

Supporting Information

Iodine-mediated Thio-arylation under Electrochemistry

Jiajia Yu¹, Tong Li², Qi Sun^{*1} and Zhiyong Wang^{*1,2}

¹Institute of Advanced Technology, University of Science and Technology of China, Hefei 230000, China. ^{*}Hefei National Center for Physical Sciences at Microscale, Key Laboratory of Precision and Intelligent Chemistry, School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China.

^{*}E-mail: zwang3@ustc.edu.cn.

Table of Contents

1. General Information	S2
2. Experimental Procedure	S2
3. Optimization of Reaction Conditions	S3
4. Cyclic Voltammetry Studies	S3
5. Control experiments	S5
6. Detail Descriptions for Products	S5
7. Supporting Refrence.....	S14
8. NMR Spectra for the Products.....	S15

1. General Information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker AV-500 (^1H : 500 MHz, ^{13}C : 125 MHz, ^{19}F NMR: 470 MHz) spectrometer using TMS as internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. GC-MS was Shimadzu QP-5050 GC-MS system. Commercially available compounds were used without further purification. All substances were known compounds and synthesized according to the references. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and the time-of-flight (TOF) mass analyzer. The anode electrode and cathode electrode all are Pt ($1.0 \times 1.0 \text{ cm}^2$). These electrodes are commercially available from GaossUnion, China.

2. Experimental Procedure

Typical Procedure for 4-aminophenyl phenyl sulfide: A mixture of diphenyl disulfide (0.15 mmol), aniline (0.9 mmol), Et_4NI (0.3 mmol), DMSO = 3 mL and H_2O = 0.3 mL was added to an undivided cell. The cell was equipped with platinum electrode as both the anode and cathode. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 120 °C for corresponding time. When the reaction was finished, the solution was extracted with EtOAc ($3 \times 10 \text{ ml}$). The solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (PE/EtOAc = 4:1) to afford the desired product.

Gram-scale synthesis of 3aa: A mixture of diphenyl disulfide (3 mmol) benzylamine (15 mmol), ammonium tetrafluoroborate (5 mmol) and aniline (18 mmol), Et_4NI (6 mmol), DMSO = 60 mL and H_2O = 6 mL was added to an undivided cell. The cell was equipped with platinum electrode as both the anode and cathode. The reaction mixture was stirred and electrolyzed ($J = 10 \text{ mA/cm}^2$, $I = 23 \text{ mA}$) under 120 °C for 2 days. When the reaction was finished, the solution was extracted with EtOAc ($3 \times 100 \text{ mL}$). The combined organic layer was dried with Na_2SO_4 , filtered. The solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel (PE/EtOAc = 4:1) to afford the desired product.

3. Optimization of Reaction Conditions

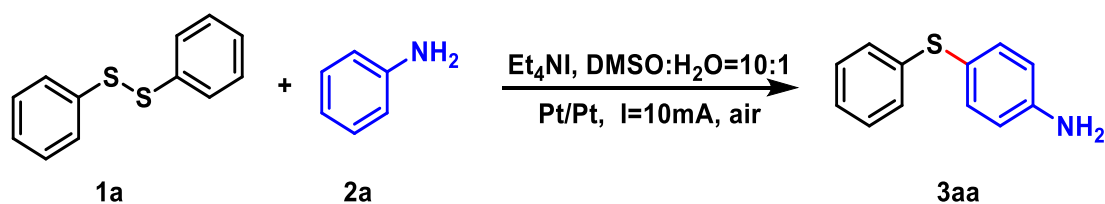


Table S1. the optimization of temperature of reaction.^a

Entry	Temperature(°C)	Yield[%] ^b
1	25	trace
2	40	trace
3	50	trace
4	60	trace
5	80	trace
6	100	40
7	120	86
8	140	80

^a Standard condition: platinum plate (10 mm × 10 mm × 0.2mm) as the anode, platinum plate (10 mm × 10 mm × 0.2mm) as the cathode, undivided cell, 1a (0.15 mmol), 2a (0.9 mmol), Et_4NI (0.3 mmol), and DMSO (3 mL), Air, 120°C, 4h. ^b Isolated yield.

4. Cyclic Voltammetry Studies

Cyclic voltammetry data were measured with a Shanghai Chenhua potentiostat (CHI760E).

Working electrode: The working electrode is a 3 mm diameter Pt disk working electrode. Polished with 0.3 μm aluminum oxide and then sonicated in distilled water before drying.

Reference electrode: The reference electrode consisted of a silver wire covered with silver chloride immersed in a saturated solution of potassium chloride.

Counter electrode: The counter electrode is a platinum wire that was polished with sand paper.

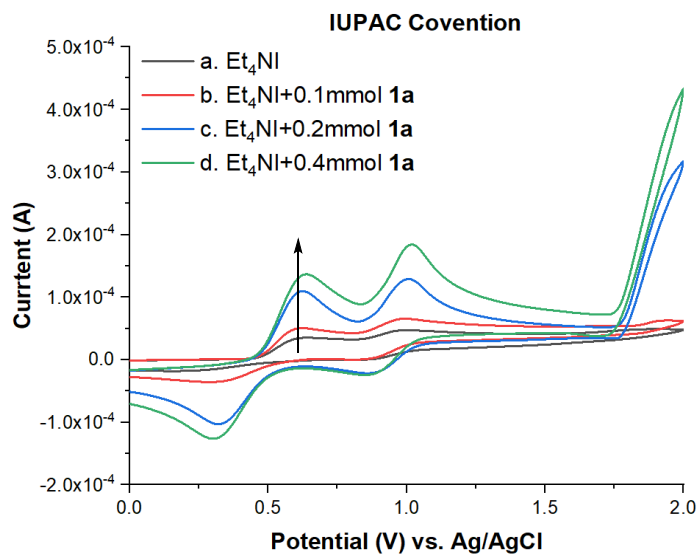


Figure S1. Cyclic voltammetry experiments: Cyclic voltammograms of **1a**, and 0.1 mmol Et₄NI in 0.1 M *n*-Bu₄NBF₄/MeCN = 10 mL using a Pt disk as the working electrode, and Pt wire and Ag/AgCl as the counter and reference electrodes, respectively, at a scan rate of 100 mV·s⁻¹; background (curve a), **1a** (10 mmol·L⁻¹, curve b), **1a** (20 mmol·L⁻¹, curve c) and **1a** (40 mmol·L⁻¹, curve d).

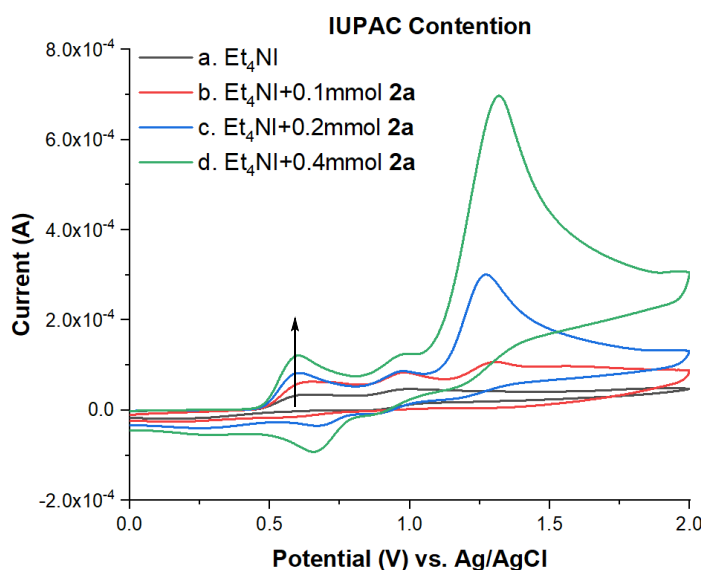
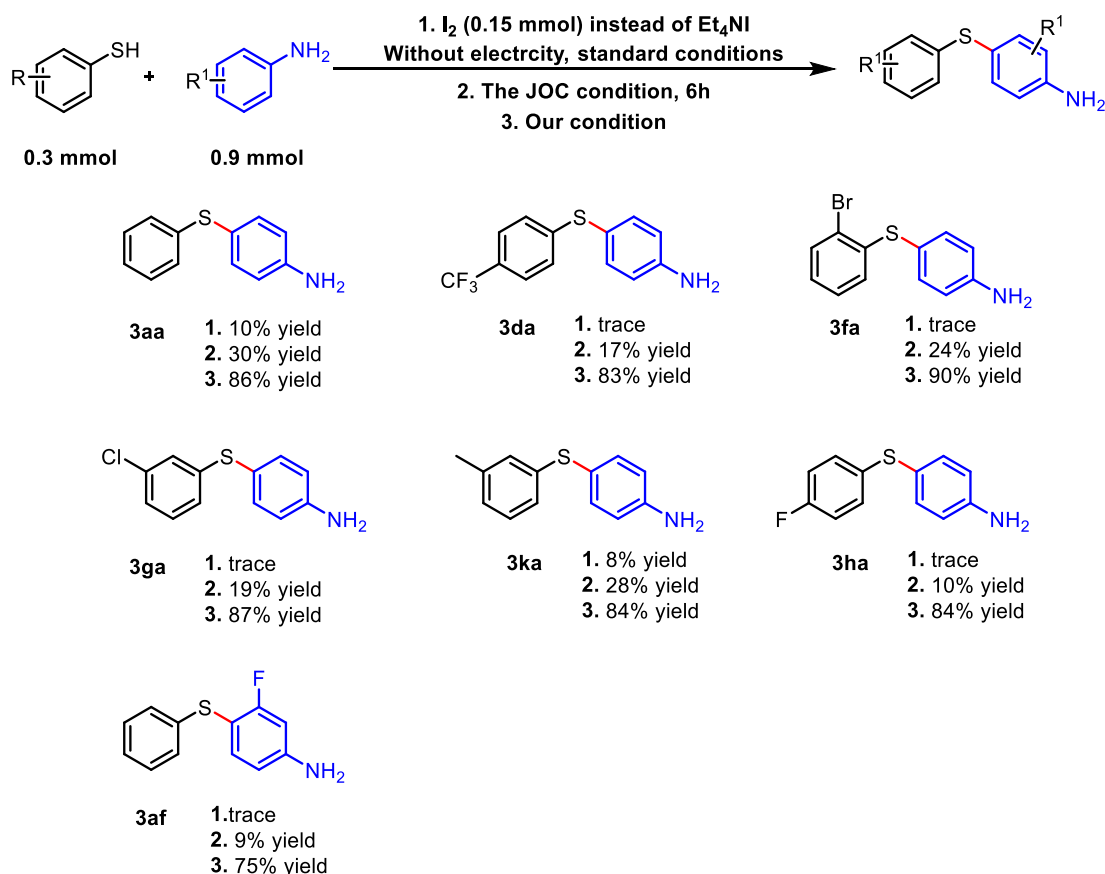


Figure S2. Cyclic voltammetry experiments: Cyclic voltammograms of **2a**, and 0.1 mmol Et₄NI in 0.1 M *n*-Bu₄NBF₄/MeCN = 10 mL using a Pt disk as the working electrode, and Pt wire and Ag/AgCl as the counter and reference electrodes, respectively, at a scan rate of 100 mV·s⁻¹; background (curve a), **2a** (10 mmol·L⁻¹, curve b), **2a** (20 mmol·L⁻¹, curve c) and **2a** (40 mmol·L⁻¹, curve d).

Figure S1 and **Figure S2** investigated the catalytic activity of Et₄NI. It can be observed that excessive treatment of Et₄NI with **1a** and **2a** led to a significant increase in the anodic peak of the mediator Et₄NI, which confirmed the catalytic role of Et₄NI in the reaction.

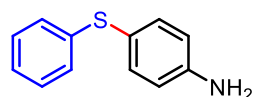
5. Control experiments

We conducted experiments without the addition of oxidants on all substrates. It was ultimately found that when thiols were used as substrates for the reaction, the corresponding products could not be obtained under the condition that iodine was not added as an oxidant. And under I₂/DTBP conditions, the yield after 6 hours of reaction is very low.



6. Detail Descriptions for Products

4-(phenylthio)aniline (3aa)

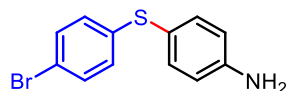


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 86% yield, 51.9 mg. M.P. = 76-78 °C. HRMS (ESI) m/z: calcd for C₁₂H₁₂NS [M+H]⁺ 202.0685, found: 202.0690.

¹H NMR (500 MHz, CDCl₃) δ 7.36 – 7.32 (m, 2H), 7.26 – 7.21 (m, 2H), 7.21 – 7.03 (m, 3H), 6.71 – 6.65 (m, 2H), 3.72 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 147.1, 139.7, 136.2, 128.9, 127.3, 125.3, 120.43, 115.9.

4-((4-bromophenyl)thio)aniline (**3ba**)^{S1}

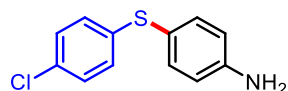


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 86% yield, 72.2 mg.

¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, *J* = 8.0 Hz, 4H), 6.97 (m, 2H), 6.70 – 6.65 (m, 2H), 3.81 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 147.4, 139.3, 136.3, 131.8, 128.6, 119.6, 118.8, 116.0.

4-((4-chlorophenyl)thio)aniline (**3ca**)^{S2}

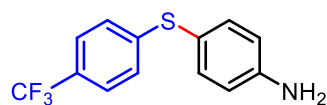


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 81% yield, 57.1 mg. M.P. = 73-75 °C.

¹H NMR (500 MHz, CDCl₃) δ 7.33 – 7.28 (m, 2H), 7.21 – 7.16 (m, 2H), 7.08 – 7.03 (m, 2H), 6.70 – 6.65 (m, 2H), 3.79 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 147.3, 138.5, 136.2, 131.1, 128.9, 128.5, 119.9, 116.0.

4-((4-(trifluoromethyl)phenyl)thio)aniline (**3da**)



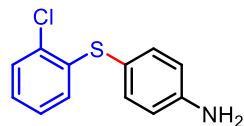
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 82% yield, 66.2 mg. M.P. = 85-87 °C. HRMS (ESI) *m/z*: calcd for C₁₃H₁₀F₃NS [M+H]⁺ 270.0559, found 270.0561.

¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 8.3 Hz, 2H), 7.33 (t, *J* = 5.6 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 148.0, 145.9, 137.1, 126.8 (q, *J* = 32.5 Hz), 125.9, 125.6 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.5 Hz), 117.8, 116.1.

¹⁹F NMR (470 MHz, CDCl₃) δ -62.25.

4-((2-chlorophenyl)thio)aniline (**3ea**)^{S3}

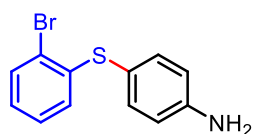


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 81% yield, 57.1mg.

¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.29 (m, 3H), 7.03 (m, 2H), 6.75 – 6.69 (m, 3H), 3.74 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 147.8, 139.7, 137.4, 130.4, 129.3, 127.0, 126.9, 125.7, 117.8, 116.2.

4-((2-bromophenyl)thio)aniline (**3fa**)^{S4}

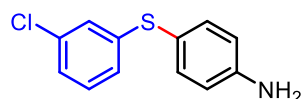


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 90% yield, 75.6 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.49 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.36 – 7.31 (m, 2H), 7.10 – 7.06 (m, 1H), 6.93 (td, $J = 7.6, 1.5$ Hz, 1H), 6.73 – 6.70 (m, 2H), 6.68 (dd, $J = 8.0, 1.5$ Hz, 1H), 3.75 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.8, 141.7, 137.4, 132.6, 127.6, 126.9, 125.9, 120.1, 118.3, 116.2.

4-((3-chlorophenyl)thio)aniline (**3ga**)^{S3}



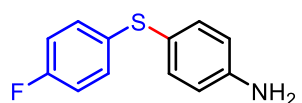
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a

yellow oil. 87% yield, 61.3 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.41 – 7.27 (m, 2H), 7.16 – 7.09 (m, 1H), 7.09 – 7.00 (m, 2H), 7.02 – 6.93 (m, 1H), 6.85 – 6.62 (m, 2H), 3.74 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.5, 142.4, 136.7, 134.8, 129.8, 126.3, 125.2, 124.8, 118.9, 116.1.

4-((4-fluorophenyl)thio)aniline (**3ha**)^{S5}



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a

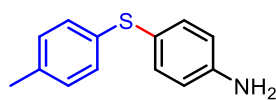
yellow oil. 64% yield, 42.0 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.23 (m, 2H), 7.16 – 7.12 (m, 2H), 6.95 – 6.90 (m, 2H), 6.70 – 6.64 (m, 2H), 3.38 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 161.3 (d, $J = 245.2$ Hz), 146.6, 135.4, 134.2 (d, $J = 3.2$ Hz), 130.0 (d, $J = 8.0$ Hz), 121.6, 116.0, 115.9 (d, $J = 22.5$ Hz).

^{19}F NMR (470 MHz, CDCl_3) δ -117.06.

4-(p-tolylthio)aniline (**3ia**)^{S6}



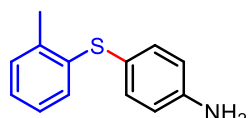
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a

yellow oil. 83% yield, 53.5 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.33 – 7.28 (m, 2H), 7.14 – 7.04 (m, 4H), 6.69 – 6.64 (m, 2H), 3.73 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 146.7, 135.6, 135.5, 135.4, 129.7, 128.3, 121.7, 115.9, 21.0.

4-(o-tolylthio)aniline (**3ja**)^{S3}

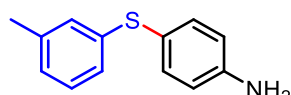


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 88% yield, 56.7 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.27 (m, 2H), 7.20 – 7.16 (m, 1H), 7.10 – 7.04 (m, 2H), 6.93 (m, 1H), 6.71 – 6.67 (m, 2H), 3.68 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 146.8, 138.5, 136.0, 135.8, 130.1, 127.6, 126.4, 125.4, 120.4, 116.1, 20.3.

4-(m-tolylthio)aniline (**3ka**)^{S3}

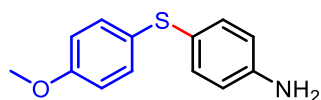


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 84% yield, 54.1 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.35 – 7.31 (m, 2H), 7.12 (t, J = 7.7 Hz, 1H), 7.00 (s, 1H), 6.97 – 6.91 (m, 2H), 6.71 – 6.66 (m, 2H), 3.65 (s, 2H), 2.28 (s, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ 146.9, 139.3, 138.7, 136.0, 128.8, 128.0, 126.3, 124.5, 120.8, 116.0, 21.4.

4-((4-methoxyphenyl)thio)aniline (**3la**)^{S7}

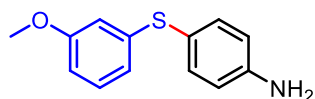


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 68% yield, 47.1 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.26 – 7.18 (m, 4H), 6.82 (d, J = 8.7 Hz, 2H), 6.62 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 3.64 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 158.6, 146.2, 134.0, 131.5, 128.9, 123.5, 115.9, 114.7, 55.4.

4-((3-methoxyphenyl)thio)aniline (**3ma**)^{S8}

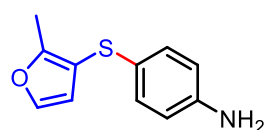


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 76% yield, 52.6 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.32 (m, 2H), 7.15 (t, J = 8.0 Hz, 1H), 6.75 – 6.65 (m, 5H), 3.80 – 3.68 (m, 5H).

^{13}C NMR (125 MHz, CDCl_3) δ 160.0, 147.2, 141.3, 136.4, 129.7, 119.9, 119.4, 116.0, 112.6, 110.9, 55.2.

4-((2-methylfuran-3-yl)thio)aniline (**3na**)



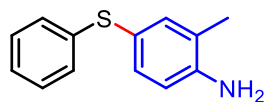
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 55% yield, 33.8 mg. HRMS (ESI) m/z : calcd for

C₁₁H₁₁NOS [M+H]⁺ 206.0634, found 206.0634.

¹H NMR (500 MHz, CDCl₃) δ 7.29 (d, *J* = 1.9 Hz, 1H), 7.08 – 7.04 (m, 2H), 6.61 – 6.58 (m, 2H), 6.32 (d, *J* = 1.9 Hz, 1H), 3.45 (s, 2H), 2.36 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 155.1, 144.9, 140.8, 130.3, 125.3, 115.9, 115.0, 110.6, 11.9.

2-methyl-4-(phenylthio)aniline (**3ab**)^{S9}

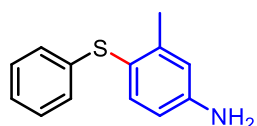


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 88% yield, 56.8 mg.

¹H NMR (500 MHz, CDCl₃) δ 7.24 – 7.16 (m, 4H), 7.13 – 7.05 (m, 3H), 6.64 (d, *J* = 8.1 Hz, 1H), 3.69 (s, 2H), 2.12 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 145.4, 140.0, 137.1, 134.0, 128.9, 127.1, 125.2, 123.4, 120.0, 115.7, 17.3.

3-methyl-4-(phenylthio)aniline (**3ac**)

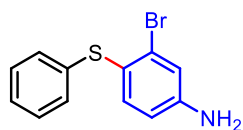


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil: 81% yield, 52.2 mg. HRMS (ESI) *m/z*: calcd for C₁₃H₁₃NS [M+H]⁺ 216.0841, found 216.0843.

¹H NMR (500 MHz, CDCl₃) δ 7.36 (d, *J* = 8.2 Hz, 1H), 7.22 (m, 2H), 7.12 – 7.08 (m, 1H), 7.06 (m, 2H), 6.65 (d, *J* = 2.4 Hz, 1H), 6.55 (dd, *J* = 8.2, 2.5 Hz, 1H), 3.72 (s, 2H), 2.32 (s, 3H).

¹³C NMR (125 MHz, CDCl₃) δ 147.7, 144.0, 139.5, 138.0, 128.9, 126.3, 124.8, 119.2, 117.3, 113.6, 20.9.

3-bromo-4-(phenylthio)aniline (**3ad**)

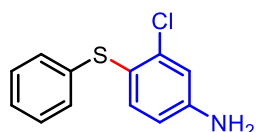


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 85% yield, 71.4 mg. HRMS (ESI) *m/z*: calcd for C₁₂H₁₀ClNS [M+H]⁺ 279.9790, found 279.9789.

¹H NMR (500 MHz, CDCl₃) δ 7.24 (m, 3H), 7.17 – 7.10 (m, 3H), 6.96 (d, *J* = 2.5 Hz, 1H), 6.53 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.70 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 148.2, 137.6, 137.1, 130.2, 129.1, 128.0, 125.9, 121.6, 119.4, 115.0.

3-chloro-4-(phenylthio)aniline (**3ae**)



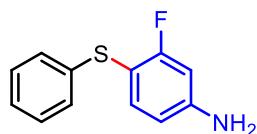
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 80% yield, 56.4 mg. HRMS (ESI) *m/z*: calcd for

C₁₂H₁₀CINS [M+H]⁺ 236.0295, found 236.0298.

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.19 (m, 3H), 7.15 – 7.10 (m, 3H), 6.77 (d, *J* = 2.5 Hz, 1H), 6.50 (dd, *J* = 8.4, 2.5 Hz, 1H), 3.73 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 148.3, 139.4, 137.5, 137.4, 129.0, 127.8, 125.8, 119.4, 116.2, 114.3.

3-fluoro-4-(phenylthio)aniline (**3af**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 75% yield, 49.3 mg. M.P. = 73-75 °C HRMS (ESI)

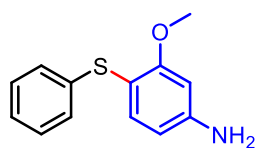
m/z: calcd for C₁₂H₁₀FNS [M+H]⁺ 220.0591, found 220.0591.

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.25 (m, 1H), 7.24 – 7.18 (m, 2H), 7.17 – 7.06 (m, 3H), 6.48 – 6.40 (m, 2H), 3.85 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 163.9 (d, *J* = 246.0 Hz), 149.8, 149.7, 138.2, 138.2, 138.1, 128.9, 127.1, 125.5, 111.5 (d, *J* = 2.8 Hz), 106.7 (d, *J* = 19.0 Hz), 102.4 (d, *J* = 26.6 Hz).

¹⁹F NMR (470 MHz, CDCl₃) δ -106.28.

3-methoxy-4-(phenylthio)aniline (**3ag**)



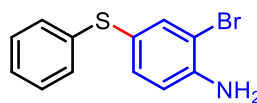
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 70% yield, 48.5 mg. HRMS (ESI) *m/z*: calcd for

C₁₃H₁₃NOS [M+H]⁺ 232.0791, found 232.0792.

¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.25 (m, 1H), 7.23 – 7.18 (m, 2H), 7.14 – 7.07 (m, 3H), 6.34 – 6.28 (m, 2H), 3.78 (s, 3H), 3.52 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 160.9, 149.2, 138.9, 138.0, 128.7, 126.8, 124.9, 108.1, 107.9, 98.8, 55.9.

