Supplementary Material (ESI) for Chemical Communications

Supplementary Information

for

Isolating Fluorinated Carbocations

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(19 pages)

General. All operations were performed using helium filled donor solvent glovebox or non-donor glovebox or chloro glovebox, according to the chemicals used (O_2, H_20 <5 ppm) or by using Schlenk techniques. All glassware was dried at 160˚C for 12 hours before use. Et_3SiH, $C_6H_5CF_3$, p-$CH_3C_6F_4CF_3$, p-$FC_6H_4CF_3$, CH_3CN, o-$Cl_2C_6H_4$, $C_6H_5CH_3$ and C_6H_5F were purchased from Aldrich, purified by literature methods methods (Perin, D. D.; Armarego, W. F. L.; Perrin, D. R. Purification of Laboratory Chemicals; 2nd Ed.; Pergamon; Sydney, 1980) and distilled under argon prior to use. CH_3CF_3 was purchased from Synquest Labs and used as received. $Et_3Si(CHB_{11}Cl_{11})$ and $Ag(CHB_{11}I_{11})$ were prepared according to previous procedures. NMR spectra were recoded on Varian 500 or Bruker 300 spectrometers for ^1H, ^{13}C, ^{11}B NMR, and ^{19}F (referenced externally to $C_6H_5CF_3$) and. IR spectra were recorded on a Shimadzu FTIR-8300 placed inside a glovebox filled with nitrogen. GCMS data were obtained with the use of a Hewlett-Packard 5989A instrument. The $[(p\text{-}C_6H_5F)_2CF]^+$, $[(p\text{-}C_6H_5F)(CH_3)CF^+]$ and $[(p\text{-}C_6H_5F)_3C]^+$ cations were identified by their NMR spectra as previously reported.[1-3]

1. H. Volz and W. D. Mayer, *Liebigs Ann. Chem*. 1981, 1407-1414.
2. H. Volz and H.-J Streicher, *Tetrahedron*, 1977, **33**, 3133-3135.
3. Pozdnyakovich, Y. V.; Shteingarts, V. D. *J. Fluorine Chem.* 1974, 297-316.

Preparation of $Ph_3C(CHB_{11}I_{11})$

A solution of Ph_3CBr (0.59 g, 1.83 mmol) in $C_6H_5CH_3$ (10 mL) was added with stirring to a solution of $AgCHB_{11}I_{11}$ (1.00 g, 0.61 mmol) in $C_6H_5CH_3$:CH_3CN (50:30 mL) over 30 min. The mixture was stirred at room temperature for 1h and at 70˚C for 5 days inside the glovebox. After this time, it was brought to room temperature, filtered to remove AgBr, washed with $C_6H_5CH_3$:CH_3CN (10:10 mL), and the volume was reduced to 20 mL to precipitate a dark red solid. This was filtered and dried at high vacuum for 12 h to give 46% of $Ph_3C(CHB_{11}I_{11})$ (0.50 g, 0.28 mmol). ^1H NMR (δ ppm in $CDCl_3$): 3.60 (s, 1H, CH), 7.77 (d, 6H, Ph), 7.97 (t, 6H, Ph), 8.02 (t, 3H, Ph), ^{11}B NMR (δ ppm in $CDCl_3$): -8.5 (1B), -11.0 (5B), -18.0(5B), IR (KBr, cm^{-1}): 3051, 3003, 1578, 1479, 1448, 1353, 1293, 1181, 1092, 993, 916, 765, 700, 607.

Preparation of $Et_3Si(CHB_{11}I_{11})$

$Ph_3C(CHB_{11}I_{11})$ (0.30 g, 0.17 mmol) was suspended in o-dichlorobenzene (10 mL) and excess of Et_3SiH (0.4 mL) was added with stirring. After 7 days, the solution had turned completely colorless from the original dark red. Upon addition of hexanes (15 mL) a white precipitate formed, filtered and washed with more hexanes (10 mL) and dried under high vacuum for 12h to give $Et_3Si(CHB_{11}I_{11})$ in 29% yield (0.08 g, 0.05 mmol) ^1H NMR (δ ppm in SO_2): 2.49 (br s, 15H), 5.1 (br s, 1H); ^{11}B NMR (δ ppm in SO_2): -8.8 (1B), -13.1 (5B), -19.8(5B); IR (KBr, cm^{-1}): 3042, 2959, 2872, 1660, 1451, 1395, 1379, 1222, 1087, 1019, 915, 834, 739, 560.

Reaction between $Et_3Si(CHB_{11}I_{11})$ and $(p\text{-}FC_6H_4)CF_3$.
Inside the glovebox, freshly prepared $Et_3Si(CHB_{11}I_{11})$ (400 mg, 0.24 mmol) was dissolved in C_6H_5F (0.3 mL) in a J-young NMR tube and cooled down to -40˚C. $(p\text{-}FC_6H_4)CF_3$ (500 μL) was syringed in and the mixture warmed up slowly to room temperature. An exothermic reaction occurred and the color of the mixture changed from colorless to orange. In addition to the peaks of the reactant and solvent (-61.1, -106.5 and -112.0), ^{19}F NMR spectroscopy showed (Figure S1) the formation of Et_3SiF (173.9 ppm) and the resonances corresponding to the formation of $[(p\text{-}C_6H_4F)_2CF]^+[CHB_{11}I_{11}^-]$ (see below for values of this compound). After 12 h, new resonances for Et_2SiF_2 (146 ppm) and $[(p\text{-}C_6H_4F)_3C]^+[CHB_{11}I_{11}^-]$ (Figure S2) appeared. Upon layering with hexanes and after 15 days two kind of crystals, yellow and orange, were deposited in the interface which were analyzed by X-ray crystallography to be $[(p\text{-}C_6H_4F)_2CF^+][CHB_{11}I_{11}^-]\cdot C_6H_5F$, **1**, and $[(p\text{-}C_6H_4F)_3C^+]$ $[CHB_{11}I_{11}^-]\cdot 1.5C_6H_5F$, **3**, respectively.
$[(p\text{-}C_6H_4F)_2CF^+][CHB_{11}I_{11}^-]$. ^{19}F NMR (δ ppm in C_6H_5F): +5.1 (t, C^+-F) ($J_{H\text{-}F}$ = 10 Hz), -67.8 (m) (C_6H_5F), ^{11}B NMR (δ ppm in C_6H_5F): -1.9 (1B), -9.4 (5B), -12.4 (5B), IR (KBr): 3105, 3025, 1589, 1578, 1493, 1483, 1438, 1430, 1406, 1365, 1266, 1229, 1155, 1121, 1033, 1011, 935, 531 (Figure S3, S4).
$[(p\text{-}C_6H_4F)_3C^+][CHB_{11}I_{11}^-]$. ^{19}F NMR (δ ppm in C_6H_5F): -81.7 (s) (C_6H_5F), ^{11}B NMR (δ ppm in C_6H_5F): -0.9 (1B), -9.3 (5B), -19.5 (5B).

