Supporting Information

DMSO-Mediated Palladium-Catalyzed Cyclization of Two Isothiocyanates *via* C-H Sulfurization: A New Route to 2-Aminobenzothiazoles

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(A) General information

All regents were obtained form commercial sources and used as received. All reactions were carried out with flame-dried glassware using standard Schlenk techniques under in atmosphere. ^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance 500 instrument (500 MHz for ^{1}H, 126 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ and DMSO-d_6 as the solvent and calibrated using residual deuterated solvents as an internal reference ($CDCl_3$: δ 7.26 ppm for ^{1}H NMR, δ 77.16 ppm for ^{13}C NMR; DMSO-d_6: δ 2.50 ppm for ^{1}H NMR, δ = 39.52 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Mass spectra were measured on an Agilent GC-MS-5975C Plus spectrometer (EI). HRMS (ESI) analyses were measured on a Thermo Scientific LTQ Orbitrap XL instrument.

(B) ESI-MS detection for intermediate A

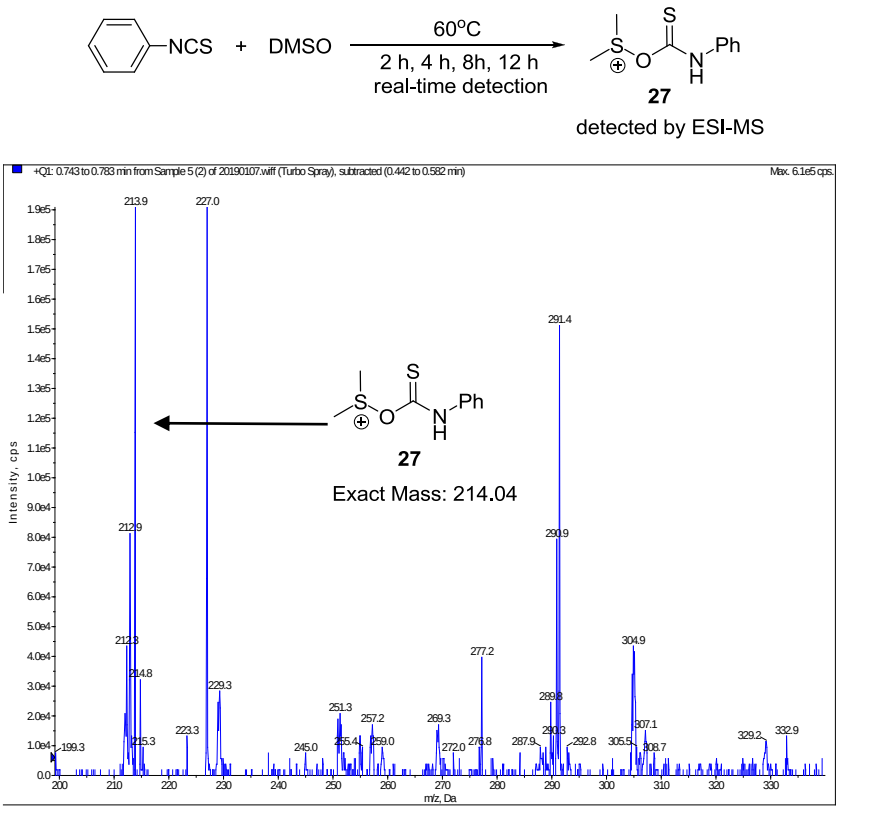


Figure S1. The real-time ESI-MS detection for intermediate A

(C) Theoretical calculation for NBO charge of DMSO and PhNCS

All calculations were performed with the Gaussian 09 package.[1] Geometry optimization were performed with B3LYP [2,3] and 6-31+G (d, p) basis set. Normal vibrational mode analysis at the same level of theory confirmed that the optimized structures are minimal (zero imaginary frequency) or saddle

points (one imaginary frequency). Single point energies and solvent effects in DMSO were computed with the dispersion-corrected density functional methods using the CPCM solvent model.

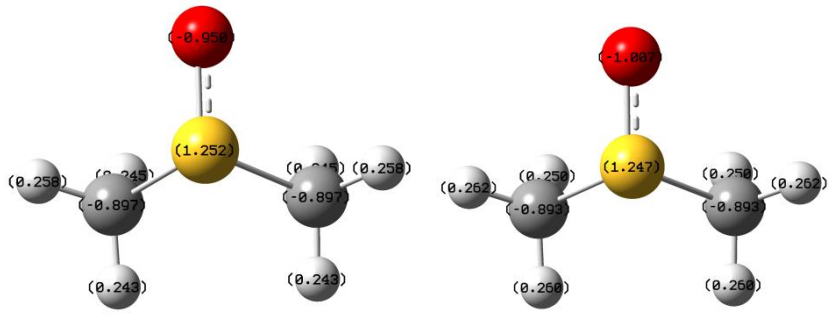


Figure S2. NBO charges of DMSO (Left: gas, Right: DMSO solvent)

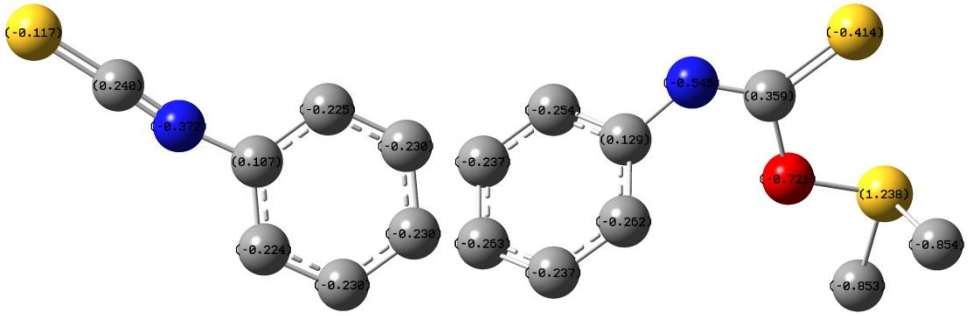
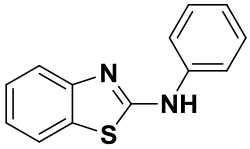


Figure S3. NBO charge of PhNCS and compound A

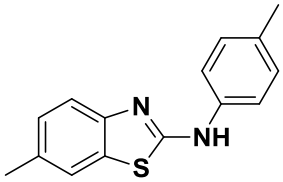
(D) Analytical data for 2-10 and 12-23

N-Phenylbenzo[*d*]thiazol-2-amine (2) [4]



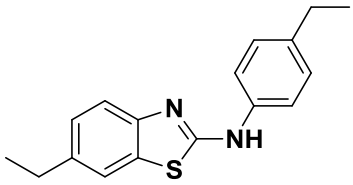
White solid. (37 mg, 82% yield). M.P.: 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.24 – 7.11 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 151.3, 140.00, 129.8, 129.6, 126.2, 124.5, 122.4, 120.9, 120.5, 119.3. IR (ATR, cm^{-1}): 1627, 1569, 1456, 743. LRMS (EI, 70 Ev) m/z (%): 226 (M^+, 100).

6-Methyl-*N*-(*p*-tolyl)benzo[*d*]thiazol-2-amine (3) [4]



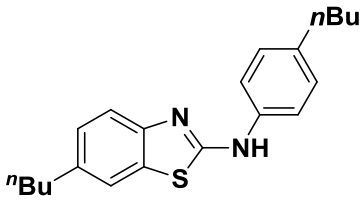
White solid. (39 mg, 76% yield). M.P.: 154-157 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.33 (br, 1H), 7.47 – 7.39 (m, 2H), 7.37 (dd, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 149.3, 137.6, 134.2, 131.8, 130.0, 129.8, 127.2, 121.0, 120.8, 118.6, 21.2, 20.9. IR (ATR, cm^{-1}): 1612, 1538, 1451, 810. LRMS (EI, 70 Ev) m/z (%): 254 (M^+, 100).

6-Ethyl-*N*-(4-ethylphenyl)benzo[*d*]thiazol-2-amine (4)



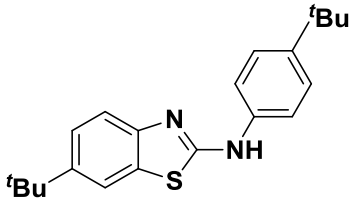
Yellow solid. (44 mg, 78% yield). M.P.: 137-139 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.28 (s, 1H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.60 (s, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.15 (dd, *J* = 8.3, 1.8 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.60 – 2.53 (m, 2H), 1.19 (dt, *J* = 15.4, 7.6 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.0, 150.3, 138.5, 137.9, 137.3, 130.0, 128.2, 128.1, 125.7, 119.7, 118.8, 118.1, 117.8, 28.0, 27.6, 16.0, 15.7. IR (ATR, cm^{-1}): 2951, 2856, 1605, 1541, 1451, 1251. LRMS (EI, 70 Ev) m/z (%): 282 (M^+, 100). HRMS (ESI) for $C_{17}H_{19}N_2S$ ($M+H^+$): calcd. 283.1263, found 283.1272.

6-Butyl-*N*-(4-butylphenyl)benzo[*d*]thiazol-2-amine (5)



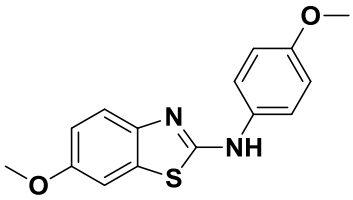
Yellow oil. (55 mg, 81% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.27 (s, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.57 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.12 (dd, *J* = 8.2, 1.7 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.53 (d, *J* = 6.7 Hz, 2H), 1.63 – 1.44 (m, 4H), 1.36 – 1.24 (m, 4H), 0.89 (td, *J* = 7.5, 1.3 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.5, 150.7, 139.0, 136.9, 136.4, 130.5, 129.1, 126.7, 120.7, 119.2, 118.3, 35.1, 34.7, 34.0, 33.8, 22.18, 14.26. IR (ATR, cm^{-1}): 2955, 2922, 2850, 1608, 1540, 1456, 815. LRMS (EI, 70 Ev) m/z (%): 338 (M^+, 100). HRMS (ESI) for $C_{21}H_{27}N_2S$ ($M+H^+$): calcd. 339.1889, found 339.1873.

6-(tert-Butyl)-*N*-[4-(tert-butyl)phenyl]benzo[*d*]thiazol-2-amine (6)



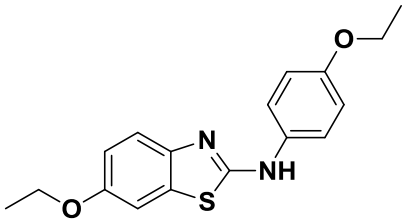
White solid. (57 mg, 84% yield). M.P.: 177-179 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.02 (br, 1H), 7.64 (s, 1H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.42 (s, 4H), 7.40 – 7.35 (m, 1H), 1.37 (d, *J* = 8.1 Hz, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9, 149.2, 147.3, 145.6, 137.5, 129.9, 126.4, 123.8, 120.1, 120.1, 118.6, 117.2, 34.8, 34.5, 31.7, 31.4. IR (ATR, cm^{-1}): 2961, 2904, 2867, 1607, 1539, 1516, 1451, 820. LRMS (EI, 70 Ev) m/z (%): 338 (M^+, 100). HRMS (ESI) for $C_{21}H_{26}N_2S$ ($M+H^+$): calcd. 339.1890, found 339.1891.

6-Methoxy-*N*-(4-methoxyphenyl)benzo[*d*]thiazol-2-amine (7) [4]



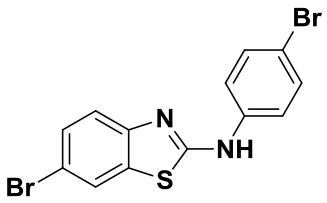
Yellow solid. (43 mg, 75% yield). M.P.: 157-159 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.09 (s, 1H), 7.71 – 7.60 (m, 2H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 6.96 – 6.92 (m, 2H), 6.90 (dd, *J* = 8.8, 2.7 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.7, 155.5, 154.9, 146.8, 134.7, 131.5, 119.8, 119.7, 114.7, 113.8, 105.8, 56.0, 55.7. IR (ATR, cm^{-1}): 1611, 1541, 1502, 1246, 1055. LRMS (EI, 70 Ev) m/z (%): 286 (M^+, 100). HRMS (ESI) for $C_{15}H_{15}N_2O_2S$ $[M+H]^+$: calcd. 287.0849, found 287.0851.

6-Ethoxy-*N*-(4-ethoxyphenyl)benzo[*d*]thiazol-2-amine (8)



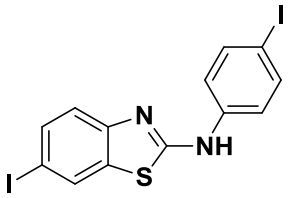
Yellow solid. (48 mg, 77% yield). M.P.: 146-148 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.08 (s, 1H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 2.6 Hz, 1H), 6.97 – 6.90 (m, 2H), 6.88 (dd, *J* = 8.7, 2.6 Hz, 1H), 4.01 (dq, *J* = 15.7, 7.0 Hz, 4H), 1.33 (q, *J* = 6.7 Hz, 6H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.2, 154.2, 153.6, 146.2, 134.1, 130.9, 119.2, 119.2, 114.7, 113.8, 106.0, 63.5, 63.1, 14.7, 14.6. IR (ATR, cm^{-1}): 1614, 1540, 1507, 1457, 1244. LRMS (EI, 70 Ev) m/z (%): 314 (M^+, 100).

