Supplemental Materials

Table S1: pH dependent formation of thiophene in the presence of NiS.

Table S2: Identified thiophene derivatives and their retention times.

Figure S1: GC/MS chromatograms comparing thiophene and commercially available thiophene derivatives.

Figure S2: GC/MS mass spectra comparing reaction products to commercially available thiophene standards and mass spectra from NIST14 library.

Table S1. pH dependent formation of thiophene in the presence of NiS. Reactions were performed with 5.36 mmol acetylene and 1 mmol freshly precipitated nickel sulfide under aqueous conditions at 105°C. Reactions were performed for 1d and pH values were measured at the end of the reaction time.

pH	H_2SO_4 [mmol]	NaOH [mmol]	Supernatant [mM]	Solid [mM]	Total [mM]
1.9	1.0	-	0.001	0.013	**0.03**
2.8	0.5	-	0.027	0.025	**0.11**
4.0	0.2	-	0.003	0.051	**0.11**
6.5	-	-	0.336	1.242	**3.16**
8.3	-	0.5	0.060	1.148	**2.42**
9.7	-	1.0	0.091	0.971	**2.02**
10.7	-	1.5	0.212	0.255	**0.94**

Table S2: Identified thiophene derivatives (x) and their retention times (RT, min) from experiments with acetylene and metal sulfides as described in Table 1. Numbers corresponding to Figure 3 are given in brackets. The amounts were not quantified, but indicated by x, if detected. The ratio thiophene to thiophene derivatives is calculated from peak areas.

Run	RT [min]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Product																			
2-Ethylthiophene (2)	7.5	x	x	x	x	x	x	x	x	x	x	x	x	x	-	-	x	-	-
3-Ethylthiophene (3)	8.2	x	-	x	x	x	x	-	-	x	x	-	x	-	-	-	-	-	-
2,3-Dimethylthiophene (4)	7.7	x		x	x	x	x	-	-	x	x	-	x						
Ethylvinylsulfide (5)	4.0	-	-	-	-		-	-		-	-	-	-	-	-	-	-	-	-
Tetrahydrothiophene (6)	6.2	x	x	x	-	x	x	x	x	-	x	x	x	-	-	-	-	-	-
3-Ethynylthiophene (7)	8.0	-	-	-	-		-	-	-	-	-	-	-	-	-	-	-	-	-
3-Thiophene thiol (8)	10.2	x	x	x	x	x	x	x	-	x	x	-	x	x	-	x	x	-	-
5-Methylthiophene-carboxaldehyde (9)	11.5	-	-	x	-		-	-	-	-	x	-	-	x	x	x	-	-	-
2[5H]-5-Methylthiophenon (10)	11.8	-	-	-	-		-	-	-	-	x	-	x	-	-	-	-	-	-
2-Vinylthiophene (11)	8.1	x	-	x	x	x	x	-	-	x	x	-	x	x	-	-	x	-	-
2-Acetyl-5-methylthiophene (12)	12.5	-	-	-	-		-	-	-	-	-	-	x	-	-	-	-	-	-
2-Acetylthiophene (13)	11.5	x	-	-	x	x	-	-	-	-	-	-	x	-	-	-	-	-	-
Thiophene-carboxaldehyde (14)	9.9	-	-	-	-		-	-	-	-	x	-	-	-	-	-	-	-	-
Cyclohex-2-enthion (15)	9.2	x	-	x	x	x	x	-	-	x	x	-	x	-	-	-	-	-	-
cis-1,4-Dithiapentalene (16)	13.5	x	-	-	x	x	x	x	x	x	x	-	x	-	-	-	-	-	-
trans-1,4-Dithiapentalene (17)	13.6	x	-	x	x	x	x	-	-	x	x	-	x	-	-	-	-	-	-
Benzo[*b*]thiophene (18)	13.3	x	-	x	x	x	x	-	-	x	x	-	x	-	-	-	-	-	-
Ratio thiophene : Σthiophene derivatives		**12.5**	**<0.1**	**0.3**	**9.6**	**19.3**	**2.7**	**<0.1**	**0.8**	**25.4**	**1.3**	**0.1**	**3.2**	**17.9**	**0.1**	**2.8**	**1.0**	**-**	**-**

