Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Selective synthesis of azoxybenzenes from nitrobenzenes by the visible light irradiation using flow microreactors

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1. General information

Spectrograde solvents (ethanol, methanol and water) were used throughout the work. All commercially available reagents were used without further purification. Particularly, 1,3,5-trimethoxybenzene as an internal standard was purchased with the qNMR grade. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded at 400 and 100 MHz (Bruker Co. Ltd. Avance 400 and Ⅲ 400 HD), respectively, and chemical shifts were represented as δ-values relative to internal standard TMS. GC-MS spectra were recorded by Agilent Technology Inc. 6890N (GC) and JEOL Ltd. JMS-K9 (MS).

2. Photoreaction set-up

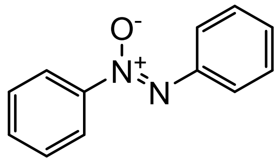
Tape-type green LED (5050type 60 LED/m Non-waterproof, Consumed electric power 6 W/m)) was utilized as the light source. Three different lengths of tape-type LED were made to match the length of the tube (2 m (120 tips) for batch reactor and 3 m tubes; 4.4 m (261 tips) for 7 m and 14 m tubes; ca. 5 m (297 tips) for 28 m tubes). As shown in Figure 1 and 2, the tape-type LED was stuck inside the beaker in order to emit the light inward. The beaker which LEDs were attached was immersed in isothermal bath to release the heat from the LED. The Pyrex test tube (inner diameter (i.d.) 16 mm) was used as a batch. It was set at center of the LED attached beaker, and the reaction solution in test tube was photoirradiated from the outward (30 mm: the distance from the light to solution). For comparison experiments, the PTFE tube (3 m, i.d. 1 mm) was used as microreactors. In order to make the distance from the light source the same, the tubes was tightly wrapped around the Pyrex test tube (i.d. 14 mm). This test tube was also set at center of the LED attached beaker. FEP tubes (7 m, 14 m, and 28 m) were also used as microreactors. Both 7 m and 14 m tubes were tightly wrapped around the beaker (outer diameter (o.d.) 65 mm), and set in the 4.4 m LED attached beaker (o.d. 104 mm). 28 m tube was also tightly wrapped around the beaker (o.d. 104 mm), and set in the 5 m LED attached beaker (o.d. 130 mm). The distance from light source to these FEP tubes was ca. 10 mm.

Figure S1. The light source of this reaction: 120 chips (left), 261 chips (middle), 297 tips (right).

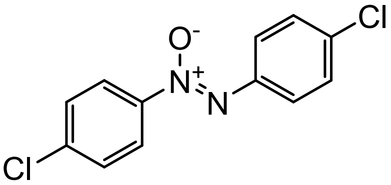
3. Photoreaction procedure

Procedure for the photoreduction of nitrobenzene derivatives as follows: Appropriate nitrobenzene or *p*-chloronitrobenzene was dissolved in ethanol or methanol and water (alcohols : water = 3 : 2) (0.4 M). Then, appropriate equivalents of triethanolamine and 1 mol% Eosin Y were added in reaction solution. In order to make a homogeneous solution, sonication was employed if necessary. The pH value of solutions was adjusted to 8.5 by adding concentrated HCl aqueous solutions, because this pH value is the best condition for this photoreaction proceeding.[1] After pH adjusting, the solution was poured in the Pyrex test tube, and argon was bubbled to the sample solutions for deaeration for 1 h. After argon bubbling, about 10 mL solution was pull out by using gastight syringe, and extracted with $CHCl_3$ (3 × 30 mL). The combined organic phase was washed with saturated $NaHCO_3$ aqueous solution (15 mL) and saturated NaCl solution (15 mL), dried over anhydrous Na_2SO_4. After concentration by using a rotary evaporator, 1,3,5-trimethoxybenzene was added, and measured ^{1}H-NMR for the before photoreaction solution. In the case of batch reaction, the Pyrex test tube containing the residue solution after pulling out the before reaction solution, was set at center of the LED attached beaker, and photoirradiated. In the case of flow microreactor, the residue solution was pulled out by using another gastight syringe, and set to the syringe pump. The outlet of syringe was connected to the irradiation unit (FEP or PTFE tube). The solution flow rate was controlled according to the target irradiation time. After irradiation, the same extraction way of the before reaction solution was conducted, and concentrated. 1,3,5-trimethoxybenzene was added, and measured ^{1}H-NMR. Both conversions and yields were determined by ^{1}H-NMR data.

