Contents:

X-ray Crystal Data and Structure Refinement

Crystal data and structure refinement for *(S)-tert*-butyl 4-selenocyanato-2-(*tert*-butoxycarbonylamino)butanoate (**15**).

Empirical formula	$C_{14}H_{24}N_2O_4Se$	
Formula weight	363.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.3393(16) Å	a= 90°.
	b = 16.636(5) Å	b= 90°.
	c = 19.468(6) Å	g = 90°.
Volume	1729.3(9) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	2.187 mm^{-1}	
F(000)	752	
Crystal size	0.52 x 0.15 x 0.12 mm^3	
Theta range for data collection	1.61 to 28.30°.	
Index ranges	-7<=h<=7, -21<=k<=21, -25<=l<=25	
Reflections collected	14681	
Independent reflections	4011 [R(int) = 0.1339]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7793 and 0.3959	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4011 / 0 / 199	
Goodness-of-fit on F^2	1.004	
Final R indices [I>2σ(I)]	R1 = 0.0505, wR2 = 0.0950	
R indices (all data)	R1 = 0.0672, wR2 = 0.1008	
Absolute structure parameter	-0.010(12)	
Largest diff. peak and hole	1.606 and -0.648 $e·Å^{-3}$	

Table S1. Bond lengths [E] and angles [°] for **15**

Se(1)-C(1)	1.859(4)
Se(1)-C(2)	1.981(4)
N(1)-C(5)	1.351(5)
N(1)-C(4)	1.439(4)
N(2)-C(1)	1.147(5)
O(1)-C(5)	1.211(4)
O(2)-C(5)	1.349(5)
O(2)-C(6)	1.481(4)
O(3)-C(10)	1.207(5)
O(4)-C(10)	1.317(5)
O(4)-C(11)	1.496(4)
C(2)-C(3)	1.513(5)
C(3)-C(4)	1.533(5)
C(4)-C(10)	1.534(5)
C(6)-C(7)	1.515(5)
C(6)-C(8)	1.518(5)
C(6)-C(9)	1.524(5)
C(11)-C(13)	1.500(5)
C(11)-C(14)	1.509(6)
C(11)-C(12)	1.527(5)
C(1)-Se(1)-C(2)	97.66(18)
C(5)-N(1)-C(4)	118.7(3)
C(5)-O(2)-C(6)	120.4(3)
C(10)-O(4)-C(11)	120.9(3)
N(2)-C(1)-Se(1)	175.2(4)
C(3)-C(2)-Se(1)	112.9(3)
C(2)-C(3)-C(4)	113.3(3)
N(1)-C(4)-C(3)	110.8(3)
N(1)-C(4)-C(10)	114.5(3)
C(3)-C(4)-C(10)	111.1(3)
O(1)-C(5)-O(2)	126.6(3)
O(1)-C(5)-N(1)	124.0(4)
O(2)-C(5)-N(1)	109.4(3)
O(2)-C(6)-C(7)	109.9(3)
O(2)-C(6)-C(8)	103.1(3)

C(7)-C(6)-C(8)	110.3(4)
O(2)-C(6)-C(9)	110.2(3)
C(7)-C(6)-C(9)	112.0(3)
C(8)-C(6)-C(9)	110.9(3)
O(3)-C(10)-O(4)	127.1(3)
O(3)-C(10)-C(4)	120.1(4)
O(4)-C(10)-C(4)	112.9(3)
O(4)-C(11)-C(13)	111.4(3)
O(4)-C(11)-C(14)	107.9(3)
C(13)-C(11)-C(14)	113.6(3)
O(4)-C(11)-C(12)	101.3(3)
C(13)-C(11)-C(12)	111.3(3)

Gaussian archive log entries for optimized geometries:

Methionine, Met

1\1\GINC-N312\FOpt\RB3LYP\6-311+G(2df,2p)\C6H13N1O2S1\MJPUSHIE\05-Jul-
2012\0\\#p RB3LYP/6-311+G(2df,2p) opt=(redundant,maxcycle=60) nosymm f
req guess=read iop(1/8=8)\\[methionine]charge neutral without continuu
m geom opt and freqs\\0,1\N,-1.2009253799,-3.6070091481,0.4665526731\C
,-0.5250778152,-2.7895917017,-0.5521547126\C,0.7192459179,-3.541338326
1,-1.0559233224\O,1.168684072,-4.4836583095,-0.2145592961\O,1.26253976
91,-3.2904403802,-2.096980694\H,-1.149554406,-2.6036981997,-1.42926766
01\C,-0.1159557302,-1.4363042365,0.0592114485\C,0.431349163,-0.4174971
09,-0.9432383666\C,0.8205310829,0.8886629221,-0.2550284302\S,1.3816126
968,2.1162876793,-1.4866970586\C,1.7636484159,3.5062882386,-0.38105685
73\H,0.5150853095,-4.5270274232,0.5139464406\H,-1.7166846884,-3.039164
9331,1.1254122467\H,-1.8460441327,-4.2690103243,0.0543316576\H,-1.0056
062262,-1.0169568412,0.5400905681\H,0.6128819931,-1.6131026023,0.85519
72174\H,-0.3259985521,-0.2160812487,-1.7045198017\H,1.2916563112,-0.83
18653227,-1.4673388452\H,-0.0292989842,1.306266058,0.2894272479\H,1.62
74641377,0.7166910421,0.4598406937\H,2.111261415,4.3234778574,-1.00930
58613\H,2.5526371,3.2441924663,0.3224077727\H,0.8779775997,3.833102661
5,0.1621726908\\Version=EM64L-G09RevC.01\HF=-840.0677176\RMSD=6.139e-0
9\RMSF=1.005e-05\Dipole=-1.6659205,0.46674,1.6680814\Quadrupole=2.4439
055,1.2997952,-3.7437007,13.1513255,4.9883515,-4.5766043\PG=C01 [X(C6H
13N1O2S1)]\\@

Selenomethionine, SeM

1\1\GINC-N309\FOpt\RB3LYP\6-311+G(2df,2p)\C6H13N1O2Se1\MJPUSHIE\05-Jul
-2012\0\\#p RB3LYP/6-311+G(2df,2p) opt=(redundant,maxcycle=60) nosymm
freq guess=read iop(1/8=8)\\[selenomethionine]charge neutral without c
ontinuum geom opt and freqs\\0,1\N,-1.2559226028,-2.6467370517,0.90565
91598\C,-0.5456578177,-1.8366948436,-0.0955127528\C,0.700714194,-2.603
4451954,-0.5707753524\O,1.1165180761,-3.5544107307,0.2778652367\O,1.27
26256142,-2.3564631386,-1.5974205206\H,-1.1466863865,-1.6424182844,-0.
9871070827\C,-0.1352139359,-0.4888177291,0.5268569126\C,0.4573781144,0
.52260356,-0.4589953035\C,0.8299662446,1.8255159701,0.239274859\Se,1.5
247183382,3.1422132124,-1.0588319549\C,1.8171082015,4.6080253027,0.212
1012943\H,0.4449162519,-3.5905420023,0.9902187612\H,-1.7774695322,-2.0
729706308,1.5547819201\H,-1.9017663248,-3.2977654113,0.4773742631\H,-1
.0326792072,-0.0558871194,0.9804172564\H,0.5672244006,-0.6745573426,1.
3441386835\H,-0.2705124801,0.7238562595,-1.2485904783\H,1.3320140698,0
.095904166,-0.9487268488\H,-0.0355173238,2.2730051247,0.7277767624\H,1
.6032078286,1.6593375173,0.988519128\H,2.2032692537,5.4462447947,-0.36
17336372\H,2.5473360729,4.3187144152,0.963048226\H,0.8802657953,4.8944
544254,0.6826466172\\Version=EM64L-G09RevC.01\HF=-2843.3965753\RMSD=4.
033e-09\RMSF=1.063e-05\Dipole=-1.7316416,0.4643737,1.6047841\Quadrupol
e=0.6333541,1.1750022,-1.8083562,10.0453333,3.4856962,-0.9520797\PG=C0
1 [X(C6H13N1O2Se1)]\\@

Trifluoromethionine (TFM)

1\1\GINC-N311\FOpt\RB3LYP\6-311+G(2df,2p)\C6H10F3N1O2S1\MJPUSHIE\06-Ju
l-2012\0\\#p RB3LYP/6-311+G(2df,2p) opt=(redundant,maxcycle=60) nosymm
freq guess=read iop(1/8=8)\\[methionineCF3]charge neutral without con
tinuum geom opt and freqs\\0,1\N,-1.2442268607,-2.6357104984,0.8981733
732\C,-0.5352128579,-1.8191853801,-0.0970449079\C,0.7169349463,-2.5767
223808,-0.5746207561\O,1.1236160206,-3.5455460219,0.2554596103\O,1.298
8427105,-2.3040918159,-1.5894716289\H,-1.1350888377,-1.6237449159,-0.9
892583025\C,-0.1314213084,-0.4721965376,0.5310573684\C,0.4737223126,0.
5341341118,-0.4511224362\C,0.839576013,1.8353367258,0.2605686261\S,1.5
165589164,3.0195165302,-0.9669895309\C,1.7928724419,4.4338836842,0.129
2480112\H,0.4490281326,-3.5941590294,0.9644987899\H,-1.759836445,-2.06
91337508,1.5582155314\H,-1.89452377,-3.2798366497,0.4663913021\H,-1.03
27887226,-0.0375834616,0.9743315046\H,0.5624969588,-0.6585764142,1.355
2391278\H,-0.2442252603,0.7400462832,-1.2481035927\H,1.3536026944,0.10
61520231,-0.9297240517\H,-0.0354923081,2.2873885136,0.7247422709\H,1.5
948261578,1.6600179825,1.0247484965\F,2.28175612,5.4456865557,-0.59953
24237\F,2.6708957185,4.1757244563,1.1173517983\F,0.6670736585,4.866463
6601,0.7313274021\\Version=EM64L-G09RevC.01\HF=-1137.8986607\RMSD=7.71
8e-09\RMSF=7.364e-06\Dipole=-2.040305,-0.6355008,1.1354477\Quadrupole=
3.6407449,-7.0186359,3.377891,5.3202648,2.0961734,-4.1717461\PG=C01 [X
(C6H10F3N1O2S1)]\\@

Trifluoroselenomethionine (TFSeM)

1\1\GINC-N309\FOpt\RB3LYP\6-311+G(2df,2p)\C6H10F3N1O2Se1\MJPUSHIE\06-J
ul-2012\0\\#p RB3LYP/6-311+G(2df,2p) opt=(redundant,maxcycle=60) nosym
m freq guess=read iop(1/8=8)\\[selenomethionineCF3]charge neutral with
out continuum geom opt and freqs\\0,1\N,-1.3284999095,-2.6447392382,0.
8333955924\C,-0.4167807302,-1.8595791169,-0.0138924128\C,0.7957560918,
-2.7377223783,-0.3939906797\O,0.5974472939,-4.0472703145,-0.2074574803
\O,1.8184492393,-2.2981900431,-0.8460896643\H,-0.9385685342,-1.6815826
206,-0.9586358804\C,-0.0014411983,-0.502620877,0.5818677441\C,0.556733
8949,0.5021549132,-0.4337769647\C,0.8953258246,1.8291615171,0.23586897
17\Se,1.5531711046,3.1086359515,-1.1252248348\C,1.6501588115,4.6636357
747,0.0740920705\H,-0.2882061964,-4.1281588056,0.2051802258\H,-1.11382
69382,-2.5304529462,1.8172113622\H,-2.294281619,-2.3800080055,0.697086
3849\H,-0.8881445271,-0.0717015092,1.0545401349\H,0.7305977882,-0.6702
220494,1.3767397908\H,-0.1872365024,0.6671408745,-1.2181482301\H,1.438
7284722,0.0786995946,-0.9104170352\H,0.0213743981,2.2791975718,0.70147
09099\H,1.6791661804,1.7104282362,0.9797985006\F,2.0549774237,5.728519
9294,-0.6318200614\F,2.5155387442,4.4897784108,1.0886609381\F,0.463914
9639,4.9680851624,0.6335302239\\Version=EM64L-G09RevC.01\HF=-3141.2250
055\RMSD=5.328e-09\RMSF=5.987e-06\Dipole=-2.0281276,-0.5419253,0.91174
95\Quadrupole=2.6332395,-10.6480759,8.0148364,5.2179076,1.4728544,-4.2
833754\PG=C01 [X(C6H10F3N1O2Se1)]\\@

Methionine, Met, CHelpG output from B3LYP/6-31G(d)-optimized geometry

1\1\GINC-N257\SP\RB3LYP\6-31G(d)\C6H13N1O2S1\MJPUSHIE\27-Jul-2012\0\\#
p RB3LYP/6-31G(d) iop(1/8=8) pop=(chelpg)\\[methionine]charge neutral
without continuum CHELPG\\0,1\N,0,-1.3740169732,-3.3538669726,0.661102
6855\C,0,-0.4792856029,-2.5295033665,-0.174227603\C,0,0.7616016665,-3.
3705461757,-0.5472705815\O,0,0.5890722754,-4.6903621899,-0.3860018133\
O,0,1.7832231287,-2.9013268259,-0.9722996392\H,0,-1.0005909862,-2.3643
681245,-1.1236293626\C,0,-0.1136135802,-1.1623309336,0.4306477061\C,0,
0.384049488,-0.1245980201,-0.5828208926\C,0,0.7022259419,1.2100274176,
0.0871555879\S,0,1.1693805288,2.4593493626,-1.1709247626\C,0,1.4862238
4,3.8868496185,-0.0827216364\H,0,-0.3033714979,-4.7902430724,0.0151877
986\H,0,-1.1658969809,-3.2338133916,1.6483999468\H,0,-2.3461610978,-3.
1024120586,0.5254166291\H,0,-1.0132245895,-0.7746967994,0.9211313886\H
,0,0.6372192925,-1.3071950002,1.2152564192\H,0,-0.3877664989,0.0290423
728,-1.345369647\H,0,1.2682588875,-0.5068675916,-1.0926177558\H,0,-0.1
648568131,1.5839281624,0.639049864\H,0,1.5321948003,1.0961069914,0.789
0770933\H,0,1.7762918229,4.7157483473,-0.7276598987\H,0,2.3013556829,3
.6766631028,0.6106105426\H,0,0.5883562651,4.1661671473,0.4699409308\\V
ersion=EM64L-G09RevC.01\State=1-A\HF=-839.8628473\RMSD=5.906e-09\Dipol
e=-1.7992981,0.4982078,1.4882054\Quadrupole=1.5589606,-2.7066872,1.147
7266,8.880444,0.6337162,-0.3167806\PG=C01 [X(C6H13N1O2S1)]\\@

