# Syntheses and Anion Binding Capabilities of *Bis*(diarylboryl) Ferrocenes and Related Systems

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**Supporting information (14 pages)**

## 1. Details of the crystal structure of [K(18-crown-6)][*rac*-1,2-fc(BMes$_2$F)(SiMe$_2$OH)]

$M_r$= 830.78, monoclinic, $P2_1/c$, a = 12.4769(2), b = 14.4345(2), c = 24.4216(4) Å, β = 92.385(1)°, V = 4394.5(1) Å$^3$, Z = 4, $\rho_c$ = 1.256 Mg m$^{-3}$, T = 150 K, 76059 reflections collected, 9984 independent [R(int) = 0.036]. $R_1$ = 0.0495, $wR_2$ = 0.0980 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1$ = 0.0820, $wR_2$ = 0.1099 for all unique reflections. Max. and min. residual electron densities 0.66 and -0.66 e Å$^{-3}$. CSD reference: 923316.

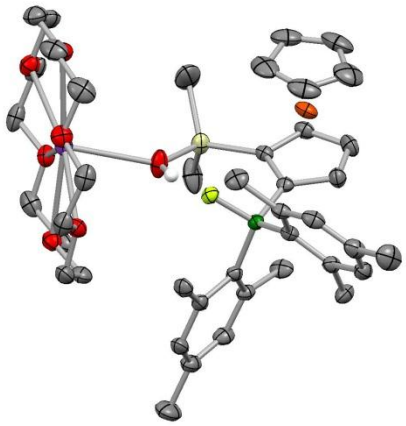


**Figure s1**: Molecular structure of [K(18-crown-6)][*rac*-1,2-fc(BMes$_2$F)(SiMe$_2$OH)] as determined by X-ray crystallography. Hydrogen atoms [except that attached to O(8)] omitted for clarity and thermal ellipsoids set at the 35% probability level.

## 2. Details of the crystal structure of [$^{n}$Bu$_4$N][*rac*-1,2-fc(BMes$_2$CN)(SiMe$_2$OH)]

$M_r$= 775.93, monoclinic, $P2_1/c$, a = 12.8131(1), b = 17.3681(2), c = 20.2116(2) Å, β = 90.377(1)°, V = 4497.8(1) Å$^3$, Z = 4, $\rho_c$ = 1.146 Mg m$^{-3}$, T = 150 K, 48187 reflections collected, 9386 independent [R(int) = 0.036]. $R_1$ = 0.0537, $wR_2$ = 0.1239 for observed unique reflections [$F^2 > 2\sigma(F^2)$] and $R_1$ = 0.0599, $wR_2$ = 0.1317 for all unique reflections. Max. and min. residual electron densities 1.54 and -0.85 e Å$^{-3}$. CSD reference: 924826.

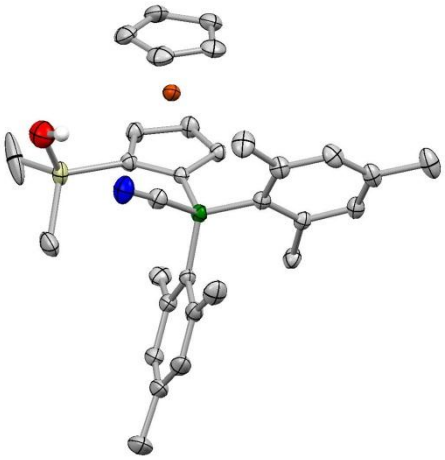


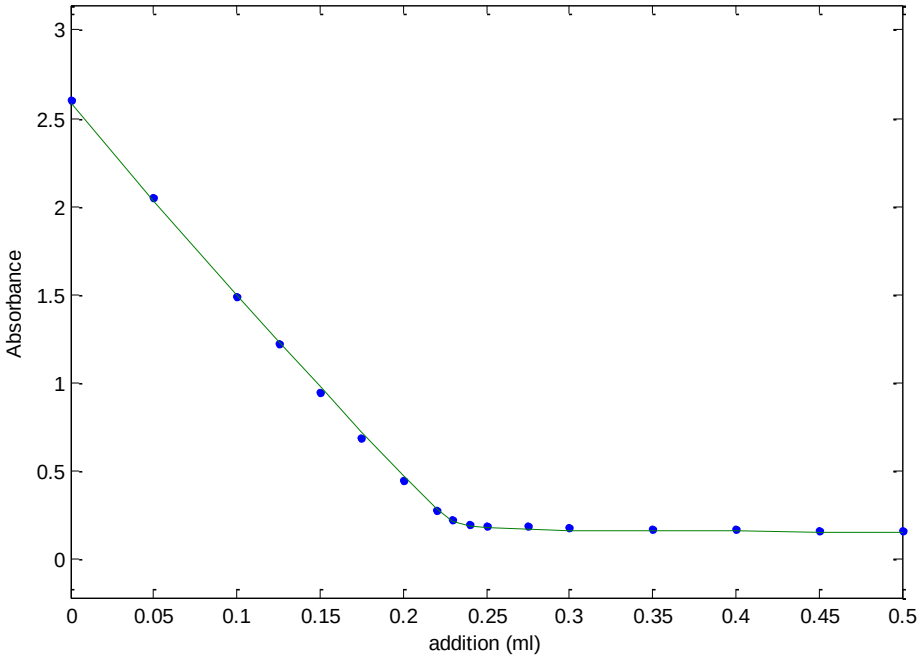
**Figure s2**: Molecular structure of the anionic component of [$^{n}$Bu$_4$N][*rac*-1,2-fc(BMes$_2$CN)(SiMe$_2$OH)] as determined by X-ray crystallography. Hydrogen atoms [except that attached to O(29)] and counter-ion omitted for clarity and thermal ellipsoids set at the 35% probability level.

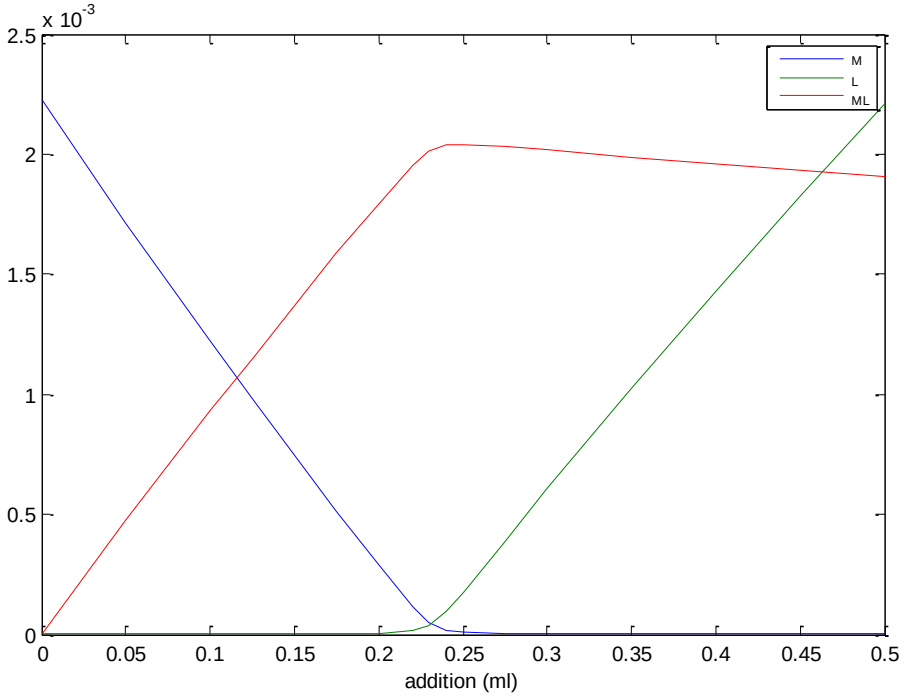
**3. Fluoride binding isotherms – least squares fits from ReactLab software**

