Supporting Information:

Synergistic Photocatalytic Aerobic Oxidation of Sulfides and Amines on TiO_2 under Visible Light Irradiation

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General:

The UV-visible absorption spectra of benzylamine, thioaniosole and the mixture of benzylamine and thioaniosole were recorded on a Shimadzu UV 2550 UV-vis Spectrophotometer. The detailed recording concentration: 2×10^{-3} M of benzylamine in MeOH; 2×10^{-4} M of thioanisole in CH_3OH; a mixture of 6.7×10^{-4} M of benzylamine and 2×10^{-4} M of thioanisole in CH_3OH.

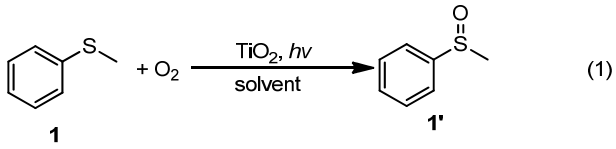
The UV-visible absorption spectra of the solid samples were recorded on the same machine with a diffuse reflectance measurement accessory.

The phase composition of the Degussa P25 TiO_2 sample was identified by X-ray diffraction (XRD) using a Shimadzu 6000 X-ray diffractometer with Cu K_α radiation (λ = 1.541 78 Å).

The TEM image of Degussa P25 TiO_2 sample was recorded on a JEOL JEM-2010 transmission electron microscope (TEM) operating at 200 kV to obtain the detailed nanostructures.

X-ray Photoelectron Spectroscopy (XPS) were measured by a ESCALAB250XI. The incident radiation was Mg K_α X-ray (1253.6 eV) at 400 W and a charge neutralizer was turned on for acquisition. The binding energy of N1s was corrected by C 1s peak (284.8 eV) from residual carbon.

Table S1: Control experiments for the photocatalytic oxidation of thioanisole on TiO_2 in organic solvent[a]

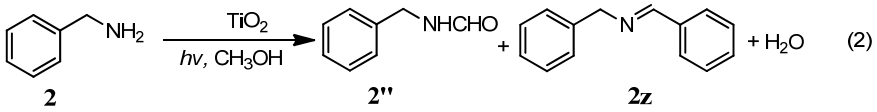


(1)

Entry	Solvent	Conditions	Conv. (mol%)[b]	Select. (mol%)[b]
1	CH_3CN	>350 nm	10	40
2	CH_3OH	>350 nm	5	95
3	CH_3CN	>400 nm	10	63
4	CH_3OH	>400 nm	6	93

Reaction conditions: 0.3 mmol of thioanisole, 0.1 MPa of O_2, 40 mg of TiO_2 (Degussa P25), 300 W Xe lamp, 5 mL of solvent, 3 h. Longpass cutoff filters are used to control the irradiation wavelength. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole **1**, selectivity of methyl phenyl sulfoxide **1'**.

Table S2: Control experiment for the photocatalytic oxidation of benzylamine on Degussa P25 TiO_2 in organic solvent[a]



(2)

Entry	Solvent	Conditions	Conv. (mol%)[b]	Select. (mol%)[b]
1	CH_3CN	>400 nm	100	85 (imine)
2	CH_3OH	>400 nm	100	38 (formamide)
3	CH_3OH	>350 nm	100	10 (formamide)

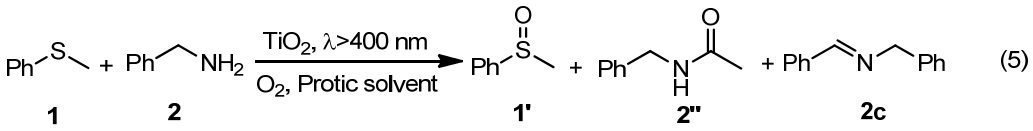
[a] Reaction conditions: 0.1 mmol of benzylamine, 0.1 MPa of O_2, 40 mg of Degussa P25 TiO_2, 5 mL of solvent, 3 h. [b] Determined by GC using chlorobenzene as the internal standard.

Table S3: The aerobic oxidation of thioanisole and benzylamine in inert organic solvent on TiO_2 under visible light irradiation[a]

Entry	Solvent	Conv1. (mol%)[b]	Select1. (mol%)[b]	Conv2. (mol%)[b]	Select2. (mol%)[b]
1	CH_3CN	10	63	--	--
1'[c]	CH_3CN	16	86	100	74
2	BTF	5	38	--	--
2'[c]	BTF	5	66	100	58
3	EtOAc	6	42	--	
3'[c]	EtOAC	12	80	100	75
4	DCM	4	65	--	--
4'[c]	DCM	8	90	100	58

[a] Reaction conditions: 0.3 mmol of thioanisole, 5 mL of solvent, 40 mg of Degussa P25 TiO_2, 300 W Xe lamp λ>400 nm, 0.1 MPa of O_2, 3 h, [b] Determined by GC using chlorobenzene as the internal standard. [c] 0.1 mmol of benzylamine was added. BTF, Benzotrifluoride; EtOAc, ethyl acetate; DCM, dichloromethane.

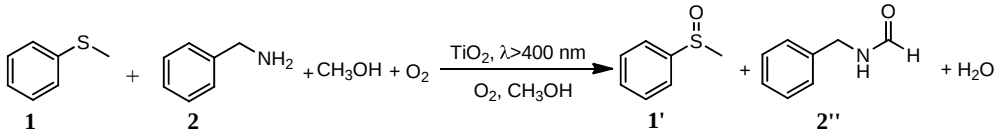
Table S4: The selective aerobic oxidation of thioanisole and benzylamine on TiO_2 in protic solvents under visible light irradiation[a]



Entry	Solvent	Thioanisole		Benzylamine	
		Conv1. (mol%)[b]	Select1. (mol%)[b]	Conv2. (mol%)[c]	Select2. (mol%)[c]
1	IPA	2	100	--	--
1'[d]	IPA	28	85	100	**2c** (64)[e]
2	C_2H_5OH	1	100	--	--
2'[d]	C_2H_5OH	45	88	100	**2c** (35)[e]
3	CH_3OH	6	93	--	--
3'[d]	CH_3OH	77	93	100	**2''** (79)[e]

[a] Reaction conditions: 0.3 mmol of **2**, 0.1 MPa of O_2, 40 mg Degussa P25 TiO_2, 300 W Xe lamp, 5 mL of solvent, λ>400 nm, 3 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of **2**, selectivity of **2b**. [c] Determined by GC using chlorobenzene as the internal standard, conversion of benzylamine. [d] 0.1 mmol of **1** was added. [e] Data in the parentheses is the selectivity for the indicated product for the oxidation of **1**, IPA, isopropanol.

Table S5: The scale-up for the synergistic photocatalytic oxidation of sulfide to amines [a]

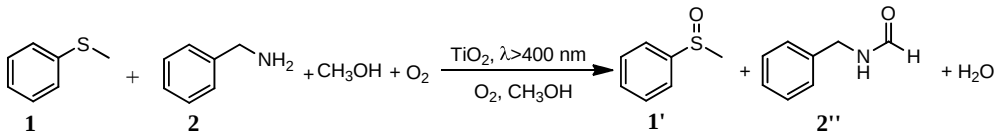


1 2 1' 2''

Entry	Substrates (mmol)	Time (h)	Conv1. (mol%)[b]	Select1. (mol%)[b]	Conv2. (mol%)[c]	Select2. (mol%)[c]
1	0.05+ 0.15	2	85	92	100	77
2	0.1+ 0.3	4	83	92	100	78
3	0.2+ 0.6	8	88	89	100	82
4[d]	0.3+ 0.9	12	83	91	100	42

[a] Reaction conditions: 5 mL of CH_3OH, 40 mg of TiO_2, 300 W Xe lamp, λ>400 nm, 0.1 MPa of O_2, [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole **1**, selectivity of sulfoxide **1'**; [c] Determined by GC using chlorobenzene as the internal standard, conversion of benzylamine **2**, selectivity of *N*-benzylformamide **2''**. [d] 15% of benzaldehyde **2y** and 5% of imine **2z** were the other products detected.