Selenomethionine, SeM, CHelpG output from B3LYP/6-31G(d)-optimized geometry

1\1\GINC-N312\SP\RB3LYP\6-31G(d)\C6H13N1O2Se1\MJPUSHIE\27-Jul-2012\0\\
#p RB3LYP/6-31G(d) pop=(chelpg,readatradii)\\[selenomethionine]charge
neutral without continuum CHELPG\\0,1\N,0,-1.4211761795,-2.5535437112,
1.0536429835\C,0,-0.7314067401,-1.7248106853,0.049197517\C,0,0.5253532
318,-2.4699022627,-0.4348058953\O,0,0.9563681747,-3.4220176126,0.40705
75367\O,0,1.0919954562,-2.2061610554,-1.4613524931\H,0,-1.3436528783,-
1.5393286154,-0.8384315148\C,0,-0.3403173292,-0.3712778747,0.673358605
5\C,0,0.2303993679,0.6520848263,-0.3150008443\C,0,0.5912660862,1.95783
58689,0.3857850317\Se,0,1.2496384773,3.2951669964,-0.9181022262\C,0,1.
5420924151,4.7594368168,0.3624830397\H,0,0.2810138405,-3.4679011038,1.
1200088306\H,0,-1.9438878025,-1.9863985342,1.7114583201\H,0,-2.0721925
56,-3.2009830581,0.6217999969\H,0,-1.2440863628,0.0464089869,1.1331035
278\H,0,0.3710714758,-0.5474572724,1.4875089916\H,0,-0.5090564615,0.84
63208226,-1.0981555775\H,0,1.1077165342,0.2375552487,-0.814077696\H,0,
-0.2762132504,2.3904816588,0.8874638175\H,0,1.3792105135,1.8009088966,
1.1239035088\H,0,1.908852687,5.6072956397,-0.2133355773\H,0,2.28903213
41,4.4727193215,1.1002799815\H,0,0.6064091661,5.0293967024,0.848630135
5\\Version=EM64L-G09RevC.01\State=1-A\HF=-2841.0526939\RMSD=6.396e-09\
Dipole=-1.7497048,0.3925263,1.6030729\Quadrupole=3.3917801,-1.6102301,
-1.78155,11.4669884,-0.2454874,-2.385676\PG=C01 [X(C6H13N1O2Se1)]\\@

Trifluoromethionine (TFM), CHelpG output from B3LYP/6-31G(d)-optimized geometry

1\1\GINC-N256\SP\RB3LYP\6-31G(d)\C6H10F3N1O2S1\MJPUSHIE\27-Jul-2012\0\
\#p RB3LYP/6-31G(d) iop(1/8=8) pop=(chelpg)\\[methionineCF3]charge neu
tral without continuum CHELPG\\0,1\N,0,-1.4119816626,-2.5331339943,1.0
501443724\C,0,-0.7279139826,-1.6965950551,0.0498042992\C,0,0.526636141

4,-2.436303226,-0.4505808532\O,0,0.9512183632,-3.4117109622,0.36497373
39\O,0,1.0953383552,-2.1456598249,-1.4690622841\H,0,-1.3455703612,-1.5
028004822,-0.8323927965\C,0,-0.3316230128,-0.3488113903,0.6825310484\C
,0,0.2480675741,0.6712940254,-0.3028663128\C,0,0.611843704,1.971188664
7,0.4132071335\S,0,1.2547349089,3.1757493837,-0.8222489961\C,0,1.49373
06908,4.5980221903,0.2737696822\H,0,0.2797031584,-3.4688198193,1.08081
96911\H,0,-1.9206891816,-1.9736307817,1.7252773383\H,0,-2.0744413776,-
3.1682021835,0.6174381877\H,0,-1.2334880481,0.0730136919,1.1414029176\
H,0,0.3774118592,-0.5325897074,1.4968234338\H,0,-0.486470456,0.8760234
374,-1.0873756063\H,0,1.1256735291,0.2539135371,-0.7986539683\H,0,-0.2
608661933,2.4132442179,0.8945125709\H,0,1.3856531846,1.8006020893,1.16
17711847\F,0,1.9561127405,5.623047539,-0.4575638642\F,0,2.3796266329,4
.3651753117,1.2638068762\F,0,0.3556974335,5.0028043387,0.8768792118\\V
ersion=EM64L-G09RevC.01\State=1-A\HF=-1137.5744888\RMSD=5.507e-09\Dipo
le=-1.9956185,-0.5444505,1.2495399\Quadrupole=6.7771022,-6.4774269,-0.
2996753,11.0790746,-0.0787281,-6.0995991\PG=C01 [X(C6H10F3N1O2S1)]\\@

Trifluoroselenomethionine (TFSeM), CHelpG output from B3LYP/6-31G(d)-optimized geometry

1\1\GINC-N312\SP\RB3LYP\6-31G(d)\C6H10F3N1O2Se1\MJPUSHIE\27-Jul-2012\0
\\#p RB3LYP/6-31G(d) pop=(chelpg,readatradii)\\[selenomethionineCF3]ch
arge neutral without continuum CHELPG\\0,1\N,0,-1.4202119906,-2.553446
152,1.0695383216\C,0,-0.7389616132,-1.7282999042,0.0578819069\C,0,0.51
18610075,-2.4754818531,-0.4405513836\O,0,0.9372891588,-3.4444853534,0.
3820835884\O,0,1.0775480568,-2.1953321647,-1.4637825247\H,0,-1.3603995
294,-1.5423398708,-0.8233319678\C,0,-0.3367913263,-0.3749219189,0.6750
415459\C,0,0.2388002044,0.6359017687,-0.3239797879\C,0,0.6138882721,1.
9378771284,0.3770767006\Se,0,1.3049162504,3.2370411412,-0.9559412328\C
,0,1.5217913278,4.7267117098,0.3096936995\H,0,0.2676347893,-3.49414900
55,1.1004374922\H,0,-1.9210121241,-1.9864292308,1.7442073661\H,0,-2.08
80748501,-3.1895143061,0.6469063637\H,0,-1.2348910224,0.0531885413,1.1
35407623\H,0,0.3773664818,-0.5516729032,1.4863825355\H,0,-0.5031692433
,0.8335999144,-1.1035255377\H,0,1.1090089923,0.2071392593,-0.823339158
9\H,0,-0.2480018155,2.4001664266,0.856476186\H,0,1.3986361603,1.781106
3738,1.1154702976\F,0,1.9797083997,5.7976587799,-0.3570063905\F,0,2.39
49568139,4.452797518,1.2980128731\F,0,0.3665115997,5.0787051015,0.9092
584838\\Version=EM64L-G09RevC.01\State=1-A\HF=-3138.7646675\RMSD=6.783
e-09\Dipole=-1.9659483,-0.5288961,1.1577669\Quadrupole=6.7313934,-6.90
26622,0.1712688,12.4678408,-1.1290624,-7.3584799\PG=C01 [X(C6H10F3N1O2
Se1)]\\@

Table S2. HOMO and LUMO energies from B3LYP/6-311+G(2df,2p) density functional calculations.

	Met	**SeM**	**TFM**	**TFSeM**
HOMO (AU)	-0.2246	-0.2151	-0.2698	-0.2521
LUMO (AU)	-0.0208	-0.0214	-0.0275	-0.0359
HOMO-LUMO Gap (kJ/mol)	535.2	508.7	636.1	567.7
Gap Relative to Met	***0.0***	***-26.5***	***+100.9***	***+32.5***
Gap Relative to SeM	***+26.5***	***0.0***	***+127.4***	***+59.0***

Table S3. CHelpG charges from B3LYP/6-311+G(2df,2p)-optimized geometries, calculated at the same level of theory.

		CHelpG Charges			
Atom No.	**Atom Type**	**Met**	**SeM**	**TFM**	**TFSeM**
1	N	-0.904	-0.881	-0.886	-0.870
2	H1	0.330	0.326	0.329	0.324
3	H2	0.342	0.328	0.344	0.331
4	C	0.721	0.704	0.705	0.595
5	O1	-0.534	-0.528	-0.520	-0.492
6	O2	-0.578	-0.578	-0.570	-0.533
7	H3	0.339	0.331	0.336	0.315
8	CA	0.309	0.361	0.295	0.469
9	HA	-0.039	-0.044	-0.026	-0.027
10	CB	-0.058	-0.226	-0.168	-0.388
11	HB1	0.029	0.059	0.068	0.064
12	HB2	0.009	0.046	0.052	0.092
13	CG	-0.048	0.164	0.002	0.330
14	HG1	0.041	-0.019	0.043	-0.058
15	HG2	0.078	0.028	0.089	-0.004
16	CD	-0.052	-0.089	-0.032	-0.135
17	HD1	0.071	0.061	0.067	0.078
18	HD2	0.080	0.065	0.072	0.069
19	Hetero (S/Se)	-0.261	-0.207	-0.193	-0.111
20	CZ	-0.049	-0.004	0.506	0.444
21	XZ1 (H/F)	0.097	0.068	-0.144	-0.144
22	XZ2 (H/F)	0.039	0.021	-0.183	-0.168

23	XZ3 (H/F)	0.038	0.014	-0.186	-0.181

Table S4. CHelpG charges from B3LYP/6-31G(d)-optimized geometries, calculated at the same level of theory.

		CHelpG Charges			
Atom No.	**Atom Type**	**Met**	**SeM**	**TFM**	**TFSeM**
1	N	-0.956	-0.923	-0.929	-0.906
2	H1	0.350	0.351	0.351	0.348
3	H2	0.360	0.352	0.363	0.354
4	C	0.521	0.617	0.613	0.618
5	O1	-0.499	-0.509	-0.503	-0.503
6	O2	-0.476	-0.526	-0.520	-0.526
7	H3	0.343	0.342	0.346	0.341
8	CA	0.523	0.372	0.338	0.349
9	HA	-0.041	-0.041	-0.031	-0.027
10	CB	-0.285	-0.261	-0.205	-0.376
11	HB1	0.037	0.064	0.069	0.105
12	HB2	0.057	0.064	0.064	0.105
13	CG	0.074	0.157	0.014	0.246
14	HG1	0.017	-0.007	0.038	-0.018
15	HG2	0.023	0.030	0.079	0.035
16	CD	-0.039	-0.129	-0.019	-0.164
17	HD1	0.071	0.076	0.063	0.082
18	HD2	0.086	0.080	0.069	0.080
19	Hetero (S/Se)	-0.289	-0.208	-0.213	-0.120
20	CZ	-0.080	-0.074	0.398	0.340
21	XZ1 (H/F)	0.110	0.094	-0.100	-0.098
22	XZ2 (H/F)	0.049	0.042	-0.141	-0.130

23	XZ3 (H/F)	0.044	0.037	-0.144	-0.135

Table S5. Force constants for new chemical groups from B3LYP/6-31G(d)-optimized geometries, calculated at the same level of theory.

	Force Constants [a]			
Bond Type	**Met**	**SeM**	**TFM**	**TFSeM**
CH_2–S	33223	-	85563	-
CH_2–Se	-	69108	-	69126
S–CH_3	98422	-	-	-
S–CF_3	-	-	110004	-
Se–CH_3	-	62362	-	-
Se–CF_3	-	-	-	32235
(S)CH_2–H	389056	-	-	-
(S)CF_2–F	-	-	378016	-
(Se)CH_2–H	-	394856	-	-
(Se)CF_2–F	-	-	-	420014

a – Units are in kJ/mol/nm^2

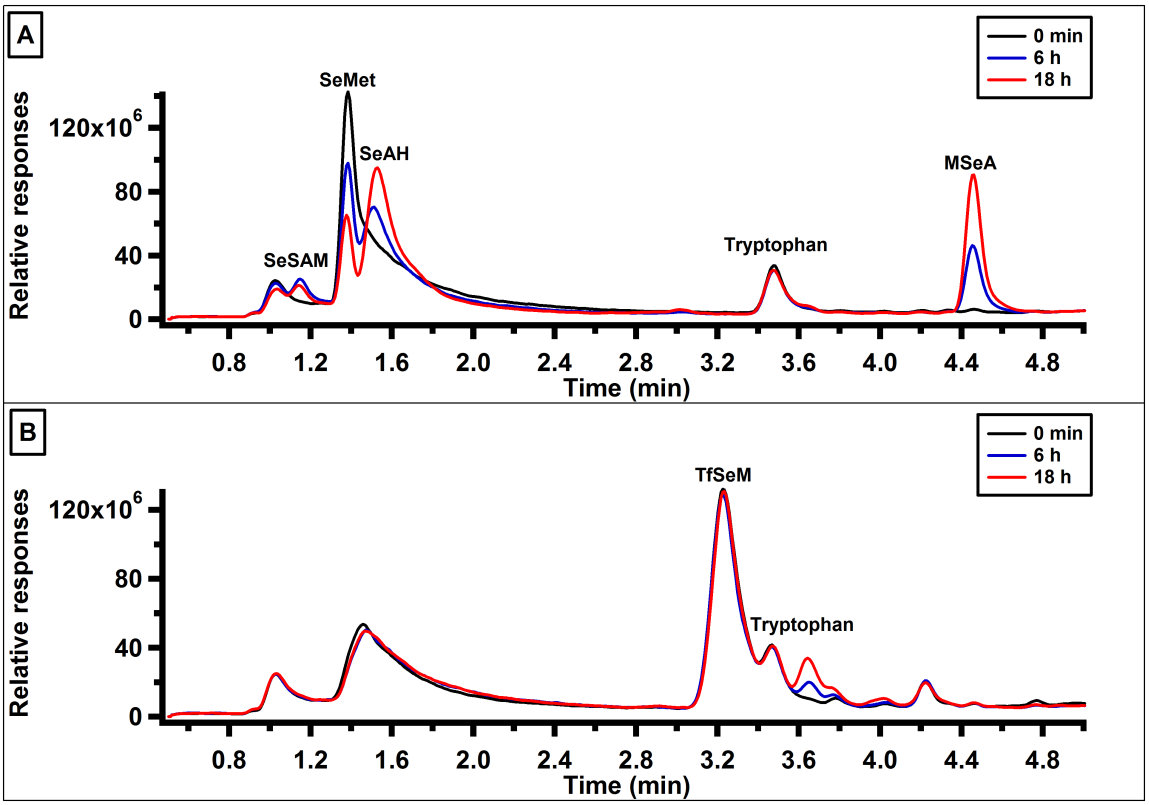


Figure S1. Total ion chromatograms (TIC) of time-dependent consumption of (A) SeMet (= SeM) or (B) TFSeM in reactions with MAT. Consumption of SeMet and formation of both SeSAM and SeAH in panel A indicated MAT was active and contaminated with a methyltransferase, whereas TFSeM remained constant over 18 h, indicating it is not a suitable substrate of MAT.

