

SUPPORTING INFORMATION

Hydrosilane-Promoted Cyclization of 2-Aminothiophenols by CO₂ to Benzothiazoles

Xiang Gao, Bo Yu, Yanfei Zhao, Leiduan Hao and Zhimin Liu✉

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Colloid, Interface
and Chemical Thermodynamics, Institute of Chemistry, Chinese Academy of Sciences,
Beijing 100190, China. Fax: 8610-62562821; E-mail: liuzm@iccas.ac.cn.

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1. Materials

CO₂ (99.99%) was provided by Beijing Analytical Instrument Company. 2-Aminothiophenol (1a: 98%), 2-amino-4-chlorothiophenol (1e: 97%), 2-amino-6-methylbenzothiazole (98%), 2-amino-6-methoxybenzothiazole (99%), TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene, 98%), NMP (1-methyl-2-pyrrolidinone) were purchased from J&K Scientific Ltd. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 98%), DBN (1,5-diazabicyclo[4.3.0]non-5-ene, 98%), PMHS (poly(methylhydrosiloxane), ca 1900), Et₂SiH₂ (diethylsilane, 98%), Et₃SiH (triethylsilane, 99%), 4-nitroacetophenone (98%) were purchased from Alfa Aesar. 2-Amino-5-bromobenzenethiol (1d: 98%), 2-Amino-5-nitrobenzenethiol (1f: 98%) were purchased from Beijing Kaida Technology Development Co., Ltd. The deuterated solvent (DMSO-d₆) was obtained from Cambridge Isotope Laboratories, Inc. 2-Amino-5-methylbenzenethiol (1b) and 2-amino-5-methoxybenzenethiol (1c) were synthesized according to the published procedures, the other chemicals were used as received.

2. Synthesis of 2-amino-5-methylbenzenethiol (1b) and 2-amino-5-methoxybenzenethiol (1c)

2-Amino-5-methylbenzenethiol (1b) and 2-amino-5-methoxybenzenethiol (1c) were synthesized according to the published procedures.¹⁻³ The mixture of 2-amino-6-methylbenzothiazole (10 mmol) and KOH (100 mmol) in H₂O (20 mL) was heated at 120 °C. The mixture was kept on reflux for 24 h and then cooled to room temperature. The mixture was filtered to remove the scraps and the filtrate was neutralized by acetic acid (50% in water) to pH = 6. Finally, the precipitate was collected by filtration and the target compound 1b was obtained as a light yellow solid. Similarly, compound 1c was obtained by the same method using 2-amino-6-methoxybenzothiazole as raw material and it was a yellow green solid.

3. Synthesis of benzothiazoles

The cyclization of 2-aminothiophenol by CO₂ in the presence of hydrosilane was conducted in a 22 ml Teflon-lined stainless steel autoclave equipped with a magnetic stirrer. In a typical experiment to synthesize benzothiazole, 2-aminothiophenol (2 mmol, 0.2504 g), DBN (1 equiv, 0.2483 g), Et₂SiH₂ (1.5 equiv, 0.2645 g) and NMP (2 mL) were successively added into the reactor, and then CO₂ was charged into the reactor until the desired pressure (5 MPa) at room temperature. Subsequently, the reactor was moved into an oil bath of desired temperature (150 °C) and the stirrer started. After a certain time (24 h), the reactor was moved to ice water and CO₂ was slowly released. The product yields were determined by ¹H NMR using 4-nitroacetophenone as the internal standard of the crude mixture.

Similarly, the other benzothiazole derivatives were obtained using the corresponding substituted 2-aminothiophenols as the substrates. The pure products were obtained via column chromatography separation and characterized by NMR. The yields were the isolated products. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) study was carried out with a Bruker Avance III 400 HD spectrometer with DMSO-d₆ as the solvent at ambient temperature.

4. NMR data of the as-prepared products

The characterization data for the as-prepared products were identical to the previously reported in the literature.

Compound 2 (benzothiazolone):

^1H NMR (400 MHz, DMSO) δ 11.87 (s, 1H), 7.54 (d, $J = 7.9$ Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.11 (d, $J = 4.9$ Hz, 2H).

^{13}C NMR (100 MHz, DMSO) δ 170.47, 136.79, 126.85, 123.76, 123.14, 123.04, 111.94.

