

Supporting Information

Visible-light-induced mono-bromination of arenes with BrCCl₃

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1. General information

All commercially available reagents were obtained from chemical suppliers and used without further purification. Flash column chromatography was performed on silica gel (300-400 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV lamp (254 nm).

The ^1H NMR spectra were recorded on 400 MHz spectrometers and ^{13}C NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and all combinations thereof can be explained by their integral parts. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Mechanistic Studies

1) Ultraviolet-visible Absorption Experiments

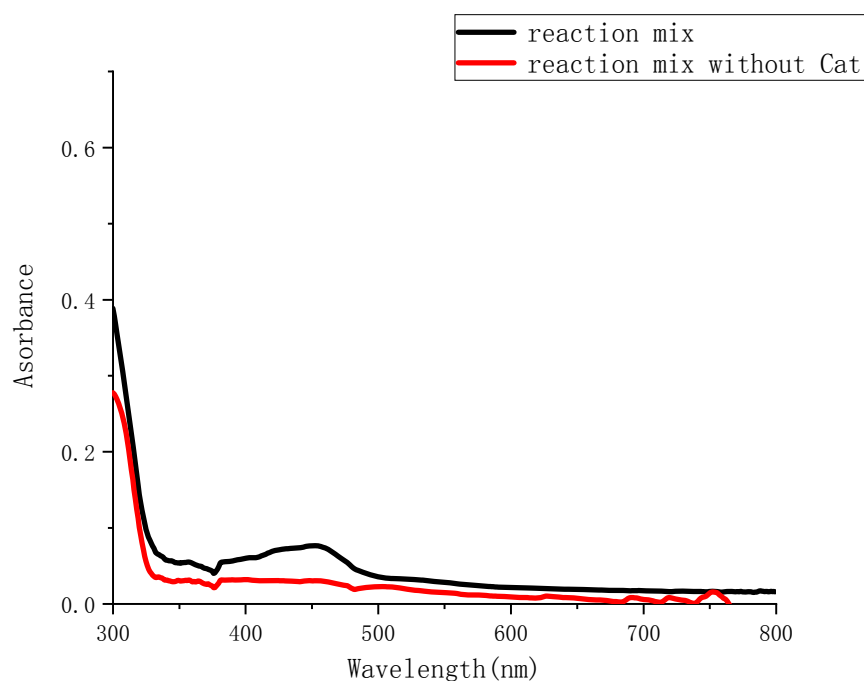


Figure S1: Ultraviolet-visible Absorption Analysis.

2) Stern-Volmer Fluorescent Quenching Experiments

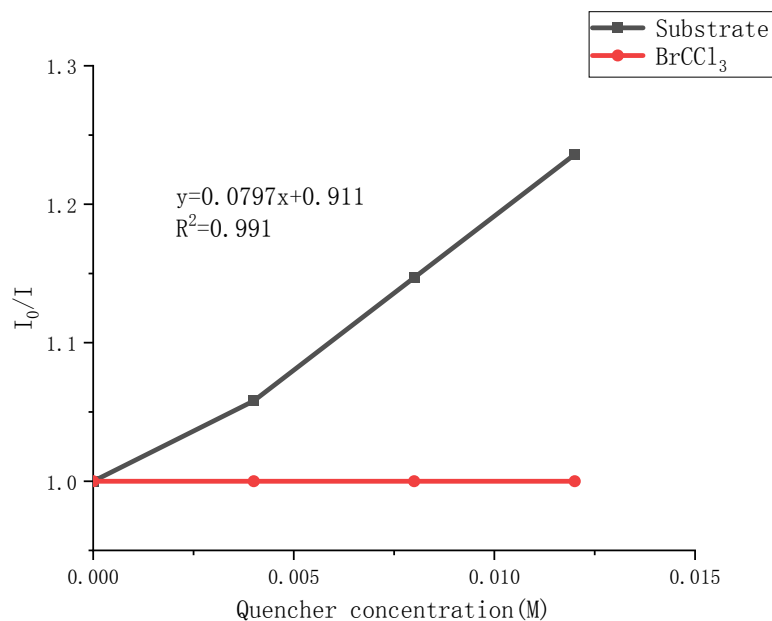


Figure S2: Stern-Volmer Fluorescent Quenching Analysis.

3) Electron Paramagnetic Resonance (EPR) Experiments

EPR measurements were recorded on a Bruker A200-6/1 CW-EPR spectrometer operating in X-band. After the reaction was stirred at room temperature under 23 W CFL for 30 min, DMPO (45 μ L) was added. After 10 min, a certain amount of sample was sealed in melting-point capillary and submitted for the EPR experiments. For the experiment without DMPO, the reaction mixture was submitted directly in melting-point capillary for EPR experiment. (DMPO = 5,5-dimethyl-1-pyrroline-1-oxide)

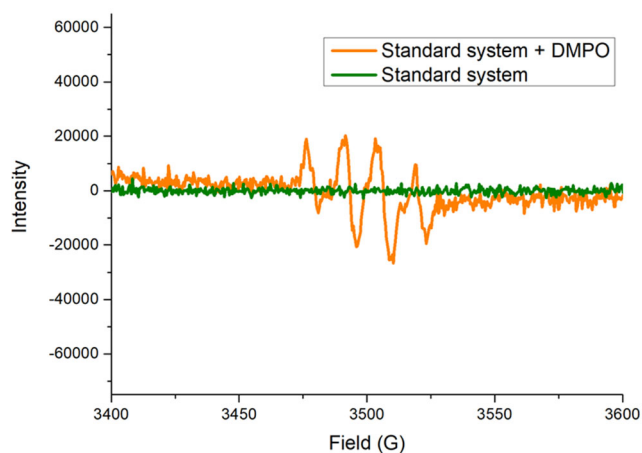
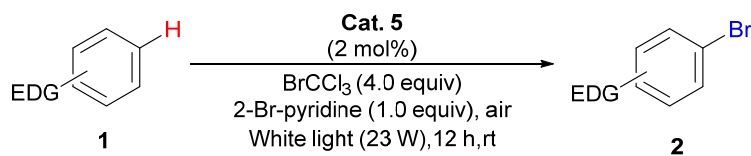


Figure S3: EPR spectra

3. General procedure for bromination of arenes



In the air, to an 8 mL vial equipped with a magnetic stir bar, were added **Cat. 5** ($\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$) (3.0 mg, 2.0 mol%), 2-Br-pyridine (31 mg, 0.20 mmol, 1.0 equiv.), BrCCl_3 (158 mg, 0.80 mmol, 4.0 equiv.), substrate (0.20 mmol) and *N,N*-dimethylformamide (DMF, 1 mL). The reaction was then placed in the photoreactor and stirred at room temperature for 12 h. The mixture was proportioned with water (5 mL) and extracted by EtOAc (5 mL \times 3). The combined organic layer were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulted residue was purified by column chromatography on silica gel, eluted with the mixture of ethyl acetate/hexanes, to give the corresponding products.

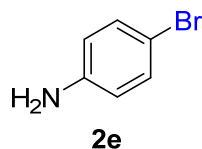
2a **4-Bromo-*N,N*-dimethylaniline (2a)**^[1] Yellow oil (31.6 mg, 85%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.26 (d, $J = 8.0$ Hz, 2H), 6.49 (d, $J = 8.3$ Hz, 2H), 2.81 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.39, 132.00, 114.07, 108.94, 30.85.

2b **4-Bromo-*N,N*-dimethylaniline (2b)**^[2] Light yellow oil (31.2 mg, 78%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.30 (d, $J = 9.1$ Hz, 2H), 6.59 (d, $J = 9.1$ Hz, 2H), 2.92 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 149.64, 131.82, 114.23, 108.64, 40.72.

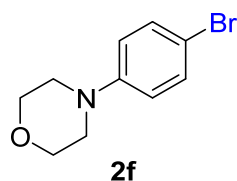
2c **4-Bromo-*N,N*-diethylaniline (2c)**^[3] Light yellow oil (36.9 mg, 81%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.27 (d, $J = 8.2$ Hz, 2H), 6.56 (d, $J = 8.2$ Hz, 2H), 3.32 (q, $J = 7.1$ Hz, 4H), 1.14 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 146.79, 131.97, 113.48, 107.03, 44.58, 12.51.

2d **4-Bromo-*N,N*-diisopropylaniline (2d)**^[4] Light yellow oil (38.4 mg, 75%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.26 (d, $J = 8.9$ Hz, 1H), 6.74 (d, $J = 8.9$ Hz,

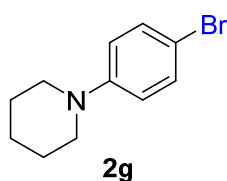
2H), 3.78 – 3.68 (m, 2H), 1.20 (d, $J = 6.8$ Hz, 12H). ^{13}C NMR (101 MHz, Chloroform- d) δ 147.18, 131.32, 120.35, 109.99, 47.71, 21.32.



4-Bromoaniline (2e)^[1] Yellow oil (15.5 mg, 44%). ^1H NMR (400 MHz, Chloroform- d) δ 7.23 (d, $J = 8.8$ Hz, 2H), 6.56 (d, $J = 8.8$ Hz, 2H), 3.60 (br, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 145.50, 132.15, 116.85, 110.37.

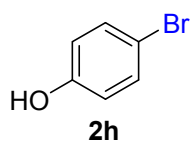


4-(4-Bromophenyl)morpholine (2f)^[5] White solid (25.0 mg, 52%). ^1H NMR (400 MHz, Chloroform- d) δ 7.36 (d, $J = 9.1$ Hz, 2H), 6.78 (d, $J = 9.1$ Hz, 2H), 3.85 (t, $J = 4.9$ Hz, 4H), 3.12 (t, $J = 4.9$ Hz, 4H). ^{13}C NMR (101 MHz, Chloroform- d) δ 150.40, 132.06, 117.42, 112.31, 66.87, 49.26.

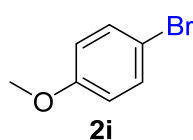


1-(4-Bromophenyl)piperidine (2g)^[1] Colorless oil (45.1 mg, 94%). ^1H NMR (400 MHz, Chloroform- d) δ 7.31 (d, $J = 9.1$ Hz, 2H), 6.79 (d, $J = 9.0$ Hz, 2H), 3.12 (t, $J = 5.5$ Hz, 4H), 1.72 – 1.66 (m, 4H), 1.60 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 151.30, 131.87, 118.15, 111.23, 50.59, 25.79,

24.31.

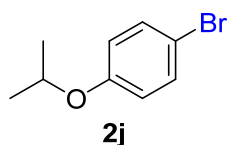


4-Bromophenol (2h)^[2] Brown solid (24.6 mg, 71%). ^1H NMR (400 MHz, Chloroform- d) δ 7.33 (d, $J = 8.9$ Hz, 2H), 6.72 (d, $J = 8.9$ Hz, 2H), 4.92 (s, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 154.82, 132.59, 117.32, 112.92.



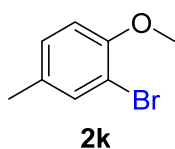
1-Bromo-4-methoxybenzene (2i)^[5] Light yellow oil (34.4 mg, 92%). ^1H NMR (400 MHz, Chloroform- d) δ 7.38 (d, $J = 9.1$ Hz, 2H), 6.78 (d, $J = 9.1$ Hz, 2H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 158.78, 132.36, 115.83,

112.92, 55.57.

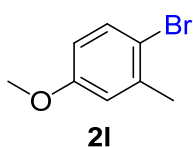


1-Bromo-4-isopropoxybenzene (2j)^[5] Colorless oil (35.8 mg, 83%). ^1H NMR (400 MHz, Chloroform- d) δ 7.35 (d, $J = 9.0$ Hz, 2H), 6.76 (d, $J = 9.0$ Hz,

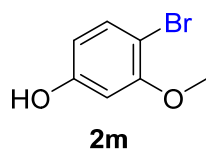
2H), 4.54 – 4.45 (m, 1H), 1.32 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (101 MHz, Chloroform- d) δ 157.12, 132.39, 117.82, 112.67, 70.39, 22.06.



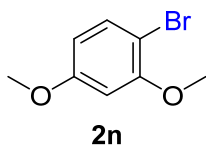
2-Bromo-1-methoxy-4-methylbenzene (2k)^[3] Colorless oil (32.2 mg, 80%). ^1H NMR (400 MHz, Chloroform- d) δ 7.36 (d, $J = 2.1$ Hz, 1H), 7.06 (dd, $J = 8.3, 2.1$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 1H), 3.87 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 153.79, 133.86, 131.55, 129.00, 111.88, 111.32, 56.39, 20.29.



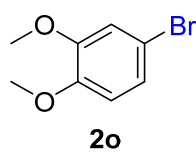
1-Bromo-4-methoxy-2-methylbenzene (2l)^[5] Colorless oil (30.5 mg, 76%). ^1H NMR (400 MHz, Chloroform- d) δ 7.40 (d, $J = 8.7$ Hz, 1H), 6.79 (d, $J = 3.0$ Hz, 1H), 6.61 (dd, $J = 8.7, 3.0$ Hz, 1H), 3.77 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 158.84, 138.89, 132.88, 116.56, 115.48, 112.99, 55.48, 23.27.



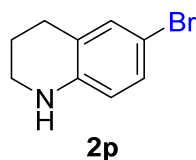
4-Bromo-3-methoxyphenol (2m)^[6] Colorless oil (28.8 mg, 71%). ^1H NMR (400 MHz, Chloroform- d) δ 7.34 (d, $J = 8.5$ Hz, 1H), 6.45 (d, $J = 2.7$ Hz, 1H), 6.33 (dd, $J = 8.5, 2.7$ Hz, 1H), 4.99 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 156.83, 156.26, 133.45, 108.62, 102.32, 100.56, 56.30.



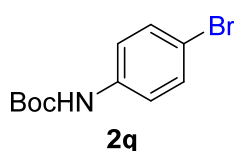
1-Bromo-2,4-dimethoxybenzene (2n)^[5] Colorless oil (29.0 mg, 67%). ^1H NMR (400MHz, Chloroform- d) δ 7.40 (d, $J = 8.7$ Hz, 1H), 6.49 (d, $J = 2.7$ Hz, 1H), 6.40 (dd, $J = 8.7, 2.7$ Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 160.34, 156.64, 133.26, 105.99, 102.54, 100.07, 56.25, 55.68.



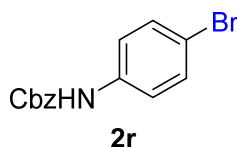
4-Bromo-1,2-dimethoxybenzene (2o)^[5] Colorless oil (35.6 mg, 82%). ^1H NMR (400 MHz, Chloroform- d) δ 7.03 (dd, $J = 8.6, 2.4$ Hz, 1H), 6.98 (d, $J = 2.5$ Hz, 1H), 6.74 (d, $J = 8.6$ Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 149.76, 148.36, 123.46, 114.76, 112.79, 112.45, 56.19, 56.13.



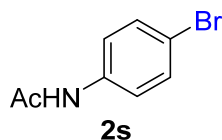
6-Bromo-1,2,3,4-tetrahydroquinoline (2p)^[7] Colorless oil (29.8 mg, 71%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.05 – 7.01 (m, 2H), 6.35 (d, *J* = 8.3 Hz, 1H), 3.28 (t, *J* = 5.5 Hz, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 1.94 – 1.88 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.72, 132.02, 129.50, 123.61, 115.73, 108.46, 41.93, 26.94, 21.79.



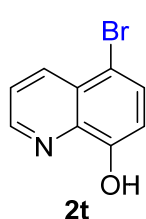
tert-Butyl (4-bromophenyl)carbamate (2q)^[5] White solid (44.6 mg, 82%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 8.9 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 1.51 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 152.63, 137.56, 131.98, 115.52, 81.02, 28.42.



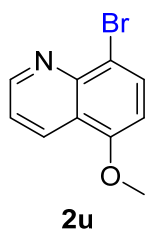
Benzyl (4-bromophenyl)carbamate (2r)^[8] White solid (52.1 mg, 85%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.35 (m, 7H), 7.27 – 7.29 (m, 2H), 6.78 (s, 1H), 5.19 (s, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) 153.41, 136.95, 135.79, 131.90, 128.63, 128.43, 128.27, 120.27, 115.98, 67.16.



N-(4-Bromophenyl)acetamide (2s)^[5] White solid (21.8 mg, 51%) ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.06 (s, 1H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.9 Hz, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 168.50, 138.71, 131.51, 120.86, 114.51, 24.07.

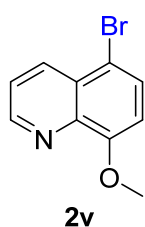


5-Bromoquinolin-8-ol (2t) White solid (33.5 mg, 75%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 10.85 (s, 1H), 8.87 (dd, *J* = 4.3, 1.7 Hz, 2H), 8.27 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.38 (dd, *J* = 8.1, 4.3 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 155.79, 151.25, 146.20, 136.38, 128.42, 123.36, 119.24, 118.90, 106.41. HRMS (ESI) *calcd* for C₉H₆BrNO [M + H]⁺ 223.9711, found 223.9707.

