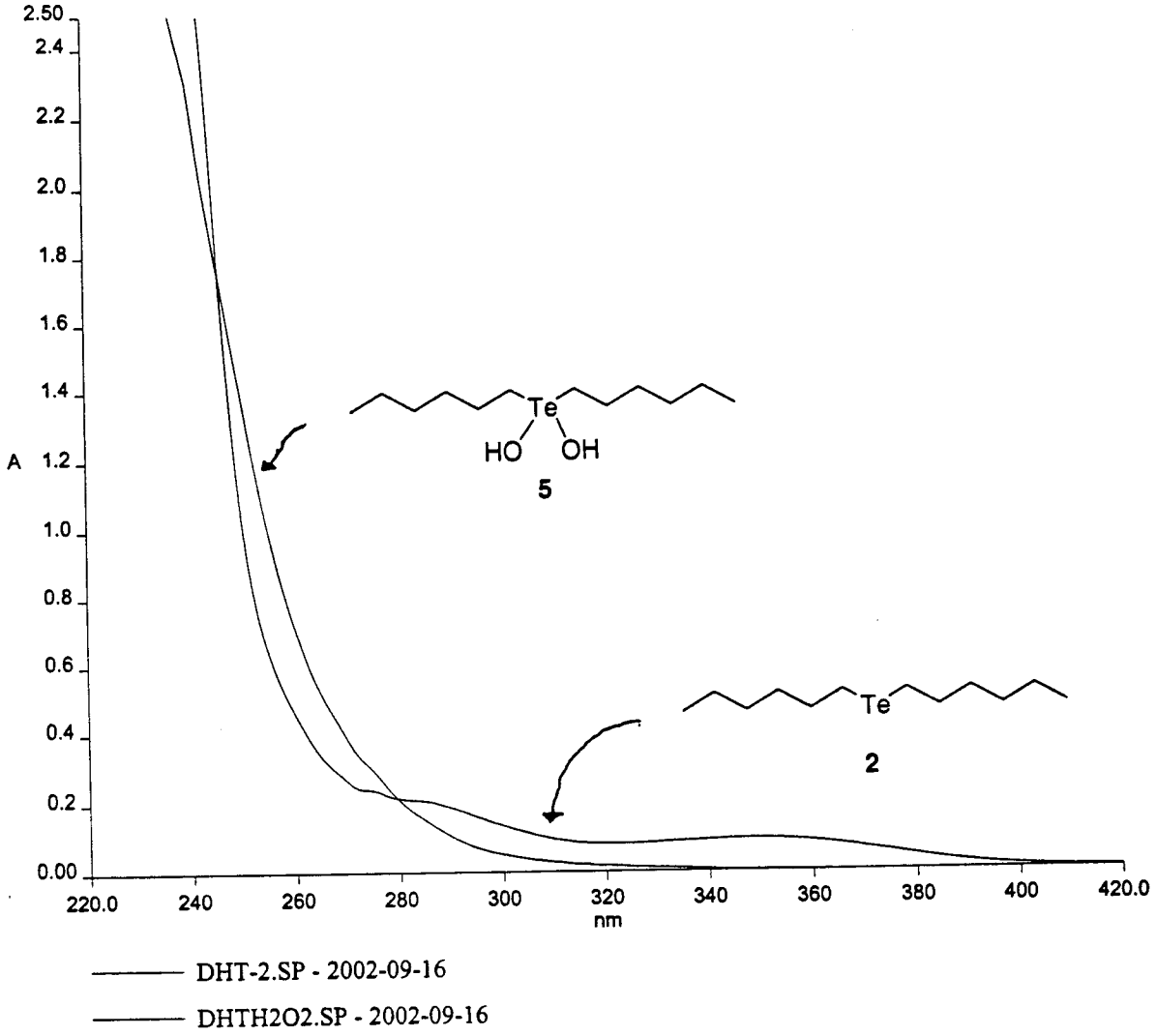

Figure S1. Absorption spectra of 2.5 x 10^{-4} M **2** and 2.5 x 10^{-4} M **5** in MeOH in 1-cm quartz cuvettes. Compound **2** was oxidized to **5** with 2.5 x 10^{-3} M H_2O_2.

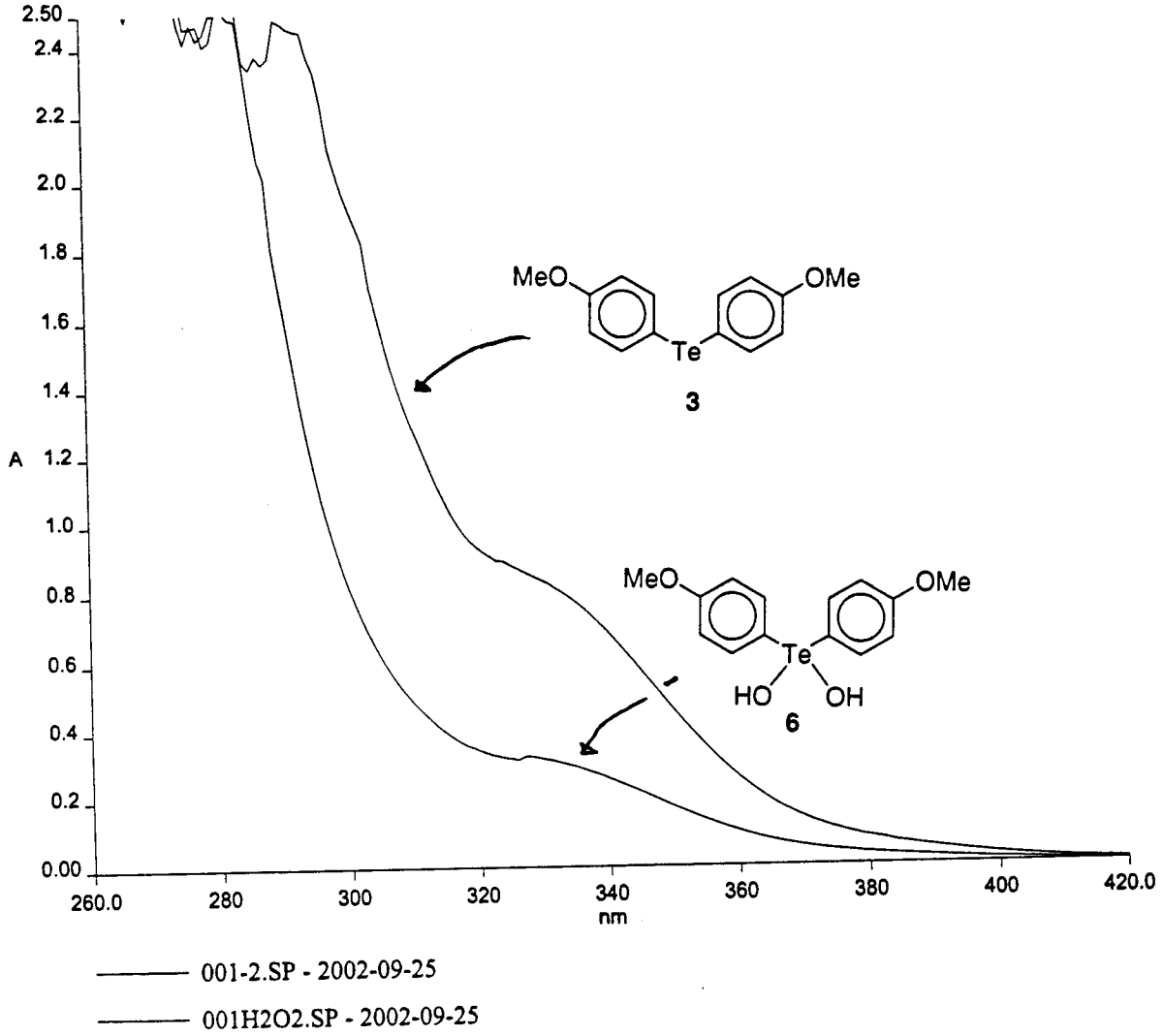

Figure S2. Absorption spectra of 1.0 x 10^{-3} M **3** and 1.0 x 10^{-3} M **6** in MeOH in 1-cm quartz cuvettes. Compound **3** was oxidized to **6** with 1.0 x 10^{-2} M H_2O_2.

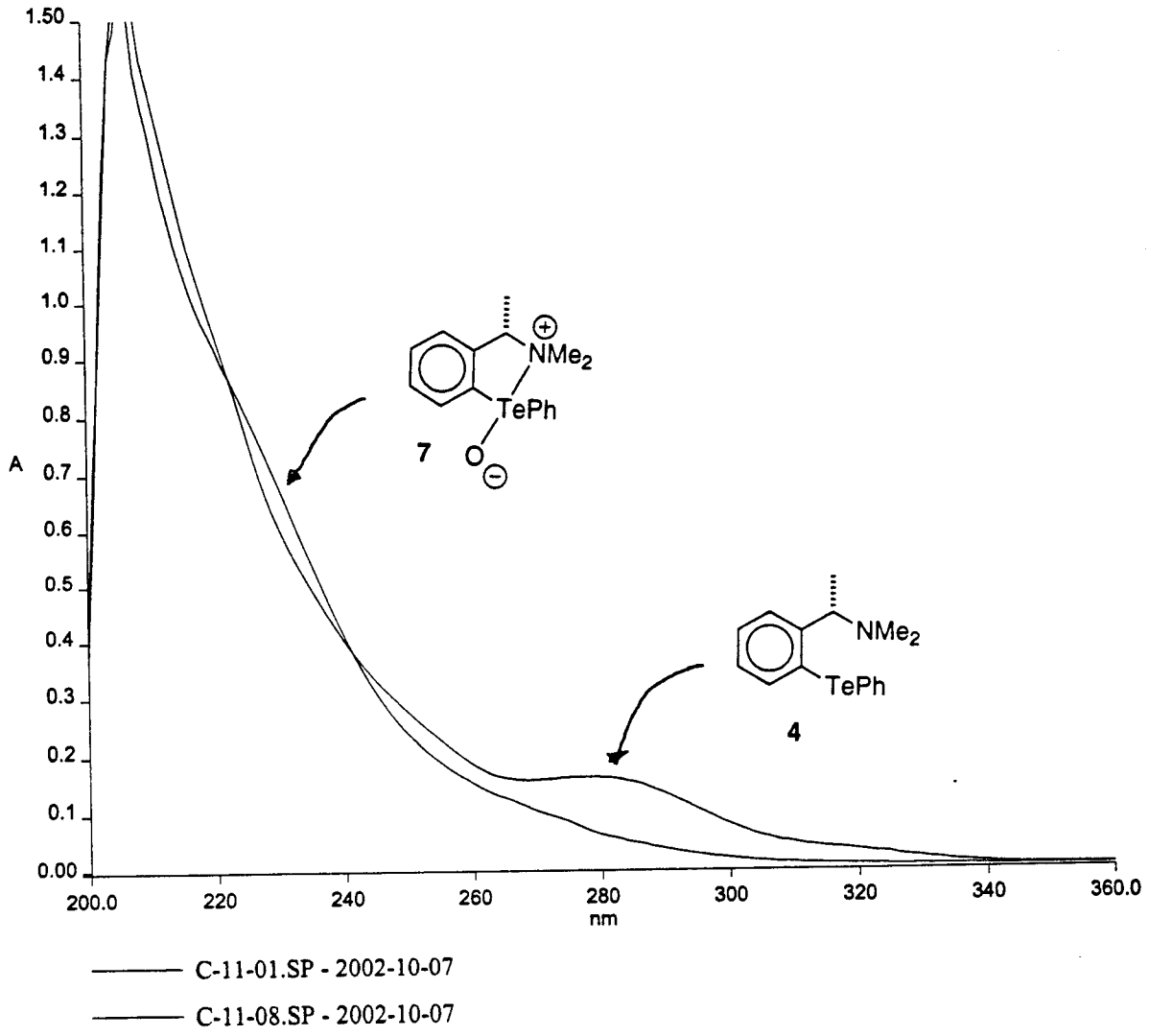

Figure S3. Absorption spectra of 1.0×10^{-3} M **4** and 1.0×10^{-3} M **7** in MeOH in 1-cm quartz cuvettes. Compound **4** was oxidized to **7** with 1.0×10^{-2} M H_2O_2.

