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Supporting Information for

Regioselective C−H Dithiocarbamation of Indolizines with Tetramethylthiuram Disulfide under Metal-Free Conditions

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1. General considerations

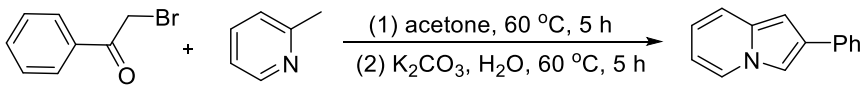
^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using $CDCl_3$ as solvent. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). The data of HRMS was carried out on a waters G2-XS high-resolution mass spectrometer (HR-ESI-MS). IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a PerkinElmer Frontier spectrometer. Melting points were determined with a Büchi Melting Point B-545 instrument. Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification.

2. Experimental procedures and characterization data

2.1 Experimental procedures

Synthesis of substrates 1 according to the following procedure:

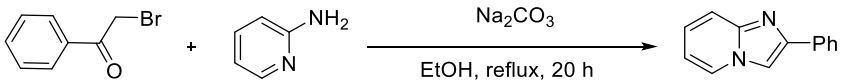
The substrates **1a**-**1x** are known and were prepared according to the procedures in the literature.[1-3] As exemplified for **1a**:



A solution of 2-picoline (0.93 g, 10 mmol, 1.0 equiv.) and 2 bromoacetophenone (1.99 g, 10 mmol, 1.0 equiv.) in acetone (50 mL) were added to a 100 mL round bottom flask and heated with a heating mantle at 60 °C for 5 hours. The precipitate obtained by filtration separation was redissolved in 20 mL of hot water (60 °C). Then, K_2CO_3 (1.38 g, 10 mmol, 1.0 equiv.) was added and heated at 60 °C for 5 hours. After filtration and drying in vacuo, a white solid compound was obtained in 50% overall yield (0.965 g, 5 mmol) without further purification.

Synthesis of substrates 6 according to the following procedure:

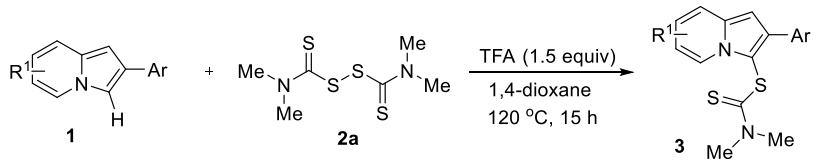
The substrates **6a-6d** are known and were prepared according to the procedures in the literature.[4-6] As exemplified for **6a**:



Pyridin-2-amine (100.0 mmol) was dissolved in C_2H_5OH (20.0 mL) and then Na_2CO_3 (200.0 mmol) and 2-bromo-1-phenylethan-1-one (130.0 mmol) were added, respectively. The reaction mixture was refluxed for 20 h, then cooled to room temperature, and the solvent was removed to afford an oily residue. The water (100.0 mL) was added into residue. The aqueous solution was extracted with EtOAc (5×30.0 mL) and the combined extract was dried with anhydrous Na_2SO_4. The solvent was removed and the crude product was separated by column chromatography (eluted with petroleum ether : ethyl acetate=1:1)to give a pure sample of 2-phenylimidazo[1,2-*a*]pyridine.

Synthesis of products 3 and 7 according to the following procedure:

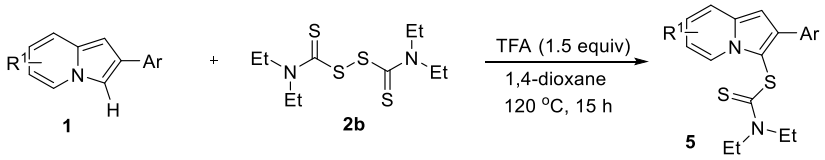
As exemplified for **3a**:



A pressure tube was charged with 2-phenylindazine **1a** (0.058 g，0.3 mmol), tetramethylthiuram disulfide **2a** (0.108 g, 0.45 mmol) and 1,4-dioxane (2 mL). TFA (0.051 g, 0.45 mmol) was added and the mixtures were heated with a heating mantle at 120 °C for 15 h. After cooling to room temperature, the solvent was volatilized and the crude product was purified by flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v), and the target compound **3a** was obtained.

Synthesis of products 5 according to the following procedure:

As exemplified for **5a**:



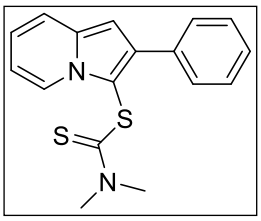
A pressure tube was charged with 2-phenylindazine **4a** (0.058 g，0.3 mmol), tetraethylthiuram disulfide **2b** (0.133 g, 0.45 mmol) and 1,4-dioxane (2 mL). TFA (0.051 g, 0.45 mmol) was added and the mixtures were heated with a heating mantle at 120 °C for 15 h. After cooling to room temperature, the solvent was volatilized and the crude product was purified by flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v), and the target compound **5a** was obtained.

Scale-up experiment:

An oven-dried 50 mL Schlenk flask was charged with a stirring bar, 2-phenylindazine **1a** (1.158 g，6.0 mmol), tetramethylthiuram disulfide **2a** (2.164 g, 9.0 mmol) and 1,4-dioxane (15 mL). TFA (1.026 g, 9.0 mmol) was added and the mixture was heated with a heating mantle at 120 °C for 15 h. After cooling to room temperature, the solution was then diluted with EtOAc and water, extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v), and the target compound **3a** (1.537 g, 82% yield) was obtained.

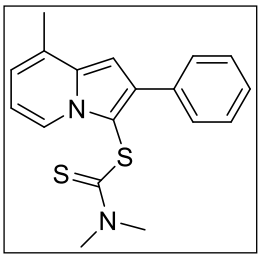
2.2 Characterization data

2-Phenylindolizin-3-yl dimethylcarbamodithioate (3a)



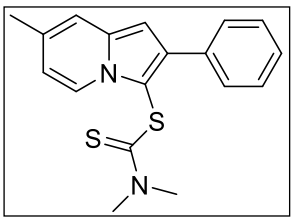
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3a**. Dark green solid (82.5 mg, 88%), mp 53.6-54.3 °C. IR (KBr): 2923, 1627, 1602, 1502, 1377, 759, 733 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 1H), 7.67 – 7.62 (m, 2H), 7.46 – 7.38 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.89 (m, 1H), 6.76 (s, 1H), 6.67 – 6.62 (m, 1H), 3.53 (s, 3H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.30, 138.08, 136.52, 135.37, 129.28, 128.29, 127.21, 124.26, 120.47, 118.93, 111.27, 104.68, 100.75, 45.88, 41.99. HRMS MALDI (m/z): calcd for $C_{17}H_{16}N_2S_2$ $[M + H]^+$: 313.0833, found: 313.0836.

8-Methyl-2-phenylindolizin-3-yl dimethylcarbamodithioate (3b)



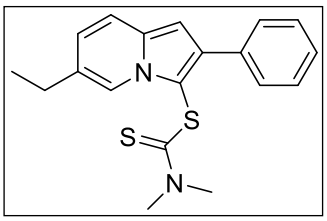
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3b**. Dark green solid (78.36 mg, 80%), mp 56.9-57.5 °C. IR (KBr): 2923, 1496, 1375, 1343, 1246, 755, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.0 Hz, 1H), 7.67 (m, 2H), 7.45 – 7.36 (m, 2H), 7.31 (m, 1H), 6.75 (s, 1H), 6.71 (d, *J* = 6.8 Hz, 1H), 6.60 (m, 1H), 3.54 (s, 3H), 3.49 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.60, 137.70, 137.32, 135.53, 129.30, 128.30, 128.03, 127.18, 122.23, 119.87, 111.46, 105.07, 99.38, 45.92, 42.02, 18.03. HRMS MALDI (m/z): calcd for $C_{18}H_{18}N_2S_2$ $[M + H]^+$: 327.0990, found: 327.0991.

7-Methyl-2-phenylindolizin-3-yl dimethylcarbamodithioate (3c)



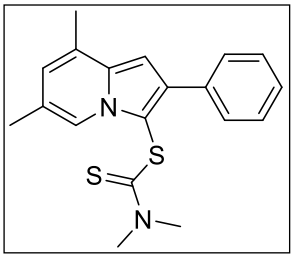
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3c**. Yellowish brown solid (74.4 mg, 76%), mp 95.4-96.3 °C. IR (KBr): 2933, 1596, 1395, 1303, 1236, 759, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.1 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.20 (d, *J* = 9.5 Hz, 1H), 6.62 (s, 1H), 6.50 – 6.44 (m, 1H), 3.52 (s, 3H), 3.47 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.77, 138.14, 136.82, 135.49, 130.81, 129.18, 128.23, 127.09, 123.68, 117.26, 113.94, 103.56, 99.38, 45.85, 41.91, 21.13. HRMS MALDI (m/z): calcd for $C_{18}H_{18}N_2S_2$ $[M + H]^+$: 326.0911, found: 326.0909.

6-Ethyl-2-phenylindolizin-3-yl dimethylcarbamodithioate (3d)



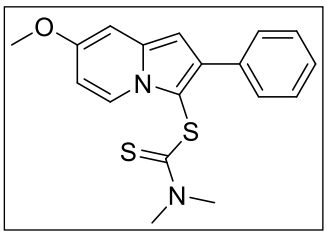
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3d**. Dark green solid (78.66 mg, 77%), mp 143.5-144.1 °C. IR (KBr): 3083, 2925, 1740, 1343, 1154, 1116, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.67 – 7.61 (m, 2H), 7.42 – 7.37 (m, 3H), 7.33 – 7.28 (m, 1H), 6.82 (d, *J* = 9.1 Hz, 1H), 6.71 (s, 1H), 3.57 (s, 3H), 3.52 (s, 3H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.80, 137.82, 135.64, 134.34, 129.29, 128.28, 127.14, 127.08, 122.66, 121.28, 118.63, 104.30, 100.46, 45.94, 42.02, 26.39, 15.49. HRMS MALDI (m/z): calcd for $C_{19}H_{20}N_2S_2$ $[M + H]^+$: 341.1146, found: 341.1148.

6,8-Dimethyl-2-phenylindolizin-3-yl dimethylcarbamodithioate (3e)



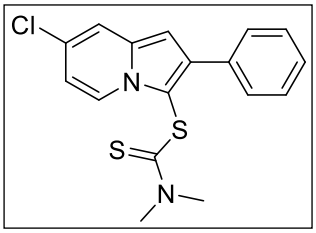
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3e**. Purplish black solid (72.5 mg, 71%), mp 102.8-103.4 °C. IR (KBr): 2917, 1503, 1406, 1376, 1337, 1247, 759 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.69 – 7.63 (m, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.33 – 7.27 (m, 1H), 6.70 (s, 1H), 6.58 (s, 1H), 3.56 (s, 3H), 3.51 (s, 3H), 2.44 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.97, 137.25, 136.18, 135.69, 129.21, 128.25, 127.38, 127.02, 123.32, 120.86, 119.79, 104.48, 99.04, 45.92, 41.98, 18.76, 17.87. HRMS MALDI (m/z): calcd for $C_{19}H_{20}N_2S_2$ $[M + H]^+$: 340.1062, found: 340.1065.

7-Methoxy-2-phenylindolizin-3-yl dimethylcarbamodithioate (3f)



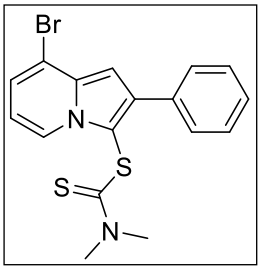
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3f**. Yellowish brown solid (77.1 mg, 75%), mp 146.7-147.2 °C. IR (KBr): 2924, 1646, 1504, 1374, 1244, 1225, 1022 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.57 (s, 1H), 6.42 – 6.38 (m, 1H), 3.84 (s, 3H), 3.57 (s, 3H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.35, 154.73, 138.83, 137.38, 135.55, 129.16, 128.28, 127.17, 125.55, 106.30, 102.62, 99.03, 95.82, 55.42, 45.97, 41.96. HRMS MALDI (m/z): calcd for $C_{18}H_{18}N_2OS_2$ $[M + H]^+$: 342.0855, found: 342.0856.

7-Chloro-2-phenylindolizin-3-yl dimethylcarbamodithioate (3g)



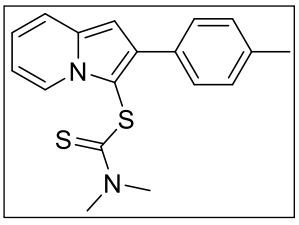
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3g**. Yellowish brown solid (67.6 mg, 65%), mp 91.2-91.8 °C. IR (KBr): 2922, 1623, 1501, 1372, 1246, 757, 696 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.47 – 7.39 (m, 3H), 7.34 (d, *J* = 7.3 Hz, 1H), 6.71 (s, 1H), 6.66 – 6.59 (m, 1H), 3.57 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.82, 139.13, 136.14, 134.96, 129.28, 128.41, 127.54, 126.92, 125.14, 117.56, 112.68, 105.54, 100.88, 45.98, 42.13. HRMS MALDI (m/z): calcd for $C_{17}H_{15}ClN_2S_2$ $[M + H]^+$: 346.0360, found: 346.0363.

8-Bromo-2-phenylindolizin-3-yl dimethylcarbamodithioate (3h)



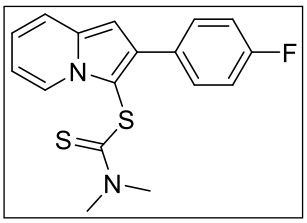
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3h**. Yellowish brown solid (82.2 mg, 70%), mp 98.9-99.6 °C. IR (KBr): 2924, 1496, 1374, 1337, 1246, 750, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.1 Hz, 1H), 6.93 (s, 1H), 6.53 (t, *J* = 7.1 Hz, 1H), 3.54 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.48, 138.57, 135.38, 134.85, 129.32, 128.38, 127.53, 123.61, 123.08, 112.96, 111.08, 107.12, 102.63, 45.91, 42.11. HRMS MALDI (m/z): calcd for $C_{17}H_{15}BrN_2S_2$ $[M + H]^+$: 389.9855, found: 389.9854, 391.9850.

2-(P-tolyl)indolizin-3-yl dimethylcarbamodithioate (3i)



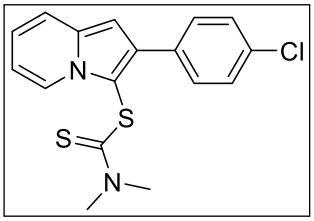
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3i**. Brown solid (81.3 mg, 83%), mp 79.9-80.6 °C. IR (KBr): 2922, 1505, 1373, 1334, 1243, 968, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.47 – 7.41 (m, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.93 – 6.87 (m, 1H), 6.74 (s, 1H), 6.65 (t, *J* = 6.8 Hz, 1H), 3.57 (s, 3H), 3.53 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.53, 138.21, 136.97, 136.56, 132.49, 129.19, 129.10, 124.30, 120.45, 118.93, 111.21, 104.57, 100.69, 45.94, 42.04, 21.42. HRMS MALDI (m/z): calcd for $C_{18}H_{18}N_2S_2$ $[M + H]^+$: 327.0990, found: 327.0994.

2-(4-Fluorophenyl)indolizin-3-yl dimethylcarbamodithioate (3j)



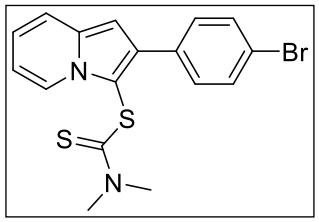
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3j**. Brown solid (77.3 mg, 78%), mp 61.9-62.3 °C. IR (KBr): 2919, 1516, 1378, 1156, 809, 798, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.1 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.10 (t, *J* = 8.7 Hz, 2H), 6.95 – 6.90 (m, 1H), 6.73 (s, 1H), 6.71 – 6.64 (m, 1H), 3.58 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.32, 162.46 (d, *J* = 245.0 Hz), 137.28, 136.60, 131.47 (d, *J* = 3.0 Hz), 130.88 (d, *J* = 8.0 Hz), 124.30, 120.67, 118.99, 115.27 (d, *J* = 21.3 Hz), 111.45, 104.70, 100.71, 46.01, 42.08. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.59. HRMS MALDI (m/z): calcd for $C_{17}H_{15}FN_2S_2$ $[M + H]^+$: 331.0739, found: 331.0738.

2-(4-Chlorophenyl)indolizin-3-yl dimethylcarbamodithioate (3k)



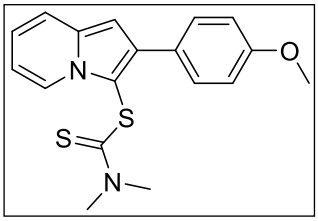
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3k**. Yellowish brown solid (77.0 mg, 74%), mp 68.1-68.9 °C. IR (KBr): 2920, 1501, 1369, 1242, 774, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.88 (m, 1H), 6.73 (s, 1H), 6.67 (t, *J* = 6.9 Hz, 1H), 3.56 (s, 3H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.10, 136.97, 136.61, 133.91, 133.25, 130.55, 128.51, 124.28, 120.71, 119.01, 111.53, 104.80, 100.66, 45.97, 42.06. HRMS MALDI (m/z): calcd for $C_{17}H_{15}ClN_2S_2$ $[M + H]^+$: 346.0360, found: 346.0367.

2-(4-Bromophenyl)indolizin-3-yl dimethylcarbamodithioate (3l)



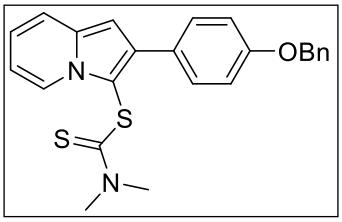
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3l**. Yellowish brown solid (89.2 mg, 76%), mp 83.5-84.4 °C. IR (KBr): 2930, 2018,1506, 1315, 1205, 1034, 786 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.1 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.44 (d, *J* = 8.9 Hz, 1H), 6.93 – 6.87 (m, 1H), 6.72 (s, 1H), 6.66 (t, *J* = 6.8 Hz, 1H), 3.54 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.94, 136.86, 136.54, 134.31, 131.39, 130.83, 124.21, 121.45, 120.67, 118.95, 111.49, 104.70, 100.54, 45.91, 42.01. HRMS MALDI (m/z): calcd for $C_{17}H_{15}BrN_2S_2$ $[M + H]^+$: 389.9855, found: 389.9857, 391.9838.

2-(4-Methoxyphenyl)indolizin-3-yl dimethylcarbamodithioate (3m)



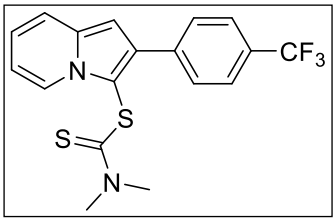
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3m**. Brown solid (81.2 mg, 79%), mp 49.7-50.6 °C. IR (KBr): 2925, 1505, 1375, 1245, 1175, 1031, 774 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.0 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 6.98 – 6.94 (m, 2H), 6.93 – 6.87 (m, 1H), 6.72 (s, 1H), 6.68 – 6.61 (m, 1H), 3.84 (s, 3H), 3.58 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.64, 159.08, 137.98, 136.60, 130.40, 127.95, 124.28, 120.47, 118.85, 113.86, 111.15, 104.40, 100.52, 55.40, 45.97, 42.05. HRMS MALDI (m/z): calcd for $C_{18}H_{18}N_2OS_2$ $[M + H]^+$: 343.0939, found: 343.0946.

2-(4-(Benzyloxy)phenyl)indolizin-3-yl dimethylcarbamodithioate (3n)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3n**. Yellowish brown solid (91.7 mg, 73%), mp 106.3-107.0 °C. IR (KBr): 2924,, 1505,1375, 1241, 1174,968, 732 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.1 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.46 – 7.36 (m, 5H), 7.35 – 7.30 (m, 1H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.92 – 6.85 (m, 1H), 6.71 (s, 1H), 6.67 – 6.60 (m, 1H), 5.09 (s, 2H), 3.55 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.50, 158.30, 137.85, 137.16, 136.54, 130.37, 128.69, 128.14, 128.05, 127.60, 124.23, 120.45, 118.82, 114.73, 111.13, 104.35, 100.48, 70.09, 45.93, 42.02. HRMS MALDI (m/z): calcd for $C_{24}H_{22}N_2OS_2$ $[M + H]^+$: 418.1168, found: 418.1171.

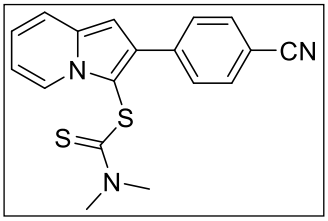
2-(4-(Trifluoromethyl)phenyl)indolizin-3-yl dimethylcarbamodithioate (3o)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford 3o. Yellowish brown solid (98.2 mg, 86%), mp 185.8-186.7 °C. IR (KBr): 3056, 1750, 1536, 1254, 1136, 975, 789 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.1 Hz, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.43 – 7.34 (m, 1H), 6.87 – 6.80 (m, 1H), 6.71 (s, 1H), 6.61 (t, J = 6.8 Hz, 1H), 3.46 (s, 3H), 3.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.41, 138.95, 136.42, 136.22, 129.29, 128.70 (q, J = 32.0 Hz), 125.03 (q, J = 3.8 Hz), 124.06, 120.63, 120.42 (q, J = 537.0 Hz), 118.89,

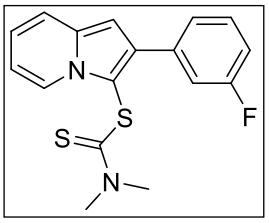
111.57, 104.99, 100.69, 45.69, 41.79. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.11. HRMS MALDI (m/z): calcd for $C_{18}H_{15}F_3N_2S_2$ $[M + H]^+$: 380.0623, found: 380.0635.

2-(4-Cyanophenyl)indolizin-3-yl dimethylcarbamodithioate (3p)



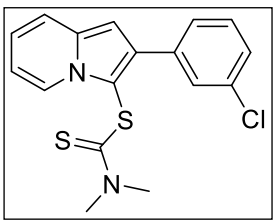
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3p**. Brown solid (72.9 mg, 72%), mp 210.5-211.4 °C. IR (KBr): 2223, 1608, 1503, 1379, 1244, 774, 729 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.1 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 1H), 6.97 – 6.92 (m, 1H), 6.77 (s, 1H), 6.73 – 6.68 (m, 1H), 3.57 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.48, 140.22, 136.71, 136.03, 132.11, 129.78, 129.60, 124.25, 121.02, 119.21, 112.01, 110.56, 105.21, 100.85, 46.01, 42.11. HRMS MALDI (m/z): calcd for $C_{18}H_{15}N_3S_2$ $[M + H]^+$: 338.0786, found: 338.0787.

2-(3-Fluorophenyl)indolizin-3-yl dimethylcarbamodithioate (3q)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford 3q. Yellowish brown solid (69.4 mg, 70%), mp 76.4-77.2 °C. IR (KBr): 2919, 1516, 1378, 1156, 809, 798, 706 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.1 Hz, 1H), 7.44 (t, J = 8.2 Hz, 2H), 7.40 – 7.31 (m, 3H), 7.04 – 6.98 (m, 1H), 6.94 – 6.88 (m, 1H), 6.75 (s, 1H), 6.66 (t, J = 6.8 Hz, 1H), 3.54 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.85, 162.74 (d, J = 244.5 Hz), 137.57 (d, J = 8.5 Hz), 136.70, 136.50, 129.71 (d, J = 8.4 Hz), 124.96 (d, J = 2.8 Hz), 124.23, 120.68, 119.03, 115.98 (d, J = 22.1 Hz), 113.98 (d, J = 21.1 Hz), 111.56, 104.88, 100.77, 45.92, 42.04. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.69. HRMS MALDI (m/z): calcd for $C_{17}H_{15}FN_2S_2$ $[M + H]^+$: 331.0739, found: 331.0738.

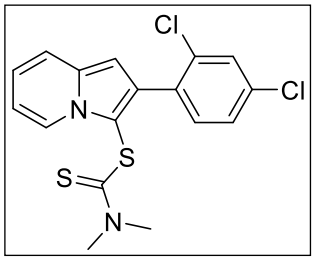
2-(3-Chlorophenyl)indolizin-3-yl dimethylcarbamodithioate (3r)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3r**. Dark green solid (76.0 mg, 73%), mp 55.6-56.4 °C. IR (KBr): 3456, 2921, 1512, 1246, 1053, 813, 547 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.46 (d, *J* = 8.9 Hz, 1H),

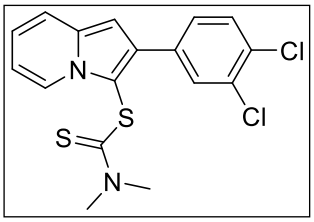
7.35 – 7.27 (m, 2H), 6.94 – 6.89 (m, 1H), 6.74 (s, 1H), 6.67 (t, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 3.53 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 194.98, 137.26, 136.60, 136.56, 134.03, 129.55, 129.22, 127.50, 127.22, 124.29, 120.72, 119.08, 111.60, 105.00, 100.78, 45.94, 42.10. HRMS MALDI (m/z): calcd for $C_{17}H_{15}ClN_2S_2$ $[M + H]^+$: 347.0443, found: 347.0443.

2-(2,4-Dichlorophenyl)indolizin-3-yl dimethylcarbamodithioate (3s)



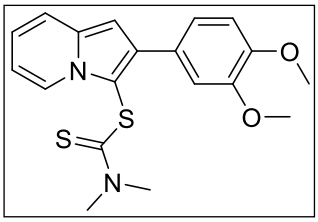
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3s**. Gray green solid (84.7 mg, 74%), mp 244.1-244.9 °C. IR (KBr): 2925, 1501, 1379, 1243, 969, 776, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 1H), 7.51 – 7.46 (m, 3H), 7.27 (d, *J* = 2.2 Hz, 1H), 6.95 – 6.90 (m, 1H), 6.77 (s, 1H), 6.68 (t, *J* = 6.9 Hz, 1H), 3.52 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.90, 136.09, 134.42, 134.29, 133.82, 133.59, 132.94, 129.37, 126.81, 124.32, 120.57, 119.28, 111.59, 106.23, 102.50, 45.88, 42.05. HRMS MALDI (m/z): calcd for $C_{17}H_{14}Cl_2N_2S_2$ $[M + H]^+$: 379.9970, found: 379.9968.

2-(3,4-Dichlorophenyl)indolizin-3-yl dimethylcarbamodithioate (3t)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3t**. Dark green solid (84.7 mg, 74%), mp 107.8-108.2 °C. IR (KBr): 2923, 1495, 1349, 1241, 1026, 769, 729 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.0 Hz, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.50 – 7.43 (m, 3H), 6.96 – 6.90 (m, 1H), 6.72 (s, 1H), 6.71 – 6.65 (m, 1H), 3.56 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.76, 136.61, 135.63, 135.54, 132.21, 131.23, 130.93, 130.26, 128.60, 124.27, 120.89, 119.10, 111.79, 105.07, 100.66, 45.99, 42.12. HRMS MALDI (m/z): calcd for $C_{17}H_{14}C_{l2}N_2S_2$ $[M + H]^+$: 379.9970, found: 379.9971.

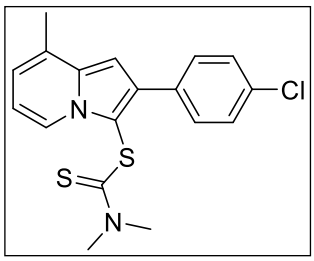
2-(3,4-Dimethoxyphenyl)indolizin-3-yl dimethylcarbamodithioate (3u)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3u**. Dark green solid (83.8 mg, 75%), mp 59.5-60.5 °C. IR (KBr): 2926, 1505, 1376, 1256, 1233, 1139, 1023 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14

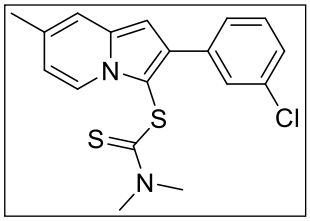
(d, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.25 – 7.16 (m, 2H), 6.95 – 6.87 (m, 2H), 6.73 (s, 1H), 6.65 (t, *J* = 6.8 Hz, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.56 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.91, 148.58, 148.43, 138.18, 136.57, 128.24, 124.20, 121.44, 120.55, 118.86, 112.82, 111.27, 111.14, 104.48, 100.54, 56.00, 55.87, 45.92, 42.03. HRMS MALDI (m/z): calcd for $C_{19}H_{20}N_2O_2S_2$ $[M + H]^+$: 373.1044, found: 373.1039.

2-(4-Chlorophenyl)-8-methylindolizin-3-yl dimethylcarbamodithioate (3v)



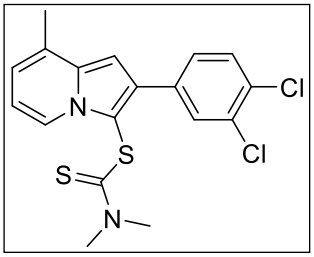
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3v**. Dark green solid (82.3 mg, 76%), mp 194.8-195.2 °C. IR (KBr): 2924, 1497, 1374, 1250, 1087, 769, 757 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.40 – 7.34 (m, 2H), 6.72 (d, *J* = 4.5 Hz, 2H), 6.61 (t, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 3.50 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.21, 137.32, 136.46, 134.00, 133.12, 130.49, 128.45, 128.03, 122.15, 120.02, 111.65, 105.12, 99.19, 45.92, 42.00, 17.98. HRMS MALDI (m/z): calcd for $C_{18}H_{17}ClN_2S_2$ $[M + H]^+$: 360.0516, found: 360.0521.

2-(4-Bromophenyl)-7-chloroindolizin-3-yl dimethylcarbamodithioate (3w)



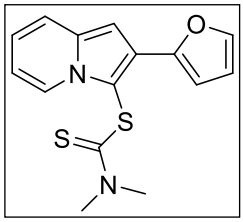
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3w**. Green solid (83.0 mg, 65%), mp 84.5-85.4 °C. IR (KBr):2924, 1496, 1375, 1244, 968, 773, 737 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 1.7 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.34 – 7.27 (m, 2H), 7.22 (s, 1H), 6.61 (s, 1H), 6.54 – 6.49 (m, 1H), 3.57 (s, 3H), 3.55 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.57, 137.43, 136.93, 136.74, 134.01, 131.17, 129.52, 129.18, 127.45, 127.14, 126.31, 123.76, 117.44, 114.35, 103.92, 99.45, 45.99, 42.09, 21.22. HRMS MALDI (m/z): calcd for $C_{18}H_{17}ClN_2S_2$ $[M + H]^+$: 360.0516, found: 360.0526.

2-(3,4-Dichlorophenyl)-8-methylindolizin-3-yl dimethylcarbamodithioate (3x)



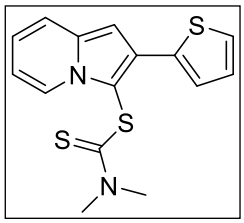
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3x**. Yellowish brown solid (89.0 mg, 75%), mp 202.1-202.6 °C. IR (KBr): 2923, 1491, 1352, 1245, 1131, 779, 753 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 6.76 – 6.68 (m, 2H), 6.62 (t, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 3.52 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.86, 137.32, 135.63, 135.09, 132.12, 131.07, 130.82, 130.20, 128.53, 128.14, 122.13, 120.19, 111.90, 105.38, 99.18, 45.94, 42.06, 17.96. HRMS MALDI (m/z): calcd for $C_{18}H_{16}Cl_2N_2S_2$ $[M + H]^+$: 394.0126, found: 394.0128.

2-(Furan-2-yl)indolizin-3-yl dimethylcarbamodithioate (3y)



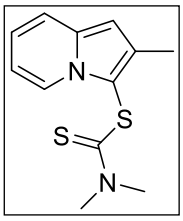
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3y**. Brown solid (70.7 mg, 78%), mp 101.7-102.3 °C. IR (KBr): 1509, 1378, 1360, 1330, 1245, 770, 727 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.1 Hz, 1H), 7.49 – 7.41 (m, 2H), 6.94 – 6.86 (m, 2H), 6.81 (d, *J* = 3.3 Hz, 1H), 6.64 (td, *J* = 6.8, 1.2 Hz, 1H), 6.47 – 6.44 (m, 1H), 3.59 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.41, 149.47, 141.84, 136.66, 128.06, 124.00, 120.61, 119.08, 111.53, 111.50, 107.50, 103.33, 98.50, 45.92, 42.09. HRMS MALDI (m/z): calcd for $C_{15}H_{14}N_2OS_2$ $[M + H]^+$: 303.0626, found: 303.0625.

2-(Thiophen-2-yl)indolizin-3-yl dimethylcarbamodithioate (3z)



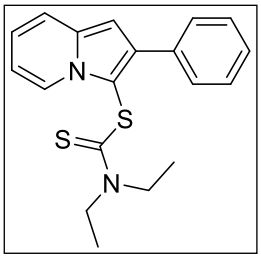
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3z**. Light yellow solid (72.5 mg, 76%), mp 87.4-87.9 °C. IR (KBr): 1504, 1490, 1375, 1343, 1248, 771, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.32 – 7.26 (m, 1H), 7.10 – 7.03 (m, 1H), 6.92 – 6.85 (m, 1H), 6.83 (s, 1H), 6.63 (td, *J* = 6.9, 1.2 Hz, 1H), 3.58 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.77, 136.94, 136.59, 131.29, 127.30, 125.64, 125.49, 124.18, 120.80, 118.82, 111.43, 104.56, 99.90, 45.94, 42.12. HRMS MALDI (m/z): calcd for $C_{15}H_{14}N_2S_3$ $[M + H]^+$: 319.0397, found: 319.0394.

2-Methylindolizin-3-yl dimethylcarbamodithioate (3aa)



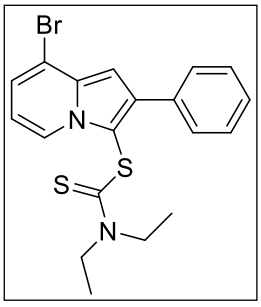
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **3aa**. Grey liquid (66.0 mg, 88%). IR (KBr): 1506, 1388, 1372, 1245, 972, 766, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.0, 1.0 Hz, 1H), 7.33 (dt, *J* = 8.7, 1.2 Hz, 1H), 6.84 – 6.77 (m, 1H), 6.55 (td, *J* = 6.8, 1.2 Hz, 1H), 6.47 (s, 1H), 3.50 (s, 3H), 3.48 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.39, 136.26, 134.58, 123.79, 119.68, 119.63, 118.16, 110.29, 101.12, 45.75, 41.79, 12.54. HRMS MALDI (m/z): calcd for $C_{12}H_{14}N_2S_2$ $[M + H]^+$: 251.0677, found: 251.0675.

2-Phenylindolizin-3-yl diethylcarbamodithioate (5a)



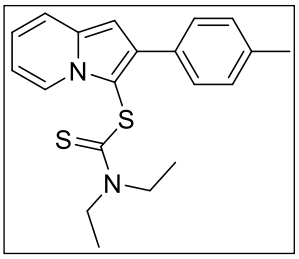
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5a**. Brown solid (81.7 mg, 80%), mp 88.4-89.2 °C. IR (KBr): 2928, 1490, 1418, 1351, 1268, 1202, 763 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.92 – 6.86 (m, 1H), 6.76 (s, 1H), 6.65 (t, *J* = 6.8 Hz, 1H), 4.11 – 3.79 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.87, 137.90, 136.47, 135.43, 129.26, 128.21, 127.14, 124.29, 120.42, 118.89, 111.24, 104.90, 100.63, 50.12, 47.24, 13.27, 11.82. HRMS MALDI (m/z): calcd for $C_{19}H_{20}N_2S_2$ $[M + H]^+$: 340.1062, found: 340.1073.

8-Bromo-2-phenylindolizin-3-yl diethylcarbamodithioate(5b)



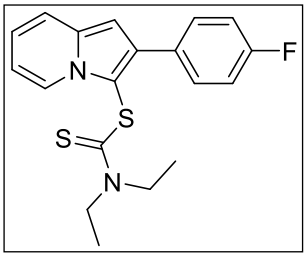
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5b.** Brown liquid (94.4 mg, 75%). IR (KBr): 1490, 1421, 1337, 1269, 1201, 765, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.0 Hz, 1H), 7.68 – 7.63 (m, 2H), 7.40 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.13 (dd, *J* = 7.2, 0.9 Hz, 1H), 6.93 (d, J = 0.9 Hz, 1H), 6.53 (t, J = 7.1 Hz, 1H), 4.13 – 3.76 (m, 4H), 1.39 (t, J = 7.1 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.03, 138.38, 135.33, 134.90, 129.30, 128.31, 127.47, 123.65, 123.03, 112.92, 111.05, 107.34, 102.50, 50.18, 47.40, 13.30, 11.81. HRMS MALDI (m/z): calcd for $C_{19}H_{19}BrN_2S_2$ $[M + H]^+$: 419.0251, found: 419.0248, 421.0227.

2-(P-tolyl)indolizin-3-yl diethylcarbamodithioate (5c)



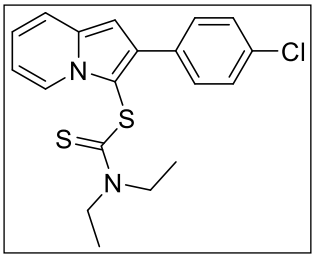
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5c**. Purplish black solid (80.8 mg, 76%), mp 68.9-69.2 °C. IR (KBr): 2974, 1490, 1418, 1350, 1270, 1202, 771 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 6.92 – 6.87 (m, 1H), 6.75 (s, 1H), 6.65 (t, *J* = 6.8 Hz, 1H), 4.06 – 3.85 (m, 4H), 2.38 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.08, 138.01, 136.88, 136.53, 132.56, 129.16, 129.03, 124.33, 120.39, 118.89, 111.17, 104.80, 100.57, 50.15, 47.26, 21.40, 13.37, 11.87. HRMS MALDI (m/z): calcd for $C_{20}H_{22}N_2S_2$ $[M + H]^+$: 354.1219, found: 354.1212.

2-(4-Fluorophenyl)indolizin-3-yl diethylcarbamodithioate (5d)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5d**. Dark green solid (64.5 mg, 60%), mp 110.5-111.4 °C. IR (KBr): 2964, 1486, 1320, 1269, 1101, 1092, 788 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.95 – 6.89 (m, 1H), 6.73 (s, 1H), 6.70 – 6.65 (m, 1H), 4.15 – 3.77 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.82, 162.41 (d, *J* = 245.9 Hz), 137.11, 136.55, 131.55 (d, *J* = 3.0 Hz), 130.84 (d, *J* = 7.9 Hz), 124.32, 120.62, 118.94, 115.28, 115.07, 111.42, 104.92, 100.58, 50.25, 47.30, 13.34, 11.86. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.69. HRMS MALDI (m/z): calcd for $C_{19}H_{19}FN_2S_2$ $[M + H]^+$: 358.0968, found: 358.0962.

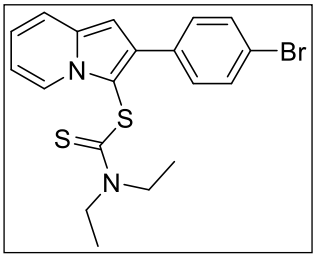
2-(4-Chlorophenyl)indolizin-3-yl diethylcarbamodithioate (5e)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5e**. Yellowish brown solid (76.5 mg, 68%), mp 149.8-150.7 °C. IR (KBr): 2974, 1490, 1420, 1269, 1201, 1092, 778 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 6.0 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.49 – 7.39 (m, 1H), 7.40 – 7.32 (m, 2H), 6.94 – 6.88 (m, 1H), 6.73 (s, 1H), 6.67 (t, *J* = 6.2 Hz, 1H), 4.17 –

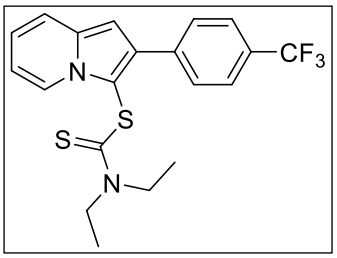
3.79 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.61, 136.80, 136.57, 133.99, 133.18, 130.53, 128.44, 124.30, 120.66, 118.98, 111.51, 105.01, 100.55, 50.24, 47.32, 13.36, 11.84. HRMS MALDI (m/z): calcd for $C_{19}H_{19}ClN_2S_2$ $[M + H]^+$: 374.0673, found: 374.0673.

2-(4-Bromophenyl)indolizin-3-yl diethylcarbamodithioate (5f)



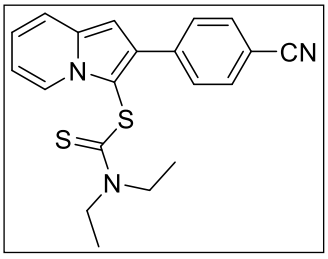
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5f**. Brown solid (95.6 mg, 76%), mp 154.8-155.1 °C. IR (KBr): 3012, 1509, 1460, 1369, 1301, 1192, 878 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 6.8 Hz, 1H), 7.51 (d, *J* = 1.9 Hz, 4H), 7.43 (d, *J* = 8.9 Hz, 1H), 6.90 (t, *J* = 7.8 Hz, 1H), 6.72 (s, 1H), 6.66 (t, *J* = 6.8 Hz, 1H), 4.12 – 3.75 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.29, 136.52, 136.35, 134.24, 131.16, 130.65, 124.09, 121.22, 120.47, 118.78, 111.33, 104.77, 100.31, 50.02, 47.12, 13.21, 11.68. HRMS MALDI (m/z): calcd for $C_{19}H_{19}BrN_2S_2$ $[M + H]^+$: 418.0168, found: 418.0172, 420.0144.

2-(4-(Trifluoromethyl)phenyl)indolizin-3-yl diethylcarbamodithioate (5g)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5g**. Yellowish brown solid (98.0 mg, 80%), mp 159.9-160.6 °C. IR (KBr): 2253, 1706, 1501, 1423, 1331, 1302, 794 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.9 Hz, 1H), 6.94 – 6.88 (m, 1H), 6.77 (s, 1H), 6.68 (t, *J* = 6.9, 1.2 Hz, 1H), 4.11 – 3.79 (m, 4H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.26, 139.16, 136.59, 136.38, 129.42, 128.97 (q, *J* = 32 Hz), 125.11 (q, *J* = 3.8 Hz), 124.55 (q, *J* = 271 Hz)124.26, 120.76, 119.07, 111.72, 105.32, 100.77, 50.25, 47.34, 13.30, 11.78. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.22. HRMS MALDI (m/z): calcd for $C_{20}H_{19}F_3N_2S_2$ $[M + H]^+$: 408.0936, found: 408.0932.

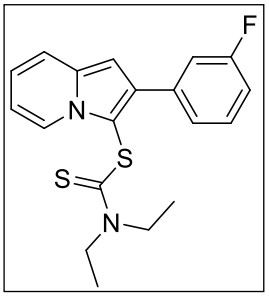
2-(4-Cyanophenyl)indolizin-3-yl diethylcarbamodithioate (5h)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5h**. Gray green solid (79.0 mg, 72%), mp 85.4-86.3 °C. IR (KBr): 2223,

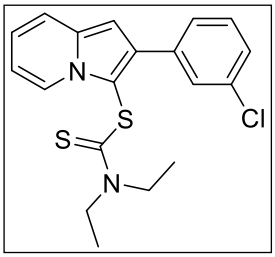
1606, 1491, 1419, 1351, 1202, 774 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.9 Hz, 1H), 6.97 – 6.91 (m, 1H), 6.77 (s, 1H), 6.71 (t, *J* = 6.8 Hz, 1H), 4.15 – 3.77 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.92, 140.29, 136.64, 135.85, 132.01, 129.73, 124.24, 120.96, 119.36, 119.16, 111.99, 110.45, 105.40, 100.74, 50.30, 47.37, 13.34, 11.80. HRMS MALDI (m/z): calcd for $C_{20}H_{19}N_3S_2$ $[M + H]^+$: 365.1015, found: 365.1024.

2-(3-Fluorophenyl)indolizin-3-yl diethylcarbamodithioate (5i)



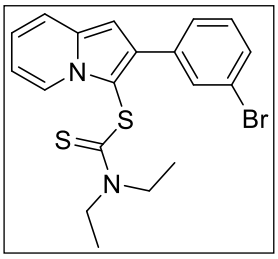
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5i**. Green solid (75.3 mg, 70%), mp 78.2-78.9 °C. IR (KBr): 2919, 1516, 1378, 1156, 809, 798, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.1 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.30 (m, 2H), 7.04 – 6.96 (m, 1H), 6.94 – 6.88 (m, 1H), 6.76 (s, 1H), 6.68 (t, *J* = 6.8 Hz, 1H), 4.14 – 3.77 (m, 4H), 1.42 (t, *J* = 8.4, 5.7 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.52, 163.98, 161.55, 137.66 (d, *J* = 8.5 Hz), 136.51 (d, *J* = 2.7 Hz), 129.64 (d, *J* = 8.4 Hz), 124.92 (d, *J* = 2.8 Hz), 124.30, 120.66, 119.03, 116.02 (d, *J* = 22.3 Hz), 113.92 (d, *J* = 21.1 Hz), 111.57, 105.16, 100.66, 50.24, 47.36, 13.30, 11.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.90. HRMS MALDI (m/z): calcd for $C_{19}H_{19}FN_2S_2$ $[M + H]^+$: 358.0968, found: 358.0970.

2-(3-Chlorophenyl)indolizin-3-yl diethylcarbamodithioate (5j)



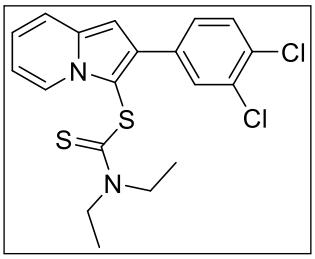
Flash column chromatography on silica gel (eluent: PE/EtOAc = 6/1, v/v) to afford **5j**. Yellowish brown solid (76.5 mg, 68%), mp 82.8-83.4 °C. IR (KBr): 2975, 1490, 1419, 1270, 1202, 772, 735 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.0 Hz, 1H), 7.64 (t, *J* = 1.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.34 – 7.26 (m, 2H), 6.94 – 6.88 (m, 1H), 6.75 (s, 1H), 6.68 (t, *J* = 6.8 Hz, 1H), 4.07 – 3.85 (m, 4H), 1.42 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.61, 137.28, 136.51, 136.28, 133.99, 129.49, 129.24, 127.38, 127.12, 124.32, 120.68, 119.03, 111.58, 105.26, 100.59, 50.27, 47.42, 13.33, 11.82. HRMS MALDI (m/z): calcd for $C_{19}H_{19}ClN_2S_2$ $[M + H]^+$: 374.0673, found: 374.0673.

2-(3-Bromophenyl)indolizin-3-yl diethylcarbamodithioate (5k)



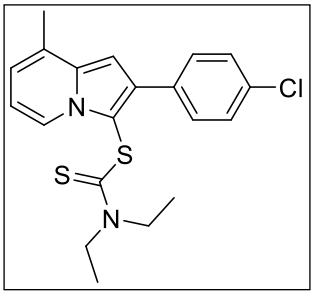
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5k**. Yellowish brown solid (93.1 mg, 74%), mp 69.2-70.1 °C. IR (KBr): 2929, 1490, 1420, 1270, 1202, 771, 731 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.1 Hz, 1H), 7.79 (t, *J* = 1.8 Hz, 1H), 7.59 – 7.54 (m, 1H), 7.49 – 7.41 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 1H), 6.92 (dd, *J* = 8.8, 6.6 Hz, 1H), 6.75 (s, 1H), 6.68 (t, *J* = 6.9 Hz, 1H), 4.11 – 3.80 (m, 4H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.64, 137.59, 136.53, 136.19, 132.18, 130.04, 129.79, 127.85, 124.35, 122.29, 120.71, 119.06, 111.61, 105.29, 100.60, 50.30, 47.46, 13.39, 11.87. HRMS MALDI (m/z): calcd for $C_{19}H_{19}BrN_2S_2$ $[M + H]^+$: 418.0168, found: 418.0172, 420.0145.

2-(3,4-Dichlorophenyl)indolizin-3-yl diethylcarbamodithioate (5l)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5l**. Brown solid (76.1 mg, 62%), mp 60.9-61.6 °C. IR (KBr): 2975, 1490, 1453,1351, 1270, 1202, 773 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.1 Hz, 1H), 7.73 (d, *J* = 1.8 Hz, 1H), 7.51 – 7.40 (m, 3H), 6.91 (dd, *J* = 9.0, 6.5 Hz, 1H), 6.72 (s, 1H), 6.68 (td, *J* = 6.8, 1.2 Hz, 1H), 4.03 (q, *J* = 8.3, 4.1 Hz, 2H), 3.95 – 3.77 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.27, 136.53, 135.55, 135.26, 132.12, 131.08, 130.89, 130.16, 128.46, 124.26, 120.82, 119.03, 111.74, 105.27, 100.45, 50.31, 47.43, 13.34, 11.80. HRMS MALDI (m/z): calcd for $C_{19}H_{18}Cl_2N_2S_2$ $[M + H]^+$: 408.0283, found: 408.0289.

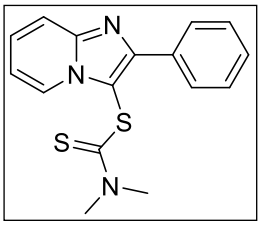
2-(4-Chlorophenyl)-8-methylindolizin-3-yl diethylcarbamodithioate (5m)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 6/1, v/v) to afford **5m**. Blue solid (71.2 mg, 61%), mp 124.1-124.8 °C. IR (KBr): 2931, 1492, 1421, 1270, 1201, 1090, 776 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.0 Hz, 1H), 7.61 – 7.57 (m, 2H), 7.39 – 7.34 (m, 2H), 6.74 – 6.70 (m, 2H), 6.62 (t, *J* = 6.9 Hz, 1H), 4.09 – 3.82 (m, 4H), 2.47 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.84,

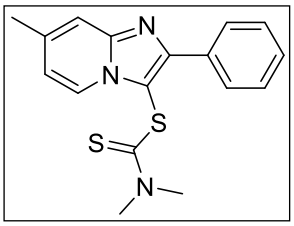
137.36, 136.39, 134.14, 133.12, 130.52, 128.43, 128.06, 122.25, 120.02, 111.67, 105.40, 99.15, 50.24, 47.30, 18.02, 13.36, 11.85. HRMS MALDI (m/z): calcd for $C_{20}H_{21}ClN_2S_2$ $[M + H]^+$: 388.0829, found: 388.0837.

2-Phenylimidazo[1,2-a]pyridin-3-yl dimethylcarbamodithioate (7a)



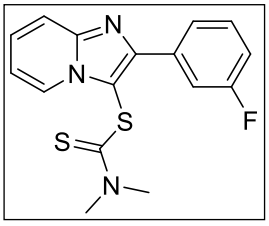
Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **7a**. Pale yellow solid (73.3 mg, 78%), mp 136.7-137.4 ºC. IR (KBr): 3374, 1499, 1489, 1341, 973, 783, 757 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.15 (m, 1H), 8.03 – 7.98 (m, 2H), 7.75 – 7.71 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.32 (m, 2H), 6.91 (t, *J* = 6.8 Hz, 1H), 3.59 (s, 3H) 3.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.81, 152.97, 147.45, 133.43, 128.85, 128.65, 128.36, 127.07, 124.91, 117.67, 112.98, 106.54, 45.93, 42.13. HRMS MALDI (m/z): calcd for $C_{16}H_{15}N_3S_2$ $[M + H]^+$: 313.0702, found: 313.0706.

7-Methyl-2-phenylimidazo[1,2-a]pyridin-3-yl dimethylcarbamodithioate (7b)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **7b**. Yellowish brown solid (74.7 mg, 76%), mp 162.7-163.5 ºC. IR (KBr): 2912, 1496, 1378, 1356, 1248, 1239, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 6.9 Hz, 1H), 7.98 (dt, *J* = 8.2, 1.2 Hz, 2H), 7.50 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.35 (m, 1H), 6.75 (dd, *J* = 6.9, 1.5 Hz, 1H), 3.61 (s, 3H), 3.51 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.32, 152.88, 147.83, 138.41, 133.53, 128.86, 128.61, 128.37, 124.12, 116.32, 115.65, 105.79, 45.99, 42.14, 21.57. HRMS MALDI (m/z): calcd for $C_{17}H_{17}N_3S_2$ $[M + H]^+$: 327.0858, found: 327.0863.

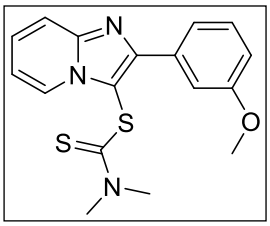
2-(3-Chlorophenyl)imidazo[1,2-a]pyridin-3-yl dimethylcarbamodithioate (7c)



Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **7c**. Brown solid (75.1 mg, 72%), mp 180.2-180.8 ºC. IR (KBr): 2919, 1416, 1378, 1256, 889, 808, 706 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (dt, *J* = 6.9, 1.2 Hz, 1H), 7.79 – 7.68 (m, 2H), 7.43 – 7.35 (m, 2H), 7.25 – 7.15 (m, 2H), 6.95 (td, *J* = 6.8, 1.2 Hz, 1H), 3.61 (s, 3H), 3.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.90, 160.32 (d, *J* = 250.5 Hz), 149.10, 147.62, 132.35 (d, *J* = 2.9 Hz), 130.52 (d, *J* = 8.2 Hz), 127.08, 125.11,

124.08 (d, J = 3.6 Hz), 121.60 (d, J = 13.6 Hz), 117.98, 115.98 (d, J = 22.0 Hz), 113.13, 108.86, 45.85, 42.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.95. HRMS MALDI (m/z): calcd for $C_{16}H_{14}FN_3S_2$ $[M + H]^+$: 331.0613, found: 331.0620.

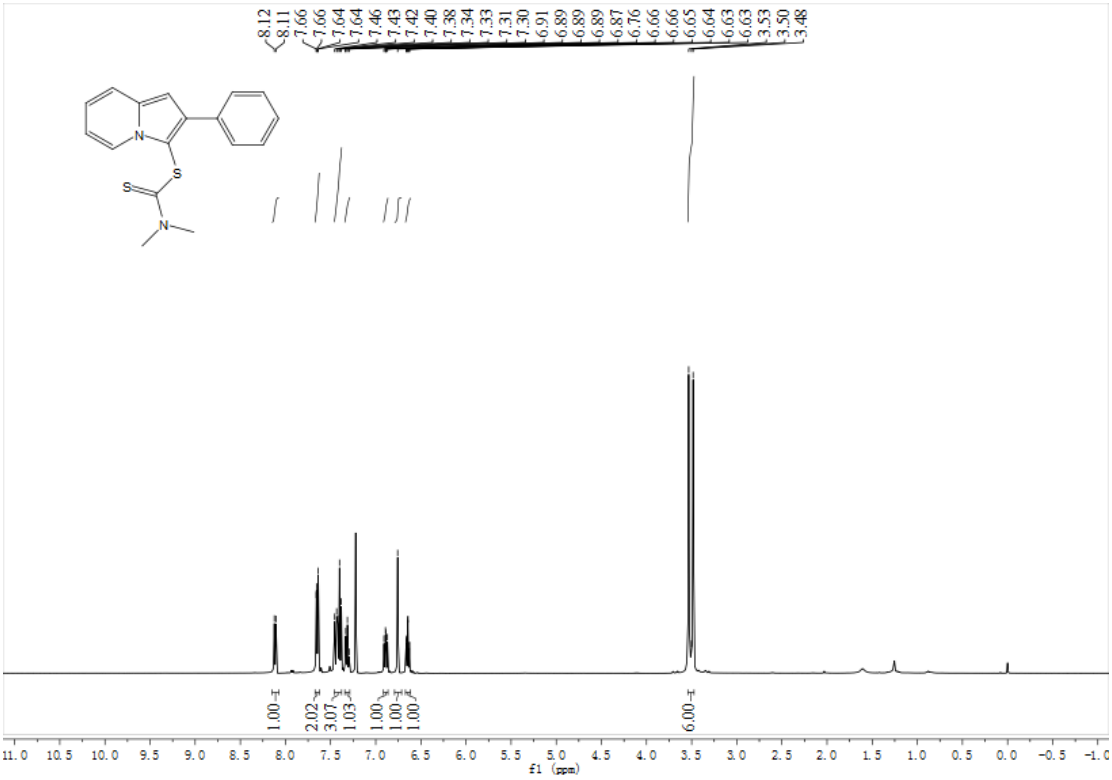
2-(3-Methoxyphenyl)imidazo[1,2-a]pyridin-3-yl dimethylcarbamodithioate (7d)

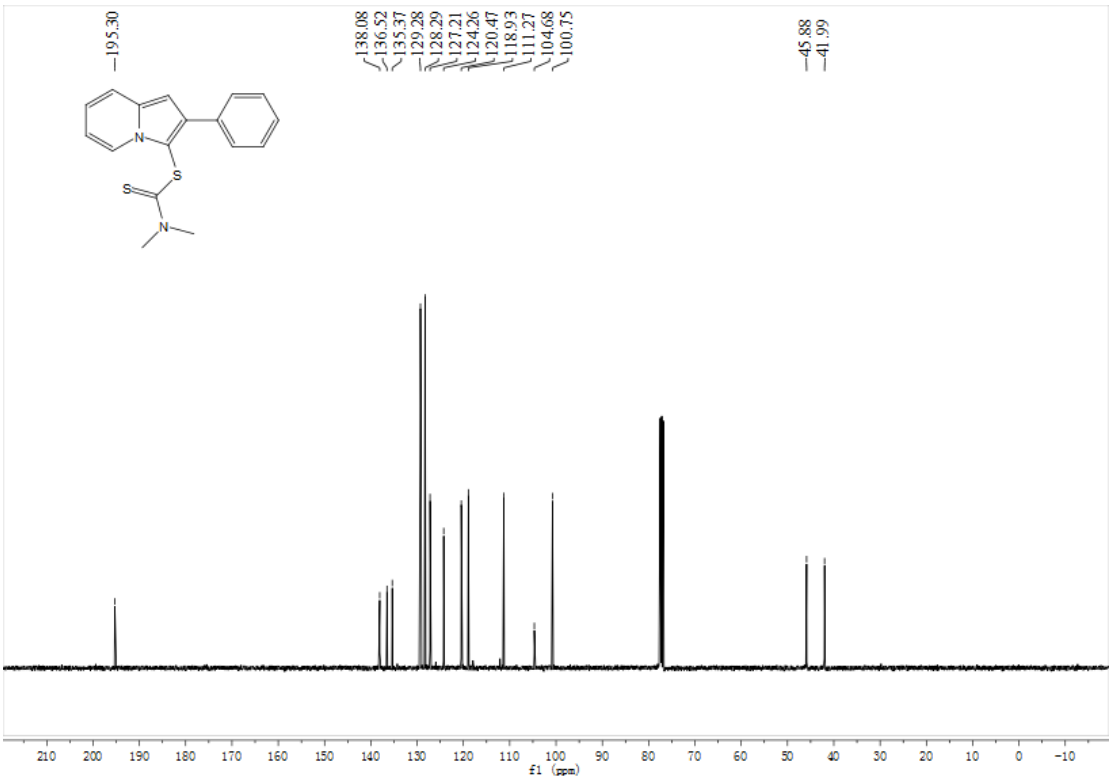


Flash column chromatography on silica gel (eluent: PE/ EtOAc = 2/1, v/v) to afford **7d**. Yellow and white solid (76.2 mg, 74%), mp 114.5-115.2 ºC. IR (KBr): 22923, 1495, 1341, 1247, 1232, 969,756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.18 (m, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.59 (dt, J = 4.0, 1.6 Hz, 2H), 7.37 (dt, J = 10.5, 7.5 Hz, 2H), 6.98 – 6.91 (m, 2H), 3.87 (s, 3H), 3.57 (d, J = 7.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.88, 159.63, 152.82, 147.36, 134.63, 129.43, 127.27, 124.98, 121.45, 117.75, 115.25, 113.76, 113.18, 106.82, 55.47, 45.99, 42.22. HRMS MALDI (m/z): calcd for $C_{17}H_{17}N_3OS_2$ $[M + H]^+$: 343.0808, found: 343.0816.

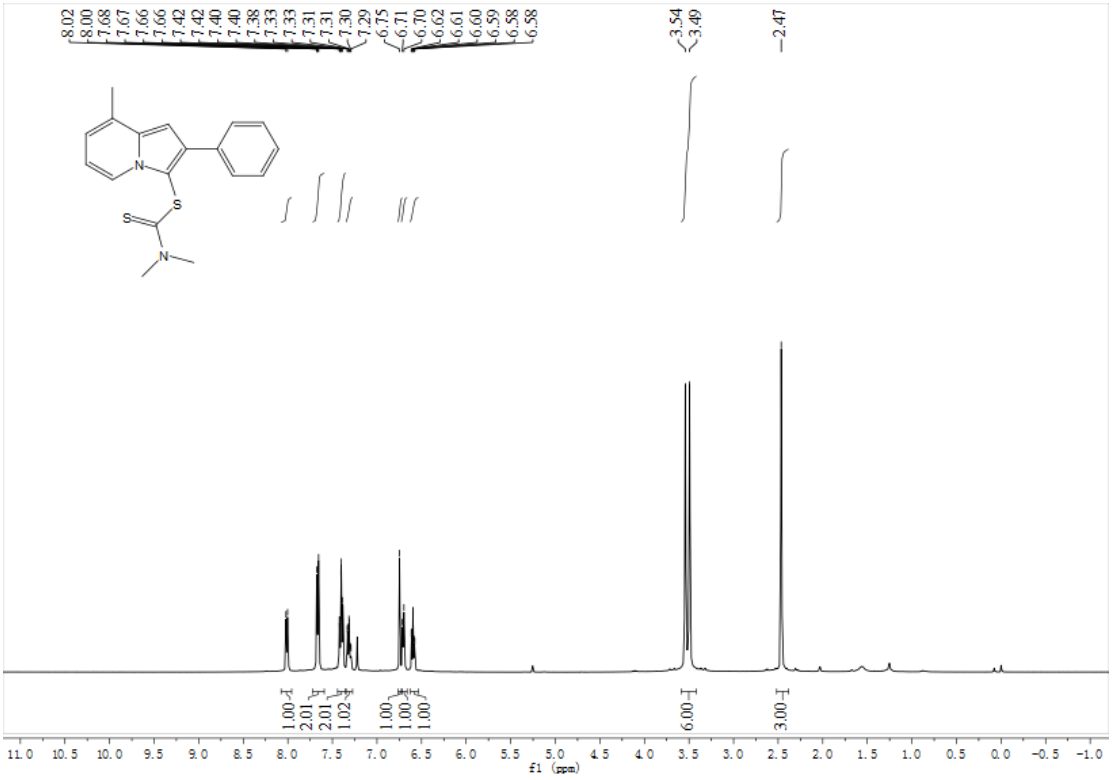
3. NMR spectra for new compounds

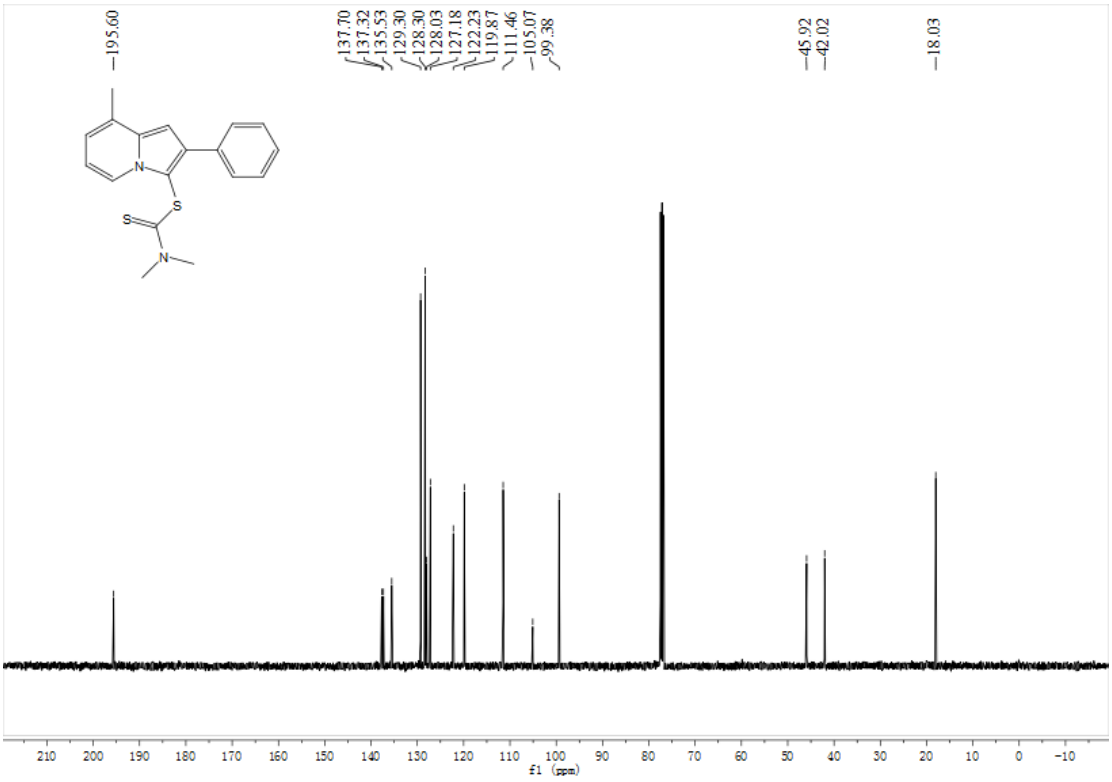
^{1}H NMR and ^{13}C NMR spectrum of compound **3a**



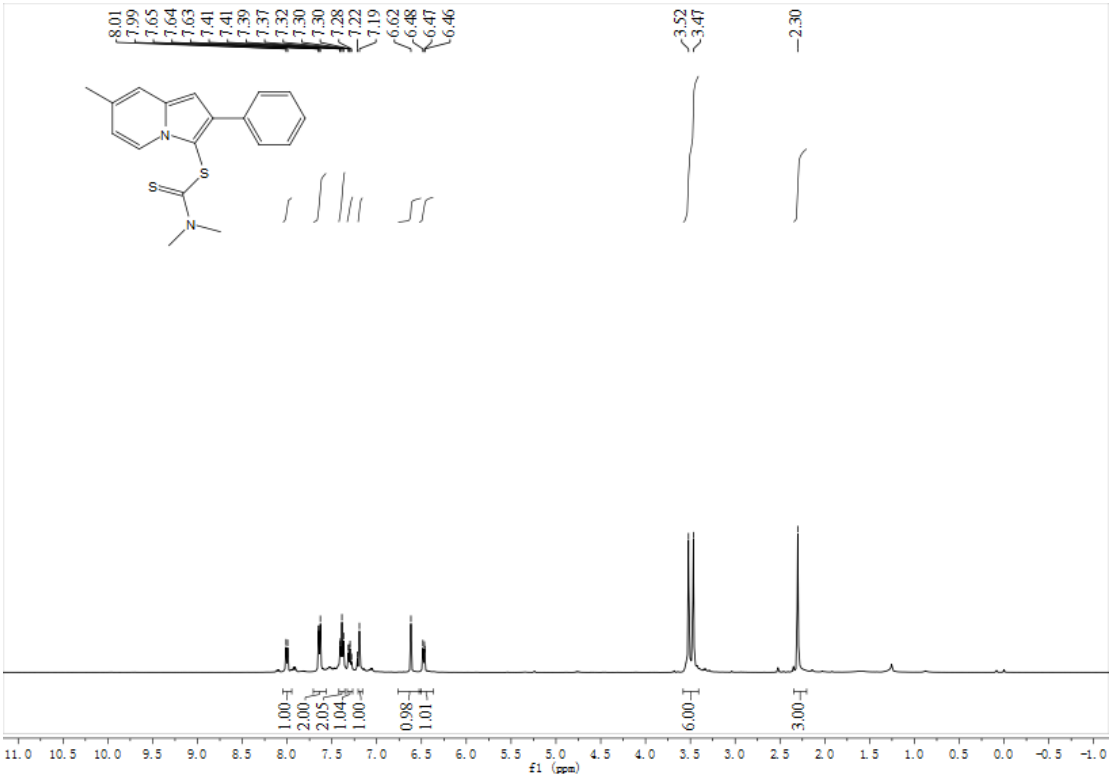


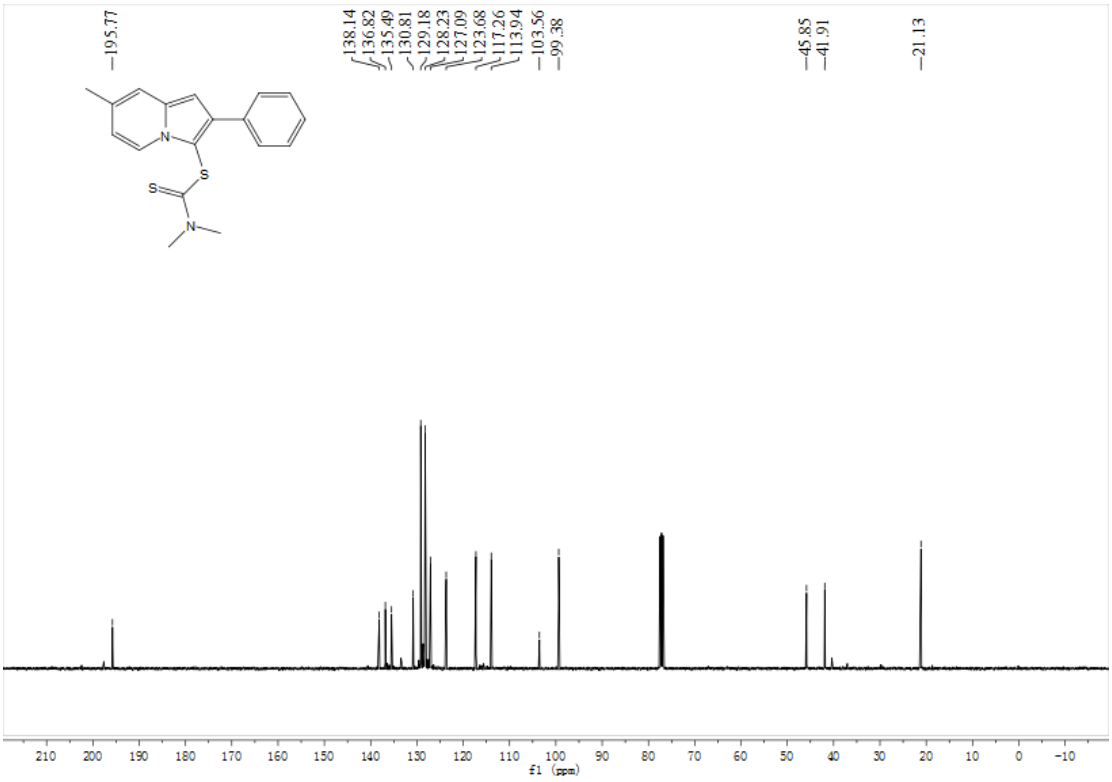
^{1}H NMR and ^{13}C NMR spectrum of compound **3b**



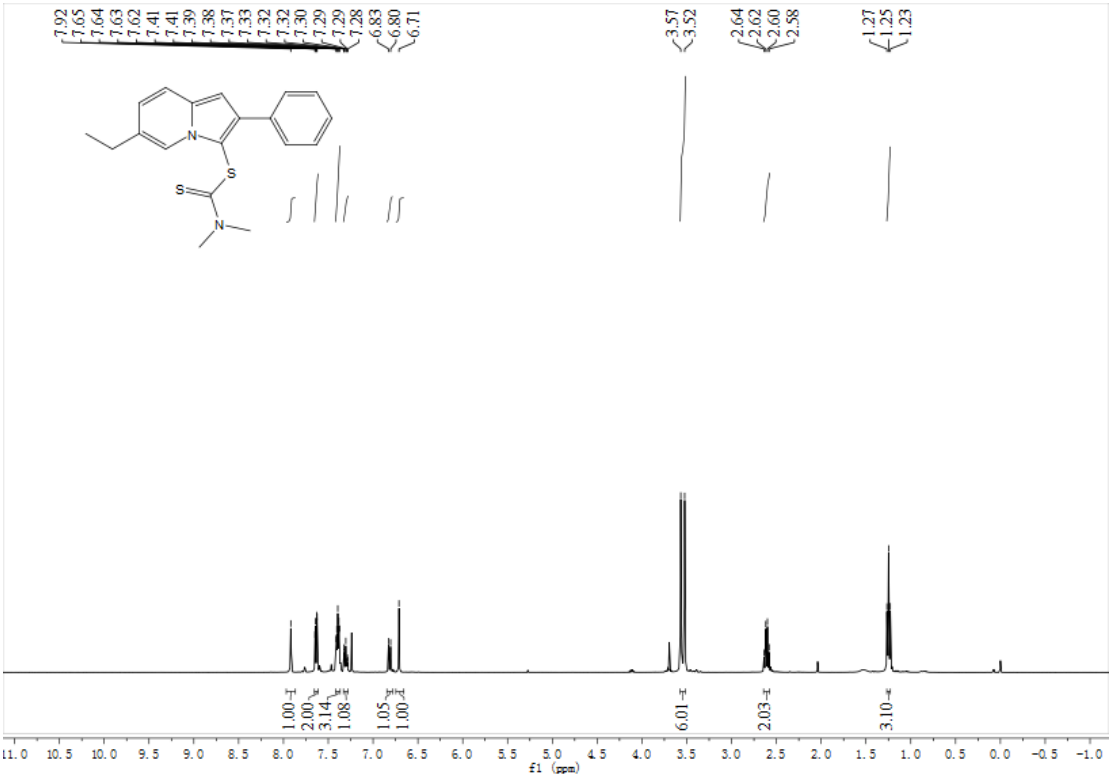


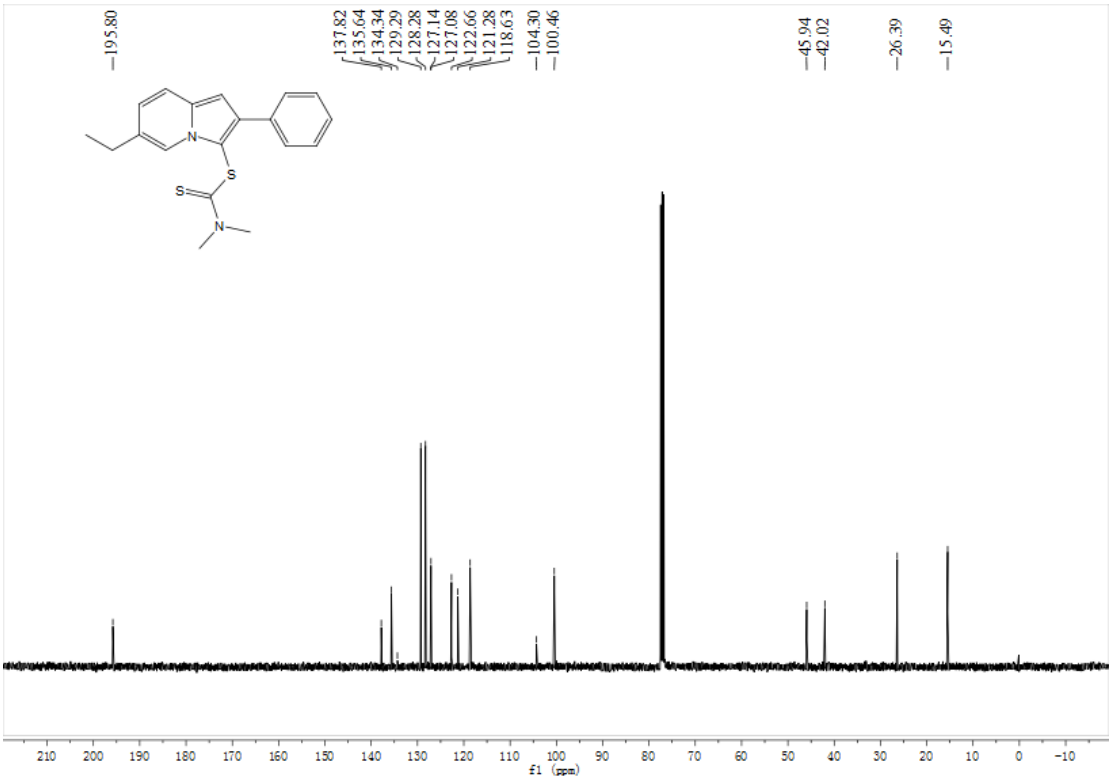
^{1}H NMR and ^{13}C NMR spectrum of compound **3c**



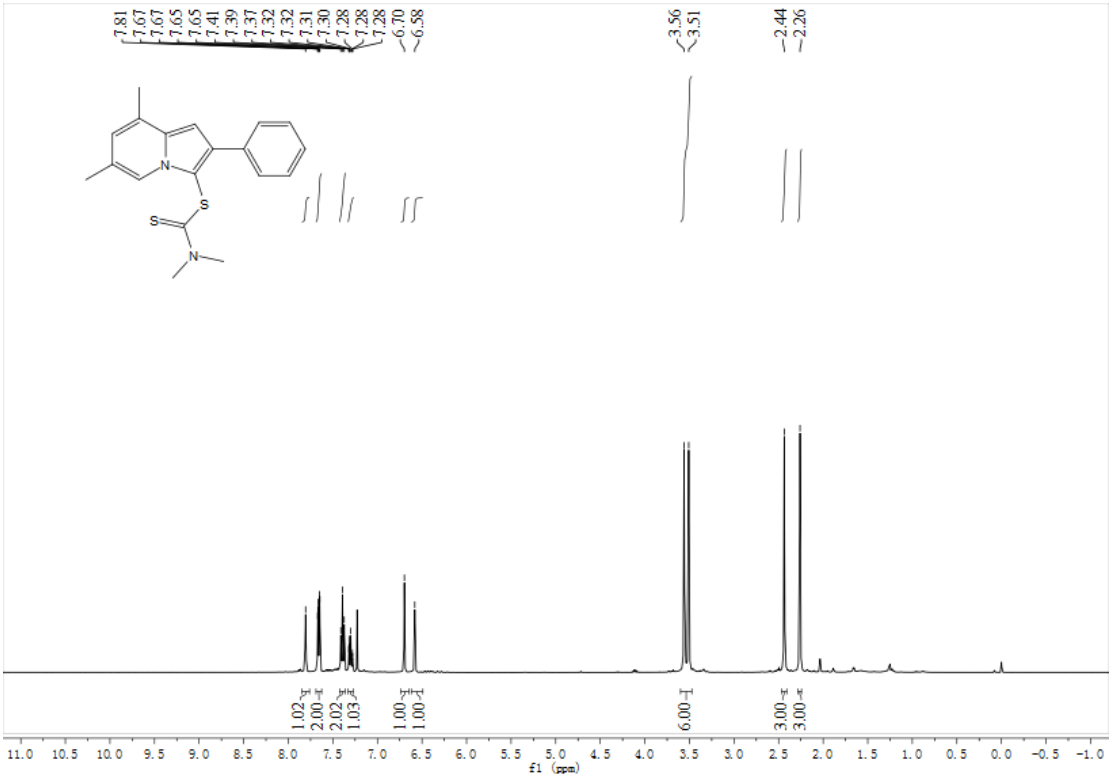


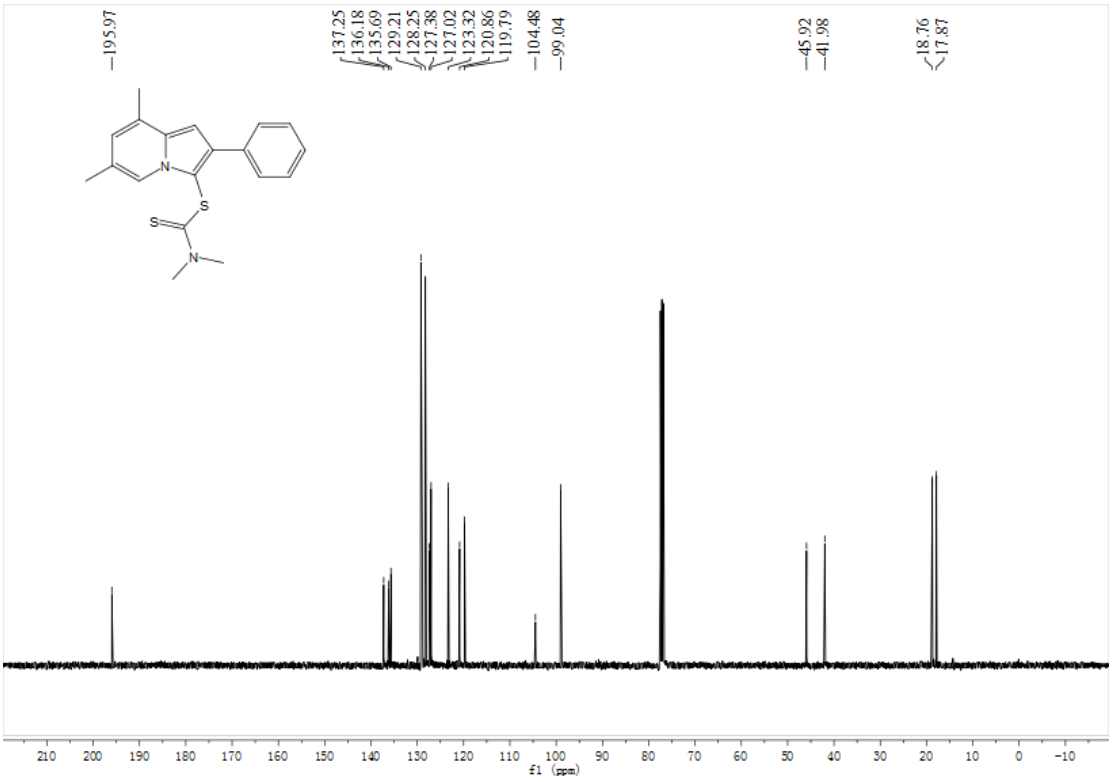
^{1}H NMR and ^{13}C NMR spectrum of compound **3d**



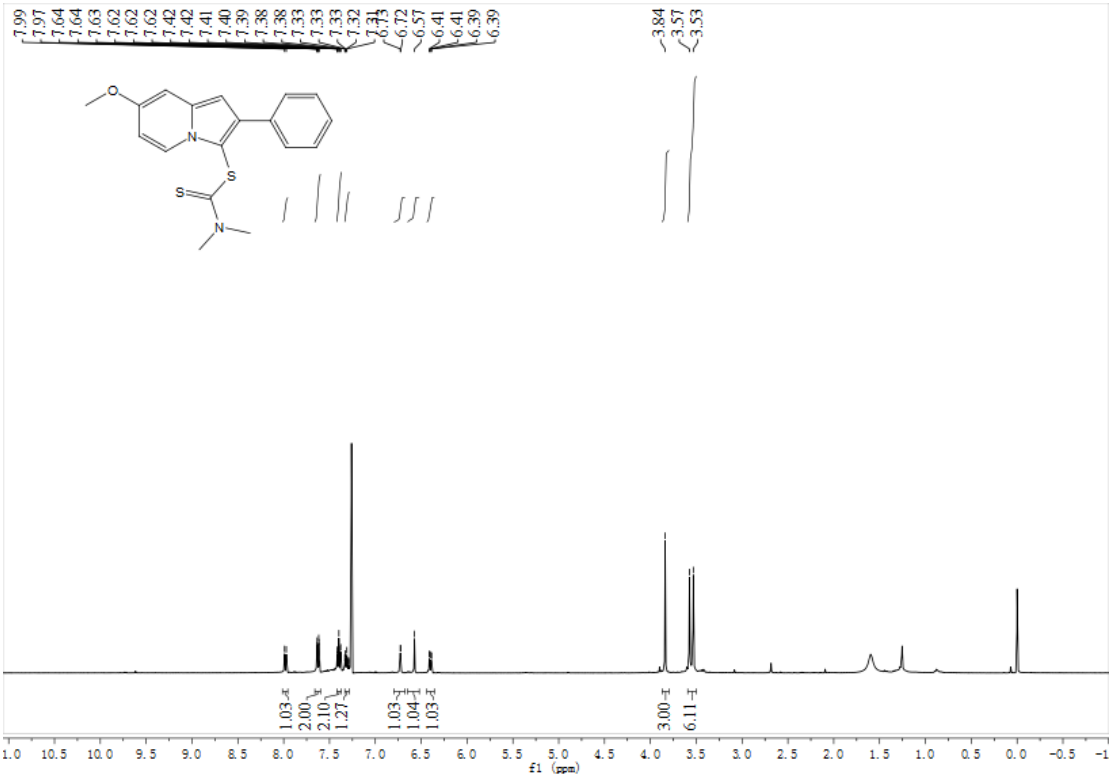


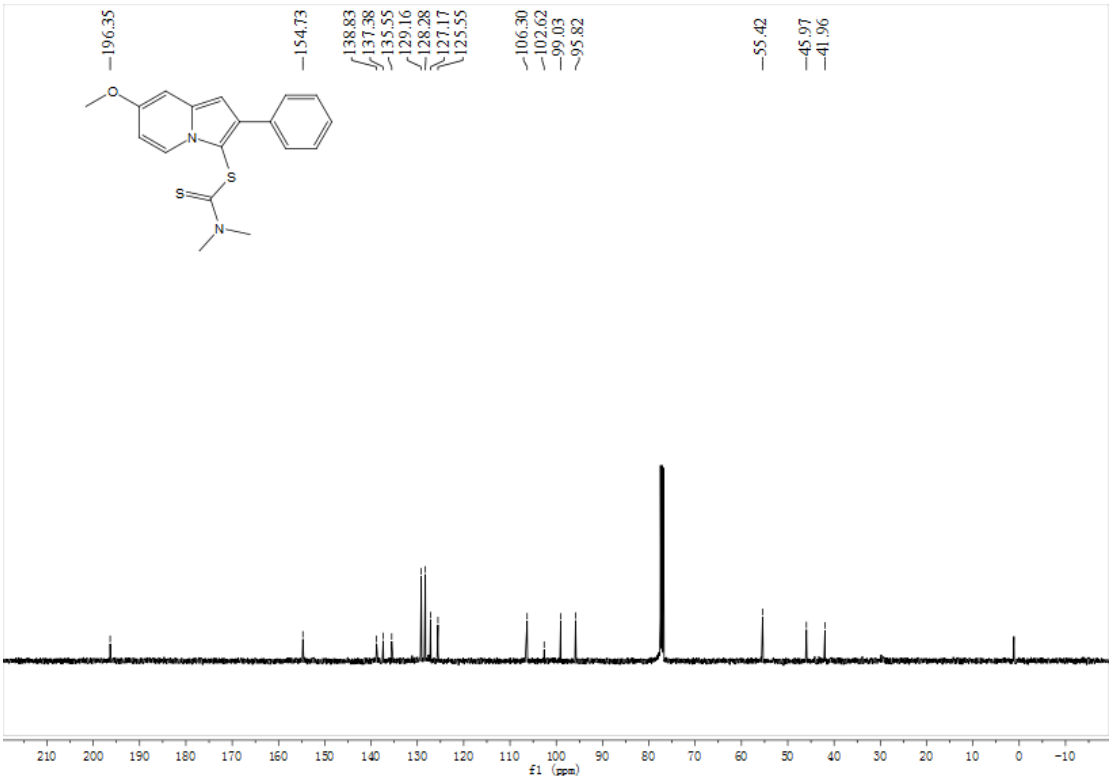
^{1}H NMR and ^{13}C NMR spectrum of compound **3e**



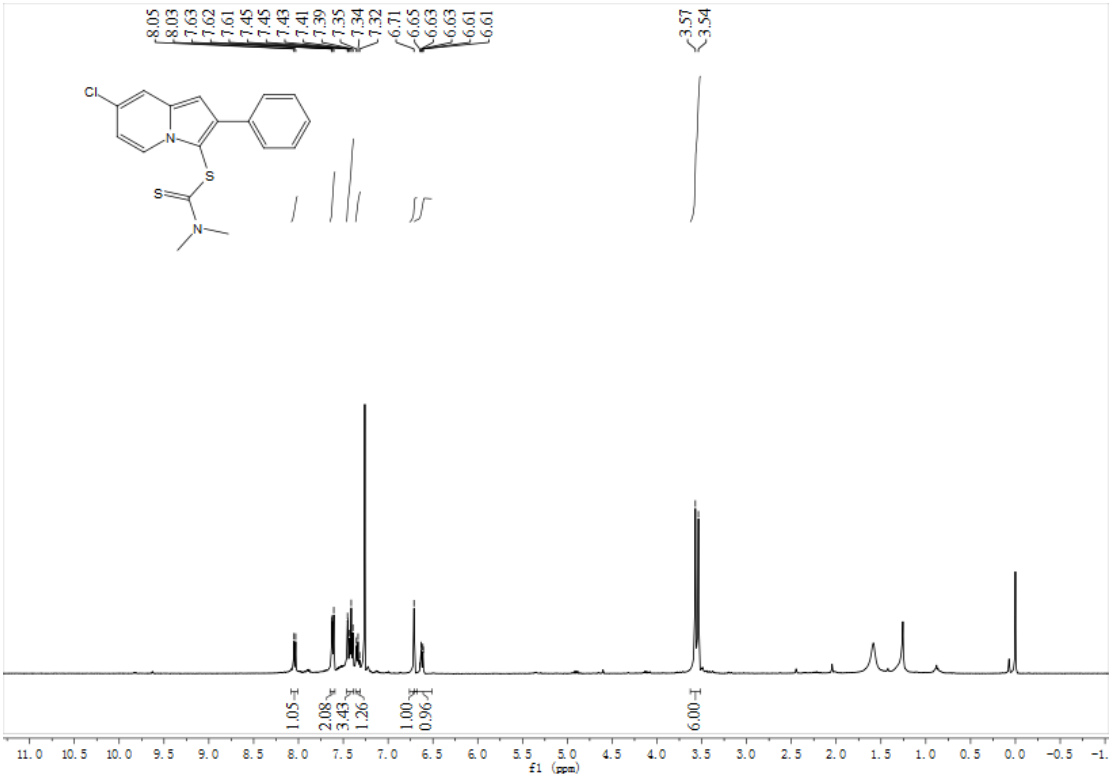


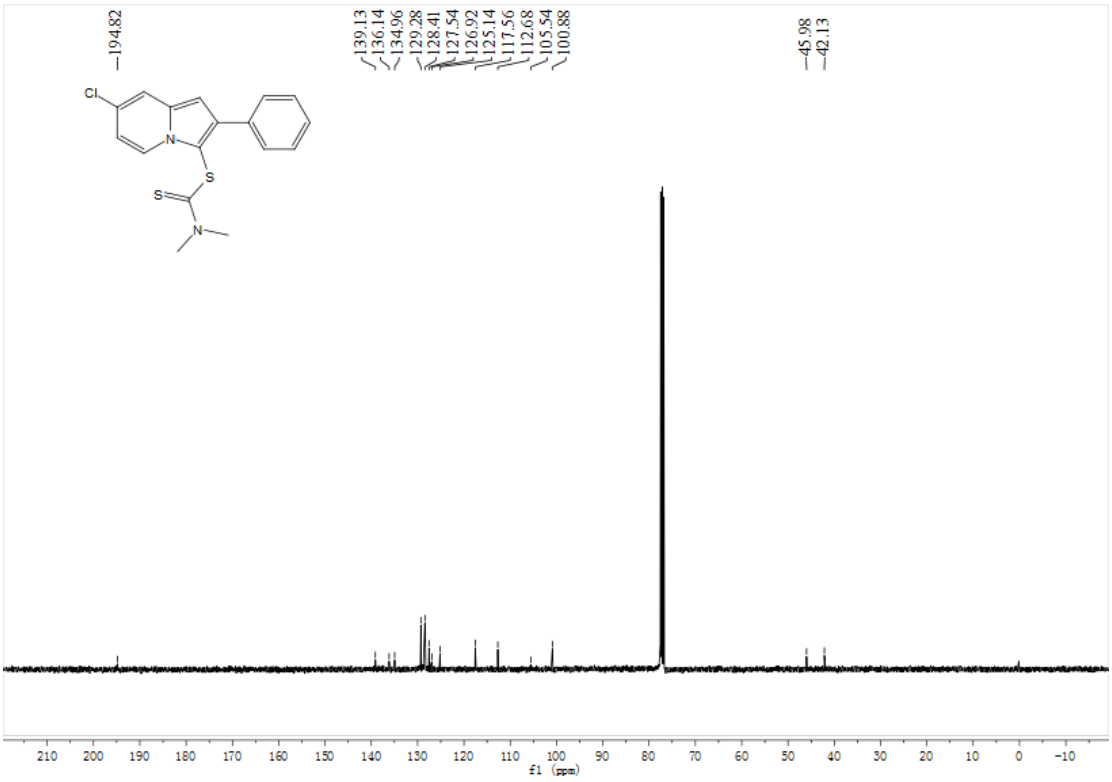
^{1}H NMR and ^{13}C NMR spectrum of compound **3f**



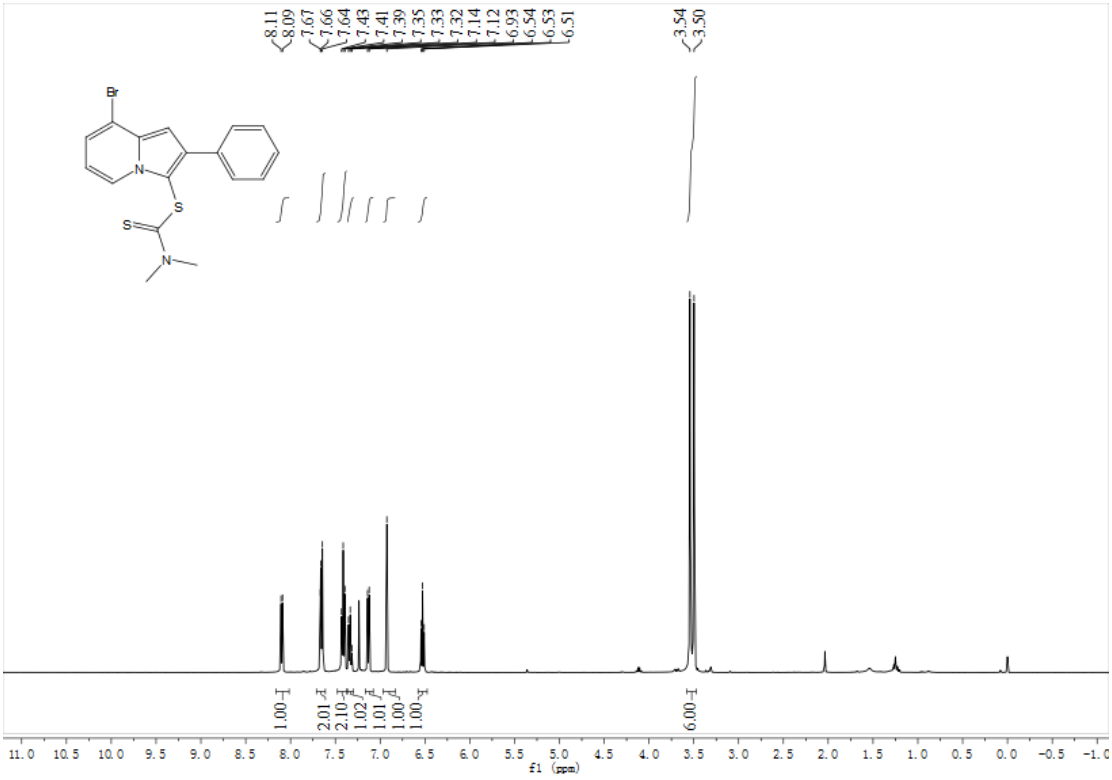


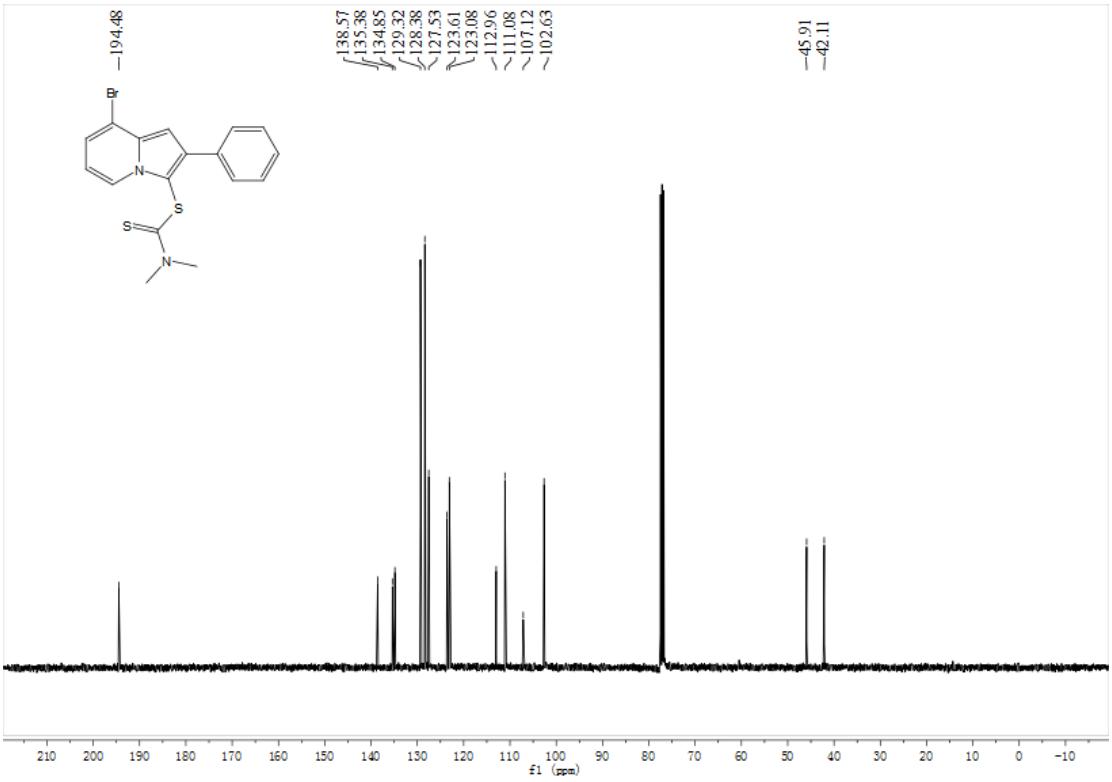
^{1}H NMR and ^{13}C NMR spectrum of compound **3g**



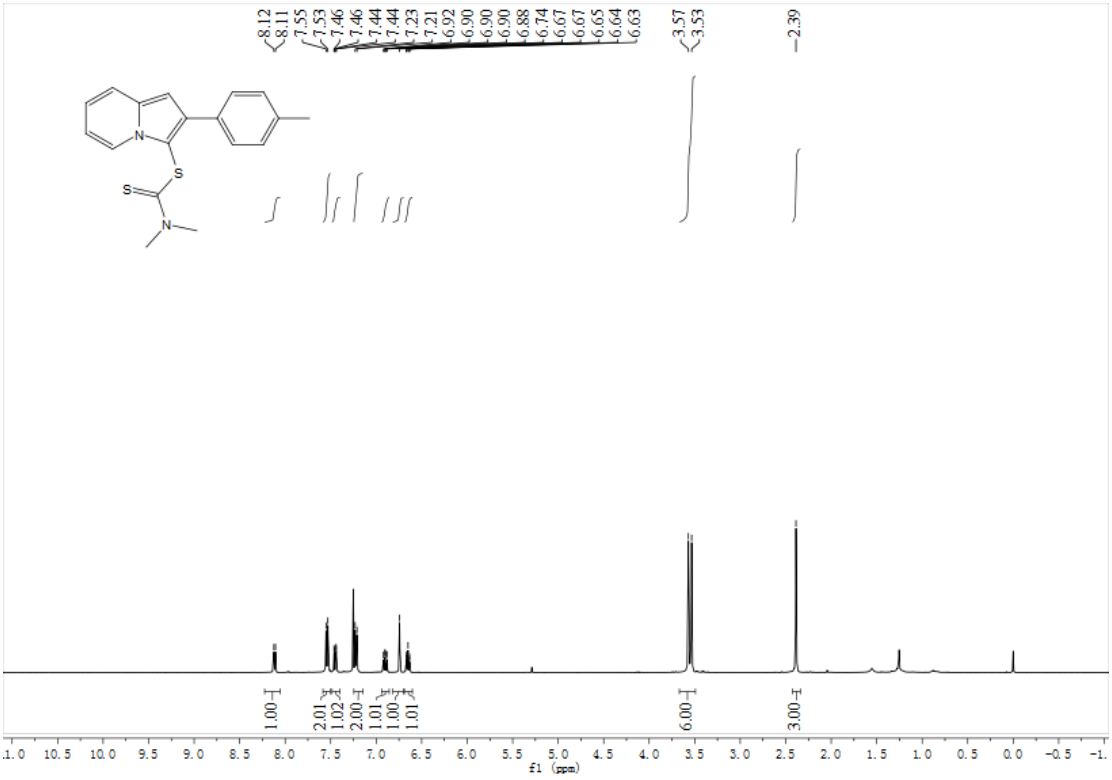


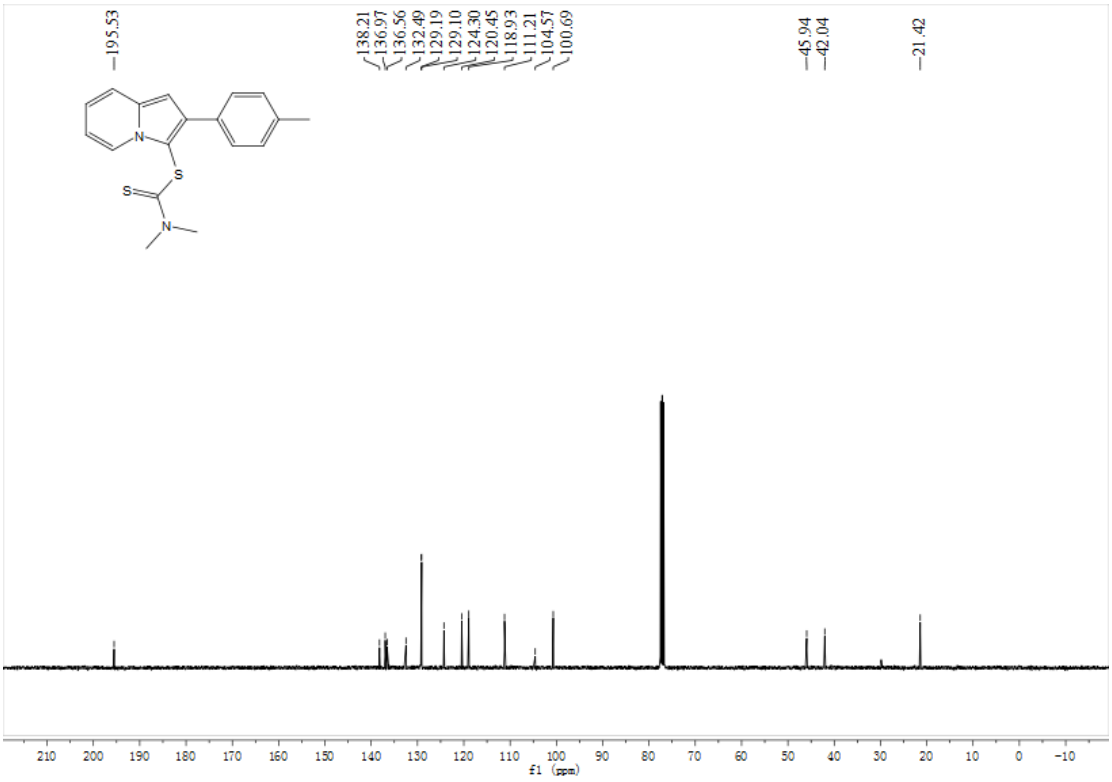
^{1}H NMR and ^{13}C NMR spectrum of compound **3h**



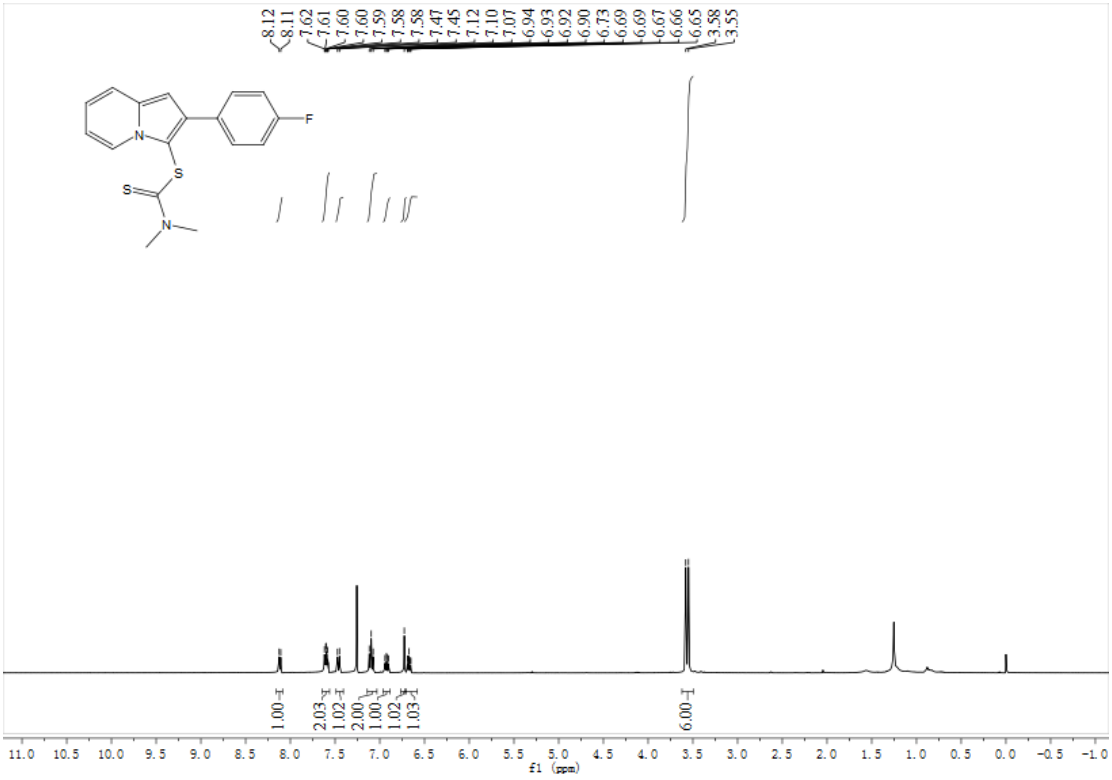


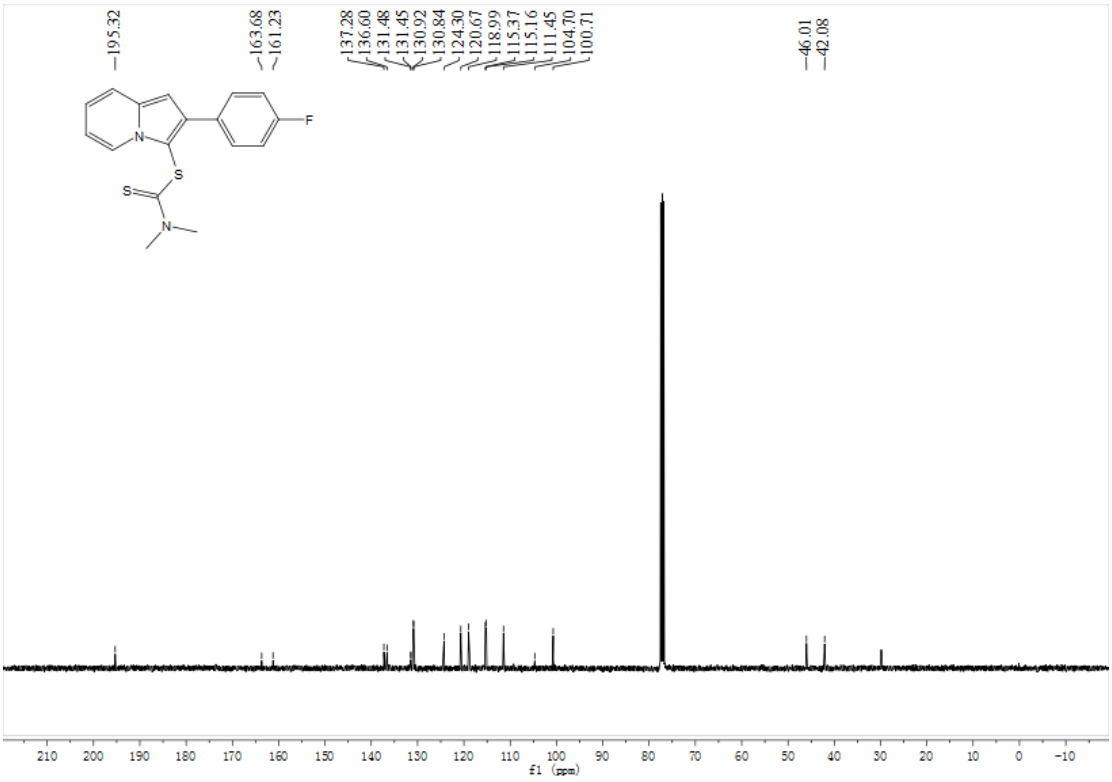
^{1}H NMR and ^{13}C NMR spectrum of compound **3i**



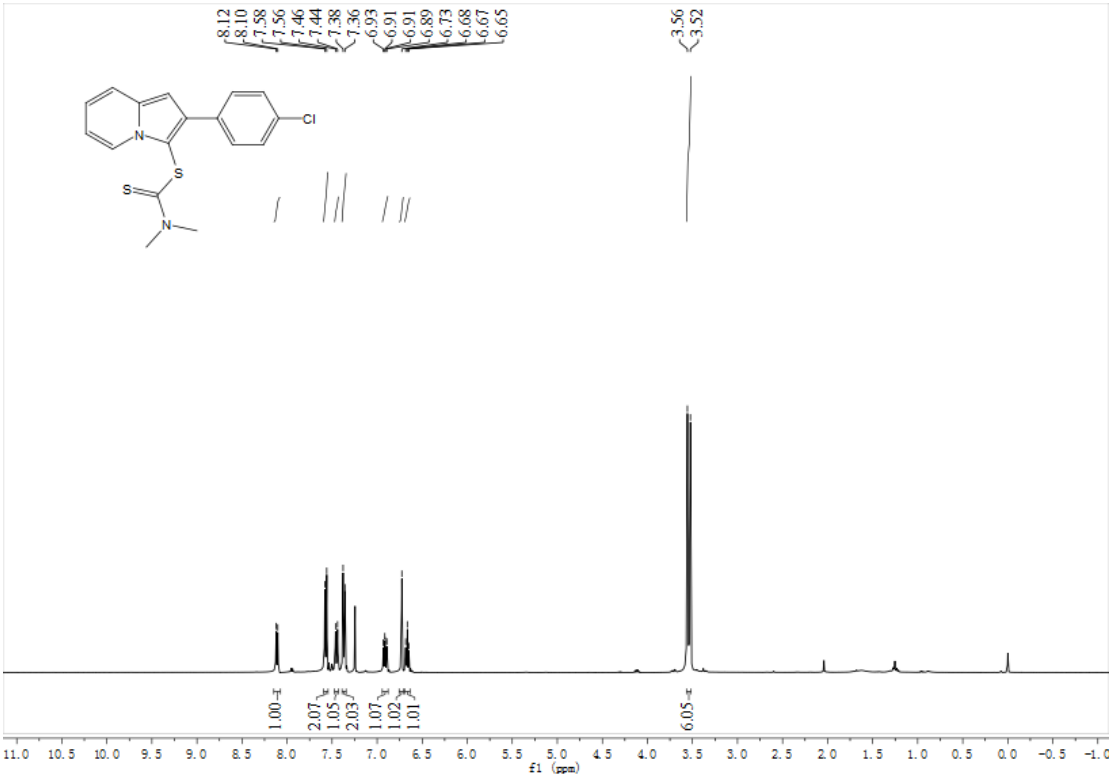


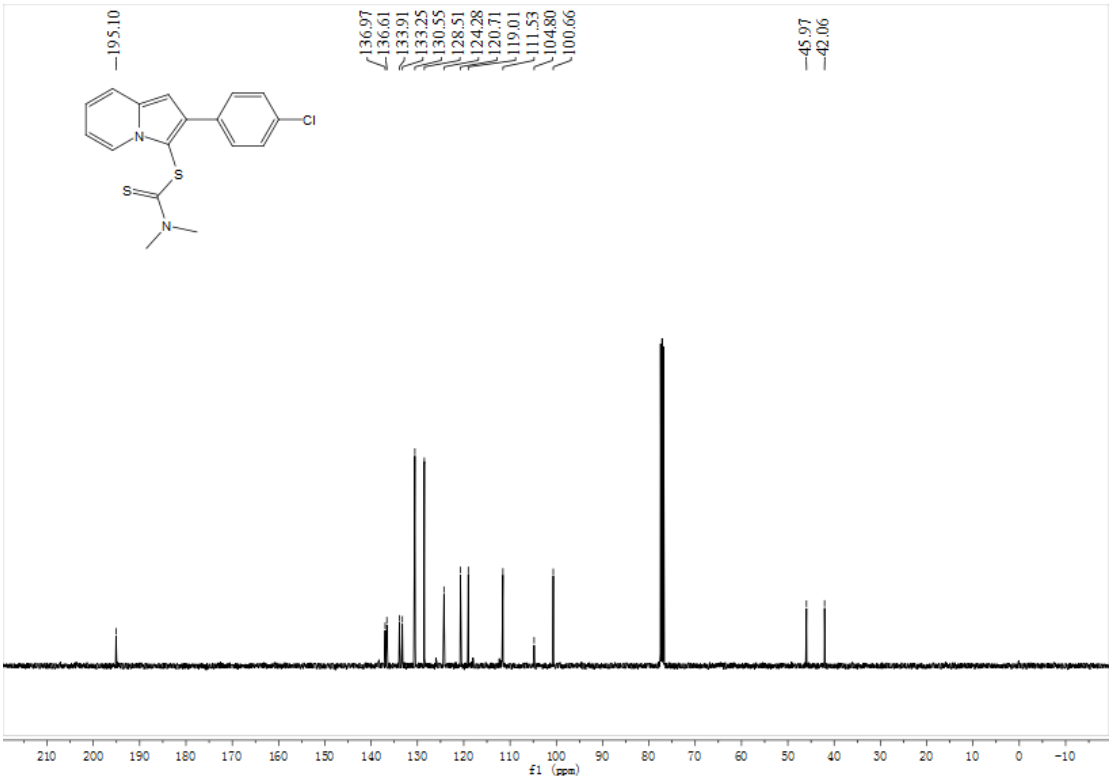
^{1}H NMR and ^{13}C NMR spectrum of compound **3j**



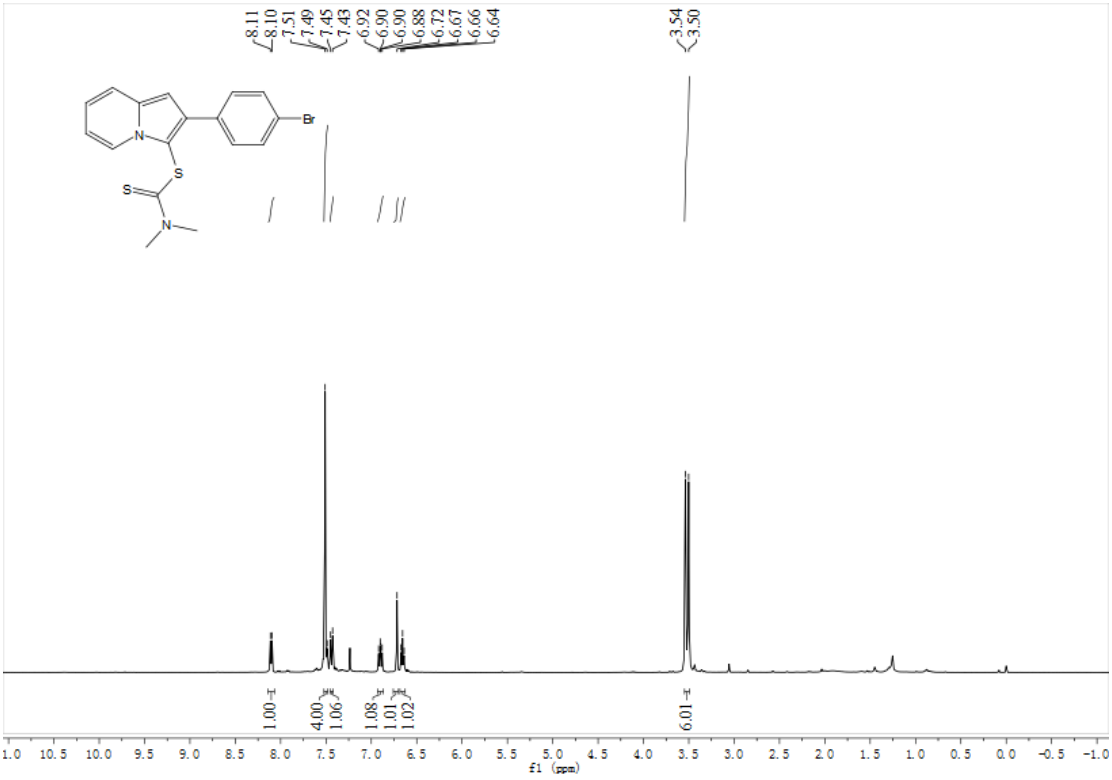


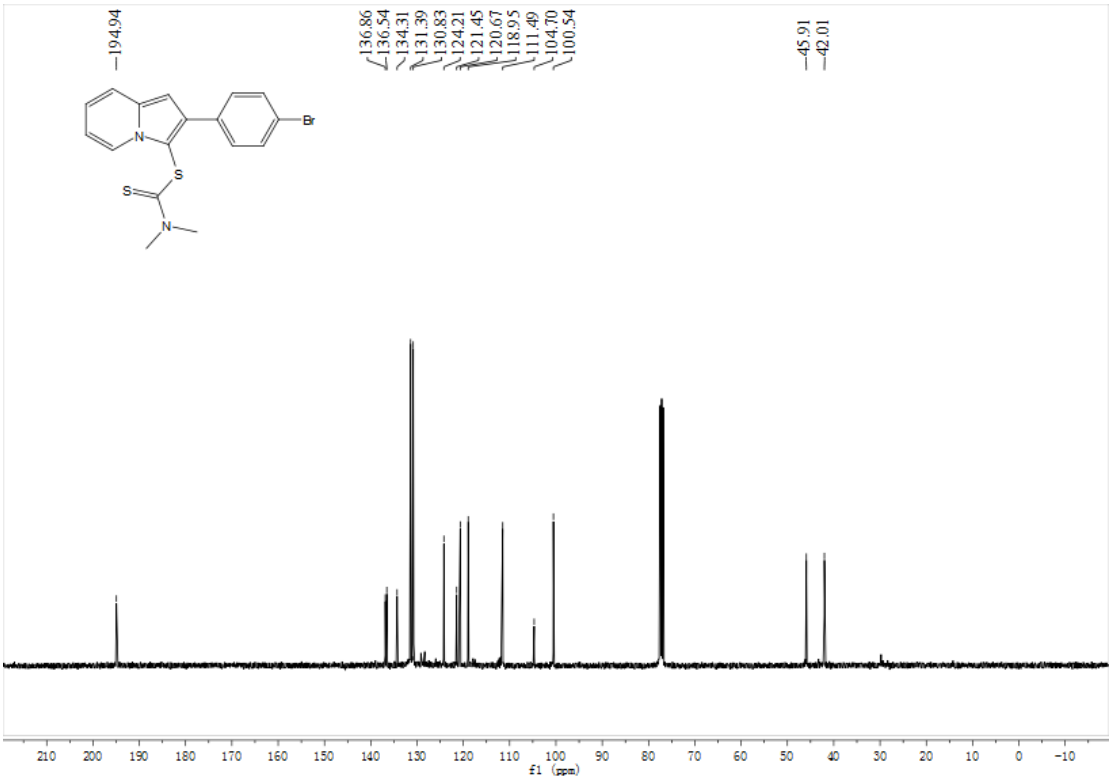
^{1}H NMR and ^{13}C NMR spectrum of compound **3k**



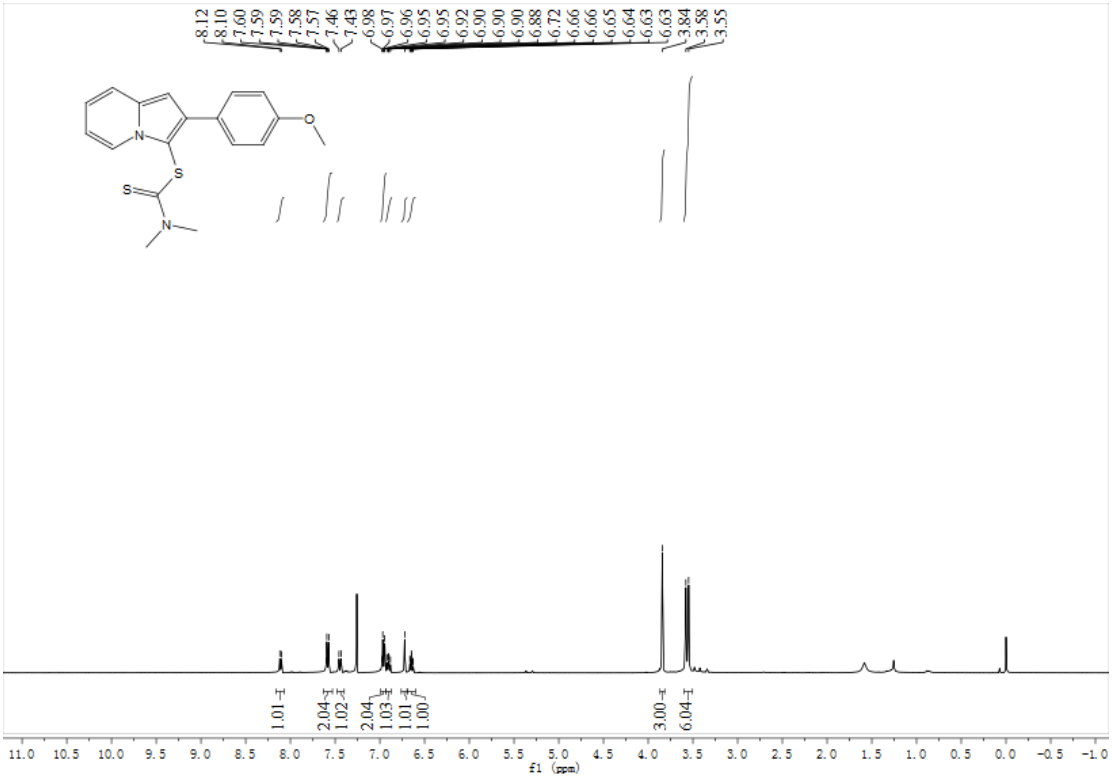


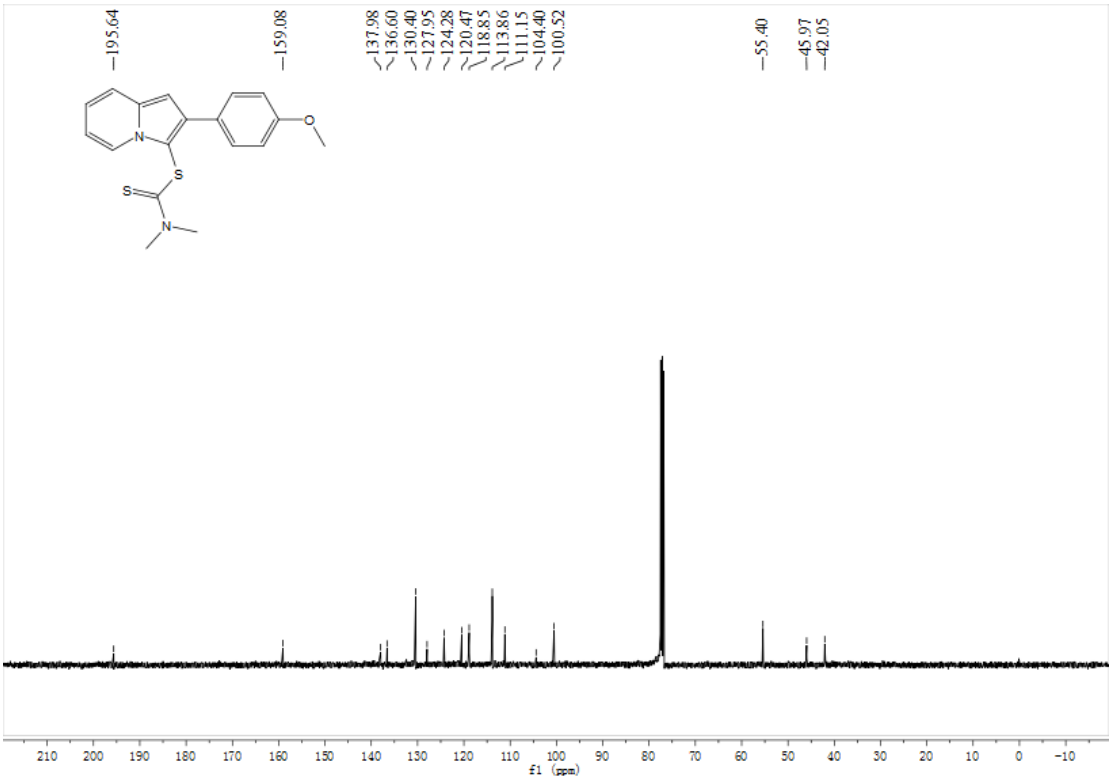
^{1}H NMR and ^{13}C NMR spectrum of compound **3l**



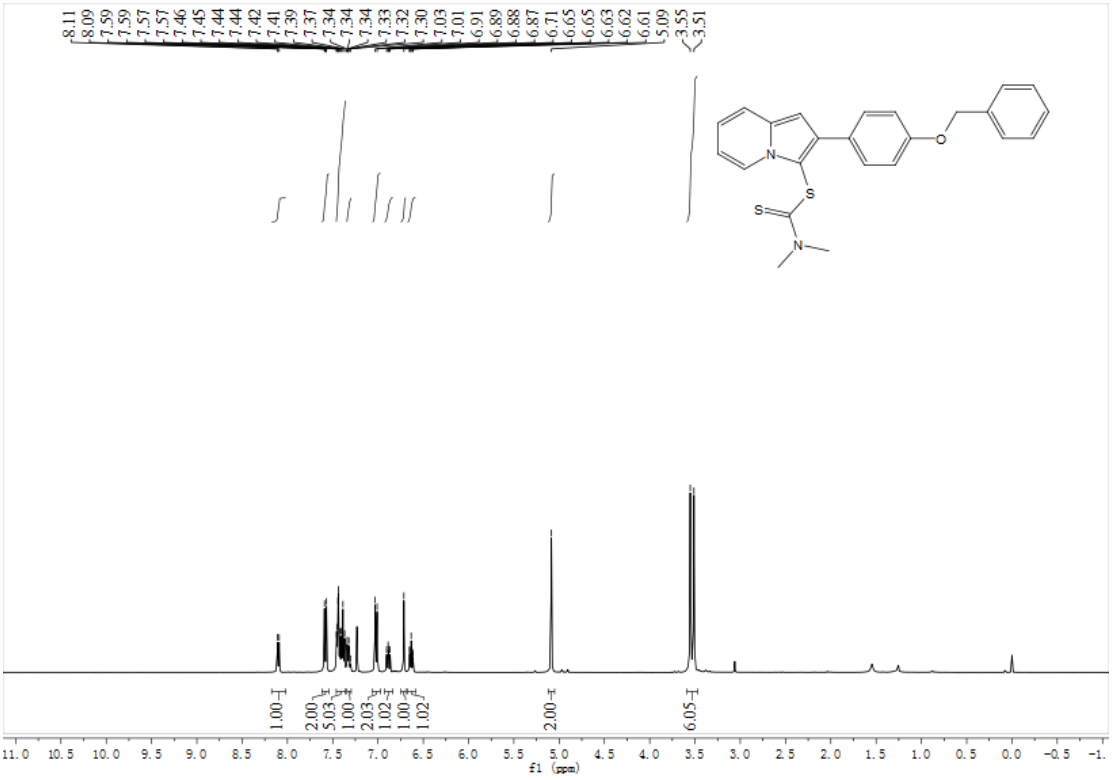


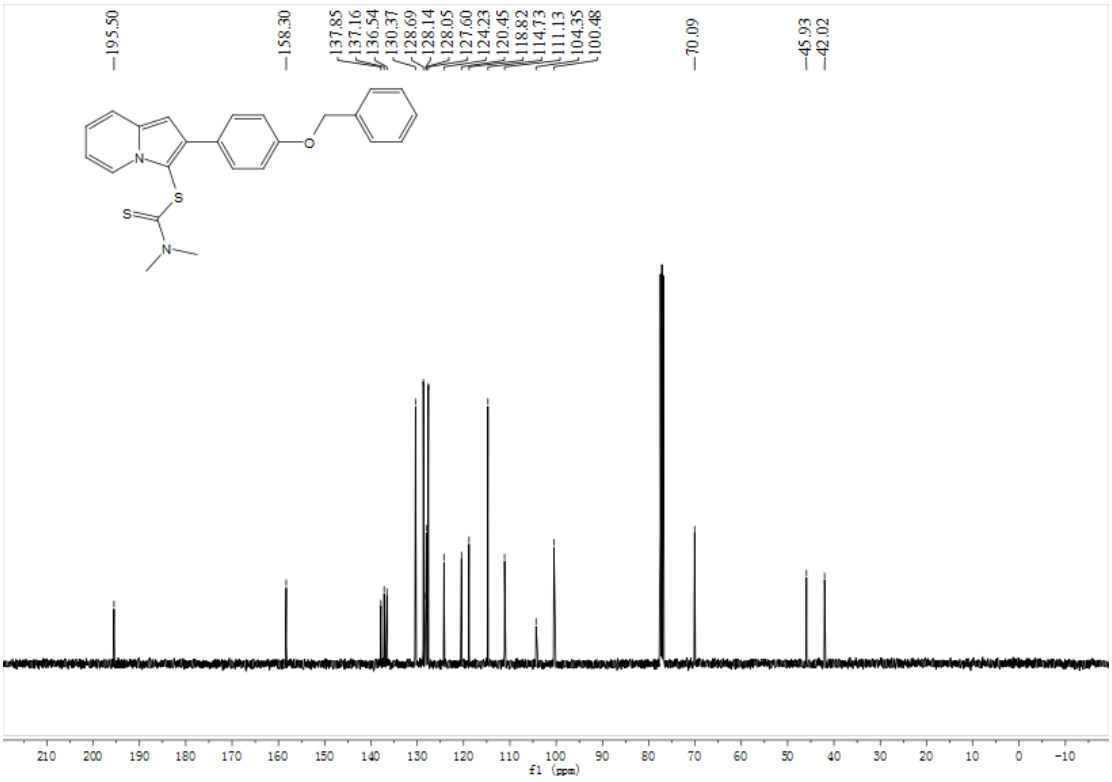
^{1}H NMR and ^{13}C NMR spectrum of compound **3m**



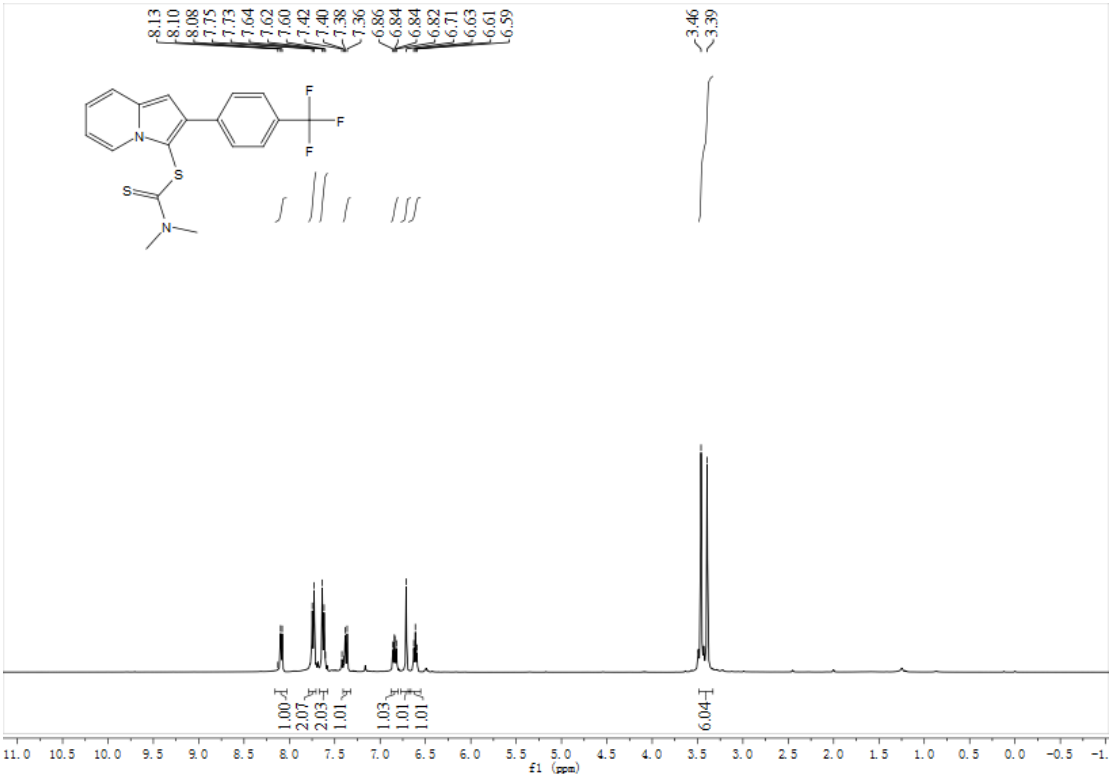


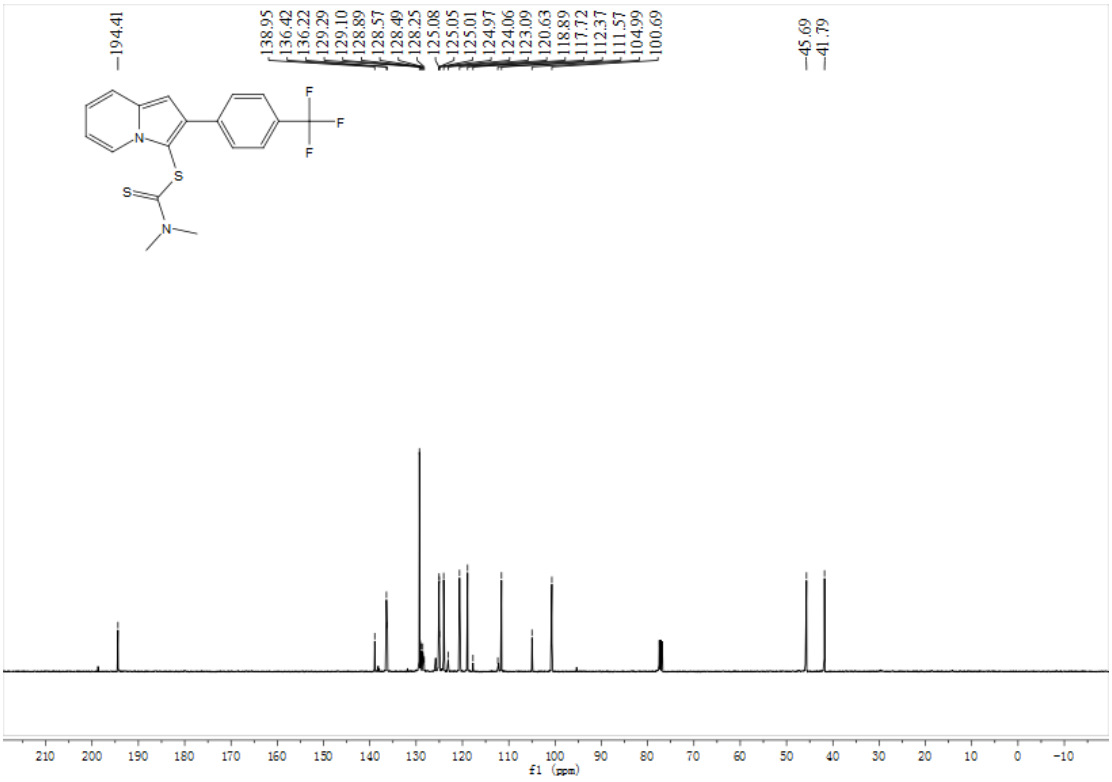
^{1}H NMR and ^{13}C NMR spectrum of compound **3n**



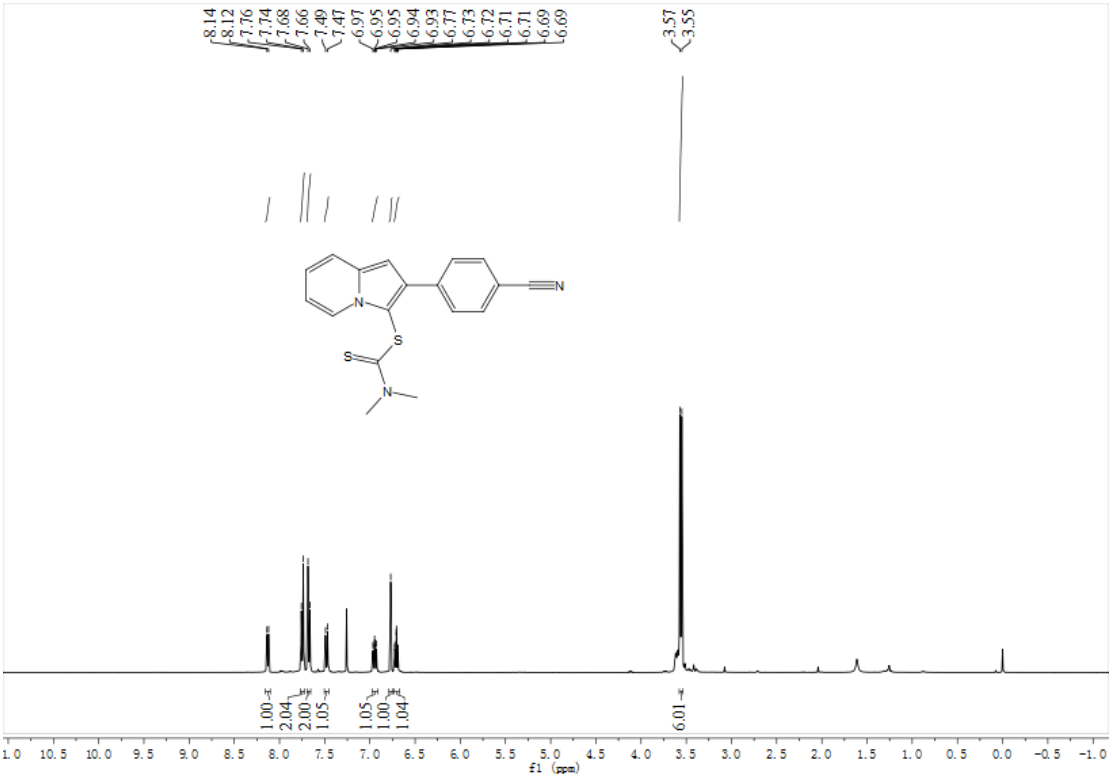


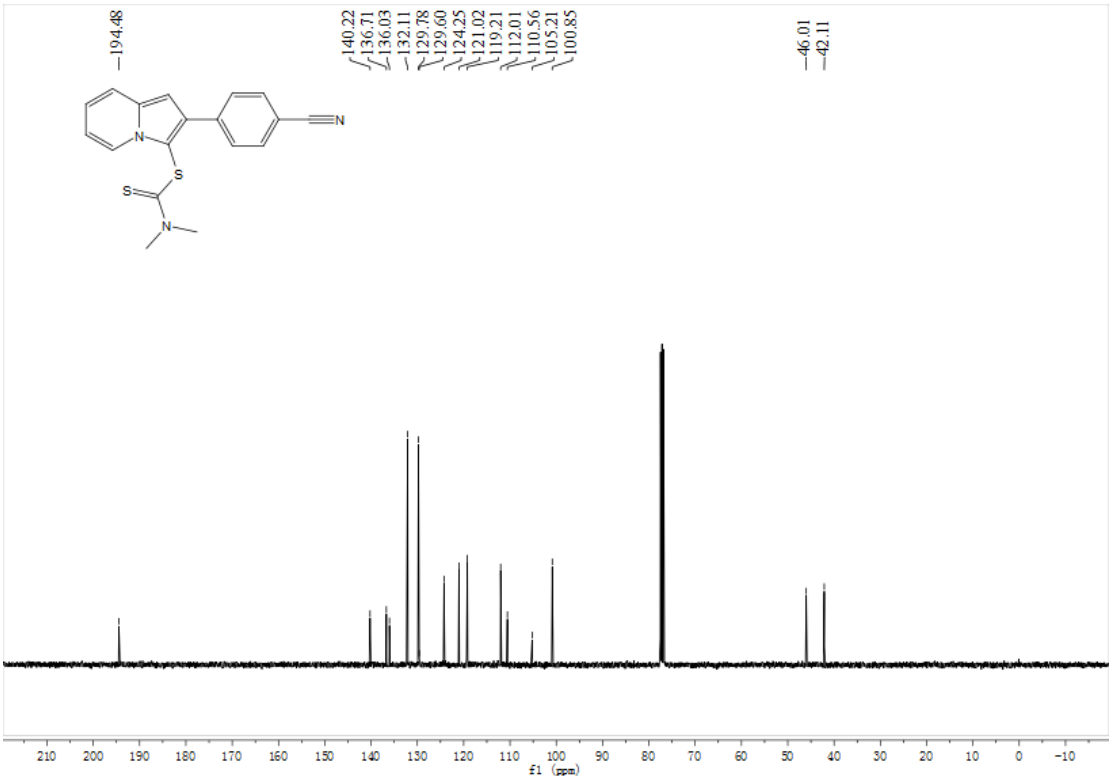
^{1}H NMR and ^{13}C NMR spectrum of compound **3o**



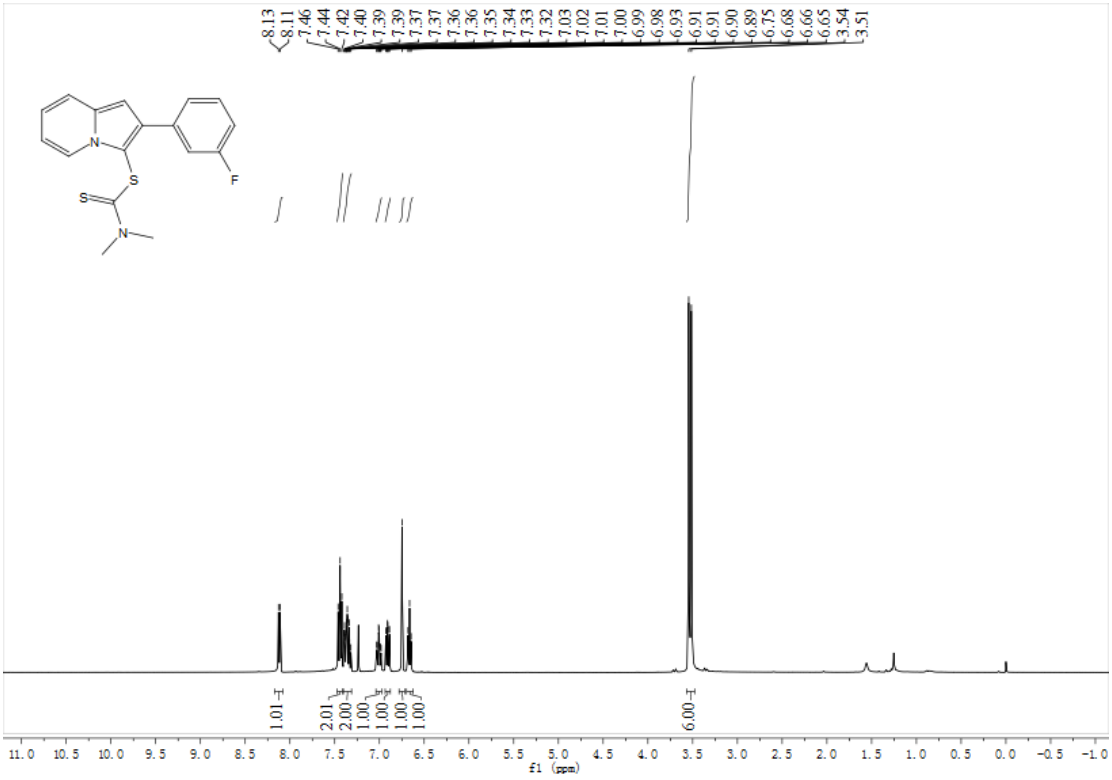


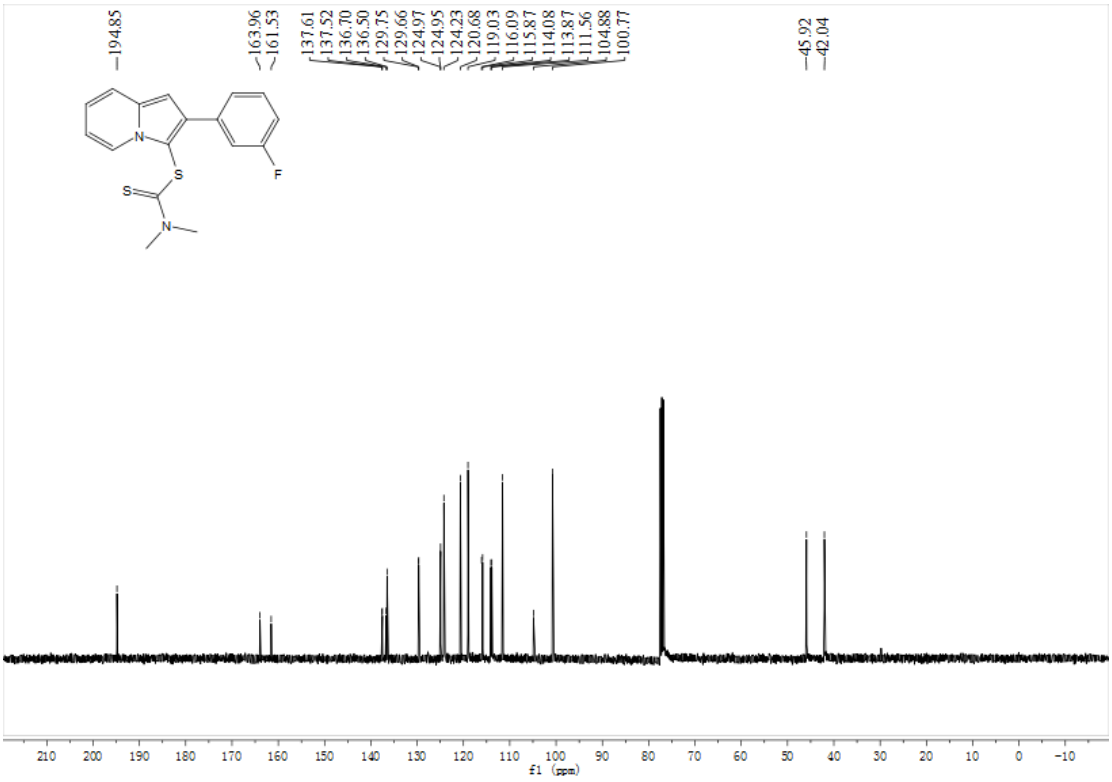
^{1}H NMR and ^{13}C NMR spectrum of compound **3p**



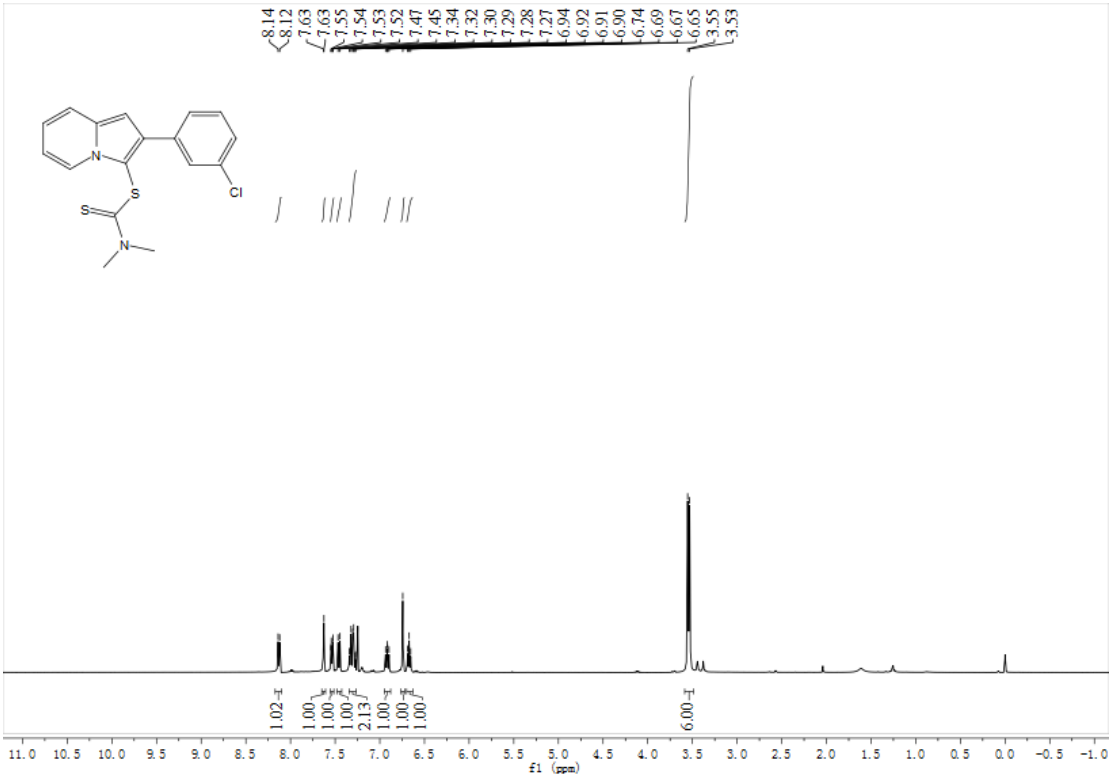


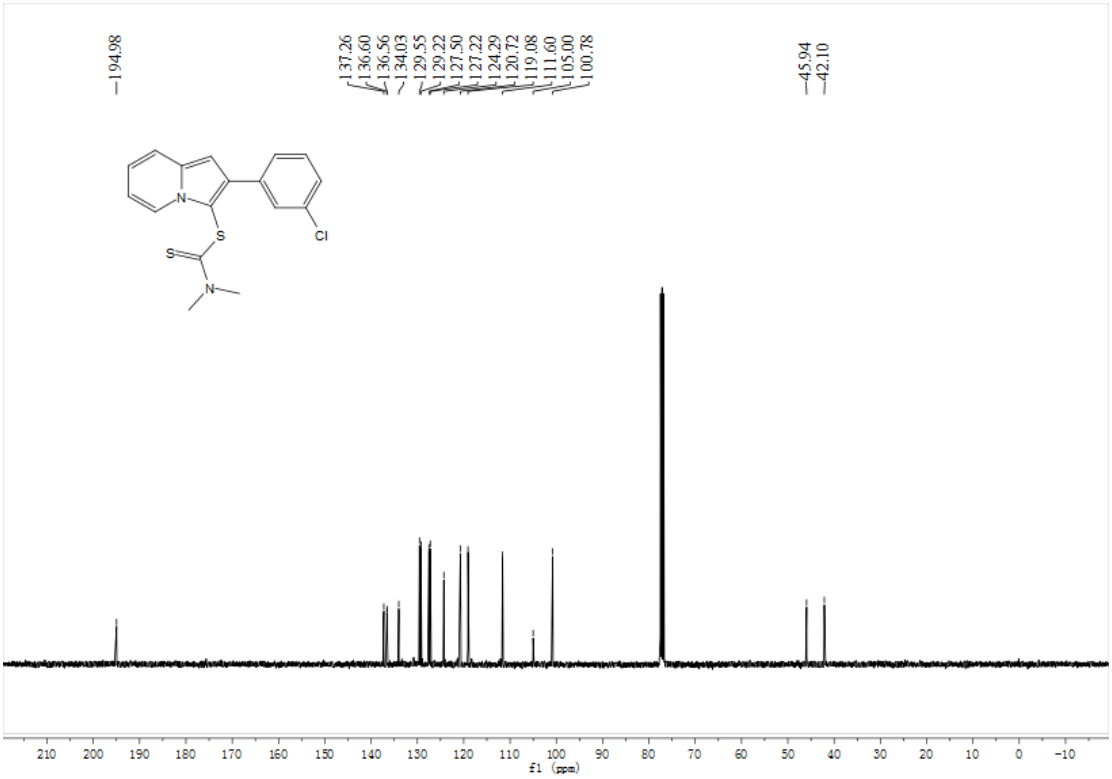
^{1}H NMR and ^{13}C NMR spectrum of compound **3q**



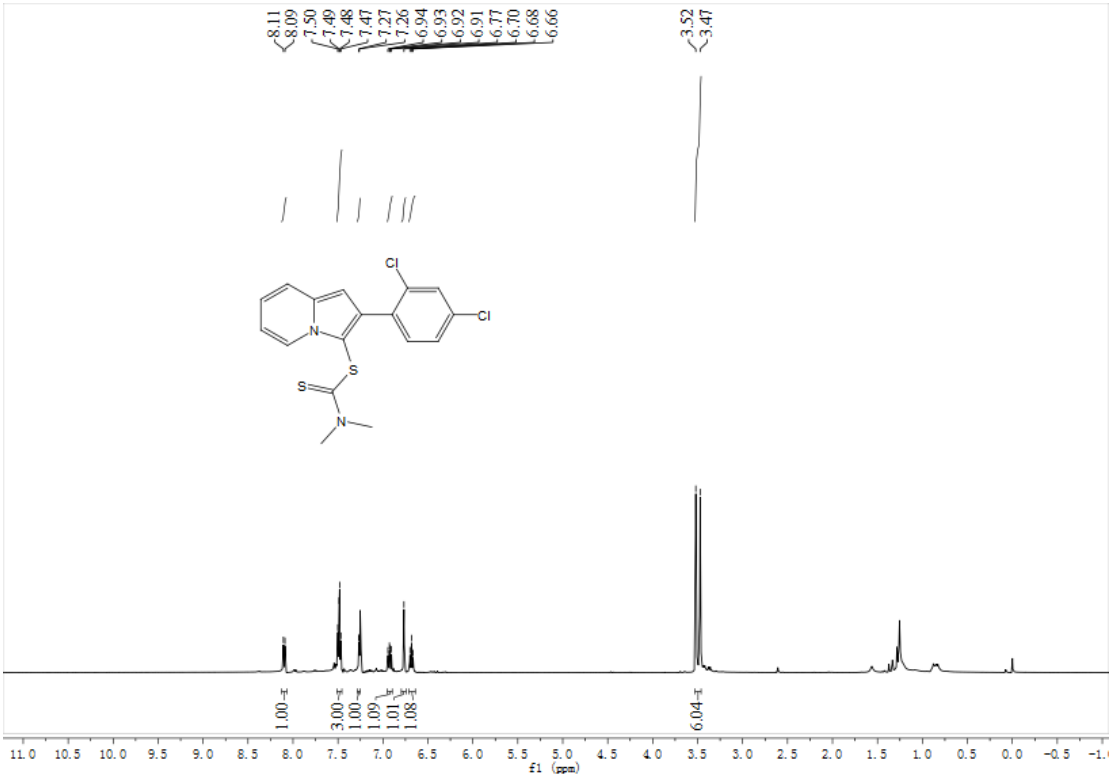


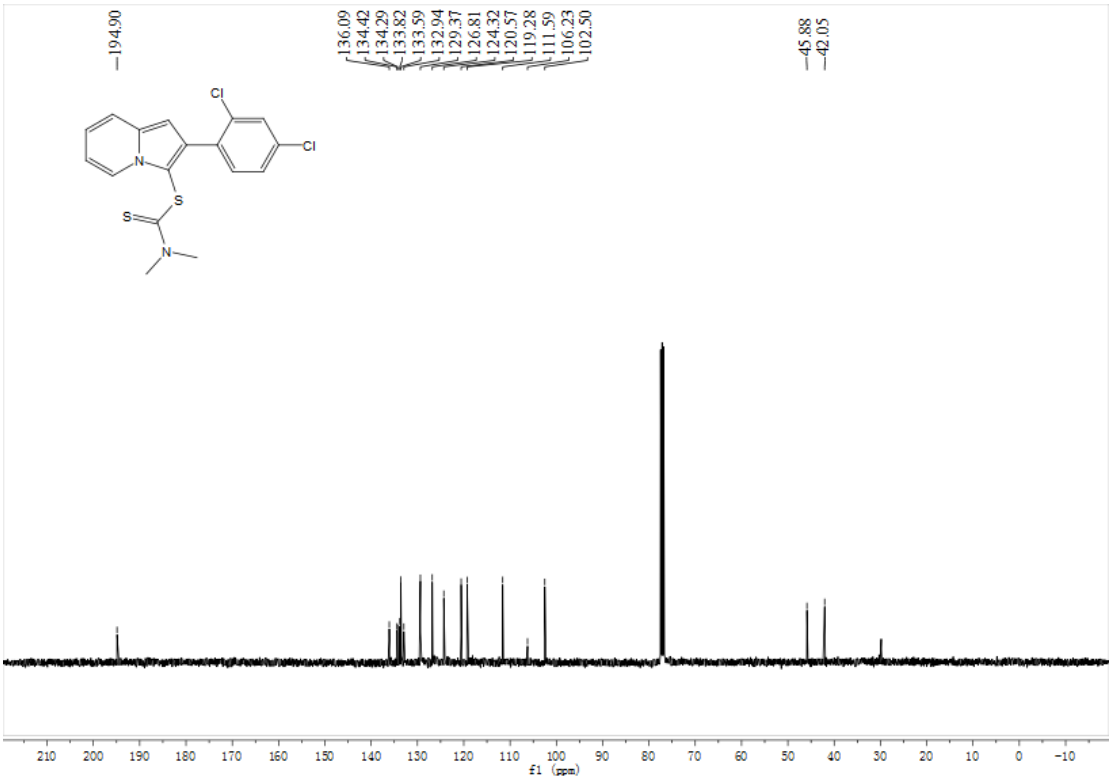
^{1}H NMR and ^{13}C NMR spectrum of compound **3r**



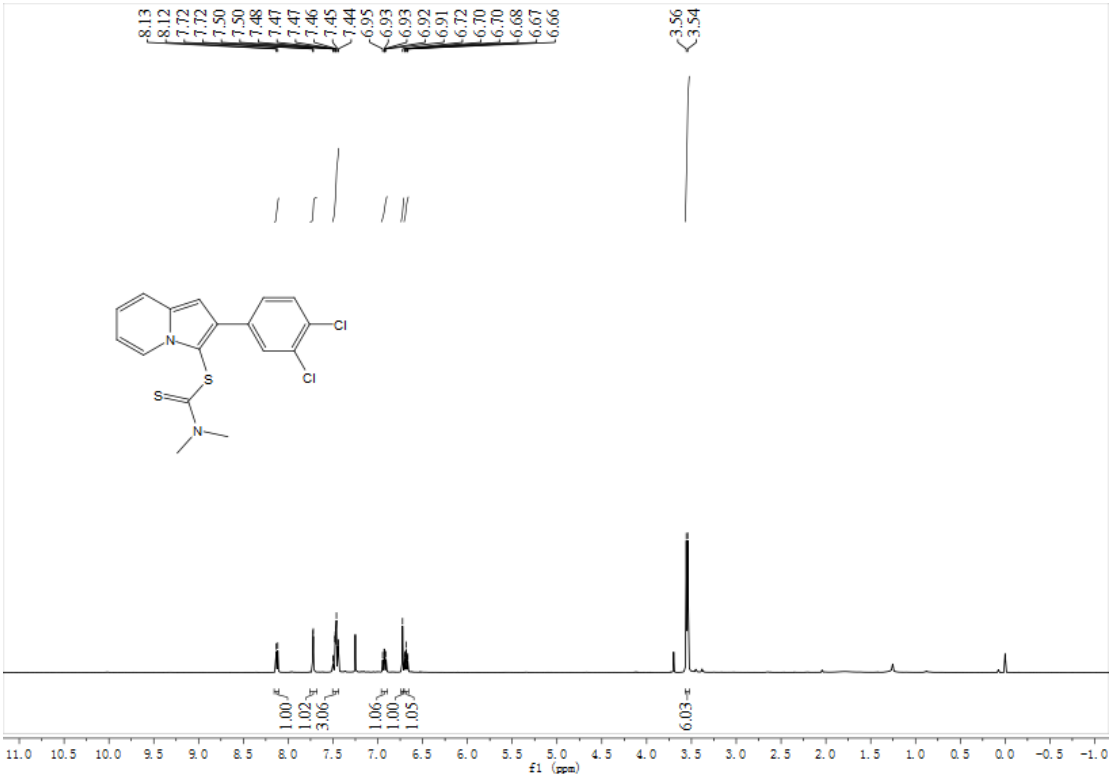


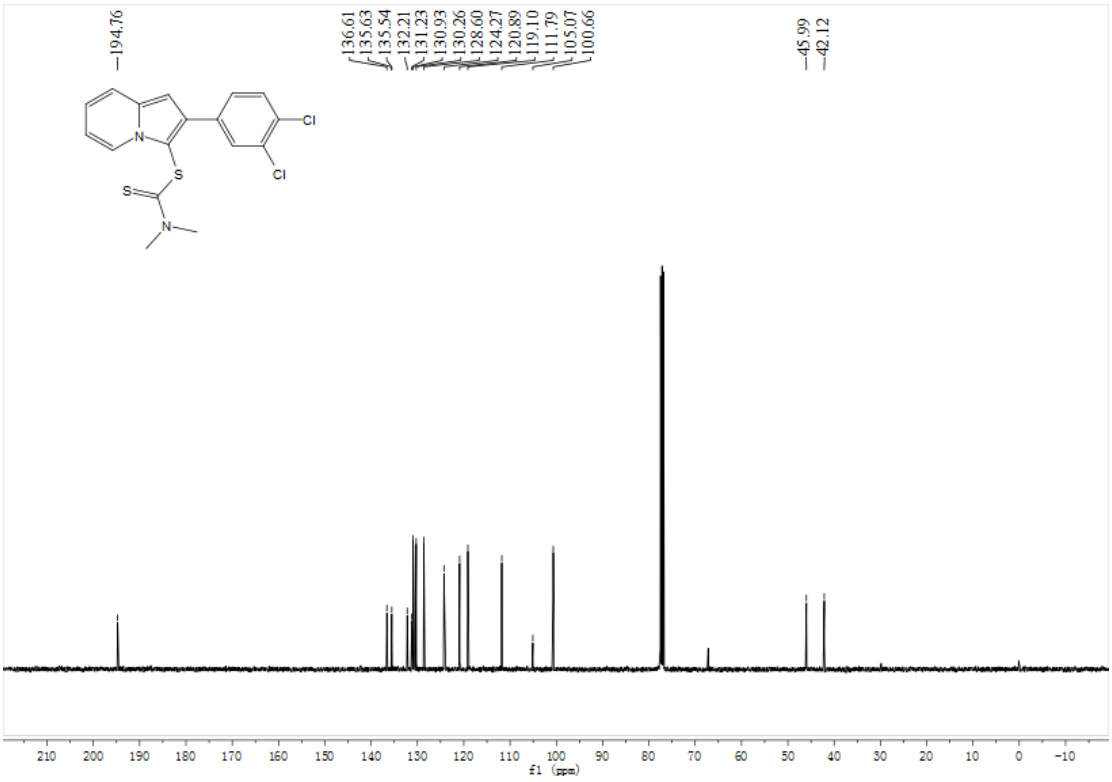
^{1}H NMR and ^{13}C NMR spectrum of compound **3s**



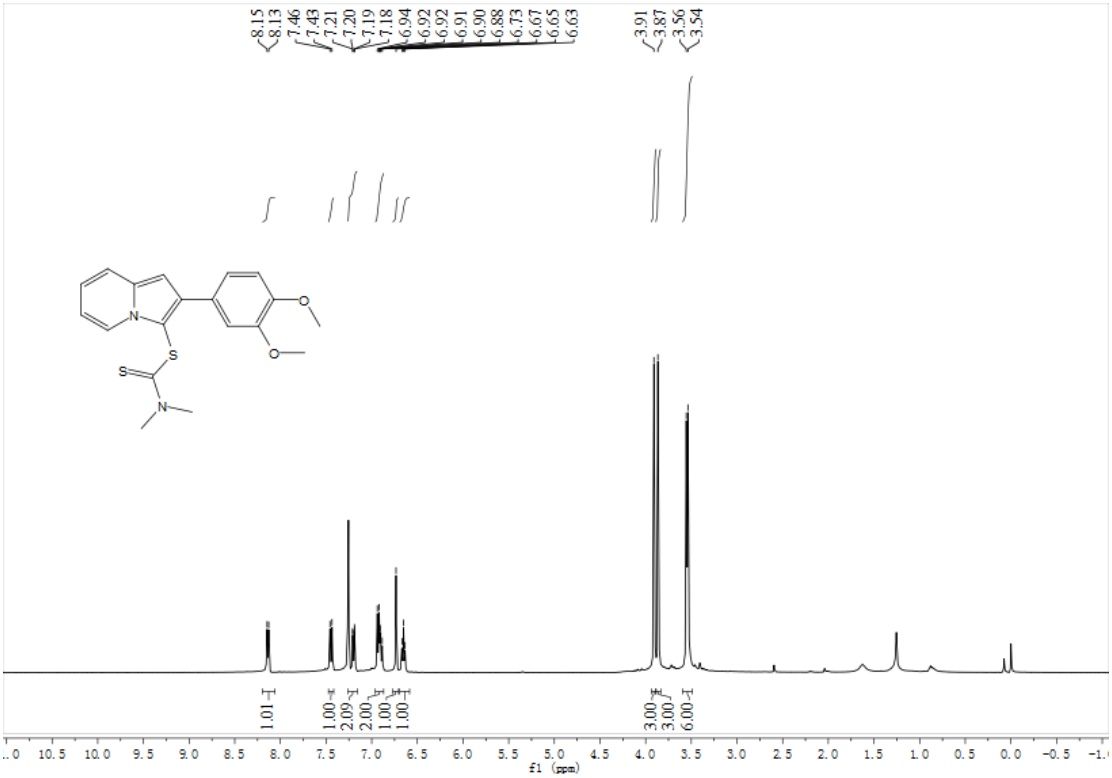


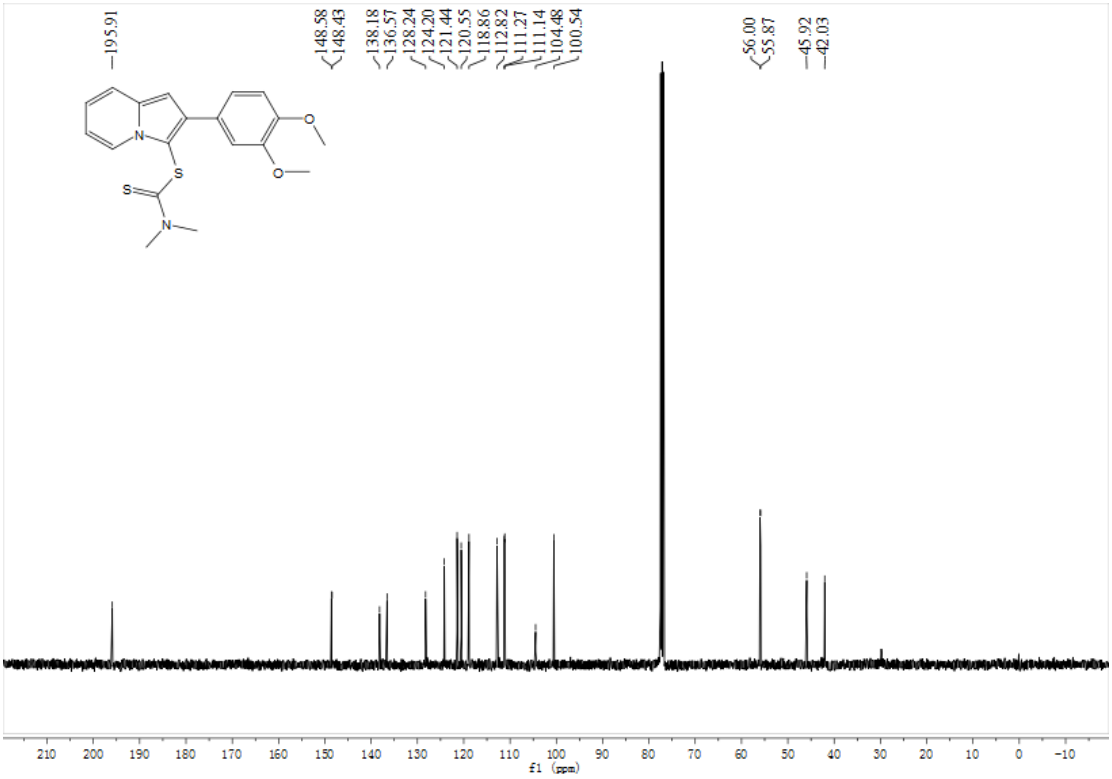
^{1}H NMR and ^{13}C NMR spectrum of compound **3t**



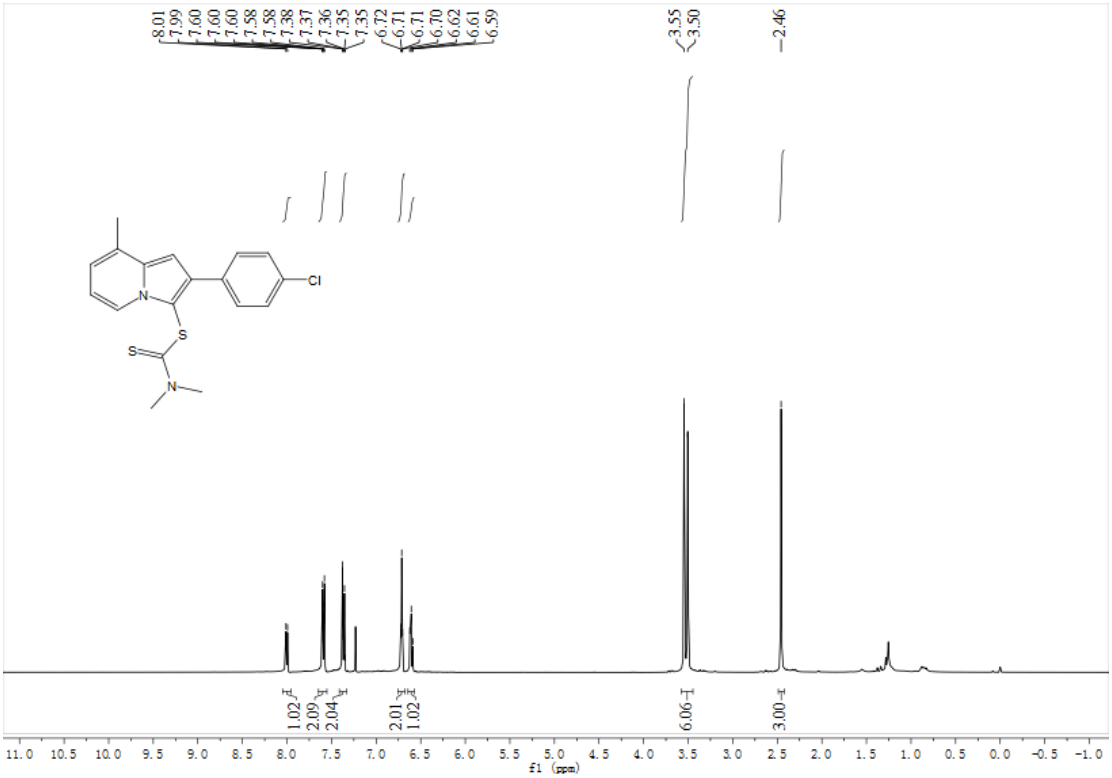


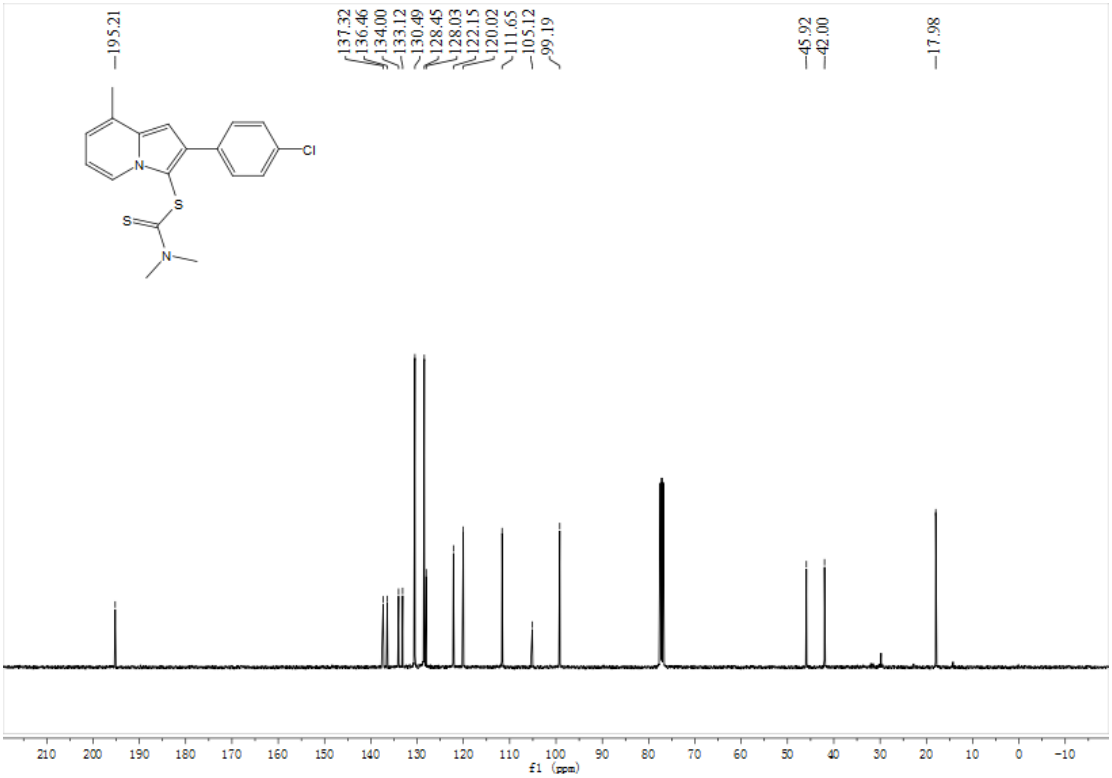
^{1}H NMR and ^{13}C NMR spectrum of compound **3u**



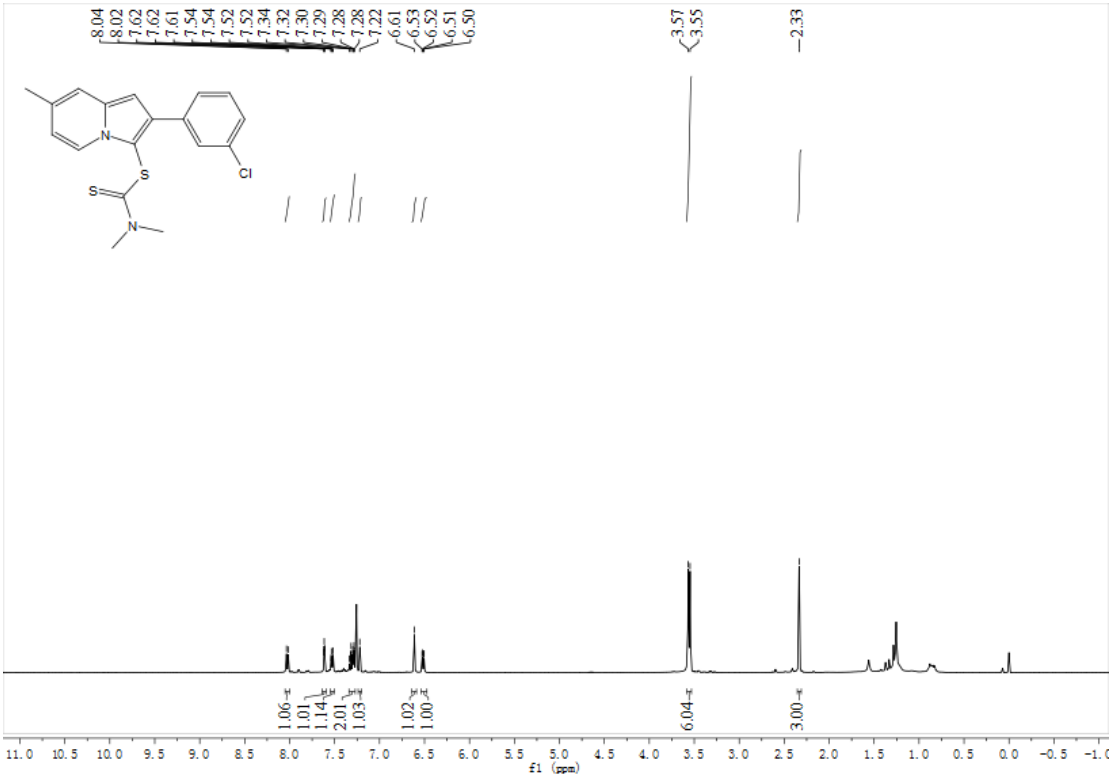


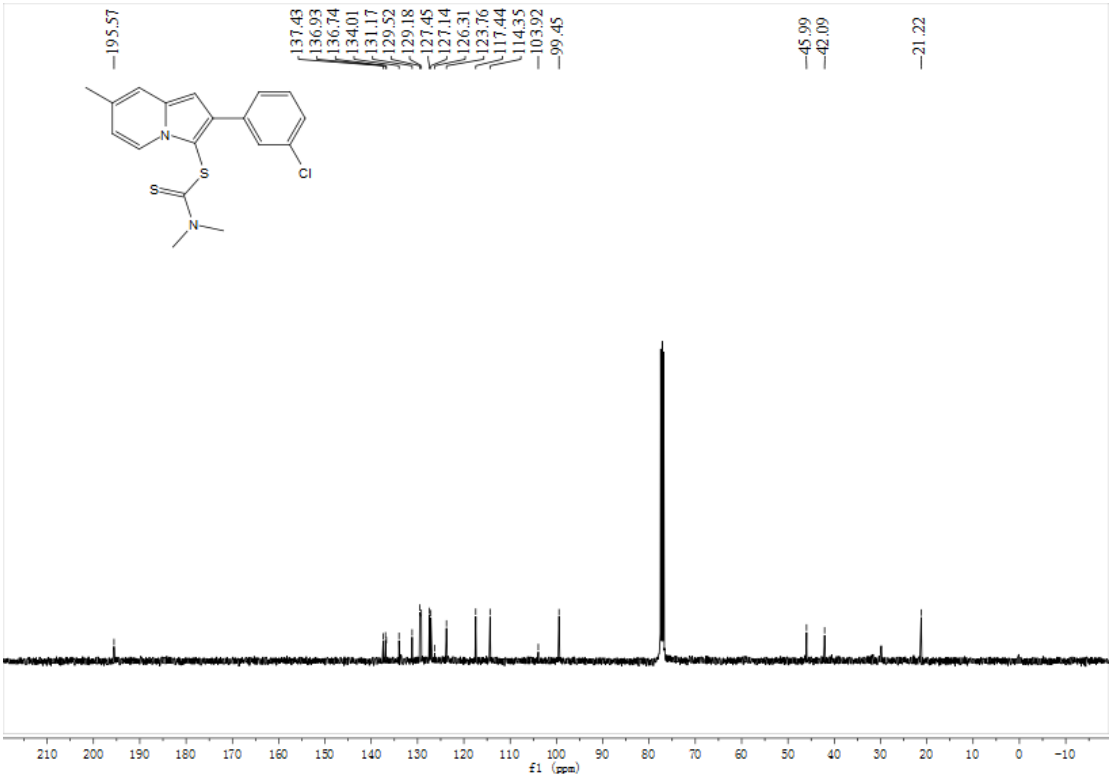
^{1}H NMR and ^{13}C NMR spectrum of compound **3v**



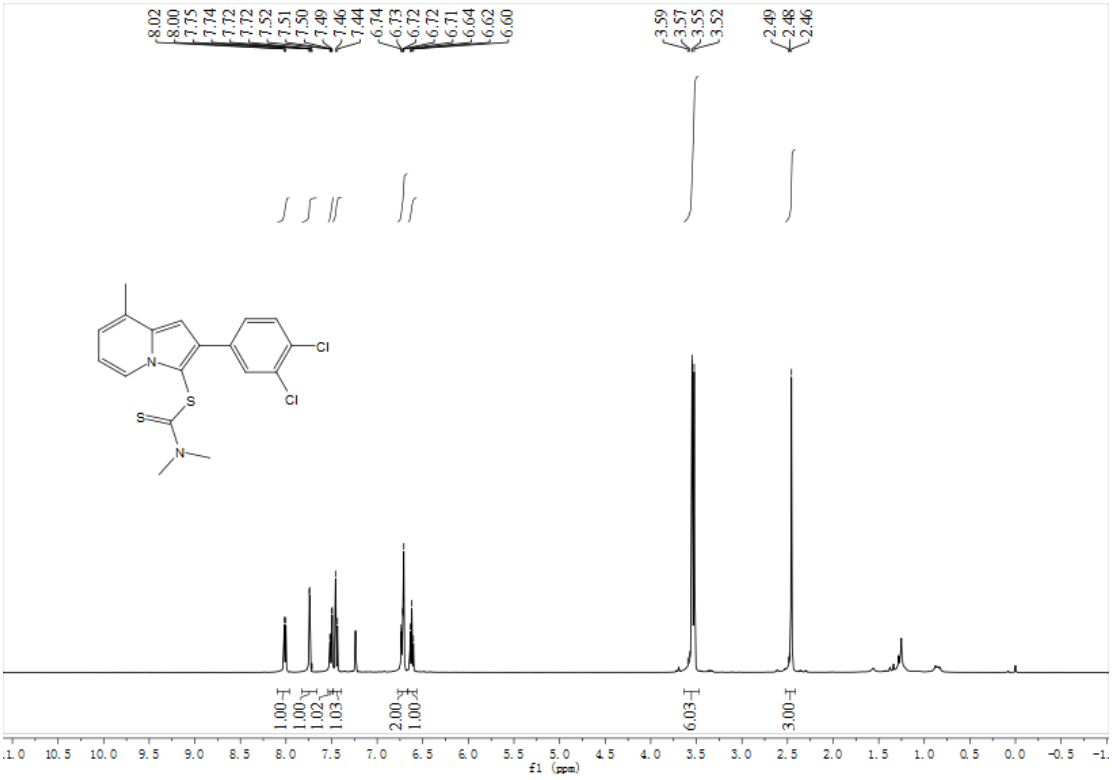


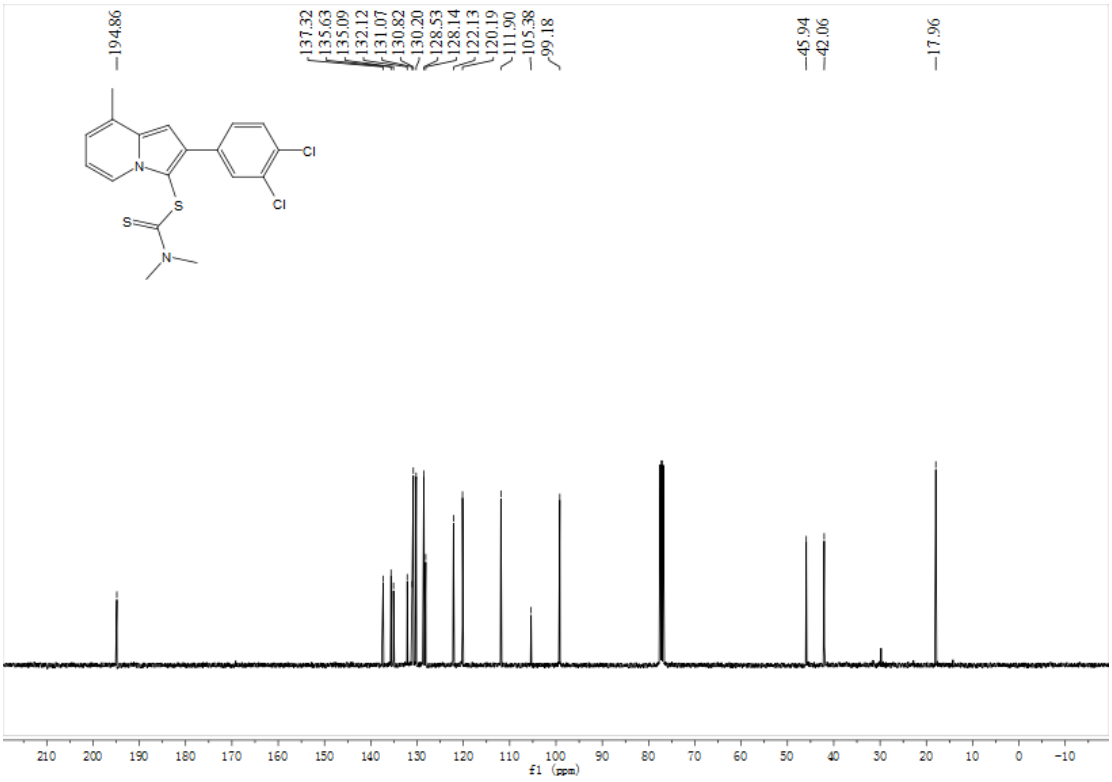
^{1}H NMR and ^{13}C NMR spectrum of compound **3w**



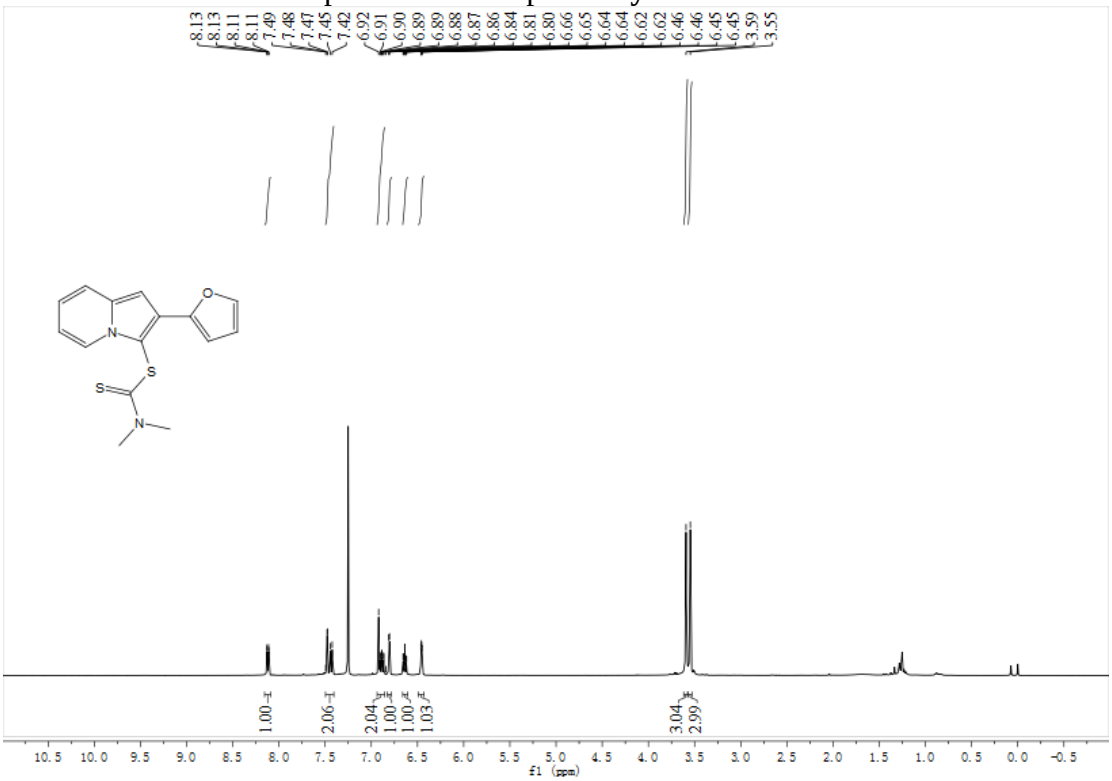


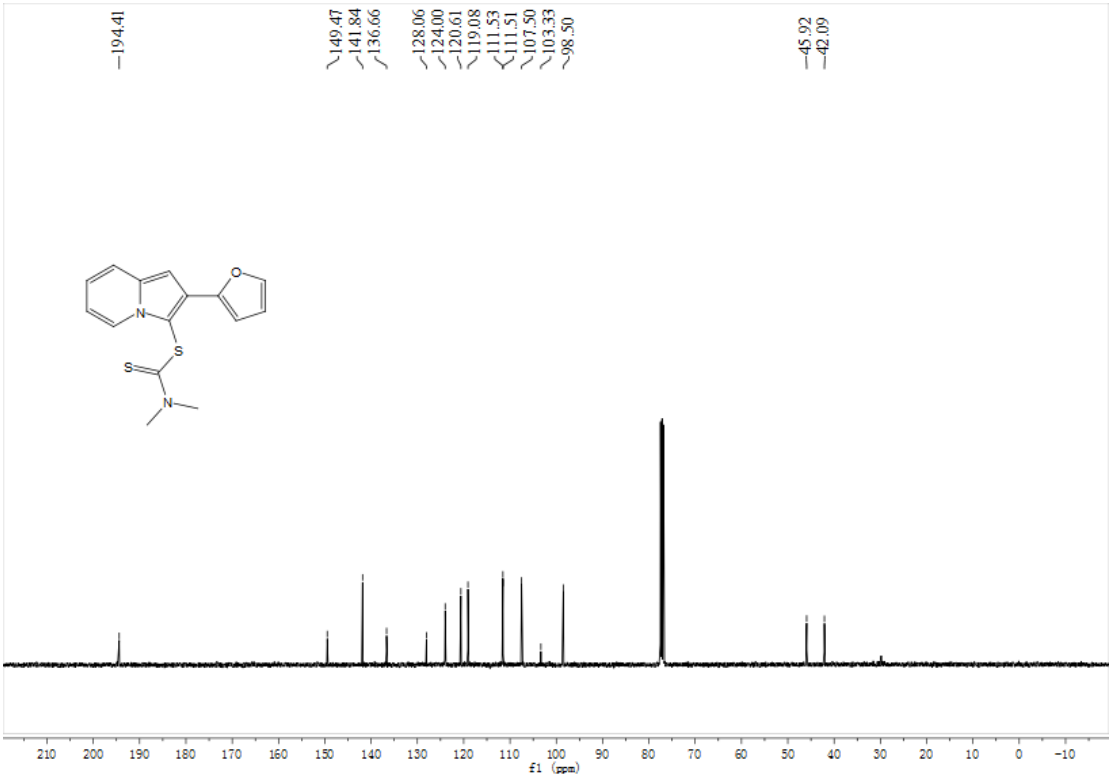
^{1}H NMR and ^{13}C NMR spectrum of compound **3x**



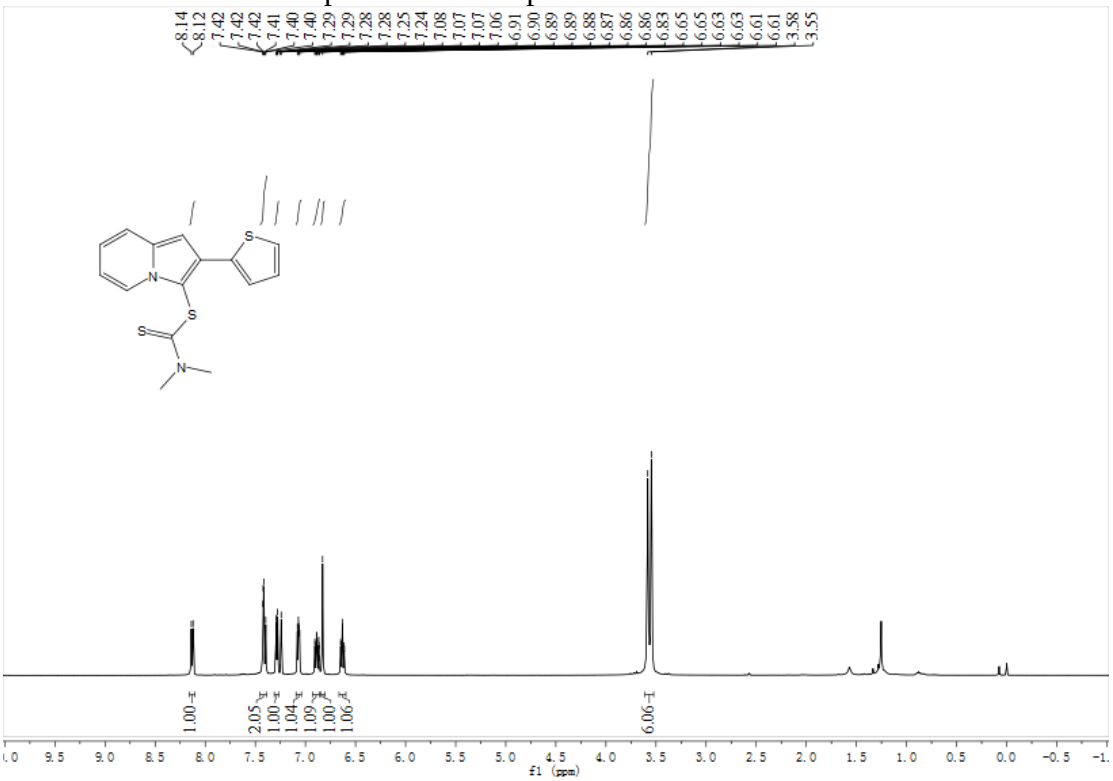


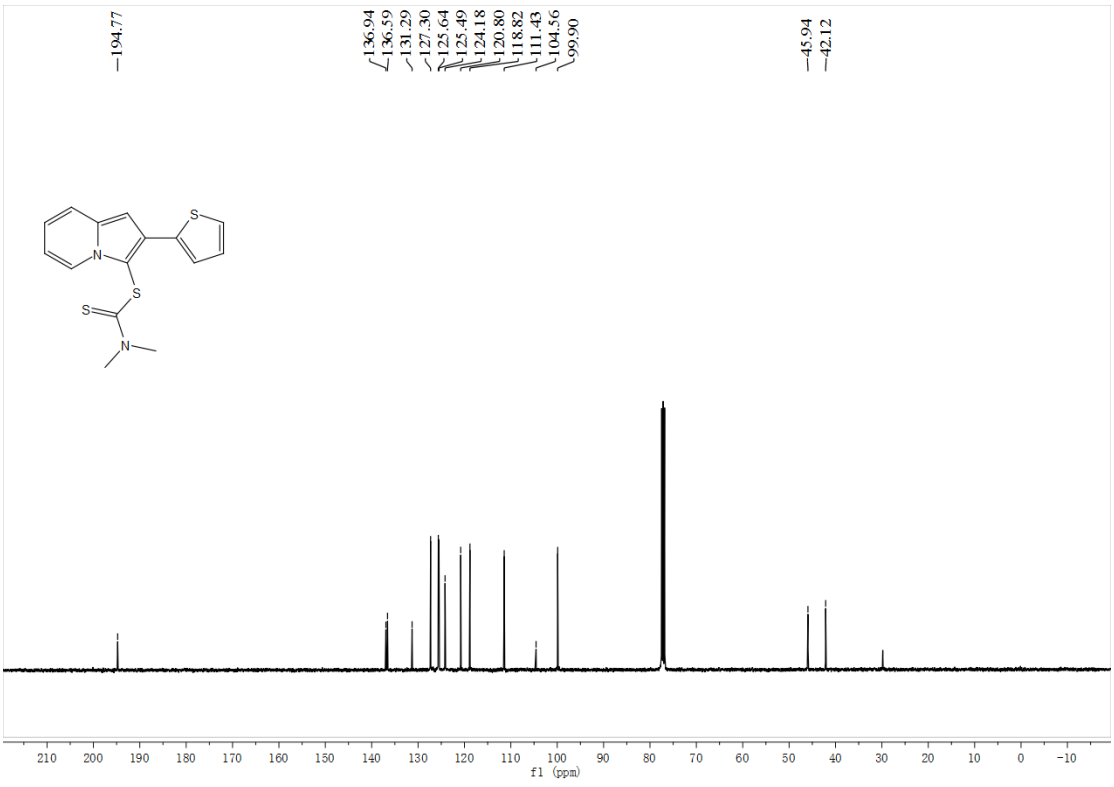
^{1}H NMR and ^{13}C NMR spectrum of compound **3y**



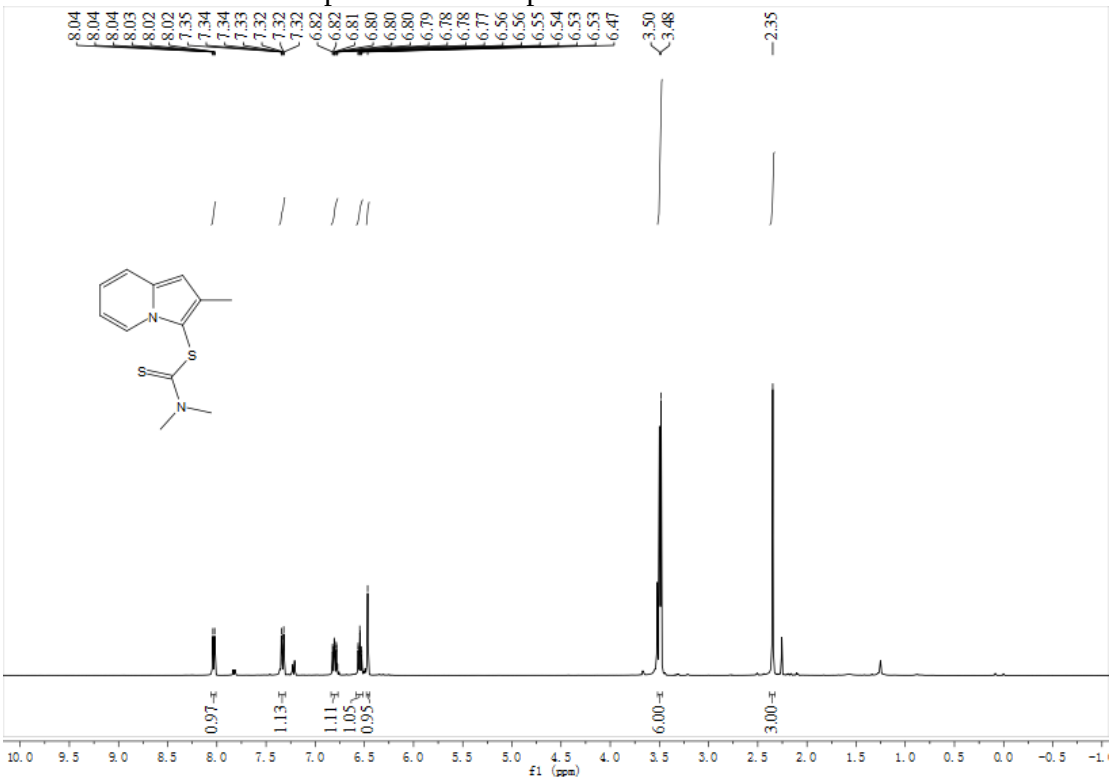


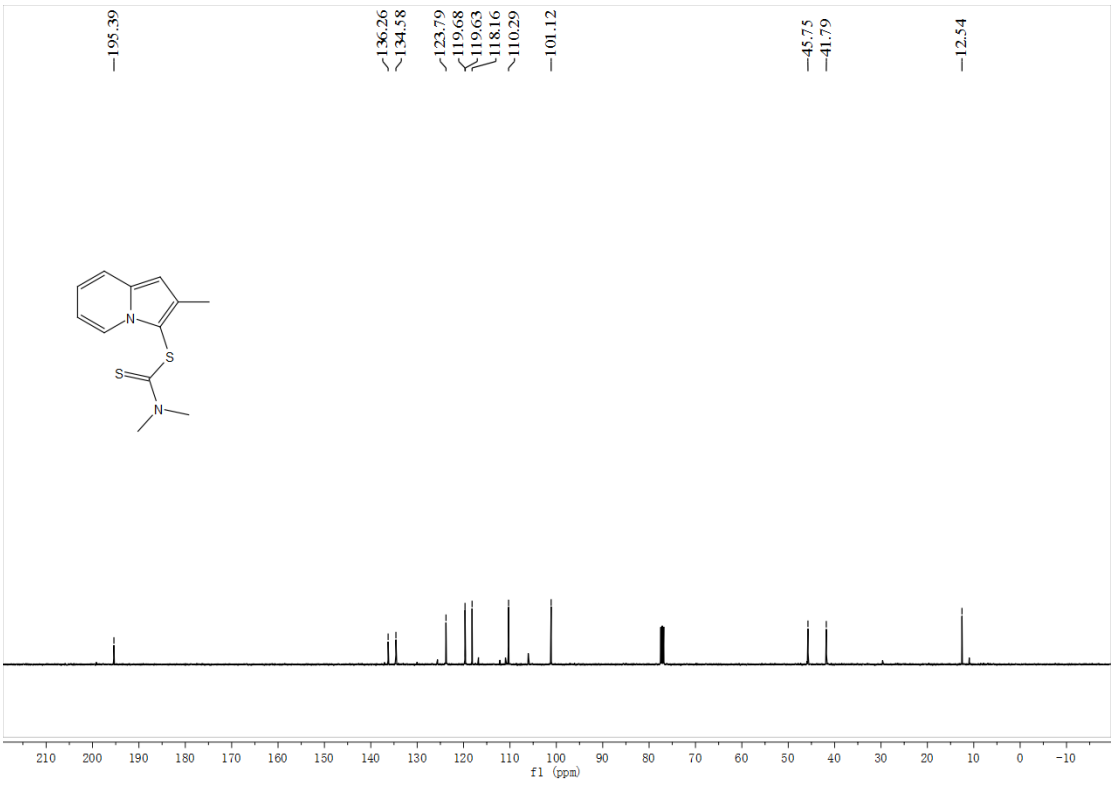
^{1}H NMR and ^{13}C NMR spectrum of compound **3z**



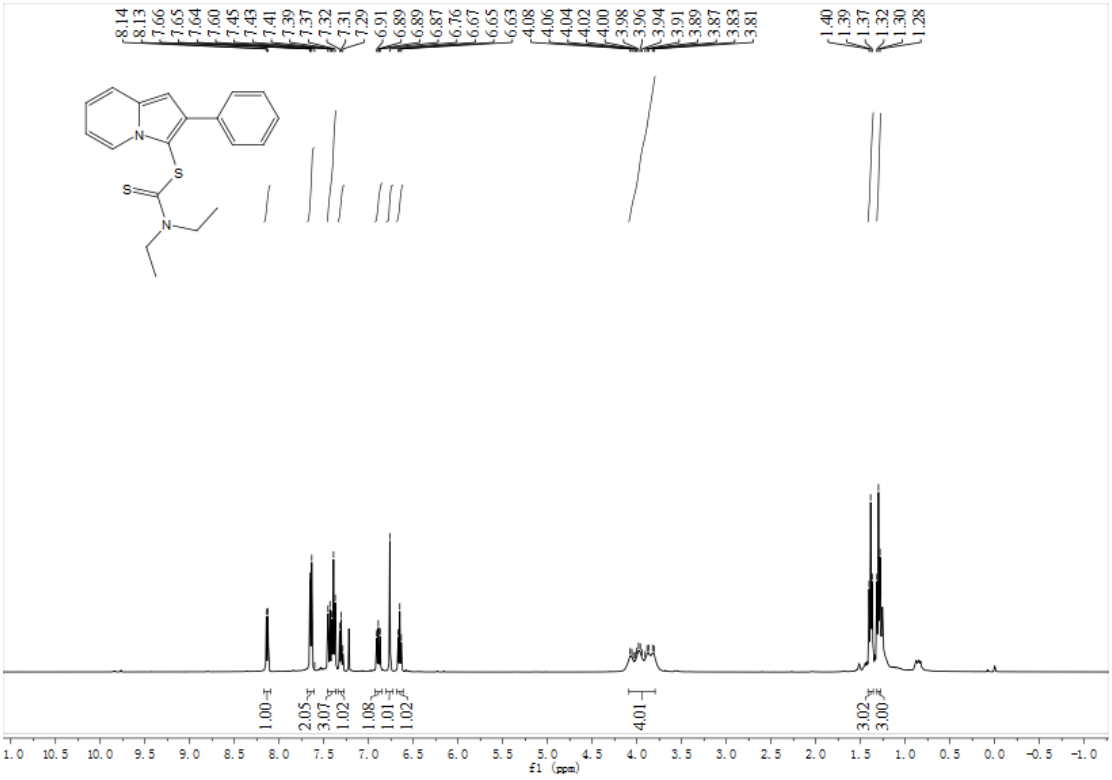


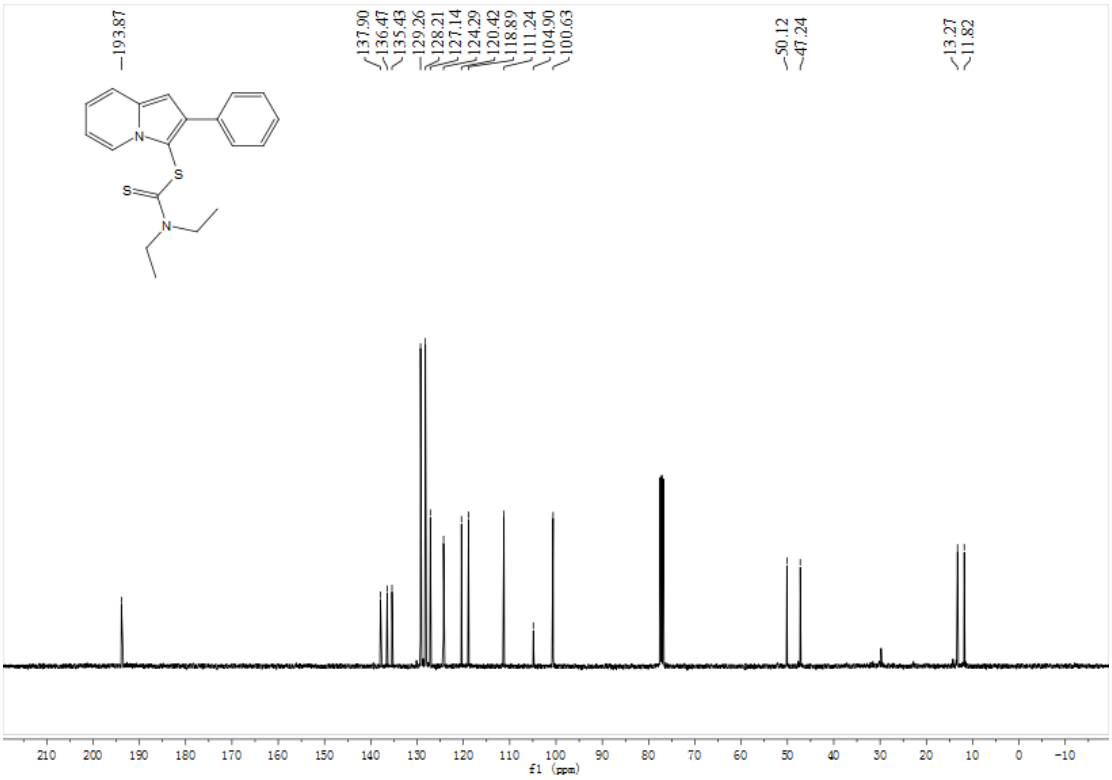
^{1}H NMR and ^{13}C NMR spectrum of compound **3aa**



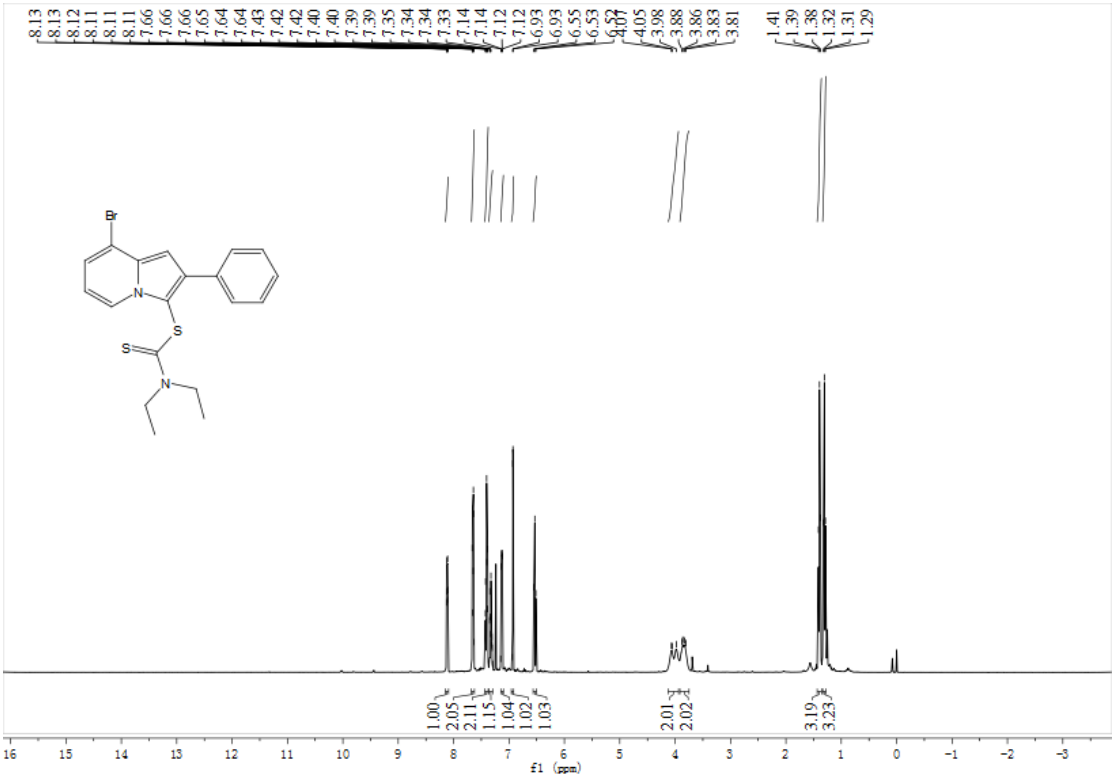


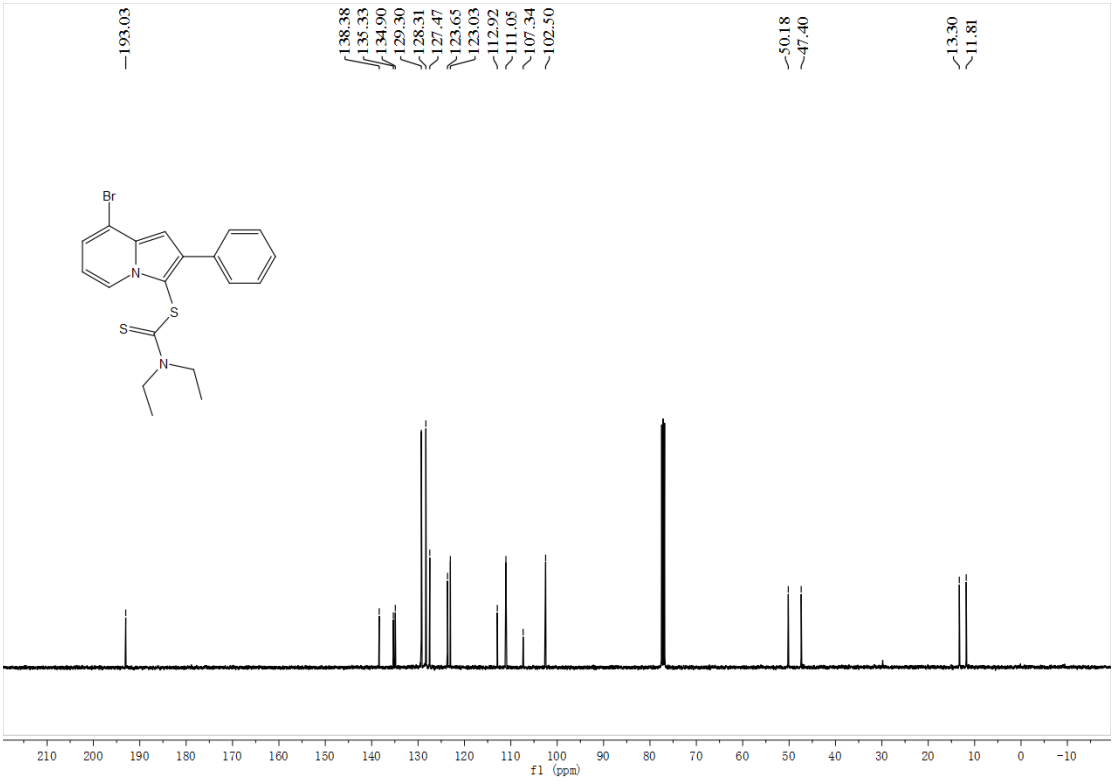
^{1}H NMR and ^{13}C NMR spectrum of compound **5a**



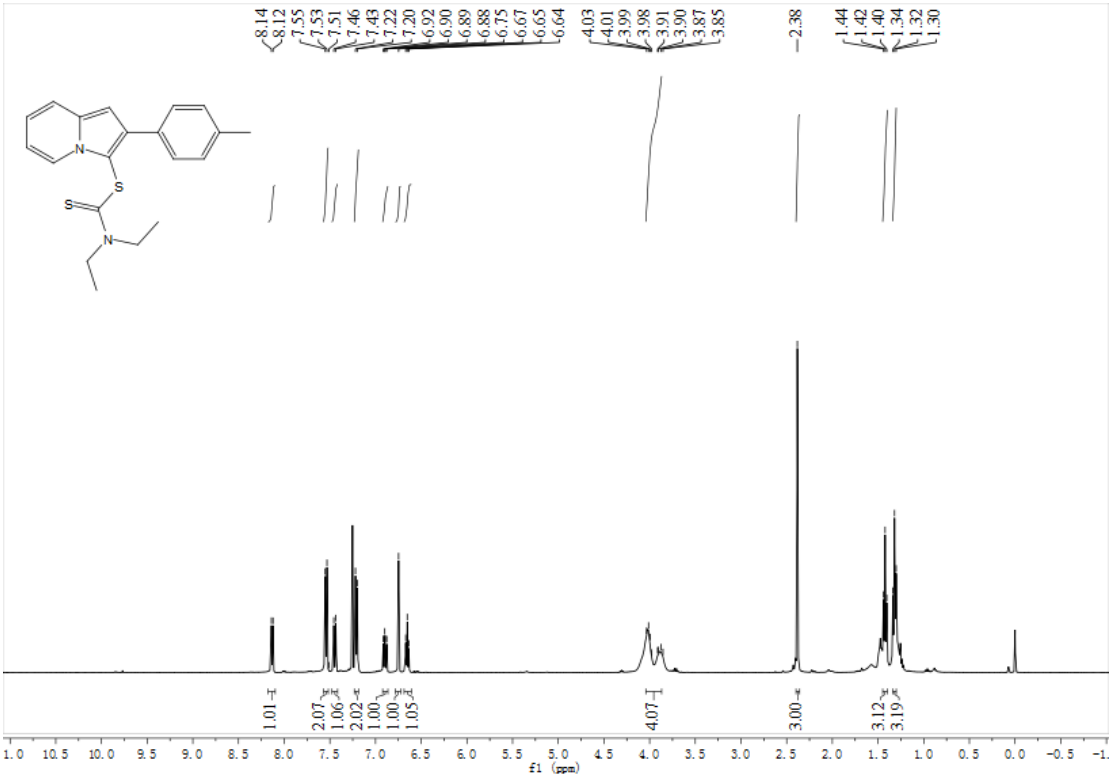


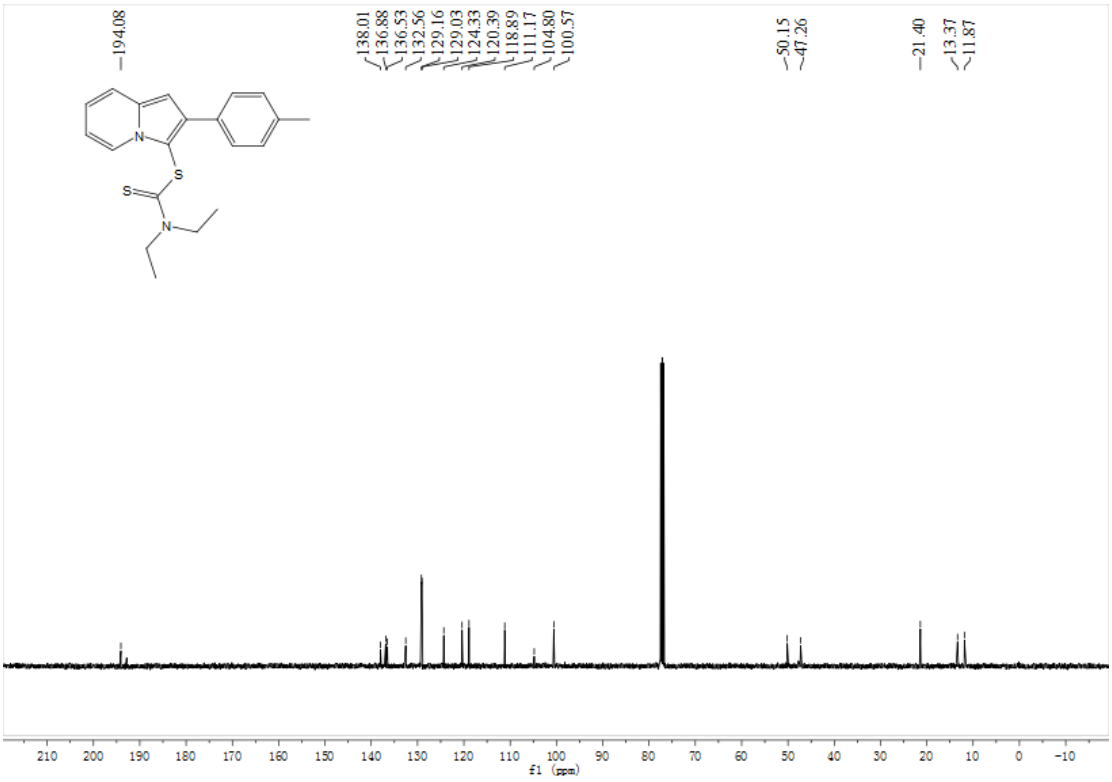
^{1}H NMR and ^{13}C NMR spectrum of compound **5b**



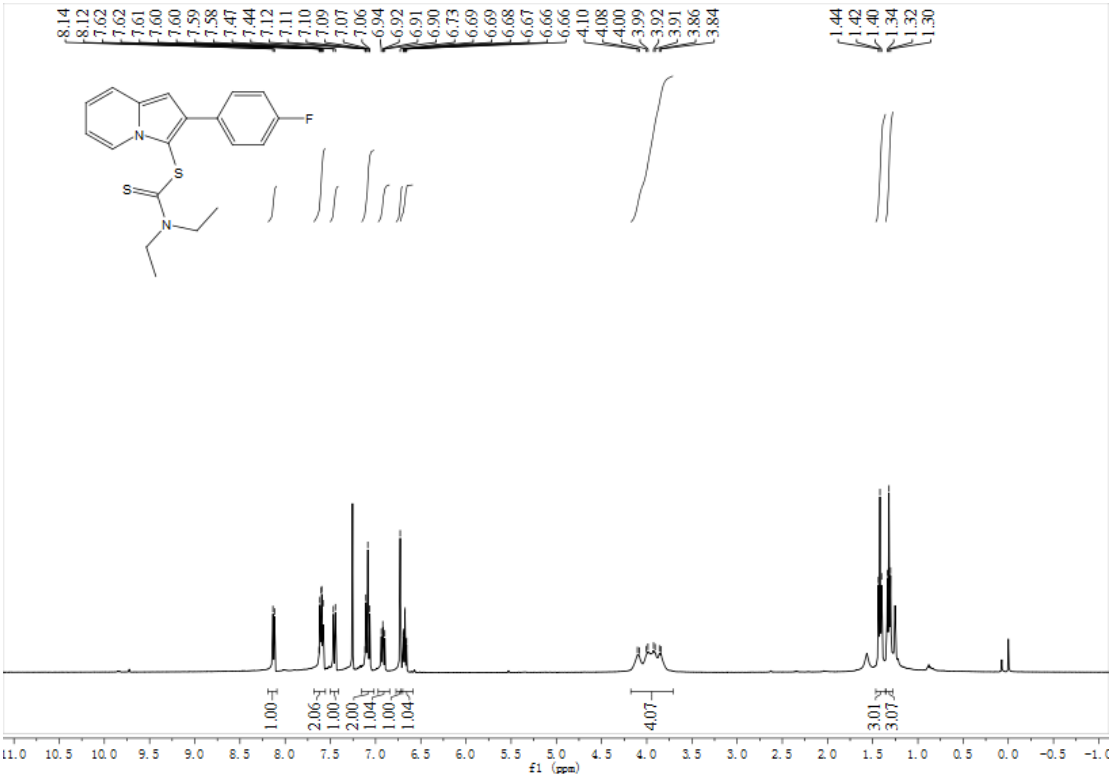


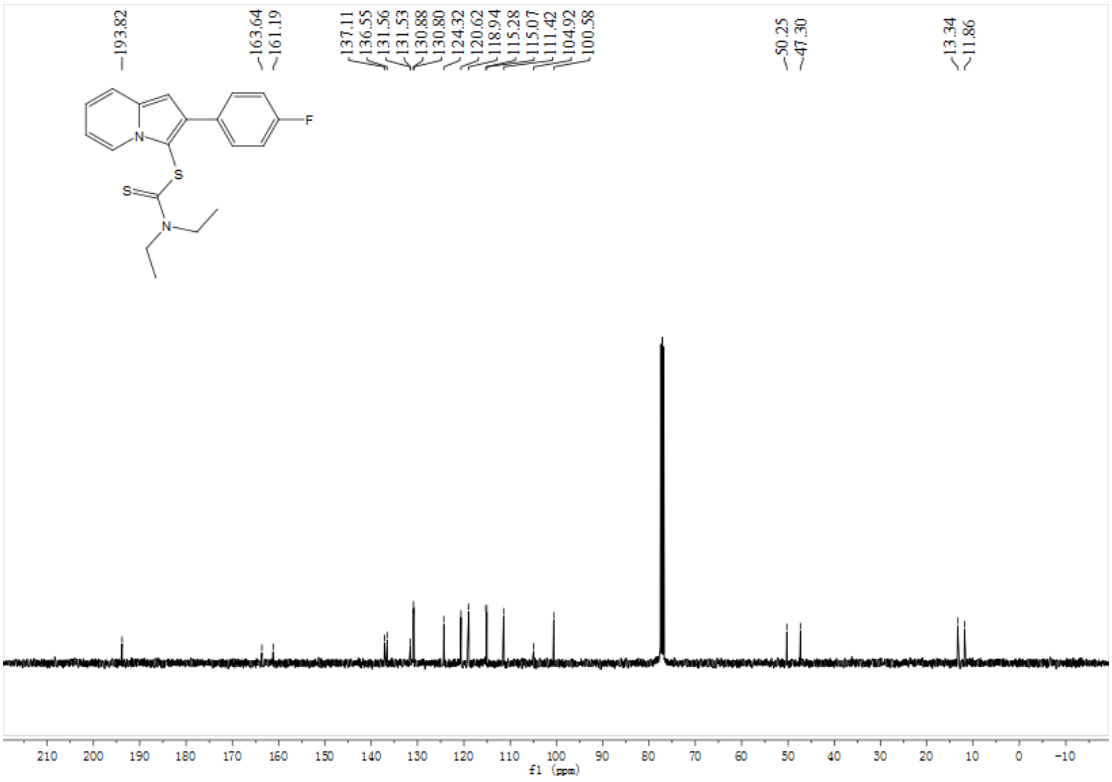
^{1}H NMR and ^{13}C NMR spectrum of compound **5c**



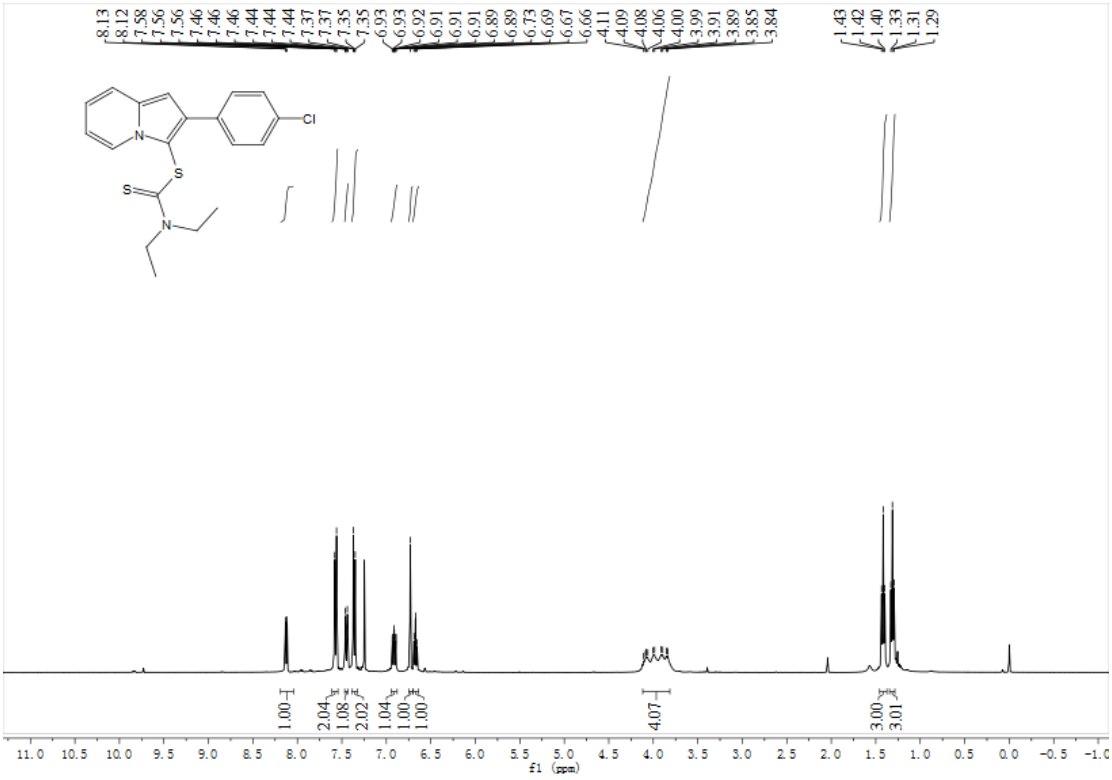


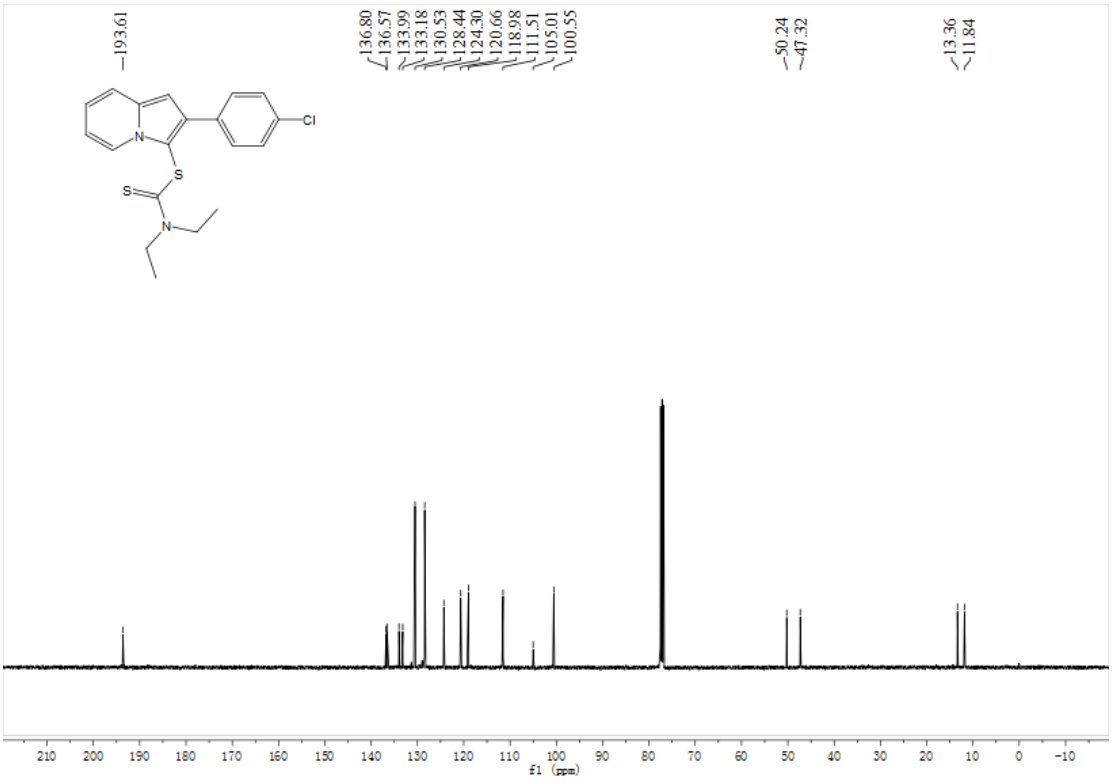
^{1}H NMR and ^{13}C NMR spectrum of compound **5d**



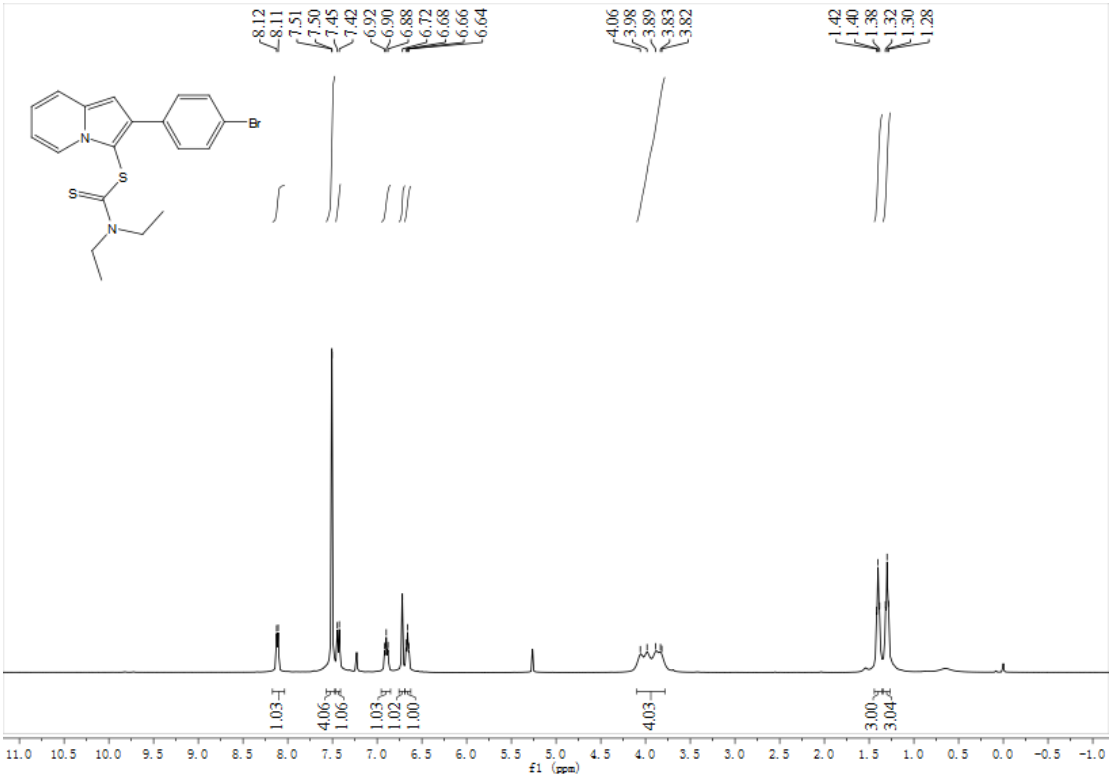


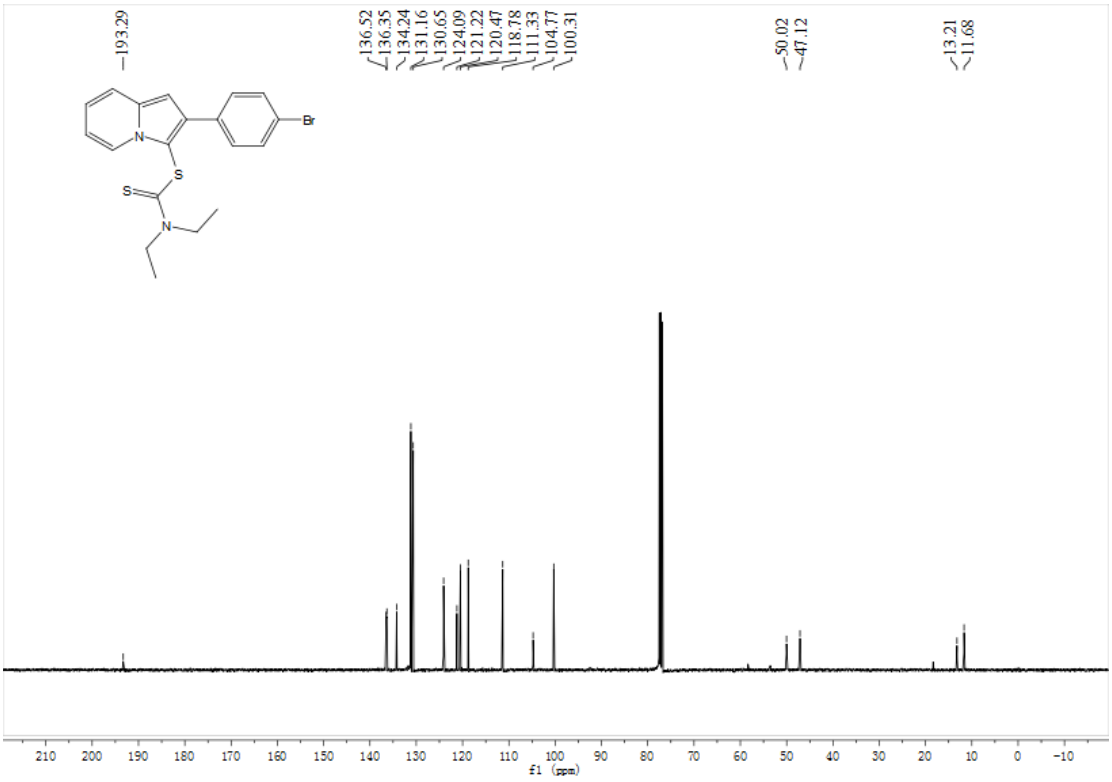
^{1}H NMR and ^{13}C NMR spectrum of compound **5e**



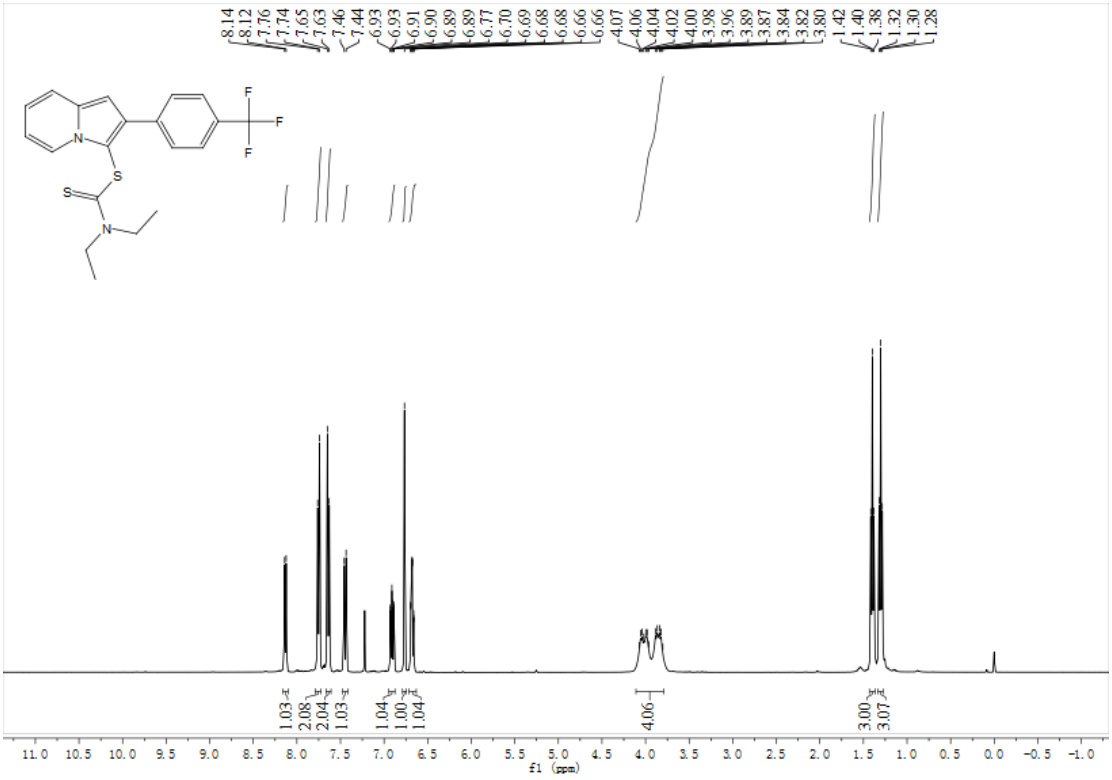


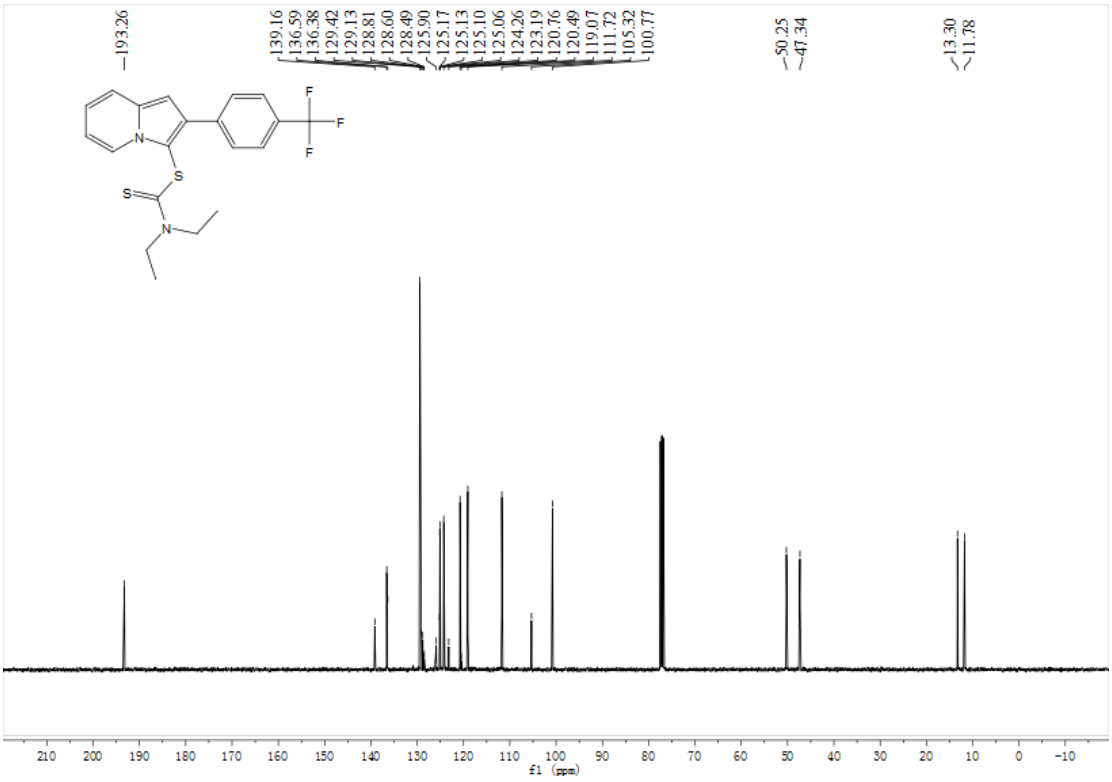
^{1}H NMR and ^{13}C NMR spectrum of compound **5f**



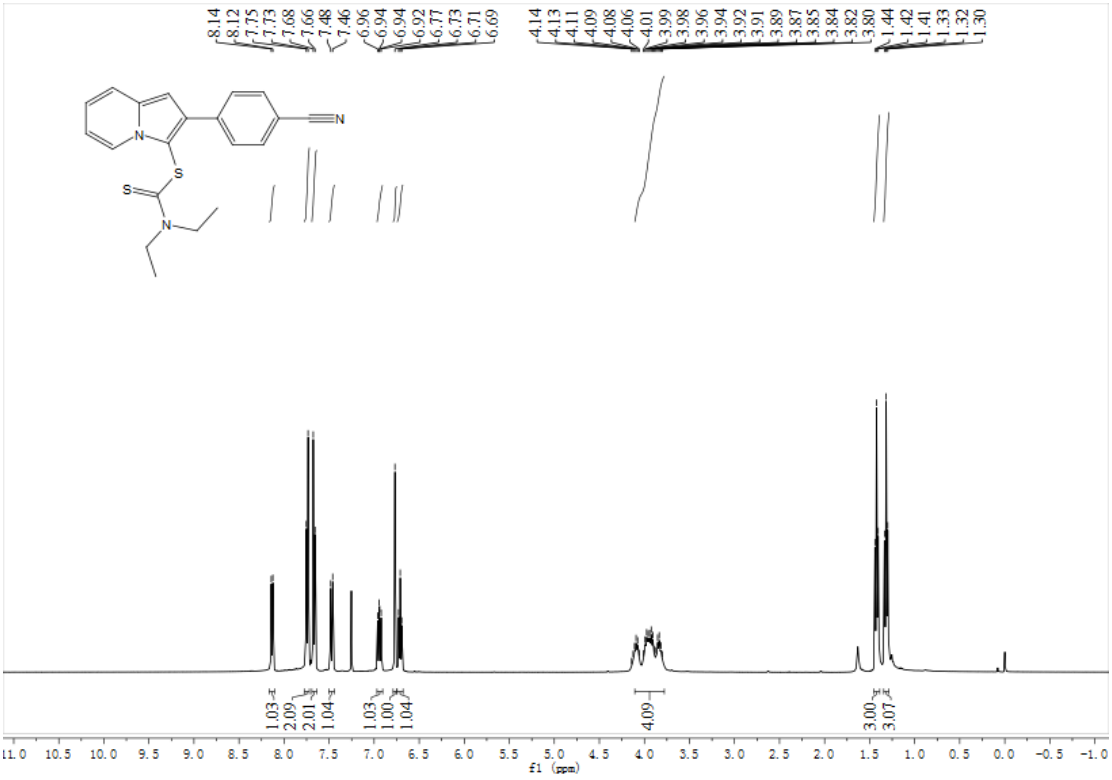


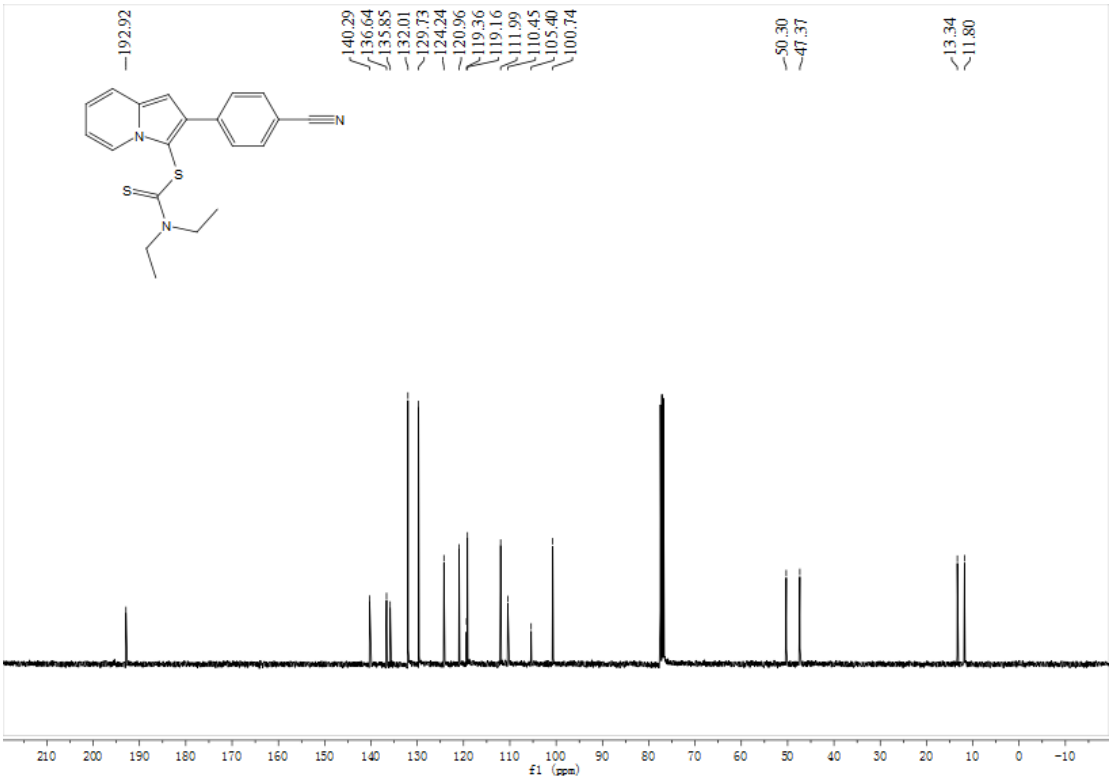
^{1}H NMR and ^{13}C NMR spectrum of compound **5g**



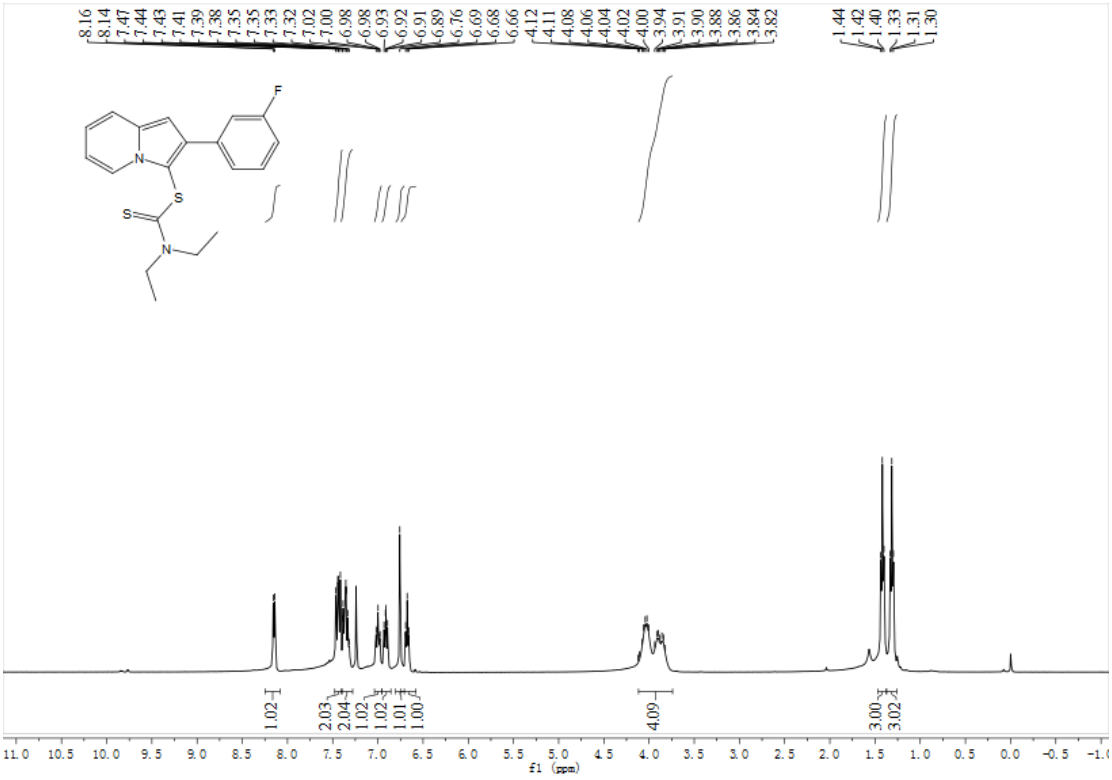


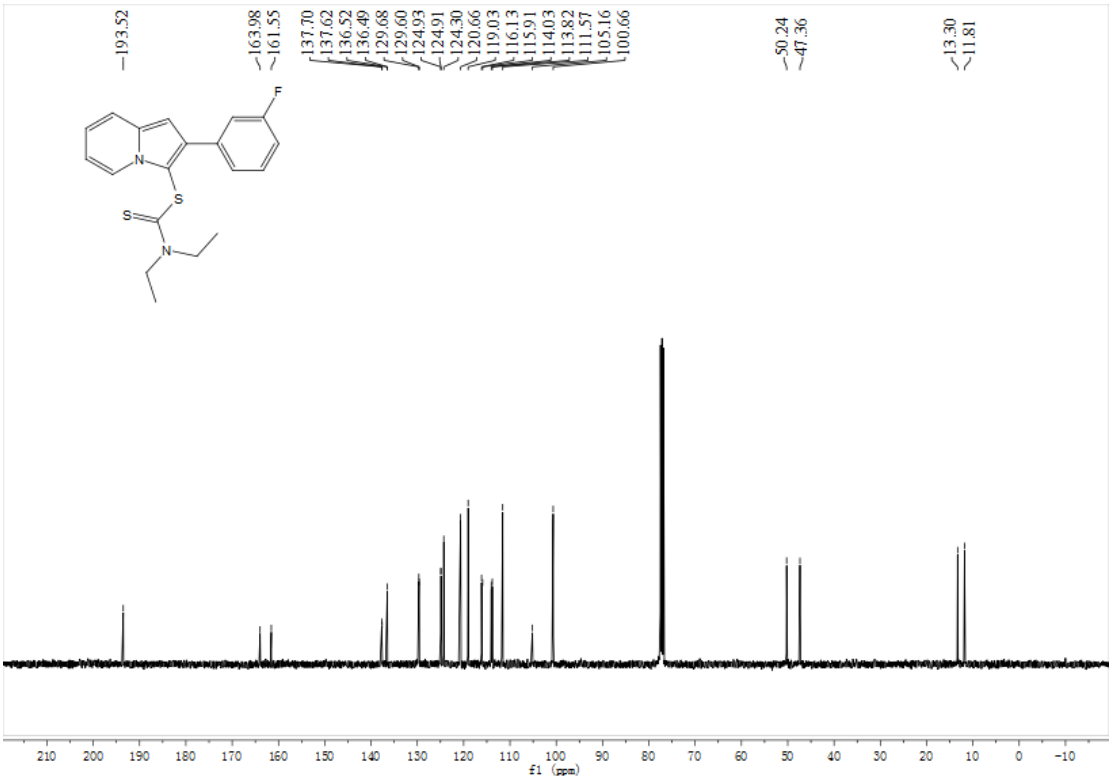
^{1}H NMR and ^{13}C NMR spectrum of compound **5h**



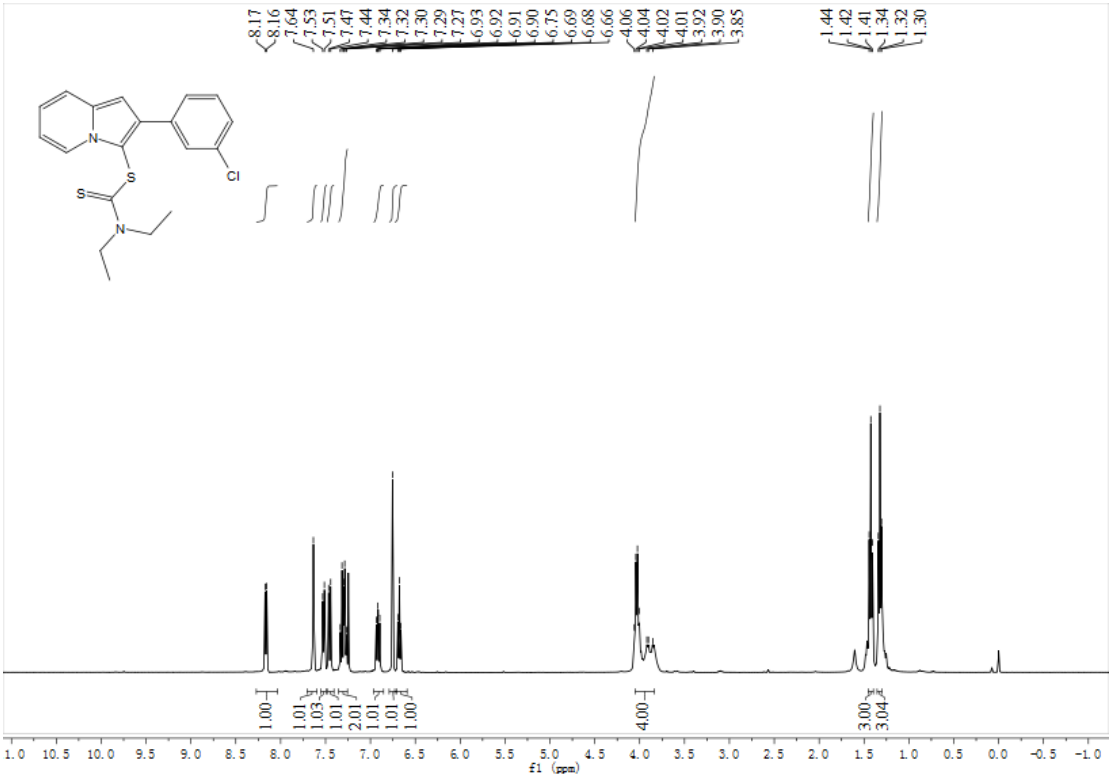


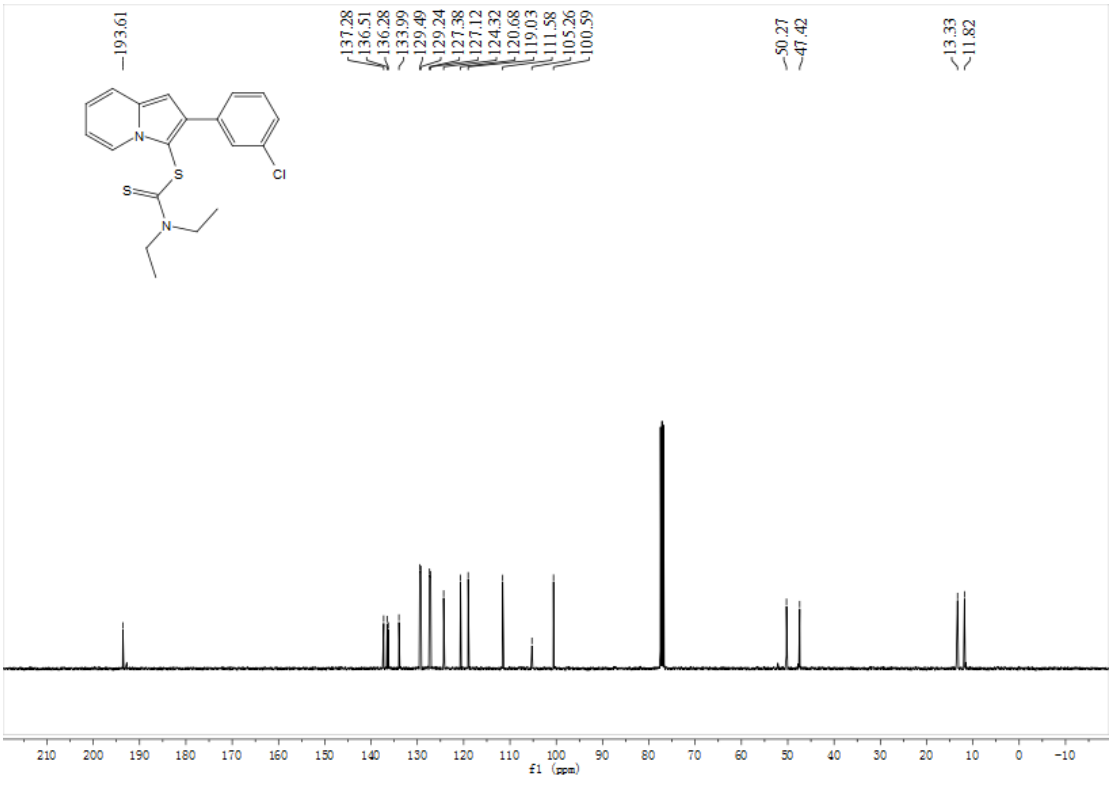
^{1}H NMR and ^{13}C NMR spectrum of compound **5i**