Table S6: Control experiment for the synergistic photocatalytic oxidation of thioanisole on Degussa P25 TiO_2 in organic solvent[a]



1 2 1' 2''

Entry	Conditions	Conv1. (mol%)[b]	Select1. (mol%)[b]	Conv2. (mol%)[c]	Select2. (mol%)[c]
1	>350 nm	30	92	100	10
2	>400 nm	83	92	100	78
3[d]	>400 nm	0	--	0	--
4[e]	>400 nm	0	--	0	--
4[f]	--	0	--	0	--
5	>420 nm	0	--	15	0

[a] Reaction conditions: 5 mL of methanol, 40 mg of Degussa P25 TiO_2, 300 W Xe lamp λ>400 nm, 0.1 MPa of O_2, 4 h. [b] Determined by GC using chlorobenzene as the internal standard, conversion of thioanisole, selectivity of sulfoxide; [c] Determined by GC using chlorobenzene as the internal standard, conversion of benzylamine, selectivity of *N*-benzylformamide. [d] Without O_2 with 0.1 MPa of N_2 as the atmosphere. [e] Without TiO_2. [f] Without λ>400 nm visible light irradiation.

Table S7: Adsorption difference of benzylamine on Degussa P25 TiO_2 in CH_3OH and CH_3CN

Entry	Solvent	Adsorption amounts
1	CH_3OH	3 μmol
2	CH_3CN	10 μmol

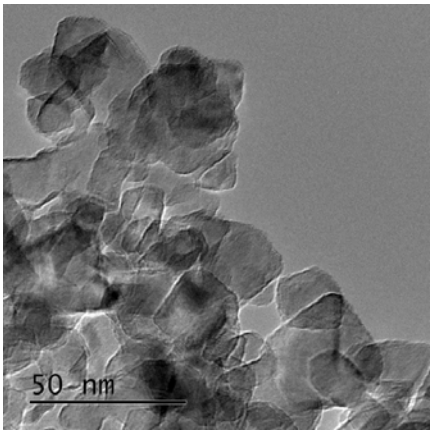


Figure S1: Transmission electron microscopy (TEM) images of Degussa P25 TiO_2

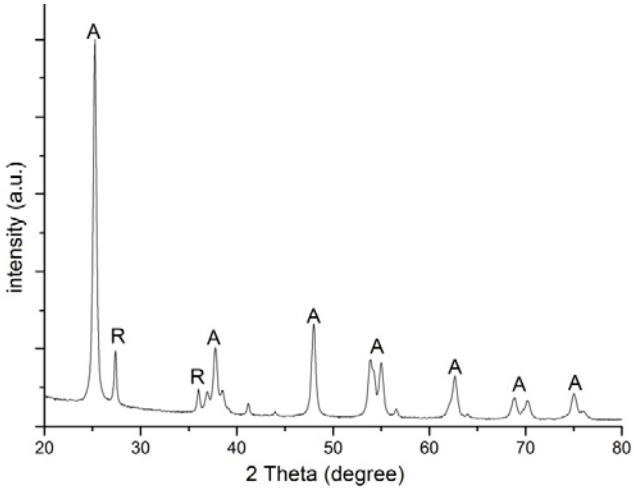


Figure S2: X-ray diffraction spectroscopy (XRD) of Degussa P25 TiO_2

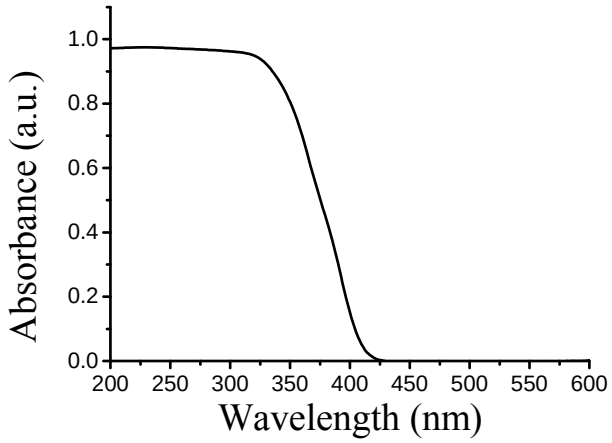


Figure S3: UV-visible absorbance spectroscopy of Degussa P25 TiO_2

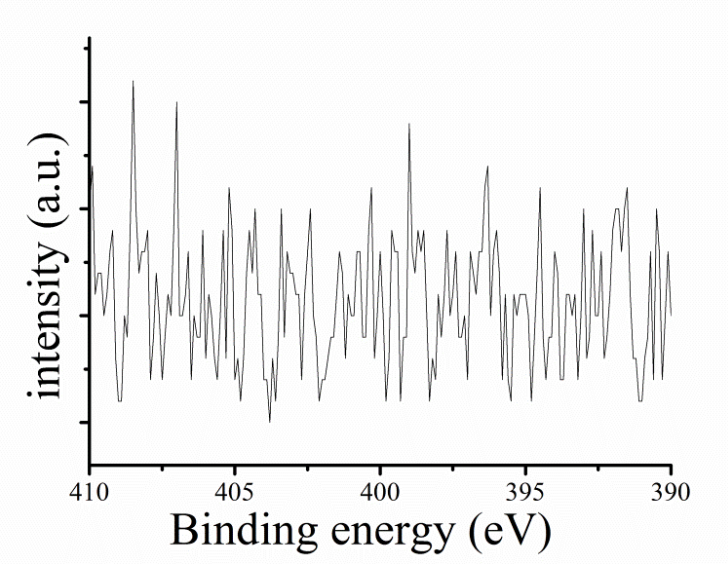


Figure S4: XPS spectroscopy of Degussa P25 TiO_2

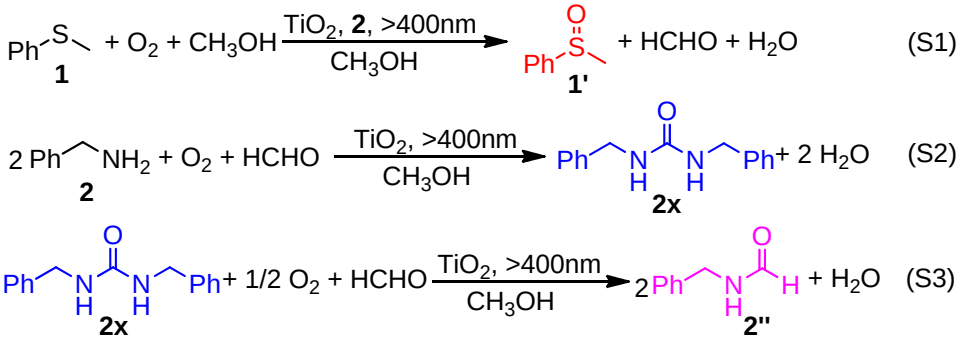


Figure S5: Products formation processes for the synergetic photocatalytic aerobic oxidation of sulfides and amines on TiO_2 under visible light irradiation