Reaction between $Et_3Si(CHB_{11}I_{11})$ and CH_3CF_3.
Freshly prepared $Et_3Si(CHB_{11}I_{11})$ (400 mg, 0.24 mmol) was dissolved in C_6H_5F (0.2 mL) in a J-young NMR tube and cooled down to -78˚C. CH_3CF_3 (0.3 mL) was vacuum transferred into the solution. The mixture was slowly warmed up to -20˚C during which time a reaction occurred and the color of the mixture changed from colorless to deep orange, while deep orange solid precipitated in the bottom of the tube. After 10 days upon standing at -20˚C, crystals of $[(p\text{-}C_6H_4F)(CH_3)CF^+][CHB_{11}I_{11}^-]$, **2**, had been formed which were analyzed by X-ray crystallography.
$[(p\text{-}C_6H_4F)(CH_3)CF^+][CHB_{11}I_{11}^-]$. ^{19}F NMR (δ ppm in C_6H_5F, -25˚C): +32.2 (C-F_a), -46.2 (C_6H_5F), ^{11}B NMR (δ ppm in C_6H_5F, -25˚C): -5.1 (1B), -9.3 (5B), -19.6 (5B), IR (KBr, cm^{-1}): 3383, 3227, 3002, 2959, 1697, 1593, 1508, 1488, 1457, 1257, 1189, 1158, 1094, 1033, 917, 877, 845, 642 (Figure S5).

Reaction between $Et_3Si(CHB_{11}Cl_{11})$ and $p\text{-}CH_3C_6F_4CF_3$.
The same procedure as for $(p\text{-}FC_6H_4)CF_3$ was followed, and crystals of $[(p\text{-}C_6H_4F)_2(p\text{-}CH_3C_6F_4)C^+][CHB_{11}Cl_{11}^-]$, **4**, grew after 3 weeks and were analyzed by X-ray crystallography.
$[(p\text{-}C_6H_4F)_2(p\text{-}CH_3C_6F_4)C]^+[CHB_{11}Cl_{11}^-]$. ^{19}F NMR (δ ppm in o-$C_6D_4Cl_2$): -70.9 (s, p-C_6H_5F), -129.1, (m, $C_6F_4CH_3$), -135.0 (m, $C_6F_4CH_3$) (Figure S6), ^1H NMR (δ ppm in o-$C_6D_4Cl_2$): 2.31 (s, 3H, CH_3), 3.04 (s, 1H, CH), 6.99 (s, 2H, C_6H_4F), 7, 25 (s, 2H, C_6H_4F) (Figure S7), ^{11}B NMR (δ ppm in o-$C_6D_4Cl_2$): -2.2 (s, 1B), -9.7 (s, 5B), -12.8 (s, 5B) (Figure S8).

Figure S1: ^{19}F NMR of the reaction between $Et_3Si(CHB_{11}Cl_{11})$ and p-$FC_6H_4CF_3$ in C_6H_5F after 10 min.

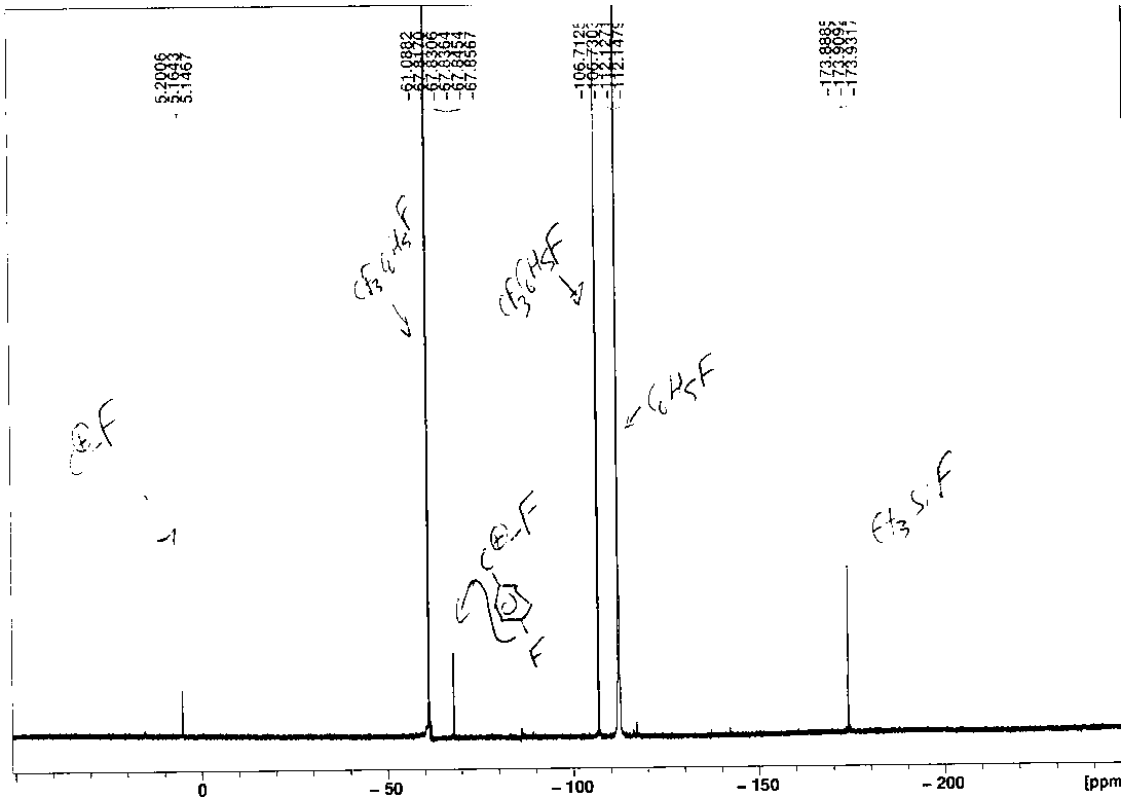

Figure S2: ^{19}F NMR of the reaction between $Et_3Si(CHB_{11}Cl_{11})$ and p-$FC_6H_4CF_3$ in C_6H_5F after 4 days.

