Electronic Supplementary Information

TsCl-Promoted Thiolation of Quinoline N-Oxides with Thiophenols

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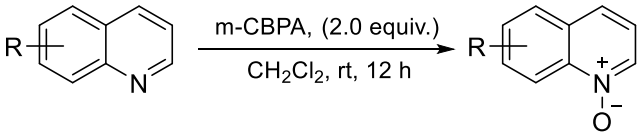
Contents

1. General information

All chemicals were purchased from Energy Chemical Reagent, Ltd, Zane Chemical Technology company, Aladdin Ltd, Crystal pure bio-tech company and so forth. Unless otherwise stated, all experiments were conducted in a seal tube under argon atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on Nuclear Magnetic Resonance spectrometer (400 MHz for ^{1}H or 600 MHz for ^{1}H, 151 MHz for ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$(δ = 7.26 for ^{1}H-NMR， δ = 77.00 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using ZAB-HS Bifocal high resolution mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz).

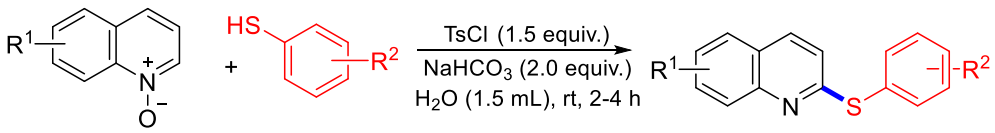
2. Experimental section

2.1 Typical procedure for the preparation of quinoline *N*-oxides[1]



To a 50 mL dry flask equipped with a stirring magnet was added 5 mL CH_2Cl_2 and substituted quinoline (10 mmol, 1.0 equiv) and a mixture of m-CPBA (20 mmol, 2.0 equiv.) dissolved in CH_2Cl_2 (5 mL) was added in batches under ice bath conditions. The reaction mixture was then left to stir at room temperature overnight. After completion, the reaction mixture was diluted with 10 mL of CH_2Cl_2, burst with 1 M aqueous KOH and extracted with saturated saline and CH_2Cl_2. The organic phase was combined and washed three times with saline, dried with anhydrous Na_2SO_4, concentrated under reduced pressure and purified by column chromatography (pure EA) to give quinoline *N*-oxides.

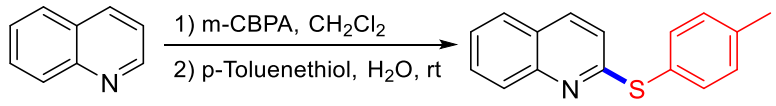
2.2 General procedure for the preparation of 2-thiolquinolines



1 **2** **3 and 4**

Add quinoline *N*-oxides **1** (0.2 mmol), 2 mL of water as solvent, benzenethiols **2** (0.4 mmol, 2.0 equiv), TsCl (0.3 mmol, 1.5 equiv) and sodium bicarbonate (0.4 mmol, 2.0 equiv) to a 5 mL clear colourless reaction flask and stir at room temperature for 2 hours. After complete reaction, extract the reaction solution with diethyl ether and repeat three times, combine the organic layers and concentrate under reduced pressure. The organic layer was concentrated under reduced pressure and dried overnight with anhydrous sodium sulphate. The dried solution was concentrated under reduced pressure by filtration and purified by column chromatography (EA/PE =1/40, v/v) to obtain the 2-thioquinoline product **3** and **4**. The pure sample obtained was characterised by ^{1}H NMR and ^{13}C NMR.

2.3 One-pot, two-step synthesis of 2-thiolquinoline from quinoline



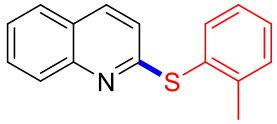
5a, 7 mmol **3aa,** 1.055 g, 60%

To a 25 mL dry flask equipped with a stirring magnet was added 5 mL CH_2Cl_2 with quinoline **5a**(7 mmol) and a mixture of m-CPBA (14 mmol, 2.0 equiv) dissolved in CH_2Cl_2 (4 mL) was added in batches under the conditions of an ice bath. The reaction mixture was then left to stir at room temperature overnight. After completion, the reaction mixture was diluted with 6 mL of CH_2Cl_2, burst with 1 M aqueous KOH, concentrated under reduced pressure to remove excess CH_2Cl_2, followed by the addition of benzenethiol (14 mmol, 2.0 equiv), TsCl (10.5 mmol, 1.5 equiv), $NaHCO_3$ (14 mmol, 2.0 equiv) and stirred at room temperature for 4 h. After the reaction was complete, the reaction solution was extracted with diethyl, repeated three times, the organic layers were combined and concentrated under reduced pressure. The organic layer was combined and concentrated under reduced pressure and dried overnight with anhydrous sodium sulphate. The dried solution was concentrated under reduced pressure by filtration and purified by column chromatography (EA/PE =1/40, v/v) to give 2-tosylquinoline. A pure sample of 1.055 g was obtained and characterised by ^{1}H NMR and ^{13}C NMR.

3. Characterization Data of Products

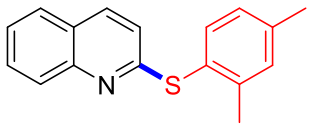
2-(*p*-Tolylthio)quinoline (3aa)[2]

Colorless liquid, 42.2 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.70-7.63 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2, 148.0, 139.6, 136.3, 135.3, 130.5, 129.4, 129.3, 127.5, 127.1, 125.7, 125.6, 119.2, 21.3.



2-*o*-Tolylsulfanylquinoline (3ab)[3]

Colorless liquid, 41.2 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.70-7.64 (m, 3H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.40-7.38 (m, 2H), 7.30-7.27 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 148.2, 143.0, 136.8, 136.4, 131.0, 130.0, 129.9, 129.8, 128.3, 127.5, 127.1, 125.7, 125.6, 118.7, 21.0.

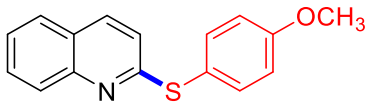


2-(2,4-Xylenethio)quinoline (3ac)

Colorless liquid, 47.2 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.70-7.66 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 6.8 Hz, 1H), 7.21 (s, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H) ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 148.2, 142.8, 140.3, 136.9, 136.3, 131.9, 129.9, 128.2, 127.9, 127.5, 126.2, 125.7, 125.5, 118.4, 21.3, 20.9.

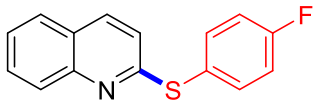
2-(*m*-Tolylthio)quinoline (3ad)

White Solid; M.p. 80-82 °C, 40.7 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.4 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.71-7.64 (m, 2H), 7.49-7.43 (m, 3H), 7.34 (t, J = 7.6 Hz, 1H), 7.27-7.25 (m, 1H), 6.97 (d, J = 8.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 148.0, 139.6, 136.4, 135.7, 132.1, 130.5, 130.1, 130.0, 129.5, 128.3, 127.5, 125.8, 125.7, 119.5, 21.3.



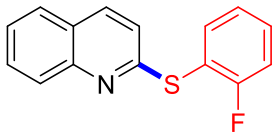
2-(*p*-Methoxyphenylthio)quinoline (3ae)

White Solid; M.p. 70-73 °C, 46.5 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.70-7.63 (m, 2H), 7.60 (d, J = 8.8 Hz, 2H), 7.43 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 160.8, 147.9, 137.3, 136.4, 130.0, 128.2, 127.5, 125.7, 125.6, 121.0, 118.8, 115.3, 55.4.



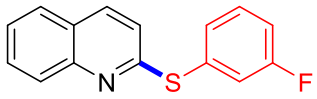
2-(*p*-Fluorophenylthio)quinoline (3af)

White Solid; M.p. 75-76 °C, 37.2 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 8.0, 5.6 Hz, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.68-7.63 (m, 3H), 7.45 (td, J = 8.0, 1.2 Hz, 1H), 7.16 (t, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 162.6, 161.1, 148.0, 137.4 (d, $J_{C\text{-}F}$ = 9.0 Hz), 136.5, 130.0, 128.3, 127.5, 125.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 125.8, 125.7, 119.2, 116.8, 116.7 (d, $J_{C\text{-}F}$ = 21.9 Hz).



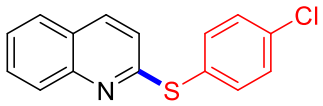
2-(*o*-Fluorophenylthio)quinoline (3ag)

Colorless liquid, 33.2 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.4 Hz, 2H), 7.72-7.63 (m, 3H), 7.50-7.42 (m, 2H), 7.26-7.20 (m, 2H), 7.01 (d, J =8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 162.1, 159.4, 148.1, 137.2, 136.5, 131.8 (d, J = 8.0 Hz), 130.0, 128.4, 127.5, 126.0, 125.8, 125.0 (d, $J_{C\text{-}F}$ = 3.9 Hz), 119.1, 117.9 (d, $J_{C\text{-}F}$ = 18.3 Hz), 116.4 (d, $J_{C\text{-}F}$ = 7.6 Hz)



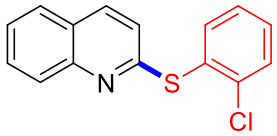
2-(*m*-Fluorophenylthio)quinoline (3ah)

Colorless liquid, 27.6 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.93 (m, 2H), 7.72 (d, J = 8.4 Hz, 1H), 7.70-7.65 (m, 1H), 7.49-7.45 (m, 1H), 7.44-7.38 (m, 3H), 7.16-7.11 (m, 1H), 7.06 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 162.0, 160.0, 148.1, 136.6, 133.7 (d, $J_{C\text{-}F}$ = 9.1 Hz), 130.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.1, 128.5, 127.6, 126.0,121.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 119.9, 116.1 (d, $J_{C\text{-}F}$ = 21.0 Hz).



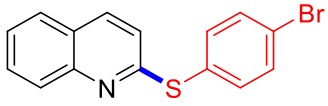
2-(*p*-Chlorophenylthio)quinoline (3ai)[3]

White Solid; M.p. 83-85 °C, 36.9 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 8.0, 7.2 Hz, 1H), 7.60-7.58 (m, 2H), 7.48-7.41 (m, 3H), 7.01 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.4, 148.1, 136.6, 136.2, 135.4, 130.1, 129.7, 129.4, 128.4, 127.5, 126.0, 125.9, 119.6.



2-(*o*-Chlorophenylthio)quinoline (3aj)

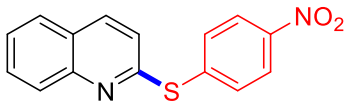
Colorless liquid, 23.3 mg, 43%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, J = 8.8 Hz, 2H), 7.76-7.70 (m, 3H), 7.66-7.46 (m, 2H), 7.40-7.33 (m, 2H), 6.69 (d, J = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 148.2, 139.0, 137.0, 136.6, 130.7, 130.5, 130.3, 130.0, 128.4, 127.6, 127.5, 126.0, 125.9, 119.6.



2-(*p*-Bromophenylthio)quinoline (3ak)

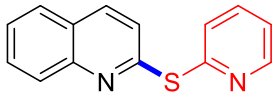
Colorless liquid, 29.6 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.70-7.67 (m, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.42-7.35 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ

159.9, 148.1, 136.7, 135.3, 135.0, 134.3, 133.0, 132.7, 130.5, 130.1, 129.2, 128.5, 127.6, 126.0, 119.9.



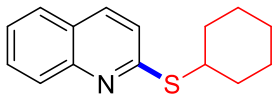
2-(*p*-Nitrophenylthio)quinoline (3al)

White Solid; M.p. 127-128 °C, 31.6 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.2 Hz, 2H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.80-7.69 (m, 4H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.9, 147.2, 144.0, 141.3, 137.1, 132.8, 130.4, 128.6, 127.6, 126.7, 126.6, 126.4, 124.4, 124.1, 121.4.



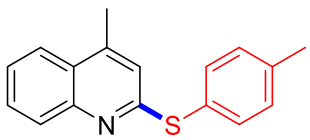
2-(2-Pyridylthio)quinoline (3am)

Colorless liquid, 36.7 mg, 77%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.8 Hz, 1H), 8.01 (dd, *J* = 13.6, 8.8 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71-7.60 (m, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 5.6 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.6, 156.3, 150.2, 148.3, 137.0, 136.6, 129.9, 128.8, 127.6, 126.7, 126.6, 126.4, 122.7, 122.0.



2-(Cyclohexylthio)quinoline (3an)[4]

Colorless liquid, 28.2 mg, 58%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 4.8 Hz, 2H), 1.69-1.67 (m, 1H), 1.60-1.48 (m, 4H), 1.39-1.34 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 148.4, 135.1, 130.2, 129.4, 128.1, 127.5, 127.0, 125.9, 125.5, 121.3, 42.7, 33.2, 26.1, 25.9.

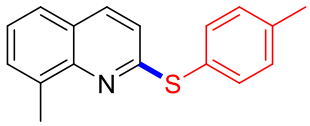


4-Methyl-2-*p*-tolylthio-quinoline (4aa)[2]

White Solid. M.p. 138-139 °C, 44.0 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.65 (dt, *J* = 6.8, 1.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.27-7.25 (m, 2H), 6.80 (s, 1H), 2.53 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 147.9, 144.6, 139.4, 135.2, 130.4, 129.6, 128.9, 127.3, 126.0, 125.4, 123.7, 119.6, 21.3, 18.7.

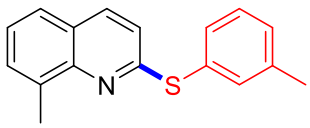
3-Methyl-2-*p*-tolylthio-quinoline (4ab)

White Solid. M.p. 95-97 °C, 42.4 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.2 Hz, 2H), 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 3H), 7.39 (td, *J* = 8.0, 1.2 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.51 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 146.8, 138.4, 135.0, 134.7, 129.7, 129.5, 128.4, 128.3, 127.0, 126.7, 126.6, 125.4, 21.3, 19.0.



8-Methyl-2-*p*-tolylthio-quinoline (4ac)

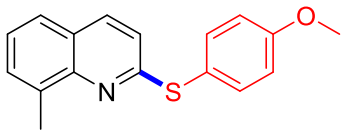
White Solid. M.p. 94-95 °C, 45.1 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* =8.4 Hz, 1H), 7.58 (d, *J* = 8.0, Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 2.65 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.3, 147.1, 139.3, 136.4, 136.2, 135.3, 130.1, 130.0, 127.2, 125.7, 125.4, 125.3, 119.0, 21.3, 17.6.



8-Methyl-2-*m*-tolylthio-quinoline (4ad)

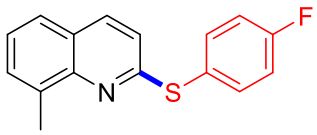
Colorless liquid, 37.6 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.54 (s, 2H), 7.49 (d, *J* = 6.4 Hz, 2H), 7.33 (dd, *J* = 15.6, 7.6 Hz, 2H), 7.24 (s, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 2.63 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8,

147.1, 139.1, 136.4, 136.3, 135.8, 132.1, 130.5, 130.0, 129.8, 129.1, 125.8, 125.4, 125.3, 119.3, 21.3, 17.6.



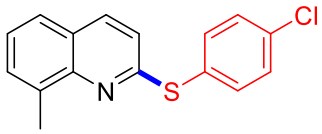
8-Methyl-2-*p*-methoxyphenylthio-quinoline (4ae)

White Solid. M.p. 66-68 °C, 44.4 mg, 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* =8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.99 (dd, *J* = 8.4,6.4 Hz, 3H), 3.88 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.7, 160.6, 147.1, 137.3, 136.4, 136.2, 132.6, 129.9, 125.6, 125.4, 125.2, 121.2, 118.7, 114.9, 114.6, 55.4, 17.6.



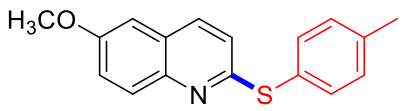
8-Methyl-2-*p*-fluorophenylthio-quinoline (4af)

Colorless liquid, 30.1 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.68 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.32 (t, *J* = 8.8 Hz, 1H), 7.16 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.08 (dd, *J* =8.4, 1.2 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 162.5, 159.0, 147.0, 137.6, 137.5, 136.5, 136.2, 130.0, 125.8, 125.7 (d, $J_{C\text{-}F}$ =3.5 Hz), 125.4, 125.3, 119.0, 116.3 (d, $J_{C\text{-}F}$ =21.8 Hz), 17.5.



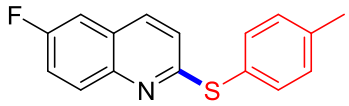
8-Methyl-2-*p*-chlorophenylthio-quinoline (4ag)

White Solid. M.p. 104-106 °C, 34.8 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 1H), 7.65-7.62 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.44-7.41 (m, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 2.58 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 147.1, 136.6, 136.4, 136.3, 135.1, 130.1, 129.3, 129.2, 125.9, 125.6, 125.4, 119.3, 17.5.



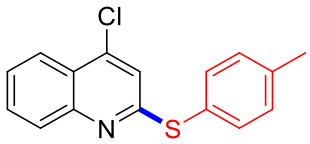
6-Methoxy-2-*p*-tolylthio-quinoline (4ah)

White Solid. M.p. 146-148 °C, 46.7 mg, 83%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 9.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 2.8 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.0, 157.2, 144.1, 139.3, 135.3, 135.1, 130.4, 129.8, 127.7, 126.7, 122.3, 119.8, 105.4, 55.9, 21.3.



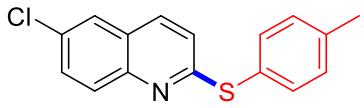
6-Fluoro-2-*p*-tolylthio-quinoline (4ai)

White Solid; M.p. 89-91 °C, 28.5 mg, 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 9.2, 5.6 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.42 (dt, *J* = 9.2, 2.8 Hz, 1H), 7.32-7.26 (m, 3H), 7.96 (d, *J* = 8.8 Hz, 1H), 2.56 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 160.7, 159.0, 145.1, 139.7, 135.6 (d, $J_{C\text{-}F}$ = 4.5 Hz), 135.3, 130.6 (d, $J_{C\text{-}F}$ = 9.0 Hz), 130.5, 126.9, 126.2 (d, $J_{C\text{-}F}$ = 10.5 Hz), 120.0, 119.9, 119.8, 110.7, (d, $J_{C\text{-}F}$ = 21.0 Hz), 21.3.



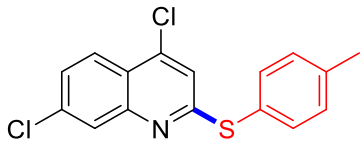
4-Chloro-2-*p*-tolylthio-quinoline (4aj)

White Solid; M.p. 129-131 °C, 35.3 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.95 (dd, *J* = 8.8, 0.4 Hz, 1H), 7.71 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.56-7.51 (m, 3H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.00 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 148.7, 143.0, 140.1, 135.4, 130.9, 130.7, 128.6, 126.5, 126.3, 124.1, 124.0, 118.7, 21.4.



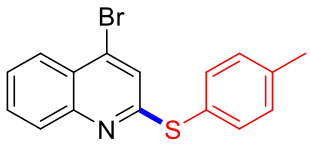
6-Chloro-2-*p*-tolylthio-quinoline (4ak)

White Solid; M.p. 133-134 °C, 31.4mg, 55%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.8 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.59-7.53 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.8, 146.4, 139.8, 135.4, 135.3, 131.1, 130.7, 130.5, 129.8, 126.6, 126.3, 126.2, 120.0, 21.3.



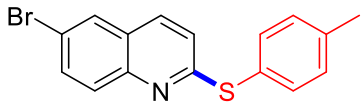
4,7-Dichloro-2-*p*-tolylthio-quinoline (4al)

White Solid; M.p. 155-156 °C, 28.7 mg, 45%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01(d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.99 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8, 149.0, 142.8, 140.3, 136.9, 135.5, 130.7, 127.6, 127.3, 125.7, 125.4, 122.6, 118.8, 21.4.



4-Bromo-2-*p*-tolylthio-quinoline (4am)

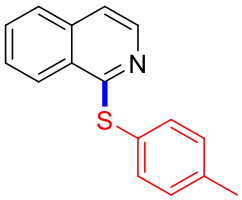
White Solid; M.p. 137-140 °C, 42.1 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.78 (dd, *J* = 12.0, 8.8 Hz, 2H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.546 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2, 148.4, 140.0, 135.4, 134.5, 130.9, 130.7, 128.7, 126.7, 126.7, 126.2, 125.4, 122.5, 21.4.



6-Bromo-2-*p*-tolylthio-quinoline (4an)

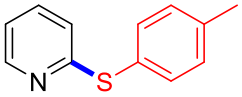
White Solid; M.p. 116-118 °C, 44.1 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 8.24 (t, *J* = 4.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.38 (t, *J* = 4.0 Hz, 1H), 7.24 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 142.4, 138.8, 135.9, 135.0,

130.4, 130.0, 127.2, 127.1, 127.0, 126.7, 124.9, 118.4, 21.4.



1-*p*-Tolylthio-isoquinoline (4ao)[2]

White Solid; M.p. 134-136 °C, 36.7 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 6.8 Hz, 1H), 7.55-7.50 (m, 3H), 7.28 (t, *J* = 7.6 Hz, 3H), 7.20 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0, 146.6, 139.8, 135.4, 135.2, 133.3, 130.5, 130.0, 129.6, 126.8, 126.6, 119.9, 119.1, 21.4.



2-*p*-Tolylthio-pyridine (4ap)

White Solid; M.p. 128-130 °C, 16.5 mg, 41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.41 (s, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 147.3, 138.4, 136.8, 132.8, 130.3, 129.5, 123.7, 21.1.

References

(1) W. C. Hu, F. Y. Zhang, G. Y. Qian and Z. T. Rong, Chem. Commun. 2021, 57, 6995-6998.

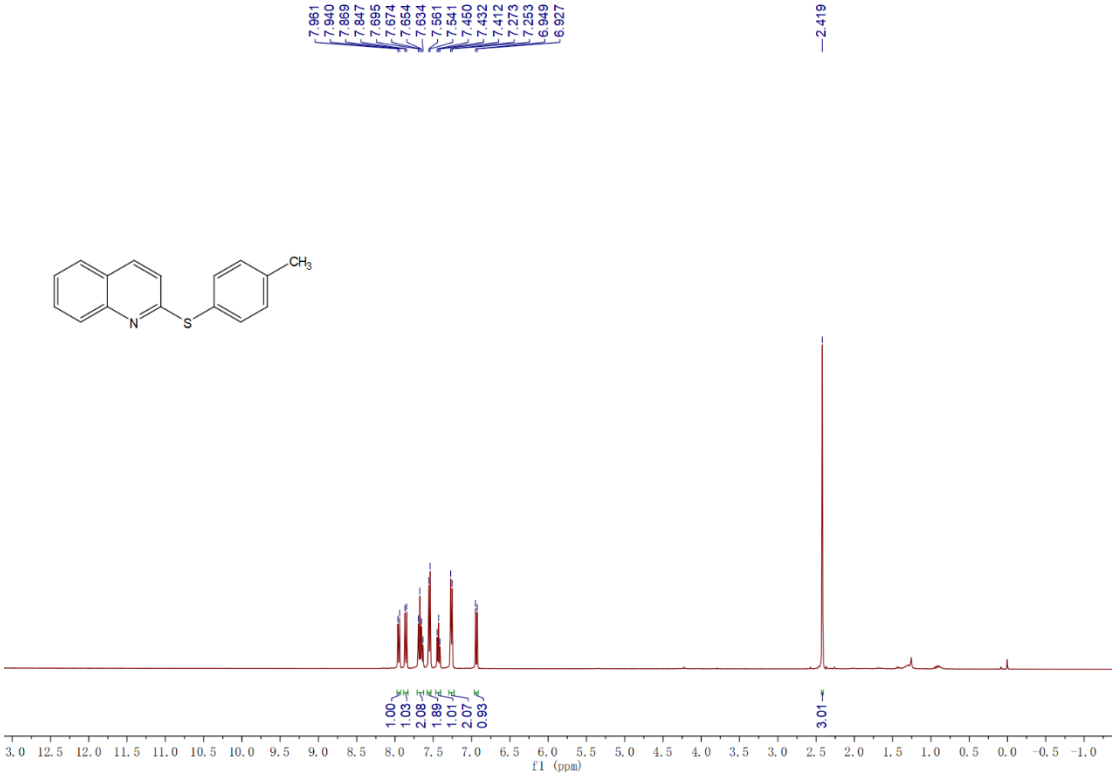
(2) D. Liu, H. X. Ma, P. Fang and T. S. Mei, Angew. Chem. Int. Ed. 2019, 58, 5033-5037.

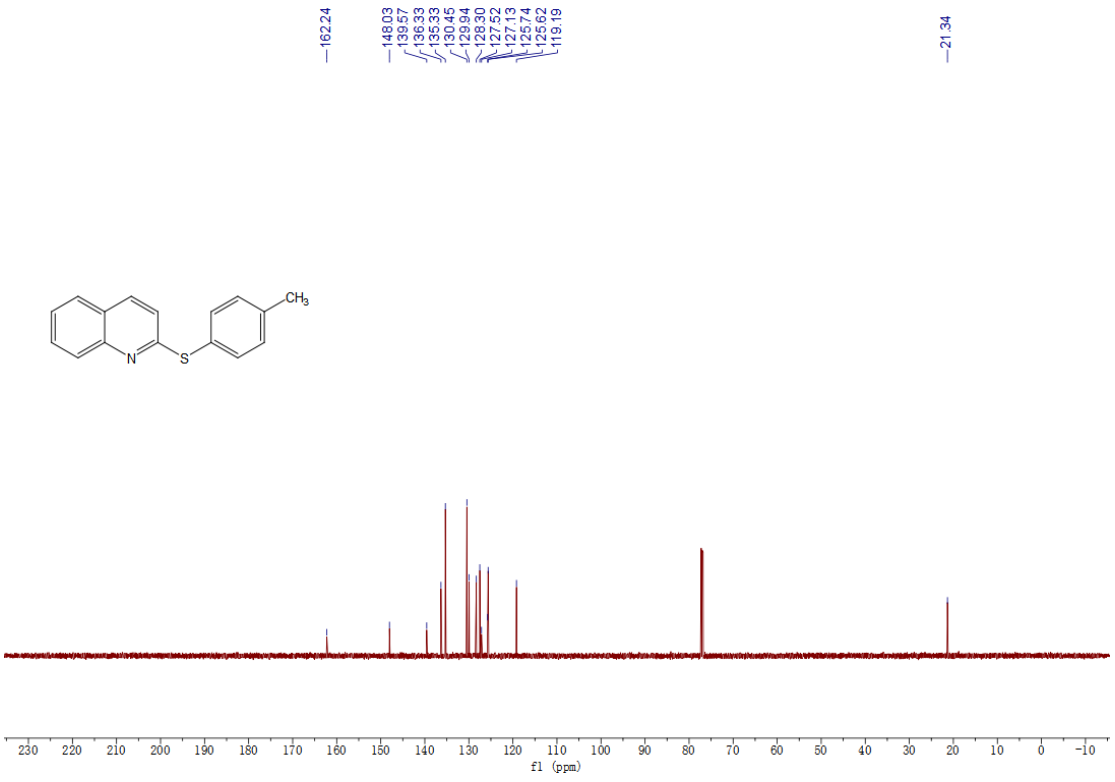
(3) B. Sreedhar, P. S. Reddy and M. A. Reddy, Synthesis 2009, 10, 1732-1738.

(4) S. C. Lee, H. H. Liao and A. Chatupheeraphat, Chem. Eur. J. 2018, 24, 3608-3612.

