Electronic Supplementary Information for Dalton Transactions

Fluoride anion binding by cyclic boronic esters: influence of backbone chelate on receptor integrity

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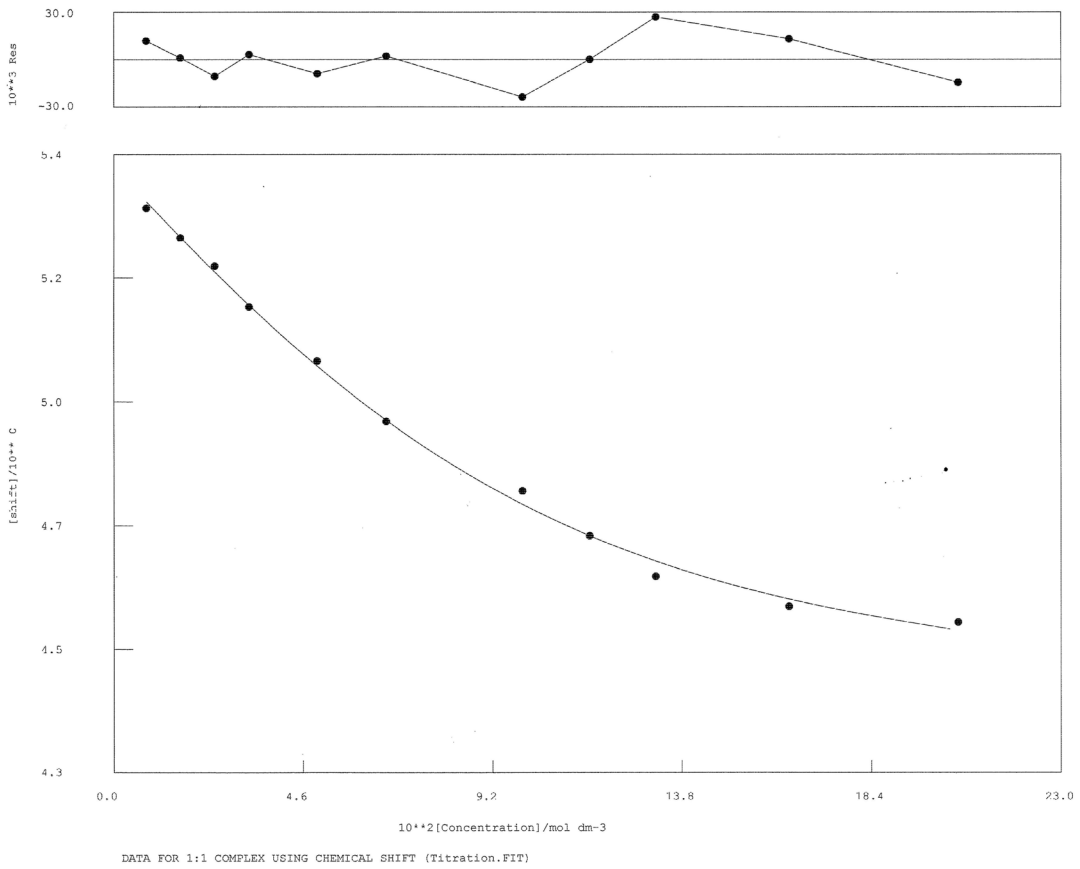
Supporting Information

1. WinEQNMR fit of ^{1}H NMR titration data and determination of K for $FcBO_2C_2H_2Ph_2$ (4)



Calculations by WinEQNMR Version 1.20 by Michael J. Hynes
Program run at 13:44:34 on 03/09/2006

DATA FOR 1:1 COMPLEX USING CHEMICAL SHIFT (Titration.FIT)
Reaction: FcB(OR)2 + F- = [FcB(OR)2F]-
FILE: titration.FIT
IDEAL DATA: K1 = 30; DELTA FcB(OR)2 = 5.32; DELTA complex = 4.35
File prepared by S. Aldridge, February 01 2006

