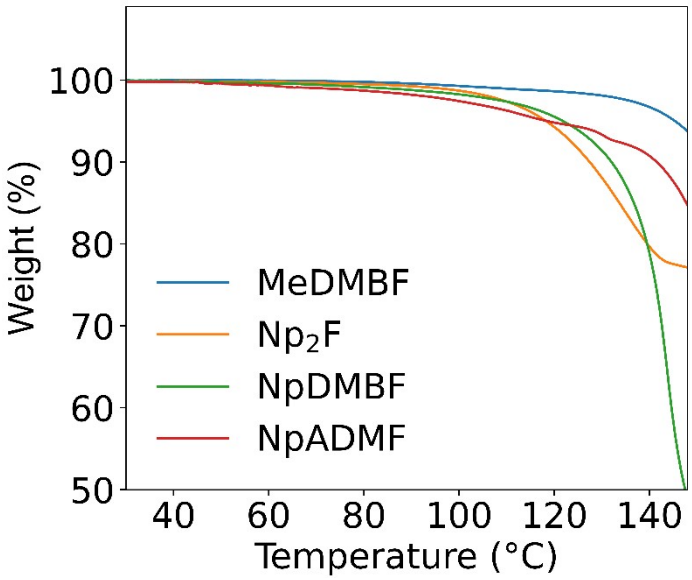


Figure S5. Thermogravimetric analysis of anhydrous MeDMBF, Np_2F, NpDMBF and NPADMF, measured at a heating rate of 1 °C min^{-1}.

Stability in Organic Solvents

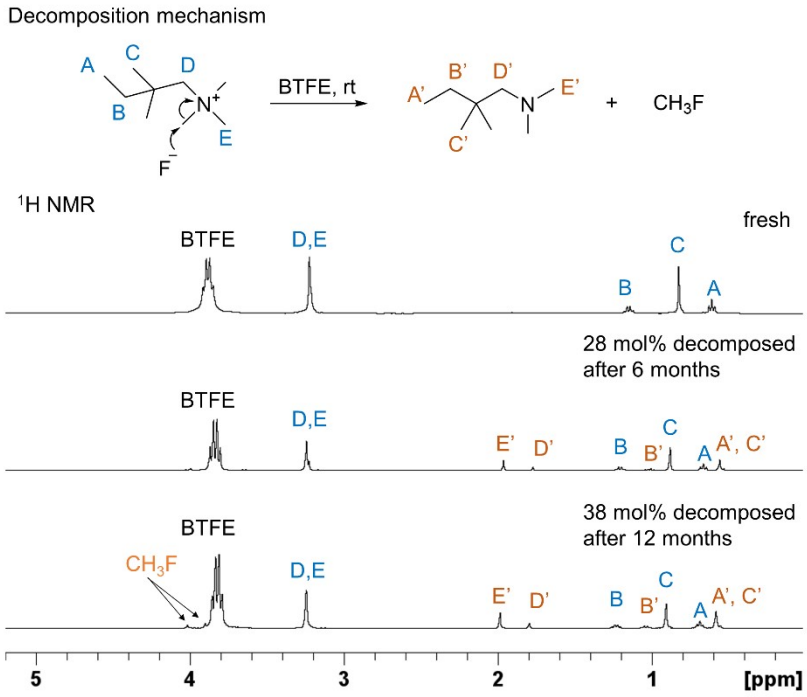


Figure S6. Long term stability of 0.9M MeDMBF/ BTFE solution at room temperature.

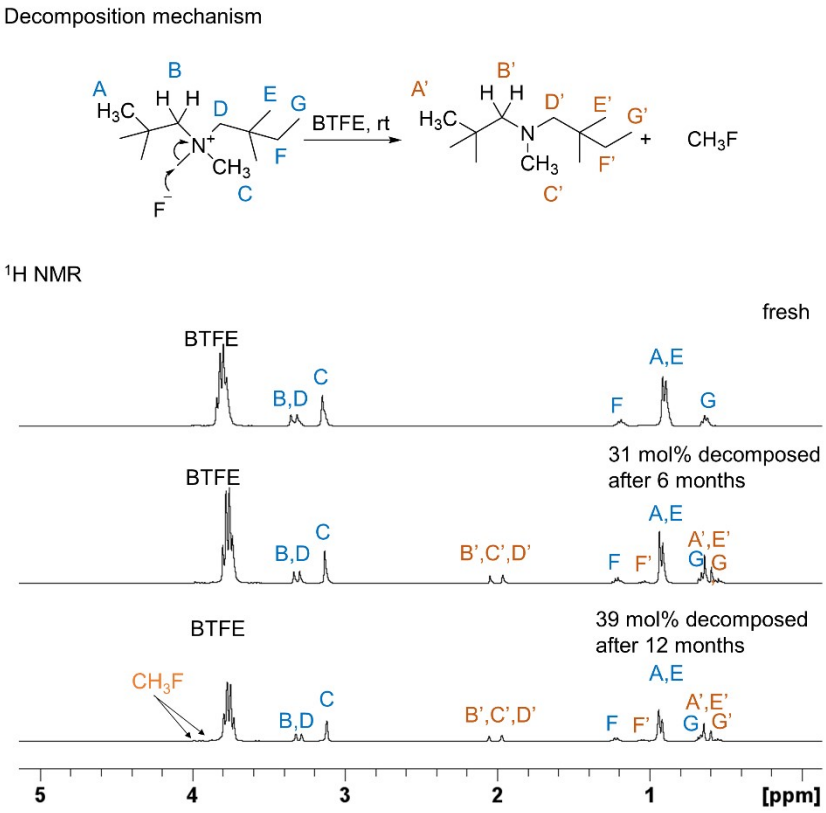


Figure S7. Long term stability of 0.9M NpDMBF/ BTFE solution at room temperature.

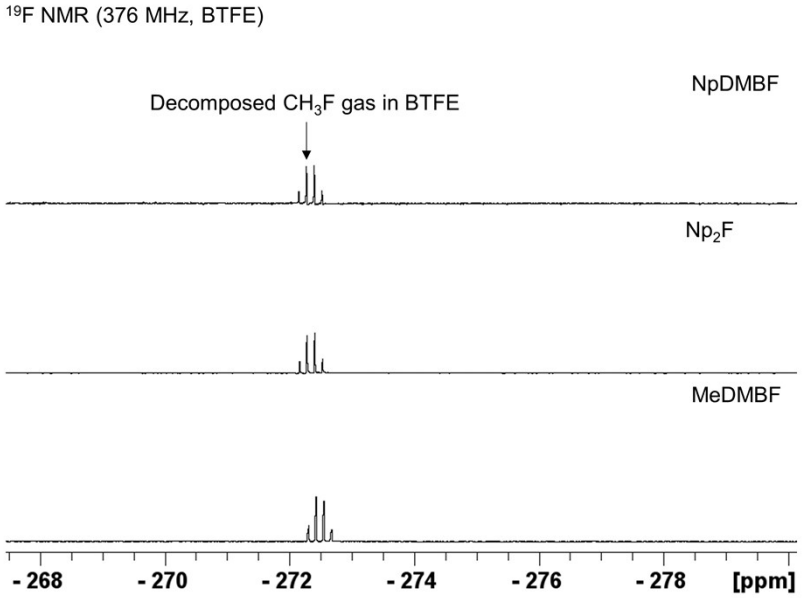


Figure S8. ^{19}F NMR for 0.9M MeDMBF, Np_2F, NpDMBF/ BTFE solution after keeping at room temperature for 12 months.

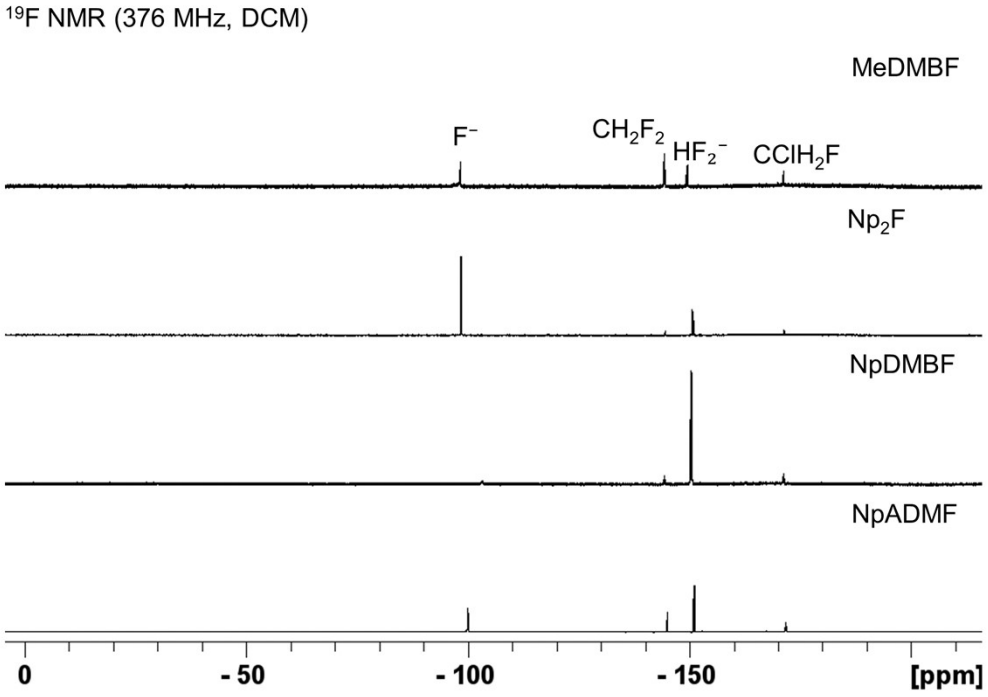


Figure S9. ^{19}F NMR for MeDMBF, Np_2F, NpDMBF and NPADMF in DCM.