2-bromo-4-(phenylthio)aniline (**3ah**)



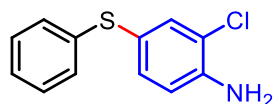
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a

yellow oil. 55% yield, 46.2 mg. HRMS (ESI) *m/z*: calcd for C₁₂H₁₀BrNS [M+H]⁺ 279.9790, found 279.9792.

¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 2.0 Hz, 1H), 7.23 (m, 3H), 7.16 – 7.11 (m, 3H), 6.73 (d, *J* = 8.3 Hz, 1H), 4.13 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 144.5, 138.7, 138.2, 134.7, 129.0, 127.9, 125.8, 122.1, 116.2, 109.3.

2-chloro-4-(phenylthio)aniline (**3ai**)^{S10}

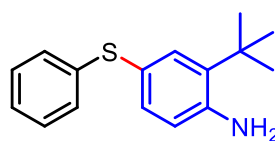


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 50% yield, 35.3 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, J = 2.0 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.17 – 7.11 (m, 3H), 6.73 (d, J = 8.3 Hz, 1H), 3.96 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 143.3, 138.6, 135.1, 134.0, 129.0, 128.0, 125.8, 121.8, 119.5, 116.3.

2-(tert-butyl)-4-(phenylthio)aniline (**3aj**)

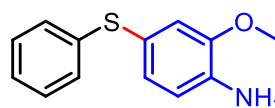


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 70% yield, 54.0 mg. HRMS (ESI) m/z : calcd for $\text{C}_{16}\text{H}_{19}\text{NS}$ $[\text{M}+\text{H}]^+$ 258.1311, found 258.1313.

^1H NMR (500 MHz, CDCl_3) δ 7.39 (d, J = 2.1 Hz, 1H), 7.22 – 7.15 (m, 3H), 7.13 – 7.06 (m, 3H), 6.61 (d, J = 8.1 Hz, 1H), 3.82 (s, 2H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, CDCl_3) δ 145.4, 139.9, 134.6, 133.6, 133.6, 128.9, 127.1, 125.2, 120.1, 118.6, 34.4, 29.5.

2-methoxy-4-(phenylthio)aniline (**3ak**)^{S11}

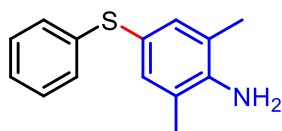


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 66% yield, 45.7 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.23 (t, J = 7.6 Hz, 2H), 7.16 – 7.09 (m, 3H), 7.01 (dd, J = 8.0, 1.8 Hz, 1H), 6.96 (d, J = 1.7 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 2H).

^{13}C NMR (125 MHz, CDCl_3) δ 147.6, 139.8, 137.0, 128.9, 128.3, 127.1, 125.2, 120.1, 116.7, 115.2, 55.6.

2,6-dimethyl-4-(phenylthio)aniline (**3al**)

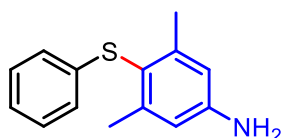


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 83% yield, 57.0 mg. HRMS (ESI) m/z : calcd for $C_{14}H_{15}NS$ $[M+H]^+$ 230.0998, found 230.1002.

1H NMR (500 MHz, $CDCl_3$) δ 7.18 (m, 2H), 7.14 – 7.04 (m, 5H), 3.63 (s, 2H), 2.13 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 140.2, 135.0, 128.8, 127.1, 125.1, 122.8, 119.2, 17.6.

3,5-dimethyl-4-(phenylthio)aniline (**3am**)

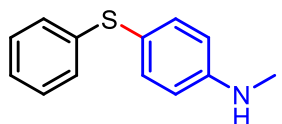


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow solid. 73% yield, 50.1mg. M.P. = 103-105 °C HRMS (ESI) m/z : calcd for $C_{13}H_{13}NS$ $[M+H]^+$ 230.0998, found 230.1003.

1H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 2H), 7.08 – 7.03 (m, 1H), 6.95 (m, 2H), 6.55 (s, 2H), 3.60 (s, 2H), 2.36 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 145.4, 139.4, 128.8, 125.0, 124.2, 118.3, 115.0, 21.9.

N-methyl-4-(phenylthio)aniline (**3an**)

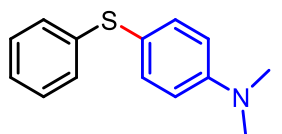


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 73% yield, 47.1 mg. HRMS (ESI) m/z : calcd for $C_{13}H_{13}NS$ $[M+H]^+$ 216.0841, found 216.0846.

1H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.25 – 7.21 (m, 2H), 7.16 – 7.08 (m, 3H), 3.76 (s, 1H), 2.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 140.3, 136.4, 128.8, 126.9, 125.1, 118.4, 113.2, 30.6.

N,N-dimethyl-4-(phenylthio)aniline (**3ao**)



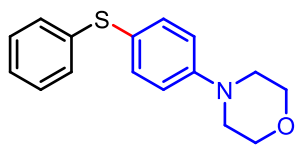
The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 77% yield, 52.9 mg. HRMS (ESI) m/z : calcd for $C_{14}H_{15}NS$ $[M+H]^+$ 230.0998, found 230.0994.

1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.26 – 7.22 (m, 2H), 7.17 – 7.09

(m, 3H), 6.77 – 6.73 (m, 2H), 3.02 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ 150.7, 140.4, 136.2, 128.8, 126.9, 125.0, 113.1, 40.4.

4-(4-(phenylthio)phenyl)morpholine (**3ap**)^{S12}

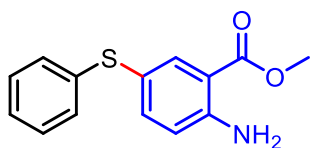


The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a White solid. 65% yield, 52.8 mg.

^1H NMR (500 MHz, CDCl_3) δ 7.40 (dd, J = 6.8, 4.8 Hz, 2H), 7.23 (t, J = 7.6 Hz, 2H), 7.20 – 7.10 (m, 3H), 6.90 (d, J = 8.7 Hz, 2H), 3.90 – 3.84 (m, 4H), 3.24 – 3.18 (m, 4H).

^{13}C NMR (125 MHz, CDCl_3) δ 151.1, 138.9, 135.2, 128.9, 128.0, 125.6, 122.6, 116.1, 66.8, 48.7.

Methyl 2-amino-5-(phenylthio)benzoate (**3aq**)



The title compound was prepared according to the general working procedure and purified by column chromatography (petroleum ether/ethyl acetate = 4:1) to give the product as a yellow oil. 60% yield, 46.6 mg. HRMS (ESI) m/z : calcd for

$\text{C}_{14}\text{H}_{13}\text{NO}_2\text{S}$ $[\text{M}+\text{Na}]^+$ 282.0559, found 282.0545.

^1H NMR (500 MHz, CDCl_3) δ 8.10 (d, J = 2.1 Hz, 1H), 7.39 (dd, J = 8.5, 2.2 Hz, 1H), 7.22 (t, J = 7.7 Hz, 2H), 7.14 – 7.09 (m, 3H), 6.68 (d, J = 8.6 Hz, 1H), 5.90 (s, 2H), 3.86 (s, 3H).

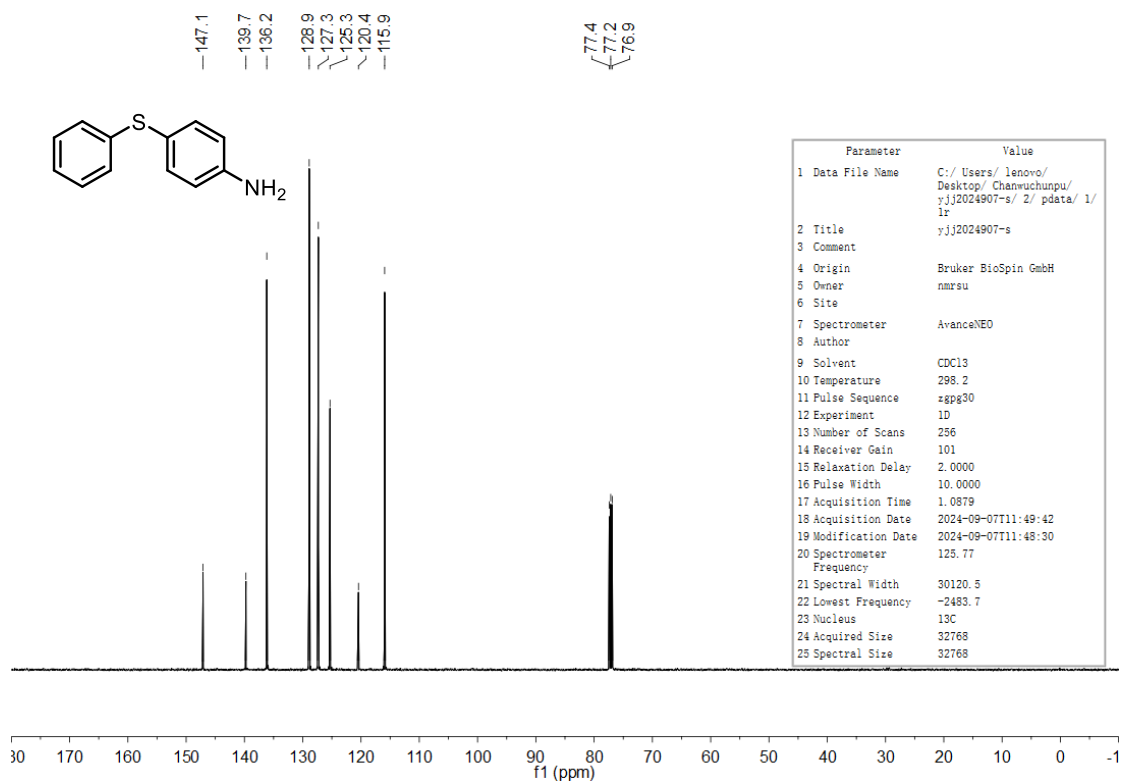
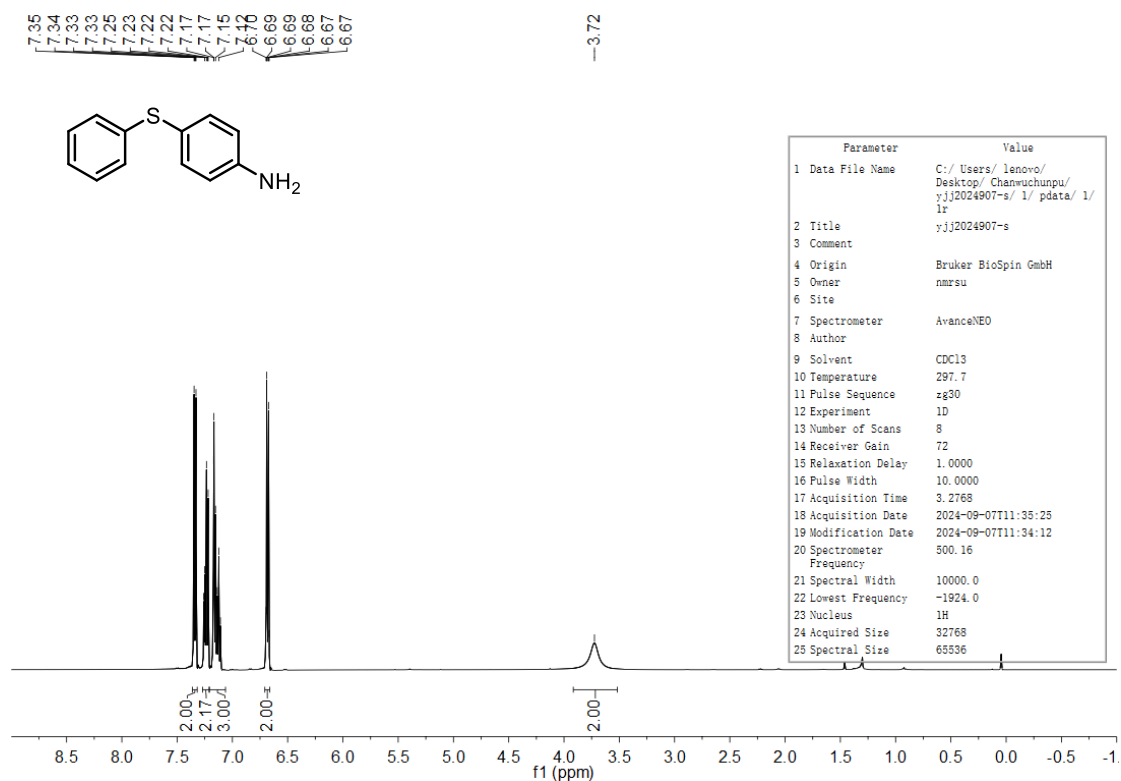
^{13}C NMR (126 MHz, CDCl_3) δ 168.0, 150.7, 140.6, 139.3, 138.3, 128.9, 127.24, 125.4, 118.3, 118.0, 111.5, 51.7.

7. Supporting Reference

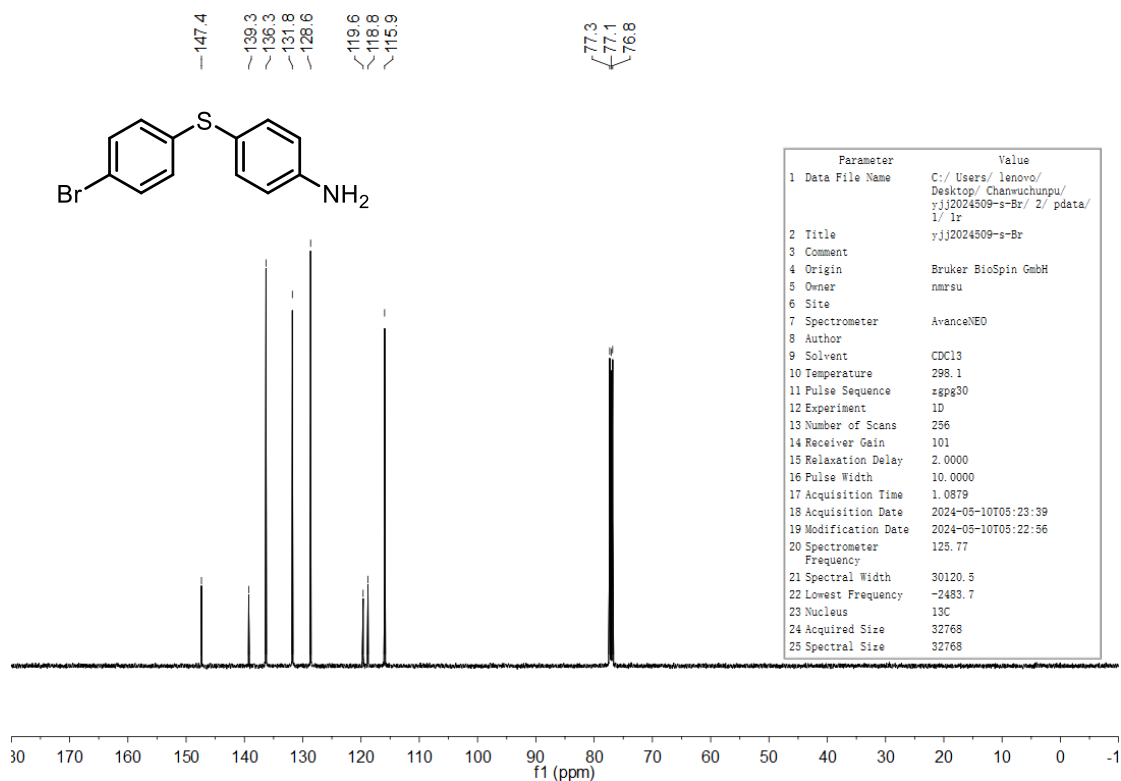
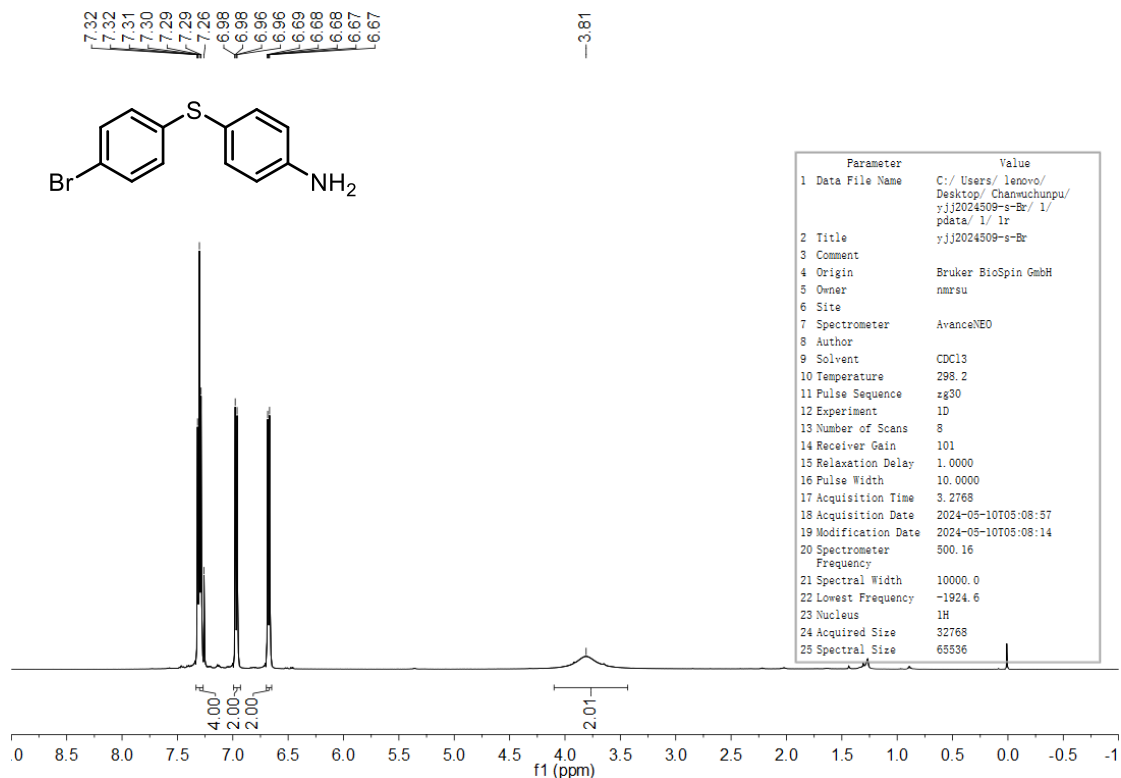
- [S1] J. Vicente, J. A. Abad, R. M. López-Nicolás, *Tetrahedron* **2008**, 64, 6281-6288.
- [S2] D. Yang, K. Yan, W. Wei, J. Zhao, M. Zhang, X. Sheng, G. Li, S. Lu, H. Wang, *J. Org. Chem.* **2015**, 80, 6083-6092.
- [S3] X. Jiang, Z. Shen, C. Zheng, *Tetrahedron Letters*. 61, (2020) 152141.
- [S4] W. Zhao, F. Zhang, G. Deng, *J. Org. Chem.* **2021**, 86, 291-301.
- [S5] X.-L. Fang, R.-Y. Tang, X.-G. Zhang, J.-H. Li, *Synthesis* 2011, **2011**,1099-1105.
- [S6] H. Tian, H. Yang, C. Zhu, H. Fu, *Adv. Synth. Catal.* **2015**, 357, 481-488.
- [S7] D. Yang, K. Yan, W. Wei, J. Zhao, M. Zhang, X. Sheng, G. Li, S. Lu, H. Wang, *J. Org. Chem.* **2015**, 80, 6083-6092.
- [S8] M. Kabir, M. Lorenz, M. Van Linn, *J. Org. Chem.* **2010**, 75, 3626–3643.
- [S9] D. S. Raghuvanshi and N. Verma, *RSC Adv.*, **2017**, 7, 22860-22868.
- [S10] F. Kwong, S. L. Buchwald, *Org. Lett.*, Vol. 4, No. 20, **2002**.
- [S11] Miura S, Shimada M, Marui S, inventors; Patent PCT Int. Appl. WO 2007052843. *Chem. Abstr.* **2007**, 146, 501048.
- [S12] Y. Liu, L. Lam, J. Ye, *Adv. Synth. Catal.* **2020**, 362, 2326-2331.

8. NMR Spectra for the Products

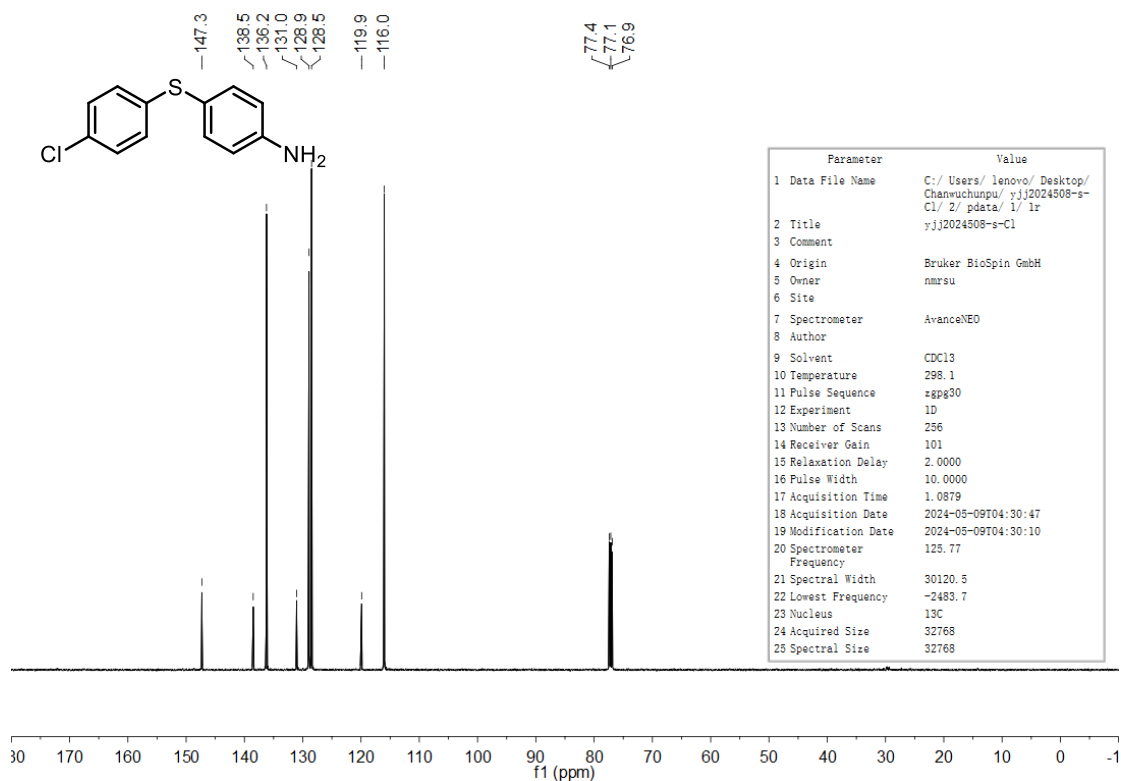
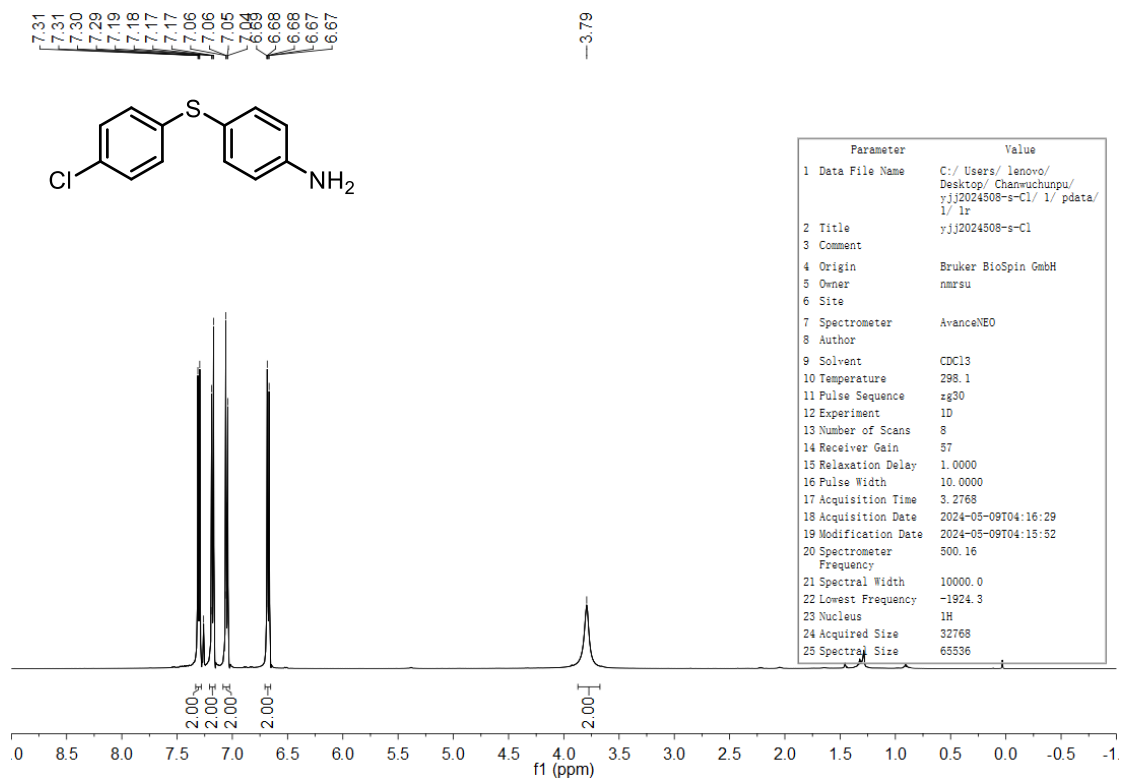
4-(phenylthio)aniline (**3aa**)



