Synthesis, crystal structure and immobilization of a new cobalt (II) complex with 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligand on modified magnetic nanoparticles as a catalyst for the oxidation of alkanes

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Supporting information:

Materials and instrumentation

All materials were of commercial reagent grade and used without further purification. FTIR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using KBr pellets over the range of 4,000–400 cm^{-1}. Raman spectra were measured on a **NRS-4100** Dispersive Raman spectrometer equipped with 633 nm argon ion laser. Elemental analyses were performed on a Heraeus CHN-O-Rapid elemental analyzer. The amount of cobalt and iron in the Fe_3O_4@SiO_2@APTMS@ [Co(tptz)Cl_2]. 2H_2O nanocatalyst was determined by atomic absorption spectroscopy (AAS) with a GBC flame spectrophotometer (0.30% (2988 ppm) Co, 77.64 % Fe). Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (BHV-55, Riken, Japan) in the magnetic field range of -8000 to 8000 Oe at room temperature. TGA/DSC (Thermogravimetric analysis & Differential Scanning Calorimetry) were recorded on a METTLER TOLEDO instrument using 12 mg of [Co(tptz)Cl_2]. 2H_2O. The X-ray powder diffraction (XRD) data were recorded on a Siefert XRD 3003 PTS diffractometer, using Cu Kα1 radiation (k = 1.5406 Å). X-ray photoelectron spectroscopy (XPS) measurements were carried out with a Thermo Scientific, ESCALAB 250Xi using an Mg X-ray source. Scanning electron microscopy (SEM) images were taken by KYKY-EM3200-26 KV. Transmission electron microscopy (TEM) images were taken by Zeiss-EM10C-100 KV. Energy Dispersive X-Ray Analysis (EDX) were recorded on a VEGA3 LMU analysis was performed by TESCAN Company. Data oxidation products were analyzed by GC and GC-Mass using Agilent 6890 series with a FID detector, HP-5, 5% phenylmethylsiloxane capillary and Agilent 5973 network, mass selective detector, HP-5 MS 6989 network GC system, respectively.

Characterization Fe_3O_4, Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2@APTMS

FT-IR spectra:

Observation of a broad band in the spectrum of Fe_3O_4 with relatively low intensity centered at 3400 cm^{-1} to 1600 cm^{-1} should be attributed either to Fe-OH group surface, or stretching and bending vibrations of the adsorbed water (Figure S3a). The stretching vibration of Fe-O also appears at 580 cm^{-1}. The band appears at 1050 cm^{-1} due to Si-O stretching demonstrates the presence of SiO_2 components (Figure S3b) [1,2]. After functionalizing of silica coated magnetic nanoparticles with APTMS, a new bands appeared at 2858-2922 cm^{-1} due to the N-H and C-H stretching vibrations [3].

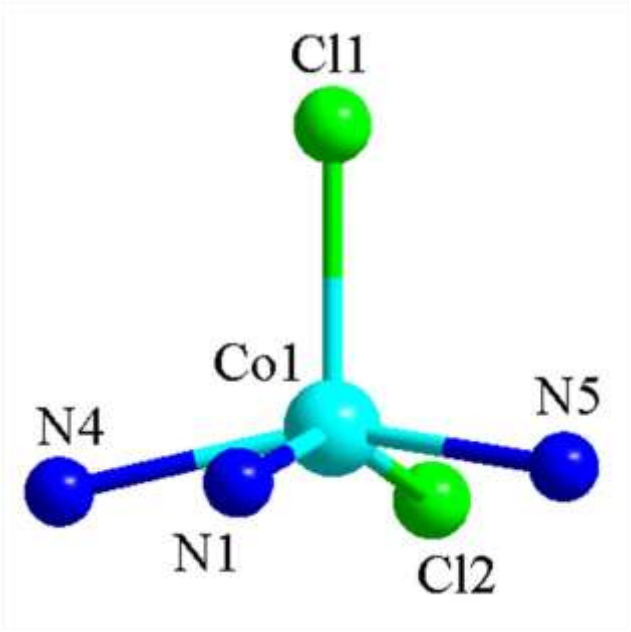


Figure S1. The distorted square pyramidal coordination sphere of complex 1.

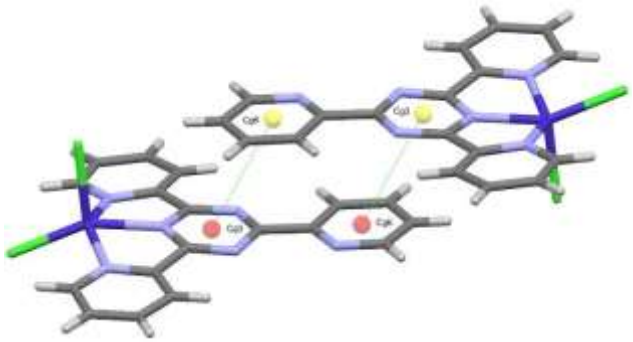


Figure S2. Inversion related π…π stacking interactions between adjacent complex 1 molecules, shown as green dotted lines with ring centroids shown as coloured spheres.

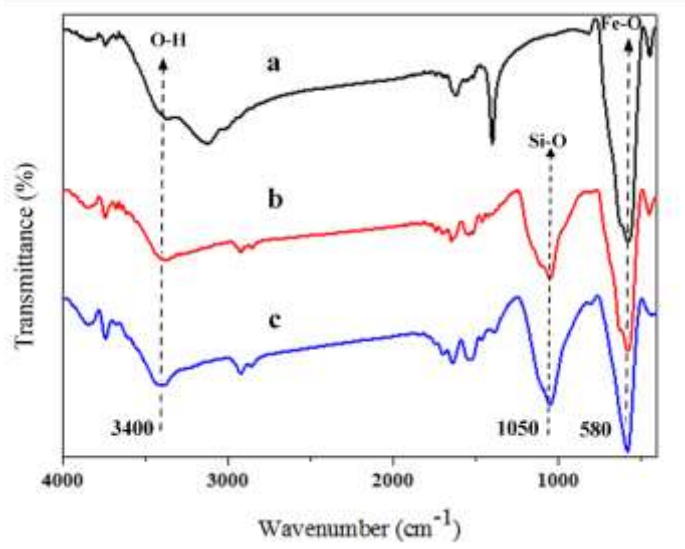


Figure S3. The FT-IR spectra of (a) Fe_3O_4, (b) Fe_3O_4@SiO_2, (c) Fe_3O_4@SiO_2@APTMS.

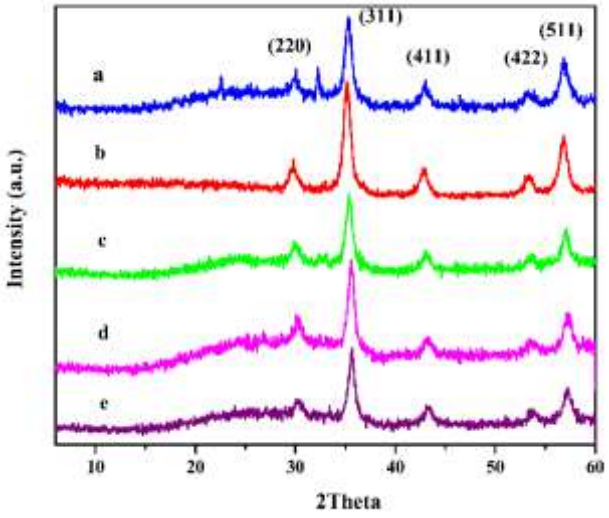


Figure S4. XRD pattern for(a) Fe_3O_4, (b) Fe_3O_4@SiO_2, (c) Fe_3O_4@SiO_2@APTMS (d) Fe_3O_4@SiO_2@APTMS@complex 1 (catalyst B) before using and (e) after using as catalyst.

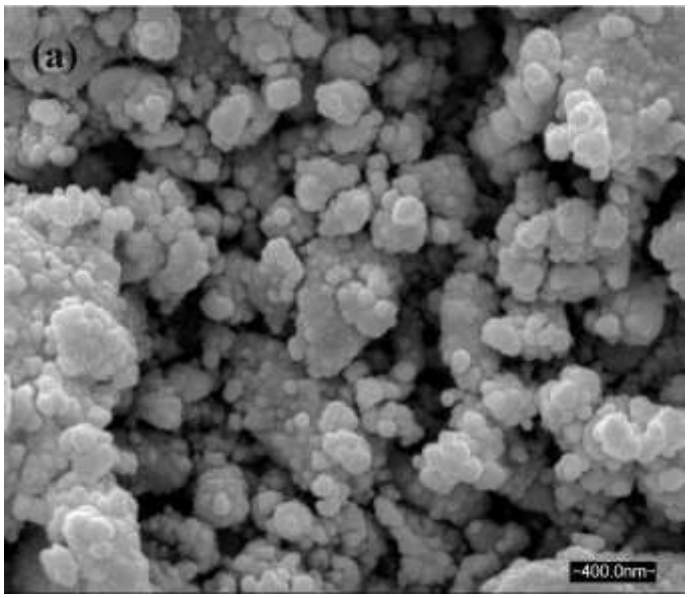


Figure S5. Scanning electron microscopy (SEM) images of nanoparticles Fe_3O_4@SiO_2@APTMS@complex 1 (catalyst B)