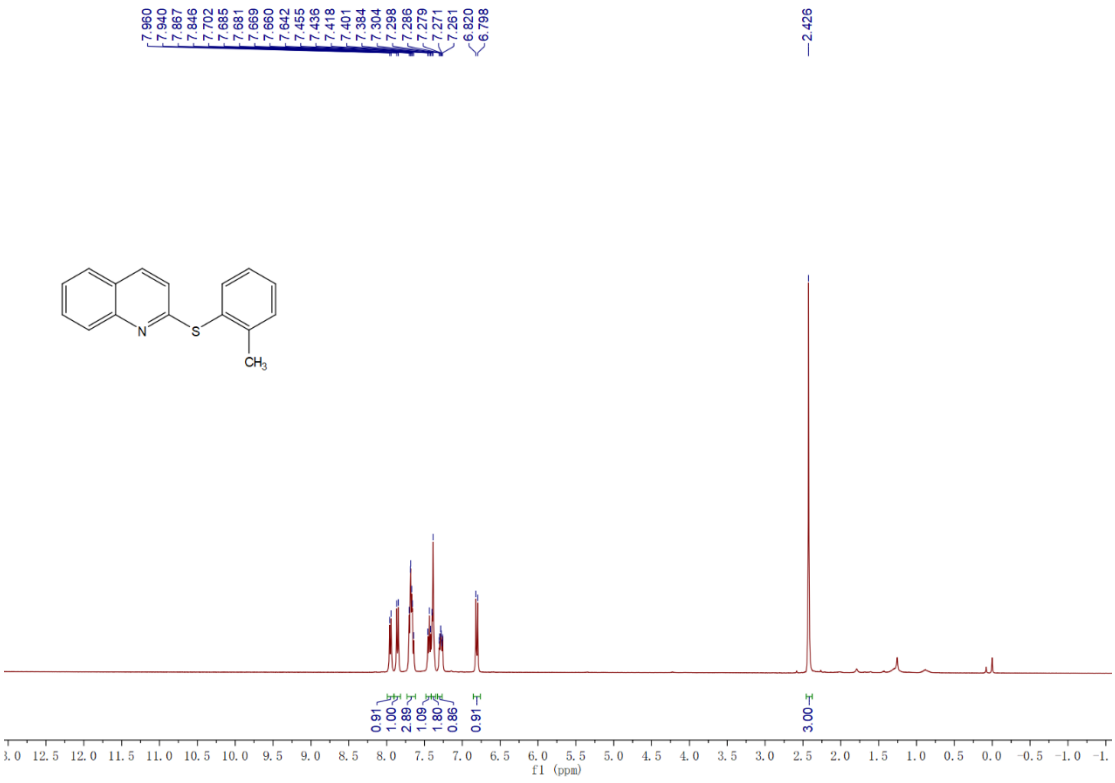
4. NMR Spectra Copies of Products

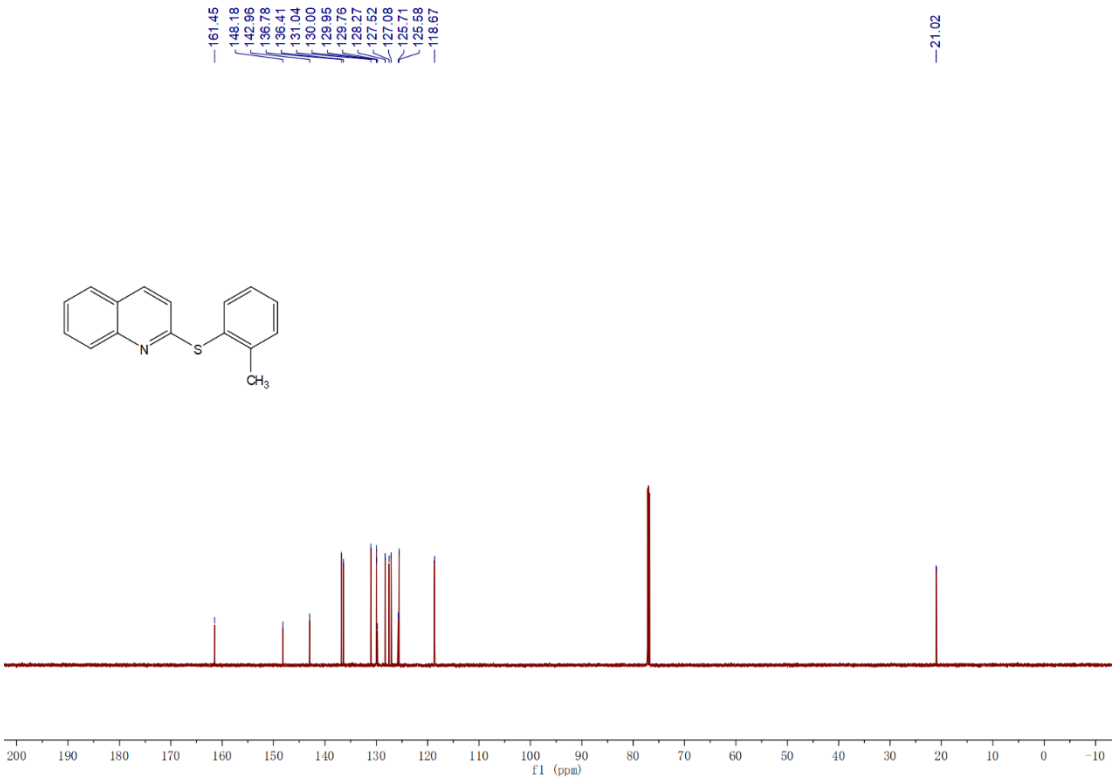
2-(*p*-Tolylthio)quinoline (3aa)



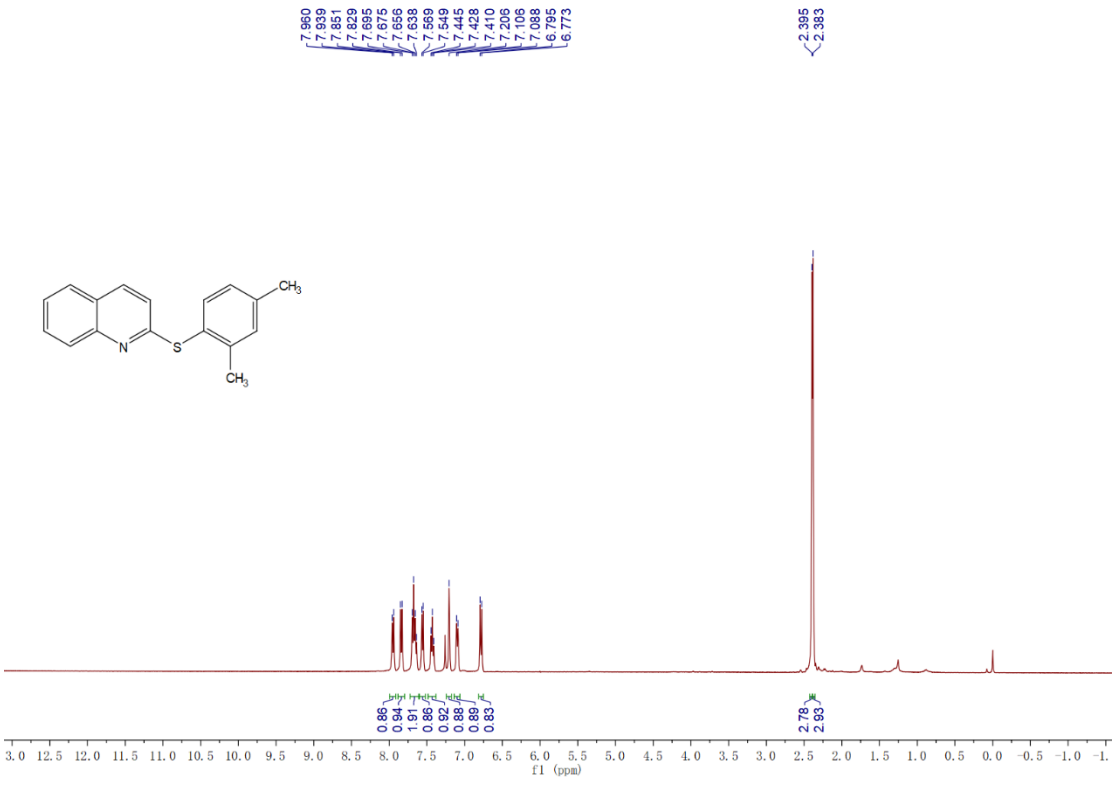


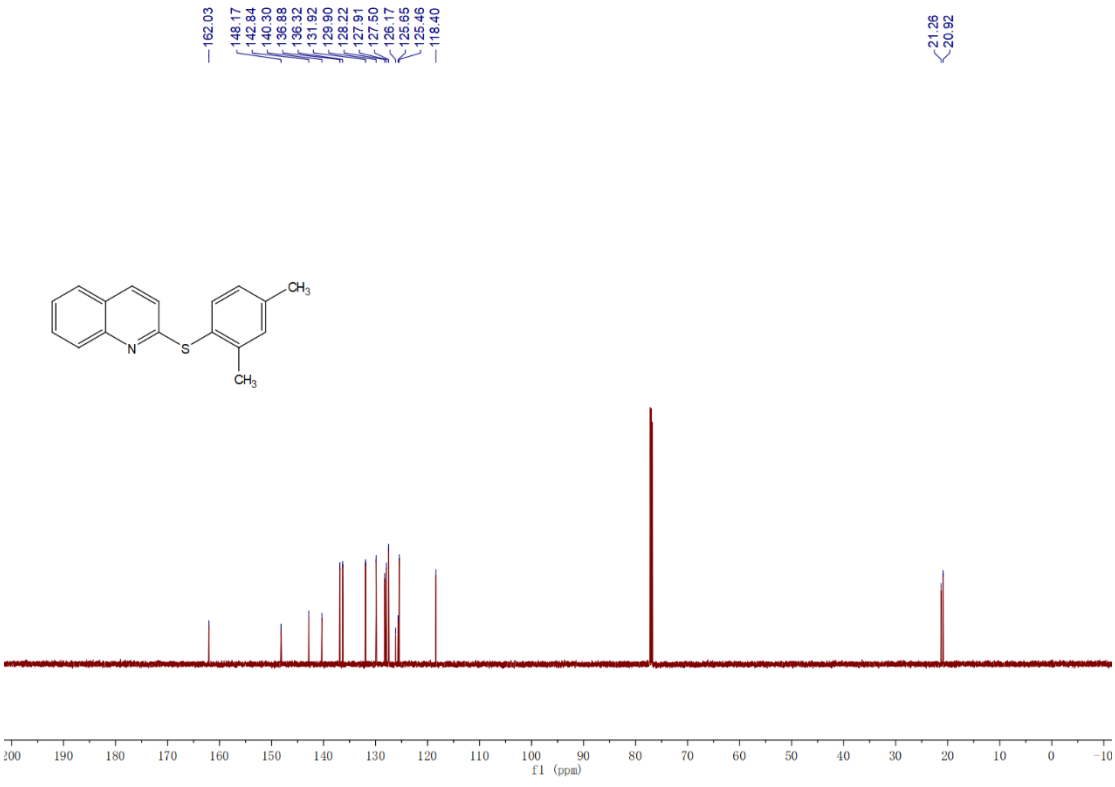
2-*o*-Tolylsulfanylquinoline (3ab)



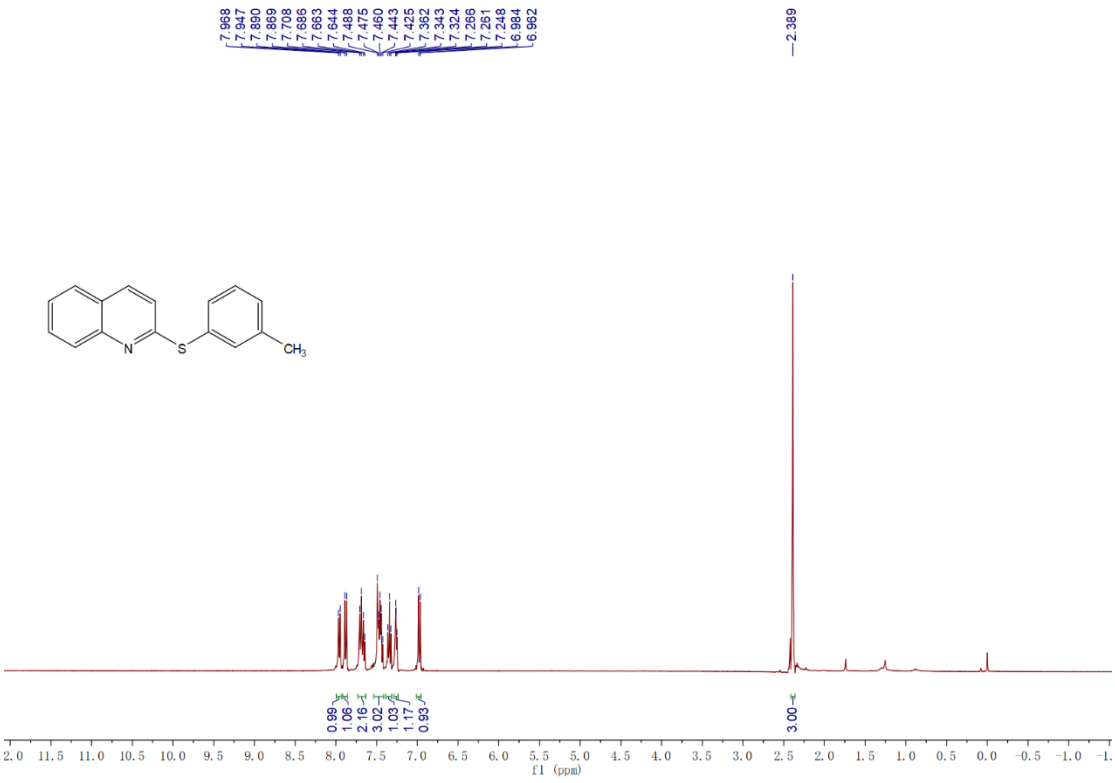


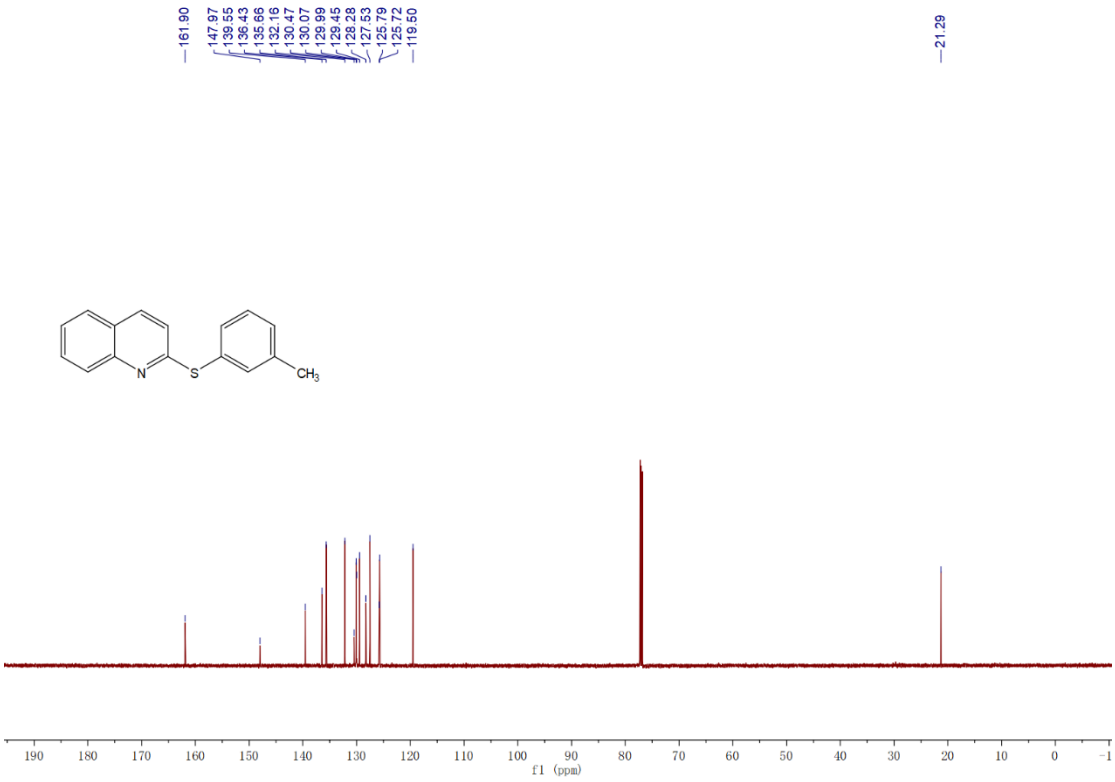
2-(2,4-Xylenethio)quinoline (3ac)



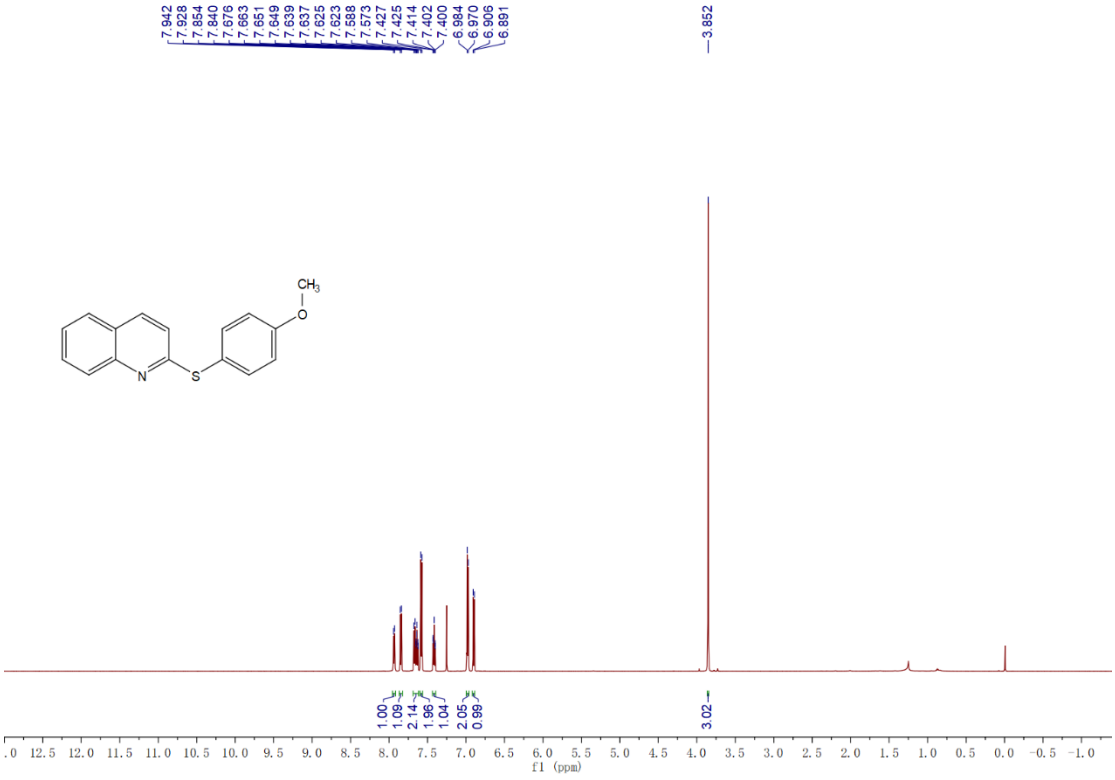


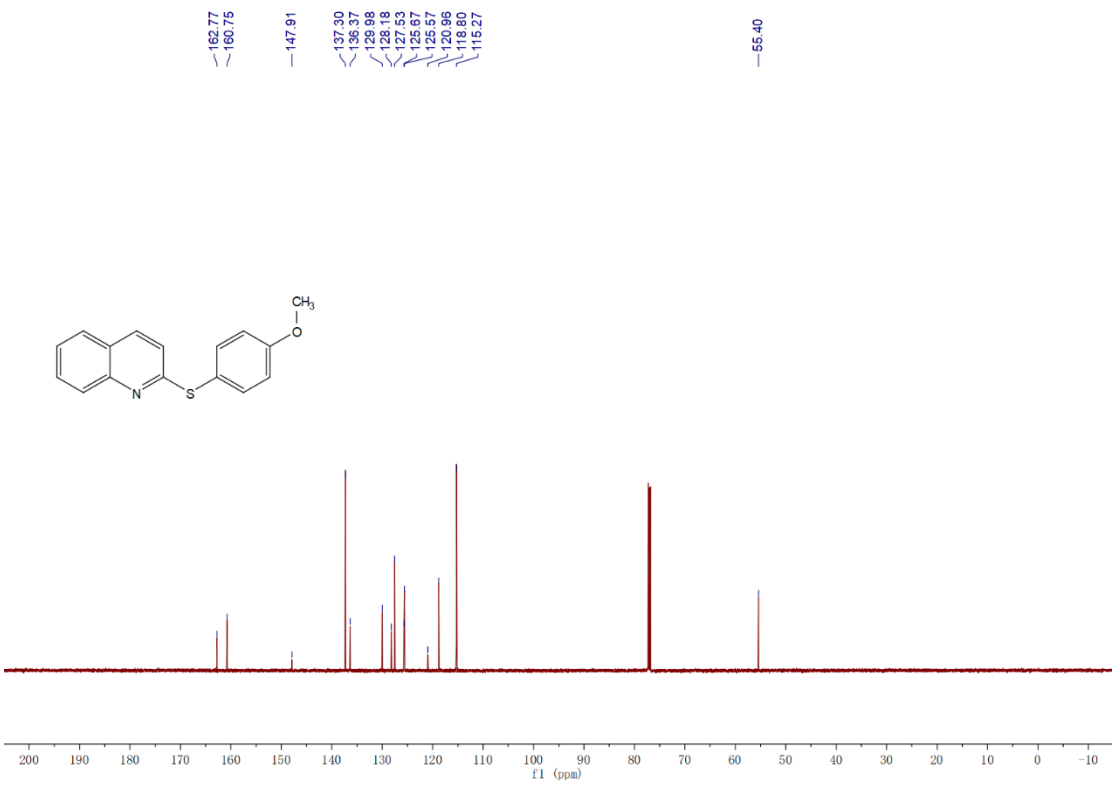
2-(*m*-Tolylthio)quinoline (3ad)



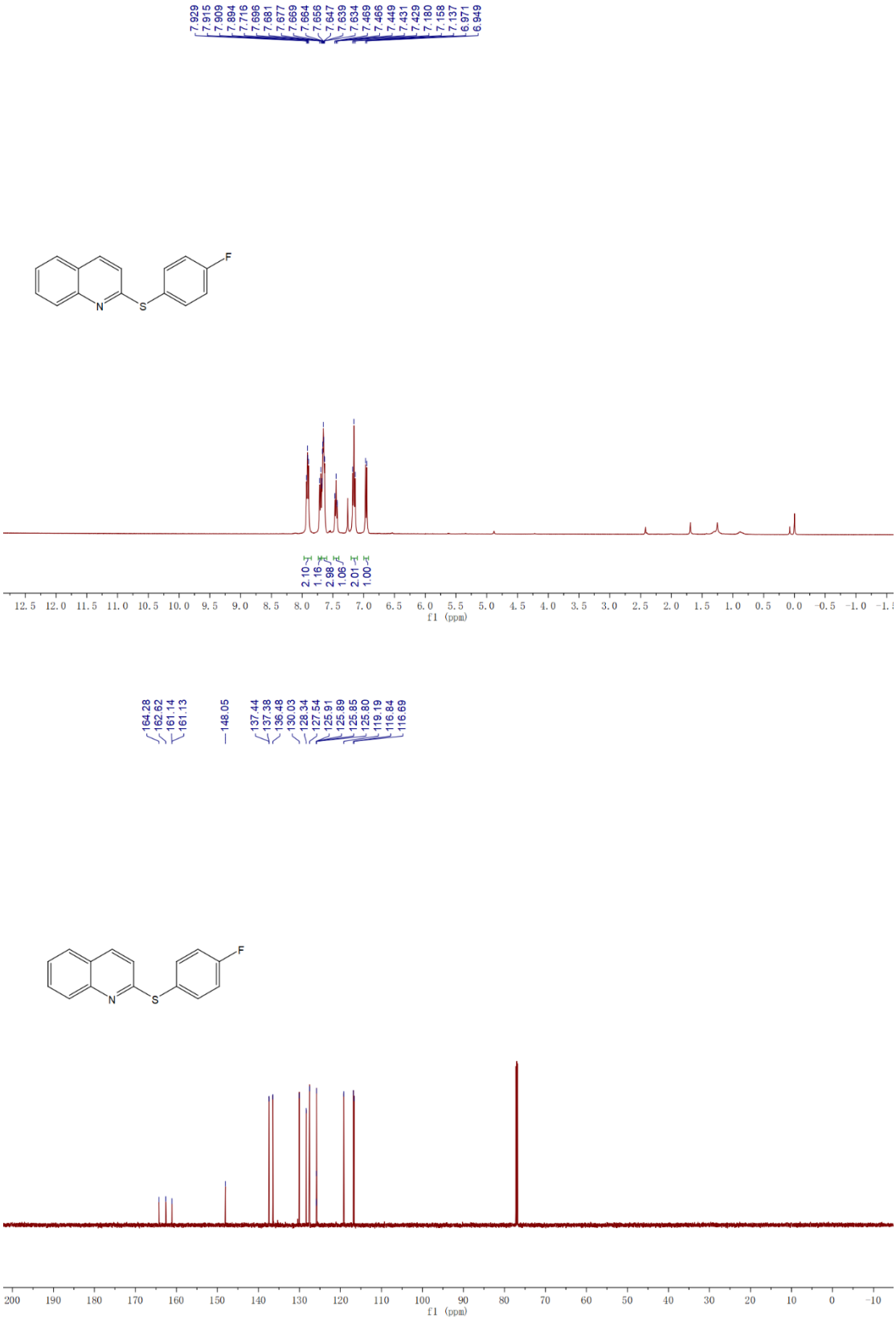


2-(*p*-Methoxyphenylthio)quinoline (3ae)

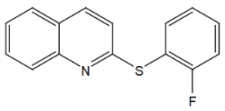


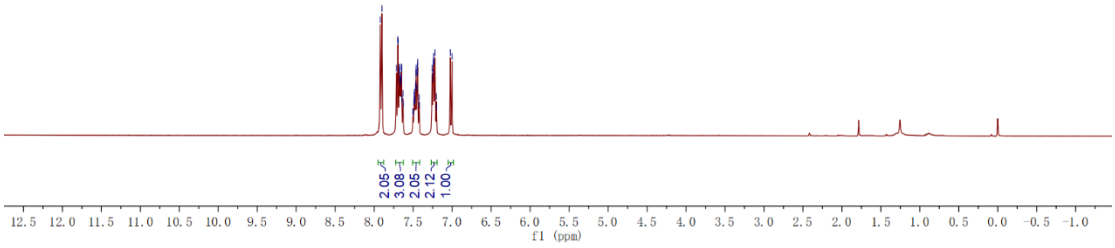


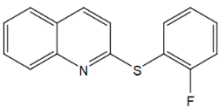
2-(*p*-Fluorophenylthio)quinoline (3af)

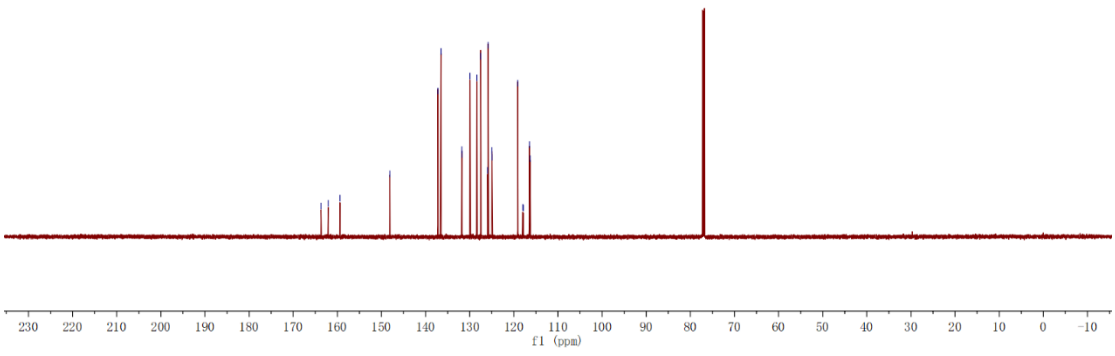


2-(*o*-Fluorophenylthio)quinoline (3ag)

