7-Selenabicyclo[2.2.1]heptane†

Phoebe E. Macdougall,[a,b] Heather M. Aitken,[a,b] Peter J. Scammells,[a,c] Yvonne Kavanagh,[a,b] Sara H. Kyne,[a,b,d] and Carl H. Schiesser*[a,b]

Electronic Supplementary Information

Details of computational methods employed, M05-2X/6-311++G(d,p)-optimised geometry of **5** as Figure S1, Gaussian Archive Entries for **10** at all optimised levels of theory used; G3(MP2)-RAD calculated Arrhenius parameters for the cyclization of **9**; experimental details for the preparation of **5**; ^{1}H and ^{13}C NMR spectra of compounds **5**, **11**, **13**, **14** (27 pages).

Computational Details

Standard ab initio molecular orbital and DFT calculations were performed in Gaussian 09.[S1] All geometry optimisations, frequency and single point energy calculations on open-shell species were performed using unrestricted wavefunctions. (U)RCCSD(T) calculations were performed using MOLPRO, version 2009.1.[S2]

Geometries of all species were optimised at the levels of theory listed in Table 1 and frequency calculations were also performed at these levels. Improved energies were then obtained using G3(MP2)-RAD, a high-level composite method that approximates (U)RCCSD(T) calculations with a large triple-ζ basis set via additivity corrections at the R(O)MP2 levelof theory.[S3] This approach has been shown to reproduce a large test set of gas-phase experimental data to within chemical accuracy,[S3] and we have had success with the use of this method to model the kinetics and thermodynamics of radical cyclization reactions.[S4,S5]

Gas-phase rate coefficients were calculated using standard transition state theory as has previously been described by us.[S5]

References

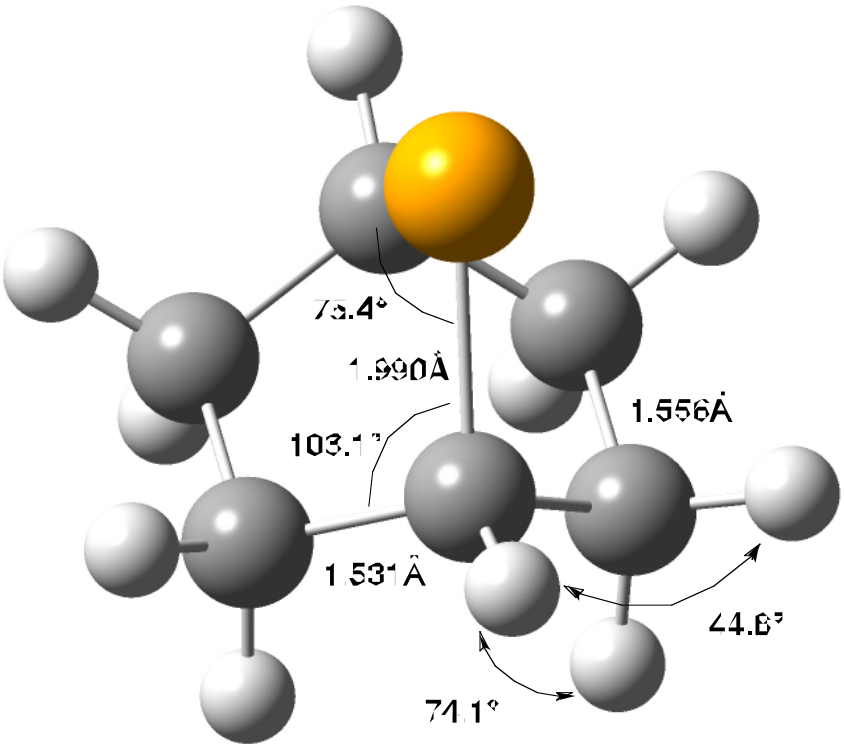
S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Peterson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H.P.; Izmayl, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, K.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S.S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R.E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; J. Ochterski, J.; Martin, R, L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *GAUSSIAN 09 (Revision B.01),* Gaussian, Inc., Wallingford, CT, **2010**.

S2. Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schu¨tz, M.; Celani, P.; Korona, T.; Rauhut, G.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C. Hetzer, G.; Lloyd, A. W.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteins- son, T. MOLPRO, version 2009.1, a package of ab initio programs.

S3. D. J. Henry, M. B. Sullivan and L. Radom, *J. Chem. Phys,* 2003, **118**, 4849.

S4. S. Lobachevsky, C. H. Schiesser, C. Y. Lin and M. L. Coote, *J. Phys. Chem. A*, 2009, **112**, 13622.

S5. S. H. Kyne, C. Y. Lin, I. Ryu, M. L. Coote and C. H. Schiesser, *Chem. Commun.*, 2010, **46**, 6521.



Gaussian Archive Entries

Transition State **10:**

HF/6-311G(d,p)

1\1\GINC-MERRI012\FTS\UHF\6-311G(d,p)\C13H17Se1(2)\SHKYNE\11-Sep-2011\
0\\# HF/6-311G** opt=(maxcyc=300,ts,noeigentest,readfc,nofreeze) freq
geom=checkpoint guess=check\\Cyclization to form selenabicyclo[2.1.1]h
eptane - benzyl radical leaving group\\0,2\C,0.1628911897,-0.000520890
9,-0.5331069242\Se,-0.1675786837,0.0023824777,2.0506501963\C,1.7338969
346,0.0012585699,1.4927200006\C,1.9791737005,1.2501967968,0.643495971\
C,1.9784844952,-1.2496633212,0.6462187384\C,0.9627482254,1.277423926,-
0.5286777832\C,0.9619659467,-1.2789286738,-0.525823263\H,-0.793351468,
-0.0007715073,-1.0291219754\H,2.3465337415,0.0020696936,2.3845251567\H
,1.8835598777,2.1440278378,1.2480807828\H,1.8824263338,-2.1421180223,1
.252763493\H,3.0009353751,1.2238373633,0.2692825466\H,3.0002383649,-1.
2246659785,0.2718913764\H,0.2997607491,2.1292287977,-0.4396633185\H,0.
29847741,-2.1301366005,-0.434853566\H,1.4854406647,1.3845524542,-1.481
071649\H,1.4845338196,-1.3885158387,-1.4780054815\C,0.3009165297,0.004
3714732,4.4698424832\H,0.8759155281,0.9127949782,4.4769569737\H,0.8751
780717,-0.9045031577,4.478594364\C,-0.9518949966,0.005527099,5.1858863
704\C,-1.5910169222,1.2186507042,5.5313343816\C,-1.5920334901,-1.20645
10394,5.5334676\C,-2.8059136357,1.2172040944,6.208977075\H,-1.12788448
36,2.1516850405,5.2625899459\C,-2.8069277567,-1.2027937184,6.211105728
8\H,-1.1296841564,-2.1403440957,5.2663629899\C,-3.4201017364,0.0077651
794,6.5541285502\H,-3.2742496019,2.1501781562,6.4676060976\H,-3.276045
8509,-2.1349183302,6.4713749626\H,-4.3590950813,0.0086193896,7.0778789
734\\Version=AM64L-G09RevB.01\State=2-A\HF=-2902.0278008\S2=1.754355\S
2-1=0.\S2A=1.942011\RMSD=6.864e-09\RMSF=1.186e-06\Dipole=0.5796575,-0.
0003877,-0.1214073\Quadrupole=1.0009095,-0.494178,-0.5067314,-0.003873
9,-4.0414179,0.0020474\PG=C01 [X(C13H17Se1)]\\@

BHandHLYP/6-311++G(d,p)

1\1\GINC-MERRI046\FTS\UBHandHLYP\6-311++G(d,p)\C13H17Se1(2)\SHKYNE\13-
Sep-2011\0\\# BHandHLYP/6-311++G** opt=(maxcyc=300,ts,noeigentest,read
fc,nofreeze) freq geom=checkpoint guess=check\\Cyclization to form sel
enabicyclo[2.1.1]heptane - benzyl radical leaving group\\0,2\C,0.05406
30365,-0.000091521,-0.1886920687\Se,-0.0798780783,0.0023246736,2.09266
39911\C,1.8281778713,0.0011812348,1.5526179645\C,2.0076981988,1.244368
6666,0.6891620648\C,2.0069440859,-1.2439061402,0.6917459806\C,0.865649
3721,1.2570152635,-0.3590139377\C,0.8648971836,-1.258032316,-0.3564116
331\H,-0.9476236917,-0.0002066827,-0.5891881393\H,2.459348513,0.001901
9726,2.4313624334\H,1.974027306,2.1401039301,1.2988205767\H,1.97272003
35,-2.1383538833,1.3032616509\H,2.9838204505,1.2163146575,0.2078590086
\H,2.9830880613,-1.2174485388,0.2103960999\H,0.2400352534,2.1331769977
,-0.2376918286\H,0.2387559846,-2.1335655546,-0.2332853591\H,1.27247720
42,1.2936098202,-1.3716138161\H,1.2717121641,-1.2969634896,-1.36892921
31\C,0.3385556354,0.0042813601,4.3255131407\H,0.9217906713,0.906380985
6,4.4145550469\H,0.9211533685,-0.8980564095,4.4162911521\C,-0.93013937
37,0.0054179703,5.0421524995\C,-1.5607030544,1.2038937489,5.3825053967
\C,-1.5615372713,-1.1919572642,5.3848241532\C,-2.7698194767,1.20478799
39,6.0506458065\H,-1.0933578479,2.1377356899,5.1177078328\C,-2.7706537
591,-1.1907168035,6.0529640803\H,-1.094841594,-2.1266352489,5.12183679
08\C,-3.3806340756,0.007575719,6.3903712846\H,-3.2373189217,2.13983649
39,6.3085576353\H,-3.2388036354,-2.1249387102,6.3126852065\H,-4.322304
5195,0.0084082412,6.9117369972\\Version=AM64L-G09RevB.01\State=2-A\HF=
-2906.8425088\S2=0.820679\S2-1=0.\S2A=0.752784\RMSD=7.409e-09\RMSF=6.8
05e-06\Dipole=0.5487958,-0.00058,-0.365297\Quadrupole=0.9840982,0.0221
908,-1.006289,-0.0033918,-3.278654,0.0002475\PG=C01 [X(C13H17Se1)]\\@

BHandHLYP/aug-cc-pVDZ

1\1\GINC-MERRI022\FTS\UBHandHLYP\Aug-CC-pVDZ\C13H17Se1(2)\SHKYNE\14-Se
p-2011\0\\# BHandHLYP/aug-cc-pVDZ opt=(maxcyc=300,ts,noeigentest,readf
c,nofreeze) freq geom=checkpoint guess=check\\Cyclization to form sele
nabicyclo[2.1.1]heptane - benzyl radical leaving group\\0,2\C,0.050230
8268,-0.0000851336,-0.1826805956\Se,-0.0802000875,0.0023248257,2.09547
50817\C,1.8287333192,0.0011825385,1.5546554028\C,2.0070270995,1.245196

0761,0.6904142695\C,2.0062736994,-1.2447339819,0.6930042436\C,0.862744
4734,1.2579712159,-0.3560052637\C,0.8619964806,-1.2589802363,-0.353402
5122\H,-0.9568289608,-0.0002025204,-0.5855956538\H,2.465663509,0.00190
77262,2.4364581771\H,1.9748983167,2.1440737472,1.3045143732\H,1.973583
5274,-2.1423136344,1.3089707981\H,2.9865689951,1.2159935825,0.20506287
08\H,2.9858400501,-1.21714429,0.2076075655\H,0.2337860915,2.1378710958
,-0.2336722807\H,0.2325111501,-2.1382504688,-0.2292665359\H,1.26943837
9,1.2926843746,-1.374043705\H,1.2686832072,-1.2960325978,-1.3713610595
\C,0.3469257004,0.0042786147,4.3228140037\H,0.9321071184,0.9119225944,
4.4120238665\H,0.931468536,-0.9036035184,4.4137647662\C,-0.9235397394,
0.005415888,5.0418012942\C,-1.5570134932,1.2070287047,5.3806371115\C,-
1.5578509546,-1.1950976937,5.3829581409\C,-2.7717031377,1.2082027673,6
.0471678219\H,-1.0869107491,2.14614915,5.116188343\C,-2.7725409572,-1.
194136746,6.0494888728\H,-1.0884027967,-2.1350551615,5.1203264812\C,-3
.3855367708,0.0075730866,6.3859790936\H,-3.2426364714,2.1483631029,6.3
051796837\H,-3.2441295475,-2.1334680985,6.3093168197\H,-4.3338877193,0
.0084078474,6.9076293225\\Version=AM64L-G09RevB.01\State=2-A\HF=-2906.
7845999\S2=0.820128\S2-1=0.\S2A=0.75278\RMSD=7.292e-09\RMSF=3.629e-05\
Dipole=0.5518076,-0.0005903,-0.3765205\Quadrupole=0.9443308,0.0175133,
-0.9618441,-0.0031594,-3.0547201,0.0002332\PG=C01 [X(C13H17Se1)]\\@

