

Supporting Information

Synthesis of Benzothiazole Compounds Based on 2D Graphene Oxide Membrane

Nanoreactors

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General information:

Single-layer graphene oxide dispersion (GO, >500 nm, 2 mg/mL, solvent: water) was purchased from XFNANO (Nanjing, China). All the reagents in this study were of analytical reagent grade (AR grade) and were used as purchased without further purification. X-ray diffraction (XRD) of samples were recorded using a Bruker D8 focus diffractometer using Cu K α radiation ($\lambda=1.5406$ Å). Fourier transform infrared (FT-IR) spectra were recorded by Bruker INVENIO S. NMR spectra were recorded in CDCl₃ with tetramethylsilane as the internal standard for ¹H (600 MHz) NMR. X-ray photoelectron spectroscopy (XPS) data was taken on an ultrahigh-vacuum system (Thermo escalab 250Xi). The obtained data was converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting. Surface topography images were obtained using an atomic force microscope (AFM, Bruker Dimension FastscanBio). Raman measurements were performed on an inVia-Qontor Spectrometer under ambient conditions with a 532 nm (2.33 eV) laser in the back-scattering configuration. SEM images were captured from a field-emission scanning electron microscope (HITACHI S-4800). Gas chromatography-mass spectrometry (GCMS) was used to identify each molecule in products by a Thermo Fisher Exactive GC gas chromatograph-mass spectrometer equipped with a TG-5SilMS capillary column. The products were analyzed by Shimadzu GC-2014C equipped with an AOC-20i PLUS Auto-Injector and a TG-5SilMS capillary column. The column oven and injection temperature were set at 50°C and 250°C, respectively. The column temperature was increased from 50°C to 320°C using a ramp rate of 35°C/min and held at 320°C for 4 min.

Preparation of Graphene Oxide (GO) membrane:

Use deionized water to dilute the GO dispersion and obtain a uniform dispersion (0.05 mg mL⁻¹) by ultrasound. The dispersion was then vacuum filtered into a highly uniform membrane, which was subsequently dried at room temperature and stored for further reactions. GO membranes of varying thicknesses (1.2, 1.4, 1.9, and 2.4 μ m) were prepared by adjusting the volume of the GO dispersion used.

Preparation of TGO-120 Membranes:

To obtain TGO-120 membrane, the freshly prepared GO membrane was applied to a thermal annealing process under vacuum for 12 hours at 120°C.

Preparation of bGO Membranes:

The single-layer GO dispersion (25 mL, 2 mg/mL) was dispersed in 55 mL DI water. 300 mg of NaOH plate was added to the GO dispersion. The mixture was refluxed in a round-bottom flask under constant magnetic stirring for 1 h. Subsequently, the base-treated GO was filtered and washed with DI water. Finally, the obtained bGO dispersion was further diluted to 50 mL, after homogeneous dispersion by ultrasound, and stored in a reagent bottle (1 mg/mL, determined by the concentration of GO).

Use DI water to dilute the bGO dispersion and obtain a uniform dispersion (0.05 mg mL^{-1}) by ultrasound. The dispersion was then vacuum filtered into a highly uniform membrane, which was subsequently dried at room temperature.

Membranes (GO/ TGO-120/ bGO) for the Confined Reactions:

The membrane was cleaned by blowing with nitrogen to remove any floating dust particles. A flat and smooth section of the membrane was selected, cut into a suitable shape, and securely fixed in a microfiltration device with an inner diameter of 15 mm to create a filter membrane. The membrane was carefully clamped to ensure a tight seal. The effective mass of the catalyst is less than a quarter of the mass of the prepared membrane. Subsequently, a reaction solution containing benzaldehyde (0.1 mol L^{-1}), 2-aminothiophenol (0.1 mol L^{-1}), and ethanol was added to the upper measuring cylinder, which was then sealed with aluminum foil. Driven by the pressure difference (0.9 atm), the reaction solution flowed through the 2D confined space of the membrane at 22°C . Under constant pressure, specific reactions were conducted to completion, and it is dried naturally. The products were extracted from the system along with the solvent. The filtrate was collected and analyzed using gas chromatography to determine the conversion.

Measurement of the interlayer spacing of the GO membrane in the wet state:

Due to the expansion effect of the solvent, the wet d-spacing of the GO membrane under dry conditions may be significantly larger than the d-spacing under dry conditions. The preparation process of wet GO membrane was similar to the reaction process, except that the reaction solution was replaced by solvent. After a few hours, the wet GO membrane was removed and XRD characterization was performed immediately.

Calculation of the reaction time of the limiting reaction:

Pang et al. calculated the retention time of the solution passing through the GO-NH₂ laminar flow membrane. ¹Our calculation formula is as follows:

$$t_R = \frac{V_M}{k} = \frac{A \times h}{k}$$

where V_M is the total volume of the membrane; k is the slope of the reactant flow volume as a function of with time; A is the channel cross-sectional area of the microfiltration device, $A = \frac{\pi}{4} \times 15^2 = 176.7 \text{ mm}^2$; h is the thickness of the membrane. The meaning of t_R represents the time required for the reaction solution to fill the total volume of the GO membrane. Considering the thickness of single-layer graphene ($\approx 0.34 \text{ nm}$), the GO nanosheets account for a portion of the total volume of the GO membrane except for the laminar flow nanochannels. Therefore, the effective volume filled by the reaction solution is less than V_M , making the actual reaction time less than t_R . t_R approximately represents the reaction time of the interlayer confined reaction.

