Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Efficient Access to 1*H*-Indazoles via Copper-Catalyzed Cross-Coupling/Cyclization of 2-Bromoaryl Oxime Acetates and Amines

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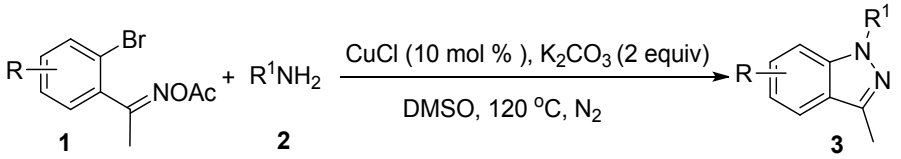
General Information

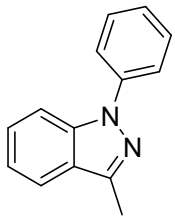
^1H and ^{13}C NMR spectra were recorded on BRUKER DRX-400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS-QP5000 spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. 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]

General Procedure for the Synthesis of 1*H*-Indazoles



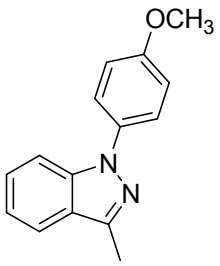
The mixture of oxime acetates **1** (0.5 mmol), amines **2** (0.6 mmol), CuCl (10 mol %) and K_2CO_3 (1.0 mmol) in a 25 mL Schlenk tube was stirred in DMSO (2.0 mL) at 120 °C, under N_2 for 6 h. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL) or CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding pyrroles **3** with hexanes/ethyl acetate as the eluent.

Analysis Data for Compounds 3a-3y



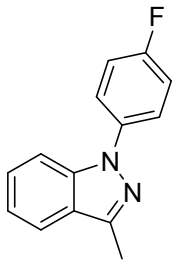
3-methyl-1-phenyl-1H-indazole (3a)[2]

Yellow oil (89 mg, 86 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 4H), 7.54 – 7.50 (m, 2H), 7.44 – 7.40 (m, 1H), 7.32 (dd, *J* = 14.6, 7.3 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.3, 139.5, 129.4, 127.2, 126.1, 124.9, 122.4, 120.8, 120.6, 110.4, 11.9. MS (EI, 70 eV) m/z : 208 (M^+), 193, 167, 139, 104, 77. IR (KBr): 1594, 1507, 1443, 750 cm^{-1}.



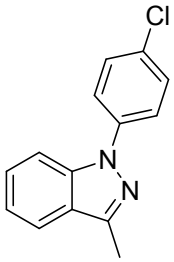
1-(4-methoxyphenyl)-3-methyl-1H-indazole (3b)[2]

Red oil (107 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.61 – 7.58 (m, 3H), 7.41 – 7.36 (m, 1H), 7.21 – 7.17 (m, 1H), 7.05 – 7.02 (m, 2H), 3.87 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 143.4, 139.8, 133.5, 126.9, 124.5, 124.3, 120.5,120.5, 114.6, 110.1, 55.6, 11.9. MS (EI, 70 eV) m/z : 238 (M^+), 223, 195, 167, 154, 128, 92, 77. IR (KBr):1604, 1517, 1447, 1249, 744 cm^{-1}.



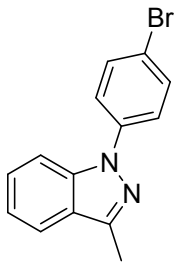
1-(4-fluorophenyl)-3-methyl-1H-indazole (3c)[2]

Red oil (103 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.61 (m, 3H), 7.44 – 7.40 (m, 1H), 7.23 – 7.19 (m, 3H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9 (d, *J* = 244.2 Hz), 144.1, 139.6, 136.5 (d, *J* = 2.5 Hz), 127.3, 124.8,123.2, 124.2 (d, *J* = 8.3 Hz), 120.8 (d, *J* = 18.9 Hz), 116.3, 116.1, 110.0, 11.9. MS (EI, 70 eV) m/z : 226 (M^+), 184, 157, 131, 95, 75. IR (KBr): 1603, 1516, 1442, 1222, 747 cm^{-1}.



1-(4-chlorophenyl)-3-methyl-1H-indazole (3d)[2]

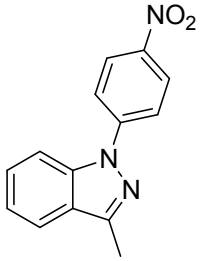
Yellow solid (100 mg, 83 %), m.p. = 91 – 92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.65 (m, 3H), 7.50 – 7.41 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 139.4, 138.9, 131.4, 129.5, 127.4, 125.1, 123.3, 121.1, 120.8, 110.1, 11.9. MS (EI, 70 eV) m/z : 242 (M^+), 206, 192, 166, 140, 111, 103, 75. IR (KBr): 1598, 1502, 1434, 1085, 747 cm^{-1}.



1-(4-bromophenyl)-3-methyl-1H-indazole (3e)

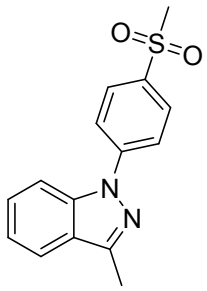
Yellow solid (120 mg, 84 %), m.p. = 89 – 90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.5 Hz, 1H), 7.64 – 7.59 (m, 4H), 7.44 (dd, *J* = 11.4, 4.0 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 2.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 139.4, 139.3, 132.5, 127.5, 125.2,

123.7, 121.1, 120.8, 119.1, 110.2, 11.9. MS (EI, 70 eV) m/z : 286 (M^+), 206, 166, 139, 103, 76. HRMS-ESI (m/z): calcd for $C_{14}H_{12}BrN_2$, $[M+H]^+$: 287.0178; found, 287.0172. IR (KBr): 1591, 1492, 1019, 822, 745 cm^{-1}.



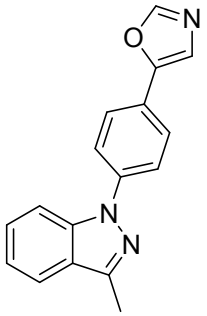
3-methyl-1-(4-nitrophenyl)-1H-indazole (3f)[2]

Yellow solid (109 mg, 86 %), m.p. = 144 – 145 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.37 (m, 2H), 7.95 (t, *J* = 6.0 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 145.6, 144.5, 139.3, 128.2, 126.2, 125.3, 122.2, 121.2, 120.6, 110.6, 12.0. MS (EI, 70 eV) m/z : 253 (M^+), 223, 205, 192, 166, 140, 102, 76. IR (KBr): 1590, 1506, 1328, 845, 745 cm^{-1}.



3-methyl-1-(4-(methylsulfonyl)phenyl)-1H-indazole (3g)

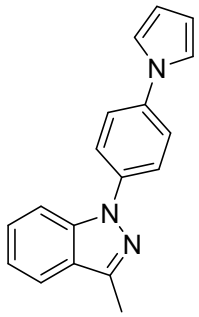
Yellow solid (116 mg, 81 %), m.p. = 122 – 123 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.7 Hz, 2H), 7.95 – 7.92 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.48 – 7.44 (m, 1H), 7.24 – 7.22 (m, 1H), 3.07 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.2, 144.8, 139.2, 136.6, 129.0, 128.1, 126.0, 121.9, 121.3, 121.1, 110.5, 44.7, 12.0. MS (EI, 70 eV) m/z : 286 (M^+), 223, 207, 192, 166, 139, 128, 102, 76. HRMS-ESI (m/z): calcd for $C_{15}H_{15}N_2O_2S$, $[M+H]^+$: 287.0849; found, 287.0852. IR (KBr): 1587, 1510, 1439, 1146, 756 cm^{-1}.



5-(4-(3-methyl-1H-indazol-1-yl)phenyl)oxazole (3h)

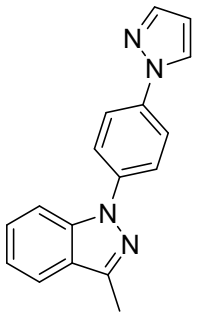
Yellow oil (100 mg, 73 %). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 (s,1H), 7.80 (s, 4H), 7.76 – 7.73 (m, 2H), 7.47 – 7.40 (m, 2H), 7.23 (d, *J* = 7.8 Hz,1H), 2.67 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 150.5, 144.7, 140.5, 139.3, 127.5, 125.9, 125.3, 125.2, 122.3, 121.5, 121.2, 120.8, 110.4, 12.0. MS (EI, 70 eV) m/z : 275 (M^+), 246, 219, 205, 178, 137, 110, 89, 76. HRMS-ESI (m/z): calcd for $C_{17}H_{14}N_3O$, $[M+H]^+$: 276.1131; found, 276.1130. IR (KBr): 1597, 1513, 1438, 1021,

750 cm^{-1}.



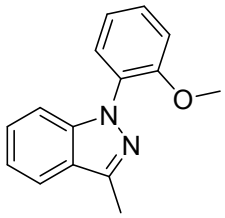
1-(4-(1H-pyrrol-1-yl)phenyl)-3-methyl-1H-indazole (3i)

Red solid (105 mg, 77 %), m.p. = 104 – 105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 4H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.20 (dd, *J* = 14.3, 7.0 Hz, 1H), 7.13 – 7.10 (m, 2H), 6.38 – 6.37 (m, 2H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 139.5, 138.6, 137.9, 127.3, 125.0, 123.3, 121.3, 121.0, 120.8, 119.4, 110.7, 110.2, 12.0. MS (EI, 70 eV) m/z: 273 (M^+), 231, 204, 182, 154, 115, 102, 89, 76. HRMS-ESI (m/z): calcd for $C_{18}H_{16}N_3$, $[M+H]^+$: 274.1339; found, 274.1337. IR (KBr): 1517, 1457, 1325, 1022, 829, 733 cm^{-1}.



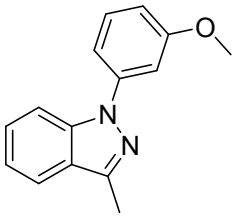
1-(4-(1H-pyrazol-1-yl)phenyl)-3-methyl-1H-indazole (3j)

Yellow oil (104 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.3 Hz, 1H), 7.86 – 7.80 (m, 4H), 7.76 – 7.70 (m, 3H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.50 (t, *J* = 2.0 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 144.4, 141.3, 139.5, 138.6, 138.0, 127.4, 126.8, 125.1, 123.1, 121.0, 120.8, 120.1, 110.2, 107.8, 12.0. MS (EI, 70 eV) m/z : 274 (M^+), 246, 205, 195, 137, 103, 89, 76. HRMS-ESI (m/z): calcd for $C_{17}H_{15}N_4$, $[M+H]^+$: 275.1291; found, 275.1289. IR (KBr): 1581, 1526, 1444, 1393, 838, 747 cm^{-1}.



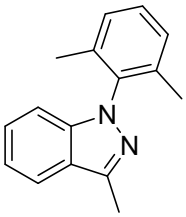
1-(2-methoxyphenyl)-3-methyl-1H-indazole (3k)[2]

Brown oil (90 mg, 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.34 (m, 3H), 7.21 – 7.16 (m, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 143.6, 141.3, 129.2, 128.6, 128.5, 126.5, 123.8, 121.0, 120.2, 120.2, 112.3, 111.0, 55.8, 12.0. MS (EI, 70 eV) m/z: 238 (M^+), 221, 207, 196, 167, 143, 119, 77. IR (KBr): 1593, 1513, 1461, 1251, 750 cm^{-1}.



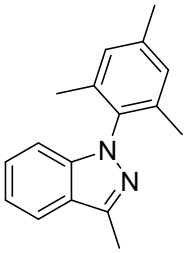
1-(3-methoxyphenyl)-3-methyl-1H-indazole (3l)[2]

Red oil (84 mg, 71 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.44 – 7.39 (m, 2H), 7.31 – 7.28 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.87 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.89 (s, 3H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 144.0, 141.4, 139.5, 130.1, 127.2, 125.1, 120.9, 120.6, 114.5, 112.1, 110.5, 108.1, 55.9, 12.3. MS (EI, 70 eV) m/z: 238 (M^+), 208, 167, 154, 127, 92, 77. IR (KBr): 1598, 1495, 1348, 844, 745 cm^{-1}.



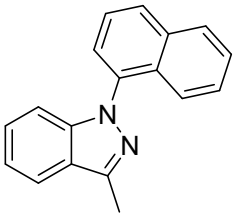
1-(2,6-dimethylphenyl)-3-methyl-1H-indazole (3m)

Brown oil (106 mg, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.34 – 7.25 (m, 2H), 7.18 – 7.14 (m, 3H), 6.94 (dd, *J* = 22.0, 11.5 Hz, 1H), 2.67 (s, 3H), 1.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.0, 137.5, 137.1, 129.0, 128.3, 126.7, 123.1, 120.4, 120.0, 109.5, 17.5, 12.1. MS (EI, 70 eV) m/z : 236 (M^+), 221, 194, 180, 117, 103, 77. HRMS-ESI (m/z): calcd for $C_{16}H_{17}N_2$, $[M+H]^+$: 237.1386; found, 237.1381. IR (KBr): 1580, 1507, 1352, 1025, 751 cm^{-1}.



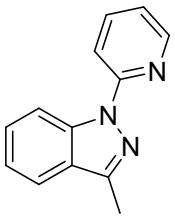
1-mesityl-3-methyl-1H-indazole (3n)

Red oil (105 mg, 84 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.99 – 6.97 (m, 3H), 2.67 (s, 3H), 2.37 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.2, 138.7, 137.1, 134.5, 129.0, 126.6, 123.1, 120.3, 119.9, 109.6, 21.2, 17.4, 12.1. MS (EI, 70 eV) m/z: 250 (M^+), 235, 208, 194, 117, 91, 77. HRMS-ESI (m/z): calcd for $C_{17}H_{19}N_2$, $[M+H]^+$: 251.1543; found, 251.1539. IR (KBr): 1586, 1509, 1349, 1022, 747 cm^{-1}.



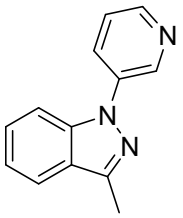
3-methyl-1-(naphthalen-1-yl)-1H-indazole (3o)

Red oil (101 mg, 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.50 (m, 4H), 7.42 (dd, *J* = 13.9, 6.7 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.24 – 7.16 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 143.8, 142.1, 136.0, 134.6, 130.1, 128.8, 128.2, 126.9, 126.9, 126.6, 125.4, 124.6, 123.9, 123.7, 120.6, 120.4, 110.4, 12.1. MS (EI, 70 eV) m/z : 258 (M^+), 241, 216, 189, 127, 107, 73. HRMS-ESI (m/z): calcd for $C_{18}H_{15}N_2$, $[M+H]^+$: 259.1230; found, 259.1229. IR (KBr): 1506, 1418, 1345, 1018, 751 cm^{-1}.



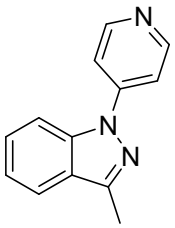
3-methyl-1-(pyridin-2-yl)-1H-indazole (3p)[3]

Yellow oil (89 mg, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.5 Hz, 1H), 8.49 (t, *J* = 14.6 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.84 – 7.75 (m, 1H), 7.68 – 7.66 (m, 1H), 7.52 – 7.45 (m, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.06 (m, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 147.7, 145.6, 139.5, 138.1, 127.9, 125.8, 121.9, 120.0, 119.3, 115.3, 113.1, 12.1. MS (EI, 70 eV) m/z : 209 (M^+), 194, 168, 140, 131, 78. IR (KBr): 1588, 1521, 1454, 1076, 755 cm^{-1}.



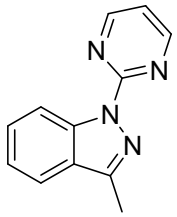
3-methyl-1-(pyridin-3-yl)-1H-indazole (3q)

Red oil (92 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.56 (d, *J* = 4.5 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 9.0 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.26 (d, *J* = 5.6 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.0, 145.4, 143.2, 139.5, 137.1, 129.2, 127.7, 125.3, 124.0, 121.4, 120.9, 110.0, 12.0. MS (EI, 70 eV) m/z : 209 (M^+), 168, 140, 114, 77. HRMS-ESI (m/z): calcd for $C_{13}H_{12}N_3$, $[M+H]^+$: 210.1026; found, 210.11026. IR (KBr): 1579, 1518, 1450, 1074, 750 cm^{-1}.



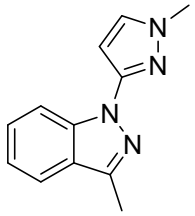
3-methyl-1-(pyridin-4-yl)-1H-indazole (3r)

Brown oil (100 mg, 96 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 2H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 147.1, 146.5, 139.2, 128.2, 126.3, 122.1, 121.1, 110.9, 12.0. MS (EI, 70 eV) m/z: 209 (M^+), 168, 140, 114, 77. HRMS-ESI (m/z): calcd for $C_{13}H_{12}N_3$, $[M+H]^+$: 210.1026; found, 210.1027. IR (KBr): 1592, 1508, 1439, 1022, 749 cm^{-1}.



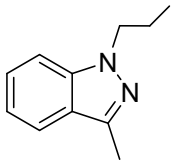
3-methyl-1-(pyrimidin-2-yl)-1H-indazole (3s)

Yellow solid (101 mg, 96 %). m.p. = 106 – 107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.62 (d, *J* = 8.5 Hz, 1H), 8.32 (d, *J* = 17.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.3, 140.0, 139.0, 136.2, 128.3, 126.0, 122.7, 120.2, 115.0, 12.1. MS (EI, 70 eV) m/z: 210 (M^+), 195, 169, 142, 131, 102,77. HRMS-ESI (m/z): calcd for $C_{12}H_{11}N_4$, $[M+H]^+$: 211.0978; found, 211.0974. IR (KBr): 1579, 1529, 1448, 1018, 751 cm^{-1}.



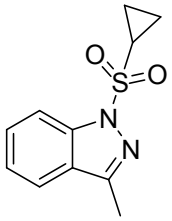
3-methyl-1-(1-methyl-1H-pyrazol-3-yl)-1H-indazole (3t)

Red oil (99 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.37 (s, 1H), 7.20 (t, J = 7.4 Hz, 1H), 6.53 (s, 1H), 3.94 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2, 144.2, 139.2, 131.0, 127.4, 124.5, 121.0, 120.1, 112.5, 96.3, 39.2, 12.0. MS (EI, 70 eV) m/z: 212 (M^+), 170, 131, 102, 77. HRMS-ESI (m/z): calcd for $C_{12}H_{13}N_4$, $[M+H]^+$: 213.1135; found, 213.1124. IR (KBr): 1581, 1526, 1445, 1028, 750 cm^{-1}.



3-methyl-1-propyl-1H-indazole (3u)

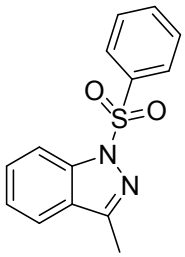
Red oil (57 mg, 65 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 12.8 Hz, 2H), 7.15 – 7.02 (m, 1H), 4.27 (t, *J* = 7.0 Hz, 2H), 2.58 (s, 3H), 1.98 – 1.87 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 140.4, 126.0, 123.2, 120.4, 119.5, 108.9, 50.2, 23.4, 11.9, 11.5. MS (EI, 70 eV) m/z : 174 (M^+), 145, 128, 91, 77. HRMS-ESI (m/z): calcd for $C_{11}H_{15}N_2$, $[M+H]^+$: 175.1230; found, 175.1224. IR (KBr): 1583, 1473, 1349, 1027, 747 cm^{-1}.



1-(cyclopropylsulfonyl)-3-methyl-1H-indazole (3v)

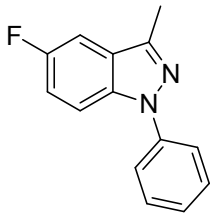
Red oil (96 mg, 81 %). ^{1}H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 8.4 Hz, 1H), 7.68 (d, J = 8.0 Hz,

1H), 7.52 (t, J = 7.7 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 2.69 – 2.65 (m, 1H), 2.61 (s, 3H), 1.42 – 1.41 (m, 2H), 1.01 – 0.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 141.3, 129.1, 125.8, 123.7, 120.6, 113.1, 31.0, 12.3, 6.1. MS (EI, 70 eV) m/z: 236 (M^+), 171, 157, 145, 132, 103, 77. HRMS-ESI (m/z): calcd for $C_{11}H_{13}N_2O_2S$, $[M+H]^+$: 237.0692; found, 237.0696. IR (KBr): 1618, 1520, 1440, 1368, 1169, 755 cm^{-1}.



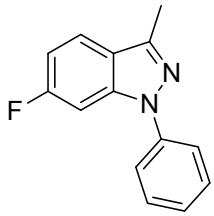
3-methyl-1-(phenylsulfonyl)-1H-indazole (3w)

Red oil (120 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 7.7 Hz, 2H), 7.59 (d, J = 7.9 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 141.1, 137.7, 133.9, 129.2, 129.1, 127.4, 126.2, 124.0, 120.6, 113.4, 12.3. MS (EI, 70 eV) m/z: 272 (M^+), 253, 218, 208, 141, 131, 103, 77. HRMS-ESI (m/z): calcd for $C_{14}H_{13}N_2O_2S$, $[M+H]^+$: 273.0692; found, 273.0699. IR (KBr): 1585, 1443, 1373, 1250, 1180, 757 cm^{-1}.



5-fluoro-3-methyl-1-phenyl-1H-indazole (3x)

Yellow oil (90 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 3H), 7.52 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.1 Hz, 2H), 7.18 (t, J = 8.9 Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5 (d, *J* = 223Hz), 143.6, 140.1, 136.5, 129.5, 126.4, 125.1(d, *J* = 9.5Hz), 122.3, 116.4 (d, *J* = 26.9Hz), 111.5 (d, *J* = 9.2Hz), 104.8, (d, *J* =23.1Hz) ,11.9. MS (EI, 70 eV) m/z: 226 (M^+), 221, 184, 158, 113, 77. HRMS-ESI (m/z): calcd for $C_{14}H_{12}FN_2$, $[M+H]^+$: 227.0979; found, 227.0970. IR (KBr): 1594, 1445, 1026, 748 cm^{-1}.



6-fluoro-3-methyl-1-phenyl-1H-indazole (3y)

Red oil (89 mg, 79 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 –7.63 (m, 3H), 7.54 – 7.50 (m, 2H), 7.35 – 7.33 (m, 2H), 6.99 – 6.95 (m, 1H), 2.63 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, *J* = 243.6Hz), 144.2, 139.9, 139.8 (d, *J* = 12.5Hz) 129.51, 126.5, 122.3, 122.0 (d, *J* = 11.1Hz), 121.8, 110.5 (d, *J* = 25.8Hz), 96.34 (d, *J* = 27.2Hz), 11.9. MS (EI, 70 eV) m/z: 226 (M^+), 221, 185, 157, 149, 77. HRMS-ESI (m/z): calcd for $C_{14}H_{12}FN_2$, $[M+H]^+$: 227.0979; found, 227.0972. IR (KBr):

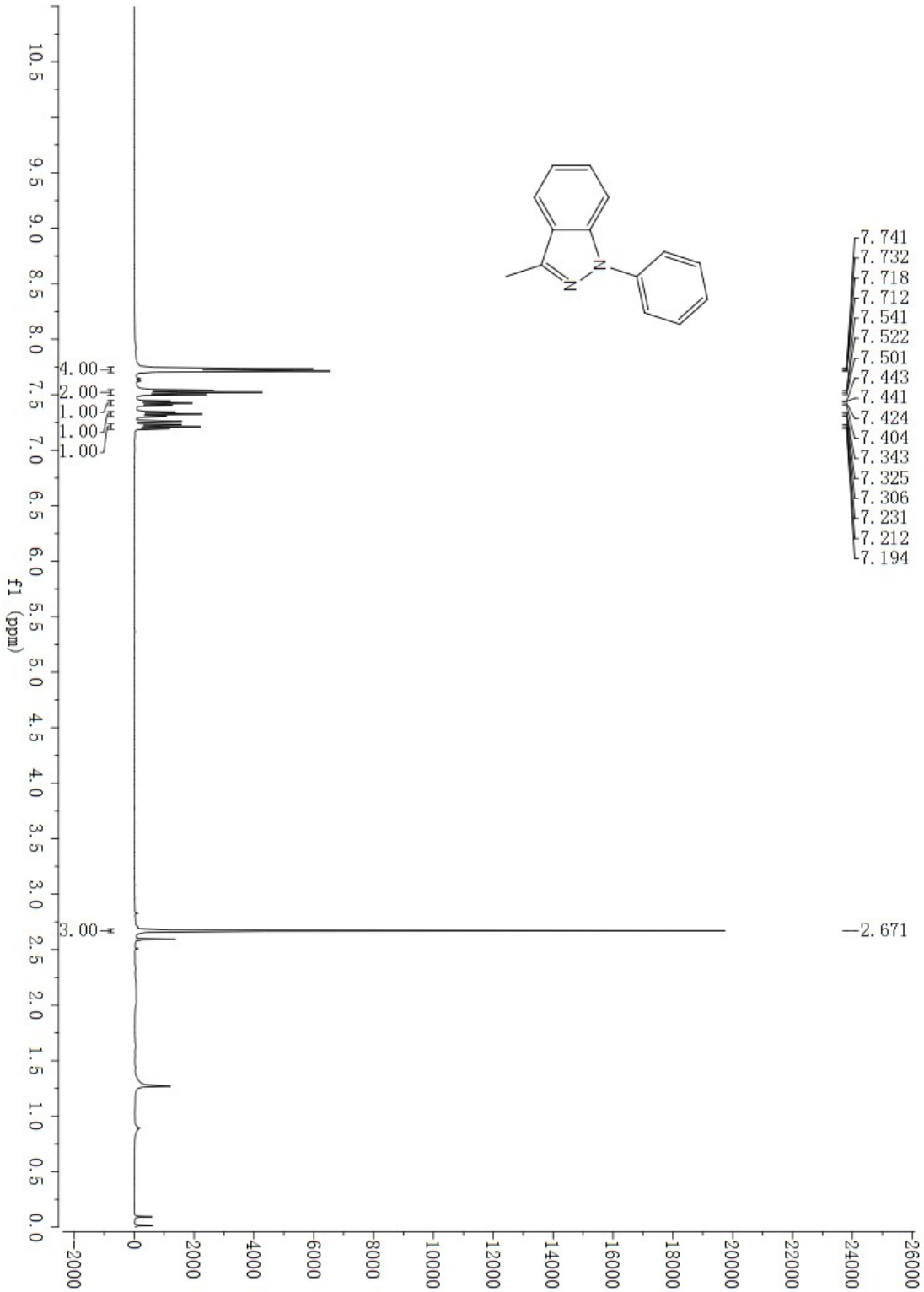
1587, 1504, 1428, 1028, 757 cm^{-1}.