M05-2X/6-311++G(d,p)

1\1\GINC-MERRI027\FTS\UM052X\6-311++G(d,p)\C13H17Se1(2)\SHKYNE\24-Nov-
2011\0\\# M052X/6-311++G** opt=(maxcyc=300,ts,noeigentest,readfc,nofre
eze) freq geom=checkpoint guess=check\\Cyclization to form selenabicyc
lo[2.1.1]heptane - benzyl radical leaving group\\0,2\C,0.015484077,0.0
207257057,-0.1174750318\Se,-0.0950158929,-0.2709655778,2.1150970149\C,
1.8208777885,-0.192927011,1.58080762\C,1.9849505529,1.1566183745,0.886
1255479\C,1.997842281,-1.3131459539,0.5592836074\C,0.8408577321,1.2851
196231,-0.1610771252\C,0.8241000477,-1.2091690197,-0.4576325563\H,-0.9
953914815,0.0732854041,-0.5023224188\H,2.447853897,-0.3077116534,2.460
2976697\H,1.9268693187,1.9667827772,1.6118046051\H,1.9890983548,-2.283
1547358,1.0524820146\H,2.9673633199,1.2053759378,0.4098899062\H,2.9632
397316,-1.1983689687,0.0606874969\H,0.2203139742,2.1525875989,0.052710
4373\H,0.2014510993,-2.1006281876,-0.4174553256\H,1.2540684627,1.41529
63396,-1.1673897228\H,1.207411349,-1.1215796756,-1.480763448\C,0.37538
02307,0.0589087741,4.2751835956\H,0.9014048134,1.0056694712,4.26105304
46\H,1.015216474,-0.794643272,4.467179536\C,-0.8947321917,0.0579467556
,5.0011935444\C,-1.6024891878,1.2470356185,5.2094649482\C,-1.452667803
2,-1.1404028358,5.4614049819\C,-2.8196367024,1.2403240905,5.8745174328
\H,-1.1879102629,2.177958494,4.8440814562\C,-2.6695011975,-1.146722255
8,6.1267313333\H,-0.9213659415,-2.0680683551,5.2905659261\C,-3.3575667
19,0.0438867657,6.3380051533\H,-3.3509511916,2.1689565906,6.0325945161
\H,-3.0832270915,-2.0807879447,6.4815652328\H,-4.3060287464,0.03923998
32,6.8567998046\\Version=AM64L-G09RevB.01\State=2-A\HF=-2907.0789966\S
2=0.778723\S2-1=0.\S2A=0.750368\RMSD=9.610e-09\RMSF=6.530e-06\Dipole=0
.6268147,0.1220366,-0.4834892\Quadrupole=1.1833502,0.1874319,-1.370782
1,-0.4871312,-3.4335431,-0.8335578\PG=C01 [X(C13H17Se1)]\\@

M05-2X/aug-cc-pVDZ

1\1\GINC-MERRI052\FTS\UM052X\Aug-CC-pVDZ\C13H17Se1(2)\SHKYNE\30-Nov-20
11\0\\# M052X/aug-cc-pVDZ opt=(maxcyc=300,ts,noeigentest,readfc,nofree
ze) freq geom=checkpoint guess=check\\Cyclization to form selenabicycl
o[2.1.1]heptane - benzyl radical leaving group\\0,2\C,0.0129675764,0.0
199151307,-0.1169177627\Se,-0.0943196129,-0.2470382455,2.1209304385\C,
1.8208879876,-0.1780111206,1.5818082407\C,1.9860274078,1.1645642766,0.
8718999047\C,1.9952204095,-1.3105163551,0.5718853478\C,0.8376246976,1.
2858963227,-0.1720091867\C,0.8216590824,-1.2142506084,-0.4466217657\H,
-1.0043805203,0.0686534546,-0.500756619\H,2.4525984783,-0.2841519863,2
.4656367955\H,1.9341759426,1.9844064807,1.5938935622\H,1.9835005457,-2
.2780193738,1.0800512769\H,2.9700123706,1.2036353228,0.3877877812\H,2.
9647444088,-1.202401951,0.0699206194\H,0.2129149928,2.1566643625,0.039
9498919\H,0.1943446841,-2.1077153785,-0.3989489461\H,1.2488950234,1.40
9148949 5,-1.1848605175\H,1.2072435208,-1.1332072552,-1.4743020808\C,0.
3873443558,0.0539436286,4.2821817889\H,0.918423166,1.0037186086,4.2725
87478\H,1.0232510963,-0.8108341167,4.4640837623\C,-0.887031588,0.05365
30096,5.0058849303\C,-1.5917263108,1.247923302,5.2195972661\C,-1.45462
63668,-1.1488778135,5.4540517416\C,-2.8161443394,1.2419581455,5.879540
1853\H,-1.1692277863,2.1845805108,4.862128148\C,-2.6788623156,-1.15446

09762,6.1140990062\H,-0.9248704326,-2.0828807701,5.2784514992\C,-3.364
2652308,0.0411797207,6.3316818457\H,-3.3469439023,2.176756482,6.042651
1838\H,-3.1016033383,-2.0940613877,6.460987902\H,-4.3205349079,0.03727
24881,6.8481370797\\Version=AM64L-G09RevB.01\State=2-A\HF=-2907.025324
8\S2=0.779201\S2-1=0.\S2A=0.750376\RMSD=8.402e-09\RMSF=5.742e-06\Dipol
e=0.6329045,0.1101335,-0.497164\Quadrupole=1.1197145,0.1820109,-1.3017
254,-0.4275038,-3.225983,-0.7632679\PG=C01 [X(C13H17Se1)]\\@

M06-2X/6-311++G(d,p)

1\1\GINC-MERRI026\FTS\UM062X\6-311++G(d,p)\C13H17Se1(2)\SHKYNE\23-Nov-
2011\0\\# M062X/6-311++G** opt=(maxcyc=300,ts,noeigentest,readfc,nofre
eze) freq geom=checkpoint guess=check\\Cyclization to form selenabicyc
lo[2.1.1]heptane - benzyl radical leaving group\\0,2\C,-0.000281939,-0
.0253490772,-0.0544031441\Se,-0.0737350886,0.3875241385,2.1335357298\C
,1.8340736513,0.2659517604,1.5885560785\C,2.005259447,1.324663467,0.49
9083029\C,1.9771656542,-1.1267590986,0.9736700445\C,0.8024347532,1.185
4552467,-0.4803239202\C,0.8289631465,-1.2930762895,-0.0653440953\H,-1.
0165741777,-0.0994183416,-0.4314718637\H,2.4748491137,0.4296773813,2.4
535046481\H,2.0324117799,2.3232420428,0.9364027407\H,1.9077066888,-1.8
945861071,1.746910726\H,2.9564063194,1.1619697422,-0.0174225651\H,2.96
08245528,-1.222651645,0.5025435188\H,0.1842288007,2.0839150187,-0.4629
817971\H,0.2106950558,-2.1577220237,0.1772759342\H,1.1557790539,1.0531
986386,-1.5115717532\H,1.2391954202,-1.4564739979,-1.0698403326\C,0.38
16172156,-0.075683266,4.2265055733\H,1.0595177651,0.7348049092,4.48665
22395\H,0.8791055764,-1.0414125506,4.1863786727\C,-0.8870746153,-0.067
1241903,4.9689701344\C,-1.3939016579,1.1241224222,5.5037758867\C,-1.64
86161374,-1.2345459733,5.1042292164\C,-2.6112812189,1.1432970254,6.171
3464524\H,-0.8213235792,2.039062092,5.3905120499\C,-2.86674176,-1.2157
148223,5.7710191814\H,-1.274417763,-2.1613865706,4.6815936191\C,-3.352
3474531,-0.027269056,6.3099106484\H,-2.9843611761,2.0731848769,6.58460
41616\H,-3.4399239957,-2.1301972884,5.8712174793\H,-4.3023543379,-0.01
32556067,6.830572504\\Version=AM64L-G09RevB.01\State=2-A\HF=-2906.9928
657\S2=0.767439\S2-1=0.\S2A=0.750134\RMSD=9.213e-09\RMSF=7.753e-06\Dip
ole=0.6001883,-0.1434535,-0.47757\Quadrupole=1.3167092,0.2501167,-1.56
68259,0.6931004,-3.1010302,1.2143009\PG=C01 [X(C13H17Se1)]\\@

M06-2X/aug-cc-pVDZ

1\1\GINC-MERRI049\FTS\UM062X\Aug-CC-pVDZ\C13H17Se1(2)\SHKYNE\30-Nov-20
11\0\\# M062X/aug-cc-pVDZ opt=(maxcyc=300,ts,noeigentest,readfc,nofree
ze) freq geom=checkpoint guess=check\\Cyclization to form selenabicycl
o[2.1.1]heptane - benzyl radical leaving group\\0,2\C,-0.0004397195,-0
.0283075459,-0.055338062\Se,-0.0764027004,0.3737204816,2.1326250473\C,
1.8314169765,0.2605073,1.5893187511\C,2.0014147109,1.3247340711,0.5050
470265\C,1.9792015795,-1.1288742814,0.9680410117\C,0.8010834713,1.1856
512602,-0.4765454692\C,0.8313167325,-1.2950345027,-0.0705224067\H,-1.0
210185579,-0.1029782135,-0.4358129599\H,2.474338631,0.4221249398,2.459
6316527\H,2.0244219571,2.3247168505,0.9507773332\H,1.9137709758,-1.902
3484197,1.7420272878\H,2.9575759225,1.1657551784,-0.012854092\H,2.9666
367369,-1.2173454181,0.4930064143\H,0.1774450598,2.0857265731,-0.45832
7867\H,0.2109231501,-2.1638410145,0.1717490428\H,1.1585382835,1.054061
5392,-1.5112855925\H,1.2434287059,-1.4545099464,-1.0797341061\C,0.3862
880003,-0.074242019,4.2261162402\H,1.0629406348,0.7456985632,4.4801343
278\H,0.8864949996,-1.0443069713,4.1885641893\C,-0.8833913977,-0.06517
21278,4.9696127645\C,-1.3914285034,1.1288453701,5.5049441774\C,-1.6471
744918,-1.2350409221,5.1040372798\C,-2.6124886255,1.1486580955,6.17283
55675\H,-0.8159099073,2.0484512992,5.3927180232\C,-2.8689594441,-1.215
9570238,5.7710805806\H,-1.2715881448,-2.1667167274,4.6796730191\C,-3.3
560676904,-0.0244505444,6.3107513624\H,-2.9876878709,2.0830593879,6.58
86228718\H,-3.4458784615,-2.134838772,5.8712503324\H,-4.3115019183,-0.
0103036028,6.8332670493\\Version=AM64L-G09RevB.01\State=2-A\HF=-2906.9
389898\S2=0.767063\S2-1=0.\S2A=0.750128\RMSD=9.684e-09\RMSF=5.989e-06\
Dipole=0.599415,-0.1343931,-0.4849631\Quadrupole=1.2378723,0.2611731,-
1.4990454,0.6602561,-2.8892169,1.1820524\PG=C01 [X(C13H17Se1)]\\@

ROMP2/6-311++G(d,p)//BHandHLYP/6-311++G(d,p)

