Evidence for the Contribution of Degenerate Hydrogen Atom Transport to the Persistence of Sulfanyl radicals Anchored to Nanostructured Hybrid Materials

François Vibert,[a] Emily Bloch,[b] Michèle P. Bertrand,[a] Séverine Queyroy,*[a] Stéphane Gastaldi,*[a] Eric Besson*[a]

[a] Aix Marseille Univ, CNRS, ICR, Marseille, France.

[b] Aix Marseille Univ, CNRS, MADIREL, Marseille, France.

E-mail : stephane.gastaldi@univ-amu.fr, eric.besson@univ-amu.fr

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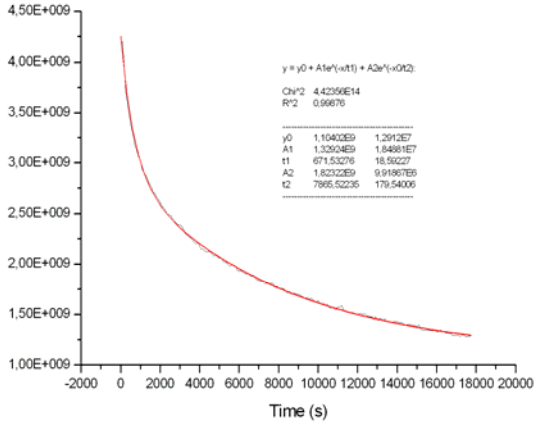
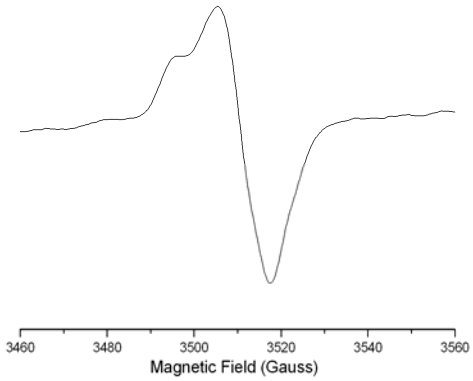
EPR spectra and their decay curves

Under photochemical irradiation at 293 K:

SBA_{27}-1:





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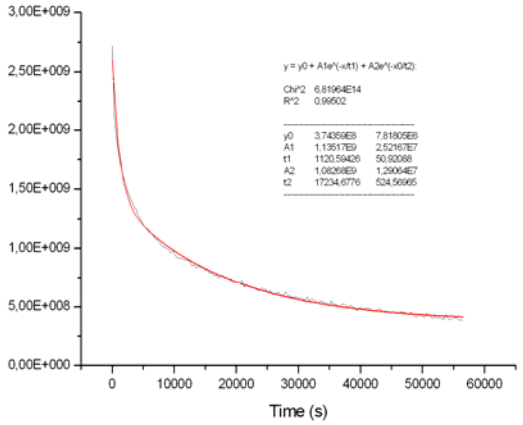

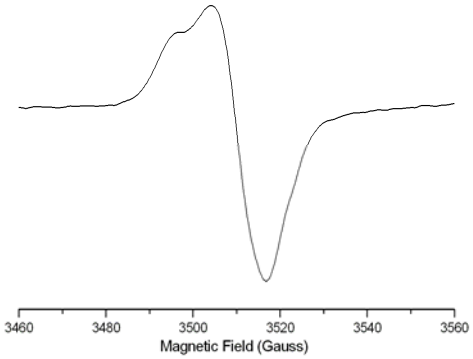

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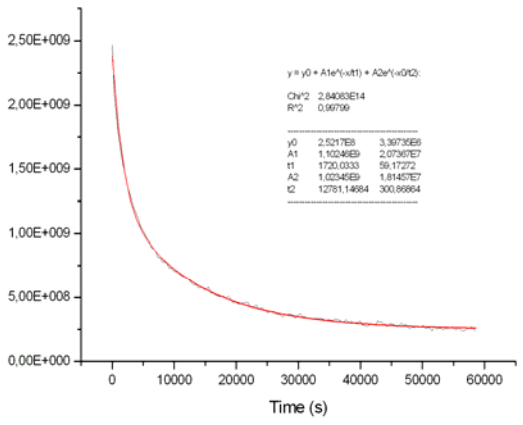

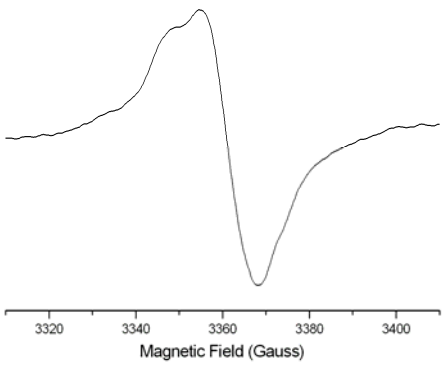

Under thermal conditions at 473 K:

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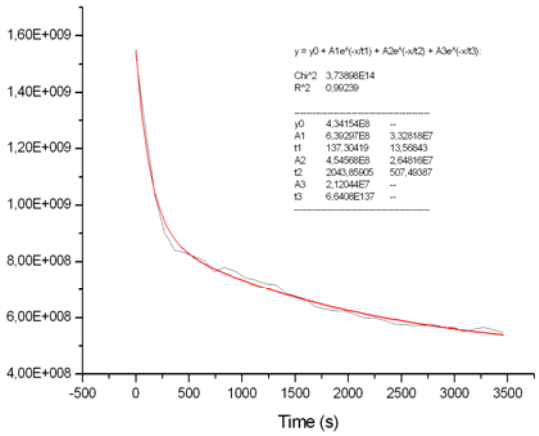

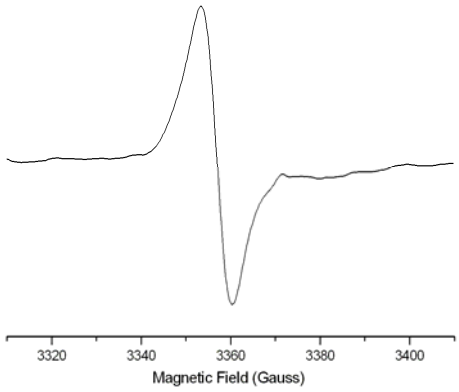

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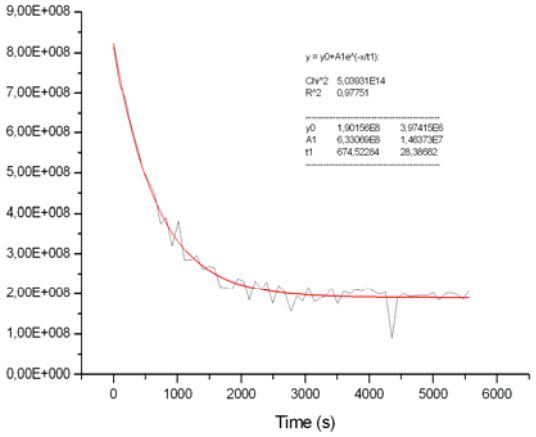

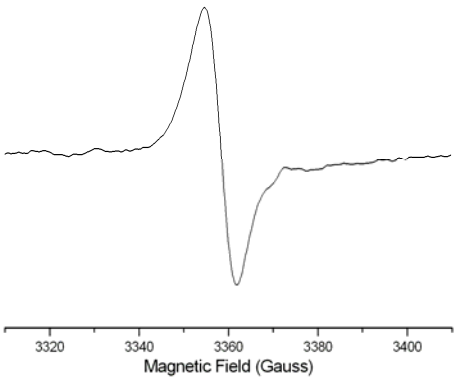

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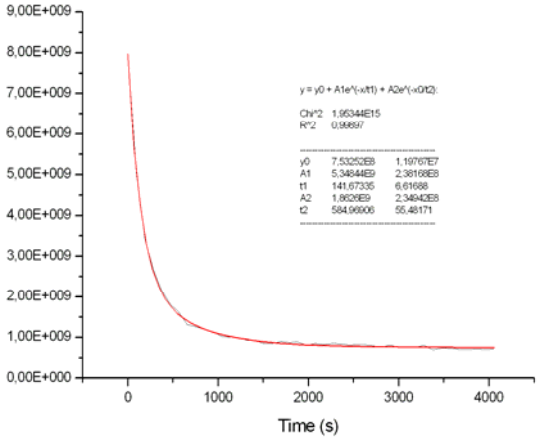
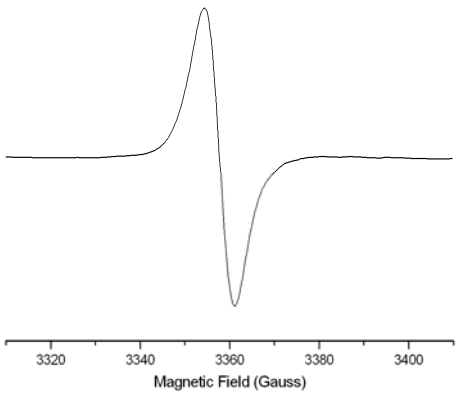




Simulations

All simulations have been performed using gaussian 09.
The scan over the dihedral angle have been performed using the following command:
#opt=(ts,noeigen,modredundant) b3lyp/6-311+g(d,p)
D 18 21 42 39 S 24 15.0
This, in principle, ensures that the 24 stationary points found during the scan are transition states. We have checked that the transition states found really correspond to the hydrogen atom transfer (frequency is then approximately i1250 cm^{-1}).
In practice, it happens that some of these stationary points have a second very low imaginary frequency. The geometry has properly converged to the correct transition state, but numerical inaccuracies in the Hessian are probably the source of this second nearly zero imaginary frequency.[1] Unfortunately, we were unable to remove this second imaginary frequency neither by using smaller optimization step, tighter energy gradient threshold, tighter scf orbital gradient threshold, tighter electron integral accuracy and tighter grid accuracy, nor by trying to deform the geometry in the direction of the strongest vector corresponding to this second imaginary frequency.

Tunneling effects on reaction coordinate motion can be evaluated by the means of the Wigner's multiplicative transmission coefficient $\chi(T)$,[2] so that: $k^{TST/T}(T) = \chi(T) \times k^{TST}(T)$, where $k^{TST}(T)$ is the reaction rate in the transition state theory and $k^{TST/T}(T)$ is the reaction rate taking into account tunneling effects. In this relatively simple treatment, the imaginary frequency (ν) is used to compute the correction $\chi(T)=1-1/24*(h\ Im(\nu)/k/T)^2$.
In our case, where ν=1250 cm^{-1}, the transmission coefficient is 2.5 at 300K. This means that the degenerate hydrogen atom transfer is more than two times faster than classical thermodynamics would have predicted.
We can also use the Skodje-Truhlar[3] definition of the mutliplicative transmission coefficient. In that case $\chi(T)=\pi\beta/\alpha/\sin(\pi\beta/\alpha)+\beta\exp((\beta-\alpha)\Delta H)/(\beta-\alpha)\approx 7$, which would imply even faster kinetics.

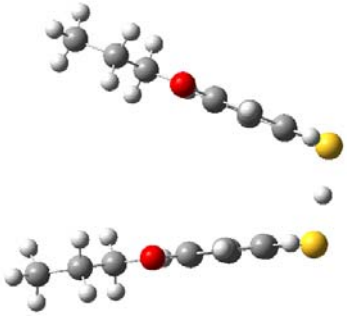
Six of these transition states structures have been used as starting points for IRC scans (30 steps of 0.1 Bohr in each direction) in order to evaluate the energy barrier for HAT.
The end points of the IRC scans were fully optimized at the same level of theory b3lyp/6-311+g(d,p) leading to two minima per TS.
The energies of the stationary points of these IRC are given in the table below and the geometry of the starting transition states is given further below.

	Transition State		Minimum 1		Minimum 2	
	H (u.a.)	G (u.a.)	H (u.a.) *ΔH(kcal/mol)*	G (u.a.) *ΔG(kcal/mol)*	H (u.a.) *ΔH(kcal/mol)*	G (u.a.) *ΔG(kcal/mol)*
d=7.7 Å φ=3°	-1646.448454 *2ImF*	-1646.531224 *2ImF*	-1646.455552 *4.5*	-1646.544456 *8.3*	-1646.455494 *4.4*	-1646.545594 *9.0*
d=7.4 Å φ=18°	-1646.447911	-1646.533973	-1646.455494 *4.8*	-1646.545591 *7.3*	-1646.455526 *4.8*	-1646.544790 *6.8*

[1] M. Malagoli and J. Baker, "The effect of grid quality and weight derivatives in density functional calculations of harmonic vibrational frequencies" *J Chem Phys*, 2003, ***119***,12763-12768.
[2] E. Wigner, *Z. Phys. Chem. B*, 1932, ***19***, 203-216.
[3] R. T. Skodje and D. G. Truhlar, *J. Phys. Chem*., 1981, ***85***, 624-628

d=14.9 Å φ=67°	-1646.448508	-1646.535082	-1646.455880 *4.6*	-1646.546347 *7.0*	-1646.455552 *4.4*	-1646.544480 *5.9*
d=12.9 Å φ=-72°	-1646.449555 *2ImF*	-1646.531996 *2ImF*	-1646.455551 *3.8*	-1646.544469 7.8	-1646.455881 *4.0*	-1646.546389 *9.0*
d=19.4 Å φ=168	-1646.448114	-1646.534022	-1646.455103 *4.4*	-1646.545805 *7.4*	-1646.454710 *4.1*	-1646.546225 *7.7*
d=19.4 Å φ=-177°	-1646.447940	-1646.535601	-1646.455528 *4.8*	-1646.544794 *5.8*	-1646.455892 *5.0*	-1646.545783 *6.4*

First TS structure, with d=7.7 Å and φ=3°:



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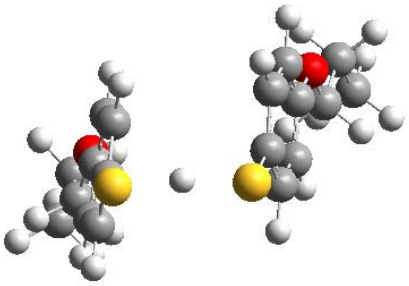
C,-.708767,3.622219,0.371789\H,-4.026047,2.790827,1.008613\
H,-3.528047,4.475421,1.032552\C,-2.400062,3.245662,-0.303939\
H,-2.029585,4.073185,-0.921681\H,-2.533431,2.368288,-0.94925\
C,-0.183464,2.588405,0.374705\C,0.691268,2.328415,1.44297\
C,0.278058,2.473383,-0.943506\C,1.999747,1.961752,1.19693\
H,0.31564,2.427927,2.454272\C,1.596002,2.098644,-1.17989\
H,-0.375228,2.671604,-1.782364\C,2.483395,1.836048,-0.123325\
H,2.674412,1.773927,2.023315\H,1.953678,2.00865,-2.198408\
S,4.164285,1.434013,-0.444652\C,-5.078864,-3.726869,-0.677102\
H,-5.214074,-2.961788,-1.447967\H,-6.044923,-3.877898,-0.190268\
H,-4.812835,-4.662158,-1.17898\C,-4.014723,-3.315391,0.344202\
H,-3.914548,-4.083609,1.116919\H,-4.312735,-2.393203,0.852364\
C,-2.655912,-3.098254,-0.302109\H,-2.705203,-2.300833,-1.054308\
H,-2.309319,-4.014712,-0.795608\C,-0.432554,-2.504157,0.412835\
C,0.409789,-2.182974,1.490345\C,0.095924,-2.576338,-0.883179\
C,1.75284,-1.94366,1.275569\H,-0.01803,-2.135705,2.484529\
C,1.448482,-2.327666,-1.088862\H,-0.53207,-2.823379,-1.728459\
C,2.304911,-2.009818,-0.0219\H,2.401513,-1.709905,2.11096\
H,1.857866,-2.383248,-2.090223\S,4.026178,-1.780642,-0.295122\
H,4.103064,-0.167717,-0.239992\O,-1.732615,-2.730045,0.728508\
O,-1.445328,2.946975,0.72056

Freq (cm^{-1}): i1256.2582, i12.3997, 6.7787, 17.9288, 25.4849, 33.2133, 38.0628, 56.4345, 78.8237, 83.0765, 91.5270, 92.7999, 110.8642, 133.1393, 154.0233, 167.7945, 231.4581, 234.4092, 237.5597, 239.3183, 255.6268, 273.8458, 277.1786, 318.4449, 330.1760, 331.9349, 334.2666, 414.8387, 416.6571, 440.7858, 445.6612, 460.7407, 505.2200, 506.1780, 517.8438, 518.0716, 641.6260, 642.2355, 684.2987, 684.5099, 706.9945, 709.5496, 772.0010, 772.4099, 812.6132, 815.9254, 837.2028, 837.7796, 840.9994, 842.5863, 910.8416, 911.6343, 916.3724, 916.7810, 954.9221, 955.4714, 979.0589, 982.1831, 1019.8061, 1020.3802, 1030.7959, 1031.7145, 1041.0126, 1053.5935, 1054.5402, 1098.3946, 1105.9478, 1128.2013, 1129.9054, 1144.4884, 1145.1260, 1181.5172, 1181.7713, 1191.1429, 1196.3441, 1270.3795, 1270.9571, 1271.3678, 1278.5612, 1309.2585, 1311.6769, 1323.9302, 1324.9425, 1325.4765, 1325.9835, 1339.6876, 1339.9811, 1417.0974, 1417.9624, 1426.3838, 1426.8777, 1440.6200, 1441.8594, 1494.4547, 1495.5803, 1501.8994, 1502.6772, 1504.1501, 1504.7751, 1509.5882, 1510.2564, 1523.3163, 1524.0021, 1576.9448, 1577.6716, 1617.3521, 1622.7002, 2994.0483, 2994.5217, 3023.4274, 3023.6681, 3031.4189, 3031.8841, 3036.9719, 3037.2982, 3065.5090, 3065.8798, 3089.5638, 3090.0794, 3096.3860, 3096.6815, 3183.4634, 3183.9431, 3187.5744, 3188.1386, 3198.3380, 3198.9748, 3206.9516, 3209.4802

Second TS structure, with d=7.4 Å and φ=18°:



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H,-3.011527,4.866354,0.750056\C,-2.162002,3.184606,-0.261695\
H,-1.89537,3.731765,-1.174477\H,-2.423405,2.156213,-0.540482\
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C,0.343493,2.050744,-1.039837\C,2.415468,2.135601,0.831869\
H,0.996918,3.117387,2.120309\C,1.591352,1.524438,-1.354172\

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93,-0.416019\H,-5.087852,-4.543748,-0.846137\C,-4.325274,-2.774252,0.1
82393\H,-4.409255,-3.195861,1.188566\H,-4.571446,-1.711053,0.263743\C,
-2.883764,-2.907102,-0.281842\H,-2.752926,-2.461089,-1.275833\H,-2.589
908,-3.962526,-0.338263\C,-0.704295,-2.222596,0.484287\C,0.04317,-1.57
618,1.482723\C,-0.045759,-2.810749,-0.604091\C,1.420777,-1.524008,1.39
6732\H,-0.484146,-1.131765,2.318192\C,1.340334,-2.740707,-0.687522\H,-
0.598367,-3.316264,-1.384367\C,2.102838,-2.10358,0.305646\H,1.992875,-
1.036597,2.176307\H,1.850179,-3.188366,-1.531977\S,3.857721,-2.091993,
0.206607\H,4.085128,-0.554296,-0.22847\O,-2.050035,-2.227379,0.663554\
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Frequencies (cm^{-1}): i1250.503500,4.760800,10.941900,20.974300,32.502400,37.743200,40.371100,57.599300,82.150900,85.864600,
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3090.129000,3090.545100,3096.783500,3097.118300,3182.470800,3185.553200,3187.509100,3188.033500,3197.517000,3200.698100,320
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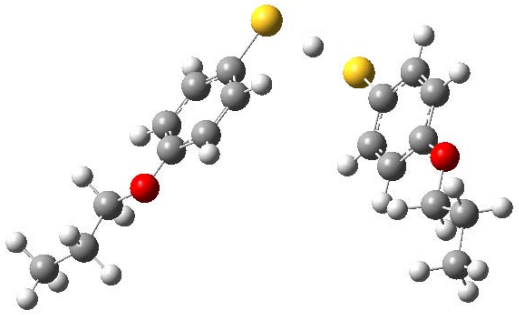
Third TS structure, with d=14.9 Å and φ=67°:



Coordinates (Å): C,-6.7069145046,4.1875472403,-0.3886186848\H,-7.664101
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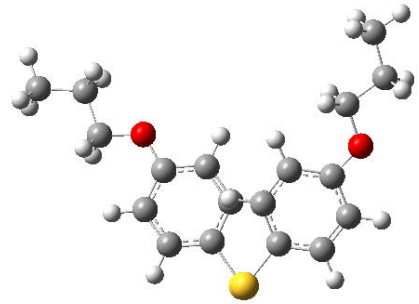
Frequencies (cm^{-1}): i1234.1619, 4.2759, 15.7419, 18.3362, 28.2501, 30.9972, 43.6104, 50.9919, 80.2350, 83.2829, 92.9530, 94.1515, 113.5958, 127.5817, 155.1982, 161.4877, 235.5275, 236.5540, 240.4074, 242.0287, 266.5673, 272.4292, 290.6653, 315.2224, 332.6294, 333.6593, 339.2265, 417.1788, 418.0346, 444.6214, 446.4286, 505.1026, 505.4330, 516.1050, 516.7148, 642.0738, 642.1963, 683.5086, 684.3975, 697.8655, 703.9361, 750.3458, 766.1916, 772.8592, 773.9714, 813.1615, 815.1218, 837.6814, 838.0168, 844.3833, 846.1677, 911.6117, 913.4342, 917.0974, 917.3806, 955.0954, 955.9536, 978.9142, 981.4350, 1020.3383, 1020.4998, 1030.3285, 1031.3964, 1053.3501, 1054.4212, 1098.7709, 1107.0157, 1128.8756, 1129.1114, 1144.9235, 1145.2673, 1181.4625, 1182.1258, 1192.5628, 1196.6398, 1272.2248, 1272.3729, 1273.5835, 1278.2019, 1310.5444, 1311.3275, 1324.9790, 1325.9633, 1326.2595, 1327.4674, 1339.8540, 1340.8119, 1417.9950, 1418.2614, 1426.7279, 1427.0993, 1441.1987, 1441.5003, 1494.9925, 1495.5504, 1502.9553, 1503.1733, 1504.4781, 1505.1219, 1509.9075, 1510.5208, 1523.0984, 1524.1044, 1577.8371, 1578.4196, 1617.8701, 1622.7878, 2995.6131, 2995.9910, 3024.0400, 3024.1720, 3033.2313, 3033.8275, 3036.9905, 3037.7618, 3066.4463, 3066.7178, 3090.5311, 3090.7971, 3096.5725, 3096.8585, 3182.2874, 3184.1441, 3186.8203, 3187.7494, 3197.4149, 3199.0446, 3207.8160, 3210.1206

Fourth TS structure, with d=12.9 Å and φ=-72°:



Coordinates (Å): C,-7.13024,-3.26009,-0.973961\H,-7.464065,-4.299621,-0.942265\
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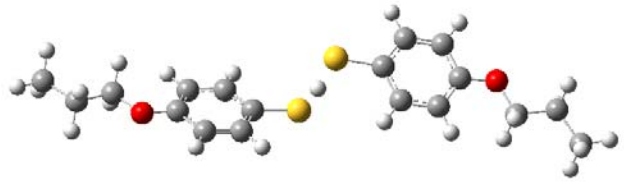
H,-5.843594,-3.432033,0.763341\C,-5.284687,-1.664976,-0.303562\
H,-5.994464,-1.003459,0.20836\H,-5.168724,-1.31199,-1.335846\
C,-3.370388,-0.432311,0.485808\C,-2.14284,-0.474106,1.167743\
C,-3.844538,0.788269,-0.014207\C,-1.406907,0.681531,1.346966\
H,-1.79637,-1.426591,1.550621\C,-3.094141,1.94461,0.168827\
H,-4.786751,0.846463,-0.541913\C,-1.866096,1.919206,0.848847\
H,-0.464337,0.64705,1.879353\H,-3.459836,2.887683,-0.218779\
S,-0.953925,3.398889,1.118233\C,5.59962,-4.693341,0.20593\
H,4.670314,-5.133491,0.58037\H,6.429155,-5.24921,0.648529\
H,5.633652,-4.855258,-0.875776\C,5.696156,-3.205,0.553825\
H,6.641697,-2.791471,0.190193\H,5.687121,-3.067898,1.639361\
C,4.552076,-2.405057,-0.047935\H,3.586087,-2.765783,0.326906\
H,4.550629,-2.491765,-1.141581\C,3.835051,-0.105178,-0.099216\
C,4.091315,1.216731,0.303276\C,2.711174,-0.384346,-0.888441\
C,3.242794,2.237475,-0.078959\H,4.965991,1.410975,0.912341\
C,1.861153,0.650511,-1.26379\H,2.492903,-1.392945,-1.212096\
C,2.105172,1.976625,-0.871757\H,3.44597,3.255662,0.22948\
H,0.991483,0.43555,-1.872683\S,1.045767,3.278864,-1.396762\
H,0.056876,3.332827,-0.130193\O,4.728944,-1.033136,0.323859\
O,-4.018531,-1.617986,0.364985

Frequencies (cm^{-1}): i1234.701600,i14.208500,6.897900,23.787300,27.561700,30.926600,42.945900,52.789200,81.352900,83.494100,93.150300,95.672800,111.704500,127.385200,153.881500,163.170800,233.018500,237.067800,240.374500,242.549000,267.250900,272.844700,289.858700,315.176100,331.364900,334.104400,340.896600,417.451800,418.522600,442.971400,446.519700,504.691400,505.242500,512.808700,518.162700,640.135500,642.178200,643.778100,684.424700,686.025300,711.441400,724.292900,772.473000,772.917600,813.522000,813.817800,830.663400,836.386200,839.445900,844.595100,863.942500,911.456200,911.483100,916.755800,916.914200,956.169200,957.212600,981.238900,984.143000,1020.215300,1021.296100,1030.827700,1031.910200,1053.550100,1054.821100,1098.748200,1107.245900,1128.942400,1129.905200,1145.075900,1145.591000,1181.506700,1181.802000,1191.005700,1196.316600,1271.412200,1272.283700,1273.338000,1280.170400,1311.295900,1311.418400,1325.453300,1326.542500,1326.730000,1328.880300,1340.350900,1340.920600,1416.448100,1417.261600,1427.351900,1427.684700,1440.406400,1441.274900,1495.427400,1495.560900,1501.978900,1502.662000,1504.652300,1505.223200,1510.102500,1510.846400,1522.901900,1524.512600,1577.544800,1579.874900,1618.142200,1623.077300,2994.799600,2995.297600,3024.000300,3024.288500,3032.563300,3033.248500,3037.026100,3038.411000,3066.246000,3066.730200,3090.281000,3090.894700,3096.164300,3096.893700,3183.074100,3184.380200,3187.698500,3188.406200,3198.966100,3199.639800,3208.293300,3209.637400

Fifth TS structure, with d=19.4 Å and φ=168°:



Coordinates (Å): C,-9.4530438448,1.6041065925,0.2301530286\H,-1
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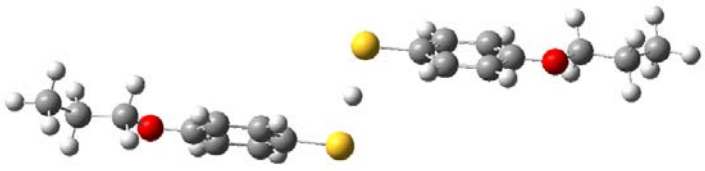
0.0873220649\H,-9.4652099297,1.5904748882,1.324348551\C,-8.596045974,0
.4679085529,-0.3360072079\H,-8.6182700136,0.4855755615,-1.4298565681\H
,-8.9997347456,-0.5009925874,-0.026804131\C,-7.1493453563,0.5598881317
,0.1225853031\H,-7.0841418332,0.5105301109,1.2166853982\H,-6.695299820
3,1.5026634685,-0.2070549875\C,-5.1141572717,-0.6951221426,-0.18474095
85\C,-4.4974051276,-1.8092932141,-0.7775088967\C,-4.3581047902,0.16820
211,0.6202520694\C,-3.1530269897,-2.0524151313,-0.5712812264\H,-5.0976
3551,-2.4629030566,-1.3989670658\C,-3.0082895916,-0.091822735,0.830672
3008\H,-4.8096575214,1.0331499764,1.0868852798\C,-2.3774406315,-1.2005
048014,0.2428738998\H,-2.6787608355,-2.9070913494,-1.037958352\H,-2.42
94390656,0.5706794708,1.4628813944\S,-0.6793536386,-1.5524114904,0.535
6088153\C,9.7929388506,-0.5678668393,-0.1647418945\H,9.6592863858,-1.6
323694295,-0.3803275383\H,10.7073928502,-0.4631474385,0.4233643954\H,9
.9516122797,-0.051845985,-1.1166118194\C,8.5919089059,0.0070819874,0.5
923301306\H,8.7583139627,1.0644997139,0.8193219286\H,8.4667873237,-0.5
065724392,1.5503370069\C,7.3015310113,-0.1221441242,-0.2013389601\H,7.
0791209676,-1.1752434395,-0.4138143796\H,7.377407024,0.4130629777,-1.1
560450802\C,4.9803982373,0.4593346369,0.0876518967\C,4.0055482676,1.03
20864493,0.9221630139\C,4.608898441,-0.0447972122,-1.1657994391\C,2.68
95697226,1.1049750088,0.5083999732\H,4.3129643282,1.4169533613,1.88711
2761\C,3.2792978848,0.0231040377,-1.5681448472\H,5.3392759638,-0.49322
42535,-1.8253920117\C,2.2954746267,0.5996674209,-0.7490150461\H,1.9453
957698,1.5577862523,1.1522846108\H,2.9904067785,-0.3770713716,-2.53242
59321\S,0.6322519506,0.7179234025,-1.307405269\H,-0.0415998098,-0.2966
626514,-0.2482324428\O,6.2434424604,0.4423825832,0.5821666862\O,-6.435
7737317,-0.5424398186,-0.4497227723

Frequencies (cm^{-1}): i1248.6170, 7.0612, 12.5980, 23.3334, 24.9767, 37.9051, 43.7570, 49.6705, 80.8454, 84.5586, 91.1043, 93.0630, 116.9358, 122.2685, 154.6986, 158.0814, 230.4495, 235.8525, 239.7155, 241.1984, 266.1890, 272.0537, 278.8548, 314.1041, 329.9592, 332.3384, 346.7832, 416.5665, 420.1053, 443.4989, 446.6703, 503.8962, 504.9412, 519.1510, 521.8429, 589.4875, 642.1571, 642.6422, 683.4827, 683.9565, 717.8594, 722.1172, 771.6906, 773.4682, 814.0353, 814.7101, 837.4197, 837.7244, 841.1643, 843.2273, 910.8308, 912.9817, 916.0717, 916.5658, 953.4479, 955.2194, 979.1151, 980.8018, 1020.2877, 1020.4813, 1030.3600, 1030.6896, 1051.1550, 1053.4746, 1054.3433, 1098.1582, 1107.4663, 1129.7342, 1131.0756, 1144.7648, 1145.1487, 1181.4820, 1182.3525, 1193.1989, 1197.0132, 1270.5749, 1272.8196, 1273.0657, 1278.2178, 1310.4908, 1313.3797, 1324.7054, 1325.2632, 1326.3299, 1328.0910, 1339.4492, 1340.6142, 1416.3660, 1416.5148, 1425.5419, 1427.7565, 1441.4930, 1442.0305, 1495.1206, 1495.1856, 1502.3223, 1503.0748, 1504.8399, 1505.0654, 1510.1881, 1510.5071, 1523.2135, 1523.7174, 1578.3028, 1578.5244, 1617.7840, 1623.5970, 2994.5853, 2995.5990, 3023.7751, 3023.9073, 3032.5172, 3033.4414, 3037.1914, 3037.4214, 3066.2130, 3066.6034, 3090.3894, 3090.8066, 3096.7890, 3096.8309, 3183.1875, 3184.5134, 3186.2261, 3187.1085, 3198.1402, 3199.4712, 3207.9015, 3208.5638

Sixth TS structure, with d=19.4 Å and φ=-177°:

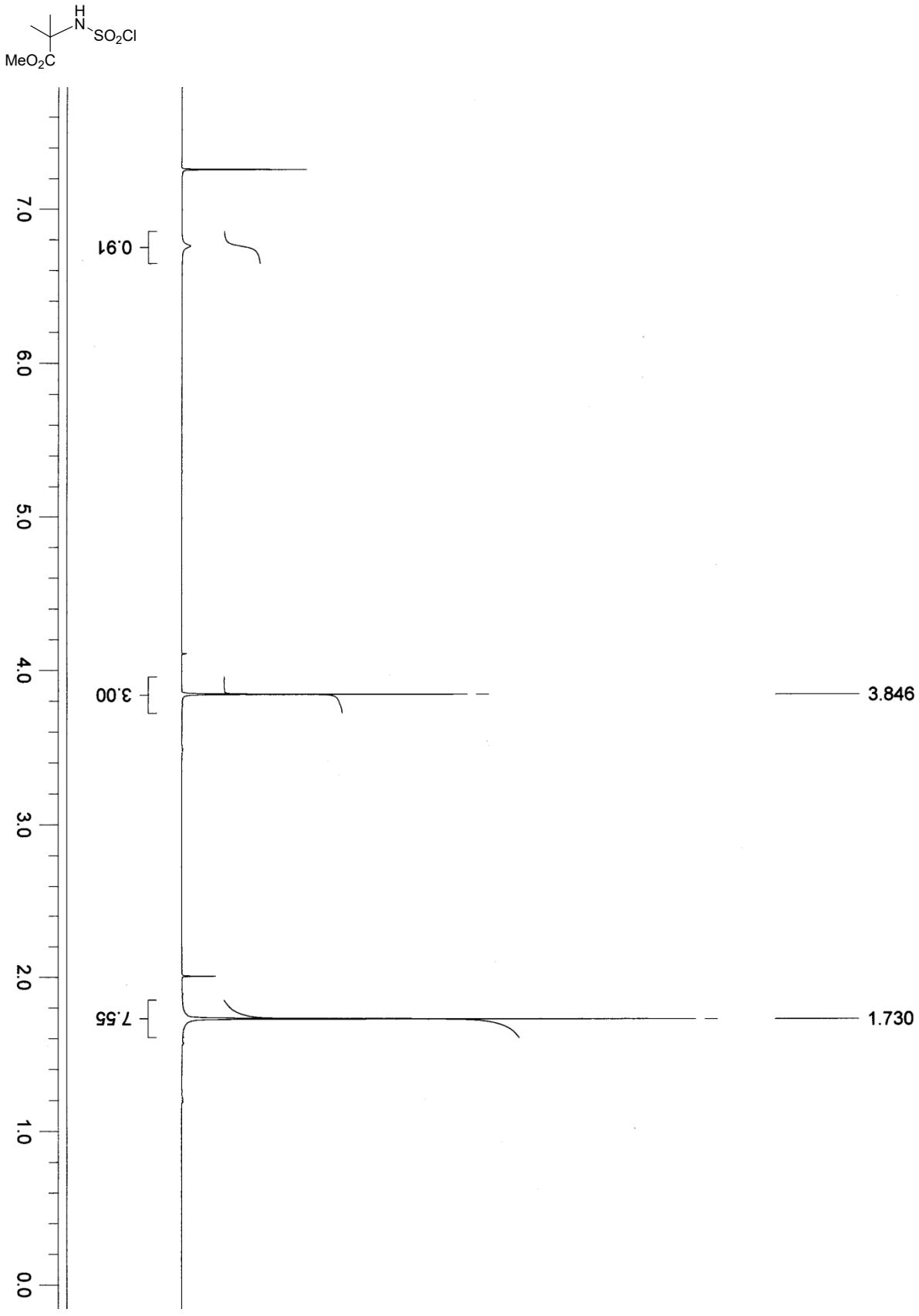


Coordinates (Å): C,-9.531825,1.388165,-0.279556\H,-10.51612,1.214941,-0.720296\
H,-9.175489,2.35845 9,-0.638709\H,-9.663876,1.461448,0.804303\
C,-8.56392,0.261493,-0.652479\H,-8.466204,0.1902,-1.739981\
H,-8.951257,-0.70129,-0.305506\C,-7.183192,0.474786,-0.053074\
H,-7.236929,0.513846,1.042037\H,-6.745028,1.415164,-0.409876\
C,-5.059149,-0.662858,-0.053219\C,-4.314438,-1.7653,-0.503747\
C,-4.446545,0.302015,0.758214\C,-2.983496,-1.8951,-0.156082\
H,-4.805515,-2.499454,-1.131087\C,-3.109899,0.15544,1.112561\
H,-4.998931,1.158797,1.119556\C,-2.350817,-0.937297,0.663536\
H,-2.409111,-2.740118,-0.515522\H,-2.641778,0.896964,1.748731\
S,-0.666431,-1.134718,1.129705\C,9.705807,-0.87644,-0.537121\

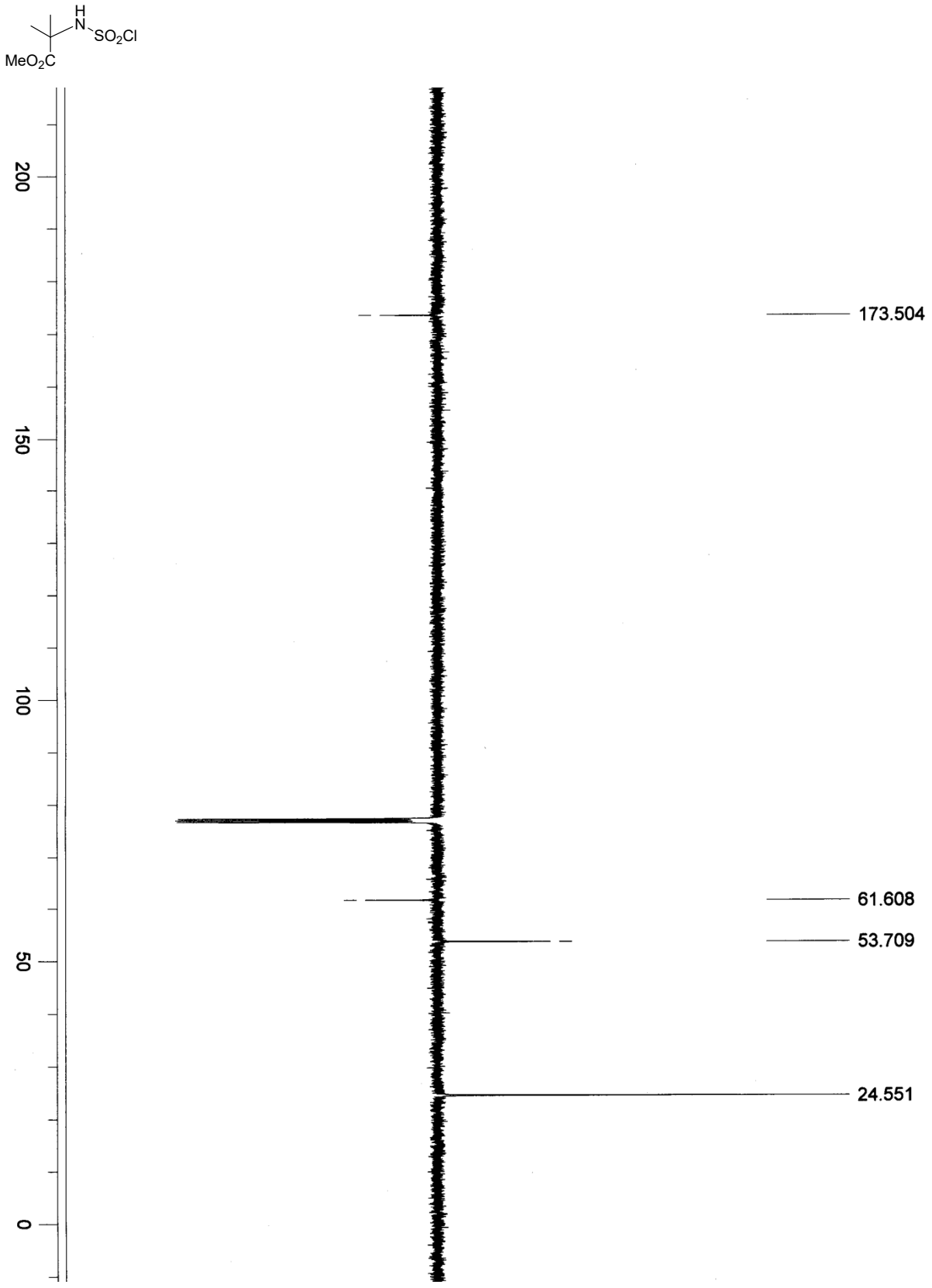
H,9.466877,-1.925348,-0.737628\H,10.676682,-0.849596,-0.037362\
H,9.816421,-0.369305,-1.500519\C,8.63123,-0.211127,0.327752\
H,8.90107,0.829066,0.533979\H,8.556853,-0.716781,1.295284\
C,7.266262,-0.236631,-0.34089\H,6.944874,-1.268645,-0.52869\
H,7.293245,0.29519,-1.300182\C,5.033174,0.513947,0.164853\
C,4.187727,1.157564,1.084373\C,4.507517,0.03761,-1.04347\
C,2.846874,1.326191,0.797879\H,4.61382,1.519762,2.012265\
C,3.153757,0.201448,-1.316755\H,5.136786,-0.462876,-1.766709\
C,2.298147,0.848249,-0.411144\H,2.202665,1.833518,1.505775\
H,2.744744,-0.177598,-2.24541\S,0.600747,1.083221,-0.805296\
H,-0.044949,0.09712,0.296678\O,6.333004,0.404399,0.5365\
O,-6.354403,-0.622205,-0.454181

