Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information for:

Synthesis of imidazolium-based pentacoordinated organofluorosilicate and germanate salts

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Table of content

S1 NMR Spectroscopy

S1.1 [IPrH][Ph$_3$SiF$_2$] (1)

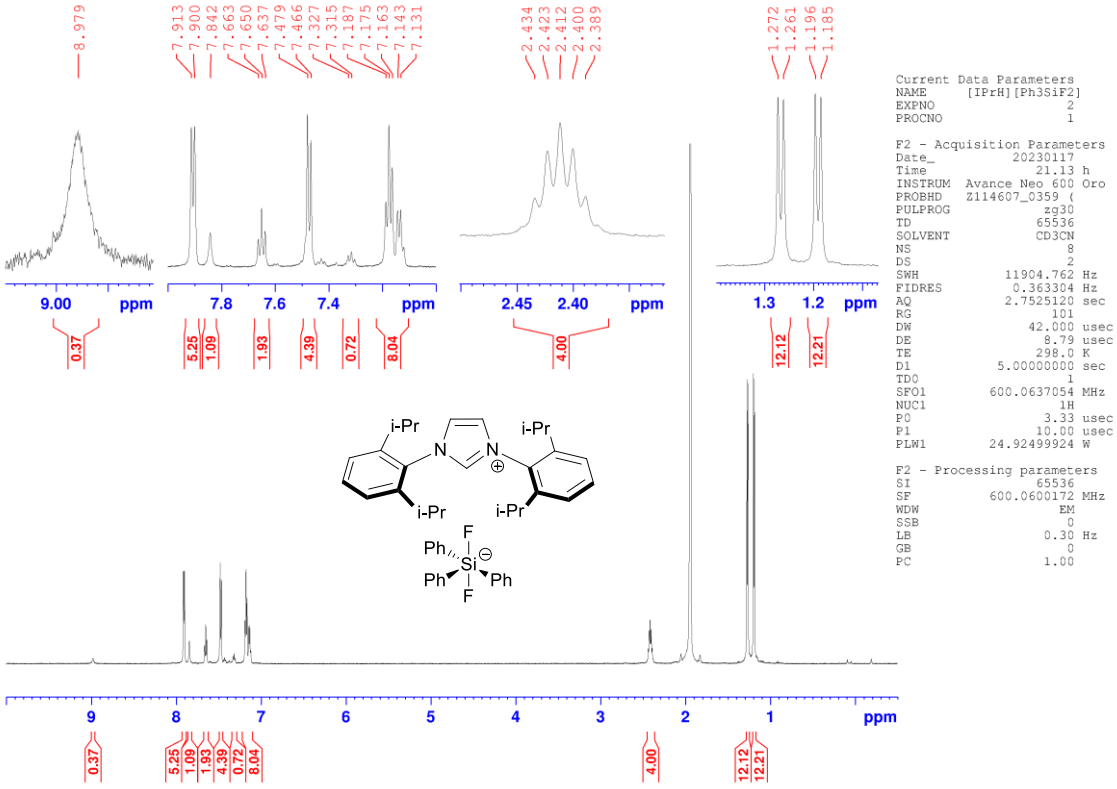


Figure S1 ^{1}H NMR spectrum of [IPrH][Ph$_3$SiF$_2$] (**1**) in MeCN-d^3 solution.

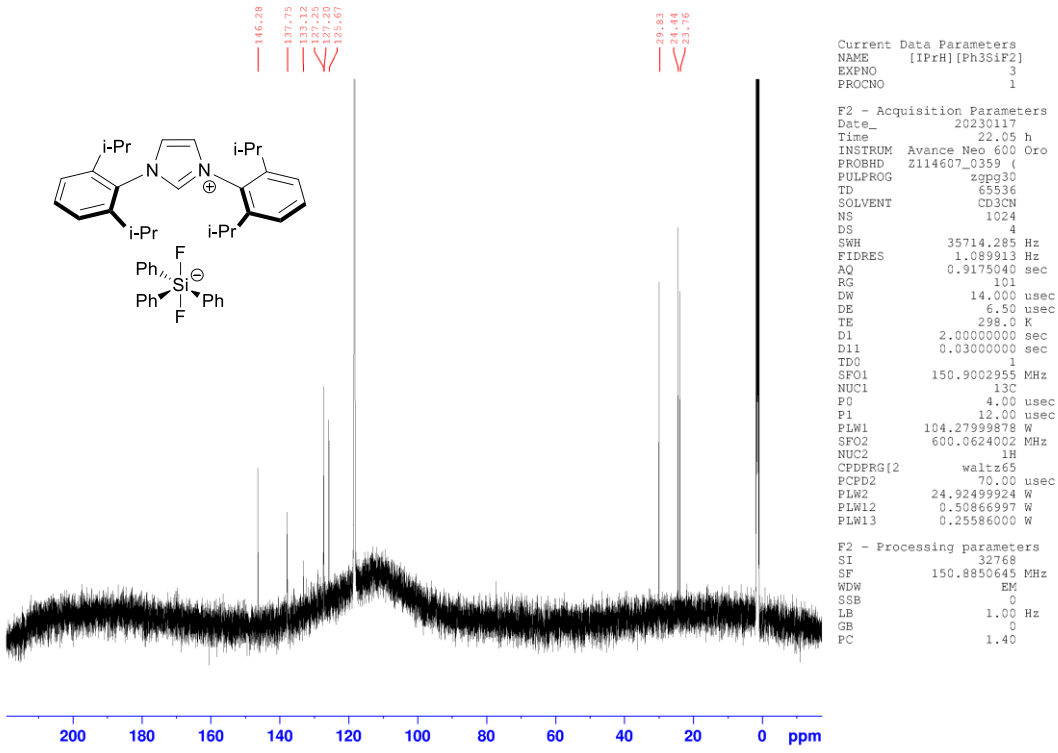


Figure S2 ^{13}C NMR spectrum of [IPrH][Ph$_3$SiF$_2$] (**1**) in MeCN-d^3 solution.

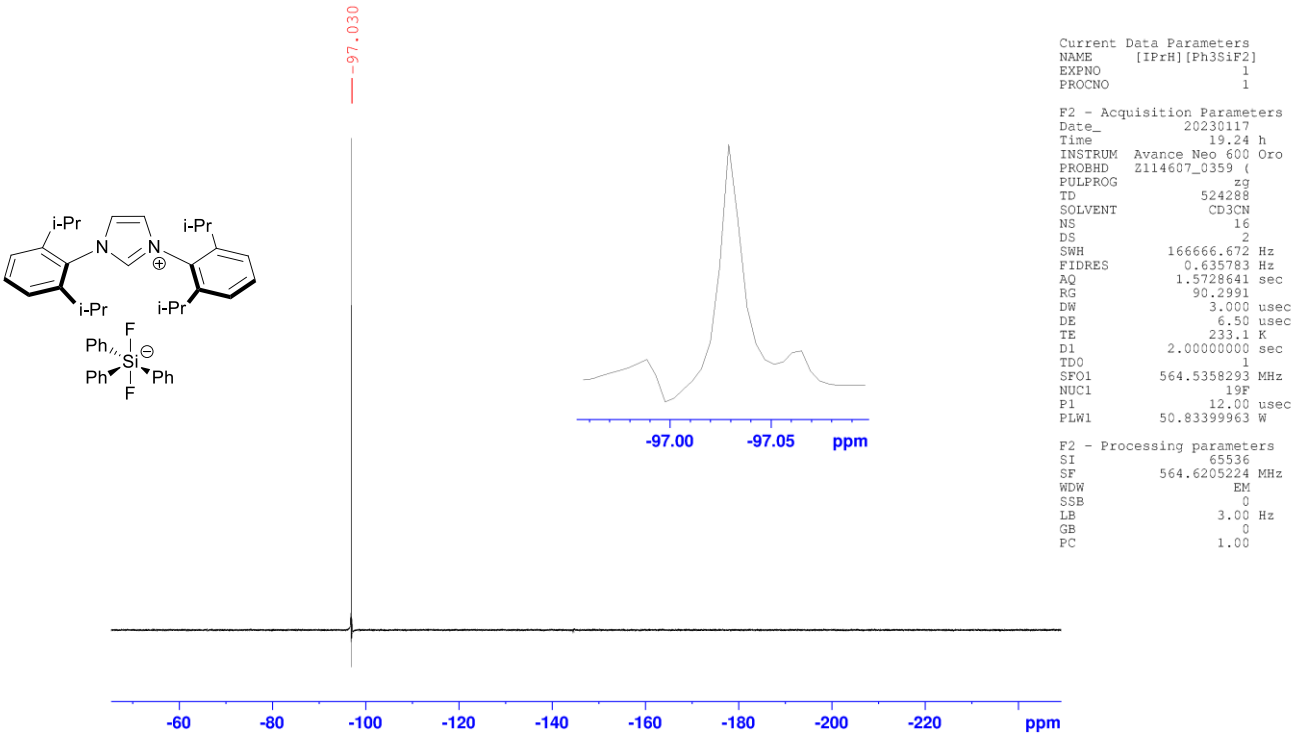


Figure S3 ^{19}F NMR spectrum of [IPrH][Ph_3SiF_2] (**1**) in MeCN-d^3 solution.

S1.2 Attempted synthesis of [IPrH][Et$_3$SiF$_2$] (2)

Reaction between Et_3SiF and [IPrH][F] was carried out in MeCN-d^3 for 24h. Afterwards the ^1H and ^{19}F NMR spectra were measured at room temperature and at −40°C. Below, the ^{19}F NMR spectrum of the reaction mixture measured at room temperature is shown in Figure S4, while a comparison of ^{19}F NMR spectra of Et_3SiF and the reaction mixture measured at −40°C is shown in Figure S5. Both spectra show that only the starting compounds are present in the reaction mixture. Note that in Figure S5 the signal for [IPrH][F] is disproportionally weaker than the signal of Et_3SiF due to its lower solubility at −40°C.

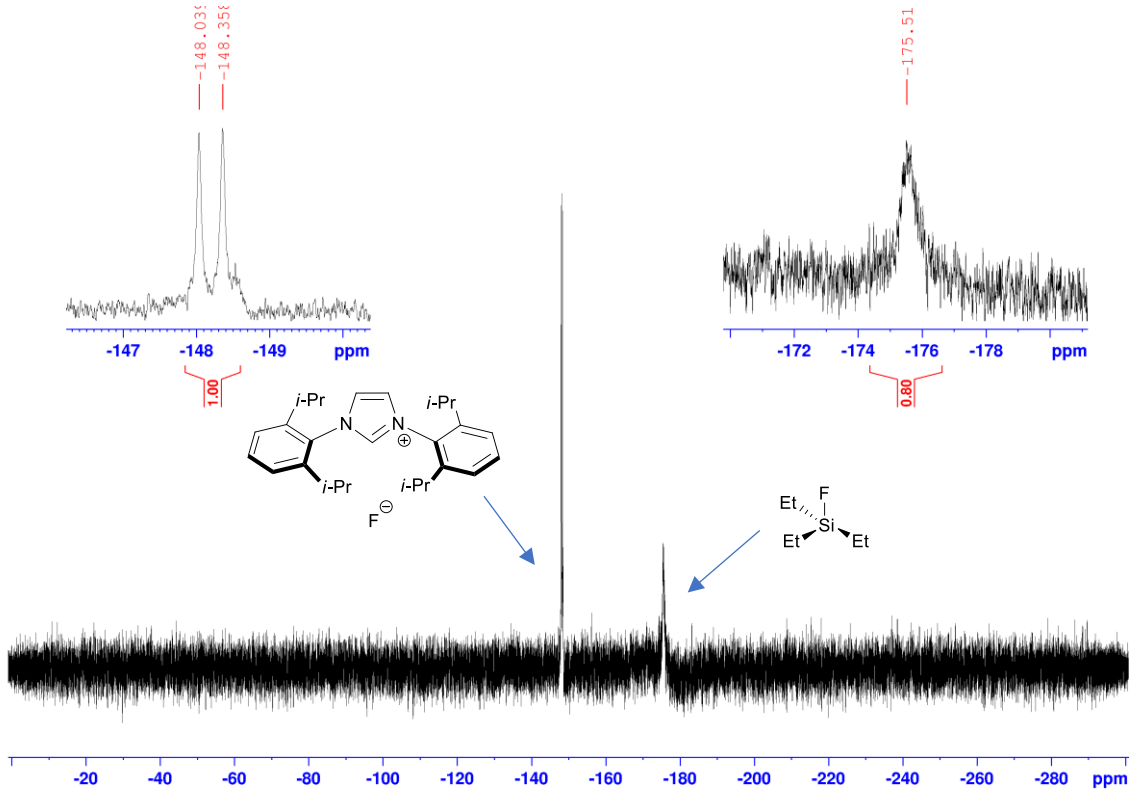


Figure S4: ^{19}F NMR spectrum of the Et_3SiF and [IPrH][F] reaction mixture at 298K.

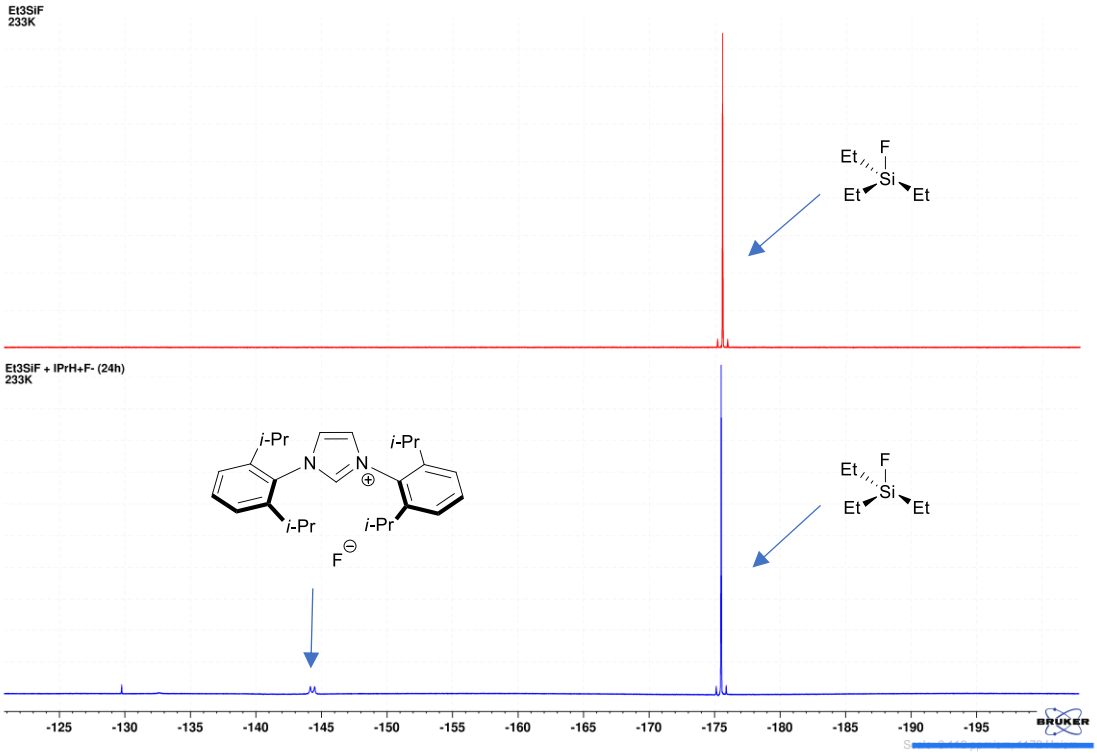


Figure S5 Comparison of ^{19}F NMR spectra of Et_3SiF and reaction mixture of Et_3SiF and [IPrH][F] at 233K.