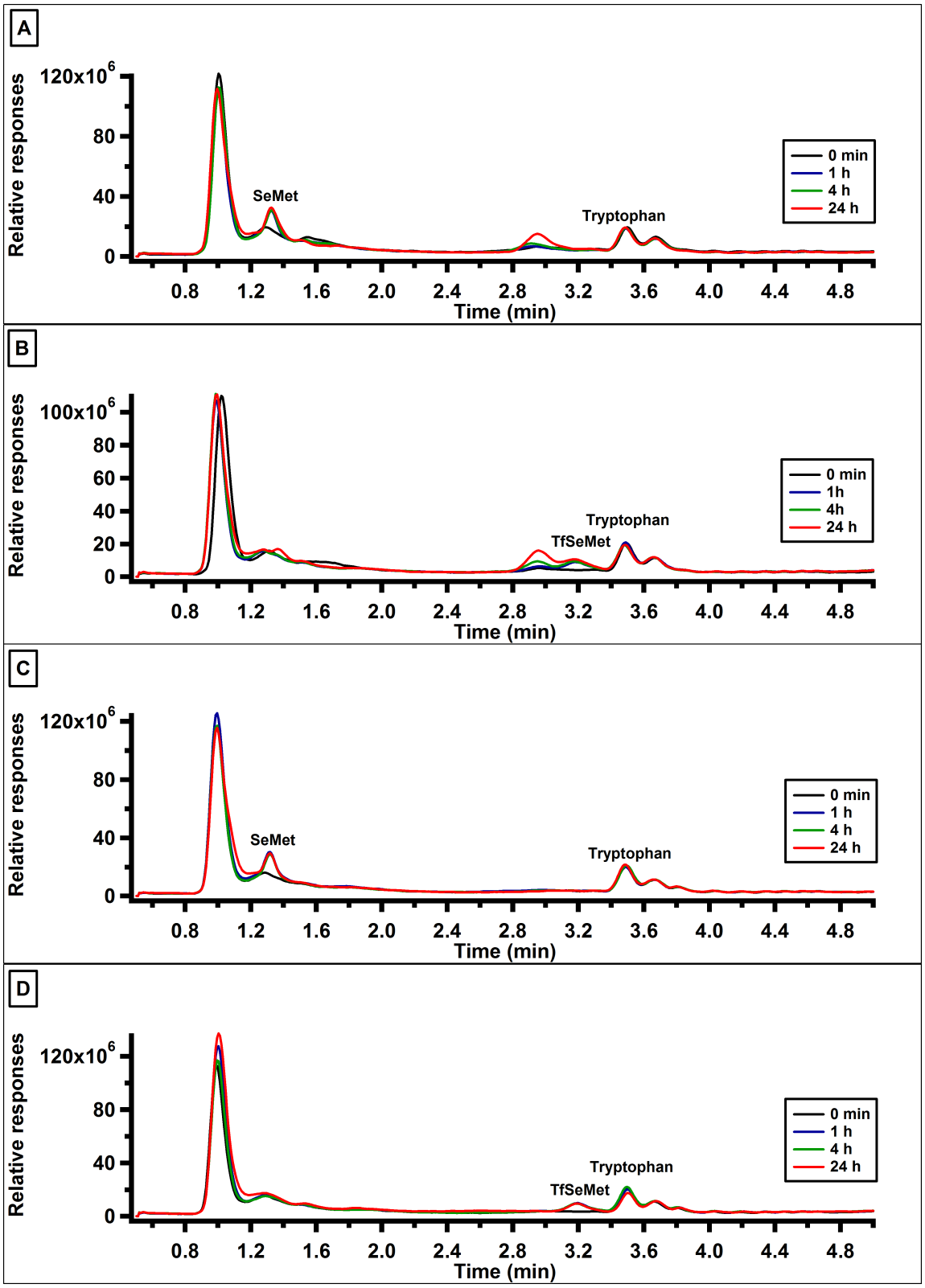
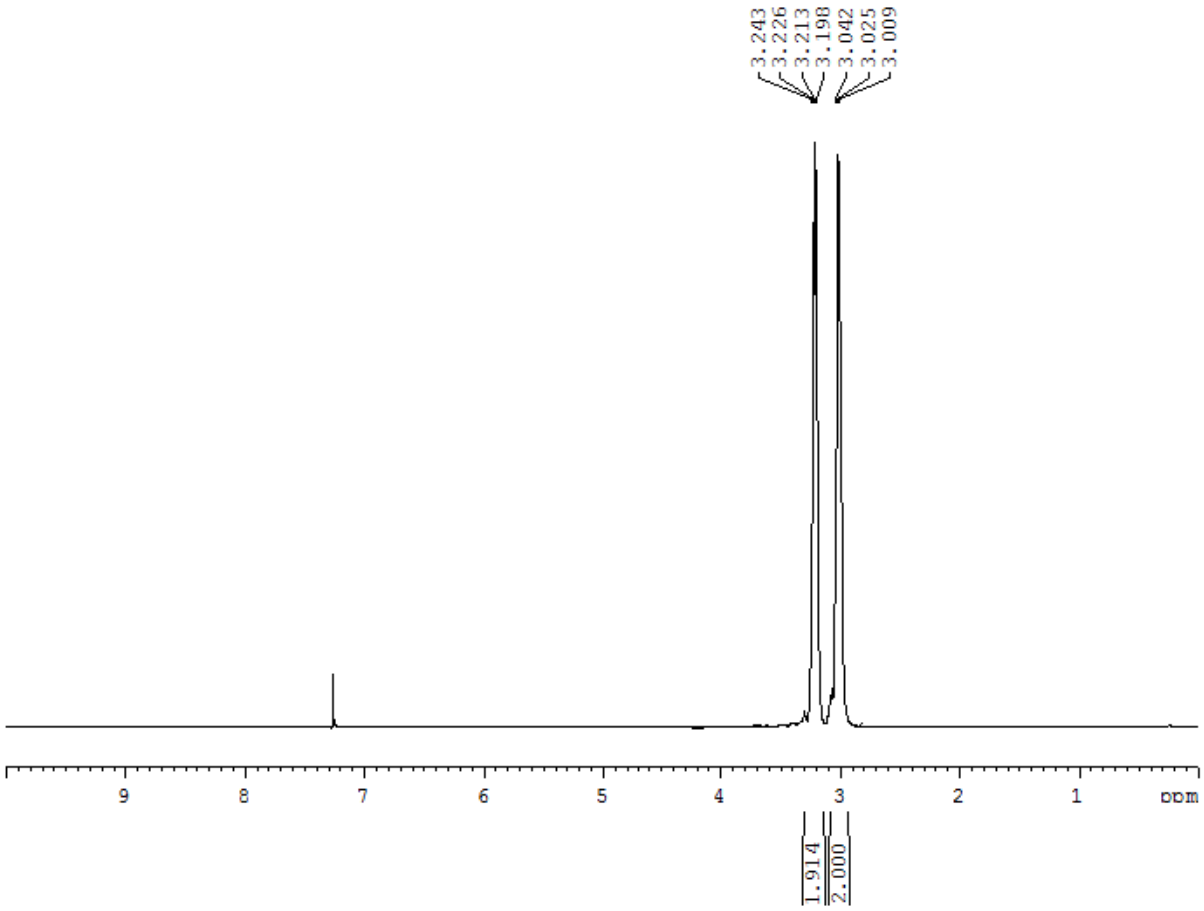


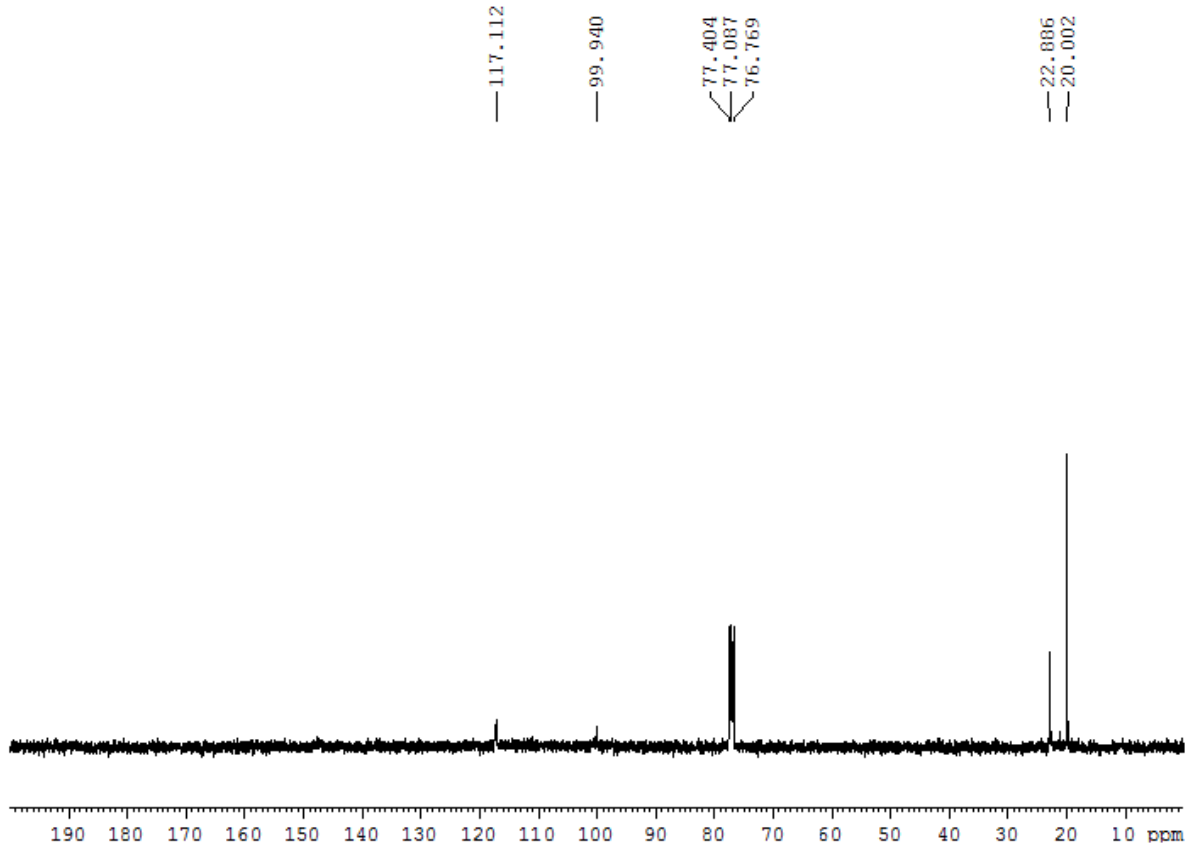
Figure S2. Total ion chromatograms of boiled crude lysate with (A) SeM (= SeMet) or (B) TFSeM and crude lysate filtrate with (C) SeM or (D) TFSeM (= TFSeMet). In each experiment SeM and TFSeM remained constant throughout the 24 h incubation.

Synthesis and Purity

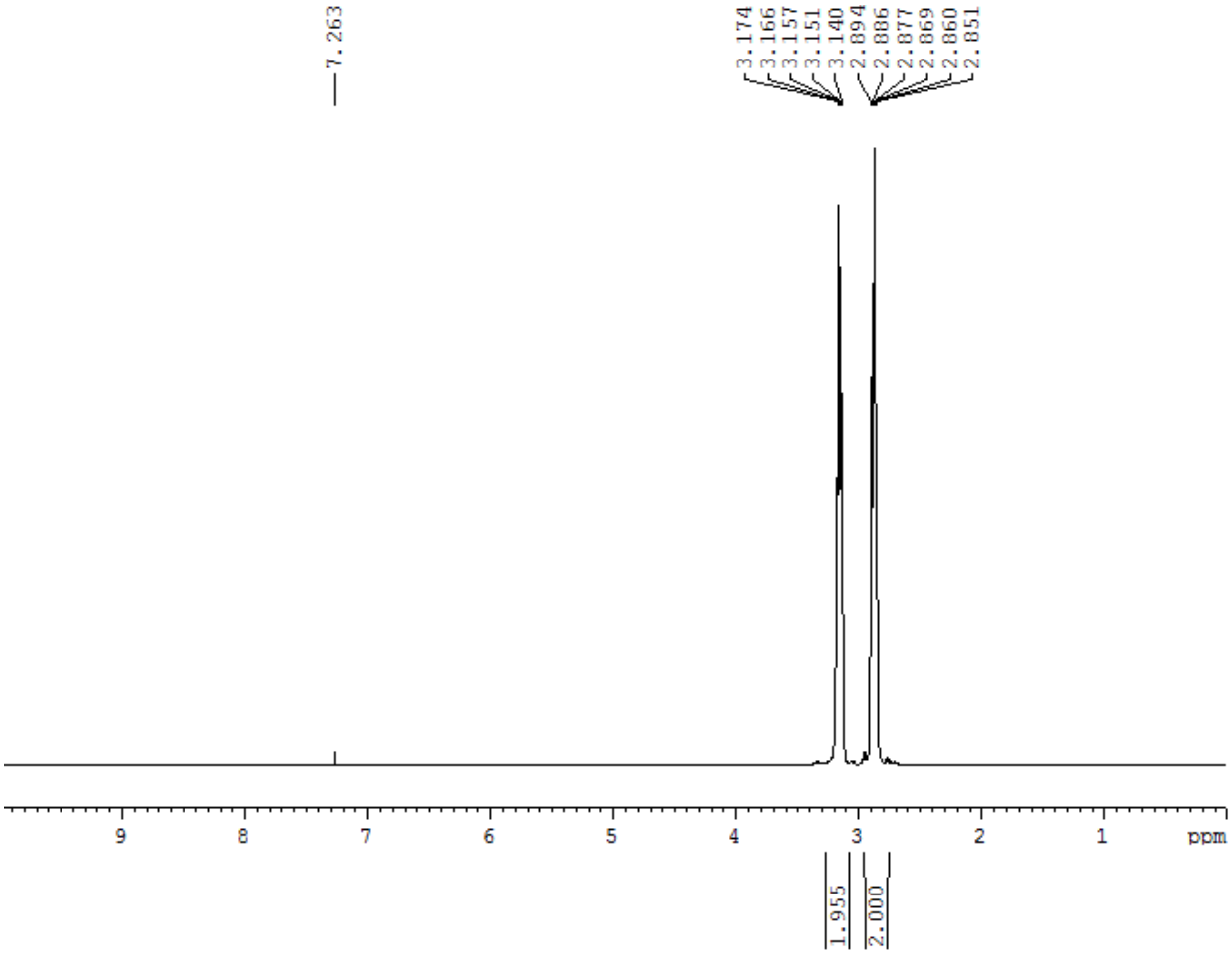
^{1}H NMR of 3-selenocyanatopropanenitrile (17)