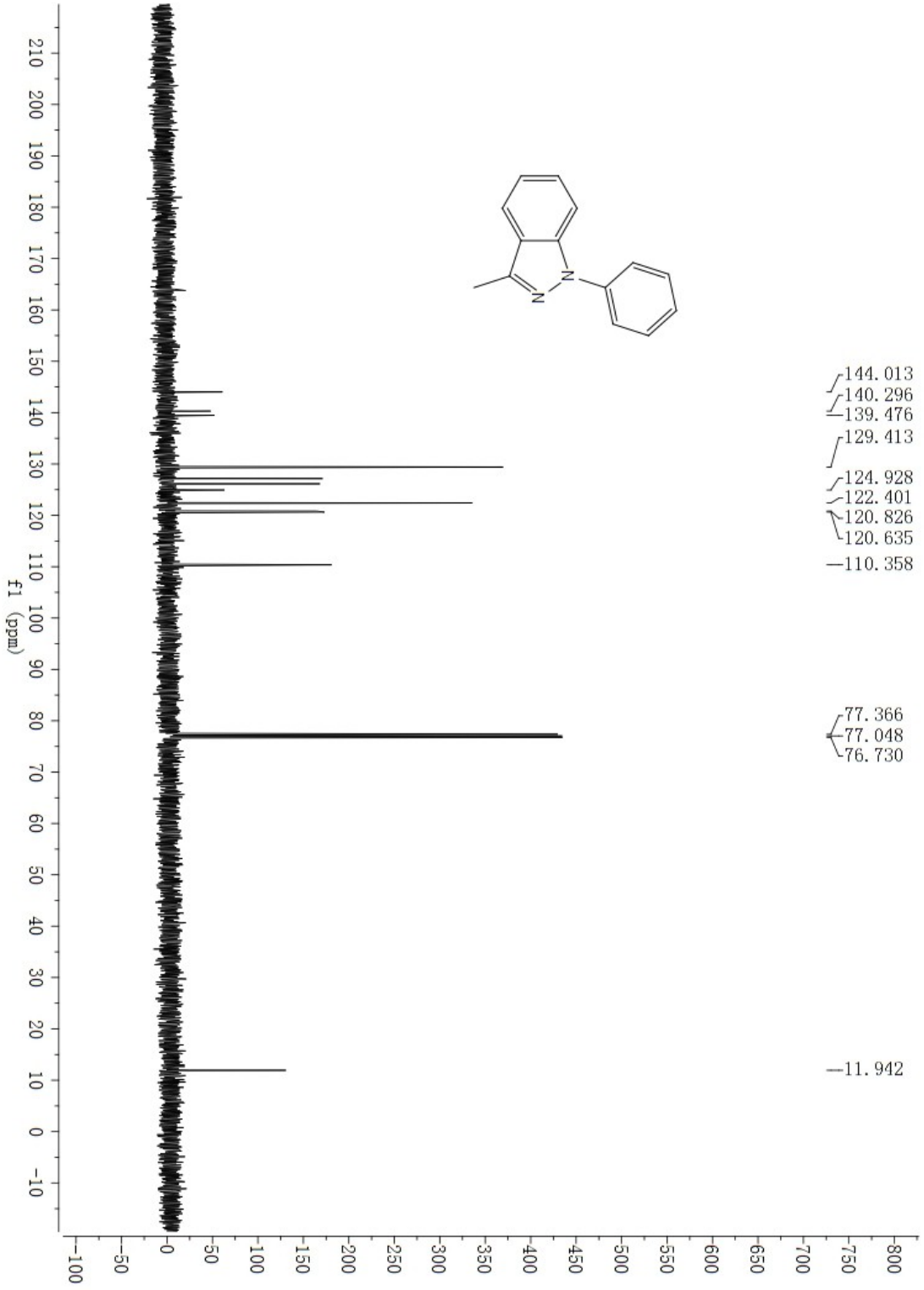
References

1. P. C. Too, Y-F. Wang, S. Chiba, *Org. Lett*. 2010, **12**, 5688.
2. B. C. Wray, J. P. Stambuli, *Org. Lett*. 2010, **12**, 4576.
3. X. D. Xiong, Y. W. Jiang, D. W. Ma, *Org. Lett*. 2012, **14**, 2552.

NMR Spectra for Compounds 3a-3y

3a

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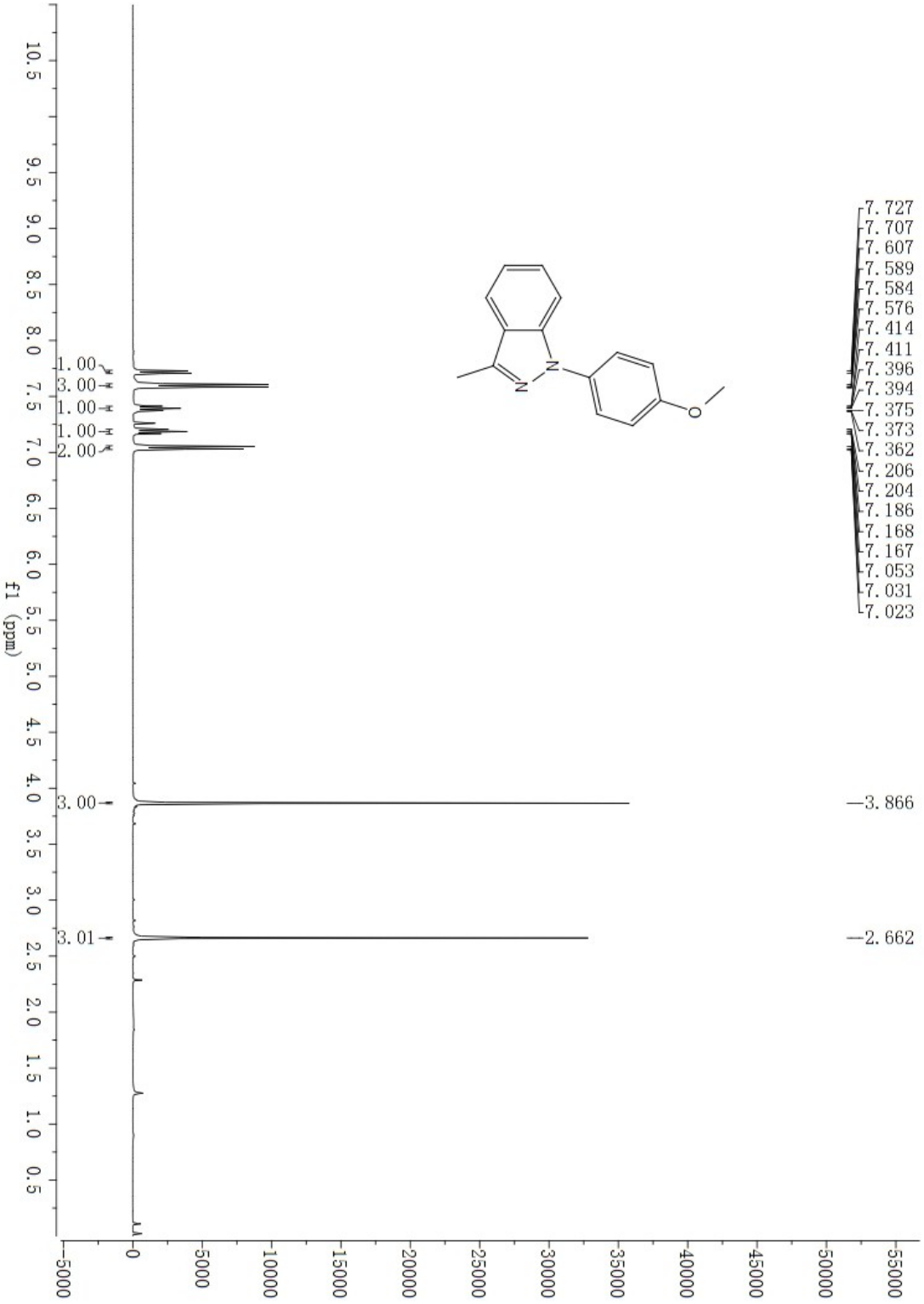
3b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7.204
7.186
7.168
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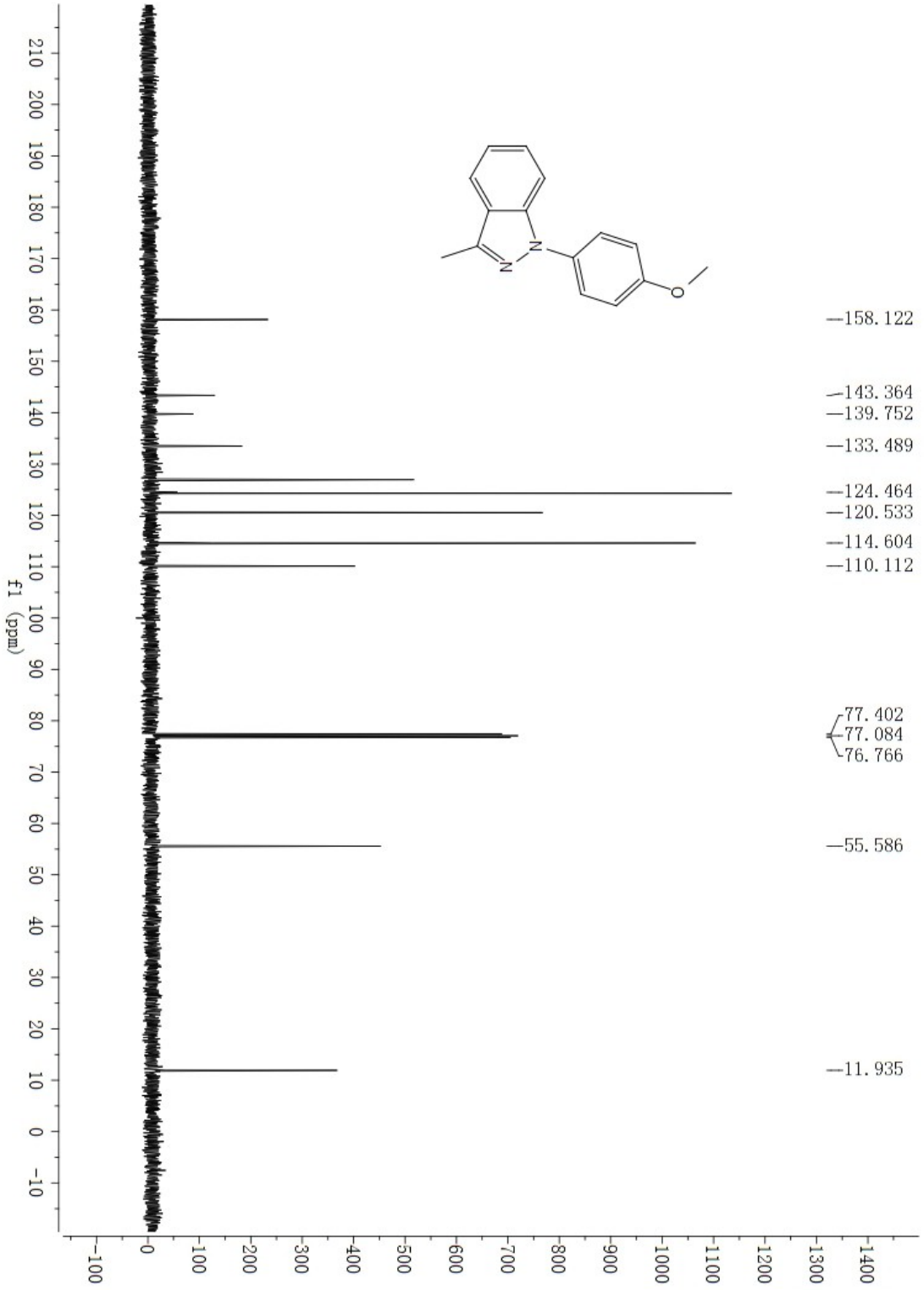
3.01
f1 (ppm)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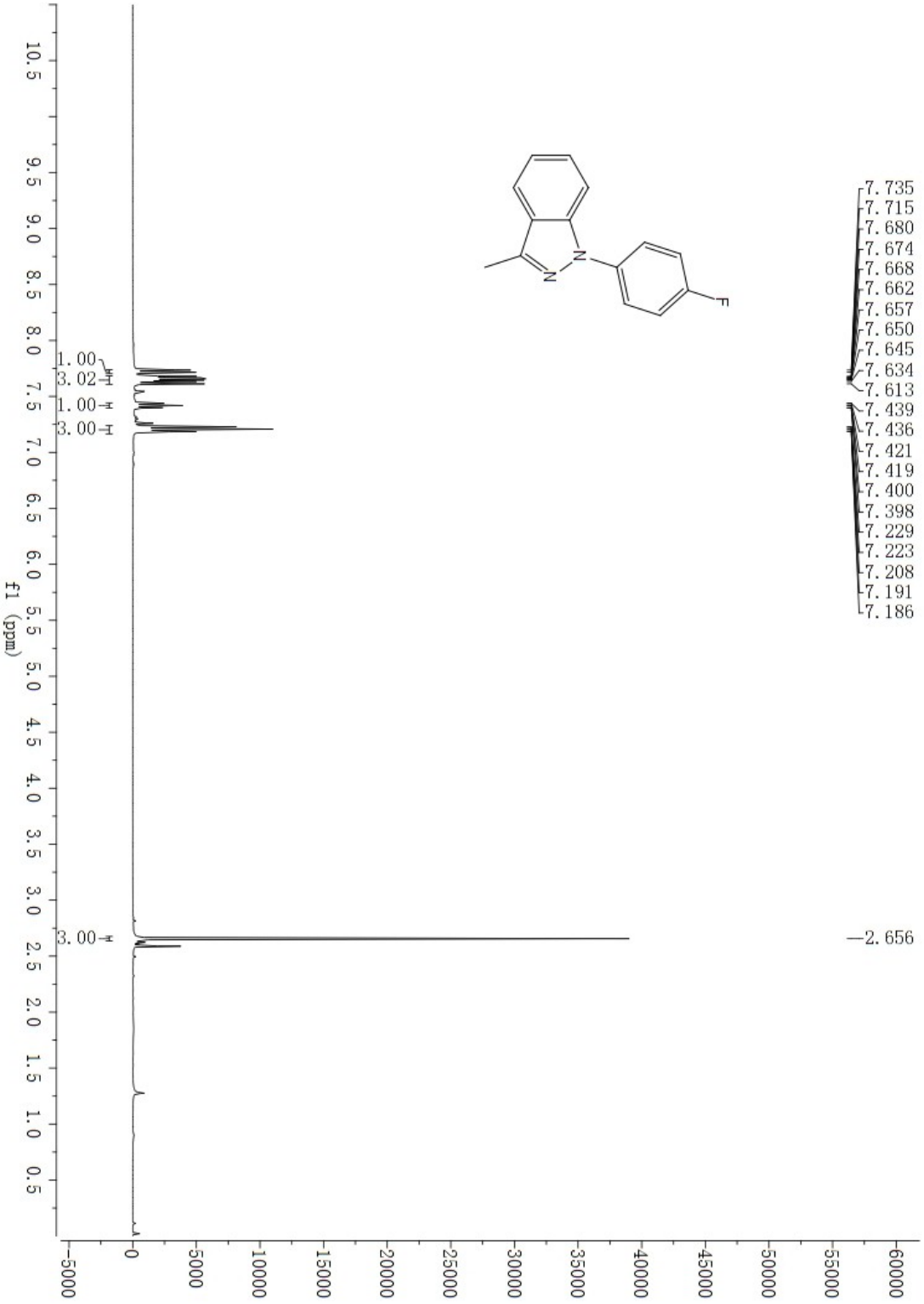
f1 (ppm)

3c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7.419
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7.223
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3.02
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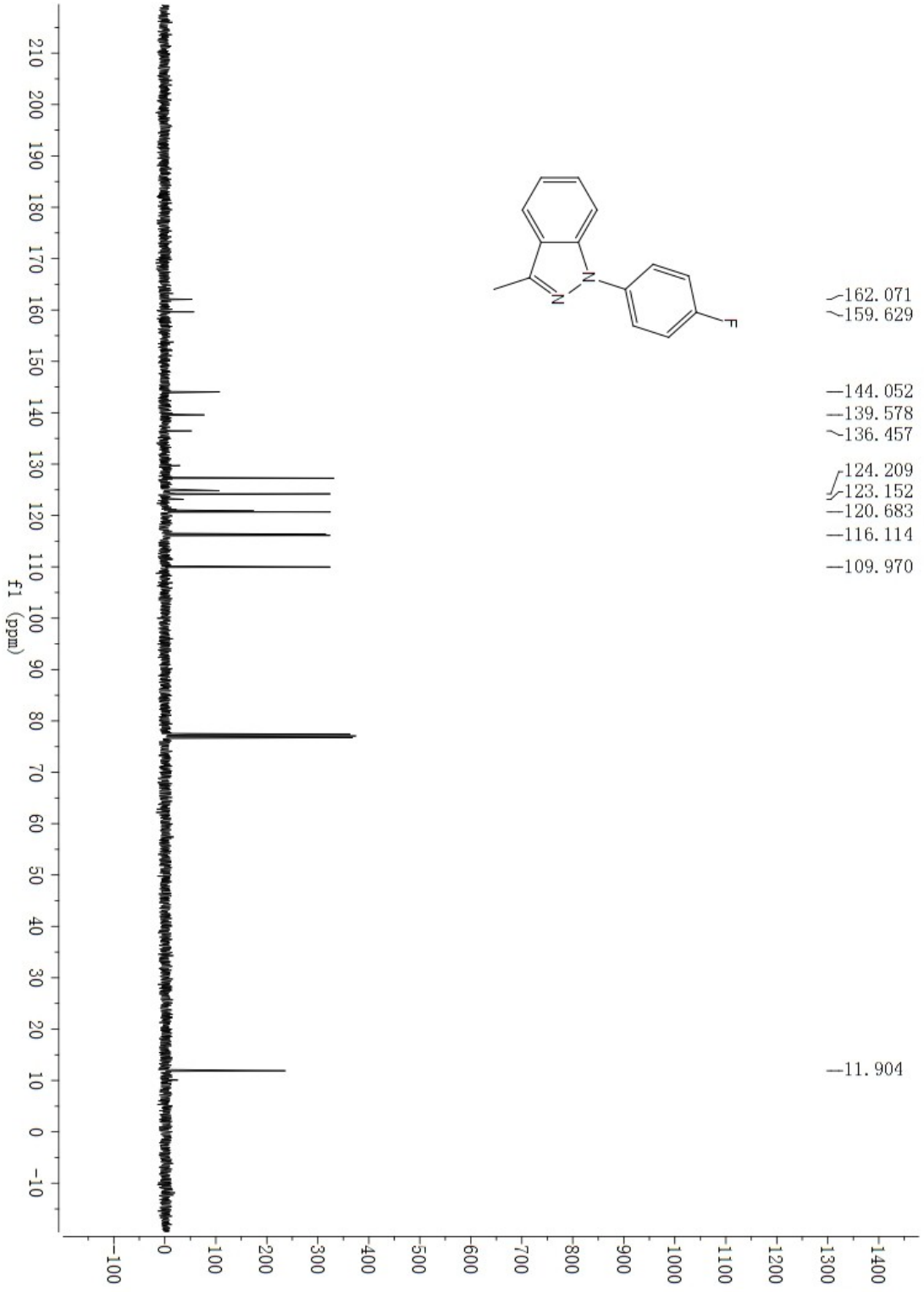
3.00
3.00
N
N
F
f1 (ppm)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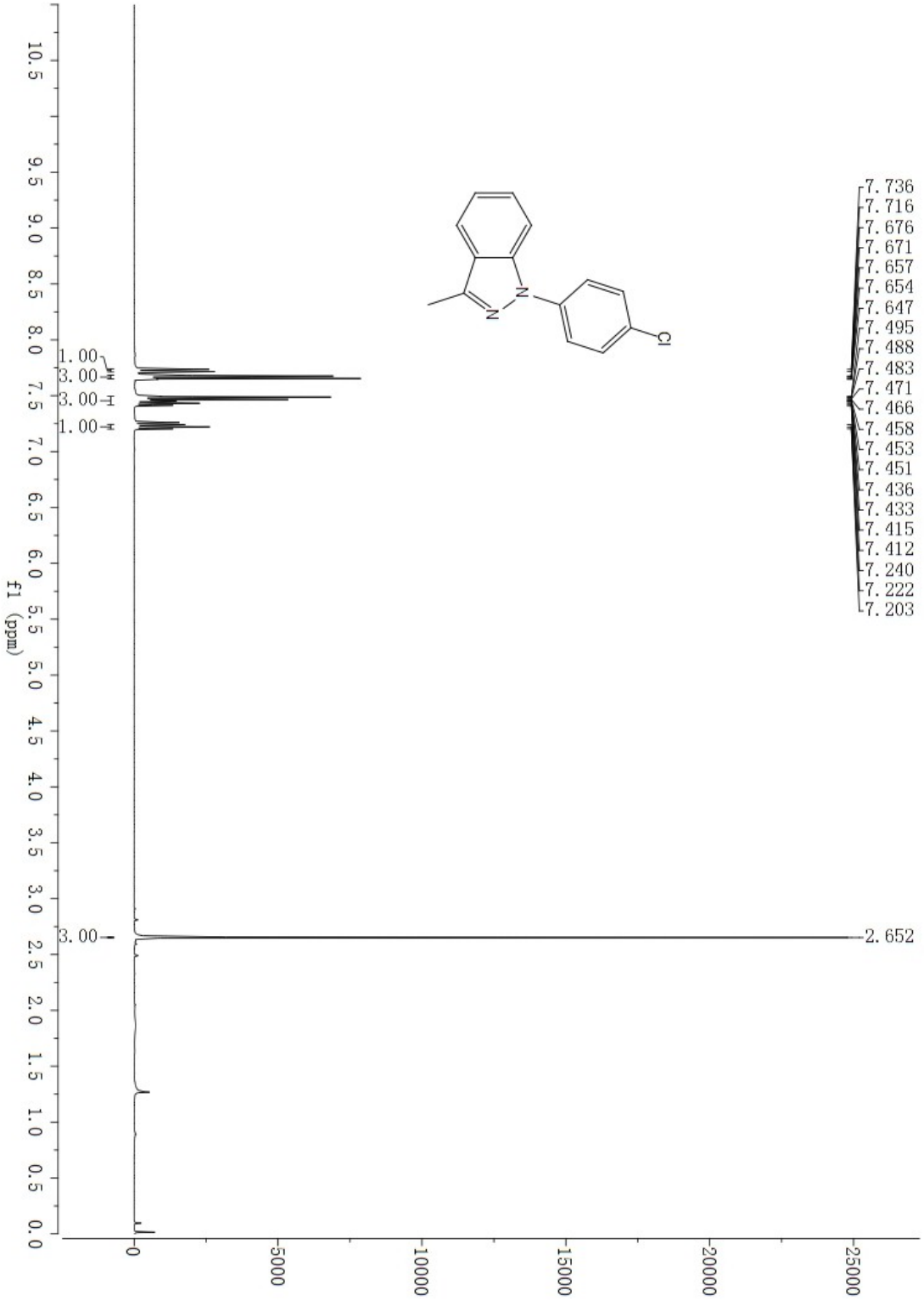
f1 (ppm)