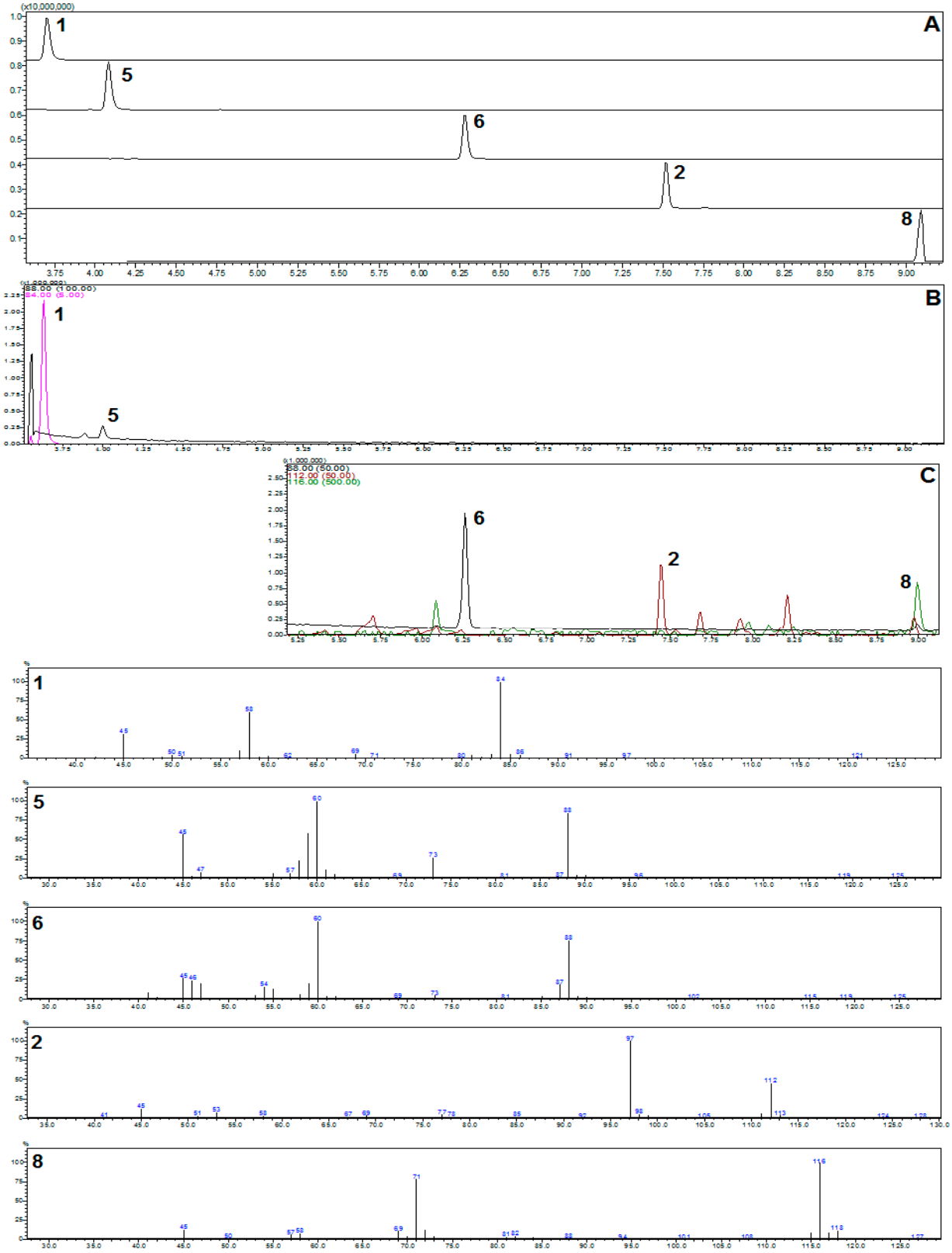
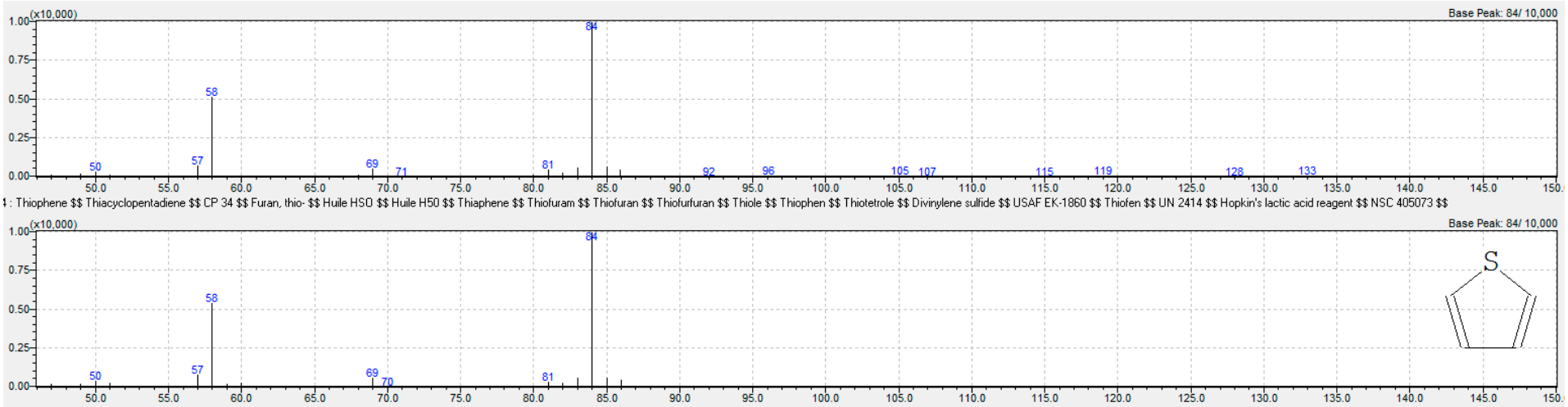
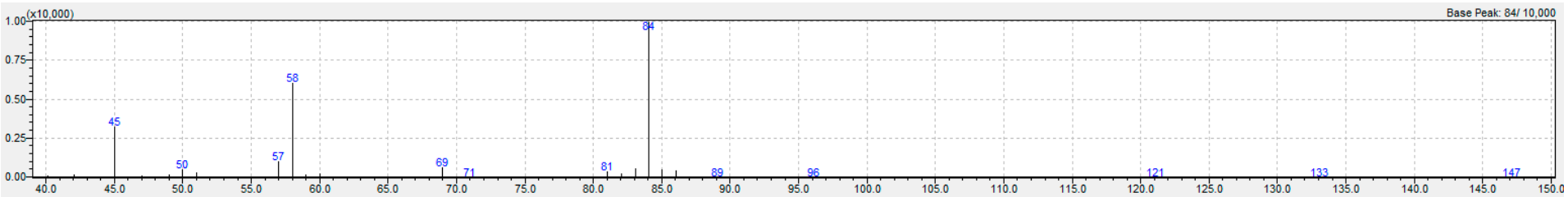


Figure S1: GC/MS chromatograms comparing thiophene and commercially available thiophene derivatives (**A**) to reaction products (**B**,**C**). Numbers correspond to structures in Figure 3