4. Analytical data of azoxy products



Azoxybenzene :[2] ^{1}H-NMR (400 MHz, CDCl$_3$): δ = 8.30 (2 H, d, J = 7.2 Hz), 8.15 (2 H, d, J = 8.4 Hz), 7.57-7.38 (6 H, m); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 148.38, 144.03, 131.60, 129.61, 128.80, 128.71. 125.53, 122.36 ppm; GC-MS: m / z = 198



4,4'-dichloroazoxybenzene :[2] ^{1}H-NMR (400 MHz, CDCl$_3$):δ = 8.25 (2 H, d, J = 9.2 Hz), 8.16 (2 H, d, J = 8.8 Hz) 7.50-7.44 ppm (4 H, m); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 146.53, 142.22, 138.07, 135.24, 129.01, 128.95, 127.06. 123.69 ppm; GC-MS: m / z = 266

[1]: X.-J. Yang, B. Chen, L.-Q. Zheng, L.-Z. Wu and C.-H. Tung, *Green Chem.*, 2014, **16**, 1082-1086.

[2]: Y.-F. Chen, J. Chen, L.-j. Lin and G. J. Chuang, *J. Org. Chem.*, 2017, **82**, 11626-11630.

5. ^{1}H-NMR chart and GC-MS chart

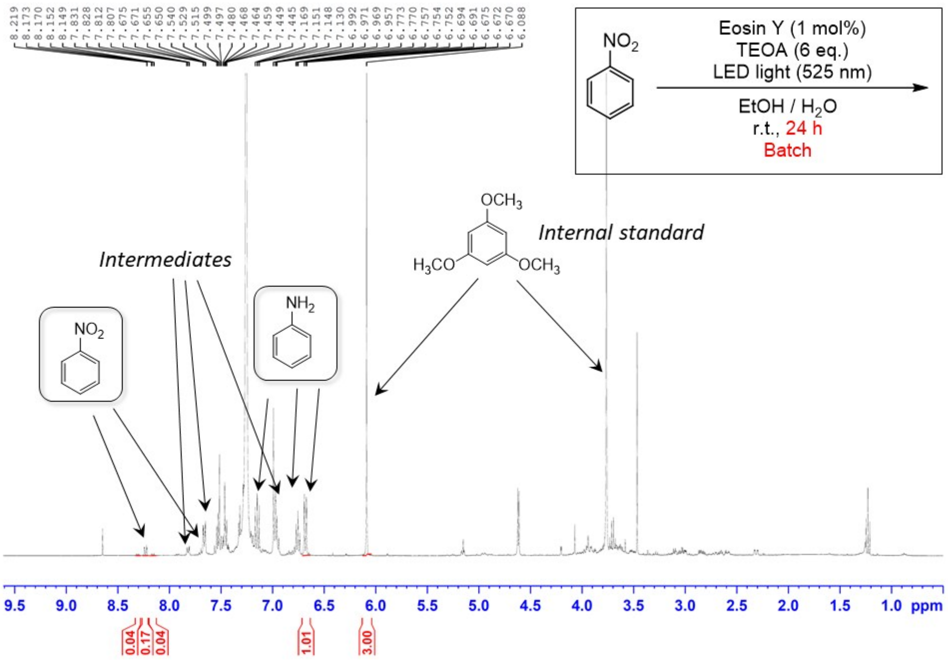


Figure S2. ^{1}H-NMR chart of sample solution after photoreduction of nitrobenzene in a batch.

