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Cs_2CO_3 Promoted Direct C-H Bond Sulfenylation of Imidazo[1,2-a]pyridines And Related Heteroarenes in Ionic Liquid

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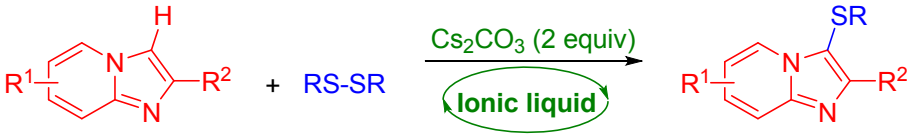
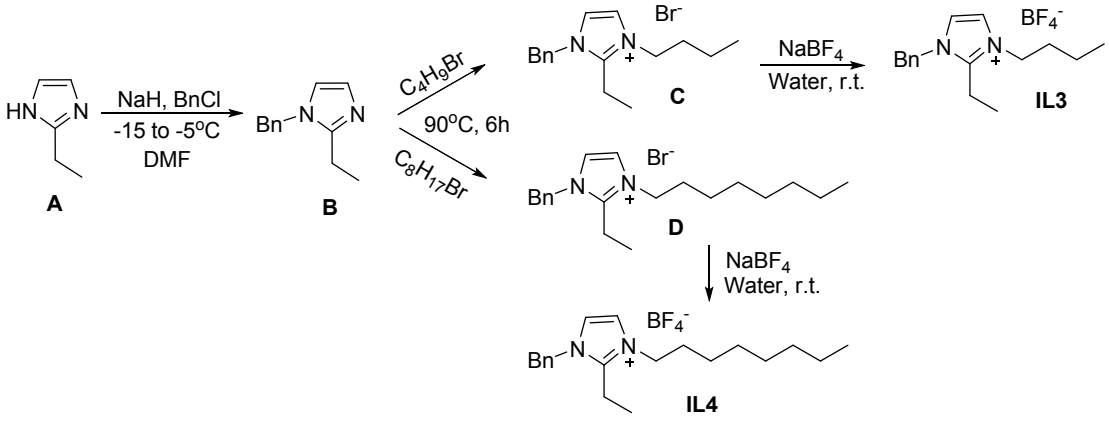


General Consideration:

All chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60-90 °C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/ UV 254 plates). Column chromatography was performed on Silicycle silica gel (200-300 mesh). Melting points were obtained using a Yamato melting point apparatus Model MP-21 and are uncorrected. IR spectra were recorded on a Shimadzu spectrophotometer using KBr discs. ^1H and ^{13}C NMR spectra were obtained using a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard. All the products are known compounds and they were identified by comparison of their physical and spectral data with those reported in the literature.

Experimental

General procedure for the synthesis of aryl-substituted imidazolium-based ionic liquid

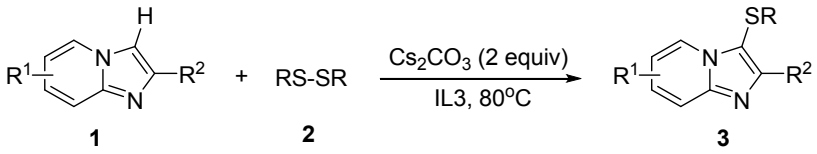


(1) Sodium hydride (60% suspension, 40 mmol) was placed in a two-necked flask and 2-ethyl imidazole (20 mmol) in DMF (20 mL) was added under nitrogen atmosphere at -15°C. The reaction mixture was stirred for another 30 min at -15°C, and then benzyl chloride (20 mmol) was added. The temperature of the reaction was raised to -5°C and the reaction mixture was stirred for another 3 hours under N_2. After completion, reaction was quenched with methanol (5 mL) and solvent was evaporated to give the crude product which was purified using silica gel column chromatography to obtain **B** in 92% yield.

(2) Alkyl bromide (25 mmol) was added to **B** (20 mmol) in THF (20 mL) and the reaction was stirred for 4-6 hours at 80°C. The reaction mixture was dried under reduced pressure and column chromatography over silica gel provided the desired compounds **C** and **D** in the yield of 91% and 90%.

(3) To the solutions of the imdazolium halides **C** and **D** (20 mmol) in water (20 mL) was added $NaBF_4$ (21 mmol) and the reaction mixture was stirred for 1.5 h at room temperature. Reaction mixture was extracted with dichloromethane (3*10mL) and purified by column chromatography to obtain ionic liquid IL3 and IL4 in the yield of 95% and 94%.

General procedure for sulfenyltion of heterocycles with disulfides



1 2 3

A mixture of heterocycle (0.5 mmol), disulfide (0.5 mmol) and Cs_2CO_3 (1 mmol) were added in IL3 (1ml) at 80°C in a flask. The reaction was carried out under an air atmosphere for about 15h until complete consumption of starting material as monitored by TLC. The solution was extracted with Ethyl ether (3×10 mL). And then the organic layer was separated and concentrated under vacuum and the crude product was purified by column chromatography (PE:EtOAc, 15:1) or recrystallization (PE:EtOAc, 5:1) to provide the analytically pure product. The ionic liquid layer was washed with water (2×2 mL) and separated via simple work-up manipulation. And the ionic liquid can be easily recycled after drying under vacuum.

1-Benzyl-2-ethyl-imidazole (B)

Colorless Oil; Yield: 3.42g (18.4 mmol, 92%); (Lit.[16g]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.23-7.31 (m, 3H), 7.01 (d, 2H, J=7.0Hz), 6.95 (d, 1H, J=1.5Hz), 6.79 (d, 1H, J=1.5Hz), 5.01 (s, 2H), 2.59 (q, 2H, J=7.5Hz), 1.24 (t, 3H, J=7.5Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 149.53, 136.60, 128.90, 127.88, 127.33, 126.59, 119.84, 49.32, 11.96.

MS (EI, m/z): 187 [M^+].

1-Benzyl-3-butyl 2-ethyl-imidazolium bromide (C)

Colorless Oil; Yield: 5.86g (18.2 mmol, 91%); (Lit.[16g]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.69 (s, 1H), 7.65 (s, 1H), 7.29 (s, 5H), 5.57 (s, 2H), 4.16 (t, 2H, J=7.5Hz), 3.14 (q, 2H, J=7.5Hz), 1.75-1.81 (m, 2H), 1.31-1.38 (m, 2H), 1.01 (t, 3H, J=7.5Hz), 0.89 (t, 3H, J=7.5Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 147.56, 133.40, 129.35, 129.07, 128.14, 122.62, 121.56, 52.30, 48.39, 32.22, 19.67, 17.84, 13.57, 11.75.

MS (EI, m/z): 243 [M^+].

1-Benzyl-3-octyl 2-ethyl-imidazolium bromide (D)

Colorless Oil; Yield: 6.81g (18.0 mmol, 90%); (Lit.[16g]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.65 (d, 1H, J=2.0Hz), 7.56 (d, 1H, J=2.0Hz), 7.25-7.27 (m, 5H), 4.10 (t, 2H, J=7.5Hz), 3.09 (q, 2H, J=7.5Hz), 1.72-1.78 (m, 2H), 1.13-1.26 (m, 10H), 0.98 (t, 3H, J=7.5Hz), 0.77 (t, 3H, J=7.5Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 147.52, 133.42, 129.31, 129.02, 128.09, 122.63, 121.45, 52.25, 48.59, 31.59, 30.23, 28.95, 26.36, 22.50, 17.75, 14.00, 11.72.

MS (EI, m/z): 299 [M^+].

1-Benzyl-3-butyl 2-ethyl-imidazolium tetrafluoroborate (IL3)

Colorless Oil; Yield: 6.27g (19.0 mmol, 95%); (Lit.[16g]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.28-7.33 (m, 4H), 7.21-7.24 (m, 3H), 5.27 (s, 2H), 4.03 (t, 2H, J=7.5Hz), 2.99 (q, 2H, J=7.5Hz), 1.72-1.78 (m, 2H), 1.29-1.37 (m, 2H), 1.03 (t, 3H, J=7.5Hz), 0.89 (t, 3H, J=7.5Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 147.64, 129.38, 129.10, 128.04, 122.05, 121.31, 51.84, 48.11, 31.99, 19.53, 16.92, 13.49, 11.36.

MS (EI, m/z): 243 [M^+].

1-Benzyl-3-octyl 2-ethyl-imidazolium tetrafluoroborate (IL4)

White solid; Mp 59-60 ^{o}C; Yield: 7.27g (18.8 mmol, 94%); (Lit.[16g]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.29-7.36 (m, 4H), 7.23-26 (m, 3H), 5.29 (s, 2H), 4.04 (t, 2H, J=7.5Hz), 3.01 (q, 2H, J=7.5Hz), 1.76-1.82 (m, 2H), 1.19-1.33 (m, 10H), 1.06 (t, 3H, J=7.5Hz), 0.84 (t, 3H, J=7.5Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 147.65, 133.29, 129.41, 129.12, 128.05, 122.12, 121.22, 51.91, 48.38, 31.67, 30.09, 29.00, 26.34, 22.57, 17.00, 14.06, 11.38.

MS (EI, m/z): 299 [M^+].

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

Yellow solid; mp 96-97^{o}C; Yield: 134 mg (0.445 mmol, 89%); (Lit.[11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.30 (d, 1 H, J=7.0Hz), 8.22 (d, 2H, J=7.5Hz), 7.77 (d, 1H, J=9.0 Hz), 7.46 (t, 2H, J=7.5Hz), 7.38 (m, 2H), 7.24 (t, 2H, J=7.5Hz), 7.16 (t, 1H, 7.5Hz), 7.02 (d, 2H, J=8.0Hz), 6.90 (t, 1H, J=7.5Hz).

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

White solid; mp 121-122^{o}C; Yield: 144 mg (0.455 mmol, 91%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.27 (d, 1H, J=7.0Hz), 8.11 (d, 2H, J=8.0Hz), 7.73 (d, 1H, J=9.0 Hz), 7.33 (t, 1H, J=8.0Hz), 7.19-7.26 (m, 4H), 7.13 (t, 1H, J=7.5Hz), 7.00 (d, 2H, J=8.0Hz), 6.86 (t, 1H, J=7.0Hz), 2.38 (s, 3H).

2-(o-Tolyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3c)

White solid; mp 114-116^{o}C; Yield: 138 mg (0.435 mmol, 87%); (Lit. [10c] 115-117^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.23 (d, 1H, J=6.5Hz), 7.73 (d, 1H, J=9.0Hz), 7.33-7.39 (m, 2H), 7.29-7.30 (m, 2H), 7.17-7.22 (m, 3H), 7.11 (t, 1H, J=7.5Hz), 2.39 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 153.7, 146.9, 137.6, 135.4, 133.1, 130.8, 130.4, 129.3, 128.6, 126.3, 126.0, 125.8, 125.3, 124.7, 117.8, 113.0, 108.2.

2-(4-Methoxy-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3d)

White solid; mp 110-111^{o}C; Yield: 154 mg (0.465 mmol, 93%); (Lit. [10c] 109-110^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.25 (d, 1H, J=7.0Hz), 8.17 (d, 2H, J=9.0Hz), 7.71 (d, 1H, J=9.0Hz), 7.31 (t, 1H, J=8.0Hz), 7.20 (t, 2H, J=8.0Hz), 7.13 (t, 1H, J=7.5Hz), 6.95-7.01 (m, 4H), 6.84 (t, 1H, J=6.5Hz), 3.83 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 160.1, 151.3, 147.1, 135.3, 129.7, 129.5, 126.6, 126.0, 125.9,

125.5, 124.5, 117.4, 113.9, 113.0, 105.4, 55.3.

2-(4-Chloro-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3e)

White solid; mp 84-85^{o}C; Yield: 148 mg (0.440 mmol, 88%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.27 (d, 1H, J=7.0Hz), 8.17 (d, 2H, J=9.0Hz), 7.72 (d, 1H, J=9.0Hz), 7.40 (d, 2H, J=8.5Hz), 7.33-7.36 (m, 1H), 7.21 (t, 2H, J=7.5Hz), 7.14 (t, 1H, J=7.5Hz), 6.98 (d, 2H, J=7.5Hz), 6.88 (t, 1H, J=7.0Hz).

2-(4-Bromo-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3f)

White solid; mp 148-150^{o}C; Yield: 167 mg (0.440 mmol, 88%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.28 (d, 1H, J=7.0Hz), 8.11 (d, 2H, J=8.5Hz), 7.73 (d, 1H, J=9.0Hz), 7.56 (d, 2H, J=8.5Hz), 7.35 (t, 1H, J=8.0Hz), 7.22 (t, 2H, J=7.5Hz), 7.15 (t, 1H, J=7.5Hz), 6.98 (d, 2H, J=7.5Hz), 6.89 (t, 1H, J=7.0Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 150.2, 147.1, 134.8, 132.3, 131.6, 129.9, 129.5, 127.0, 126.3, 125.6, 124.6, 123.0, 117.7, 113.3, 106.6.

2-(4-Nitro-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3g)

Yellow solid; mp 199-200^{o}C; Yield: 144 mg (0.415 mmol, 83%); (Lit. [10c] 199-201^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.45 (d, 2H, J=9.0Hz), 8.33 (d, 1H, J=7.0Hz), 8.29 (d, 2H, J=9.0Hz), 7.77 (d, 1H, J=9.0Hz), 7.41 (t, 1H, J=8.0Hz), 7.24 (t, 2H, J=7.5Hz), 7.17 (t, 1H, J=7.5Hz), 7.0 (d, 2H, J=7.5Hz), 6.95 (t, 1H, J=7.0Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 148.5, 147.7, 147.2, 139.7, 134.2, 129.7, 128.9, 127.5, 126.6, 125.7, 124.7, 123.7, 118.0, 113.8, 108.4.

2-Methyl-3-(phenylthio)-imidazo[1,2-a] pyridine (3h)

White solid; mp 87-89^{o}C; Yield: 101 mg (0.420 mmol, 84%); (Lit. [10c] 86-88^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.14 (d, 1H, J=7.0Hz), 7.59 (d, 1H, J=9.0Hz), 7.25 (t, 1H, J=8.0Hz), 7.17 (t, 2H, J=7.0Hz), 7.10 (t, 1H, J=7.5Hz), 6.92 (d, 2H, J=7.0Hz), 6.80 (t, 1H, J=7.0).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 151.7, 147.0, 135.6, 129.3, 126.1, 125.9, 125.7, 124.4, 117.0, 112.6, 107.4, 14.0.

2-Furan-2-yl-3-(phenylthio)-imidazo[1,2-a] pyridine (3i)

White solid; mp 144-146^{o}C; Yield: 127 mg (0.435 mmol, 87%); (Lit. [10c] 143-145^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.26 (d, 1H, J=7.0Hz), 7.71 (d, 1H, J=9.0Hz), 7.58 (s, 1H), 7.31 (t, 1H, J=8.0Hz), 7.18-7.21 (m, 3H), 7.12 (t, 1H, J=7.0Hz), 7.03 (d, 2H, J=7.0Hz), 6.86 (t, 1H, J=7.0Hz), 6.49 (s, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 148.0, 147.3, 143.6, 143.2, 134.6, 129.4, 126.8, 126.3, 126.1, 124.3, 117.8, 113.3, 111.6, 110.0, 105.8.

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

White solid; mp 130-132 ^{o}C; Yield: 136 mg (0.405 mmol, 81%); (Lit. [10c] 130-131^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.23 (d, 2H, J=7.0Hz), 8.21 (dd, 1H, J=1.0Hz, 7.0Hz), 7.43 (t, aH, J=7.5Hz), 7.36-7.40 (m, 2H), 7.21 (t, 2H, J=7.5Hz), 7.14 (t, 1H, J=7.5Hz), 6.99 (d, 2H, J=7.5Hz), 6.79 (t, 1H, J=7.0Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 152.1, 144.4, 134.7, 132.9, 129.6, 128.9, 128.7, 128.4, 126.3, 125.8, 125.6, 123.5, 123.3, 112.6,108.5.

2-Phenyl-3-(p-Tolylthio)-imidazo[1,2-a] pyridine (3k)

White solid; mp 146-148^{o}C; Yield: 142 mg (0.450 mmol, 90%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.30 (d, 1 H, J=7.0Hz), 8.23 (d, 2H, J=7.5Hz), 7.76 (d, 1H, J=9.0 Hz), 7.46 (t, 2H, J=7.5Hz), 7.34-7.41 (m, 2H), 7.04 (d, 2H, J=8.0Hz), 6.93 (d, 2H, J=7.5Hz), 6.90 (t, 1H, J=6.5Hz), 2.28 (s, 3H).

2-Phenyl-3-(4-methoxy-phenylthio)-imidazo[1,2-a] pyridine (3l)

White solid; mp 93-94^{o}C; Yield: 153 mg (0.460 mmol, 92%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.25 (d, 1H, J=6.5Hz), 8.17 (d, 2H, J=9.0Hz), 7.71 (d, 1H, J=9.0Hz), 7.32 (t, 1H, J=8.0Hz), 7.20 (t, 2H, J=7.5Hz), 7.13 (t, 1H, J=7.5Hz), 6.96-7.01 (m, 4H), 6.84 (t, 1H, J=7.0Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 158.7, 145.9, 134.2, 128.6, 128.3, 125.5, 124.9, 124.8, 124.4, 123.3, 116.3, 112.8, 111.8, 105.5, 54.9.

2-Phenyl-3-[(4-Chlorophenyl)thio]-imidazo[1,2-a] pyridine (3m)

White solid; mp 116-118^{o}C; Yield: 150 mg (0.445 mmol, 89%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.15 (d, 1 H, J=7.0Hz), 7.99 (d, 2H, J=7.5Hz), 7.89 (s, 1H), 7.67 (d, 1H, J=9.0Hz), 7.46 (t, 2H, J=7.5Hz), 7.36 (t, 1H, J=7.5Hz), 7.20 (t, 1H, 7.5Hz), 6.81 (t, 1H, J=6.5Hz).

2-Phenyl-3-[(4-Bromophenyl)thio]-imidazo[1,2-a] pyridine (3n)

White solid; mp 127-129^{o}C; Yield: 171 mg (0.450 mmol, 90%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.27 (d, 1 H, J=6.5Hz), 8.19 (d, 2H, J=7.0Hz), 7.80 (d, 1H, J=9.0 Hz), 7.47 (t, 2H, J=7.0Hz), 7.38-7.43 (m, 2H), 7.35 (dt, 2H, J=2.5Hz, 9.0Hz), 6.94 (t, 1H, 7.0Hz), 6.88 (dt, 2H, J=2.5Hz, 9.0Hz).

