Identification of Guest Molecules within Hydrogen Bonded Frameworks Extracted from TGA Exhaust Gas Using Solid Phase Microextraction Fibers

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Electronic Supplementary Information

General Procedures:

Powder XRD

Crystals of **1** were collected from growth solutions and washed with methanol (1x) and acetone (2x). The crystals were then dried under vacuum to remove any remaining surface residues. The crystals were finely ground immediately prior to powder XRD analysis. The ground sample was place onto a glass slide and pressed flat with microscope slide. PXRD patterns were collected on a Rigaku Ultima IV X-ray diffractometer containing a CuKα source (λ =1.54051Å) and viewed with MDI Jade 9 software. XRD patterns were then collected from 2θ = 2° to 40°.

Thermogravimetric Analysis

Crystals of **1** were collected from growth solutions and washed with methanol (1x) and acetone (2x). The crystals were then dried under vacuum to remove any remaining surface residues. The crystals were immediately transferred to a platinum TGA pan for analysis. TGA data was then collected using a Thermal Advantage TGA Q50 (TA Instruments) and TA Universal Analysis software for data analysis. TGA data was collected from 40°C up to 550°C depending on the sample with an initial 3 minute hold at 40°C. The heating rate was 10°C/minute.

Gas Chromatography/Mass Spectrometer

An HP gas chromatograph 5900 and HP gas chromatography mass spectrometer 5988A were used to collect all chromatographic data. For GC/GCMS method development, the isolated crystals were placed inside of a 20mL GC headspace vial (Xpertek, PJ. Cobert, Cat#954040) with a high temperature rated septa within the cap (Xpertek, PJ. Cobert, Cat#952237). The standalone GC was only used for initial aspects of **1**·toluene analysis. The GC oven temperature was initially 30°C for 3.0 minutes, then ramped to 150°C at a rate of 20°C/min and held for 1.0 minute. The injection port temperature was 250°C. The total analysis time was 10.50 minutes. The GC used an 15m SPB-1 column, 10µm film thickness, 0.2mm ID, bonded, 100% dimethyl siloxane stationary phase. The GCMS oven temperature was initially 30°C for 3.0 minutes, then ramped to 150°C at a rate of 20°C/min and held for 1.0 minute. The injection port temperature was 250°C. The total analysis time was 10.50 minutes. GCMS guest determinations were performed using an 11m HP-1 Ultra column, with a 0.2mm I.D x 0.33µm film.

The following SPME fibers were used during the course of this research:

a) 100 µm polydimethyl siloxane (PDMS) coated SPME fiber (Supelco, Cat# 57300-U
b) 7µm PDMS coated SPME fiber (Supelco, Cat#57302)
c) 85µm polyacrylate (PA) coated SPME fiber (Supelco, Cat# 57305)

Guest Evolution Studies

A new approach was used to determine that the toluene guest molecule was still evolving from the framework and was not just part of the head space. To show this, a new crystal (20mg) was placed in a headspace vial and then placed into a heating block well. The block had been pre-heated to 110°C. 110°C was a peak maximum from the TGA derivative plot. 10uL of headspace was sampled every minute for ten minutes using a gastight syringe with built-in valve and injected into the GCMS (Table S.1). The hole created by the syringe was covered with fresh Para film in between sample injections. The area count increased to a maximum within two minutes. After two minutes, the peaks did not increase greatly in intensity other than what could be explained by fluctuations due to sampling error since the test was performed manually.

Table S.1 – Measured peak areas for timed extractions of the toluene guest

Time (Mins)	Injection Number	Peak Area (Abundance)
0	1	368440
1	2	734970
2	3	6336325
3	4	4683424
4	5	4315510
5	6	8186782
6	7	2483174
7	8	4255166
8	9	3837816
9	10	4949555
10	11	3824192

Guest Evolution and TGA Analysis

GCMS parameters were used for detection of the guest. The average weight of the sample for this series was 23mg. An 85 µm polyacrylate SPME fiber was used for this study. The TGA was loaded with a platinum tray and the guest-containing crystal. The TGA program was set to immediately increase to 40°C and then perform an isotherm for 3 minutes. A heating ramp would then increase the temperature by 10°C/min until 500°C. It was assumed from the TGA that guest would not be detectable at 145°C. The fiber was left to the side of the instrument well away from the exhaust while the temperature ramped. At a specific temperature, the fiber was then introduced to the exhaust port of the TGA and immediately exposed for absorption

At each temperature point, the fiber was exposed until the TGA reached 145°C. Working backwards from 130°C - 100°C, the absorption time for the fiber is increase because of the heating ramp of 10°C/min. For example, the fiber would be exposed to off-gas for 1.5 minutes from 130°C -145°C and injected. On a new sample, the fiber would then be exposed to off-gas for 2.5 minutes from 120°C - 145°C and so on. It was expected that the concentration of the guest molecule should increase and thus give an increase in peak area once the fiber has desorbed into the GCMS. To compensate for the long exposure time of the fiber at lower temperatures, the total time (+30s) of exposure from 100°C to 145°C was used for 140°C to show that little guest remained at the tail of the TGA peak at that temperature. The temperature ramp was held at an isotherm at 140°C for the five minute interval. If the peak area is compared between 130°C and 140°C, based on the longer exposure time, there is likely a lower concentration of guest molecule left in the framework at 140°C than 130°C. This is comparable to what is seen in the TGA derivative overlay plot.

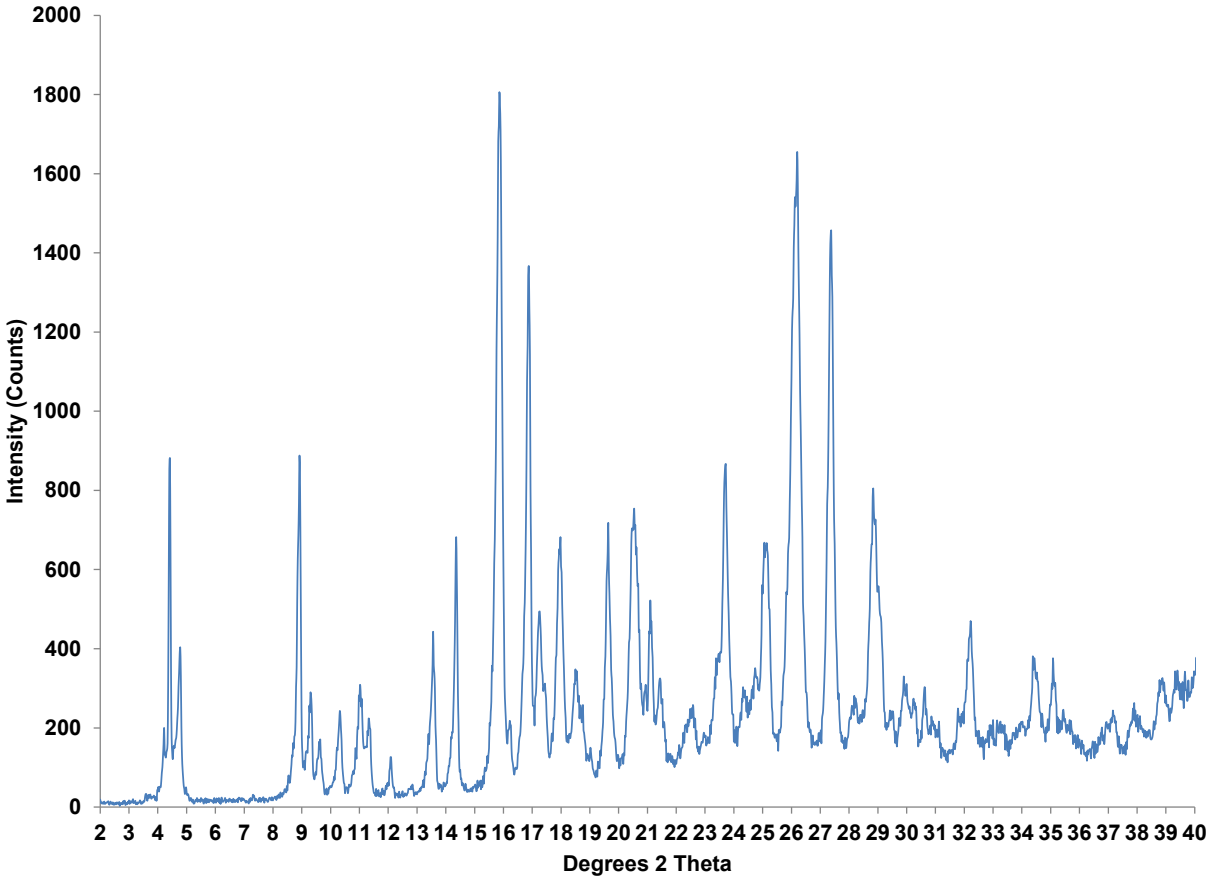

Figure S.1. – Powder XRD of **1**•toluene guest filled framework

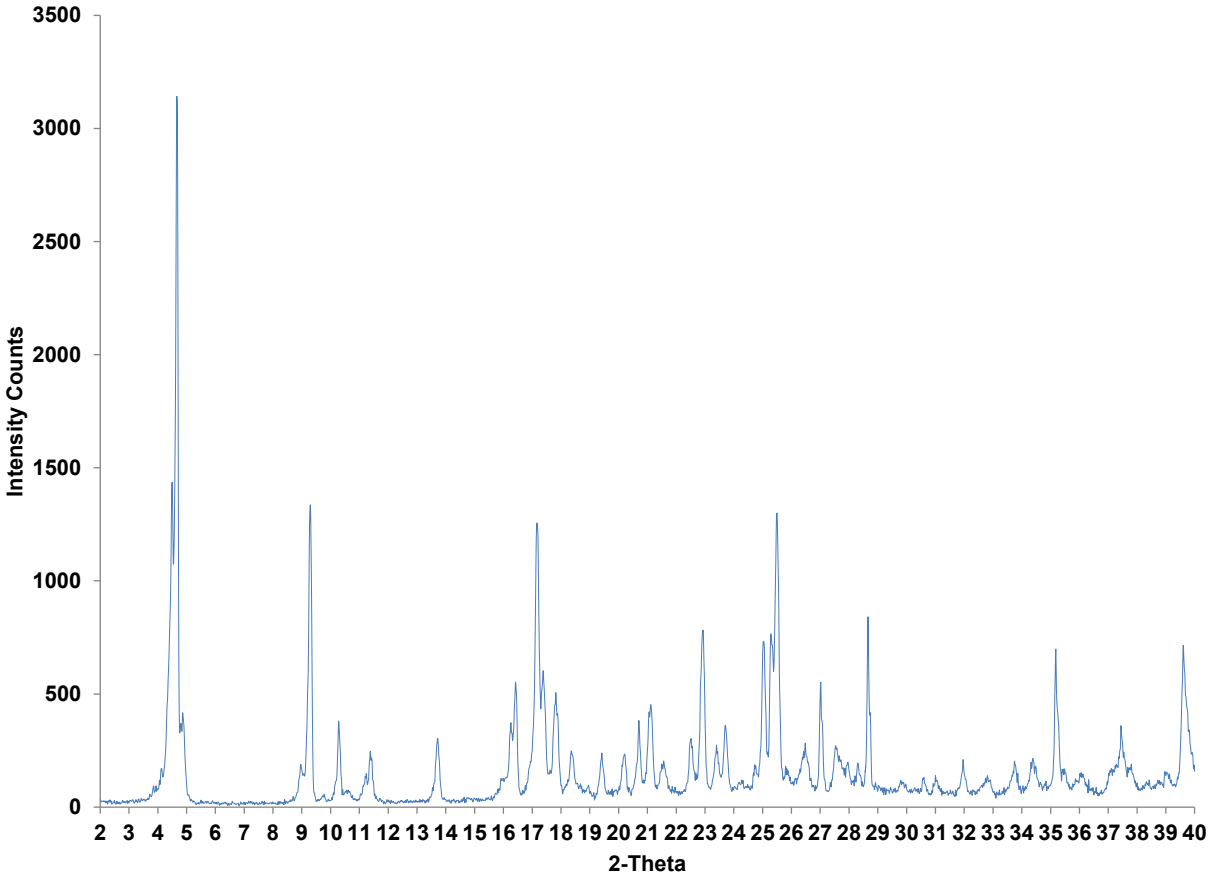

Figure S.2 – Powder XRD of **1**•m-xylene and 1,3-diethylbenzene guest filled framework

```
File       : C:\HPCHEM\1\DATA\MATT_F\JUN13\06192013\TOL_60C.D
Operator   : Matt
Acquired   : 19 Jun 2013  21:31      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: Tol guest in Framwork, DB-1 Column
Misc Info  : Ti=30C,3mins, Tf=150C, 20C/min, 1min
Vial Number: 1
```

