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Supporting Information

Iodine-Triphenylphosphine Mediated Sulfenylation of Imidazoheterocycles with Sodium Sulfinates

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Content

1. General information

^{1}H-NMR spectra were recorded on a Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$, ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$(δ = 77.00 ppm). High Resolution Mass spectra were recorded using a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (APEX IV, Bruker). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM).

2. General procedure

Iodine (0.3 mmol) was added to a solution of imidazoheterocycle **1** or **4** (0.3 mmol), sodium sulfinate (0.6 mmol) and triphenylphosphine (0.6 mmol) in DMF (3 mL), and the reaction mixture was stirred at 80℃ for 12 h. The reaction mixture was quenched by the addition of sat. aq. $Na_2S_2O_3$ (5 mL). Further stirring was followed by extraction with EtOAc (3*15 mL). The combined organic extracts were washed with water (10 mL) and brine (10 mL), dried with Na_2SO_4. After removal of solvents with a rotary evaporater, the residue was purified on a silica gel column using petroleum-ethyl acetate as eluent to afford the desired product.

3. Characterization data

2-Phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3a)[19d]

White solid; mp 96-97^{o}C (Lit. mp 95-97^{o}C); Yield: 95%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.8 Hz, 1H), 8.24 - 8.14 (m, 2H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 - 7.27 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.03 - 6.95 (m, 2H), 6.85 (td, *J* = 6.8, 0.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 147.2, 135.3, 133.5, 129.5, 128.7, 128.5, 128.4, 126.7, 126.1, 125.7, 124.6, 117.7, 113.1, 106.4.

6-Fluoro-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3b)

White solid; mp 118-121^{o}C; Yield: 90%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 - 8.18 (m, 3H), 7.72 (dd, *J* = 9.7, 4.9 Hz, 1H), 7.51 - 7.36 (m, 3H), 7.31 - 7.22 (m, 3H), 7.21 - 7.15 (m, 1H), 7.06 - 6.99 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9 (d, *J* = 237 Hz), 152.6 (d, *J* = 2.5 Hz), 144.7, 134.6, 133.2,129.7, 128.8, 128.6, 128.3, 126.4, 125.9, 118.6 (d, *J* = 2.4 Hz), 118.1 (d, *J* = 1.0 Hz), 111.6 (d, *J* = 4.2 Hz), 108.1.

HRMS (ESI): exact mass calculated for $C_{19}H_{14}FN_2S$ ($[M+H]^+$) 321.0862, found 321.0858.

6-Bromo-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3c)[19d]

White solid; mp 166-168^{o}C; Yield: 92%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.1 Hz, 1H), 8.25 - 8.13 (m, 2H), 7.61 (d, *J* = 9.4 Hz, 1H), 7.47 - 7.33 (m, 4H), 7.25 - 7.21 (m, 2H), 7.19 - 7.11 (m, 1H), 7.04 - 6.95 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 145.6, 134.7, 133.0, 130.2, 129.7, 128.9, 128.6, 128.4, 126.4, 125.8, 124.8, 118.4, 108.1, 107.2.

6-Chloro-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3d)[19a]

White solid; mp 150-152°C; Yield: 84%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 2.0, 0.8 Hz, 1H), 8.23 - 8.16 (m, 2H), 7.66 (dd, *J* = 9.5, 0.7 Hz, 1H), 7.48 - 7.34 (m, 3H), 7.29 (dd, *J* = 9.4, 2.0 Hz, 1H), 7.25 - 7.19 (m, 2H), 7.18 - 7.12 (m, 1H), 7.04 - 6.96 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 145.5, 134.7, 133.0, 129.7, 128.9, 128.6, 128.4, 128.1, 126.4, 125.8, 122.5, 121.6, 118.1, 107.3.

2-Phenyl-3-(phenylthio)-6-(trifluoromethyl)imidazo[1,2-a]pyridine (3e)

White solid; mp 106-108°C; Yield: 89%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.23 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 9.3 Hz, 1H), 7.53 - 7.35 (m, 4H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 - 7.13 (m, 1H), 7.08 - 6.97 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 146.9, 134.2, 132.7, 129.8, 129.2, 128.7, 128.5, 126.7, 126.0, 123.5 (q, *J* = 5.8 Hz), 123.4 (q, *J* = 271 Hz), 122.7 (q, *J* = 2.8 Hz), 118.5, 117.6 (q, *J* = 34.4 Hz), 108.7.

HRMS (ESI): exact mass calculated for $C_{20}H_{14}F_3N_2S$ ($[M+H]^+$) 371.0824, found 371.0827.

6-Methyl-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3f)[19d]

White solid; mp 130-133°C; Yield: 96%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.4 Hz, 2H), 8.06 (s, 1H), 7.62 (d, *J* = 9.1 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.23 - 7.09 (m, 4H), 7.00 (d, *J* = 7.4 Hz, 2H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 146.3, 135.7, 133.6, 129.8, 129.5, 128.6, 128.5, 128.4, 126.0, 125.5, 123.0, 122.3, 117.1, 105.8, 18.4.

8-Methyl-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3g)[19d]

White solid; mp 126-128°C; Yield: 91%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.5 Hz, 2H), 8.12 (d, *J* = 6.7 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.3 Hz, 2H), 6.98 (d, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 6.8 Hz, 1H), 2.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 147.5, 135.6, 133.8, 129.4, 128.6, 128.5, 128.4, 127.8, 126.0, 125.7, 125.5, 122.4, 113.1, 106.6, 16.9.

7-Methyl-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3h)[19d]

White solid; mp 170-172°C; Yield: 88%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.5 Hz, 2H), 8.11 (d, *J* = 6.9 Hz, 1H), 7.47 (s, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 - 7.29 (m, 1H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.66 (d, *J* = 6.7 Hz, 1H), 2.41 (s, 3H) .

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 147.5, 137.8, 135.5, 133.5, 129.4, 128.5, 128.4, 128.3, 125.9, 125.5, 123.6, 116.2, 115.6, 105.4, 21.3.

8-(Benzyloxy)-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3i)

White solid; mp 107-109°C; Yield: 90%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.2 Hz, 2H), 7.90 (dd, *J* = 6.6, 0.7 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 2H), 7.46 - 7.28 (m, 6H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 7.04 - 6.93 (m, 2H), 6.71 - 6.63 (m, 1H), 6.60 (d, *J* = 7.1 Hz, 1H), 5.43 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 148.1, 141.7, 136.3, 135.4, 133.4, 129.5, 128.8, 128.7, 128.5, 128.3, 128.2, 127.4, 126.1, 125.7, 117.6, 112.9, 107.5, 105.6, 71.2.
HRMS (ESI): exact mass calculated for $C_{26}H_{21}N_2OS$ ($[M+H]^+$) 409.1375, found 409.1365.

6-Bromo-8-methyl-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3j)

White solid; mp 144-145°C; Yield: 89%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.18 (d, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.35 (dd, *J* = 8.5, 5.9 Hz, 1H), 7.23 - 7.17 (m, 3H), 7.13 (t, *J* = 7.0 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 2.69 (s, 3H) .
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 146.0, 135.1, 133.3, 129.6, 129.0, 128.9, 128.7, 128.5, 128.5, 126.3, 125.8, 122.5, 108.0, 107.3, 16.7.
HRMS (ESI): exact mass calculated for $C_{20}H_{16}BrN_2S$ ($[M+H]^+$) 395.0212, found 395.0215.

2-(4-Methoxyphenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3k)[19b]

White solid; mp 106-108°C (Lit. mp 109-110°C); Yield: 99%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.8 Hz, 1H), 8.21 - 8.13 (m, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.12 (t, *J* = 7.3 Hz, 1H), 7.02 - 6.93 (m, 4H), 6.83 (t, *J* = 8.0 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 151.4, 147.2, 135.4, 129.7, 129.5, 126.6, 126.1, 126.1, 125.6, 124.5, 117.5, 113.9, 112.9, 105.4, 55.3.

2-(p-Tolyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3l)[19b]

White solid; mp 121-123°C (Lit. mp 122-123°C); Yield: 90%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 6.8 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.31 (t, *J* = 8.4, Hz, 1H), 7.28 - 7.16 (m, 4H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.02 - 6.96 (m, 2H), 6.84 (t, *J* = 6.8 Hz, 1H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 147.2, 138.6, 135.4, 130.6, 129.5, 129.2, 128.3, 126.6, 126.1, 125.6, 124.5, 117.6, 113.0, 106.0, 21.4.

2-(4-Nitrophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3m)[19b]

Yellow solid; mp 195-197°C (Lit. mp 199-201°C); Yield: 80%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.4 Hz, 2H), 8.32 (d, *J* = 6.8 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.25 - 7.12 (m, 3H), 6.99 (d, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 6.7 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.7, 147.4, 139.8, 134.3, 129.7, 129.0, 127.5, 126.6, 125.8, 124.7, 123.8, 118.1, 113.8, 108.5.

2-(4-Chlorophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3n)[19b]

White solid; mp 80-82°C (Lit. mp 83-85°C); Yield: 91%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dt, *J* = 6.9, 1.1 Hz, 1H), 8.16 (dt, *J* = 8.0, 2.4 Hz ,2H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.40 (d, *J* = 9.2 Hz ,2H), 7.36 - 7.32 (m, 1H), 7.24 - 7.17 (m, 2H), 7.17 - 7.10 (m, 1H), 7.02 - 6.95 (m, 2H), 6.88 (td, *J* = 6.8, 1.1 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 147.2, 134.9, 134.7, 131.9, 129.7, 129.6, 128.7, 127.0, 126.3, 125.7, 124.6, 117.7, 113.3, 106.6.

2-(2-Chlorophenyl)-3-(phenylthio)imidazo[1,2-a]pyridine (3o)[19d]

White solid; mp 135-137°C; Yield: 81%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.8 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.40 - 7.27 (m, 3H), 7.17 (t, *J* = 7.5 Hz, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.00 - 6.83 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 147.0, 134.9, 134.2, 132.9, 132.4, 129.9, 129.9, 129.4, 126.6, 126.5, 126.1, 126.1, 124.7, 118.1, 113.3, 109.3.

3-(Phenylthio)-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (3p)[19d]

White solid; mp 158-160°C; Yield: 89%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 6.8 Hz, 1H), 7.98 (dd, *J* = 3.6, 0.9 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.37 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.16 - 7.07 (m, 2H), 7.08 - 6.99 (m, 2H), 6.85 (t, *J* = 6.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 146.9, 136.3, 134.7, 129.5, 127.8, 126.9, 126.9, 126.7, 126.3, 126.0, 124.4, 117.5, 113.2, 105.6.

2-Methyl-3-(phenylthio)imidazo[1,2-a]pyridine (3q)[19b]

White solid; mp 80-82°C (Lit. mp 86-88°C); Yield: 72%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 6.6 Hz, 1H), 7.60 (d, *J* = 8.9 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 2H), 6.81 (t, *J* = 6.7 Hz, 1H), 2.58 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.7, 147.0, 135.7, 129.3, 126.1, 126.0, 125.7, 124.4, 117.1, 112.7, 107.5, 14.0.

3-(Phenylthio)imidazo[1,2-a]pyridine (3r)[19d]

White solid; mp 85-88°C; Yield: 77%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 6.8 Hz, 1H), 7.99 (s, 1H), 7.71 (d, *J* = 9.0 Hz, 1H), 7.30 (t, *J* = 8.5 Hz, 1H), 7.24 - 7.17 (m, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.03 - 6.96 (m, 2H), 6.87 (t, *J* = 6.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 142.5, 135.3, 129.3, 126.3, 126.2, 126.05, 124.4, 118.2, 113.2, 110.8.

2-Phenyl-3-(p-tolylthio)imidazo[1,2-a]pyridine (3s)[19b]

White solid; mp 141-144°C (Lit. mp 145-147°C); Yield: 99%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 6.7 Hz, 1H), 8.21 (d, *J* = 7.4 Hz, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 - 7.27 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.84 (t, *J* = 6.7 Hz, 1H), 2.25 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 147.1, 136.1, 133.5, 131.6, 130.3, 128.6, 128.5, 126.6, 125.9, 124.6, 117.7, 113.1, 107.0, 20.9.

3-((4-Chlorophenyl)thio)-2-phenylimidazo[1,2-a]pyridine (3t)[19d]

White solid; mp 165-167°C; Yield: 93%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 6.8, 0.8 Hz, 1H), 8.21-8.13 (m, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.48 - 7.41 (m, 2H), 7.41 - 7.31 (m, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.97 - 6.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 147.3, 133.9, 133.3, 132.2, 129.7, 128.8, 128.6, 128.4, 127.0, 126.9, 124.4, 117.9, 113.3, 105.8.

3-((4-Bromophenyl)thio)-2-phenylimidazo[1,2-a]pyridine (3u)[19a]

White solid; mp 179-181°C; Yield: 87%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 6.6 Hz, 1H), 8.17 (d, *J* = 7.4 Hz, 2H), 7.73 (d, *J* = 9.0 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.40 - 7.28 (m, 4H), 6.88 - 6.84 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 147.3, 134.6, 133.2, 132.5, 128.8, 128.5, 128.4, 127.2, 126.9, 124.4, 119.9, 117.8, 113.3, 105.6.

8-((2-Phenylimidazo[1,2-a]pyridin-3-yl)thio)quinolone (3v)

White solid; mp 217-218°C; Yield: 87%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.26 (m, 3H), 8.18 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.78 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 8.3, 4.3 Hz, 1H), 7.43 - 7.28 (m, 4H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.83 (t, *J* = 6.8 Hz, 1H), 6.64 (d, *J* = 7.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 149.7, 147.6, 145.3, 136.5, 135.6, 133.4, 128.8, 128.6, 128.5, 128.4, 127.0, 126.7, 125.1, 124.8, 123.7, 122.0, 117.8, 113.1, 105.4.

HRMS (ESI): exact mass calculated for $C_{22}H_{16}N_3S$ ($[M+H]^+$) 354.1065, found 354.1059.

2-Phenyl-3-(pyridin-3-ylthio)imidazo[1,2-a]pyridine (3w)

White solid; mp 114-117°C; Yield: 88%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 2.5 Hz, 2H), 8.28 (d, *J* = 6.8 Hz, 1H), 8.19 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.47 - 7.34 (m, 4H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.91 (t, *J* = 6.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 147.4, 147.4, 147.1, 133.3, 133.1, 132.7, 128.9, 128.6, 128.4, 127.0, 124.3, 124.2, 118.0, 113.5, 104.6.

HRMS (ESI): exact mass calculated for $C_{18}H_{14}N_3S$ ([M+H]+) 304.0908, found 304.0903.

3-(Methylthio)-2-phenylimidazo[1,2-a]pyridine (3x)[19c]

White solid; mp 66-67°C; Yield: 43%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.8 Hz, 1H), 8.29 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.27 (t, *J* = 8.0 Hz,1H), 6.91 (t, *J* = 6.7 Hz, 1H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 146.4, 133.9, 128.4, 128.3, 125.9, 124.3, 117.7, 112.7, 111.4, 18.2.

3-(Cyclopropylthio)-2-phenylimidazo[1,2-a]pyridine (3y)

Yellow oil; Yield: 75%;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.8 Hz, 1H), 8.27 (d, *J* = 7.7 Hz, 2H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.32 - 7.23 (t, *J* = 8.0 Hz, 1H), 6.91 (t, *J* = 6.8 Hz, 1H), 2.19 - 2.07 (m, 1H), 0.72 (q, *J* = 6.5 Hz, 2H), 0.60 (q, *J* = 6.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 146.4, 133.9, 128.5, 128.2, 125.9, 124.4, 117.6, 112.6, 111.3, 16.4, 8.0.
HRMS (ESI): exact mass calculated for $C_{16}H_{15}N_2S$ ($[M+H]^+$) 267.0956, found 267.0951.

3-(Butylthio)-2-phenylimidazo[1,2-a]pyridine (3z)[19a]

Yellow oil; Yield: 74%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (dt, *J* = 6.9, 1.1 Hz, 1H), 8.36 - 8.28 (m, 2H), 7.66 (dt, *J* = 9.0, 1.0 Hz, 1H), 7.52 - 7.42 (m, 2H), 7.42 - 7.34 (m, 1H), 7.31 - 7.23 (m, 1H), 6.91 (td, *J* = 6.8, 1.1 Hz, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.48 - 1.23 (m, 4H), 0.76 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 146.4, 134.0, 128.4, 128.3, 128.2, 125.9, 124.4, 117.6, 112.6, 110.5, 35.5, 31.6, 21.8, 13.6.

6-Phenyl-5-(phenylthio)imidazo[2,1-b]thiazole (5a)[19d]

White solid; mp 130-132°C; Yield: 95%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.4 Hz, 2H), 7.41 - 7.39 (m, 3H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 4.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 151.5, 135.9, 133.6, 129.5, 128.5, 128.2, 127.6, 126.2, 126.0, 118.1, 113.0, 107.9.

6-Phenyl-5-(p-tolylthio)imidazo[2,1-b]thiazole (5b)

White solid; mp 100-101°C; Yield: 95%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 2H), 7.41 - 7.39 (m, 3H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 4.1 Hz, 1H), 2.26 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 151.3, 136.2, 133.7, 132.3, 130.3, 128.5, 128.2, 127.6, 126.3, 118.1, 112.9, 108.5, 21.0.
HRMS (ESI): exact mass calculated for $C_{18}H_{15}N_2S_2$ ($[M+H]^+$) 323.0671, found 323.0673.

5-((4-Bromophenyl)thio)-6-phenylimidazo[2,1-b]thiazole (5c)

White solid; mp 111-113°C; Yield: 90%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 2H), 7.44 - 7.28 (m, 6H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 4.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 151.8, 135.2, 133.4, 132.5, 128.5, 128.4, 127.5, 127.4, 120.0, 118.0, 113.3, 107.1.
HRMS (ESI): exact mass calculated for $C_{17}H_{12}BrN_2S_2$ ($[M+H]^+$) 386.9619, found 386.9626.

2-Phenyl-3-(phenylthio)benzo[d]imidazo[2,1-b]thiazole (5d)[19d]

White solid; mp 149-151°C; Yield: 90%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 - 8.31 (m, 1H), 8.09 (d, *J* = 7.0 Hz, 2H), 7.68 - 7.66 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.36 - 7.27 (m, 3H), 7.27 - 7.19 (m, 2H), 7.17 - 7.11 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 150.9, 136.6, 133.5, 133.3, 130.3, 129.7, 128.5, 128.4, 127.9, 126.4, 126.2, 125.7, 125.0, 124.1, 114.5, 110.0.

3-((4-Chlorophenyl)thio)-2-phenylbenzo[d]imidazo[2,1-b]thiazole (5e)

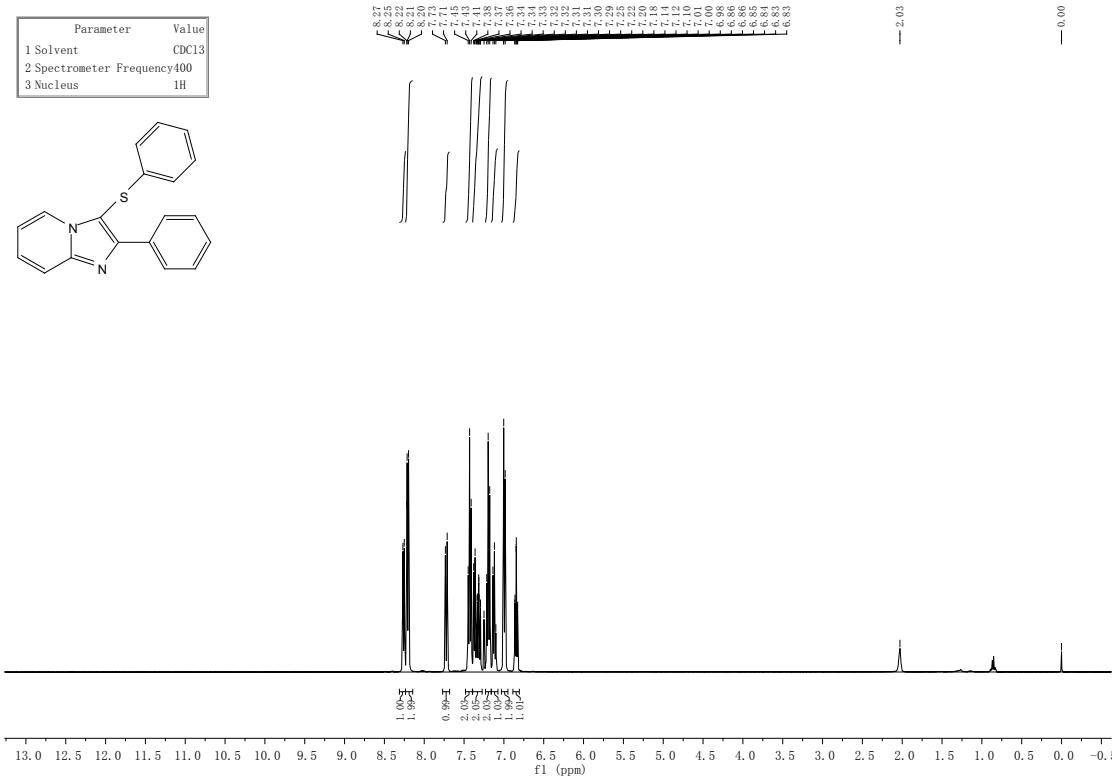
White solid; mp 167-169^{o}C; Yield: 95%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.21 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.74 - 7.64 (m, 1H), 7.41 (t, *J* = 10.0 Hz, 2H), 7.37 - 7.28 (m, 3H), 7.23 - 7.16 (m, 2H), 7.12 - 7.03 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 151.1, 135.2, 133.5, 133.1, 132.3, 130.3, 129.9, 128.6, 128.5, 127.9, 127.0, 126.6, 125.2, 124.2, 114.3, 109.4.
HRMS (ESI): exact mass calculated for $C_{21}H_{14}ClN_2S_2$ ($[M+H]^+$) 393.0281, found 393.0287.

2-Phenyl-3-(phenylthio)imidazo[1,2-a]pyrimidine (5f)[19a]

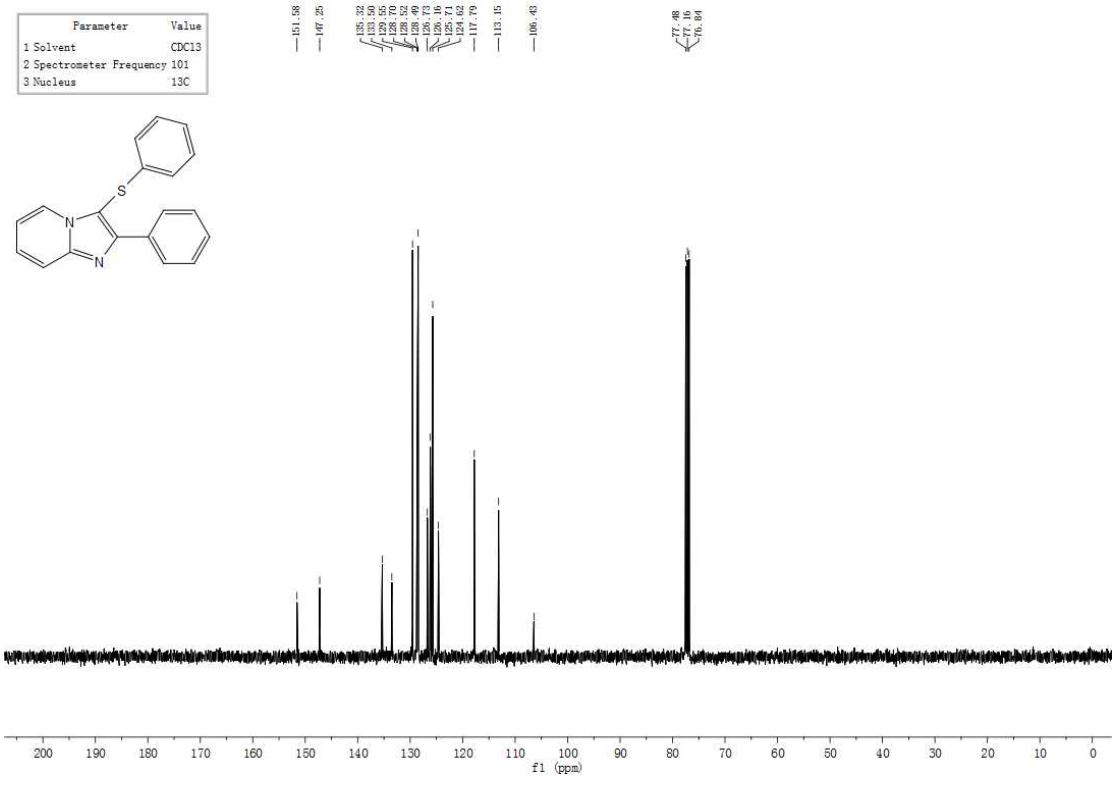
White solid; mp 125-126^{o}C; Yield: 91%;
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68-8.66 (m, 1H), 8.56 - 8.53 (m, 1H), 8.41 - 8.32 (m, 2H), 7.53 - 7.37 (m, 3H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.20 - 7.13 (m, 1H), 7.03 (d, *J* = 7.5 Hz, 2H), 6.96-6.94 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 151.7, 150.1, 134.3, 132.8, 132.2, 129.7, 129.2, 128.7, 128.6, 126.5, 125.9, 109.4, 105.4.

