

Supporting Information

**Iodine-Triphenylphosphine Mediated Sulfenylation of
Imidazoheterocycles with Sodium Sulfinates**

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1. General information

¹H-NMR spectra were recorded on a Bruker AVANCE III-400 spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in CDCl₃, ¹³C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl₃ (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°C for 12 h. The reaction mixture was quenched by the addition of sat. aq. Na₂S₂O₃ (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 Na₂SO₄. After removal of solvents with a rotary evaporator, 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°C (Lit. mp 95-97°C); Yield: 95%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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°C; Yield: 90%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₁₉H₁₄FN₂S ([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°C; Yield: 92%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₀H₁₄F₃N₂S ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₆H₂₁N₂OS ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₀H₁₆BrN₂S ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₂H₁₆N₃S ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₄N₃S ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₁₆H₁₅N₂S ([M+H]⁺) 267.0956, found 267.0951.

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

Yellow oil; Yield: 74%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₁₈H₁₅N₂S₂ ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₁₇H₁₂BrN₂S₂ ([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%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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°C; Yield: 95%;

¹H NMR (400 MHz, CDCl₃) 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).

¹³C NMR (101 MHz, CDCl₃) 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 C₂₁H₁₄ClN₂S₂ ([M+H]⁺) 393.0281, found 393.0287.

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

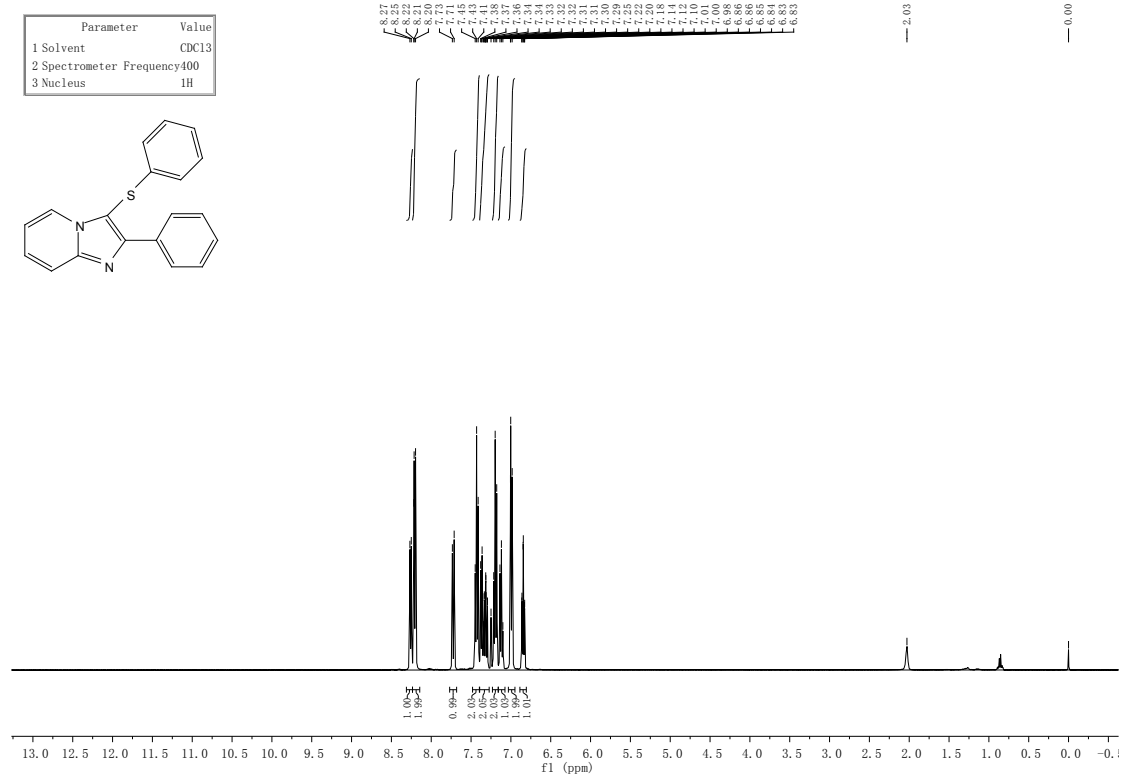
White solid; mp 125-126°C; Yield: 91%;

¹H NMR (400 MHz, CDCl₃) 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).

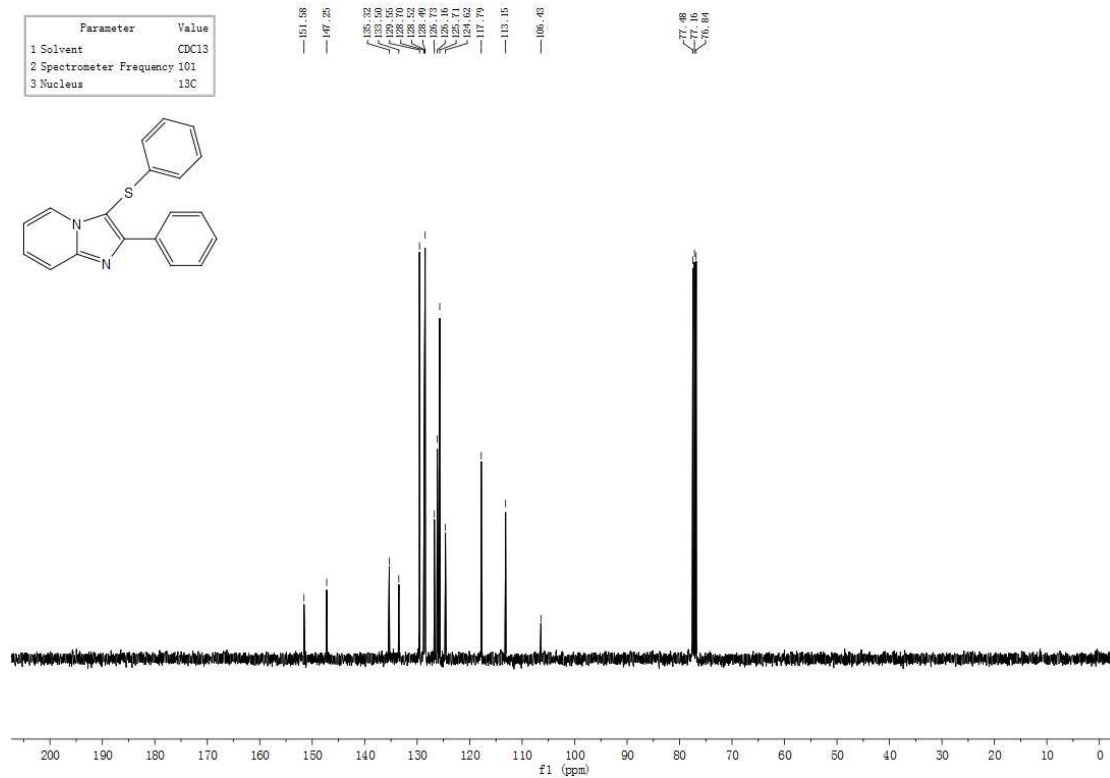
¹³C NMR (101 MHz, CDCl₃) δ 152.9, 151.7, 150.1, 134.3, 132.8, 132.2, 129.7, 129.2, 128.7, 128.6, 126.5, 125.9, 109.4, 105.4.

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

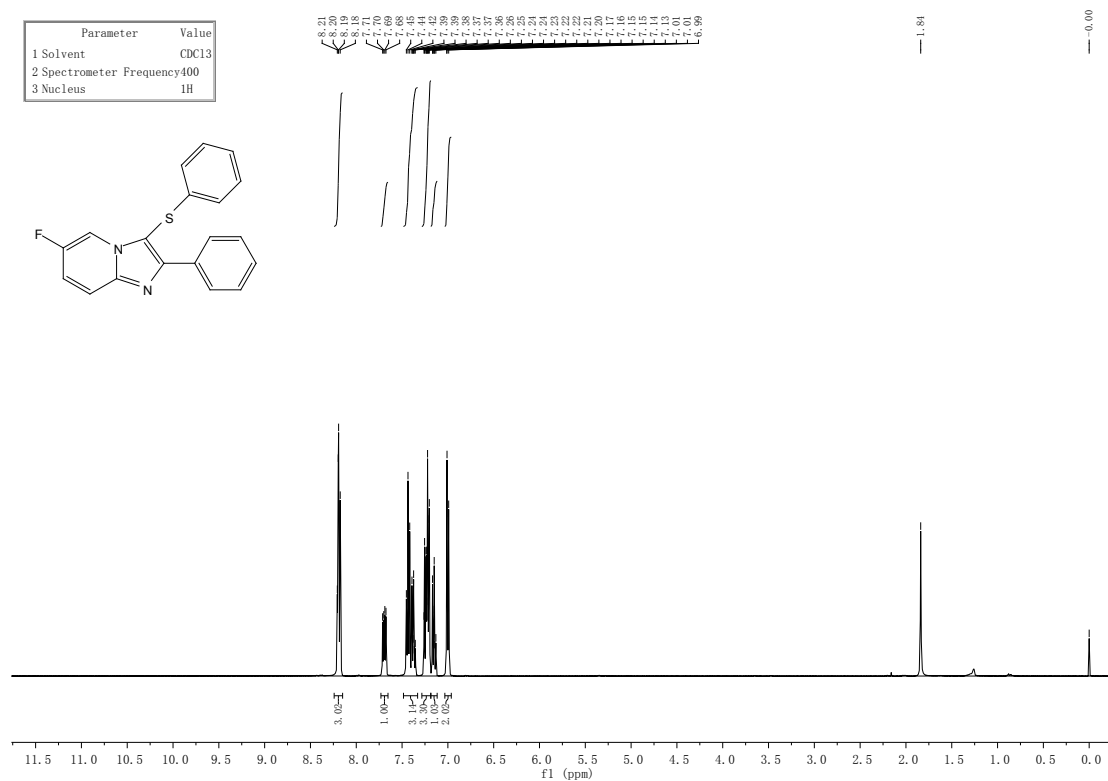
^1H NMR (400 MHz, CDCl_3) of **3a**



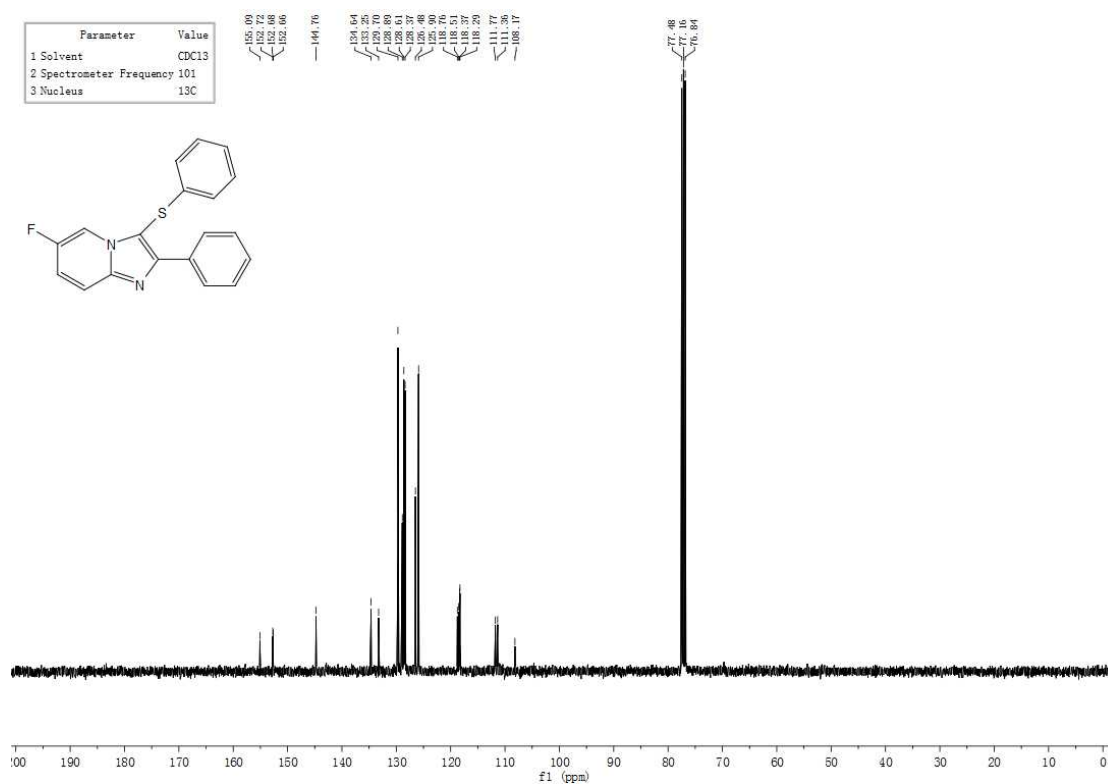
^{13}C NMR (101 MHz, CDCl_3) of **3a**



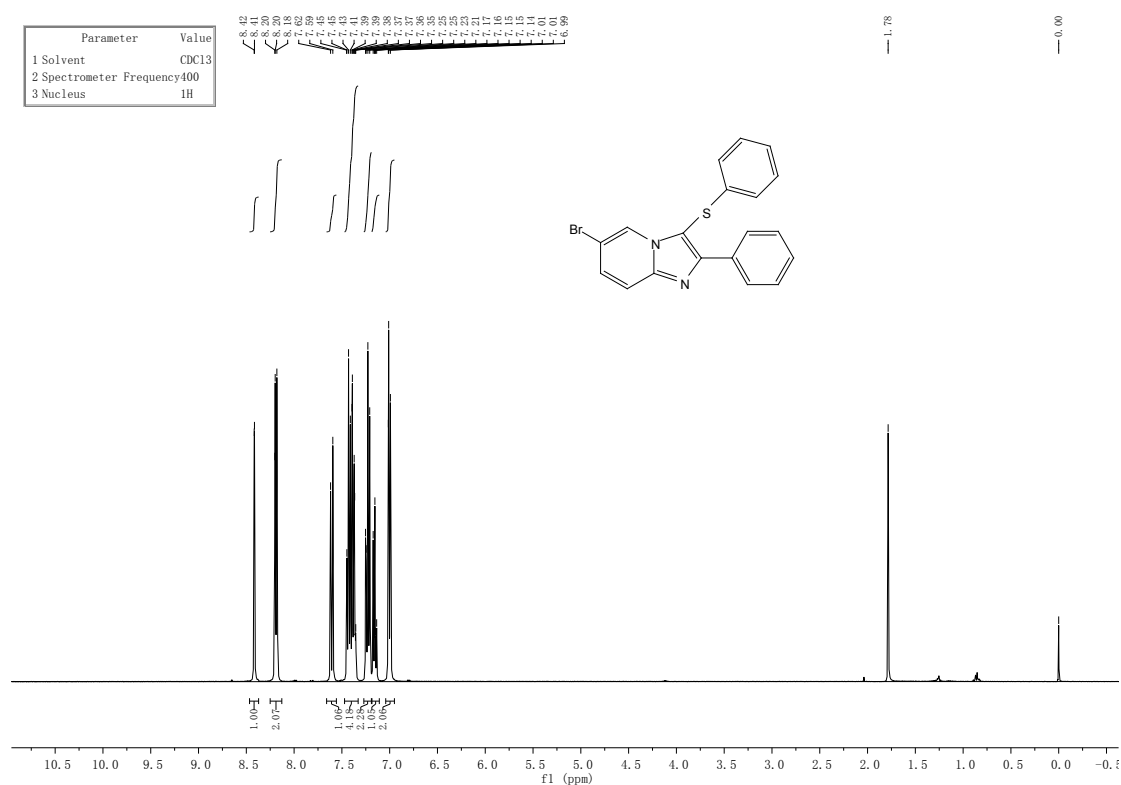
¹H NMR (400 MHz, CDCl₃) of **3b**



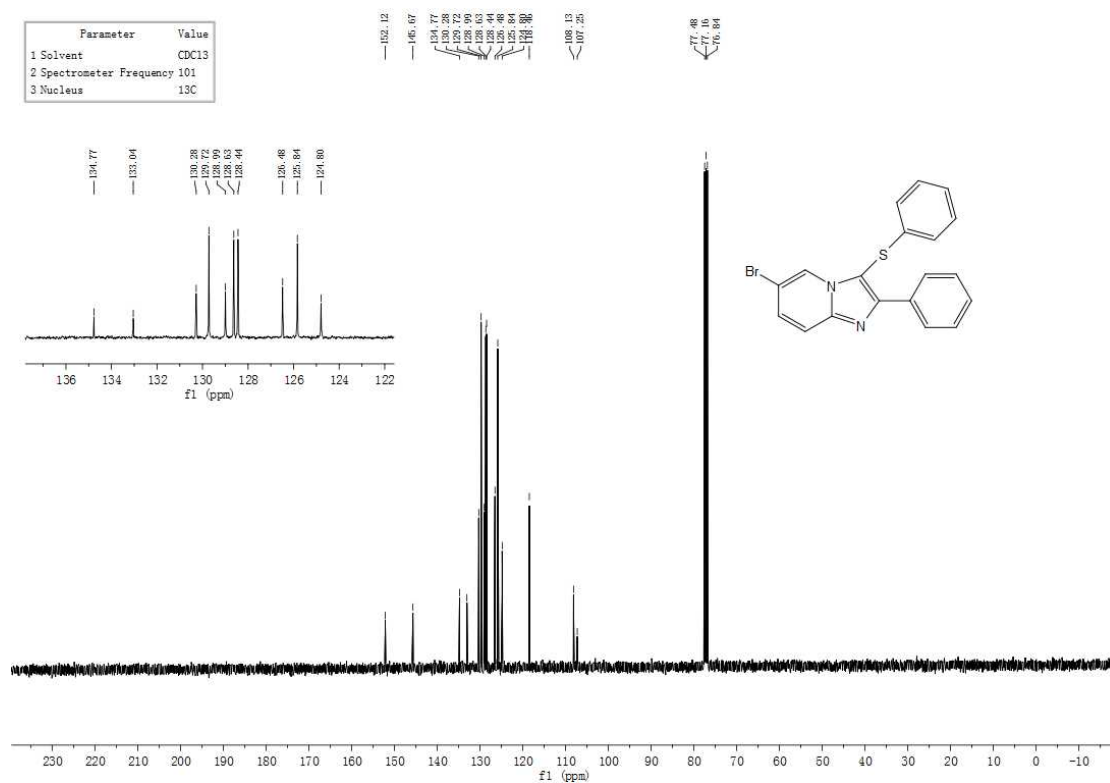
¹³C NMR (101 MHz, CDCl₃) of **3b**



¹H NMR (400 MHz, CDCl₃) of **3c**



¹³C NMR (101 MHz, CDCl₃) of **3c**



[illegible]