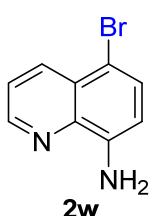


8-Bromo-5-methoxyquinoline (2u) Colorless oil (19.3 mg, 41%). ¹H NMR (400 MHz, Chloroform-*d*) δ 9.05 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.60 (dd, *J* = 8.4, 1.7 Hz, 3H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.45 (dd, *J* = 8.4, 4.3 Hz, 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 4.00 (s, 3H).

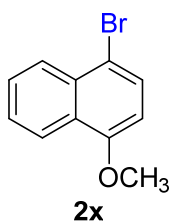
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.15, 151.60, 145.64, 132.72, 131.61, 122.32, 121.11, 114.92, 105.20, 56.10. HRMS (ESI) *calcd* for $\text{C}_{10}\text{H}_8\text{BrNO}$ $[\text{M}]^+$ 236.9789, found 236.9791.



5-Bromo-8-methoxyquinoline (2v)^[9] Colorless oil (30.7 mg, 65%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.95 (dd, $J = 4.2, 1.6$ Hz, 1H), 8.50 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.55 (dd, $J = 8.5, 4.2$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 1H), 4.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.35, 149.88, 140.94, 135.76, 130.23, 128.34, 122.93, 112.02, 108.29, 56.33.

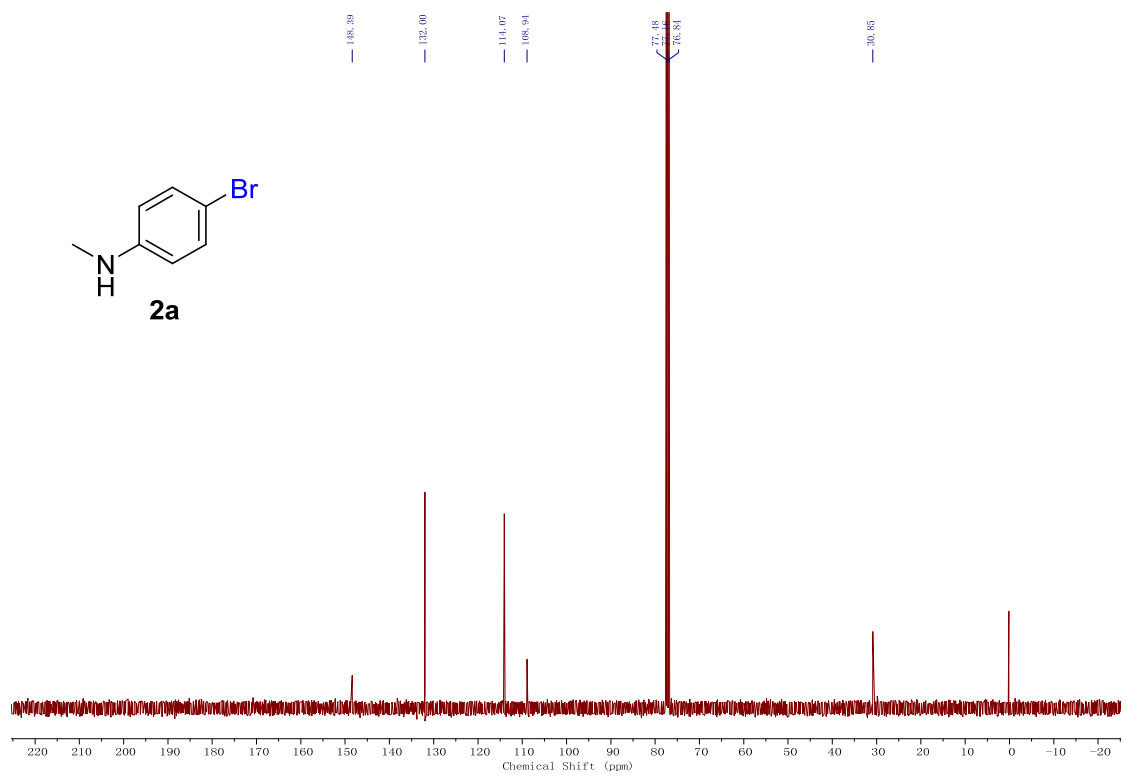
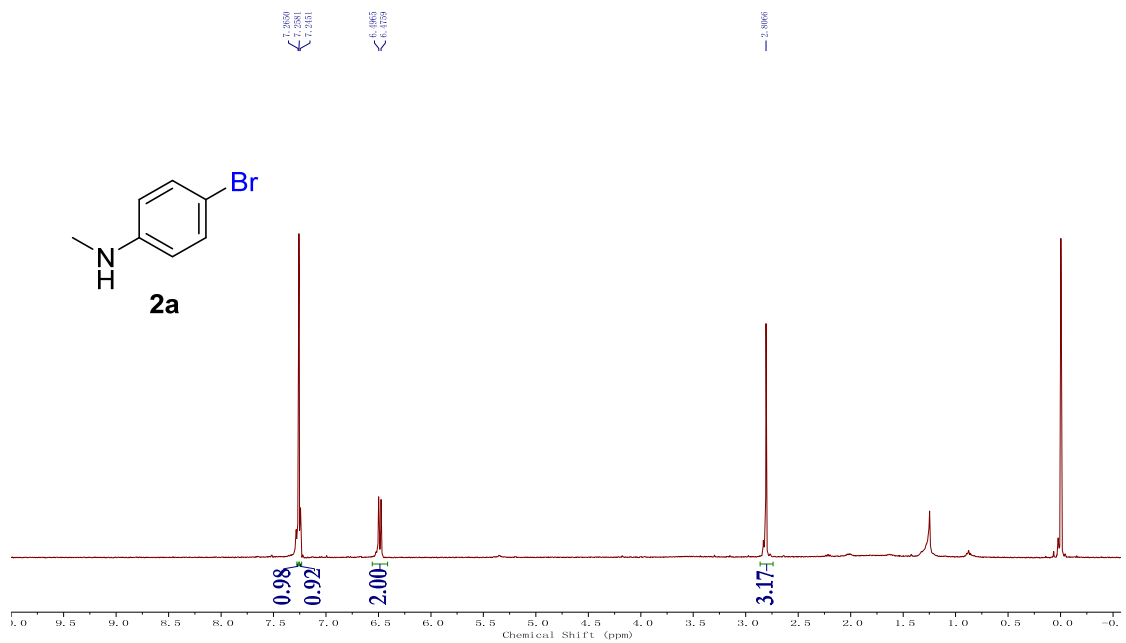


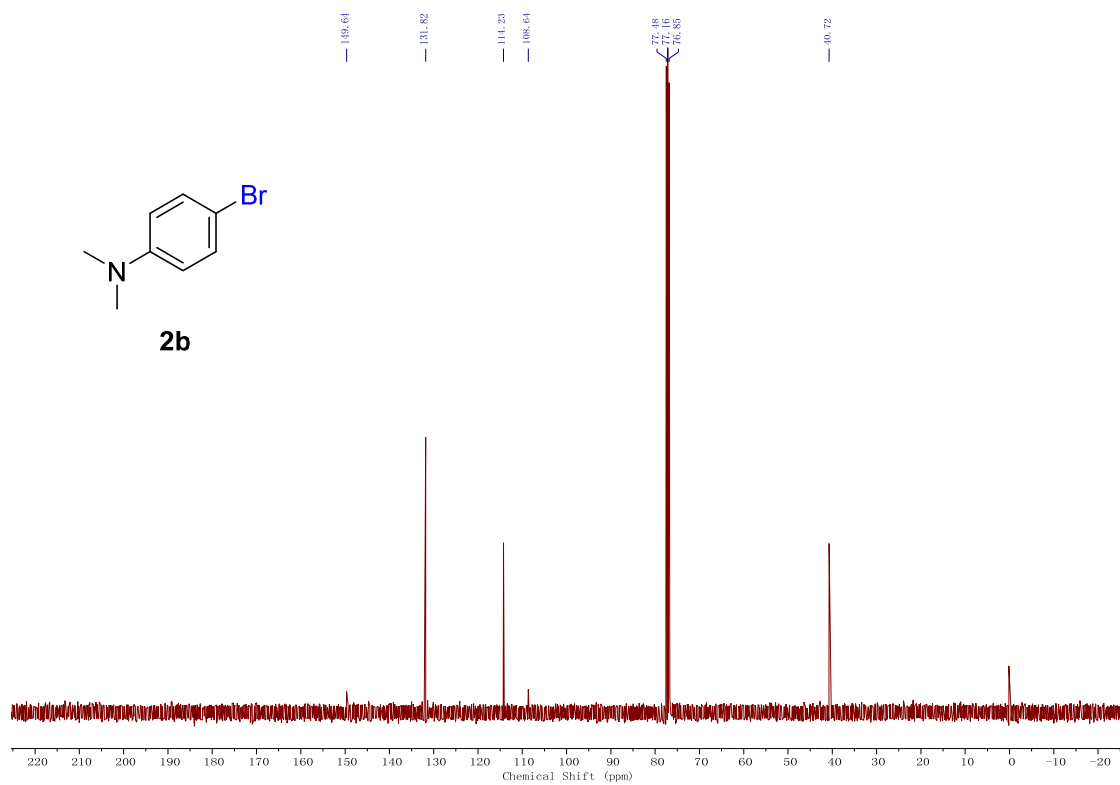
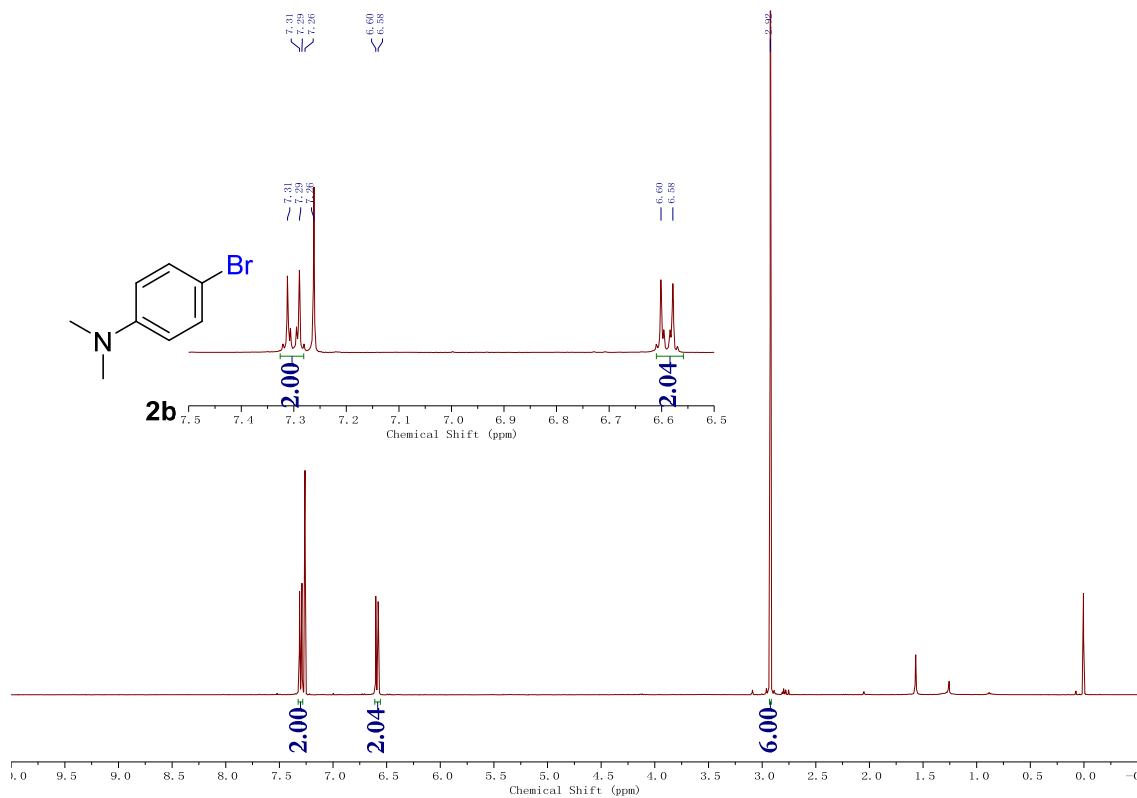
5-Bromoquinolin-8-amine (2w)^[10] Yellow solid (14.3 mg, 32%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.81 (dd, $J = 4.2, 1.5$ Hz, 1H), 8.49 (dd, $J = 8.6, 1.5$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H), 7.57 (dd, $J = 8.5, 4.2$ Hz, 1H), 7.08 (d, $J = 8.2$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.13, 148.52, 139.02, 136.03, 131.21, 127.72, 123.09, 110.81, 109.91.

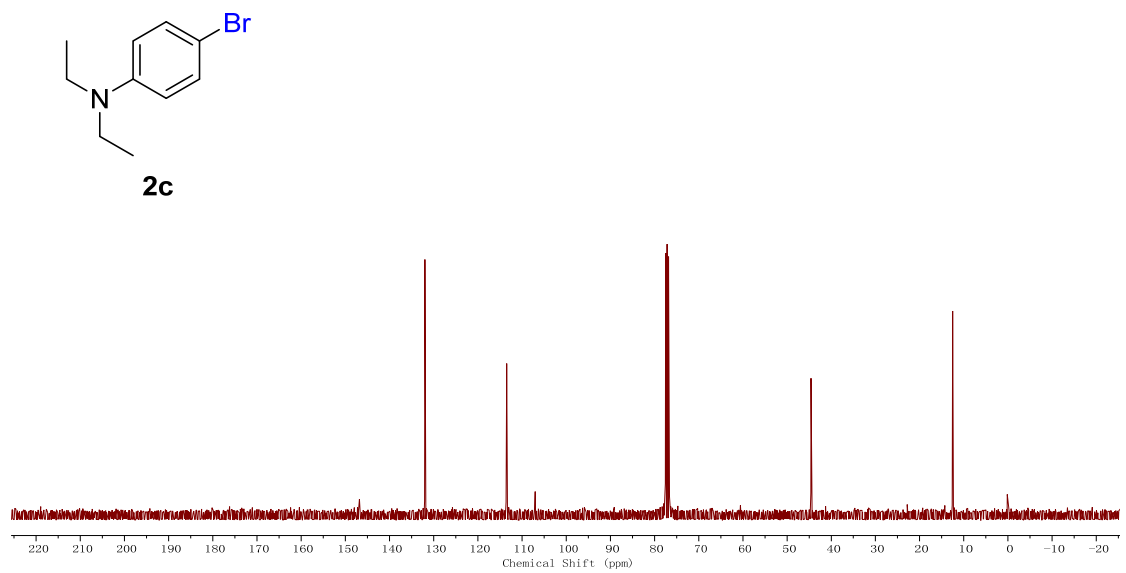
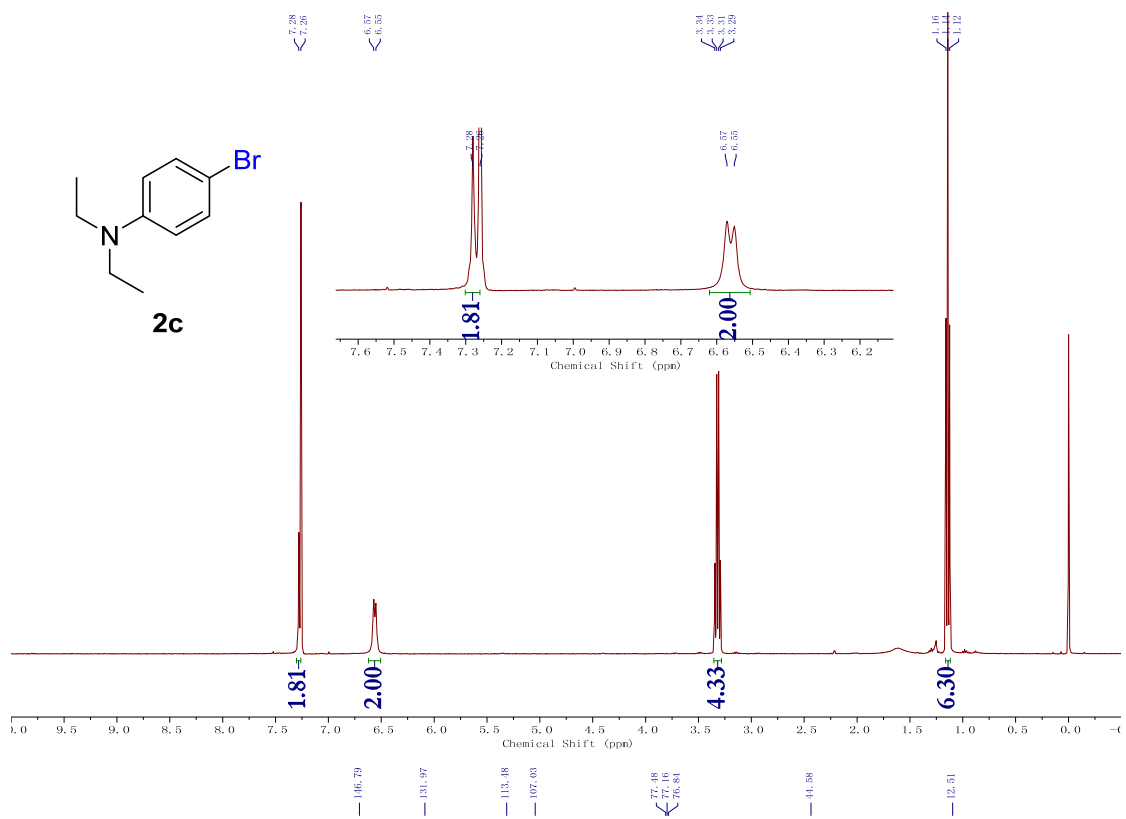