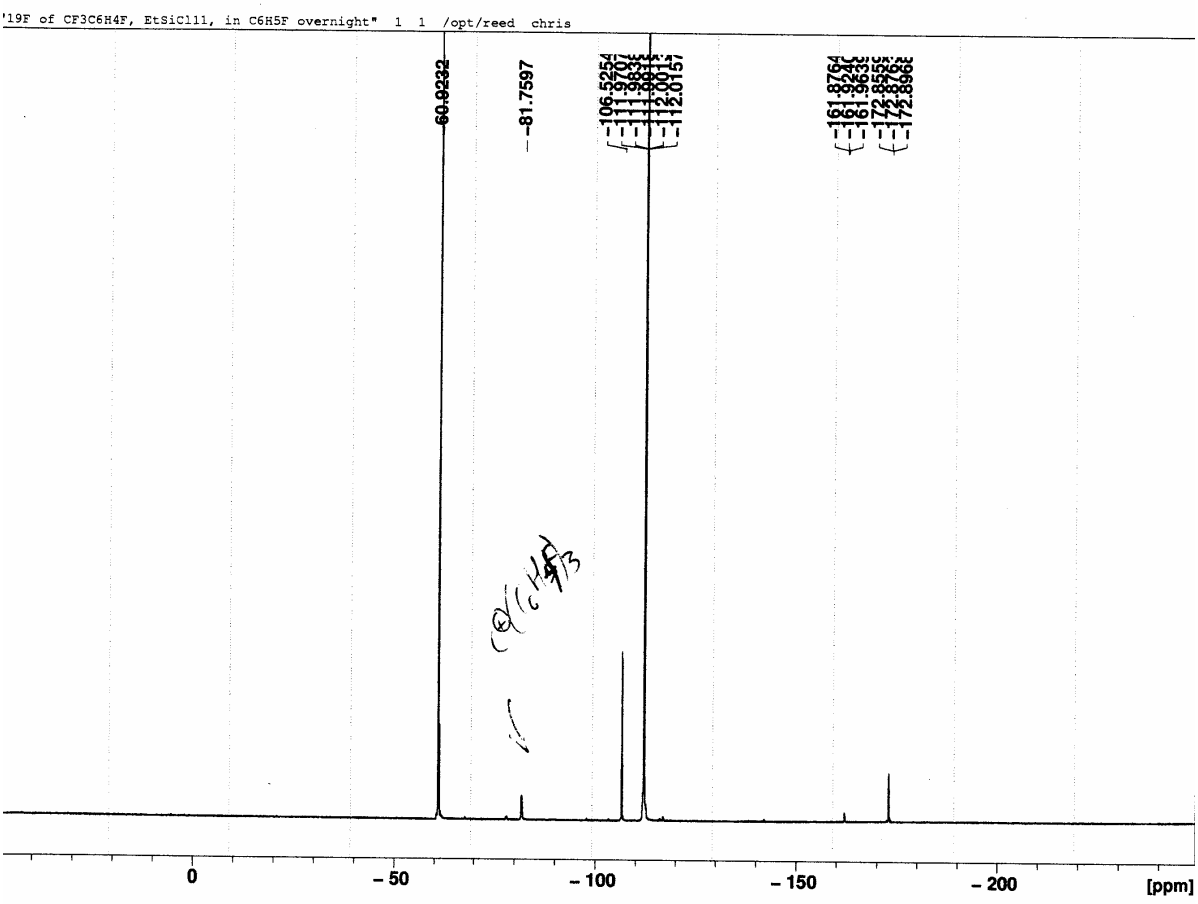

Figure S3: IR of the $[(C_6H_4F)_2CF]^+[CHB_{11}I_{11}^-]$ crystal in KBr.

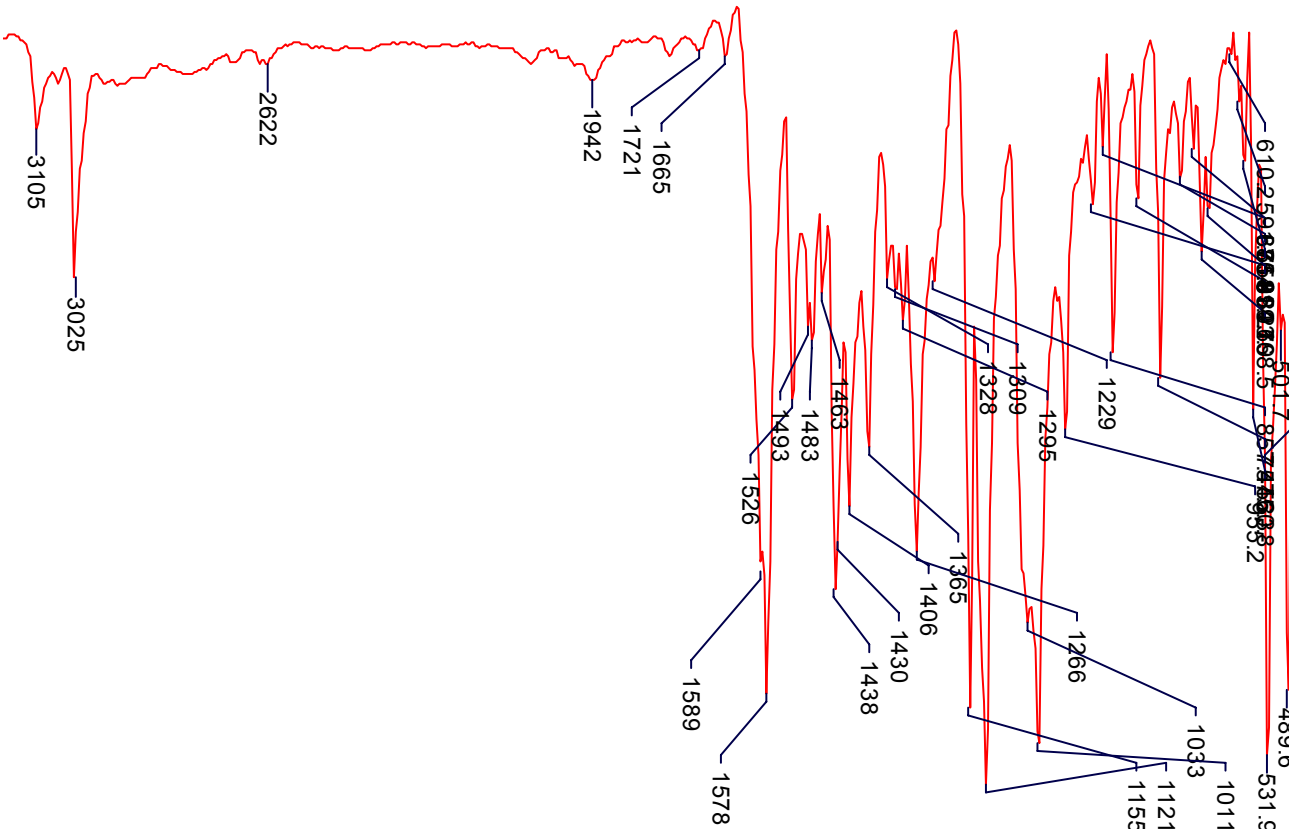

Figure S4: IR of the $[(C_6H_4F)_2CF]^+$ in KBr where the anion peaks have been subtracted from the original spectrum of the crystal.