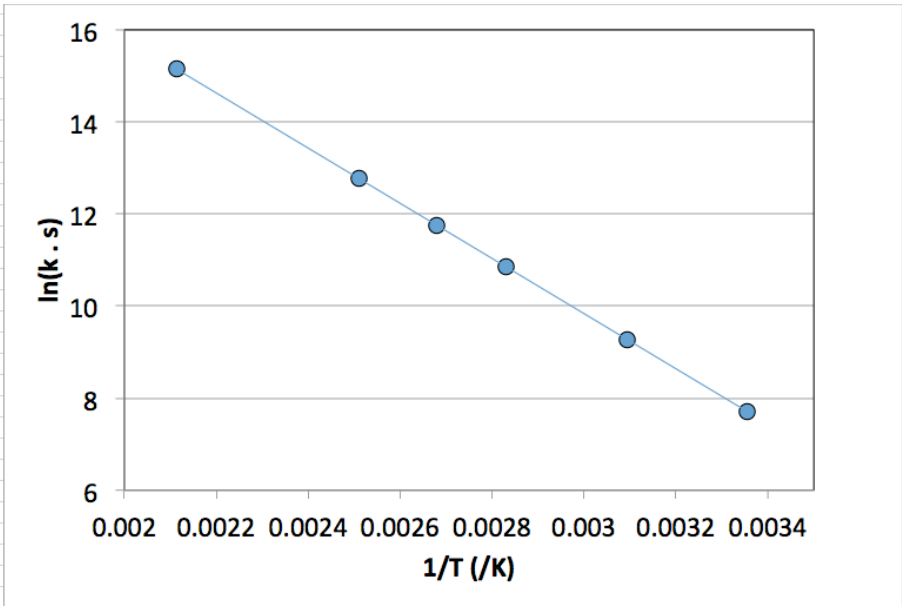
MP2=-2904.00949

ROMP2/aug-cc-pVDZ//BHandHLYP/aug-cc-pVDZ

MP2=-2903.976276

Calculated Arrhenius Data

$k_{T(K)}$	
$k_{298.15}$	2.2E+03
$k_{323.15}$	1.1E+04
$k_{353.15}$	5.1E+04
$k_{373.15}$	1.3E+05
$k_{398.15}$	3.5E+05
$k_{473.15}$	3.8E+06
A (plot)	1.197E+12
Ea (plot)	49.8
A (formula)	1.221E+12
Ea (formula)	49.9
1/T	ln(k)
0.003354016	7.715101476
0.003094538	9.269804643
0.002831658	10.84443602
0.002679887	11.75342687
0.002511616	12.76141922
0.002113495	15.148172



Experimental Details

Experimental Procedure A:

Ethyl 4-(methanesulfonyloxy)cyclohexanecarboxylate (**13**).
A solution of ethyl 4-hydroxycyclohexanecarboxylate (0.95g, 5.54mmol), Et_3N (1.16mL, 8.31mmol) in distilled DCM (27mL) was reduced to -20°C under a nitrogen atmosphere. Mesyl chloride (0.9mL, 11.64mmol) was added and the solution was maintained at this temperature for 1 hour. The reaction mixture was washed with 5% HCl x 2, 10% $NaHCO_3$ x 2 and saturated NaCl before being reduced *in vacuo*. The crude mesylate was purified by flash column chromatography (1:4 EtOAc:PS) to give the title compound as a clear oil and as a 2.2:1 mixture of isomers in a yield of 1.31g, (94%). ^{1}H-NMR ($CDCl_3$): δ 1.23-1.26 (m, 3H), 1.54-2.39 (m, 9H), 3.02 (s, 3H), 4.12 (q, J = 7.2, 14.4Hz, 2H), 4.64 (major, quin, J = 5.2, 6Hz, 1H) 4.92 (minor, m, 1H). ^{13}C-NMR ($CDCl_3$): δ 13.39 (major), 13.43 (minor), 22.69 (minor), 25.64 (major), 29.20 (minor), 30.63 (major), 37.56 (minor), 37.60 (minor), 39.99 (minor), 40.35 (major), 59.48 (minor), 59.52 (major), 77.66 (minor), 79.51 (major), 173.73 (major), 173.78 (minor). MS (ESI): 273 ($[M + Na]^+$).

Experimental Procedure B:

Ethyl 4-(4-methoxybenzylseleno)cyclohexanecarboxylate
To a solution of bis(4-methoxybenzyl) selenide (4.03g, 10.06mmol) in distilled EtOH (183mL) maintained at 0°C under a nitrogen atmosphere, was added $NaBH_4$ (~1.00g) until the solution remained colourless. The solution was stirred for a further 30 mins before ethyl 4-(methanesulfonyloxy)cyclohexanecarboxylate (1.26g, 5.03mmol) in distilled EtOH (10mL)

was added dropwise. The mixture was refluxed overnight after which it was cooled and the solvent removed *in vacuo*. The product was taken up in H_2O, extracted into Et_2O x 2, dried over $MgSO_4$ and the solvent evaporated. The crude benzylselenide was purified by flash column chromatography (1:80 EtOAc:PS) to give the title compound as a yellow oil and as a mixture of isomers in a yield of 1.03g (60%). ^{13}C-NMR ($CDCl_3$): δ 14.09 (minor), 14.12, 25.37 (minor), 25.97, 26.11, 29.60, 30.75 (minor), 31.11, 33.30, 36.88 (minor), 37.75, 41.33, 42.35 (minor), 55.09, 60.04, 113.73, 113.78, 129.62, 129.66, 129.86 (minor), 131.35, 158.16, 174.88. ^{77}Se-NMR ($CDCl_3$): δ 233.07. MS (ESI): 463 ([M + Ag]$^+$). HRMS calcd for $C_{17}H_{24}AgO_3Se$ [M + Ag]$^+$ 462.9936, found 462.9937.

A small quantity was further purified by flash chromatography to afford samples of each isomer.

^{1}H-NMR ($CDCl_3$) major isomer: δ 1.21-1.25 (m, 3H), 1.64-1.70 (m, 2H), 1.78-1.81 (m, 4H), 1.90-1.98 (m, 2H), 2.35 (p, J = 4.5, 8.5Hz, 1H), 3.06 (t, J = 5Hz, 1H), 3.73 (s, 2H), 3.76 (s, 3H), 4.11 (q, J = 7.5, 14.5Hz, 2H), 6.80 (dd, J = 3, 9.5Hz, 2H), 7.19 (dd, J = 2, 6.5Hz, 2H).

^{1}H-NMR ($CDCl_3$): minor isomer: δ 1.21-1.25 (m, 3H), 1.61-1.65 (m, 2H), 1.71-1.78 (m, 2H), 1.91-1.97 (m, 2H), 2.27-2.31 (m, 2H), 2.73-2.81 (m, 1H), 3.74 (s, 2H), 3.77 (s, 3H), 4.12 (q, J = 8, 15.2Hz, 2H), 6.79 (dd, J = 2, 6.8Hz, 2H), 7.18 (dd, J = 2, 6.4Hz, 2H).

Ethyl 4-(benzylseleno)cyclohexanecarboxylate

The title compound was prepared from ethyl 4-(methanesulfonyloxy)cyclohexanecarboxylate (**13**) and dibenzyl diselenide according to Experimental Procedure B as a yellow oil in 53% yield. ^{1}H-NMR ($CDCl_3$): δ 1.19-1.24 (m, 3H), 1.62-1.69 (m, 2H), 1.73-1.80 (m, 4H), 1.88-2.07 (m, 2H), 2.34 (sep, J = 5, 10.5, 16Hz, 1H), 3.05 (quin, J = 6.5, 13Hz, 1H), 3.74 (t, J = 7.5Hz, 2H), 4.10 (q, J = 8.5, 17.5Hz, 2H), 7.13-7.19 (m, 1H), 7.22-7.28 (m, 3H). ^{13}C-NMR ($CDCl_3$): δ 14.04, 25.99, 26.40, 29.47, 30.95, 33.16, 37.72, 41.17, 59.93, 126.30, 128.19, 128.24, 128.49, 128.53, 139.35, 174.70. ^{77}Se-NMR ($CDCl_3$): δ 355.13. MS (ESI): 349 ([M + Na]$^+$). HRMS calcd for $C_{16}H_{22}NaO_2Se$ [M + Na]$^+$ 349.0678, found 349.0677.

Experimental Procedure C:

4-(4-Methoxybenzylseleno)cyclohexanecarboxylic acid

To a round bottom flask, under a nitrogen atmosphere, fitted with a condenser and drying tube was added ethyl 4-(4-methoxybenzylseleno)cyclohexanecarboxylate (1.06g, 2.99mmol) and distilled EtOH (4.3mL). The reaction mixture was heated to ~65°C after which a solution of KOH (0.20g, 3.58mmol) in EtOH (4.3mL) was added dropwise. The mixture was heated for a further 4 hours, cooled and the solvent removed *in vacuo*. The residue was acidified with 5% HCl, extracted into Et_2O x 3, dried over $MgSO_4$ and evaporated. The crude acid was then purified by flash column chromatography (1:10 EtOAc:PS) to give the title compound as a pale oil and as a 2.4:1 mixture of isomers in a yield of 0.65g, (66%). ^{1}H-NMR ($CDCl_3$): δ 1.42-1.54 (m, 1H), 1.67-2.14 (m, 7H), 2.31-2.37 (minor, m, 1H), 2.44 (major, sep, J = 4, 8.5, 12.5Hz, 1H), 2.69-3.09 (minor, m, 1H), 3.07 (major, quin, J = 5, 10Hz, 1H), 3.75 (s, 2H), 3.79 (d, J = 1.5Hz, 3H), 6.82 (dd, J = 2.5, 6Hz, 2H), 7.21 (dd, J = 1.5, 6.5Hz, 2H), 11.52 (bs, 1H). ^{13}C-NMR ($CDCl_3$): major δ 25.55 (minor), 25.99, 26.10, 29.43, 31.08, 33.25, 36.82 (minor), 37.62, 41.09 (minor), 42.15, 55.24, 113.88, 113.93, 129.74, 129.79, 131.37 (minor), 131.43, 158.29, 181.41. MS (ESI): 435 ([M + Ag]$^+$). HRMS calcd for $C_{15}H_{20}AgO_3Se$ [M + Ag]$^+$ 434.9623, found 434.9625.

4-(Benzylseleno)cyclohexanecarboxylic acid

The title compound was prepared from ethyl 4-(benzylseleno)cyclohexanecarboxylate according to Experimental Procedure C as a pale oil and as a 2.3:1 mixture of isomers in 82% yield. ^{1}H-NMR ($CDCl_3$): δ 1.41-1.56 (m, 1H), 1.69-2.14 (m, 7H), 2.31-2.38 (minor, m, 1H), 2.41-2.48 (major, m, 1H), 2.71-2.76 (minor, m, 1H), 3.08-3.12 (major, m, 1H), 3.78-3.84 (m, 3H), 7.18-7.37 (m, 4H), 11.83 (bs, 1H). ^{13}C-NMR ($CDCl_3$): major δ 25.84, 25.96 (minor), 26.52, 29.27, 30.91, 33.09, 36.81 (minor), 37.60, 40.99, 42.06, 126.45, 126.50 (minor), 128.32, 128.36 (minor), 128.60, 129.64, 139.35 (minor), 139.39, 181.69, 181.95 (minor). ^{77}Se-NMR ($CDCl_3$): δ 353.69. MS (ESI): 321 ([M + Na]$^+$). HRMS calcd for $C_{14}H_{18}NaO_2Se$ [M + Na]$^+$ 321.0365, found 321.0364.

Experimental Procedure D:

N-[4-*p*-(Methoxybenzyl)selenocyclohexanoyl]-*N*,*S*-dimethyldithiocarbamate (**14**)

To a solution of 4-(4-methoxybenzylseleno)cyclohexanecarboxylic acid (0.65g, 1.98mmol), DCC (0.62g, 2.96mmol), DMAP (48.3mg, 0.40mmol) and distilled DCM (5mL) was added *N*,*S*-dimethl-*N*-hydroxydithiocarbamate (0.41g, 2.96mmol) in distilled DCM (1.2mL) dropwise. The reaction mixture was stirred overnight at room temperature after which it was filtered through celite. The filtrate was washed with saturated $NaHCO_3$ x 2, dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude dithiocarbamate was purified by flash column chromatography (1:40 EtOAc:PS) to give the title compound as a clear oil and as a mixture of isomers in a yield of 0.78g, (88%). ^{77}Se-NMR ($CDCl_3$): δ 329. MS (ESI): 554 ([M + Ag]$^+$). HRMS calcd for $C_{18}H_{25}AgNO_3S_2Se$ [M + Ag]$^+$ 553.9487, found 553.9490.