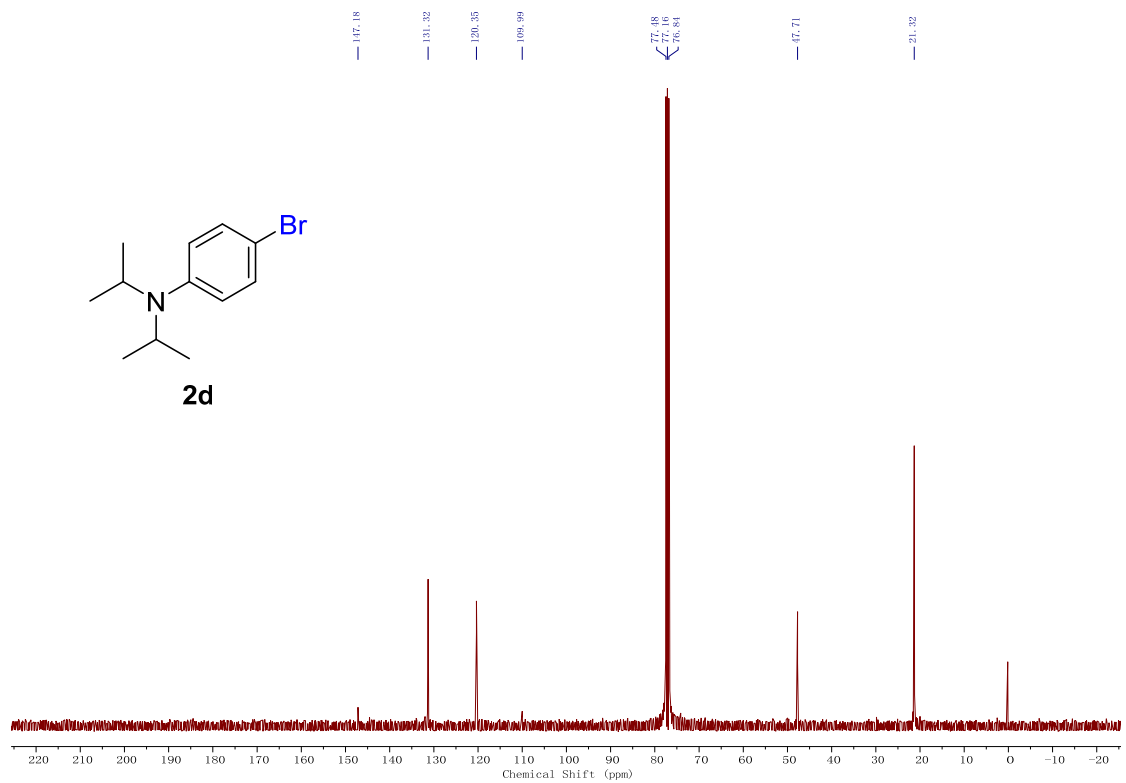
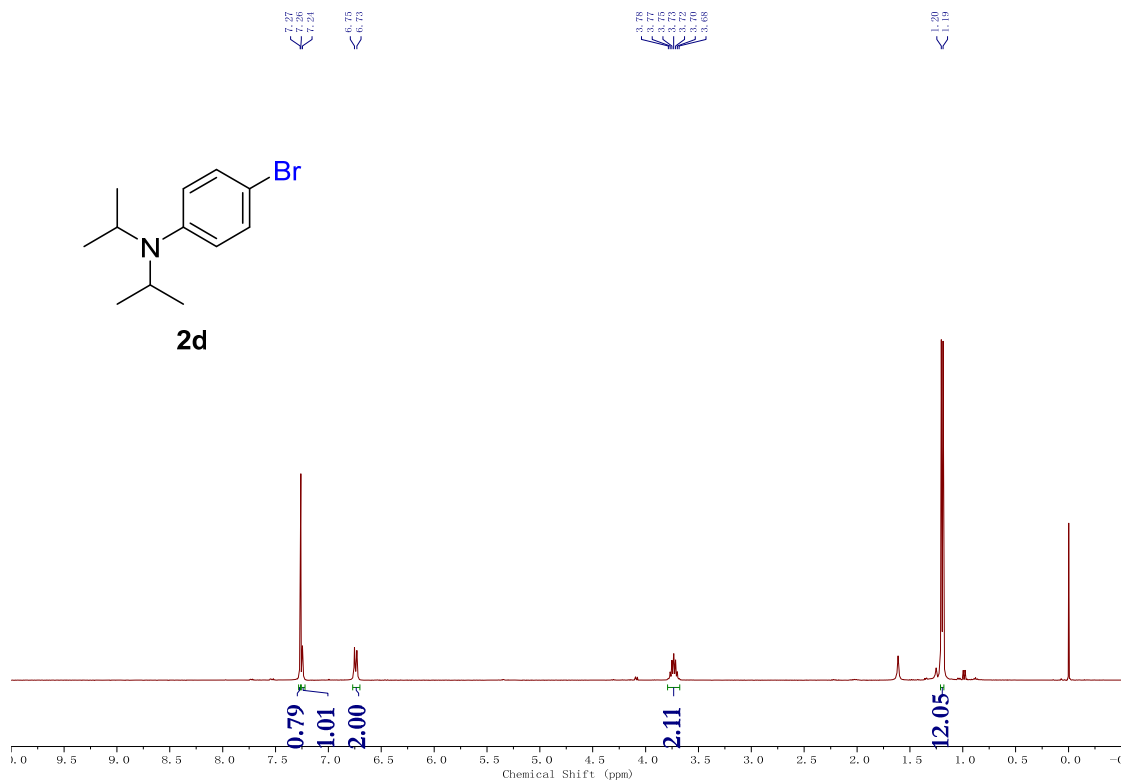
1-Bromo-4-methoxynaphthalene (2x)^[5] Colorless liquid (10.9 mg, 23%, 65% (Conversion yield)). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.4$ Hz, 1H), 8.24 (d, $J = 8.4$ Hz, 1H), 7.71 – 7.61 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 6.68 – 6.55 (m, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.19, 132.39, 129.50, 127.79, 126.85, 126.77, 125.97, 122.47, 113.22, 104.48, 55.63.

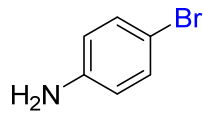
4. NMR spectra



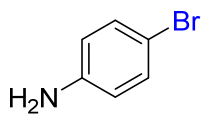
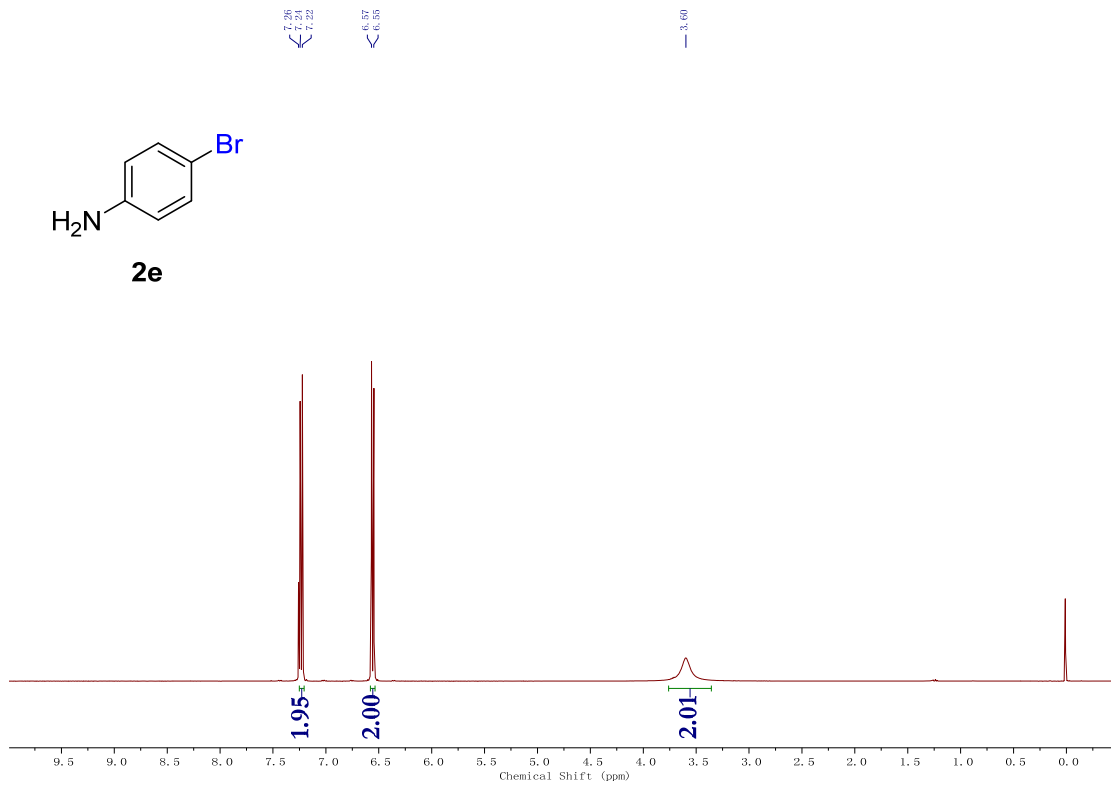




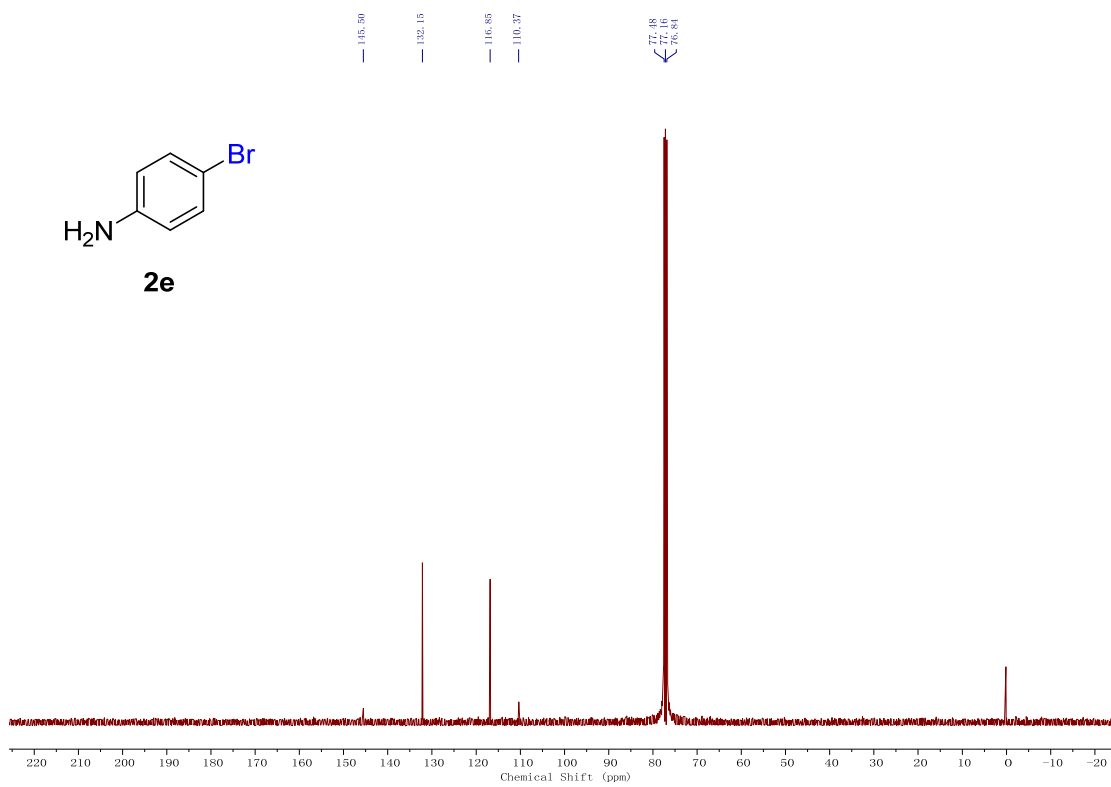


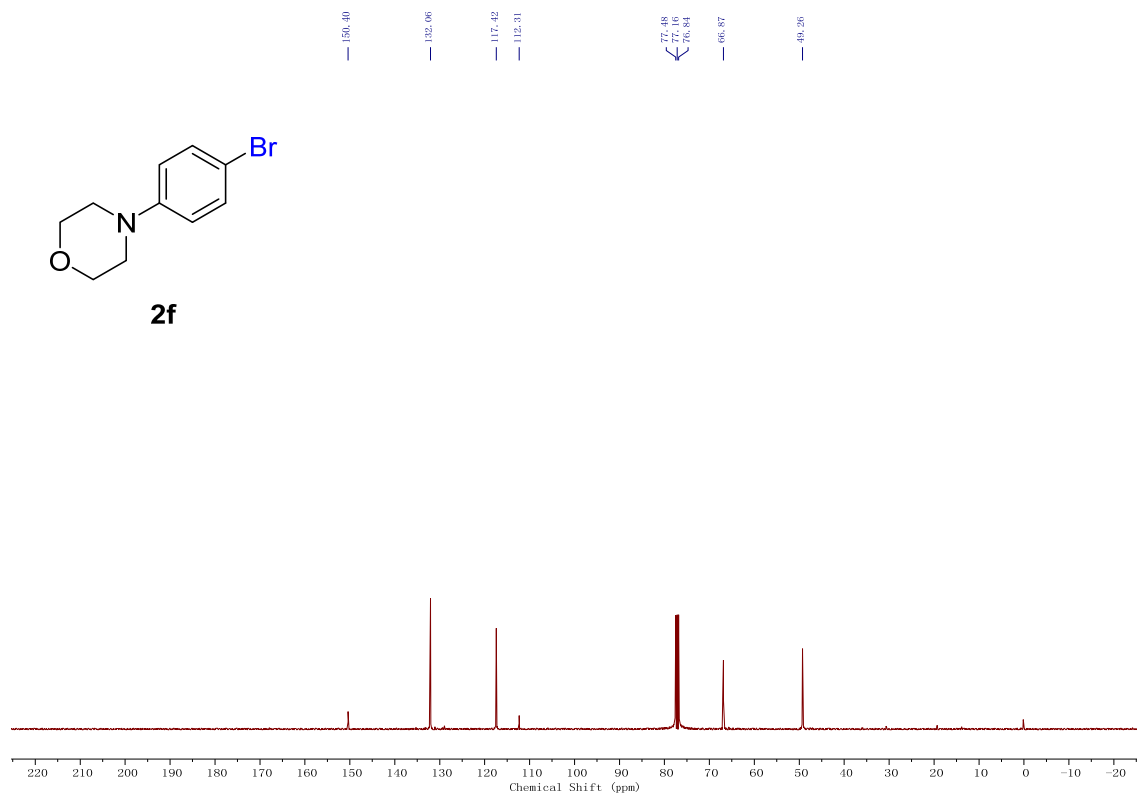
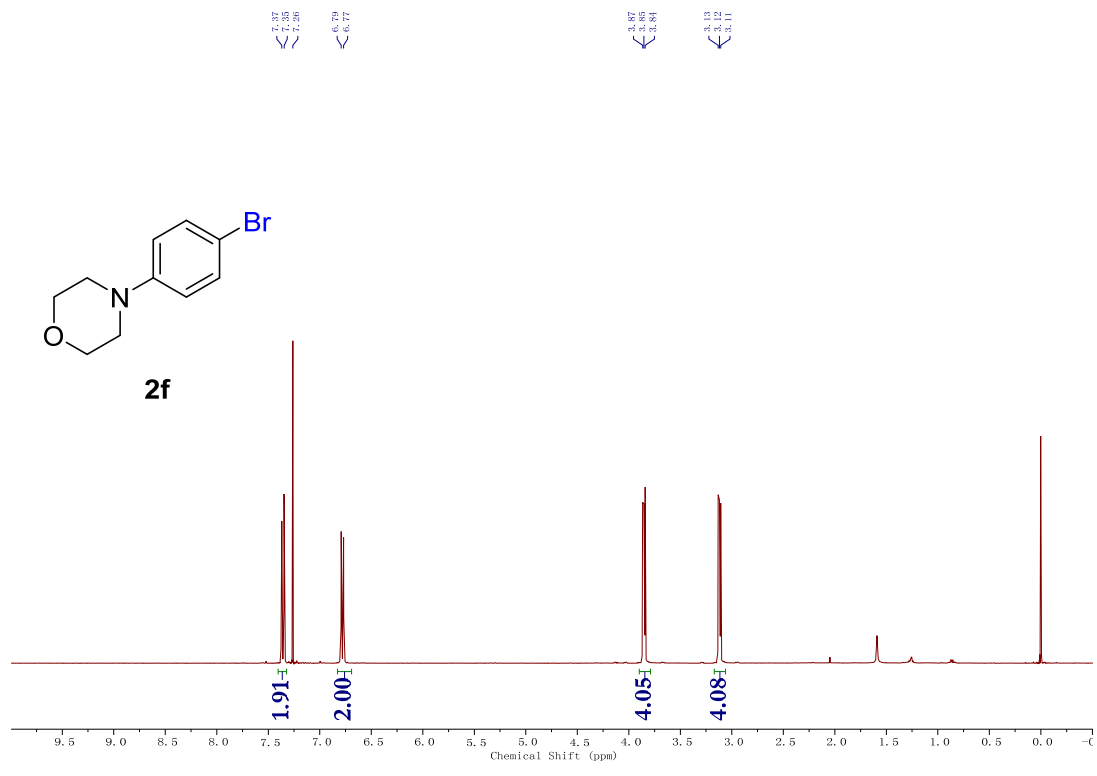