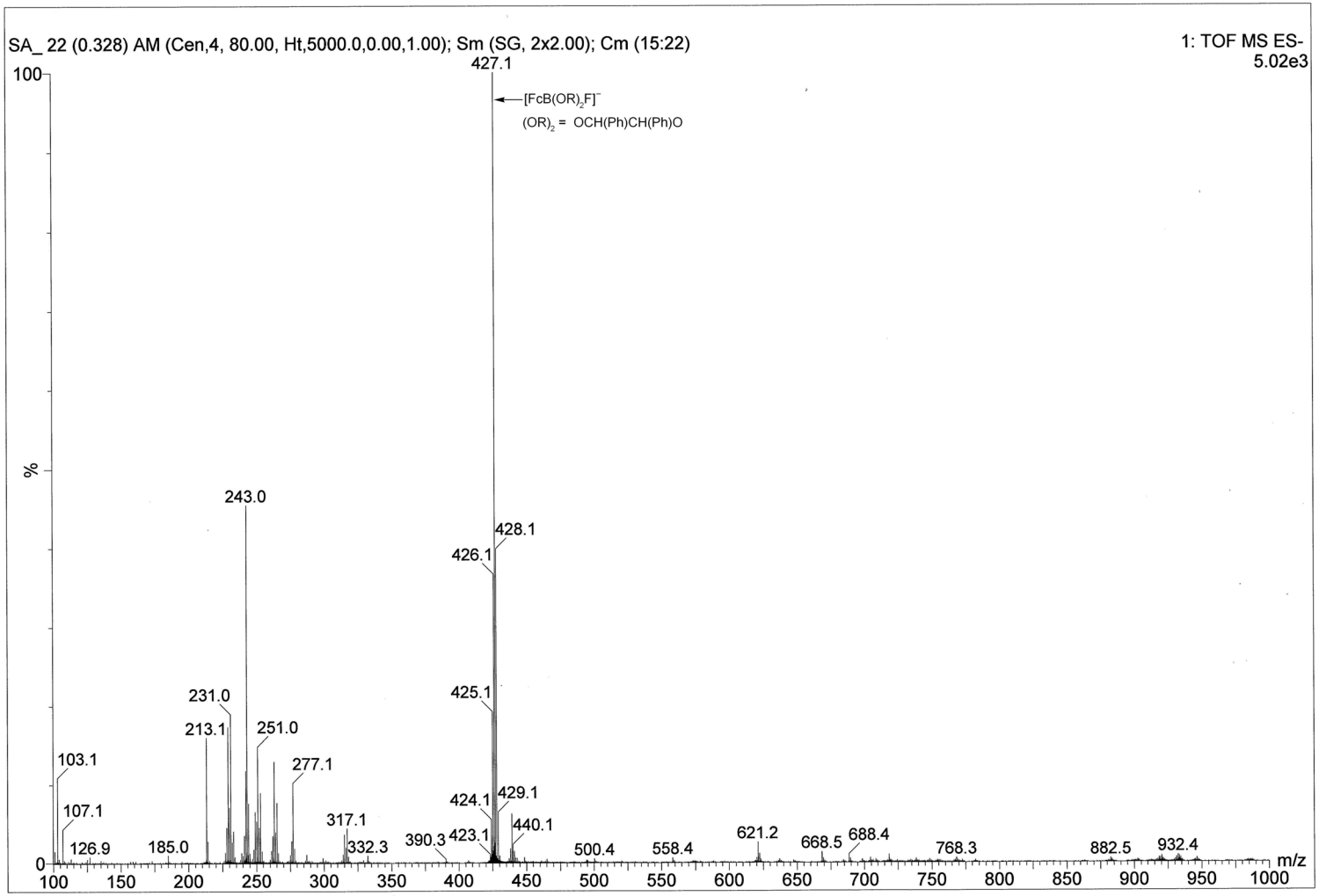
NO.	A	PARAMETER	DELTA	ERROR	CONDITION	DESCRIPTION
1	1	3.57930E+01	1.000E+00	9.817E+00	4.399E+01	K1
2	1	5.37827E+00	5.000E-02	1.044E-02	1.761E+00	SHIFT FcB(OR)2
3	1	4.36904E+00	5.000E-02	5.889E-02	4.049E+01	SHIFT complex

