

Electronic Supplementary Information

Extending the π -conjugated molecules on TiO_2 for selective photocatalytic aerobic oxidation of sulfides triggered by visible light

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1. Experimental section

1.1. Reagents and solvents

All the reagents were procured from commercial suppliers such as Sigma-Aldrich, Alfa Aesar and TCI, J&K Scientific, etc. Anatase TiO₂ (ST-01) was obtained from Ishihara Sangyo Kaisha, Ltd., Japan. P90 and P25 was kindly supplied by Evonik Industries, China. Rutile TiO₂ was purchased from Sakai chemical Industry CO., Ltd., Japan. The solvents were supplied by Merck, Fischer Scientific and Sinopharm Chemical Reagent Co. Ltd., China. All the reagents and solvents were directly used without further purification.

1.2. General procedure for the photocatalytic oxidation of sulfide

Firstly, 40 mg of TiO₂ (ST-01), 1.2×10^{-3} mmol 1H2NA, 0.015 mmol of TEMPO and 0.3 mmol of methyl phenyl sulfide were put into the solution of 1 mL CH₃OH in a 10 mL pyrex vessel. After 5 min of ultrasonic treatment at room temperature, the suspension was stirred for 30 min in dark to reach adsorption-desorption equilibrium. Subsequently, the rubber septum of Pyrex reactor was punched a hole to connect with aerial O₂. The reactor was vigorously stirred at 1500 rpm and illuminated with 460 nm blue LEDs (Shenzhen Ouying Lighting Science and Technology Co., Ltd. China) concurrently. It's worth noting that all of these reactions take place at room temperature. Finally, 1H2NA-TiO₂ nanoparticles were separated from the reaction mixture by centrifugation and the reaction products were analyzed by gas chromatography

equipped with a flame ionization detector (GC-FID, Agilent 7890B) using bromobenzene as the internal standard. The structures of products were confirmed by comparison with the retention time with authentic samples by GC-FID and further confirmed by gas chromatography–mass spectrometry (GC–MS).

Conversion, selectivity and yield for oxidation of sulfide to the desired sulfoxide were defined as follows:

$$\text{Conv. [\%]} = [(C_0 - C_S)/C_0] \times 100$$

$$\text{Sel. [\%]} = [C_{SO} / (C_0 - C_S)] \times 100$$

$$\text{Yield [\%]} = (C_{SO} / C_0) \times 100$$

where C_0 is the initial concentration of sulfide, and C_S and C_{SO} are the concentrations of sulfide and sulfoxide at a certain time during the photocatalytic reaction. For conversions, selectivities and yields, the mean standard deviation was $\pm 3\%$. The products were confirmed by the retention time comparison with that of standard samples and further verified by gas chromatography–mass spectrometry.

1.3. Characterization of photocatalytic materials

X-ray powder diffraction (PXRD) measurement was carried out using a Rigaku/Miniflex 600 diffractometer with filtered Cu $K\alpha$ radiation, and the data were collected from 10° to 80° . Fourier transform infrared (FT-IR) spectroscopy was performed by Nicolet 5700 FTIR Spectrometer. The UV-visible absorbance of 1H2NA,

1H2NA-TiO₂ and TiO₂ samples were measured on UV-3600 UV-vis spectrophotometer (Shimadzu, Japan) equipped with a diffuse reflectance measurement accessory, BaSO₄ was used as a reflectance standard.

1.4. EPR experimental procedures

The EPR experiments was carried out on an electron paramagnetic resonance (EPR) spectrometer (JEOL, JES-FA300). The EPR tube was added with 0.3 mmol of methyl phenyl sulfide, 40 mg of 1H2NA-TiO₂, 0.3 mmol of 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), 1 mL of CH₃OH. The signals of DMPO- \cdot OOH were collected at 0 min, 2 min and 4 min respectively under air irradiated by a high-pressure Hg lamp with a filter to select the band of 460 nm in the light chamber of the EPR spectrometer. Next, 0.015 mmol of TEMPO was added to the same EPR tube under air and irradiated with the same light source to collect the signals in situ at 0 min, 2 min and 4 min respectively.