GO nanosheets used for the bulk reaction:

The catalytic reaction was performed in 10-mL glass flasks. First, bulk GO nanosheet powder (excess relative to the membrane reaction) was dissolved in 2 mL ethanol solution containing benzaldehyde (0.1 M) and ethyl cyanoacetate (0.1 M). Then, the mixture was continuously stirred at 22°C, 40°C, and 60°C for 48 h, respectively, with samples being collected every 12 h. The reaction solution was filtered and detected by gas chromatography at different reaction temperatures and times.

GO Recovery:

After the reaction, the surface of the GO membrane was meticulously cleaned, breaking the GO membrane, and then soaked and filtered several times with ethanol. The retrieved GO powder was then amassed and dried at 22°C for 24 h in preparation for further testing.

Determination of main products:

The quantitative determination of each reaction product proceeded as follows. In general, after the reaction, ethyl acetate was added to clean the filter element to collect the filtrate, which was subsequently analyzed by a Thermo Fisher Exactive GC-MS and the structure of the main product was determined according to its mass spectrum. The filtrate was then analyzed using the external standard method. The calibration curves were created by standard solutions with different amounts of samples. In addition, the structures of some typical products were performed by NMR.

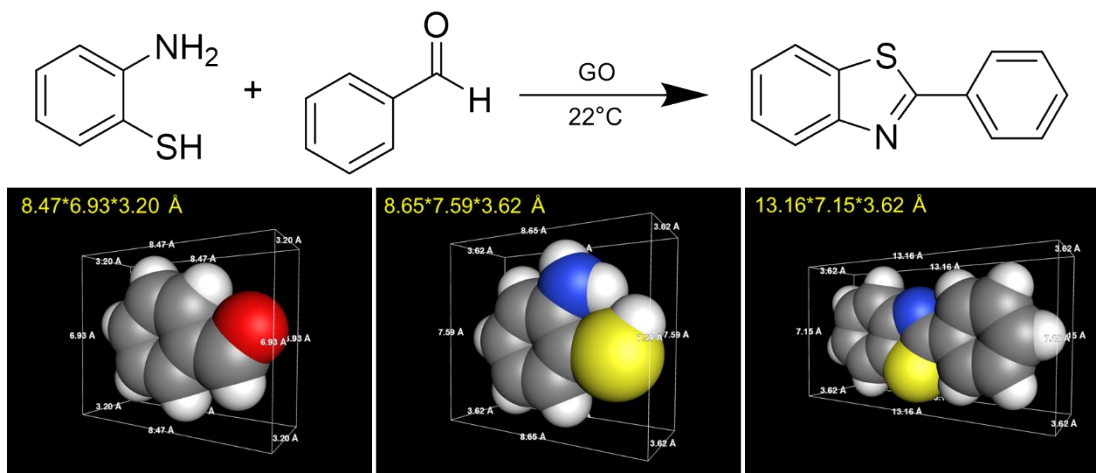


Figure S1: Perspective view of reactants and products molecules. The sub-nanochannels provided by GO allow reactants and products to pass through.

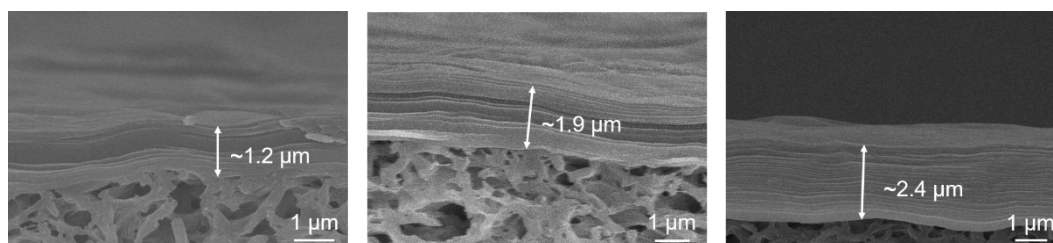


Figure S2: SEM observation of cross-sections of the GO membrane with different thicknesses, showing compact multilayer structures.

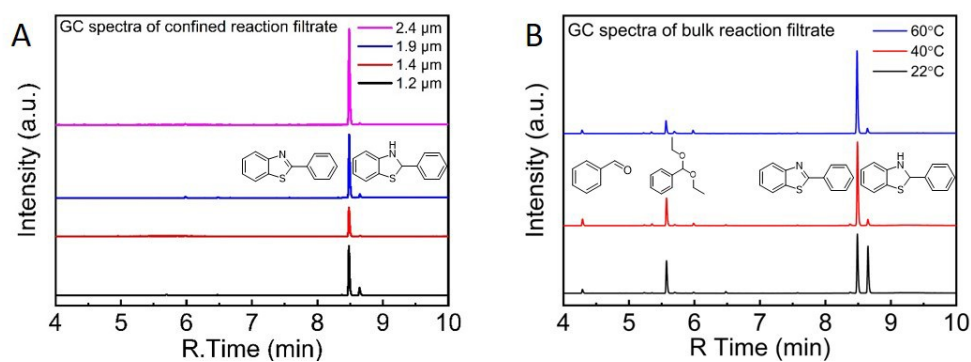


Figure S3: Typical GC spectrum of confined reaction and bulk reaction filtrate. A) Confined reaction catalyzed by different GO membranes thickness. B) Bulk reaction catalyzed by GO nanosheets after 48 h of continuous stirring at different temperature.