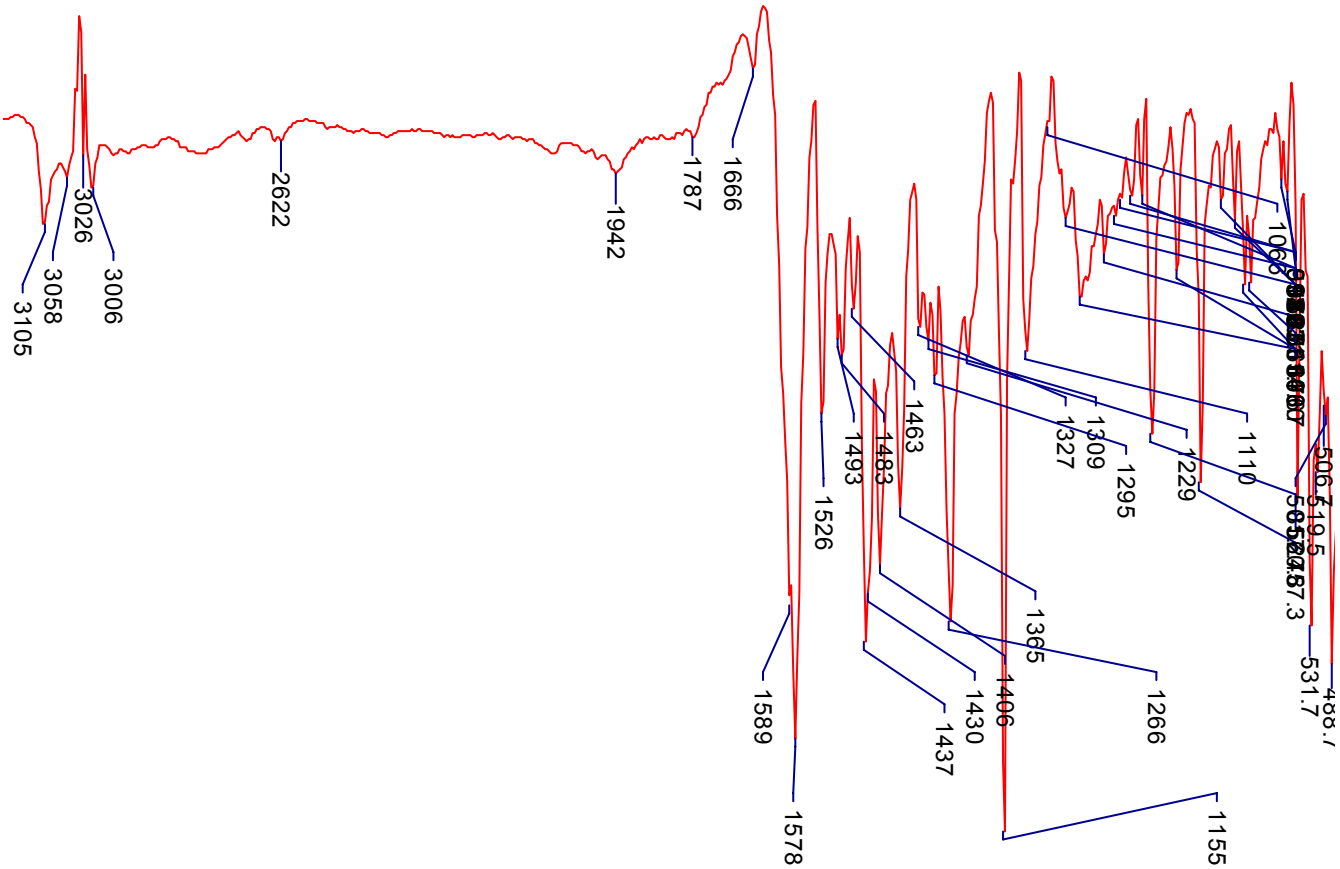

Figure S5: IR spectrum of [(p-C_6H_5F)(CH_3)CF^+] in the frequency range of stretch CH_3 vibrations. Very broad and intense absorption indicate to the strong H-bonding of CH_3 group with iodine atoms of the counterion. Band marked with asterisk can arise from Fermi-resonance with overtone 2νCC.

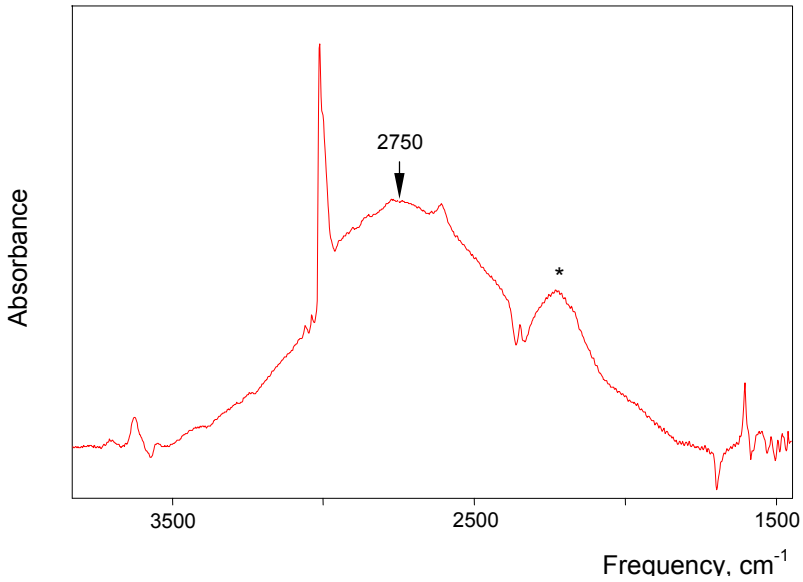

Figure S6: ^{19}F NMR of $[(p\text{-}C_6F_4CH_3)(C_6H_4F)_2C]^+[CHB_{11}Cl_{11}^-]$ in o-dichlorbenzene-*d*.