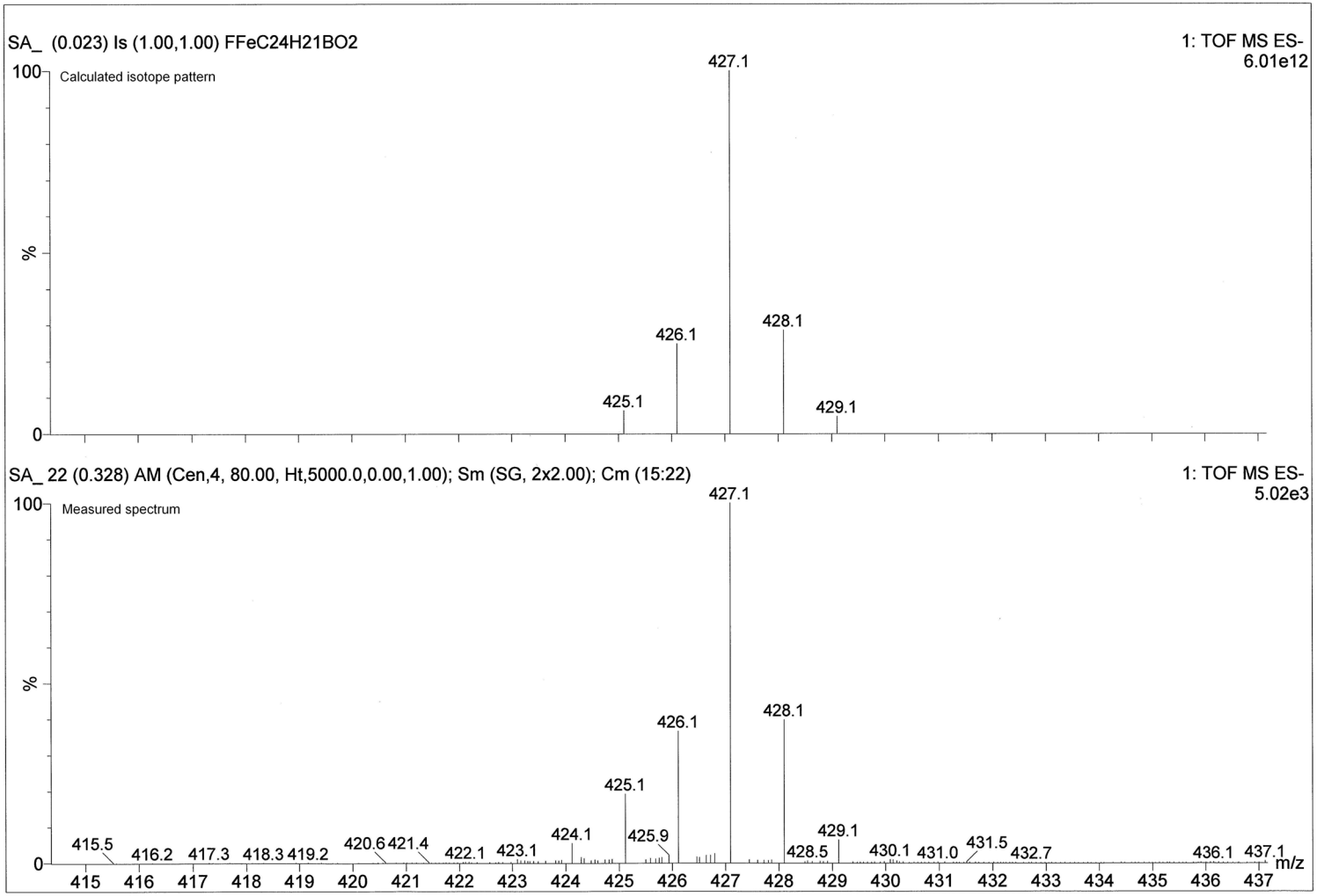
0RMS ERROR = 1.59E-02 MAX ERROR = 2.69E-02 AT OBS.NO. 9
RESIDUALS SQUARED = 2.02E-03
RFACTOR = 0.2746 PERCENT

NO.	A	EXPT. DEL	CALC. DEL	RESIDUAL	% DEV	WEIGHT	Fluoride	FcB(OR)2	pH
1	1	5.3041E+00	5.3158E+00	-1.1693E-02	-2.2046E-01	1.0000E+00	7.8700E-03	9.7664E-02	0.0000E+00
2	1	5.2514E+00	5.2524E+00	-1.0300E-03	-1.9613E-02	1.0000E+00	1.6130E-02	9.7664E-02	0.0000E+00
3	1	5.2013E+00	5.1906E+00	1.0710E-02	2.0591E-01	1.0000E+00	2.4510E-02	9.7664E-02	0.0000E+00
4	1	5.1283E+00	5.1314E+00	-3.1276E-03	-6.0987E-02	1.0000E+00	3.2890E-02	9.7664E-02	0.0000E+00
5	1	5.0326E+00	5.0236E+00	9.0141E-03	1.7911E-01	1.0000E+00	4.9400E-02	9.7664E-02	0.0000E+00
6	1	4.9249E+00	4.9271E+00	-2.2011E-03	-4.4693E-02	1.0000E+00	6.6170E-02	9.7664E-02	0.0000E+00
7	1	4.8019E+00	4.7782E+00	2.3716E-02	4.9389E-01	1.0000E+00	9.9190E-02	9.7664E-02	0.0000E+00
8	1	4.7221E+00	4.7222E+00	-6.1989E-05	-1.3127E-03	1.0000E+00	1.1557E-01	9.7664E-02	0.0000E+00
9	1	4.6503E+00	4.6772E+00	-2.6946E-02	-5.7945E-01	1.0000E+00	1.3157E-01	9.7664E-02	0.0000E+00
10	1	4.5966E+00	4.6096E+00	-1.2972E-02	-2.8222E-01	1.0000E+00	1.6396E-01	9.7664E-02	0.0000E+00
11	1	4.5683E+00	4.5537E+00	1.4612E-02	3.1985E-01	1.0000E+00	2.0498E-01	9.7664E-02	0.0000E+00