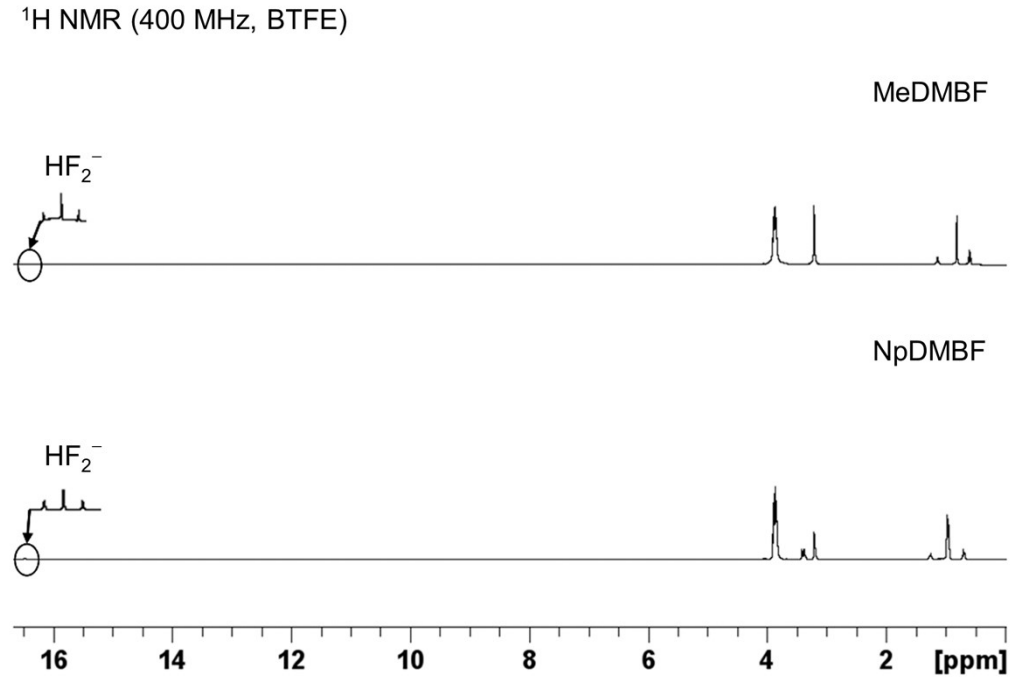


Figure S10. ^{1}H NMR for MeDMBF and NpDMBF in BTFE.

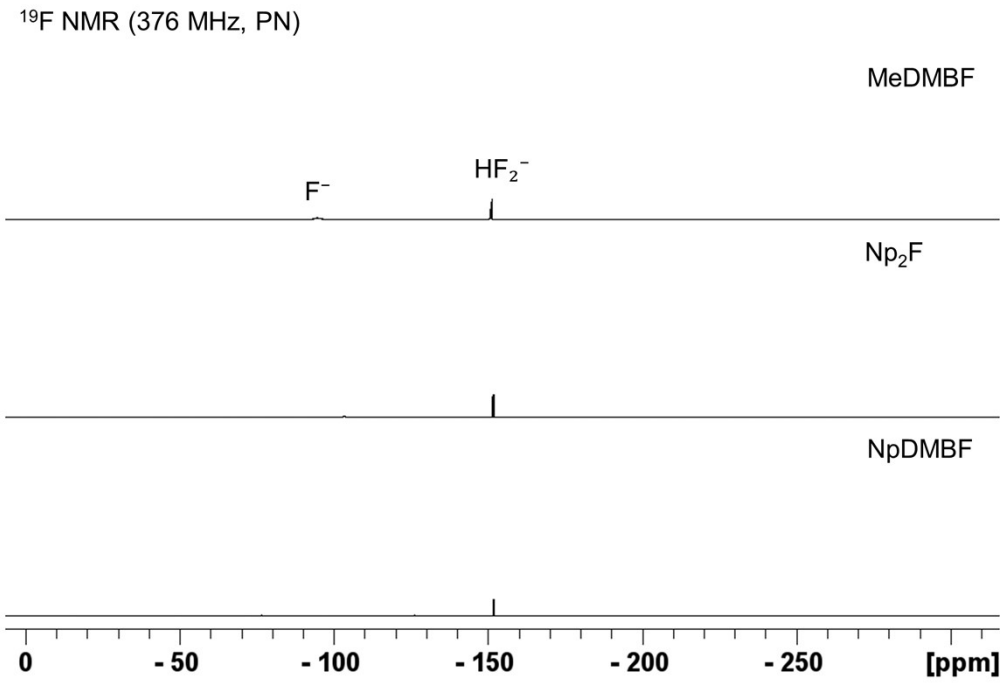


Figure S11. ^{19}F NMR for MeDMBF, Np_2F, NpDMBF in PN.

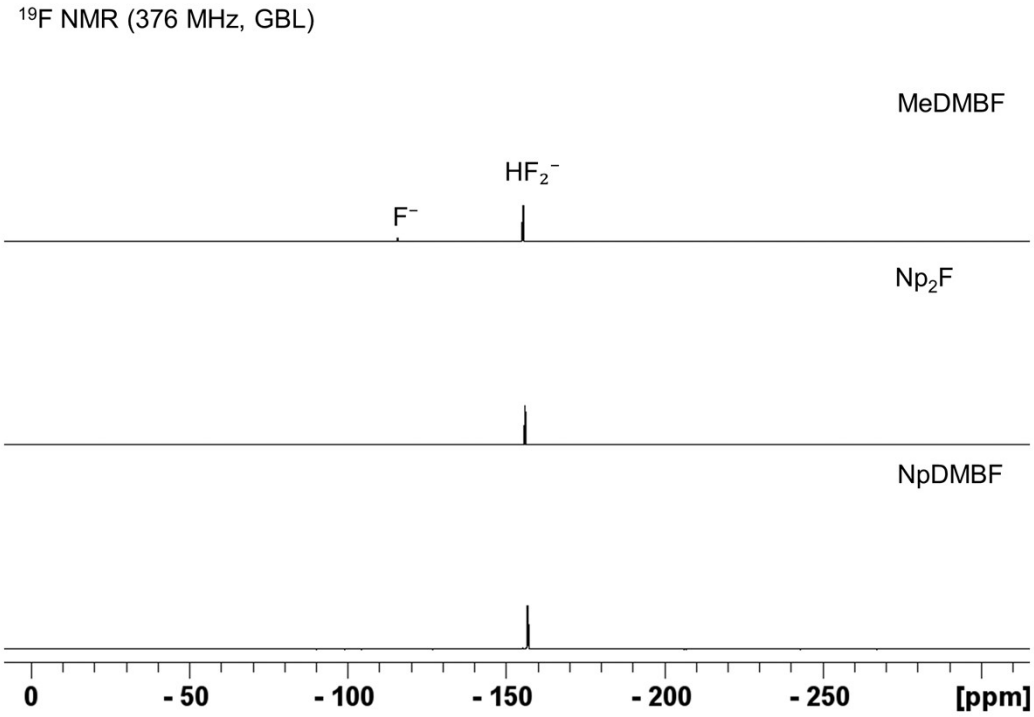


Figure S12. ^{19}F NMR for MeDMBF, Np_2F, NpDMBF in GBL.

Theoretical Calculations

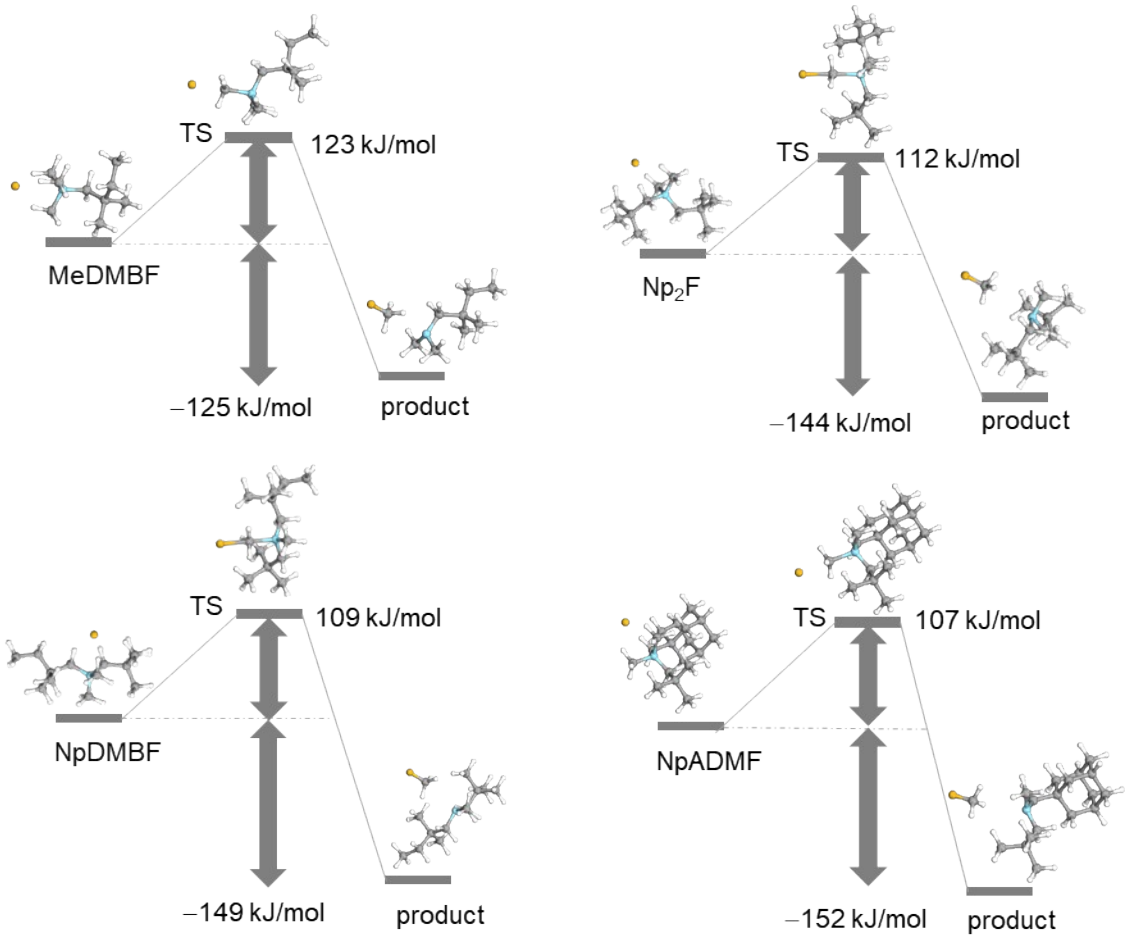


Figure S13**.** Energy diagram of MeDMBF, Np_2F, NpDMBF, and NPADMF at M062X/Def2-TZVPP level.