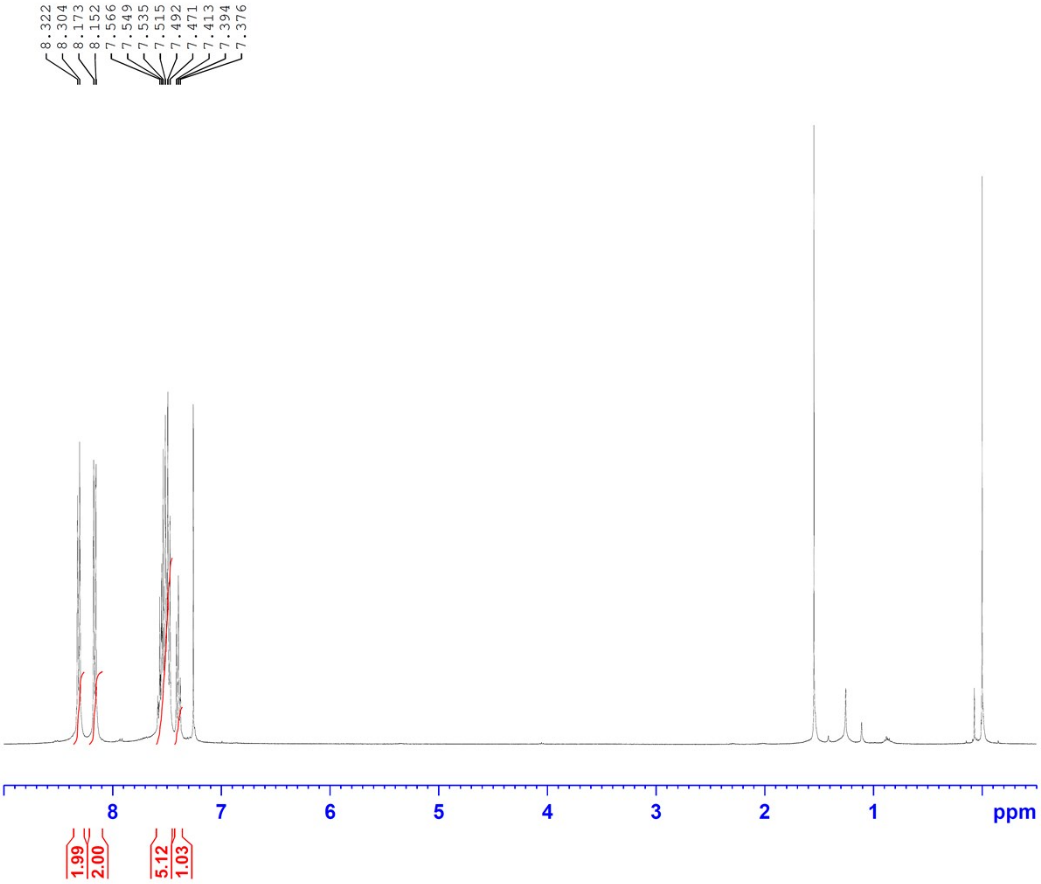


Figure S3. ^{1}H-NMR chart of purified azoxybenzene.