Frequencies(cm^{-1}) : i1250.7542, 2.0859, 9.3634, 20.7667, 23.0907, 37.2823, 43.7442, 47.9985, 81.1000, 81.6553, 91.1013, 93.2797, 115.8705, 121.2859, 154.3133, 158.1941, 226.7756, 230.3089, 233.0110, 239.9807, 268.0059, 272.3757, 277.5374, 314.2927, 331.3905, 332.4557, 354.0549, 416.8739, 420.4872, 443.6880, 446.4941, 504.5363, 505.0480, 518.8499, 523.6502, 565.2976, 642.3631, 642.6747, 683.8452, 684.2481, 717.6533, 721.6685, 772.7176, 773.0383, 814.5449, 814.7584, 837.7297, 837.8625, 841.4028, 843.0974, 910.8868, 911.9905, 916.1817, 916.4624, 954.3976, 954.9605, 979.7658, 980.6427, 1020.5114, 1020.7137, 1030.7259, 1031.0456, 1053.3500, 1053.6859, 1058.5568, 1098.4736, 1106.7893, 1130.3090, 1131.0487, 1144.9541, 1145.2518, 1181.5573, 1181.7373, 1193.9901, 1197.8613, 1270.6646, 1271.5936, 1273.5059, 1278.6898, 1310.8408, 1313.6304, 1325.3140, 1325.7274, 1326.6688, 1326.8561, 1339.9197, 1340.4735, 1416.0135, 1416.2408, 1427.1242, 1427.3434, 1441.8692, 1442.4700, 1495.3050, 1495.4411, 1501.3010, 1501.4344, 1505.2411, 1505.3080, 1510.4769, 1510.9168, 1523.8974, 1524.2380, 1578.9594, 1579.4049, 1618.1183, 1623.8413, 2994.7407, 2995.4898, 3023.4933, 3023.6877, 3032.6451, 3033.1242, 3037.1654, 3037.3509, 3066.0576, 3066.0786, 3090.2388, 3090.3026, 3096.2035, 3096.6235, 3183.2227, 3184.4750, 3186.4612, 3187.5293, 3198.1186, 3199.4056, 3209.2238, 3209.5531

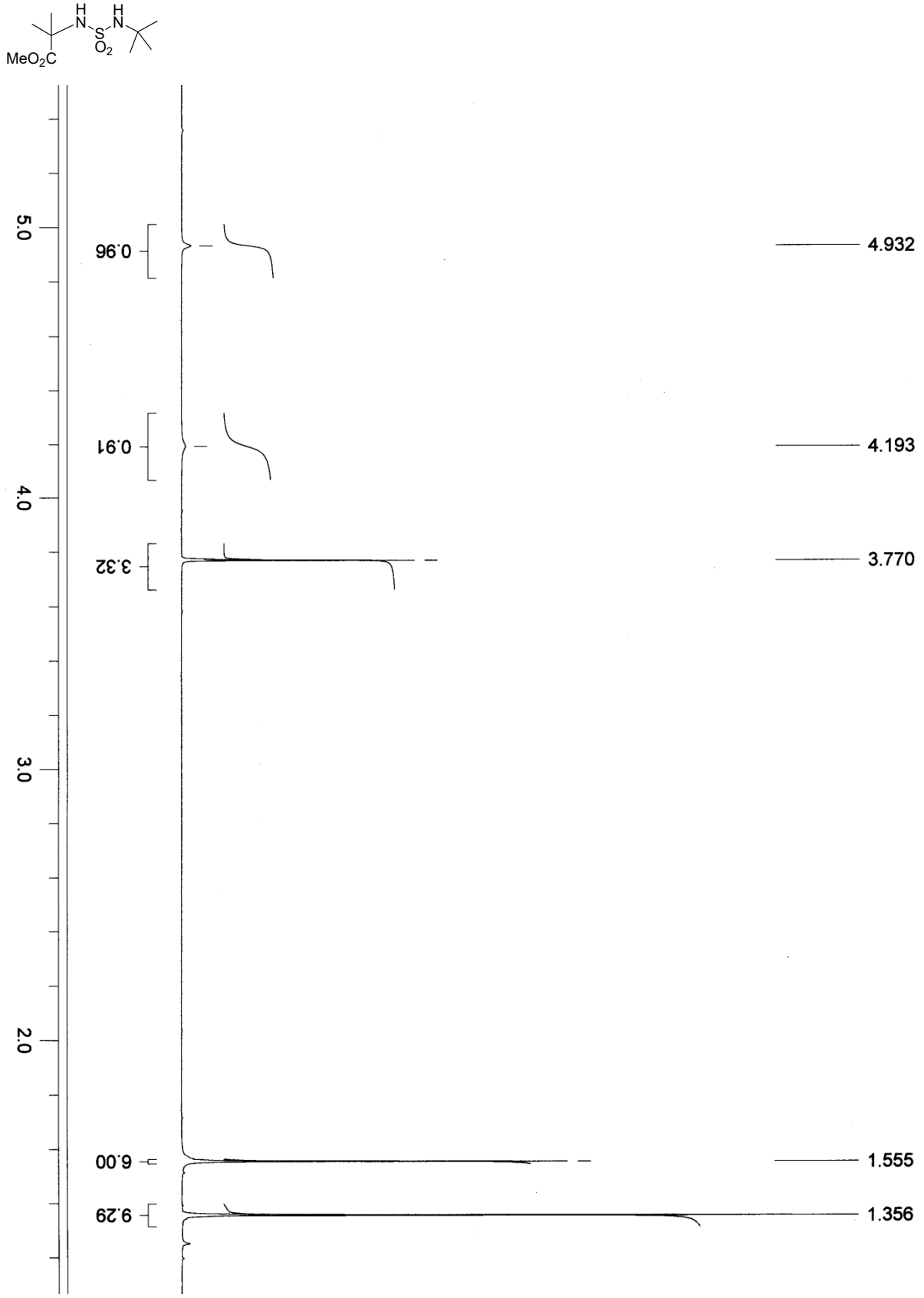
Methyl 2-methyl-2-(sulfonsulfonoylamino)propanoate: ^{1}H NMR



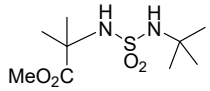
Methyl 2-methyl-2-(sulfonsulfonoylamino)propanoate: ^{13}C NMR (APT)

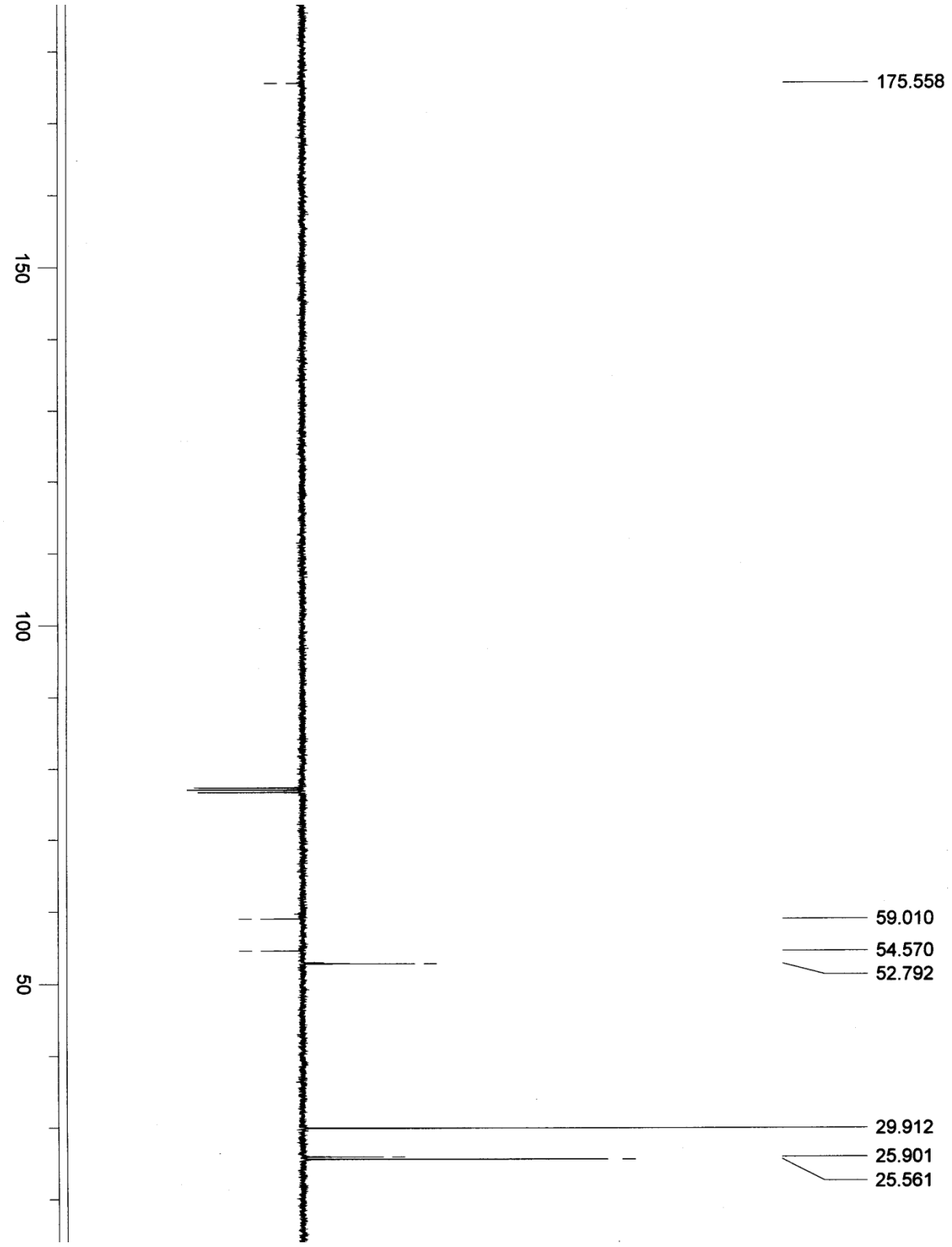


Methyl 2-[*N*-(tert-butyl)aminosulfonamido]-2-methylpropanoate (8): ^{1}H NMR

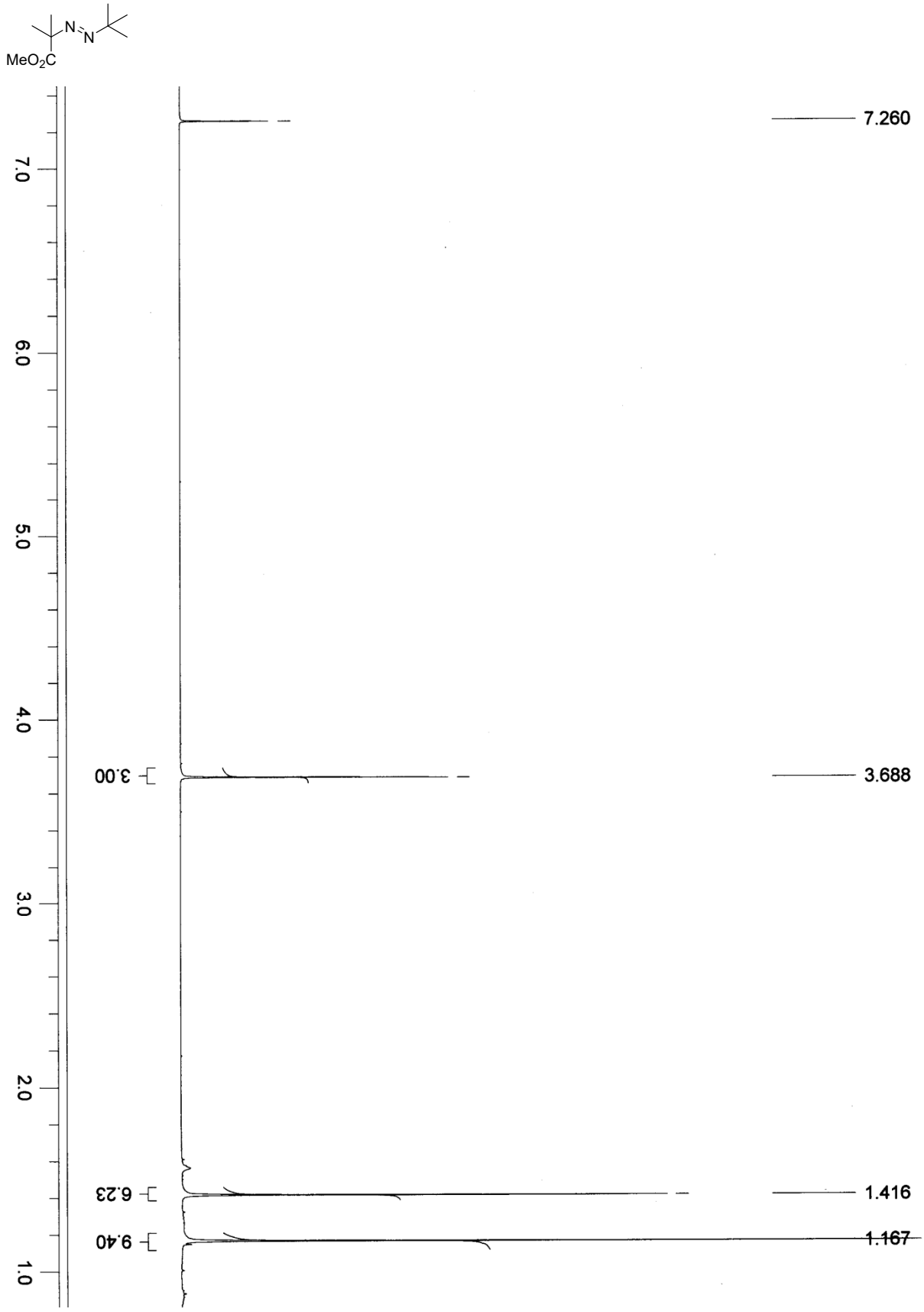


Methyl 2-[*N*-(tert-butyl)aminosulfonamido]-2-methylpropanoate (8): ^{13}C NMR (APT)