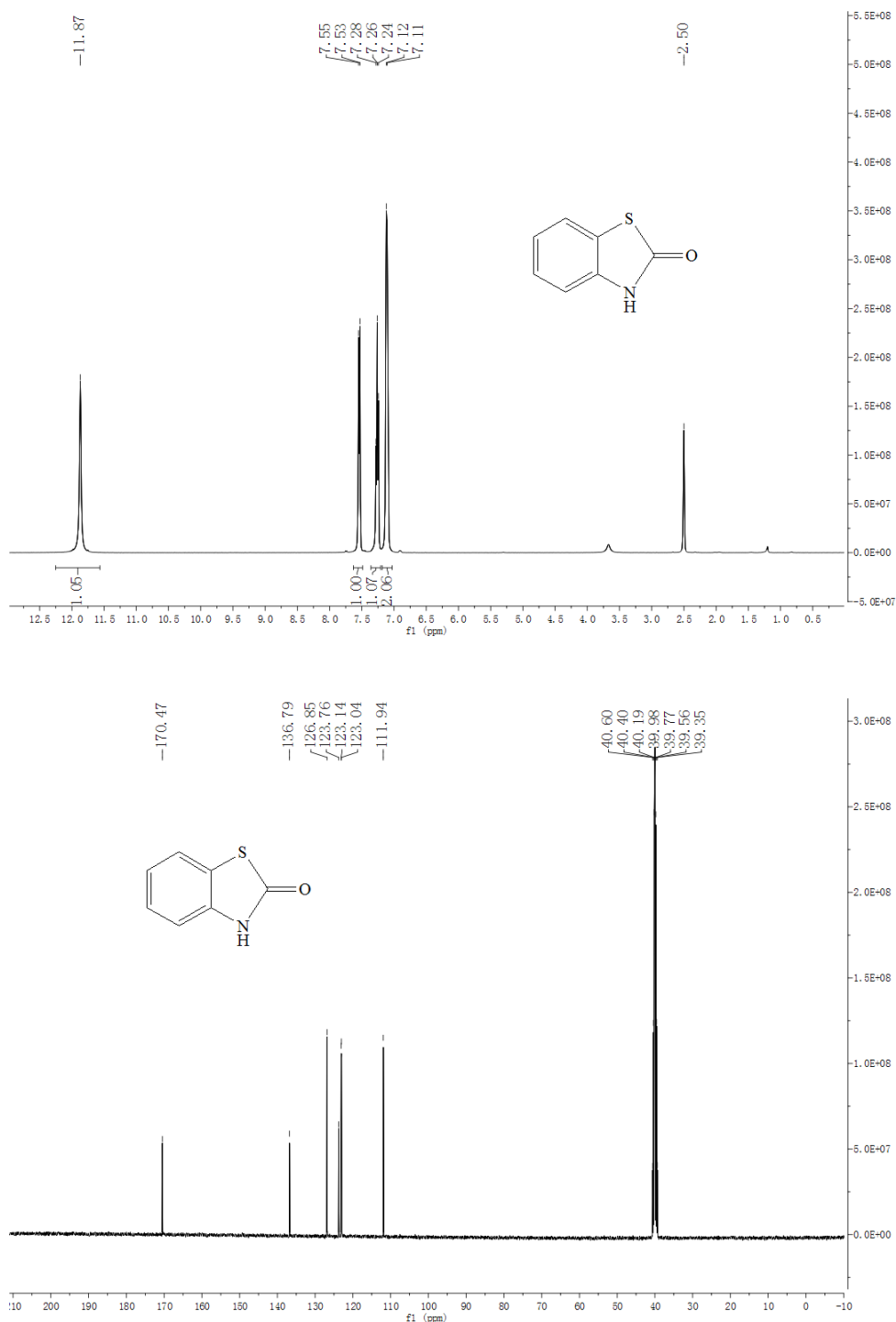


Figure S1. ^1H NMR and ^{13}C NMR spectra of benzothiazolone

Compound 1b (2-amino-5-methylbenzenethiol):

^1H NMR (400 MHz, DMSO) δ 6.92 (d, $J = 8.1$ Hz, 1H), 6.81 (s, 1H), 6.65 (d, $J = 8.1$ Hz, 1H), 5.22 (s, 2H), 2.05 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 147.84, 136.08, 132.35, 125.02, 117.12, 115.36, 20.13.