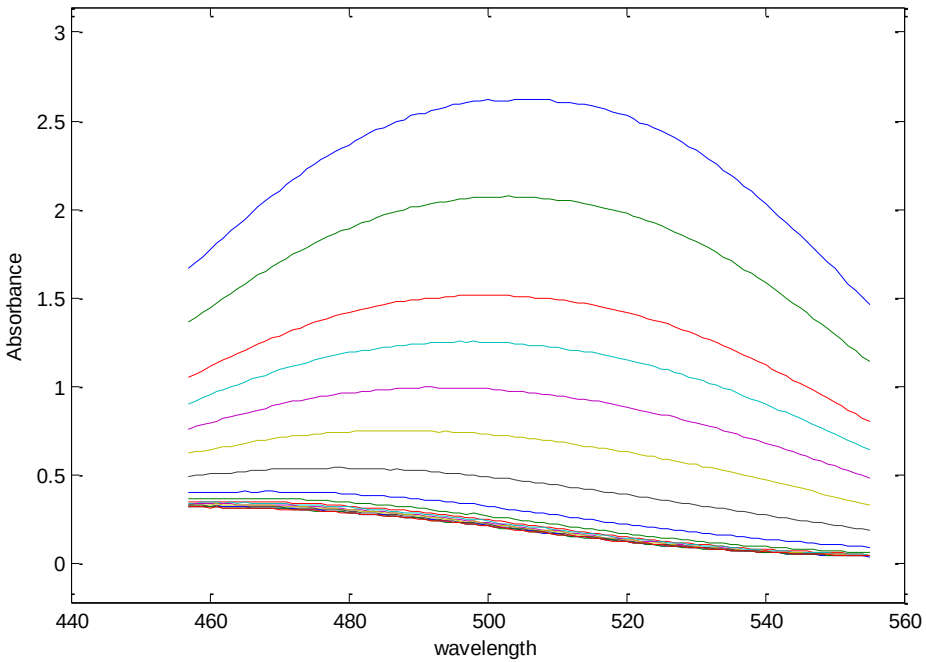
(ReactLab$^{TM}$ equlibria, Version 1.0, JPlus Consulting Pty Ltd., 2010)

(i) Fluoride binding by $FcBMes_2$ in thf

K2 LogK/LogB = 6.057(0.057), sigmar($1.75x10^{-2}$), ssq(0.484).

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wavelength
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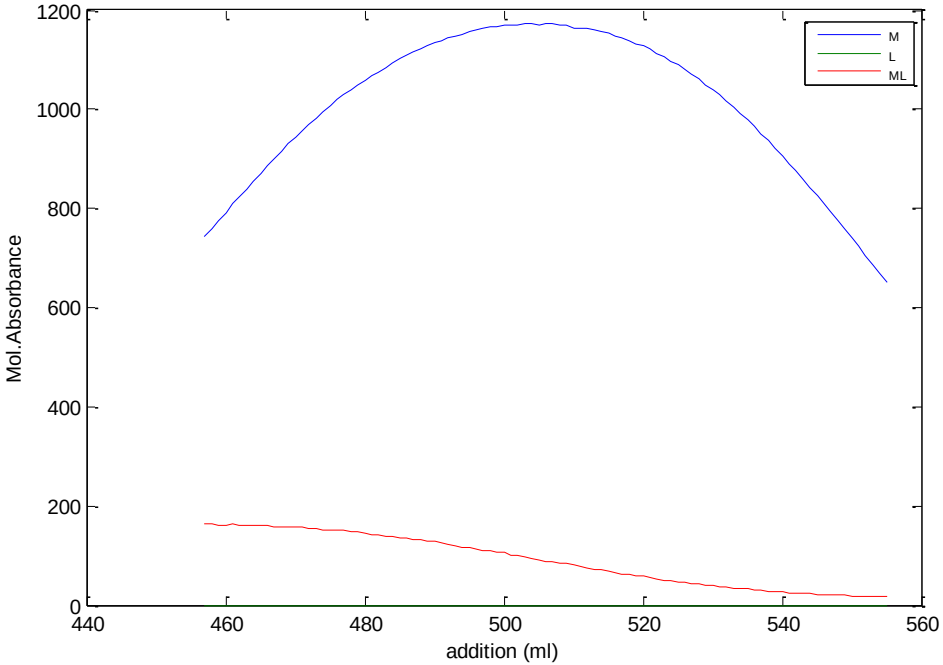
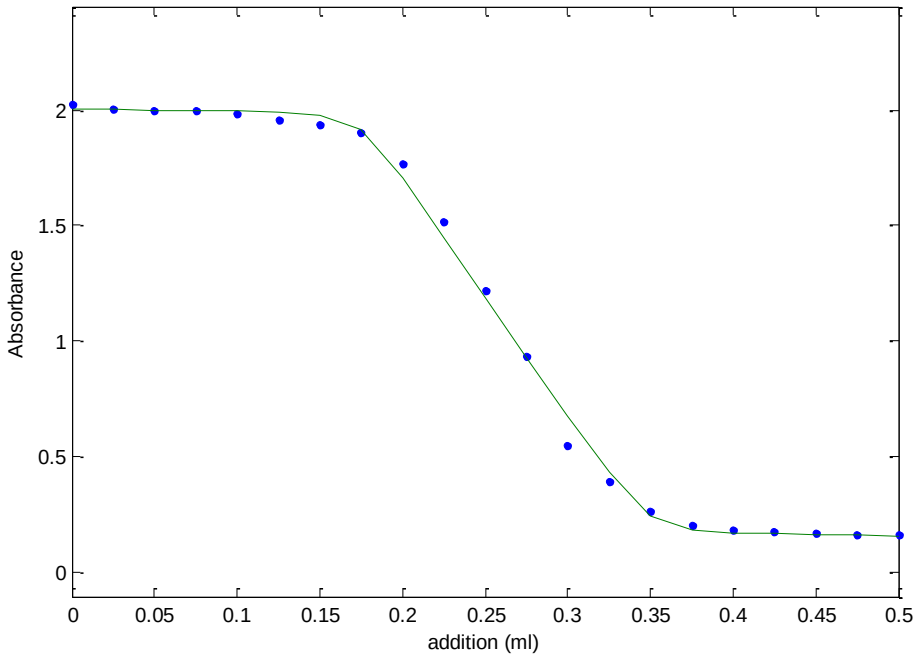
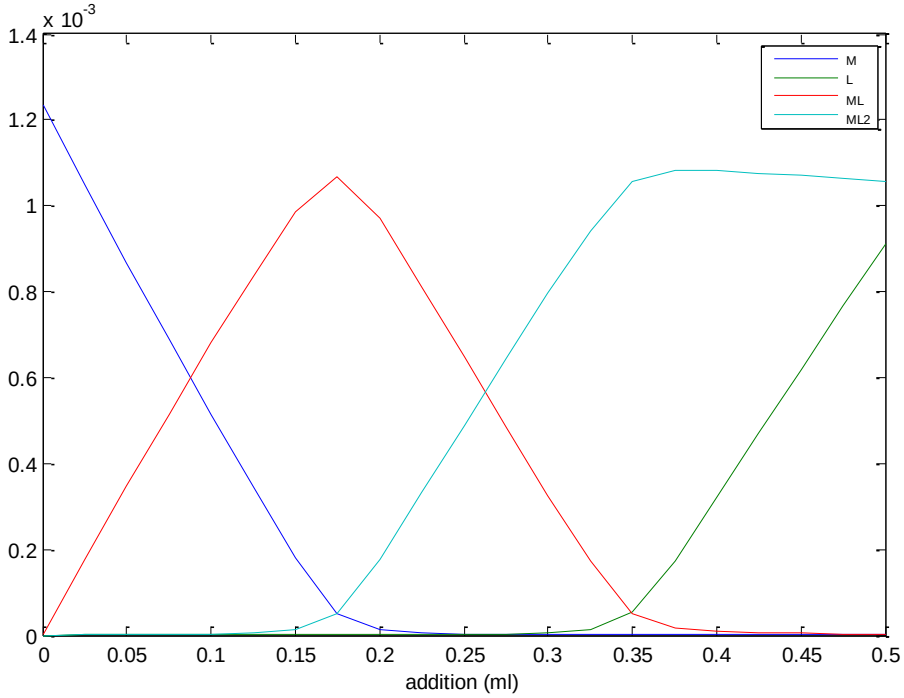
2.5
2
1.5
1
0.5
0
440
460
480
500
520
540
560