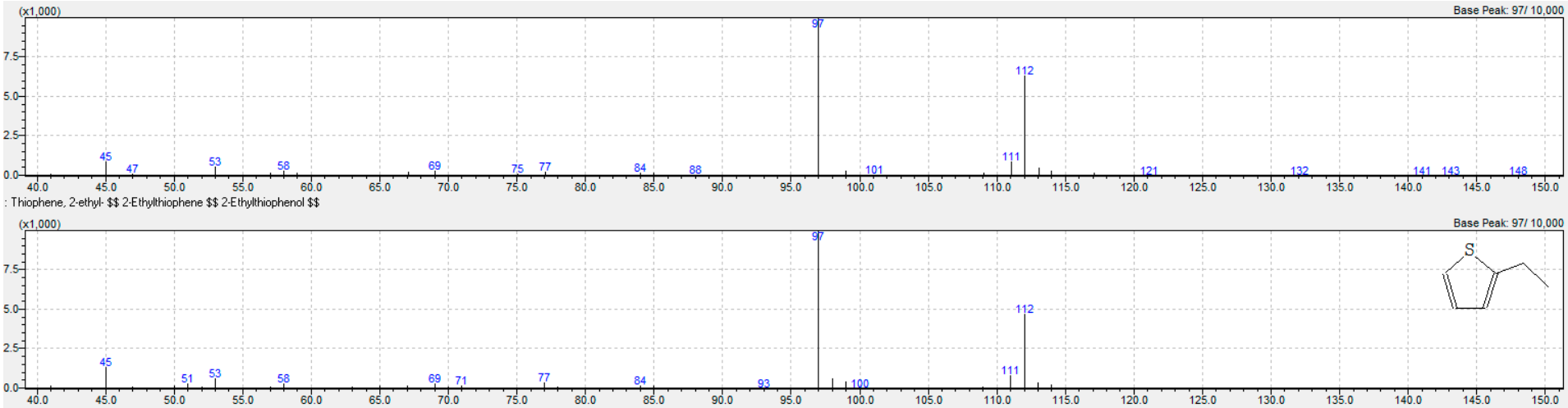
Thiophene (1) similarity to NIST14 database: 96%



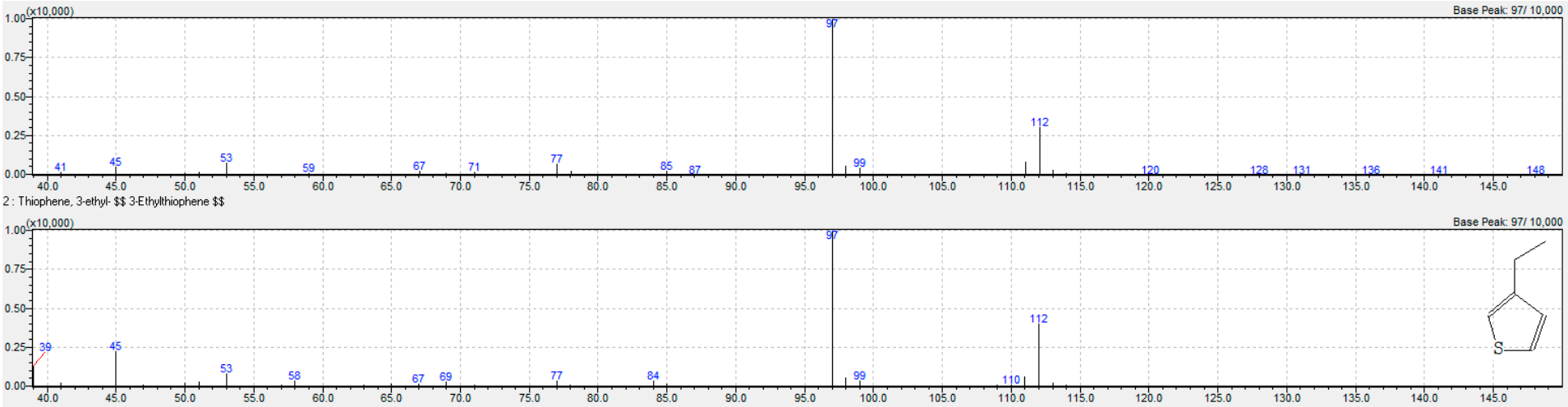
Thiophene analytical standard (Sigma Aldrich)



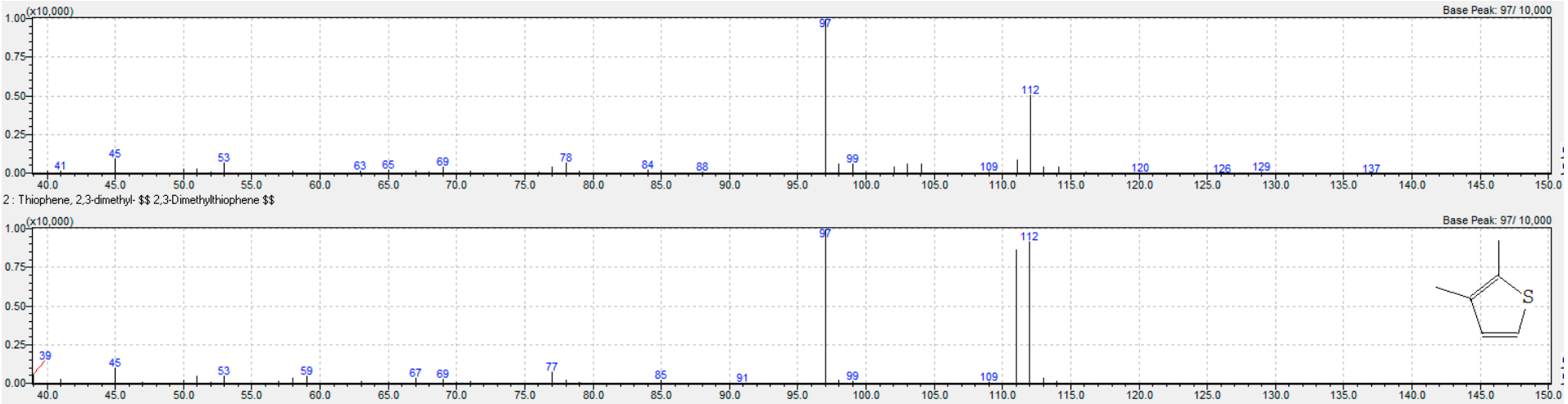
2-Ethylthiophene (2) similarity to NIST14 database: 93%



