Supporting information

Labile Dioxy-Functionalised Zwitterionic Imidazolinium Salt: Access to Zwitterionic and Neutral Imidazolidin-2-ylidene Derivatives and π-Acceptor Properties of Imidazolidine-2-selones

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Contents

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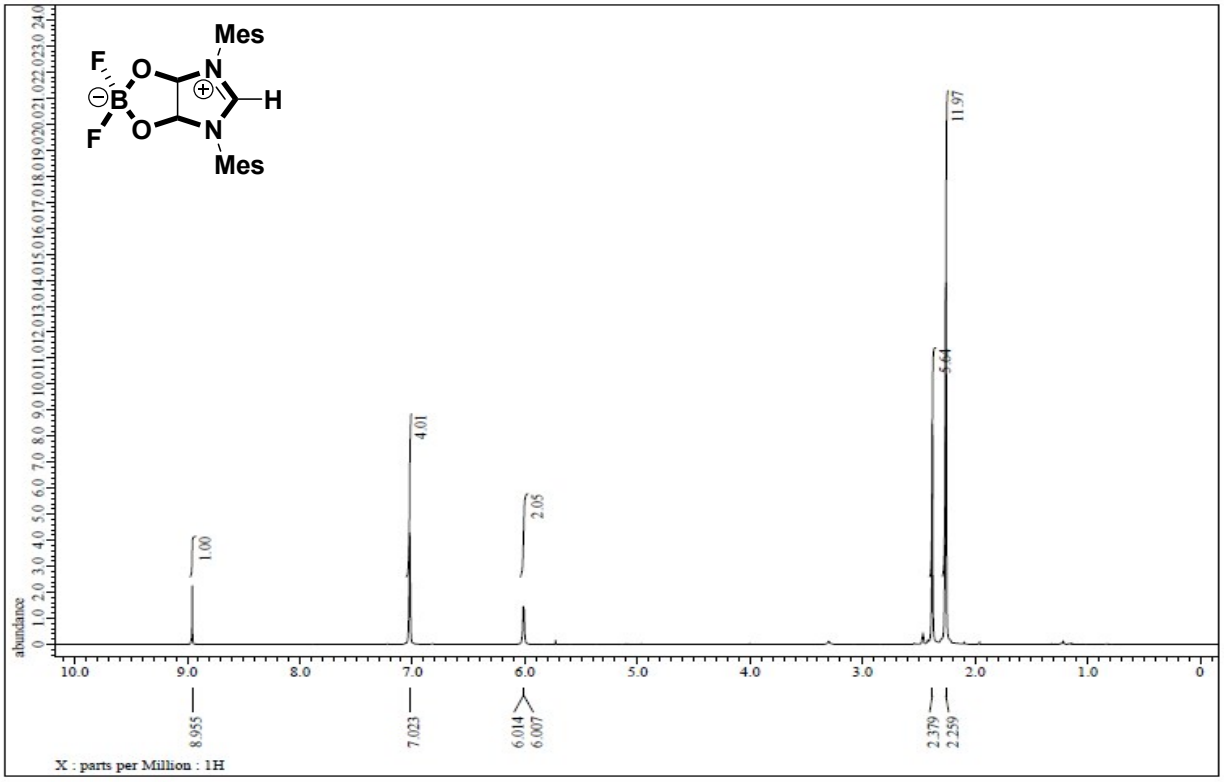
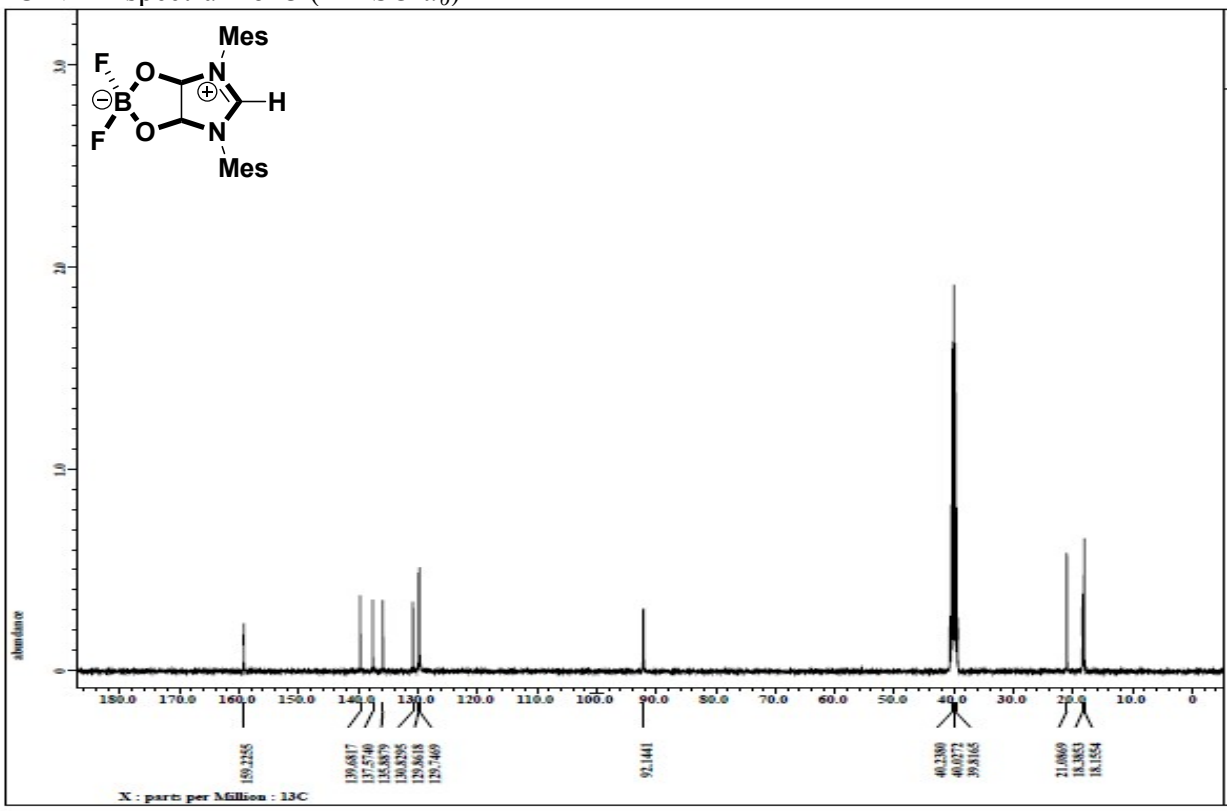
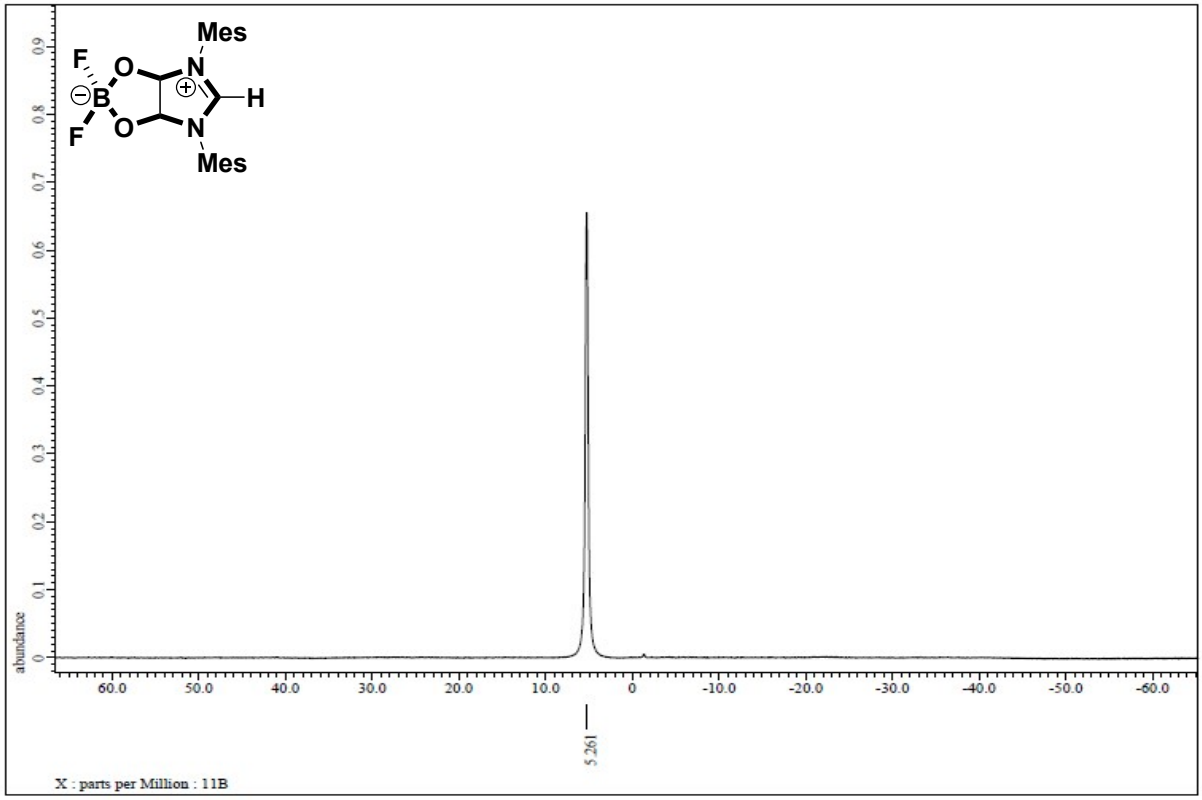
^{1}H NMR spectrum of **3** (DMSO-d_6)



^{13}C NMR spectrum of **3** (DMSO-d_6)



^{11}B NMR spectrum of **3** (DMSO-d_6)



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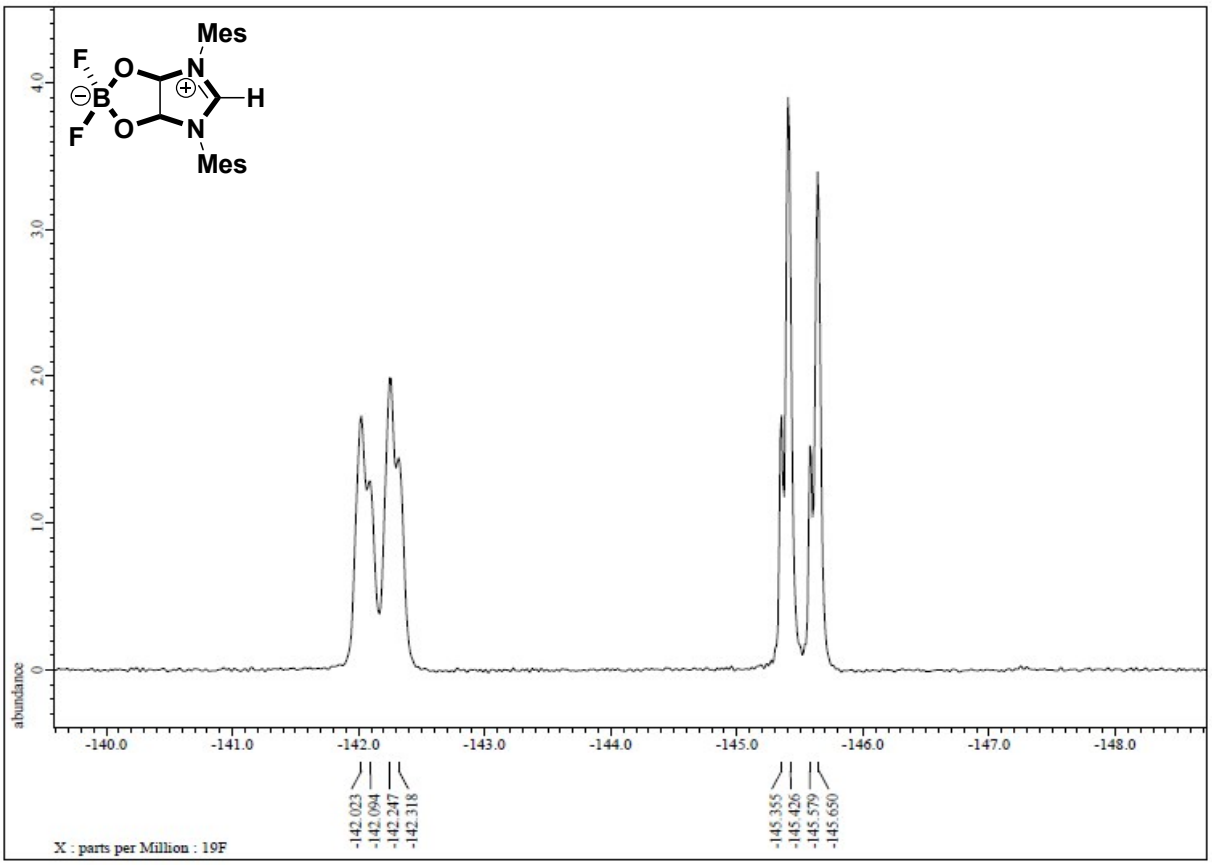

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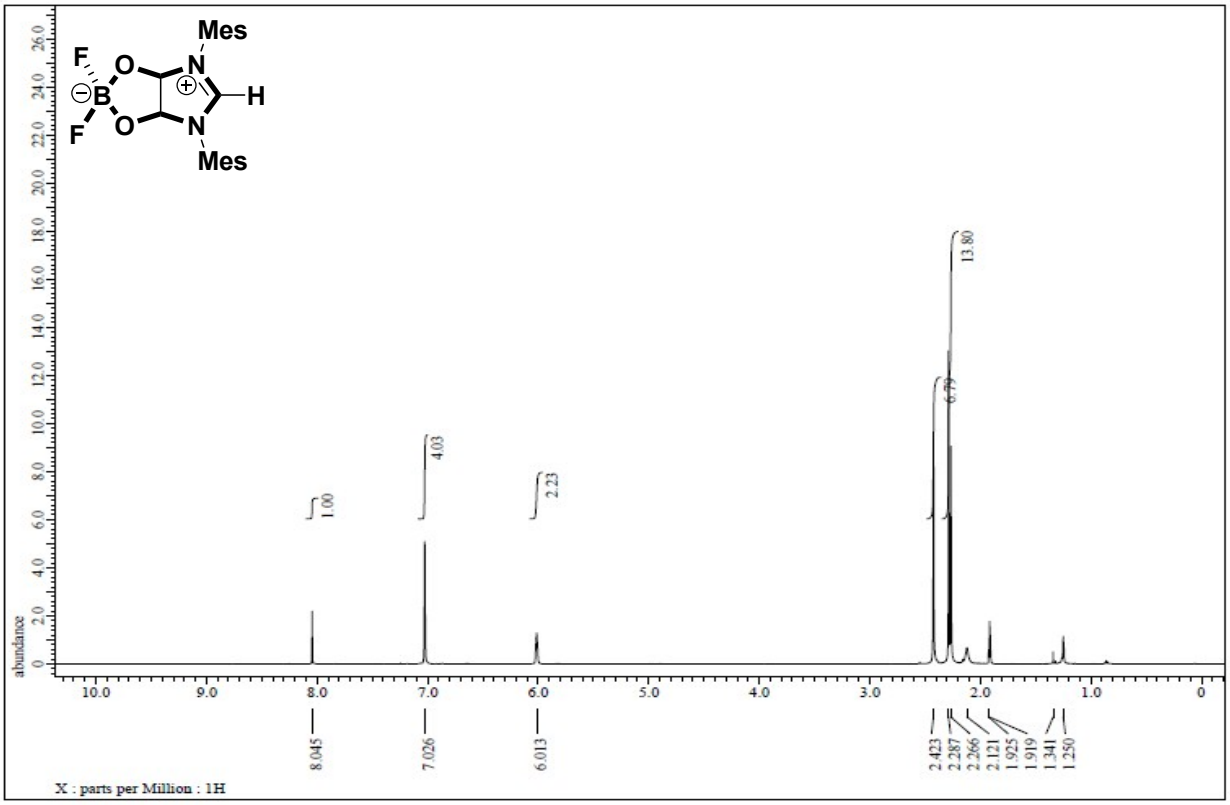

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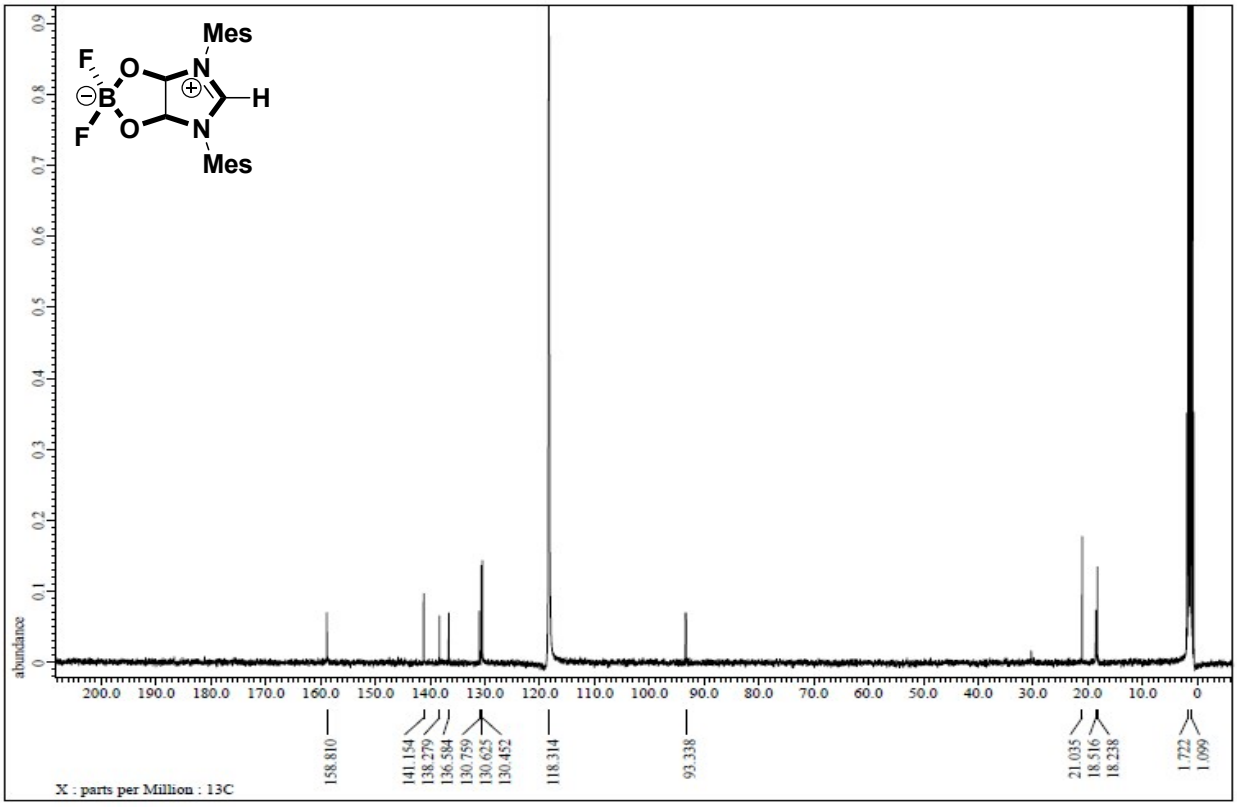