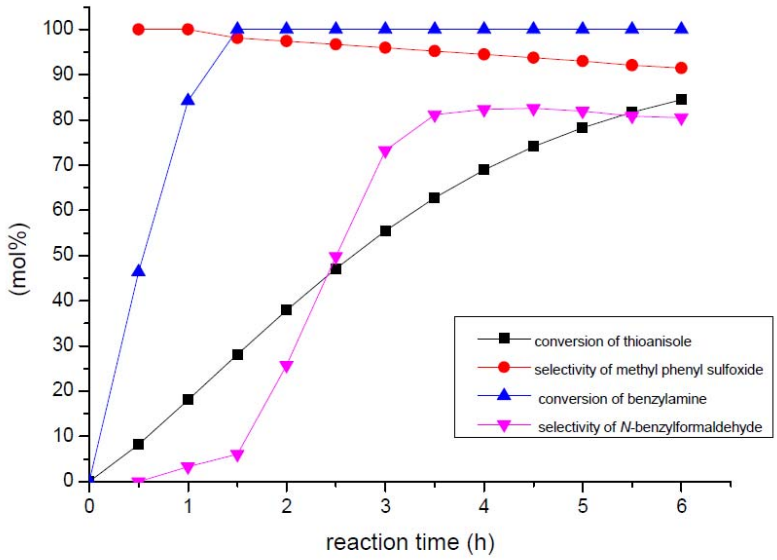
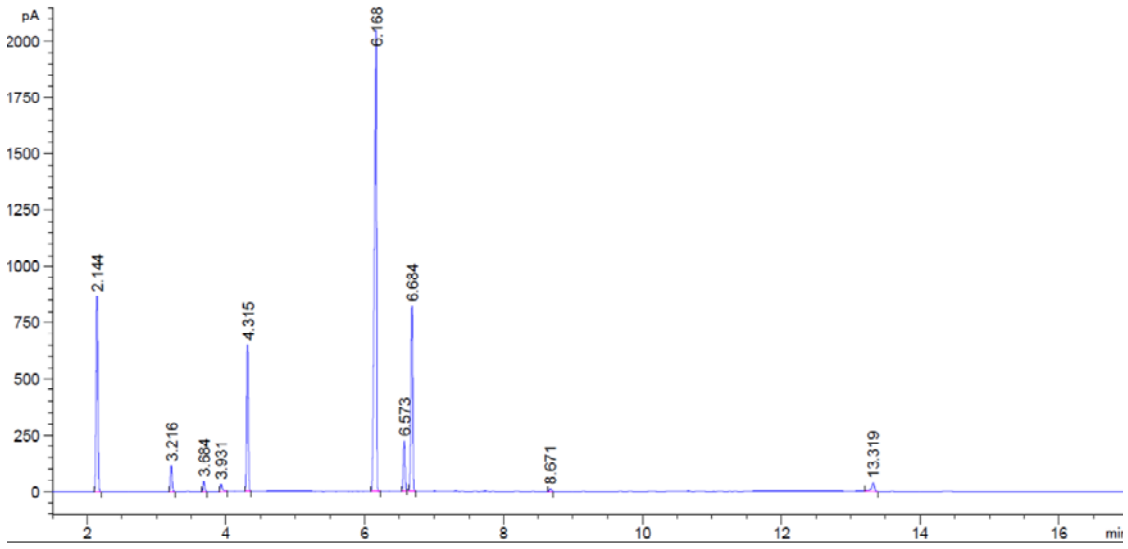


Figure S6: Reaction kinetic plot for the synergetic photocatalytic aerobic oxidation of sulfides and amines on TiO_2 under visible light irradiation. Reaction conditions: 0.3 mmol of thioanisole, 0.1 mmol of benzylamine, 40 mg of Degussa P25 TiO_2, 300 W Xe lamp, 5 mL of CH_3OH, λ>400 nm, 0.1 MPa of air



The GC-FID of Table 2 entry 1:

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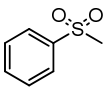
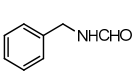
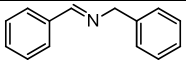
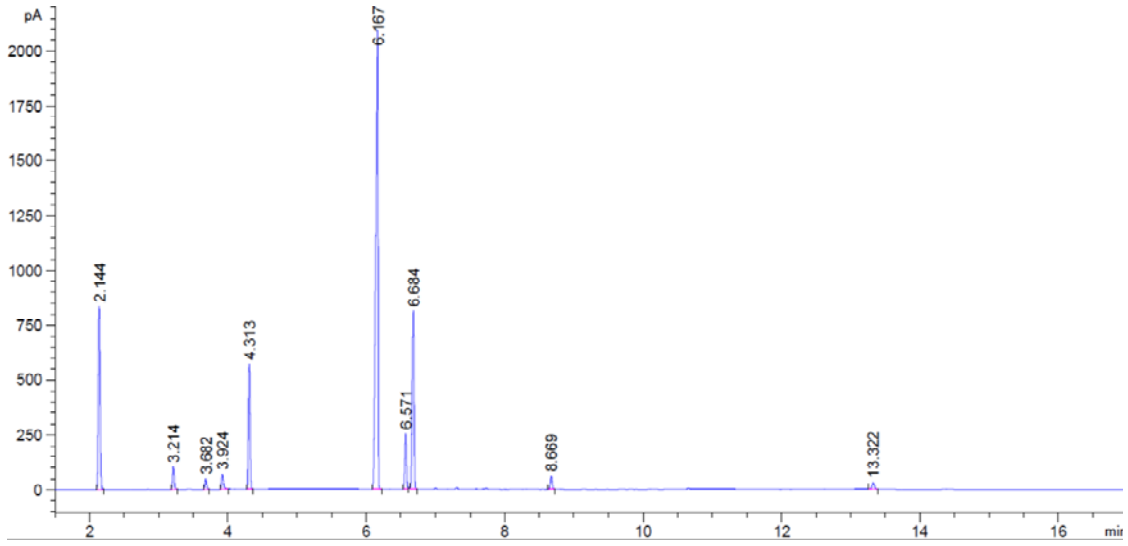
Chemical							



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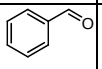
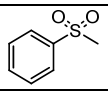
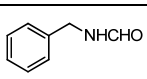
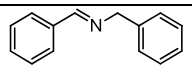
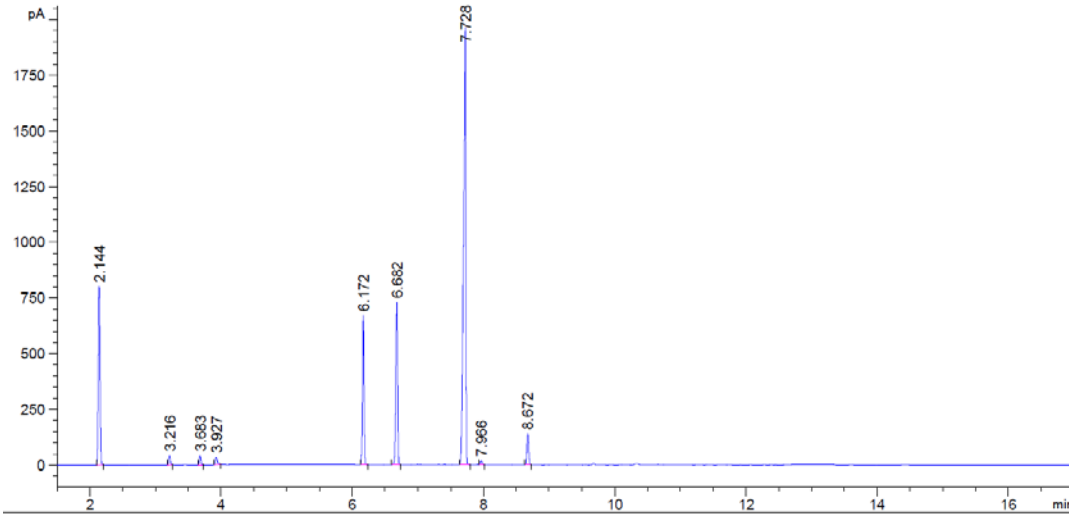
Retention time (min)	2.144	3.216	4.315	6.168	6.573	6.684	8.669
Chemical							



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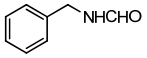
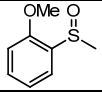
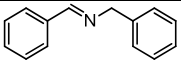
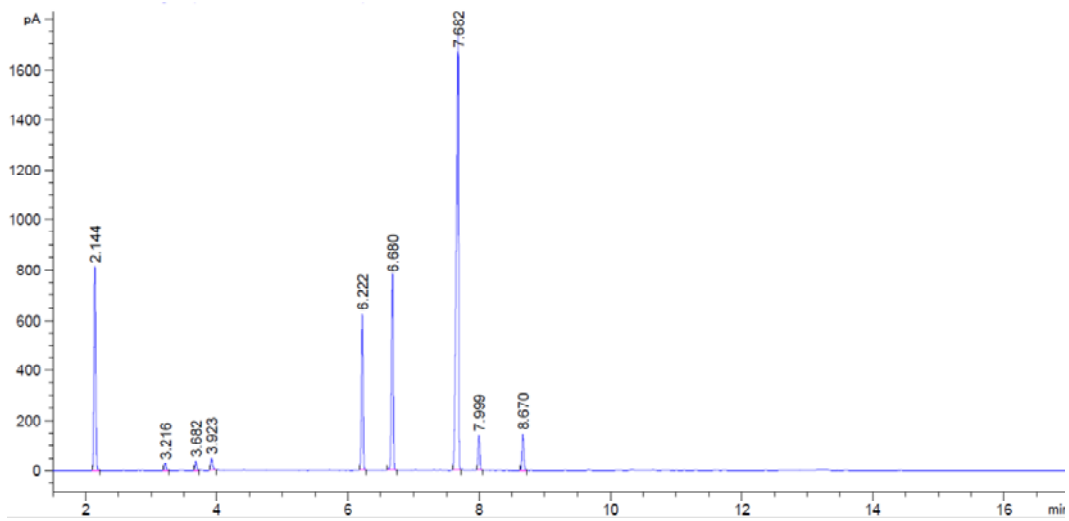
Chemical							