2-Phenyl-3-[(4-nitrophenyl)thio]-imidazo[1,2-a] pyridine (3o)

White solid; mp 227-228^{o}C; Yield: 149 mg (0.430 mmol, 86%); (Lit. [11c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.22 (dt, 1H, J=7.0Hz, J=1.0Hz), 8.12-8.14 (m, 2H), 8.08 (dt, 2H, J=9.0Hz, J=2.0Hz), 7.81(d, 1H, J=9.0Hz), 7.40-7.45 (m, 4H), 7.09 (d, 2H, J=9.0Hz), 6.96 (t, 1H, J=7.0Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 152.4, 147.6, 146.1, 145.0, 132.8, 129.1, 128.6, 128.3, 127.4, 125.3, 124.7, 124.2, 118.1, 113.8, 103.6.

2-Phenyl-3-(benzylthio)-imidazo[1,2-a] pyridine (3p)

Pale yellow Oil. Yield: 120 mg (0.380 mmol, 76%); (Lit. [10c]).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.26 (d, 2H, J=8.0Hz), 8.05 (d, 2H, J=7.0Hz), 7.58(d, 1H, J=9.0Hz), 7.46 (t, 2H, J=7.5Hz), 7.38 (t, 1H, J=7.5Hz), 7.16 (t, 1H, J=7.5Hz), 7.02-7.09 (m, 3H), 6.9 (d, 2H, J=8.0Hz), 6.64 (t, 1H, J=7.0Hz), 3.79 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ= 150.1, 146.4, 137.1, 133.8, 128.7, 128.5, 128.33, 128.29, 127.4, 126.1, 124.2, 117.2, 112.3, 109.4, 40.6.

2-Phenyl-3-(phenylselanyl)-imidazo[1,2-a] pyridine (3r)

White solid; mp 142-144 ^{o}C; Yield: 144 mg (0.410 mmol, 82%); (Lit.[13f] 142-143^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.37 (d, 1 H, J=7.0Hz), 8.17 (d, 2H, J=7.0Hz), 7.75 (d, 1H, J=8.0 Hz), 7.47 (t, 2H, J=7.5Hz), 7.40 (t, 1H, J=7.5Hz), 7.34 (t, 1H, J=7.5Hz), 7.18-7.21 (m, 3H), 7.12-7.13 (m, 2H), 6.88 (t, 1H, J=7.0Hz).

3-(Phenylthio)-*1H*-indole (3s)

White solid; mp 150-152^{o}C; Yield: 99 mg (0.440 mmol, 88%); (Lit.[12m] 149-151^{o}C).

IR (KBr): 3412, 3126, 3051, 1651, 1579, 1477, 1438, 1406, 1234, 736.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 11.68 (br s,1 H), 7.76 (s, 1H), 7.49 (d, 1H, J=8.0 Hz), 7.39 (d, 1H, J=7.5 Hz), 7.17-7.21 (m, 3H), 7.05-7.08 (m, 2H), 7.02 (d, 2H, J=8.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ=139.2, 136.5, 130.7, 129.1, 128.7, 125.9, 124.8, 123.1, 120.9, 119.7, 111.6, 102.8.

2-Methyl-3-(phenylthio)-*1H*-indole (3t)

White solid; mp110-112^{o}C; Yield: 110 mg (0.460 mmol, 92%); (Lit.[11e]110.9-111.2^{o}C).

IR (KBr): 3402, 3053, 2912, 2835, 1768, 1614, 1583, 1477, 1220, 1078, 1022, 744.

^{1}H NMR (500 MHz, $CDCl_3$): δ=8.22 (br s, 1 H), 7.59 (d, 1H, J=8.0 Hz), 7.37 (d, 1H, J=8.0 Hz), 7.21-7.25 (m, 1H), 7.15-7.20 (m, 3H), 7.06-7.09 (m, 3H), 2.54 (s, 3H).

5-Bromo-3-(phenylthio)-*1H*-indole (3u)

White solid; mp 120-121^{o}C; Yield: 132 mg (0.435 mmol, 87%); (Lit. [11e] 120.9-123.1^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.45 (br s, 1 H), 7.78 (s, 1H), 7.52 (d, 1H, J=2.5 Hz), 7.33-7.39 (m, 2H), 7.19-7.22 (m, 2H), 7.08-7.11 (m, 3H).

5-Methoxy-3-(phenylthio)-*1H*-indole (3v)

Colorless crystals; mp 77-79^{o}C; Yield: 117 mg (0.460 mmol, 92%); (Lit.[12i] 78-79^{o}C).

IR (KBr): 3412, 3066, 2958, 2937, 2835, 1680, 1627, 1577, 1475, 1282, 1201, 1095, 862, 738.

^{1}H NMR (500 MHz, $CDCl_3$): δ=8.34 (br s, 1 H), 7.47 (dd, 1H, J=2.5Hz, 10.0 Hz), 7.35 (d, 1H, J=8.5 Hz), 7.18-7.21 (m, 2H), 7.12-7.14 (m, 2H), 7.06-7.10 (m, 2H), 6.94 (dd, 1H, J= 2.5 Hz, 10.0 Hz), 3.81 (s, 3H).

3-(Phenylselanyl)-*1H*-indole (3w)

White solid; mp 141-142^{o}C; Yield: 116 mg (0.425 mmol, 85%); (Lit.[13d] 142^{o}C).

^{1}H NMR (500 MHz, $CDCl_3$): δ=8.44 (br s, 1 H), 7.66 (d, 1H, J=7.5 Hz), 7.52 (d, 1H, J=2.5 Hz), 7.47 (d, 1H, J=8.0Hz), 7.29-7.32 (m, 1H), 7.26 (d, 1H, J=7.5Hz), 7.20 (t, 1H, J=7.5Hz), 7.10-7.17 (m, 3H).

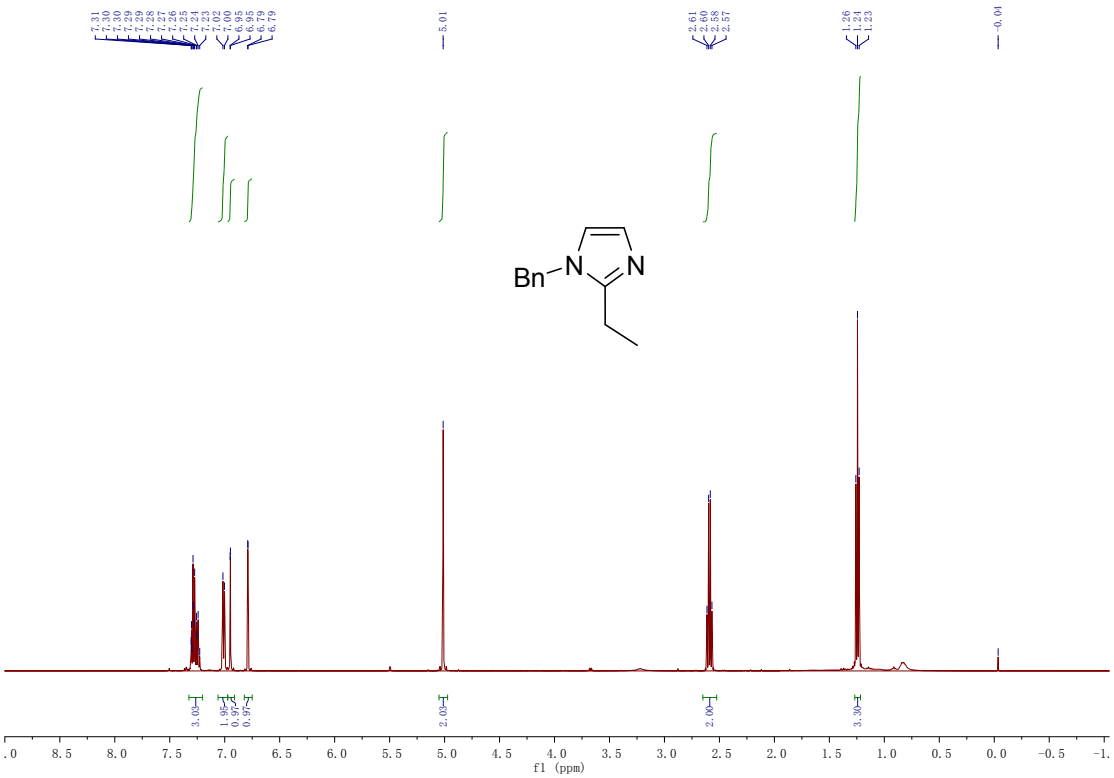
2-(Phenylthio)-*1H*-pyrrole (3x)

White solid; mp 86-88 ^{o}C; Yield: 65 mg (0.370 mmol, 74%); (Lit.[13c] 86-87^{o}C).

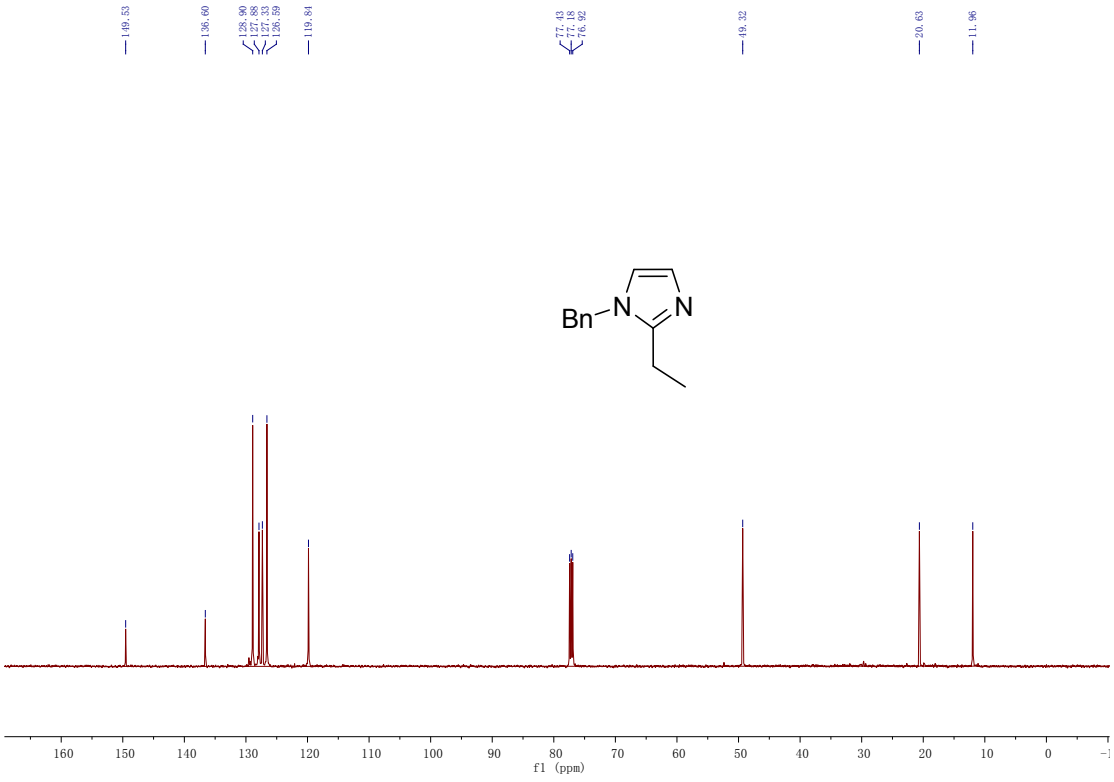
^{1}H NMR (500 MHz, $CDCl_3$): δ= 8.28 (br s, 1 H), 7.23 (t, 2H, J=7.5Hz), 7.11 (t, 1H, J=7.5 Hz), 7.03-7.05 (m, 2H), 6.59-6.60 (m, 1H), 6.34 (q, 1H, J=2.5Hz).

1-Benzyl-2-ethyl-imidazole (B)

^{1}H NMR (500 MHz, $CDCl_3$)

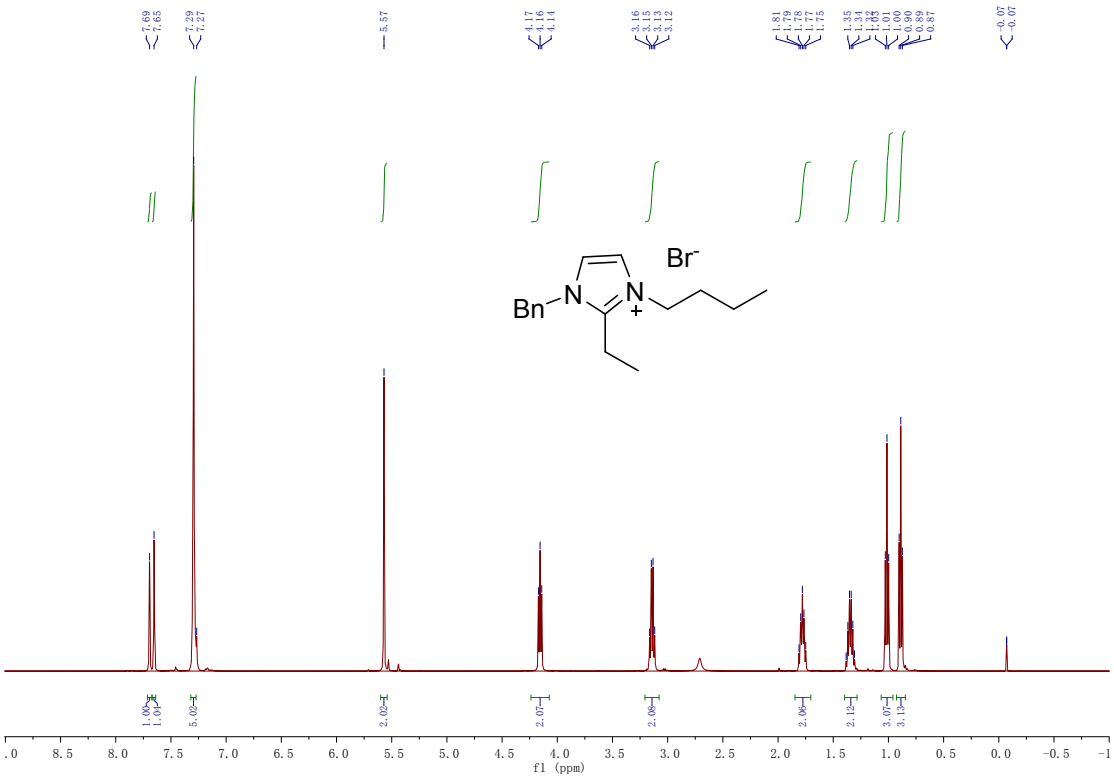


^{13}C NMR (125 MHz, $CDCl_3$)

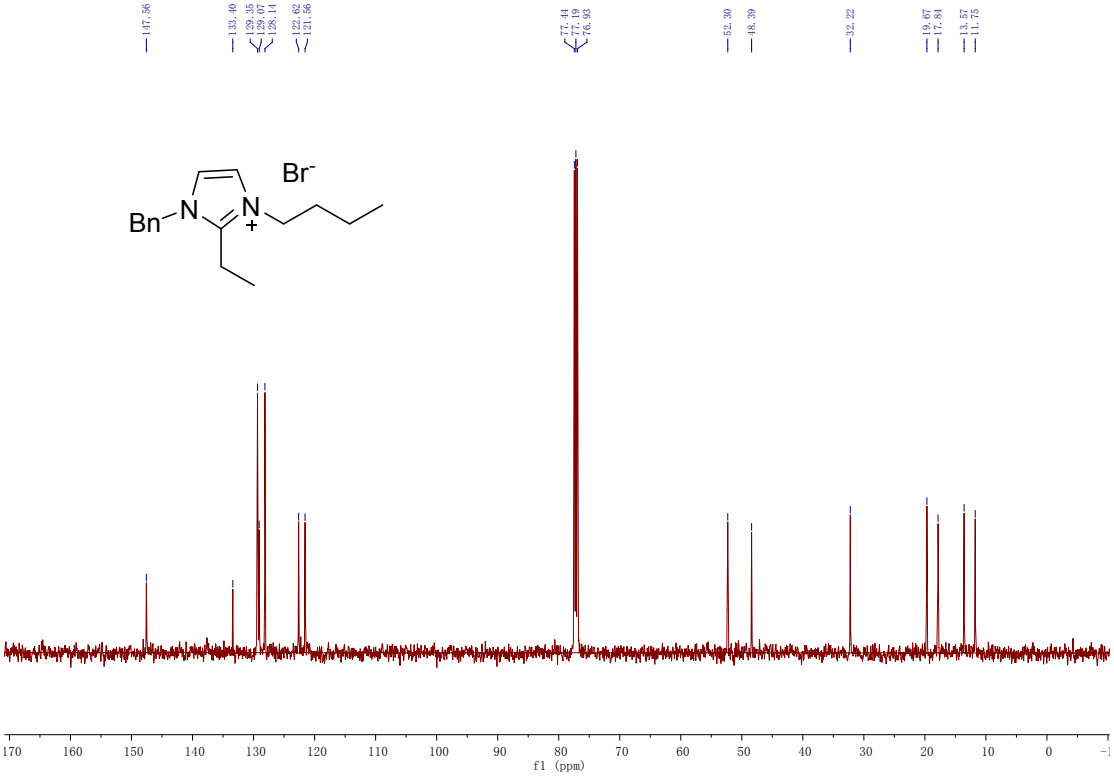


1-Benzyl-3-butyl 2-ethyl-imidazolium bromide (C)

^{1}H NMR (500 MHz, $CDCl_3$)