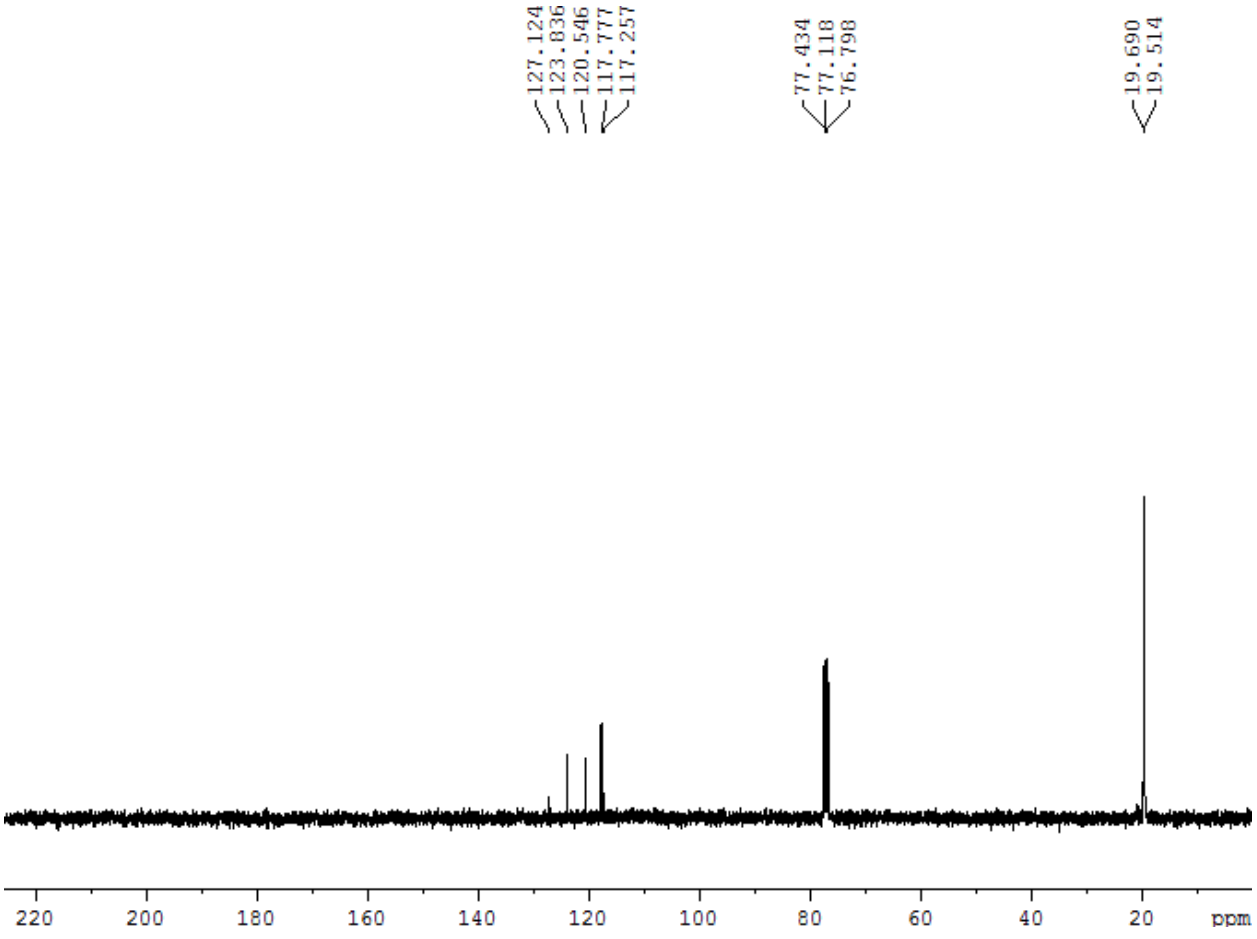
^{13}C NMR of 3-selenocyanatopropanenitrile (17)



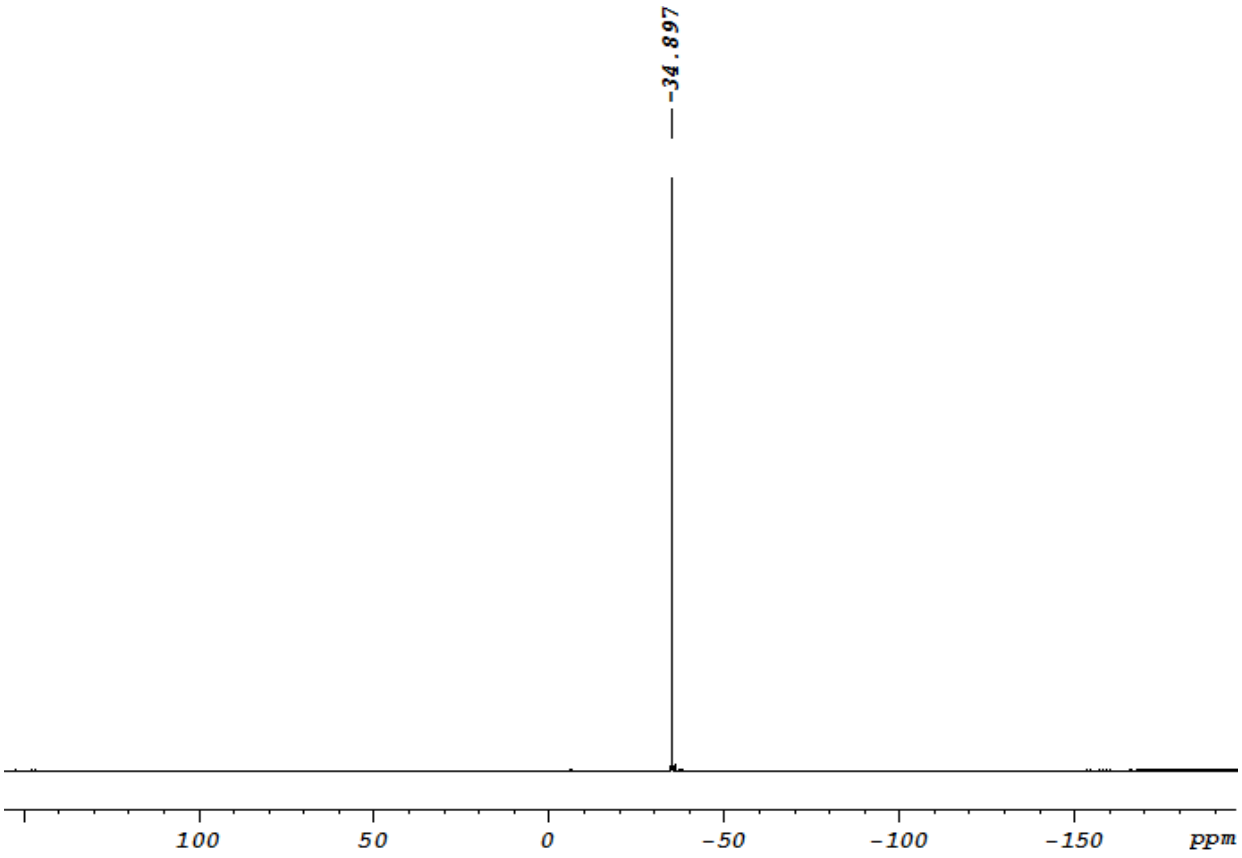
^{1}H NMR of **3-(Trifluoromethylselanyl)propionitrile (18)**



^{13}C NMR of **3-(Trifluoromethylselanyl)propionitrile (18)**

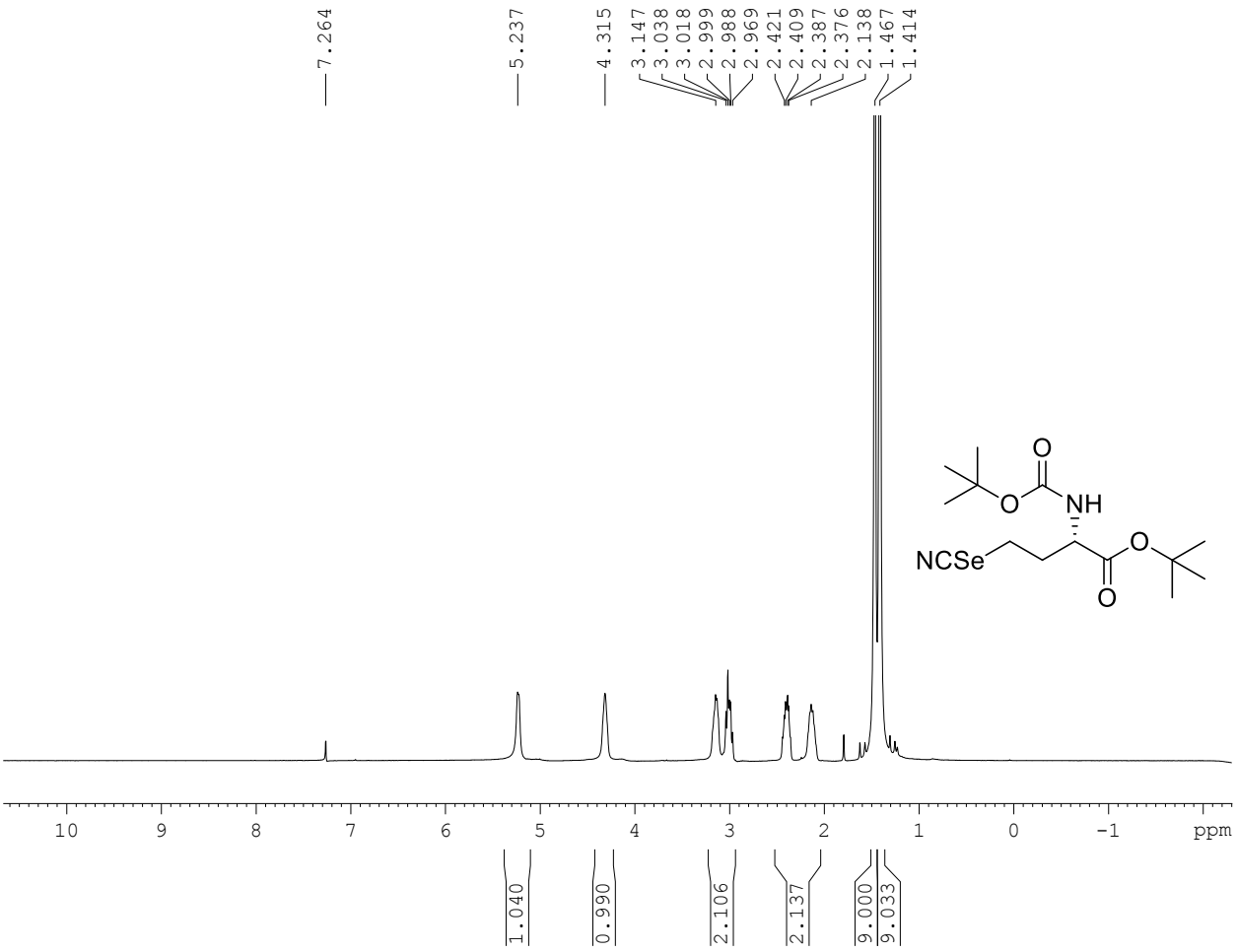


^{19}F NMR of **3-(Trifluoromethylselanyl)propionitrile (18)**

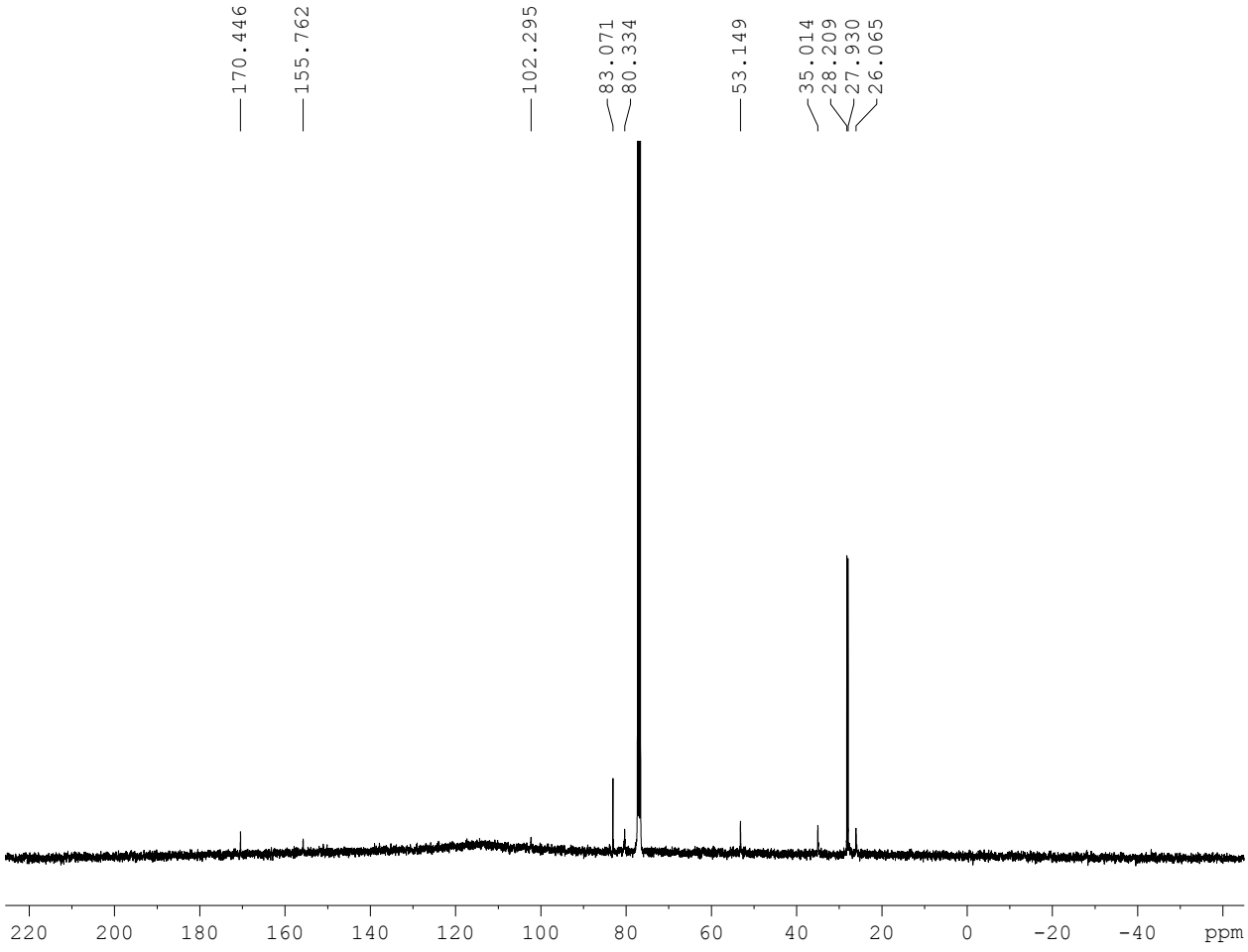


***(S)-tert*-Butyl 4-selenocyanato-2-(*tert*-butoxycarbonylamino)butanoate (15)**

^{1}H NMR in $CDCl_3$ (400 MHz)