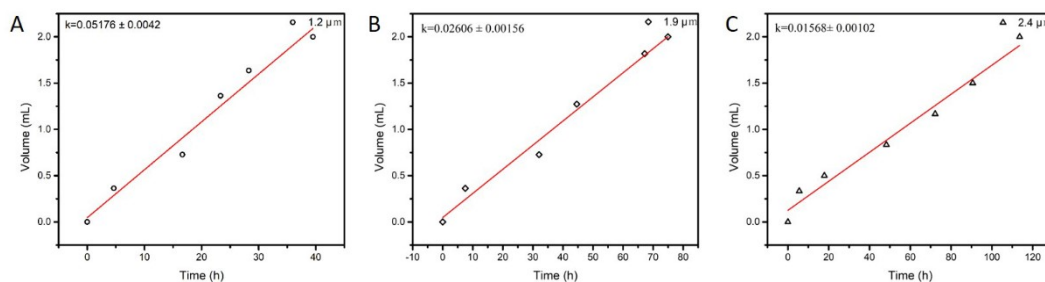


Figure S4: Flow curves of reaction solution of 2-Aminothiophenol and Benzaldehyde in EtOH.

The curves corresponding to GO membranes with different thickness.

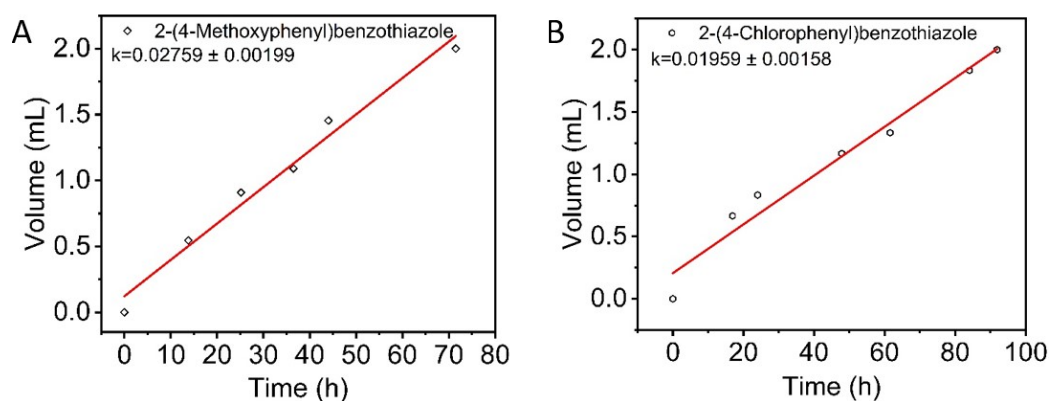


Figure S5: Flow curves of reaction solution of 2-Aminothiophenol and 4-Methoxybenzaldehyde

(A) and 4-Chlorobenzaldehyde (B) in EtOH.

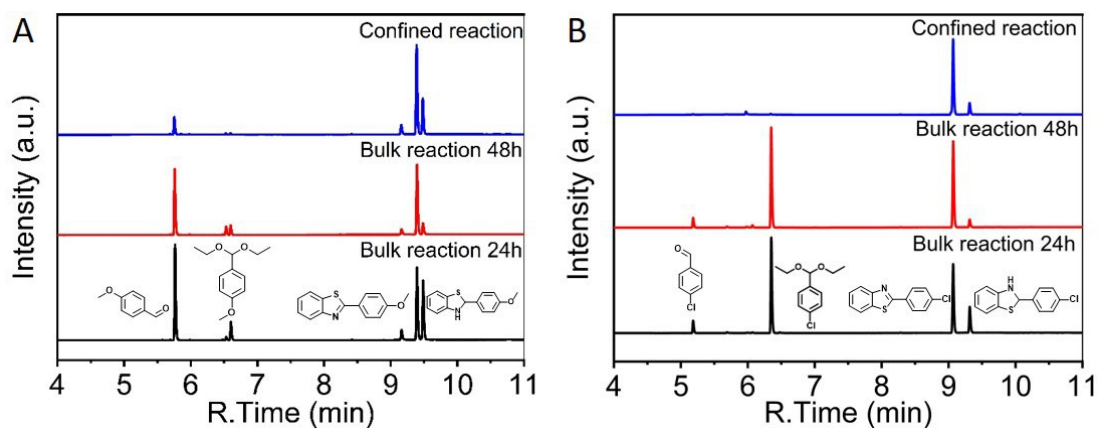


Figure S6: Typical GC spectrum of confined reaction and bulk reaction filtrate. A) Reaction

between 4-Methoxybenzaldehyde and 2-Aminothiophenol. B) Reaction 4-Chlorobenzaldehyde

between and 2-Aminothiophenol.

