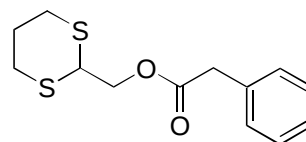


Supporting Information, Page 1:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

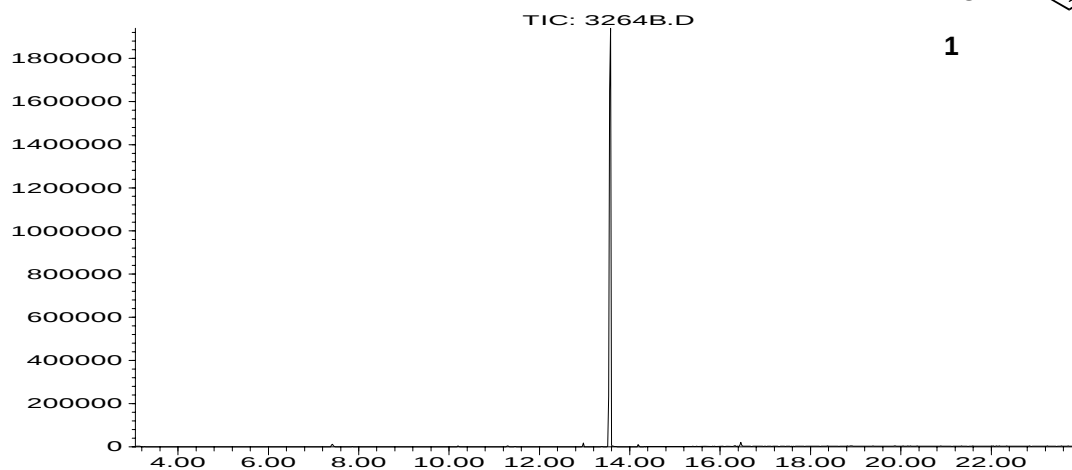
Dim Phenylacetate (1)

GC-MS (M.W. = 268.40(±9)) + ^1H NMR

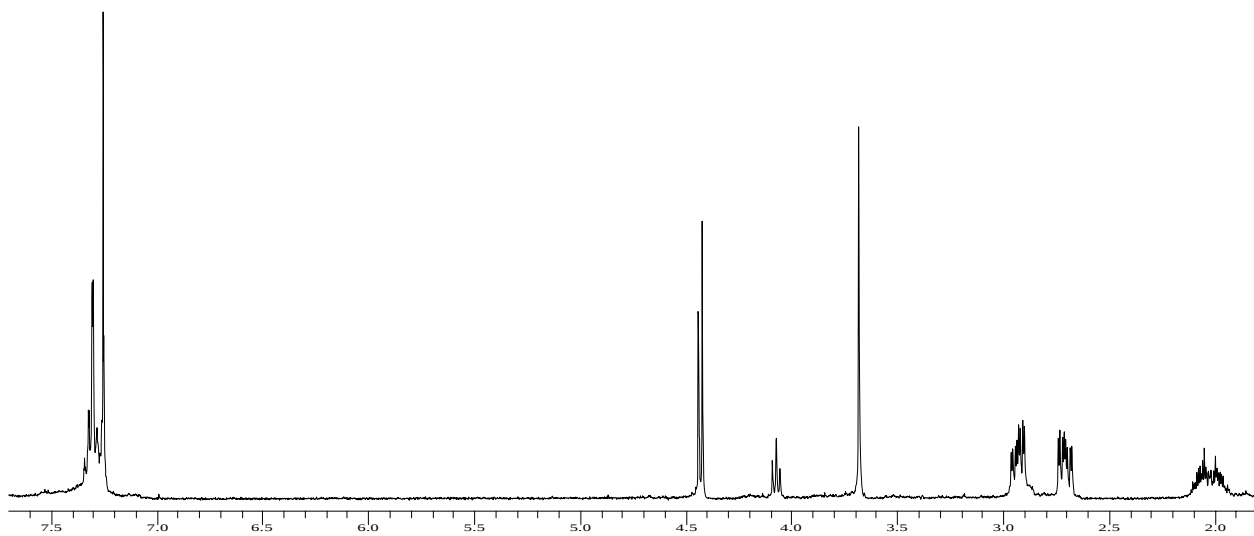
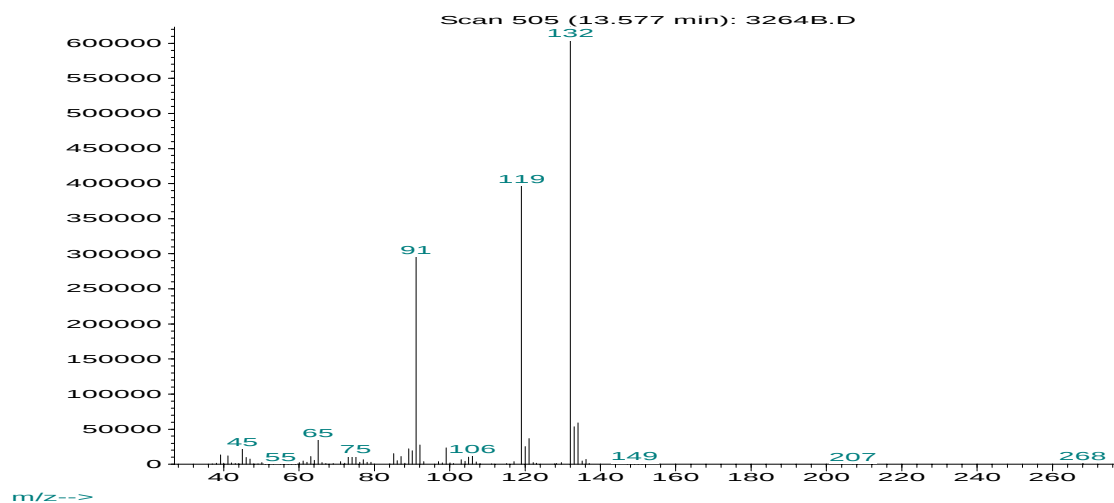