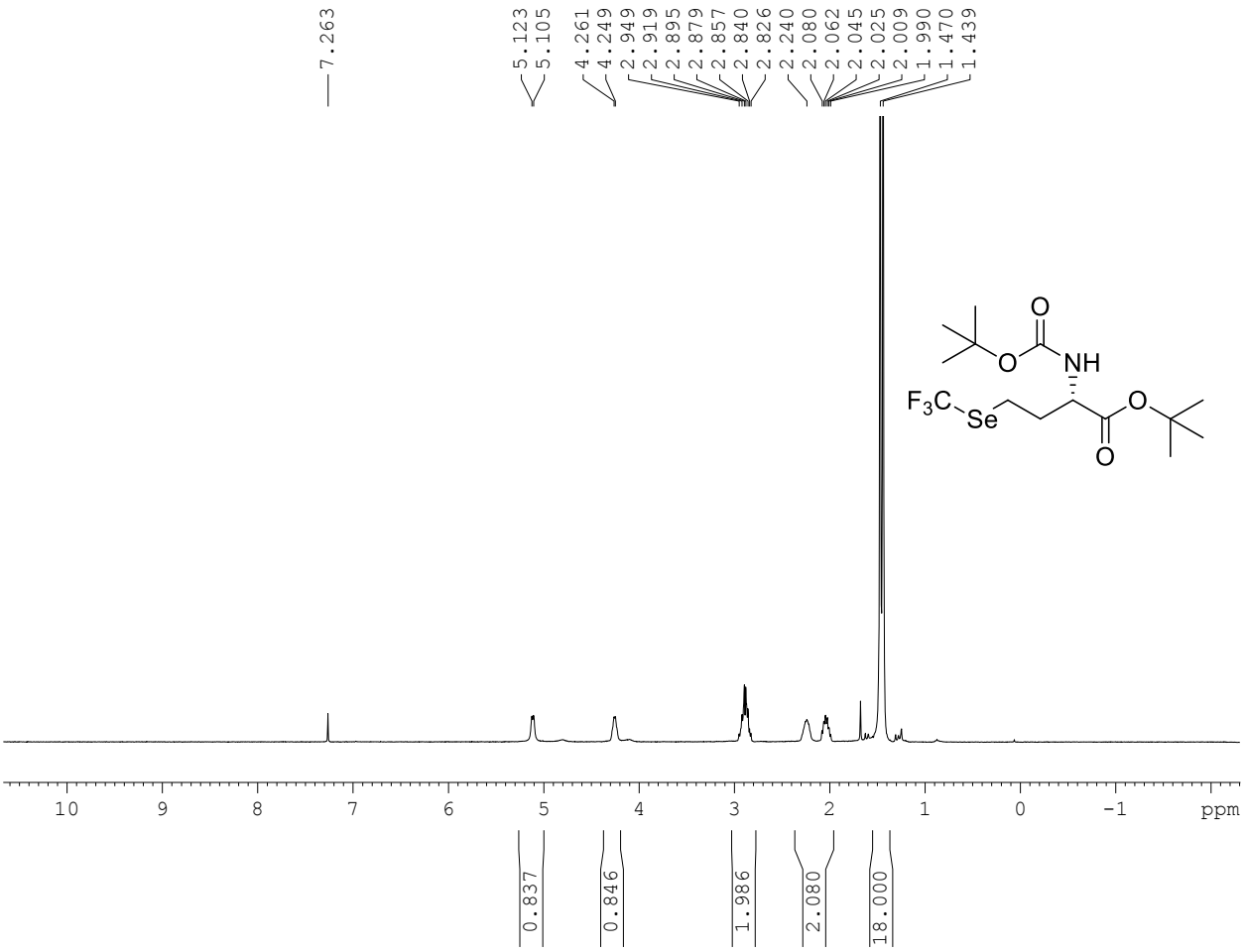
^{13}C NMR in $CDCl_3$ (100 MHz)



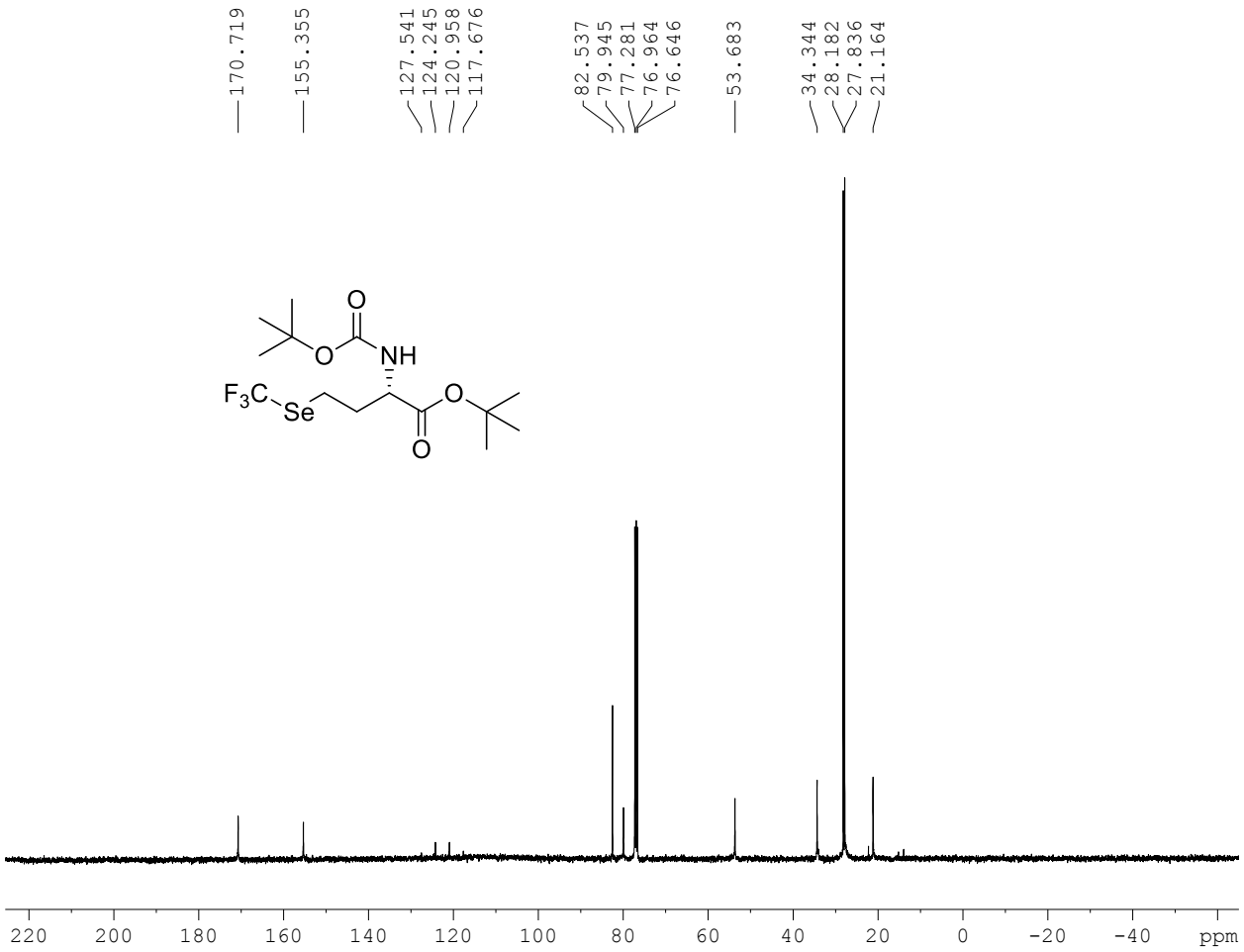
(S)-tert-Butyl 4-trifluoro

methylselanyl-2-(*tert*-butoxycarbonylamino) butanoate (16).

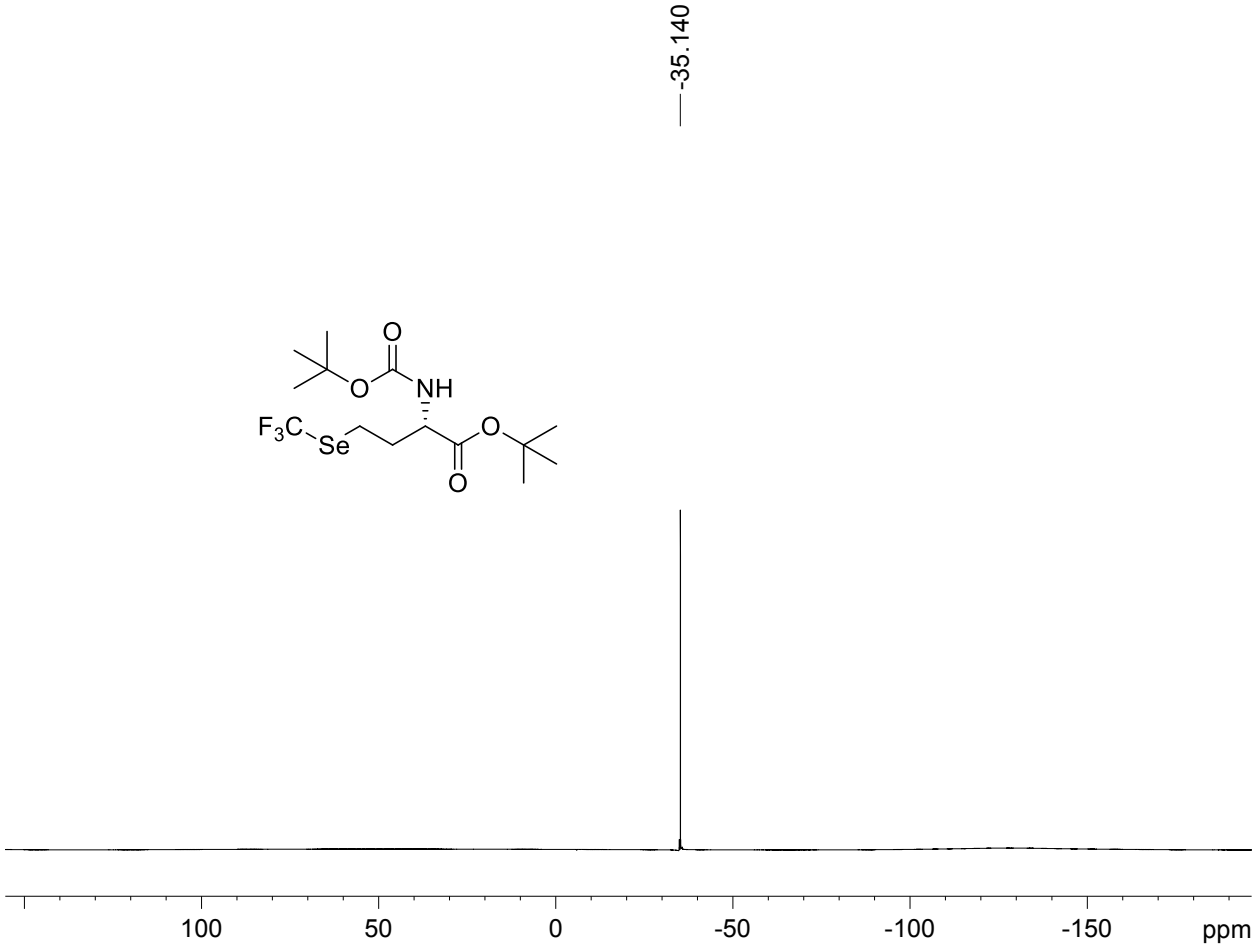
^{1}H NMR in $CDCl_3$ (400 MHz)



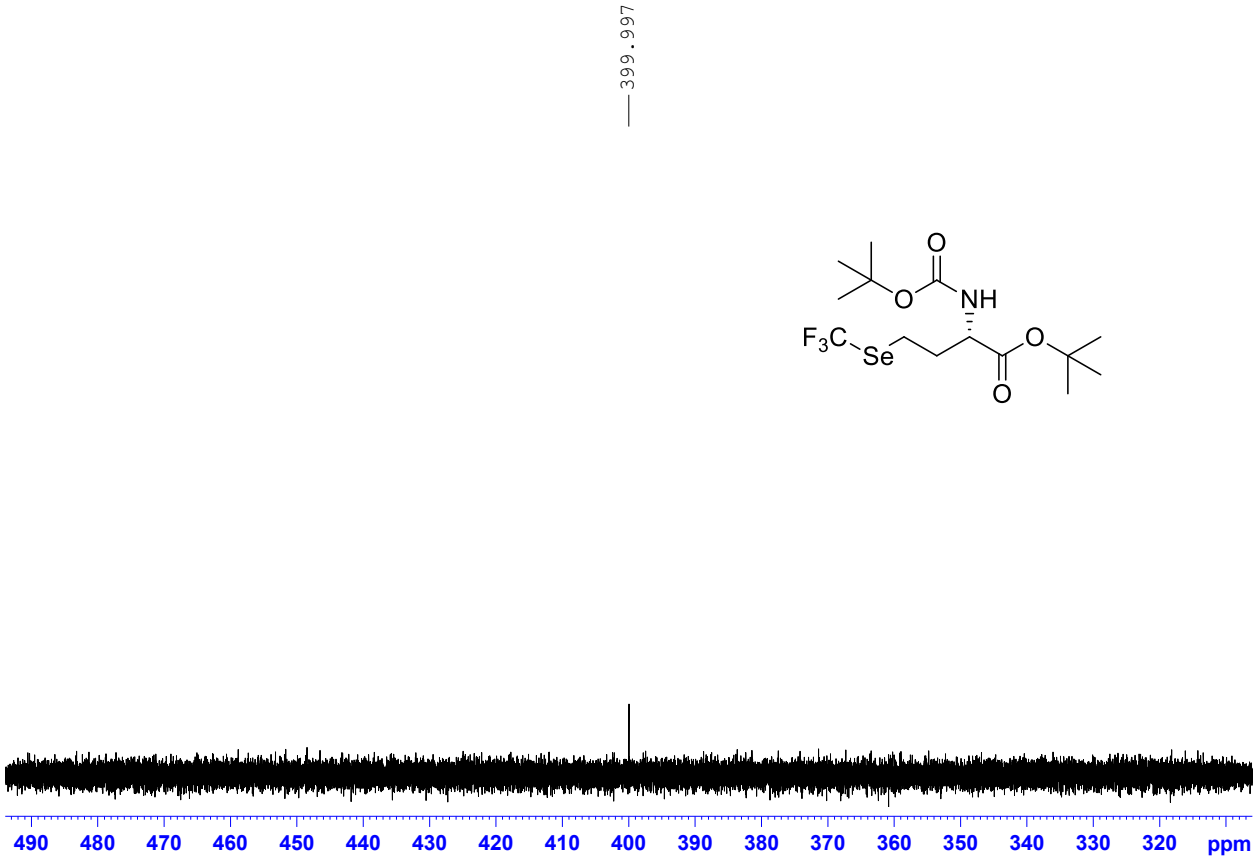
^{13}C NMR in $CDCl_3$ (100 MHz)