4. ^{1}H & ^{13}C-NMR Spectra

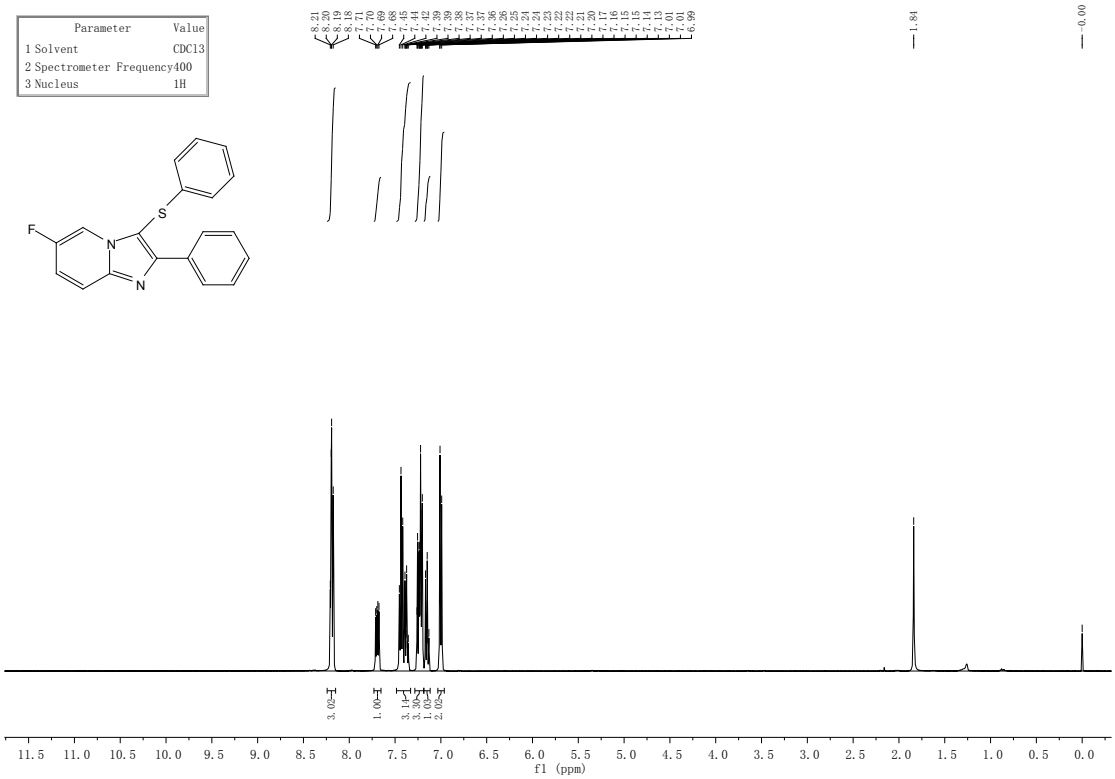
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



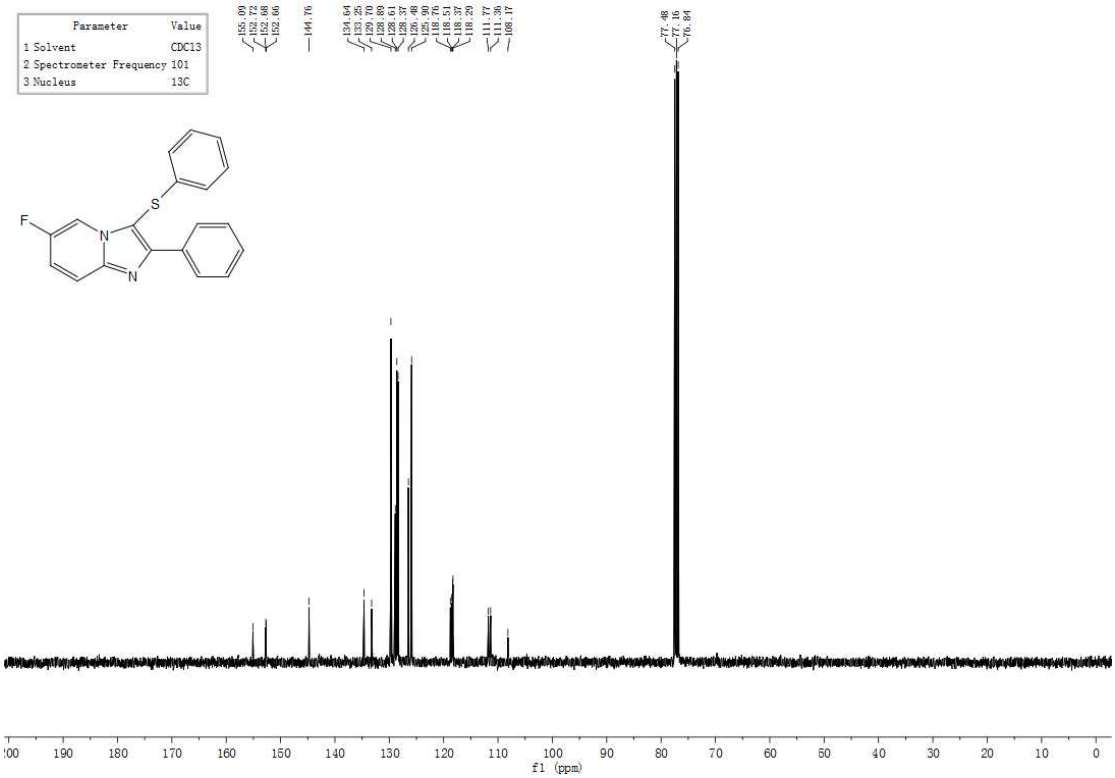
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



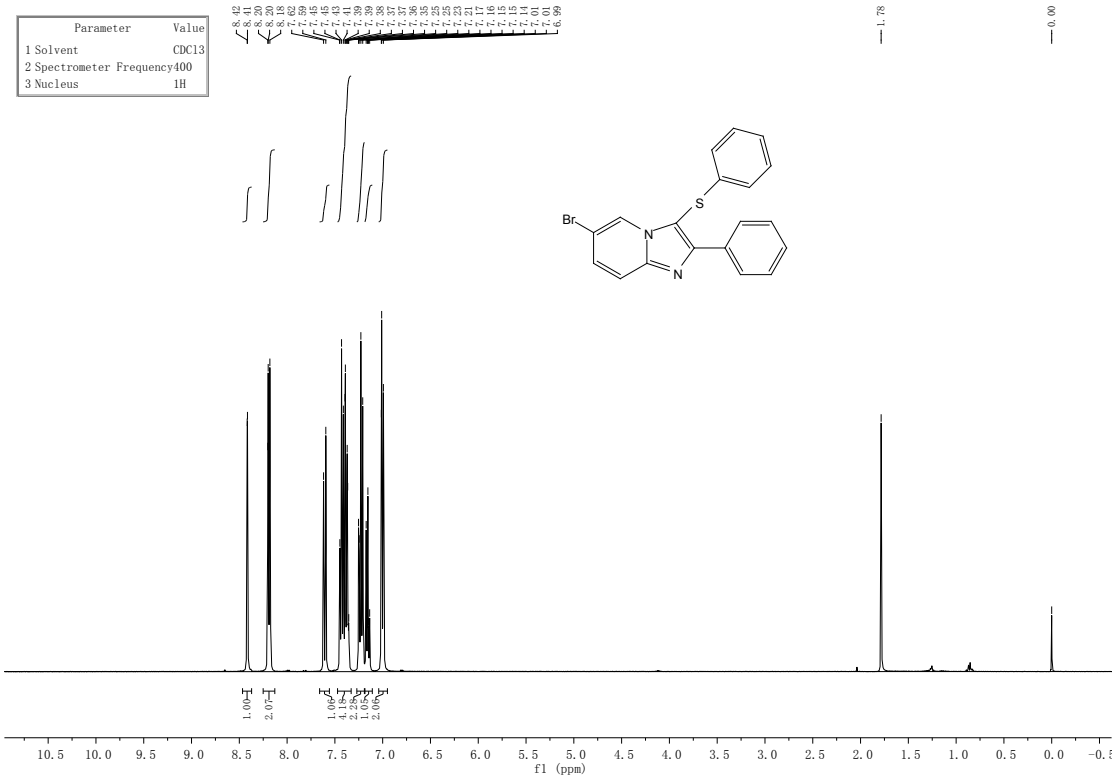
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



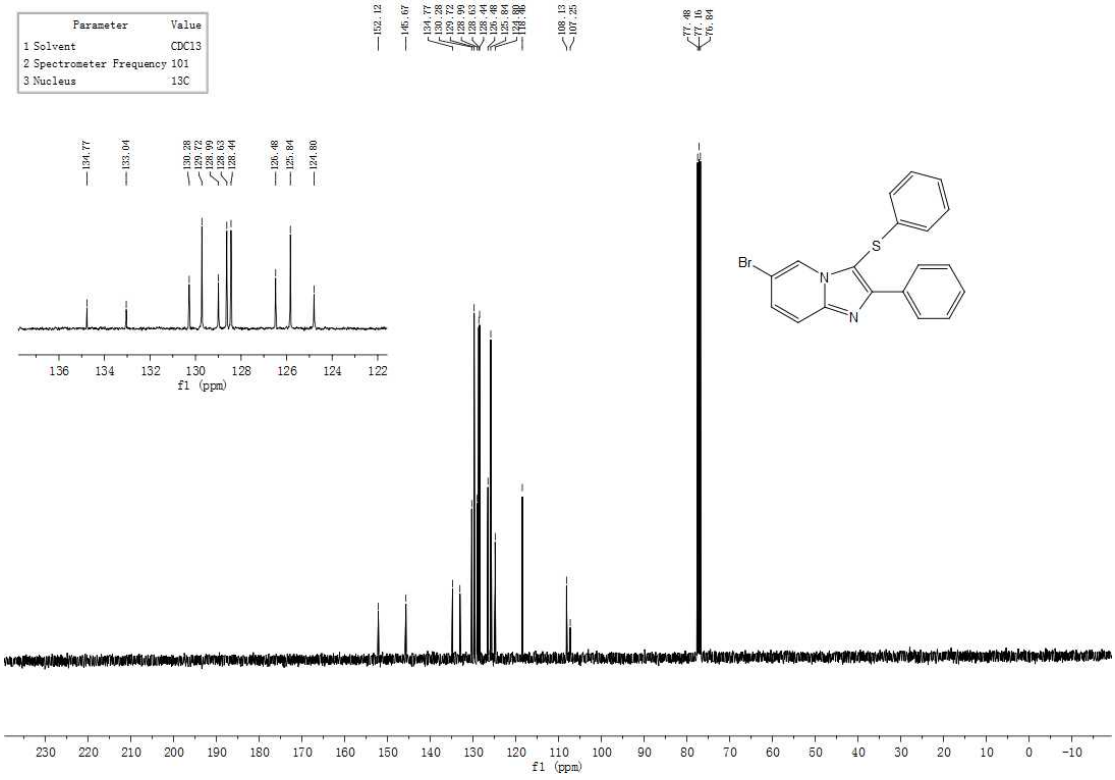
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



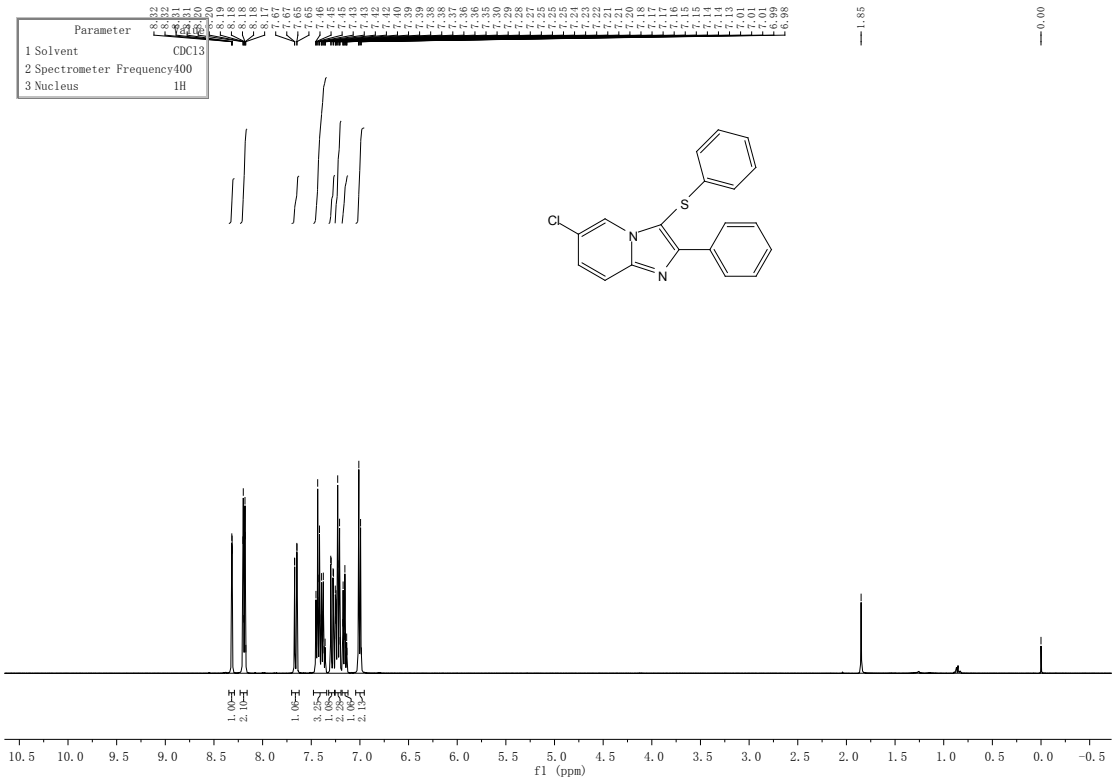
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



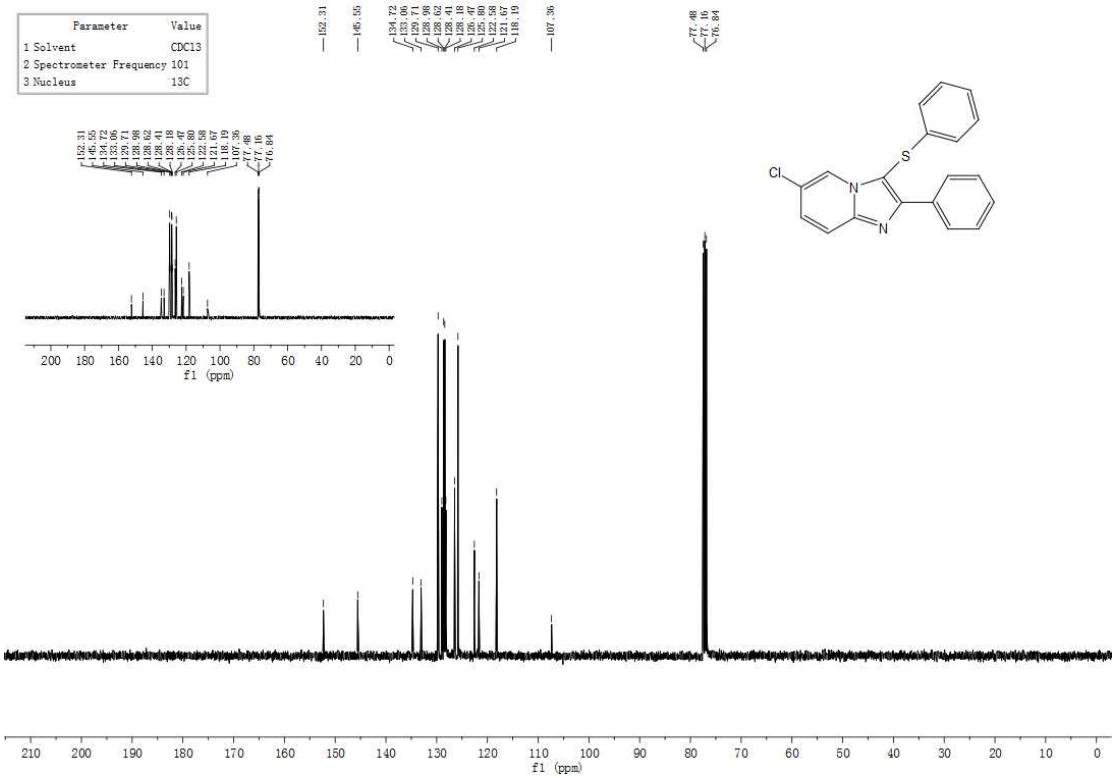
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



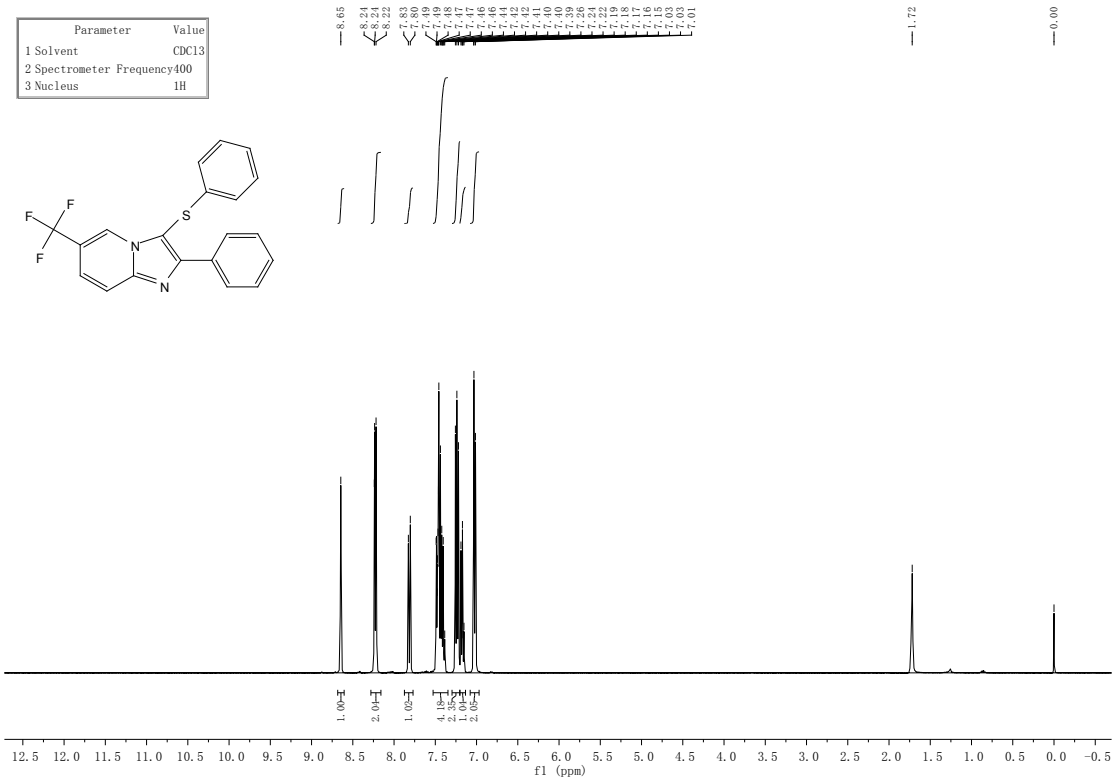
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



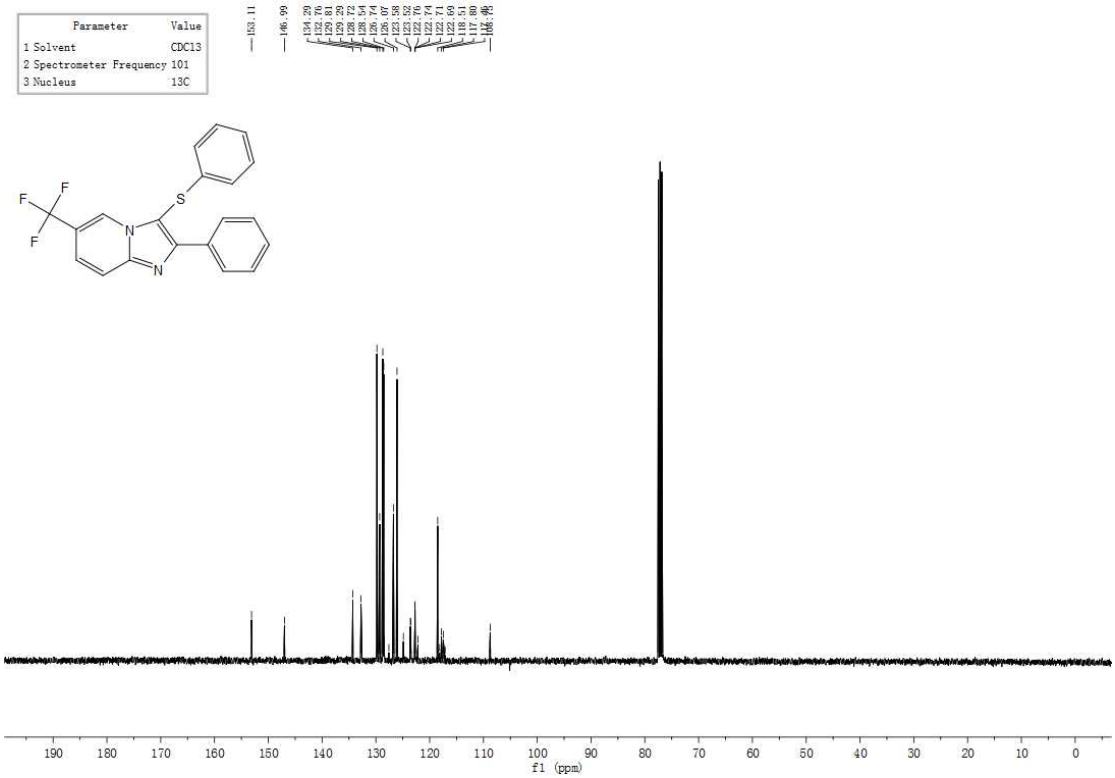
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