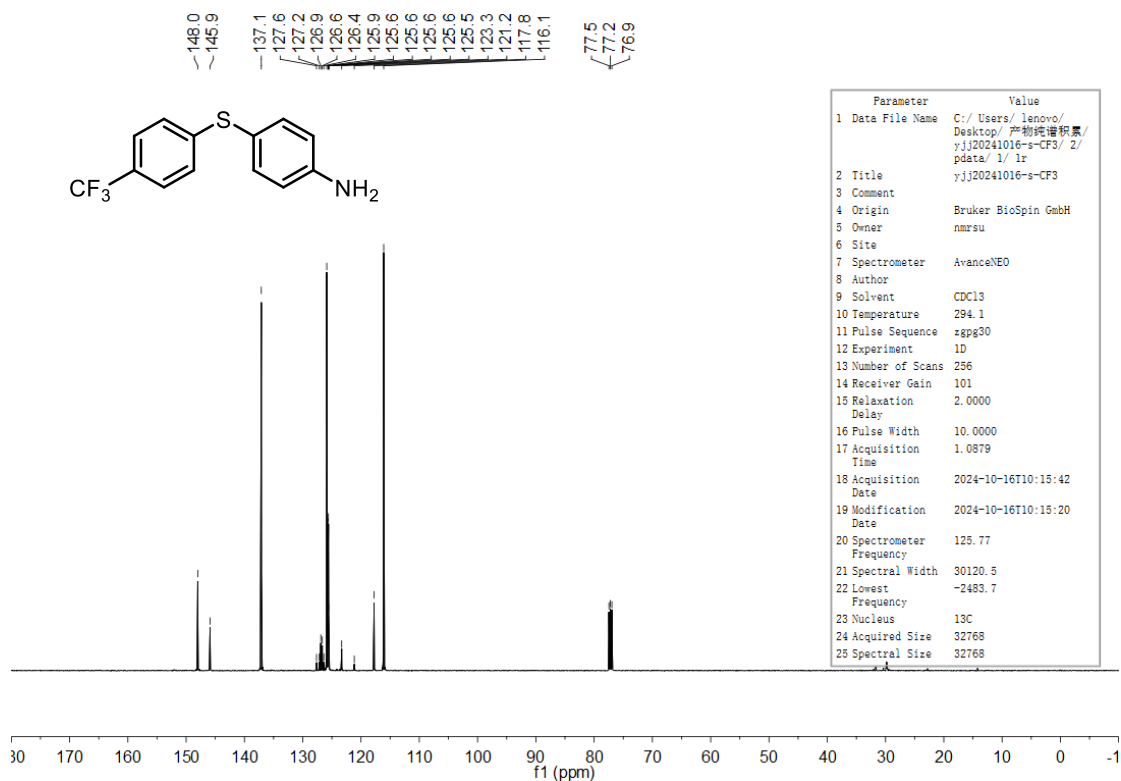
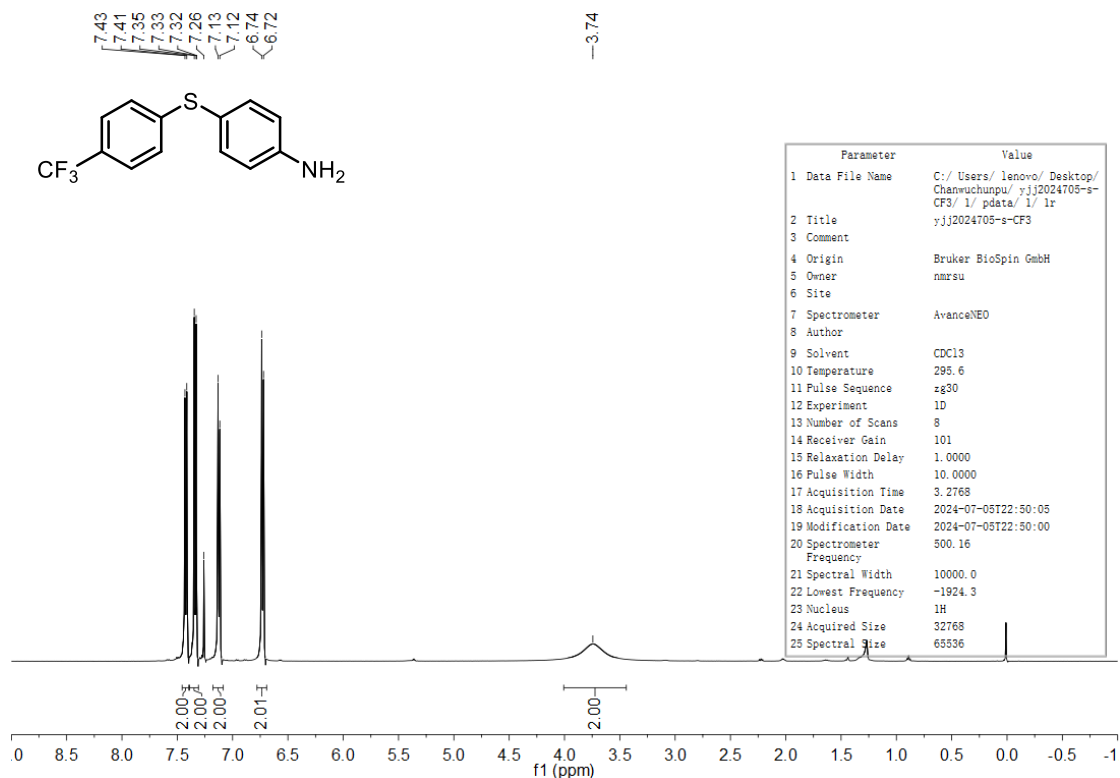
4-((4-bromophenyl)thio)aniline (**3ba**)

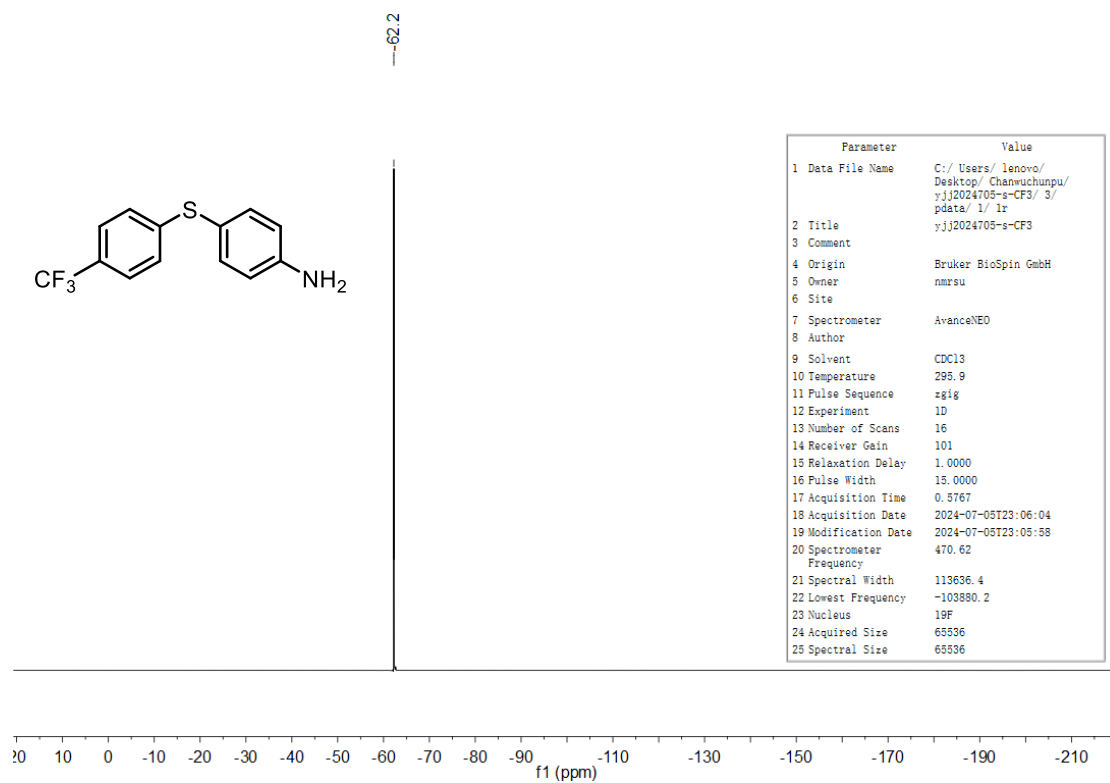


4-((4-chlorophenyl)thio)aniline (**3ca**)

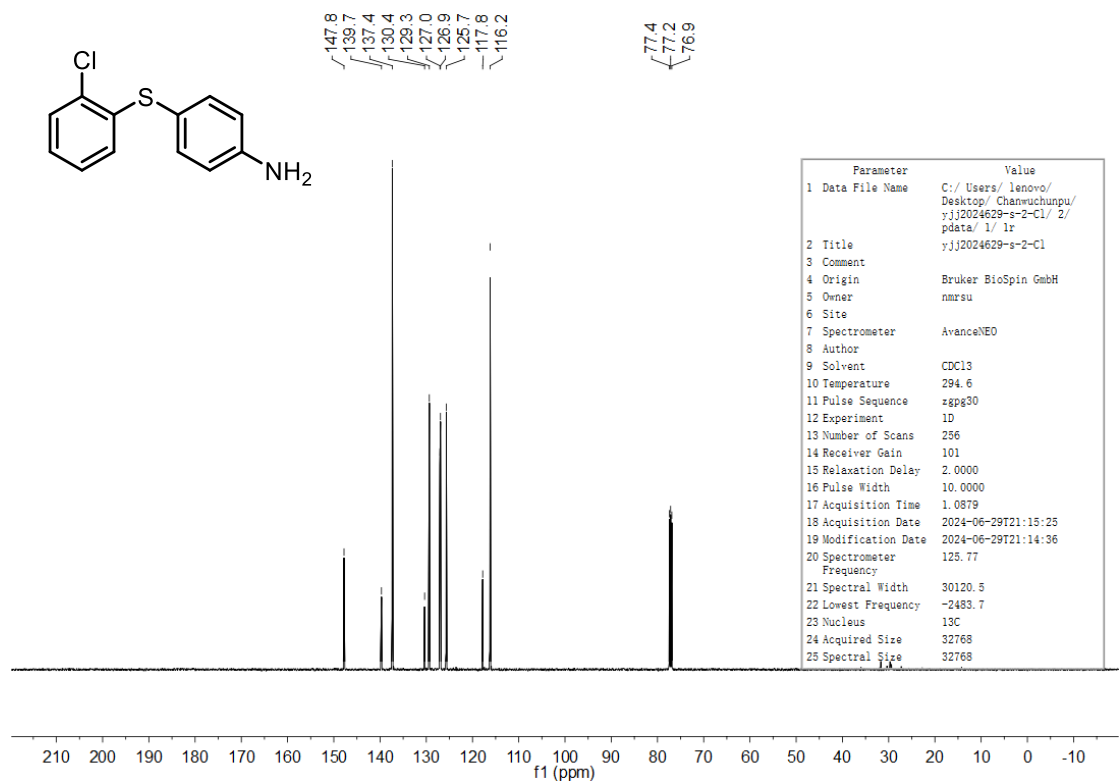
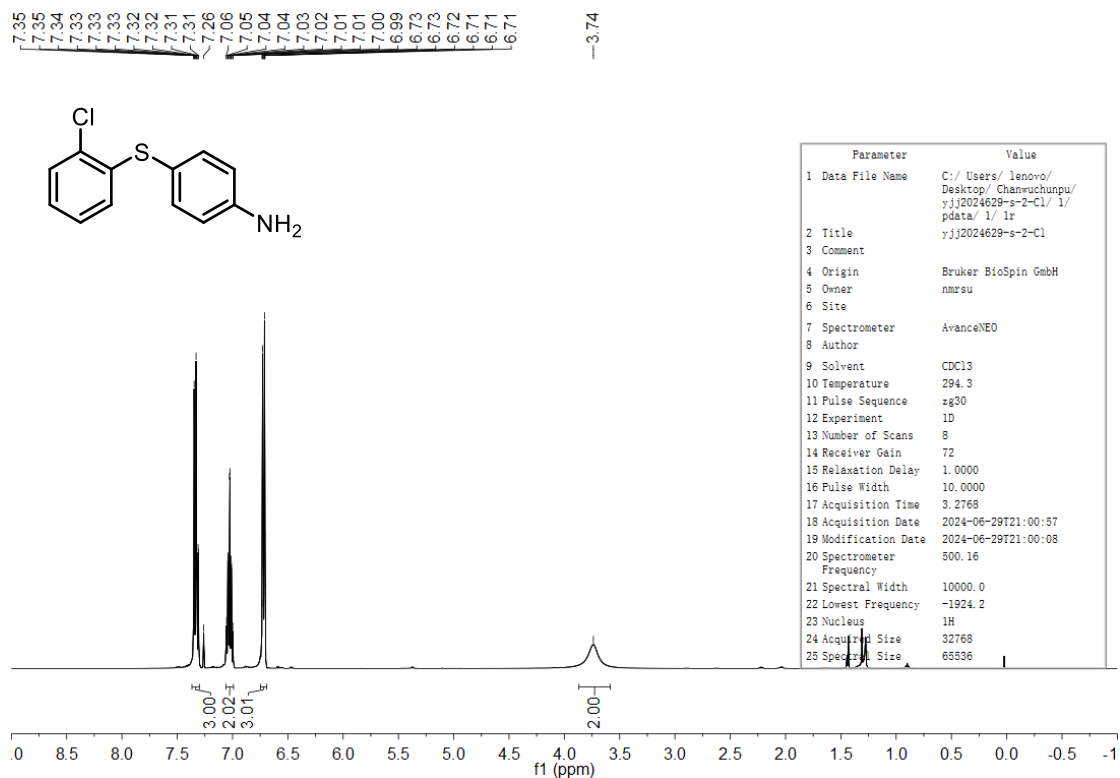


4-((4-(trifluoromethyl)phenyl)thio)aniline (**3da**)

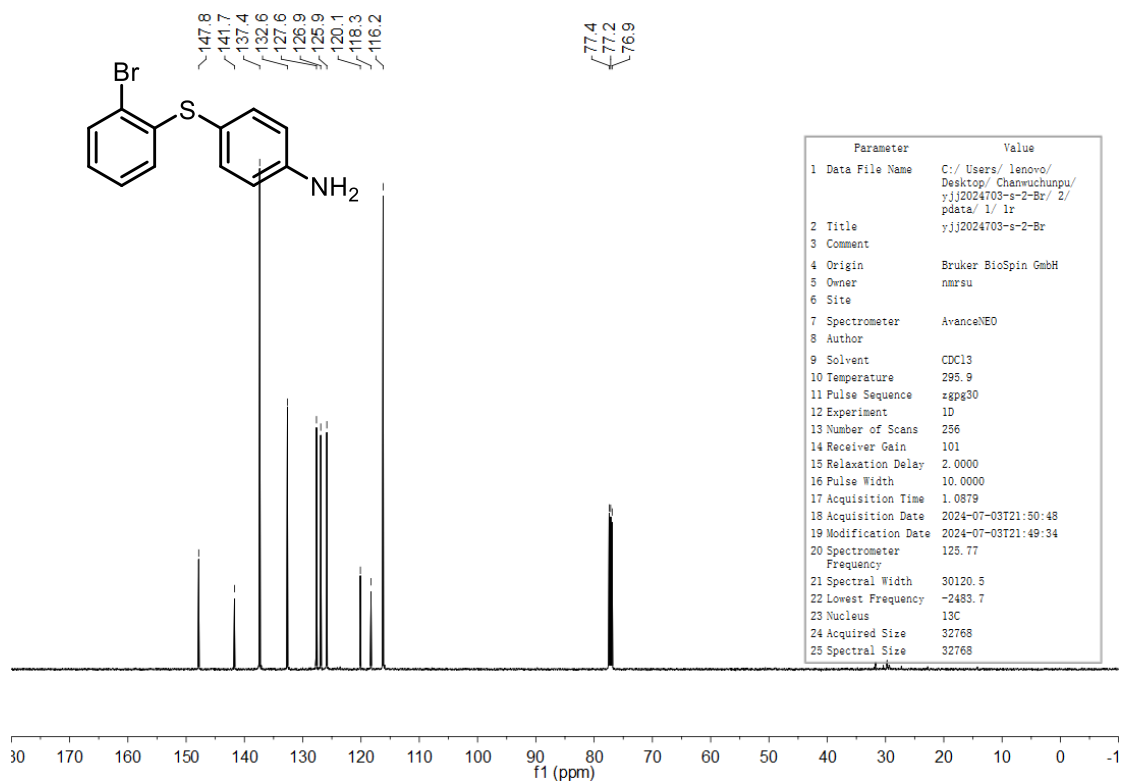
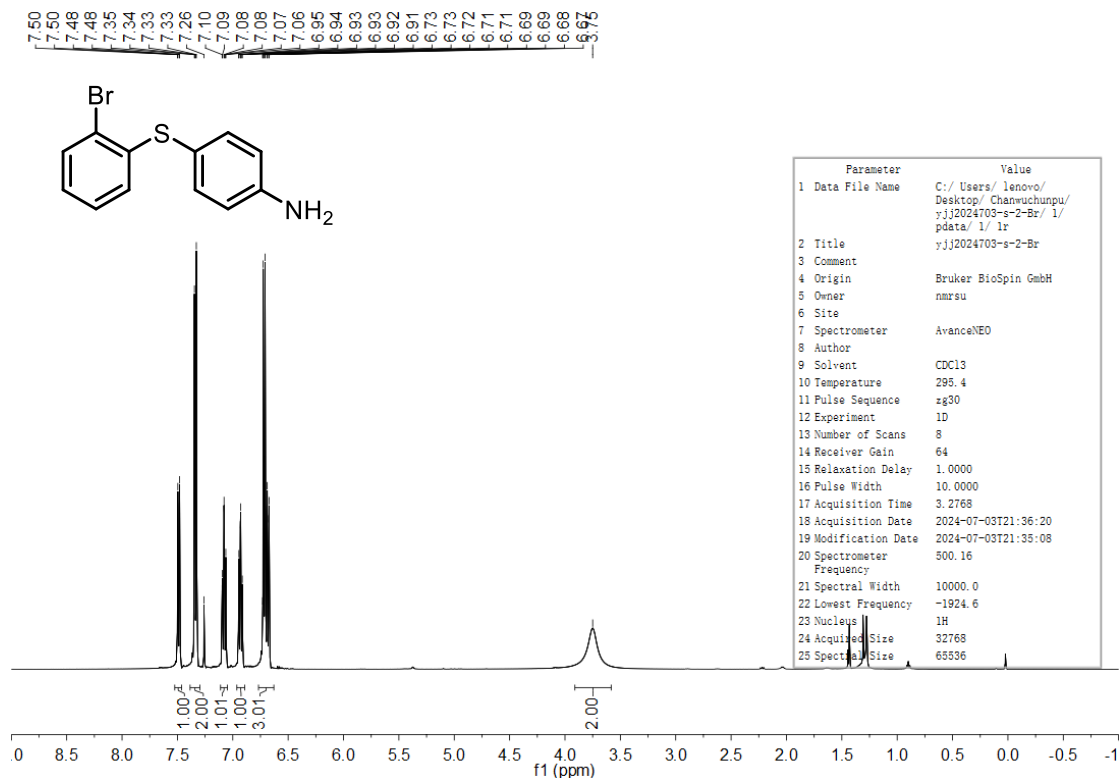




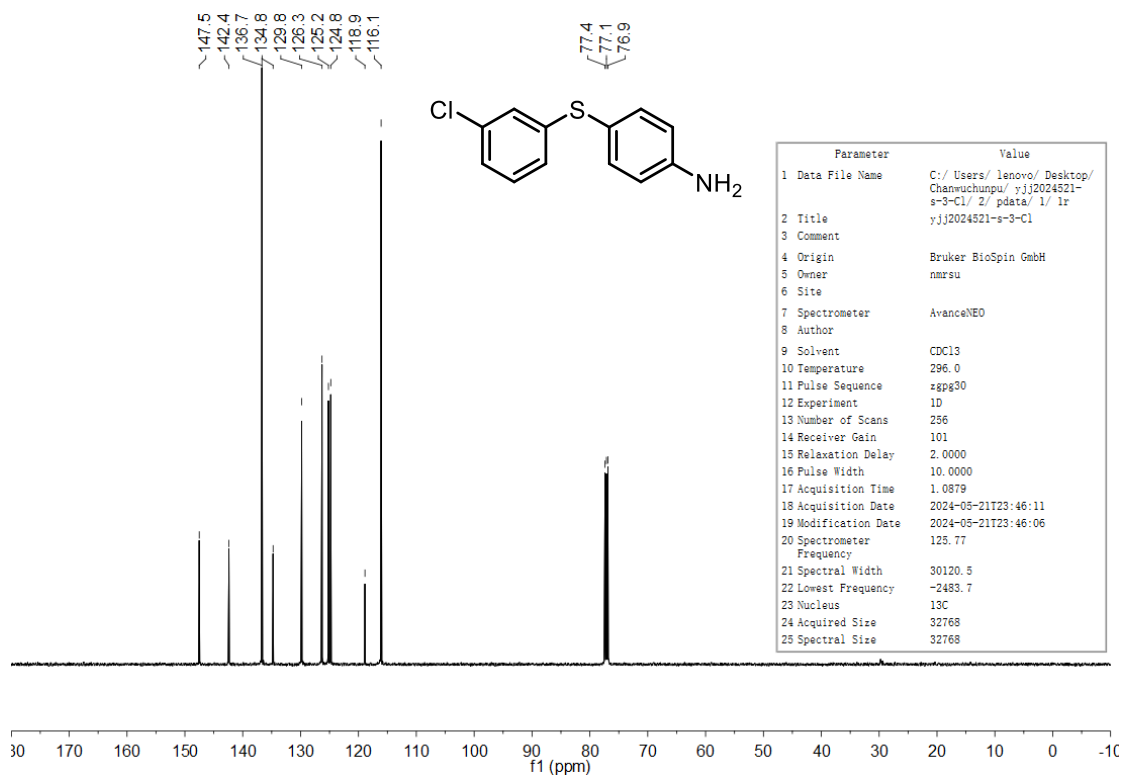
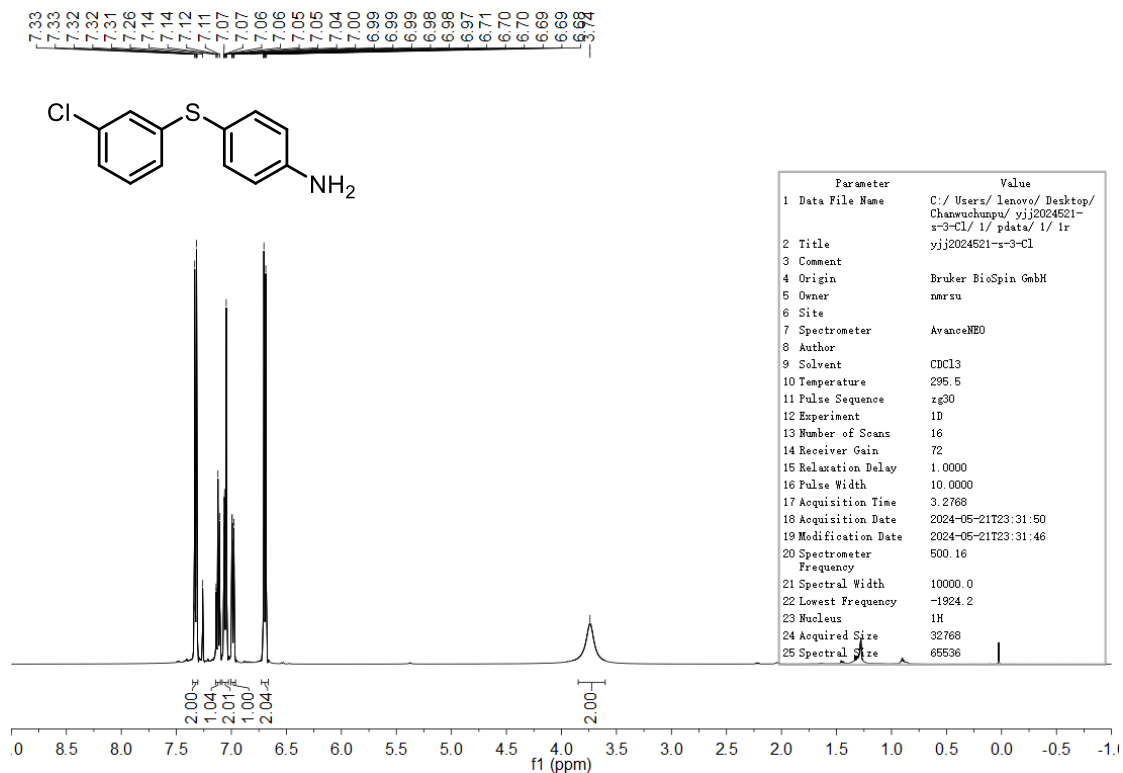
4-((2-chlorophenyl)thio)aniline (3ea)