I-KA-101a

Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
INOVA-400 "cosy.chem.buffalo.edu"
PULSE SEQUENCE
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Pulse 29.1 degrees
Acq. time 1.499 sec
Width 12001.2 Hz
16 repetitions
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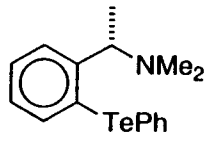
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 10 sec



4

I-KA-101A

Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
GEMINI-300 "roesy.chem.buffalo.edu"

PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 90.0 degrees
Acq. time 1.706 sec
Width 18761.7 Hz
64 repetitions
OBSERVE C13, 75.4536665 MHz
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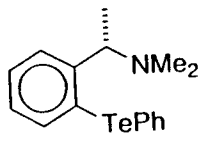
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536



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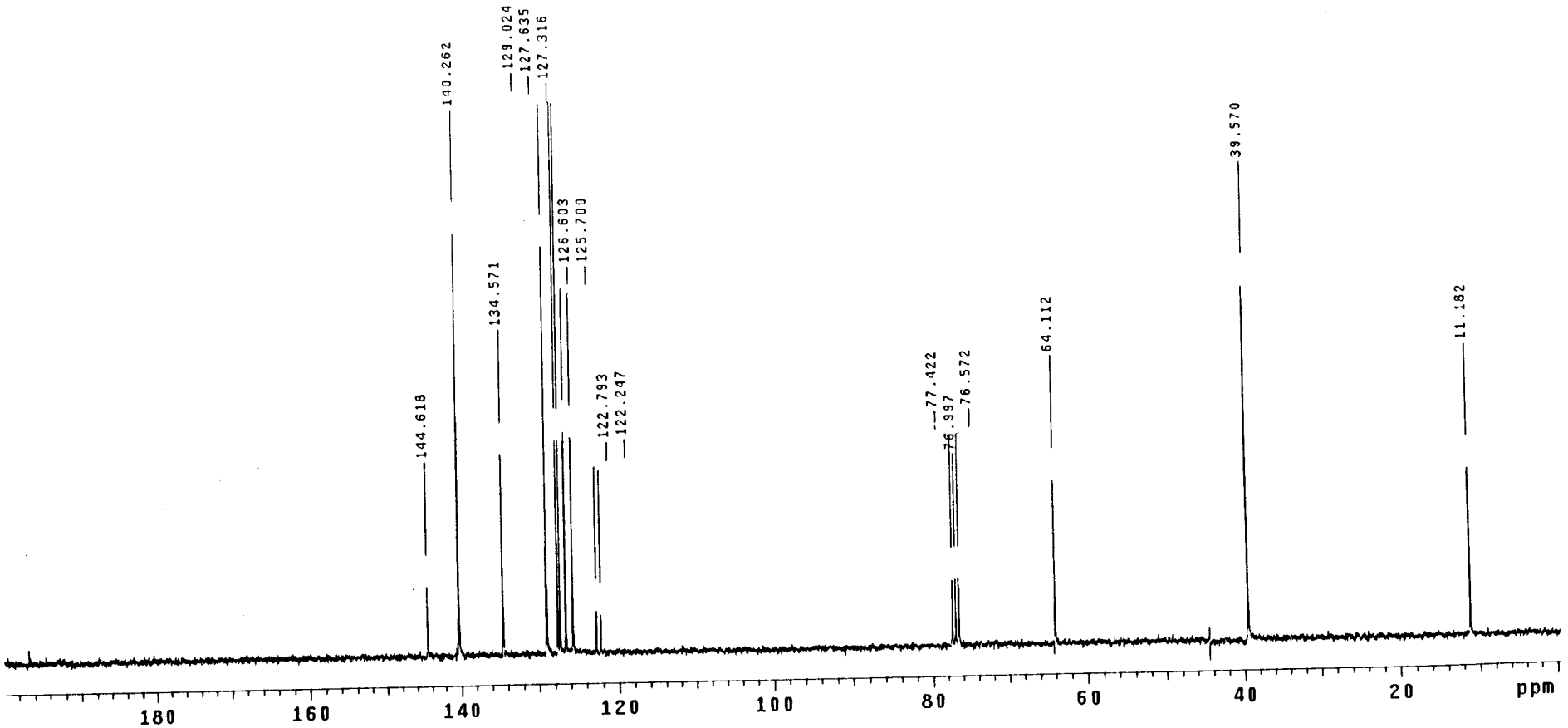

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10/08/02 06:08:04 PM

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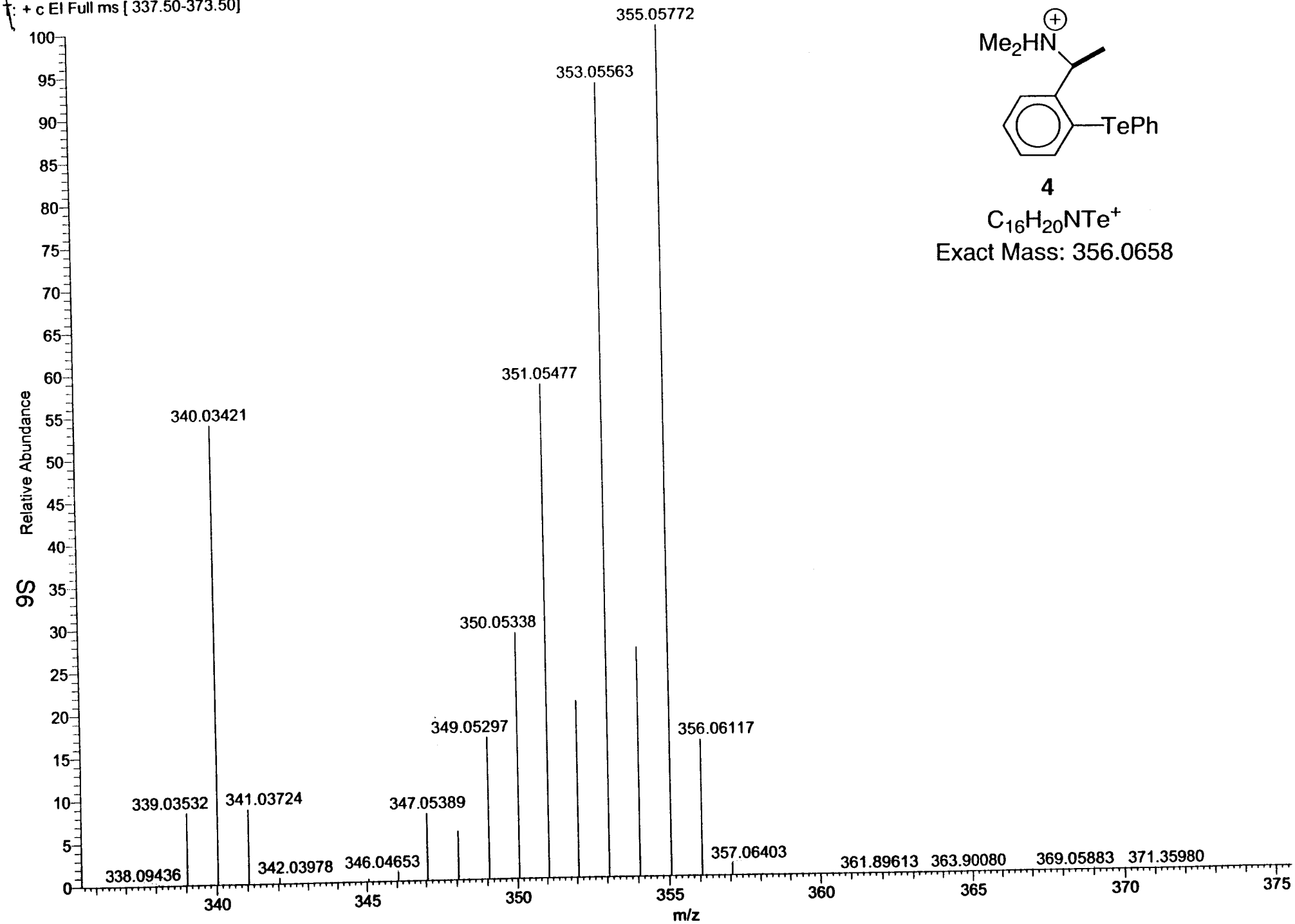
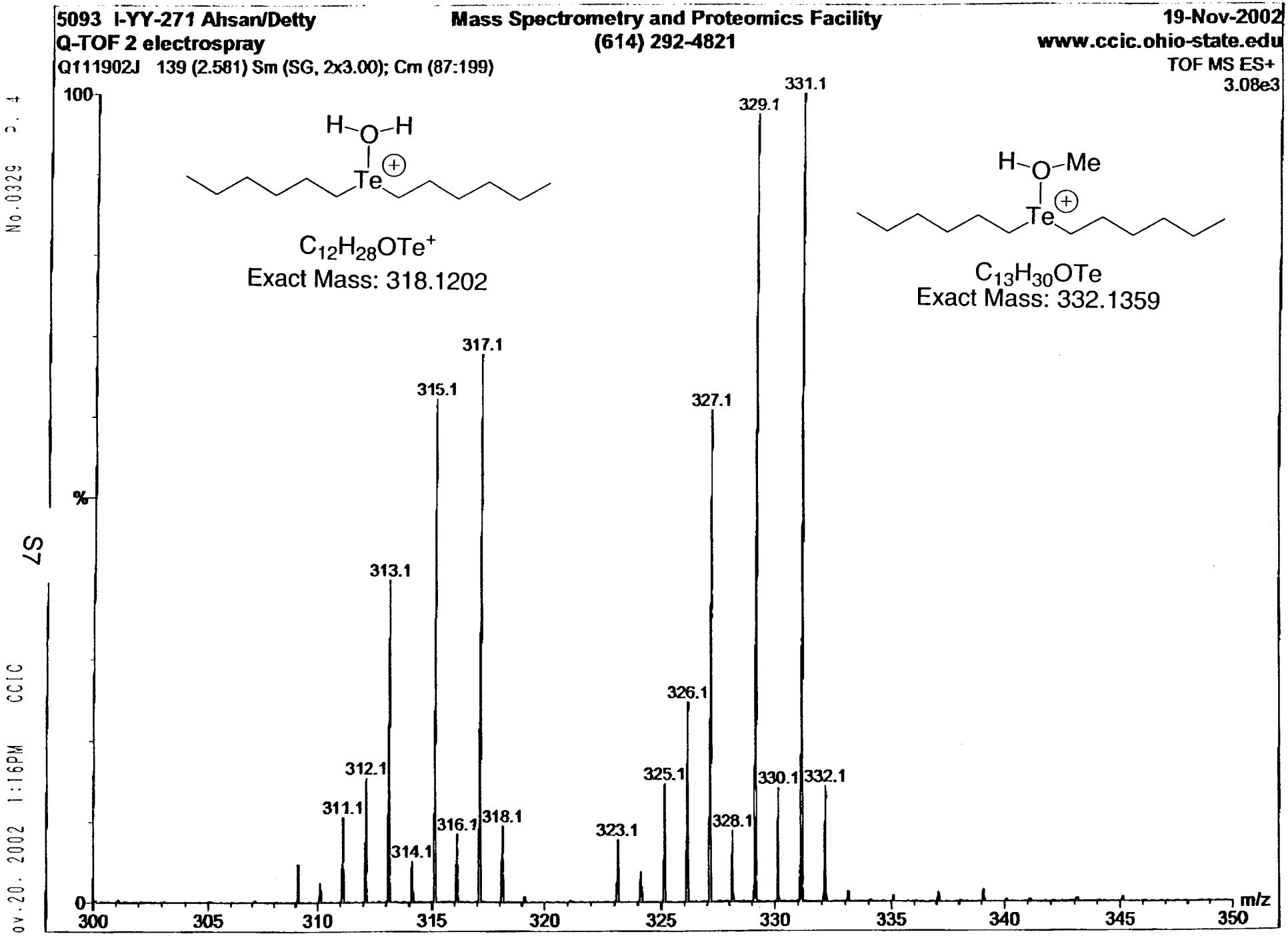


