

Supplementary Materials

Iodine-Mediated One-Pot Synthesis of Imidazo[1,5-*a*]Pyridines

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1. General Information

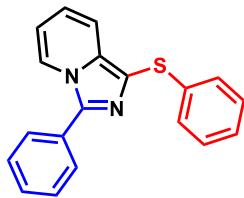
All starting materials were purchased from commercial suppliers and used without further purification unless otherwise stated. Yields refer to isolated compounds estimated to be >95 % pure as determined by ^1H NMR and capillary GC analysis. NMR spectra were recorded on a Bruker AM400 or Bruker AM600 NMR instrument in CDCl_3 using TMS as an internal standard. Chemical shifts are given in ppm and coupling constants (J) are given in Hz. All melting points were determined on a RY-1G melting point instrument without correction. High-resolution mass spectra (HRMS) were recorded on a Finnigan MAT 95Q or Finnigan 90 mass instrument (ESI). TLC was performed using aluminum plates coated with SiO_2 (Merck 60, F-254) and visualized with UV light at 254 nm. Column chromatography was performed on silica gel (150–300 mesh) with PE (petroleum ether)-EA (ethyl acetate) as eluent.

2. Typical procedure (TP) for 3-sulfinylimidazo[1,5-*a*]pyridines

A mixture of pyridin-2-ylmethanamine (**1a**, 1 mmol), benzaldehyde (**2a**, 0.5 mmol), and iodine (0.1 mmol) in DMF (3 mL) were added into the reaction tube, then TBHP (1.0 eq., based on **2a**) was added, the mixture was stirred at 100 °C for 2 hours. Then sodium benzenesulfite (**3a**, 1 mmol), iodine (0.5 mmol), PPh_3 (2.0 eq., based on **2a**) was added, the mixture was stirred at 100 °C and monitored by TLC until the starting material (**1a** or **2a**) was consumed. The reaction was then quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution (about 5 mL), extracted with ethyl acetate. The original solution was dried with anhydrous Na_2SO_4 and evaporated in vacuo. The crude product was purified by column chromatography to give **4a**.

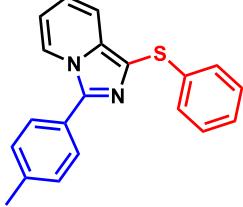
3. Analytical data for all compounds

3-phenyl-1-(phenylthio)imidazo[1,5-a]pyridine (4a)



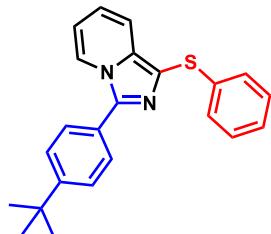
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **4a**, 104 mg (yield: 69%), a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.32 (d, J = 7.2 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.65 (d, J = 9.1 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.09 (t, J = 6.9 Hz, 1H), 6.87 (dd, J = 9.2, 6.4 Hz, 1H), 6.67 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.3, 138.4, 135.1, 129.5, 129.2, 129.0, 128.8, 128.3, 127.1, 125.5, 122.1, 121.1, 120.1, 118.5, 113.9. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{S}^+$ (303.0950), found 303.0953.

*1-(phenylthio)-3-(*p*-tolyl)imidazo[1,5-a]pyridine (4b)*



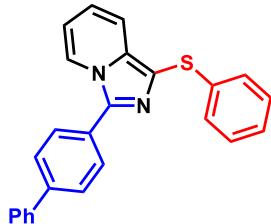
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4b**. 72 mg (yield: 46%), a white solid. M.P.: 142–146 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.29 (d, J = 7.2 Hz, 1H), 7.74 – 7.72 (m, 2H), 7.64 (d, J = 9.2 Hz, 1H), 7.35 – 7.33 (m, 2H), 7.23 – 7.16 (m, 4H), 7.08 (t, J = 7.0 Hz, 1H), 6.85 (dd, J = 9.2, 6.4 Hz, 1H), 6.65 (t, J = 6.8 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 139.5, 139.3, 138.4, 135.0, 129.7, 128.8, 128.2, 127.1, 126.6, 125.5, 122.2, 121.0, 119.7, 118.5, 113.8, 21.5. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{S}^+$ (317.1107), found 317.1104.

3-(4-(tert-butyl)phenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4c)



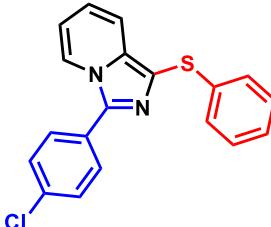
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4c**. 82 mg (yield: 46%), a green solid. M.P.: 140-148 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.31 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.77 (m, 2H), 7.62 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.54 (m, 2H), 7.23 – 7.16 (m, 4H), 7.07 (t, *J* = 7.1 Hz, 1H), 6.82 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.62 (t, *J* = 6.8 Hz, 1H), 1.38 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 152.4, 139.5, 138.5, 135.0, 128.8, 128.0, 127.0, 126.7, 126.0, 125.5, 122.2, 121.0, 119.8, 118.4, 113.7, 34.9, 31.3. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₂₃H₂₃N₂S⁺ (359.1576), found 359.1572.

3-(1,1'-biphenyl-4-yl)-1-(phenylthio)imidazo[1,5-a]pyridine (4d)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4d**. 84 mg (yield: 44%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.39 (d, *J* = 7.3 Hz, 1H), 7.96 (s, 1H), 7.94 (s, 1H), 7.80 (s, 1H), 7.77 (s, 1H), 7.70-7.67 (m, 3H), 7.52-7.48 (m, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.28-7.20 (m, 4H), 7.12 (t, *J* = 7.1 Hz, 1H), 6.90 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.71 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 141.8, 140.3, 139.0, 138.4, 135.2, 129.0, 128.9, 128.6, 128.4, 127.8, 127.7, 127.1, 127.1, 125.6, 122.2, 121.2, 120.3, 118.5, 114.0. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₂₅H₁₉N₂S⁺ (379.1263), found 379.1260.

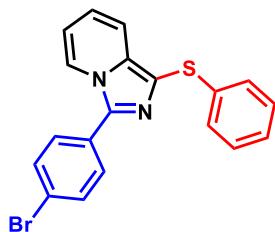
3-(4-chlorophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4e)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4e**. 121 mg (yield: 72%), a yellow solid. M.P.: 104-1110 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.25 (d, *J* = 7.2 Hz, 1H), 7.79 (s, 1H), 7.77 (s, 1H), 7.65 (d, *J* = 9.1 Hz, 1H), 7.50 (s, 1H), 7.48 (s,

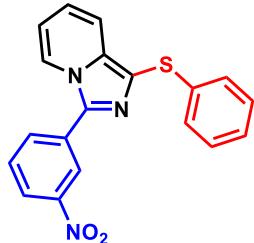
1H), 7.22 - 7.17 (m, 4H), 7.09 (t, J = 6.7 Hz, 1H), 6.88 (dd, J = 9.2, 6.5 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 138.1, 135.3, 135.0, 129.4, 129.3, 128.9, 128.0, 127.2, 125.6, 122.4, 121.9, 121.3, 120.5, 118.6, 114.3. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{19}\text{H}_{14}\text{ClN}_2\text{S}^+$ (337.0561), found 337.0565.

3-(4-bromophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4f)



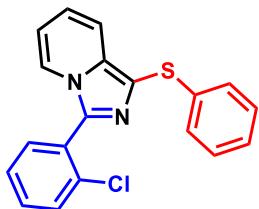
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4f**. 95 mg (yield: 50%), a yellow solid. M.P.: 118-126 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.25 (d, J = 7.2 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.65 – 7.73 (m, 3H), 7.22 – 7.16 (m, 4H), 7.09 (t, J = 6.7 Hz, 1H), 6.88 (dd, J = 9.0, 6.6 Hz, 1H), 6.69 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 138.1, 135.3, 132.3, 129.6, 128.9, 128.5, 127.2, 125.6, 123.2, 121.9, 121.3, 120.6, 118.6, 114.3. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{19}\text{H}_{13}\text{BrN}_2\text{S}^+$ (381.0056), found 381.0053.

3-(3-nitrophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4g)



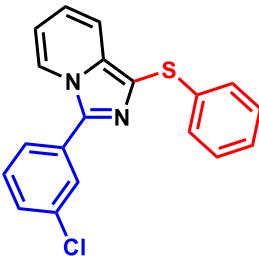
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4g**. 105 mg (yield: 61%), a yellow solid. M.P.: 116-120 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.70 (s, 1H), 8.34 (d, J = 7.5 Hz, 1H), 8.27 – 8.21 (m, 2H), 7.72 – 7.68 (m, 2H), 7.22 – 7.16 (m, 4H), 7.09 (t, J = 6.6 Hz, 1H), 6.95 (dd, J = 8.9, 6.7 Hz, 1H), 6.79 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 148.6, 137.8, 136.6, 135.7, 134.0, 131.3, 130.3, 128.9, 127.3, 125.8, 123.5, 122.3, 121.9, 121.6, 121.5, 118.7, 115.1. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{19}\text{H}_{14}\text{N}_3\text{O}_2\text{S}^+$ (348.0801), found 348.0805.

3-(2-chlorophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4h)



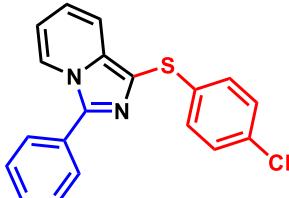
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4h**. 67 mg (yield: 40%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.69 – 7.65 (m, 3H), 7.55 (d, *J* = 7.7 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.20 – 7.19 (m, 4H), 7.11 – 7.06 (m, 1H), 6.92 (dd, *J* = 9.9, 6.6 Hz, 1H), 6.69 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.5, 136.9, 134.7, 134.3, 133.4, 131.1, 130.0, 128.8, 128.8, 127.3, 127.0, 125.5, 122.9, 121.3, 119.6, 118.1, 113.5. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₄ClN₂S⁺ (337.0561), found 337.0564.

3-(3-chlorophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine (4i)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4i**. 69 mg (yield: 41%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.32 (d, *J* = 7.2 Hz, 1H), 7.86 (s, 1H), 7.74 (d, *J* = 7.3 Hz, 1H), 7.68 (d, *J* = 9.2 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.24 – 7.17 (m, 4H), 7.12 – 7.08 (m, 1H), 6.91 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.74 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 137.9, 137.7, 135.3, 135.1, 131.0, 130.3, 129.3, 128.9, 128.2, 127.4, 126.2, 125.7, 121.9, 121.5, 118.7, 114.5. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₄ClN₂S⁺ (337.0561), found 337.0565.

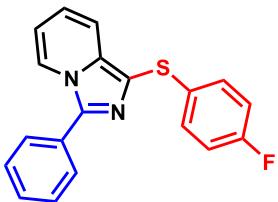
1-((4-chlorophenyl)thio)-3-phenylimidazo[1,5-a]pyridine (4j)



According to TP, the residue was purified by flash chromatography on silica gel

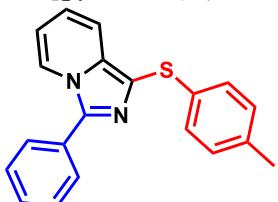
(petroleum ether/ethyl acetate = 20:1) to give the target compound **4j**. 101 mg (yield: 60%), a white solid. M.P.: 104-110 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.32 (d, *J* = 7.3 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.47 (t, *J* = 7.3 Hz, 1H), 7.15 (s, 4H), 6.90 (dd, *J* = 9.1, 6.4 Hz, 1H), 6.69 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.4, 136.9, 135.0, 131.5, 129.3, 129.1, 128.9, 128.5, 128.3, 122.2, 121.5, 119.5, 118.3, 114.1. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₄ClN₂S⁺ (337.0561), found 337.0563.

1-((4-fluorophenyl)thio)-3-phenylimidazo[1,5-*a*]pyridine (4k)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4k**. 104 mg (yield: 65%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.32 (d, *J* = 7.2 Hz, 1H), 7.85 – 7.83 (m, 2H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.56 – 7.52 (m, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.25 (m, 2H), 6.94 – 6.87 (m, 3H), 6.68 (t, *J* = 6.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 161.4 [d, *J*(C-F) = 244.0 Hz], 139.3, 134.9, 133.2, 129.5, 129.5 [d, *J*(C-F) = 8.0 Hz], 129.2, 129.1, 128.3, 122.1, 121.3, 120.5, 118.3, 115.9 [d, *J*(C-F) = 21.0 Hz], 113.9. ¹⁹F NMR (377 MHz, CDCl₃) δ -117.0. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₄FN₂S⁺ (321.0856), found 321.0853.

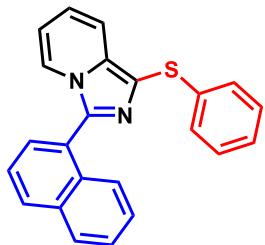
3-phenyl-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4l)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4l**. 82 mg (yield: 52%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.29 (d, *J* = 7.2 Hz, 1H), 7.84 – 7.82 (m, 2H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.54 – 7.50 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.18 – 7.16 (m, 2H), 7.02 – 7.00 (m, 2H), 6.84 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.64 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 139.1, 136.5, 135.5, 134.8, 134.6, 129.6, 129.6, 129.1, 129.0, 128.3, 127.8, 122.0, 121.0, 118.5, 113.9, 21.0. HRMS (ESI)

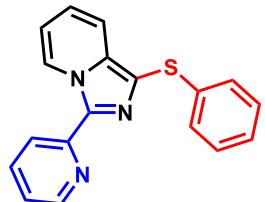
m/z [(M + H)⁺] Calcd for C₂₀H₁₇N₂S⁺ (317.1107), found 317.1104.

3-(naphthalen-1-yl)-1-(phenylthio)imidazo[1,5-a]pyridine (4m)



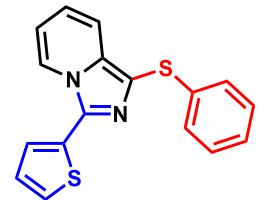
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4m**. 109 mg (yield: 62%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.01 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.1 Hz, 1H), 7.74 – 7.70 (m, 3H), 7.63 – 7.59 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.24 – 7.20 (m, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 6.89 (dd, *J* = 9.6, 6.4 Hz, 1H), 6.58 – 6.54 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.6, 138.1, 134.7, 134.0, 131.8, 130.3, 129.0, 128.9, 128.7, 127.2, 126.6, 126.5, 125.5, 125.4, 125.3, 122.5, 121.3, 119.8, 118.3, 113.5. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₂₃H₁₇N₂S⁺ (353.1107), found 353.1104.

1-(phenylthio)-3-(pyridin-2-yl)imidazo[1,5-a]pyridine (4n)



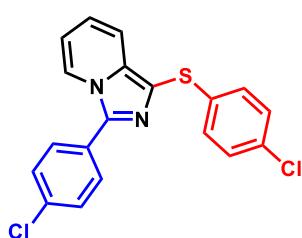
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4n**. 110 mg (yield: 73%), a white solid. M.P.: 100–110 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 10.00 (d, *J* = 7.3 Hz, 1H), 8.61 (d, *J* = 4.0 Hz, 1H), 8.43 (d, *J* = 8.1 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 9.1 Hz, 1H), 7.20 – 7.15 (m, 5H), 7.09 – 7.0 (m, 1H), 6.93 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.76 (t, *J* = 6.9 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 150.6, 148.1, 138.3, 136.6, 136.4, 136.3, 128.9, 126.9, 126.8, 125.5, 122.4, 122.2, 120.3, 117.6, 114.2. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₈H₁₄N₃S⁺ (304.0903), found 304.0906.

1-(phenylthio)-3-(thiophen-2-yl)imidazo[1,5-a]pyridine (4o)



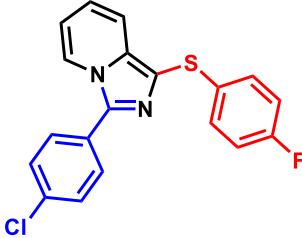
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4o**. 49 mg (yield: 32%), a yellow solid. M.P.: 112–116 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.40 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 9.1 Hz, 1H), 7.60 (d, J = 3.7 Hz, 1H), 7.45 (d, J = 5.1 Hz, 1H), 7.21 – 7.16 (m, 5H), 7.10 – 7.07 (m, 1H), 6.89 (dd, J = 9.1, 6.4 Hz, 1H), 6.76 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 138.2, 135.1, 134.0, 131.5, 128.8, 127.7, 127.1, 126.6, 125.8, 125.6, 122.4, 121.1, 120.5, 118.5, 114.4. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{17}\text{H}_{13}\text{N}_2\text{S}_2^+$ (309.0515), found 309.0518.

3-(4-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine (4p)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **4p**. 138 mg (yield: 74%), a yellow solid. M.P.: 140–148 °C. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.26 (d, J = 7.3 Hz, 1H), 7.78 – 7.76 (m, 2H), 7.64 (d, J = 9.2 Hz, 1H), 7.51 – 7.49 (m, 2H), 7.14 (s, 4H), 6.91 (dd, J = 9.2, 6.5 Hz, 1H), 6.71 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 138.3, 136.7, 135.3, 135.2, 131.5, 129.4, 129.4, 128.9, 128.5, 127.9, 121.9, 121.6, 112.0, 118.4, 114.3. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{19}\text{H}_{13}\text{Cl}_2\text{N}_2\text{S}^+$ (371.0171), found 371.0175.

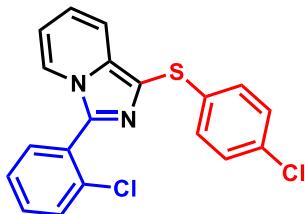
3-(4-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-a]pyridine (4q)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4q**. 122 mg (yield: 69%), a white oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.27 (d, J = 7.2 Hz, 1H), 7.81 (s, 1H), 7.79 (s, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.54 (s, 1H), 7.52 (s, 1H), 7.29 – 7.25 (m, 2H), 6.95 – 6.91 (m, 3H), 6.73 (t, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 161.5

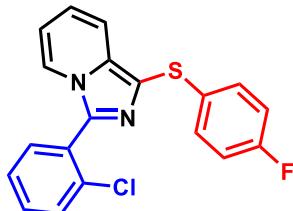
[d, $J(C-F) = 244.0$ Hz], 138.1, 135.2, 135.0, 132.9, 129.7 [d, $J(C-F) = 7.0$ Hz], 129.5, 129.4, 127.8, 121.9, 121.5, 120.9, 118.5, 115.9 [d, $J(C-F) = 22.0$ Hz], 114.3. ^{19}F NMR (377 MHz, CDCl₃) δ -116.7. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃ClFN₂S⁺ (355.0467), found 355.0465.

3-(2-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine (4r)



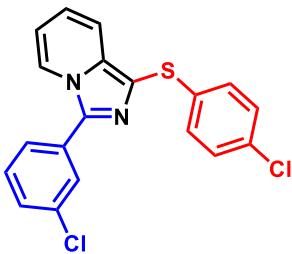
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the target compound **4r**. 145 mg (yield: 78%), a yellow solid. M.P.: 150-152 °C. 1H NMR (400 MHz, CDCl₃) δ (ppm): 7.69 – 7.64 (m, 3H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.49 – 7.40 (m, 2H), 7.15 – 7.12 (m, 4H), 6.94 (dd, $J = 9.1$, 6.5 Hz, 1H), 6.70 (t, $J = 6.7$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ (ppm): 137.1, 134.7, 134.3, 133.3, 131.4, 131.3, 130.0, 128.9, 128.6, 128.3, 127.3, 123.0, 121.7, 119.1, 117.9, 113.6. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃Cl₂N₂S⁺ (371.0171), found 371.0174.

3-(2-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-a]pyridine (4s)



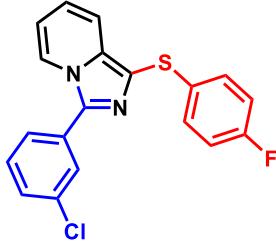
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4s**. 130 mg (yield: 73%), a white solid. M.P.: 80-92°C. 1H NMR (400 MHz, CDCl₃) δ (ppm): 7.68 – 7.62 (m, 3H), 7.54 (s, 1H), 7.53 (s, 1H), 7.47 – 7.39 (m, 2H), 7.24 – 7.21 (m, 2H), 6.94 – 6.87 (m, 3H), 6.69 – 6.66 (m, 1H). ^{13}C NMR (100 MHz, CDCl₃) δ (ppm): 161.4 [d, $J(C-F) = 244.0$ Hz], 136.9, 134.5, 134.3, 133.3, 131.2, 130.0, 129.3 [d, $J(C-F) = 8.0$ Hz], 128.7, 127.3, 122.9, 121.5, 120.0, 118.0, 115.9 [d, $J(C-F) = 22.0$ Hz], 113.5. ^{19}F NMR (377 MHz, CDCl₃) δ -117.1. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃ClFN₂S⁺ (355.0467), found 355.0464.

3-(3-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine(4t)



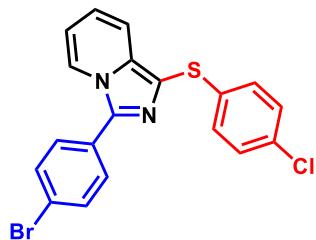
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4t**. 150 mg (yield: 81%), a yellow solid. M.P.: 98-102 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.30 (d, *J* = 7.2 Hz, 1H), 7.84 (s, 1H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 9.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.17 – 7.12 (m, 4H), 6.92 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.73 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 137.9, 136.7, 135.4, 135.1, 131.6, 131.1, 130.4, 129.3, 128.9, 128.5, 128.2, 126.1, 122.0, 121.8, 120.2, 118.4, 114.5. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃Cl₂N₂S⁺ (371.0171), found 371.0175.

3-(3-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-a]pyridine (4u)



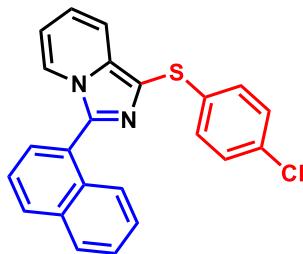
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4u**. 126 mg (yield: 71%), a yellow solid. M.P.: 98-100°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.30 (d, *J* = 7.3 Hz, 1H), 7.85 (s, 1H), 7.74 – 7.67 (m, 2H), 7.49 – 7.42 (m, 2H), 7.27 – 7.24 (m, 2H), 6.95 – 6.89 (m, 3H), 6.74 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.5 [d, *J*(C-F) = 243.0 Hz], 137.7, 135.1, 132.9, 131.1, 130.3, 129.7 [d, *J*(C-F) = 8.0 Hz], 129.3, 128.2, 126.1, 121.9, 121.6, 121.1, 118.5, 115.9 [d, *J*(C-F) = 23.0 Hz], 114.4. ¹⁹F NMR (377 MHz, CDCl₃) δ -116.7. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃ClFN₂S⁺ (355.0467), found 355.0463.

3-(4-bromophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine (4v)



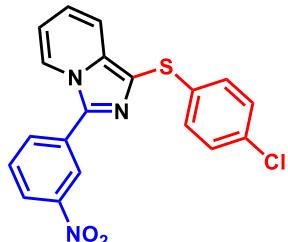
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4v**. 133 mg (yield: 64%), a white solid. M.P.:150-156°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.26 (d, J = 7.2 Hz, 1H), 7.72 (s, 1H), 7.70 (s, 1H), 7.66 – 7.62 (m, 3H), 7.14 (s, 4H), 6.91 (dd, J = 9.2, 6.5 Hz, 1H), 6.71 (t, J = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.3, 136.7, 135.3, 132.3, 131.5, 129.6, 128.9, 128.5, 128.3, 123.4, 121.9, 121.6, 120.0, 118.4, 114.4. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃BrClN₂S⁺ (414.9666), found 414.9669.

