
Supporting Information

Copper-Catalyzed Coupling of Oxime Acetates with Isothiocyanates: A Strategy for 2-Aminothiazoles

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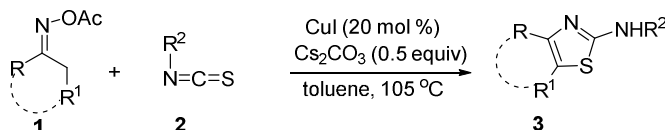
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General Information

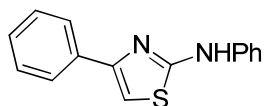
^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using CDCl_3 as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. Oxime acetates were synthesized according to the literature procedure.¹

Experimental Section for Products 3



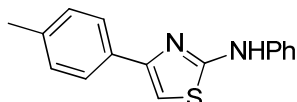
General procedure for products **3**: oxime acetates **1** (0.5 mmol), isothiocyanate **2** (0.5 mmol), CuI (20 mol %), Cs_2CO_3 (0.25 mmol), in toluene (3 mL) were added to a 25 mL tube with magnetic stirrer bar. The mixture was stirred at 105 °C (oil bath temperature) for 12 h under air. After the reaction was finished (monitored by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified by column chromatography (EtOAc/hexanes) on silica gel.

Characterization Data for All Products



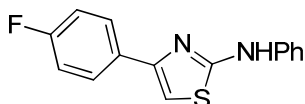
N,4-Diphenylthiazol-2-amine (**3aa**)²

Red solid (101 mg, 80 %), m.p. = 136 – 137 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 7.9 Hz, 2H), 7.43 – 7.29 (m, 7H), 7.07 (t, J = 7.0 Hz, 1H), 6.83 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.6, 151.4, 140.4, 134.6, 129.5, 128.7, 127.9, 126.2, 123.0, 118.3, 101.8. MS (EI, 70 eV) m/z : 252 (M^+), 224, 150, 134, 104, 89, 77. IR (KBr): 3388, 1600, 1543, 1444, 1309, 753, 700 cm^{-1} .



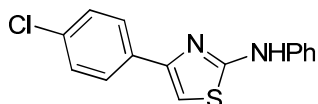
N-Phenyl-4-(*p*-tolyl)thiazol-2-amine (**3ba**)³

Red solid (112 mg, 84 %), m.p. = 94 – 95 °C. ^1H NMR (400 MHz, CDCl_3) 7.75 (d, J = 7.8 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.21 (d, J = 7.8 Hz, 2H), 7.06 (t, J = 6.5 Hz, 1H), 6.77 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.6, 151.4, 140.4, 137.7, 131.9, 129.4, 129.3, 126.1, 122.9, 118.2, 101.0, 21.3. MS (EI, 70 eV) m/z : 266 (M^+), 207, 147, 132, 118, 104, 77. IR (KBr): 1624, 1401, 1126, 749, 691 cm^{-1} .



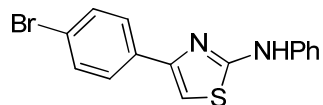
4-(4-Fluorophenyl)-*N*-phenylthiazol-2-amine (**3ca**)²

Red solid (105 mg, 78 %), m.p. = 126 – 127 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (dd, J = 8.0, 5.8 Hz, 2H), 7.35 (d, J = 5.9 Hz, 4H), 7.07 (t, J = 8.3 Hz, 3H), 6.74 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.8, 162.6 (d, J = 246 Hz), 150.3, 140.3, 130.9, 129.5, 127.8 (d, J = 8 Hz), 123.1, 118.3, 115.5 (d, J = 22 Hz), 101.3. MS (EI, 70 eV) m/z : 270 (M^+), 242, 198, 152, 122, 104, 77. IR (KBr): 1625, 1401, 1133, 746, 692 cm^{-1} .



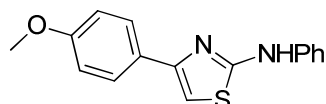
4-(4-Chlorophenyl)-*N*-phenylthiazol-2-amine (**3da**)⁴

Yellow solid (106 mg, 74 %), m.p. = 141 – 142 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 6H), 7.10 – 7.06 (m, 1H), 6.78 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 150.1, 140.2, 133.6, 133.0, 129.5, 128.8, 127.4, 123.3, 118.5, 102.1. MS (EI, 70 eV) *m/z* : 286 (M⁺), 207, 168, 150, 133, 104, 89, 77. IR (KBr): 3370, 1552, 1268, 833, 744 cm⁻¹.



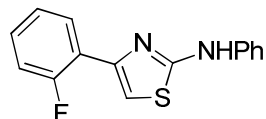
4-(4-Bromophenyl)-N-phenylthiazol-2-amine (3ea)⁴

Red solid (118 mg, 71 %), m.p. = 137 – 138 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 8.2, 6.0 Hz, 4H), 7.08 (td, *J* = 5.6, 3.0 Hz, 1H), 6.82 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 150.3, 140.2, 133.5, 131.7, 129.5, 127.7, 123.2, 121.8, 118.4, 102.3. MS (EI, 70 eV) *m/z* : 332 (M⁺), 250, 212, 150, 133, 125, 89, 77. IR (KBr): 1628, 1401, 1130, 762, 680 cm⁻¹.



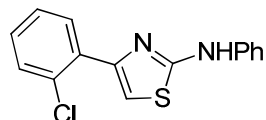
4-(4-Methoxyphenyl)-N-phenylthiazol-2-amine (3fa)²

Yellow solid (121 mg, 86 %), m.p. = 142 – 143 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.05 (t, *J* = 6.4 Hz, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.69 (s, 1H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.6, 159.4, 151.1, 140.4, 129.4, 127.6, 127.4, 122.9, 118.2, 114.0, 100.0, 55.3. MS (EI, 70 eV) *m/z* : 282 (M⁺), 267, 165, 149, 134, 121, 77. IR (KBr): 3383, 1602, 1544, 1488, 1247, 747, 689 cm⁻¹.



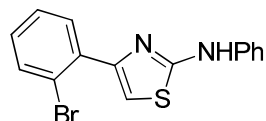
4-(2-Fluorophenyl)-N-phenylthiazol-2-amine (3ga)

Yellow solid (101 mg, 75 %), m.p. = 104 – 105 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (br, 1H), 8.10 (t, *J* = 7.7 Hz, 1H), 7.33 – 7.23 (m, 4H), 7.19 (t, *J* = 6.7 Hz, 1H), 7.14 – 7.05 (m, 3H), 7.00 (t, *J* = 6.3 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 160.4 (d, *J* = 248 Hz), 144.8 (d, *J* = 3 Hz), 140.5, 130.0 (d, *J* = 3 Hz), 129.5, 124.4 (d, *J* = 3 Hz), 123.1, 122.3 (d, *J* = 12 Hz), 118.4, 116.0, 115.8, 106.9 (d, *J* = 15 Hz). MS (EI, 70 eV) *m/z* : 270 (M⁺), 225, 207, 152, 124, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂FN₂S, [M+H]⁺: 271.0700; found, 271.0704. IR (KBr): 3392, 1599, 1549, 1314, 1217, 751, 698 cm⁻¹.



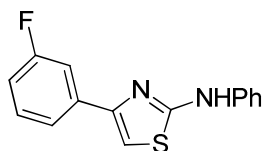
4-(2-Chlorophenyl)-N-phenylthiazol-2-amine (3ha)

Yellow solid (103 mg, 72 %), m.p. = 130 – 131 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.50 (br, 1H), 7.86 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.15 (m, 6H), 7.07 (s, 1H), 7.00 (t, *J* = 7.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 147.5, 140.4, 133.4, 132.0, 131.4, 130.4, 129.4, 128.8, 126.9, 123.1, 118.6, 106.8. MS (EI, 70 eV) *m/z* : 286 (M⁺), 207, 168, 150, 125, 104, 89, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂ClN₂S, [M+H]⁺: 287.0404; found, 287.0407. IR (KBr): 3390, 1600, 1552, 1462, 1308, 1039, 748 cm⁻¹.



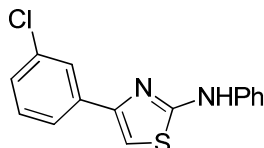
4-(2-Bromophenyl)-N-phenylthiazol-2-amine (3ia)

Yellow solid (114 mg, 69 %), m.p. = 126 – 127 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.70 (br, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.20 (m, 3H), 7.19 – 7.08 (m, 3H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.96 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 149.1, 140.4, 135.7, 133.6, 131.6, 129.4, 129.2, 127.4, 123.0, 121.9, 118.6, 106.3. MS (EI, 70 eV) *m/z* : 330 (M⁺), 251, 207, 184, 150, 134, 89, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂BrN₂S, [M+H]⁺: 330.9899; found, 330.9897. IR (KBr): 3384, 1630, 1556, 1460, 1267, 753 cm⁻¹.



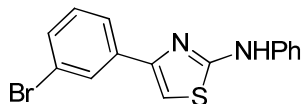
4-(3-Fluorophenyl)-N-phenylthiazol-2-amine (3ja)

Yellow solid (100 mg, 74 %), m.p. = 124 – 125 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (br, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.30 (m, 5H), 7.11 – 7.05 (m, 1H), 7.00 (t, *J* = 8.3 Hz, 1H), 6.83 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 163.2 (d, *J* = 243 Hz), 150.1 (d, *J* = 3 Hz), 140.3, 136.8 (d, *J* = 8 Hz), 130.2 (d, *J* = 8 Hz), 129.5, 123.2, 121.8 (d, *J* = 3 Hz), 118.5, 114.7 (d, *J* = 21 Hz), 113.1 (d, *J* = 22 Hz), 102.7. MS (EI, 70 eV) *m/z* : 270 (M⁺), 242, 207, 152, 122, 204, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂FN₂S, [M+H]⁺ : 271.0700; found, 271.0705. IR (KBr): 1607, 1402, 1149, 870, 748 cm⁻¹.



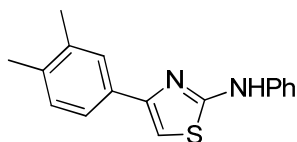
4-(3-Chlorophenyl)-N-phenylthiazol-2-amine (3ka)

Yellow solid (107 mg, 75 %), m.p. = 127 – 128 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (br, 1H), 7.81 (s, 1H), 7.70 – 7.65 (m, 1H), 7.33 – 7.27 (m, 4H), 7.27 – 7.17 (m, 2H), 7.08 – 7.00 (m, 1H), 6.78 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 150.0, 140.2, 136.3, 134.6, 129.9, 129.5, 127.9, 126.3, 124.3, 123.3, 118.6, 102.8. MS (EI, 70 eV) *m/z* : 286 (M⁺), 250, 168, 150, 124, 104, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂ClN₂S, [M+H]⁺ : 287.0404; found, 287.0408. IR (KBr): 3391, 1598, 1546, 1461, 1305, 750 cm⁻¹.



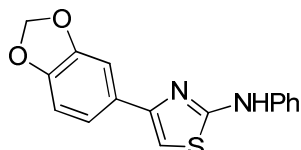
4-(3-Bromophenyl)-N-phenylthiazol-2-amine (3la)

Yellow oil (116 mg, 70 %). ¹H NMR (400 MHz, CDCl₃) δ 7.97 (s, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.28 (m, 4H), 7.21 (dd, *J* = 13.8, 5.7 Hz, 1H), 7.10 – 7.01 (m, 1H), 6.79 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.2, 149.8, 140.2, 136.6, 130.8, 130.2, 129.5, 129.2, 124.7, 123.3, 122.9, 118.5, 102.8. MS (EI, 70 eV) *m/z* : 330 (M⁺), 250, 150, 133, 125, 104, 89, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₂BrN₂S, [M+H]⁺ : 330.9899; found, 330.9900. IR (KBr): 3385, 1597, 1545, 1308, 1067, 711 cm⁻¹.



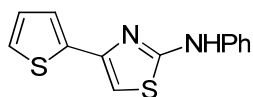
4-(3,4-Dimethylphenyl)-N-phenylthiazol-2-amine (3ma)

Red oil (113 mg, 81 %). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.32 (m, 4H), 7.15 (d, *J* = 7.7 Hz, 1H), 7.10 – 7.04 (m, 1H), 6.73 (s, 1H), 2.29 (s, 3H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.8, 150.7, 140.2, 136.8, 136.6, 131.7, 130.0, 129.5, 127.3, 123.6, 123.2, 118.4, 100.6, 19.8, 19.6. MS (EI, 70 eV) *m/z* : 280 (M⁺), 265, 207, 147, 132, 115, 91. HRMS-ESI (*m/z*): calcd for C₁₇H₁₇N₂S, [M+H]⁺ : 281.1107; found, 281.1102. IR (KBr): 1604, 1548, 1314, 1117, 748, 698 cm⁻¹.



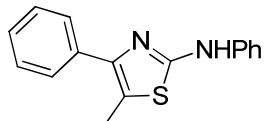
4-(Benzo[d][1,3]dioxol-5-yl)-N-phenylthiazol-2-amine (3na)

Red oil (104 mg, 70 %). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.32 (m, 6H), 7.12 – 7.03 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.65 (s, 1H), 5.98 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 164.4, 150.8, 147.9, 147.4, 140.3, 129.5, 129.0, 123.0, 120.0, 118.2, 108.4, 106.7, 101.1, 100.0. MS (EI, 70 eV) *m/z* : 296 (M⁺), 207, 178, 149, 133, 120, 104, 77. HRMS-ESI (*m/z*): calcd for C₁₆H₁₃N₂O₂S, [M+H]⁺ : 297.0692; found, 297.0692. IR (KBr): 1614, 1399, 1243, 1114, 750, 697 cm⁻¹.



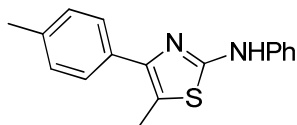
N-Phenyl-4-(thiophen-2-yl)thiazol-2-amine (30a)

Brown solid (97 mg, 75 %), m.p. = 89 – 90 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.04 (br, 1H), 7.40 – 7.35 (m, 1H), 7.30 – 7.29 (m, 4H), 7.24 – 7.19 (m, 1H), 7.09 – 6.96 (m, 2H), 6.67 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 165.0, 145.7, 140.2, 138.6, 129.5, 127.7, 124.9, 123.9, 123.2, 118.4, 100.6. MS (EI, 70 eV) m/z : 258 (M⁺), 225, 207, 149, 140, 96, 77. HRMS-ESI (m/z): calcd for C₁₃H₁₁N₂S₂, [M+H]⁺ : 259.0358; found, 259.0361. IR (KBr): 3383, 1599, 1539, 1421, 1291, 752, 701 cm⁻¹.



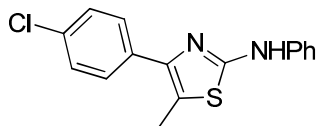
5-Methyl-N,4-diphenylthiazol-2-amine (3pa)⁵

Yellow solid (110 mg, 83 %), m.p. = 161 – 162 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 6.9 Hz, 2H), 7.32-7.22 (m, 5H), 7.01 (d, *J* = 6.7 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 146.1, 140.6, 135.1, 129.4, 128.5, 128.3, 127.4, 122.7, 118.1, 116.8, 12.3. MS (EI, 70 eV) m/z: 266 (M⁺), 251, 207, 150, 115, 104, 77. IR (KBr): 3371, 1625, 1450, 1324, 755, 694 cm⁻¹.



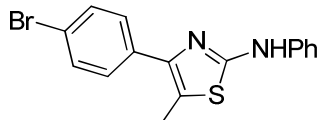
5-Methyl-N-phenyl-4-(p-tolyl)thiazol-2-amine (3qa)

Yellow solid (119 mg, 85 %), m.p. = 164 – 165 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 7.7 Hz, 2H), 7.22 – 7.13 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.8, 146.2, 140.9, 137.1, 132.3, 129.2, 129.0, 128.5, 122.5, 118.3, 115.6, 21.3, 12.3. MS (EI, 70 eV) m/z : 280 (M⁺), 265, 161, 150, 118, 91, 77. HRMS-ESI (m/z): calcd for C₁₇H₁₇N₂S, [M+H]⁺ : 281.1107; found, 281.1109. IR (KBr): 1611, 1399, 1114, 747, 693 cm⁻¹.



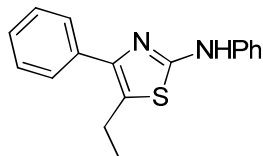
4-(4-Chlorophenyl)-5-methyl-N-phenylthiazol-2-amine (3ra)⁵

Yellow solid (119 mg, 79 %), m.p. = 169 – 170 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.35 – 7.24 (m, 4H), 7.06 (t, *J* = 7.0 Hz, 1H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.3, 144.8, 140.4, 133.4, 133.2, 129.7, 129.4, 128.5, 123.0, 118.3, 117.0, 12.3. MS (EI, 70 eV) m/z: 300 (M⁺), 285, 181, 150, 138, 103, 77. IR (KBr): 3358, 1570, 1268, 749 cm⁻¹.



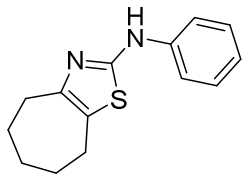
4-(4-Bromophenyl)-5-methyl-N-phenylthiazol-2-amine (3sa)

Yellow solid (139 mg, 81 %), m.p. = 173 – 174 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 4H), 7.30 – 7.24 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 145.1, 140.5, 134.0, 131.4, 130.1, 129.4, 122.9, 121.4, 118.4, 117.0, 12.3. MS (EI, 70 eV) m/z : 344 (M⁺), 331, 184, 162, 150, 132, 77. HRMS-ESI (m/z): calcd for C₁₆H₁₄BrN₂S, [M+H]⁺ : 345.0056; found, 345.0060. IR (KBr): 3360, 1622, 1399, 1132, 750 cm⁻¹.



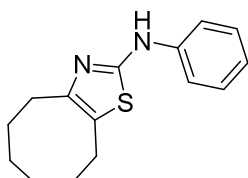
5-Ethyl-*N*,4-diphenylthiazol-2-amine (3ta)

Yellow solid (115 mg, 82 %), m.p. = 156 – 157 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.1 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.96 (t, *J* = 7.2 Hz, 1H), 2.83 (q, *J* = 7.5 Hz, 2H), 1.26 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 145.4, 140.8, 135.3, 129.3, 128.7, 128.3, 127.5, 124.5, 122.6, 118.4, 20.5, 16.8. MS (EI, 70 eV) *m/z* : 280 (M⁺), 265, 162, 147, 135, 103, 77. HRMS-ESI (*m/z*): calcd for C₁₇H₁₇N₂S, [M+H]⁺ : 281.1107; found, 281.1109. IR (KBr): 1600, 1550, 1454, 1307, 755, 696 cm⁻¹.



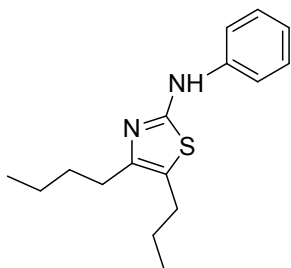
N-Phenyl-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazol-2-amine (3ua)

Yellow solid (90 mg, 74 %), m.p. = 103 – 104 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 7.00 (t, *J* = 7.1 Hz, 1H), 2.82 – 2.74 (m, 2H), 2.70 – 2.65 (m, 2H), 1.82 (d, *J* = 4.4 Hz, 2H), 1.77 – 1.67 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 149.9, 141.0, 129.3, 122.2, 120.4, 117.7, 31.8, 31.4, 28.3, 26.6, 26.1. MS (EI, 70 eV) *m/z* : 244 (M⁺), 215, 190, 135, 93, 77. HRMS-ESI (*m/z*): calcd for C₁₄H₁₇N₂S, [M+H]⁺ : 245.1107; found, 245.1111. IR (KBr): 2923, 1600, 1551, 1440, 749. cm⁻¹.



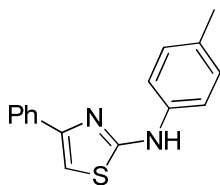
N-Phenyl-4,5,6,7,8,9-hexahydrocycloocta[*d*]thiazol-2-amine (3va)

Red solid (94 mg, 73 %), m.p. = 186 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.12 (br, 1H), 2.88 – 2.82 (m, 2H), 2.69 – 2.62 (m, 2H), 1.79 – 1.71 (m, 2H), 1.70 – 1.63 (m, 2H), 1.47 – 1.43 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 170.4, 161.1, 142.4, 129.6, 121.8, 120.2, 116.3, 31.8, 30.4, 29.2, 26.0, 25.7, 23.6. MS (EI, 70 eV) *m/z* : 258 (M⁺), 230, 215, 103, 190, 93, 77. HRMS-ESI (*m/z*): calcd for C₁₅H₁₉N₂S, [M+H]⁺ : 259.1263; found, 259.1267. IR (KBr): 2922, 1560, 1424, 1299, 746, 694. cm⁻¹.



4-Butyl-*N*-phenyl-5-propylthiazol-2-amine (3wa)

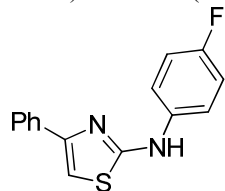
Red oil (85 mg, 62 %). ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.09 (br, 1H), 2.69 – 2.63 (m, 2H), 2.49 (t, *J* = 7.7 Hz, 2H), 1.74 (dt, *J* = 15.3, 7.6 Hz, 2H), 1.57 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.43 (dq, *J* = 14.7, 7.4 Hz, 2H), 1.03 – 0.93 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 162.3, 142.4, 129.7, 121.9, 120.1, 116.4, 31.8, 30.4, 27.3, 22.7, 22.6, 14.1, 14.0. MS (EI, 70 eV) *m/z* : 274 (M⁺), 245, 232, 203, 190, 119, 77. HRMS-ESI (*m/z*): calcd for C₁₆H₂₃N₂S, [M+H]⁺ : 275.1576; found, 275.1577. IR (KBr): 2949, 1600, 1533, 1414, 750, 691. cm⁻¹.



4-Phenyl-*N*-(*p*-tolyl)thiazol-2-amine (3ab)³

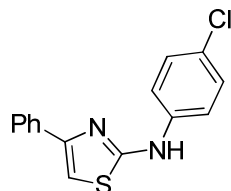
Red solid (109 mg, 82 %), m.p. = 102 – 103 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 3.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.5, 151.2, 137.8, 134.5, 133.1, 130.0, 128.6, 127.9, 126.1, 119.0, 101.5, 20.8. MS (EI, 70 eV) m/z : 266 (M^+), 207, 163, 134, 118, 104, 91, 77. IR (KBr): 1625, 1401, 1131, 756 cm^{-1} .



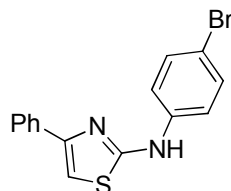
***N*-(4-Fluorophenyl)-4-phenylthiazol-2-amine (3ac)⁶**

Brown solid (108 mg, 80%), m.p. = 142 – 143 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, J = 7.9 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 7.05 (t, J = 8.3 Hz, 2H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 157.5, 151.6, 136.7, 134.6, 128.6, 128.0, 126.1, 120.8 (d, J = 8 Hz), 116.1 (d, J = 23 Hz), 101.7. MS (EI, 70 eV) m/z : 270 (M^+), 207, 168, 134, 122, 91, 77. IR (KBr): 1626, 1401, 1132, 754 cm^{-1} .



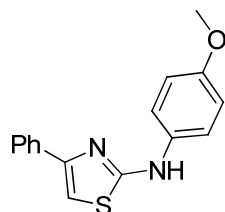
***N*-(4-Chlorophenyl)-4-phenylthiazol-2-amine (3ad)⁶**

Yellow solid (109 mg, 76 %), m.p. = 140 – 141 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, J = 7.8 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.34 – 7.28 (m, 3H), 7.27 – 7.22 (m, 2H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 151.3, 138.9, 134.3, 129.4, 128.7, 128.1, 127.8, 126.2, 119.5, 102.0. MS (EI, 70 eV) m/z : 286 (M^+), 207, 183, 134, 104, 91, 77. IR (KBr): 3379, 1629, 1584, 1132, 823, 706 cm^{-1} .



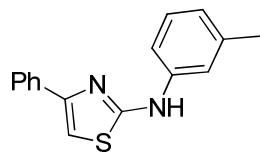
***N*-(4-Bromophenyl)-4-phenylthiazol-2-amine (3ae)³**

Red solid (125 mg, 75 %), m.p. = 146 – 147 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, J = 7.7 Hz, 2H), 7.39 (t, J = 8.0 Hz, 4H), 7.32 (t, J = 7.1 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 6.83 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 151.4, 139.5, 134.4, 132.2, 128.7, 128.1, 126.2, 119.8, 115.1, 102.1. MS (EI, 70 eV) m/z : 332 (M^+), 251, 149, 134, 125, 104, 90, 77. IR (KBr): 3378, 1629, 1589, 1328, 1064, 820, 706 cm^{-1} .



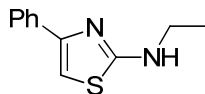
***N*-(4-Methoxyphenyl)-4-phenylthiazol-2-amine (3af)³**

White solid (124 mg, 88 %), m.p. = 142 – 143 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.4 Hz, 2H), 7.26 – 7.20 (m, 3H), 6.83 (d, J = 8.9 Hz, 2H), 6.69 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.3, 156.4, 151.4, 134.7, 133.8, 128.6, 127.8, 126.1, 122.2, 114.7, 101.2, 55.6. MS (EI, 70 eV) m/z : 282 (M^+), 267, 240, 165, 134, 91, 77. IR (KBr): 3379, 1630, 1314, 1029, 823, 702 cm^{-1} .



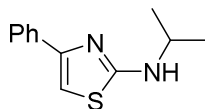
4-Phenyl-*N*-(*m*-tolyl)thiazol-2-amine (3ag)

Red oil (102 mg, 77 %). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (d, $J = 7.7$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.22 (dd, $J = 12.2, 7.8$ Hz, 2H), 7.14 (s, 1H), 6.89 (d, $J = 7.0$ Hz, 1H), 6.82 (s, 1H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.7, 151.2, 140.2, 139.5, 134.6, 129.3, 128.7, 127.9, 126.1, 124.0, 119.1, 115.3, 101.7, 21.6. MS (EI, 70 eV) m/z : 266 (M^+), 207, 164, 134, 118, 91, 77. HRMS-ESI (m/z): calcd for $\text{C}_{16}\text{H}_{15}\text{N}_2\text{S}$, $[\text{M}+\text{H}]^+$: 267.0950; found, 267.0954. IR (KBr): 1630, 1548, 1491, 770, 694 cm^{-1} .



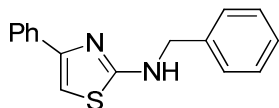
N-Ethyl-4-phenylthiazol-2-amine (3ah)

Red oil (92 mg, 90 %). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.9$ Hz, 2H), 7.37 (t, $J = 7.5$ Hz, 2H), 7.29 (d, $J = 7.4$ Hz, 1H), 6.69 (s, 1H), 5.50 (br, 1H), 3.36 – 3.27 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 169.7, 151.7, 135.0, 128.5, 127.6, 126.1, 100.6, 40.8, 14.7. MS (EI, 70 eV) m/z : 204 (M^+), 189, 176, 134, 102, 89. HRMS-ESI (m/z): calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{S}$, $[\text{M}+\text{H}]^+$: 205.0794; found, 205.0797. IR (KBr): 1558, 1334, 1244, 1059, 700 cm^{-1} .



N-Isopropyl-4-phenylthiazol-2-amine (3ai)

Yellow oil (80 mg, 73 %). ^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.3$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.30 – 7.25 (m, 1H), 6.69 (s, 1H), 5.20 (br, 1H), 3.78 – 3.67 (m, 1H), 1.28 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 168.7, 151.4, 135.0, 128.5, 127.6, 126.0, 100.6, 48.0, 22.9. MS (EI, 70 eV) m/z : 218 (M^+), 203, 176, 134, 104, 89, 77. HRMS-ESI (m/z): calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{S}$, $[\text{M}+\text{H}]^+$: 219.0950; found, 219.0954. IR (KBr): 1601, 1545, 1443, 1337, 1056, 1027, 771, 701 cm^{-1} .