Table S1. The influence of different photocatalysts on the blue light-triggered selective photocatalytic aerobic oxidation of methyl phenyl sulfide. ^a

Entry	Photocatalyst	Conv. ^b (%)	Sel. ^b (%)
1	TiO ₂ (ST-01)	78	89
2	SiO ₂	1	>99
3	λ-Al ₂ O ₃	4	99

^a Reaction conditions: photocatalyst (0.5 mmol), methyl phenyl sulfide (0.3 mmol), 1H2NA (1.2×10^{-3} mmol), TEMPO (0.015 mmol), blue LEDs (3 W \times 4), CH₃OH (1 mL), air (1 atm), 1 h. ^b Conversions for methyl phenyl sulfide, selectivities for methyl phenyl sulfoxide were determined by GC-FID using bromobenzene as an internal standard.

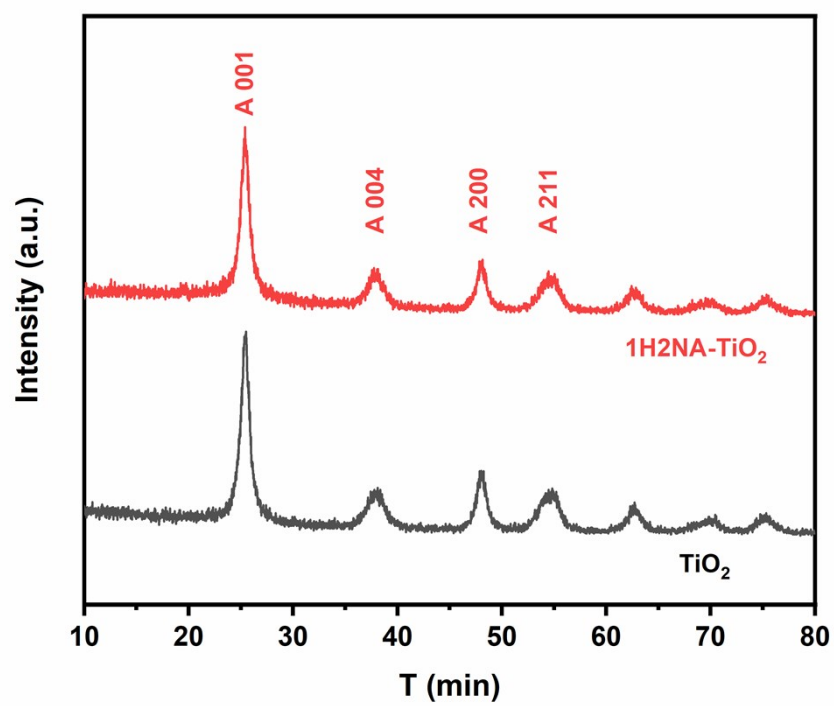


Fig. S1. The PXR D patterns of 1H2NA-TiO₂ and anatase TiO₂.

Figure S2: GC-FID results for Table 3

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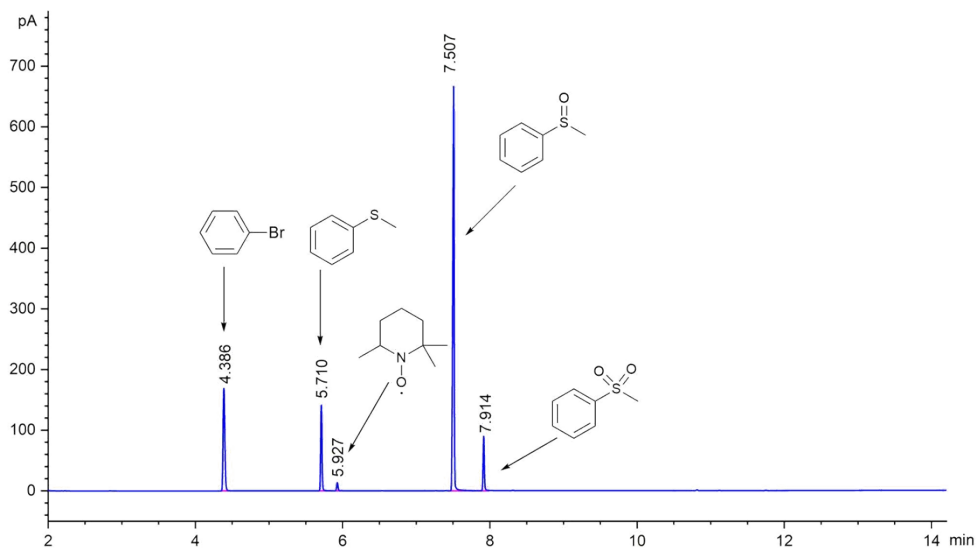