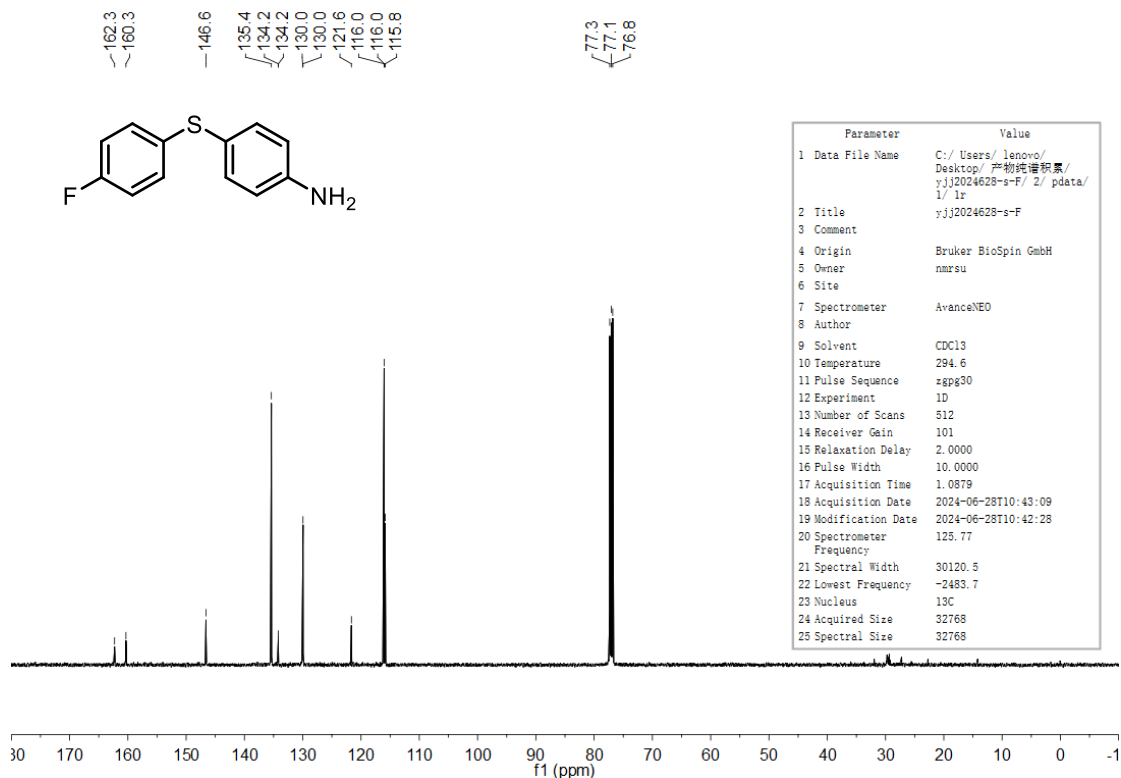
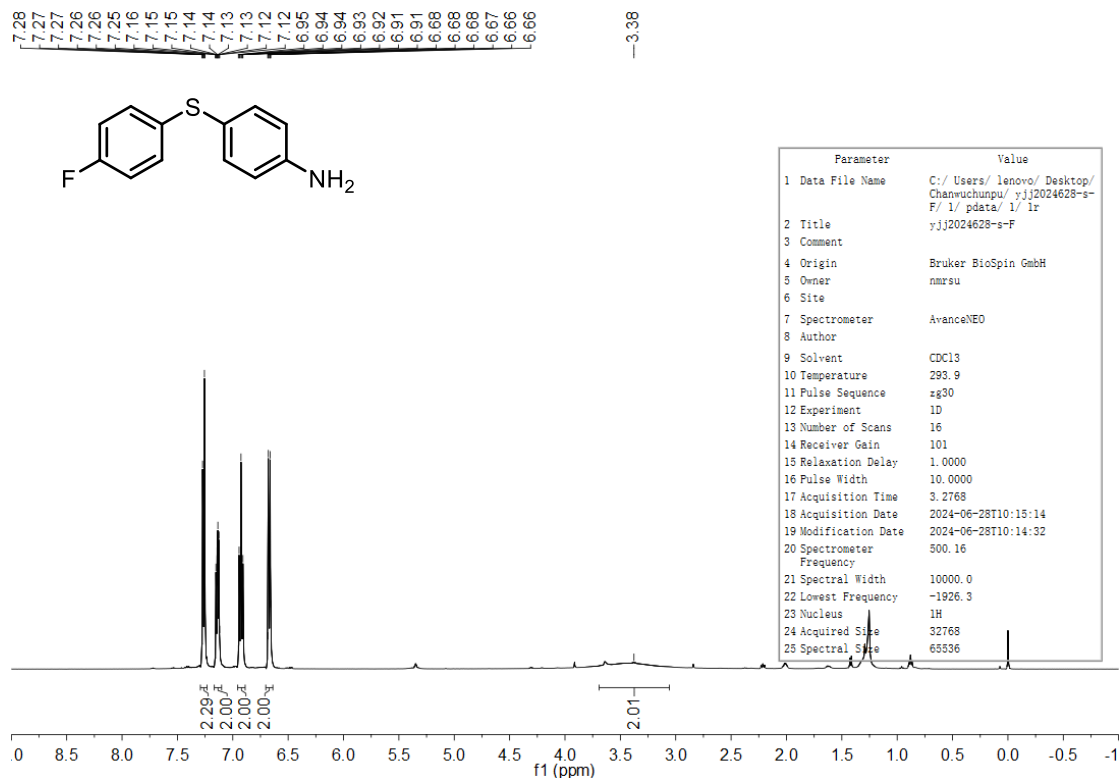
4-((2-bromophenyl)thio)aniline (3fa)

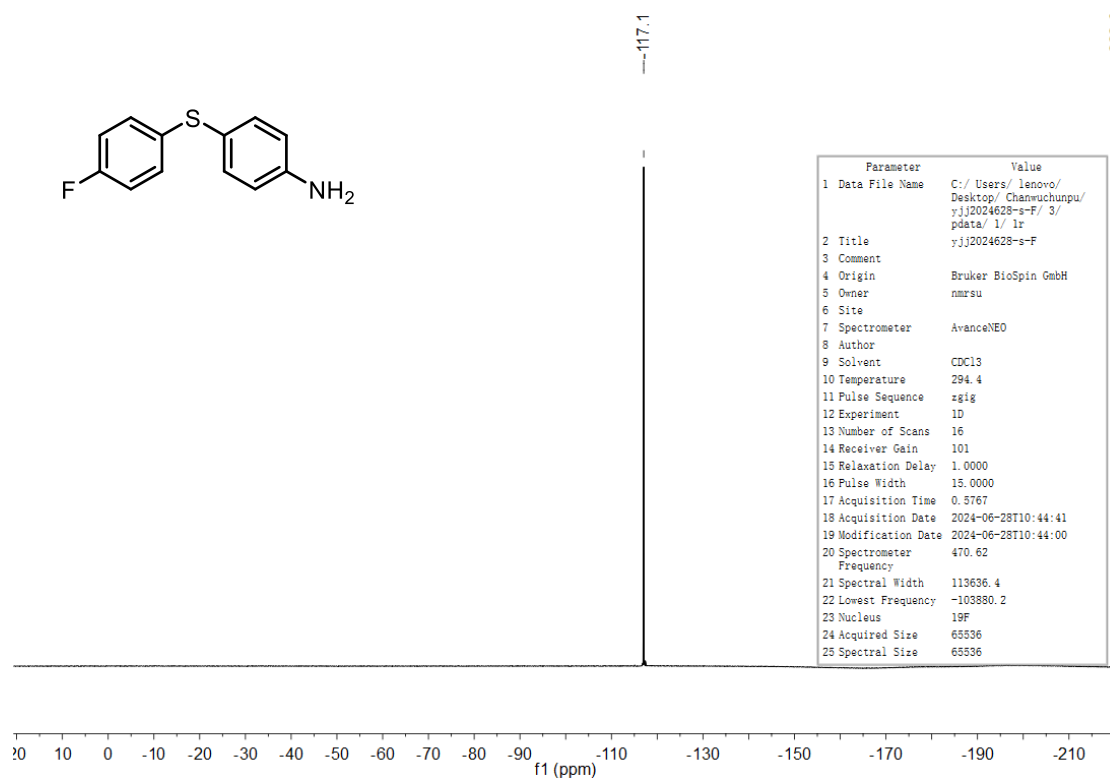


4-((3-chlorophenyl)thio)aniline (3ga)

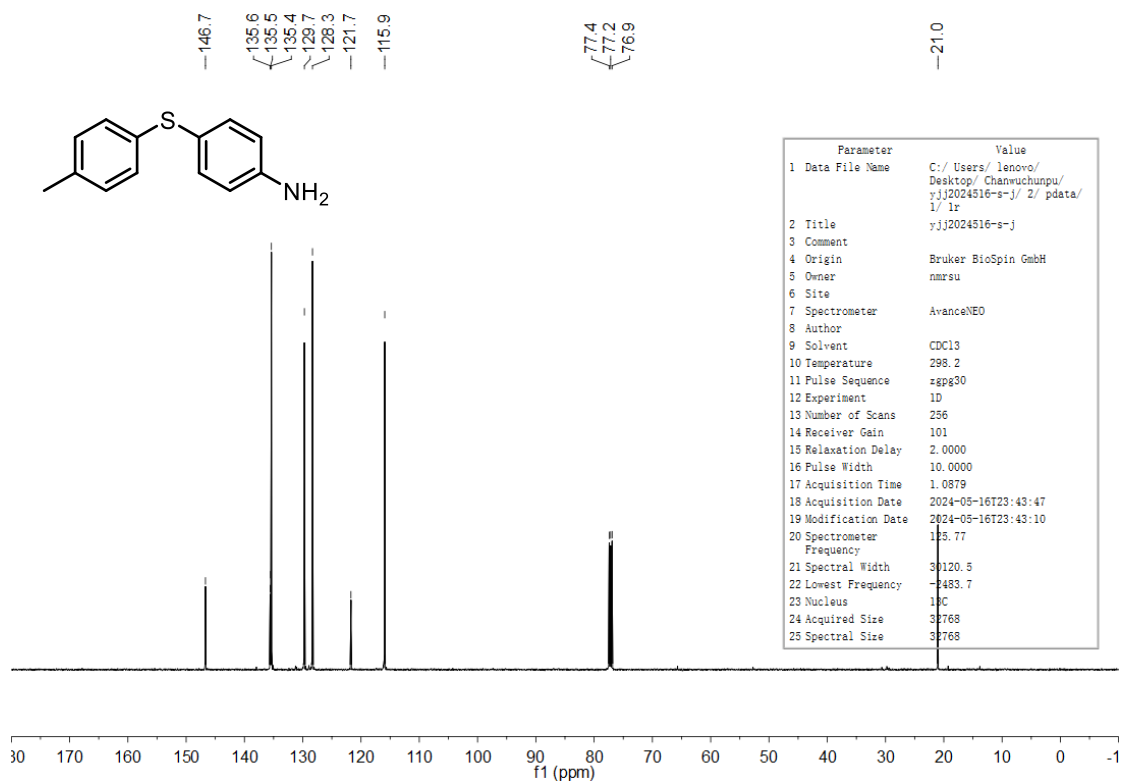
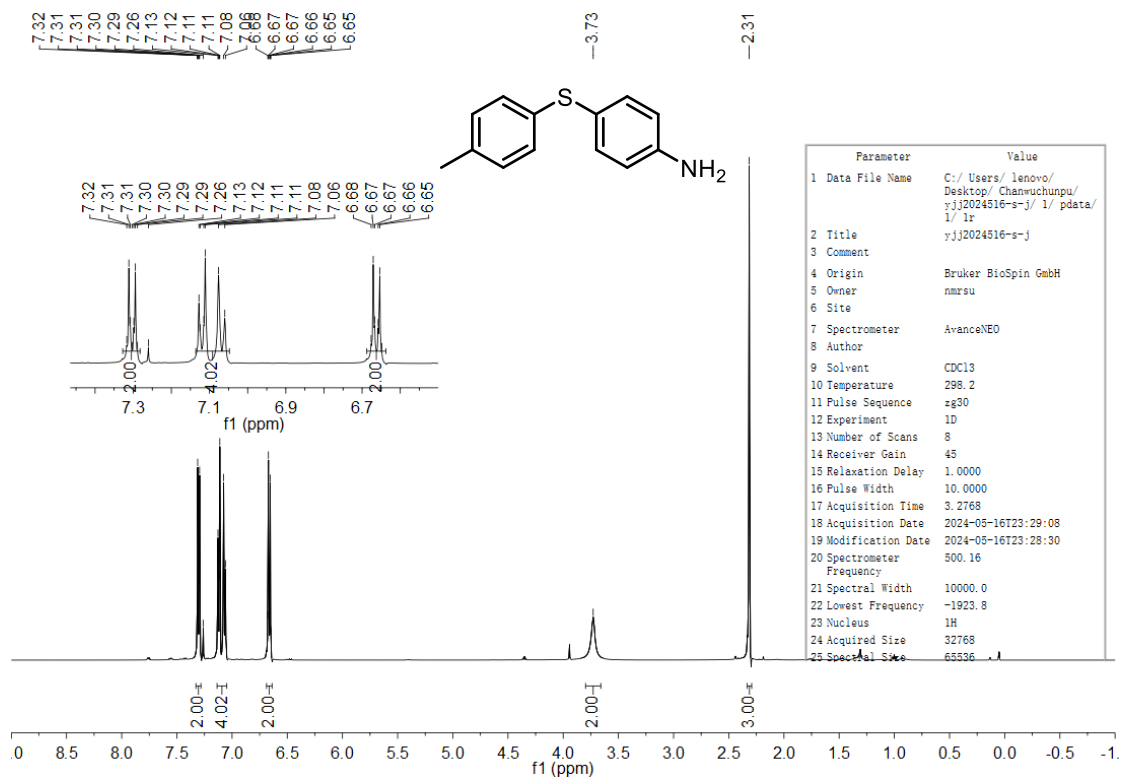


4-((4-fluorophenyl)thio)aniline (**3ha**)

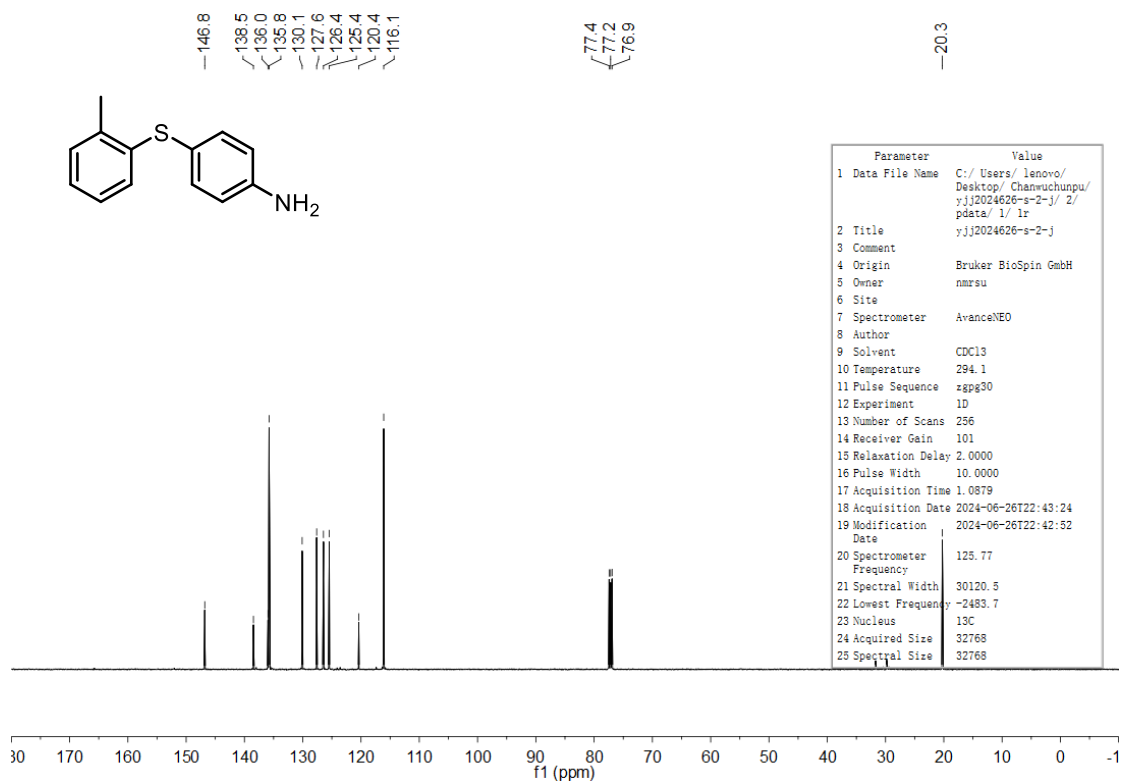
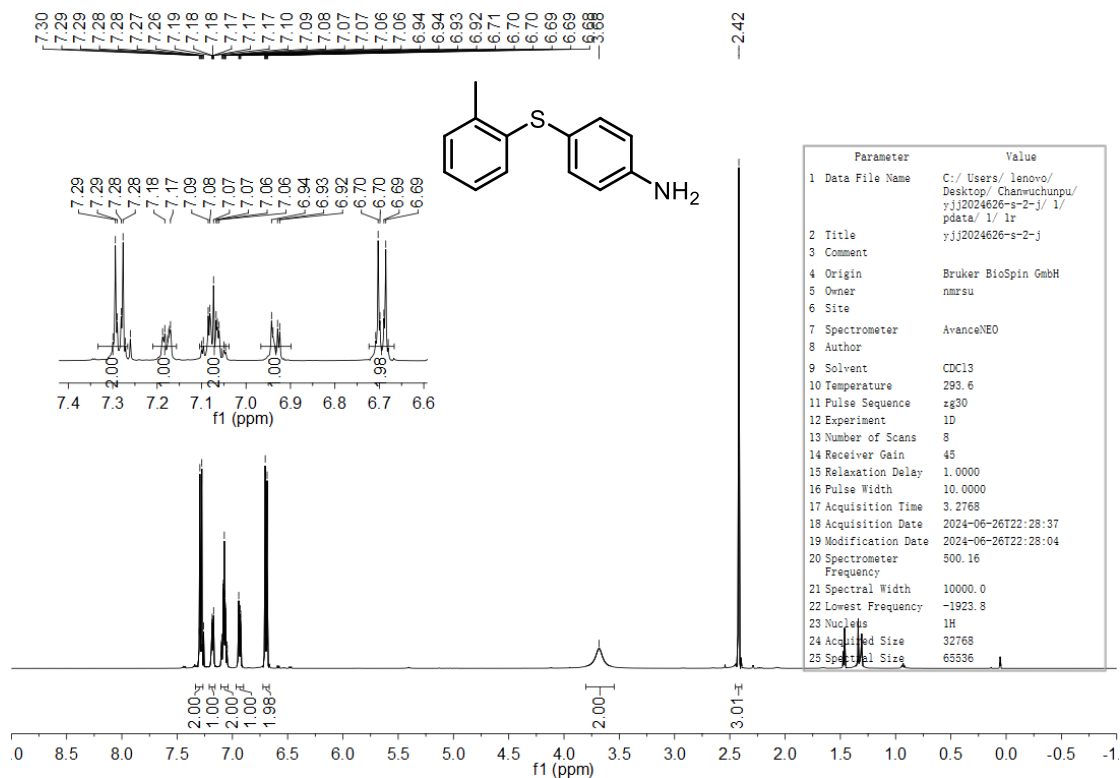




4-(p-tolylthio)aniline (3ia)

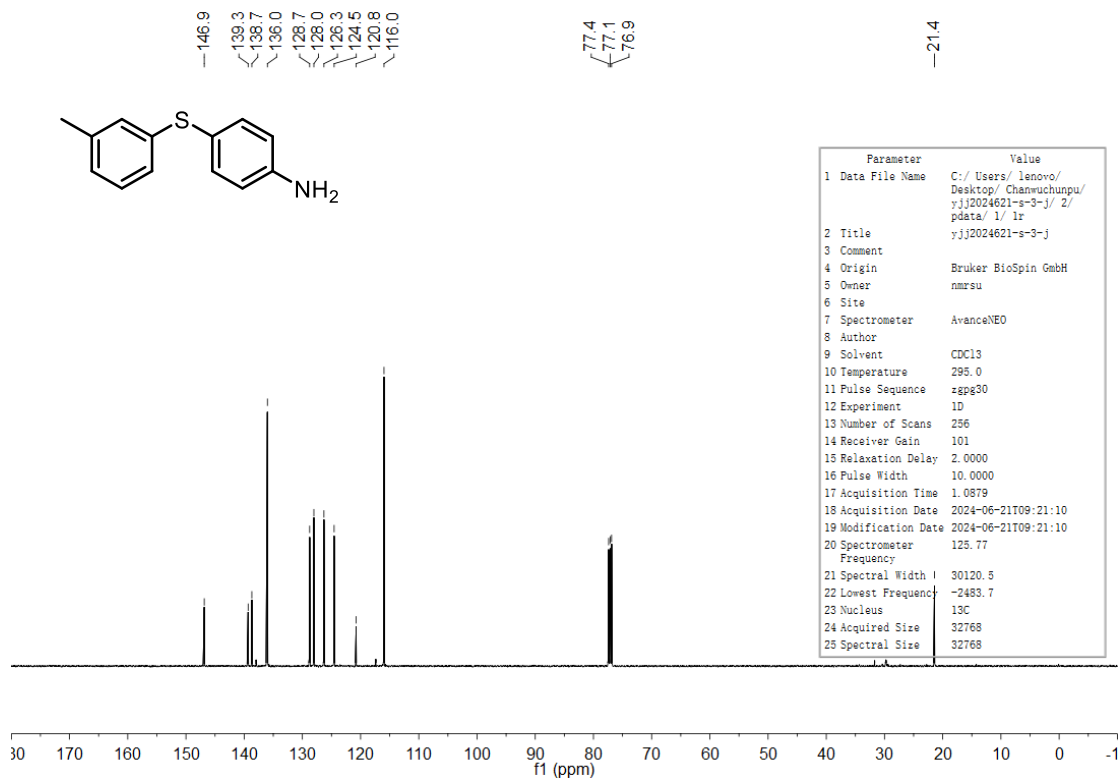


4-(o-tolylthio)aniline (3ja)