N-Benzyl-4-phenylthiazol-2-amine (3aj)⁷

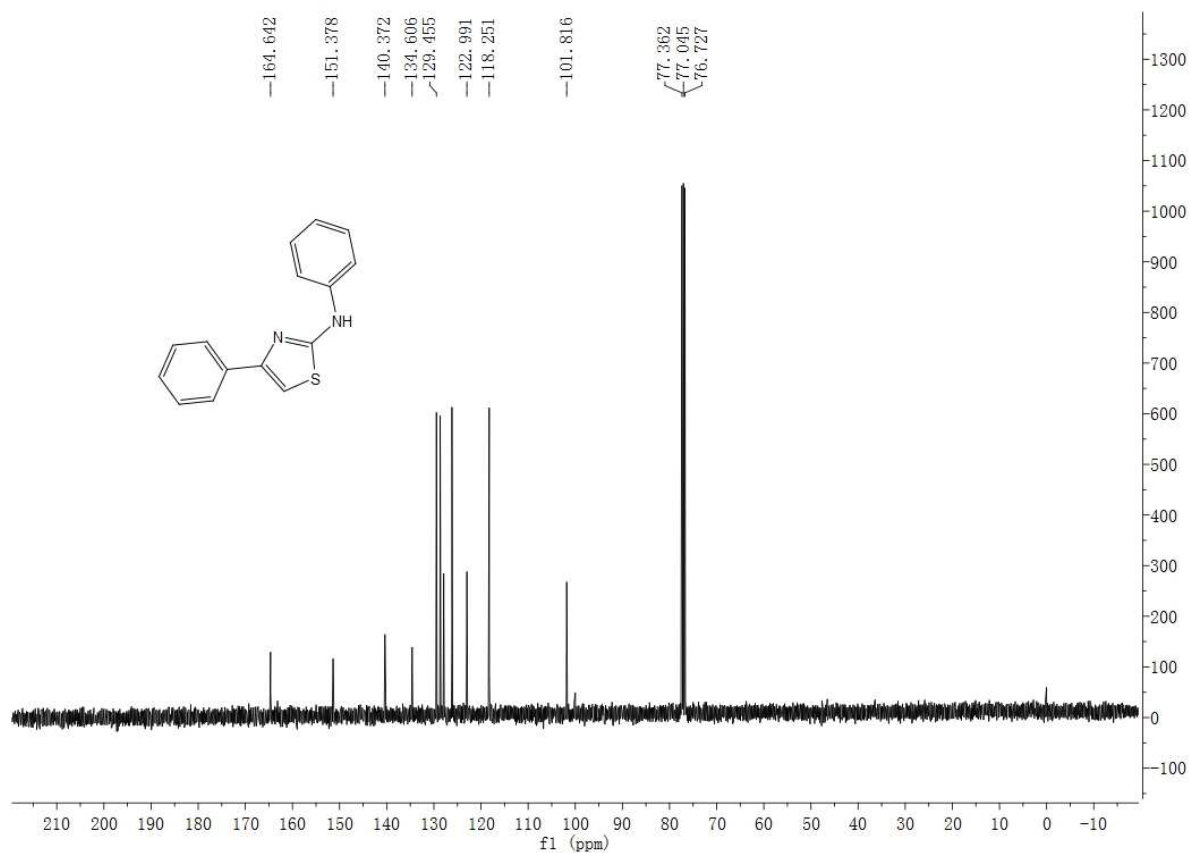
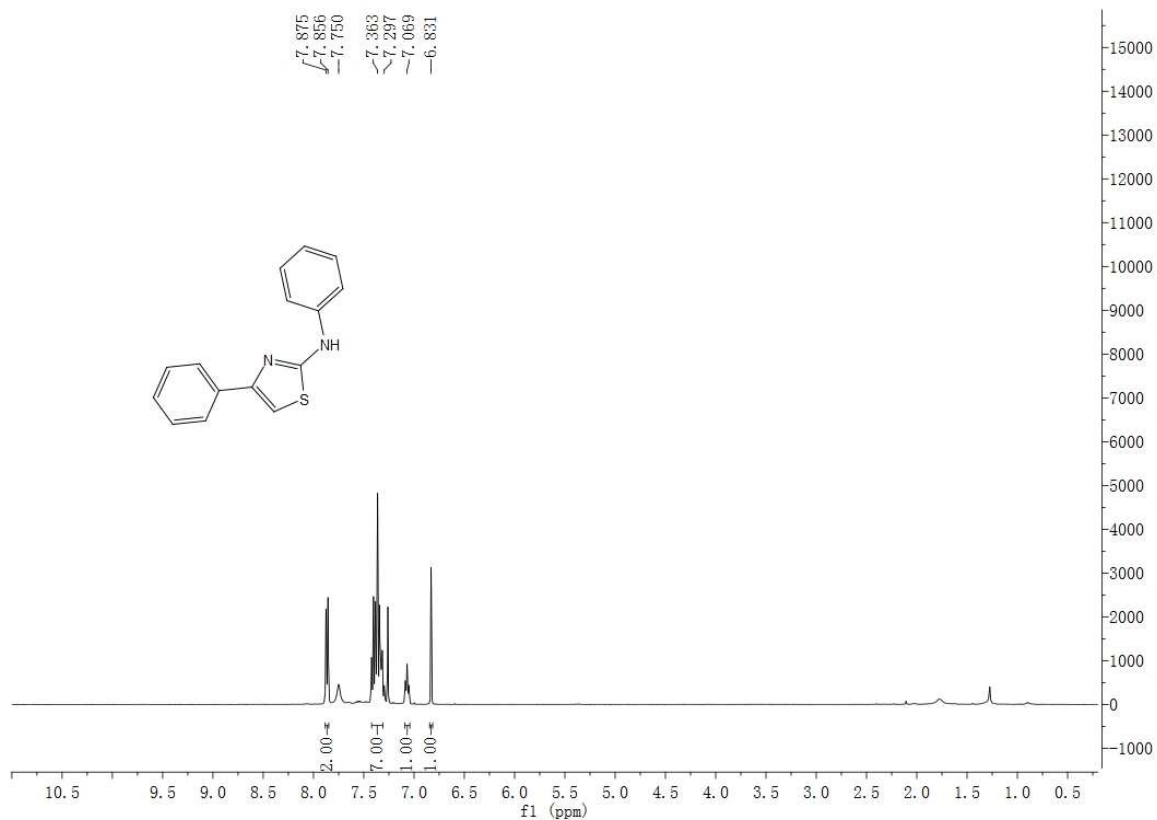
Red oil (113 mg, 85 %). ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.8$ Hz, 2H), 7.42 – 7.33 (m, 6H), 7.29 (dd, $J = 14.5, 6.7$ Hz, 2H), 6.70 (s, 1H), 5.86 (br, 1H), 4.51 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.3, 151.4, 137.7, 134.8, 128.8, 128.6, 127.8, 127.7, 126.1, 101.1, 49.9. MS (EI, 70 eV) m/z : 266 (M^+), 233, 162, 134, 106, 91. IR (KBr): 1626, 1401, 1131, 755 cm^{-1} .

References

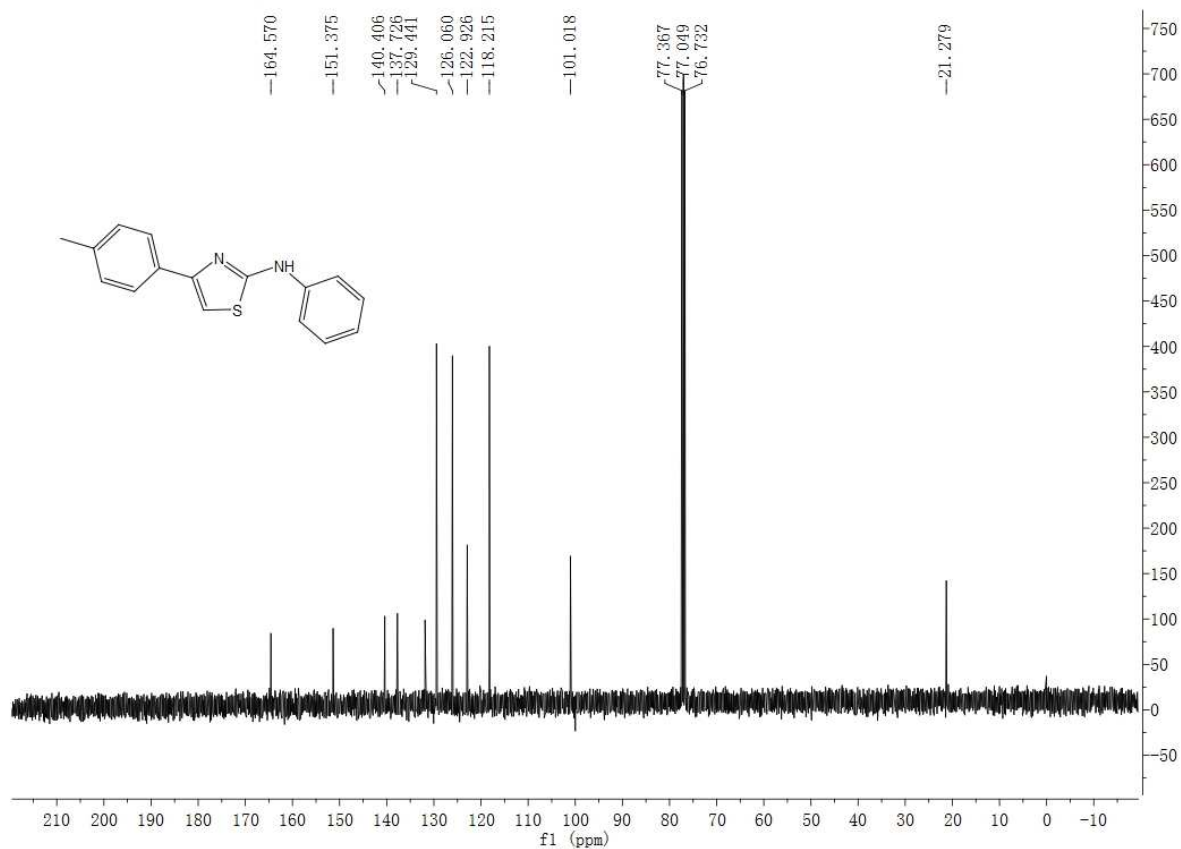
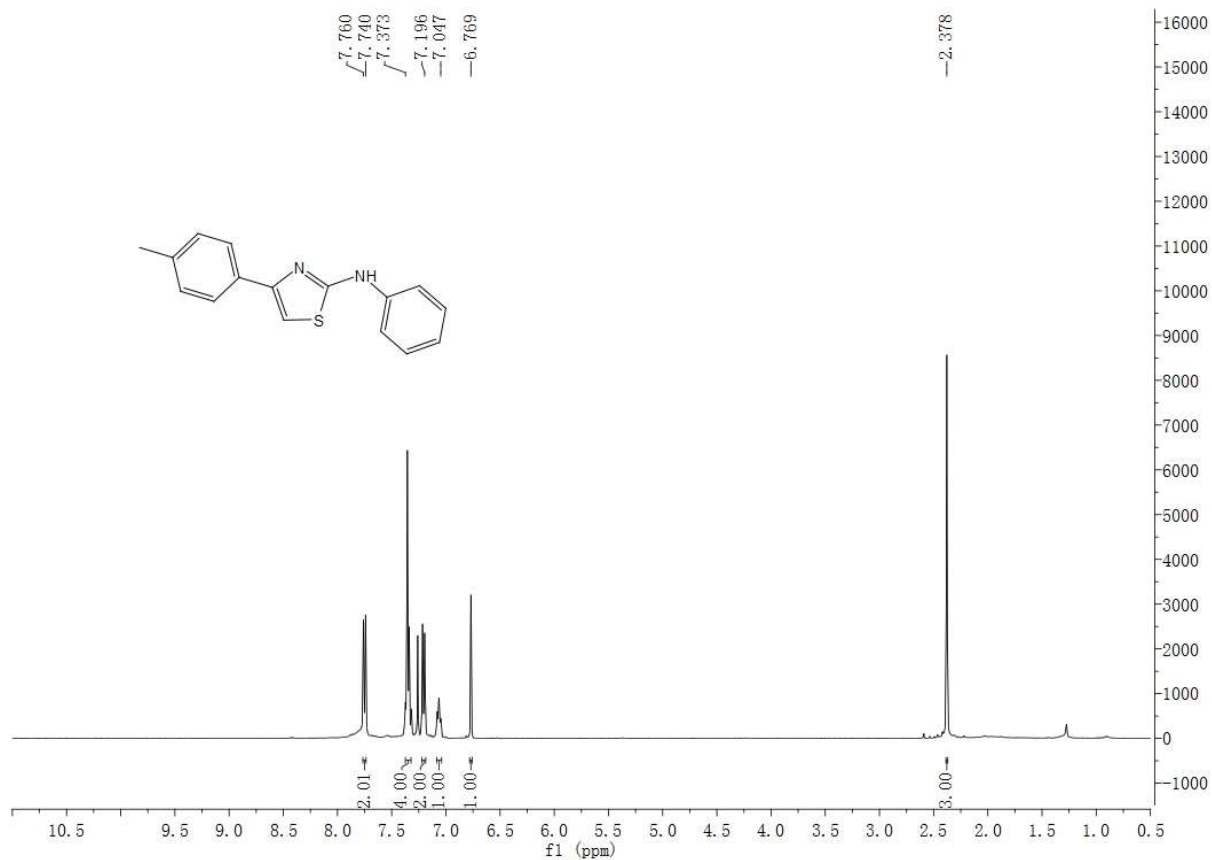
1. Too, P. C.; Wang, Y.-F.; Chiba, S. *Org. Lett.* **2010**, *12*, 5688.
2. Potewar, T. M.; Ingale, S. A.; Srinivasan, K. V. *Tetrahedron* **2008**, *64*, 5019.
3. Kidwai, M.; Chauhan, R.; Bhatnagar, D. *J. Sulfur Chem.* **2011**, *32*, 37.
4. Kidwai, M.; Bhatnagar, D.; Mothsra, P.; Singh, A. K.; Dey, S. *J. Sulfur Chem.* **2009**, *30*, 29.
5. Lagoja, I.; Pannecouque, C.; Griffioen, G.; Wera, S.; Rojaselaparra, V. M.; Aerschot, A. V.; *Eur. J. Pharm. Sci.* **2011**, *43*, 386.
6. Madhav, B.; Murthy, S. N.; Kumar, B. S. P. A.; Ramesh, K.; Nageswar, Y. V. D. *Tetrahedron Lett.* **2012**, *53*, 3835.
7. Golubev, V.; Zubkov, F.; Krasavin, M. *Tetrahedron Lett.* **2013**, *54*, 4844.