Parameter Value

1 Solvent CDCl₃

2 Spectrometer Frequency 101

3 Nucleus ¹³C

152.31, 151.72, 151.33, 150.96, 139.71, 139.65, 138.62, 138.41, 138.18, 137.89, 136.47, 135.80, 131.67, 121.19, 118.19, 117.36, 77.16, 76.94, 77.48, 77.16, 76.94, 107.36

200 180 160 140 120 100 80 60 40 20 0

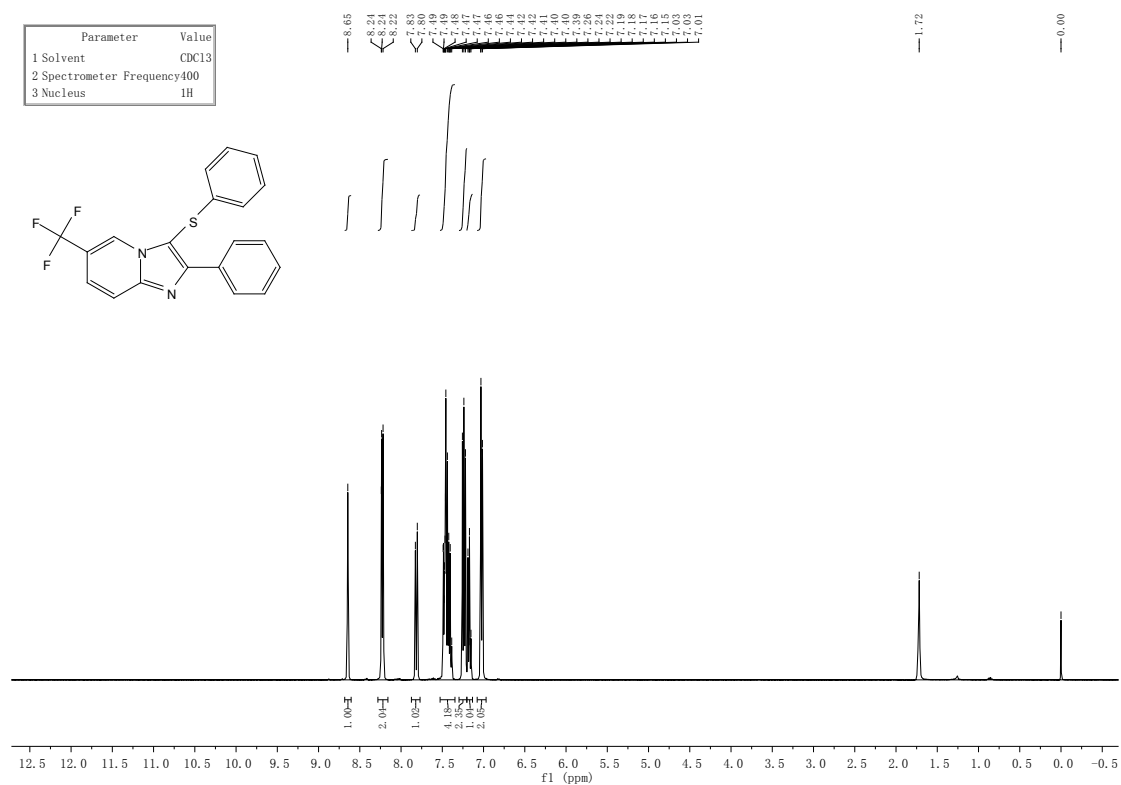
f1 (ppm)

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

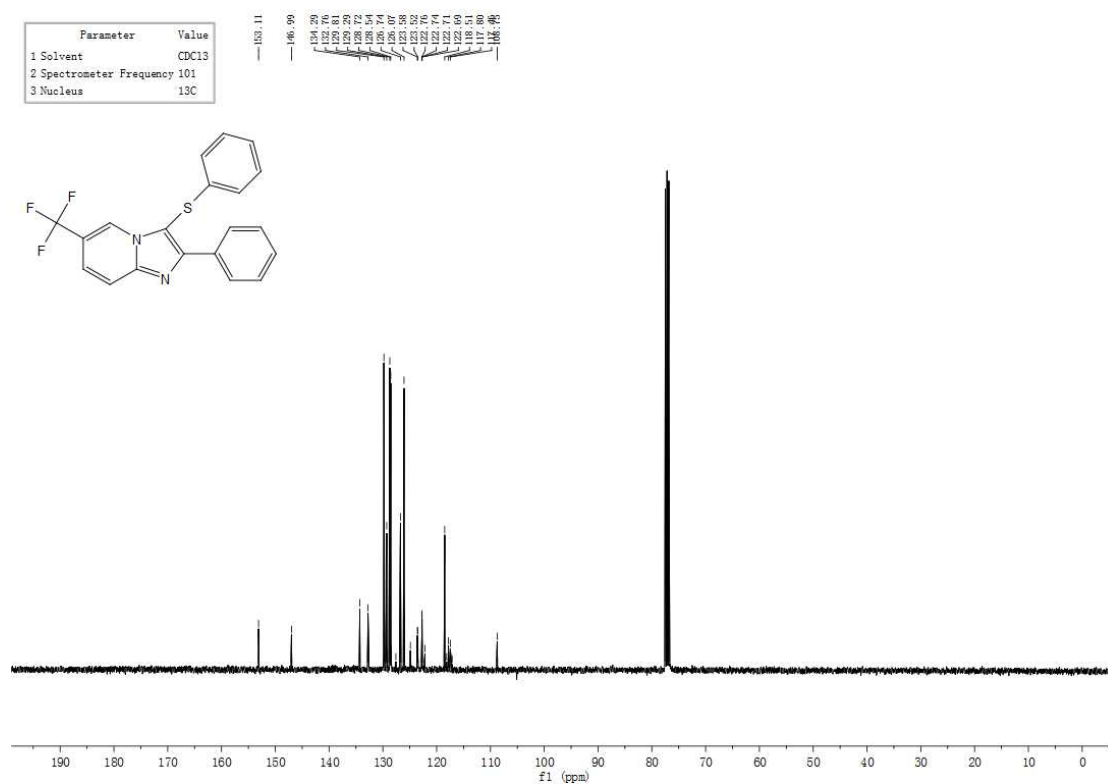
f1 (ppm)

c1ccc(cc1)-c2nc3ccc(Cl)cc3n2Sc4ccccc4

¹H NMR (400 MHz, CDCl₃) of **3e**



¹³C NMR (101 MHz, CDCl₃) of **3e**



[illegible]

Chemical structure of 2-methyl-4-phenyl-5-phenylthio-1H-benzotriazole:

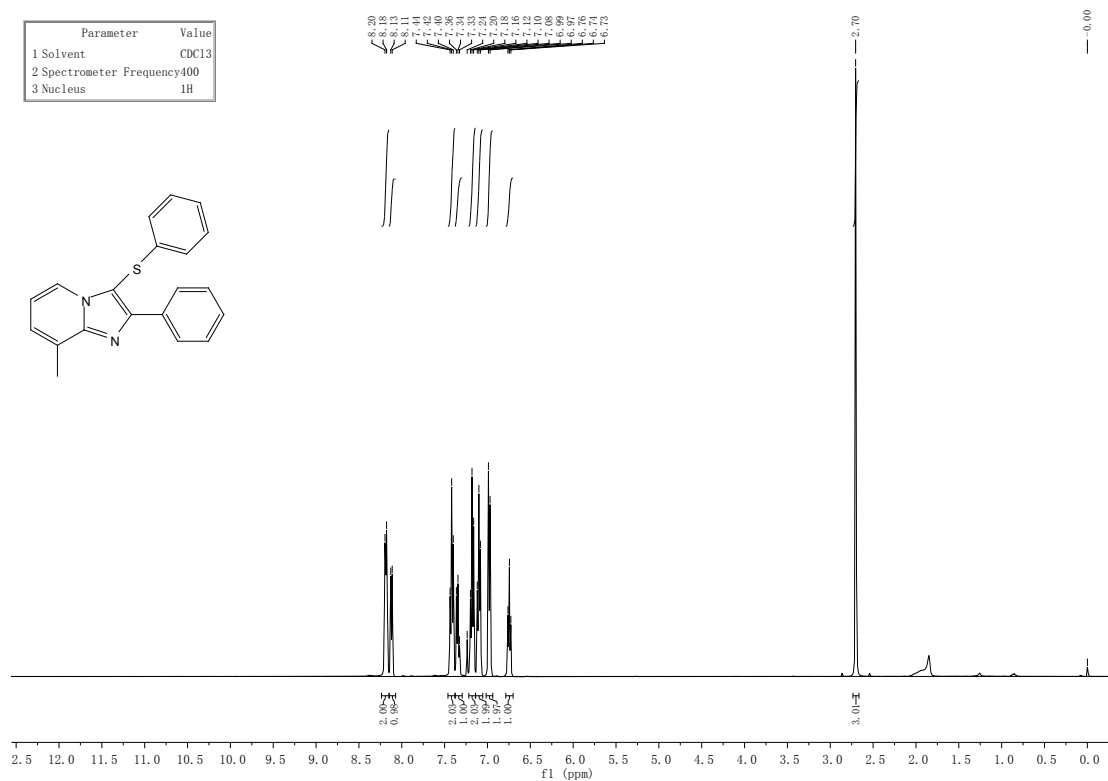
Cc1nc2ccccc2n(c1)S(c3ccccc3)c4ccccc4

¹³C NMR spectrum (CDCl₃) showing peaks at 151.43, 146.32, 135.70, 129.88, 129.54, 129.49, 129.39, 129.04, 125.56, 125.31, 125.21, 105.85, 77.48, 77.04, 76.84, 18.49, and 15.58 ppm.

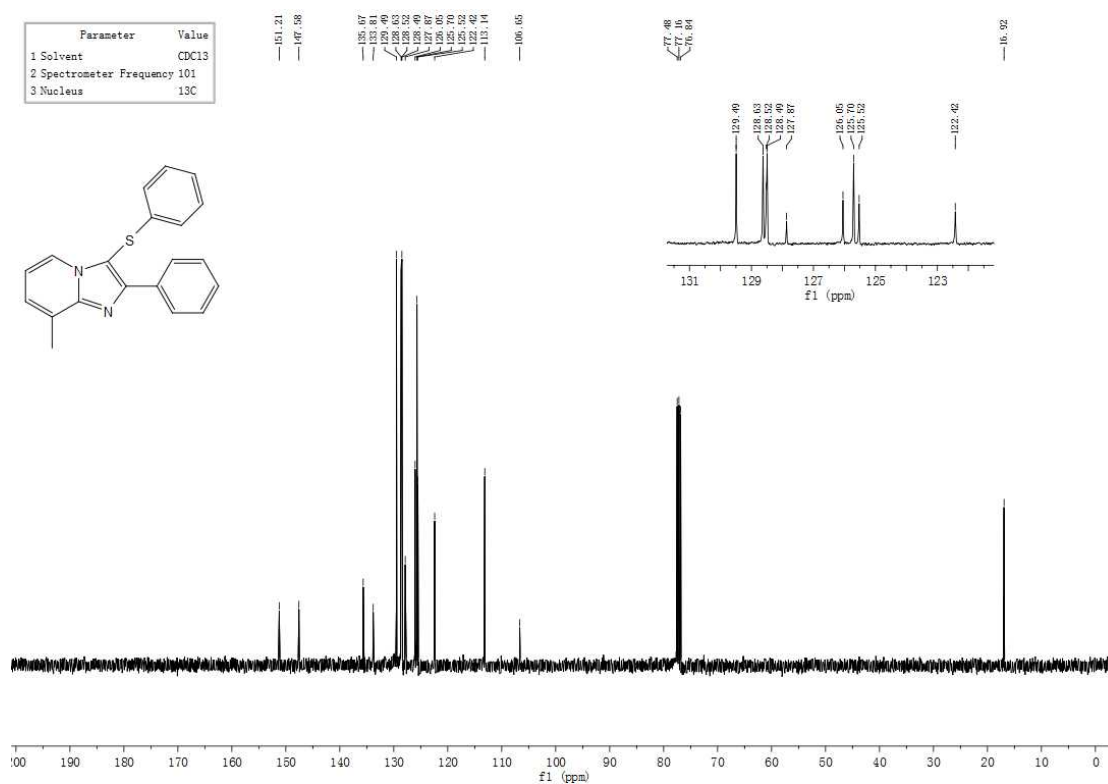
Table of peak data:

Peak Number	Chemical Shift (ppm)
1	151.43
2	146.32
3	135.70
4	129.88
5	129.54
6	129.49
7	129.39
8	129.04
9	125.56
10	125.31
11	125.21
12	105.85
13	77.48
14	77.04
15	76.84
16	18.49
17	15.58