9S

4

$C_{16}H_{20}NTe^{+}$

Exact Mass: 356.0658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Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
3.08e3
H–O–H
Te
C12H28OTe+
Exact Mass: 318.1202
H–O–Me
Te
C13H30OTe
Exact Mass: 332.1359
100
%
0
m/z
300
305
310
315
320
325
330
335
340
345
350
317.1
315.1
331.1
329.1
327.1
313.1
326.1
312.1
325.1
330.1
332.1
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316.1
318.1
328.1
323.1
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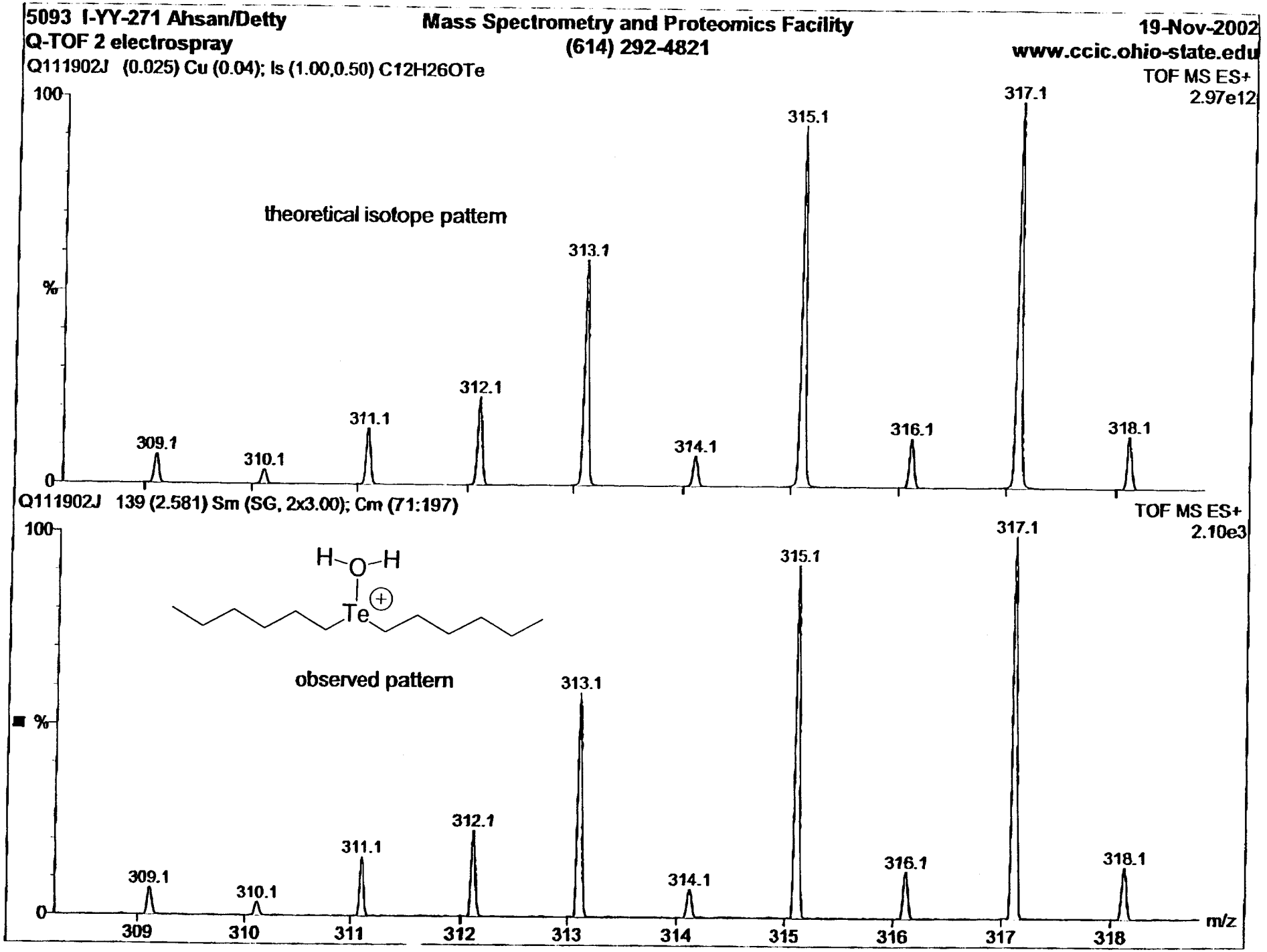
No.0329
Nov.20. 2002 1:16PM CCIC
S7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Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
2.97e12
theoretical isotope pattern
100
%
0
309.1
310.1
311.1
312.1
313.1
314.1
315.1
316.1
317.1
318.1
Q111902J 139 (2.581) Sm (SG, 2x3.00); Cm (71:197)
TOF MS ES+
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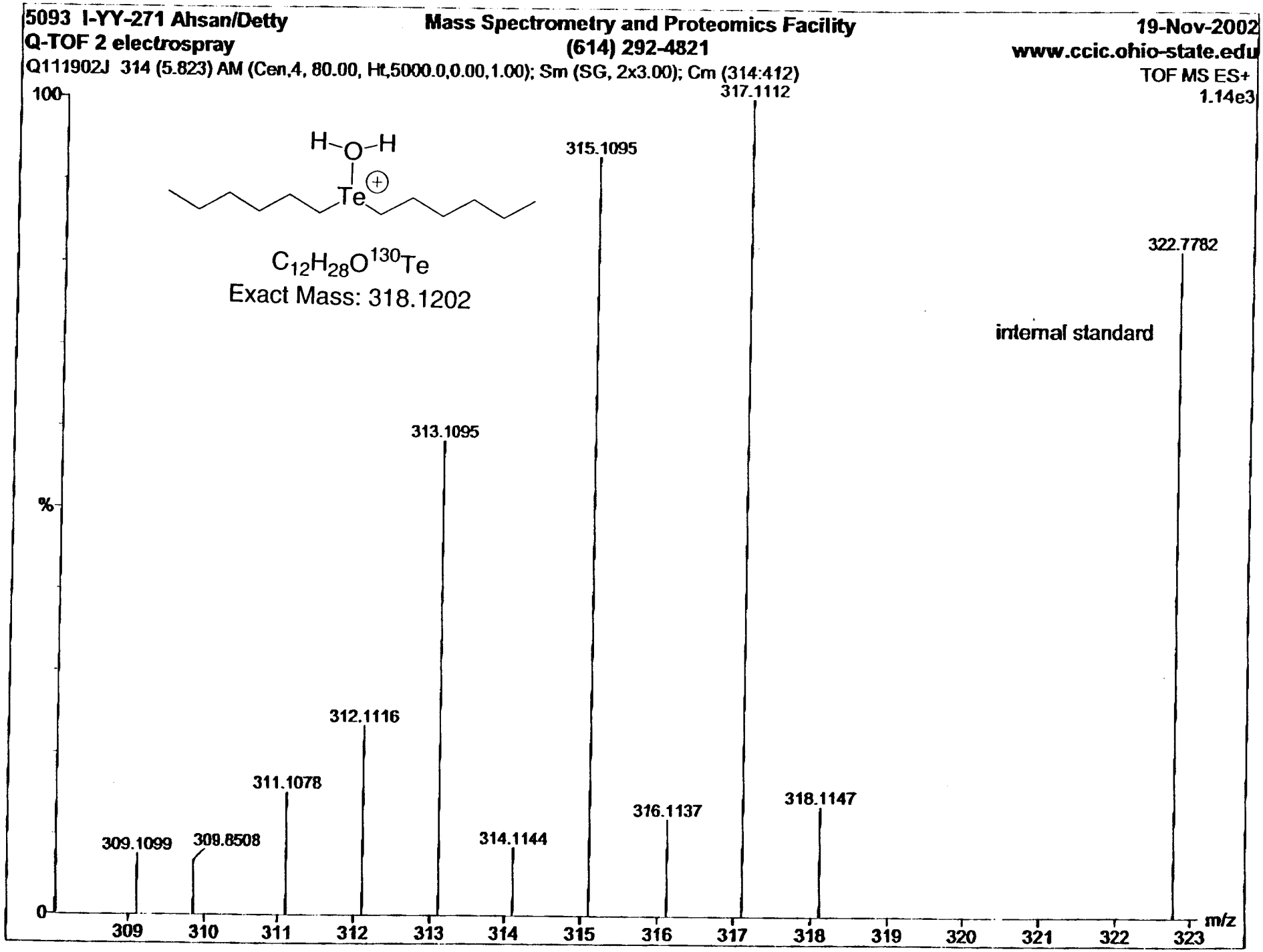
observed pattern
H–O–H
Te
309
310
311
312
313
314
315
316
317
318
m/z