NMR Spectra for All Compounds

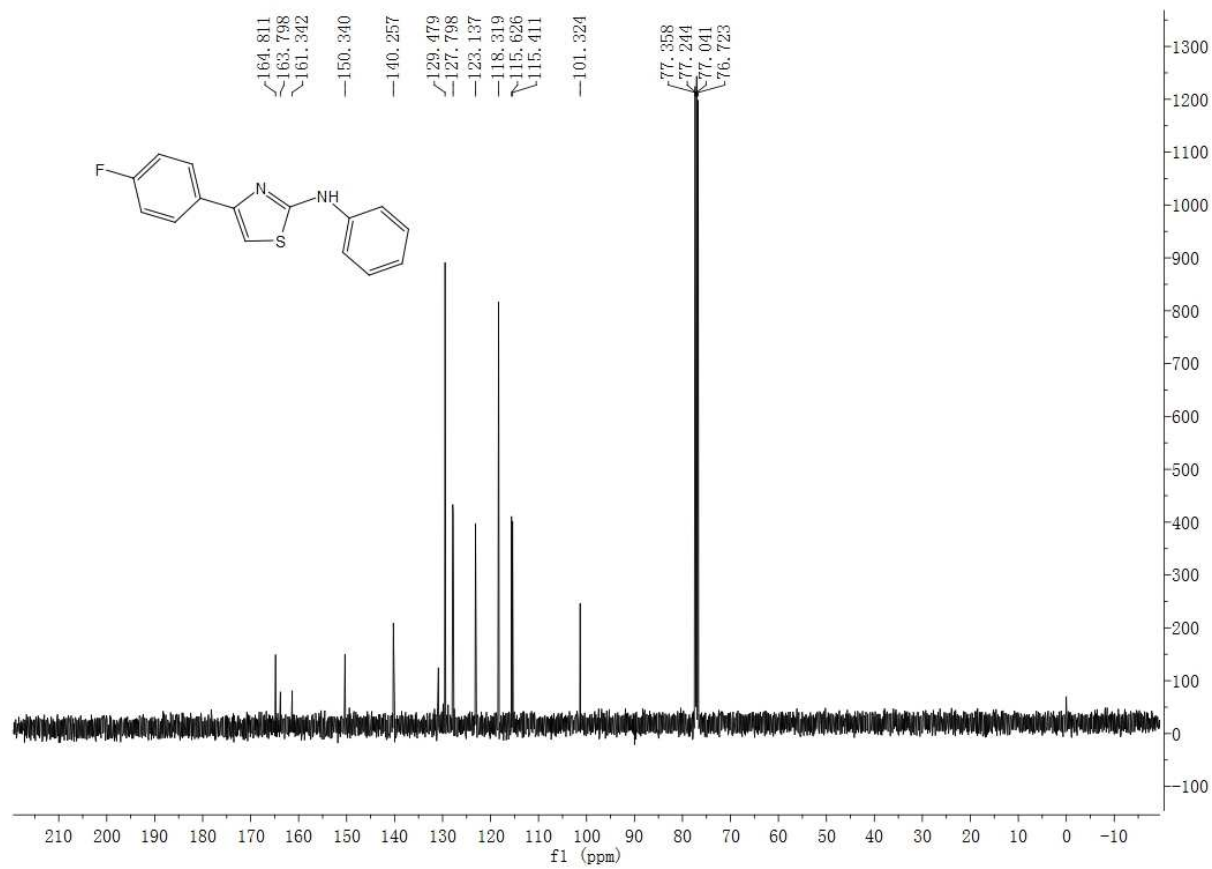
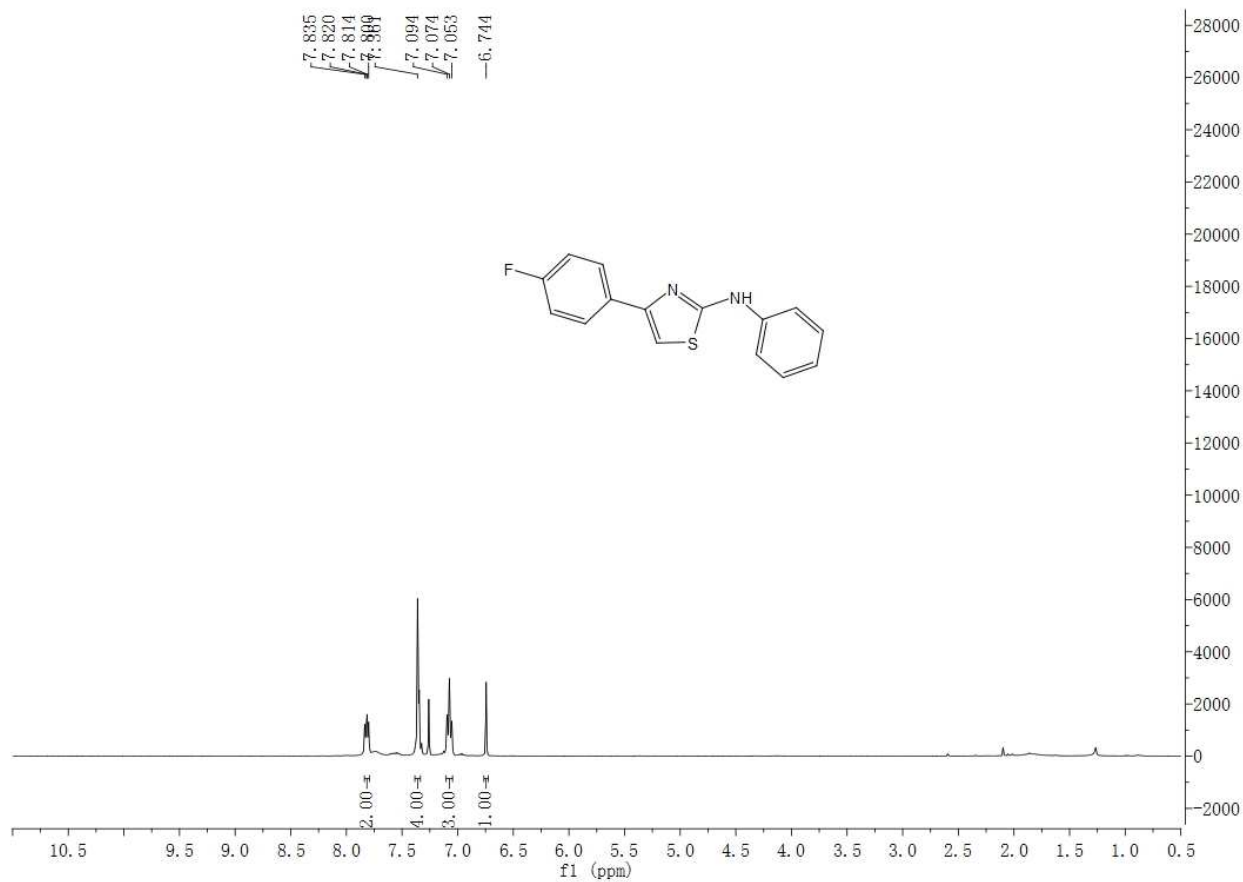
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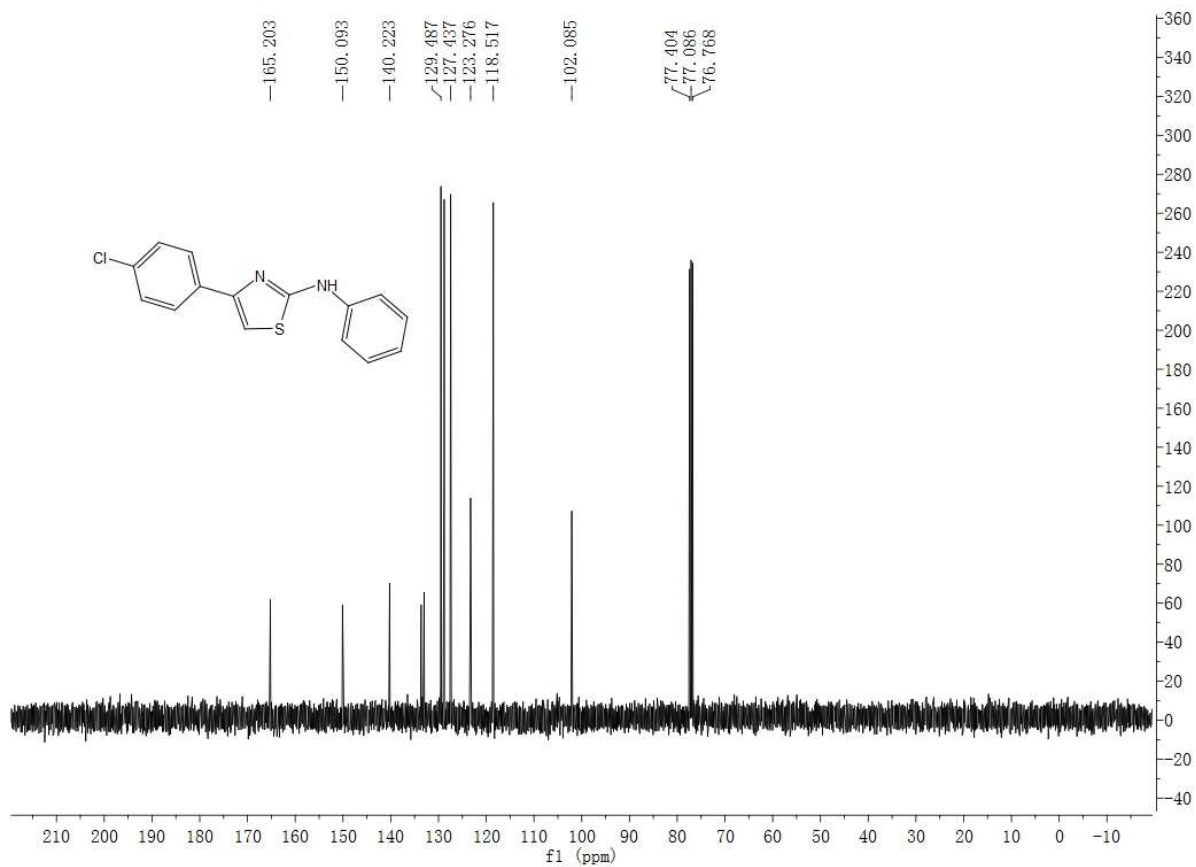
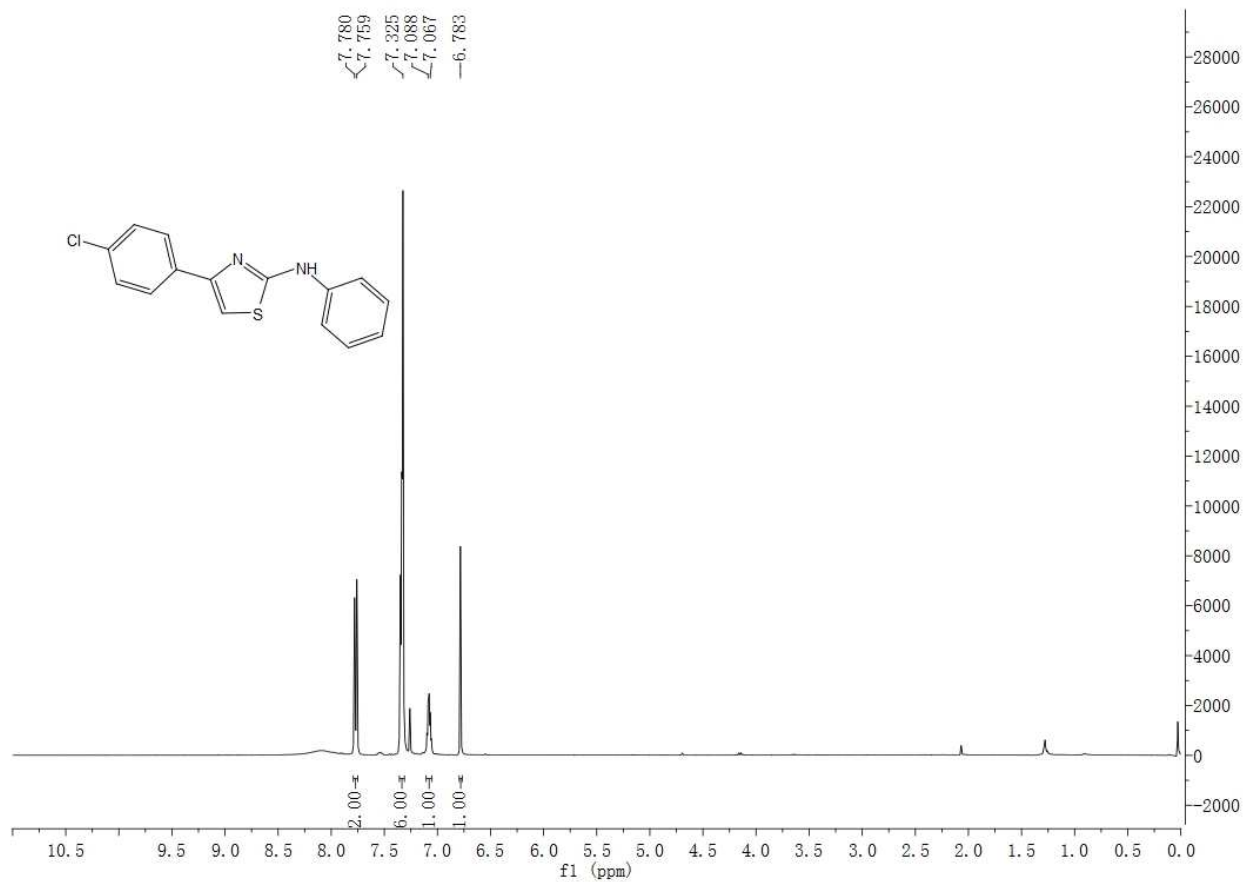
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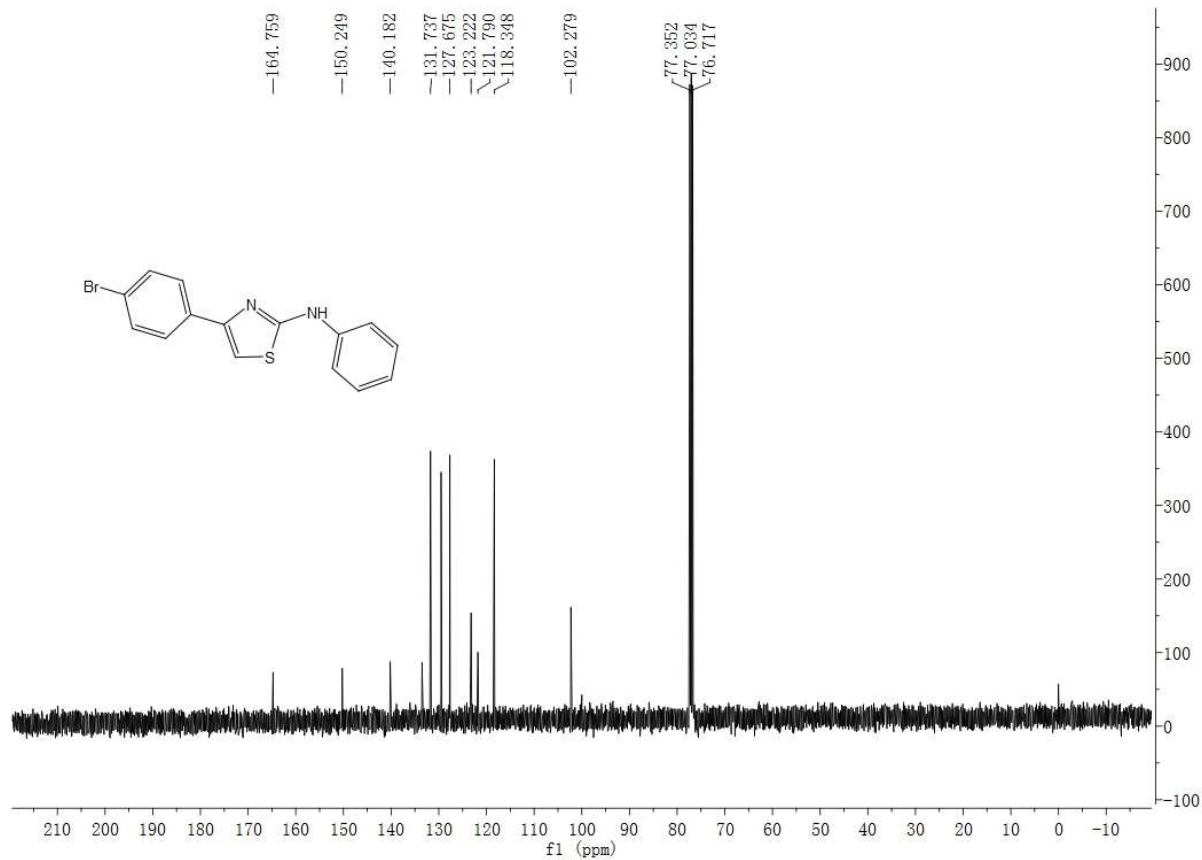
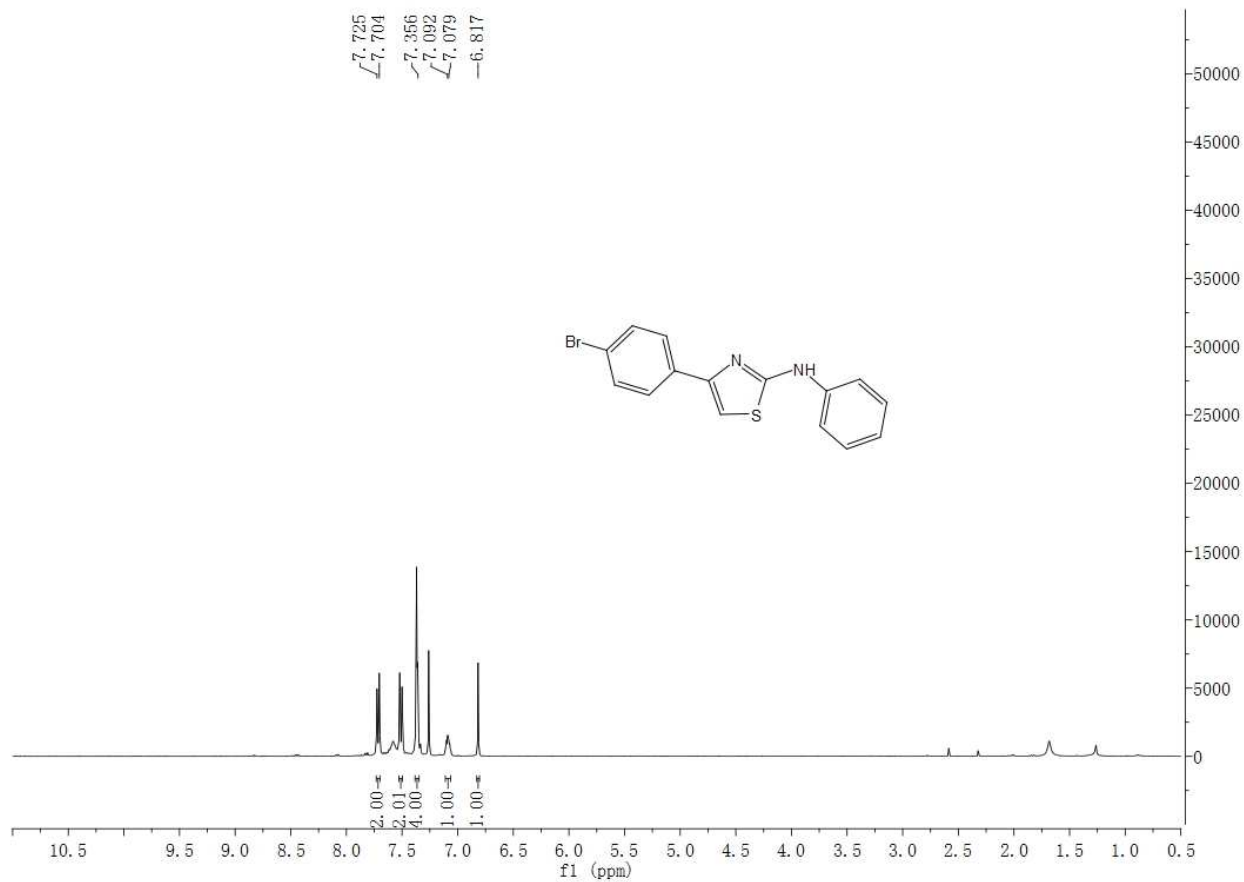
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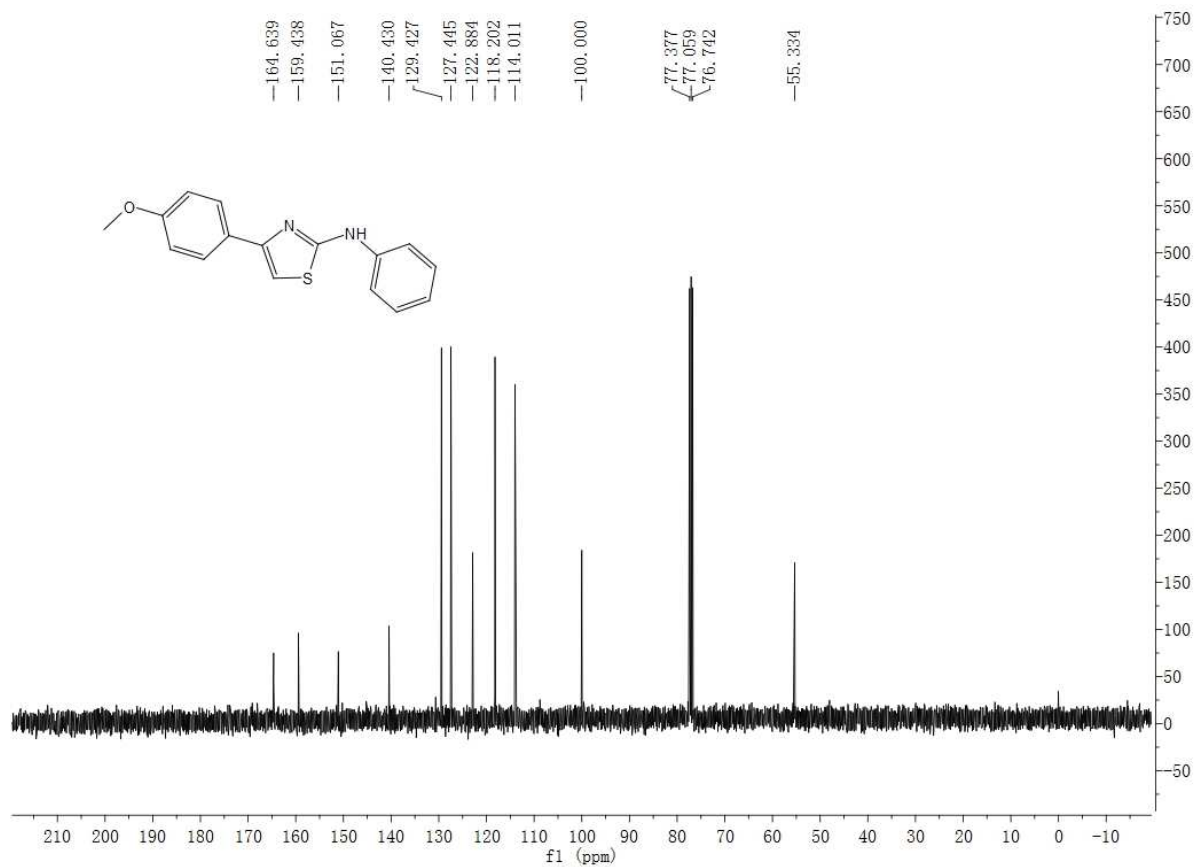
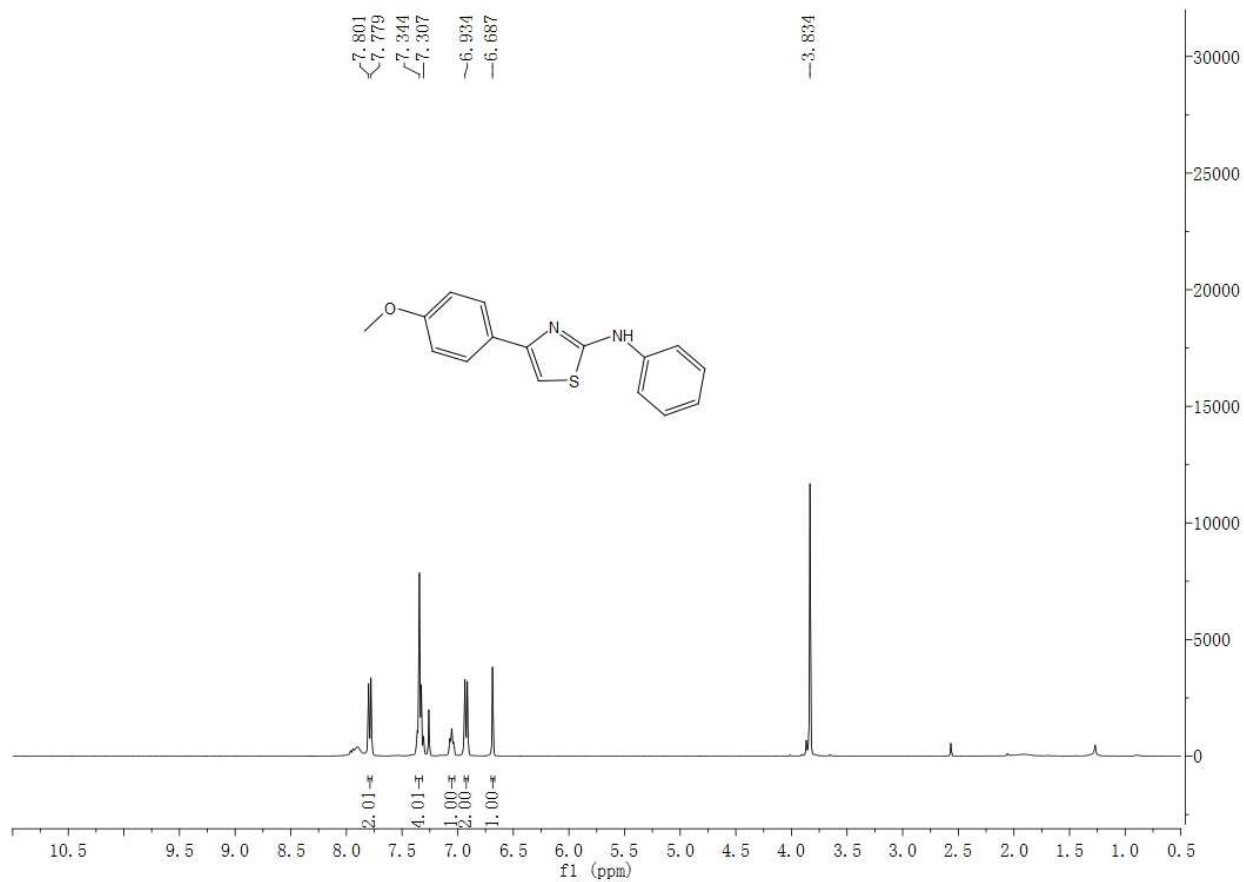
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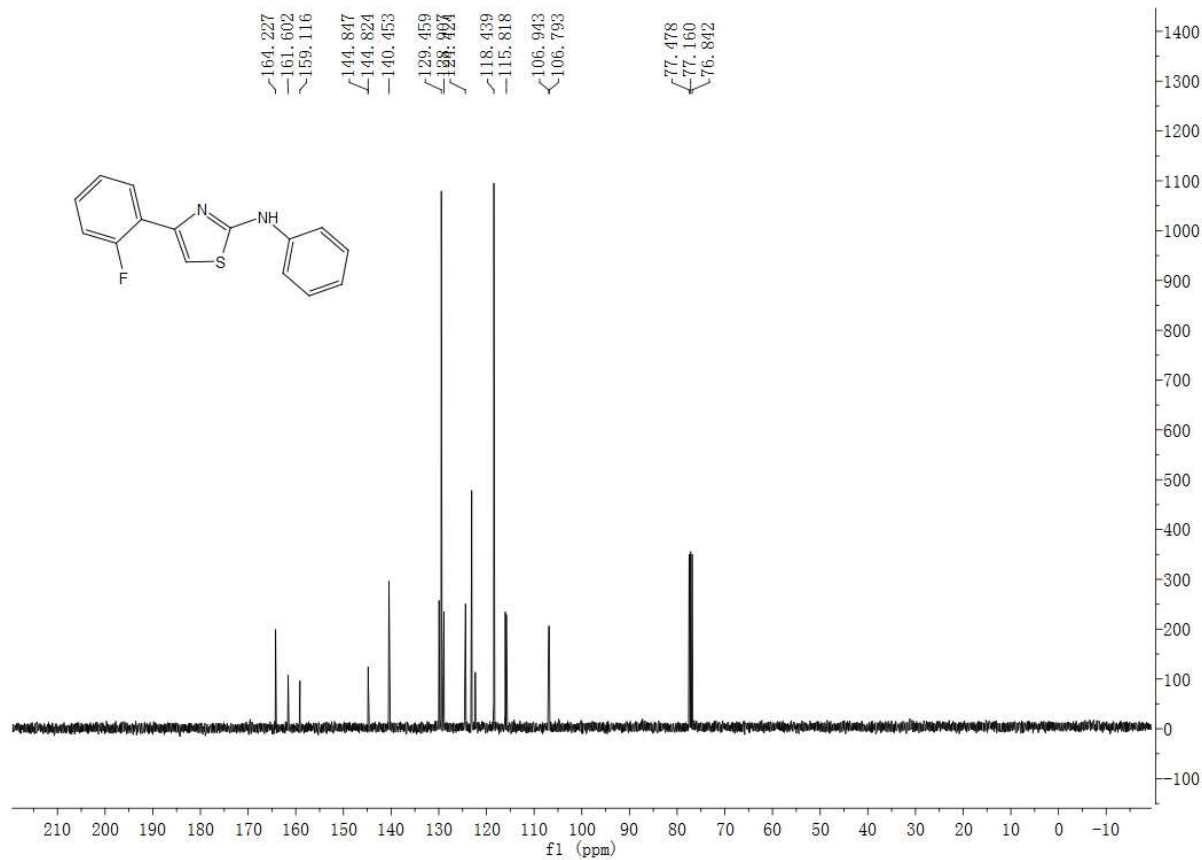
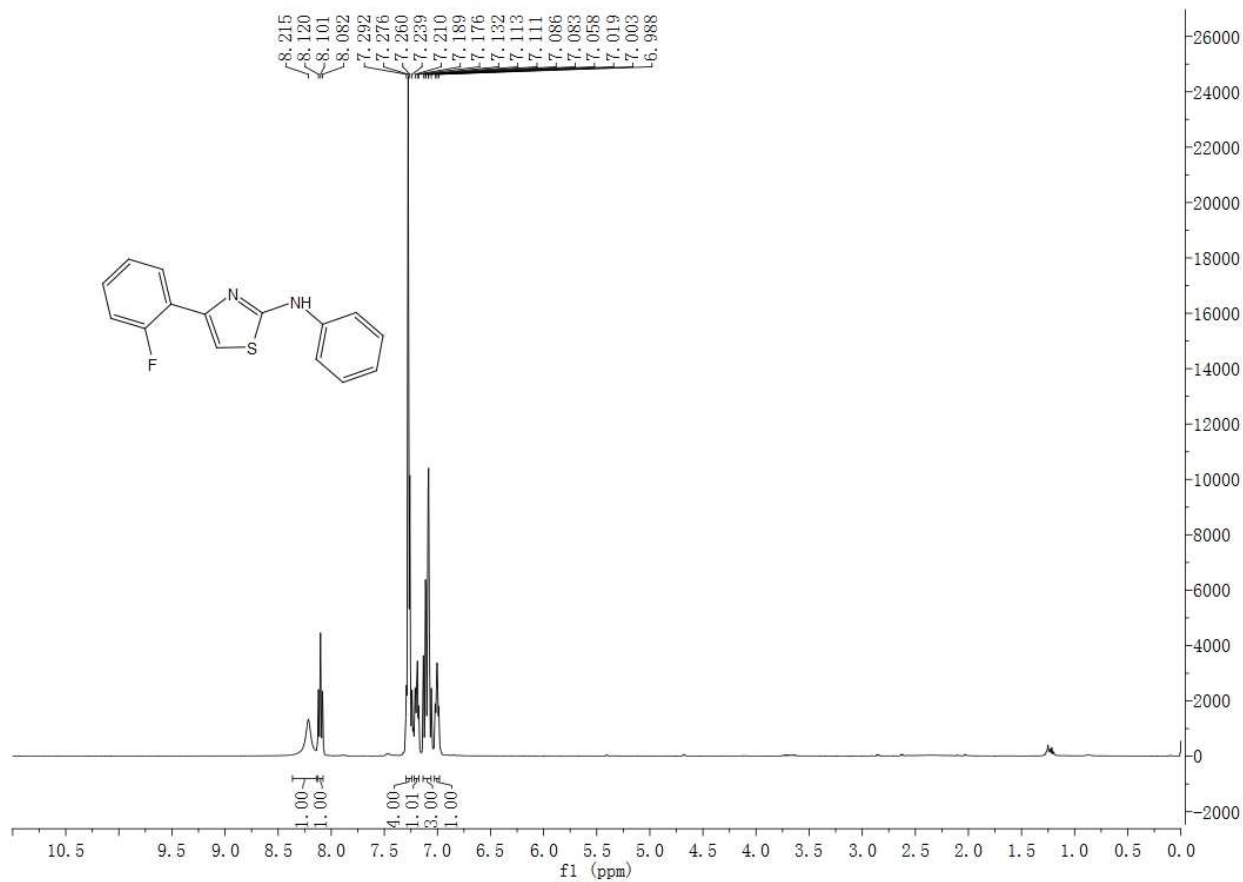
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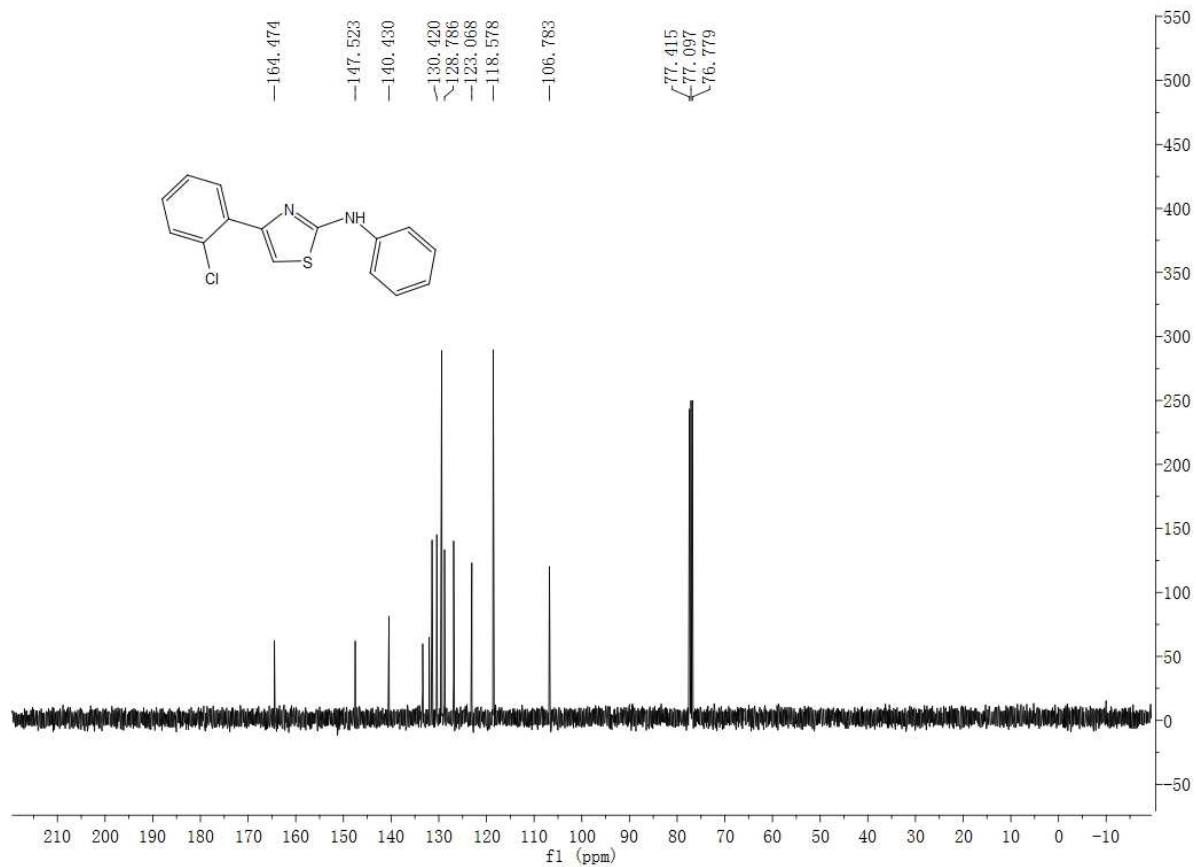
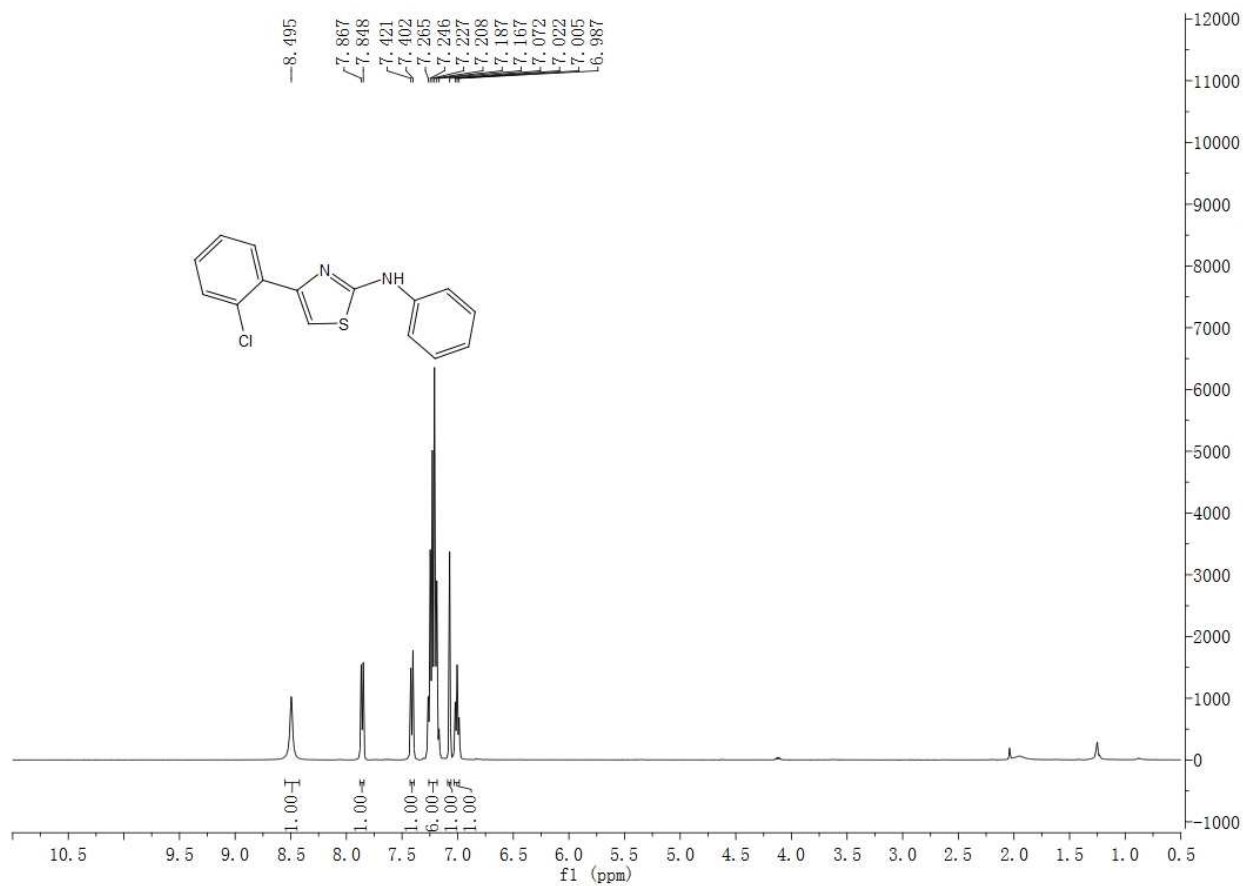
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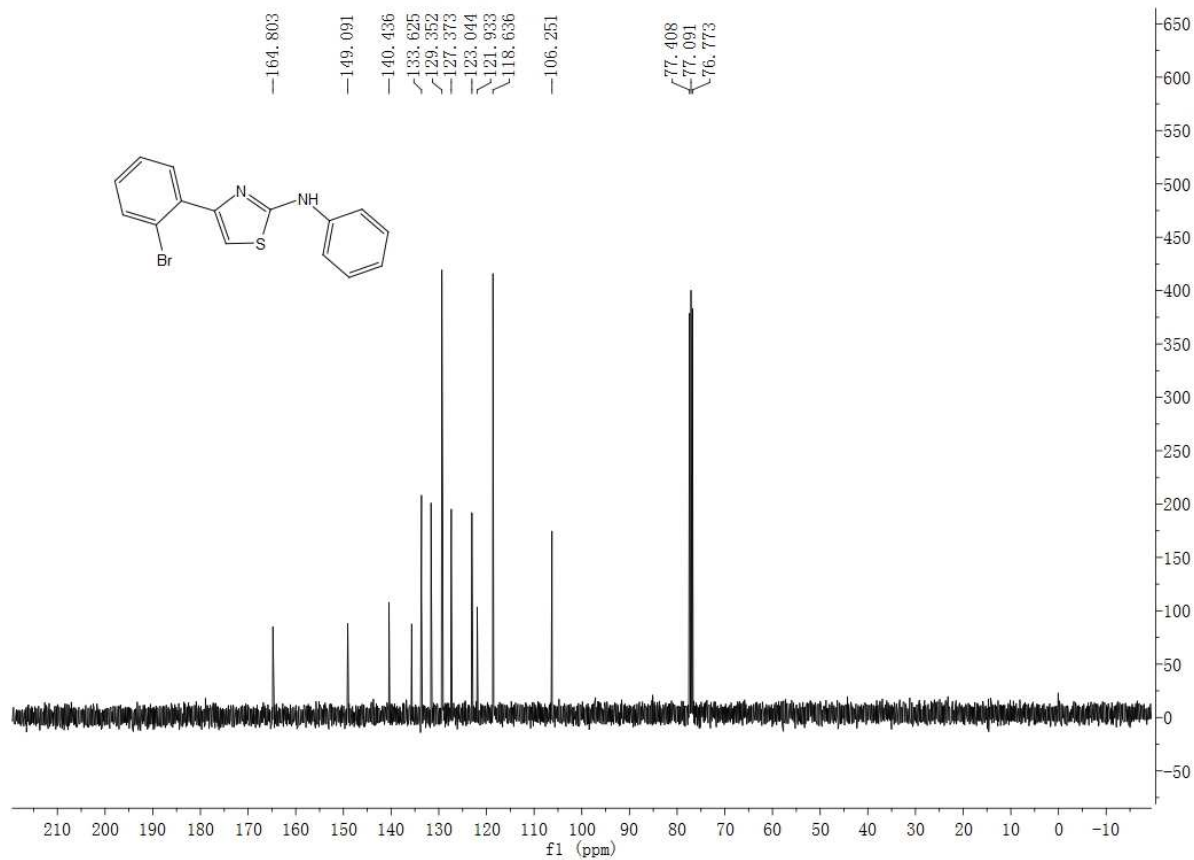