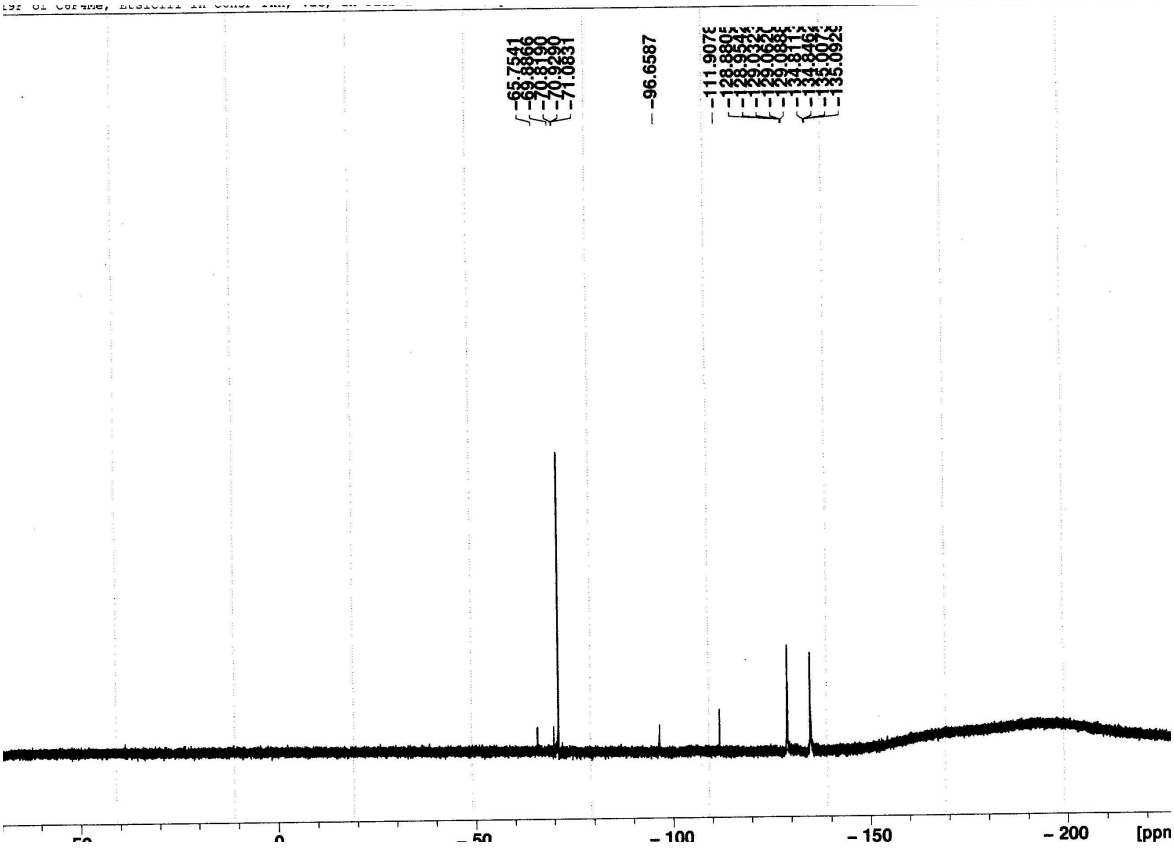

Figure S7: ^{1}H NMR of $[(p\text{-}C_6F_4CH_3)(C_6H_4F)_2C]^+[CHB_{11}Cl_{11}^-]$ in o-dichlorobenzene-*d*.

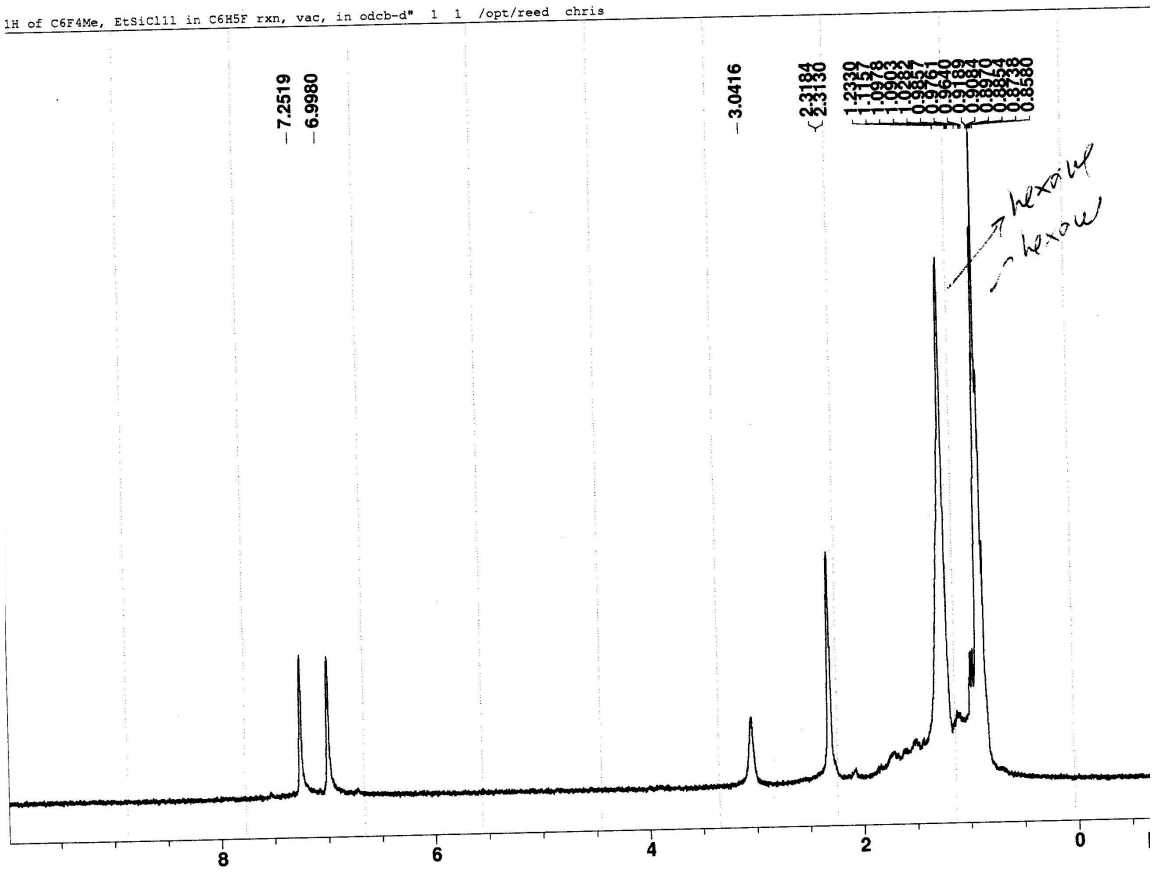

Figure S8: ^{11}B NMR of $[(p\text{-}C_6F_4CH_3)(C_6H_4F)_2C]^+[CHB_{11}Cl_{11}^-]$ in o-dichlorobenzene-*d*.