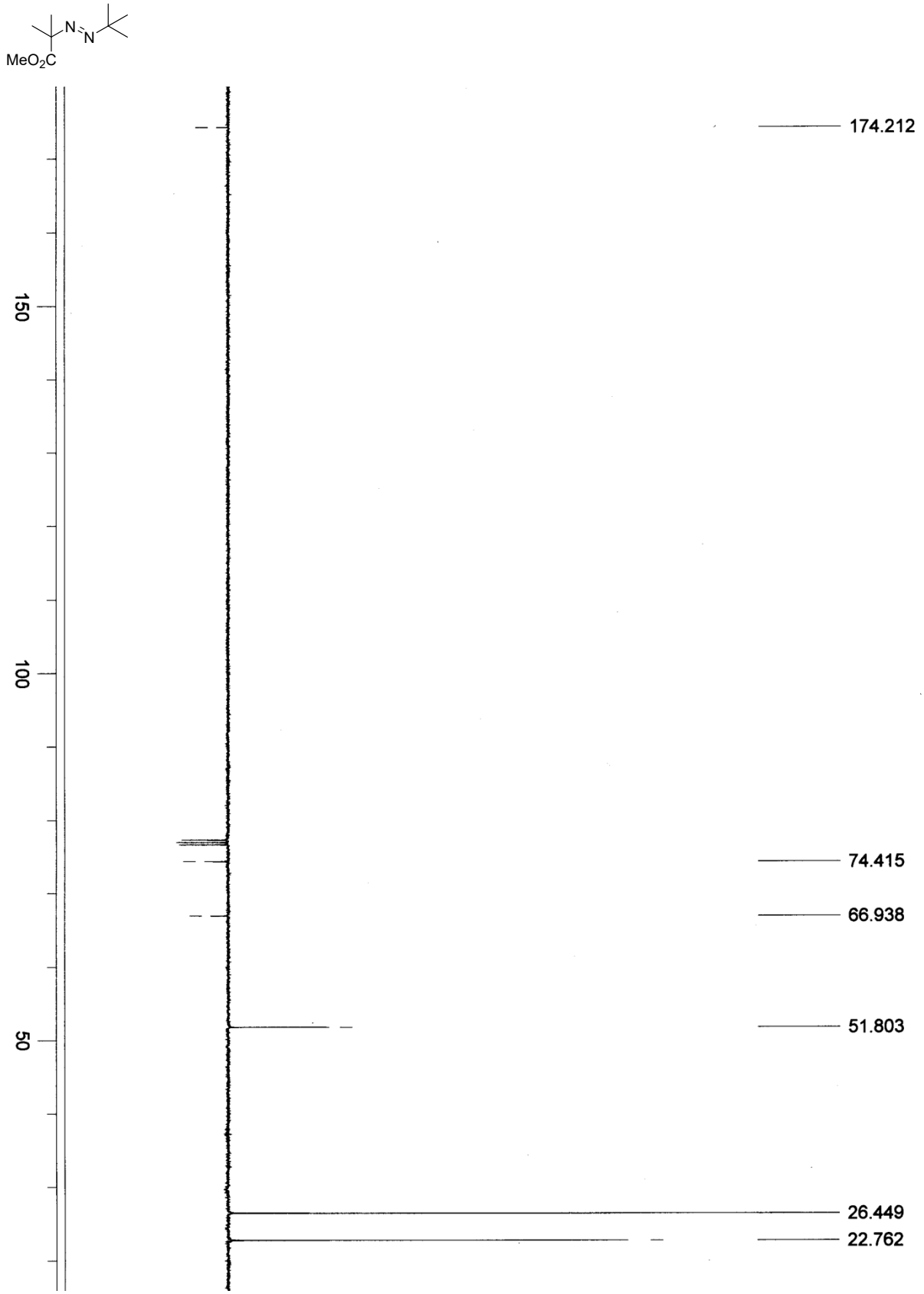




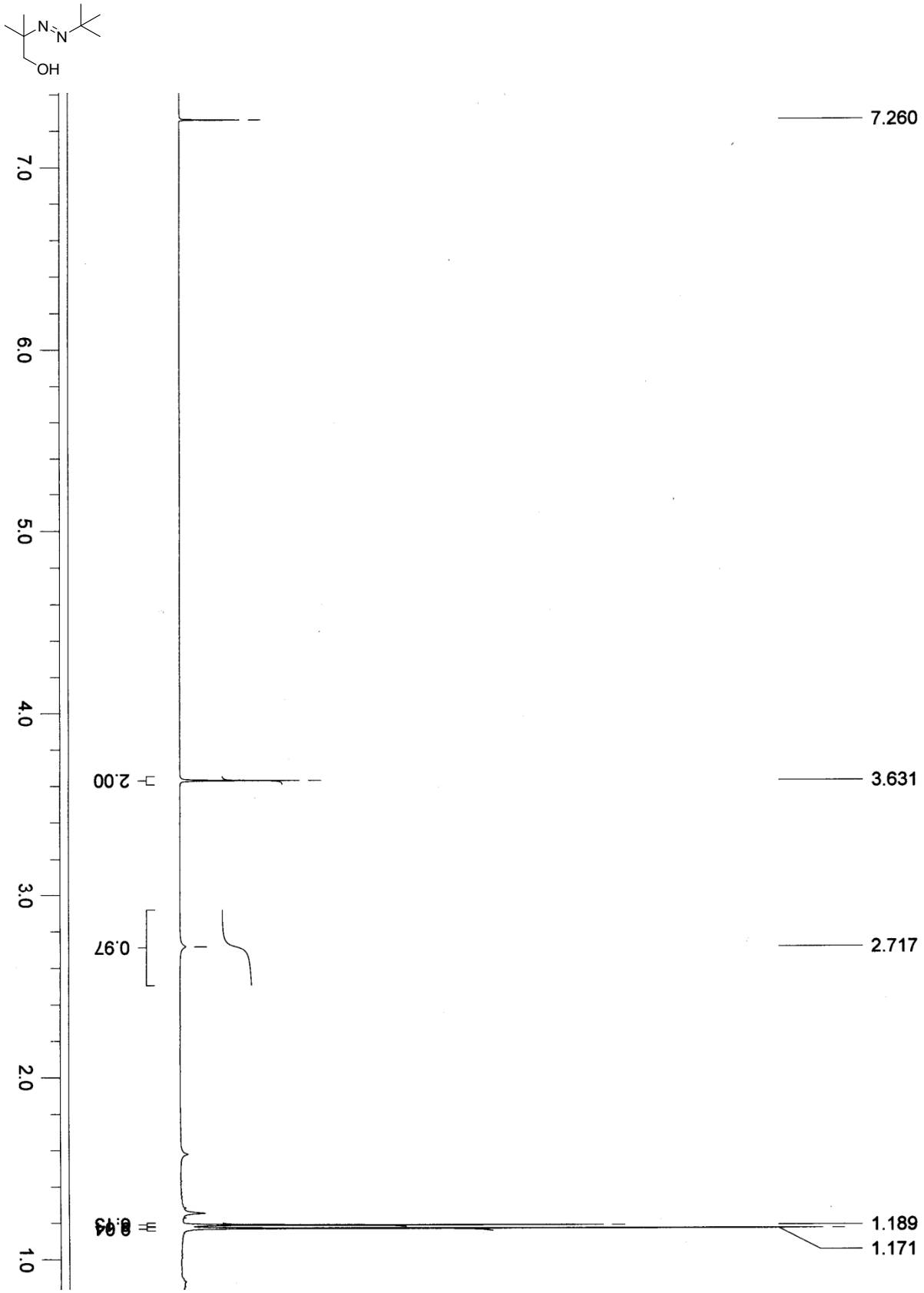
(*E*)-Methyl 2-(2-tert-butyldiazenyl)-2-methylpropanoate (7): ^{1}H NMR



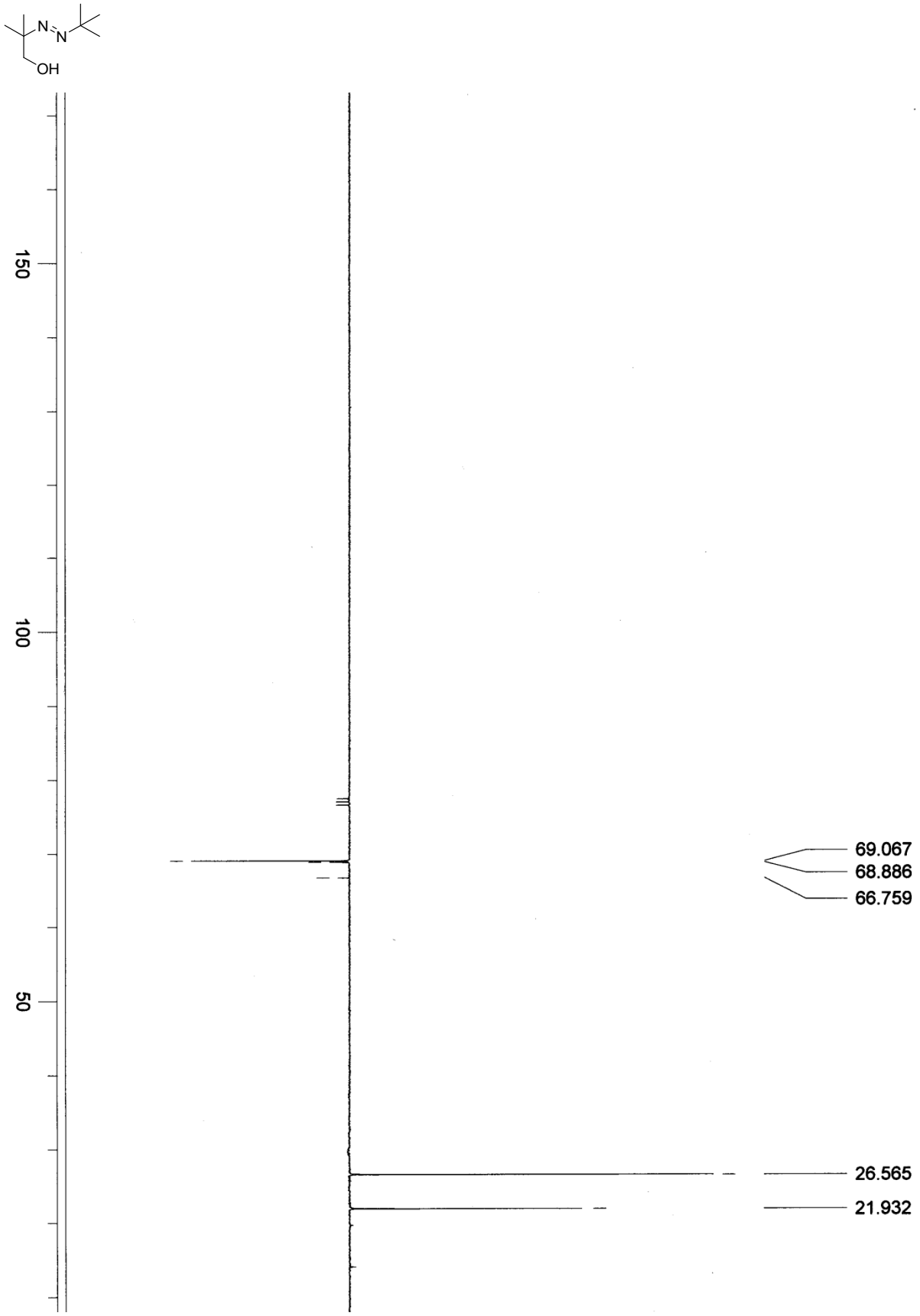
(*E*)-Methyl 2-(2-tert-butyldiazenyl)-2-methylpropanoate (7): ^{13}C NMR (APT)



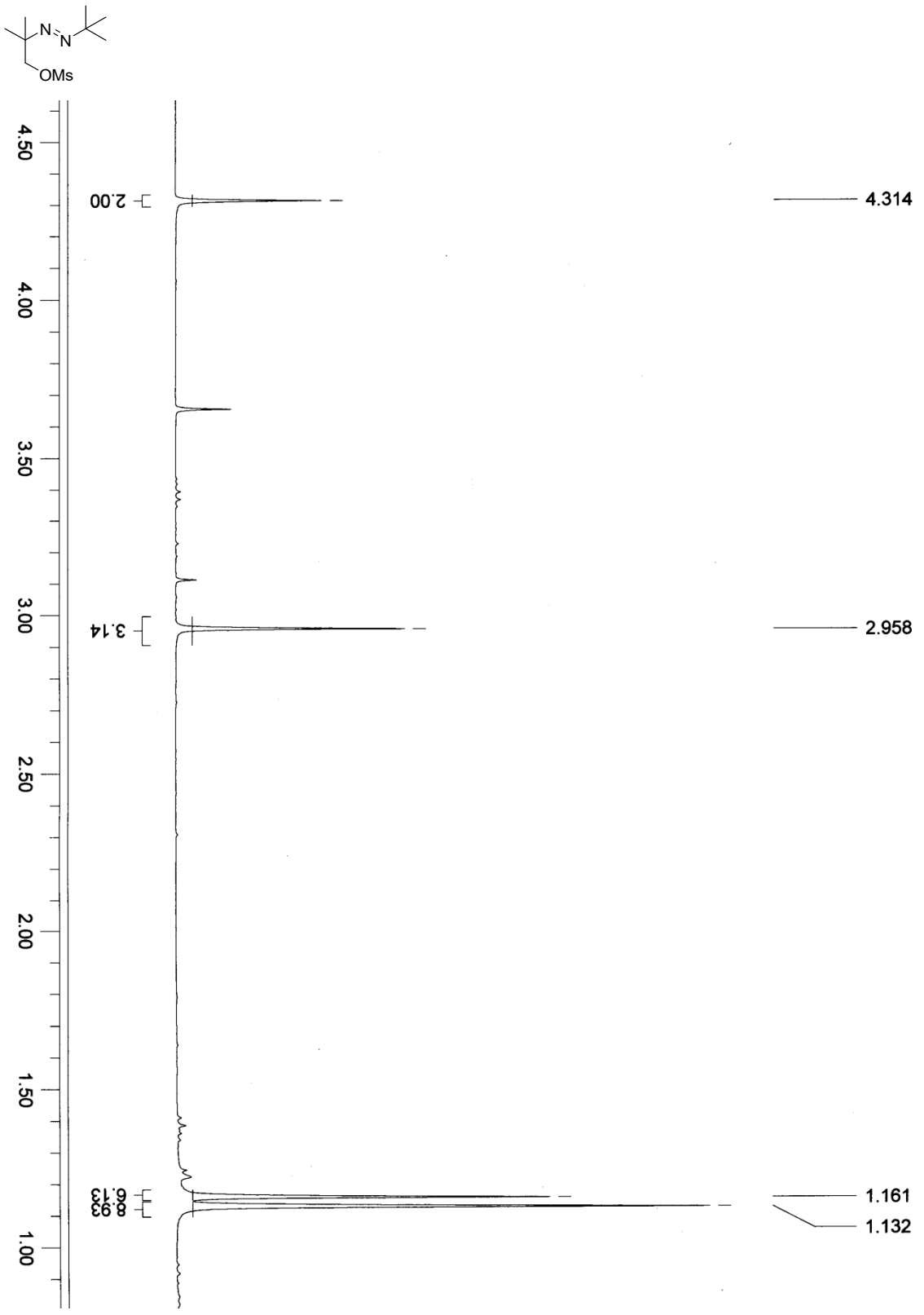
(*E*)-2-(2-tert-Butyldiazenyl)-2-methylpropan-1-ol (6): ^{1}H NMR



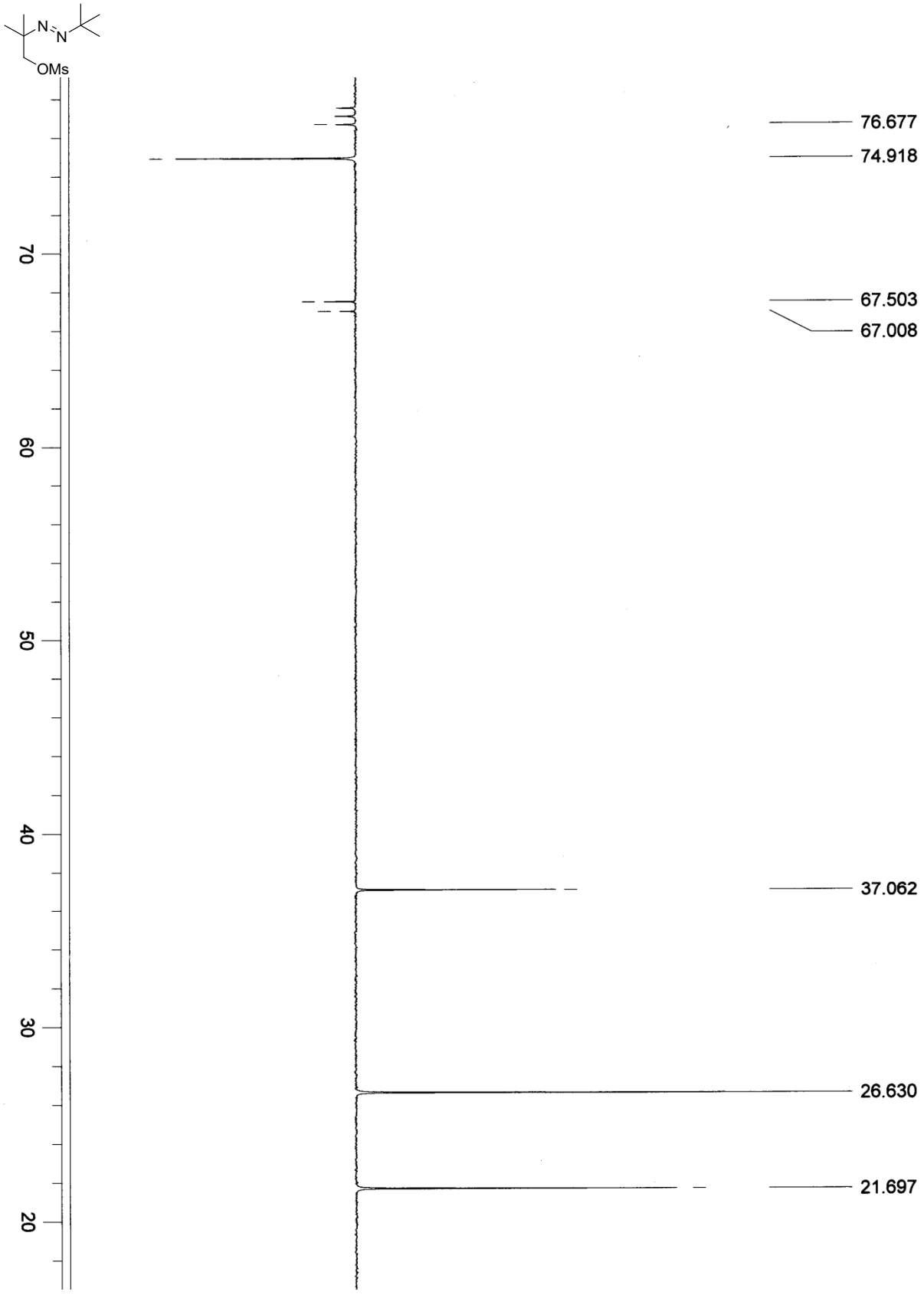
(*E*)-2-(2-tert-Butyldiazenyl)-2-methylpropan-1-ol (6): ^{13}C NMR (APT)



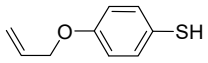
2-[(*E*)-2-[1-(Methansulfonyloxy)-2-methylpropan-2-yl]diazen-1-yl]-2-methyl propane (5): ^{1}H NMR

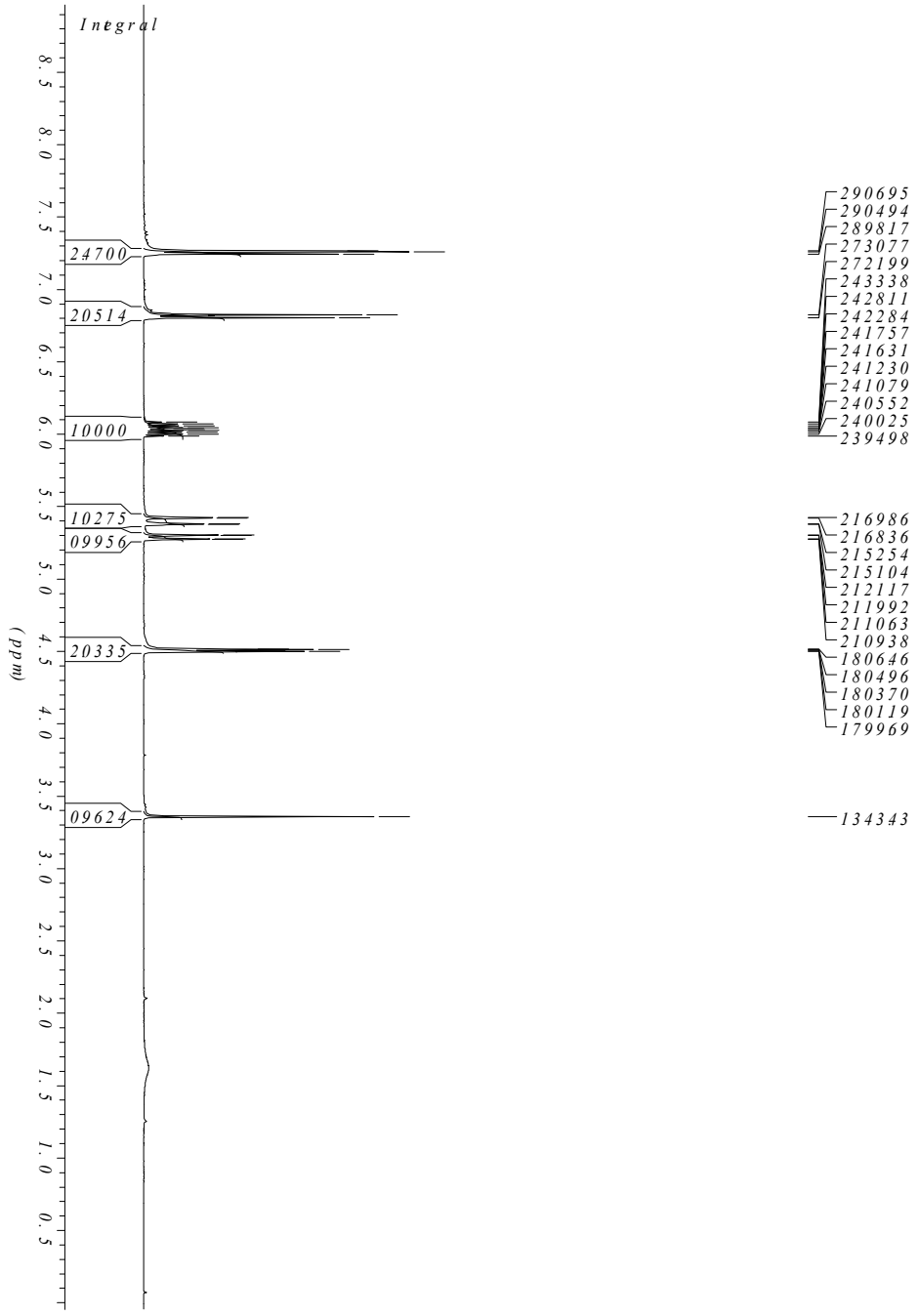


2-[(*E*)-2-[1-(Methansulfonyloxy)-2-methylpropan-2-yl]diazen-1-yl]-2-methyl propane (5): ^{13}C NMR (APT)

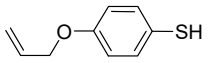


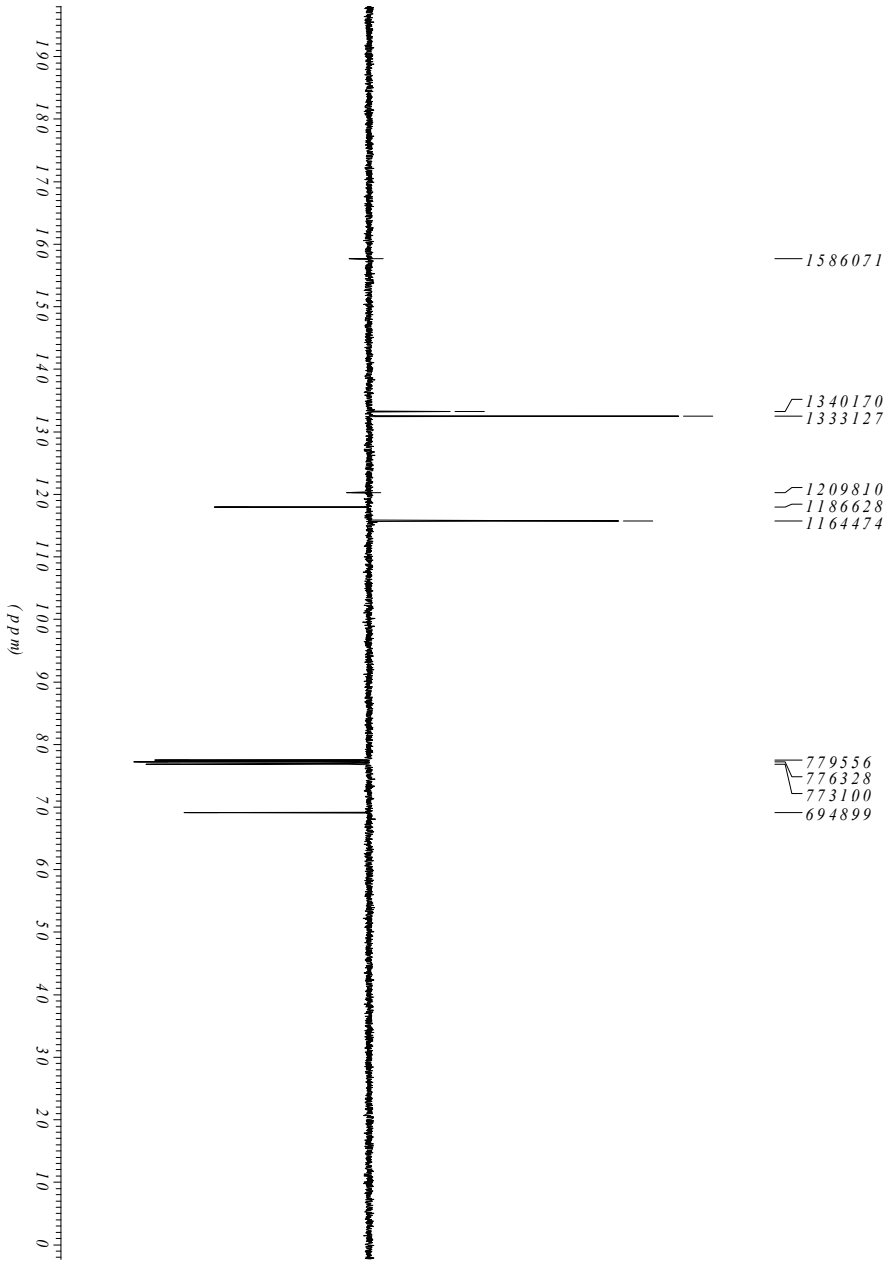
4-(Prop-2-en-1-yloxy)benzenethiol (4): ^{1}H NMR



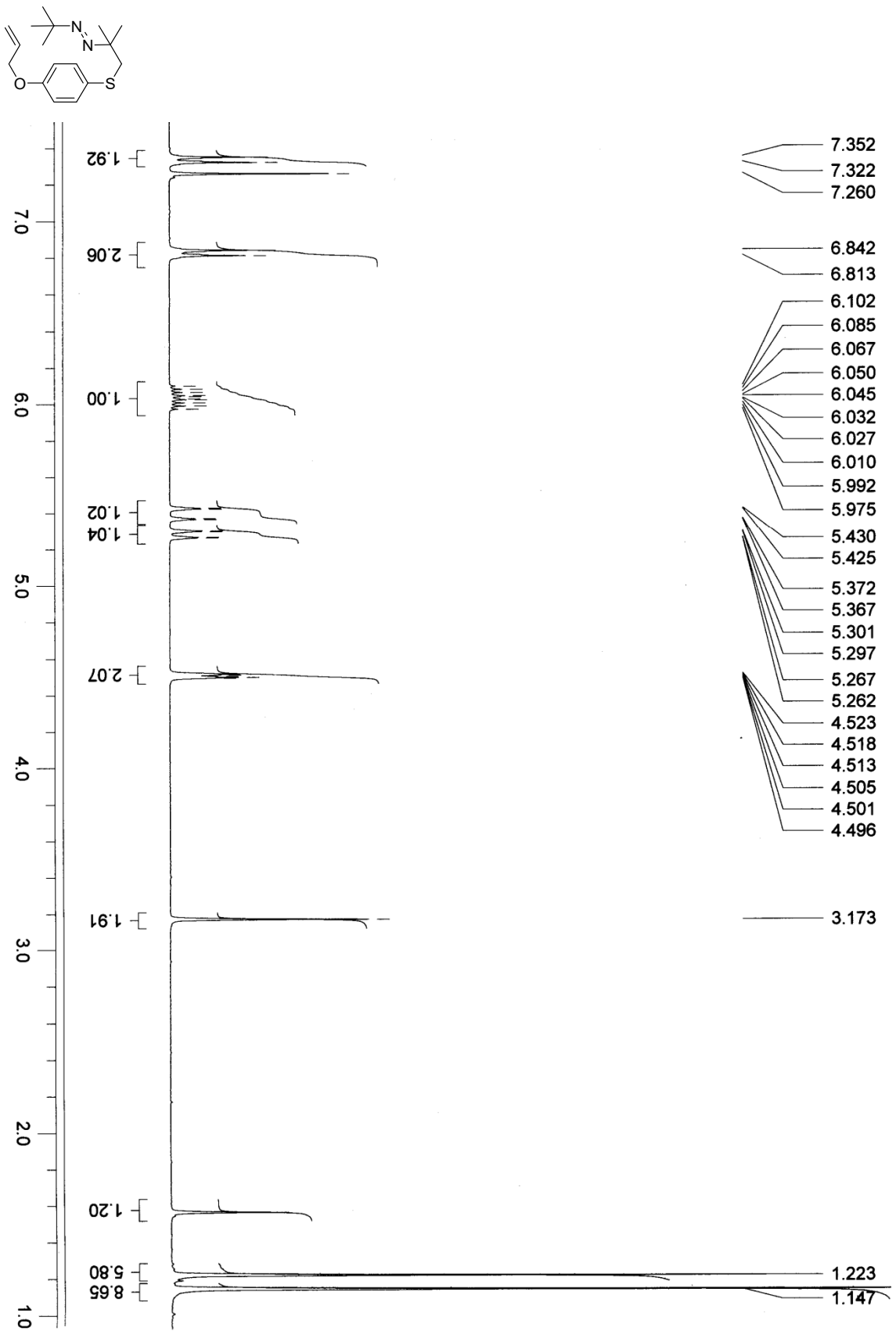


4-(Prop-2-en-1-yloxy)benzenethiol (4): ^{13}C NMR (APT)

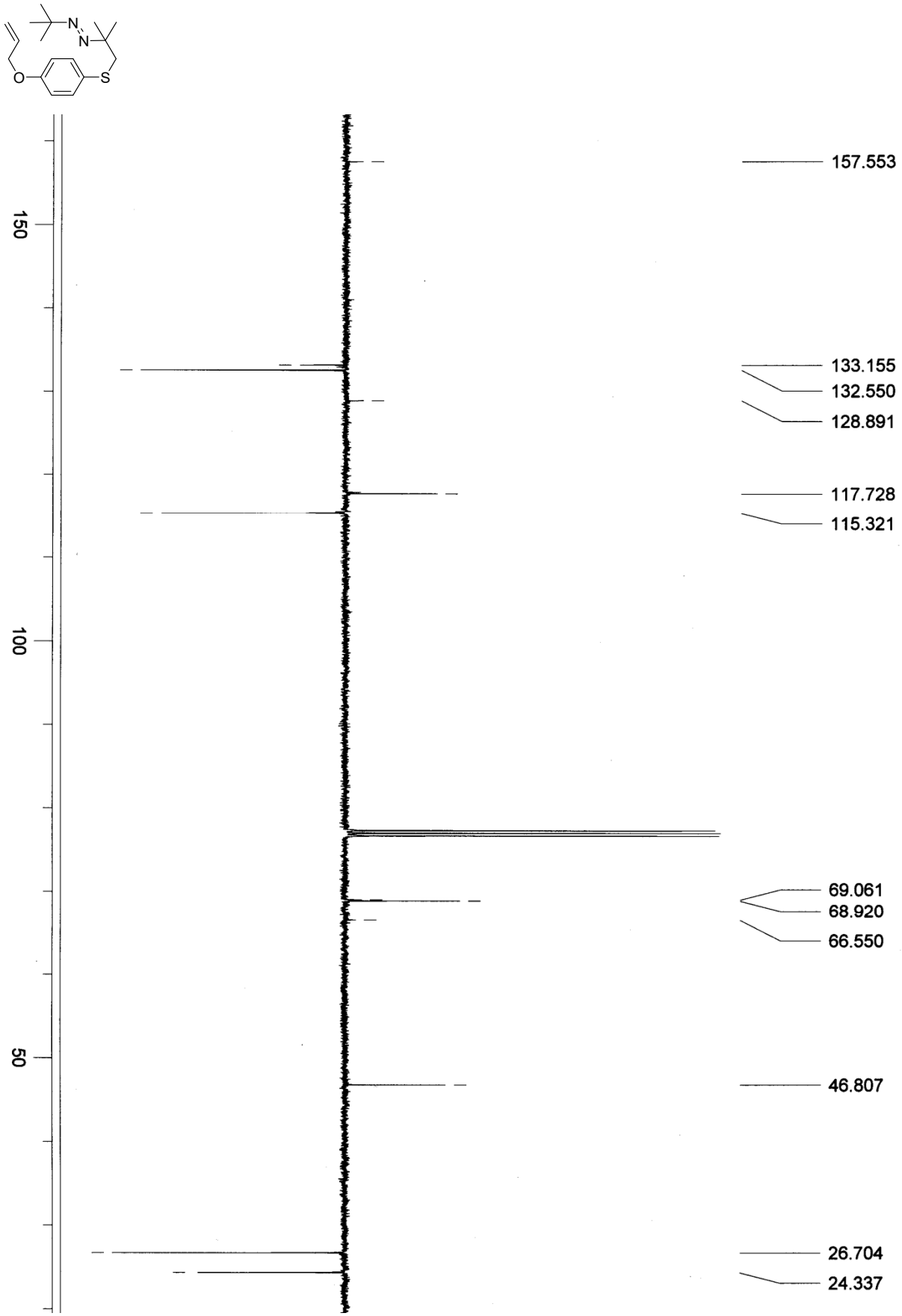




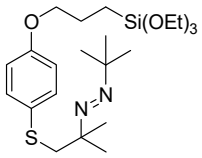
(*E*)-2-(1-(4-(Allyloxy)phenylthio)-2-methylpropan-2-yl)-1-tert-butyldiazene (3): ^{1}H NMR

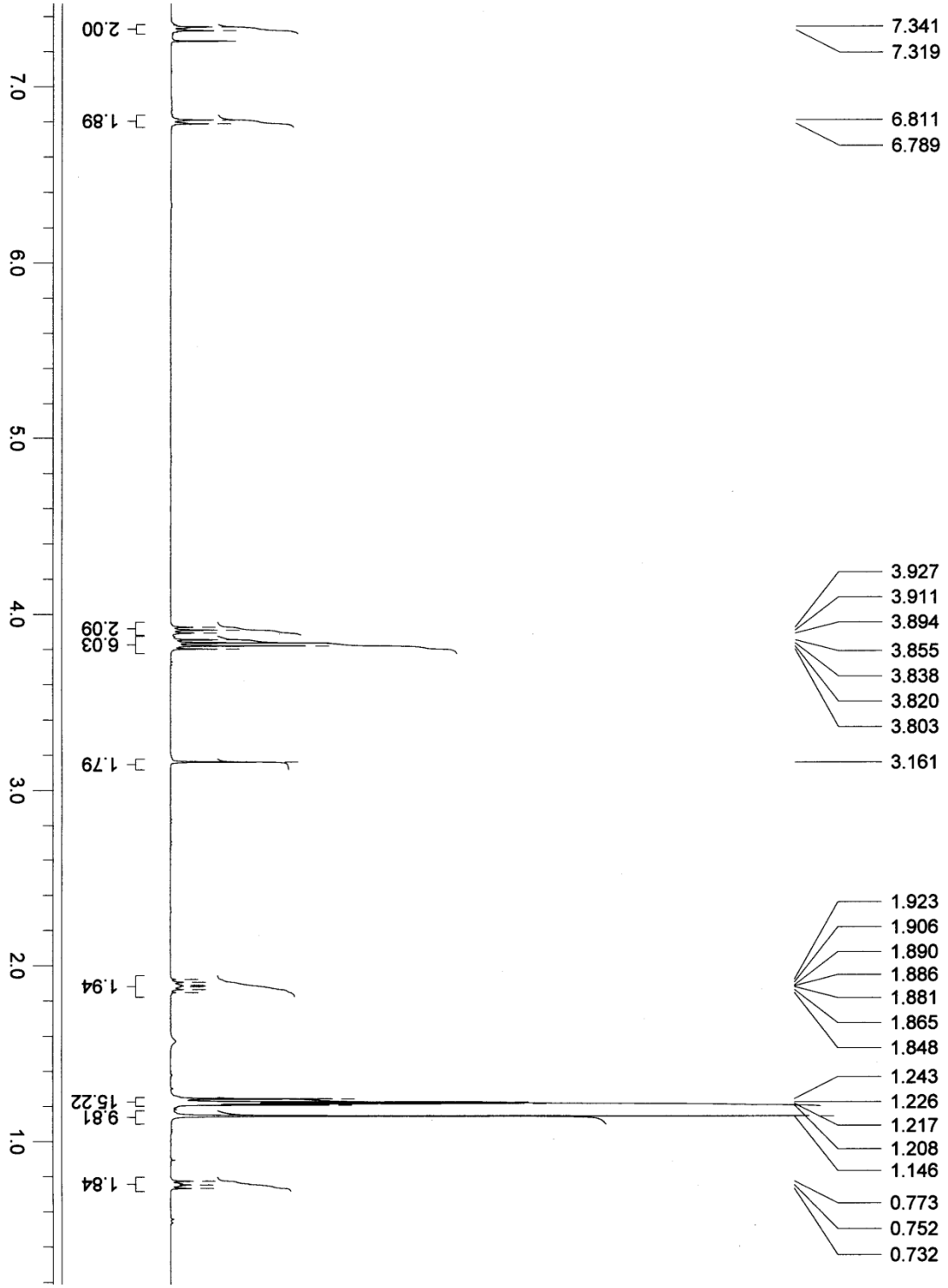


(*E*)-2-(1-(4-(Allyloxy)phenylthio)-2-methylpropan-2-yl)-1-tert-butyldiazene (3): ^{13}C NMR (APT)

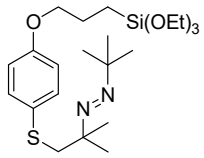


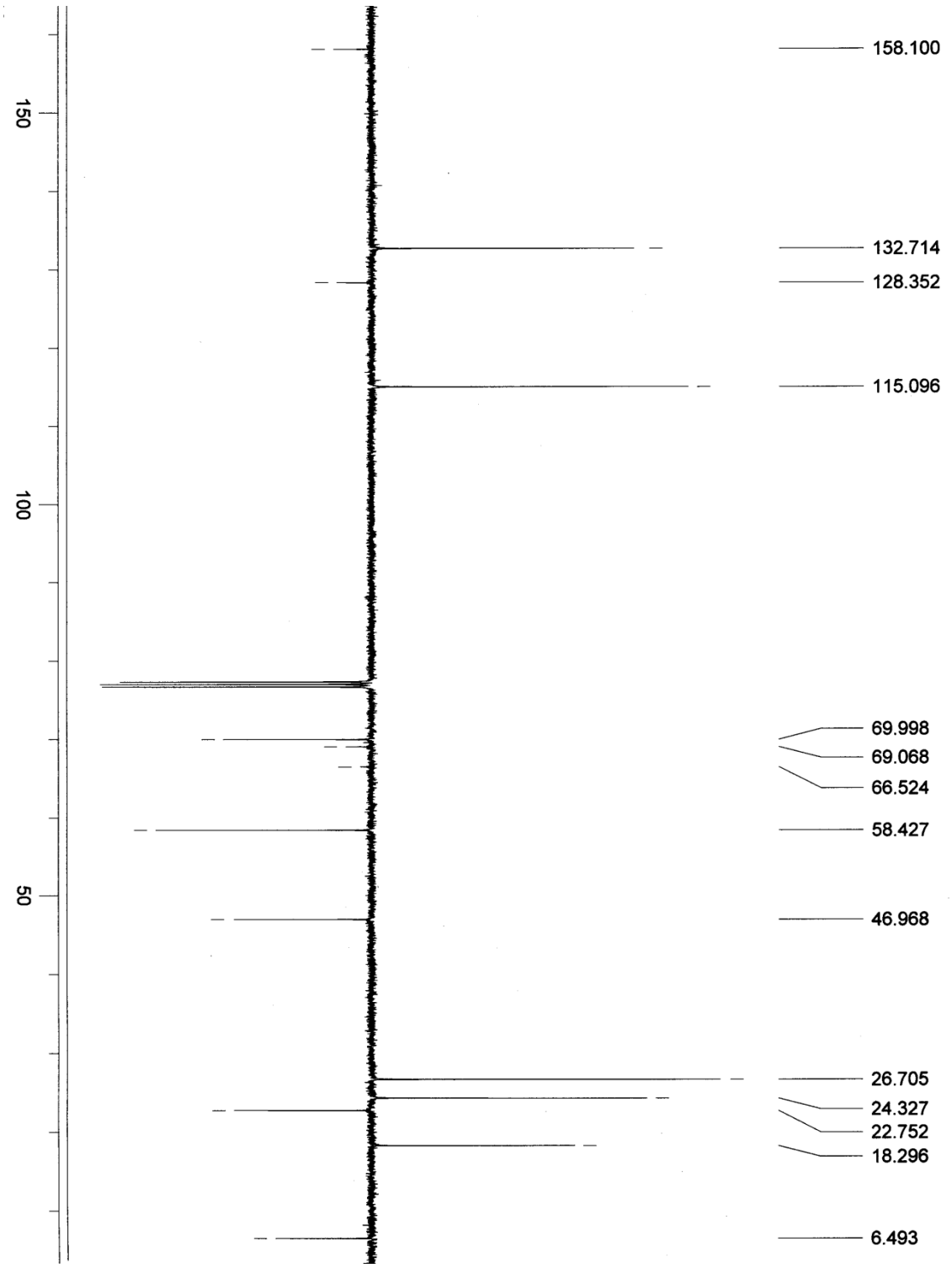
(*E*)-2-(1-(4-(3-(Triethoxysilyl)propoxy)phenylthio)-2-methylpropan-2-yl)-1-tert-butyldiazene (1): ^{1}H NMR