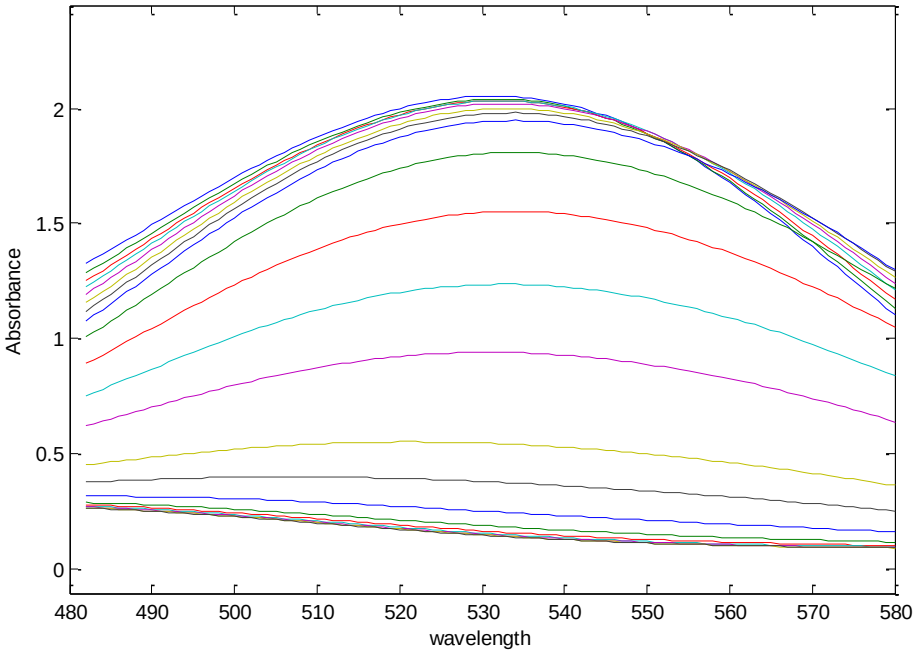

Mol.Absorbance
addition (ml)
M
L
ML
1200
1000
800
600
400
200
0
440
460
480
500
520
540
560

(ii) Fluoride binding by 1,1'-fc($BMes_2$)$_2$ (**1a**) in thf

K6 LogK/LogB= 8.255(0.090), 5.597(0.057), sigma(3.65x$10^{-2}$), ssq(2.51)