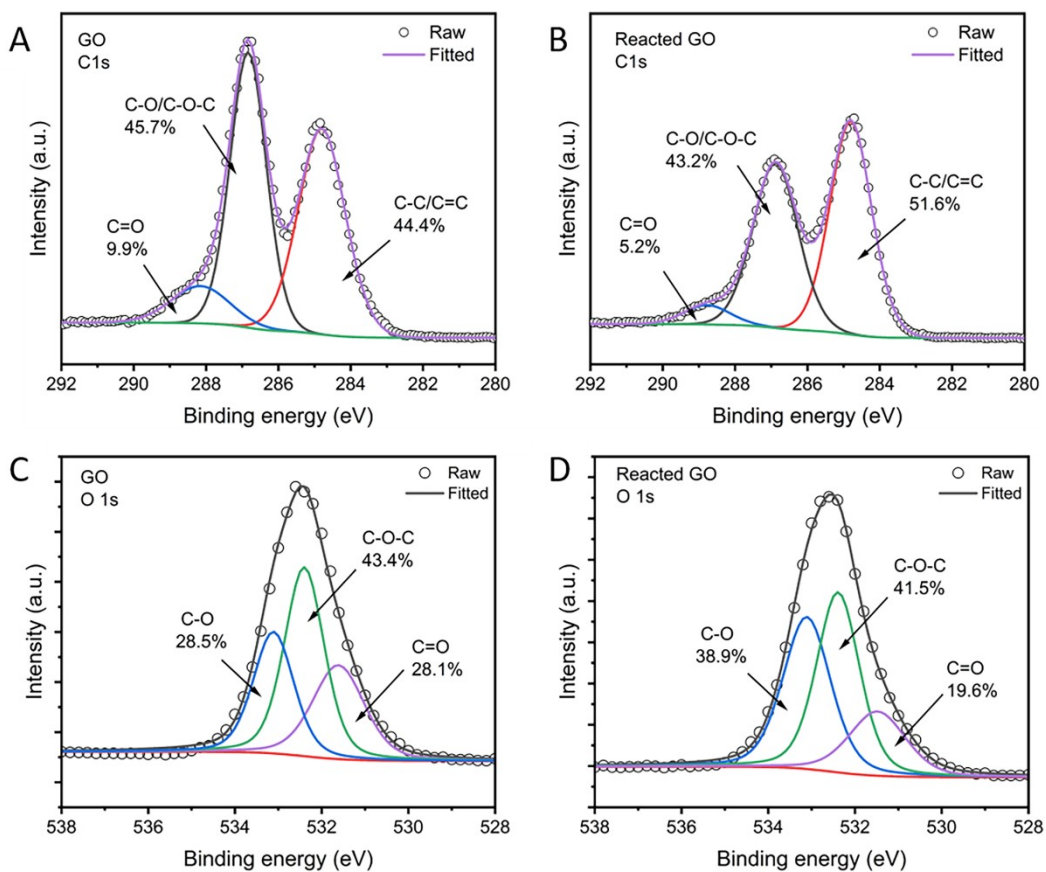


Figure S7: C 1s XPS spectra of (A) GO membranes and (B) reacted GO membranes. The high-resolution C1s spectrum of GO was deconvoluted into three major components, including C=C/C=C (~284.8 eV), C-O/C-O-C (~286.8 eV) and C=O/O-C=O (~288.2 eV).² Following the reaction, the proportion of C-C/C=C groups in the C1s spectra increased significantly, from 44.4% to 51.6%. Conversely, the intensities of the C=O and C-O/C-O-C groups decreased. XPS spectra for O 1s of (C) GO membranes and (D) reacted GO membranes. The O 1s peak can be fitted by three peaks at 531.6, 532.4 and 533.1 eV, corresponding to C=O, C-O-C and C-O, respectively.³ Following the reaction, the proportion of C-O groups in the O 1s spectra increased significantly, from 28.5% to 38.9%. Conversely, the intensities of the C-O-C and C=O groups decreased.