^{19}F NMR in $CDCl_3$ (376.5 MHz)

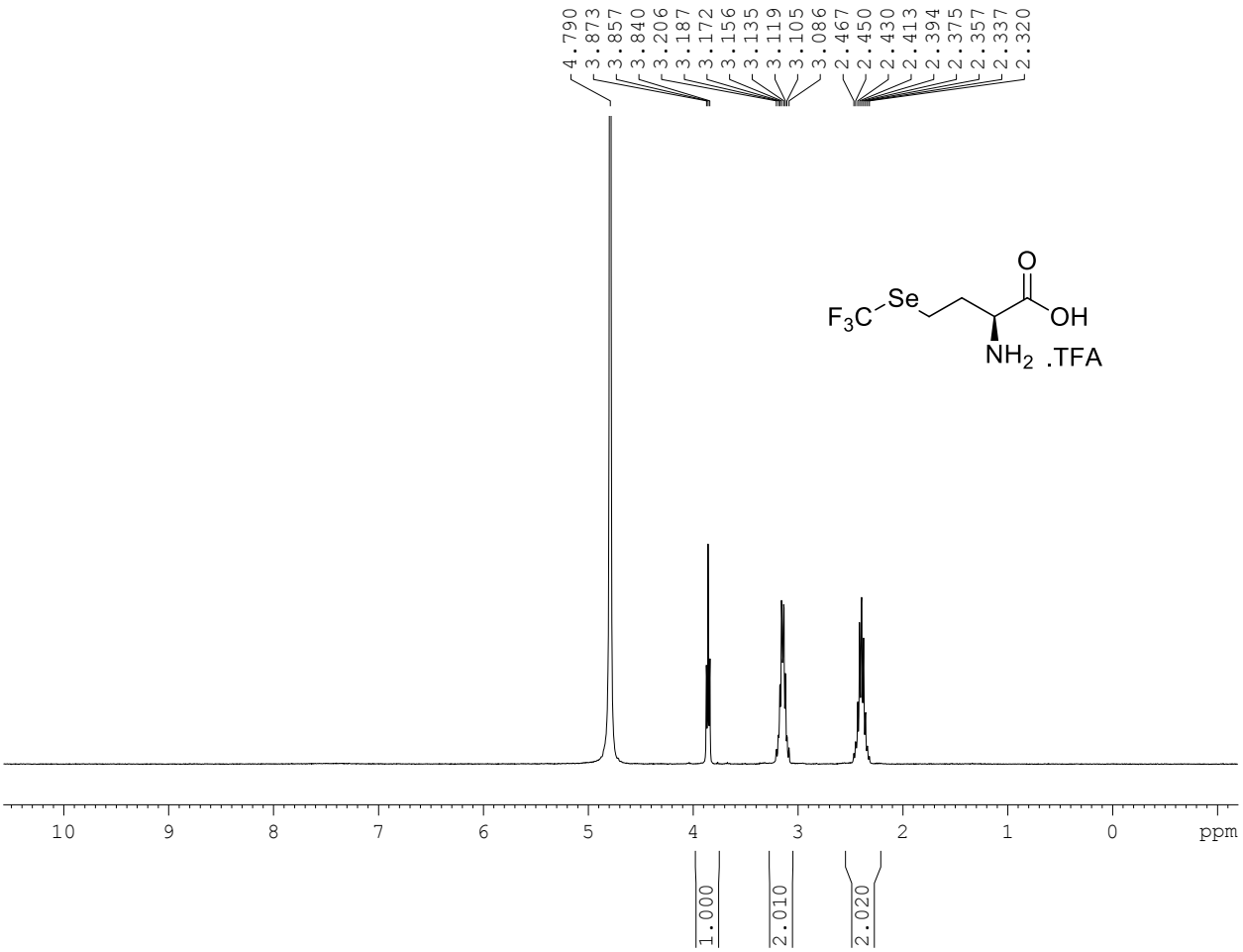


^{77}Se-NMR in $CDCl_3$ (95.3 MHz)

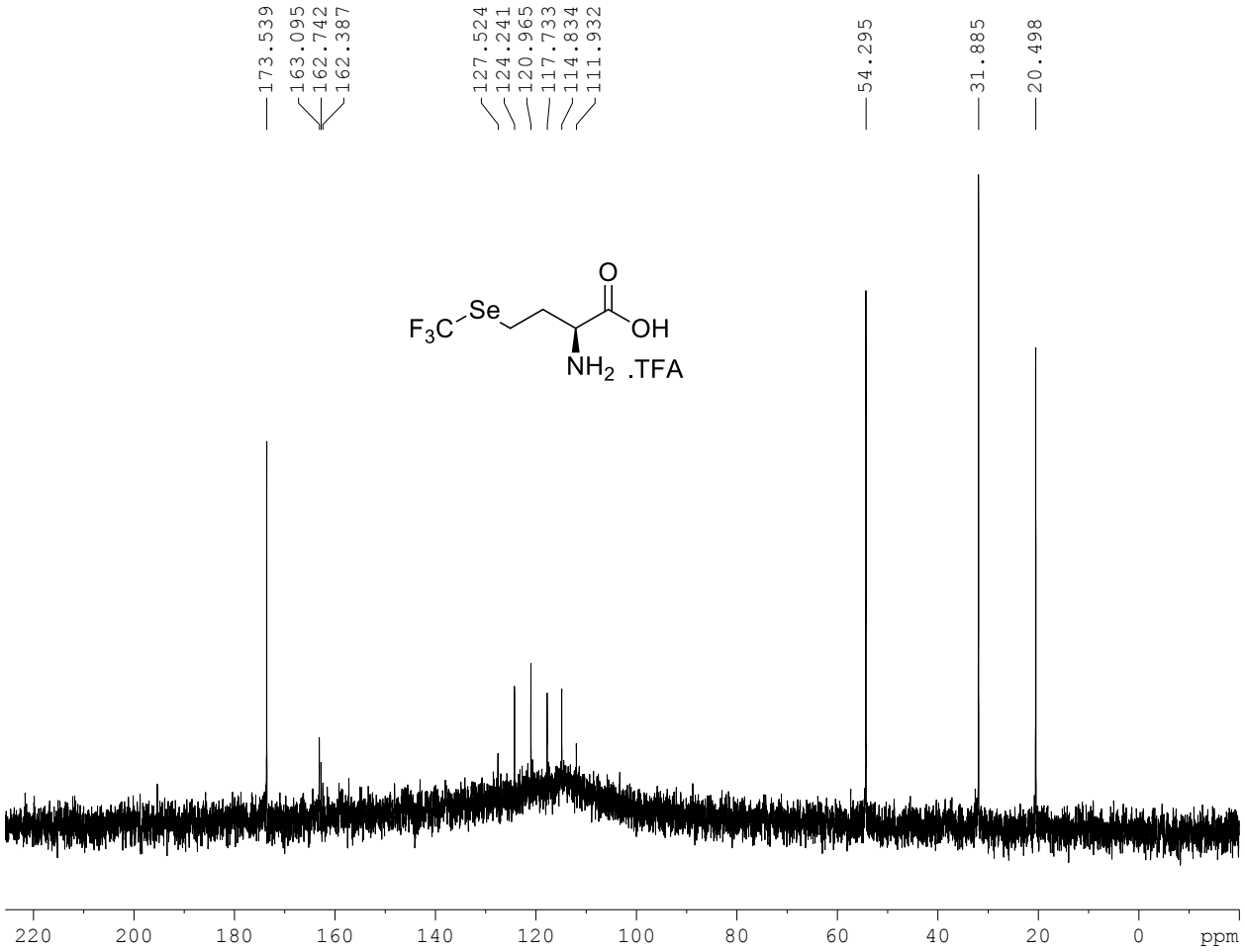


(*S*)-1-Carboxy-3-((trifluoromethyl)selanyl)propan-1-aminium 2,2,2-trifluoroacetate (7a)

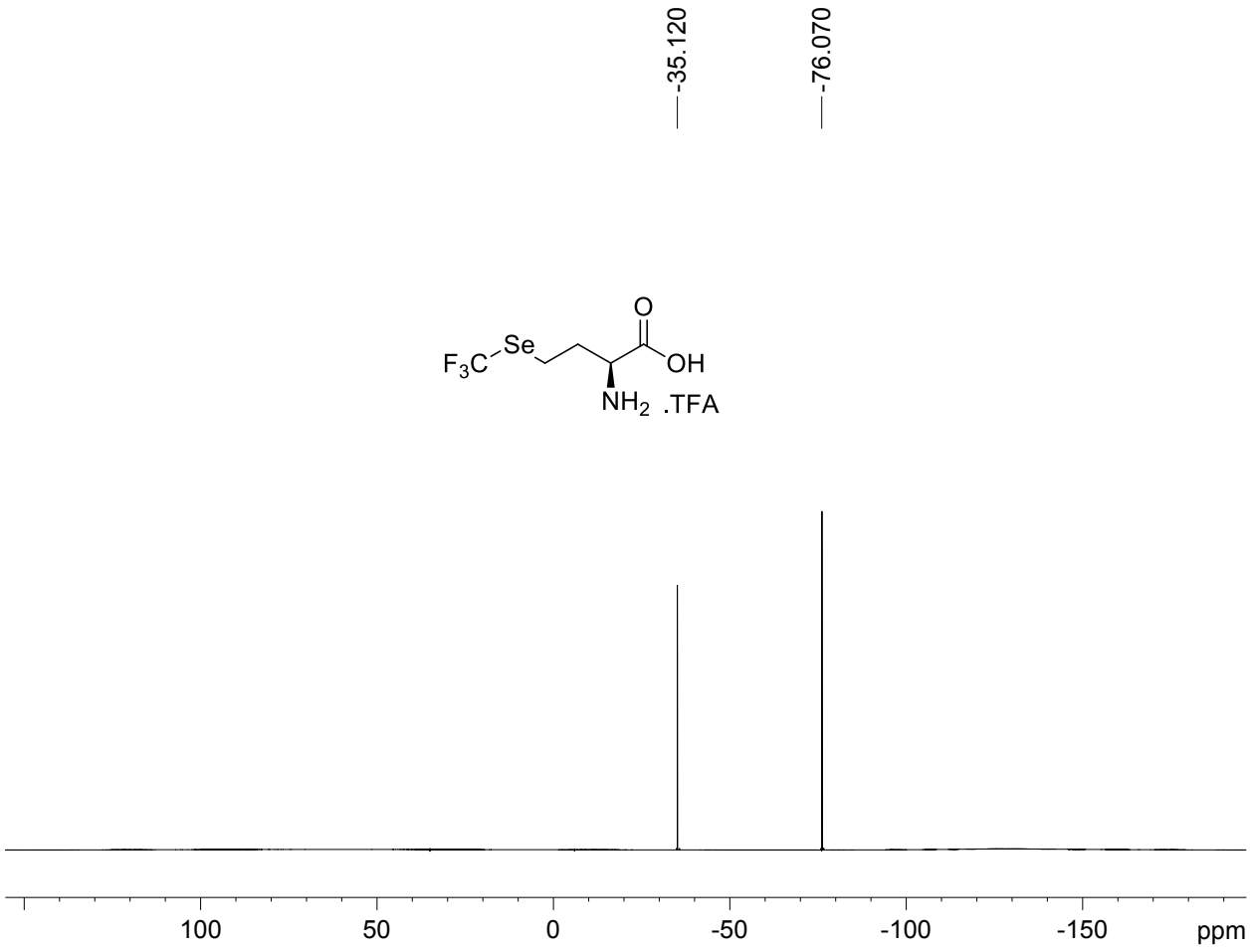
^{1}H NMR in D_2O (400 MHz)