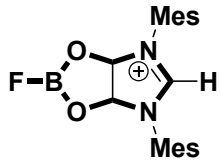

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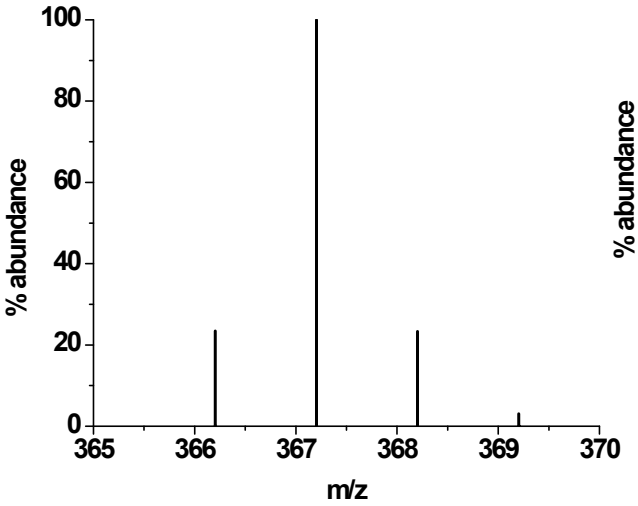

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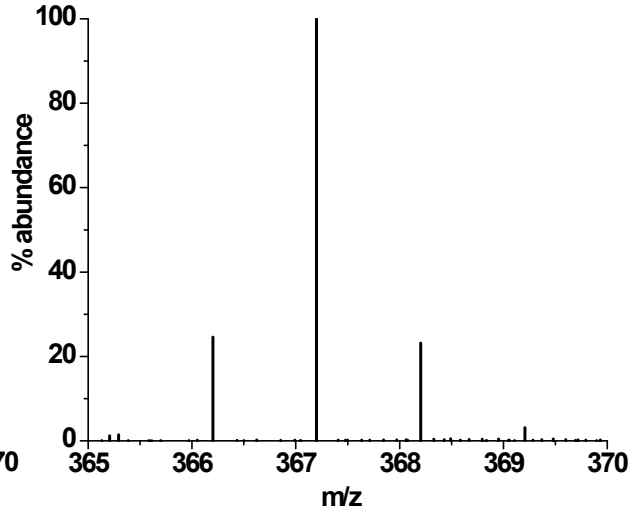

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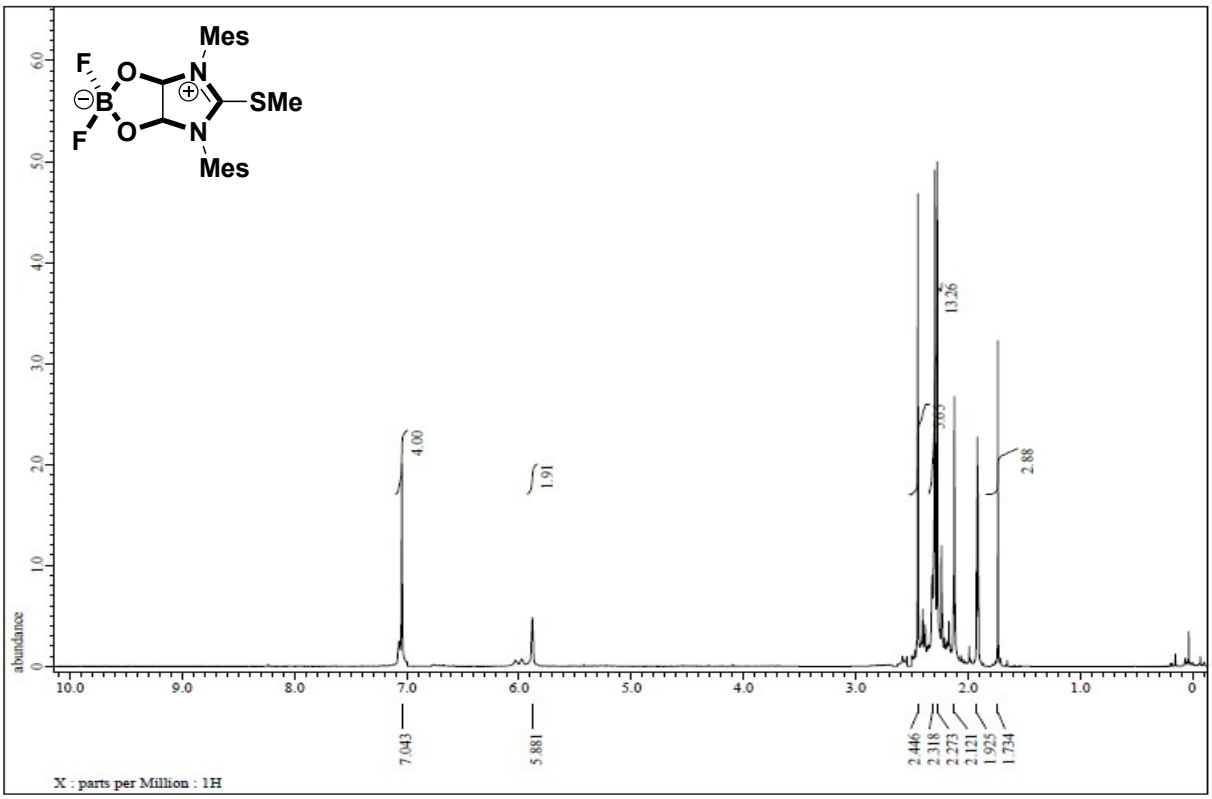

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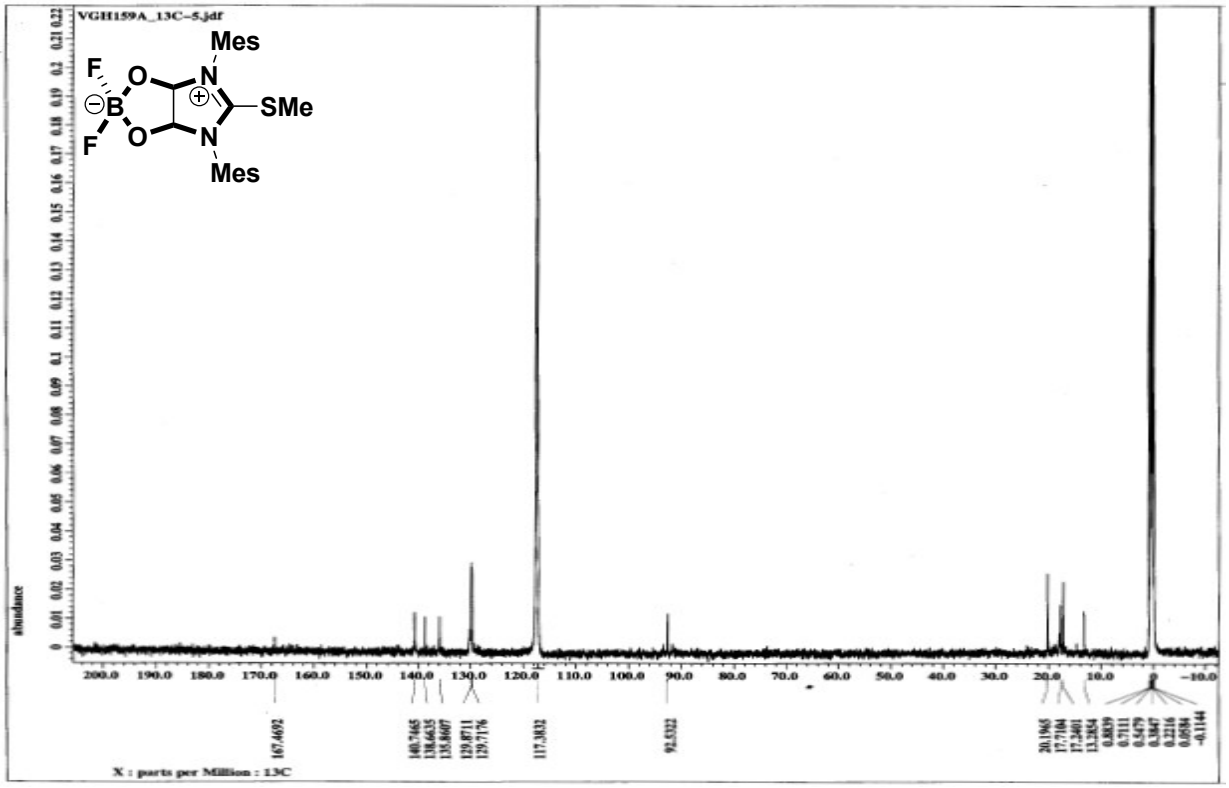

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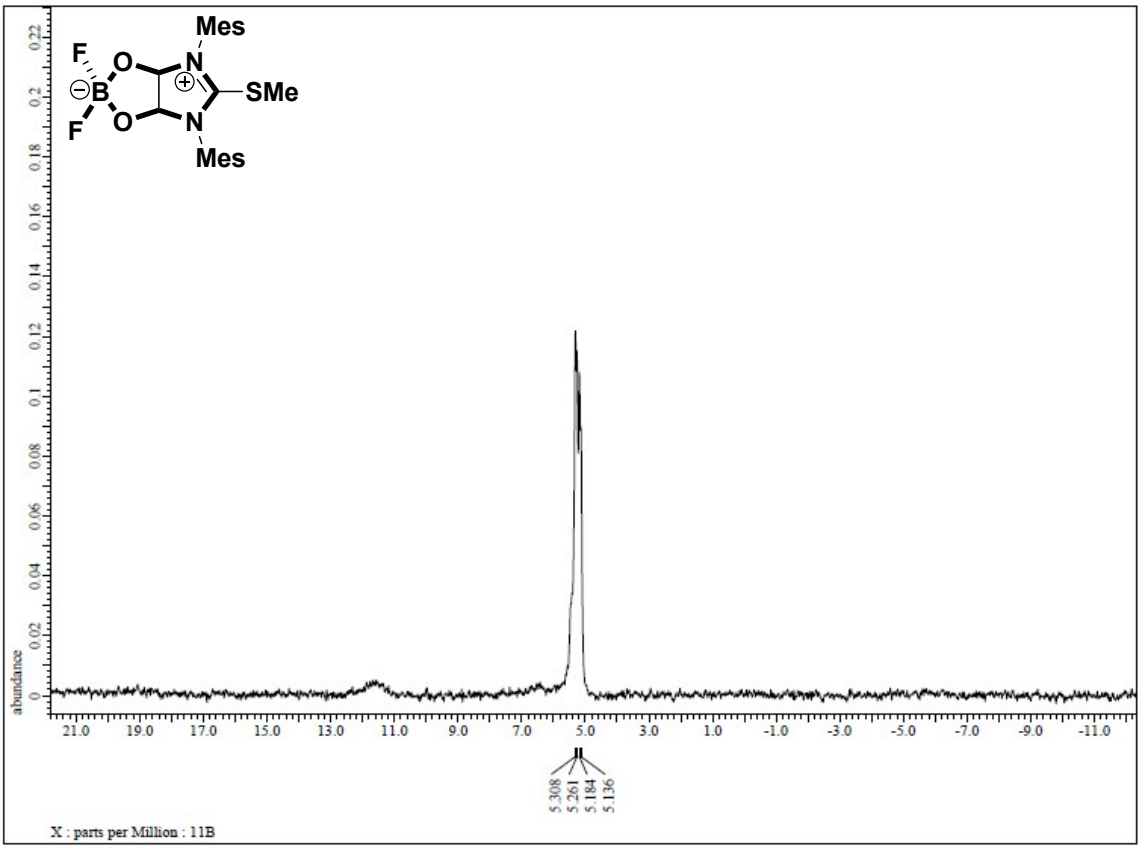

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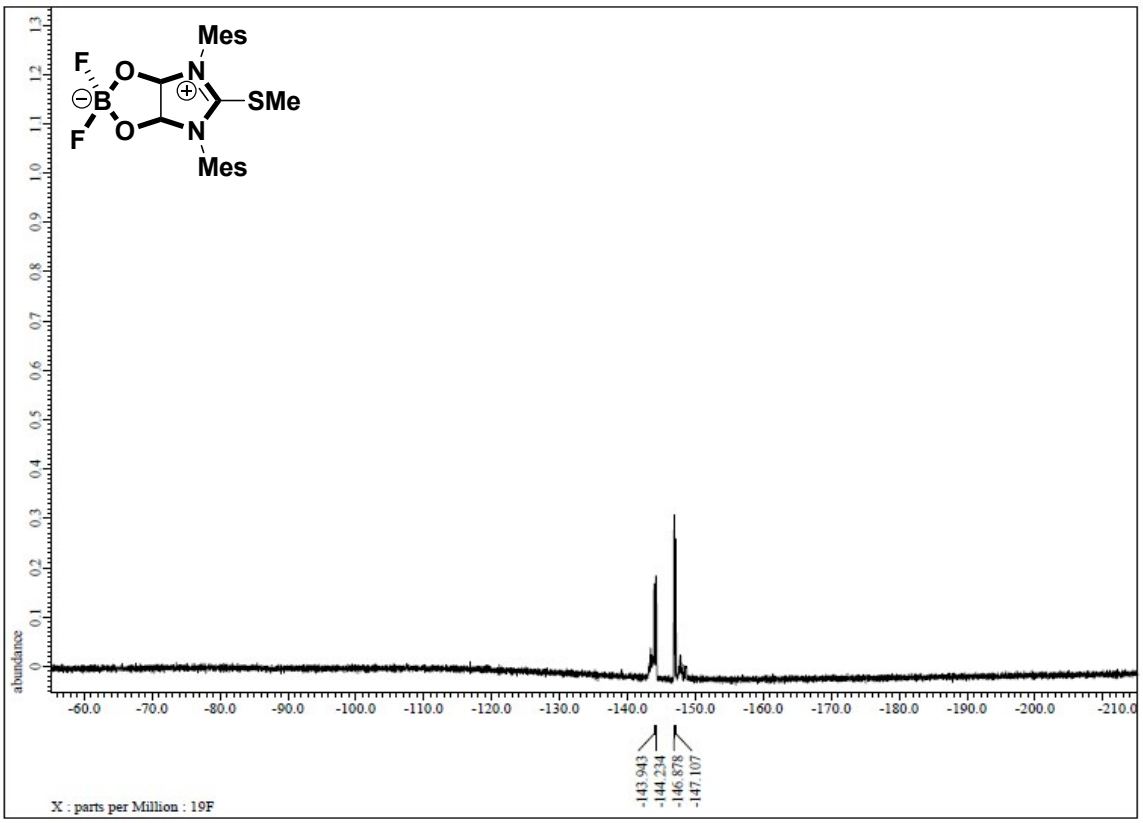

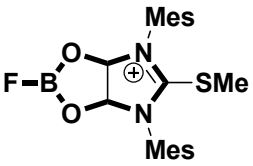
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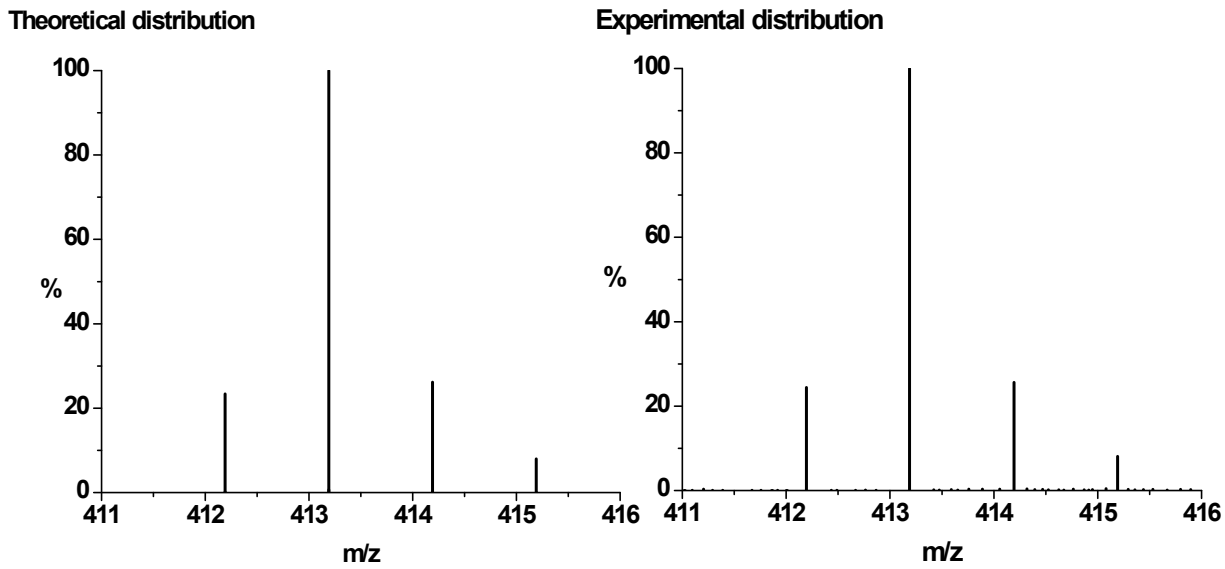
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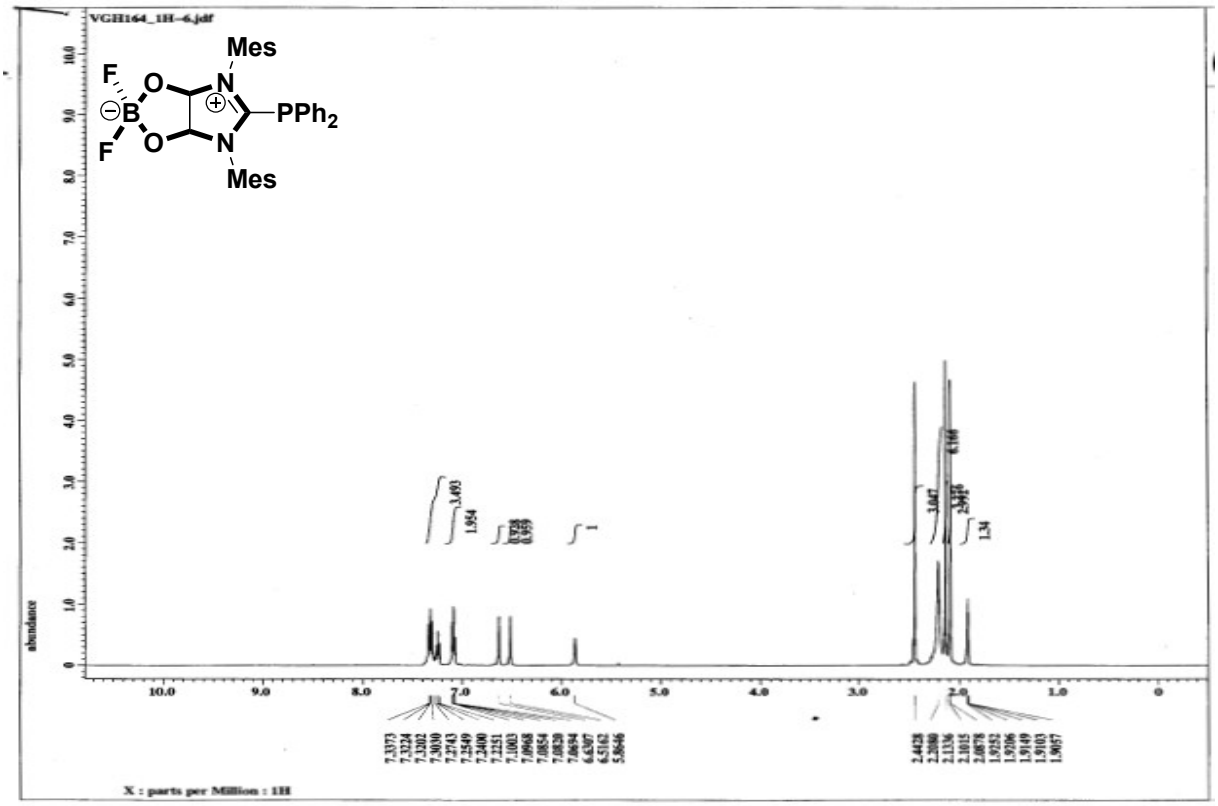