S1.3 [IPrH][Ph$_2$SiF$_3$] (3)

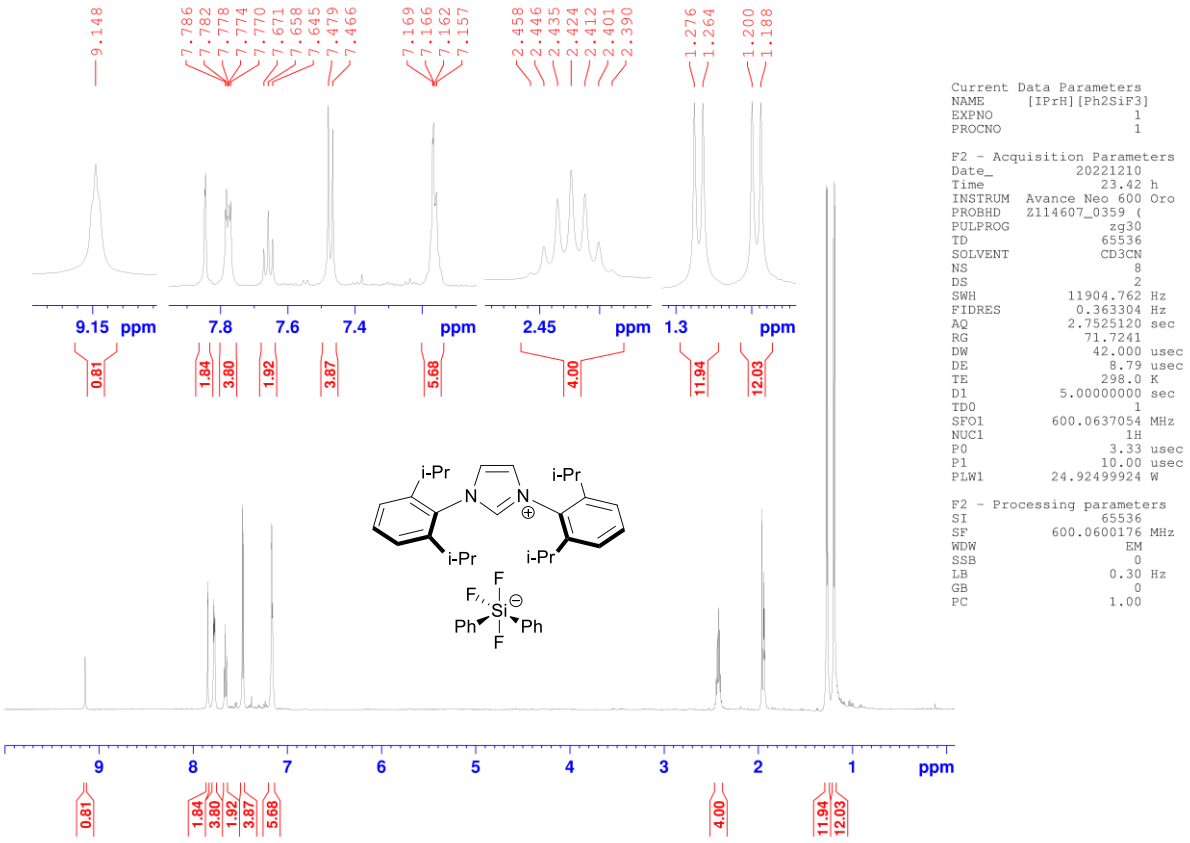


Figure S6 ^{1}H NMR spectrum of [IPrH][Ph$_2$SiF$_3$] (**3**) in MeCN-d^3 solution.

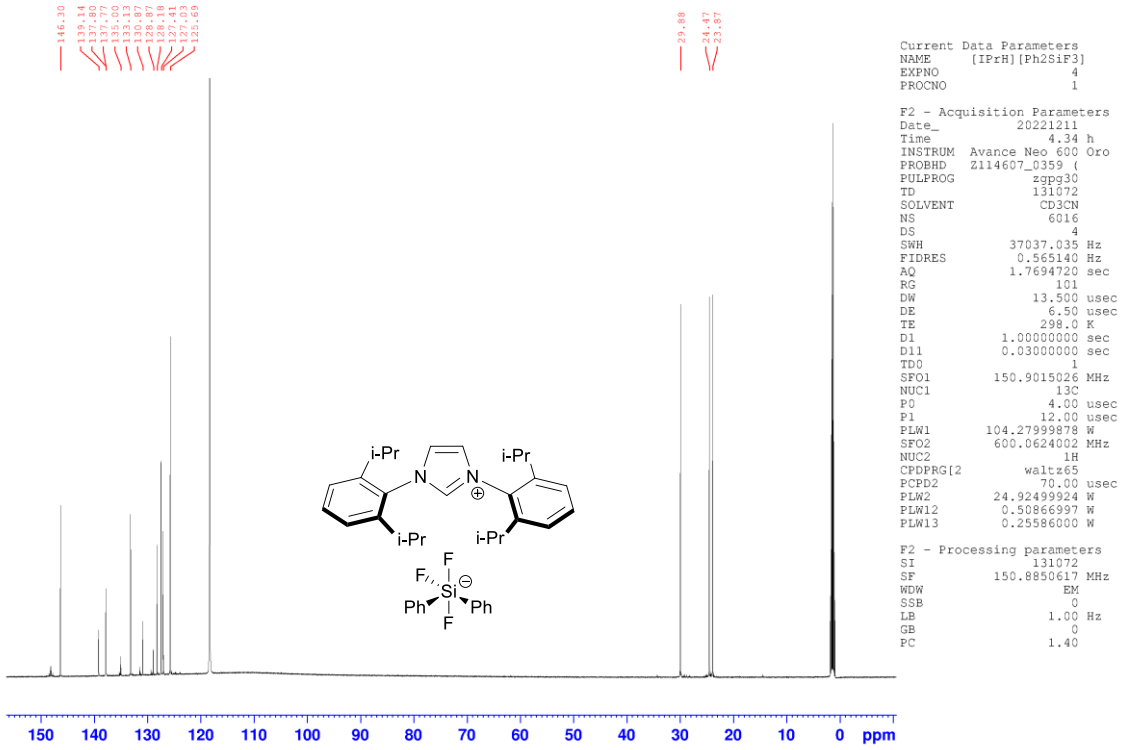


Figure S7 ^{13}C NMR spectrum of [IPrH][Ph$_2$SiF$_3$] (**3**) in MeCN-d^3 solution.

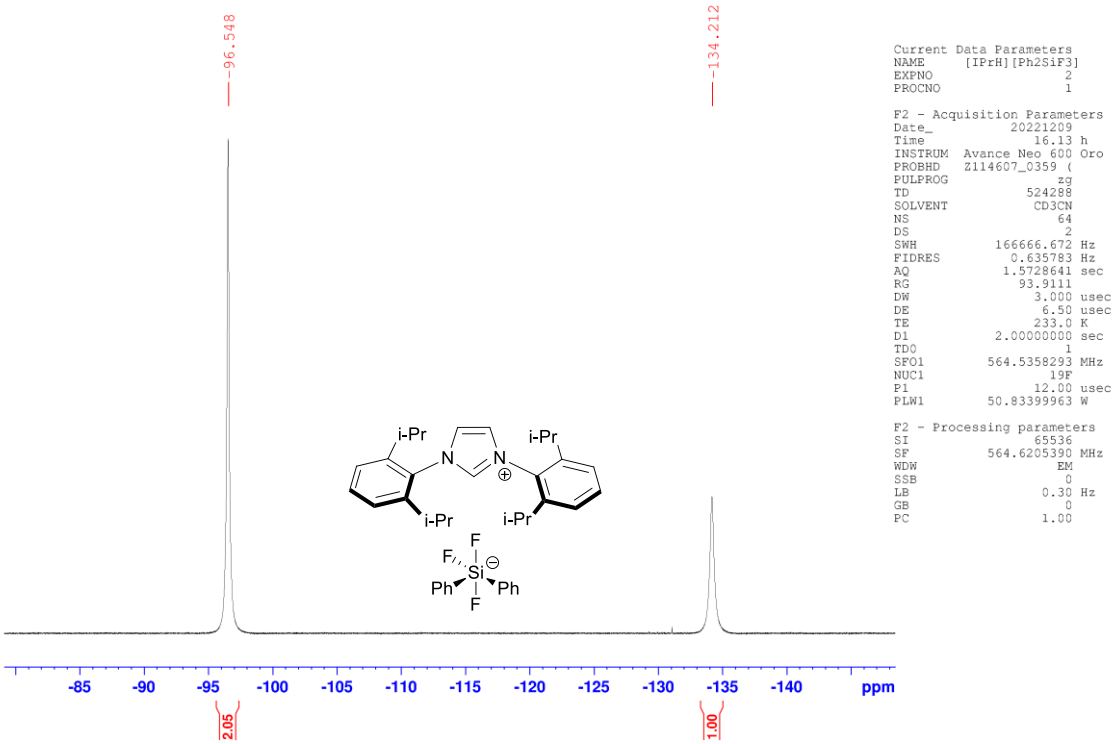


Figure S8 ^{19}F NMR spectrum of [IPrH][Ph_2SiF_3] (**3**) in MeCN-d^3 solution.

S1.4 [IPrH][Et$_2$SiF$_3$] (4)

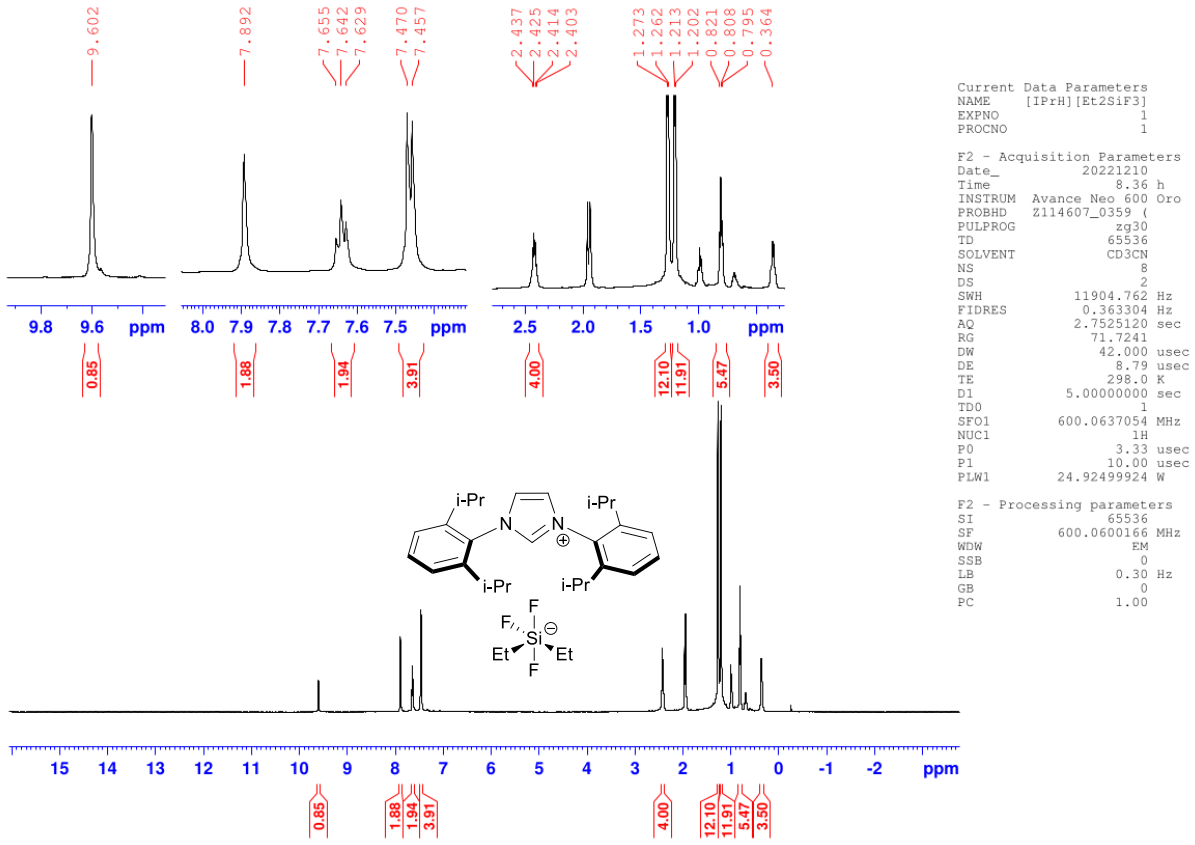


Figure S9 ^{1}H NMR spectrum of [IPrH][Et$_2$SiF$_3$] (**4**) in MeCN-d^3 solution.

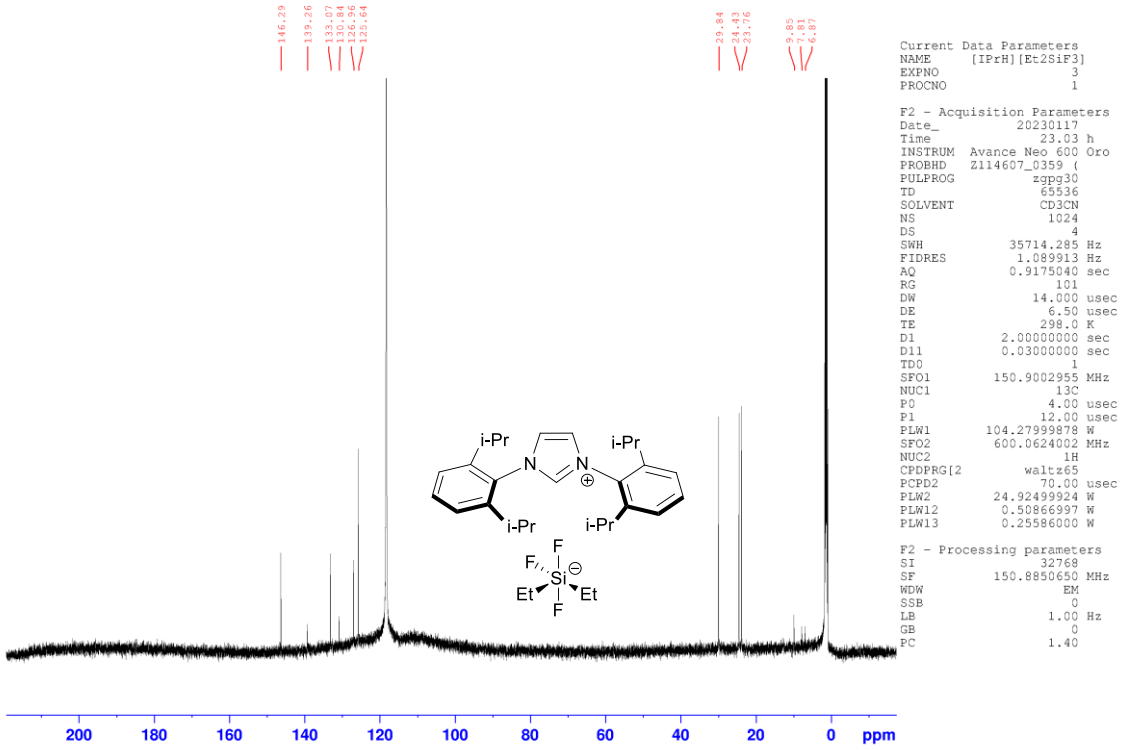


Figure S10 ^{13}C NMR spectrum of [IPrH][Et$_2$SiF$_3$] (**4**) in MeCN-d^3 solution.

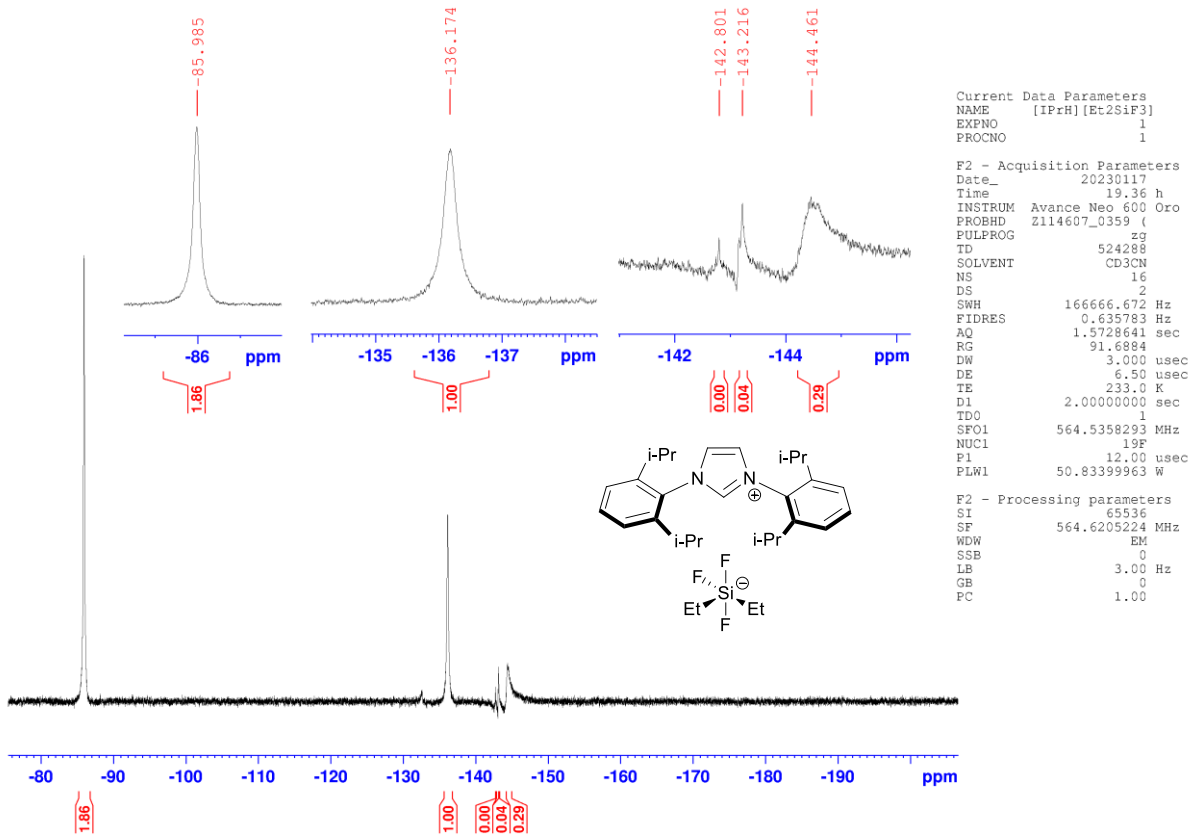


Figure S11 ^{19}F NMR spectrum of [IPrH][Et_2SiF_3] (**4**) in MeCN-d^3 solution.