1

Abundance



Abundance



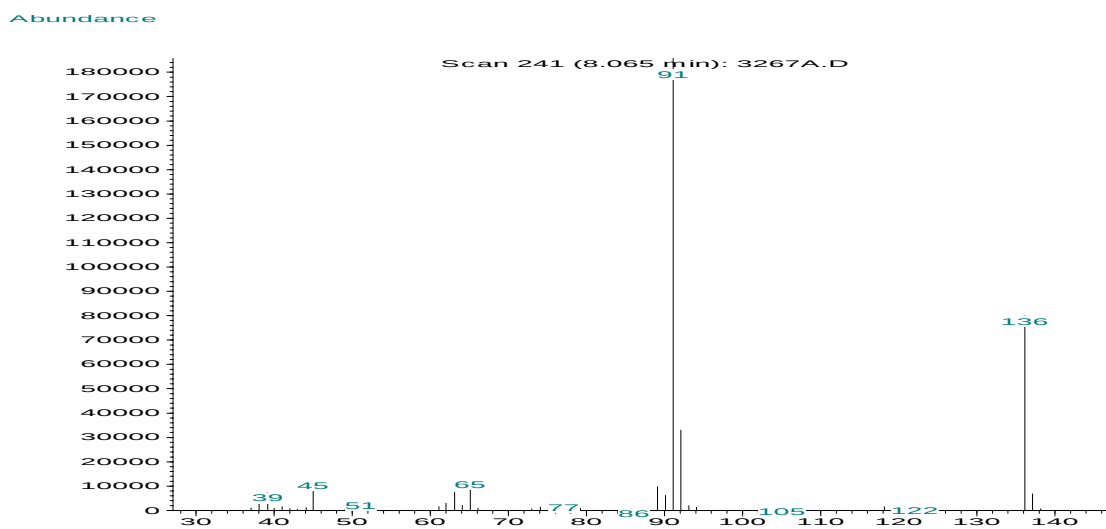
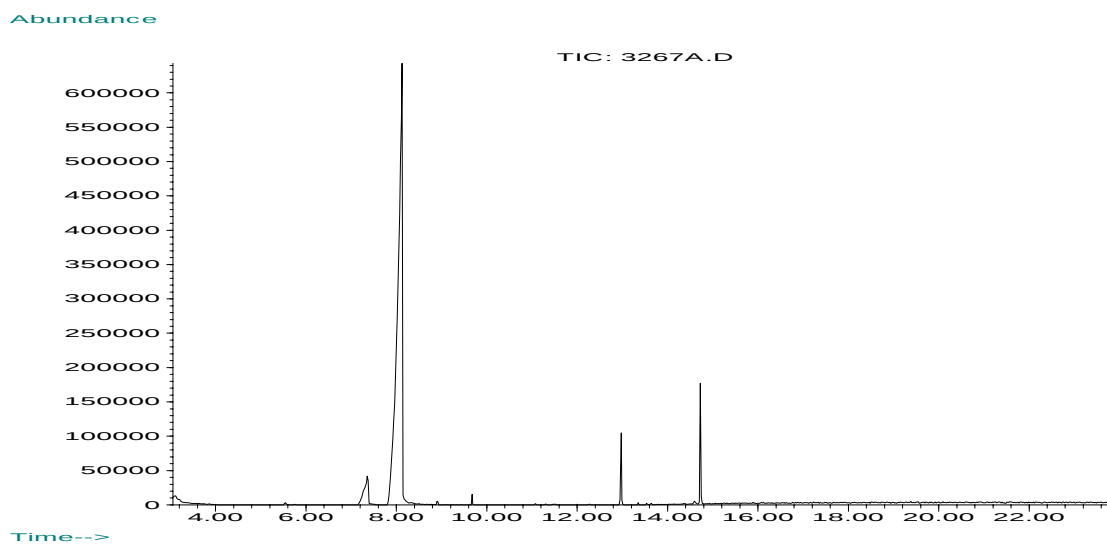
Supporting Information, Page 2:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

Electrolysis of **Dim Phenyllacetate (1)** – 2nd ether extract (from acidified solution)

GC-MS

Phenylacetic acid: M.W. = 136.150(±3)

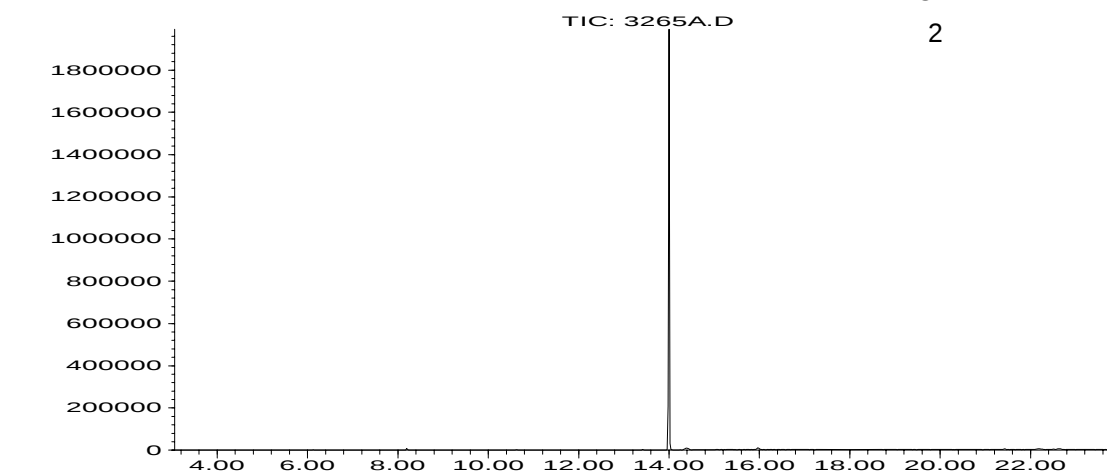
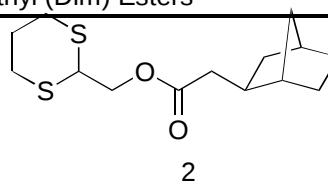