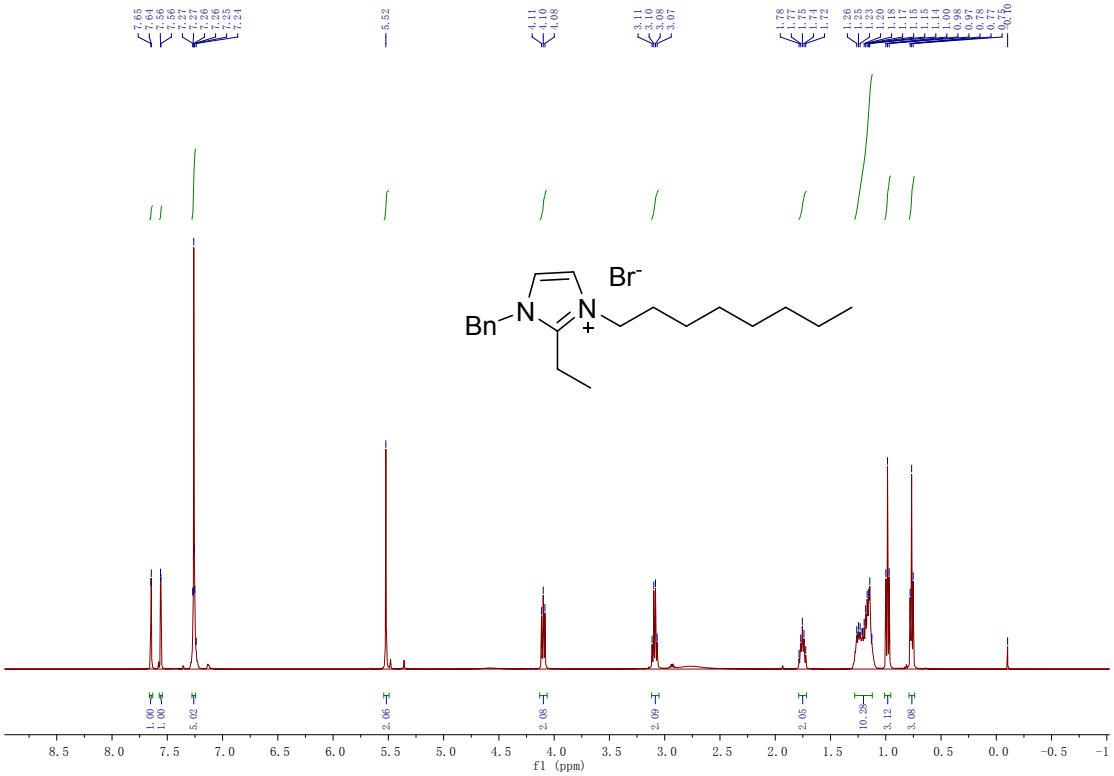


^{13}C NMR (125 MHz, $CDCl_3$)

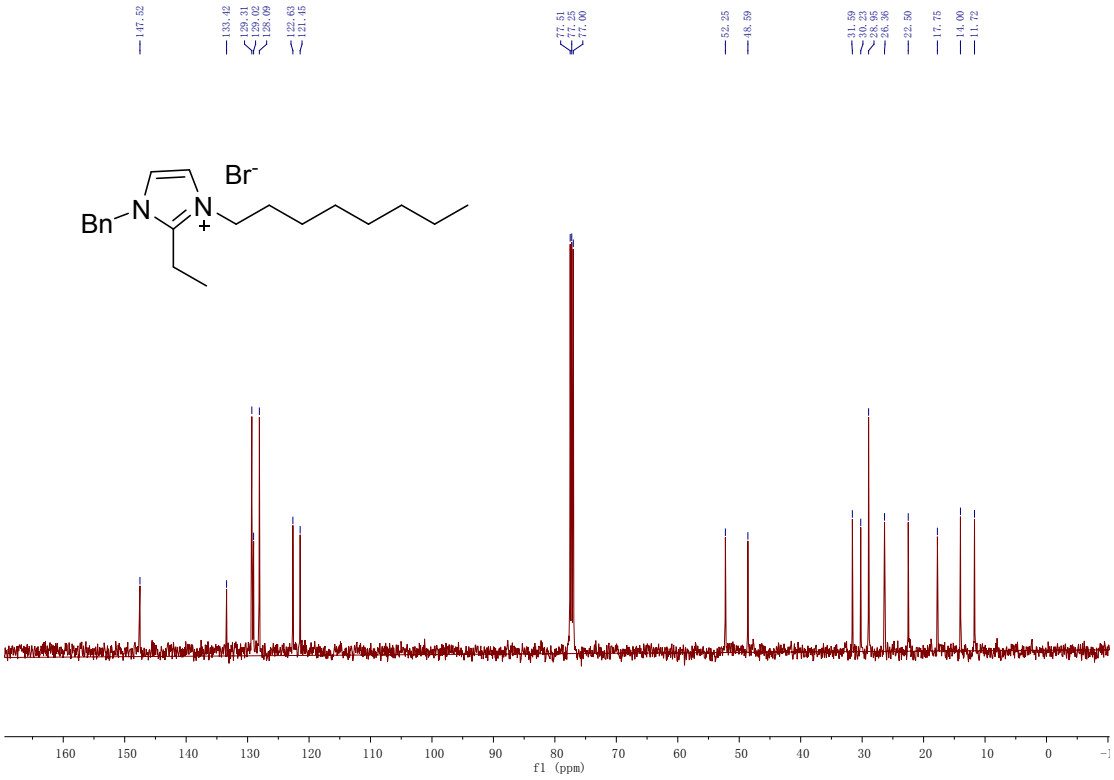


1-Benzyl-3-octyl 2-ethyl-imidazolium bromide (D)

^{1}H NMR (500 MHz, $CDCl_3$)

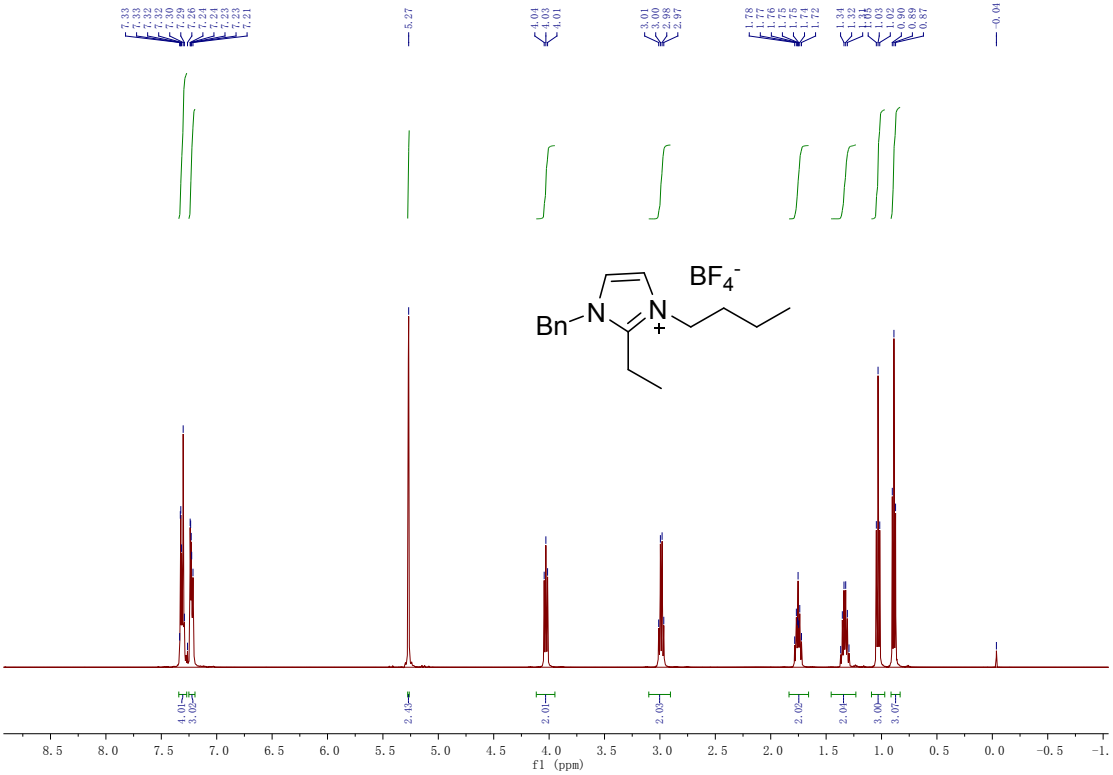


^{13}C NMR (125 MHz, $CDCl_3$)

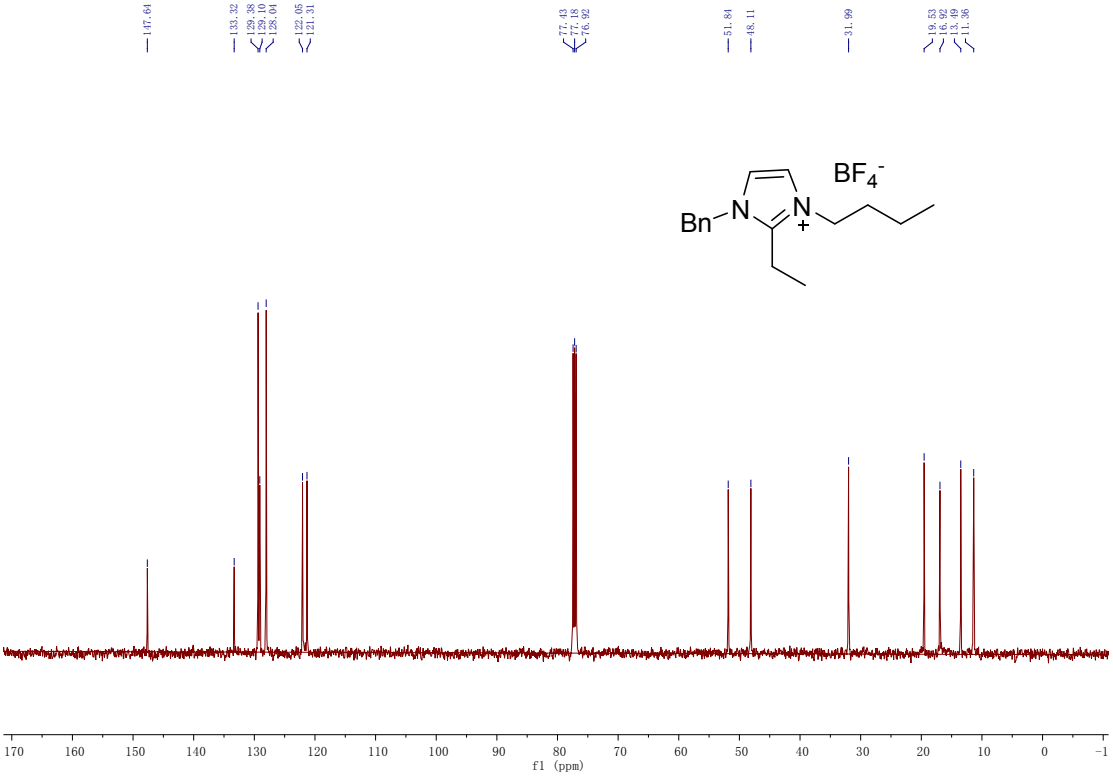


1-Benzyl-3-butyl 2-ethyl-imidazolium tetrafluoroborate (IL3)

^{1}H NMR (500 MHz, $CDCl_3$)

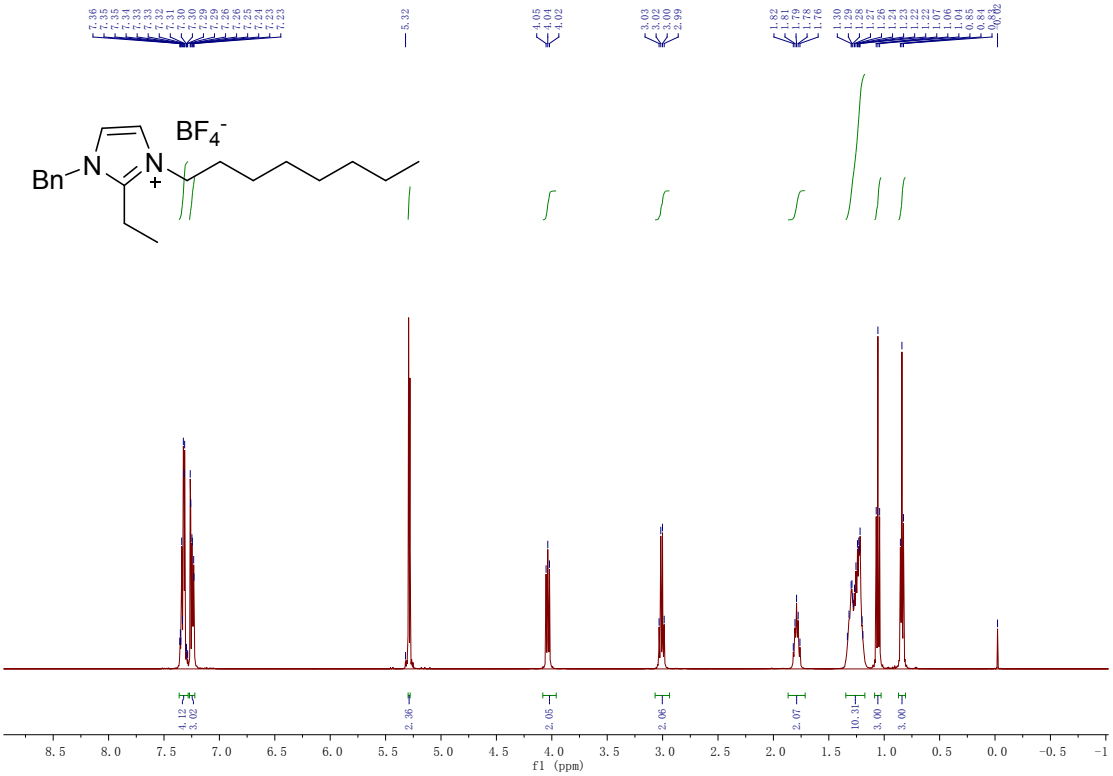


^{13}C NMR (125 MHz, $CDCl_3$)

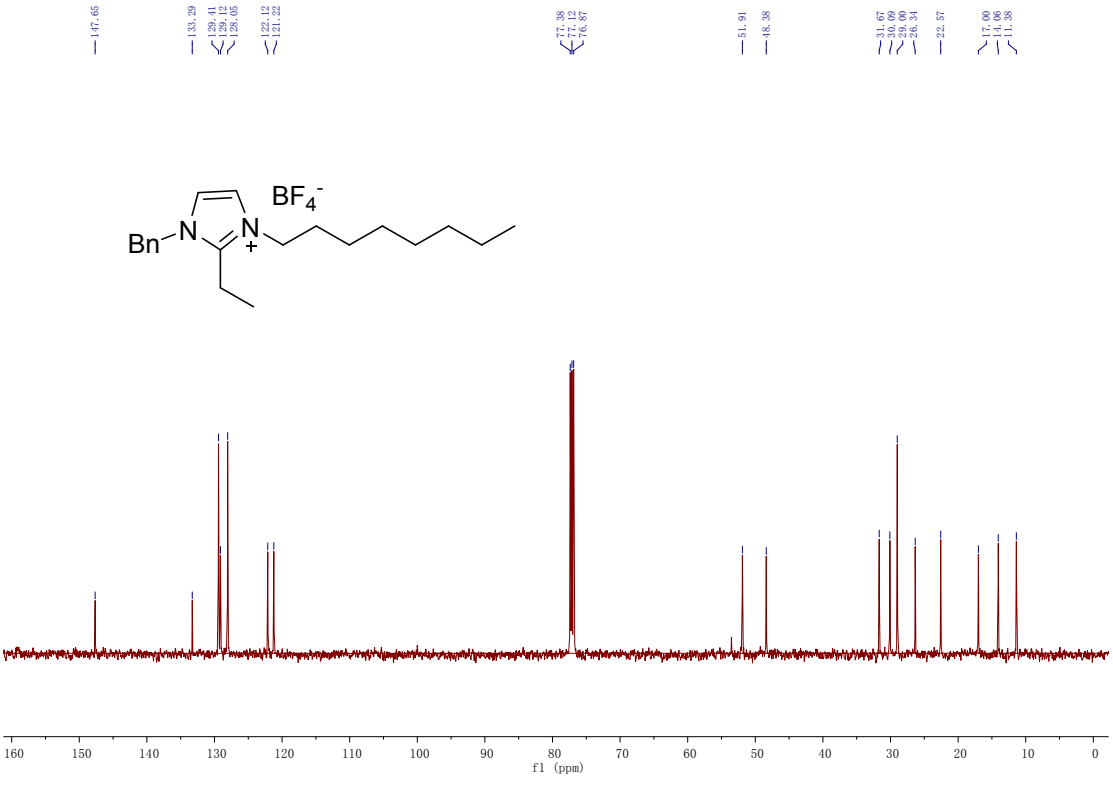


1-Benzyl-3-octyl 2-ethyl-imidazolium tetrafluoroborate (IL4)

^{1}H NMR (500 MHz, $CDCl_3$)

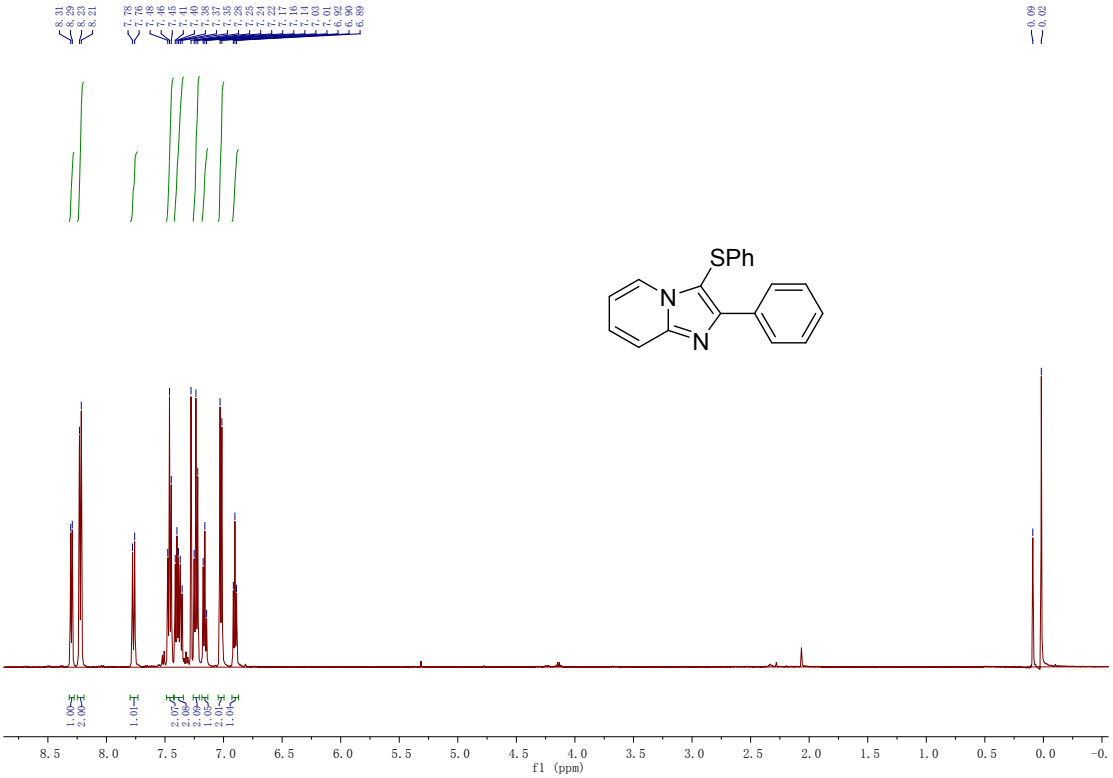


^{13}C NMR (125 MHz, $CDCl_3$)