1-((4-chlorophenyl)thio)-3-(naphthalen-1-yl)imidazo[1,5-a]pyridine (4w)



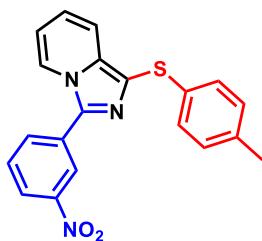
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4w**. 140 mg (yield: 72%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.02 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.1 Hz, 1H), 7.73 – 7.67 (m, 3H), 7.64 – 7.60 (m, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.24 – 7.17 (m, 4H), 6.92 (dd, J = 9.2, 6.4 Hz, 1H), 6.59 (t, J = 6.7 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 138.3, 137.0, 134.7, 134.0, 131.7, 131.5, 130.4, 129.0, 128.9, 128.7, 128.6, 127.3, 126.5, 126.3, 125.3, 125.3, 122.6, 121.6, 119.3, 118.1, 113.6. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₂₃H₁₆ClN₂S⁺ (387.0717), found 387.0720.

1-((4-chlorophenyl)thio)-3-(3-nitrophenyl)imidazo[1,5-a]pyridine (4x)



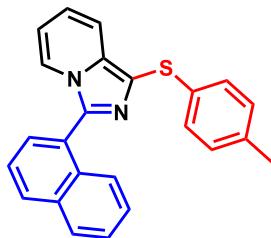
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4x**. 144 mg (yield: 75%), a yellow solid. M.P.:140-144°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.68 (s, 1H), 8.34 (d, *J* = 7.2 Hz, 1H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.65 (m, 2H), 7.13 (s, 4H), 6.97 (dd, *J* = 9.2, 6.5 Hz, 1H), 6.81 (t, *J* = 6.8 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.6, 136.7, 136.4, 135.7, 134.0, 131.7, 131.2, 130.3, 129.0, 128.6, 123.6, 122.4, 122.2, 121.7, 120.9, 118.5, 115.1. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₁₉H₁₃ClN₃O₂S⁺ (382.0412), found 382.0416.

3-(3-nitrophenyl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4y)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4y**. 120 mg (yield: 67%), a yellow solid. M.P.:140-144°C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.70 (s, 1H), 8.33 (d, *J* = 7.2 Hz, 1H), 8.28 – 7.26 (m, 2H), 7.71 – 7.68 (m, 2H), 7.18 (s, 1H), 7.16 (s, 1H), 7.02 – 7.01 (m, 2H), 6.94 (dd, *J* = 9.2, 6.4 Hz, 1H), 6.78 (t, *J* = 6.8 Hz, 1H), 2.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.6, 136.3, 135.9, 135.4, 134.0, 133.9, 131.3, 130.2, 129.7, 128.1, 123.4, 122.5, 122.3, 121.7, 121.5, 118.8, 115.0, 21.0. HRMS (ESI) m/z [(M + H)⁺] Calcd for C₂₀H₁₆N₃O₂S⁺ (362.0958), found 362.0955.

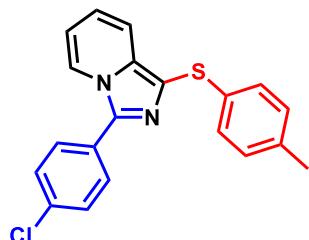
3-(naphthalen-1-yl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4z)



According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4z**. 78 mg (yield: 43%), a yellow oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.03 (d, *J* = 8.2 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.1 Hz, 1H), 7.75 – 7.71 (m, 3H), 7.65 – 7.61 (m, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.26 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H),

6.90 (dd, $J = 9.1, 6.3$ Hz, 1H), 6.59 – 6.56 (m, 1H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 137.8, 135.6, 134.7, 134.4, 134.0, 131.7, 130.3, 129.6, 129.0, 128.7, 128.0, 127.2, 126.5, 126.4, 125.4, 125.3, 122.5, 121.1, 120.7, 118.4, 113.5, 21.0. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{24}\text{H}_{19}\text{N}_2\text{S}^+$ (367.1263), found 367.1266.

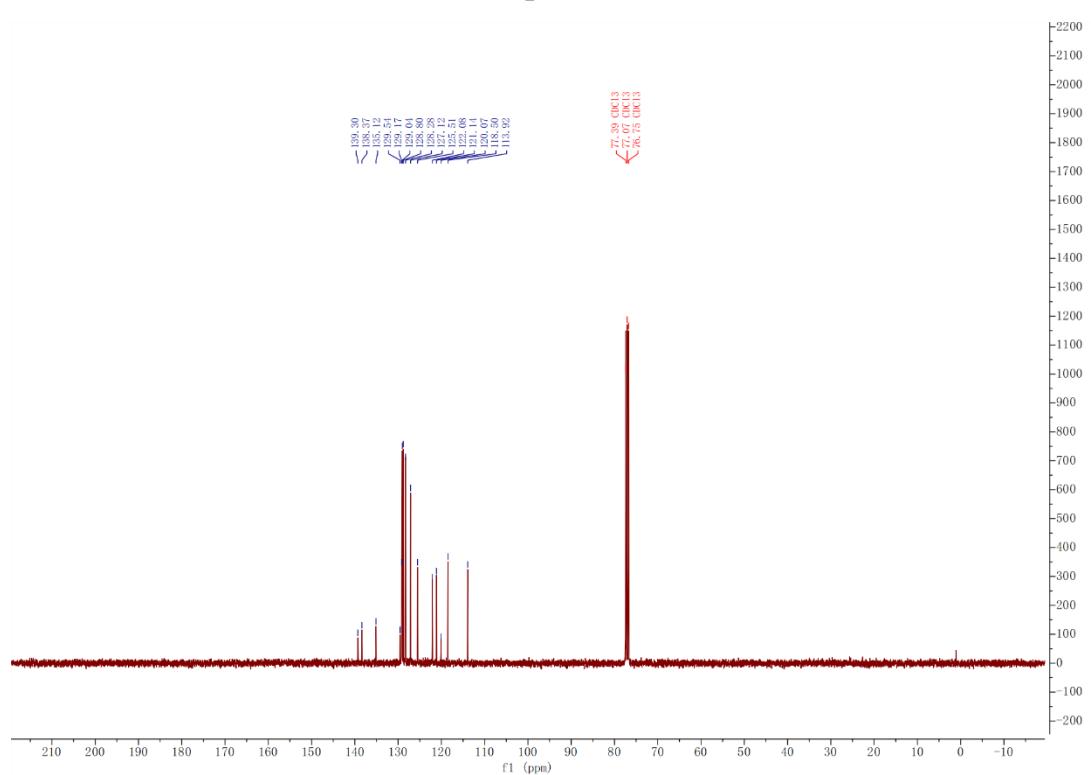
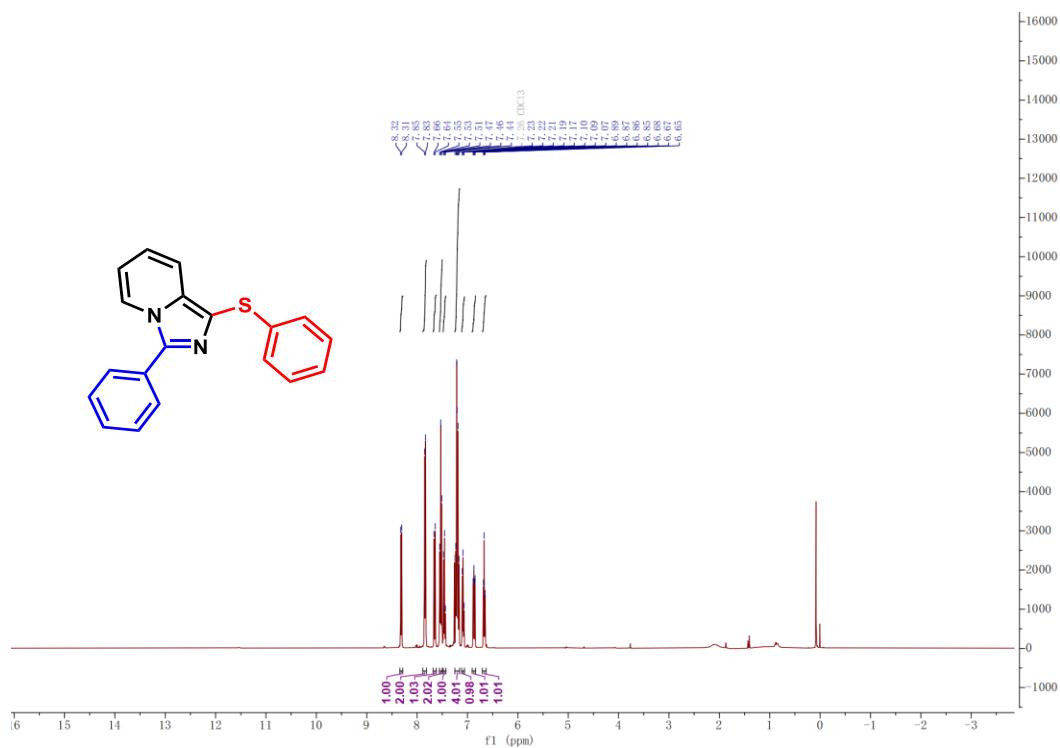
3-(4-chlorophenyl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4za)



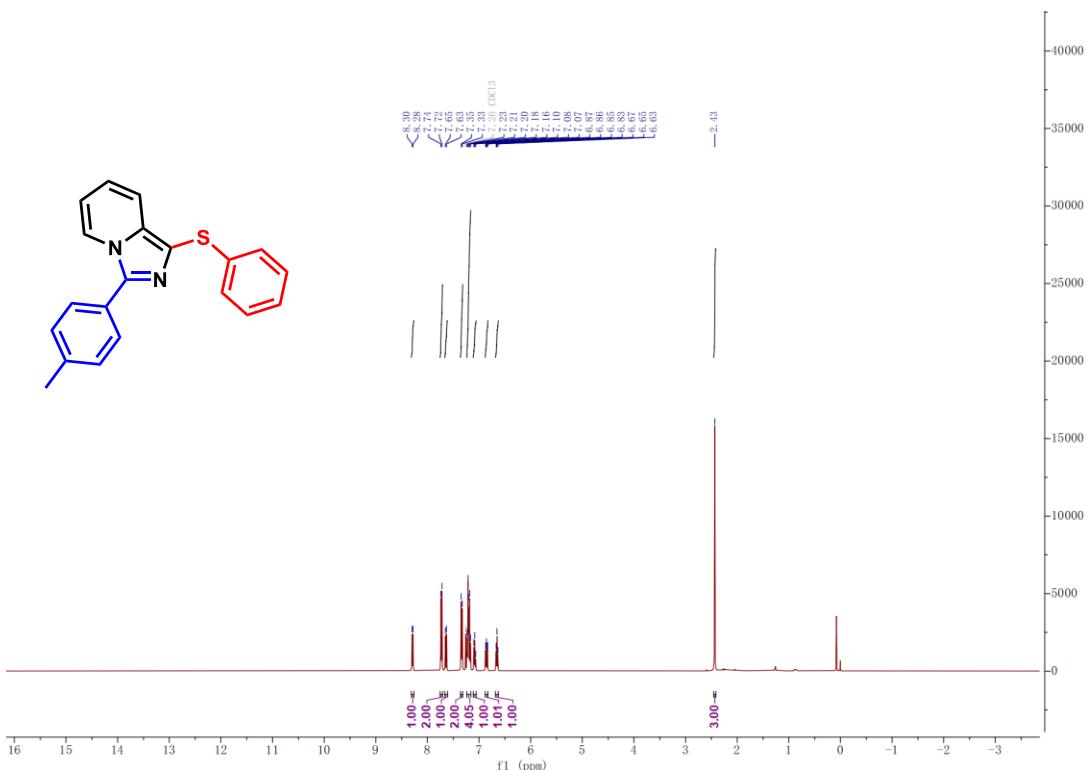
According to TP, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the target compound **4za**. 120 mg (yield: 68%), a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.22 (d, $J = 7.3$ Hz, 1H), 7.77 (m, 1H), 7.75 (m, 1H), 7.64 (d, $J = 9.1$ Hz, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 7.01 (s, 1H), 6.99 (s, 1H), 6.85 (dd, $J = 9.2, 6.4$ Hz, 1H), 6.66 (t, $J = 6.8$ Hz, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 137.9, 135.7, 135.0, 134.9, 134.4, 129.6, 129.4, 129.3, 128.1, 127.8, 121.8, 121.4, 121.1, 118.6, 114.2, 21.0. HRMS (ESI) m/z [(M + H) $^+$] Calcd for $\text{C}_{20}\text{H}_{16}\text{ClN}_2\text{S}^+$ (351.0717), found 351.0714.

4. ^1H NMR and ^{13}C NMR spectra of all products

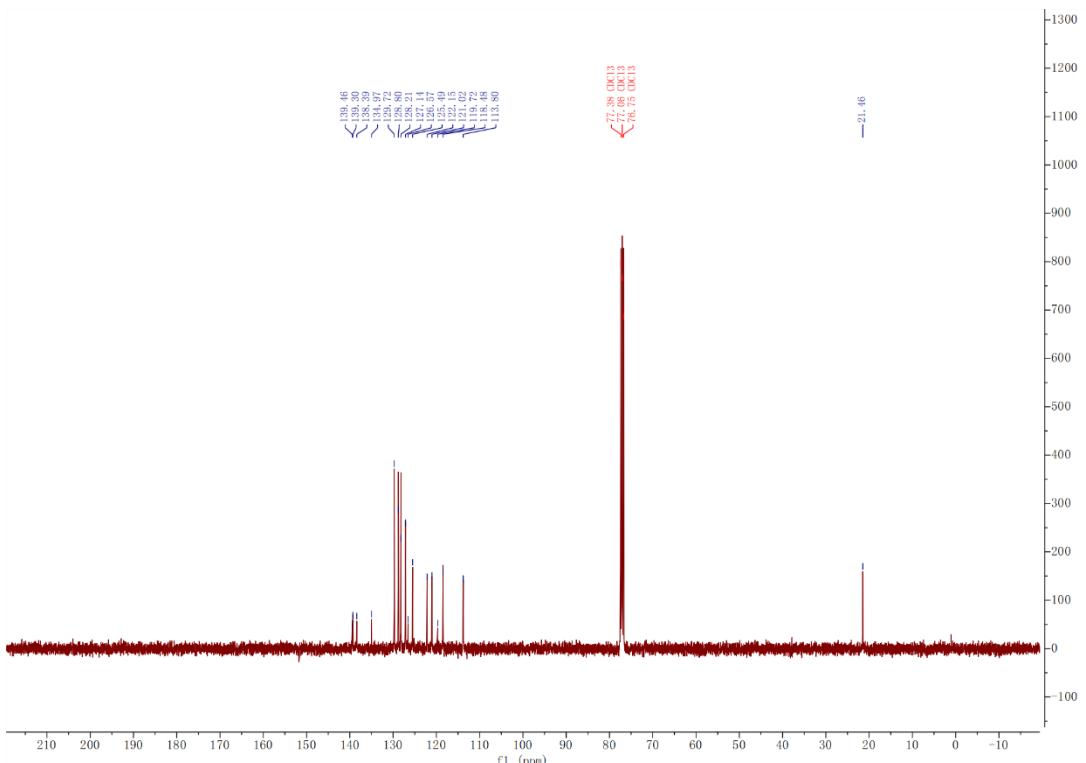
*3-phenyl-1-(phenylthio)imidazo[1,5-*a*]pyridine (4a)*



1-(phenylthio)-3-(*p*-tolyl)imidazo[1,5-*a*]pyridine (4b)

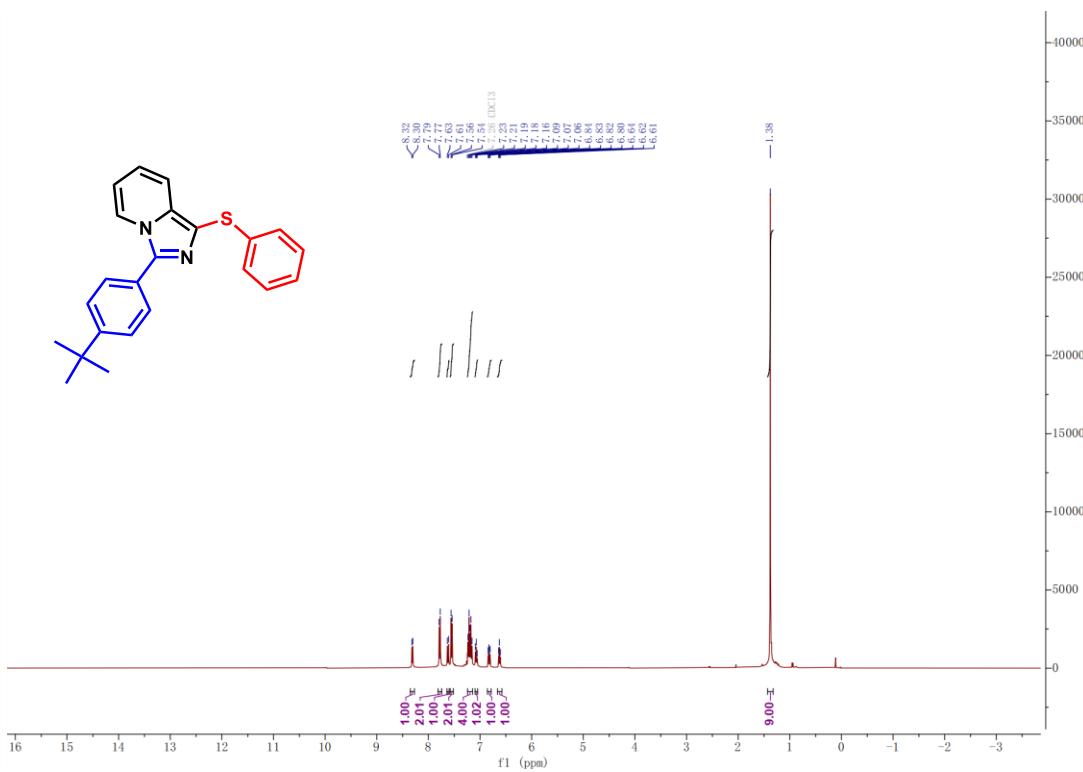


¹H NMR spectrum of 4b

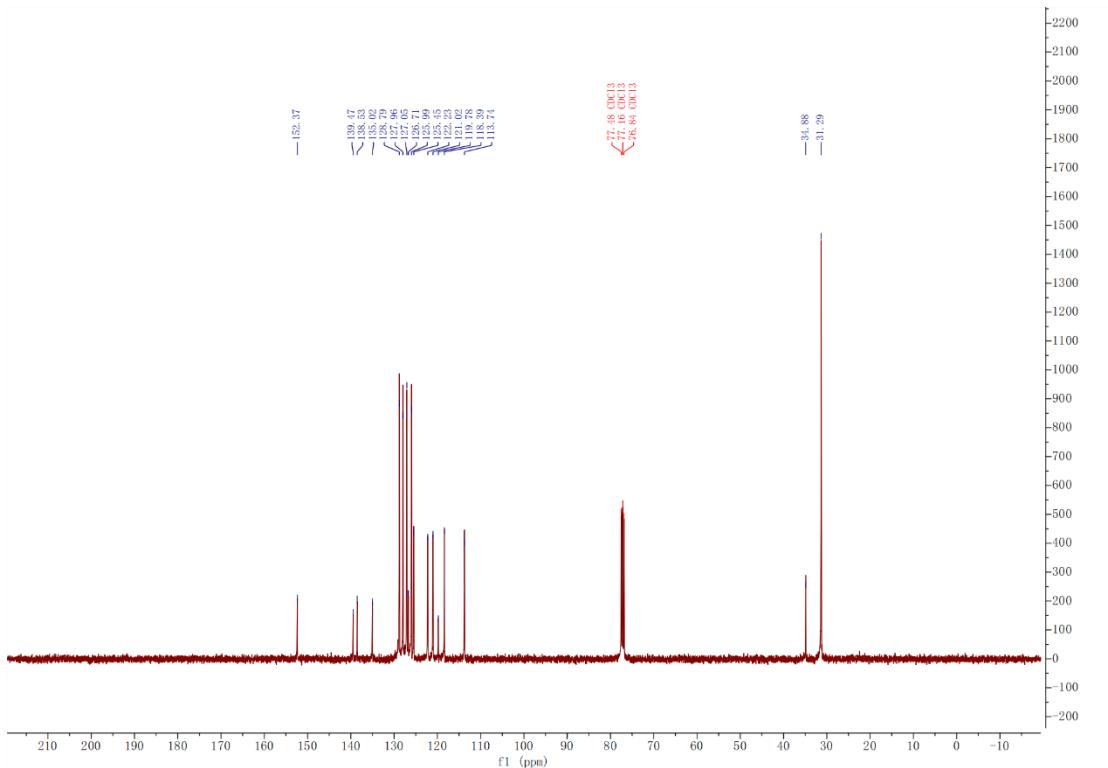


¹³C NMR spectrum of 4b

3-(4-(*tert*-butyl)phenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine(4c)