Absorbance
wavelength
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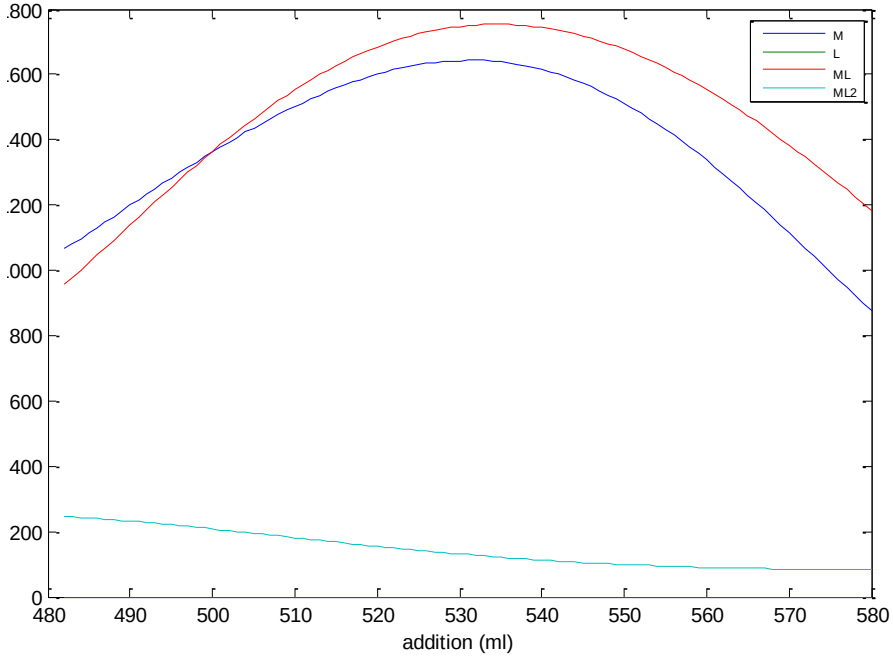
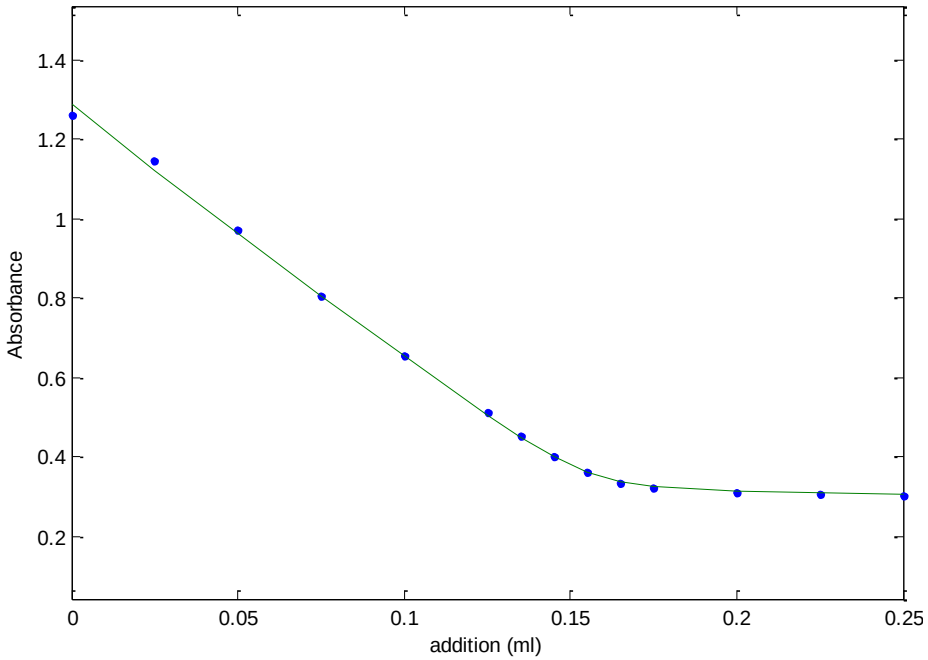
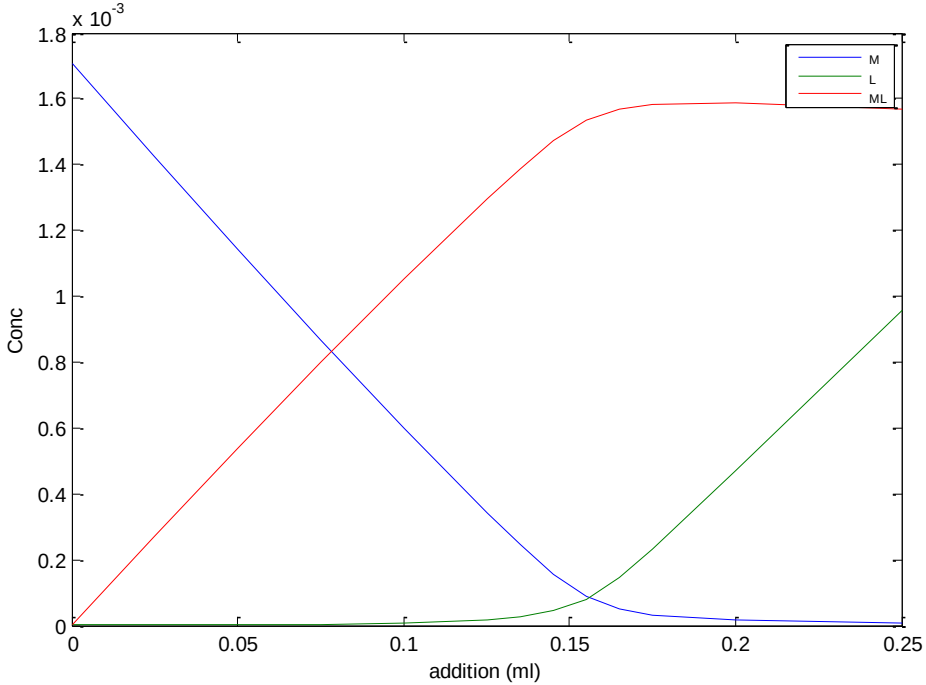
0.5
1
1.5
2
480
490
500
510
520
530
540
550
560
570
580

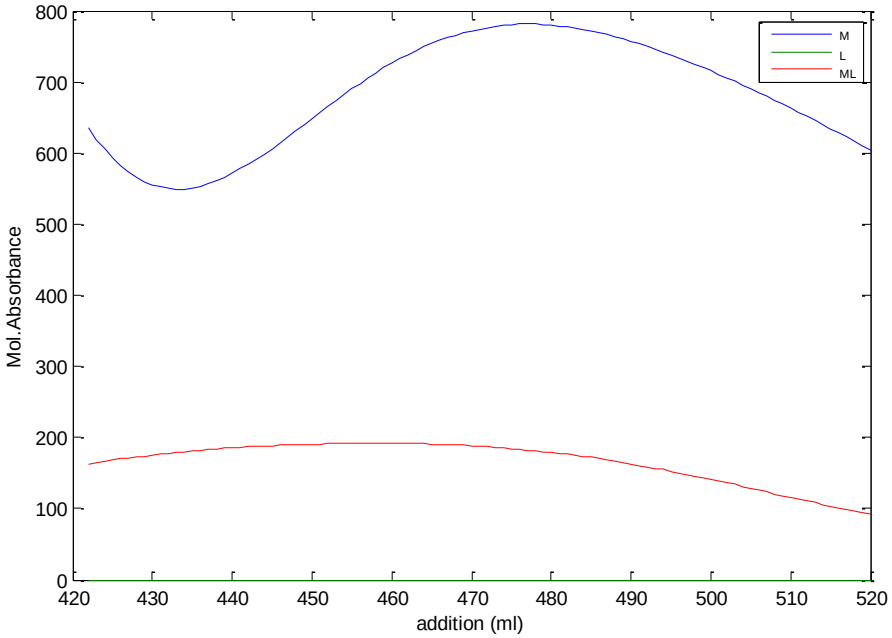

M
L
ML
ML2
addition (ml)
0
200
400
600
800
.000
.200
.400
.600
.800
480
490
500
510
520
530
540
550
560
570
580

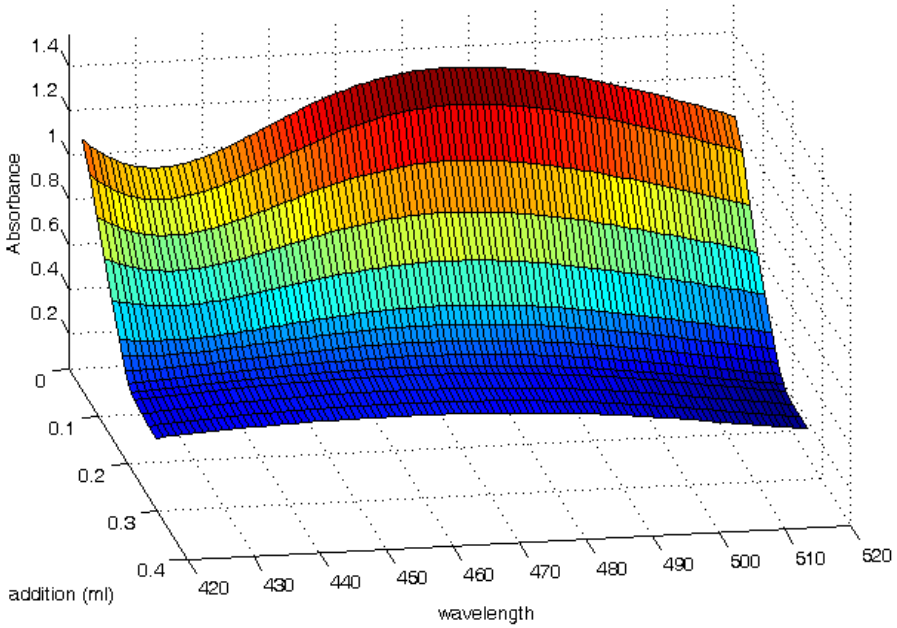
(iii) Fluoride binding by 1,2-fc($BMes_2$)($SiMe_2OMe$) (**9**) in thf