Signal at −86 ppm corresponds to the axially positioned fluorine atoms, while signal at −136 ppm belongs to the equatorial fluorine. Signals around −144 ppm are a result of [IPrH][F] and [IPrH][HF_2] impurities.

S1.5 [IPrH][EtSiF$_4$] (6)

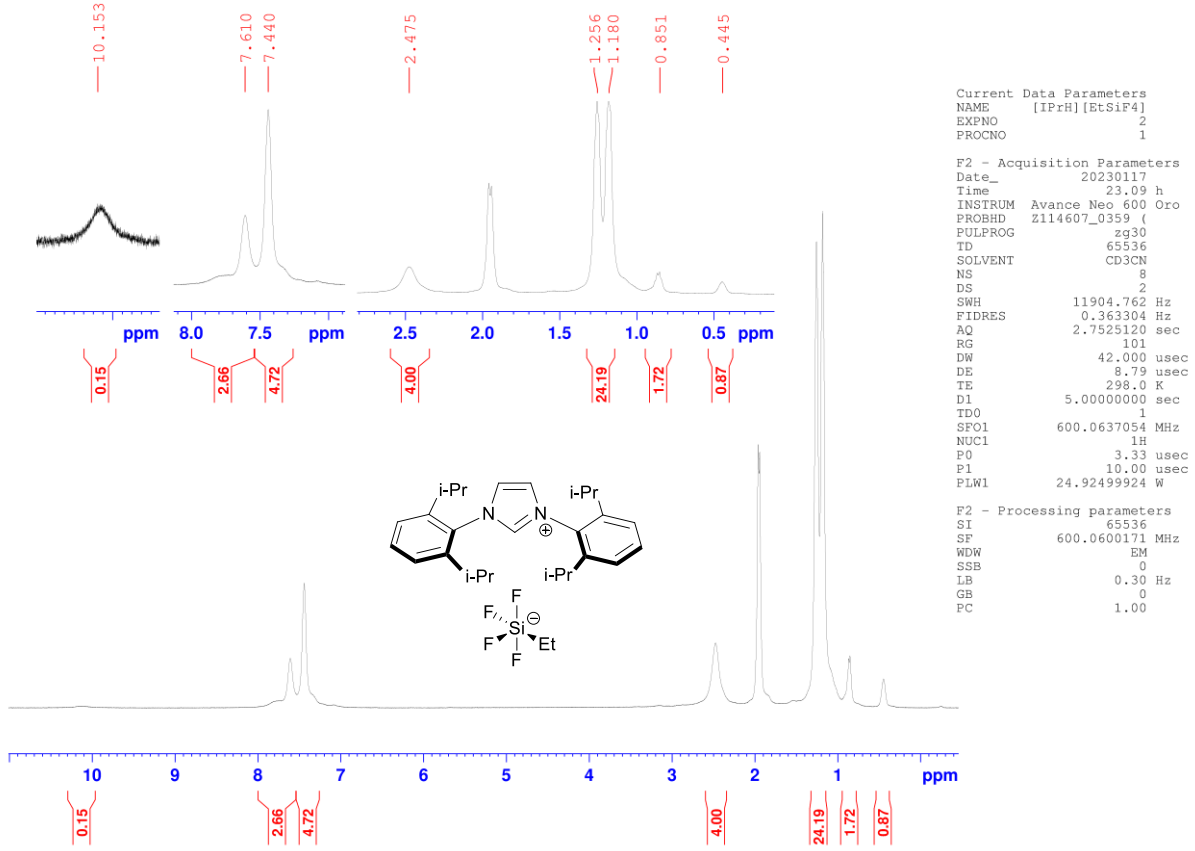


Figure S12 ^{1}H NMR spectrum of [IPrH][EtSiF$_4$] (**6**) in MeCN-d^3 solution.

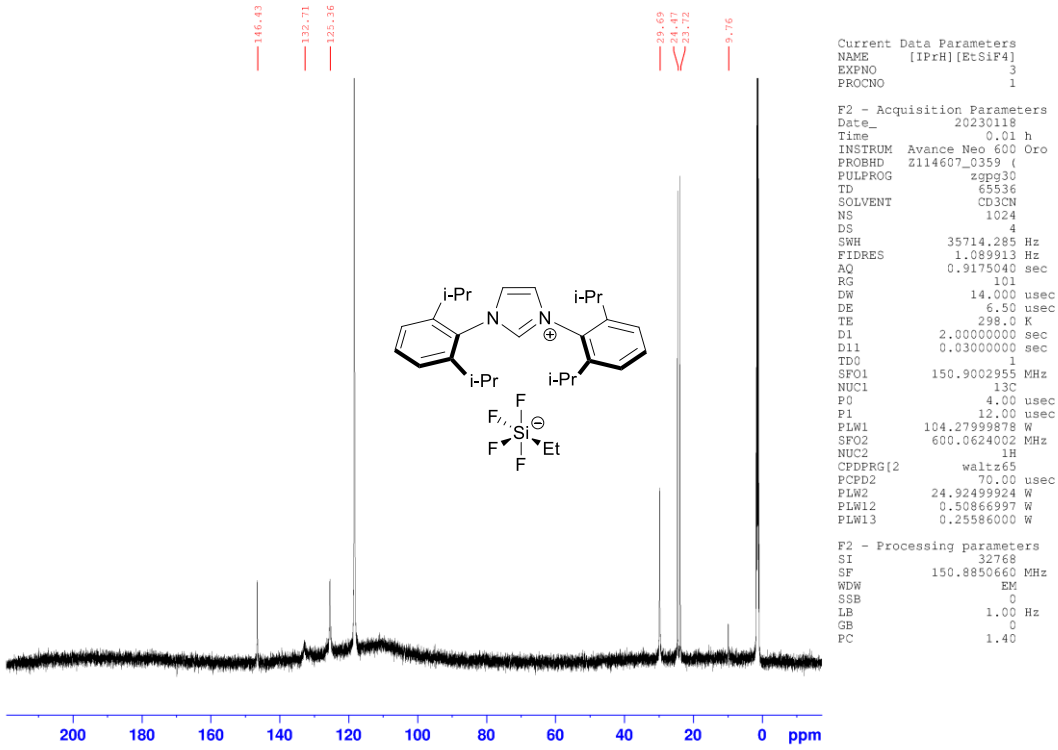


Figure S13 ^{13}C NMR spectrum of [IPrH][EtSiF$_4$] (**6**) in MeCN-d^3 solution.

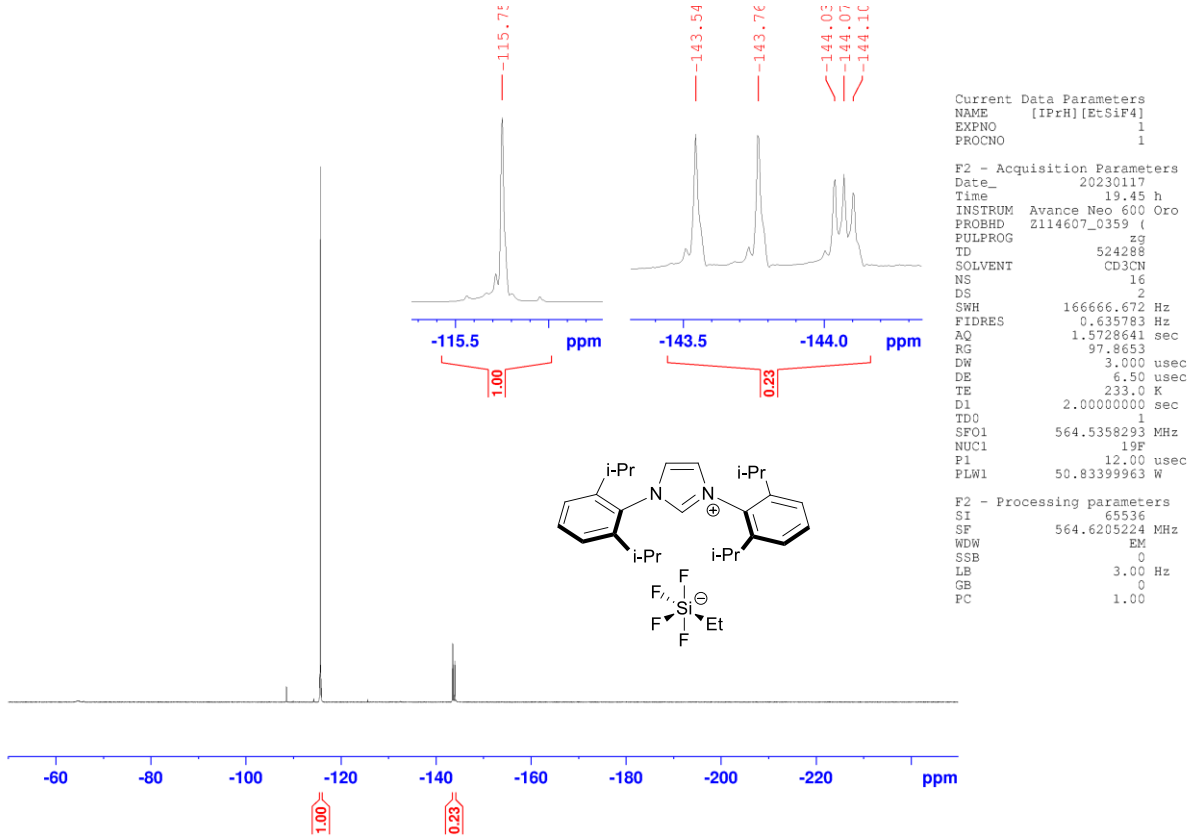


Figure S14 ^{19}F NMR spectrum of [IPrH][$EtSiF_4$] (**6**) in MeCN-d^3 solution.

Signal at −116 ppm belongs to the compound **6**, while the signals at −143 ppm and −144 ppm correspond to [IPrH][F] and [IPrH][HF_2] impurities, respectively.

S1.6 [IPrH][Ph$_3$GeF$_2$] (7)

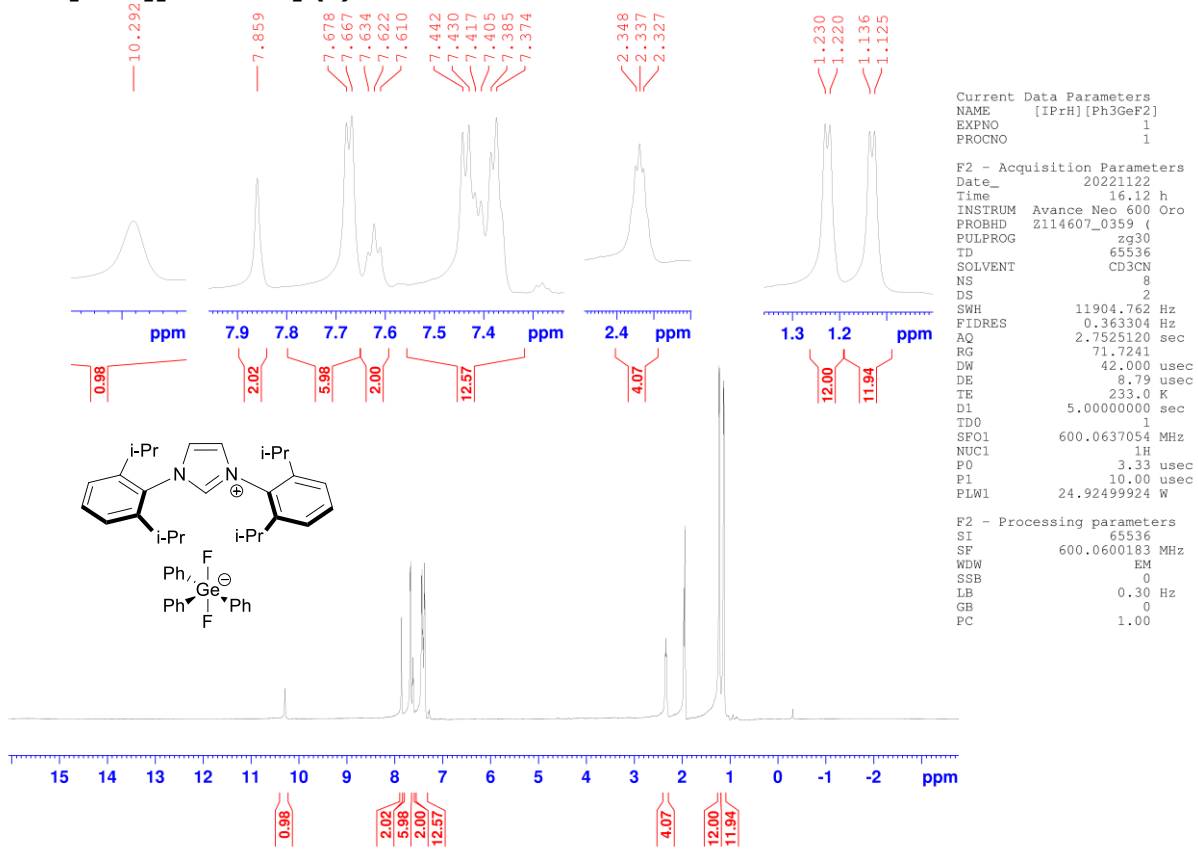


Figure S15 ^{1}H NMR spectrum of [IPrH][Ph$_3$GeF$_2$] (**7**) in MeCN-d^3 solution.

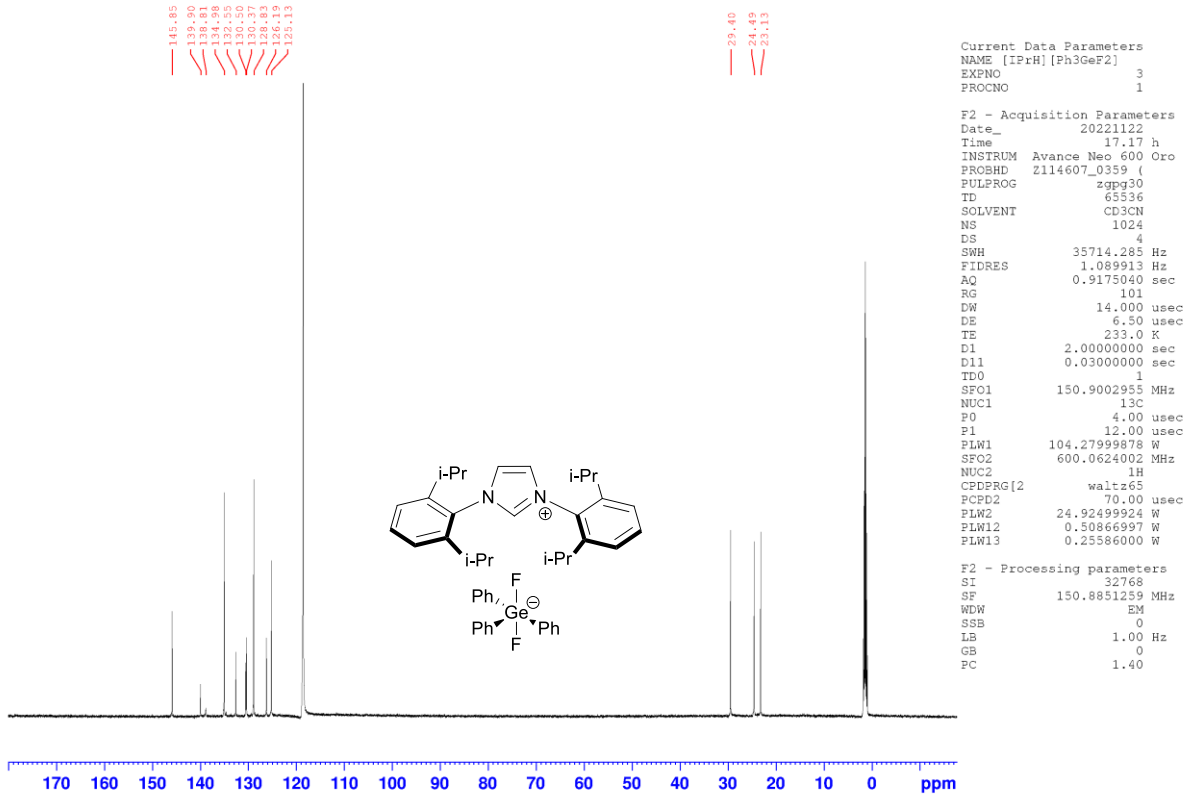
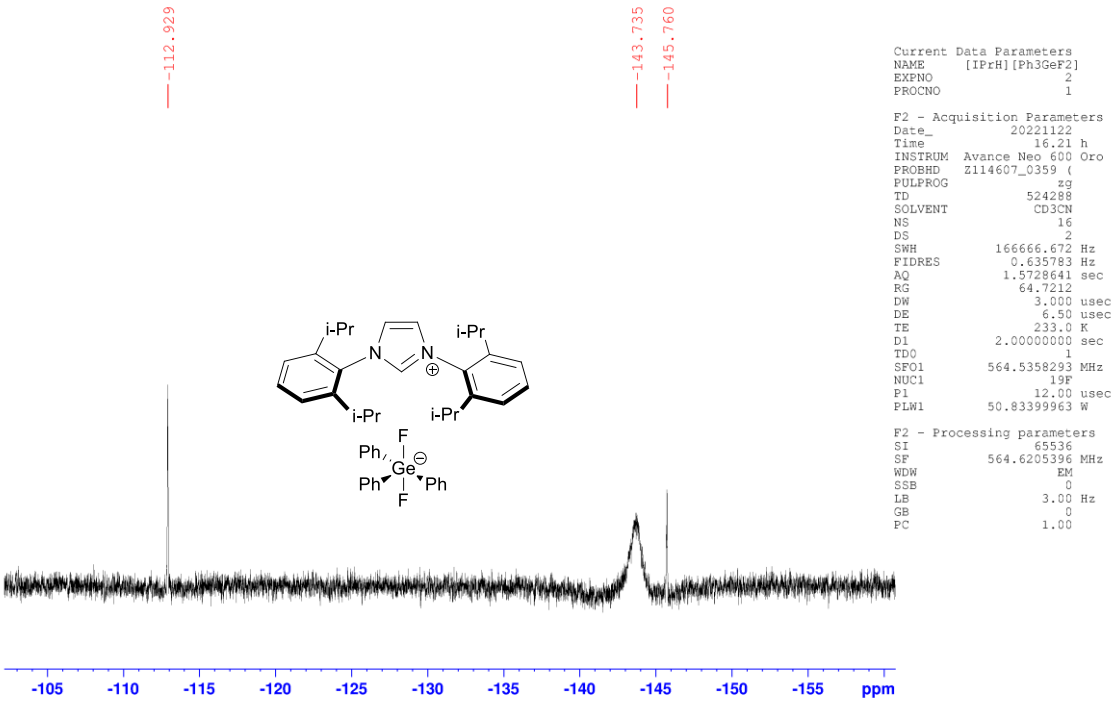


Figure S16 ^{13}C NMR spectrum of [IPrH][Ph$_3$GeF$_2$] (**7**) in MeCN-d^3 solution.