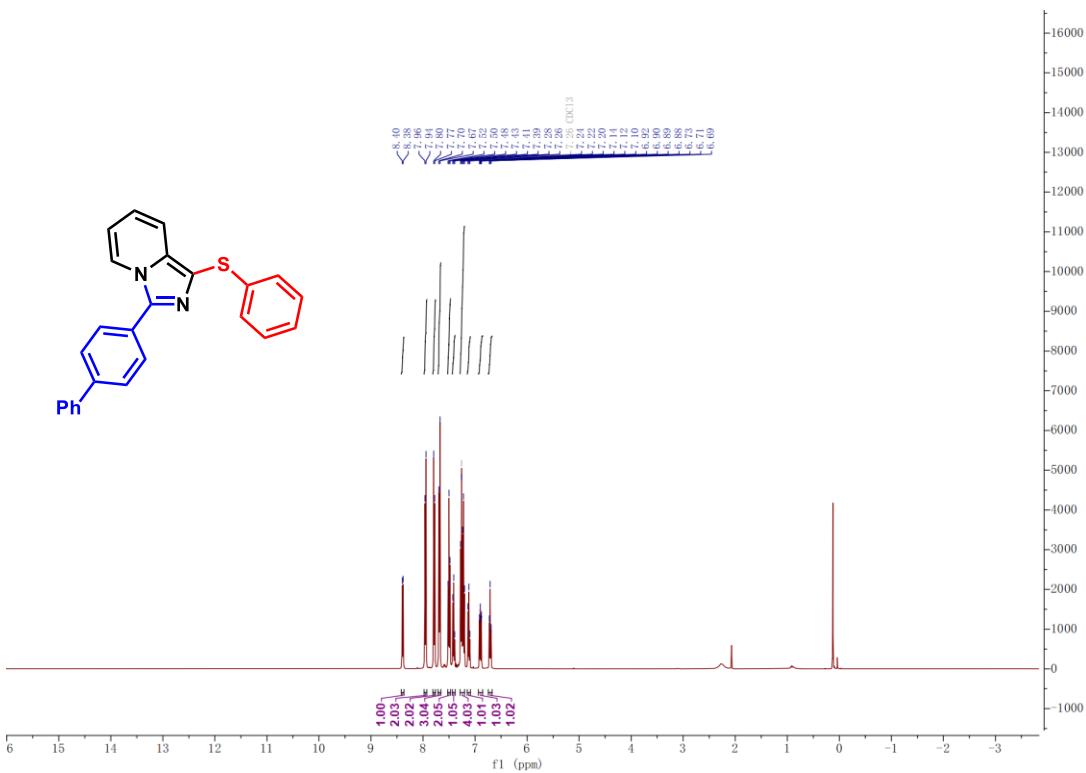


¹H NMR spectrum of 4c

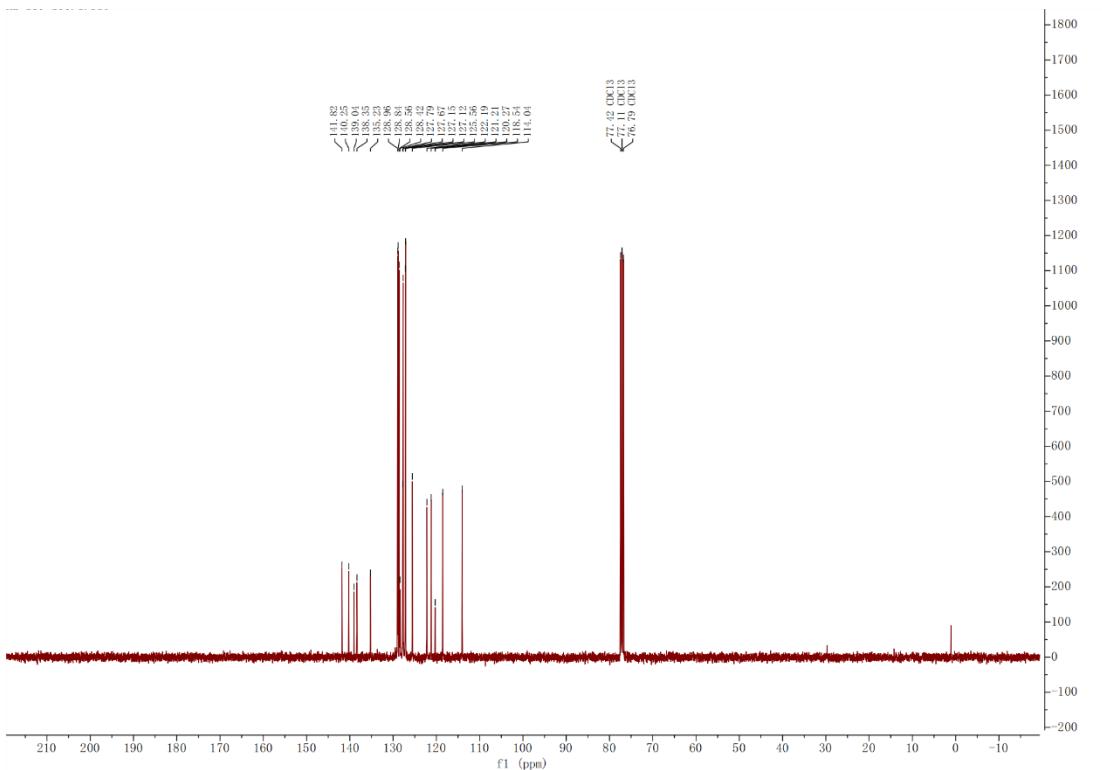


¹³C NMR spectrum of 4c

3-([1,1'-biphenyl]-4-yl)-1-(phenylthio)imidazo[1,5-a]pyridine(4d)

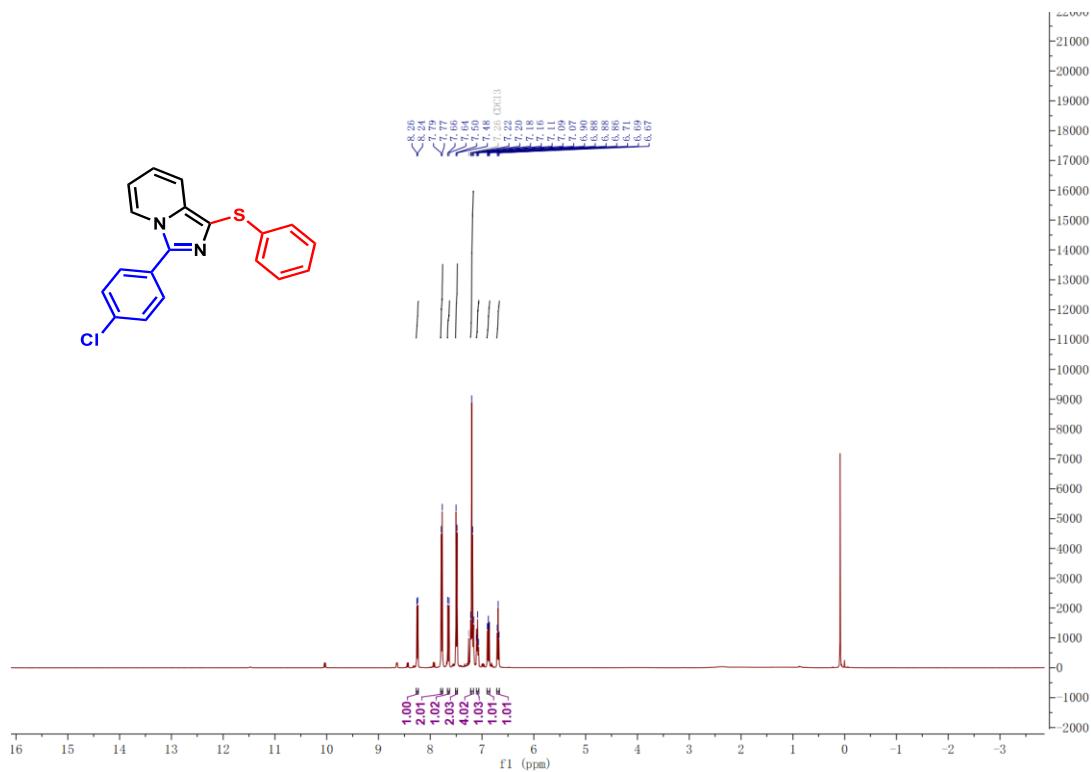


¹H NMR spectrum of 4d

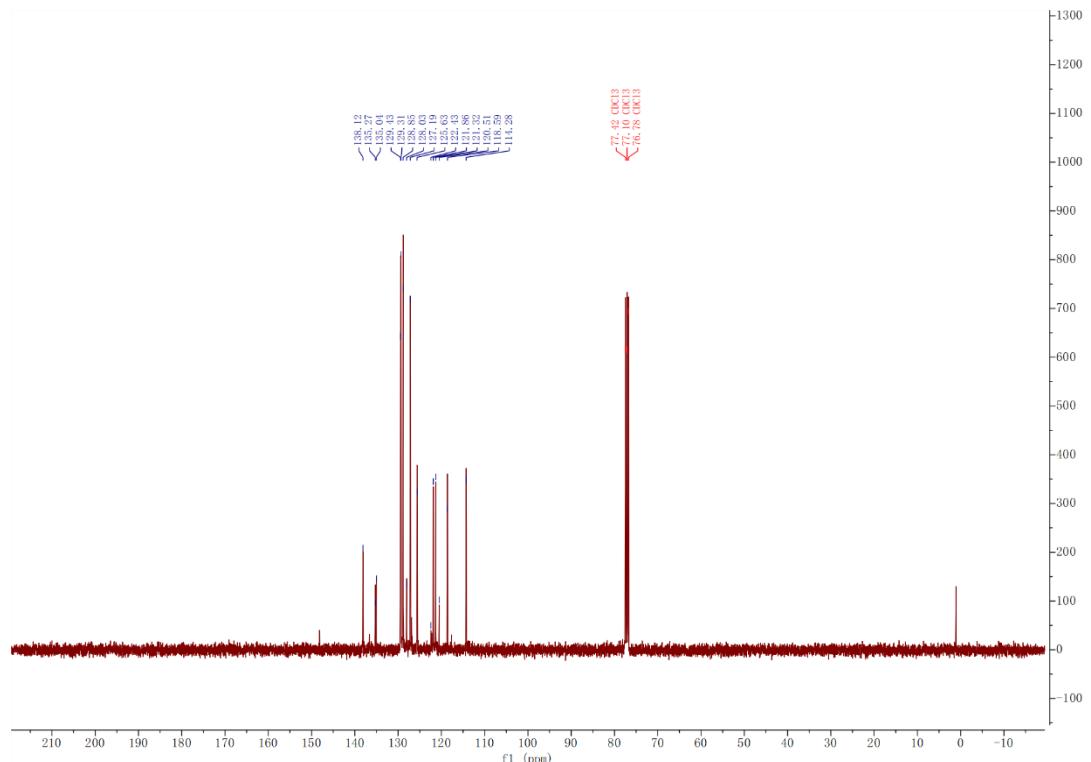


¹³C NMR spectrum of 4d

3-(4-chlorophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine(4e)

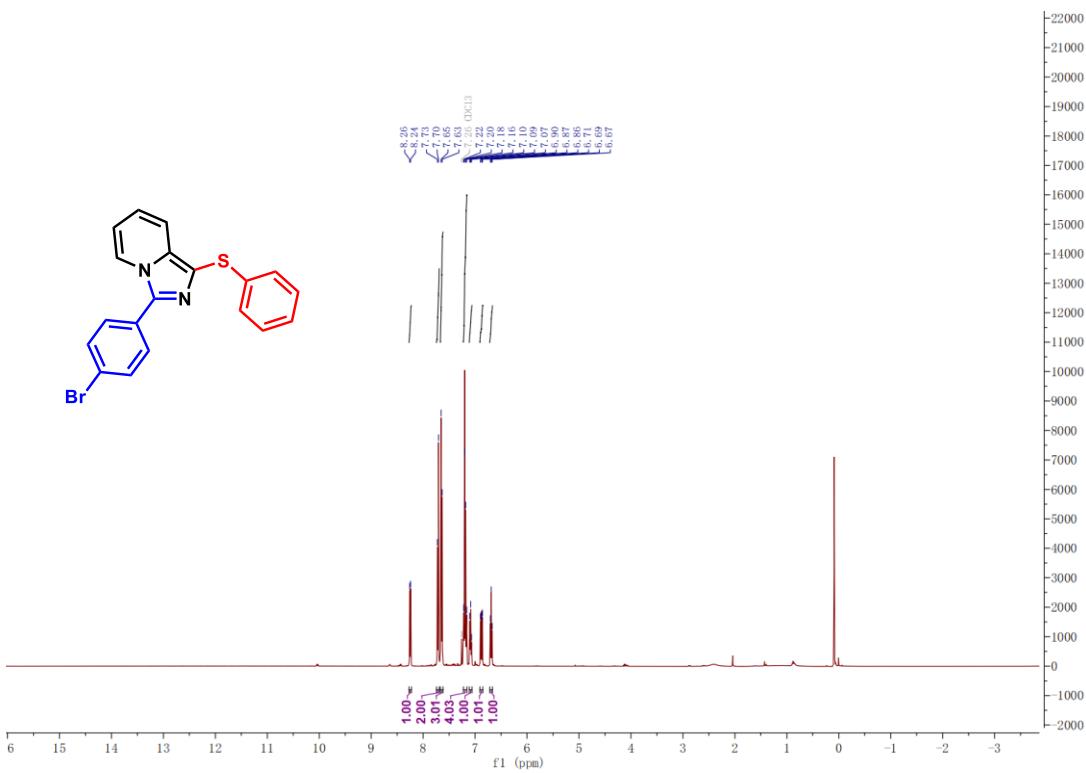


¹H NMR spectrum of 4e

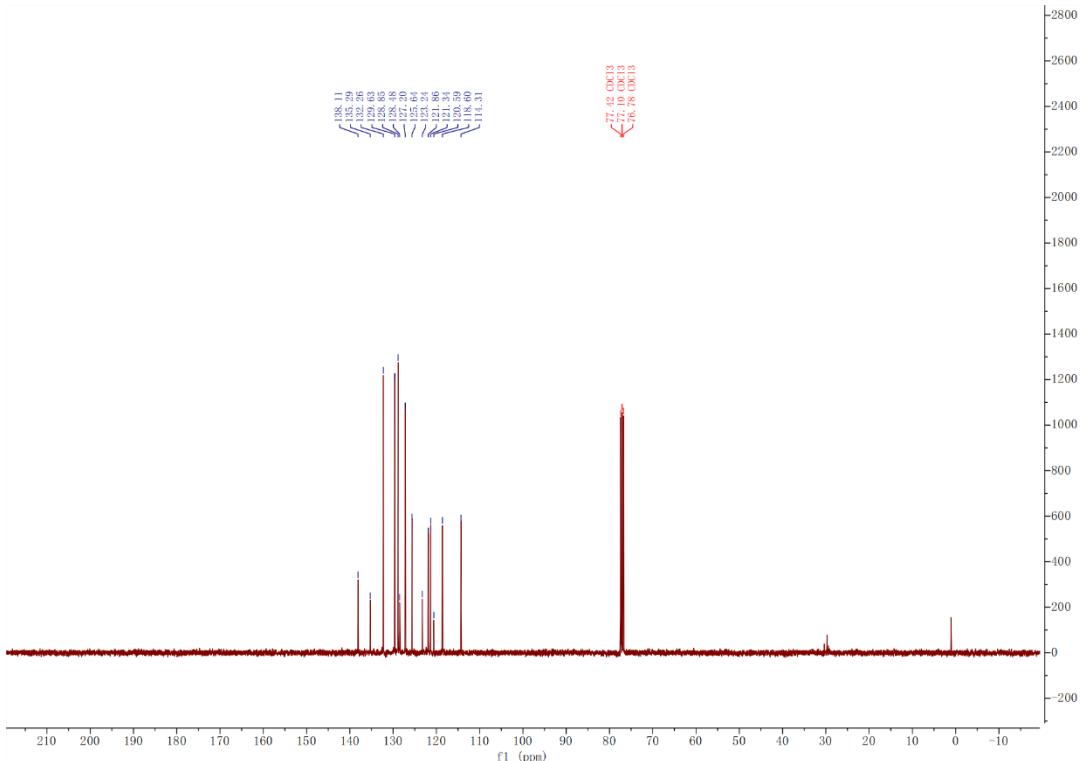


¹³C NMR spectrum of 4e

3-(4-bromophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine(4f)

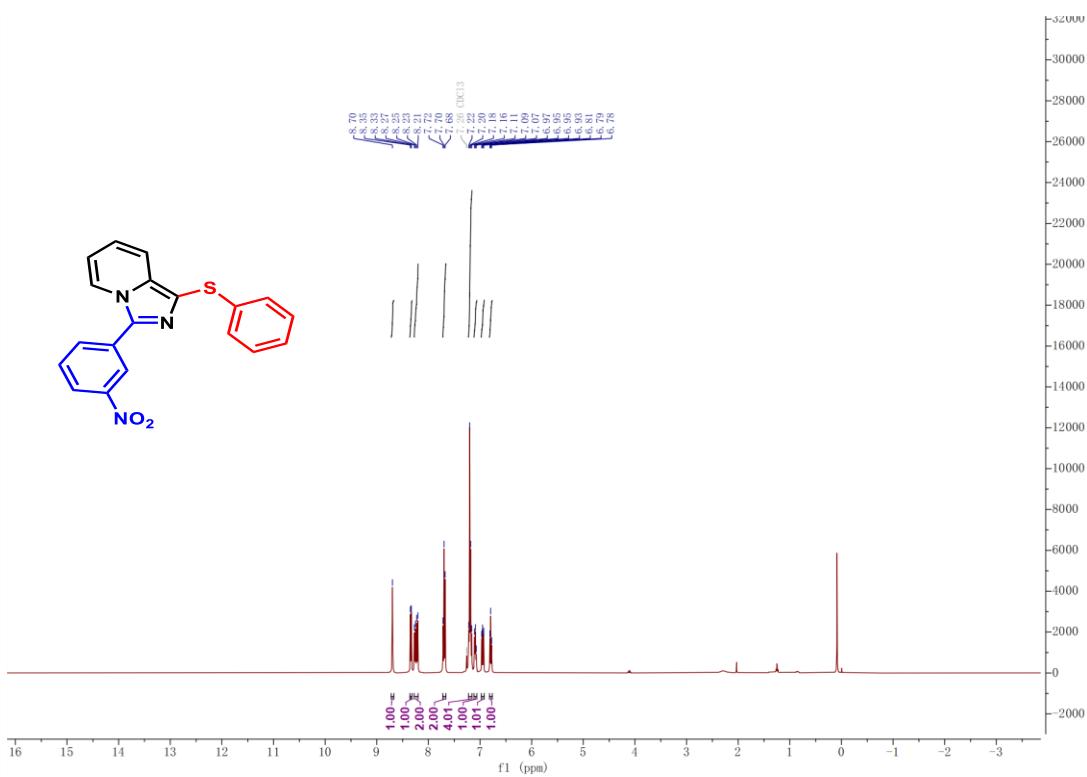


¹H NMR spectrum of 4f

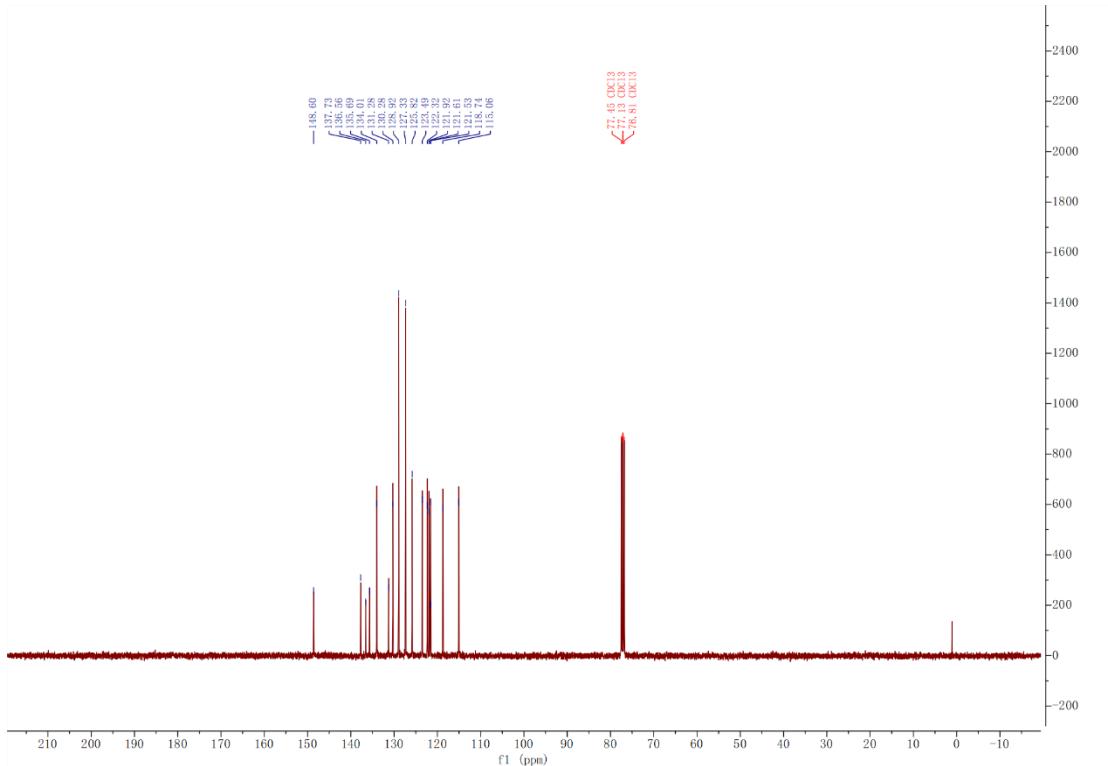


¹³C NMR spectrum of 4f

3-(3-nitrophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine(4g)

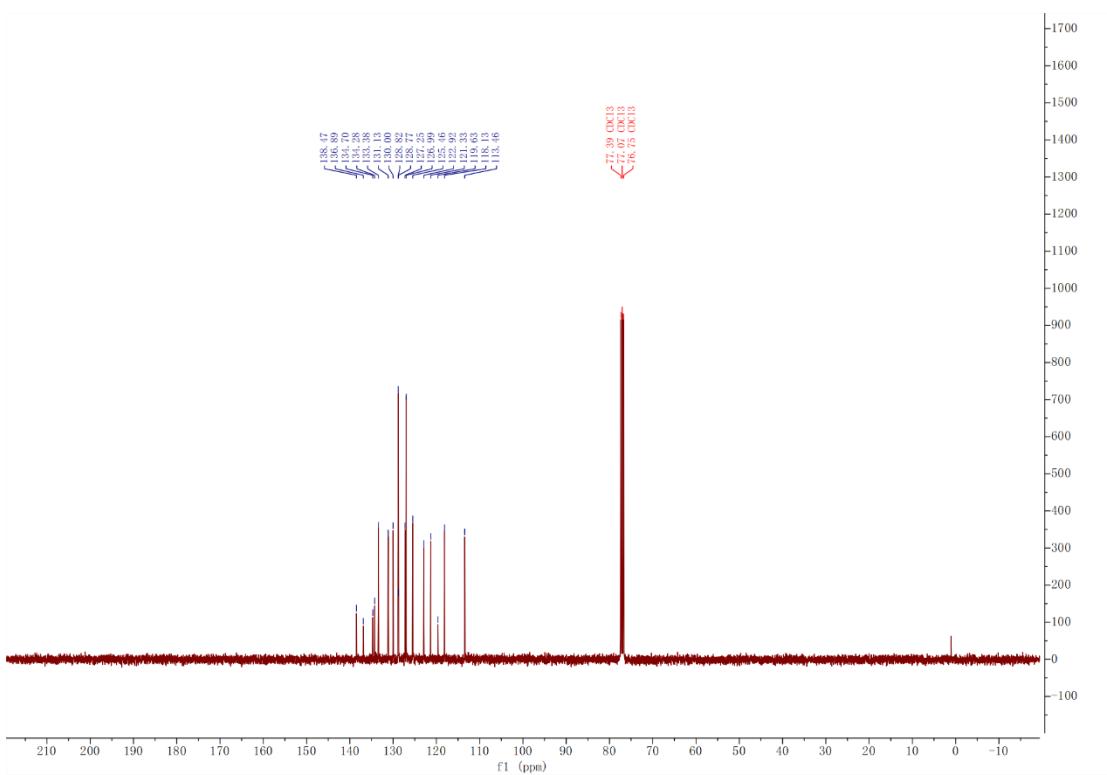
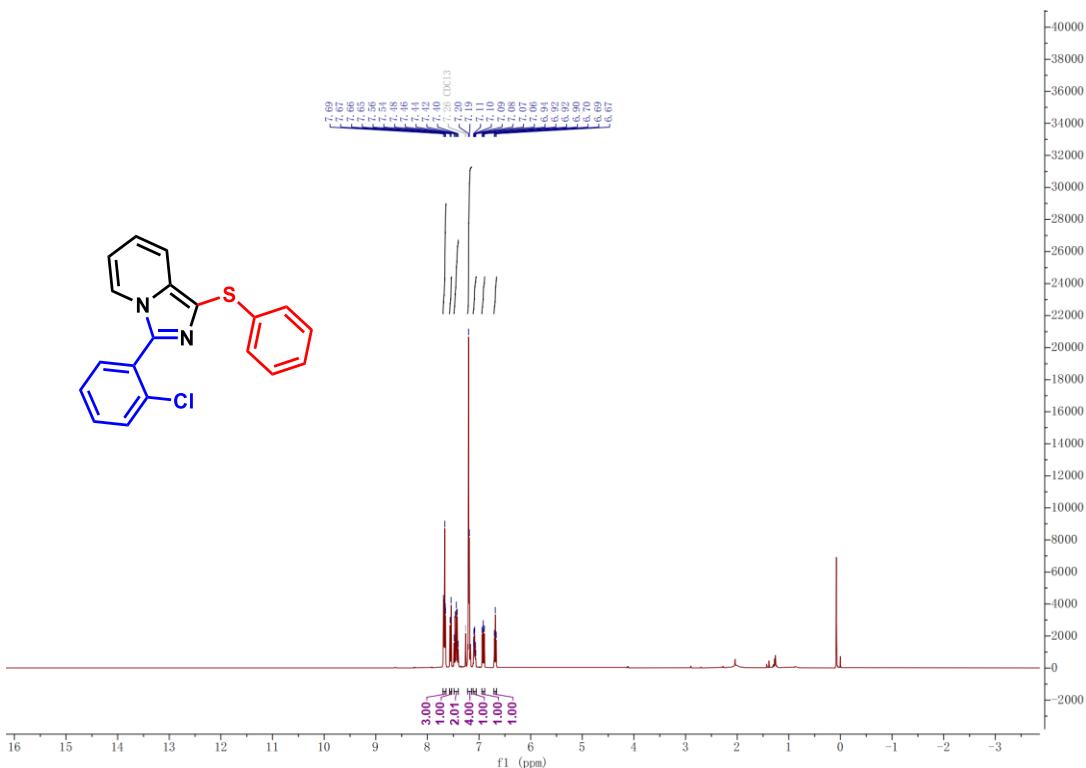