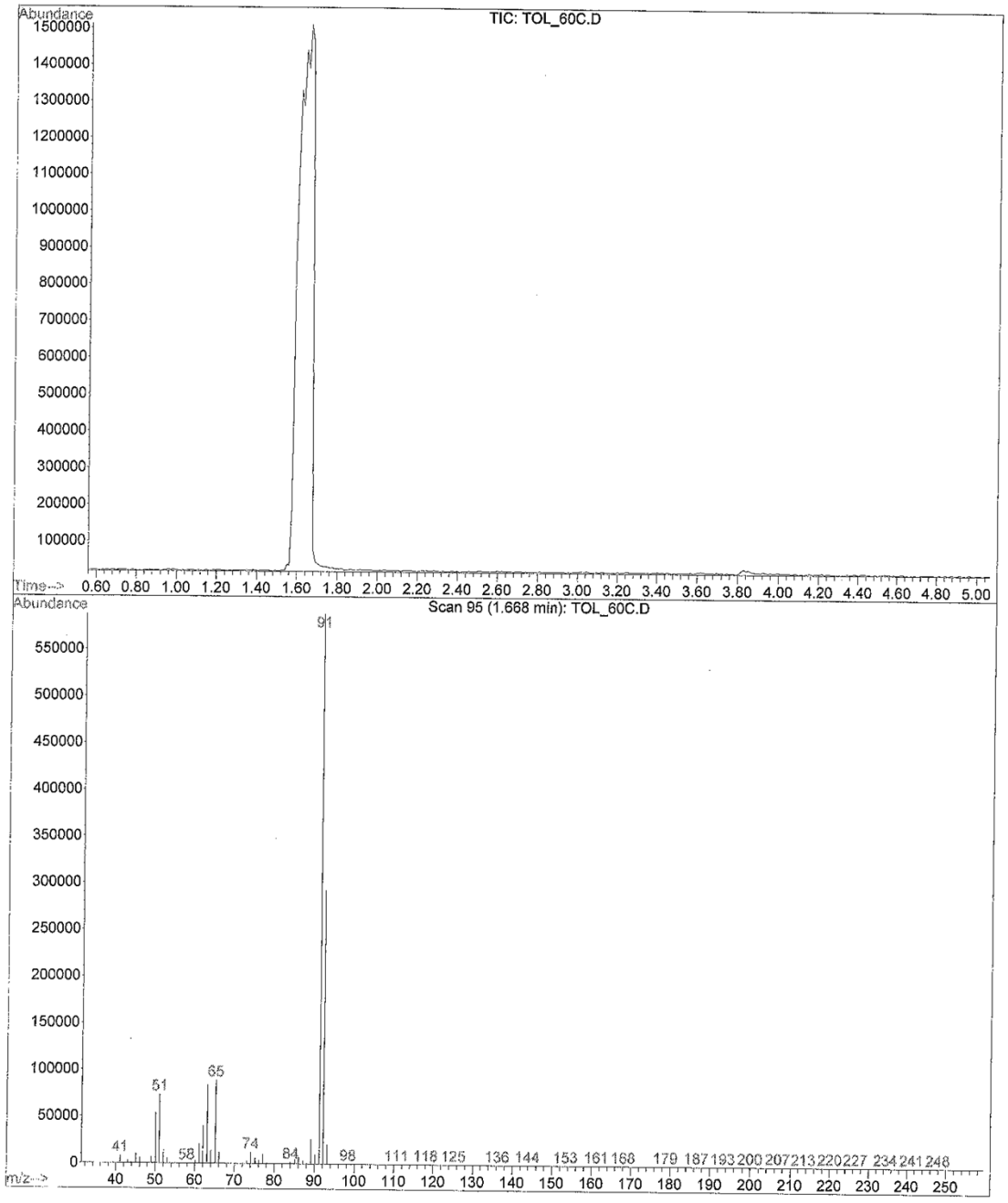

Figure S.3 – GC chromatograph of GC determination of toluene from **1** for GC parameters

```
File        : C:\HPCHEM\2\DATA\MATT_F\04112013\TOLU1.D
Operator    : Matt
Acquired    : 11 Apr 2013  20:09      using AcqMethod MATT_F2.M
Instrument :   HP5890
Sample Name: toluene,SPME determination, DB-5 Column
Misc Info   : Ti=30C, 20C/min,3m,Tf=150C, 20C/min1.00m
Vial Number: 1
```

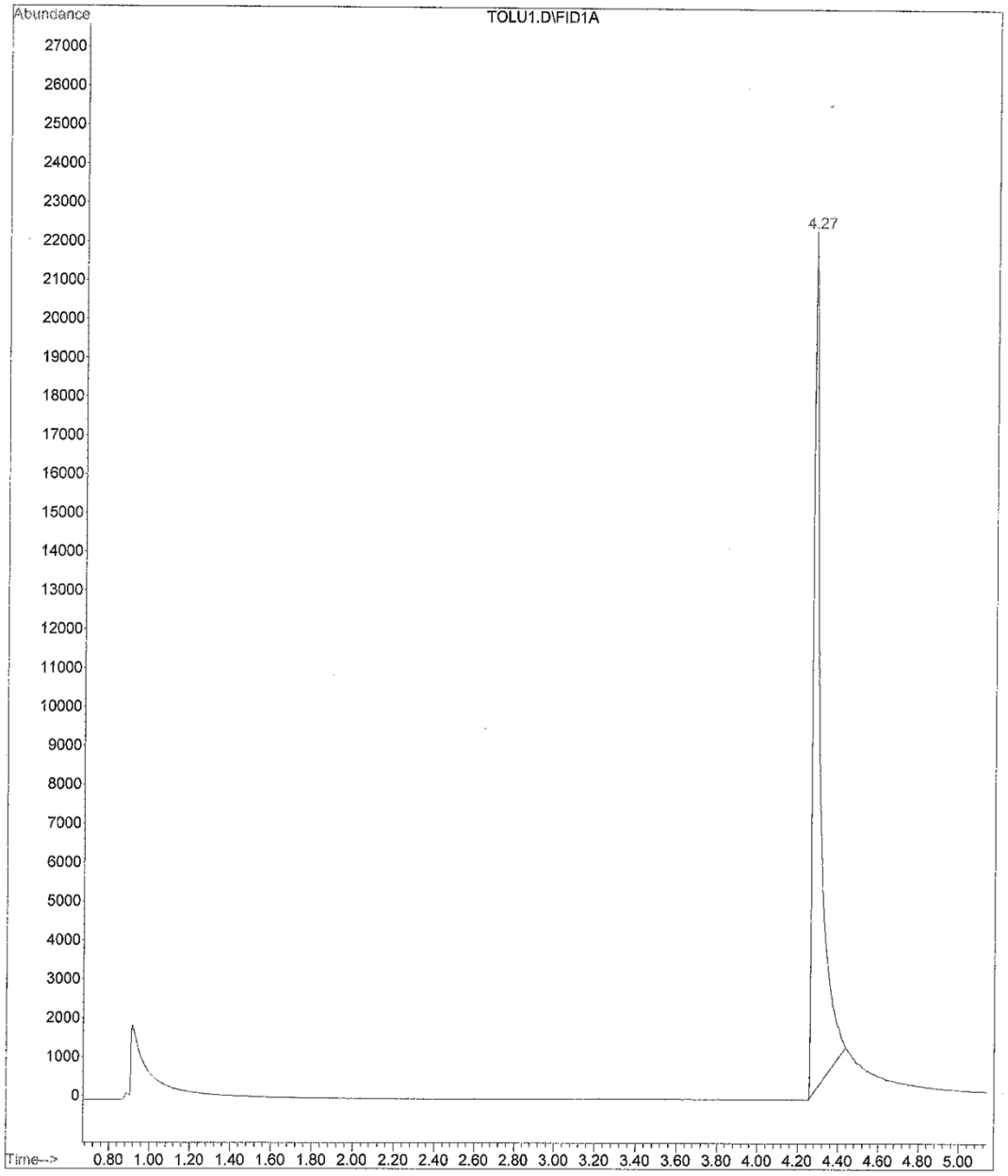

Figure S.4 – GC chromatograph of toluene from **1** using 100µm PDMS SPME fiber from TGA exhaust

TOLU1.D\FID1A

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	4.272	BB	0.035	555187	4.250	4.437
2	7.184	BV	0.006	103424	7.167	7.194

Figure S.4.1 – Peak area from Figure S.4

```
File        : C:\HPCHEM\2\DATA\MATT_F\04112013\TOLU2.D
Operator    : Matt
Acquired    : 11 Apr 2013  20:37      using AcqMethod MATT_F2.M
Instrument :    HP5890
Sample Name: Toluene in Methanol, Ret. time check
Misc Info   : Ti=30C, 20C/min,3m,Tf=150C, 20C/min1.00m
Vial Number: 1
```

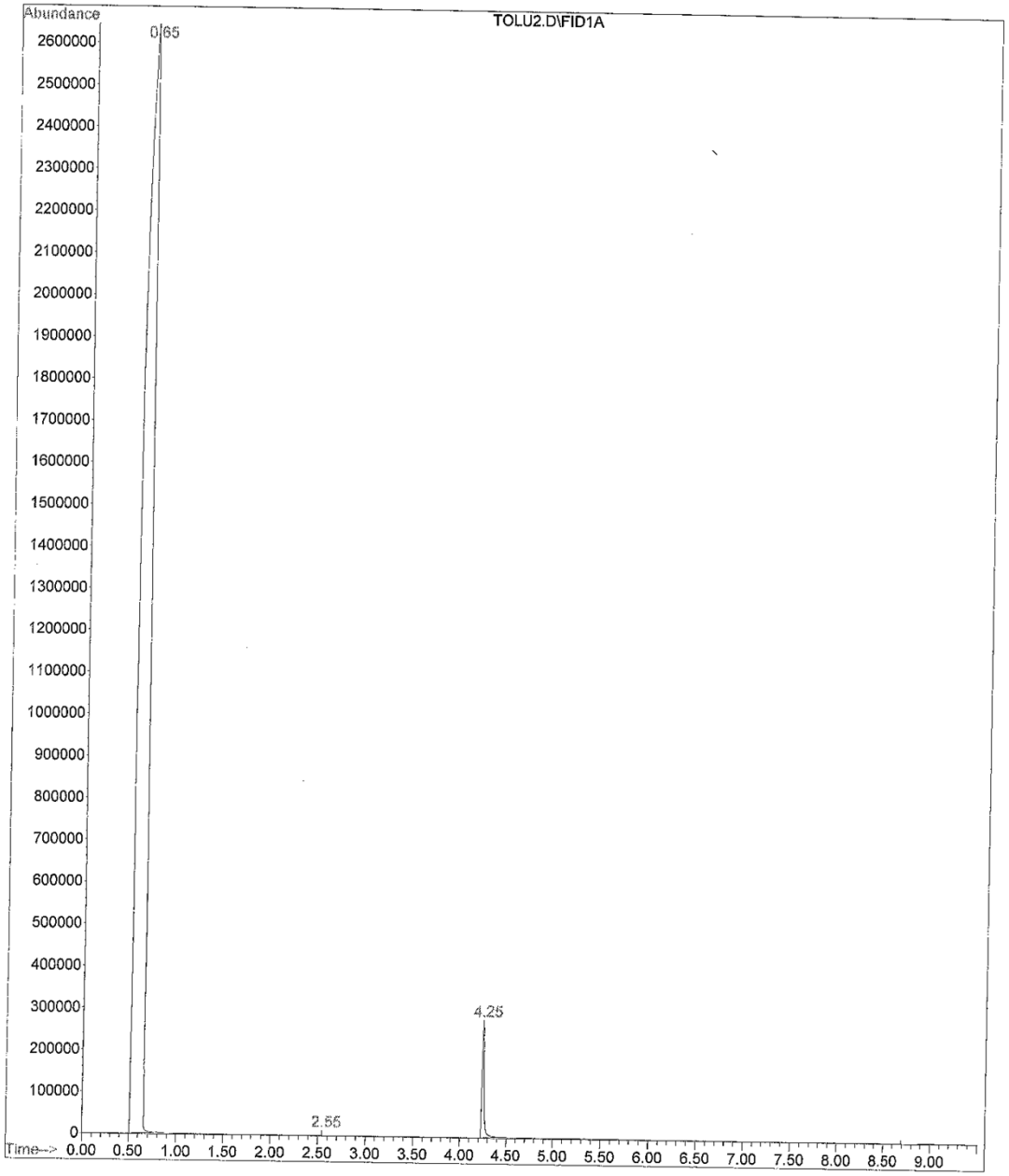

Figure S.5 – GC chromatograph of toluene in methanol solution, direct inject

TOLU2.D\FID1A

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	0.647	BV	0.084	179588773	0.493	0.782
2	2.548	BB	0.005	23628	2.536	2.566
3	4.247	BB	0.025	4518843	4.208	4.459

Figure S.5.1 – Peak area from Figure S.5

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGATOL.D
Operator    : Matt
Acquired    : 13 Jan 2014  22:18      using AcqMethod MATT_F
Instrument :     CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas, full run
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