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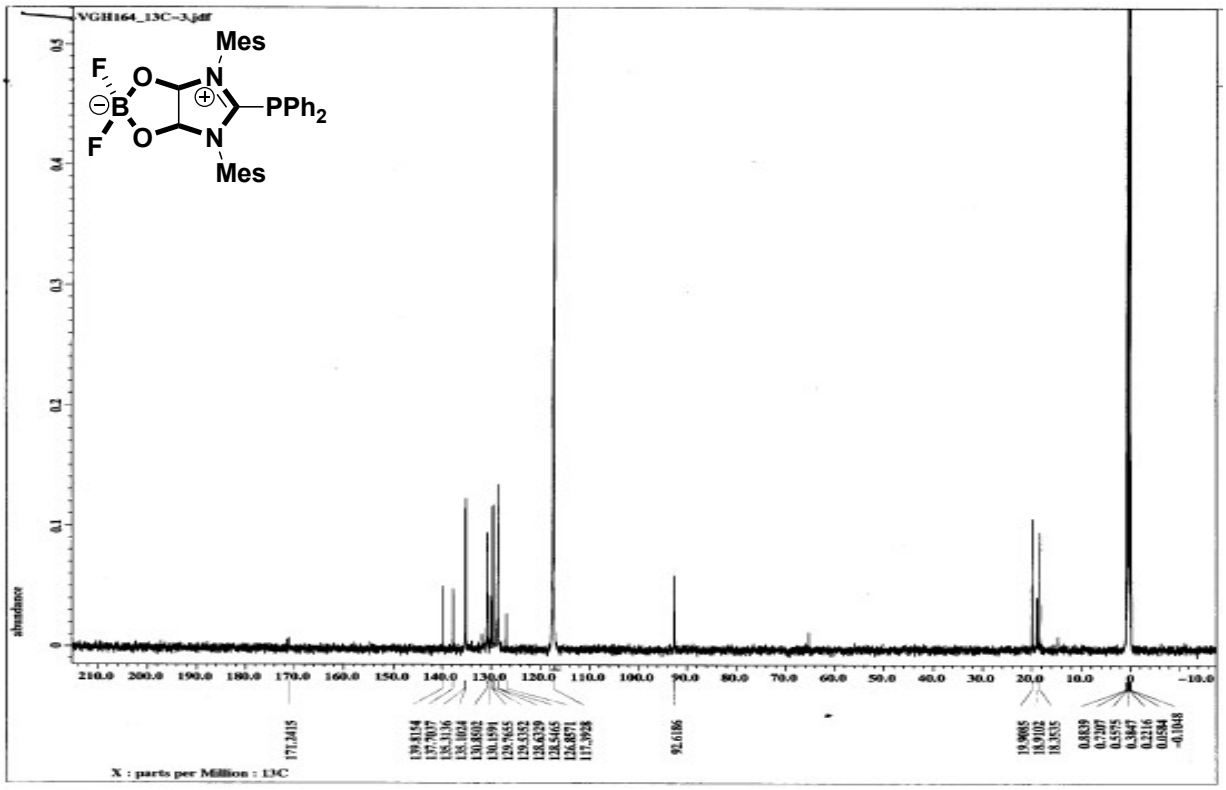

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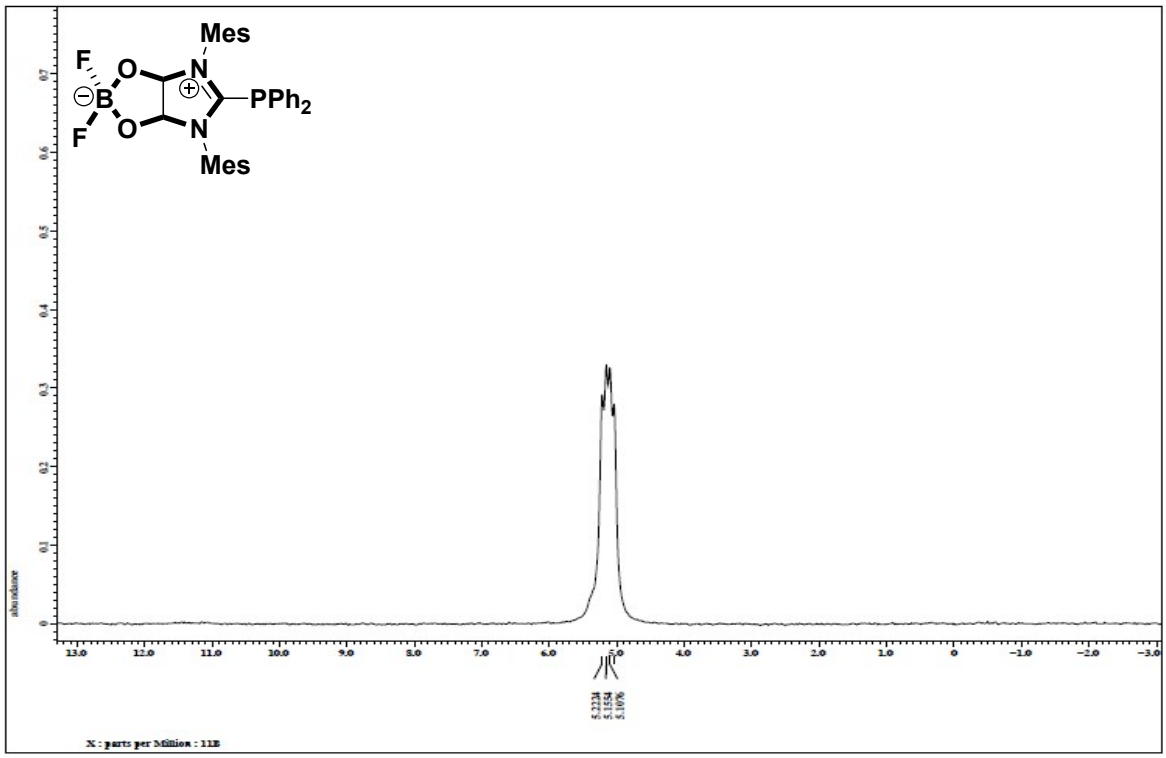

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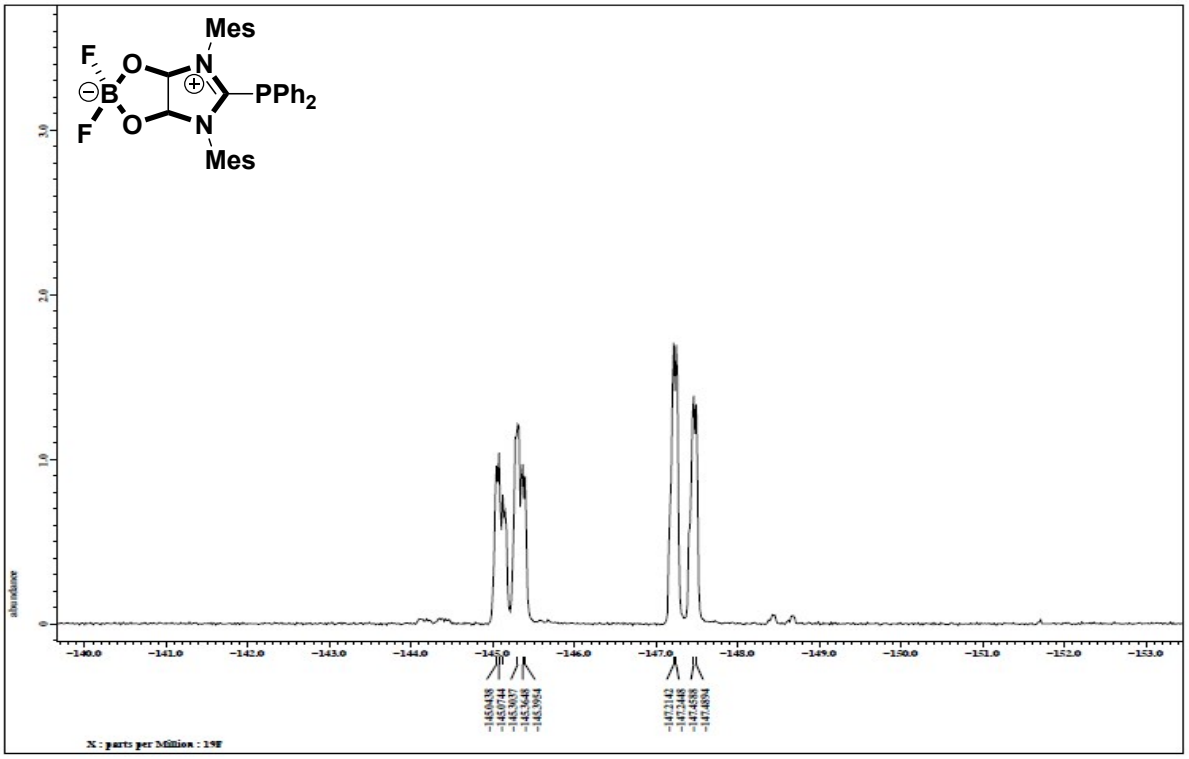

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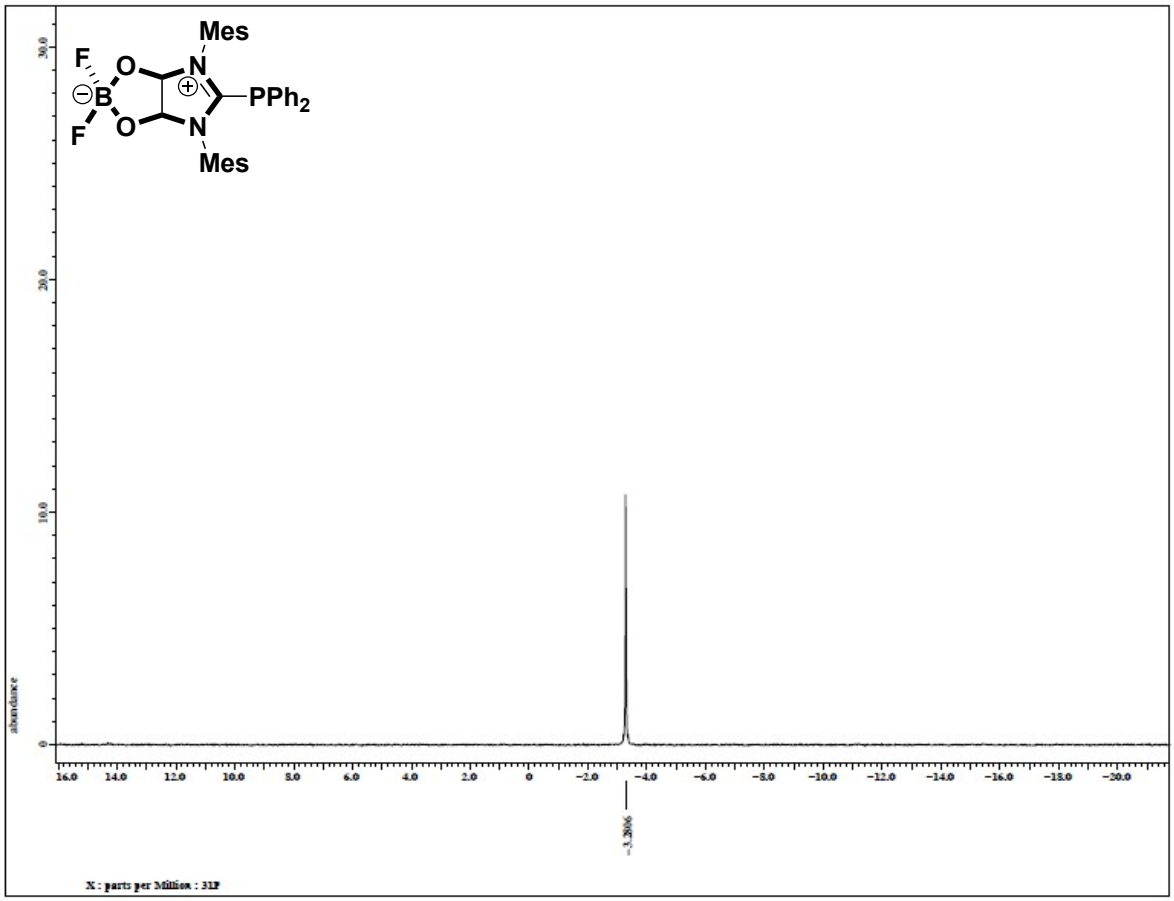

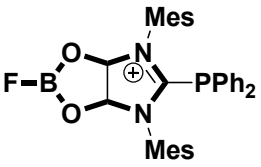

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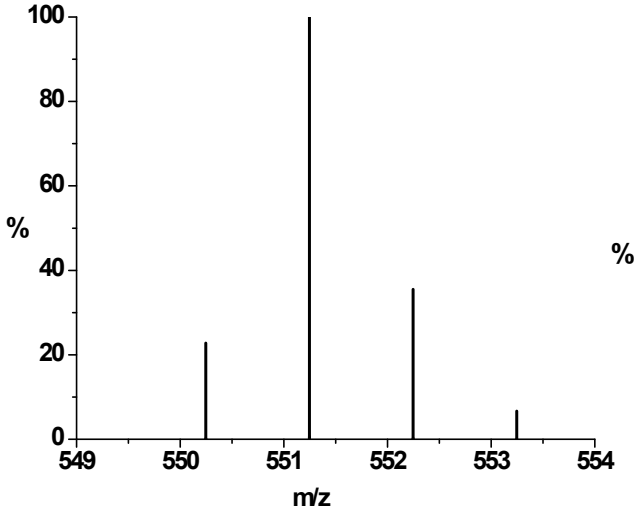

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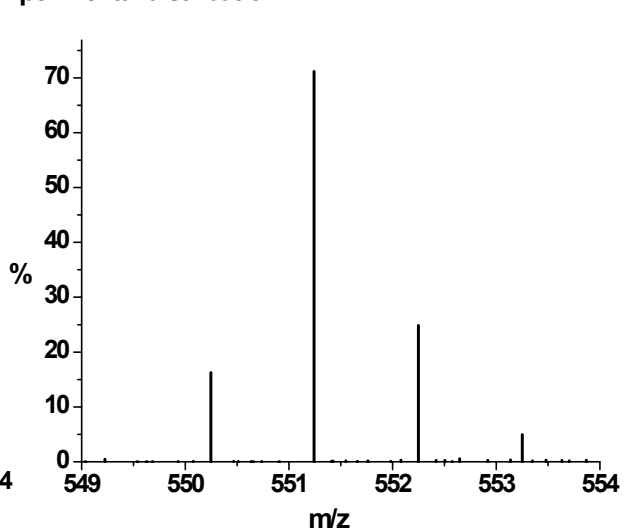

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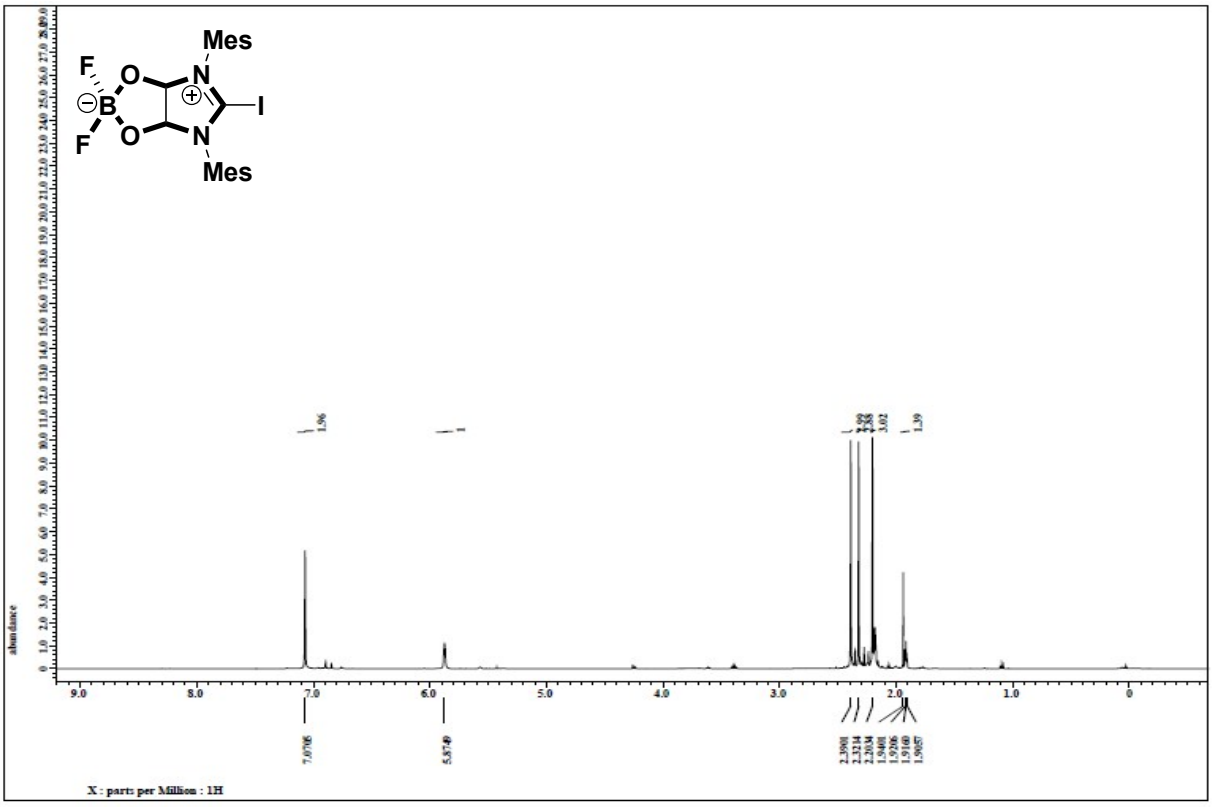