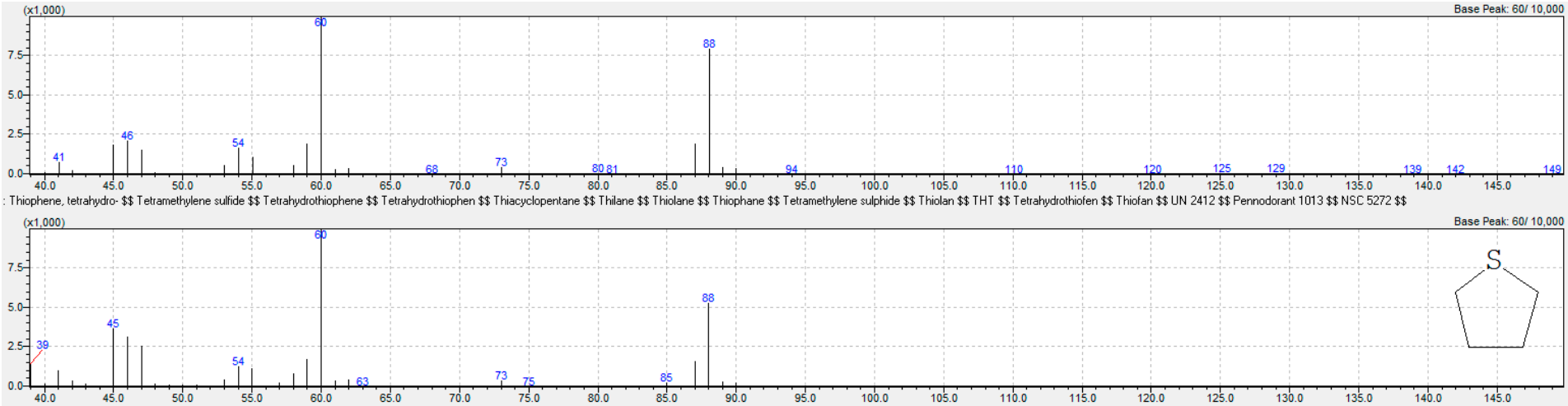
3-Ethylthiophene (3) similarity to NIST14 database: 91%



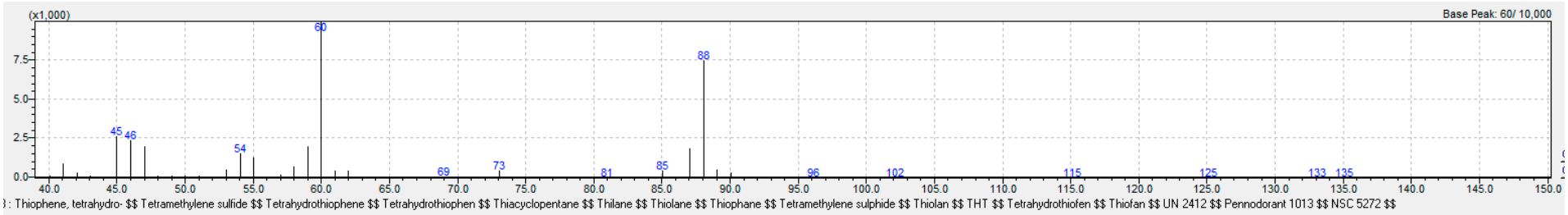
2,3-Dimethylthiophene (4) similarity to NIST14 database: 82%



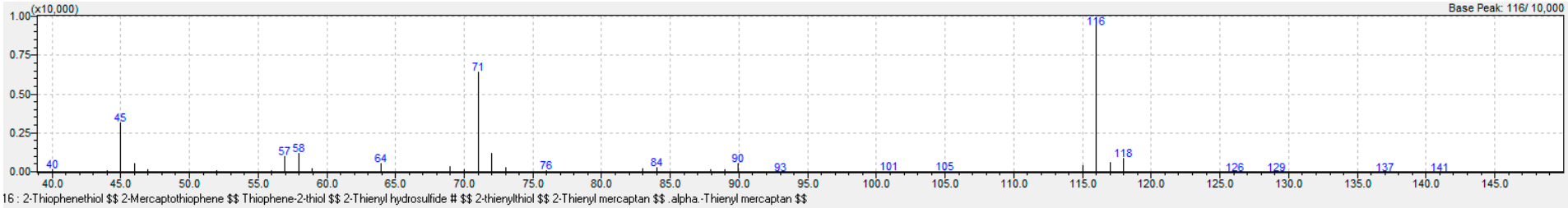
Tetrahydrothiophene (6) similarity to NIST14 database: 92%

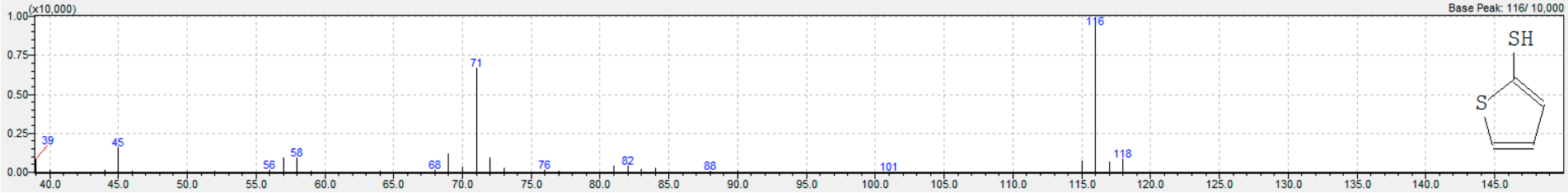


Tetrahydrothiophene analytical standard (Sigma Aldrich)