¹H NMR spectrum of 4g

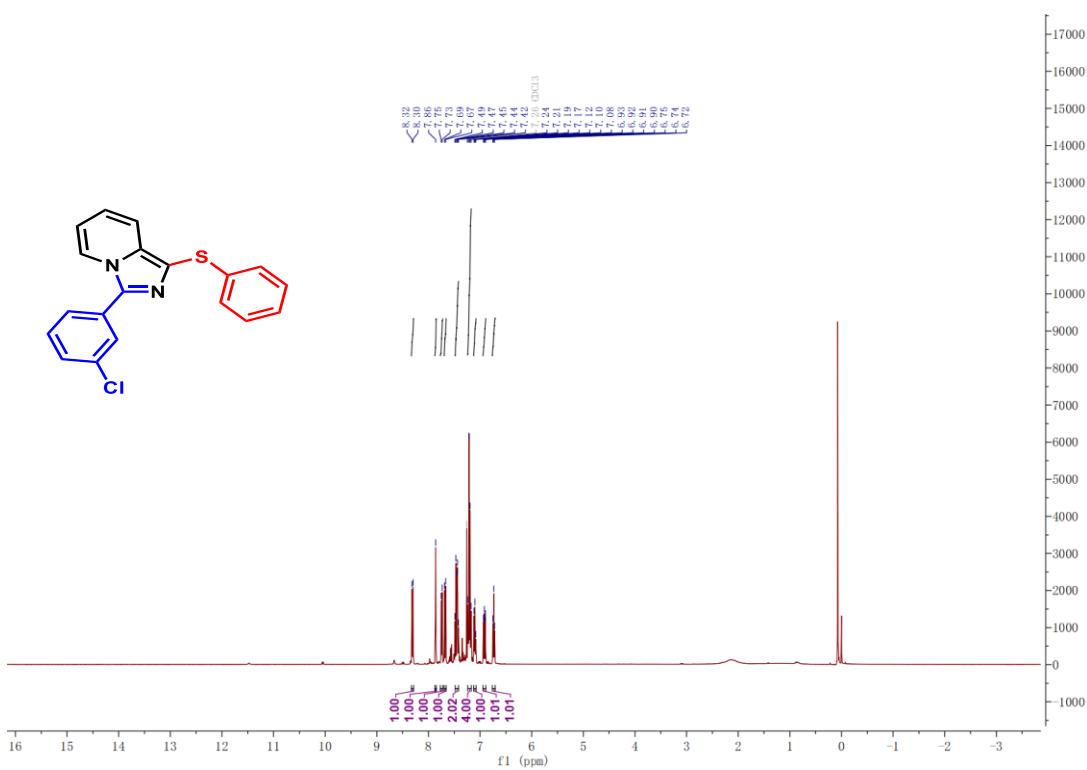


¹³C NMR spectrum of 4g

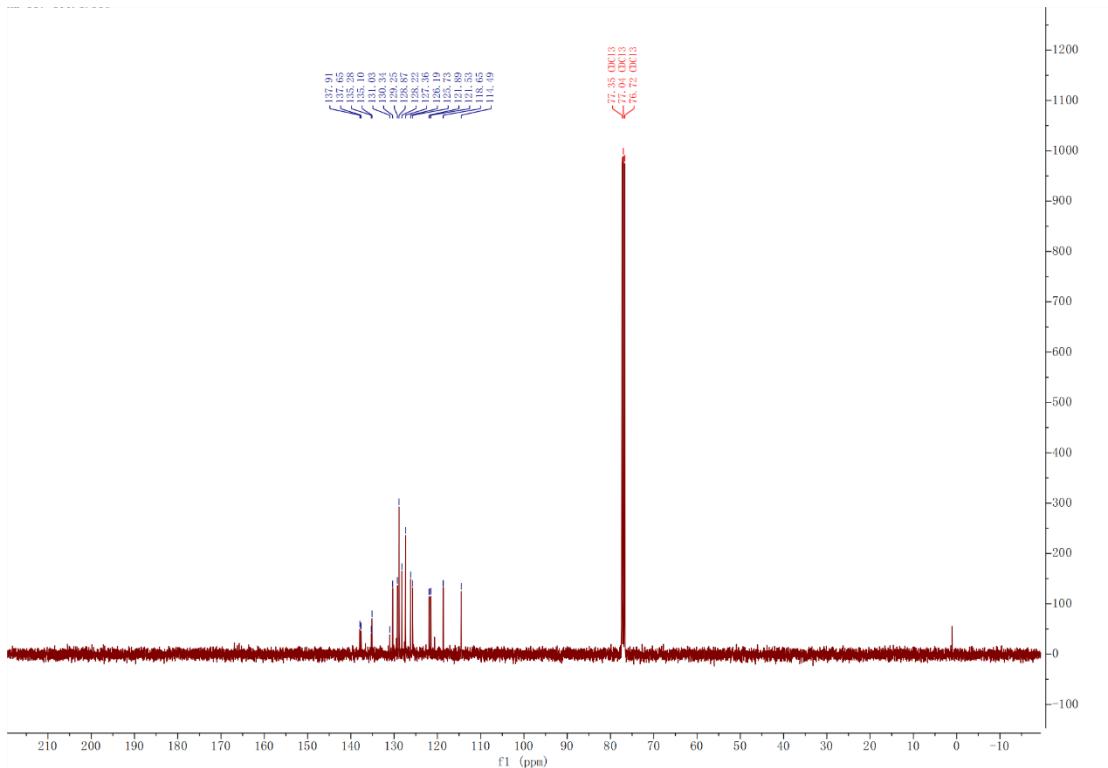
3-(2-chlorophenyl)-1-(phenylthio)imidazo[1,5-a]pyridine(4h)



3-(3-chlorophenyl)-1-(phenylthio)imidazo[1,5-*a*]pyridine(4*i*)

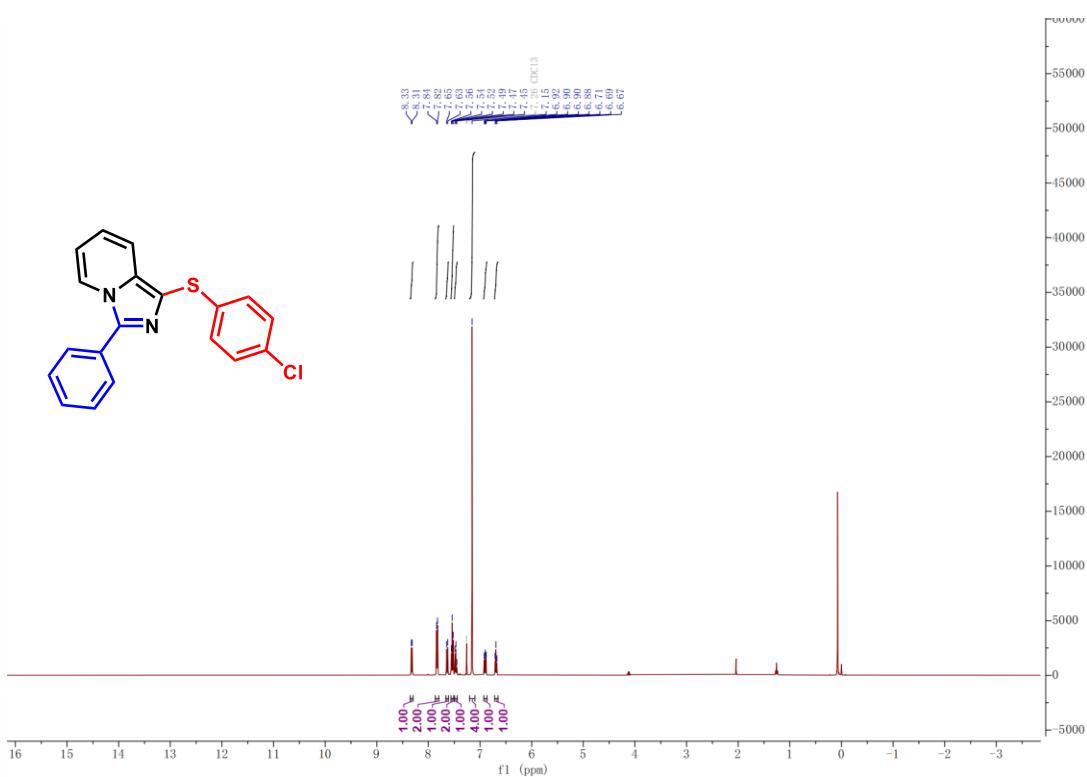


¹H NMR spectrum of 4*i*

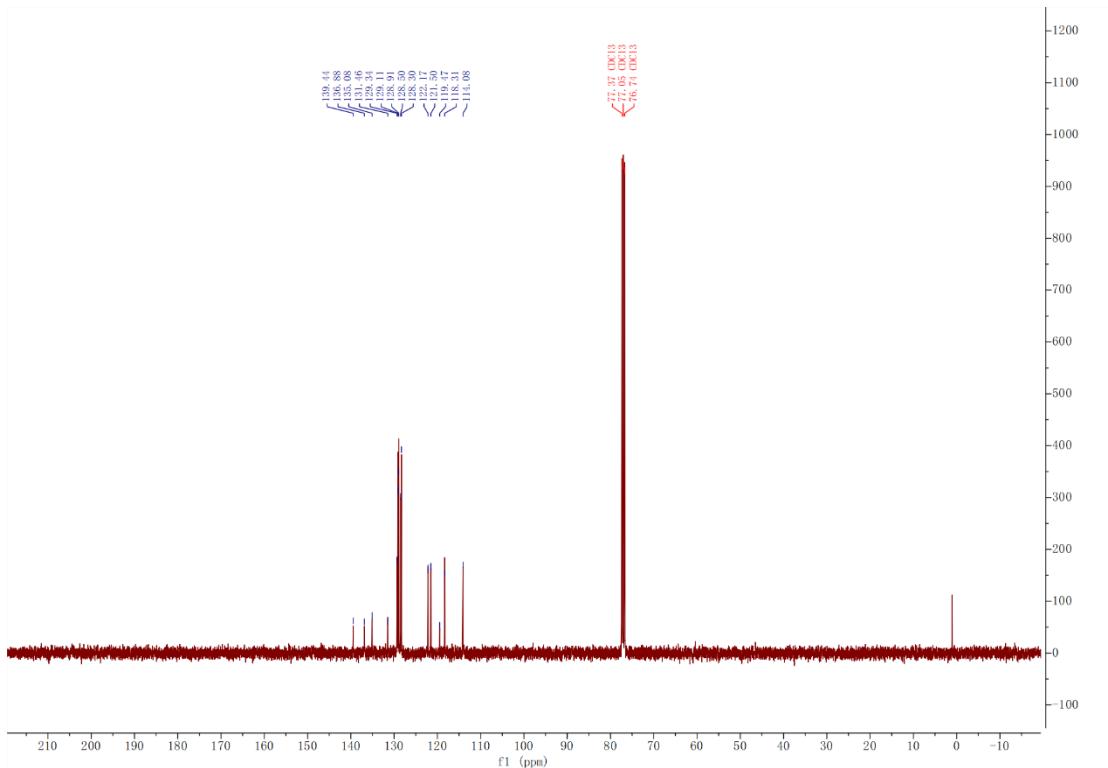


¹³C NMR spectrum of 4*i*

1-((4-chlorophenyl)thio)-3-phenylimidazo[1,5-a]pyridine (4j)

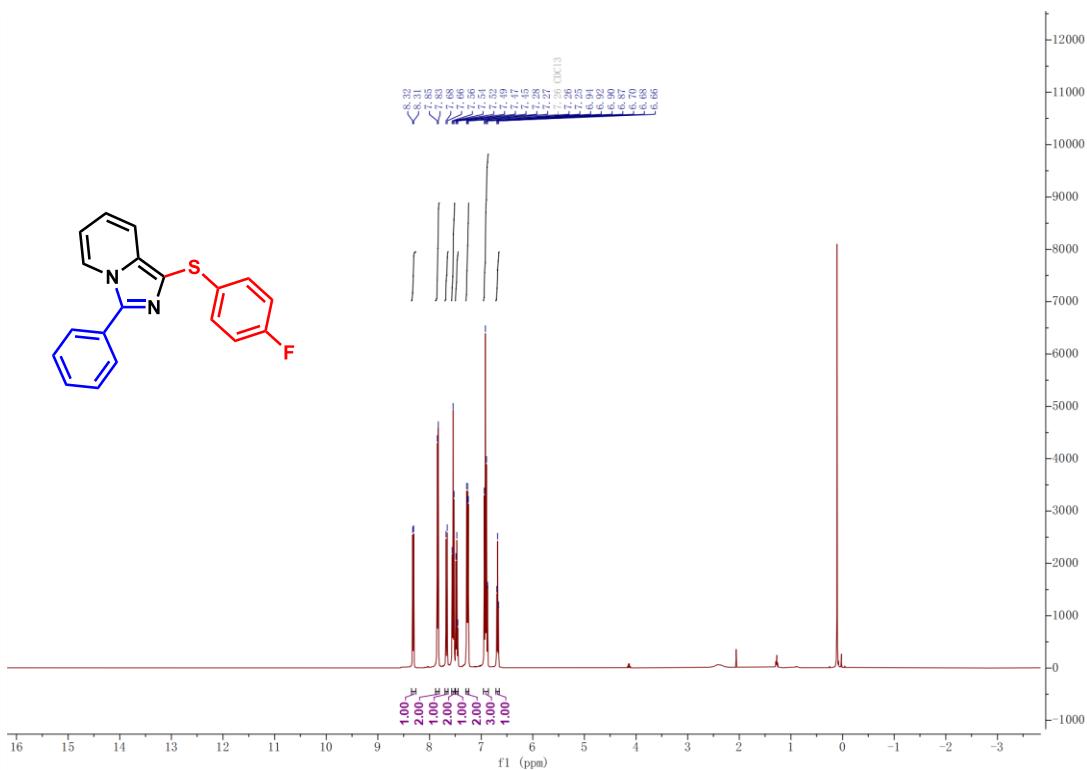


¹H NMR spectrum of 4j

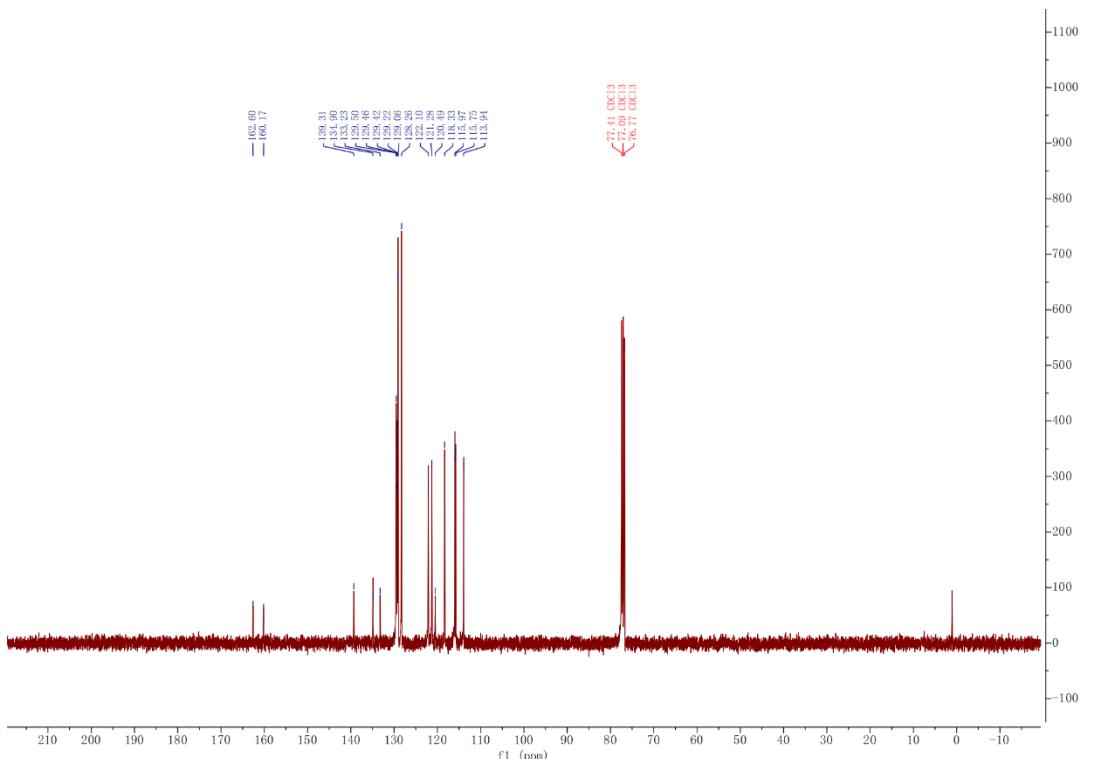


¹³C NMR spectrum of 4j

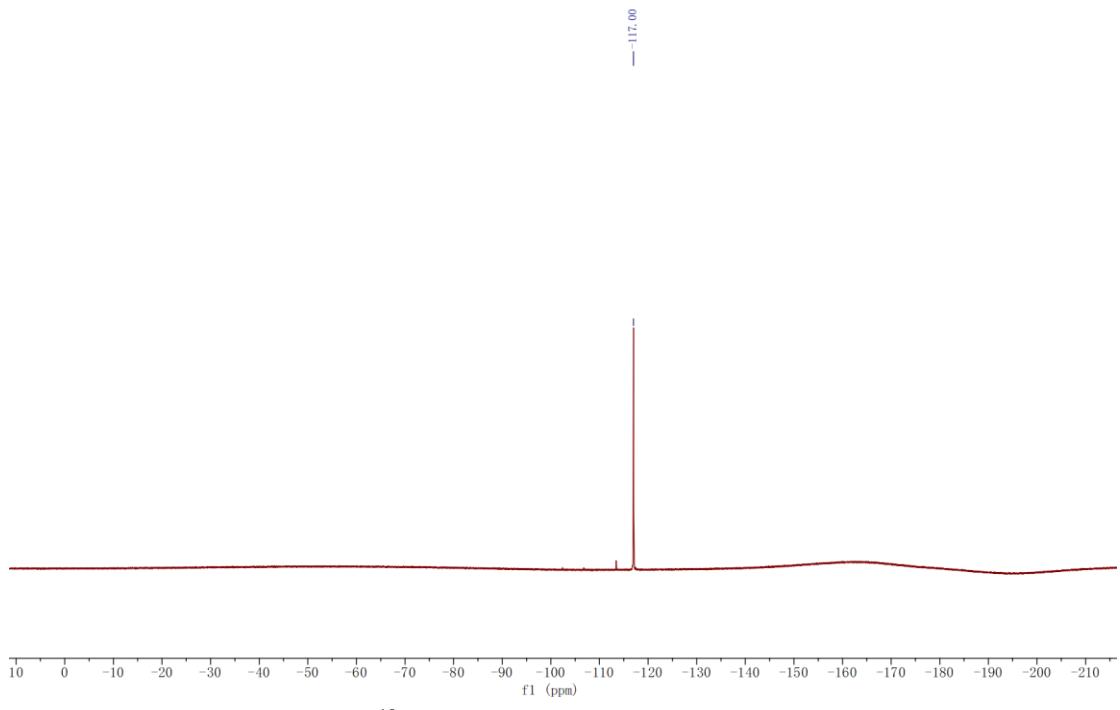
1-((4-fluorophenyl)thio)-3-phenylimidazo[1,5-*a*]pyridine(4k)