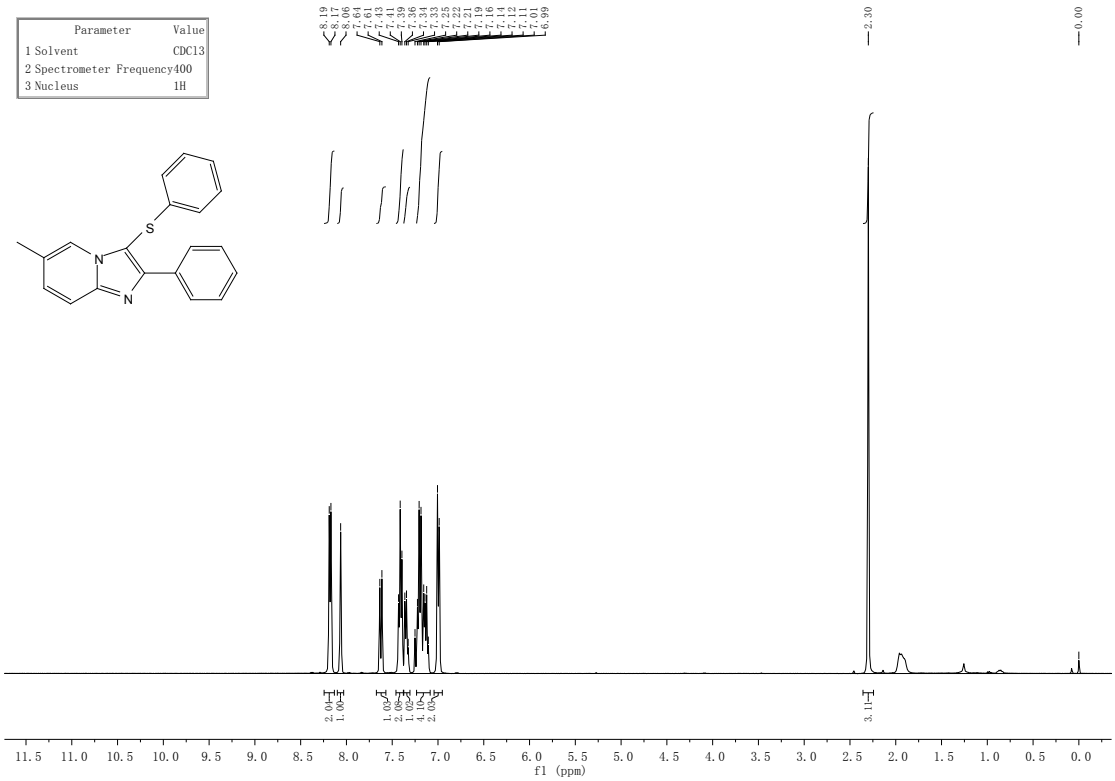
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



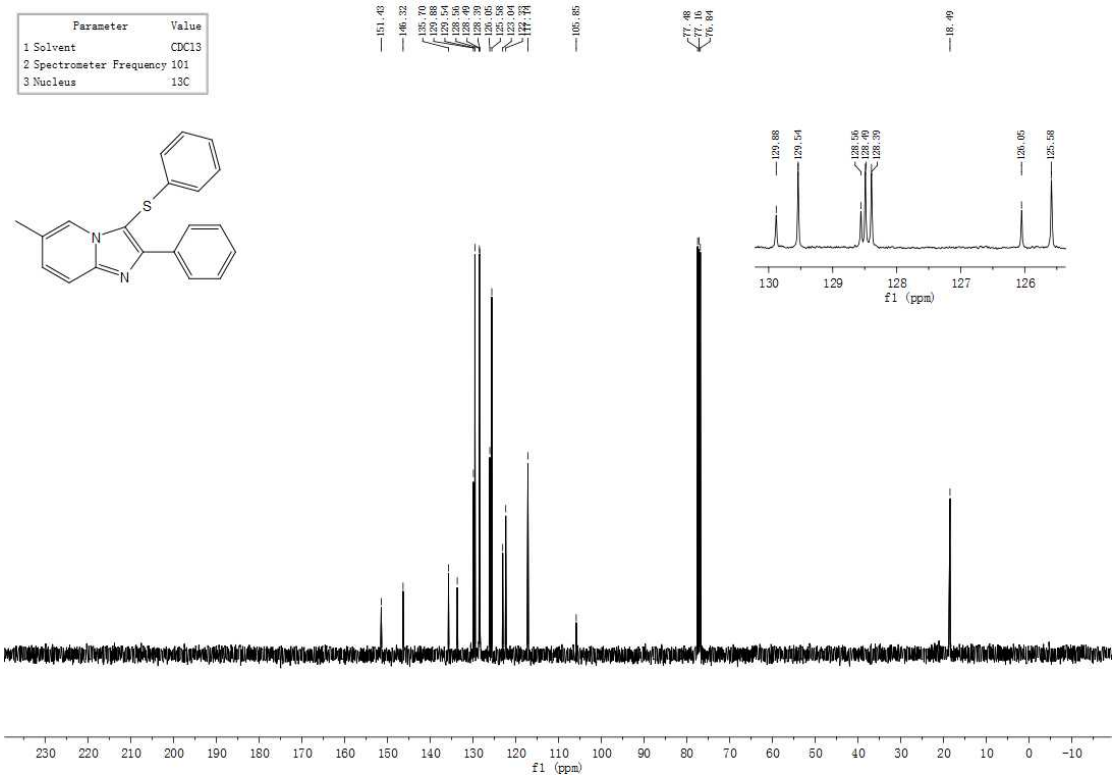
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



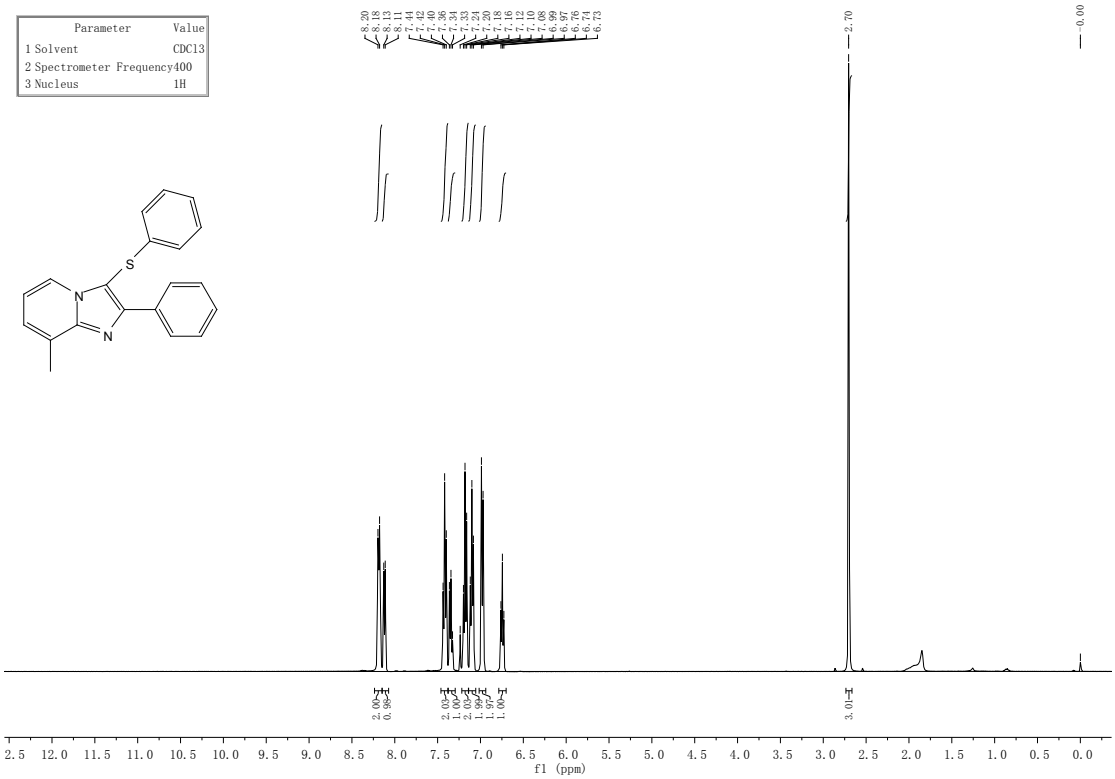
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



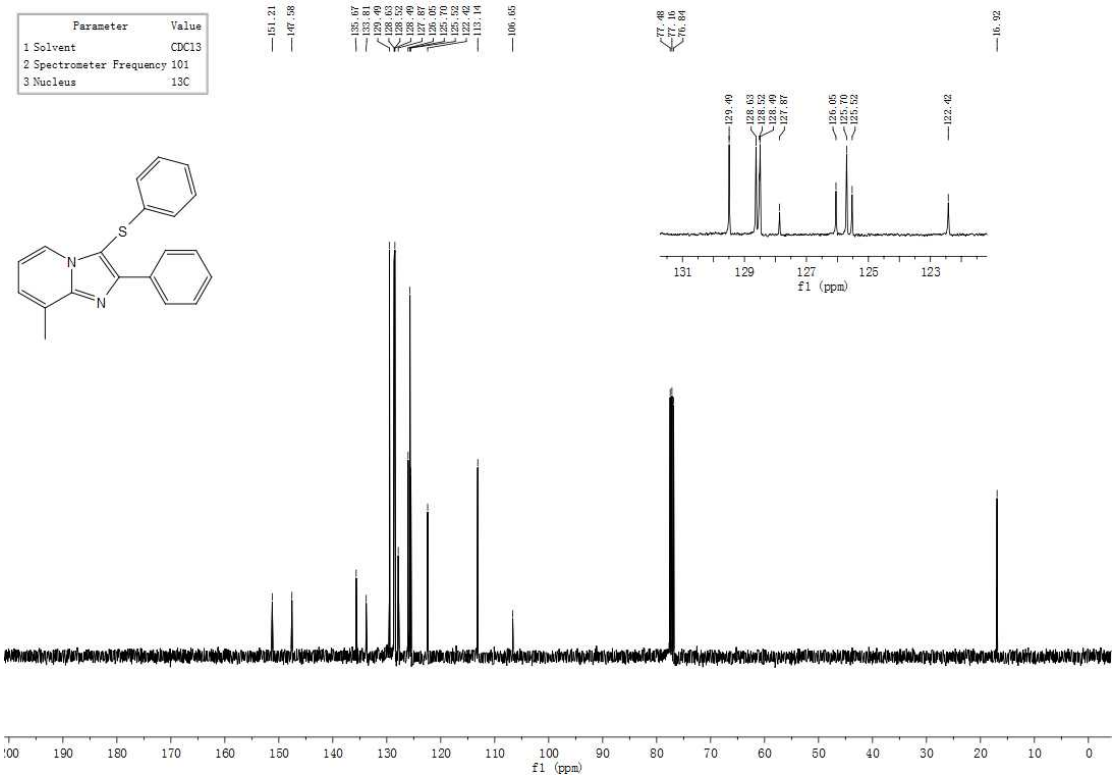
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



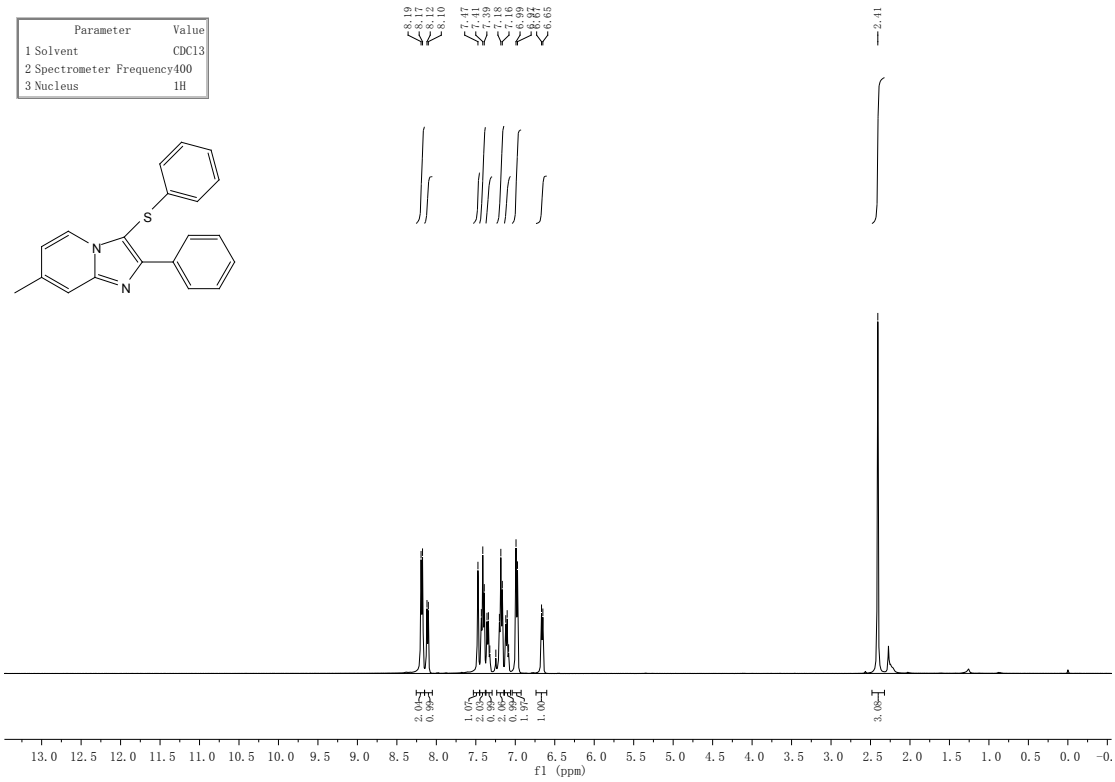
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



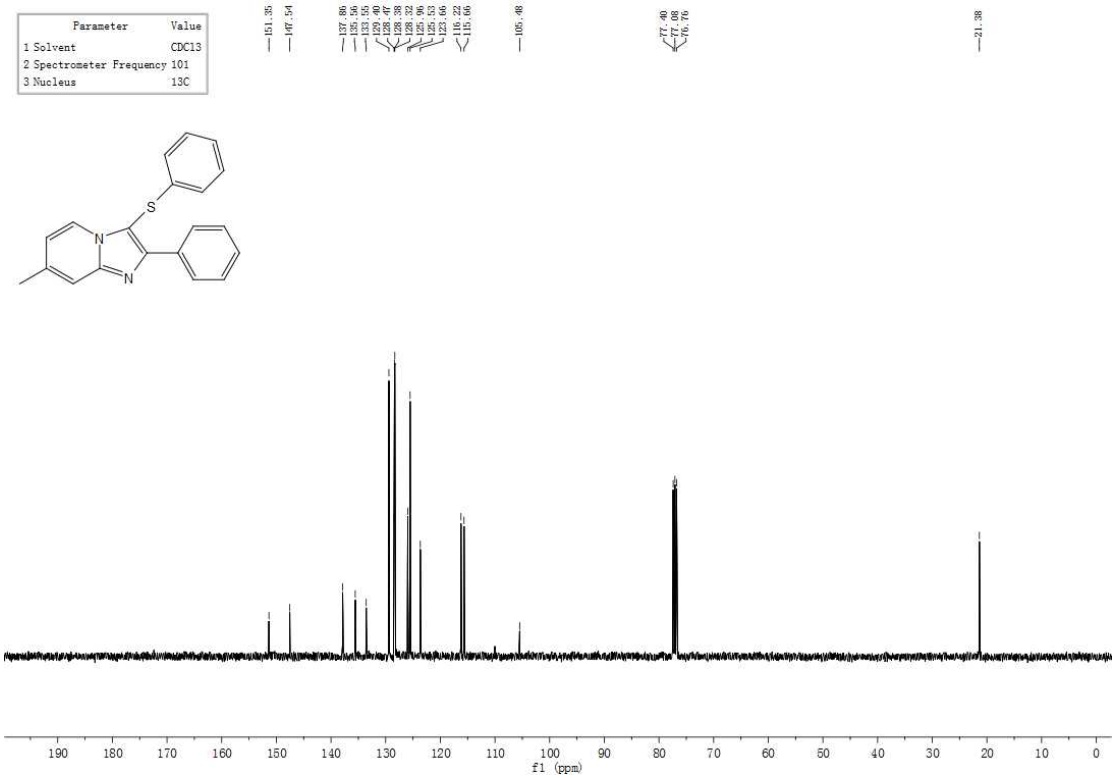
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



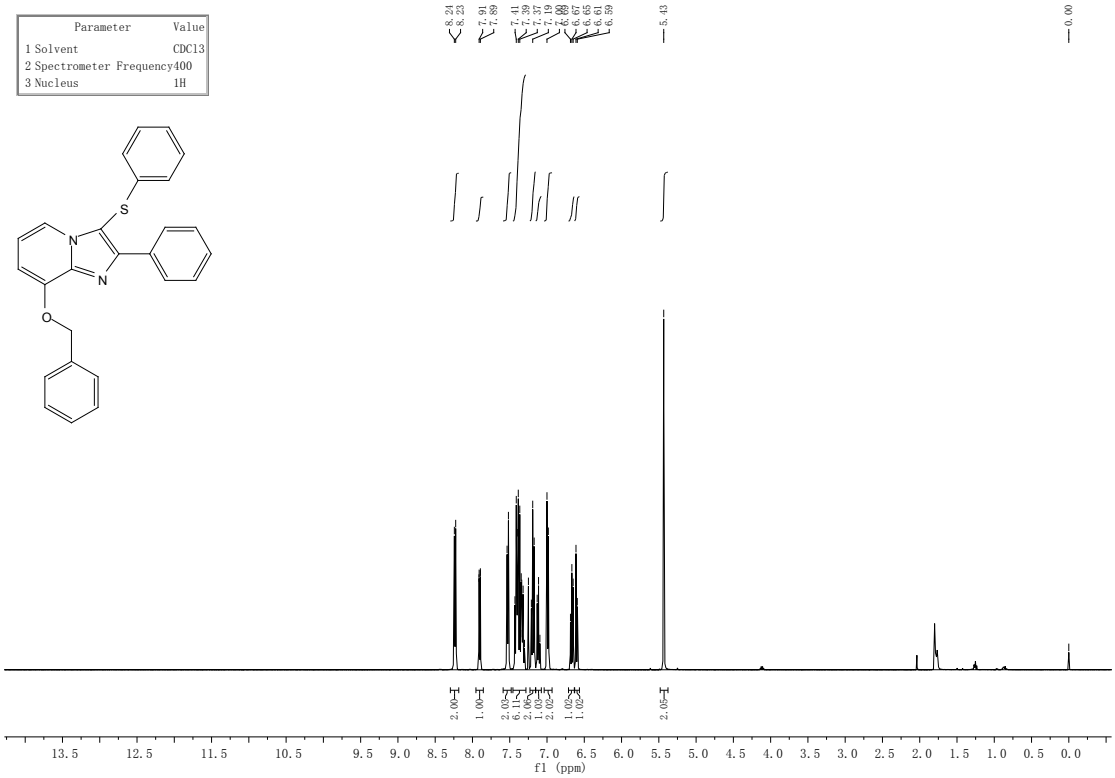
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



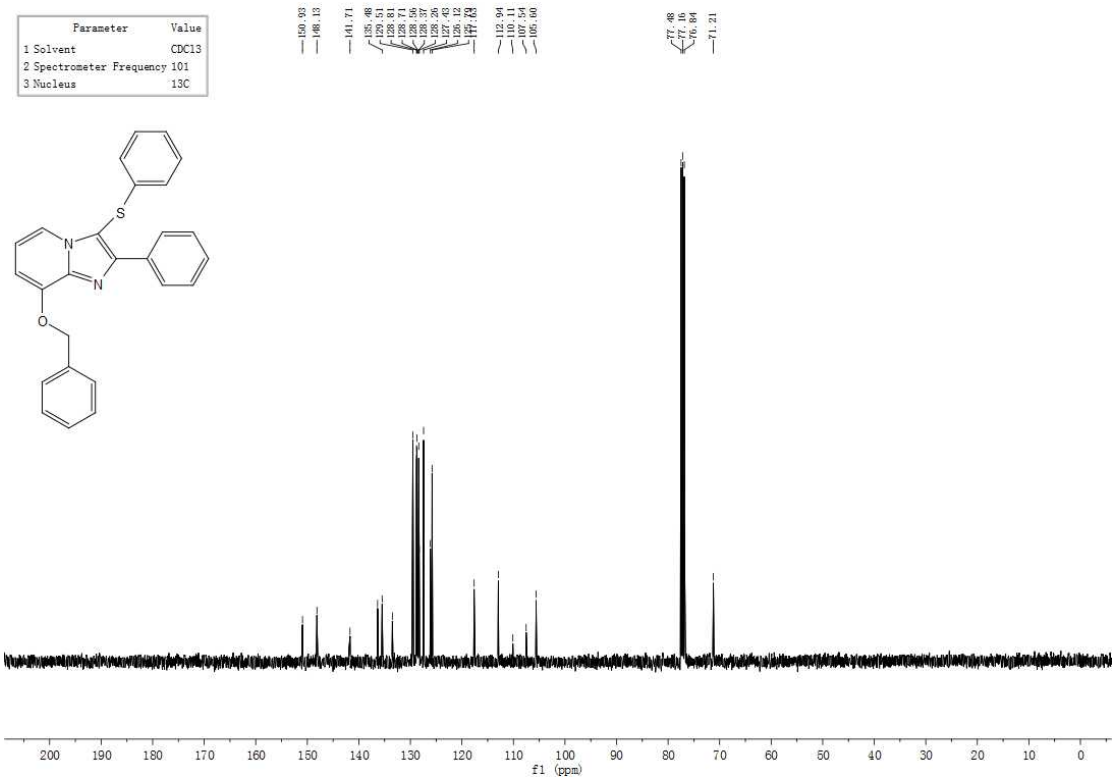
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



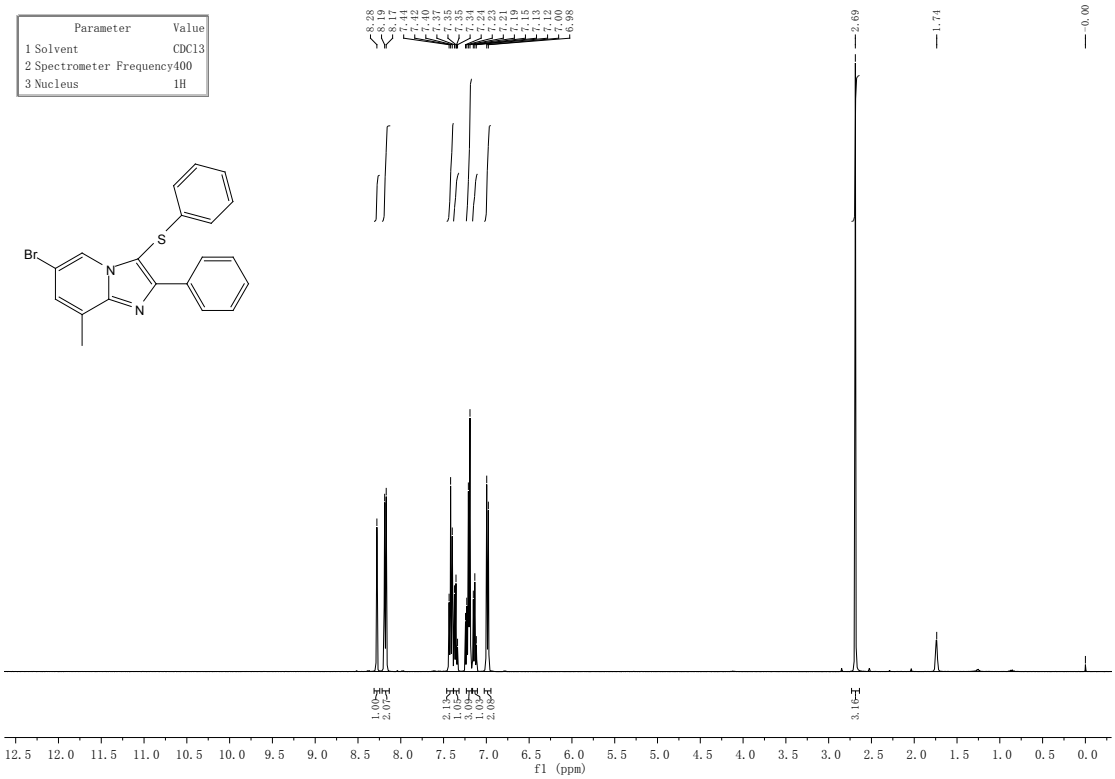
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