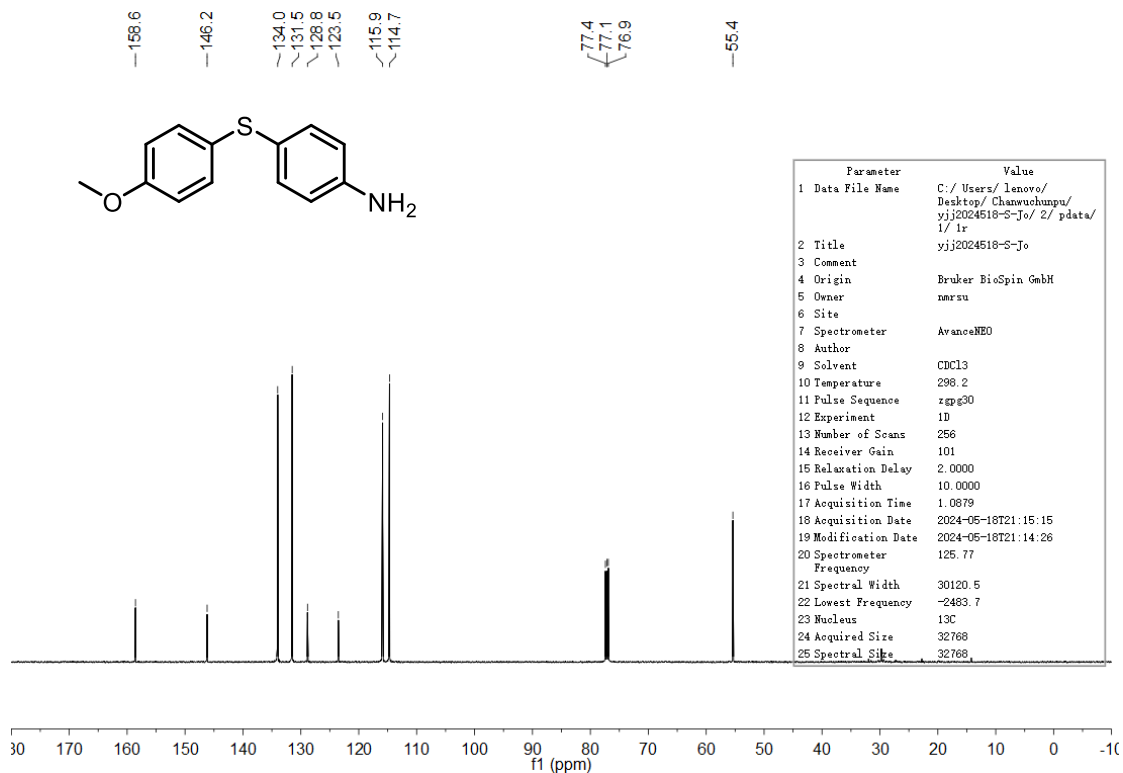
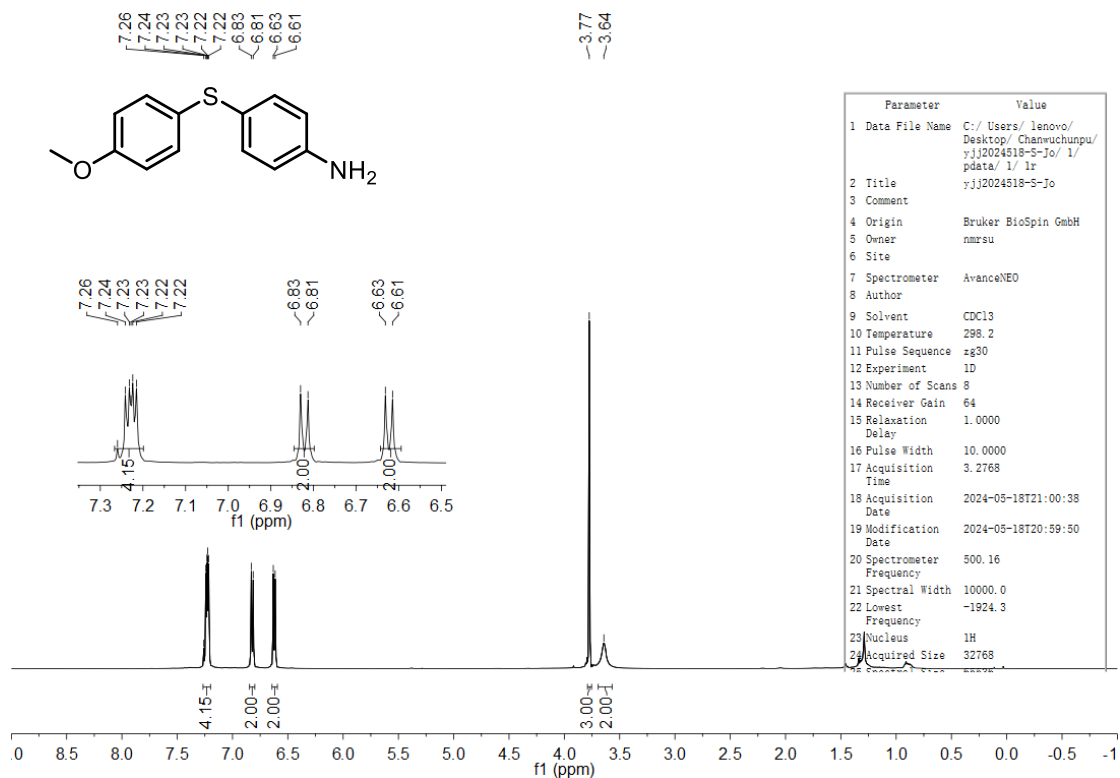


Cc1ccc(Sc2ccc(N)cc2)cc1

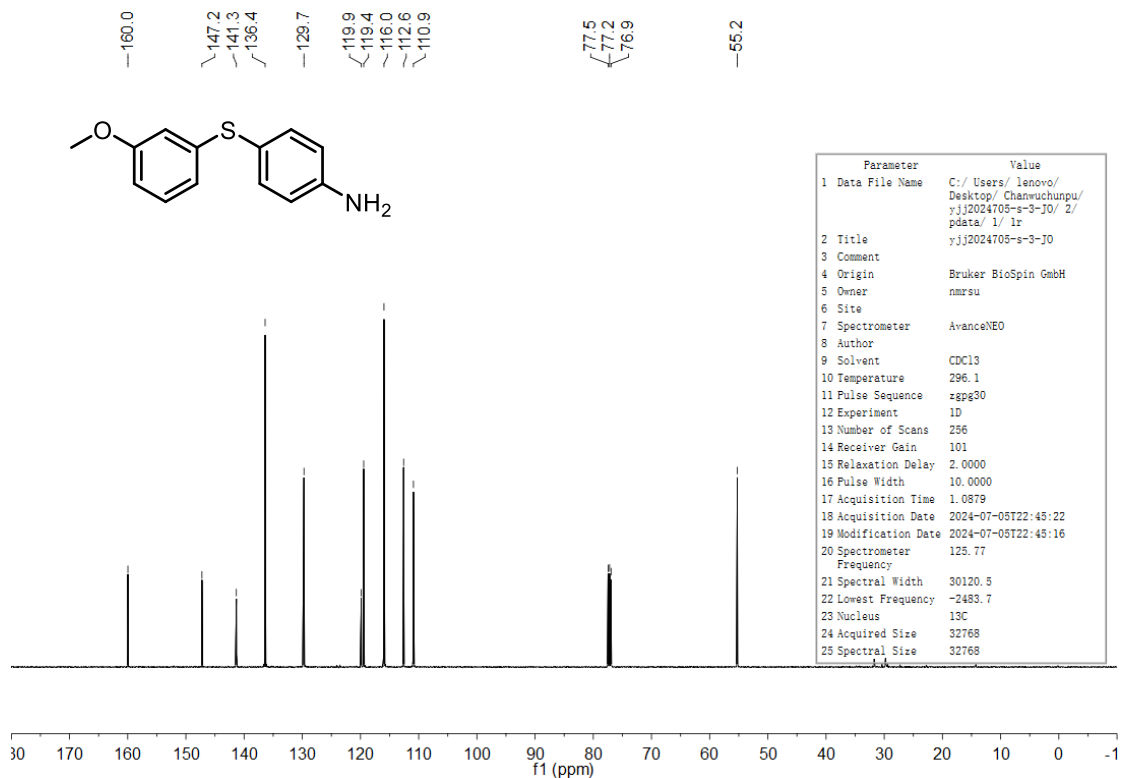
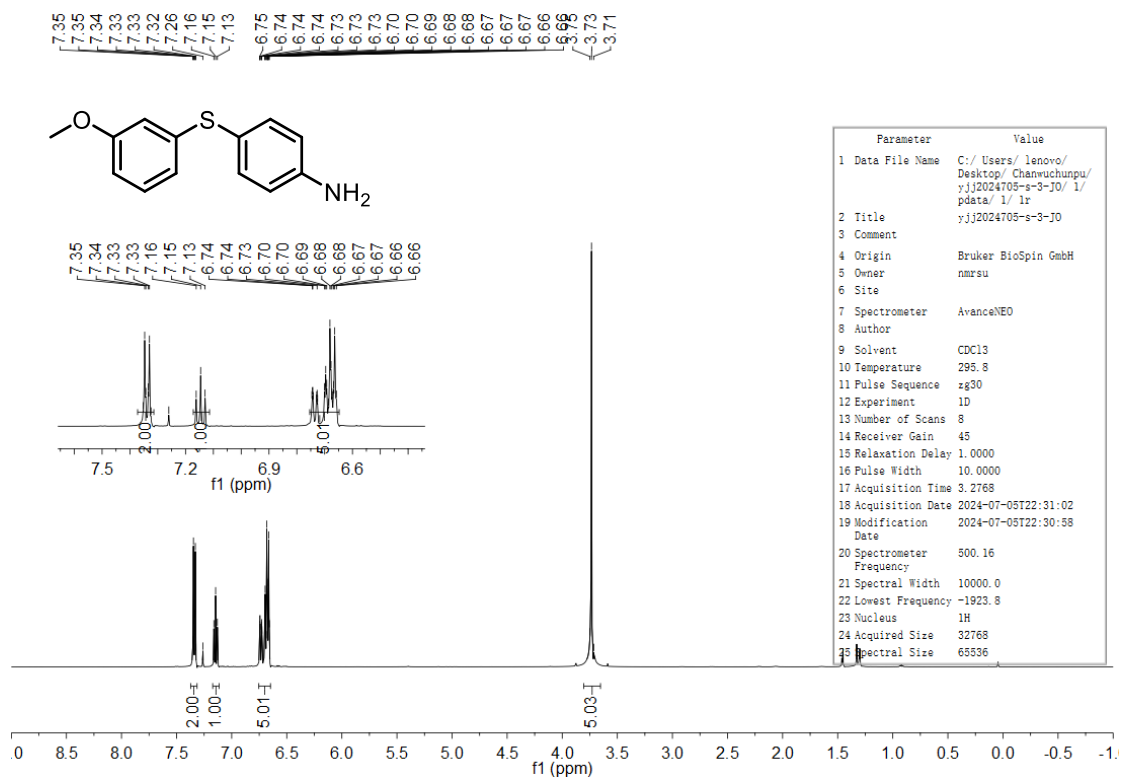
Parameter	Value
1 Data File Name	C:/Users/lanovo/Desktop/Chanwuchunpu/yj2024621-s-3-j/ 1/ pdate/ 1/ lr
2 Title	yj2024621-s-3-j
3 Comment	
4 Origin	Bruker BioSpin GmbH
5 Owner	nmsr
6 Site	
7 Spectrometer	AvanceNEO
8 Author	
9 Solvent	CDCl ₃
10 Temperature	294.5
11 Pulse Sequence	zg30
12 Experiment	1D
13 Number of Scans	8
14 Receiver Gain	72
15 Relaxation Delay	1.0000
16 Pulse Width	10.0000
17 Acquisition Time	3.2768
18 Acquisition Date	2024-06-21T09:06:56
19 Modification Date	2024-06-21T09:06:54
20 Spectrometer Frequency	500.16
21 Spectral Width	10000.0
22 Lowest Frequency	-1923.9
23 Nucleus	¹ H
24 Acquired Size	32768
25 Spectral Size	65536



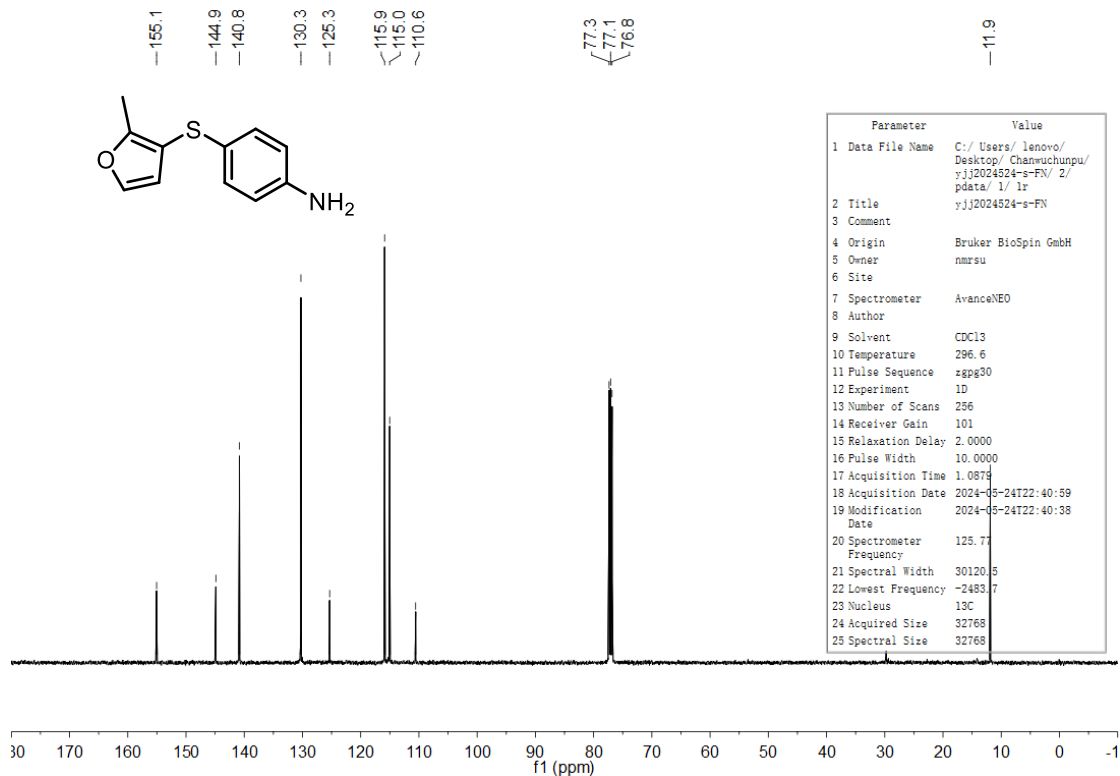
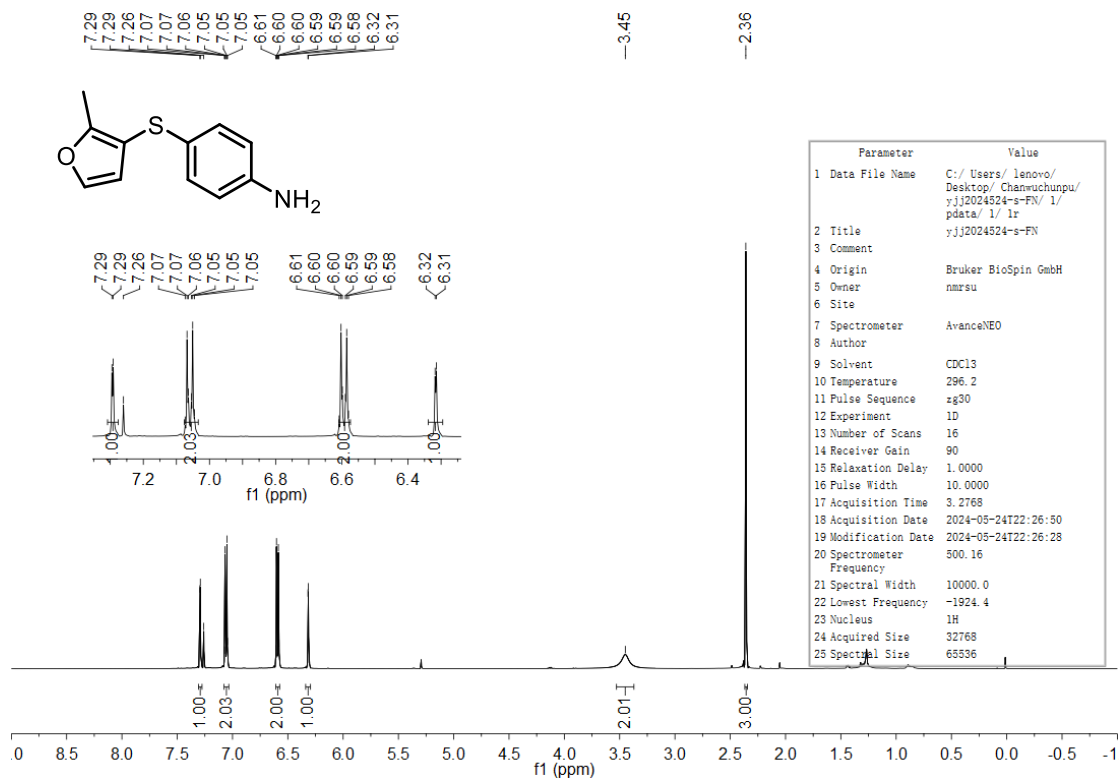
4-((4-methoxyphenyl)thio)aniline (**3la**)



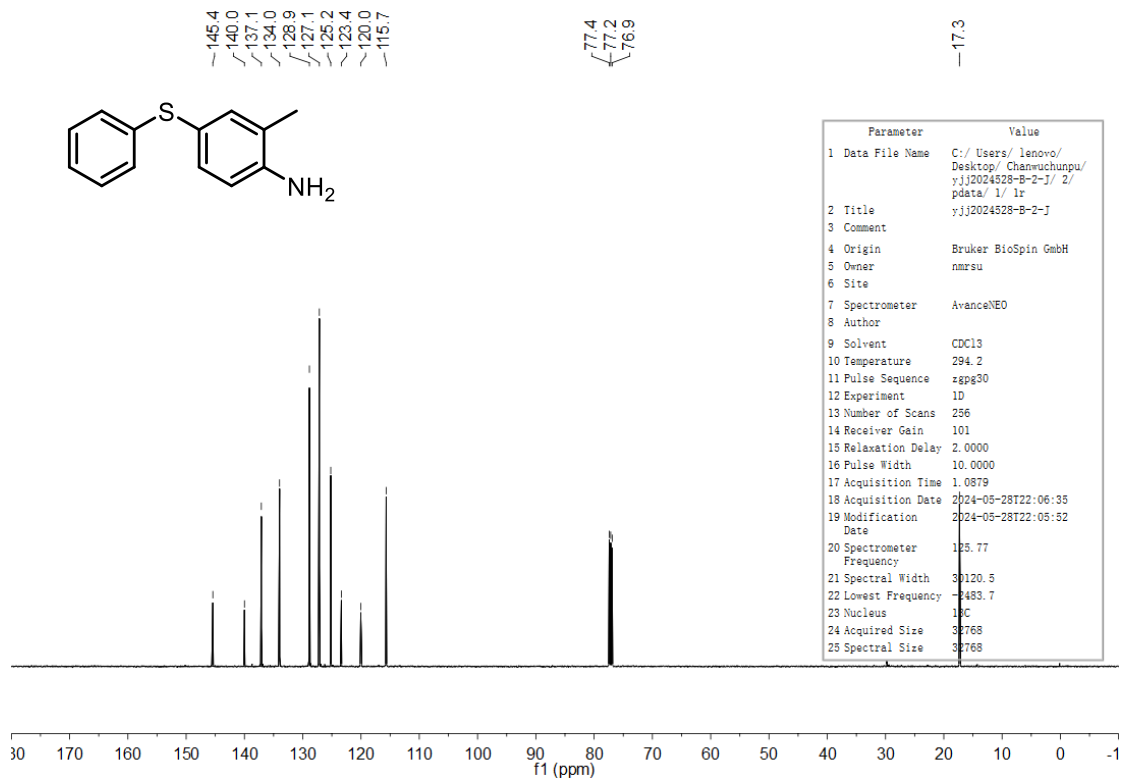
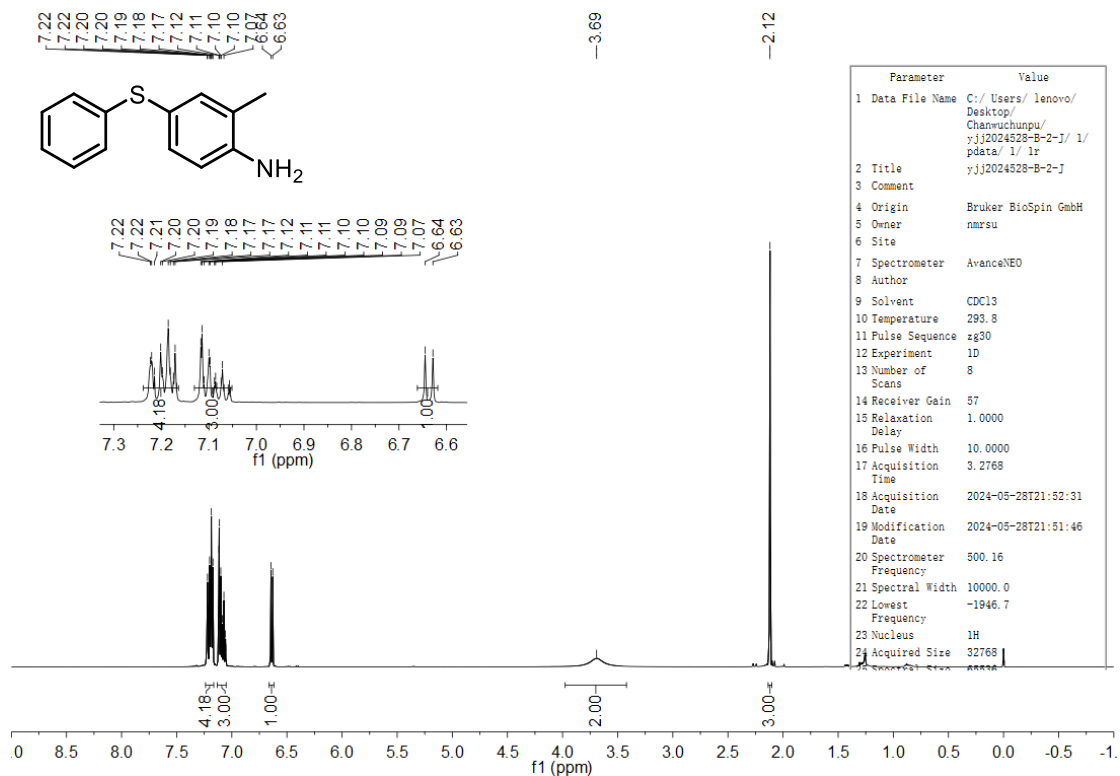
4-((3-methoxyphenyl)thio)aniline (**3ma**)



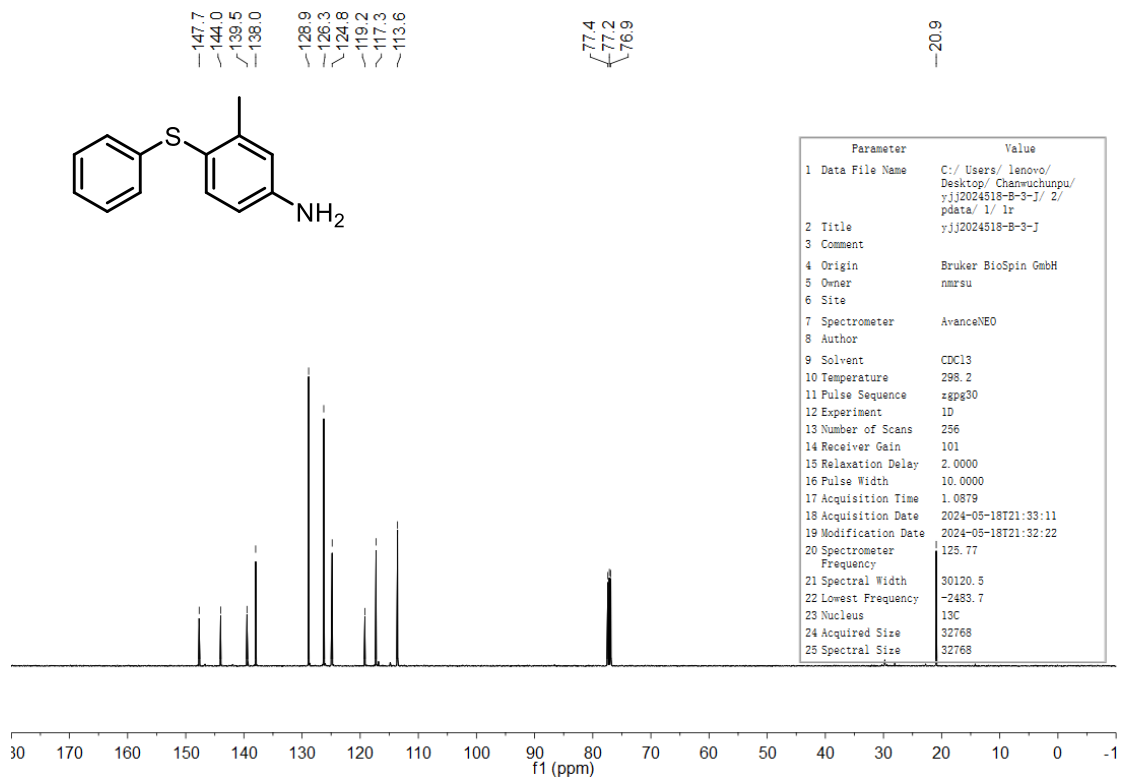
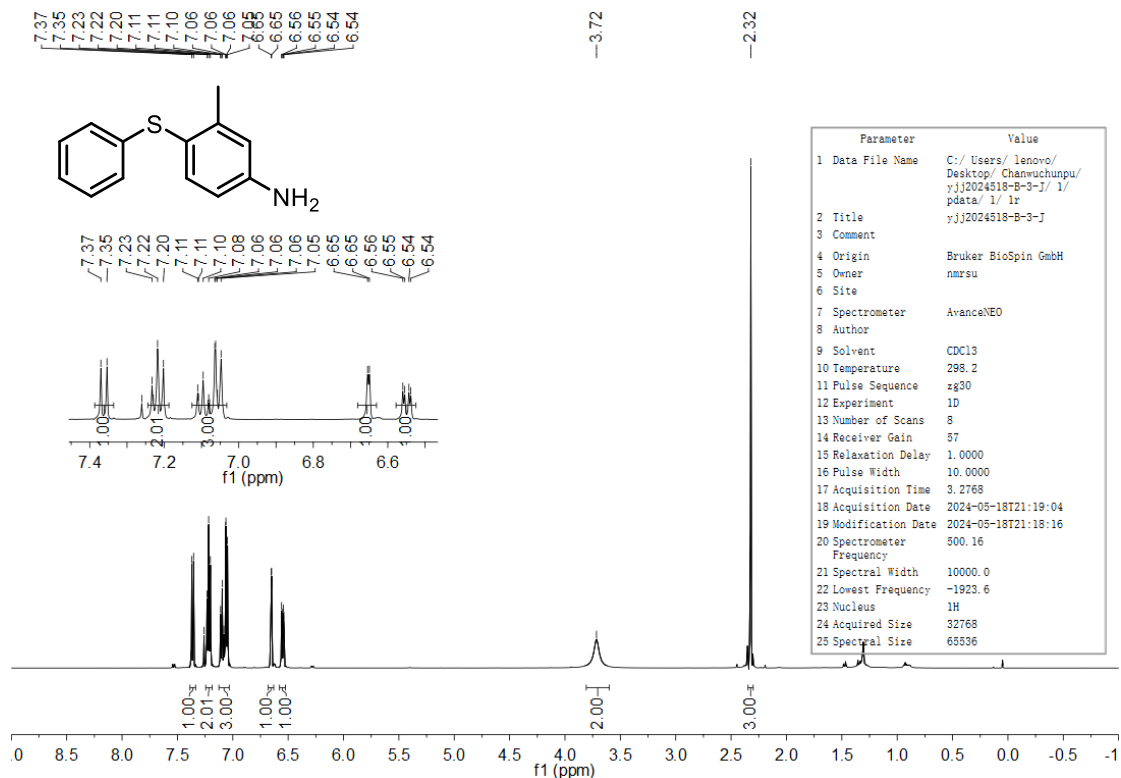
4-((2-methylfuran-3-yl)thio)aniline (**3na**)