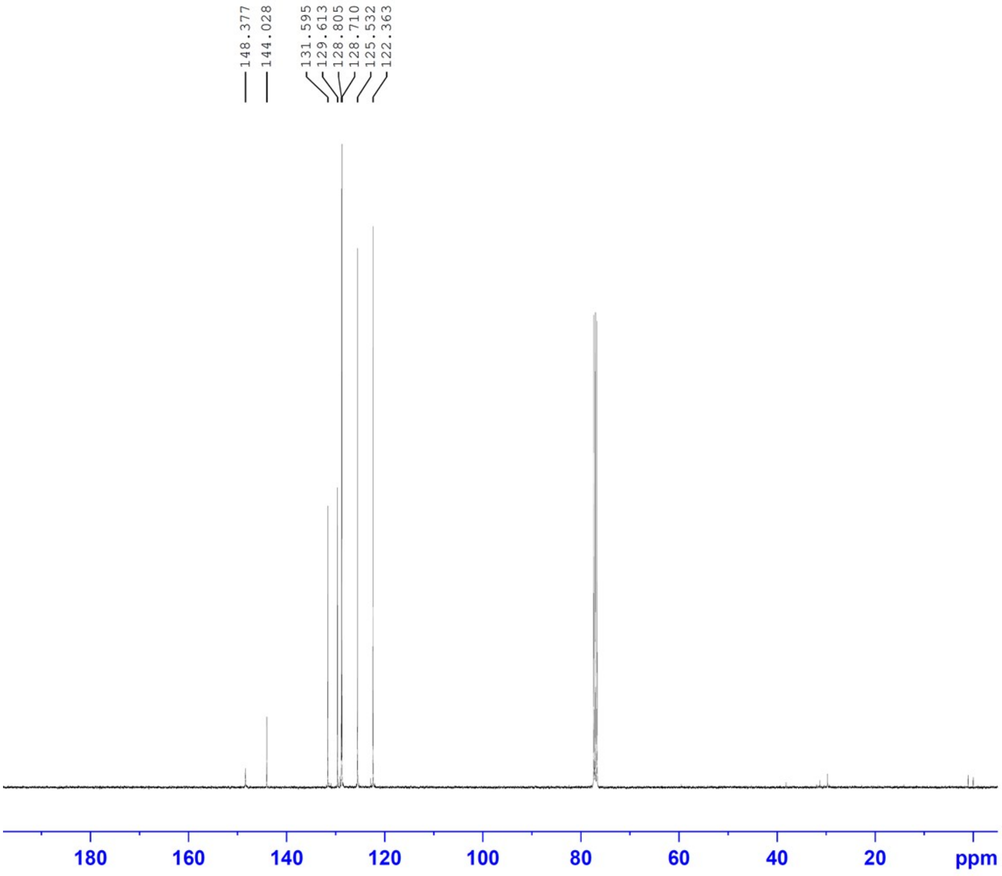


Figure S4. ^{13}C-NMR chart of purified azoxybenzene.