3d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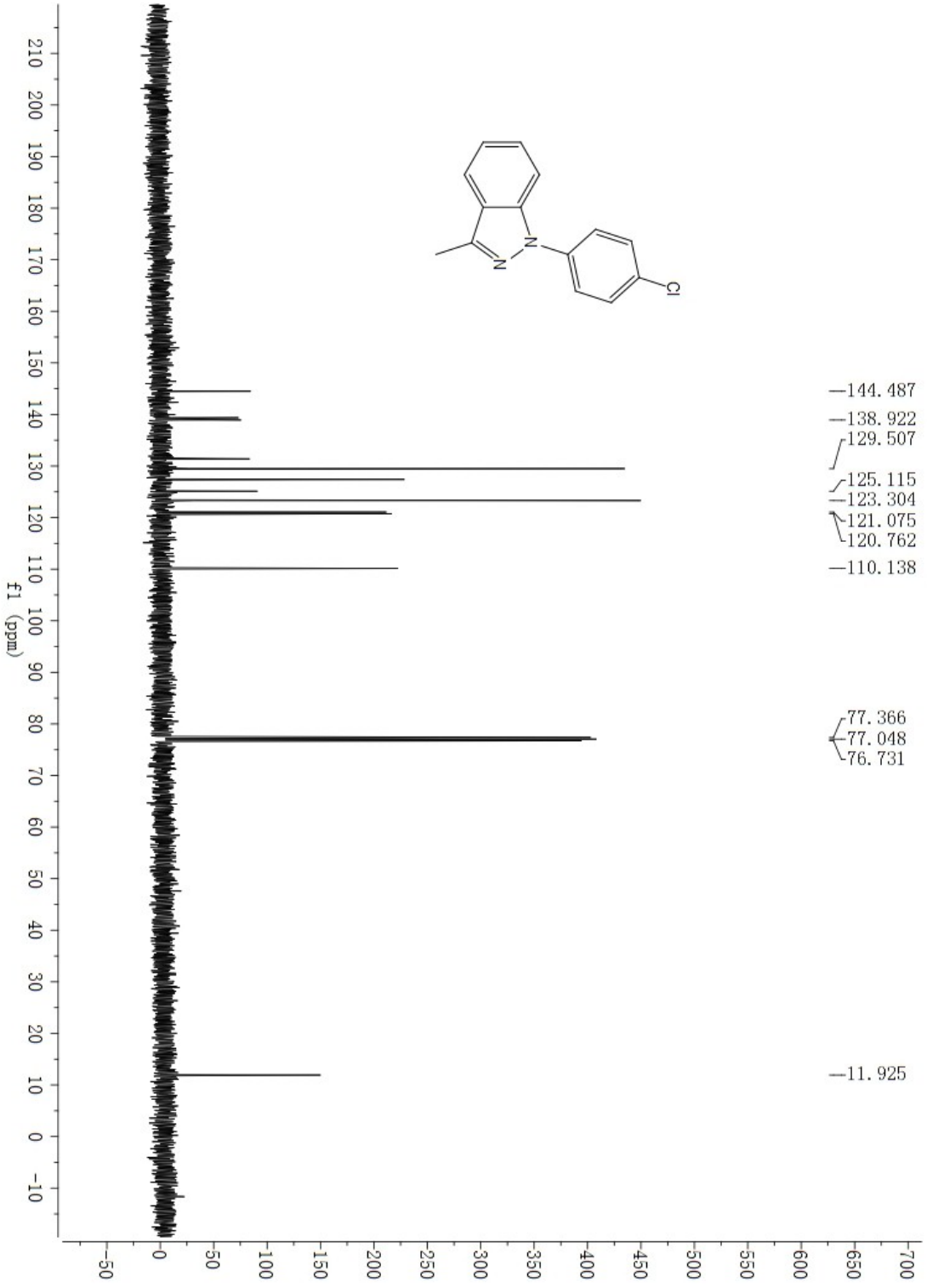
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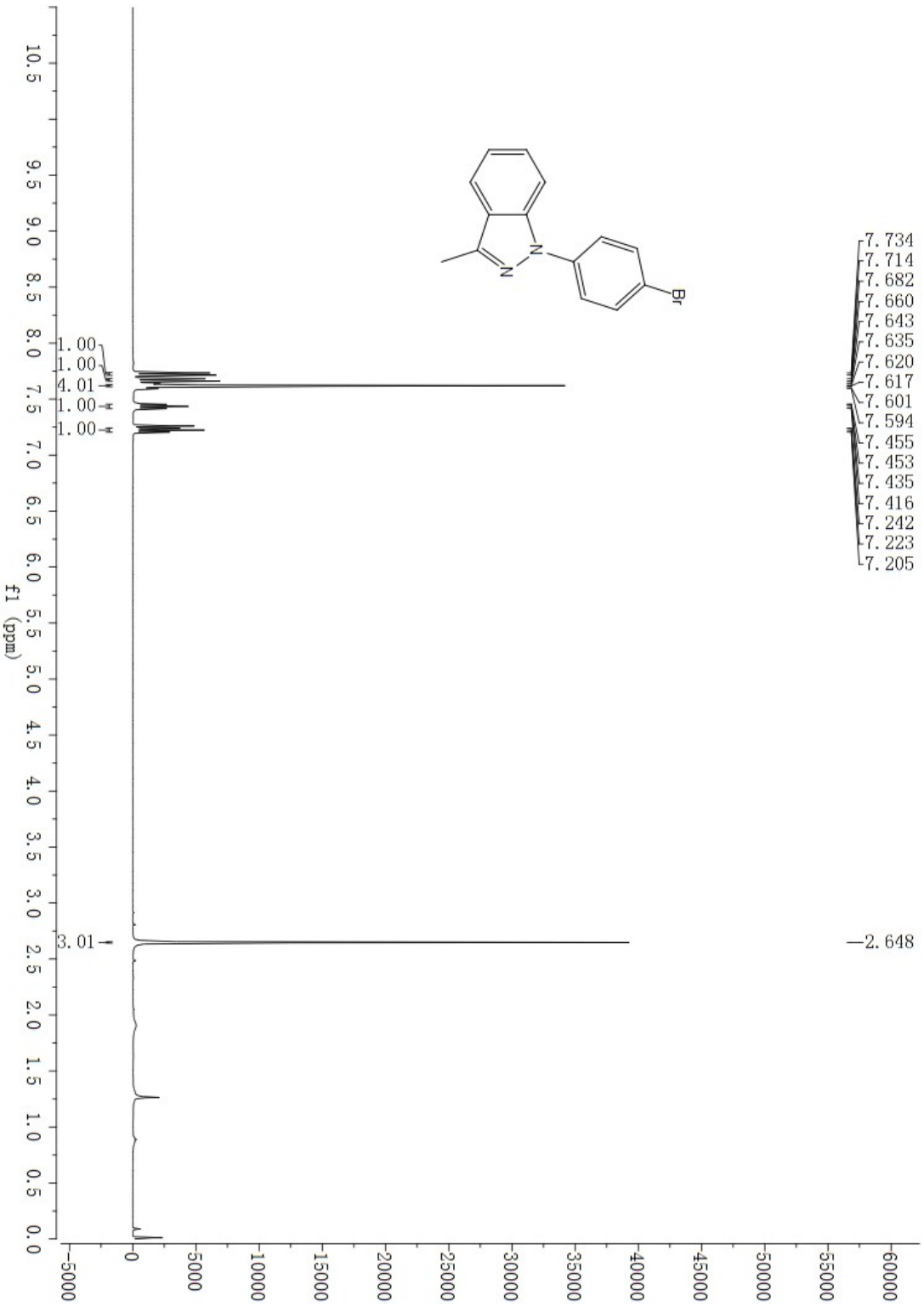
3e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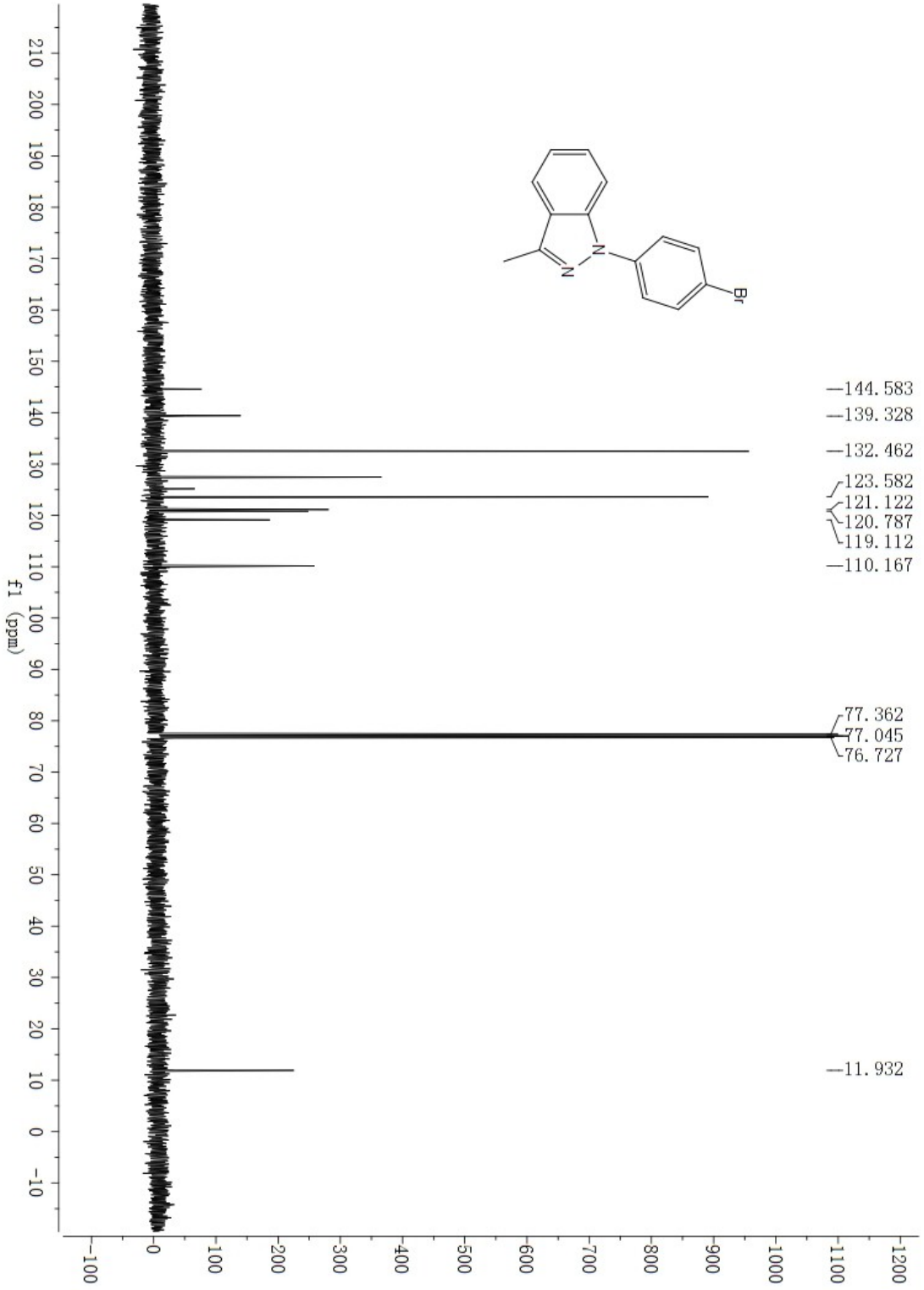
f1 (ppm)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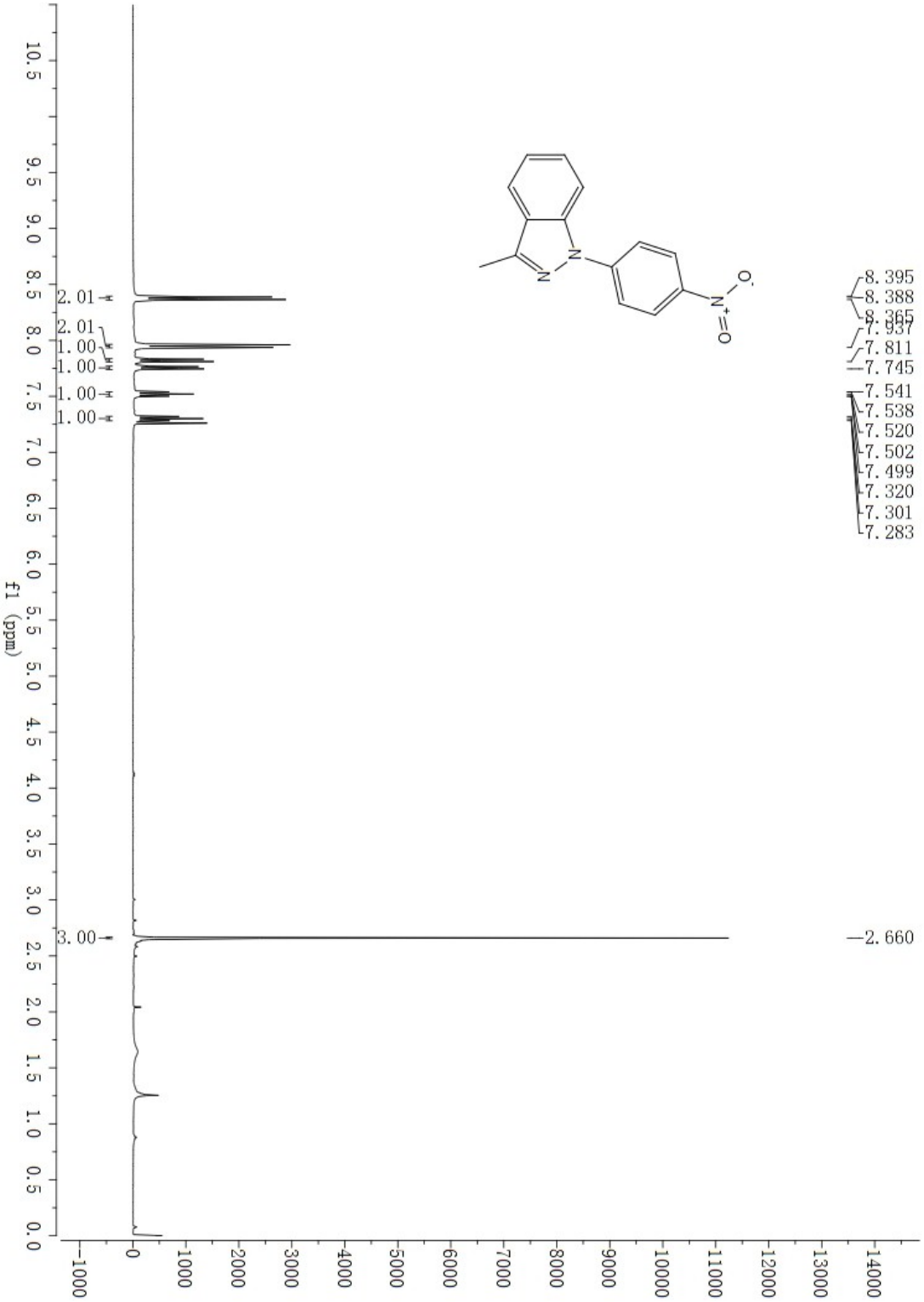
f1 (ppm)
Br
N
N

3f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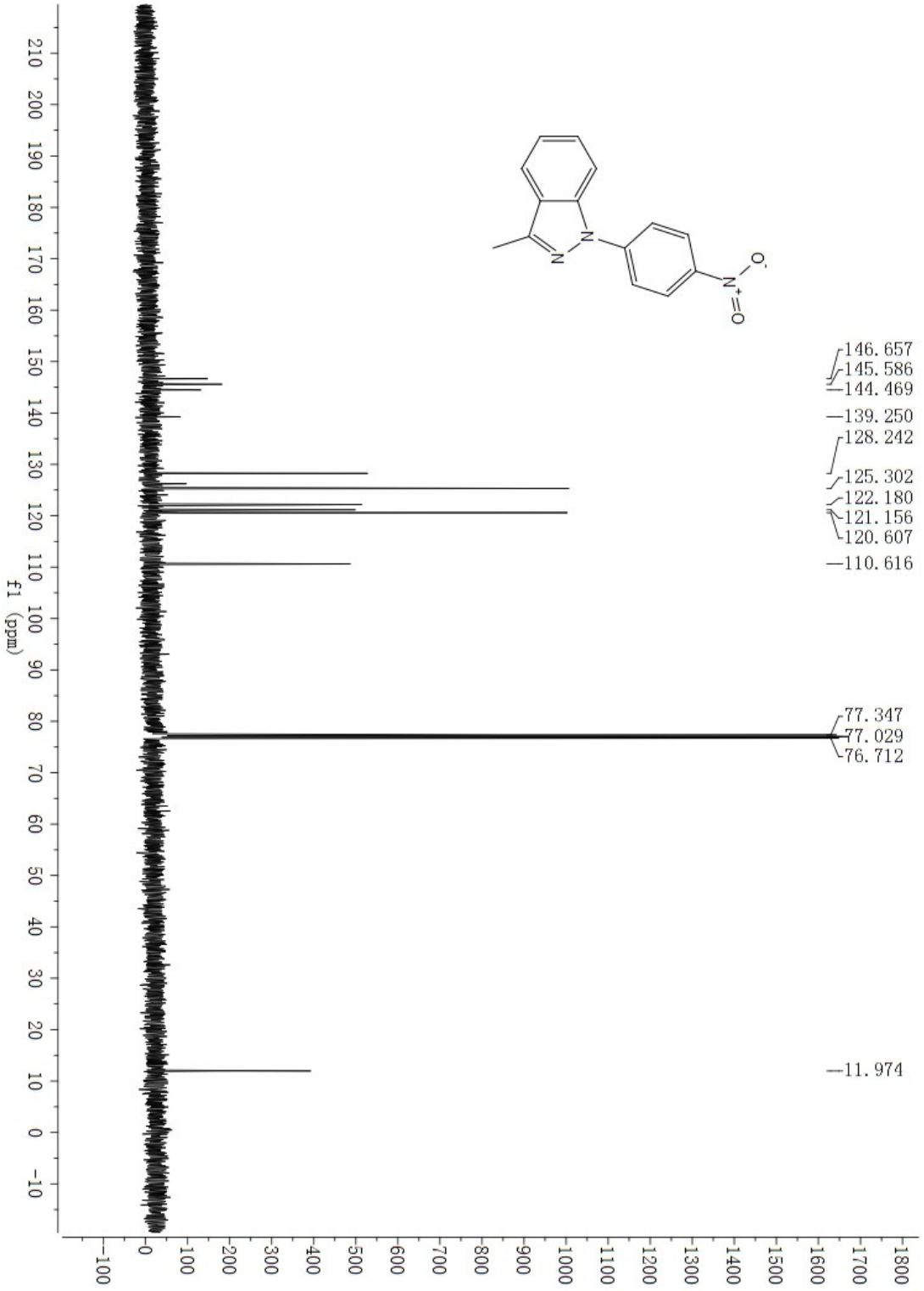
f1 (ppm)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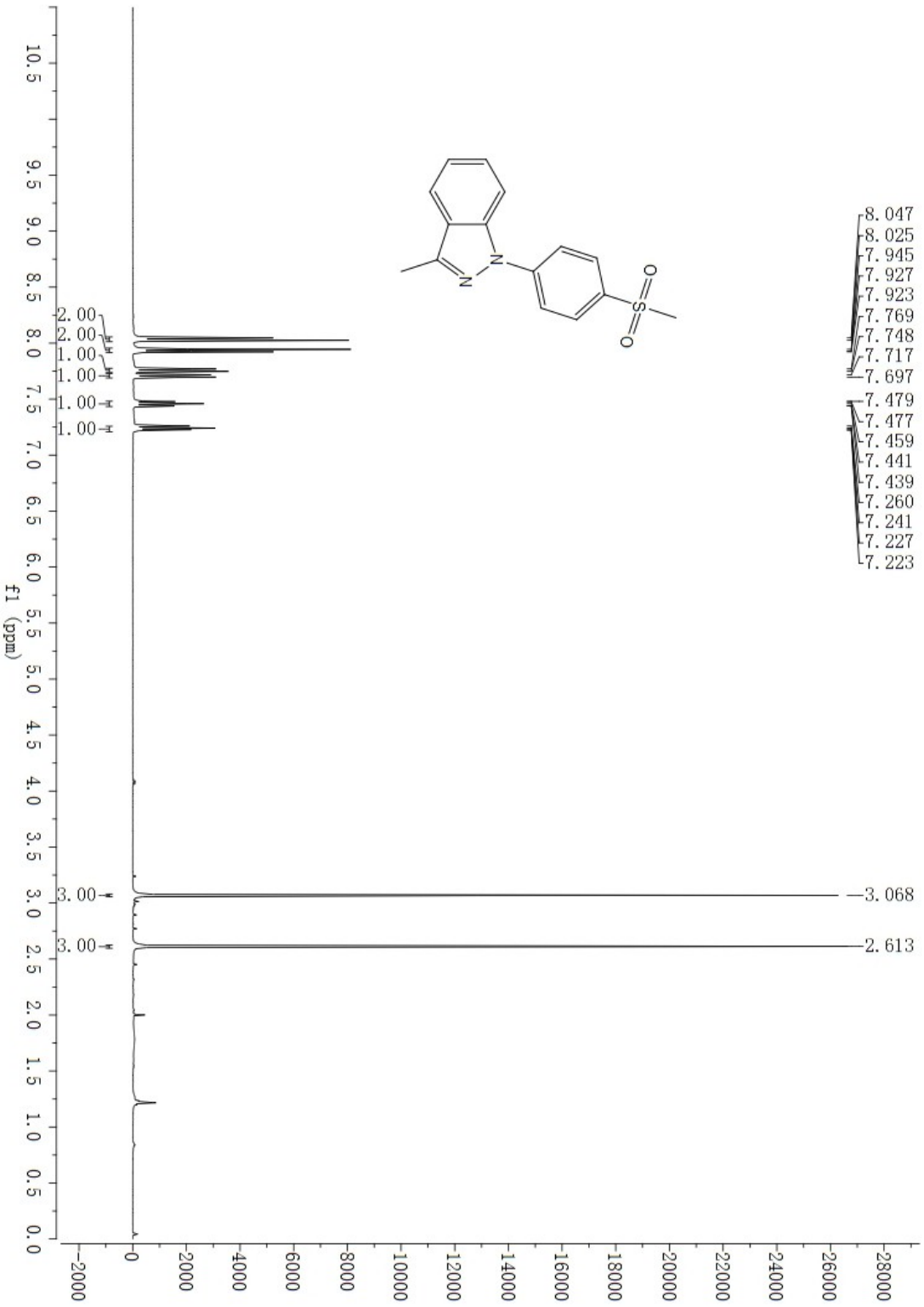
f1 (ppm)