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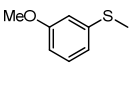
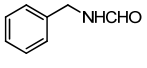
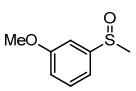
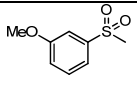
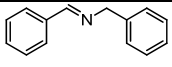
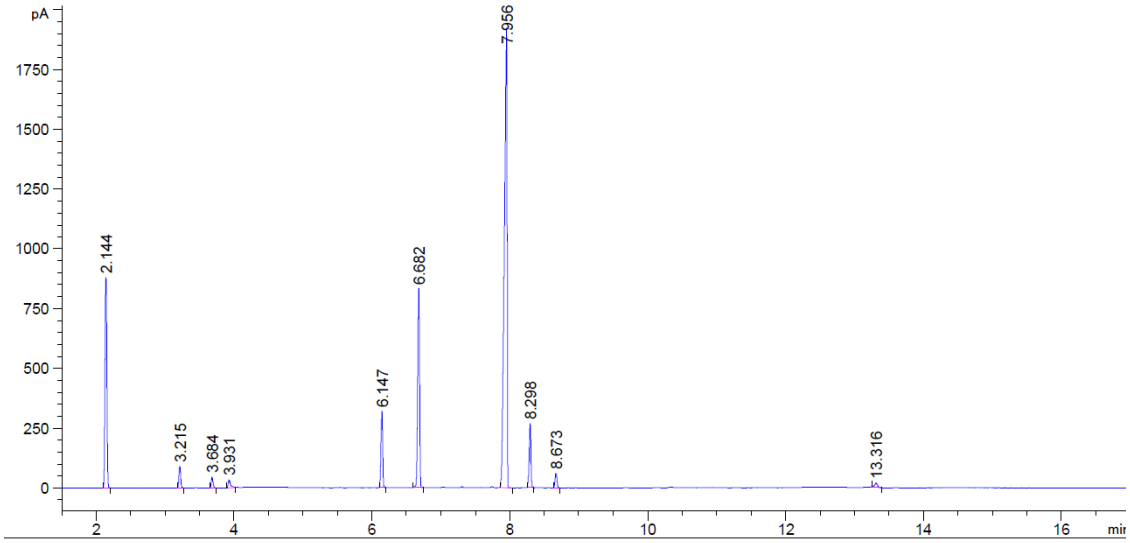
Chemical							



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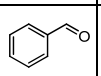
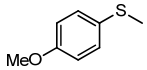
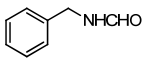
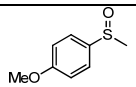
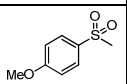
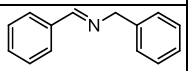
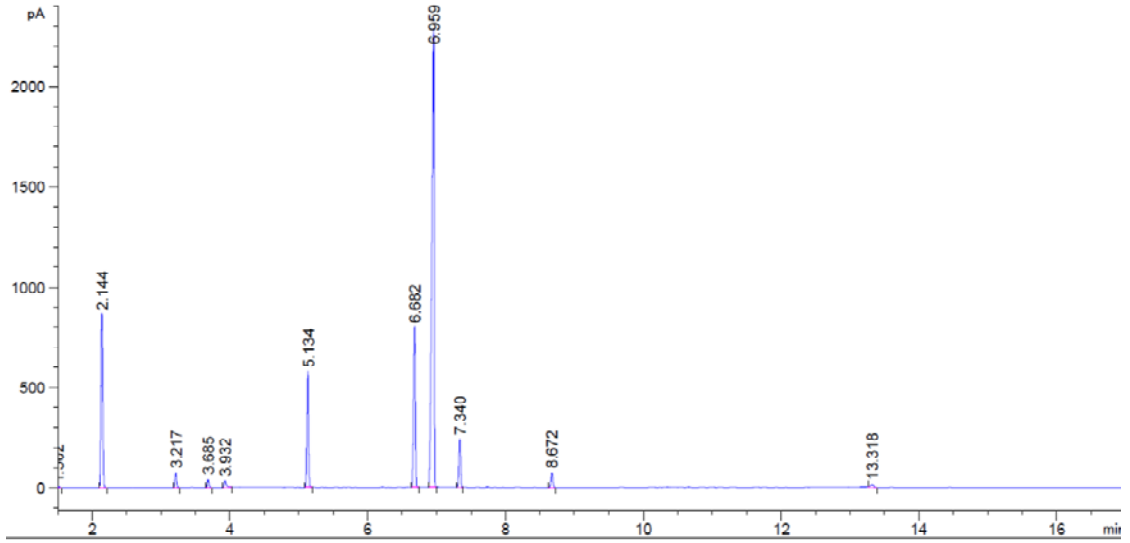
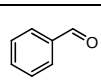
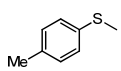
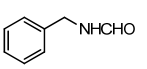
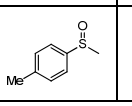
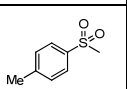
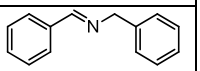
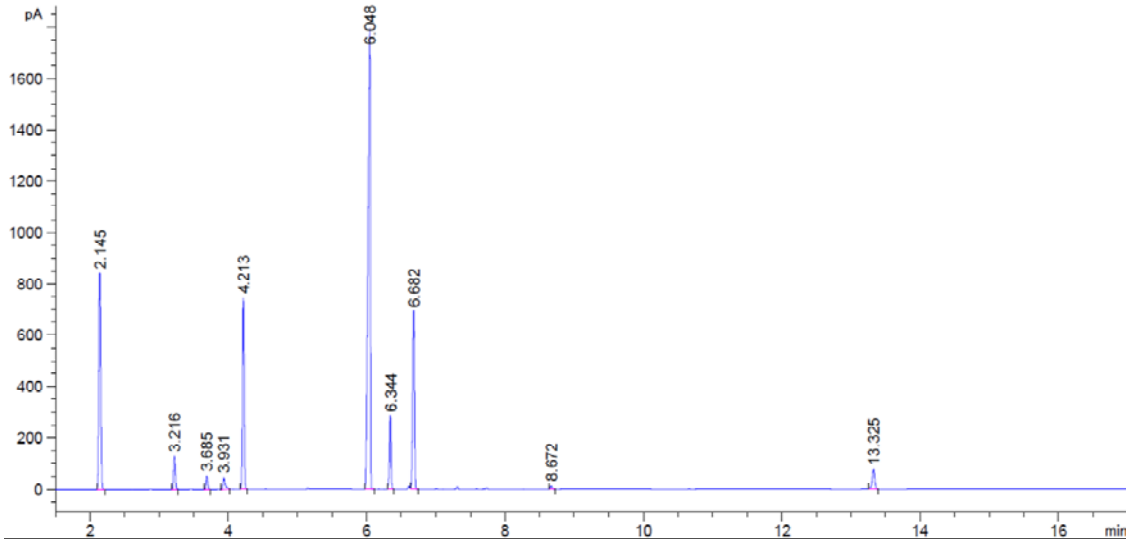
Retention time (min)	2.144	3.216	6.147	6.682	7.956	8.298	8.673
Chemical							

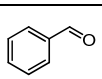
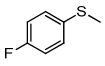
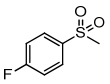
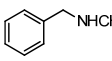
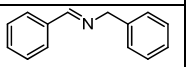