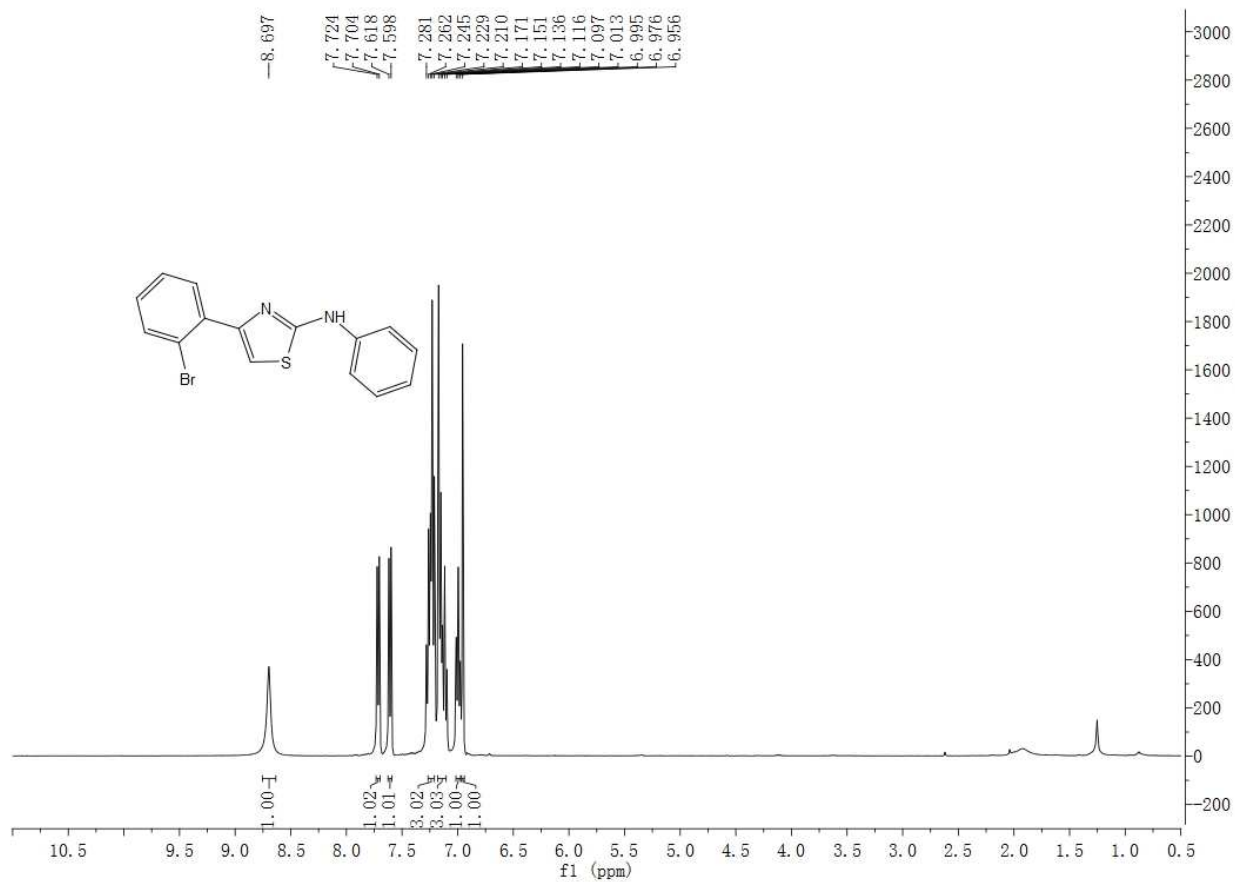
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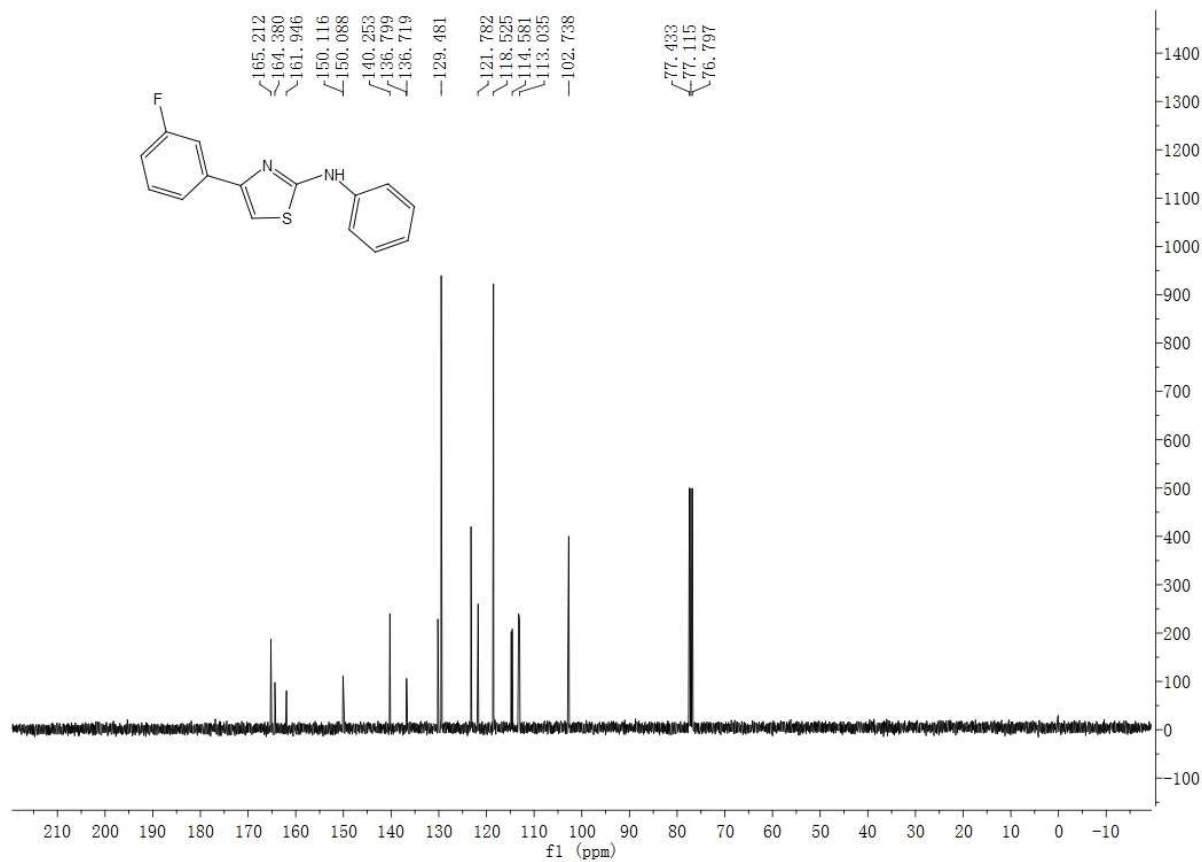
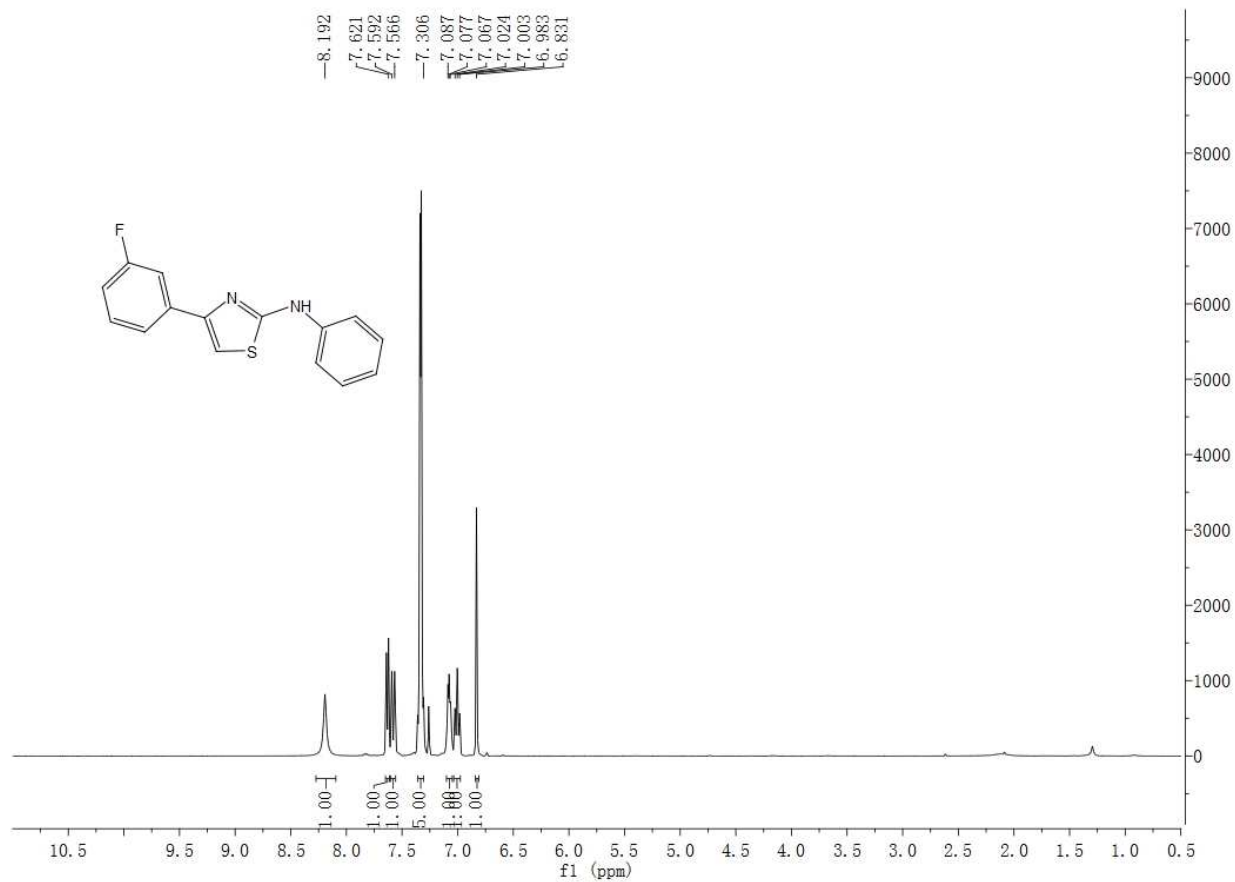
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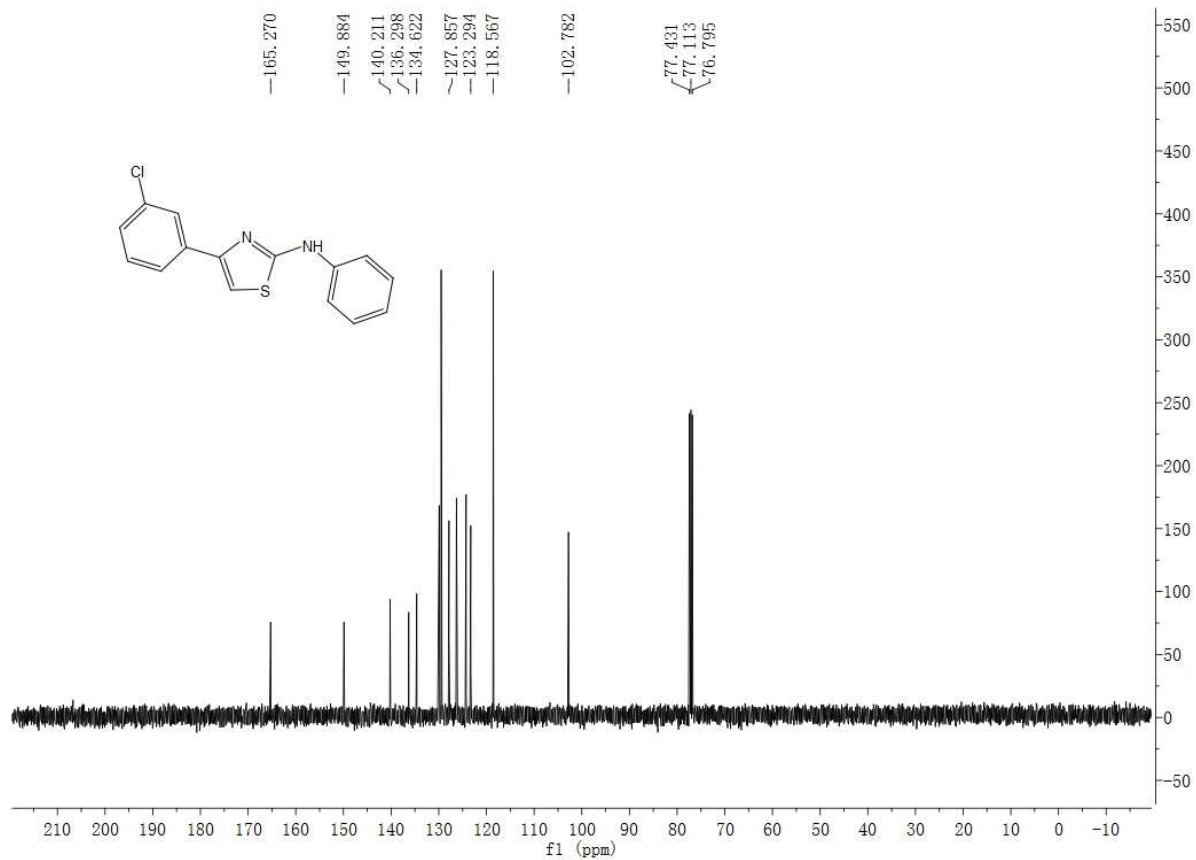
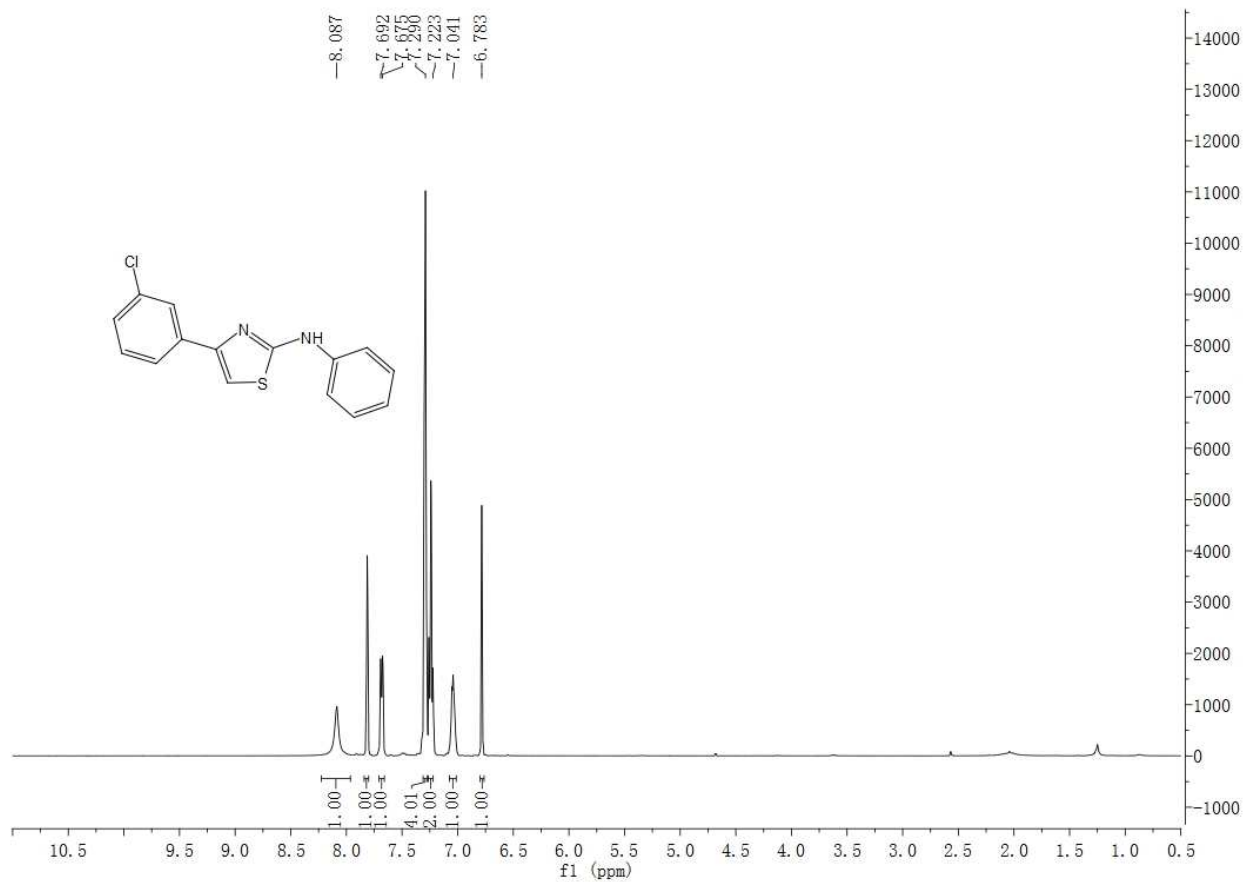
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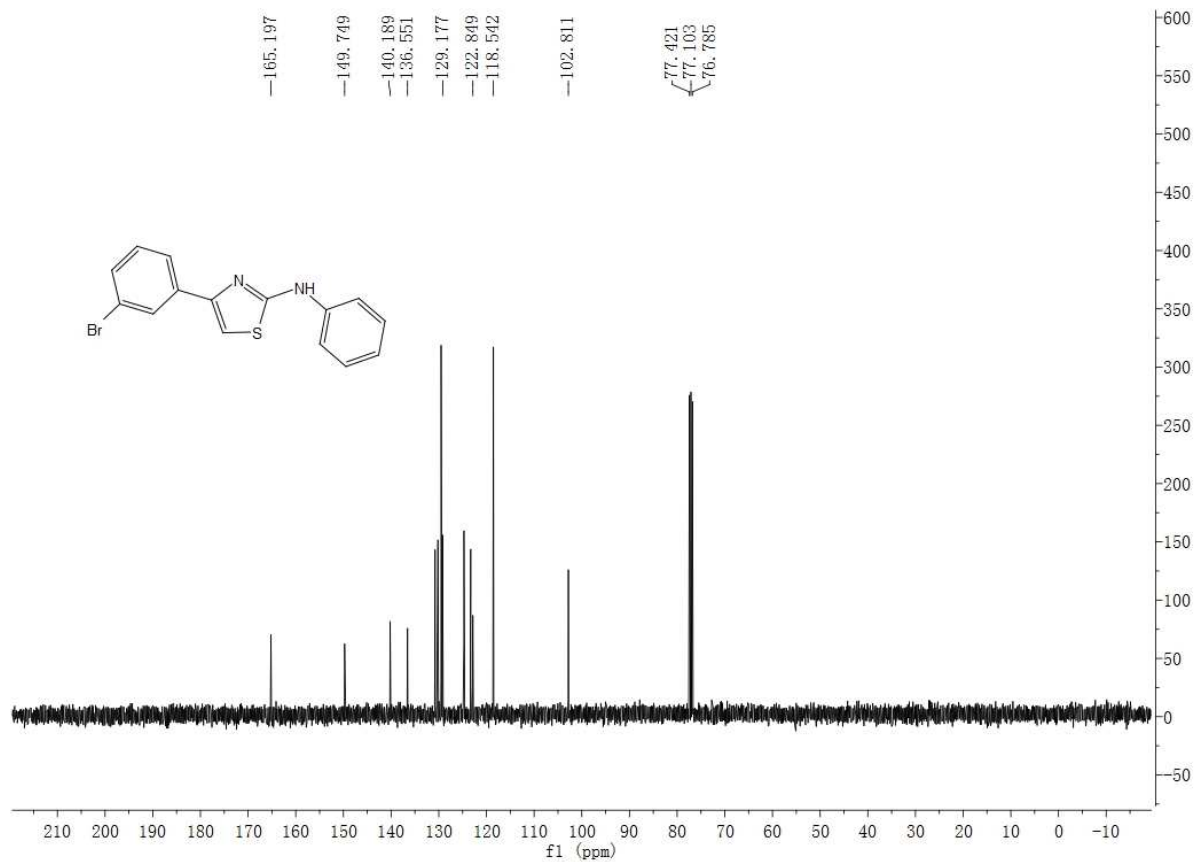
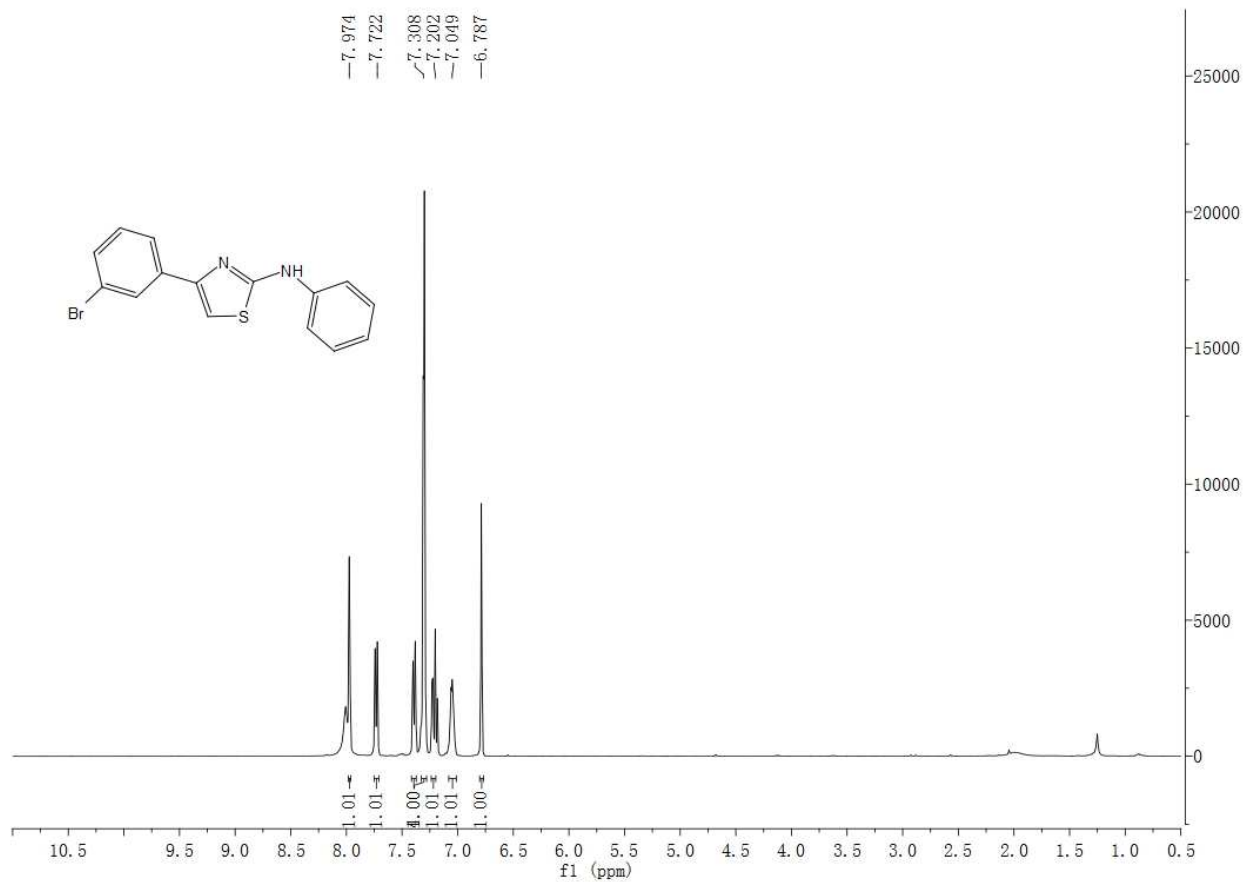
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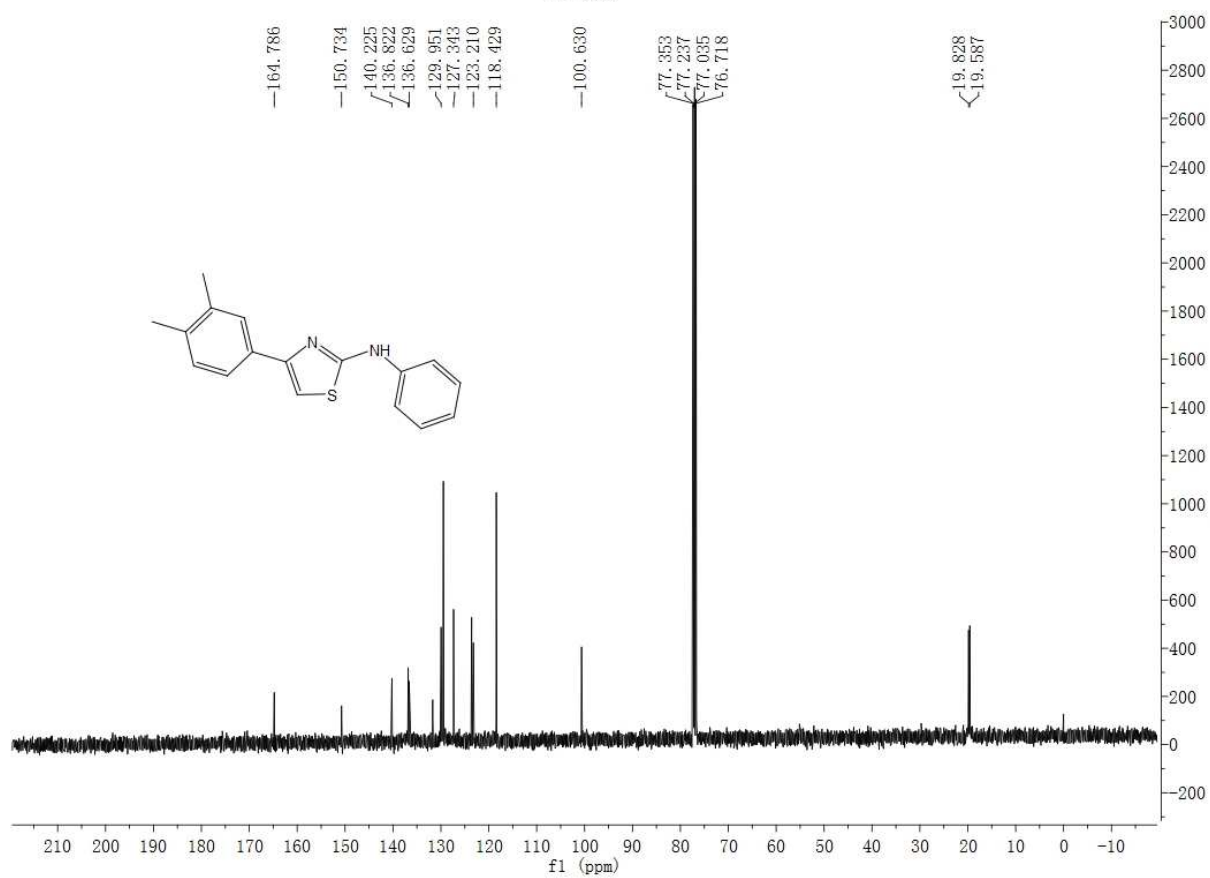
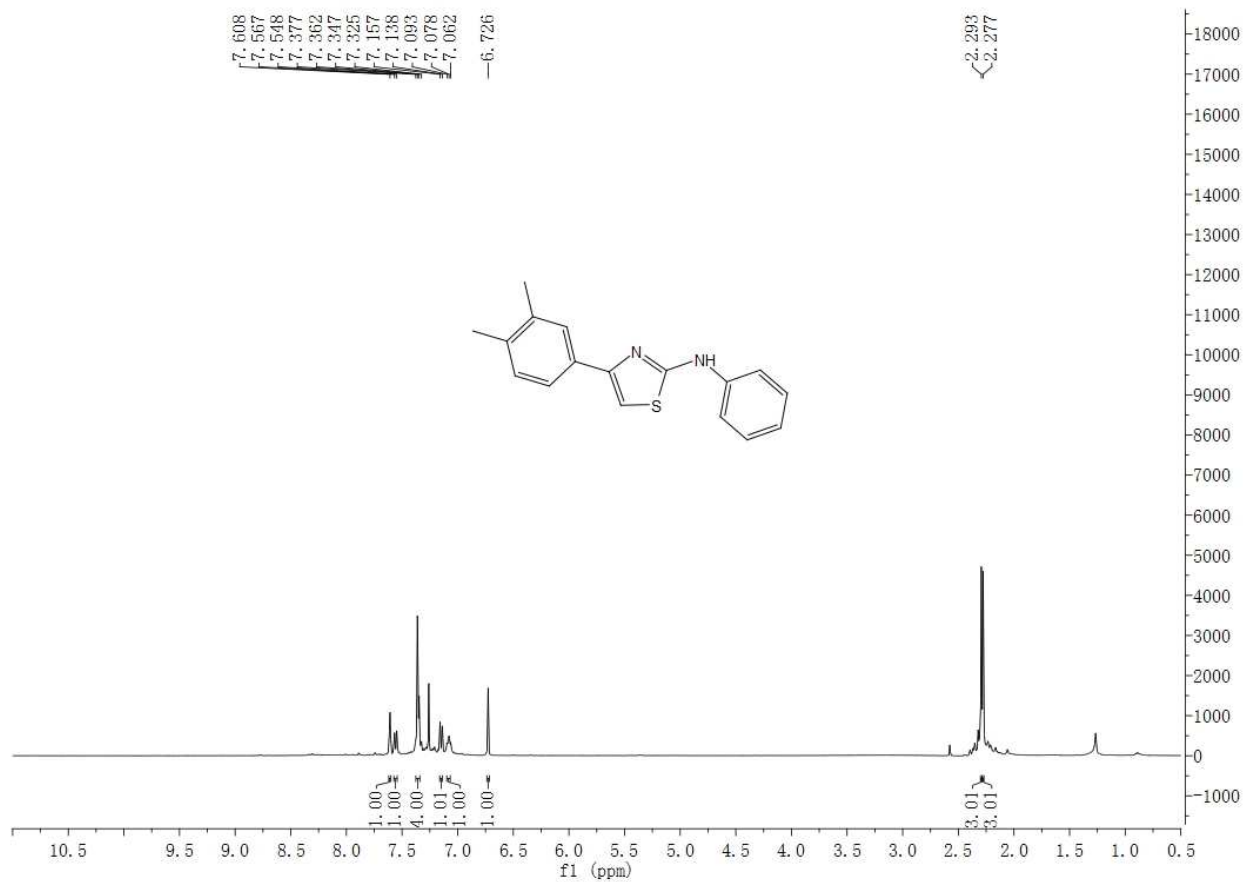
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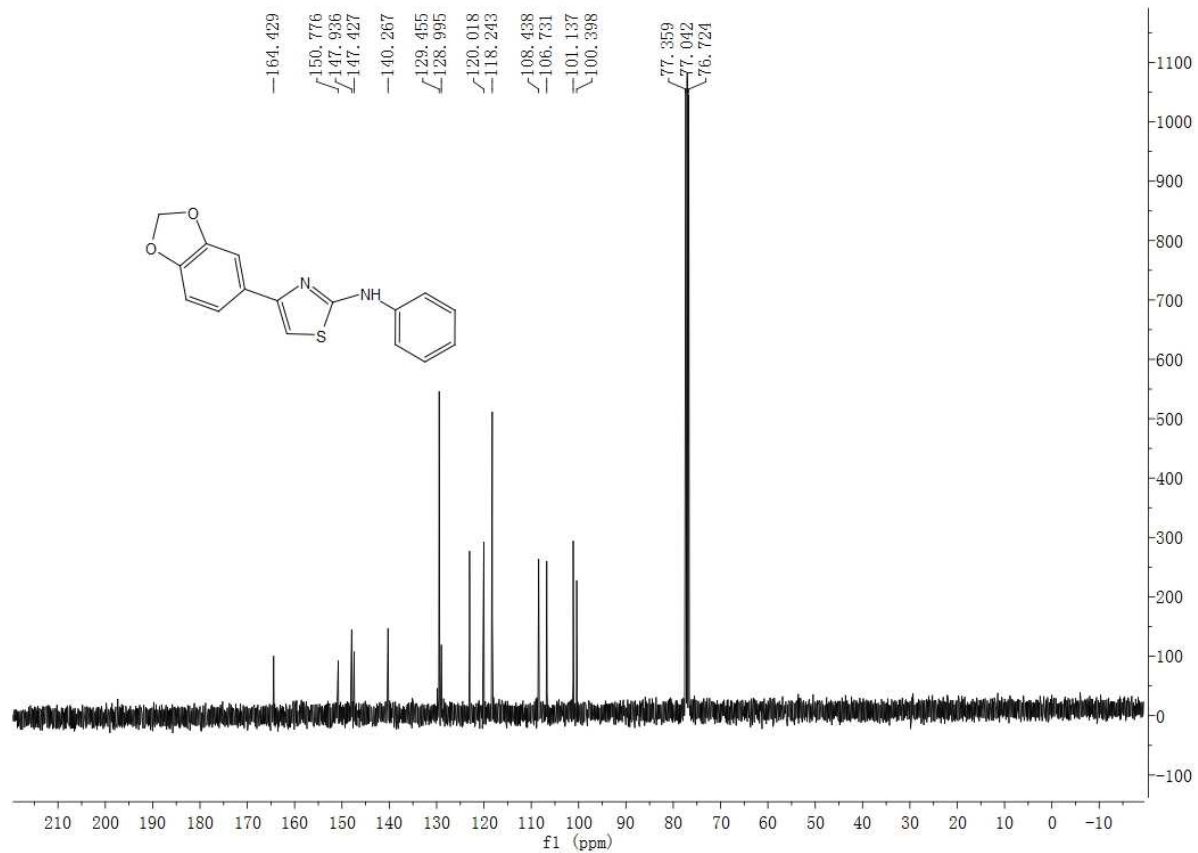
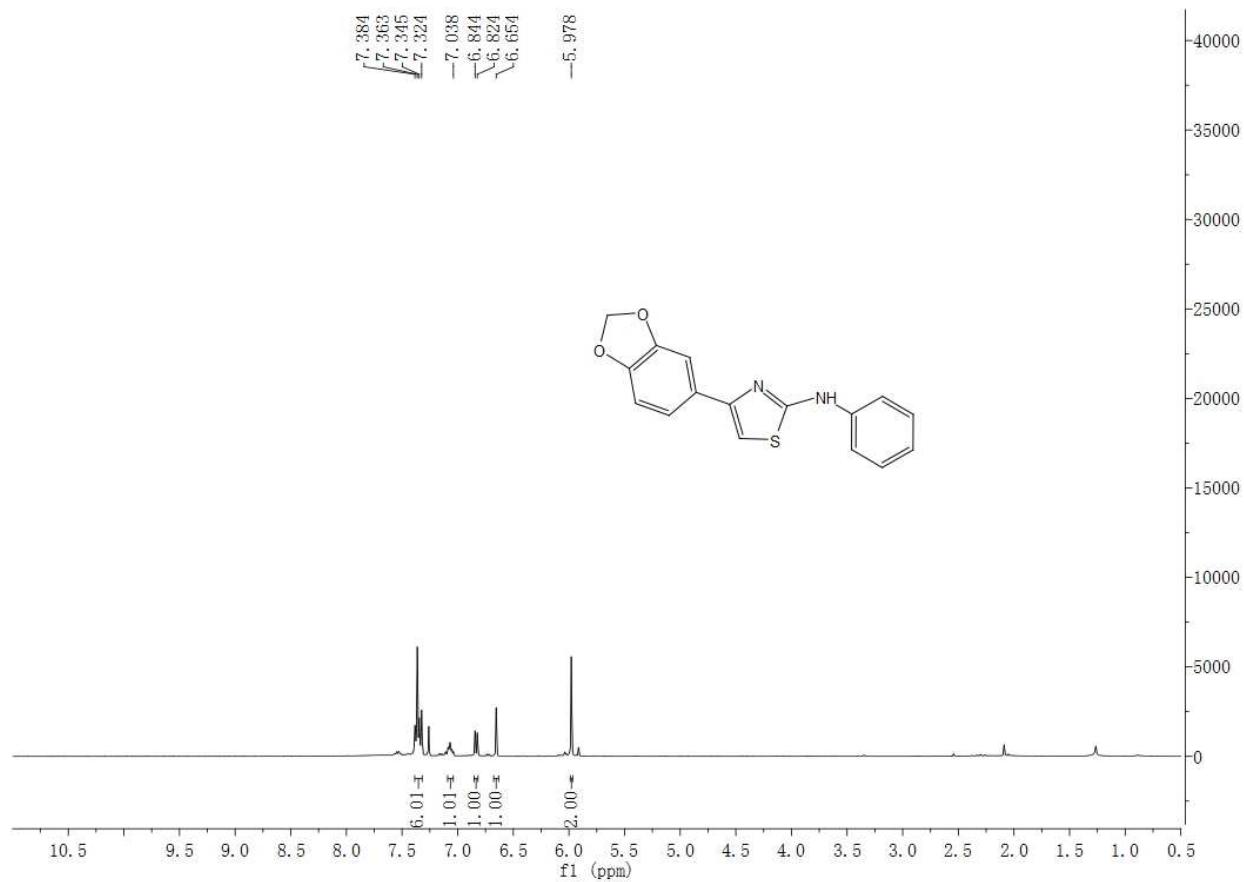
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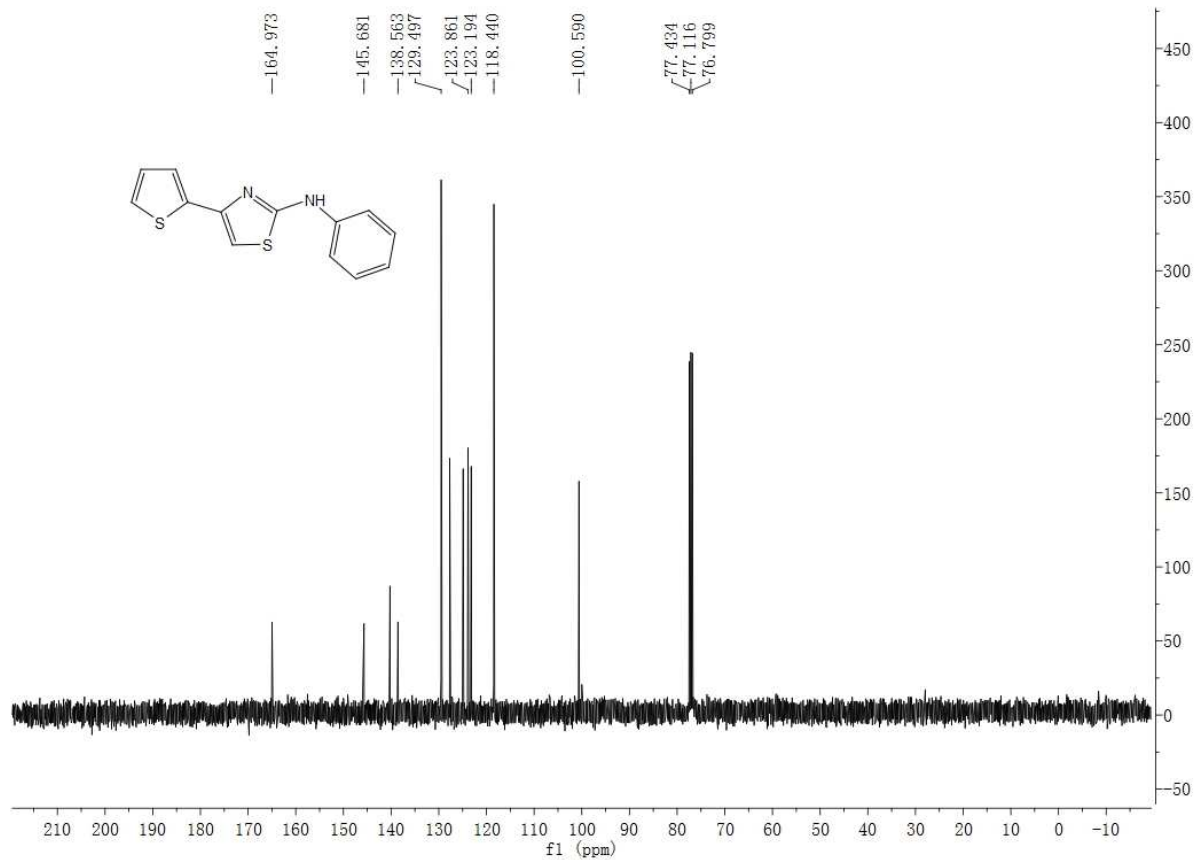
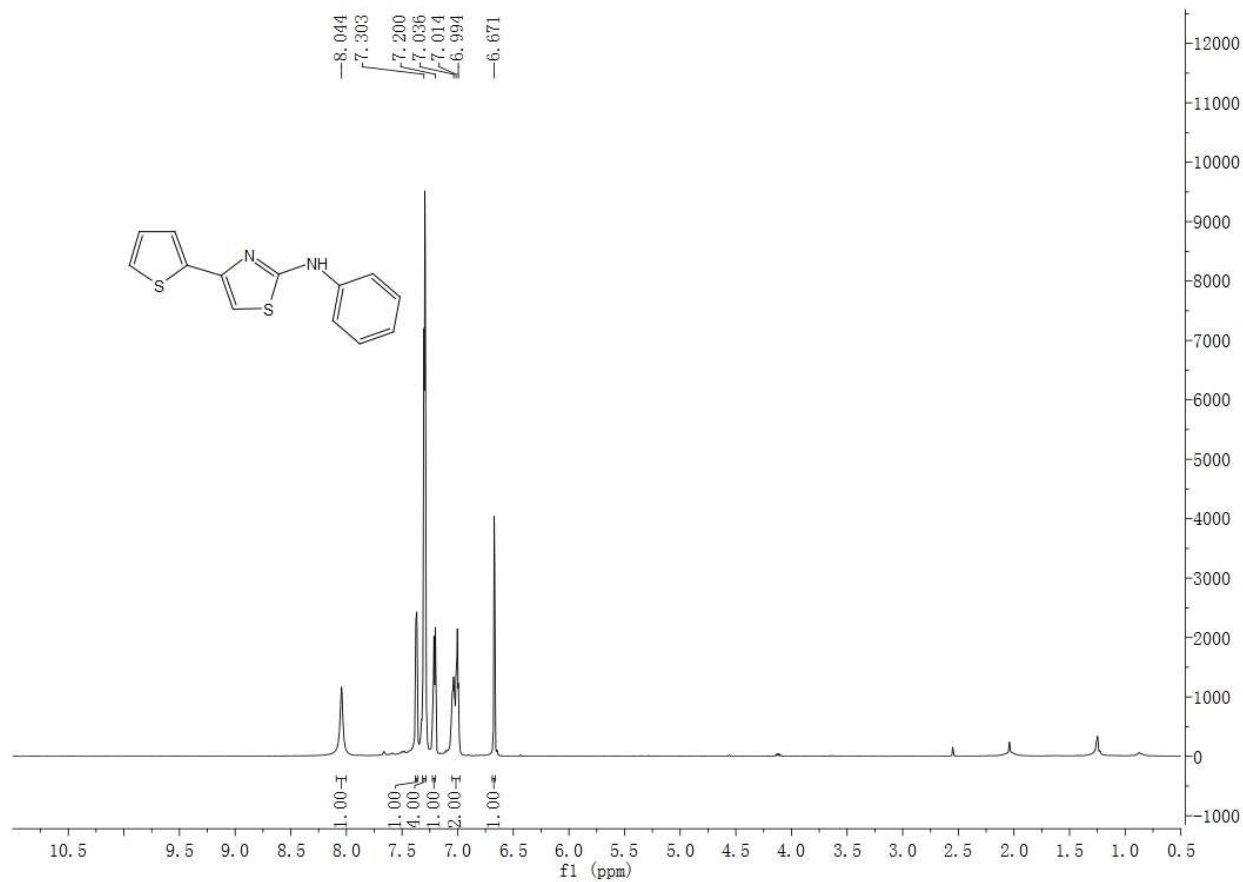
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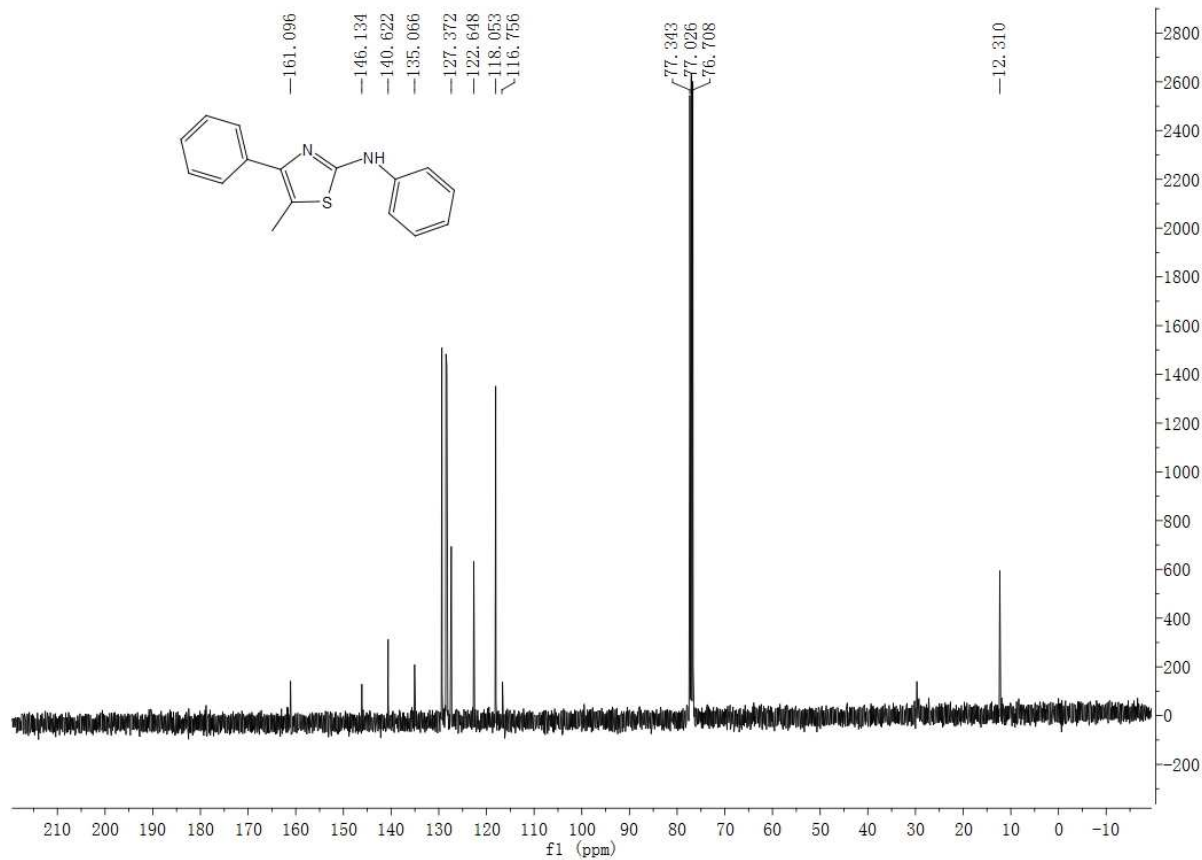