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Current Data Parameters
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EXPNO                   2
PROCNO                  1

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PULPROG               zg
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SOLVENT             CD3CN
NS                    16
DS                     2
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F2 - Processing parameters
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SSB                    0
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PC                  1.00
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Figure S17 ^{13}C NMR spectrum of [IPrH][Ph_3GeF_2] (**7**) in MeCN-d^3 solution. Signal at −146 ppm belongs to excess [IPrH][F].

S2 Raman Spectroscopy

S2.1 [IPrH][Ph_3SiF_2] (1)

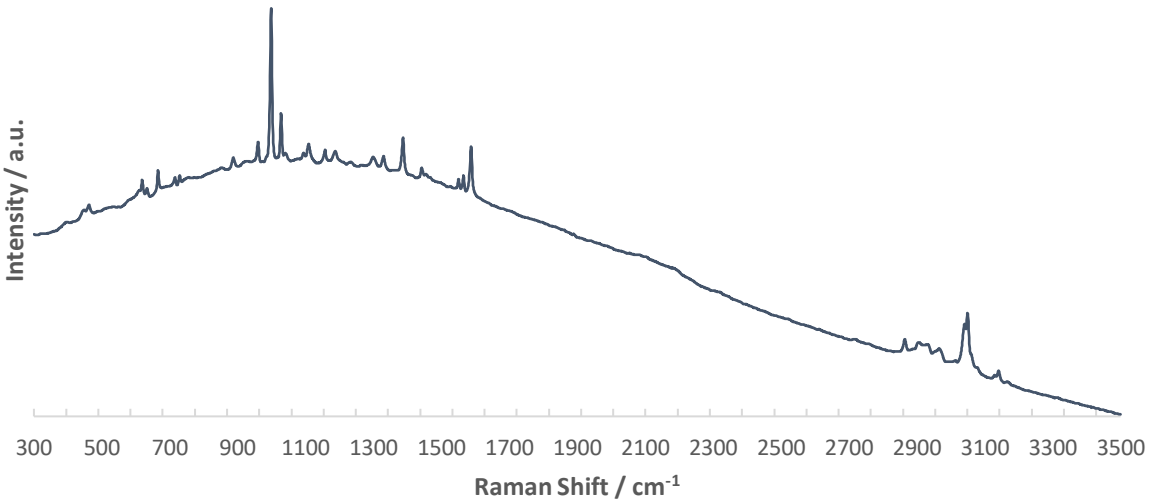


Figure S18 Raman spectrum of [IPrH][Ph_3SiF_2] (**1**)

S2.2 [IPrH][Ph_2SiF_3] (3)

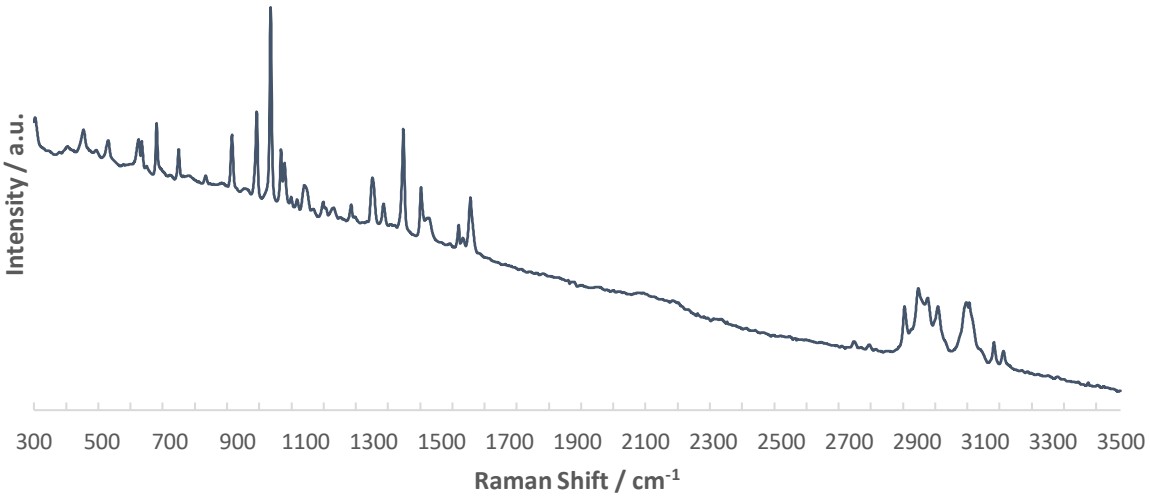


Figure S19 Raman spectrum of [IPrH][Ph_2SiF_3] (**3**)

S2.3 [IPrH][Et_2SiF_3] (4)

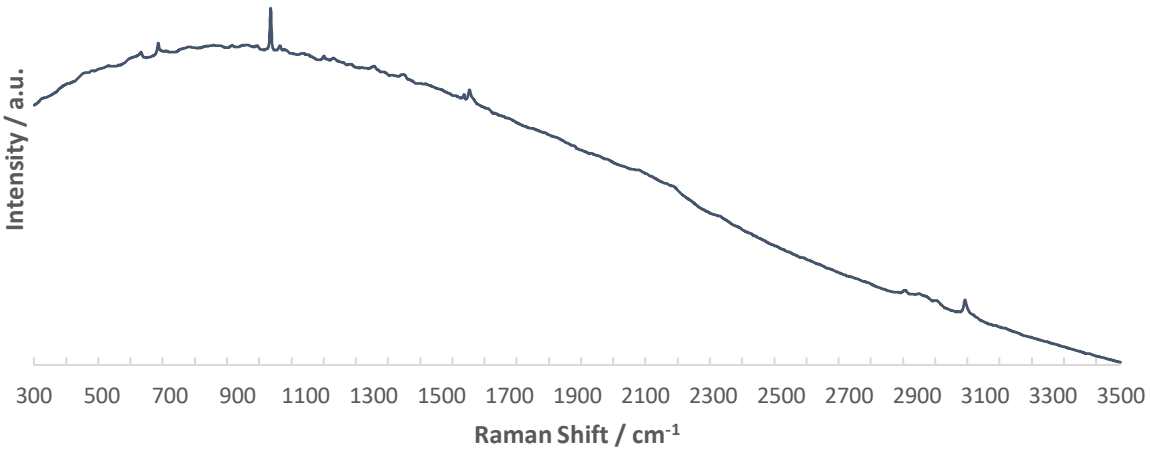


Figure S20 Raman spectrum of [IPrH][Et_2SiF_3] (**4**)

S2.4 [IPrH][$EtSiF_4$] (6)

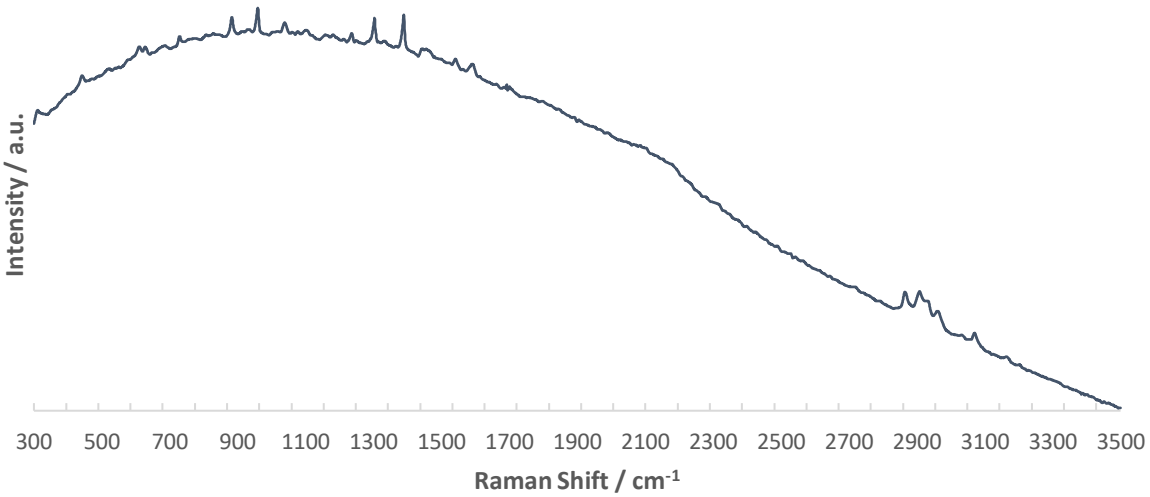


Figure S21 Raman spectrum of [IPrH][$EtSiF_4$] (**6**)

S2.5 [IPrH][Ph_3GeF_2] (7)

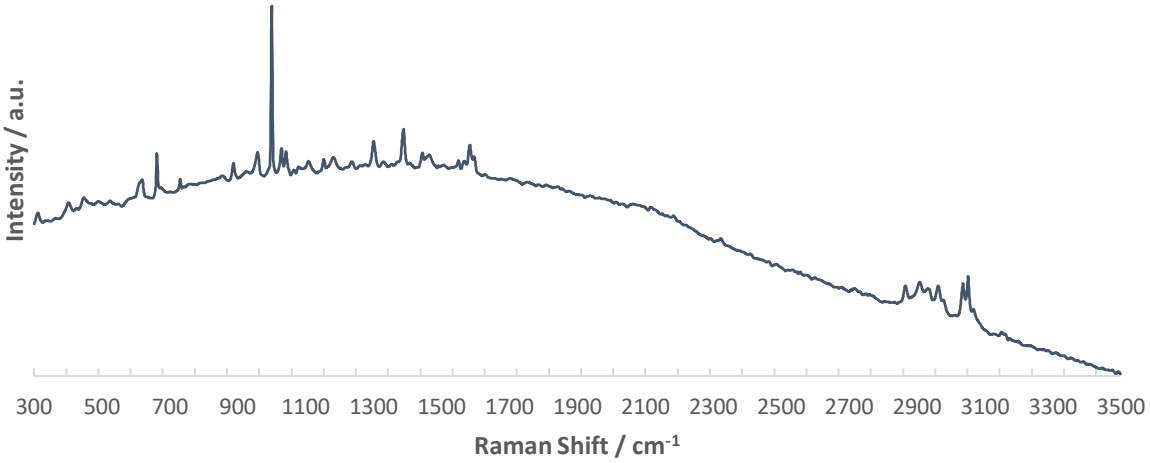


Figure S22: Raman spectrum of [IPrH][Ph_3GeF_2] (**7**)

S3 Crystal Structure Data

Table S1 Selected crystal data for [IPrH][Ph_3SiF_2] (**1**), [IPrH][Ph_2SiF_3] (**3**), [IPrH][Et_2SiF_3]·MeCN (**4**·MeCN) and [IPrH][$PhSiF_4$] (**5**).

	[IPrH][Ph_3SiF_2] (**1**)	[IPrH][Ph_2SiF_3] (**3**)	[IPrH][Et_2SiF_3] ·MeCN (**4**·MeCN)	[IPrH][$PhSiF_4$] (**5**)
CCDC No.	2240916	2240917	2240918	2240919
Chemical formula	$C_{27}H_{37}N_2$· $C_{18}H_{15}F_2Si$	$C_{27}H_{37}N_2$· $C_{12}H_{10}F_3Si$	$C_{27}H_{37}N_2$· $C_4H_{10}F_3Si$·C_2H_3N	$C_{27}H_{37}N_2$· $C_6H_5F_4Si$
F_W (g/mol)	686.97	628.87	573.85	570.77
T (K)	150	150	150	150
λ (Å)	1.54184	1.54184	1.54184	1.54184
Cristal size (mm)	0.95 × 0.57 × 0.46	0.59 × 0.46 × 0.25	0.76 × 0.48 × 0.34	0.80 × 0.62 × 0.28
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	12.4227(3)	18.4493(2)	10.54523(9)	9.8511(2)
b (Å)	18.0014(3)	19.9096(2)	16.13628(15)	17.6141(3)
c (Å)	18.7170(4)	20.1610(3)	19.75591(16)	20.1066(3)
α (°)	90	90	90	69.107(2)
β (°)	108.699(3)	107.3070(10)	91.4592(8)	82.0820(10)
γ (°)	90	90	90	88.7690(10)
V (Å^3)	3964.67(16)	7070.21(15)	3360.59(5)	3226.95(11)
Z	4	8	4	4
ρ_{calc} (g/cm^3)	1.151	1.182	1.134	1.175
μ (mm^{-1})	0.847	0.944	0.950	1.029
F(000)	1472	2688	1240	1216
Θ range (°)	3.5−72.3	2.8−72.4	3.5−72.3	2.7−72.3
Index ranges	−15 ≤ h ≤ 15 −21 ≤ k ≤ 22 −20 ≤ l ≤ 22	−20 ≤ h ≤ 22 −24 ≤ k ≤ 17 −24 ≤ l ≤ 24	−13 ≤ h ≤ 12 −19 ≤ k ≤ 19 −24 ≤ l ≤ 24	−12 ≤ h ≤ 12 −21 ≤ k ≤ 21 −24 ≤ l ≤ 24
Reflections collected	41128	40383	114300	111155
Independent reflections	7763	13662	6630	12537
Reflections with ($I > 2\sigma(I)$)	6558	10288	5722	10696
R_{int}	0.0688	0.0326	0.0649	0.0575
Data / restrains / parameters	7763 / 0 / 459	13662 / 0 / 827	6630 / 0 / 398	12537 / 0 / 1006
S[a]	1.047	1.030	1.051	1.014
R_1[b], wR_2[c] ($I > 2\sigma(I)$)	0.0480, 0.1266	0.0431, 0.1119	0.0499, 0.1334	0.0484, 0.1302
R_1[b], wR_2[c] (all data)	0.0568, 0.1362	0.0608, 0.1242	0.0565, 0.1423	0.0564, 0.1389
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	−0.412, 0.657	−0.345, 0.337	−0.219, 0.474	−0.296, 0.379

[a] $S = [\Sigma(w(F_o^2-F_c^2)^2)/(N_o-N_p)]^{1/2}$.

[b] $R_1 = ||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table S2 Selected crystal data for [IPrH][$EtSiF_4$] (**6**), [IPrH][Ph_3GeF_2] (**7**), [IPrH][Ph_3GeF_2]·MeCN (**7a**) and [IPrH][Ph_3GeF_2]·MeCN (**7b**).