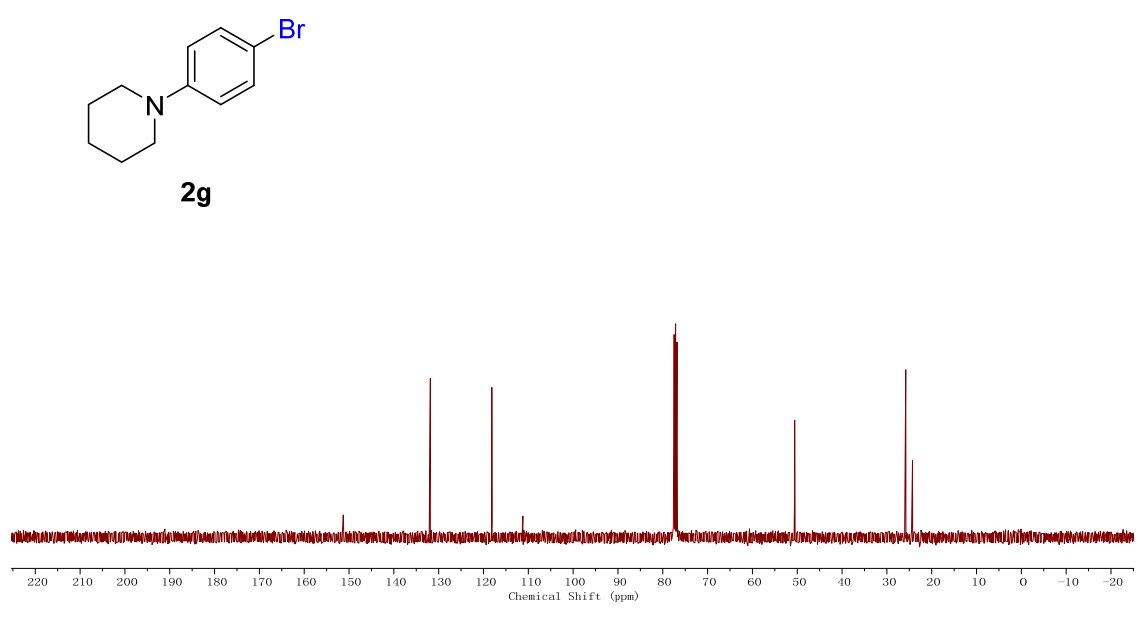
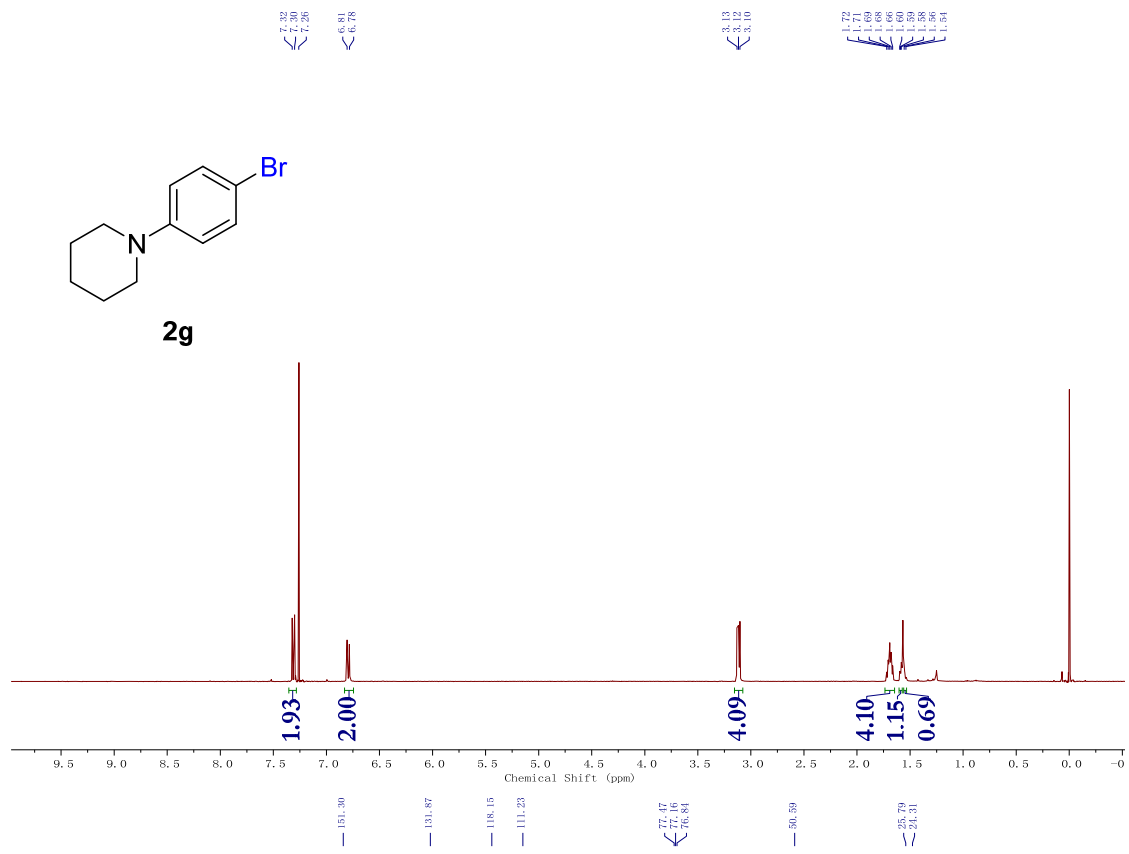
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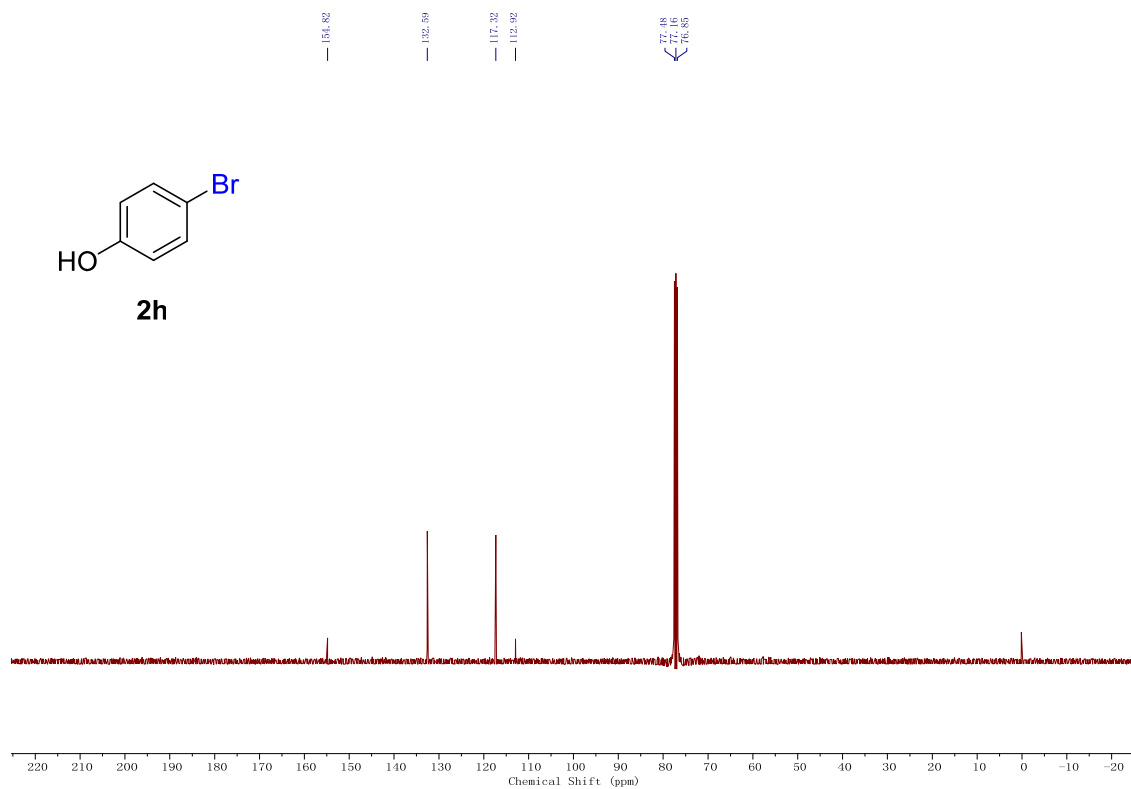
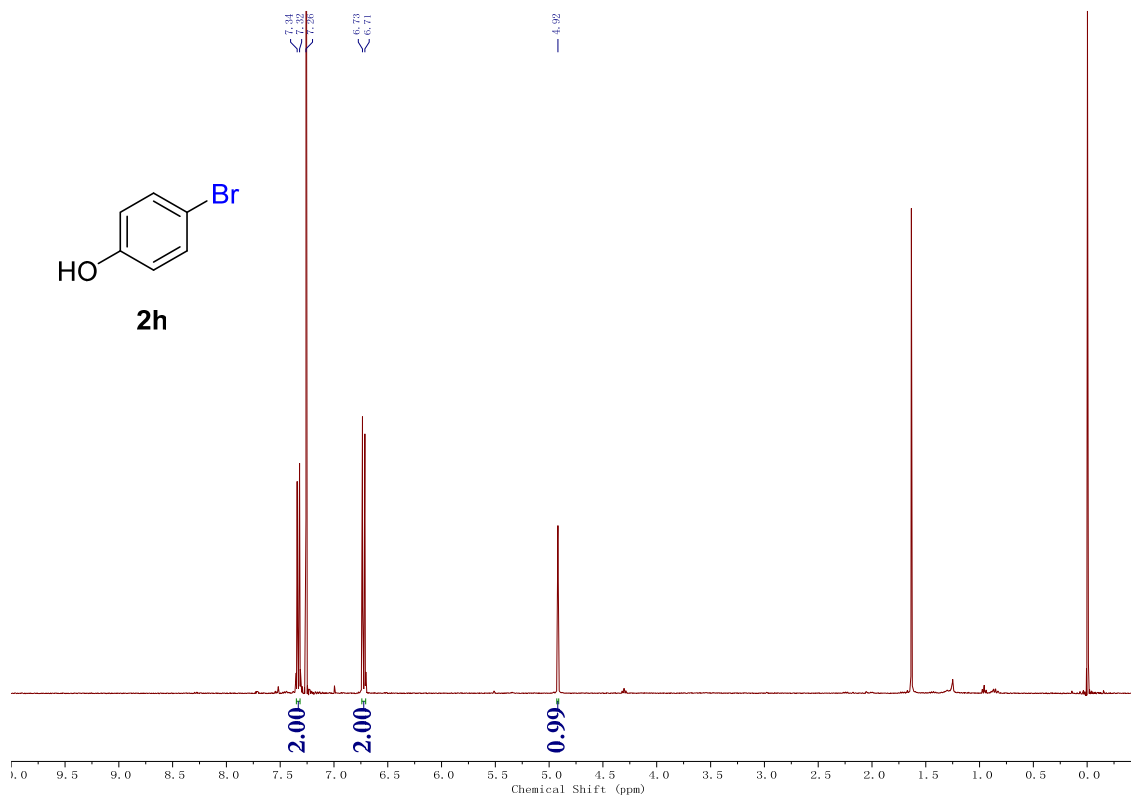