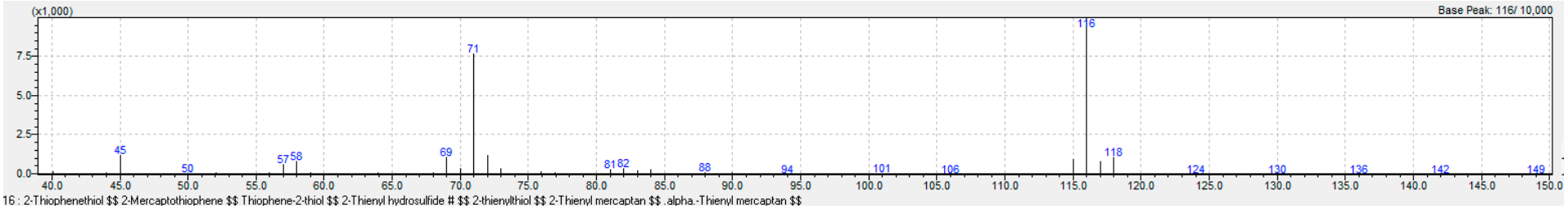


2-Thiophenthiol (8) similarity to NIST14 database: 93%

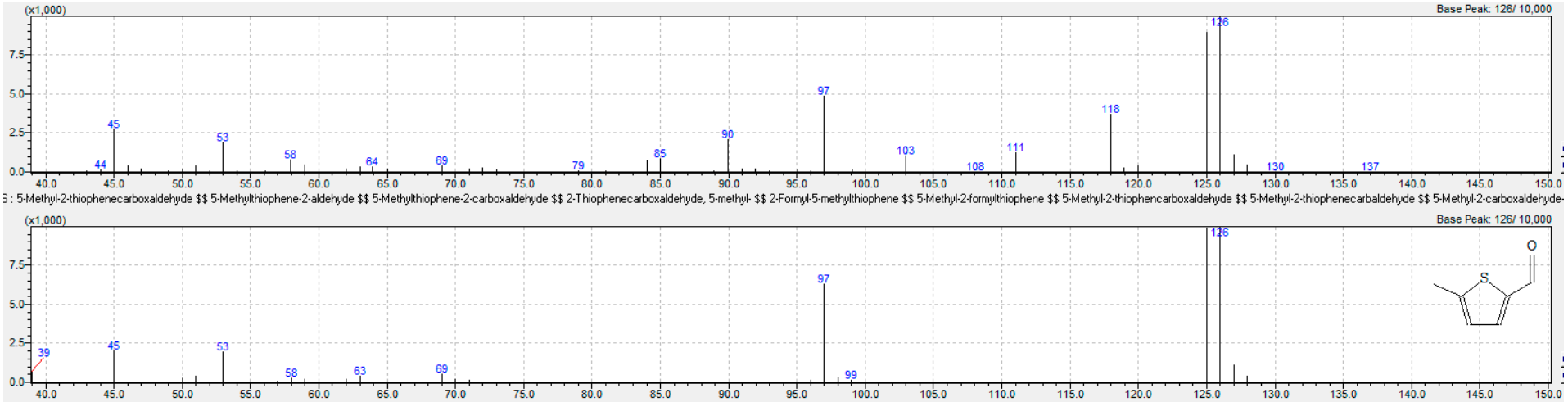




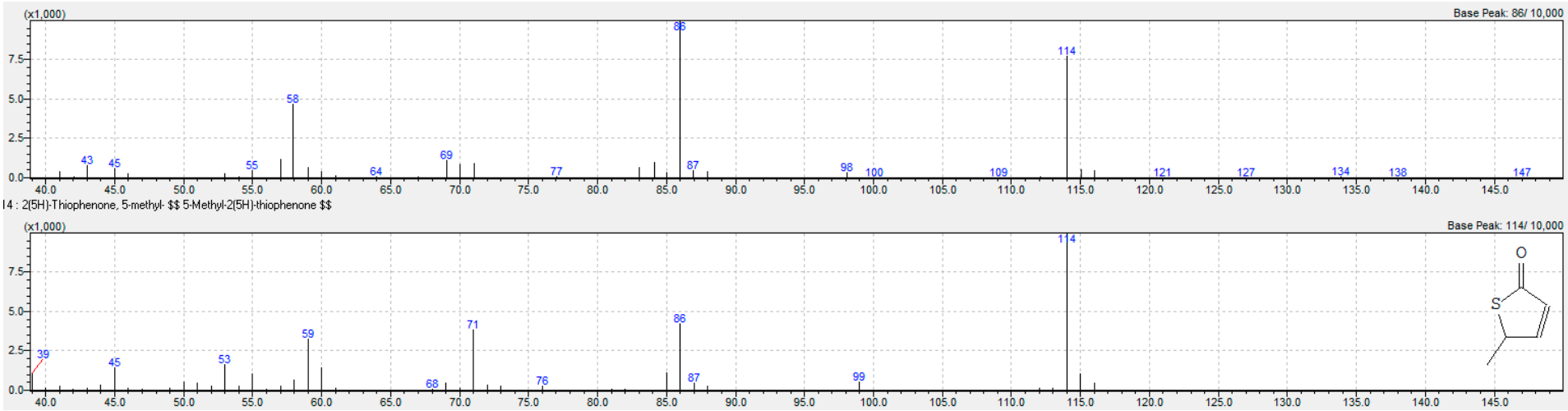
2-Thiophenthiol analytical standard (Sigma Aldrich)