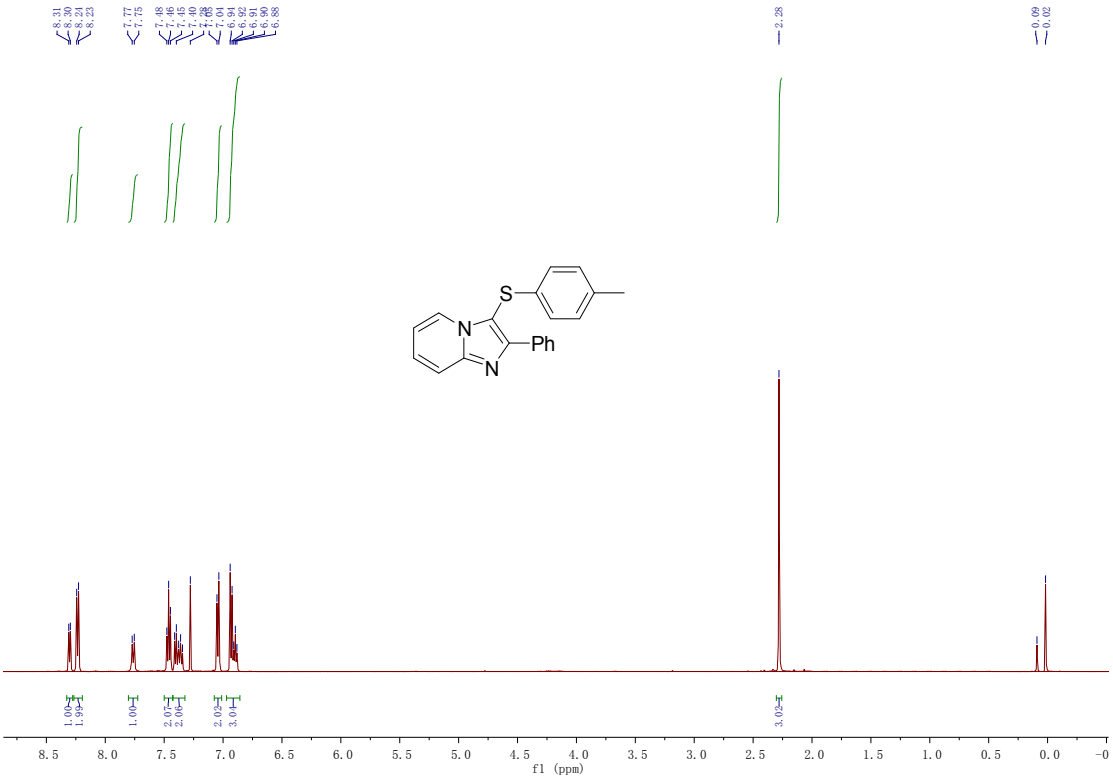
2-Phenyl-3-(phenylthio)-imidazo[1,2-a] pyridine (3a)

^{1}H NMR (500 MHz, $CDCl_3$)



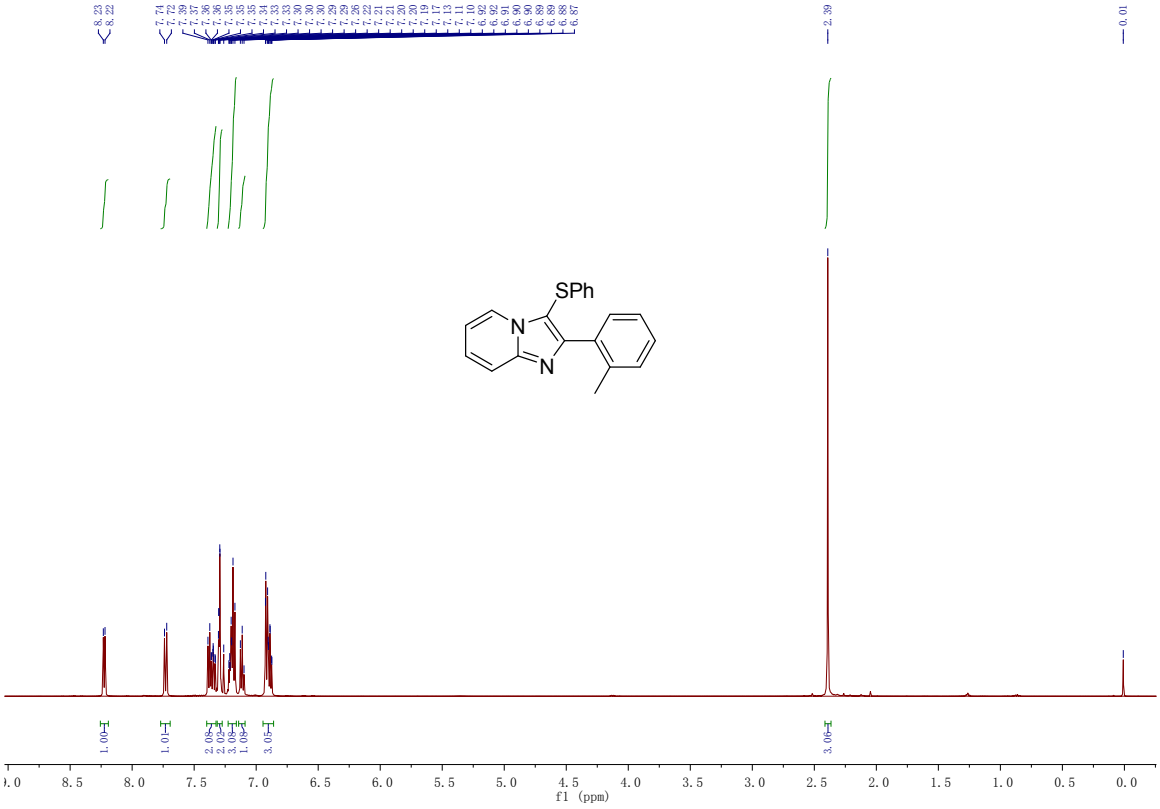
2-Phenyl-3-(p-Tolylthio)-imidazo[1,2-a] pyridine (3b)

^{1}H NMR (500 MHz, $CDCl_3$)

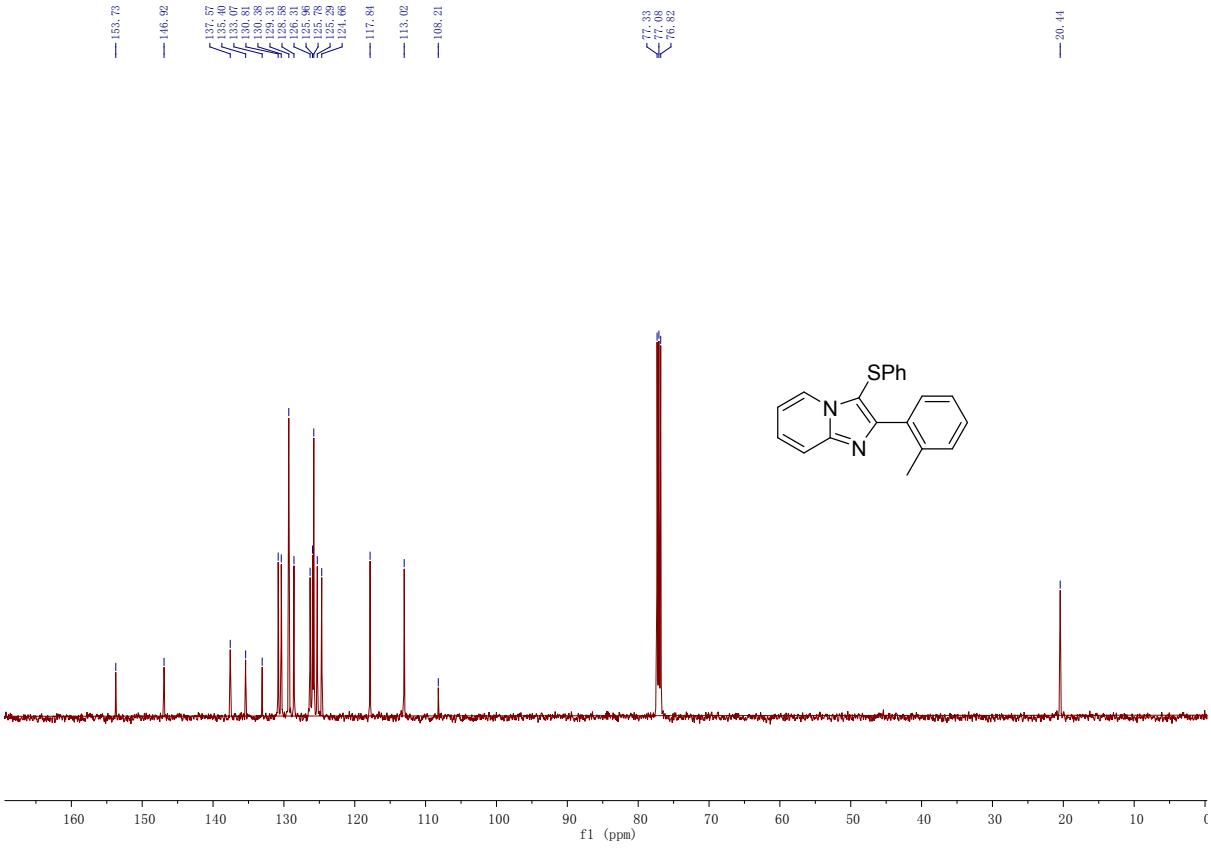


2-(o-Tolyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3c)

^{1}H NMR (500 MHz, $CDCl_3$)

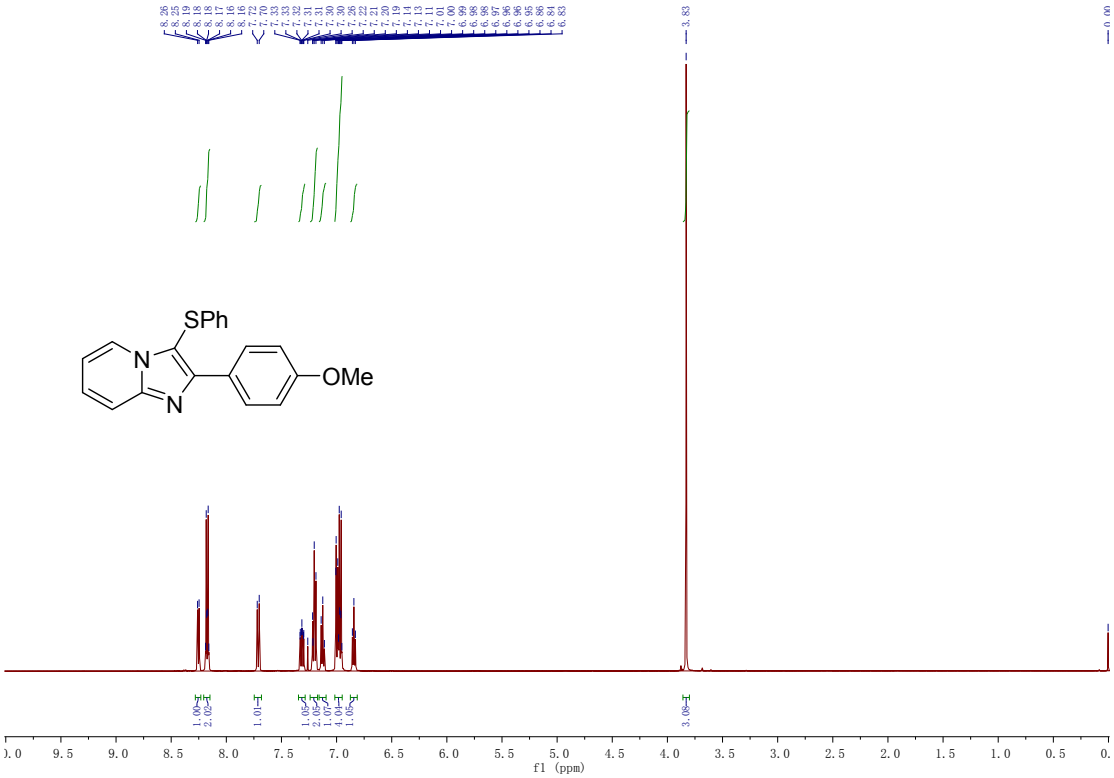


^{13}C NMR (125 MHz, $CDCl_3$)

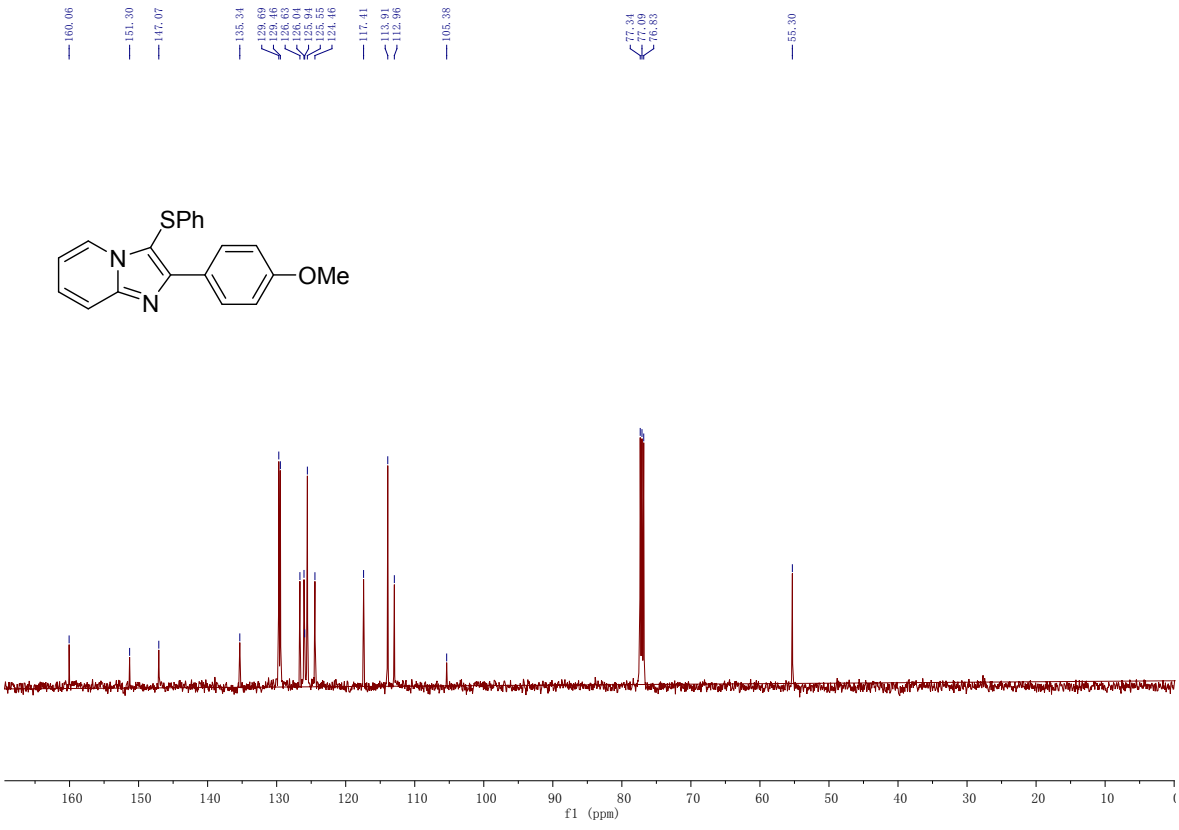


2-(4-Methoxy-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3d)

^{1}H NMR (500 MHz, $CDCl_3$)

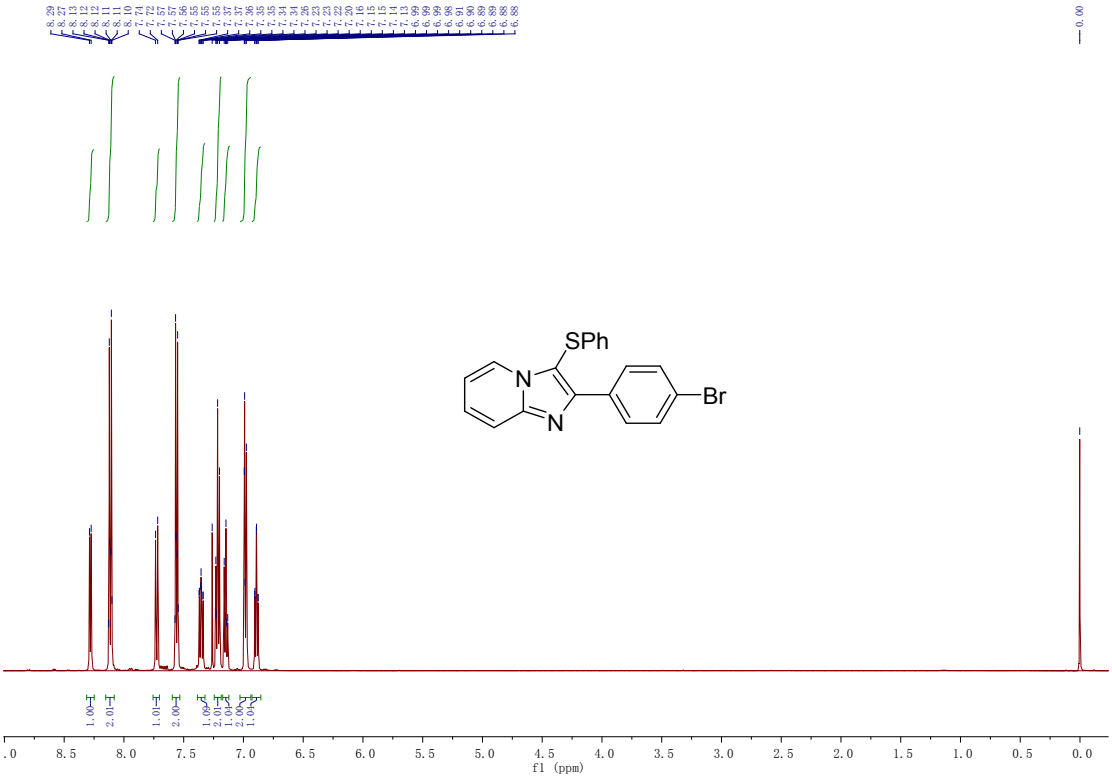


^{13}C NMR (125 MHz, $CDCl_3$)