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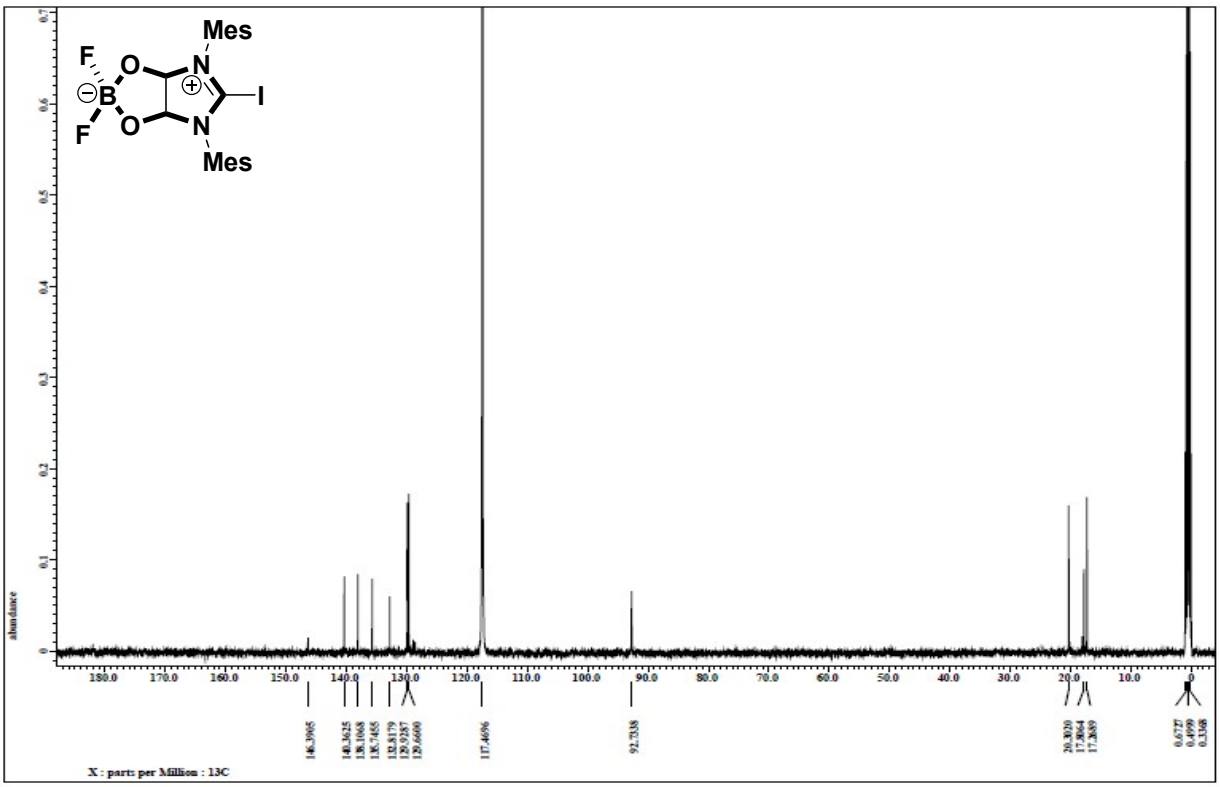

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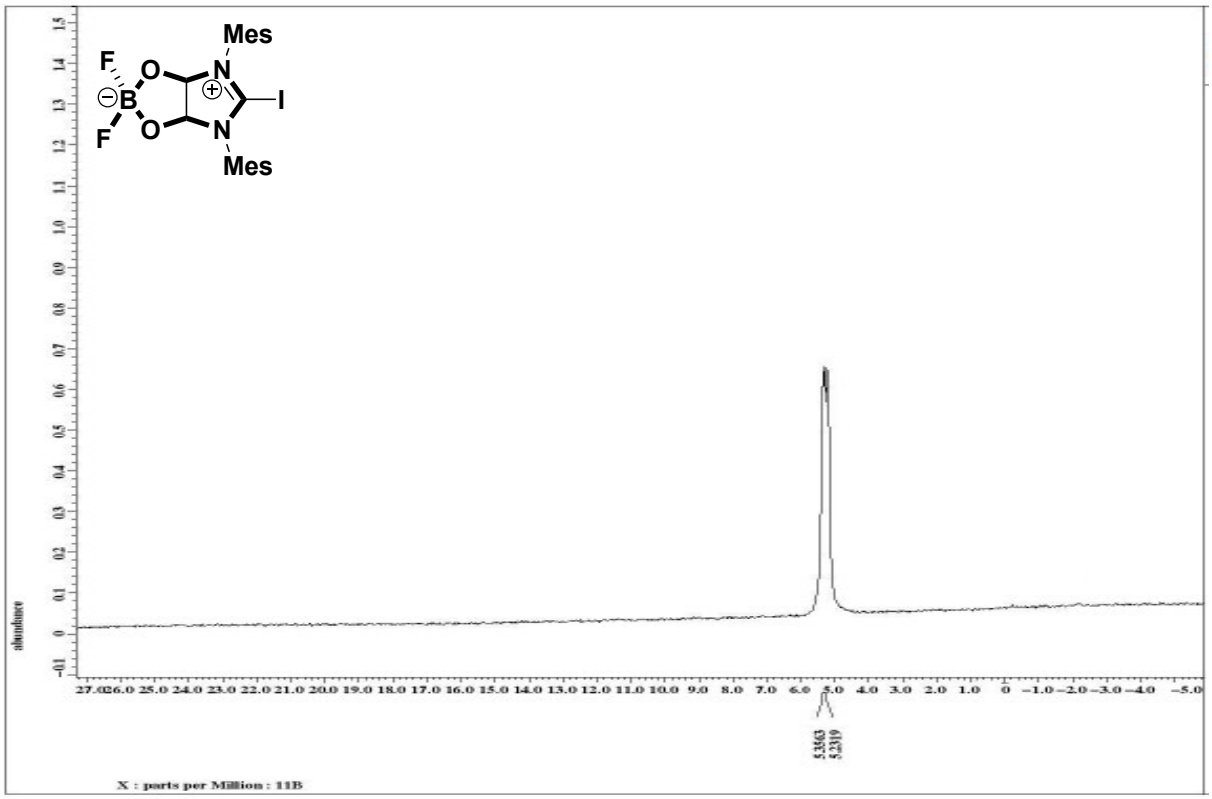

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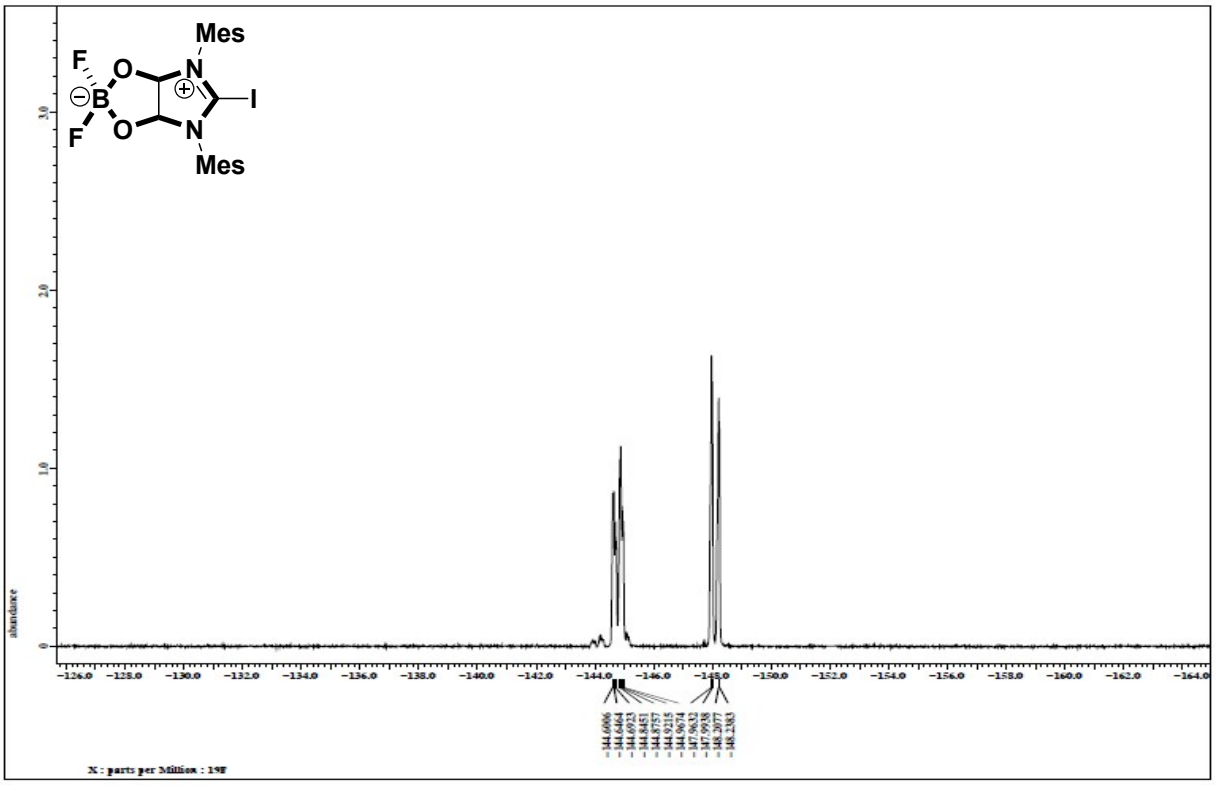

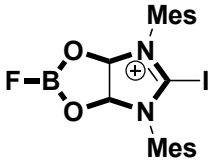

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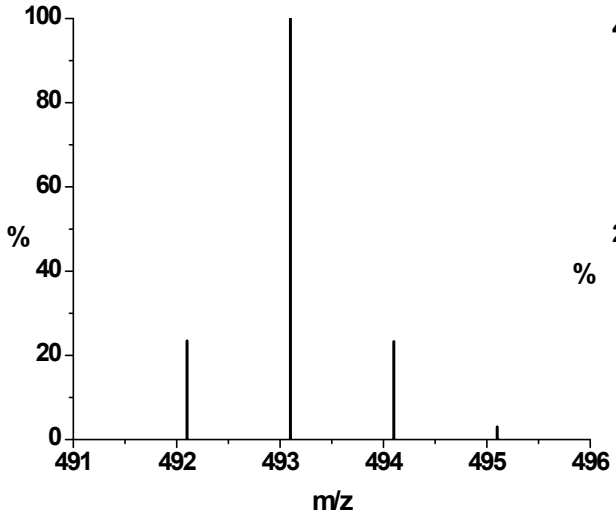

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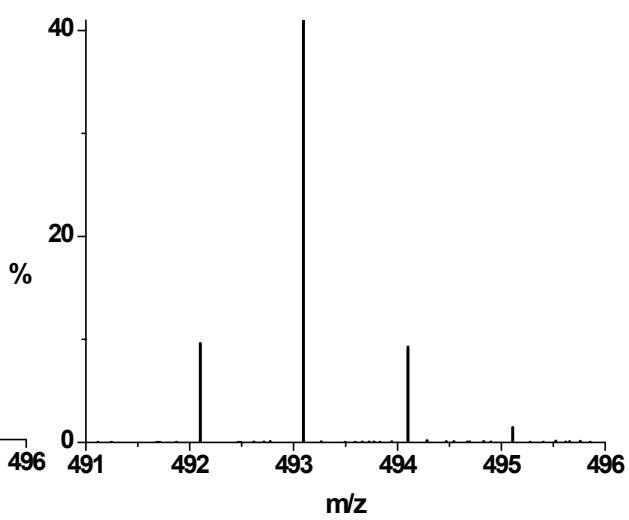

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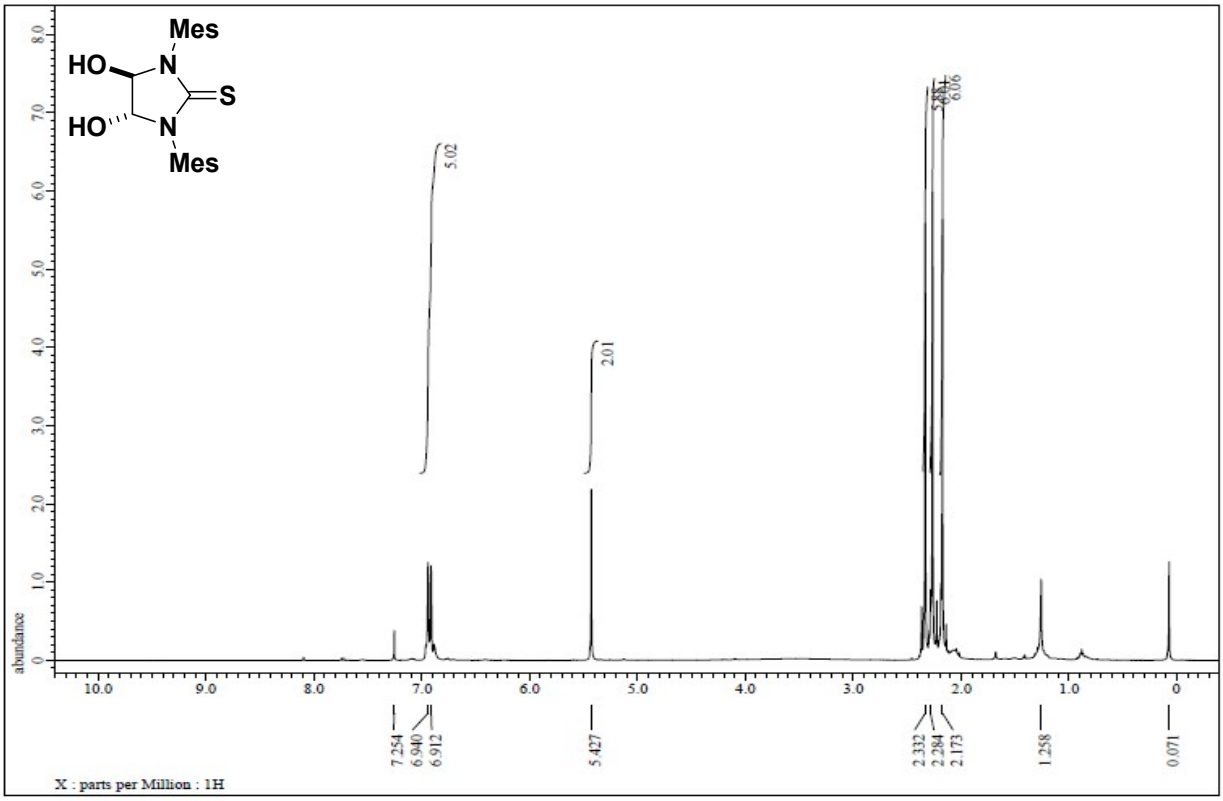

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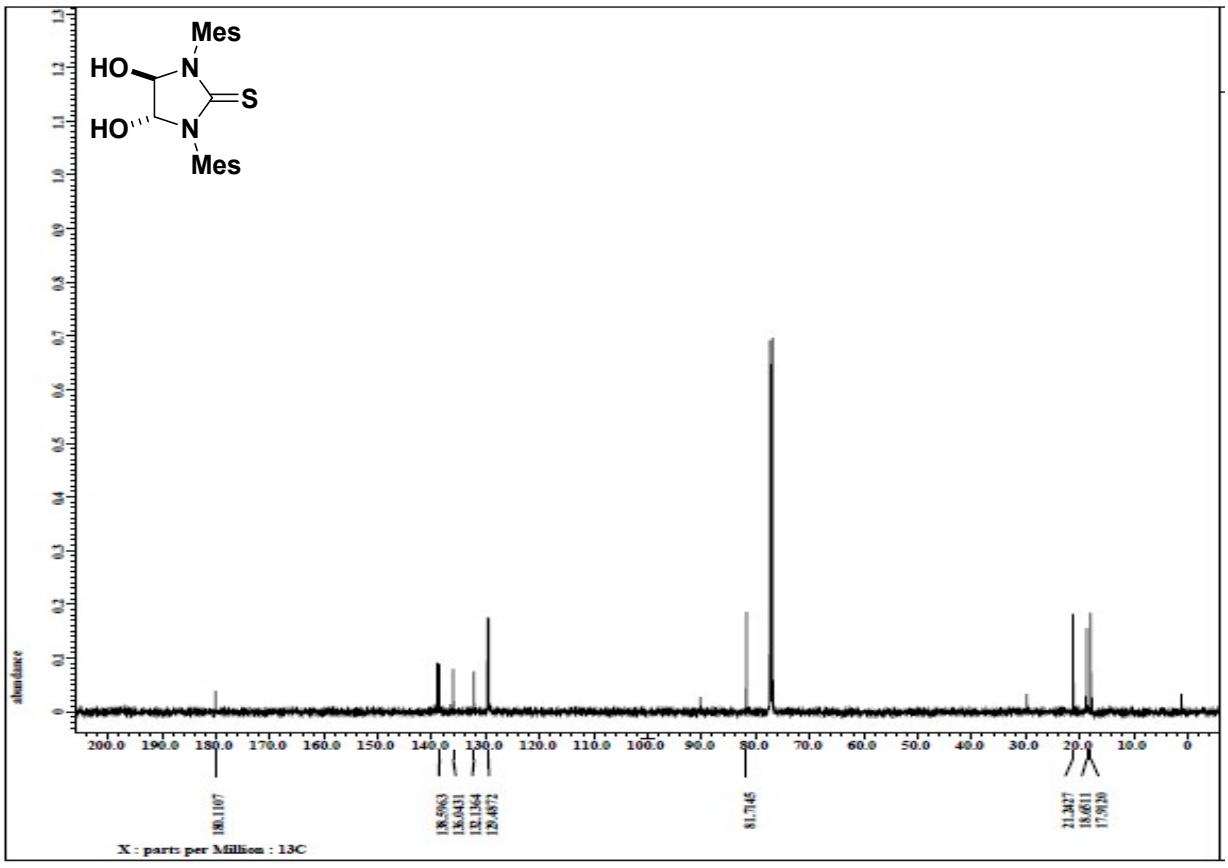

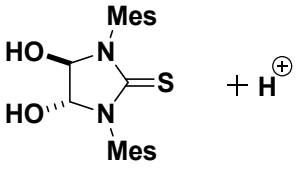

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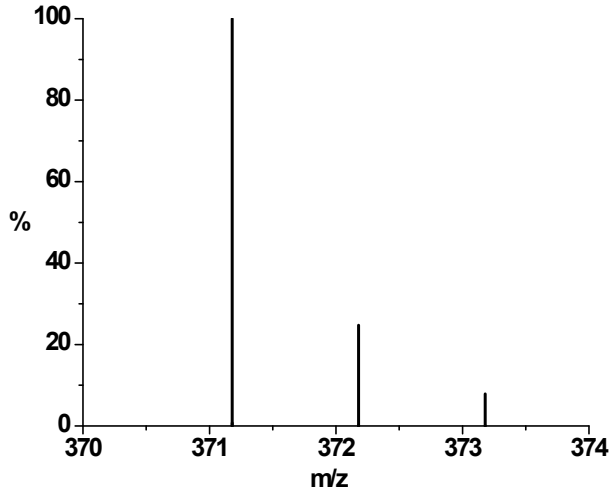

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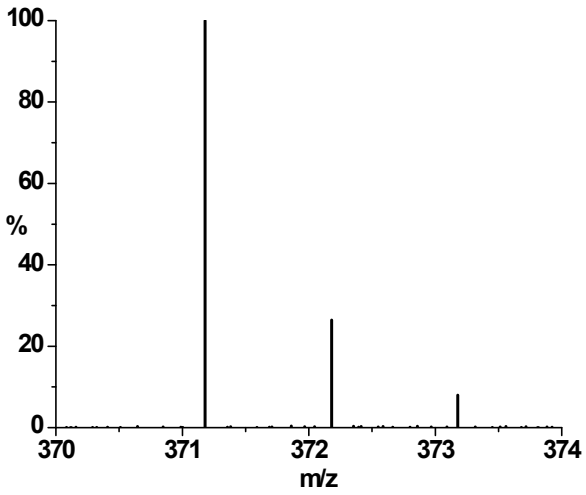