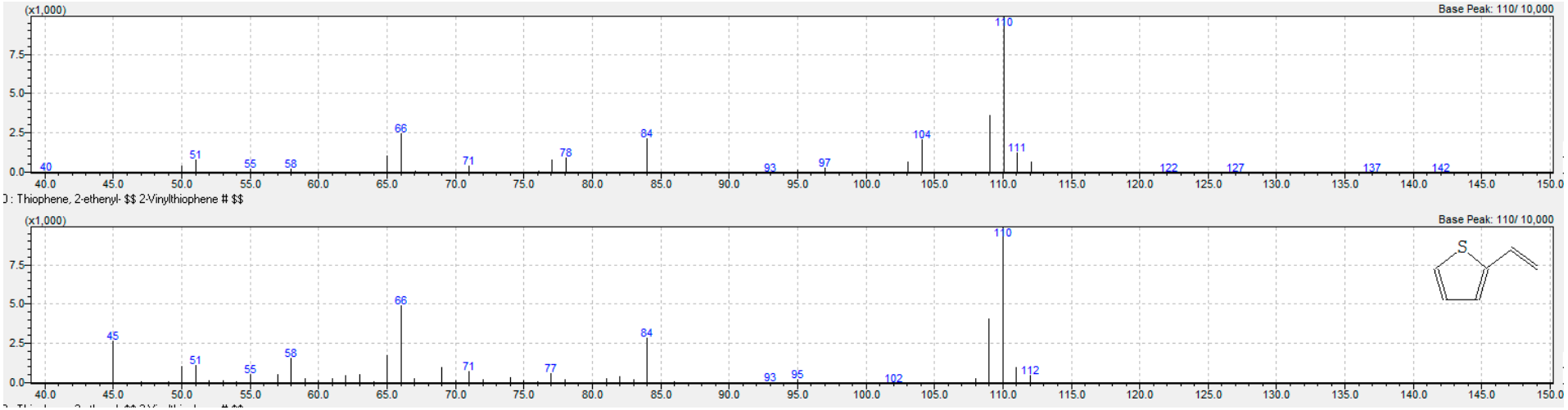
5-Methylthiophene-carboxaldehyde (9) similarity to NIST14 database: 82%



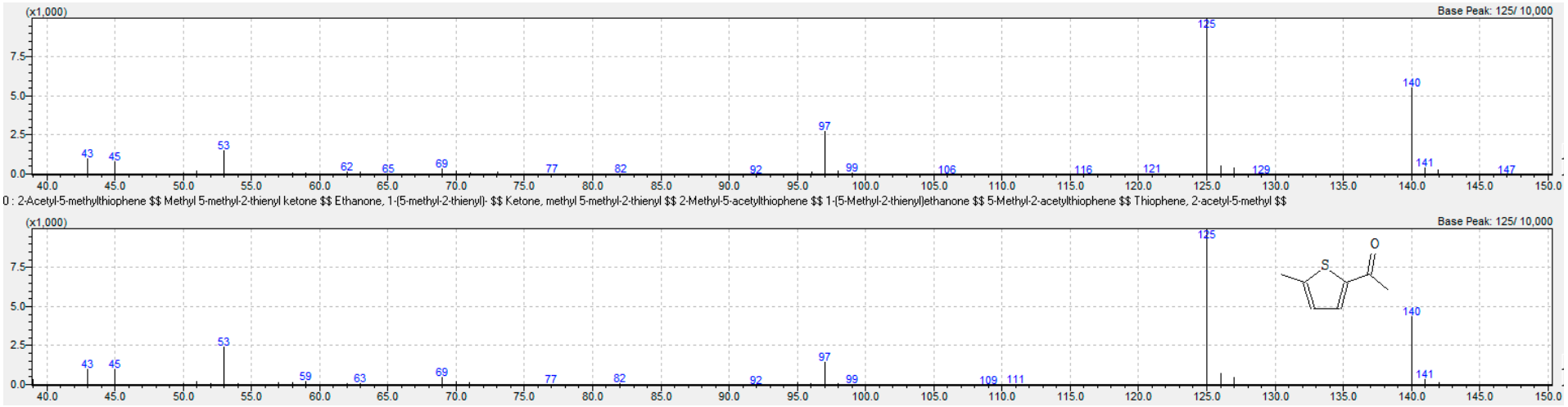
2[5H]-5-Methylthiophenon (10) similarity to NIST14 database: 77%



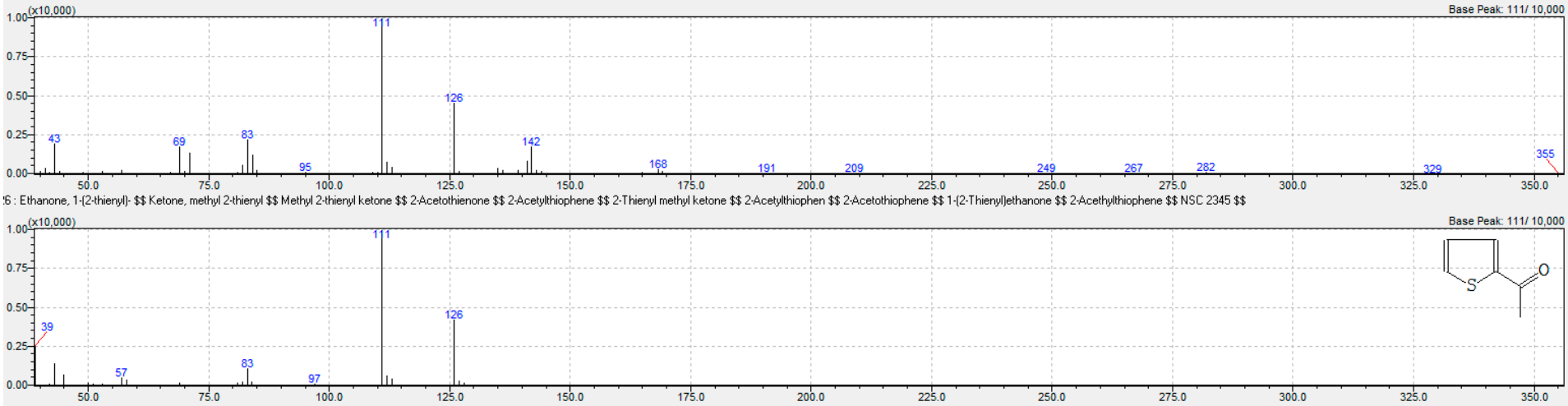
2-Vinylthiophene (11) similarity to NIST14 database: 81%