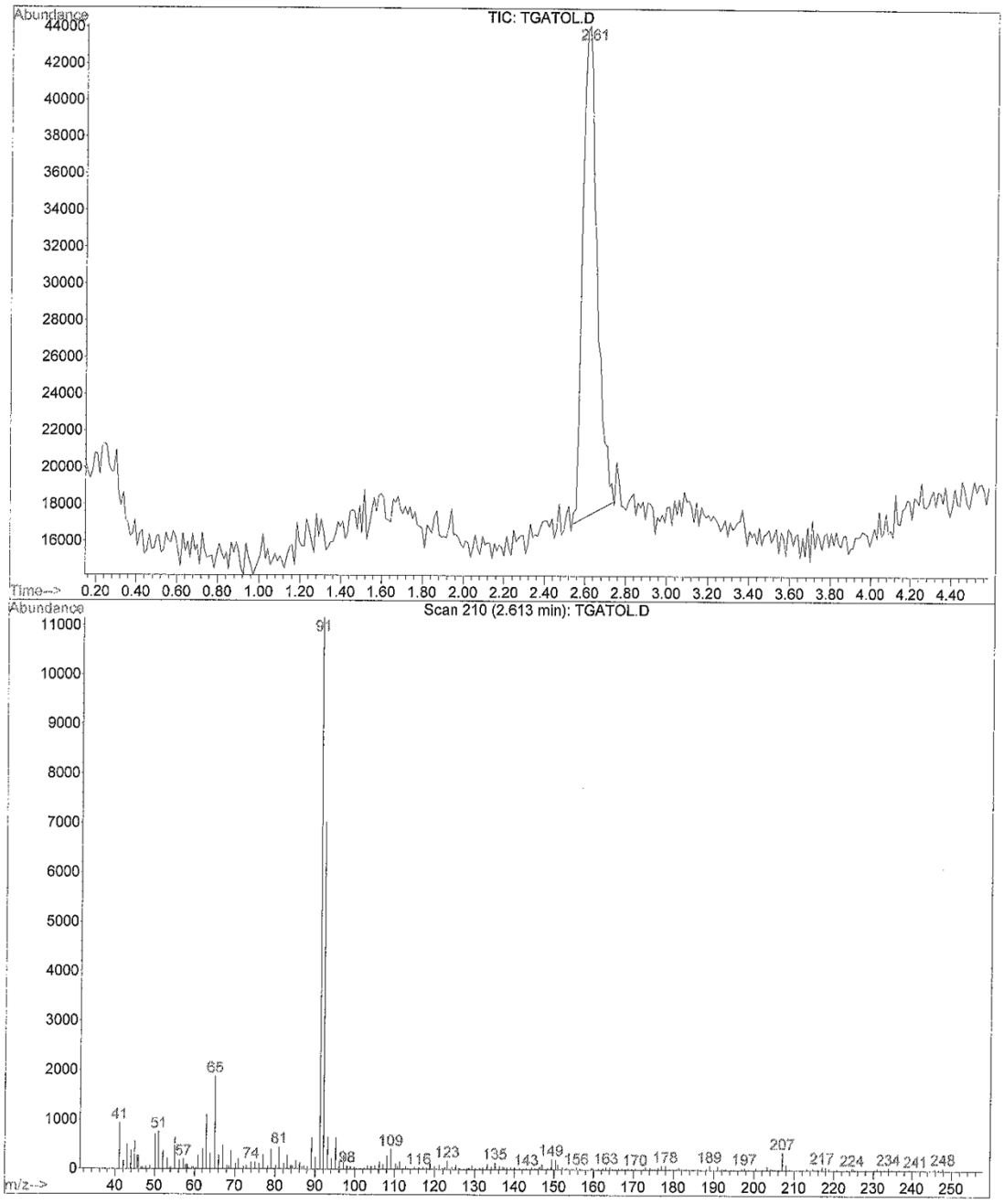

Figure S.6 – GCMS chromatograph of toluene from **1** using 85µm Polyacrylate SPME fiber from TGA exhaust

TIC: TGATOL.D

85umPolyacFiber,Tol,TGA off-gas, full run

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.614	PV	0.075	1313133	2.537	2.745

Figure S.6.1 – Peak area from Figure S.6

```
File        : C:\HPCHEM\1\DATA\MATT_F\07012013\TOL1.D
Operator    : Matt
Acquired    :  1 Jul 2013  20:50      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: Tol Guest, DB-1 Column, SPME 7um PDMS   60 C
Misc Info   : Ti=30C,20/min,3min,Tf=150C,20C/min, 1min
Vial Number: 1
```

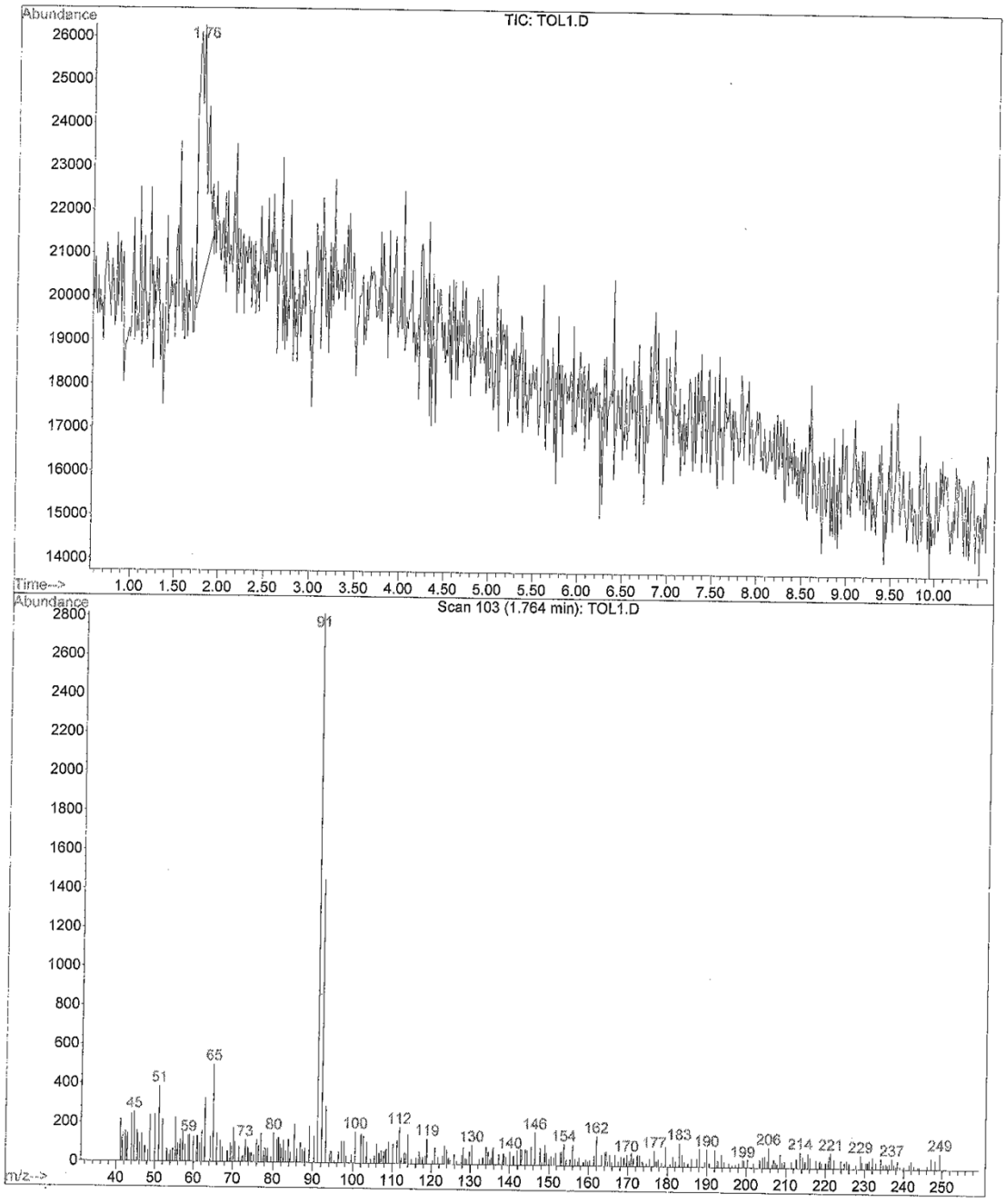

Figure S.7 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 60°C

TIC: TOL1.D

LOC

Tol Guest, DB-1 Column, SPME 7um PDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.762	M	0.105	383405	1.727	1.932

Figure S.7.1 – Peak area from Figure S.7

```
File        : C:\HPCHEM\1\DATA\MATT_F\07012013\TOL2.D
Operator    : Matt
Acquired    :  1 Jul 2013  21:21      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: Tol Guest 70C, DB-1 Column, SPME 7um PDMS
Misc Info   : Ti=30C,20/min,3min,Tf=150C,20C/min, 1min
Vial Number: 1
```

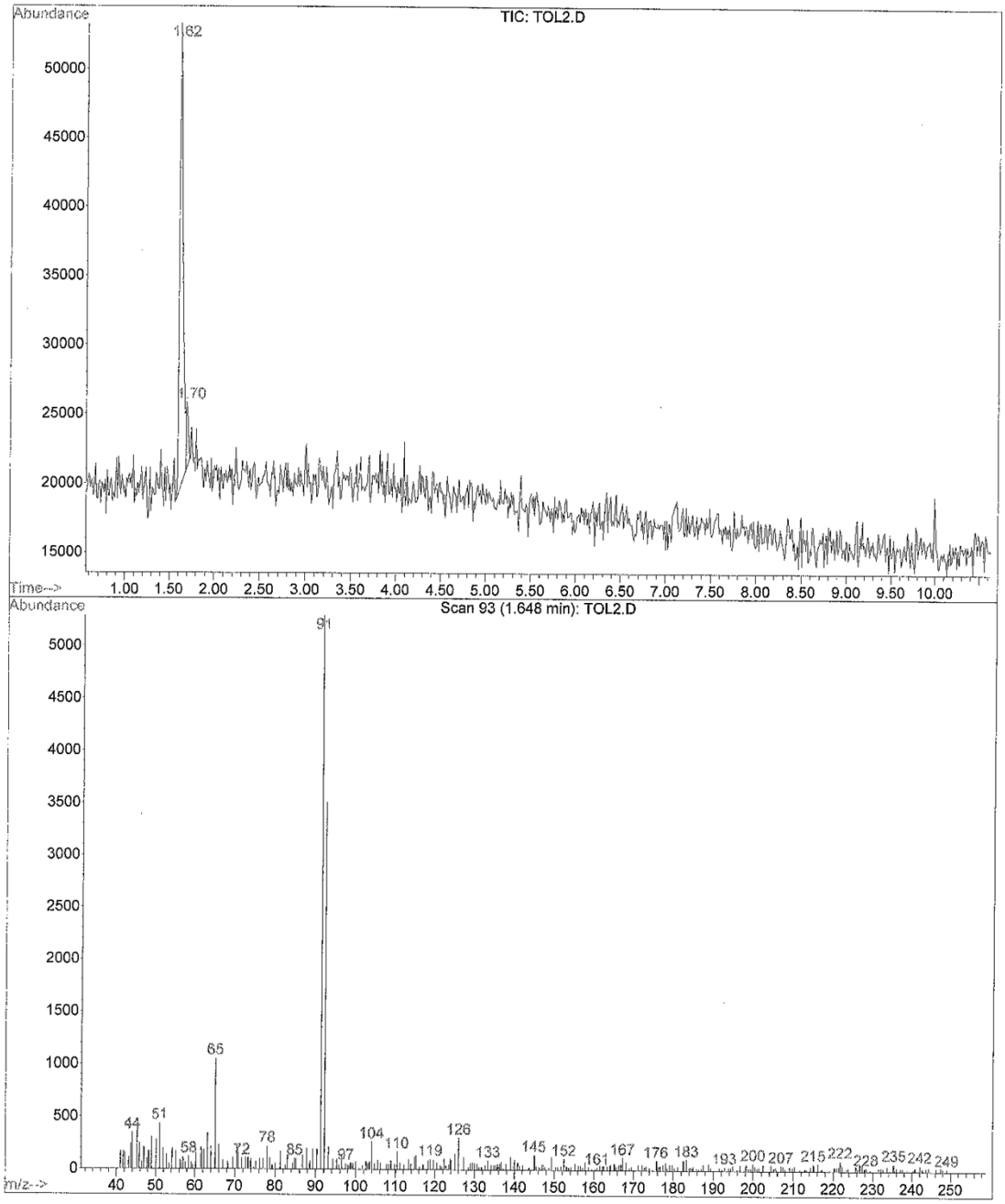

Figure S.8 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 70°C

TIC: TOL2.D

Tol Guest 70C, DB-1 Column, SPME 7um PDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.621	PV	0.042	877206	1.576	1.684
2	1.698	VV	0.030	83139	1.684	1.731