Table S3. Binding Energy of MeDMBF, Np_2F, and NpDMBF

	MeDMBF	Np_2F	NpDMBF
Energy[a] (kJ/mol)	–519	–515	–513

[a]Calculated at M062X/Def2-TZVPP level.

Crystal Data for NpADMCl (CCDC: 2385359)

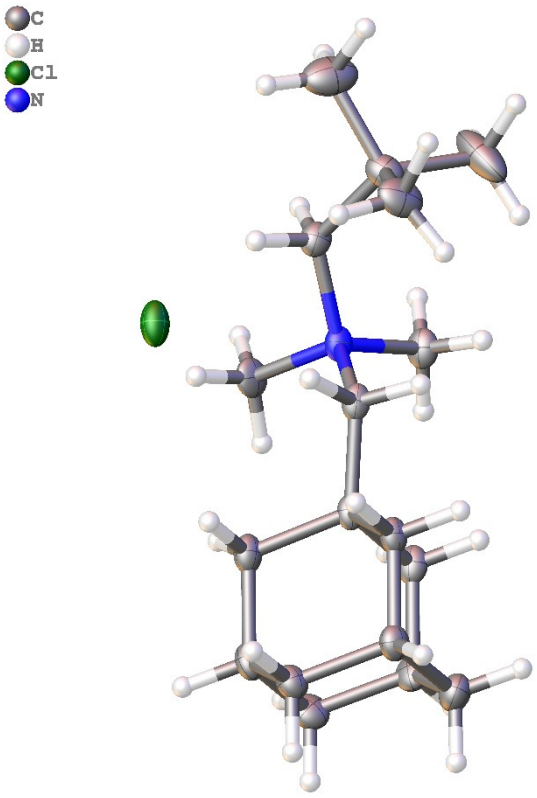


Figure S14. Crystal structure of NpADMCl.

A clear light colourless plate-shaped crystal with dimensions 0.40×0.28×0.13 mm^3 was mounted on a suitable support. Data were collected using an XtaLAB Synergy R, HyPix diffractometer operating at T = 100.00(10) K. Data were measured using w scans of 0.5° per frame for 5.0 s using Mo K_a radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku). The maximum resolution that was achieved was Q = 26.372 (0.80 Å). The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku) and the unit cell was refined using CrysAlisPro (Rigaku, V1.171.43.64a, 2023). Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.43.64a, 2023). The final completeness is 99.00 % out to 26.372 in Q. A multi-scan absorption correction was performed using CrysAlisPro 1.171.43.64a (Rigaku Oxford Diffraction, 2023) using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient m of this material is 0.207 mm^{-1} at this wavelength (l = 0.711Å) and the minimum and maximum transmissions are 0.664 and 1.000. The structure was solved and the space group P-1 (# 2) determined by the ShelXT, structure solution program using Intrinsic Phasing and refined by Least Squares with SHELXL program using OLEX2 software.[3–5]All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

Compound	**NpADMCl**
Formula	$C_{36}H_{68}Cl_2N_2$
$D_{calc.}$/ g cm^{-3}	1.112
m/mm^{-1}	0.207
Formula Weight	599.82
Colour	clear light colourless
Shape	plate
Size/mm^3	0.40×0.28×0.13
T/K	100.00(10)
Crystal System	triclinic
Space Group	P-1
a/Å	6.6435(2)
b/Å	12.1821(5)
c/Å	22.1673(7)
a/°	92.234(3)
b/°	91.070(2)
g/°	92.200(2)
V/Å^3	1790.99(11)
Z	2
Z'	1
Wavelength/Å	0.71073
Radiation type	Mo K_a
Q_{min}/°	2.438
Q_{max}/°	26.372
Measured Refl.	16411
Independent Refl.	7216
Reflections with I >2(I)	5101
R_{int}	0.0462
Parameters	371
Restraints	0
Largest Peak	0.498
Deepest Hole	-0.371
GooF	1.041
wR_2 (all data)	0.1359
wR_2	0.1249
R_1 (all data)	0.0809
R_1	0.0499

NMR Charts

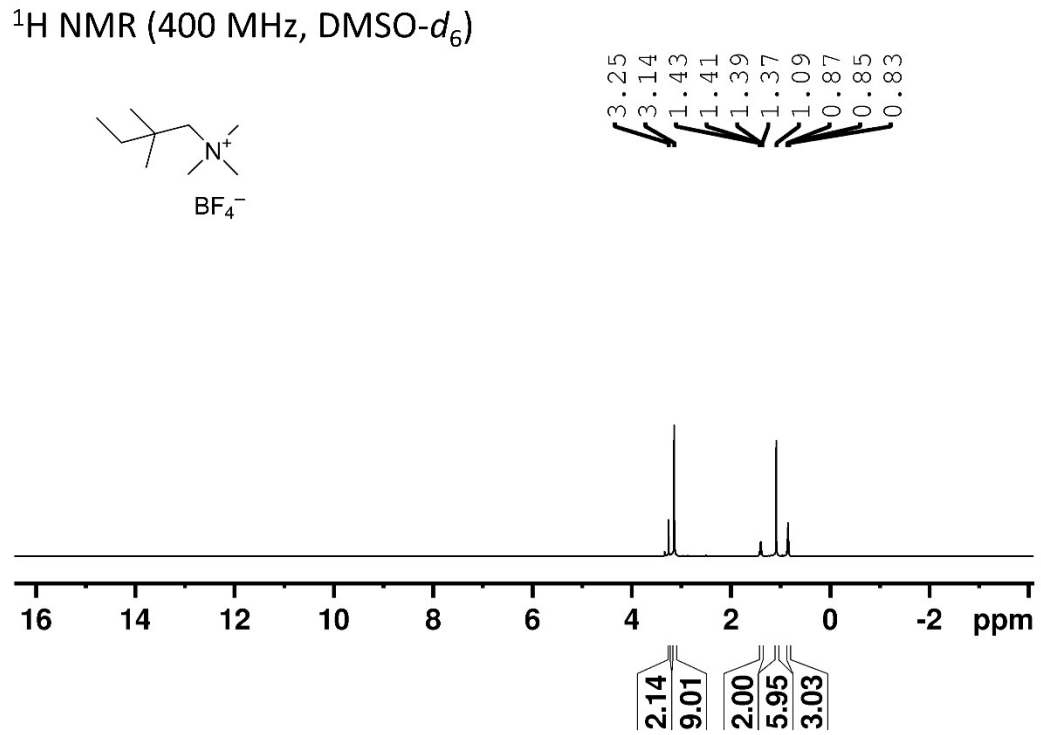


Figure S15. ^{1}H NMR for $MeDMBBF_4$

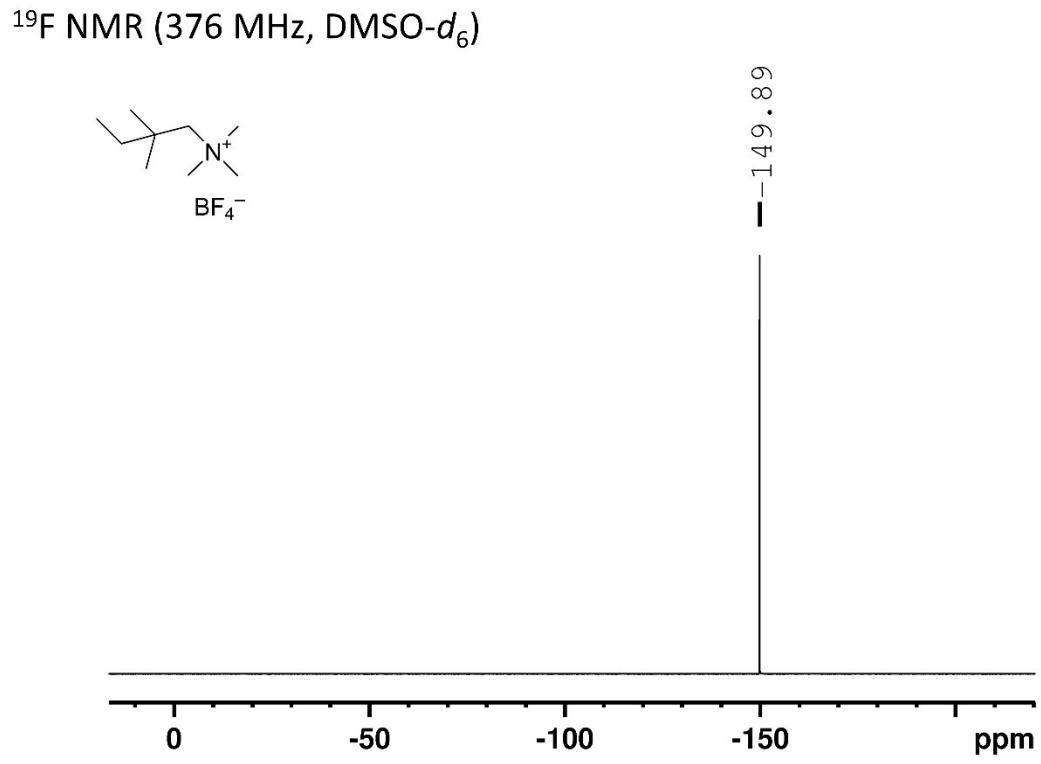


Figure S16. ^{19}F NMR for $MeDMBBF_4$.