	[IPrH][$EtSiF_4$] (**6**)	[IPrH][Ph_3GeF_2] (**7**)	[IPrH][Ph_3GeF_2] ·MeCN (**7a**)	[IPrH][Ph_3GeF_2] ·MeCN (**7b**)
CCDC No.	2240920	2240921	2240922	2240923
Chemical formula	$C_{27}H_{37}N_2 \cdot C_2H_5F_4Si$	$C_{27}H_{37}N_2 \cdot C_{18}H_{15}F_2Ge$	$C_{27}H_{37}N_2 \cdot C_{18}H_{15}F_2Ge \cdot C_2H_3N$	$C_{27}H_{37}N_2 \cdot C_{18}H_{15}F_2Ge \cdot C_2H_3N$
F_W (g/mol)	522.73	731.47	772.53	772.53
T (K)	150	150	150	150
λ (Å)	1.54184	1.54184	1.54184	1.54184
Cristal size (mm)	0.38 × 0.29 × 0.18	0.52 × 0.23 × 0.06	0.75 × 0.20 × 0.09	0.44 × 0.29 × 0.2
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*I*2*a*	*P*−1	*P*−1	$P2_12_12_1$
a (Å)	17.5233(1)	10.6533(3)	11.3519(3)	14.4757(1)
b (Å)	39.6998(4)	18.5885(5)	12.0229(3)	15.3732(2)
c (Å)	17.5322(1)	20.6911(5)	15.6446(4)	18.8377(2)
α (°)	90	94.715(2)	89.256(2)	90
β (°)	90.1310(10)	97.195(2)	81.538(2)	90
γ (°)	90	95.184(2)	80.477(2)	90
V (Å^3)	12196.62(16)	4030.37(19)	2082.73(9)	4192.10(7)
Z	16	4	2	4
ρ_{calc} (g/cm^3)	1.139	1.205	1.232	1.224
μ (mm^{-1})	1.042	1.351	1.341	1.333
F(000)	4480	1544	816	1632
Θ range (°)	2.7−72.3	3.0−72.1	3.7−72.3	2.8−72.4
Index ranges	−21 ≤ h ≤ 21 −42 ≤ k ≤ 47 −21 ≤ l ≤ 21	−12 ≤ h ≤ 12 −22 ≤ k ≤ 22 −25 ≤ l ≤ 22	−13 ≤ h ≤ 13 −14 ≤ k ≤ 14 −19 ≤ l ≤ 19	−17 ≤ h ≤ 17 −18 ≤ k ≤ 18 −23 ≤ l ≤ 23
Reflections collected	97660	33630	32767	34996
Independent reflections	11993	15341	8068	8093
Reflections with ($I > 2\sigma(I)$)	11069	11878	7139	7783
R_{int}	0.0337	0.0345	0.0418	0.0338
Data / restrains / parameters	11993 / 0 / 709	15341 / 0 / 1033	8068 / 0 / 498	8093 / 0 / 487
S[a]	1.020	1.033	1.056	1.053
R_1[b], wR_2[c] ($I > 2\sigma(I)$)	0.0384, 0.1032	0.0520, 0.1292	0.0354, 0.0851	0.0274, 0.0679
R_1[b], wR_2[c] (all data)	0.0430, 0.1073	0.0697, 0.1415	0.0419, 0.0900	0.0293, 0.0692
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (eÅ^{-3})	−0.308, 0.344	−0.349, 1.134	−0.276, 0.481	−0.229, 0.370

[a] $S = [\Sigma(w(F_o^2-F_c^2)^2)/(N_o-N_p)]^{1/2}$.

[b] $R_1 = ||F_o|-|F_c||/\Sigma|F_o|$.

[c] $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma(w(F_o^2)^2)]^{1/2}$.

Table S3 Selected bond lengths (Å) and bond angles (°) for compounds [IPrH][Ph_3SiF_2] (**1**), [IPrH][Ph_2SiF_3] (**3**), [IPrH][Et_2SiF_3]·MeCN (**4**·MeCN), [IPrH][$PhSiF_4$] (**5**), [IPrH][$EtSiF_4$] (**6**) and [IPrH][Ph_3GeF_2] (**7**).

[IPrH][Ph_3SiF_2] (**1**)			
Bond lengths			
Si(1)–F(1)	1.743(1)	Si(1)–C(1)	1.898(2)
Si(1)–F(2)	1.746(1)	Si(1)–C(7)	1.906(2)
		Si(1)–C(13)	1.907(2)
Bond angles			
F(1)–Si(1)–F(2)	177.44(5)	F(2)–Si(1)–C(7)	90.10(6)
F(1)–Si(1)–C(1)	88.98(6)	F(2)–Si(1)–C(13)	90.09(6)
F(1)–Si(1)–C(7)	91.74(6)	C(1)–Si(1)–C(7)	123.97(8)
F(1)–Si(1)–C(13)	90.35(6)	C(1)–Si(1)–C(13)	119.81(8)
F(2)–Si(1)–C(1)	88.51(6)	C(7)–Si(1)–C(13)	116.21(7)
[IPrH][Ph_2SiF_3] (**3**)			
Anion 1		Anion 2	
Bond lengths		*Bond lengths*	
Si(1)–F(1)	1.645(1)	Si(2)–F(4)	1.646(1)
Si(1)–F(2)	1.691(1)	Si(2)–F(5)	1.689(1)
Si(1)–F(3)	1.711(1)	Si(2)–F(6)	1.710(1)
Si(1)–C(1)	1.897(2)	Si(2)–C(13)	1.897(2)
Si(1)–C(7)	1.901(2)	Si(2)–C(19)	1.898(2)
Bond angles		*Bond angles*	
F(1)–Si(1)–F(2)	88.00(6)	F(4)–Si(2)–F(5)	88.00(6)
F(1)–Si(1)–F(3)	85.92(5)	F(4)–Si(2)–F(6)	85.99(5)
F(1)–Si(1)–C(1)	120.30(7)	F(4)–Si(2)–C(13)	119.87(7)
F(1)–Si(1)–C(7)	121.98(7)	F(4)–Si(2)–C(19)	121.29(7)
F(2)–Si(1)–F(3)	173.91(5)	F(5)–Si(2)–F(6)	173.97(6)
F(2)–Si(1)–C(1)	92.19(6)	F(5)–Si(2)–C(13)	92.25(7)
F(2)–Si(1)–C(7)	91.91(6)	F(5)–Si(2)–C(19)	91.83(7)
F(3)–Si(1)–C(1)	91.22(6)	F(6)–Si(2)–C(13)	91.20(7)
F(3)–Si(1)–C(7)	90.97(6)	F(6)–Si(2)–C(19)	90.84(7)
C(1)–Si(1)–C(7)	117.68(7)	C(13)–Si(2)–C(19)	118.80(8)
[IPrH][Et_2SiF_3]·MeCN (**4**·MeCN)			
Bond lengths			
Si(1)–F(1)	1.733(1)	Si(1)–C(1)	1.875(2)
Si(1)–F(2)	1.648(1)	Si(1)–C(3)	1.885(2)
Si(1)–F(3)	1.729(1)		
Bond angles			
F(1)–Si(1)–F(2)	86.41(5)	F(2)–Si(1)–C(1)	118.09(7)
F(1)–Si(1)–F(3)	173.12(6)	F(2)–Si(1)–C(3)	119.51(7)
F(1)–Si(1)–C(1)	89.95(6)	F(3)–Si(1)–C(1)	94.26(7)
F(1)–Si(1)–C(3)	91.42(7)	F(3)–Si(1)–C(3)	90.92(7)
F(2)–Si(1)–F(3)	86.81(5)	C(1)–Si(1)–C3	122.36(8)

[IPrH][$PhSiF_4$] (**5**)			
Anion 1		Anion 2	
Bond lengths		*Bond lengths*	
Si(1A)–F(1A)	1.653(2)	Si(2A)–F(5A)	1.624(4)
Si(1B)–F(1B)	1.69(1)	Si(2B)–F(5B)	1.689(7)
Si(1A)–F(2A)	1.718(2)	Si(2A)–F(6A)	1.751(3)
Si(1B)–F(2B)	1.523(7)	Si(2B)–F(6B)	1.553(6)
Si(1A)–F(3A)	1.584(3)	Si(2A)–F(7A)	1.574(5)
Si(1B)–F(3B)	1.763(9)	Si(2B)–F(7B)	1.745(7)
Si(1A)–F(4A)	1.660(2)	Si(2A)–F(8A)	1.656(3)
Si(1B)–F(4B)	1.568(9)	Si(2B)–F(8B)	1.600(7)
Si(1A)–C(1A)	1.902(5)	Si(2A)–C(11A)	1.850(7)
Si(1B)–C(1B)	1.77(2)	Si(2B)–C(11B)	1.873(7)
Bond angles		*Bond angles*	
F(1A)–Si(1A)–F(2A)	174.6(1)	F(5A)–Si(2A)–F(6A)	174.8(2)
F(1B)–Si(1B)–F(2B)	124.1(5)	F(5B)–Si(2B)–F(6B)	122.0(4)
F(1A)–Si(1A)–F(3A)	91.6(1)	F(5A)–Si(2A)–F(7A)	93.2(2)
F(1B)–Si(1B)–F(3B)	84.1(4)	F(5B)–Si(2B)–F(7B)	84.2(3)
F(1A)–Si(1A)–F(4A)	88.3(1)	F(5A)–Si(2A)–F(8A)	89.3(2)
F(1B)–Si(1B)–F(4B)	89.2(5)	F(5B)–Si(2B)–F(8B)	88.0(4)
F(1A)–Si(1A)–C(1A)	93.4(2)	F(5A)–Si(2A)–C(11A)	91.4(3)
F(1B)–Si(1B)–C(1B)	112.8(8)	F(5B)–Si(2B)–C(11B)	119.8(4)
F(2A)–Si(1A)–F(3A)	89.3(1)	F(6A)–Si(2A)–F(7A)	88.3(2)
F(2B)–Si(1B)–F(3B)	87.4(4)	F(6B)–Si(2B)–F(7B)	88.2(3)
F(2A)–Si(1A)–F(4A)	86.5(1)	F(6A)–Si(2A)–F(8A)	85.6(1)
F(2B)–Si(1B)–F(4B)	95.9(5)	F(6B)–Si(2B)–F(8B)	93.8(3)
F(2A)–Si(1A)–C(1A)	90.7(2)	F(6A)–Si(2A)–C(11A)	92.0(3)
F(2B)–Si(1B)–C(1B)	121.9(8)	F(6B)–Si(2B)–C(11B)	118.0(4)
F(3A)–Si(1A)–F(4A)	116.5(1)	F(7A)–Si(2A)–F(8A)	118.4(2)
F(3B)–Si(1B)–F(4B)	173.2(6)	F(7B)–Si(2B)–F(8B)	171.8(4)
F(3A)–Si(1A)–C(1A)	122.7(2)	F(7A)–Si(2A)–C(11A)	121.9(3)
F(3B)–Si(1B)–C(1B)	87.9(7)	F(7B)–Si(2B)–C(11B)	92.8(4)
F(4A)–Si(1A)–C(1A)	120.6(2)	F(8A)–Si(2A)–C(11A)	119.5(2)
F(4B)–Si(1B)–C(1B)	95.3(8)	F(8B)–Si(2B)–C(11B)	93.3(4)
[IPrH][$EtSiF_4$] (**6**)			
Anion 1		Anion 2	
Bond lengths		*Bond lengths*	
Si(1)–F(1)	1.701(1)	Si(2)–F(5)	1.698(1)
Si(1)–F(2)	1.672(1)	Si(2)–F(6)	1.670(1)
Si(1)–F(3)	1.618(1)	Si(2)–F(7)	1.621(1)
Si(1)–F(4)	1.614(1)	Si(2)–F(8)	1.617(1)
Si(1)–C(1)	1.862(3)	Si(2)–C(3)	1.866(3)
Bond angles		*Bond angles*	
F(1)–Si(1)–F(2)	174.87(7)	F(5)–Si(2)–F(6)	174.56(7)
F(1)–Si(1)–F(3)	88.08(7)	F(5)–Si(2)–F(7)	88.06(7)
F(1)–Si(1)–F(4)	88.10(6)	F(5)–Si(2)–F(8)	88.17(6)
F(1)–Si(1)–C(1)	89.6(1)	F(5)–Si(2)–C(3)	90.0(1)

F(2)–Si(1)–F(3)	89.36(7)	F(6)–Si(2)–F(7)	89.07(6)
F(2)–Si(1)–F(4)	89.21(7)	F(6)–Si(2)–F(8)	89.09(7)
F(2)–Si(1)–C(1)	95.5(1)	F(6)–Si(2)–C(3)	95.5(1)
F(3)–Si(1)–F(4)	118.45(7)	F(7)–Si(2)–F(8)	117.841(7)
F(3)–Si(1)–C(1)	121.90(9)	F(7)–Si(2)–C(3)	121.5(1)
F(4)–Si(1)–C(1)	119.5(1)	F(8)–Si(2)–C(3)	120.5(1)
[IPrH][Ph_3GeF_2] (**7**)			
Anion 1		Anion 2	
Bond lengths		*Bond lengths*	
Ge(1)–F(1)	1.930(1)	Ge(2)–F(3A)	1.939(9)
Ge(1)–F(2)	1.923(1)	Ge(2)–F(3B)	1.87(2)
Ge(1)–C(1)	1.946(3)	Ge(2)–F(4)	1.935(2)
Ge(1)–C(7)	1.949(3)	Ge(2)–C(21)	1.958(4)
Ge(1)–C(13)	1.963(3)	Ge(2)–C(27A)	1.970(5)
		Ge(2)–C(27B)	1.945(1)
		Ge(2)–C(33)	1.955(4)
Bond angles		*Bond angles*	
F(1)–Ge(1)–F(2)	177.23(7)	F(3A)–Ge(2)–F(4)	176.1(3)
F(1)–Ge(1)–C(1)	90.75(9)	F(3B)–Ge(2)–F(4)	170.5(7)
F(1)–Ge(1)–C(7)	89.04(9)	F(3A)–Ge(2)–C(21)	89.2(3)
F(1)–Ge(1)–C(13)	91.9(1)	F(3B)–Ge(2)–C(21)	87.7(7)
F(2)–Ge(1)–C(1)	88.36(9)	F(3A)–Ge(2)–C(27B)	100.7(5)
F(2)–Ge(1)–C(7)	89.15(9)	F(3B)–Ge(2)–C(27A)	80.4(7)
F(2)–Ge(1)–C(13)	90.8(1)	F(3A)–Ge(2)–C(33)	86.9(3)
C(1)–Ge(1)–C(7)	120.5(1)	F(3B)–Ge(2)–C(33)	99.0(7)
C(1)–Ge(1)–C(13)	121.8(1)	F(4)–Ge(2)–C(21)	90.3(1)
C(7)–Ge(1)–C(13)	117.7(1)	F(4)–Ge(2)–C(27A)	92.4(1)
		F(4)–Ge(2)–C(27B)	82.8(4)
		F(4)–Ge(2)–C(33)	90.0(1)
		C(21)–Ge(2)–C(27A)	118.6(2)
		C(21)–Ge(2)–C(27B)	120.9(4)
		C(21)–Ge(2)–C(33)	120.1(2)
		C(27A)–Ge(2)–C(33)	121.2(2)
		C(27B)–Ge(2)–C(33)	118.6(4)

Table S4 Selected bond lengths (Å) and bond angles (°) of interactions between cation and anion in crystal structures of compounds [IPrH][Ph_3SiF_2] (**1**), [IPrH][Ph_2SiF_3] (**3**), [IPrH][Et_2SiF_3]·MeCN (**4**·MeCN), [IPrH][$PhSiF_4$] (**5**), [IPrH][$EtSiF_4$] (**6**) and [IPrH][Ph_3GeF_2] (**7**).