Figure S.8.1 – Peak area from Figure S.8

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL80.D
Operator    : Matt
Acquired    : 10 Jul 2013  20:40      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: DB-1 Column Tol Guest, 80C Rel SPME7umPDMS
Misc Info   : Ti=30C,3min,Tf=150C,20min
Vial Number: 1
```

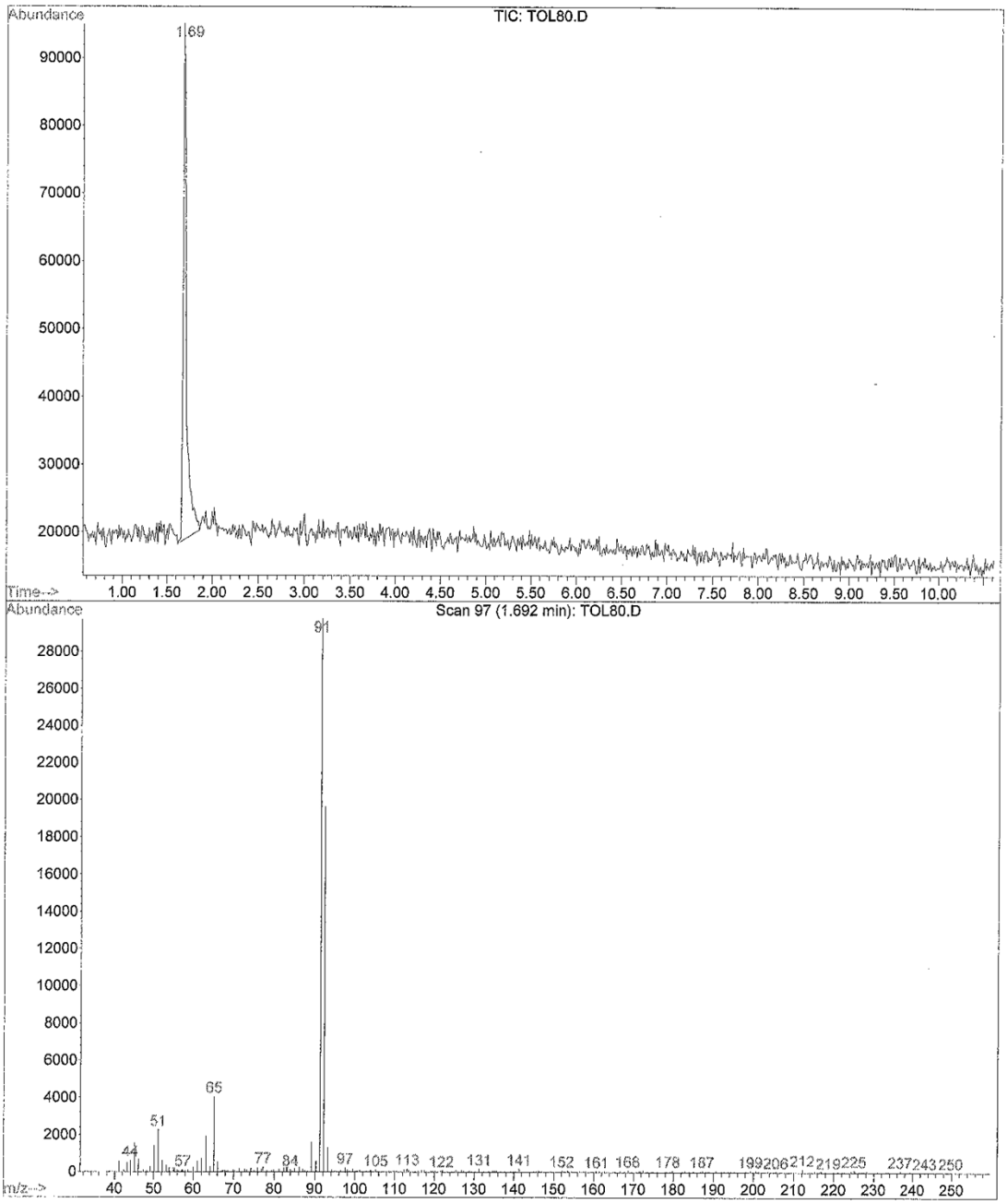

Figure S.9 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 80°C

TIC: TOL80.D

DB-1 Column Tol Guest, 80C Rel SPME7umPDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.691	PV	0.048	1950212	1.631	1.865

Figure S.9.1 – Peak area from Figure S.9

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL90.D
Operator    : Matt
Acquired    : 10 Jul 2013  21:03      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: DB-1 Column Tol Guest, 90C Rel SPME7umPDMS
Misc Info   : Ti=30C,3min,Tf=150C,20min
Vial Number: 1
```

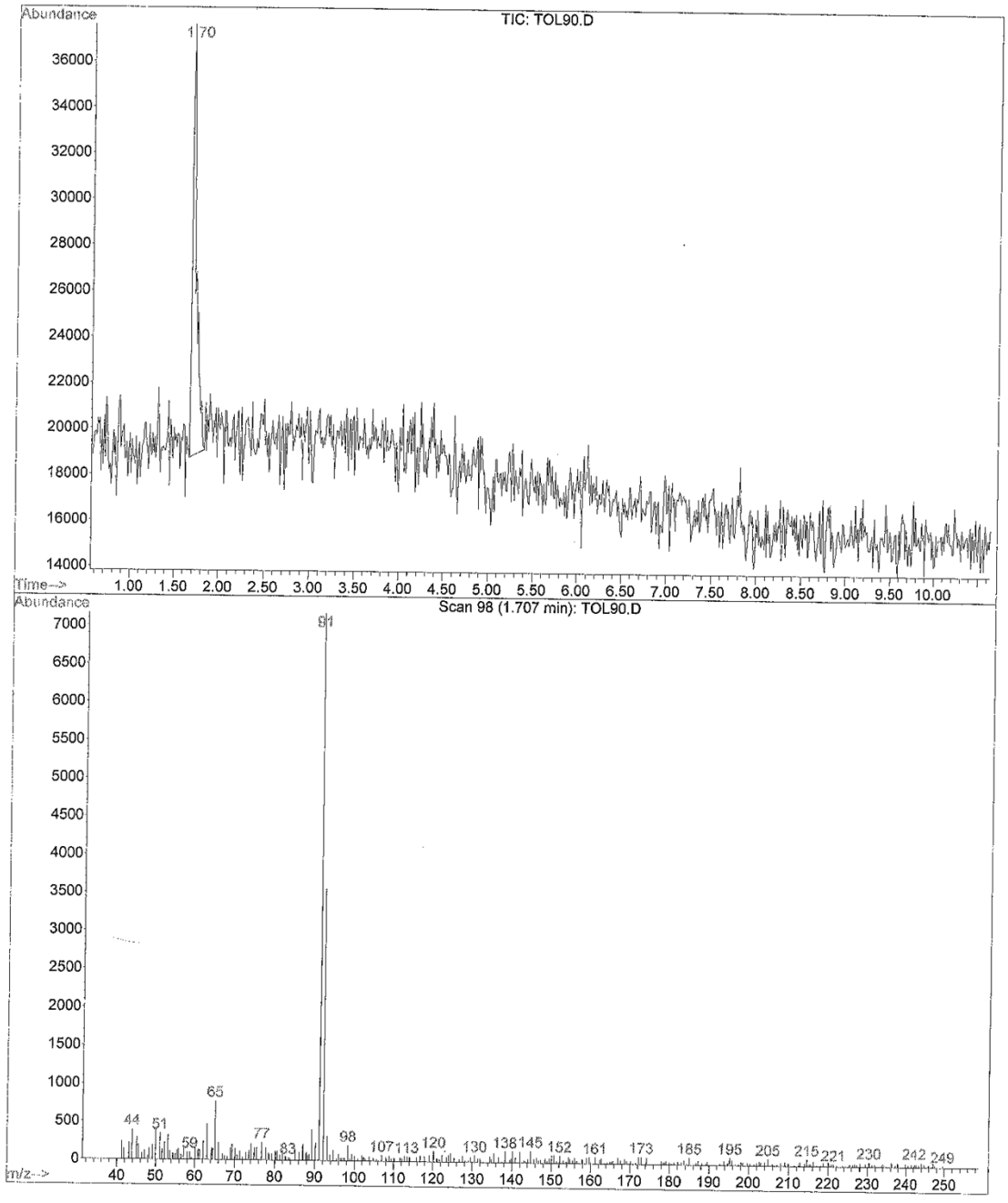

Figure S.10 - GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 90°C

TIC: TOL90.D

DB-1 Column Tol Guest, 90C Rel SPME7umPDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.700	PV	0.048	602539	1.667	1.834

Figure S.10.1 – Peak area from Figure S.10

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL100.D
Operator    : Matt
Acquired    : 10 Jul 2013  21:26      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: DB-1 Column Tol Guest, 100C Rel SPME7umPDMS
Misc Info   : Ti=30C,3min,Tf=150C,20min
Vial Number: 1
```

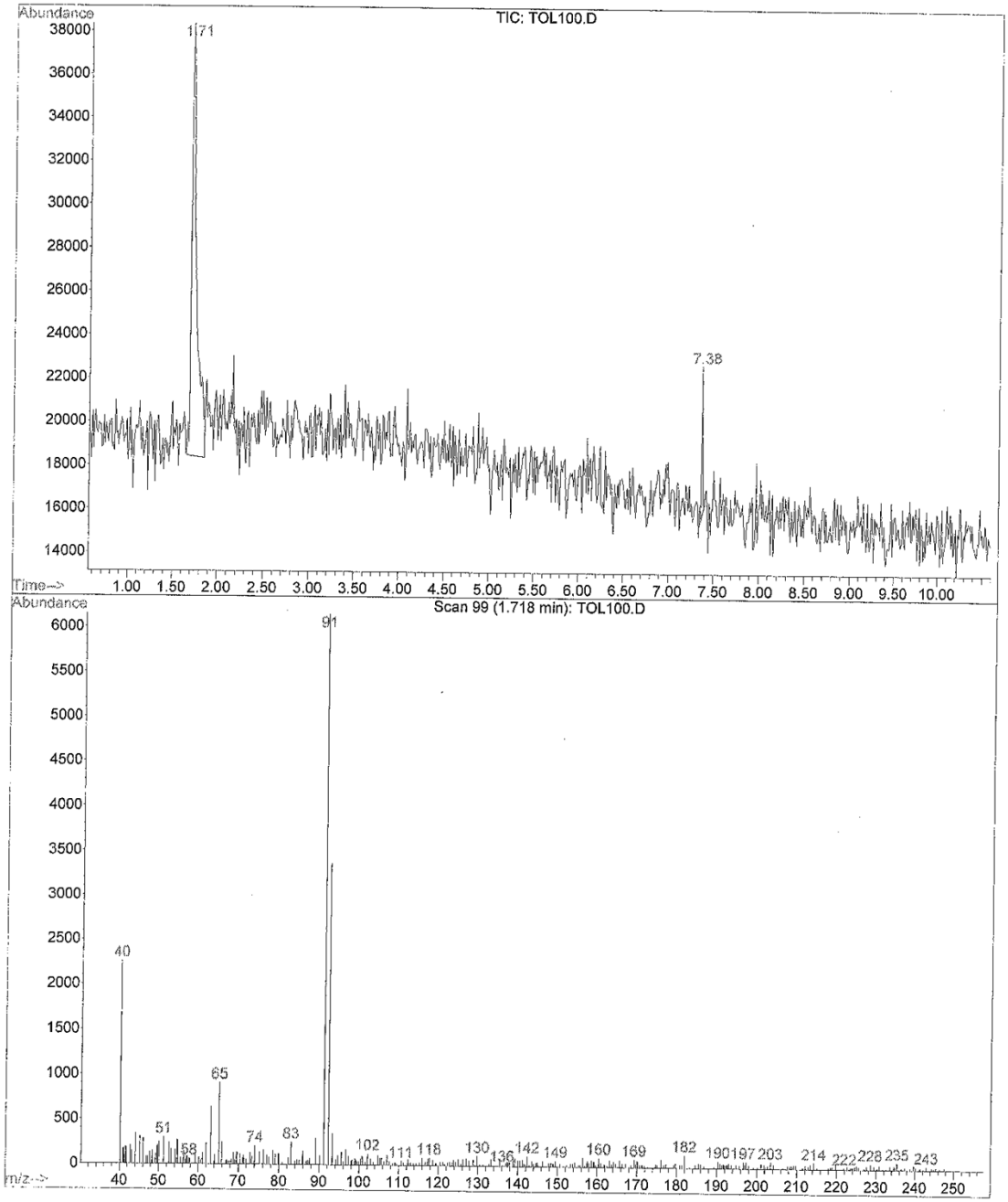

Figure S.11 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 100°C

TIC: TOL100.D

DB-1 Column Tol Guest, 100C Rel SPME7umPDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.711	VV	0.056	779687	1.655	1.856
2	7.376	PV	0.016	53002	7.342	7.398

Figure S.11.1 – Peak area from Figure S.11

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL110.D
Operator    : Matt
Acquired    : 10 Jul 2013  21:48      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: DB-1 Column Tol Guest, 110C Rel SPME7umPDMS
Misc Info   : Ti=30C,3min,Tf=150C,20min
Vial Number: 1
```

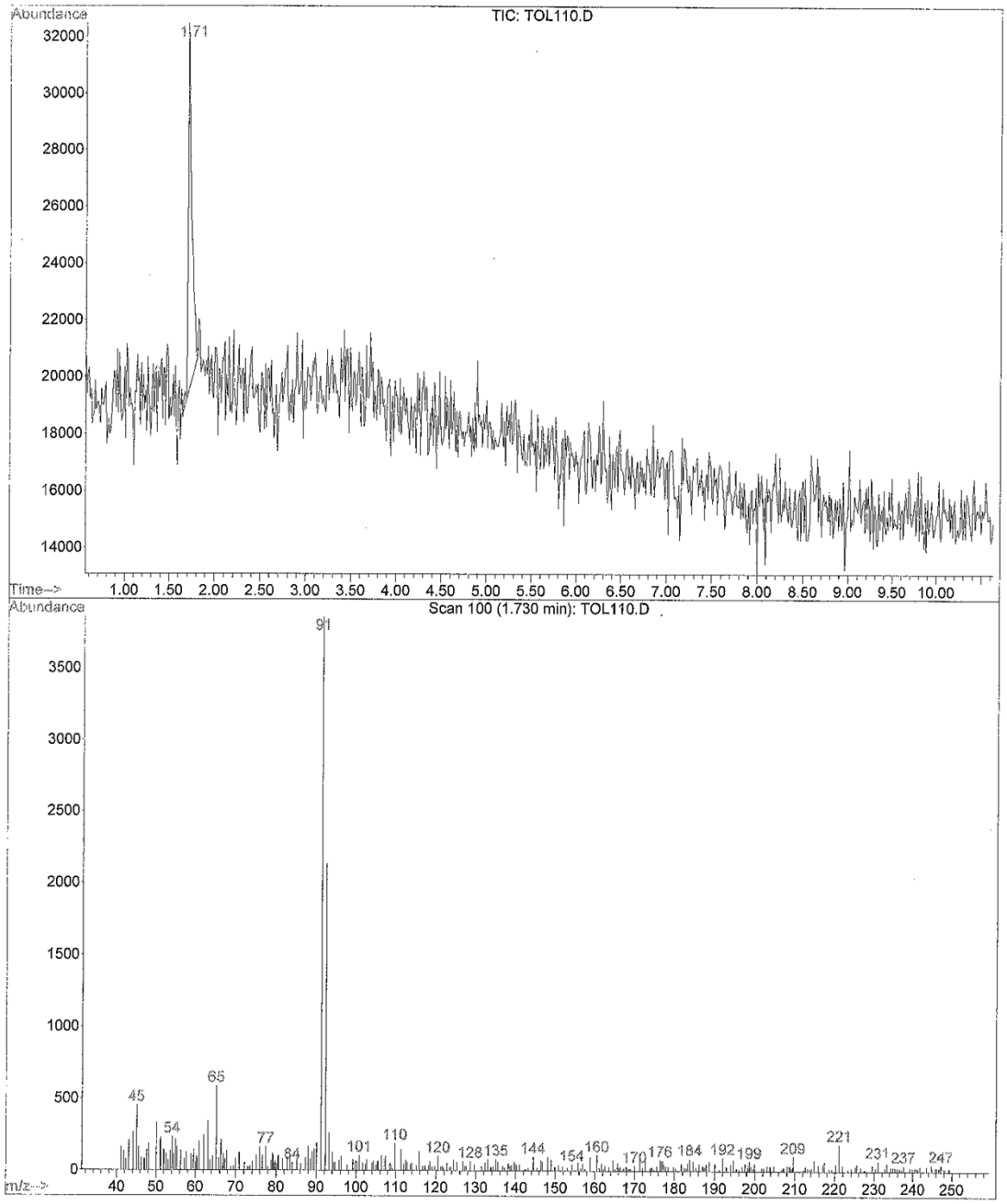

Figure S.12 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 110°C

TIC: TOL110.D

DB-1 Column Tol Guest, 110C Rel SPME7umPDMS

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	1.715	PV	0.050	326116	1.653	1.813