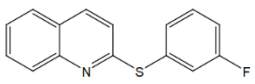


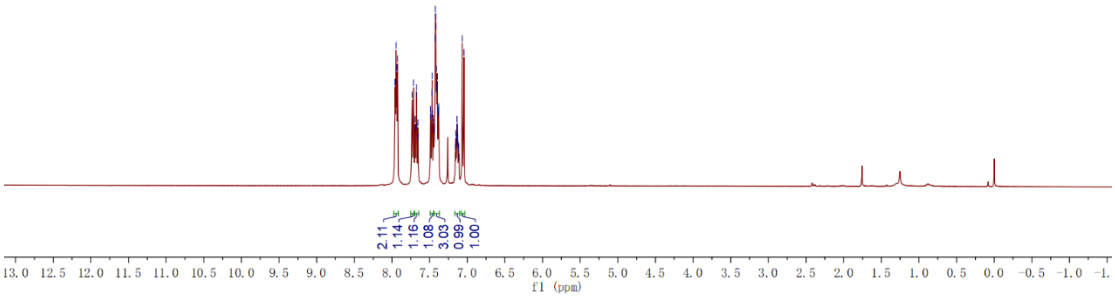


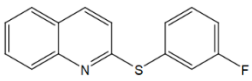


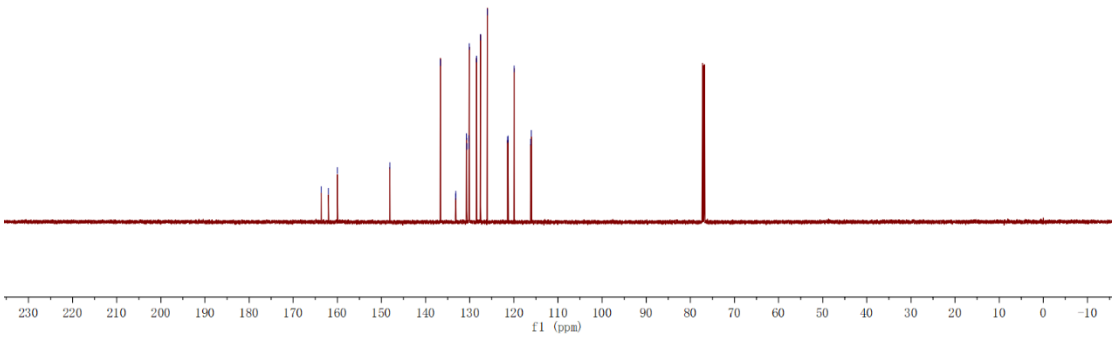


2-(*m*-Fluorophenylthio)quinoline (3ah)

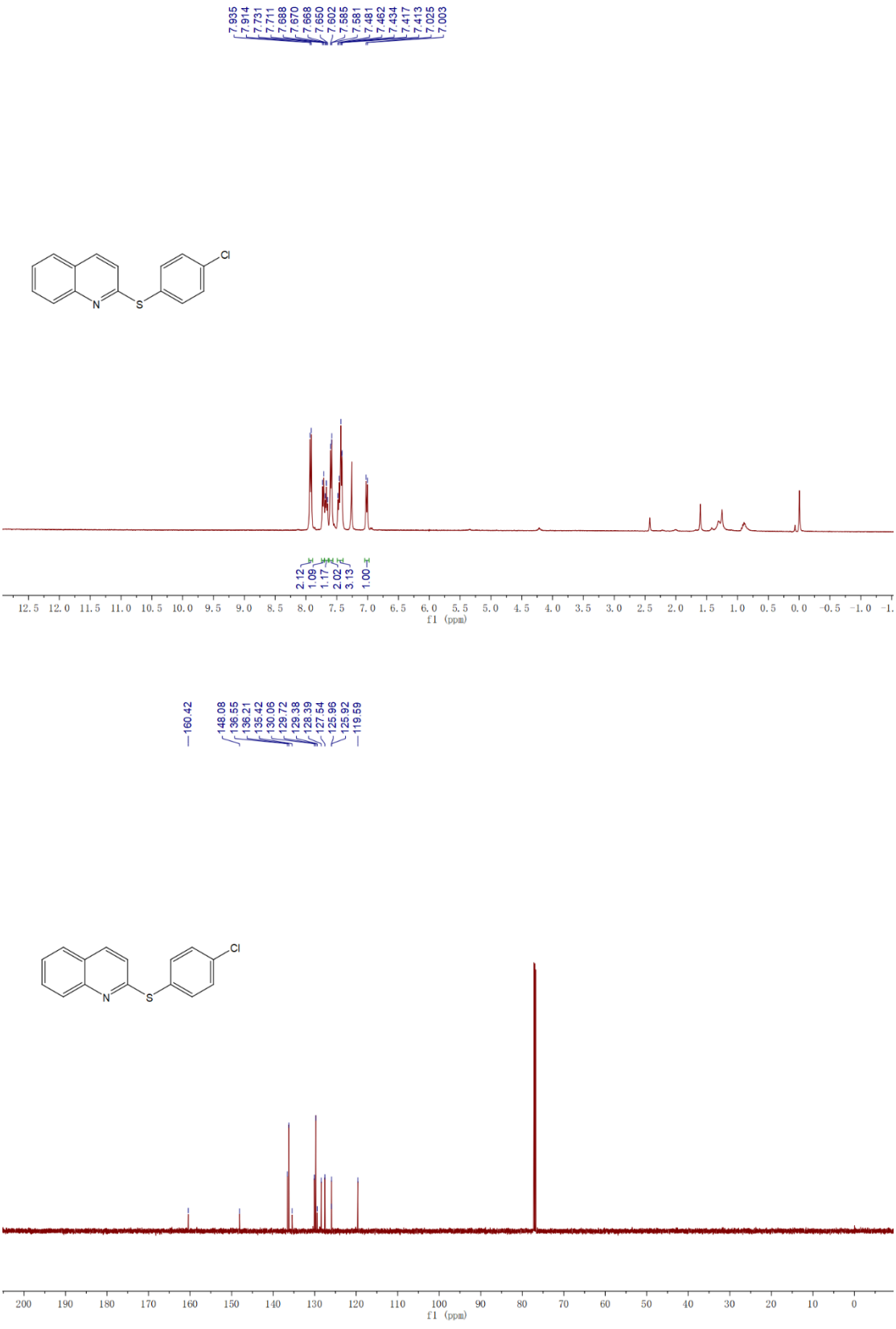




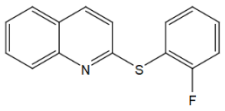


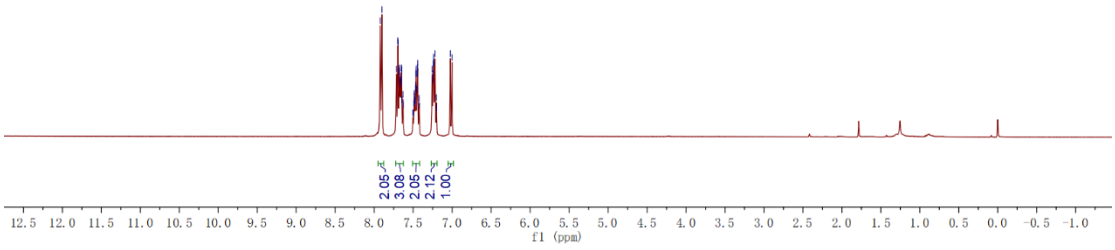


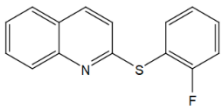
2-(*p*-Chlorophenylthio)quinoline (3ai)

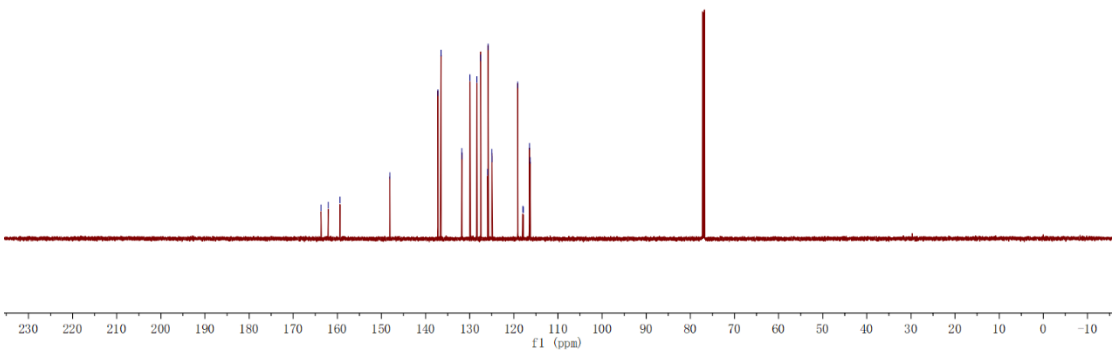


2-(*o*-Chlorophenylthio)quinoline (3aj)

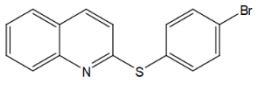


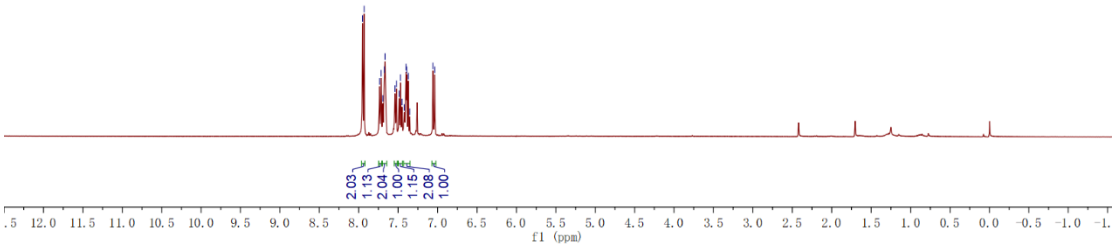


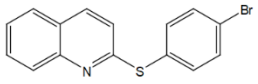




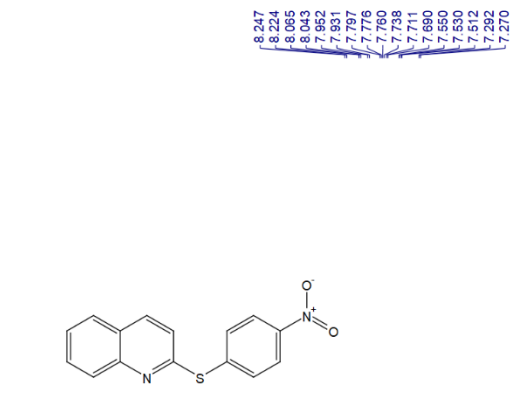
2-(*p*-Bromophenylthio)quinoline (3ak)

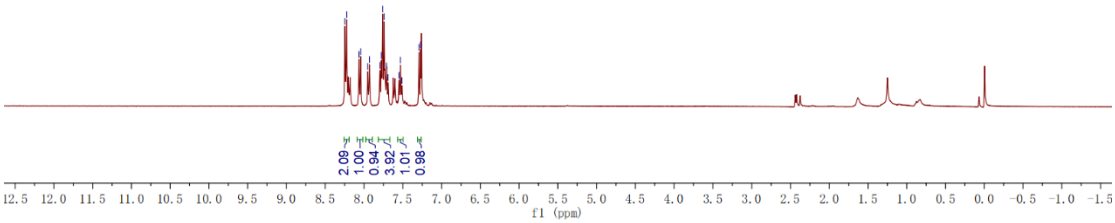


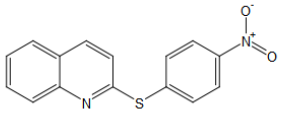




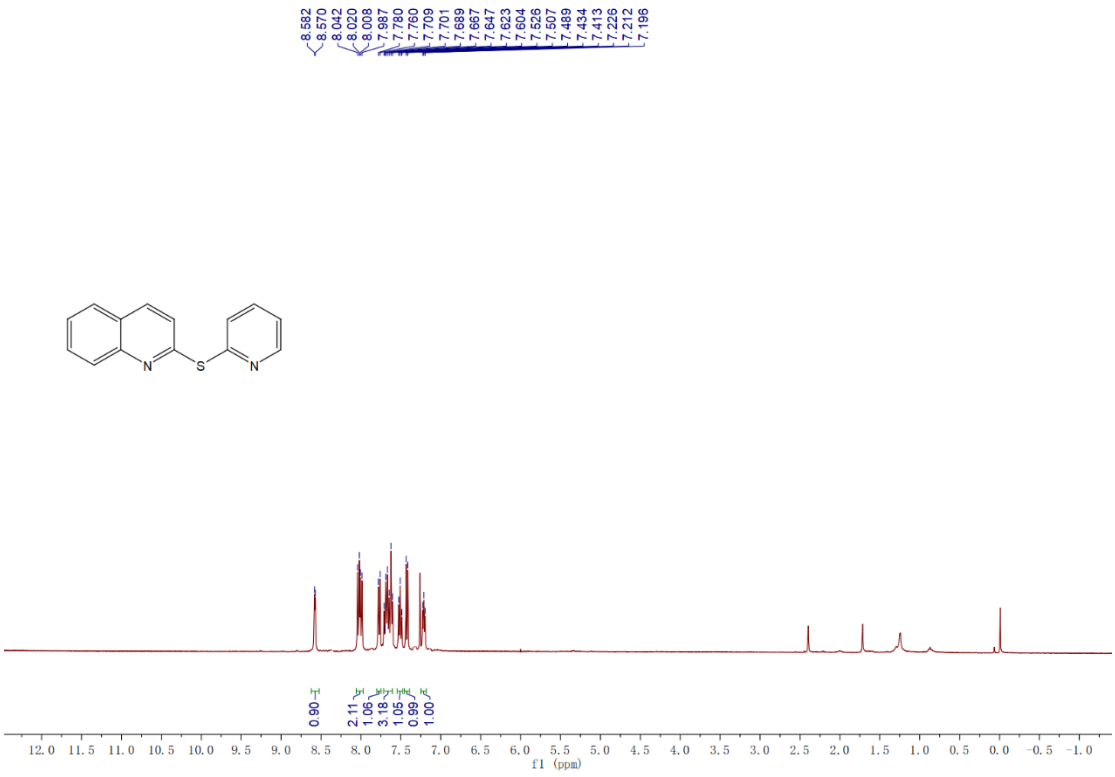
2-(*p*-Nitrophenylthio)quinoline (3al)

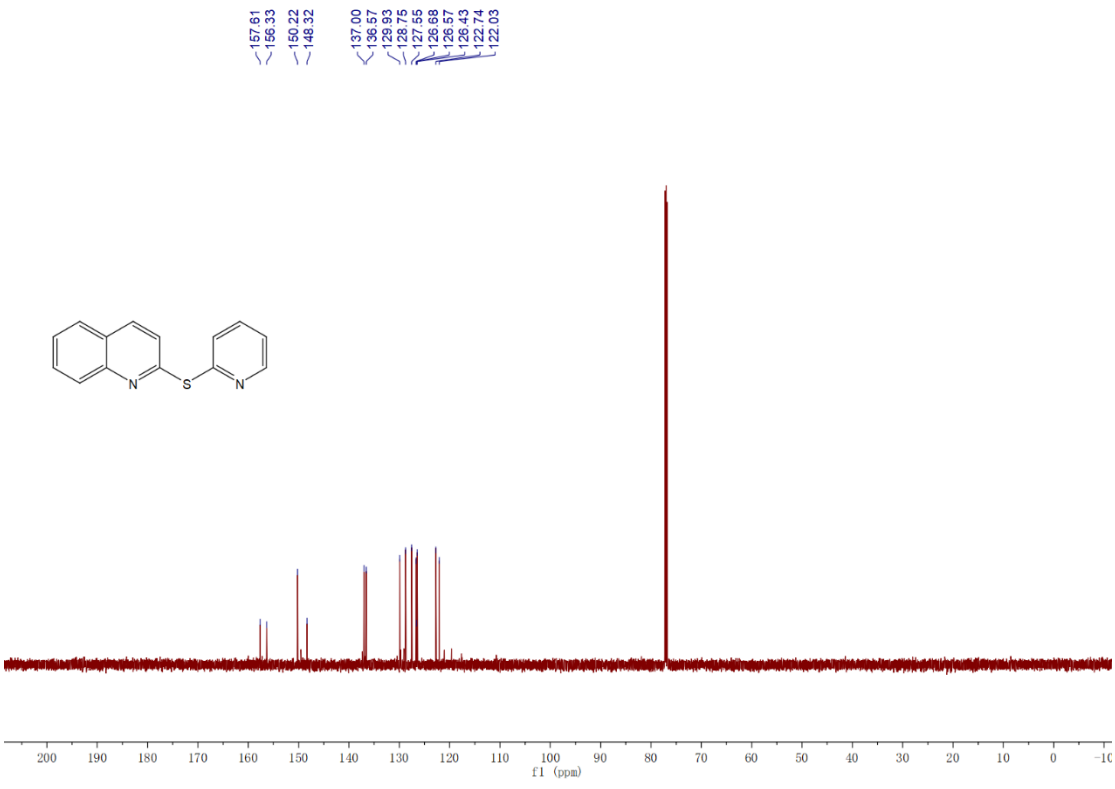




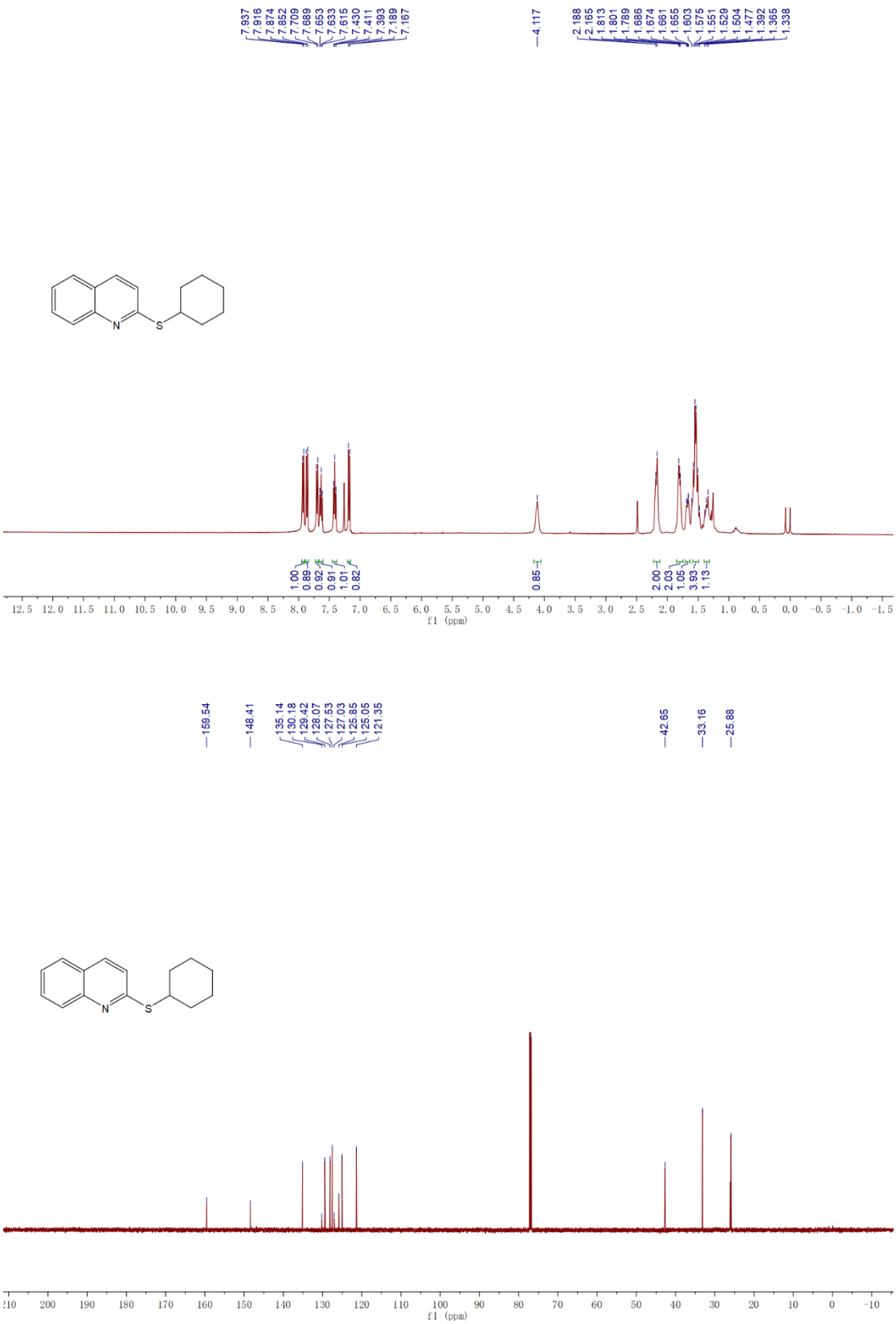


2-(2-Pyridylthio)quinoline (3am)

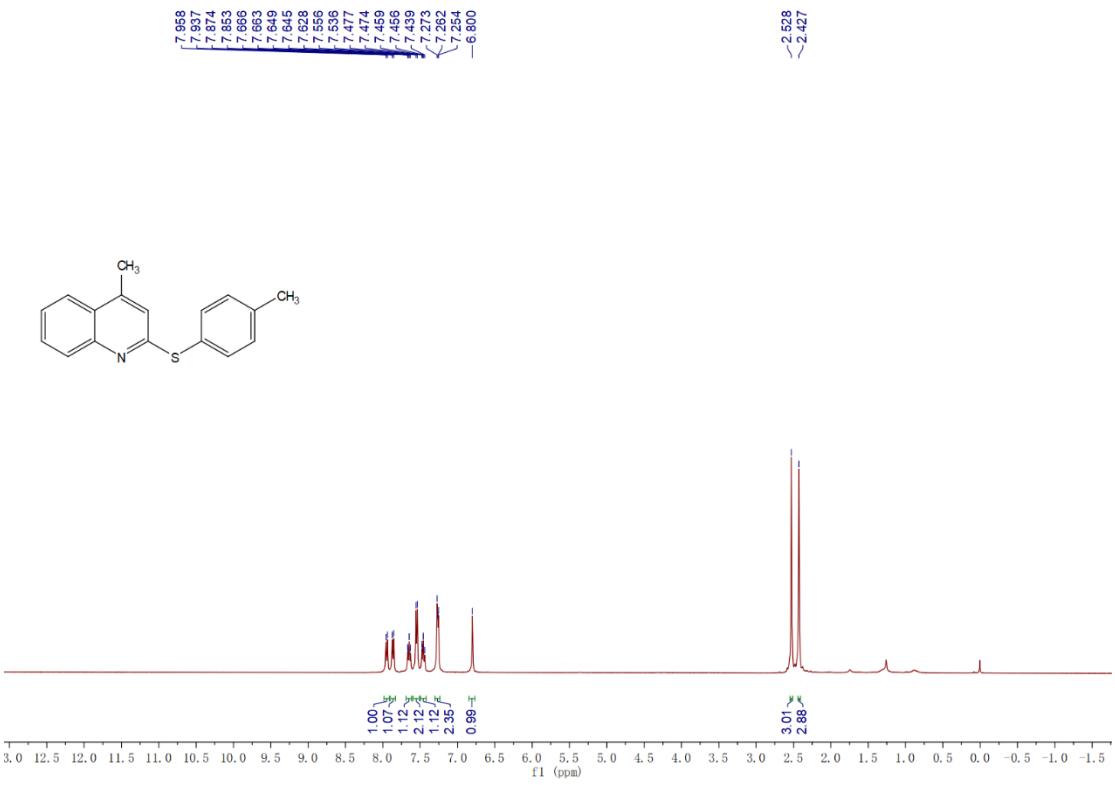


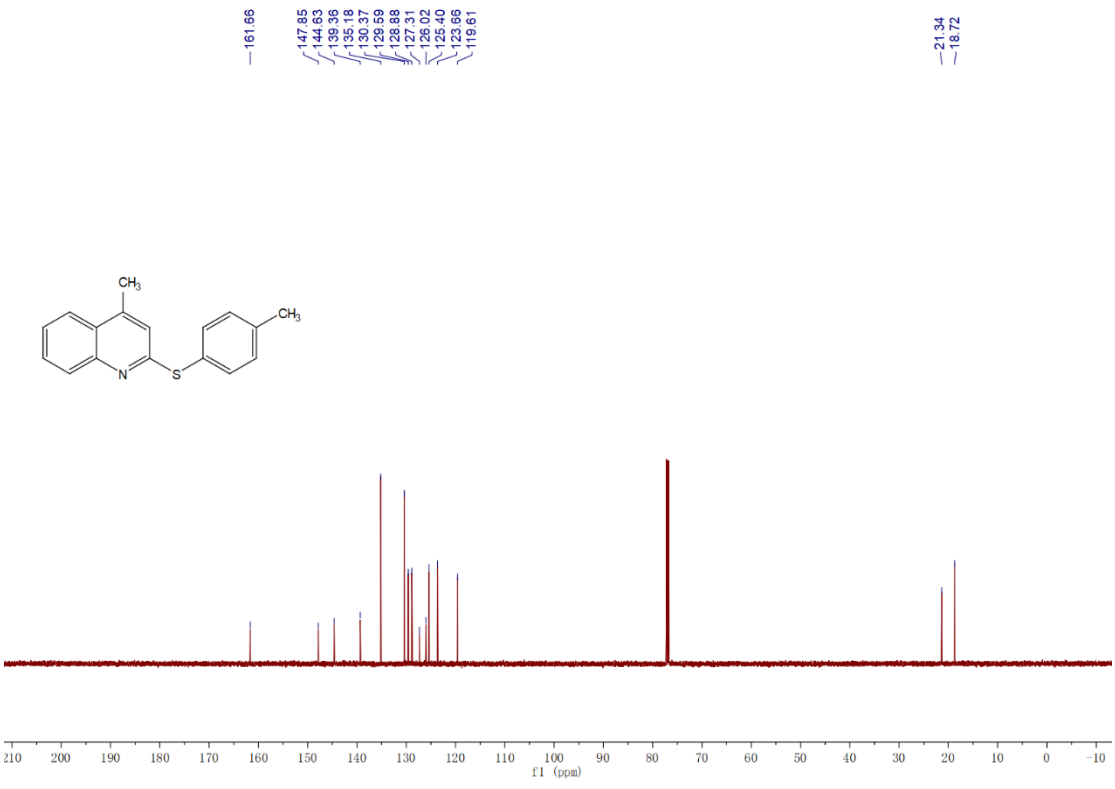


2-(Cyclohexylthio)quinoline (3an)

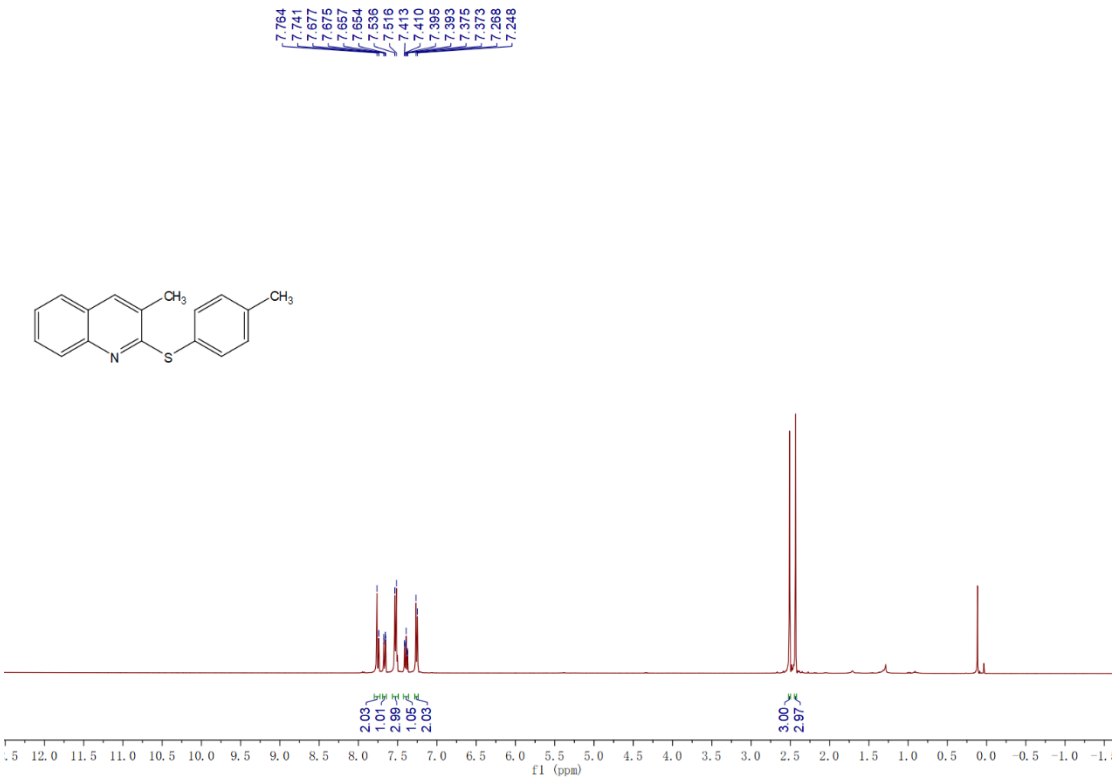


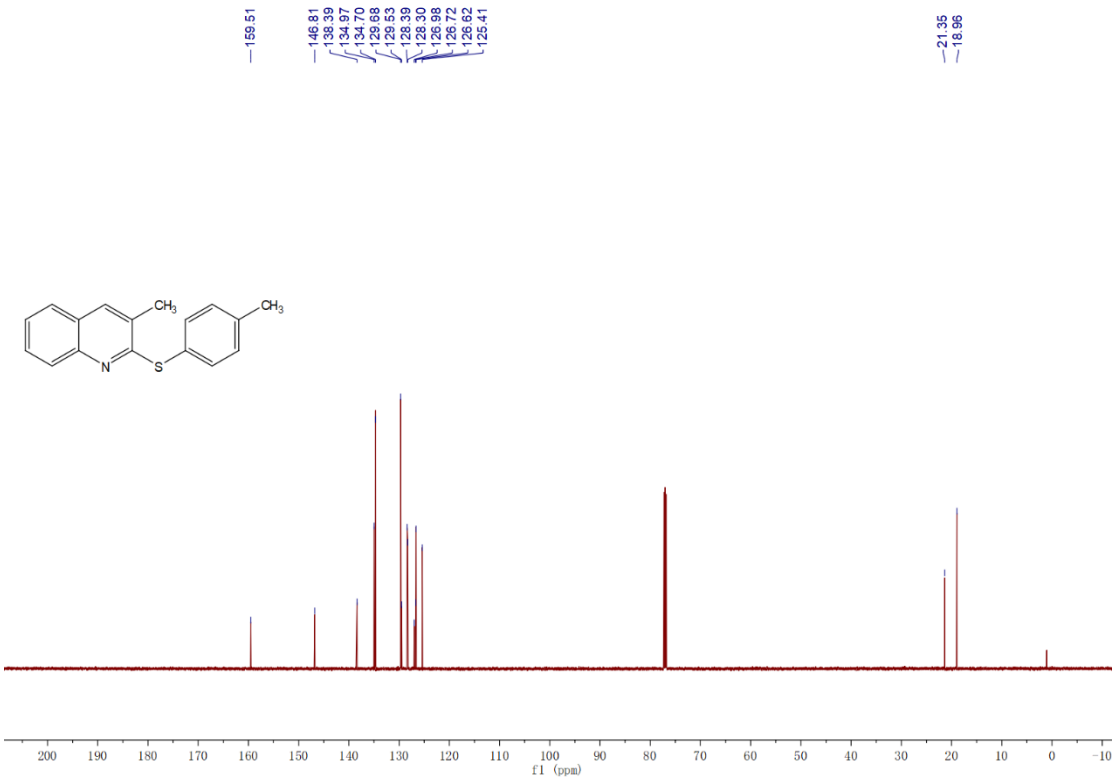
4-Methyl-2-*p*-tolylthio-quinoline (4aa)