88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Q-TOF 2 electrospray
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Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
1.14e3
100
%
0
H–O–H
Te
C12H28O130Te
Exact Mass: 318.1202
internal standard
309.1099
309.8508
311.1078
312.1116
313.1095
314.1144
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316.1137
317.1112
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316
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318
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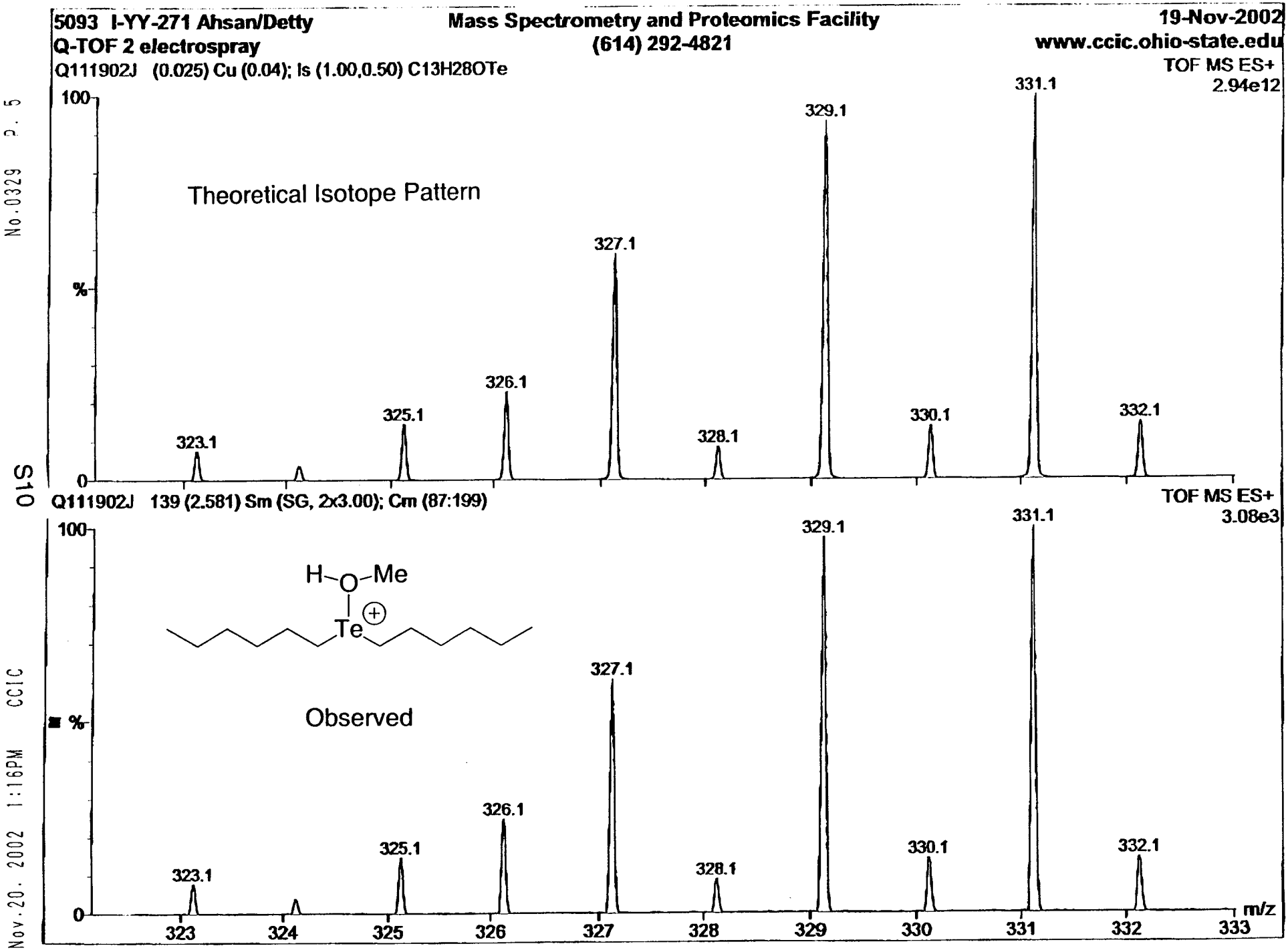
320
321
322
323
m/z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Q-TOF 2 electrospray
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
Q111902J (0.025) Cu (0.04); Is (1.00,0.50) C13H28OTe
TOF MS ES+
2.94e12
Theoretical Isotope Pattern
Q111902J 139 (2.581) Sm (SG, 2x3.00); Cm (87:199)
TOF MS ES+
3.08e3
Observed
H–O–Me
Te
323.1
325.1
326.1
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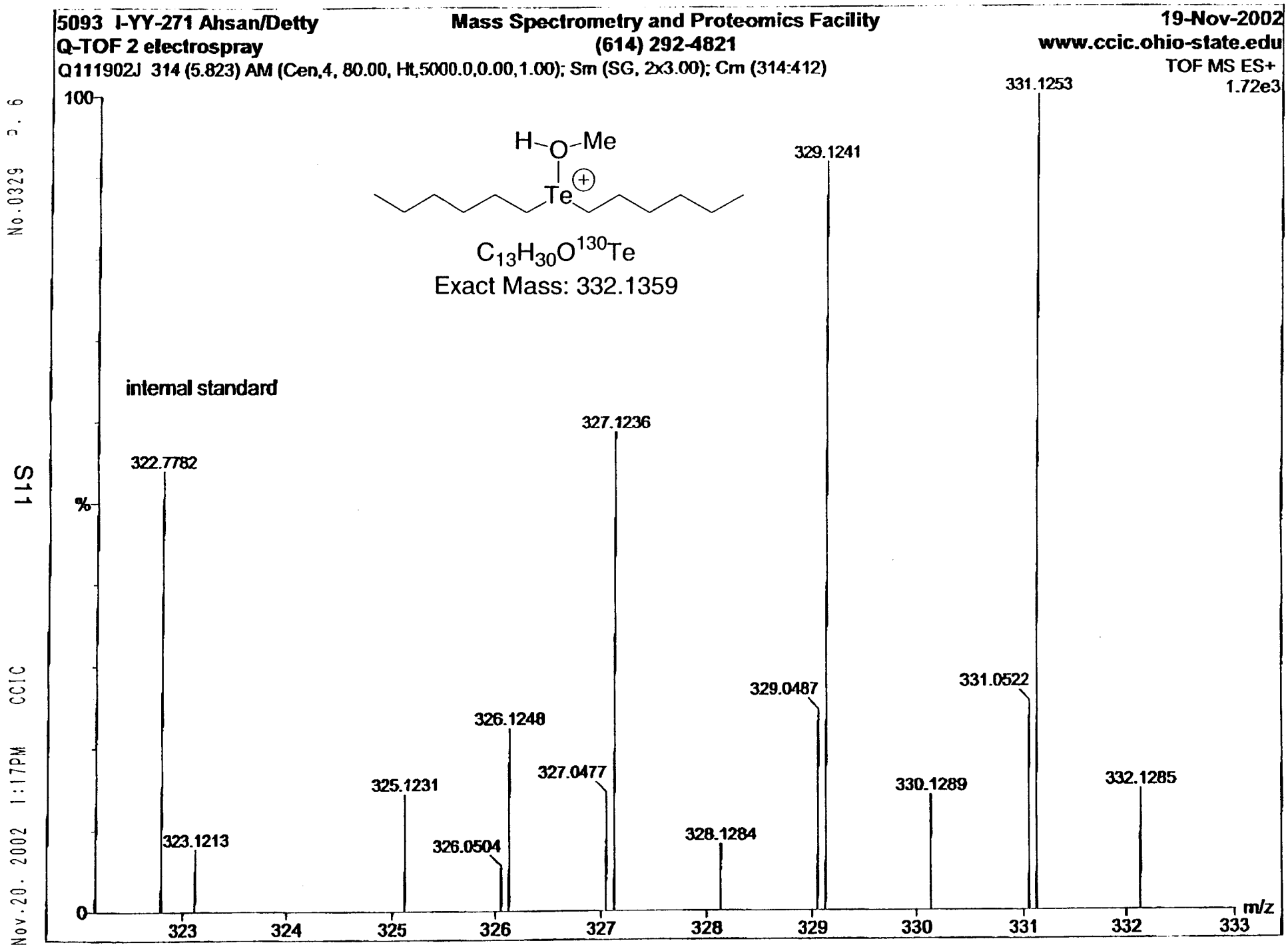
330.1
331.1
332.1
m/z
No.0329 P. 5
S10
Nov.20. 2002 1:16PM CCIC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Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
1.72e3
100
%
0
H–O–Me
Te
C13H30O130Te
Exact Mass: 332.1359
internal standard
322.7782
323.1213
325.1231
326.0504
326.1248
327.0477
327.1236
328.1284
329.0487
329.1241
330.1289
331.0522
331.1253
332.1285
323
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326
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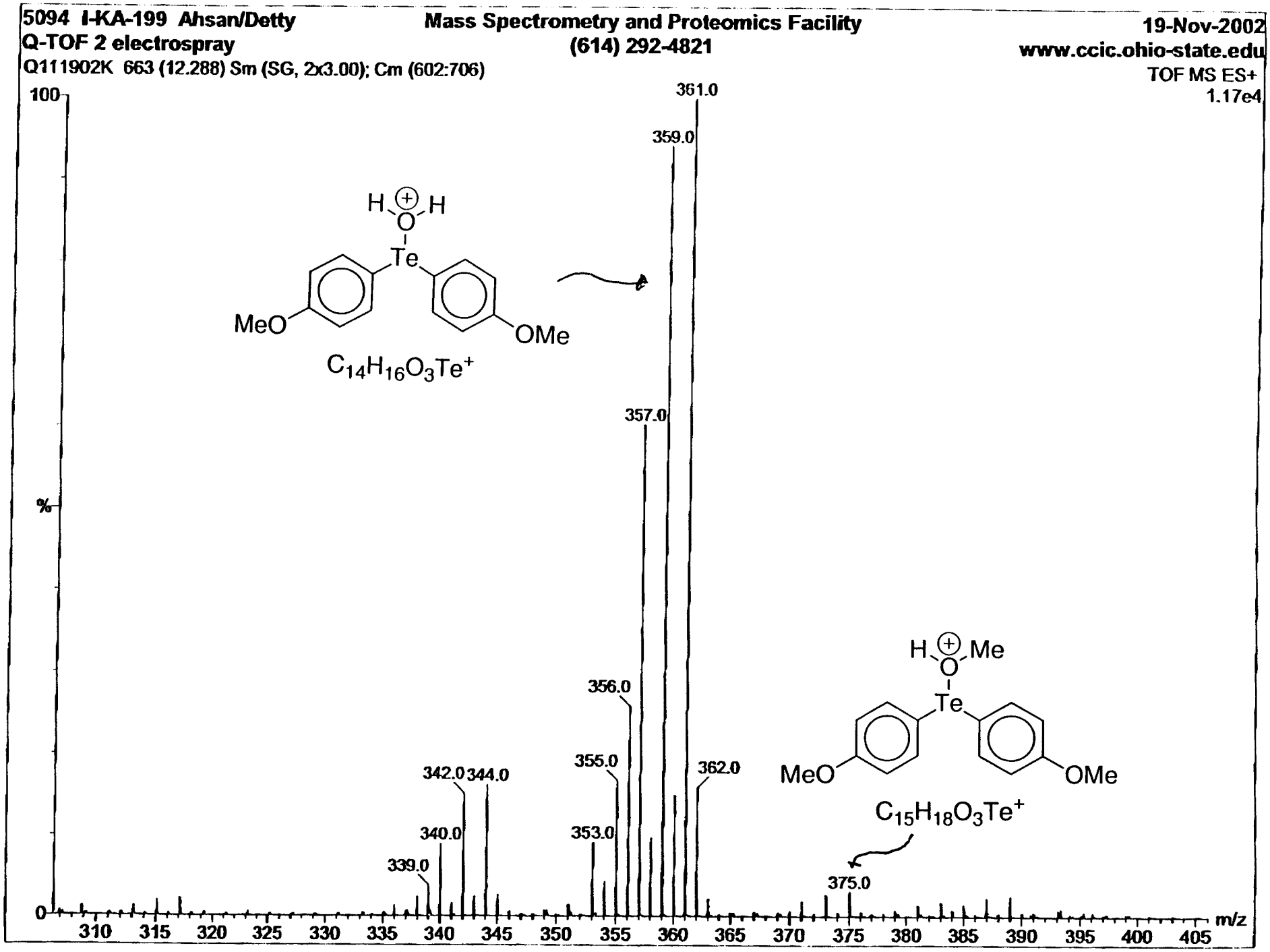
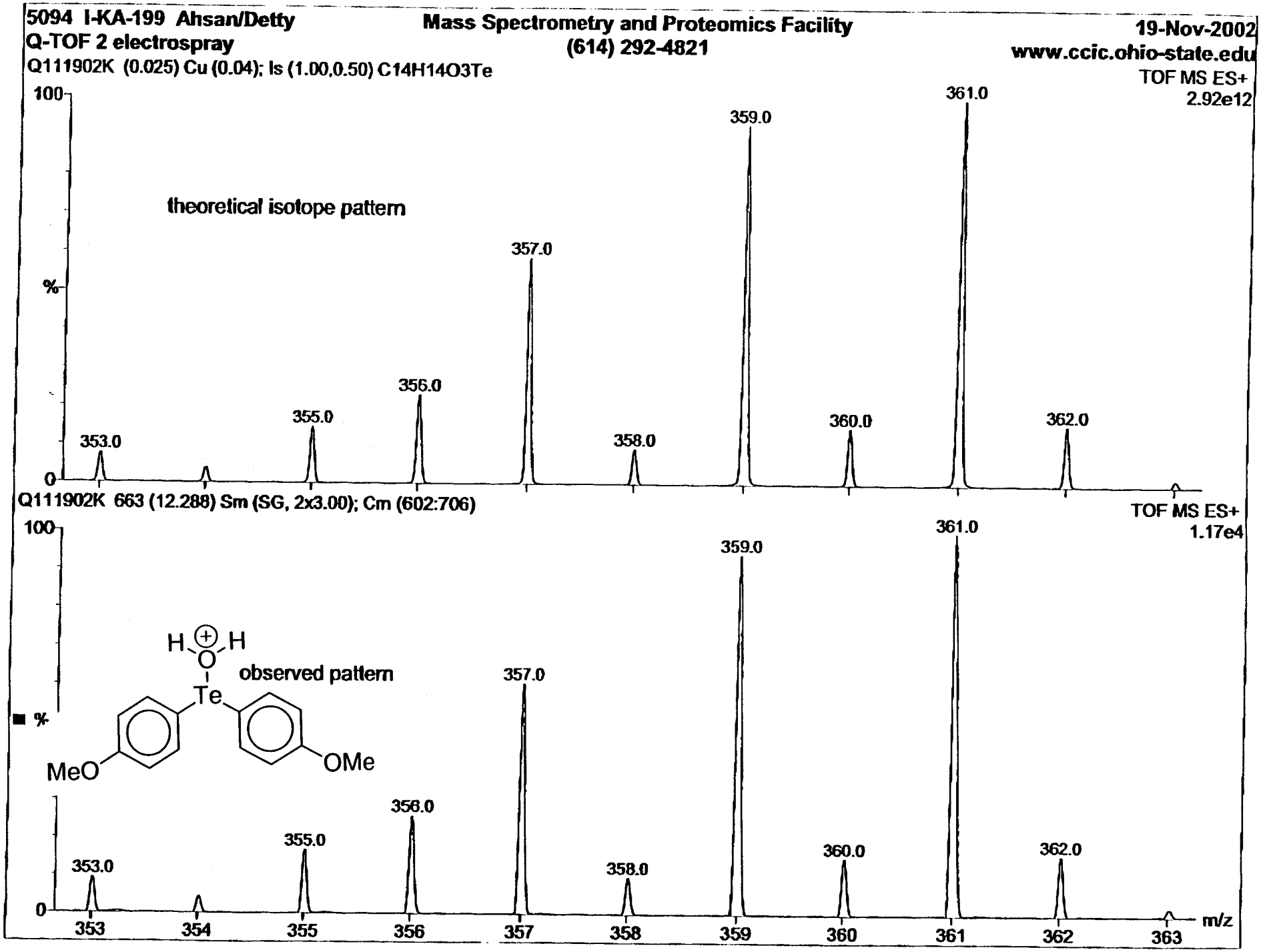
328
329
330
331
332
333
m/z
No.0329 2. 6
S11
Nov.20. 2002 1:17PM CCIC