A small quantity was further purified by flash chromatography to a small sample of each isomer.

Major isomer:

^{1}H-NMR ($CDCl_3$): δ 1.82-1.94 (m, 6H), 2.03-2.09 (m, 2H), 2.54 (s, 3H), 2.60-2.64 (m, 1H), 3.10 (bs, 1H), 3.77 (d, J = 5Hz, 8H), 6.82 (dd, J = 2, 6.5Hz, 2H), 7.21 (dd, J = 2.5, 6.5Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 18.41, 25.55, 26.07, 30.71, 36.92, 39.43, 42.43, 55.00, 113.66, 129.57, 130.97, 158.11, 170.97, 196.35.

Minor isomer:

^{1}H-NMR ($CDCl_3$): δ 1.43-1.60 (m, 4H), 2.09-2.14 (m, 4H), 2.47-2.53 (m, 4H), 2.67-2.73 (m, 1H), 3.72-3.78 (m, 8H), 6.79 (dd, J = 2, 6.5Hz, 2H), 7.18 (dd, J = 2, 6.5Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 18.54, 25.59, 29.17, 32.93, 36.18, 40.23, 42.54, 55.15, 113.84, 129.65, 131.09, 158.25, 171.44, 196.51.

N-[4-*p*-(Benzylseleno)cyclohexanoyl]-*N*,*S*-dimethyldithiocarbamate **(11)**

The title compound was prepared from 4-(benzylseleno)cyclohexanecarboxylic acid according to Experimental Procedure D as a pale oil and as a 1.7:1 mixture of isomers in 82% yield. ^{77}Se-NMR ($CDCl_3$): δ 327. MS (ESI): 524 ([M + Ag]$^+$). HRMS calcd for $C_{17}H_{23}AgNO_2S_2Se$ [M + Ag]$^+$ 523.9381, found 523.9384.

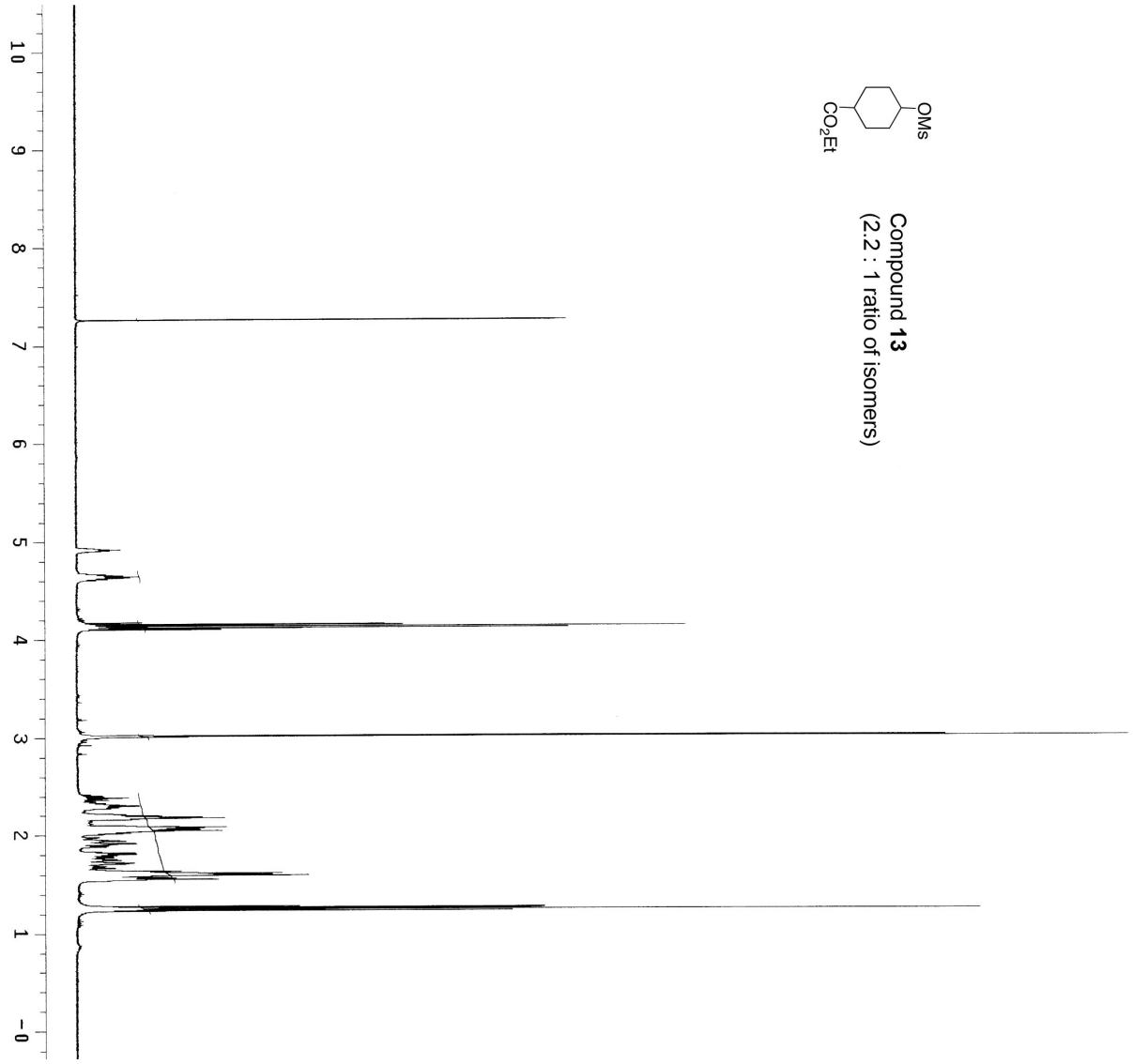
A small quantity was further purified by flash chromatography to a small sample of each isomer.

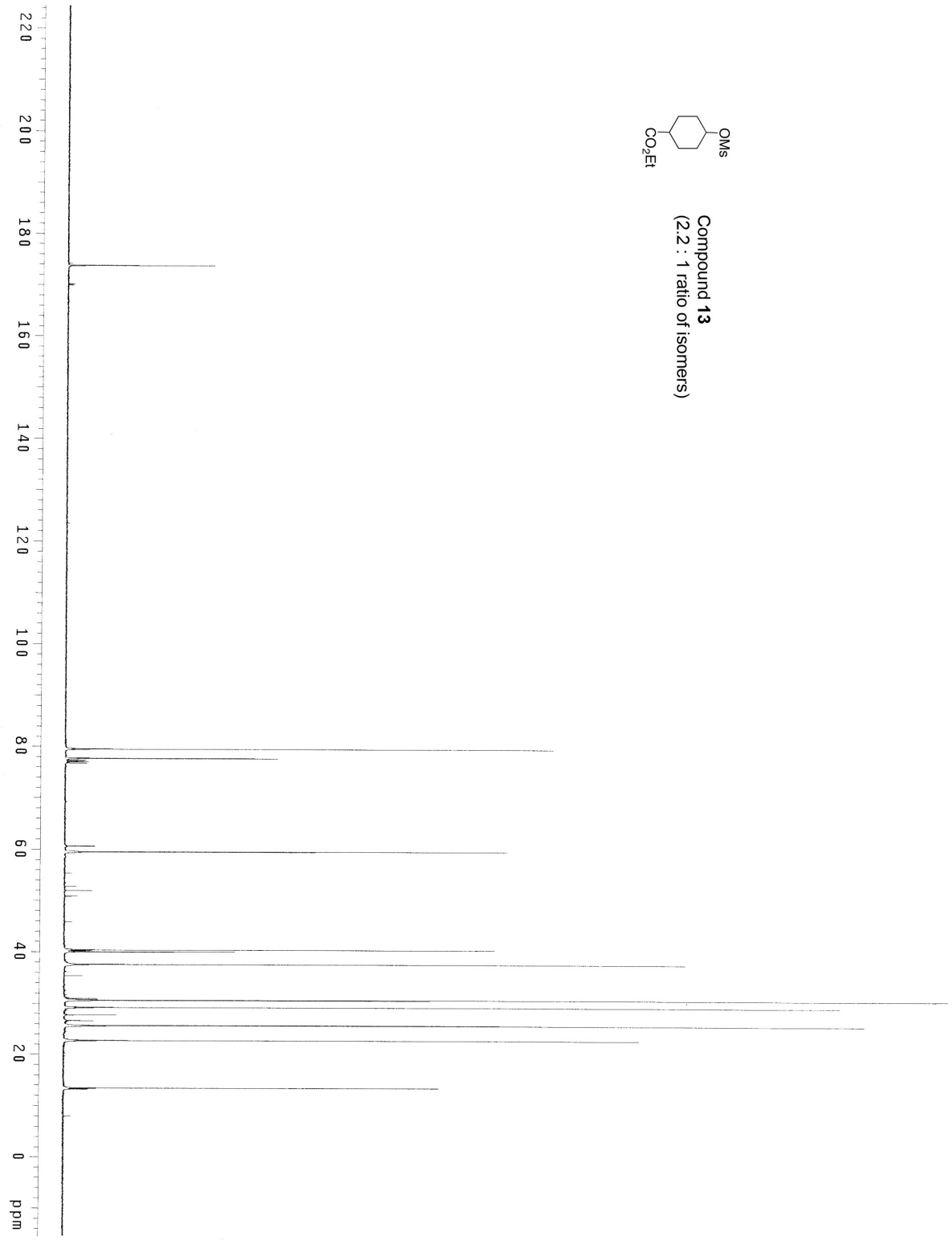
Major isomer:
^{1}H-NMR ($CDCl_3$): δ 1.83-1.96 (m, 6H), 2.05-2.12 (m, 2H), 2.56 (s, 3H), 2.65 (quin, J = 5, 9Hz, 1H), 3.15 (bs, 1H), 3.77-3.83 (m, 5H), 7.21-7.24 (m, 1H), 7.28-7.33 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 18.50, 25.60, 26.69, 29.51, 30.74, 37.09, 39.49, 42.53, 126.50, 128.33, 128.60, 139.17, 171.03, 196.47.

Minor isomer:
^{1}H-NMR ($CDCl_3$): minor δ 1.49-1.62 (m, 4H), 2.12-2.17 (m, 4H), 2.53 (s, 3H), 2.73-2.76 (m, 1H), 3.74 (s, 3H), 3.83 (s, 2H), 7.19-7.22 (m, 1H), 7.26-7.30 (m, 4H). ^{13}C-NMR ($CDCl_3$): minor δ 18.47, 26.06, 29.06, 29.49, 32.84, 36.26, 40.13, 42.46, 126.51, 128.34, 128.53, 139.16, 171.29, 196.37.