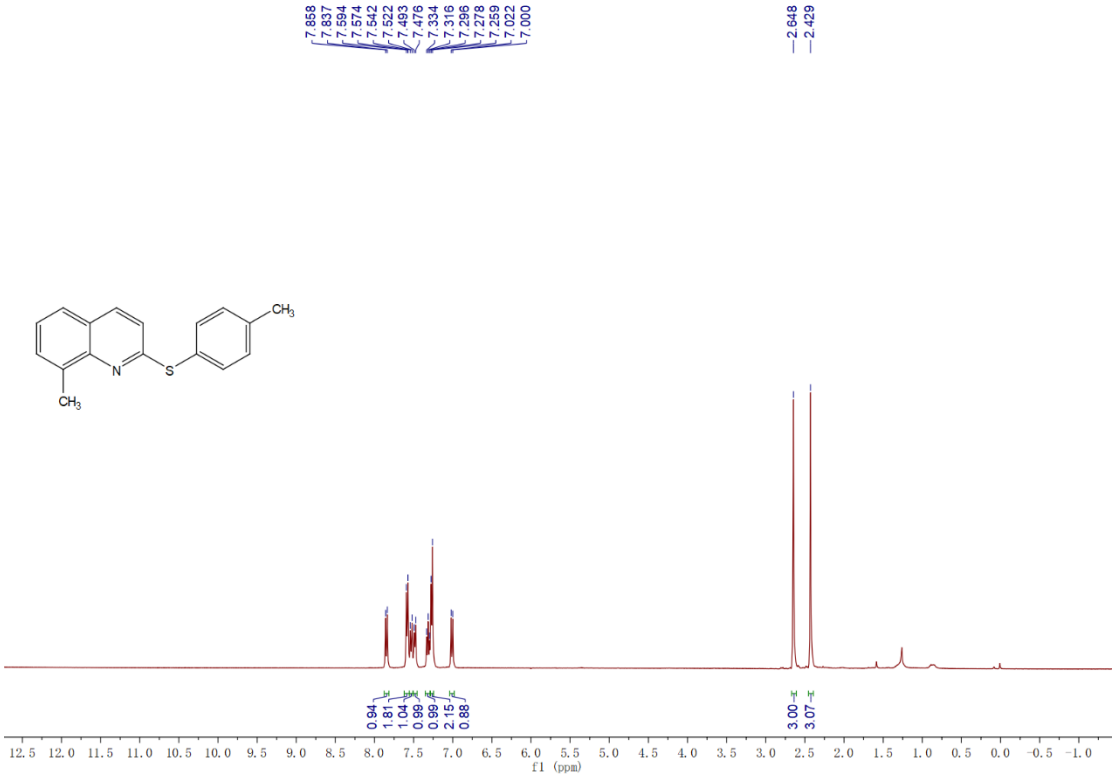


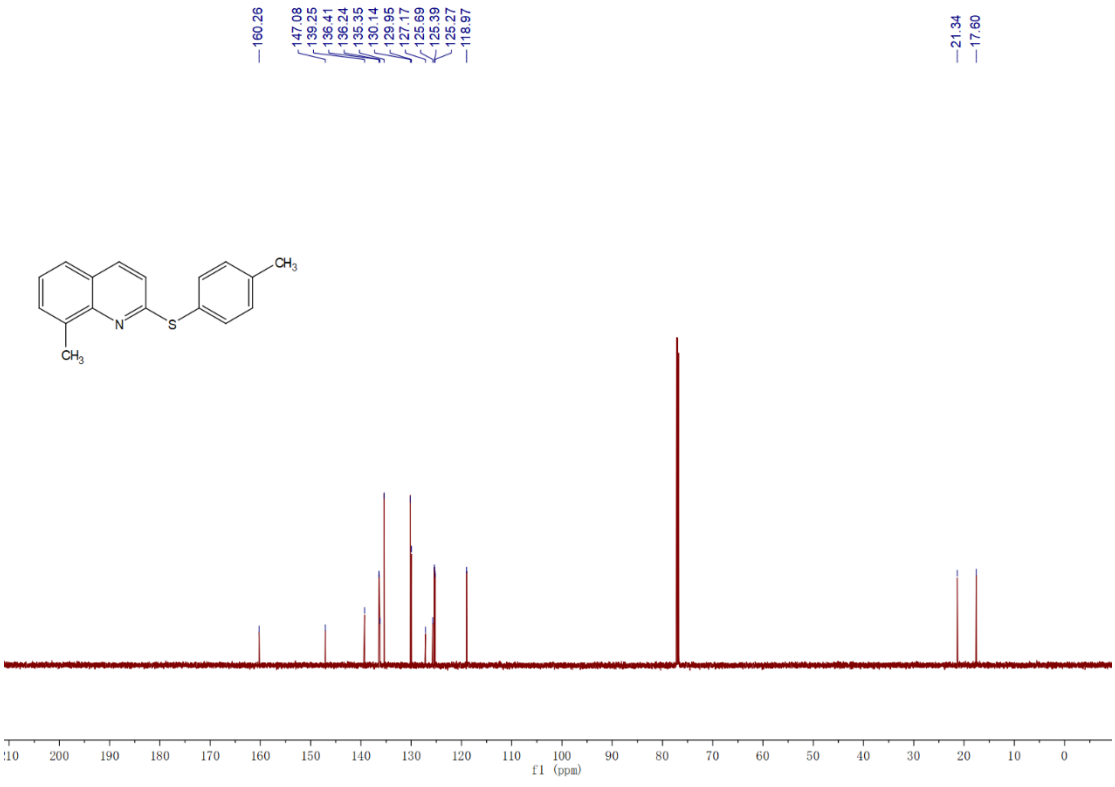
3-Methyl-2-*p*-tolylthio-quinoline (4ab)



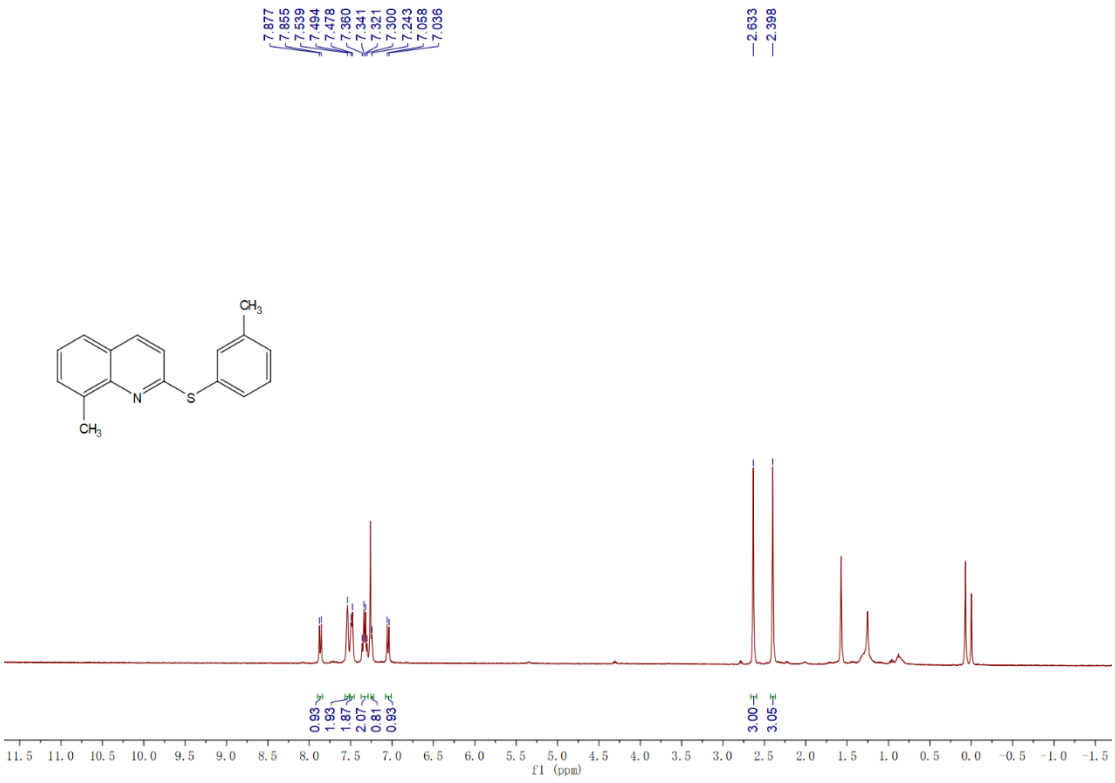


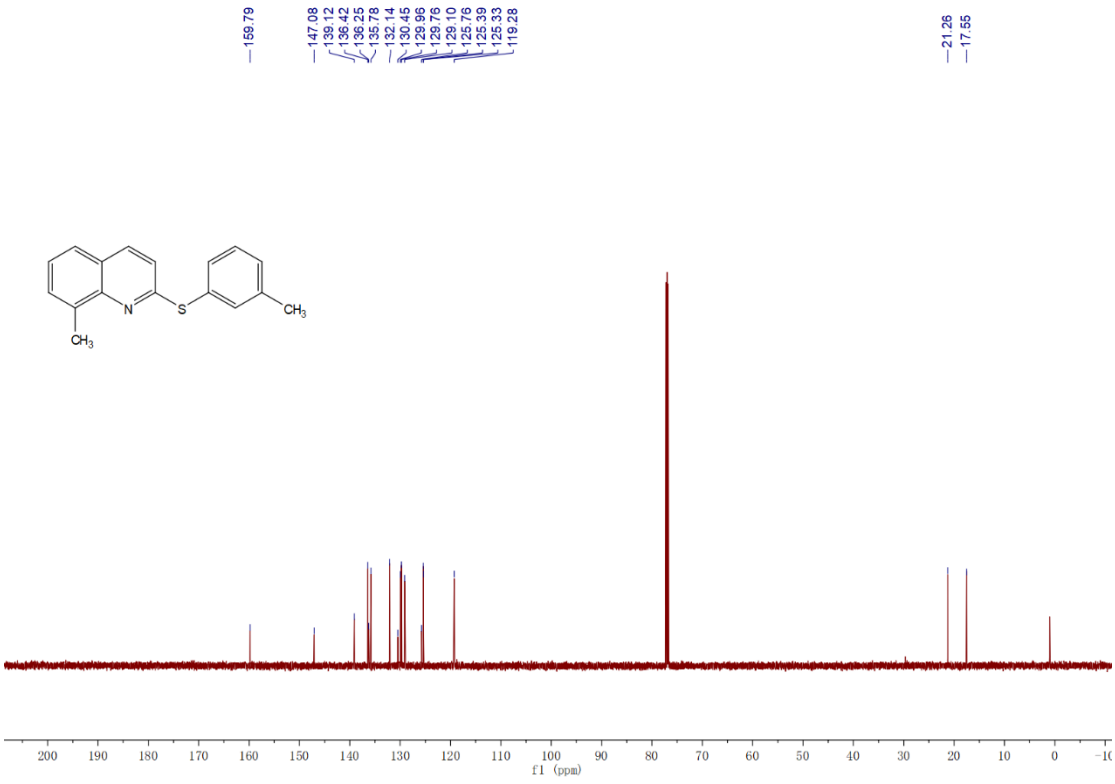
8-Methyl-2-*p*-tolylthio-quinoline (4ac)



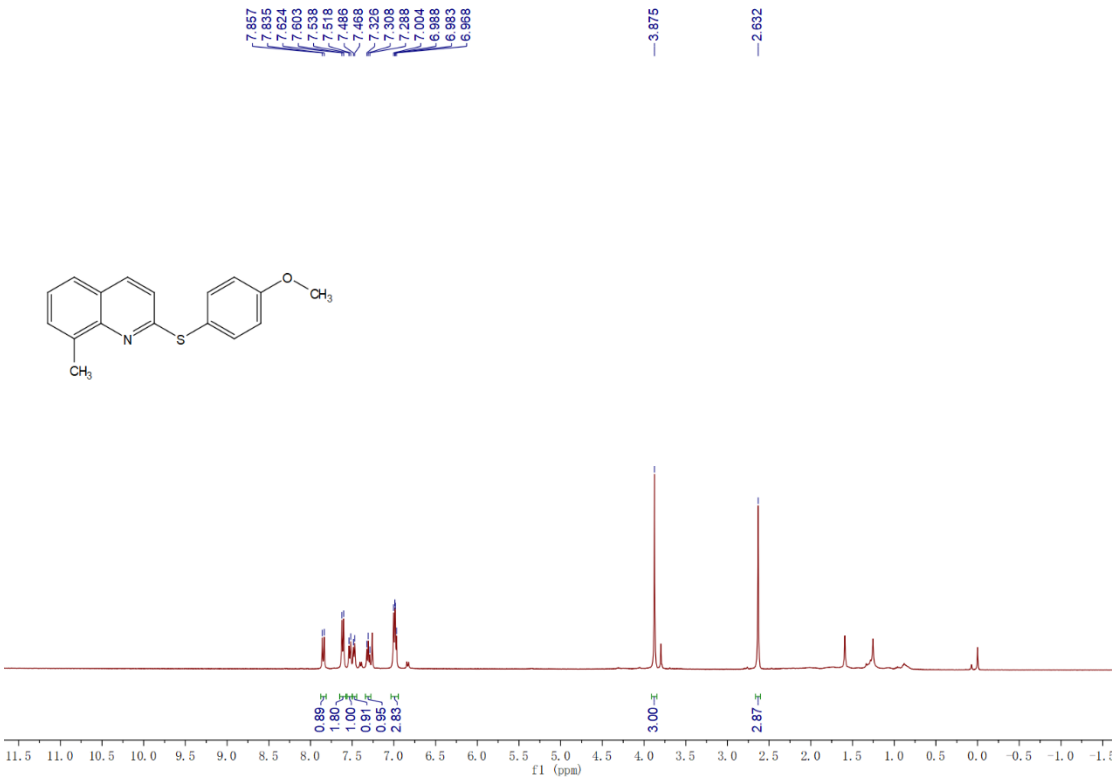


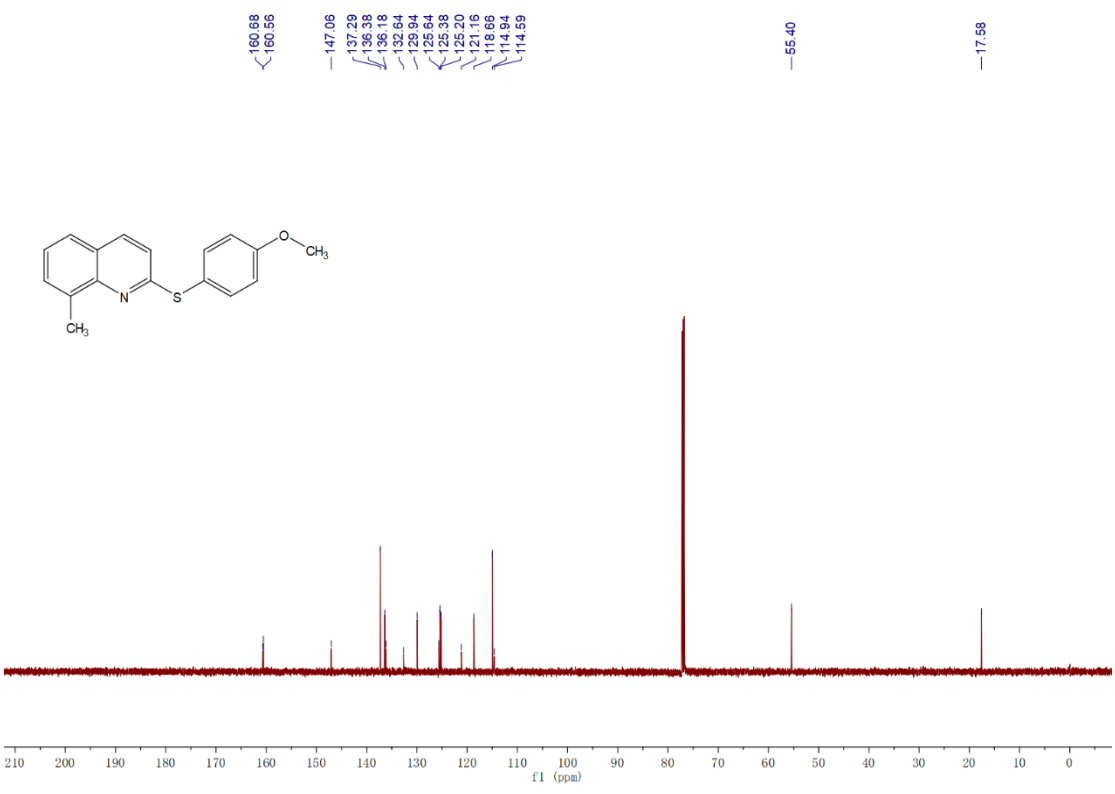
8-Methyl-2-*m*-tolylthio-quinoline (4ad)



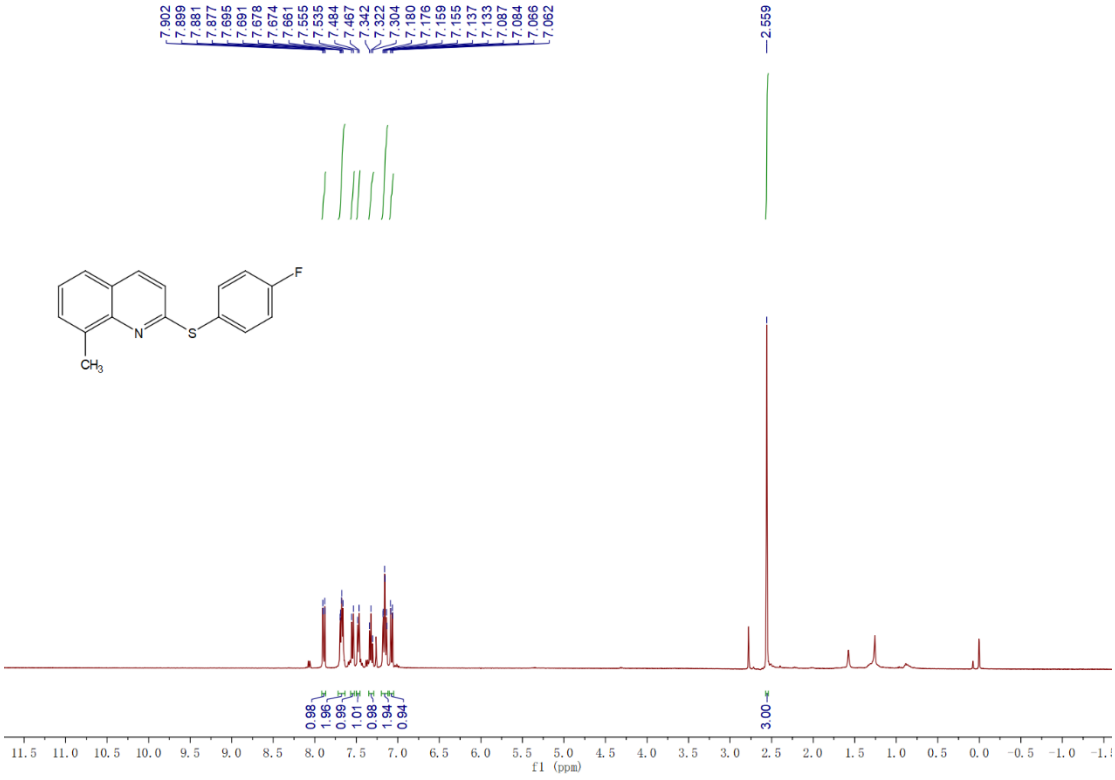


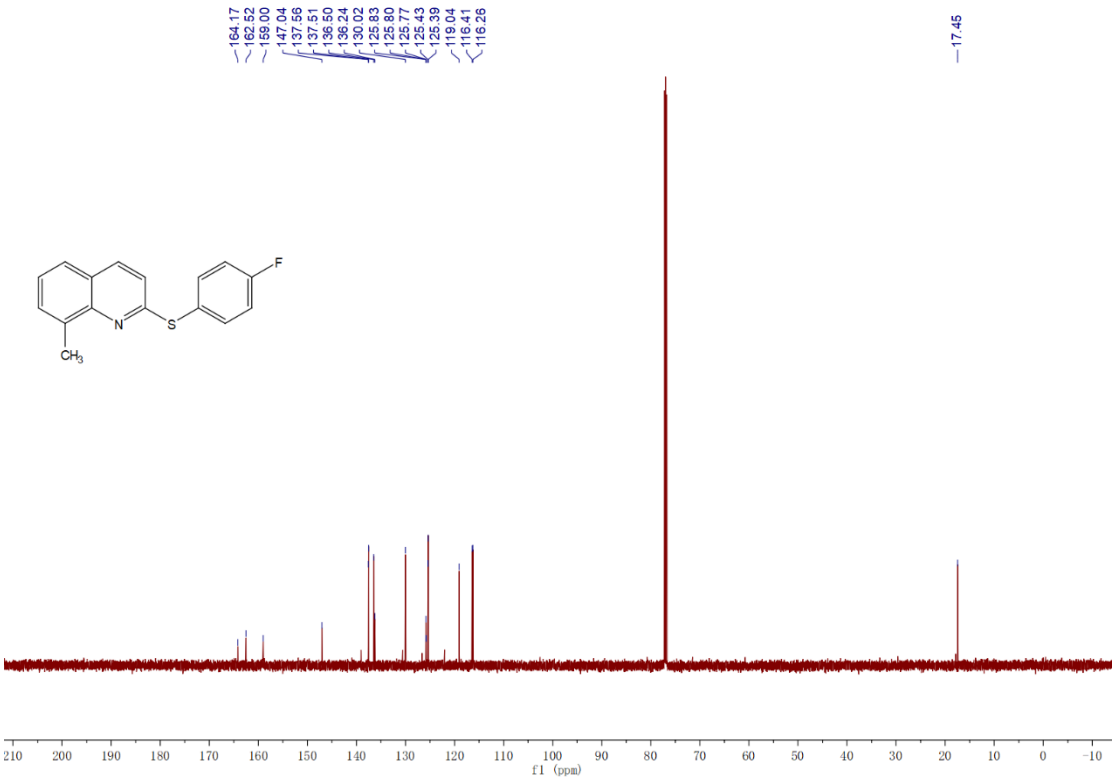
8-Methyl-2-*p*-methoxyphenylthio-quinoline (4ae)



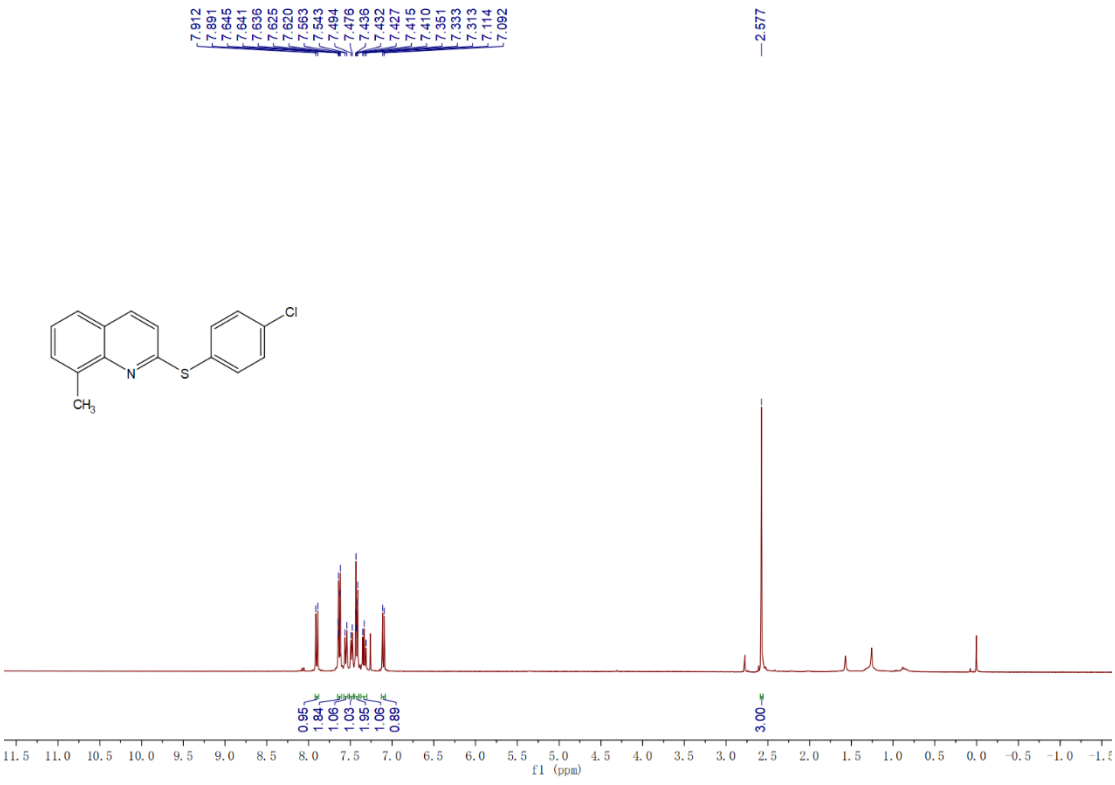


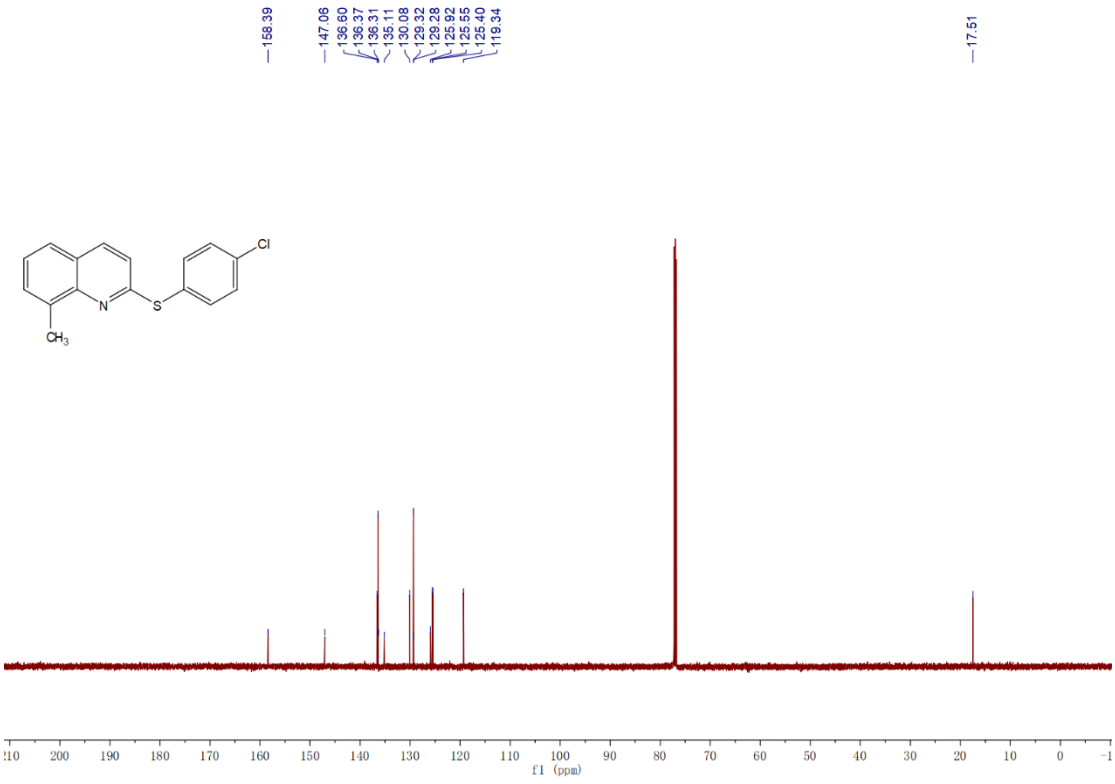
8-Methyl-2-*p*-fluorophenylthio-quinoline (4af)