Supporting Information, Page 3:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

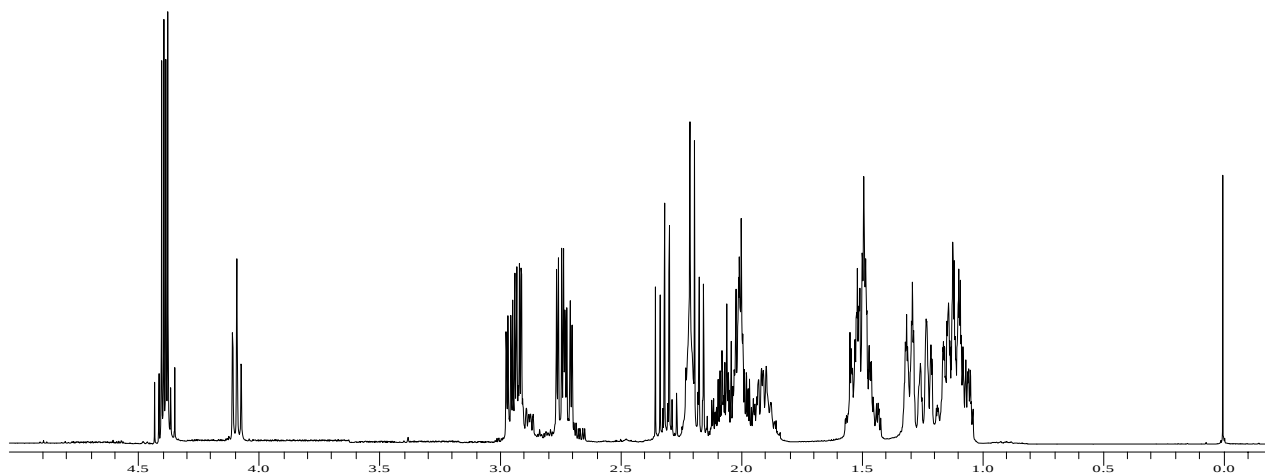
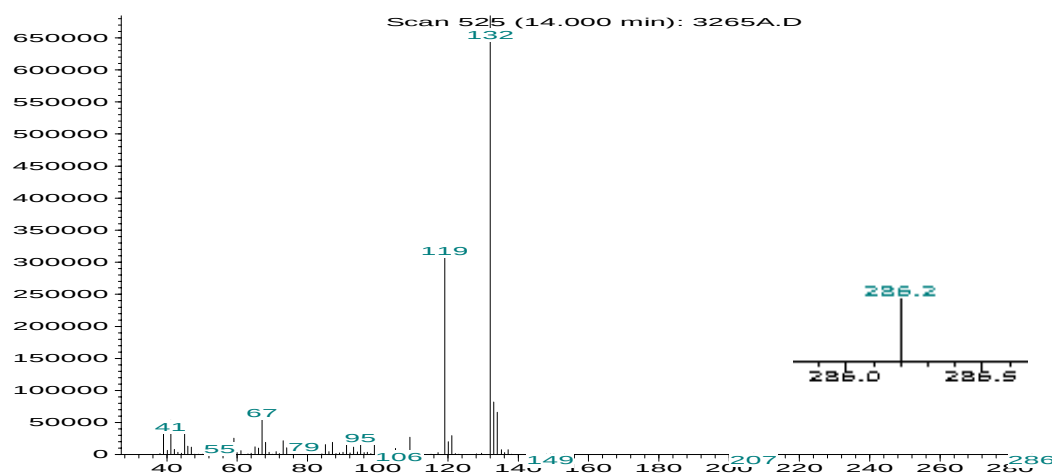
Dim Norbornylacetate (2)

GC-MS (M.W. = 286.46(±9)) + ^1H NMR



Time-->

Abundance



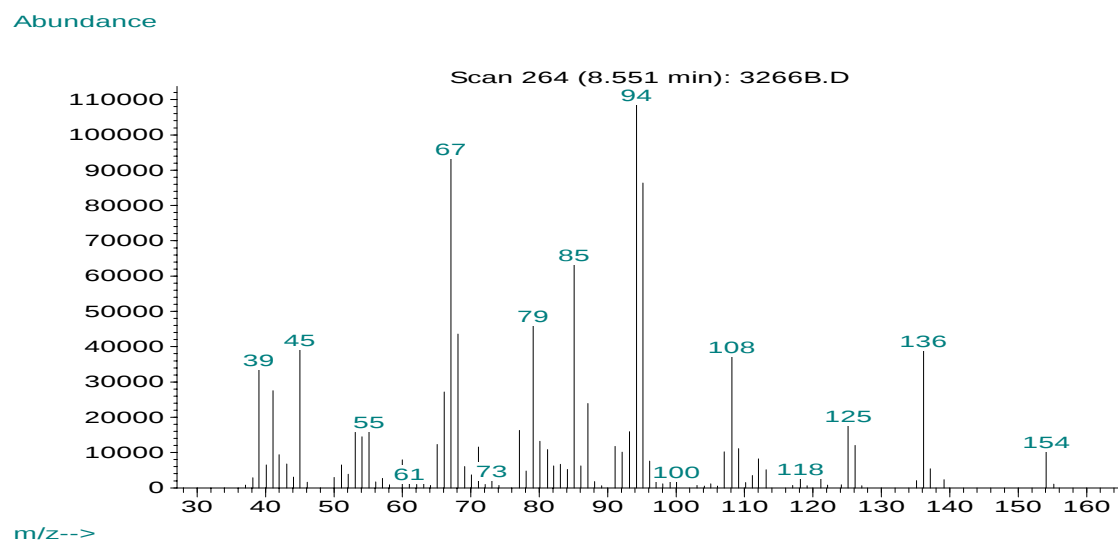
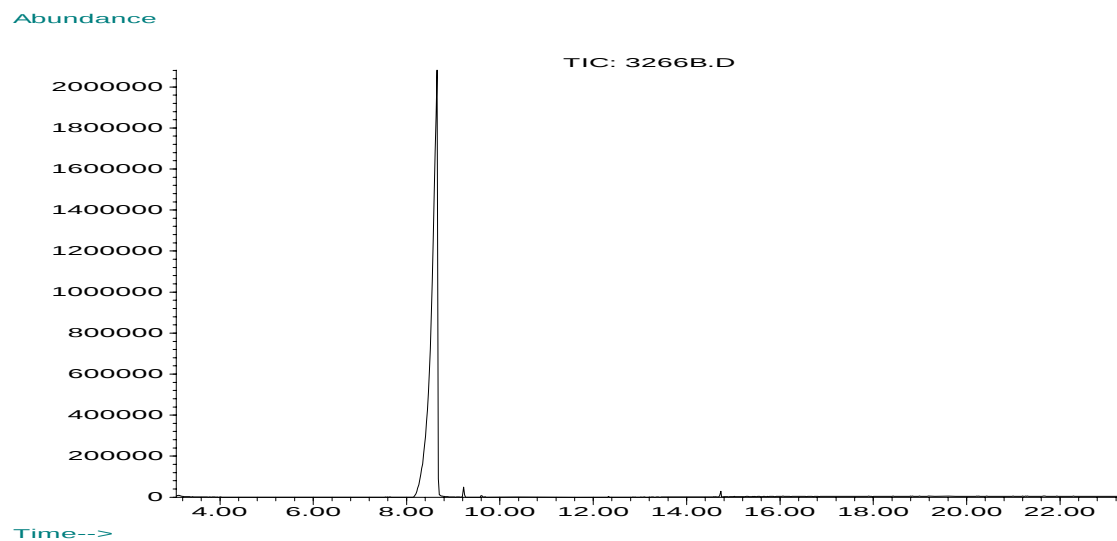
Supporting Information, Page 4:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