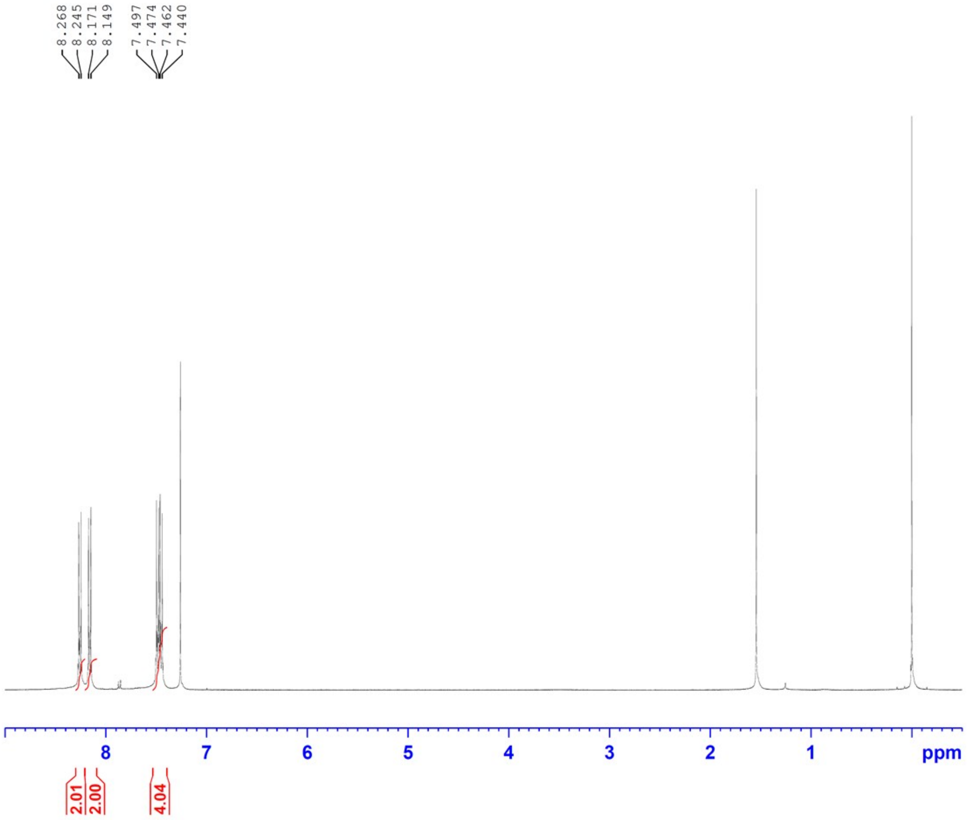


Figure S5. ^{1}H-NMR chart of purified 4,4’-dichloroazoxybenzene.

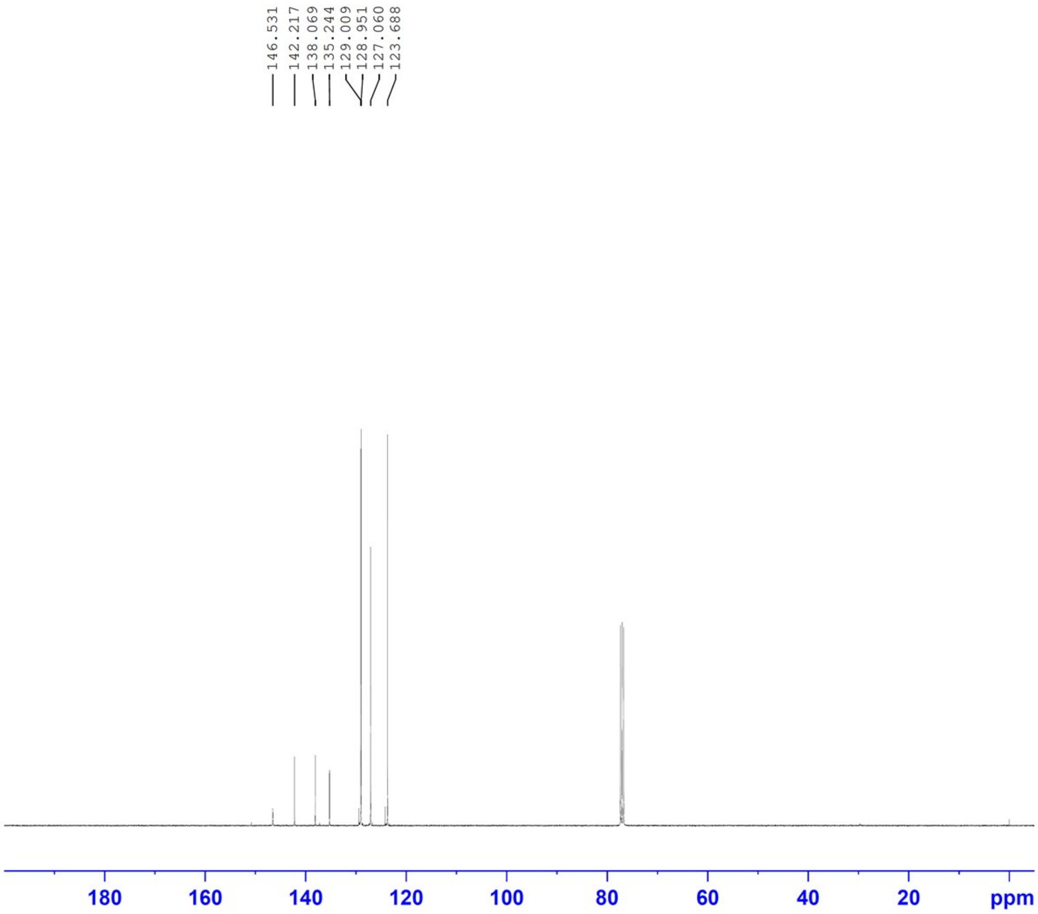


Figure S6. ^{13}C-NMR chart of purified 4,4'-dichloroazoxybenzene.