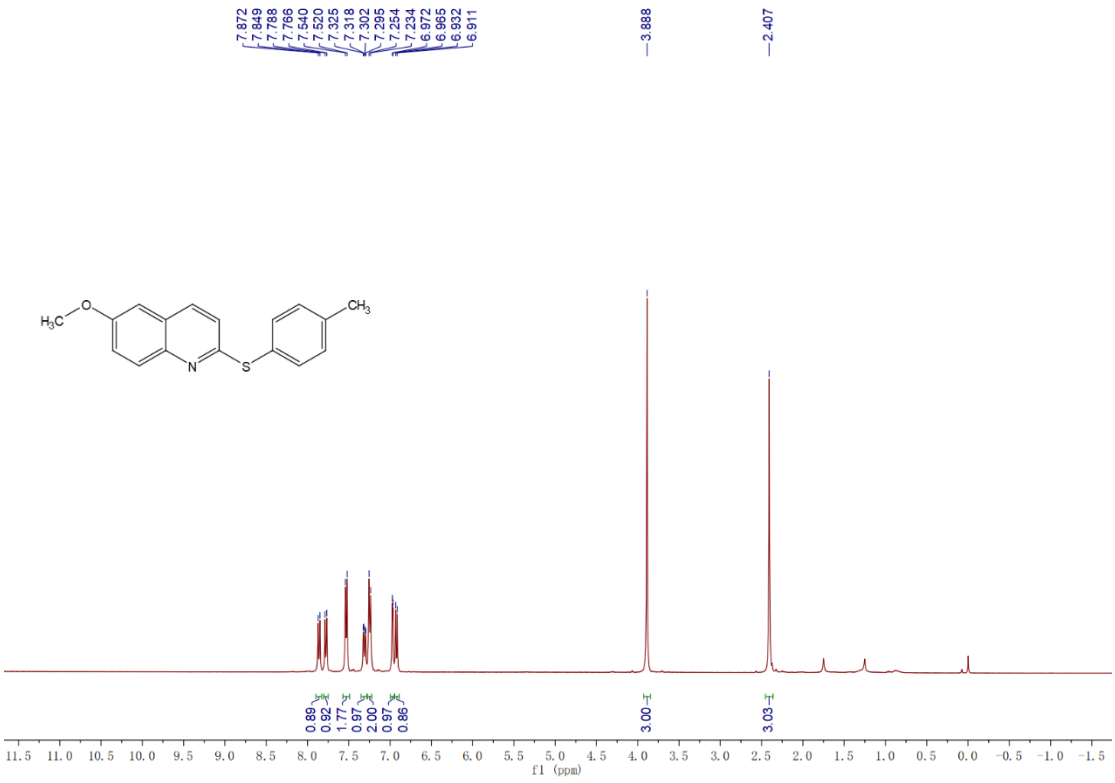


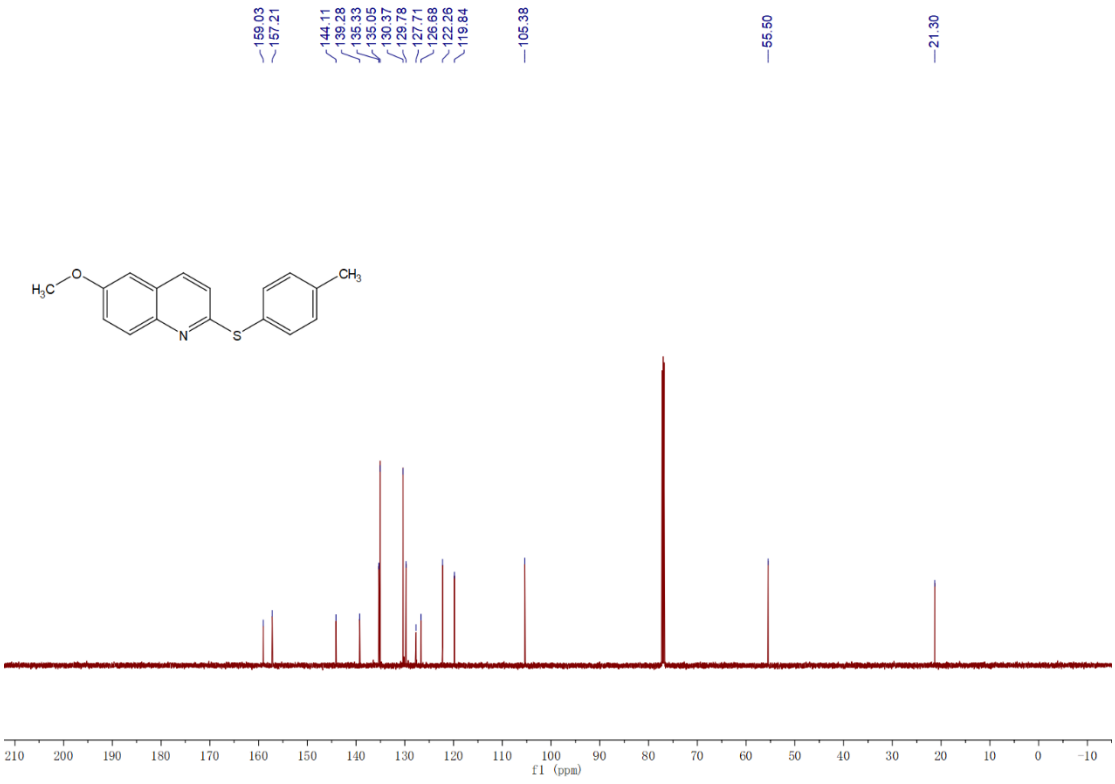
8-Methyl-2-*p*-chlorophenylthio-quinoline (4ag)



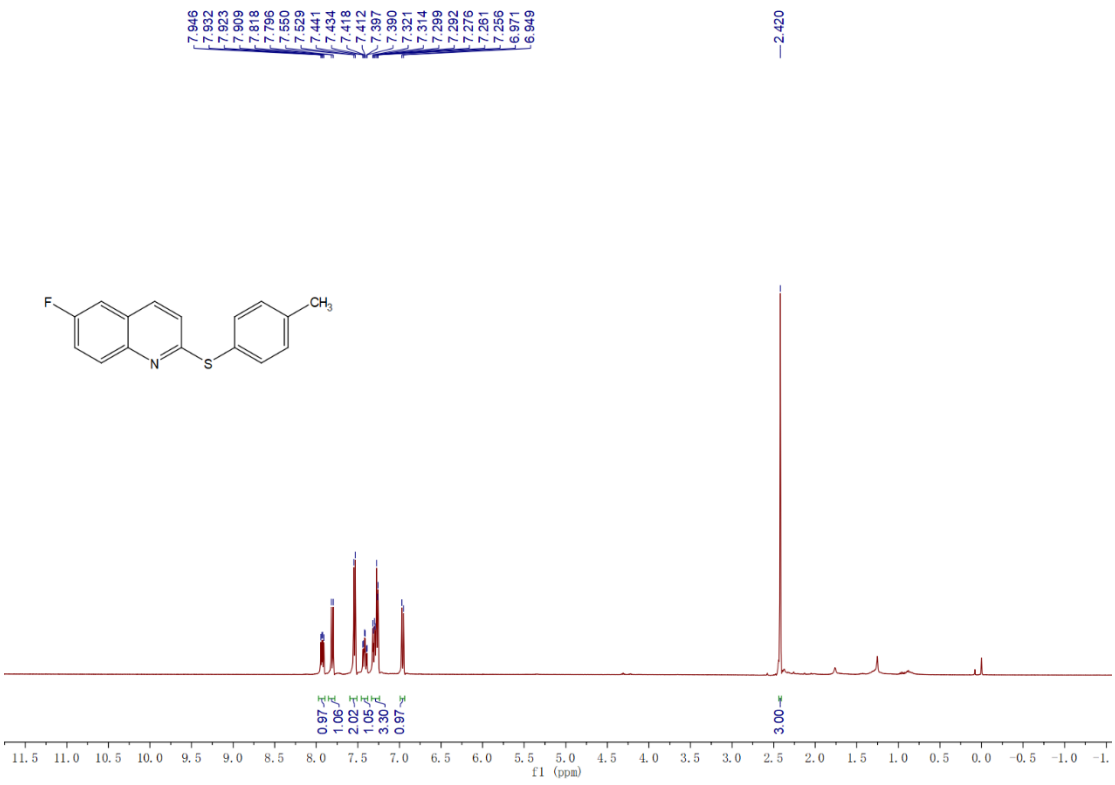


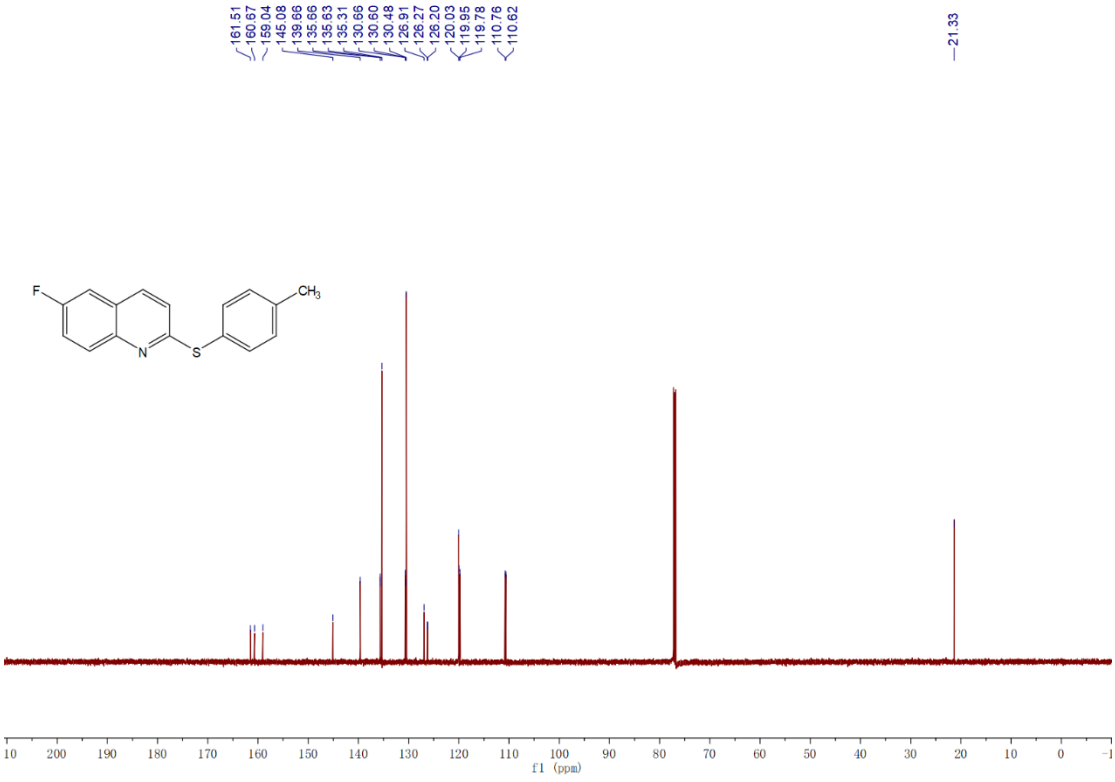
6-Methoxy-2-*p*-tolylthio-quinoline (4ah)



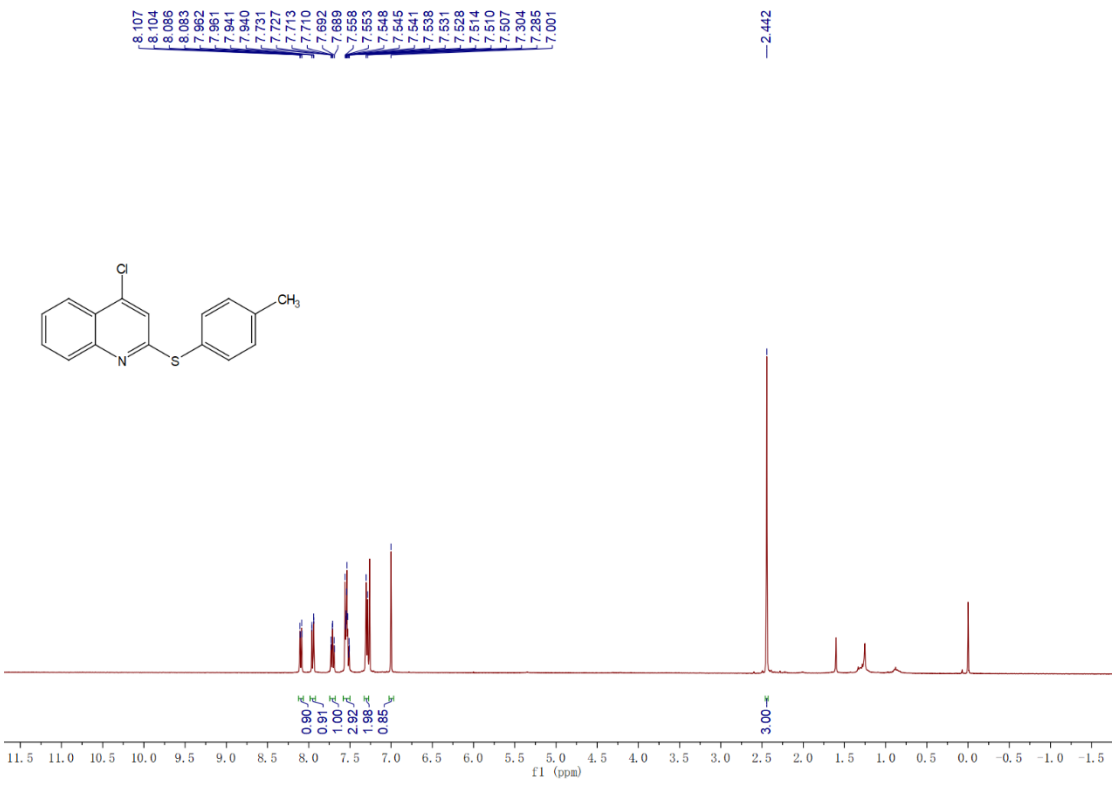


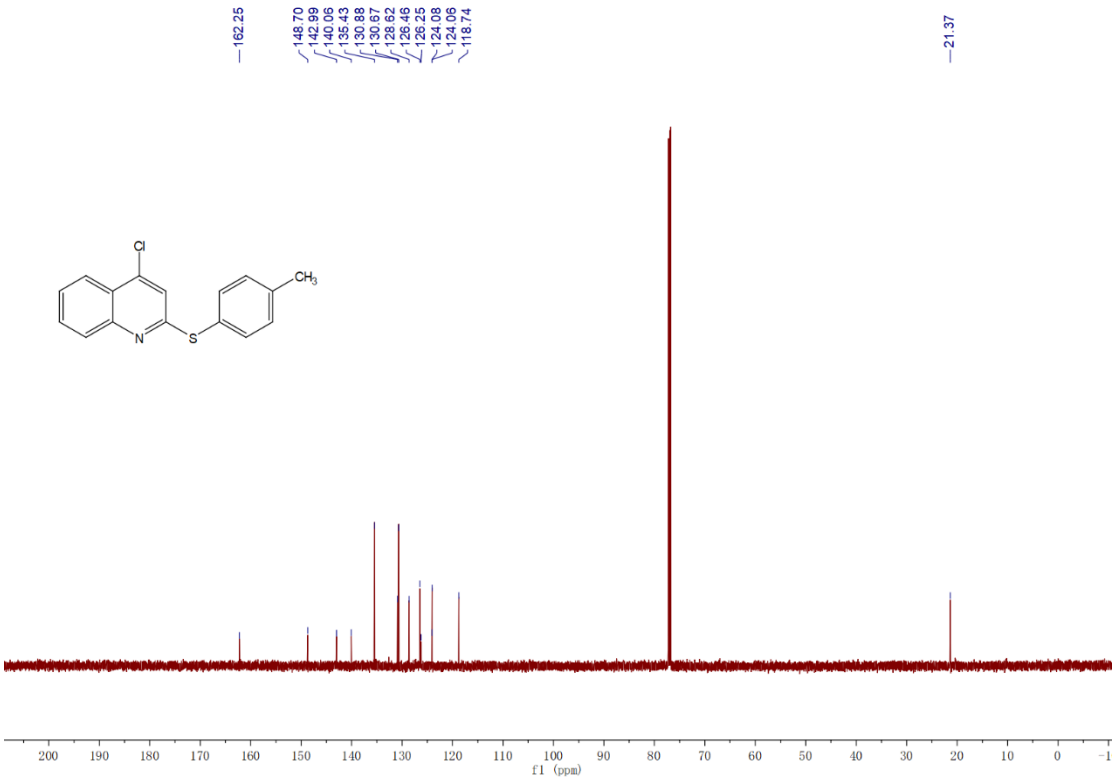
6-Fluoro-2-*p*-tolylthio-quinoline (4ai)



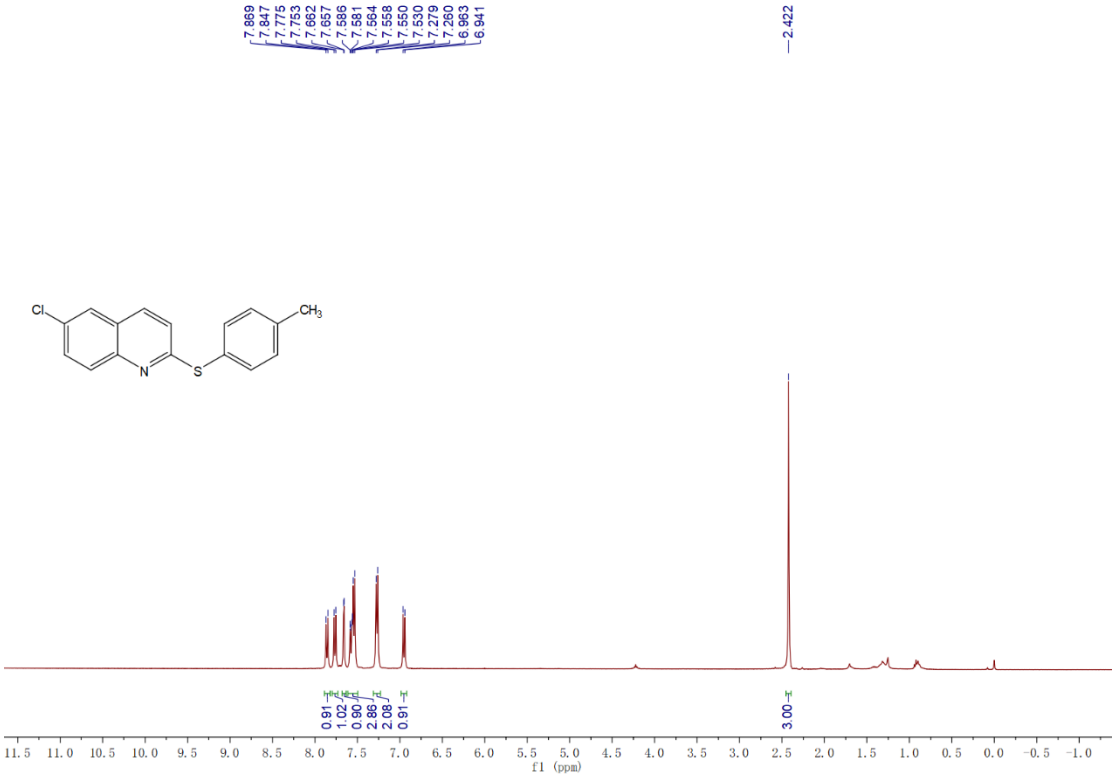


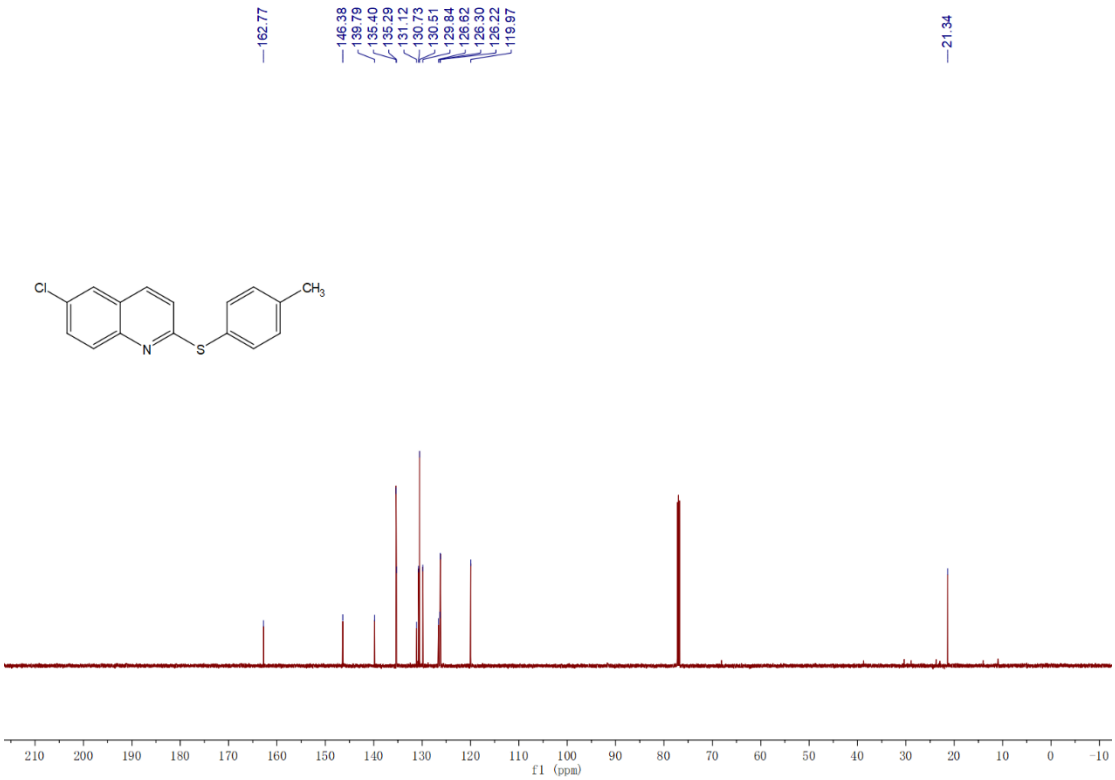
4-Chloro-2-*p*-tolylthio-quinoline (4aj)



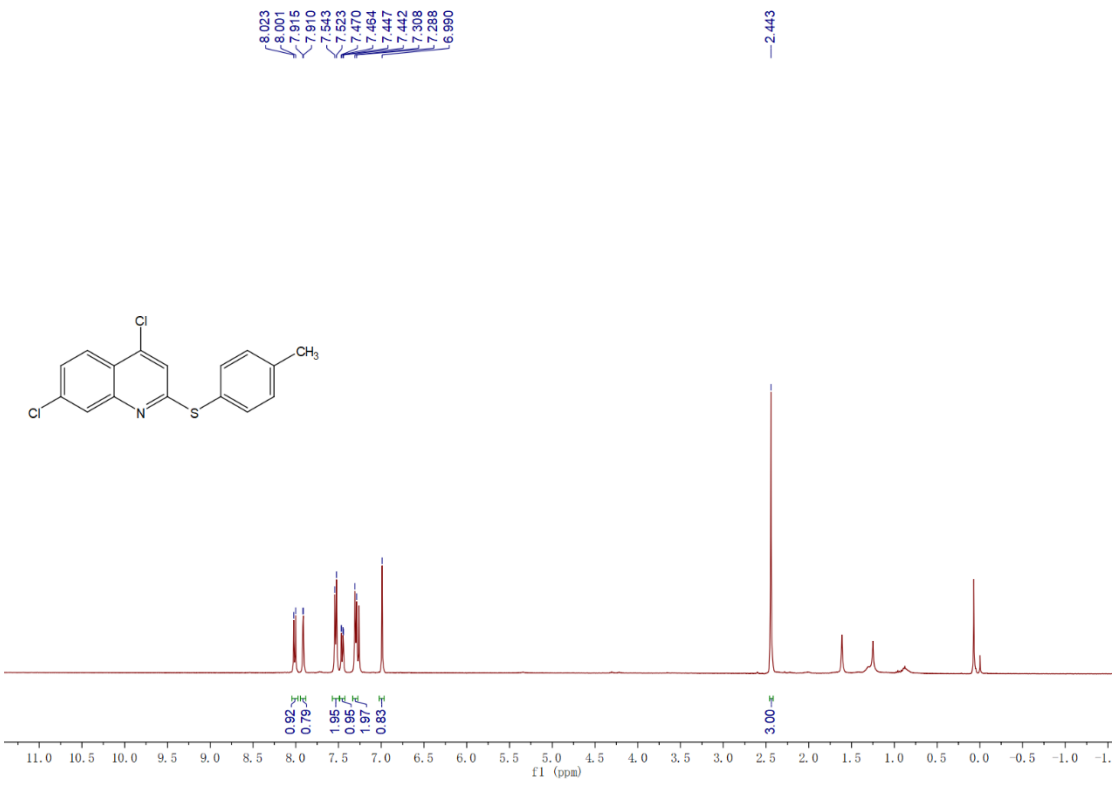


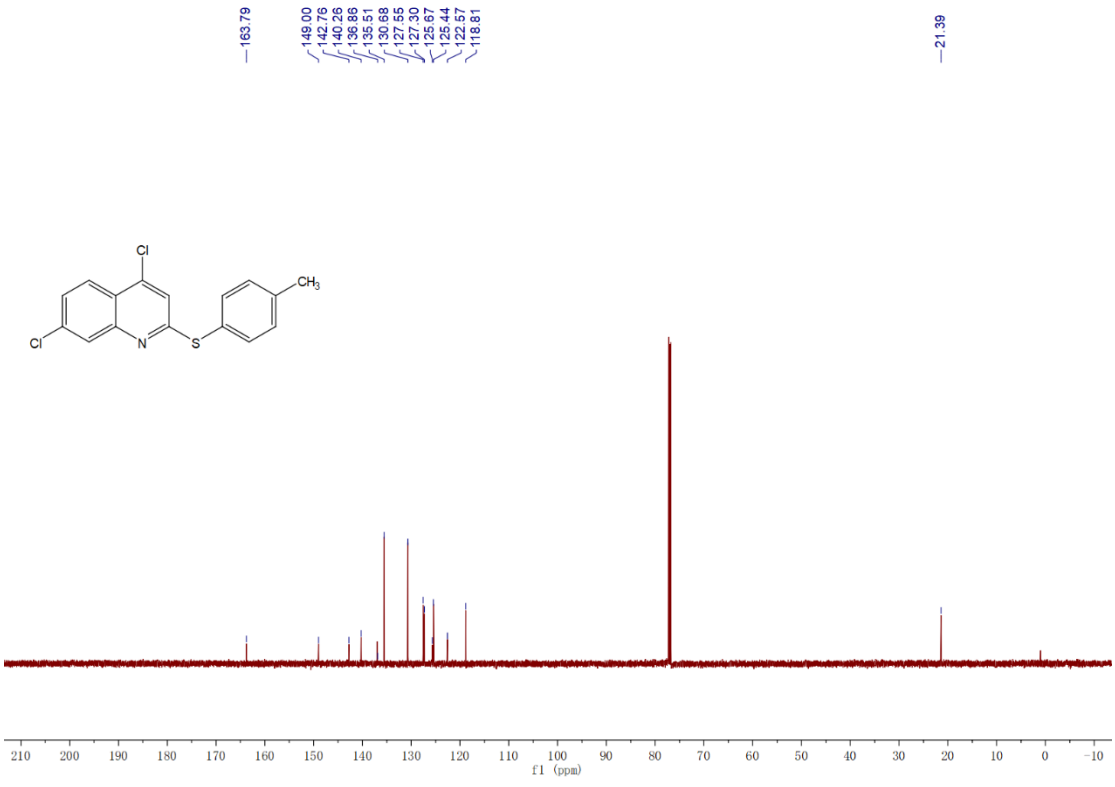
6-Chloro-2-*p*-tolylthio-quinoline (4ak)