¹H NMR spectrum of 4k

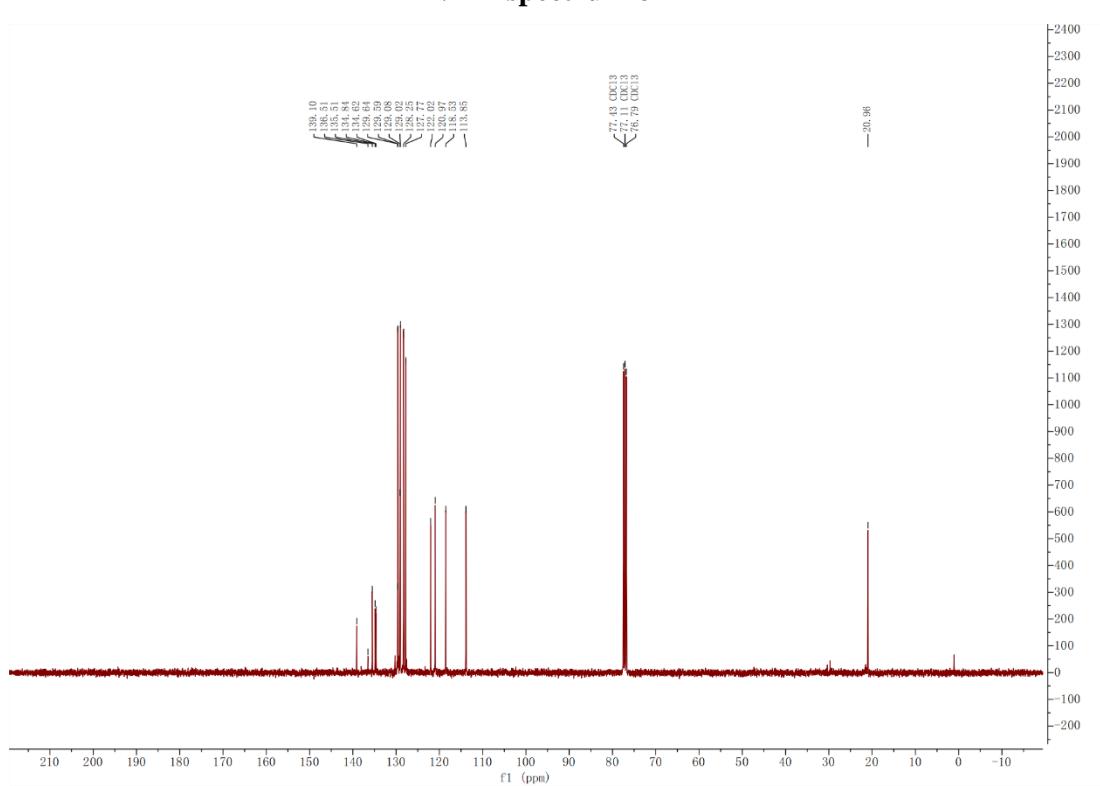
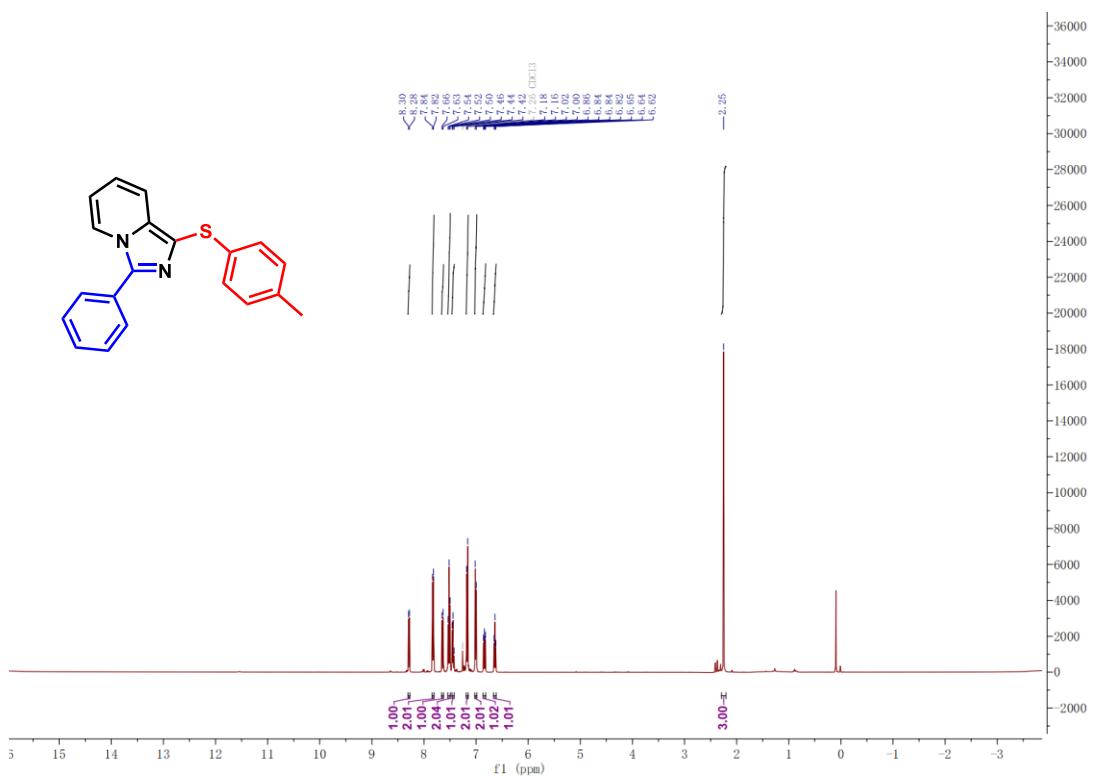


¹³C NMR spectrum of 4k

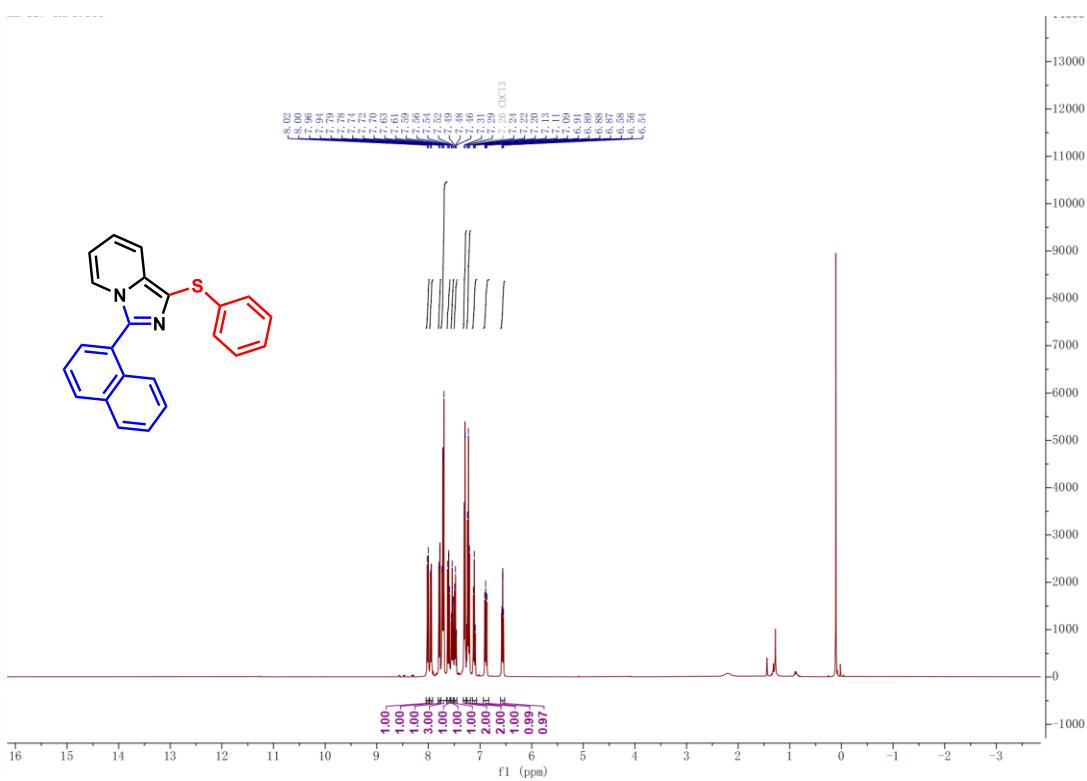


¹⁹F NMR spectrum of 4k

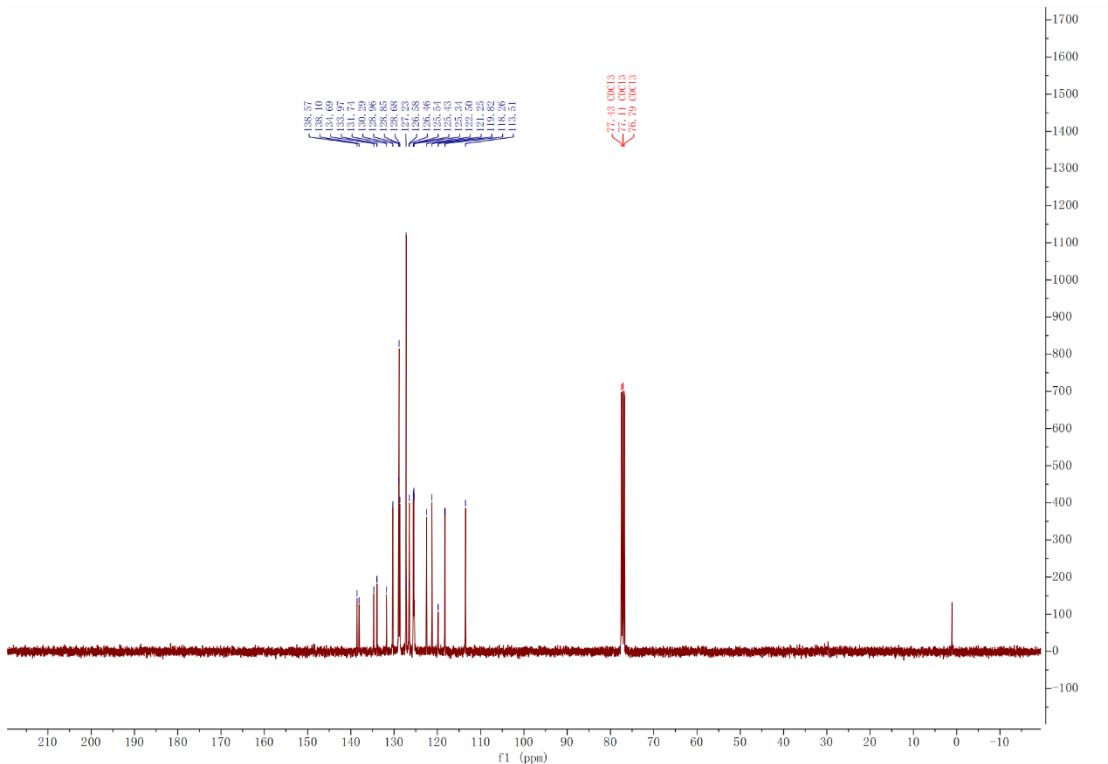
3-phenyl-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4l**)**



3-(naphthalen-1-yl)-1-(phenylthio)imidazo[1,5-*a*]pyridine(4m)

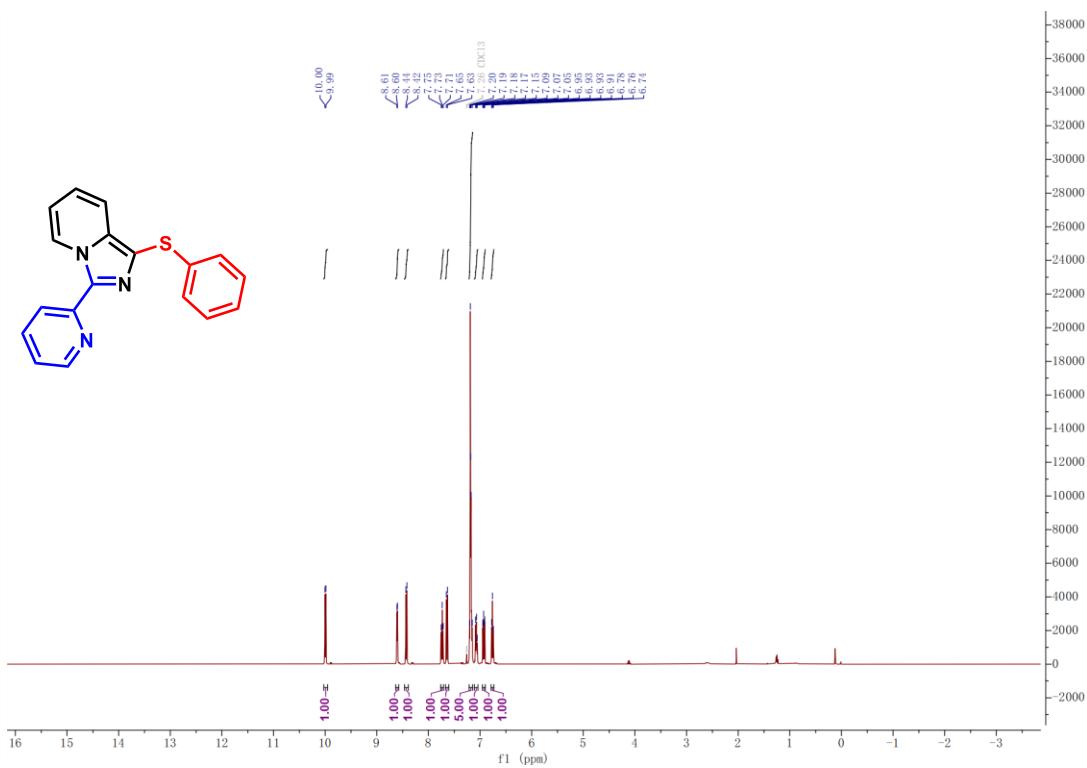


¹H NMR spectrum of 4m

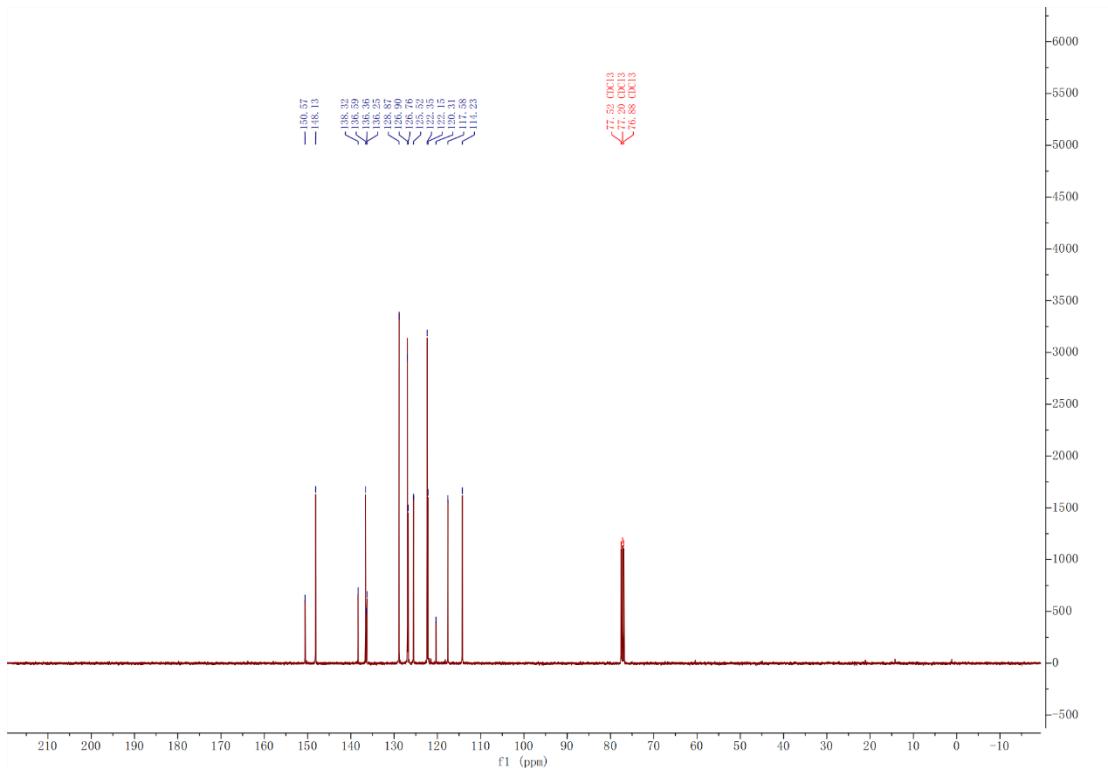


¹³C NMR spectrum of 4m

1-(phenylthio)-3-(pyridin-2-yl)imidazo[1,5-a]pyridine(4n)

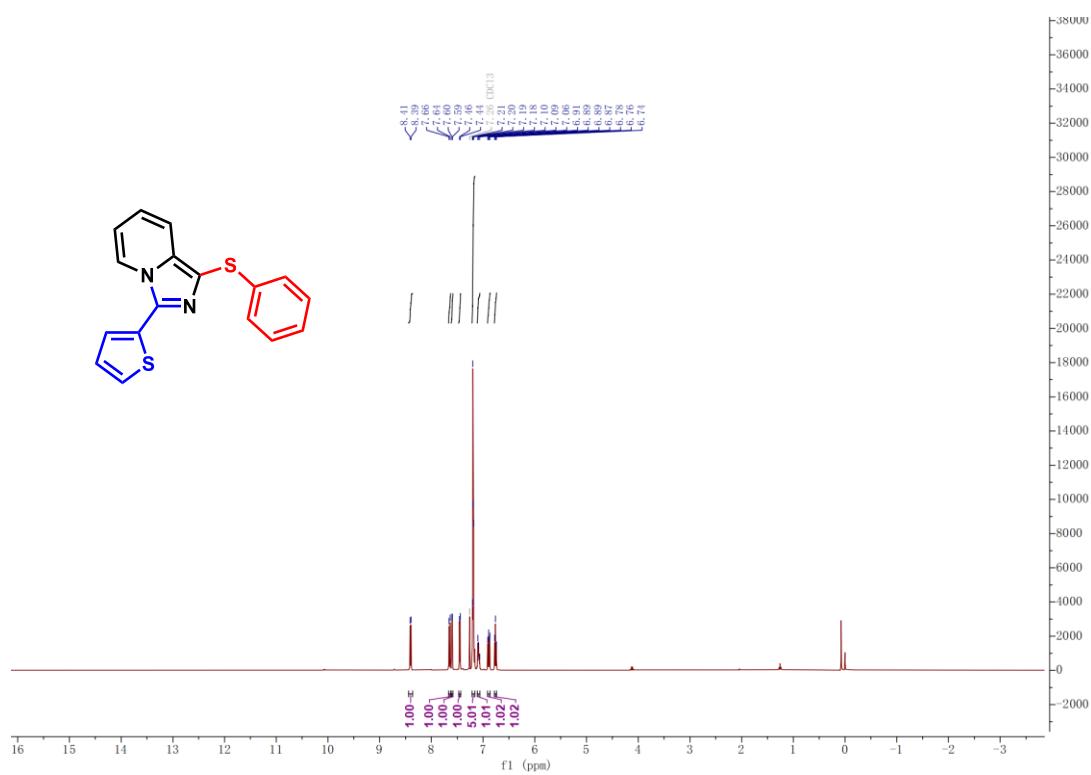


¹H NMR spectrum of 4n

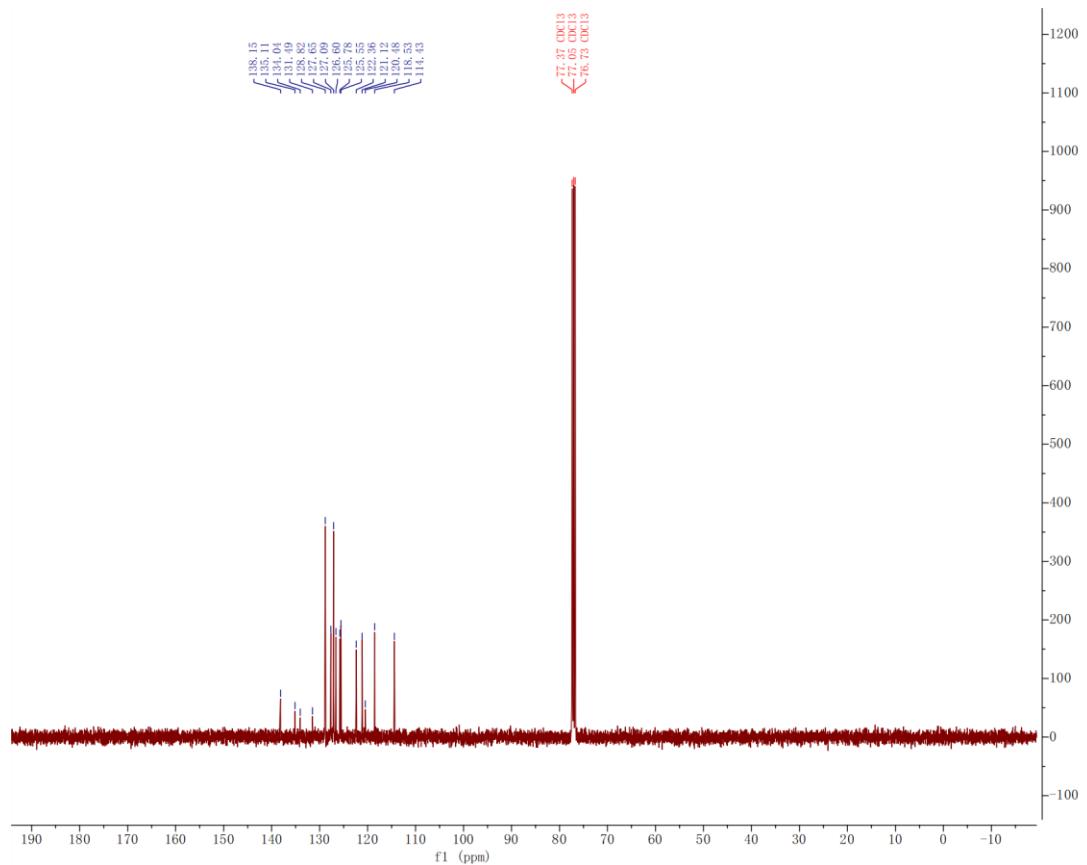


¹³C NMR spectrum of 4n

1-(phenylthio)-3-(thiophen-2-yl)imidazo[1,5-a]pyridine(4o)

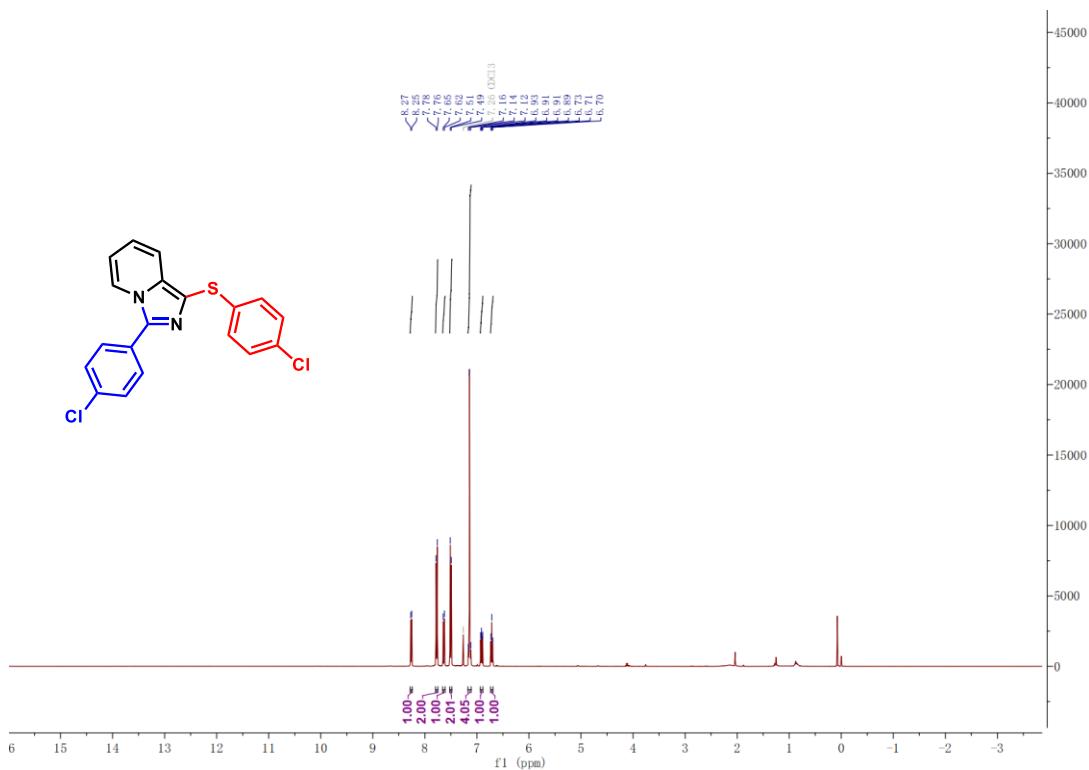


¹H NMR spectrum of 4o

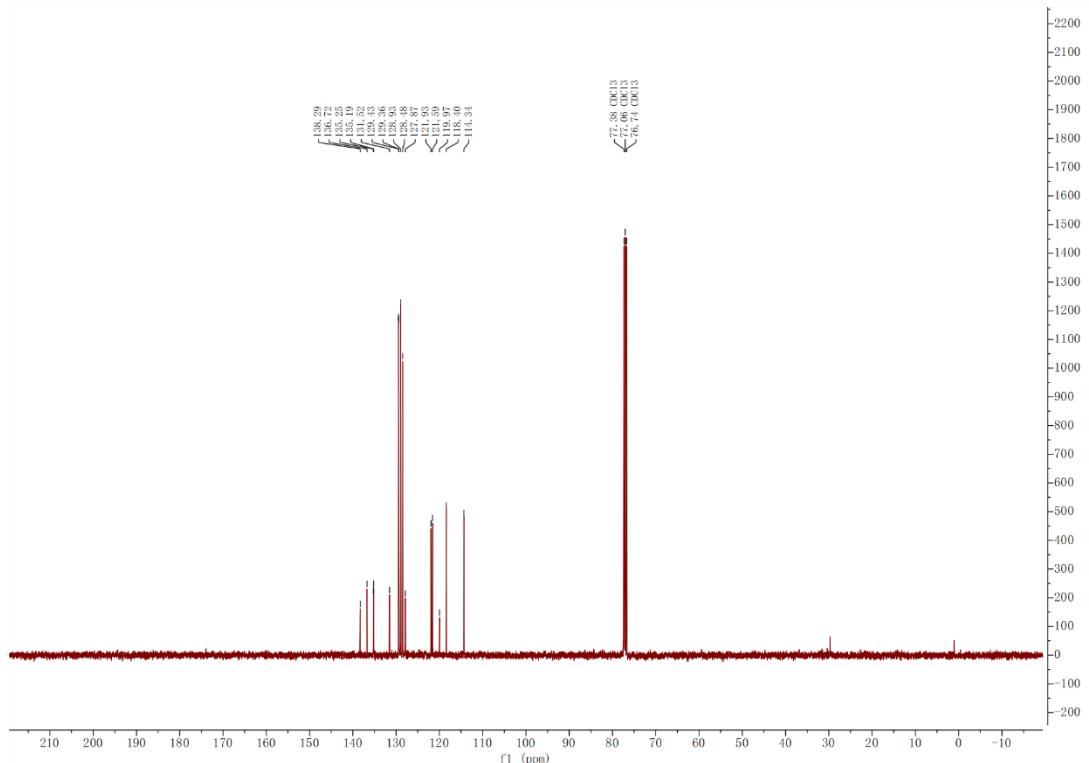


¹³C NMR spectrum of 4o

3-(4-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine(4p)