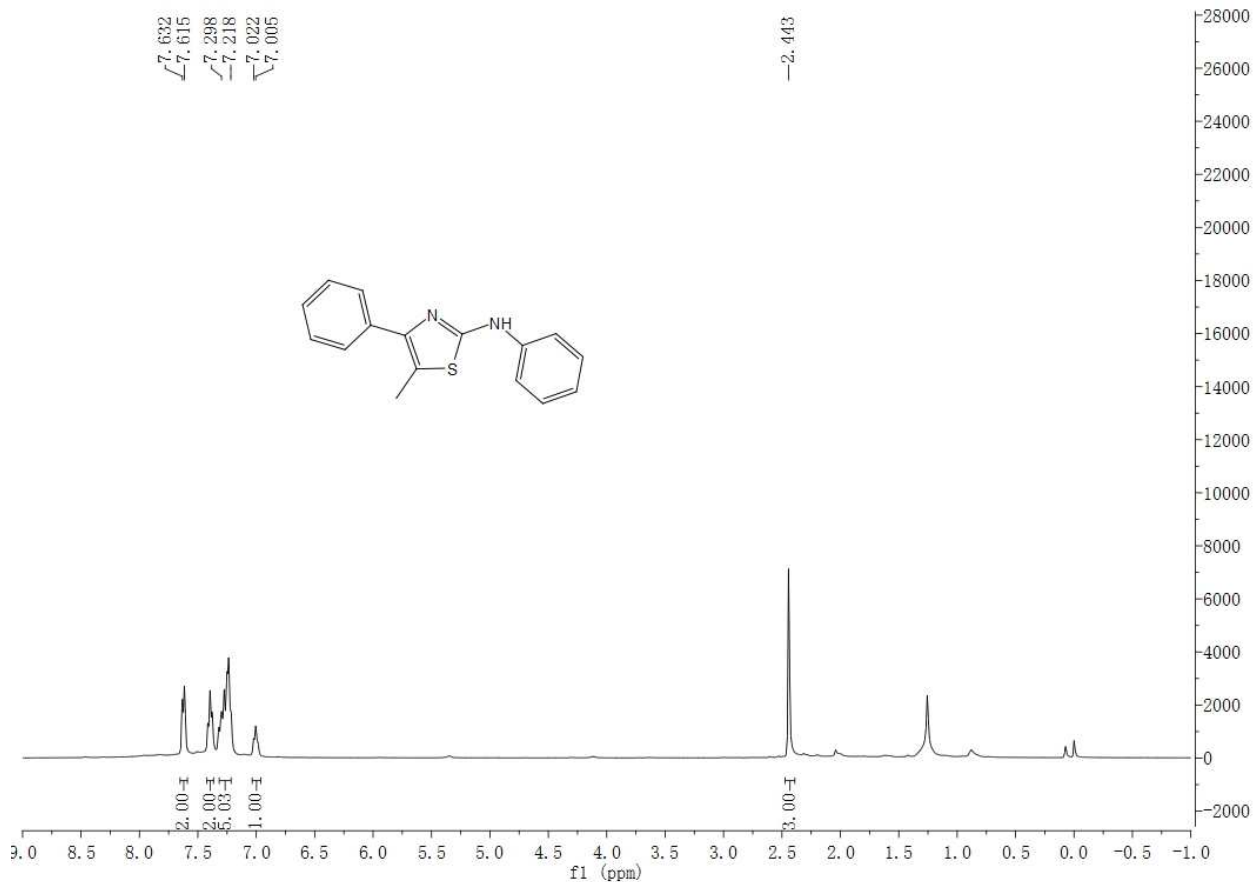
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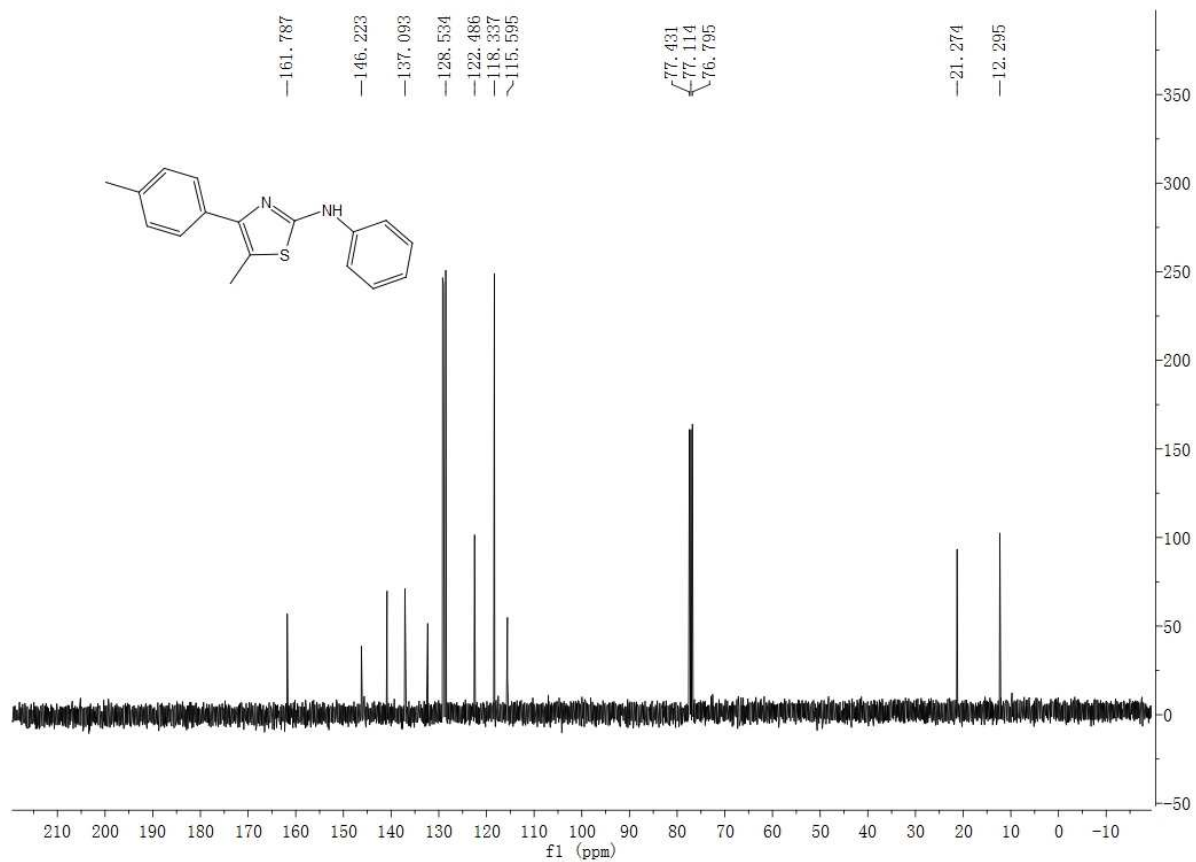
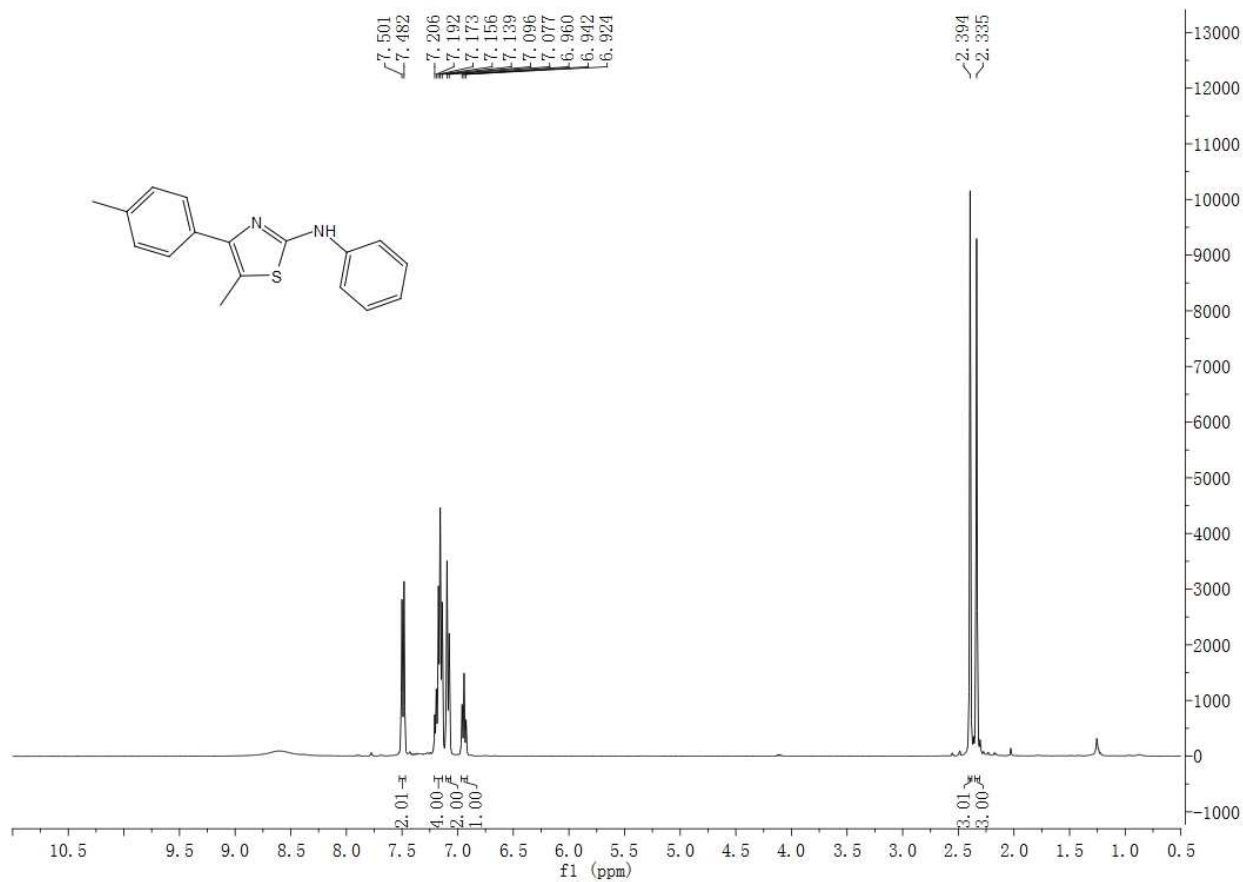
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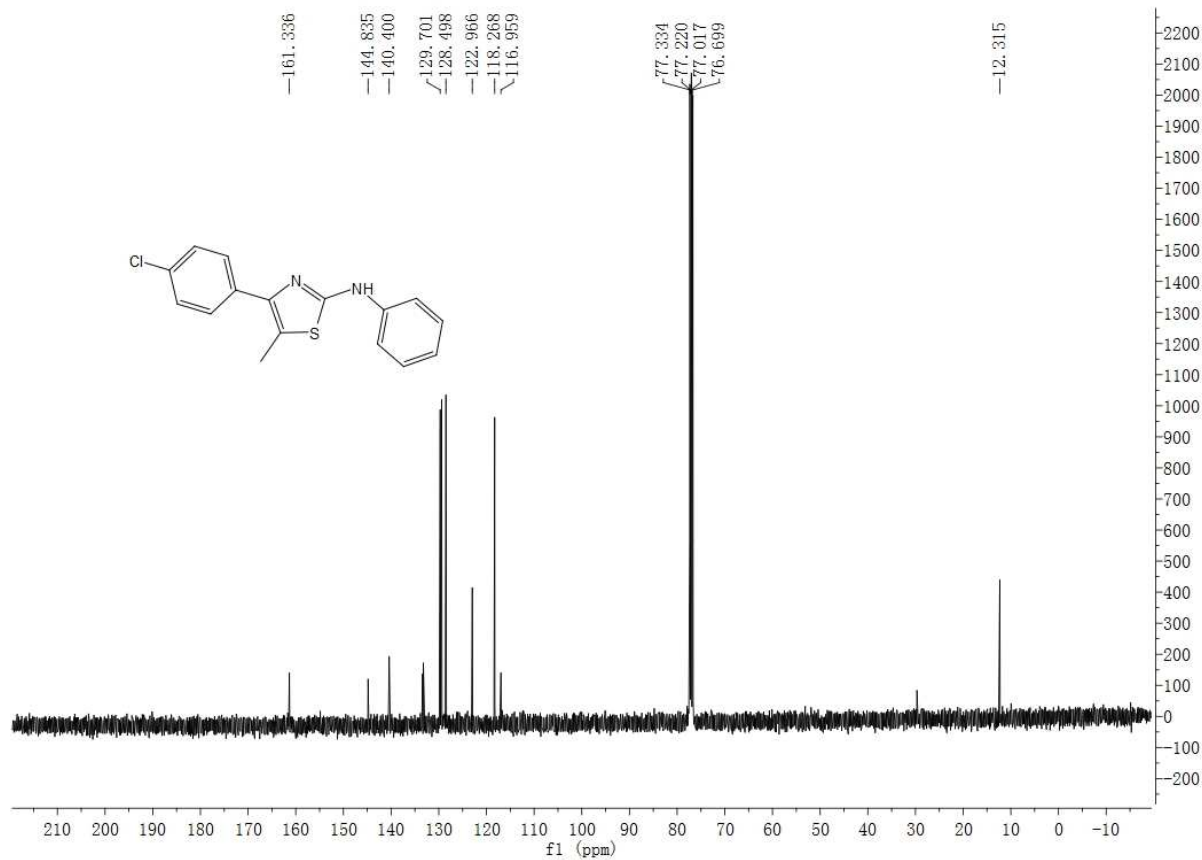
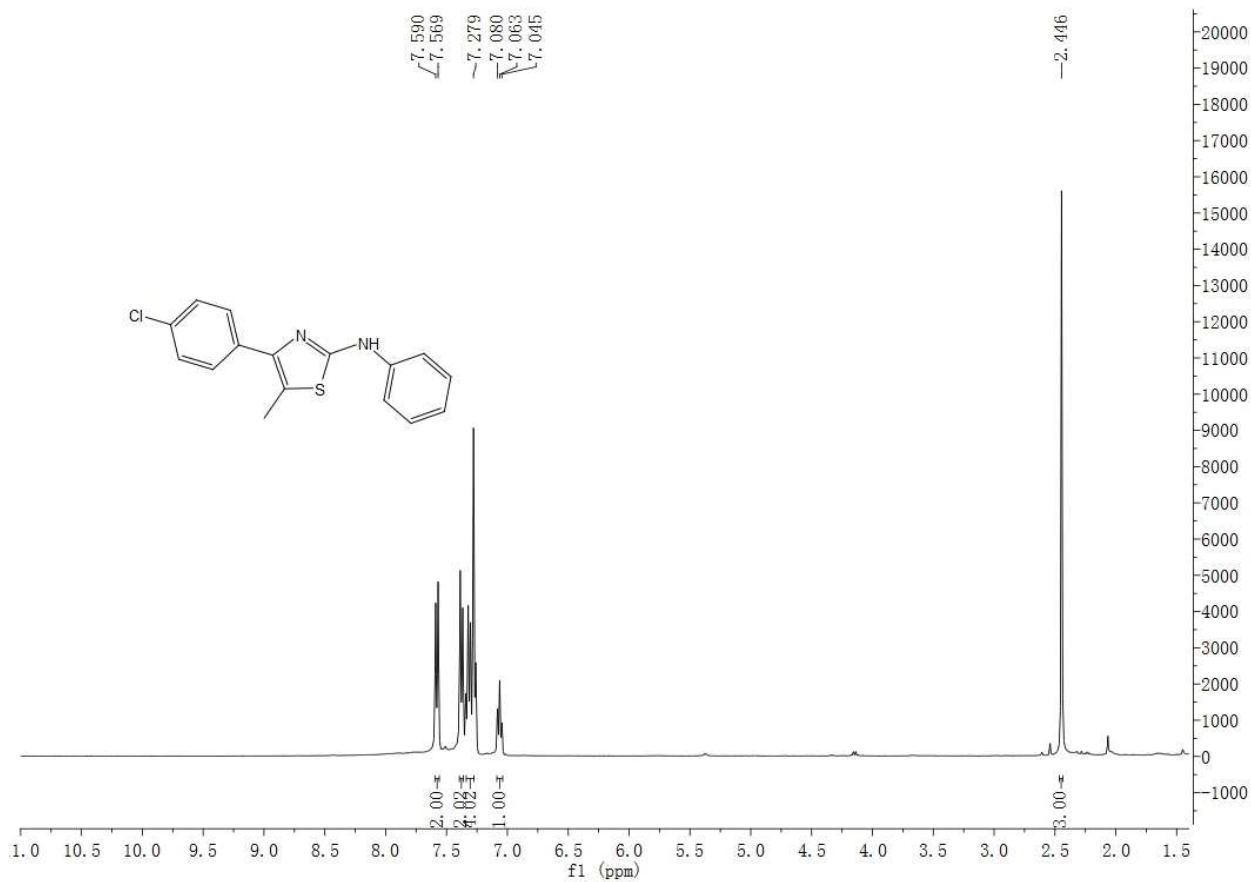
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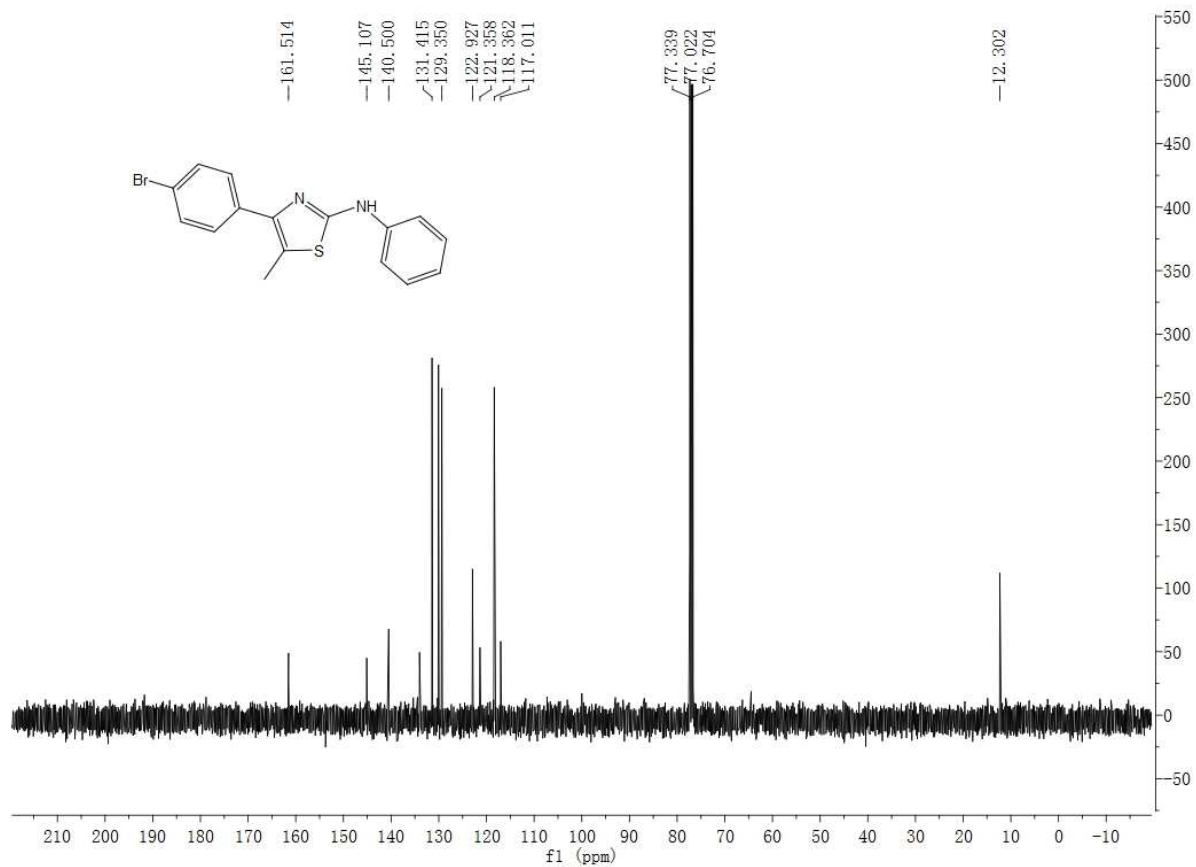
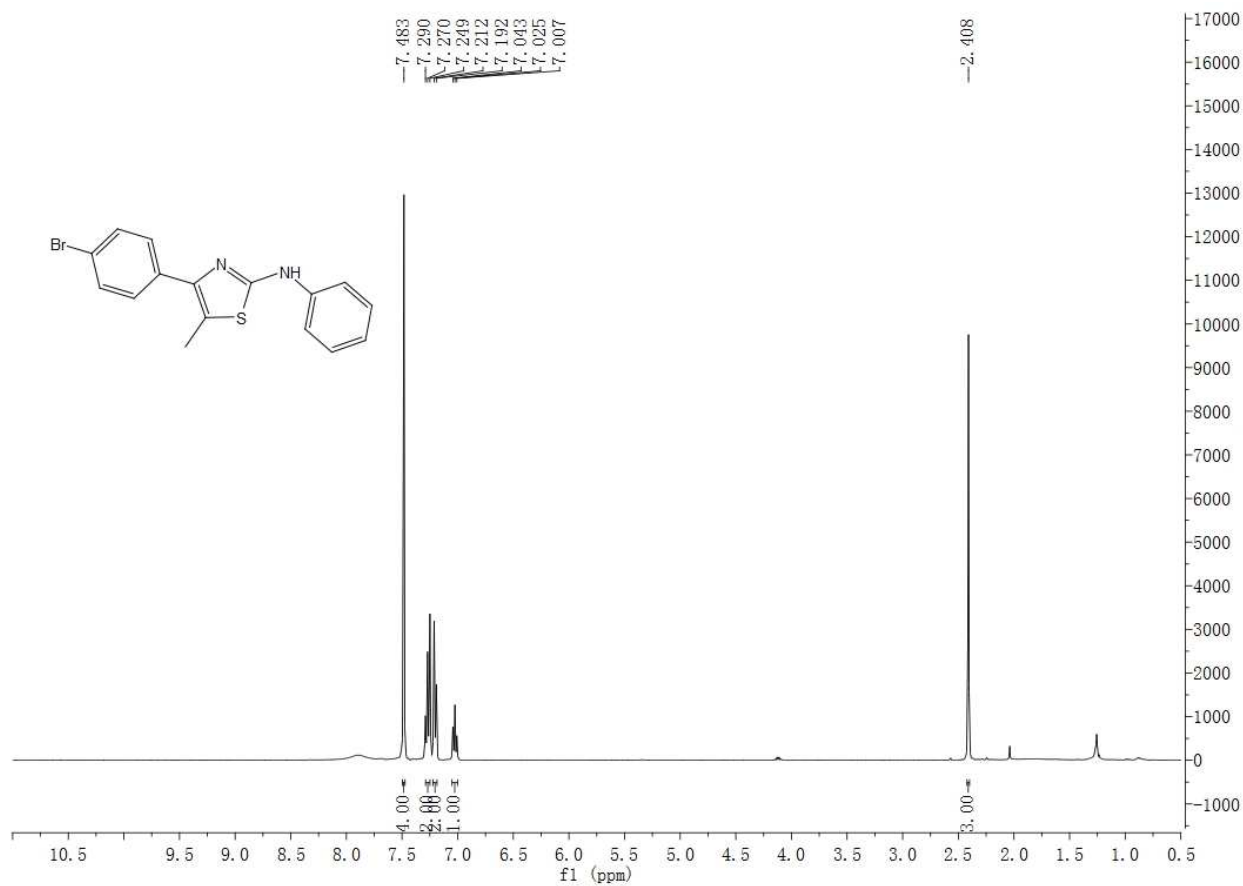
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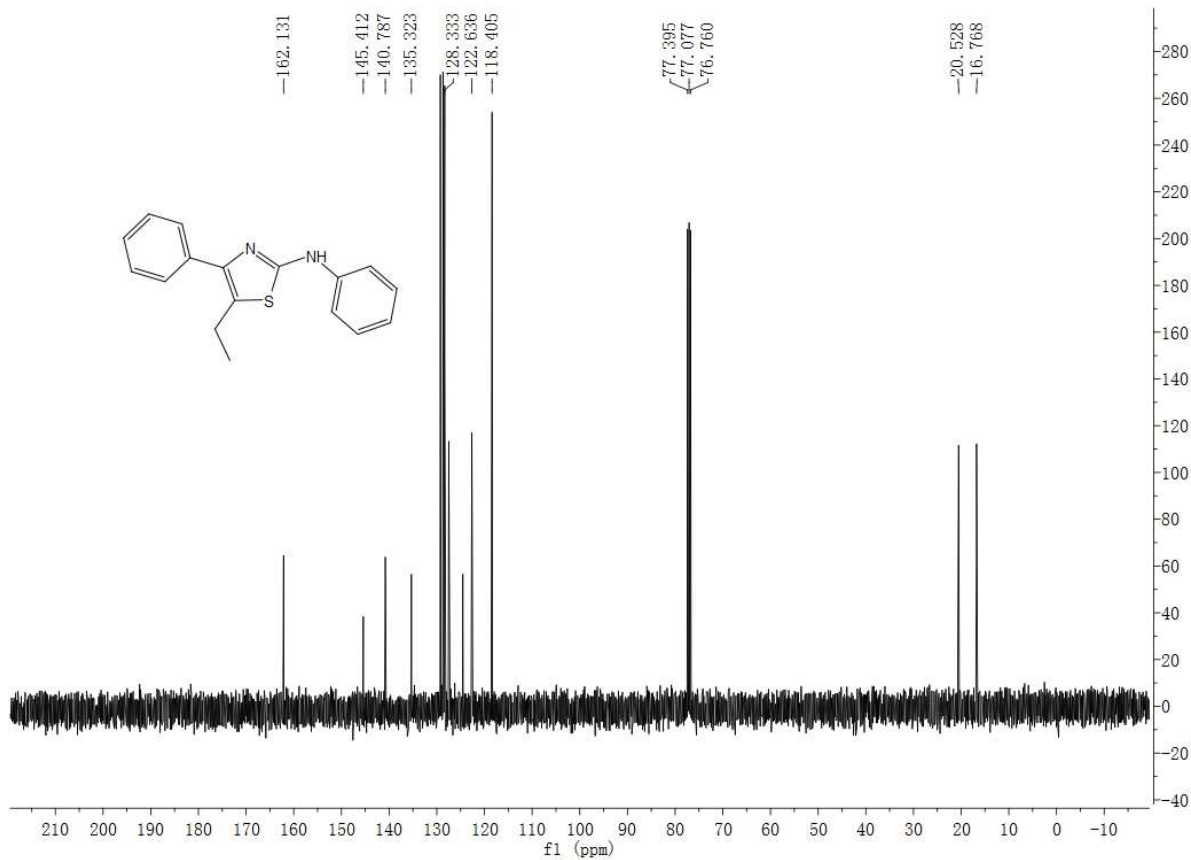
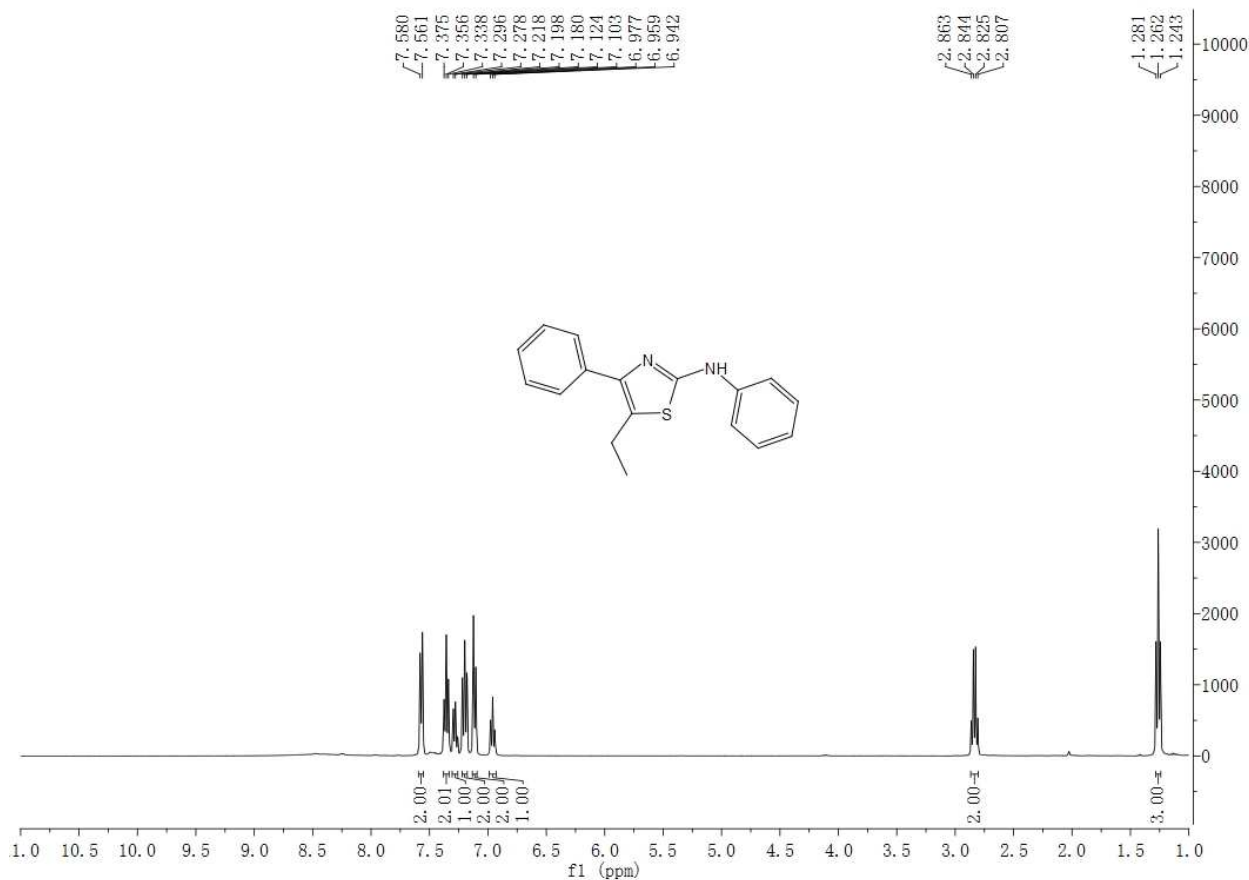
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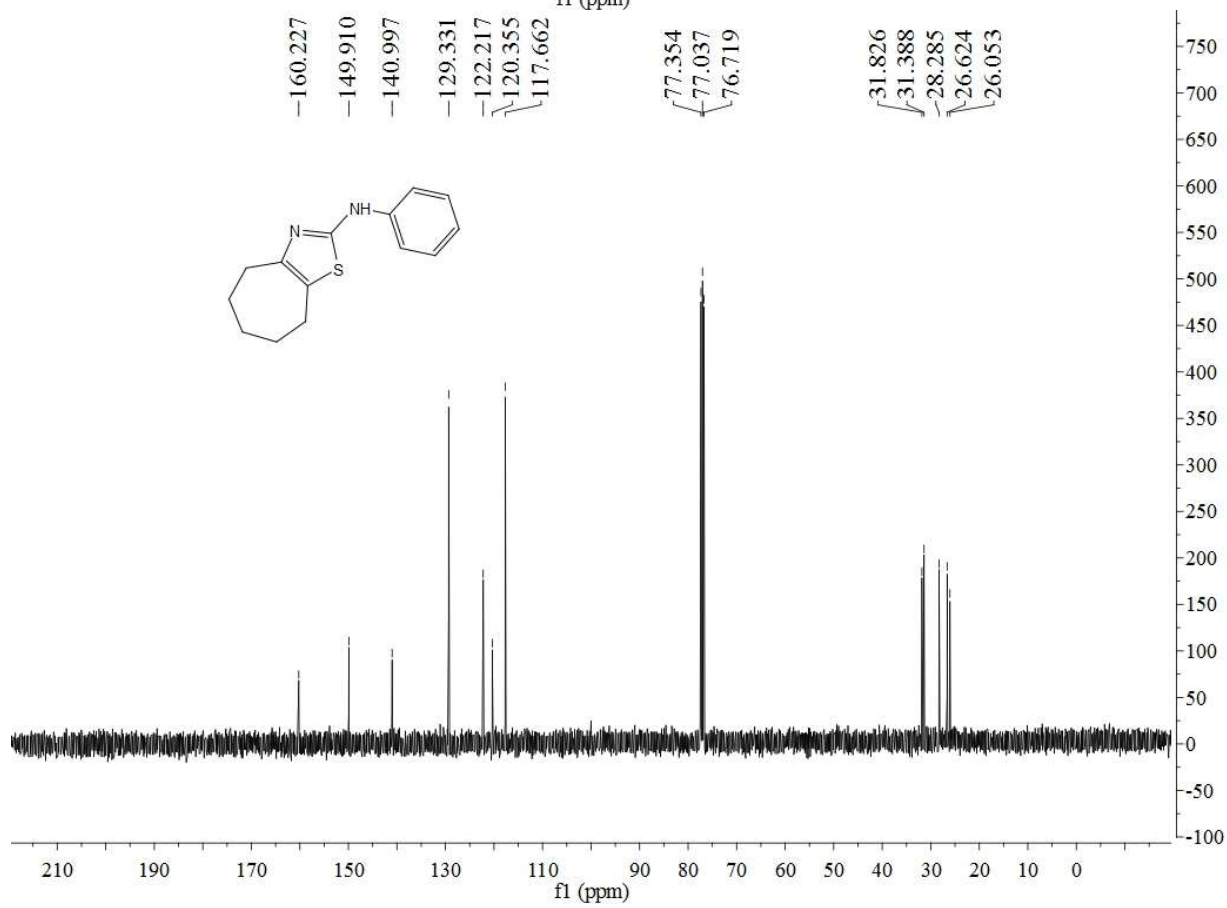
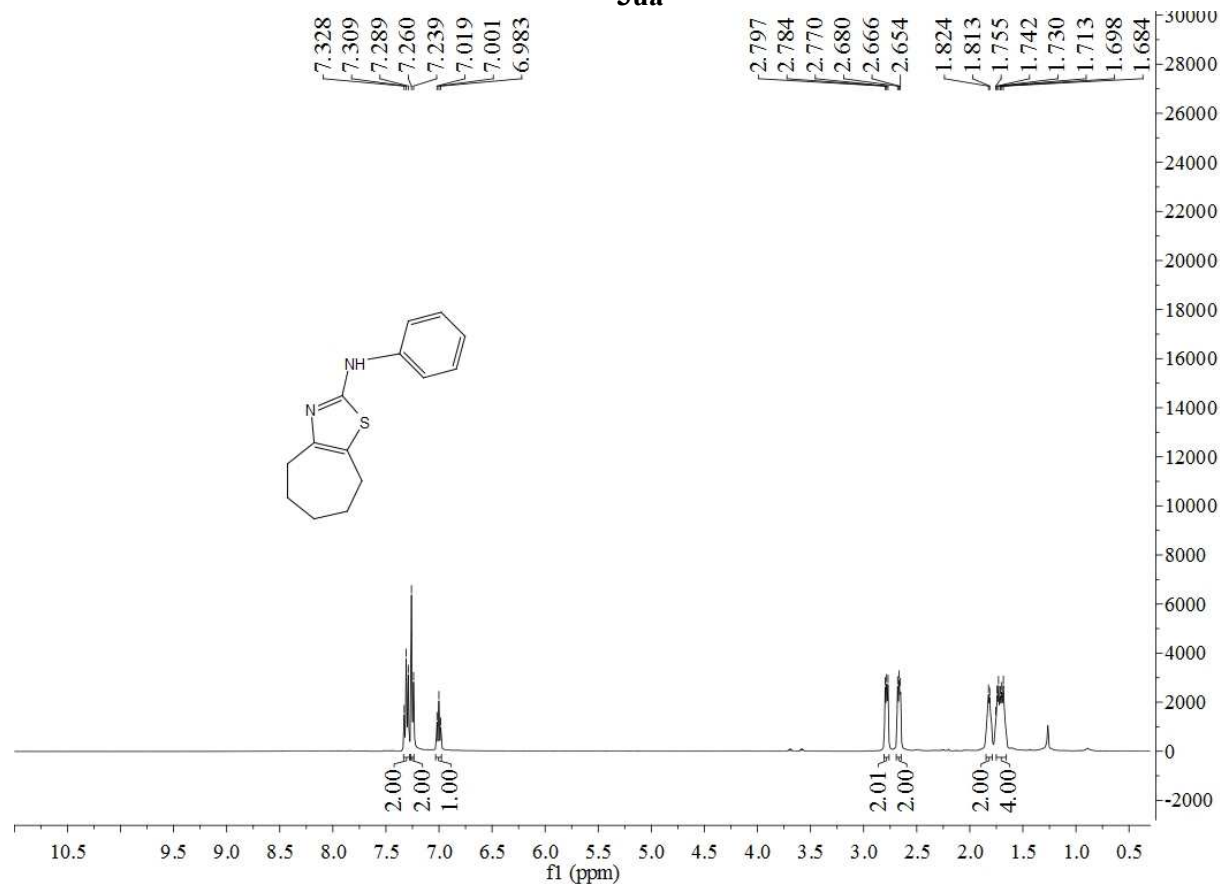
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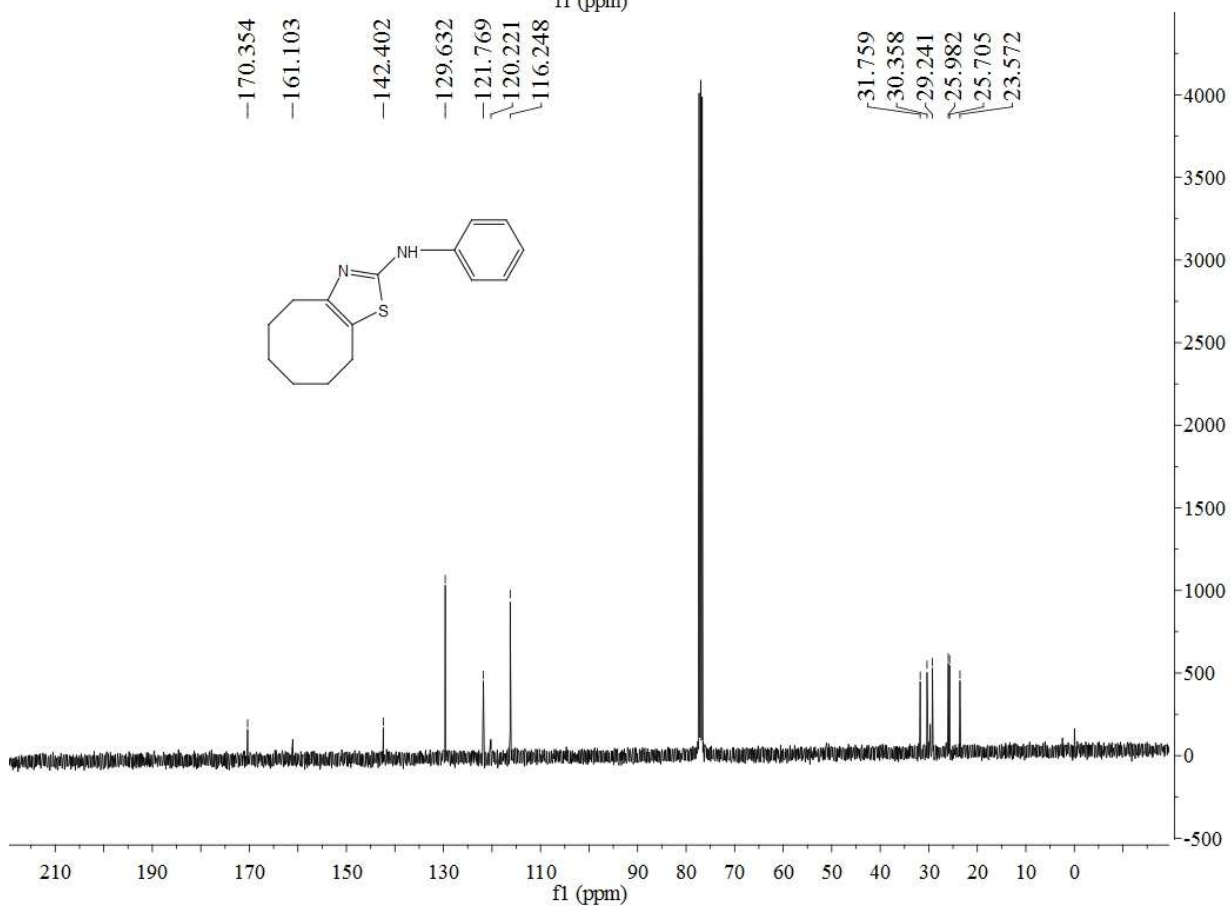
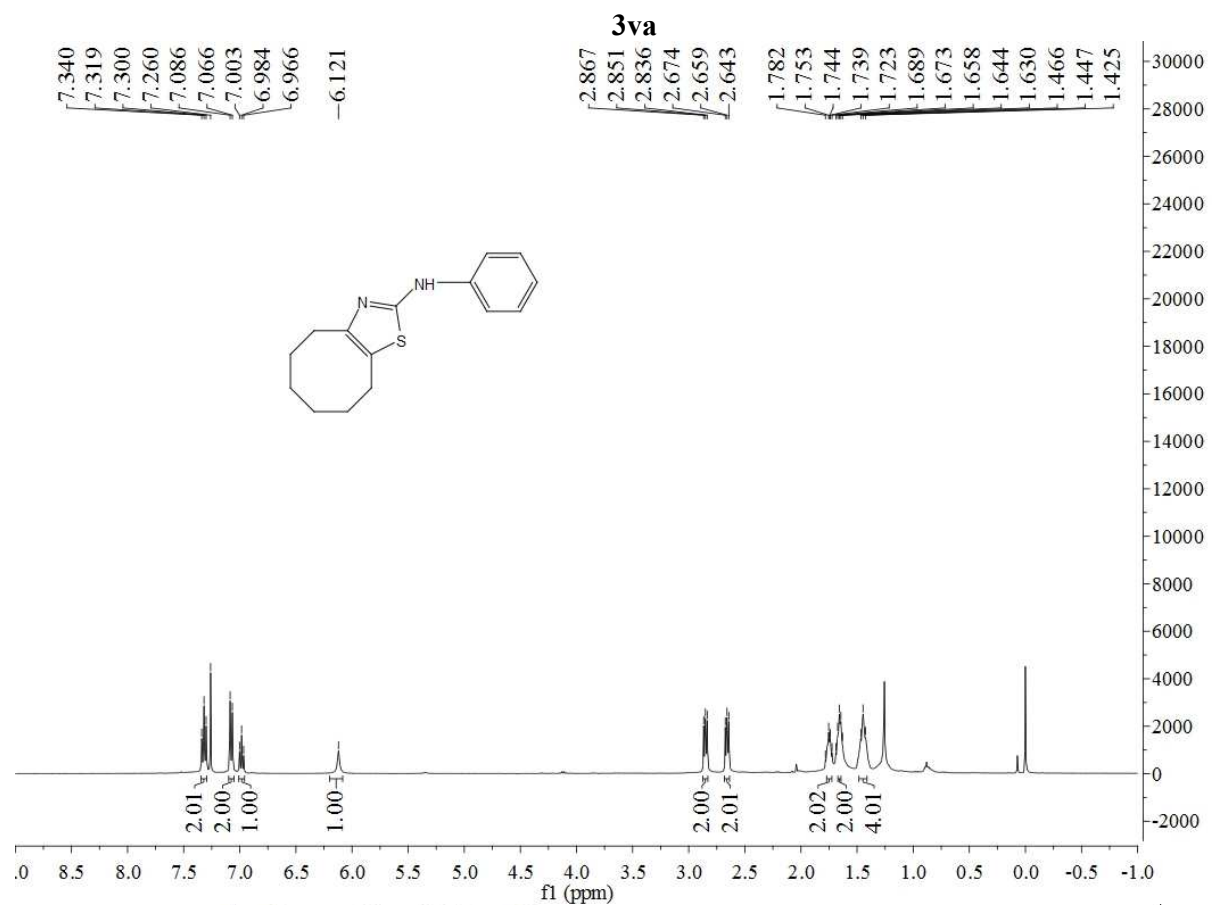