3g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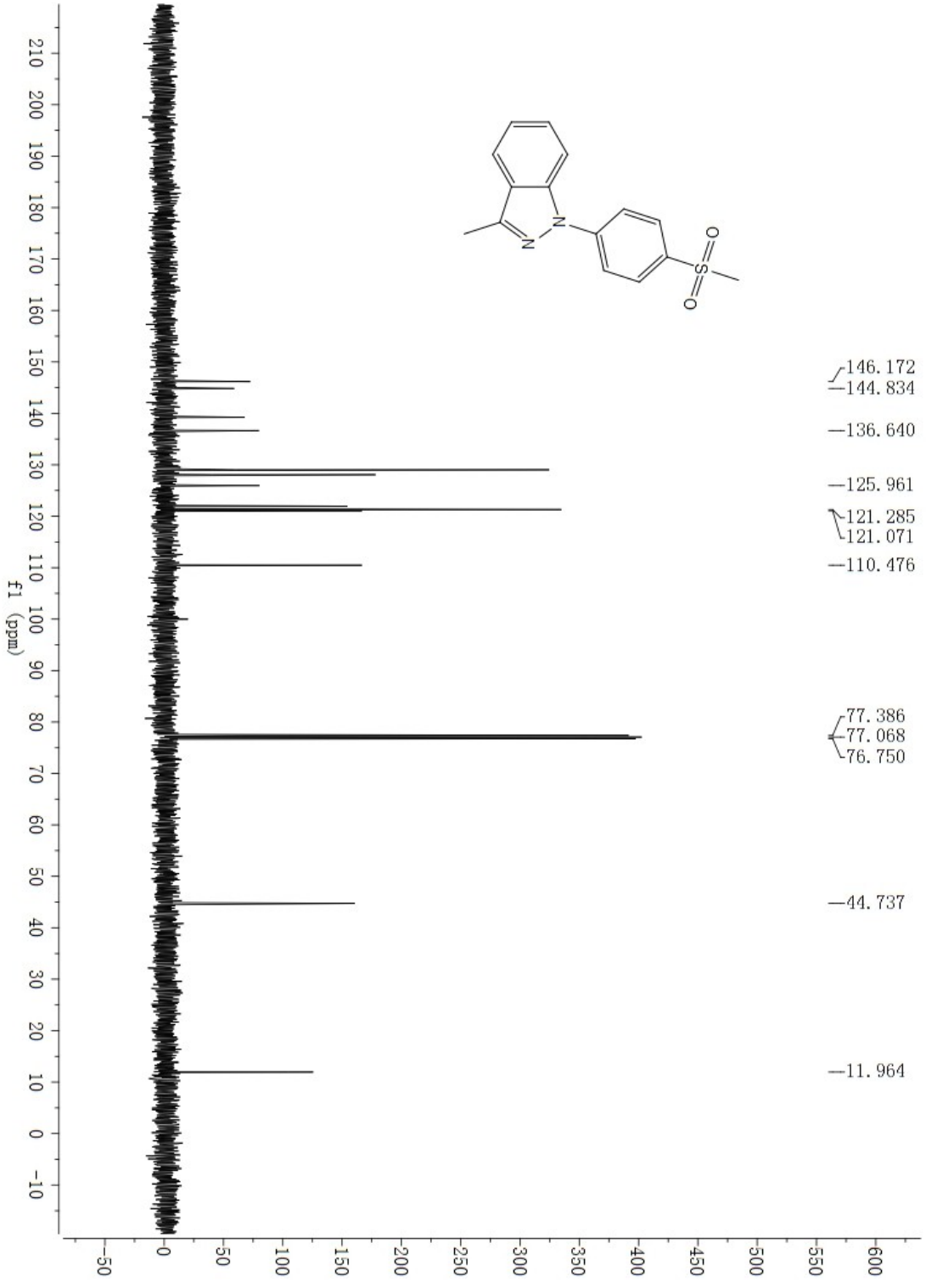
f1 (ppm)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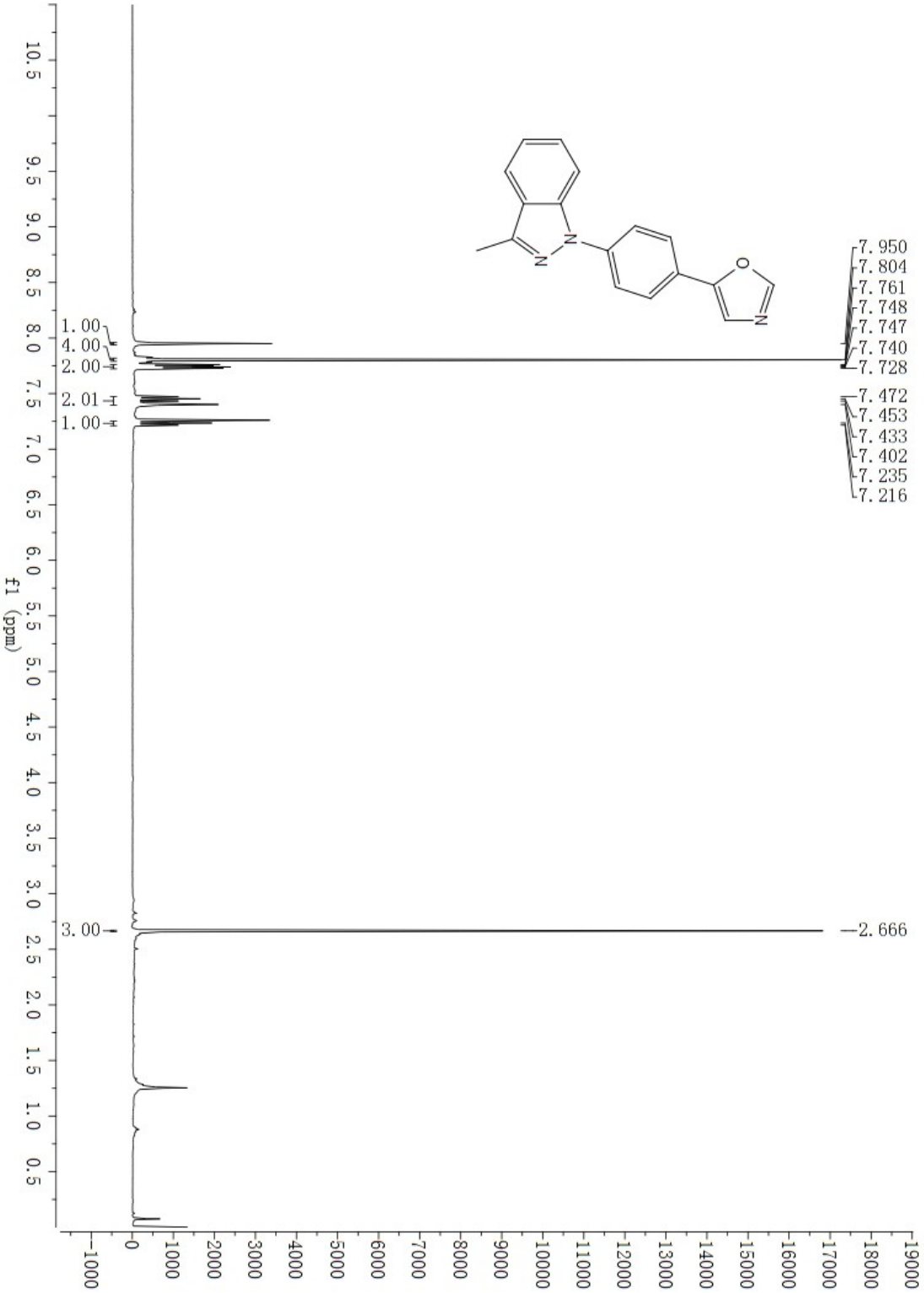
3h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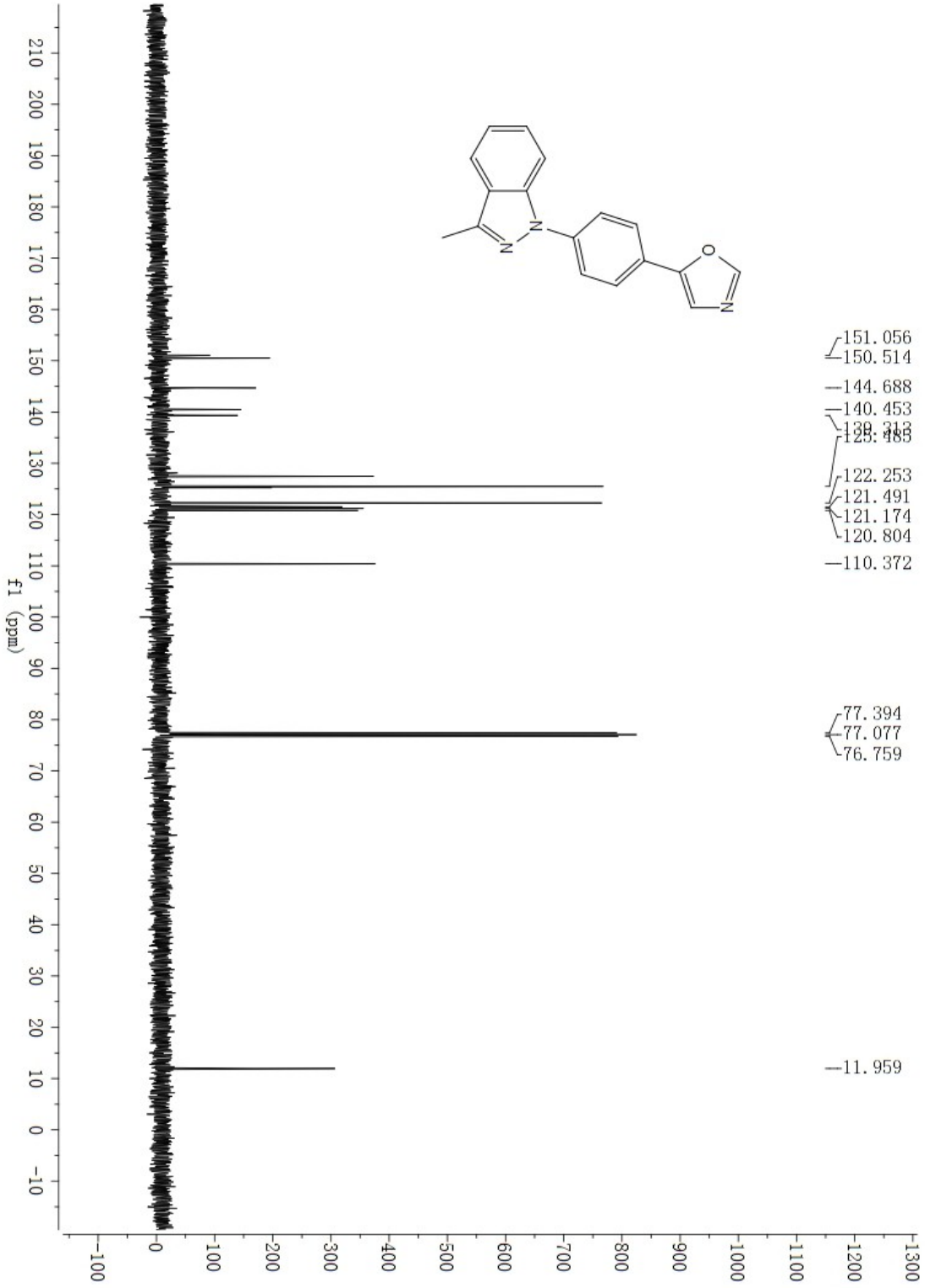
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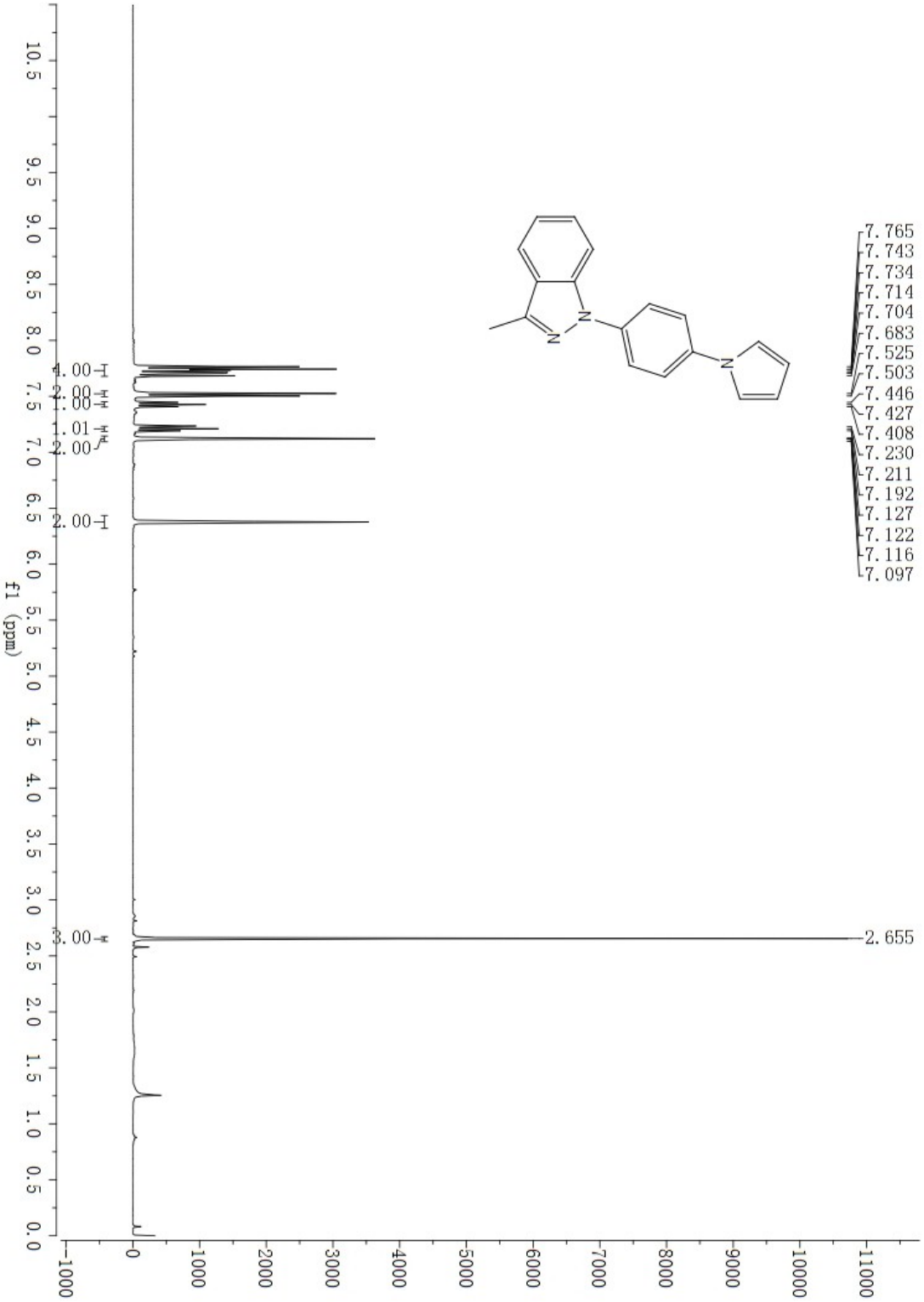
3i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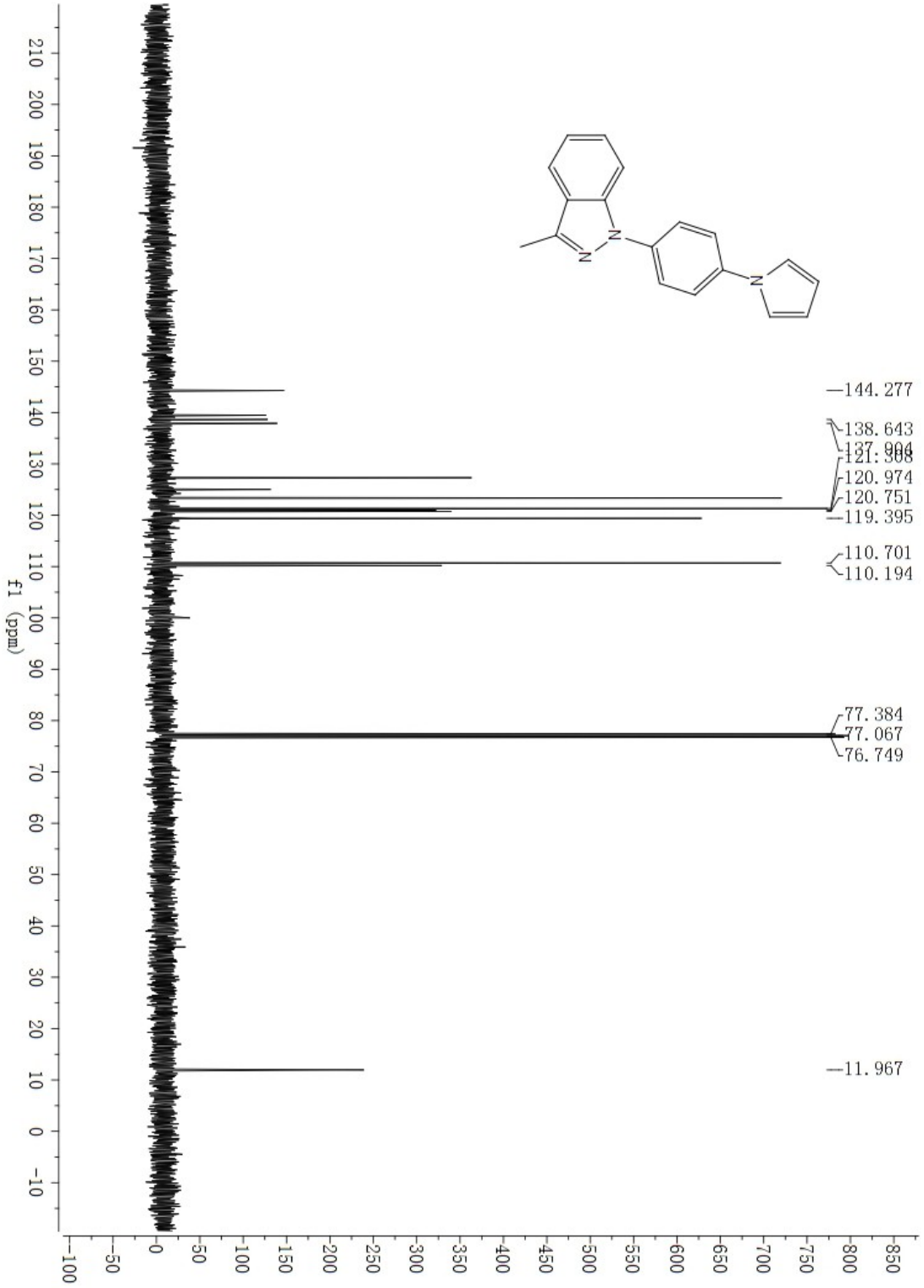
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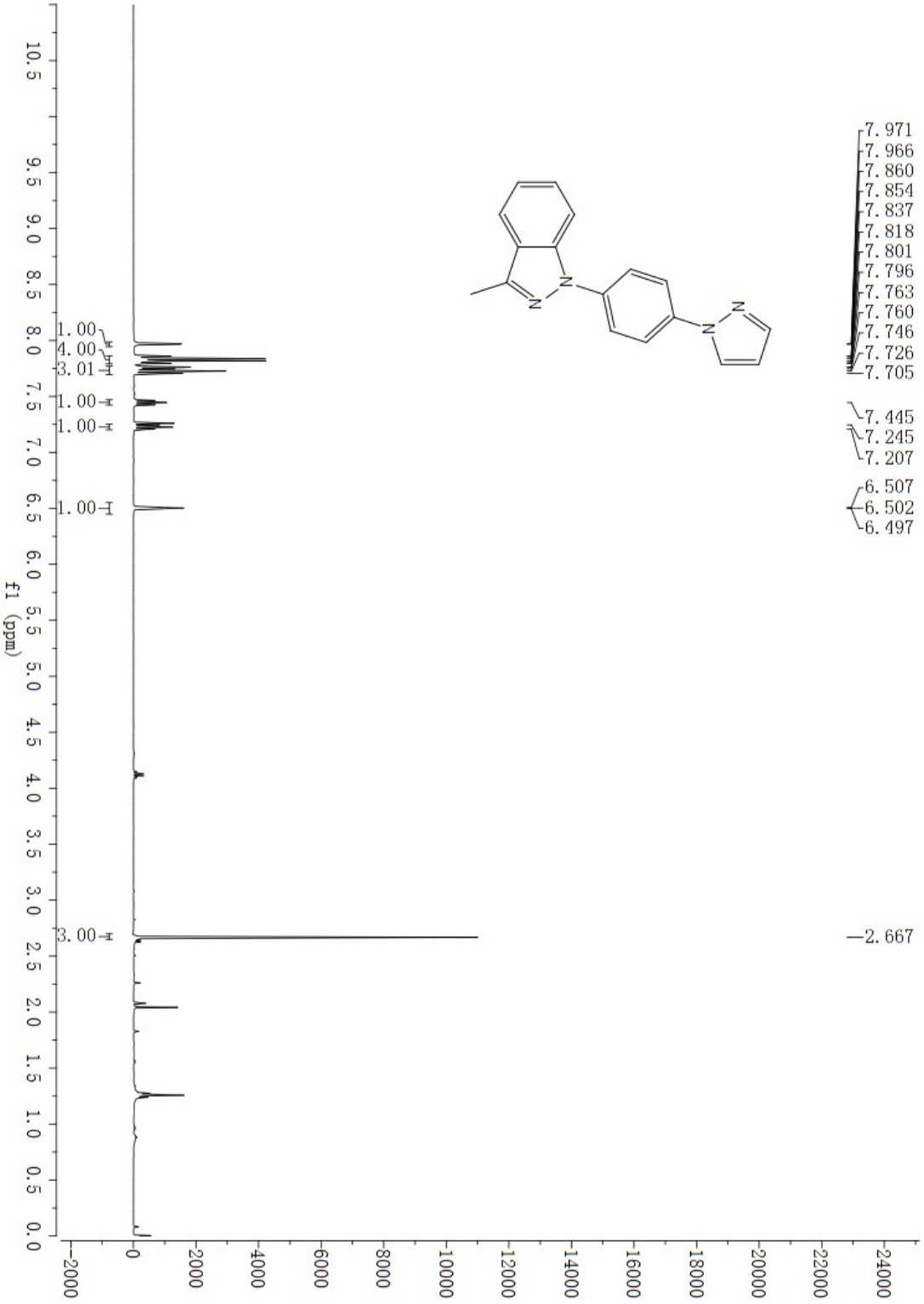
3j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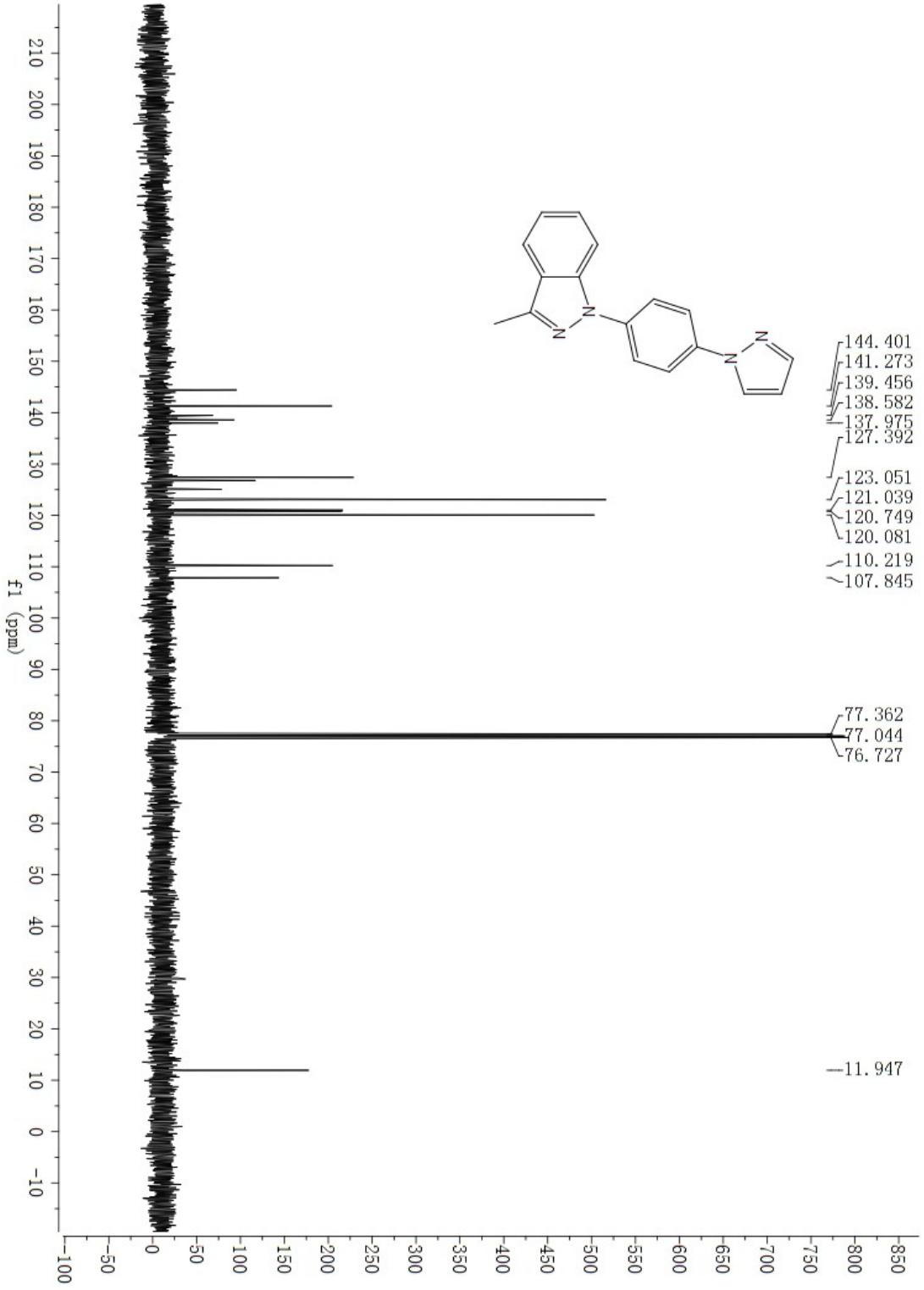
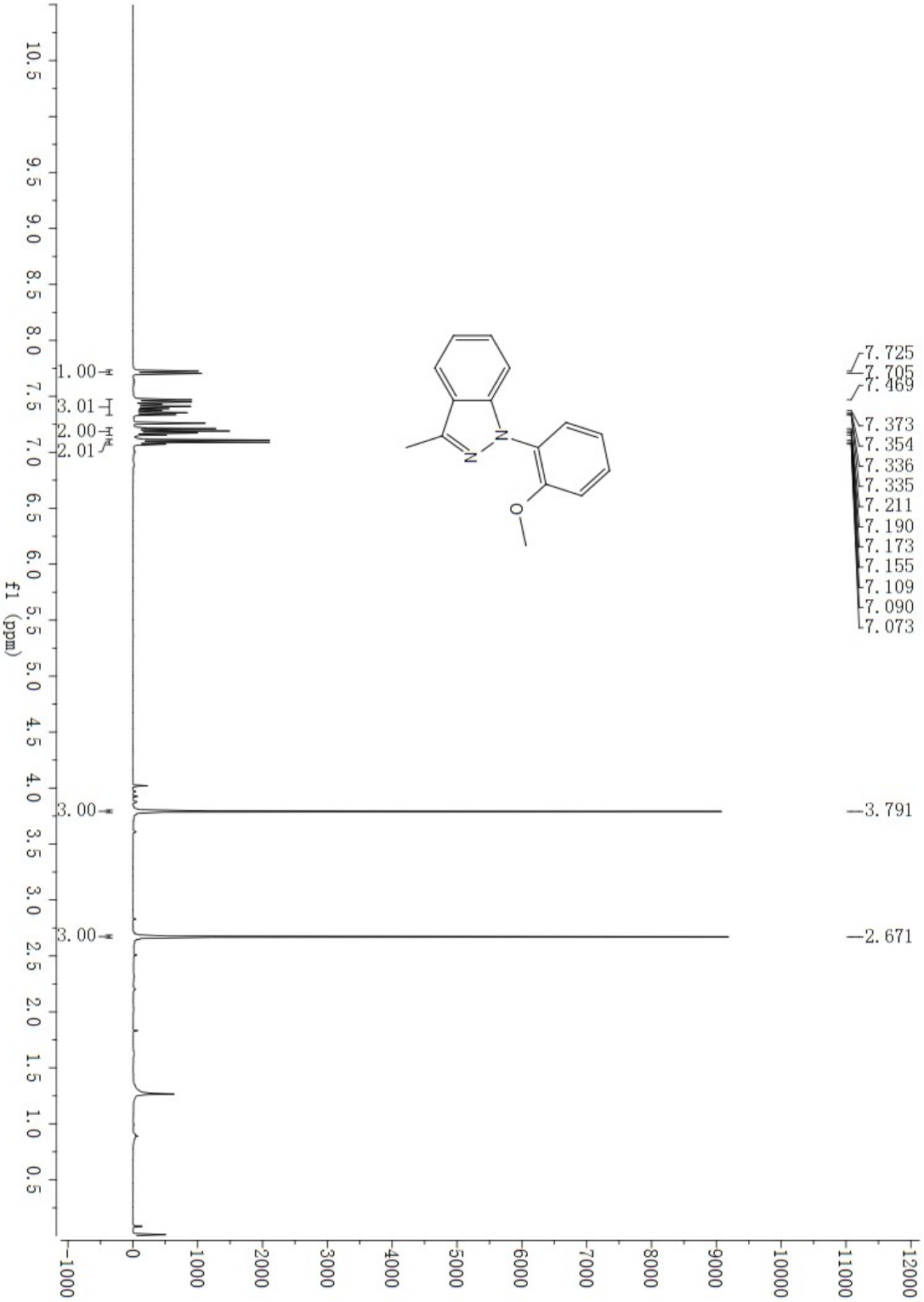
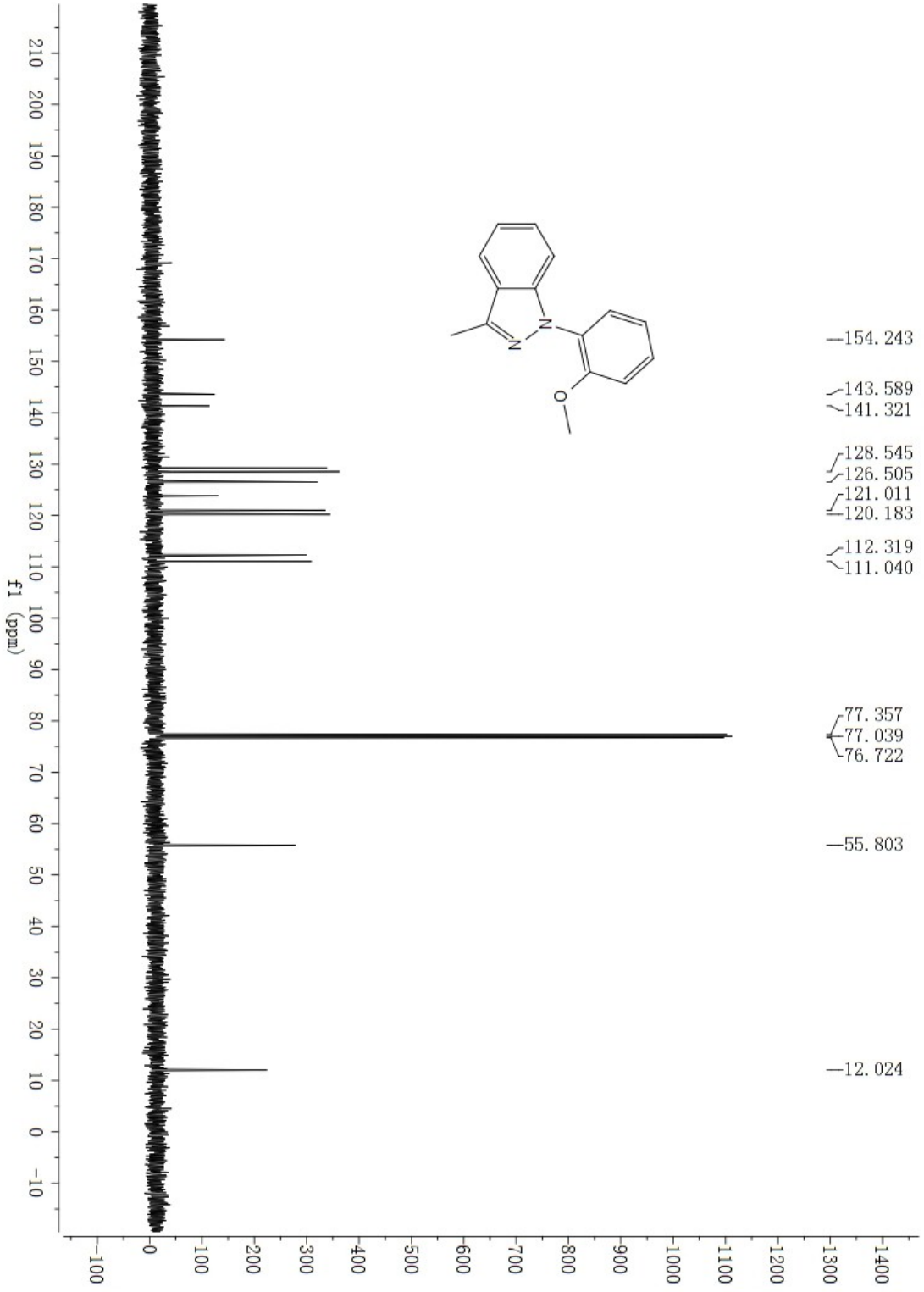
3.00
f1 (ppm)

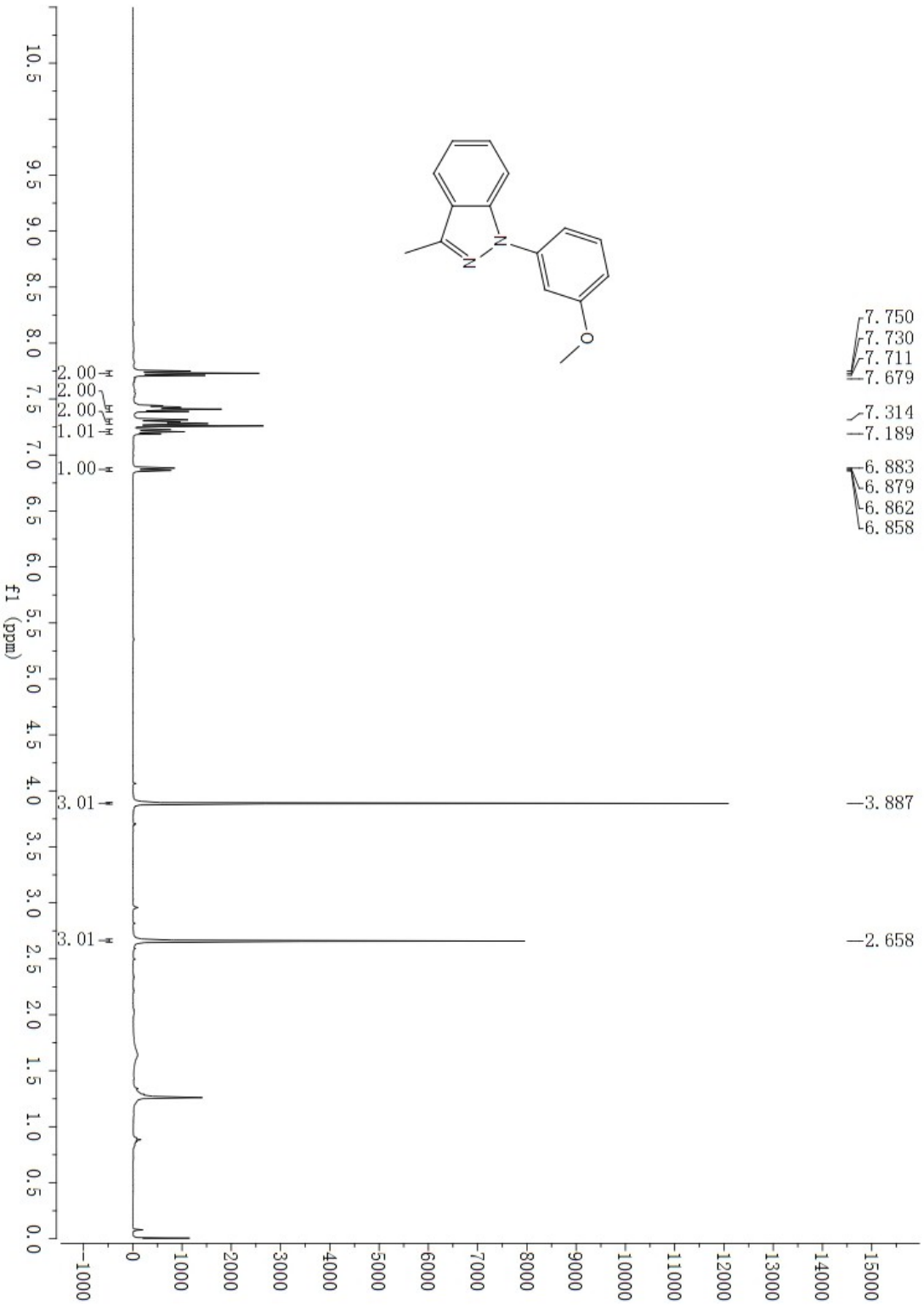

144.401
141.273
139.456
138.582
137.975
127.392
123.051
121.039
120.749
120.081
110.219
107.845
77.362
77.044
76.727
11.947
f1 (ppm)