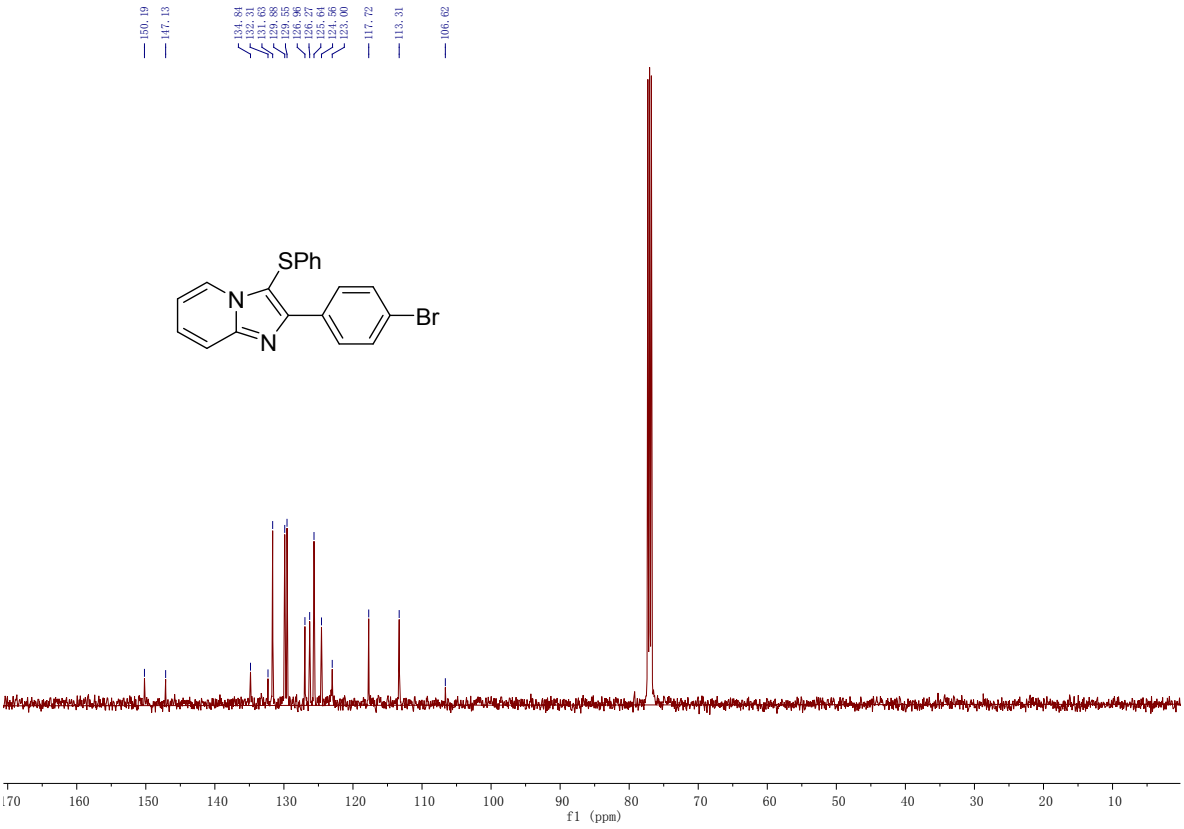


2-(4-Bromo-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3e)

^{1}H NMR (500 MHz, $CDCl_3$)

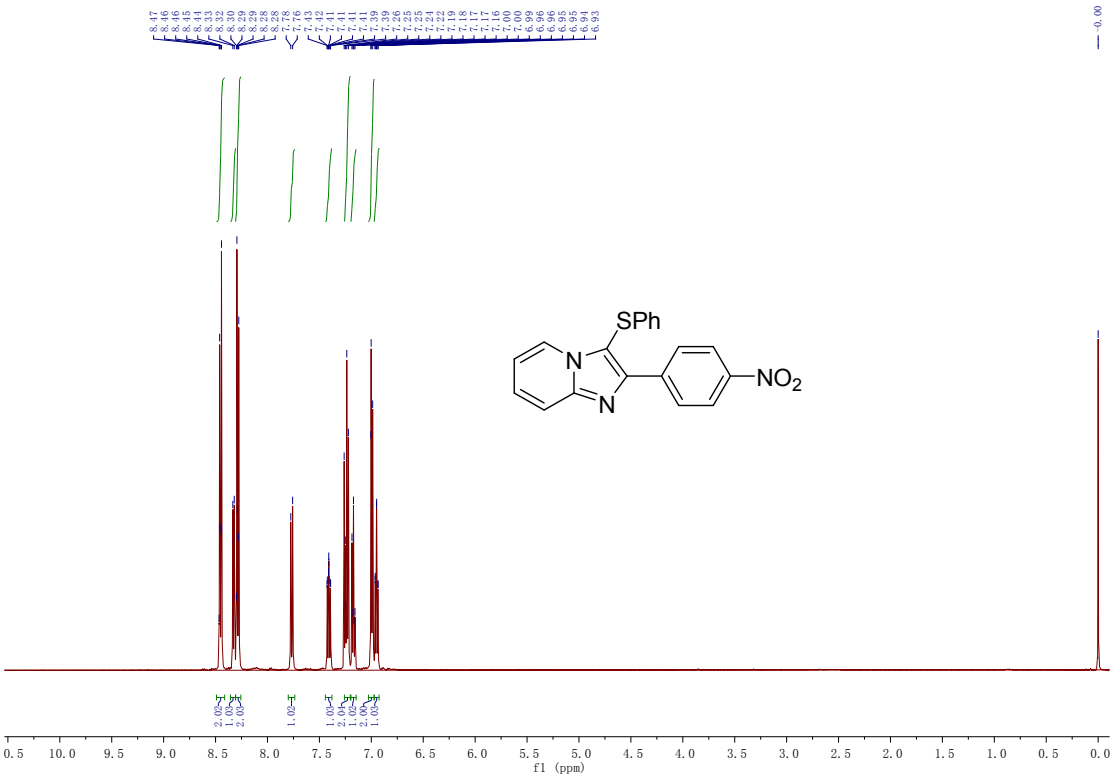


^{13}C NMR (125 MHz, $CDCl_3$)

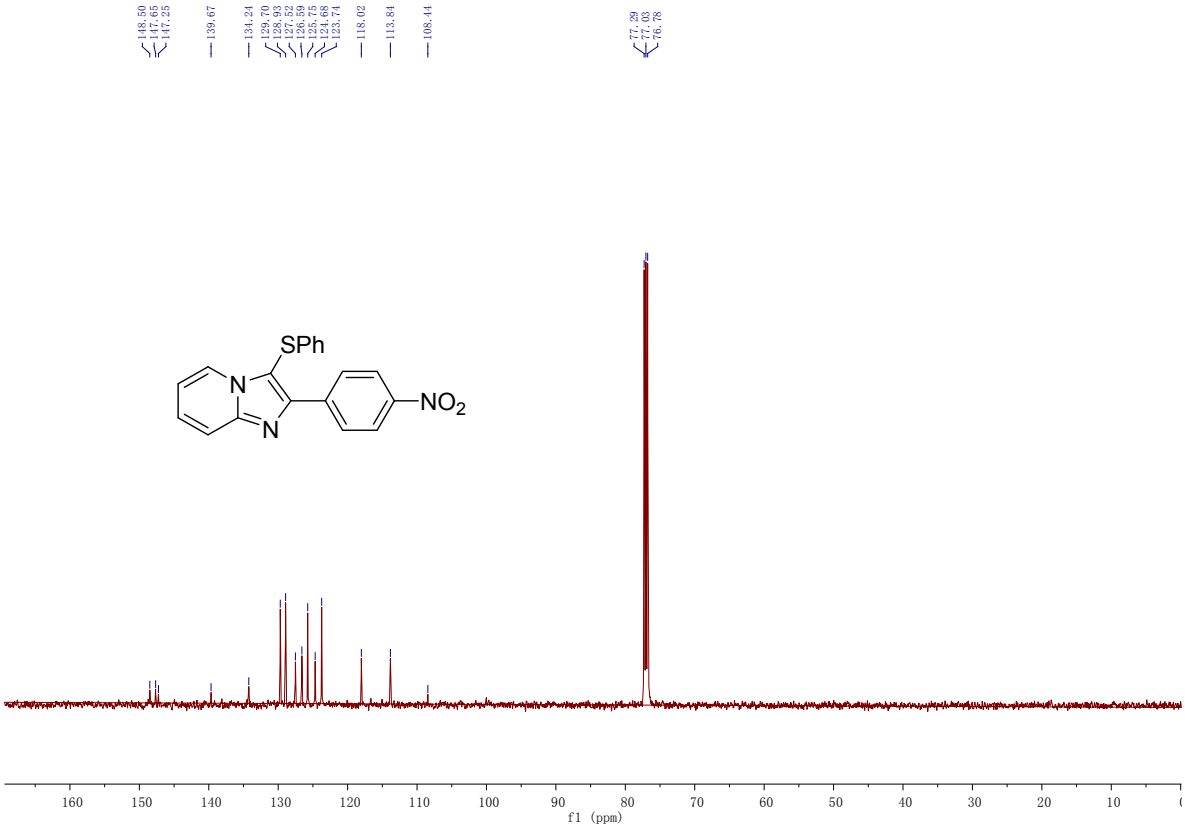


2-(4-Nitro-phenyl)-3-(phenylthio)-imidazo[1,2-a] pyridine (3f)

^{1}H NMR (500 MHz, $CDCl_3$)

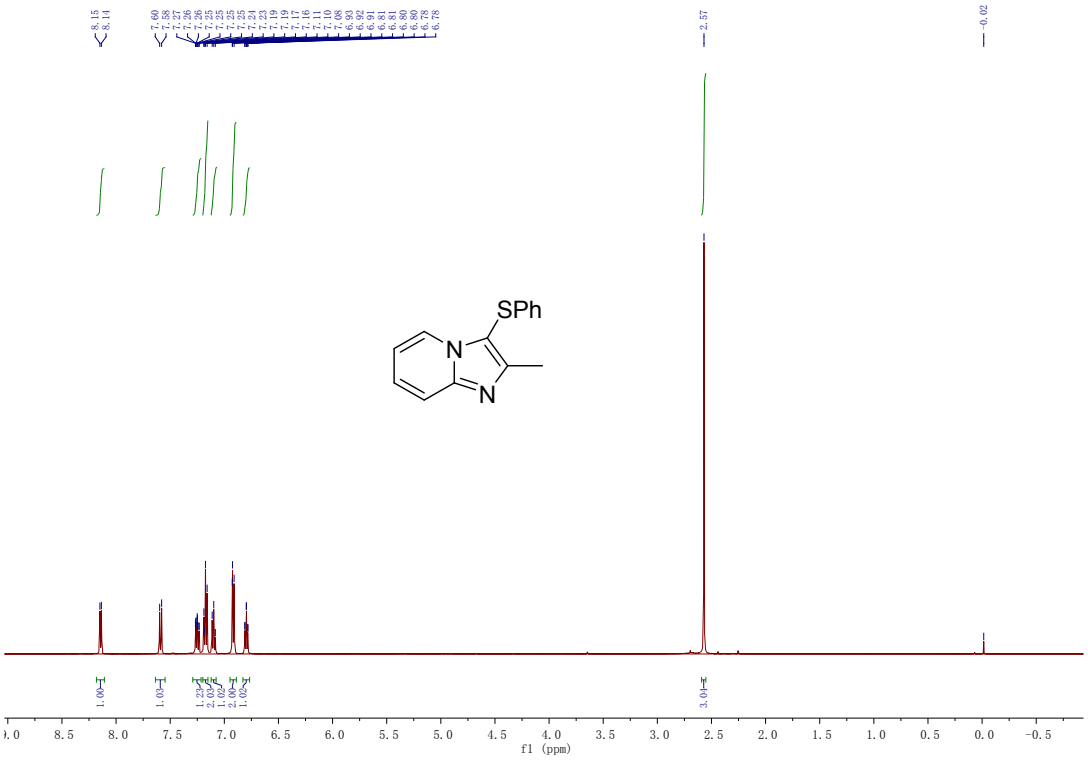


^{13}C NMR (125 MHz, $CDCl_3$)

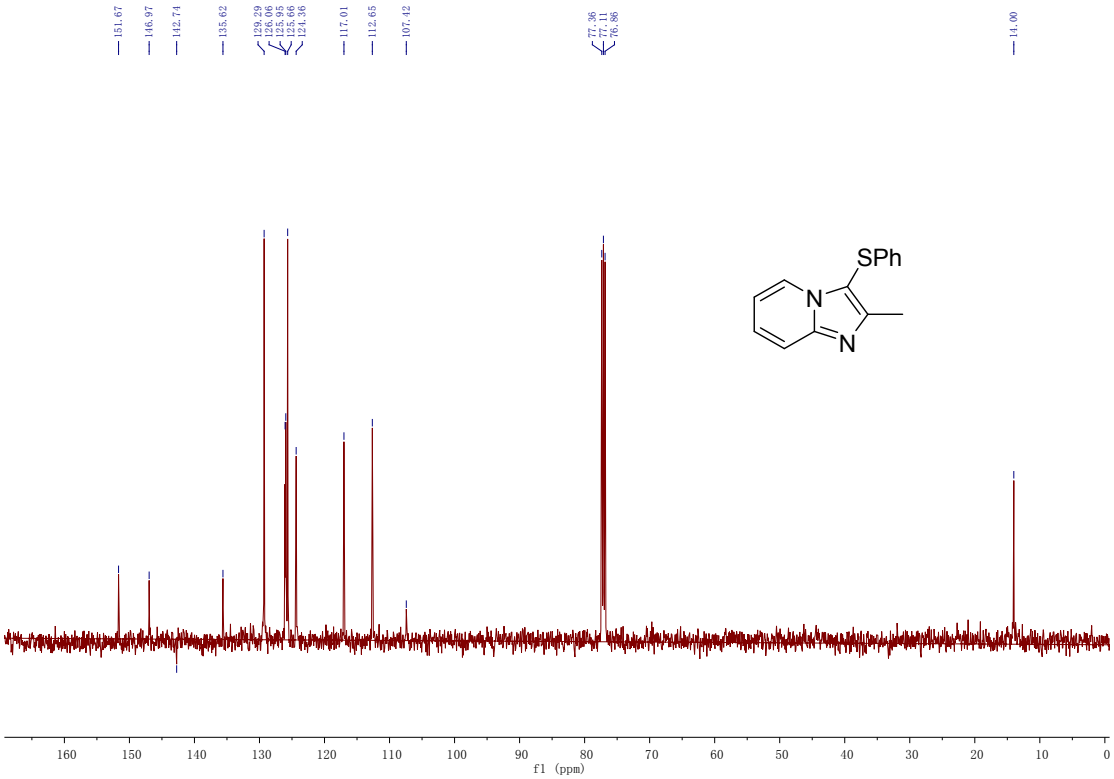


2-Methyl-3-(phenylthio)-imidazo[1,2-a] pyridine (3g)

^{1}H NMR (500 MHz, $CDCl_3$)

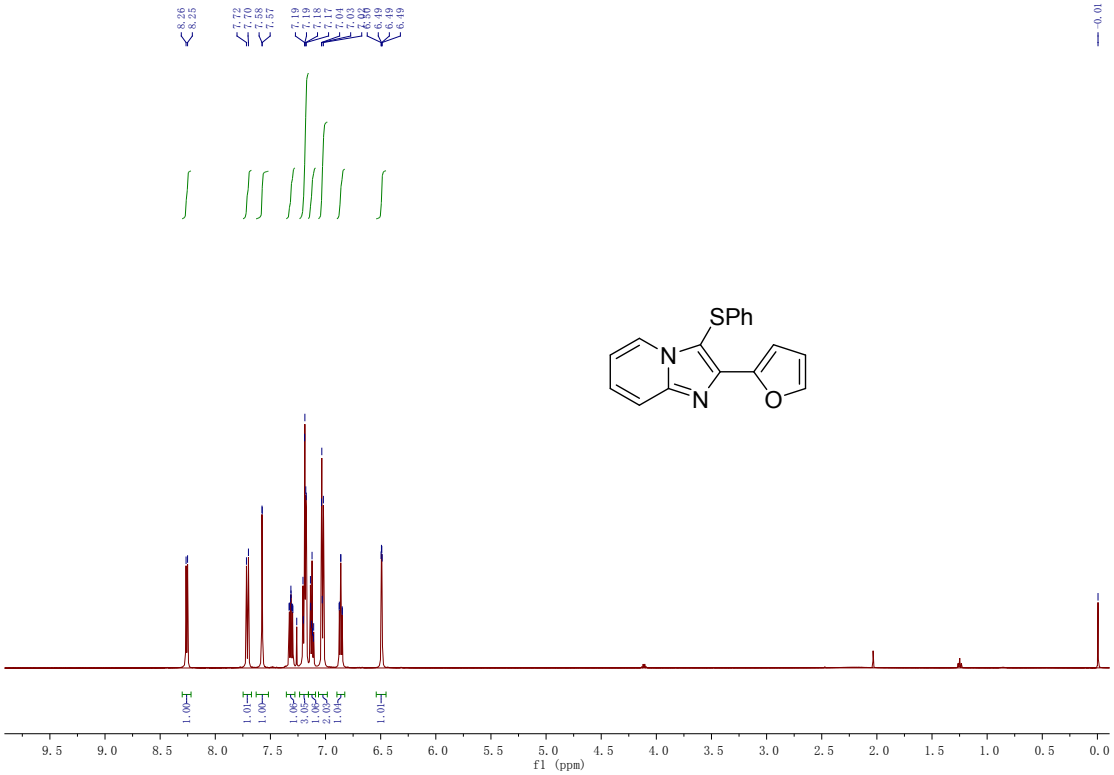


^{13}C NMR (125 MHz, $CDCl_3$)