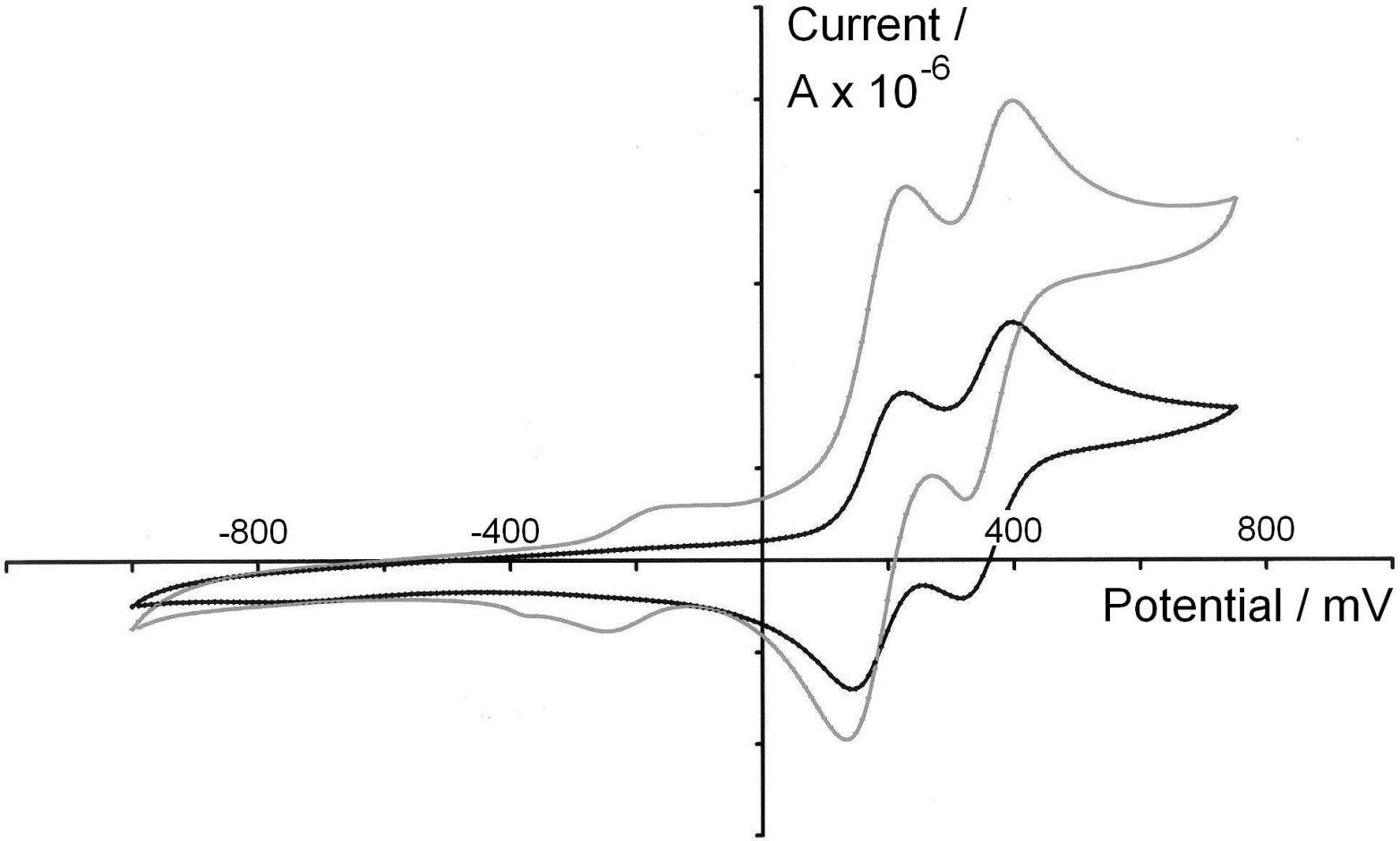
TOLERANCE ON SUM OF SQUARES 0.0300
TOLERANCE ON EIGEN VALUES 0.0001
CONVERGANCE AFTER 2 ITERATIONS