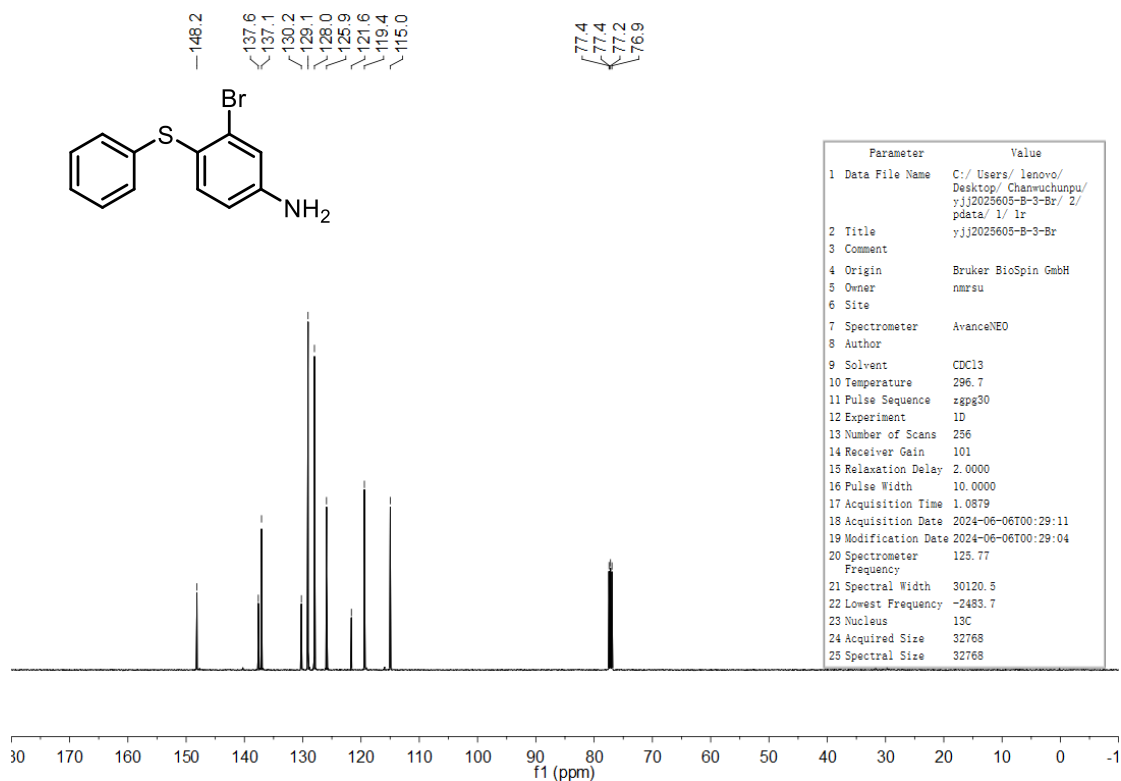
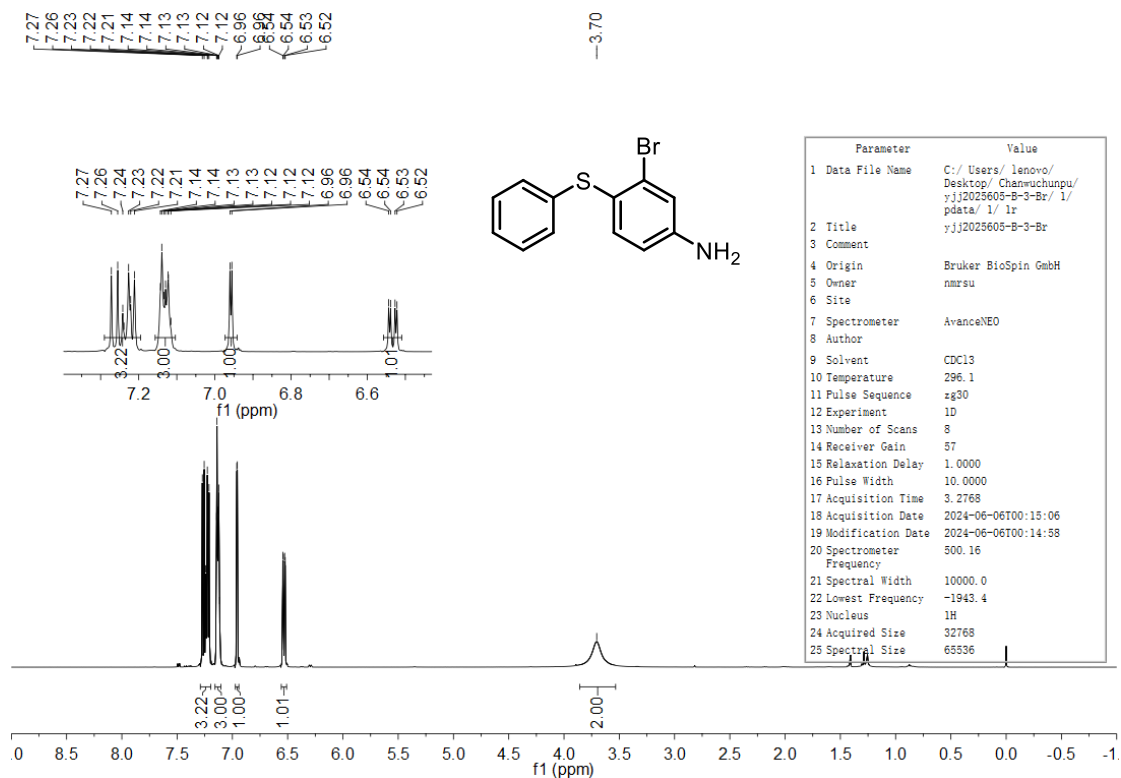
2-methyl-4-(phenylthio)aniline (**3ab**)



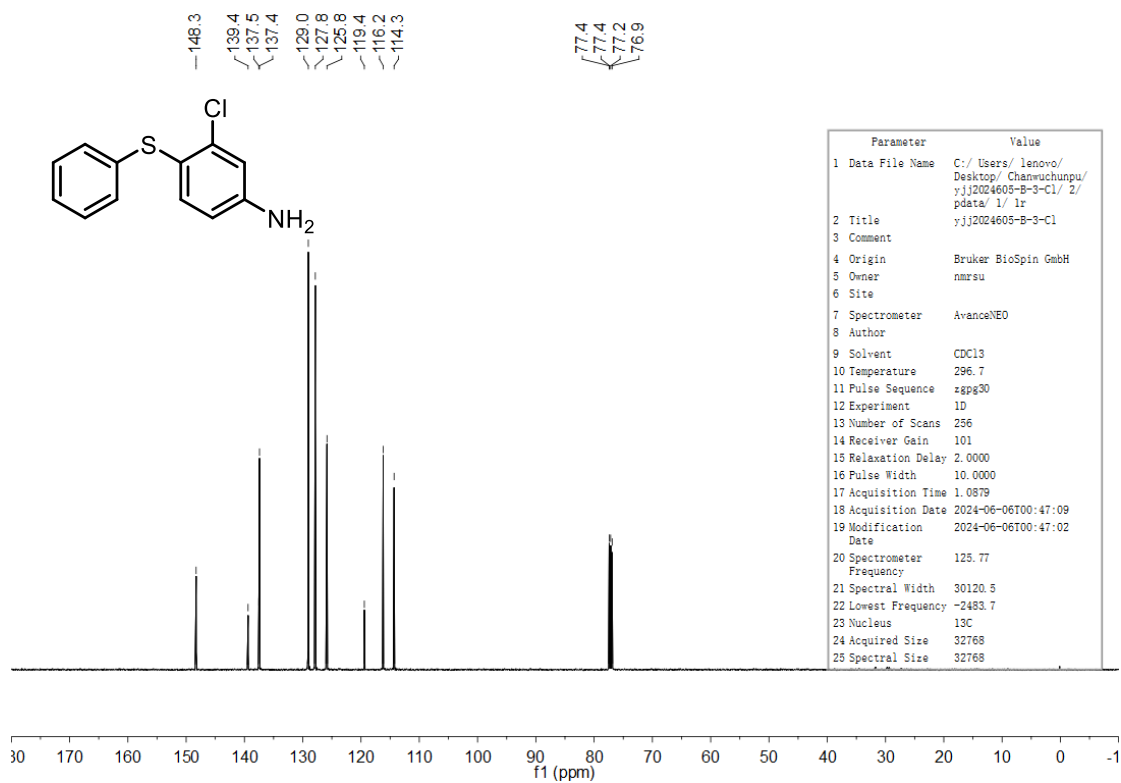
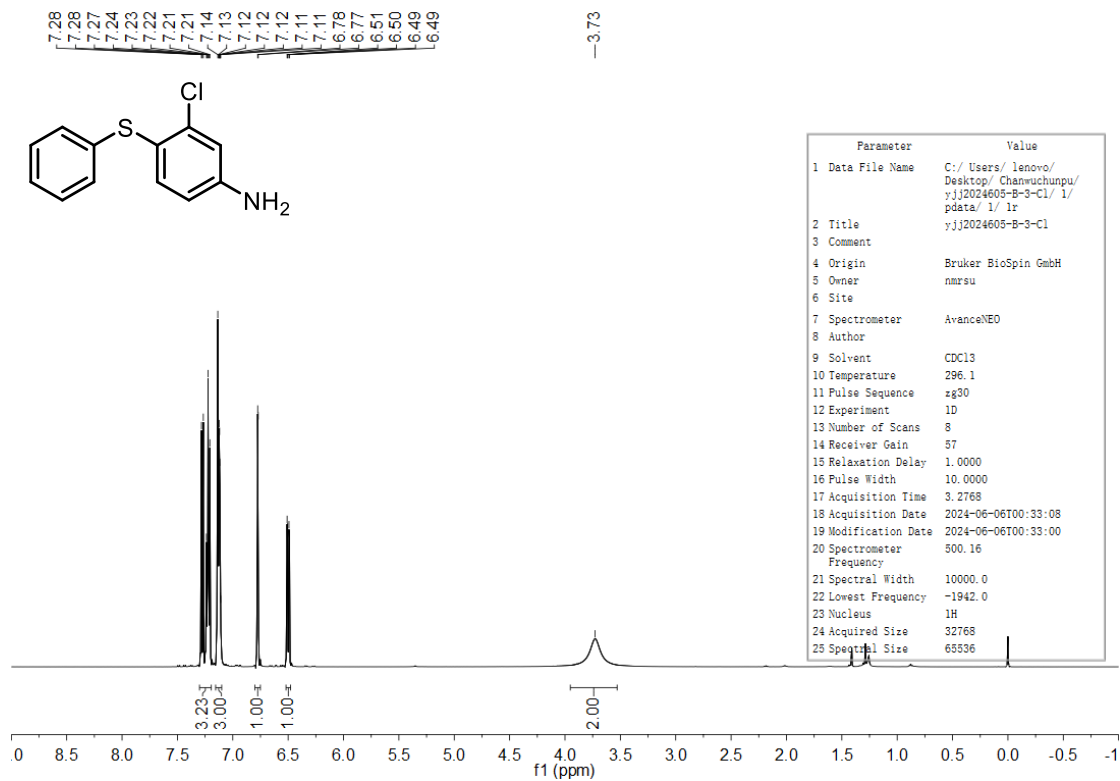
3-methyl-4-(phenylthio)aniline (**3ac**)



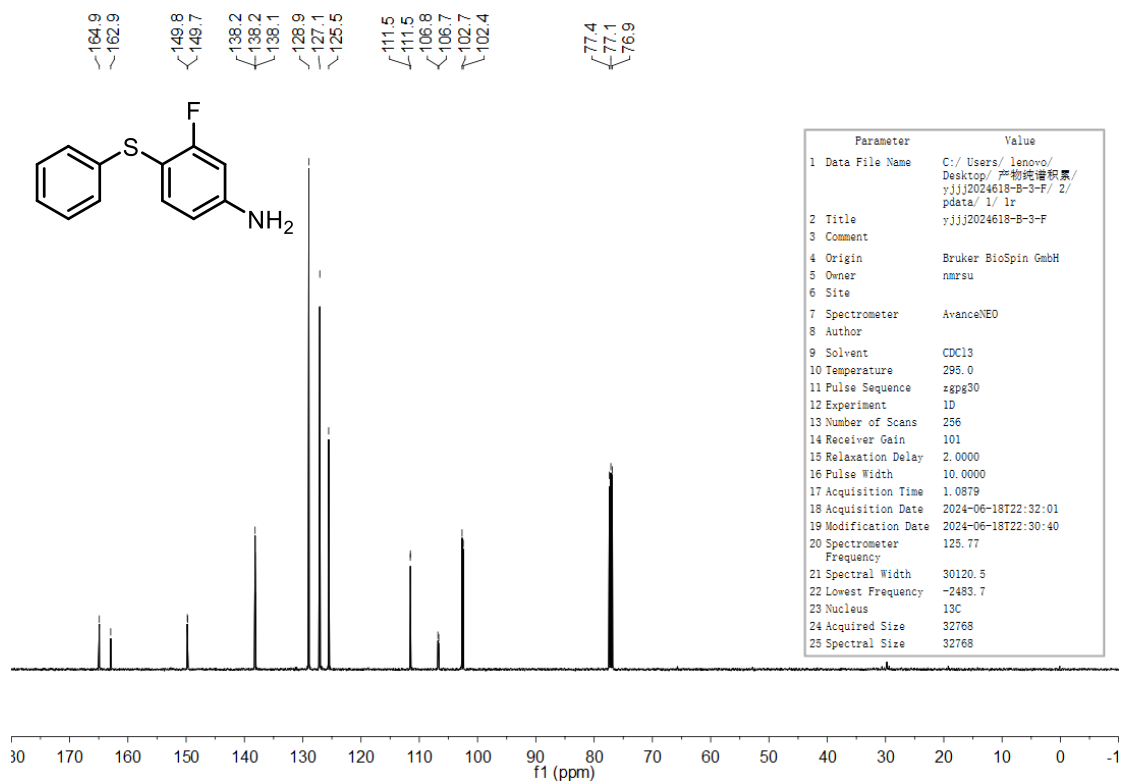
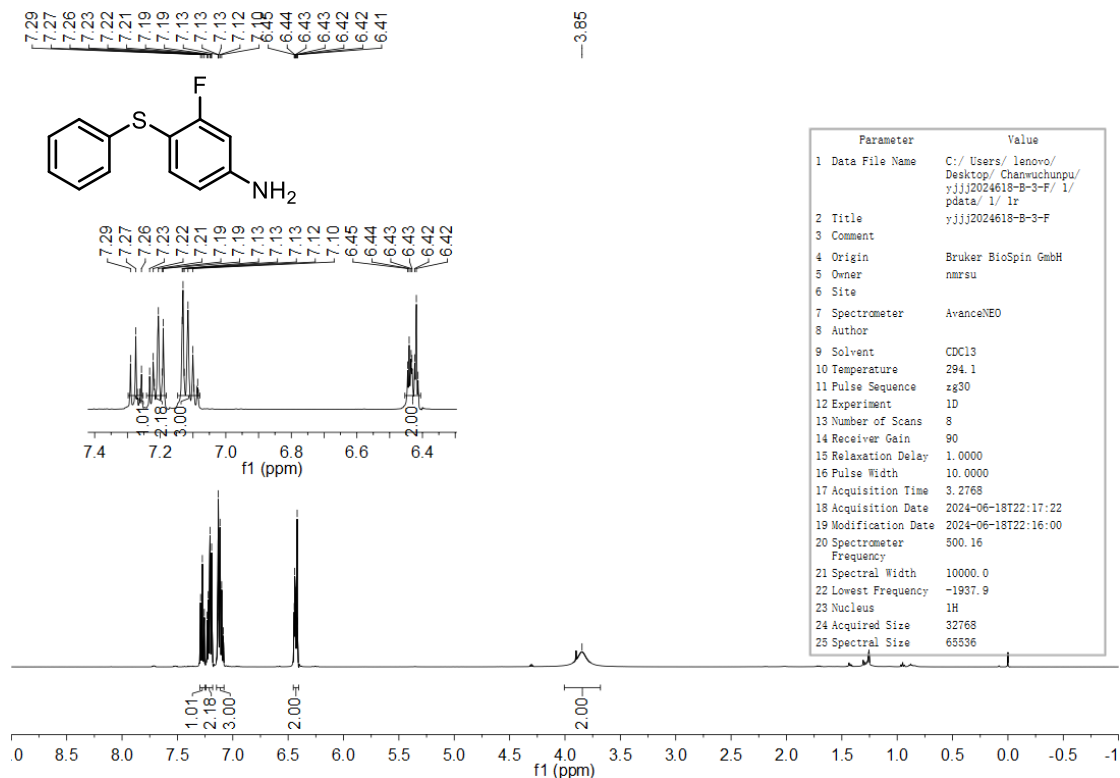
3-bromo-4-(phenylthio)aniline (**3ad**)

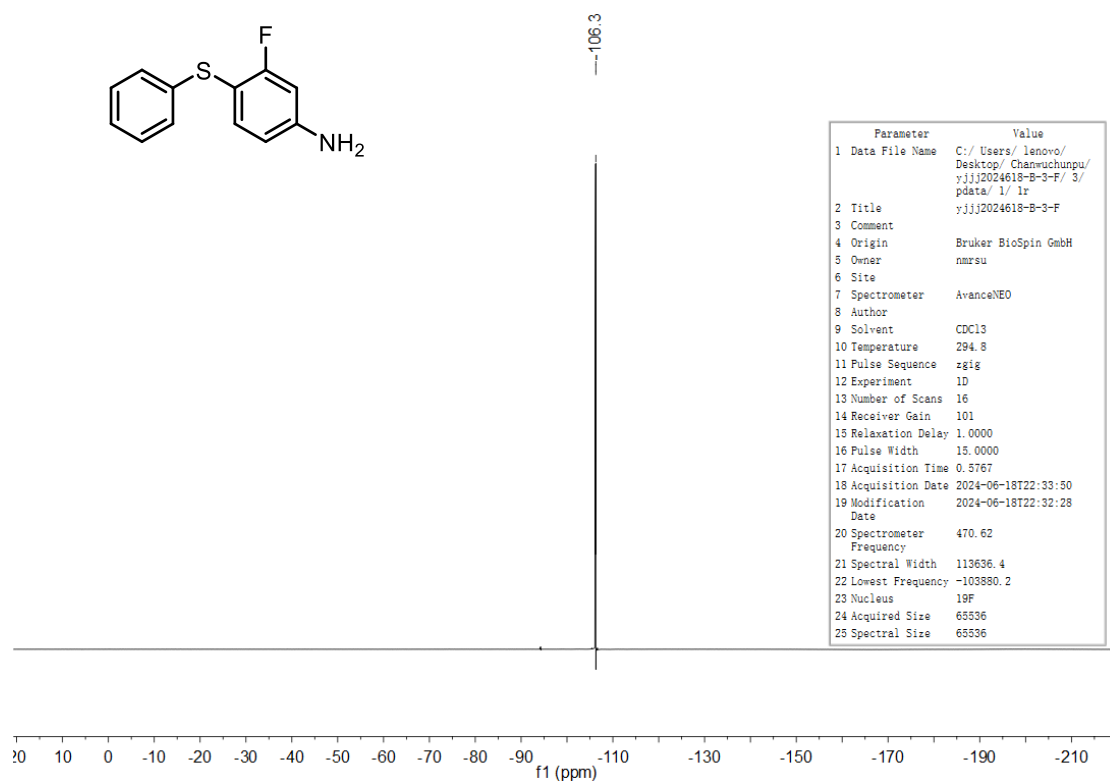


3-chloro-4-(phenylthio)aniline (**3ae**)

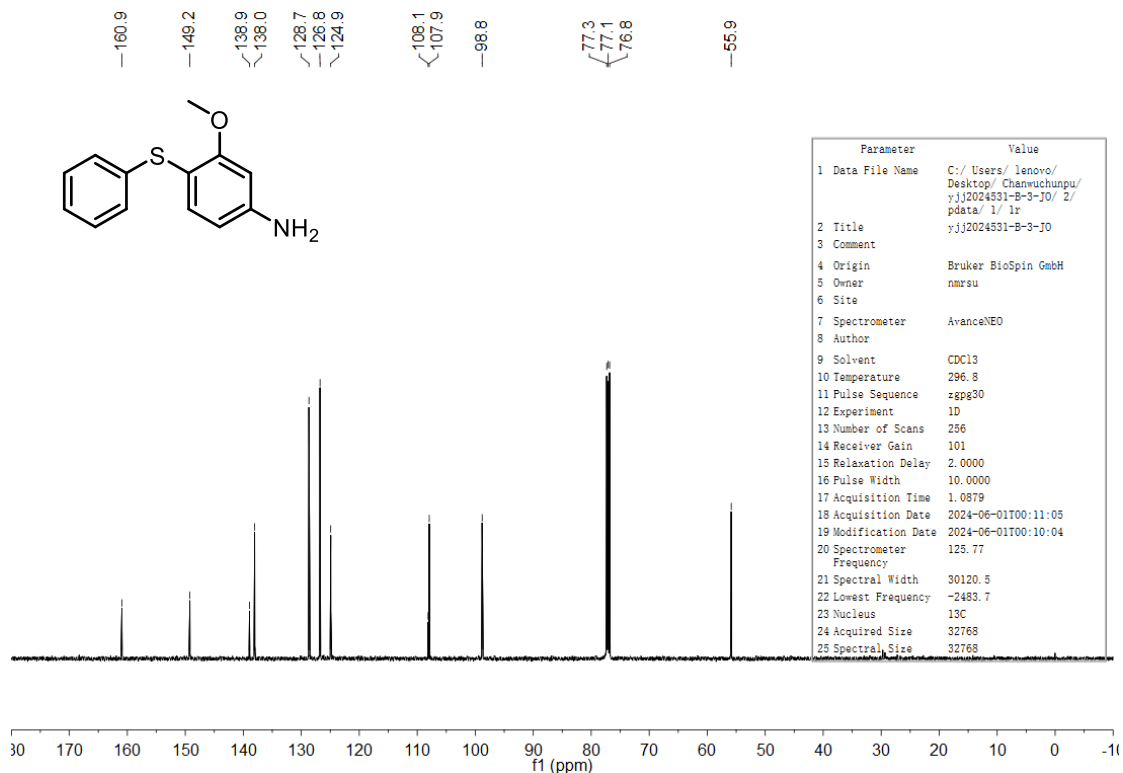
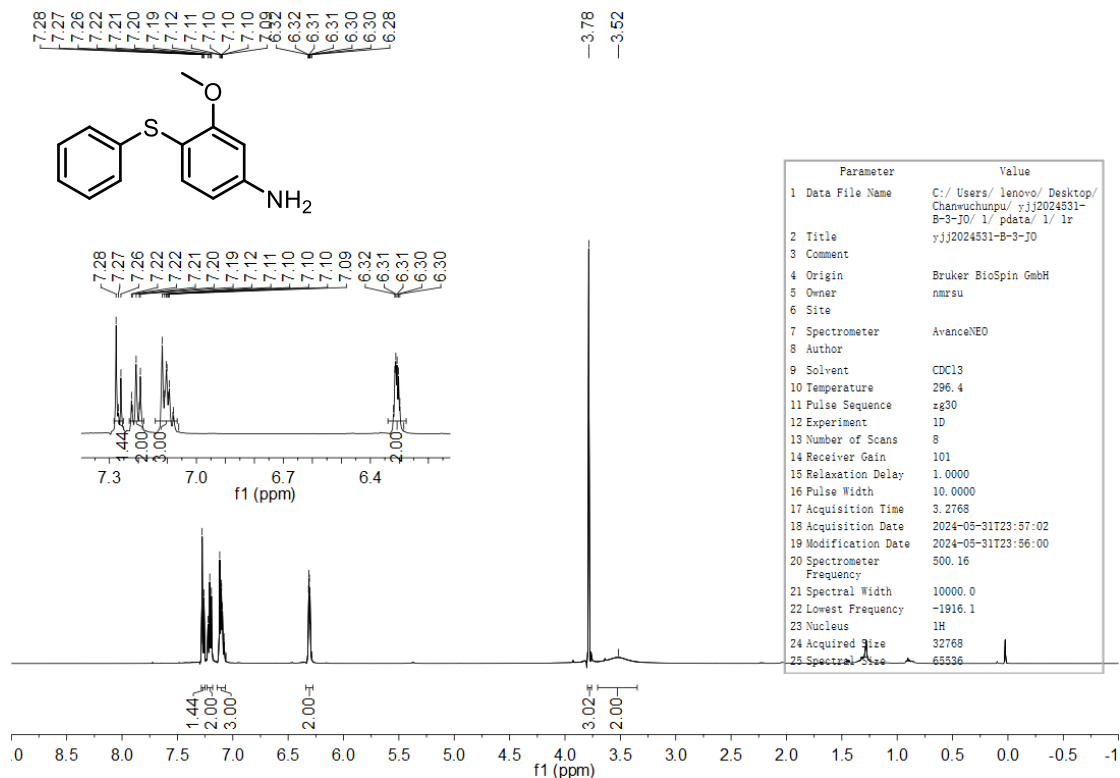