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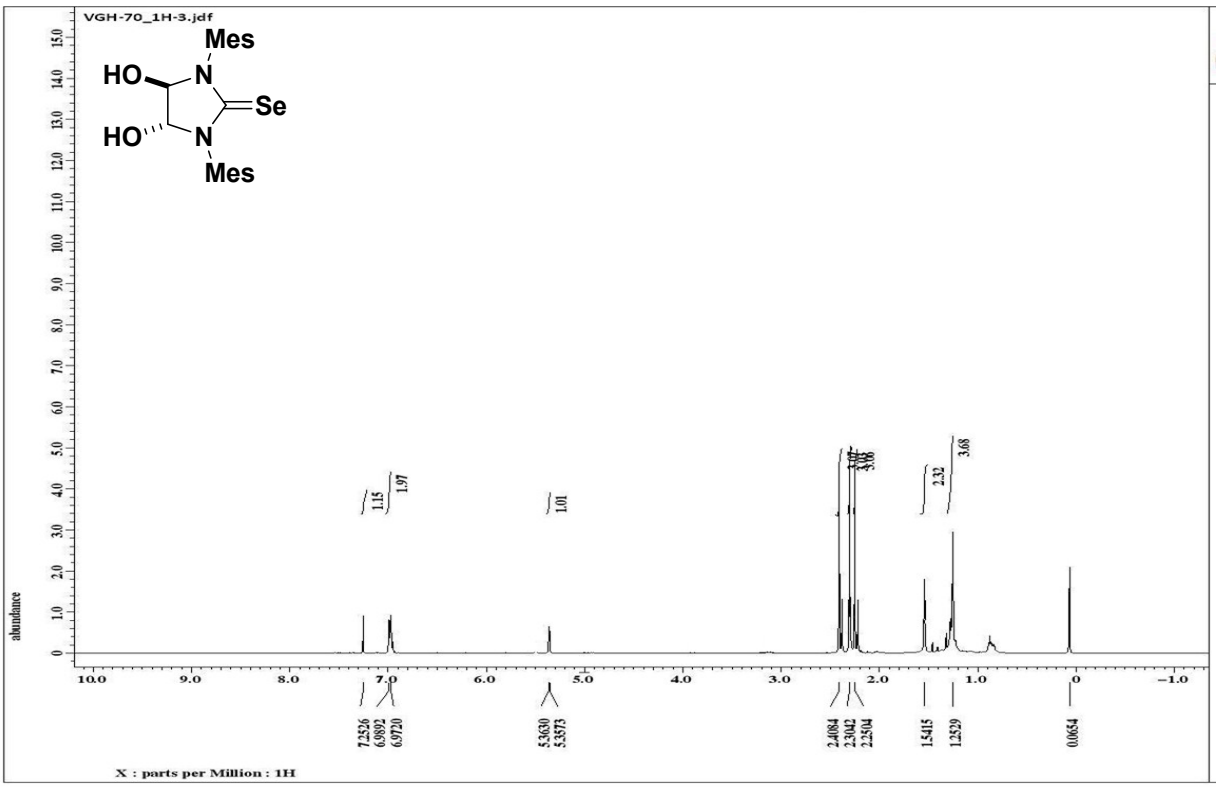

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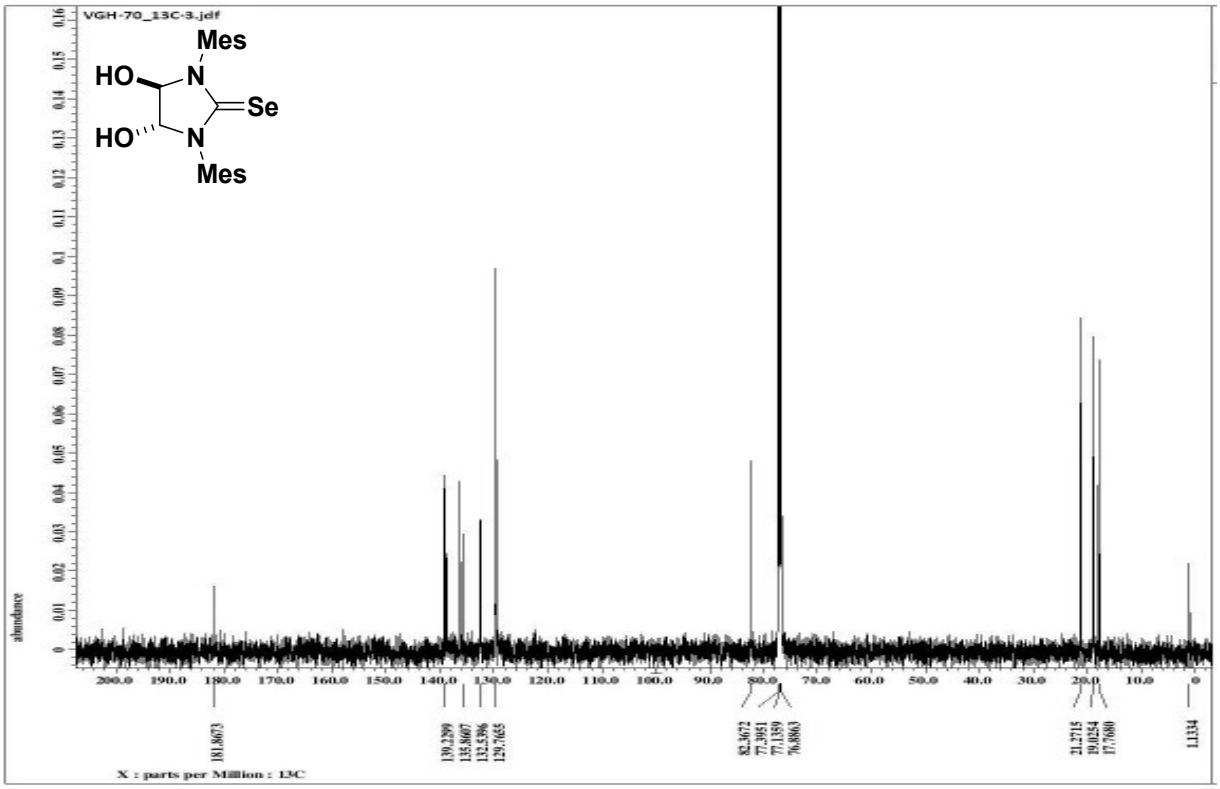

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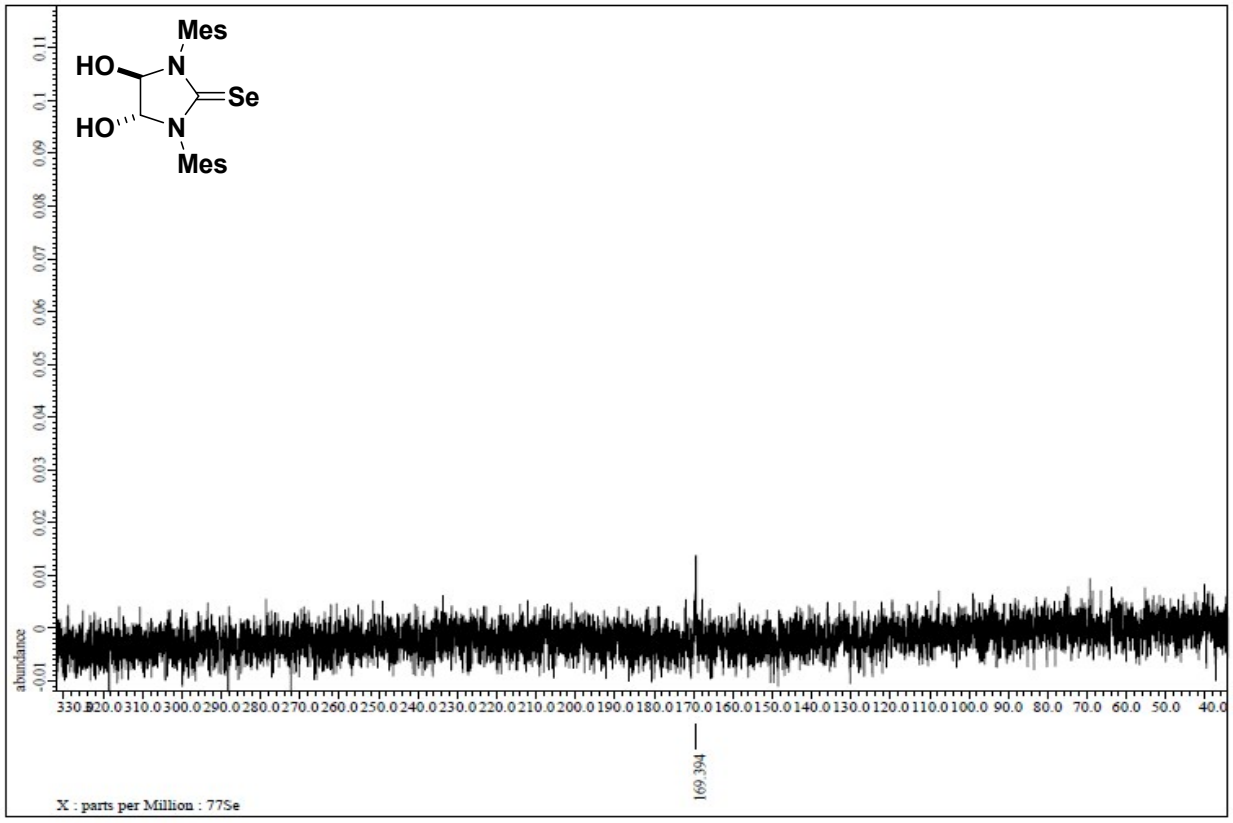

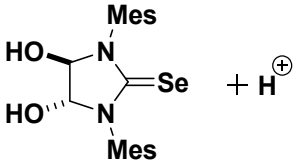

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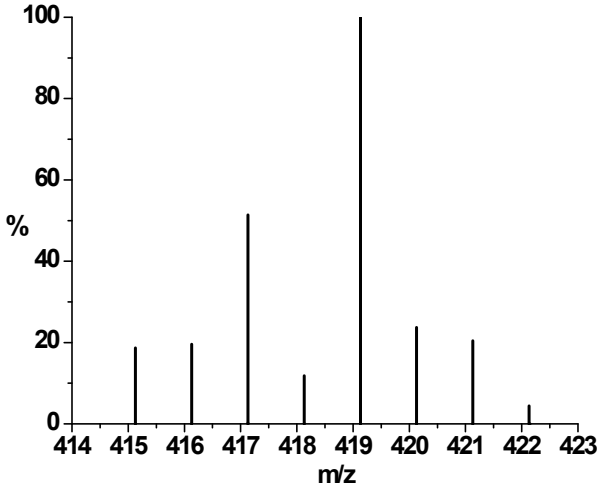

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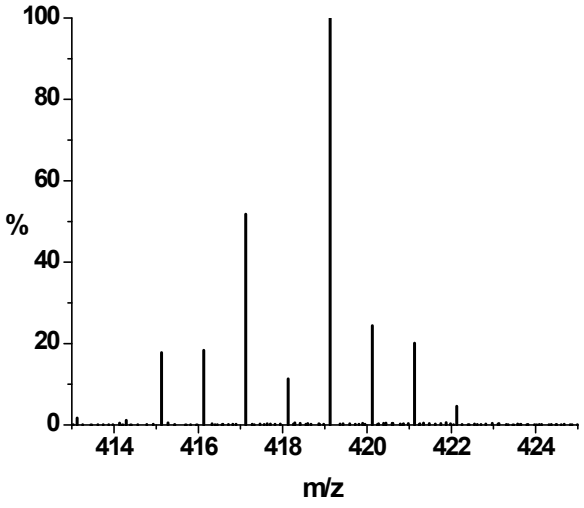

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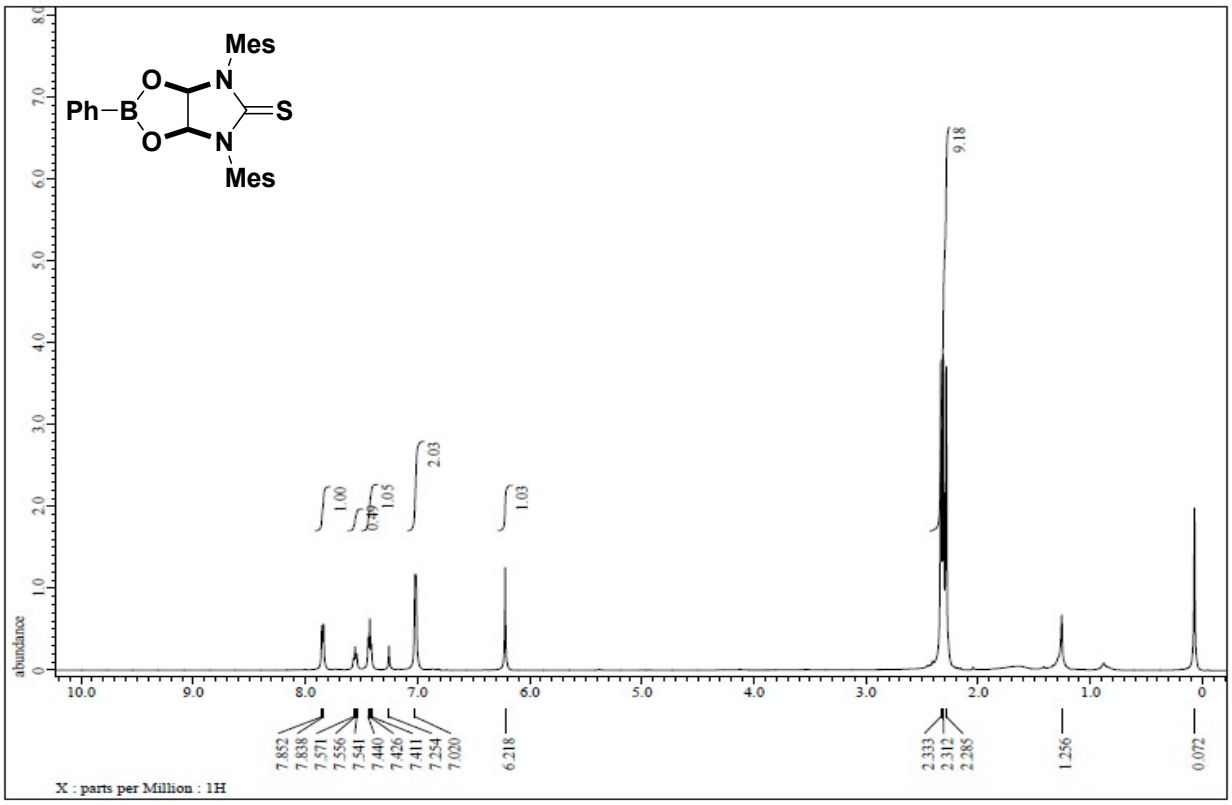

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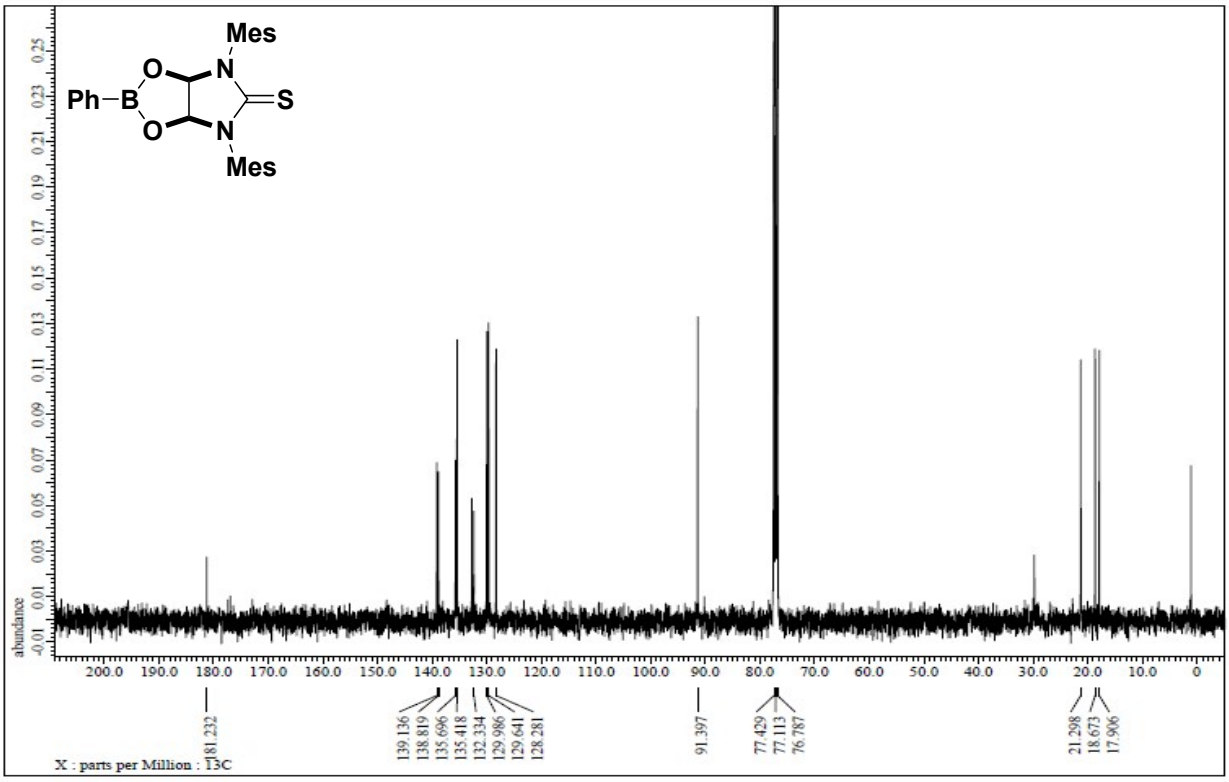