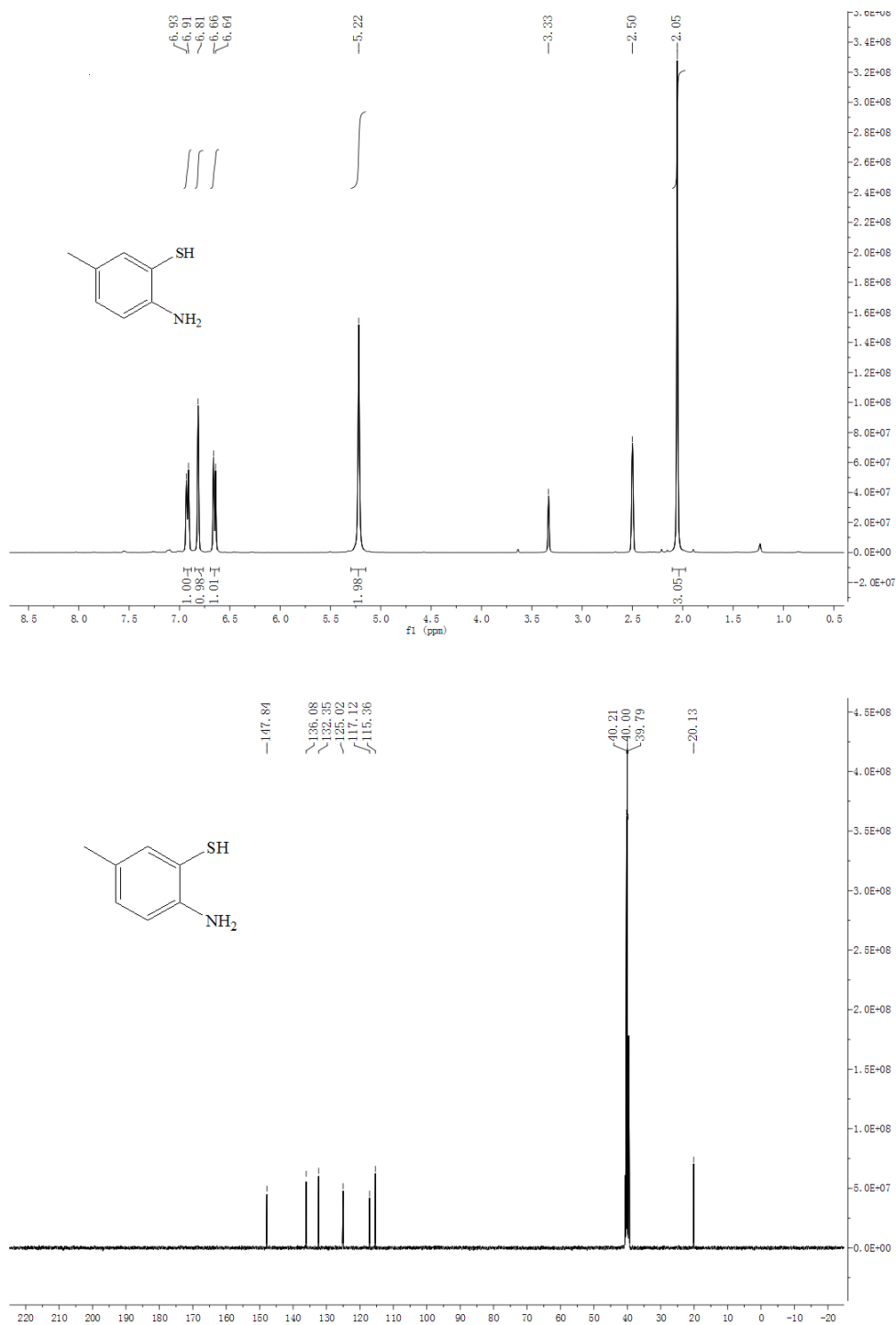


Figure S2. ^1H NMR and ^{13}C NMR spectra of 2-amino-5-methylbenzenethiol

Compound 1c (2-amino-5-methoxybenzenethiol):

$^1\text{H NMR}$ (400 MHz, DMSO) δ 6.78 (dd, $J = 8.8, 2.8$ Hz, 1H), 6.72 (d, $J = 8.8$ Hz, 1H), 6.61 (d, $J = 2.8$ Hz, 1H), 5.05 (s, 2H), 3.54 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, DMSO) δ 150.60, 144.15, 119.12, 119.00, 117.56, 116.61, 55.74.

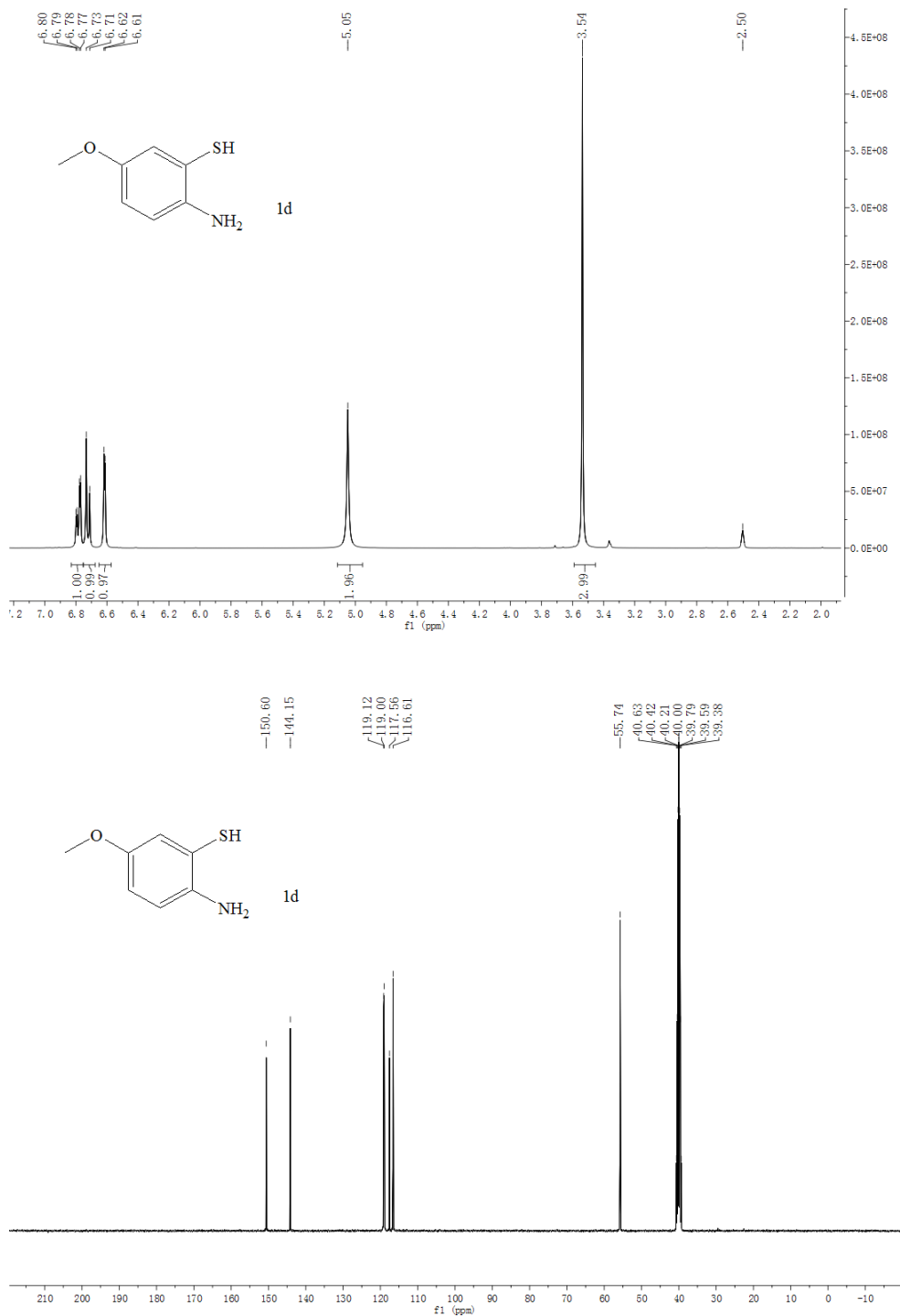


Figure S3. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of 2-amino-5-methoxybenzenethiol