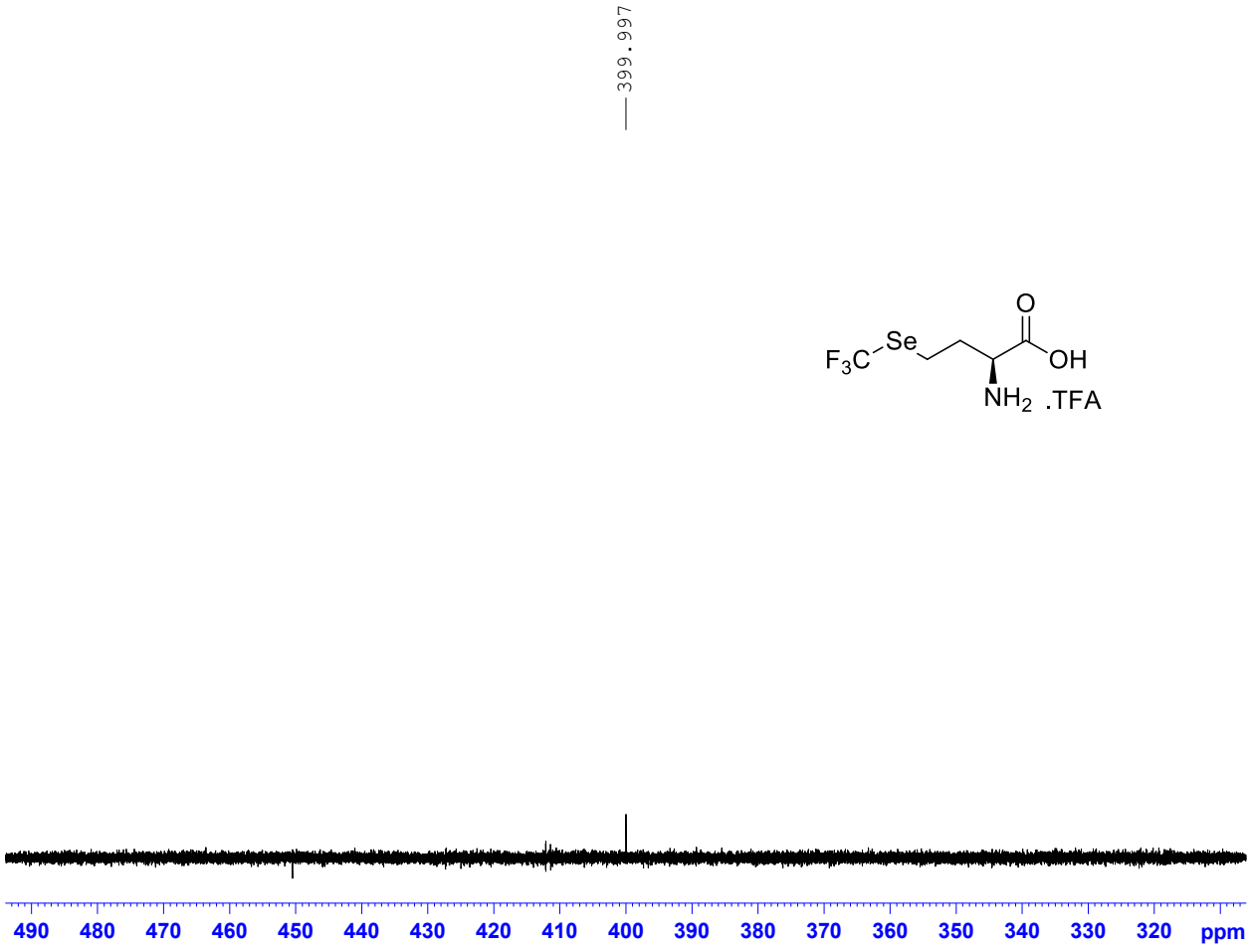
^{13}C NMR in D_2O (100 MHz)



^{19}F NMR in D_2O (376.5 MHz)

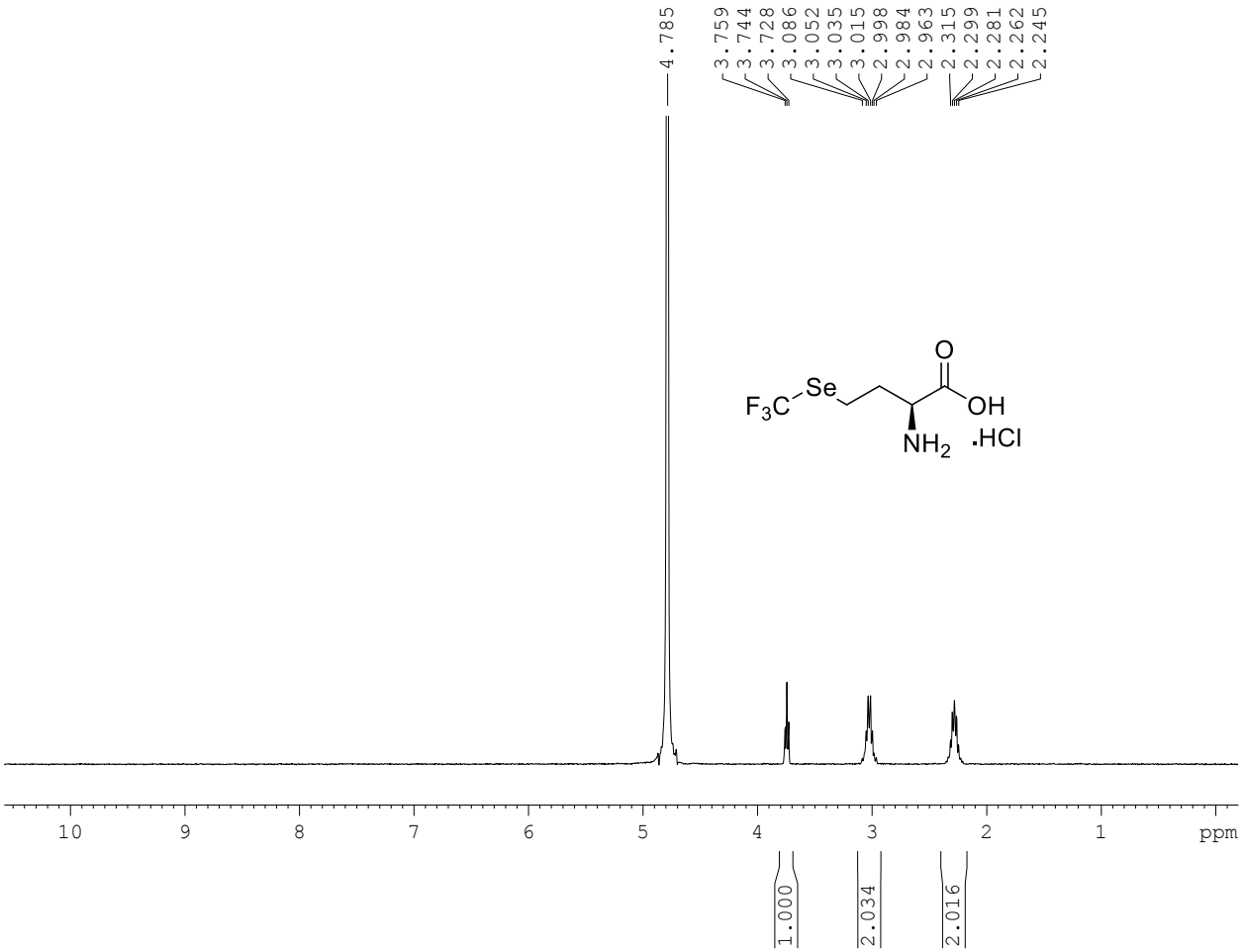


^{77}Se-NMR in D_2O (95.3 MHz)

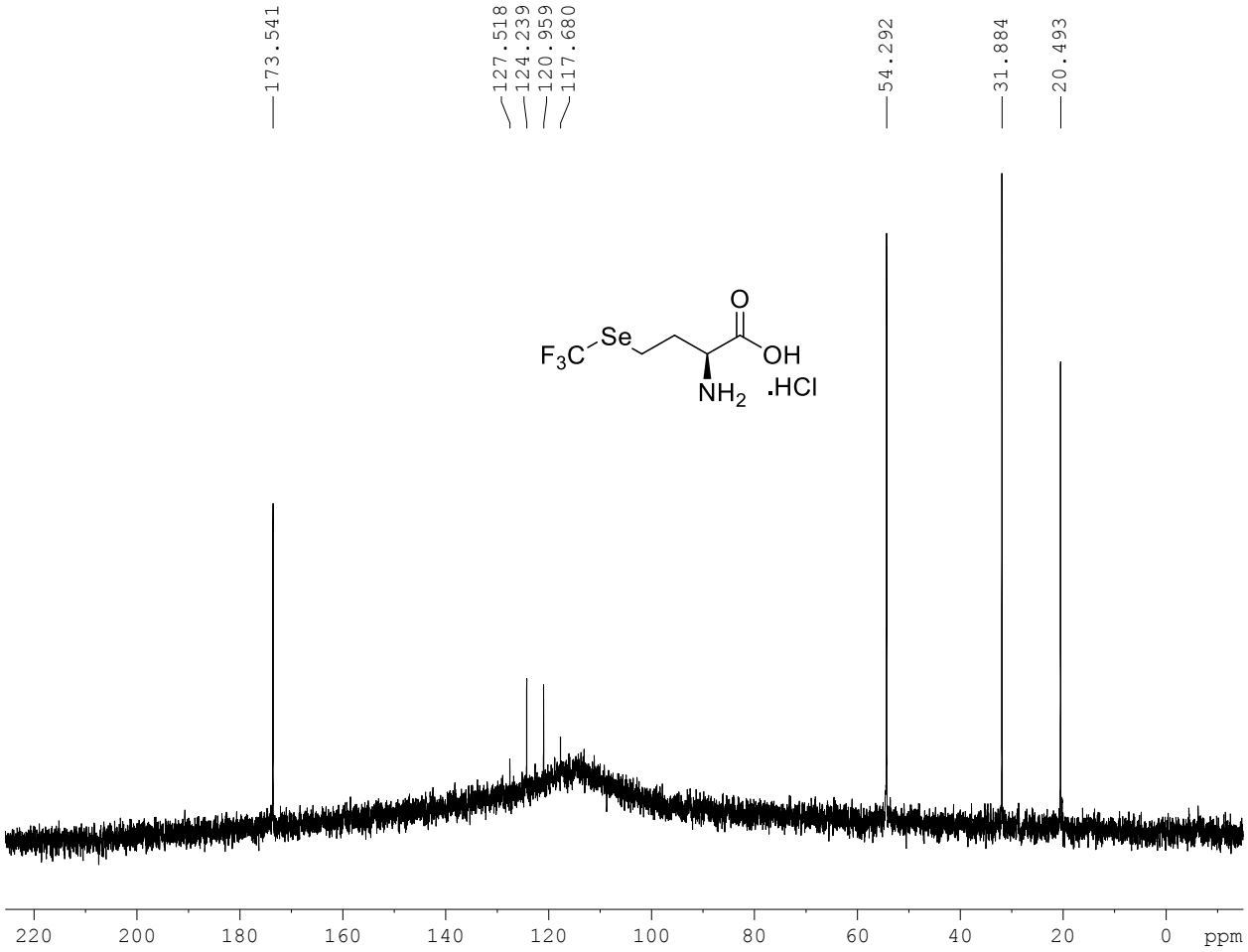


(*S*)-1-Carboxy-3-((trifluoromethyl)selanyl)propan-1-aminium chloride (7b)

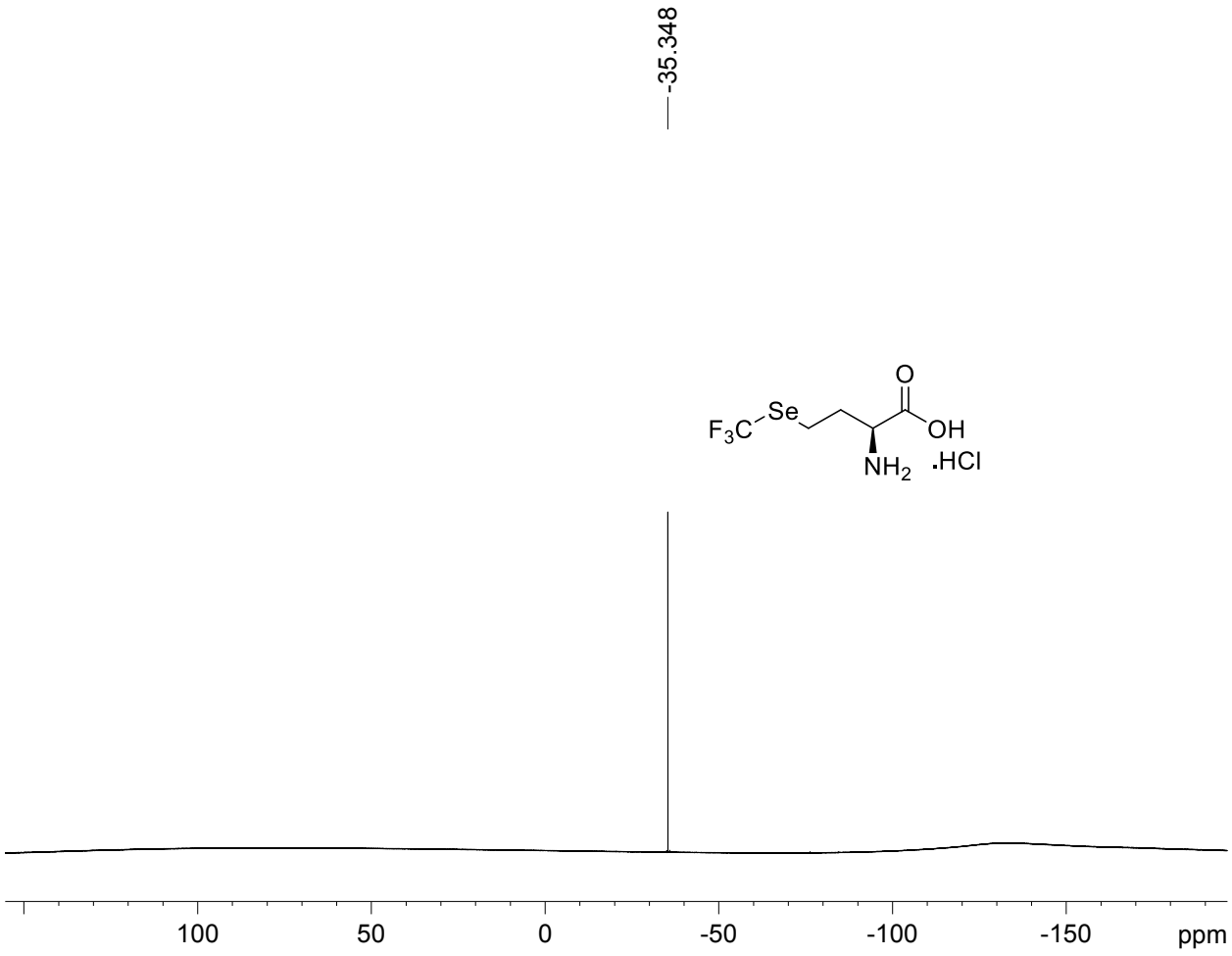
^{1}H NMR in D_2O (400 MHz)