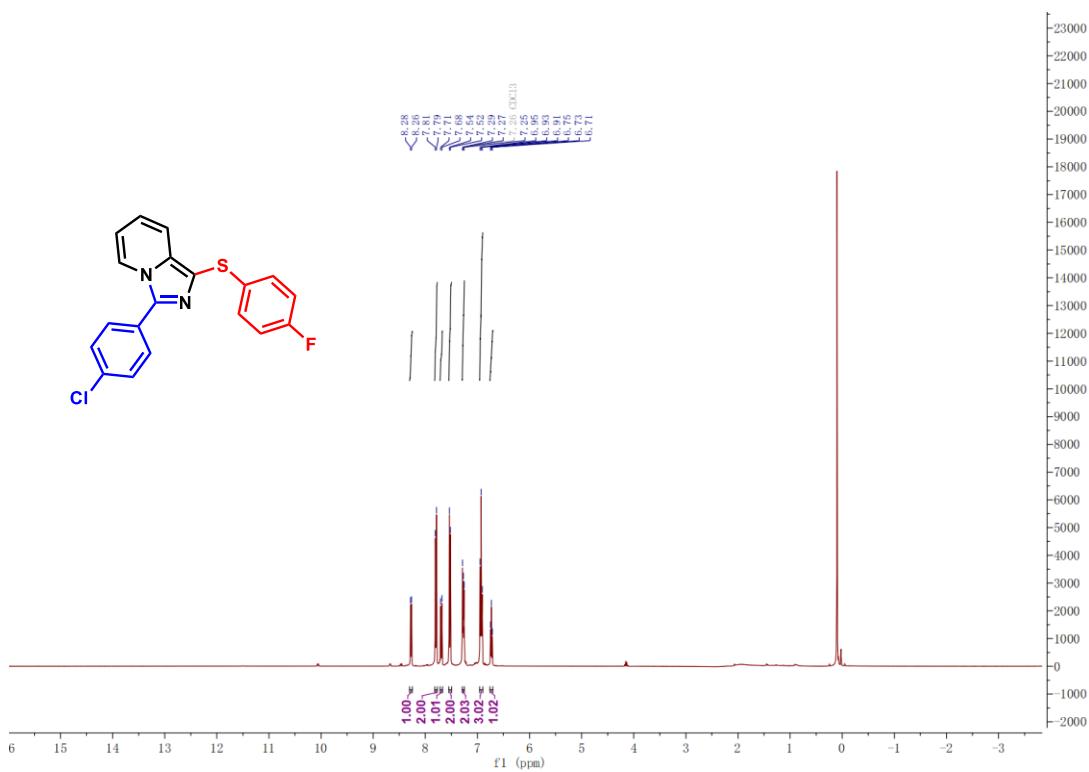


¹H NMR spectrum of 4p

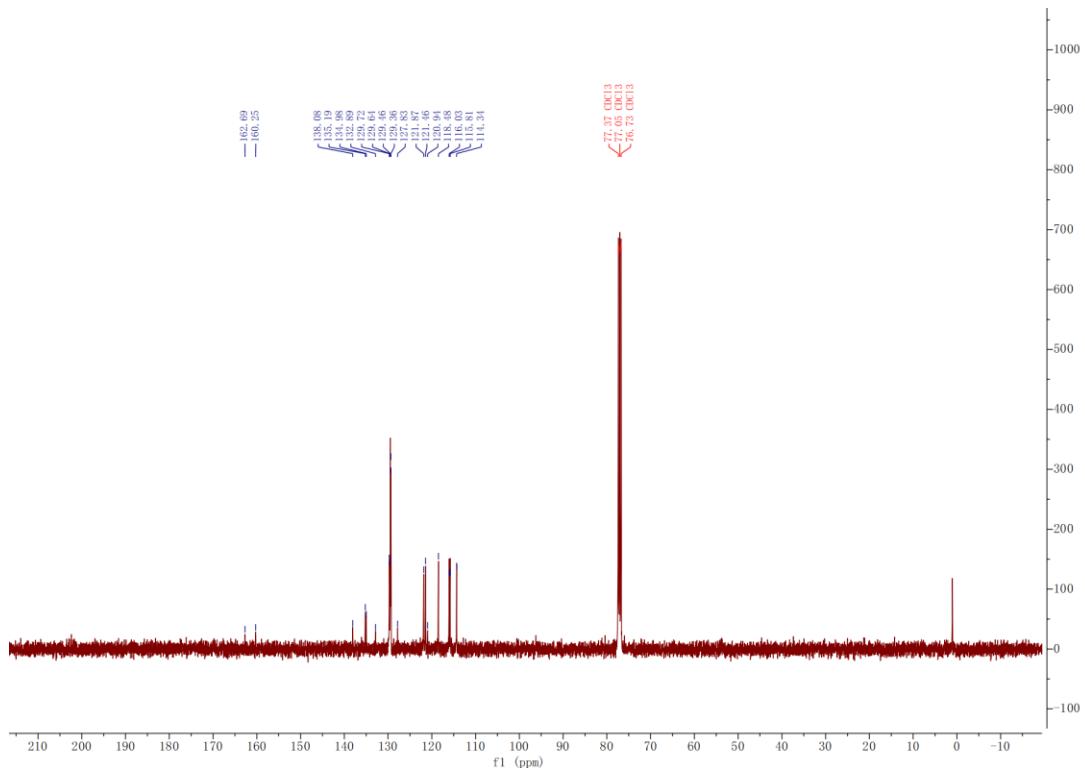


¹³C NMR spectrum of 4p

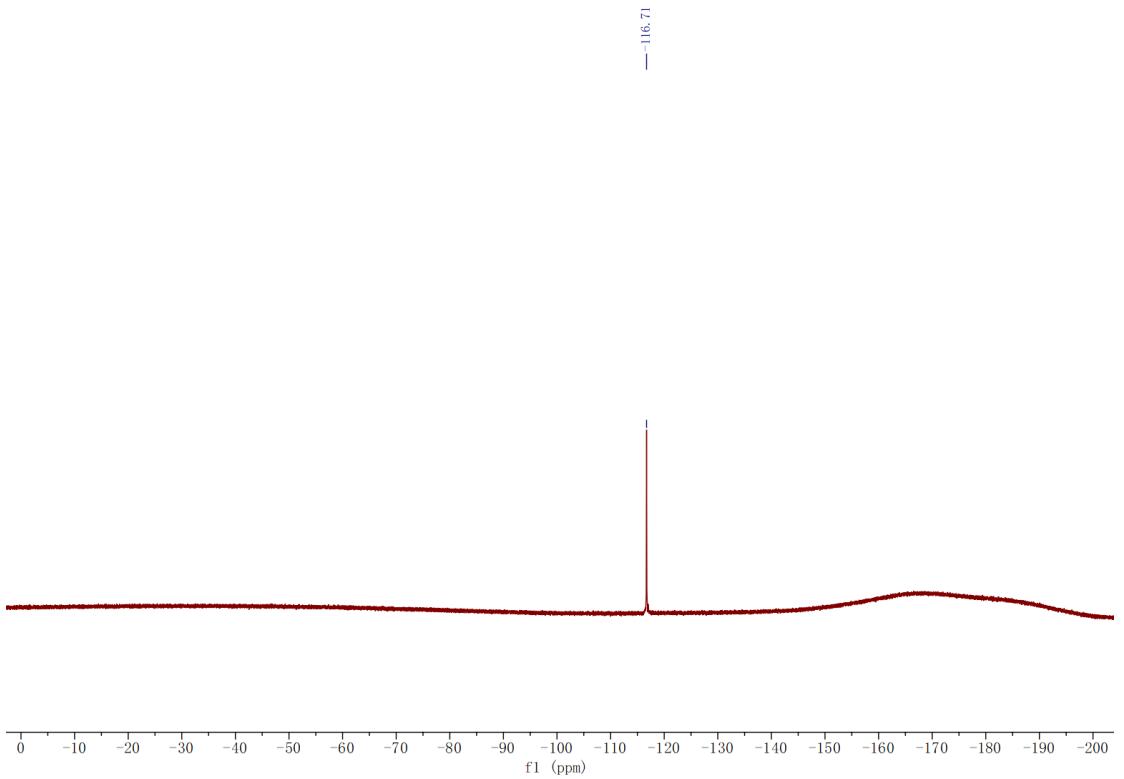
3-(4-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-*a*]pyridine(4q)



¹H NMR spectrum of 4q

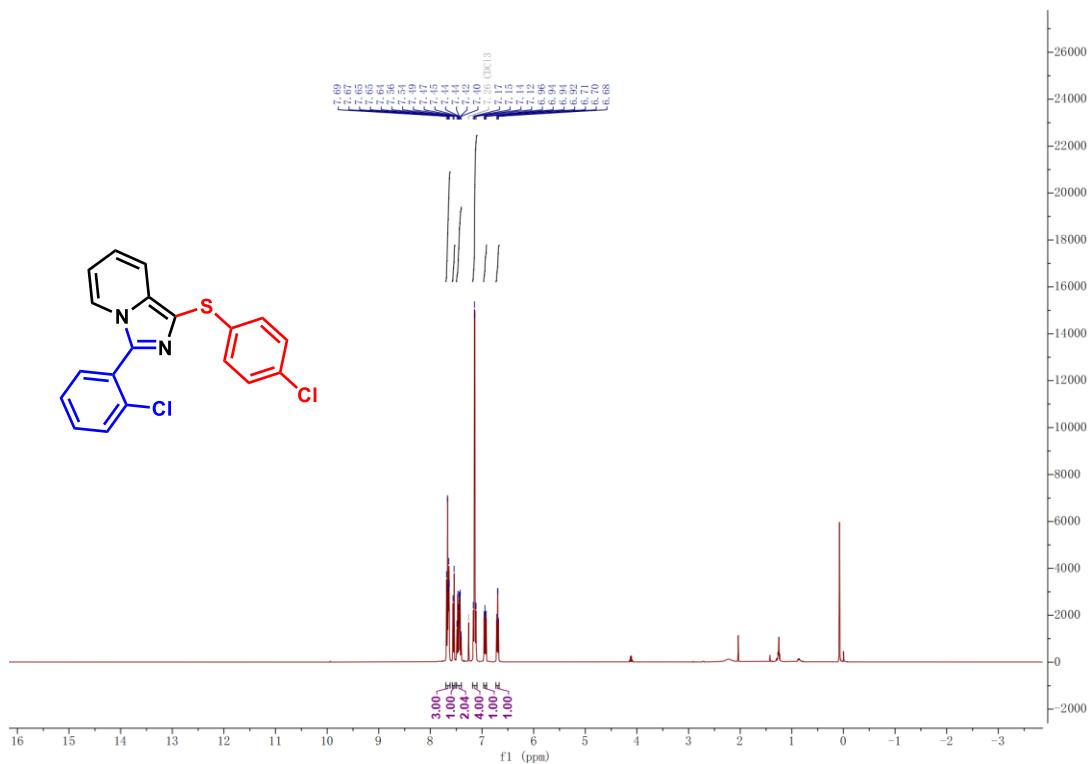


¹³C NMR spectrum of 4q

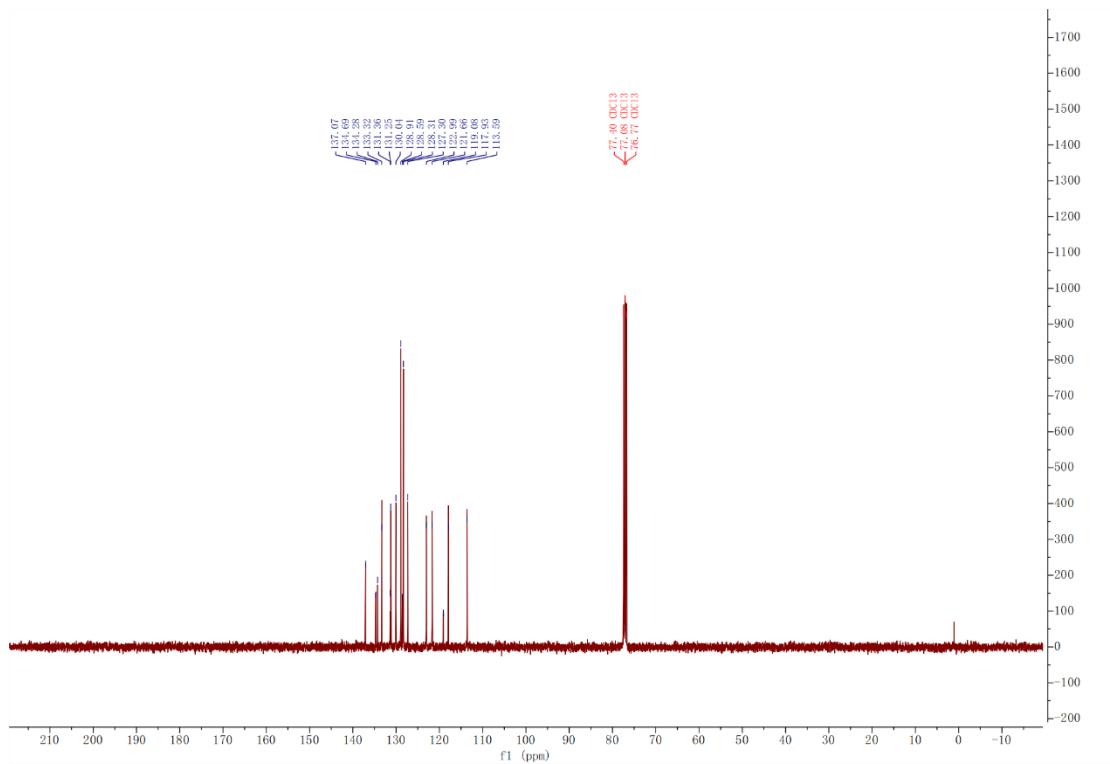


¹⁹F NMR spectrum of 4q

3-(2-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine(4r)

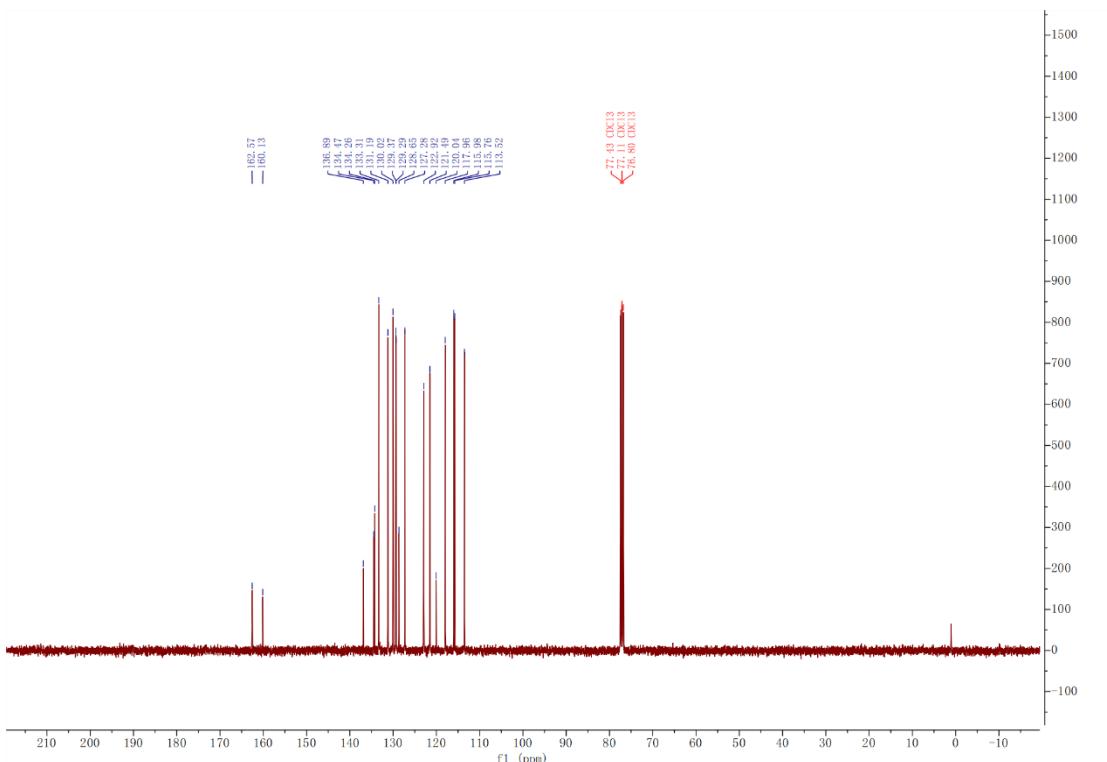
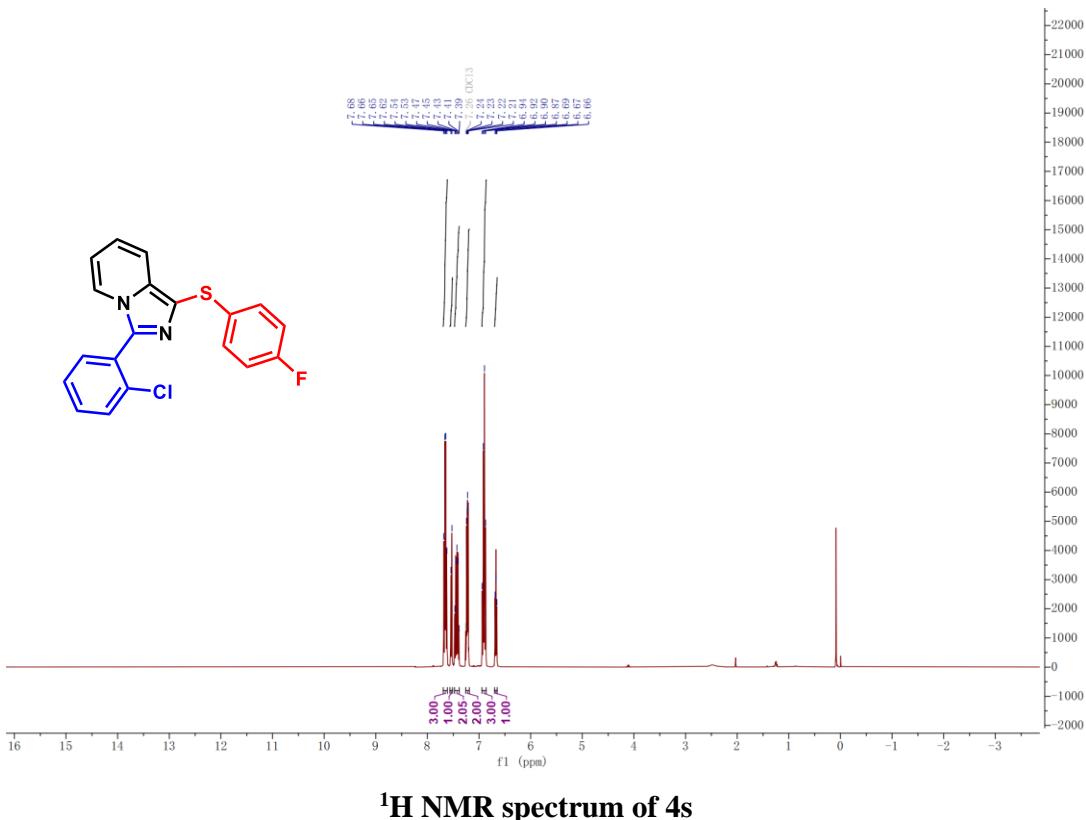