F···H−C/F	F···C	F···H	H−C	<(FHC)
[[IPrH][Ph_3SiF_2] (**1**)				
F(1)···H(22)−C(22)	2.926(2)	2.0841(9)	0.950(2)	146.83(9)
F(2)···H(24)^{I}−C(24)^{I}	2.980(2)	2.0383(9)	0.950(2)	171.0(1)
[[IPrH][Ph_2SiF_3] (**3**)				
Anion 1				
F(1)···H(32)−C(32)	3.220(2)	2.298(1)	0.950(2)	163.5(1)
F(1)···H(69)−C(69)	3.163(3)	2.368(1)	0.950(2)	141.0(1)
F(3)···H(32)−C(32)	2.990(2)	2.233(1)	0.950(2)	135.9(1)
Anion 2				
F(4)···H(62)−C(62)	3.270(2)	2.343(1)	0.950(2)	165.2(1)
F(4)···H(52)^{I}–C(52)^{I}	3.289(3)	2.424(1)	0.950(2)	151.2(1)
F(6)···H(62)−C(62)	2.970(2)	2.226(1)	0.950(2)	134.5(1)
[IPrH][Et_2SiF_3]·MeCN (**4**·MeCN)				
F(1)···H(12)−C(12)	2.958(2)	2.058(1)	0.950(1)	157.57(9)
F(2)···H(15)^{I}−C(15)^{I}	3.207(2)	2.307(1)	0.950(2)	157.84(9)
F(3)···H(14)^{I}−C(14)^{I}	3.010(2)	2.507(1)	0.950(1)	113.17(9)
[[IPrH][$PhSiF_4$] (**5**)				
Anion 1				
F(1A)···H(22)−C(22)	3.084(3)	2.155(2)	0.950(1)	165.6(1)
F(1B)···H(22)−C(22)	3.023(6)	2.122(6)	0.950(1)	157.8(2)
F(1B)···H(60)^{I}−C(60)^{I}	3.323(7)	2.549(8)	0.950(2)	138.7(2)
F(2A)···H(25)^{I}−C(25)^{I}	2.925(2)	2.393(2)	0.950(2)	115.1(1)
F(2A)···H(24)^{I}−C(24)^{I}	2.968(2)	2.490(2)	0.950(2)	111.1(1)
F(2A)···H(71A)−C(71A)	3.19(1)	2.478(2)	0.95(1)	131.6(8)
F(2B)···H(24)^{I}−C(24)^{I}	3.100(4)	2.387(4)	0.950(2)	131.6(1)
F(3A)···H(24)^{I}−C(24)^{I}	3.172(3)	2.264(2)	0.950(2)	159.7(1)
F(3B)···H(24)^{I}−C(24)^{I}	3.035(5)	2.239(4)	0.950(2)	140.8(1)
F(3B)···H(60)^{I}−C(60)^{I}	3.070(6)	2.568(6)	0.950(2)	113.3(2)
F(4A)···H(22)−C(22)	2.950(2)	2.241(2)	0.950(1)	130.8(1)
F(4A)···H(34B)−C(34)	3.327(3)	2.444(2)	0.980(3)	149.7(2)
F(4B)···H(22)−C(22)	3.007(6)	2.261(6)	0.950(1)	134.8(2)
Anion 2				
F(5A)···H(52)−C(52)	3.120(4)	2.212(3)	0.950(2)	159.7(1)
F(5B)···H(52)−C(52)	3.070(6)	2.210(6)	0.950(2)	150.1(2)
F(6A)···H(54)^{I}−C(54)^{I}	3.019(3)	2.525(2)	0.950(2)	112.5(1)

F(6A)···H(55)^{I}−C(55)^{I}	3.002(3)	2.486(2)	0.950(2)	114.2(1)
F(6B)···H(54)^{I}−C(54)^{I}	3.224(3)	2.516(3)	0.950(2)	131.4(1)
F(7A)···H(54)^{I}−C(54)^{I}	3.220(3)	2.288(3)	0.950(2)	166.6(1)
F(7B)···H(54)^{I}−C(54)^{I}	3.024(3)	2.172(3)	0.950(2)	148.7(1)
F(7B)···H(28)−C(28)	3.037(4)	2.401(4)	0.950(2)	124.0(2)
F(8A)···H(52)−C(52)	2.973(3)	2.250(3)	0.950(2)	132.3(1)
F(8A)···H(66A)−C(66)	3.302(4)	2.369(2)	0.980(3)	158.8(2)
F(8B)···H(52)−C(52)	2.943(3)	2.168(3)	0.950(2)	137.9(1)
[IPrH][$EtSiF_4$] (**6**)				
Anion 1				
F(1)···H(22)−C(22)	2.968(2)	2.050(1)	0.950(2)	162.1(1)
F(2)···H(55)^{I}−C(55)^{I}	2.958(2)	2.162(1)	0.950(2)	140.6(1)
F(2)···H(72)^{I}−C(72)^{I}	3.132(2)	2.460(1)	0.950(2)	127.7(1)
F(3)···H(54)^{I}−C(54)^{I}	3.073(2)	2.280(1)	0.950(2)	140.6(1)
F(4)···H(22)−C(22)	3.122(2)	2.379(1)	0.950(2)	134.8(1)
Anion 2				
F(5)···H(52)−C(52)	2.994(2)	2.105(1)	0.950(2)	155.4(1)
F(6)···H(24)−C(24)	2.864(2)	2.200(1)	0.950(2)	126.1(1)
F(6)···H(28)^{I}−C(28)^{I}	3.154(2)	2.478(1)	0.950(2)	128.1(1)
F(7)···H(25)−C(25)	3.118(2)	2.229(1)	0.950(2)	155.3(1)
F(8)···H(52)−C(52)	3.120(2)	2.317(1)	0.950(2)	141.9(1)
[[IPrH][Ph_3GeF_2] (**7**)				
Anion 1				
F(1)···H(72)^{I}−C(72)^{I}	2.835(3)	1.982(2)	0.950(3)	148.3(2)
F(2)···H(45)−C(45)	2.933(5)	2.078(2)	0.950(3)	149.0(2)
F(2)···H(79)^{I}−C(79)^{I}	3.268(4)	2.373(2)	0.950(4)	156.6(2)
Anion 2				
F(3A)···H(75)−C(75)	2.86(1)	1.93(1)	0.950(4)	163.8(4)
F(3B)···H(75)−C(75)	3.02(2)	2.07(2)	0.950(4)	174.0(6)
F(4)···H(42)^{I}−C(42)^{I}	2.842(3)	1.921(2)	0.950(3)	162.6(2)

S3.1 Crystal structures of the asymmetric units

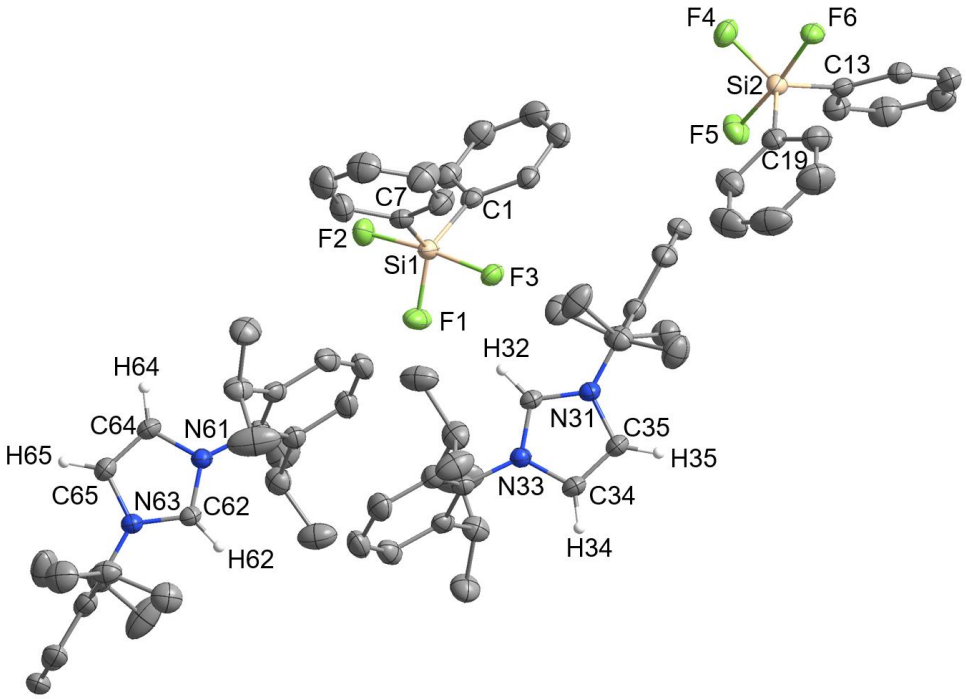


Figure S23 Crystal structure of the asymmetric unit of [IPrH][Ph_2SiF_3] (**3**). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.

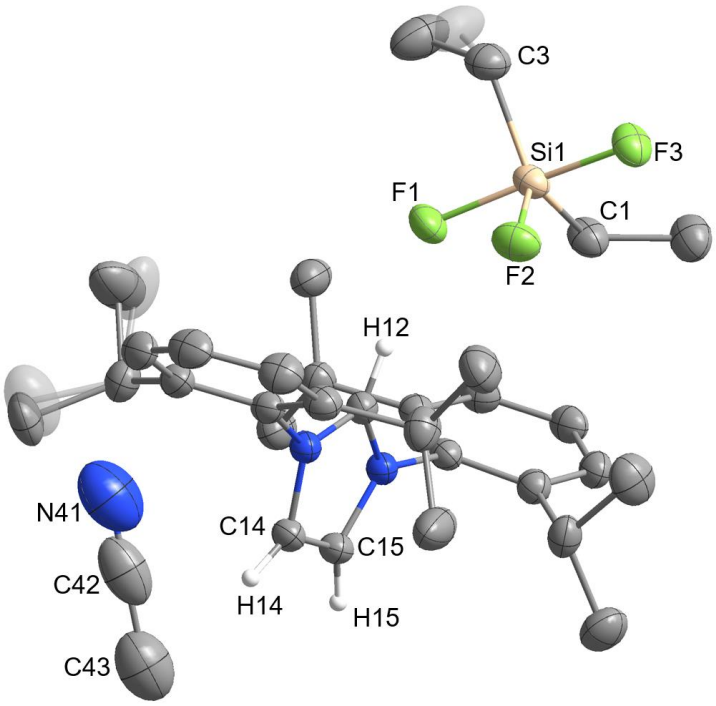


Figure S24 Crystal structure of the asymmetric unit of [IPrH][Et_2SiF_3]·MeCN (**4**·MeCN). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.

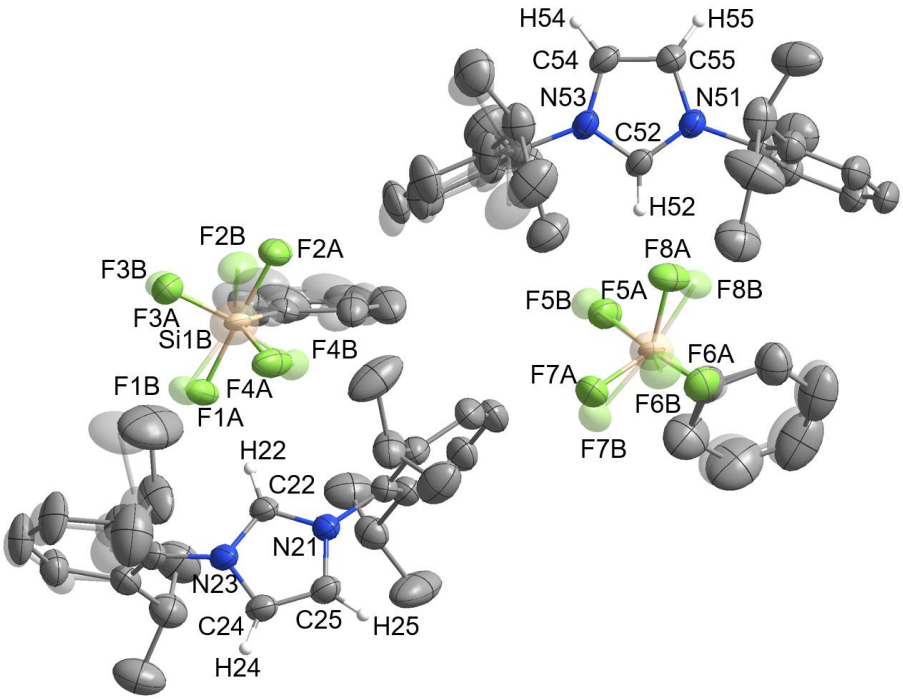
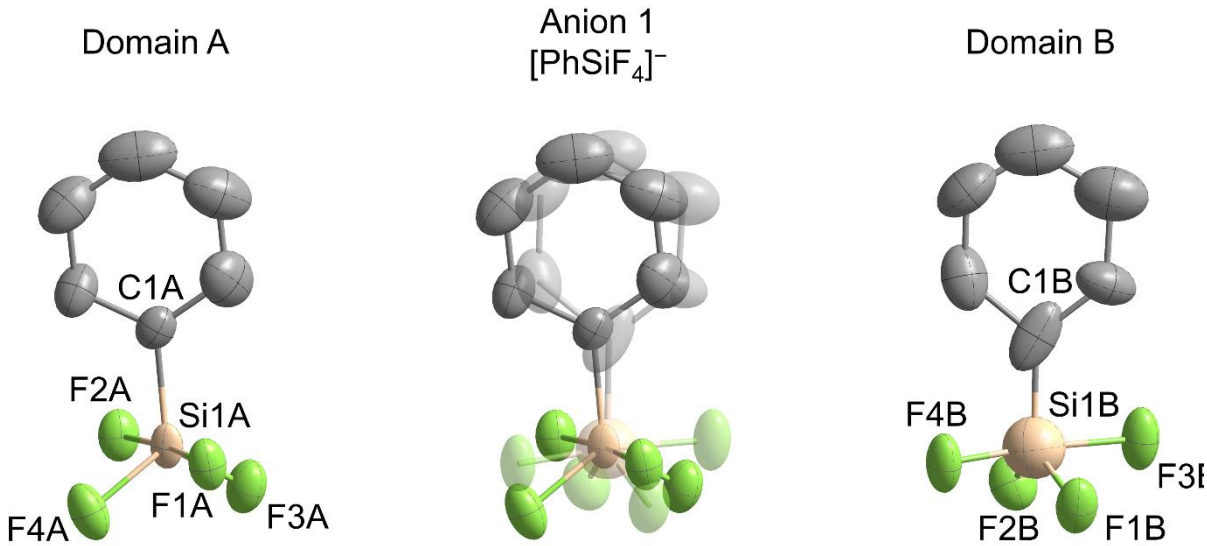
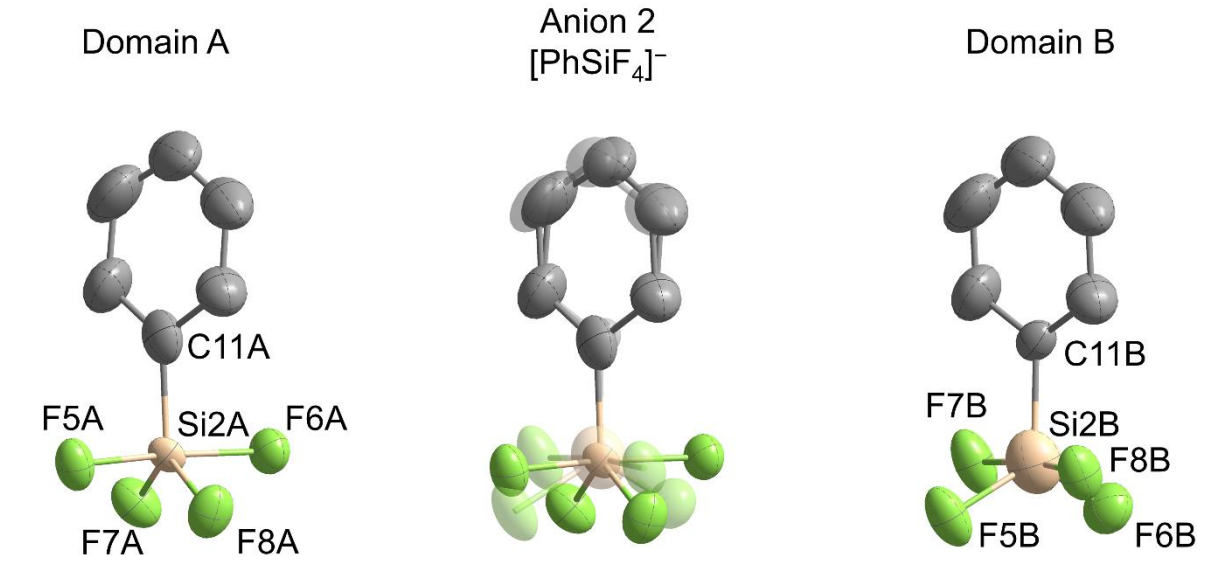


Figure S25 Crystal structure of the asymmetric unit of [IPrH][$PhSiF_4$] (**5**). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.



(a)



(b)

Figure S26 Structure of the disordered anions in the crystal structure of [IPrH][$PhSiF_4$] (**5**). (a) Disordered anion 1, and (b) disordered anion 2. The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, all hydrogen atoms are omitted. Central images represent the overlapping of domains A and B. For clarity, domain B is shaded in central images.

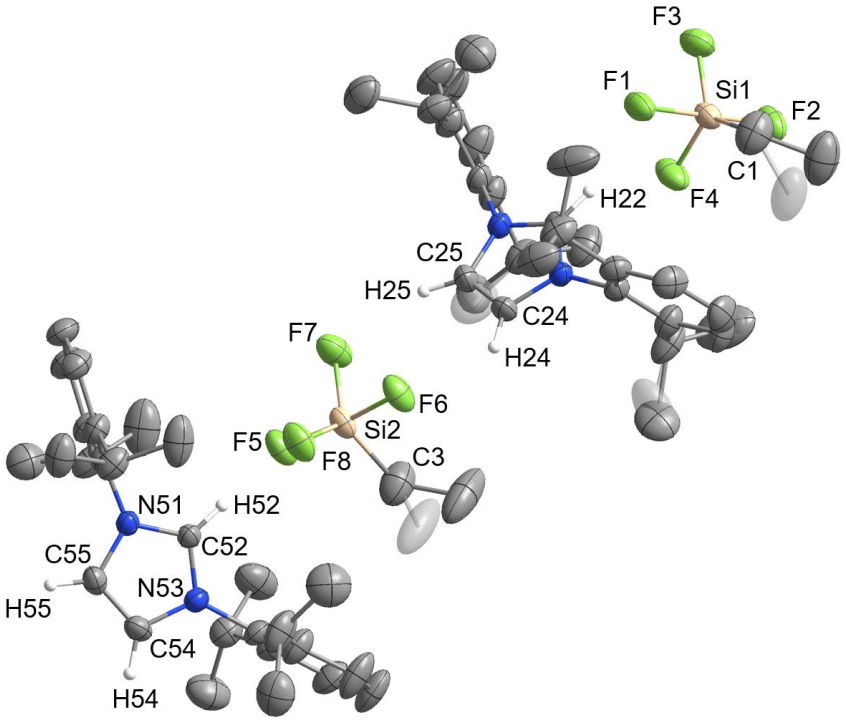


Figure S27 Crystal structure of the asymmetric unit of [IPrH][$EtSiF_4$] (**6**). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.