6-Bromo-*N*-(4-bromophenyl)benzo[*d*]thiazol-2-amine (9)



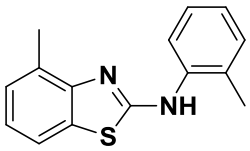
Yellow solid. (29 mg, 38% yield). M.P.: 225-227 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.72 (s, 1H), 8.08 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 8.9 Hz, 2H), 7.56-7.52 (d, *J* = 8.9 Hz, 3H), 7.47 (dd, *J* = 8.6, 2.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 151.6, 140.2, 132.7, 132.3, 129.4, 124.1, 121.3, 120.3, 114.6, 114.2. IR (ATR, cm^{-1}): 1612, 1537, 1367, 1242, 1040. LRMS (EI, 70 Ev) m/z (%): 384 (M^++2, 100), 382 (M^+, 100);

6-Iodo-*N*-(4-iodophenyl)benzo[*d*]thiazol-2-amine (10)



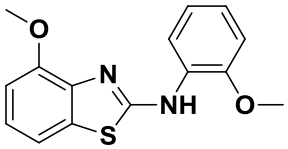
Yellow solid. (32 mg, 34% yield). M.P.: 230-231 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.67 (s, 1H), 8.20 (d, *J* = 1.8 Hz, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.57 (m, 3H), 7.40 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.2, 152.0, 140.6, 138.0, 135.0, 133.0, 129.7, 121.7, 120.6, 85.9, 85.7. IR (ATR, cm^{-1}): 1608, 1530, 1479, 1434, 1245, 1047. LRMS (EI, 70 Ev) m/z (%): 478 (M^+, 100). HRMS (ESI) for $C_{13}H_9I_2N_2S$ ($M+H^+$): calcd. 478.8570, found 478.8564.

4-Methyl-*N*-(*o*-tolyl)benzo[*d*]thiazol-2-amine (12) [5]



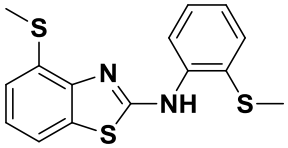
Yellow solid. (42 mg, 82% yield). M.P.: 131-133 ºC.^{1}H NMR (500 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.25 (td, *J* = 7.6, 5.9 Hz, 2H), 7.15 – 7.06 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 2.48 (s, 3H), 2.30 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 164.1, 151.5, 139.4, 131.2, 131.0, 130.2, 128.4, 127.1, 126.8, 125.1, 123.4, 122.1, 118.9, 18.6, 18.5. IR (ATR, cm^{-1}): 1558, 1540, 1456, 1258, 755. LRMS (EI, 70 Ev) m/z (%): 254 (M^+, 100).

4-Methoxy-*N*-(2-methoxyphenyl)benzo[*d*]thiazol-2-amine (13) [6]



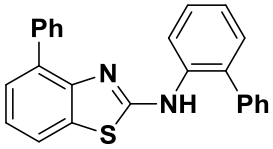
White solid. (36 mg, 63% yield). M.P.: 147-148 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (br, 1H), 7.99 – 7.89 (m, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.10 – 7.01 (m, 2H), 6.98 – 6.89 (m, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7, 151.0, 148.1, 140.9, 131.3, 129.3, 123.0, 123.0, 121.0, 117.0, 113.0, 110.4, 107.2, 55.9, 55.7. IR (ATR, cm^{-1}): 1623, 1541, 1462, 1257, 1046, 736. LRMS (EI, 70 Ev) m/z (%): 286 (M^+, 100).

4-Methylthio-*N*-[3-(methylthio)phenyl]benzo[*d*]thiazol-2-amine (14)



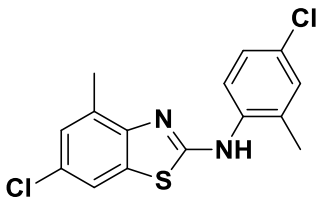
Yellow oil. (49 mg, 77% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.88 (s, 1H), 7.89 – 7.64 (m, 1H), 7.51 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.39 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.15 – 7.02 (m, 2H), 2.46 (d, *J* = 5.0 Hz, 3H), 2.42 (d, *J* = 5.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.5, 148.9, 138.1, 134.1, 130.2, 128.9, 127.8, 127.0, 126.4, 125.6, 122.8, 121.7, 117.6, 15.7, 14.5. IR (ATR, cm^{-1}): 1613, 1538, 1454, 1249, 1049. LRMS (EI, 70 Ev) m/z (%): 318 (M^+, 100); HRMS (ESI) for $C_{15}H_{15}N_2S_3$ ($M+H^+$): calcd. 319.0383, found 319.0375.

***N*-(Biphenyl-2-yl)-4-phenylbenzo[*d*]thiazol-2-amine (15)**



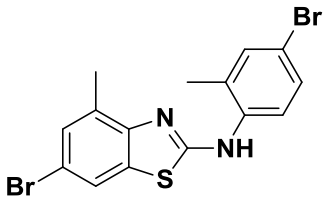
Gray oil. (63 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.64 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54 – 7.46 (m, 5H), 7.46 – 7.37 (m, 5H), 7.34 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (td, *J* = 7.5, 1.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8, 149.4, 139.4, 138.0, 137.0, 132.9, 131.4, 130.6, 129.4, 129.3, 129.1, 128.6, 128.1, 127.8, 127.2, 126.5, 124.1, 122.7, 120.4, 119.8. IR (ATR, cm^{-1}): 1609, 1544, 1379, 1266, 1037. LRMS (EI, 70 Ev) m/z (%): 378 (M^+, 100). HRMS (ESI) for $C_{25}H_{19}N_2S$ ($M+H^+$): calcd. 379.1263, found 379.1271.

6-Chloro-*N*-(4-chloro-2-methylphenyl)-4-methylbenzo[*d*]thiazol-2-amine (16)



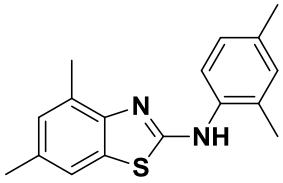
Yellow solid. (43 mg, 67% yield). M.P.: 189-191 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.78 (s, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 7.34 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 163.9, 150.2, 138.1, 132.7, 131.8, 130.6, 130.3, 128.3, 126.8, 126.8, 126.1, 124.2, 118.6, 18.4, 18.3. IR (ATR, cm^{-1}): 1627, 1538, 1451, 1257, 1046. LRMS (EI, 70 Ev) m/z (%): 322 (M^+, 100). HRMS (ESI) for $C_{15}H_{13}Cl_2N_2S$ ($M+H^+$): calcd. 323.0171, found 323.0172.

6-Bromo-*N*-(4-bromo-2-methylphenyl)-4-methylbenzo[*d*]thiazol-2-amine (17)



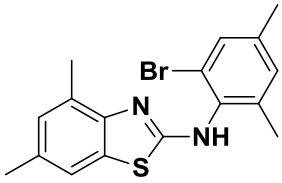
White solid. (54 mg, 66% yield). M.P.: 202-204 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.77 (s, 1H), 7.98 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 2.3 Hz, 1H), 7.47 (d, *J* = 2.5 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.30 (d, *J* = 2.2 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 163.8, 150.5, 138.5, 133.5, 133.0, 132.2, 130.7, 129.7, 129.5, 124.5, 121.4, 116.5, 113.9, 18.3, 18.2. IR (ATR, cm^{-1}): 1602, 1536, 1439, 1255, 1182. LRMS (EI, 70 Ev) m/z (%): 411 (M^++2, 100), 409 (M^+, 100). HRMS (ESI) for $C_{15}H_{12}Br_2N_2S$ ($M+H^+$): calcd. 409.9088, found 409.9092.

***N*-(2,4-dimethylphenyl)-4,6-dimethylbenzo[*d*]thiazol-2-amine (18)**



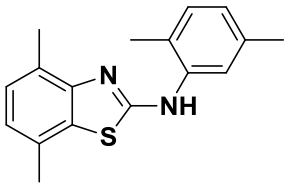
Gray solid. (27 mg, 47% yield). M.P.: 190-192 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (br, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.94 (s, 1H), 2.48 (s, 3H), 2.35 (d, *J* = 1.6 Hz, 6H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 148.8, 136.1, 135.9, 132.4, 131.9, 131.6, 130.2, 128.3, 128.1, 127.7, 124.4, 118.2, 21.2, 21.0, 18.2, 17.7. IR (ATR, cm^{-1}): 2915, 2843, 1634, 1558, 1540, 1475, 1258, 1047, 799. LRMS (EI, 70 Ev) m/z (%): 282 (M^+, 100). HRMS (ESI) for $C_{17}H_{19}N_2S$ ($M+H^+$): calcd. 283.1263, found 283.1268.

***N*-(2-Bromo-4,6-dimethylphenyl)-4,6-dimethylbenzo[*d*]thiazol-2-amine (19)**



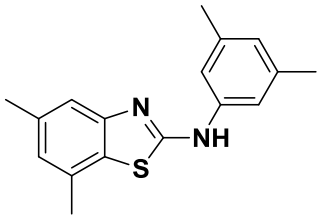
Yellow solid. (9 mg, 13% yield). M.P.: 229-230 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.0 Hz, 1H), 7.17 (s, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 2.39 (s, 3H), 2.35 (d, *J* = 4.5 Hz, 6H), 2.33 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 149.0, 139.6, 139.2, 134.8, 131.7, 131.4, 131.3, 130.4, 128.3, 128.1, 124.6, 118.4, 21.1, 20.9, 18.9, 18.2. IR (ATR, cm^{-1}): 2916, 2851, 1582, 1472, 840, 833, 741, 690. LRMS (EI, 70 Ev) m/z (%): 362 (M^++2, 100), 360 (M^+, 100). HRMS (ESI) for $C_{17}H_{17}BrN_2S$ ($M+H^+$): calcd. 361.0369, found 361.0373.

***N*-(2,5-dimethylphenyl)-4,7-dimethylbenzo[*d*]thiazol-2-amine (20)**



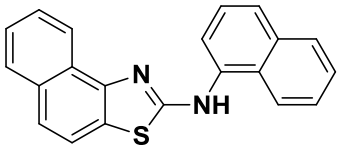
Gray solid. (40 mg, 71% yield). M.P.: 139-141 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (dd, *J* = 7.8, 2.2 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 2.53 (s, 3H), 2.40 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 150.4, 138.2, 137.0, 131.0, 130.3, 128.9, 128.2, 126.9, 126.9, 126.1, 124.6, 122.5, 21.1, 21.0, 18.0, 17.4. IR (ATR, cm^{-1}): 2914, 2840, 1611, 1551, 1232, 813, 795. LRMS (EI, 70 Ev) m/z (%): 282 (M^+, 100). HRMS (ESI) for $C_{17}H_{18}N_2S$ ($M+H^+$): calcd. 283.1264, found 283.1266.

***N*-(2,5-dimethylphenyl)-4,7-dimethylbenzo[*d*]thiazol-2-amine (21)**



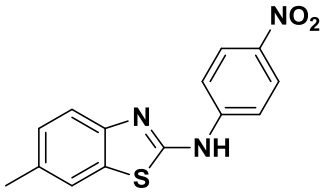
White solid. (48 mg, 85% yield). M.P.: 187-189 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.12 (s, 2H), 6.81 (d, *J* = 11.2 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 2.36 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2, 151.3, 140.0, 139.3, 136.0, 130.4, 127.0, 126.1, 124.1, 118.3, 118.2, 117.2, 21.4, 21.4, 21.1. IR (ATR, cm^{-1}): 2916, 2851, 1581, 1471, 840, 741. LRMS (EI, 70 Ev) m/z (%): 282 (M^+, 100). HRMS (ESI) for $C_{17}H_{18}N_2S$ ($M+H^+$): calcd. 283.1264, found 283.1264.

***N*-(Naphthalen-1-yl)naphtho[1,2-*d*]thiazol-2-amine (22) [4]**



White solid. (50 mg, 77% yield). M.P.: 182-185 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.19 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.84 (dd, *J* = 13.9, 8.3 Hz, 2H), 7.65 – 7.42 (m, 6H), 7.37 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 147.5, 135.9, 134.7, 132.2, 128.7, 128.7, 128.0, 126.9, 126.8, 126.7, 126.7, 126.0, 125.9, 125.5, 125.2, 123.7, 122.6, 121.7, 121.2, 118.7. IR (ATR, cm^{-1}): 1615, 1543, 1245, 1043. LRMS (EI, 70 Ev) m/z (%): 326 (M^+, 100).

6-Methyl-*N*-(4-nitrophenyl)benzo[*d*]thiazol-2-amine (23) [7]



Yellow solid. (15 mg, 27% yield). M.P.: 249-251 ºC. ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.16 (s, 1H), 8.27 (d, *J* = 9.2 Hz, 2H), 7.99 (d, *J* = 9.2 Hz, 2H), 7.69 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.21 (dd, *J* = 8.3, 1.7 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 159.8, 149.3, 146.5, 140.8, 132.7, 130.4, 129.5, 127.3, 125.4, 121.1, 119.7, 117.0, 20.9. IR (ATR, cm^{-1}): 1612, 1538, 1502, 1323, 1257. LRMS (EI, 70 Ev) m/z (%): 285 (M^+, 100).

(E) Reference

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, *et al*. Gaussian 09, rev. D. 01. Wallingford, CT: Gaussian, Inc. **2009.**

[2] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–52.

[3] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev*. **2005**, *105*, 2999–3093.

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[5] Y. He, J. Li, S. Luo, J. Huang, Q. Zhu, *Chem. Commun.* **2016**, *52*, 8444-8447.