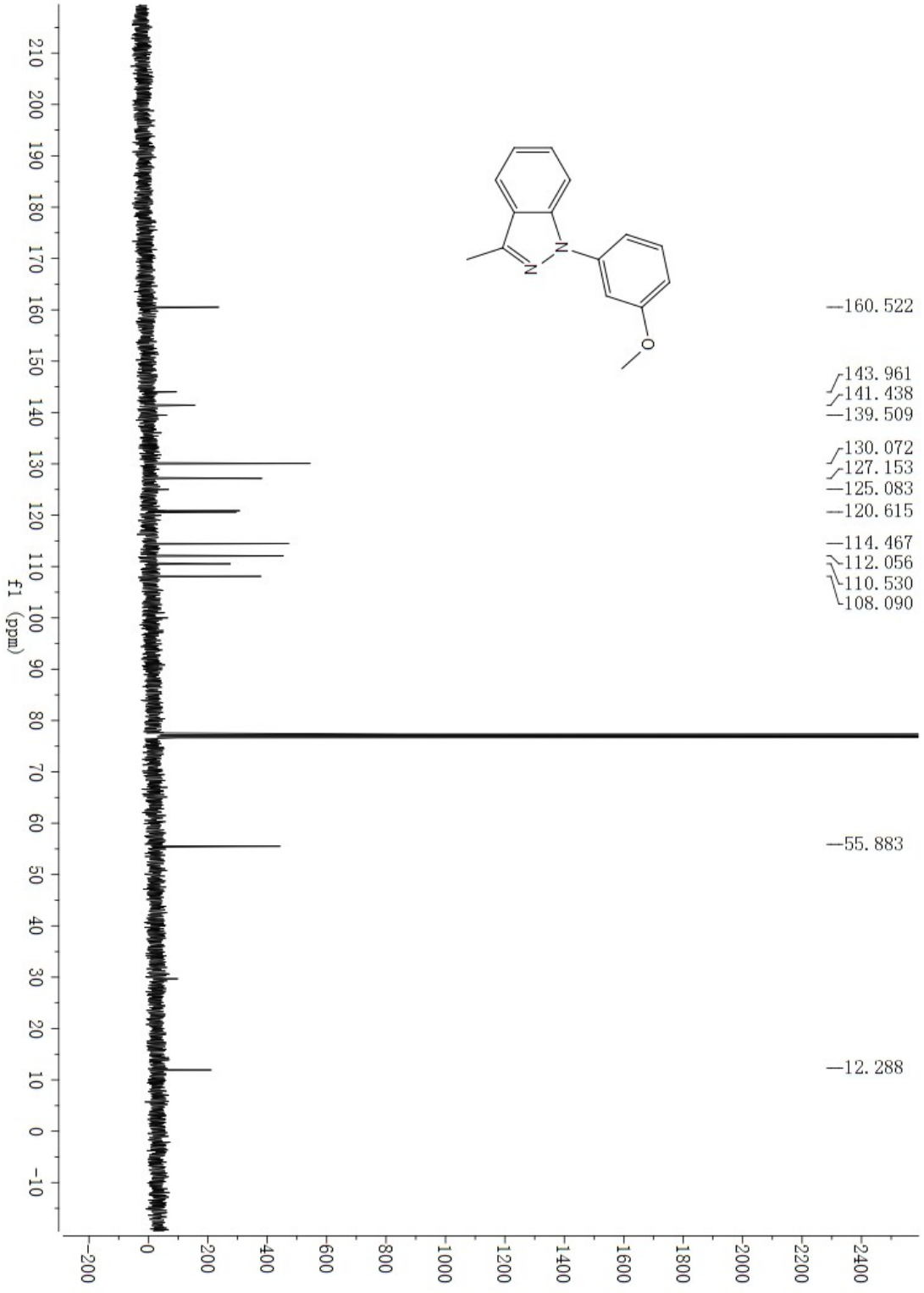
3k


7.725
7.705
7.469
7.373
7.354
7.336
7.335
7.211
7.190
7.173
7.155
7.109
7.090
7.073
3.791
2.671
1.00
3.01
2.00
2.01
3.00
3.00
f1 (ppm)

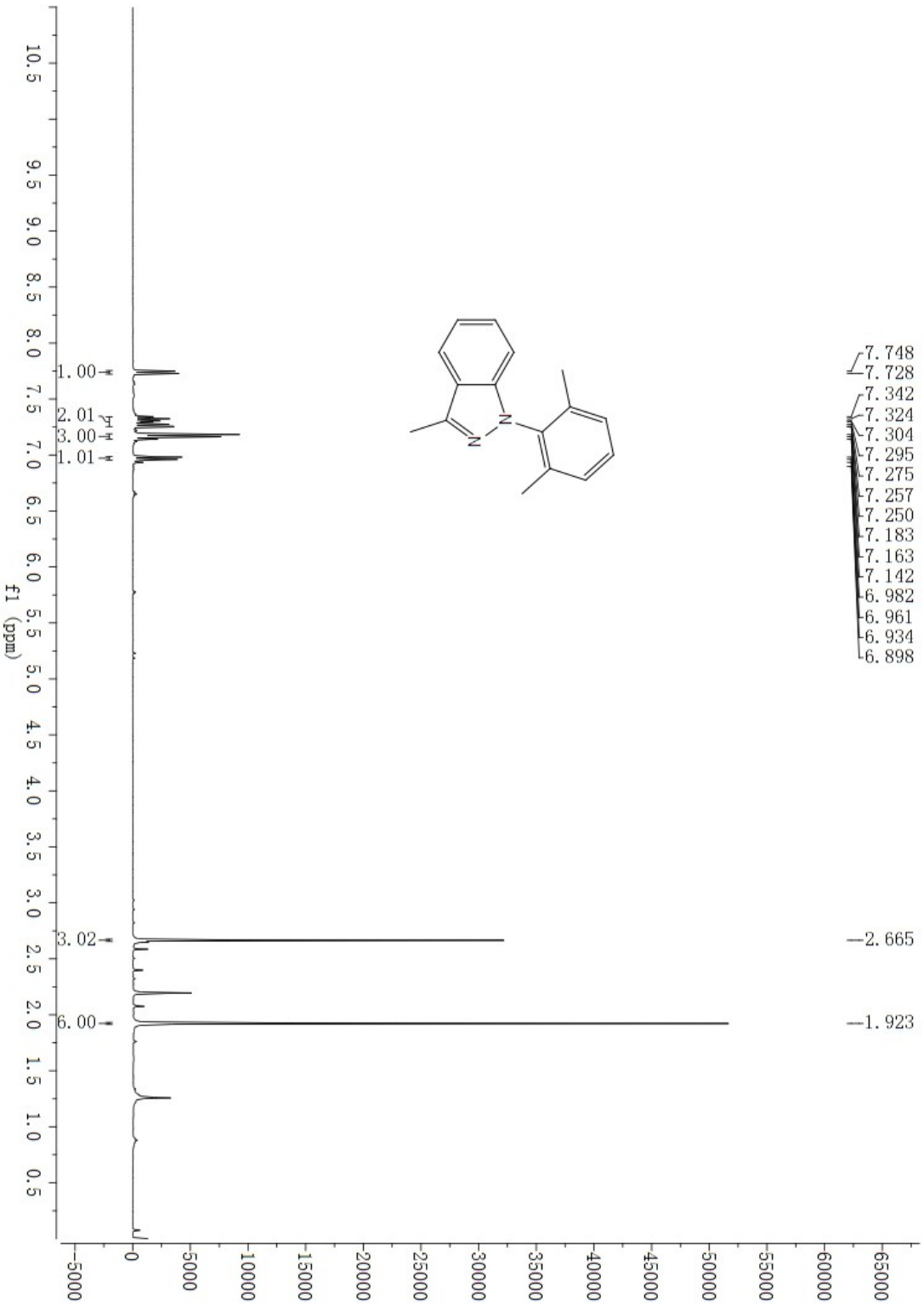

154.243
143.589
141.321
128.545
126.505
121.011
120.183
112.319
111.040
77.357
77.039
76.722
55.803
12.024
f1 (ppm)

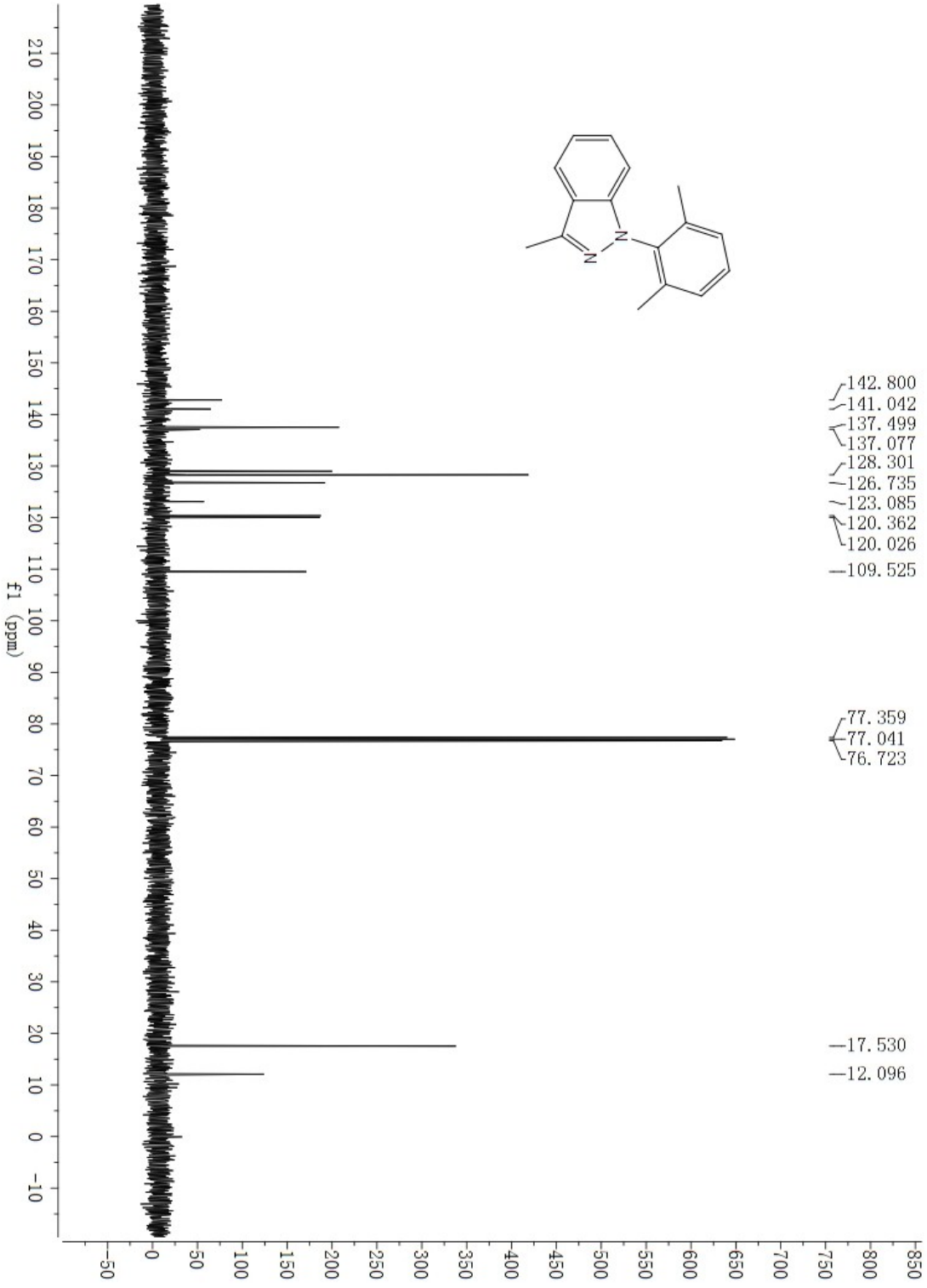
3l


7.750
7.730
7.711
7.679
7.314
7.189
6.883
6.879
6.862
6.858
3.887
2.658
2.00
2.00
2.00
1.01
1.00
3.01
3.01
f1 (ppm)

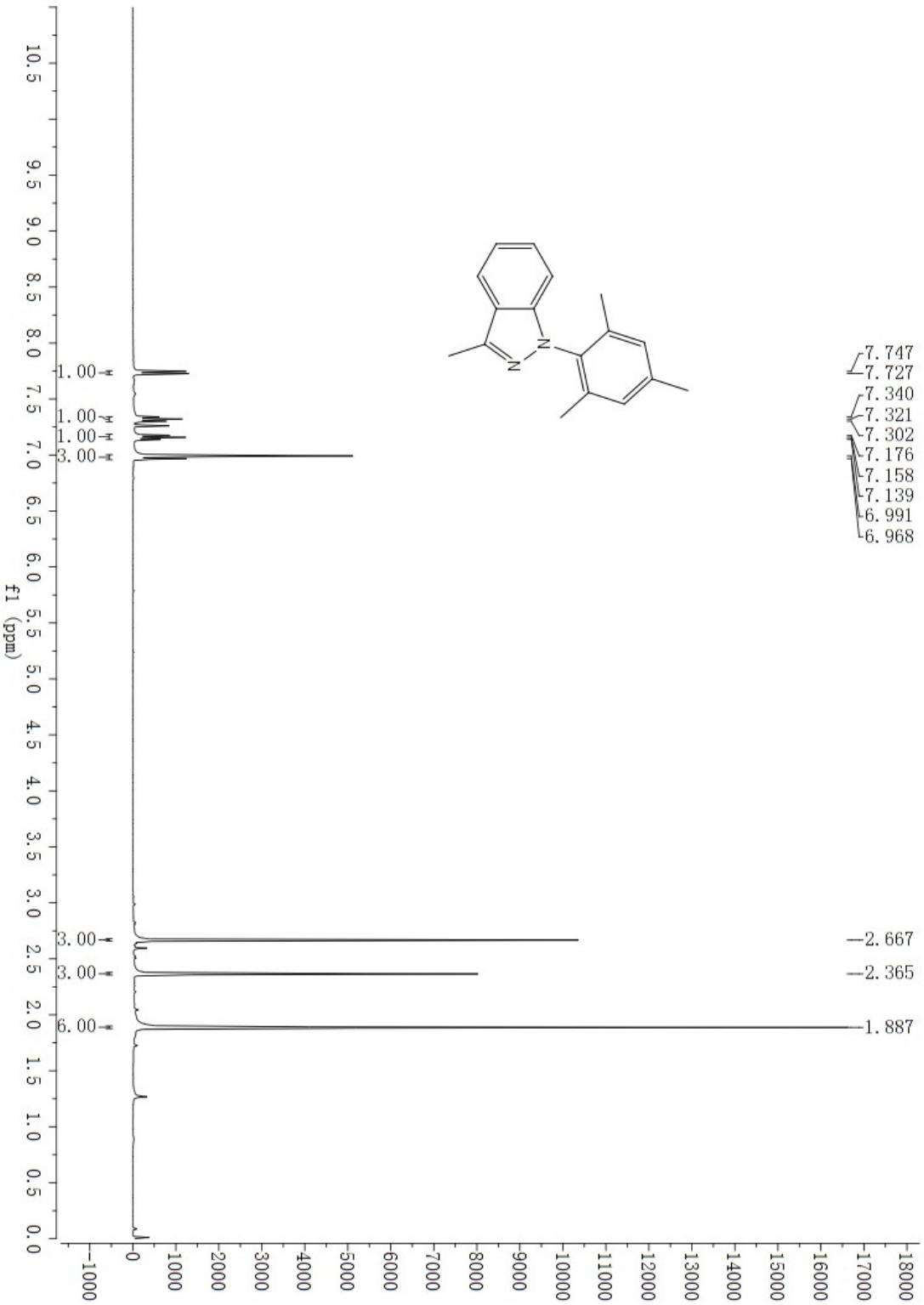

160.522
143.961
141.438
139.509
130.072
127.153
125.083
120.615
114.467
112.056
110.530
108.090
55.883
12.288
f1 (ppm)

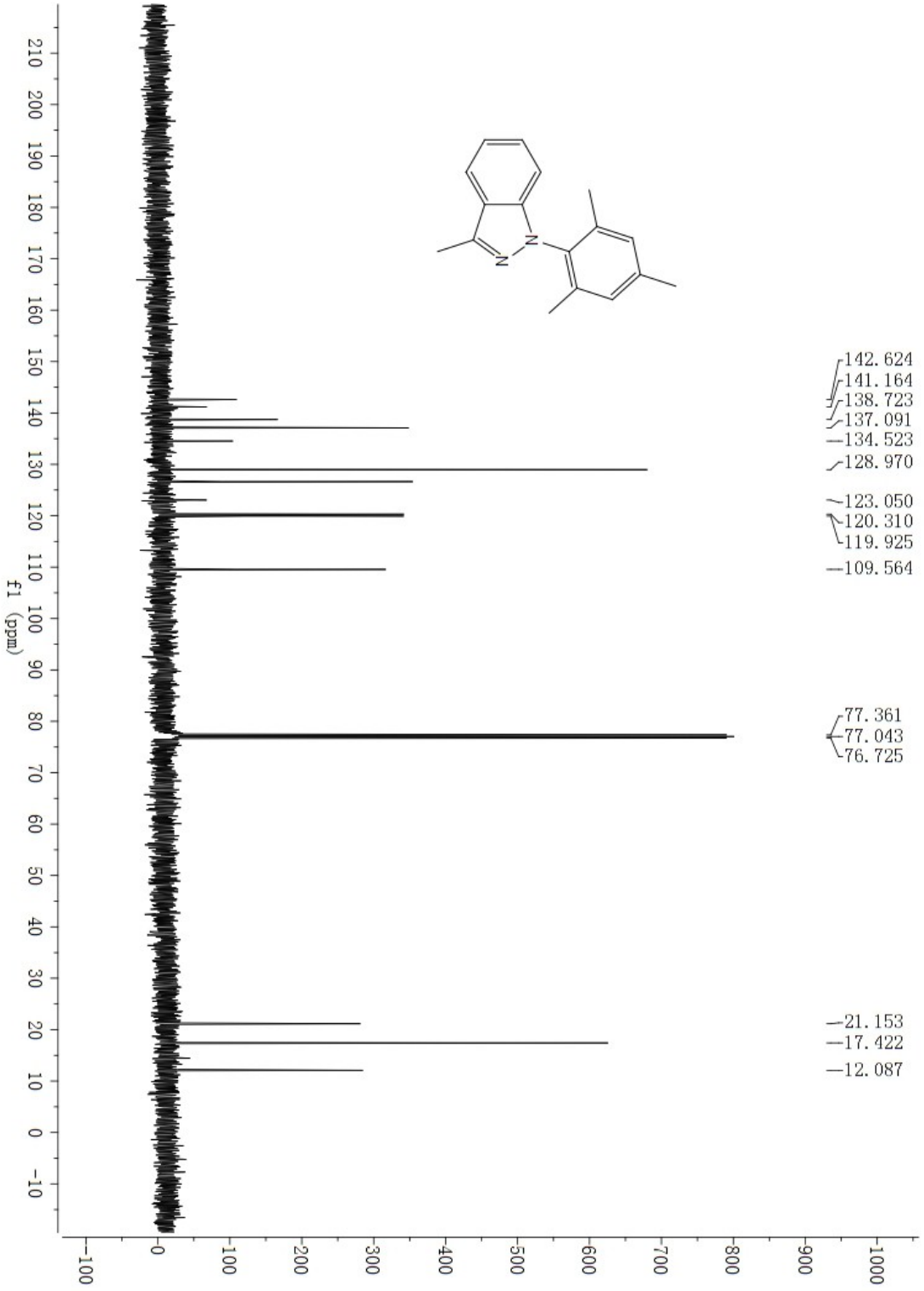
3m


7.748
7.728
7.342
7.324
7.304
7.295
7.275
7.257
7.250
7.183
7.163
7.142
6.982
6.961
6.934
6.898
2.665
1.923
1.00
2.01
3.00
1.01
3.02
6.00
f1 (ppm)

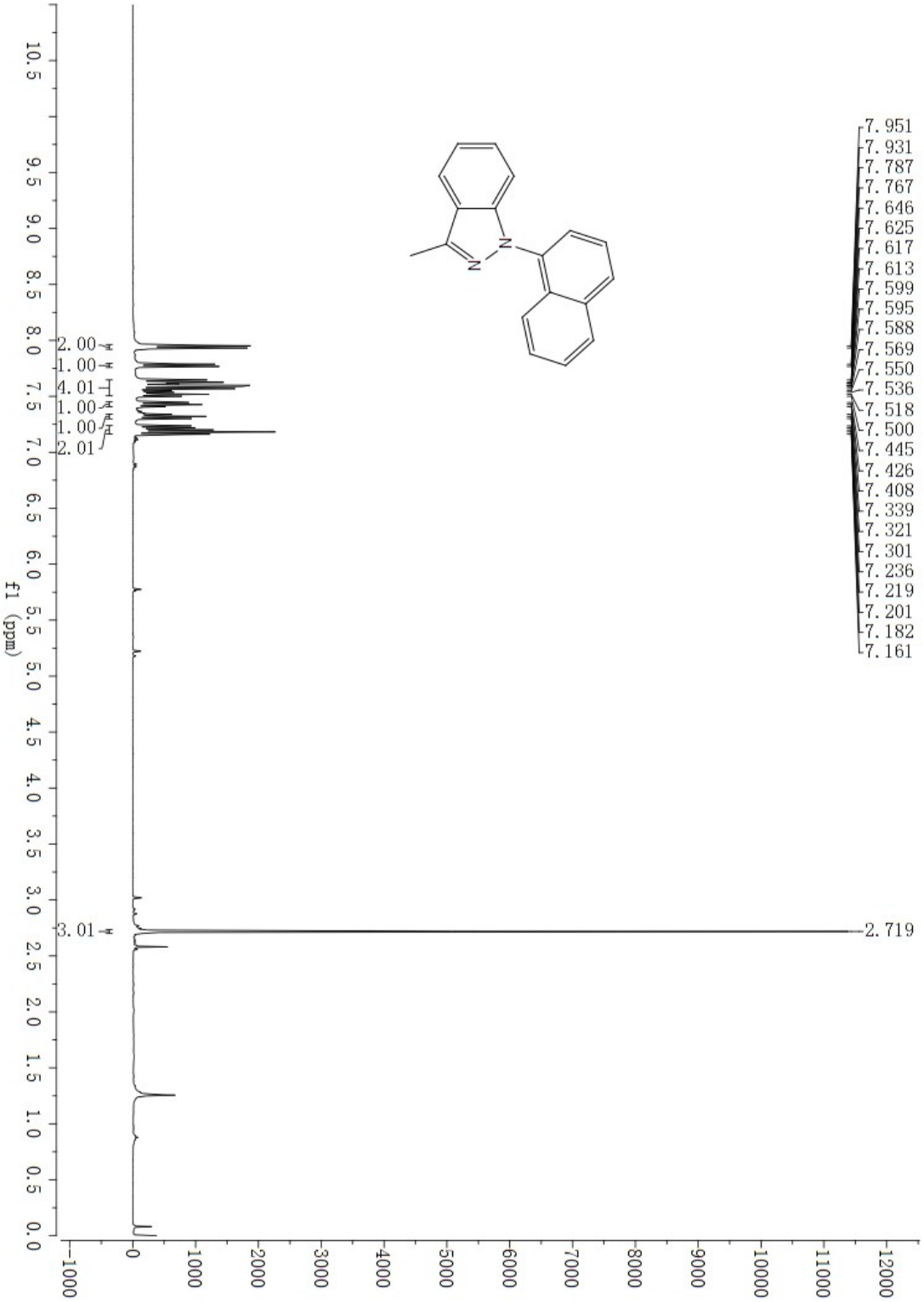

142.800
141.042
137.499
137.077
128.301
126.735
123.085
120.362
120.026
109.525
77.359
77.041
76.723
17.530
12.096
f1 (ppm)