Electrolysis of **Dim Norbornylacetate (2)** – 2nd ether extract

GC-MS

Norbornylacetic acid: M.W. = 154.209(±3)

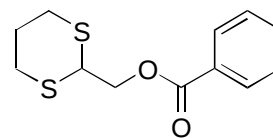


Supporting Information, Page 5:

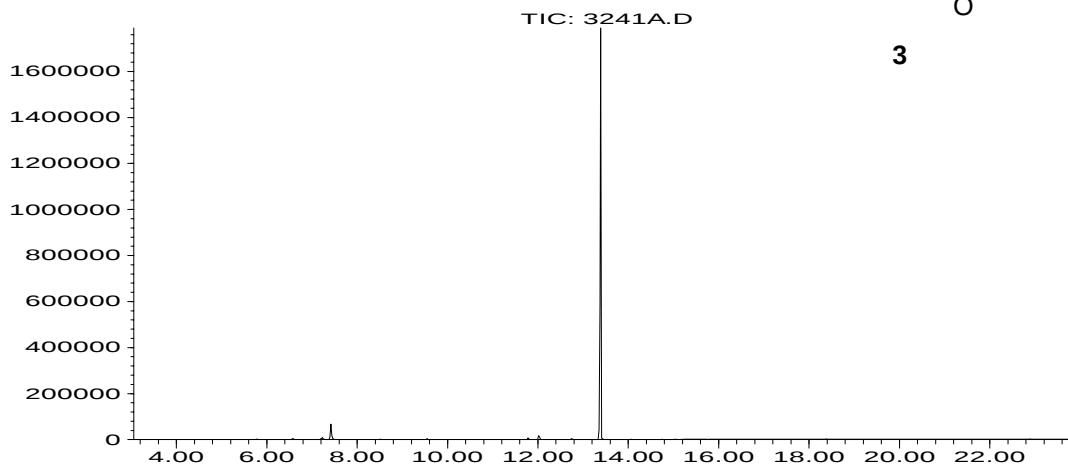
Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

Dim Benzoate (3)