5094 I-KA-199 Ahsan/Detty
Q-TOF 2 electrospray
Q111902K 663 (12.288) Sm (SG, 2x3.00); Cm (602:706)
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
1.17e4
100
%
0
361.0
359.0
357.0
356.0
355.0
353.0
342.0
344.0
340.0
339.0
362.0
375.0
MeO
OMe
$C_{14}H_{16}O_3Te^+$
Me
$C_{15}H_{18}O_3Te^+$
310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405
m/z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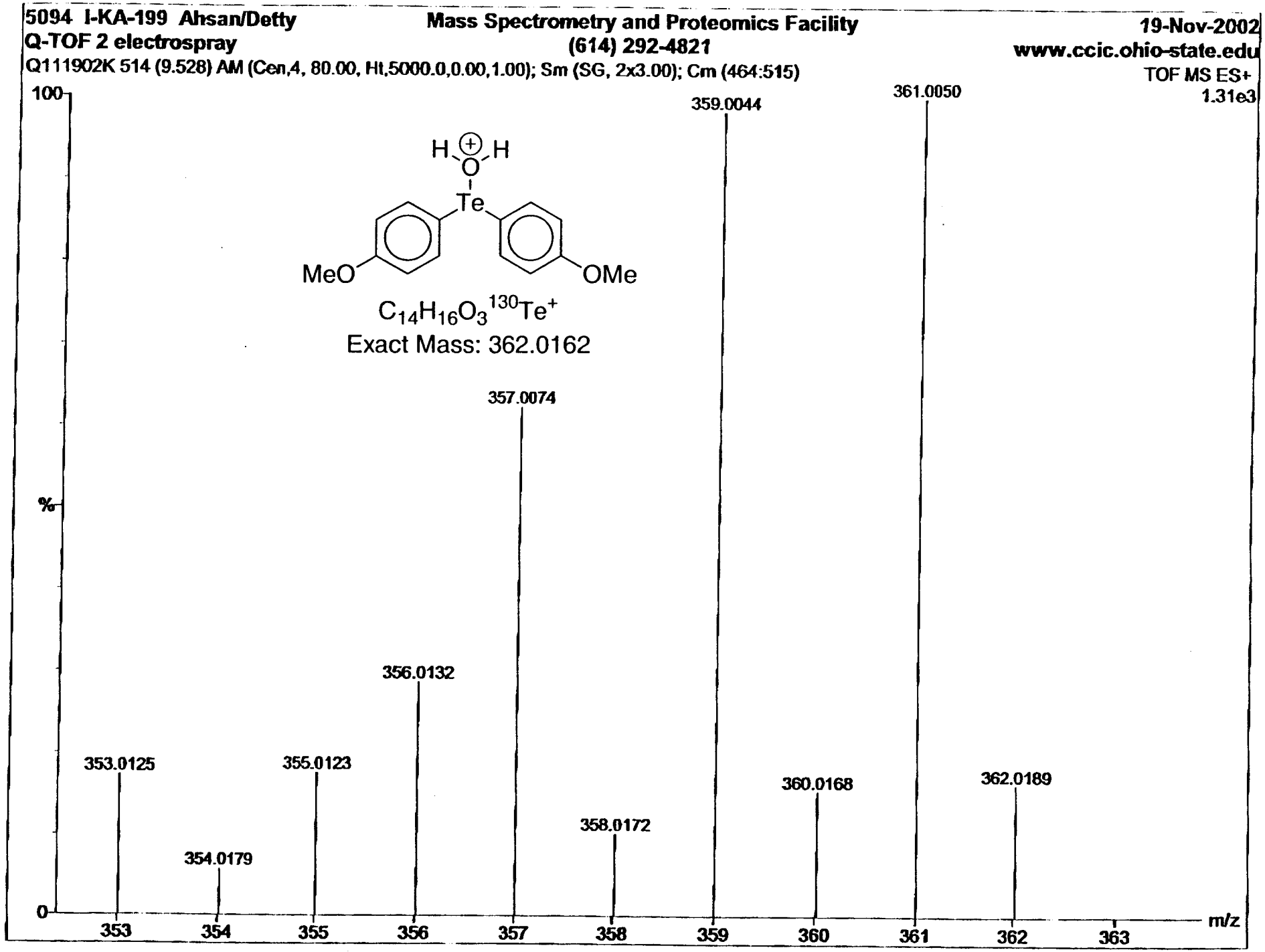
Q-TOF 2 electrospray
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
Q111902K (0.025) Cu (0.04); Is (1.00,0.50) C14H14O3Te
TOF MS ES+
2.92e12
theoretical isotope pattern
Q111902K 663 (12.288) Sm (SG, 2x3.00); Cm (602:706)
TOF MS ES+
1.17e4
observed pattern
MeO
OMe
Te
m/z