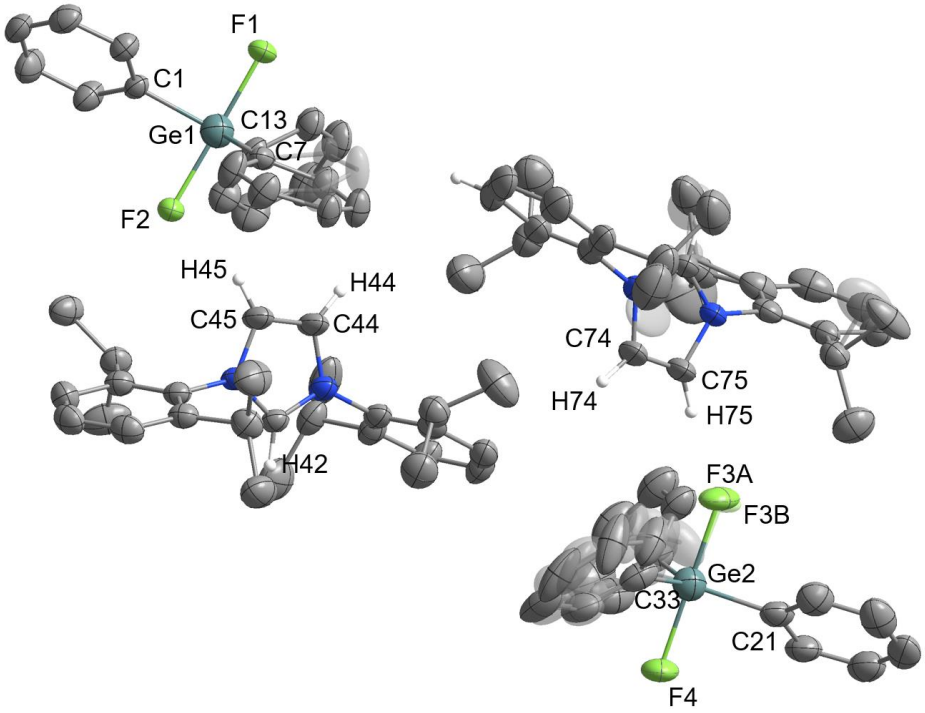


Figure S28 Crystal structure of the asymmetric unit of [IPrH][Ph_3GeF_2] (**7**). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.

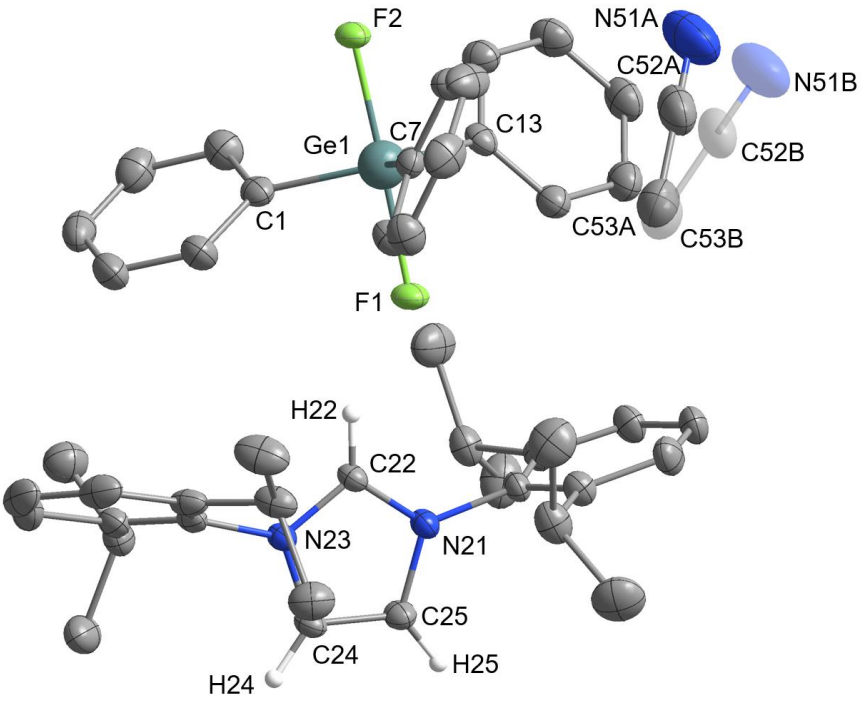


Figure S29 Crystal structure of the asymmetric unit of [IPrH][Ph_3GeF_2]·MeCN (**7a**). The ellipsoids are drawn at 50% probability. The positions of disordered atoms are shown in domains A and B. For clarity, domain B is shaded and all hydrogen atoms are omitted except for those on the imidazolium ring.

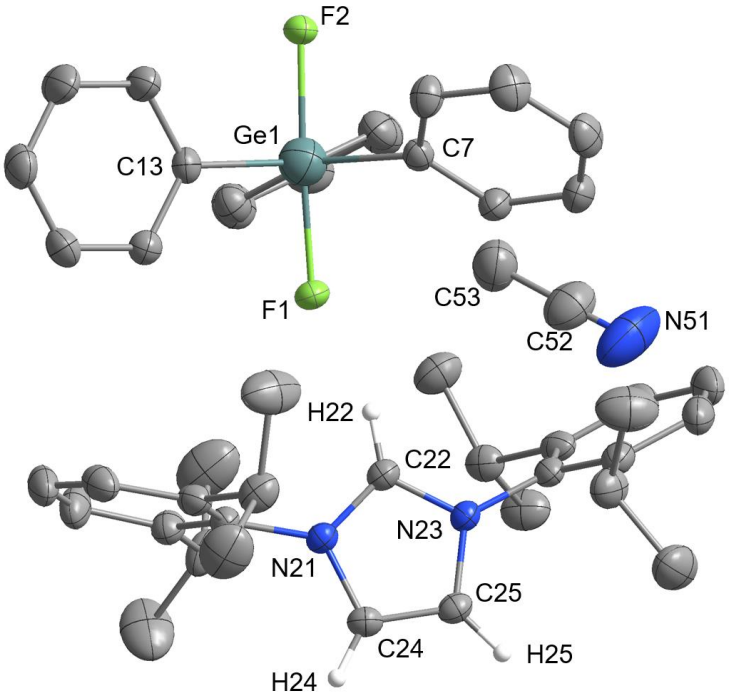


Figure S30 Crystal structure of the asymmetric unit of [IPrH][Ph_3GeF_2]·MeCN (**7b**). The ellipsoids are drawn at 50% probability. For clarity, all hydrogen atoms are omitted except for those on the imidazolium ring.

S4 Computational Results

Molecular calculations of the crystal structures were performed in gas-phase with the Gaussian 16 program[1] using the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional[2] and the D3 empirical dispersion correction of Grimme[3] with Becke−Johnson damping.[4] Electrons were described with all-electron basis sets. We used the triple-ζ basis set with polarization functions, in particular Def2-TZVP.[5,6]

Table S5 Experimental and Calculated Bond Distances of [IPrH][$Et_{4-n}SiF_{n+1}$] (n = 1−4).

Compound	*d*(Si–C) / Å		*d*(Si–F) / Å	
	Experimental	Calculated	Experimental	Calculated
[IPrH][Et_3SiF_2]	na	1.92 1.91 1.91	na	2.04[a,b] 1.71[a]
[IPrH][Et_2SiF_3]	1.875(2) 1.885(2)	1.90 1.90	1.733(1)[a,b] 1.729(1)[a] 1.648(1)[b]	1.87[a,b] 1.70[a] 1.69
[IPrH][$EtSiF_4$]	1.862(3)	1.90	1.701(1)[a,b] 1.672(1)[a] 1.618(1) 1.614(1)[b]	1.80[a,b] 1.68[a] 1.68 1.63
[IPrH][SiF_5][d]			1.62(1)[a,b,c] 1.644(4)[a,c] 1.59(1)[b,c] 1.594(4)[c] 1.585(4)[c]	1.74[a,b] 1.66[a] 1.66 1.64 1.62

[a] Axial position of fluorine atoms.
[b] Si–F distances, where fluorine atoms form the strongest hydrogen bonds with the hydrogen atom at C2 position.
[c] Si–C and Si–F distances for domain A, where the anions are disordered.
[d] Values reported in [7].

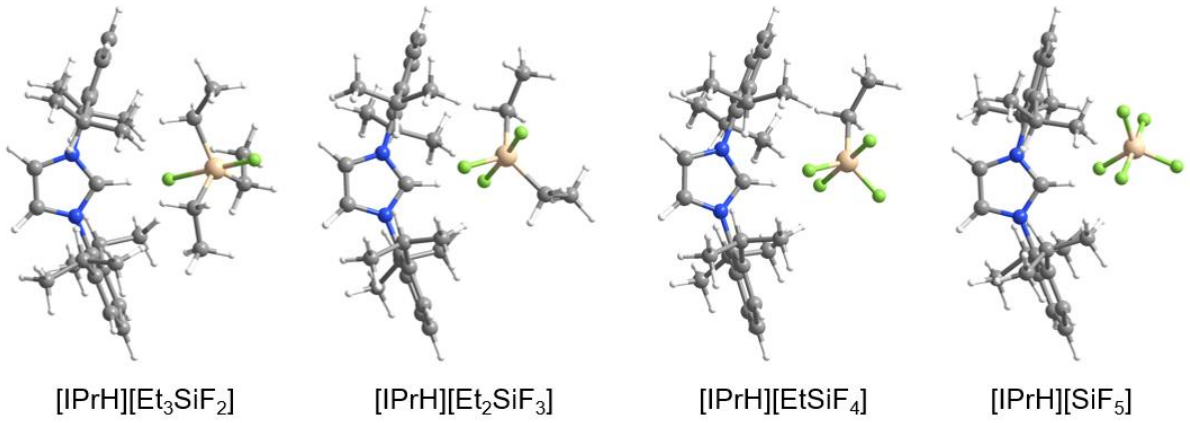


Figure S31 Optimized structures of [IPrH][$Et_{4-n}SiF_{n+1}$] (n = 1–4).

Table S6 Experimental and Calculated Bond Distances of [IPrH][$Ph_{4-n}GeF_{n+1}$] (n = 1–4) and [IPrH][$Et_{4-n}GeF_{n+1}$] (n = 1–4)

Compound	*d*(Si–C) / Å		*d*(Si–F) / Å	
	Experimental	Calcu-lated	Experimental	Calcu-lated
[IPrH] [Ph_3GeF_2]	1.946(3) 1.958(4) 1.949(3) 1.970(5) 1.963(3) 1.955(4)	1.99 1.99 1.98	1.930(1)[a,b] 1.939(9)[a,b,c] 1.923(1)[a] 1.935(2)[a]	2.07[a,b] 1.87[a]
[IPrH] [Ph_2GeF_3]	na	1.97 1.97	na	1.99[a,b] 1.84[a] 1.82
[IPrH] [$PhGeF_4$]	na	1.97	na	1.91[a,b] 1.82[a] 1.81 1.76
[IPrH] [GeF_5][d]			1.773(4)[a,b,c] 1.758(1)[c] 1.742(4)[b,c] 1.716(2)[c] 1.703(2)[c]	1.85[a,b] 1.78[a] 1.80 1.76 1.75
[IPrH] [Et_3GeF_2]	na	1.99 1.99 1.98	na	2.35[a,b] 1.85[a]
[IPrH] [Et_2GeF_3]	na	1.98 1.97	na	2.05[a,b] 1.85[a] 1.82
[IPrH] [$EtGeF_4$]	na	1.97	na	1.93[a,b] 1.82[a] 1.81 1.77
[IPrH] [GeF_5][d]			1.773(4)[a,b,c] 1.758(1)[c] 1.742(4)[b,c] 1.716(2)[c] 1.703(2)[c]	1.85[a,b] 1.78[a] 1.80 1.76 1.75

[a] Axial position of fluorine atoms.
[b] Ge–F distances, where fluorine atoms form the strongest hydrogen bonds with the hydrogen atom at C2 position.
[c] Ge–C and Ge–F distances for domain A, where the anions are disordered.
[d] Values reported in [7].

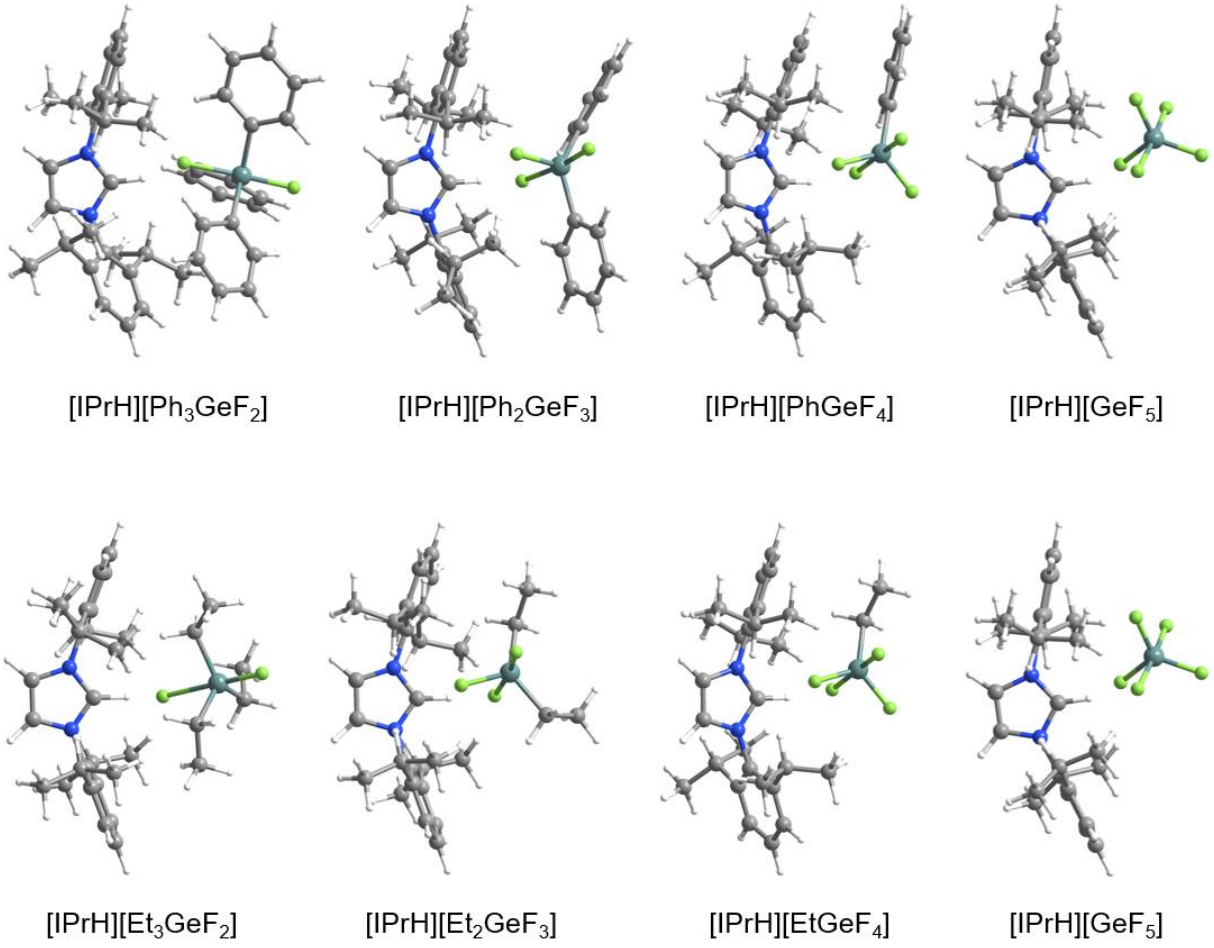


Figure S32 Optimized structures of [IPrH][$Ph_{4-n}GeF_{n+1}$] (n = 1–4) and [IPrH][$Et_{4-n}GeF_{n+1}$] (n = 1–4).

Table S7 Calculated electronic energies (*E*) at the PBE/def2TZVP level of theory and calculated energies of reactions Δ*E* in a.u. and kJ/mol.