Compound 2A (benzothiazole):

^1H NMR (400 MHz, DMSO) δ 9.41 (s, 1H), 8.12 (dd, J = 8.1, 2.8 Hz, 2H), 7.48 (m, 2H).

^{13}C NMR (100 MHz, DMSO) δ 156.26, 153.50, 134.03, 126.50, 125.80, 123.48, 122.79.

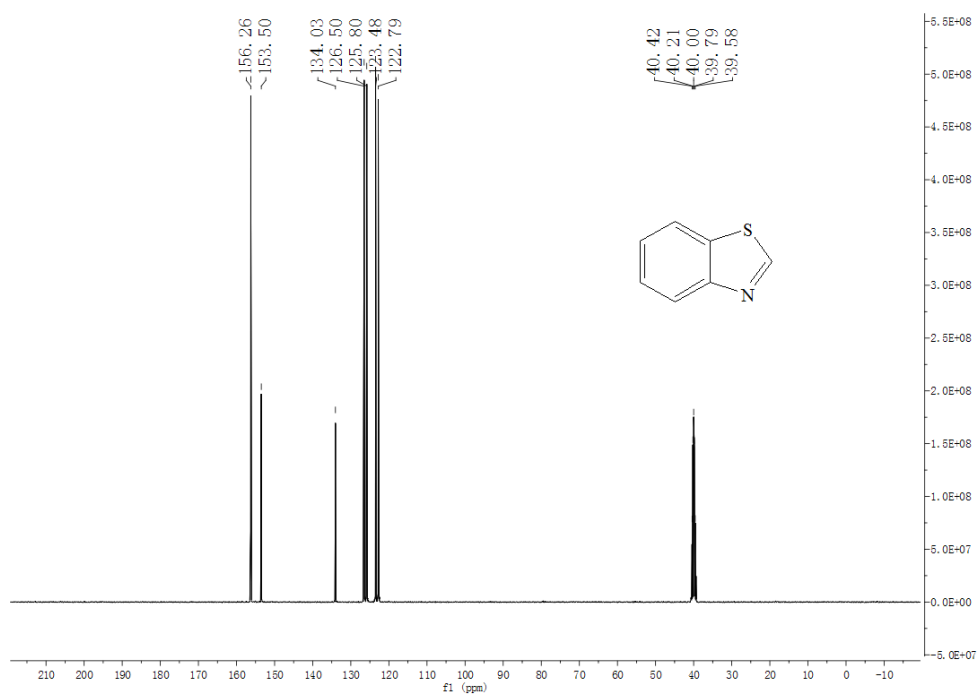
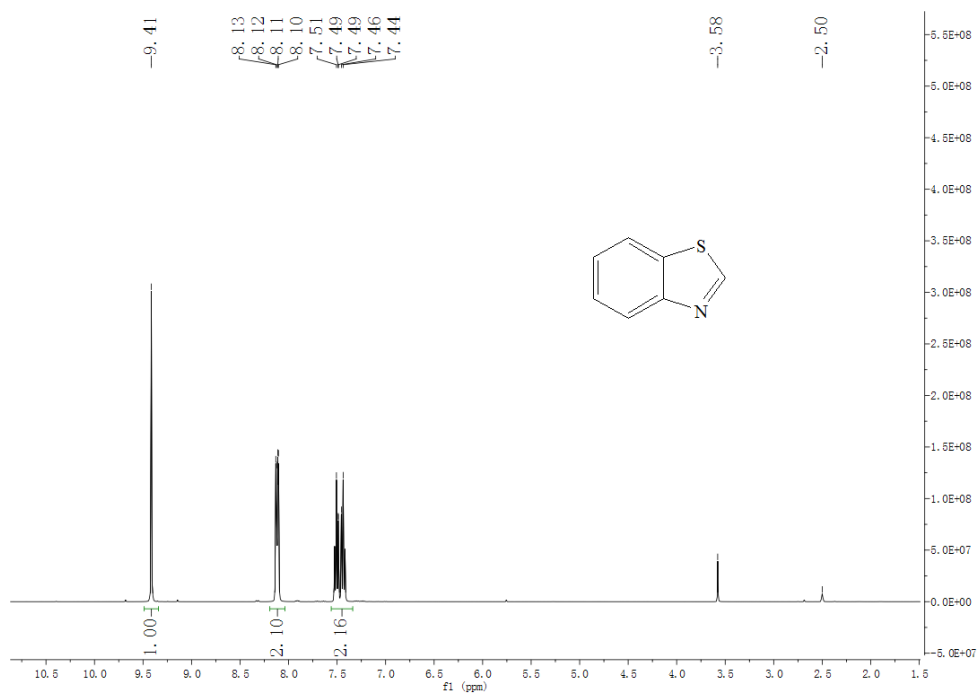


Figure S4. ^1H NMR and ^{13}C NMR spectra of benzothiazole

Compound 2B (5-methylbenzothiazole):

^1H NMR (400 MHz, DMSO) δ 9.29 (s, 1H), 8.04-7.84 (m, 2H), 7.33 (d, $J = 7.8$ Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, DMSO) δ 155.24, 151.71, 135.62, 134.19, 128.13, 123.00, 122.35, 21.44.