Table S1. Hydrogen bond distances (Å), angles (°) and π…π contacts (Å) for 1

D—H…A	D—H	H…A	D…A or Cg…Cg	‹ D—H…A
O1W—H1W...Cl1[1]	0.85(16)	2.37(16)	3.164(18)	155(15)
O2W—4W...O1W[2]	0.86(18)	2.10(15)	2.79(2)	136(1)
C5—H5...Cl2[3]	0.95	2.80	3.745(18)	172
C9—H9...O2W[4]	0.95	2.57	3.51(2)	170
C11—H11...Cl2[5]	0.95	2.76	3.674(17)	162
C18—H18...O2W[4]	0.95	2.38	3.29(2)	161
Cg3…Cg6[6]			3.794(9)	

Symmetry operations: 1 = 1+x, y, z; 2 = 2-x, 2-y, 1-z; 3 = 1-x, 1-y, -z; 4 = x, 1+y, z; 5 = -x, 2-y, -z; 6 = 2-x, 3-y,1-z Cg3 and Cg6 are the centroids of the N1, C1, N2, C13, N3, C7 and N6, C14-C18 rings respectivel

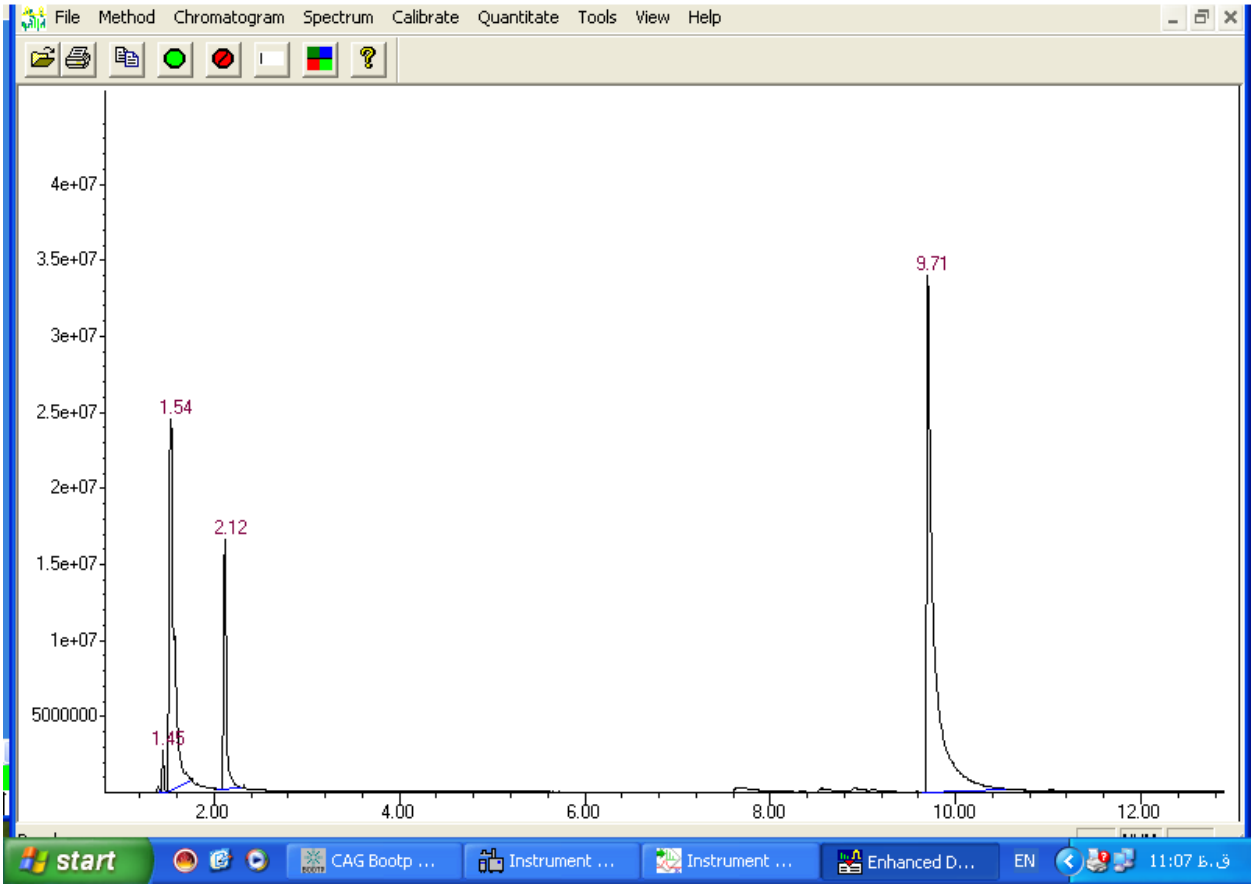
Table S2. Comparison the catalytic activity of $[Co(tptz)Cl_2].\ 2H_2O$ (catalyst A) with some soluble cobalt salts for flourene oxidation

Entry	Catalyst [a]	Substrate	Conversion (%)	Selectivity (%)	TON
1	$[Co(tptz)Cl_2].\ 2H_2O$ (catalyst A)	Flourene	99	100	10
2	$Co(OAC)_2.4H_2O$	Flourene	53	76	3
3	$Co(acac)_2$	Flourene	47	73	2

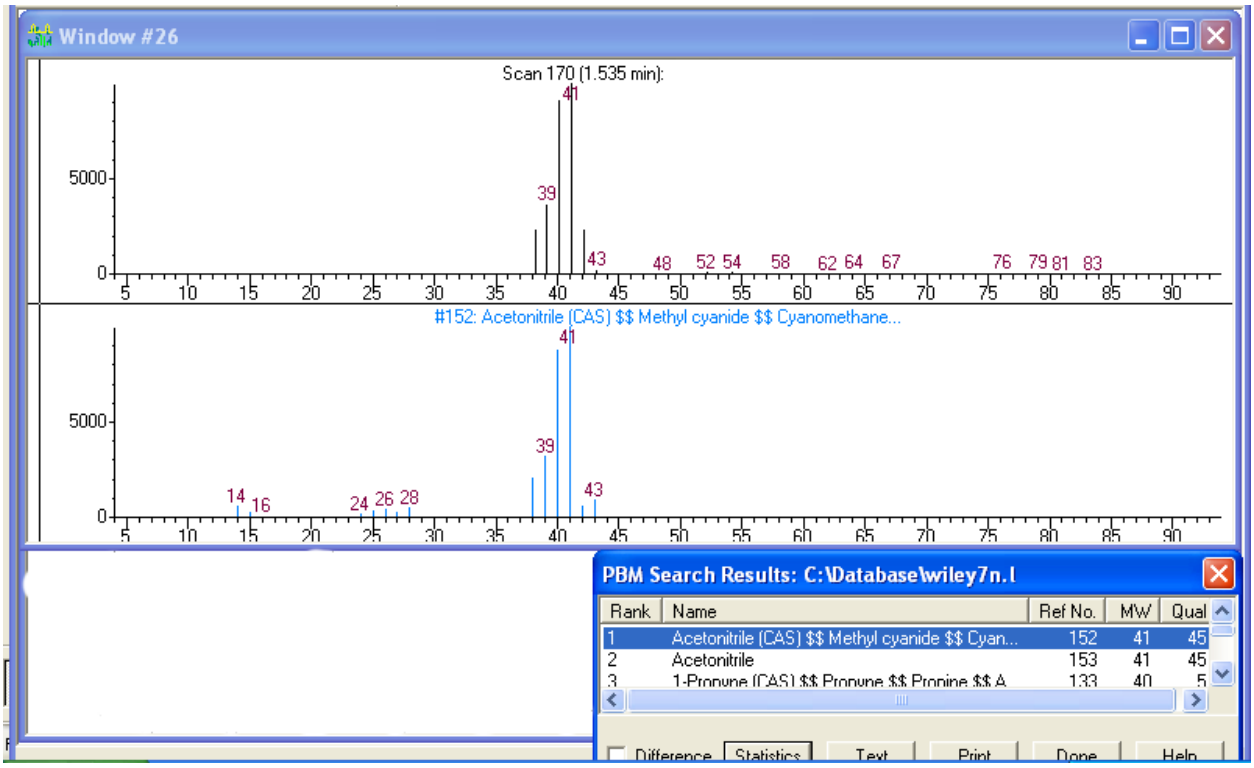
[a] Reaction conditions: catalyst, (50mg), substrate (1mmol), TBHP (1.2 mmol), solvent (acetonitrile, 5 mL, reflux at 80 °C), time (10 h).