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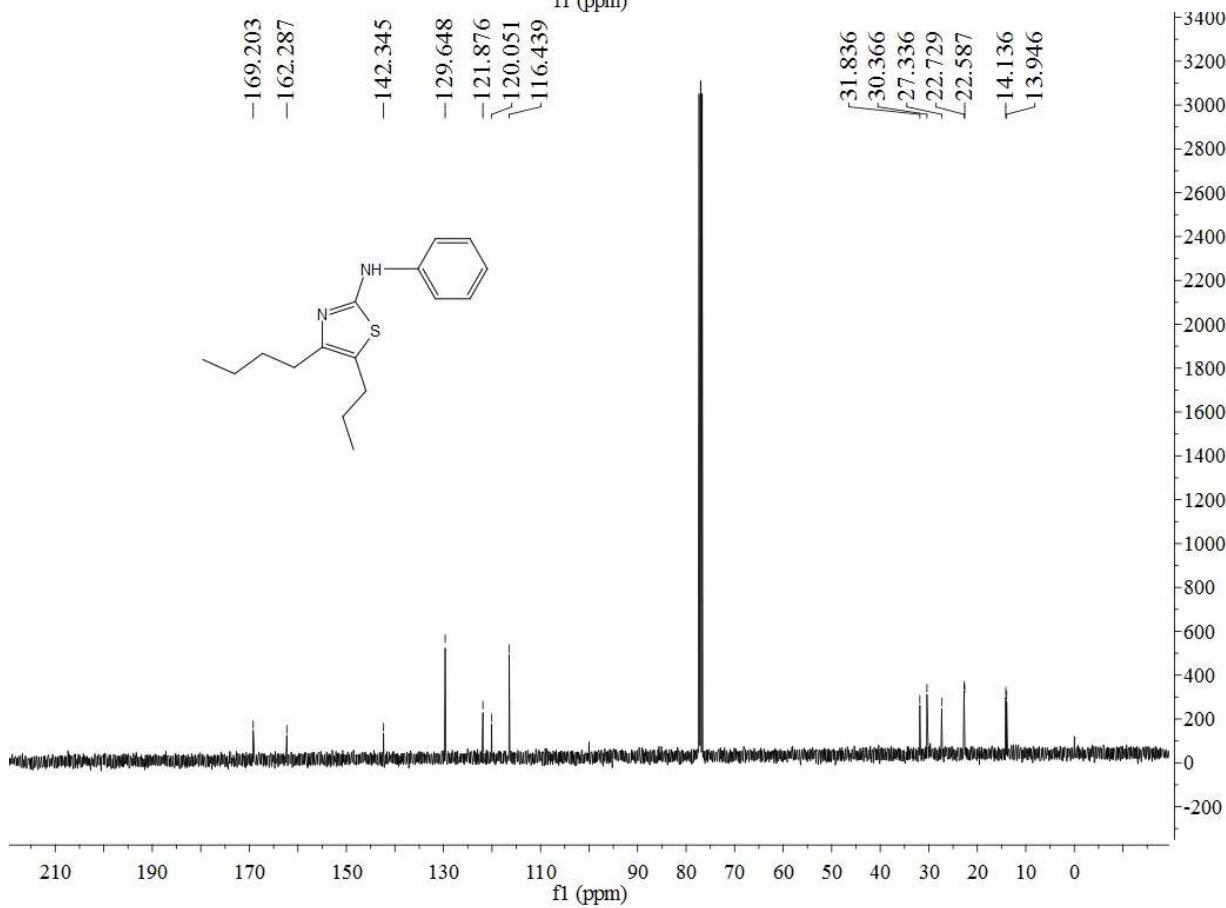
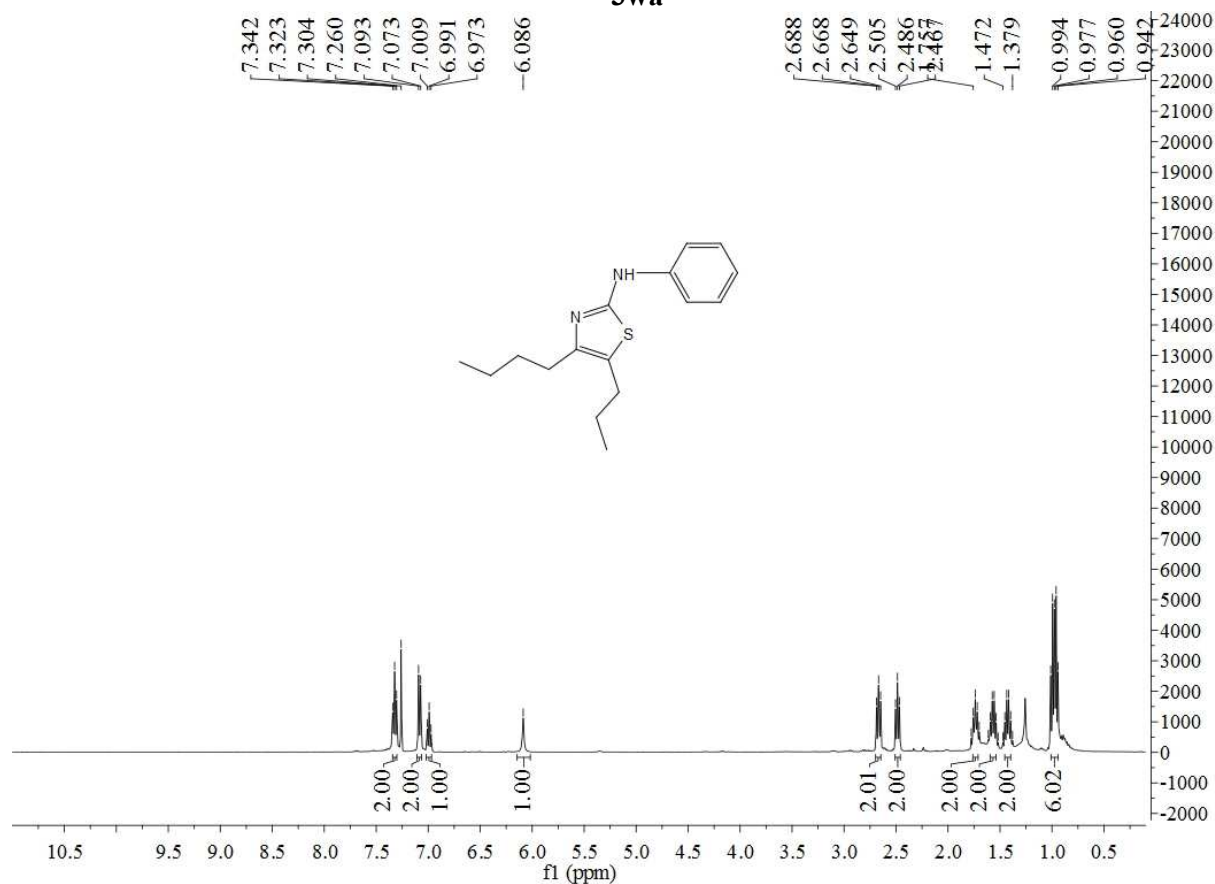