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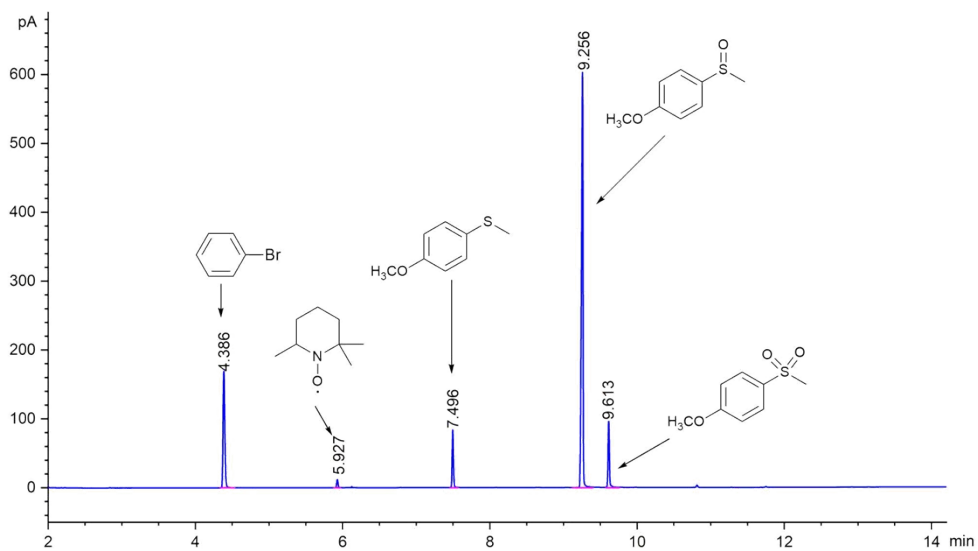


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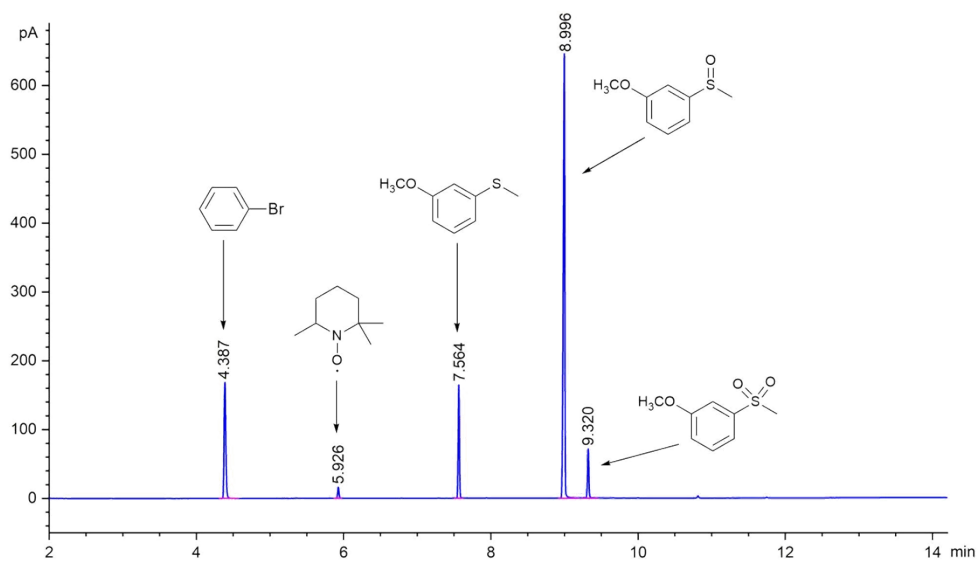


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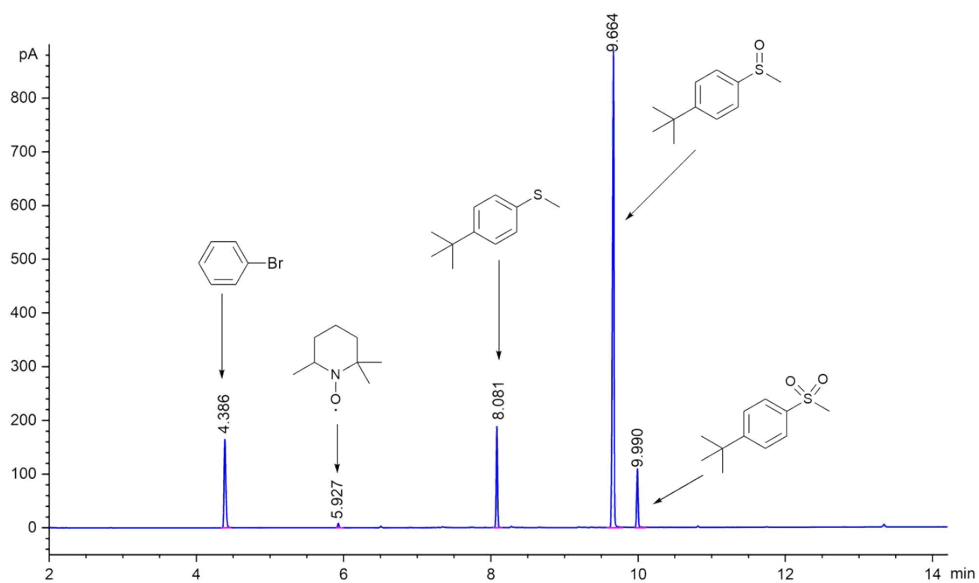