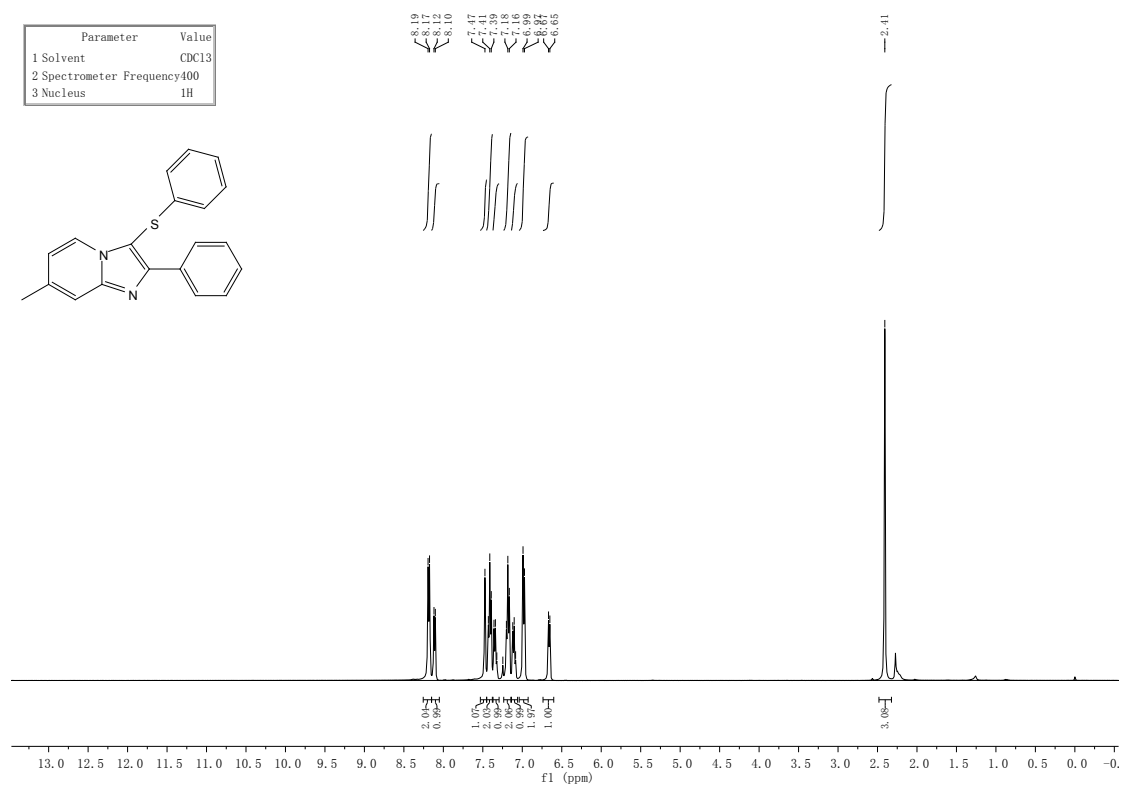
^1H NMR (400 MHz, CDCl_3) of **3g**



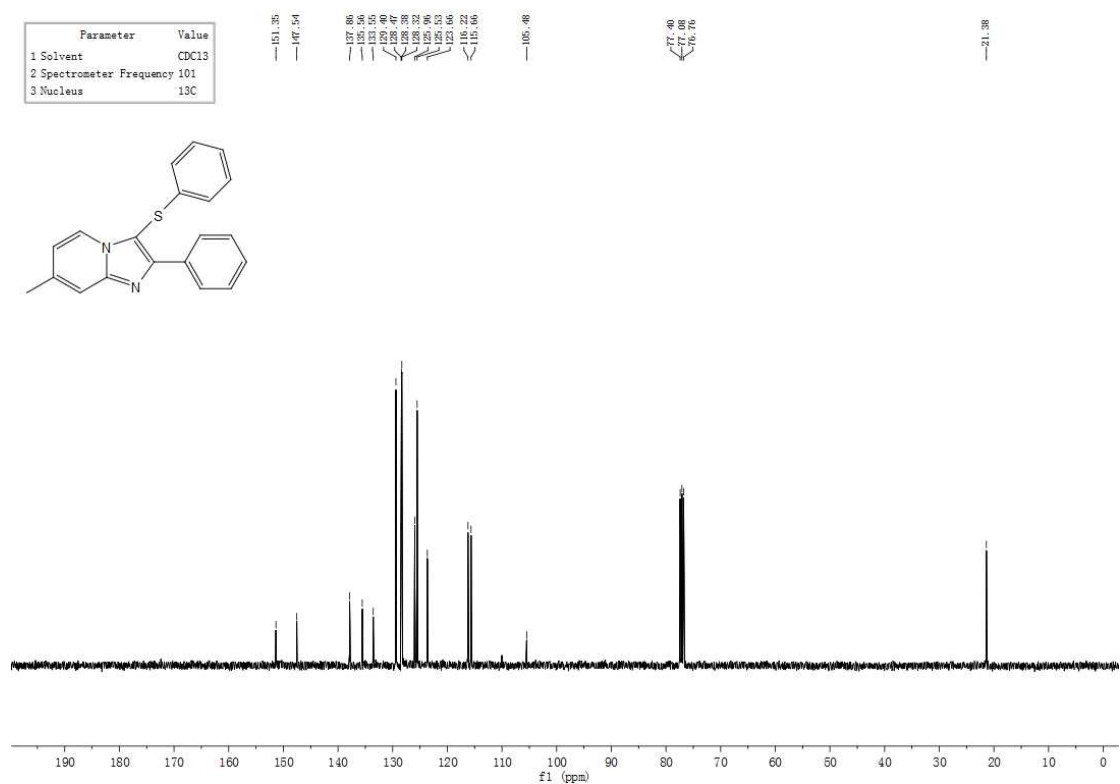
^{13}C NMR (101 MHz, CDCl_3) of **3g**



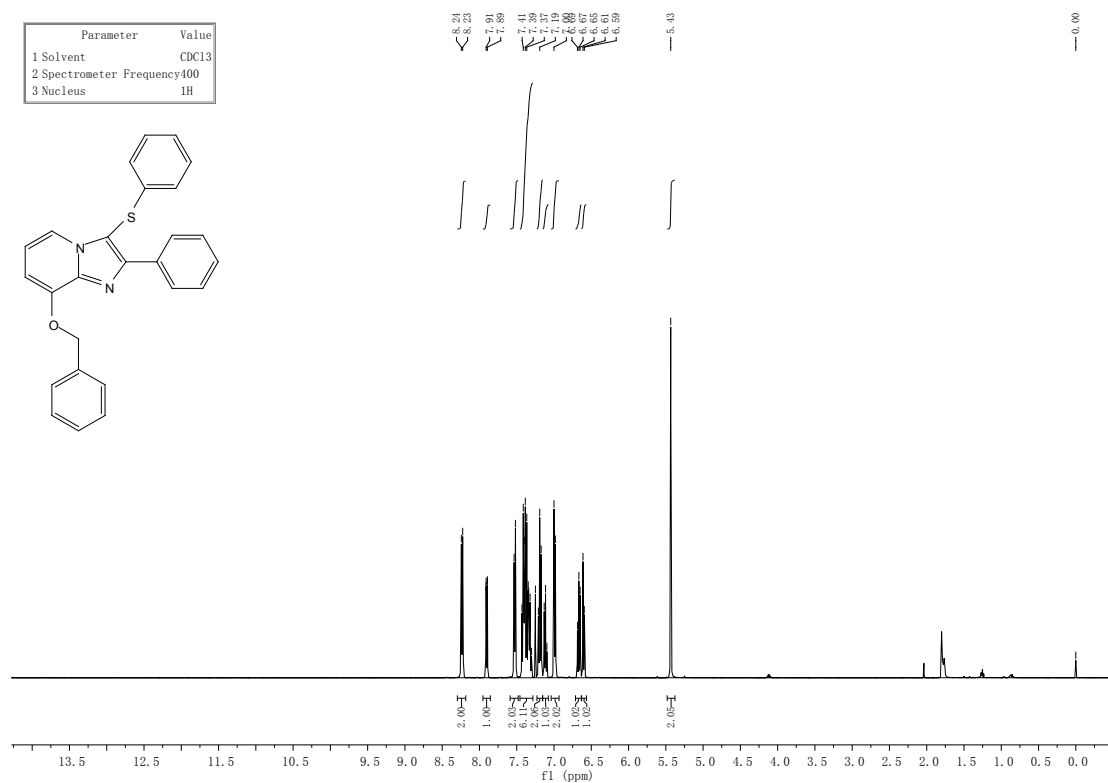
¹H NMR (400 MHz, CDCl₃) of **3h**



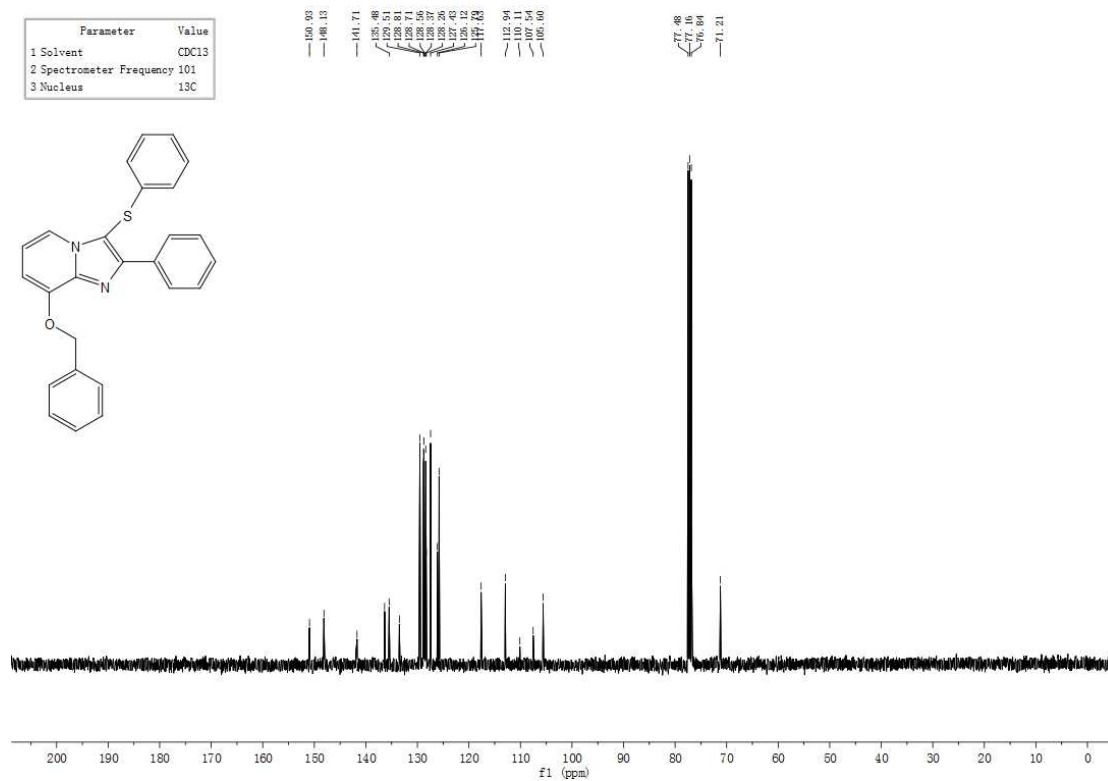
¹³C NMR (101 MHz, CDCl₃) of **3h**



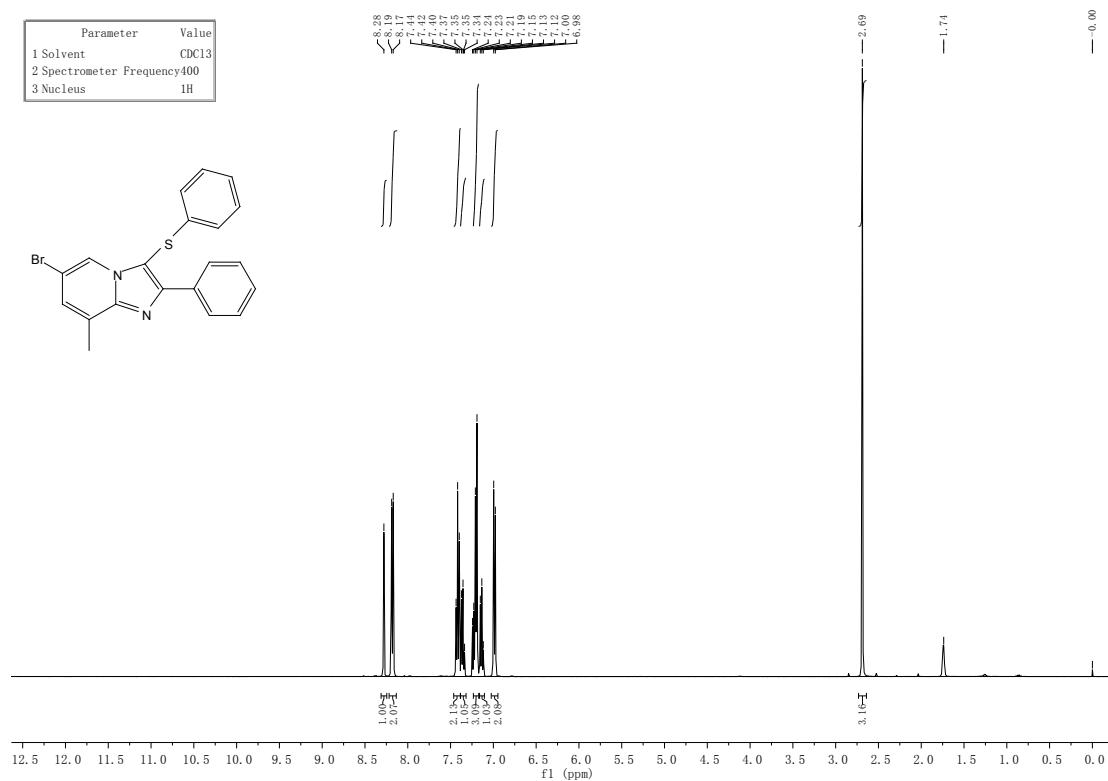
¹H NMR (400 MHz, CDCl₃) of **3i**



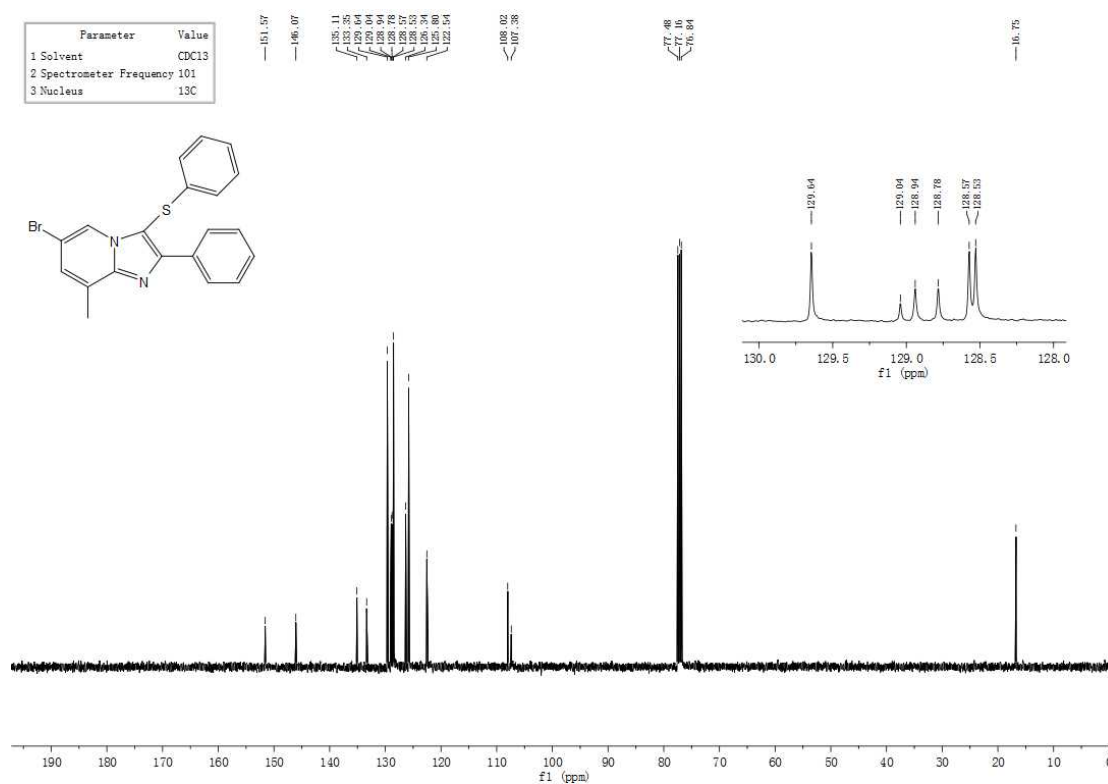
¹³C NMR (101 MHz, CDCl₃) of **3i**



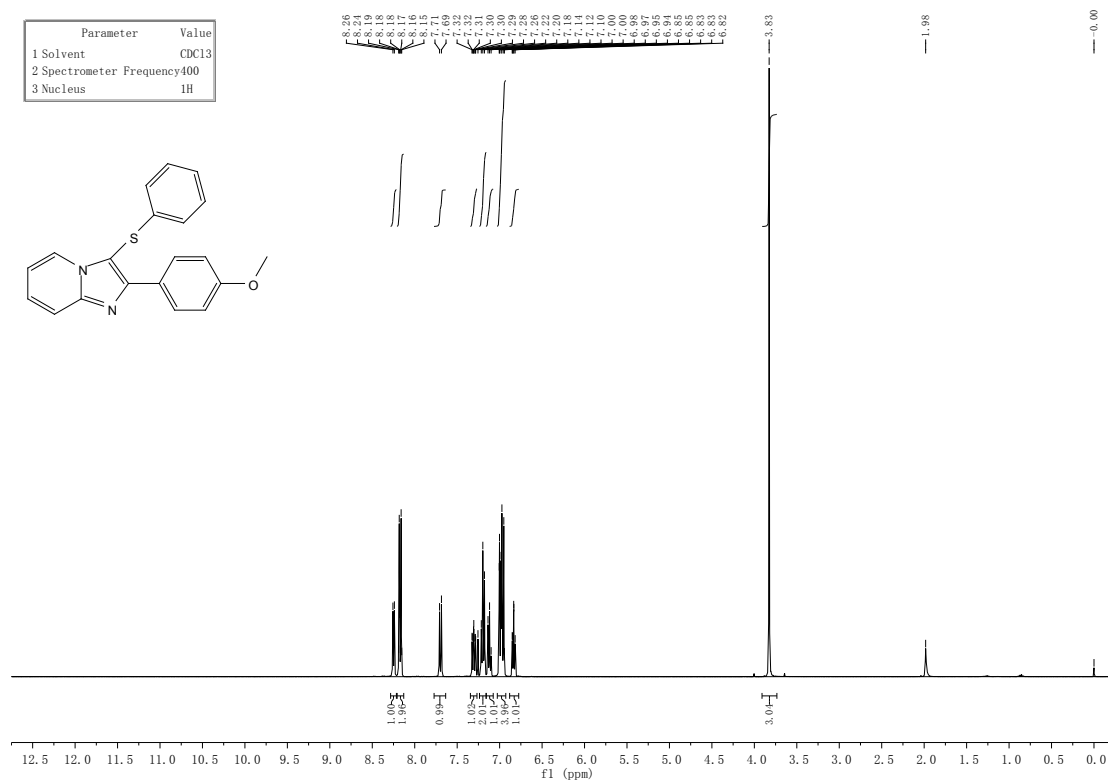
¹H NMR (400 MHz, CDCl₃) of **3j**



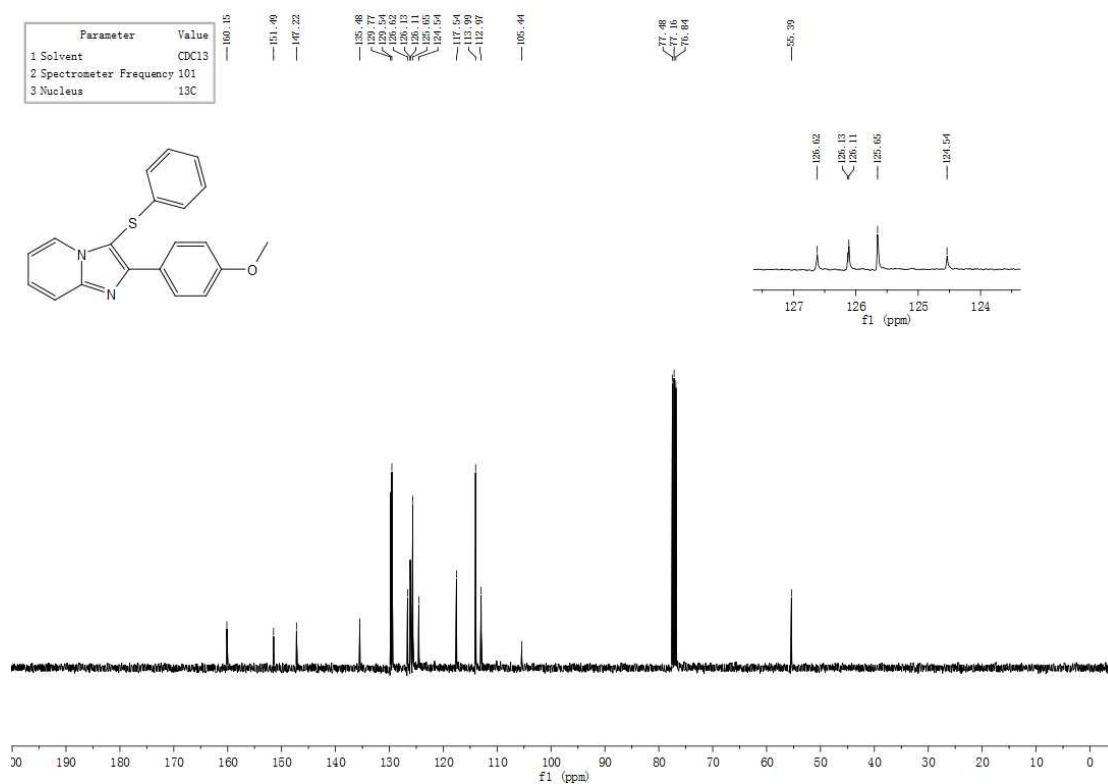
¹³C NMR (101 MHz, CDCl₃) of **3j**



¹H NMR (400 MHz, CDCl₃) of **3k**



¹³C NMR (101 MHz, CDCl₃) of **3k**



Parameter	Value
1 Solvent	CDCl3
2 Spectrometer Frequency	400
3 Nucleus	1H

Chemical structure: Cc1ccc(cc1)c2nc3ccccc3n2

1H NMR spectrum (CDCl3) showing peaks from 0 to 8 ppm. The x-axis is labeled f1 (ppm). The spectrum includes a list of peak data on the right side.