K20 logK/LogB = 5.337(0.024), sigma($1.04x10^{-2}$), ssq(1.40x10 -1)



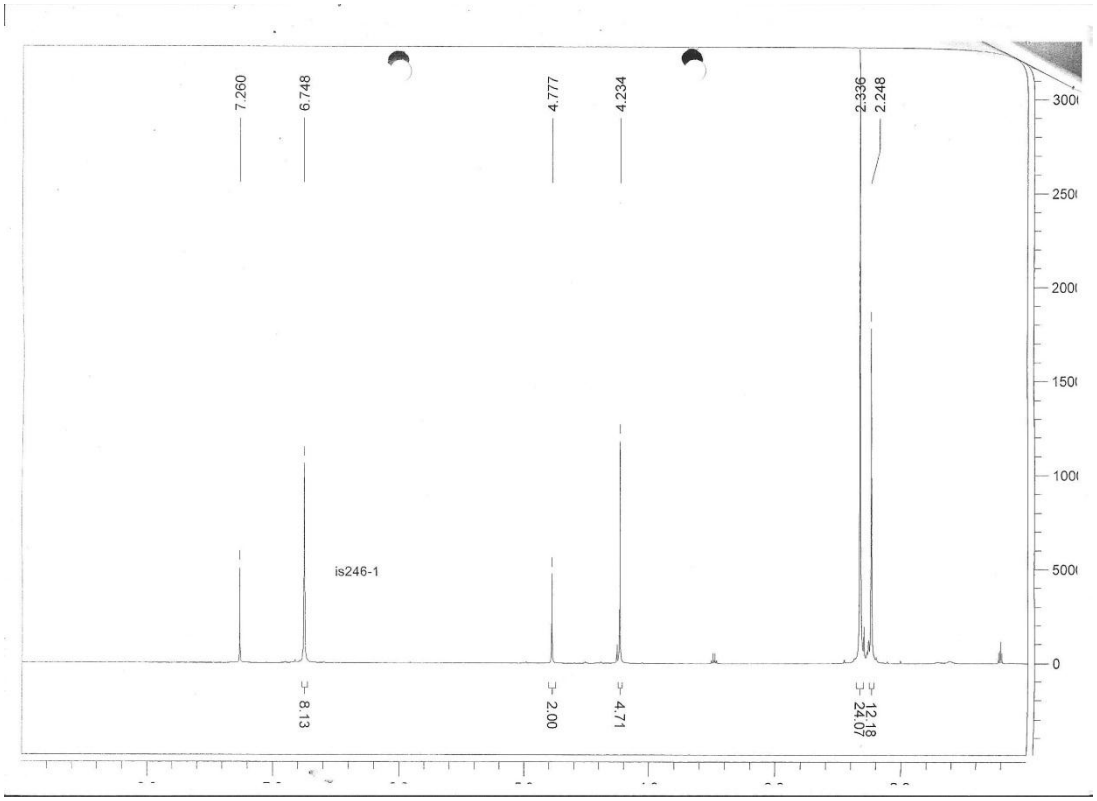



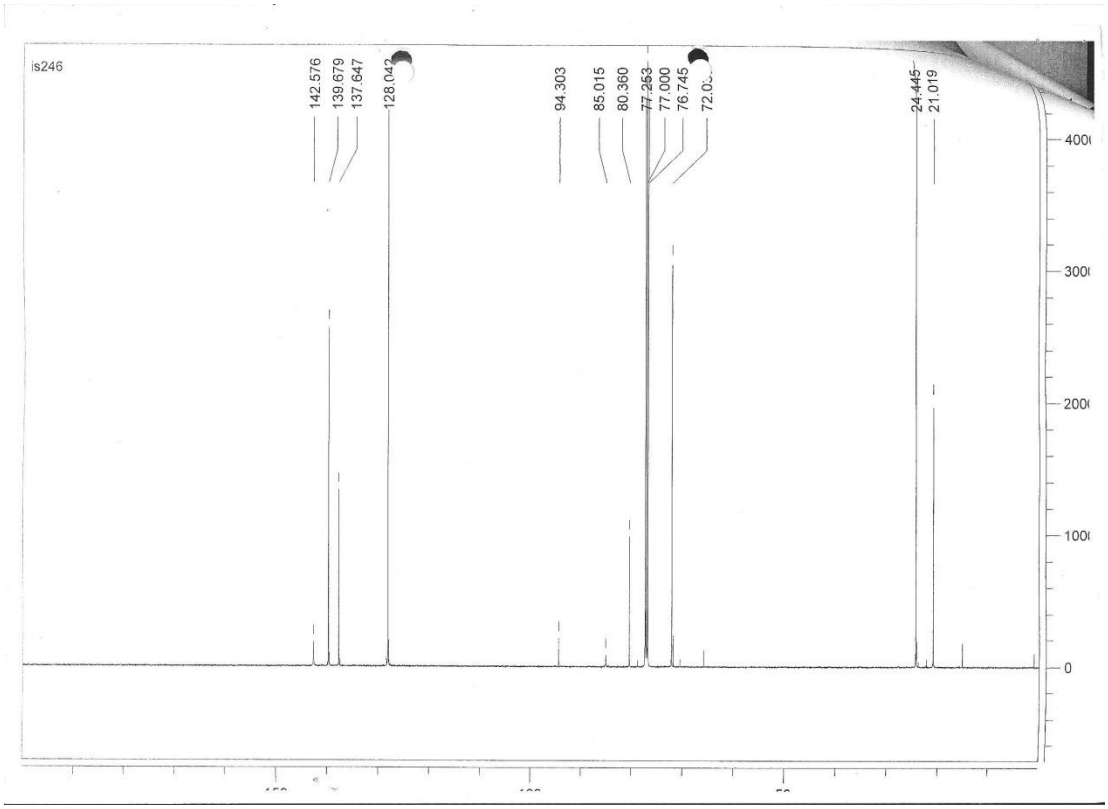

M
L
ML
Mol.Absorbance
addition (ml)
0
100
200
300
400
500
600
700
800
420
430
440
450
460
470
480
490
500
510
520


Absorbance
addition (ml)
wavelength
0
0.2
0.4
0.6
0.8
1
1.2
1.4
0.1
0.2
0.3
0.4
420
430
440
450
460
470
480
490
500
510
520