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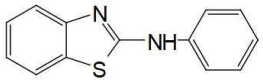
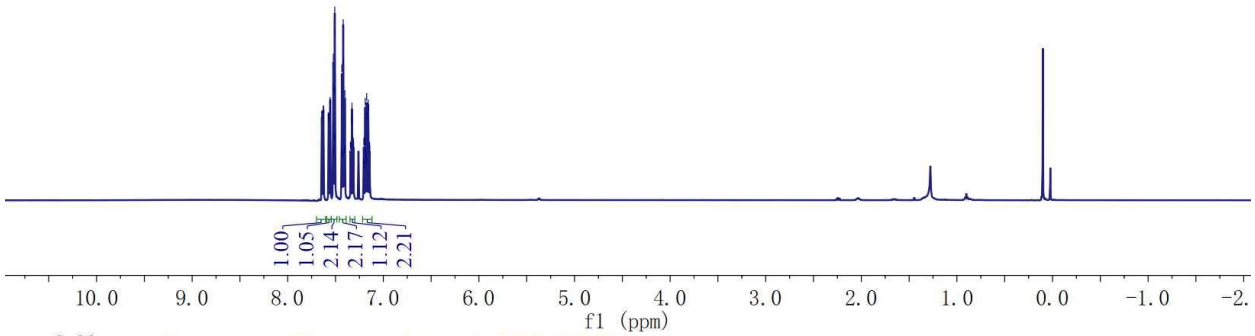
(F) *Spectra*

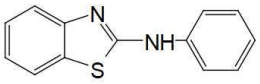
N-Phenylbenzo[*d*]thiazol-2-amine (2)

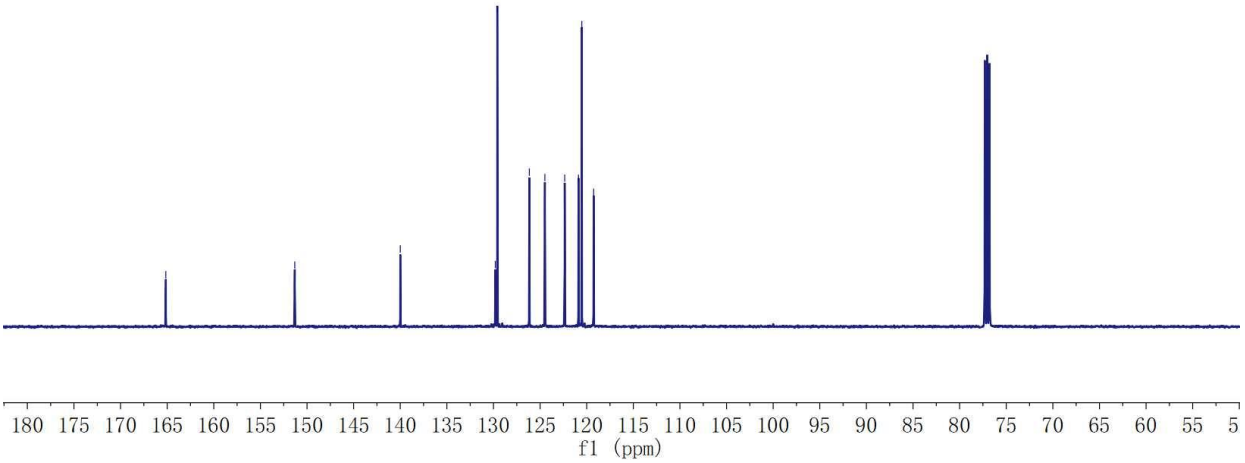




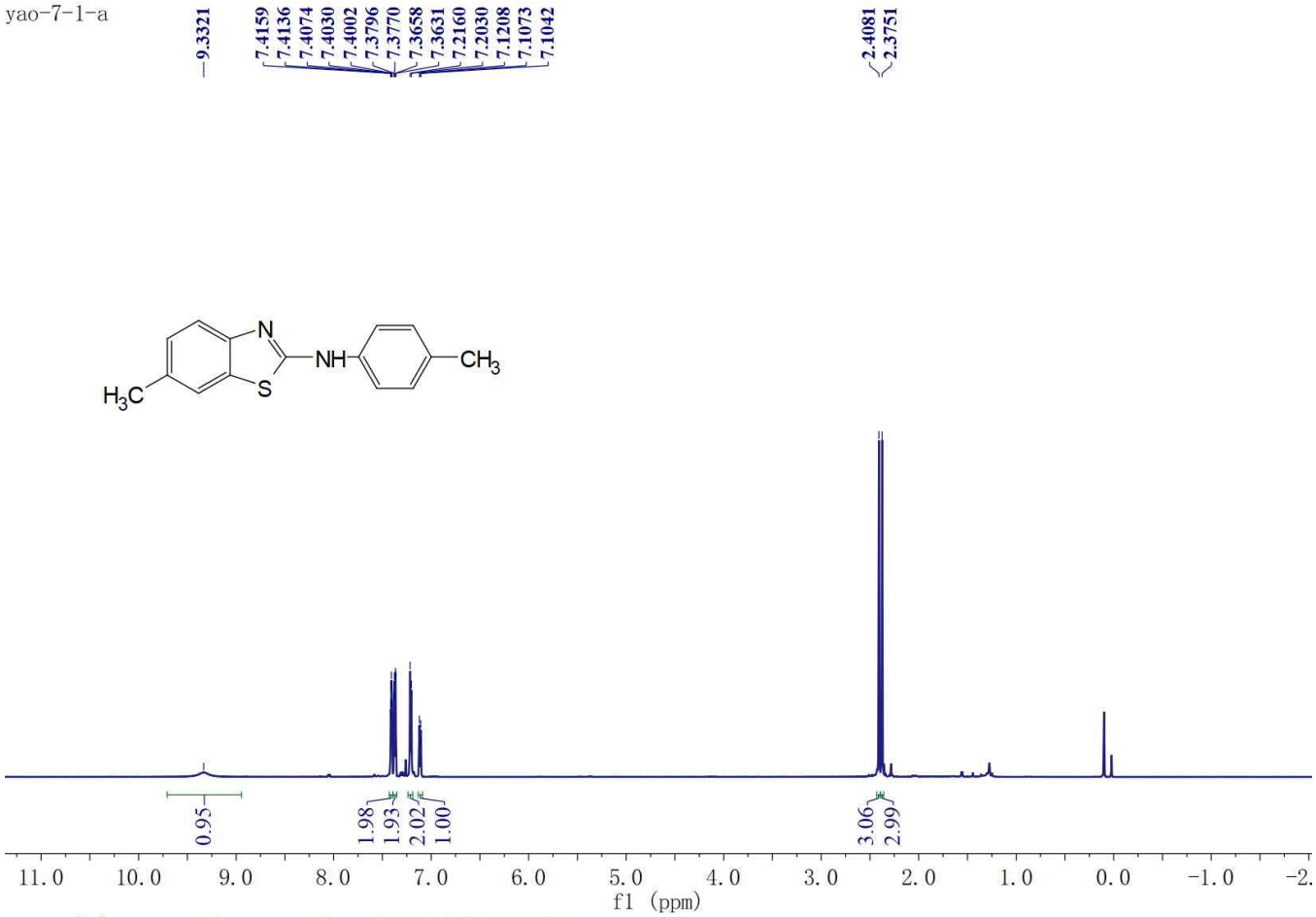
yao-6-30

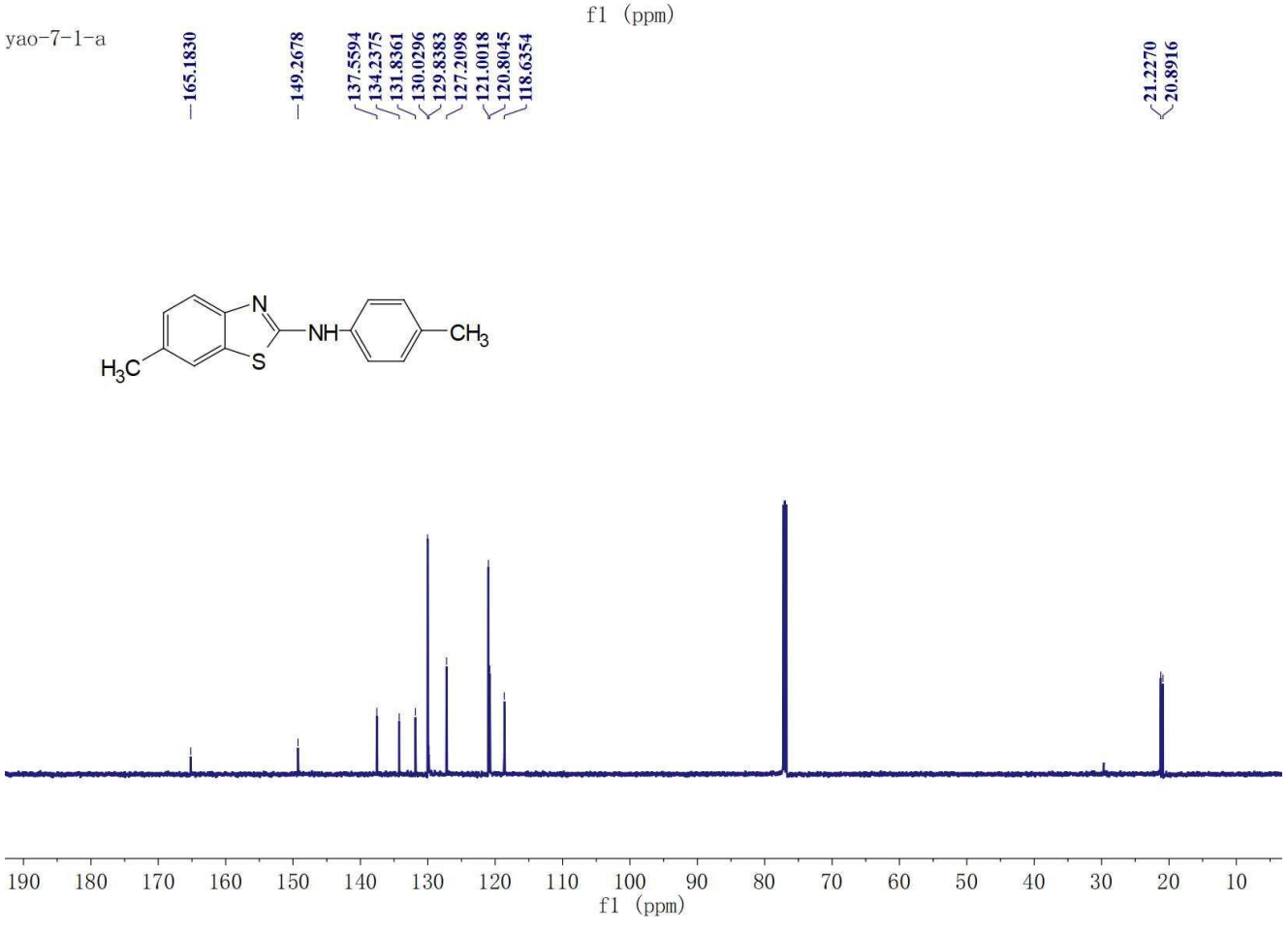
165.1437
151.3130
139.9929
129.8067
129.5906
126.1563
124.4844
122.3614
120.8822
120.5232
119.2576



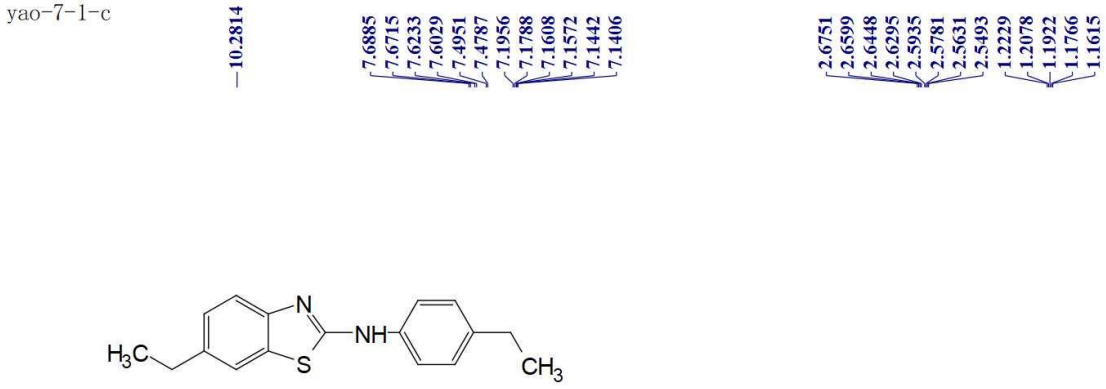


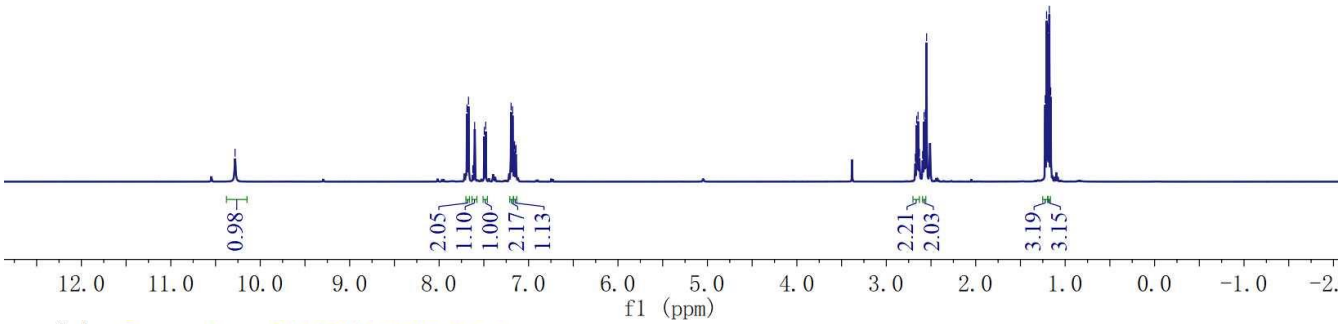
6-Methyl-*N*-p-tolylbenzo[*d*]thiazol-2-amine (3)