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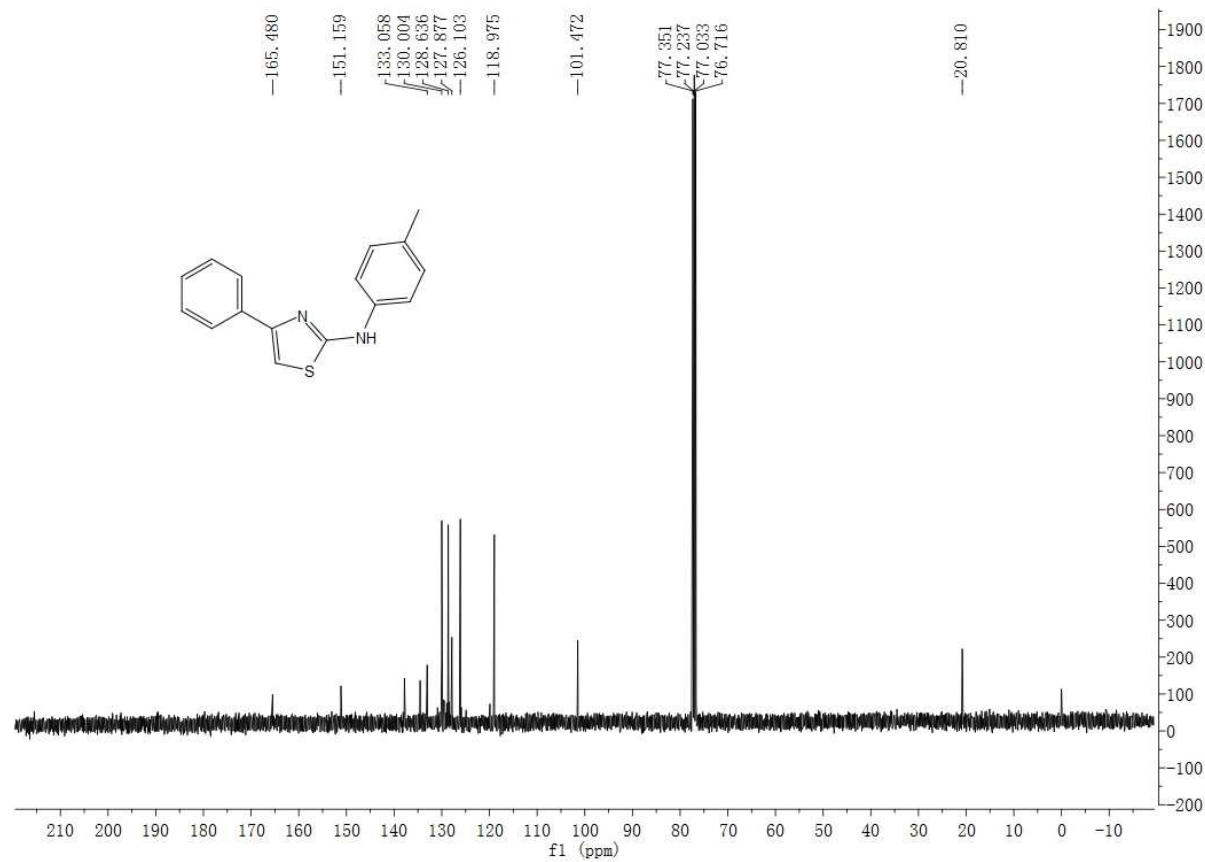
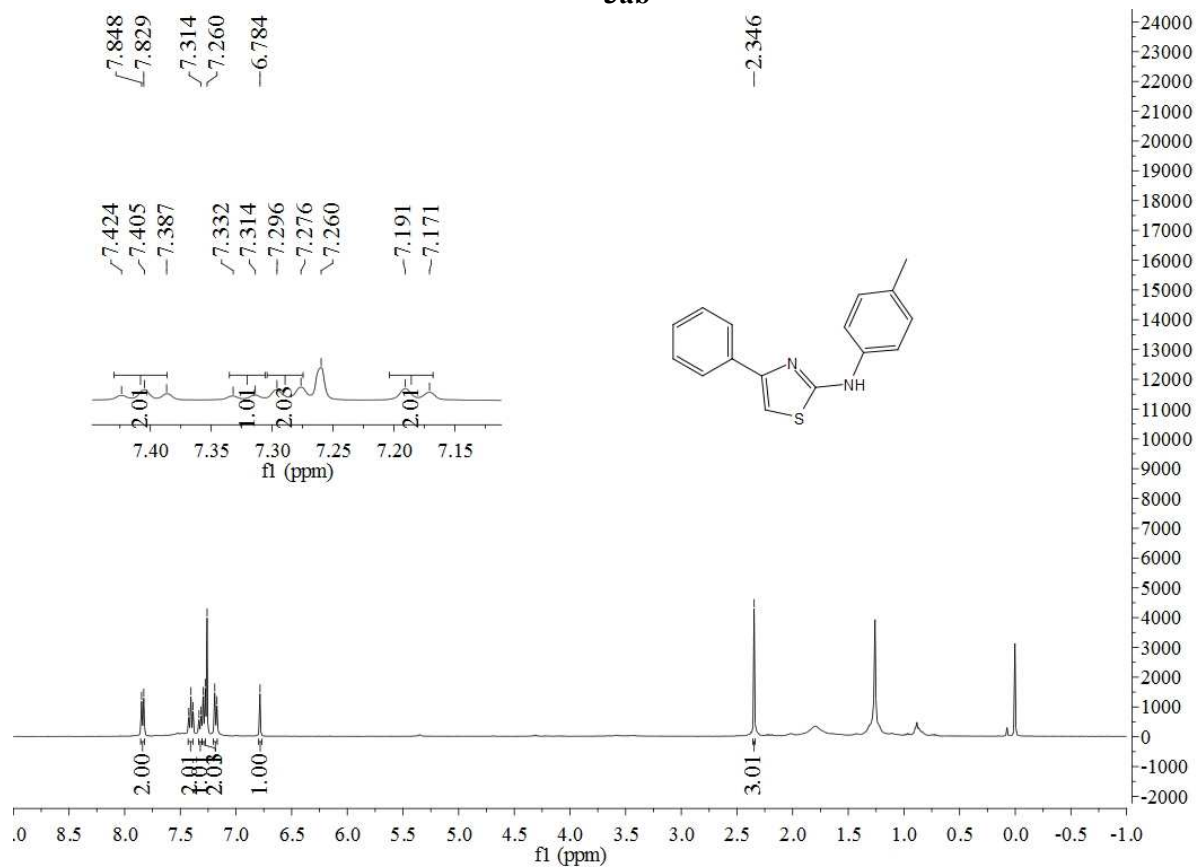