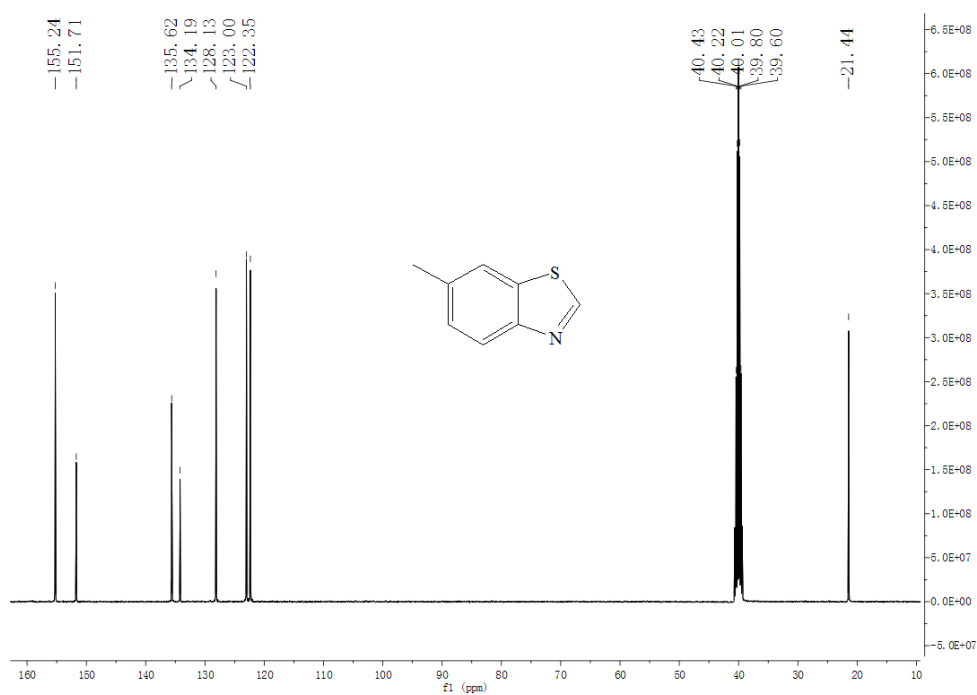
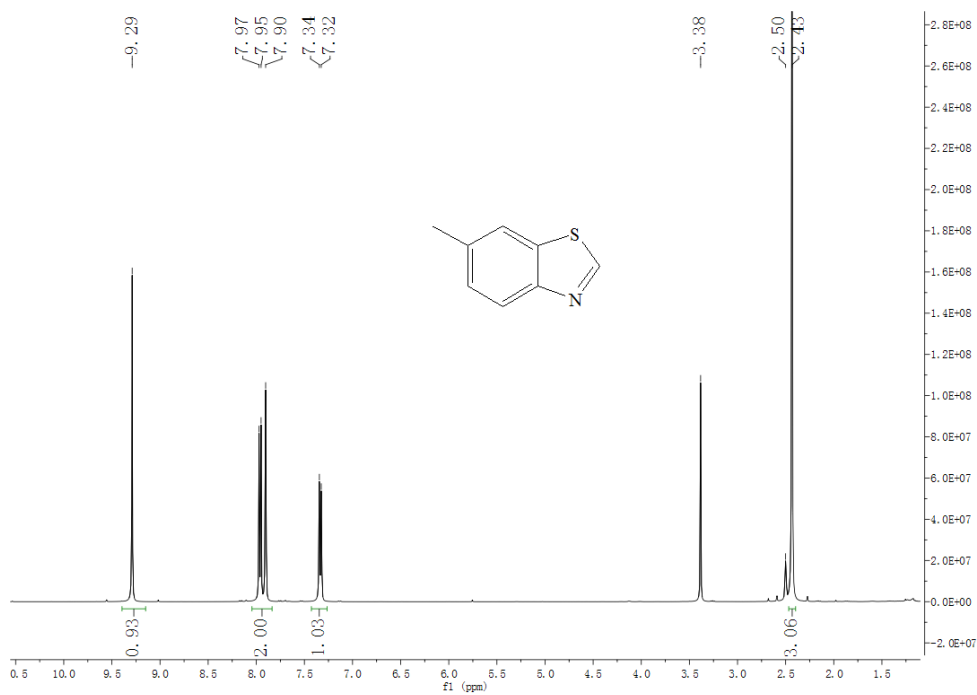


Figure S5. ^1H NMR and ^{13}C NMR spectra of 5-methylbenzothiazole

Compound 2C (5-methoxybenzothiazole):

$^1\text{H NMR}$ (400 MHz, DMSO) δ 9.18 (s, 1H), 7.96 (d, $J = 8.9$ Hz, 1H), 7.72 (d, $J = 2.5$ Hz, 1H), 7.13 (dd, $J = 8.9$, 2.5 Hz, 1H), 3.84 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, DMSO) δ 157.97, 153.78, 148.01, 135.53, 123.89, 116.15, 105.20, 56.17.