Figure S.12.1 – Peak area from Figure S.12

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL120.D
Operator    : Matt
Acquired    :  5 Dec 2013  21:17      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 7umPDMS SPME,HP1Col, 120C
Misc Info   : ti=30C,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

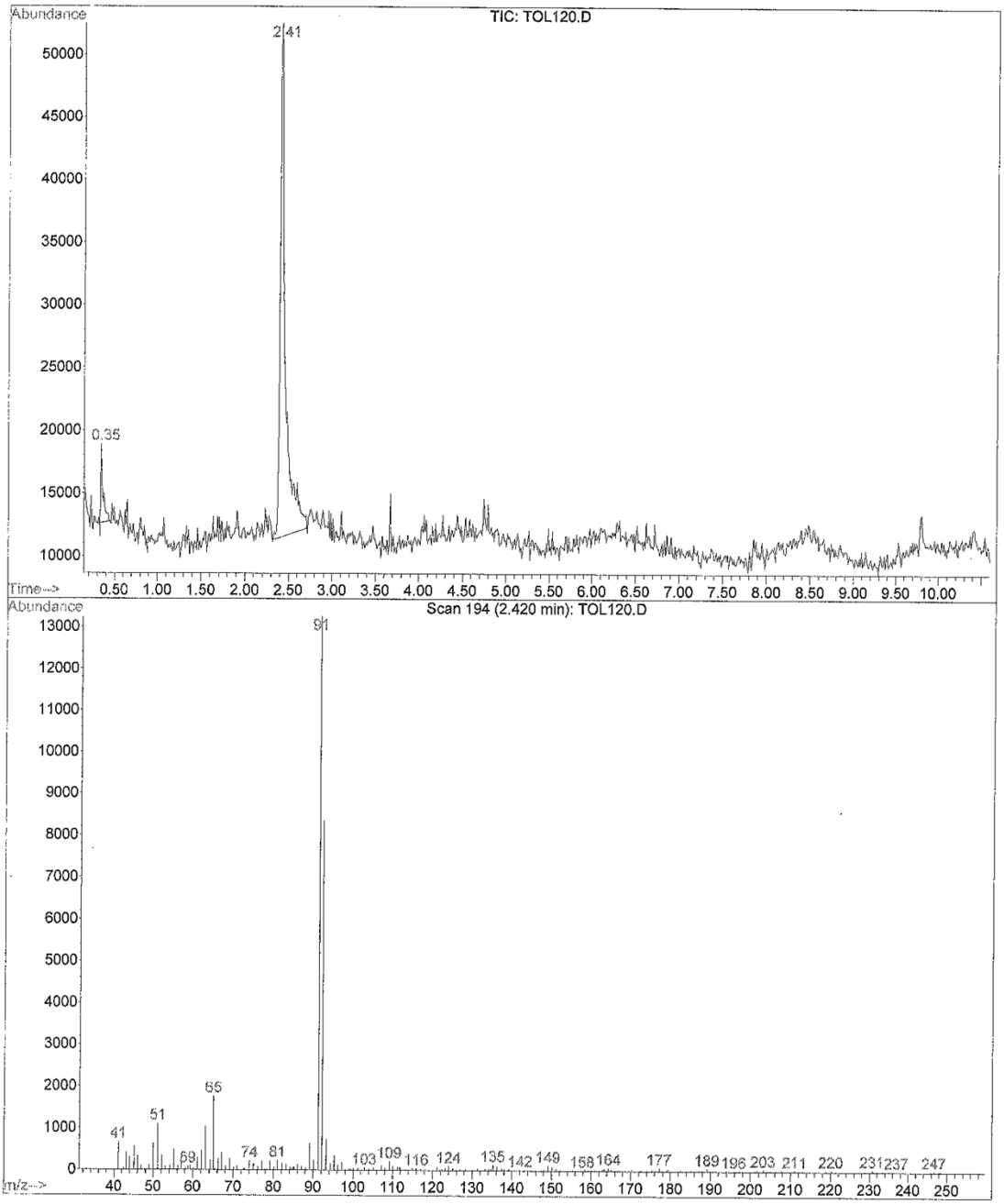

Figure S.13 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 120°C

TIC: TOL120.D

7umPDMS SPME,HP1Col, 120C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	0.348	PV	0.033	111112	0.297	0.454
2	2.410	PV	0.059	1712765	2.322	2.716

Figure S.13.1 – Peak area from Figure S.13

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL110TD.D
Operator    : Matt
Acquired    : 10 Dec 2013  21:47      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: SPME,7umPDMS,HP-1Column,Tol guest,110CTimed
Misc Info   : ti=30C,20C/min,3min,tf=150C,20C/min,1min
Vial Number: 1
```

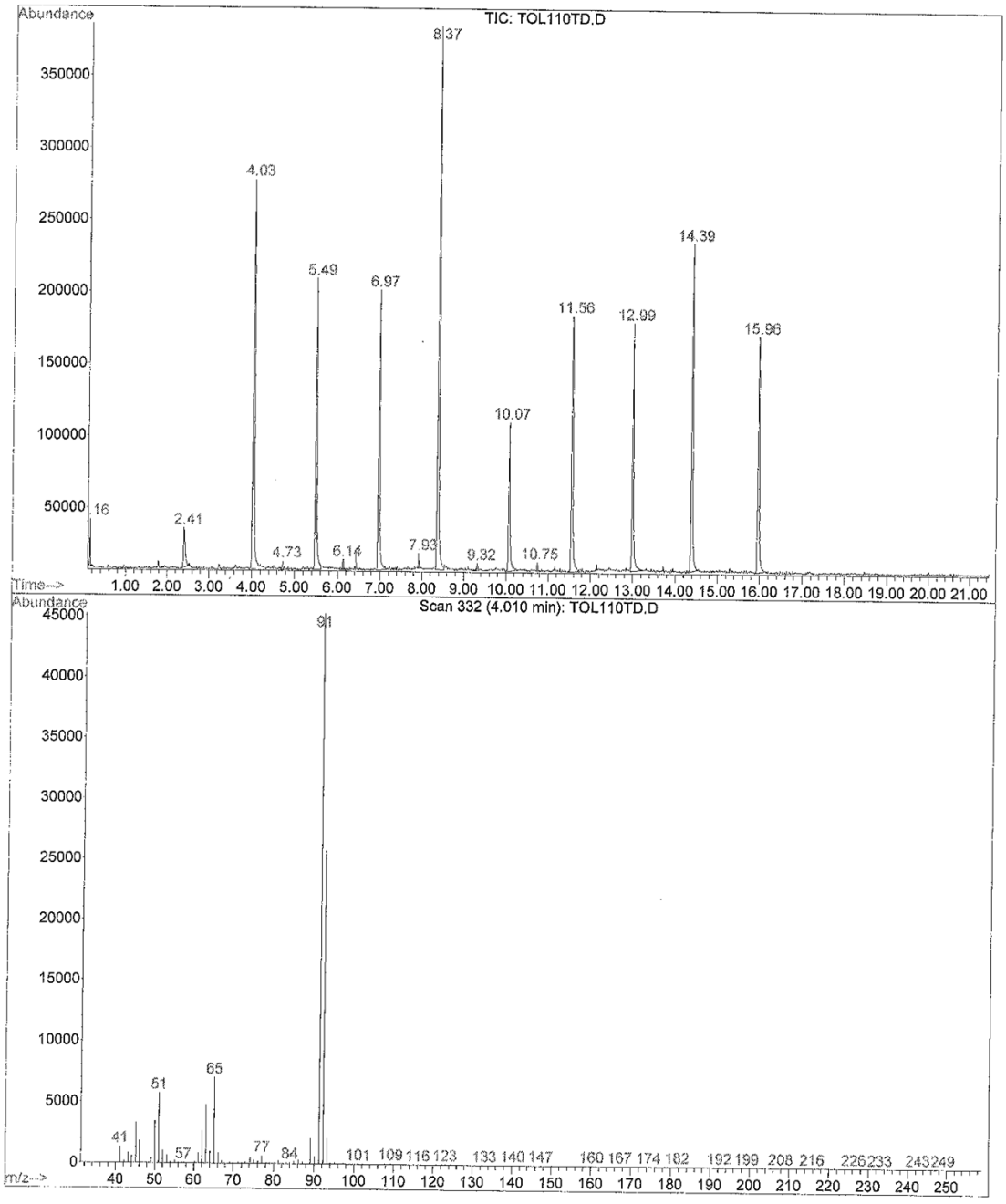

Figure S.14 – GCMS chromatograph of toluene from **1** using gas-tight syringe, sampled every 60s at 110°C

TIC: TOL110TD.D

SPME,7umPDMS,HP-1Column,Tol guest,110CTimed

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	0.161	BV	0.023	368440	0.120	0.264
2	2.414	PV	0.040	734970	2.363	2.507
3	4.031	PV	0.038	6336325	3.952	4.338
4	4.731	VV	0.025	84523	4.690	4.755
5	5.485	VV	0.036	4683424	5.403	5.611
6	6.135	VV	0.036	149385	6.051	6.200
7	6.967	PV	0.037	4315510	6.914	7.161
8	7.926	PV	0.031	128650	7.748	7.951
9	8.370	VV	0.035	8186782	8.317	8.530
10	9.323	PV	0.035	113959	9.207	9.354
11	10.071	PV	0.038	2483174	10.002	10.325
12	10.753	VV	0.027	96317	10.725	10.835
13	11.558	PV	0.037	4255166	11.467	11.793
14	12.993	PV	0.037	3837816	12.948	13.257
15	14.385	PV	0.036	4949555	14.302	14.534
16	15.964	PV	0.036	3824192	15.883	16.128

Figure S.14.1 – Peak area from Figure S.14

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL2MIN.D
Operator    : Matt
Acquired    : 10 Dec 2013  22:19      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: SPME,7umPDMS,HP-1Column,Tol guest,110C,2min
Misc Info   : ti=30C,20C/min,3min,tf=150C,20C/min,1min
Vial Number: 1
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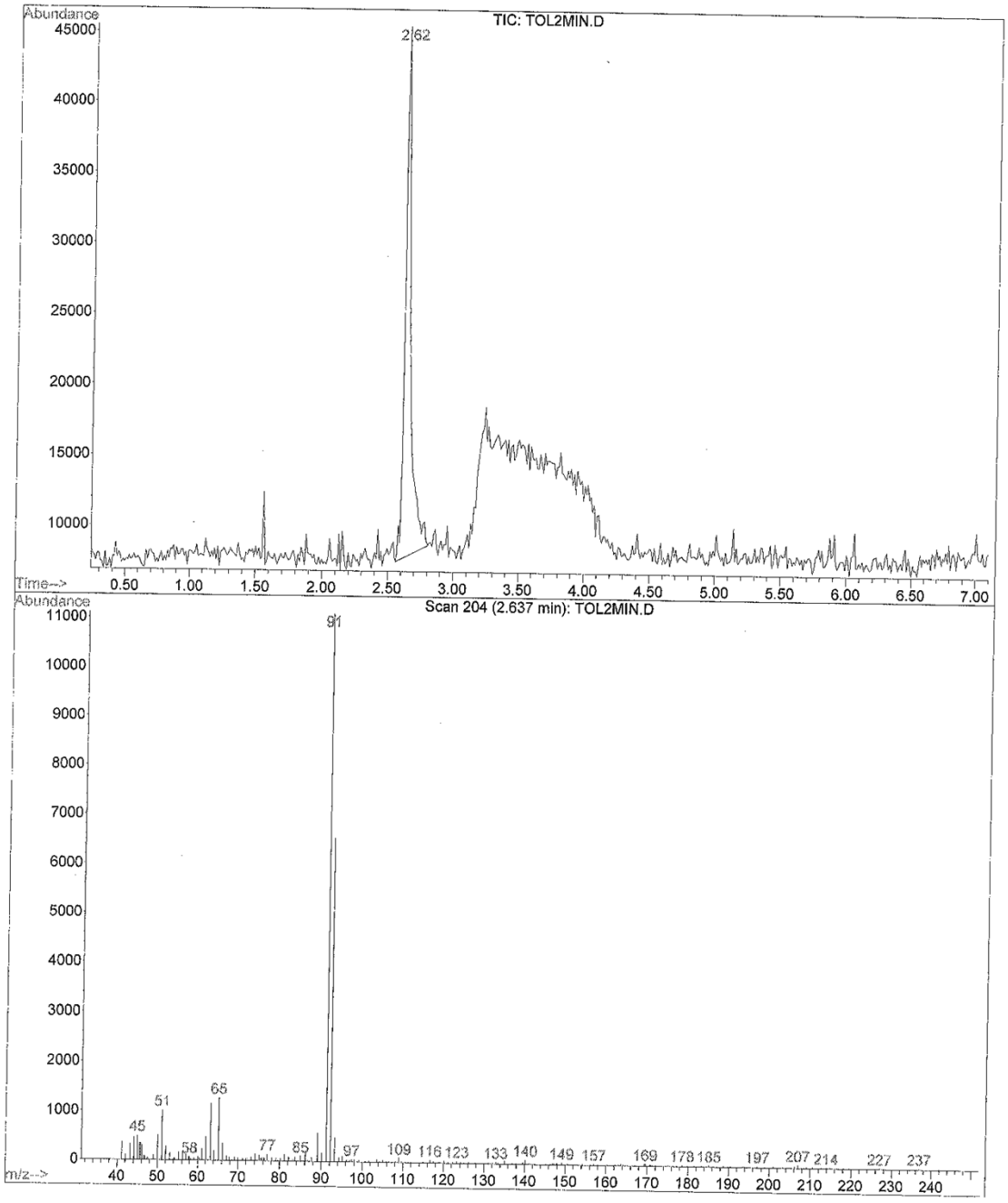

Figure S.15 – GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 120°C, 2 mins

TIC: TOL2MIN.D

SPME,7umPDMS,HP-1Column,Tol guest,110C,2min

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.624	M	0.053	1192563	2.559	2.808

Figure S.15.1 – Peak area from Figure S.15

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\TOL110P.D
Operator    : Matt
Acquired    : 10 Dec 2013  20:59      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: SPME,7umPDMS,HP-1Column,Tol guest,110C PP
Misc Info   : ti=30C,20C/min,3min,tf=150C,20C/min,1min
Vial Number: 1
```