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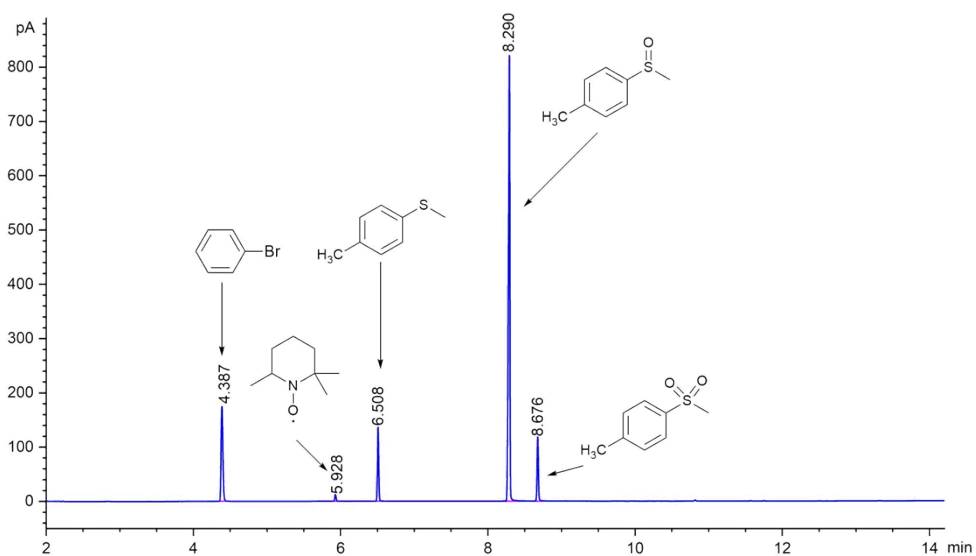


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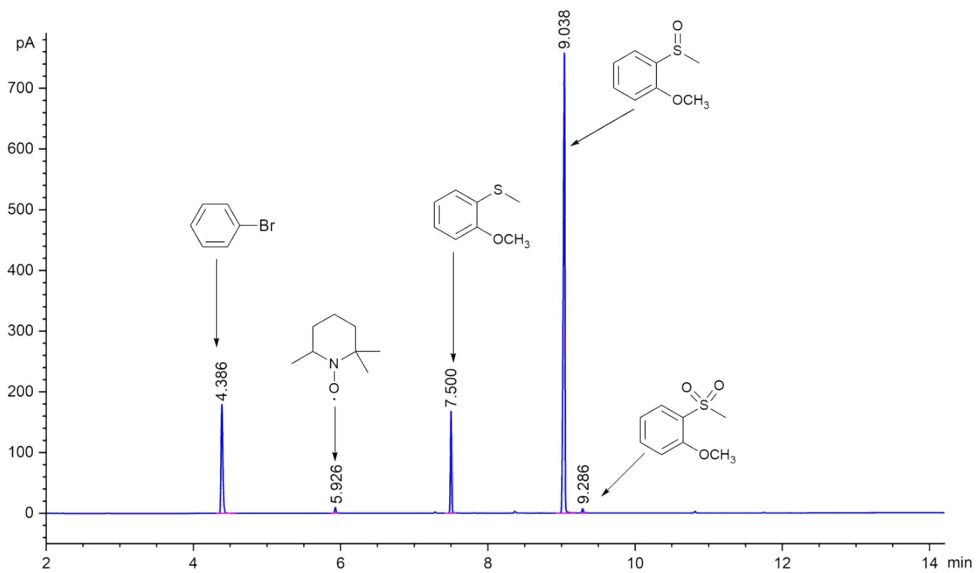