3-fluoro-4-(phenylthio)aniline (3af)

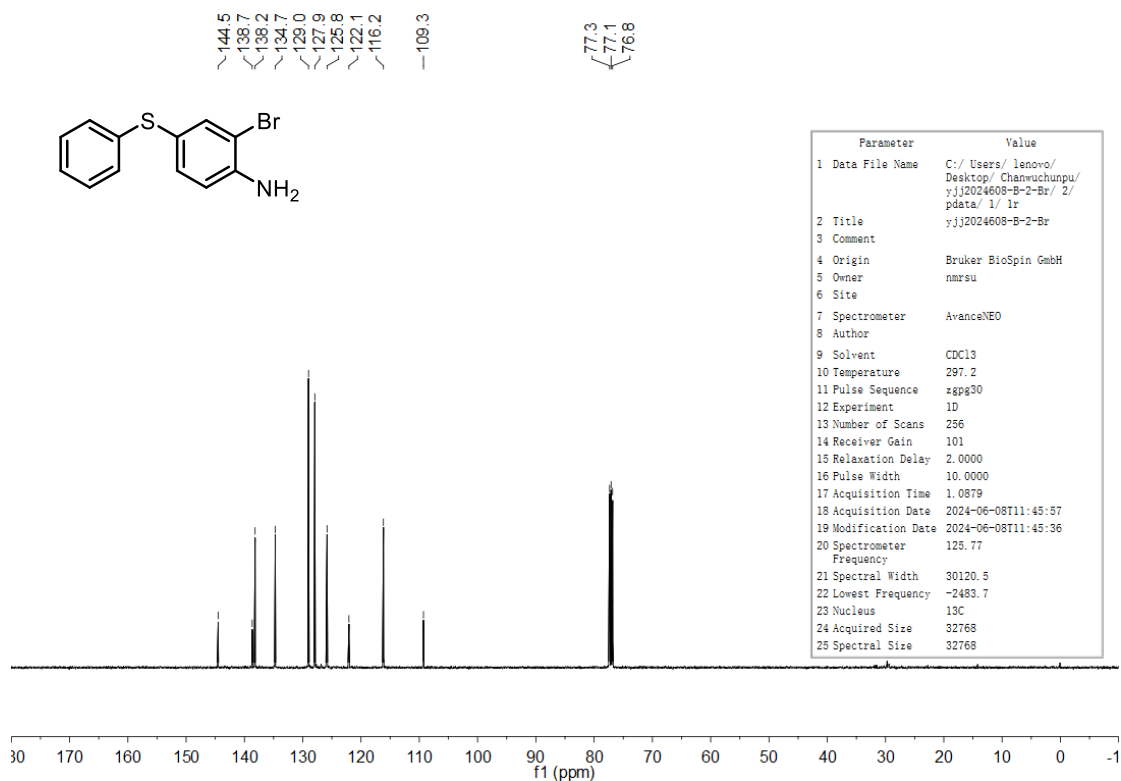
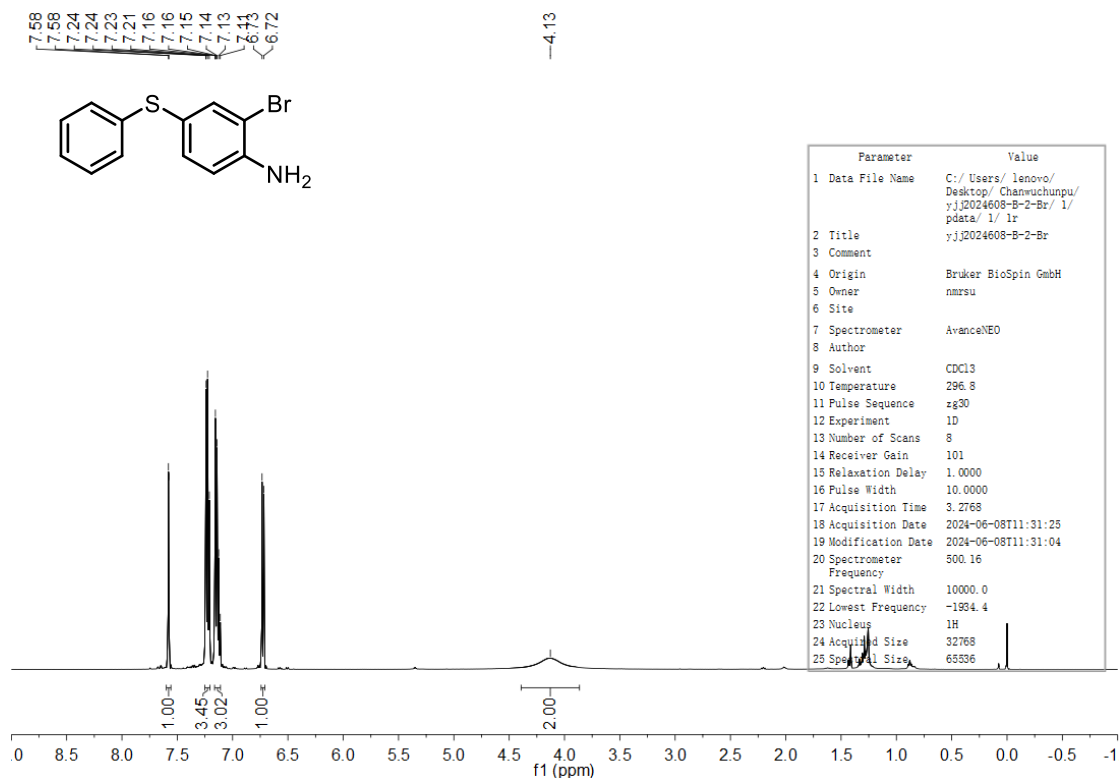




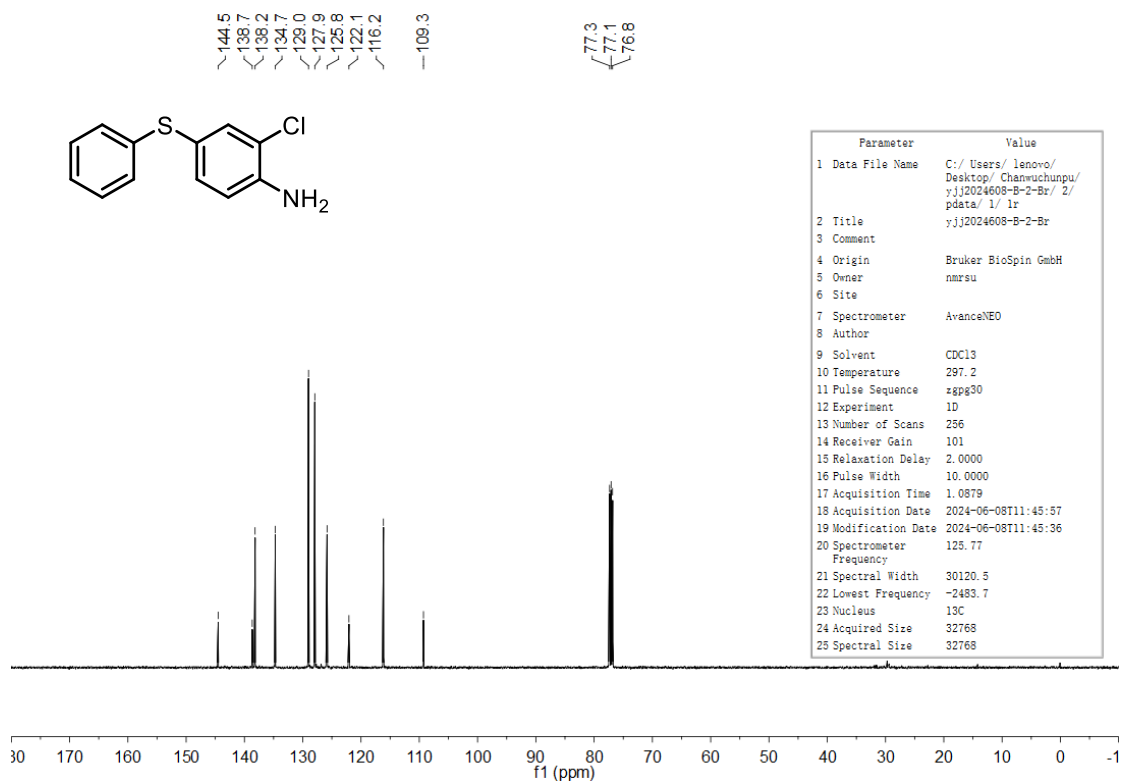
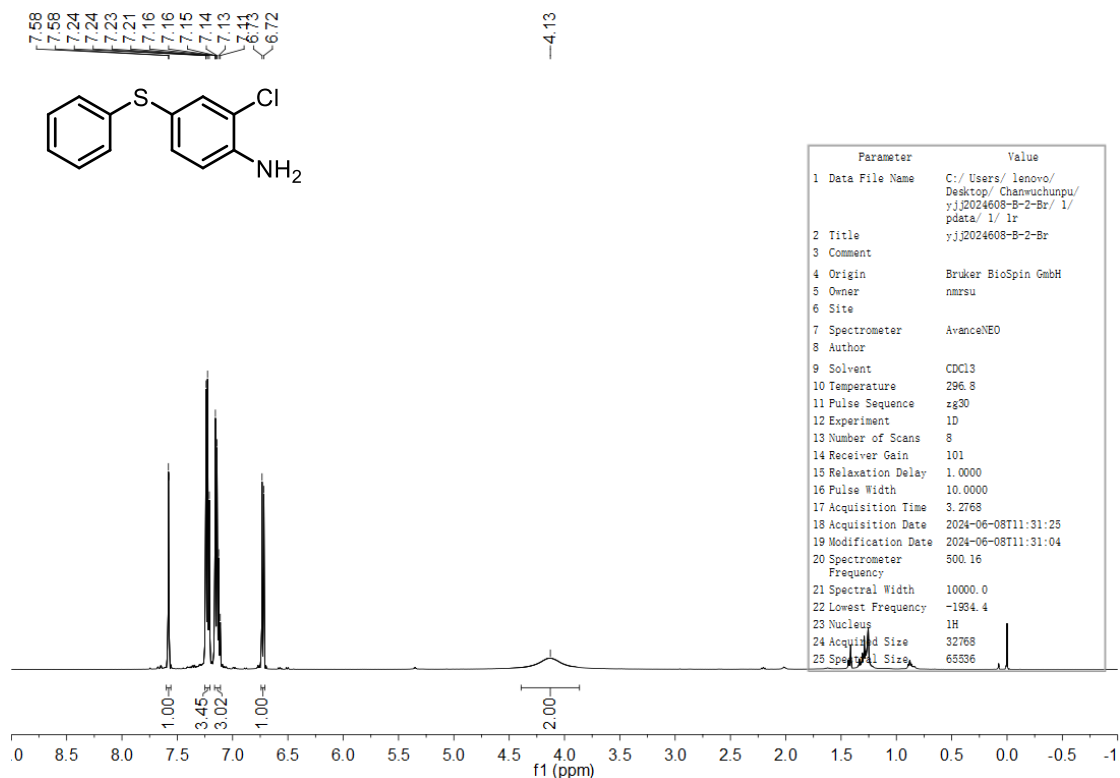
3-methoxy-4-(phenylthio)aniline (**3ag**)



2-bromo-4-(phenylthio)aniline (**3ah**)

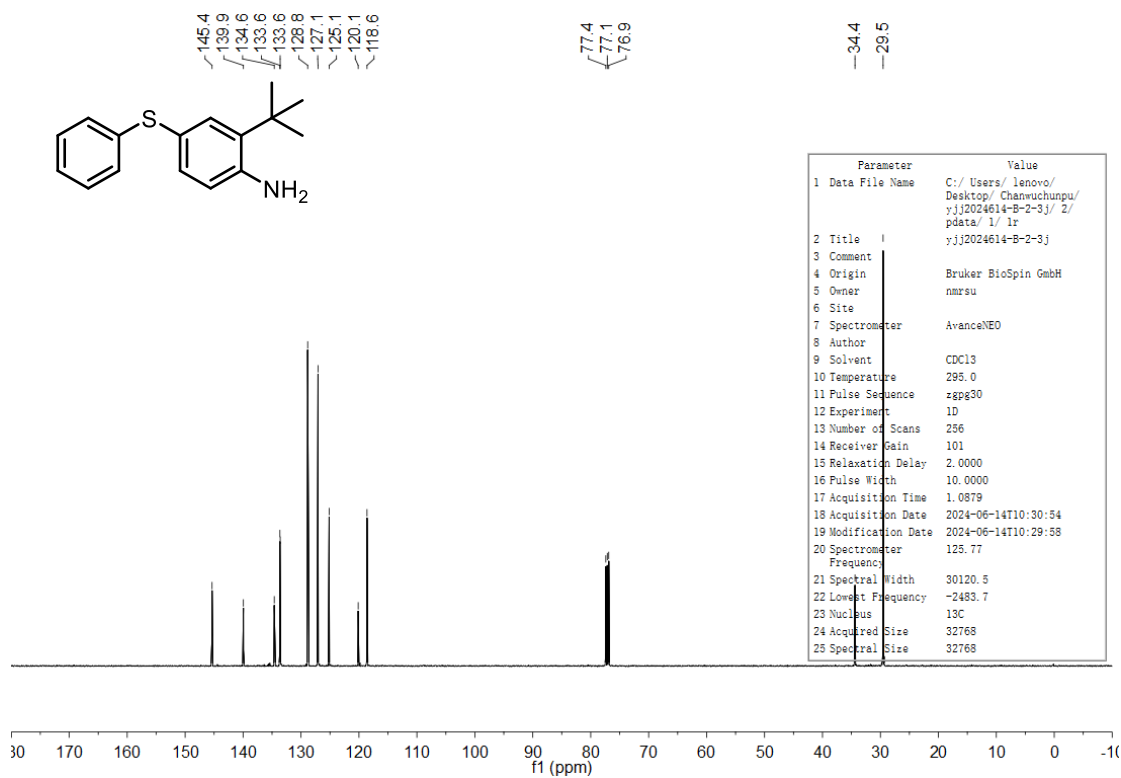


2-chloro-4-(phenylthio)aniline (**3ai**)

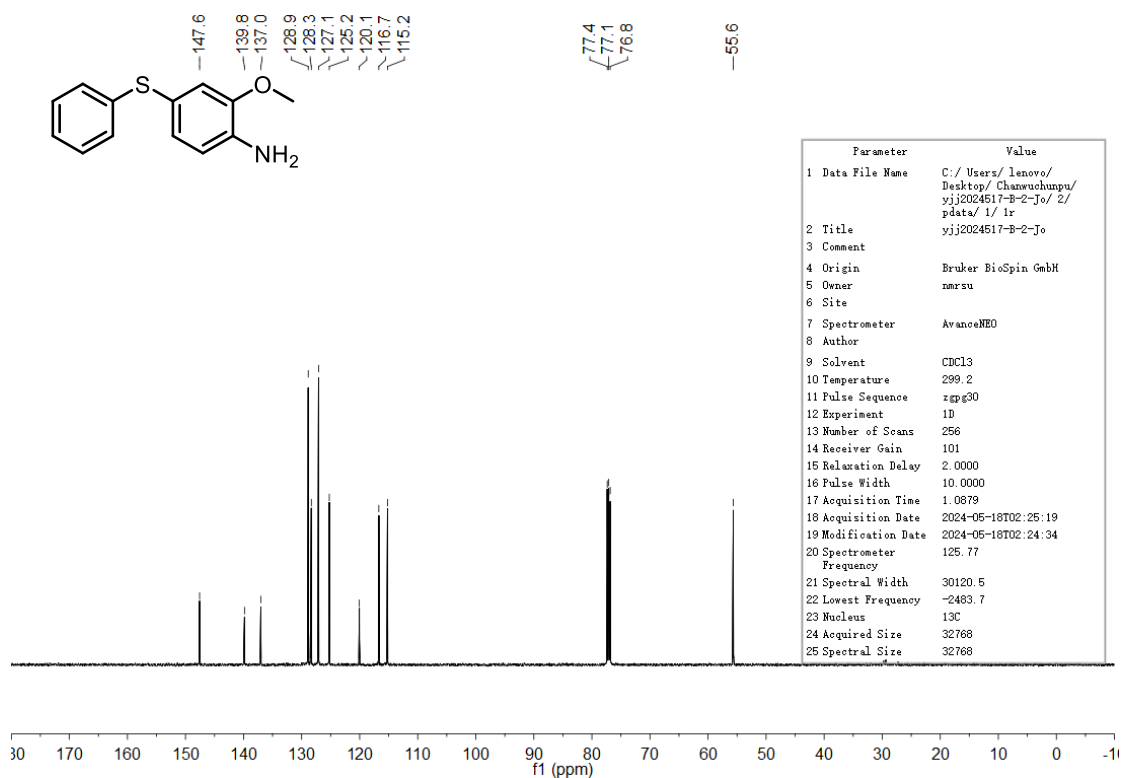
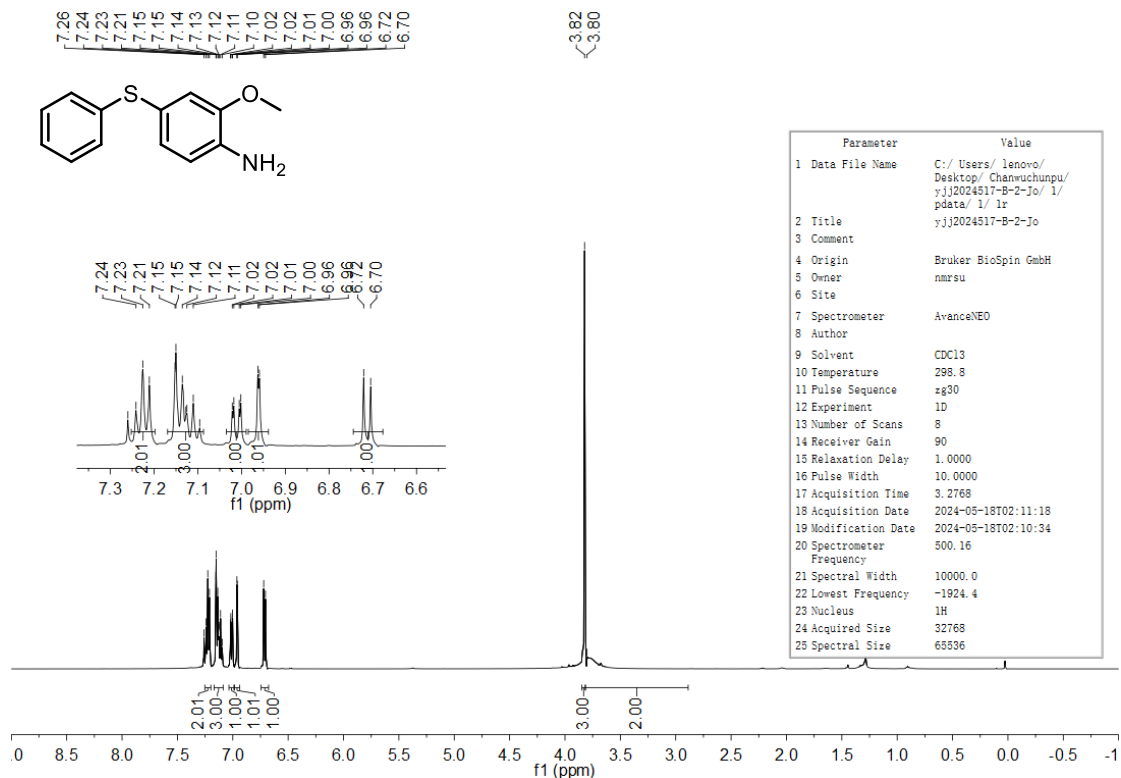


Chemical structure: CC(C)(C)c1ccc(SCc2ccc(N)cc2)cc1

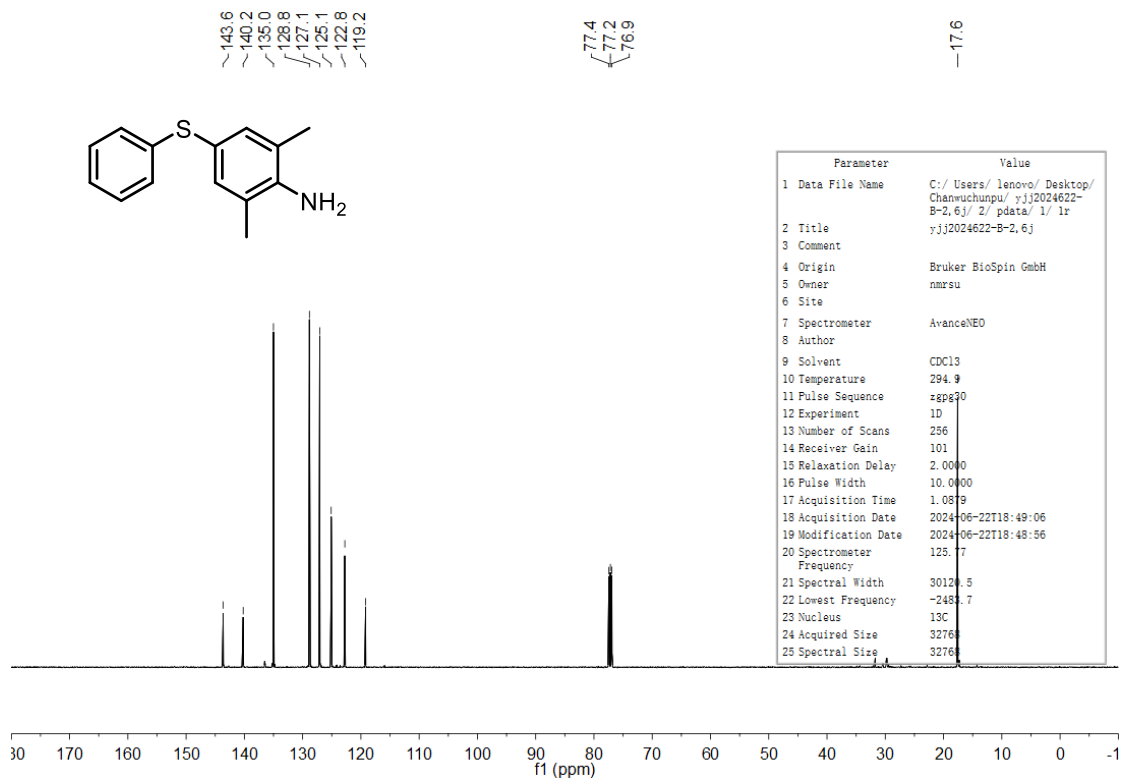
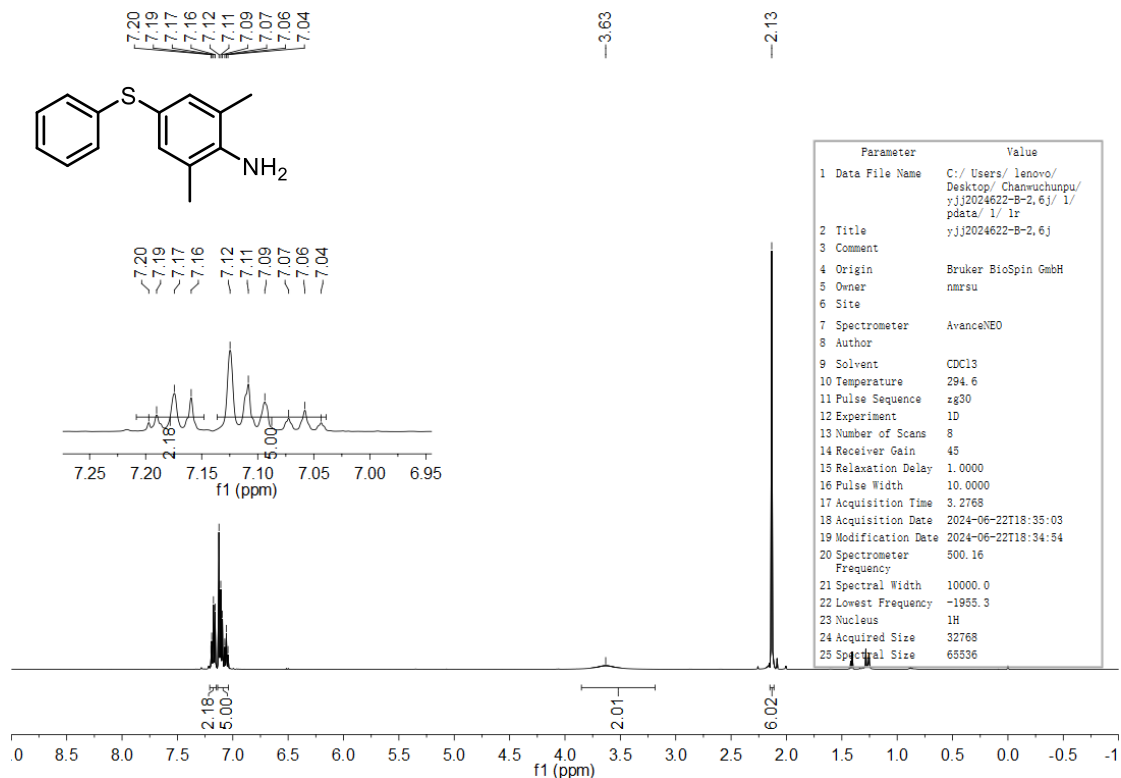
¹H NMR spectrum (DMSO-d₆) showing peaks from 6.60 to 7.40 ppm. Integration values are 1.00, 3.31, 3.00, 1.00, 2.01, and 9.01.