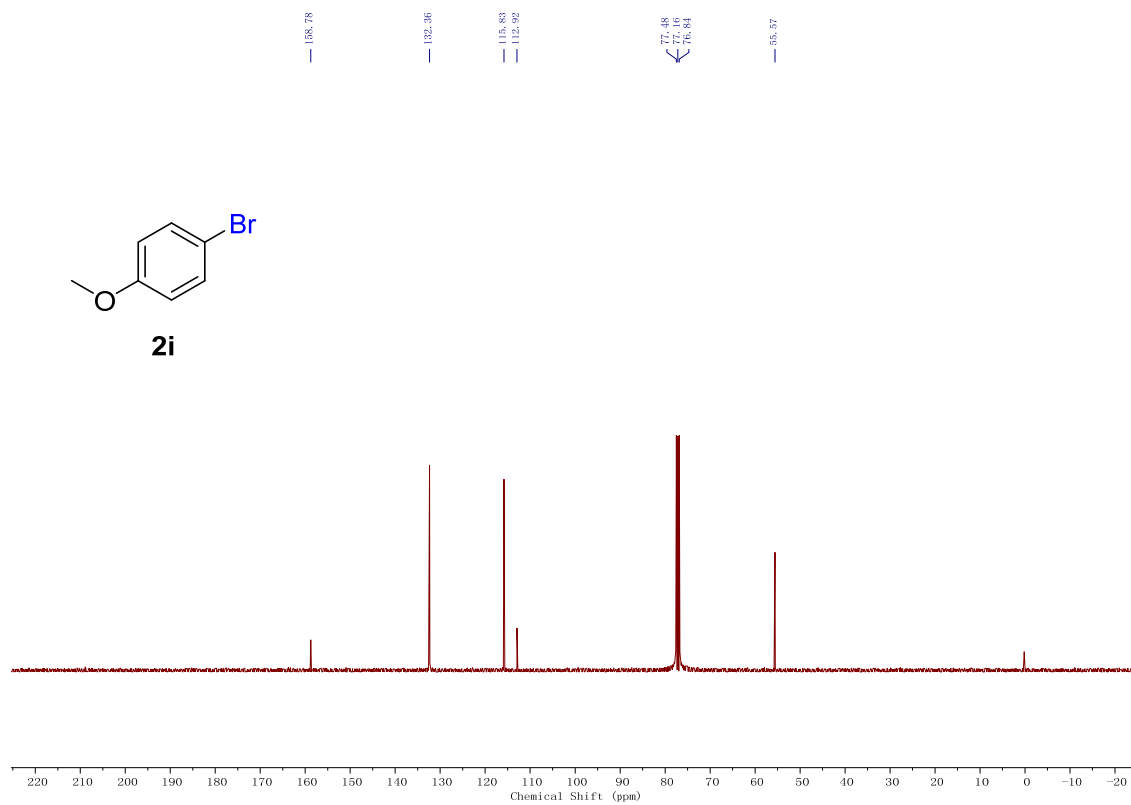
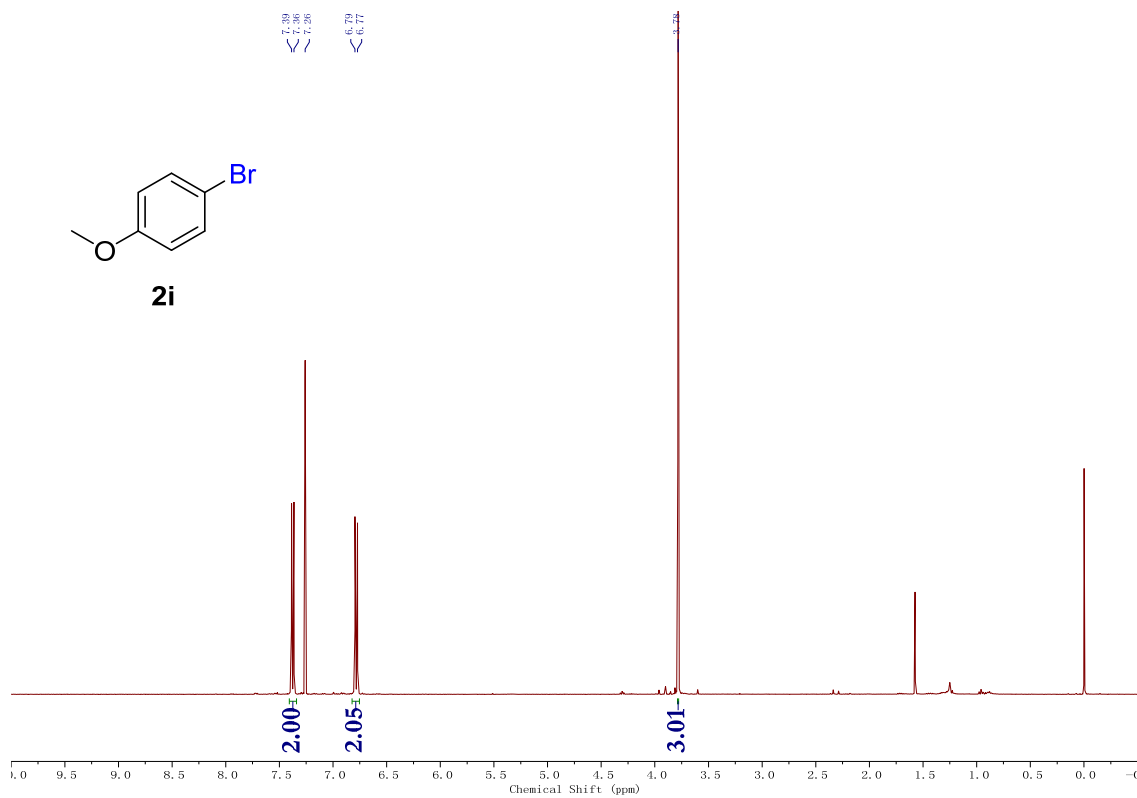
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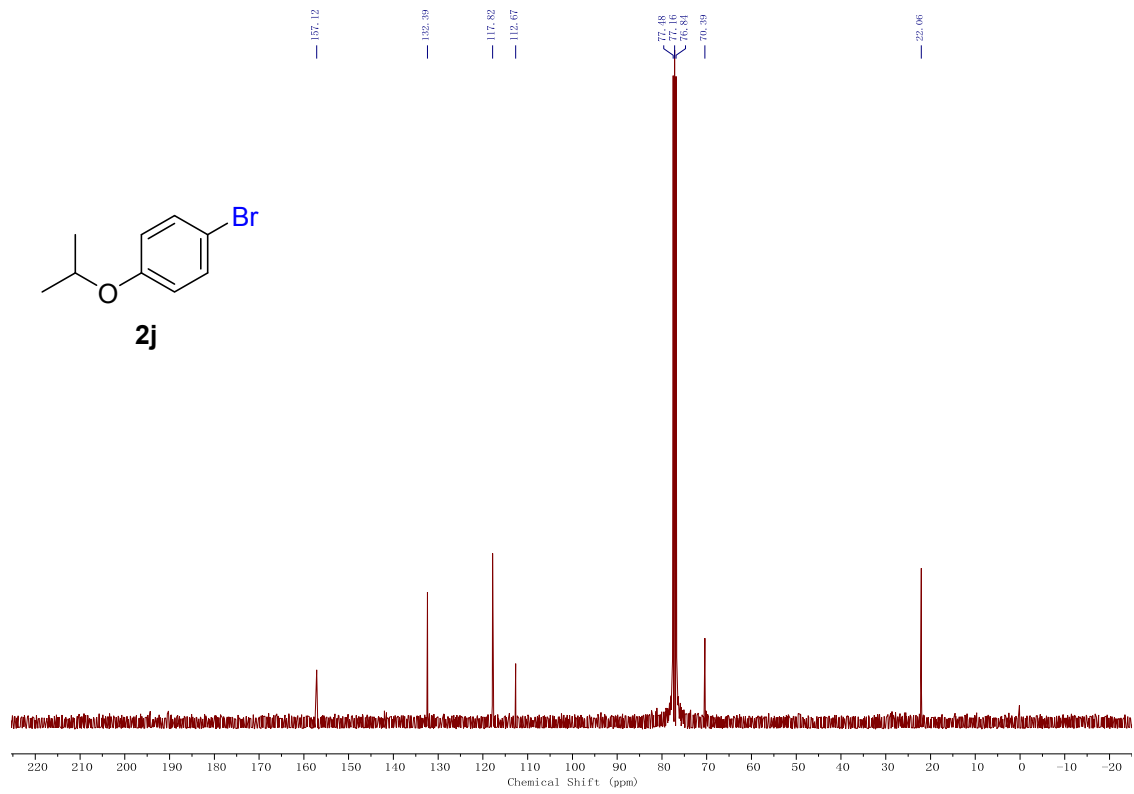
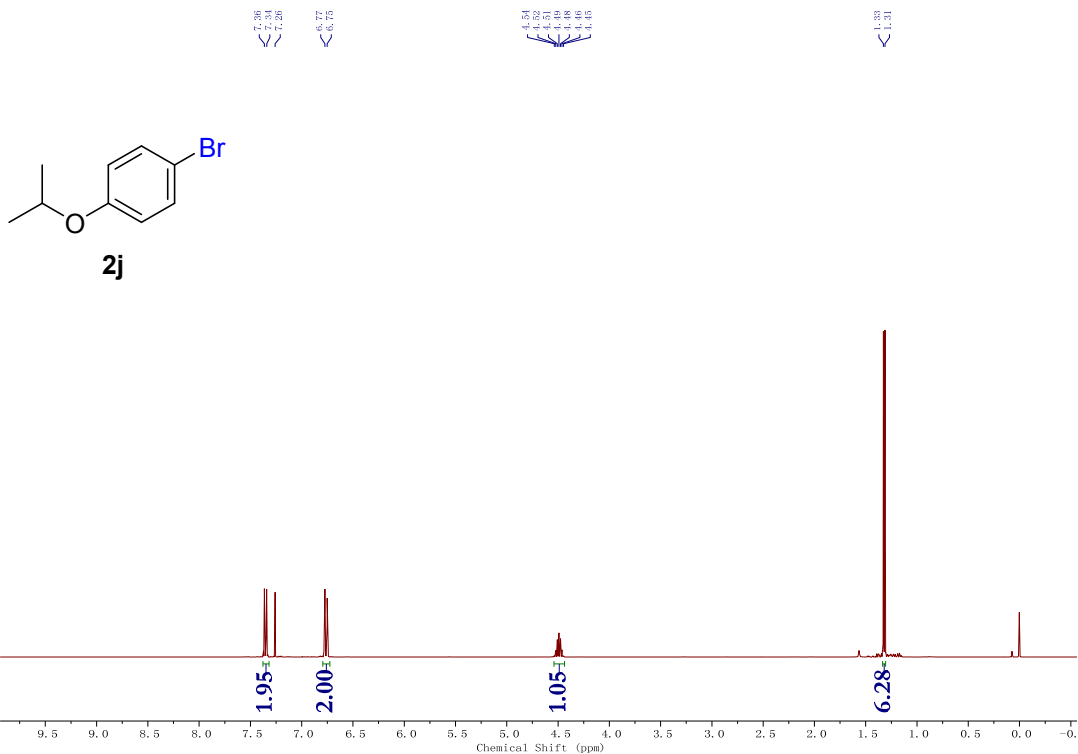


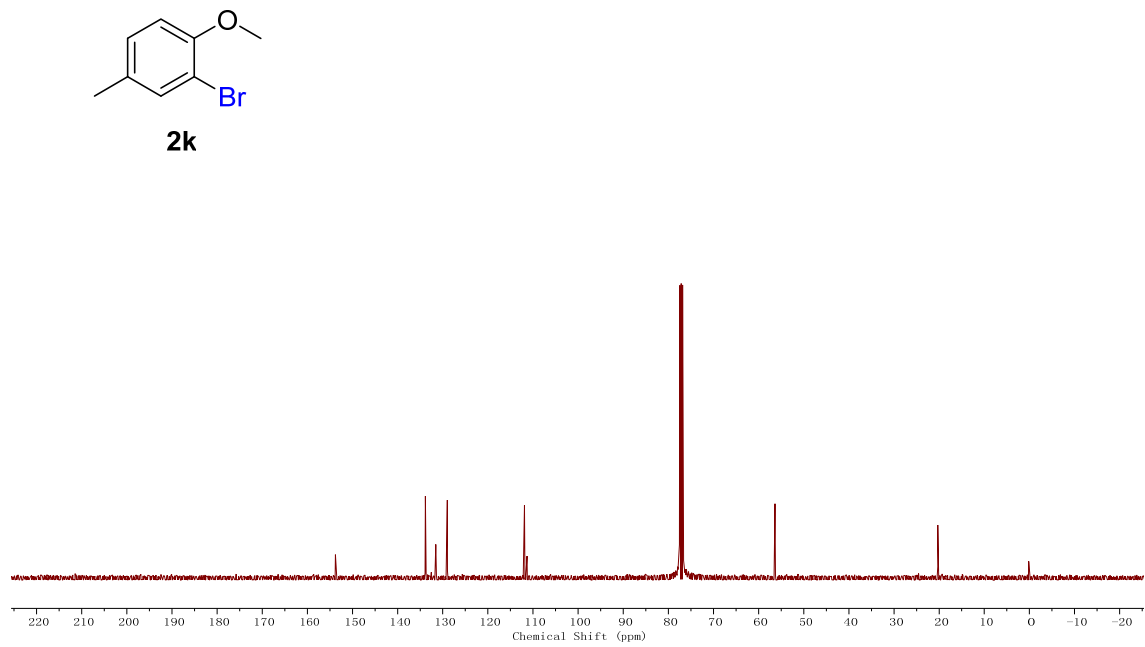
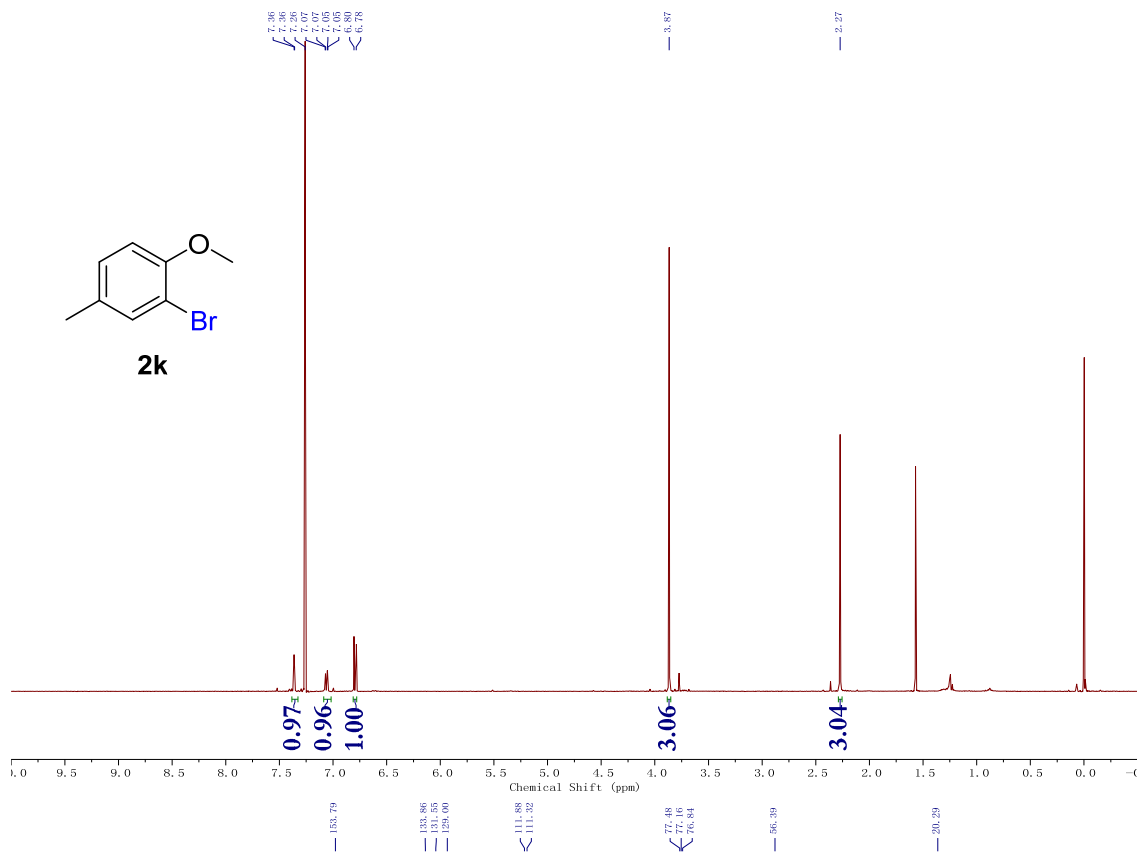


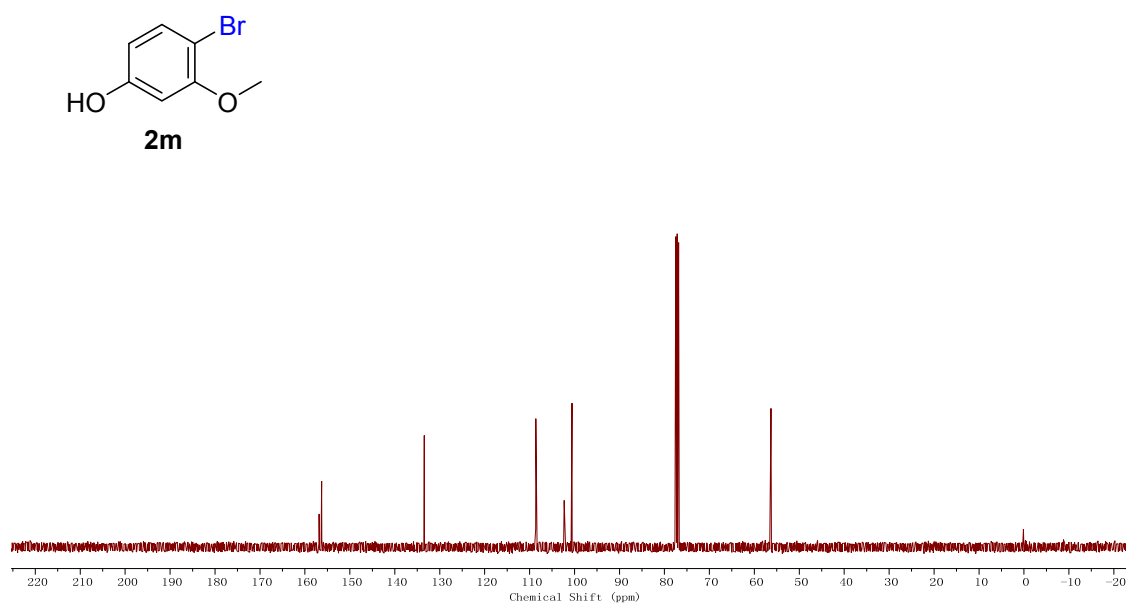
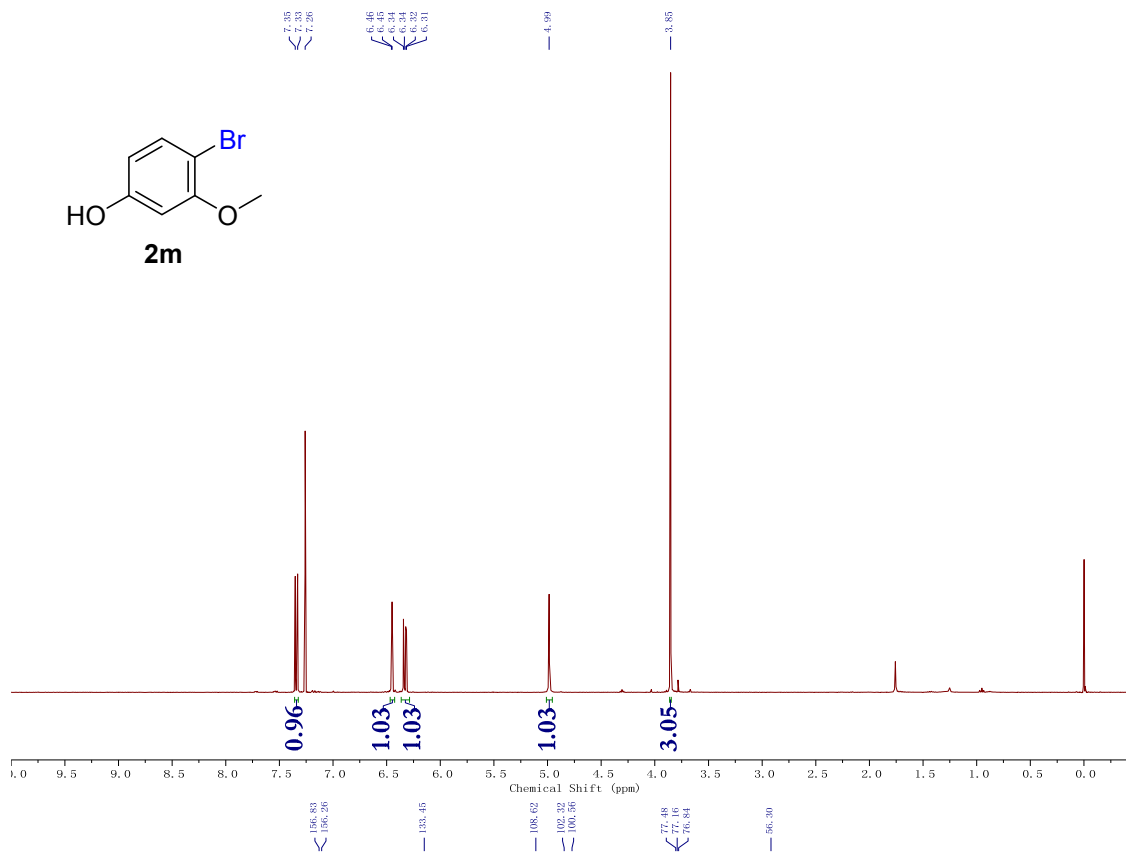