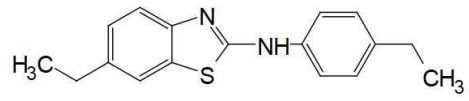


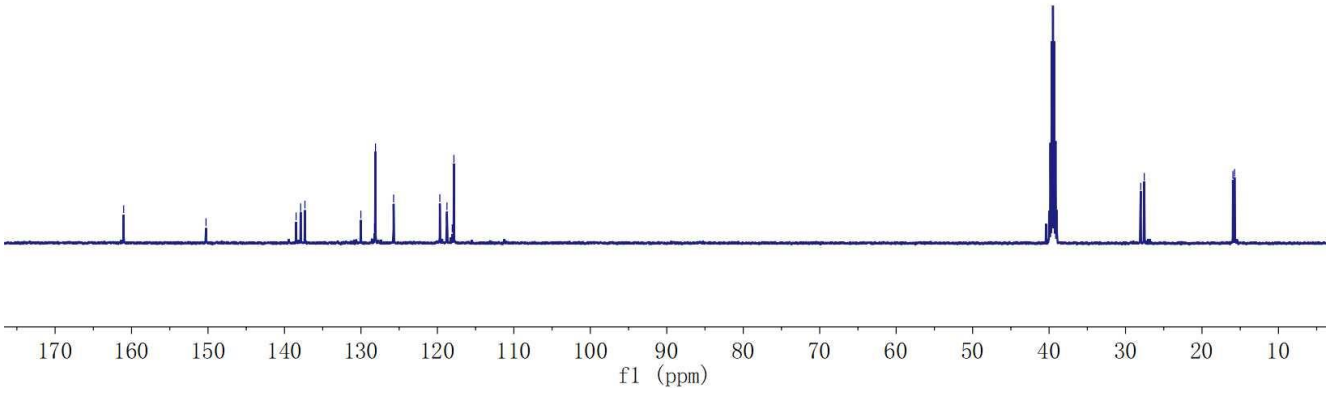


6-Ethyl-*N*-(4-ethylphenyl)benzo[*d*]thiazol-2-amine (4)