Chemical Shift (ppm)	Integration
7.85	1.00
7.82	1.99
7.72	1.00
7.31	1.05
7.29	4.25
7.25	1.00
7.21	2.00
7.13	1.04
7.12	
7.10	
7.00	
6.98	
6.97	
6.84	
6.82	
2.38	3.07

Chemical structure: Cc1ccc(cc1)c2nc3ccccc3n2S4=CC=CC=C4

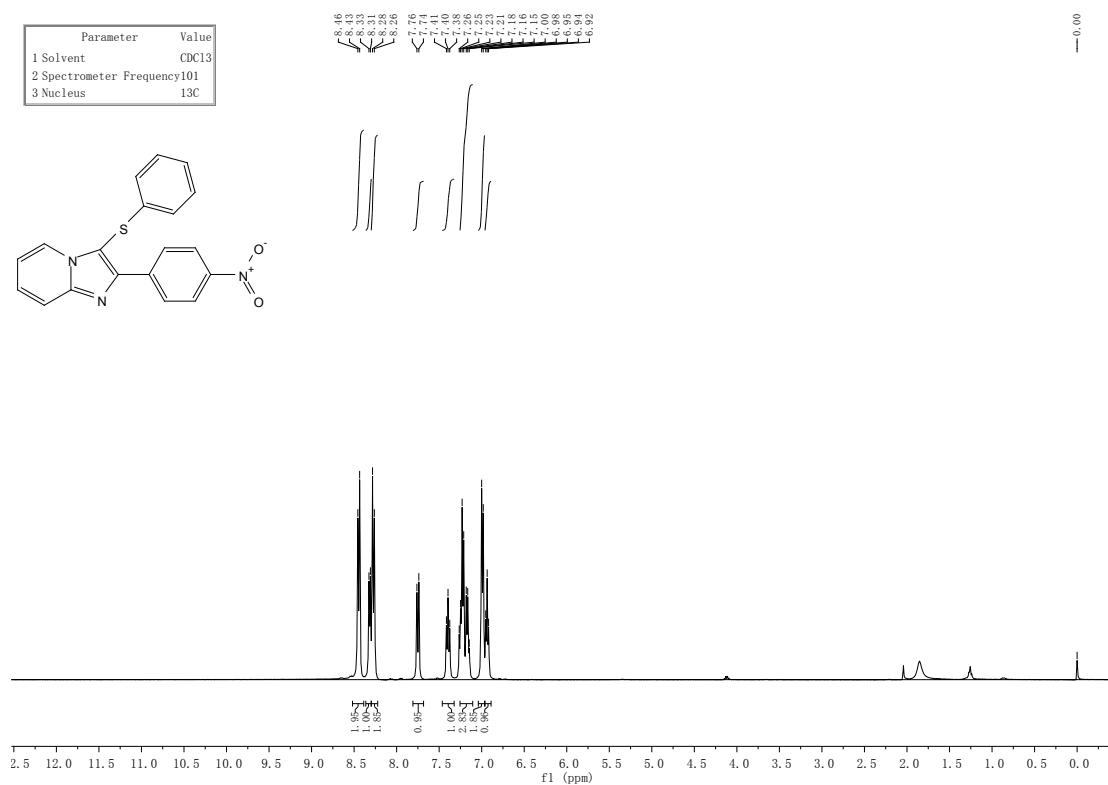
¹³C NMR spectrum (CDCl₃) showing peaks at the following chemical shifts (ppm): 197.22, 138.63, 137.43, 136.43, 129.27, 128.34, 128.34, 128.34, 126.10, 125.68, 124.57, 117.68, 113.06, 106.00, 77.48, 77.16, 76.94, and 21.47.

197.22
138.63
137.43
136.43
129.27
128.34
128.34
128.34
126.10
125.68
124.57
117.68
113.06
106.00
77.48
77.16
76.94
21.47

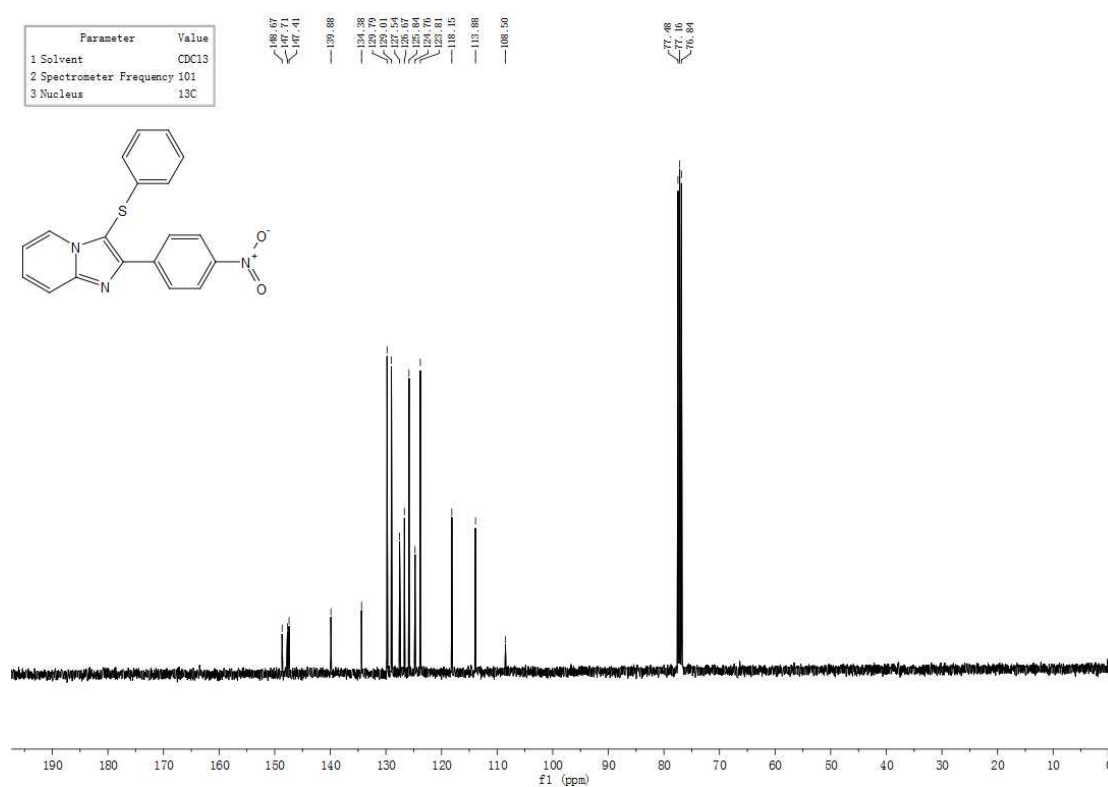
Parameter Value
1 Solvent CDCl₃
2 Spectrometer Frequency 101
3 Nucleus ¹³C

Chemical structure: Cc1ccc(cc1)c2nc3ccccc3n2S4=CC=CC=C4

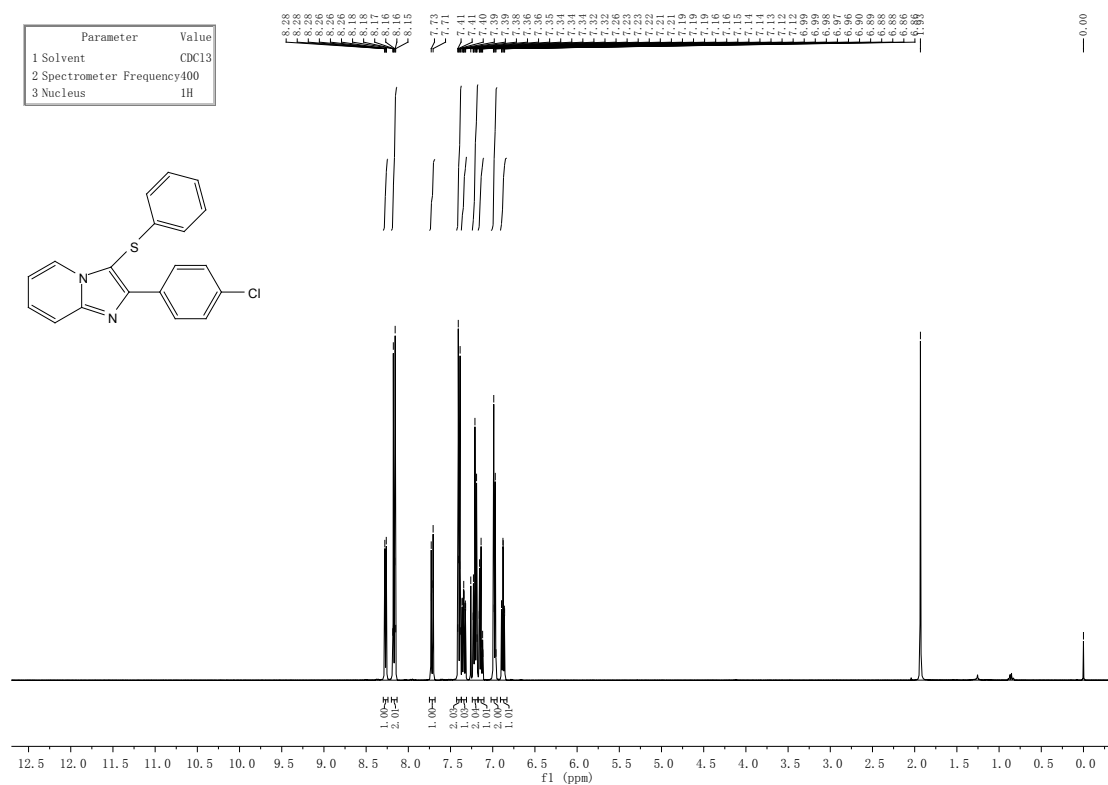
¹H NMR (400 MHz, CDCl₃) of **3m**



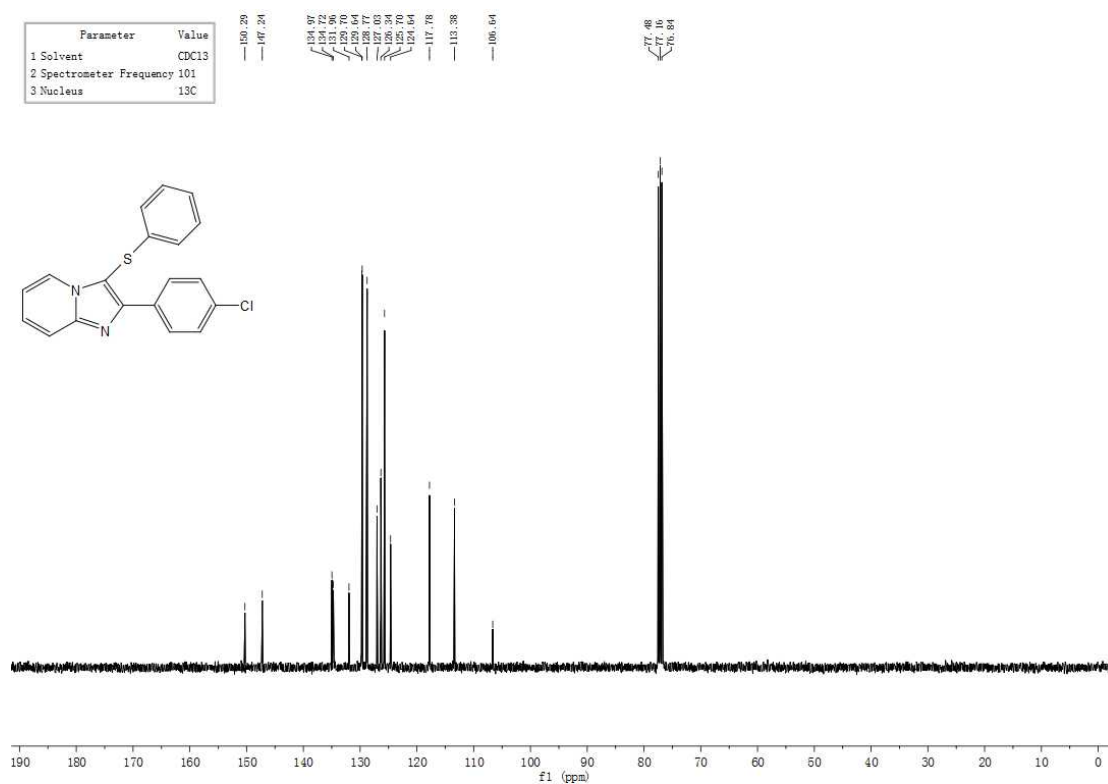
¹³C NMR (101 MHz, CDCl₃) of **3m**



¹H NMR (400 MHz, CDCl₃) of **3n**



¹³C NMR (101 MHz, CDCl₃) of **3n**



Chemical structure of 2-(benzenesulfanylmethyl)-4-chlorophenyl-1H-imidazole:

c1ccc(cc1)S[C@H]2C=NC3=CC=CC=C3N2c4ccc(Cl)cc4

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (6.5-8.2 ppm) and aliphatic region (1.8-2.0 ppm). Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
~8.20	1.00
~7.71	1.00
~7.37	1.00
~7.34	1.00
~7.28	1.00
~7.17	1.00
~7.16	1.00
~7.11	1.00
~7.10	1.00
~7.08	1.00
~6.91	1.00
~6.89	1.00
~6.57	1.00
~1.91	1.00
~1.83	1.00
~0.00	1.00

[illegible]

Chemical structure: c1ccc(cc1)S2=CN3C=CC=CC=C3N2c4ccccc4

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 8.5 ppm. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
~8.4	1.00
~8.1	0.96
~7.9	1.00
~7.7	0.96
~7.5	1.05
~7.4	0.96
~7.3	1.00
~7.2	0.96
~7.1	1.00
~7.0	0.96
~6.9	1.00
~6.8	0.96
~6.7	1.00
~6.6	0.96
~6.5	1.00
~6.4	0.96
~6.3	1.00
~6.2	0.96
~6.1	1.00
~6.0	0.96
~5.9	1.00
~5.8	0.96
~5.7	1.00
~5.6	0.96
~5.5	1.00
~5.4	0.96
~5.3	1.00
~5.2	0.96
~5.1	1.00
~5.0	0.96
~4.9	1.00
~4.8	0.96
~4.7	1.00
~4.6	0.96
~4.5	1.00
~4.4	0.96
~4.3	1.00
~4.2	0.96
~4.1	1.00
~4.0	0.96
~3.9	1.00
~3.8	0.96
~3.7	1.00
~3.6	0.96
~3.5	1.00
~3.4	0.96
~3.3	1.00
~3.2	0.96
~3.1	1.00
~3.0	0.96
~2.9	1.00
~2.8	0.96
~2.7	1.00
~2.6	0.96
~2.5	1.00
~2.4	0.96
~2.3	1.00
~2.2	0.96
~2.1	1.00
~2.0	0.96
~1.9	1.00
~1.8	0.96
~1.7	1.00
~1.6	0.96
~1.5	1.00
~1.4	0.96
~1.3	1.00
~1.2	0.96
~1.1	1.00
~1.0	0.96
~0.9	1.00
~0.8	0.96
~0.7	1.00
~0.6	0.96
~0.5	1.00
~0.4	0.96
~0.3	1.00
~0.2	0.96
~0.1	1.00
~0.0	0.96

Parameter Value

1 Solvent CDCl₃

2 Spectrometer Frequency 101

3 Nucleus ¹³C

Chemical structure: c1ccc(cc1)S[C@H]2c3ccccc3n2Cc4ccsc4

Peak list (ppm): 147.24, 146.96, 138.38, 134.73, 129.55, 127.87, 126.96, 126.96, 126.96, 126.07, 124.47, 113.25, 106.63, 77.48, 77.16, 76.84, 29.55, 27.87, 26.99, 26.96, 26.11, 26.18, 26.07, 24.47.