GC-Mass analysis:

1. Fluorene



Entry	retention time (min.)	Compund
1	1.54	Acetonitrile
2	2.12	Ditertbutylperoxide
3	8.92	Fluorene
4	9.71	Fluorene-one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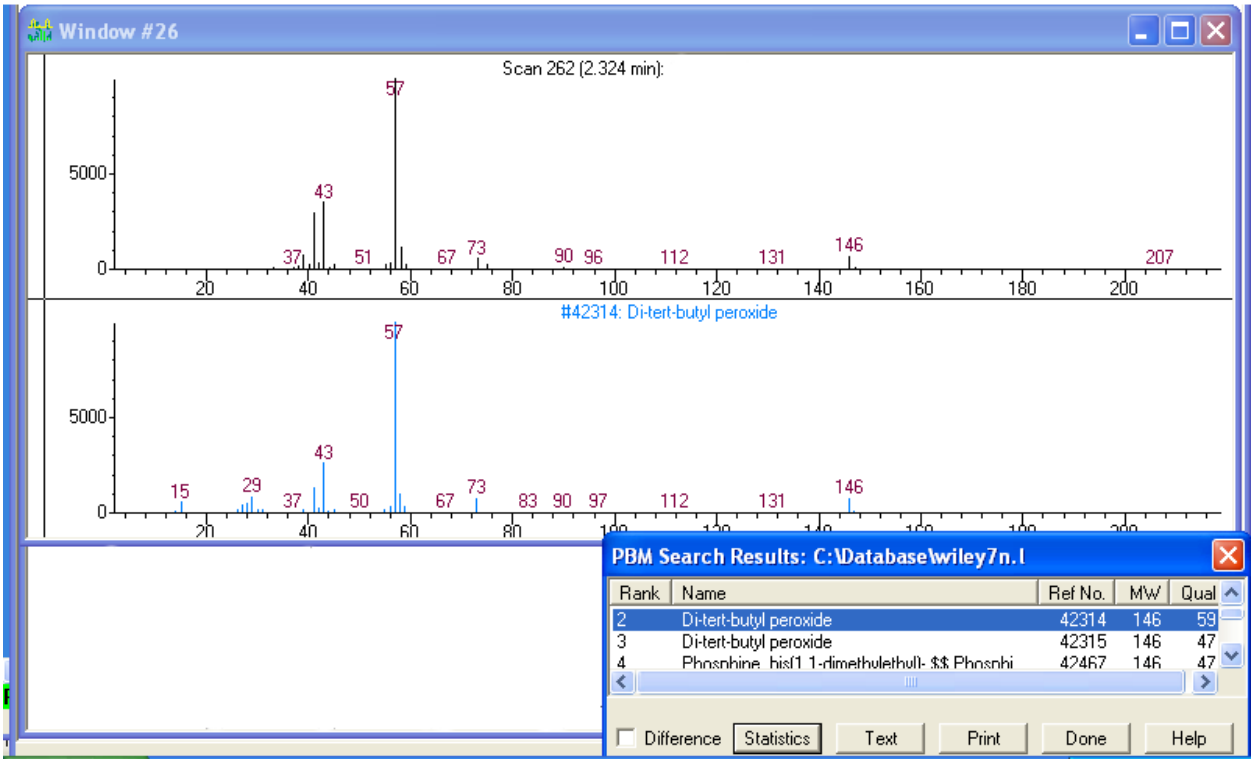
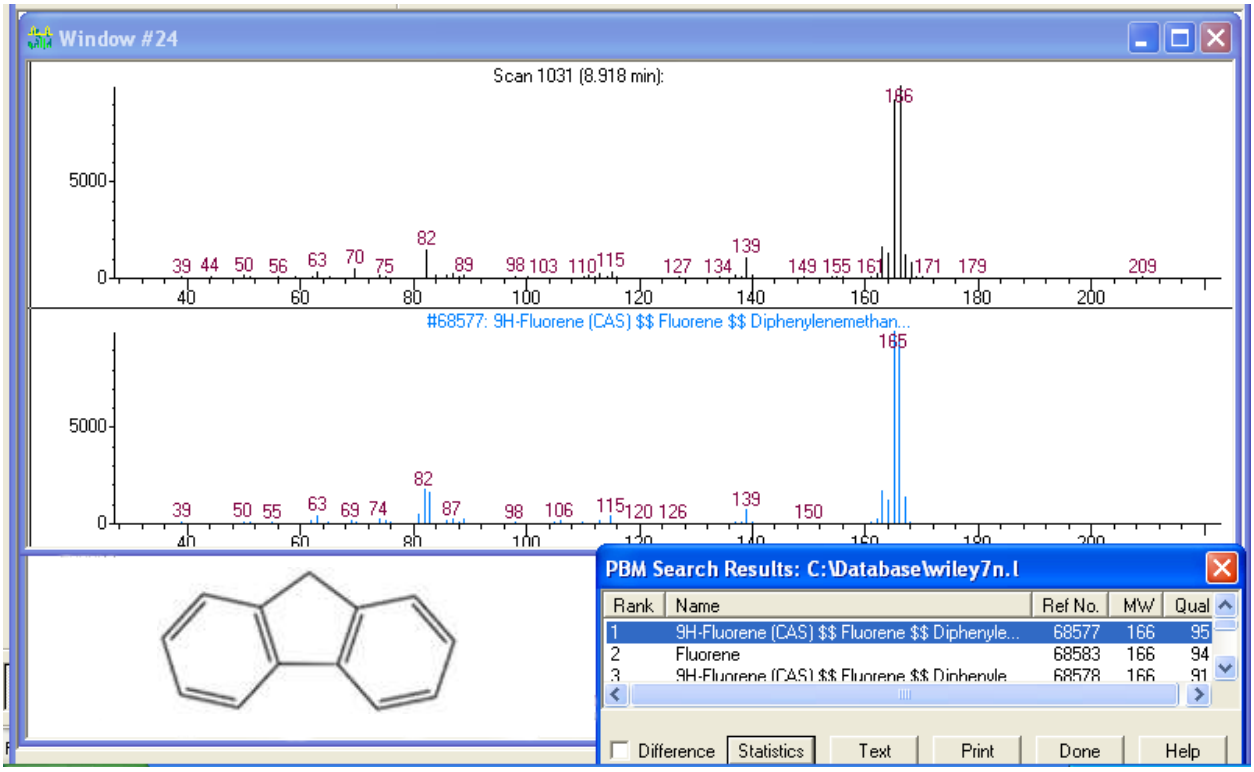
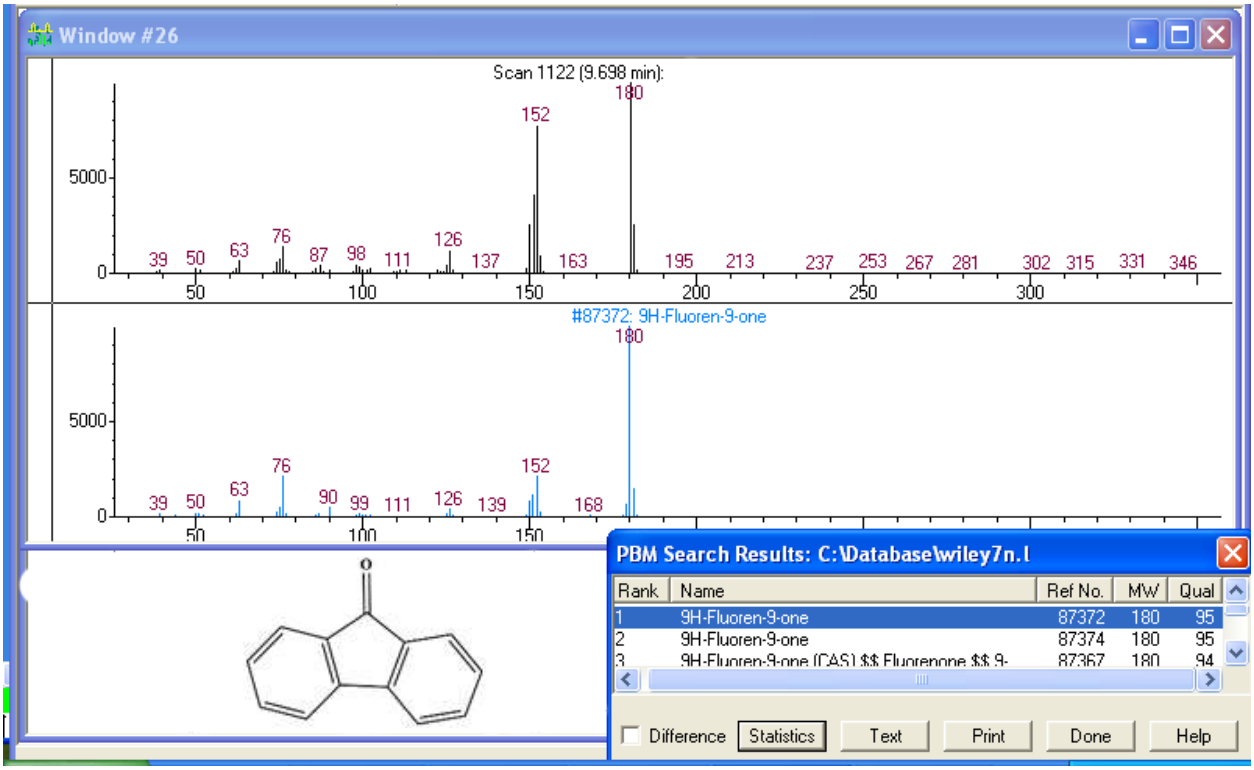
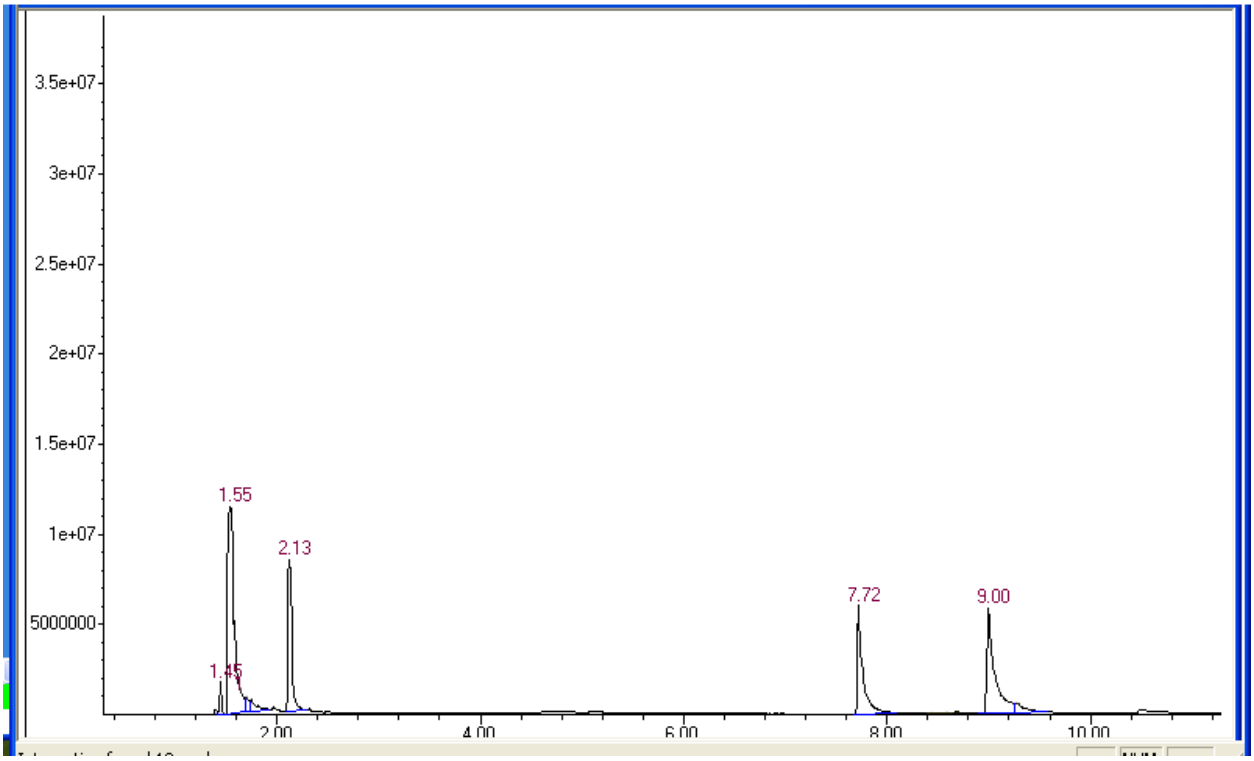
#152: Acetonitrile (CAS) $$ Methyl cyanide $$ Cyanomethane...
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 Acetonitrile (CAS) $$ Methyl cyanide $$ Cyan... 152 41 45
2 Acetonitrile 153 41 45
Difference Statistics Text Print Done Help