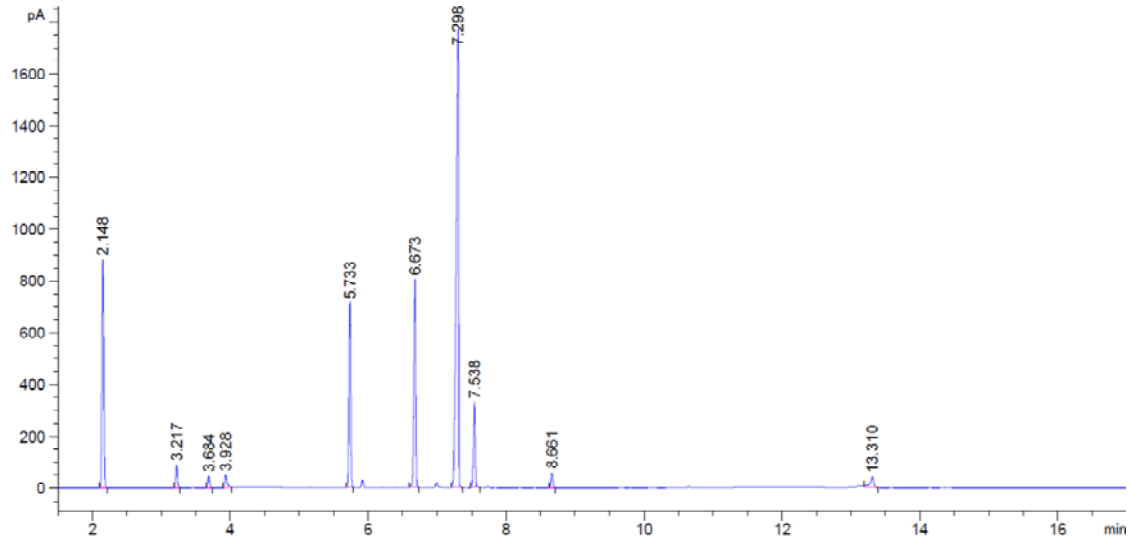
The GC-FID of Table 2 entry 5:

Retention time (min)	2.144	3.216	5.134	6.682	6.959	7.340	8.672
Chemical							

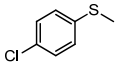
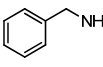
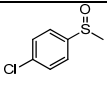
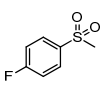
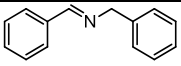


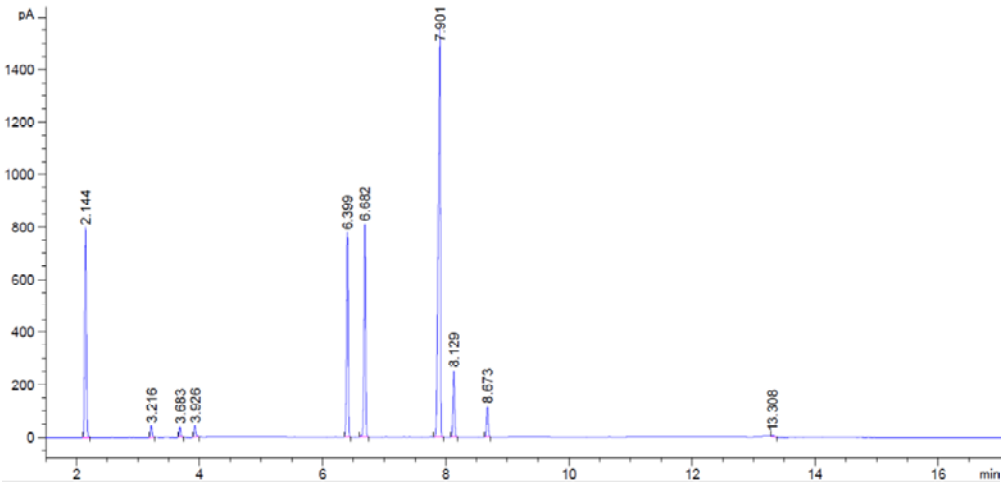
The GC-FID of Table 2 entry 6:

Retention time (min)	2.145	3.216	4.213	6.048	6.344	6.682	8.672
Chemical							

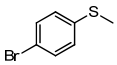
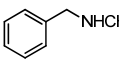
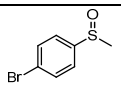
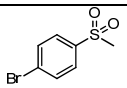
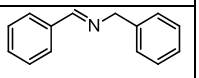


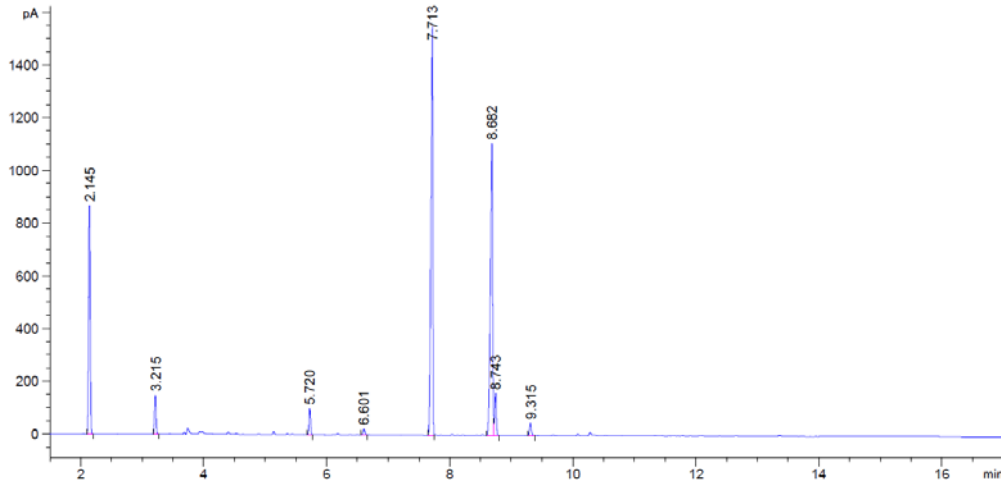
The GC-FID of Table 2 entry 7:

Retention time (min)	2.148	3.217	5.733	6.673	7.298	7.538	8.661
Chemical							

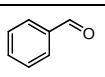
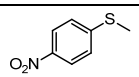
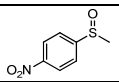
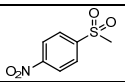


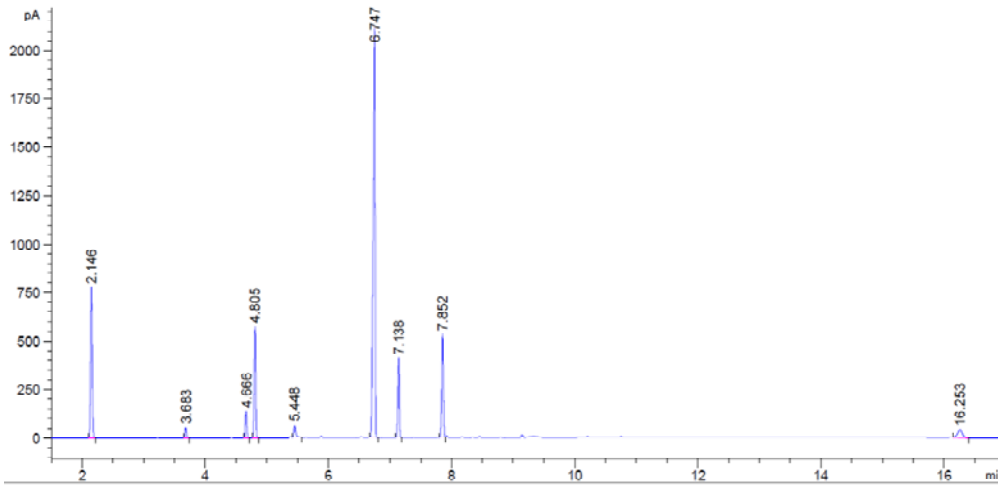
The GC-FID of Table 2 entry 8:

Retention time (min)	2.148	3.216	6.399	6.682	7.901	7.538	8.661
Chemical							

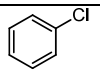
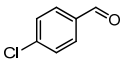
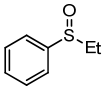
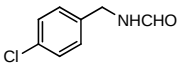