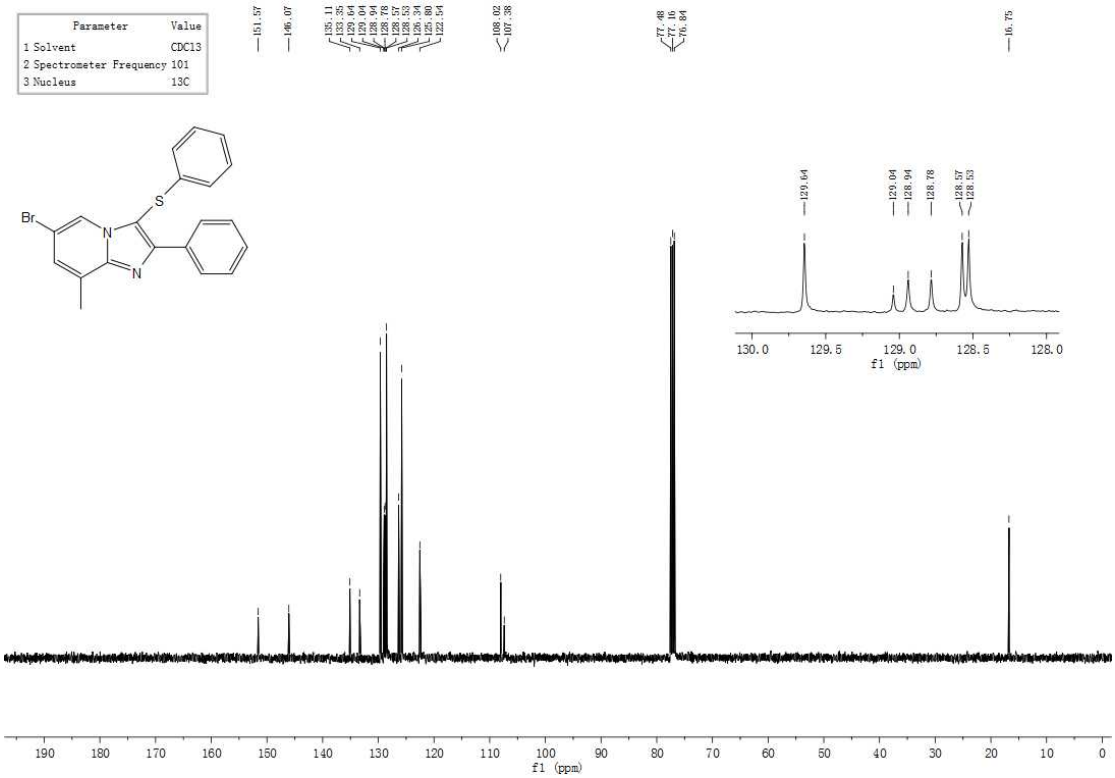
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



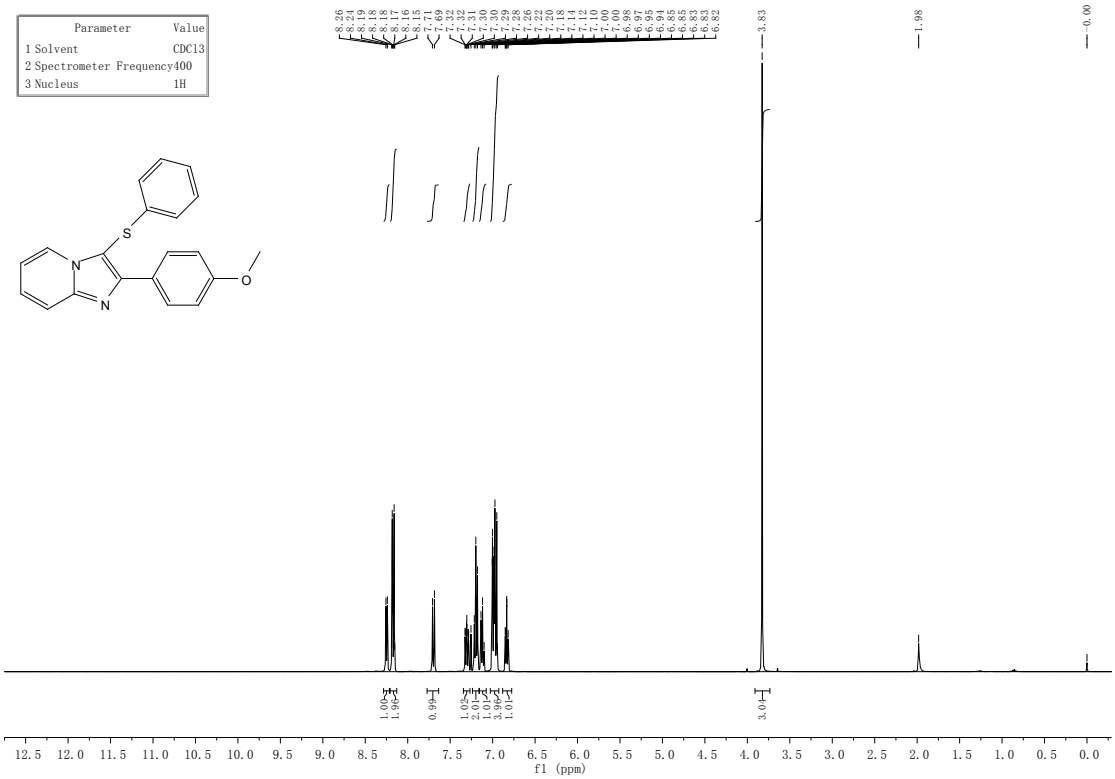
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



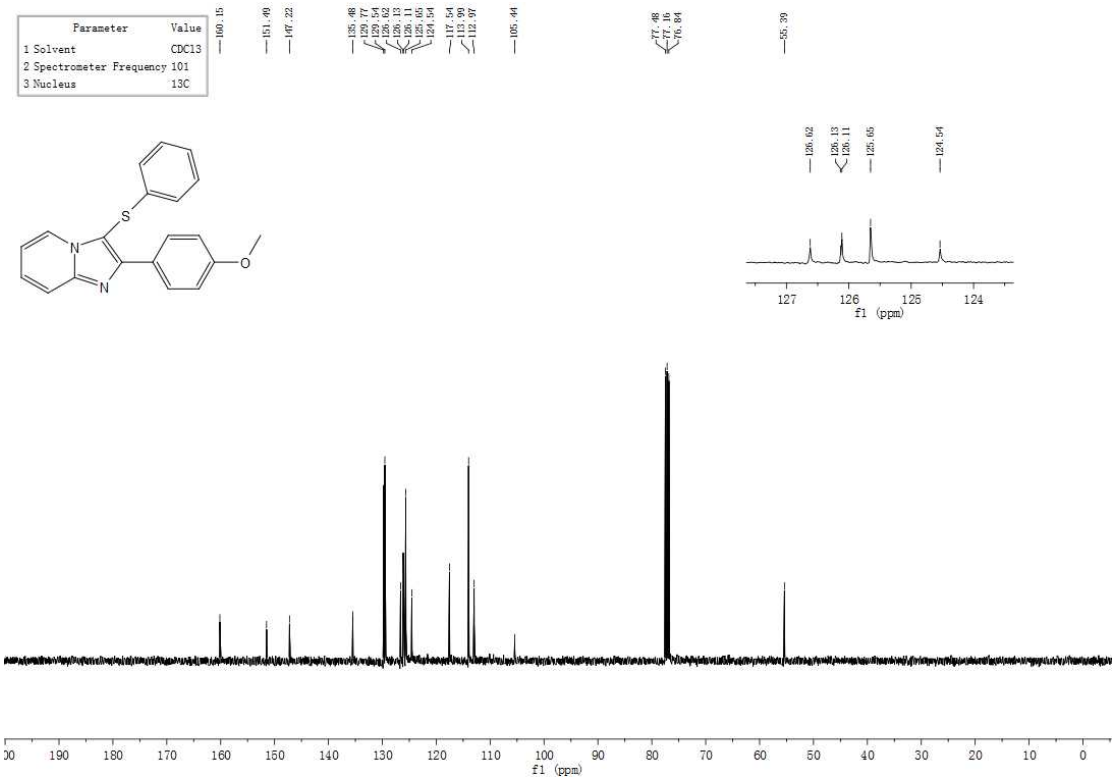
^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



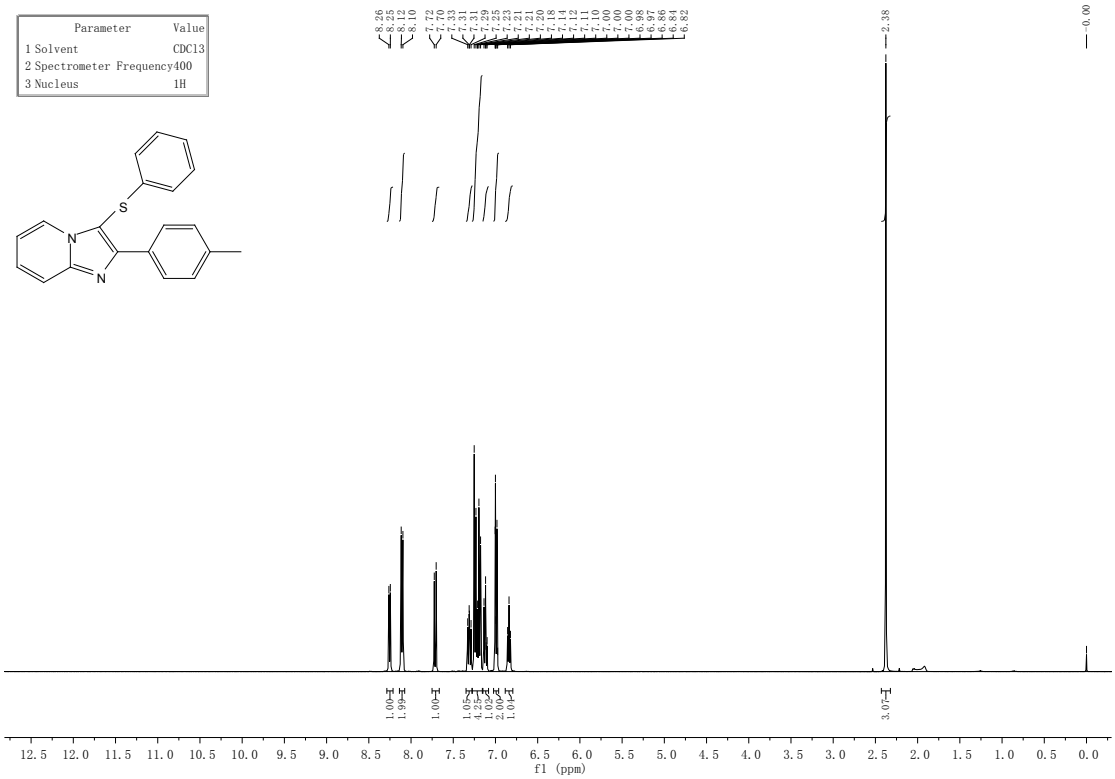
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



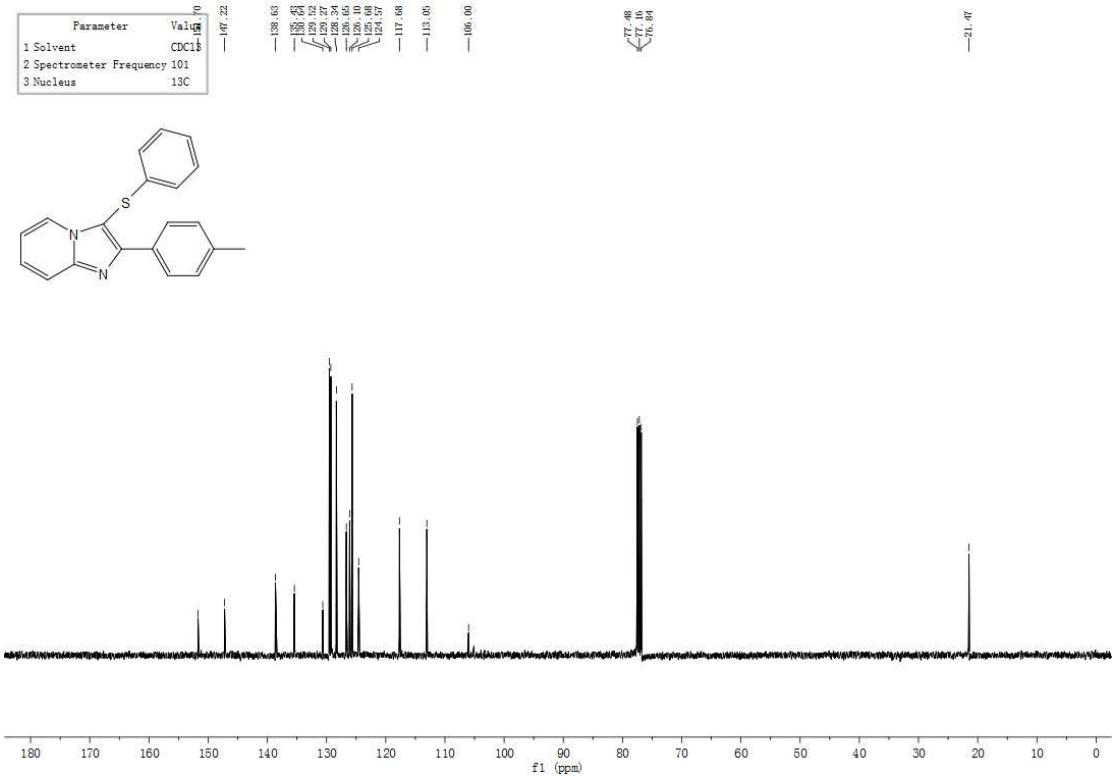
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



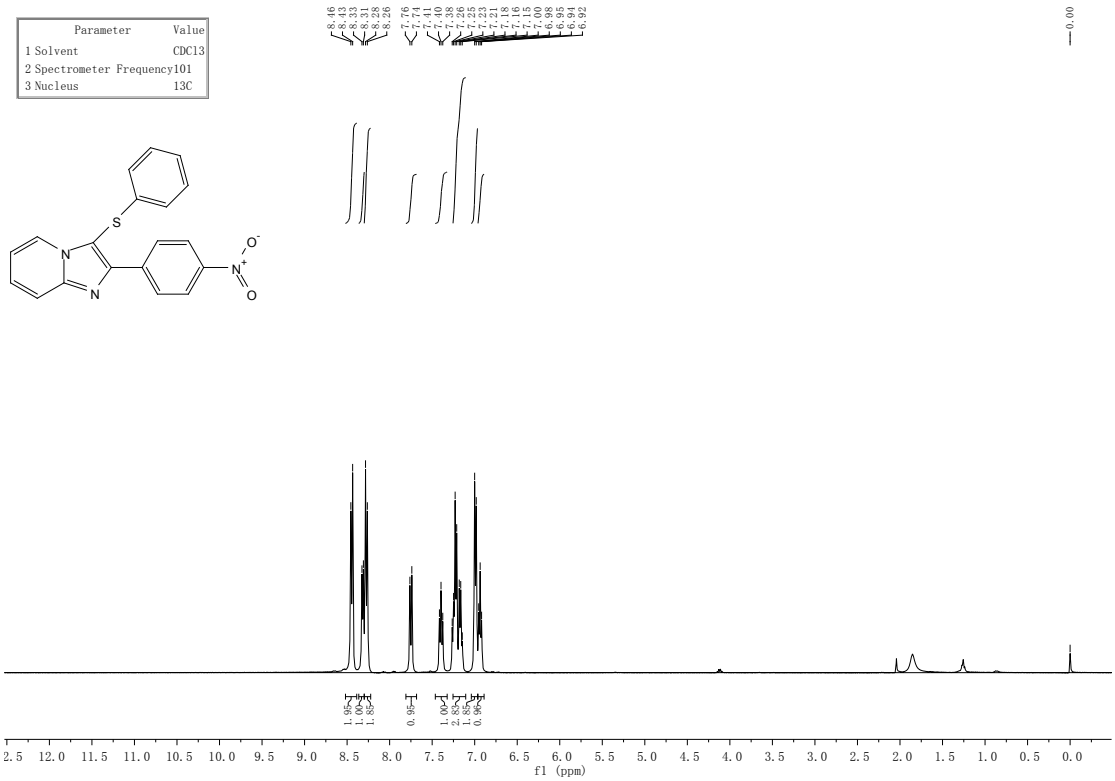
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



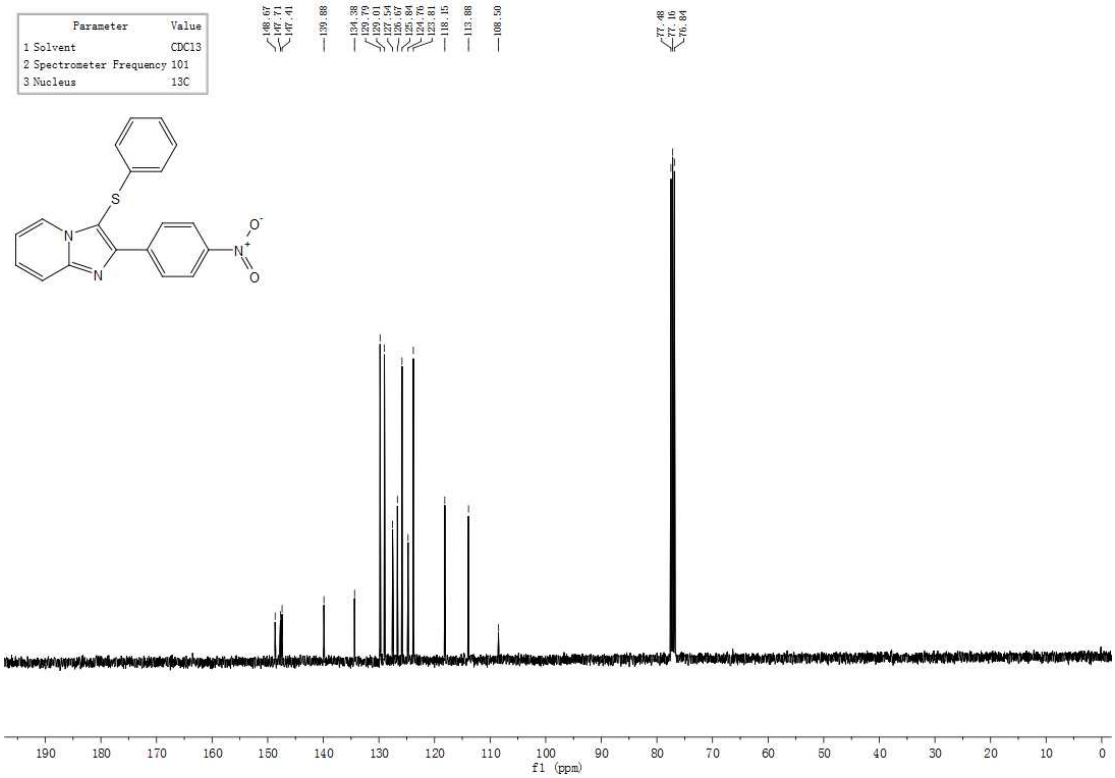
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



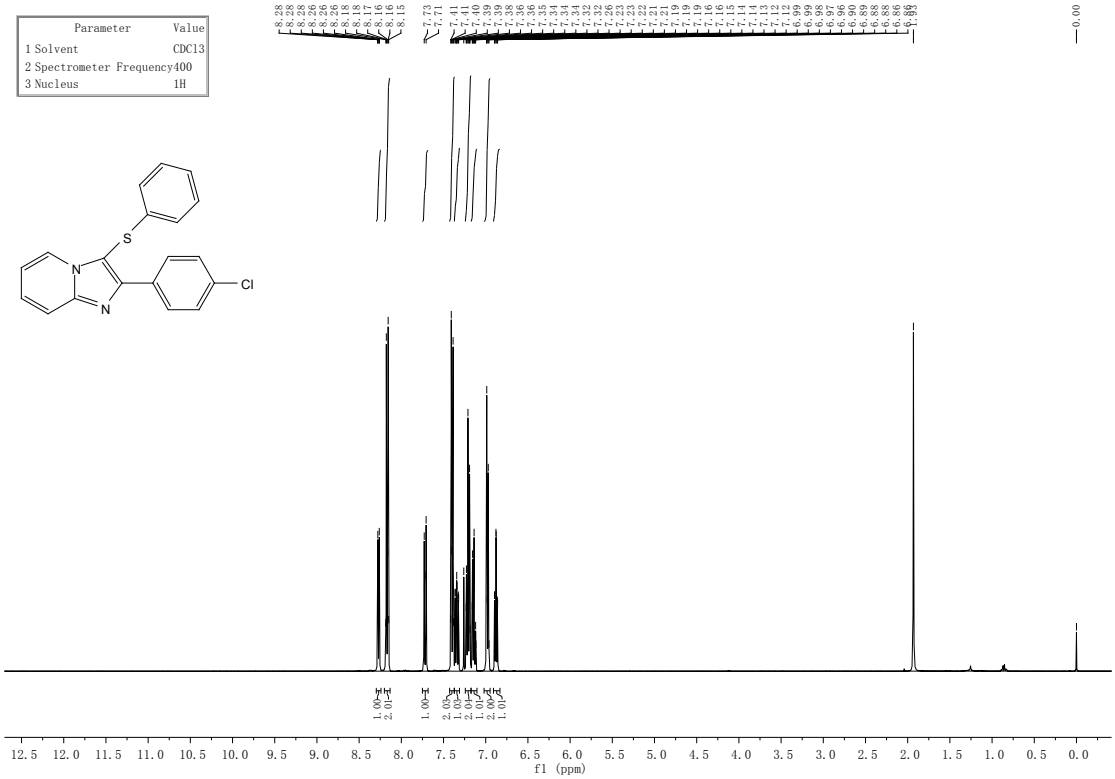
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



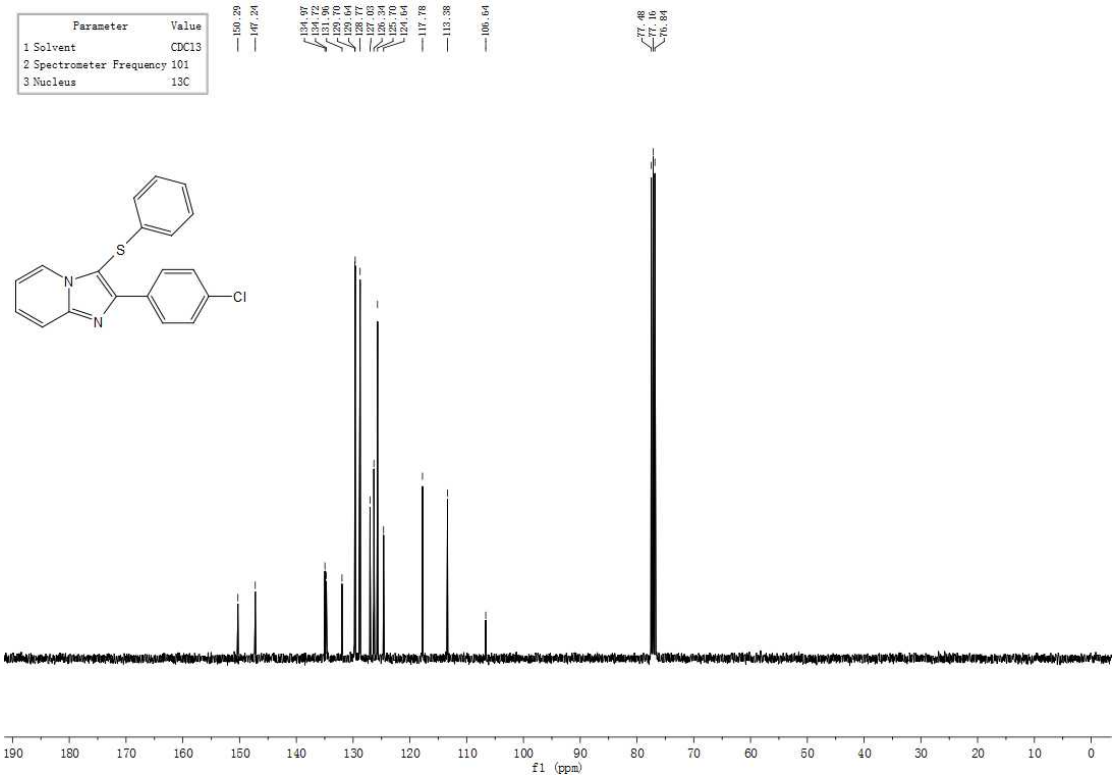
^{13}C NMR (101 MHz, $CDCl_3$) of **3m**