Window #26
Scan 262 (2.324 min):
#42314: Di-tert-butyl peroxide
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
2 Di-tert-butyl peroxide 42314 146 59
3 Di-tert-butyl peroxide 42315 146 47
Difference Statistics Text Print Done Help

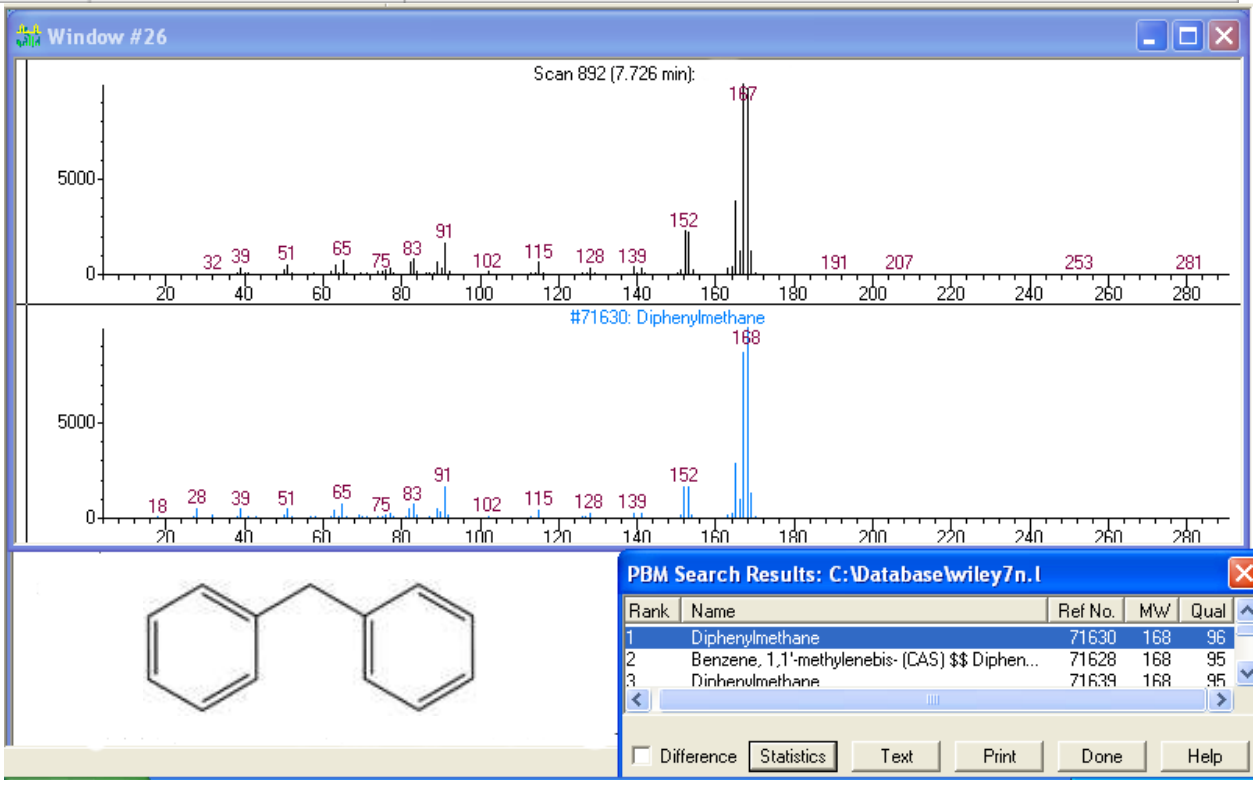

Window #24
Scan 1031 (8.918 min):
#68577: 9H-Fluorene (CAS) $$ Fluorene $$ Diphenylenemethan...
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 9H-Fluorene (CAS) $$ Fluorene $$ Diphenyle... 68577 166 95
2 Fluorene 68583 166 94
Difference Statistics Text Print Done Help

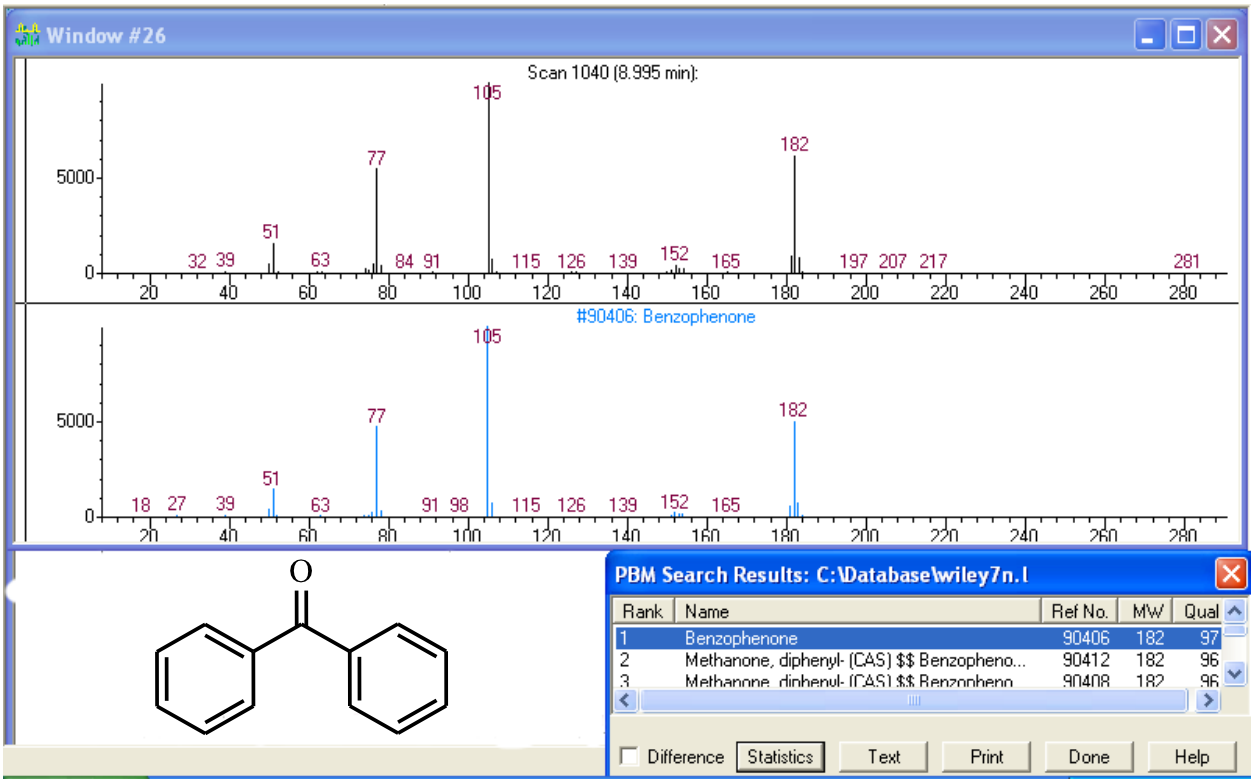

Window #26
Scan 1122 (9.698 min):
#87372: 9H-Fluoren-9-one
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 9H-Fluoren-9-one 87372 180 95
2 9H-Fluoren-9-one 87374 180 95
Difference Statistics Text Print Done Help