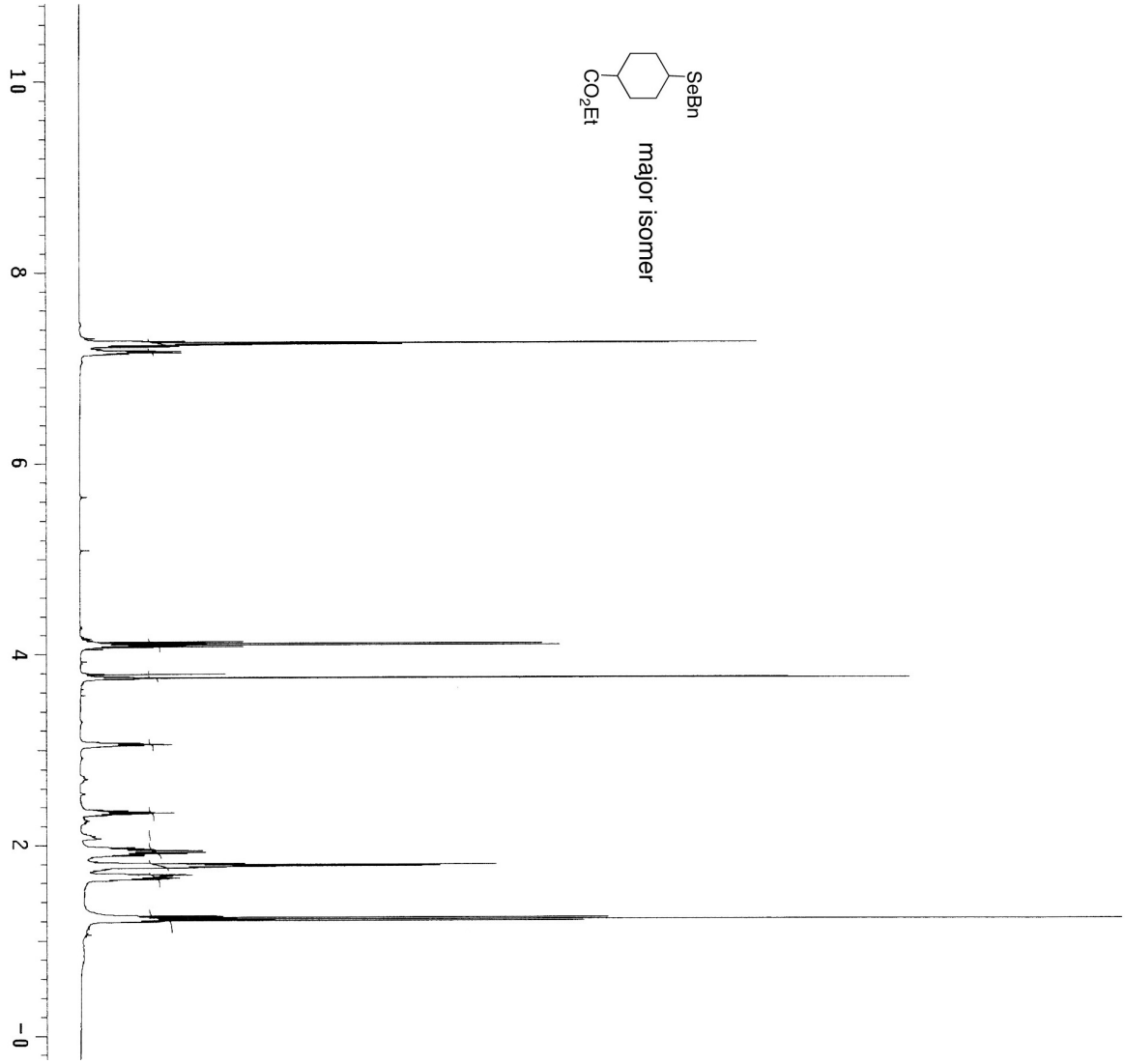
Experimental Procedure E:

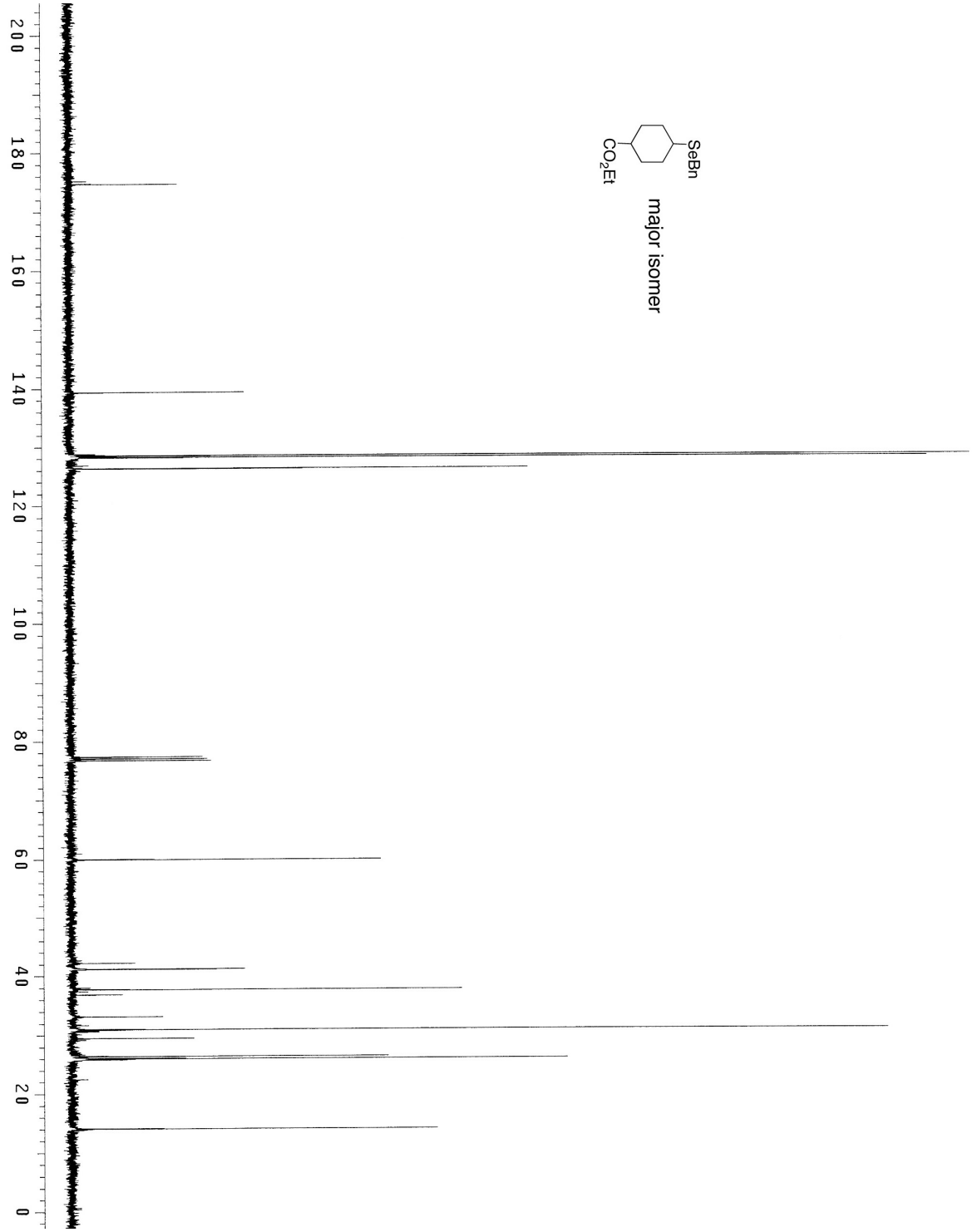
7-Selenabicyclo[2.2.1]heptane (**5**)
A solution of *N*-[4-*p*-(methoxybenzyl)seleno)cyclohexanoyl]-*N*,*S*-dimethyldithiocarbamate (0.26g, 0.58mmol) and benzene (5.8mL) was placed in a sealed tube and heated at ~200°C overnight. The solvent was removed *in vacuo* at room temperature to give the crude bicycle which was purified by flash column chromatography (distilled pentane) to give the title compound in a yield of 18.1mg, (20 %). ^{1}H-NMR ($CDCl_3$): δ 1.75 (d, J = 5.5Hz, 4H), 1.95 (d, J = 8Hz, 4H), 4.29 (s, 2H). ^{13}C-NMR ($CDCl_3$): δ 35.59, 51.30. ^{77}Se-NMR ($CDCl_3$): δ 389. MS (ESI): 177 ($[M + CH_3]^+$). HRMS calcd for $C_7H_{13}Se$ $[M + CH_3]^+$ 177.0177, found 177.0178.