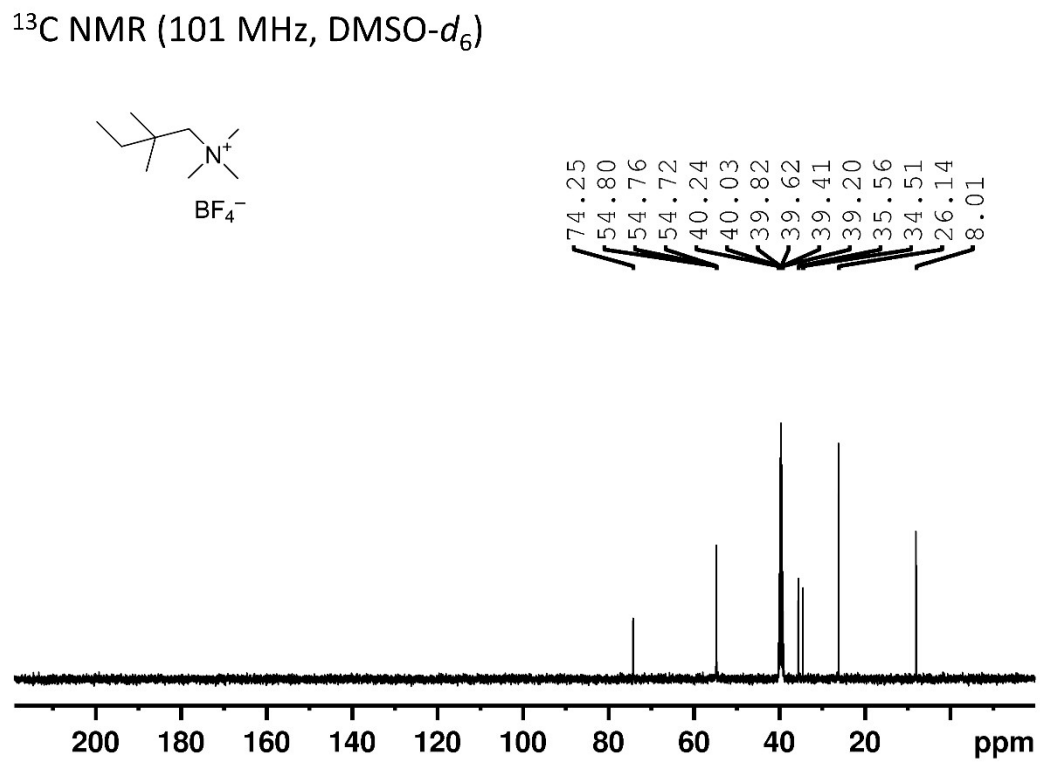


Figure S17. ^{13}C NMR for $MeDMBBF_4$.

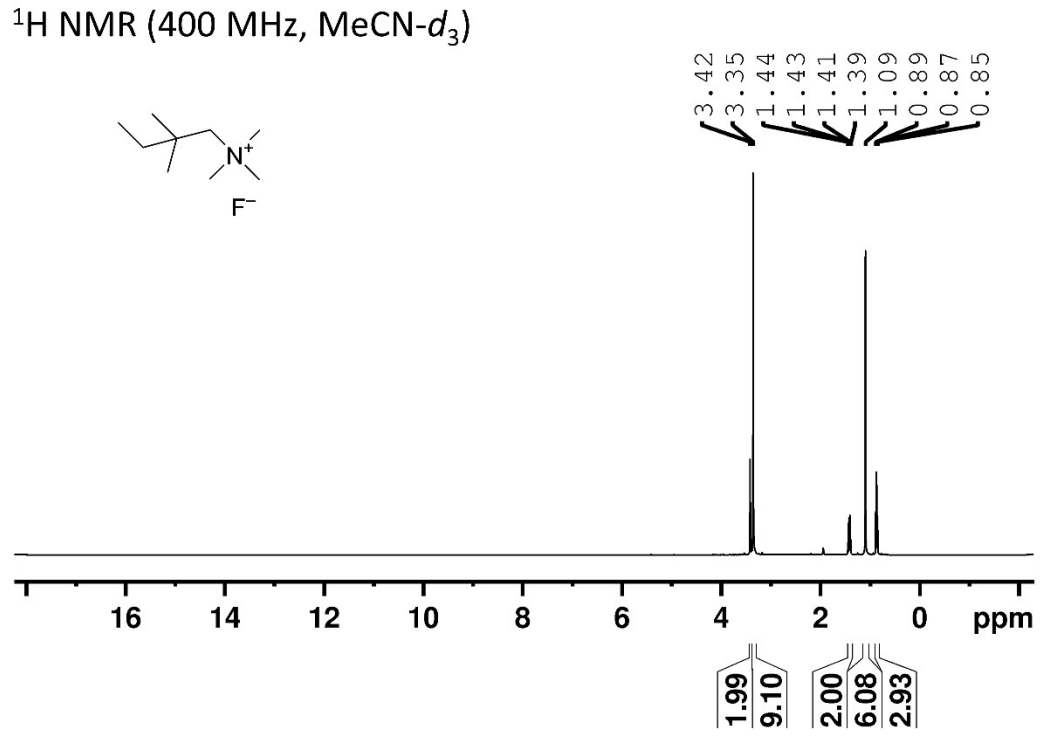


Figure S18. ^{1}H NMR for MeDMBF.

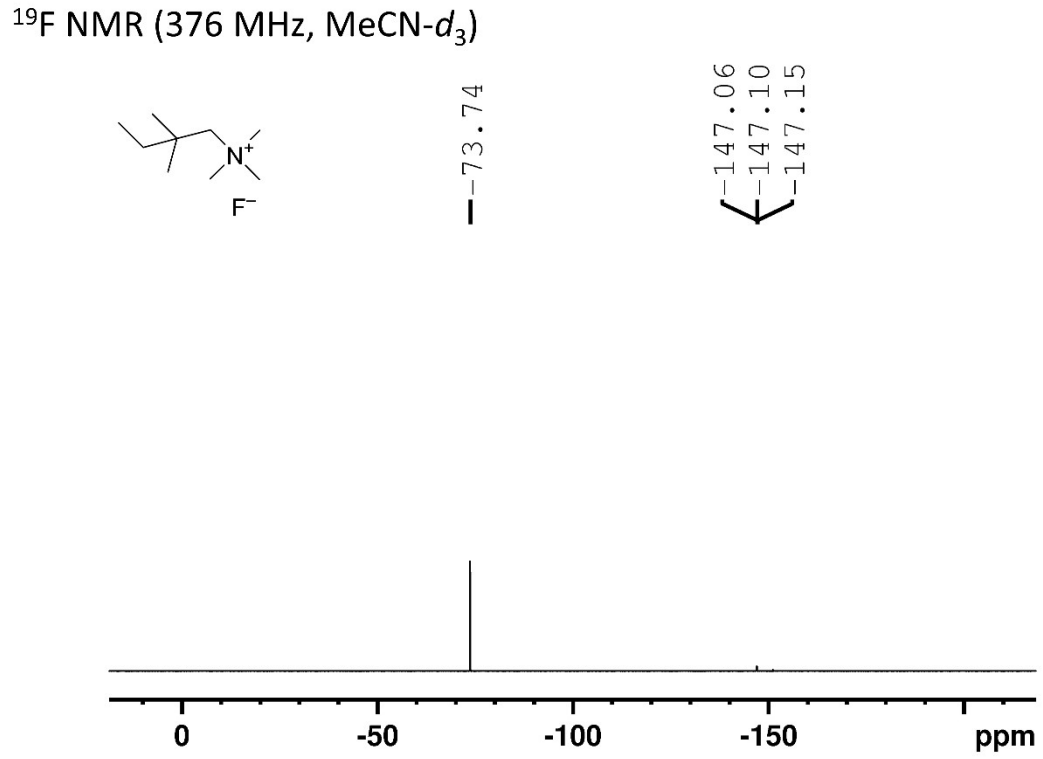


Figure S19. ^{19}F NMR for MeDMBF.

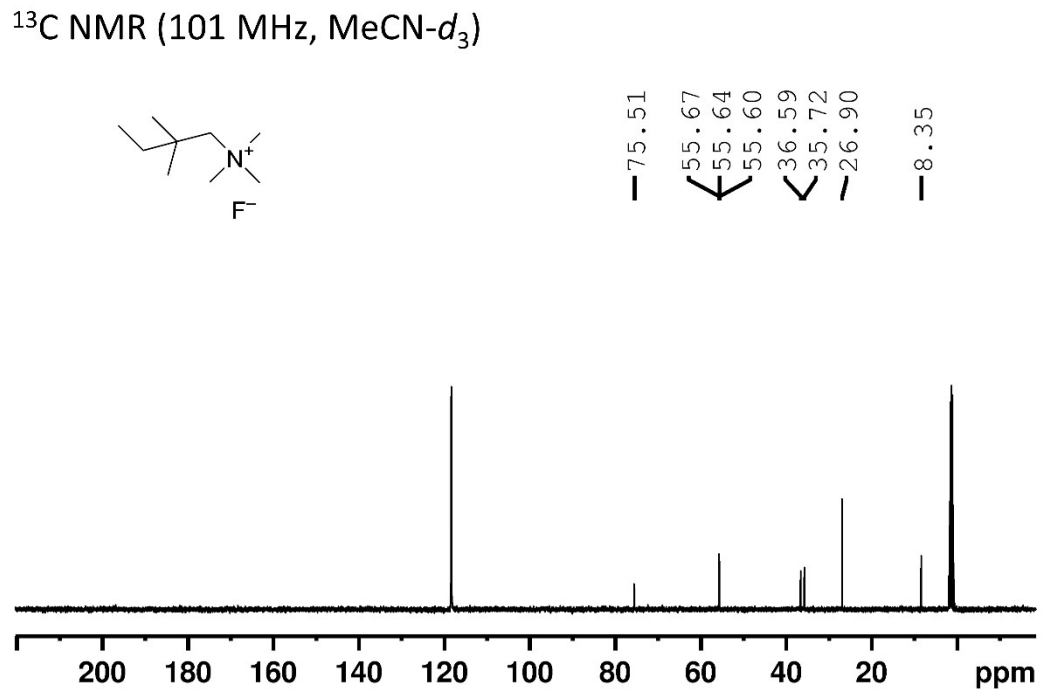


Figure S20. ^{13}C NMR for MeDMBF.