2. Diphenylmethane

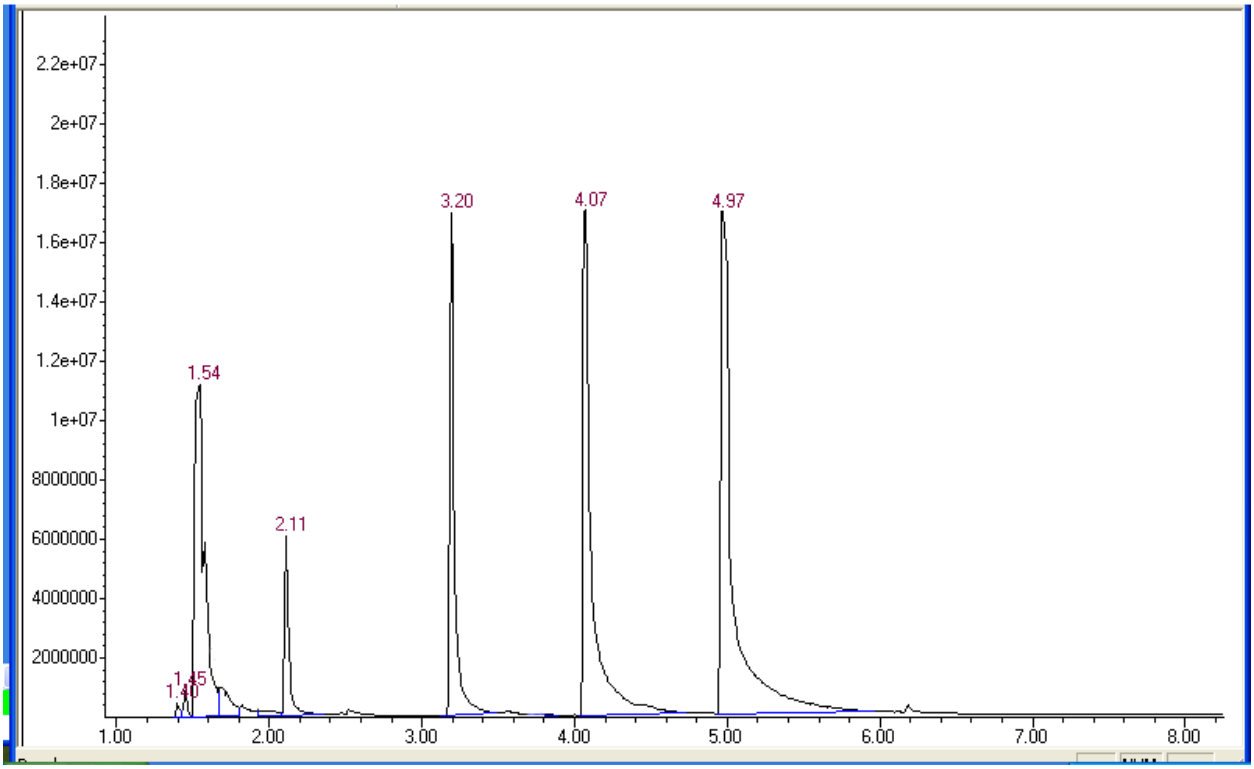


Entry	retention time (min.)	Compund
1	7.72	Diphenylmethane
2	9.00	Benzophenone

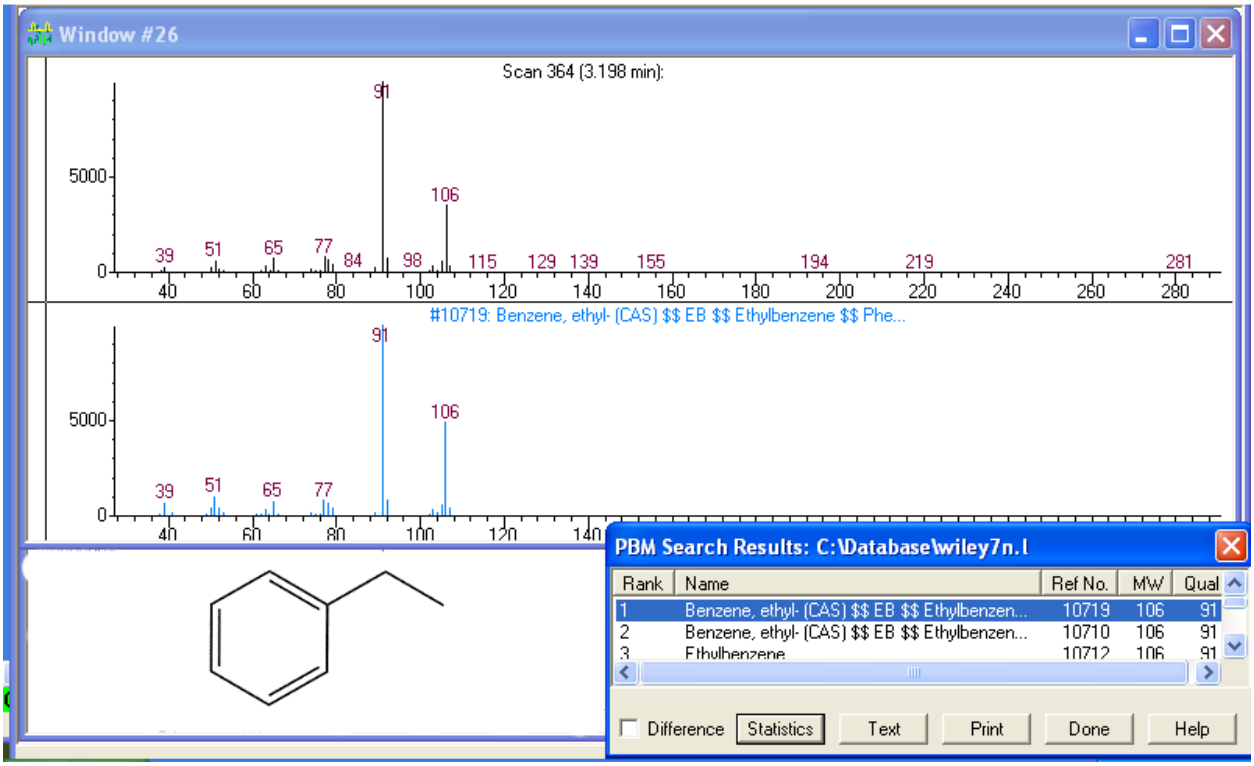


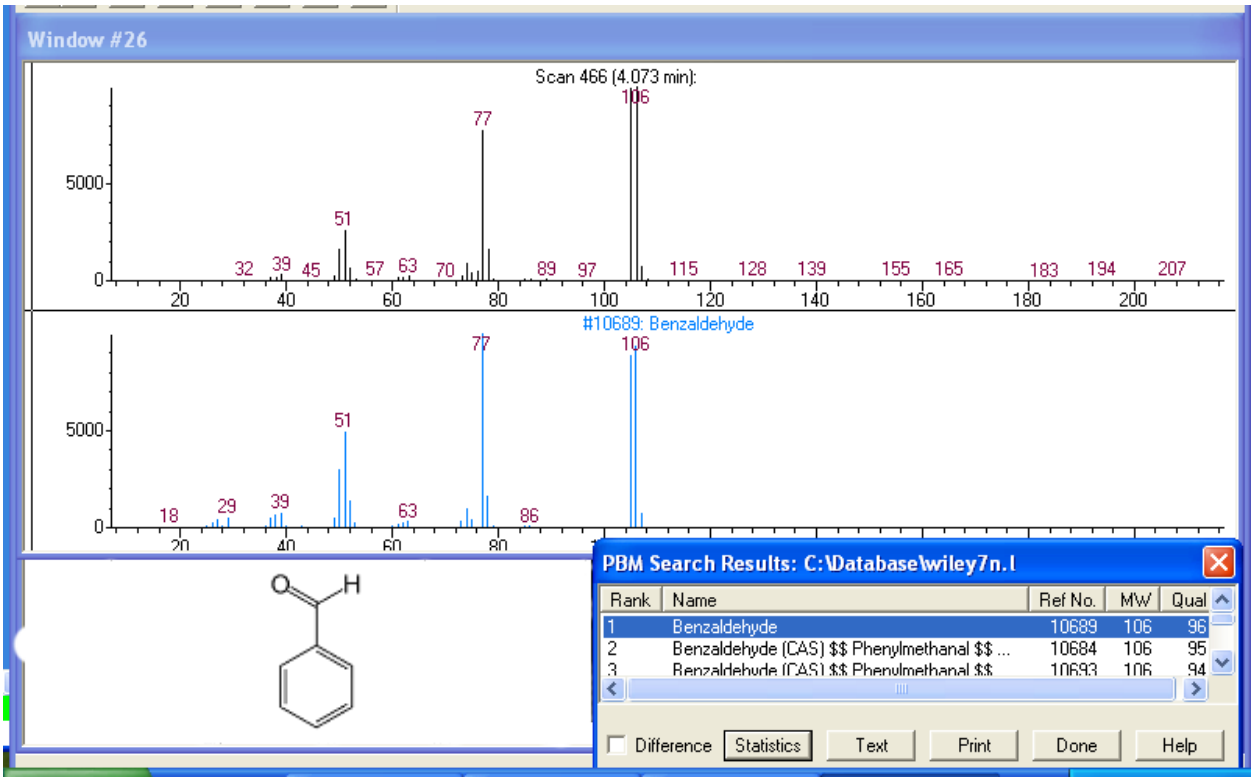


3. Ethyl benzene



Entry	retention time (min.)	Compund
1	3.20	Ethyl benzene
2	4.07	Benzaldehyde
3	4.97	Acetophenone