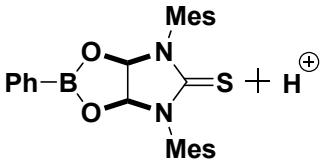
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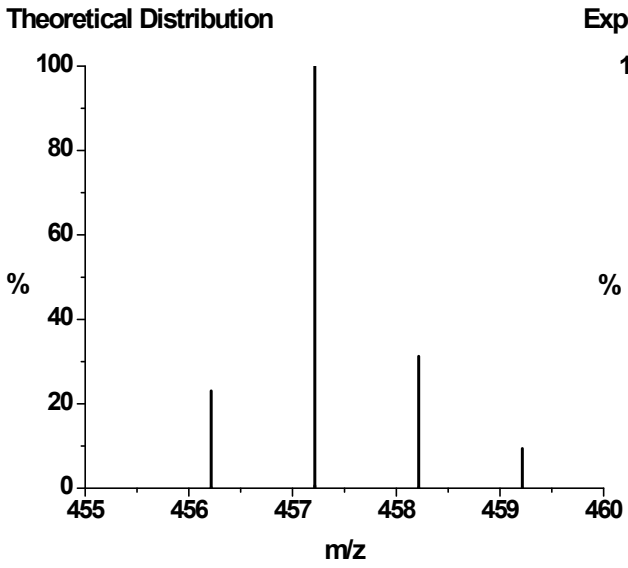
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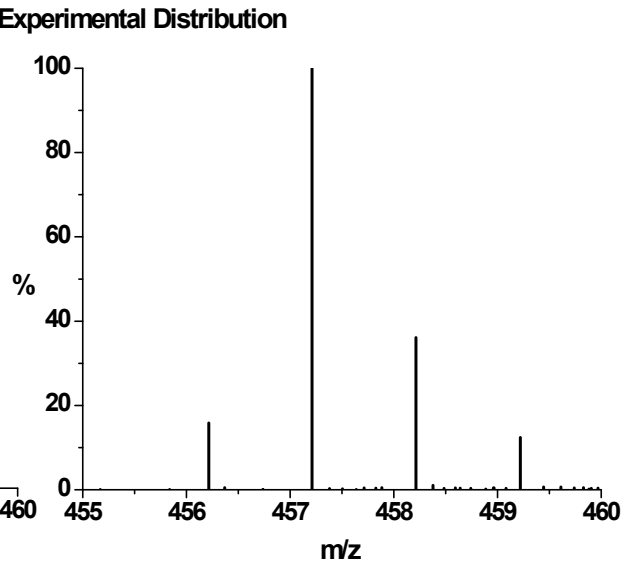
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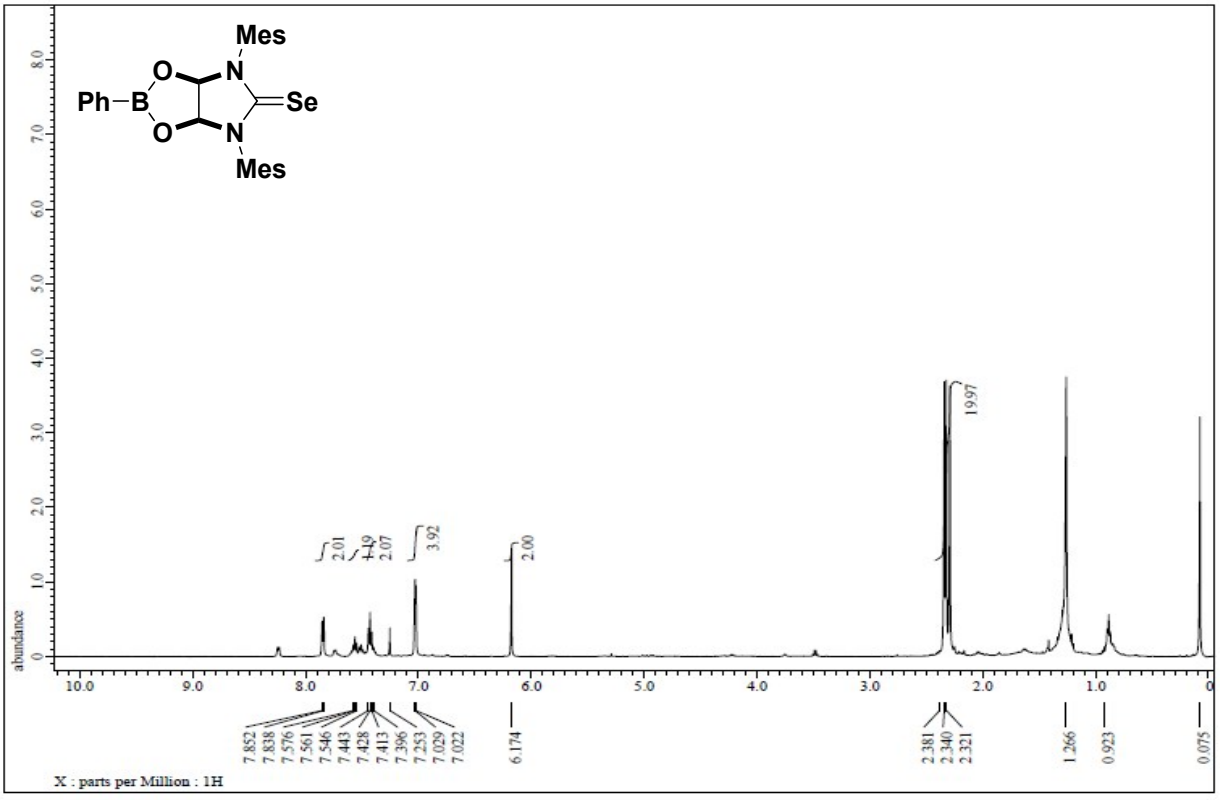

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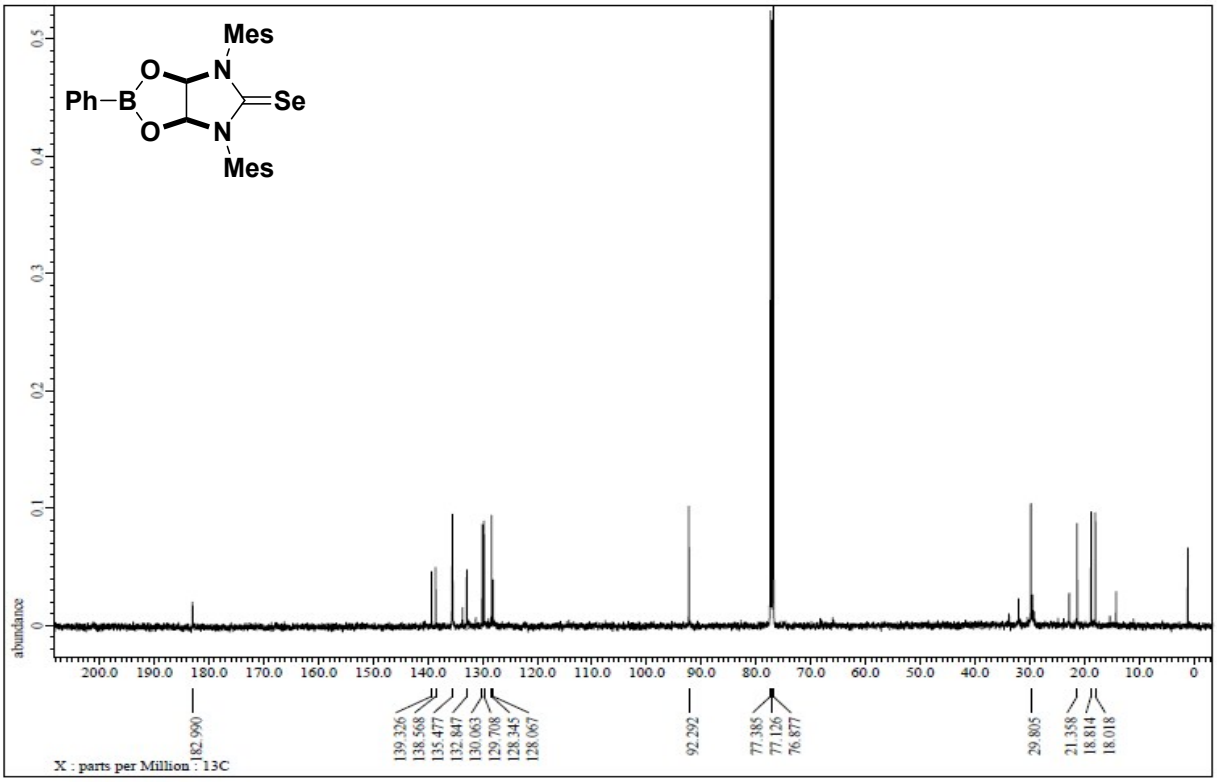

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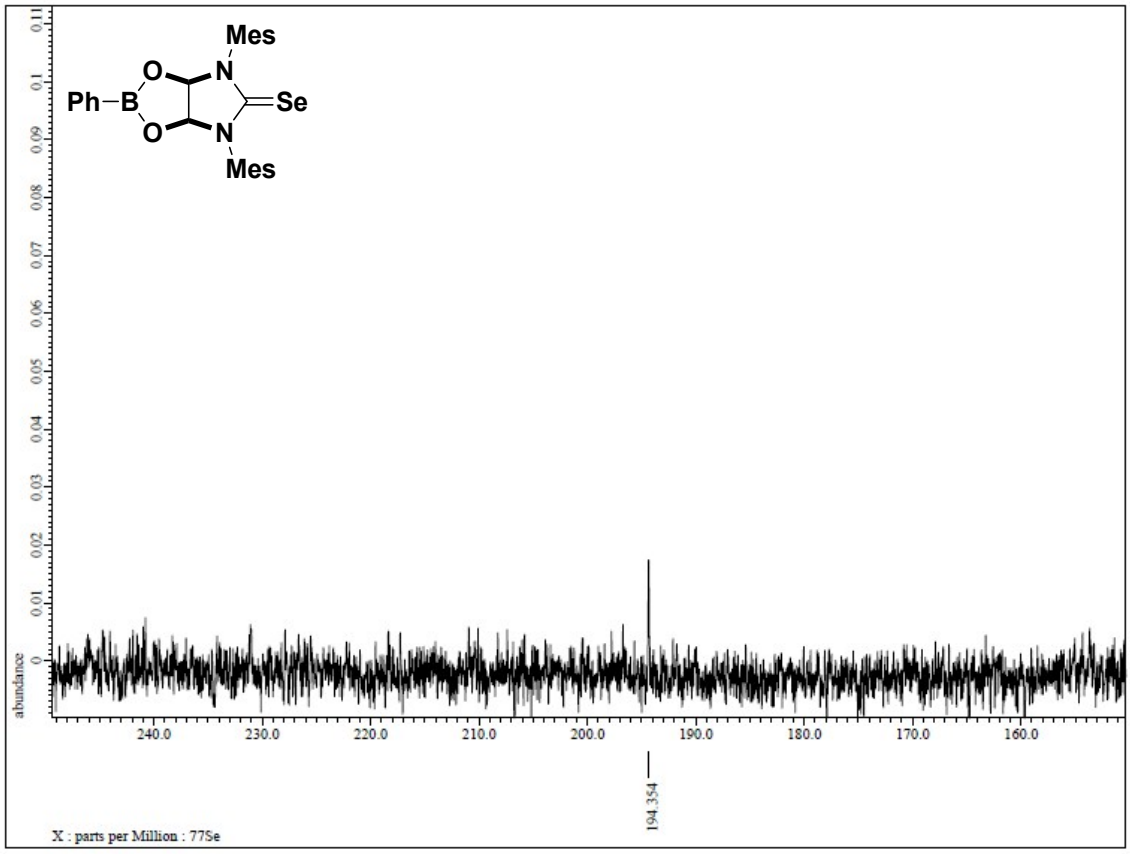

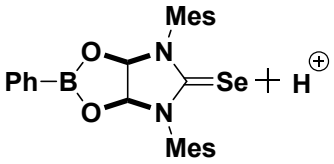

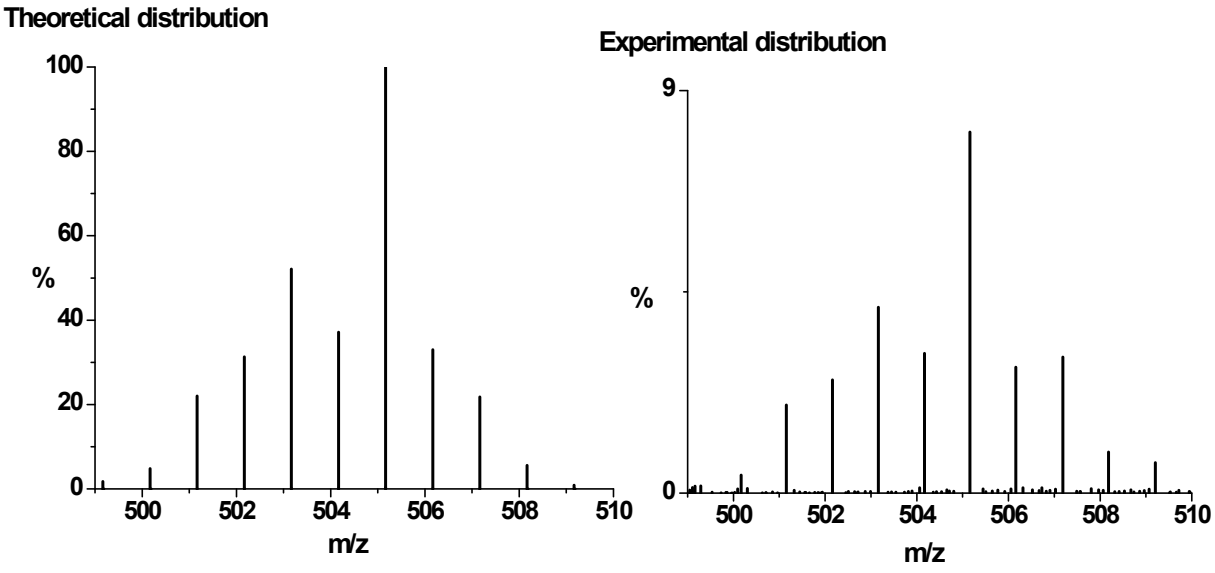

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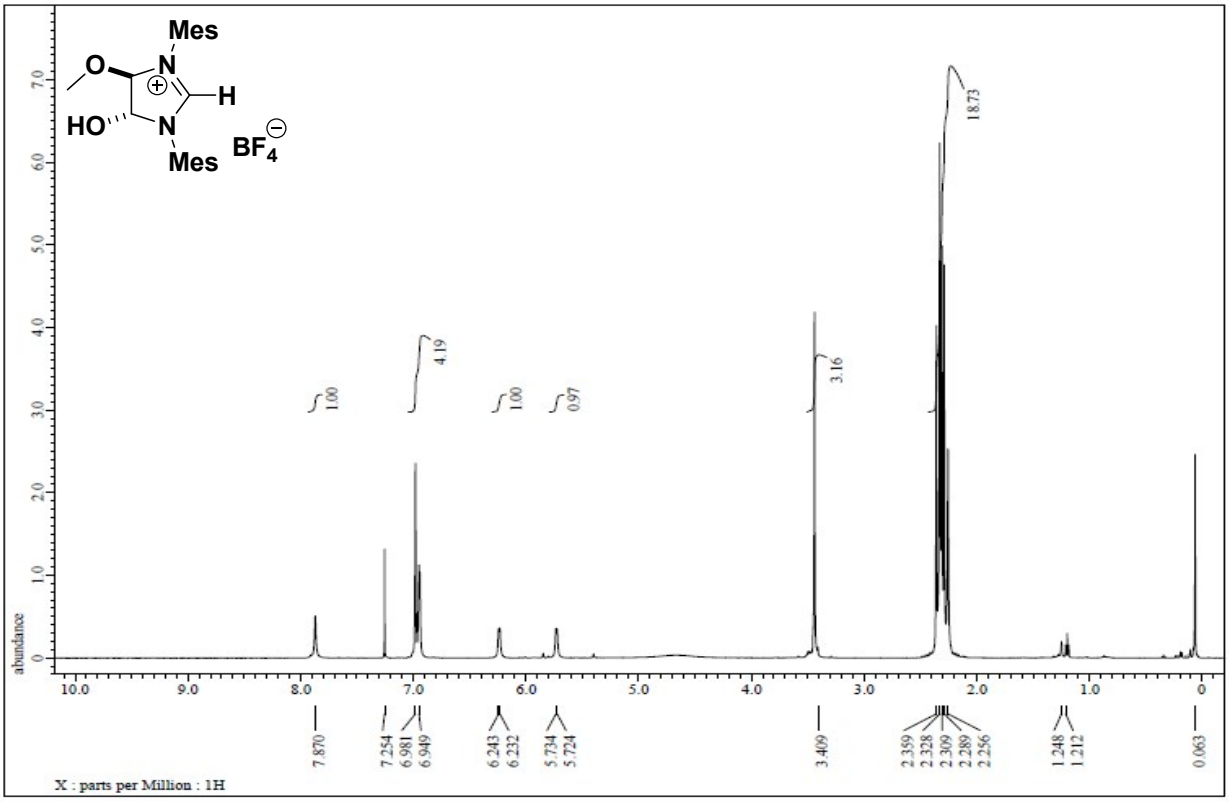

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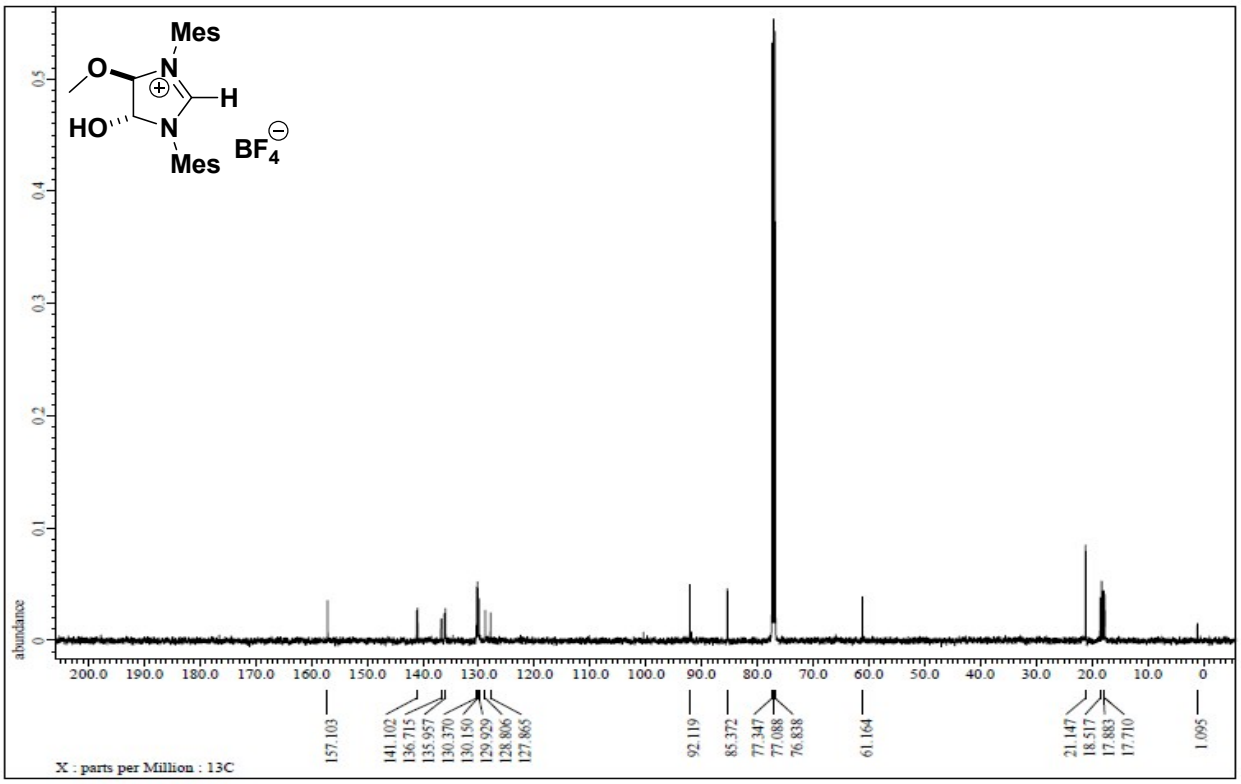
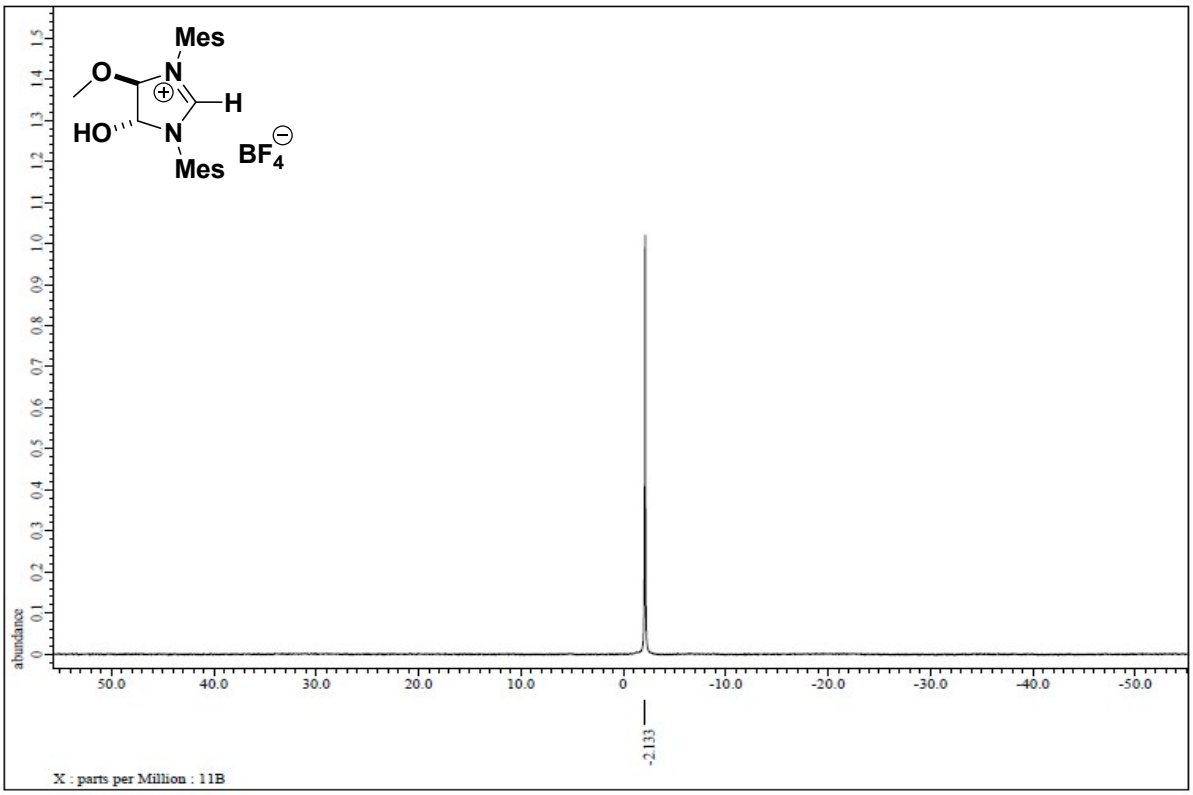
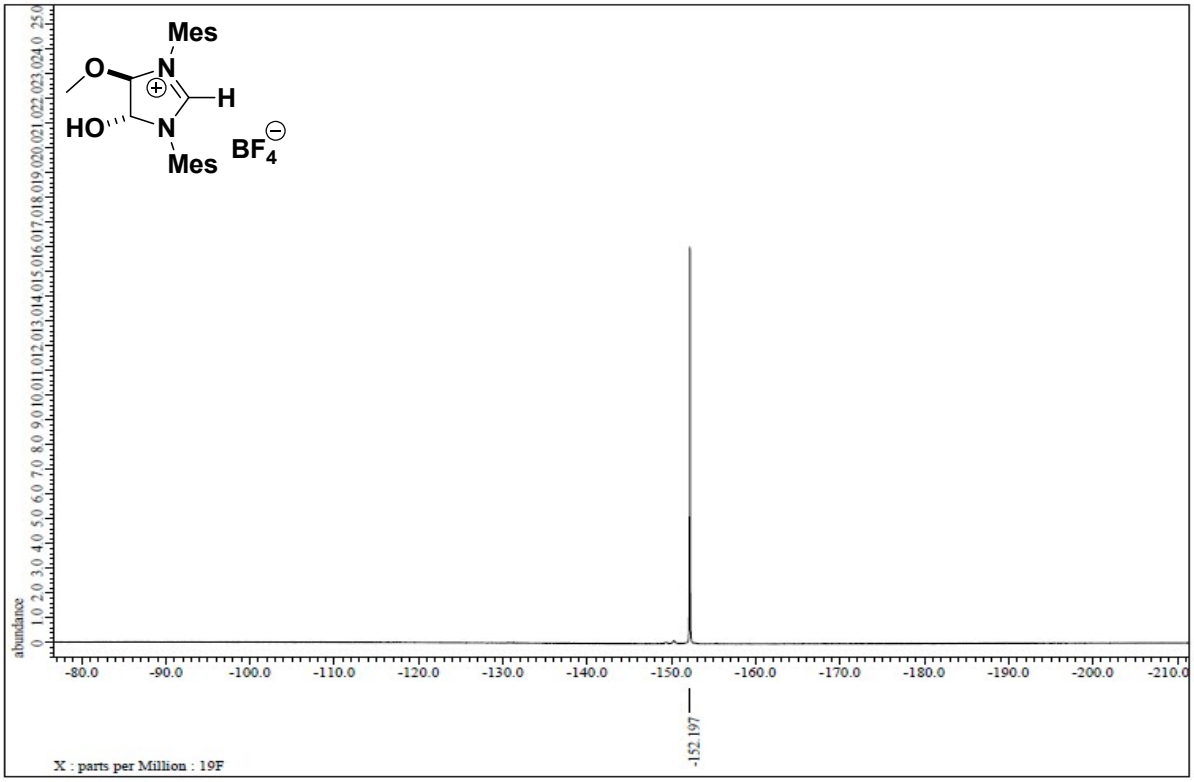
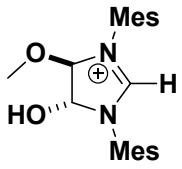