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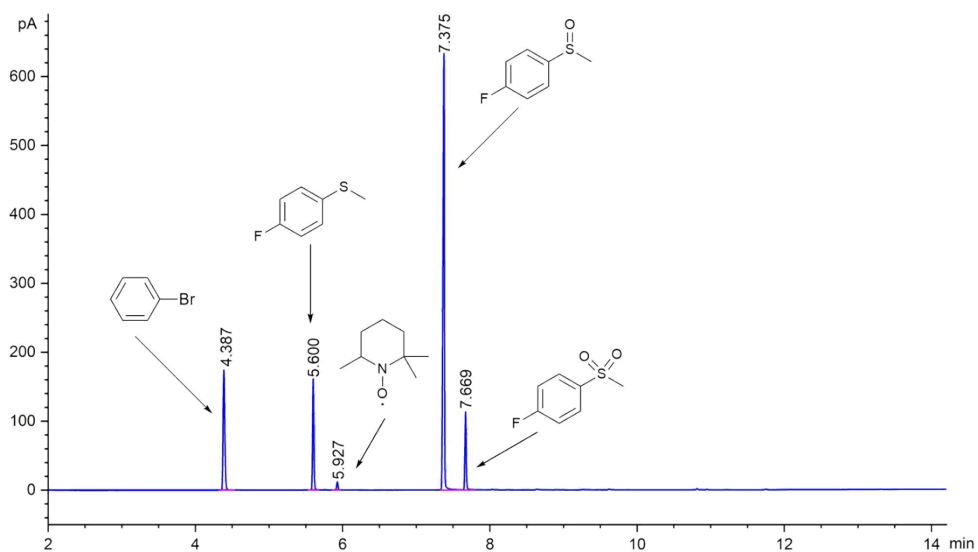


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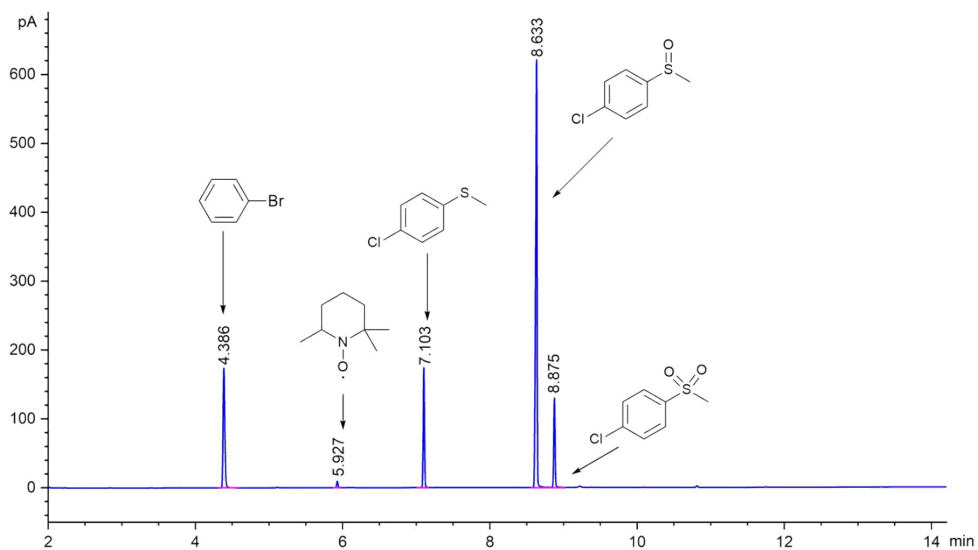


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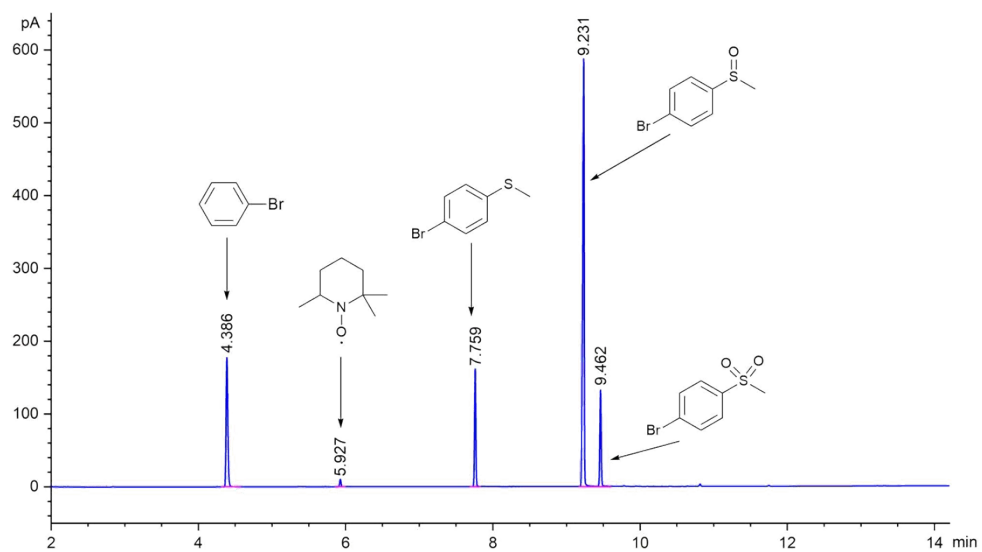