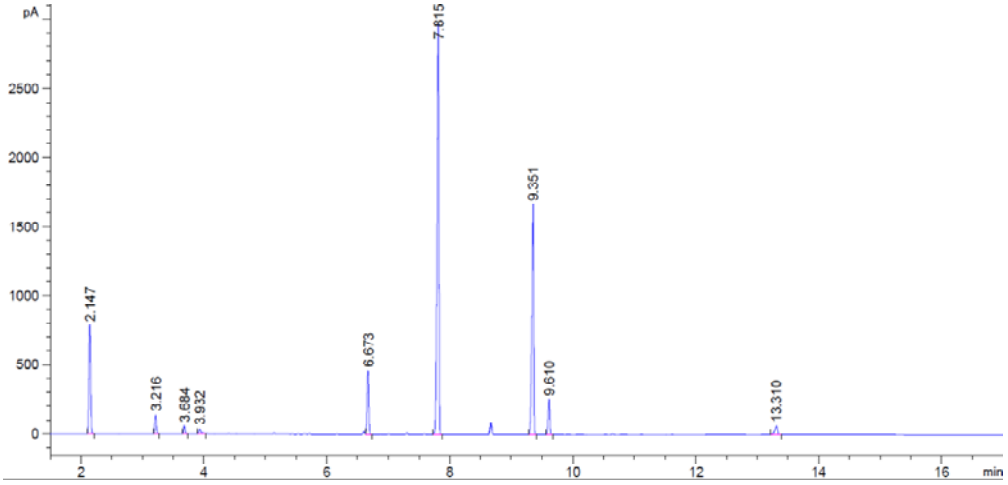
The GC-FID of Table 2 entry 9:

Retention time (min)	2.148	3.216	7.713	8.682	8.743
Chemical					

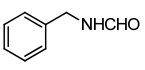
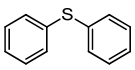
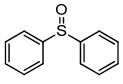
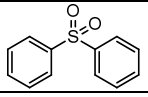


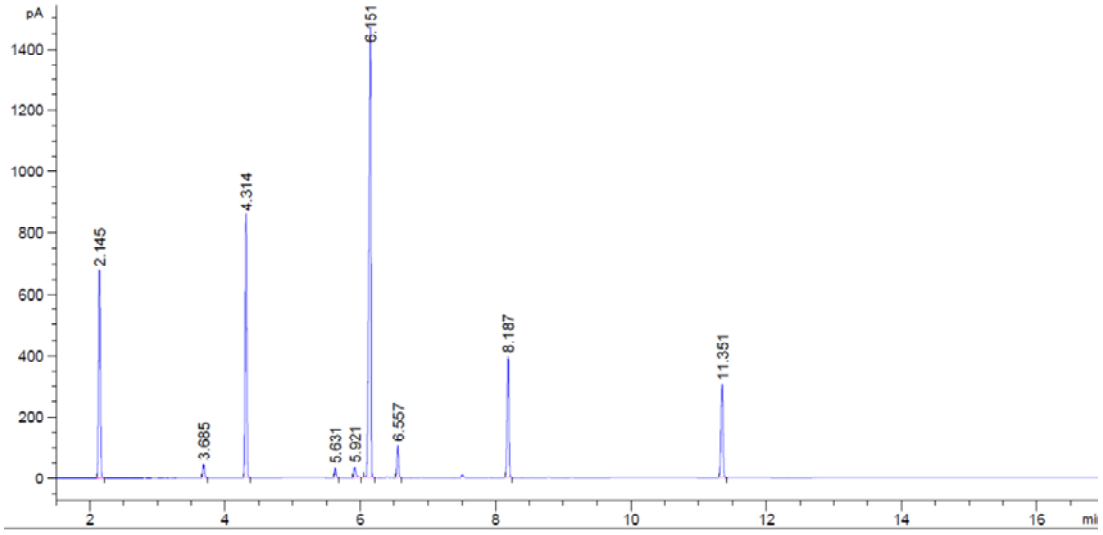
The GC-FID of Table 2 entry 10:

Retention time (min)	2.148	3.216	4.805	6.747	7.138	7.852
Chemical						

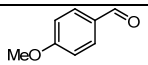
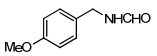
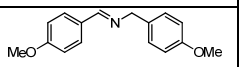


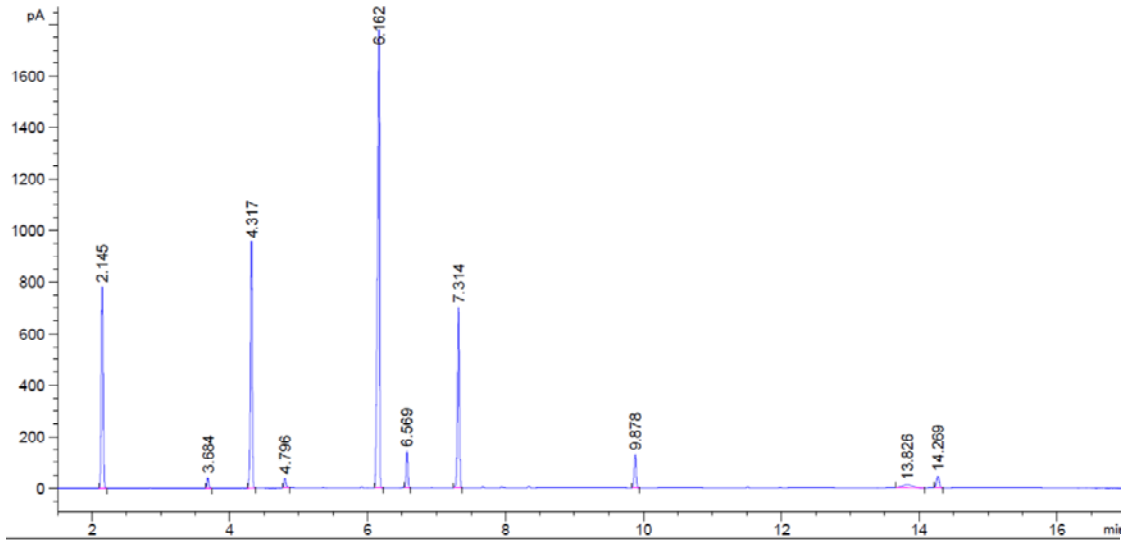
The GC-FID of Table 2 entry 11:

Retention time (min)	2.148	3.216	6.673	7.615	9.351	9.610
Chemical						

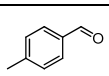
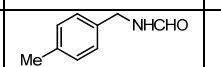
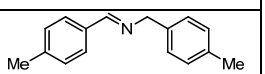


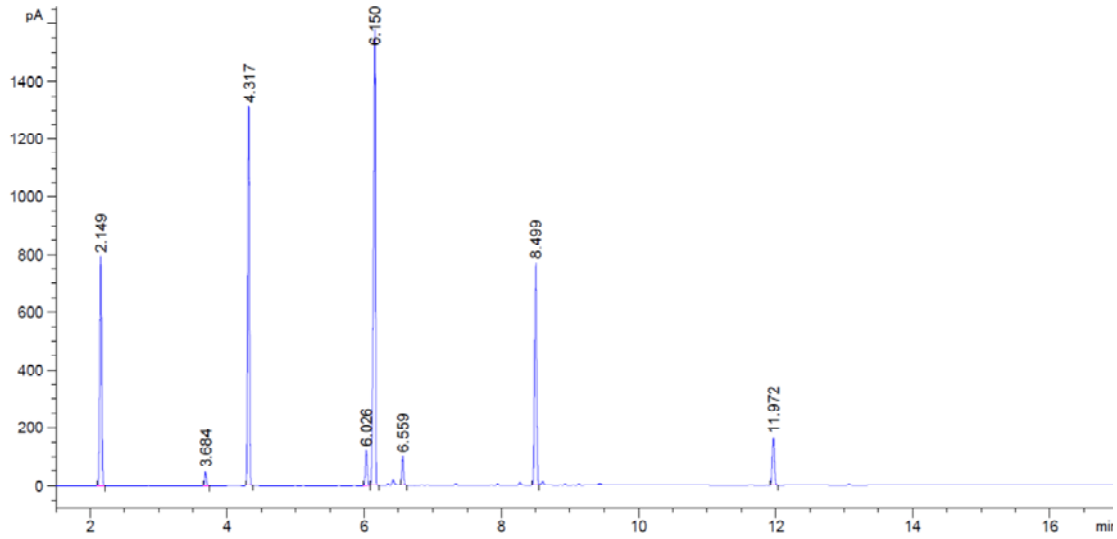
The GC-FID of Table 3 entry 1:

Retention time (min)	2.145	4.314	5.563	6.151	6.557	8.187	11.351
Chemical							

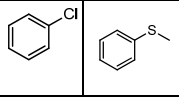
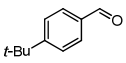
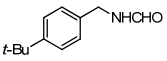
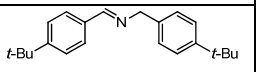


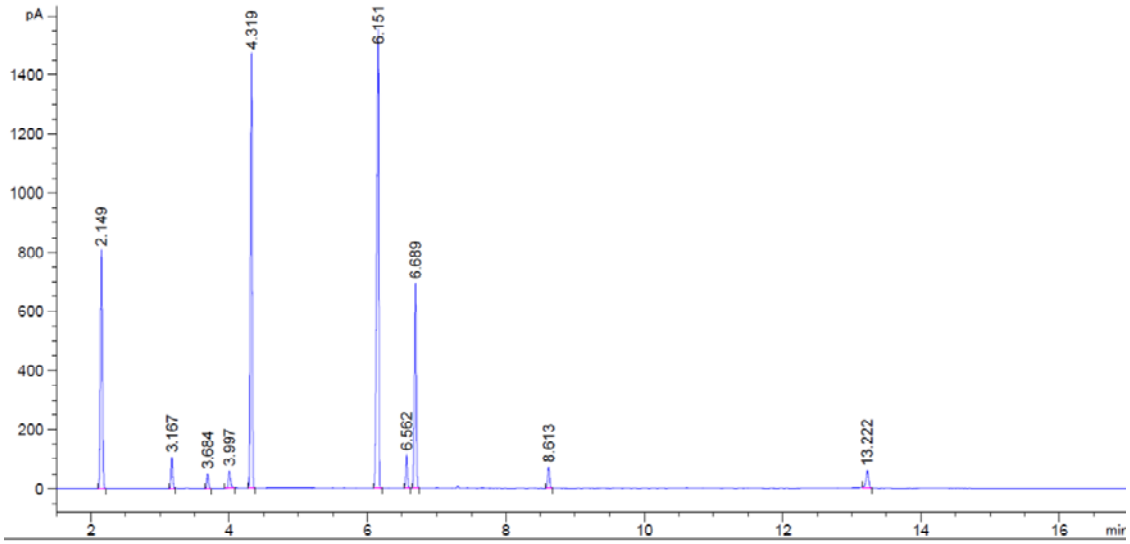
The GC-FID of Table 3 entry 2:

Retention time (min)	2.145	4.796	4.317	6.162	6.569	7.314	9.878
Chemical							

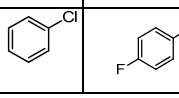
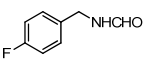
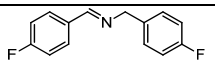


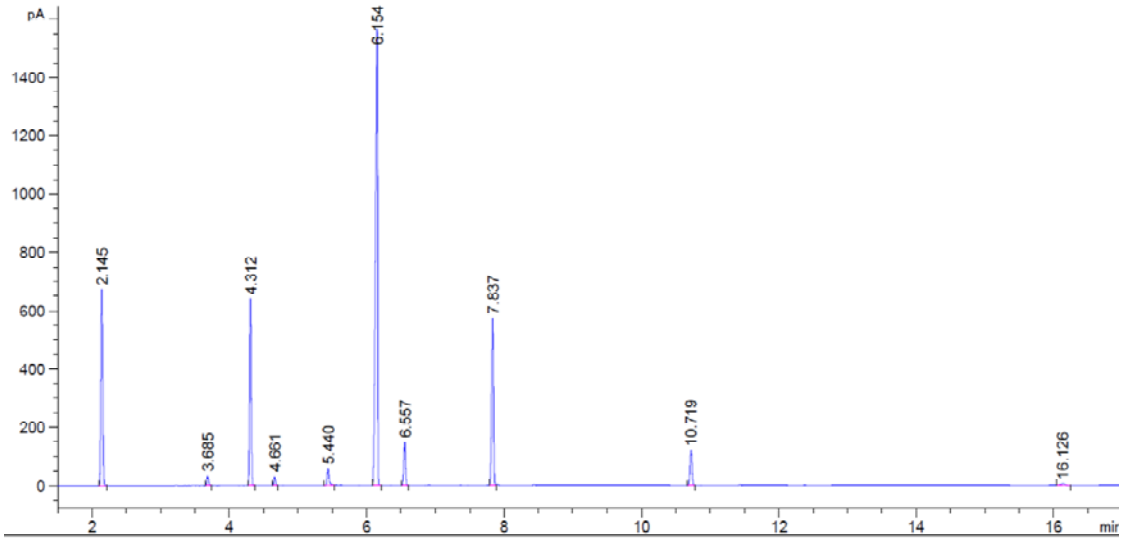
The GC-FID of Table 3 entry 3:

Retention time (min)	2.149	4.317	6.026	6.150	6.559	8.499	11.972
Chemical							

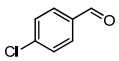
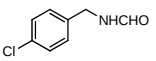
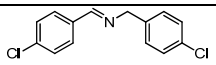


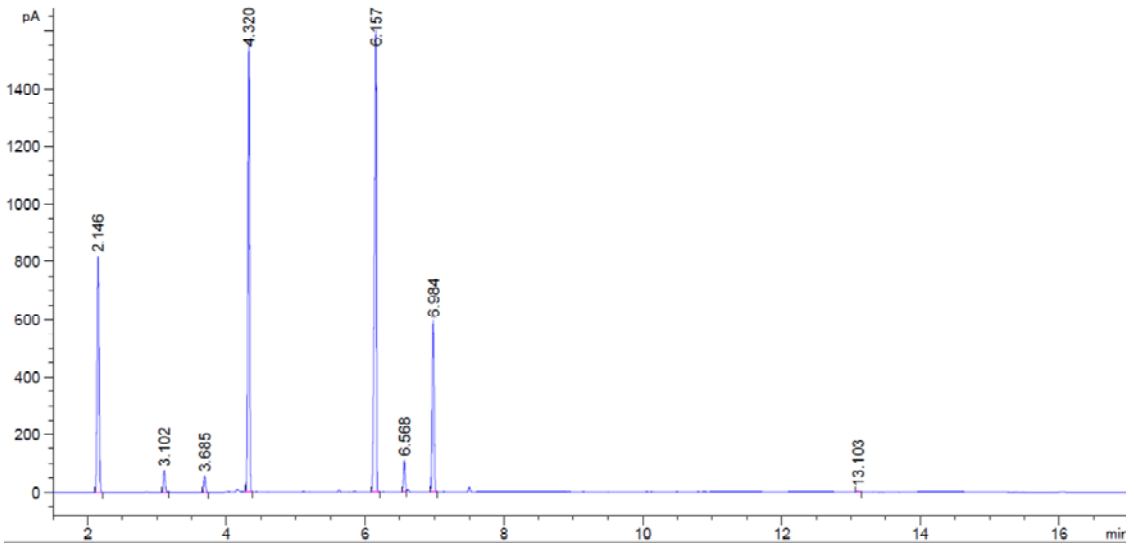
The GC-FID of Table 3 entry 4:

Retention time (min)	2.149	3.167	4.319	6.151	6.562	6.689	8.613
Chemical							

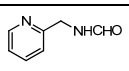


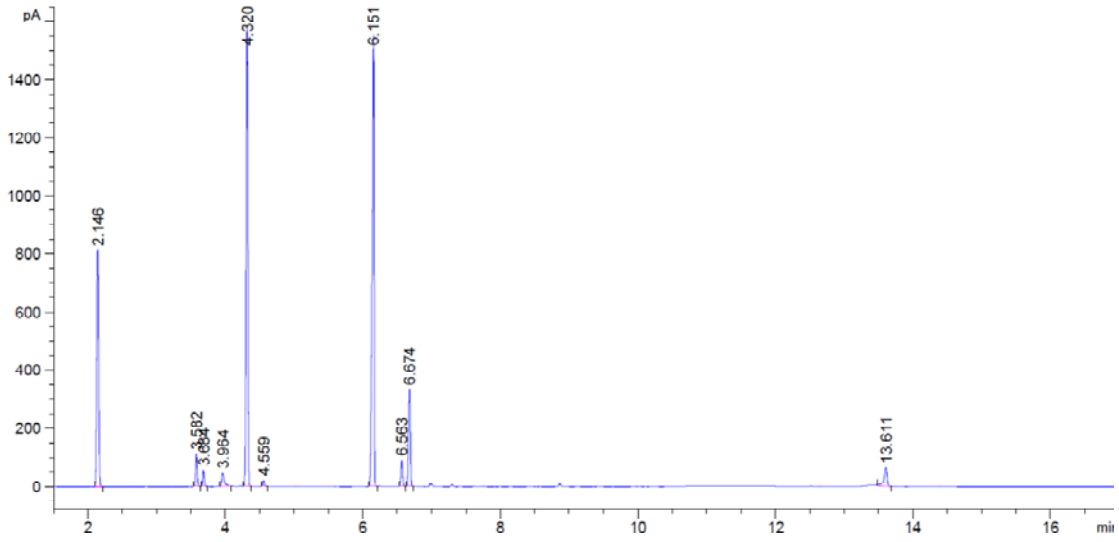
The GC-FID of Table 3 entry 5:

Retention time (min)	2.149	4.312	4.661	6.154	6.557	7.837	10.719
Chemical							

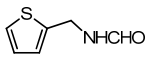


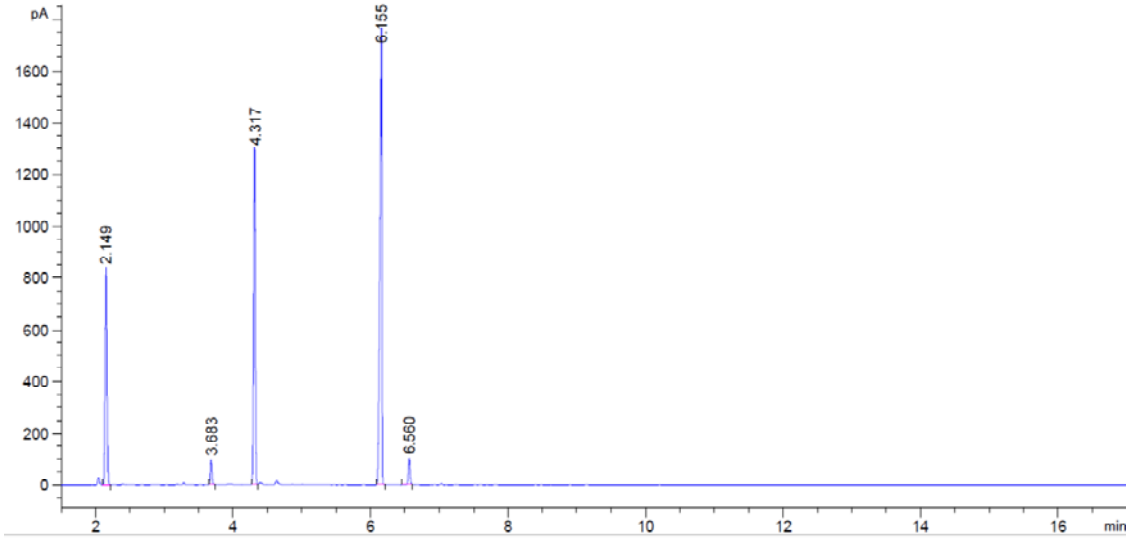
The GC-FID of Table 3 entry 6:

Retention time (min)	2.149	3.102	4.320	6.157	6.568	6.984
Chemical						



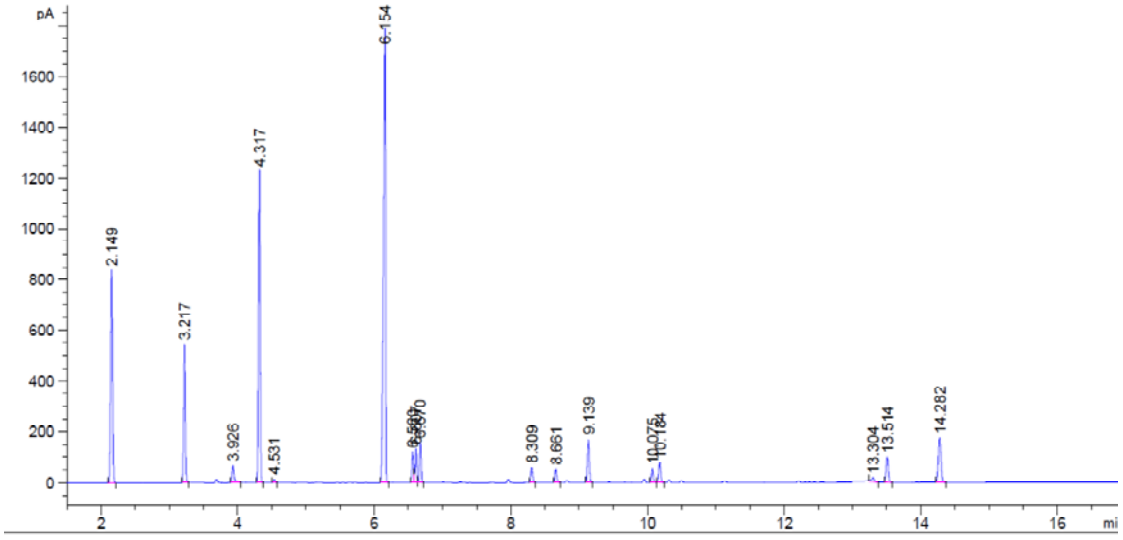
The GC-FID of Table 3 entry 7:

Retention time (min)	2.149	3.582	4.320	6.151	6.563	6.674
Chemical						

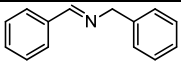


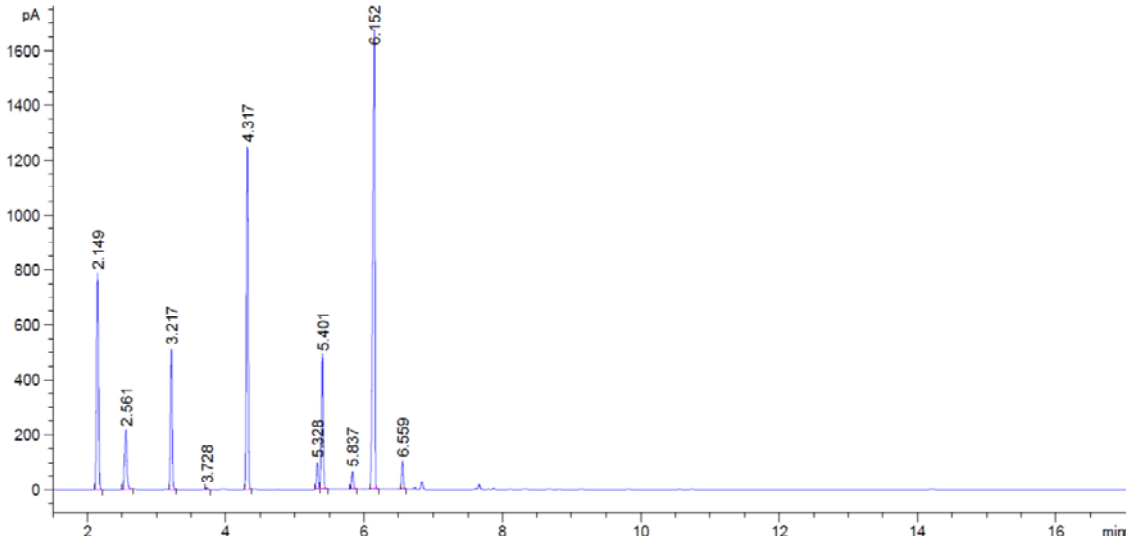
The GC-FID of Table 3 entry 8:

Retention time (min)	2.149	3.683	4.317	6.155	6.560
Chemical					



The GC-FID of Table 3 entry 9:

Retention time (min)	2.145	3.217	4.317	6.154	6.560	8.661
Chemical						



The GC-FID of Table 3 entry 10:

Retention time (min)	2.145	3.217	4.317	5.401	6.152	6.559	8.661
Chemical