^{11}B NMR spectrum of **8** ($CDCl_3$)

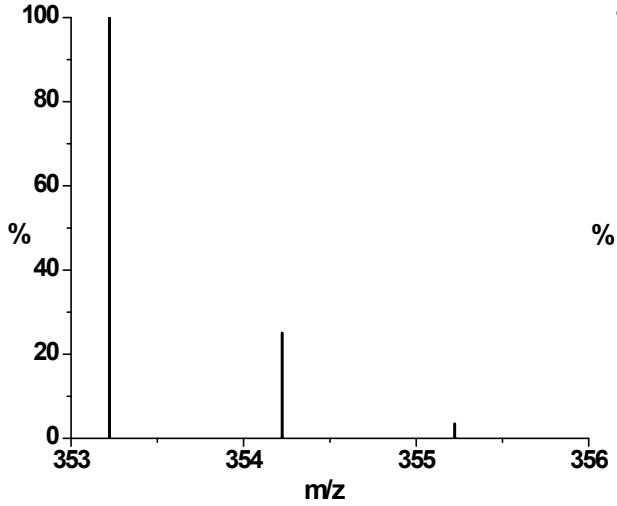


^{19}F NMR spectrum of **8** ($CDCl_3$)

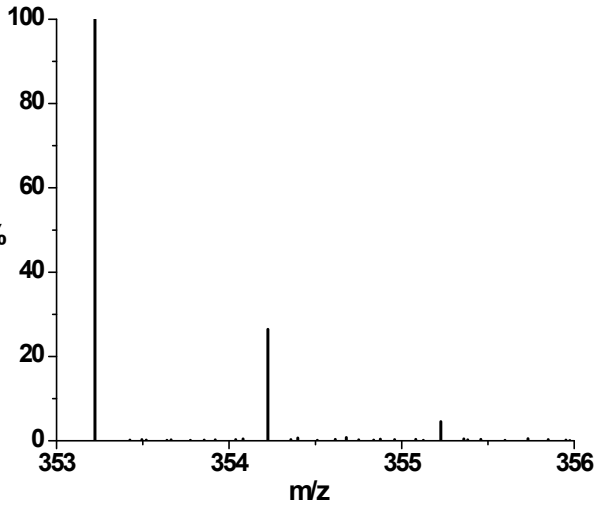




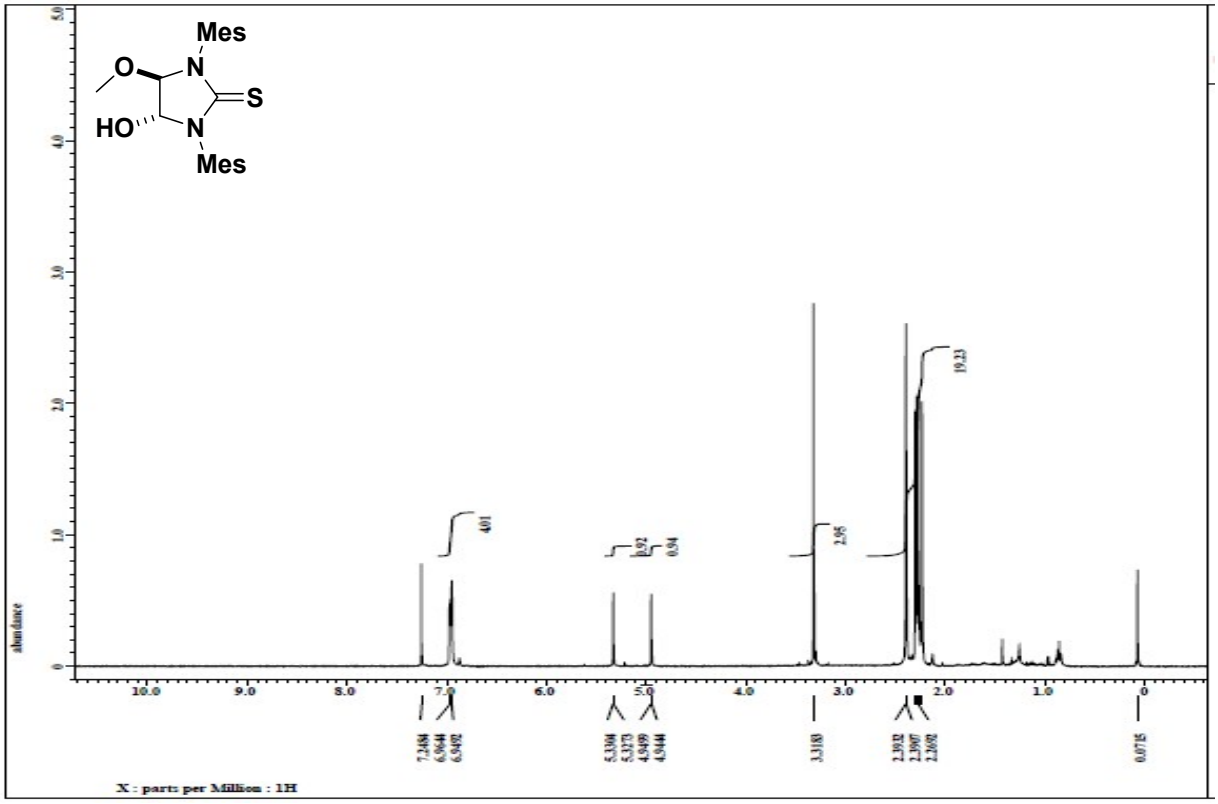
Theoretical distribution



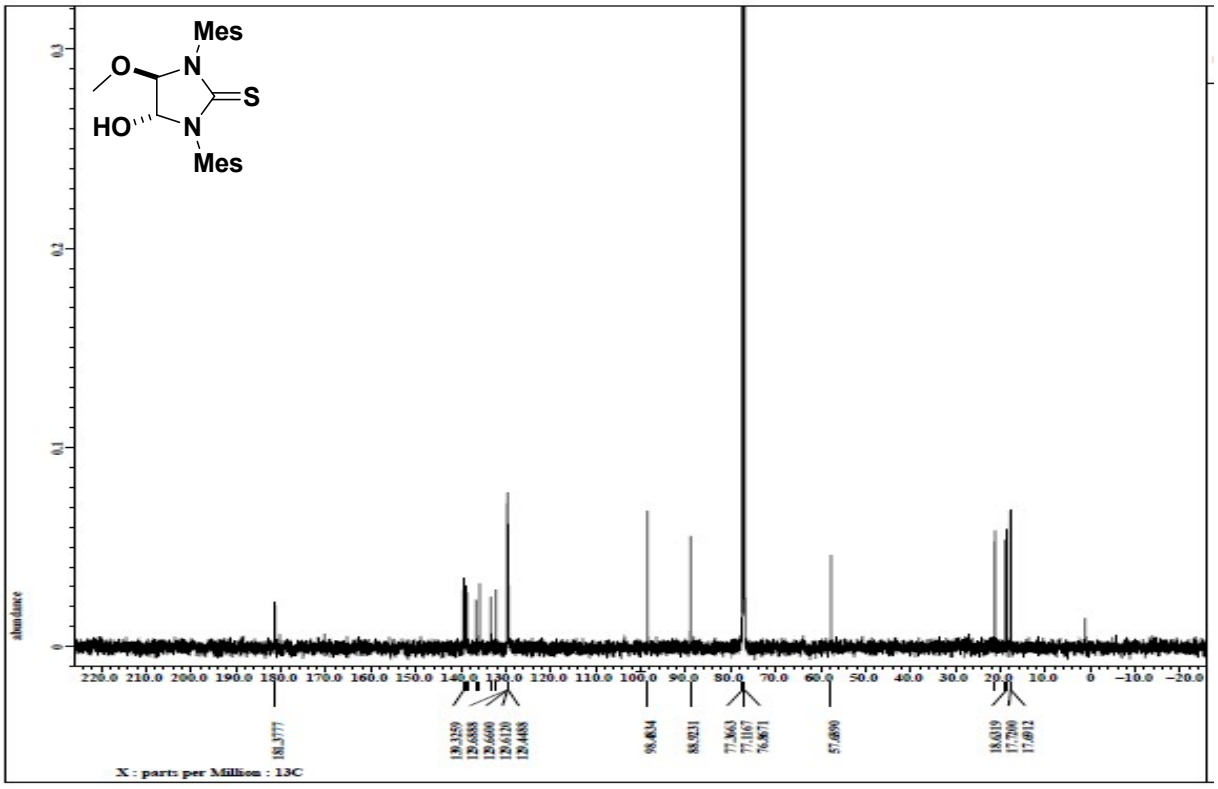
Experimental distribution

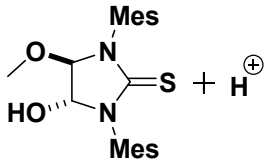


^{1}H NMR spectrum of **9a** ($CDCl_3$)

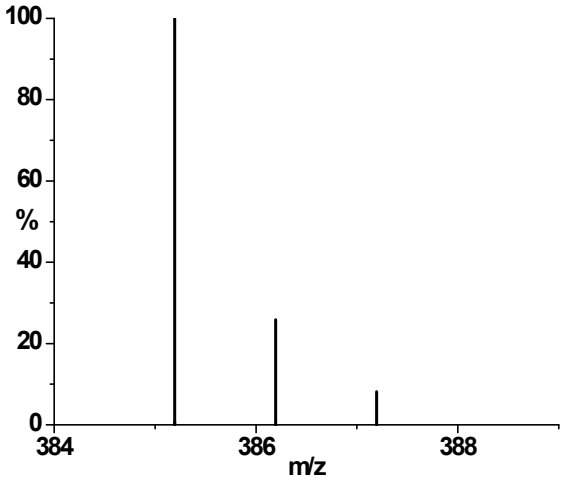


^{13}C NMR spectrum of **9a** ($CDCl_3$)