6. GC-MS chart

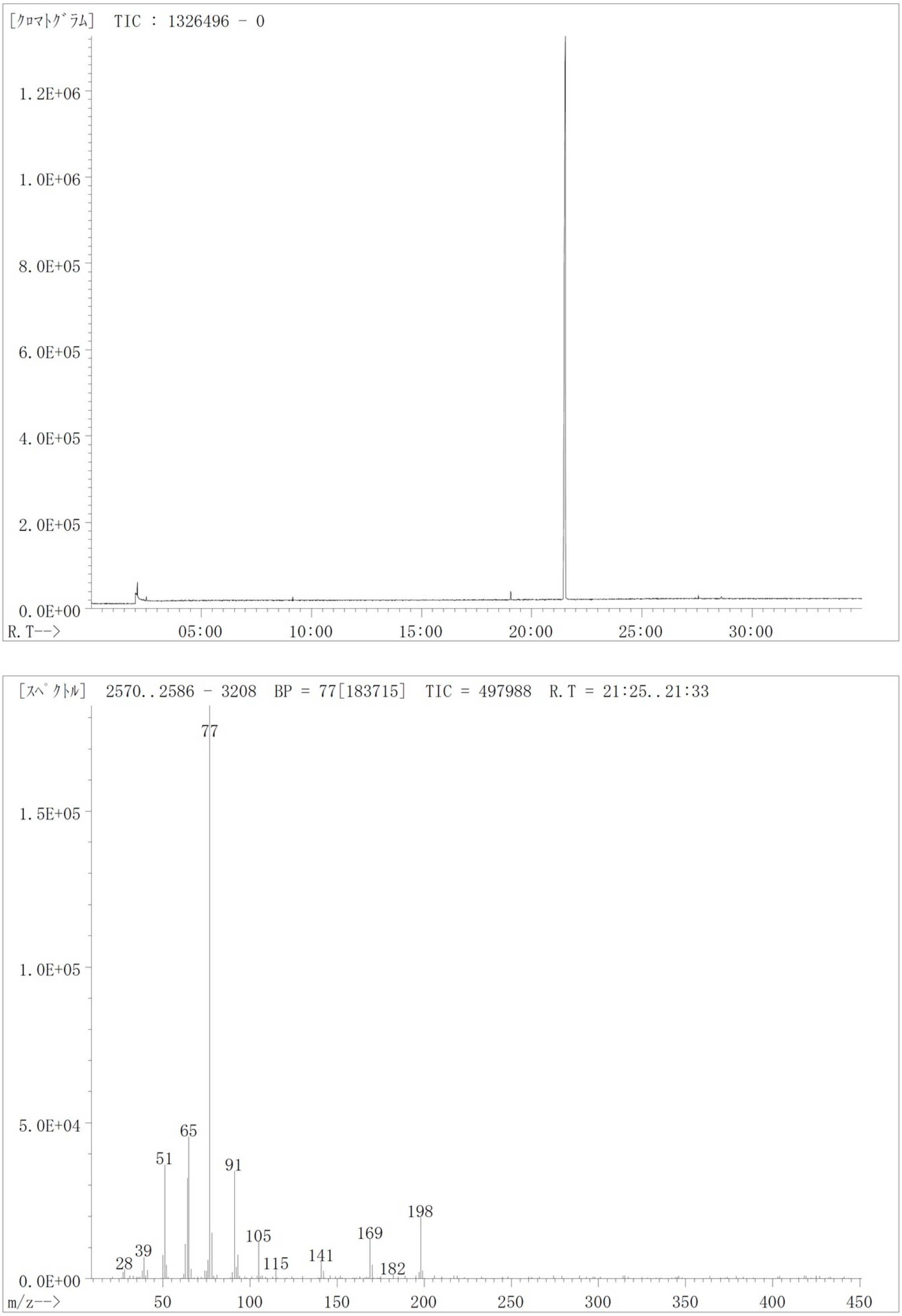


Figure S7. GC-MS chart of purified azoxybenzene.