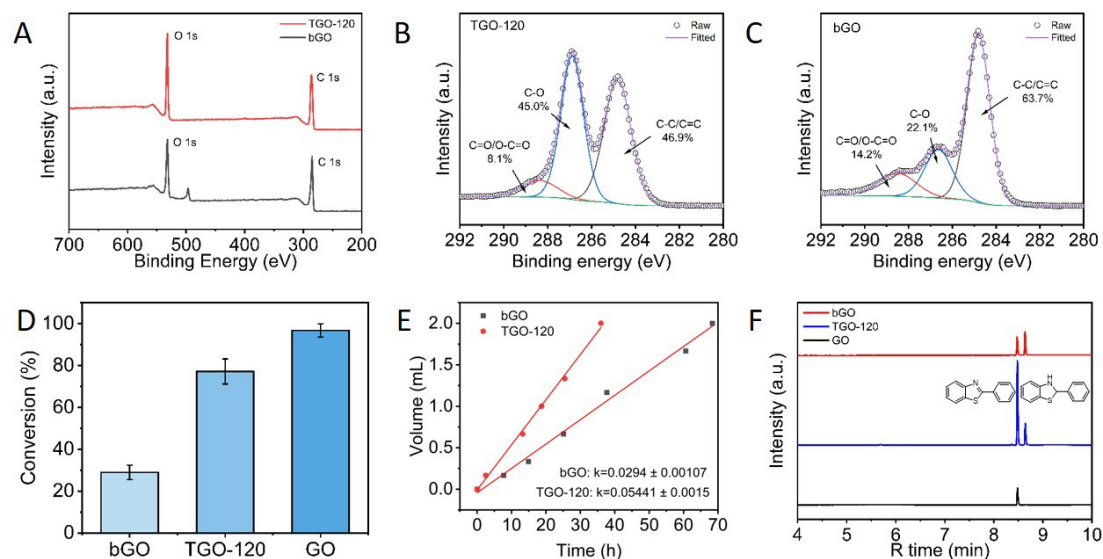


Figure S8: A) XPS spectra of TGO-120 (red line) and the bGO (black line). The XPS results demonstrate an increase in the C 1s/O 1s ratio from 2.53 for GO membranes to 2.66 for TGO-120 and 2.96 for bGO. This indicates a reduction in the number of oxygen-containing functional groups. C 1s XPS spectra of TGO-120 membranes (B) and bGO membranes (C). D) Comparison of the conversion of GO membranes with different degrees of oxidation at 22 °C. E) The flow curves of the reaction solution of benzaldehyde and 2-aminothiophenol in ethanol with TGO-120 membranes (red line) and bGO membranes (black line) at 22 °C. F) Typical GC spectrum of confined reaction catalyzed by GO membranes (black line), TGO-120 membranes (blue line) and bGO membranes (red line).

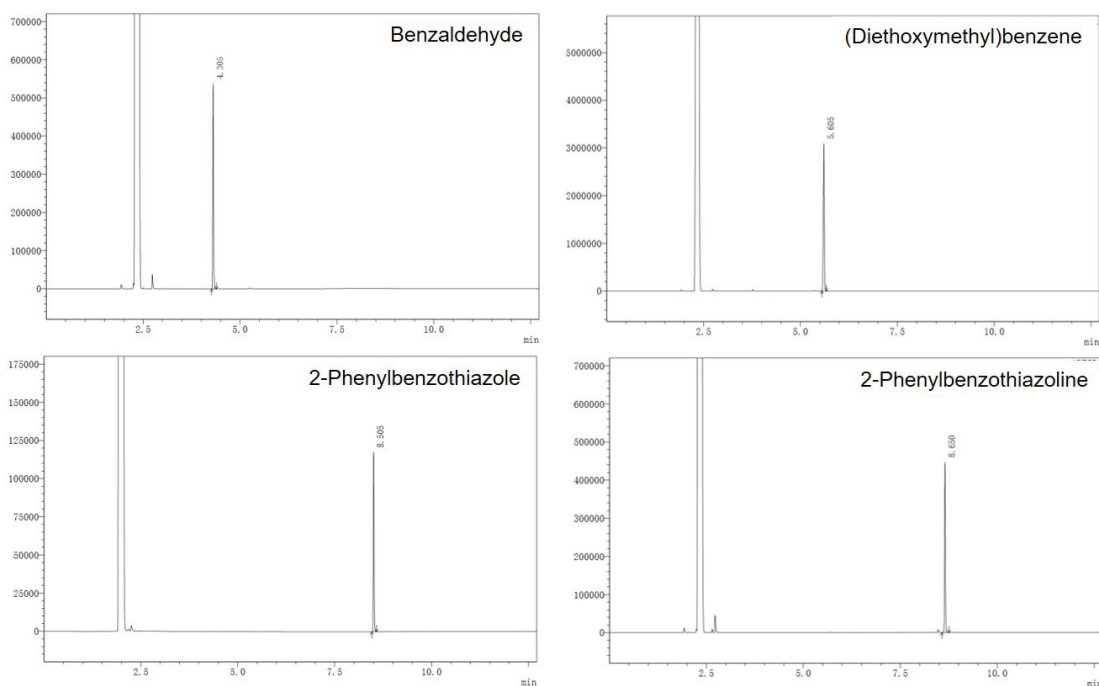
Table S1. Results comparison.

| Number | Catalyst | Reaction conditions | ^a Yield or ^b Conversion (%) | Reference |
|--------|--|---|--|-----------|
| 1 | TiO ₂ NPs | aryl aldehyde (1 mmol), 2-aminothiophenol, (1 mmol), 30% H ₂ O ₂ (4 mmol) and TiO ₂ NPs (0.1 mmol), solvent free, 50°C, 6 min. | 96% ^a | 4 |
| 2 | 4-methoxy-TEMPO | 2-aminothiophenol (5 mmol), aldehydes (5 mmol), and xylenes (15 mL; mixture of o-, m-, and p-xylene), stirred at 100°C for 9 h. 4-methoxy-TEMPO radical (5 mol%; 47 mg, 0.25 mmol), under an oxygen atmosphere. | 80% ^a | 5 |
| 3 | Co (II)-PLP-Schiff base/SBA-15 | ortho-aminothiophenol (1.0 mmol), substituted benzaldehydes (1.0 mmol), 5-10 ml of water, 0.005 g catalyst, 100°C, 3 h. | 89% ^a | 6 |
| 4 | Cu (II)-Glycerol/MCM-41 | 2-aminothiophenol (1.0 mmol), benzaldehyde (1.0 mmol), 7 mg catalyst, EtOH (3 mL), RT, 3 h. | 98% ^a | 7 |
| 5 | CoFe ₂ O ₄ @SiO ₂ @PAF-IL | aromatic aldehyde (1 mmol), o-phenylenediamine (1 mmol), or 2-aminobenzenethiol (1 mmol), 20 mg catalyst, solvent free, 70°C for an appropriate time. | 87% ^a | 8 |
| 6 | laccase | 2-aminoaromatic (10.0 mmol) and benzaldehyde derivative (10.0 mmol) in acetonitrile (10.0 mL) and acetate buffer (10.0 mL, pH 4.0), RT, 24 h. | 85% ^a | 9 |
| 7 | SnP ₂ O ₇ | benzaldehyde (1 mmol), 2-aminothiophenol (1 mmol), 2 mL EtOH, | 95% ^a | 10 |