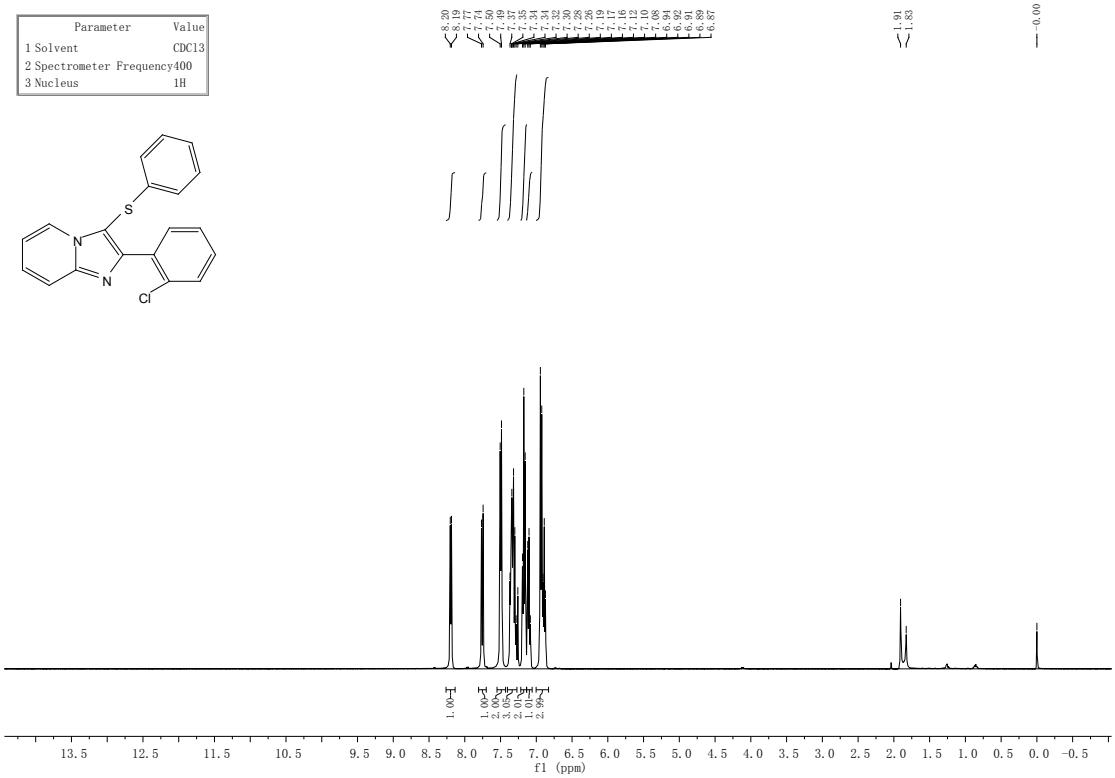
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



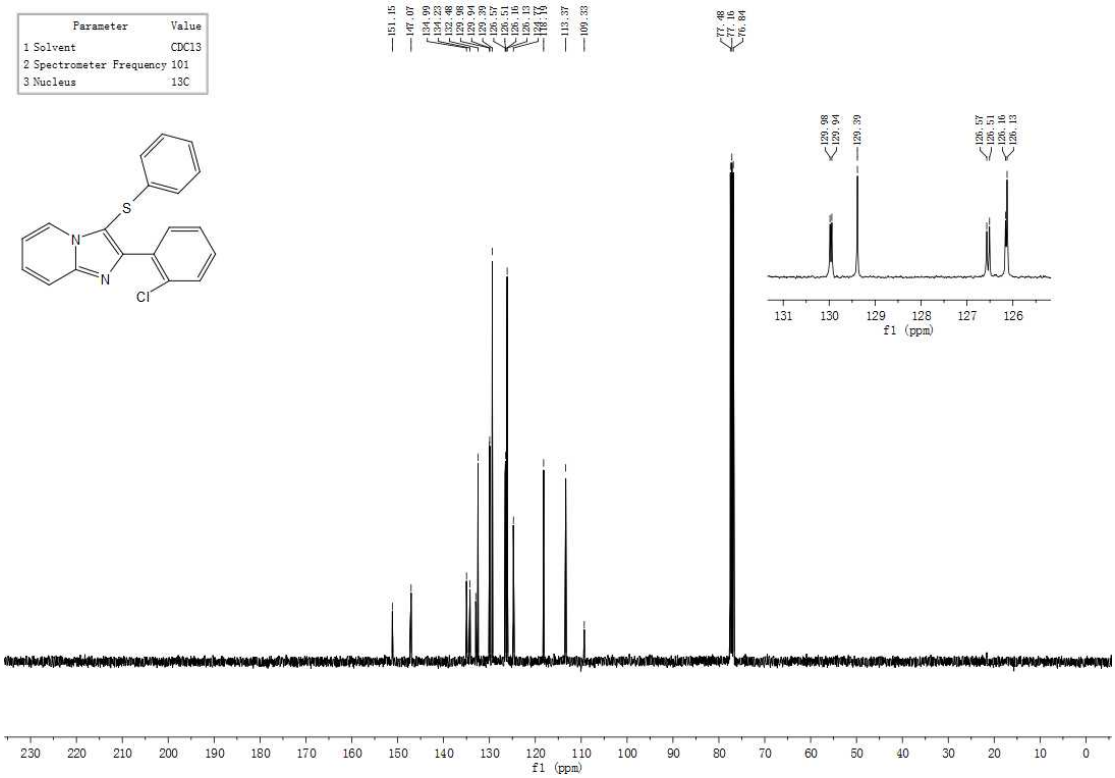
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



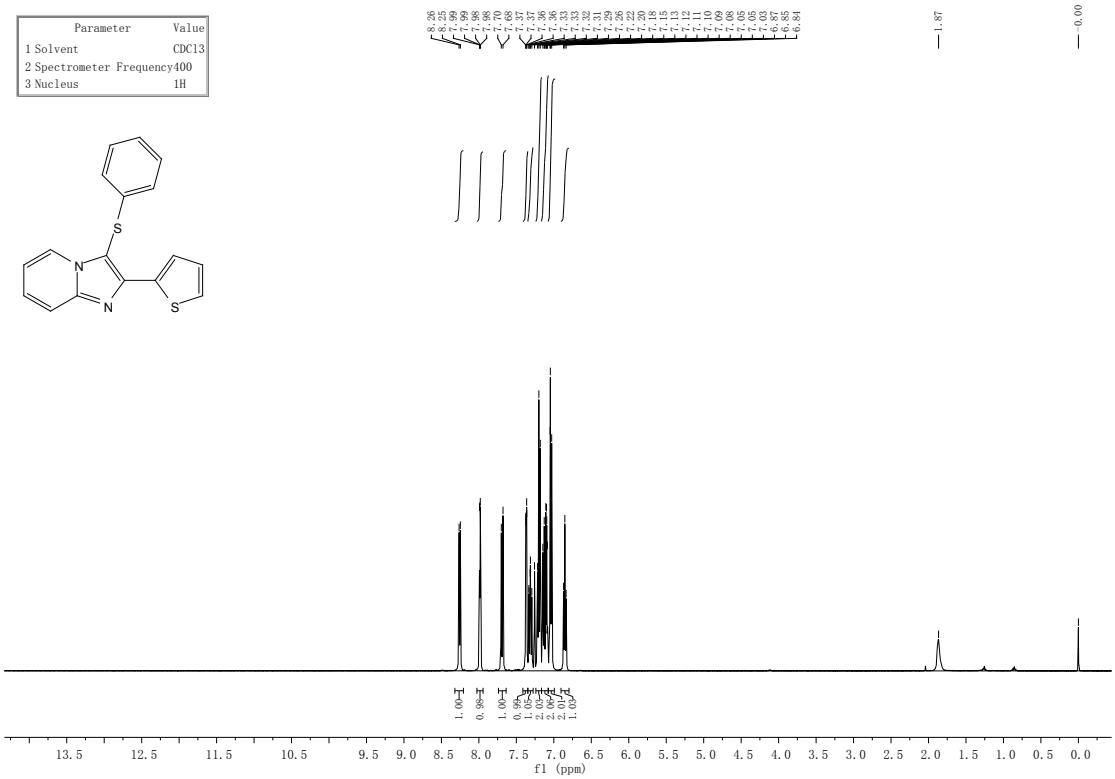
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



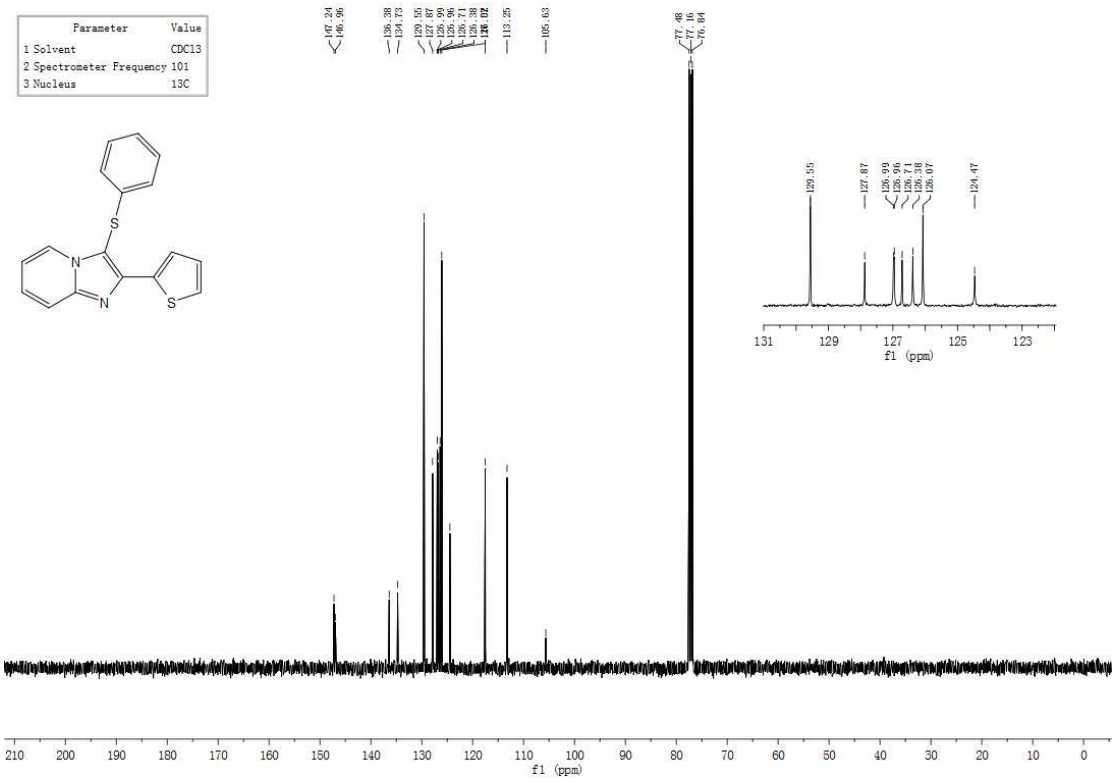
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



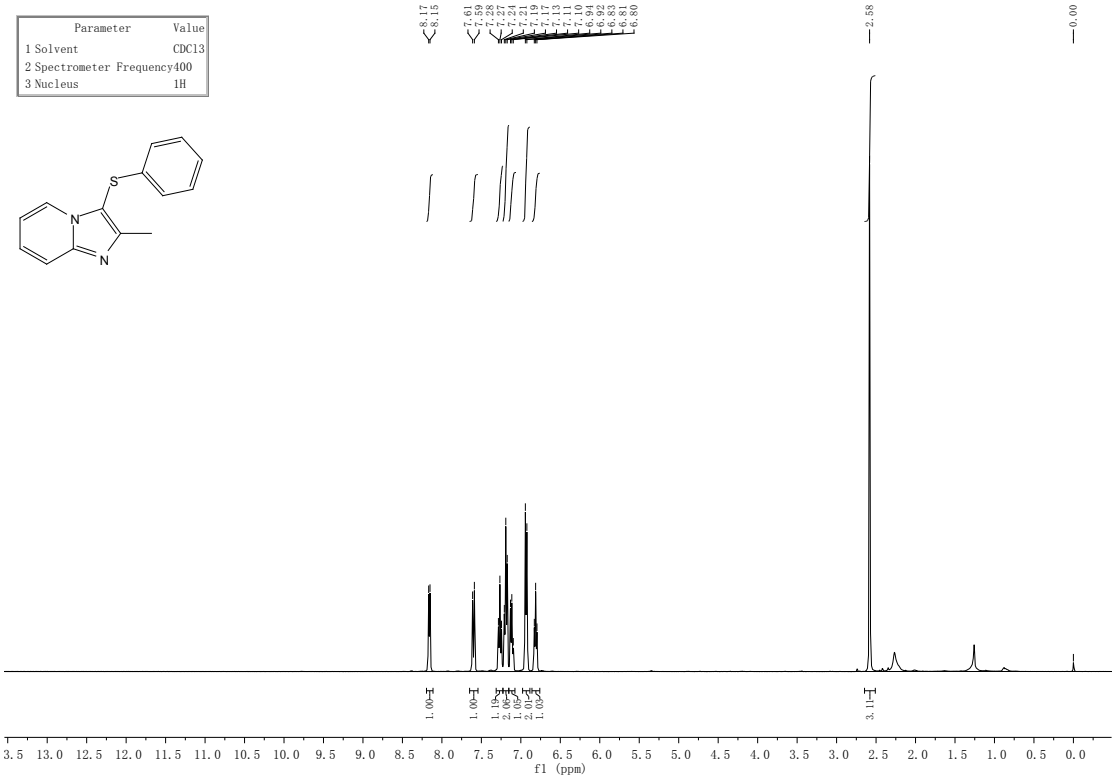
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



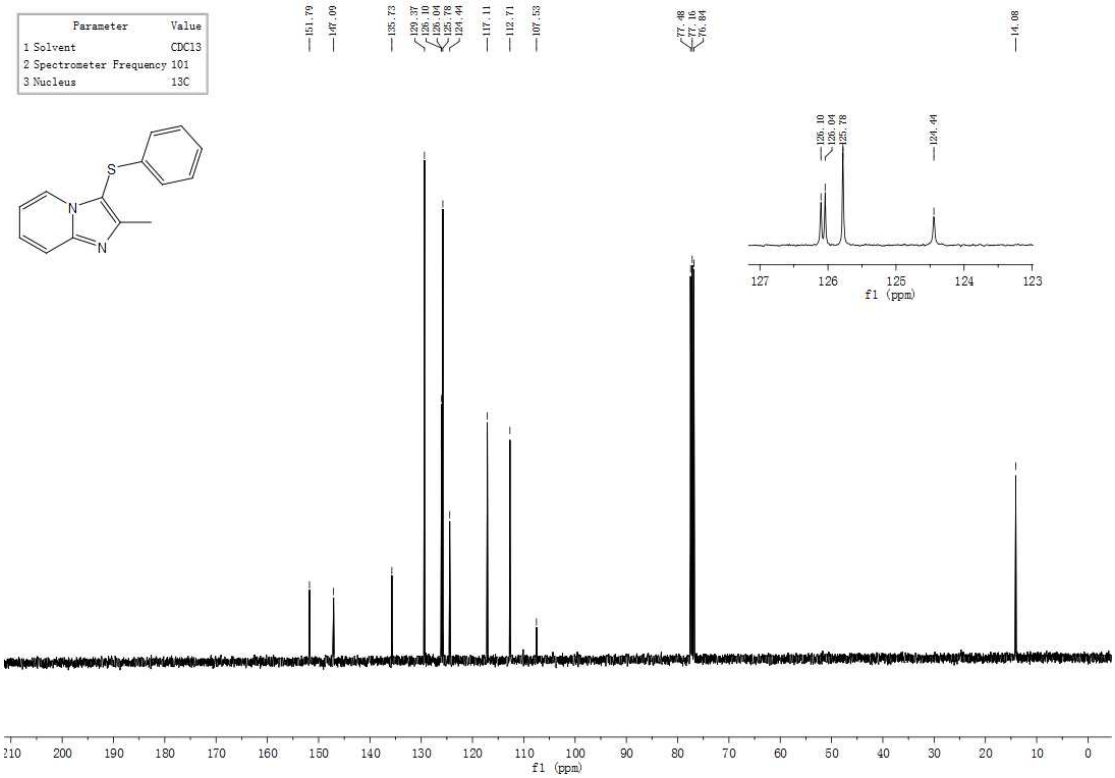
^{13}C NMR (101 MHz, $CDCl_3$) of **3p**



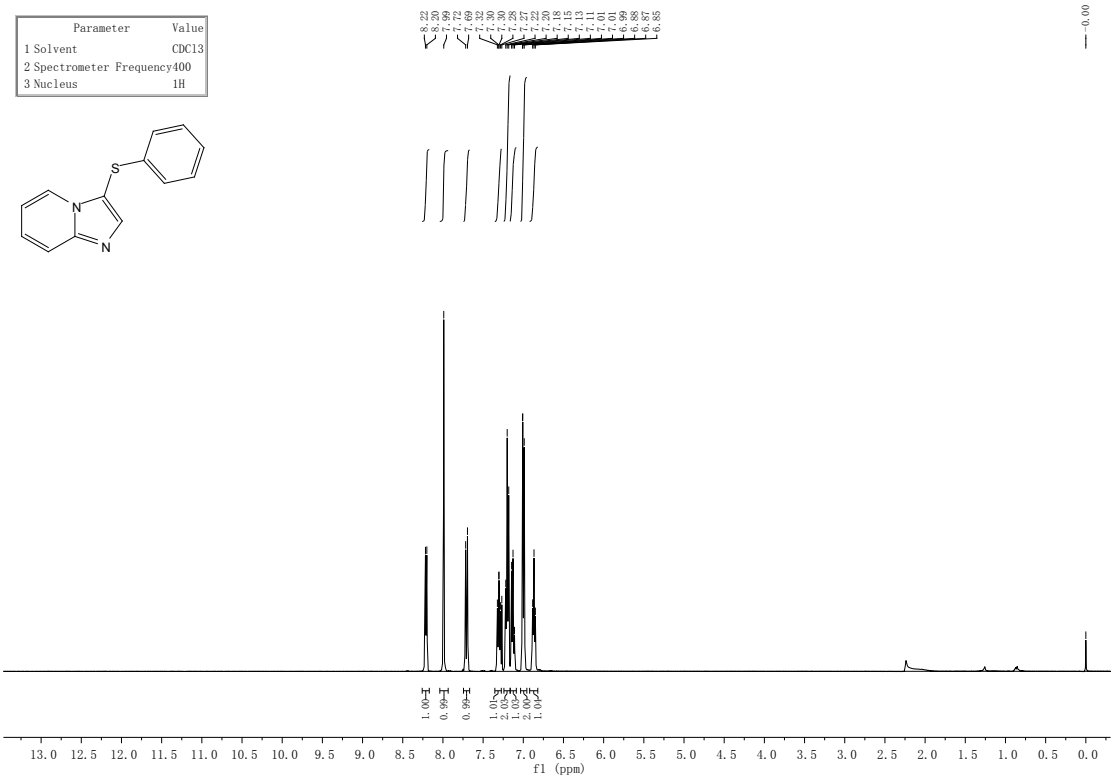
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



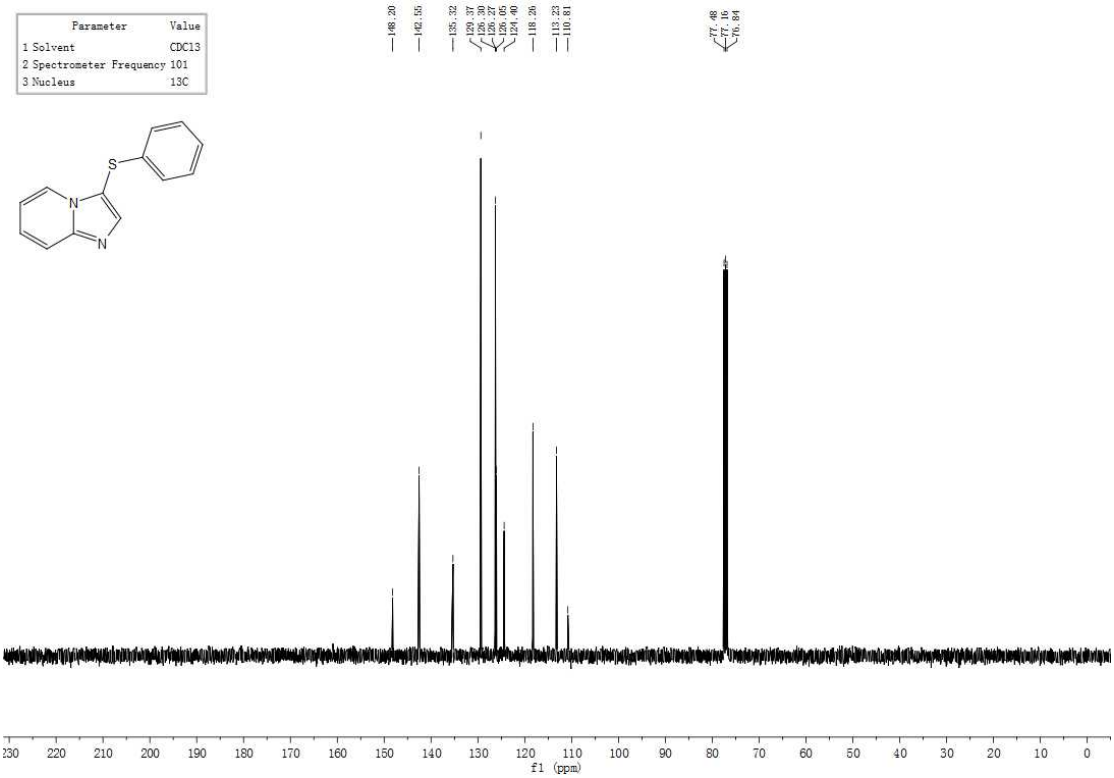
^{13}C NMR (101 MHz, $CDCl_3$) of **3q**



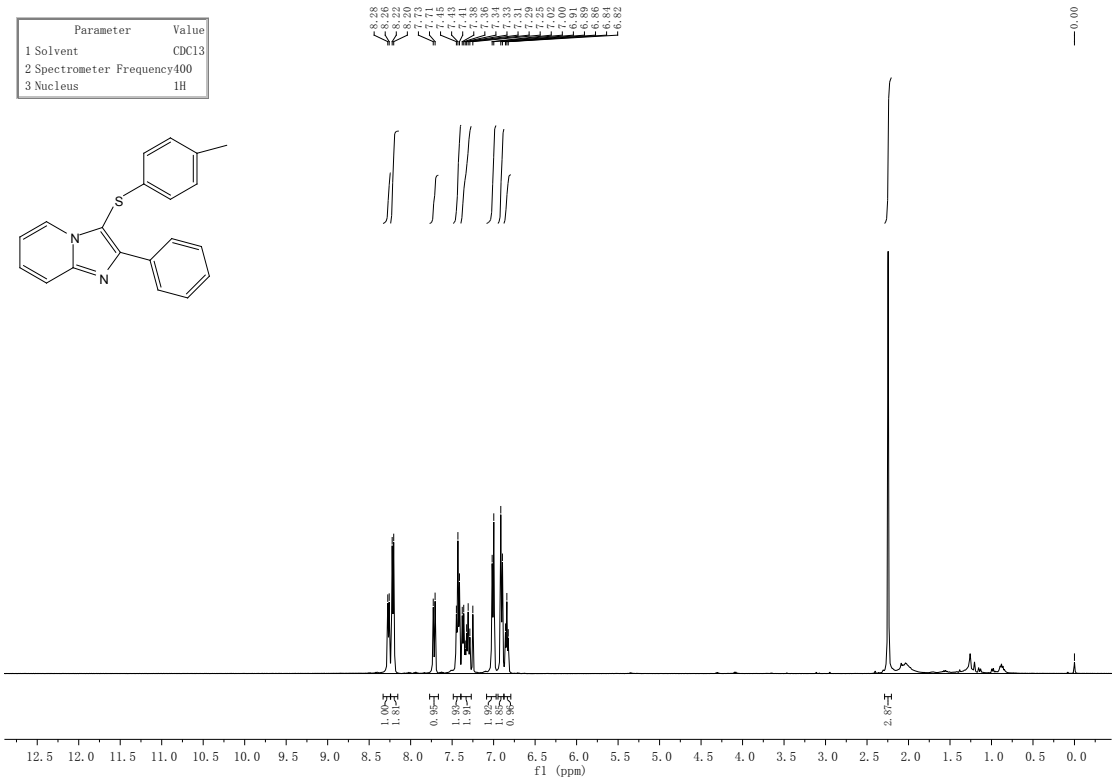
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