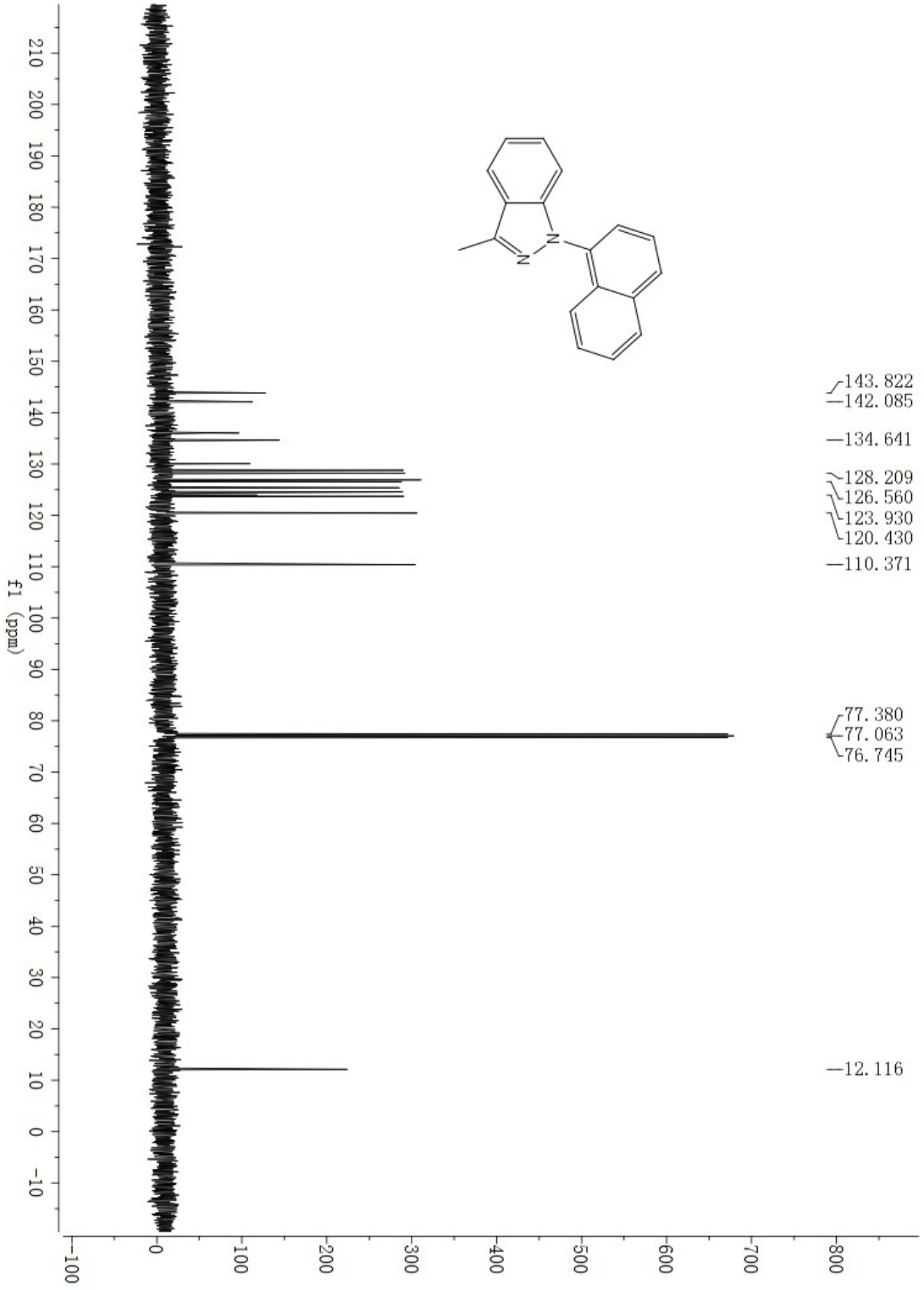
3n


7.747
7.727
7.340
7.321
7.302
7.176
7.158
7.139
6.991
6.968
2.667
2.365
1.887
1.00
1.00
1.00
3.00
3.00
3.00
6.00
f1 (ppm)

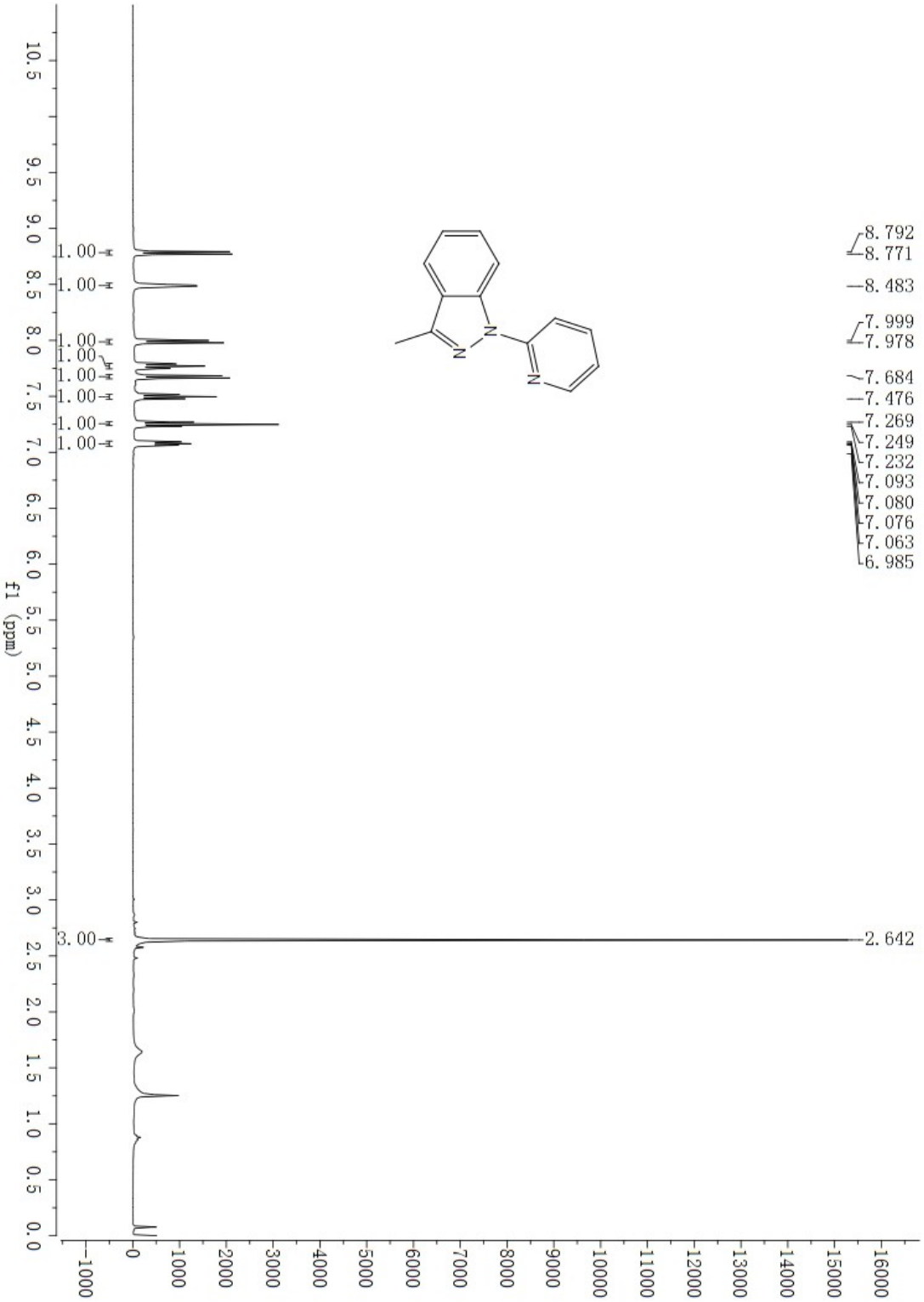

142.624
141.164
138.723
137.091
134.523
128.970
123.050
120.310
119.925
109.564
77.361
77.043
76.725
21.153
17.422
12.087
f1 (ppm)

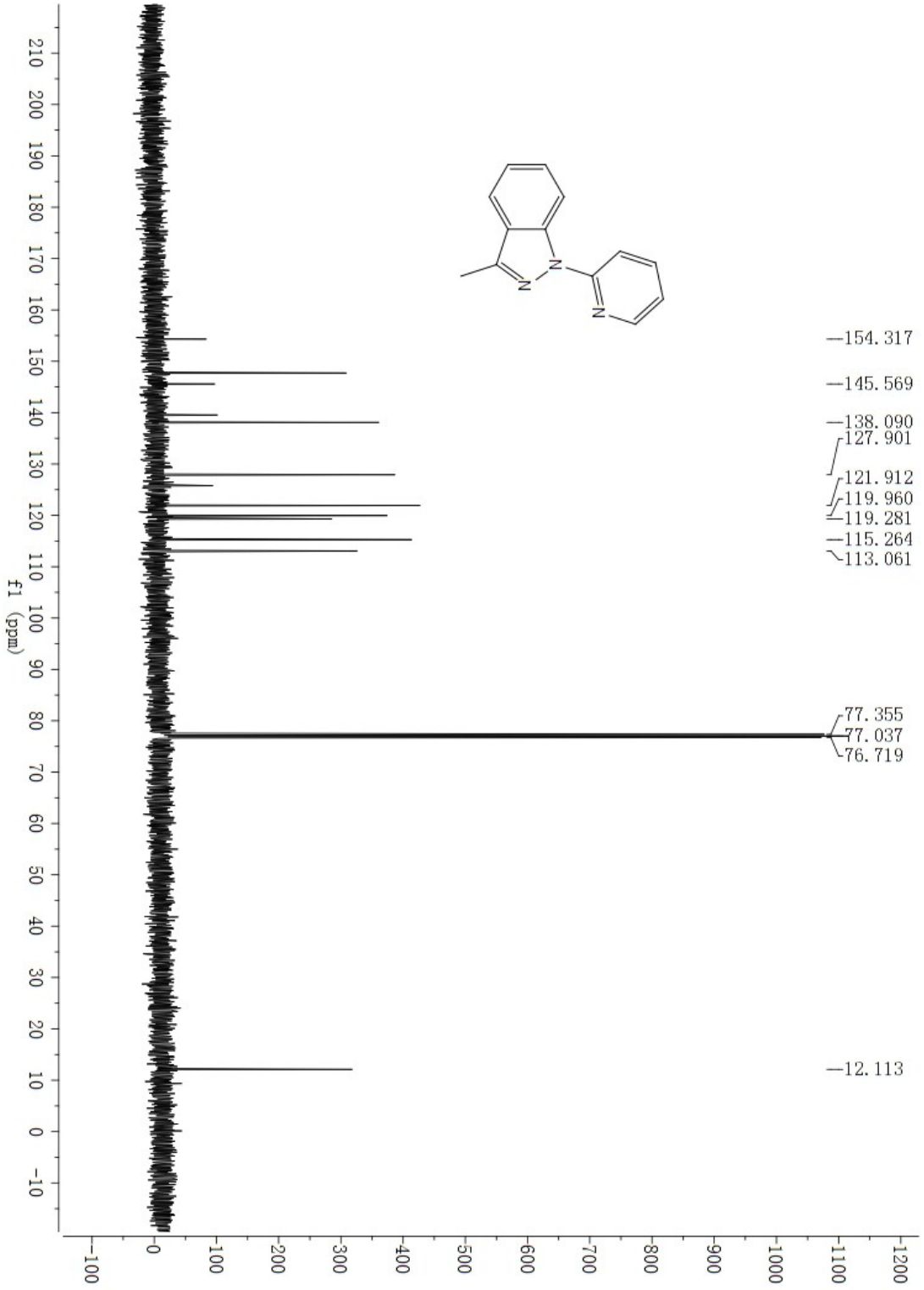
3o


7.951
7.931
7.787
7.767
7.646
7.625
7.617
7.613
7.599
7.595
7.588
7.569
7.550
7.536
7.518
7.500
7.445
7.426
7.408
7.339
7.321
7.301
7.236
7.219
7.201
7.182
7.161
2.719
2.00
1.00
4.01
1.00
1.00
2.01
3.01
f1 (ppm)

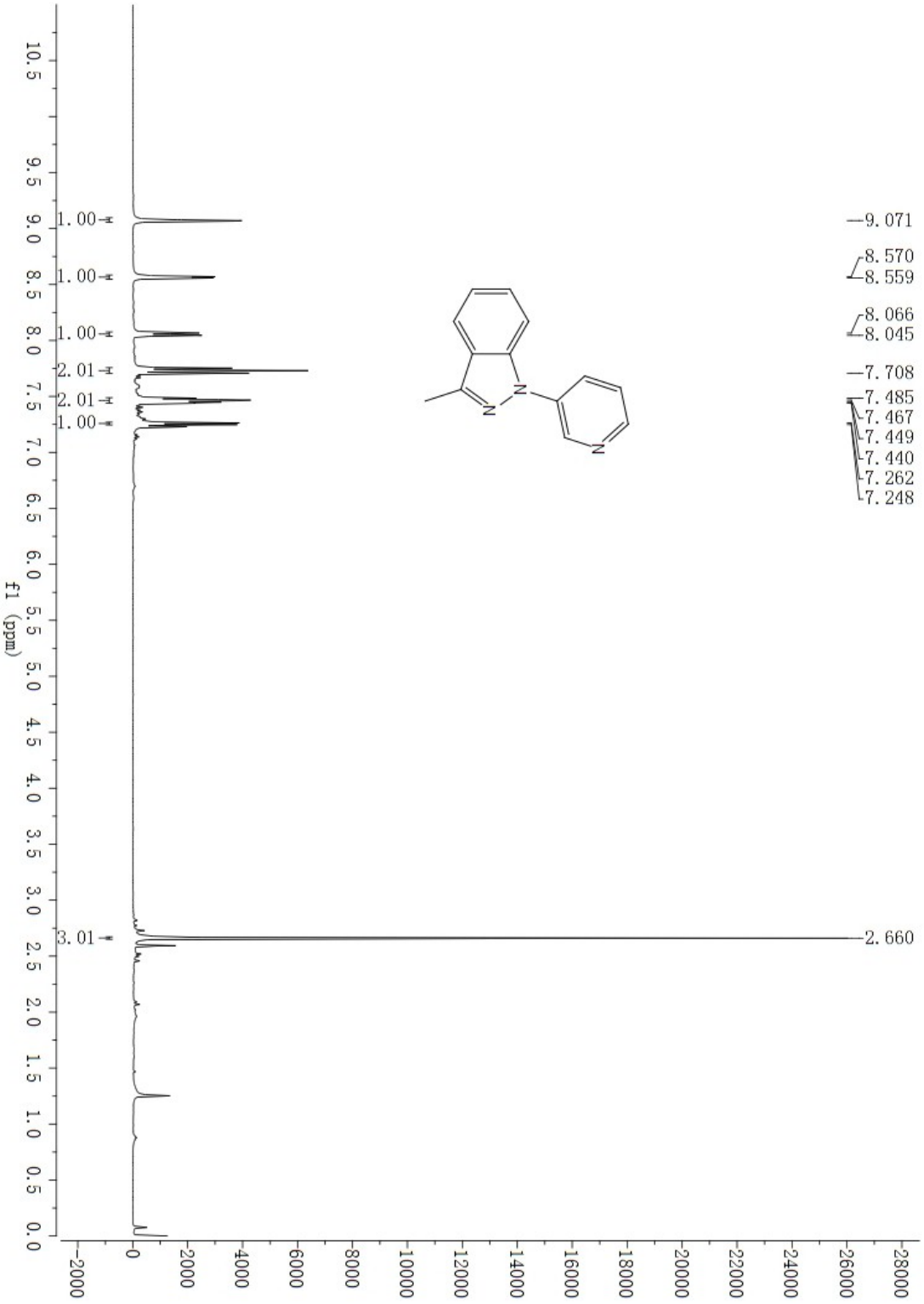

143.822
142.085
134.641
128.209
126.560
123.930
120.430
110.371
77.380
77.063
76.745
12.116
f1 (ppm)

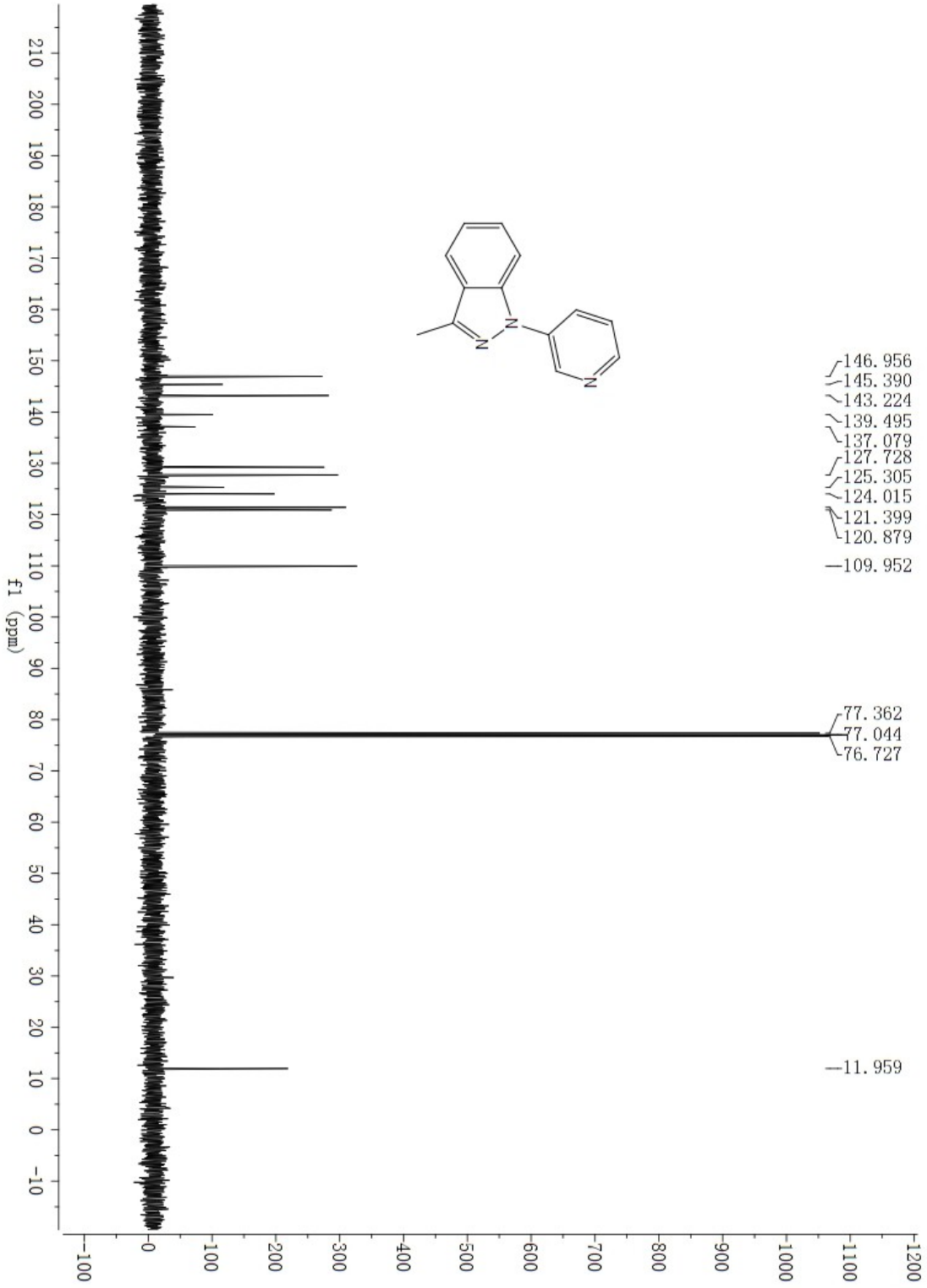
3p


8.792
8.771
8.483
7.999
7.978
7.684
7.476
7.269
7.249
7.232
7.093
7.080
7.076
7.063
6.985
2.642
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

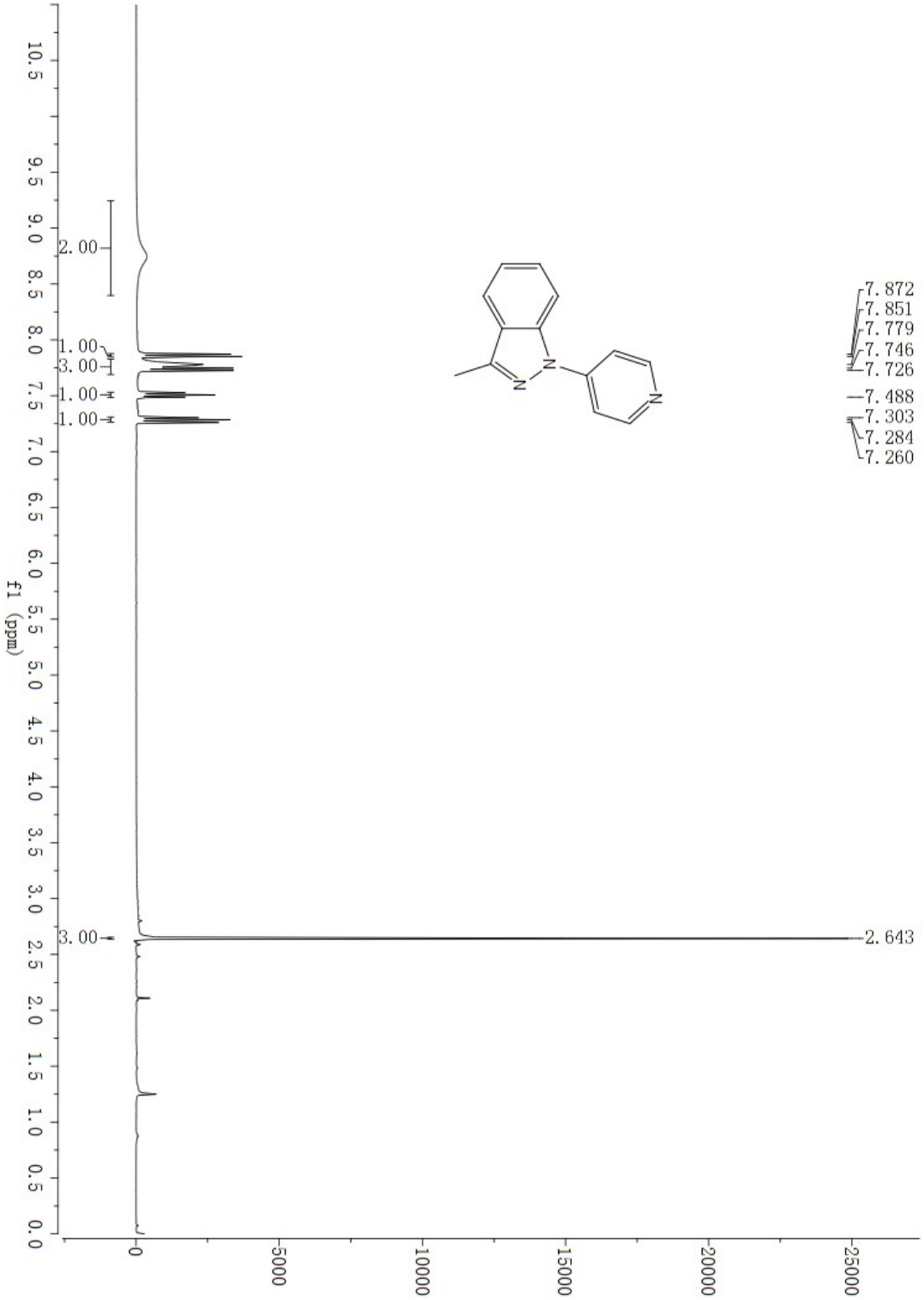

154.317
145.569
138.090
127.901
121.912
119.960
119.281
115.264
113.061
77.355
77.037
76.719
12.113
f1 (ppm)

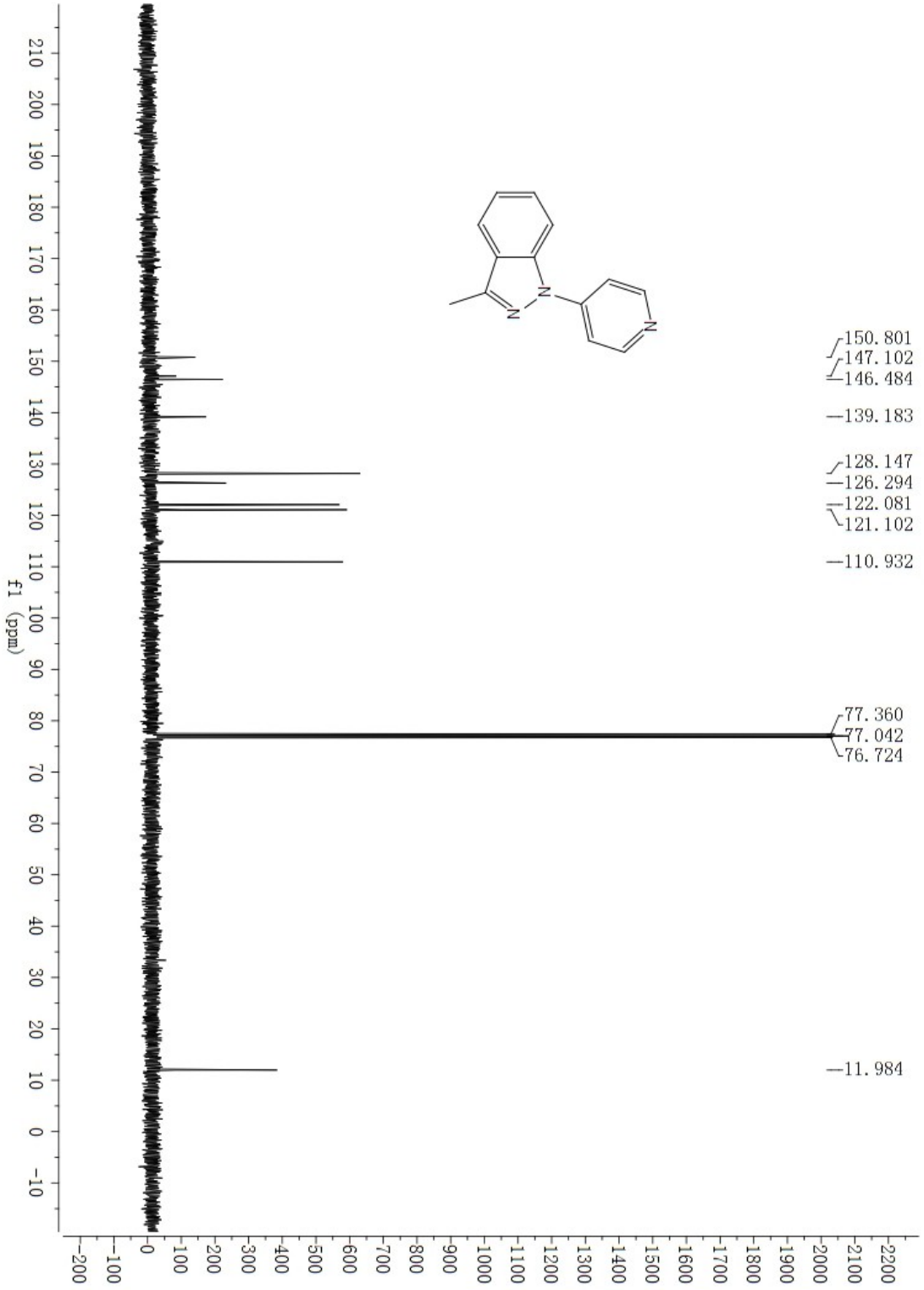
3q


9.071
8.570
8.559
8.066
8.045
7.708
7.485
7.467
7.449
7.440
7.262
7.248
2.660
1.00
1.00
1.00
2.01
2.01
1.00
3.01
f1 (ppm)

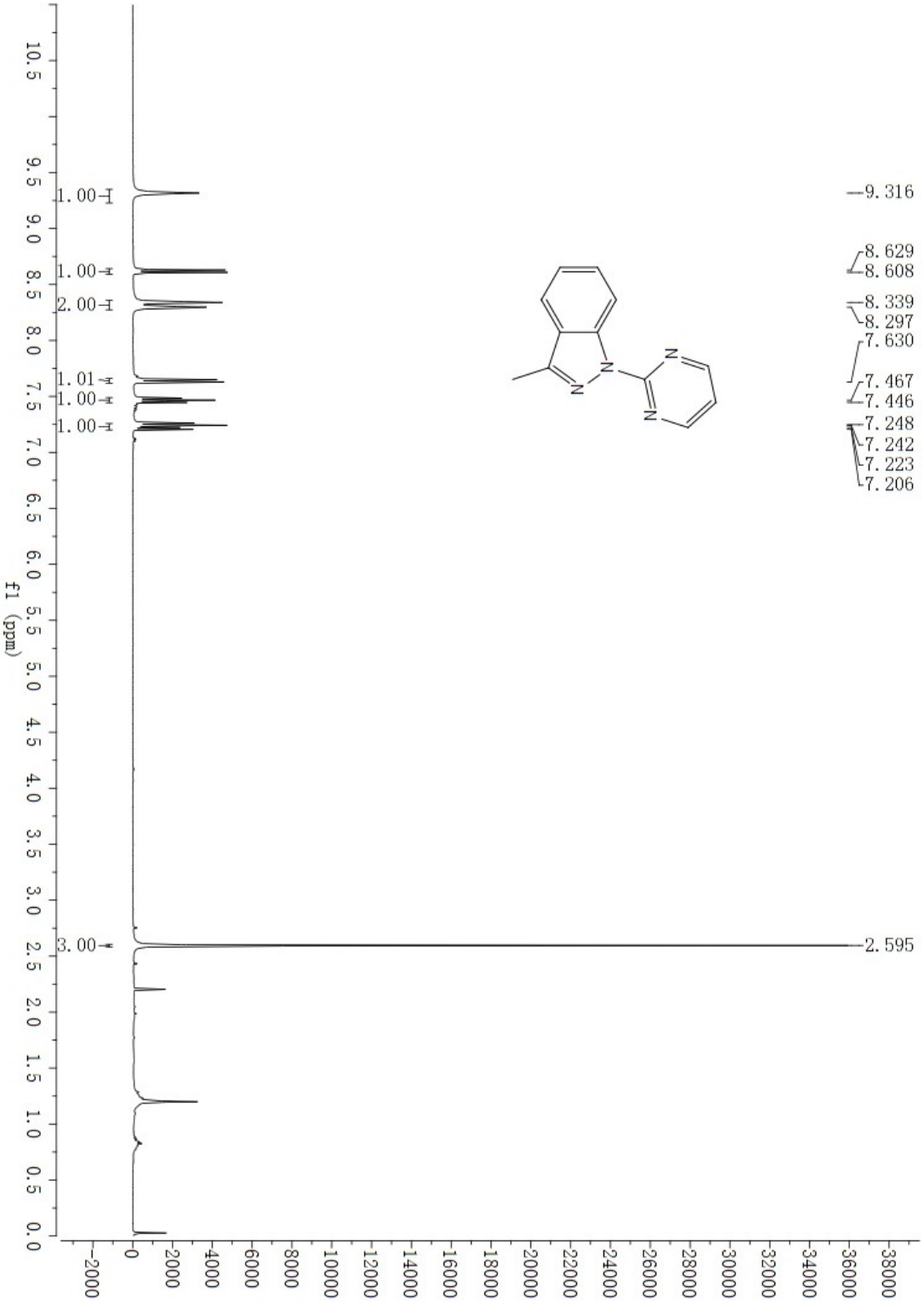

146.956
145.390
143.224
139.495
137.079
127.728
125.305
124.015
121.399
120.879
109.952
77.362
77.044
76.727
11.959
f1 (ppm)

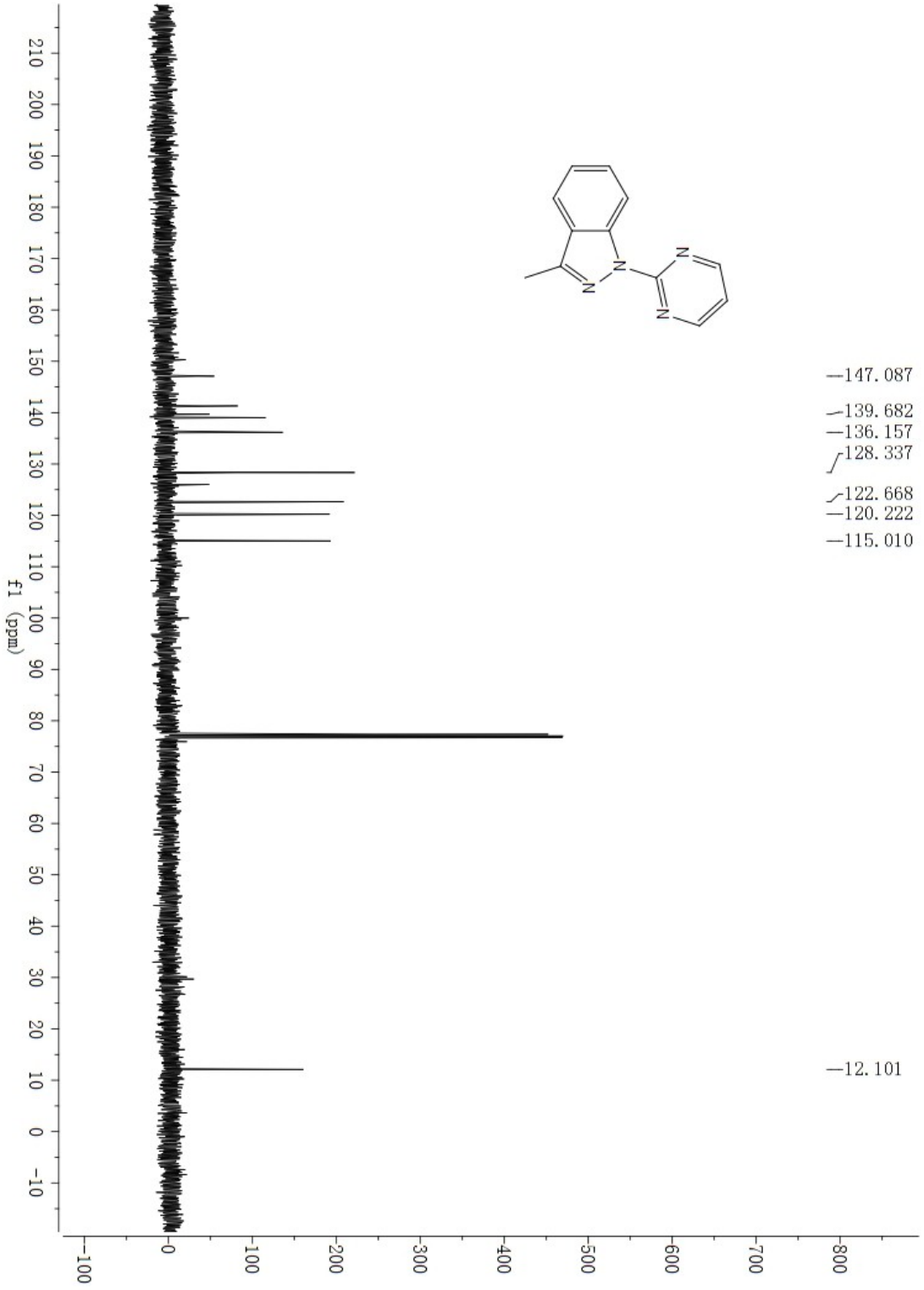
3r


7.872
7.851
7.779
7.746
7.726
7.488
7.303
7.284
7.260
2.643
2.00
1.00
3.00
1.00
1.00
3.00
f1 (ppm)

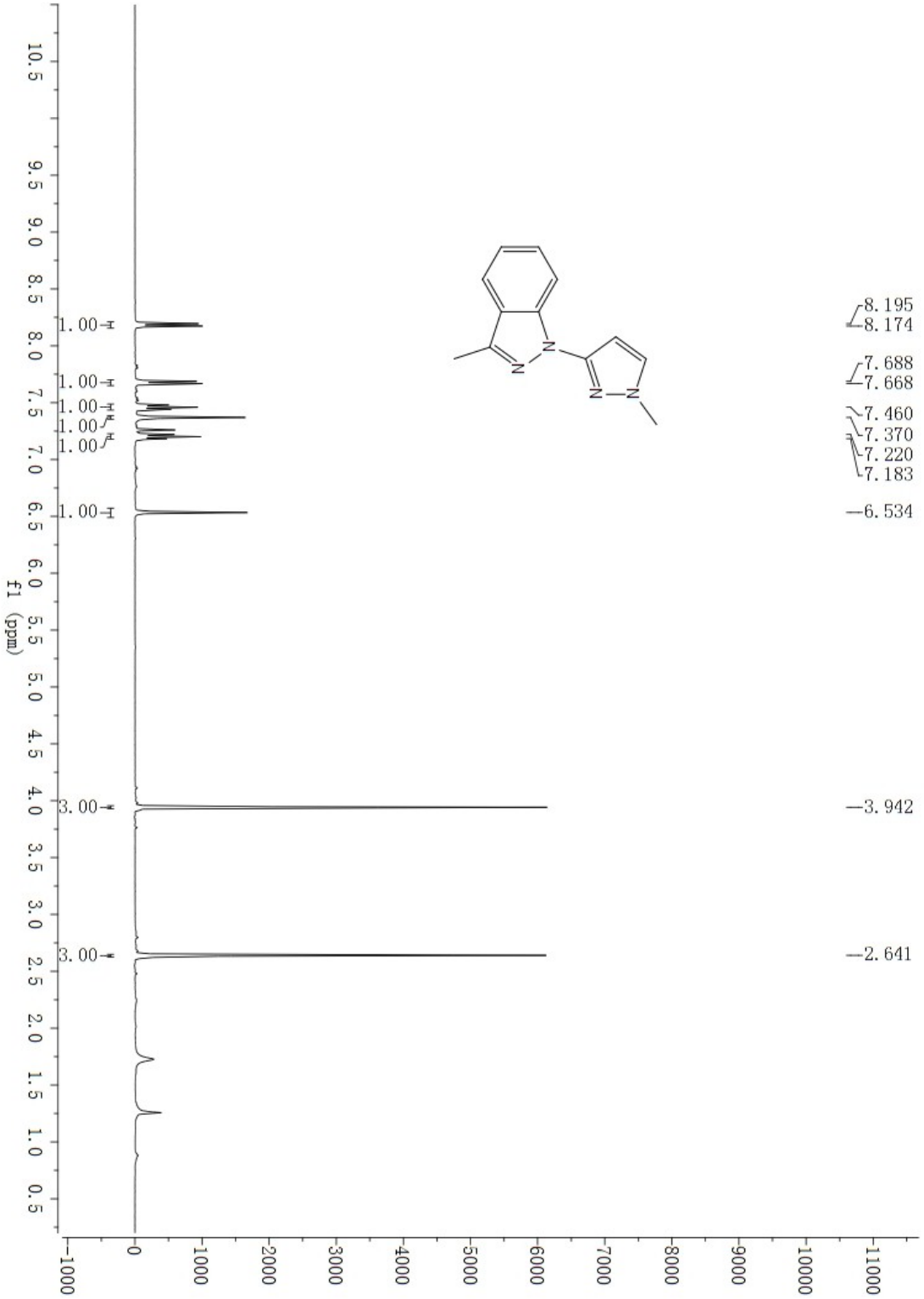

150.801
147.102
146.484
139.183
128.147
126.294
122.081
121.102
110.932
77.360
77.042
76.724
11.984
f1 (ppm)

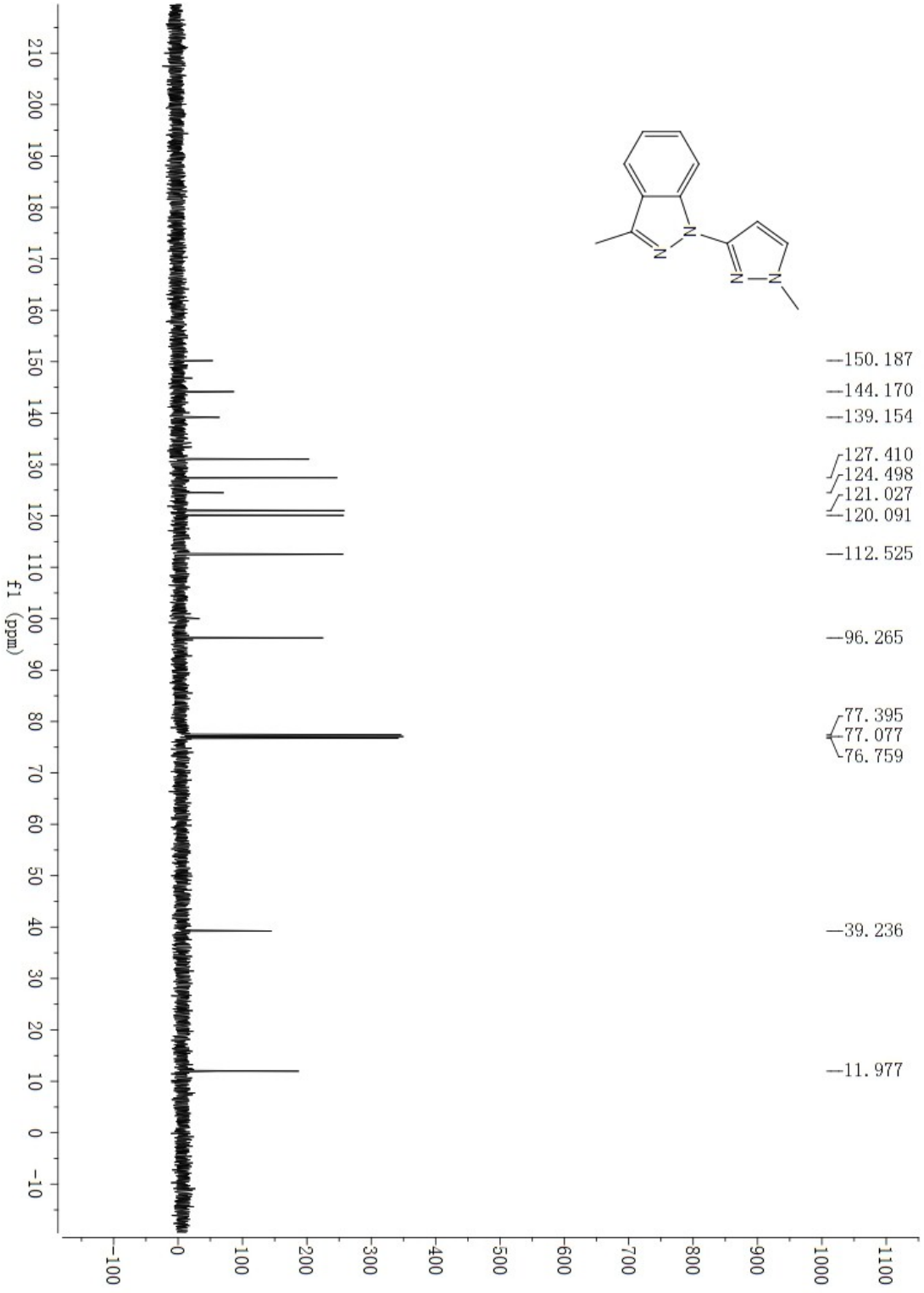
3s


9.316
8.629
8.608
8.339
8.297
7.630
7.467
7.446
7.248
7.242
7.223
7.206
2.595
1.00
1.00
2.00
1.01
1.00
1.00
3.00
f1 (ppm)

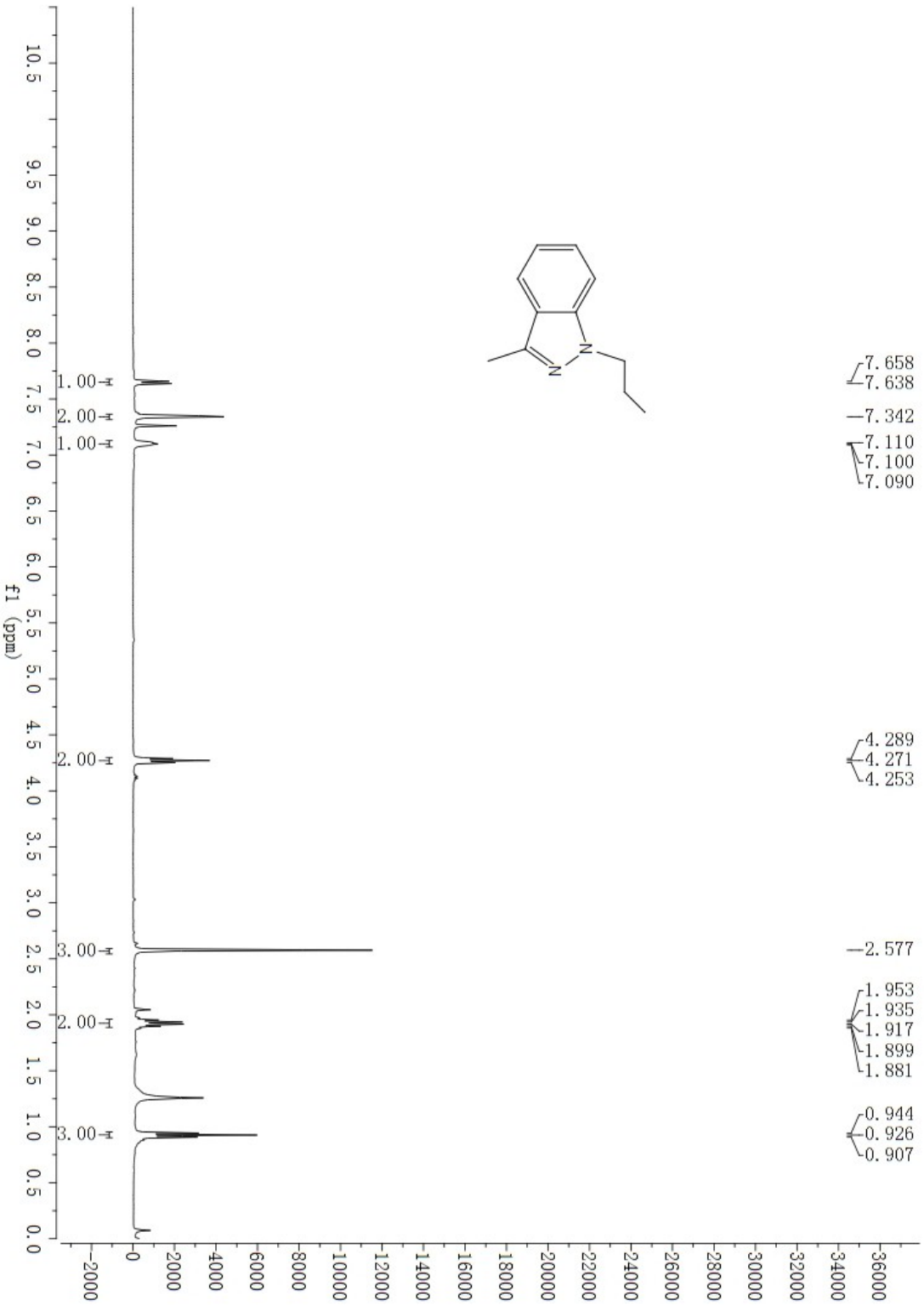

147.087
139.682
136.157
128.337
122.668
120.222
115.010
12.101
f1 (ppm)

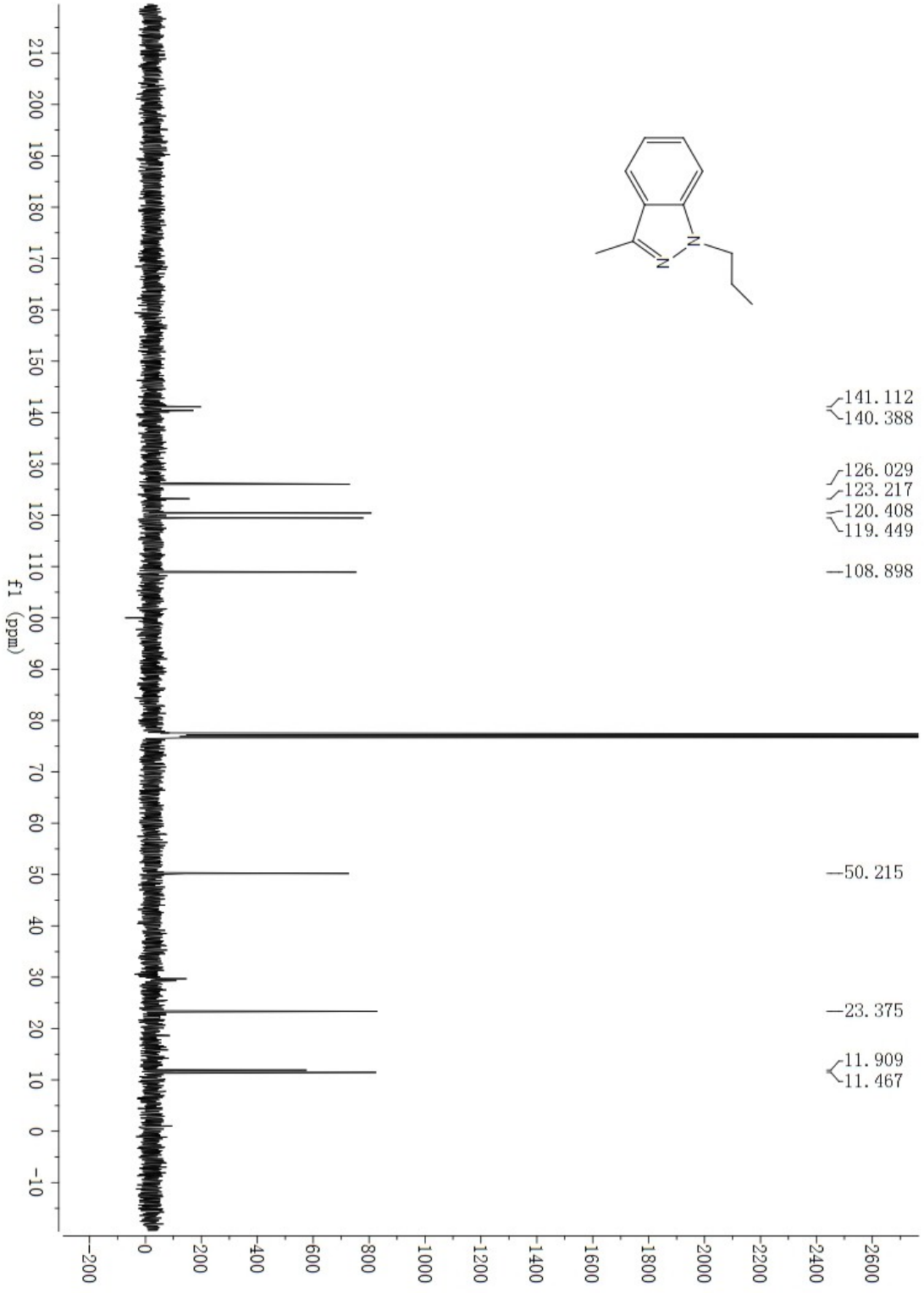
3t


8.195
8.174
7.688
7.668
7.460
7.370
7.220
7.183
6.534
3.942
2.641
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

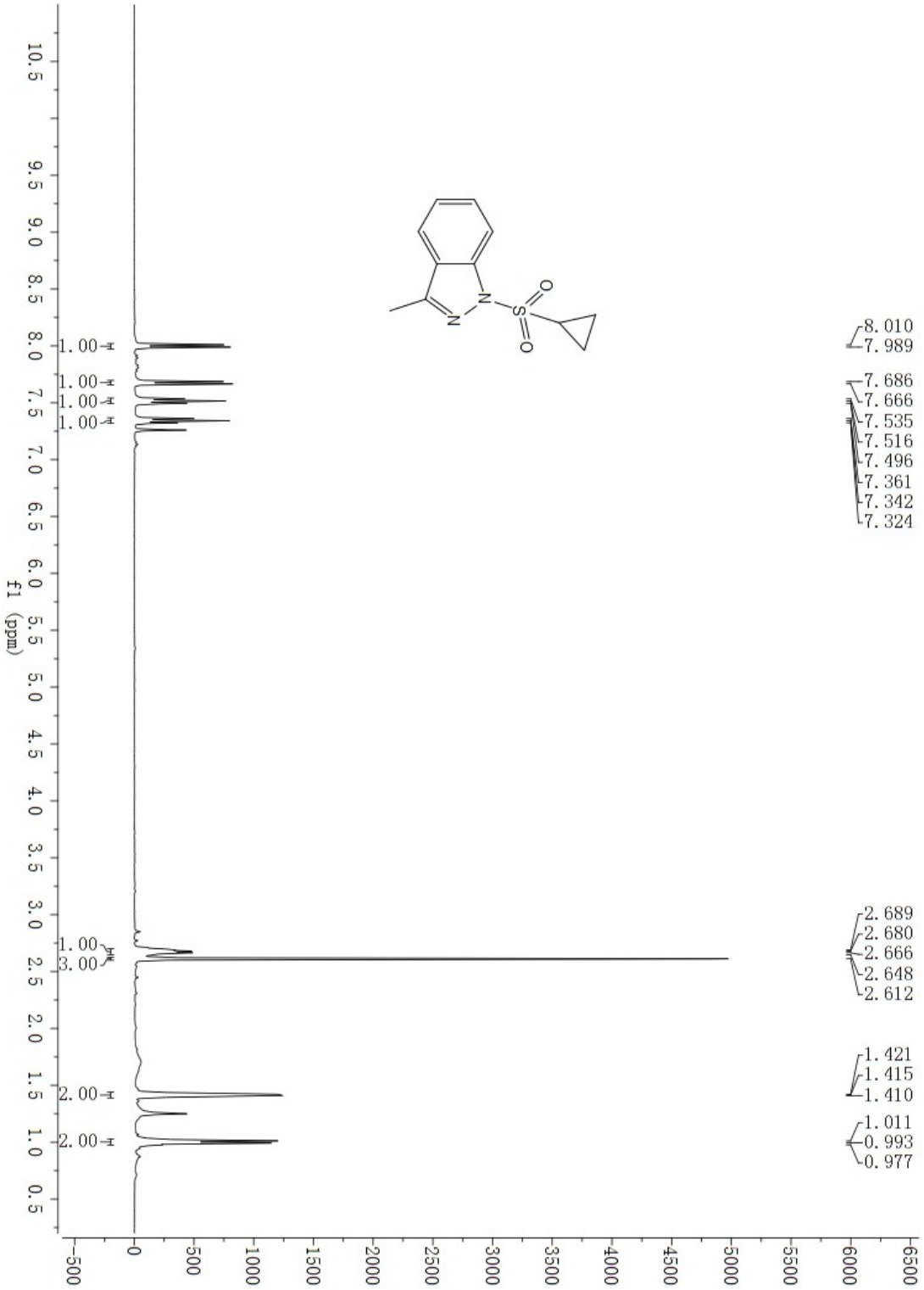

150.187
144.170
139.154
127.410
124.498
121.027
120.091
112.525
96.265
77.395
77.077
76.759
39.236
11.977
f1 (ppm)