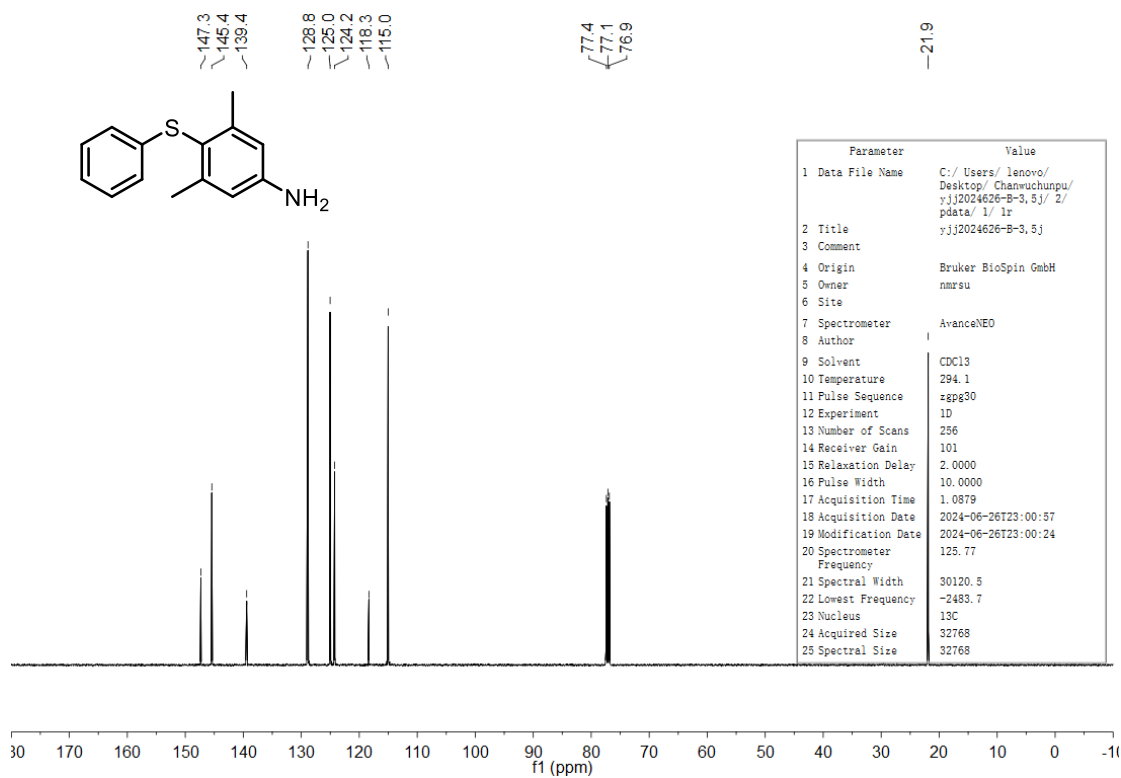
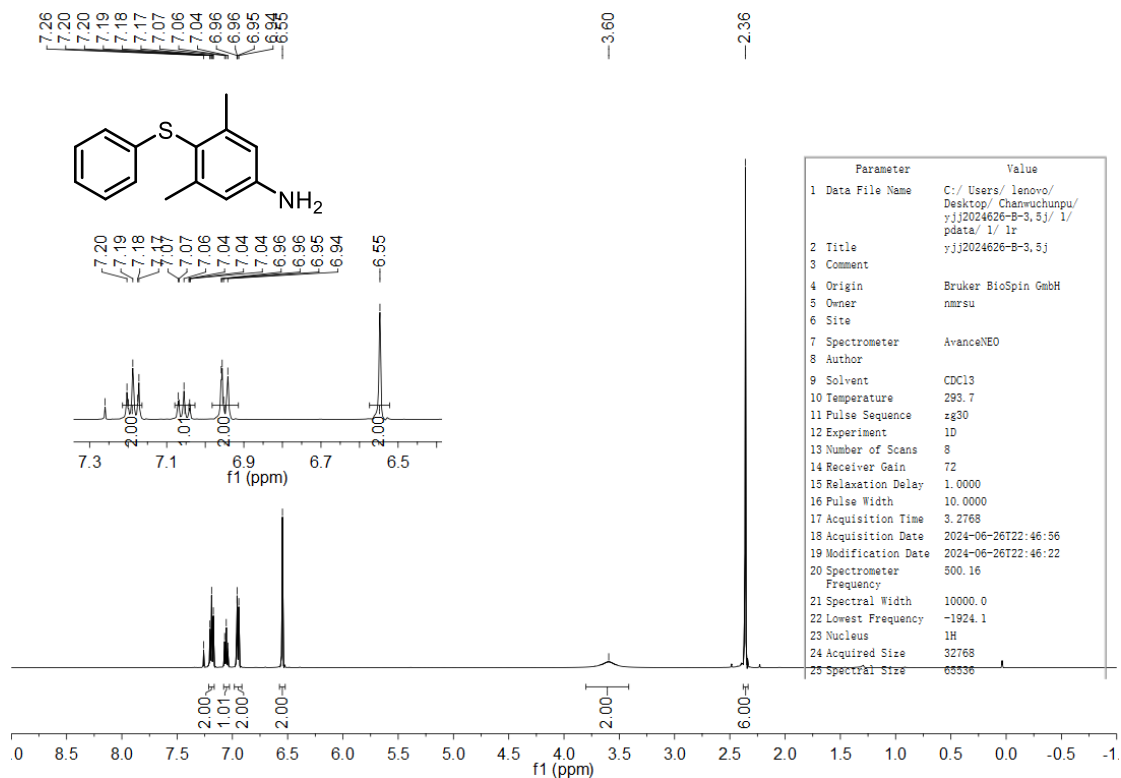
2-methoxy-4-(phenylthio)aniline (**3ak**)



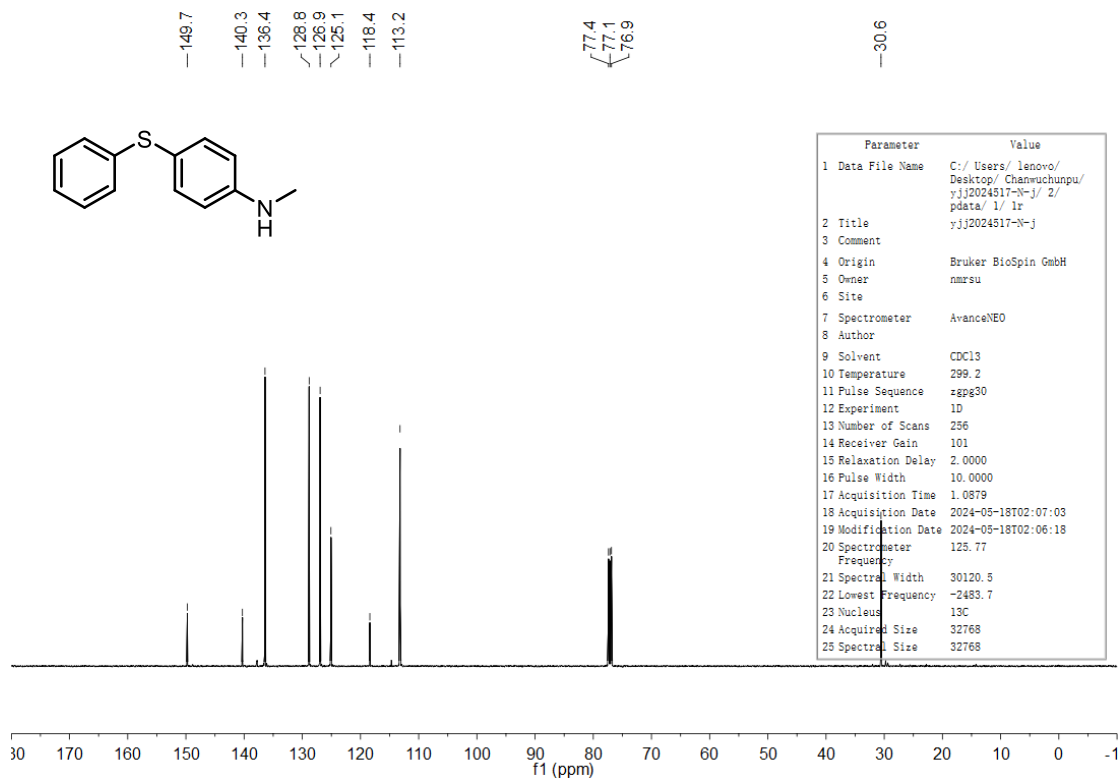
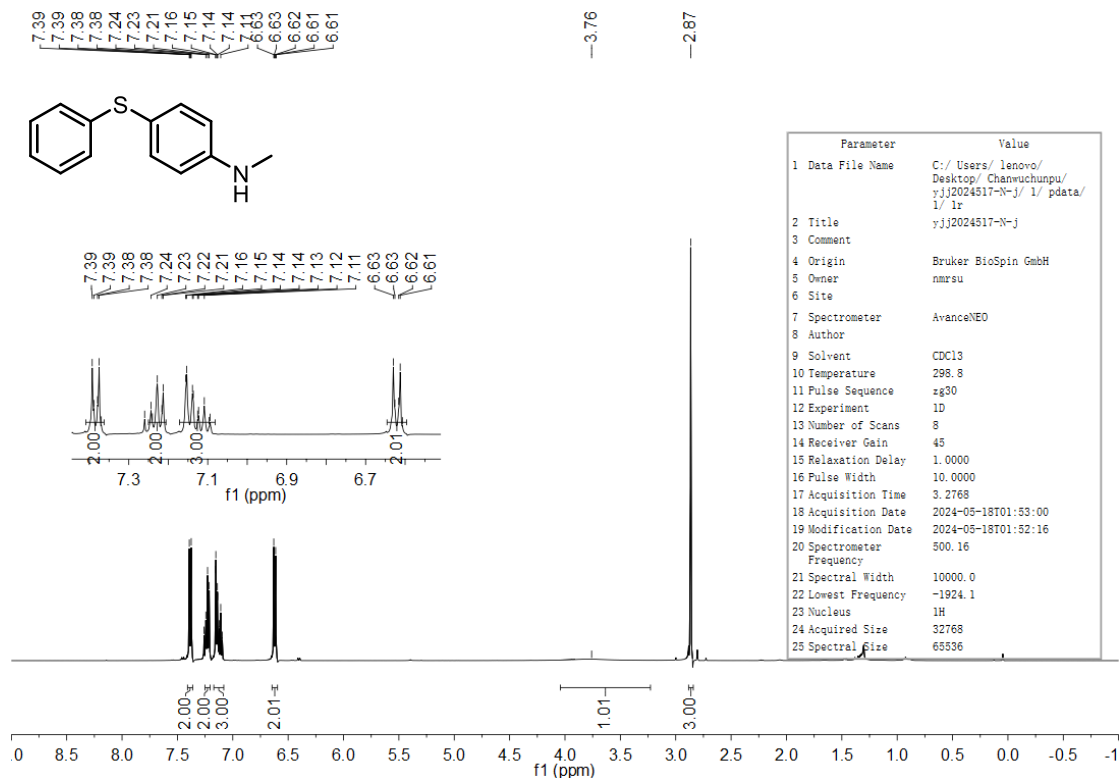
2,6-dimethyl-4-(phenylthio)aniline (**3al**)



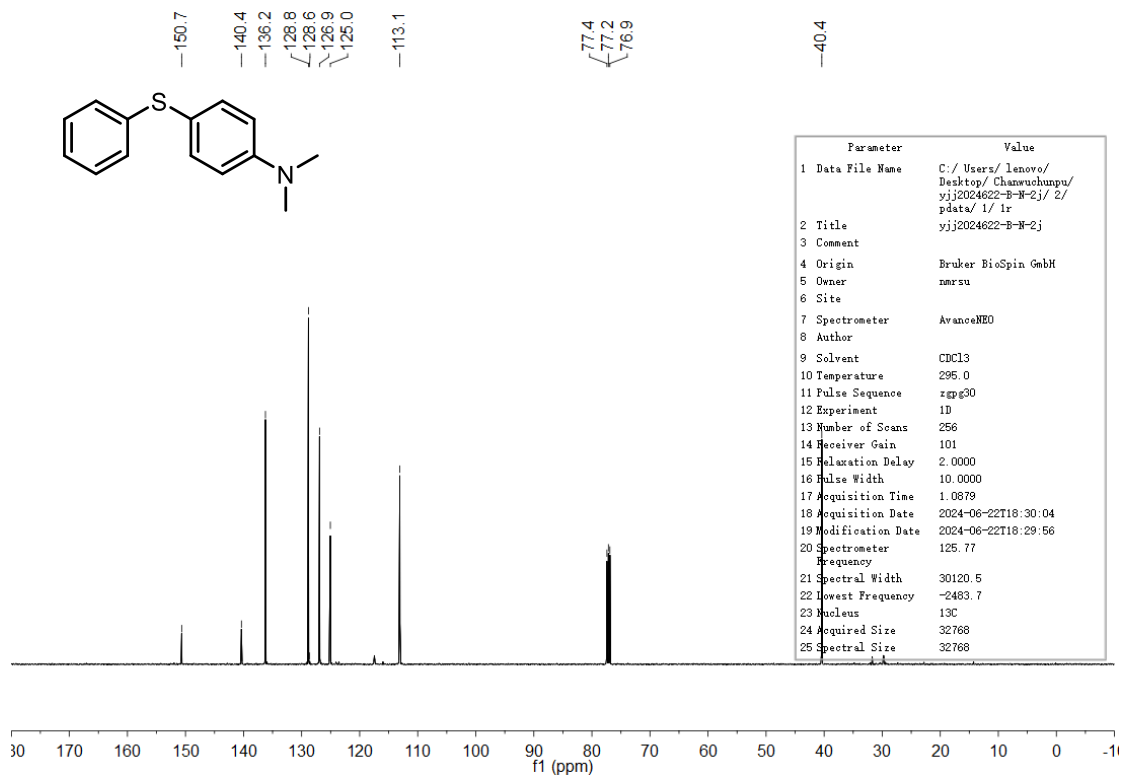
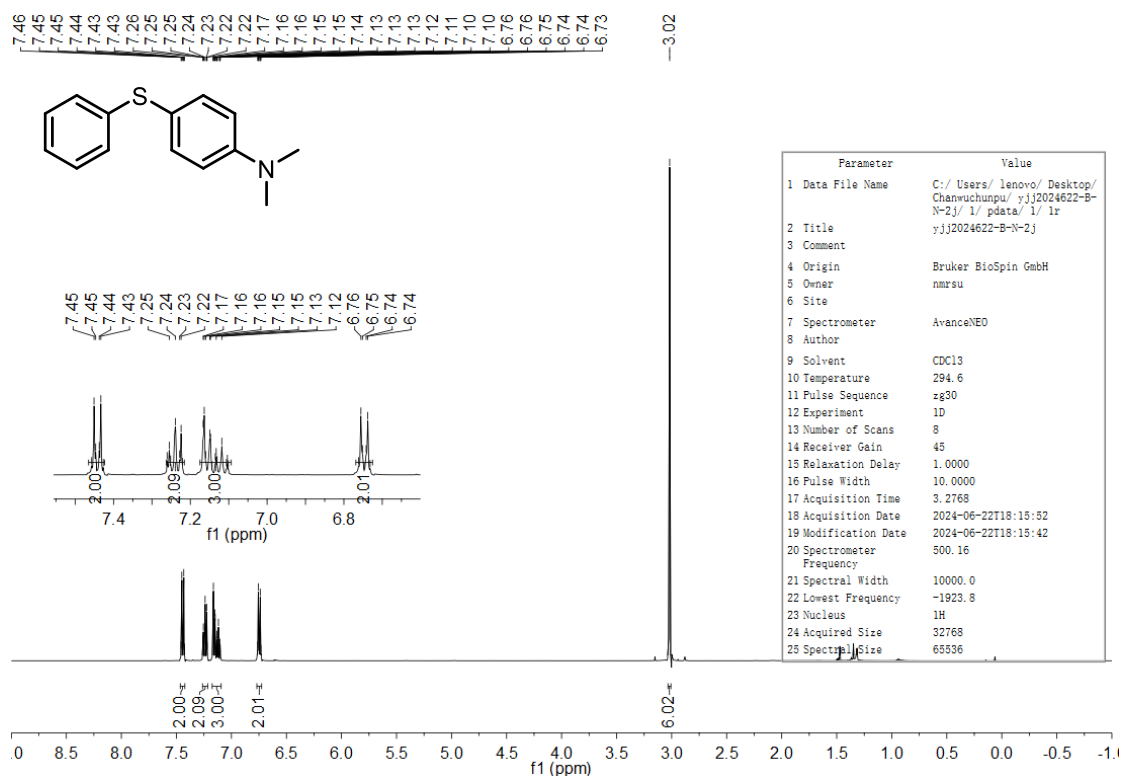
3,5-dimethyl-4-(phenylthio)aniline (**3am**)



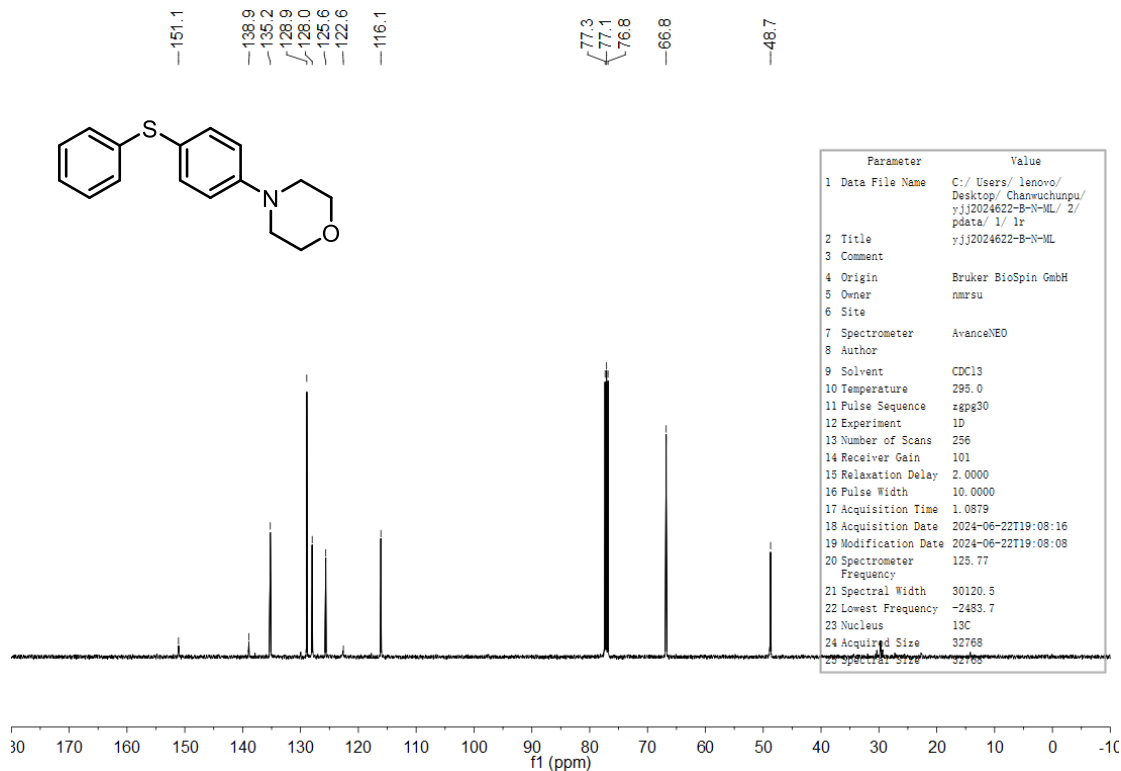
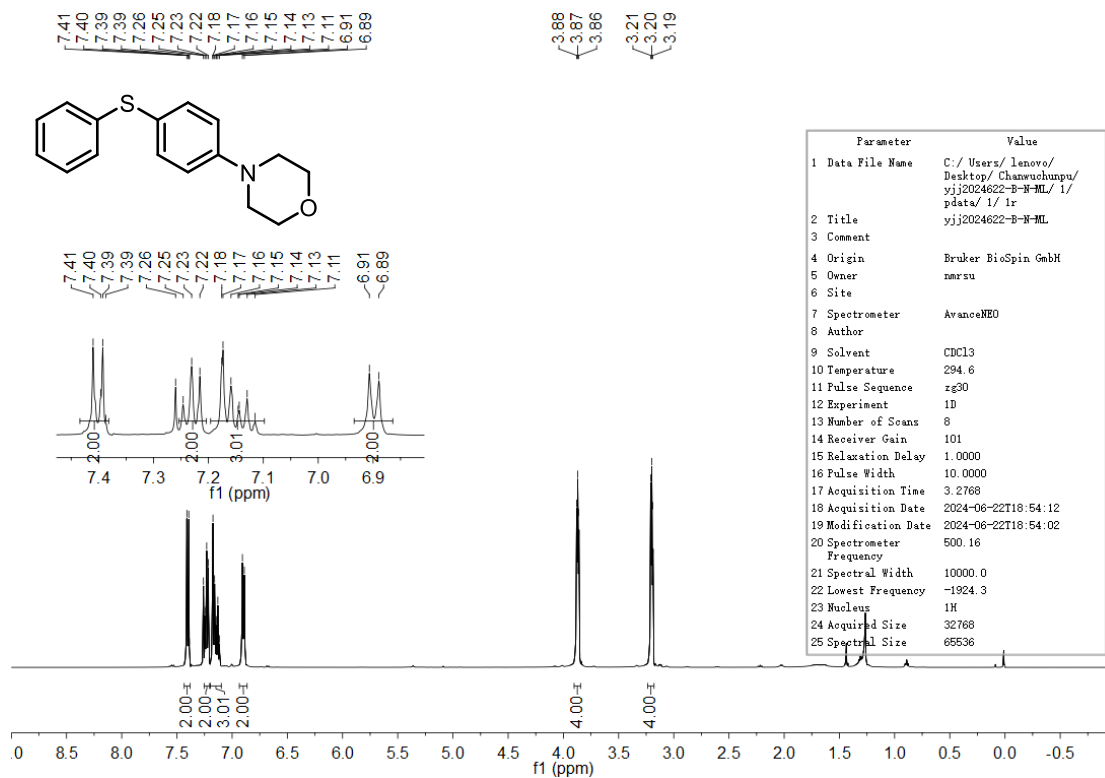
N-methyl-4-(phenylthio)aniline (**3an**)



N,N-dimethyl-4-(phenylthio)aniline (**3ao**)



4-(4-(phenylthio)phenyl)morpholine (**3ap**)



Methyl 2-amino-5-(phenylthio)benzoate (**3aq**)