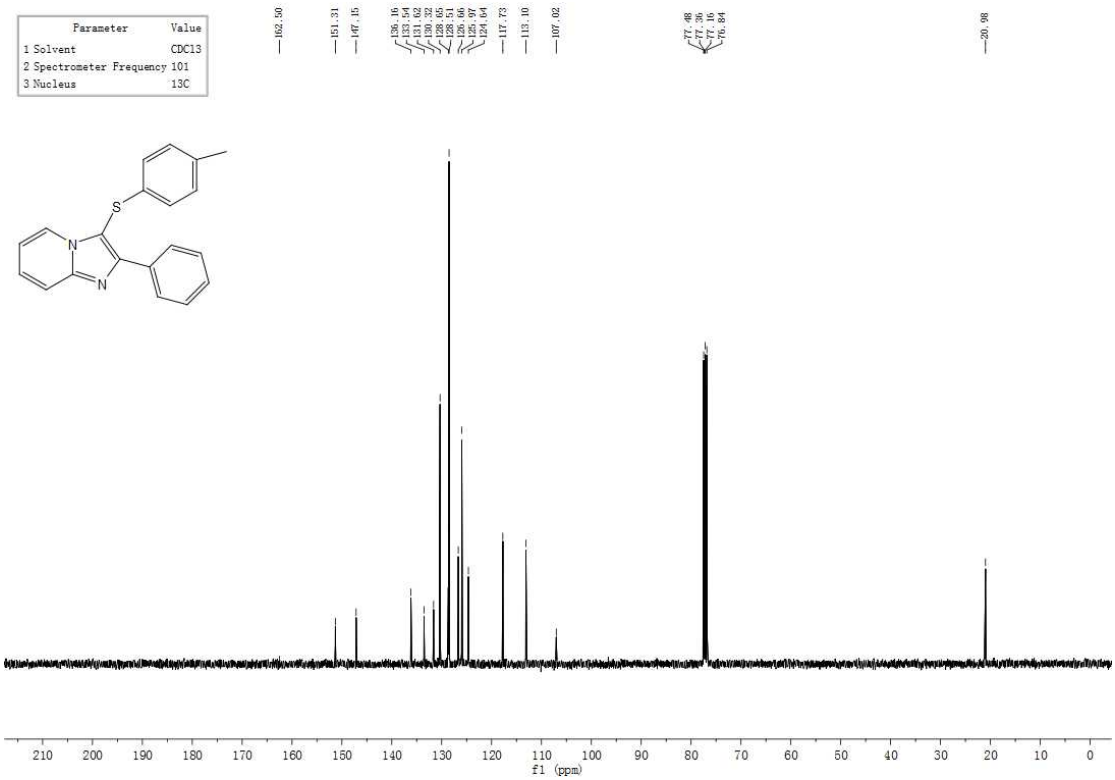
^{13}C NMR (101 MHz, $CDCl_3$) of **3r**



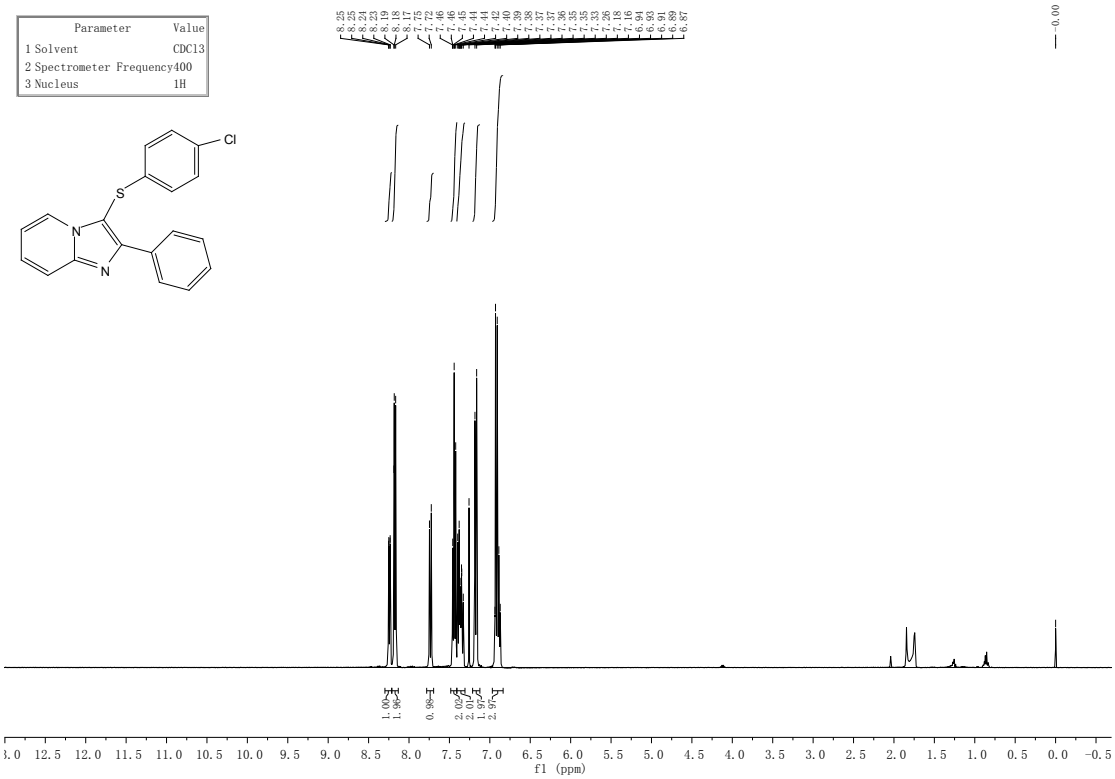
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



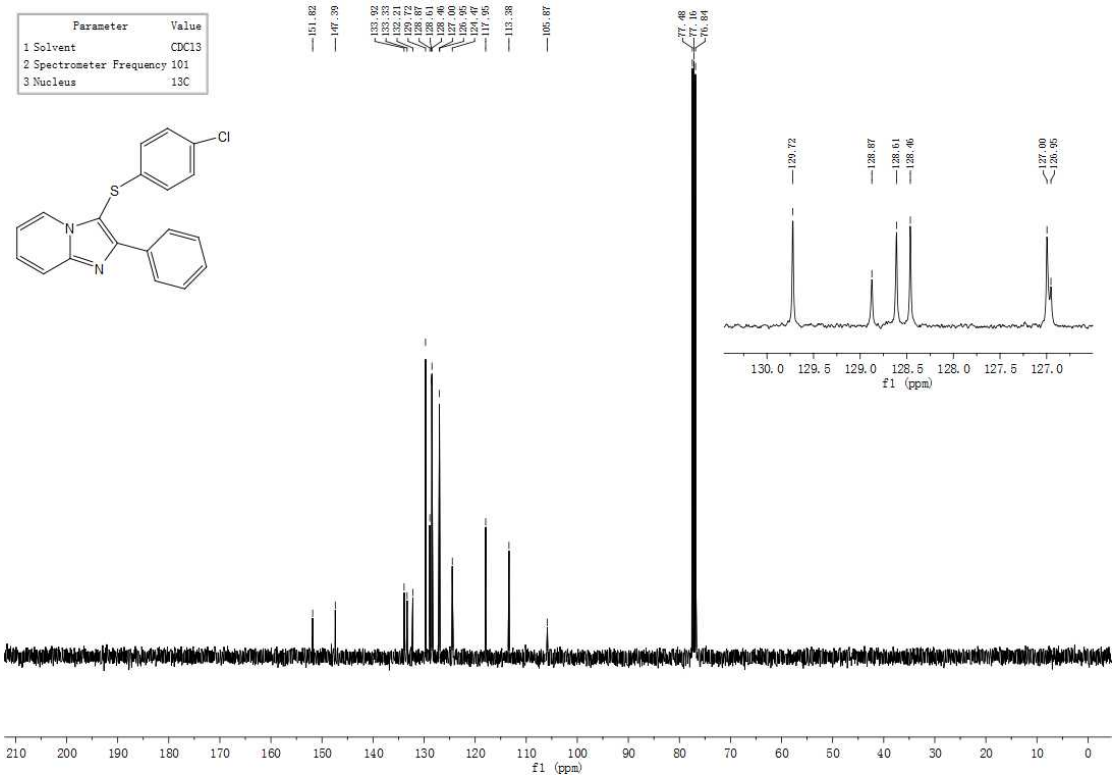
^{13}C NMR (101 MHz, $CDCl_3$) of **3s**



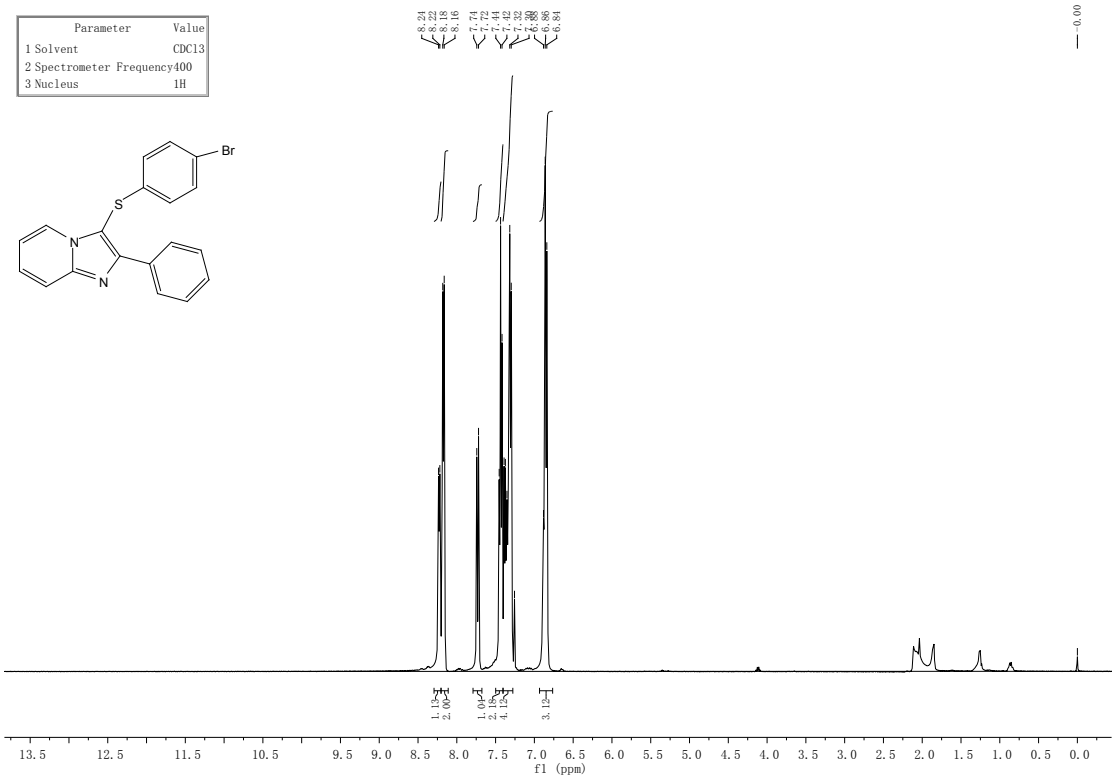
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



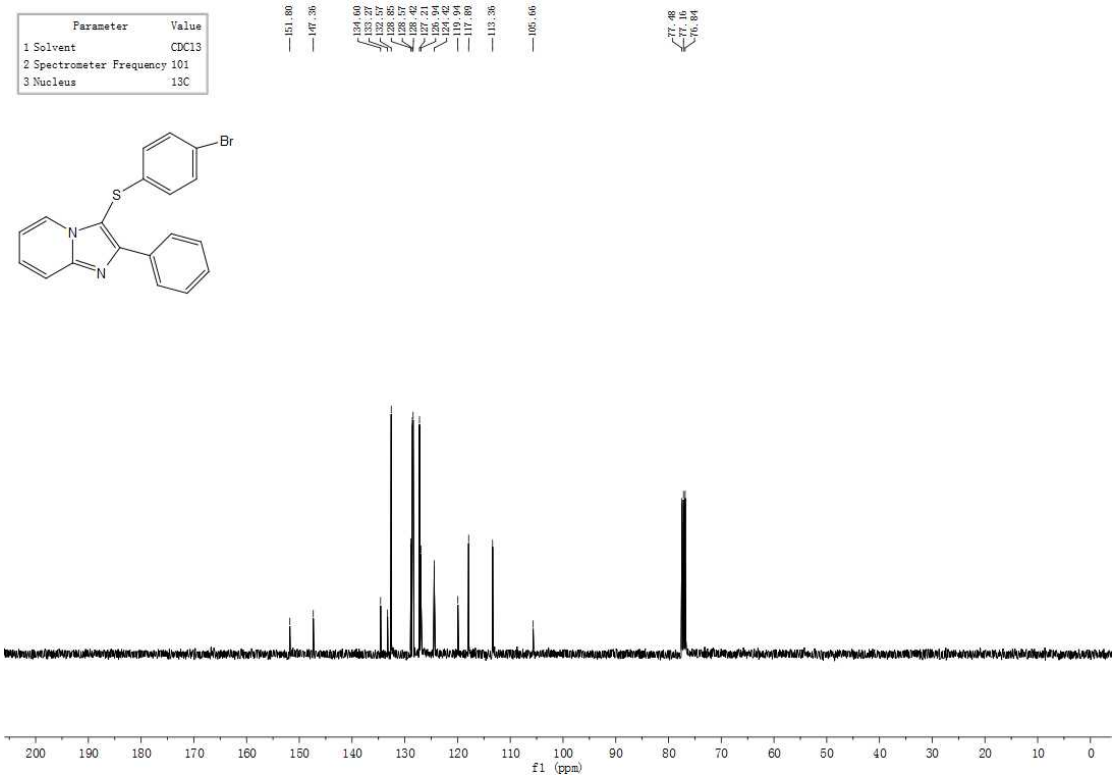
^{13}C NMR (101 MHz, $CDCl_3$) of **3t**



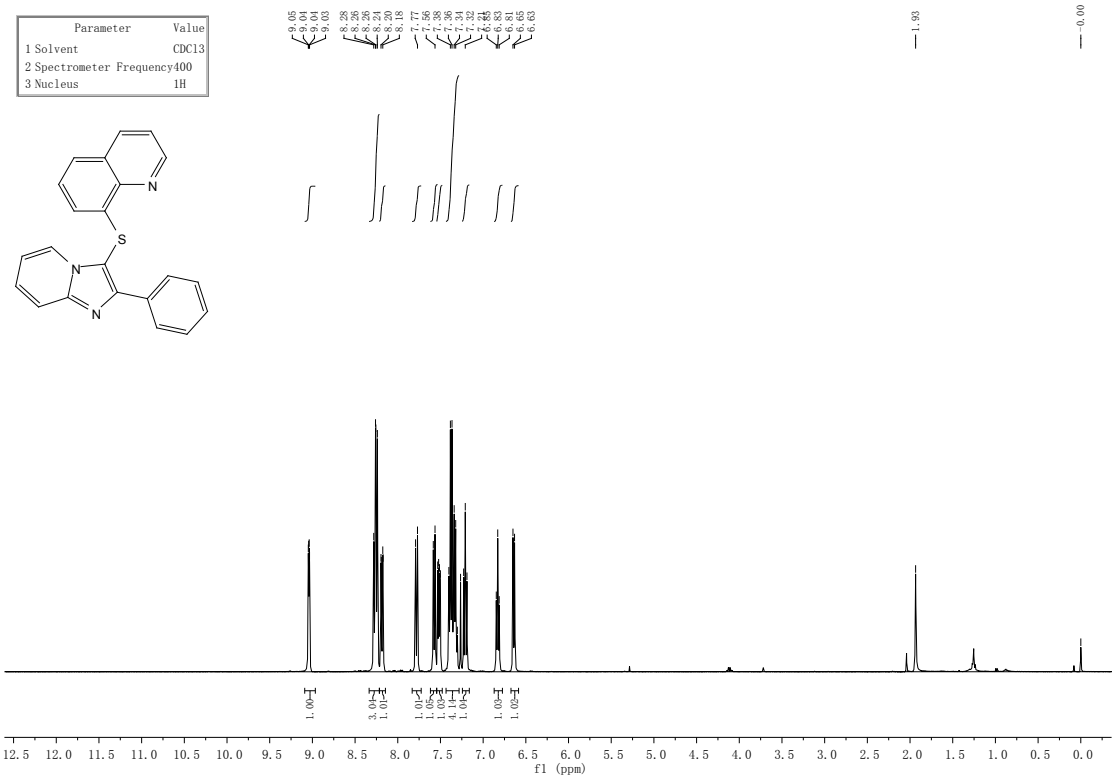
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



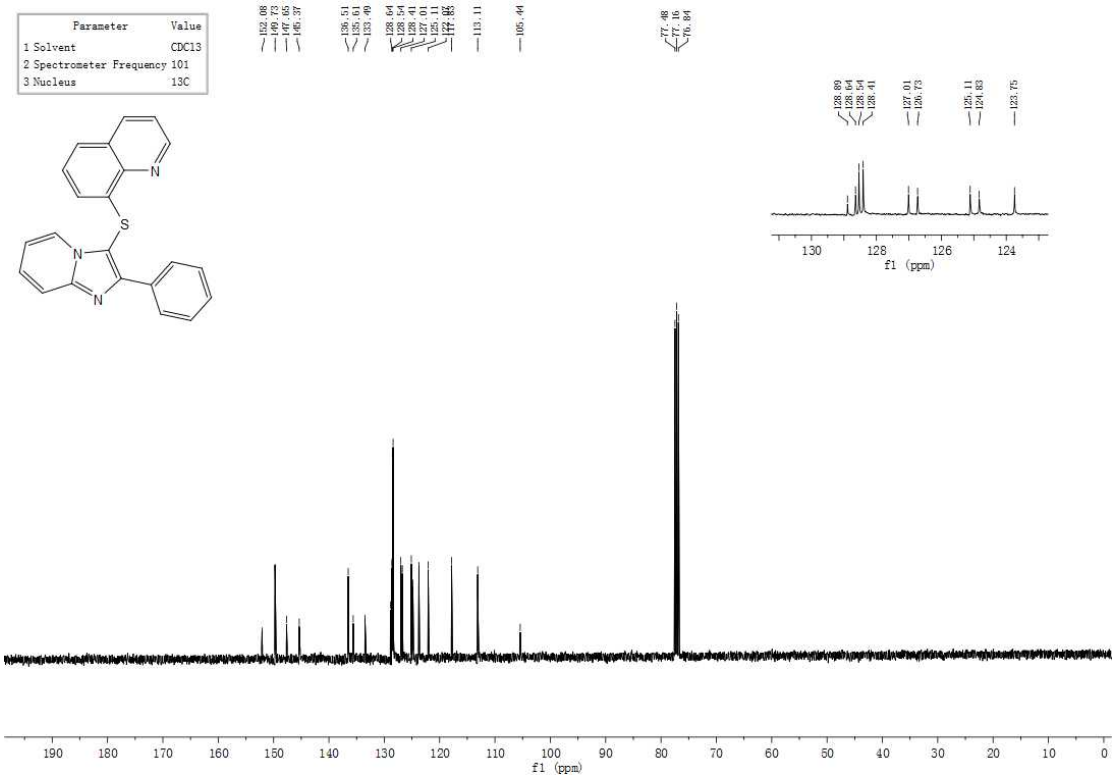
^{13}C NMR (101 MHz, $CDCl_3$) of **3u**



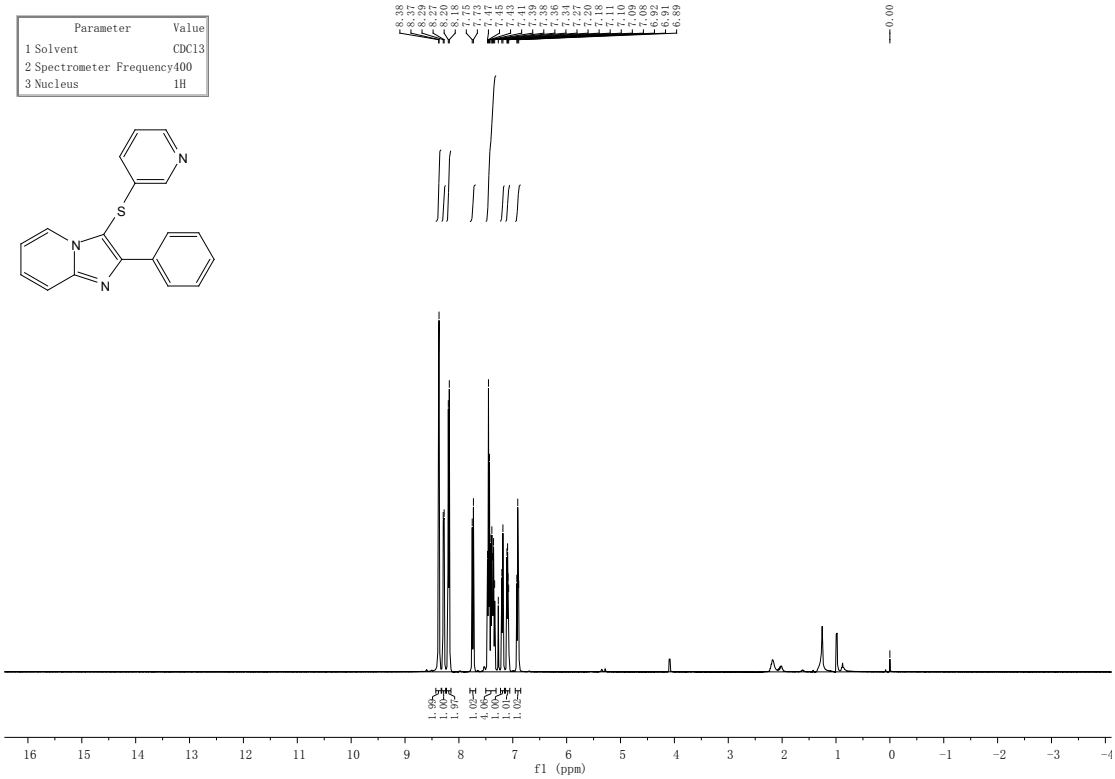
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



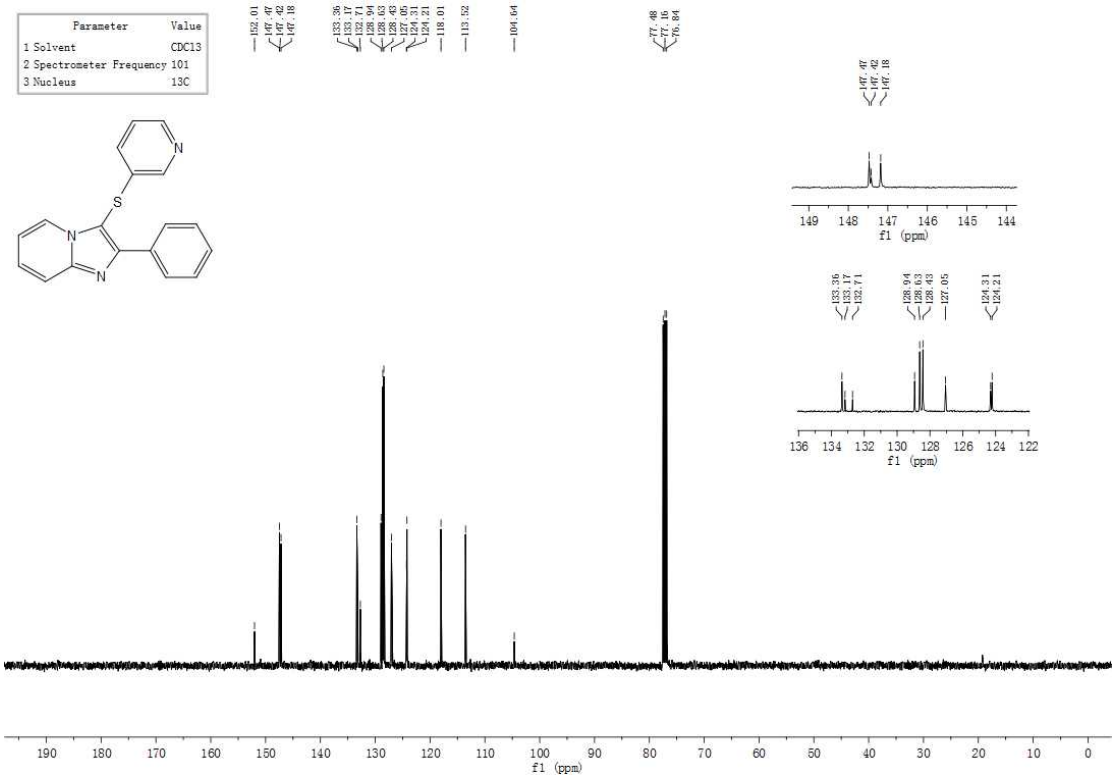
^{13}C NMR (101 MHz, $CDCl_3$) of **3v**