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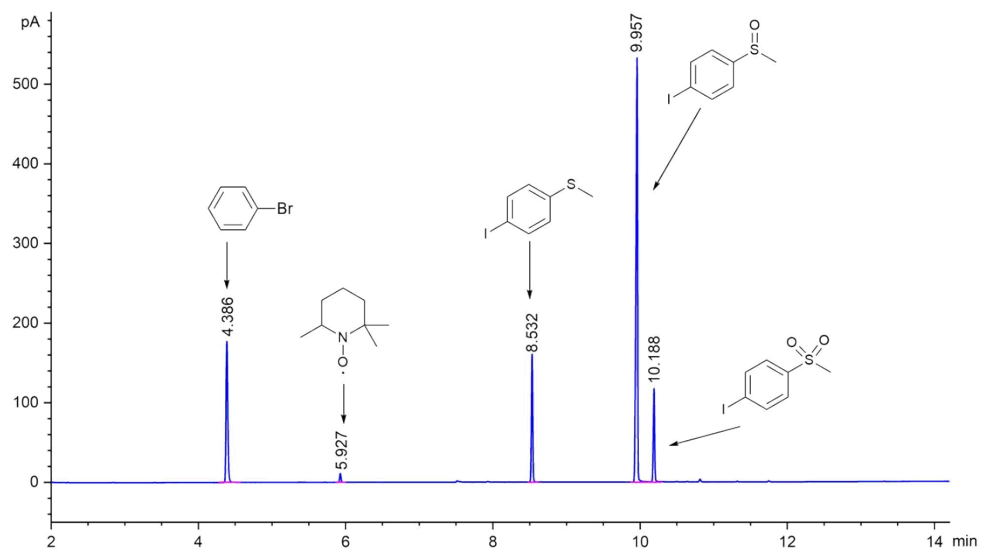


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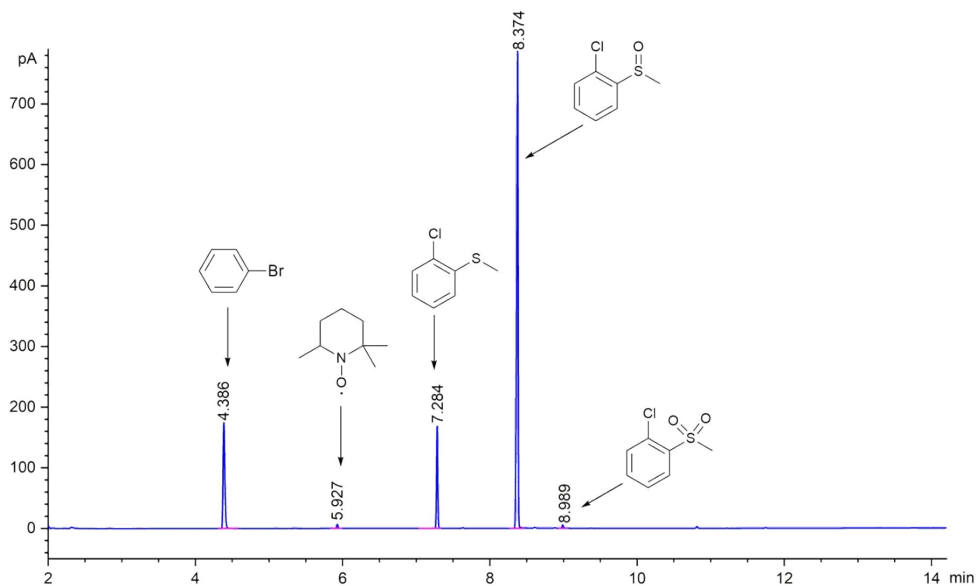