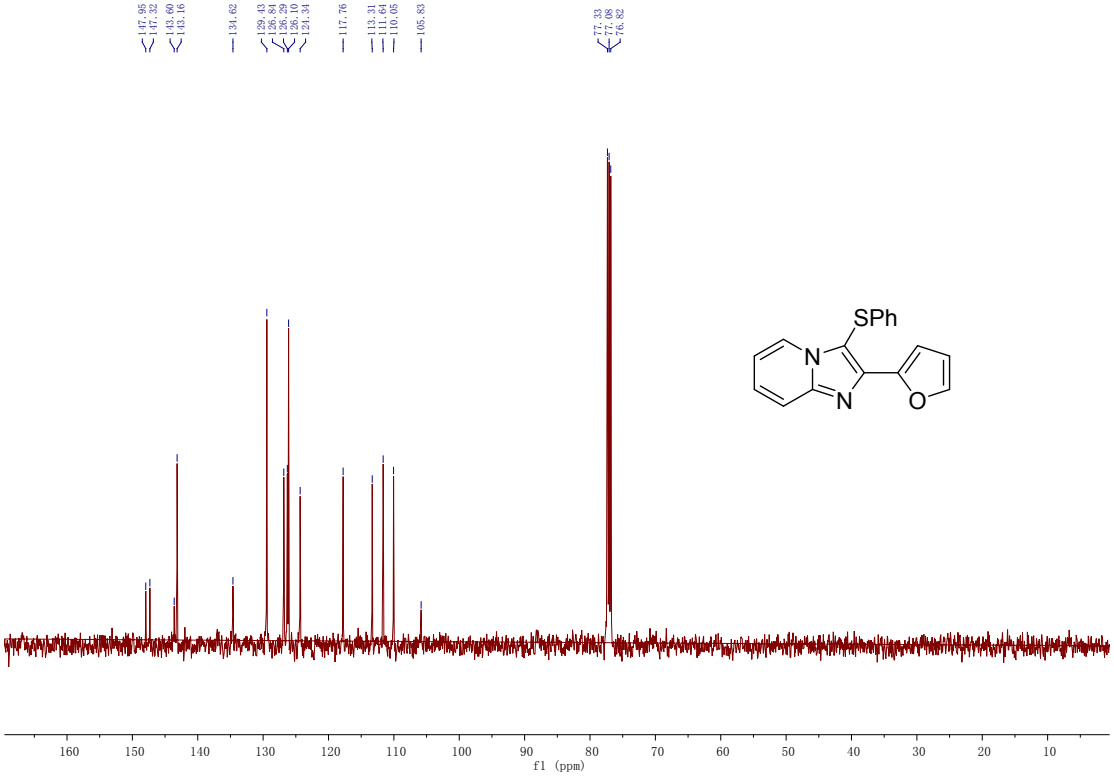


2-Furan-2-yl-3-(phenylthio)-imidazo[1,2-a] pyridine (3h)

^{1}H NMR (500 MHz, $CDCl_3$)

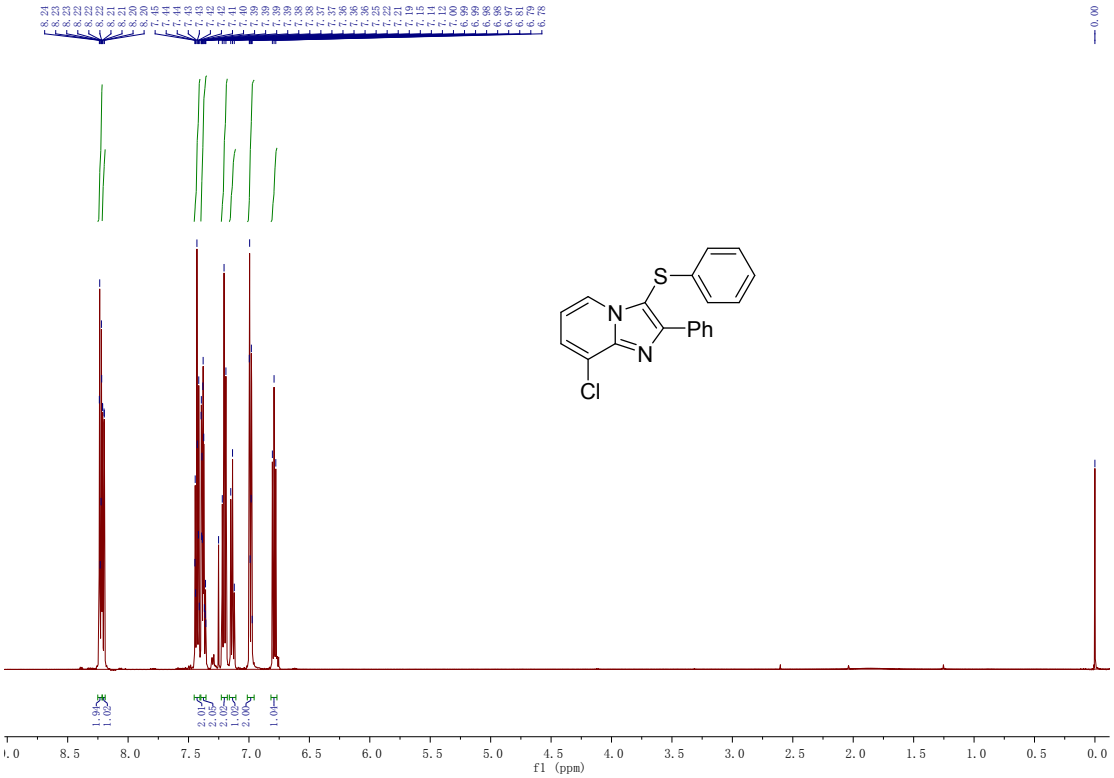


^{13}C NMR (125 MHz, $CDCl_3$)

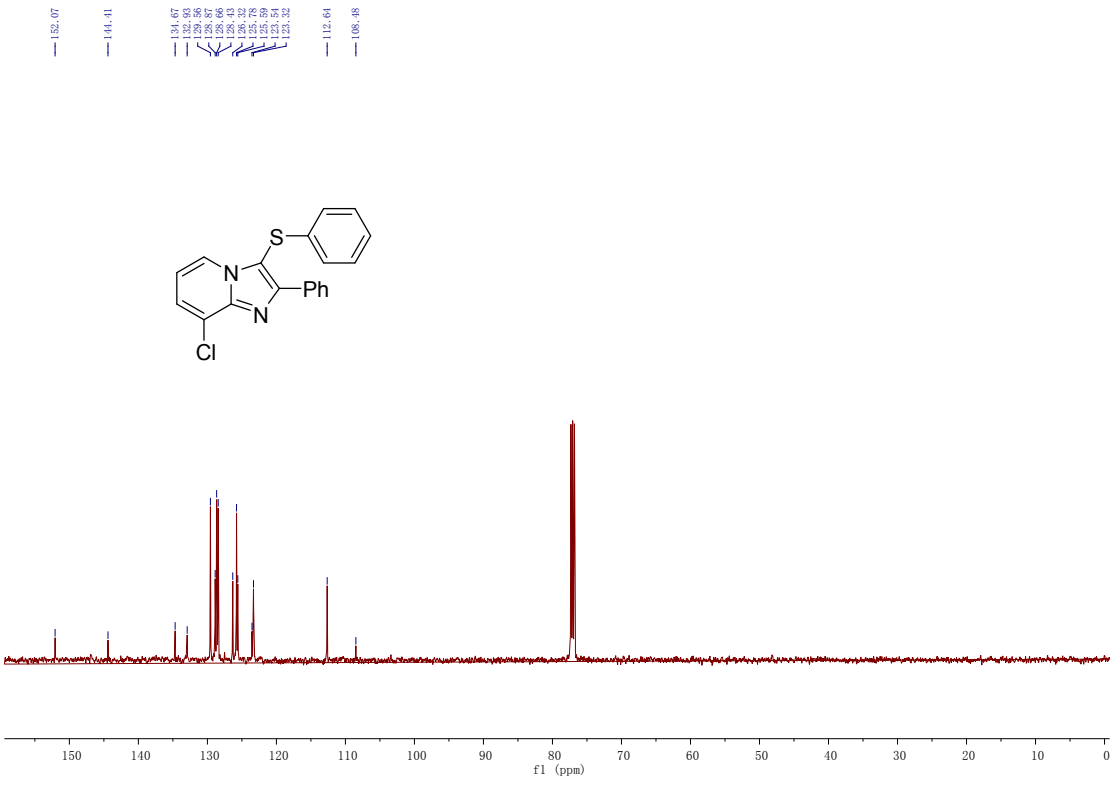


8-Chloro-2-phenyl-3-(phenylthio)imidazo[1,2-a]pyridine (3i)

^{1}H NMR (500 MHz, $CDCl_3$)

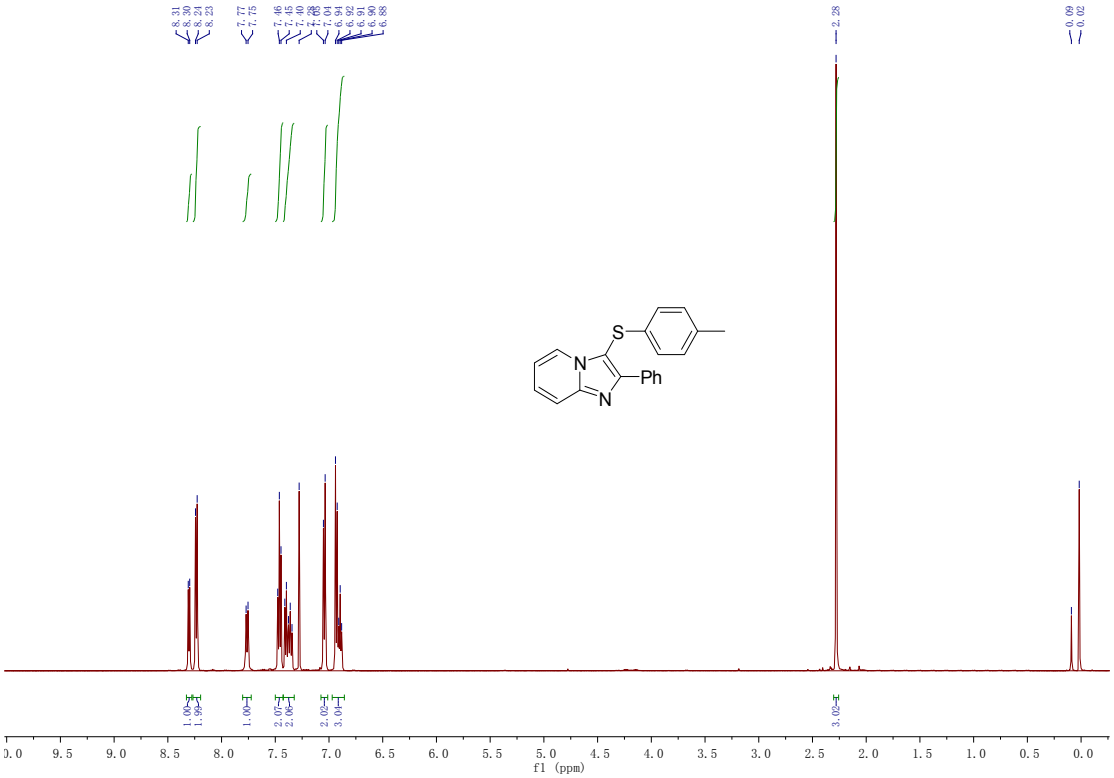


^{13}C NMR (125 MHz, $CDCl_3$)



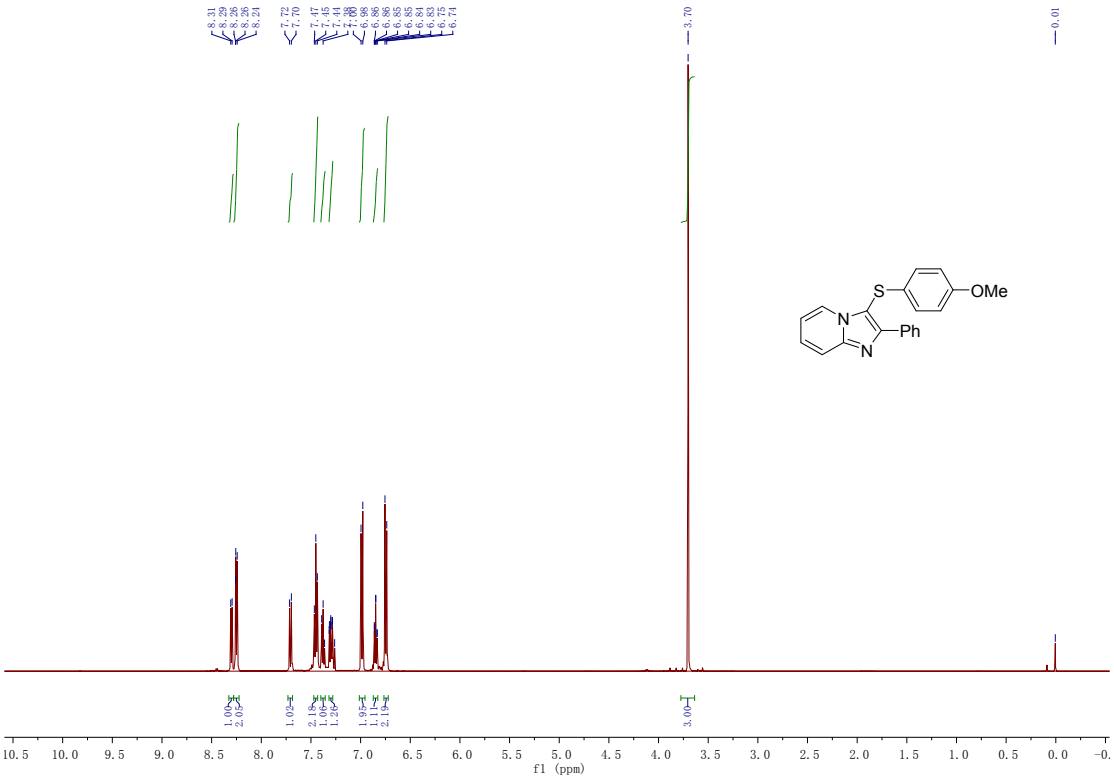
2-Phenyl-3-(p-Tolylthio)-imidazo[1,2-a] pyridine (3j)

^{1}H NMR (500 MHz, $CDCl_3$)

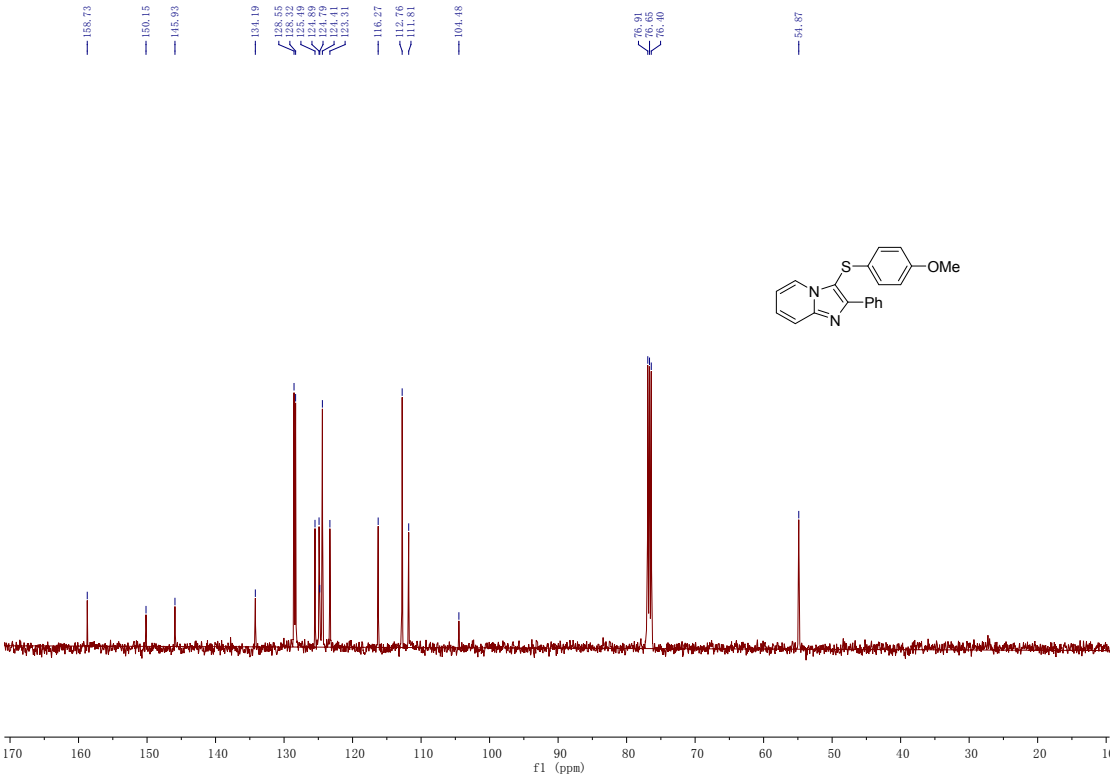


2-phenyl-3-(4-methoxy-phenylthio)-imidazo[1,2-a] pyridine (3k)

^{1}H NMR (500 MHz, $CDCl_3$)