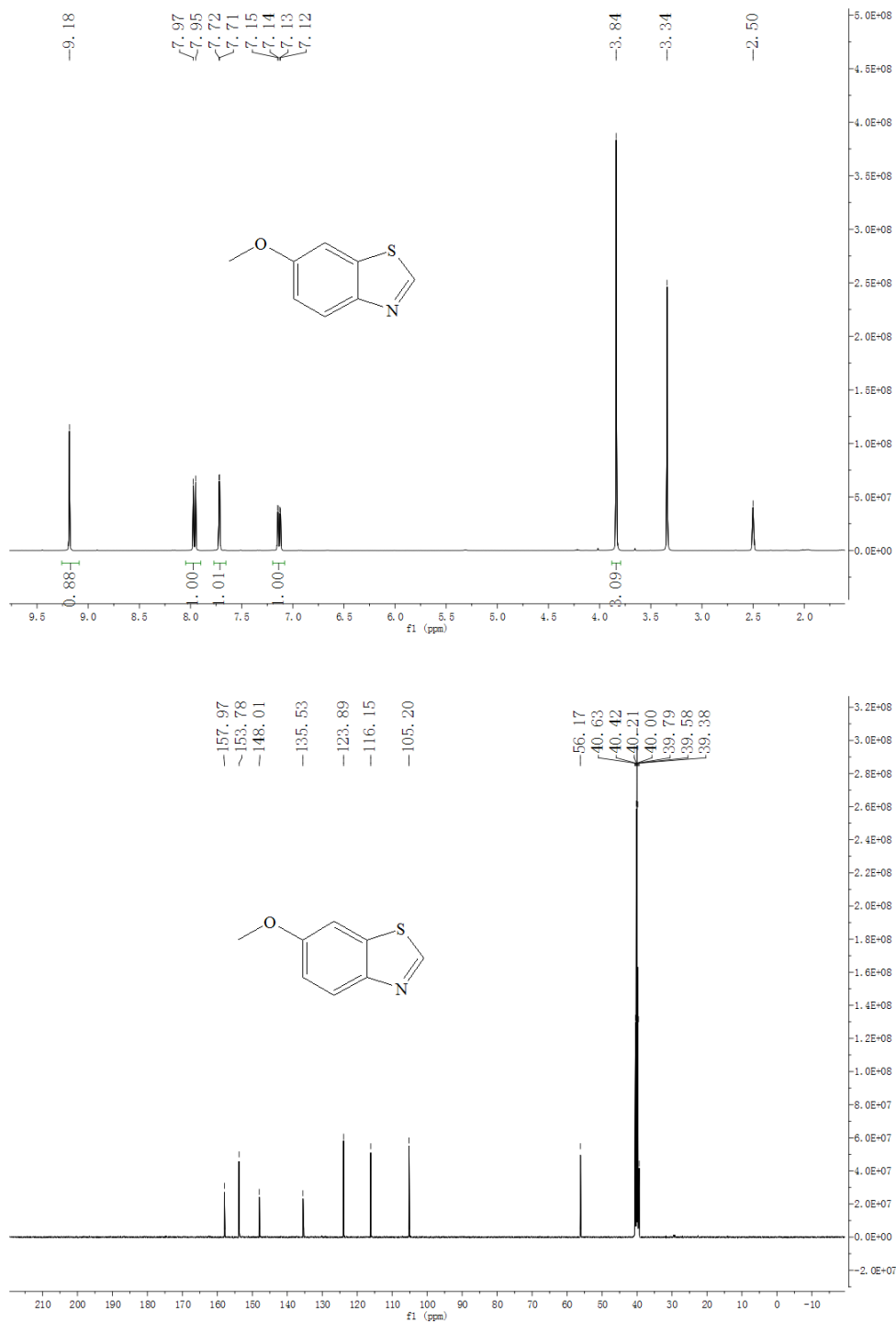


Figure S6. $^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of 5-methoxybenzothiazole

Compound 2D (5- bromobenzothiazole):

^1H NMR (400 MHz, DMSO) δ 9.40 (s, 1H), 8.47 (d, J = 1.8 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.69 (dd, J = 8.7, 1.9 Hz, 1H).

^{13}C NMR (100 MHz, DMSO) δ 157.79, 152.57, 136.22, 129.83, 125.55, 125.03, 118.73.