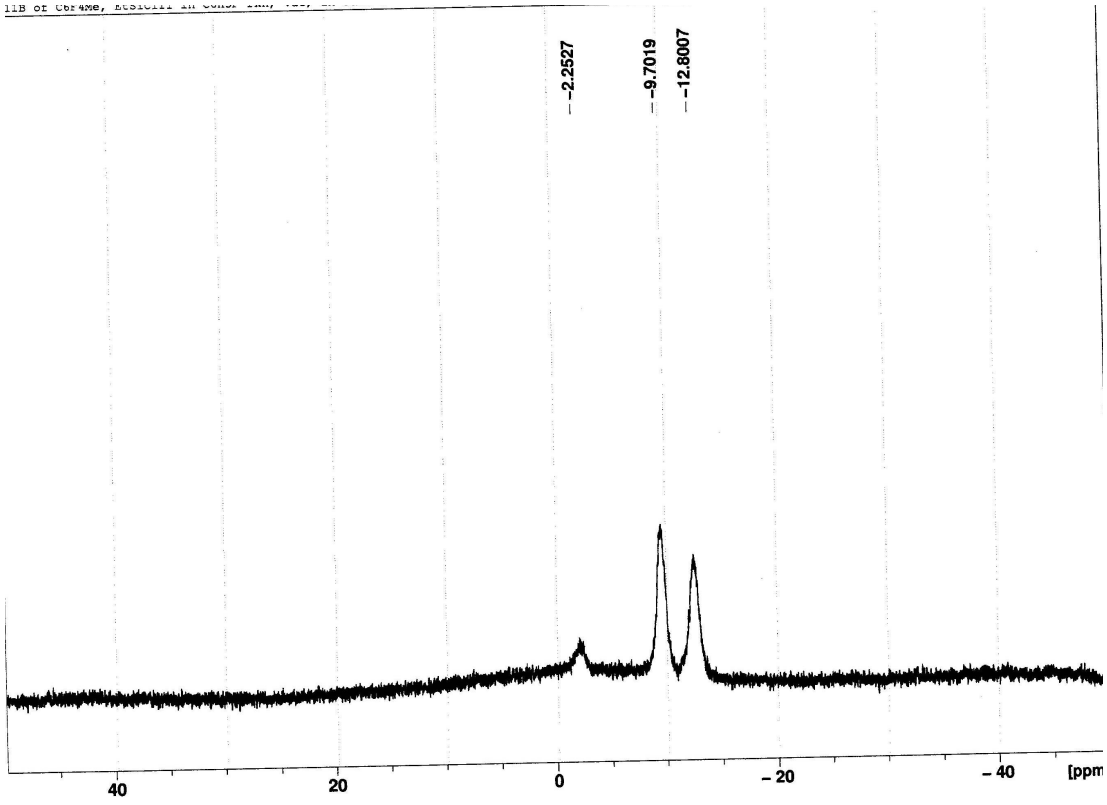

Figure S9: Crystal structure and atomic numbering of $[(p\text{-}C_6H_4F)_2CF][CHB_{11}I_{11}]\cdot C_6H_5F$, **1**. Thermal ellipsoids are shown at the 50% probability level.

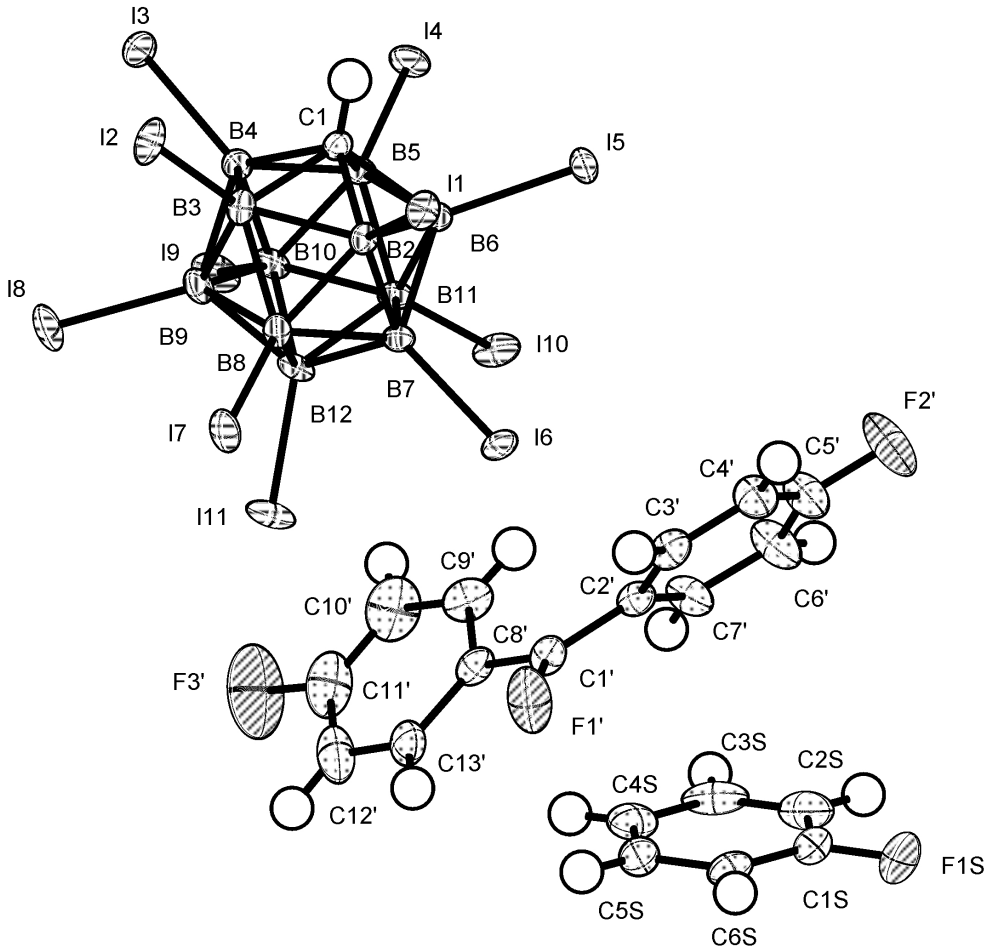

Table S1. Crystal data and structure refinement for $[(p\text{-}C_6H_4F)_2CF][CHB_{11}I_{11}]\cdot C_6H_5F$, **1**.

Identification code	cr231_0m	
Empirical formula	C20 H14 B11 F4 I11	
Formula weight	1845.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9226(2) Å	α= 81.5320(6)°.
	b = 14.4389(2) Å	β= 85.2332(6)°.
	c = 14.8328(2) Å	γ = 76.9732(6)°.
Volume	2045.10(6) $Å^3$	
Z	2	
Density (calculated)	2.996 Mg/m^3	
Absorption coefficient	8.366 mm^{-1}	
F(000)	1616	
Crystal size	0.27 x 0.23 x 0.12 mm^3	
Theta range for data collection	1.46 to 43.11°.	
Index ranges	-19<=h<=19, -27<=k<=27, -28<=l<=28	
Reflections collected	180818	
Independent reflections	30004 [R(int) = 0.0337]	
Completeness to theta = 43.11°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4463 and 0.2102	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	30004 / 291 / 541	
Goodness-of-fit on F^2	1.105	
Final R indices [I>2sigma(I)]	R1 = 0.0417, wR2 = 0.0951	
R indices (all data)	R1 = 0.0518, wR2 = 0.0993	
Largest diff. peak and hole	5.159 and -3.566 $e.Å^{-3}$	

Figure S10: Crystal structure and atomic numbering of $[(p\text{-}C_6H_4F)(CH_3)CF][CHB_{11}I_{11}]$, **2**. Thermal ellipsoids are shown at the 50% probability level.