5094 I-KA-199 Ahsan/Detty
Q-TOF 2 electrospray
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
Q111902K 514 (9.528) AM (Cen,4, 80.00, Ht,5000.0,0.00,1.00); Sm (SG, 2x3.00); Cm (464:515)
TOF MS ES+
1.31e3
100
%
0
MeO
OMe
Te
H
O
$C_{14}H_{16}O_3{}^{130}Te^+$
Exact Mass: 362.0162
353.0125
354.0179
355.0123
356.0132
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358.0172
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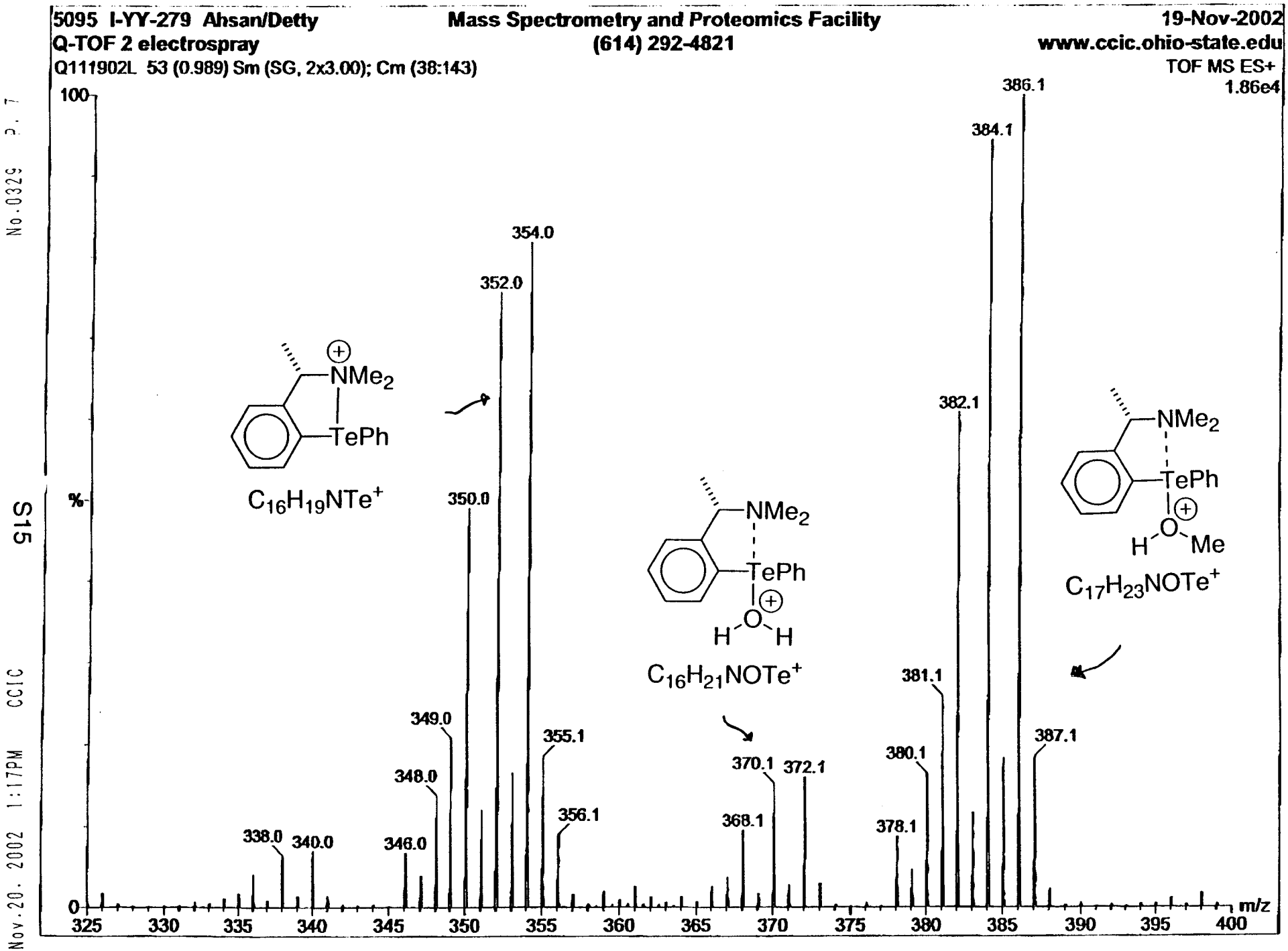
357
358
359
360
361
362
363
m/z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Q111902L 53 (0.989) Sm (SG, 2x3.00); Cm (38:143)
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
1.86e4
100
%
0
386.1
384.1
354.0
352.0
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350.0
349.0
355.1
348.0
356.1
338.0
340.0
346.0
370.1
372.1
368.1
381.1
380.1
387.1
378.1
NMe2
TePh
C16H19NTe+
NMe2
TePh
O
H
H
C16H21NOTe+
NMe2
TePh
O
H
Me
C17H23NOTe+
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330
335
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380
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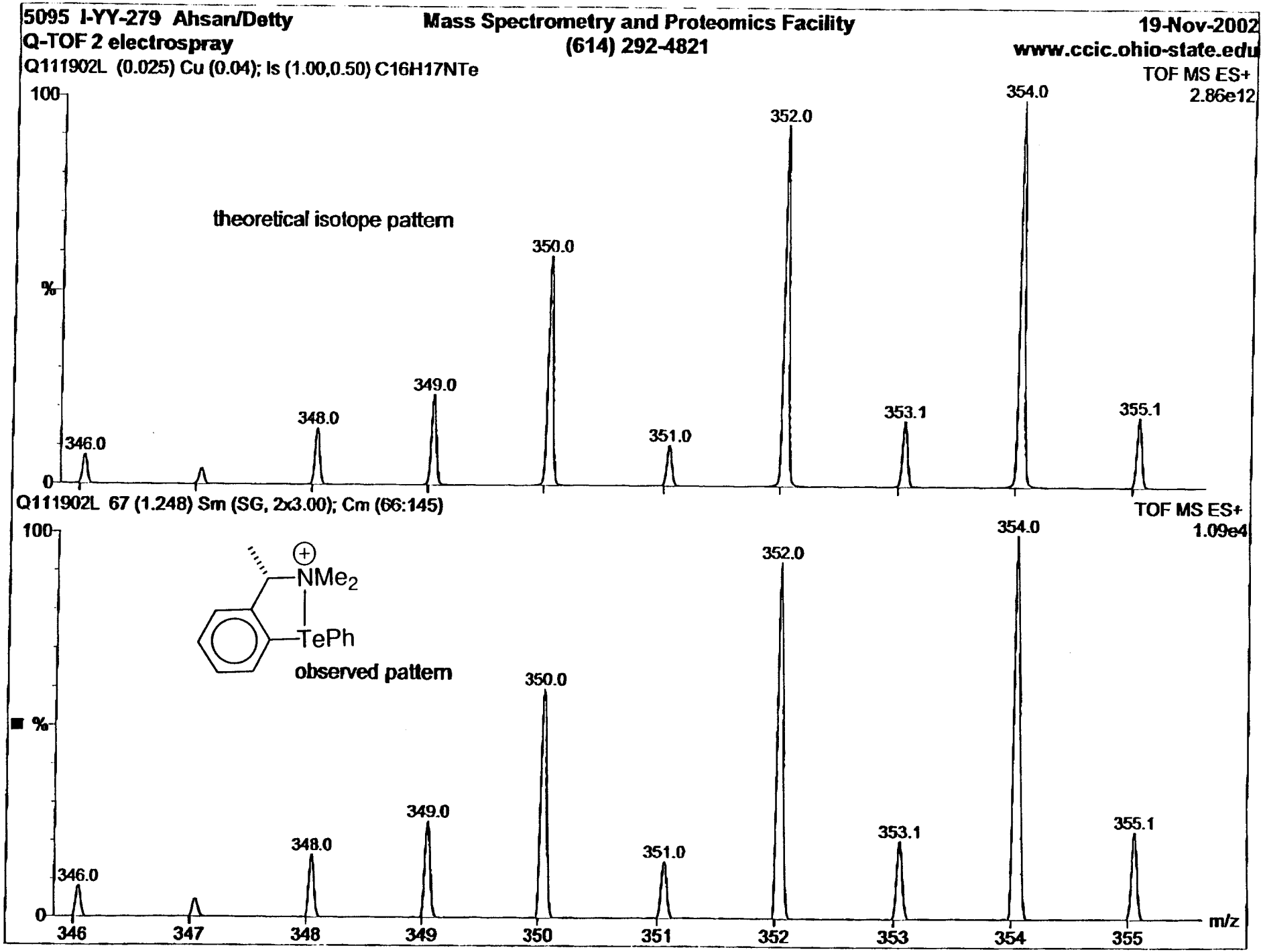
400
m/z
S15
Nov.20. 2002 1:17PM CCIC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Q-TOF 2 electrospray
Q111902L (0.025) Cu (0.04); Is (1.00,0.50) C16H17NTe
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
2.86e12
theoretical isotope pattern
100
%
0
346.0
348.0
349.0
350.0
351.0
352.0
353.1
354.0
355.1
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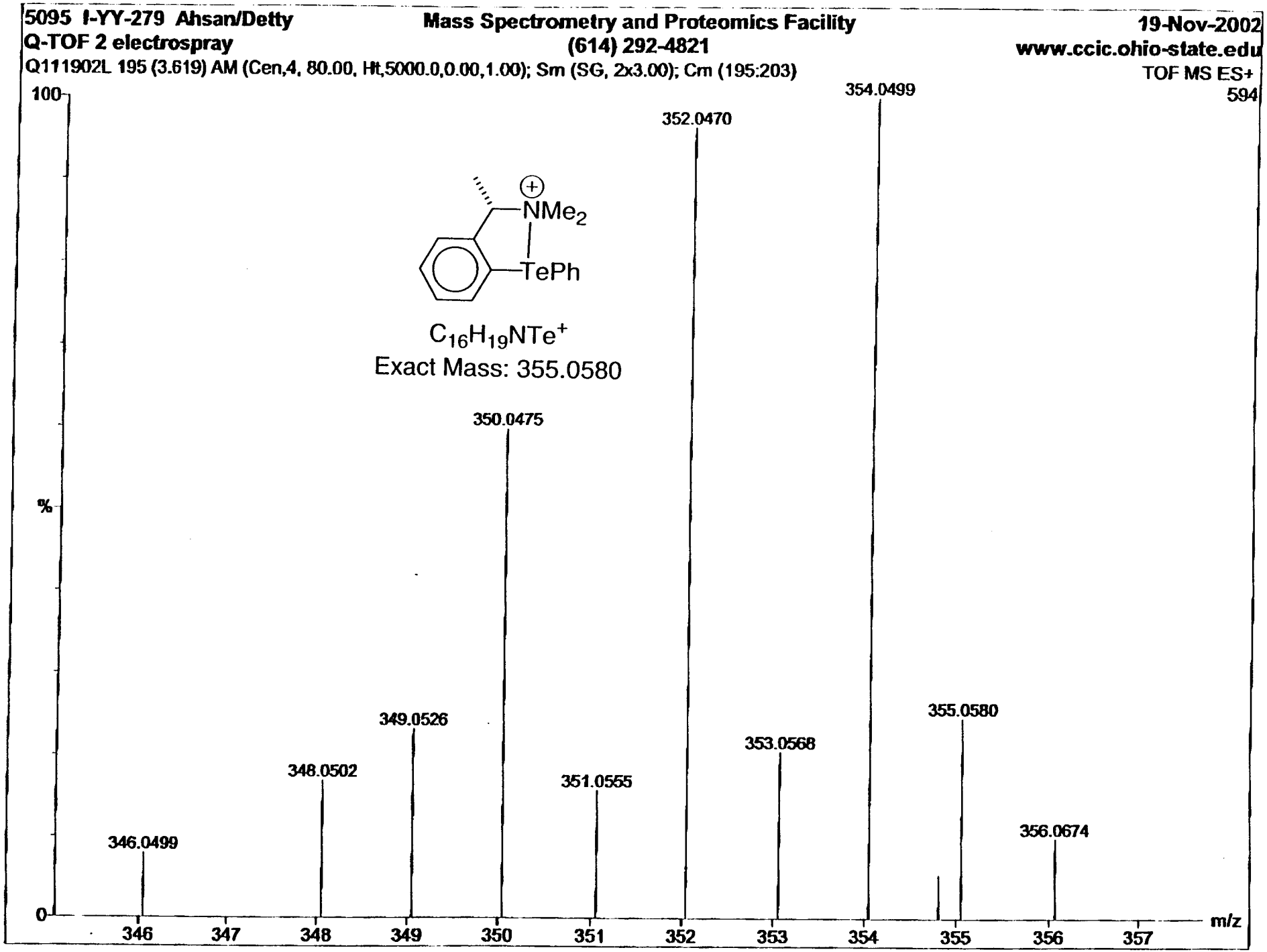
NMe2
TePh
observed pattern
m/z
346
347
348
349
350
351
352
353
354
355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Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
594
100
%
0
NMe2
TePh
C16H19NTe+
Exact Mass: 355.0580
354.0499
352.0470
350.0475
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351.0555
353.0568
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350
351
352
353
354
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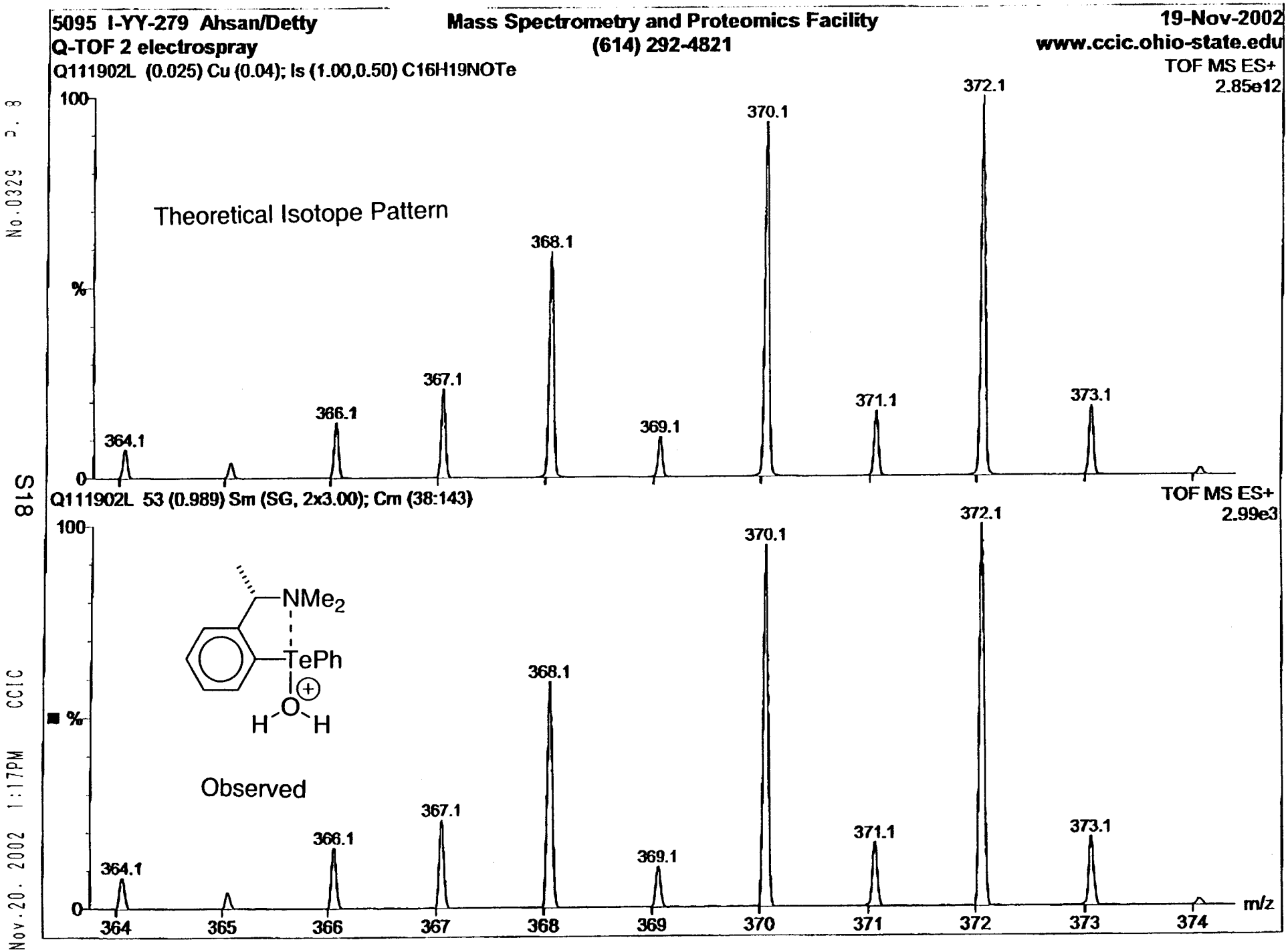
356
357
m/z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Q-TOF 2 electrospray
Q111902L (0.025) Cu (0.04); Is (1.00,0.50) C16H19NOTe
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
TOF MS ES+
2.85e12
Theoretical Isotope Pattern
100
%
0
364.1
366.1
367.1
368.1
369.1
370.1
371.1
372.1
373.1
Q111902L 53 (0.989) Sm (SG, 2x3.00); Cm (38:143)
TOF MS ES+
2.99e3
NMe2
TePh
O
H
H
Observed
m/z
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365
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367
368
369
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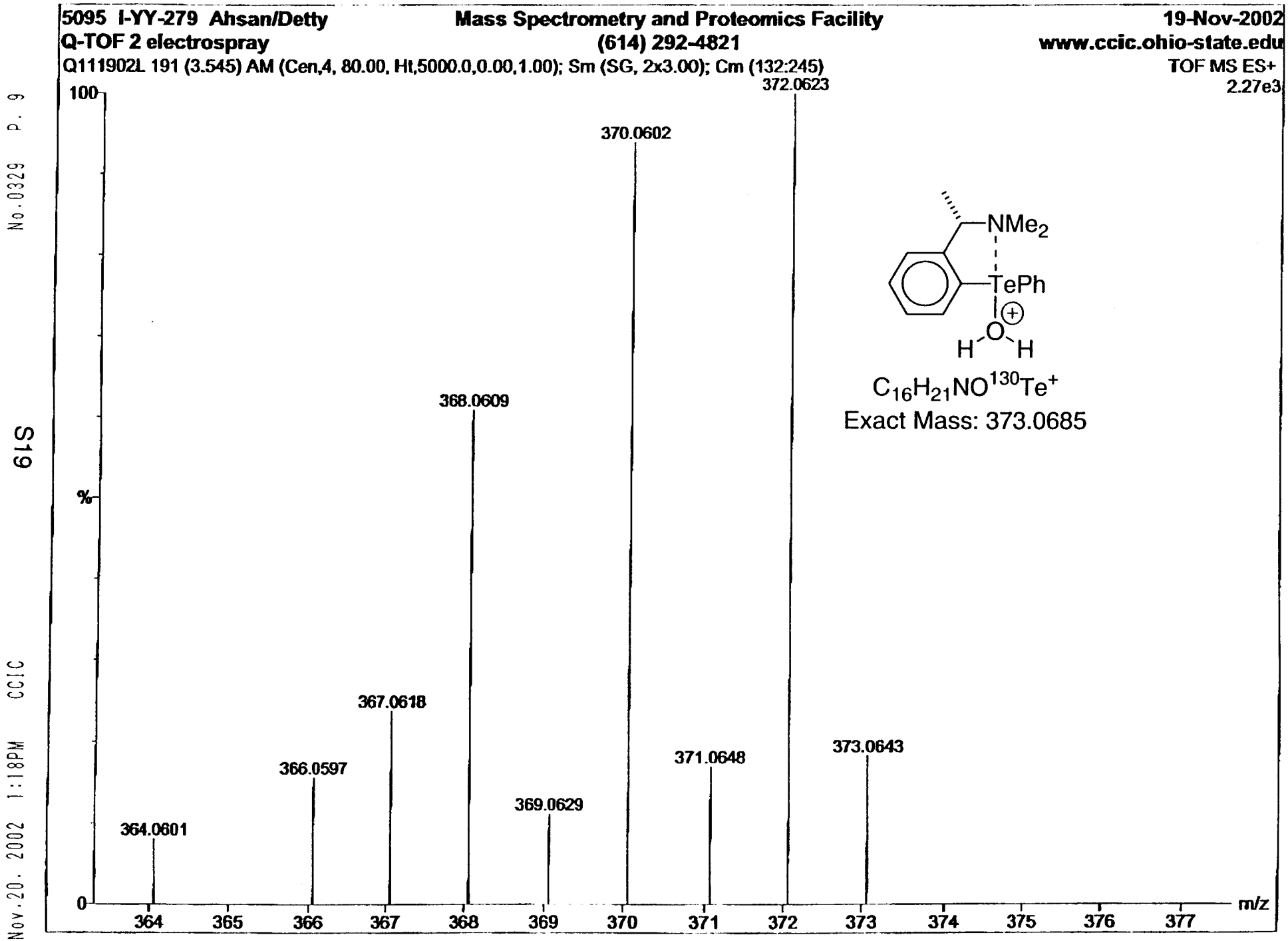
373
374
No.0329
S18
Nov.20. 2002 1:17PM CCIC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Q-TOF 2 electrospray
Mass Spectrometry and Proteomics Facility
(614) 292-4821
19-Nov-2002
www.ccic.ohio-state.edu
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100
%
0
372.0623
370.0602
368.0609
367.0618
366.0597
364.0601
369.0629
371.0648
373.0643
364
365
366
367
368
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372
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374
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376
377
m/z
NMe2
TePh
O
H
H
C16H21NO130Te+
Exact Mass: 373.0685
No.0329 P. 9
S19
Nov.20. 2002 1:18PM CCIC