¹H NMR spectrum of 4r

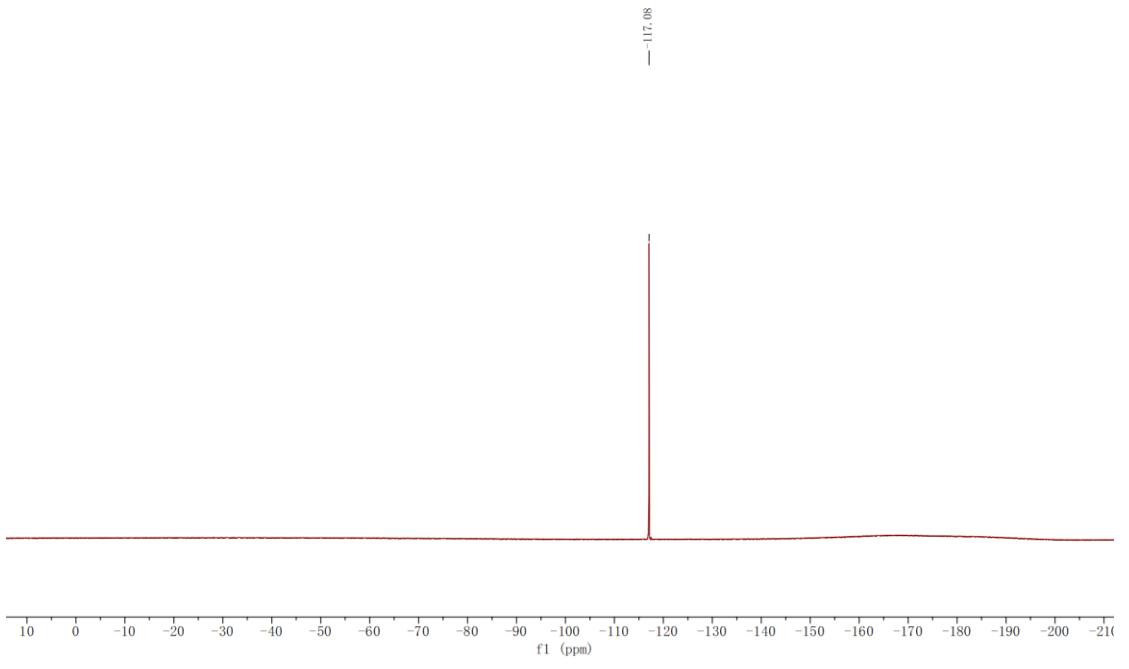


¹³C NMR spectrum of 4r

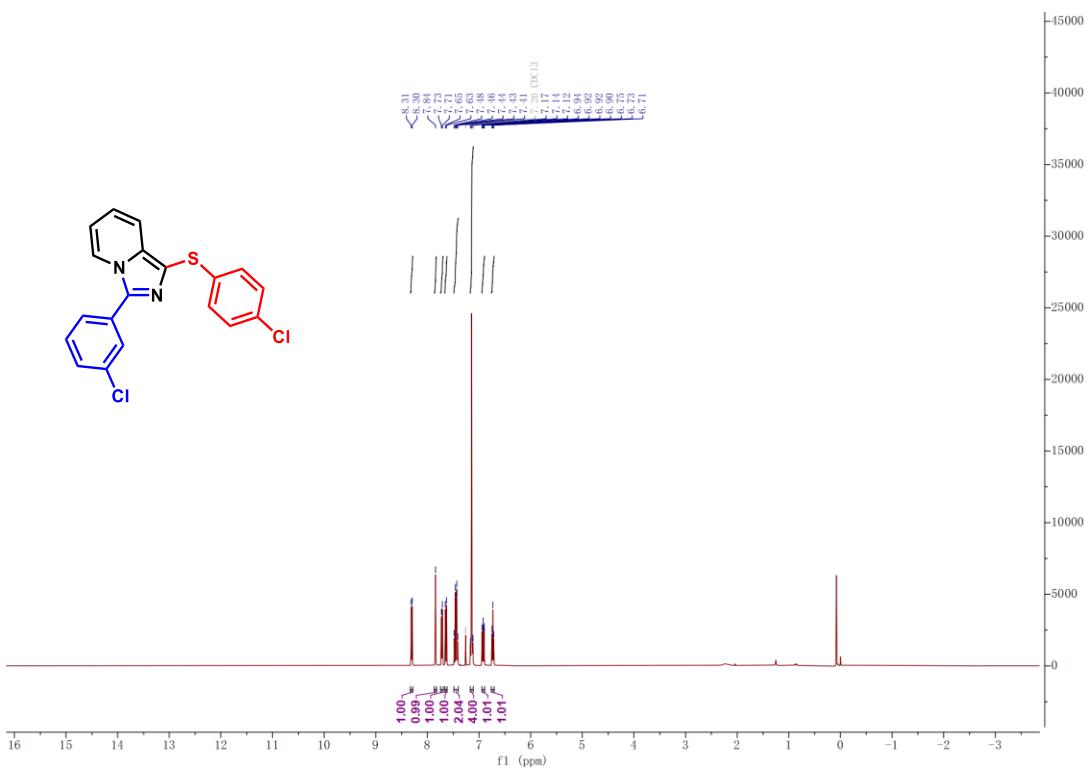
3-(2-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-a]pyridine(4s)



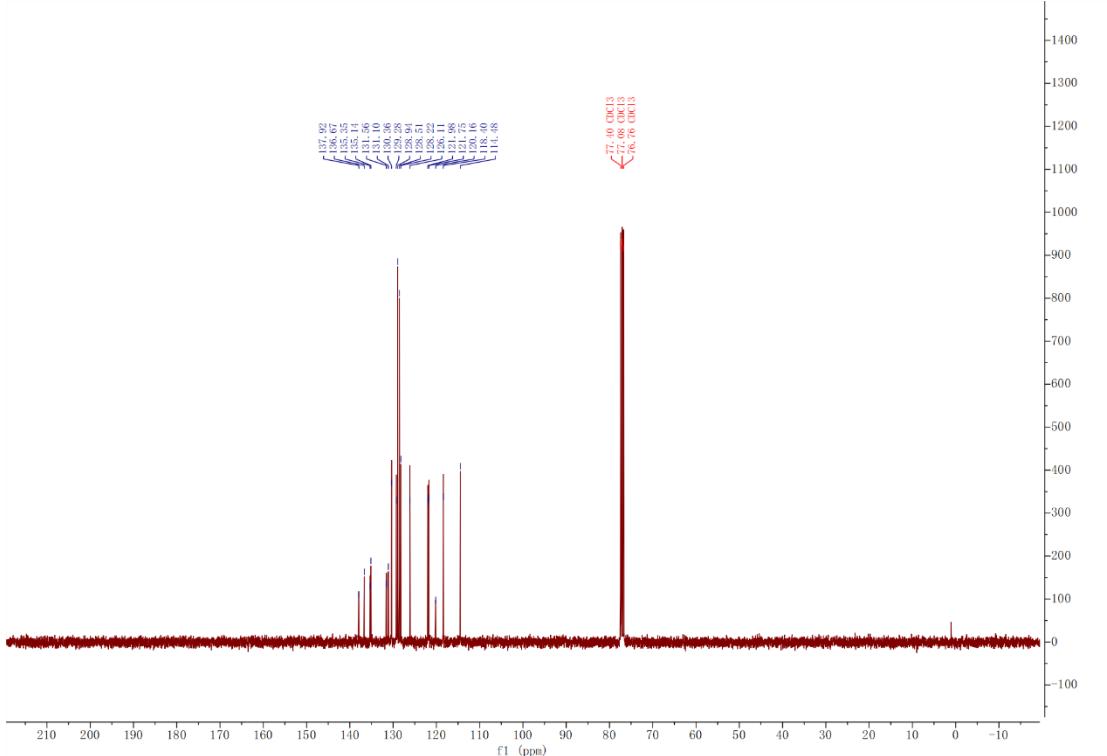
¹³C NMR spectrum of 4s



3-(3-chlorophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine (4t)

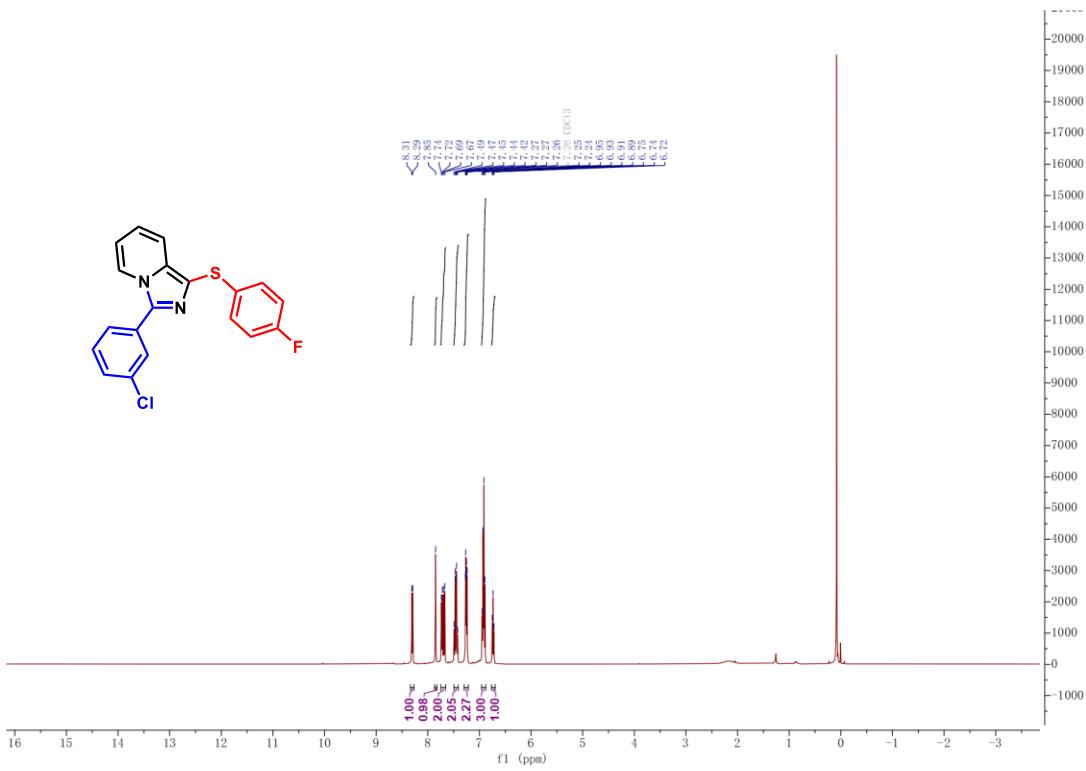


¹H NMR spectrum of 4t

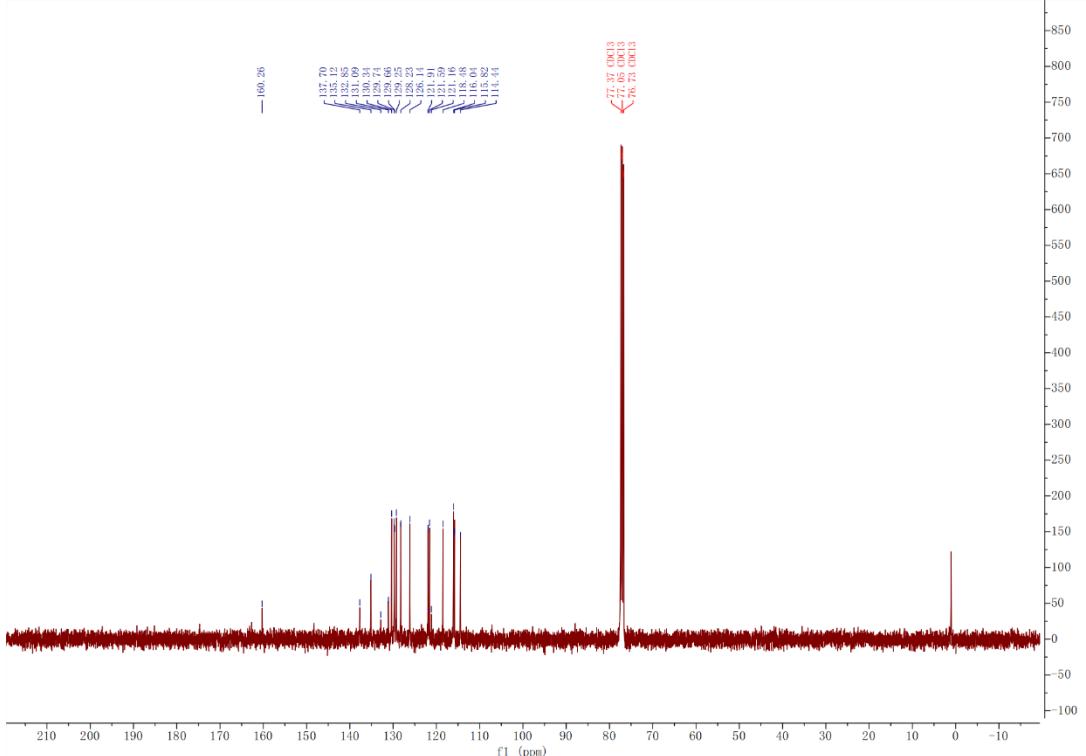


¹³C NMR spectrum of 4t

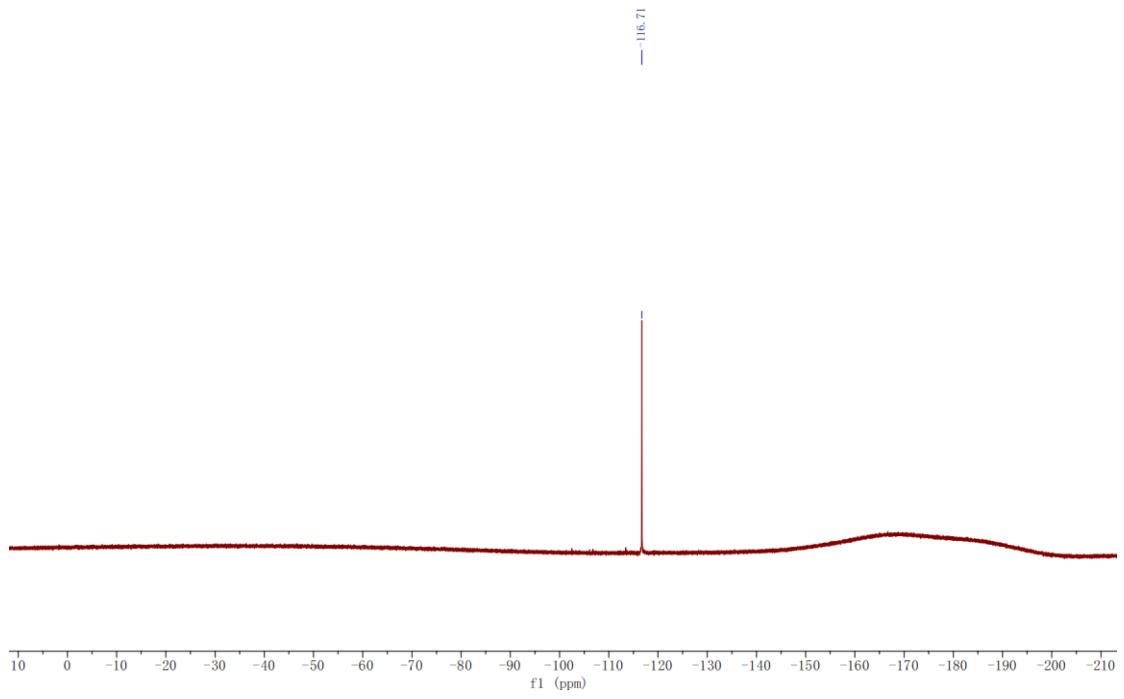
3-(3-chlorophenyl)-1-((4-fluorophenyl)thio)imidazo[1,5-a]pyridine (4u)



¹H NMR spectrum of 4u

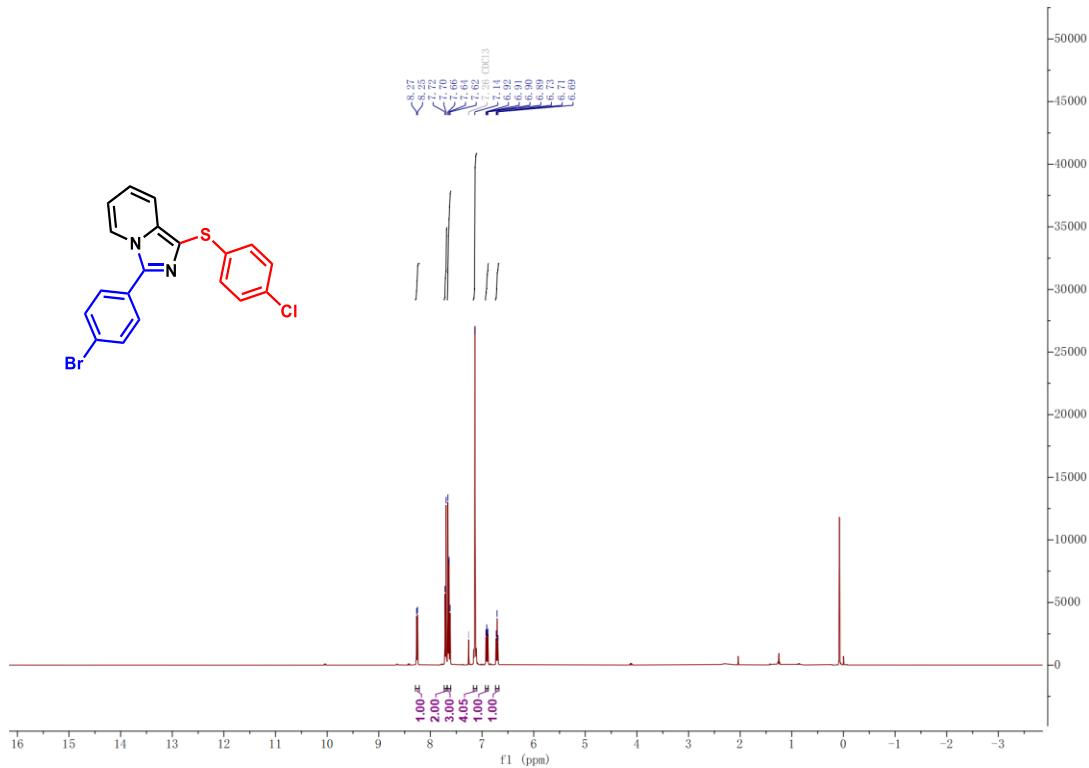


¹³C NMR spectrum of 4u

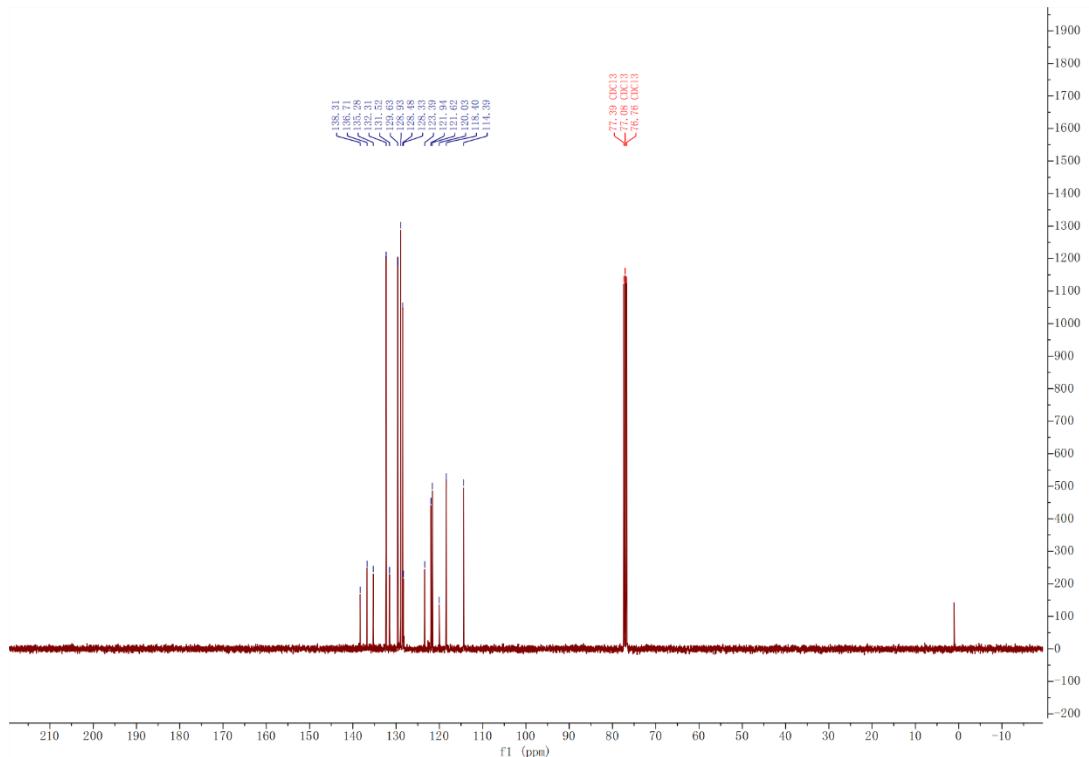


^{19}F NMR spectrum of 4u

3-(4-bromophenyl)-1-((4-chlorophenyl)thio)imidazo[1,5-a]pyridine(4v)

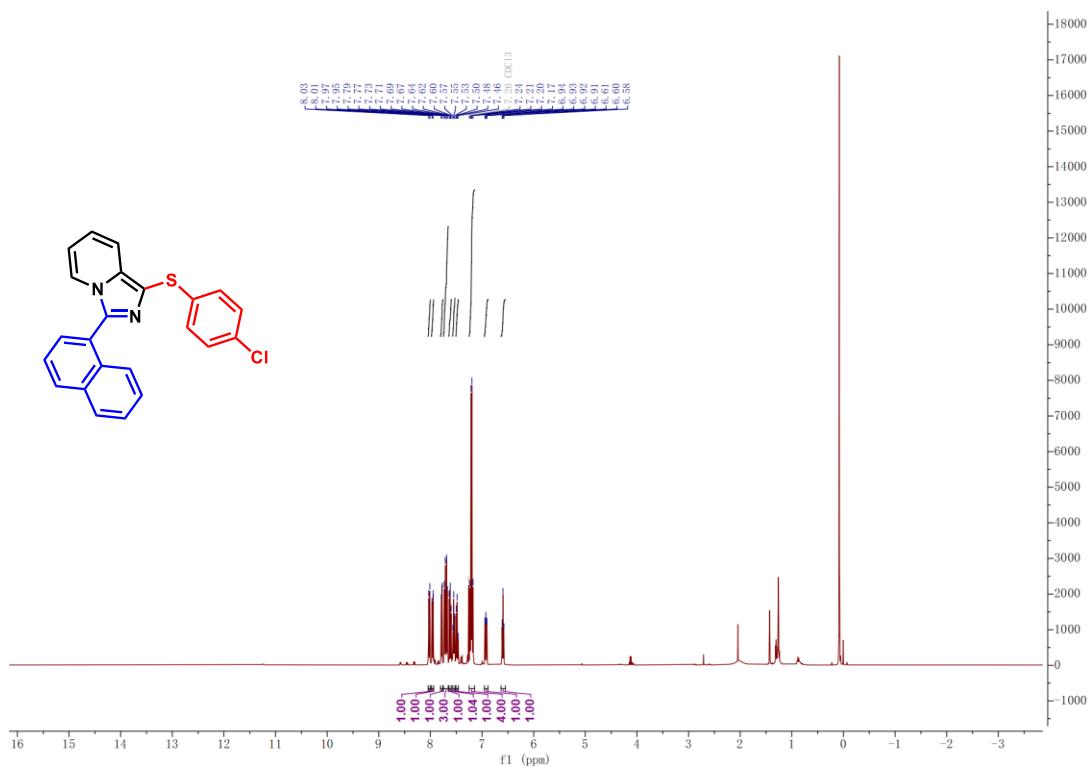


¹H NMR spectrum of 4v

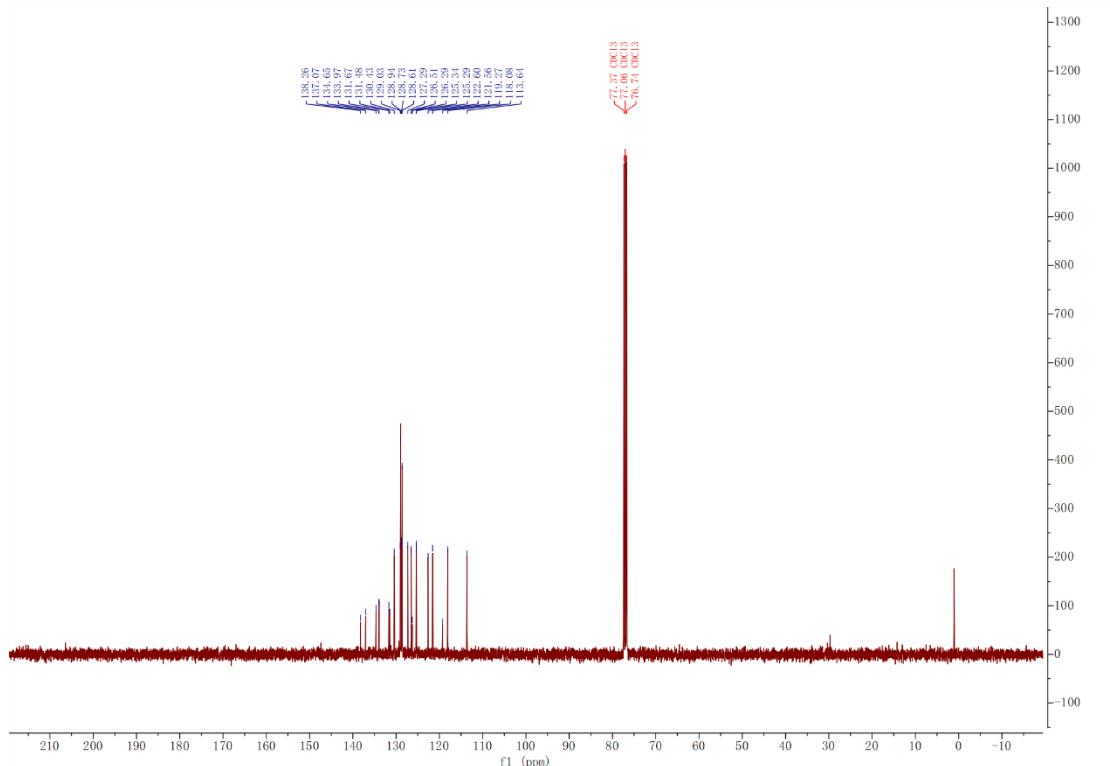


¹³C NMR spectrum of 4v

1-((4-chlorophenyl)thio)-3-(naphthalen-1-yl)imidazo[1,5-a]pyridine(4w)