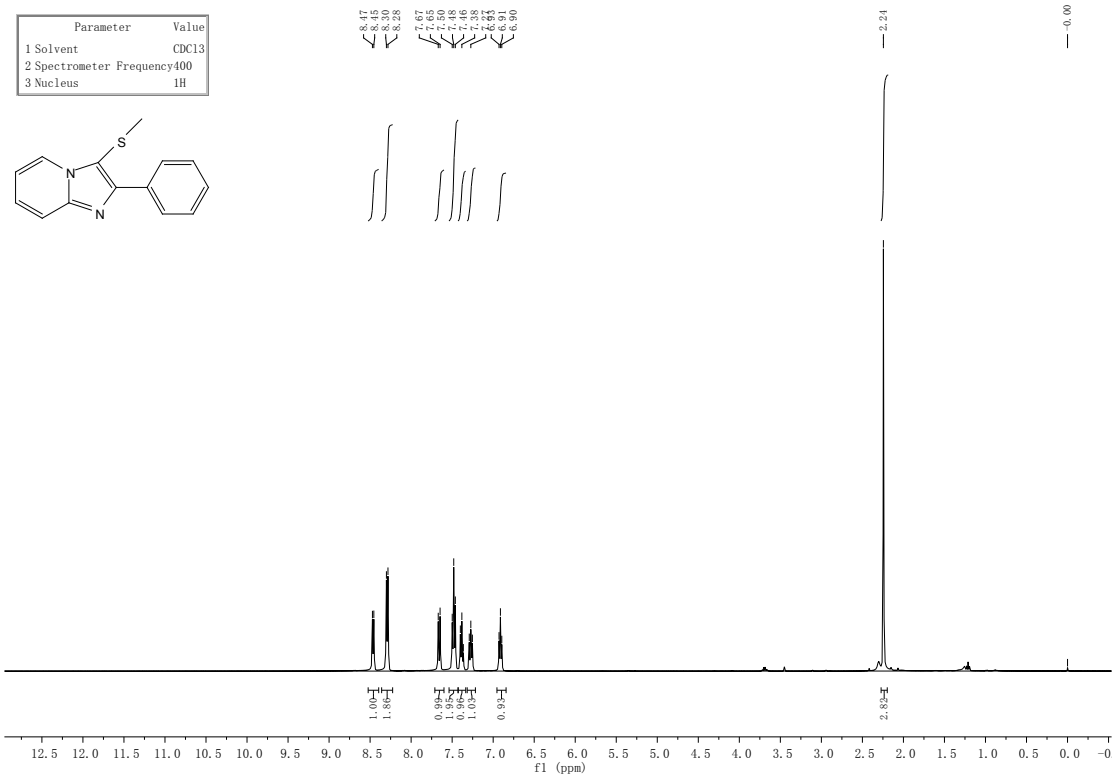
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



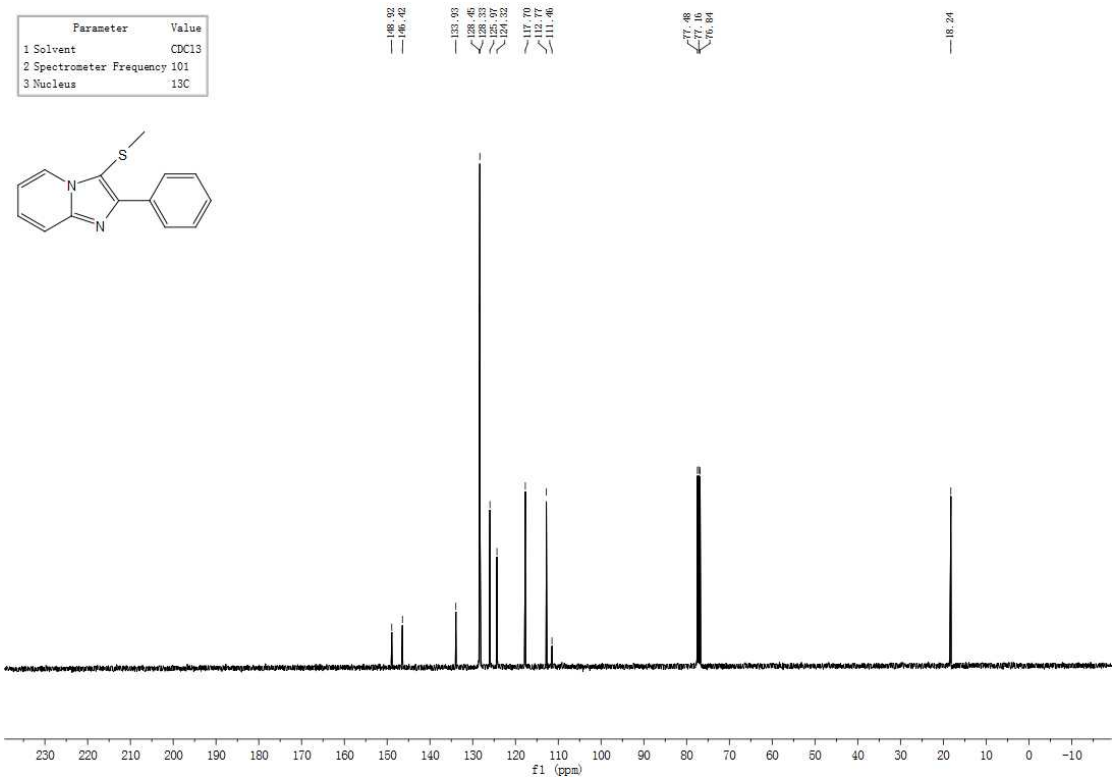
^{13}C NMR (101 MHz, $CDCl_3$) of **3w**



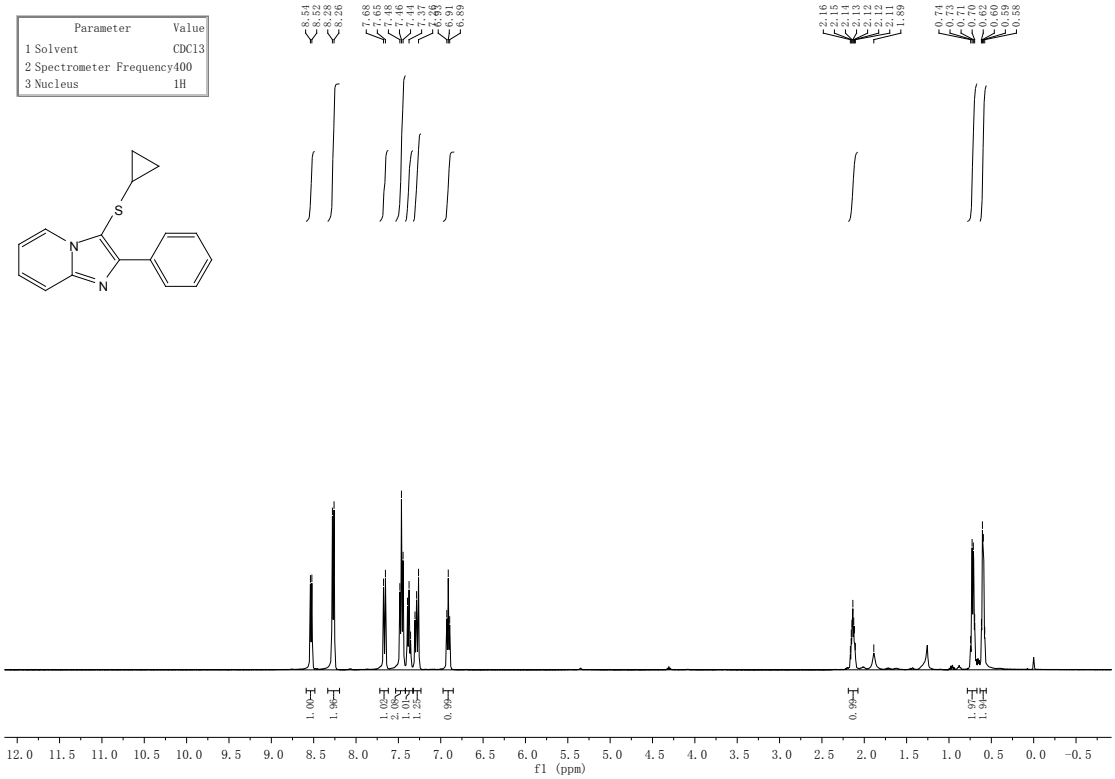
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



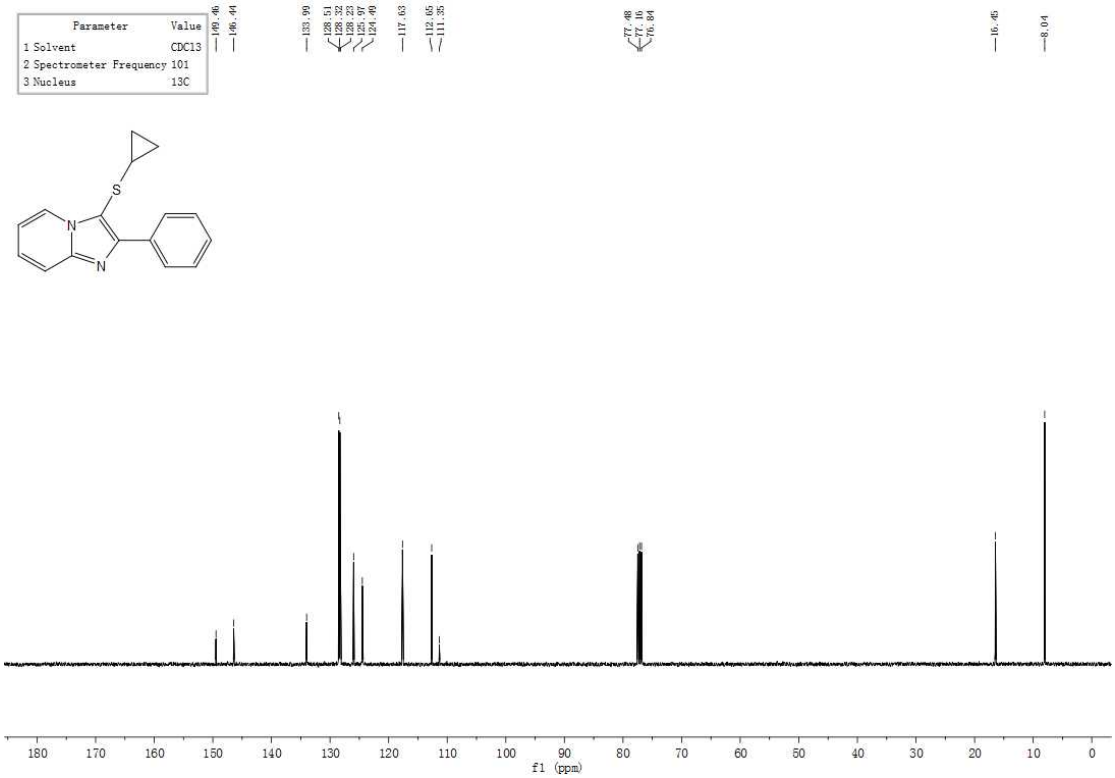
^{13}C NMR (101 MHz, $CDCl_3$) of **3x**



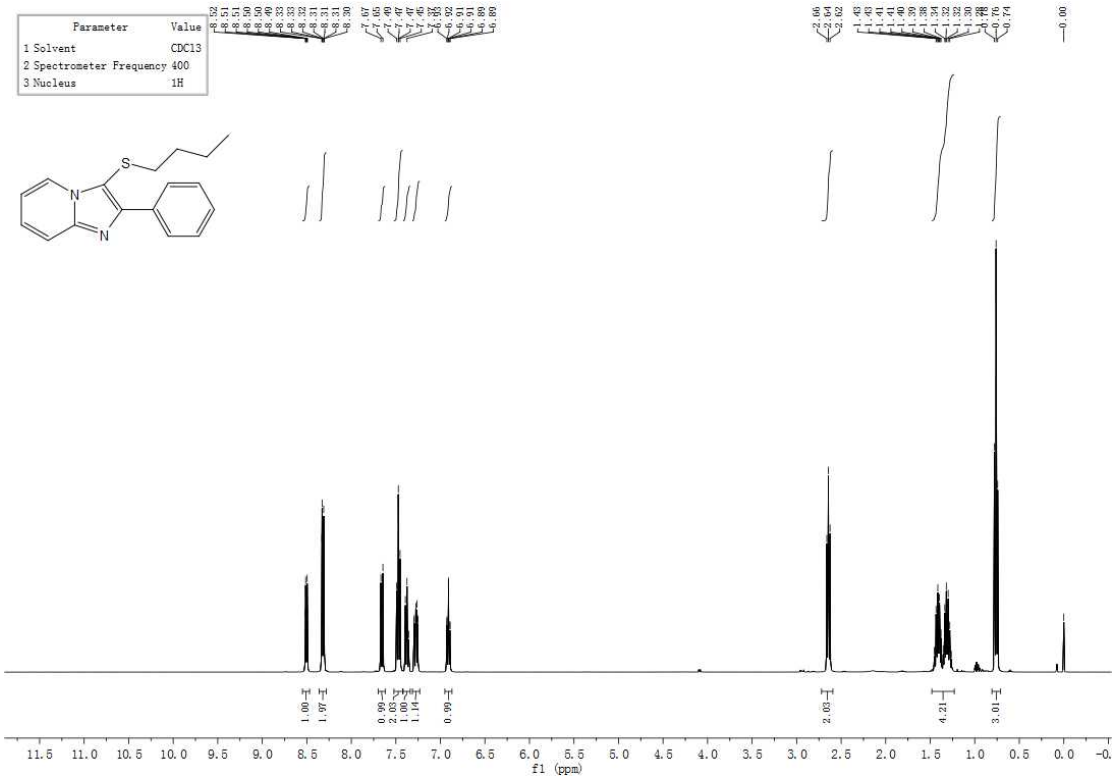
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



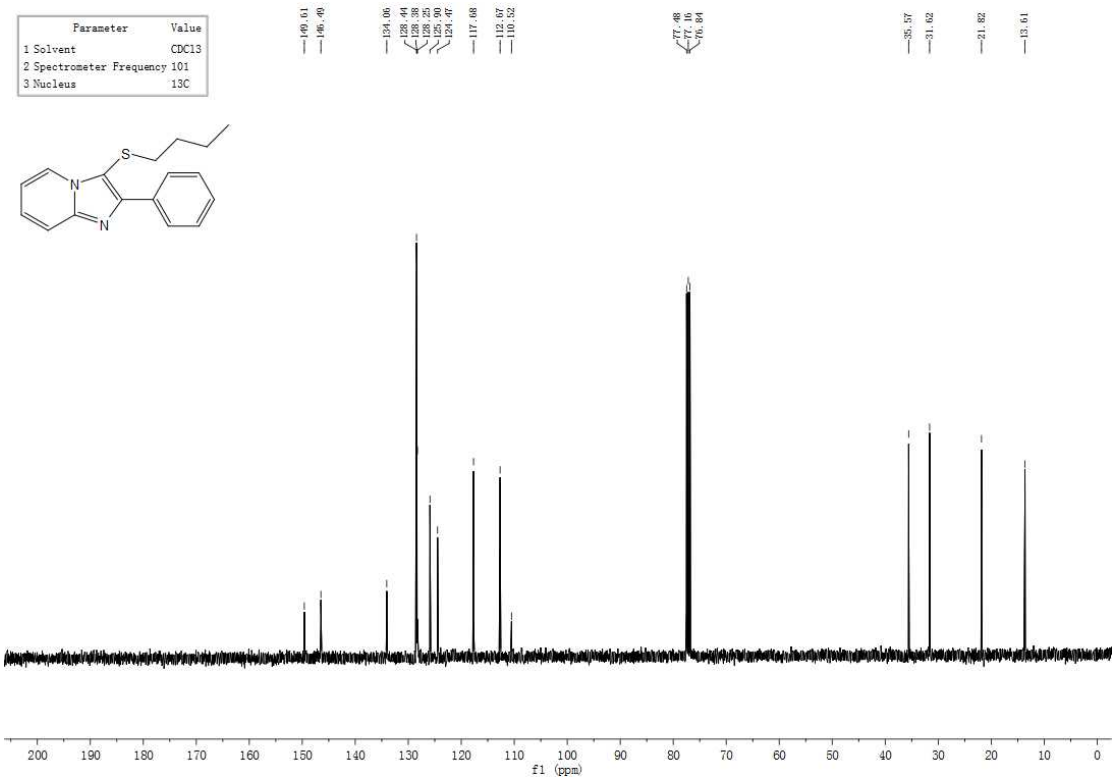
^{13}C NMR (101 MHz, $CDCl_3$) of **3y**



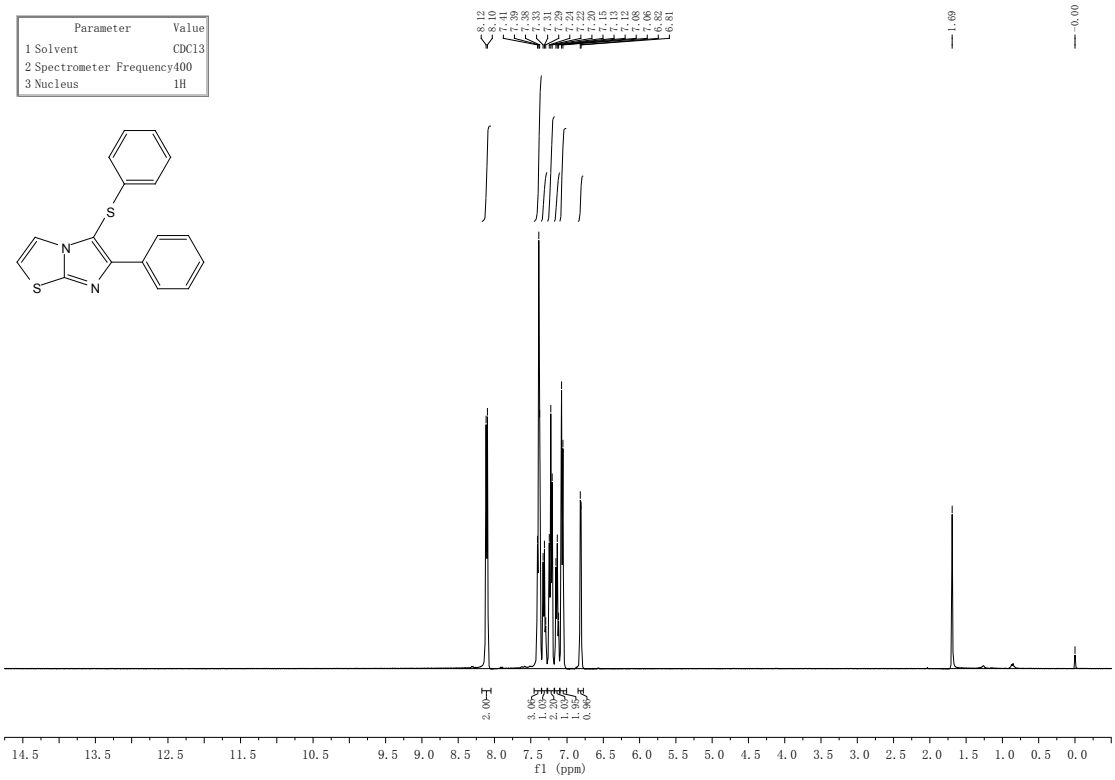
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



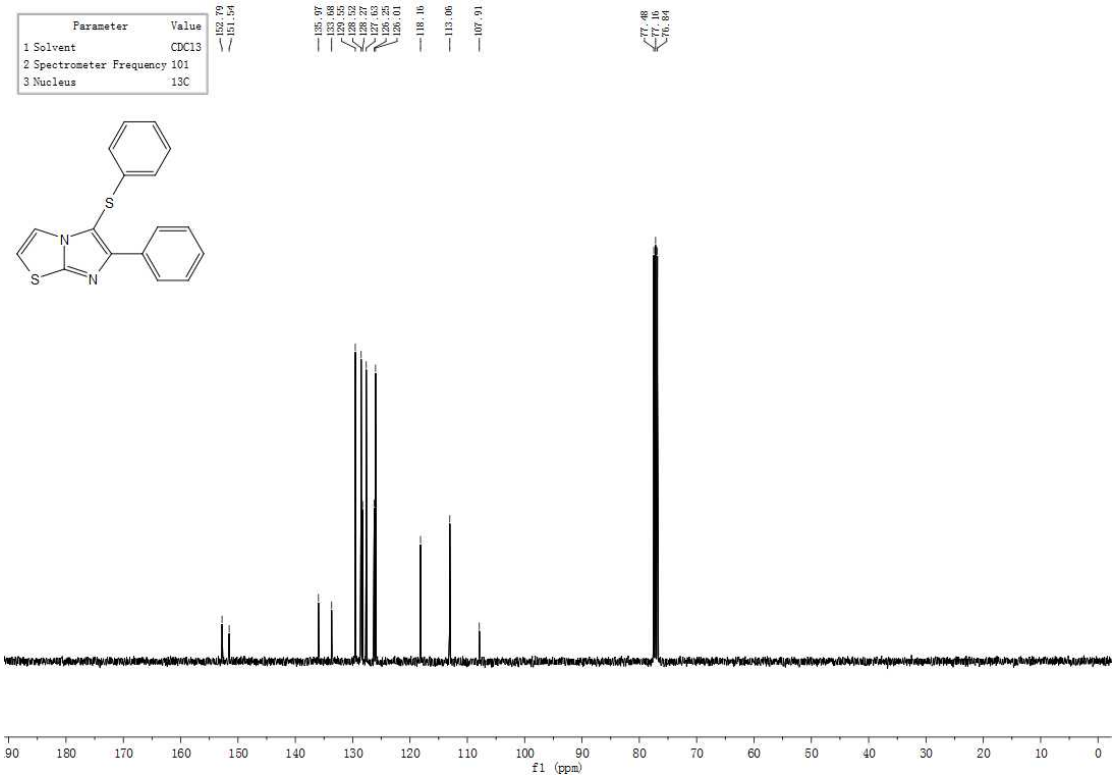
^{13}C NMR (101 MHz, $CDCl_3$) of **3z**