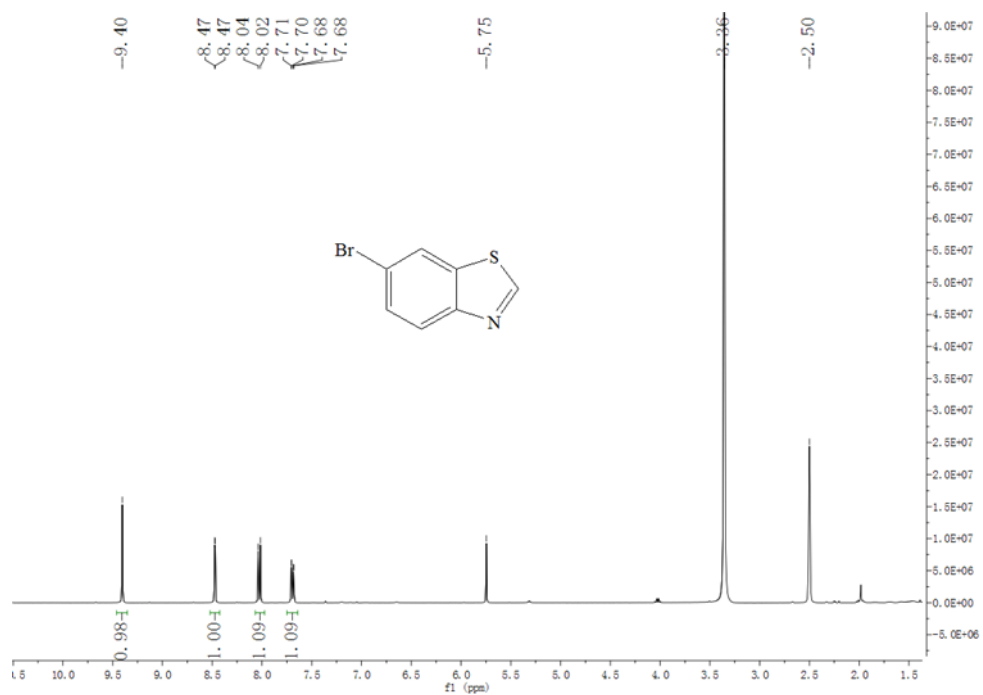


Figure S7. ^1H NMR and ^{13}C NMR spectra of 5- bromobenzothiazole

Compound 2E (6-chlorobenzothiazole):

^1H NMR (400 MHz, DMSO) δ 9.47 (s, 1H), 8.19 (dd, $J = 16.2, 5.2$ Hz, 2H), 7.54 (dd, $J = 8.6, 1.9$ Hz, 1H).

^{13}C NMR (100 MHz, DMSO) δ 159.10, 154.47, 132.93, 131.49, 126.11, 124.48, 122.96.

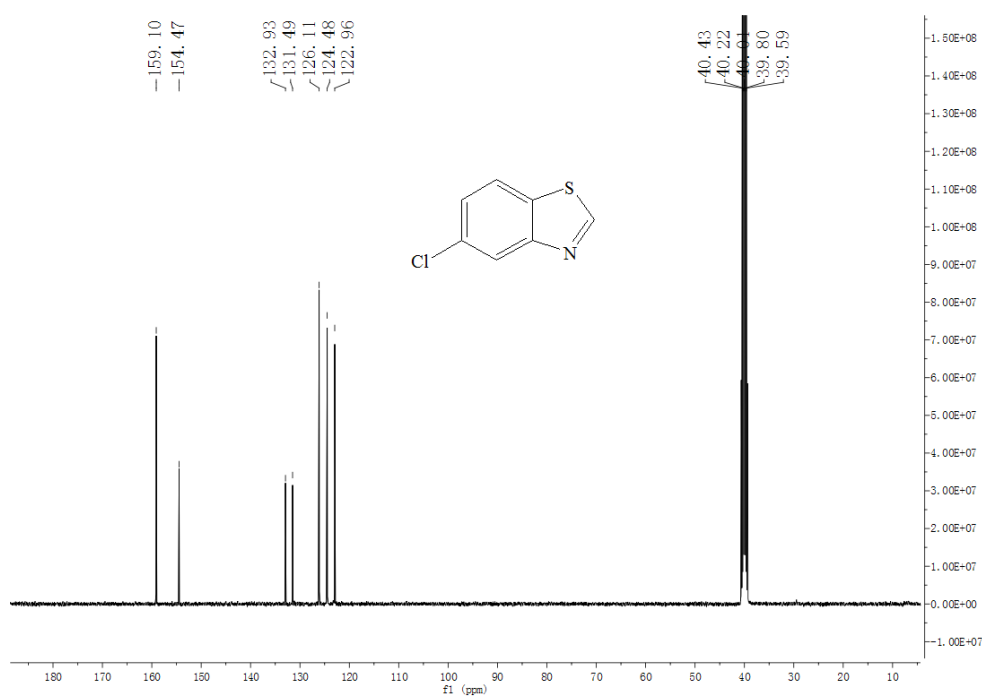
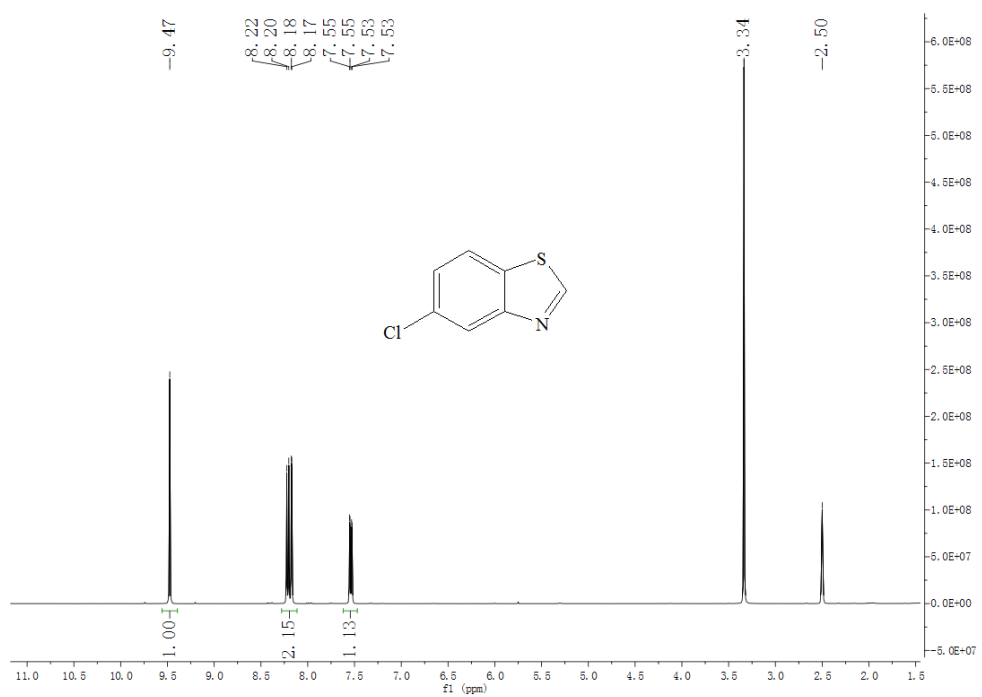