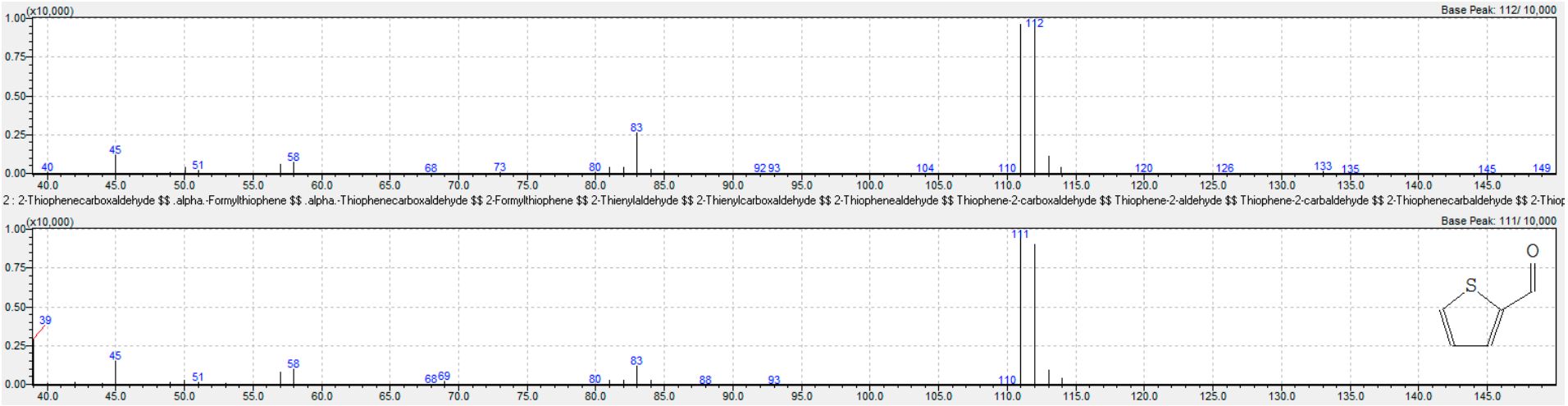
2-Acetyl-5-methylthiophene (12) similarity to NIST14 database: 93%



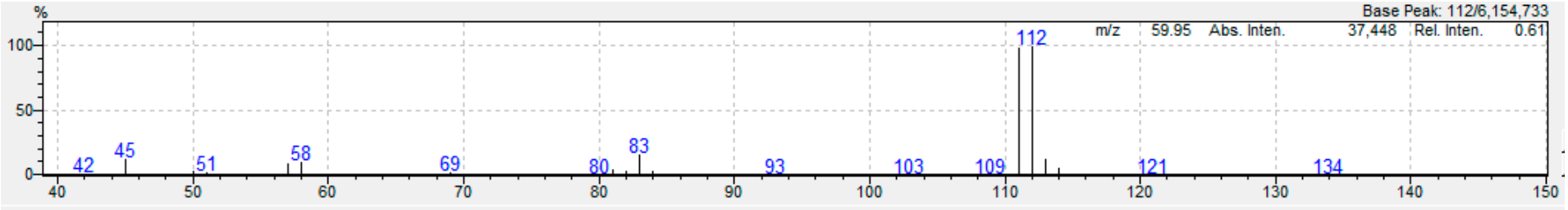
2-Acetylthiophene (13) **similarity to NIST14 database: 78%**



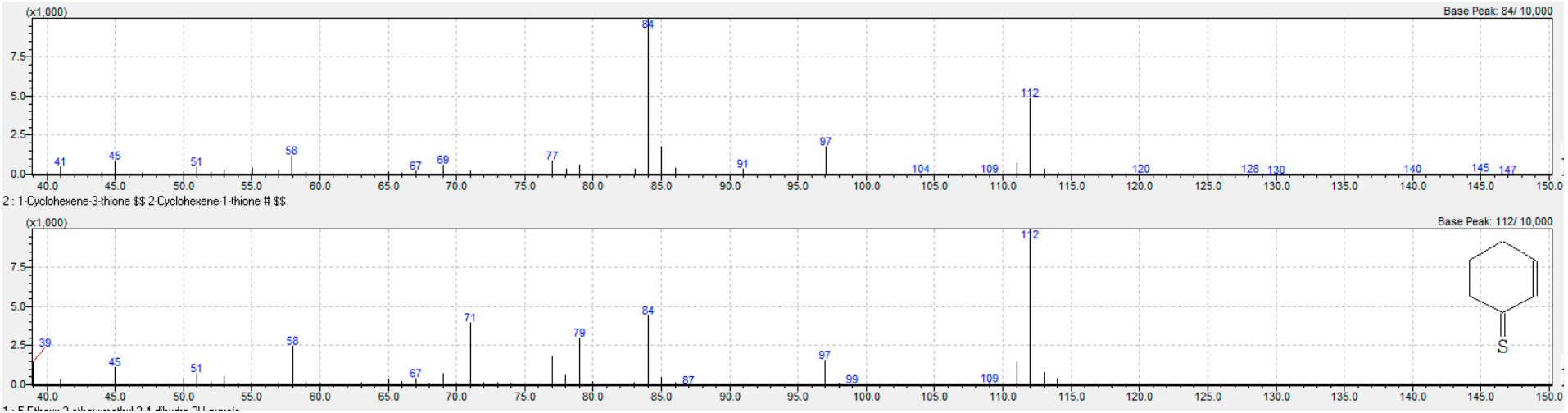
Thiophene-2-carboxaldehyde (14) similarity to NIST14 database: 84%