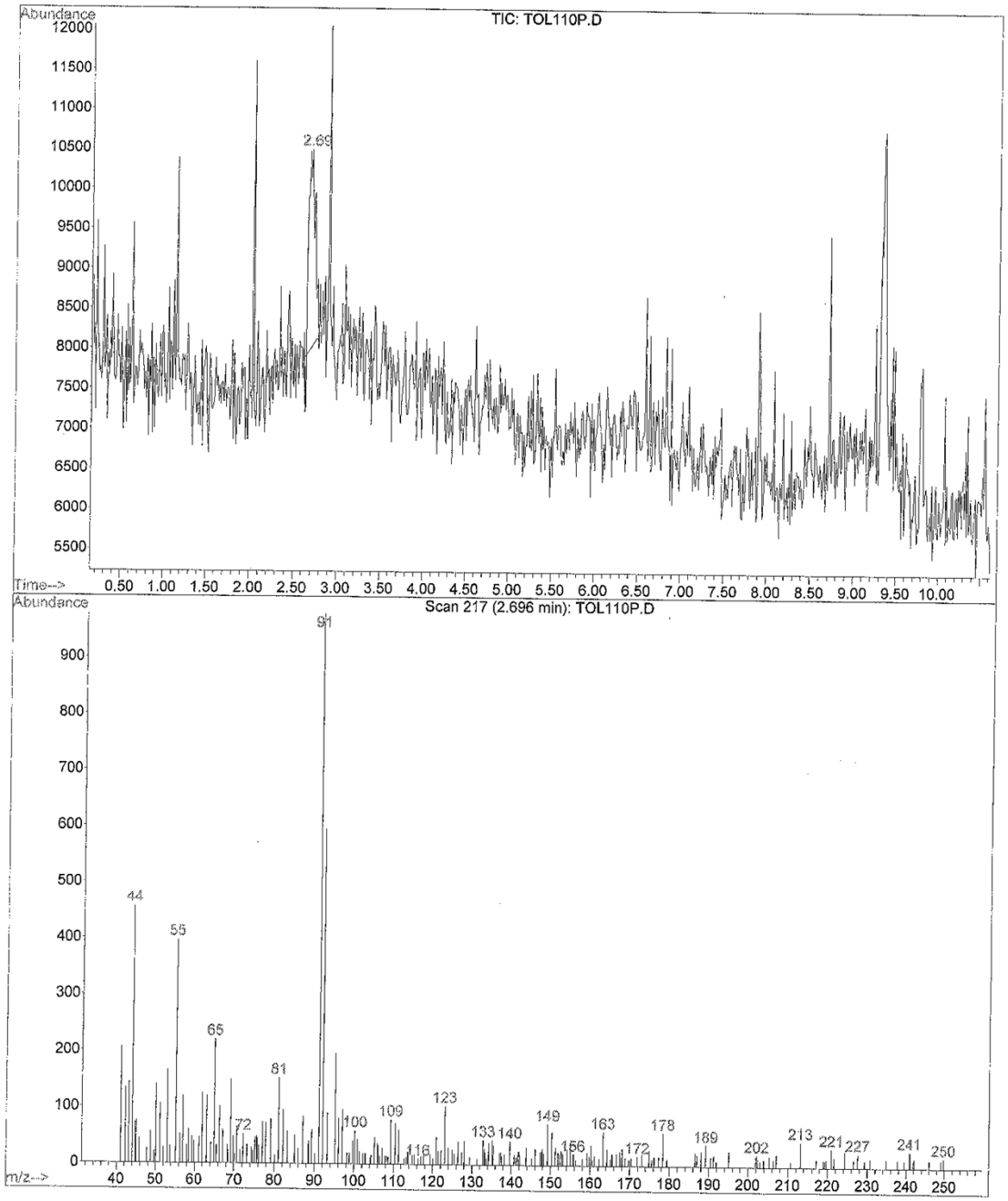

Figure S.16 - GCMS chromatograph of toluene from **1** using 7µm PDMS SPME fiber at 110°C, post-purge

TIC: TOL110P.D

SPME,7umPDMS,HP-1Column,Tol guest,110C PP

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.694	M	0.085	126836	2.628	2.780

Figure S.16.1 – Peak area from Figure S.16

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGA100.D
Operator    : Matt
Acquired    : 13 Jan 2014  21:04     using AcqMethod MATT_F
Instrument :     CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas@100C
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

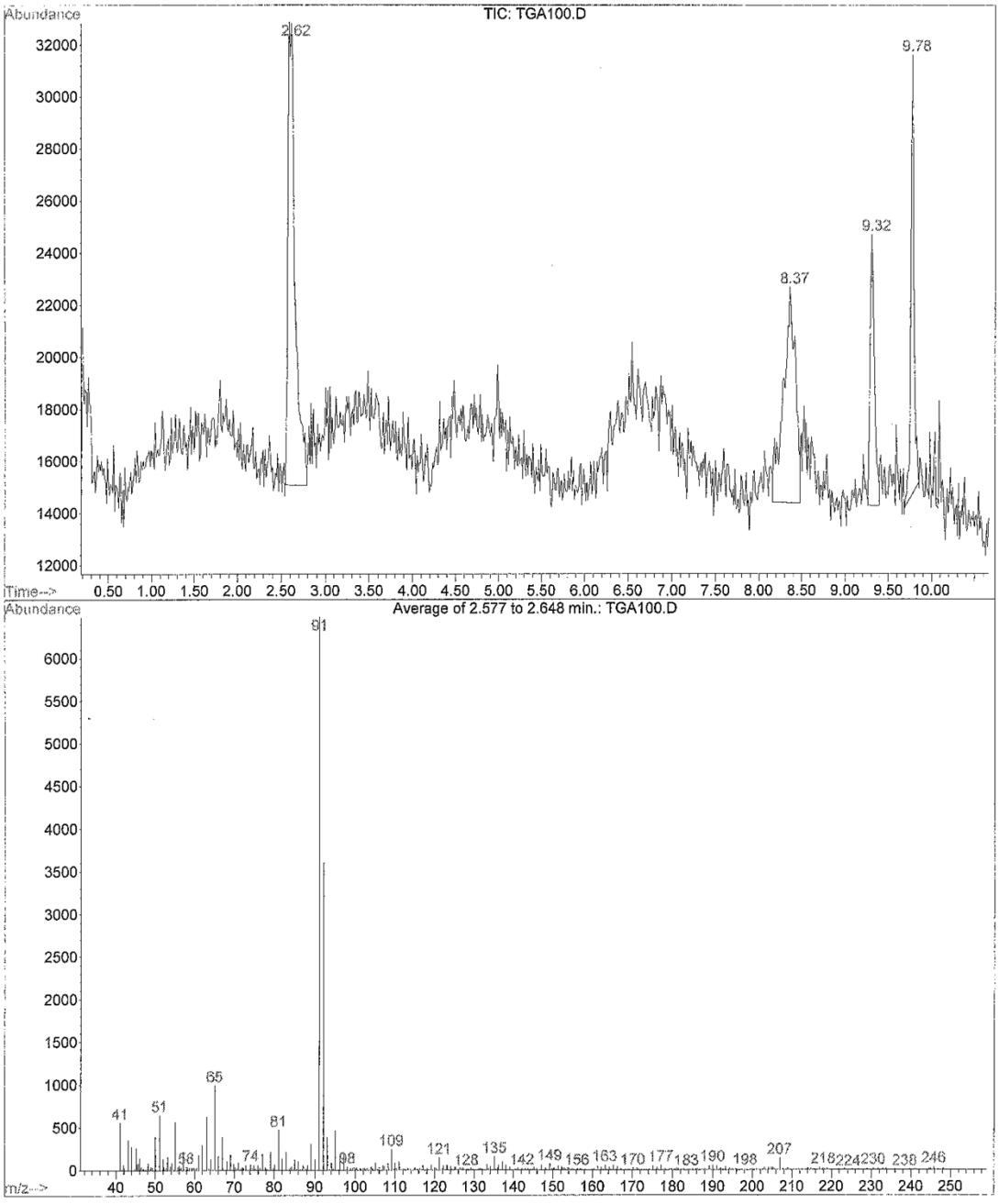

Figure S.17 - GCMS chromatograph of toluene from **1**, TGA off-gas using 85µm PA SPME fiber at 100°C

TIC: TGA100.D

85umPolyacFiber,Tol,TGA off-gas@100C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.619	PV	0.086	1004544	2.547	2.791
2	8.371	VV	0.123	802132	8.164	8.481
3	9.315	VV	0.057	369409	9.260	9.394
4	9.782	PV	0.041	411331	9.693	9.856

Figure S.17.1 – Peak area from Figure S.17

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGA110.D
Operator    : Matt
Acquired    : 13 Jan 2014   20:31      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas@110C
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

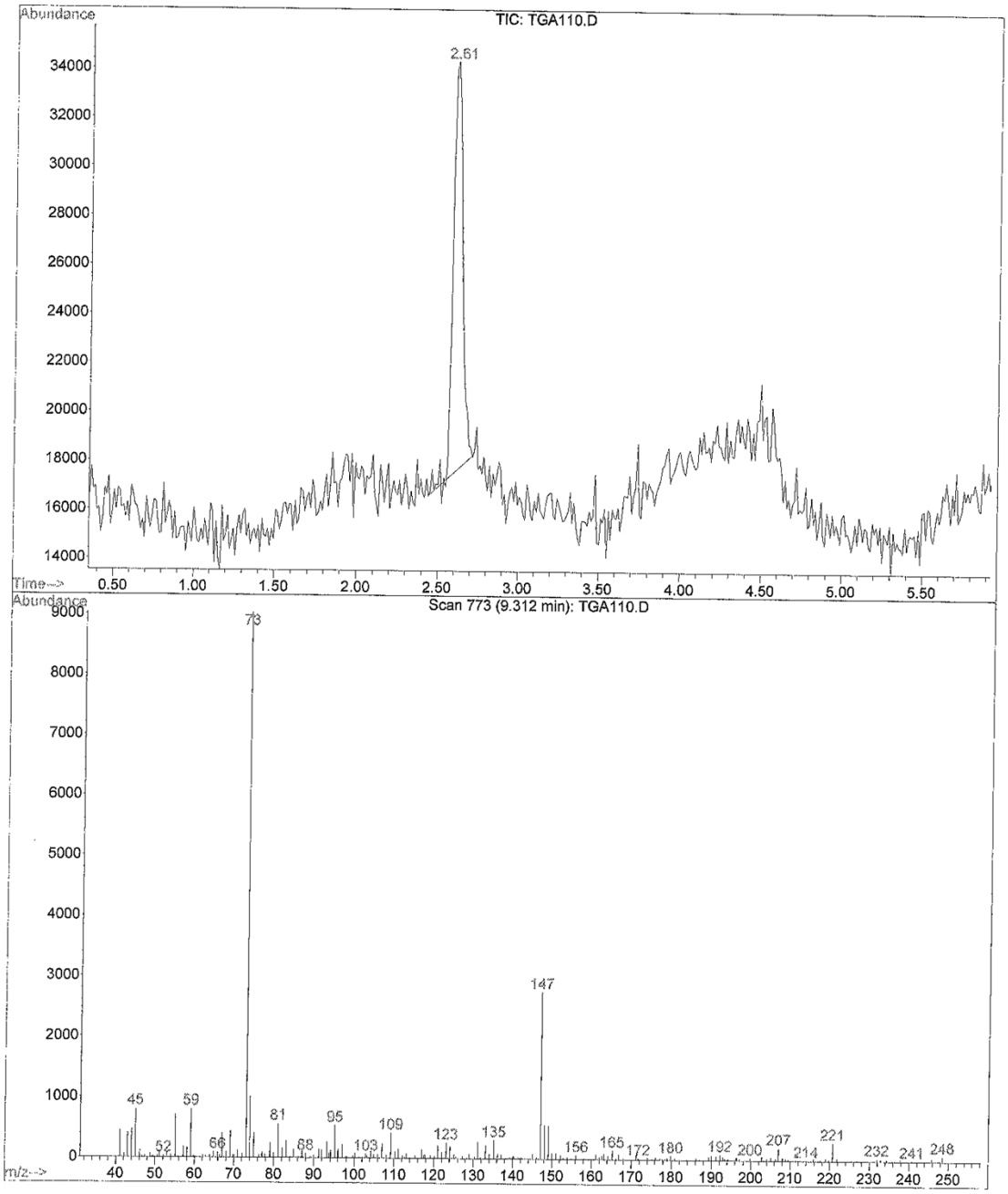

Figure S.18 - GCMS chromatograph of toluene from **1**, TGA off-gas using 85µm PA SPME fiber at 110°C