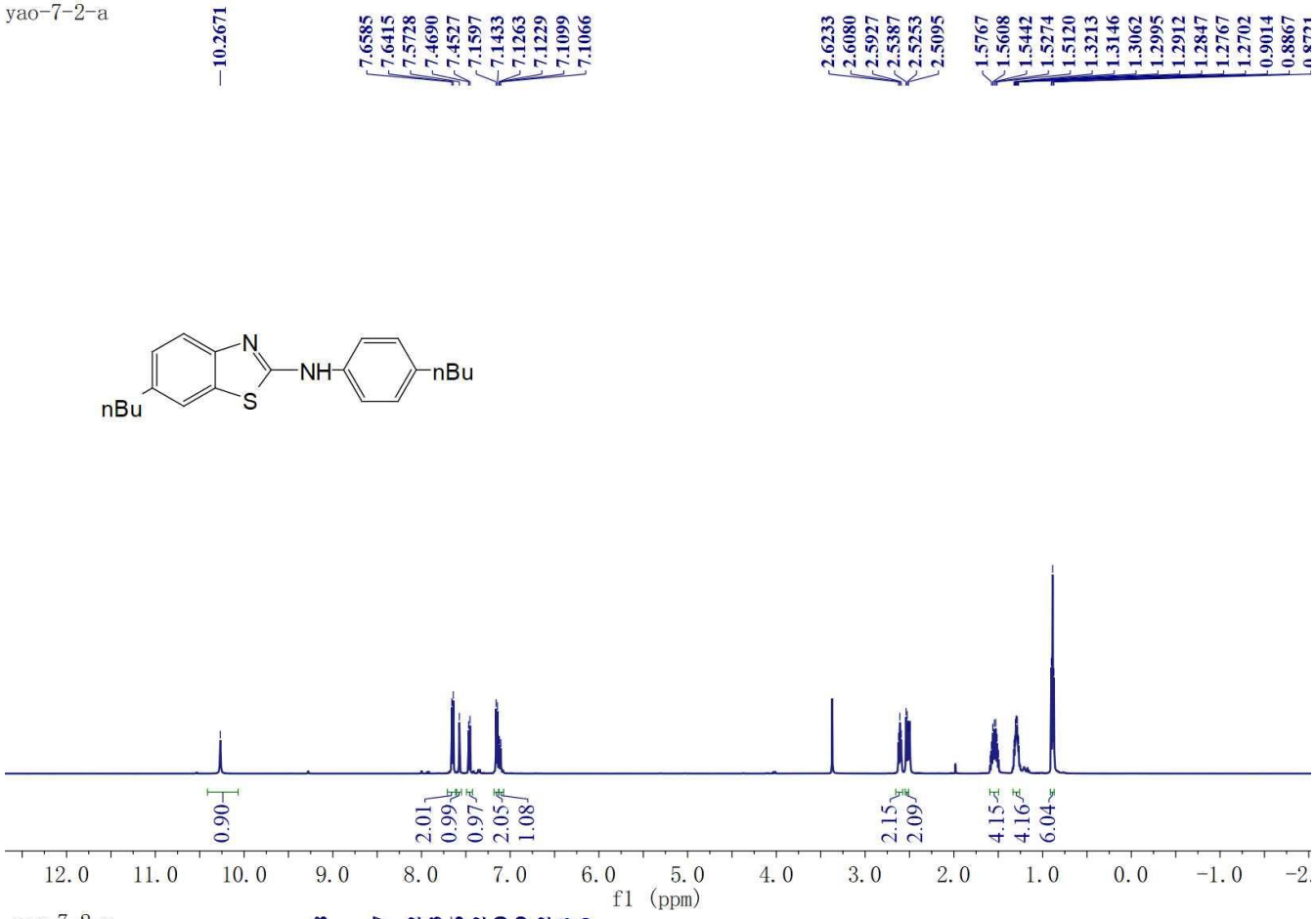


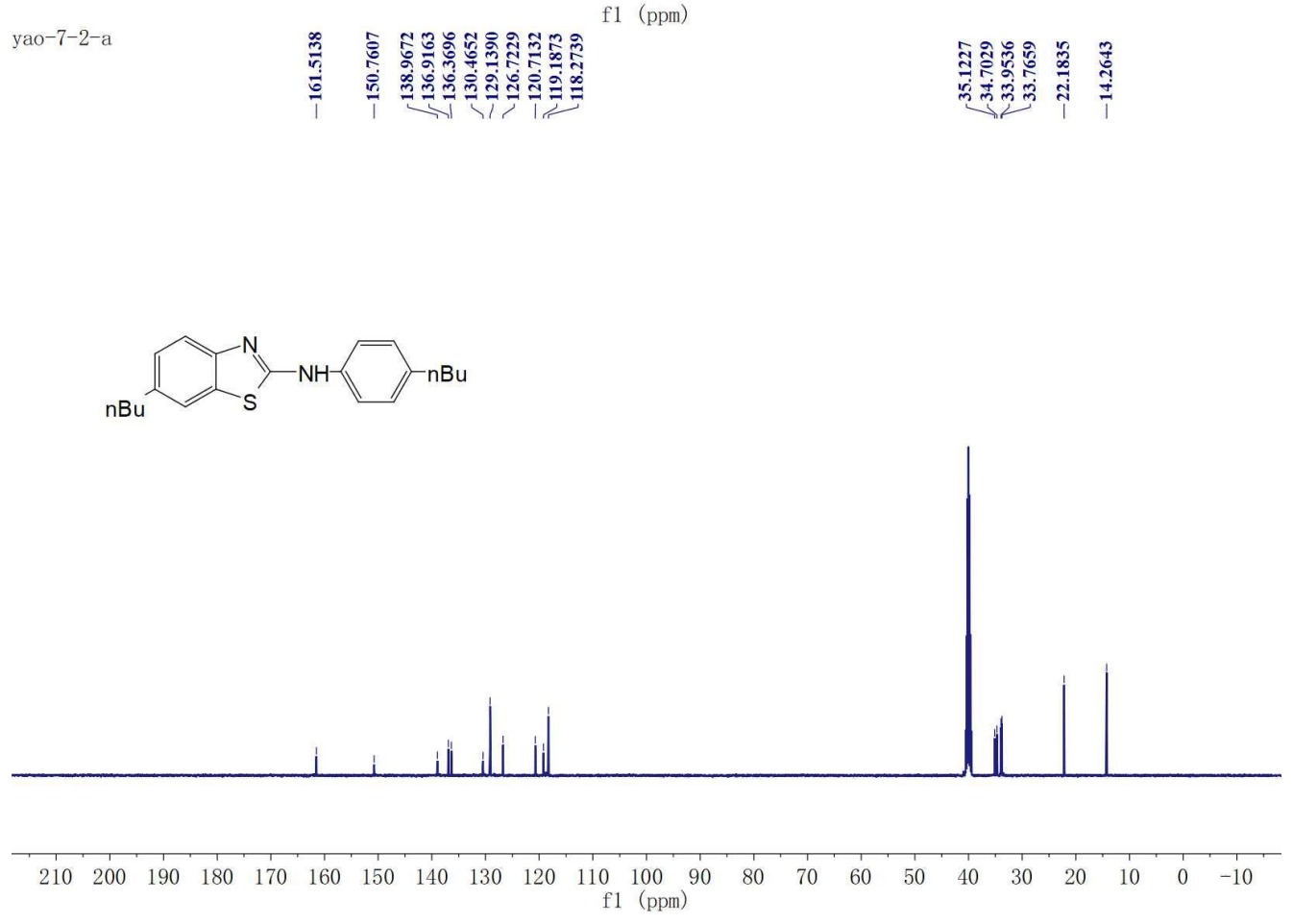




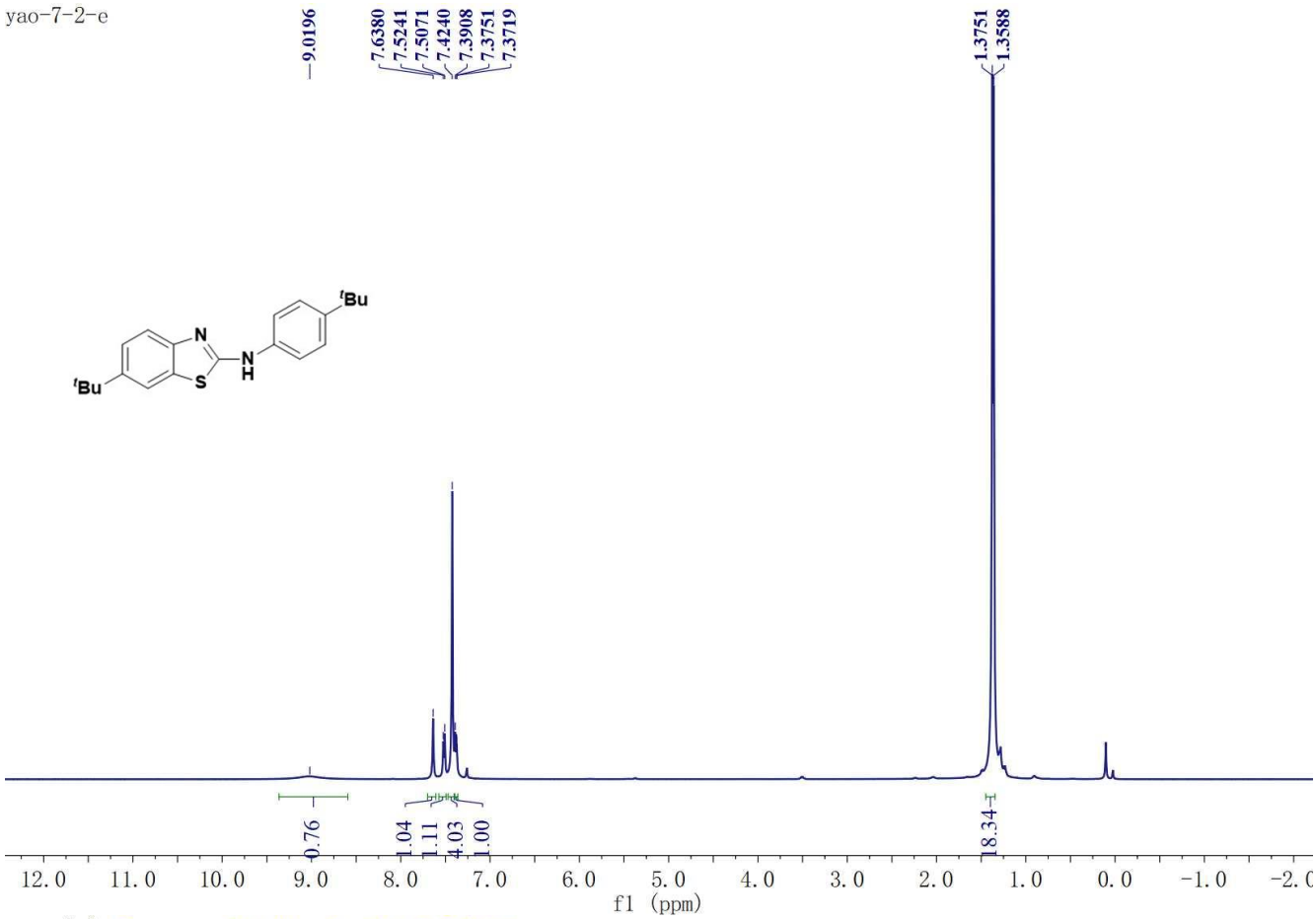


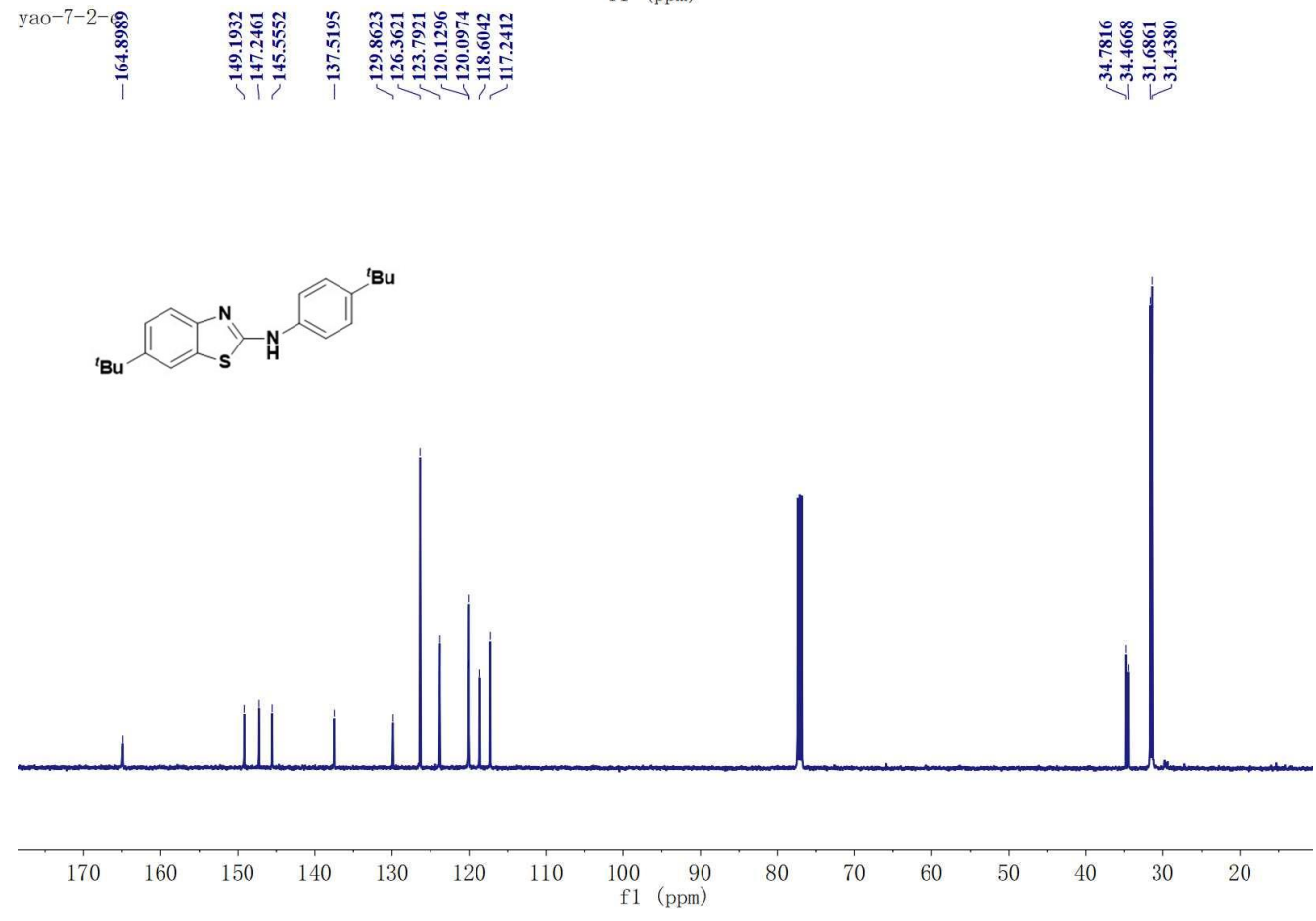
6-Butyl-*N*-(4-butylphenyl)benzo[*d*]thiazol-2-amine (5)



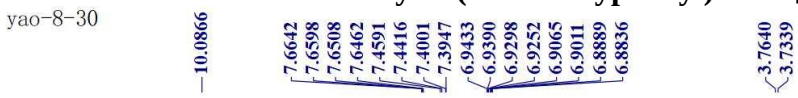


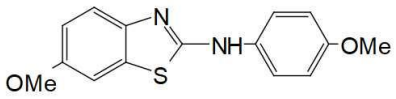
6-(tert-Butyl)-*N*-[4-(tert-butyl)phenyl]benzo[*d*]thiazol-2-amine (6)

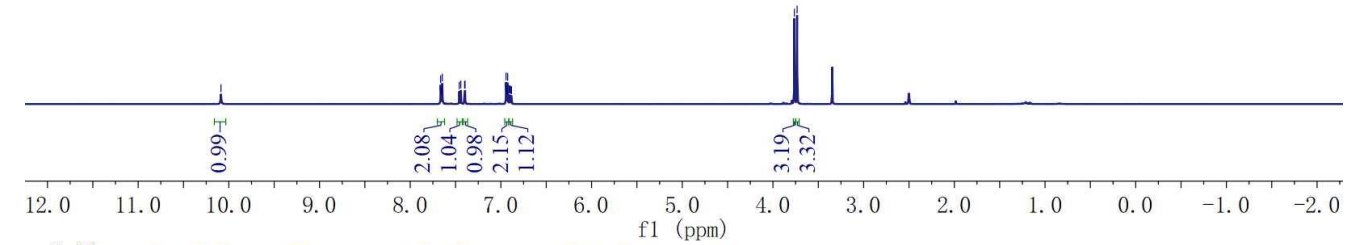


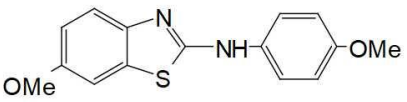


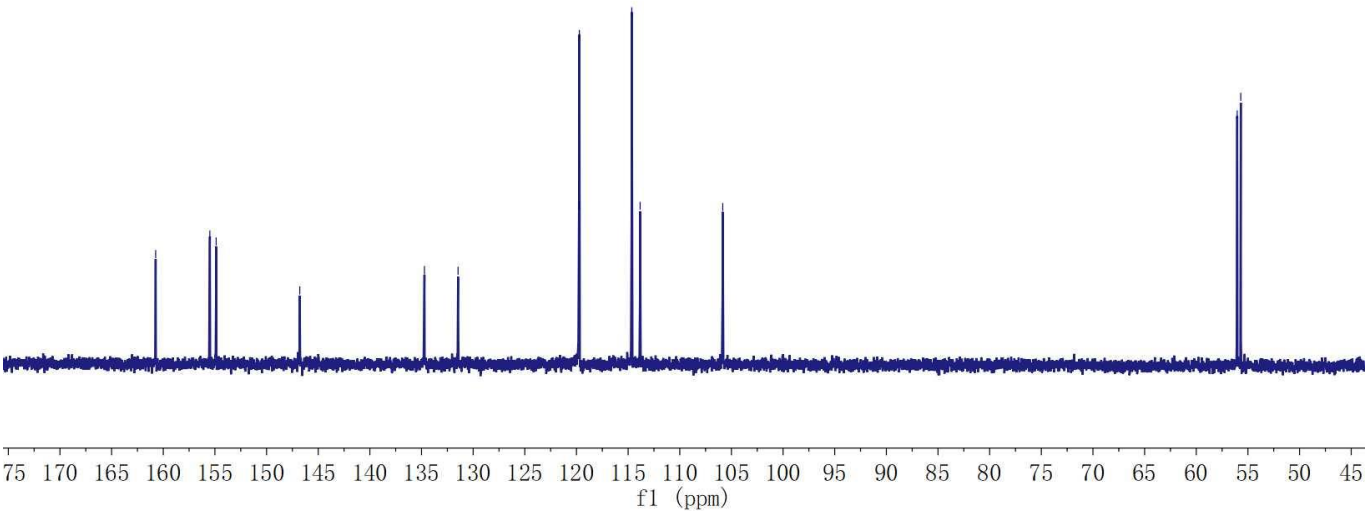
6-Methoxy-*N*-(4-methoxyphenyl)benzo[*d*]thiazol-2-amine (7)