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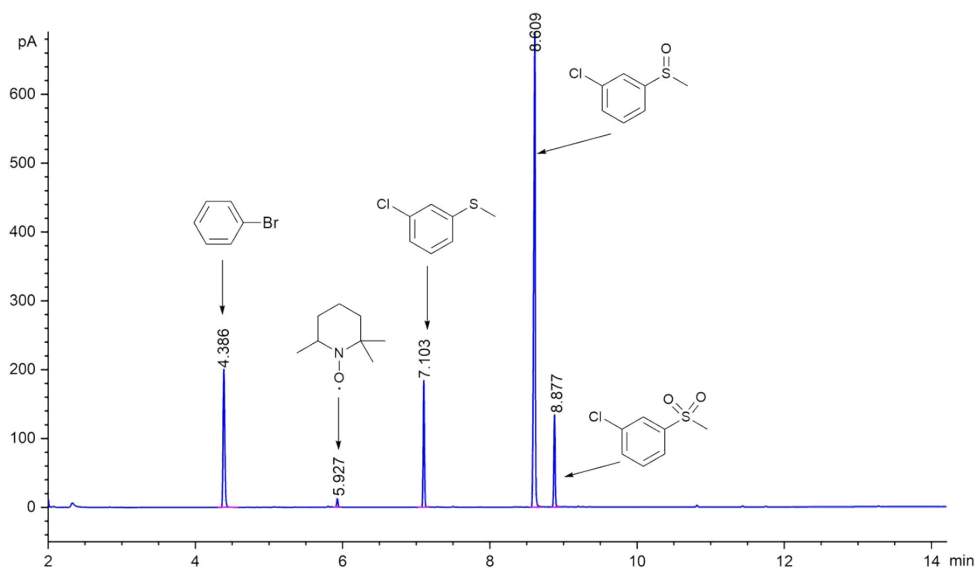


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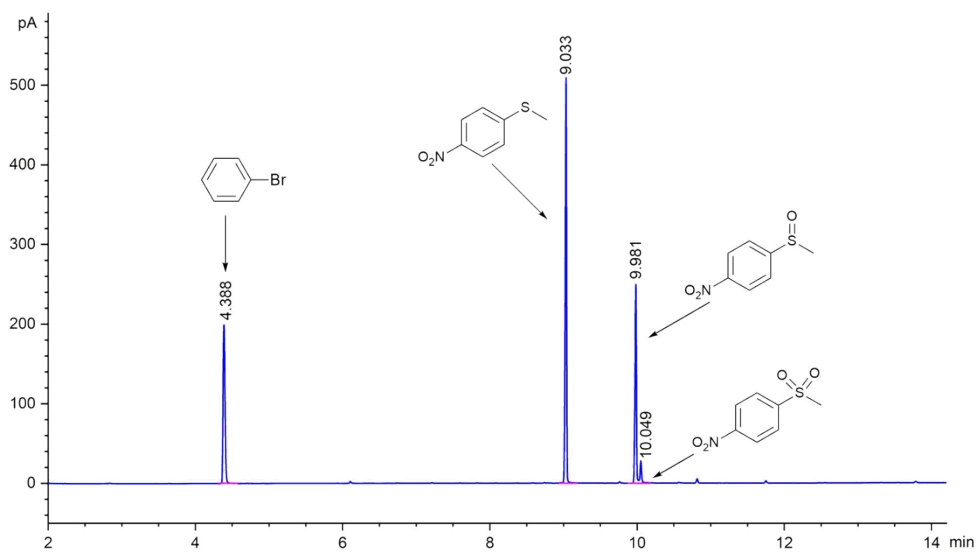