TIC: TGA110.D

85umPolyacFiber,Tol,TGA off-gas@110C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.607	PV	0.065	679366	2.549	2.718

Figure S.18.1 – Peak area from Figure S.18

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGA120.D
Operator    : Matt
Acquired    : 13 Jan 2014  19:49      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas@120C
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

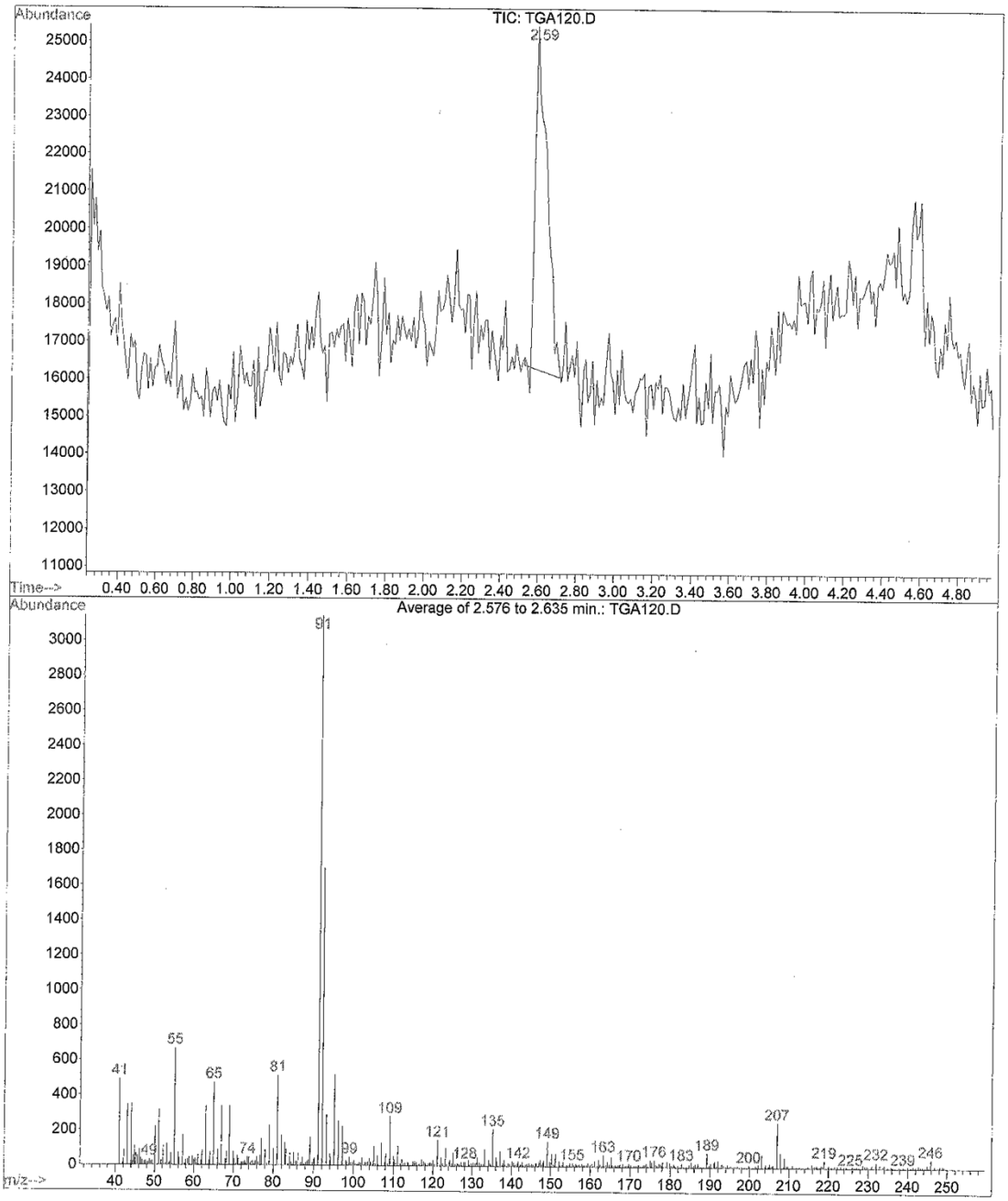

Figure S.19 - GCMS chromatograph of toluene from **1**, TGA off-gas using 85µm PA SPME fiber at 120°C

TIC: TGA120.D

85umPolyacFiber,Tol,TGA off-gas@120C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.594	BV	0.066	389800	2.525	2.722

Figure S.19.1 – Peak area from Figure S.19

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGA130.D
Operator    : Matt
Acquired    : 13 Jan 2014  19:13      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas@130C
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

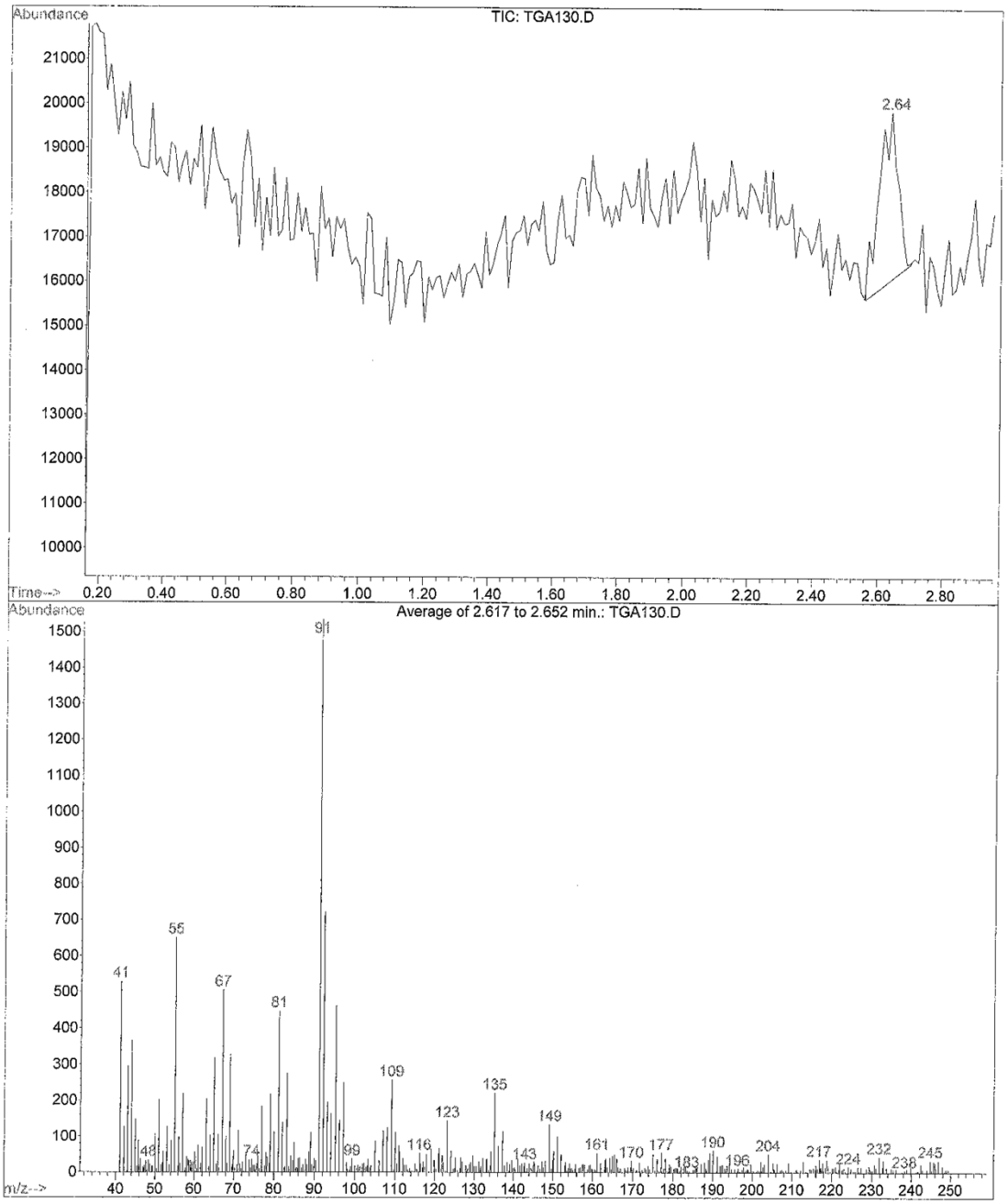

Figure S.20 – GCMS chromatograph of toluene from **1**, TGA off-gas using 85µm PA SPME fiber at 130°C

TIC: TGA130.D

85umPolyacFiber,Tol,TGA off-gas@130C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.640	M	0.067	151190	2.560	2.699

Figure S.20.1 - Peak area from Figure S.20

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\STDADD\TGA140.D
Operator    : Matt
Acquired    : 13 Jan 2014  21:44      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,Tol,TGA off-gas@140C
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

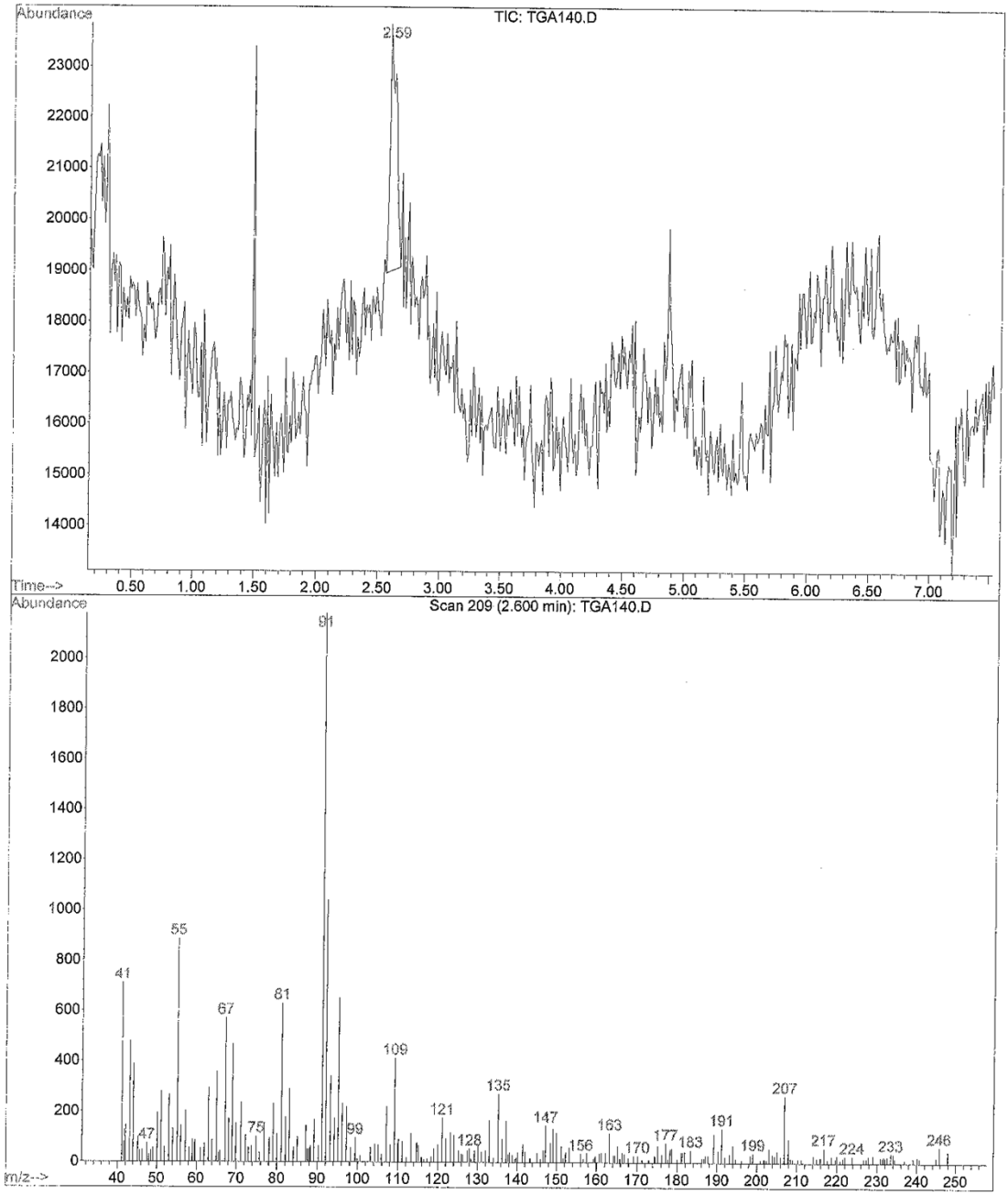

Figure S.21 - GCMS chromatograph of toluene from **1**, TGA off-gas using 85µm PA SPME fiber at 140°C