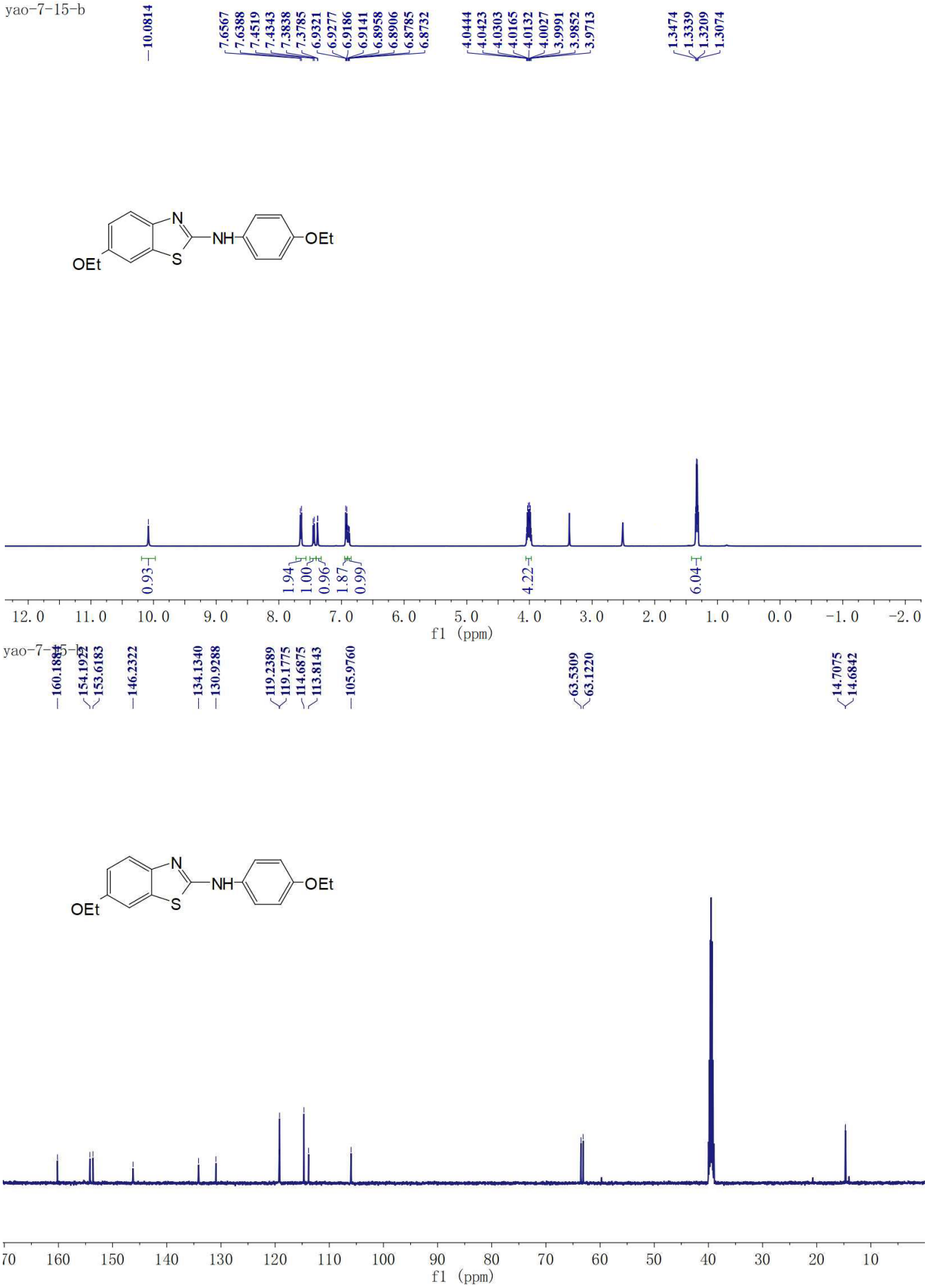




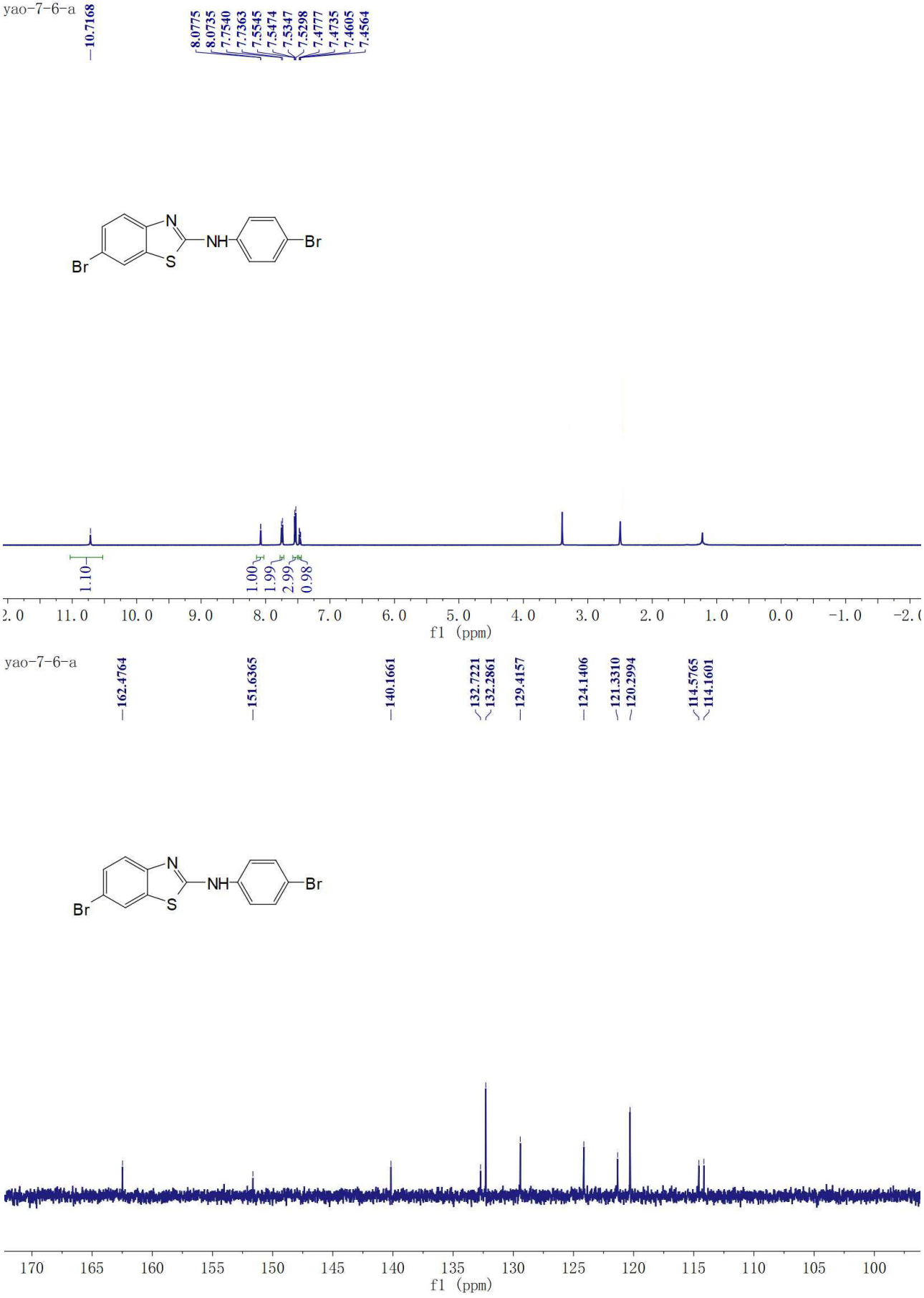




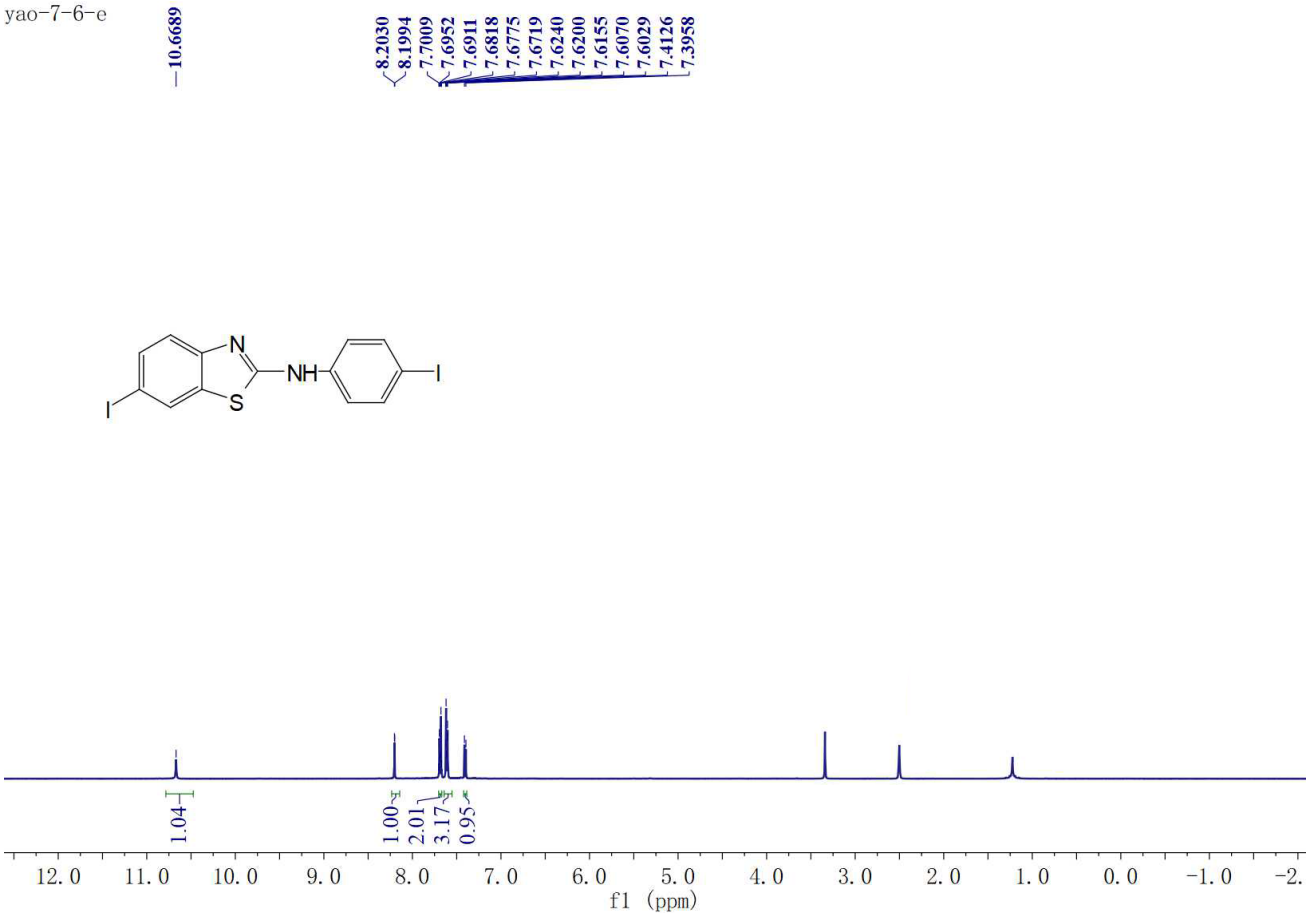
6-Ethoxy-*N*-(4-ethoxyphenyl)benzo[*d*]thiazol-2-amine (8)

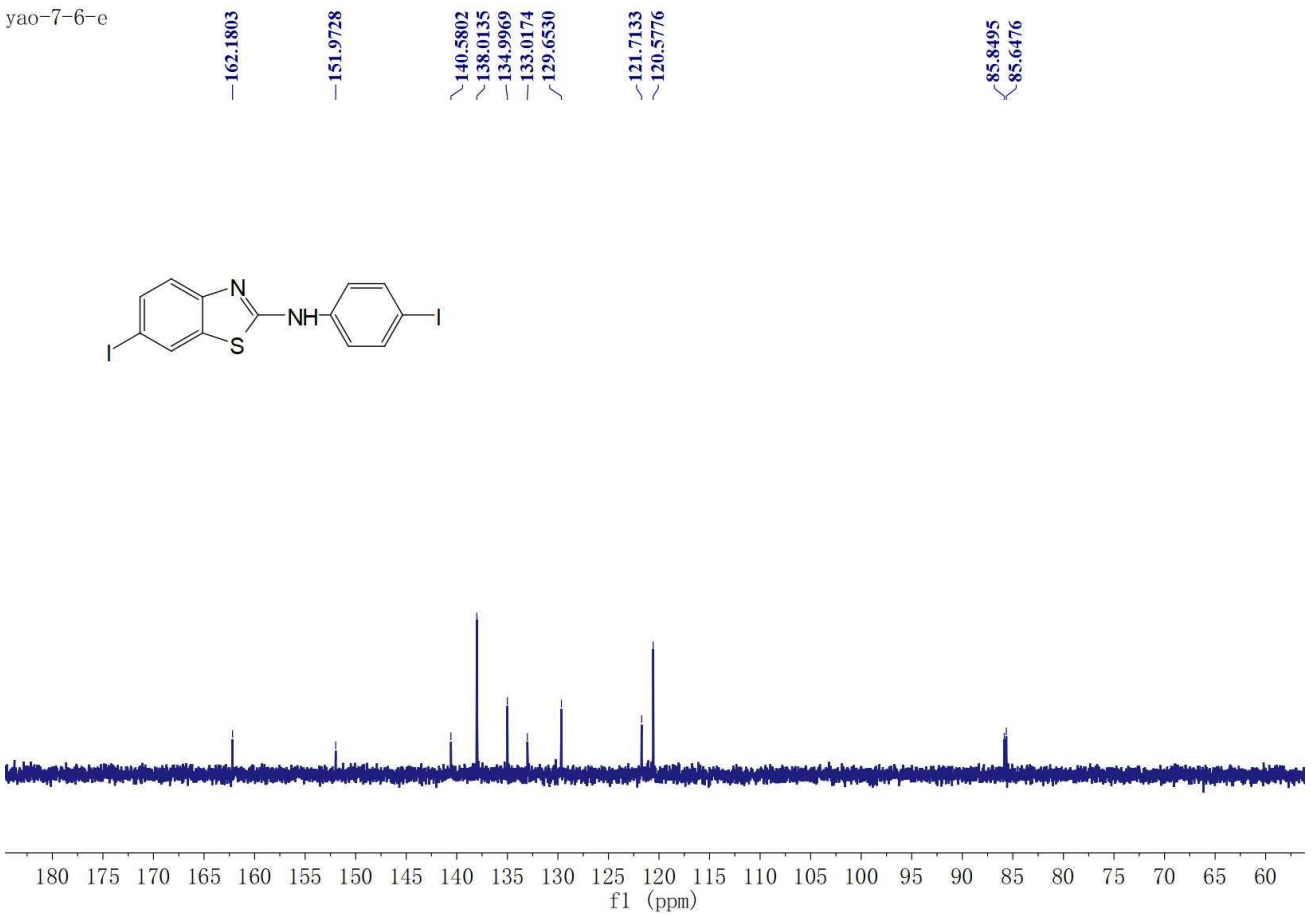


6-Bromo-*N*-(4-bromophenyl)benzo[*d*]thiazol-2-amine (9)

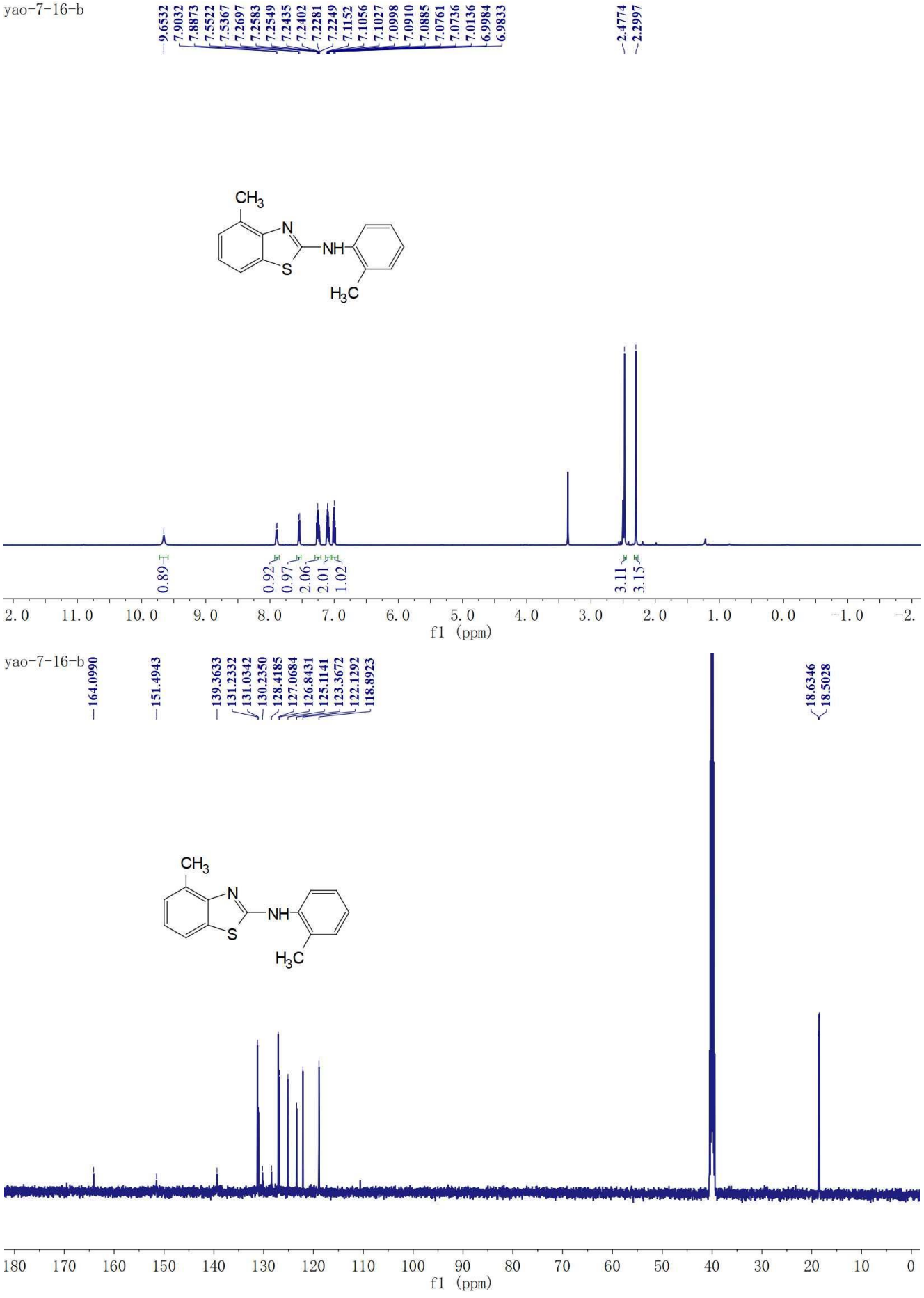


6-Iodo-*N*-(4-iodophenyl)benzo[*d*]thiazol-2-amine (10)