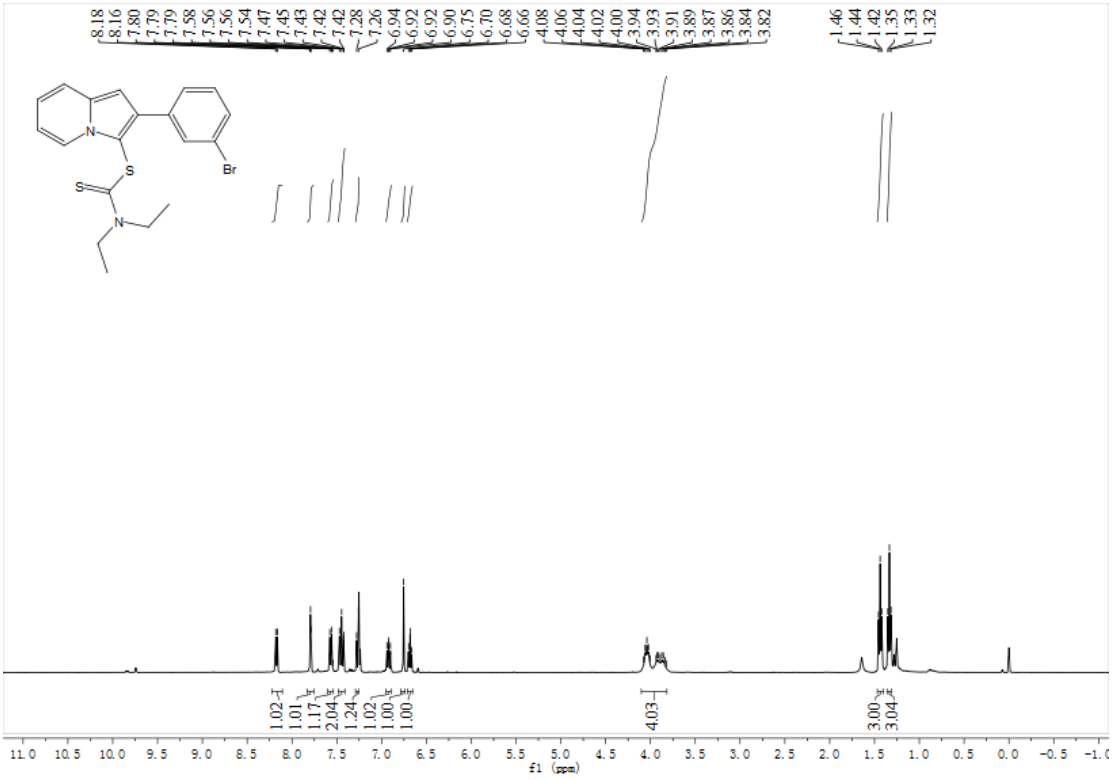


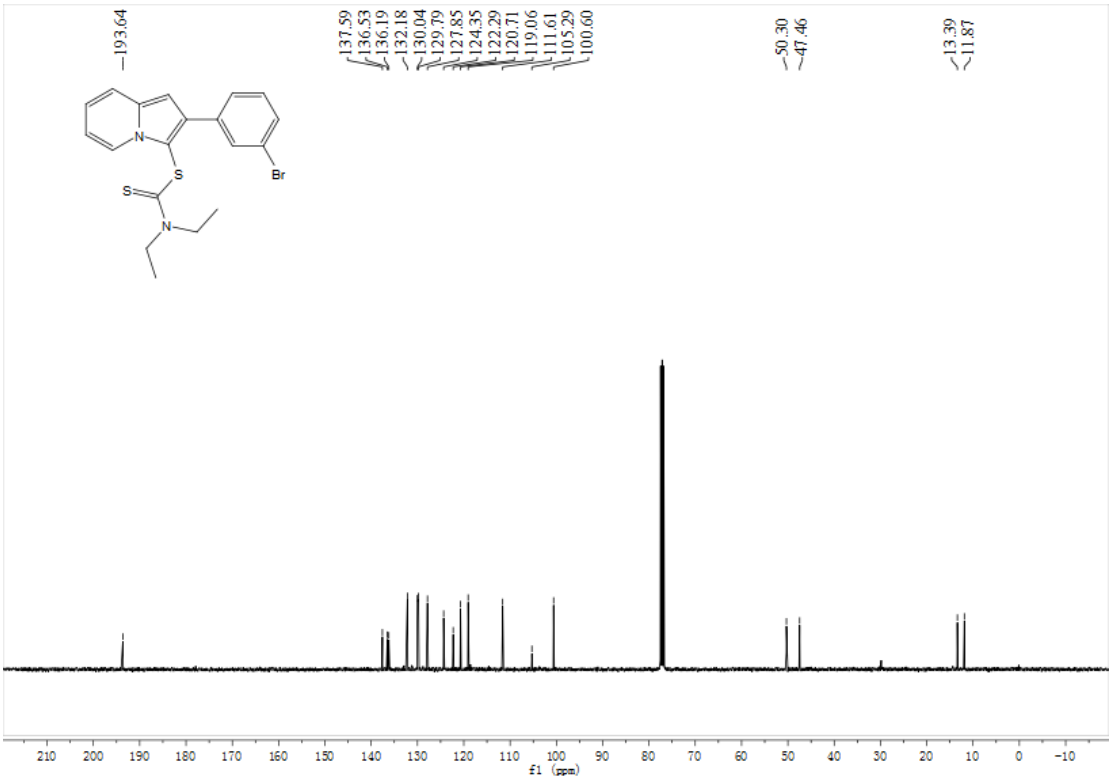
^{1}H NMR and ^{13}C NMR spectrum of compound **5j**



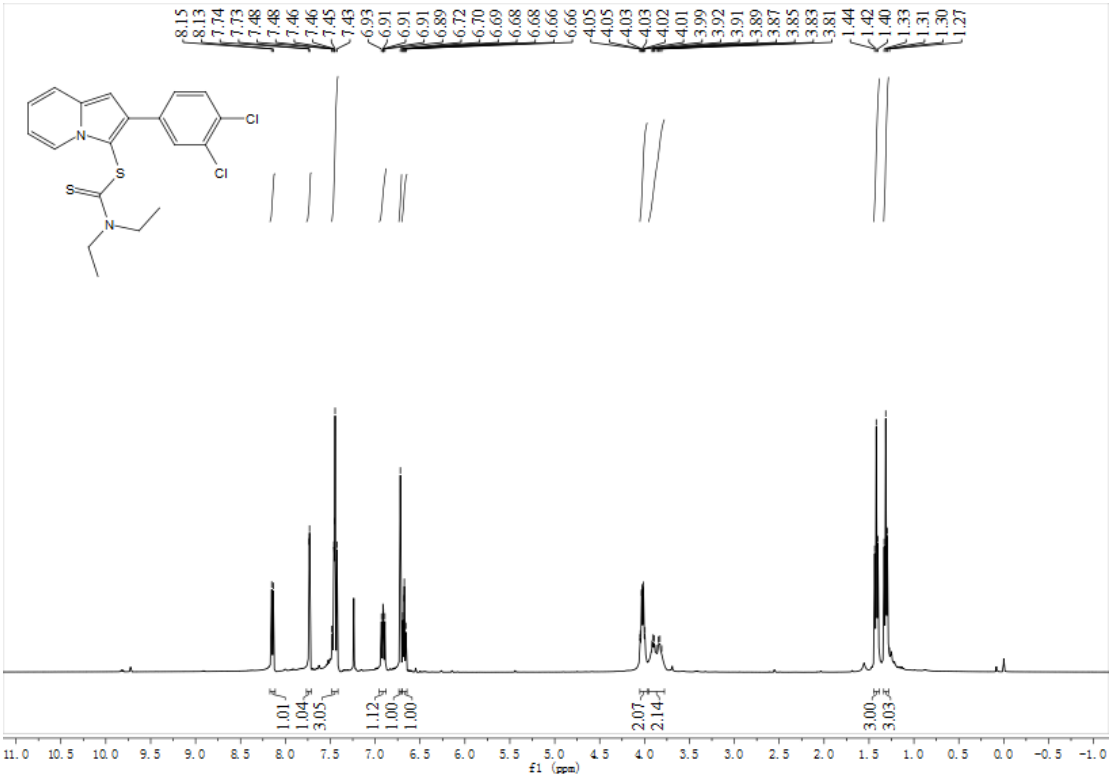


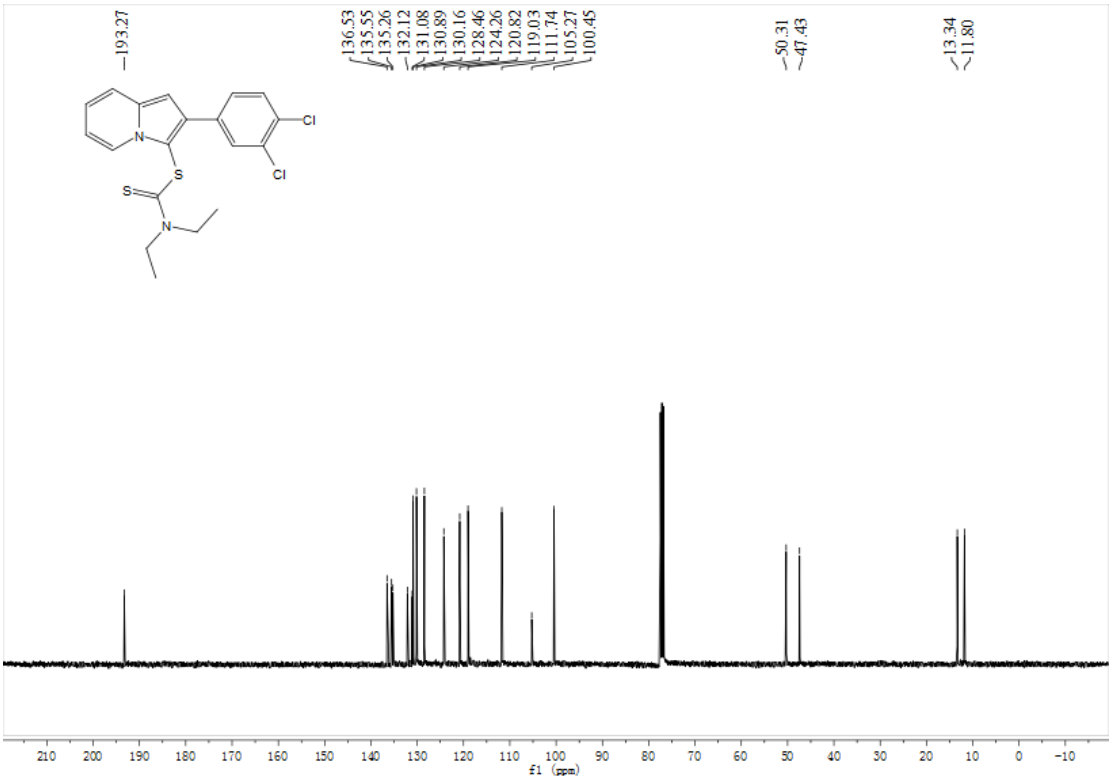
^{1}H NMR and ^{13}C NMR spectrum of compound **5k**



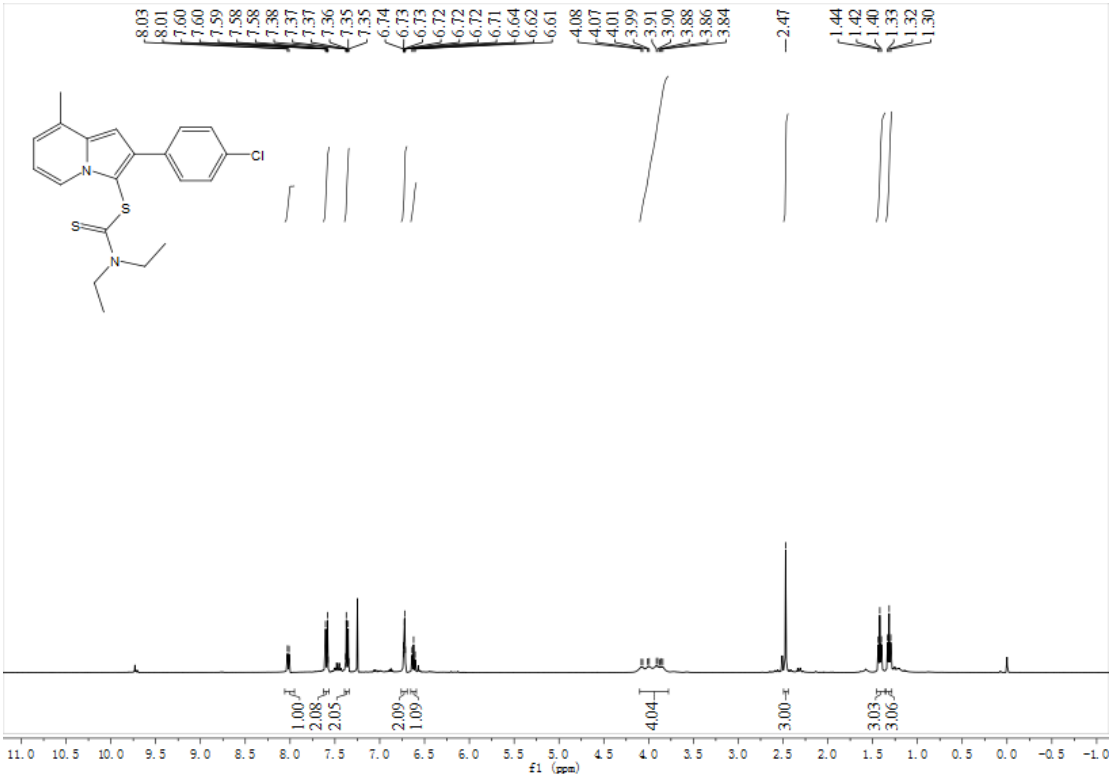


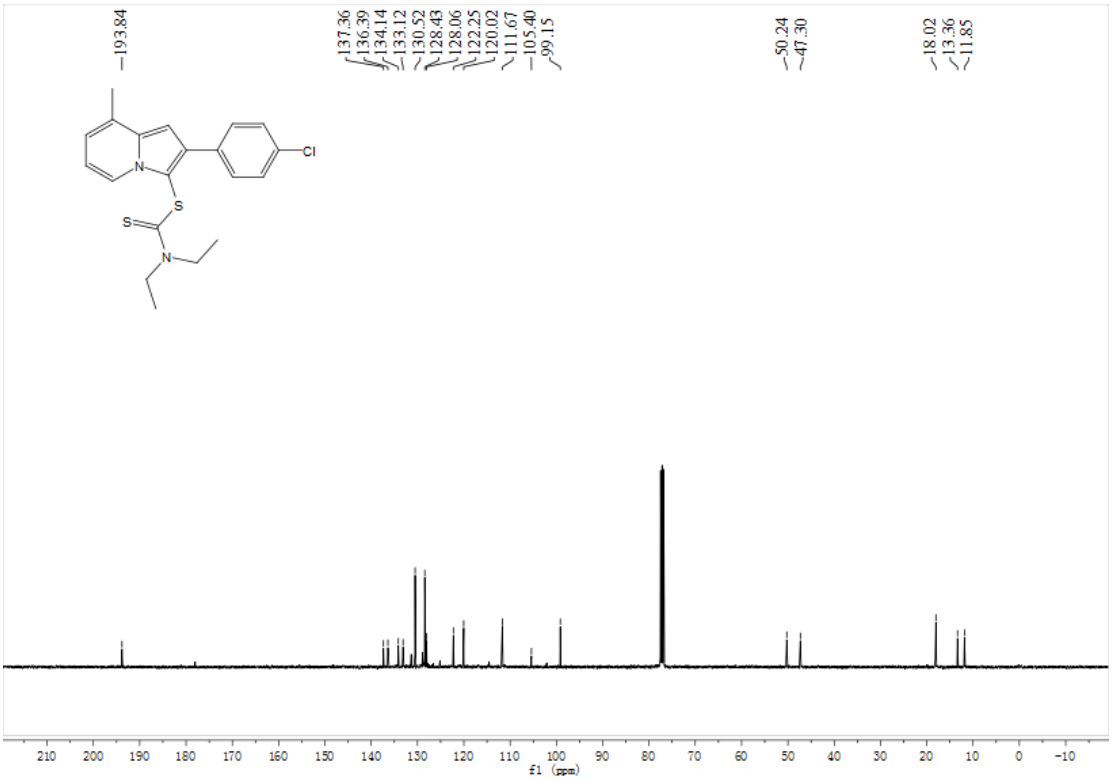
^{1}H NMR and ^{13}C NMR spectrum of compound **5l**



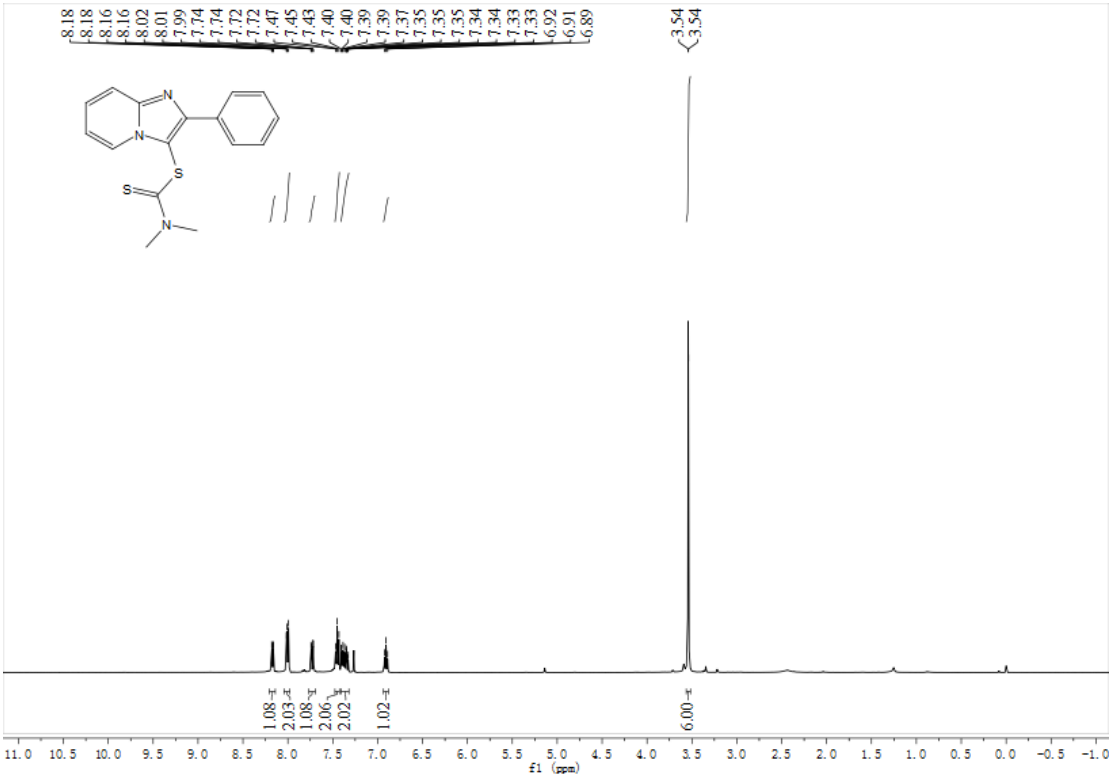


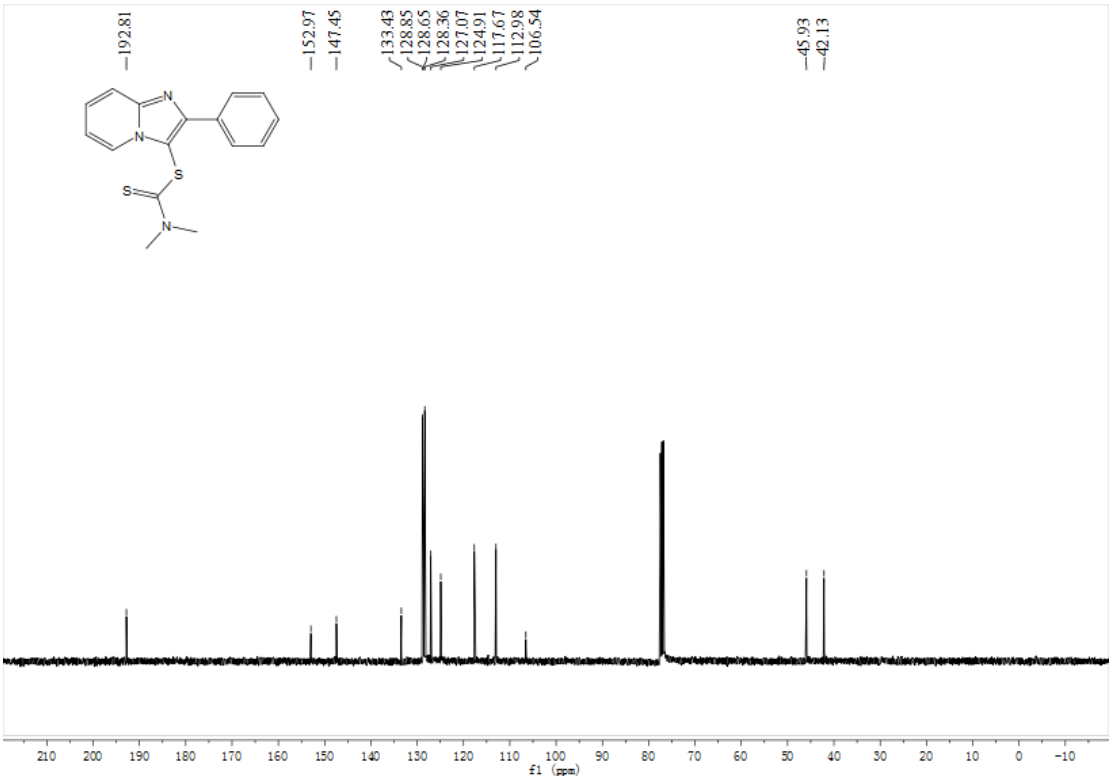
^{1}H NMR and ^{13}C NMR spectrum of compound **5m**



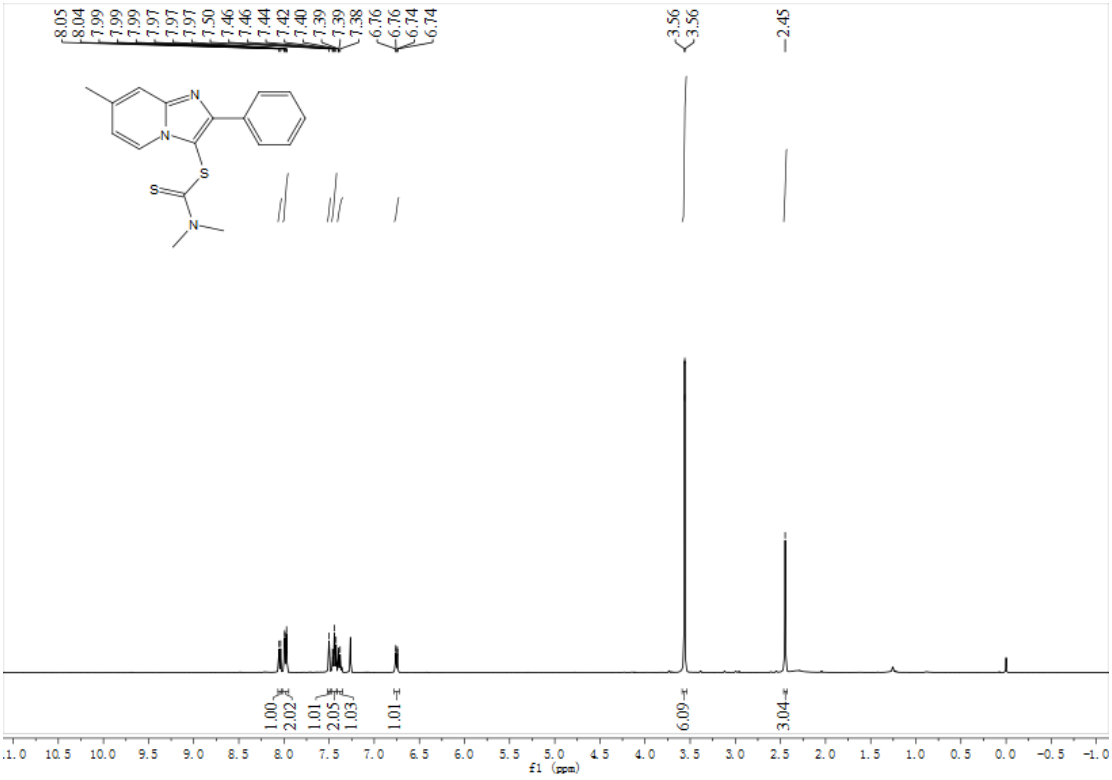


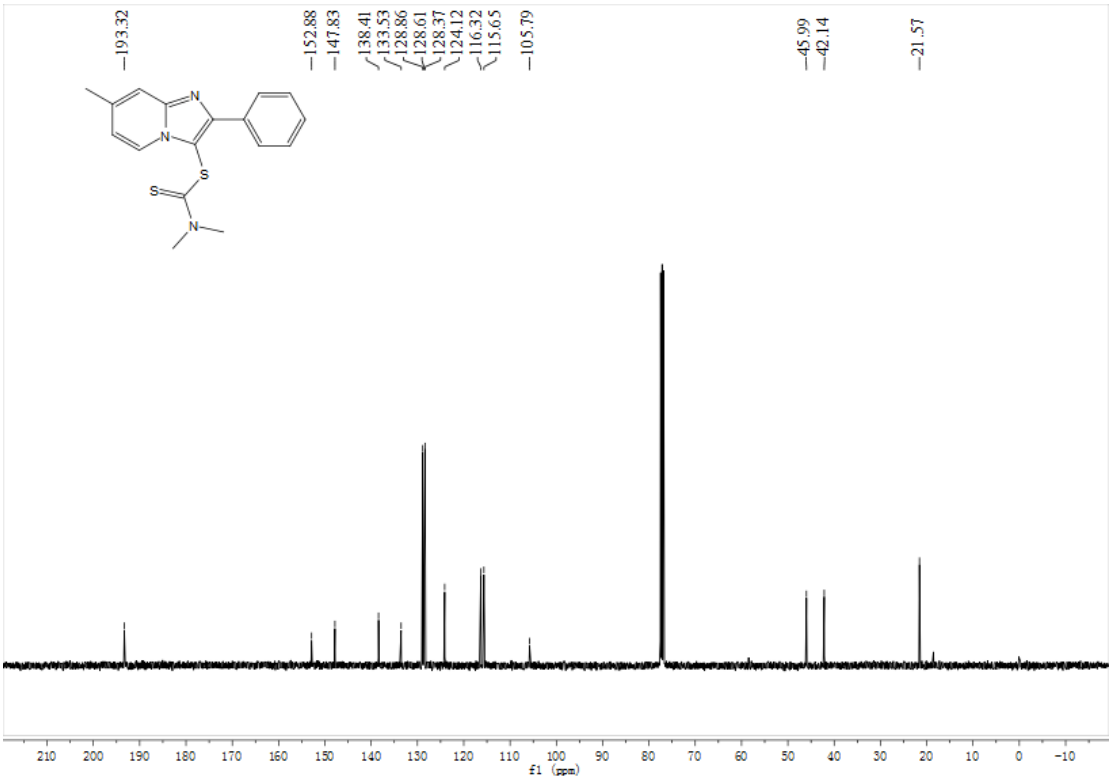
^{1}H NMR and ^{13}C NMR spectrum of compound **7a**



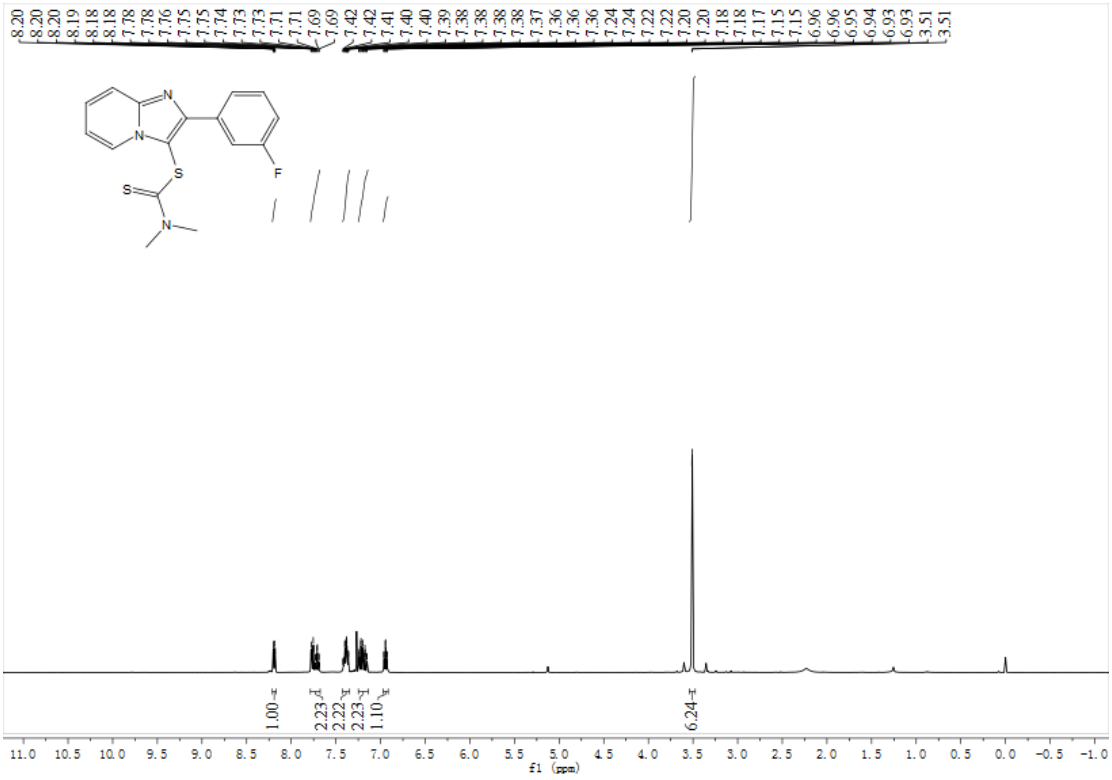


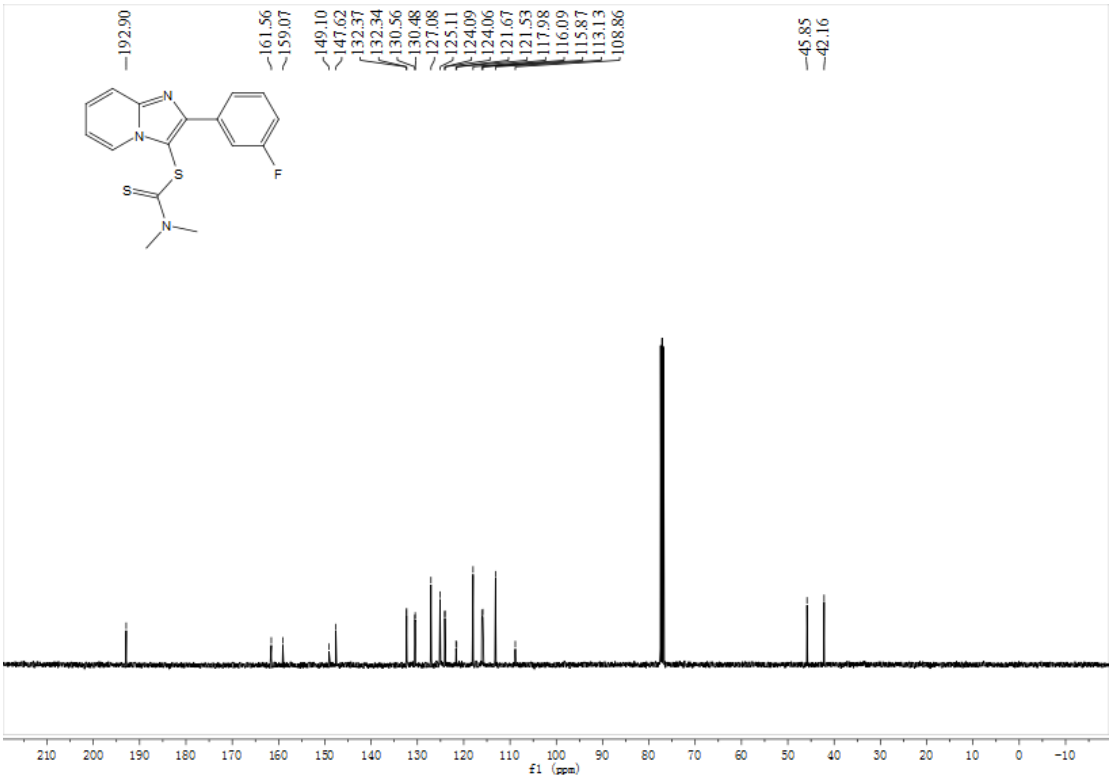
^{1}H NMR and ^{13}C NMR spectrum of compound **7b**



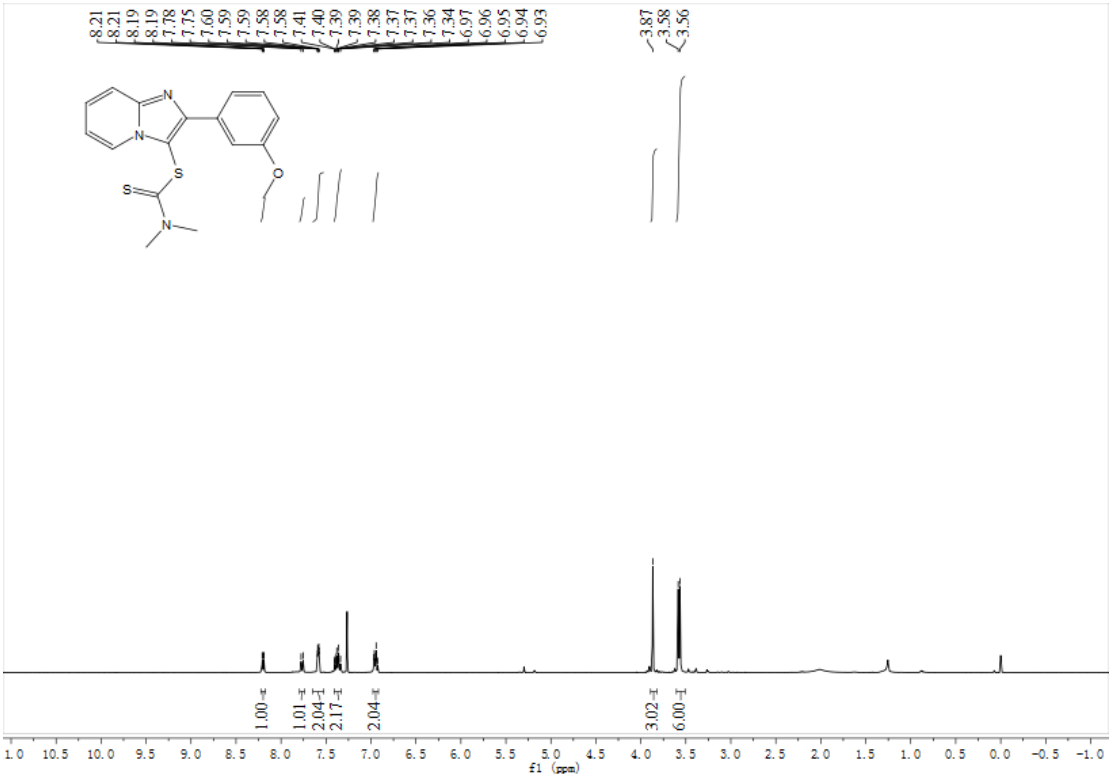


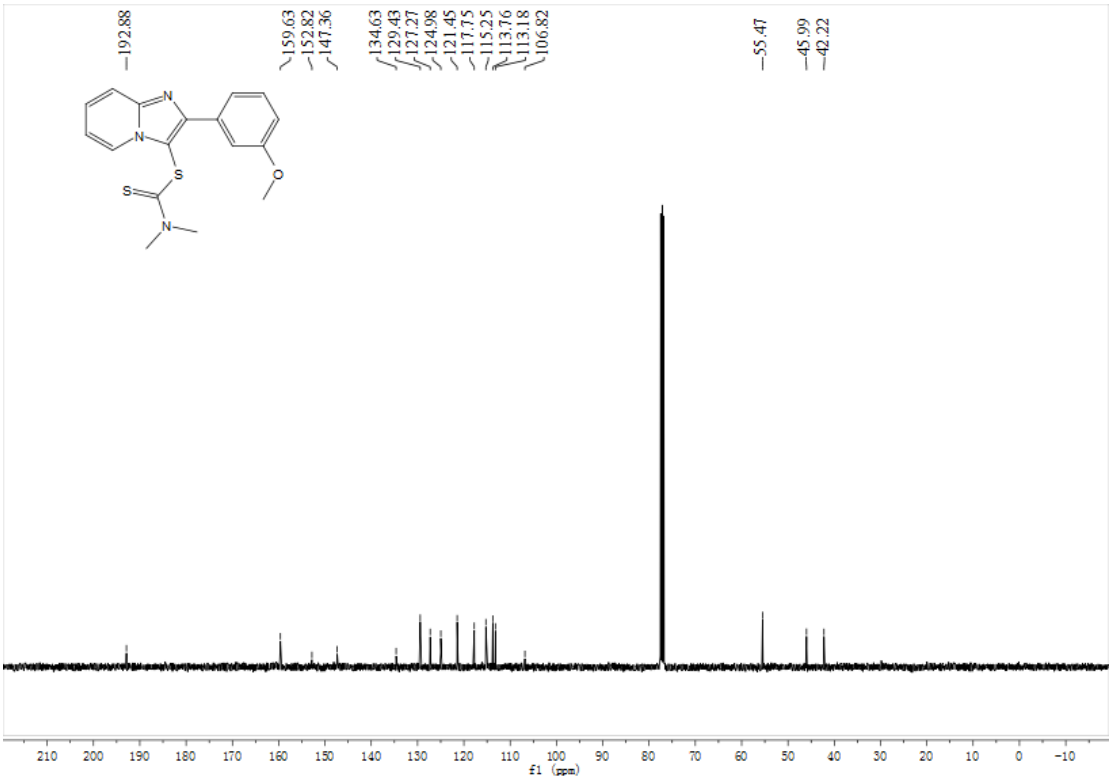
^{1}H NMR and ^{13}C NMR spectrum of compound **7c**





^{1}H NMR and ^{13}C NMR spectrum of compound **7d**





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