Window #26
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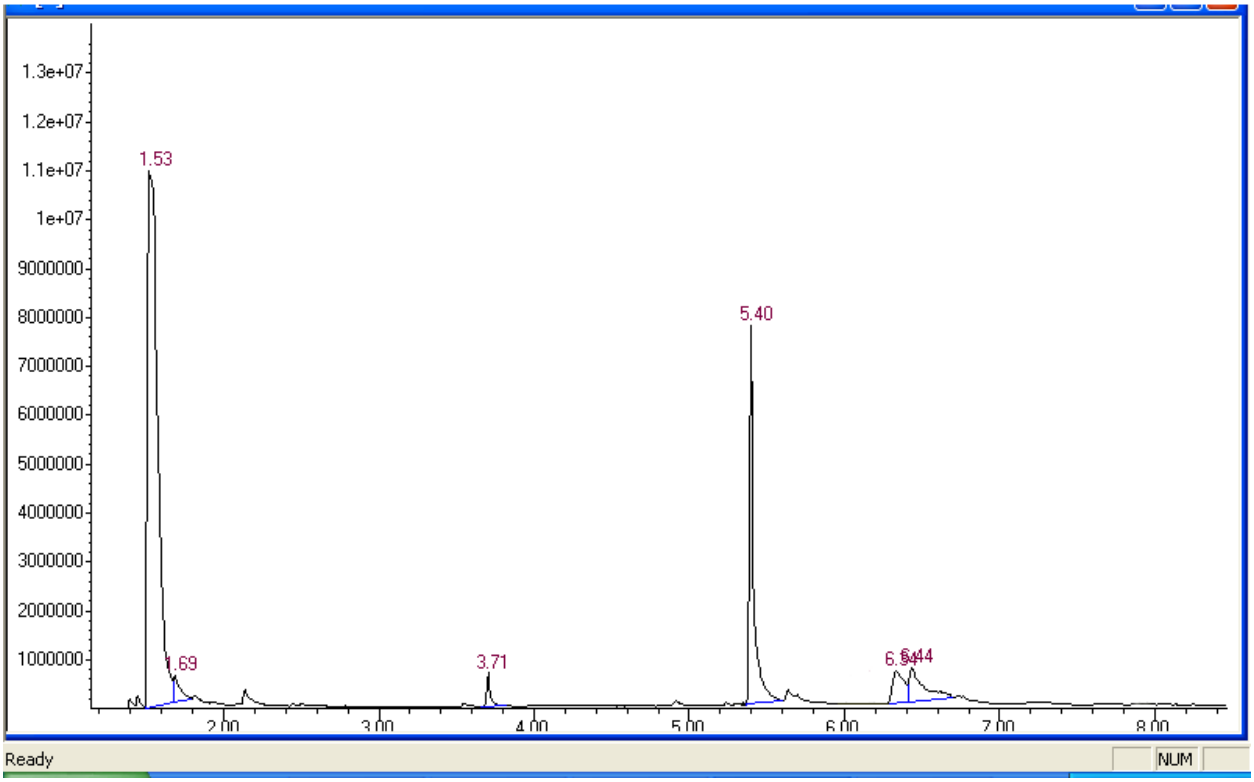
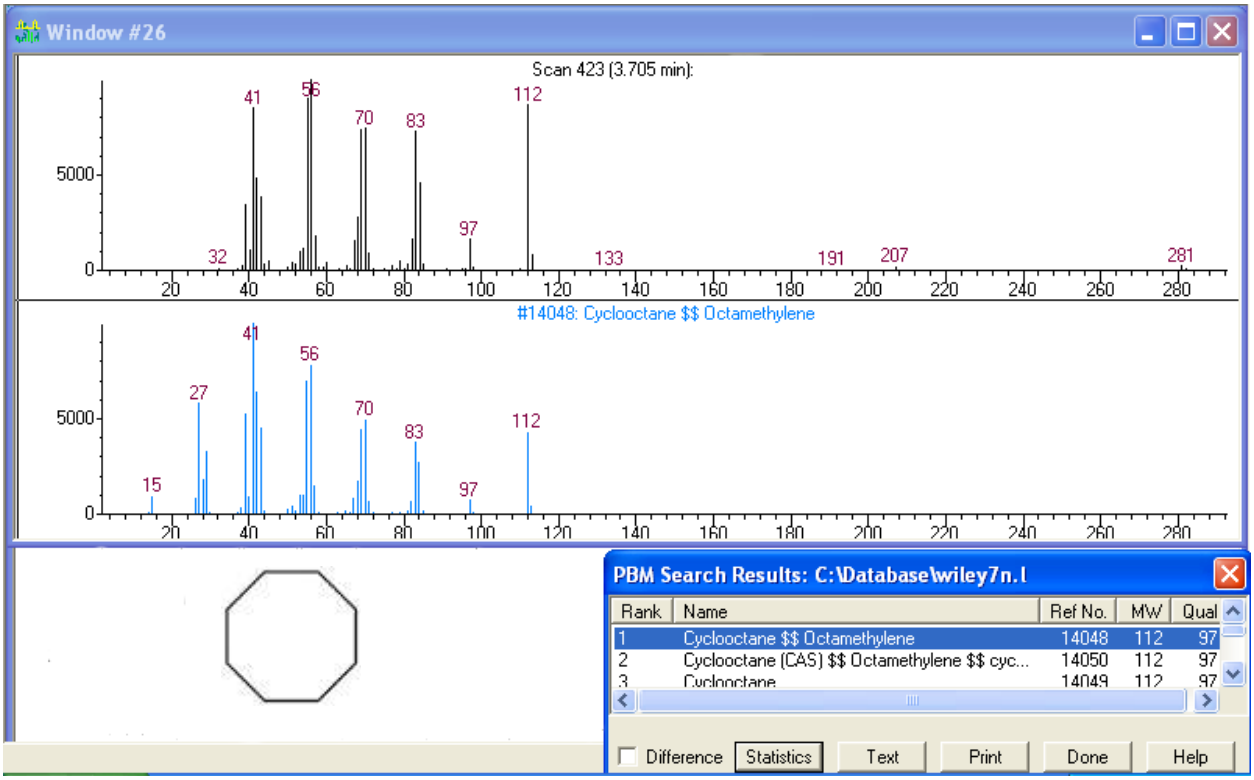
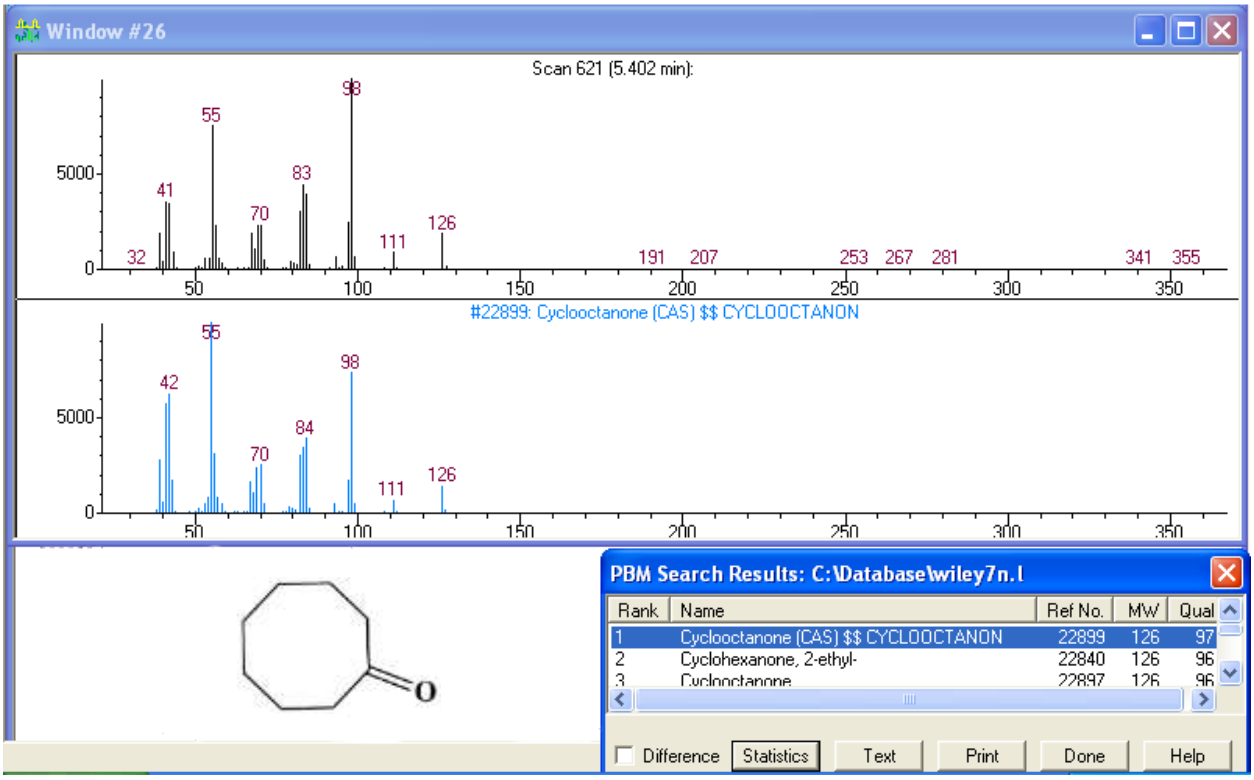
#10689: Benzaldehyde
PBM Search Results: C:\Database\wiley7n.l
Rank
Name
Ref No.
MW
Qual
1 Benzaldehyde 10689 106 96
2 Benzaldehyde (CAS) $$ Phenylmethanal $$ ... 10684 106 95
Difference
Statistics
Text
Print
Done
Help