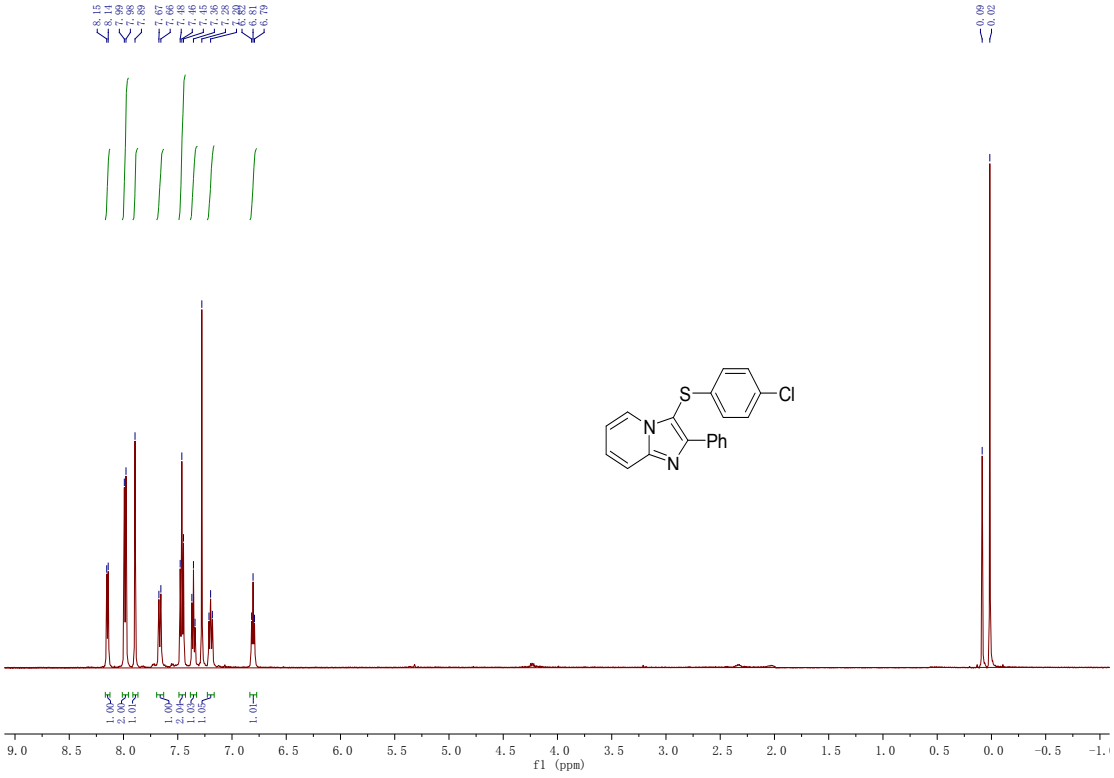


^{13}C NMR (125 MHz, $CDCl_3$)



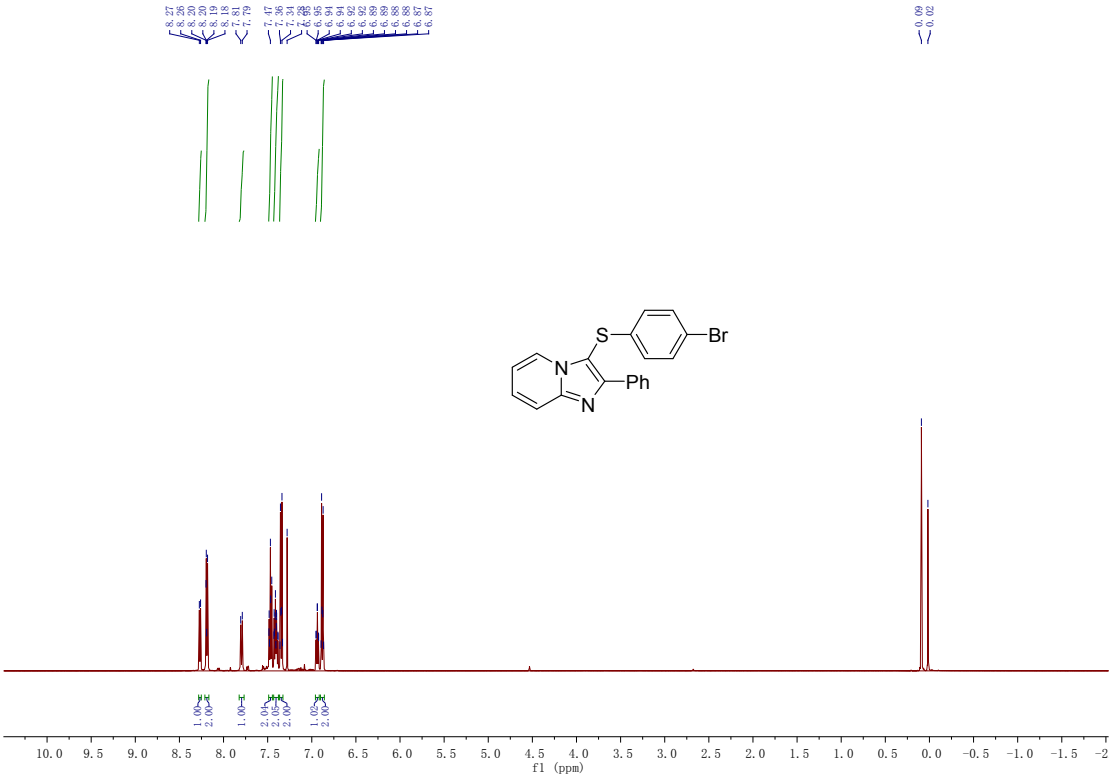
2-Phenyl-3-[(4-Chlorophenyl)thio]-imidazo[1,2-a] pyridine (3l)

^{1}H NMR (500 MHz, $CDCl_3$)



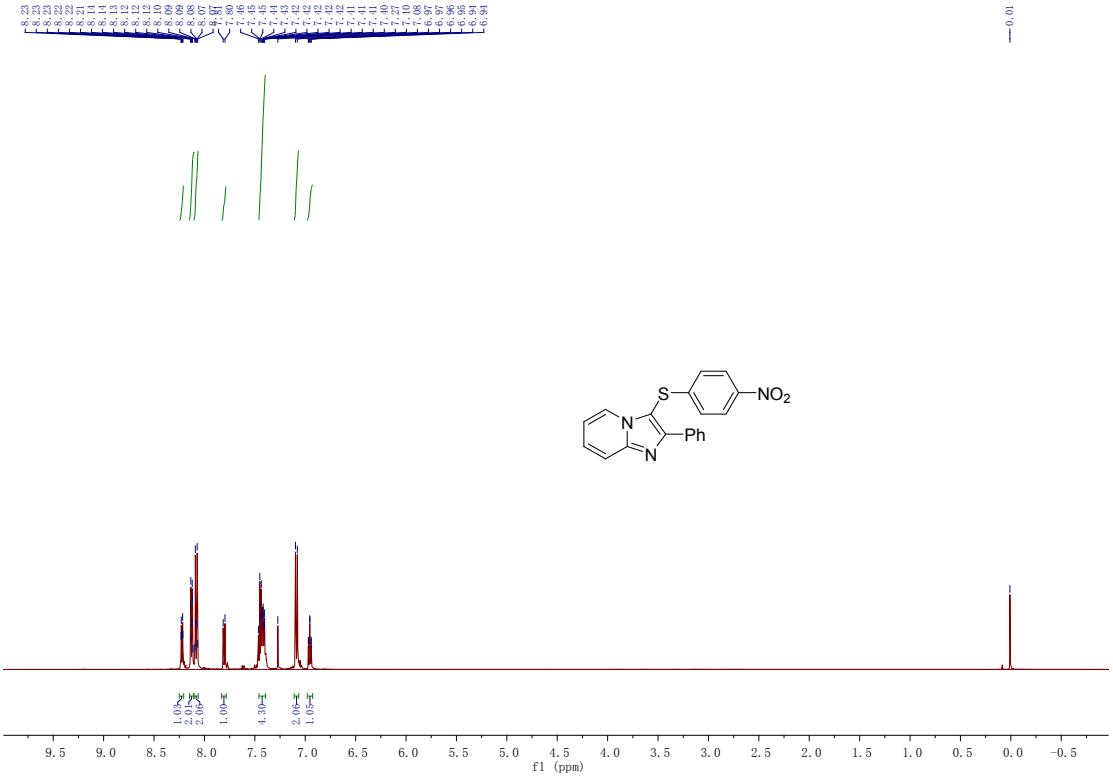
2-Phenyl-3-[(4-Bromophenyl)thio]-imidazo[1,2-a] pyridine (3m)

^{1}H NMR (500 MHz, $CDCl_3$)

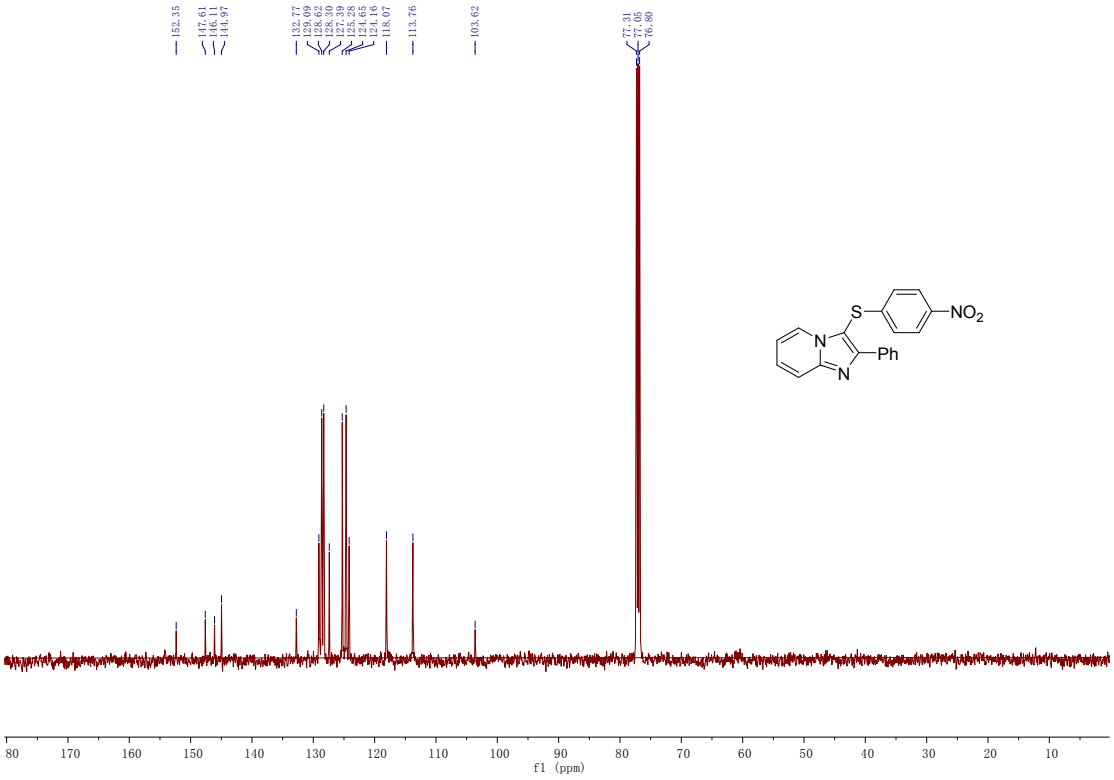


2-Phenyl-3-[(4-nitrophenyl)thio]-imidazo[1,2-a] pyridine (3n)

^{1}H NMR (500 MHz, $CDCl_3$)

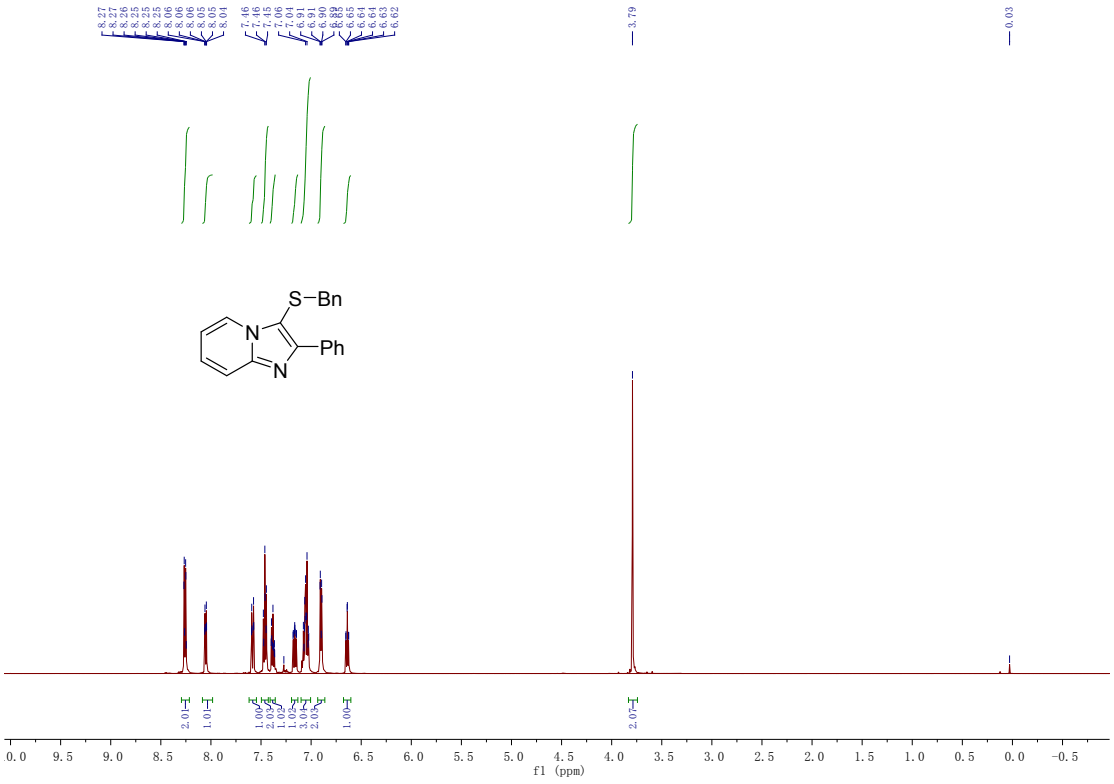


^{13}C NMR (125 MHz, $CDCl_3$)

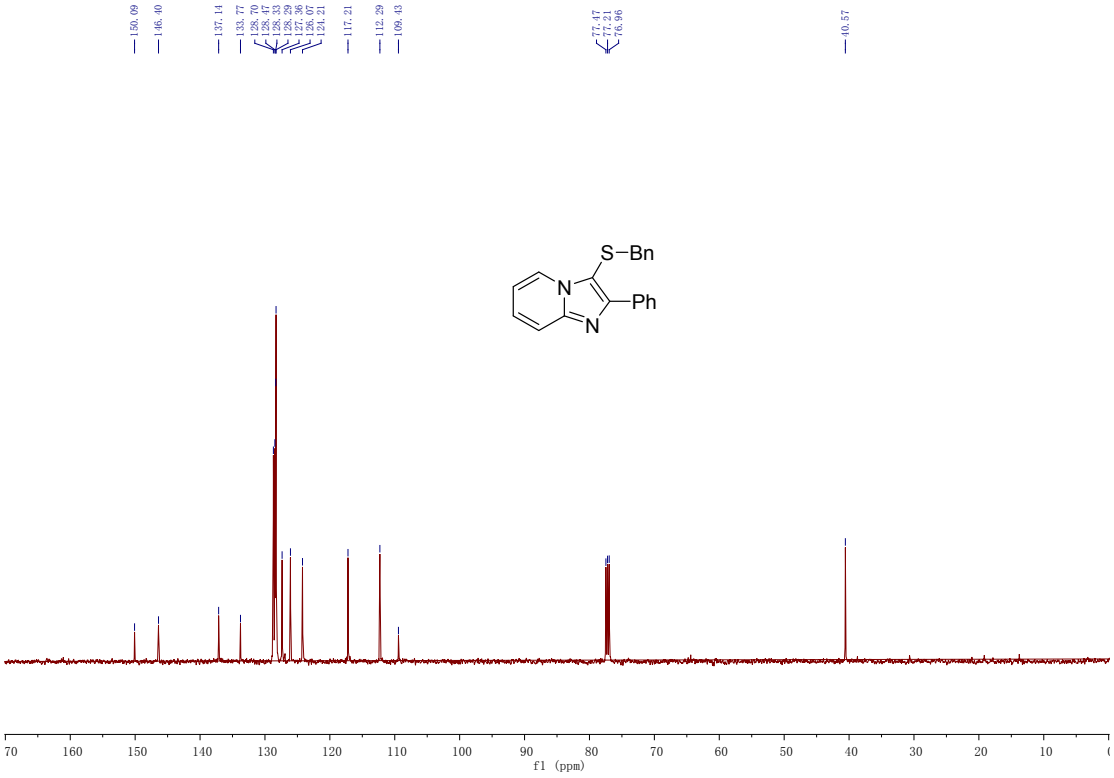


2-Phenyl-3-(benzylthio)-imidazo[1,2-a] pyridine (3o)

^{1}H NMR (500 MHz, $CDCl_3$)

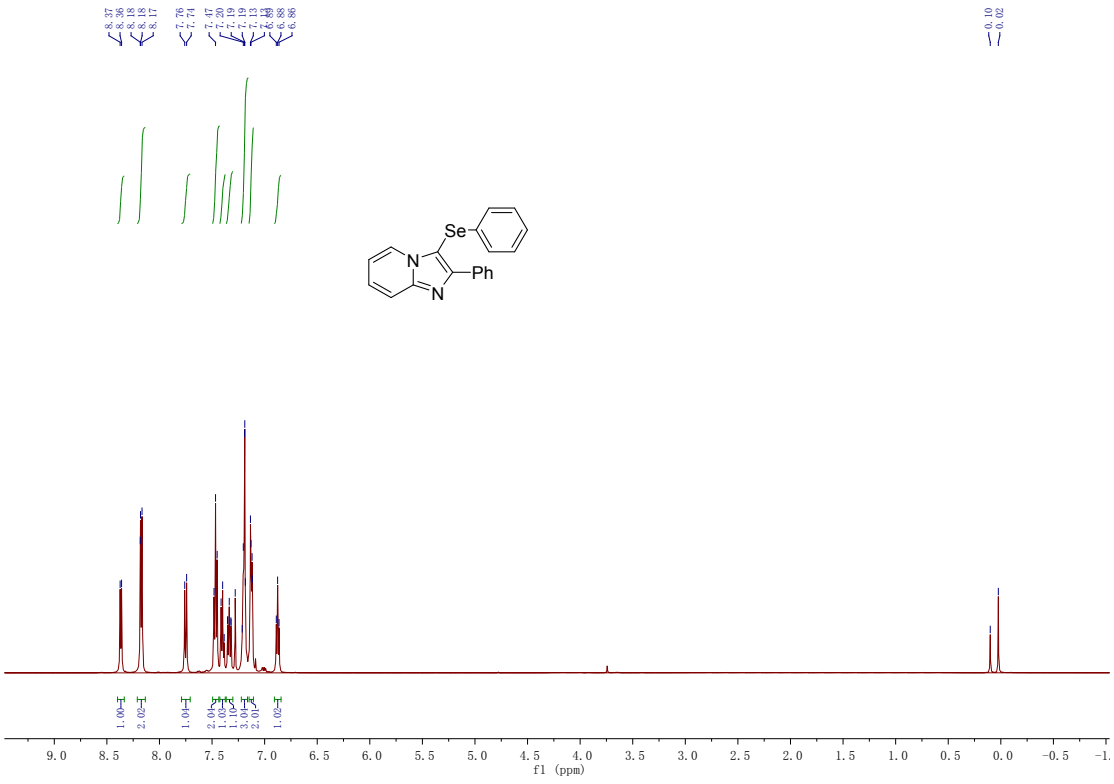


^{13}C NMR (125 MHz, $CDCl_3$)