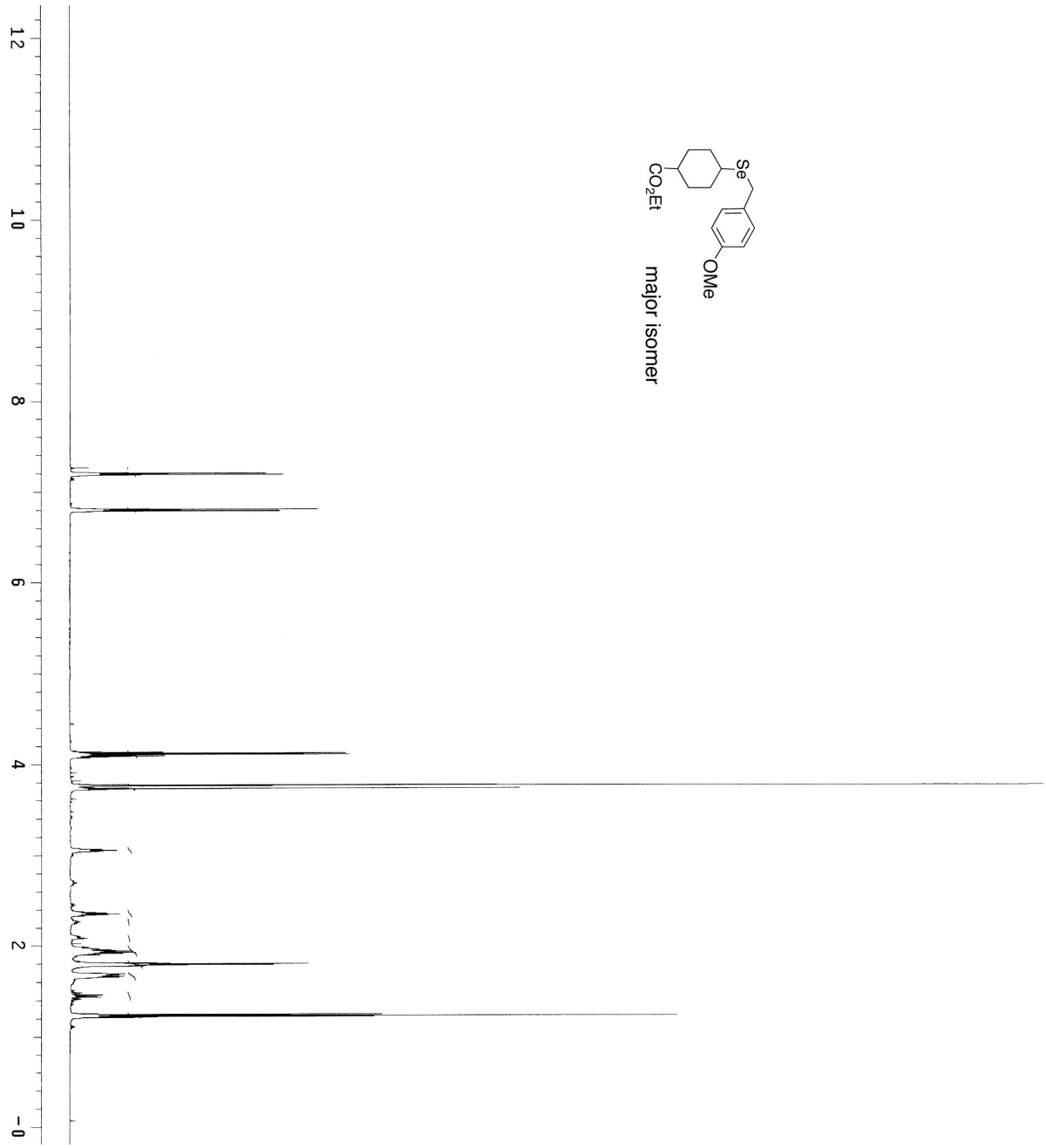


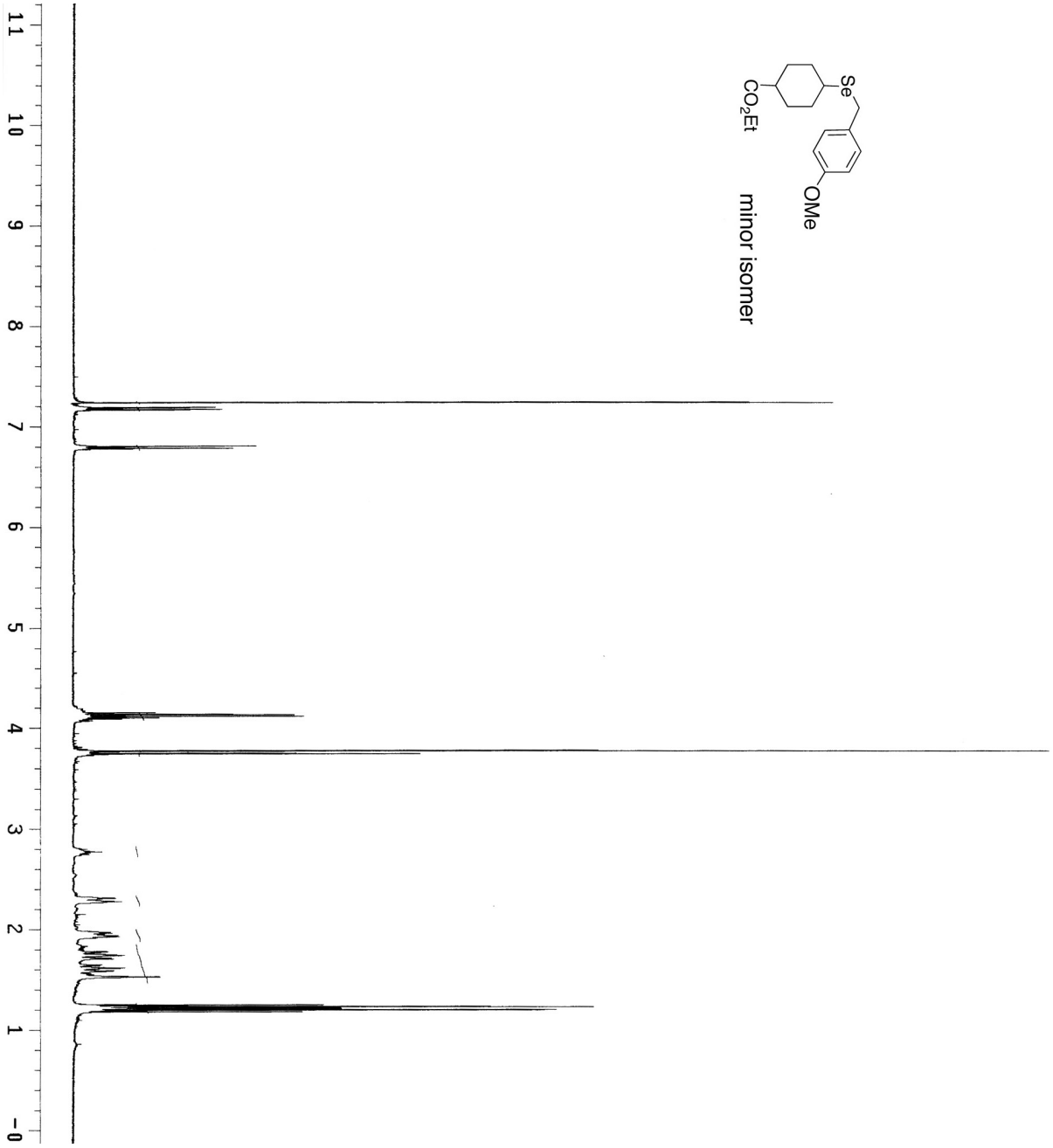


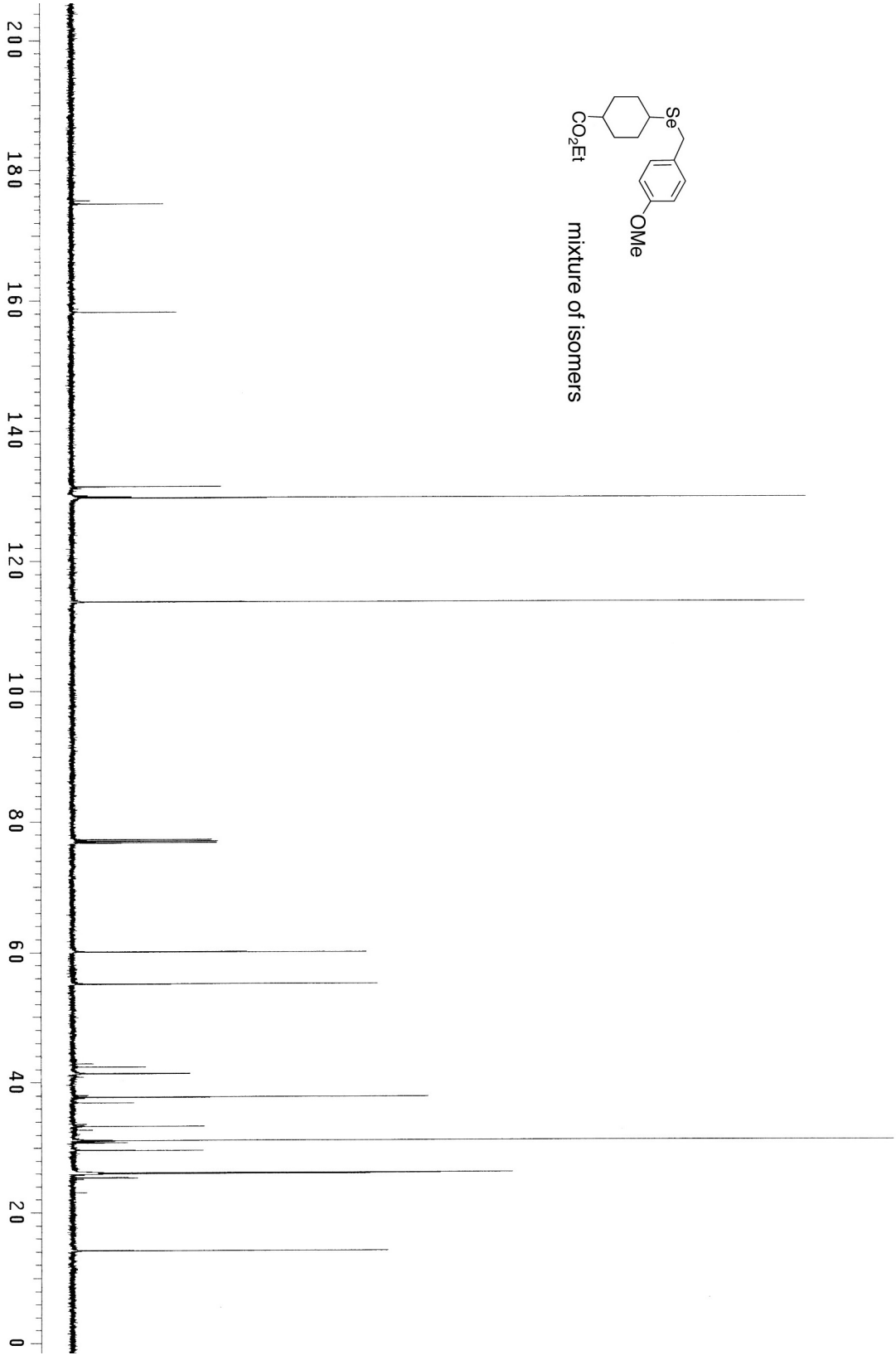
Compound **13**
(2.2 : 1 ratio of isomers)