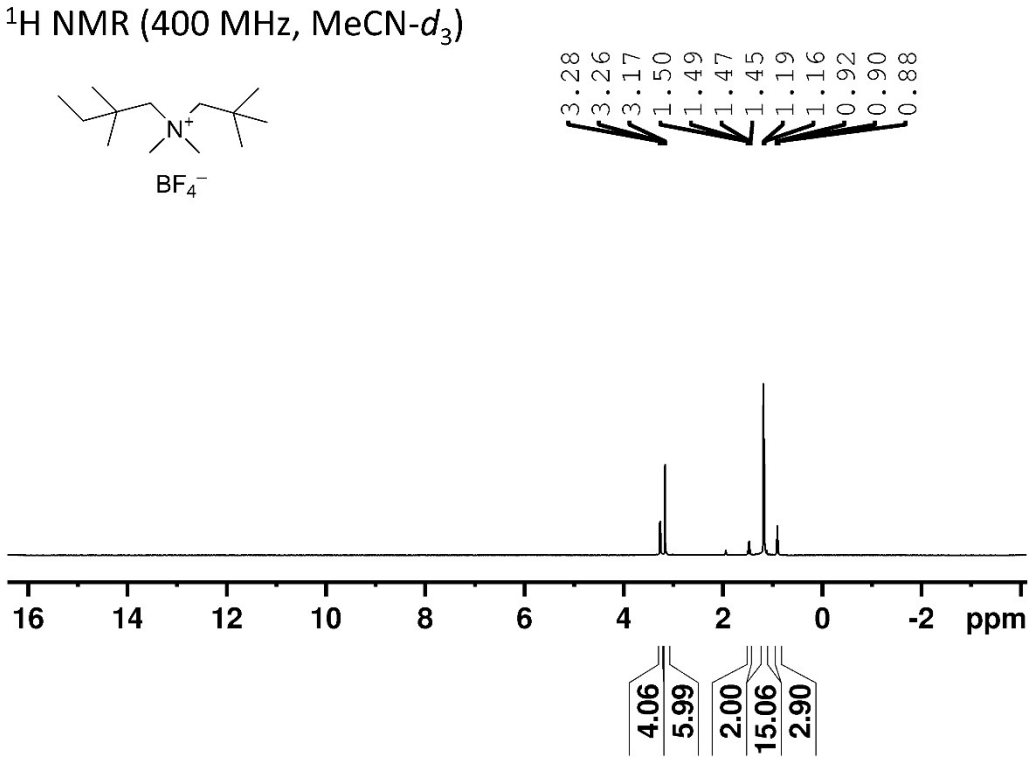


Figure S21. ^{1}H NMR for NpDMBBF$_4$.

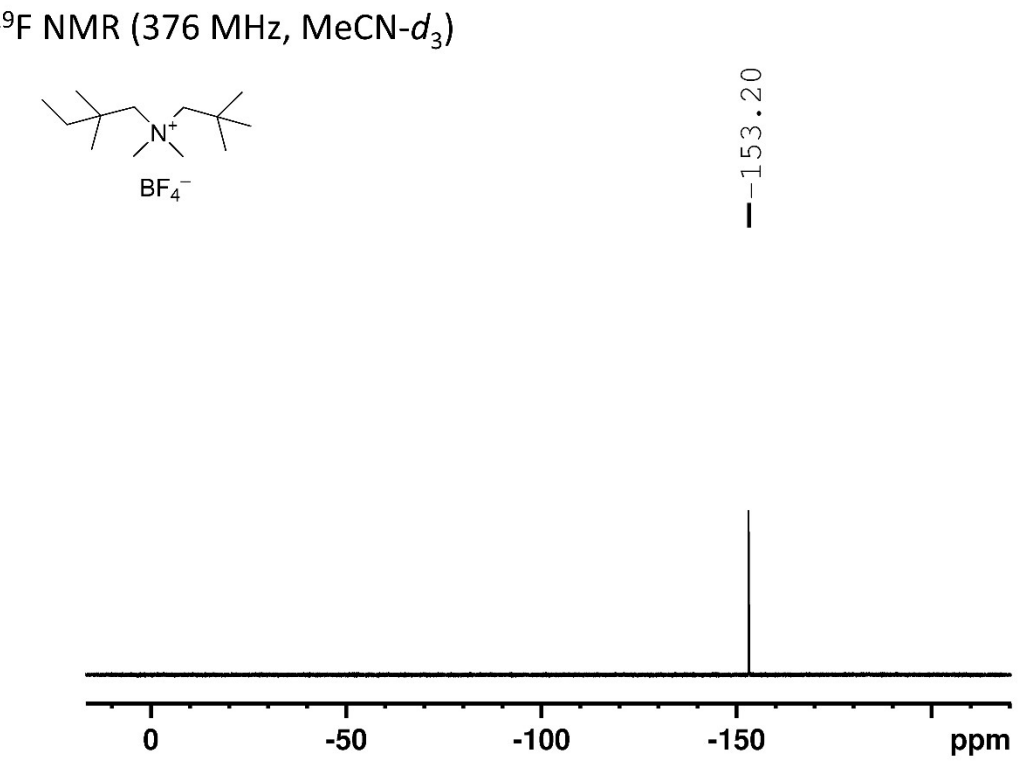


Figure S22. ^{19}F NMR for NpDMBBF$_4$.

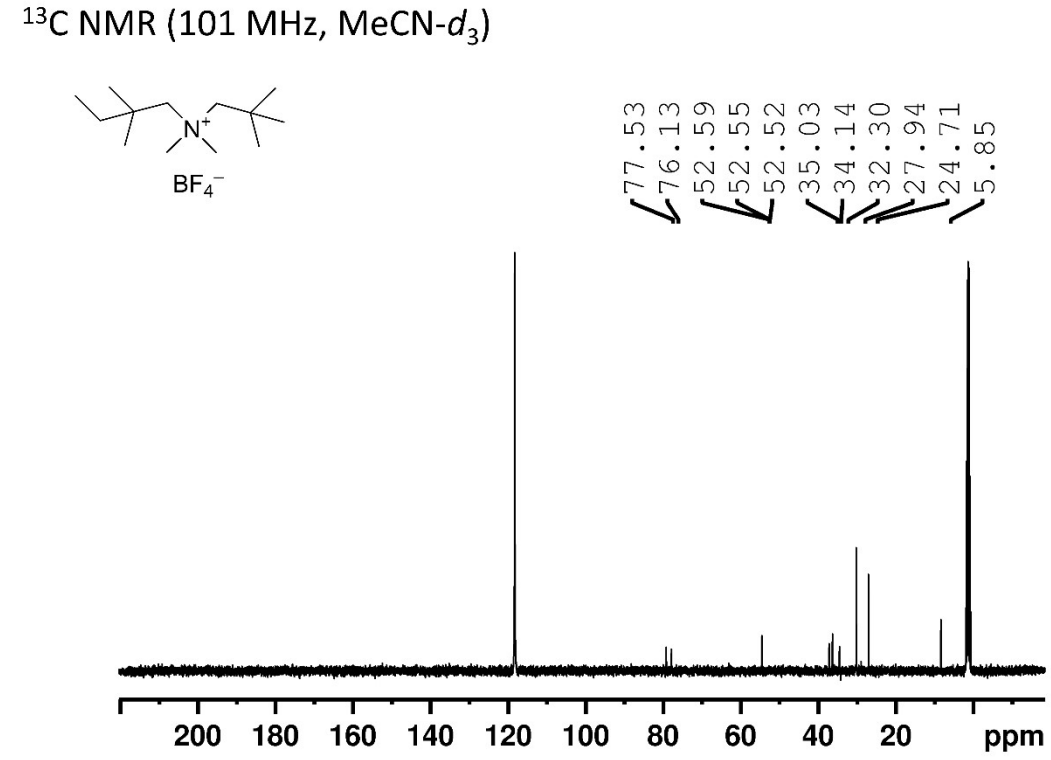


Figure S23. ^{13}C NMR for $NpDMBBF_4$.

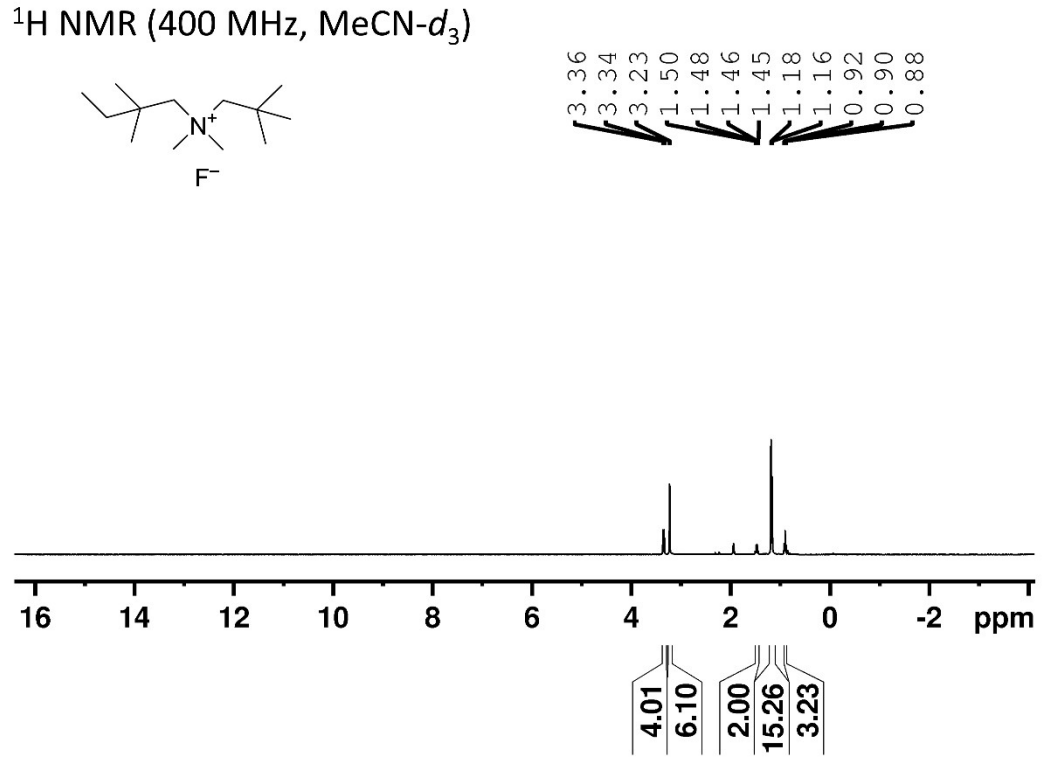


Figure S24. ^{1}H NMR for NpDMBF.