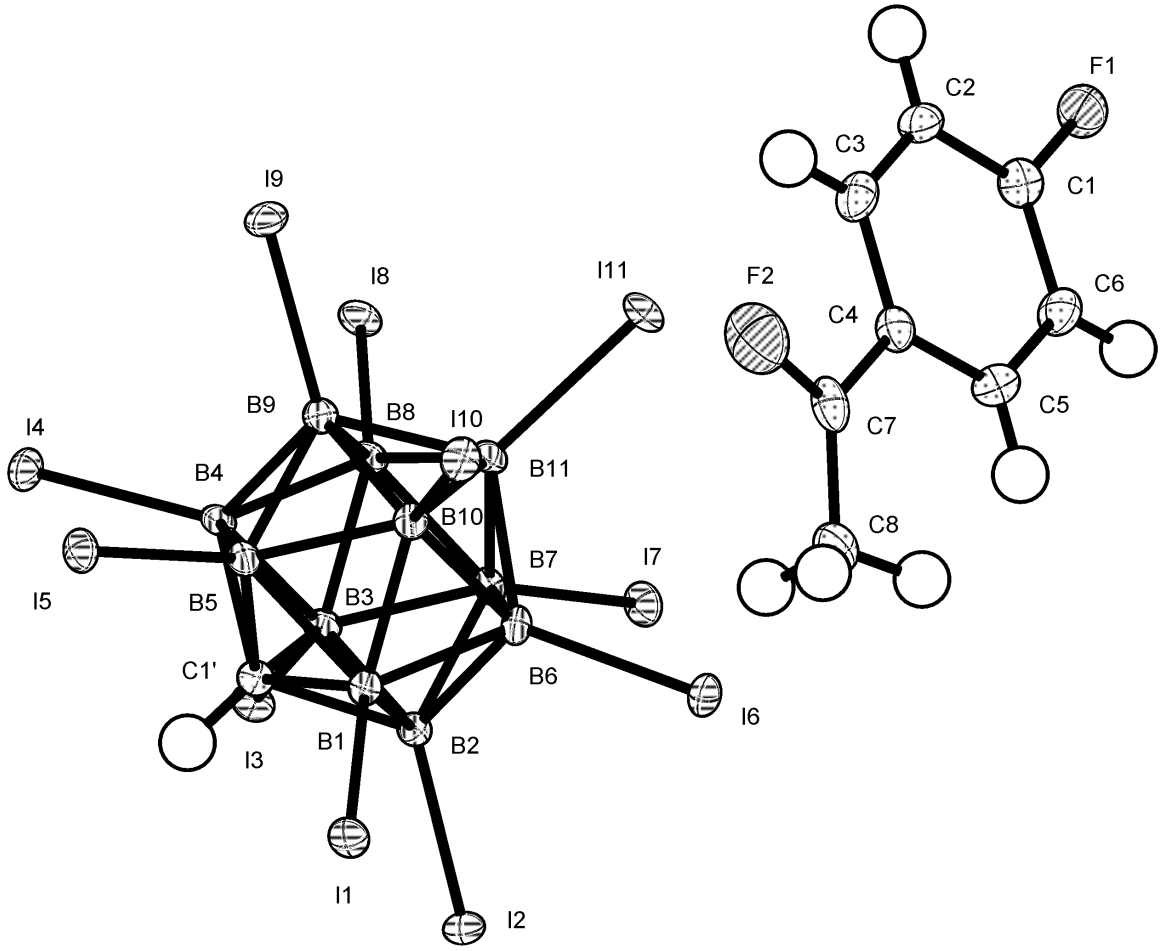

Table S2. Crystal data and structure refinement for $[(p\text{-}C_6H_4F)(CH_3)CF][CHB_{11}I_{11}]$, **2**.

Identification code	chr103006	
Empirical formula	C9 H8 B11 F2 I11	
Formula weight	1668.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.1562(5) Å	α= 90°.
	b = 21.8969(13) Å	β= 107.051(2)°.
	c = 15.0635(9) Å	γ = 90°.
Volume	3202.7(3) $Å^3$	
Z	4	
Density (calculated)	3.461 Mg/m^3	
Absorption coefficient	10.655 mm^{-1}	
F(000)	2872	
Crystal size	0.39 x 0.07 x 0.06 mm^3	
Theta range for data collection	1.69 to 36.32°.	
Index ranges	-14<=h<=16, -36<=k<=35, -25<=l<=25	
Reflections collected	41110	
Independent reflections	15009 [R(int) = 0.0304]	
Completeness to theta = 36.32°	96.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5673 and 0.1034	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15009 / 11 / 302	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0275, wR2 = 0.0496	
R indices (all data)	R1 = 0.0433, wR2 = 0.0534	
Largest diff. peak and hole	2.004 and -1.513 $e.Å^{-3}$	

Figure S11: Atomic numbering scheme for $[(p\text{-}C_6H_4F)_3C^+][CHB_{11}I_{11}^-]\cdot 1.5C_6H_5F$, **3**. Thermal ellipsoids are shown at the 50% probability level.

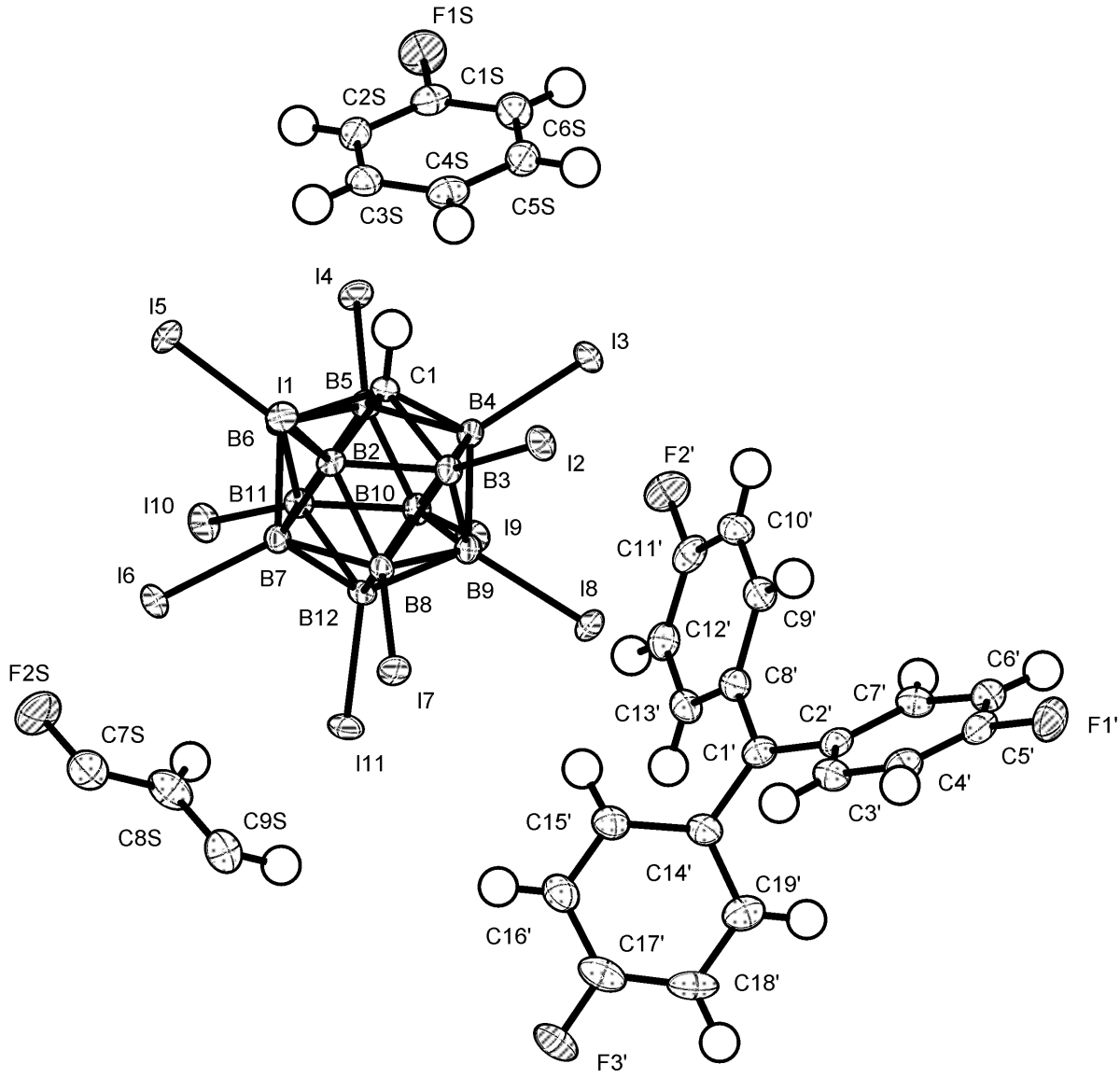

Table S3. Crystal data and structure refinement for $[(p\text{-}C_6H_4F)_3C][CHB_{11}I_{11}]\cdot 1.5C_6H_5F$, **3**.