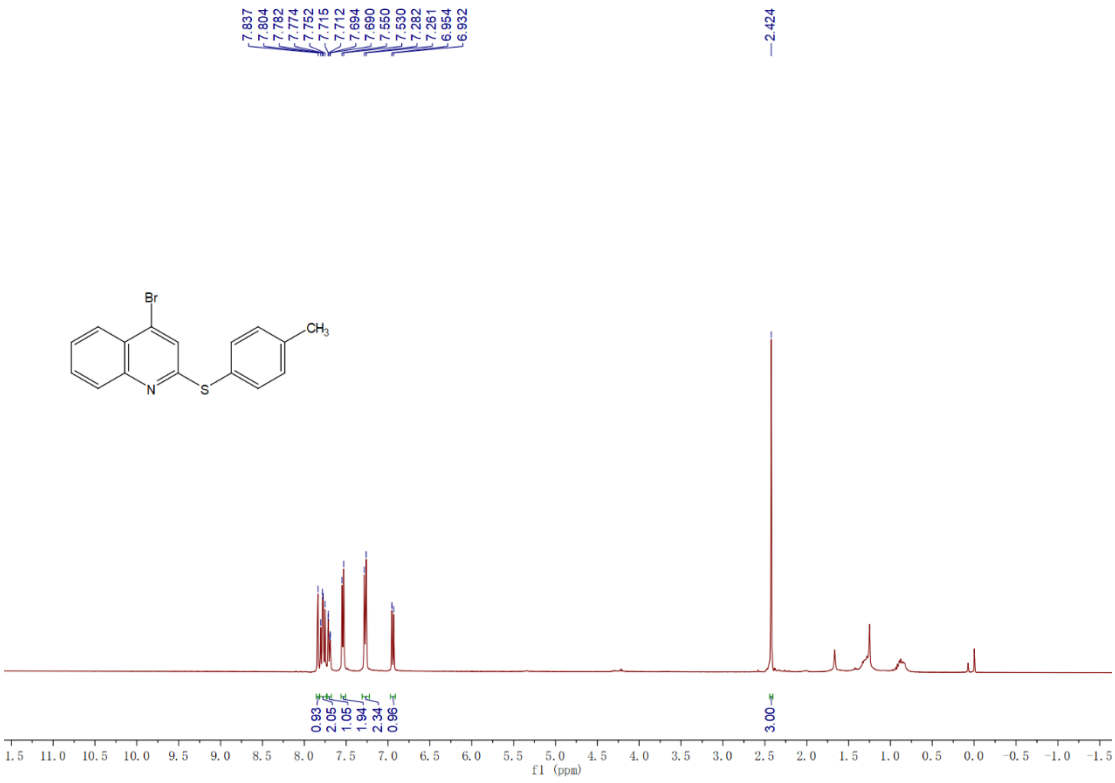


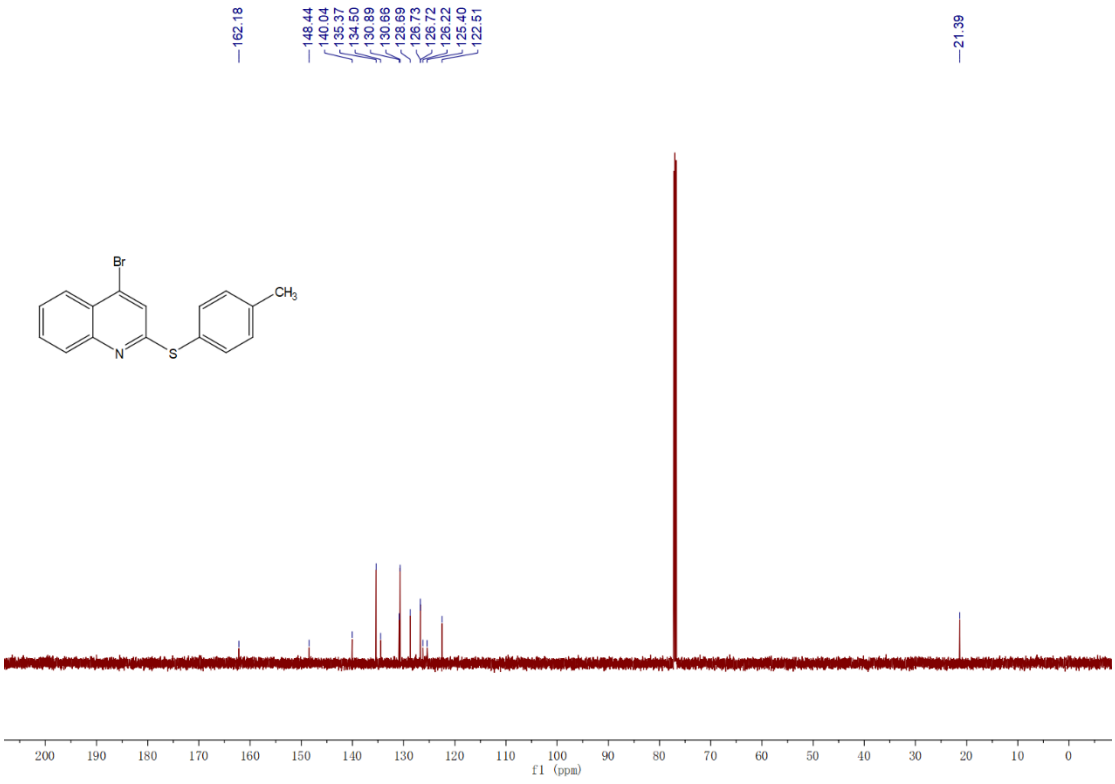
4,7-Dichloro-2-*p*-tolylthio-quinoline (4al)



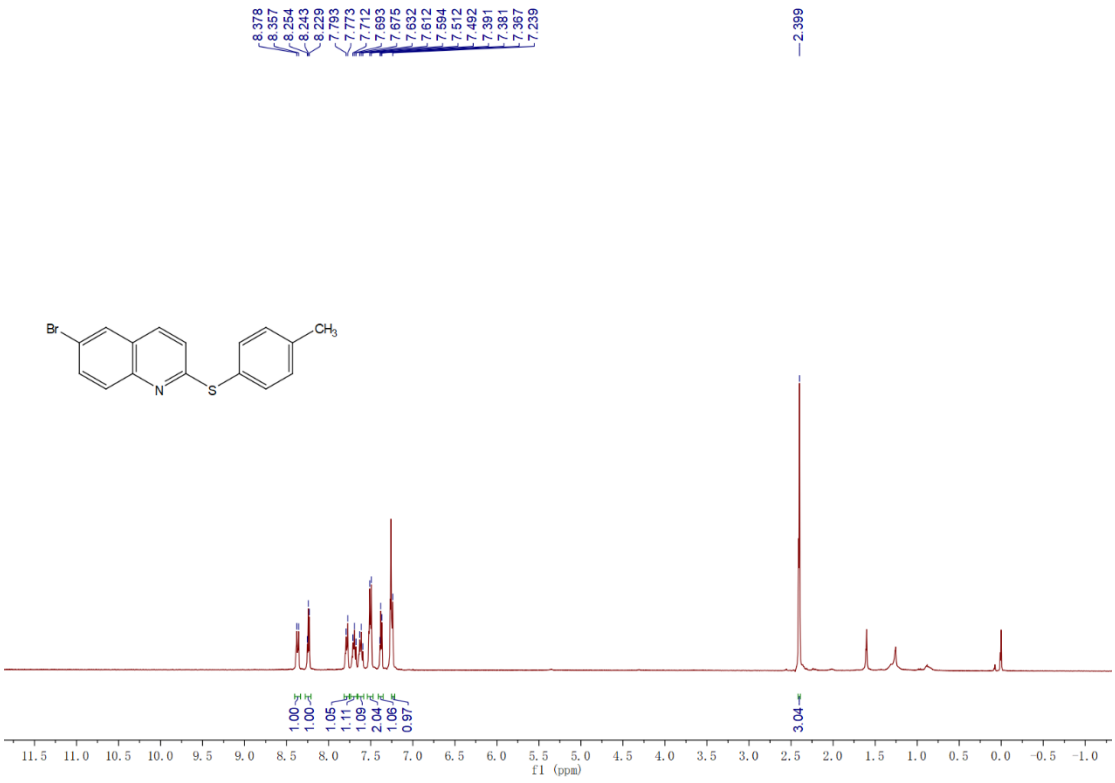


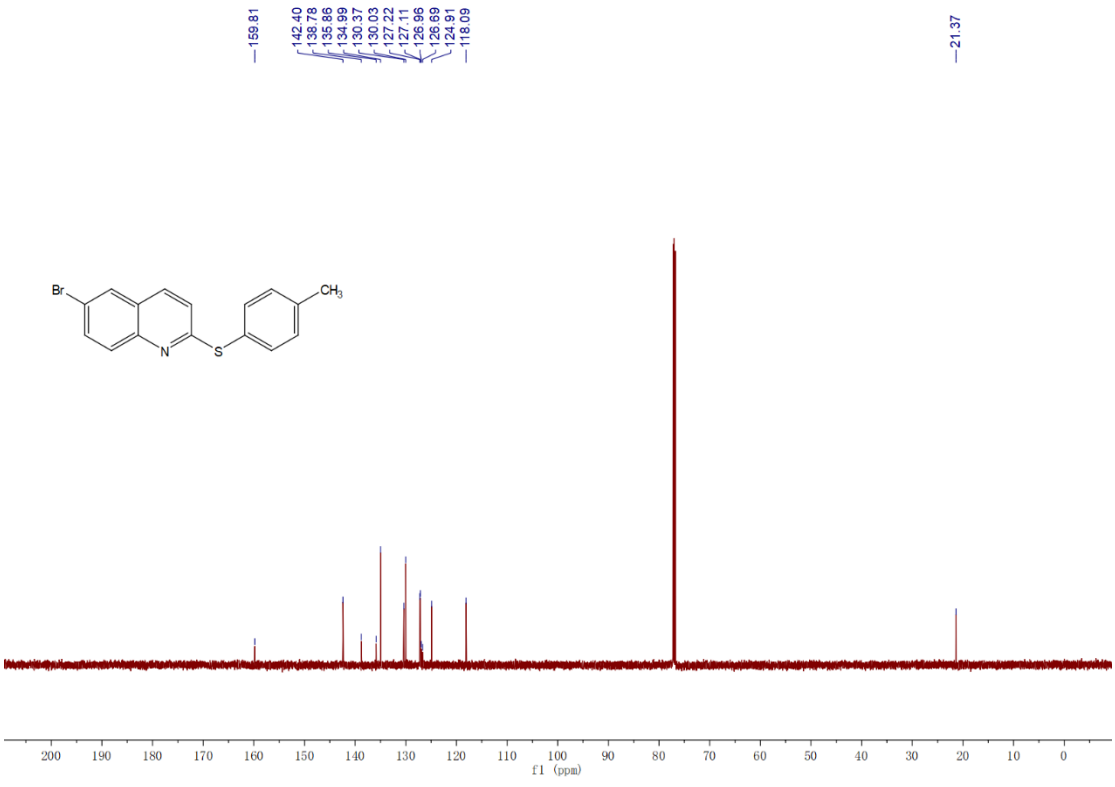
4-Bromo-2-*p*-tolylthio-quinoline (4am)



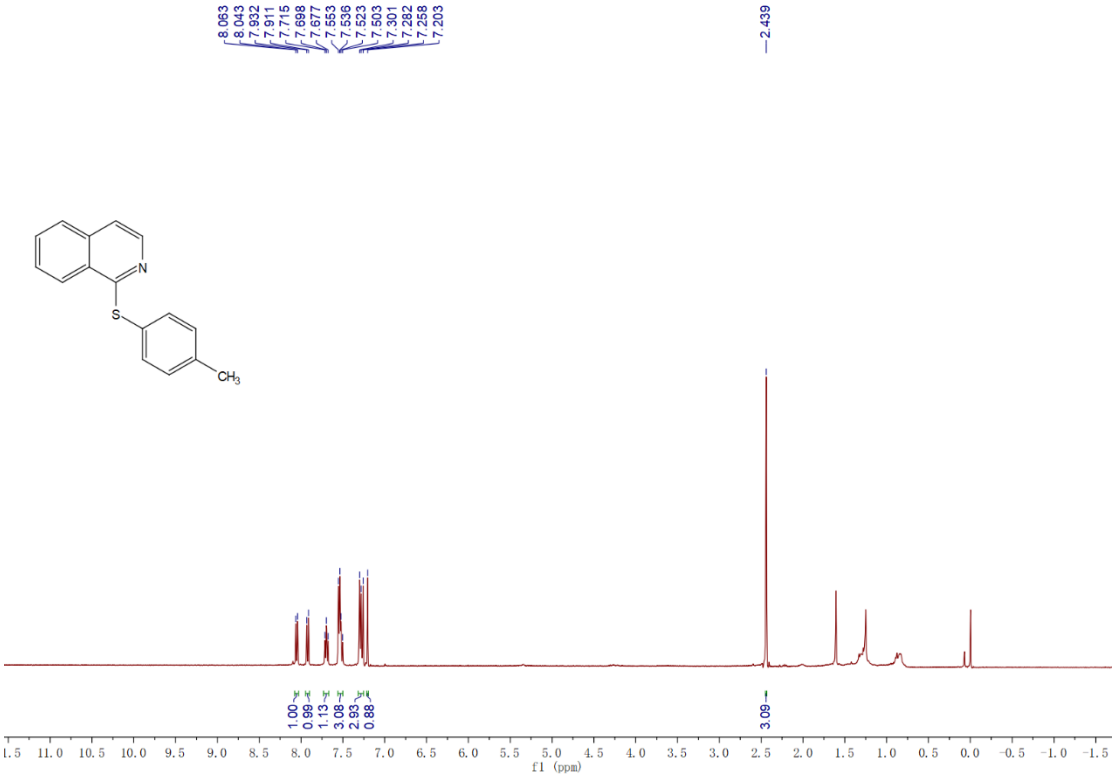


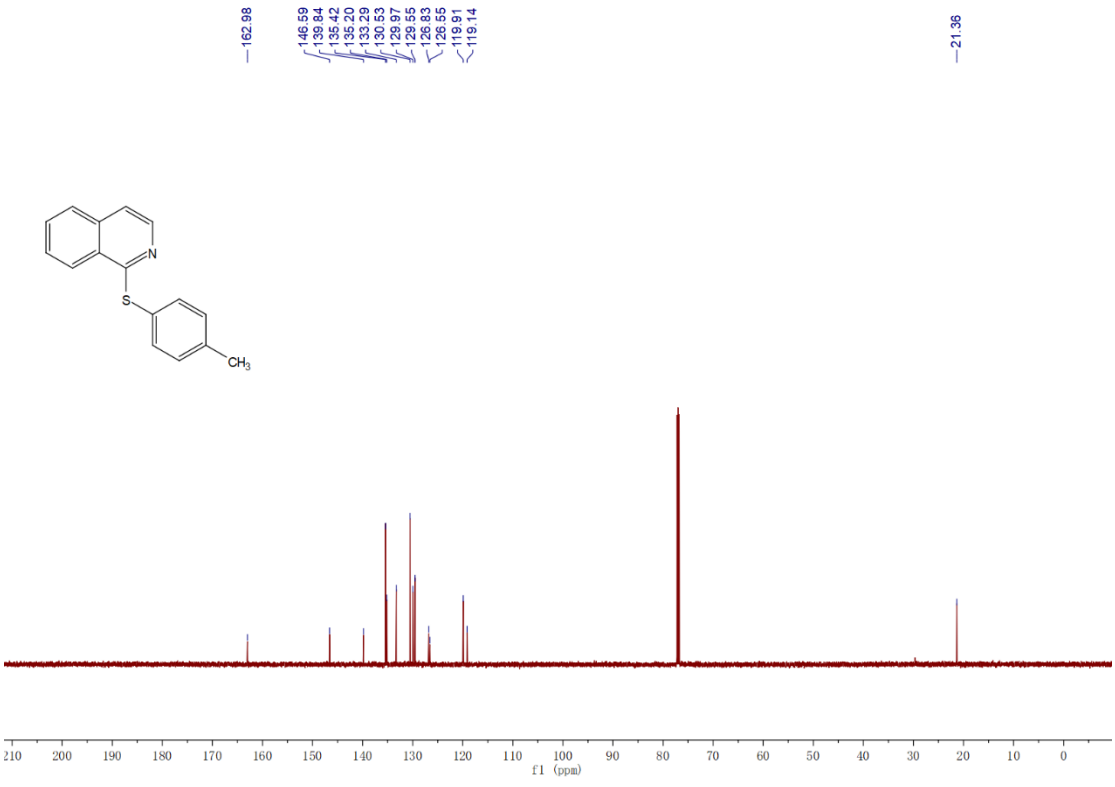
6-Bromo-2-*p*-tolylthio-quinoline (4an)



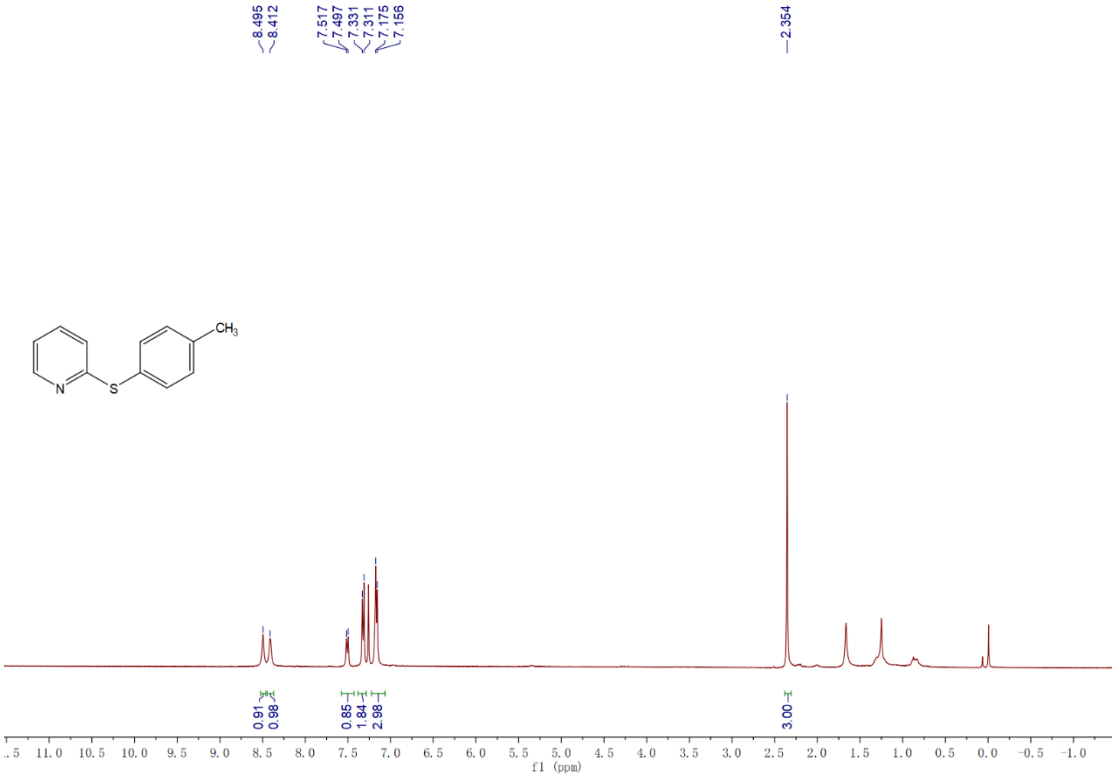


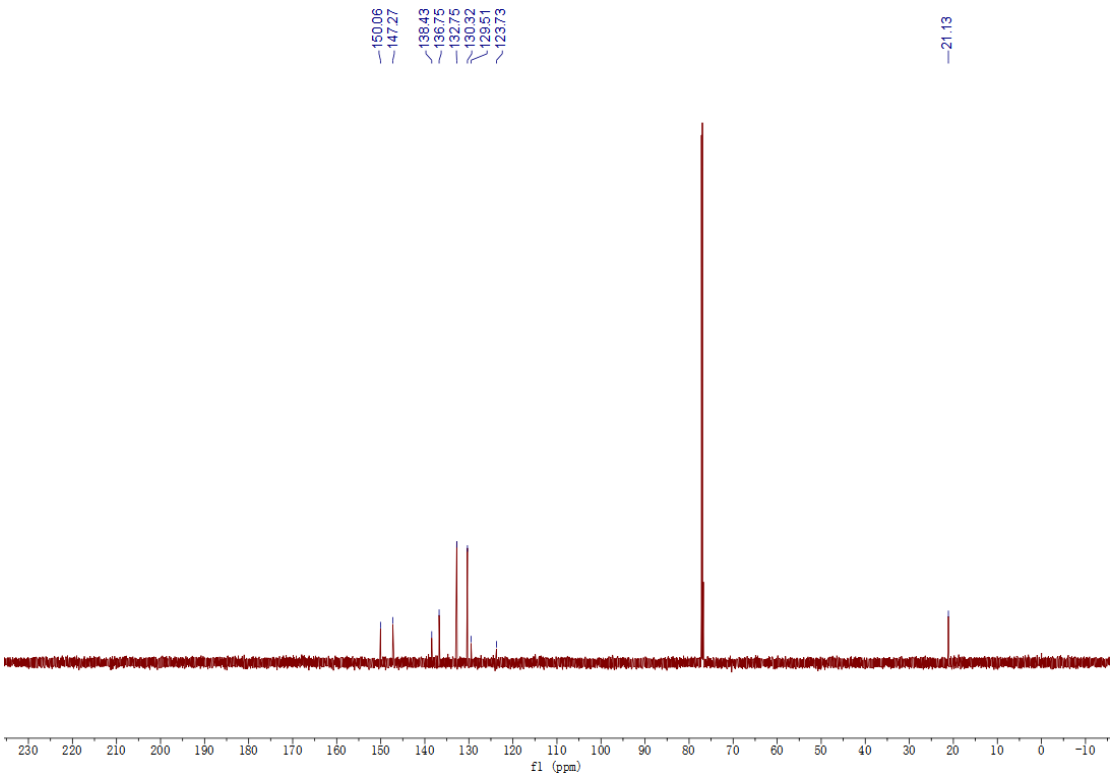
1-*p*-Tolylthio-isoquinoline (4ao)





2-*p*-Tolylthio-pyridine (4ap)

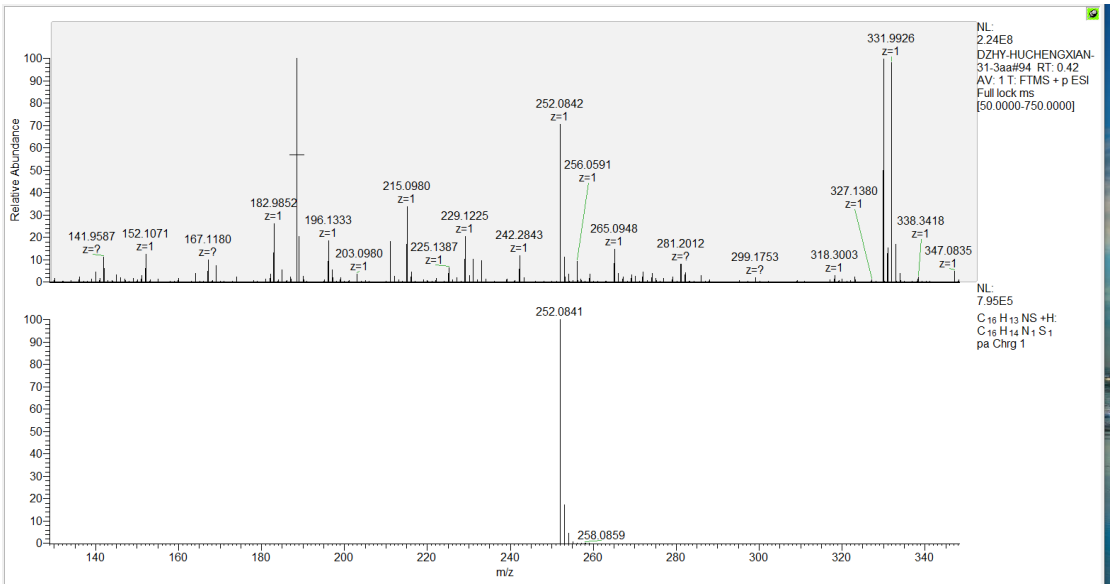




5. HRMS Spectra Copies of Products

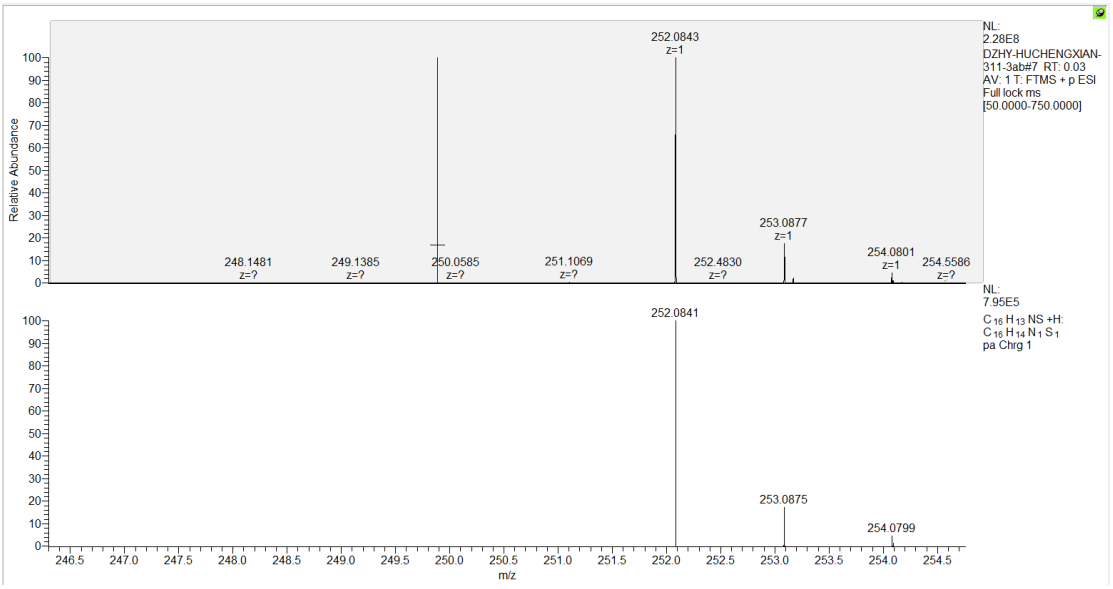
Product 3aa

HRMS (ESI) m/z calcd for $C_{16}H_{13}NS^+$, $(M+H)^+$ 252.0841, found 252.0842.