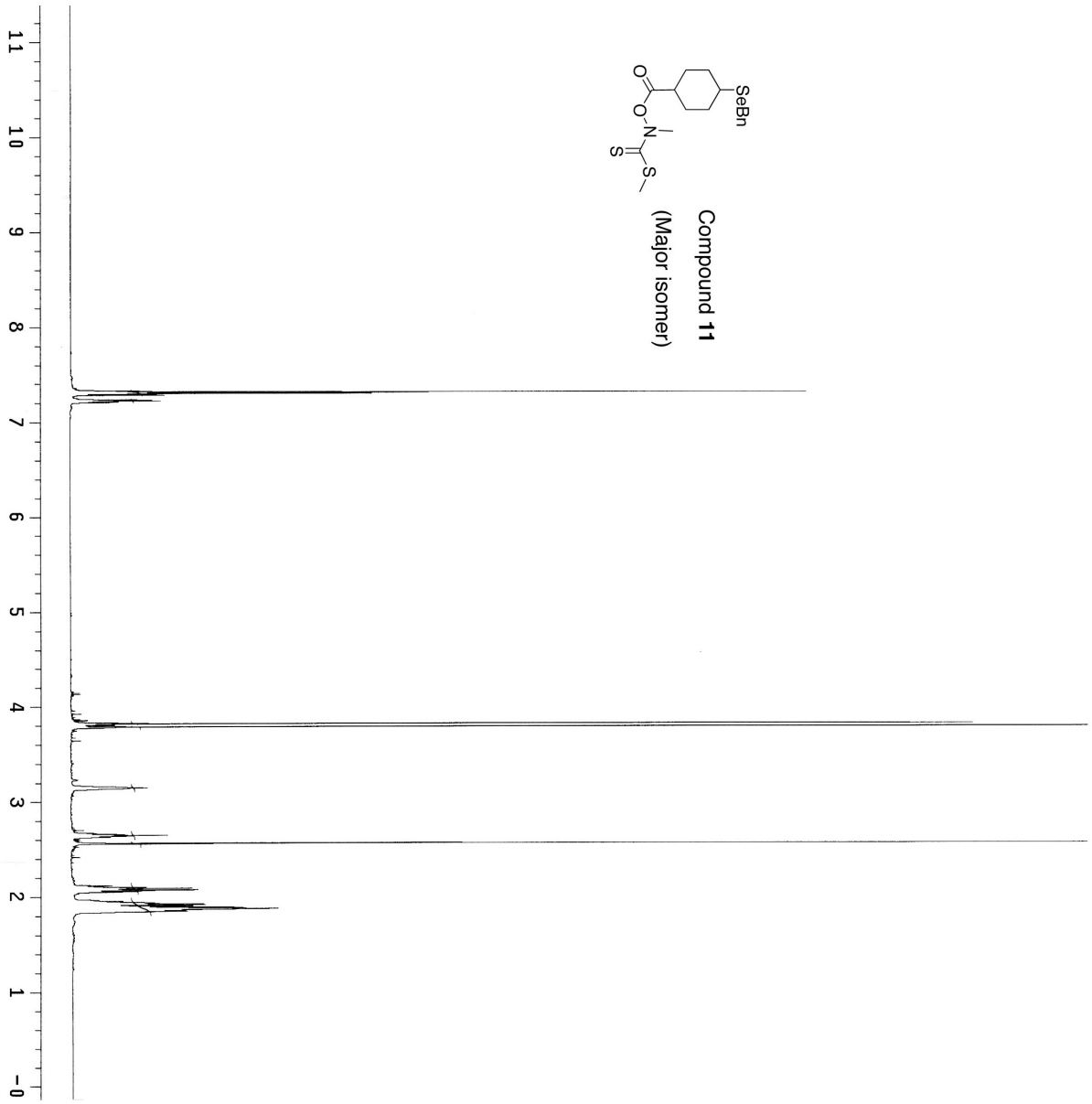


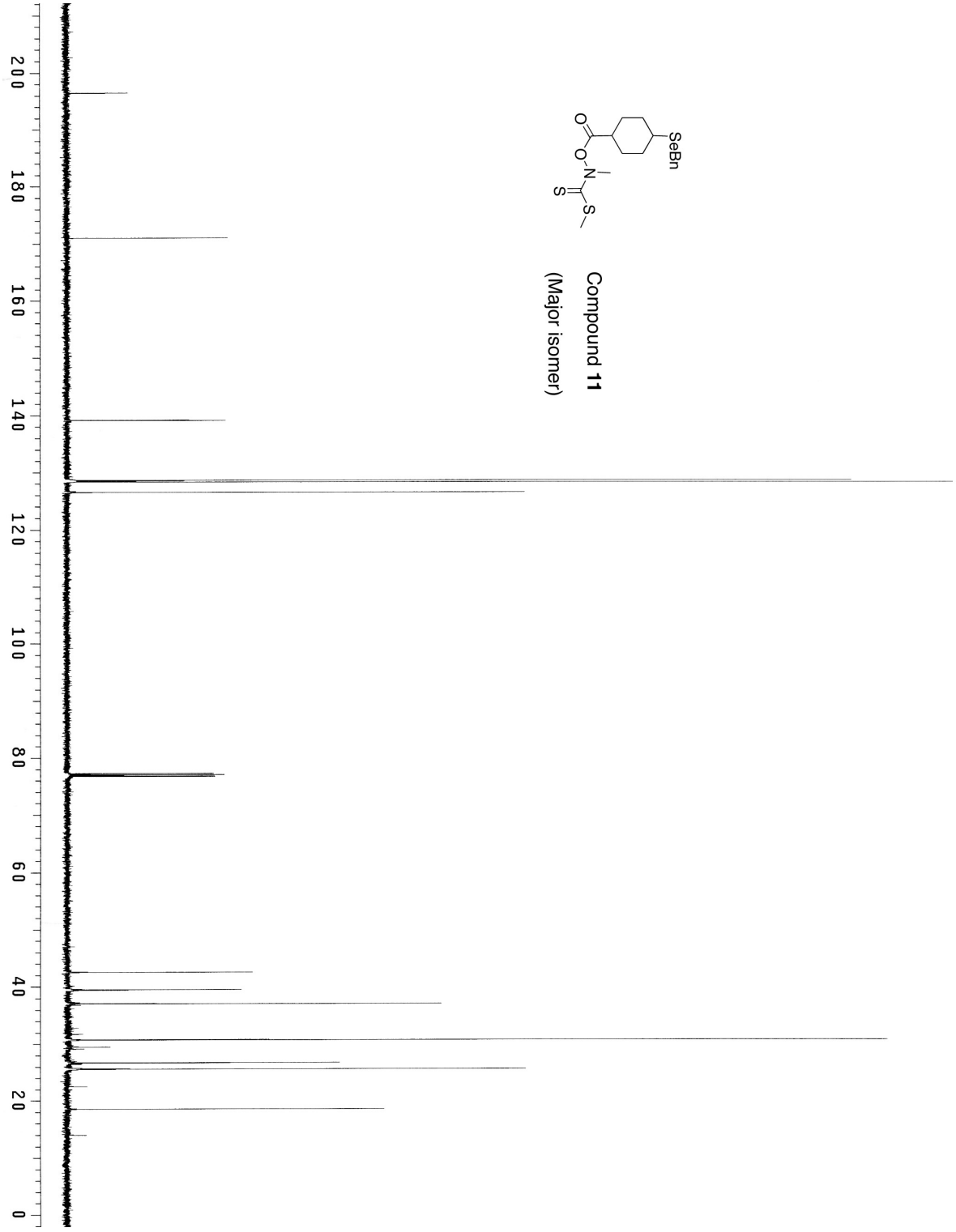






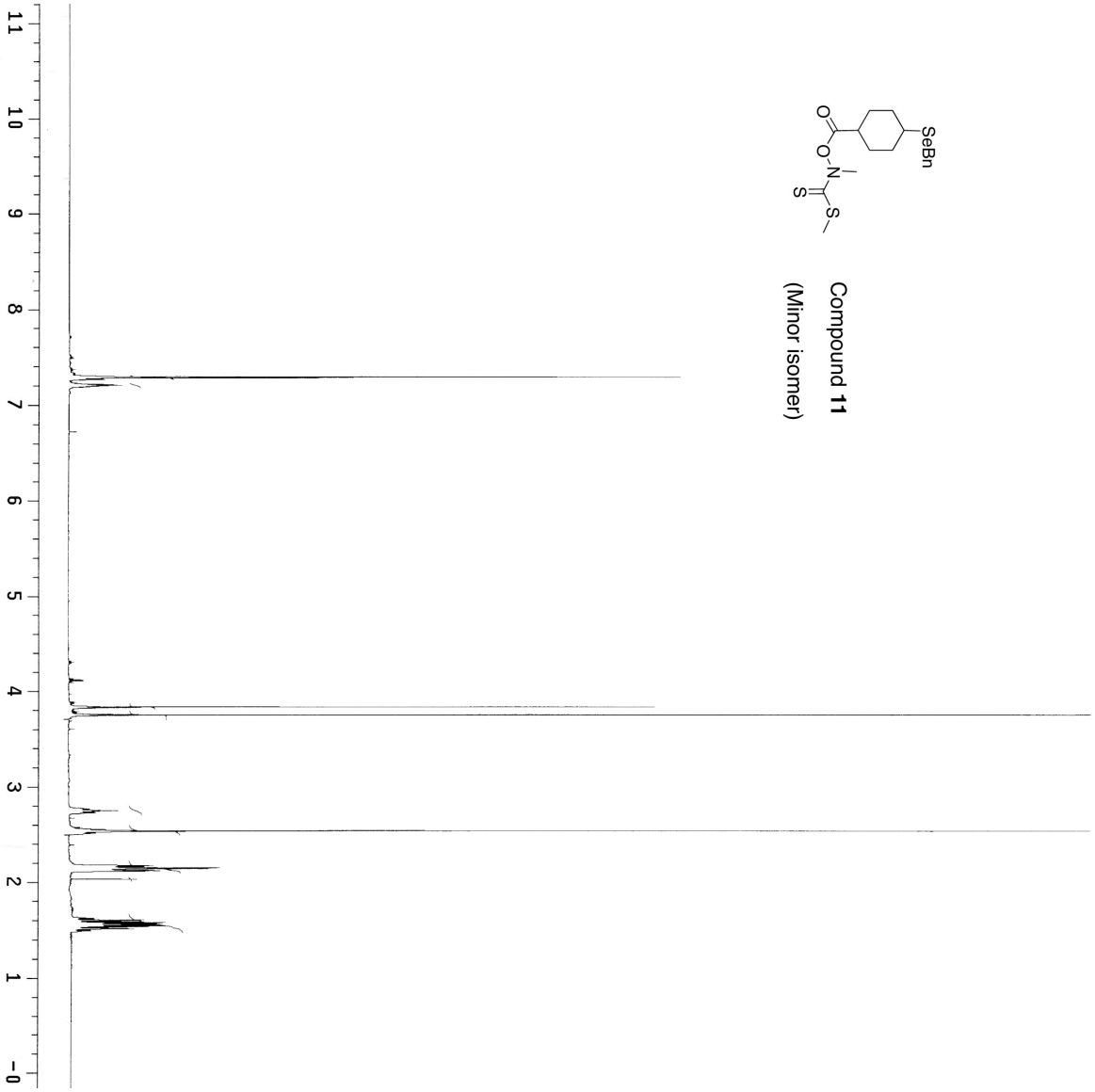


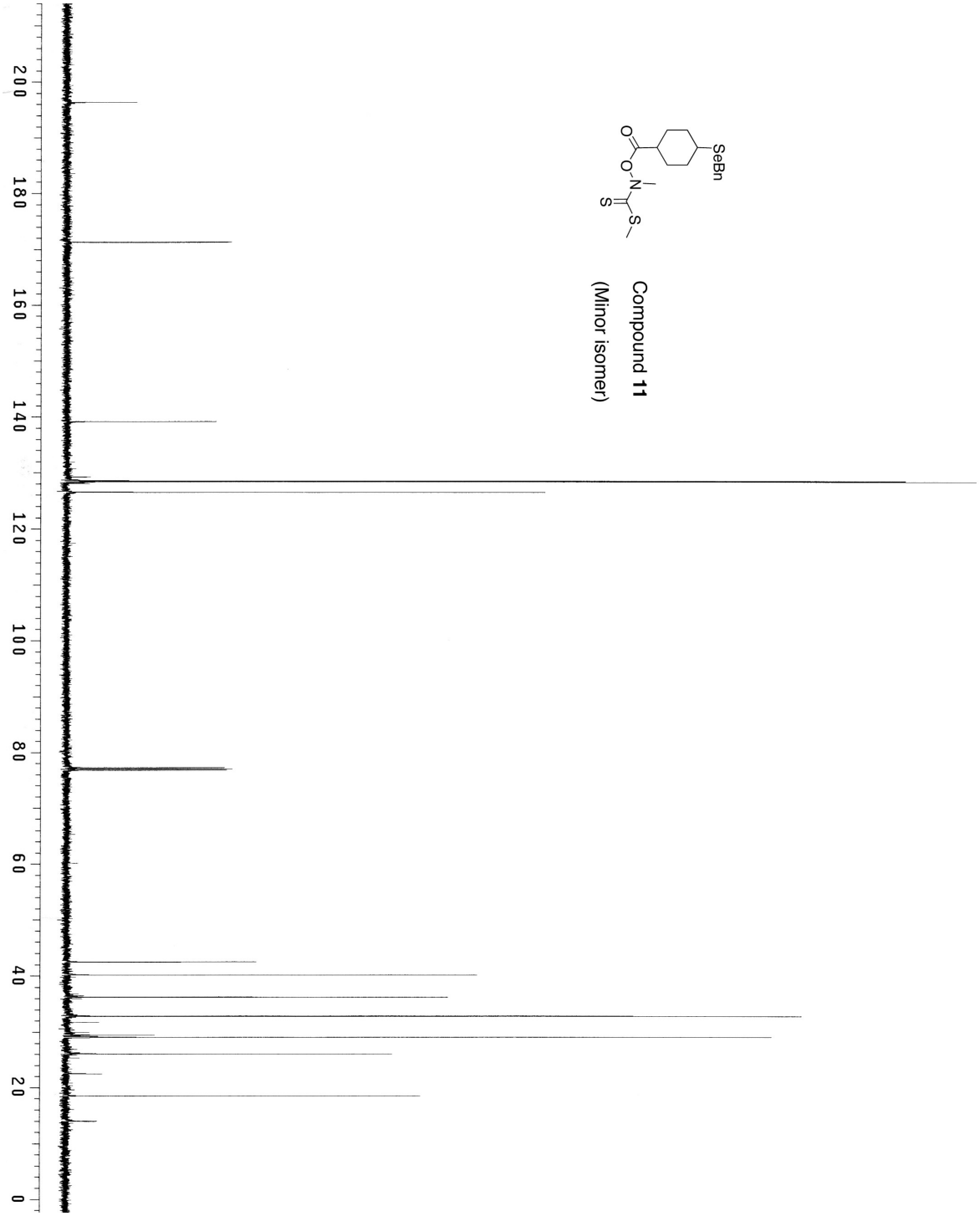




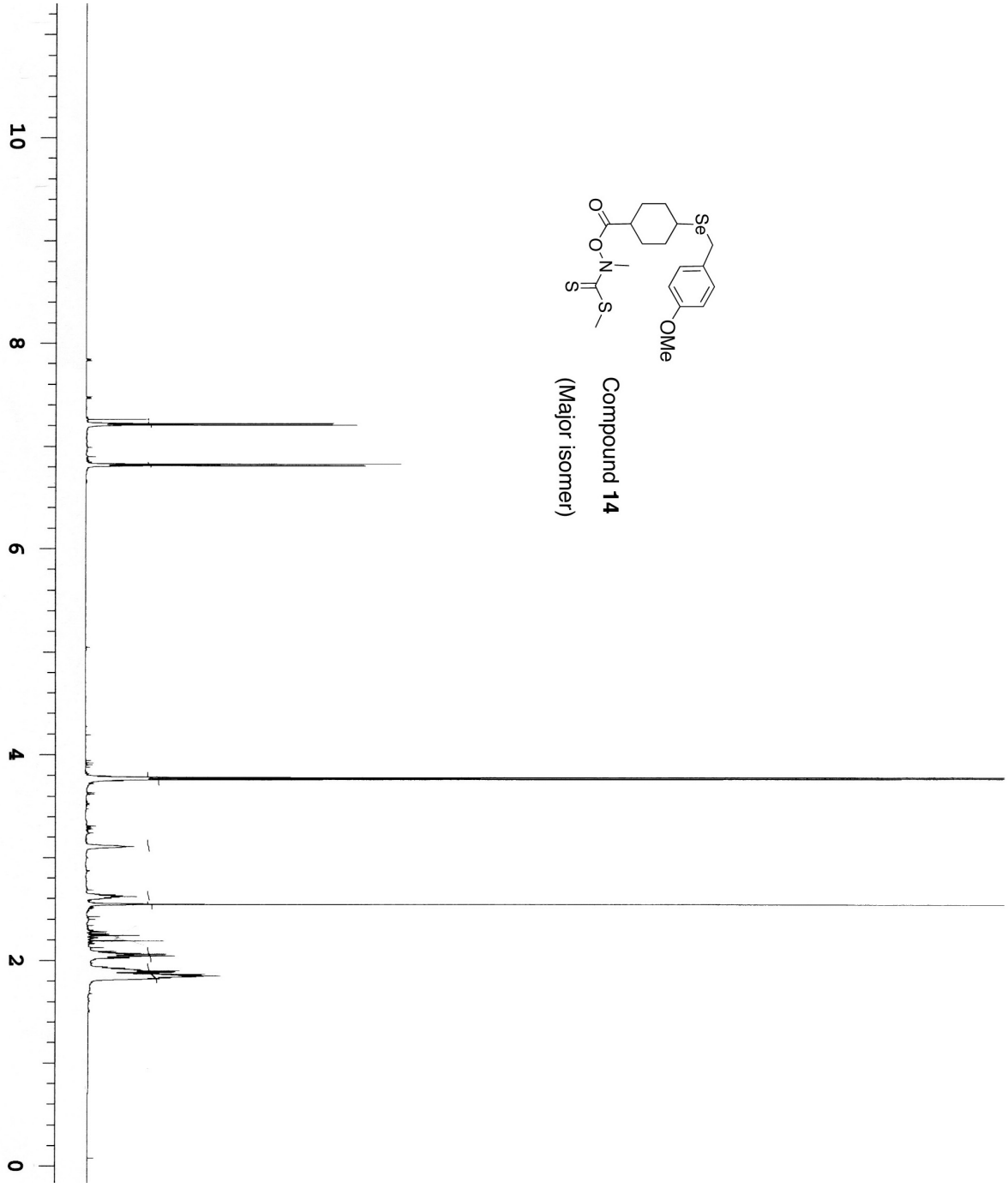
Compound **11**

(Major isomer)

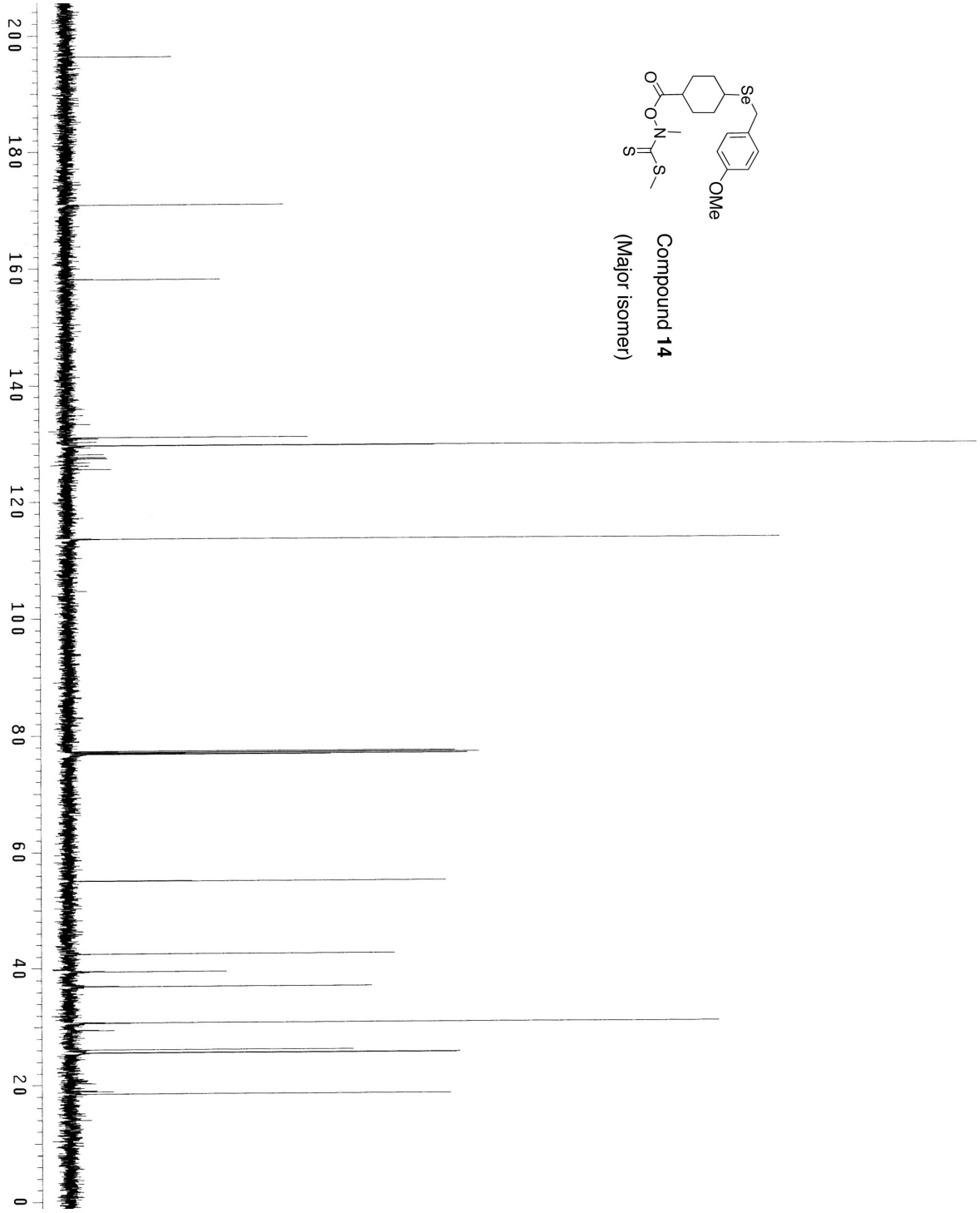