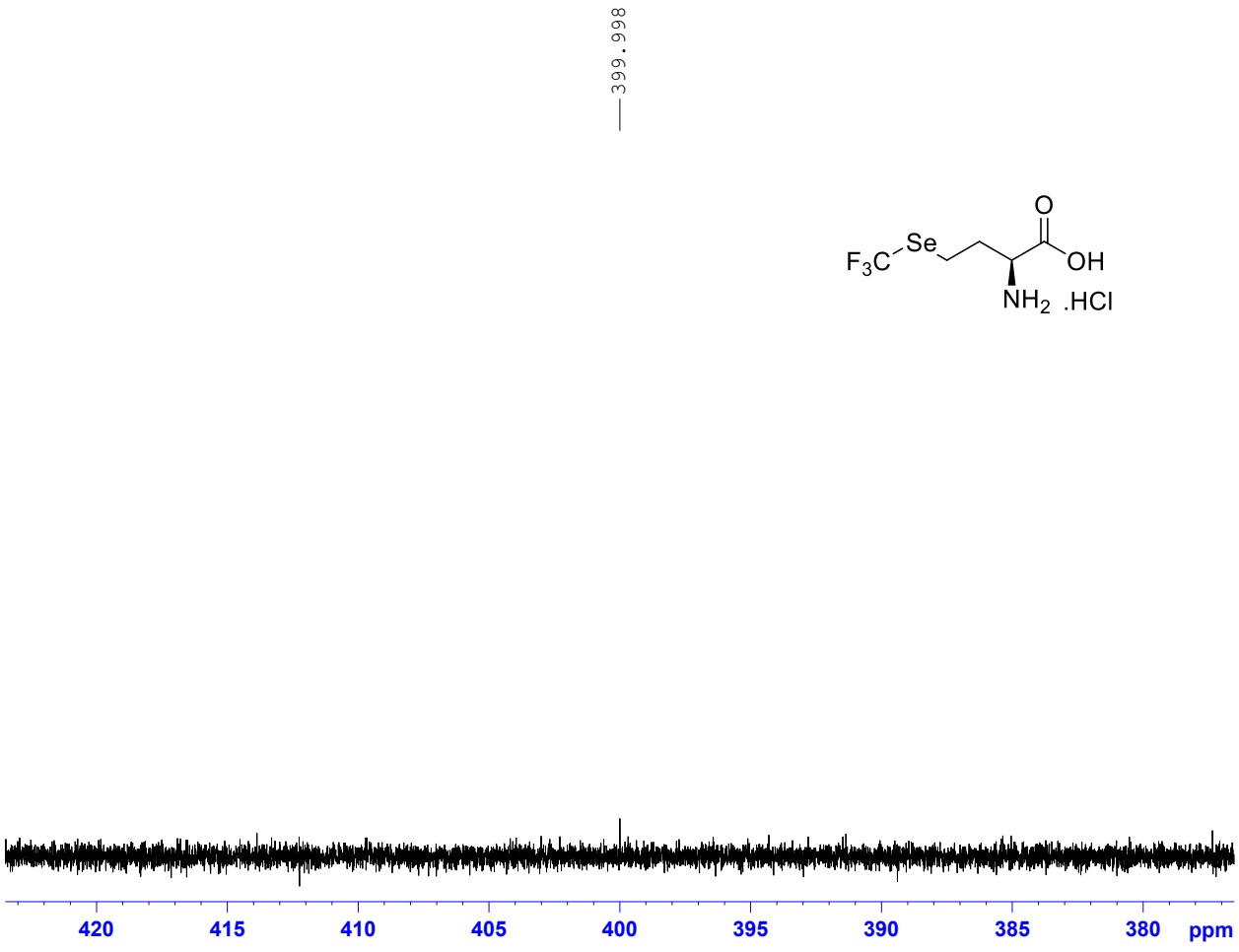
^{13}C NMR in D_2O (100 MHz)



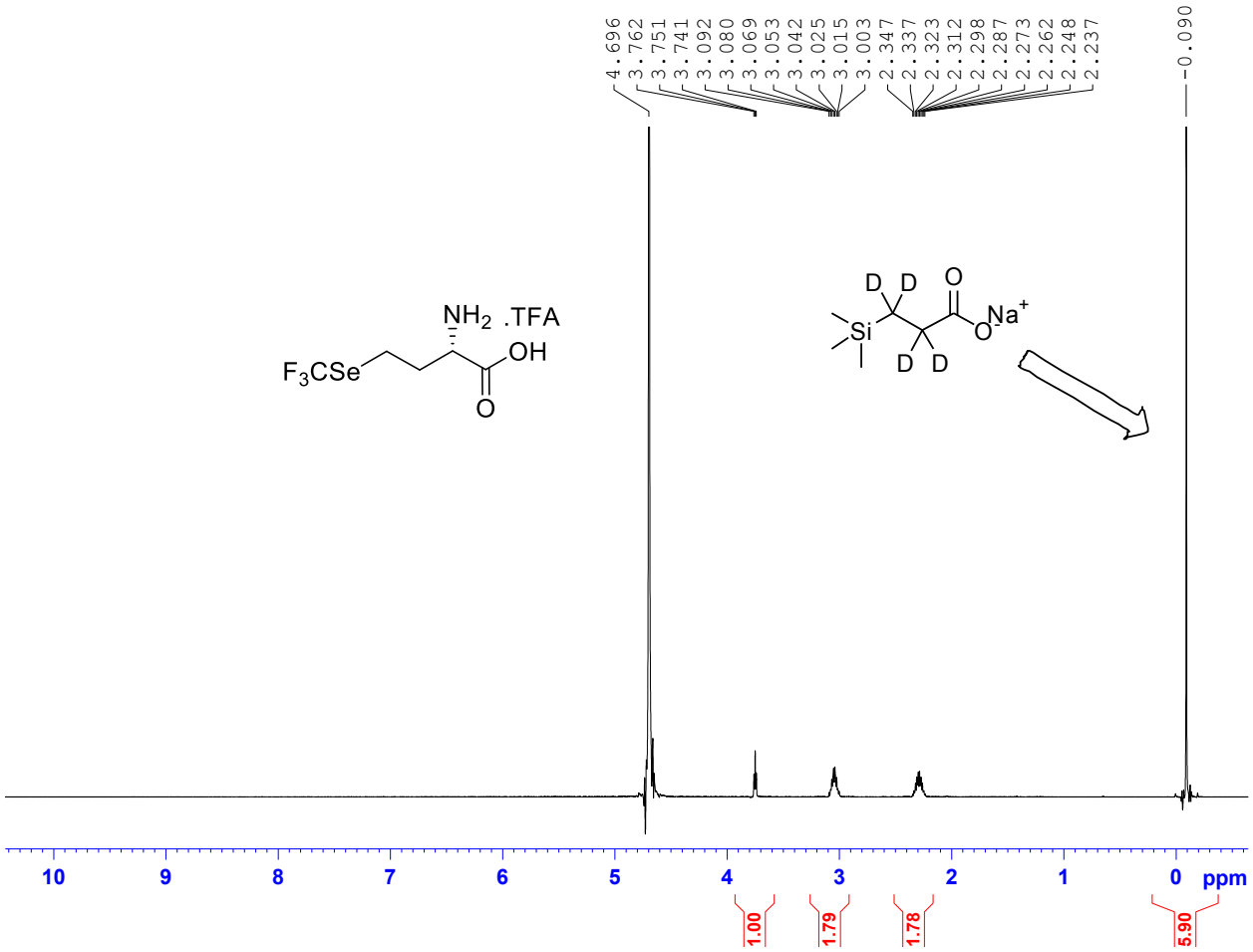
^{19}F NMR in D_2O (376.5 MHz)



^{77}Se-NMR in D_2O (95.3 MHz)



Purity of 7a by absolute qNMR



Sample preparation

7.72 mg of **7a** and 2.50 mg of sodium 3-trimethylsilylpropionate (TMSP-2,2,3,3-D_4 internal calibrant) were transferred into standard NMR tube (5 mm) to which 0.6 mL of D_2O was added.

NMR Instrument/Software Controlled Parameters

Pulse Program: Single pulse, without carbon decoupling ('zg' with 90° pulse [Bruker])
Data Points (acquired): 64 K
Zero-Filling (SI or FN): to 256 K
Dummy Scans: 4

Pulse Width (P1 or PW)	90° RT
Relaxation delay (D1)	60
Acquisition time (AQ or AT)	3.63
Spectral Window (SW)	30 ppm
Transmitter Offset	7.5 ppm
Number of Scans for 600 MHz	1

C. Hardware dependent parameters

Preacquisition Delay: DE = 10 µs (600 MHz Bruker Avance III HD equipped with quadruple resonance, HPCN, QCI-P cryoprobes): *90° Pulse Width* (P1 [Bruker] 9.60 µs)

D. Post-Acquisition Processing and Measurement of Integrals

Processing Using Line Broadening:	LB = 0.4 Hz
Zero Filling:	to 256K real data
Phasing:	Bruker-FP-Automatic
Baseline Correction:	5th order polynomial

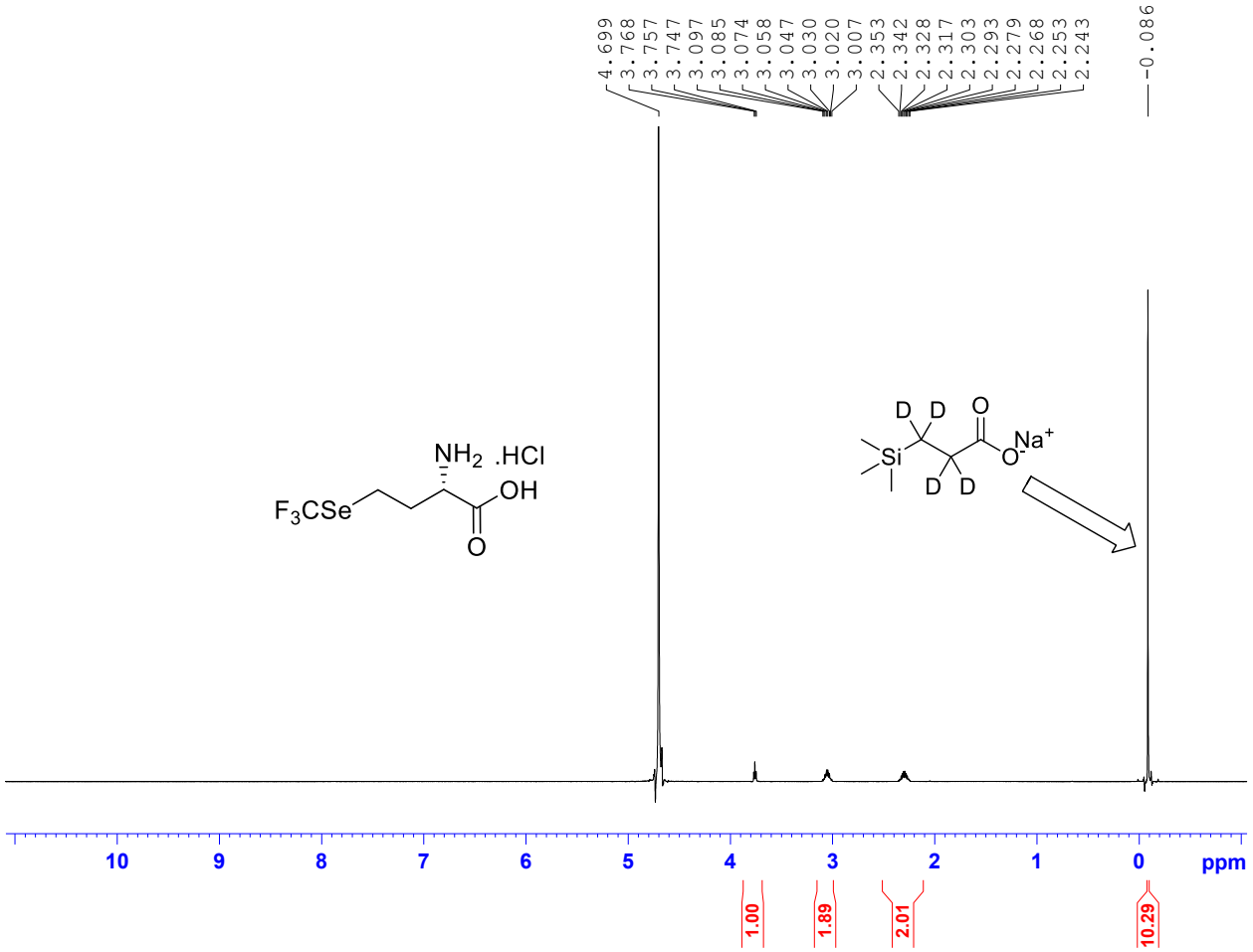
Calculation

$$P[\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.06\%$$

Where:

Weight of the internal calibrant IC (m_{IC})= 2.50 mg
Weight of the sample (m_S) = 7.72 mg
Area (integral) of the IC resonance signal being used for quantification (Int_{IC}) = 5.90
Area (integral) of the target analyte (t) resonance signal being used for
Quantification (Int_t) = 1
Number of protons that give rise to Int_{IC} (n_{IC})= 9
Number of protons of the target analyte that give rise to Int_t (n_t) = 1
Molecular weight of the internal calibrant (MW_{IC}) = 172.26
Molecular weight of the target analyte (MW_t) = 348.96 g/mol
Purity of the internal calibrant, as percent value (P_{IC}) = 98%
Purity of **7a** (P[%]) = 98.06%

Purity of 7b by absolute qNMR



Sample preparation

5.52 mg of **7b** and 3.81 mg of sodium 3-trimethylsilylpropionate (TMSP-2,2,3,3-D_4 internal calibrant, IC) were transferred into standard NMR tube (5 mm) to which 0.6 mL of D_2O was added.

NMR Instrument/Software Controlled Parameters

Pulse Program: Single pulse, without carbon decoupling ('zg' with 90° pulse [Bruker])

Data Points (acquired): 64 K
Zero-Filling (SI or FN): to 256 K
Dummy Scans: 4

Pulse Width (P1 or PW)	90° RT
Relaxation delay (D1)	60
Acquisition time (AQ or AT)	3.63

Spectral Window (SW)	30 ppm
Transmitter Offset	7.5 ppm
Number of Scans for 600 MHz	1

C. Hardware dependent parameters

Preacquisition Delay: DE = 10 µs (600 MHz Bruker Avance III HD equipped with quadruple resonance, HPCN, QCI-P cryoprobes): 90° Pulse Width (P1 [Bruker] 9.60 µs).

D. Post-Acquisition Processing and Measurement of Integrals

Processing Using Line Broadening:	LB = 0.1 Hz
Zero Filling:	to 256K real data
Phasing:	Bruker-FP- Automatic
Baseline Correction:	5th order polynomial

Calculation

$$P[\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.40\%$$

Where:

Weight of the internal calibrant IC (m_{IC}) = 3.81 mg

Weight of the sample (m_S) = 5.52 mg
Area (integral) of the IC resonance signal being used for quantification (Int_{IC}) = 10.29
Area (integral) of the target analyte (t) resonance signal being used for
Quantification (Int_t) = 1
Number of protons that give rise to Int_{IC} (n_{IC}) = 9
Number of protons of the target analyte that give rise to Int_t (n_t) = 1
Molecular weight of the internal calibrant (MW_{IC}) = 172.26
Molecular weight of the target analyte (MW_t) = 286.53 g/mol
Purity of the internal calibrant, as percent value (P_{IC}) = 98%
Purity of **7b** (P[%]) = 98.40%