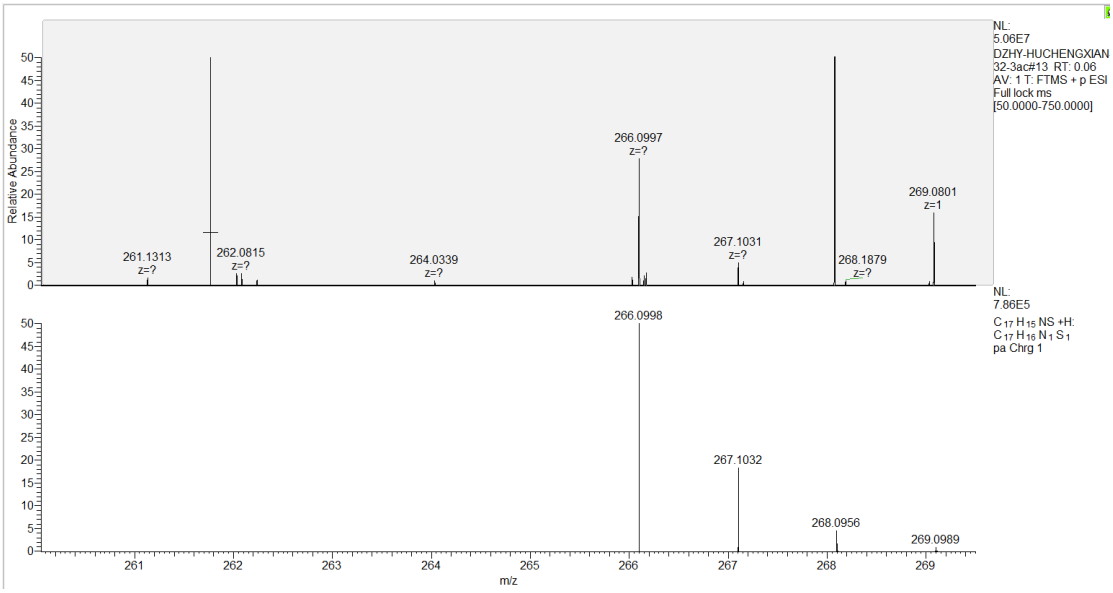
Product 3ab

HRMS (ESI) m/z calcd for $C_{16}H_{13}NS^+$, $(M+H)^+$ 252.0841, found 252.0843.



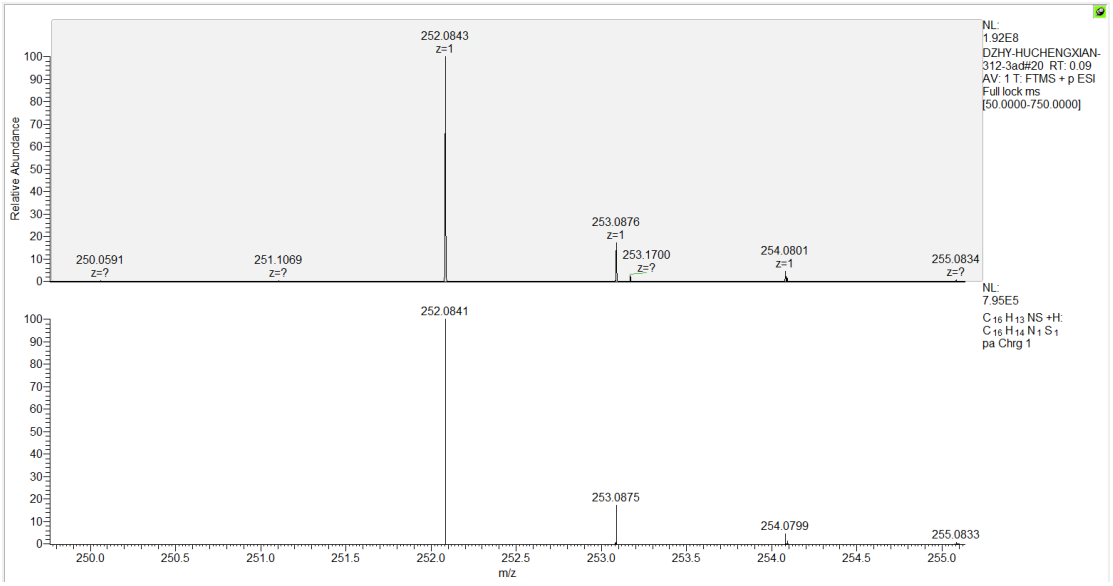
Product 3ac

HRMS (ESI) m/z calcd for $C_{17}H_{15}NS^+$, $(M+H)^+$ 266.0998, found 266.0997.



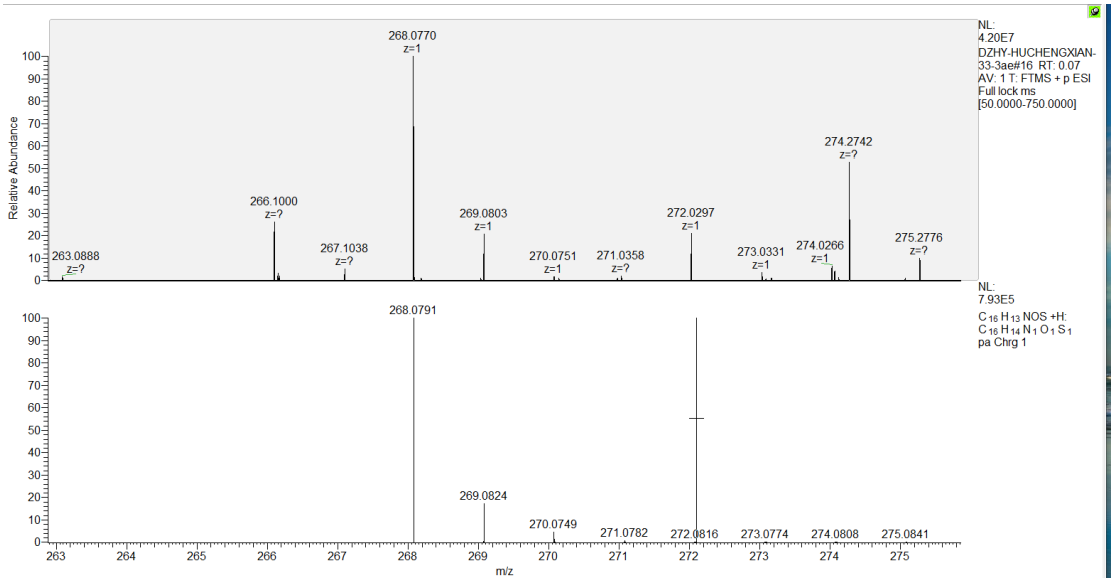
Product 3ad

HRMS (ESI) m/z calcd for $C_{16}H_{13}NS^+$, $(M+H)^+$ 252.0841, found 252.0843.



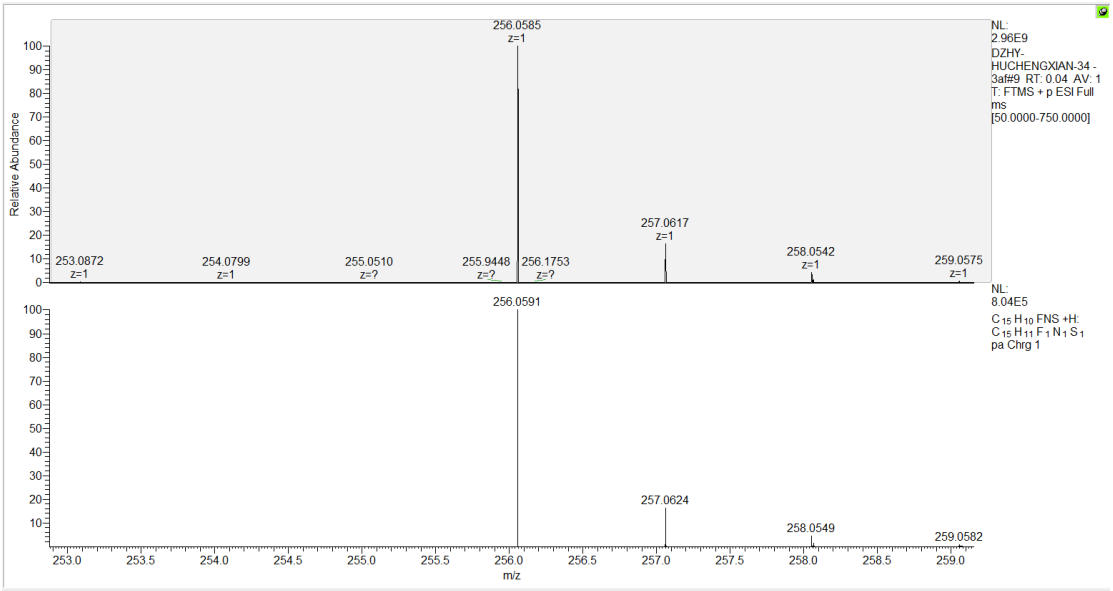
Product 3ae

HRMS (ESI) m/z calcd for $C_{16}H_{13}NOS^{+}$, $(M+H)^{+}$ 268.0791, found 268.0770.



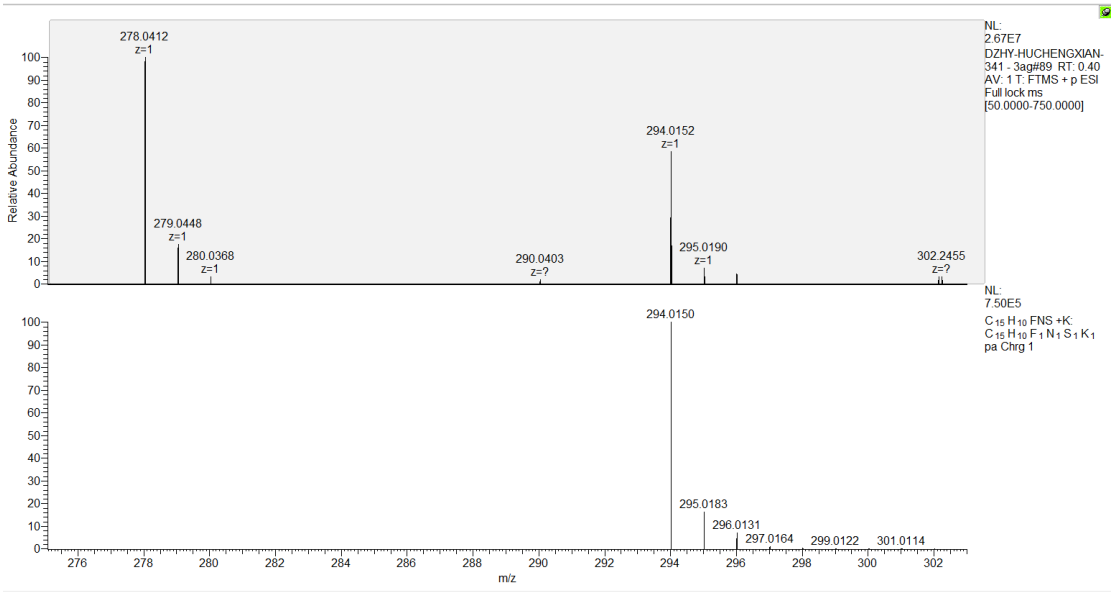
Product 3af

HRMS (ESI) m/z calcd for $C_{15}H_{10}FNS^{+}$, $(M+H)^{+}$ 256.0591, found 256.0585.



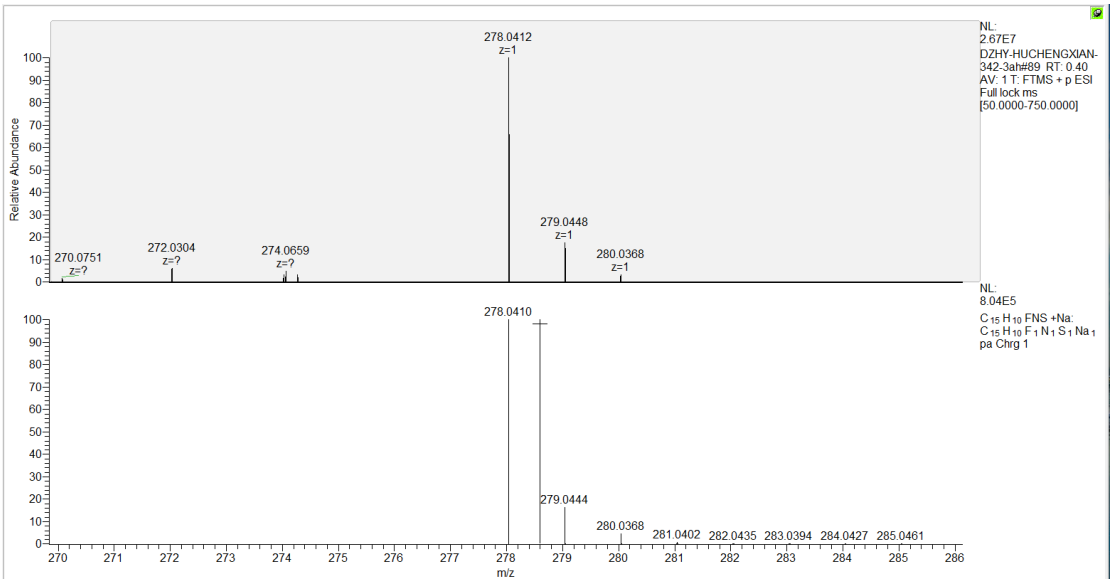
Product 3ag

HRMS (ESI) m/z calcd for $C_{15}H_{10}FNS^{+}$, $(M+K)^{+}$ 294.0150, found 294.0152.



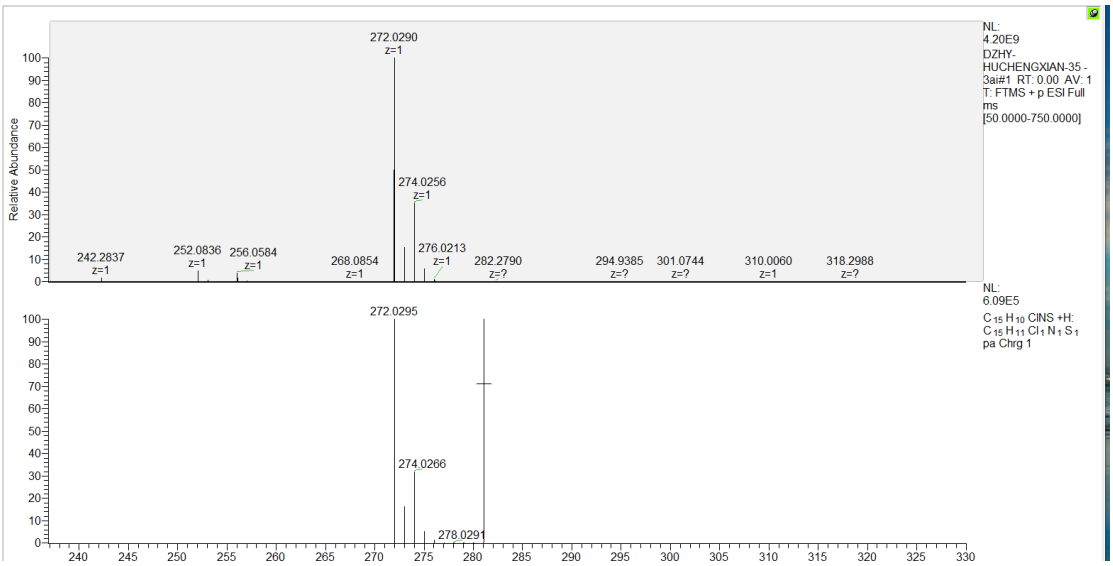
Product 3ah

HRMS (ESI) m/z calcd for $C_{15}H_{10}FNS^{+}$, $(M+Na)^{+}$ 278.0410, found 278.0412.



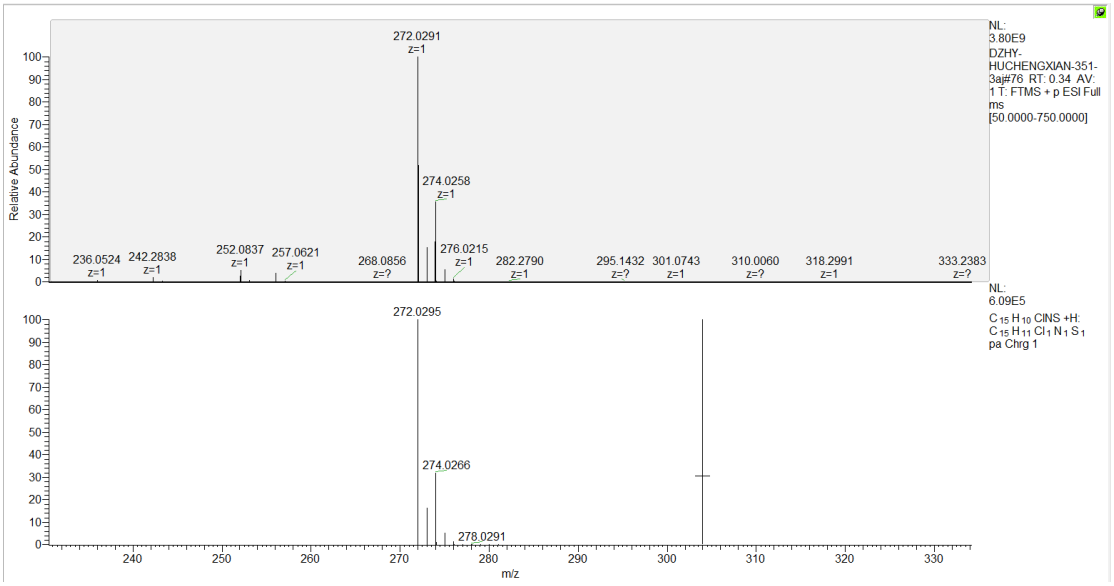
Product 3ai

HRMS (ESI) m/z calcd for $C_{15}H_{10}ClNS^+$, $(M+H)^+$ 272.0295, found 272.0290.



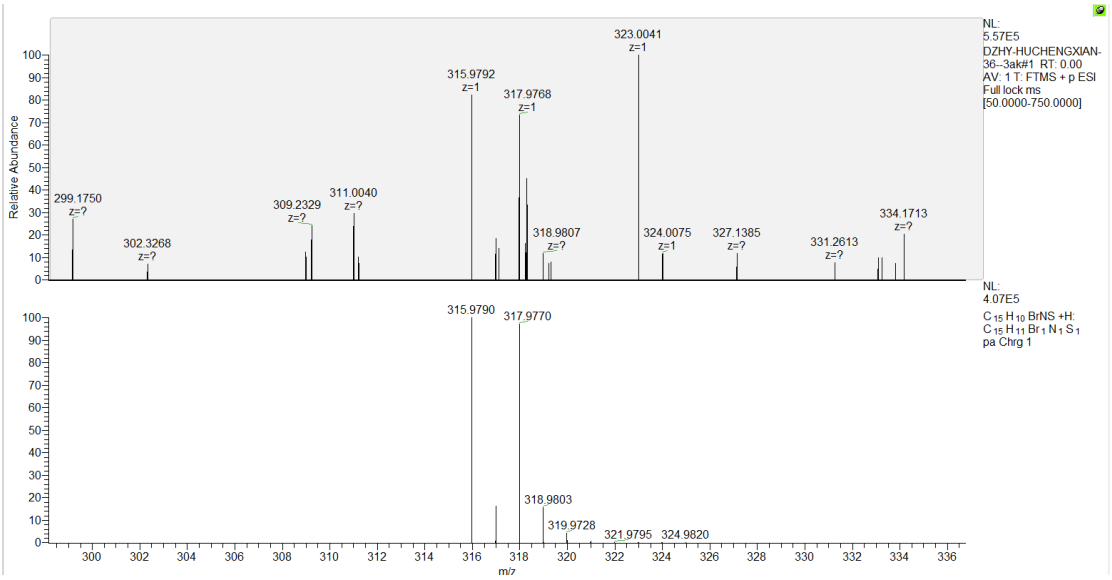
Product 3aj

HRMS (ESI) m/z calcd for $C_{15}H_{10}ClNS^+$, $(M+H)^+$ 272.0295, found 272.0291.



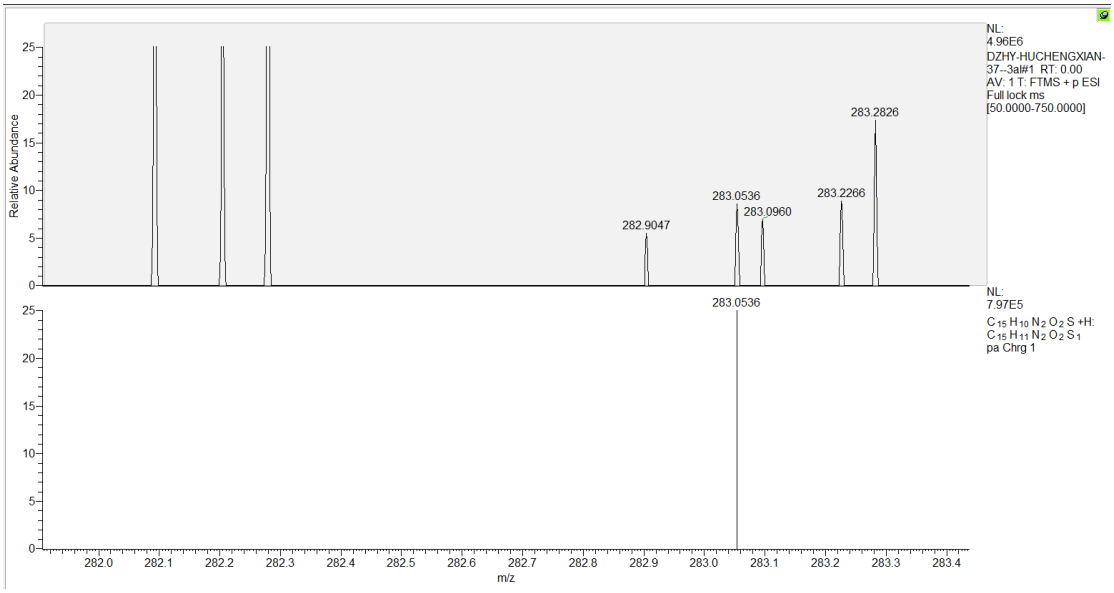
Product 3ak

HRMS (ESI) m/z calcd for $C_{15}H_{10}BrNS^+$, $(M+H)^+$ 315.9790, found 317.9792.



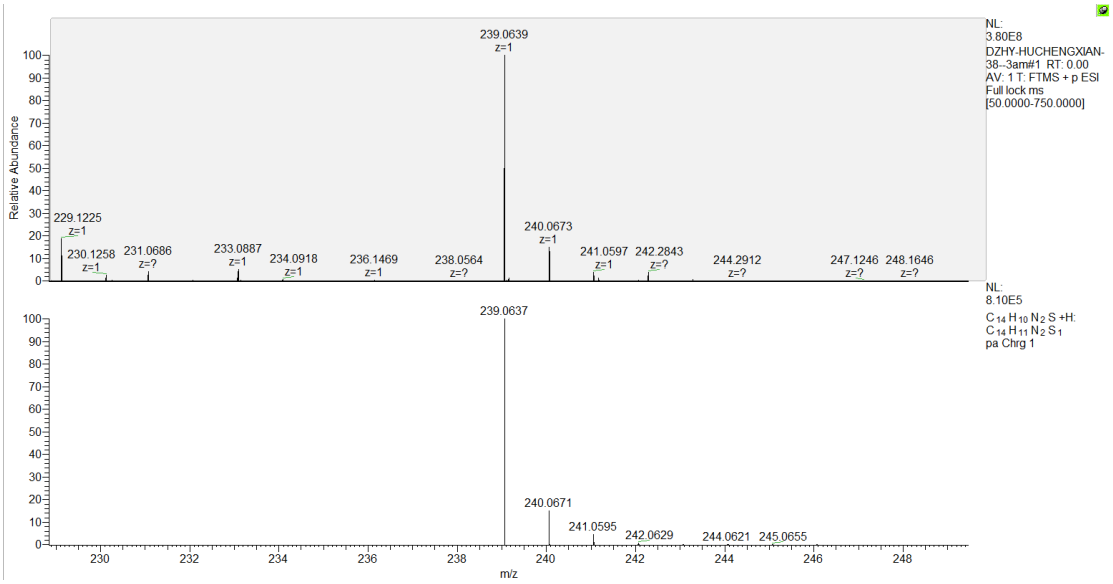
Product 3al

HRMS (ESI) m/z calcd for $C_{15}H_{10}N_2O_2S^+$, $(M+H)^+$ 283.0536, found 283.0536.



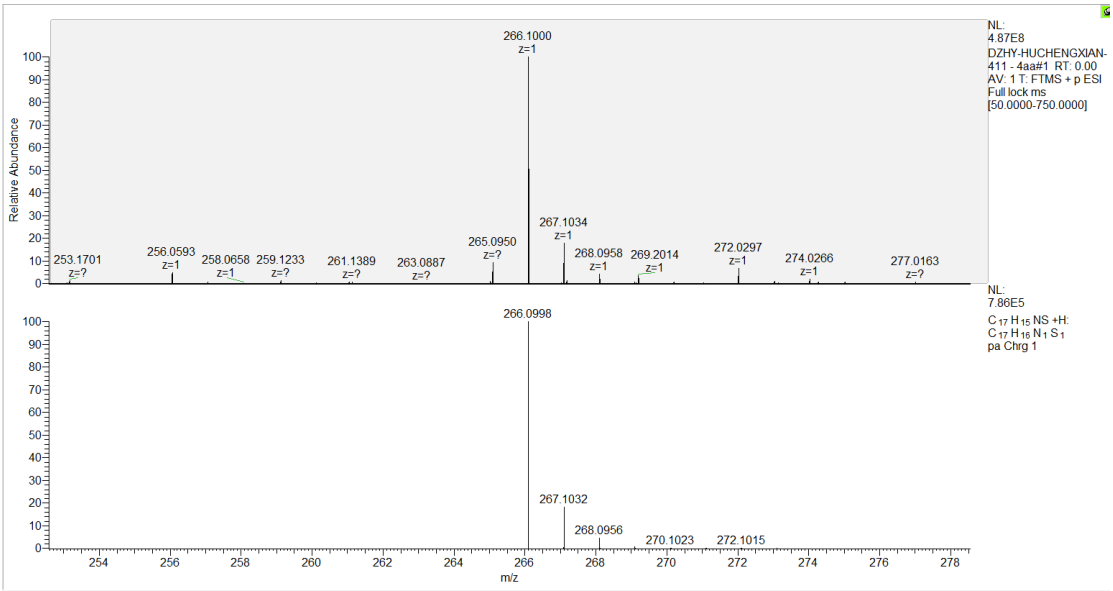
Product 3am

HRMS (ESI) m/z calcd for $C_{14}H_{10}N_2S^+$, $(M+H)^+$ 239.0637, found 239.0639.



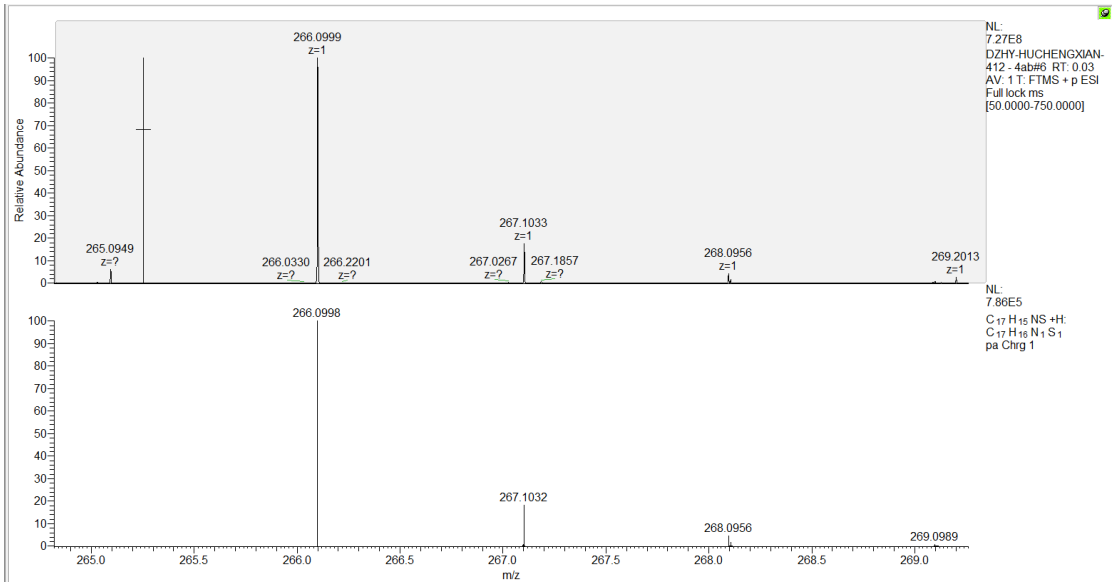
Product 4aa

HRMS (ESI) m/z calcd for $C_{17}H_{15}NS^+$, $(M+H)^+$ 266.0998, found 266.1000.