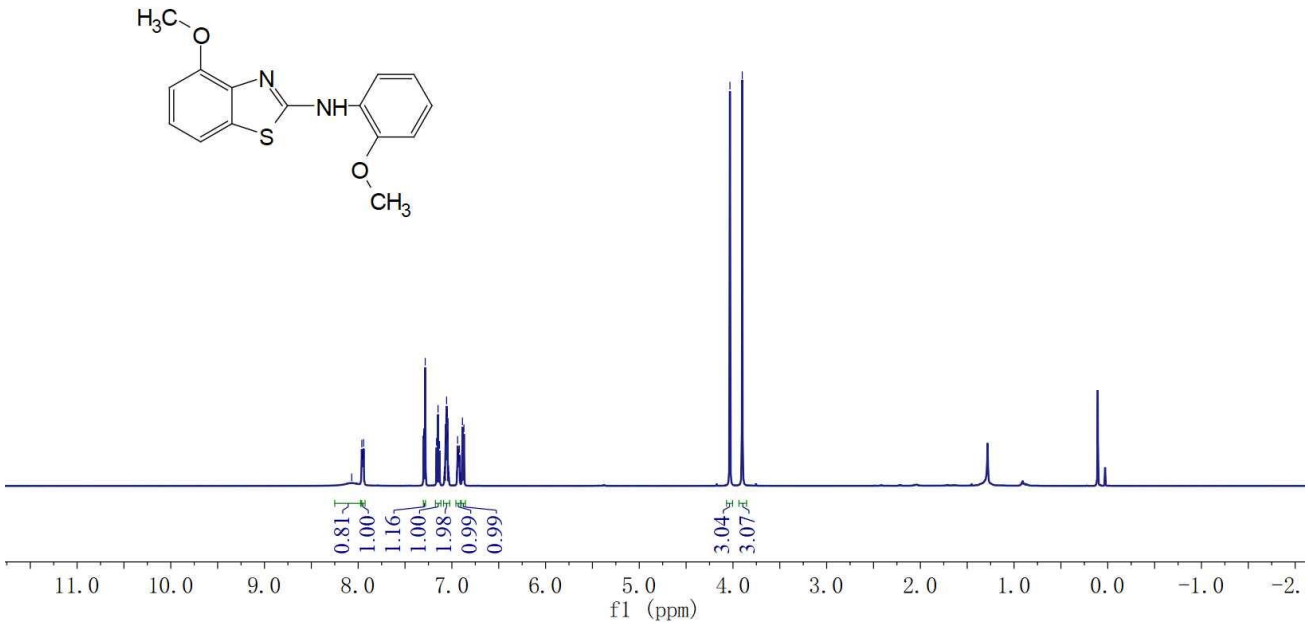


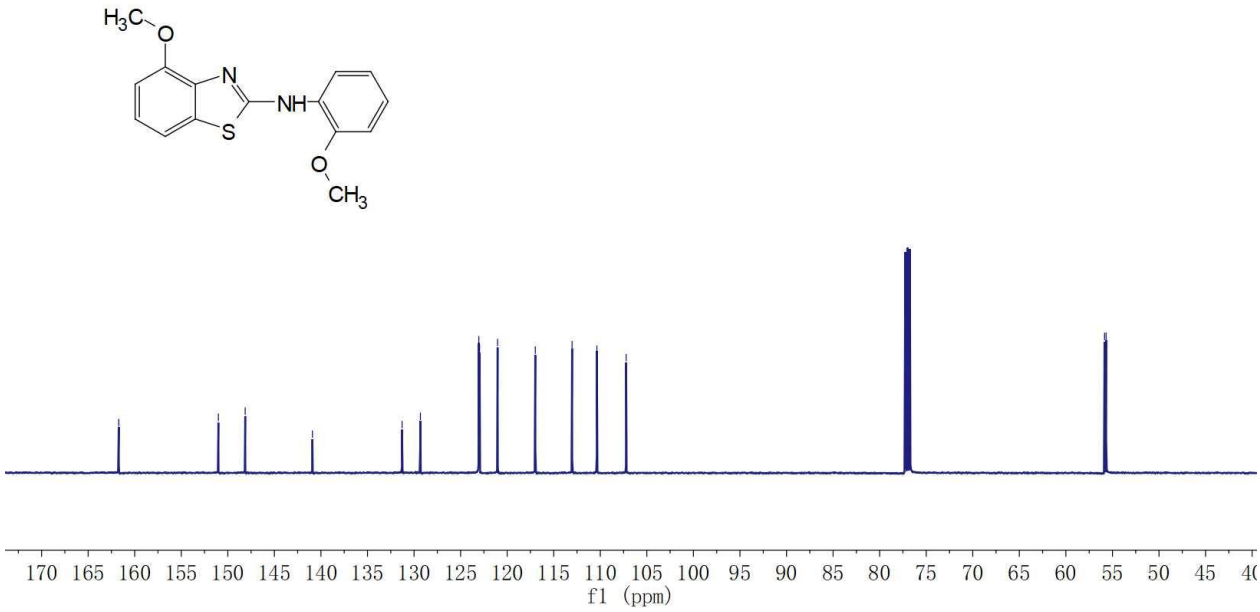


4-Methyl-*N*-(*o*-tolyl)benzo[*d*]thiazol-2-amine (12)

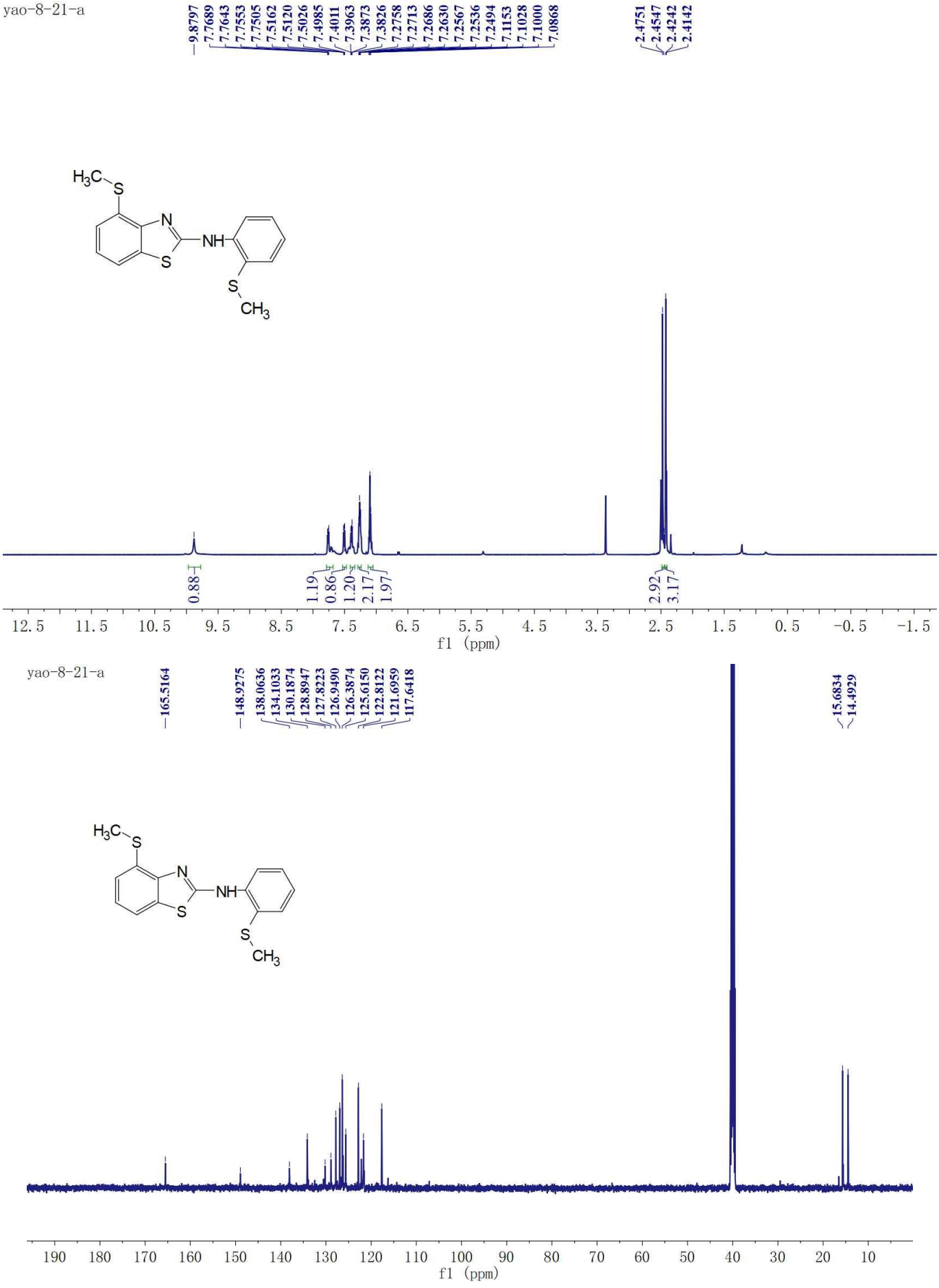


4-Methoxy-*N*-(2-methoxyphenyl)benzo[*d*]thiazol-2-amine (13)