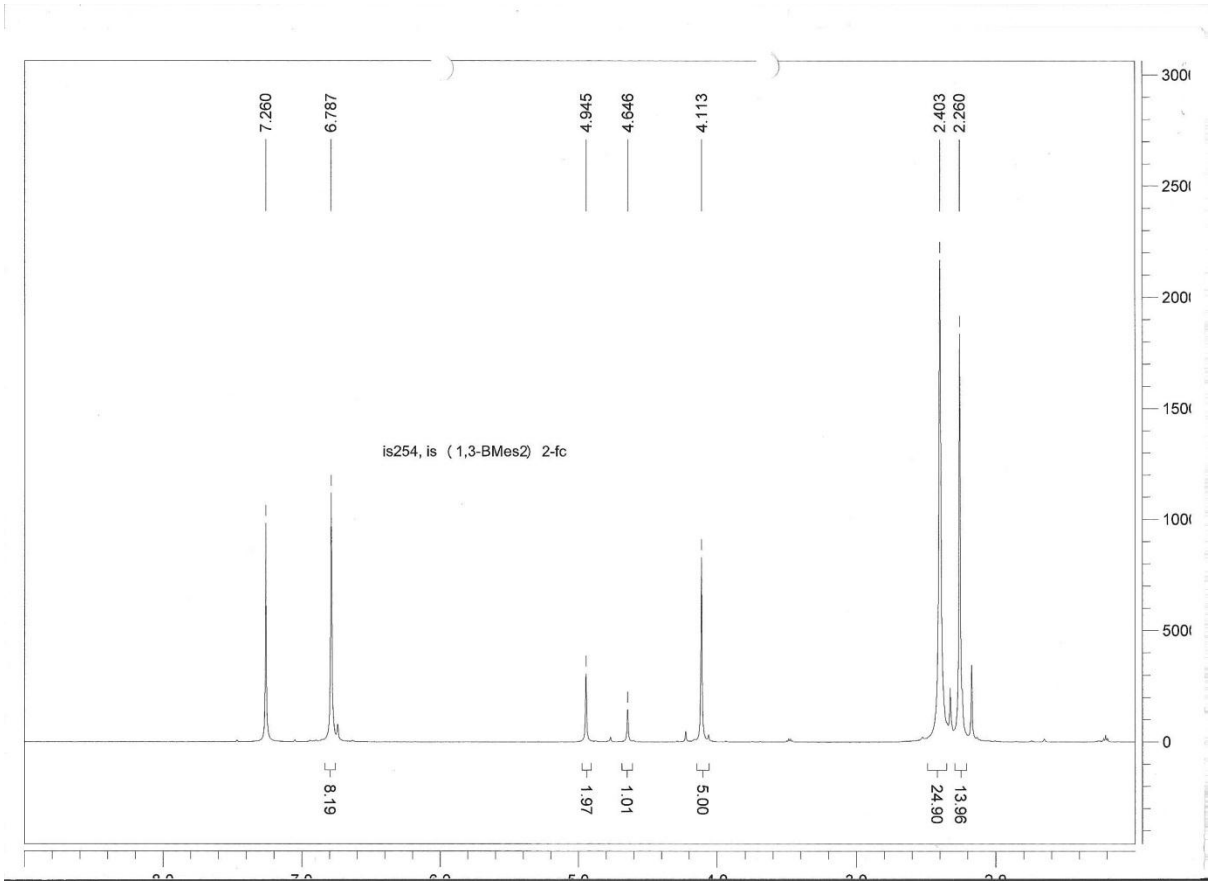
## 4. Copies of $^{1}H$, $^{13}C$ NMR spectra for selected novel compounds

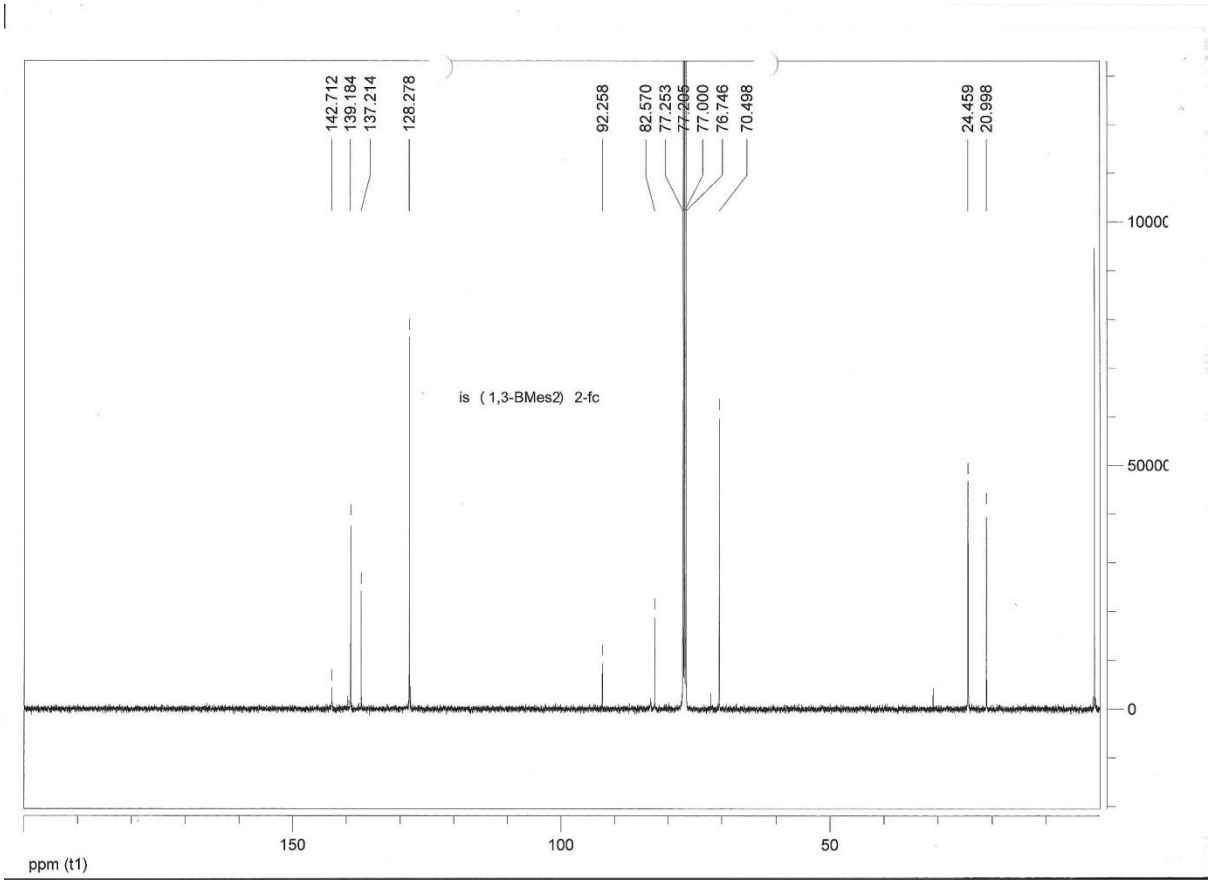
### 1,2,5-fcBr($BMes_2$)$_2$ (4)