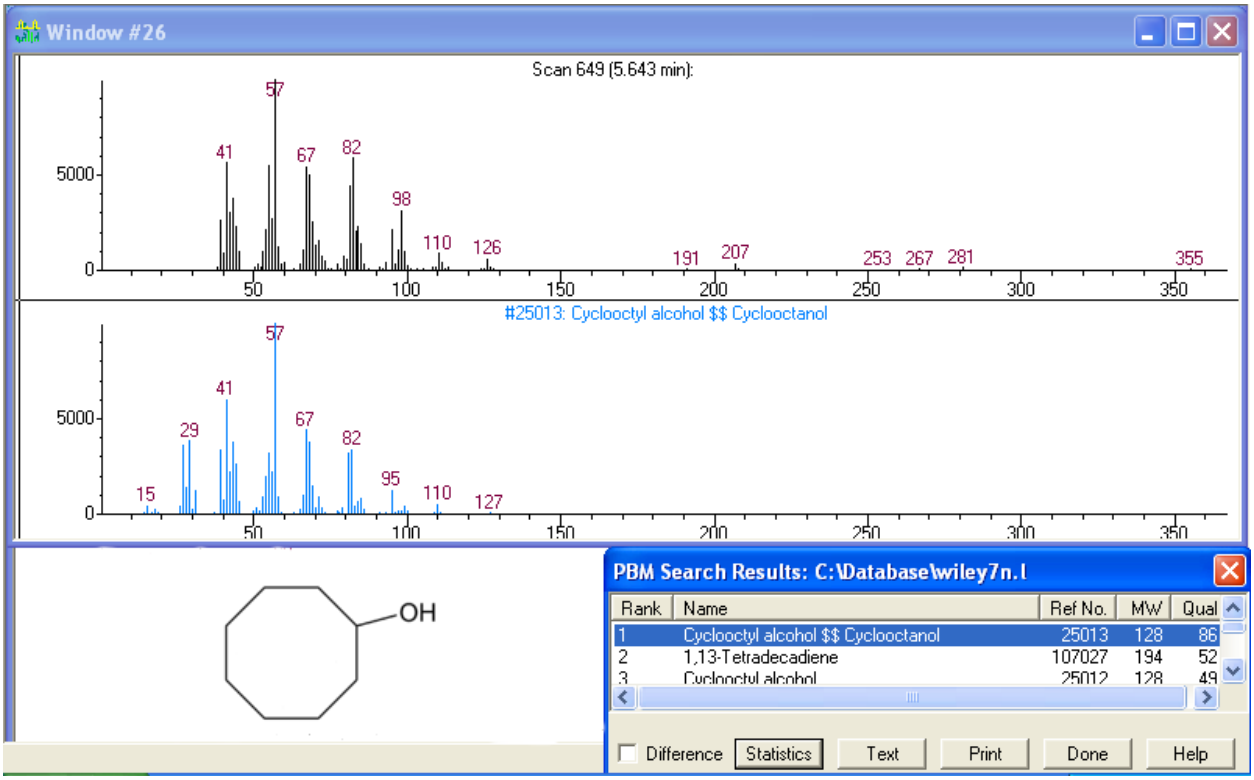
4. Cyclooctane

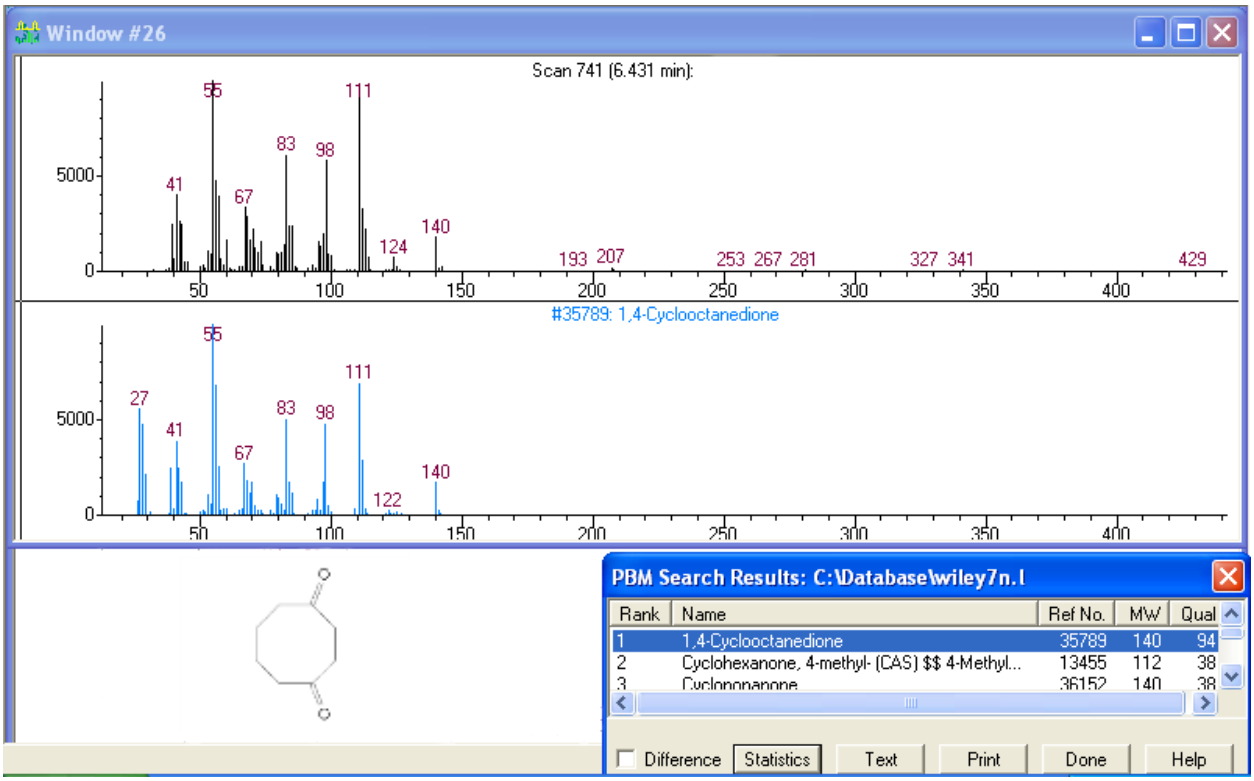


Entry	retention time (min.)	Compund
1	3.71	Cyclooctane
2	5.40	Cyclooctanone
3	5.64	Cyclooctanol
4	6.440	Cyclooctane dione


Window #26
Scan 423 (3.705 min):
#14048: Cyclooctane $$ Octamethylene
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 Cyclooctane $$ Octamethylene 14048 112 97
2 Cyclooctane (CAS) $$ Octamethylene $$ cyc... 14050 112 97
Difference
Statistics
Text
Print
Done
Help


Window #26
Scan 621 (5.402 min):
#22899: Cyclooctanone (CAS) $$ CYCLOOCTANON
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 Cyclooctanone (CAS) $$ CYCLOOCTANON 22899 126 97
2 Cyclohexanone, 2-ethyl- 22840 126 96
Difference
Statistics
Text
Print
Done
Help


Window #26
Scan 649 (5.643 min):
#25013: Cyclooctyl alcohol $$ Cyclooctanol
OH
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 Cyclooctyl alcohol $$ Cyclooctanol 25013 128 86
2 1,13-Tetradecadiene 107027 194 52
3 Cyclooctyl alcohol 25012 128 49
Difference Statistics Text Print Done Help