2. ES(-) mass spectra for $[4{\cdot}F]^-$

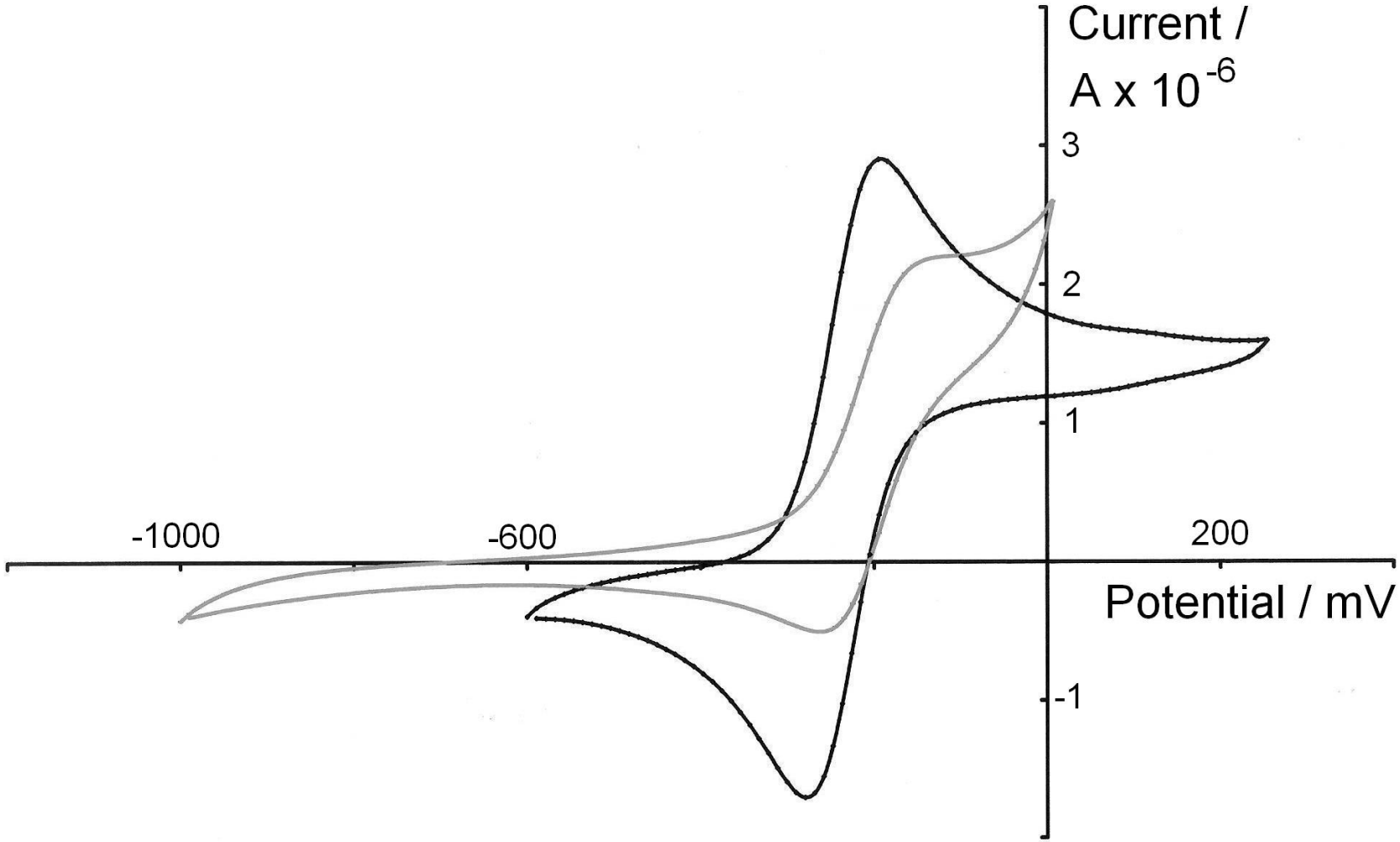



SA_ (0.023) Is (1.00,1.00) FFeC24H21BO2
1: TOF MS ES-
6.01e12
100
Calculated isotope pattern
%
0
427.1
426.1
428.1
425.1
429.1
SA_ 22 (0.328) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (SG, 2x2.00); Cm (15:22)
1: TOF MS ES-
5.02e3
100
Measured spectrum
%
0
427.1
426.1
428.1
425.1
429.1
415.5
416.2
417.3
418.3
419.2
420.6
421.4
422.1
423.1
424.1
425.9
428.5
430.1
431.0
431.5
432.7
436.1
437.1
m/z
415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437