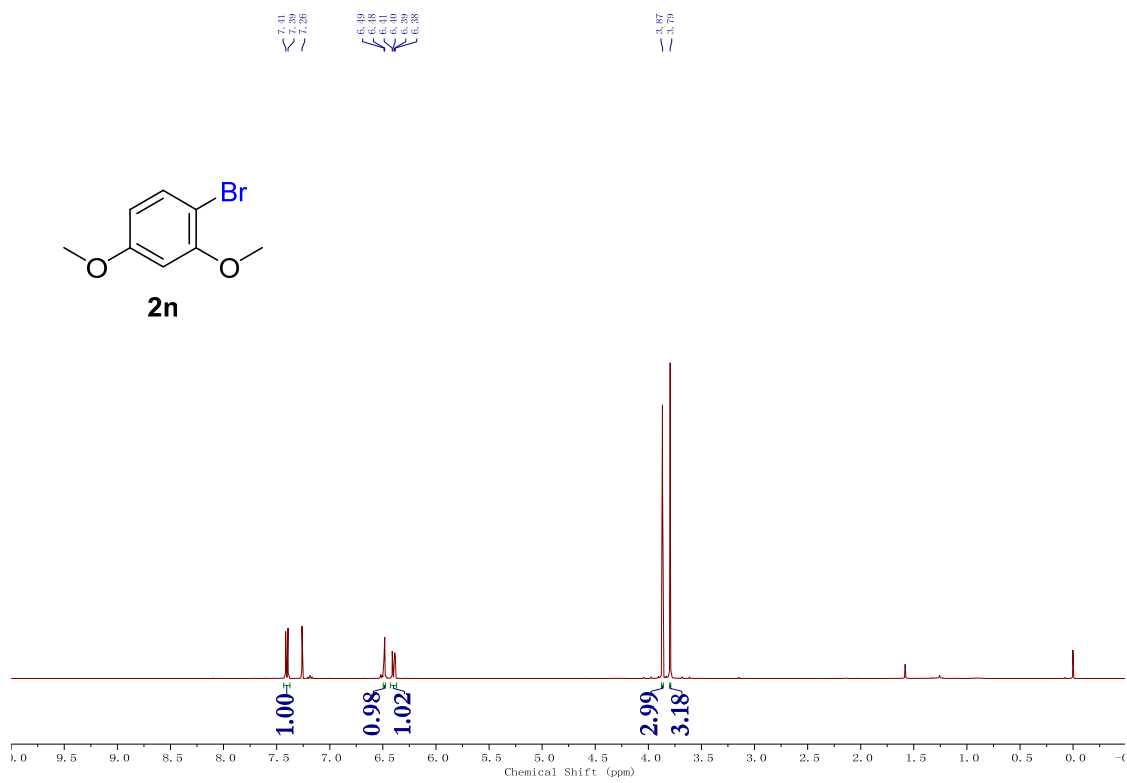


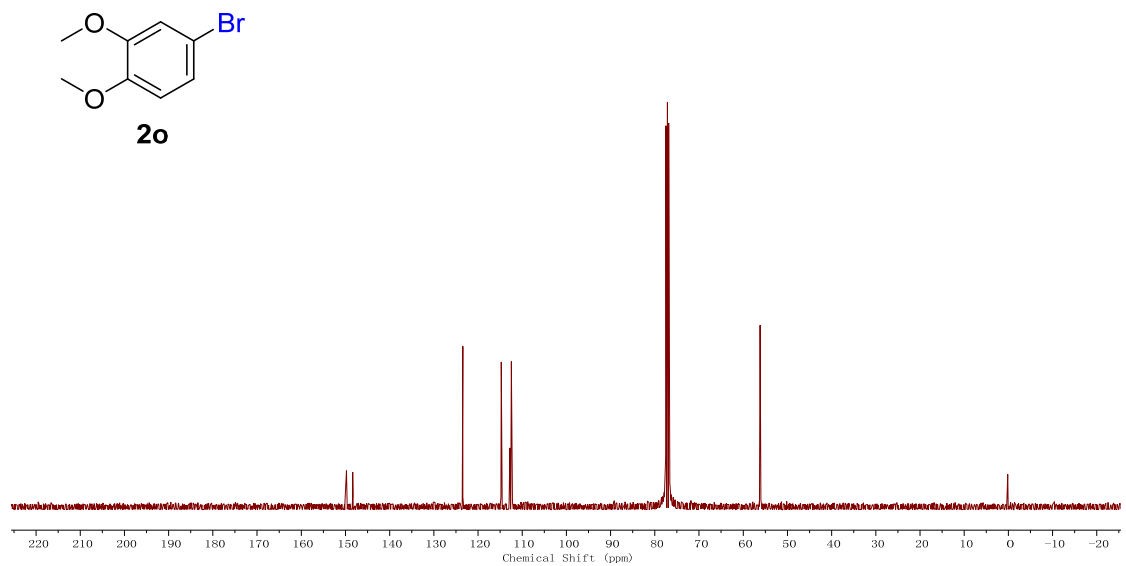
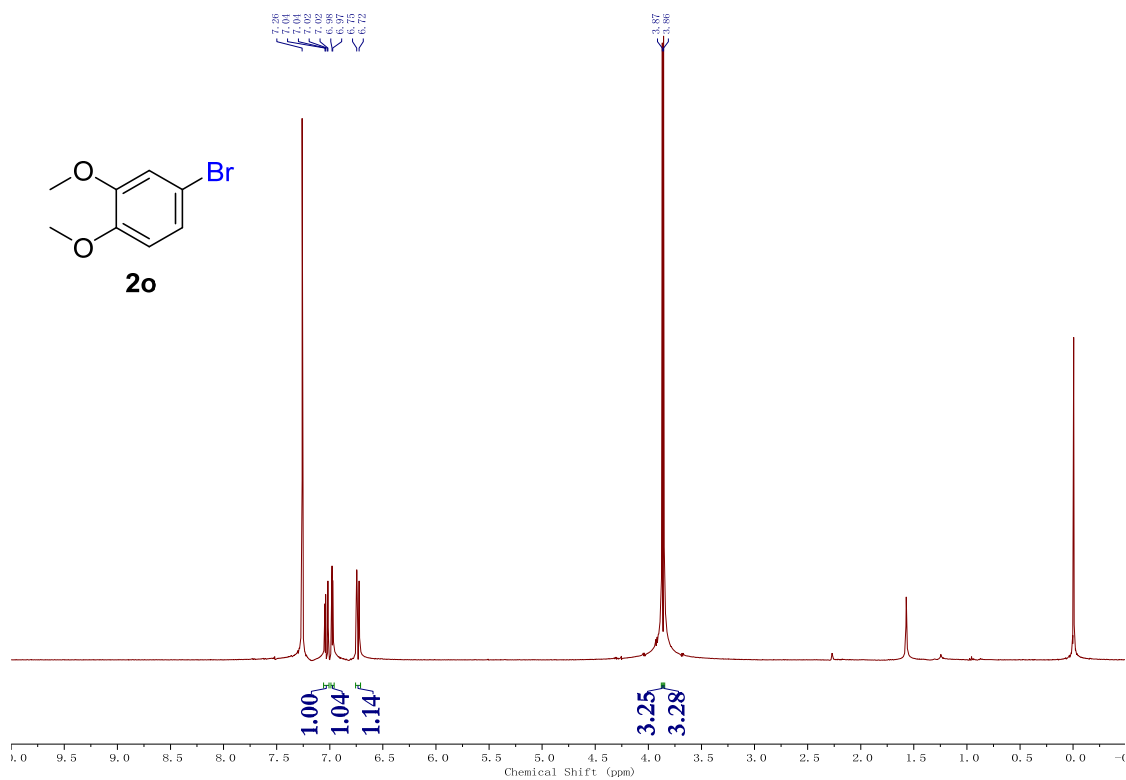


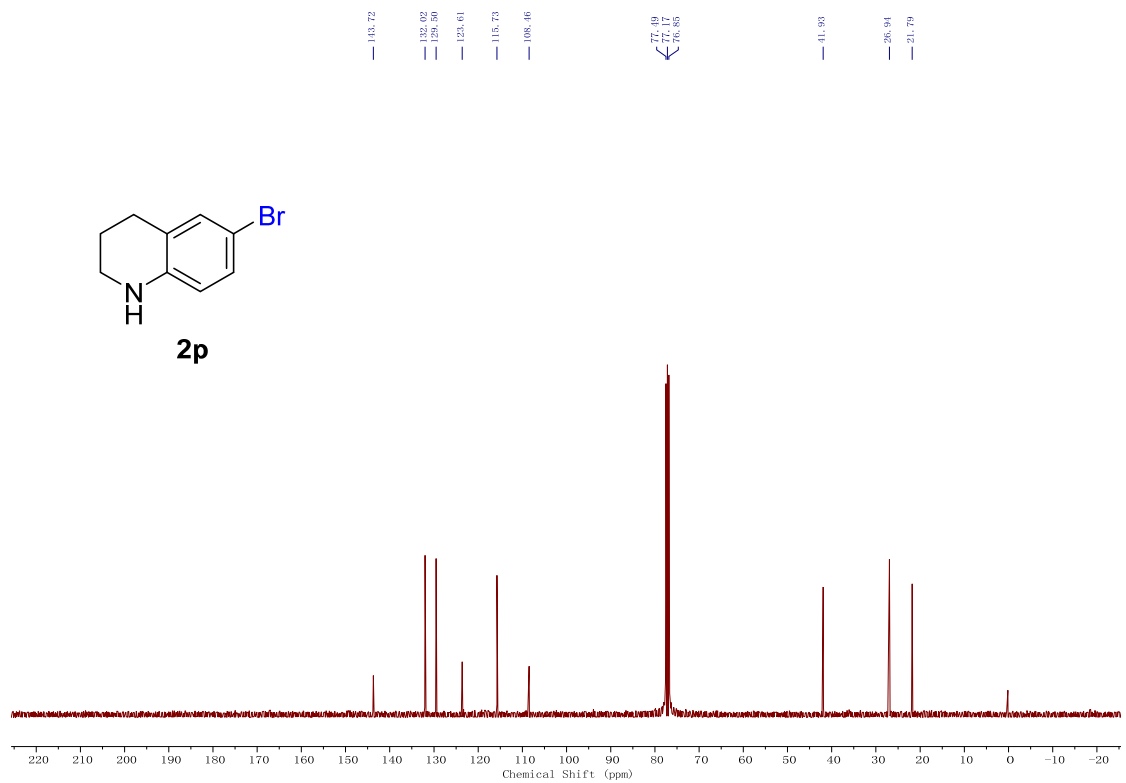
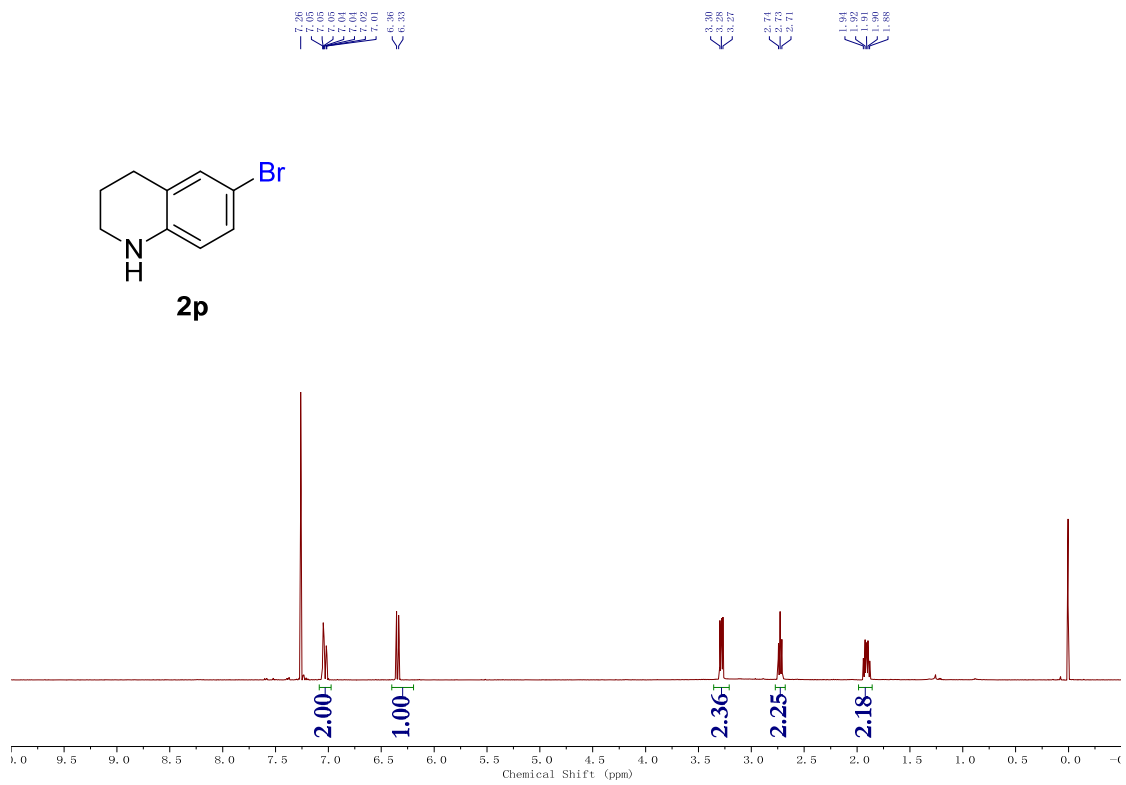