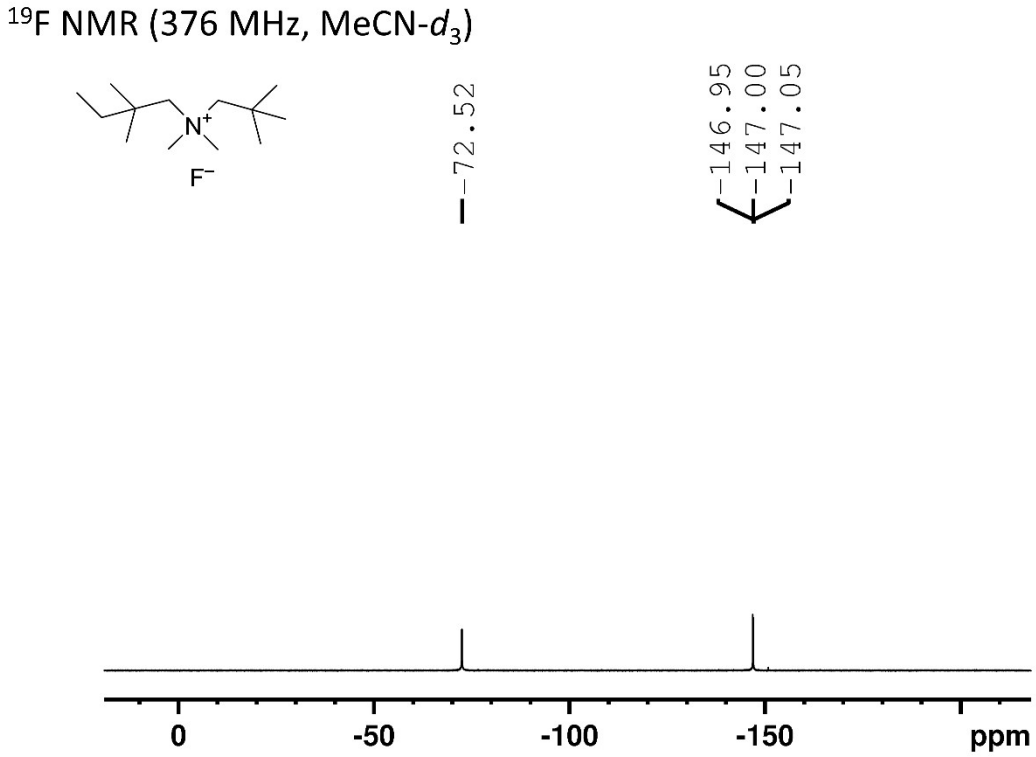


Figure S25. ^{19}F NMR for NpDMBF.

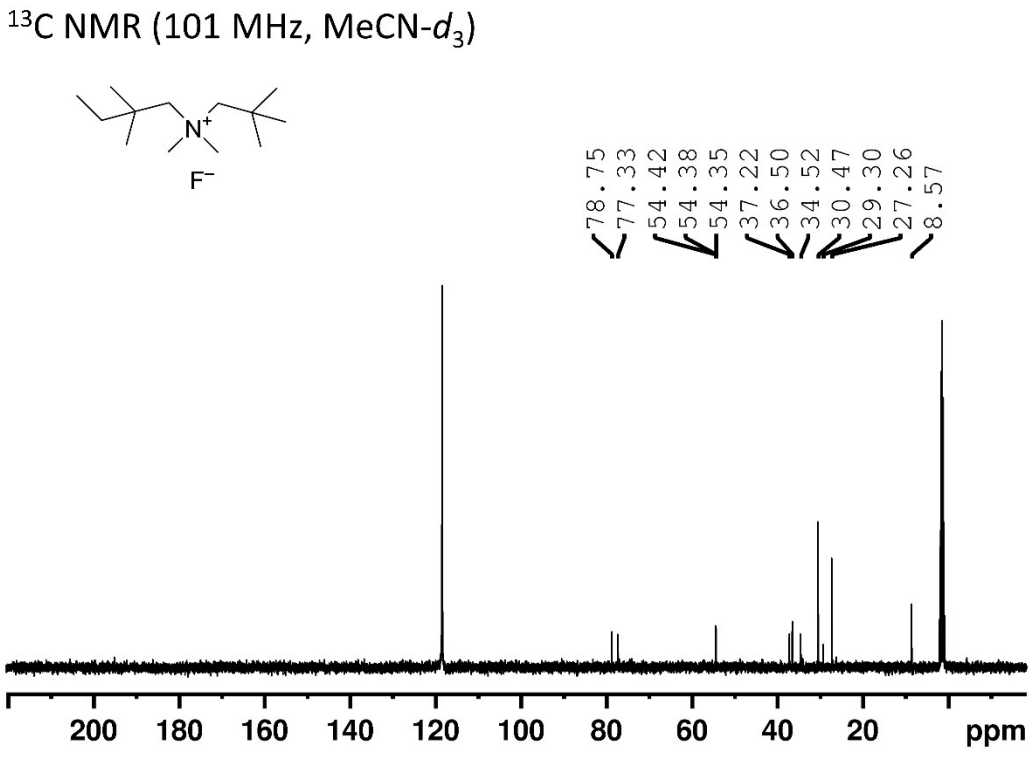


Figure S26. ^{13}C NMR for NpDMBF.

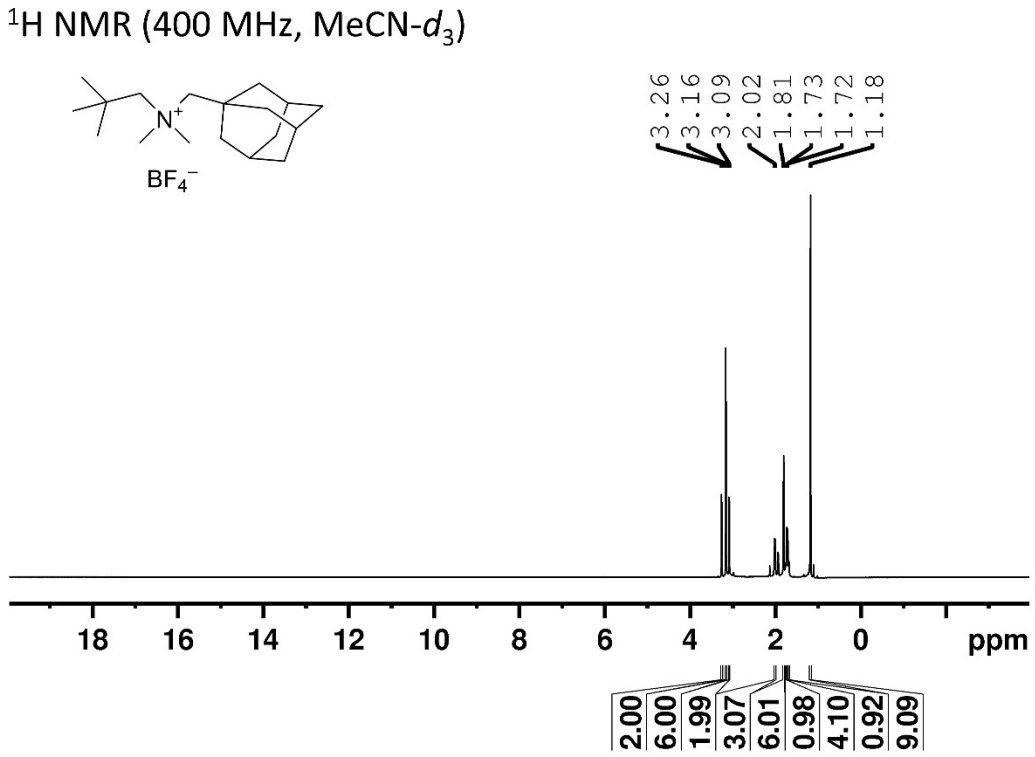


Figure S27. ^{1}H NMR for NpADMBF$_4$.

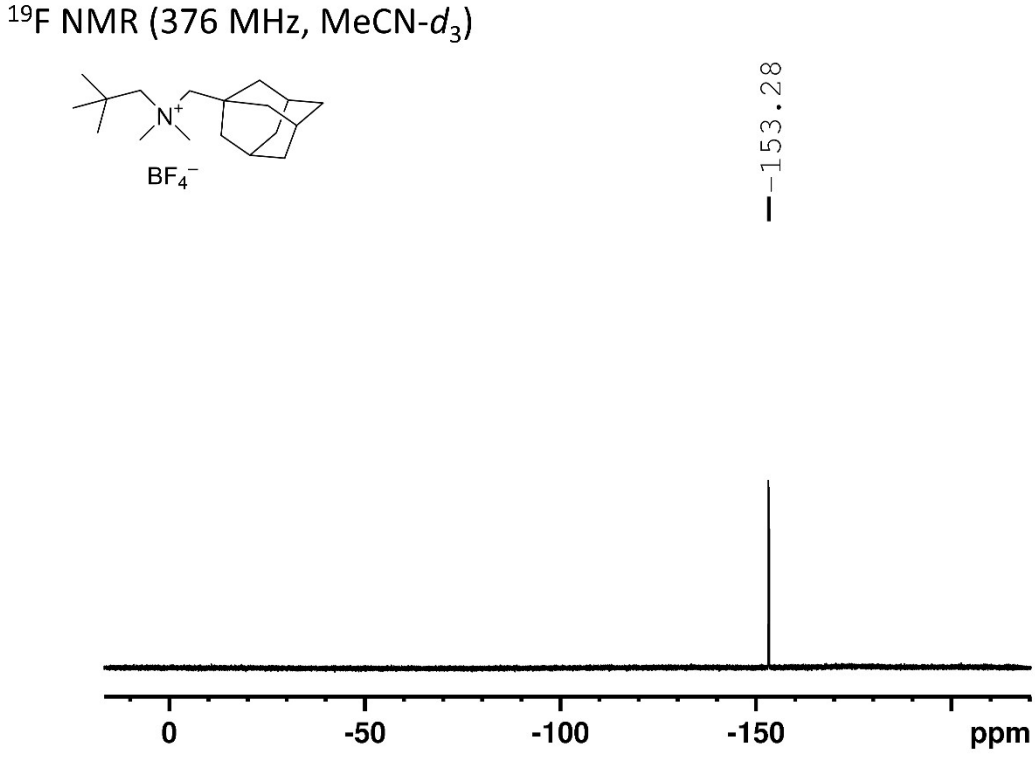


Figure S28. ^{19}F NMR for NpADMBF$_4$.