T = 50 °C

I-KA-200-CDC13/temp-50C

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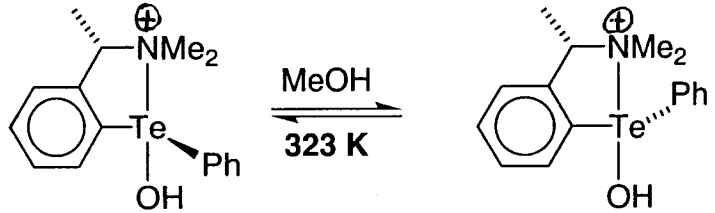
Solvent: CDC13
Temp. 54.0 C / 327.1 K
INOVA-400 "cosy.chem.buffalo.edu"

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 29.1 degrees
Acq. time 1.499 sec
Width 12001.2 Hz
16 repetitions
OBSERVE H1, 399.9388918 MHz
DATA PROCESSING
Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 10 sec



7A 7B

276 K

A B A B A B

ppm

0.01 1.96 2.39 43.01 1.95 10.57 25.38 1.27 7.46 5.85 0.00.14

Table S1. Observed Pseudo First-Order and Calculated Second-Order Rate Constants in the Reactions of Tellurides 2-4 with Hydrogen Peroxide[a]

compd	conc, M	$[H_2O_2]$, M	λ,[b] nm	k_{obs}, s^{-1}	k_{calc}, L mol^{-1} s^{-1}[c]
2	5.15×10^{-4}	5.15×10^{-3}	352	0.12 ± 0.01	–
	5.15×10^{-4}	1.03×10^{-2}	352	0.28 ± 0.02	$(2.80 \pm 0.06) \times 10^{1}$
	5.15×10^{-4}	2.06×10^{-2}	352	0.57 ± 0.08	–
3	5.15×10^{-4}	5.15×10^{-3}	310	$(1.99 \pm 0.04) \times 10^{-2}$	–
	5.15×10^{-4}	1.03×10^{-2}	310	$(5.12 \pm 0.03) \times 10^{-2}$	5.93 ± 0.04
	5.15×10^{-4}	2.06×10^{-2}	310	0.112 ± 0.001	–
4	5.15×10^{-4}	5.15×10^{-3}	286	$(1.81 \pm 0.05) \times 10^{-2}$	–
	5.15×10^{-4}	1.03×10^{-2}	286	$(3.66 \pm 0.08) \times 10^{-2}$	3.61 ± 0.02
	5.15×10^{-4}	2.06×10^{-2}	286	$(7.22 \pm 0.08) \times 10^{-2}$	–

[a] The observed rate constants, k_{obs}, are the average of 7-10 independent kinetic traces at 276.8 ± 0.4 K with twice the standard deviation given from the average. [b] Wavelength at which kinetic trace was observed. [c] Rate constant is equal to the slope of the line defined by k_{obs} plotted as a function of $[H_2O_2]$.