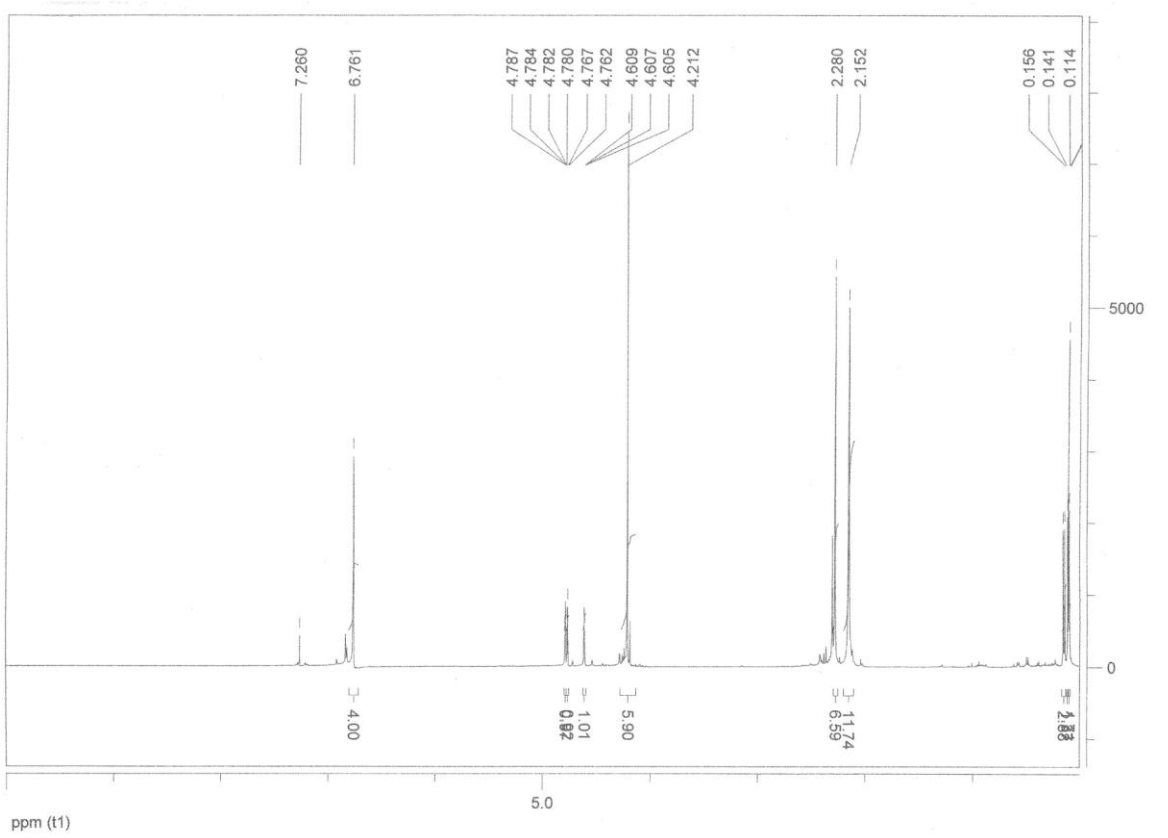



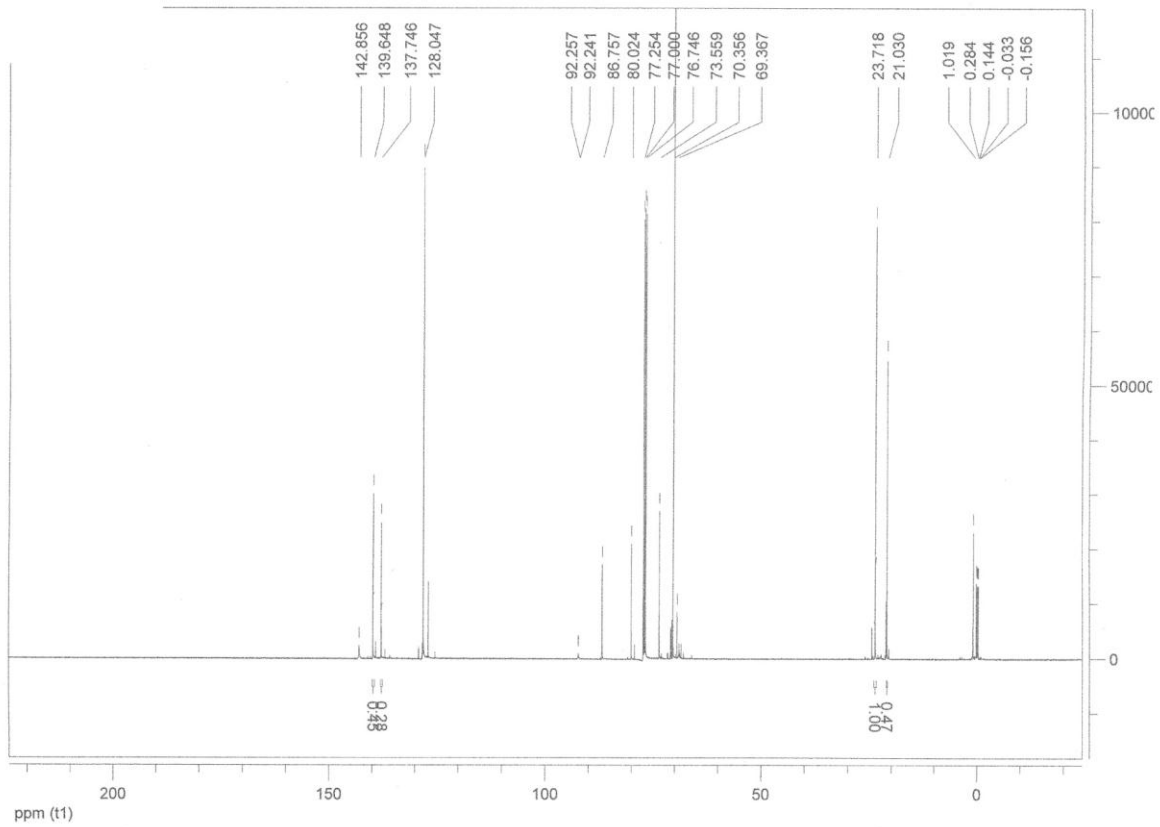
**1,3-fc($BMes_2$)$_2$ (5) (ca. 95% pure, as detailed in manuscript)**