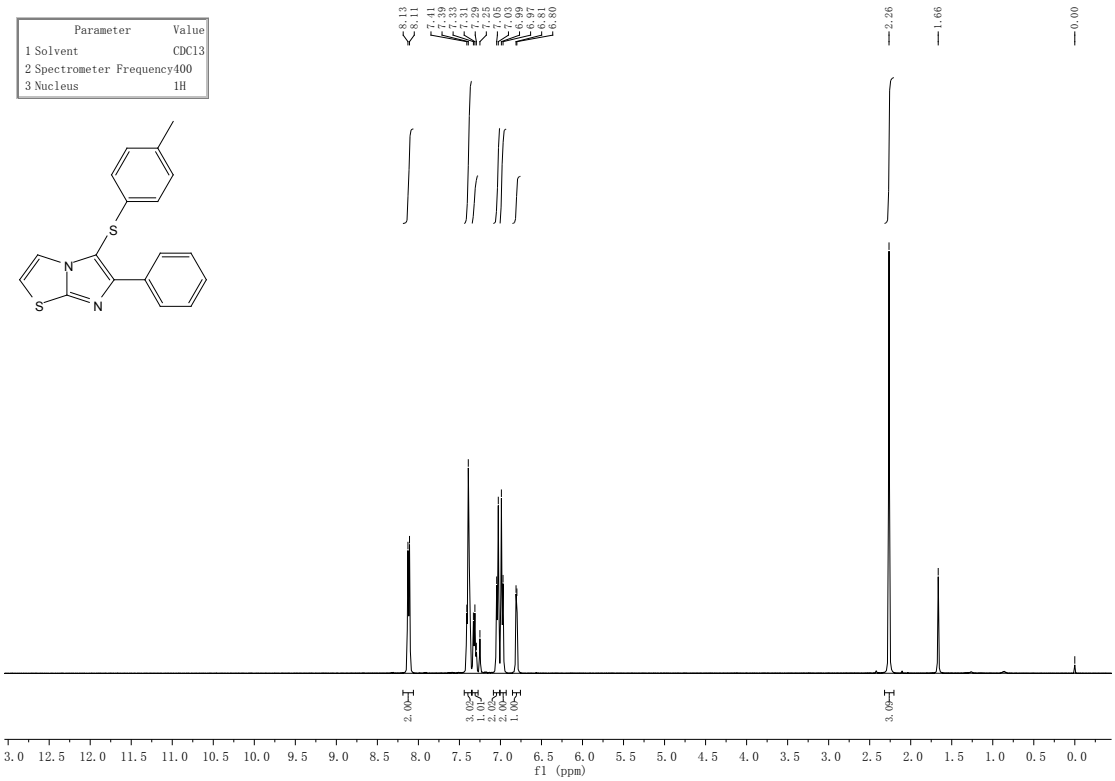
^{1}H NMR (400 MHz, $CDCl_3$) of **5a**



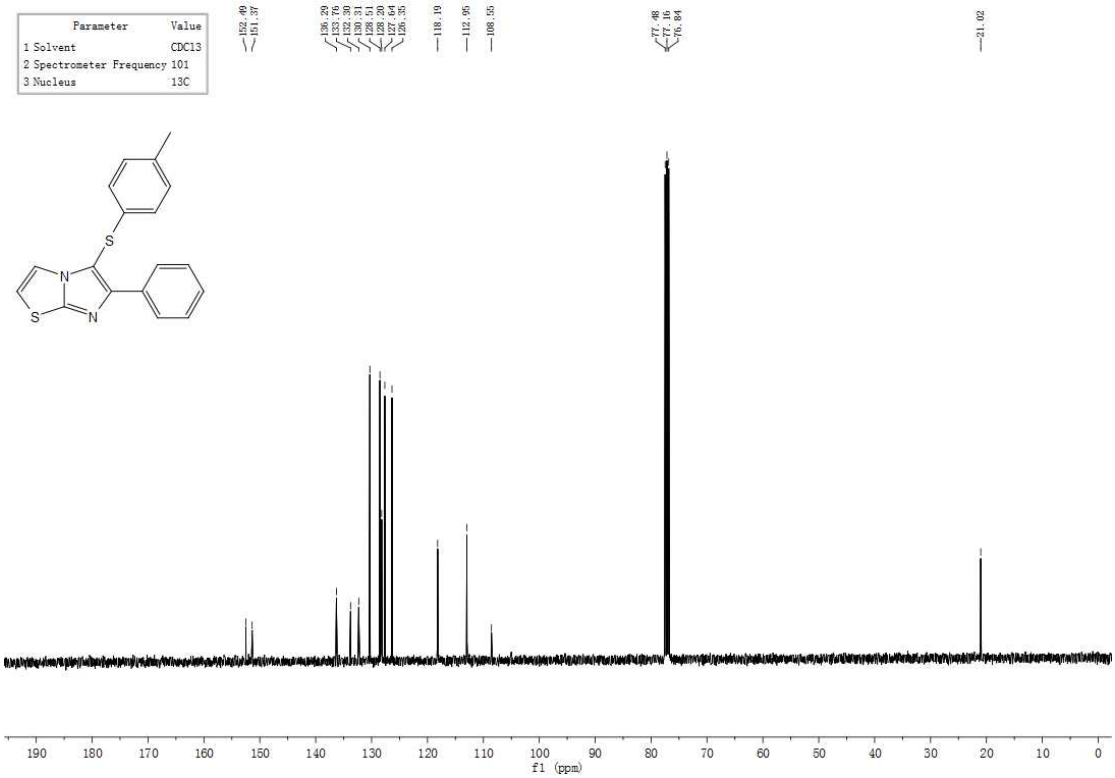
^{13}C NMR (101 MHz, $CDCl_3$) of **5a**



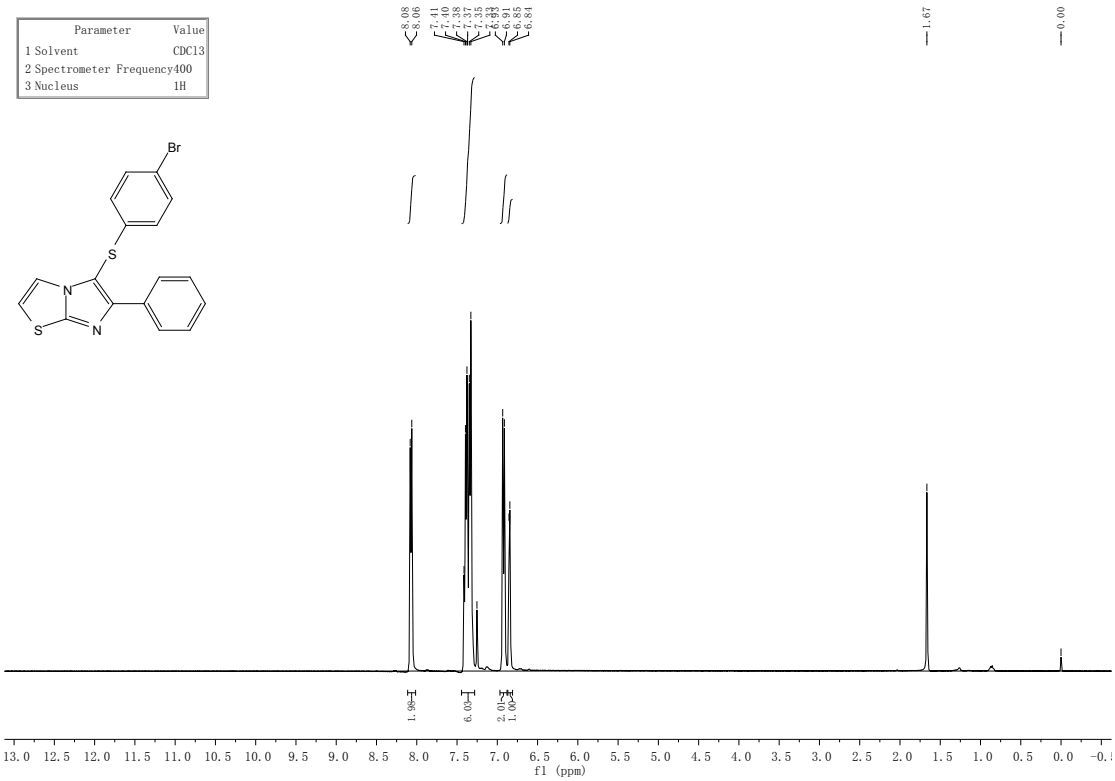
^{1}H NMR (400 MHz, $CDCl_3$) of **5b**



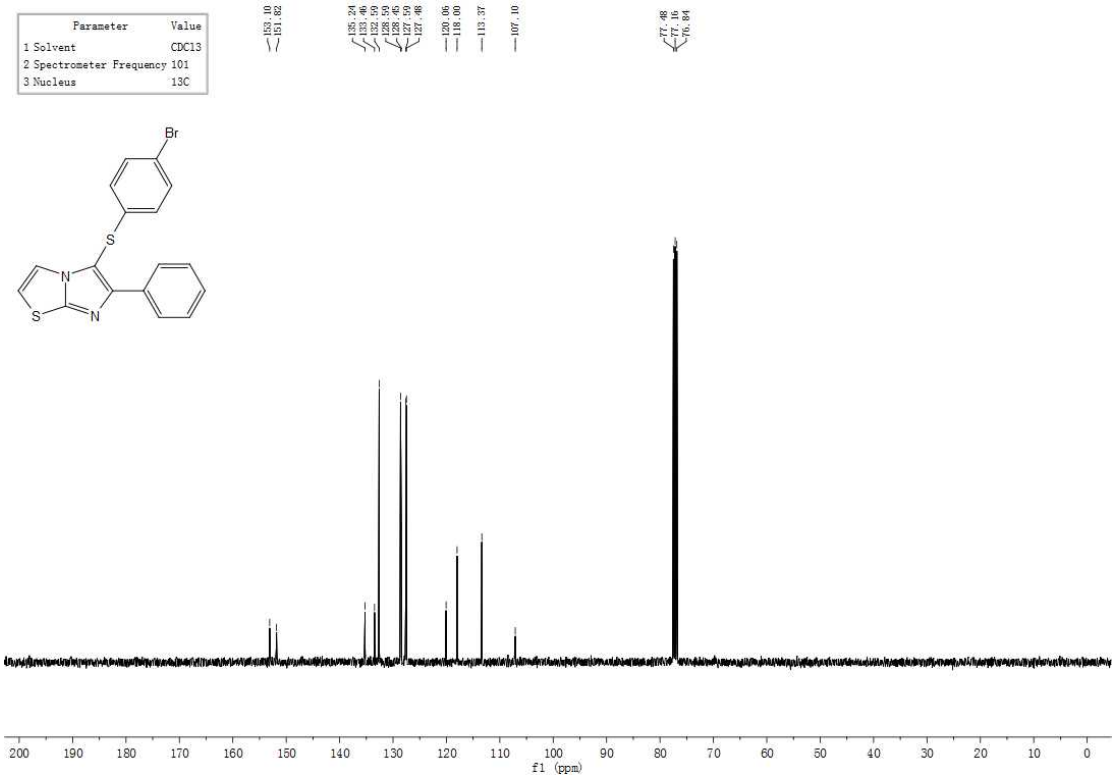
^{13}C NMR (101 MHz, $CDCl_3$) of **5b**



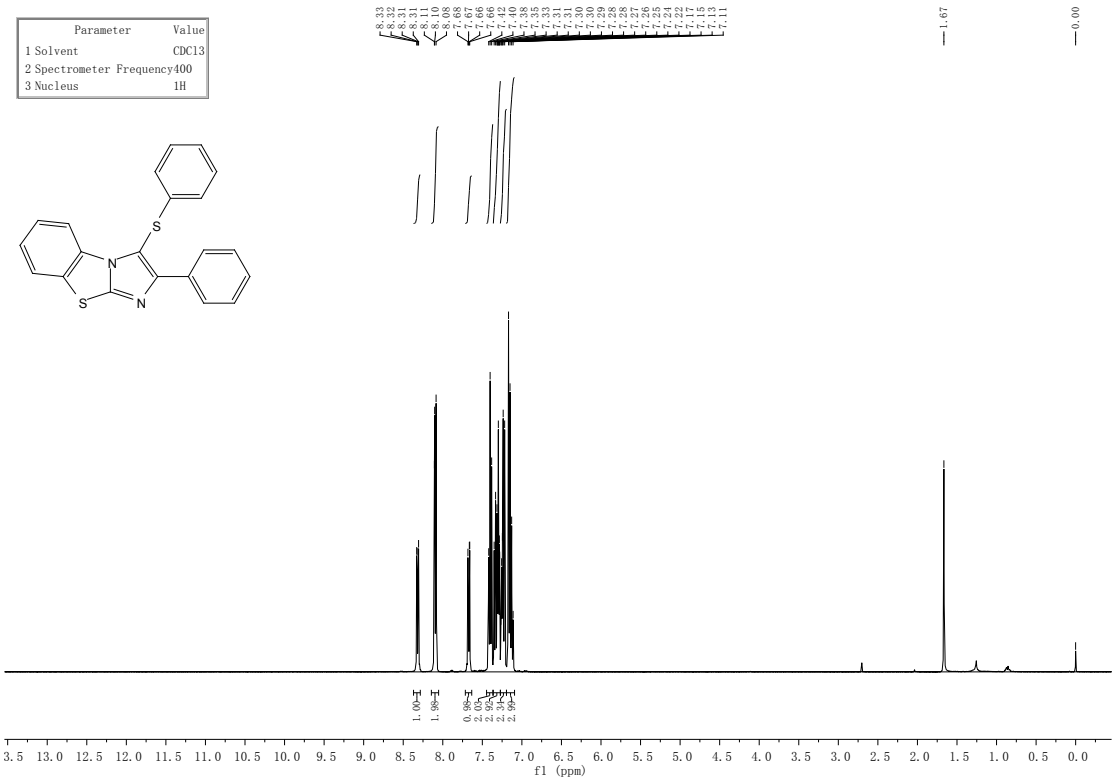
^{1}H NMR (400 MHz, $CDCl_3$) of **5c**



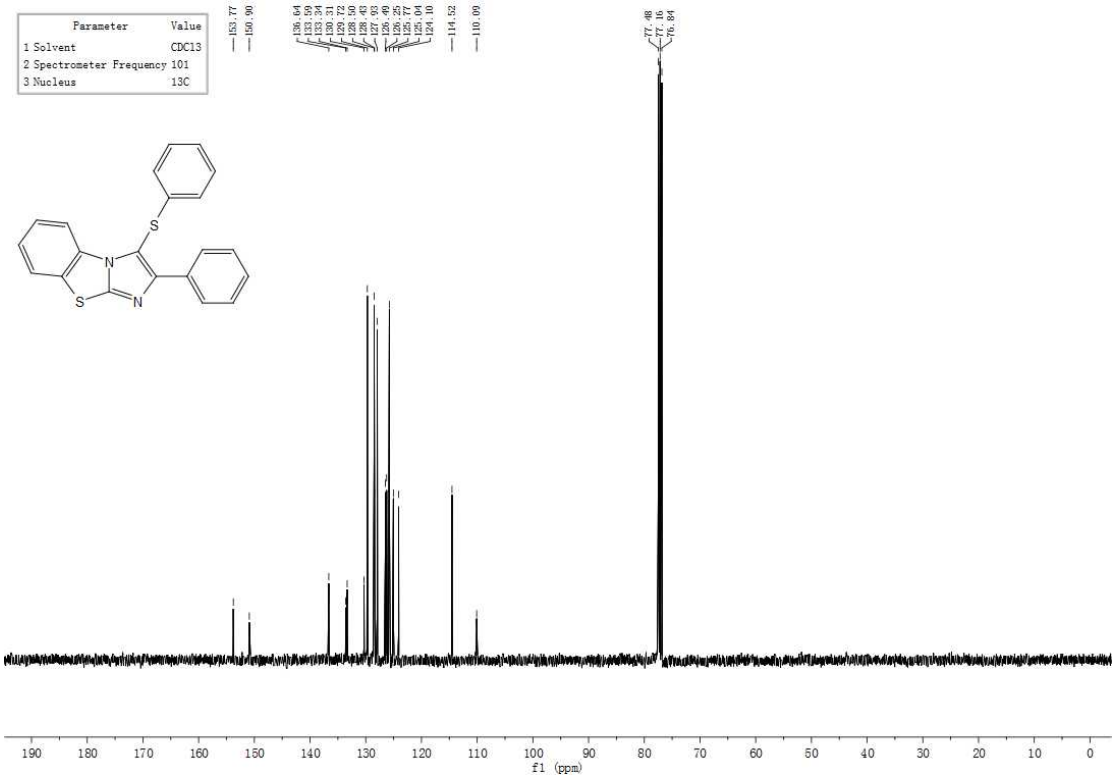
^{13}C NMR (101 MHz, $CDCl_3$) of **5c**



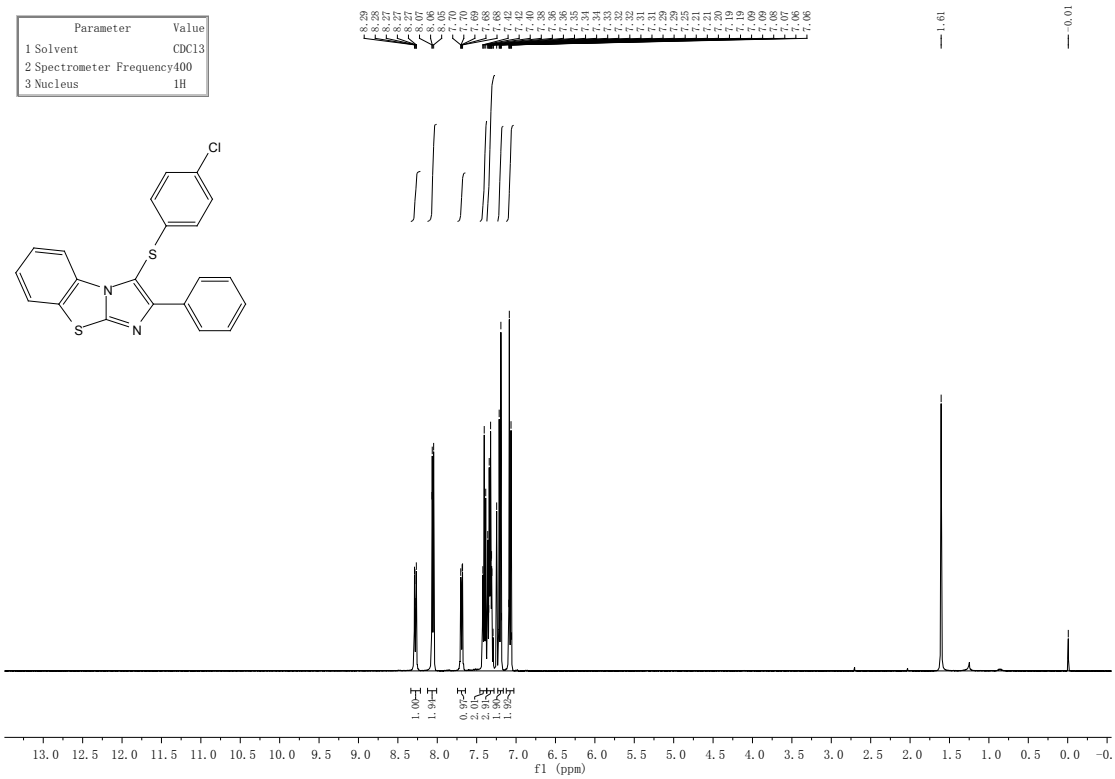
^{1}H NMR (400 MHz, $CDCl_3$) of **5d**



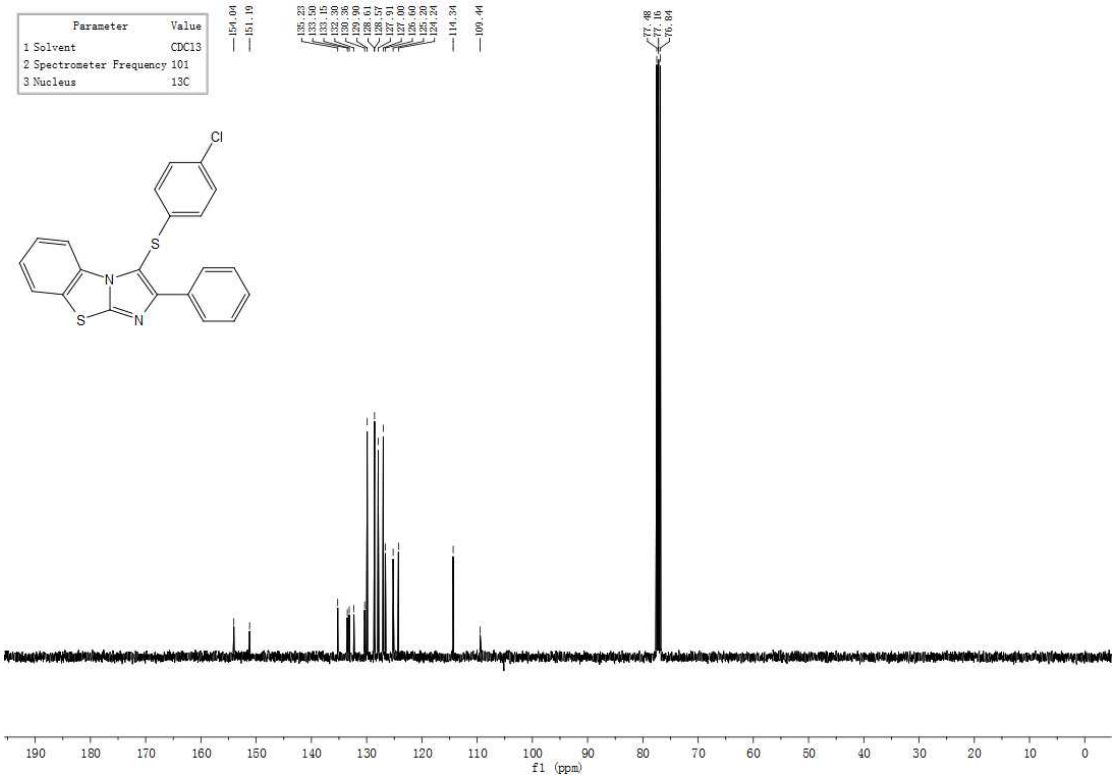
^{13}C NMR (101 MHz, $CDCl_3$) of **5d**



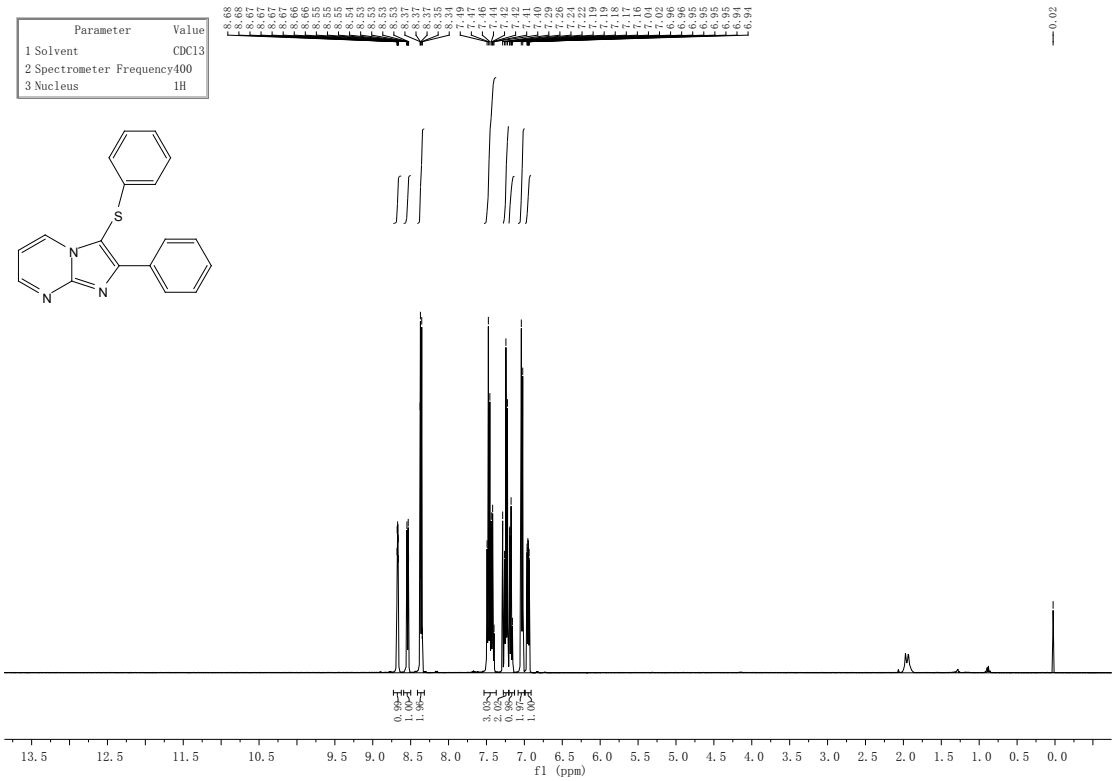
^{1}H NMR (400 MHz, $CDCl_3$) of **5e**



^{13}C NMR (101 MHz, $CDCl_3$) of **5e**



^{1}H NMR (400 MHz, $CDCl_3$) of **5f**



^{13}C NMR (101 MHz, $CDCl_3$) of **5f**