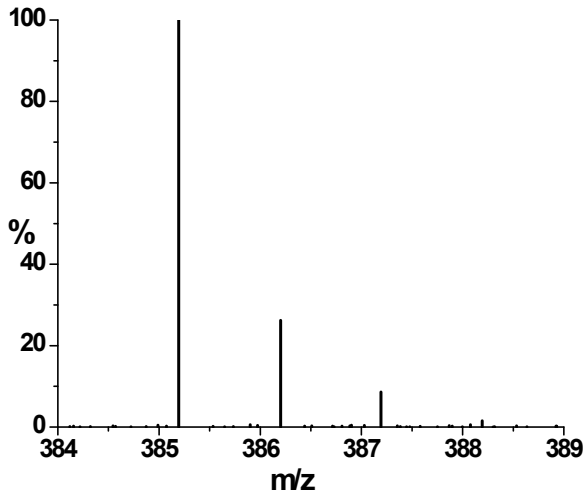




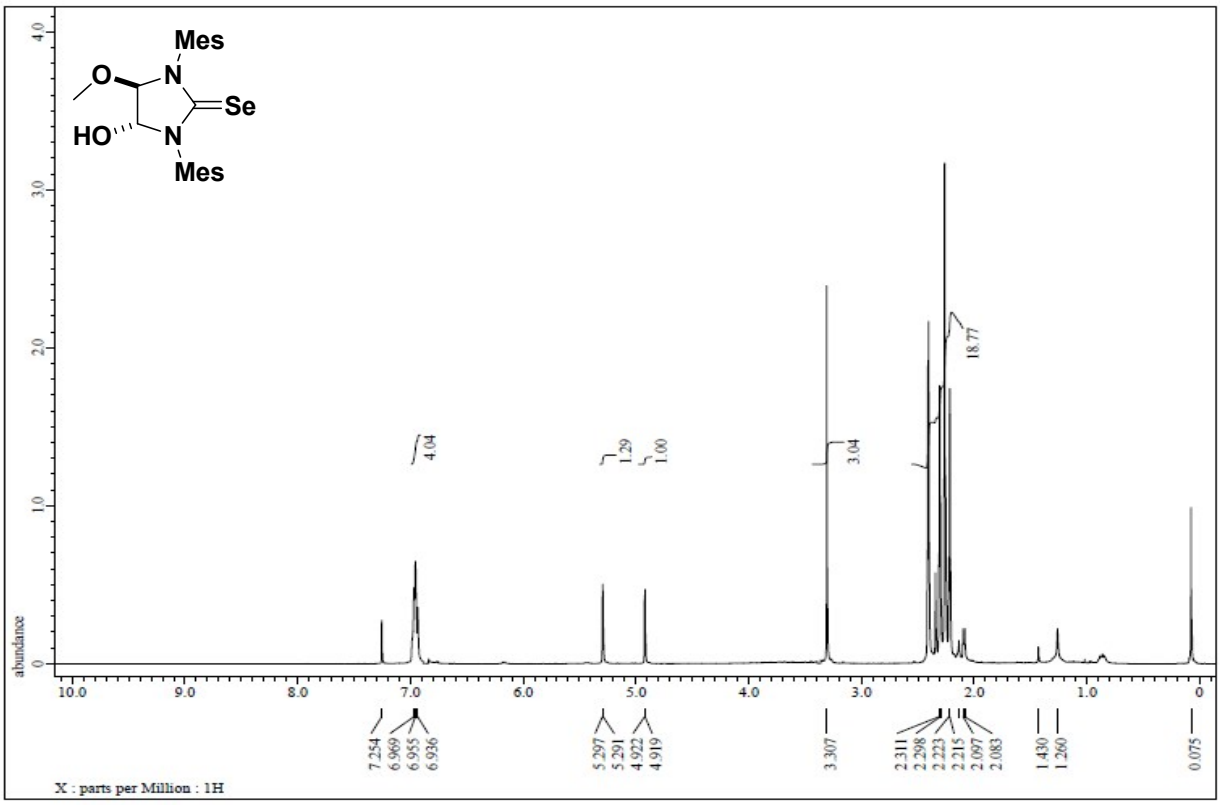
Theoretical distribution



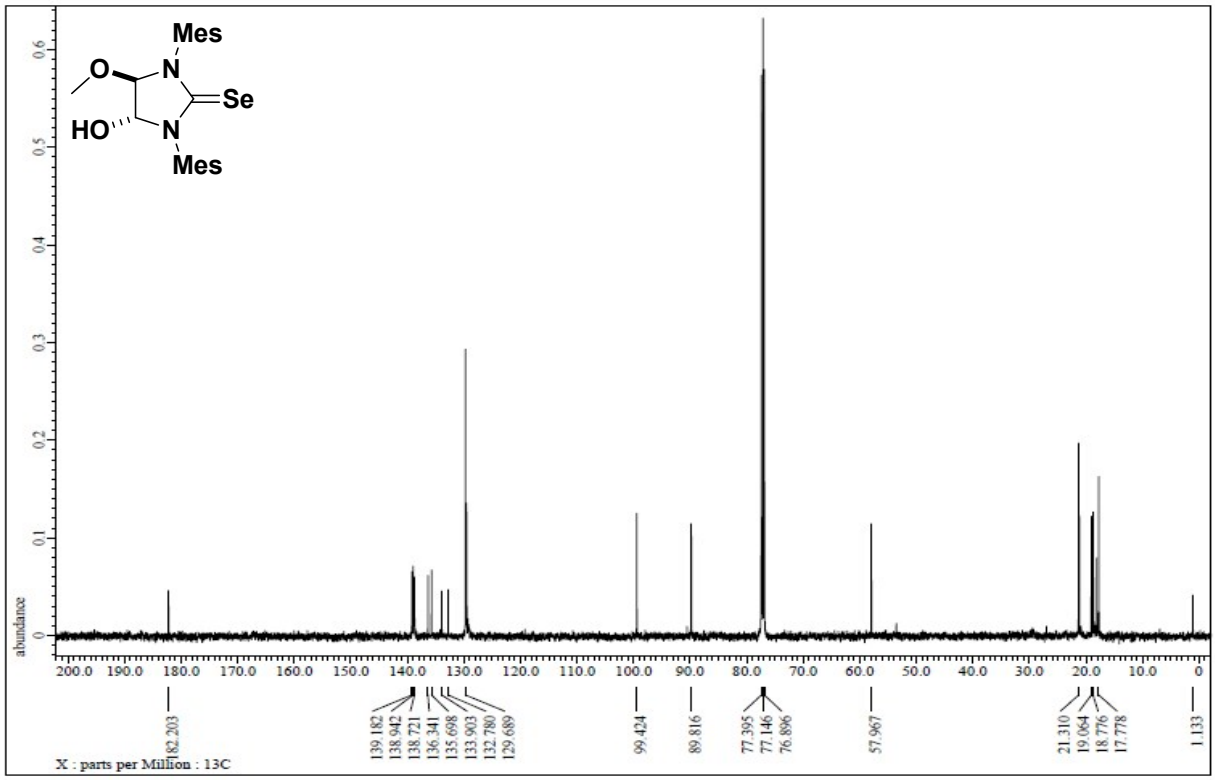
Experimental distributiom



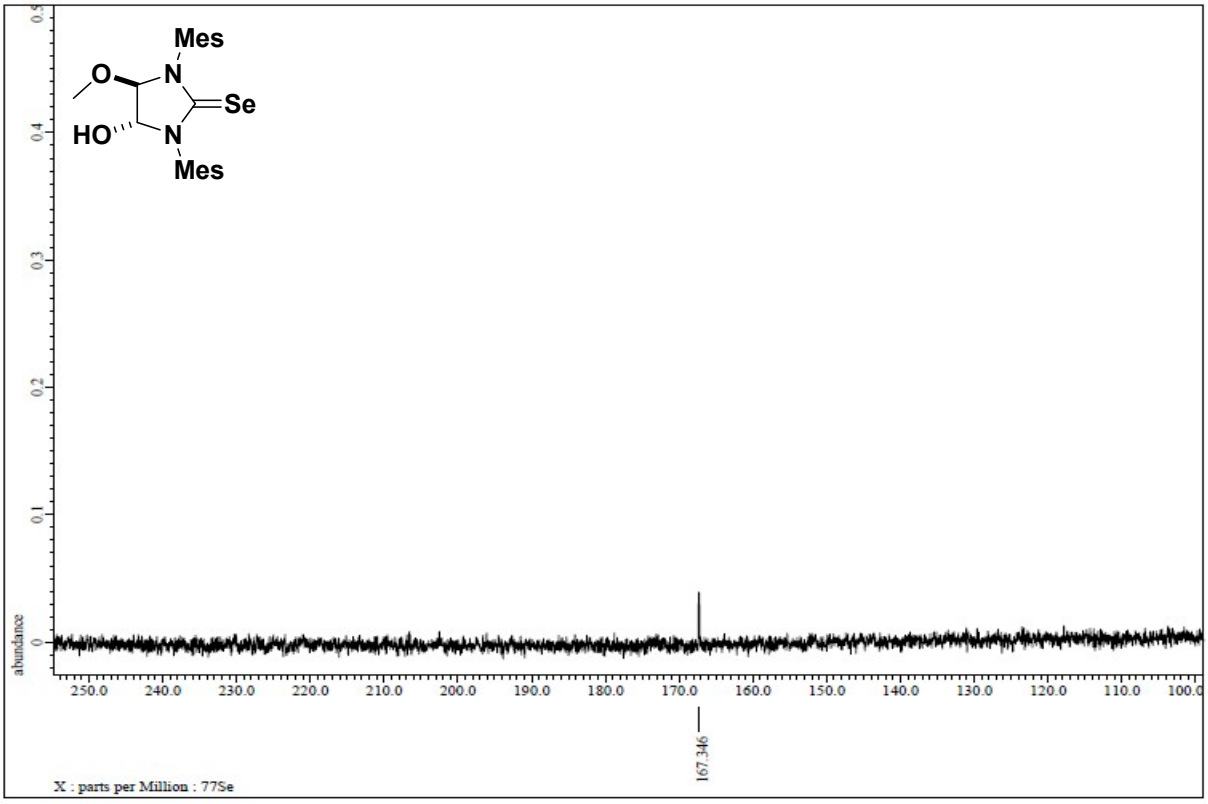
^{1}H NMR spectrum of **9b** ($CDCl_3$)

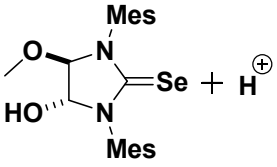


^{13}C NMR spectrum of **9b** ($CDCl_3$)

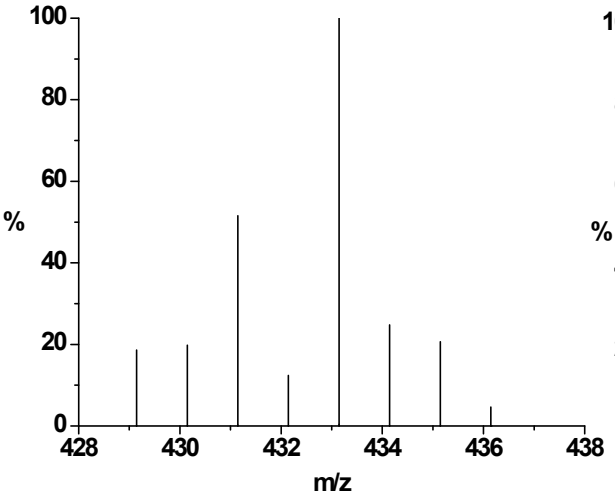


^{77}Se NMR spectrum of **9b** ($CDCl_3$)





Theoretical distribution



Experimental distribution

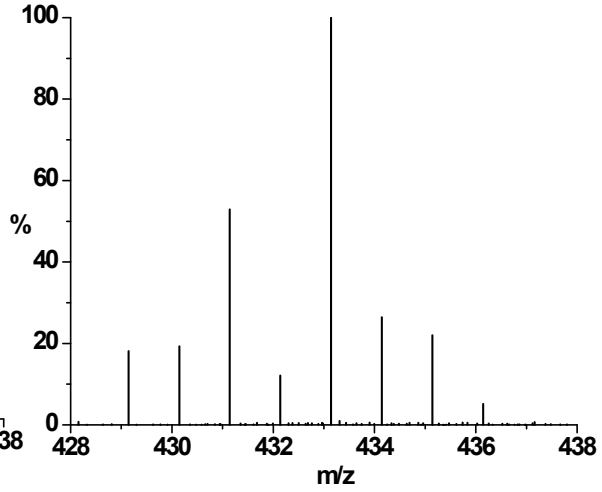


Table S1 Crystallographic data for **2**, **3**, **5a**

Identification code	**2**	**3**	**5a**
Formula	$C_{42}H_{46}N_4O_4S_2$	$C_{21}H_{25}BF_2N_2O_2$	$C_{88}H_{108}B_4F_8N_8O_8S_4$
Fw	734.97	386.24	1729.30
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space group	*Fdd*2	*C*mc2(1)	*P*-1
a, Å	20.261(4)	22.3720(18)	11.9074(6)
b, Å	46.298(9)	10.6579(9)	12.1853(6)
c, Å	8.3561(17)	8.0526(7)	17.8010(9)
α, deg	90	90	93.320(2)
β, deg	90	90	103.831(2)
γ, deg	90	90	103.498(2)
V, Å^3	7839(3)	1920.1(3)	2420.9(2)
Z	8	4	1
ρ_{Calcd}, g cm^{-3}	1.246	1.336	1.186
μ, mm^{-1}	0.182	0.098	0.168
F(000)	3120	816	912
Reflections collected	10707	6800	30629
Independent reflections, *R*(int)	3829, 0.0518	1824, 0.0317	9017, 0.0740
Completeness to *θ* (%)	99.8 %	99.5 %	99.8 %
Data / restraints / parameters	3829 / 1 / 241	1824 / 1 / 136	9017 / 0 / 555
GOF on F^2	1.070	1.059	0.960
Final *R* indices [*I*>2sigma(*I*)]	0.0481; 0.1128	0.0314; 0.0675	0.0751; 0.1772
R indices (all data)	0.0580; 0.1201	0.0384; 0.0701	0.1478; 0.1993
Largest diff. peak and hole/ e Å^{-3}	0.732 and -0.221	0.204 and -0.182	1.070 and -0.494
CCDC no.	1401392	1063837	1063842

Table S2 Crystallographic data for **5b**, **6a**, **6b**

Identification code	**5b**	**6a**	**6b**
Formula	$C_{33}H_{34}BF_2N_2O_2P$	$C_{25}H_{34}N_2O_4S$	$C_{21}H_{26}N_2O_2Se$
Fw	570.40	458.61	417.40
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	P-1
a, Å	11.811(5)	7.1062(9)	7.417(5)
b, Å	14.264(5)	22.149(3)	11.759(5)
c, Å	17.760(5)	16.237(2)	15.714(5)
α, deg	90.000(5)	90	106.783(5)
β, deg	102.367(5)	99.192(2)	98.029(5)
γ, deg	90.000(5)	90	97.972(5)
V, Å^3	2922.6(18)	2522.8(6)	1275.9(11)
Z	4	4	2
ρ_{Calcd}, g cm^{-3}	1.296	1.207	1.086
μ, mm^{-1}	0.140	0.160	1.485
F(000)	1200	984	432
Reflections collected	24836	13571	12356
Independent reflections, R(int)	5744, 0.0906	4674, 0.0473	4713, 0.0467
Completeness to θ (%)	99.9 %	99.4 %	99.6 %
Data / restraints / parameters	5744 / 0 / 376	4674 / 0 / 299	4713 / 0 / 243
GOF on F^2	1.021	1.033	0.969
Final R indices [I>2sigma(I)]	0.0608; 0.1162	0.0498; 0.1221	0.0423; 0.1008
R indices (all data)	0.1160; 0.1390	0.0722; 0.1427	0.0636; 0.1071
Largest diff. peak and hole/ e Å^{-3}	0.640 and -0.374	0.314 and -0.264	0.304 and -0.309
CCDC no.	1407615	1063838	1063839

Table S3 Crystallographic data for **7a, 7b, 9a**

Identification code	**7a**	**7b**	**9a**
Formula	$C_{27}H_{29}BN_2O_2S$	$C_{27}H_{29}BN_2O_2Se$	$C_{22}H_{28}N_2O_2S$
Fw	456.40	503.29	384.53
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	14.6181(19)	14.5257(8)	41.799(8)
b, Å	11.4652(14)	11.2585(6)	7.8933(16)
c, Å	15.805(3)	15.9893(9)	26.972(5)
α, deg	90	90	90
β, deg	107.013(4)	106.794(2)	108.32(3)
γ, deg	90	90	90
V, Å^3	2533.0(6)	2503.3(2)	8448(3)
Z	4	4	16
ρ_{Calcd}, g cm^{-3}	1.197	1.335	1.209
μ, mm^{-1}	0.153	1.526	0.172
F(000)	968	1040	3296
Reflections collected	11555	22532	27768
Independent reflections, R(int)	4964, 0.0832	5472, 0.0621	7861, 0.1004
Completeness to θ (%)	99.6 %	99.9 %	99.9 %
Data / restraints / parameters	4964 / 0 / 304	5472 / 0 / 304	7861 / 0 / 503
GOF on F^2	0.925	1.093	1.020
Final R indices [I>2sigma(I)]	0.0625; 0.1059	0.0455; 0.1059	0.0666; 0.1406
R indices (all data)	0.2440; 0.1581	0.0780; 0.1286	0.1462; 0.1721
Largest diff. peak and hole/ e Å^{-3}	0.163 and -0.154	0.578 and -0.604	0.549 and -0.534
CCDC no.	1063840	1063841	1063843

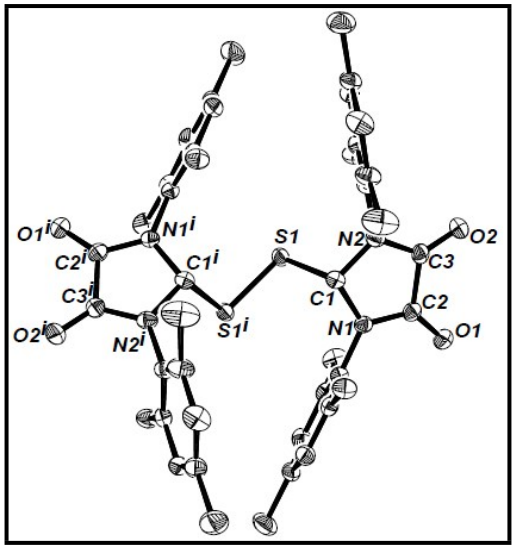


Fig. S1 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **2**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-S(1) 1.844(3), C(1)-N(1) 1.451(3), C(1)-N(2) 1.455(3), C(2)-N(1) 1.359(3), C(3)-N(2) 1.355(4), C(2)-C(3) 1.540(4), C(2)-O(1) 1.211(3), C(3)-O(2) 1.205(3), S(1)-S(1)#1 2.0307(12), N(1)-C(1)-N(2) 103.0(2).

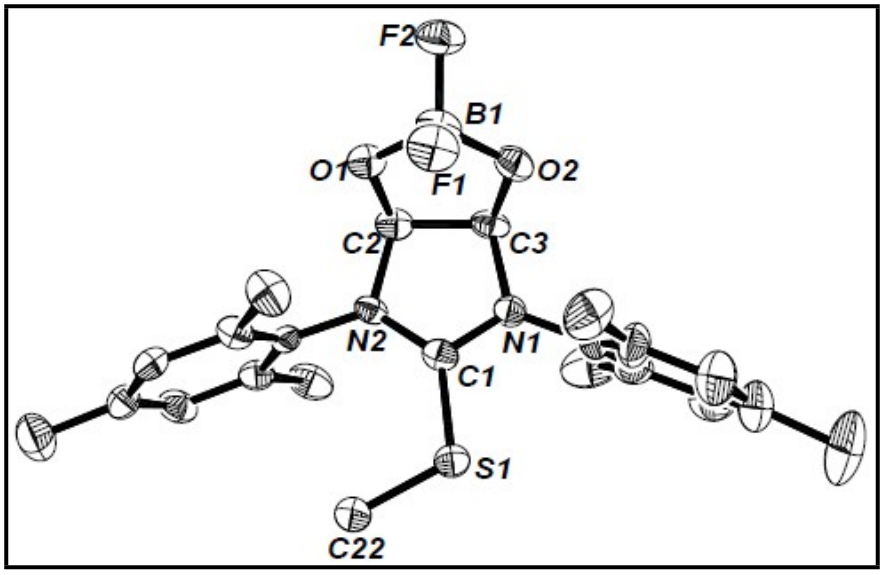


Figure S2: ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **5a**. Hydrogen atoms and one molecule have been omitted for clarity. Selected bond lengths (Å) and angles (deg): C(1)-S(1) 1.740(4), C(1)-N(1) 1.320(5), C(1)-N(2) 1.335(5), C(2)-N(2) 1.495(5), C(3)-N(1) 1.484(4), C(2)-C(3) 1.534(5), C(2)-O(1) 1.375(4), C(3)-O(2) 1.374(4), B(1)-O(1) 1.481(5), B(1)-O(2) 1.456(6), C(22)-S(1) 1.785(4), N(2)-C(1)-N(1) 112.8(3).

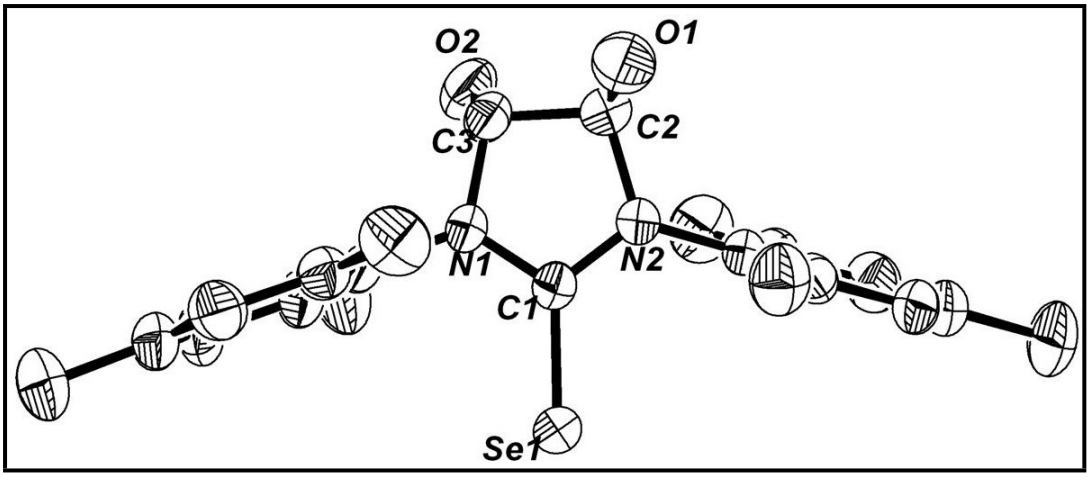


Fig. S3 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **6b**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity.

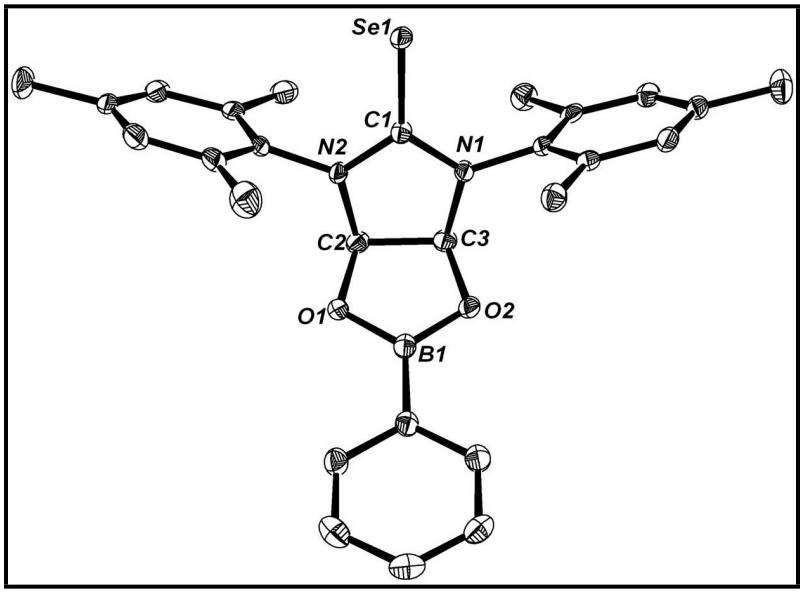


Fig. S4 ORTEP diagram showing 50% probability thermal ellipsoids and selected atom labels for **7b**. Hydrogen atoms and one ethyl acetate molecule have been omitted for clarity.