Identification code	cr218_0m	
Empirical formula	C29 H20.50 B11 F4.50 I11	
Formula weight	1969.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 10.0852(5) Å	α= 90°.
	b = 20.8766(9) Å	β= 96.2104(7)°.
	c = 22.2728(10) Å	γ = 90°.
Volume	4661.9(4) Å^3	
Z	4	
Density (calculated)	2.806 Mg/m^3	
Absorption coefficient	7.352 mm^{-1}	
F(000)	3492	
Crystal size	0.25 x 0.18 x 0.14 mm^3	
Theta range for data collection	1.84 to 30.51°.	
Index ranges	-14<=h<=14, -29<=k<=29, -31<=l<=31	
Reflections collected	73128	
Independent reflections	14223 [R(int) = 0.0418]	
Completeness to theta = 30.51°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4281 and 0.2598	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14223 / 18 / 518	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0276, wR2 = 0.0578	
R indices (all data)	R1 = 0.0376, wR2 = 0.0610	
Largest diff. peak and hole	1.648 and -0.624 e.Å^{-3}	

Figure S12: Atomic numbering scheme for $[(p\text{-}C_6H_5F)_2(p\text{-}CH_3C_6F_4)C][CHB_{11}Cl_{11}]$, **4**. Thermal ellipsoids are shown at the 50% probability level.

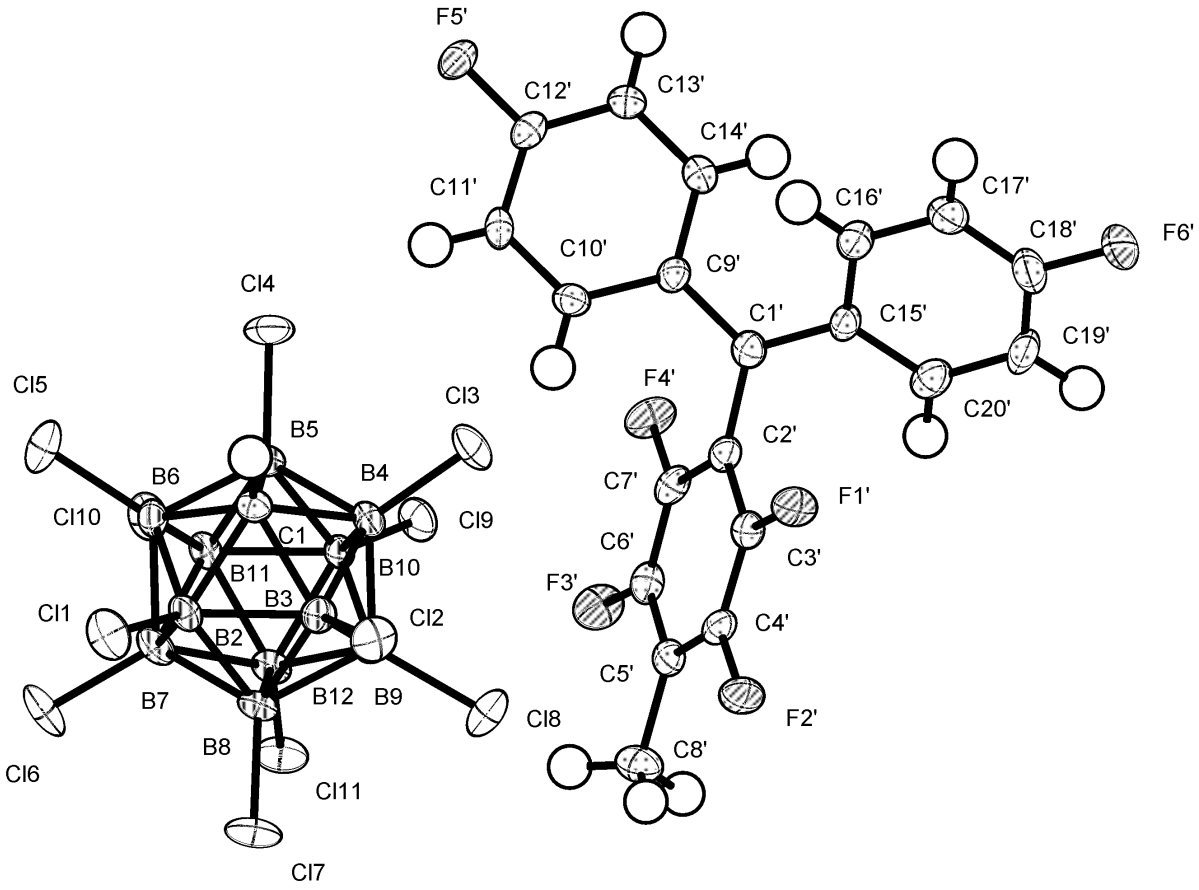

Table S4. Crystal data and structure refinement for $[(p\text{-}C_6H_4F)_2(p\text{-}CH_3C_6F_4)C][CHB_{11}Cl_{11}]$, **4**.

Identification code	cr185r_0m	
Empirical formula	C21 H12 B11 Cl11 F6	
Formula weight	887.17	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.0604(4) Å	α= 90°.
	b = 14.3581(5) Å	β= 90°.
	c = 20.1013(7) Å	γ = 90°.
Volume	3480.8(2) $Å^3$	
Z	4	
Density (calculated)	1.693 Mg/m^3	
Absorption coefficient	0.930 mm^{-1}	
F(000)	1736	
Crystal size	0.16 x 0.14 x 0.11 mm^3	
Theta range for data collection	1.74 to 30.51°.	
Index ranges	-17<=h<=17, -20<=k<=20, -28<=l<=28	
Reflections collected	55666	
Independent reflections	10625 [R(int) = 0.0707]	
Completeness to theta = 30.51°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9055 and 0.8648	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10625 / 11 / 456	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.0817	
R indices (all data)	R1 = 0.0606, wR2 = 0.0878	
Absolute structure parameter	0.02(4)	
Largest diff. peak and hole	0.430 and -0.387 $e.Å^{-3}$	