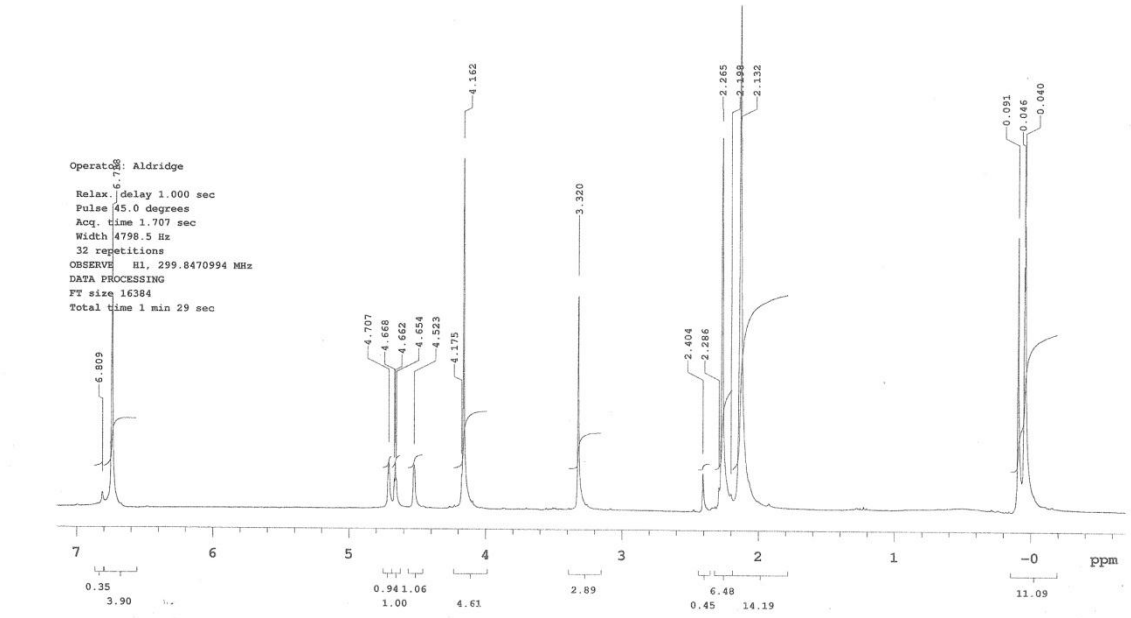



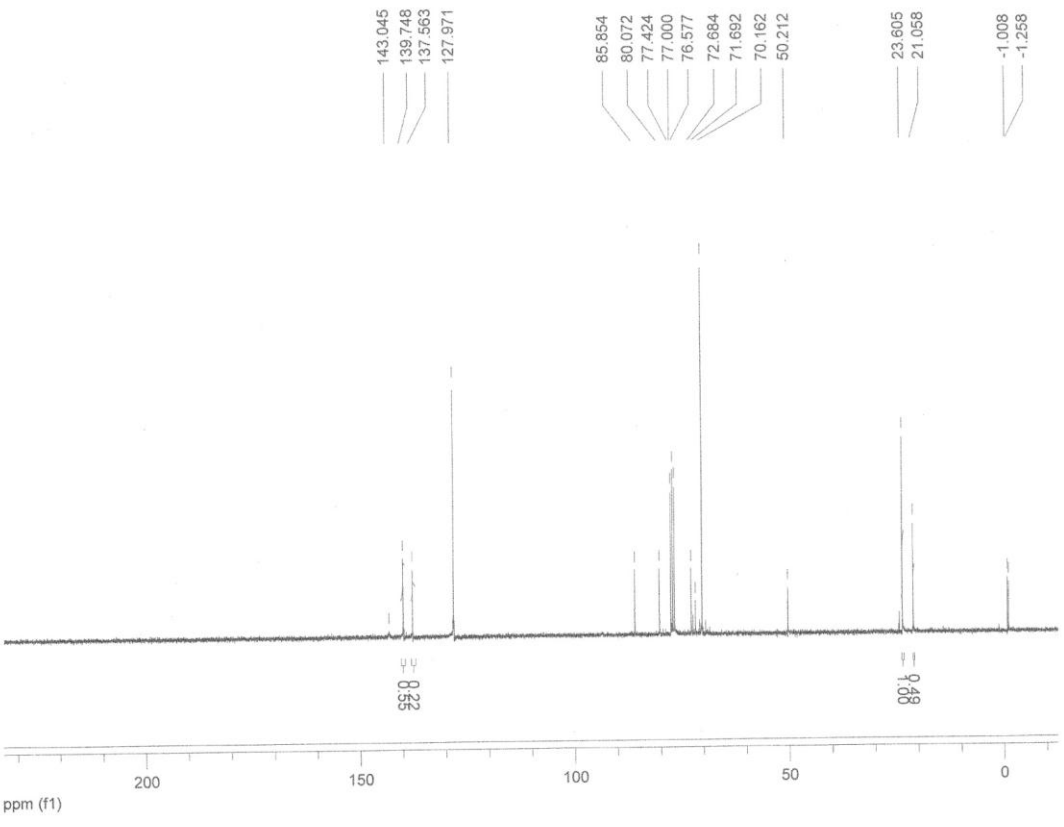
***rac*-1,2-fc(BMes$_2$)(SiMe$_2$F) (8)**



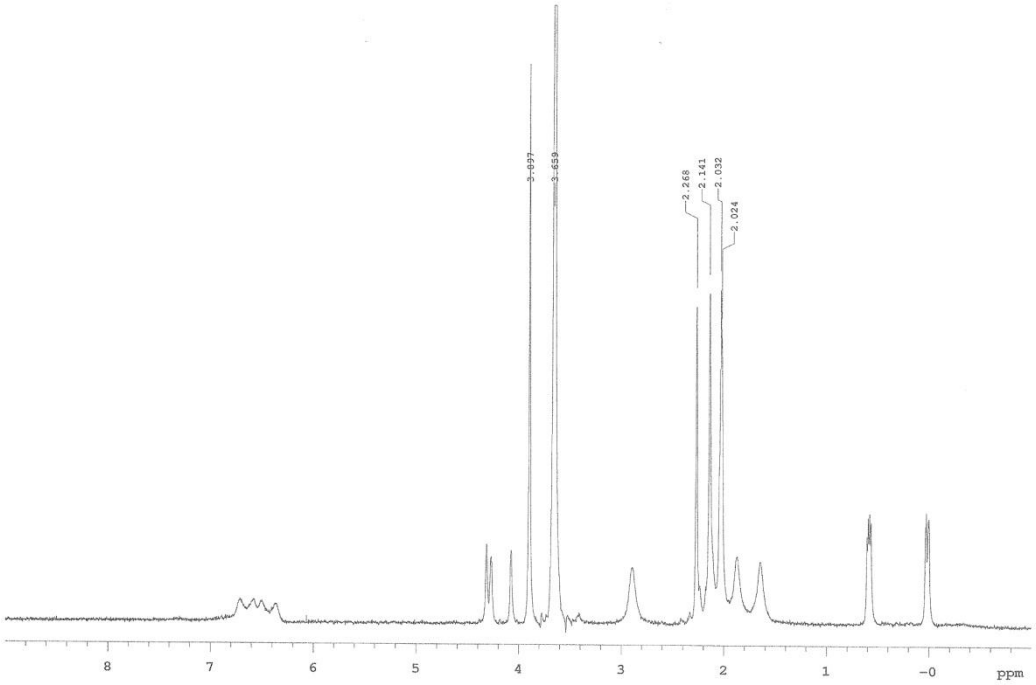
***rac*-1,2-fc(BMes$_2$)(SiMe$_2$OMe) (9)**



**[K(18-crown-6)][8·F]**

(a) $^{1}$H NMR at 20$^{o}$C:




(b) $^{1}$H NMR at 80$^{o}$C: