Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Metal-free Direct Thiocarbamation of Imidazopyridines with Carbamyl Chloride and Elemental Sulphur

Jian-Chao Deng, Shi-Bin Zhuang, Quan-Zhu Liu, Zi-Wei Lin, Yu-Liang Su, Jia-Hao Chen, Ri-Yuan Tang*

Department of Applied Chemistry, College of Materials and Energy, South China Agricultural University, Guangzhou 510642, China.

rytang@scau.edu.cn

List of Contents

1. General Information

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-III 600 instrument (600 MHz for ^{1}H, 151 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ as the solvent. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on an Agilent GC-MS-5975C Plus spectrometer (EI). LCMS (ESI) analysis was measured on an AB SCIEX, API3200. HRMS (ESI) analysis was measured on a Thermo Scientific LTQ Orbitrap XL. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

2. Experimental Procedure

(1) Typical experimental procedure for the dual C–H thiolation

To a 15-mL tube with a Teflon cap, equipped with a magnetic stirring bar was charged with **1a** (0.2 mmol), S_8 (0.4 mmol, 2 equiv), carbamyl chloride (0.4 mmol, 2 equiv), DABCO (0.4 mmol, 2 equiv) in CH_3CN (2 mL). The reaction mixture was stirred at 120 ℃ for 24 hours. After the reaction finished, the mixture was extracted with ethyl acetate, the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography (petroleum ether / ethyl acetate) to afford the desired product.

3. The data of products

***S*-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate** (**3**)

White solid, mp: 172.1 – 174.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.7 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.36 – 7.30 (m, 1H), 6.92 (t, *J* = 6.7 Hz, 1H), 3.21 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 151.9, 147.4, 133.6, 128.9, 128.4, 128.3, 126.4, 124.7, 117.7, 112.8, 103.9, 37.2. IR (KBr, cm^{-1}): 3055, 3022, 2922, 1666, 1627, 1474, 1341, 1097, 776, 762, 703. LRMS (EI, 70eV) m/z (%): 297 (21), 225 (20), 181 (9), 78 (30), 72 (100). HRMS (ESI) m/z calcd for $C_{16}H_{16}N_3OS^+$ $(M+H)^+$ 298.1008, found 298.1006.

***S*-8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate** (**4**)

Yellow solid, mp: 152.5 – 153.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 6.6 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 6.6 Hz, 1H), 6.85 (t, *J* = 6.7 Hz, 1H), 3.22 (s, 3H), 3.03 (s, 3H), 2.70 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 151.7, 147.7, 133.9, 129.0, 128.2, 128.2, 127.7, 125.2, 122.5, 112.8, 104.1, 37.1, 16.9. IR (KBr, cm^{-1}): 2984, 2943, 2916, 1849, 1665, 1471, 1445, 1355, 1257, 1096, 775, 754, 701. LRMS (EI, 70 eV) m/z (%): 311(26), 239 (29), 195 (8), 92 (24), 72 (100). HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3OS^+$ $(M+H)^+$ 312.1165, found 312.1161.

***S*-6-methoxy-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate** (**5**)

White solid, mp: 139.9 – 141.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.03 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.63 (dd, *J* = 7.4, 2.4 Hz, 1H), 3.90 (s, 3H), 3.22 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 159.4, 151.7, 148.8, 133.7, 128.6, 128.2, 125.1, 107.6, 102.4, 95.2, 55.7, 37.1. IR (KBr, cm^{-1}): 3096, 3010, 2925, 2828, 1668, 1645, 1533, 1438, 1355, 1252, 1214, 1183, 1093, 1021, 958, 831, 774, 694, 678, 571. LRMS (EI,

70 eV) m/z (%): 327(35), 255 (93), 240 (18), 211 (12), 108 (46), 93 (10), 72 (100). HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2S^+$ $(M+H)^+$ 328.1114, found 328.1112.

***S*-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (6)**

White solid, mp: 138.4 – 139.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.90 (t, *J* = 6.7 Hz, 1H), 3.86 (s, 3H), 3.22 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 159.8, 151.8, 147.3, 130.0, 126.3, 126.2, 124.6, 117.4, 113.7, 112.7, 103.0, 55.3, 37.1. IR (KBr, cm^{-1}): 3075, 3031, 2925, 2823, 1664, 1609, 1532, 1476, 1343, 1245, 1172, 1097, 1038, 837, 760, 740. LRMS (EI, 70eV) m/z (%): 327 (28), 255 (31), 240 (9), 211 (10), 78 (33), 72 (100). HRMS (ESI) m/z calcd for $C_{17}H_{18}N_3O_2S^+$ $(M+H)^+$ 328.1114, found 328.1110.

***S*-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (7)**

Light yellow solid, mp: 163.7 – 165.5 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 6.8 Hz, 1H), 8.05 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.36 – 7.33 (m, 1H), 7.16 (t, *J* = 8.7 Hz, 2H), 6.94 (t, *J* = 6.6 Hz, 1H), 3.23 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.9, 163.0 (d, $J_{C\text{-}F}$ = 248.0 Hz, 1C), 151.1, 147.3, 133.6 (d, $J_{C\text{-}F}$ = 8.2 Hz, 1C), 129.8, 126. 6, 124.7, 117.6, 115.2 (d, $J_{C\text{-}F}$ = 21.5 Hz, 1C), 112.9, 103.7, 37.1. IR (KBr, cm^{-1}): 3084, 2928, 1665, 1627, 1471, 1344, 1224, 1162, 1097, 847, 797, 759. LRMS (EI, 70eV) m/z (%): 315 (17), 243 (15), 78 (28), 72 (100). HRMS (ESI) m/z calcd for $C_{16}H_{15}FN_3OS^+$ $(M+H)^+$ 316.0879, found 316.0906.

***S*-6-methyl-2-p-tolylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (8)**

Yellow solid, mp: 162.1 – 162.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 9.1 Hz, 1H), 7.28 (s, 2H), 7.16 (d, *J* = 9.1 Hz, 1H), 3.23 (s, 3H), 3.04 (s, 3H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 151.9, 146.4, 138.0, 131.0, 129.4, 129.3, 129.3, 128.9, 128.6, 122.4, 122.4, 116.9, 103.0, 37.1, 21.4, 18. 4. IR (KBr, cm^{-1}): 3026, 2916, 2855, 1680, 1506, 1475, 1362, 1334, 1245, 1104, 828, 809, 728. LRMS (EI, 70 eV) m/z (%): 325 (38), 253 (55), 209 (11), 92 (27), 72 (100). HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3OS^+$ $(M+H)^+$ 326.1321, found 326.1317.

***S*-2-(4-methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (9)**

Brown solid, mp: 166.5 – 168.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.9 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.43 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 6.8 Hz, 1H), 3.86 (s, 3H), 3.21 (s, 3H), 3.02 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 159.7, 151.7, 147.7, 137.4, 130.0, 126.4, 123.8, 116.0, 115.2, 113.7, 102.2, 55.3, 37.1, 21.4. IR (KBr, cm^{-1}): 3008, 2931, 2837, 1671, 1606, 1468, 1344, 1238, 1180, 1097, 1029, 844, 780. LRMS (EI, 70 eV) m/z (%): 341(47), 169 (100), 225 (14), 92 (37), 72 (94), 65 (15). HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3O_2S^+$ $(M+H)^+$ 342.1270, found 342.1267.

***S*-2-(4-methoxyphenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (10)**

Brown solid, mp: 121.5 – 124.2 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 3H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.16 (dd, *J* = 9.1, 1.4 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.24 (s, 3H), 3.04 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 159.8, 151.6, 146.3, 130.0, 129.4, 126.4, 122.4, 122.4, 116.7, 113.7, 102.5, 55.3, 37.1, 18.4. IR (KBr, cm^{-1}): 2993, 2883, 1626, 1485,

1400, 1354, 1255, 1174, 1097, 1003, 833, 787. LRMS (EI, 70 eV) m/z (%): 341 (43), 269 (65), 254 (13), 225(12), 92 (32), 72 (100), 65 (16). HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3O_2S^+$ $(M+H)^+$ 342.1271, found 342.1268.

_S_-6-methoxy-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**11**)
Light yellow solid, mp: 149.8 – 152.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 3H), 6.99 – 6.96 (m, 3H), 6.60 (dd, *J* = 7.4, 2.3 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.20 (s, 3H), 3.01 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 159.7, 159.3, 151.7, 148.8, 129.8, 126.4, 125.0, 113.7, 107.3, 101.4, 95.1, 55.7, 55.3, 37.2, 37.1. IR (KBr, cm^{-1}): 2993, 2928, 2831, 1671, 1645, 1606, 1474, 1353, 1250, 1212, 1171, 1097, 1024, 838, 809. LRMS (EI, 70eV) m/z (%): 357 (27), 285 (100), 270 (15), 108 (39), 72 (48). HRMS (ESI) m/z calcd for $C_{18}H_{20}N_3O_3S^+$ $(M+H)^+$ 358.1219, found 358.1215.

_S_-2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**12**)
Light yellow solid, mp: 162.1 – 163.0 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 3H), 7.58 (d, *J* = 9.1 Hz, 1H), 7.18 (d, *J* = 1.5 Hz, 1H), 7.17 – 7.11 (m, 2H), 3.23 (s, 3H), 3.04 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.0, 162.9 (d, J_{C-F} = 247.7 Hz, 1C), 150.9, 146.3, 130.4 (d, J_{C-F} = 8.2 Hz, 1C), 130.0, 129.6, 122.7, 122.4, 116.9, 115.1 (d, J_{C-F} = 21.4 Hz, 1C), 103.2, 37.2, 37.1, 18.4. IR (KBr, cm^{-1}): 3075, 2922, 1677, 1524, 1471, 1409, 1344, 1215, 1153, 1103, 835, 803. LRMS (EI, 70eV) m/z (%): 329 (19), 257 (21), 92 (23), 72 (100), 65 (11). HRMS (ESI) m/z calcd for $C_{17}H_{17}FN_3OS^+$ $(M+H)^+$ 330.1070, found 330.1069.

_S_-2-(4-cyanophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**13**)
White solid, mp: 183.9 – 185.7 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.02 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 3.26 (s, 3H), 3.05 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.5, 149.2, 146.5, 135.2, 132.9, 132.0, 131.5, 130.1, 129.1, 123.2, 122.4, 119.0, 117.1, 112.3, 104.2, 37.3, 37.2, 18.5. IR (KBr, cm^{-1}): 3061, 2922, 2222, 1680, 1504, 1452, 1339, 1249, 1098, 894, 799. LRMS (EI, 70eV) m/z (%): 336 (12), 264 (10), 92 (17), 72 (100), 65 (10). HRMS (ESI) m/z calcd for $C_{18}H_{17}N_4OS^+$ $(M+H)^+$ 337.1117, found 337.1115.

_S_-2-(4-chlorophenyl)-6-methoxyimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**14**)
White solid, mp: 228.0 – 230.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 7.4, 2.3 Hz, 1H), 3.90 (s, 3H), 3.22 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 159.5, 150.6, 148.8, 134.2, 132.2, 129.8, 128.4, 125.1, 107.8, 102.5, 95.2, 55.7, 37.2. IR (KBr, cm^{-1}): 2966, 2931, 2828, 1671, 1642, 1530, 1350, 1244, 1212, 1171, 1094, 1021, 844, 815. LRMS (EI, 70 eV) m/z (%): 361 (15), 289(24), 253 (15), 108 (31), 72 (100). HRMS (ESI) m/z calcd for $C_{17}H_{17}ClN_3O_2S^+$ $(M+H)^+$ 362.0724, found 362.0722.

_S_-6-fluoro-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**15**)
Light yellow solid, mp: 134.8 – 137.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.65 – 7.63 (m, 1H), 7.22 (dd, *J* = 12.5, 4.9 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 3H), 3.22 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 160.0, 153.6 (d, J_{C-F} = 237.7 Hz, 1C), 152.8, 144.8, 130.0, 126.0, 118.2, 118.0, 117.8 (d, J_{C-F} = 8.7 Hz, 1C), 113.8, 111.7 (d, J_{C-}

$_F$ = 41.6 Hz, 1C), 104.8, 55.3, 37.2, 37.1. IR (KBr, cm^{-1}): 3037, 2919, 2849, 1668, 1609, 1536, 1503, 1465, 1362, 1247, 1171, 1088, 1026, 841, 823, 806. LRMS (EI, 70 eV) m/z (%): 345 (19), 273 (13), 229 (11), 96 (22), 72 (100). HRMS (ESI) m/z calcd for $C_{17}H_{17}FN_3O_2S^+$ $(M+H)^+$ 346.1020, found 346.1020.

_S_-2-phenylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**16**)

White solid, mp: 164.2 – 166.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.08 (s, 2H), 7.71 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.30 (m, 4H), 6.93 (s, 1H), 3.64 (s, 2H), 3.53 (s, 2H), 2.07 (s, 2H), 1.94 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5, 151.7, 147.3, 133. 7, 128.9, 128.3, 128.2, 126.4, 124.8, 117.6, 112.8, 104.2, 47.6, 46.4, 25.8, 24.5. IR (KBr, cm^{-1}): 2966, 2872, 1667, 1468, 1365, 1344, 1225, 1159, 891, 838, 751, 734. LRMS (EI, 70eV) m/z (%): 323 (15), 225 (17), 98 (100), 78 (37), 55 (36). HRMS (ESI) m/z calcd for $C_{18}H_{18}N_3OS^+$ $(M+H)^+$ 324.1165, found 324.1161.

_S_-8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**17**)

Yellow solid, mp: 136.0 – 138.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 6.7 Hz, 1H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 6.8 Hz, 1H), 6.84 (t, *J* = 6.8 Hz, 1H), 3.63 (t, *J* = 6.8 Hz, 2H), 3.53 (t, *J* = 6.9 Hz, 2H), 2.70 (s, 3H), 2.06 (p, *J* = 6.8 Hz, 2H), 1.93 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.7, 151.5, 147.6, 134.0, 129.0, 128.2, 128.1, 127.6, 125.1, 122.6, 112.8, 104.4, 47.6, 46.4, 25.8, 24.5, 16.9. IR (KBr, cm^{-1}): 3063, 2952, 2875, 1680, 1492, 1468, 1442, 1353, 1153, 885, 838, 782, 753, 703. LRMS (EI, 70eV) m/z (%): 337 (15), 239 (18), 98 (100), 92 (26), 55 (29). HRMS (ESI) m/z calcd for $C_{19}H_{20}N_3OS^+$ $(M+H)^+$ 338.1322, found 338.1316.

_S_-6-methoxy-2-phenylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**18**)

White solid, mp: 156.1 – 158.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.02 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 2.3 Hz, 1H), 6.63 (dd, *J* = 7.4, 2.5 Hz, 1H), 3.90 (s, 3H), 3.63 (t, *J* = 6.9 Hz, 2H), 3.54 (t, *J* = 6.9 Hz, 2H), 2.10 – 2.03 (m, 2H), 1.94 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9, 159.3, 151.5, 148.7, 133.8, 128.7, 128.2, 125.2, 107.5, 102.7, 100.00, 95.2, 55.7, 47.6, 46.4, 25.8, 24.5. IR (KBr, cm^{-1}): 3061, 2949, 2872, 1659, 1536, 1468, 1356, 1250, 1215, 1180, 1021, 832, 773, 700. LRMS (EI, 70 eV) m/z (%): 353 (29), 255 (34), 224 (11), 207 (13), 108 (31), 98 (100), 55 (31). HRMS (ESI) m/z calcd for $C_{19}H_{20}N_3O_2S^+$ $(M+H)^+$ 354.1271, found 345.1265.

_S_-6-fluoro-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**19**)

Yellow solid, mp: 188.3 – 190.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 9.3, 4.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 2H), 3.87 (s, 3H), 3.64 (t, *J* = 6.6 Hz, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.16 – 2.04 (m, 2H), 1.99 – 1.89 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.1, 160.0, 153.5 (d, $J_{C\text{-}F}$ = 237.2 Hz, 1C), 152.7, 144.7, 130.0, 126.0, 118.0 (d, $J_{C\text{-}F}$ = 25.1 Hz, 1C), 117.7 (d, $J_{C\text{-}F}$ = 8.7 Hz, 1C), 113.8, 111.8 (d, $J_{C\text{-}F}$ = 41.3 Hz, 1C), 105.0, 55.3, 47.7, 46.4, 25.8, 24.5. IR (KBr, cm^{-1}): 3090, 3028, 2972, 2925, 2878, 1665, 1609, 1542, 1503, 1459, 1359, 1241, 1177, 1032, 838, 823, 717. LRMS (EI, 70 eV) m/z (%): 371 (15), 299 (11), 98 (100), 55 (30). HRMS (ESI) m/z calcd for $C_{19}H_{19}FN_3O_2S^+$ $(M+H)^+$ 372.1177, found 372.1173.

_S_-2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**20**)

White solid, mp: 130.3–132.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (t, *J* = 7.0 Hz, 3H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.22 – 7.10 (m, 3H), 3.66 (t, *J* = 6.7 Hz, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H), 2.15 – 2.05 (m, 2H), 2.00 – 1.91 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7 (d, J_{C-F} = 247.7 Hz, 1C), 161.6, 150.8, 146.3, 130.5 (d, J_{C-F} = 8.2 Hz, 1C), 129.6, 122.7, 122.5, 116.9, 115.1 (d, J_{C-F} = 21.4 Hz, 1C), 103.4, 47.7, 46.4, 25.8, 24.5, 18.5. IR (KBr, cm^{-1}): 3081, 2975, 2919, 2878, 1671, 1521, 1456, 1365, 1339, 1156, 847, 797, 729. LRMS (EI, 70 eV) m/z (%): 355 (16), 257 (16), 98 (100), 92 (25), 55 (30). HRMS (ESI) m/z calcd for $C_{19}H_{19}FN_3OS^+$ $(M+H)^+$ 356.1227, found 356.1224.

***S*-2-(4-cyanophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (21)**

Light yellow solid, mp: 165.9 – 168.4 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.36 (d, *J* = 7.9 Hz, 1H), 8.06 (s, 1H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 9.1 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 9.1 Hz, 1H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 2.41 (s, 3H), 2.16 – 2.07 (m, 2H), 1.98 (p, *J* = 6.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 150.3, 147.7, 136.6, 134.3, 133.4, 132.9, 131.5, 130.5, 124.5, 123.9, 120.4, 118.5, 113.7, 105.9, 49.1, 47.9, 27.1, 25.9, 19.8. IR (KBr, cm^{-1}): 3058, 2952, 2922, 2875, 2225, 1680, 1503, 1453, 1371, 1339, 1297, 1247, 1171, 894, 800, 714, 682. LRMS (EI, 70 eV) m/z (%): 362 (9), 264 (7), 98 (100), 92 (23), 55 (28). HRMS (ESI) m/z calcd for $C_{20}H_{19}N_4OS^+$ $(M+H)^+$ 363.1274, found 363.1271.

***S*-2-(4-chlorophenyl)-6-methoxyimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (22)**

Yellow solid, mp: 182.7 – 184.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 6.4 Hz, 1H), 8.01 (d, *J* = 7.0 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 2H), 6.96 (s, 1H), 6.62 (d, *J* = 5.4 Hz, 1H), 3.88 (s, 3H), 3.61 (s, 2H), 3.52 (s, 2H), 2.12 – 1.85 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 159.4, 150.4, 148.7, 134.1, 132.3, 129.8, 128.4, 125.2, 107.7, 102.8, 95.1, 55.7, 47.6, 46.4, 25.8, 24.5. IR (KBr, cm^{-1}): 2972, 2928, 2881, 1668, 1642, 1457, 1364, 1246, 1211, 1173, 1080, 1016, 817, 784, 728. LRMS (EI, 70 eV) m/z (%): 387 (13), 281 (17), 254 (10), 207 (44), 108 (31), 98 (100), 73 (12), 55 (31). HRMS (ESI) m/z calcd for $C_{19}H_{19}ClN_3O_2S^+$ $(M+H)^+$ 388.0881, found 388.0885.

***S*-6-phenylimidazo[2,1-*b*]thiazol-5-yl dimethylcarbamothioate (23)**

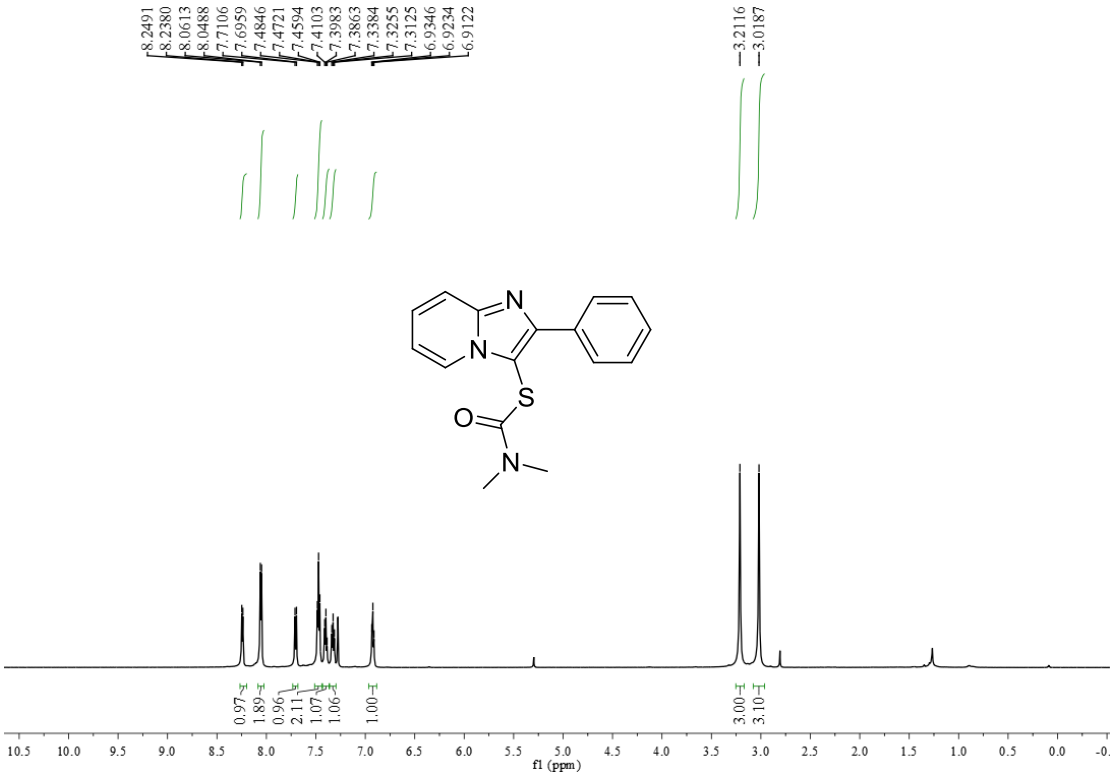
Brown solid, mp: 156.2 – 158.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.1 Hz, 3H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.89 (d, *J* = 4.2 Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 152.9, 151.7, 133.6, 128.3, 128.1, 128.0, 118.5, 112. 7, 104.9, 100.0, 37.2. IR (KBr, cm^{-1}): 3131, 3084, 2960, 2916, 1665, 1539, 1436, 1365, 1253, 1103, 906, 853, 776, 726, 703. LRMS (EI, 70eV) m/z (%): 303 (16), 187 (13), 77 (8), 72 (100). HRMS (ESI) m/z calcd for $C_{14}H_{14}N_3OS_2^+$ $(M+H)^+$ 304.0572, found 304.0570.

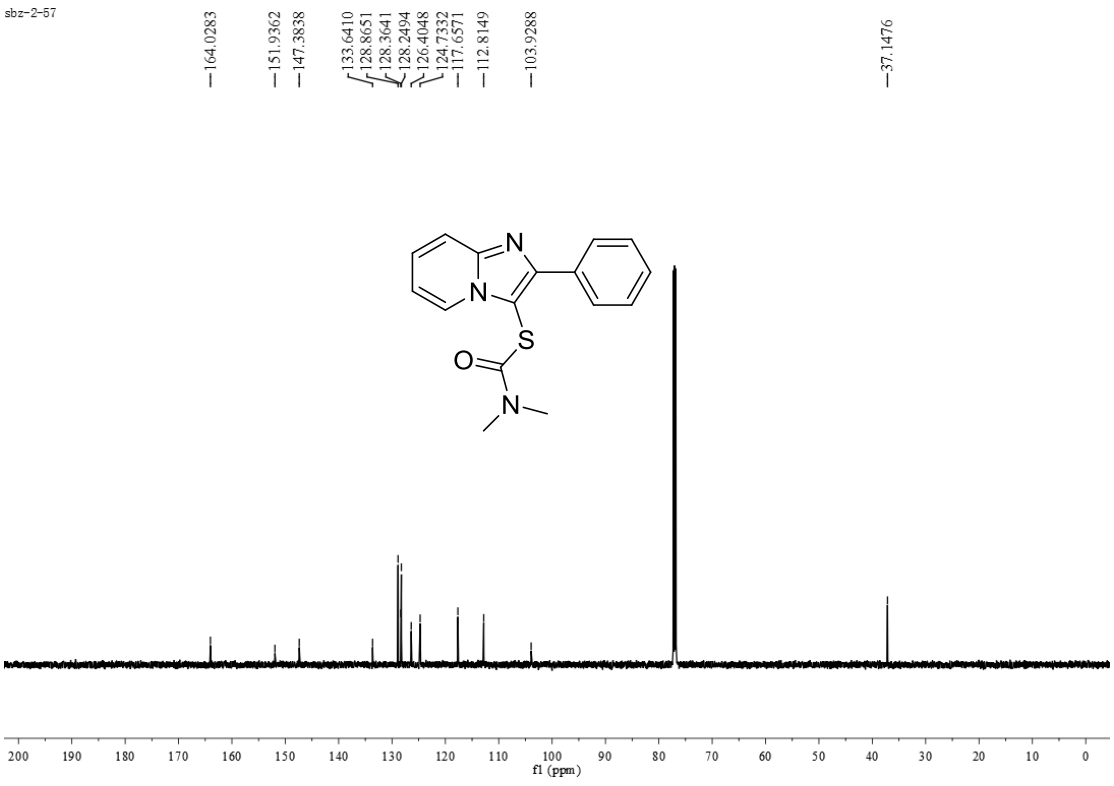
***S*-6-(4-fluorophenyl)imidazo[2,1-*b*]thiazol-5-yl dimethylcarbamothioate (24)**

Yellow solid, mp: 157.8 – 160.1 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.43 (d, *J* = 4.4 Hz, 1H), 7.12 (t, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 4.4 Hz, 1H), 3.18 (s, 3H), 3.04 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 162.7 (d, J_{C-F} = 247.5 Hz, 1C), 152.2, 151.7, 129.7 (d, J_{C-F} = 8.1 Hz, 1C), 118.4, 115.2 (d, J_{C-F} = 21.5 Hz, 1C), 112.7, 104.6, 37.2, 37.1. IR (KBr, cm^{-1}): 3134, 3105, 3061, 2919, 1662, 1524, 1462, 1368, 1256, 1224, 1106, 829, 717. LRMS (EI, 70 eV) m/z (%): 321 (12), 205 (14), 95 (5), 72 (100). HRMS (ESI) m/z calcd for $C_{14}H_{13}FN_3OS_2^+$ $(M+H)^+$ 322.0479, found 322.0475.

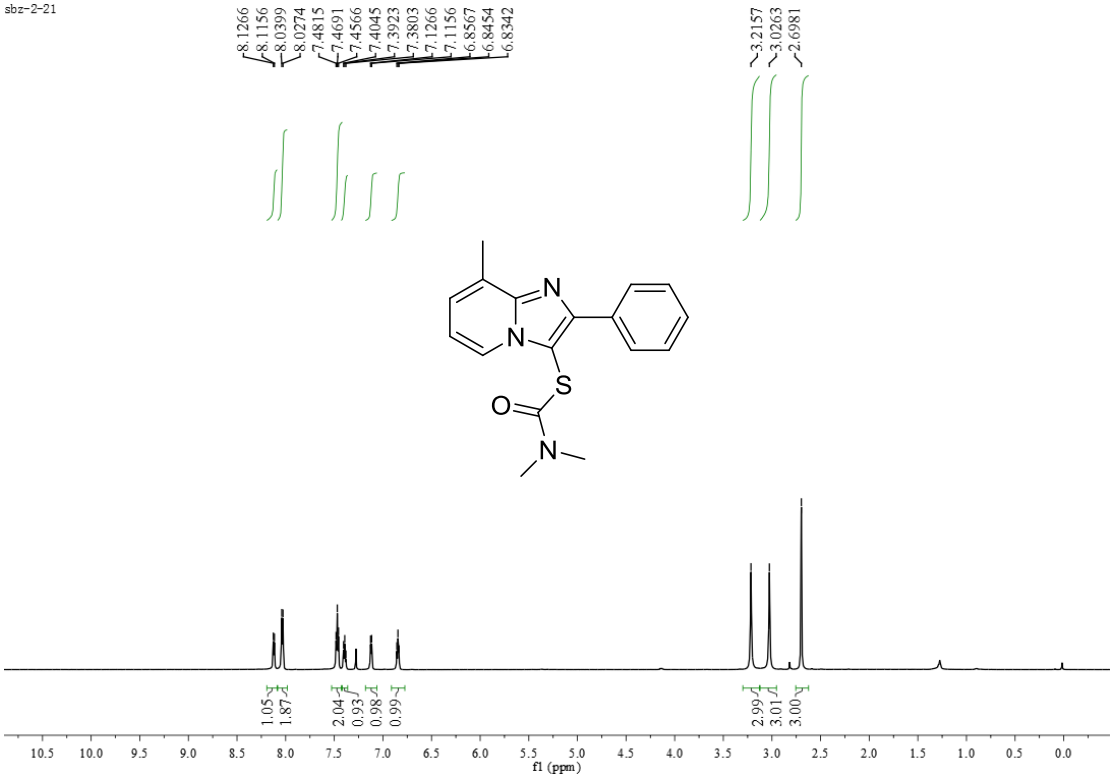
4. NMR Spectra for products

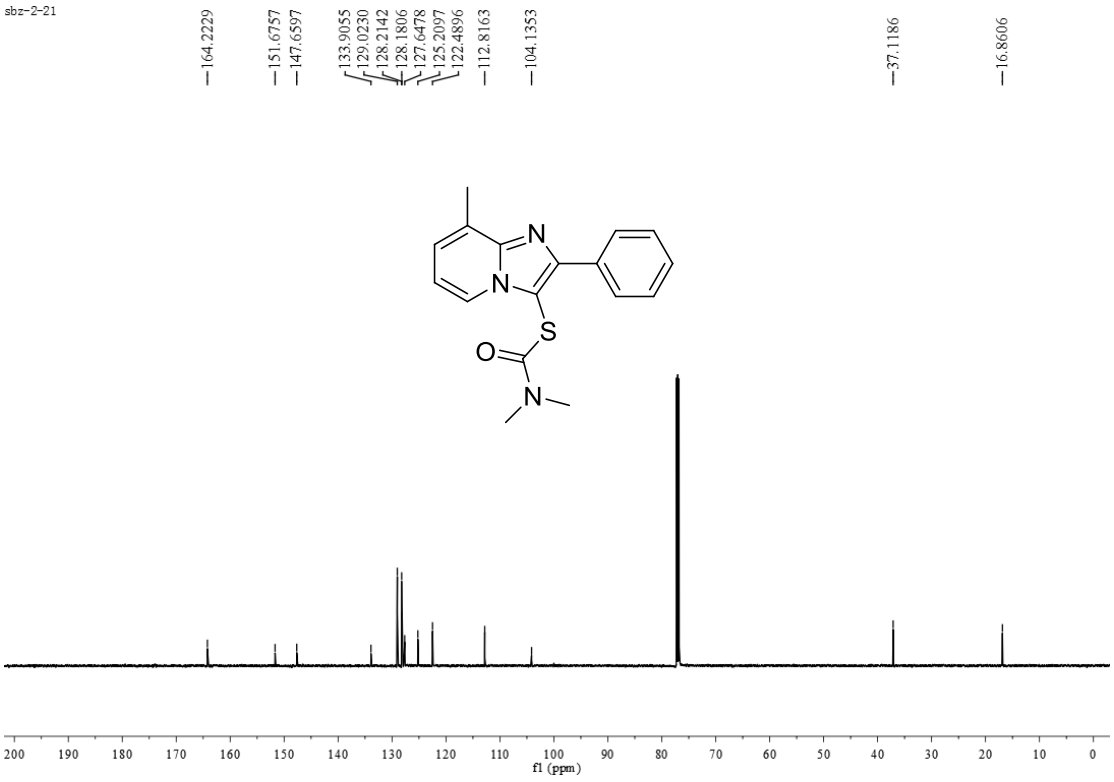
S-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (3)



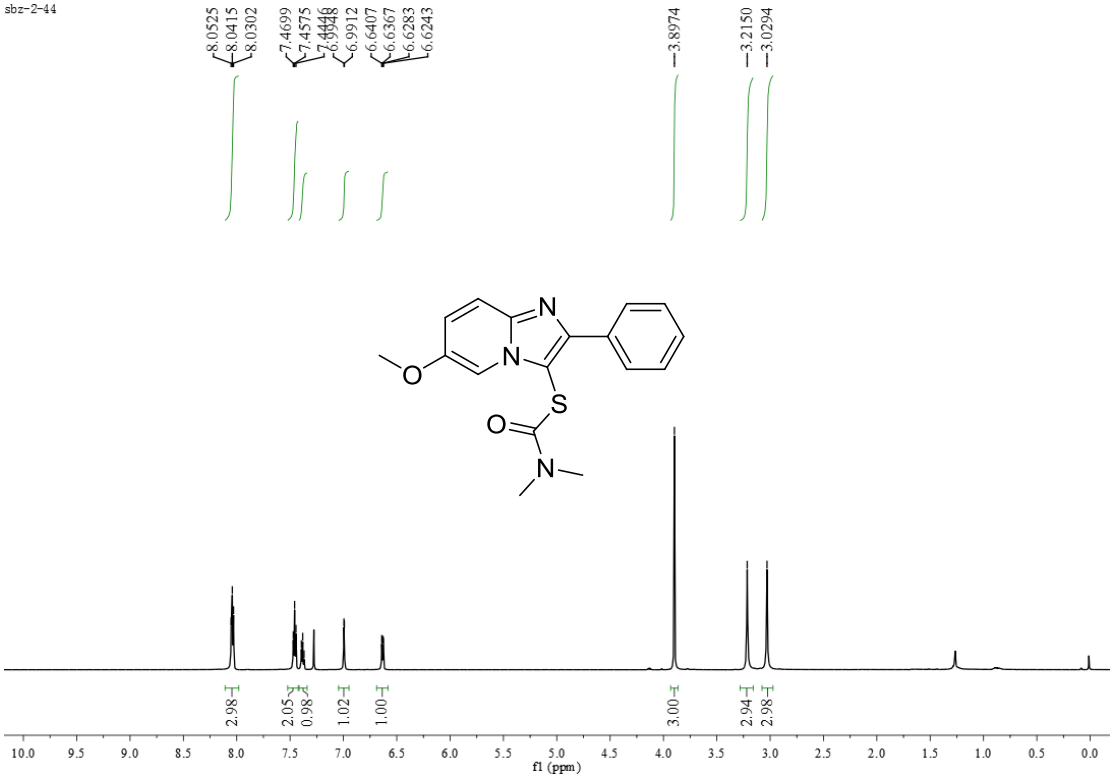


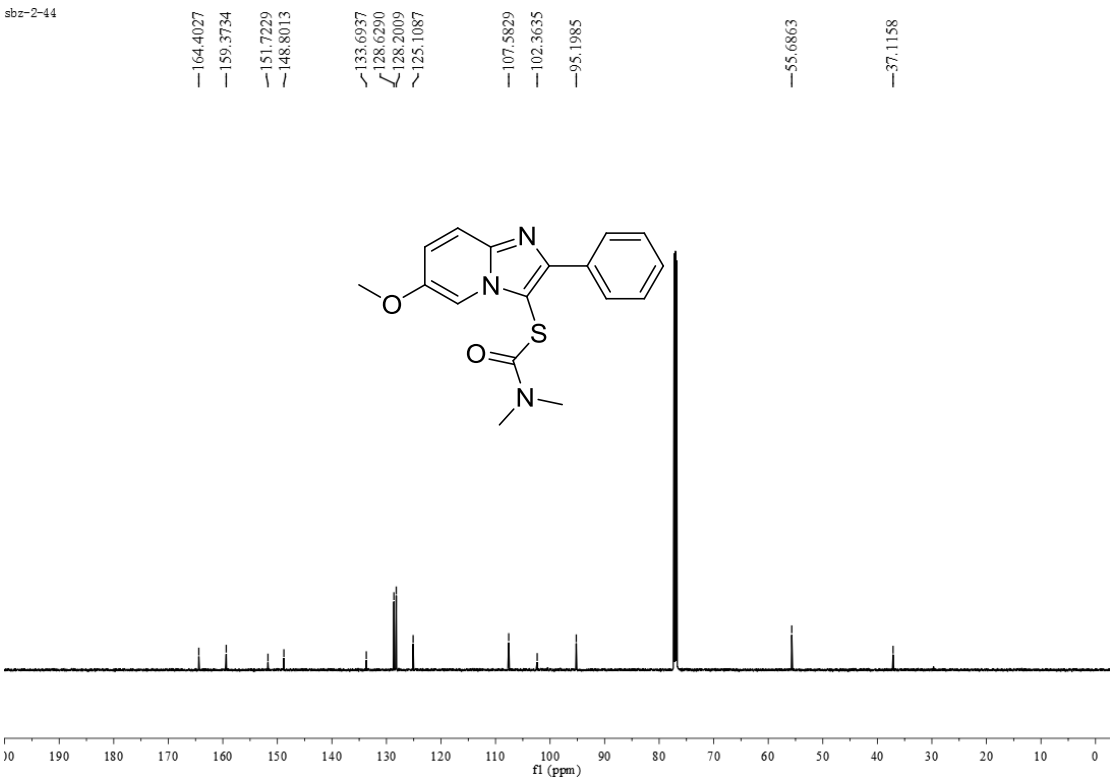
S-8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**4**)



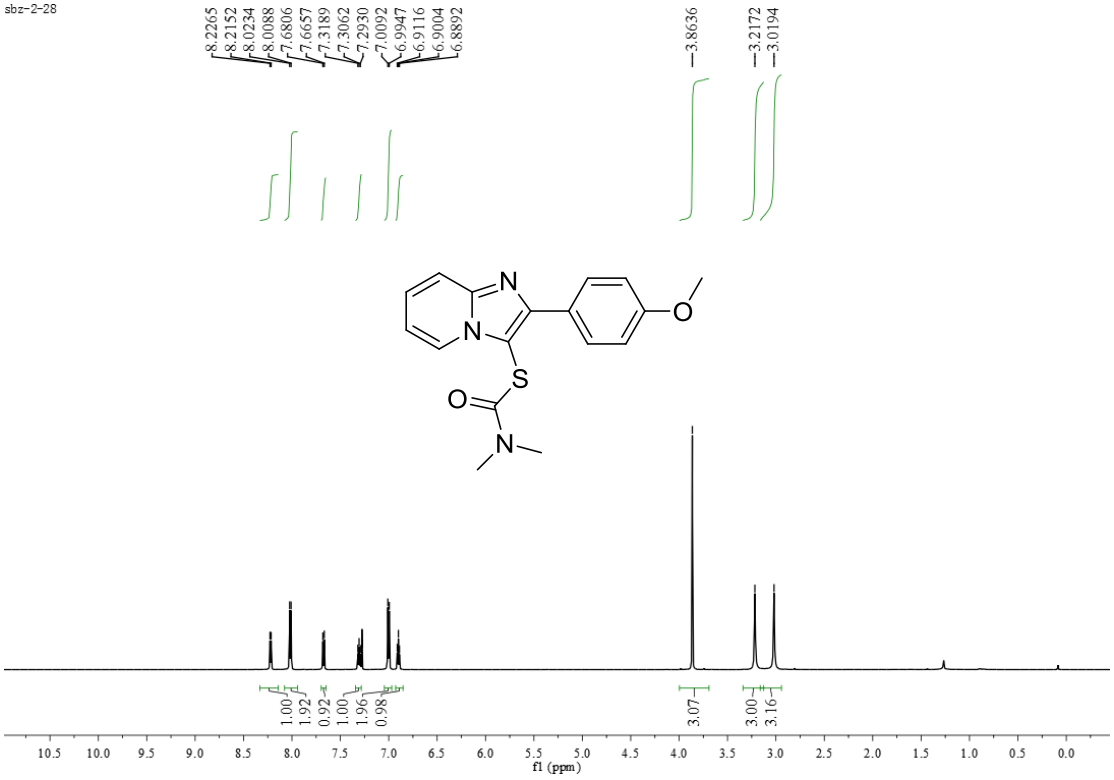


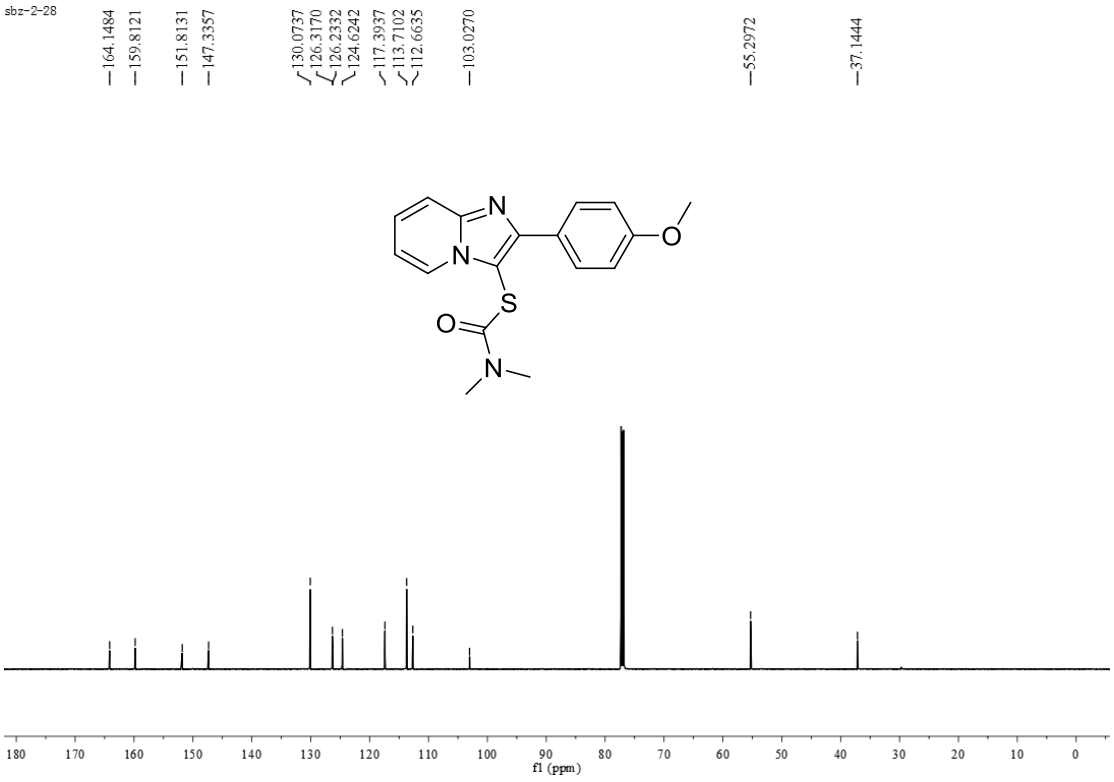
S-6-methoxy-2-phenylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (5)



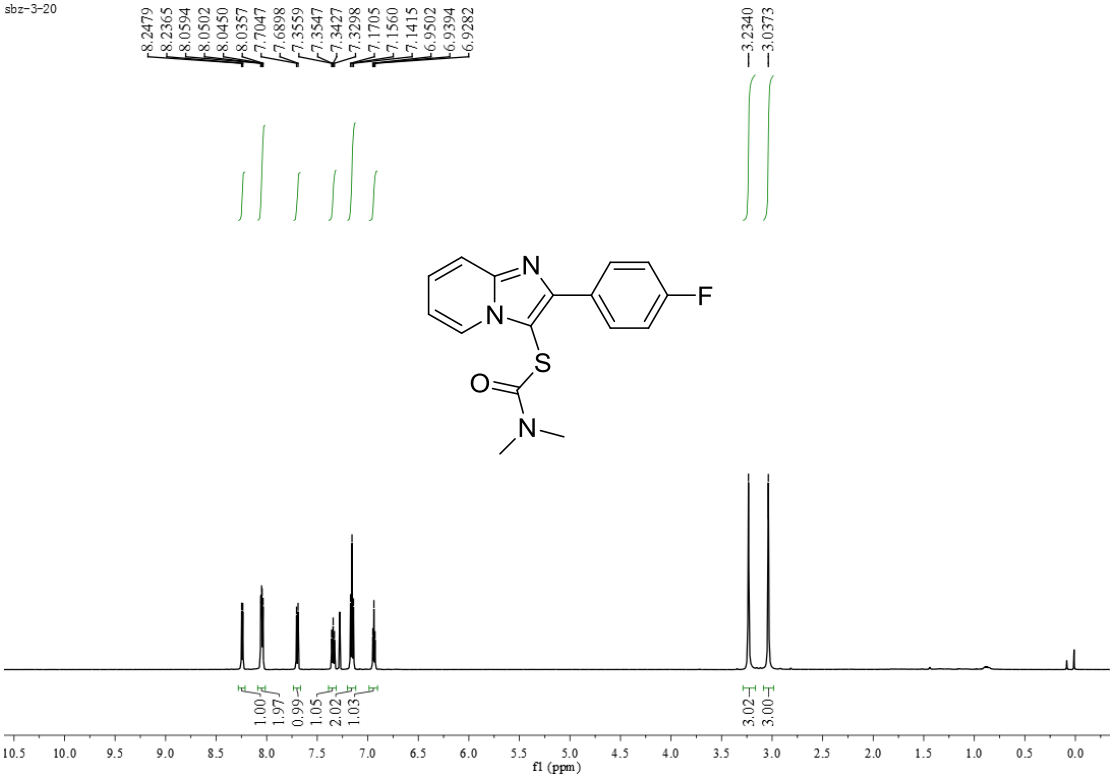


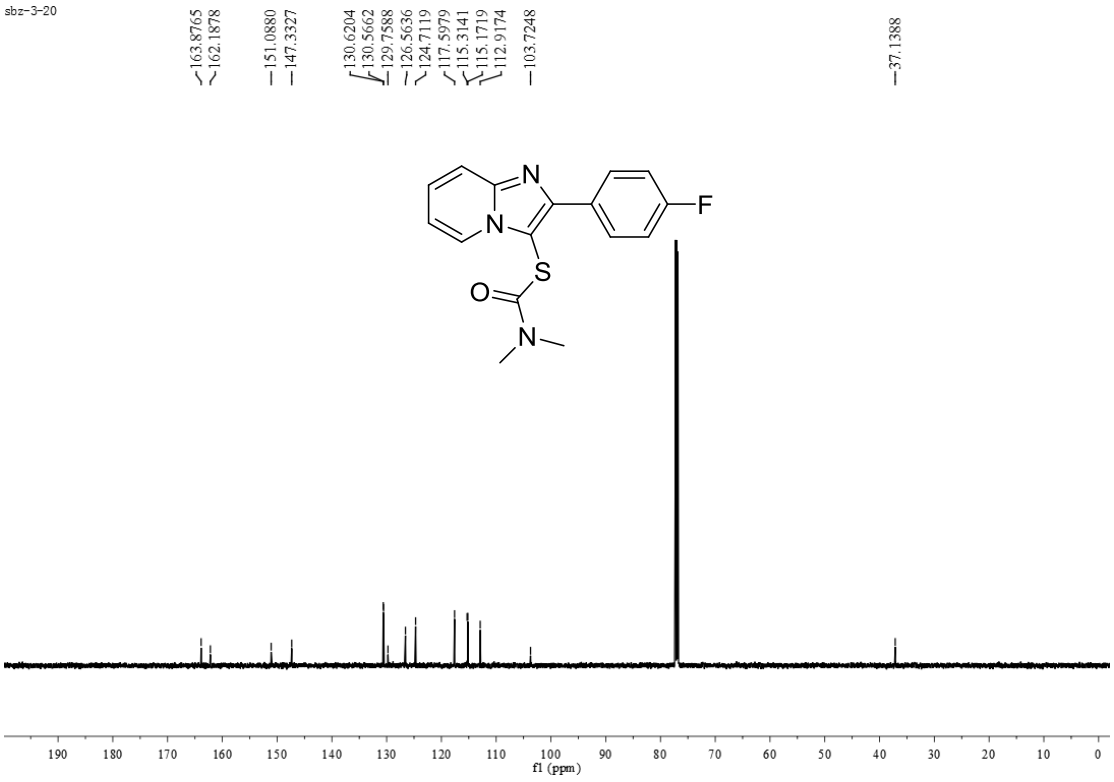
S-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**6**)



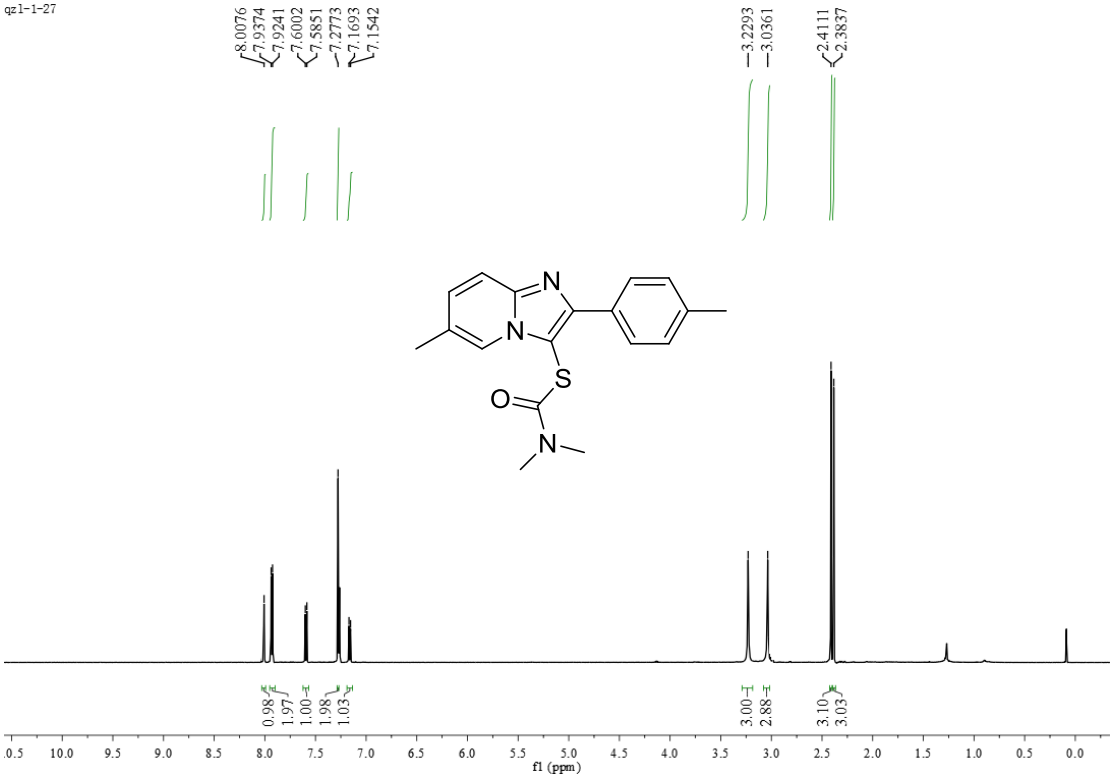


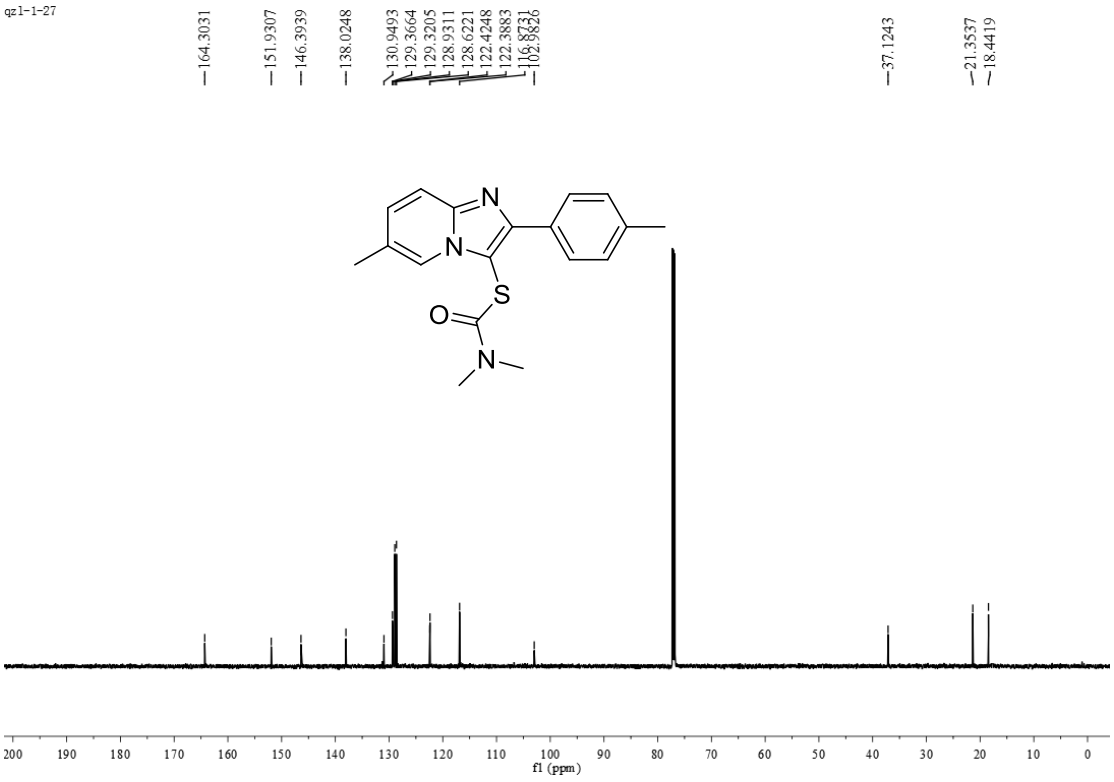
S-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (7)



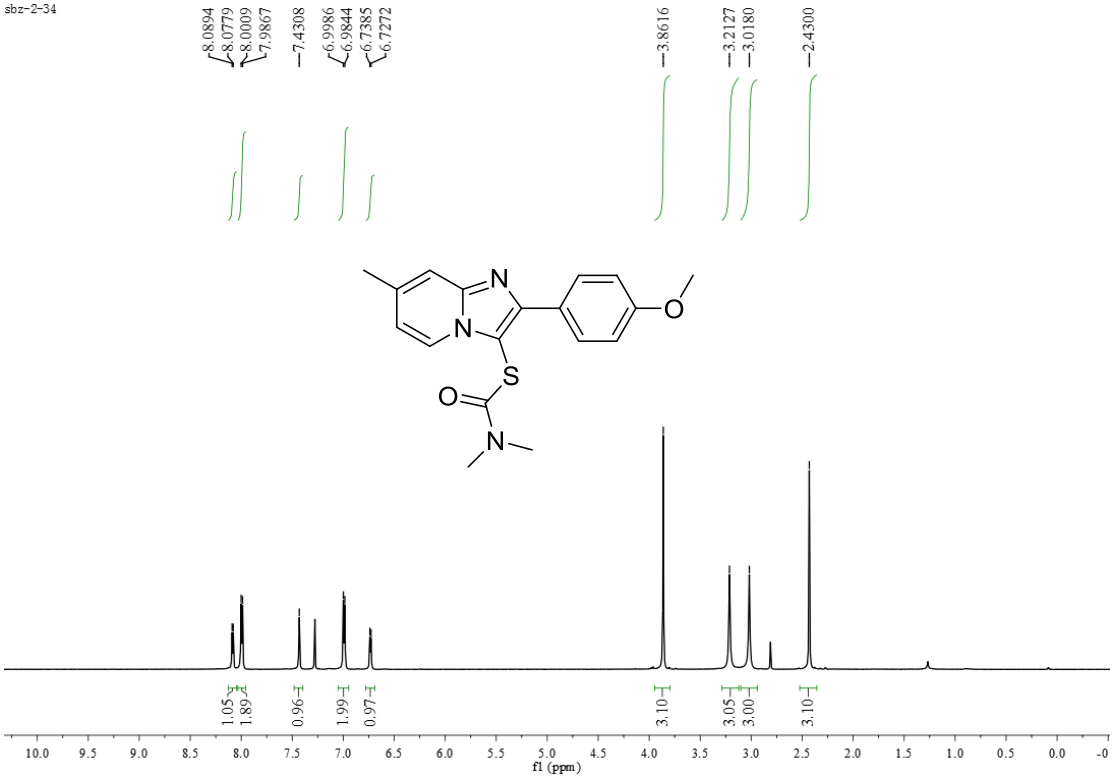


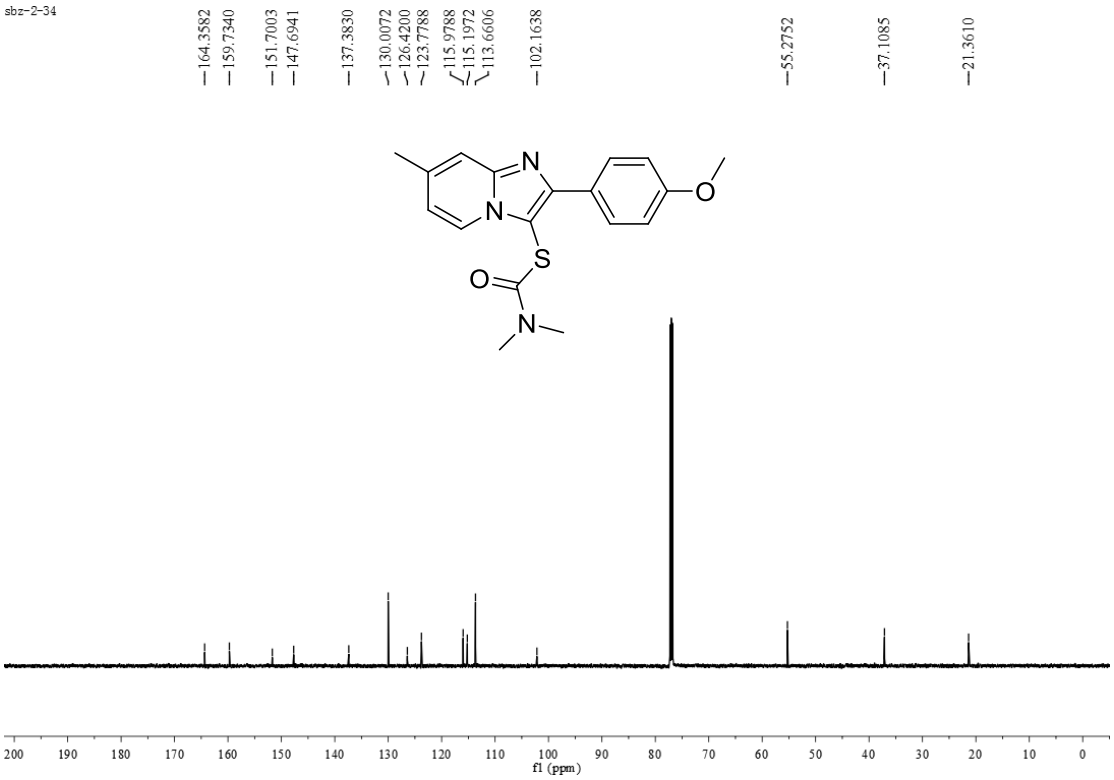
S-6-methyl-2-p-tolylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (**8**)



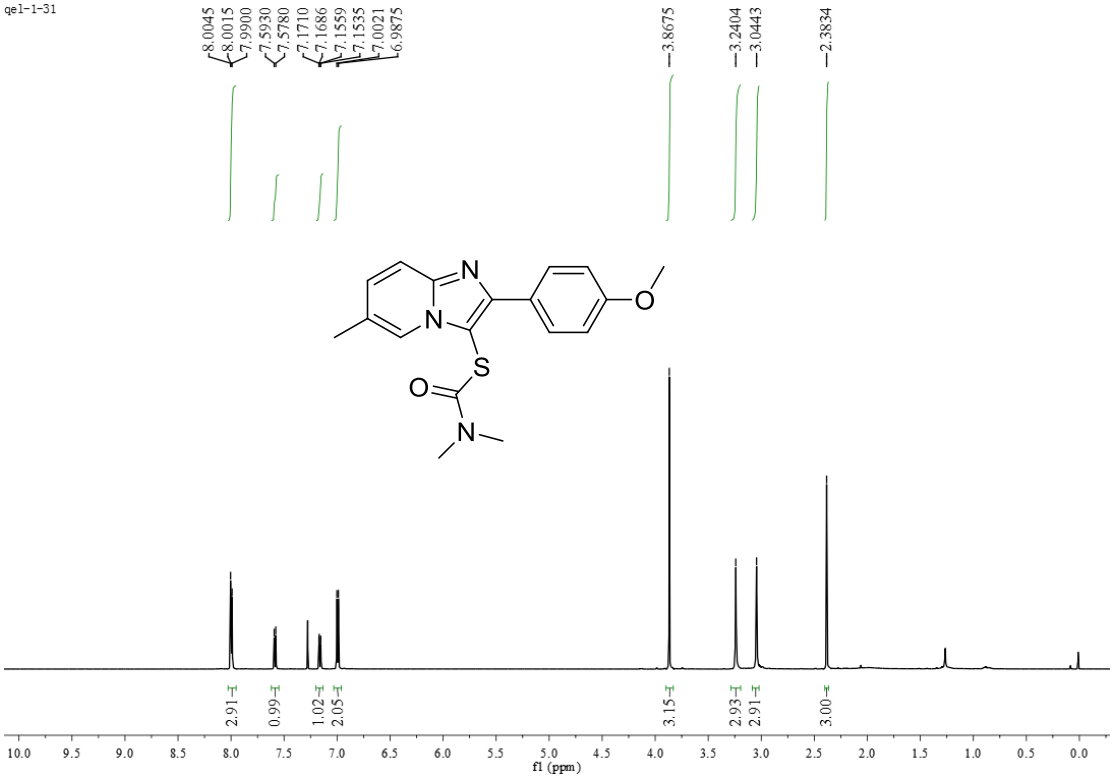


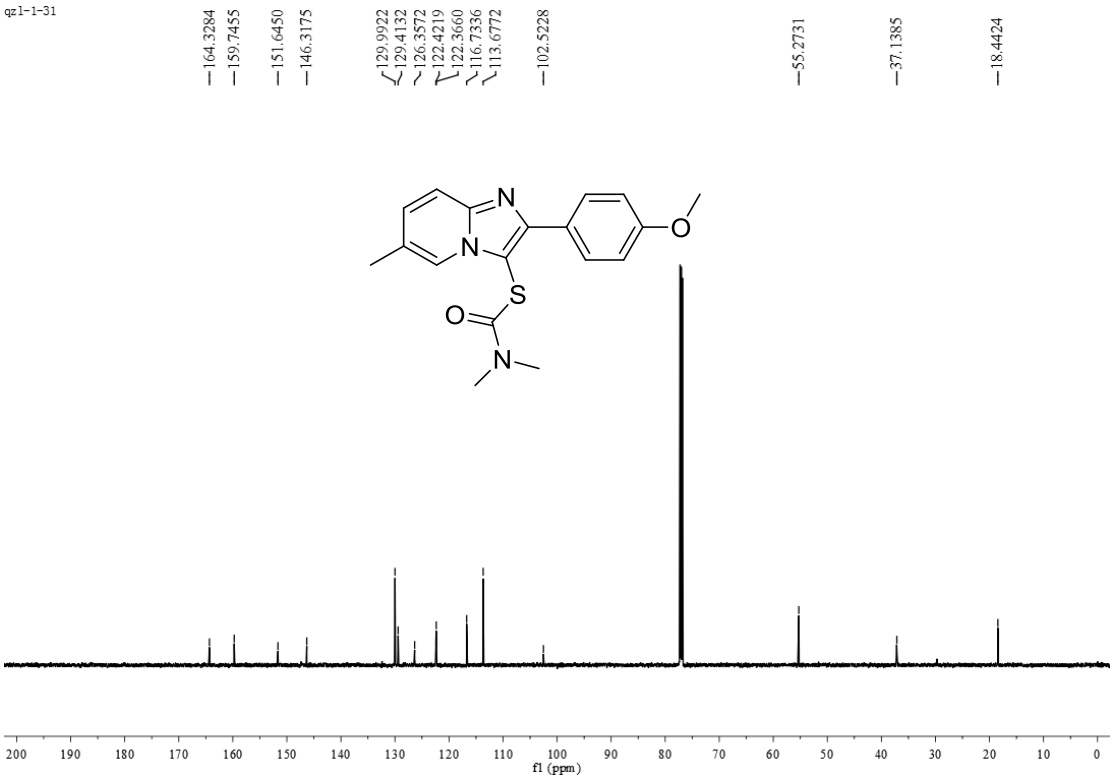
_S_-2-(4-methoxyphenyl)-7-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (9)



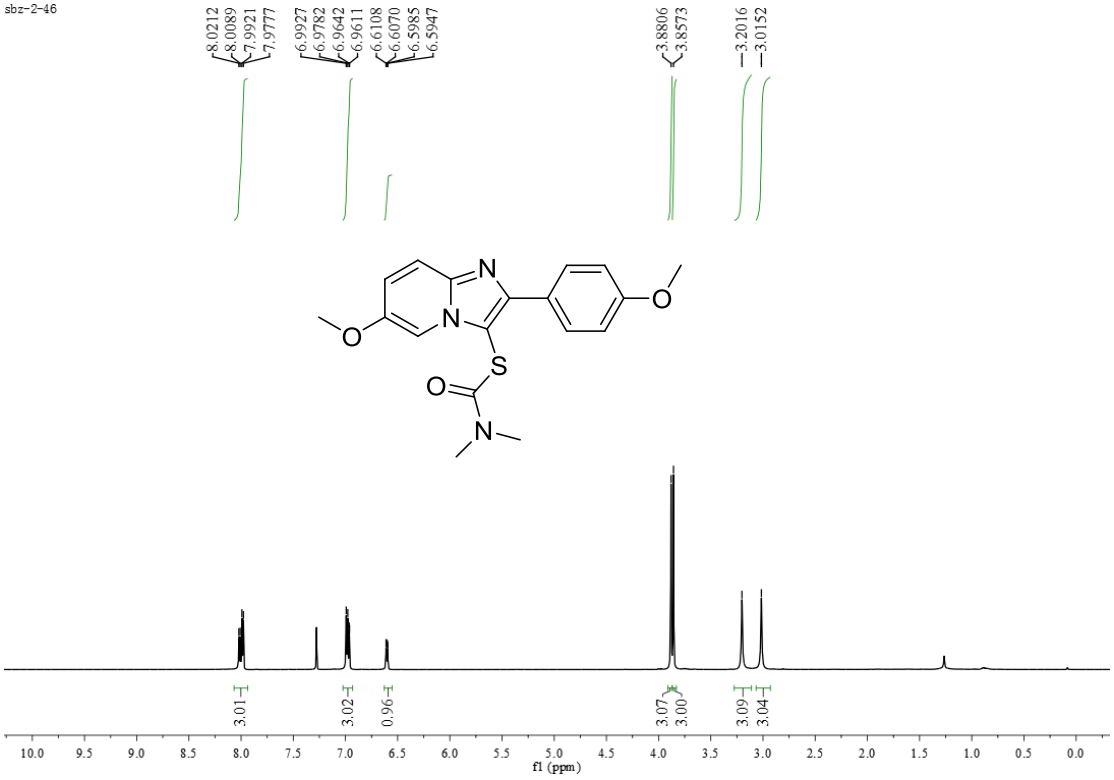


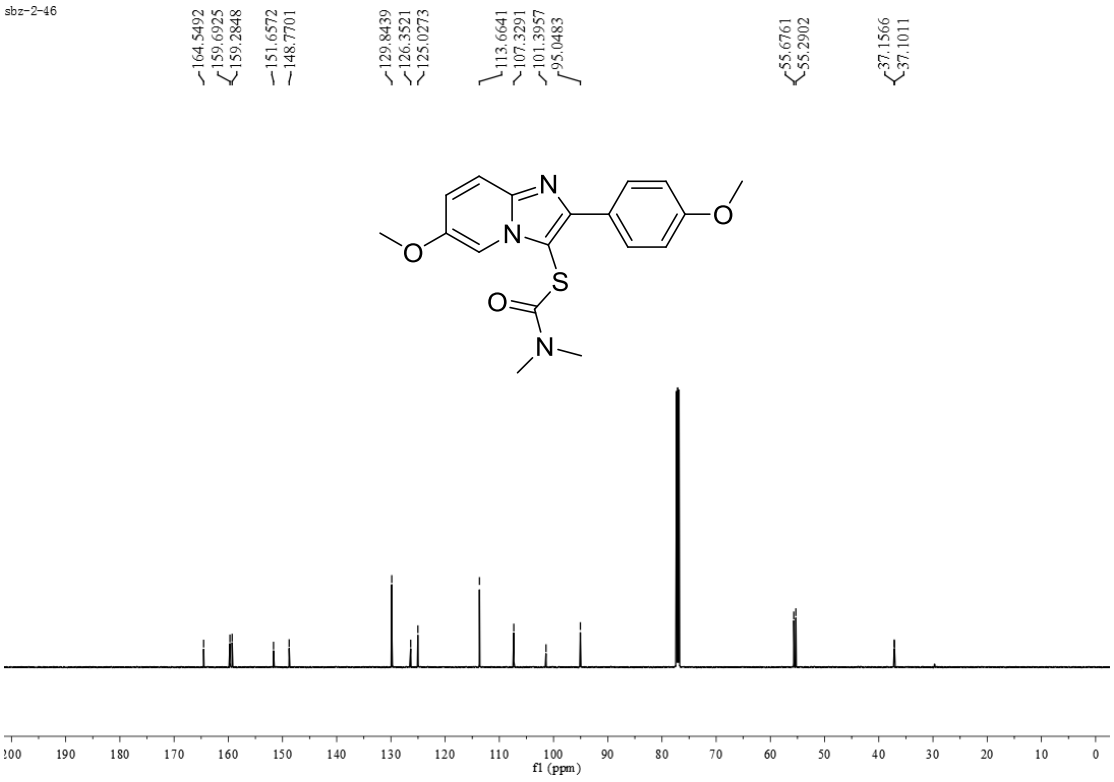
_S_-2-(4-methoxyphenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (10)



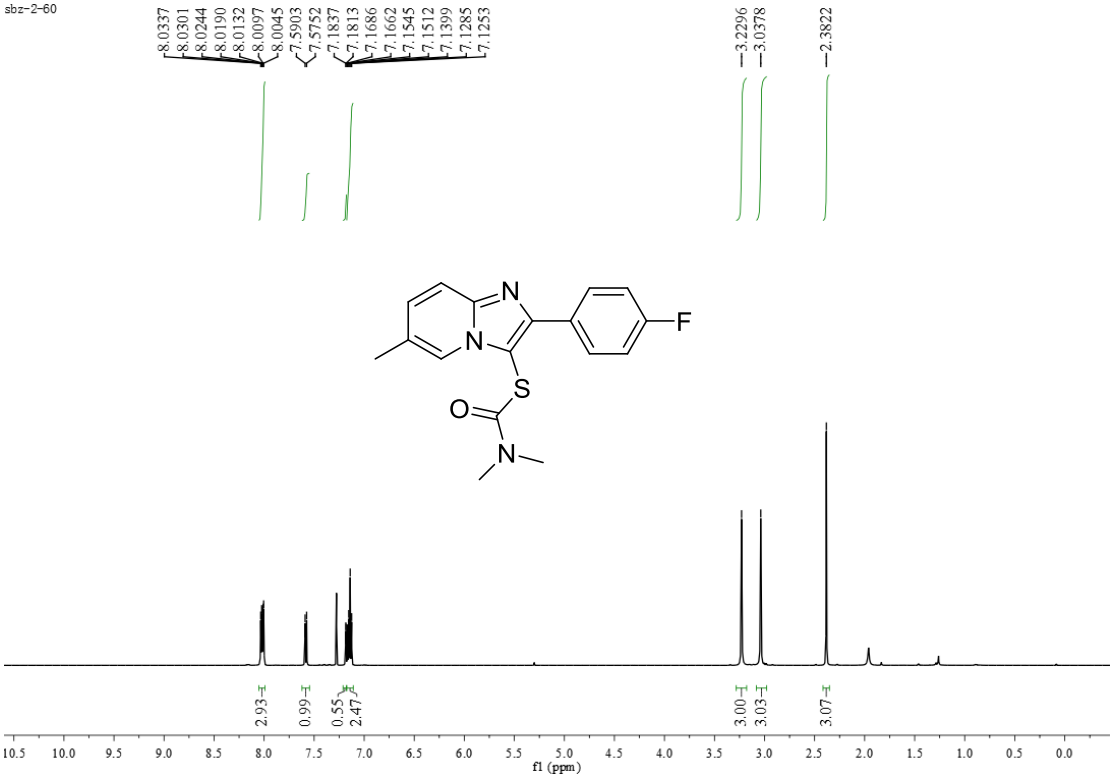


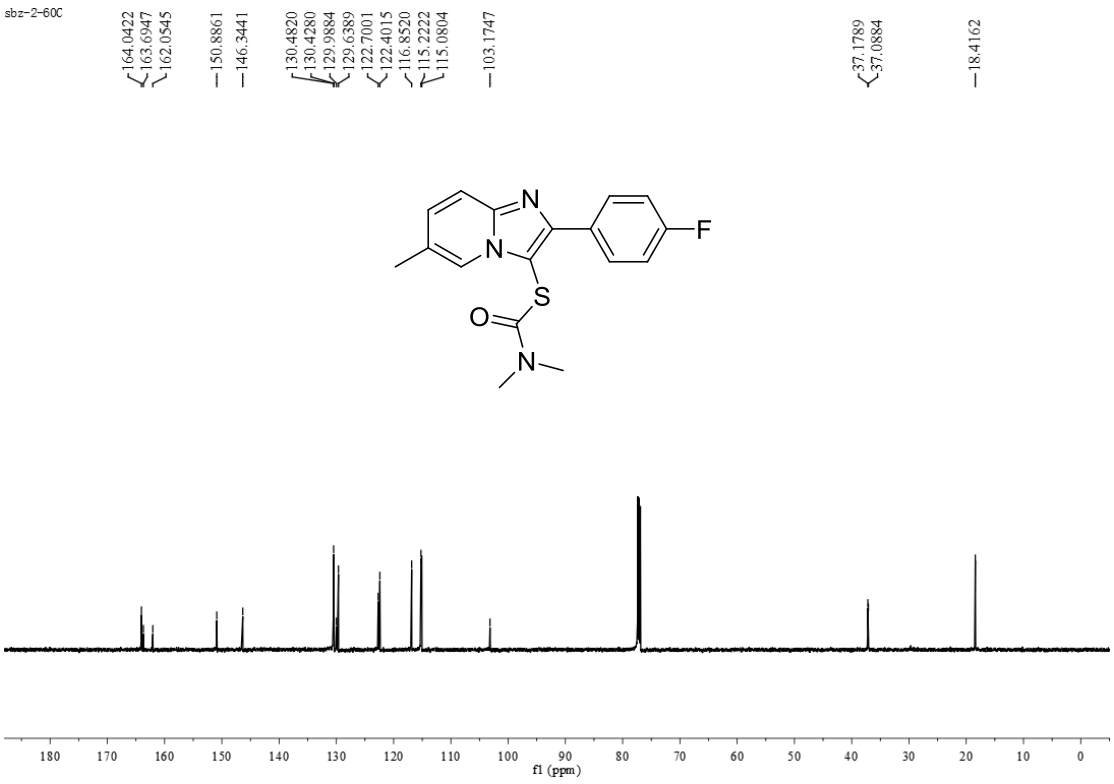
_S_-6-methoxy-2-(4-methoxyphenyl)imidazo[1,2-_a_]pyridin-3-yl dimethylcarbamothioate (11)



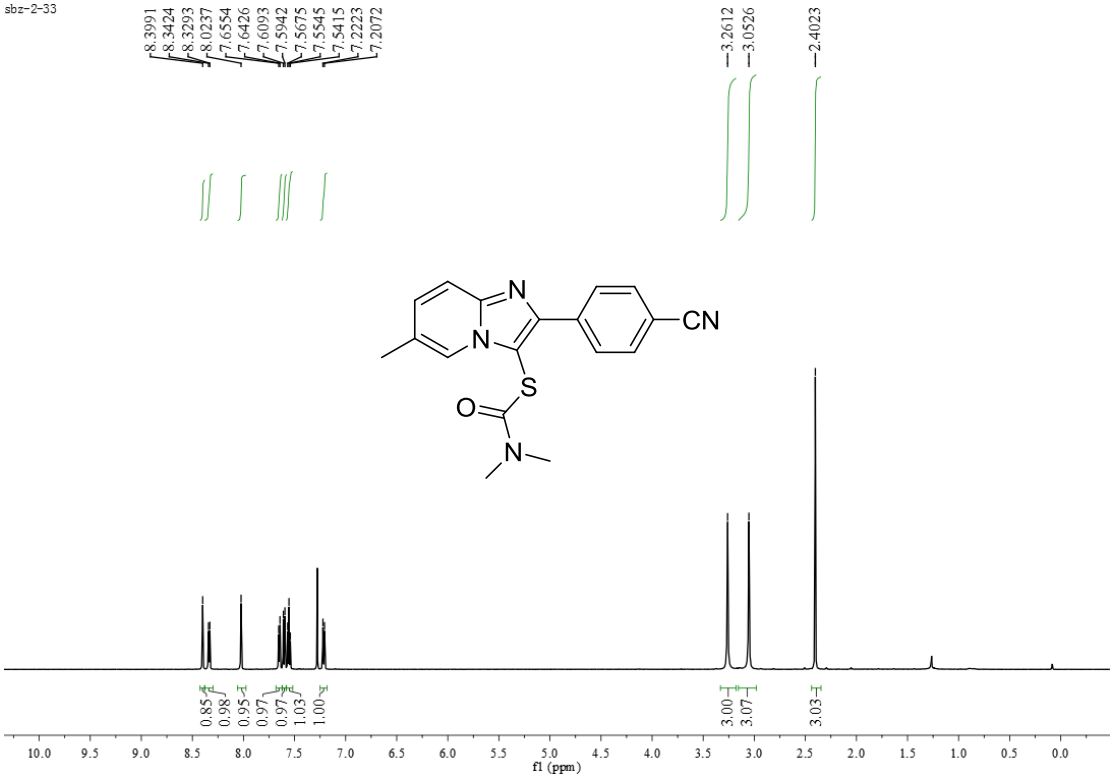


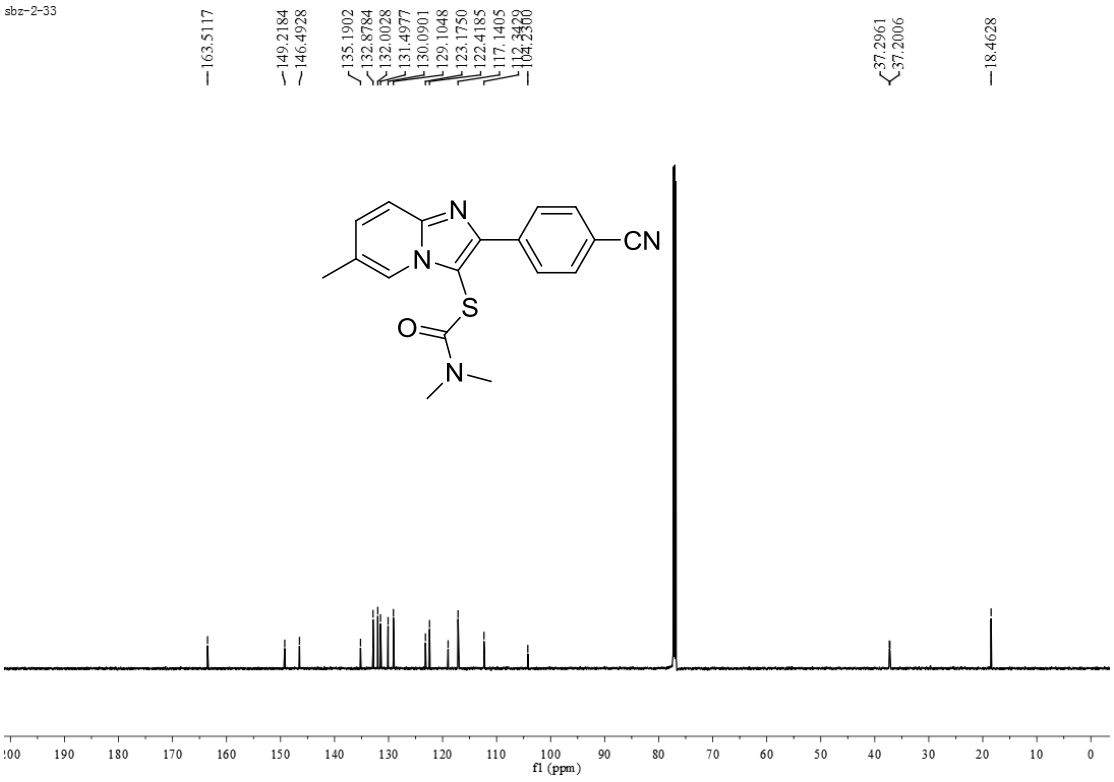
_S_-2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (12)



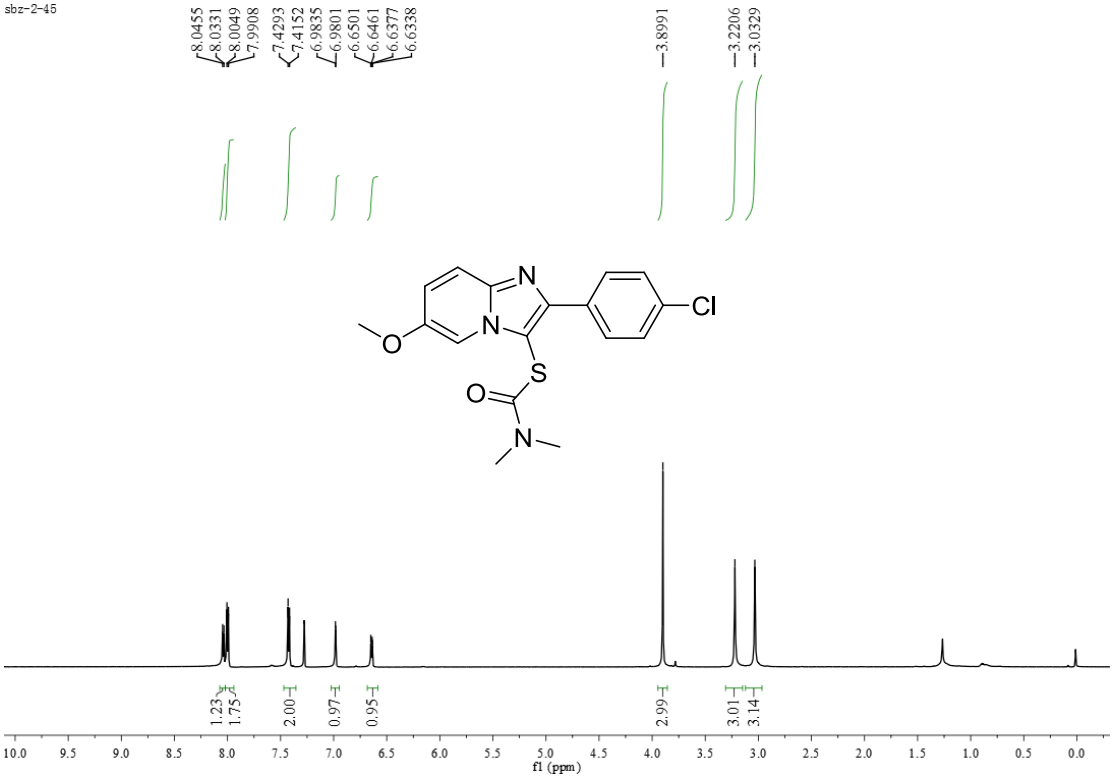


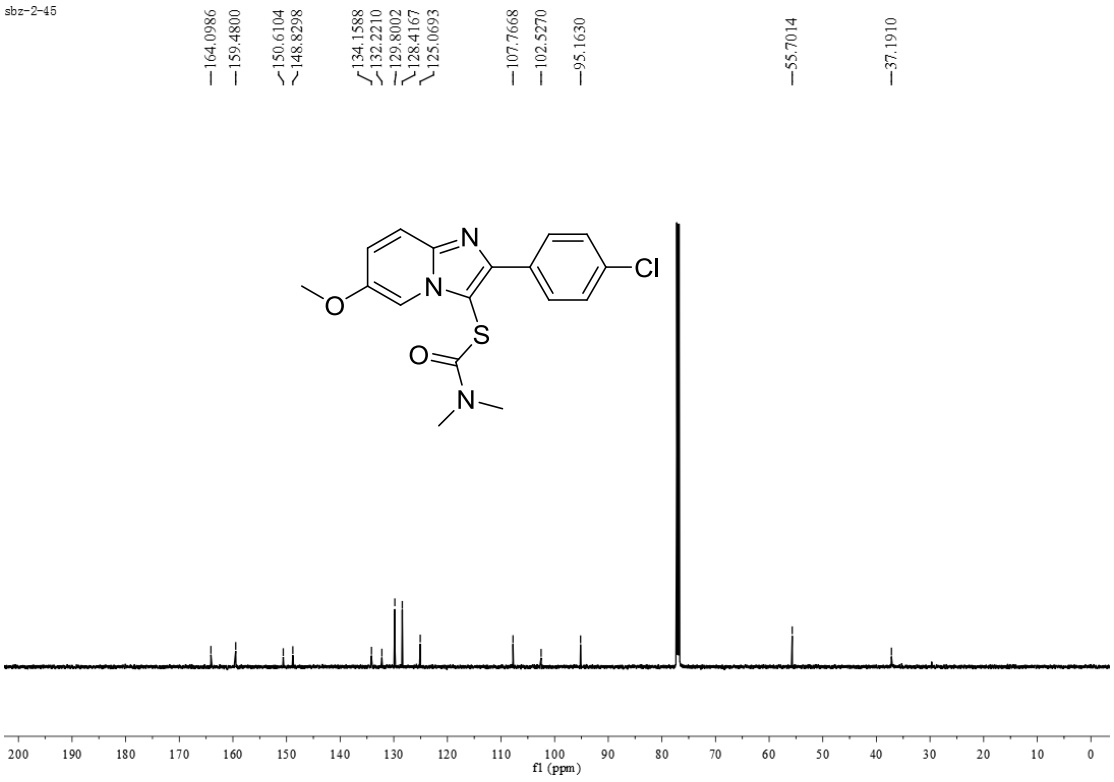
_S_-2-(4-cyanophenyl)-6-methylimidazo[1,2-_a_]pyridin-3-yl dimethylcarbamothioate (13)



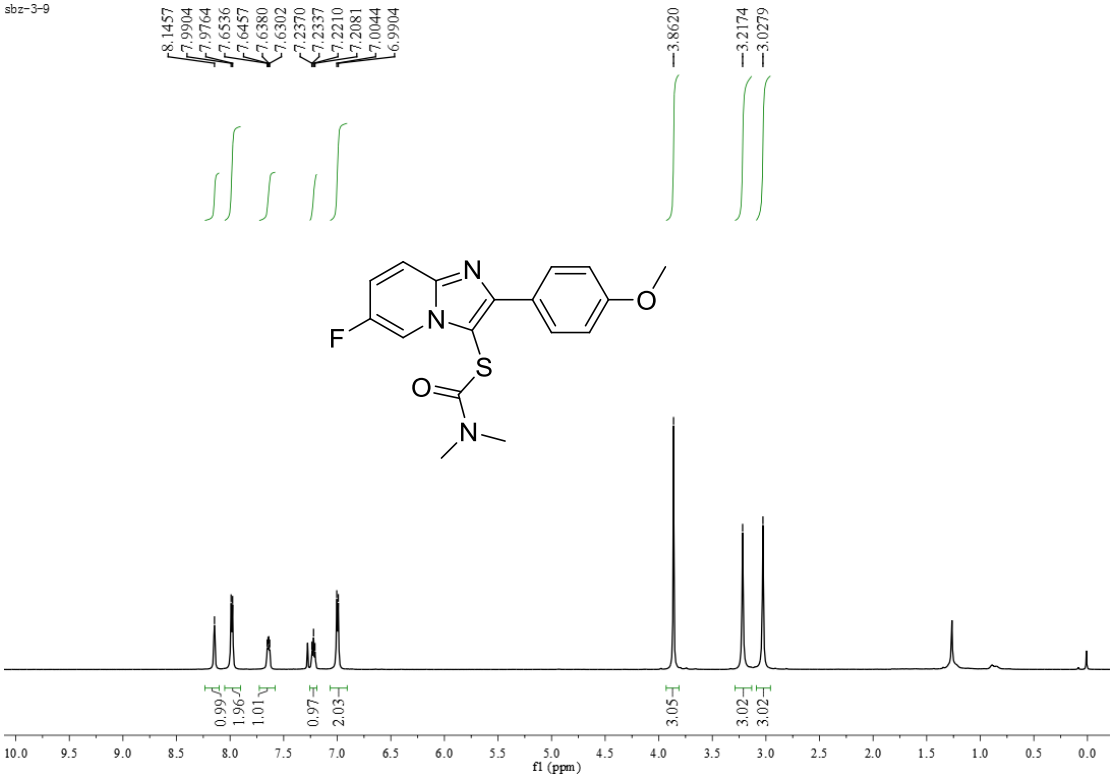


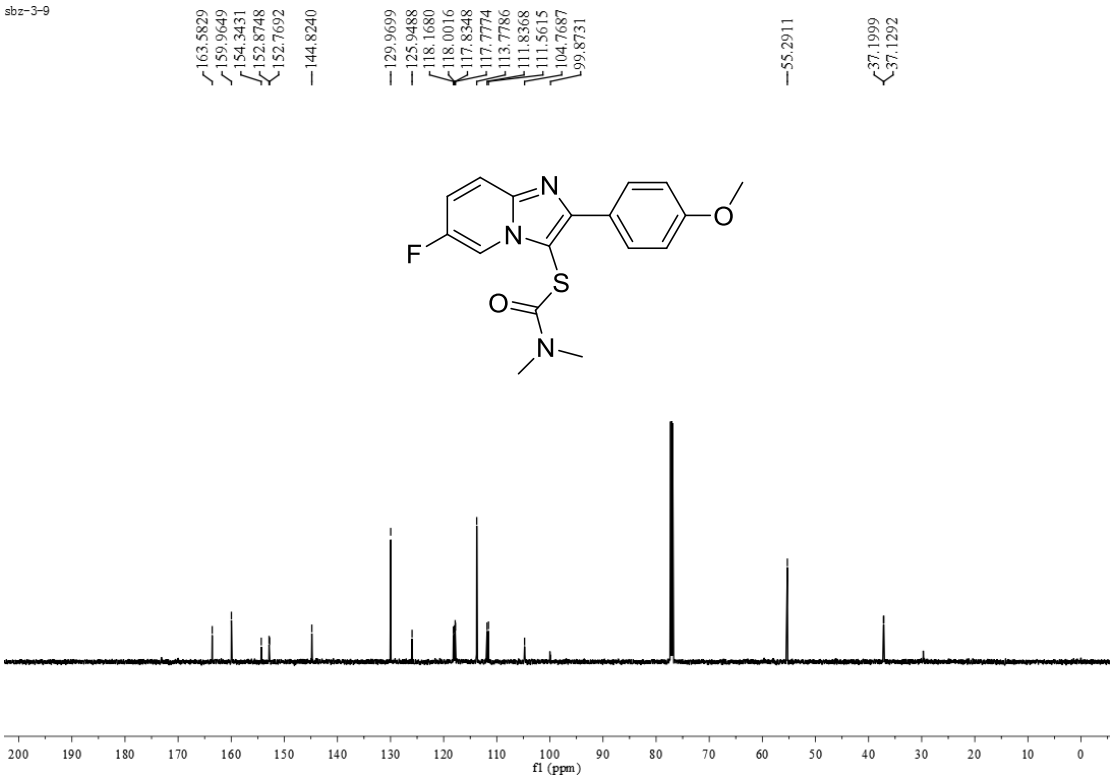
_S_-2-(4-chlorophenyl)-6-methoxyimidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (14)



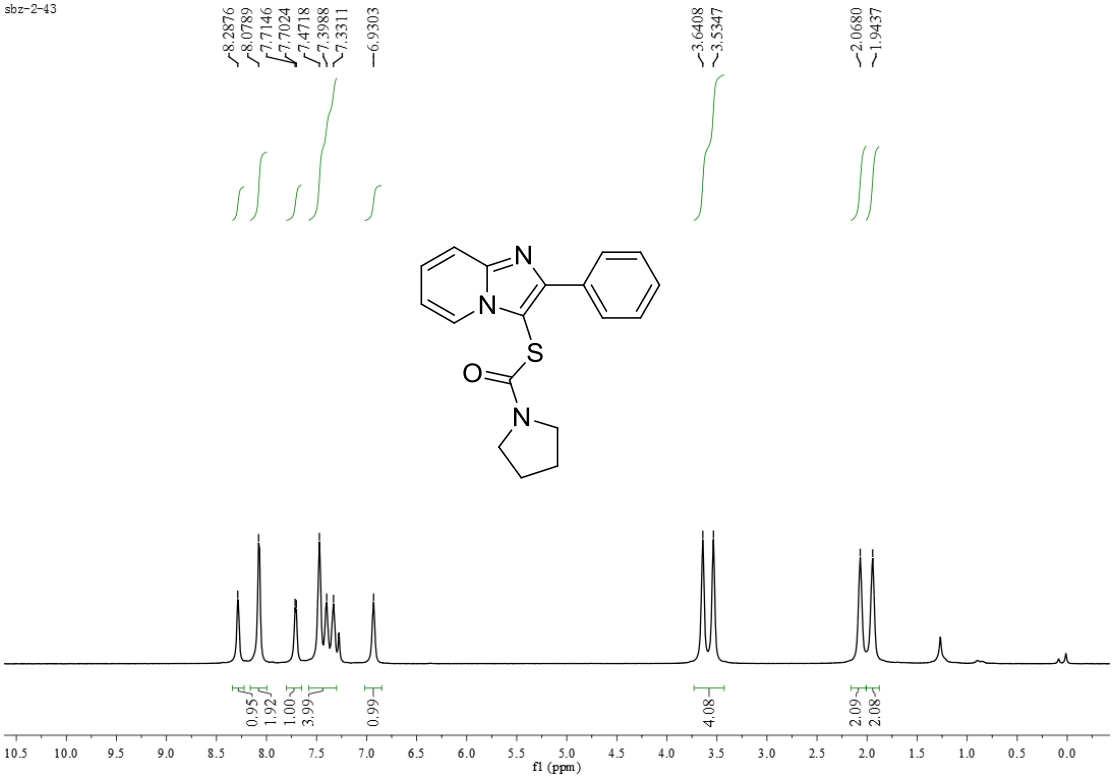


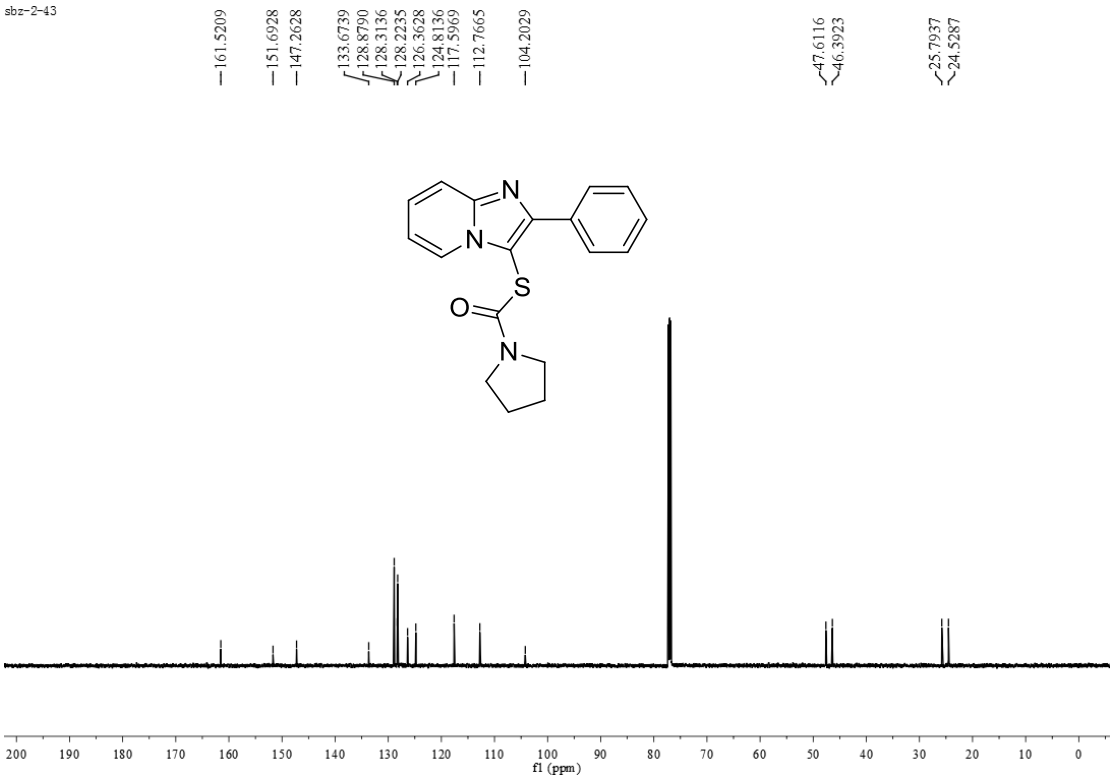
_S_-6-fluoro-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridin-3-yl dimethylcarbamothioate (15)



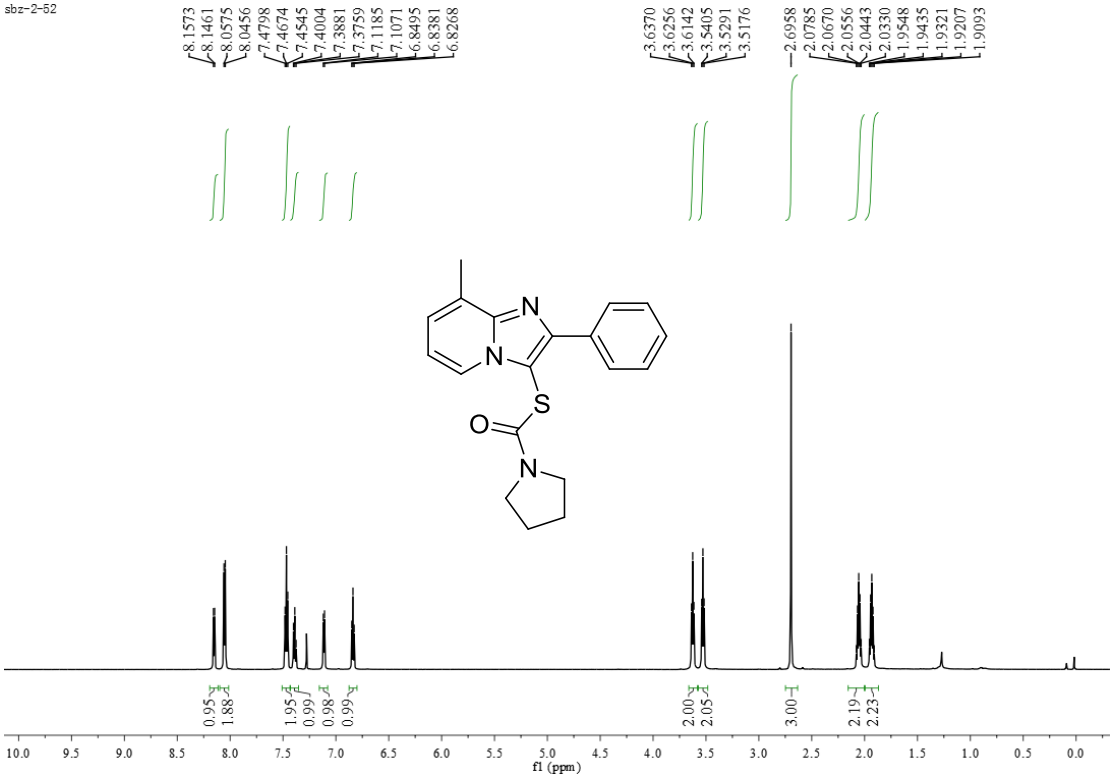


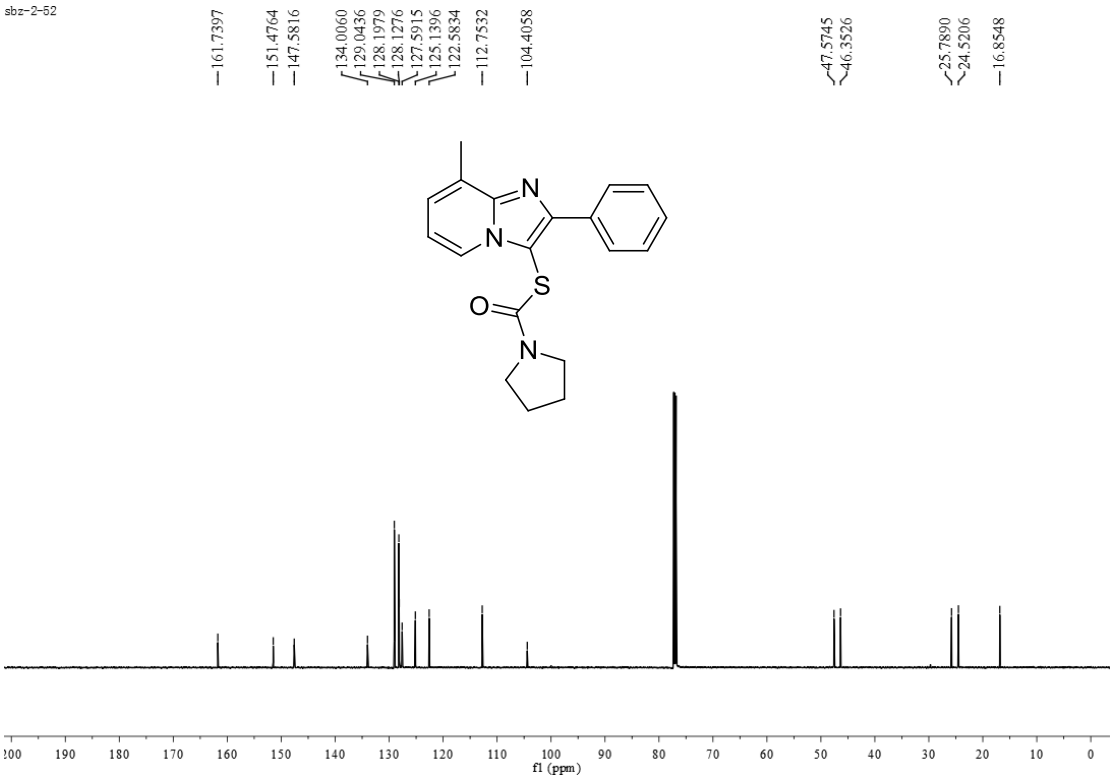
S-2-phenylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (16)



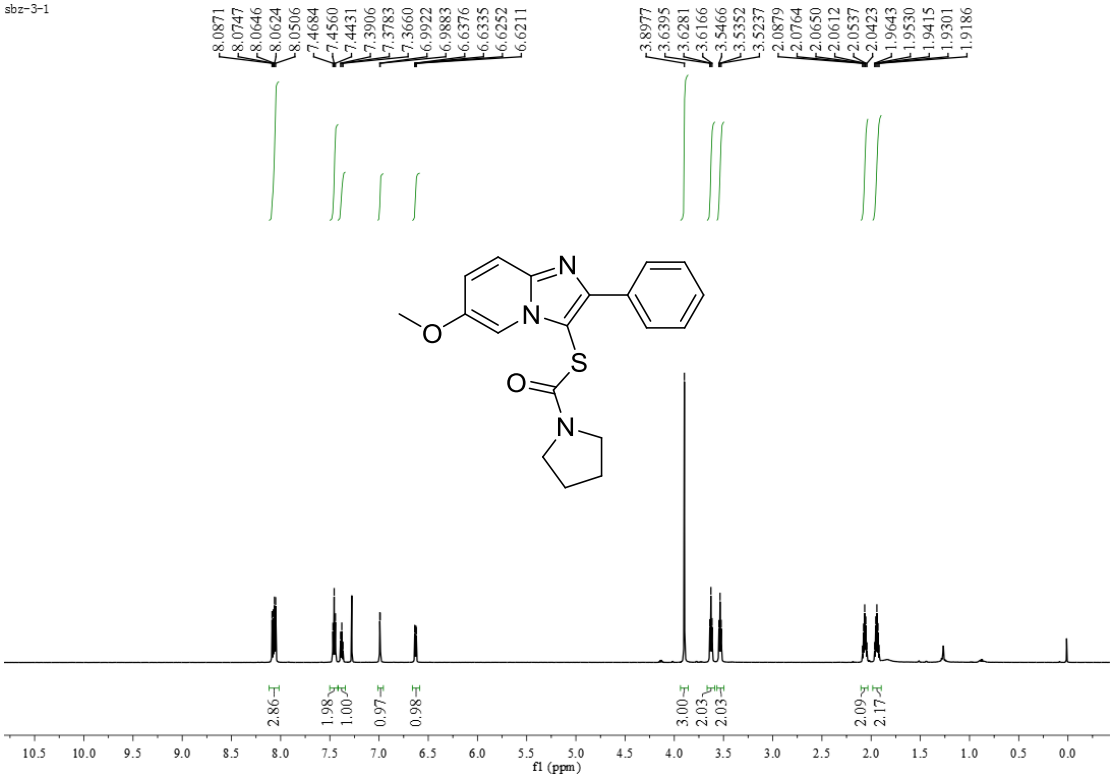


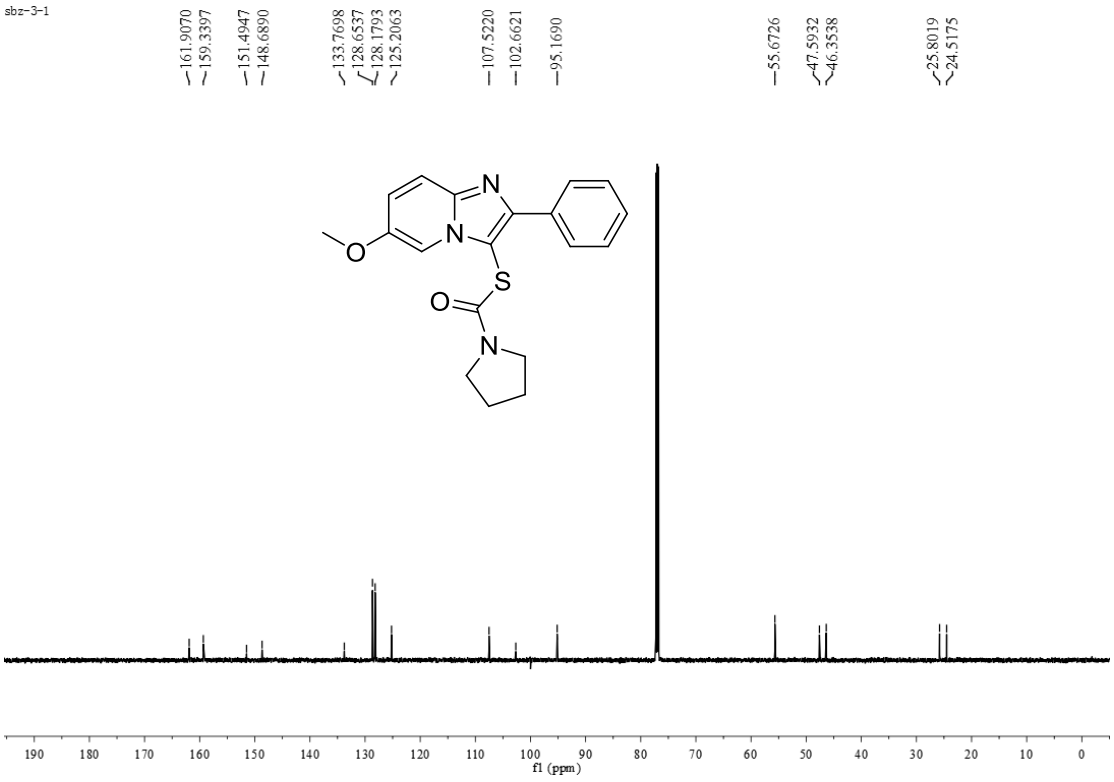
S-8-methyl-2-phenylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (**17**)



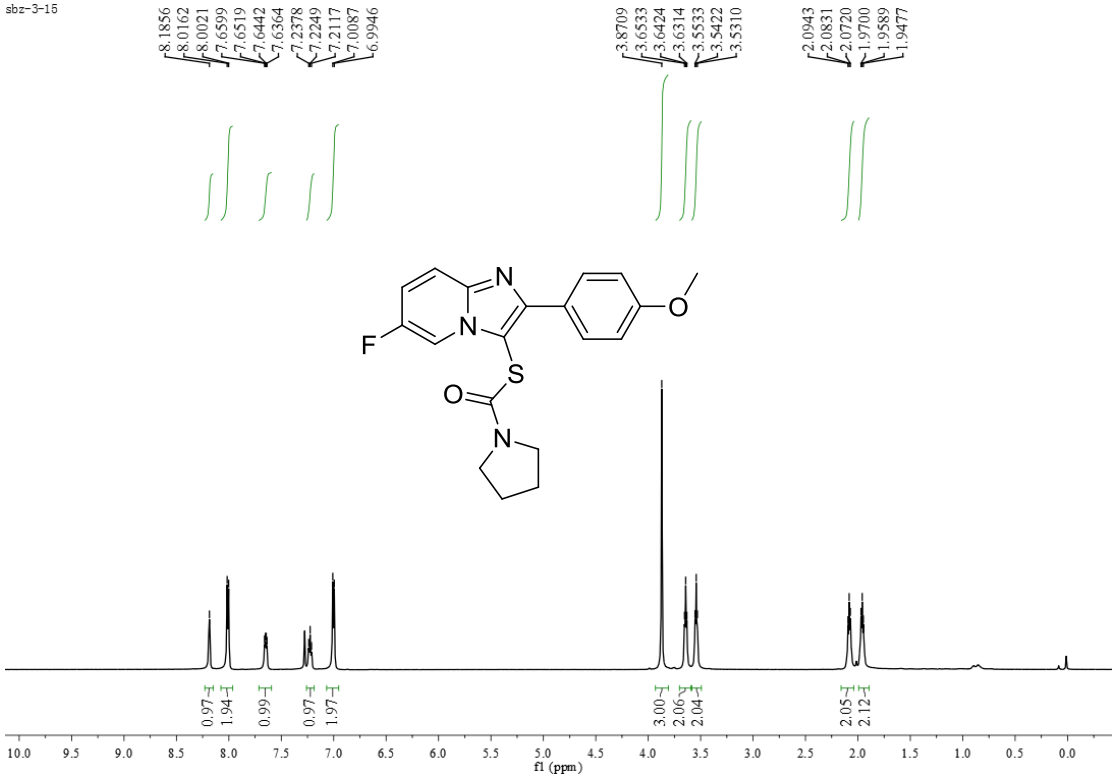


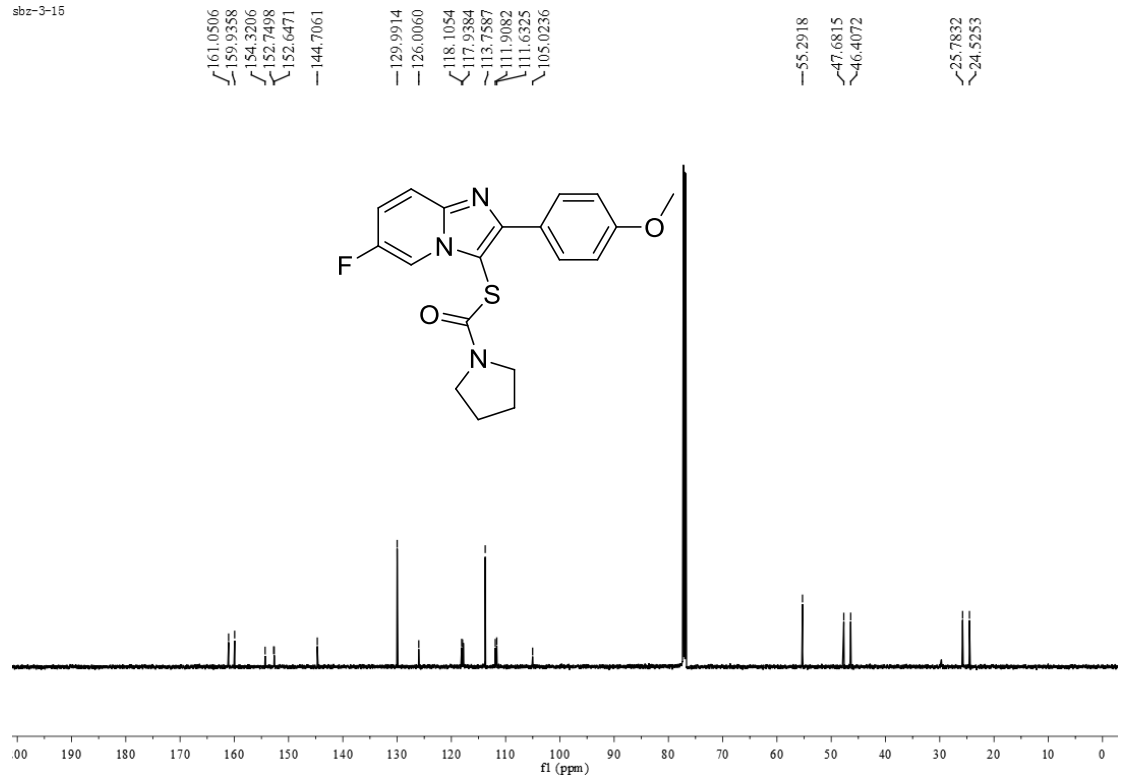
_S_-6-methoxy-2-phenylimidazo[1,2-_a_]pyridin-3-yl pyrrolidine-1-carbothioate (18)



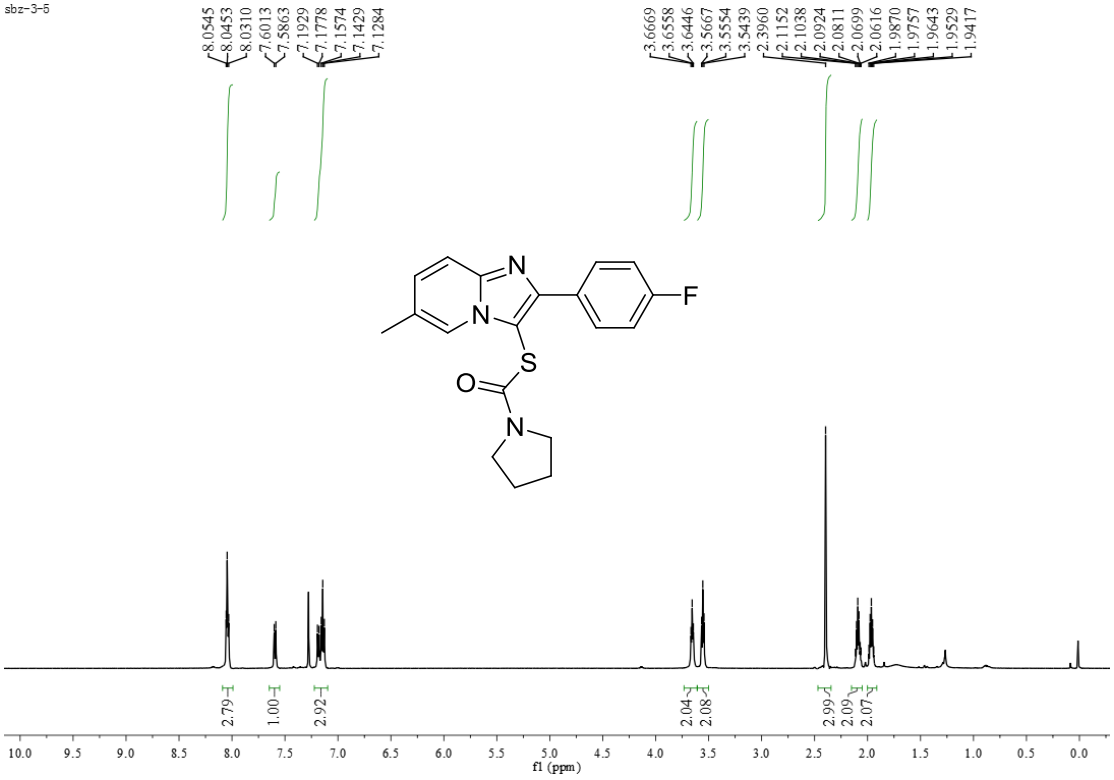


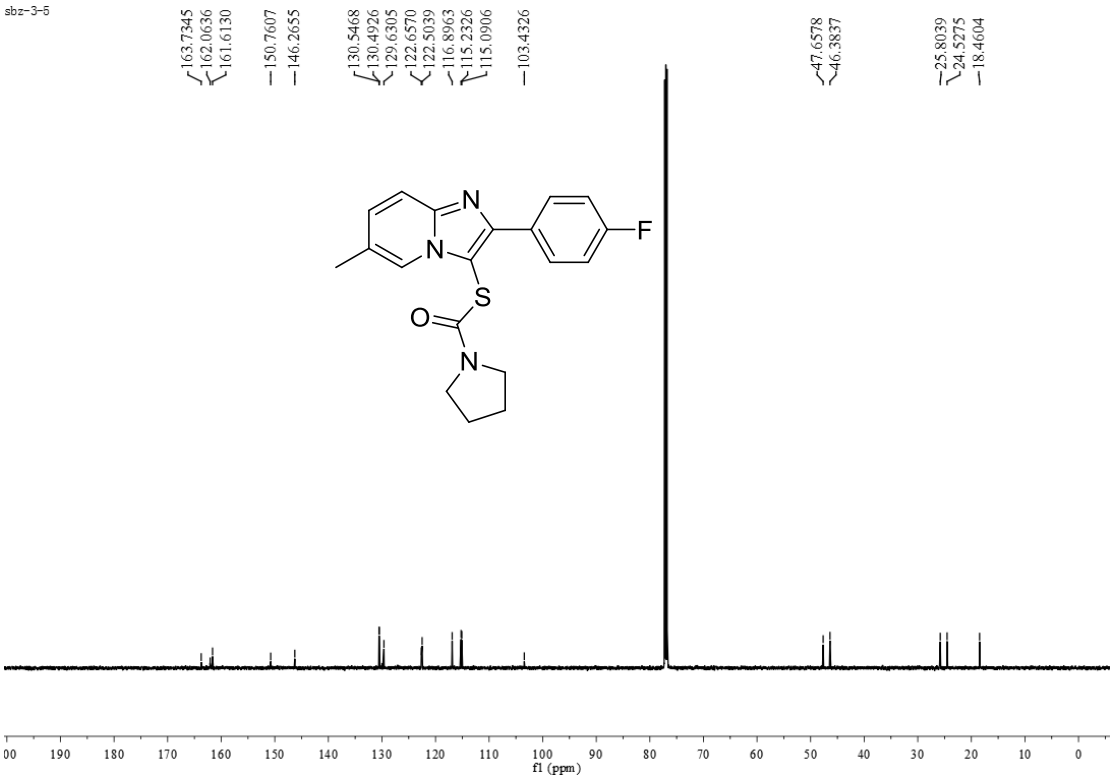
_S_-6-fluoro-2-(4-methoxyphenyl)imidazo[1,2-_a_]pyridin-3-yl pyrrolidine-1-carbothioate (19)



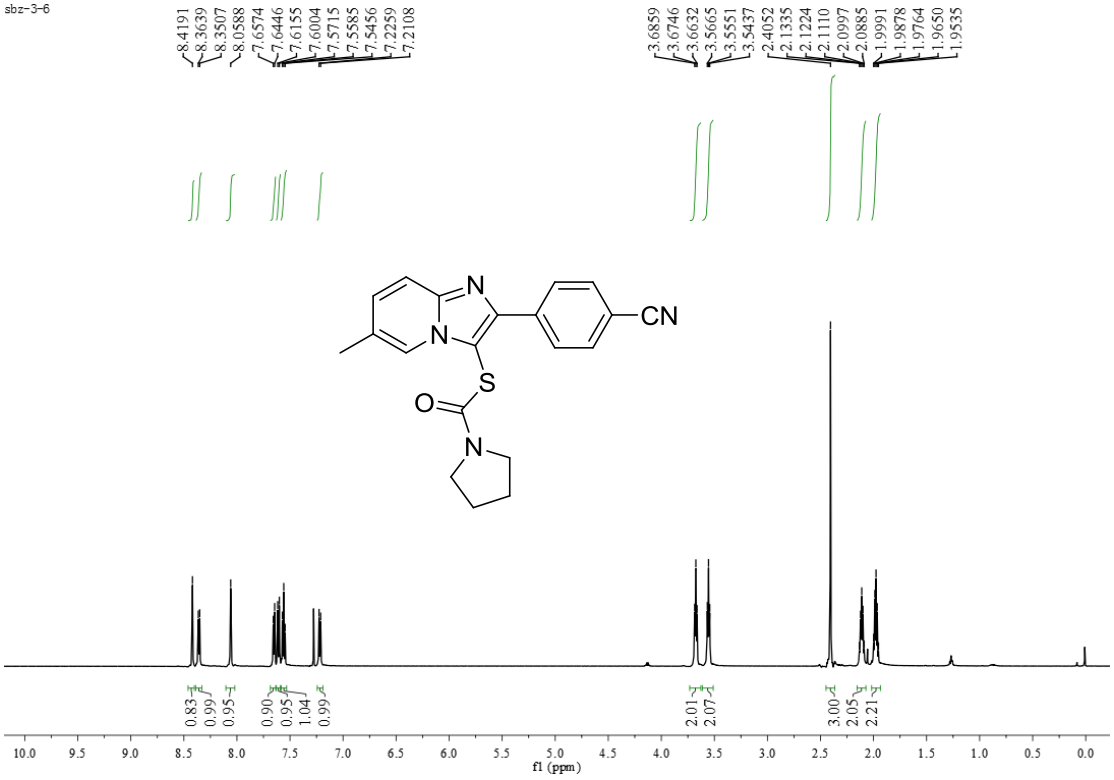


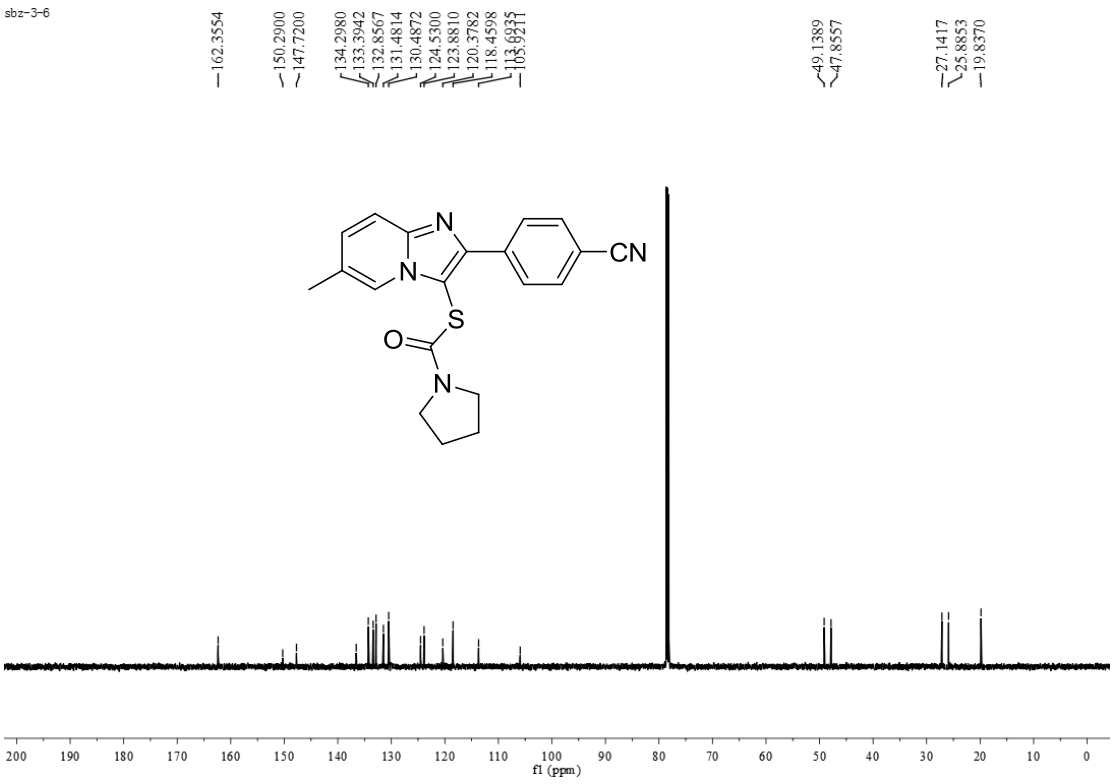
_S_-2-(4-fluorophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (20)



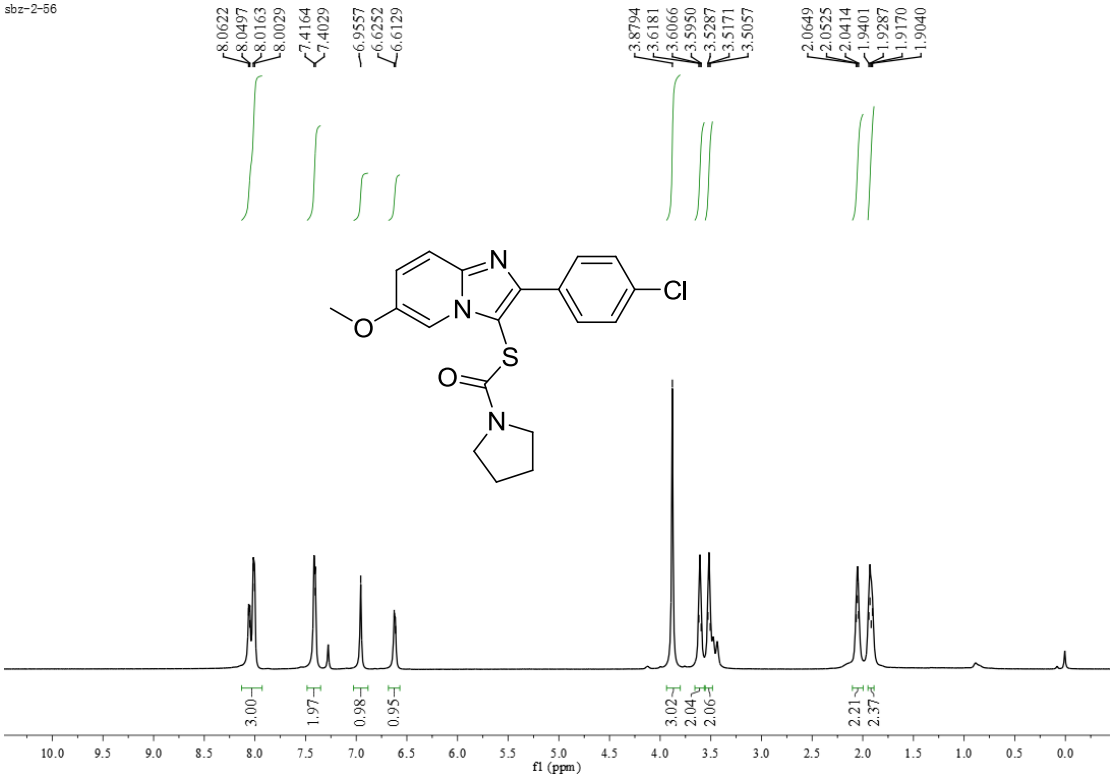


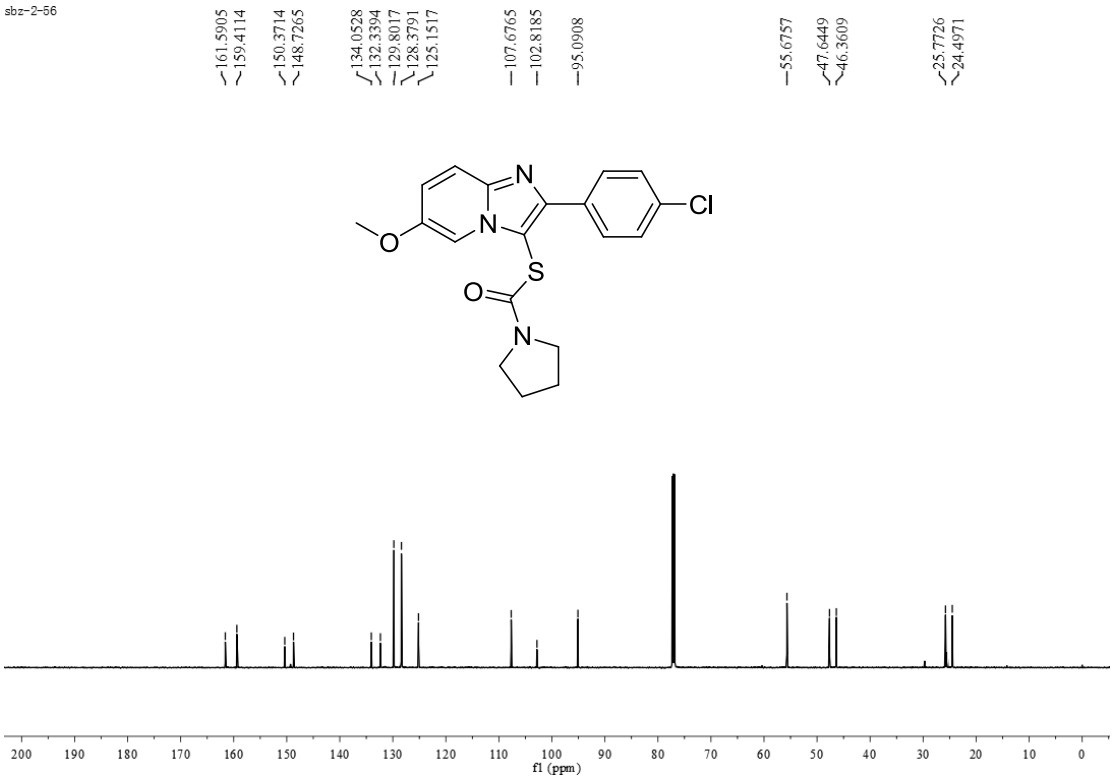
S-2-(4-cyanophenyl)-6-methylimidazo[1,2-*a*]pyridin-3-yl pyrrolidine-1-carbothioate (21)



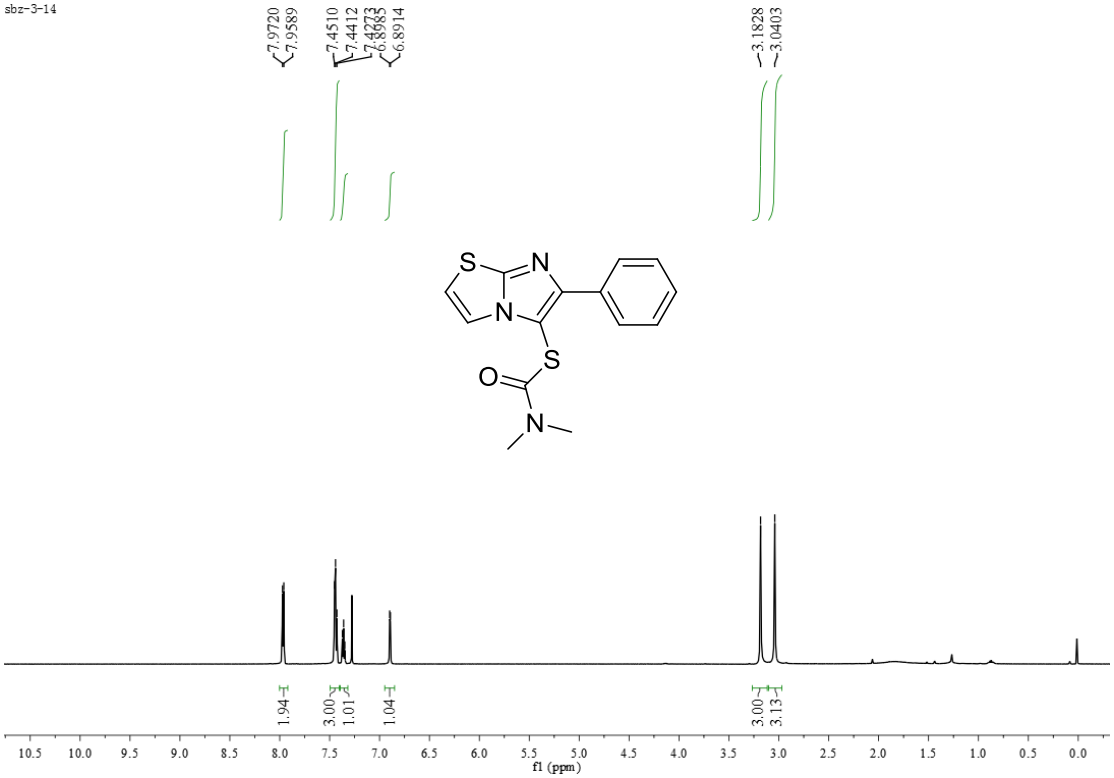


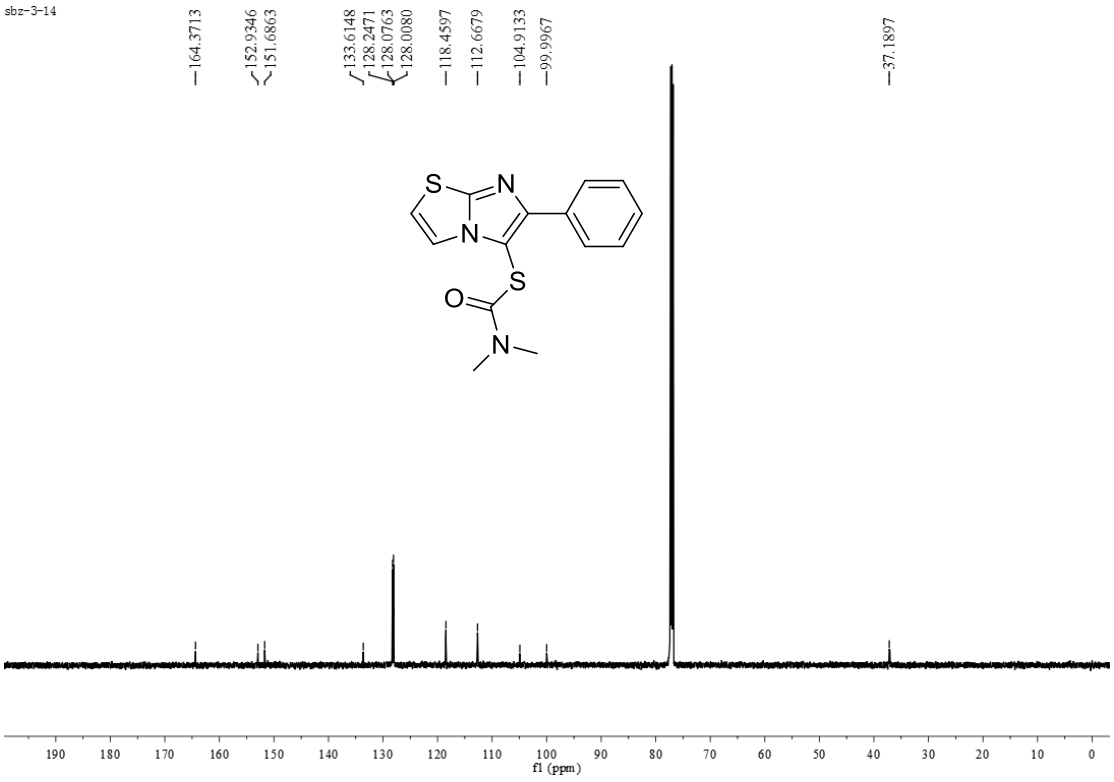
_S_-2-(4-chlorophenyl)-6-methoxyimidazo[1,2-_a_]pyridin-3-yl pyrrolidine-1-carbothioate (22)





S-6-phenylimidazo[2,1-*b*]thiazol-5-yl dimethylcarbamothioate (23)





_S_-6-(4-fluorophenyl)imidazo[2,1-_b_]thiazol-5-yl dimethylcarbamothioate (24)