GC-MS (M.W. = 254.37($\pm$ 9)) + ^1H NMR

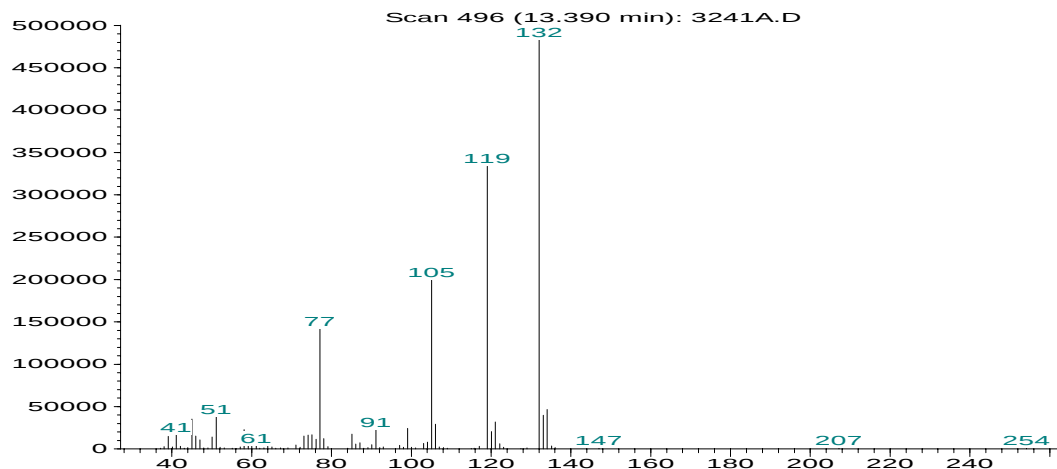


Abundance

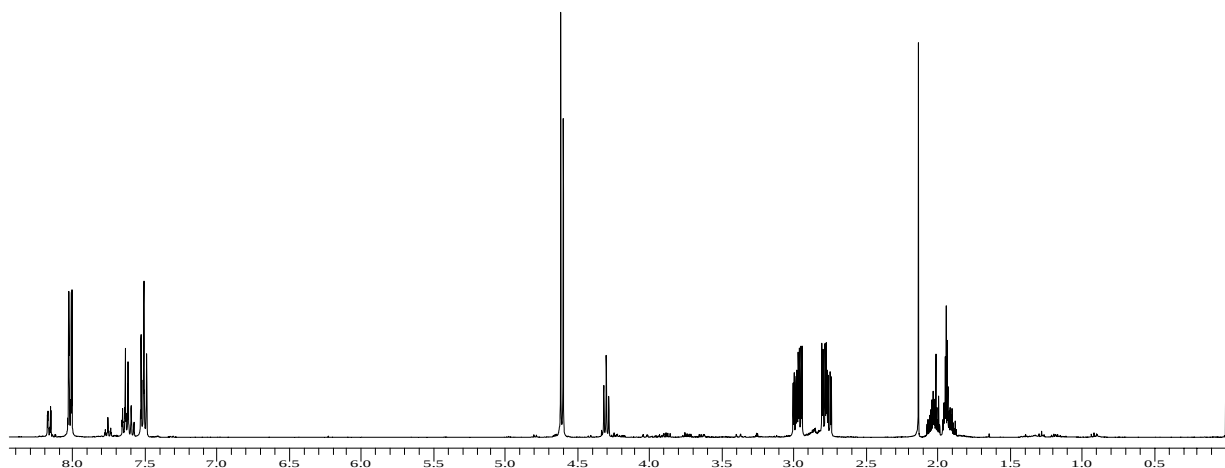


Time-->

Abundance



m/z-->



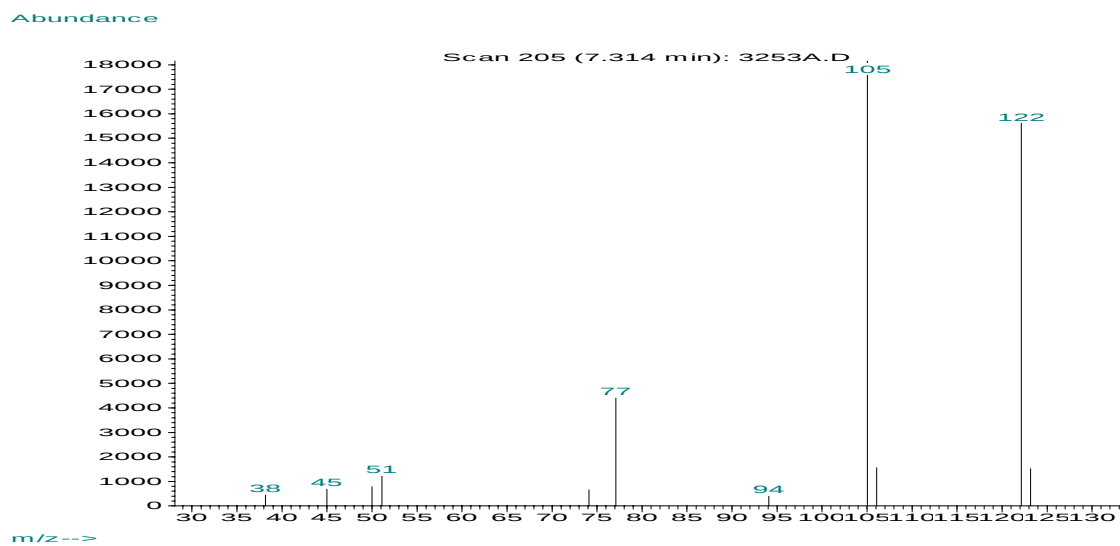
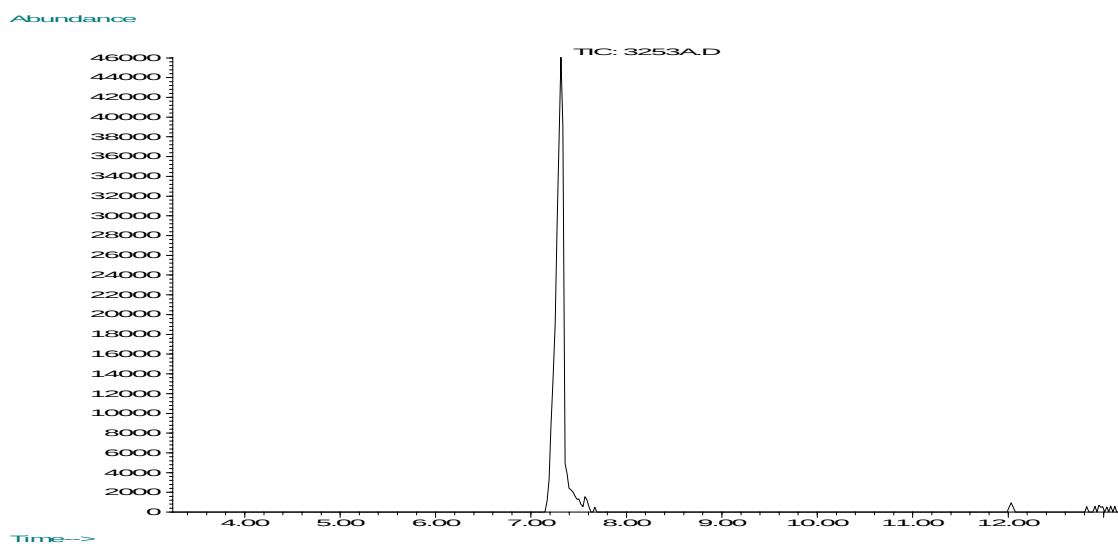
Supporting Information, Page 6:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

Electrolysis of **Dim Benzoate (3)** – 2nd ether extract (from acidified solution)

GC-MS

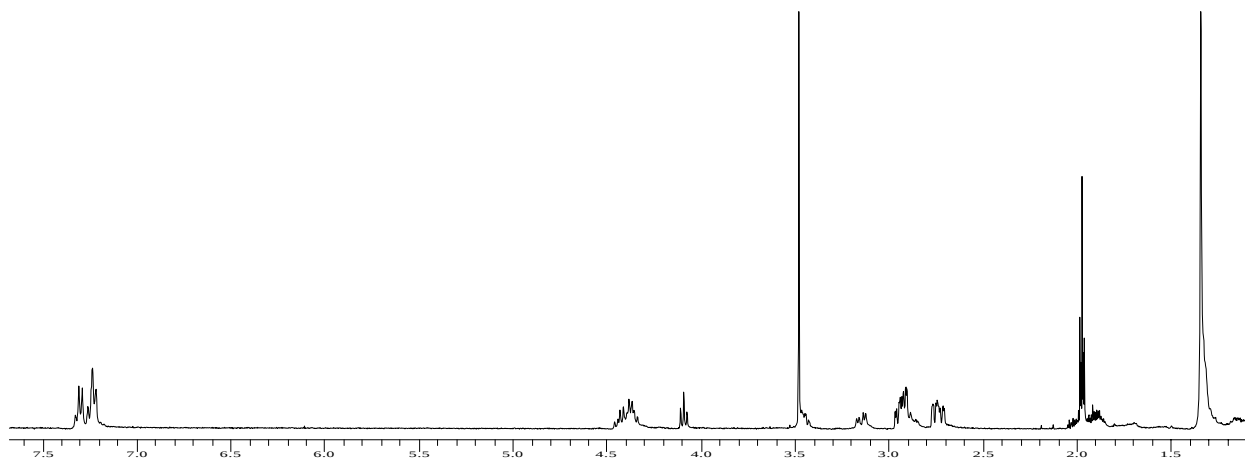
Benzoic acid: M.W. = 122.123(±3)



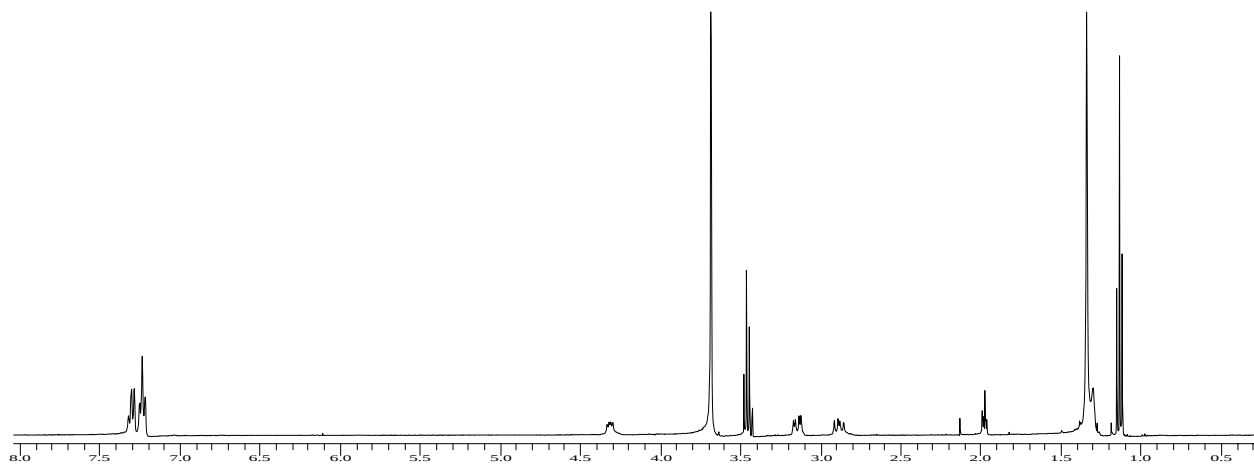
Supporting Information, Page 7:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical
Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

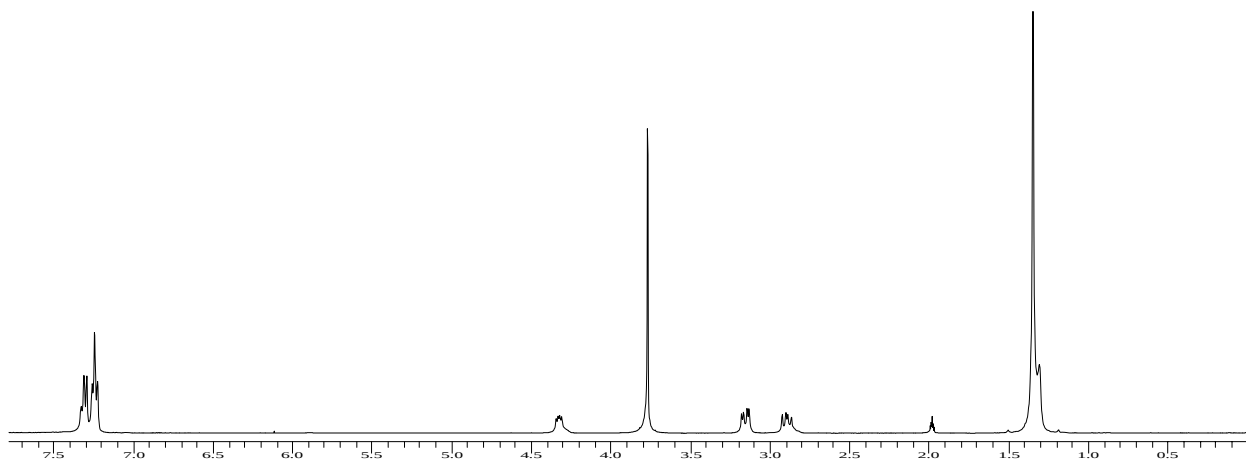
N-*t*-BOC-PheODim (CD₃CN-D₂O)



2nd Etherial extract after electrolysis (from acidified solution) – some ether is present



N-*t*-BOC-PheOH (from Aldrich)



Supporting Information, Page 8:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