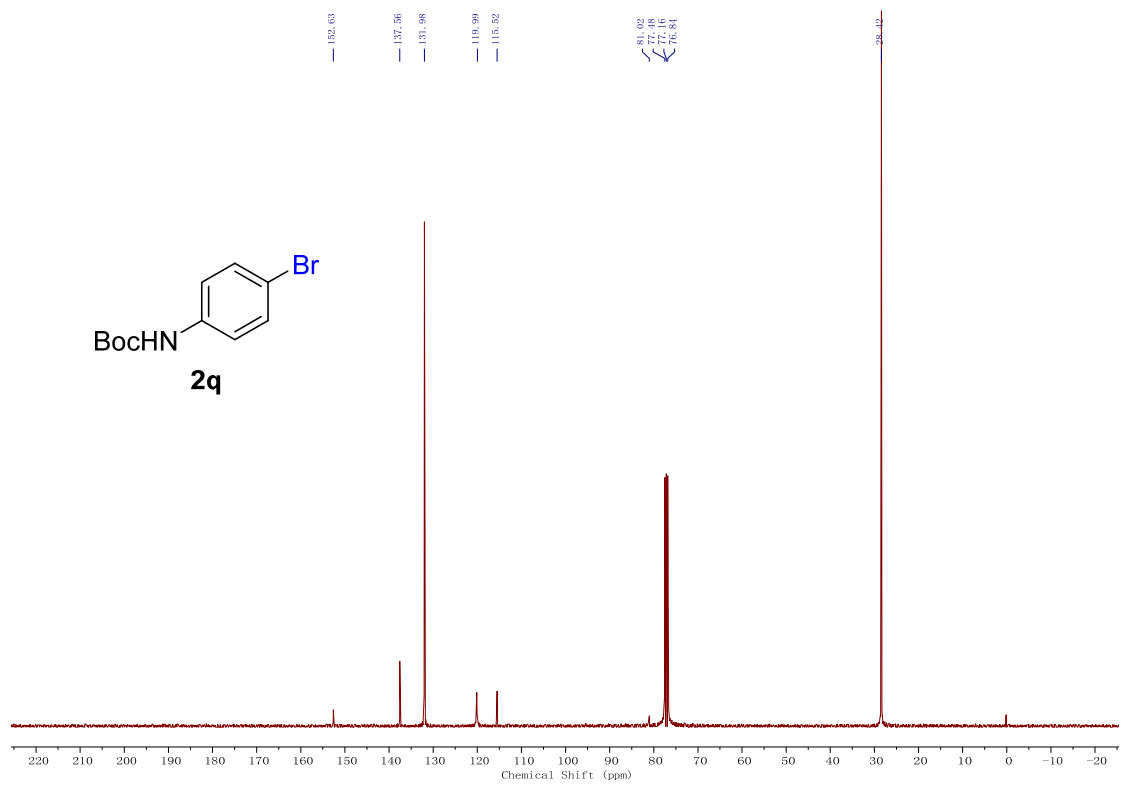
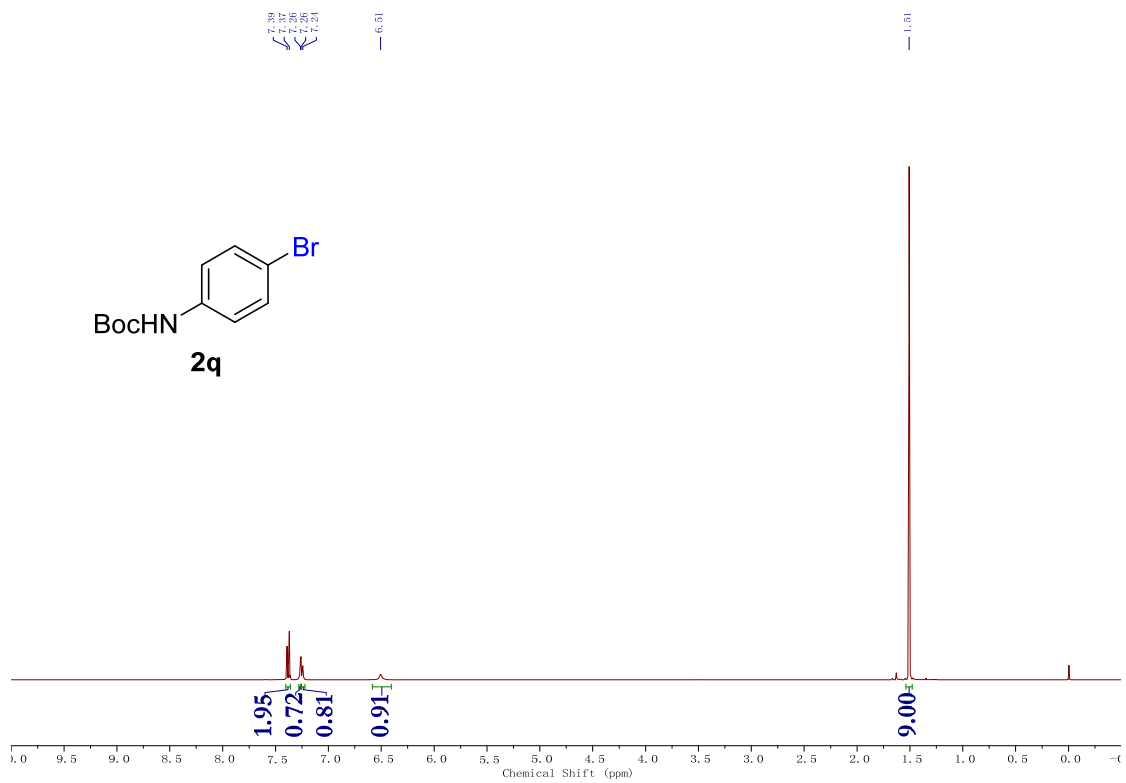


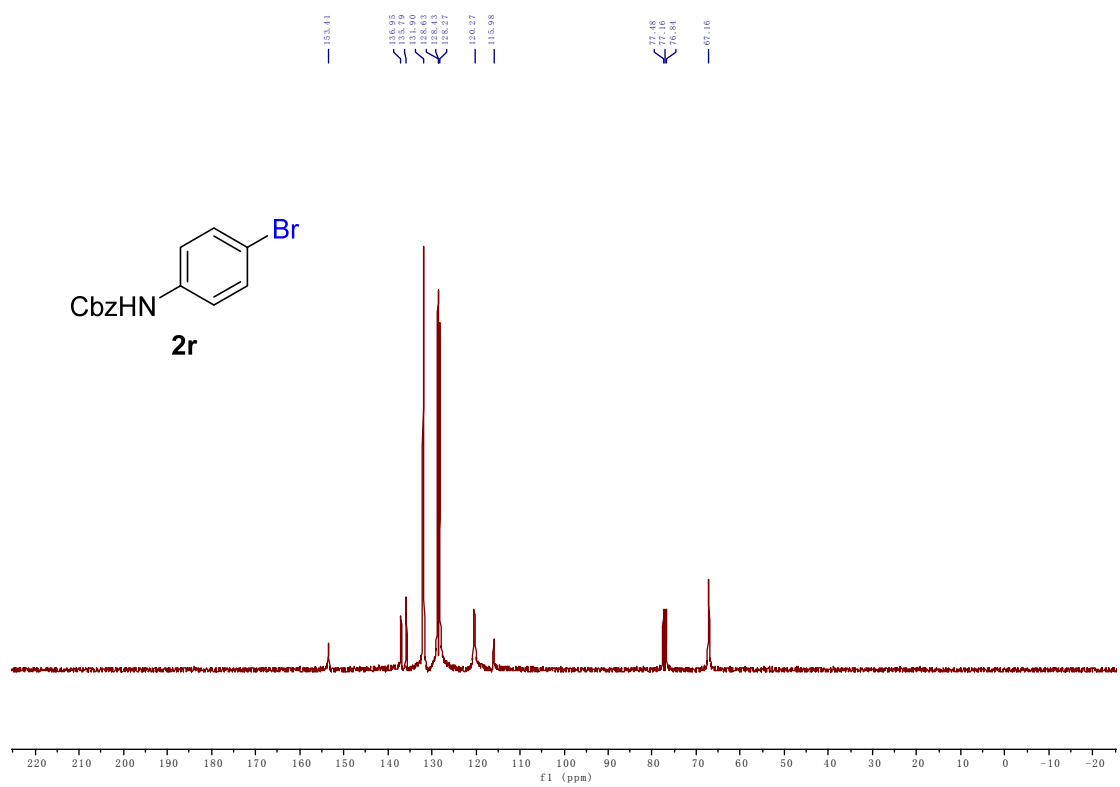
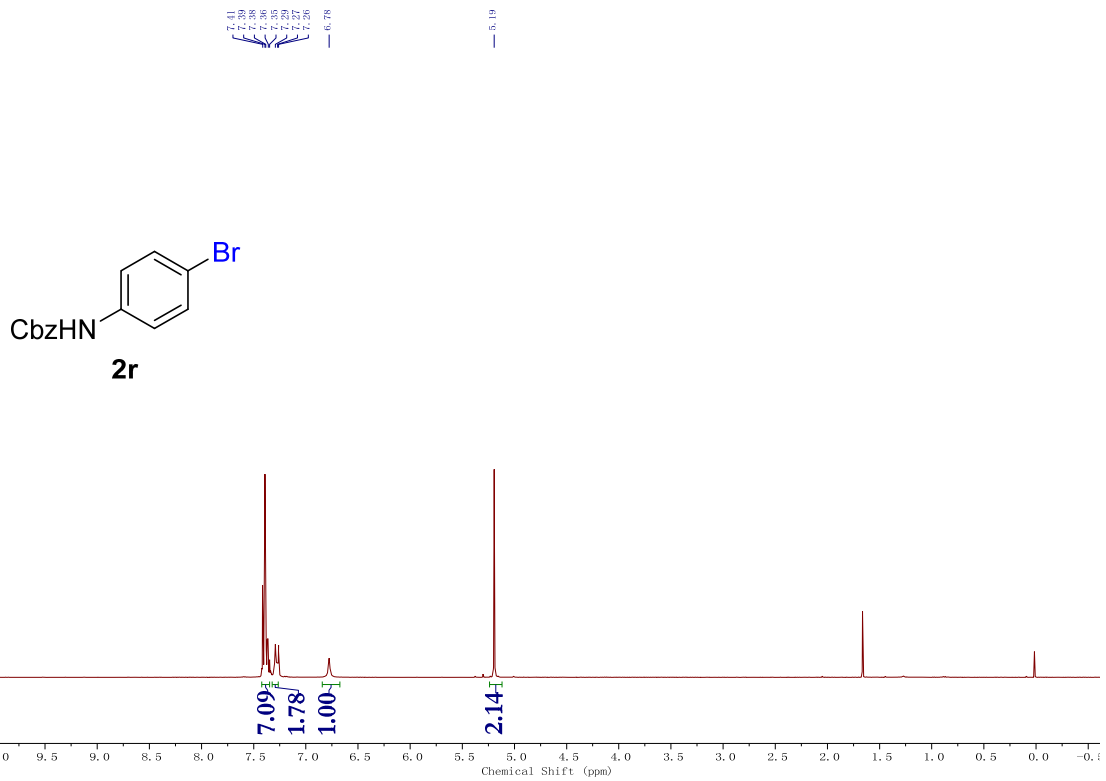


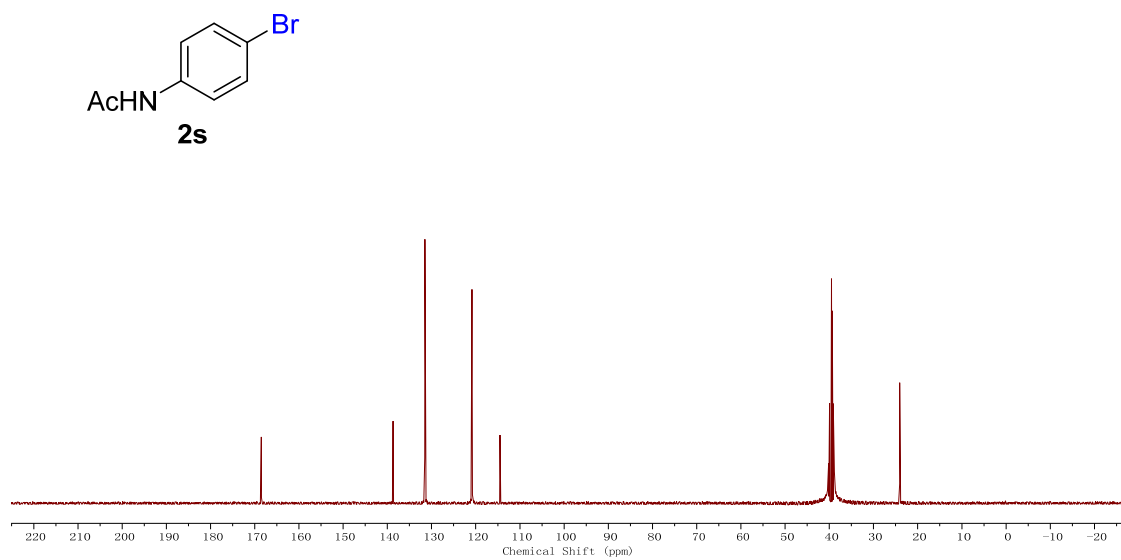
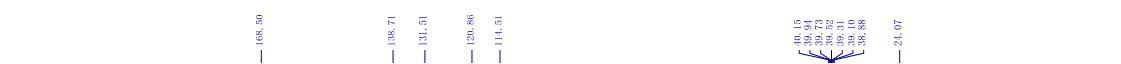
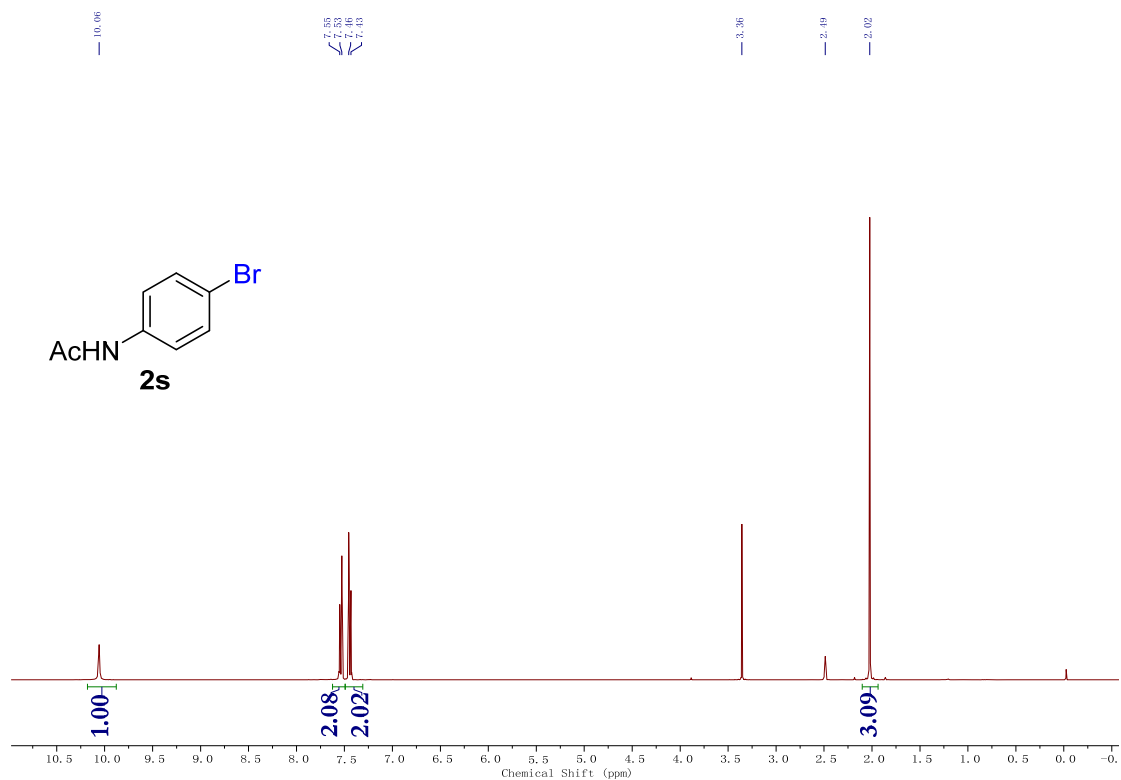


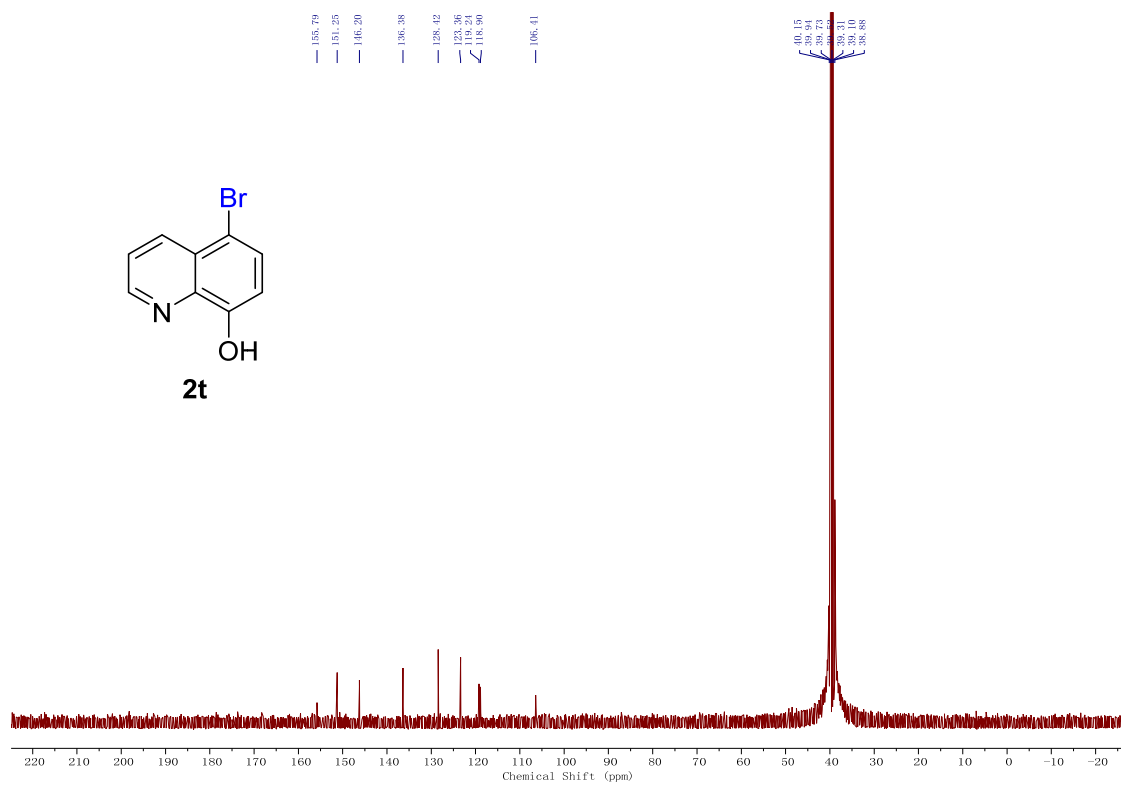
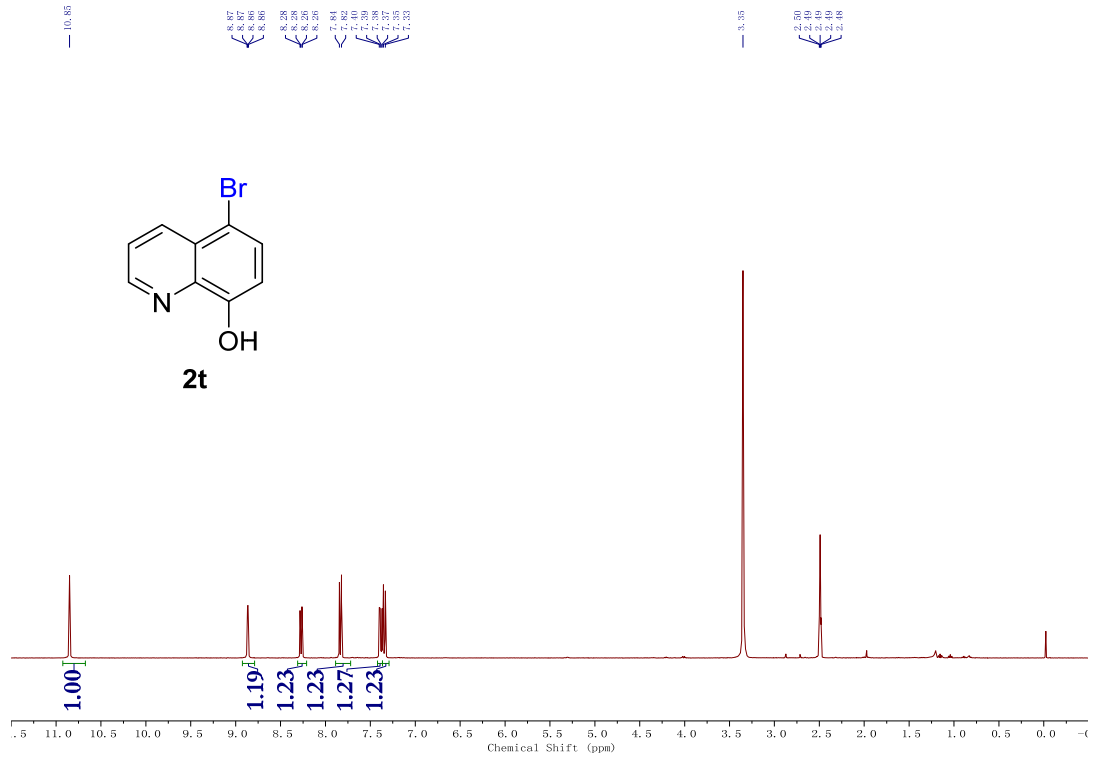