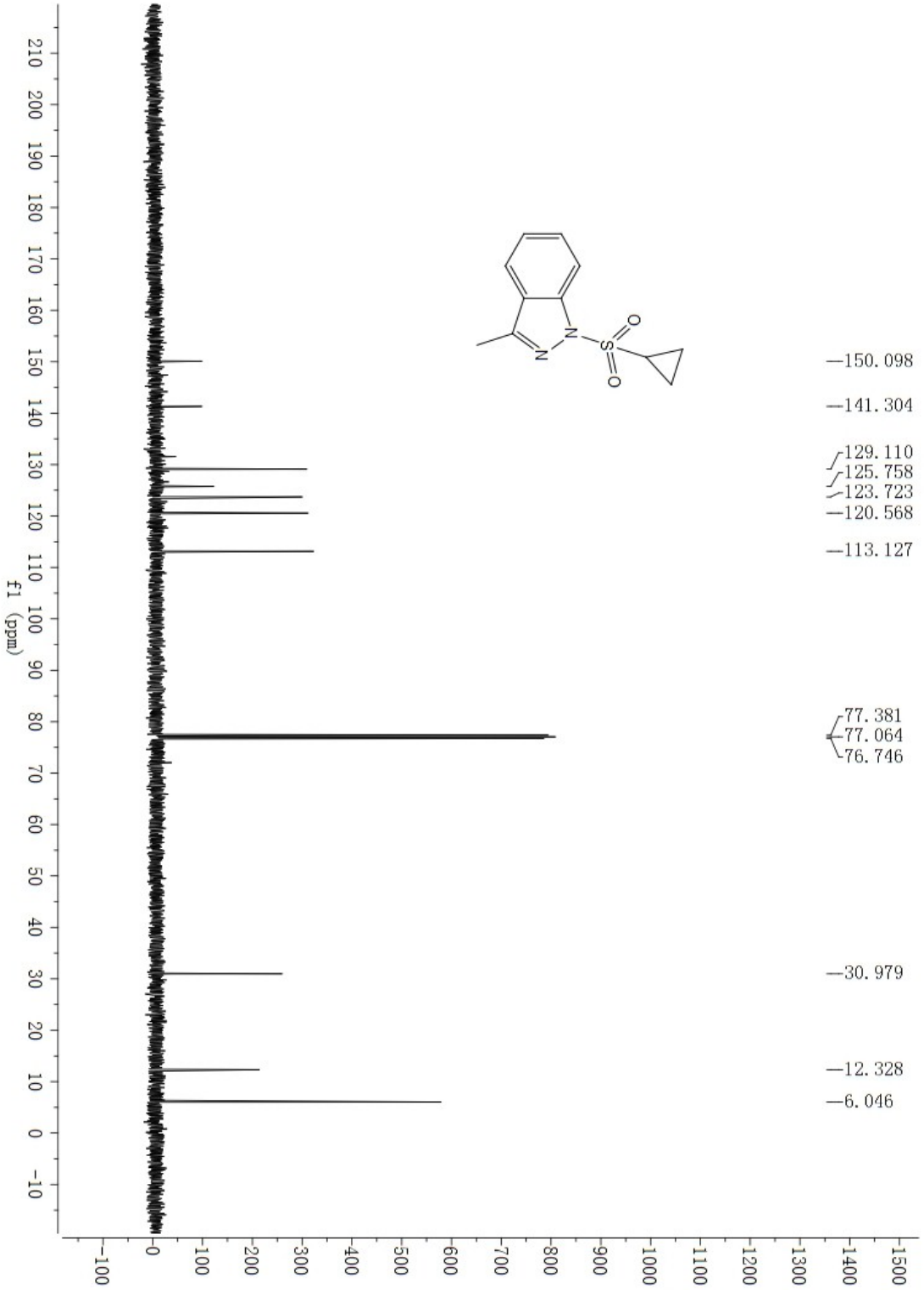
3u


7.658
7.638
7.342
7.110
7.100
7.090
4.289
4.271
4.253
2.577
1.953
1.935
1.917
1.899
1.881
0.944
0.926
0.907
1.00
2.00
1.00
2.00
3.00
2.00
3.00
f1 (ppm)

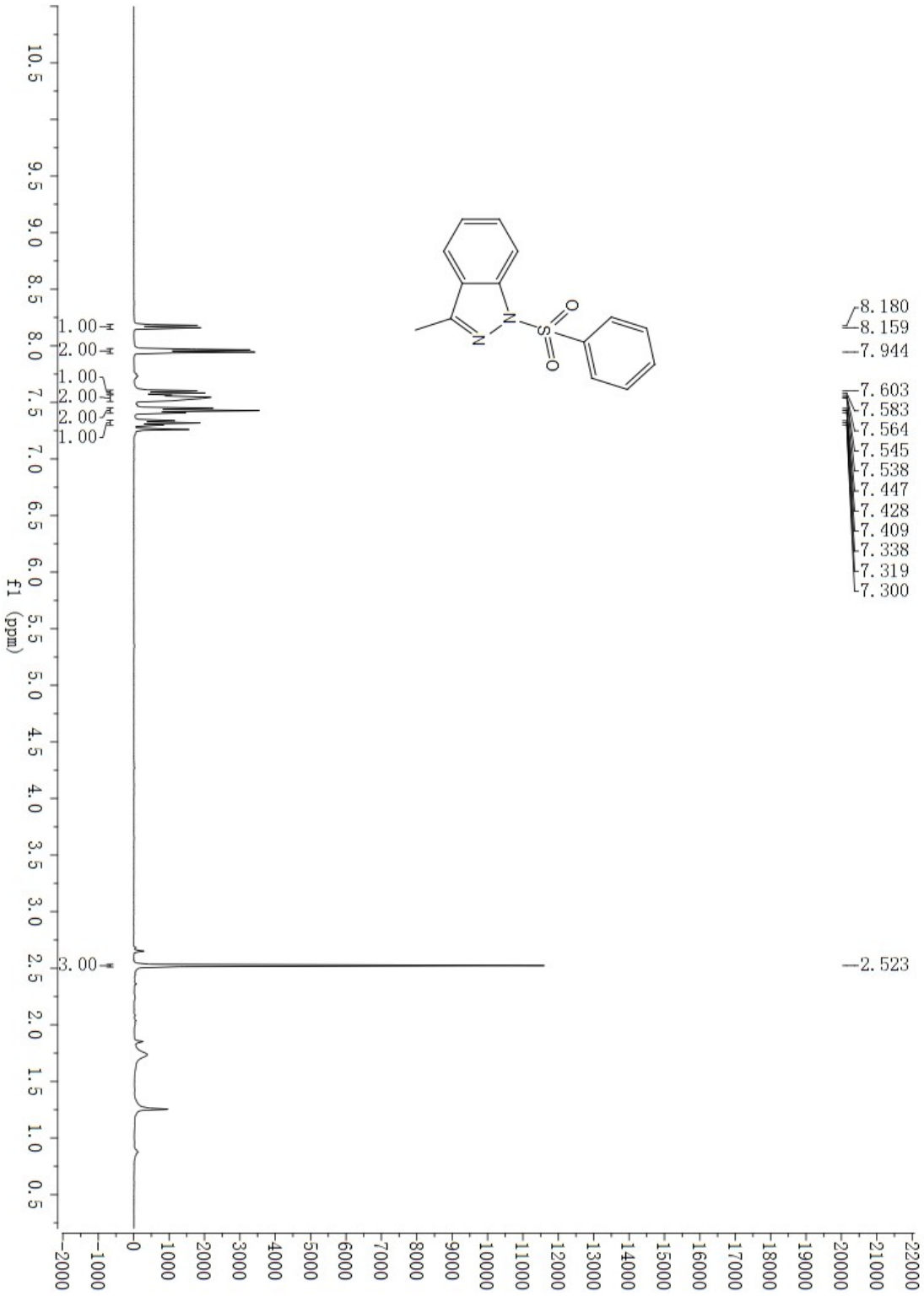

141.112
140.388
126.029
123.217
120.408
119.449
108.898
50.215
23.375
11.909
11.467
f1 (ppm)

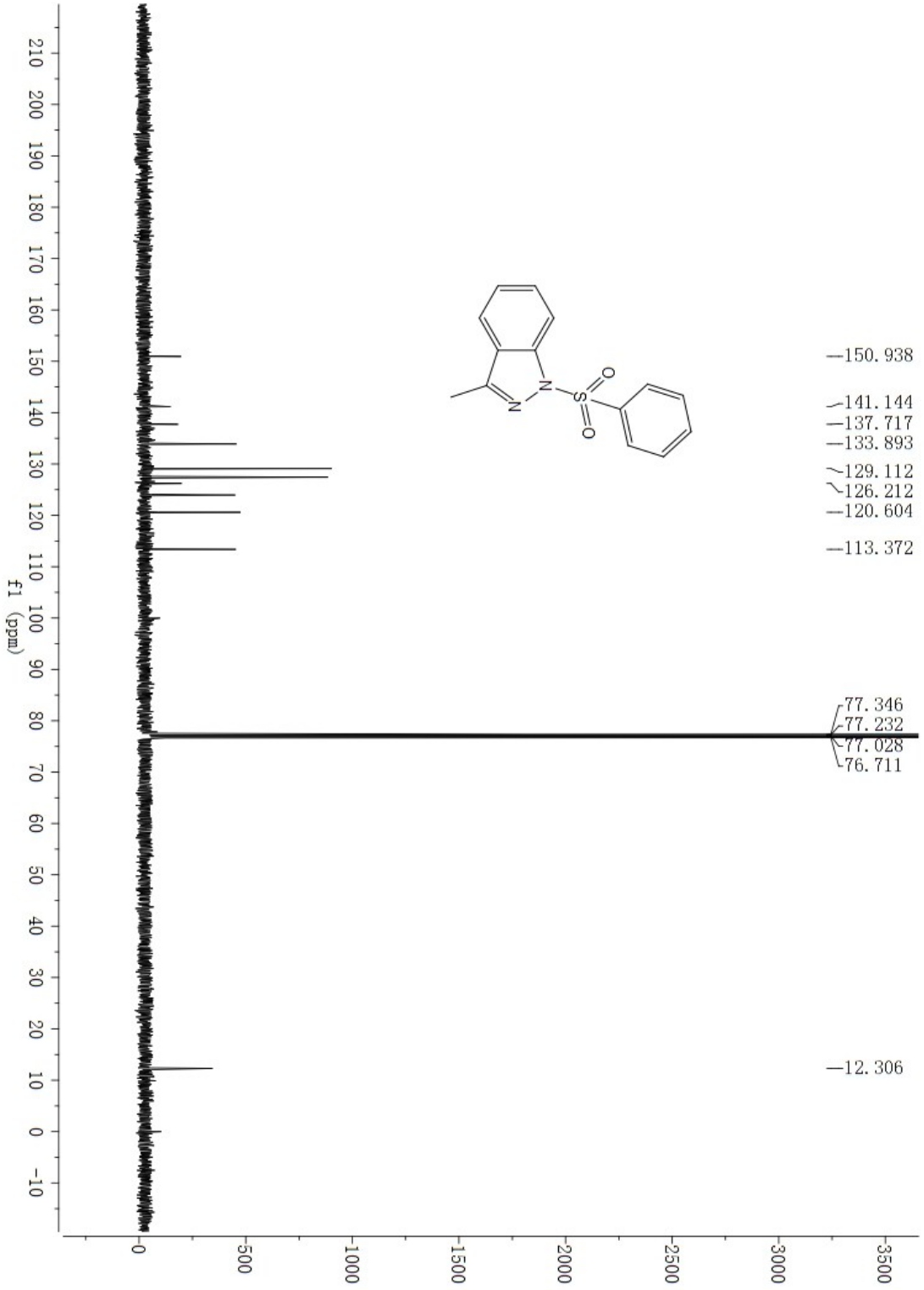
3v


8.010
7.989
7.686
7.666
7.535
7.516
7.496
7.361
7.342
7.324
2.689
2.680
2.666
2.648
2.612
1.421
1.415
1.410
1.011
0.993
0.977
1.00
1.00
1.00
1.00
1.00
3.00
2.00
2.00
f1 (ppm)

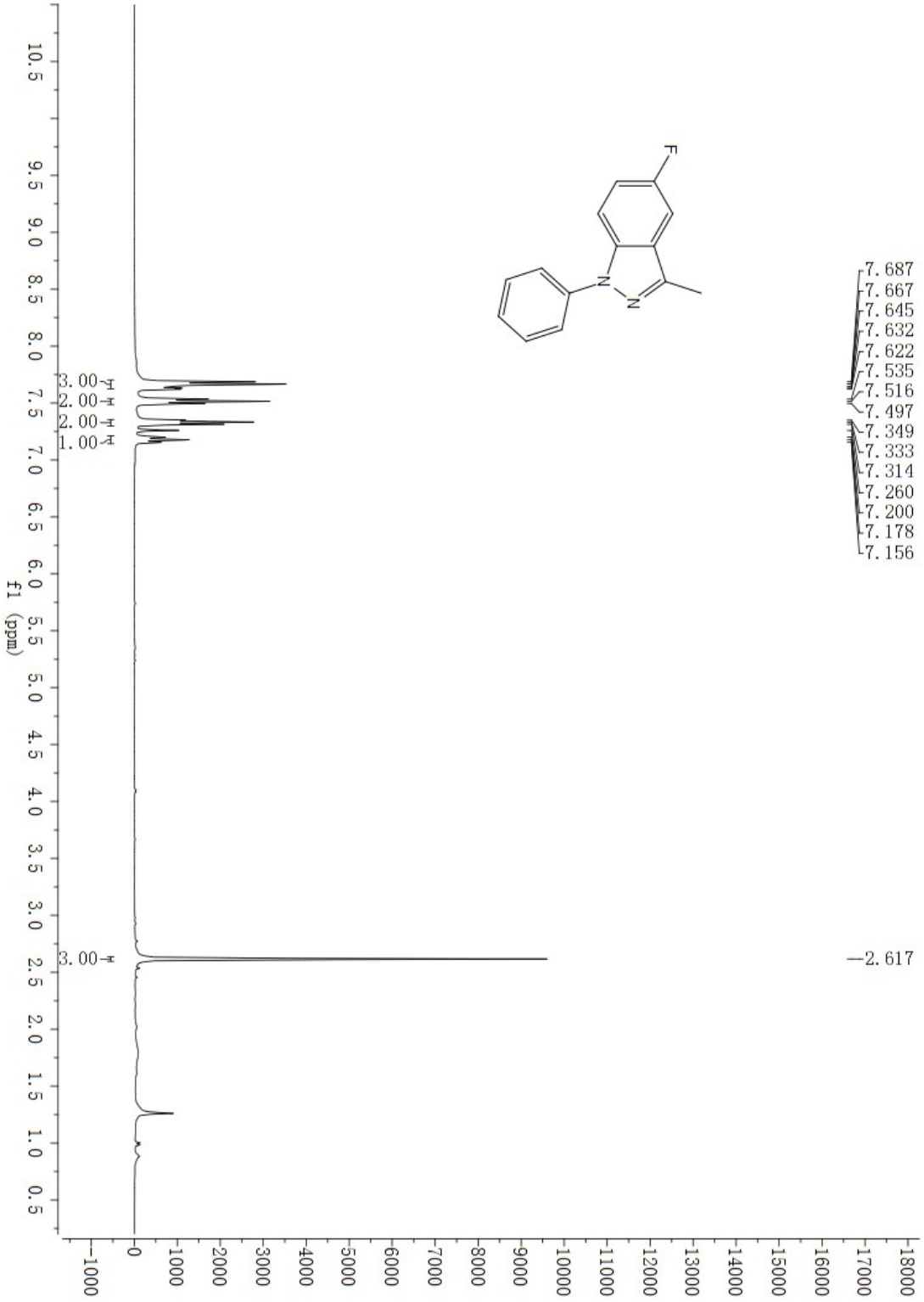

150.098
141.304
129.110
125.758
123.723
120.568
113.127
77.381
77.064
76.746
30.979
12.328
6.046
f1 (ppm)

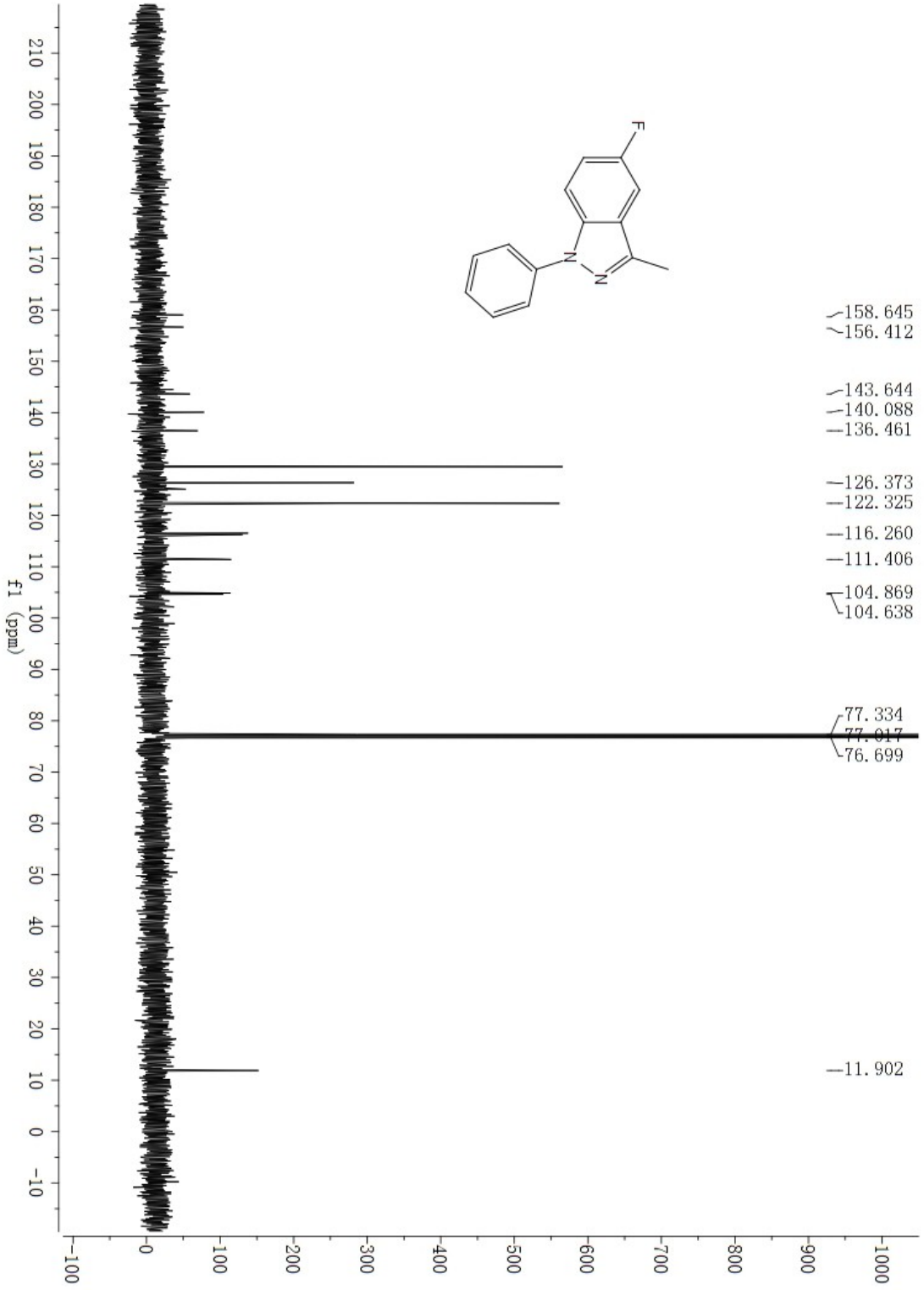
3w


8.180
8.159
7.944
7.603
7.583
7.564
7.545
7.538
7.447
7.428
7.409
7.338
7.319
7.300
2.523
1.00
2.00
1.00
2.00
2.00
1.00
3.00
f1 (ppm)

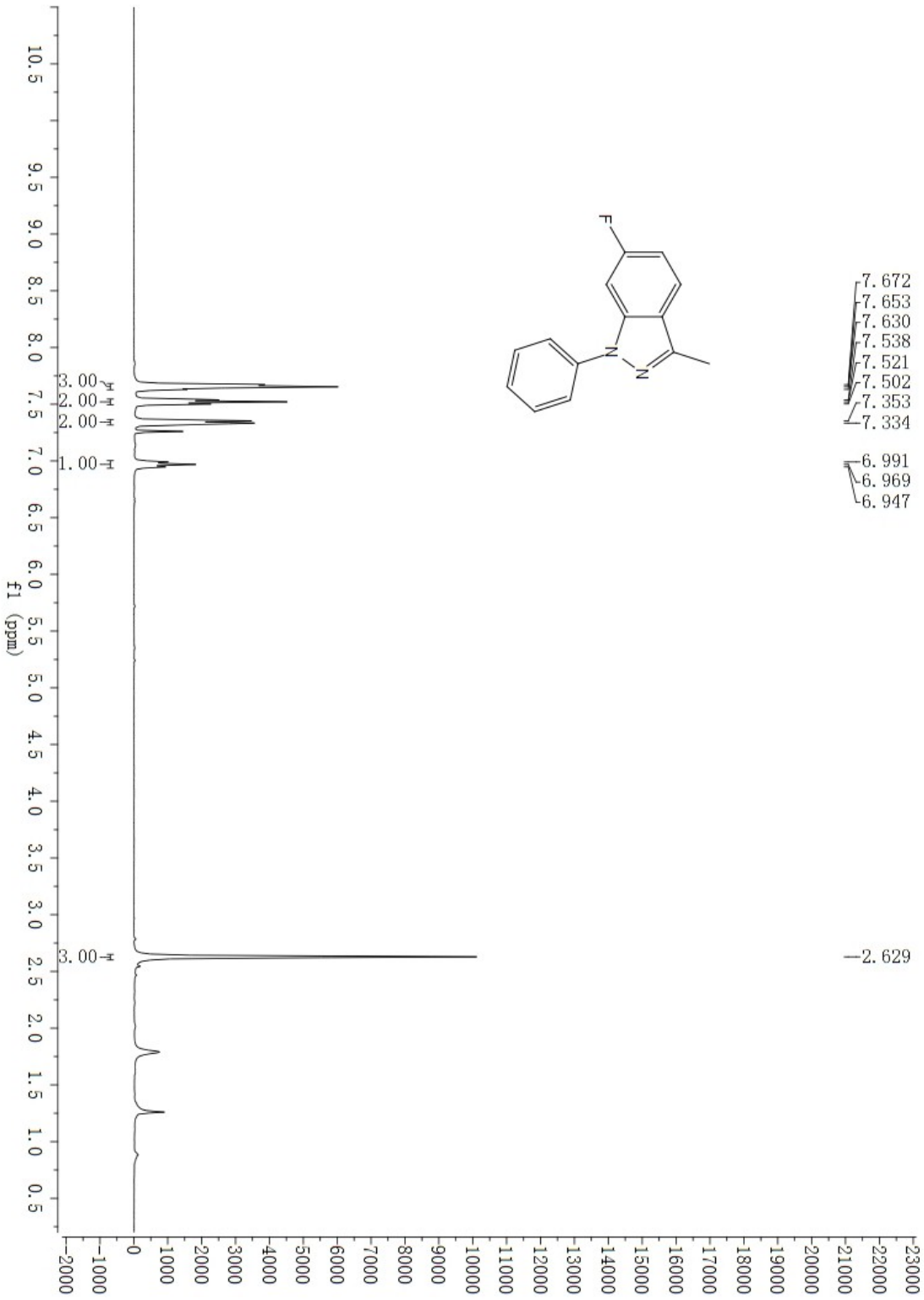

150.938
141.144
137.717
133.893
129.112
126.212
120.604
113.372
77.346
77.232
77.028
76.711
12.306
f1 (ppm)

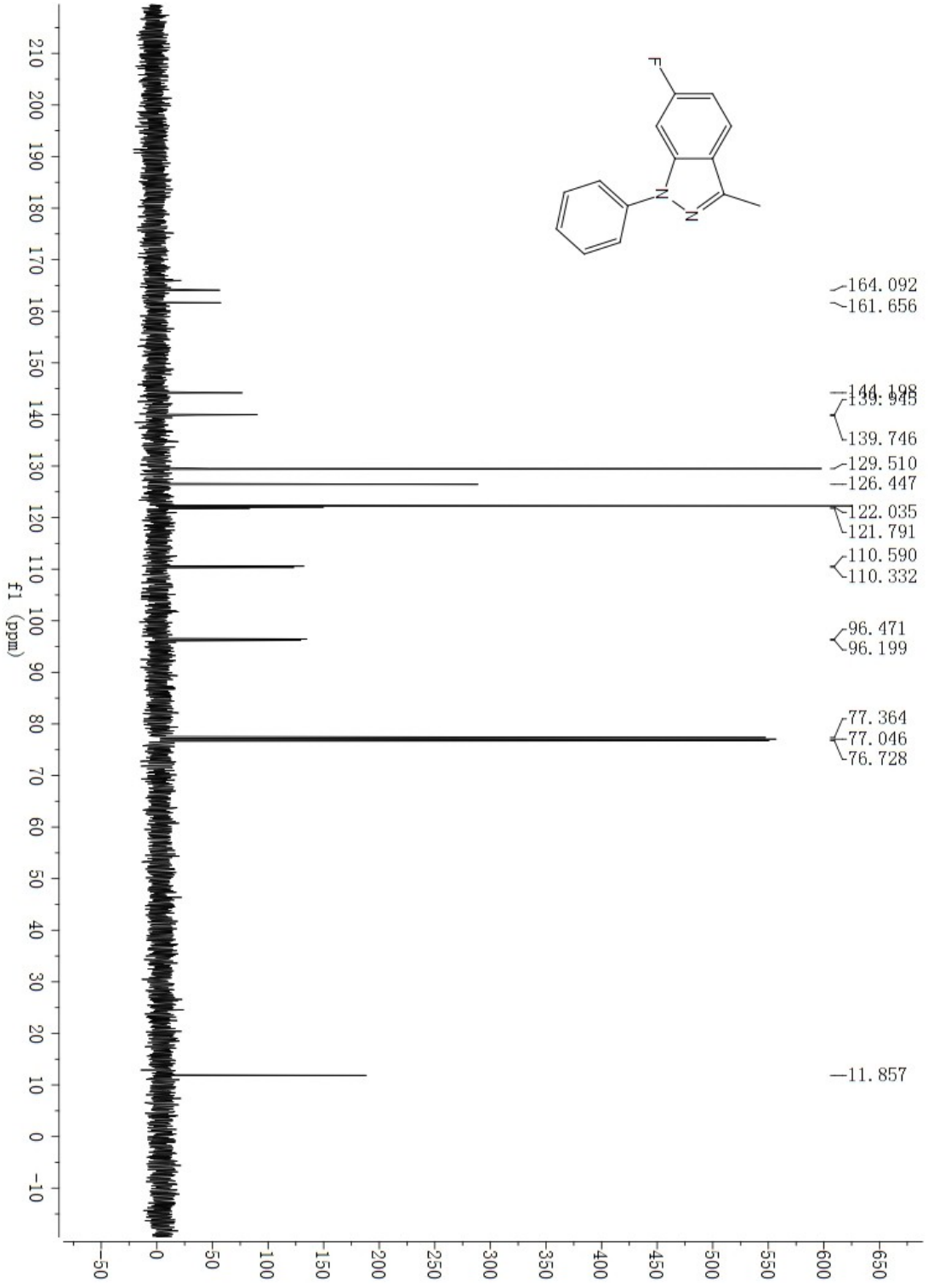
3x


F
N
N
7.687
7.667
7.645
7.632
7.622
7.535
7.516
7.497
7.349
7.333
7.314
7.260
7.200
7.178
7.156
2.617
3.00
2.00
2.00
1.00
3.00
f1 (ppm)


F
N
N
158.645
156.412
143.644
140.088
136.461
126.373
122.325
116.260
111.406
104.869
104.638
77.334
77.017
76.699
11.902
f1 (ppm)

3y


F
N
N
7.672
7.653
7.630
7.538
7.521
7.502
7.353
7.334
6.991
6.969
6.947
2.629
3.00
2.00
2.00
1.00
3.00
f1 (ppm)


F
N
N
164.092
161.656
144.198
139.945
139.746
129.510
126.447
122.035
121.791
110.590
110.332
96.471
96.199
77.364
77.046
76.728
11.857
f1 (ppm)