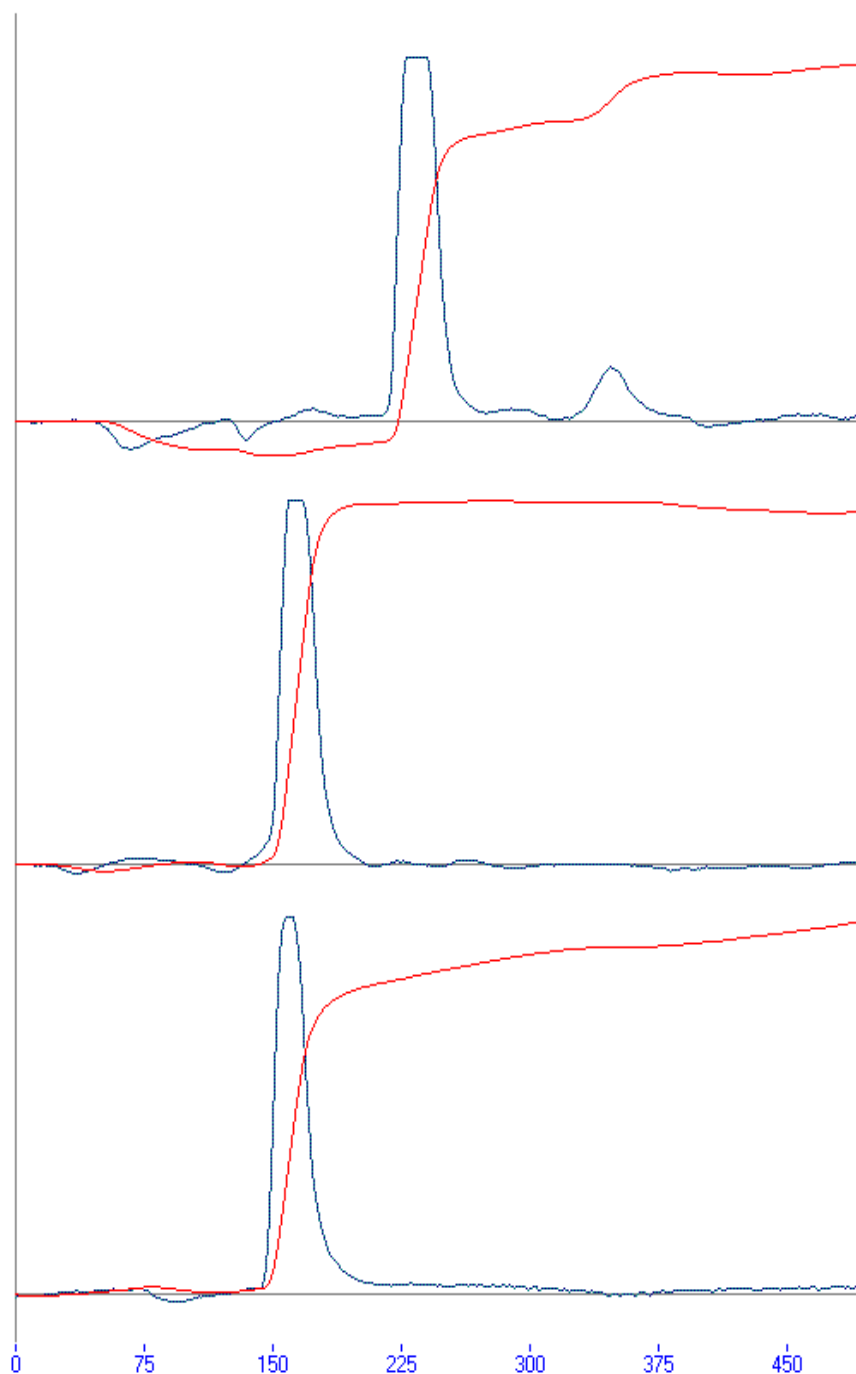
HPLC chromatograms for N-*t*-BOC-phenylalanine:

(top to bottom)

(a) Dim ester (**4**)

(b) Second ethereal extract (from acidified solution)

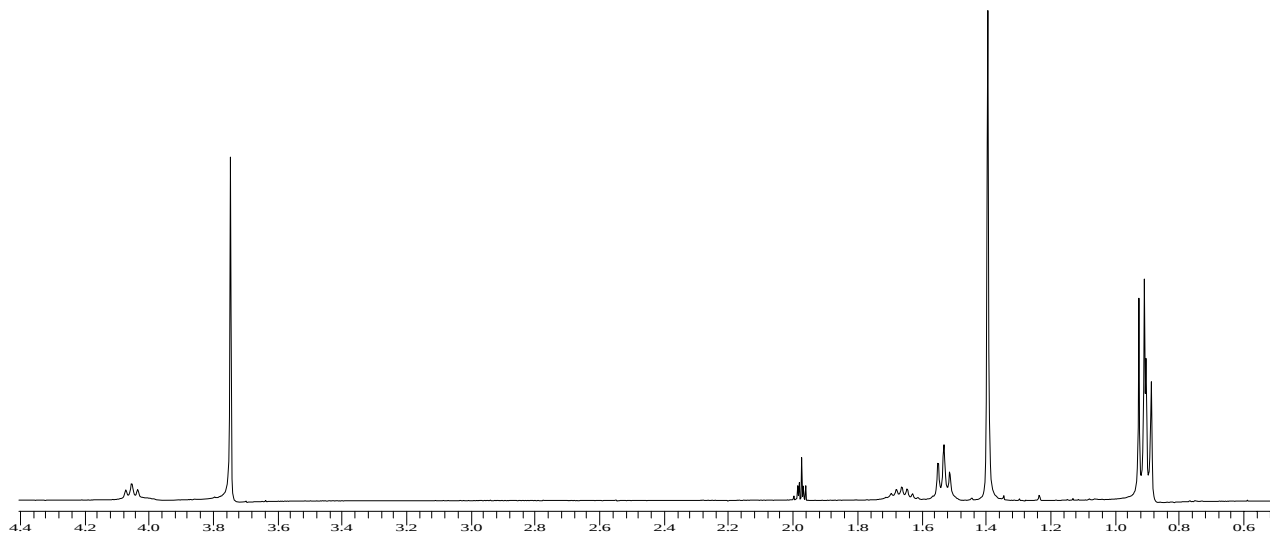
(c) N-*t*-BOC-Phe-OH (from Aldrich) – matching (b)