TIC: TGA140.D

85umPolyacFiber,Tol,TGA off-gas@140C

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	2.591	M	0.059	173877	2.553	2.671

Figure S.21.1 – Peak area from Figure S.21

```
File        : C:\HPCHEM\1\DATA\MATT_F\SPMETR\SPMEXY2.D
Operator    : Matt
Acquired    : 11 Jan 2014  10:30      using AcqMethod MATT_F
Instrument :   CSS Instr
Sample Name: 85umPolyacFiber,DOE16R5,TGA off-gas
Misc Info   : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

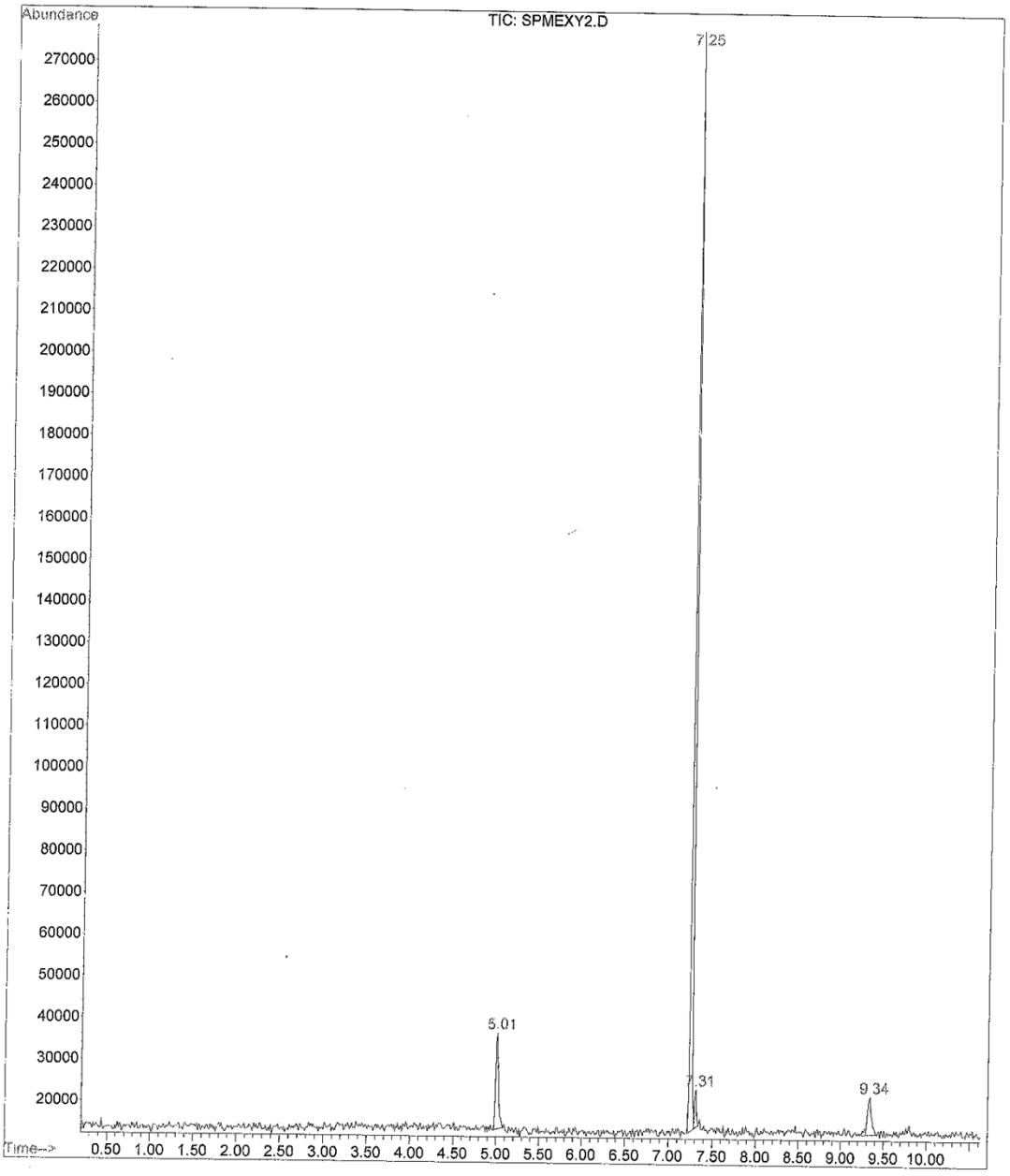

Figure S.22 - GCMS chromatograph of m-xylene and 1,3-diethylbenzene from **1** using 85µm PA SPME fiber, from TGA exhaust gas

```
File       : C:\HPCHEM\1\DATA\MATT_F\SPMETR\SPMEXY2.D
Operator   : Matt
Acquired   : 11 Jan 2014  10:30      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,DOE16R5,TGA off-gas
Misc Info  : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

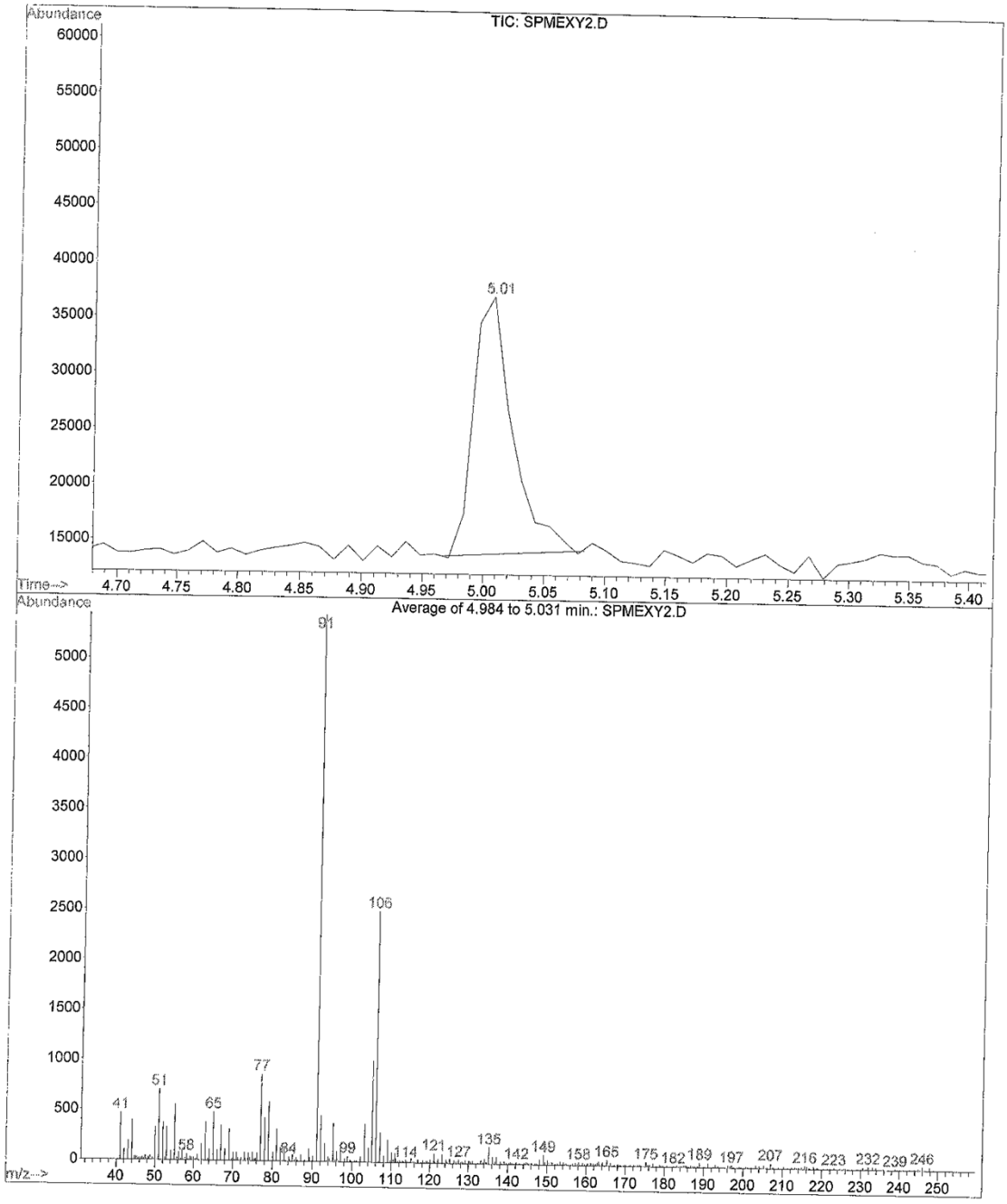

Figure S.22.1 – Expansion of GCMS peak at 5m 1s from Figure S.22, m-xylene

```
File       : C:\HPCHEM\1\DATA\MATT_F\SPMETR\SPMEXY2.D
Operator   : Matt
Acquired   : 11 Jan 2014  10:30      using AcqMethod MATT_F
Instrument :    CSS Instr
Sample Name: 85umPolyacFiber,DOE16R5,TGA off-gas
Misc Info  : Ti=30,20C/min,3min,Tf=150C,20C/min,1min
Vial Number: 1
```

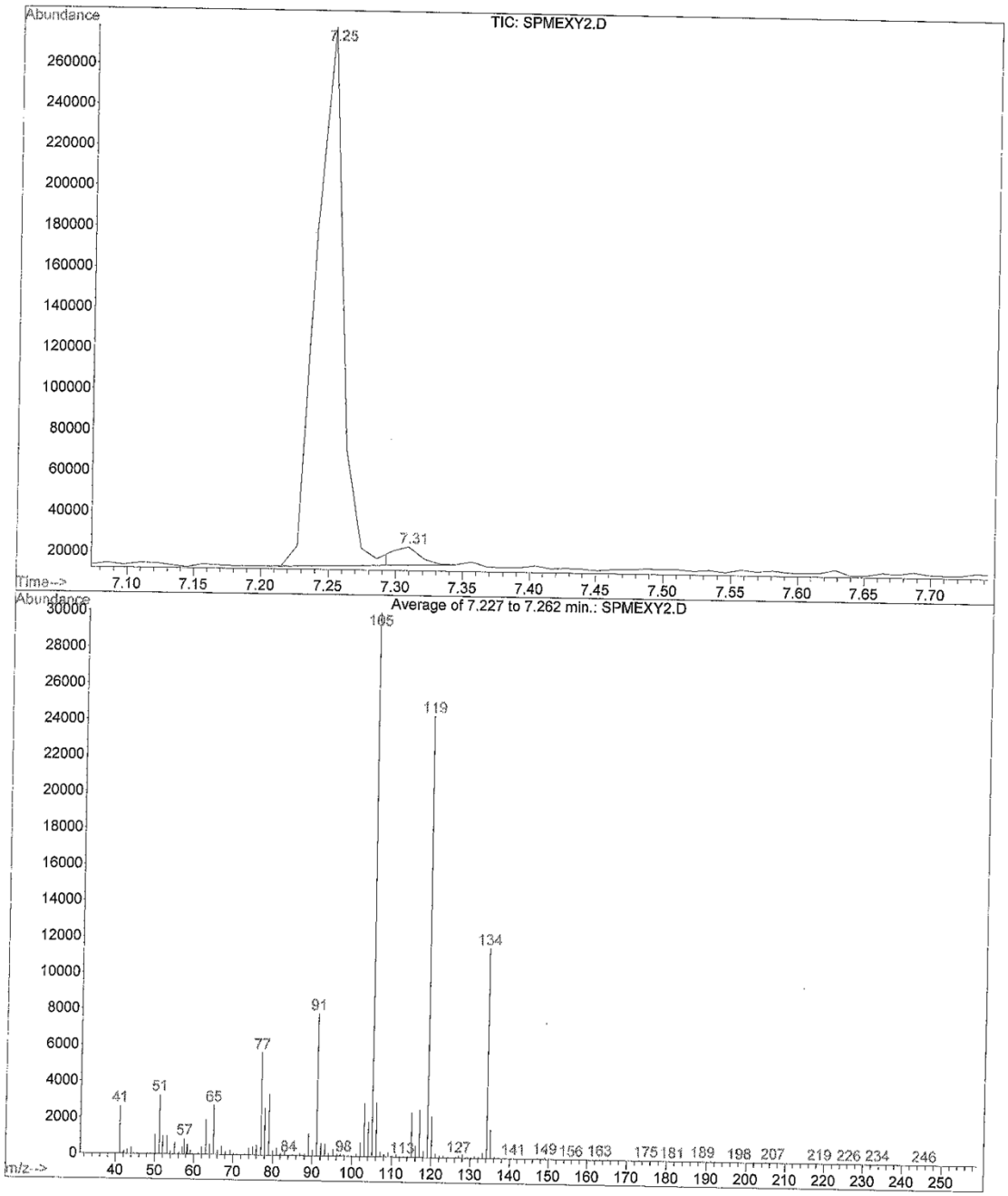

Figure S.22.2 – Expansion of GCMS peak at 7m 25s from Figure S.22, 1,3-diethylbenzene

TIC: SPMEXY2.D

85umPolyacFiber,DOE16R5,TGA off-gas

Peak#	Ret Time	Type	Width	Area	Start Time	End Time
1	5.009	PV	0.035	513353	4.967	5.083
2	7.252	BV	0.025	3593104	7.213	7.293
3	7.311	VV	0.028	140849	7.293	7.345
4	9.340	PV	0.054	317579	9.229	9.425

Figure S.22.3 – Peak area from Figure S.22