3. Cyclic voltametry traces for $(FcB)_2$calix (6)

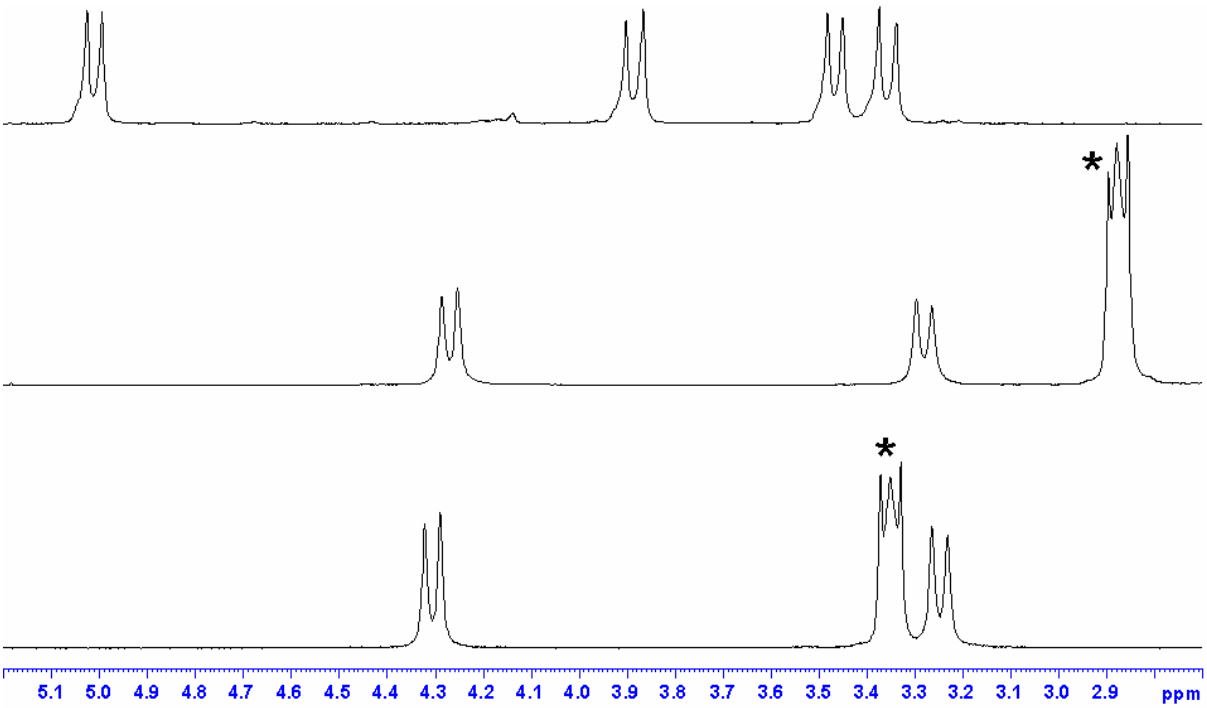


Black: CV for **6**; grey: CV for **6** plus trace fluoride.



Black: CV for $[FcBF_3]^-$; grey: CV for **6** plus excess fluoride.

4. ^{1}H NMR spectra for the reaction of $(PhB)_2$calix (8) with $[^nBu_4N]F{\cdot}xH_2O$