Chemical structure: CN1C=NC2=CC=CC=C2S1Cc3ccccc3

¹H NMR spectrum (CDCl₃, 400 MHz) showing peaks in the aromatic region (6.5-8.5 ppm) and a methine peak at 2.58 ppm. Integration values are provided below the peaks.

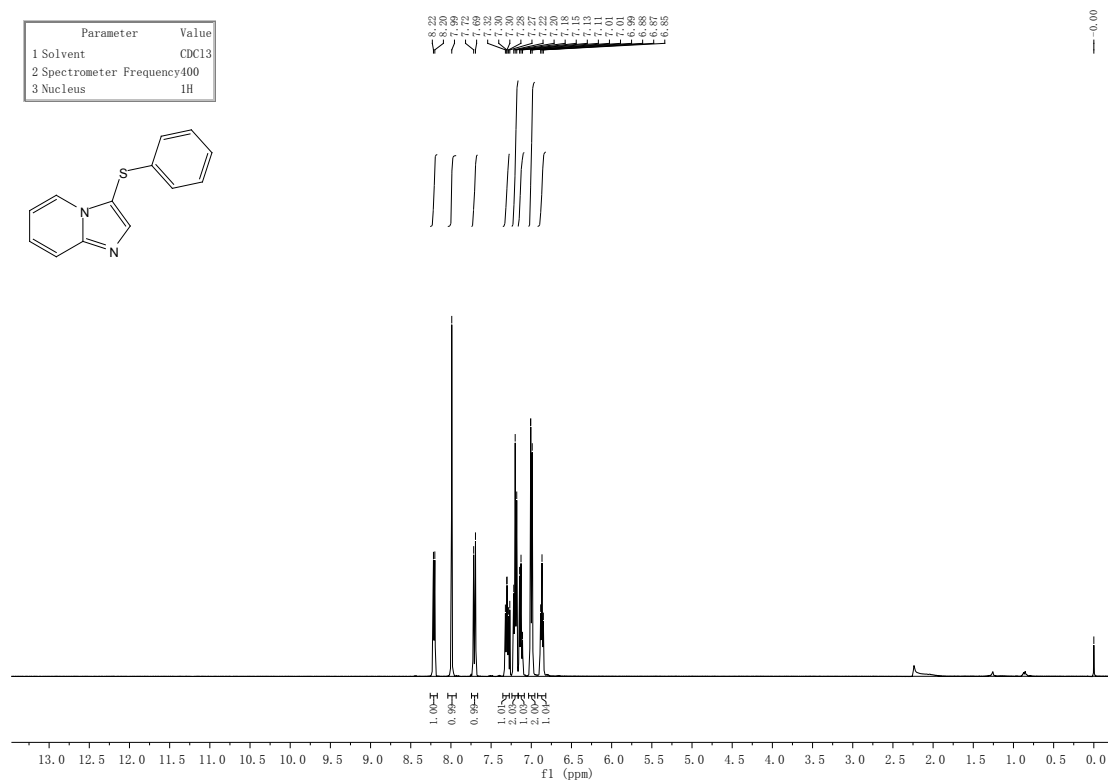
Chemical Shift (ppm)	Integration
~8.1	1.00
~7.6	1.00
~7.3	1.00
~7.2	1.00
~7.1	1.00
~7.0	2.00
~6.8	1.00
2.58	3.11

Parameter	Value
1 Solvent	CDC13
2 Spectrometer Frequency	101
3 Nucleus	¹³ C

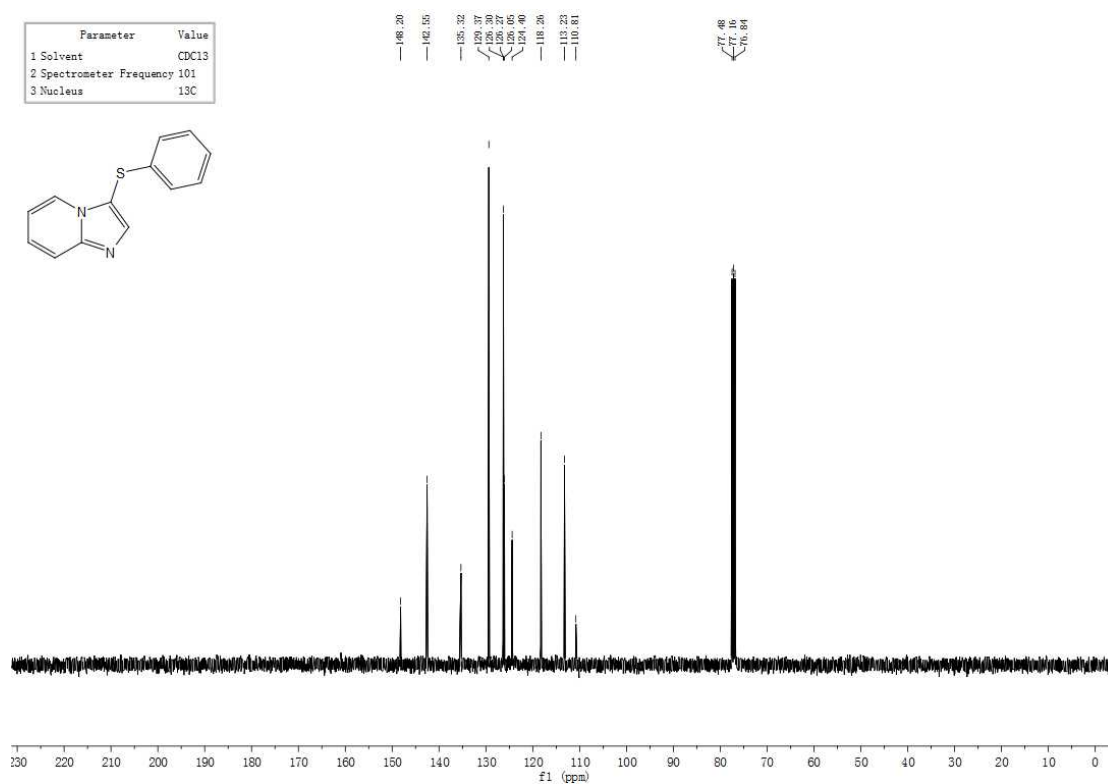
Chemical structure: Cc1nc2ccccc2n1Sc3ccccc3

Peak list (ppm): 151.79, 147.09, 135.73, 129.37, 129.44, 126.04, 125.78, 124.44, 117.11, 112.71, 107.53, 77.48, 77.16, 76.84, 14.08.