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Table 3, Entry 15

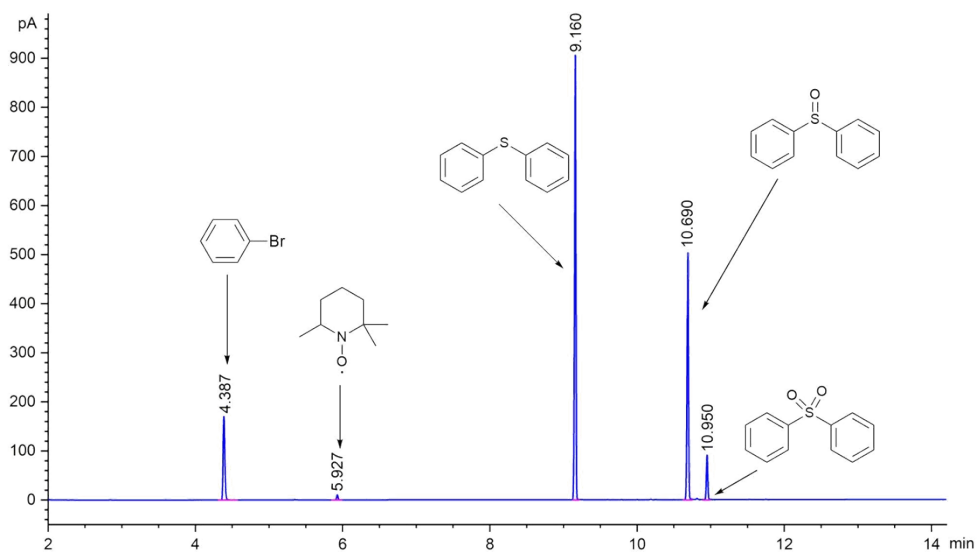


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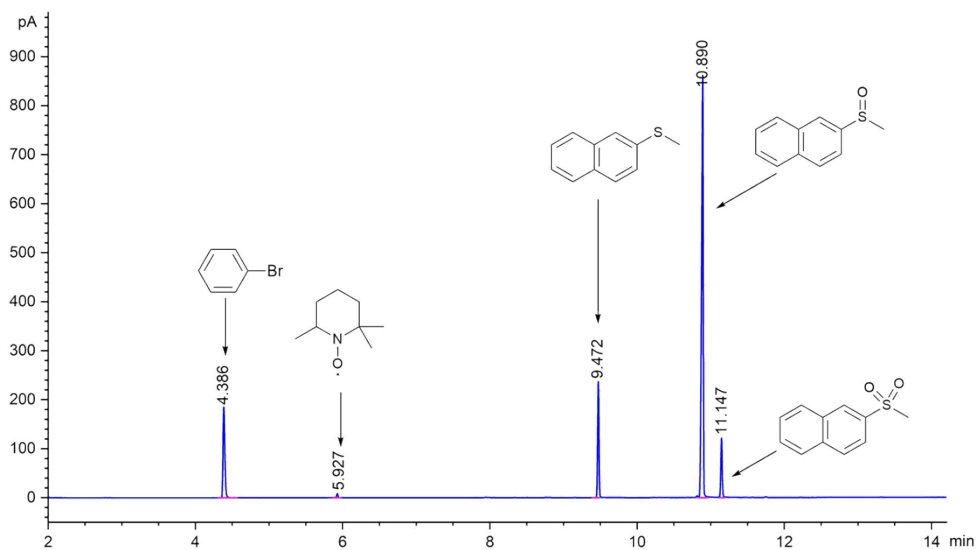


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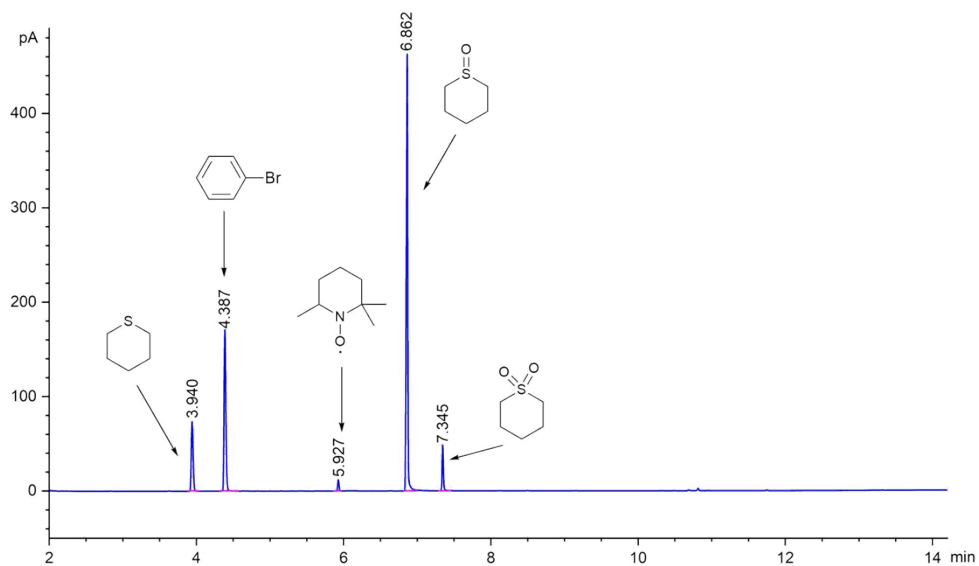


Table 3, Entry 18