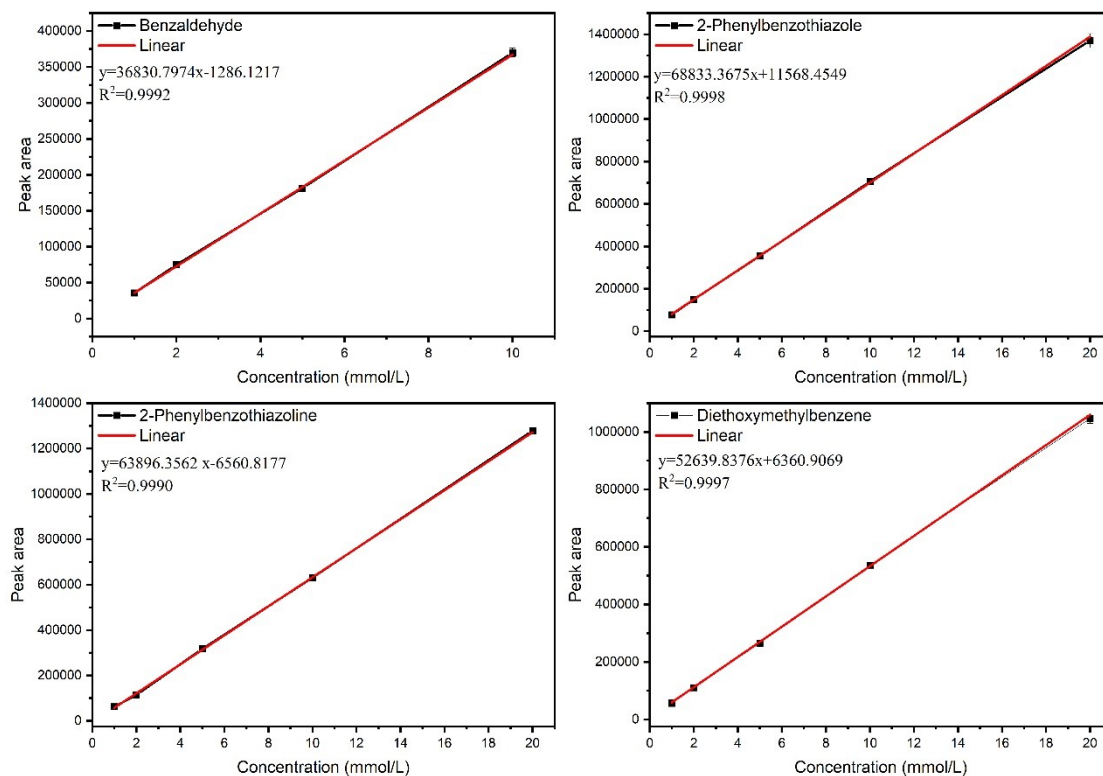
| Number | Catalyst | Reaction conditions | ^a Yield or ^b Conversion (%) | Reference |
|--------|--|---|--|-----------|
| | | 0.002 g catalyst, reflux, 10 min. | | |
| 8 | Brønsted acidic ionic liquid gel | substrate (1.0 mmol), aldehyde (1.0 mmol), BAIL gel (0.01 mmol), 130°C, solvent free, 6 h. | 91% ^a | 11 |
| 9 | NH ₂ -MIL-125(Ti) MOF | amine (1.0 mmol), aldehyde (1.0 mmol), methanol (2.0 mL), NH ₂ -MIL-125(Ti) MOF (15 mg), 60°C, 2 h. | 95% ^a | 12 |
| 10 | [(C ₆ H ₅) ₃ P(CH ₂) ₄ SO ₃ H] [OTs] | benzaldehyde (1 mmol), 2-aminothiophenol (1 mmol), 7 mol % catalyst, 120°C, 50 min. | 92% ^a | 13 |
| 11 | [bmim][FeCl ₄] | 2-aminobenzenethiol or 2-aminobenzenthionol (1 mmol), aryl aldehyde (1 mmol), [bmim][FeCl ₄] (0.5 mmol) and ethanol (5 mL), refluxed, 50 min. | 87% ^a | 14 |
| 12 | Dowex 50W | 2-aminothiophenol (5 mmol), aromatic aldehyde (5 mmol), Dowex 50W (10 mol %), water (4 mL), 70°C, 12 h. | 85% ^a | 15 |
| 13 | MoO ₃ Nanorods | 2-aminothiophenol (1 mmol), aromatic aldehyde (1 mmol) and MoO ₃ nanorods (100 mg), 80°C, 70 min. | 88% ^a | 16 |
| 14 | ZnO NPs | 2-aminothiophenol (8 mmol), aldehyde (8 mmol), ZnO NPs (0.5 mol%, 6.5 mg), 20 milling balls (5 mm) in a milling jar (80 mL) at 600 rpm, rt, 30 min. | 91% ^a | 17 |
| 15 | CTAB-Coated Bi ₂ WO ₆ | Aldehyde (1 mmol), 2-aminothiophenol (1 mmol), acetonitrile (15 | 93% ^a | 18 |