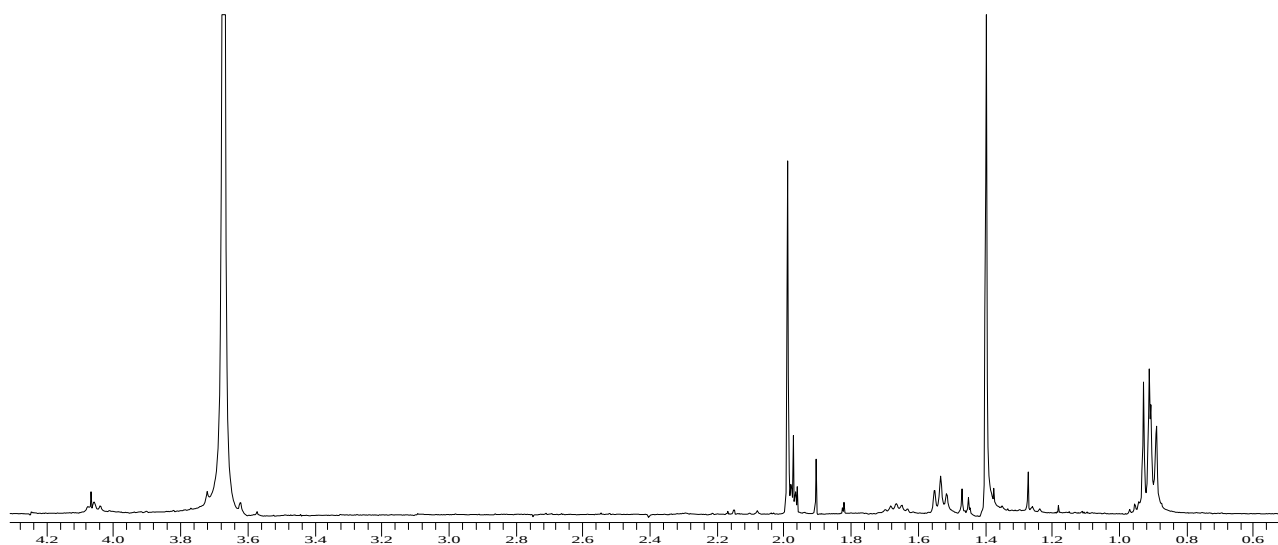
Supporting Information, Page 9:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical
Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

N-*t*-BOC-Leu-OH (Aldrich) (CD₃CN-D₂O)



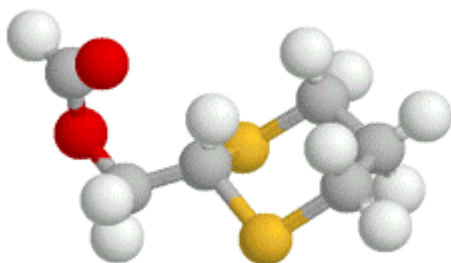
2nd Etherial extract after electrolysis of N-*t*-BOC-Leu-ODim (from acidified solution)



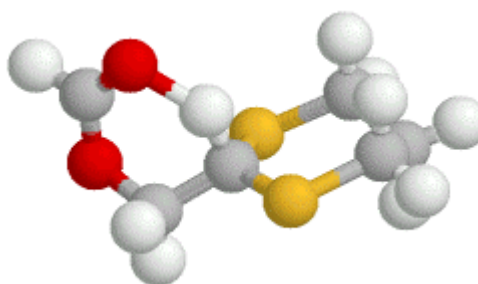
Supporting Information, Page 10:

Loren A. Barnhurst, Yongqin Wan and Andrei G. Kutateladze Efficient Electrochemical
Deprotection of Carboxylic Acids from Their 1,3-Dithianyl-2-methyl (Dim) Esters

Ab initio results:



**Starting 2-formyloxymethyl-1,3-dithiane
cation-radical**



**Transition State for concerted elimination
from the cation-radical**

Cartesian coordinates:

C 2.750855 0.595671 0.539330
C 1.600507 1.581251 0.360531
C 2.261647 -0.816350 0.888337
H 3.402362 0.923355 1.357807
H 3.355136 0.558907 -0.371789
H 1.989326 2.551154 0.033966
H 1.049029 1.739403 1.293616
S 0.444297 1.066375 -0.939303
C -0.278930 -0.351322 -0.065124
H 3.090329 -1.530117 0.909576
H 1.732206 -0.846216 1.846543
C -1.572993 -0.857066 -0.701830
H -0.422815 -0.170039 1.002258
S 1.111065 -1.447609 -0.370173
H -1.929545 -1.727271 -0.141521
H -1.436087 -1.117404 -1.753843
O -2.559055 0.175438 -0.696096
C -3.076323 0.448439 0.538080
H -3.878740 1.186189 0.440061
O -2.684143 -0.059433 1.568471

C 2.752142 0.469239 -0.005037
C 1.756121 1.544046 0.402853
C 2.384228 -0.911729 0.516702
H 3.726758 0.719797 0.428656
H 2.877817 0.455302 -1.092167
H 2.127458 2.534818 0.124447
H 1.583556 1.548723 1.483577
S 0.168686 1.420594 -0.470440
C -0.242565 -0.286889 -0.248817
H 3.146776 -1.654264 0.258963
H 2.281578 -0.915386 1.608032
C -1.507227 -0.660125 -1.043679
H -0.753675 -0.381398 0.855476
S 0.860542 -1.613956 -0.169481
H -1.776881 -1.704979 -0.856884
H -1.381191 -0.483383 -2.112008
O -2.621062 0.174292 -0.655545
C -2.871530 0.256699 0.653670
H -3.794523 0.805999 0.854584
O -2.145481 -0.211653 1.534533

MP2/6-31G(d) Energy (Hartrees):

-1178.8776251494

-1178.8369286617

ZPE (kcal/mol):

107.208

104.388