Table S2. Observed Pseudo First-Order, and Calculated Second-Order Rate Constants for the Fast Reaction of Oxidized Telluranes 5-7 with PhSH[a]

compd	conc, M	[PhSH], M	λ,[b] nm	k_{obs}, s^{-1}	k_{calc}, L mol^{-1} s^{-1}
5	4.12×10^{-5}	4.12×10^{-5}	300	156 ± 9	–
	4.12×10^{-5}	2.06×10^{-4}	300	410 ± 40	$(1.2 \pm 0.1) \times 10^{6}$[c]
	4.12×10^{-5}	4.12×10^{-4}	300	665 ± 9	–
	4.12×10^{-5}	6.18×10^{-4}	300	920 ± 20	–
6	4.12×10^{-5}	4.12×10^{-5}	300	76 ± 4	–
	4.12×10^{-5}	2.06×10^{-4}	300	180 ± 8	$(5.5 \pm 0.2) \times 10^{5}$[c]
	4.12×10^{-5}	4.12×10^{-4}	300	319 ± 4	–
	4.12×10^{-5}	6.18×10^{-4}	300	408 ± 8	–
7	2.06×10^{-4}	2.06×10^{-4}	286	10.6 ± 0.3	–
	2.06×10^{-4}	2.06×10^{-3}	286	14.3 ± 0.6	$(1.28 \pm 0.08) \times 10^{3}$[c]
	2.06×10^{-4}	4.12×10^{-3}	286	16 ± 1	–
	2.06×10^{-4}	7.05×10^{-3}	286	20 ± 1	–
	2.06×10^{-4}	1.03×10^{-2}	286	24 ± 2	–

[a] The observed rate constants, k_{obs}, are the average of 7-10 independent kinetic traces at 276.8 ± 0.4 Kwith twice the standard deviation given from the average. [b] Wavelength of measurement for kinetic trace. [c] Rate constant is equal to the slope of the line defined by k_{obs} plotted as a function of [PhSH}.

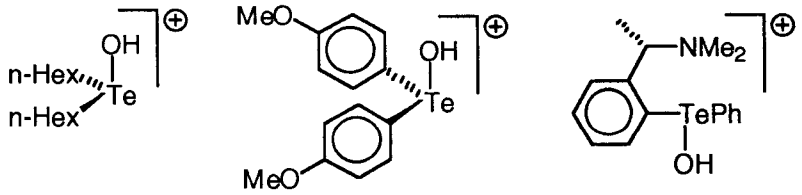
Table S3. Observed First-Order Rate Constants in the Second Reaction of Oxidized Telluranes 5-7 with PhSH[a]

compd	conc, M	[PhSH], M	λ,[b] nm	k_{obs}, s^{-1}
5	4.12×10^{-5}	4.12×10^{-5}	300	2.03 ± 0.04
	4.12×10^{-5}	2.06×10^{-4}	300	2.38 ± 0.04
	4.12×10^{-5}	4.12×10^{-4}	300	2.40 ± 0.02
	4.12×10^{-5}	8.24×10^{-4}	300	2.45 ± 0.02
	4.12×10^{-5}	1.24×10^{-3}	300	2.47 ± 0.02
	4.12×10^{-5}	1.65×10^{-3}	300	2.49 ± 0.03
	4.12×10^{-5}	2.47×10^{-3}	300	2.57 ± 0.03
	4.12×10^{-5}	3.30×10^{-3}	300	2.60 ± 0.02
	4.12×10^{-5}	4.12×10^{-3}	300	2.64 ± 0.02
	4.12×10^{-5}	6.18×10^{-3}	300	2.72 ± 0.03
	4.12×10^{-5}	8.24×10^{-3}	300	2.80 ± 0.04
	4.12×10^{-5}	1.03×10^{-2}	300	2.82 ± 0.02
	4.12×10^{-5}	1.24×10^{-2}	300	2.86 ± 0.02
	4.12×10^{-5}	1.44×10^{-2}	300	2.87 ± 0.03
	4.12×10^{-5}	1.65×10^{-2}	300	2.90 ± 0.03
	4.12×10^{-5}	2.06×10^{-2}	300	2.89 ± 0.05
6	4.12×10^{-5}	4.12×10^{-5}	300	15.8 ± 0.2
	4.12×10^{-5}	2.06×10^{-4}	300	25.3 ± 0.3
	4.12×10^{-5}	4.12×10^{-4}	300	27.8 ± 0.2
	4.12×10^{-5}	8.24×10^{-4}	300	27.8 ± 0.3
	4.12×10^{-5}	1.24×10^{-3}	300	28.0 ± 0.2
	4.12×10^{-5}	1.65×10^{-3}	300	27.9 ± 0.2
	4.12×10^{-5}	2.47×10^{-3}	300	28.5 ± 0.3
	4.12×10^{-5}	3.30×10^{-3}	300	28.9 ± 0.3
	4.12×10^{-5}	4.12×10^{-3}	300	29.2 ± 0.2
	4.12×10^{-5}	6.18×10^{-3}	300	29.9 ± 0.4
	4.12×10^{-5}	8.24×10^{-3}	300	30.8 ± 0.4
	4.12×10^{-5}	1.03×10^{-2}	300	31.5 ± 0.5
7	2.06×10^{-4}	2.06×10^{-4}	286	0.015 ± 0.001
	2.06×10^{-4}	1.03×10^{-3}	286	0.34 ± 0.03
	2.06×10^{-4}	2.06×10^{-3}	286	0.80 ± 0.01
	2.06×10^{-4}	4.12×10^{-3}	286	1.03 ± 0.01
	2.06×10^{-4}	1.03×10^{-2}	286	1.66 ± 0.03
	2.06×10^{-4}	1.65×10^{-2}	286	2.27 ± 0.03

[a] The observed rate constants, k_{obs}, are the average of 7-10 independent kinetic traces at 276.8 ± 0.4 K. Twice the standard deviation is given from the average. [b] Wavelength of measurement for kinetic trace.

General Methods. Solvents and reagents were used as received from Sigma-Aldrich Chemical Co (St. Louis, MO) unless otherwise noted. Concentration *in vacuo* was performed on a Büchi rotary evaporator. NMR spectra were recorded at 23.0 °C on a Varian Gemini-300, Inova 400, or Inova 500 instrument with residual solvent signal as internal standard: $CDCl_3$ (δ 7.26 for proton, δ77.0 for carbon). Infrared spectra were recorded on a Perkin-Elmer FT-IR instrument. UV-visible-near-IR spectra were recorded on a Perkin-Elmer Lambda 12 spectrophotometer equipped with a circulating constant-temperature bath for the sample chambers. Elemental analyses were conducted by Atlantic Microlabs, Inc. High-resolution Q-TOF mass spectrometry was conducted by the Campus Chemical Instrumentation Center of The Ohio State University (Columbus, OH).

Discussion of Electrospray Ionization Mass Spectra of 5-7. The mass spectra of compounds **5-7** using electron-impact ionization gave parent ions corresponding to the corresponding telluride plus "OH" (loss of "OH" from the dihydroxy tellurane). This type of fragmentation has been observed quite frequently in the mass spectra of dihydroxy telluranes.[1]



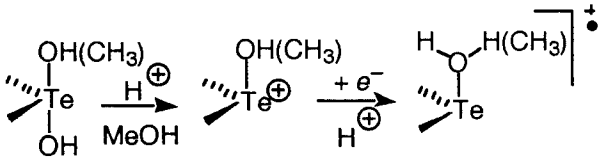
m/z 317 from **5**

m/z 361 from **6**

m/z 372 from **7**

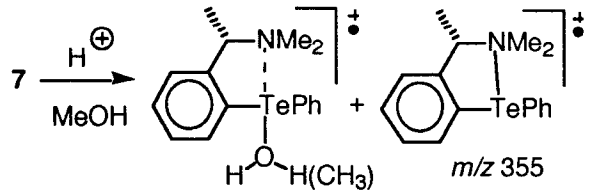
In order to observe Te(IV) derivatives incorporating MeOH as a ligand, mass spectra of MeOH solutions of **5-7** were acquired using electrospray ionization. Electrospray ionization of MeOH solutions of **5-7** gave rise to peaks corresponding to telluride plus water and telluride plus MeOH as shown in the scheme below (mass spectra can be found in Supporting Information).

These products involve a redox reaction as an artifact of the electrospray technique.[2] Reductive elimination of H_2O_2 from **5-7** can occur thermally[3] and would produce **2-4**, respectively, which could then donate an electron to the hydroxy or methoxy telluronium intermediates. Evidence in support of this process was found in the electrospray ionization of **7** where an isotope cluster containing m/z 355 corresponds to $[C_{16}H_{19}N^{130}Te]^+$ from the radical cation derived from **4** (mass spectrum in Supporting Information). This species would be stabilized by the chelating nitrogen atom. This observation can be contrasted with the electrospray ionization of telluride **4** in MeOH where an isotope cluster containing *m/z* 356 corresponds to $[C_{16}H_{19}N^{130}Te + H^+]$ (mass spectrum in Supporting Information), perhaps from protonation of the amine – but not the radical cation observed with **7**.

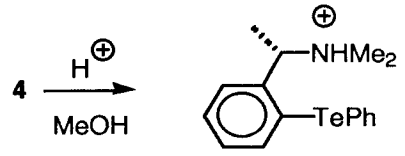


5: R = H, *m/z* 318 for $[C_{12}H_{26}{}^{130}Te\text{-}H_2O]^+$
R = Me, *m/z* 332 for $[C_{12}H_{26}{}^{130}Te\text{-}HOMe]^+$

6: R = H, *m/z* 362 for $[C_{14}H_{14}O_2{}^{130}Te\text{-}H_2O]^+$
R = Me, *m/z* 376 for $[C_{14}H_{14}O_2{}^{130}Te\text{-}HOMe]^+$



R = H, *m/z* 373 for $[C_{16}H_{19}N^{130}Te\text{-}H_2O]^+$
R = Me, *m/z* 387 for $[C_{16}H_{19}N^{130}Te\text{-}HOMe]^+$



m/z 356 for $C_{16}H_{19}N^{130}Te+H^+$

References

(1) Detty, M. R. *J. Org. Chem.* **1980**, *45*, 274.

(2) Fernandez de la Mora, J.; Van Berkel, G. J.; Enke, C. G.; Cole, R. B.; Martinez-Sanchez, M.; Fenn, J. B. *J. Mass Spectrom.* **2000**, *35*, 939.

(3) Detty, M. R.; Gibson, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 4086.