Window #26
Scan 741 (6.431 min):
#35789: 1,4-Cyclooctanedione
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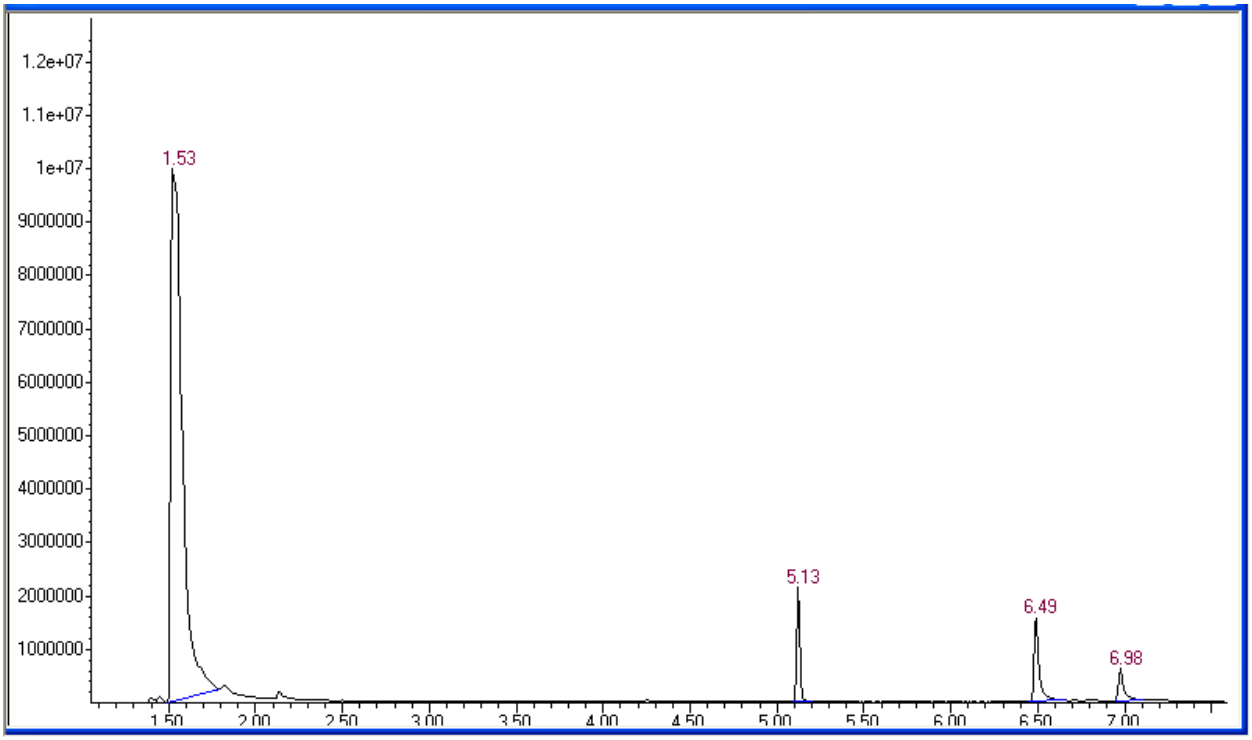
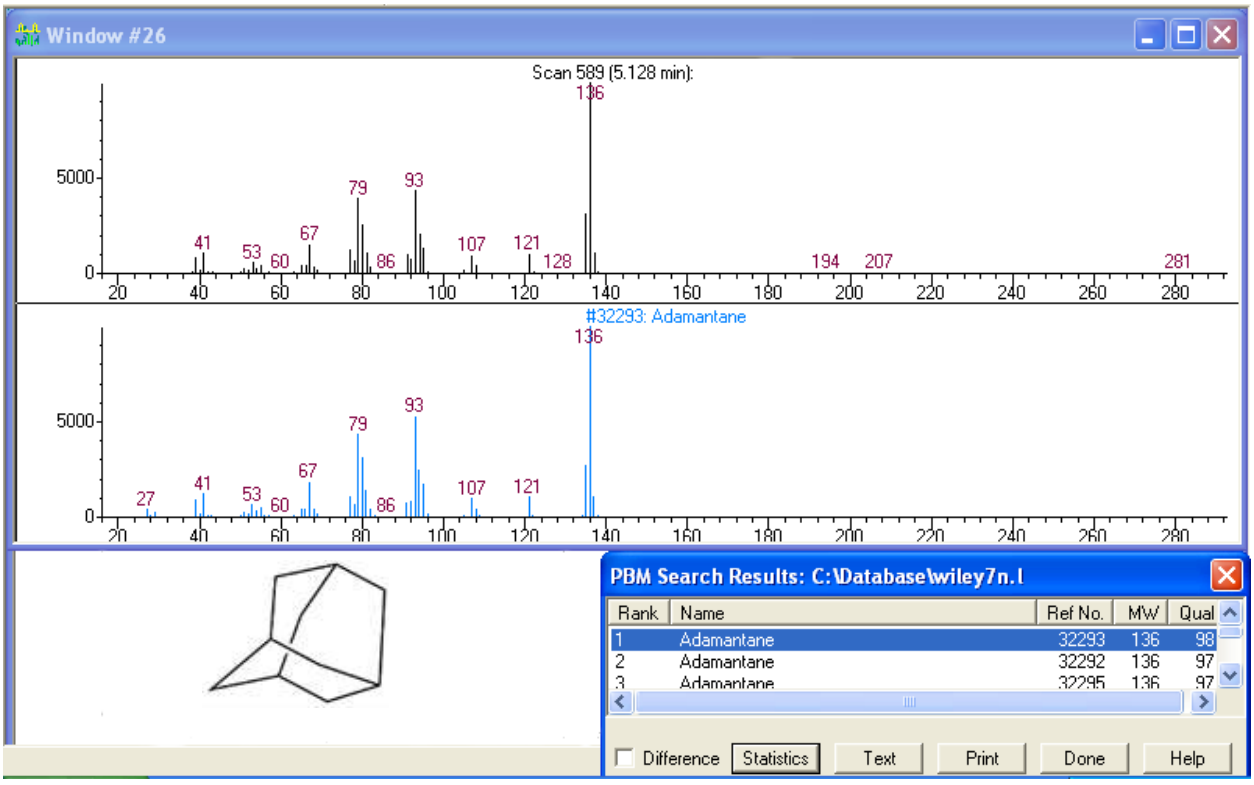
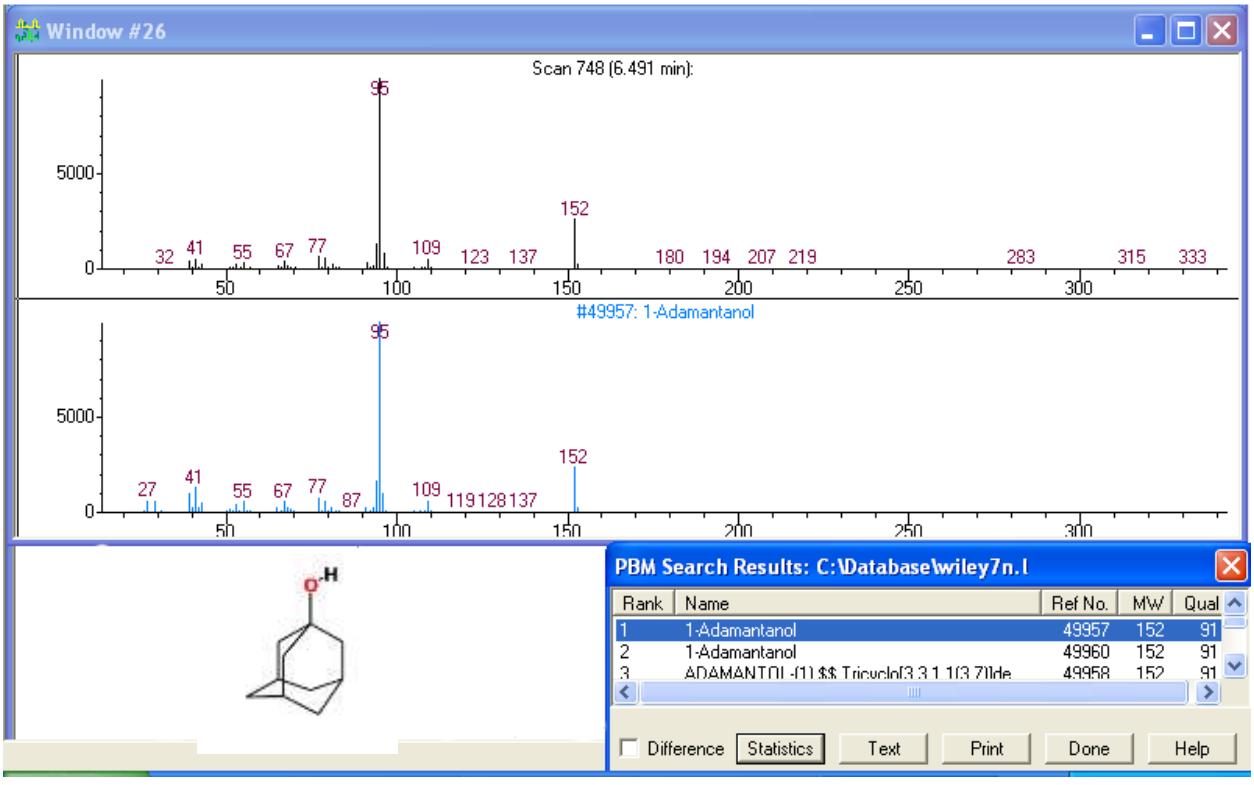
Rank Name Ref No. MW Qual
1 1,4-Cyclooctanedione 35789 140 94
2 Cyclohexanone, 4-methyl- (CAS) $$ 4-Methyl... 13455 112 38
3 Cyclononanone 36152 140 38
Difference Statistics Text Print Done Help

5. Adamantane



Entry	retention time (min.)	Compund
1	5.13	Adamantane
2	6.49	Adamantanol
3	6.98	Adamantanone


Window #26
Scan 589 (5.128 min):
#32293: Adamantane
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 Adamantane 32293 136 98
2 Adamantane 32292 136 97
Difference
Statistics
Text
Print
Done
Help


Window #26
Scan 748 (6.491 min):
#49957: 1-Adamantanol
PBM Search Results: C:\Database\wiley7n.l
Rank Name Ref No. MW Qual
1 1-Adamantanol 49957 152 91
2 1-Adamantanol 49960 152 91
Difference
Statistics
Text
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Help

How to calculate TON:

Homogeneous catalyst

1) Catalyst A: $[Co(tptz)Cl_2].\ 2H_2O$ (MW.= 478.20)

1mmol Catalyst A ($[Co(tptz)Cl_2].\ 2H_2O$) = 1mmol Co(II) (active site)

So:

50 mg Catalyst A = 0.104 mmol Catalyst A = **0.104 mmol Co(II)**

2) for example: 1mmol of flourene substrate, conversion= 99%

mmol of product= 0.99

3) TON= mmol of product/ mmol of cobalt present in catalyst= 0.99/0.104= **9.52**

Heterogeneous catalyst:

1) Fe_3O_4@SiO_2@APTMS@complex (catalyst B), **Co(II) content of catalyst B was 0.3%**

So:

70 mg Catalyst B = 0.21 mg Co(II) = **3.56×10^{-3} mmol Co(II)**

2) for example: 1mmol of flourene substrate, conversion= 42%

mmol of product= 0.42

3) TON= mmol of product/ mmol of cobalt present in catalyst = $0.42/3.56\times10^{-3}$ = **118**

References

[1] X. Liu, Z. Ma, J. Xing, H. Liu, J. Magn. Magn. Mater., 2004, **270**,1.

[2] J. Wang, S. Zheng, Y. Shao, J. L. Liu, Z. Xu, D. Zhu, J. Colloid Interface Sci., 2010, **349**, 293.

[3] S. Shylesh, W. R. Thiel, V. Schunemann, Angew. Chem. Int., 2010, **49**, 3428.