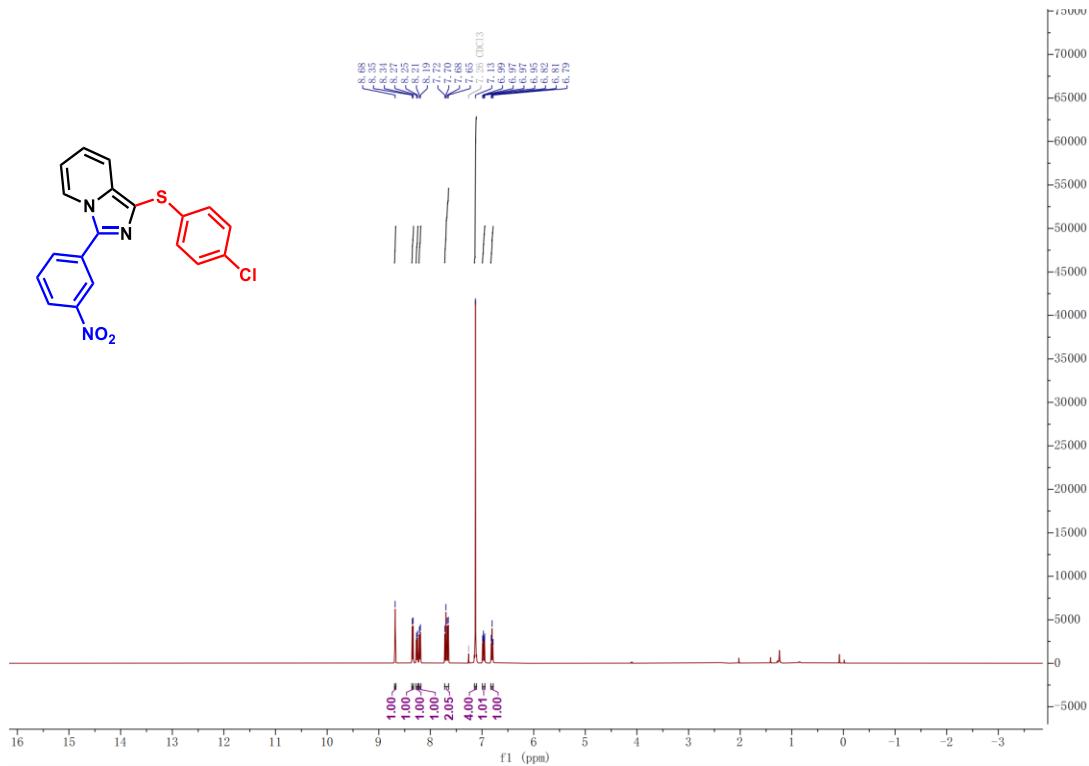


¹H NMR spectrum of 4w

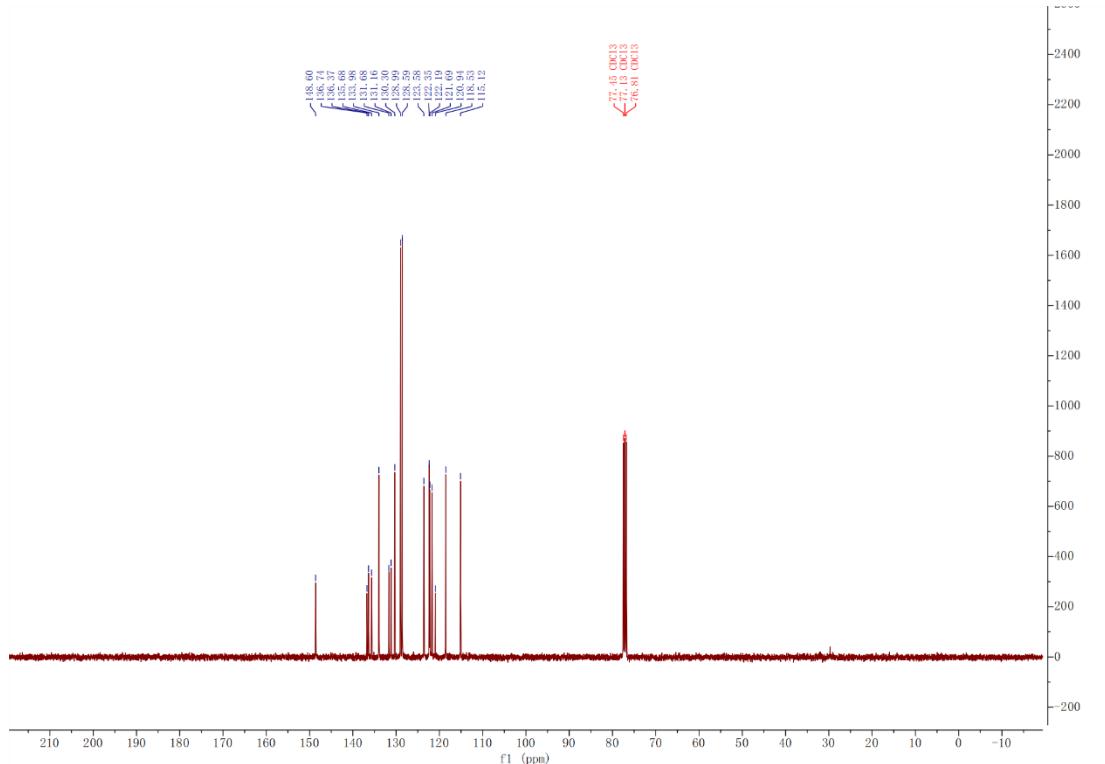


¹³C NMR spectrum of 4w

1-((4-chlorophenyl)thio)-3-(3-nitrophenyl)imidazo[1,5-a]pyridine(4x)

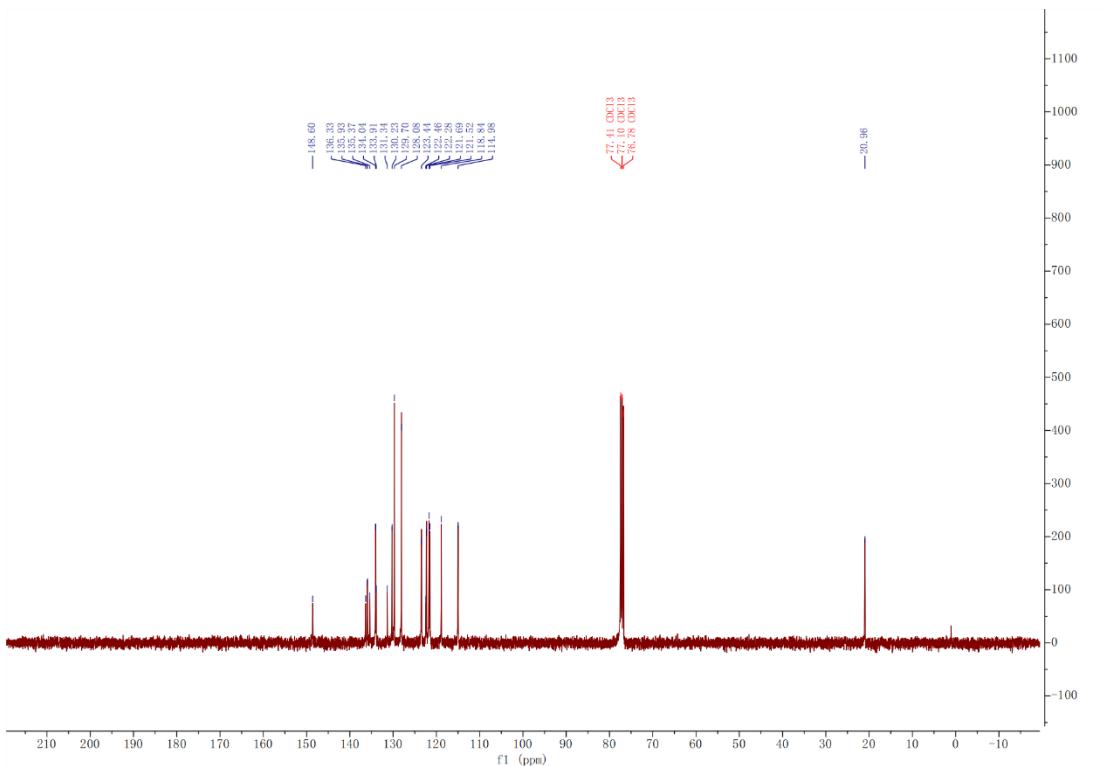
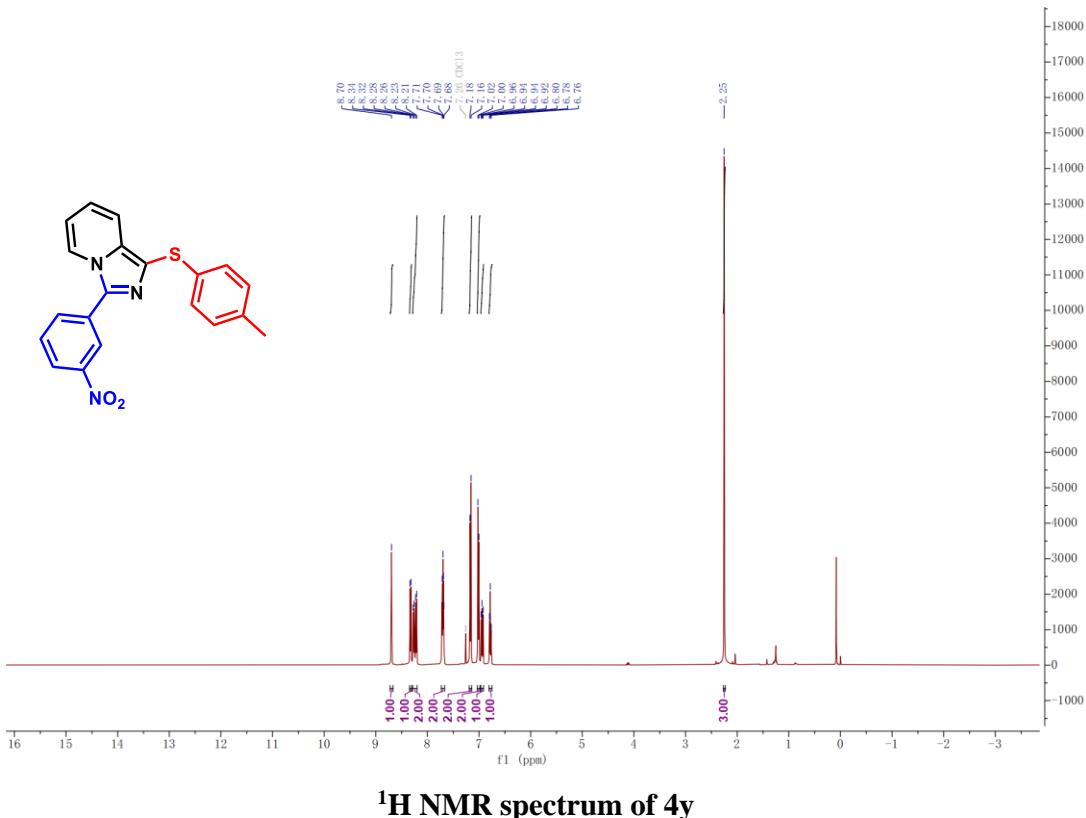


¹H NMR spectrum of 4x



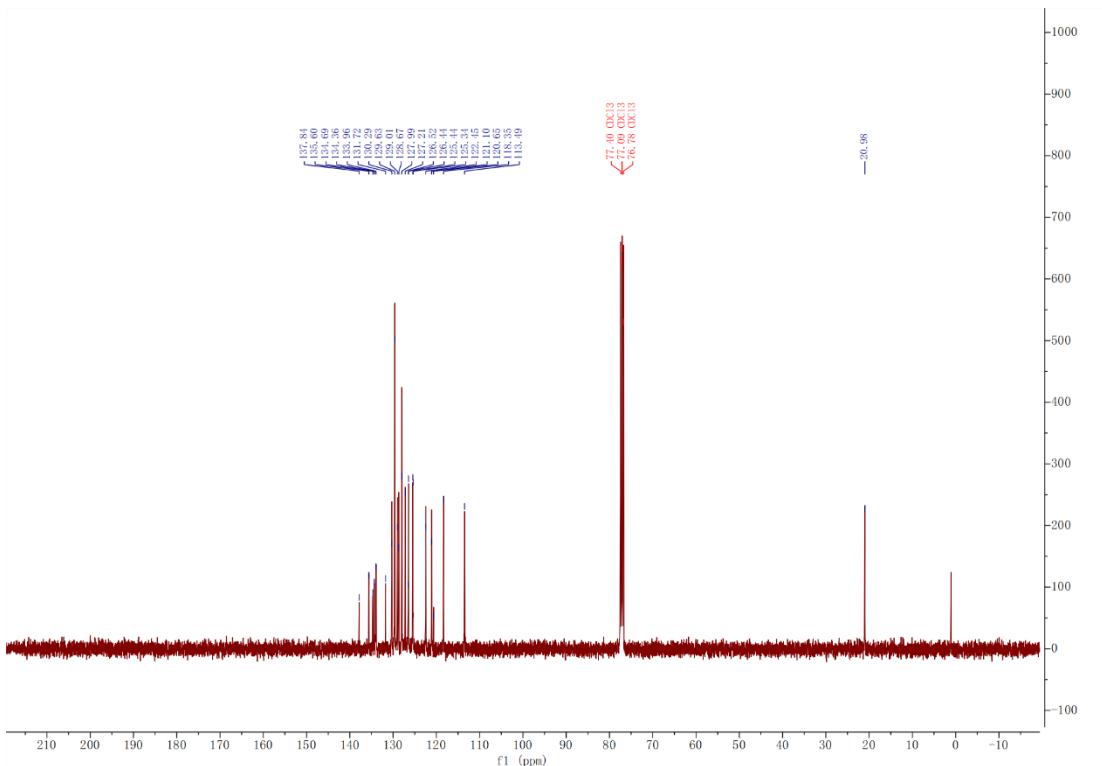
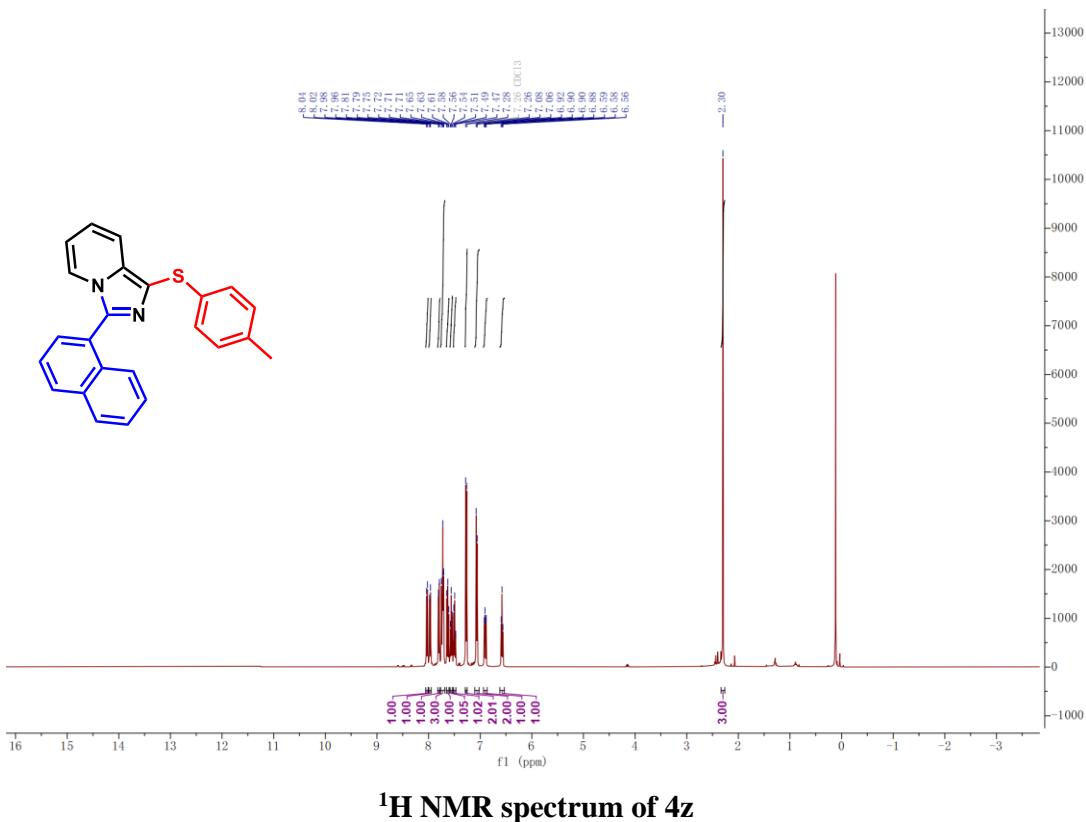
¹³C NMR spectrum of 4x

3-(3-nitrophenyl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine(4y)

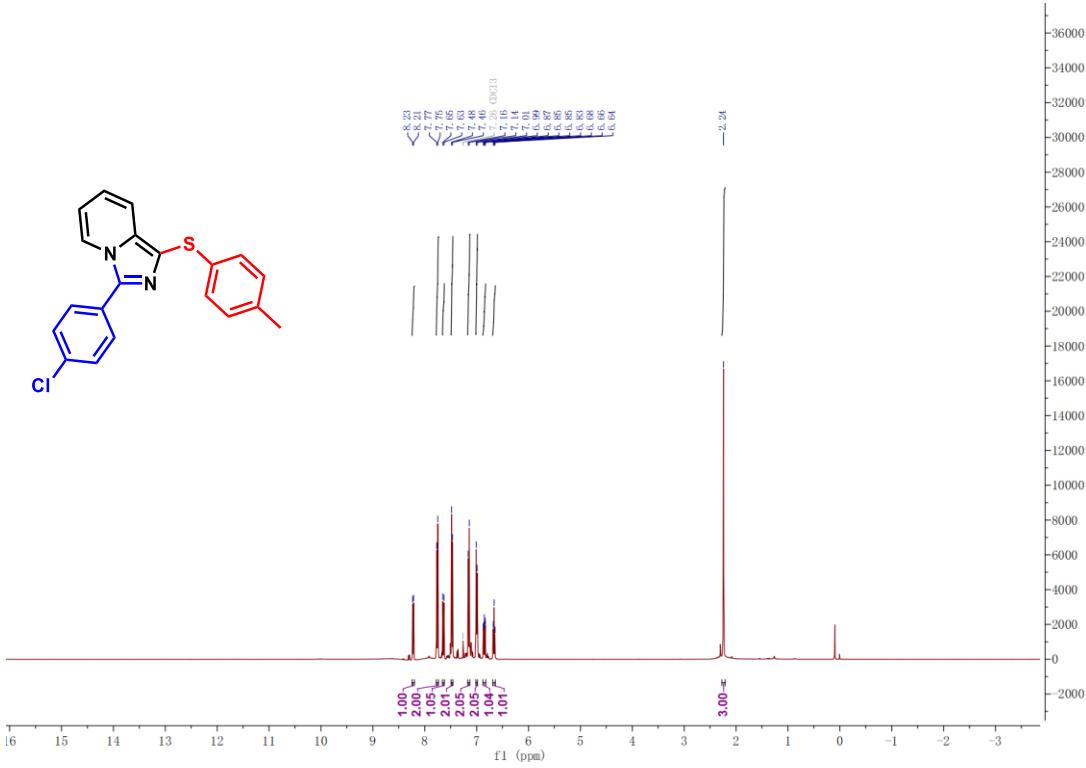


¹³C NMR spectrum of 4y

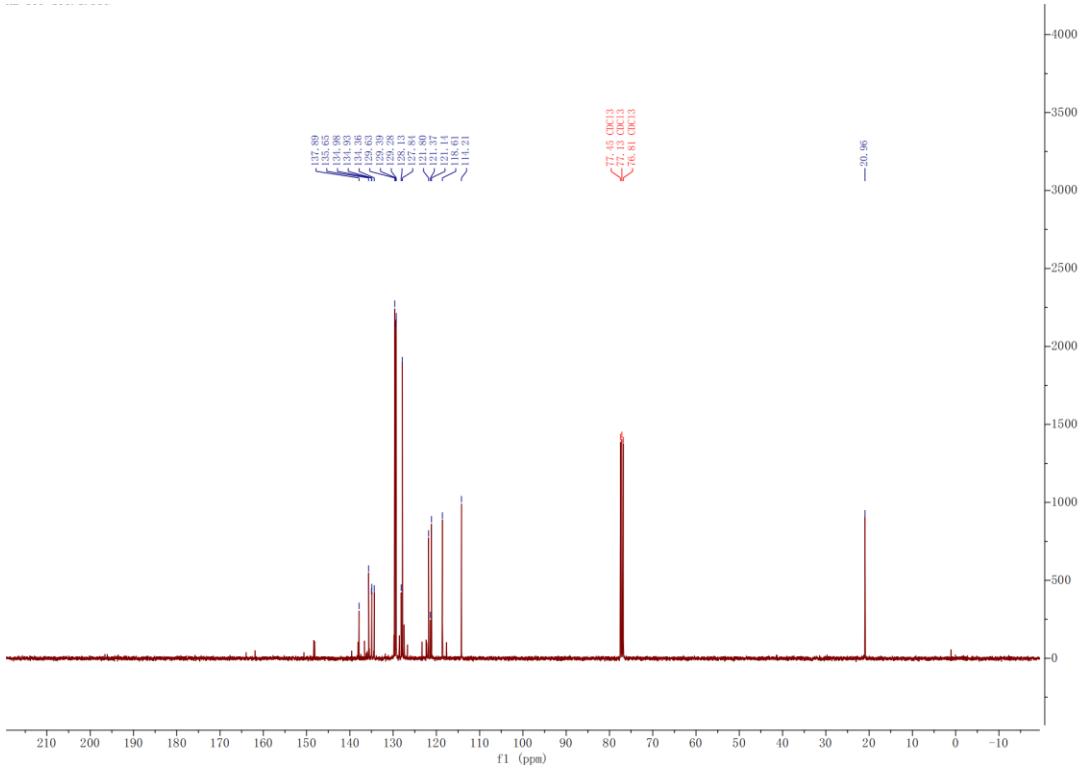
3-(naphthalen-1-yl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine(4z)



3-(4-chlorophenyl)-1-(*p*-tolylthio)imidazo[1,5-*a*]pyridine (4za)



¹H NMR spectrum of 4za



¹³C NMR spectrum of 4za