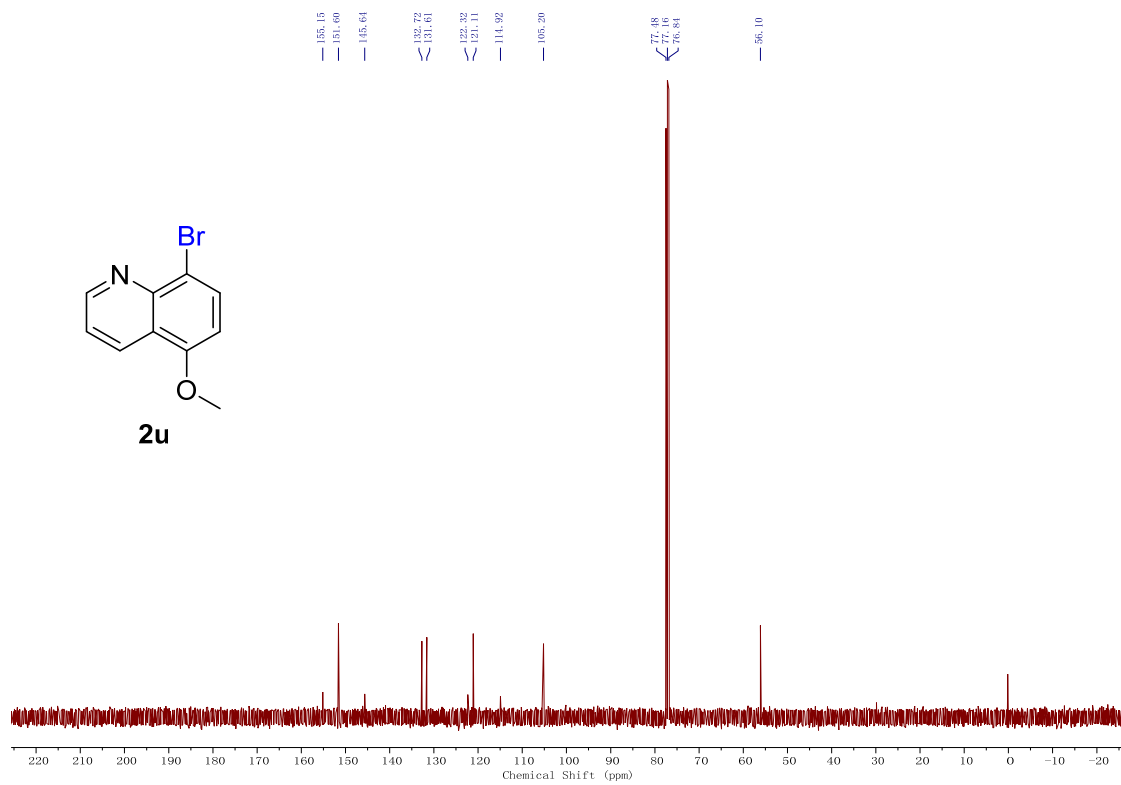
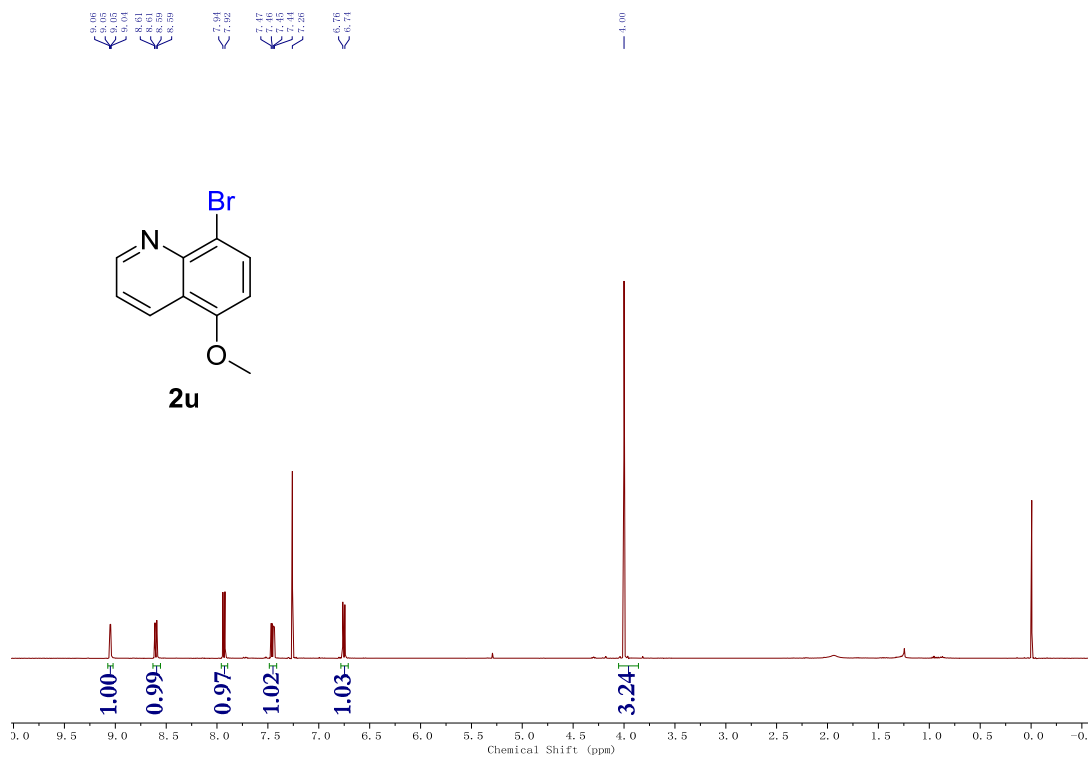


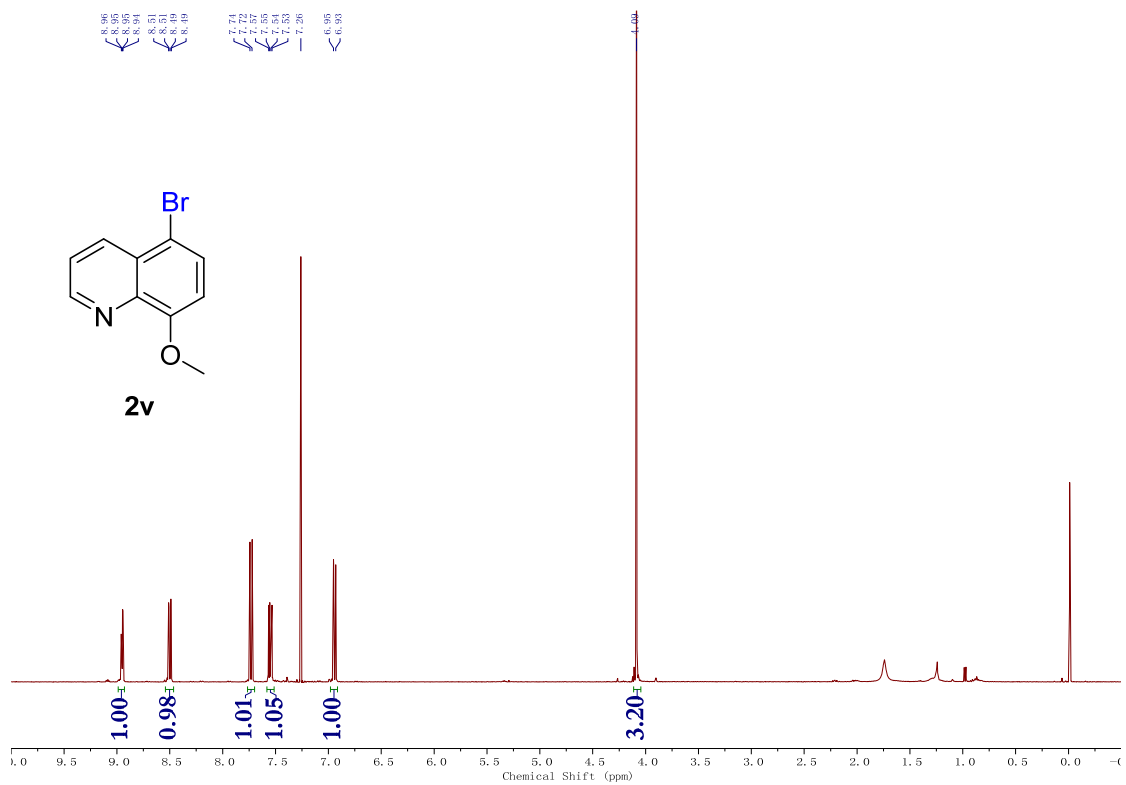


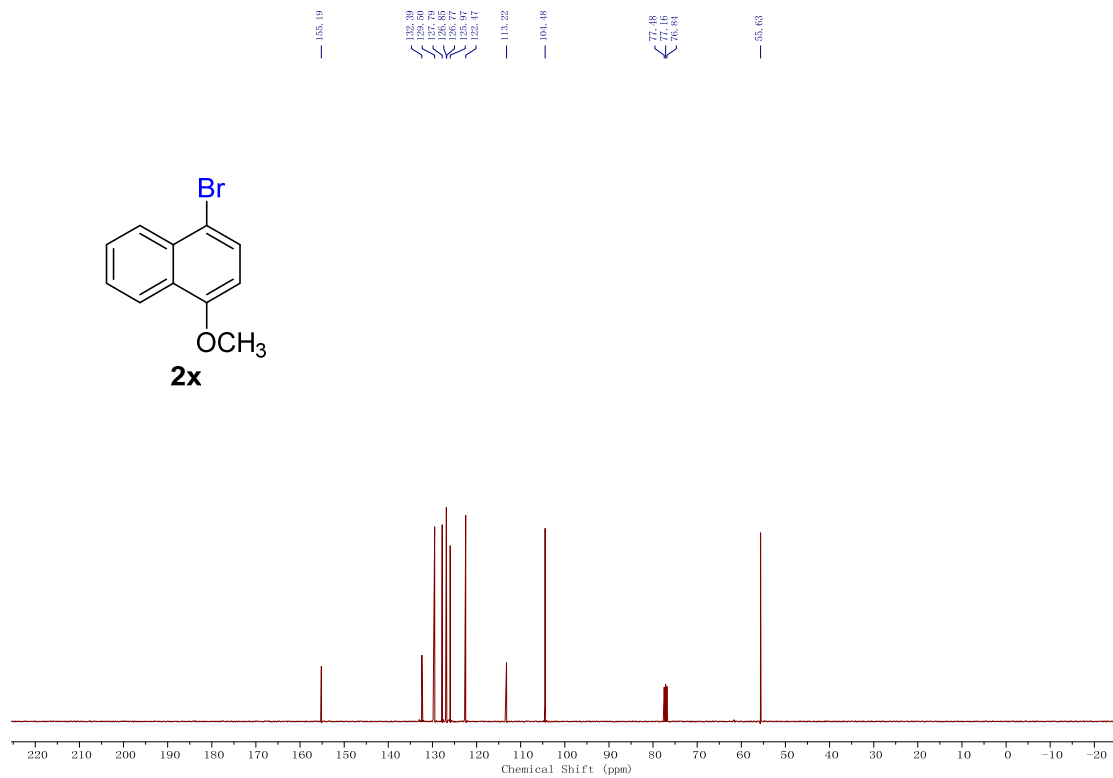
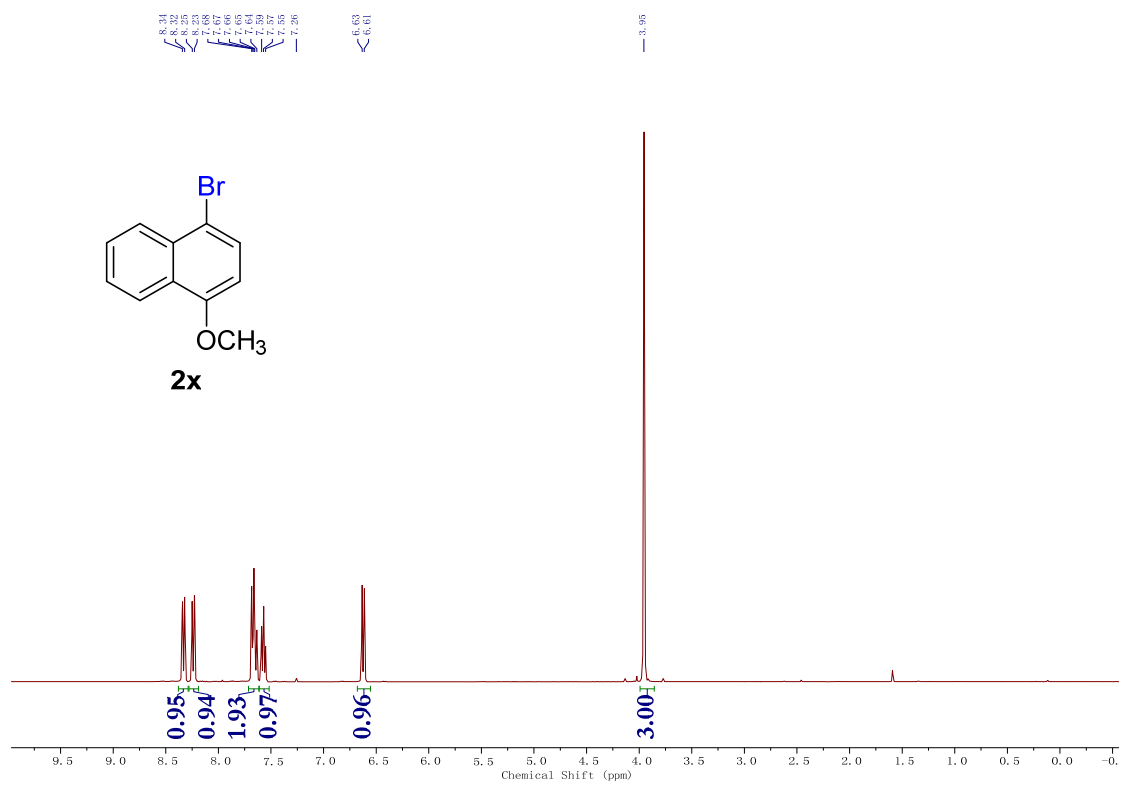












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