Figure S8. ^1H NMR and ^{13}C NMR spectra of 6-chlorobenzothiazole

Compound 2F (5-aminobenzothiazole):

^1H NMR (400 MHz, DMSO) δ 8.87 (s, 1H), 7.70 (d, $J = 8.7$ Hz, 1H), 7.11 (d, $J = 2.0$ Hz, 1H), 6.79 (dd, $J = 8.7$, 2.1 Hz, 1H), 5.38 (s, 2H).

^{13}C NMR (100 MHz, DMSO) δ 149.61, 147.78, 145.25, 135.51, 123.55, 115.38, 104.26.

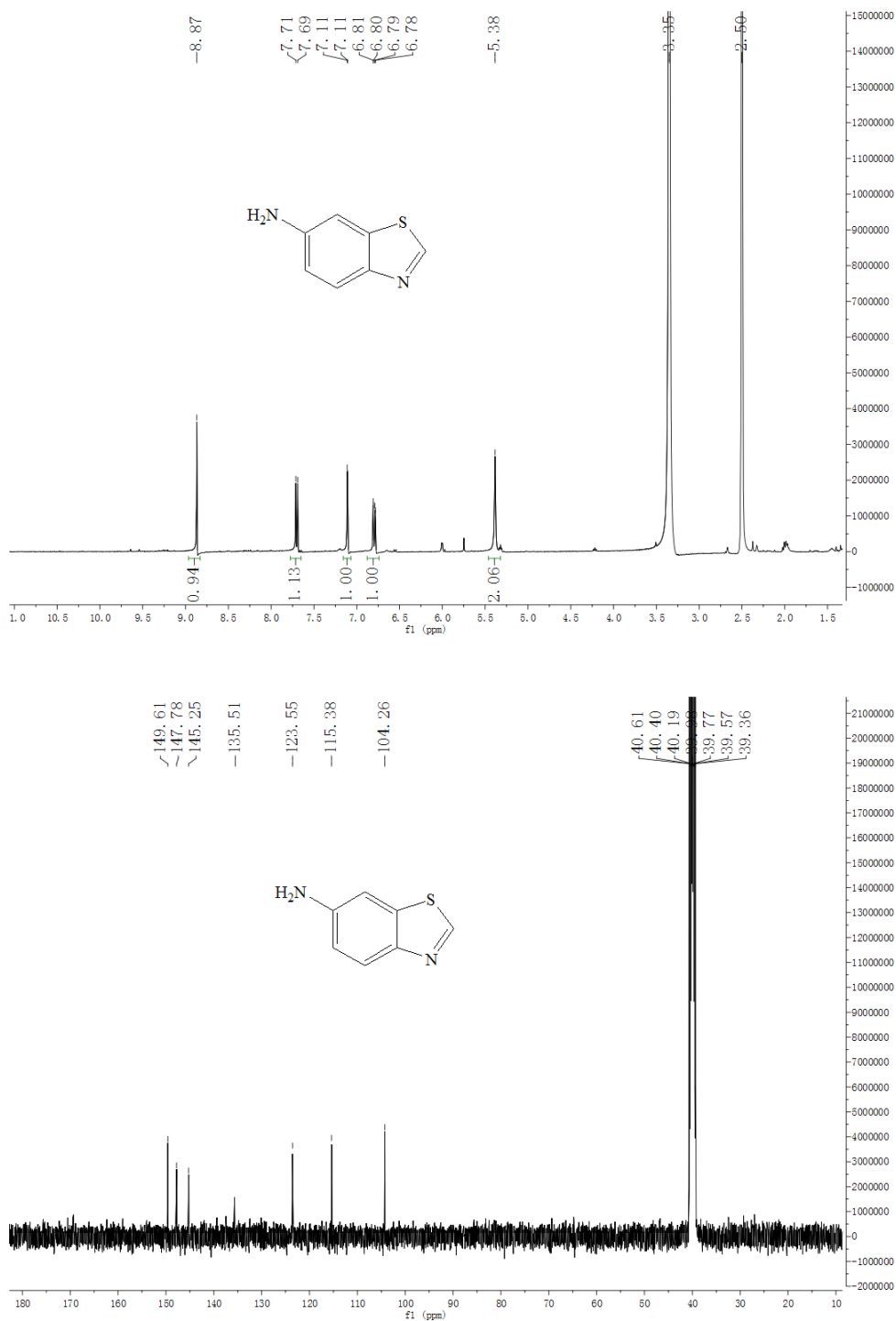


Figure S9. ^1H NMR and ^{13}C NMR spectra of 5-aminobenzothiazole

5. References

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