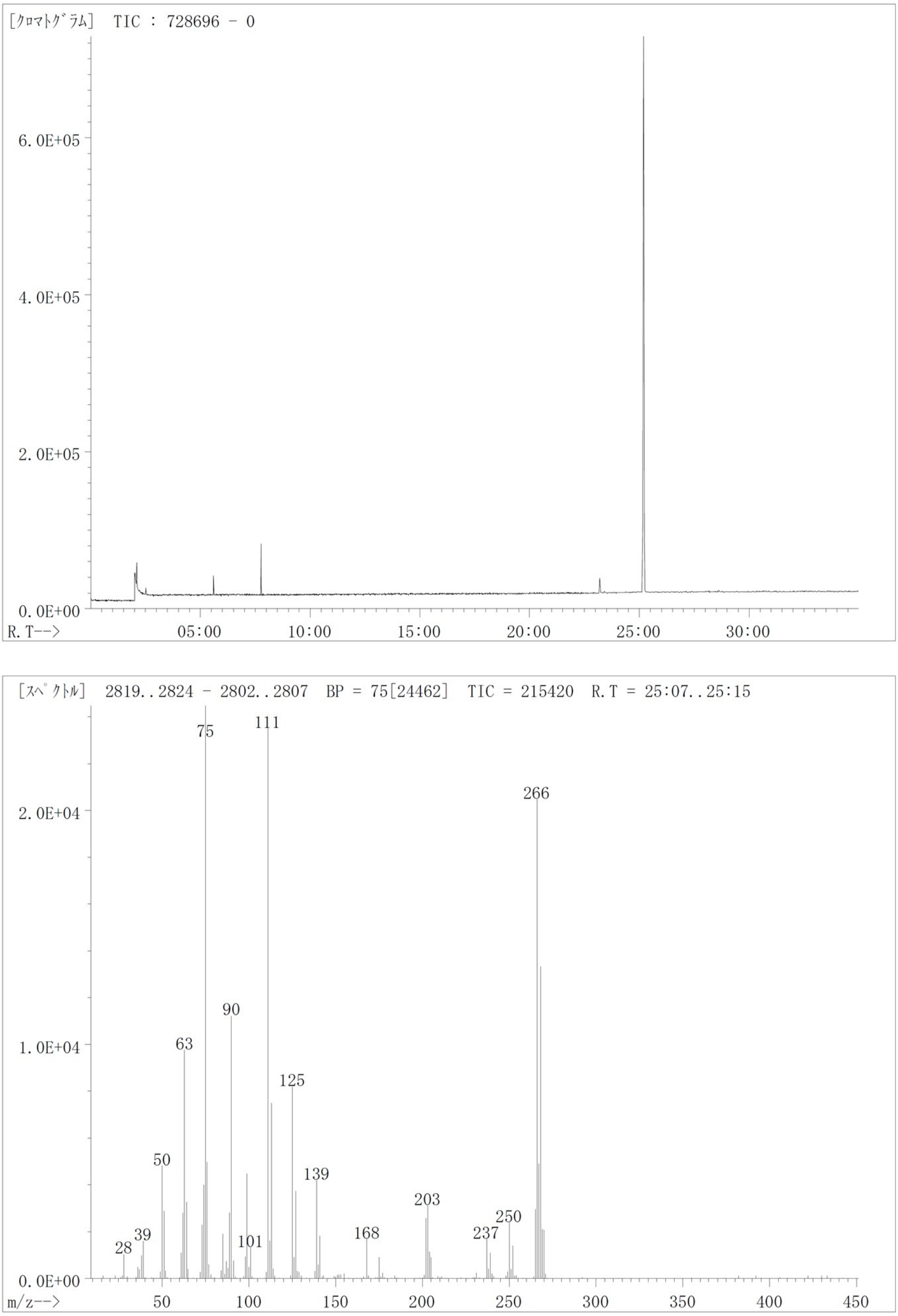


Figure S8. GC-MS chart of purified 4,4'-dichloroazoxybenzene.