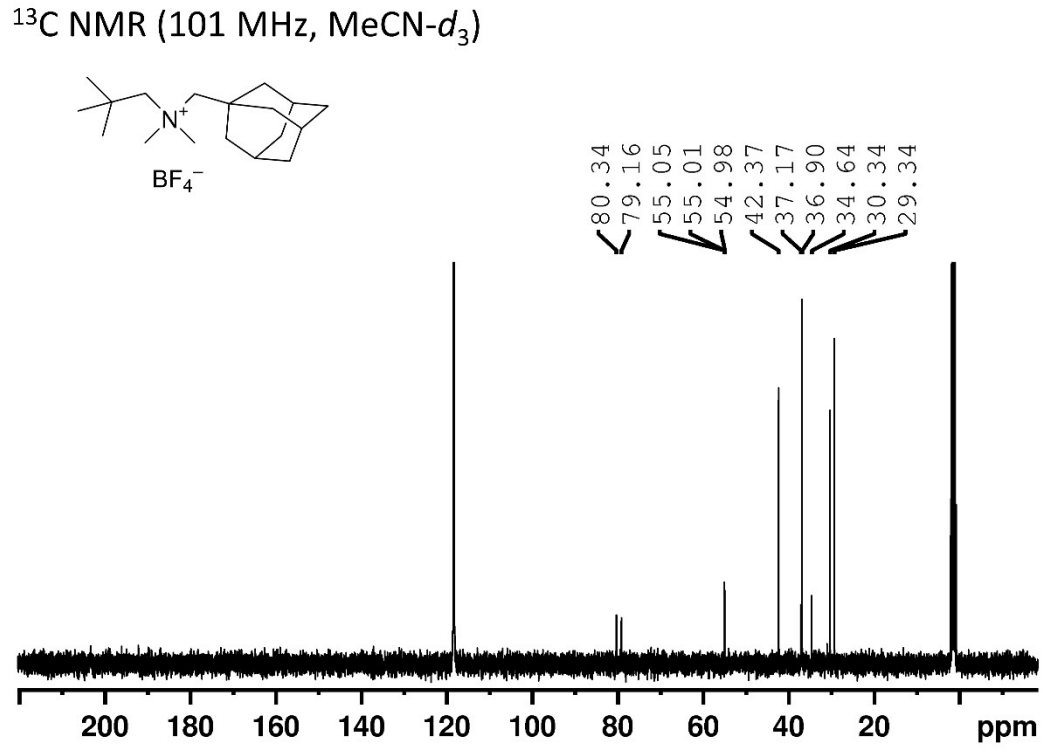


Figure S29. ^{13}C NMR for $NPADMBF_4$.

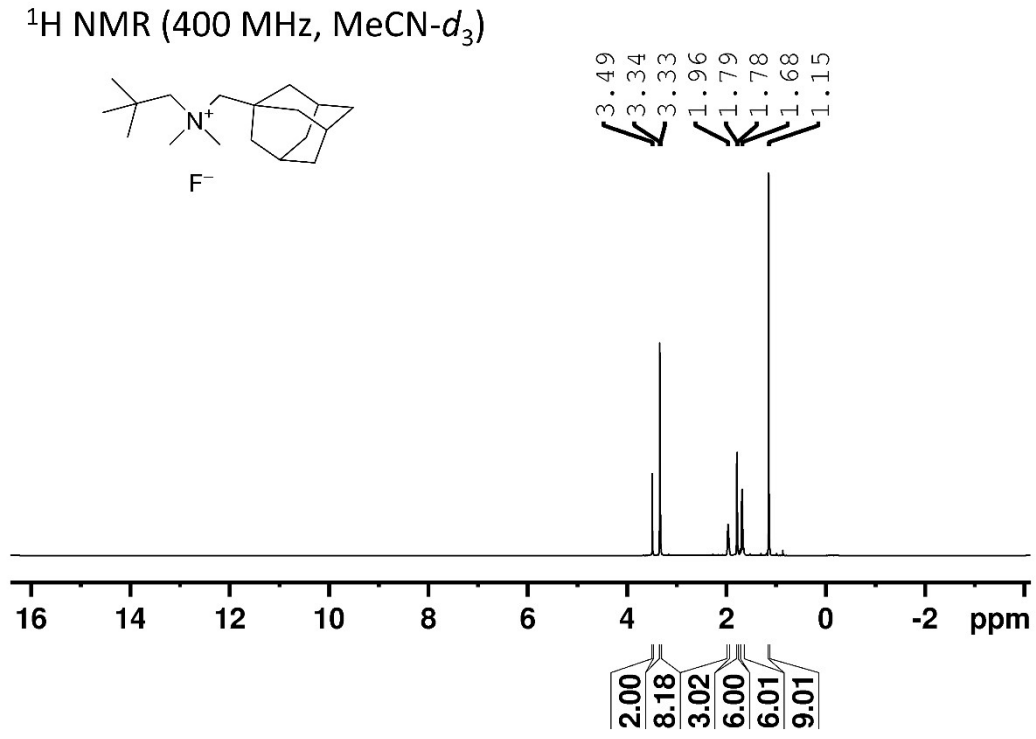


Figure S30. ^{1}H NMR for NpADMF.

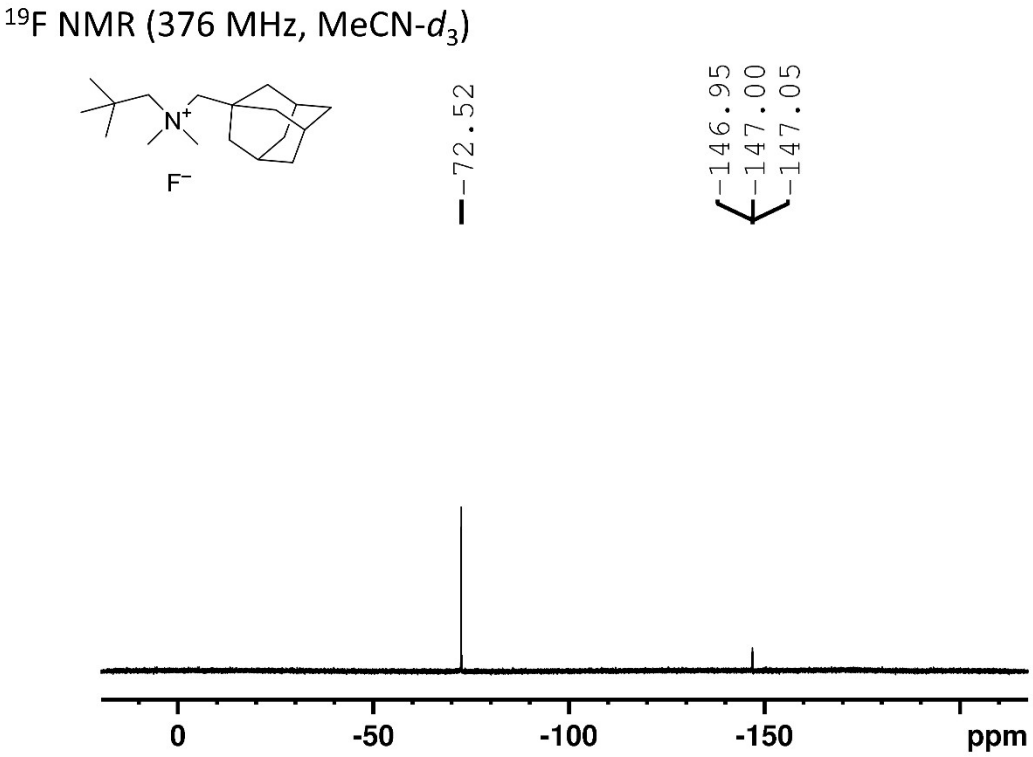


Figure S31. ^{19}F NMR for NpADMF.

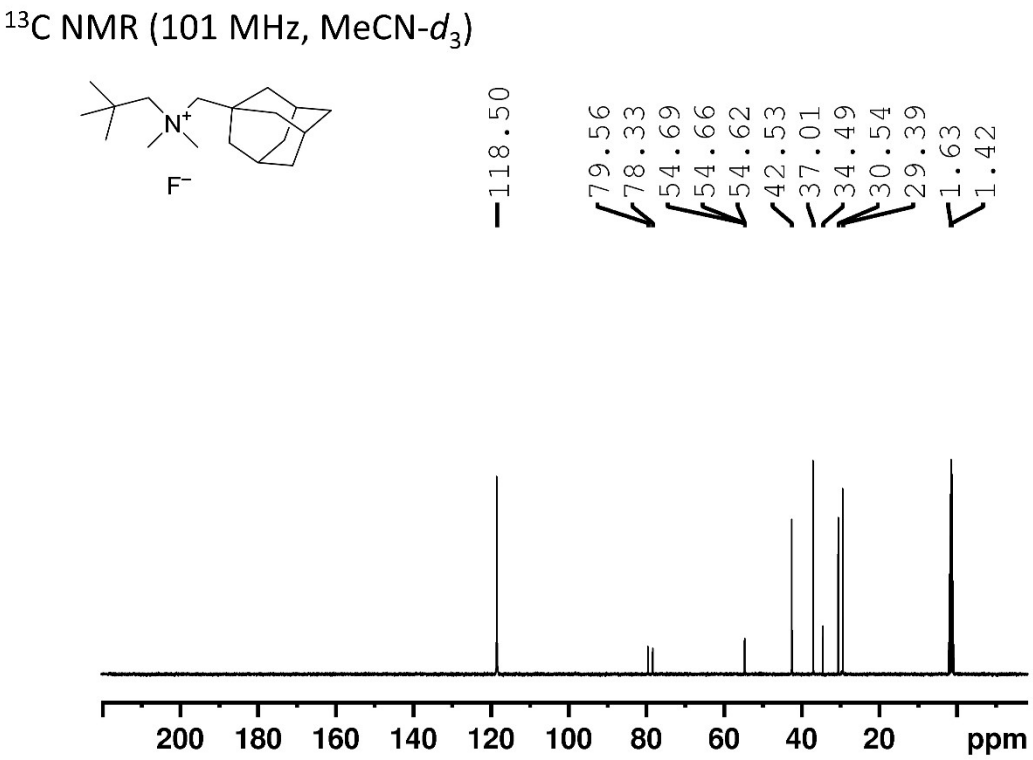


Figure S32. ^{13}C NMR for NpADMF.