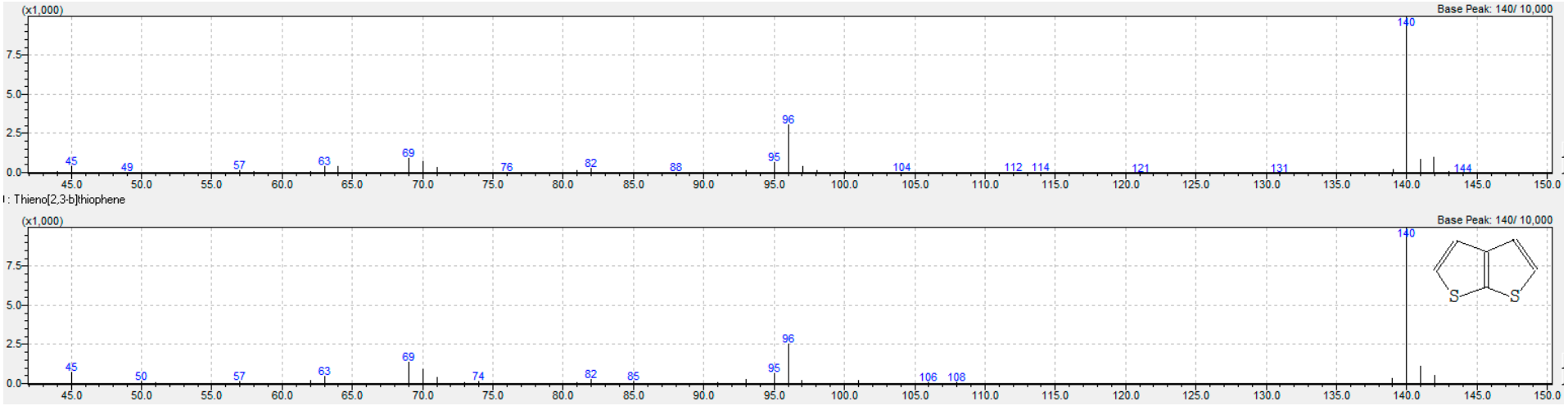
Thiophene-2-carboxaldehyde analytical standard (Sigma Aldrich)



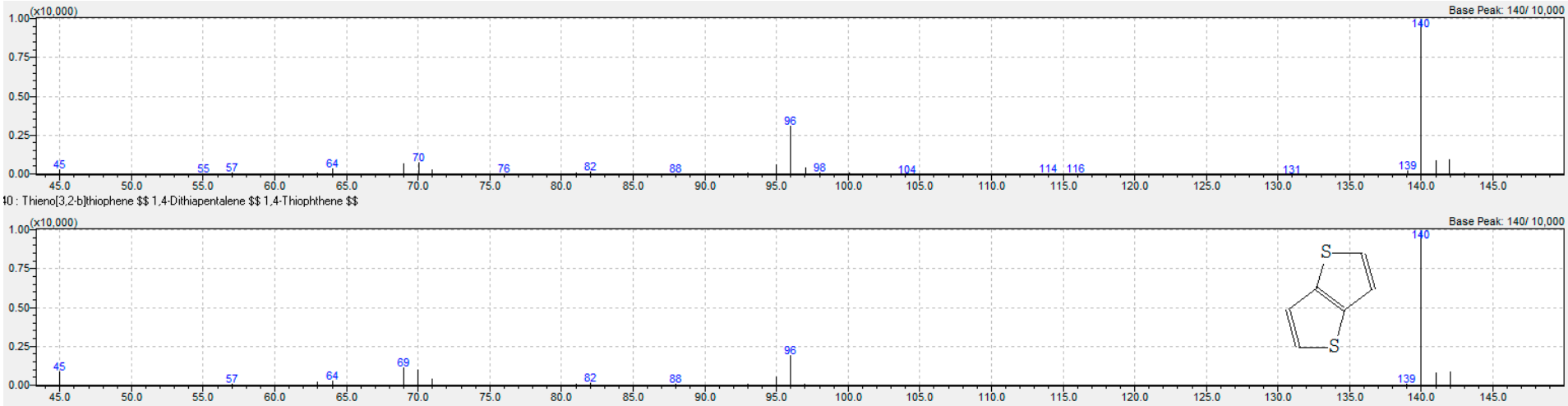
Cyclohex-2-enthion (15) **similarity to NIST14 database: 78%**



cis-1,4-Dithiapentalene (16) **similarity to NIST14 database: 89%**



trans-1,4-Dithiapentalene (17) **similarity to NIST14 database: 92%**



Benzo[*b*]thiophene (18) **similarity to NIST14 database: 97%**

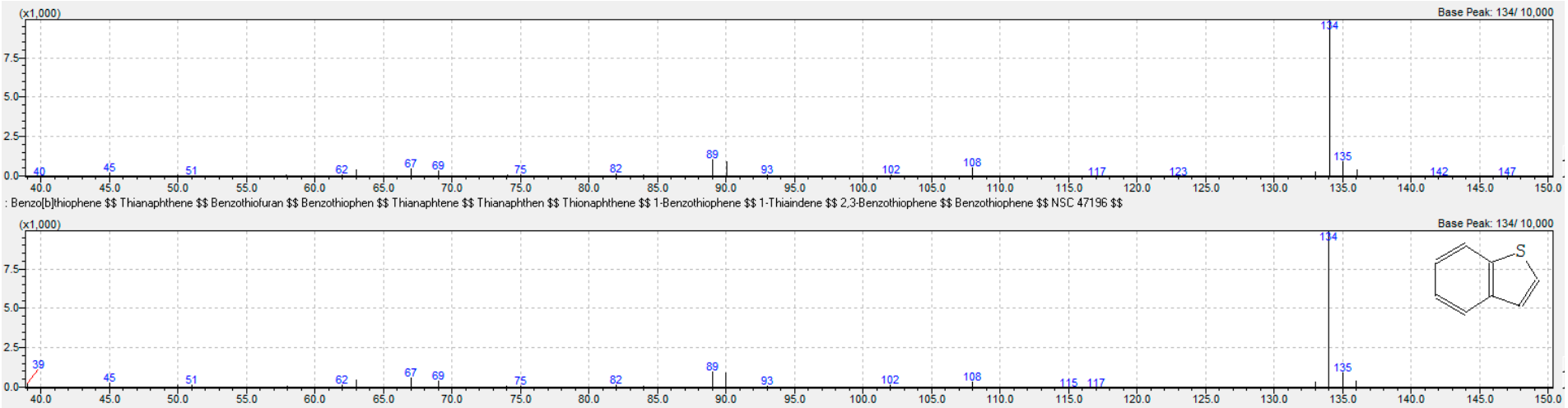


Figure S2: GC/MS mass spectra comparing reaction products to commercially available thiophene standards and mass spectra from NIST14 library. Numbers corresponding to Figure 3 in brackets.