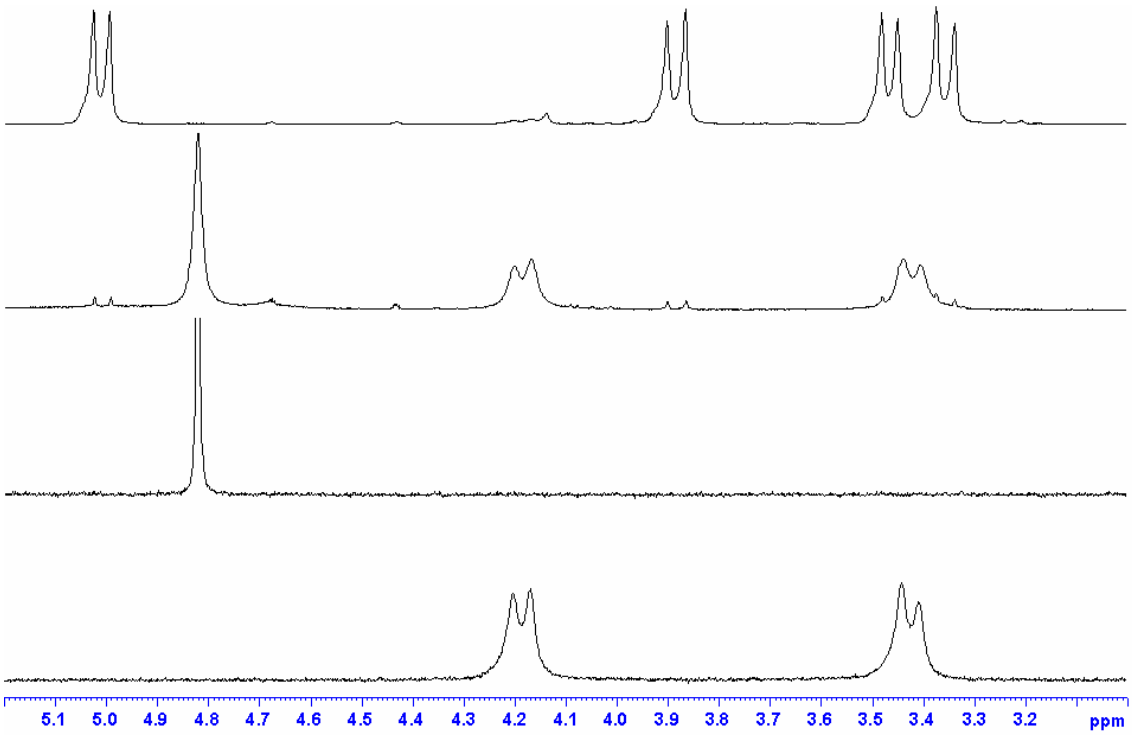
Top: $(PhB)_2$calix (**8**) in $CDCl_3$

Middle: $(PhB)_2$calix (**8**) plus excess $[^nBu_4N]F{\cdot}xH_2O$ in $CDCl_3$

Bottom: H_4(calix) plus excess $[^nBu_4N]F{\cdot}xH_2O$ in $CDCl_3$

The resonance indicated with the asterix is due to the NCH_2 protons of the $[^nBu_4N]^+$ counter-ion and is strongly dependent on concentration and ionic strength.

^{1}H NMR spectra for the reaction of $(PhB)_2$calix (8) with water



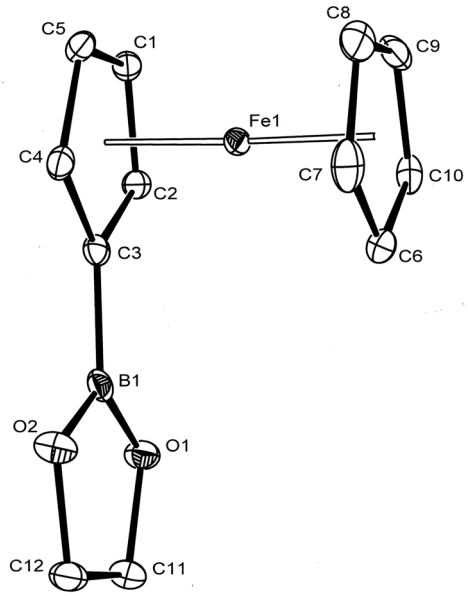
Top: $(PhB)_2$calix (**8**) in $CDCl_3$

Top Middle: $(PhB)_2$calix (**8**) plus excess water in $CDCl_3$

Bottom Middle: $PhB(OH)_2$ in $CDCl_3$

Bottom: H_4(calix) in $CDCl_3$

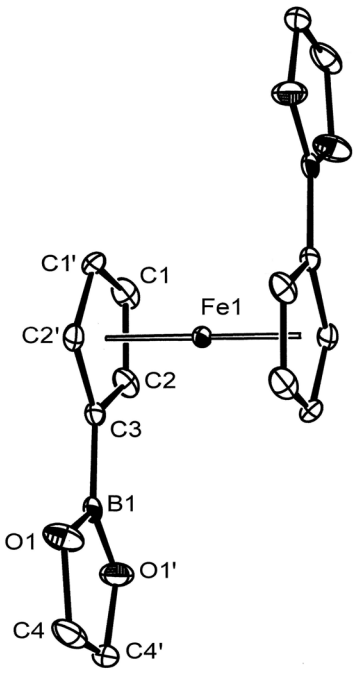
5. Crystallographic data for $FcBO_2C_2H_4$ (3a)



Crystal data and structure refinement for **3a**:

Empirical formula	C12 H13 B Fe O2	
Formula weight	255.88	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	p 21 21 21	
Unit cell dimensions	a = 5.81790(10) Å	α= 90°.
	b = 9.9233(2) Å	β= 90°.
	c = 18.4741(5) Å	γ = 90°.
Volume	1066.56(4) $Å^3$	
Z	4	
Density (calculated)	1.594 Mg/m^3	
Absorption coefficient	1.391 mm^{-1}	
F(000)	528	
Crystal size	0.60 x 0.25 x 0.20 mm^3	
Theta range for data collection	3.67 to 26.36°.	
Index ranges	-5<=h<=7, -12<=k<=12, -23<=l<=23	
Reflections collected	8431	
Independent reflections	2138 [R(int) = 0.0670]	
Completeness to theta = 26.36°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7684 and 0.4892	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2138 / 0 / 145	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0328, wR2 = 0.0795	
R indices (all data)	R1 = 0.0347, wR2 = 0.0812	
Absolute structure parameter	0.03(2)	
Largest diff. peak and hole	0.332 and -0.681 e.$Å^{-3}$	