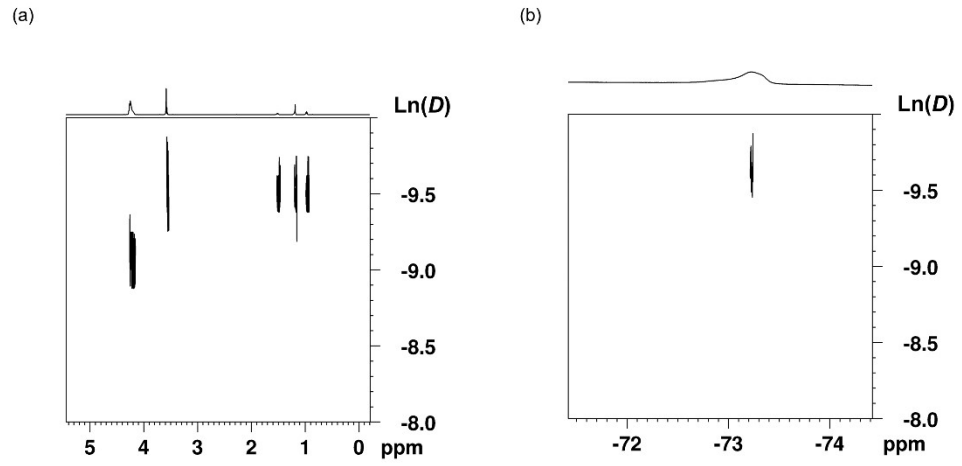


Figure S33. (a) ^{1}H DOSY spectra of MeDMBF/BTFE and (b) ^{19}F DOSY spectra of MeDMBF/BTFE.

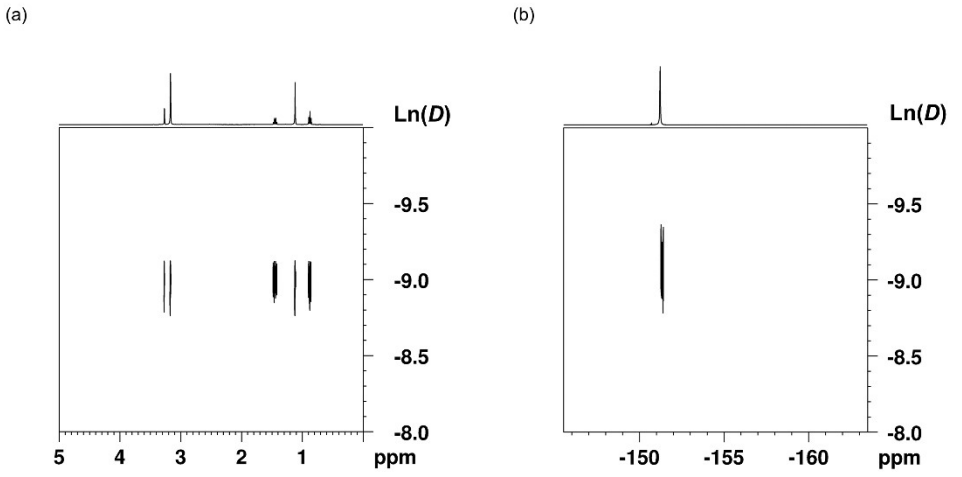


Figure S34. (a) ^{1}H DOSY spectra of MeDMBF/CD_3OD and (b) ^{19}F DOSY spectra of MeDMBF/ CD_3OD.

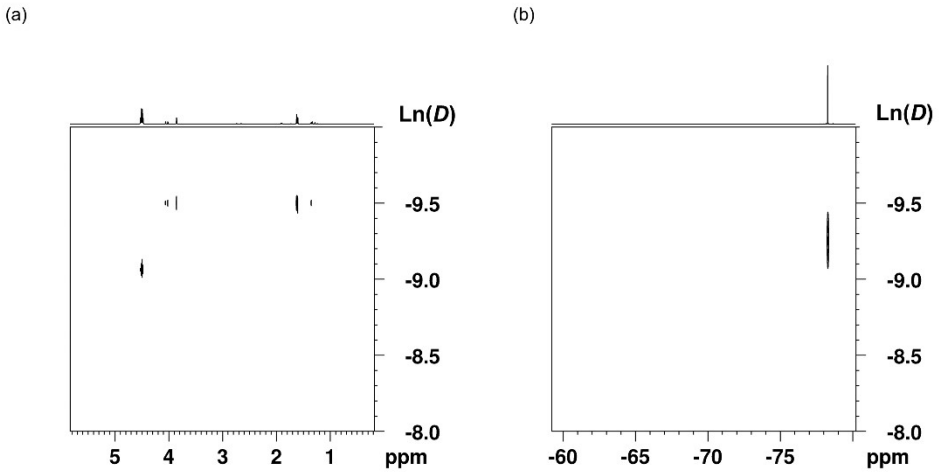


Figure S35. (a) ^{1}H DOSY spectra of NpDMBF/BTFE and (b) ^{19}F DOSY spectra of NpDMBF/BTFE.

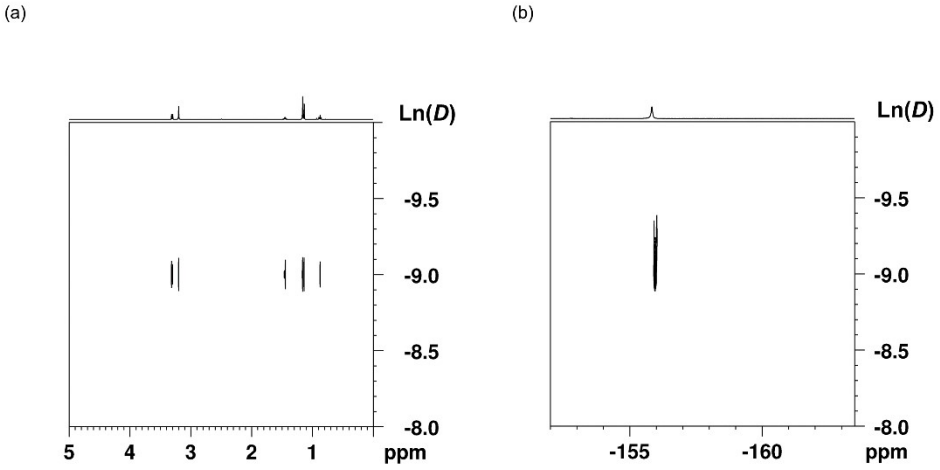


Figure S36. (a) ^{1}H DOSY spectra of NpDMBF/CD_3OD and (b) ^{19}F DOSY spectra of NpDMBF/CD_3OD.

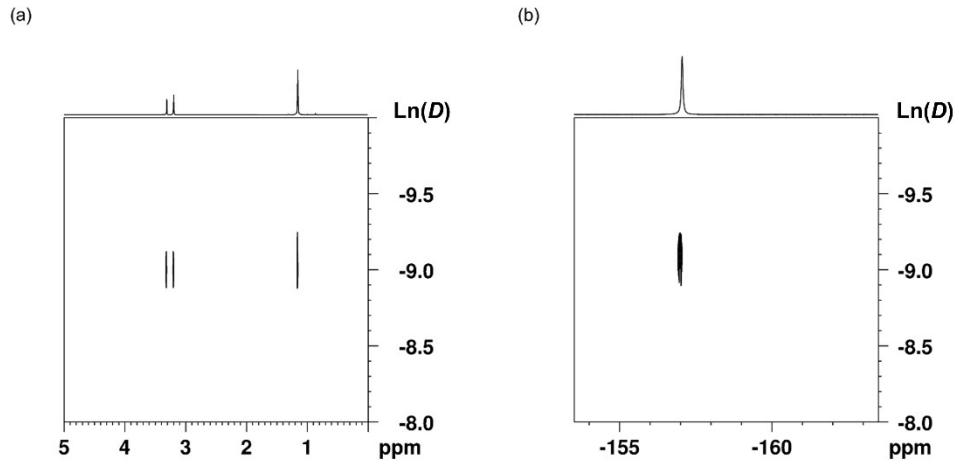


Figure S37. (a) ^{1}H DOSY spectra of Np_2F/CD_3OD and (b) ^{19}F DOSY spectra of Np_2F/CD_3OD.

Table S4. ^{19}F NMR Chemical Shifts for Fluoride Salts in Organic Solvents

Solvent	^{19}F NMR δ (ppm) of F^-			
	MeDMBF	Np_2F	NpDMBF	NpADMF
DMSO	–73	–72	–74	–[b]
GBL	–119	–116	–[a]	–[b]
MeCN	–73	–72	–74	–76
PN	–95	–103	–108	–[b]
DCM	–98	–99	–99	–100
BTFE	–71	–71	–72	–[b]

[a]Complete conversion to HF_2^-. [b]Not measured due to the low solubility.

Reference

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