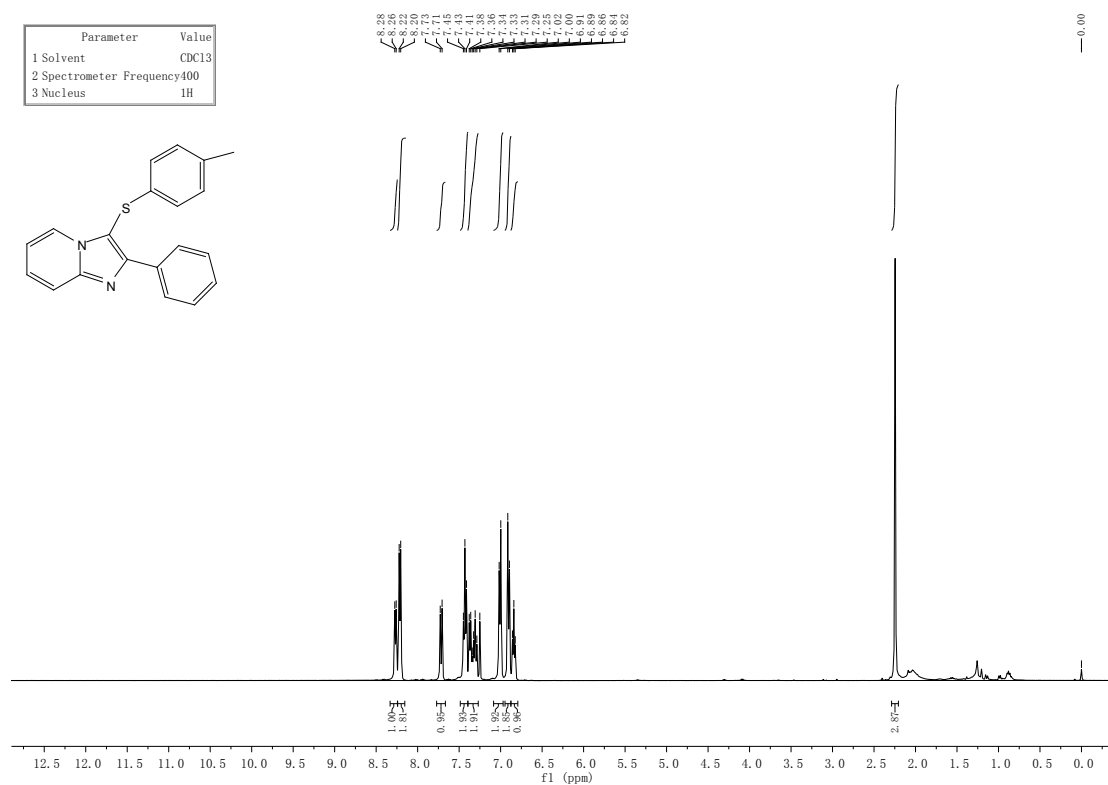
¹H NMR (400 MHz, CDCl₃) of **3r**



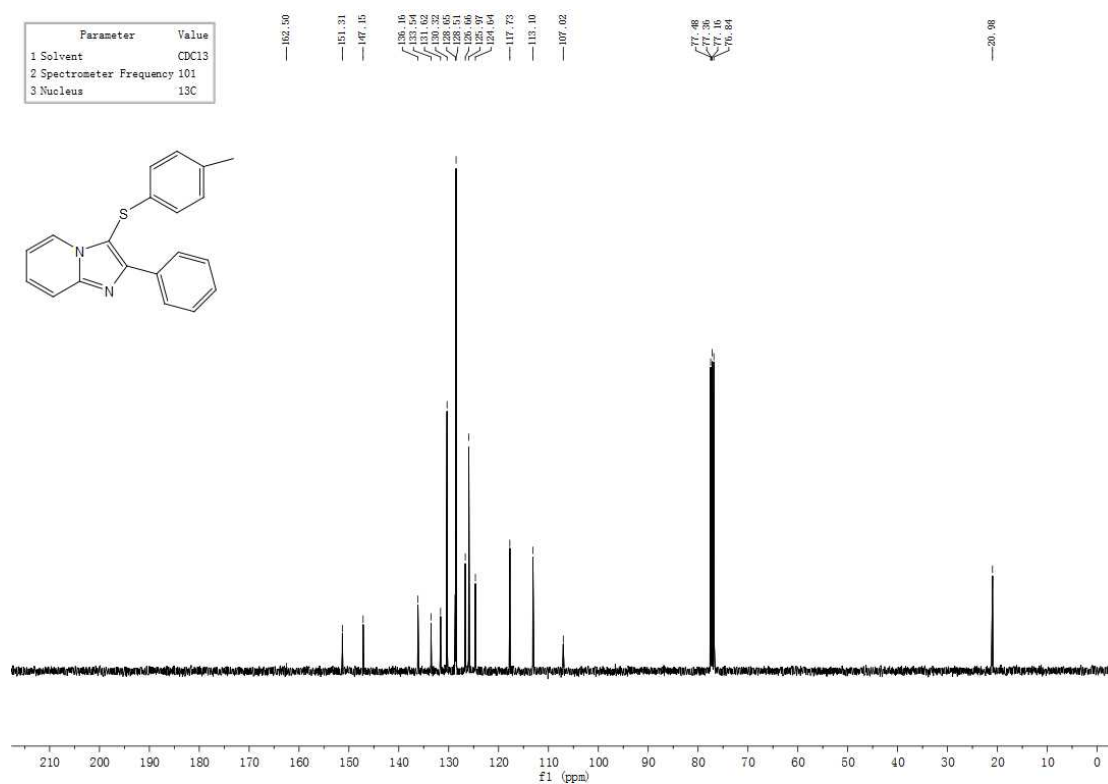
¹³C NMR (101 MHz, CDCl₃) of **3r**



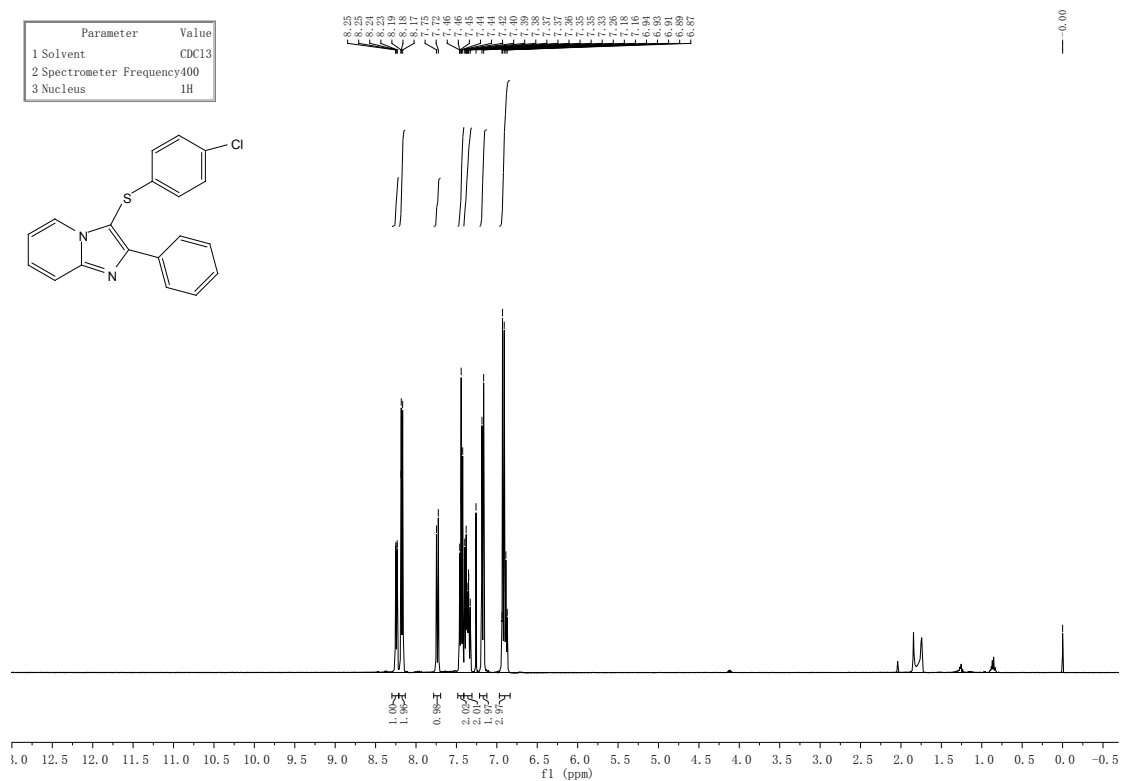
¹H NMR (400 MHz, CDCl₃) of **3s**



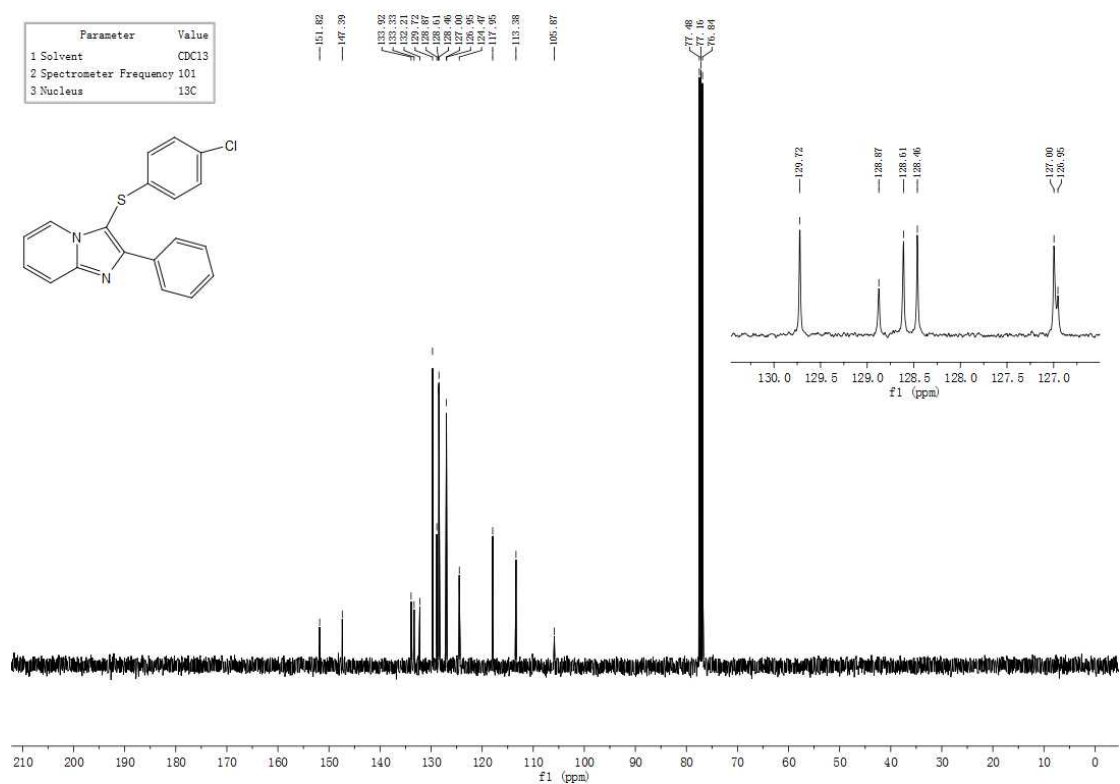
¹³C NMR (101 MHz, CDCl₃) of **3s**



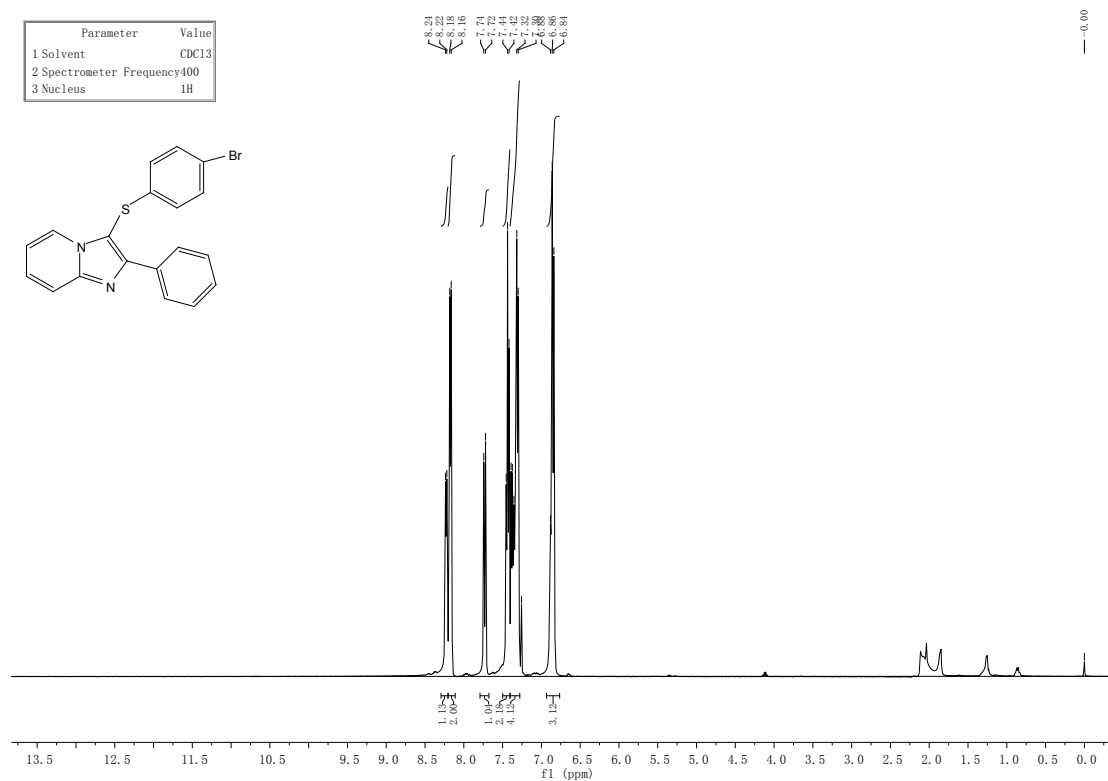
¹H NMR (400 MHz, CDCl₃) of **3t**



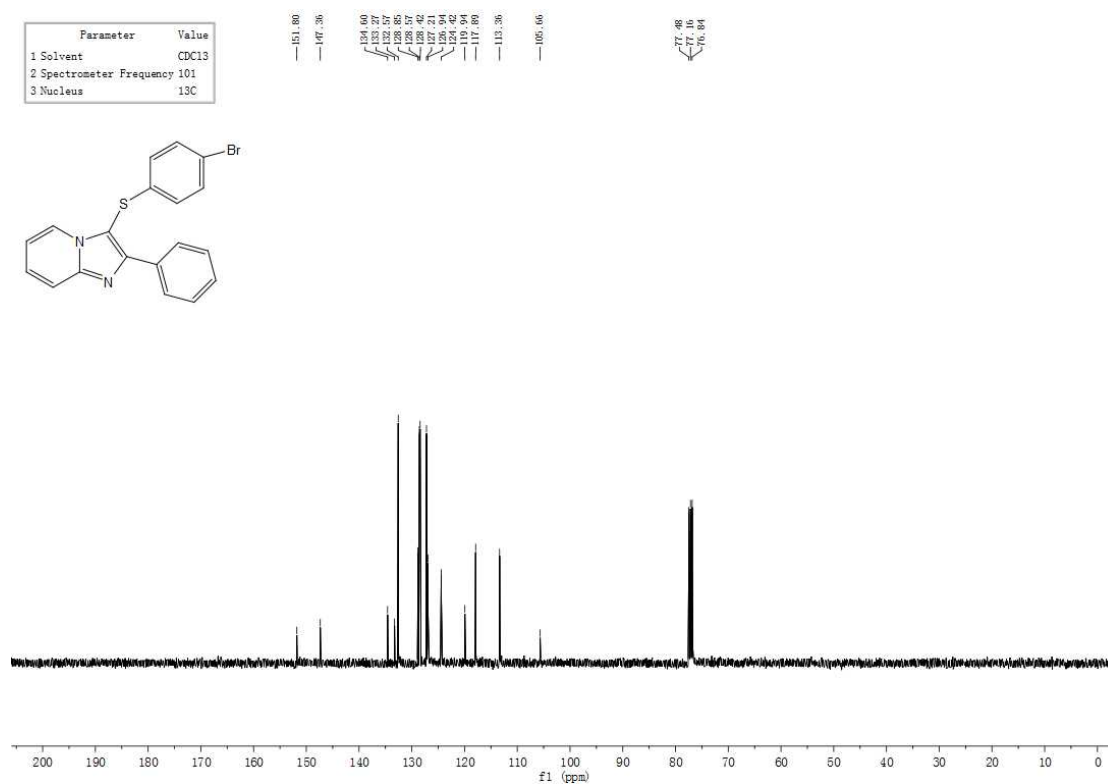
¹³C NMR (101 MHz, CDCl₃) of **3t**



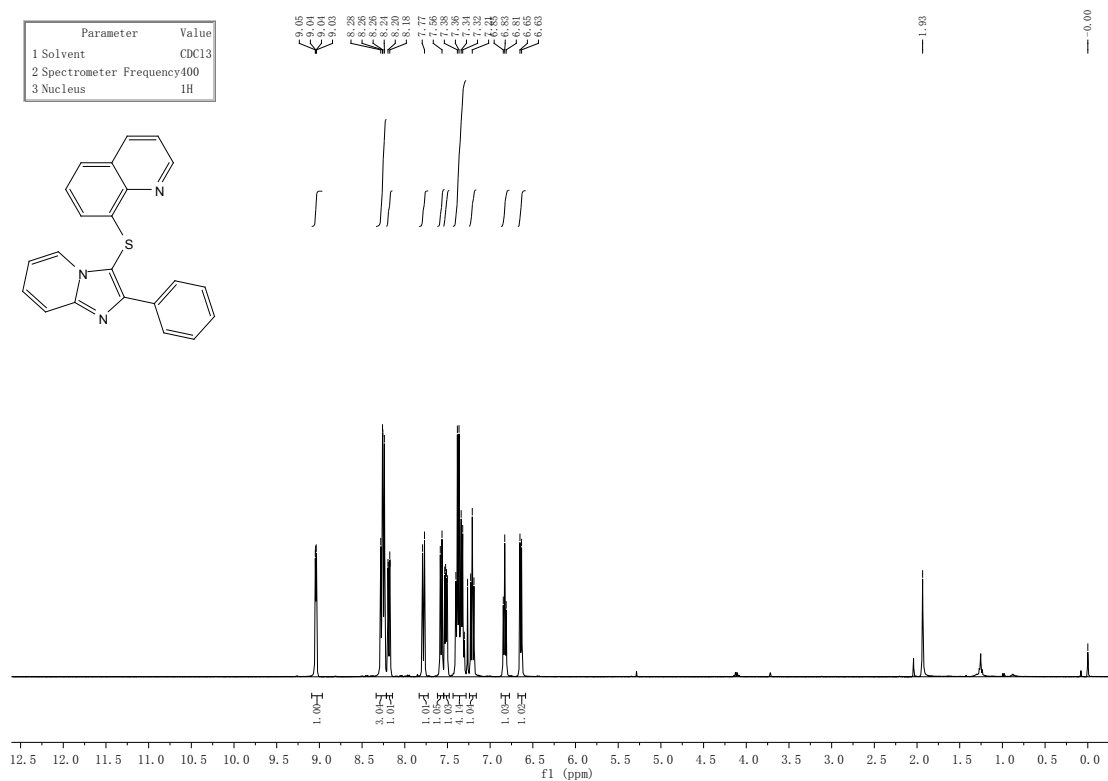
¹H NMR (400 MHz, CDCl₃) of **3u**



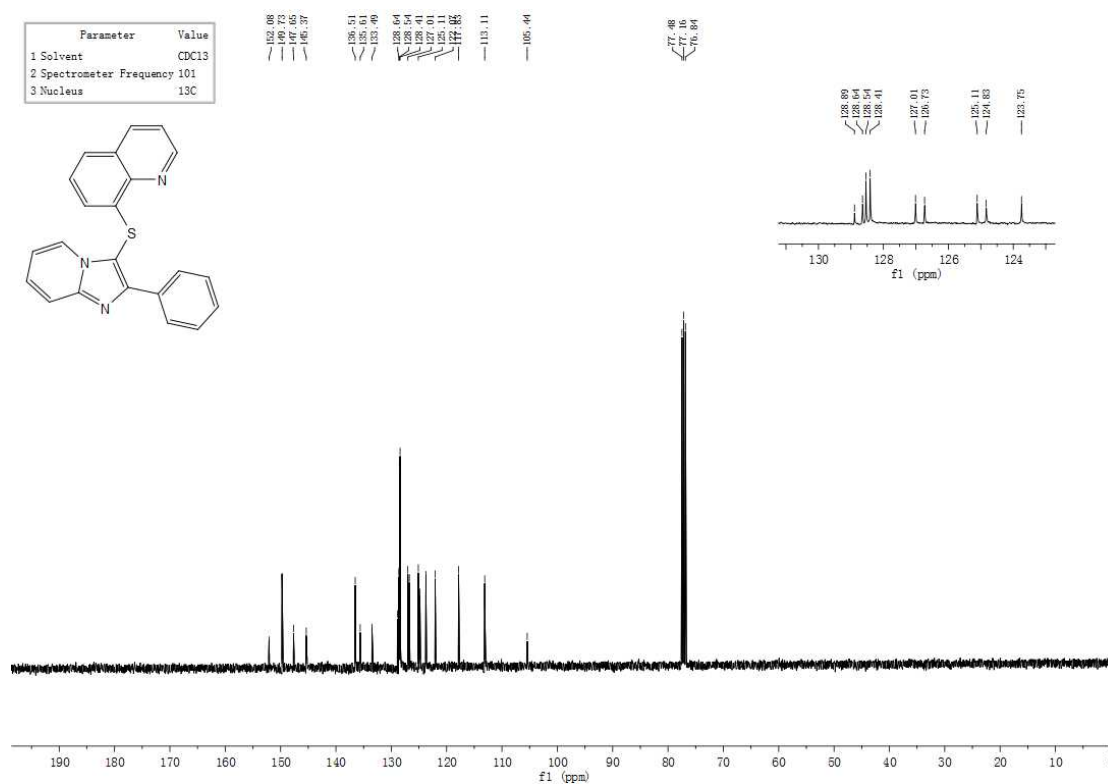
¹³C NMR (101 MHz, CDCl₃) of **3u**



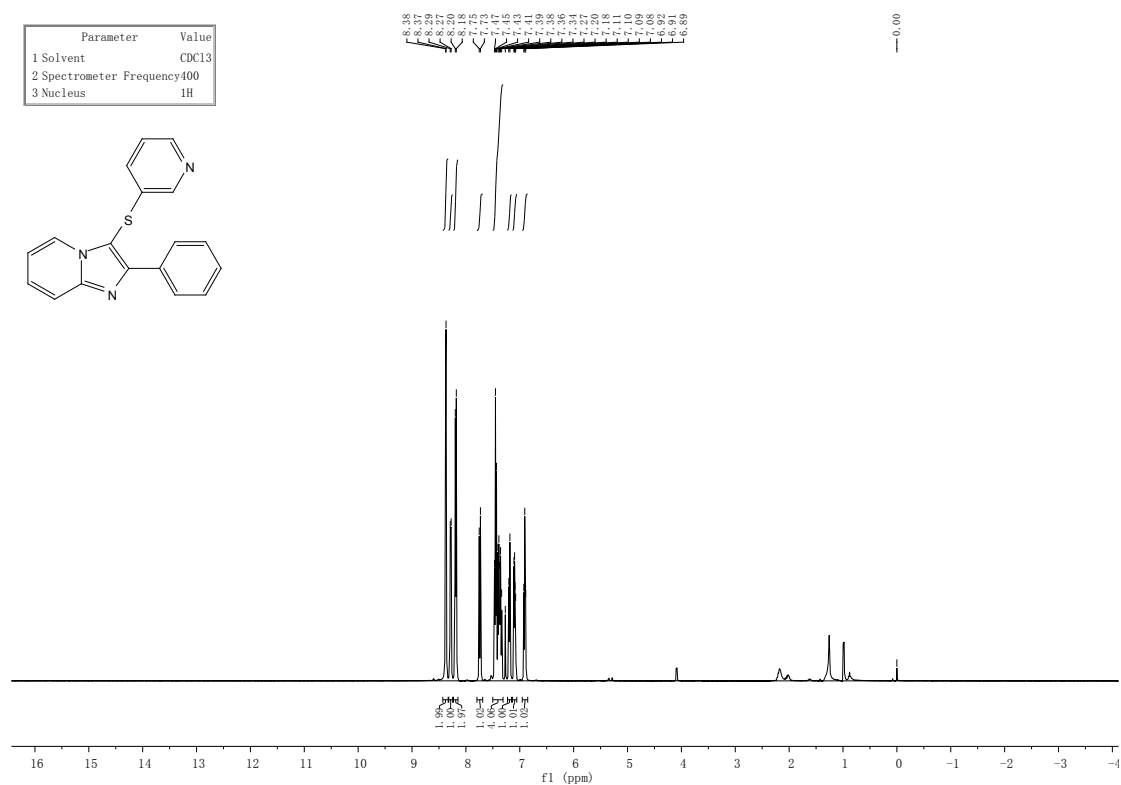
¹H NMR (400 MHz, CDCl₃) of **3v**



¹³C NMR (101 MHz, CDCl₃) of **3v**



¹H NMR (400 MHz, CDCl₃) of **3w**



[illegible]

Parameter Value

1 Solvent CDCl₃

2 Spectrometer Frequency 101

3 Nucleus ¹³C

Chemical structure: Cc1nc2ccccc2n1-c3ccccc3

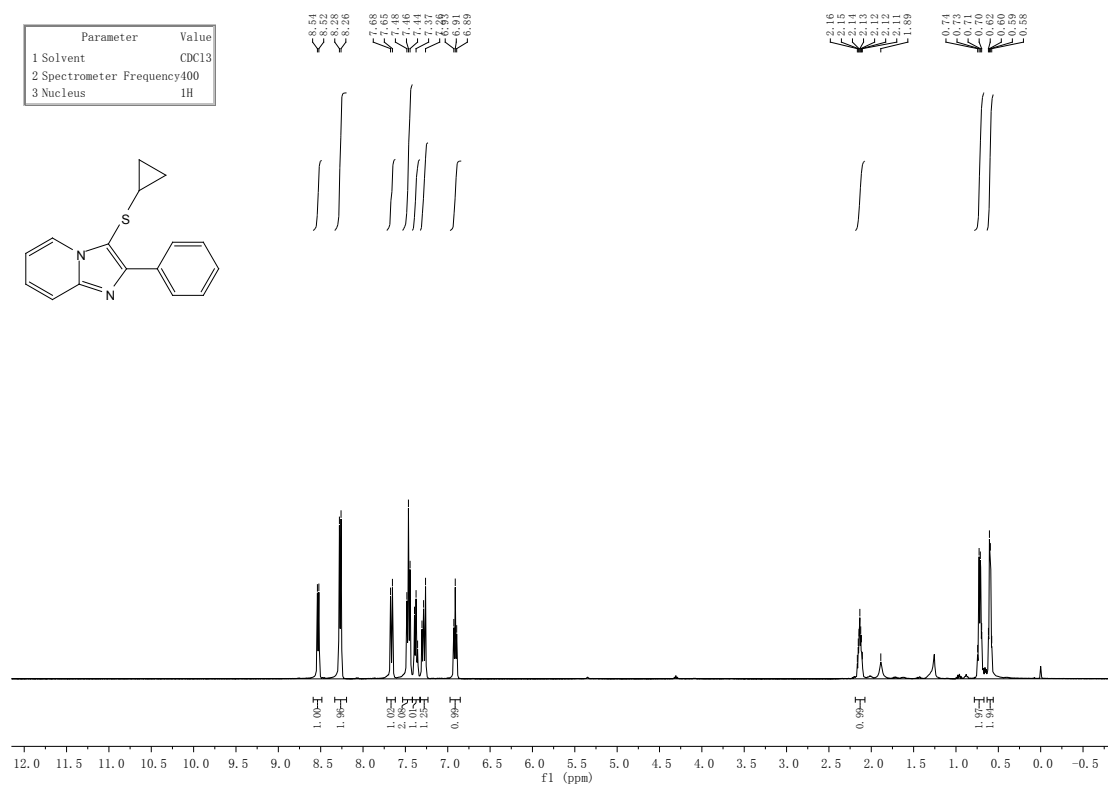
Peak list (ppm):