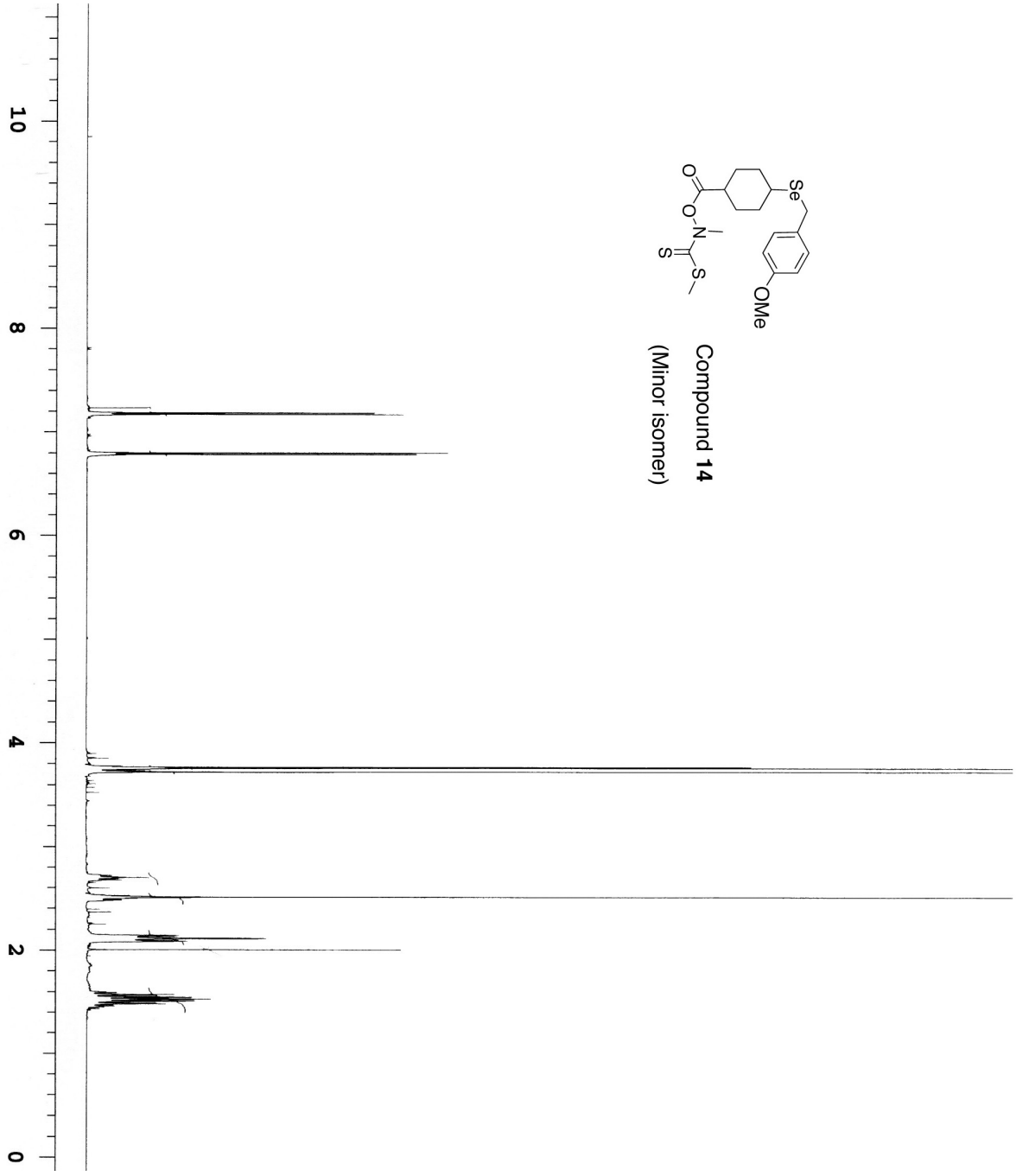


Compound **11**
(Minor isomer)

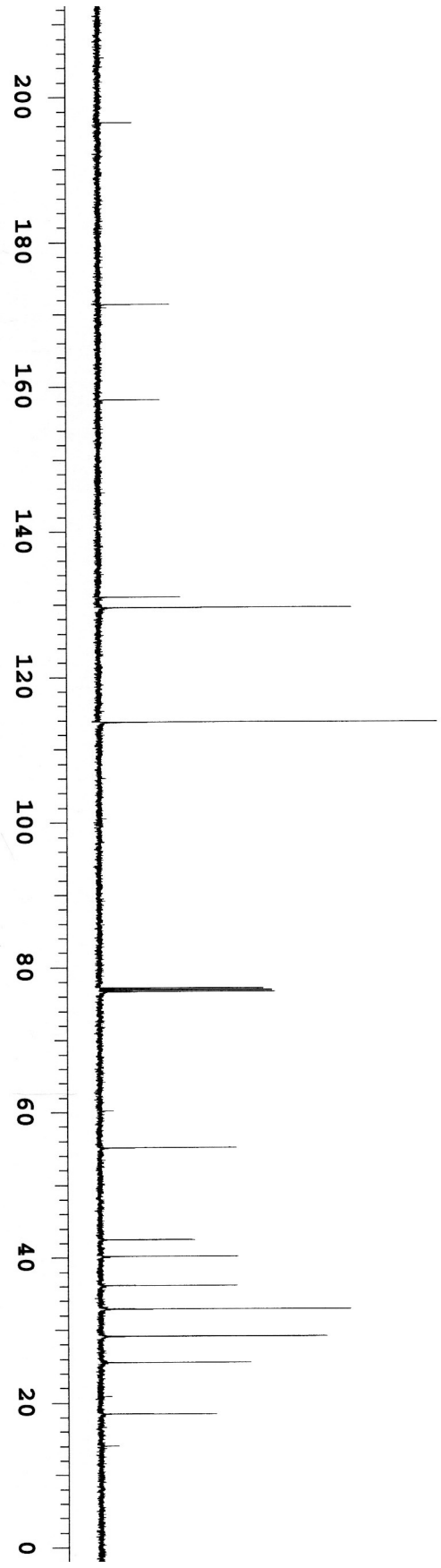


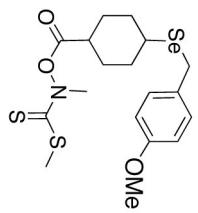
Compound **14**
(Major isomer)





Compound **14**
(Minor isomer)





Compound **14**

(Minor isomer)