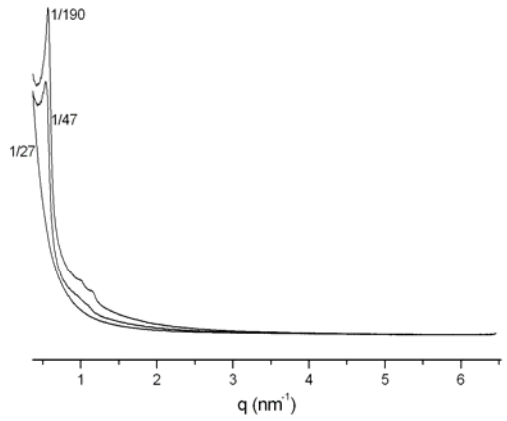


(*E*)-2-(1-(4-(3-(Triethoxysilyl)propoxy)phenylthio)-2-methylpropan-2-yl)-1-tert-butyldiazene (1): ^{13}C NMR (APT)

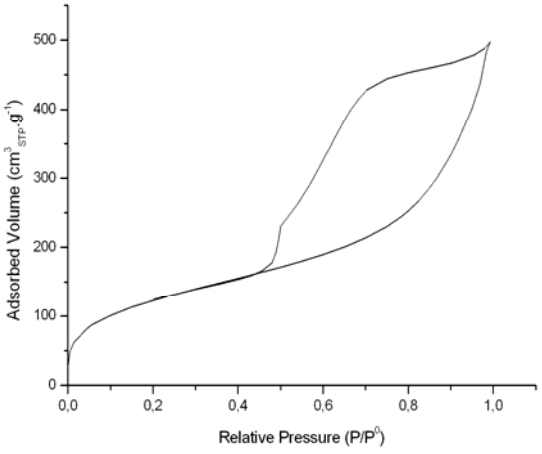




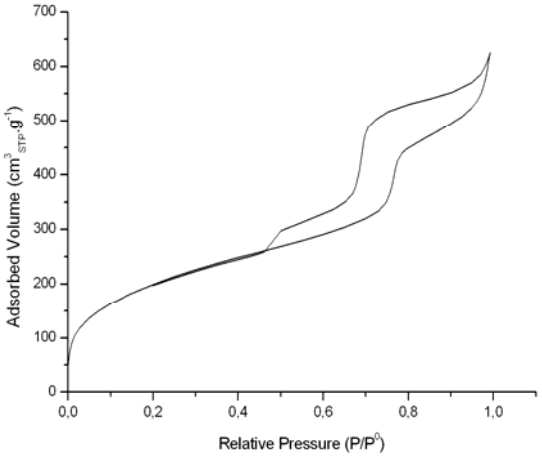
Small Angle X-Ray Scattering (SAXS): SBA_{27}-1, SBA_{47}-1, SBA_{190}-1.



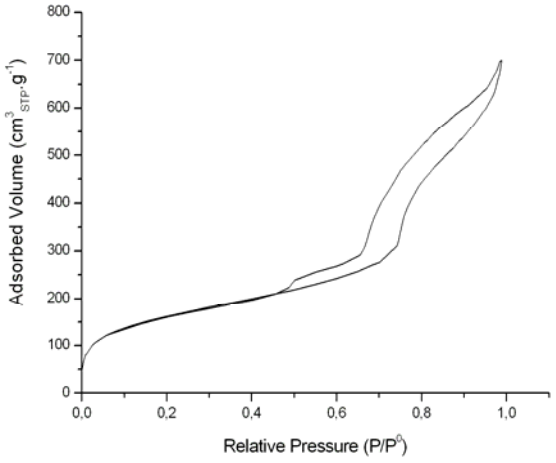
Nitrogen adsorption/desorption analysis: SBA_{27}-1



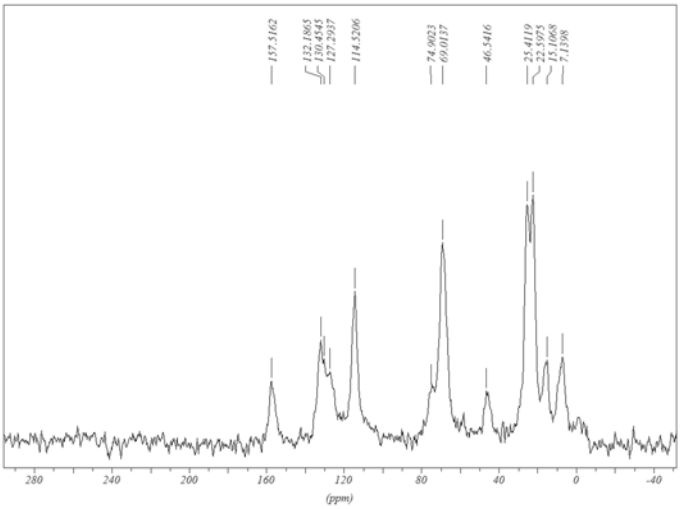
Nitrogen adsorption/desorption analysis: SBA_{47}-1



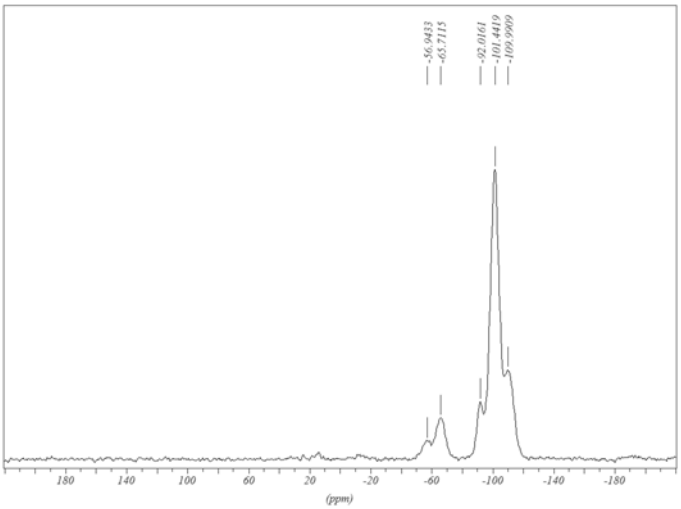
Nitrogen adsorption/desorption analysis: SBA_{190}-1



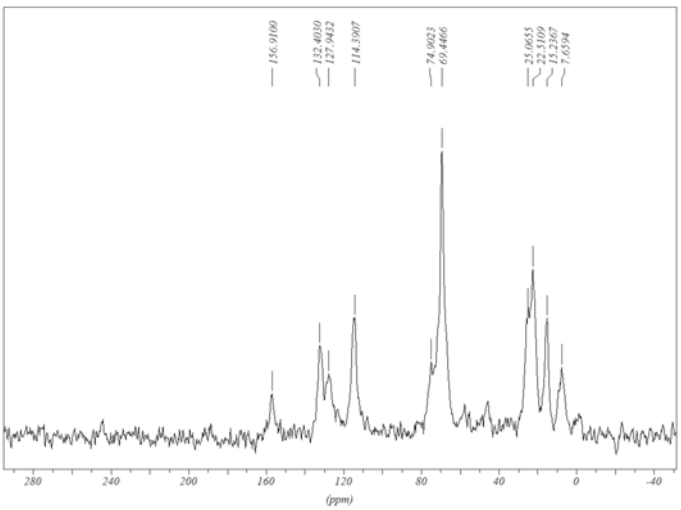
^{13}C CP-MAS solid state NMR of SBA$_{27}$-1:



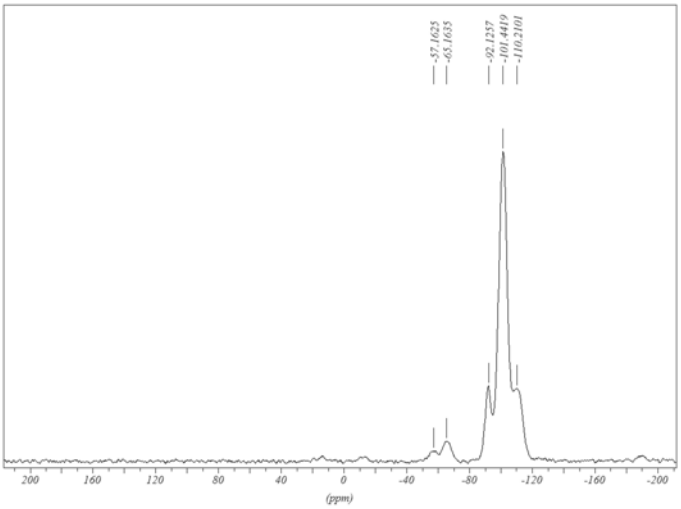
^{29}Si CP-MAS solid state NMR of SBA$_{27}$-1:



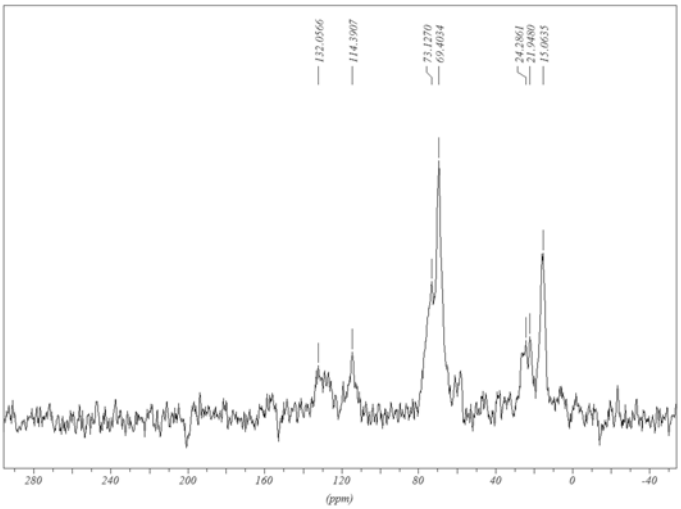
^{13}C CP-MAS solid state NMR of SBA$_{47}$-1:



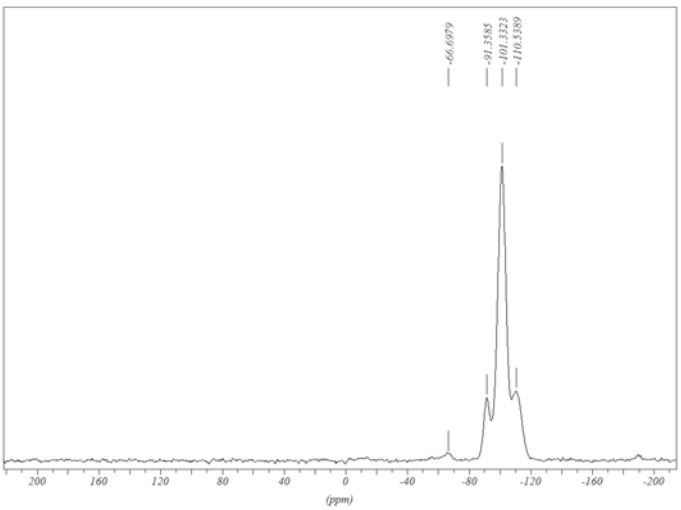
^{29}Si CP-MAS solid state NMR of SBA$_{47}$-1:



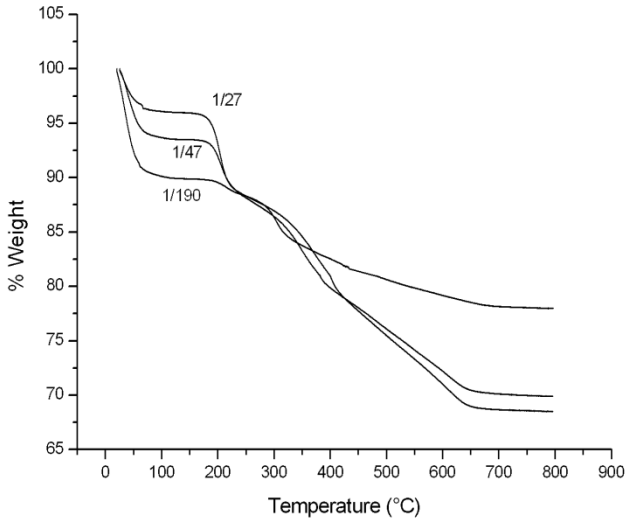
^{13}C CP-MAS solid state NMR of SBA$_{190}$-1:



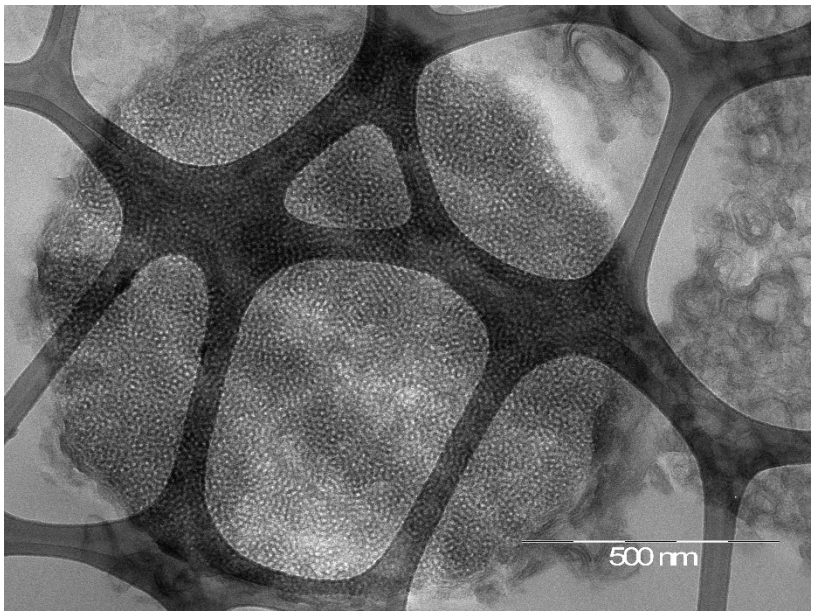
^{29}Si CP-MAS solid state NMR of SBA$_{190}$-1:



TGA for SBA_{27}-1, SBA_{47}-1, SBA_{190}-1:



TEM for SBA_{27}-1



TEM for SBA_{47}-1