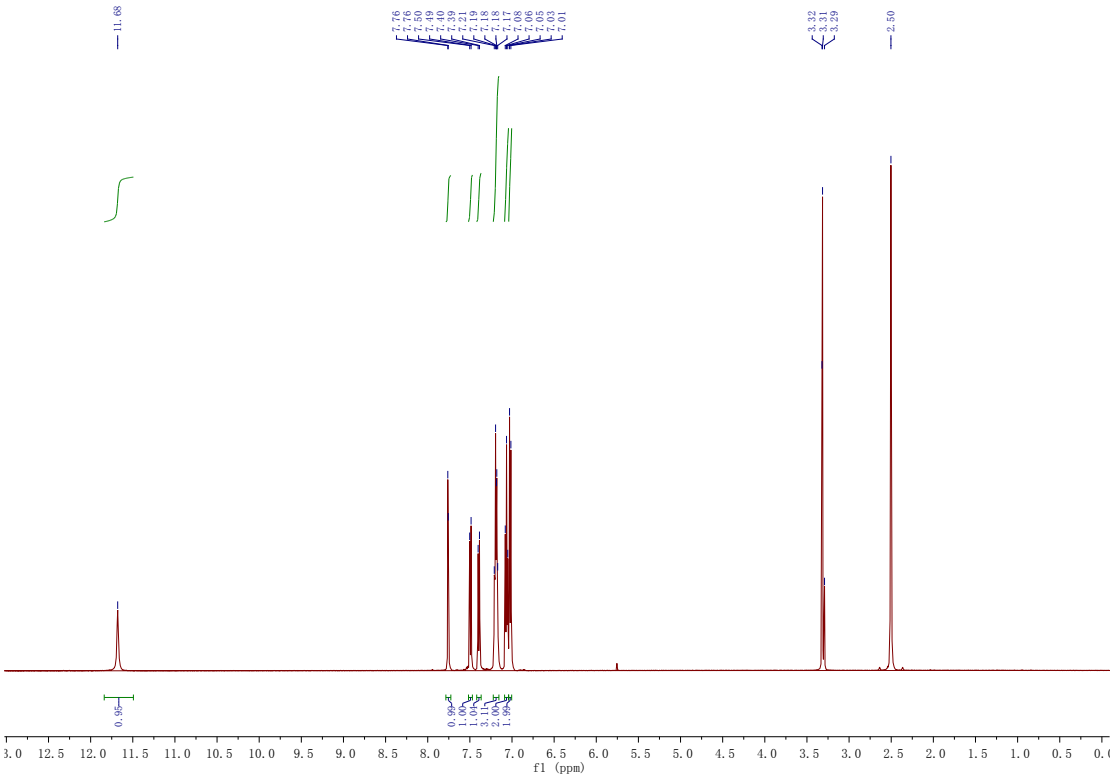
2-Phenyl-3-(phenylselanyl)-imidazo[1,2-a] pyridine (3r)

^{1}H NMR (500 MHz, $CDCl_3$)

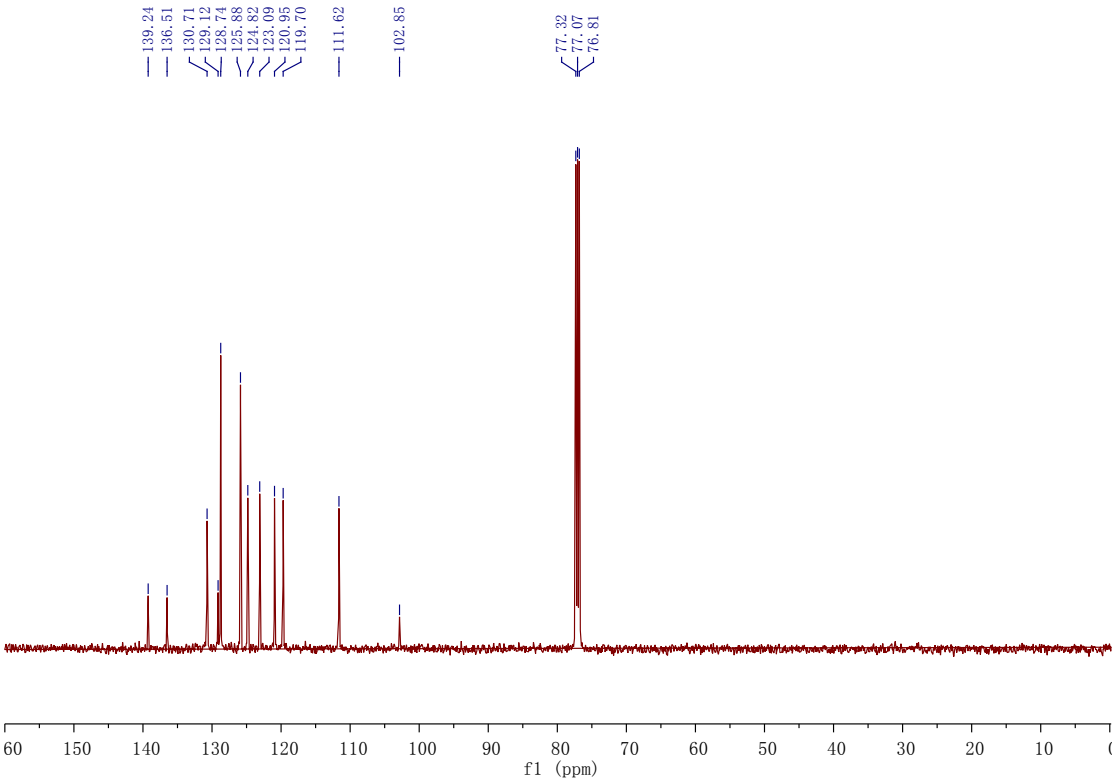


3-(Phenylthio)-*1H*-indole (3s)

^{1}H NMR (500 MHz, DMSO-d_6)

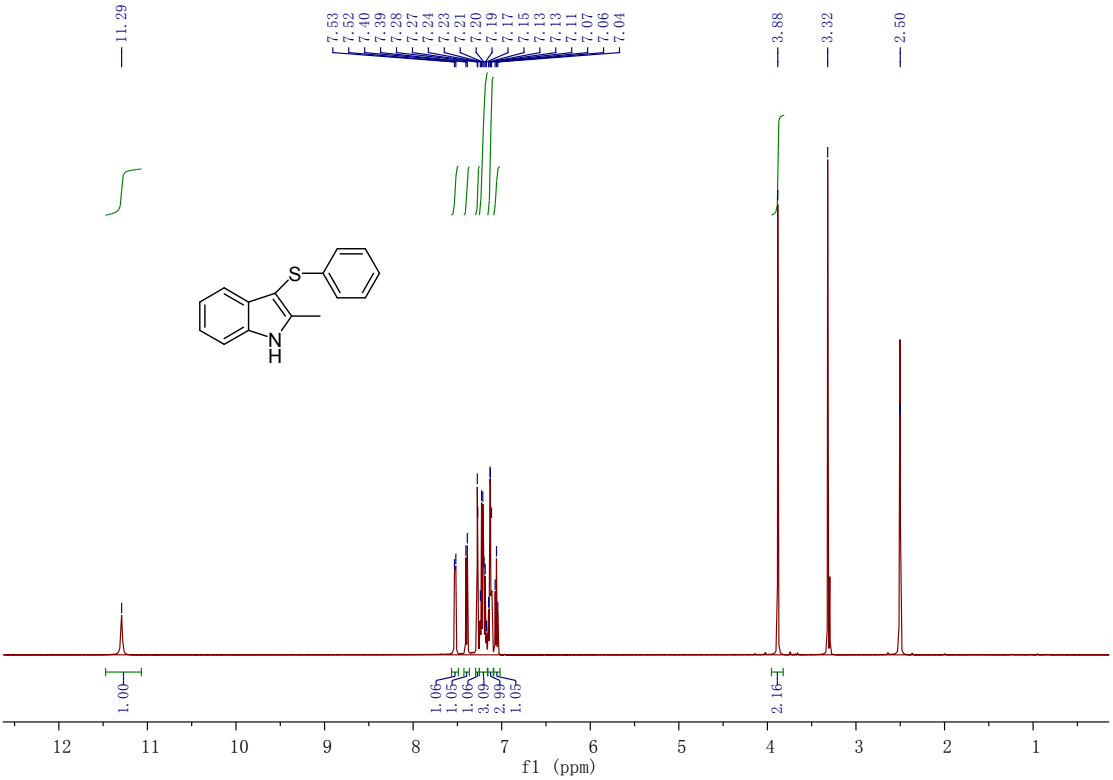


^{13}C NMR (125 MHz, $CDCl_3$)



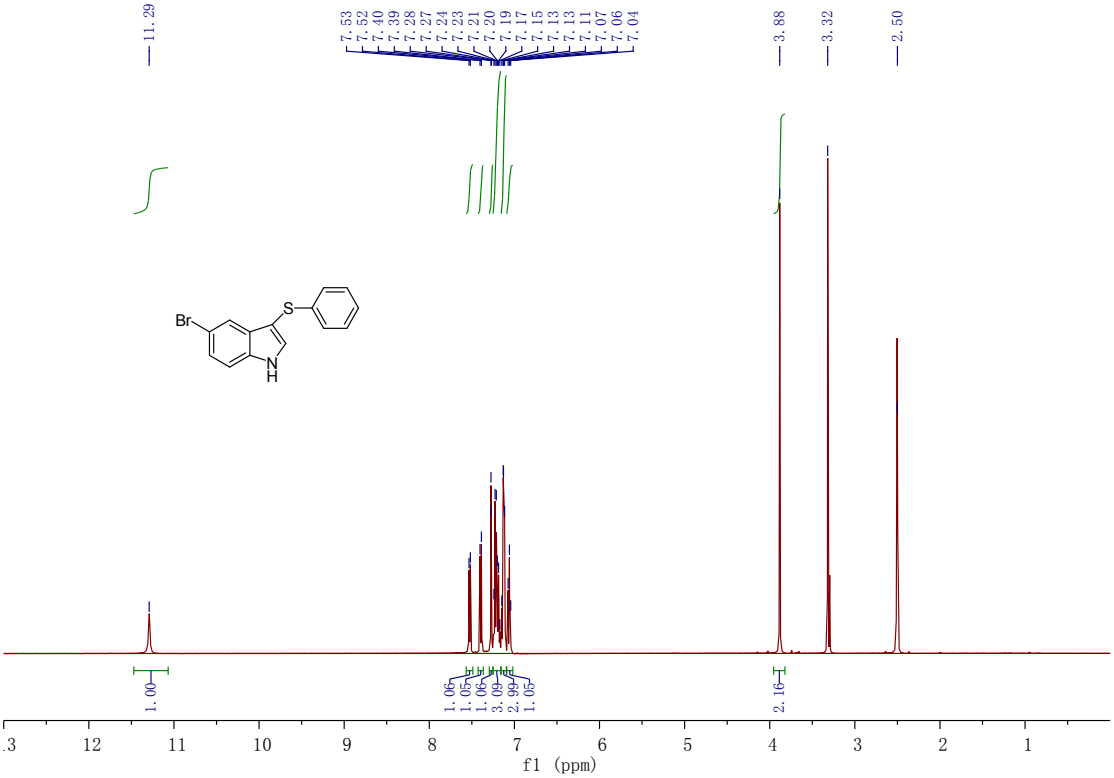
2-Methyl-3-(phenylthio)-1H-indole (3t)

^{1}H NMR (500 MHz, $CDCl_3$)



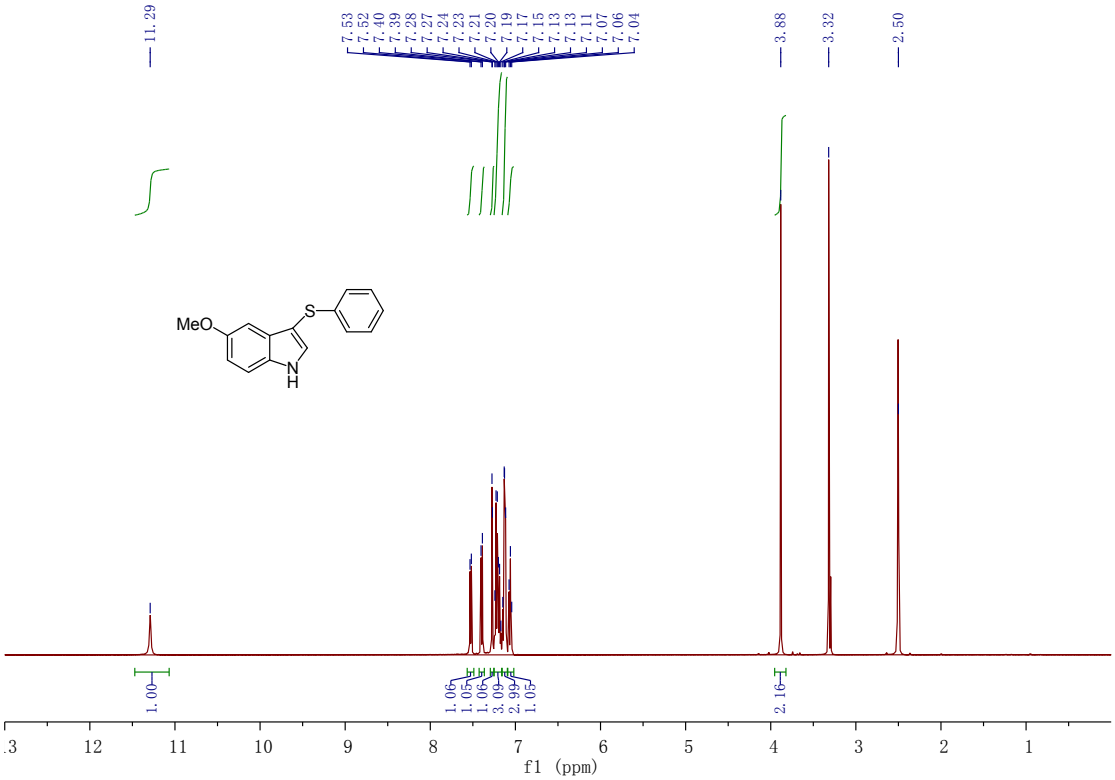
5-Bromo-3-(phenylthio)-1H-indole (3u)

^{1}H NMR (500 MHz, $CDCl_3$)



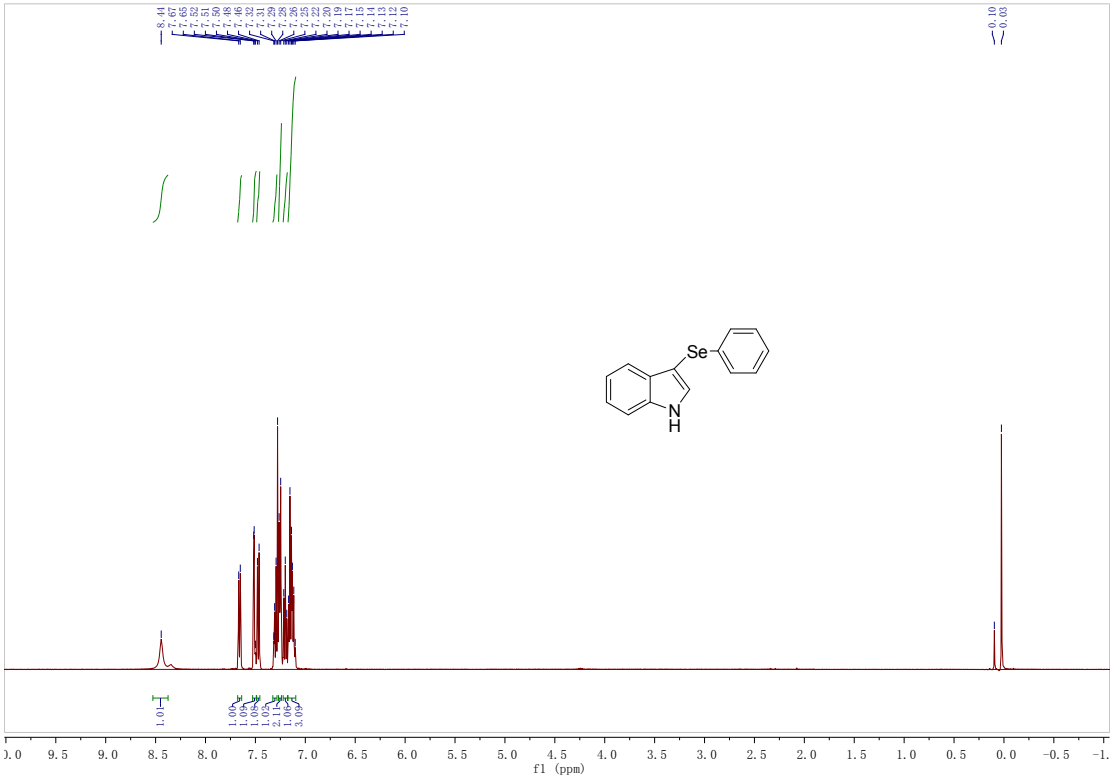
5-Methoxy-3-(phenylthio)-1H-indole (3v)

^{1}H NMR (500 MHz, $CDCl_3$)



3-(Phenylselanyl)-*1H*-indole (3w)

^{1}H NMR (500 MHz, $CDCl_3$)



2-(Phenylthio)-*1H*-pyrrole (3x)

^{1}H NMR (500 MHz, $CDCl_3$)