Peak	Chemical Shift (ppm)
1	148.82
2	146.42
3	133.93
4	129.33
5	128.97
6	128.32
7	117.70
8	112.77
9	111.46
10	77.48
11	77.16
12	76.84
13	18.24

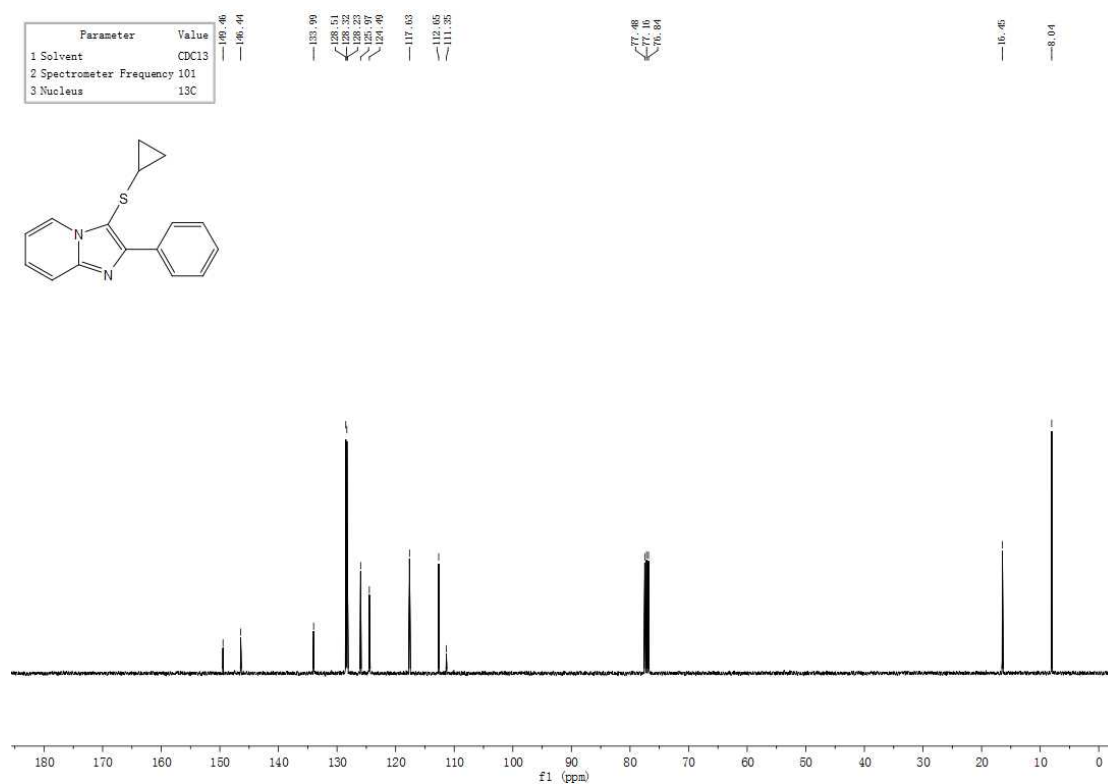
Peak list (ppm):

Peak	Chemical Shift (ppm)
1	148.82
2	146.42
3	133.93
4	129.33
5	128.97
6	128.32
7	117.70
8	112.77
9	111.46
10	77.48
11	77.16
12	76.84
13	18.24

¹H NMR (400 MHz, CDCl₃) of **3y**



¹³C NMR (101 MHz, CDCl₃) of **3y**



Parameter Value
 1 Solvent CDCl₃
 2 Spectrometer Frequency 400
 3 Nucleus ¹H

CCSC1=Cc2ccccc2N1

11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
 f1 (ppm)

1.00
 1.97
 0.82
 1.00
 1.14
 0.99
 2.03
 4.21
 3.01

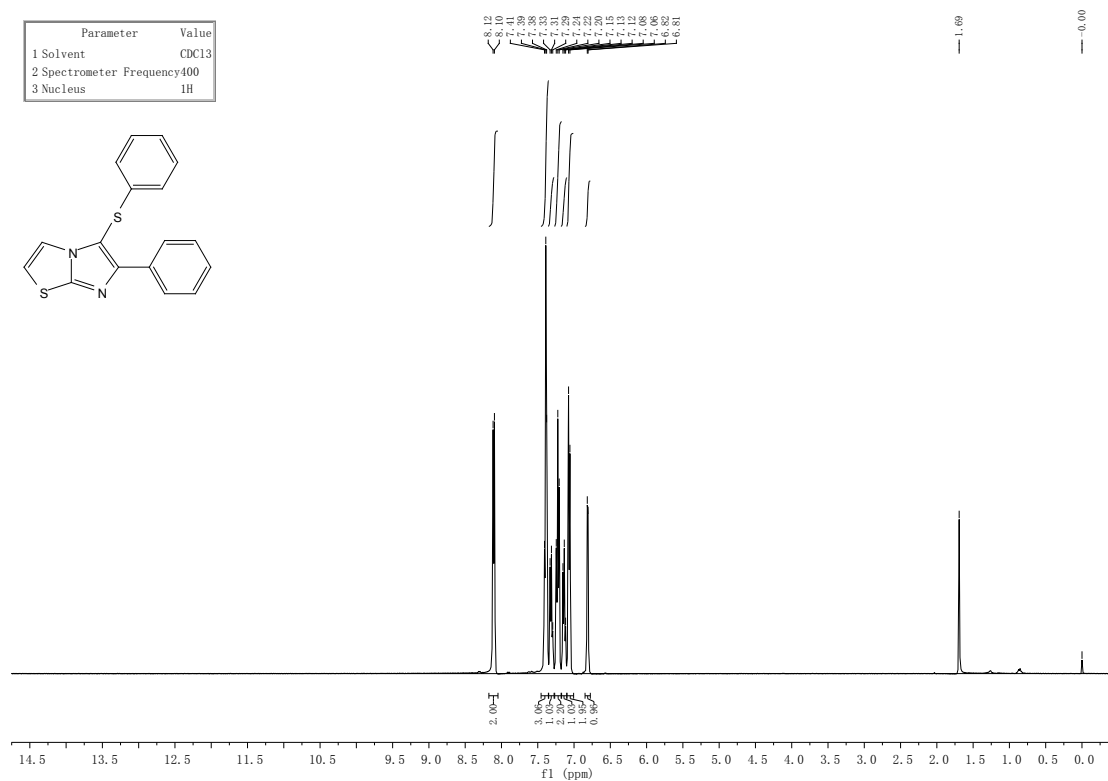
Chemical structure of 2-(4-propylphenyl)-1H-benzotriazole:

CCCC1=CC=C(C=C1)c2nc3ccccc3n2

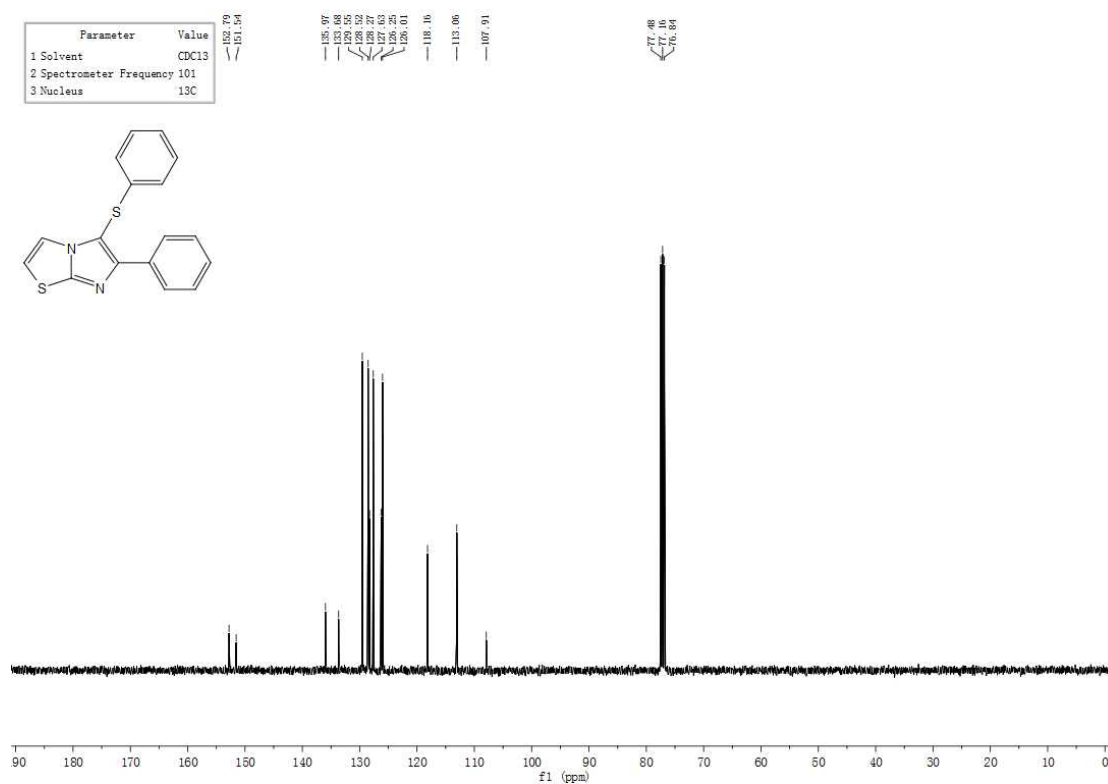
¹³C NMR spectrum (CDCl₃) showing peaks at the following chemical shifts (ppm):

Chemical Shift (ppm)
149.61
148.49
134.06
128.44
128.38
128.30
128.26
128.42
117.68
112.67
110.52
77.48
77.10
76.84
35.57
31.62
21.82
13.61