| Number | Catalyst | Reaction conditions | Yield or Conversion (%) | Reference |
|--------|-------------|--|-------------------------------|-----------|
| 16 | GO membrane | mL), catalyst (15 mg), and tungsten lamp (35 W), 60 min. Aldehyde (0.1 mol L ⁻¹), 2-aminothiophenol (0.1 mol L ⁻¹), EtOH (2 mL), 22°C, 23 s. | 96.7% ^b | This work |

Typical GC spectra of the pure compounds of the model reaction:

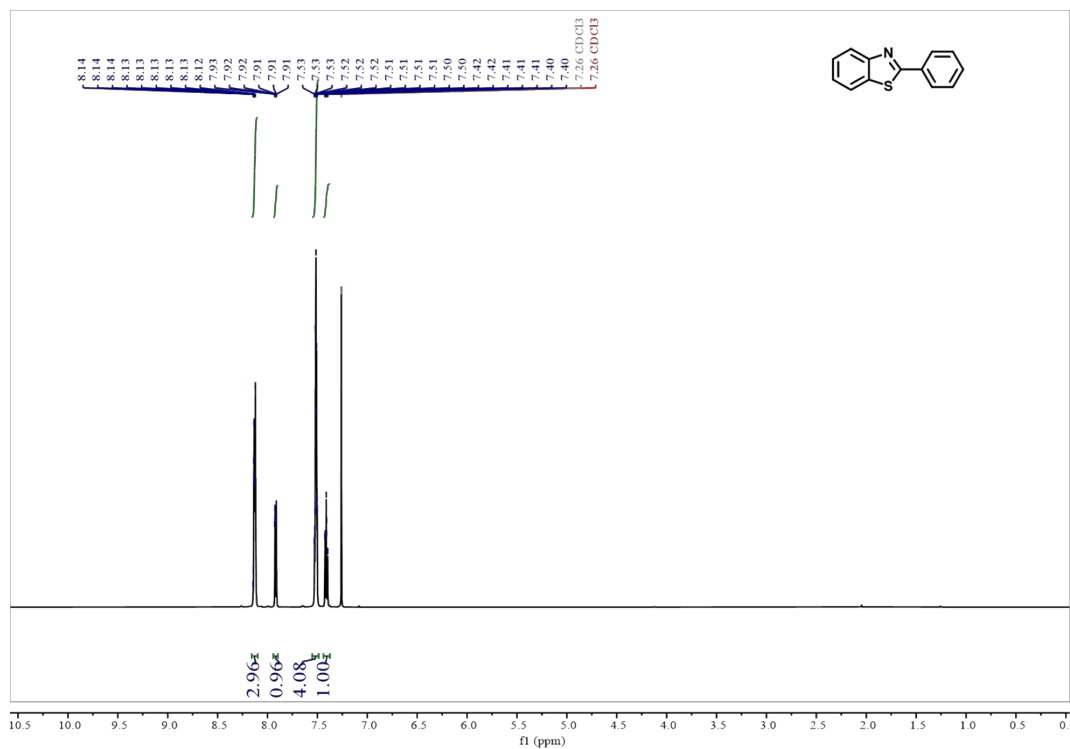


Calibration curves of benzaldehyde, 2-phenylbenzothiazole, 2-phenylbenzothiazoline and diethoxymethylbenzene:



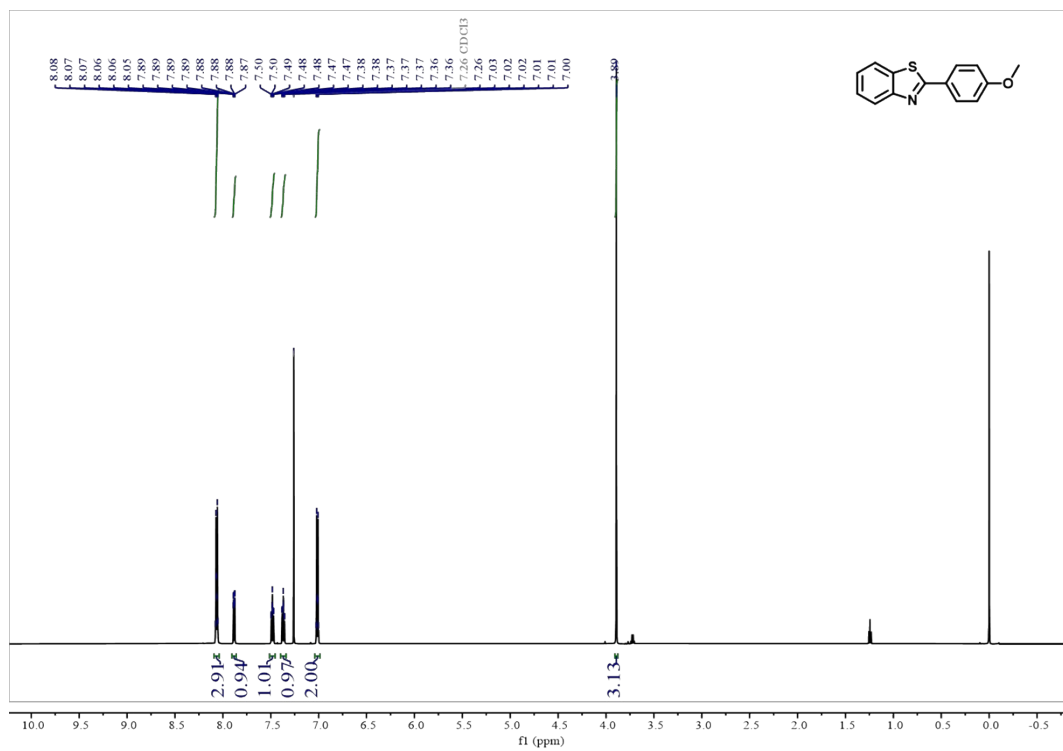
2-Phenyl-1,3-benzothiazole:

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 8.16 – 8.10 (m, 3H), 7.94 – 7.90 (m, 1H), 7.52 (pd, $J = 4.2, 1.3$ Hz, 4H), 7.41 (ddd, $J = 8.2, 7.2, 1.2$ Hz, 1H).



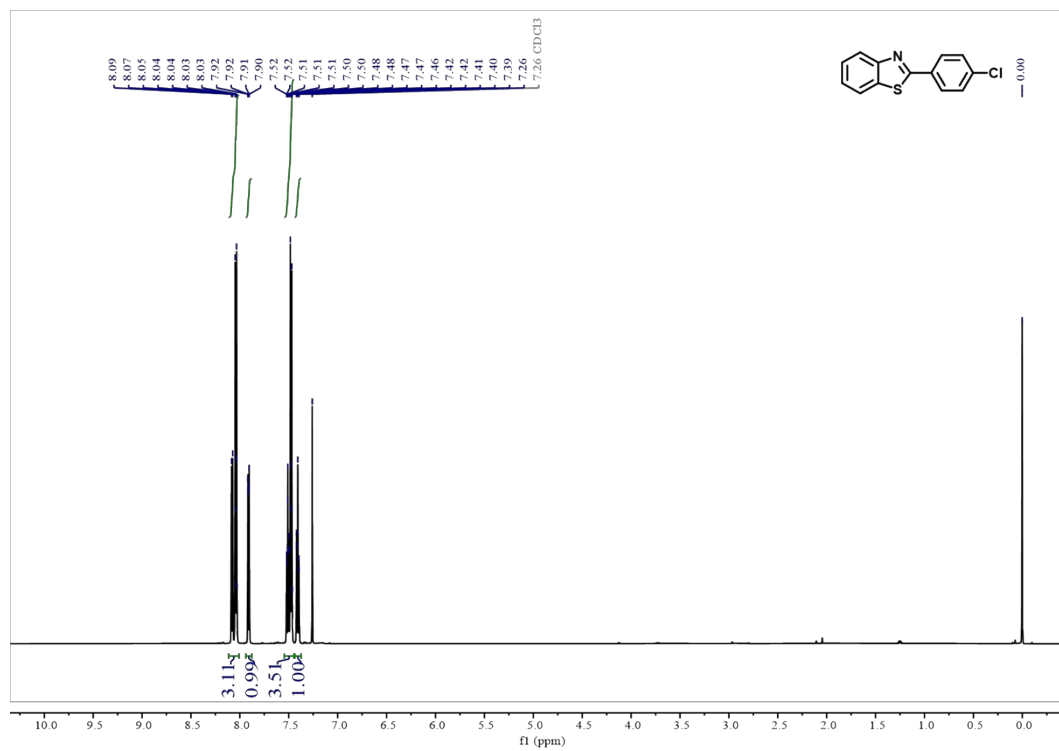
2-(4-methoxyphenyl)-1,3-benzothiazole:

$^1\text{H NMR}$ (600 MHz, Chloroform- d) δ 8.09 – 8.04 (m, 3H), 7.88 (ddd, $J = 8.0, 1.2, 0.6$ Hz, 1H), 7.48 (ddd, $J = 8.3, 7.2, 1.2$ Hz, 1H), 7.37 (ddd, $J = 8.2, 7.2, 1.1$ Hz, 1H), 7.04 – 6.99 (m, 2H), 3.89 (s, 3H).



2-(4-Chlorophenyl)-1,3-benzothiazole:

^1H NMR (600 MHz, Chloroform- d) δ 8.12 – 8.01 (m, 3H), 7.91 (dd, J = 8.0, 1.2 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.44 – 7.38 (m, 1H).



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