6. Crystallographic data for $fc(BO_2C_2H_4)_2$ (3b)



Crystal data and structure refinement for **3b**:

Empirical formula	C14 H16 B2 Fe O4	
Formula weight	325.74	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/m	
Unit cell dimensions	a = 7.0116(4) Å	α= 90°.
	b = 10.0523(7) Å	β= 104.211(3)°.
	c = 9.8912(7) Å	γ = 90°.
Volume	675.82(8) $Å^3$	
Z	2	
Density (calculated)	1.601 Mg/m^3	
Absorption coefficient	1.126 mm^{-1}	
F(000)	336	
Crystal size	0.25 x 0.20 x 0.08 mm^3	
Theta range for data collection	3.62 to 26.33°.	
Index ranges	-8<=h<=8, -10<=k<=12, -12<=l<=12	
Reflections collected	1901	
Independent reflections	740 [R(int) = 0.0634]	
Completeness to theta = 26.33°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9153 and 0.7661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	740 / 0 / 53	
Goodness-of-fit on F^2	1.097	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.0934	
R indices (all data)	R1 = 0.0535, wR2 = 0.0966	
Largest diff. peak and hole	0.606 and -0.547 e.$Å^{-3}$	

7. Crystallographic data for fcB_2calix (7)

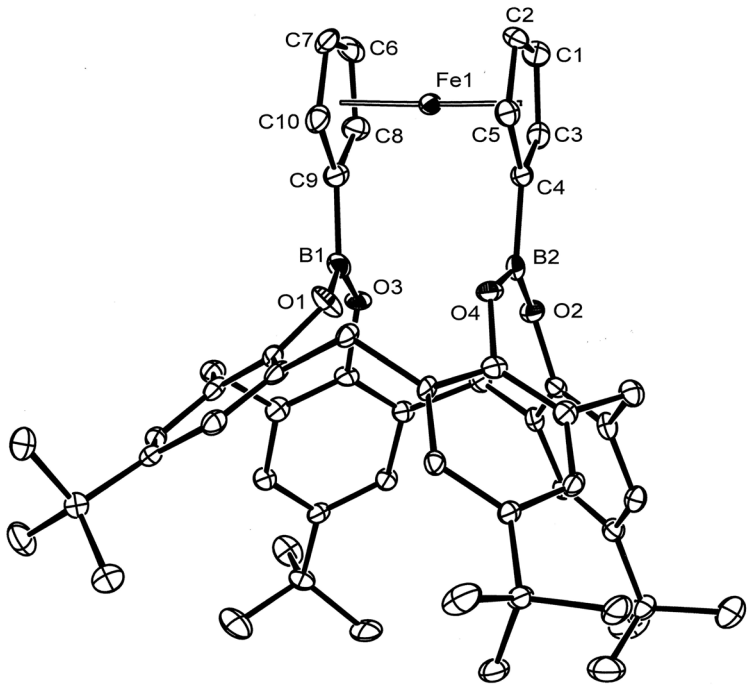


Table 1. Crystal data and structure refinement for **7**:

Empirical formula	C57 H67 B2 Fe O4	
Formula weight	893.58	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7685(3) Å	α= 89.514(2)°.
	b = 12.7505(4) Å	β= 73.968(2)°.
	c = 19.0095(6) Å	γ = 76.0250(10)°.
Volume	2429.57(13) $Å^3$	
Z	2	
Density (calculated)	1.221 Mg/m^3	
Absorption coefficient	0.356 mm^{-1}	
F(000)	954	
Crystal size	0.38 x 0.20 x 0.13 mm^3	
Theta range for data collection	2.74 to 27.21°.	
Index ranges	-13<=h<=13, -16<=k<=16, -23<=l<=24	
Reflections collected	37381	
Independent reflections	10716 [R(int) = 0.3243]	
Completeness to theta = 27.21°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9551 and 0.8764	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10716 / 6 / 587	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.1237, wR2 = 0.3054	
R indices (all data)	R1 = 0.1874, wR2 = 0.3554	
Extinction coefficient	0.017(4)	
Largest diff. peak and hole	2.075 and -2.014 e.$Å^{-3}$	