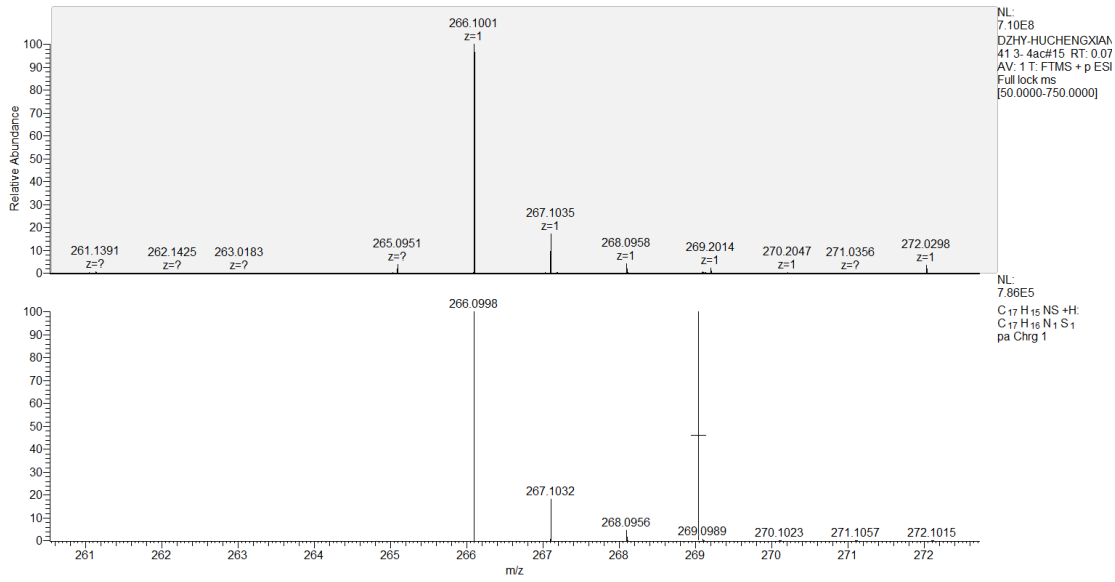
Product 4ab

HRMS (ESI) m/z calcd for $C_{17}H_{15}NS^+$, $(M+H)^+$ 266.0998, found 266.0999.



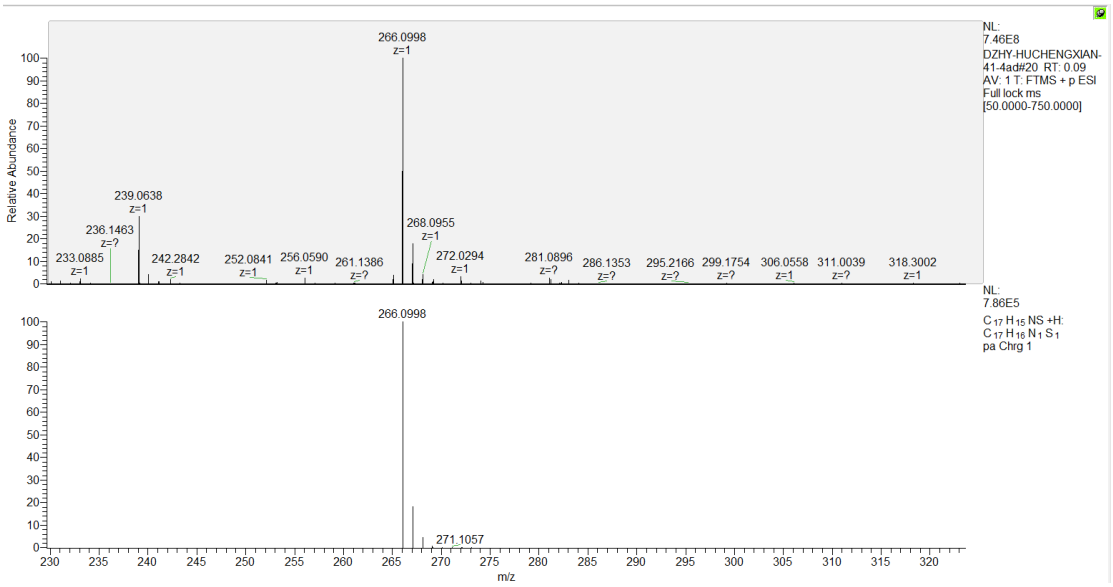
Product 4ac

HRMS (ESI) m/z calcd for $C_{17}H_{15}NS^+$, $(M+H)^+$ 266.0998, found 266.1001.



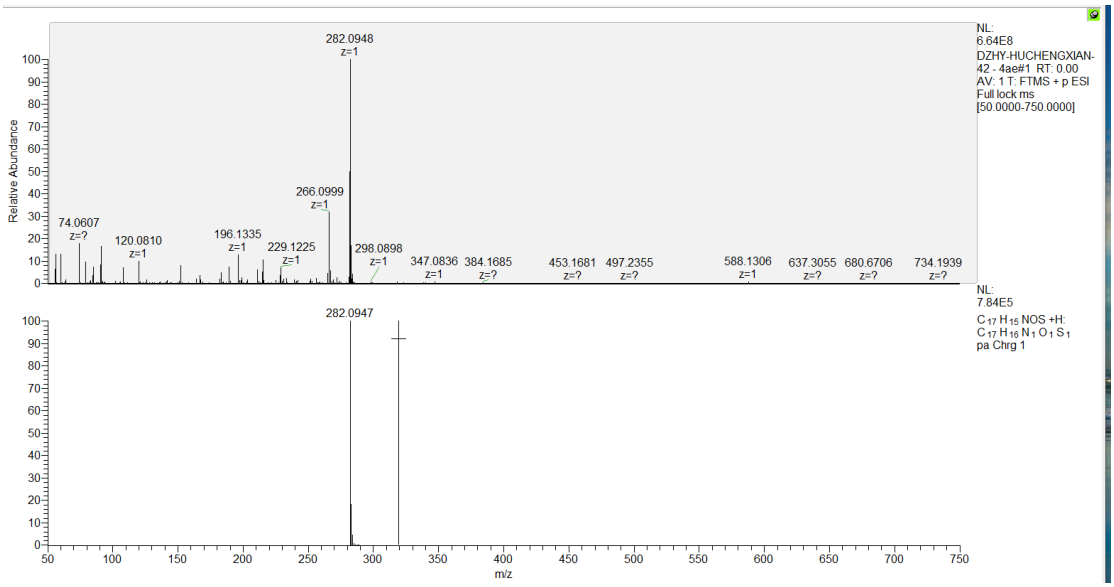
Product 4ad

HRMS (ESI) m/z calcd for $C_{17}H_{15}NS^+$, $(M+H)^+$ 266.0998, found 266.0998.



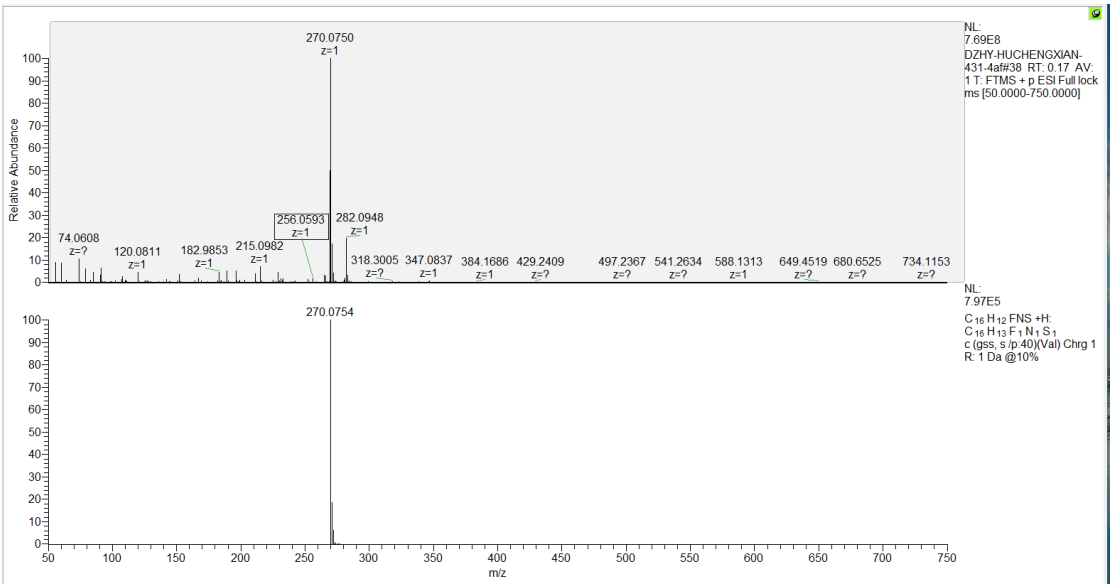
Product 4ae

HRMS (ESI) m/z calcd for $C_{17}H_{15}NOS^+$, $(M+H)^+$ 282.0947, found 282.0948.



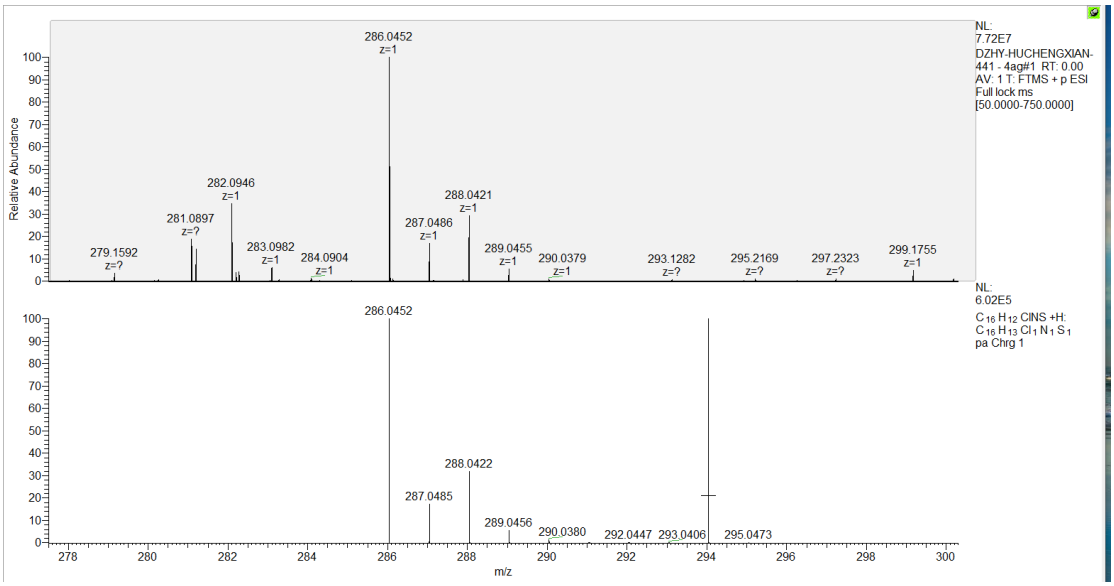
Product 4af

HRMS (ESI) m/z calcd for $C_{16}H_{12}FNS^+$, $(M+H)^+$ 270.0754, found 270.0750.



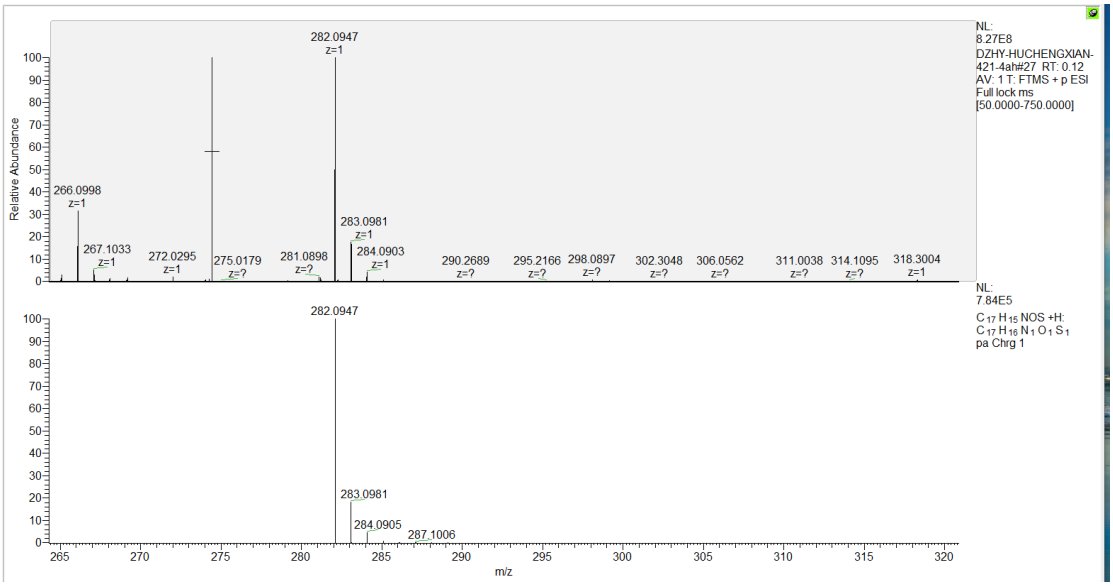
Product 4ag

HRMS (ESI) m/z calcd for $C_{16}H_{12}ClNS^+$, $(M+H)^+$ 286.0452, found 286.0452.



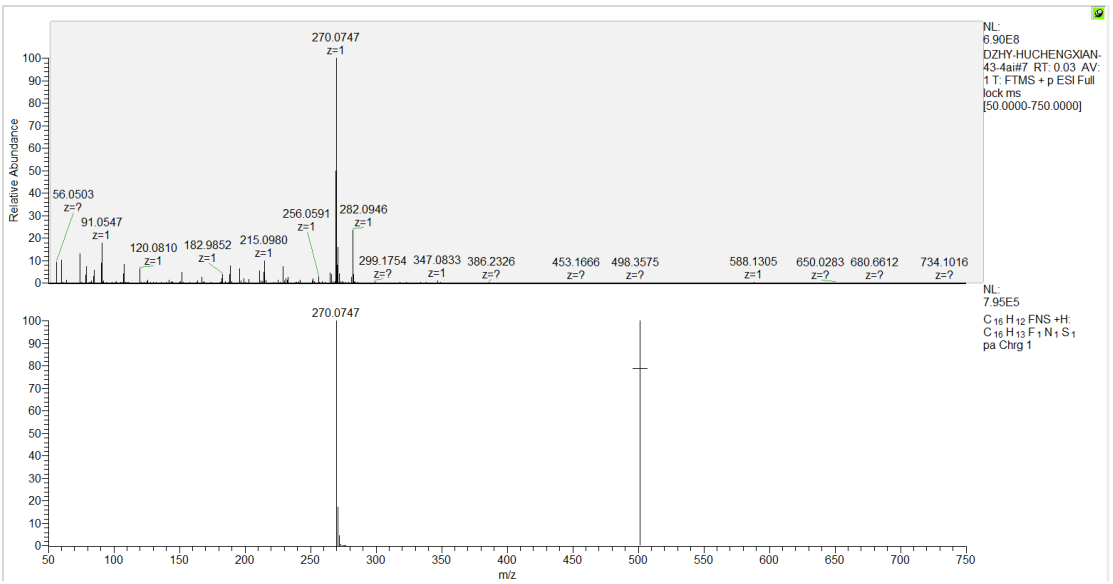
Product 4ah

HRMS (ESI) m/z calcd for $C_{17}H_{15}NOS^{+}$, $(M+H)^{+}$ 282.0947, found 282.0947.



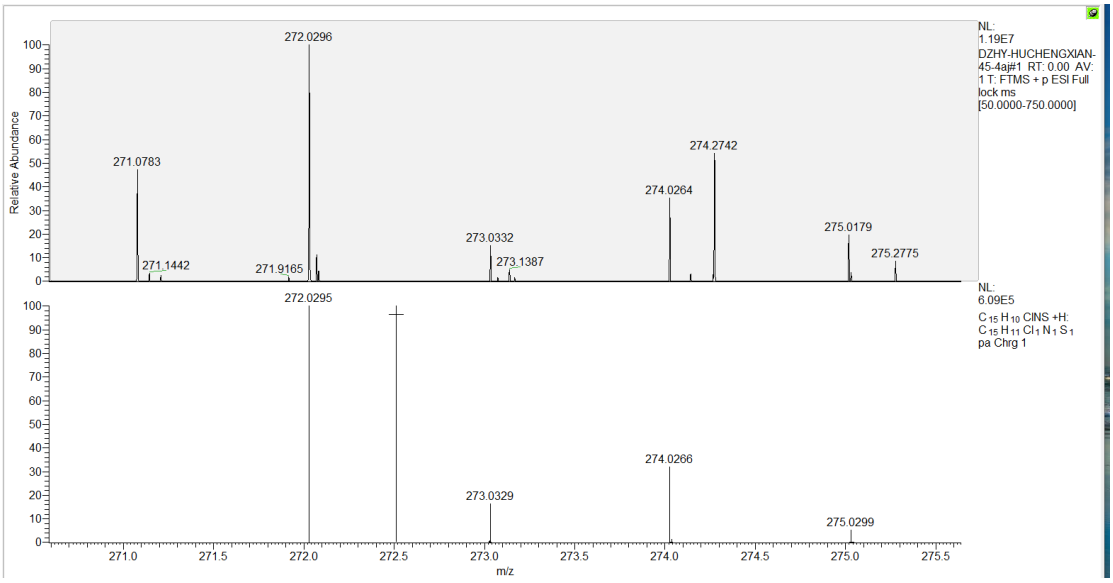
Product 4ai

HRMS (ESI) m/z calcd for $C_{16}H_{12}FNS^{+}$, $(M+H)^{+}$ 270.0747, found 270.0747.



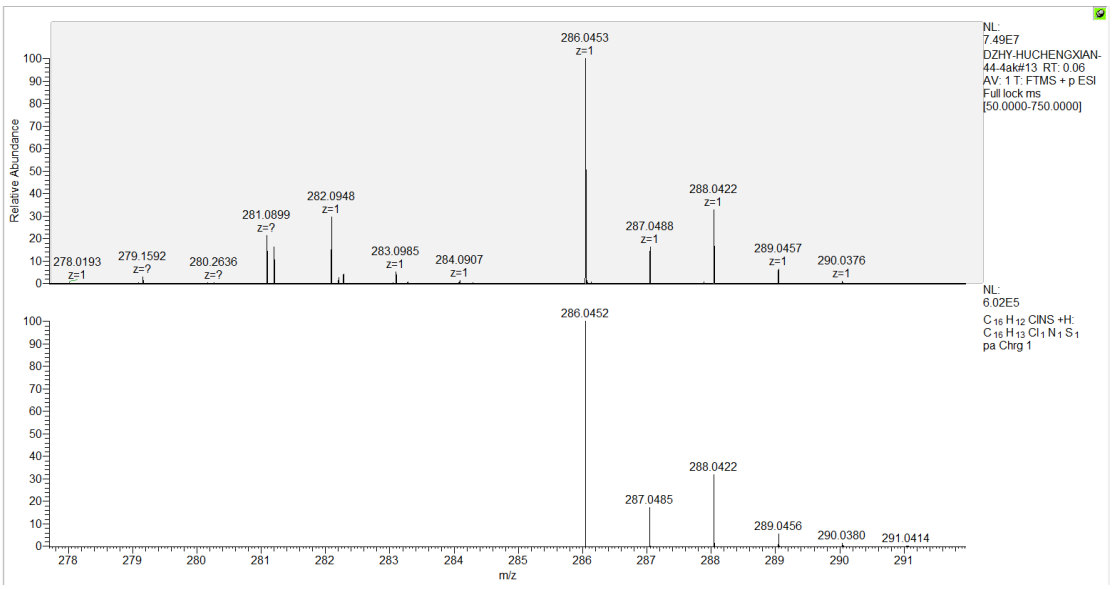
Product 4aj

HRMS (ESI) m/z calcd for $C_{15}H_{10}ClNS^+$, $(M+H)^+$ 272.0295, found 272.0296.



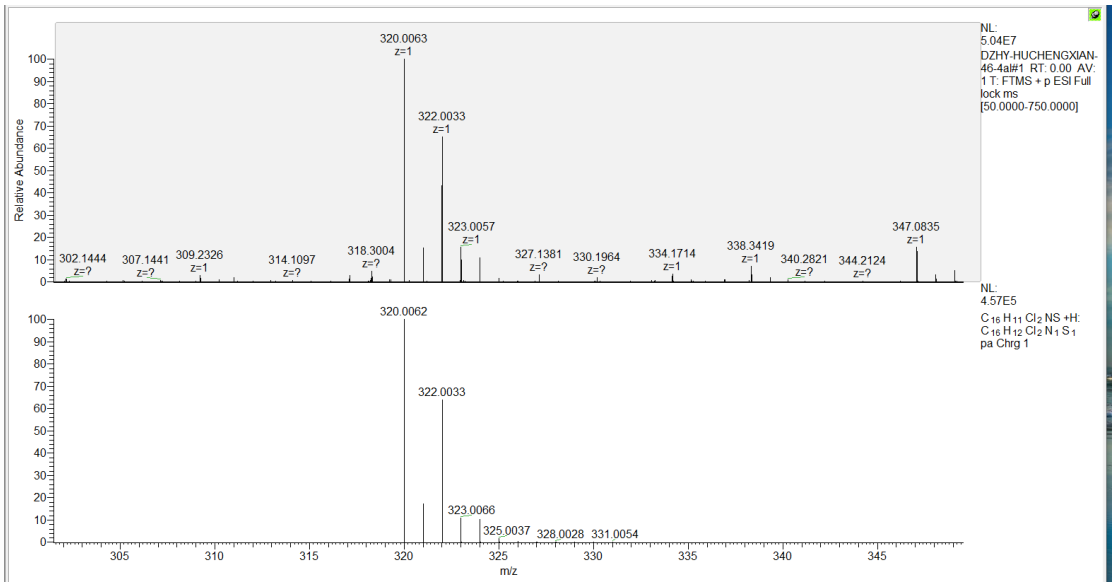
Product 4ak

HRMS (ESI) m/z calcd for $C_{16}H_{12}ClNS^+$, $(M+H)^+$ 286.0452, found 286.0453.



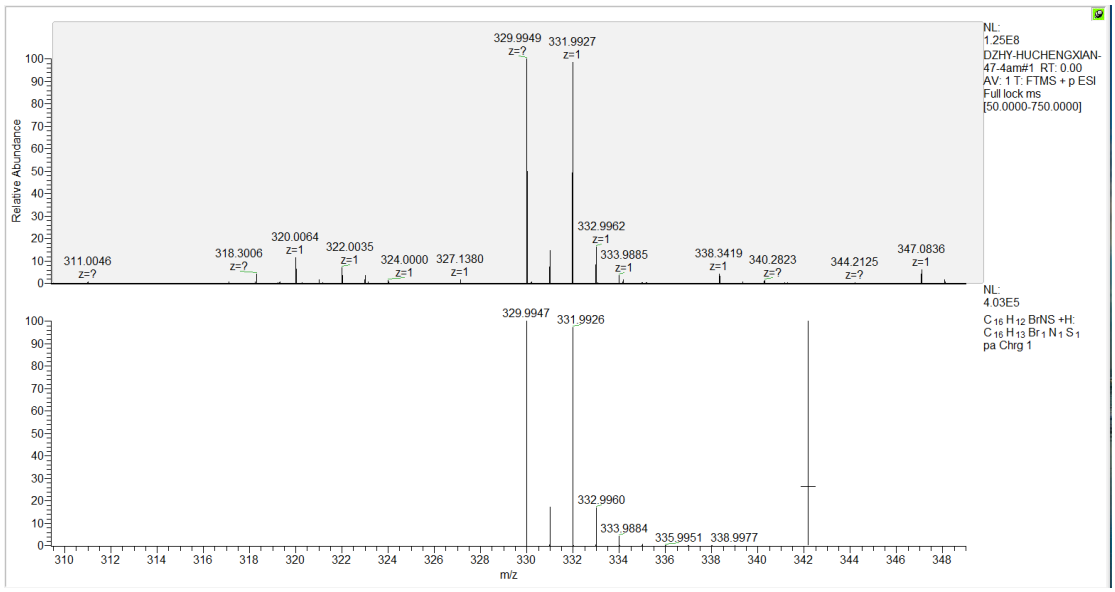
Product 4al

HRMS (ESI) m/z calcd for $C_{16}H_{11}Cl_2NS^+$, $(M+H)^+$ 320.0062, found 320.0063.



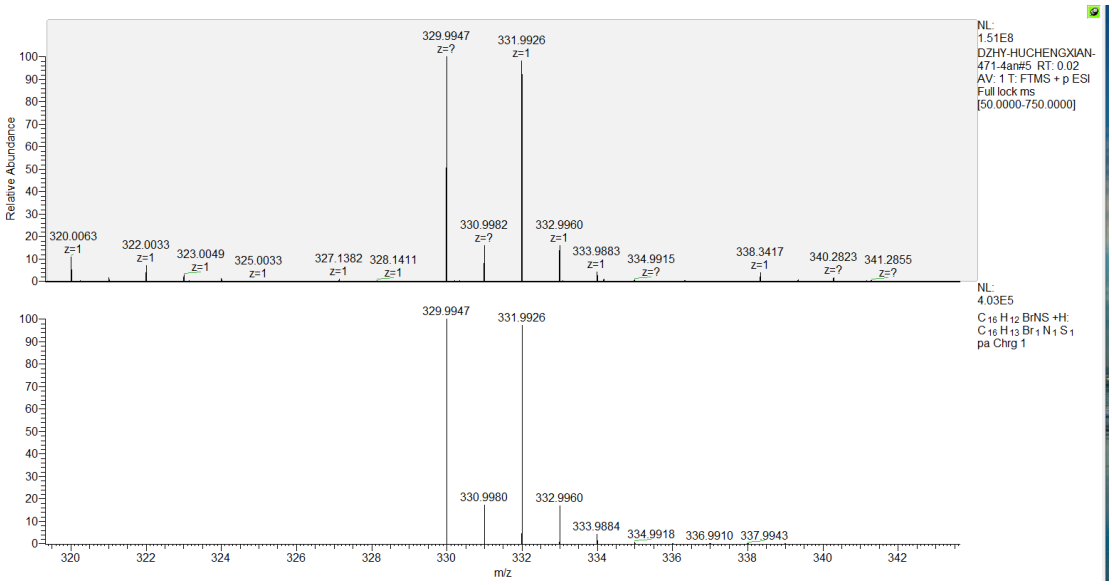
Product 4am

HRMS (ESI) m/z calcd for $C_{16}H_{12}BrNS^+$, $(M+H)^+$ 329.9947, found 329.9949.



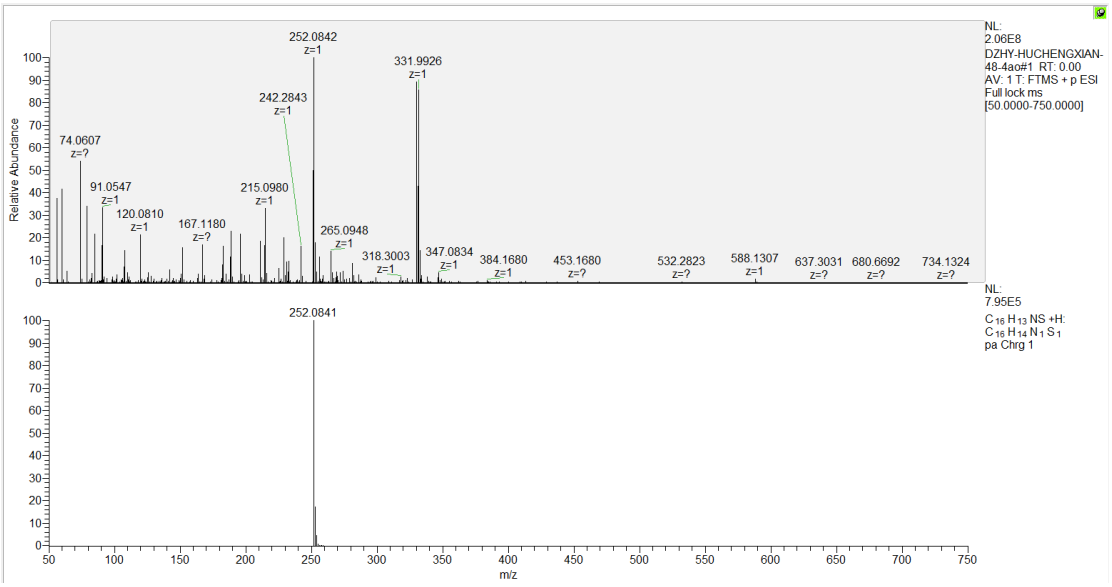
Product 4an

HRMS (ESI) m/z calcd for $C_{16}H_{12}BrNS^+$, $(M+H)^+$ 329.9947, found 329.9947.



Product 4ao

HRMS (ESI) m/z calcd for $C_{16}H_{13}NS^+$, $(M+H)^+$ 252.0841, found 252.0842.



Product 4ap

HRMS (ESI) m/z calcd for $C_{12}H_{11}NS^+$, $(M+H)^+$ 202.0685, found 202.0686.