Compound	*E* / a.u.	Reaction	Δ*E* / a.u.	Δ*E* / kJ/mol
[IPrH][F]	−1259.4111232			
Et_3SiF	−626.67114995			
Et_2SiF_2	−647.39000789			
$EtSiF_3$	−668.10336467			
SiF_4	−688.81168744			
Ph_3SiF	−1083.5715290			
Ph_2SiF_2	−951.98720139			
$PhSiF_3$	−820.40216887			
Et_3GeF	−2413.9706465			
Et_2GeF_2	−2434.6670501			
$EtGeF_3$	−2455.3540030			
GeF_4	−2476.0264617			
Ph_3GeF	−2870.8679849			
Ph_2GeF_2	−2739.2614349			
$PhGeF_3$	−2607.6499366			
[IPrH][Et_3SiF_2] (**2**)	−1886.0989692	Et_3SiF + [IPrH][F] → [IPrH][Et_3SiF_2]	−0.0166960	**−44**
[IPrH][Et_2SiF_3] (**4**)	−1906.8287845	Et_2SiF_2 + [IPrH][F] → [IPrH][Et_2SiF_3]	−0.0276534	**−73**
[IPrH][$EtSiF_4$] (**6**)	−1927.5507372	$EtSiF_3$ + [IPrH][F] → [IPrH][$EtSiF_4$]	−0.0362493	**−95**
[IPrH][SiF_5]	−1948.2696837	SiF_4 + [IPrH][F] → [IPrH][SiF_5]	−0.0468731	**−123**
[IPrH][Ph_3SiF_2] (**1**)	−2343.0148273	Ph_3SiF + [IPrH][F] → [IPrH][Ph_3SiF_2]	−0.0321751	**−84**
[IPrH][Ph_2SiF_3] (**3**)	−2211.4377454	Ph_2SiF_2 + [IPrH][F] → [IPrH][Ph_2SiF_3]	−0.0394208	**−103**
[IPrH][$PhSiF_4$] (**5**)	−2079.8560493	$PhSiF_3$ + [IPrH][F] → [IPrH][$PhSiF_4$]	−0.0427572	**−112**
[IPrH][SiF_5]	−1948.2696837	SiF_4 + [IPrH][F] → [IPrH][SiF_5]	−0.0468731	**−123**
[IPrH][Et_3GeF_2] (**7**)	−3673.4042062	Et_3GeF + [IPrH][F] → [IPrH][Et_3GeF_2]	−0.0224365	**−59**
[IPrH][Et_2GeF_3]	−3694.1140978	Et_2GeF_2 + [IPrH][F] → [IPrH][Et_2GeF_3]	−0.0359245	**−94**
[IPrH][$EtGeF_4$]	−3714.8103514	$EtGeF_3$ + [IPrH][F] → [IPrH][$EtGeF_4$]	−0.0452252	**−119**
[IPrH][GeF_5]	−3735.5005421	GeF_4 + [IPrH][F] → [IPrH][GeF_5]	−0.0629572	**−165**
[IPrH][Ph_3GeF_2]	−4130.3124792	Ph_3GeF + [IPrH][F] → [IPrH][Ph_3GeF_2]	−0.0333711	**−88**
[IPrH][Ph_2GeF_3]	−3998.7176148	Ph_2GeF_2 + [IPrH][F] → [IPrH][Ph_2GeF_3]	−0.0450567	**−118**
[IPrH][$PhGeF_4$]	−3867.1121370	$PhGeF_3$ + [IPrH][F] → [IPrH][$PhGeF_4$]	−0.0510772	**−134**
[IPrH][GeF_5]	−3735.5005421	GeF_4 + [IPrH][F] → [IPrH][GeF_5]	−0.0629572	**−165**

S5 Mass Spectrometry

S5.1 [IPrH][Ph$_3$SiF$_2$] (1)

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT (Norm)	C	H	N	F	28Si
297.0908	297.0911	-0.3	-1.0	11.5	C18 H15 F2 28Si	348.1	1.2	18	15		2	1
	297.0848	6.0	20.2	15.5	C19 H13 N2 28Si	348.0	1.1	19	13	2		1
	297.0828	8.0	26.9	16.5	C20 H10 N2 F	347.9	1.0	20	10	2	1	

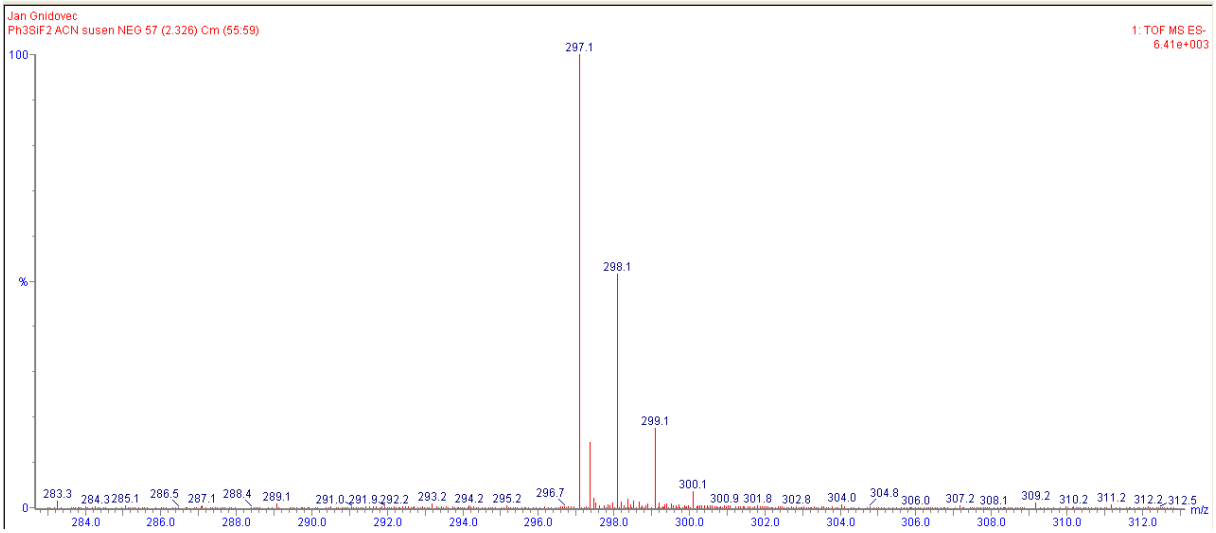


Figure S33 Mass spectrum of [IPrH][Ph$_3$SiF$_2$] (**1**).

S5.2 [IPrH][Ph$_2$SiF$_3$] (3)

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT (Norm)	C	H	N	F	28Si
239.0511	239.0504	0.7	2.9	7.5	C12 H10 F3 28Si	518.3	1.8	12	10		3	1
	239.0484	2.7	11.3	8.5	C13 H7 F4	518.2	1.7	13	7		4	
	239.0441	7.0	29.3	11.5	C13 H8 N2 F 28Si	518.4	1.9	13	8	2	1	1
	239.0421	9.0	37.6	12.5	C14 H5 N2 F2	518.3	1.8	14	5	2	2	
	239.0609	-9.8	-41.0	15.5	C17 H7 N2	518.0	1.5	17	7	2		
	239.0628	-11.7	-48.9	3.5	C8 H11 N2 F4 28Si	519.1	2.6	8	11	2	4	1

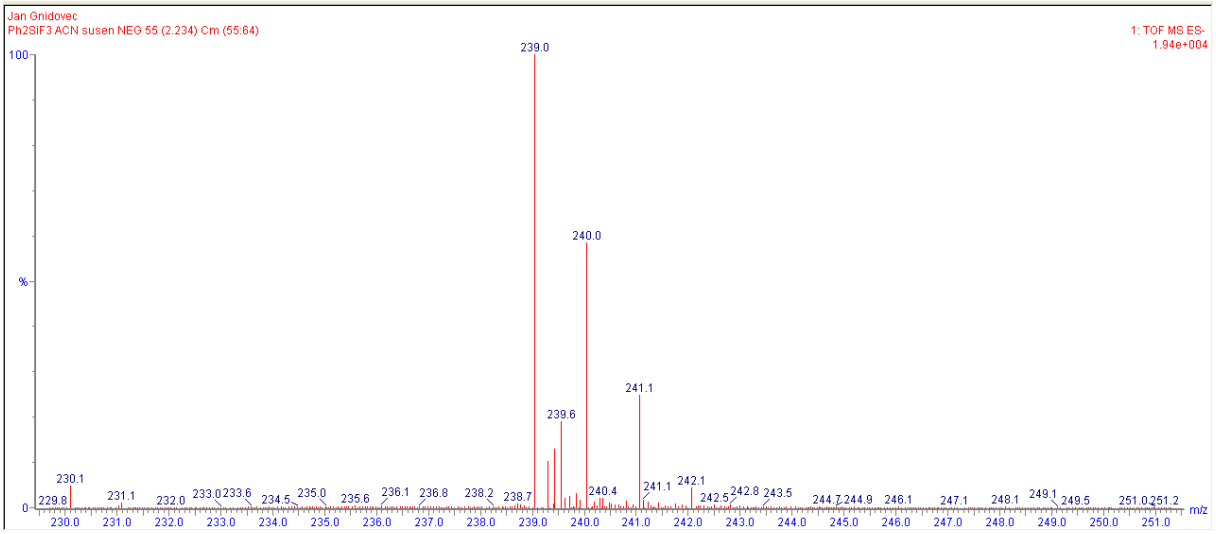


Figure S34 Mass spectrum of [IPrH][Ph$_2$SiF$_3$] (**3**).

S5.3 [IPrH][Et$_2$SiF$_3$] (4)

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT (Norm)	C	H	N	F	28Si
143.0500	143.0504	-0.4	-2.8	-0.5	C4 H10 F3 28Si	608.9	1.1	4	10		3	1
	143.0484	1.6	11.2	0.5	C5 H7 F4	609.0	1.2	5	7		4	
	143.0609	-10.9	-76.2	7.5	C9 H7 N2	609.7	1.9	9	7	2		
	143.0421	7.9	55.2	4.5	C6 H5 N2 F2	609.9	2.1	6	5	2	2	
	143.0441	5.9	41.2	3.5	C5 H8 N2 F 28Si	610.1	2.3	5	8	2	1	1

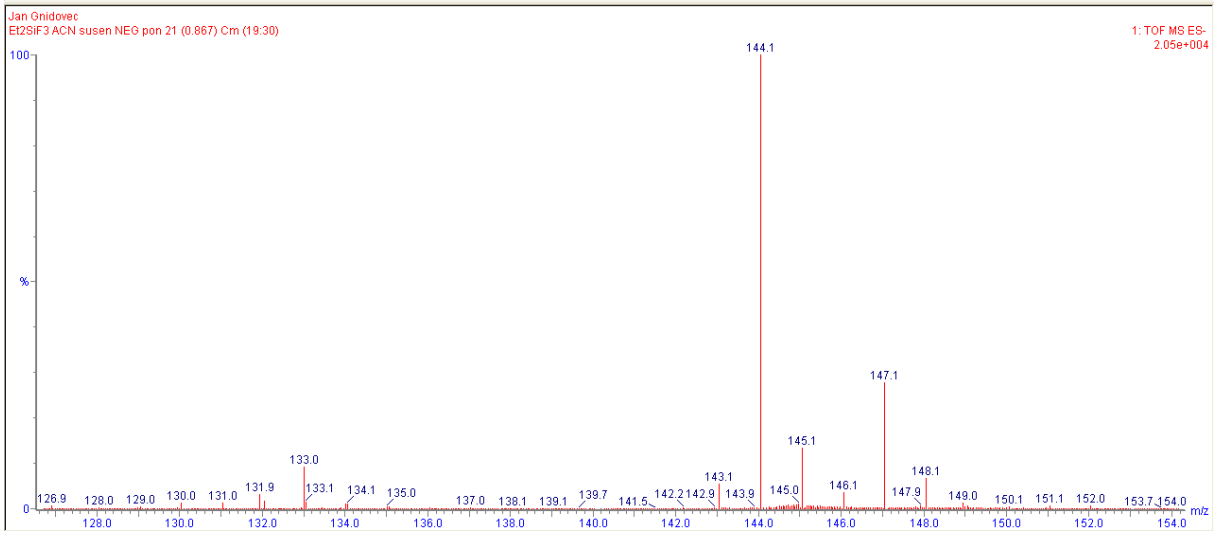


Figure S35 Mass spectrum of [IPrH][Et$_2$SiF$_3$] (**4**).

S5.4 [IPrH][EtSiF$_4$] (6)

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT (Norm)	C	H	N	F	28Si
133.0089	133.0097	-0.8	-6.0	-0.5	C2 H5 F4 28Si	470.0	2.3	2	5		4	1
	133.0034	5.5	41.4	3.5	C3 H3 N2 F2 28Si	470.3	2.6	3	3	2	2	1
	133.0014	7.5	56.4	4.5	C4 N2 F3	470.0	2.3	4		2	3	
	133.0202	-11.3	-85.0	7.5	C7 H2 N2 F	469.3	1.6	7	2	2	1	
	133.0078	1.1	8.3	11.5	C11 H	468.4	0.7	11	1			

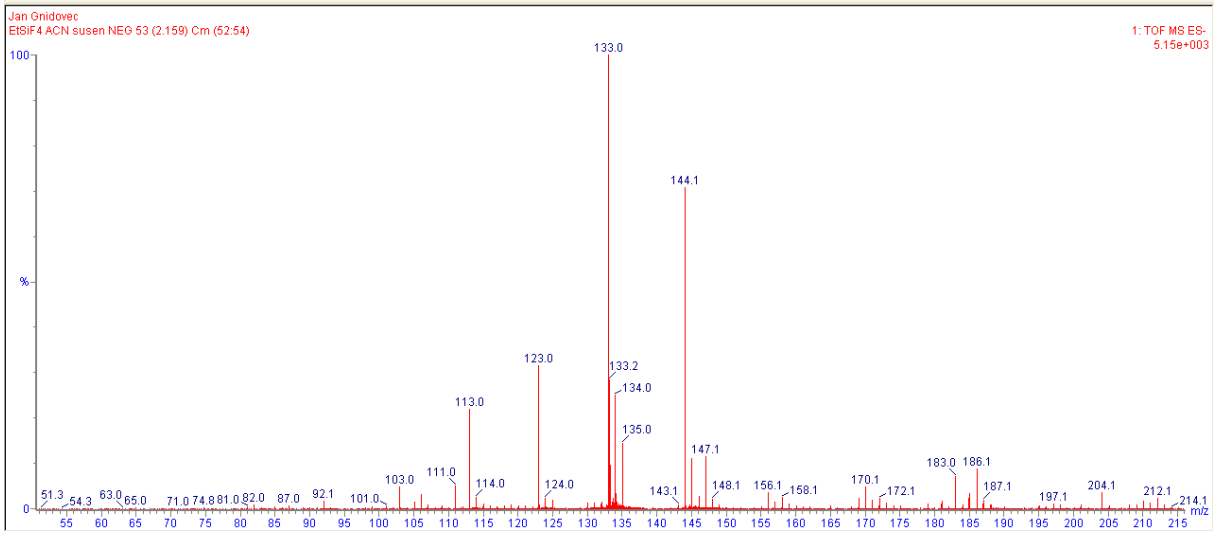


Figure S36 Mass spectrum of [IPrH][Et$_2$SiF$_3$] (**6**).

S5.6 [IPrH][Ph$_3$GeF$_2$] (7)

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT (Norm)	C	H	N	F	74Ge
343.0364	343.0354	1.0	2.9	10.5	C18 H15 F2 74Ge	178.2	1.5	18	15		2	1
	343.0291	7.3	21.3	14.5	C19 H13 N2 74Ge	178.2	1.6	19	13	2		1
	343.0359	0.5	1.5	22.5	C25 H5 F2	177.9	1.2	25	5		2	
	343.0296	6.8	19.8	26.5	C26 H3 N2	178.0	1.3	26	3	2		

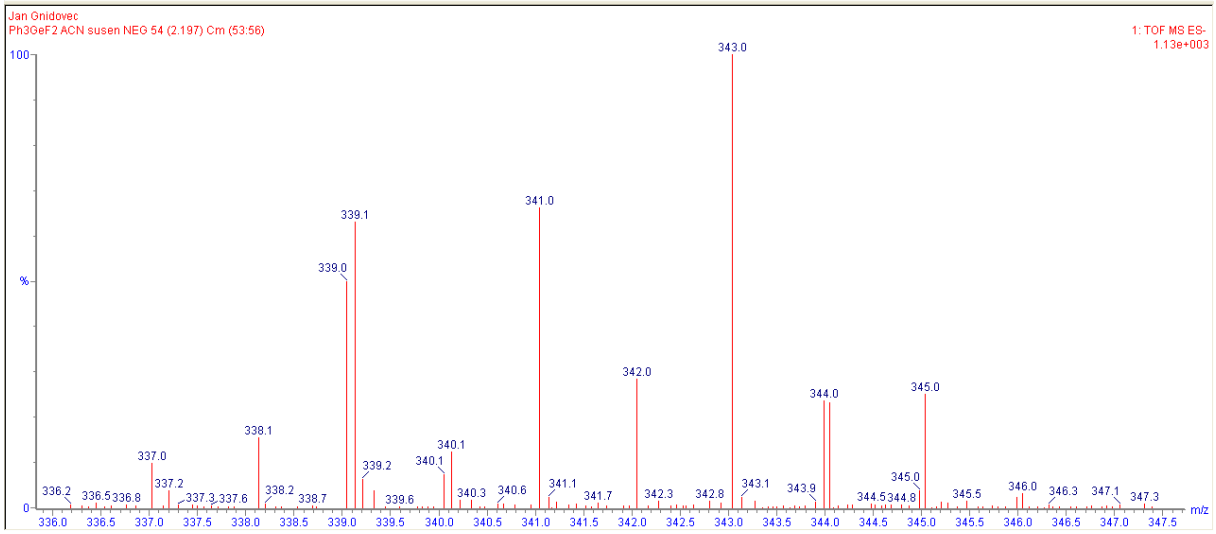


Figure S37 Mass spectrum of [IPrH][Ph$_3$GeF$_2$] (**7**).

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