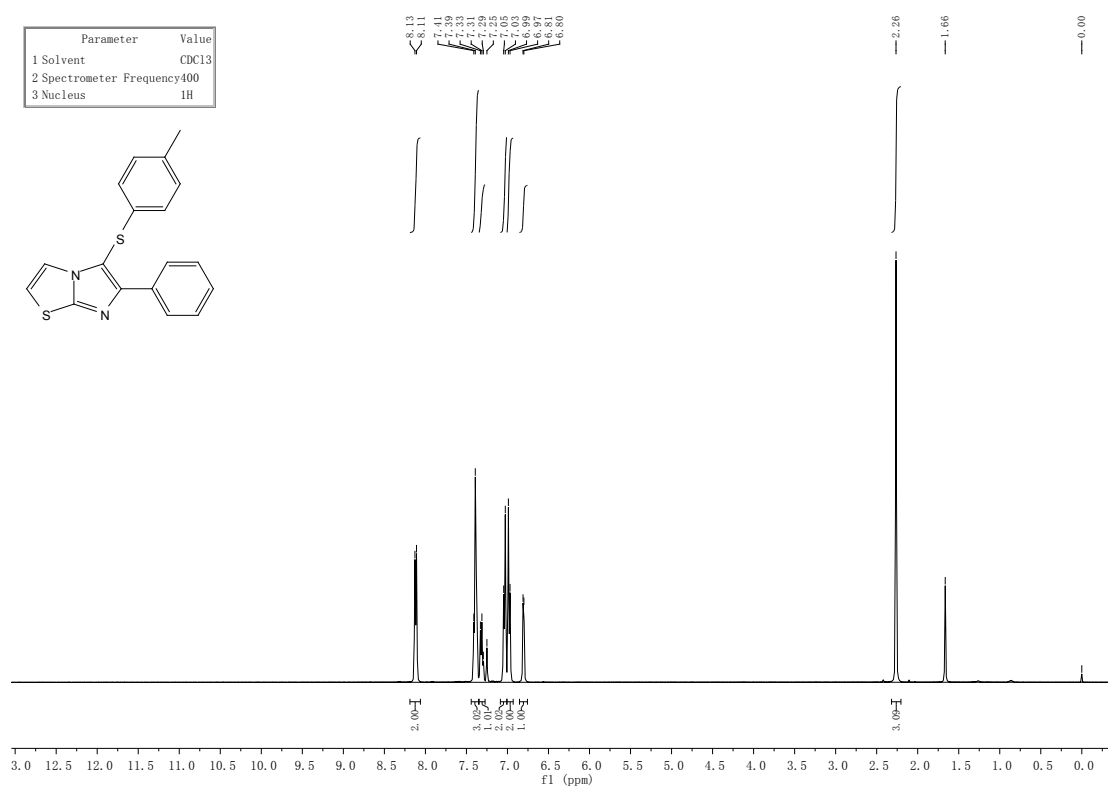
¹H NMR (400 MHz, CDCl₃) of **5a**



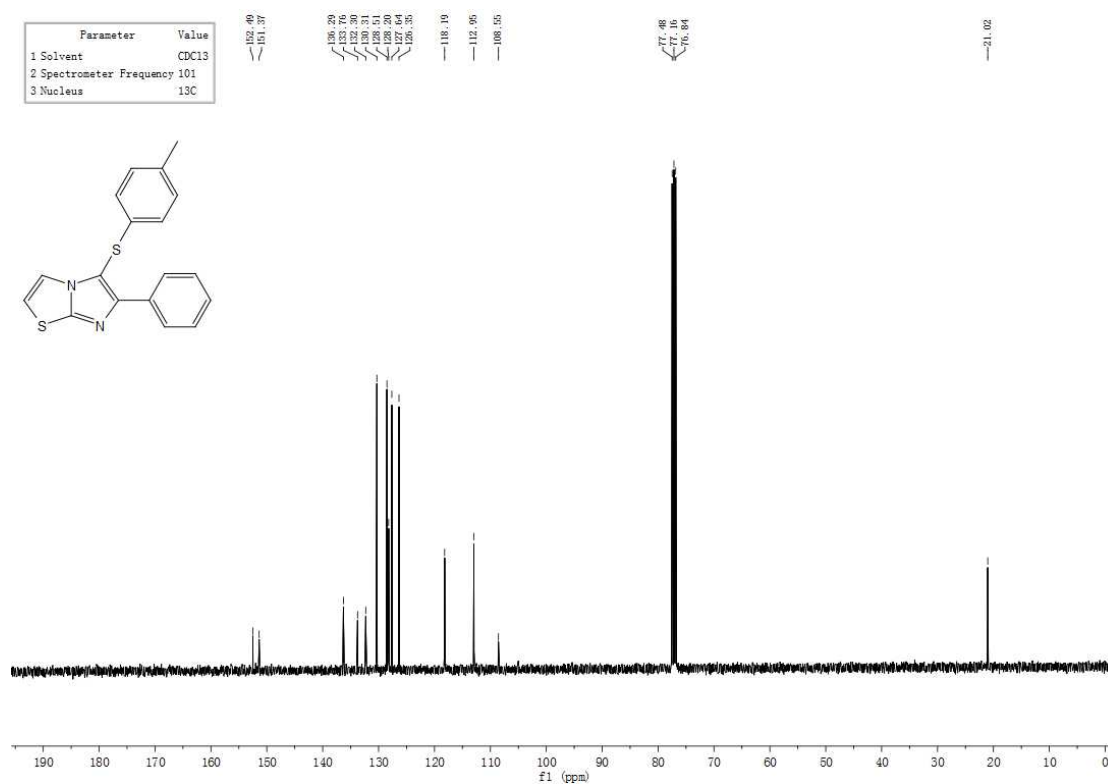
¹³C NMR (101 MHz, CDCl₃) of **5a**



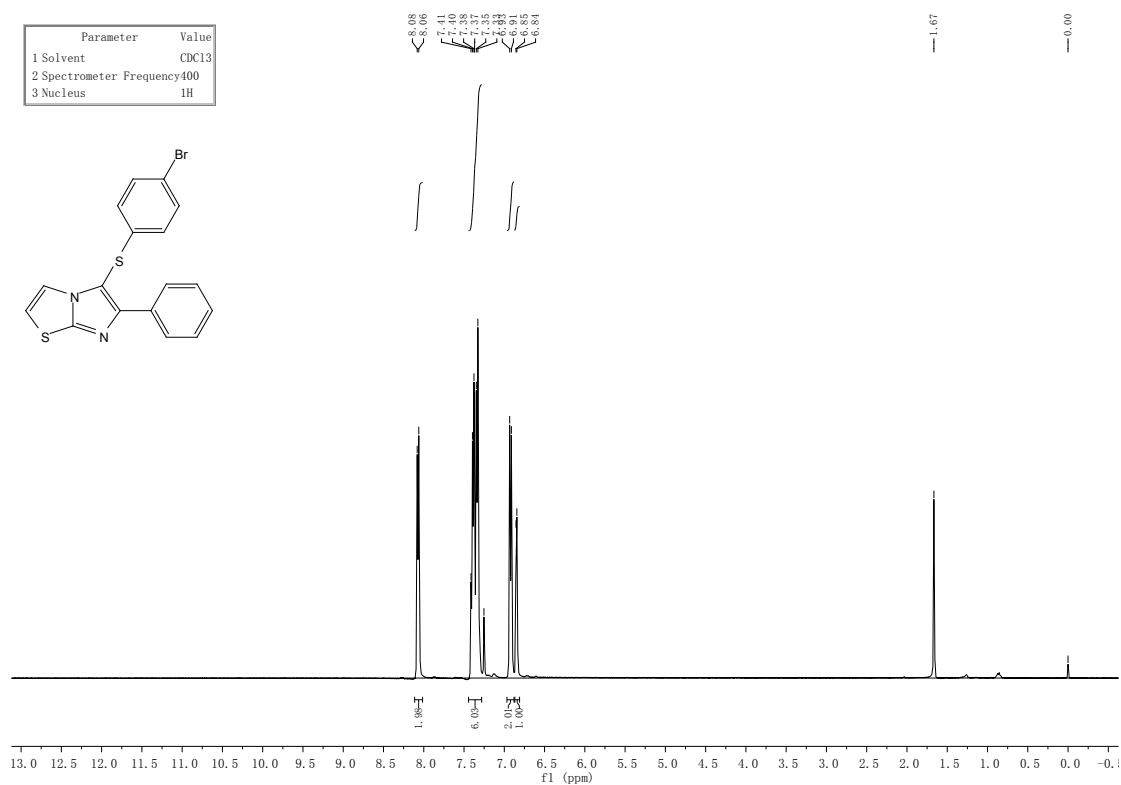
¹H NMR (400 MHz, CDCl₃) of **5b**



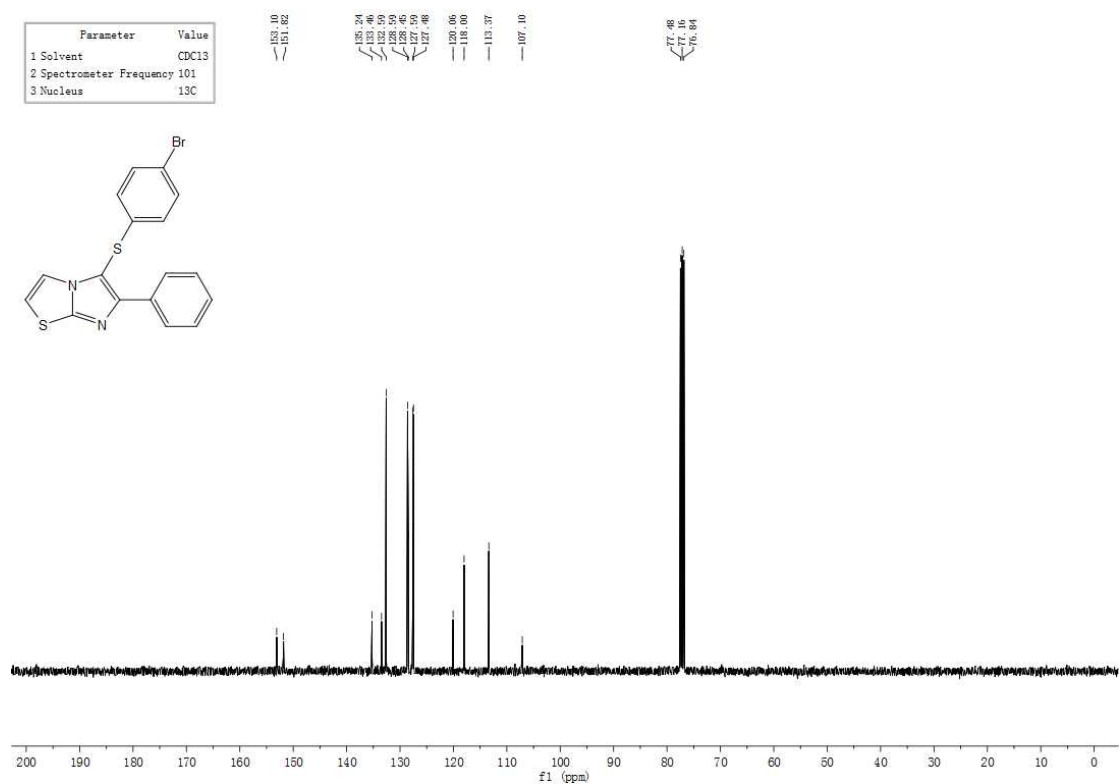
¹³C NMR (101 MHz, CDCl₃) of **5b**



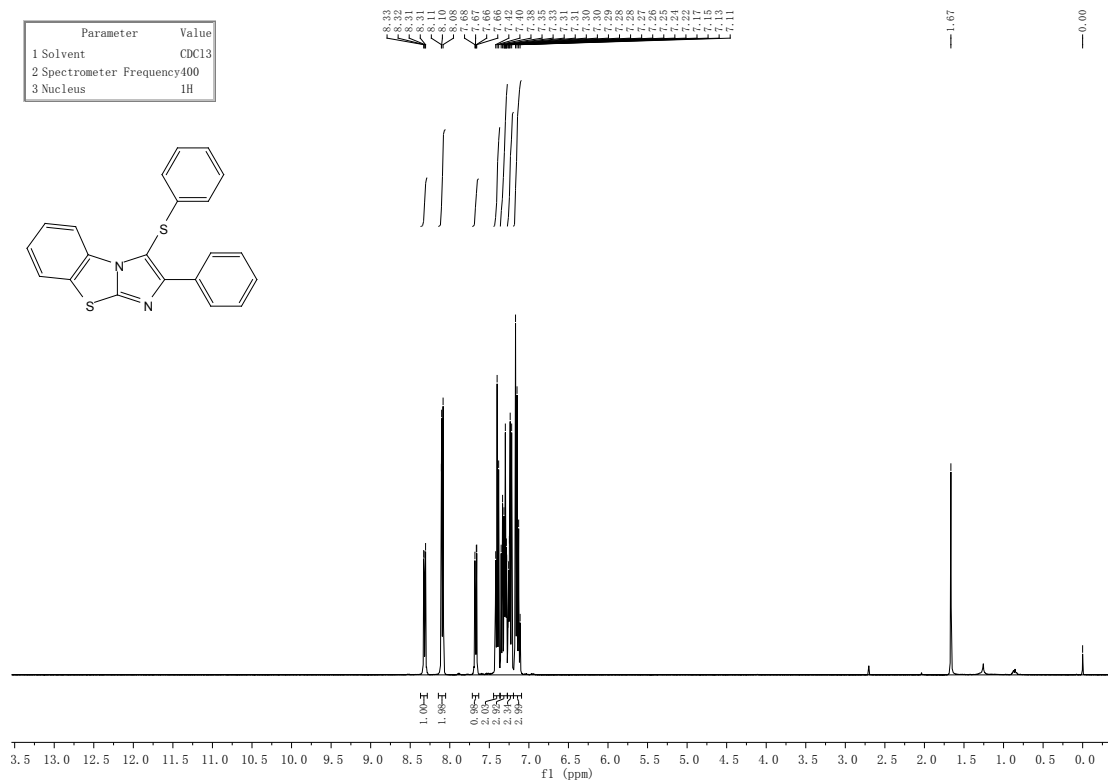
¹H NMR (400 MHz, CDCl₃) of **5c**



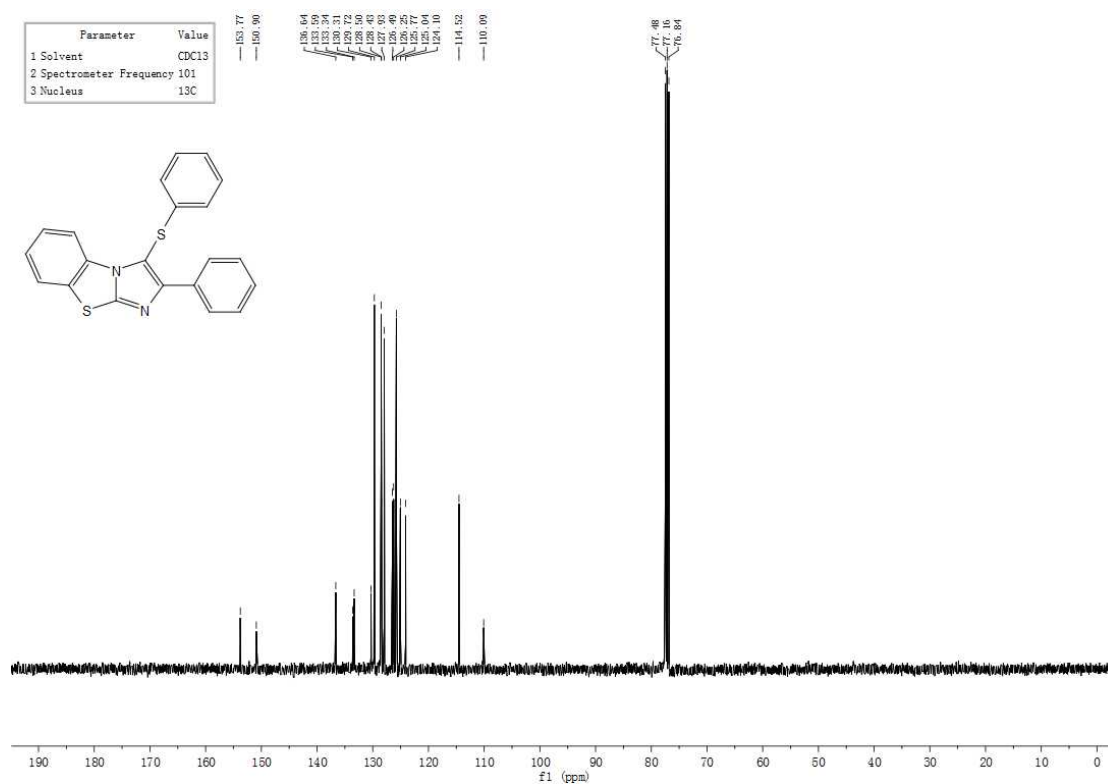
¹³C NMR (101 MHz, CDCl₃) of **5c**



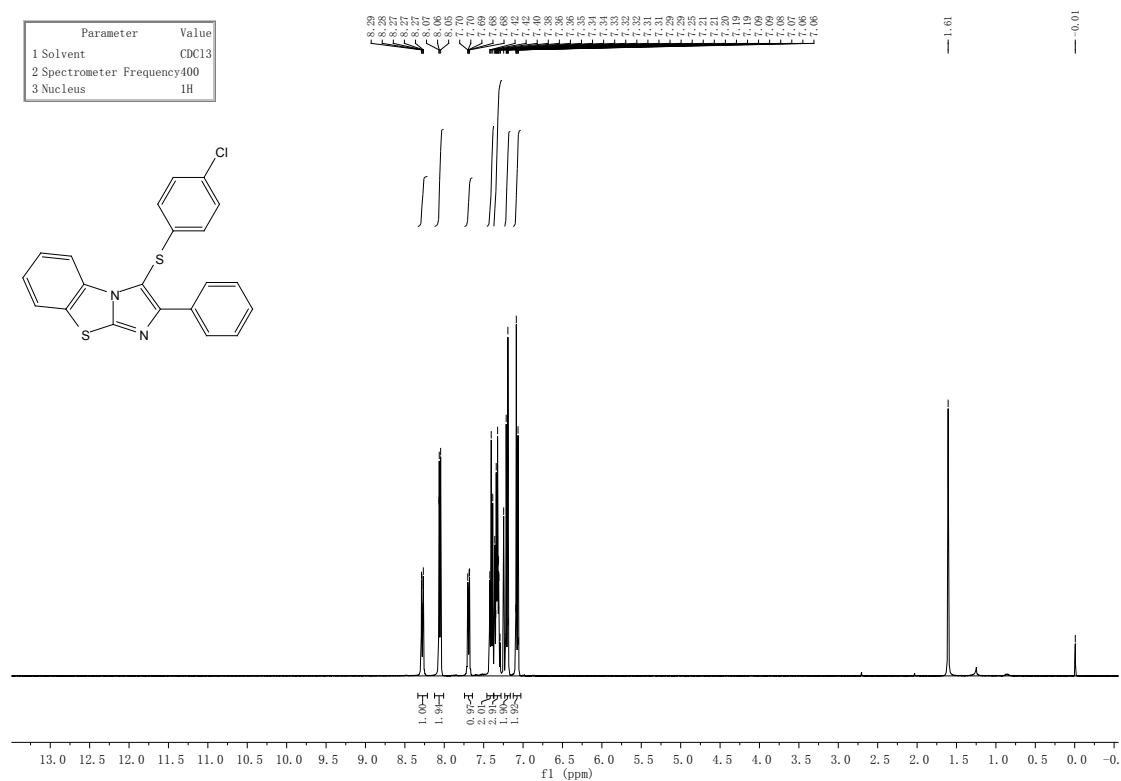
¹H NMR (400 MHz, CDCl₃) of **5d**



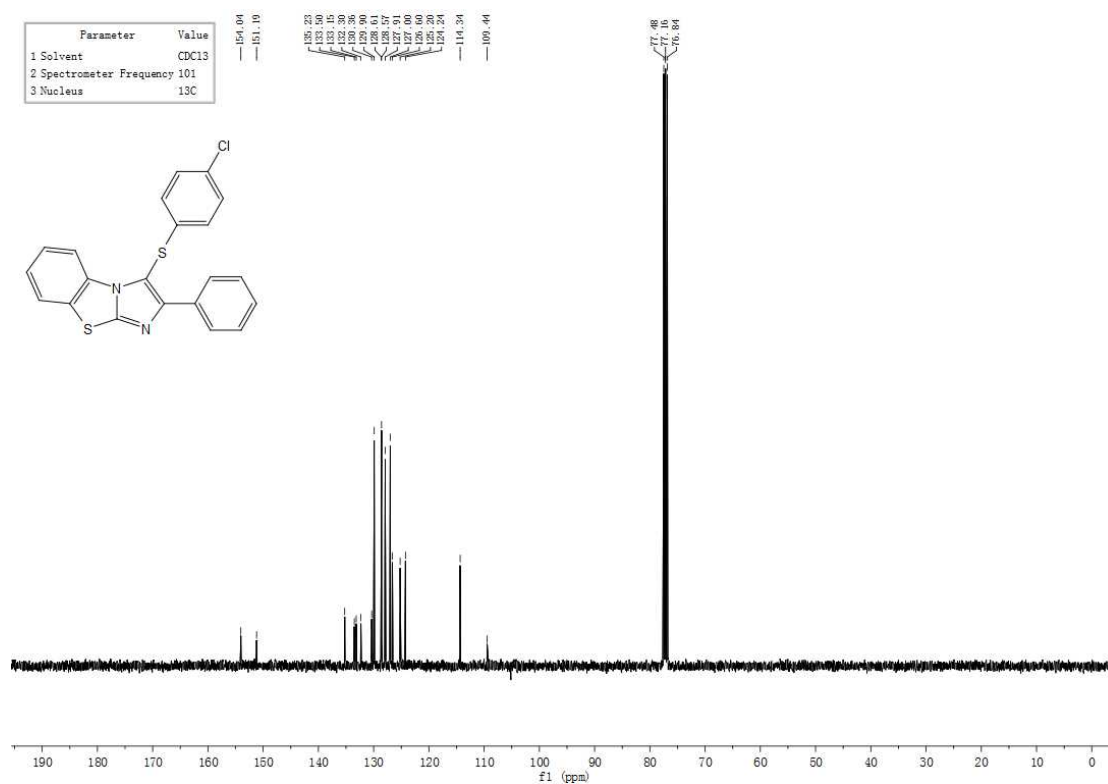
¹³C NMR (101 MHz, CDCl₃) of **5d**



¹H NMR (400 MHz, CDCl₃) of **5e**



¹³C NMR (101 MHz, CDCl₃) of **5e**



Chemical structure of the compound: c1ccc(cc1)-c2nc3ccncc3n2Sc4ccccc4

¹H NMR spectrum (CDCl₃) showing peaks in the aromatic region (7.0-8.5 ppm) and a reference peak at 0.0 ppm. The spectrum is labeled with peak numbers 1 through 35.

Integration values are provided below the peaks:

- Peak 1: 0.02
- Peak 2: 0.02
- Peak 3: 0.02
- Peak 4: 0.02
- Peak 5: 0.02
- Peak 6: 0.02
- Peak 7: 0.02
- Peak 8: 0.02
- Peak 9: 0.02
- Peak 10: 0.02
- Peak 11: 0.02
- Peak 12: 0.02
- Peak 13: 0.02
- Peak 14: 0.02
- Peak 15: 0.02
- Peak 16: 0.02
- Peak 17: 0.02
- Peak 18: 0.02
- Peak 19: 0.02
- Peak 20: 0.02
- Peak 21: 0.02
- Peak 22: 0.02
- Peak 23: 0.02
- Peak 24: 0.02
- Peak 25: 0.02
- Peak 26: 0.02
- Peak 27: 0.02
- Peak 28: 0.02
- Peak 29: 0.02
- Peak 30: 0.02
- Peak 31: 0.02
- Peak 32: 0.02
- Peak 33: 0.02
- Peak 34: 0.02
- Peak 35: 0.02

Parameter	Value
1 Solvent	CDC13
2 Spectrometer Frequency	101
3 Nucleus	¹³ C

c1ccc(cc1)Sc2c(c3ncnc3n2)c4ccccc4

Peak values (ppm): 154.33, 152.84, 151.71, 150.18, 134.33, 132.84, 131.74, 129.74, 129.28, 128.52, 128.60, 126.58, 125.91, 109.46, 105.46, 77.08, 77.04, 76.84.