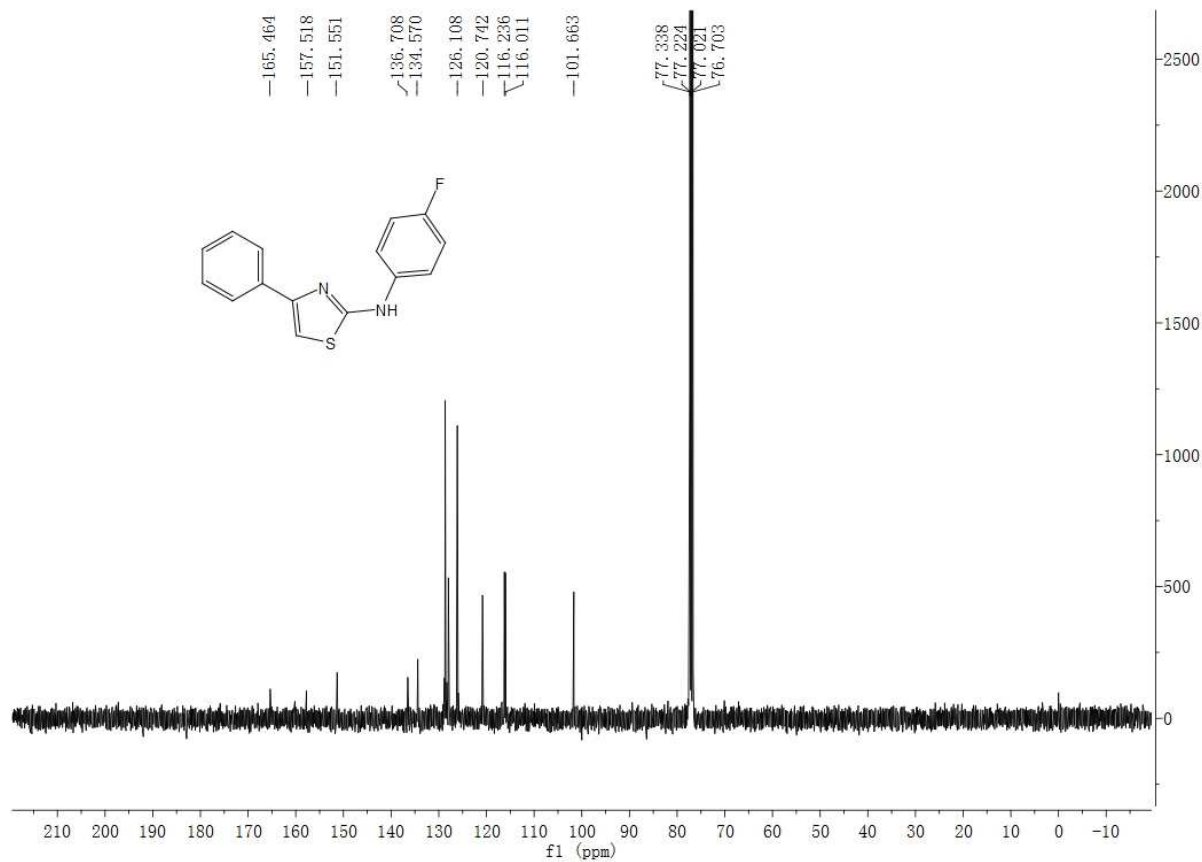
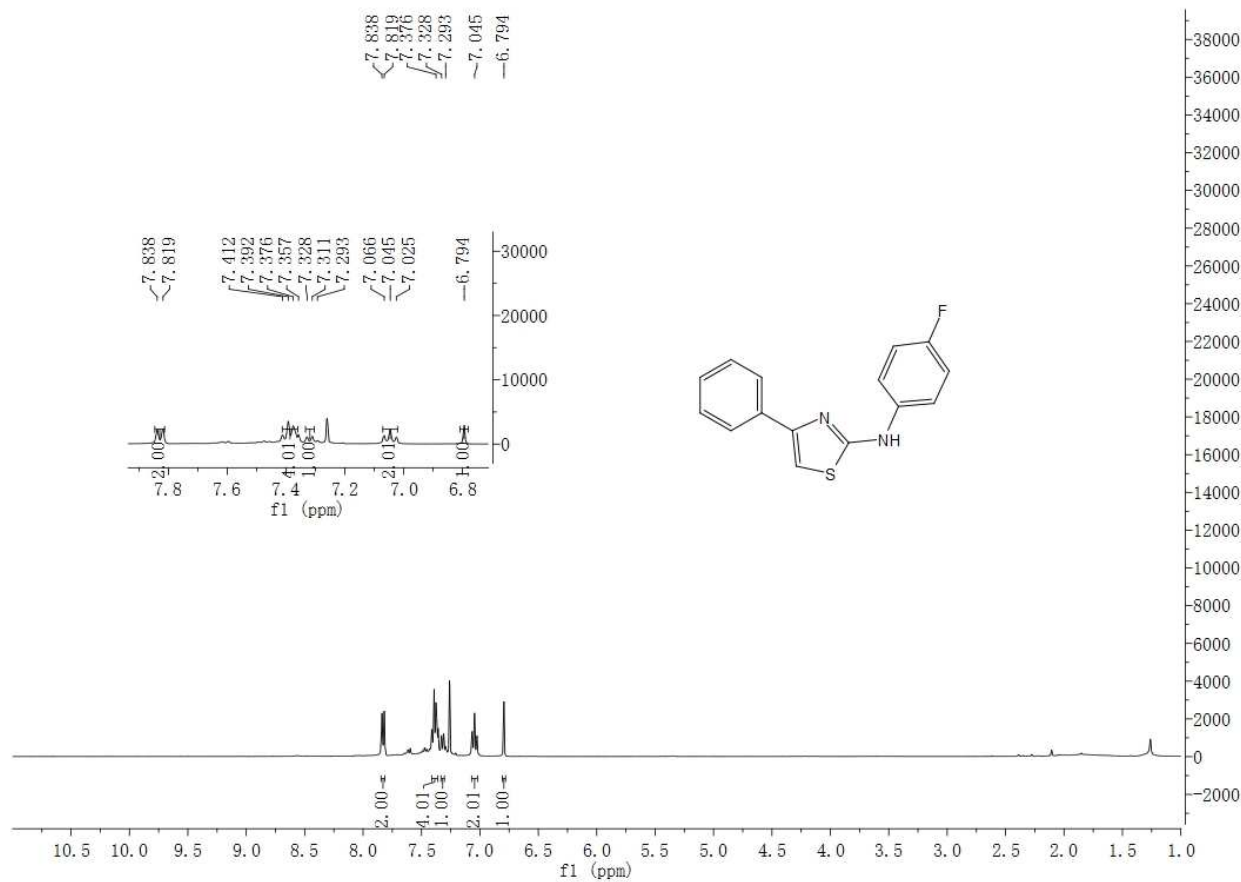
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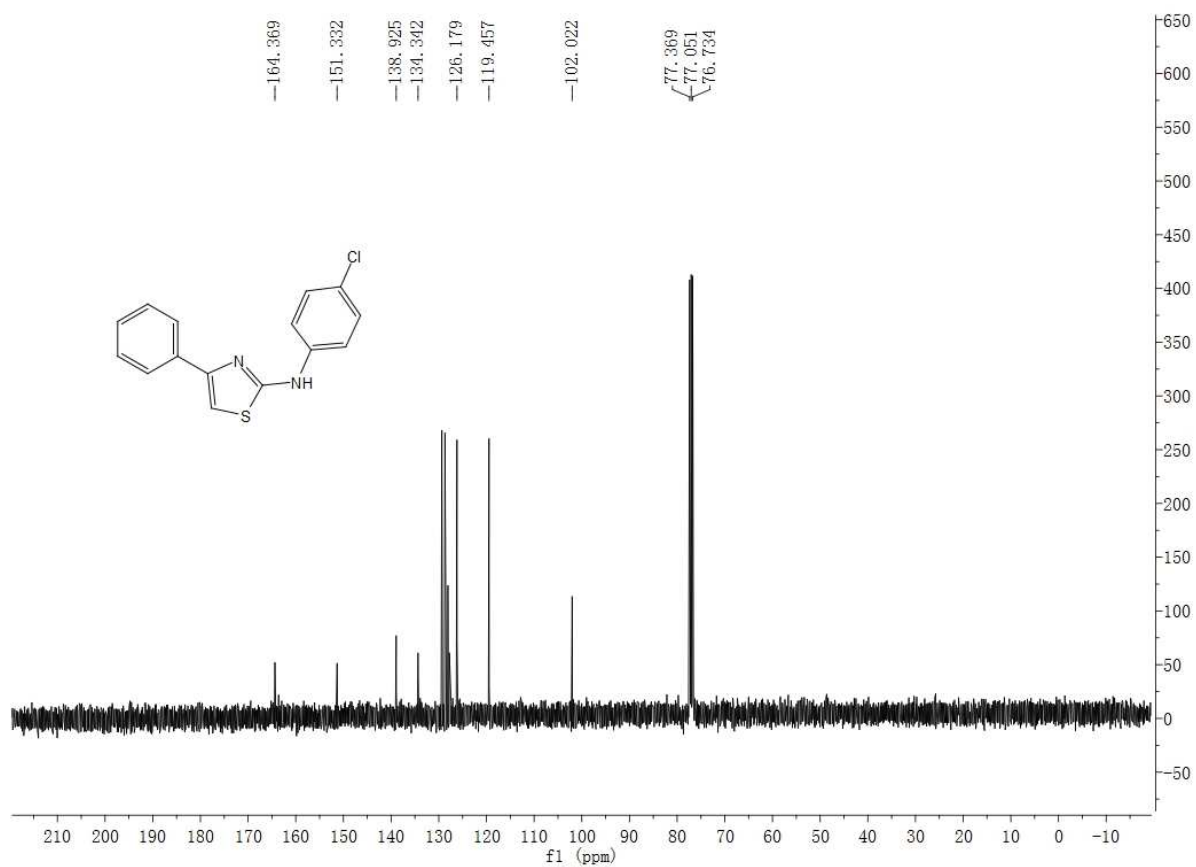
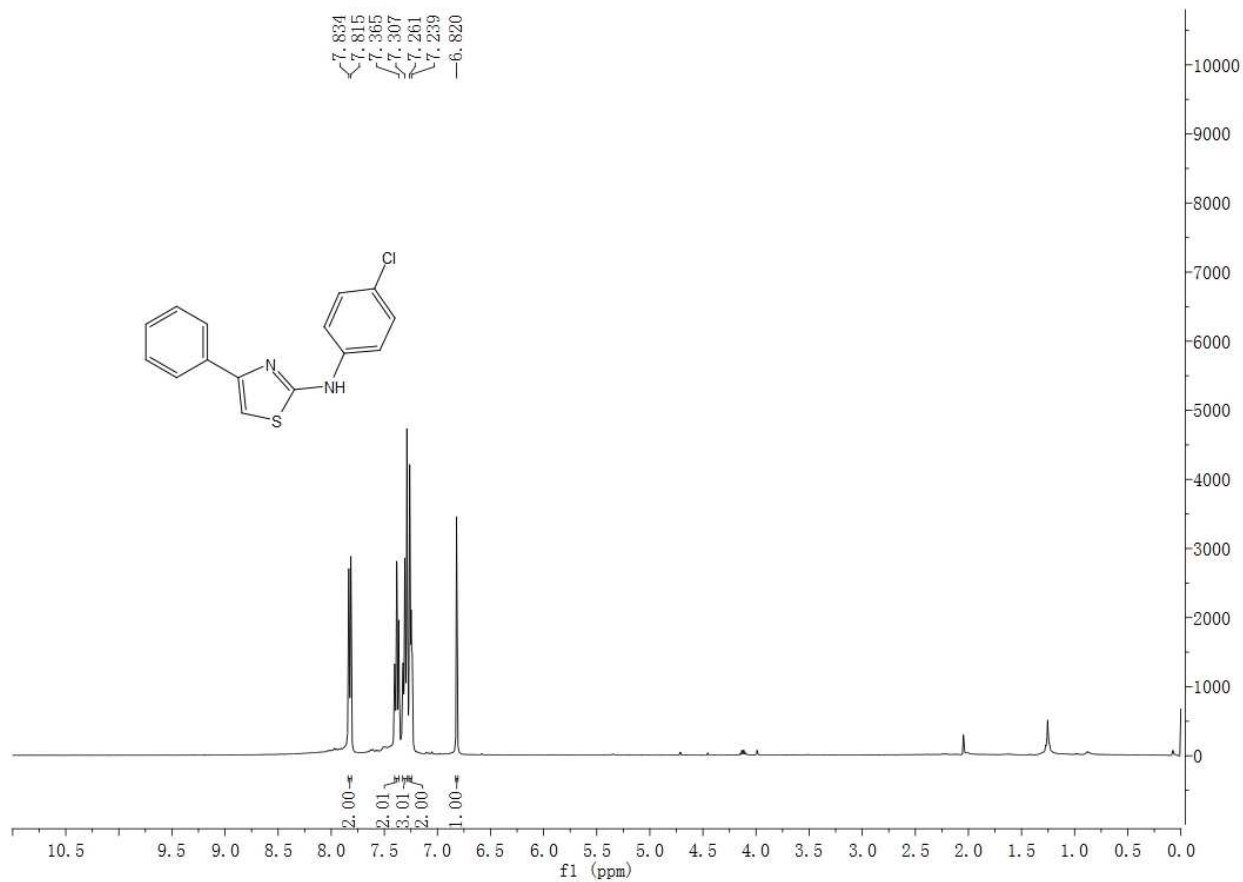
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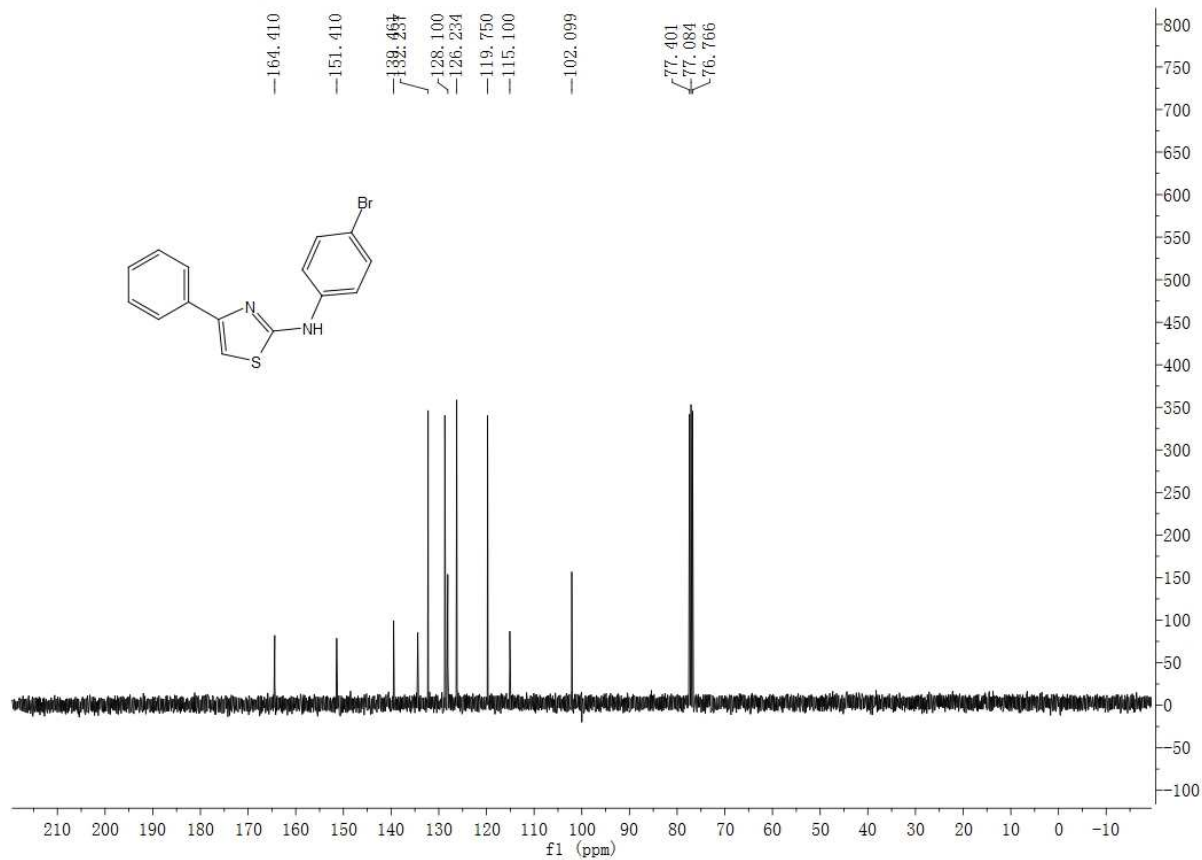
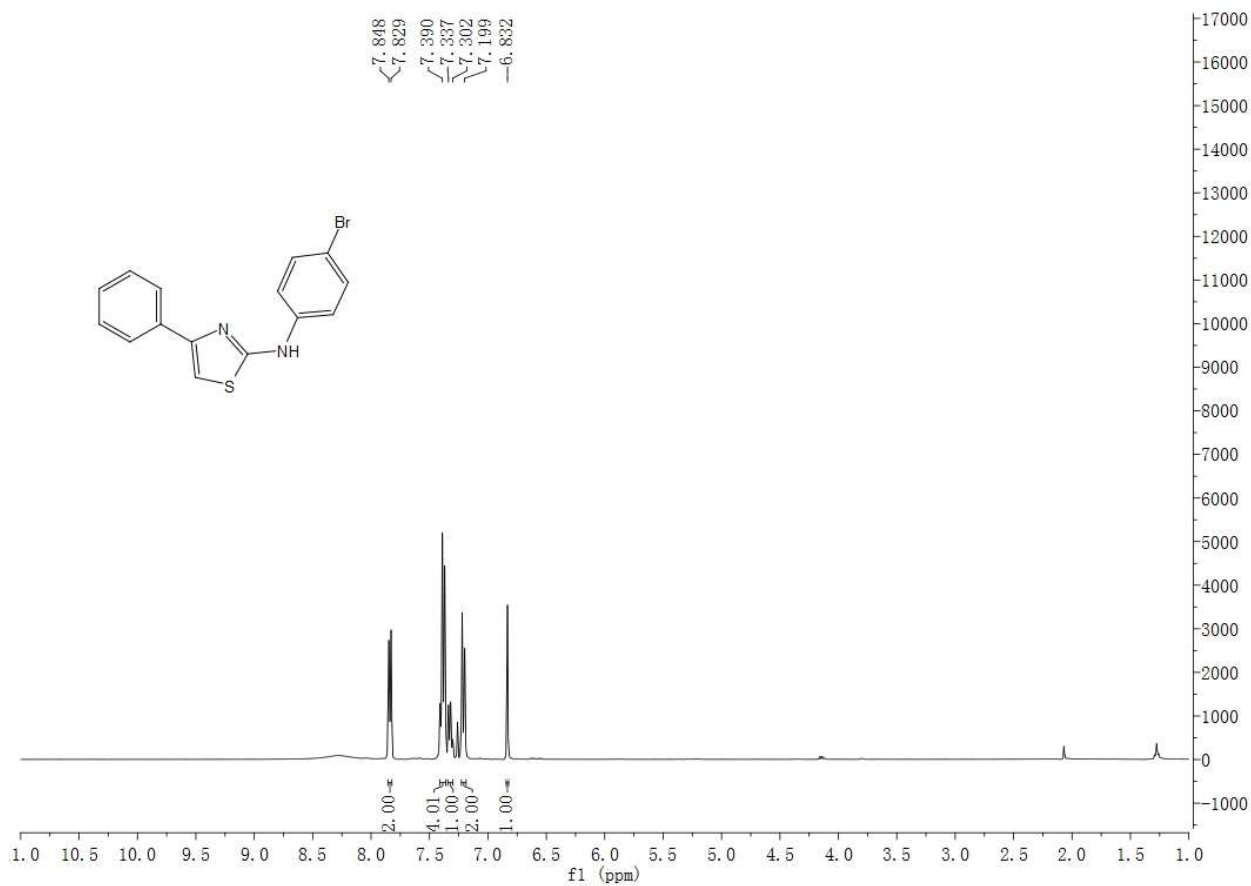
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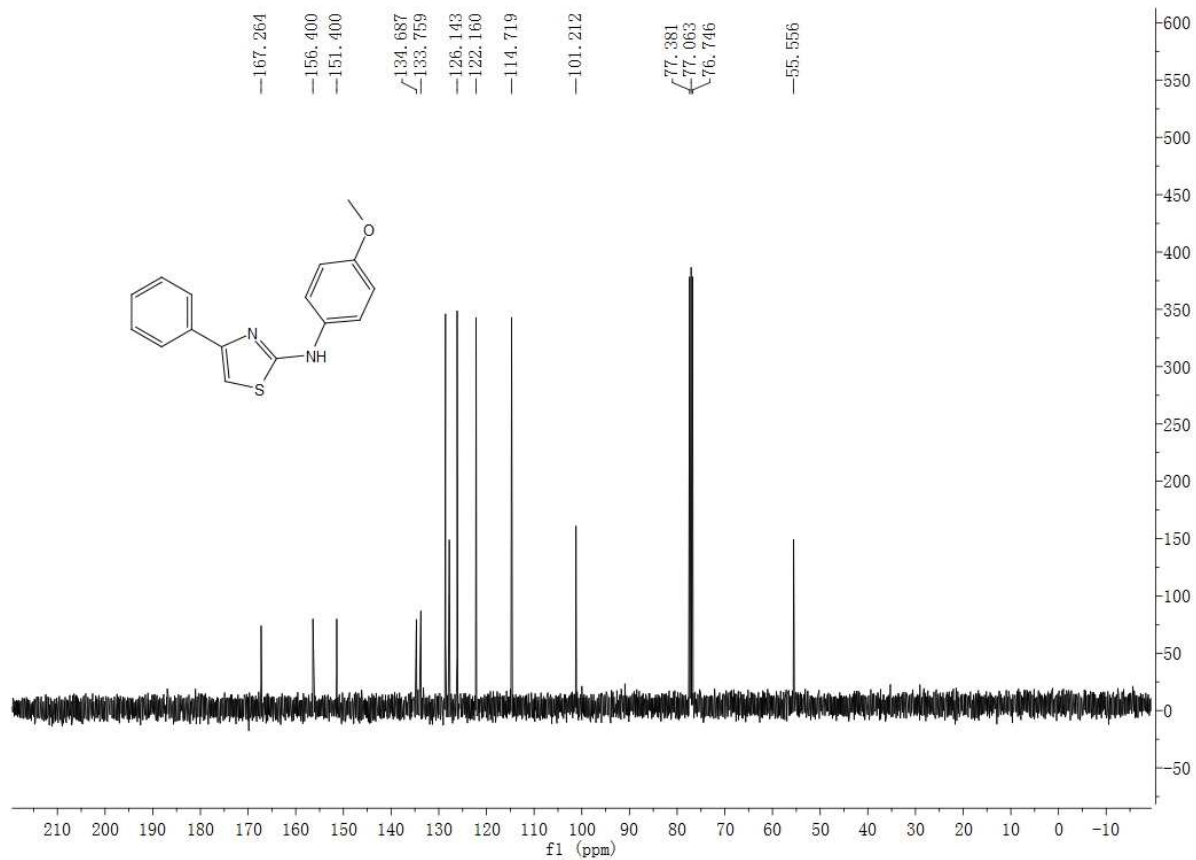
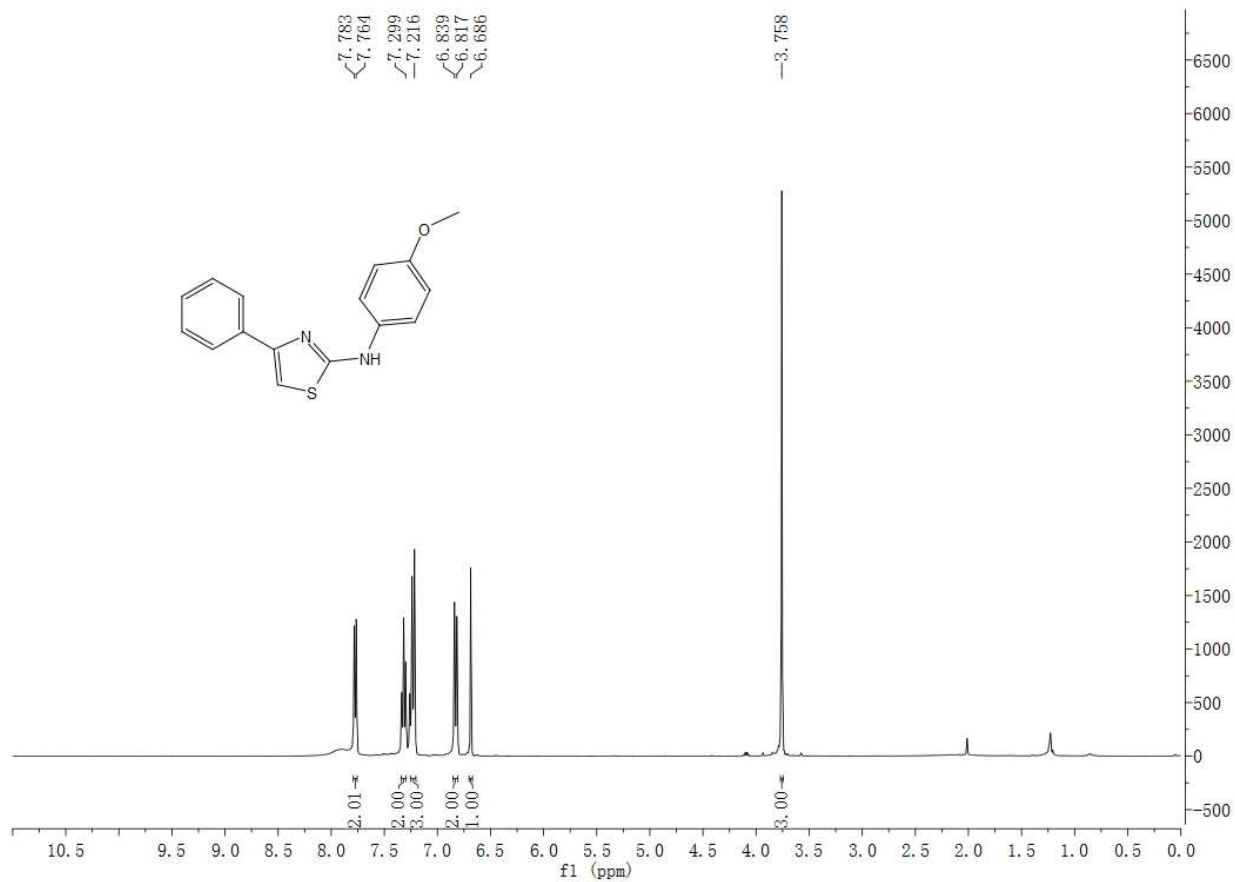
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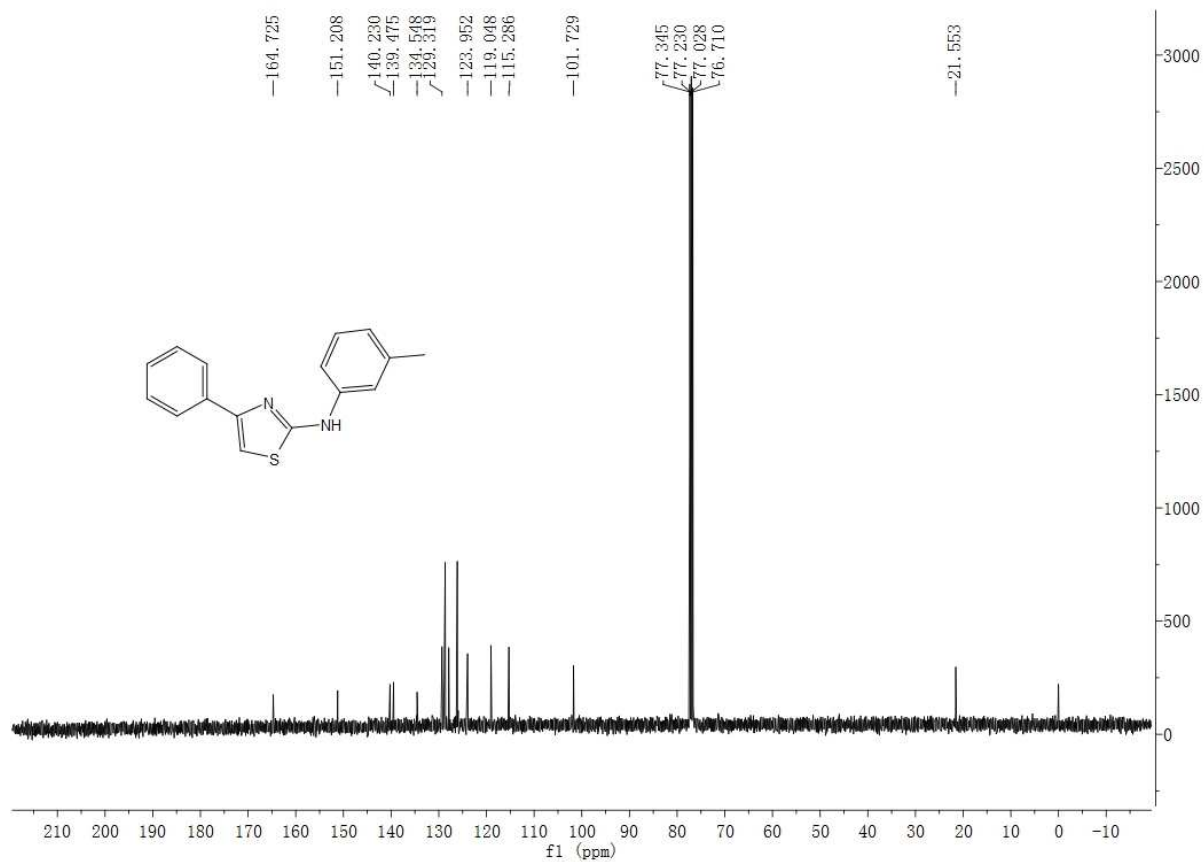
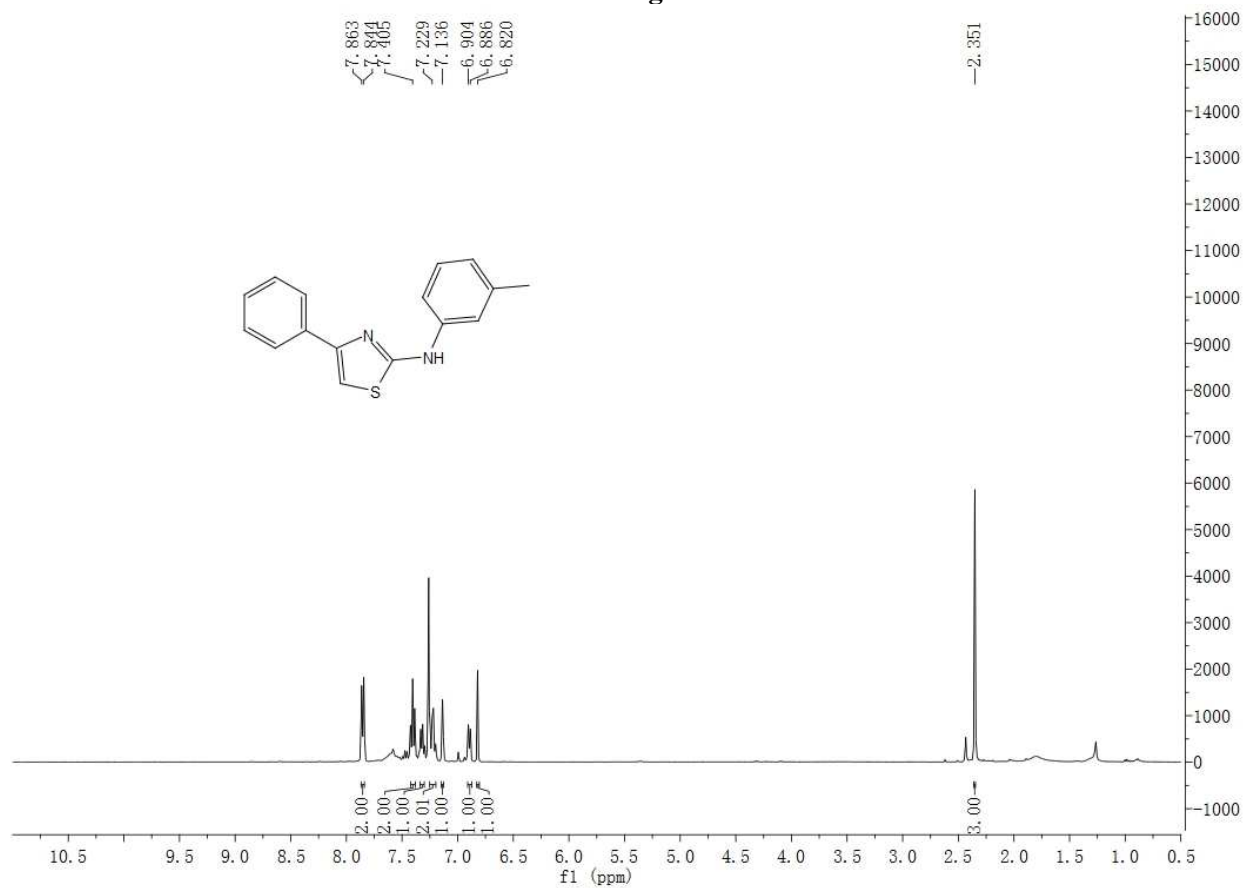
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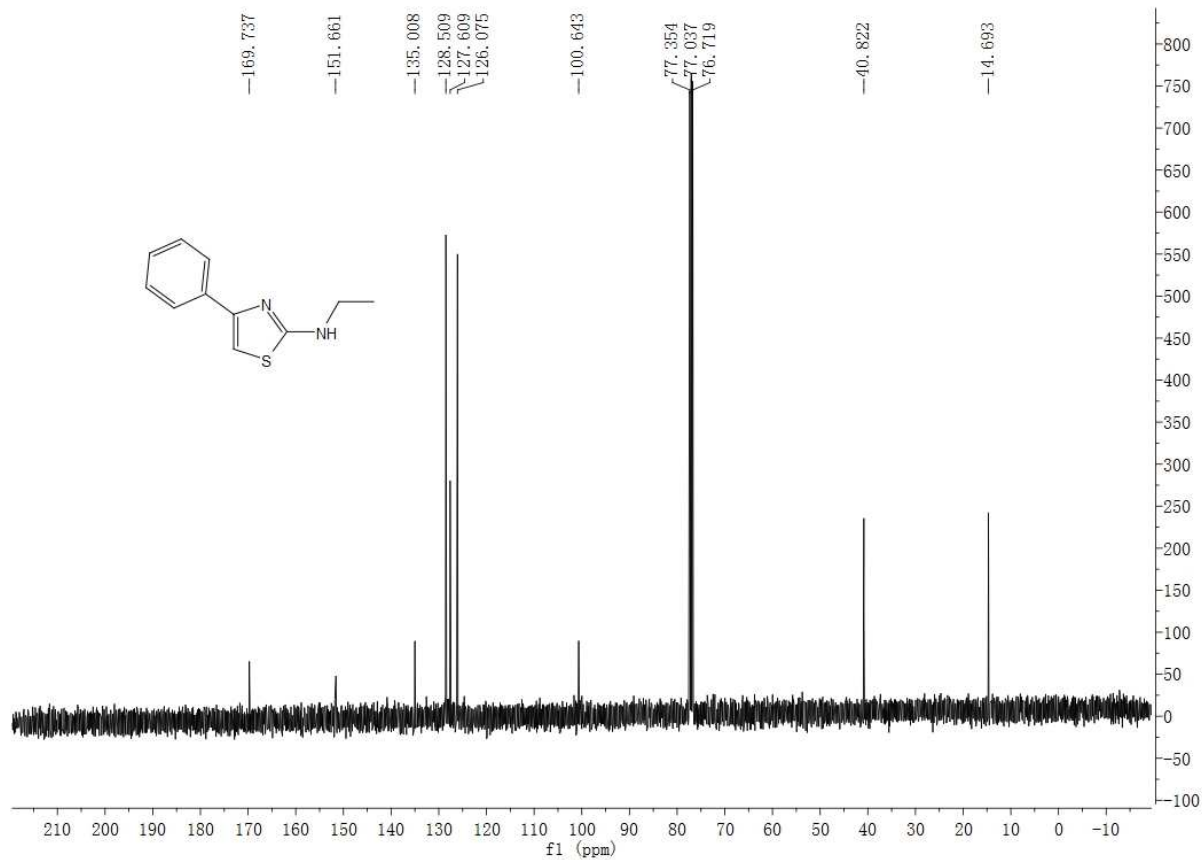
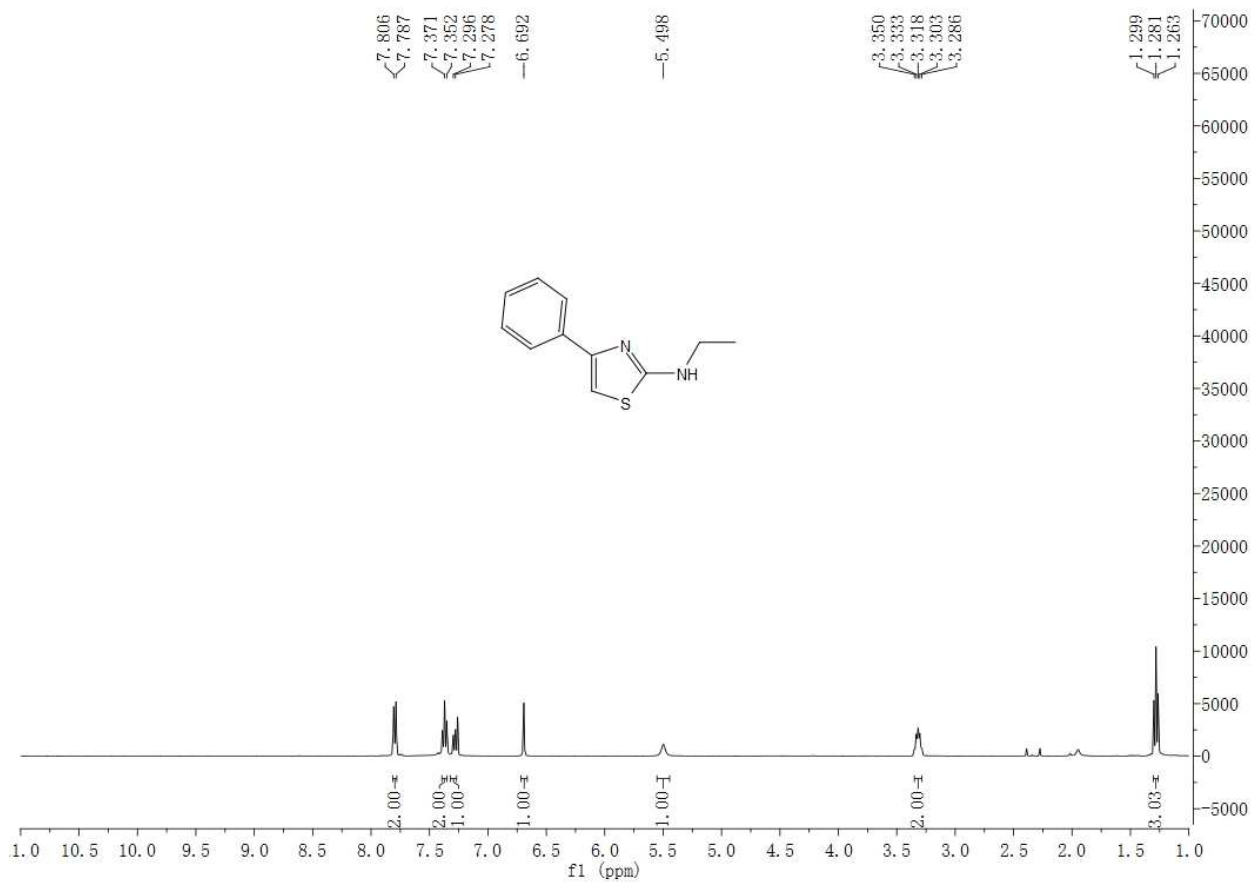
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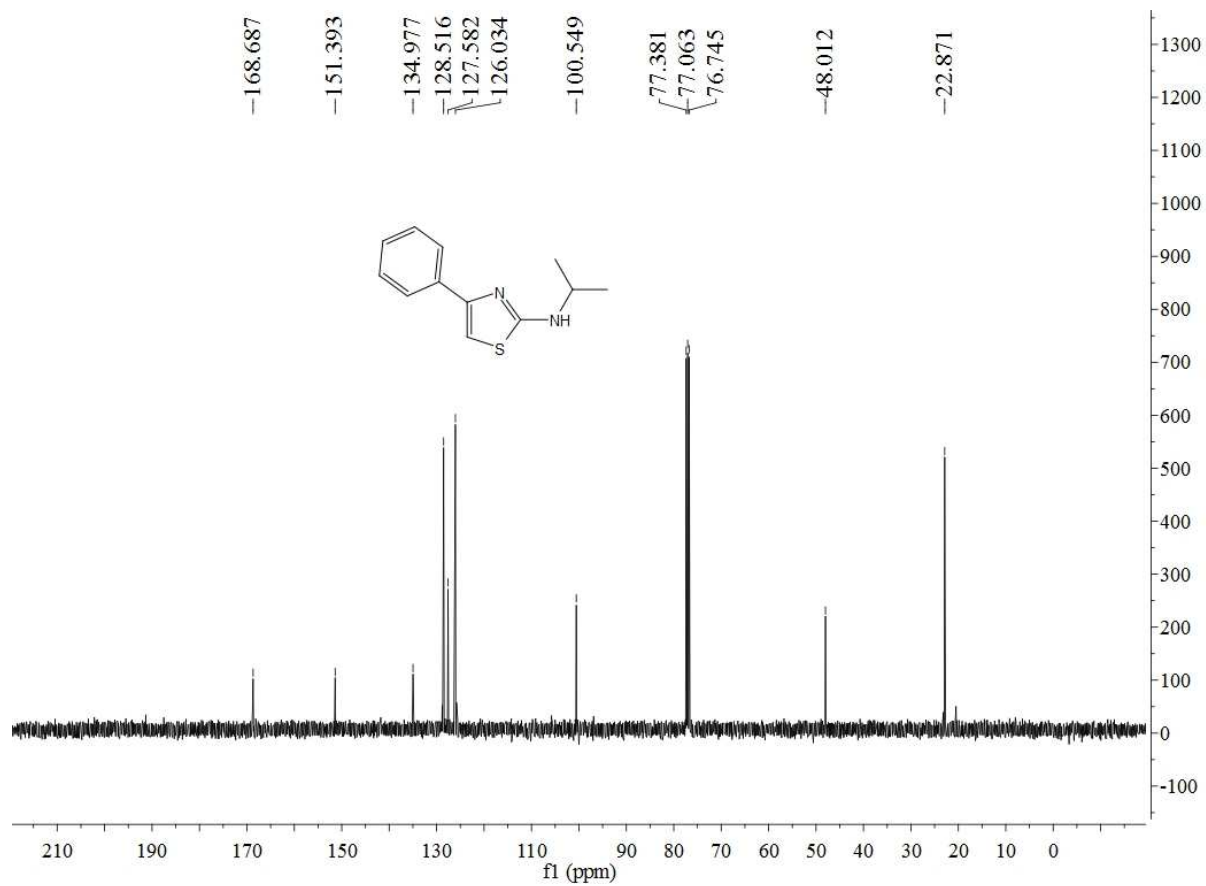
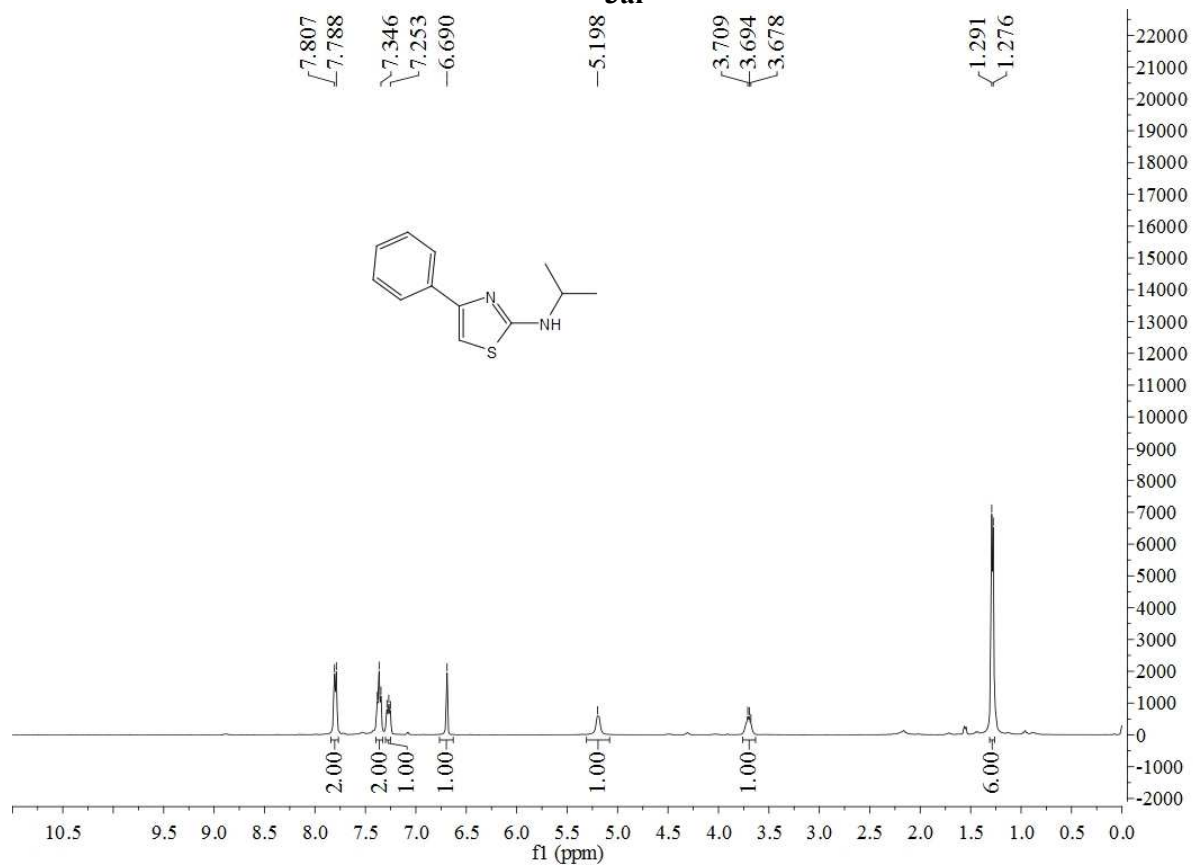
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3ah



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3aj