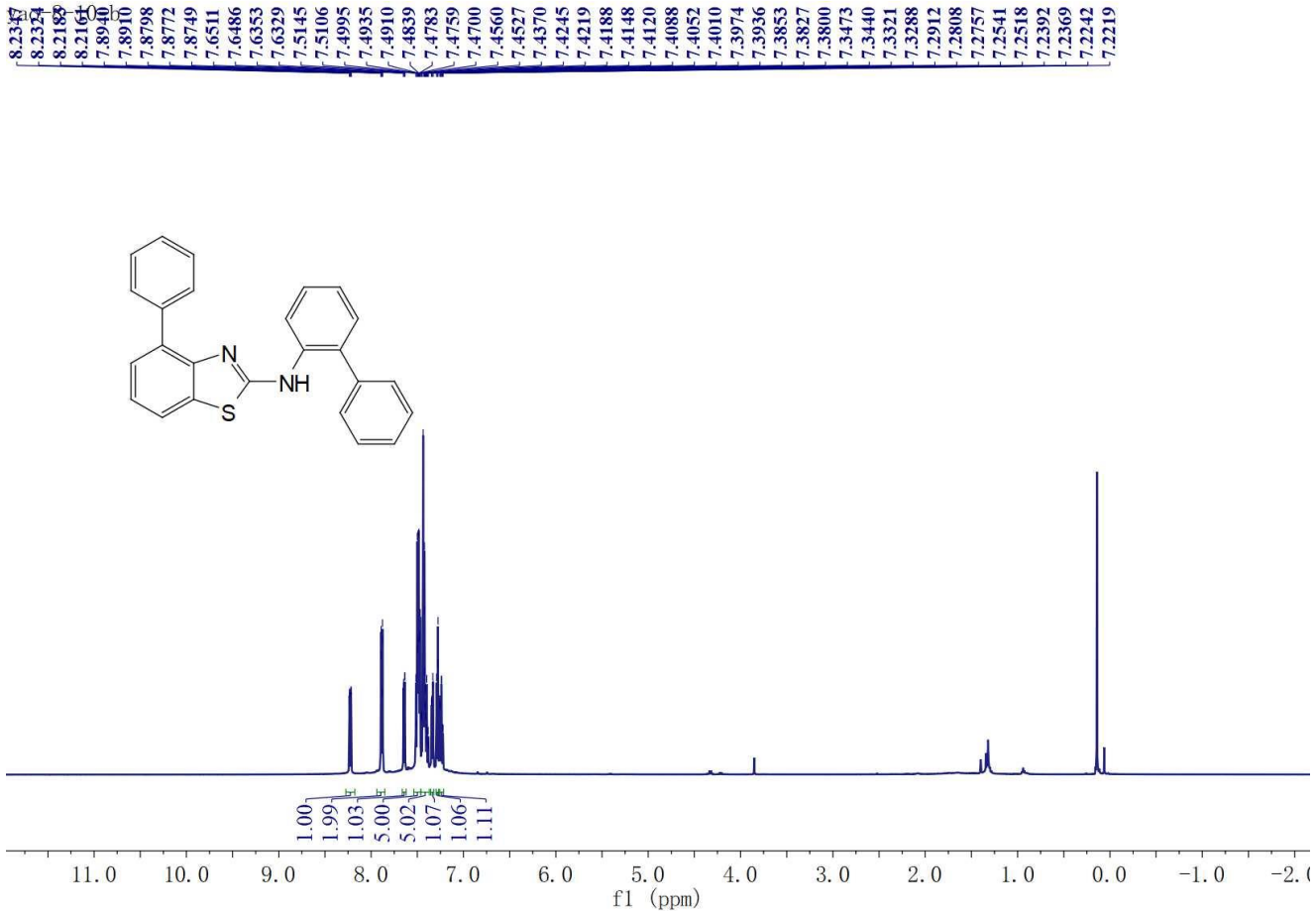


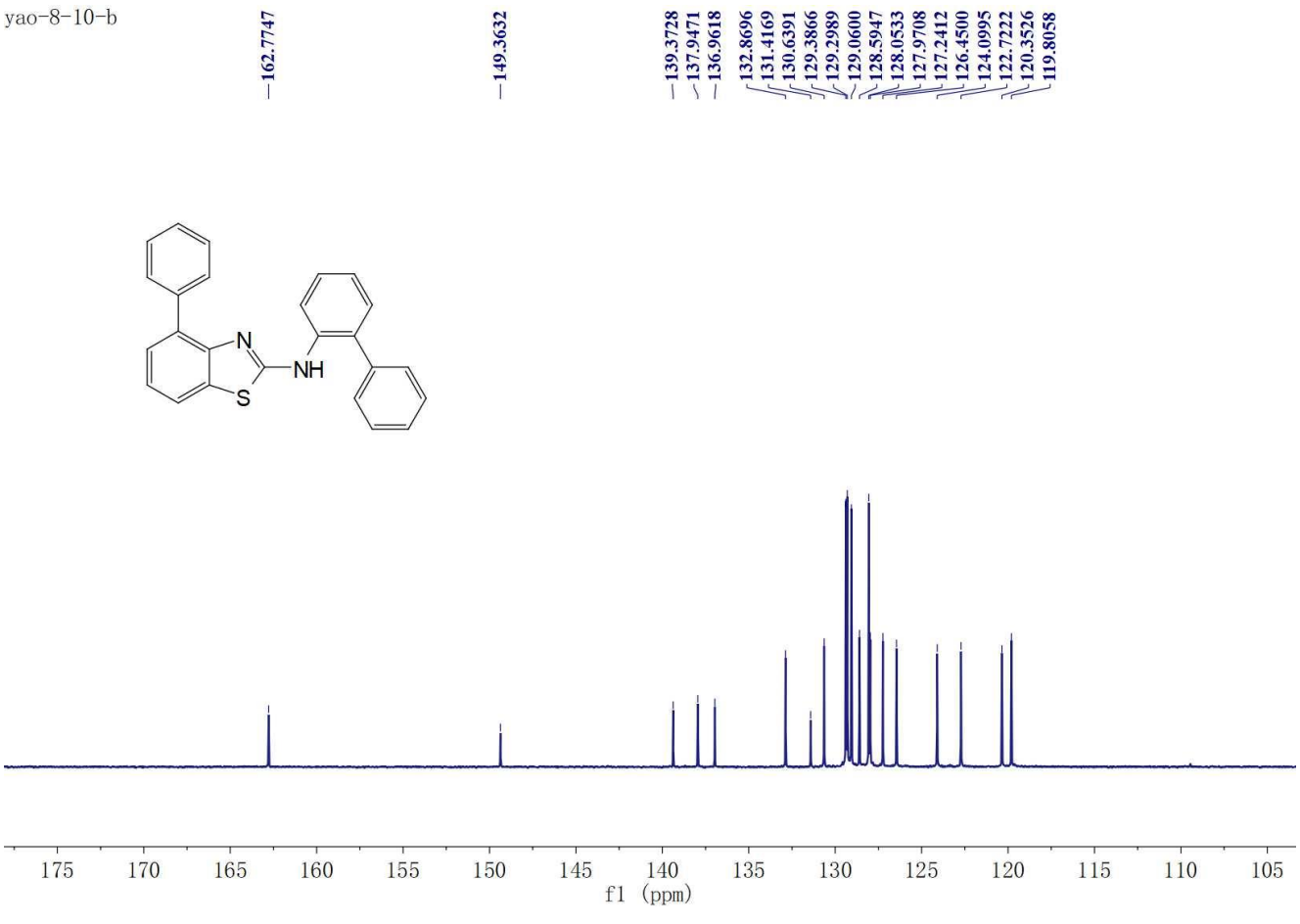


4-(Methylthio)-*N*-(3-(methylthio)phenyl)benzo[*d*]thiazol-2-amine (14)

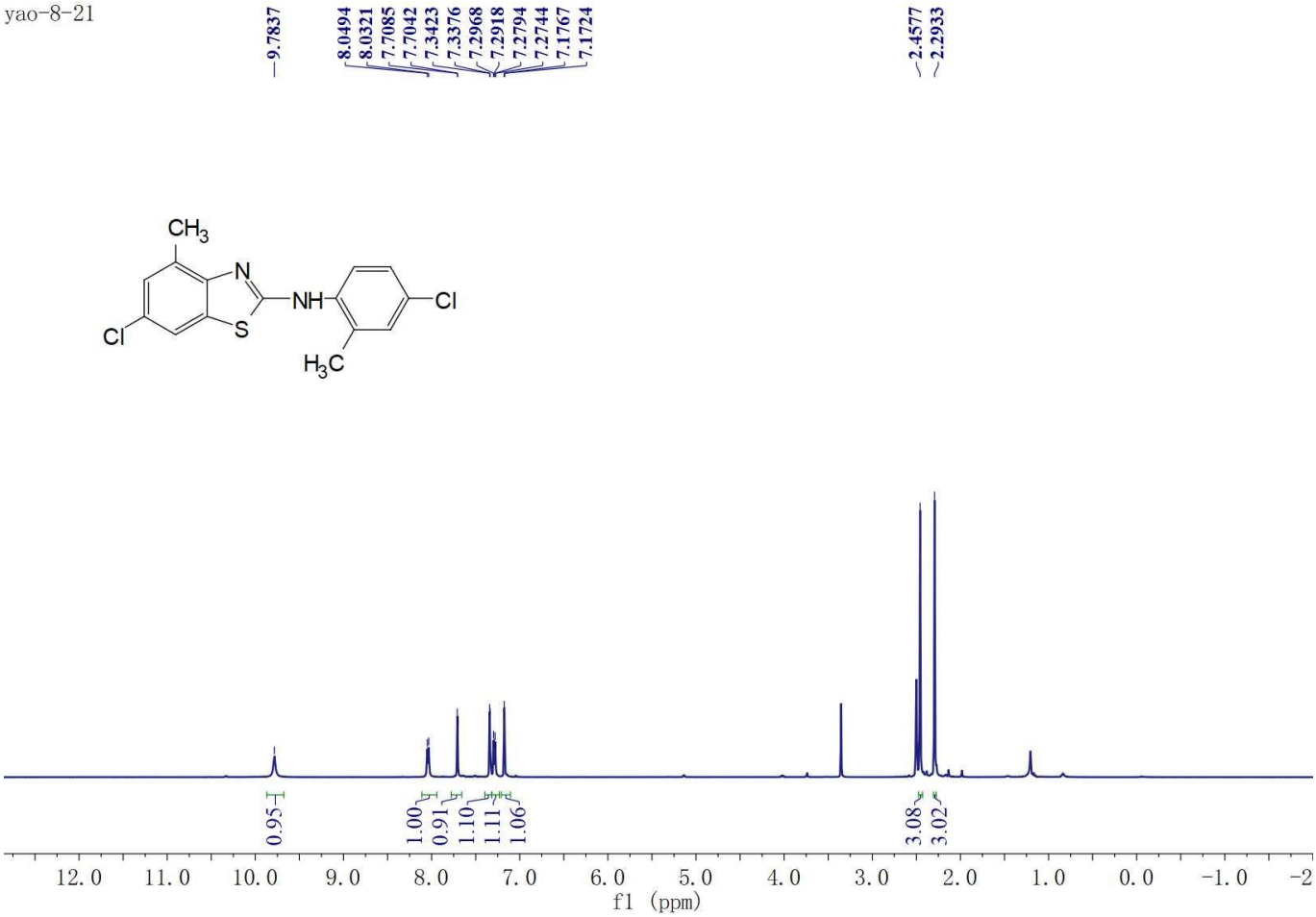


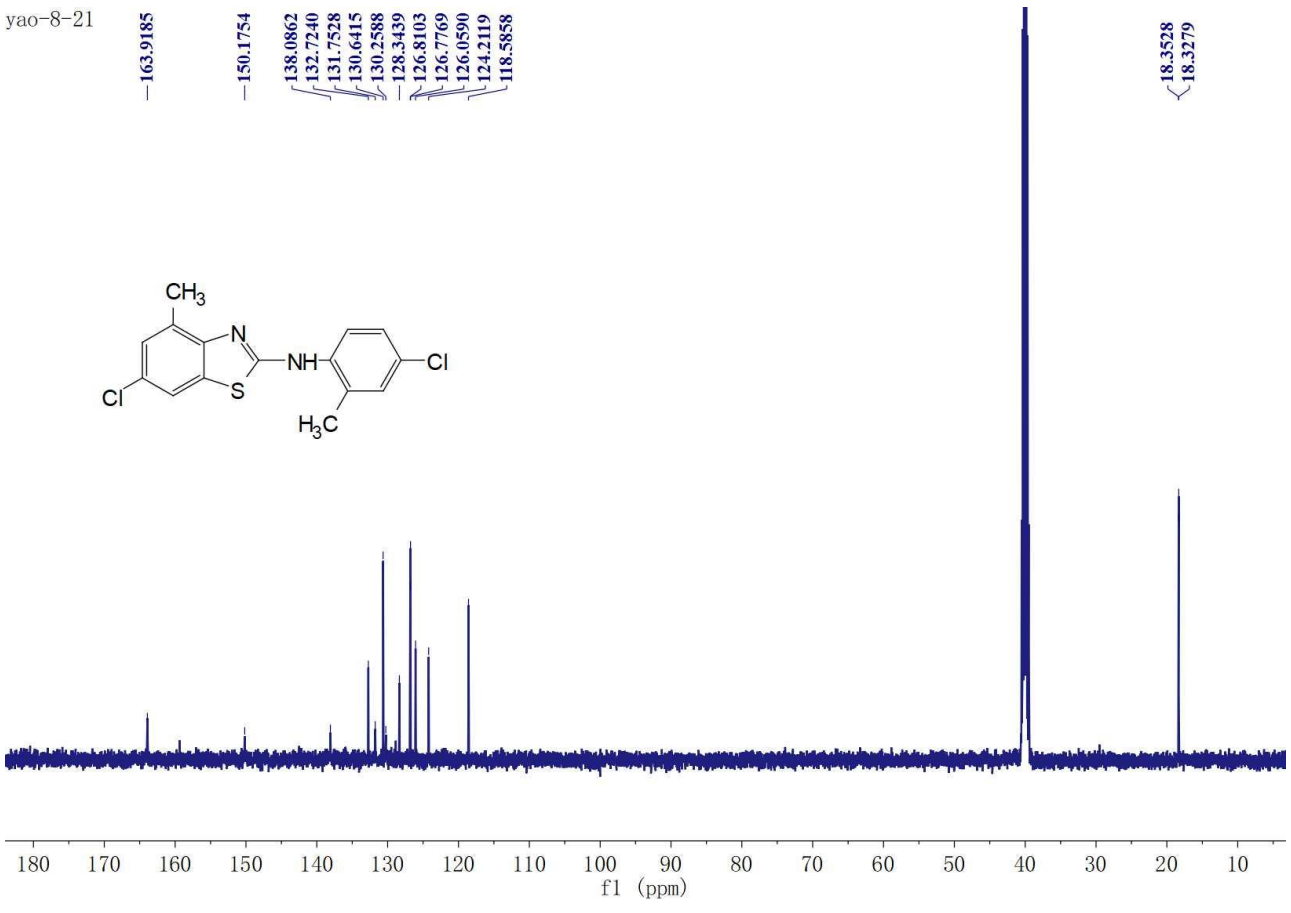
N-(Biphenyl-2-yl)-4-phenylbenzo[*d*]thiazol-2-amine (15)



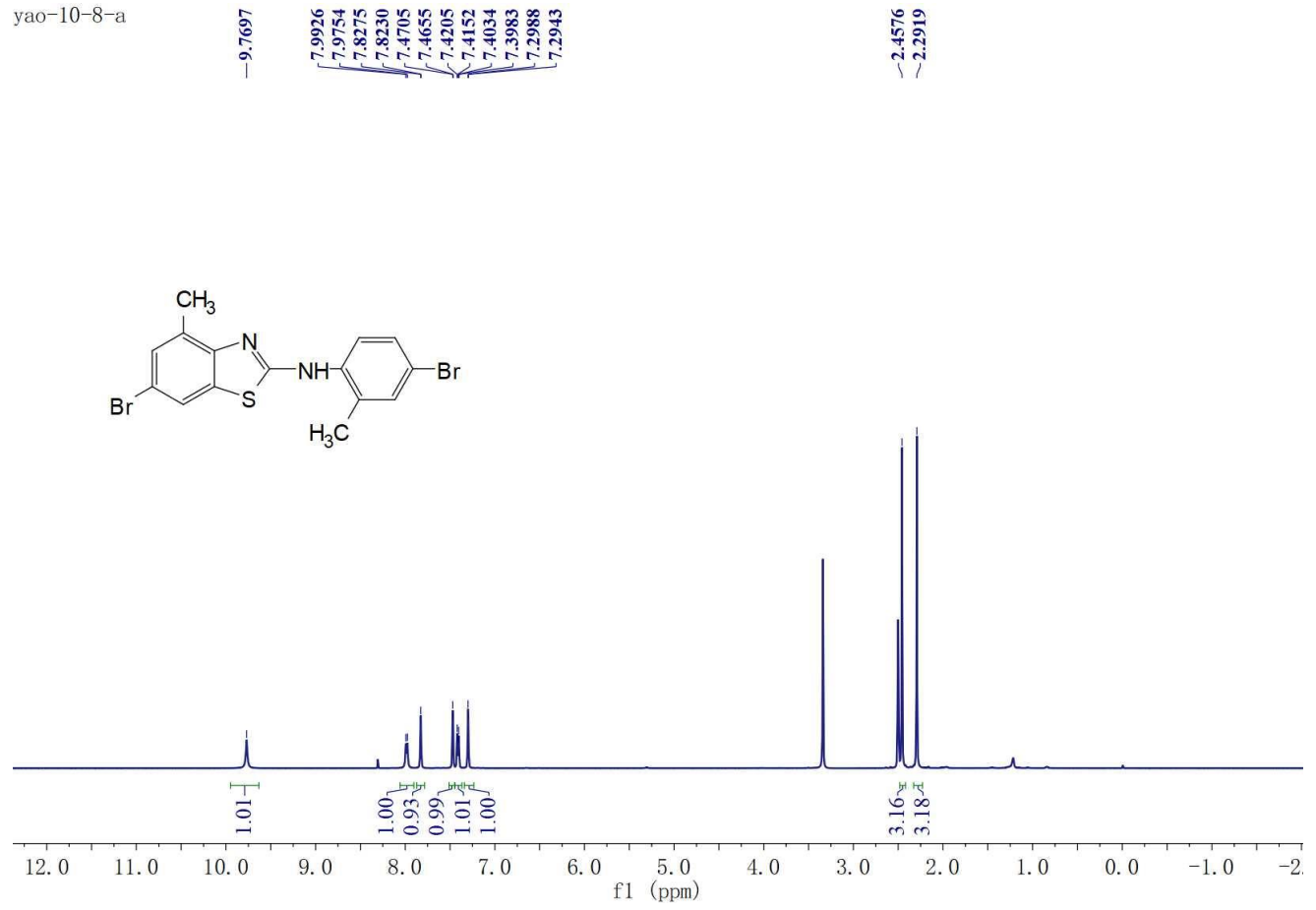


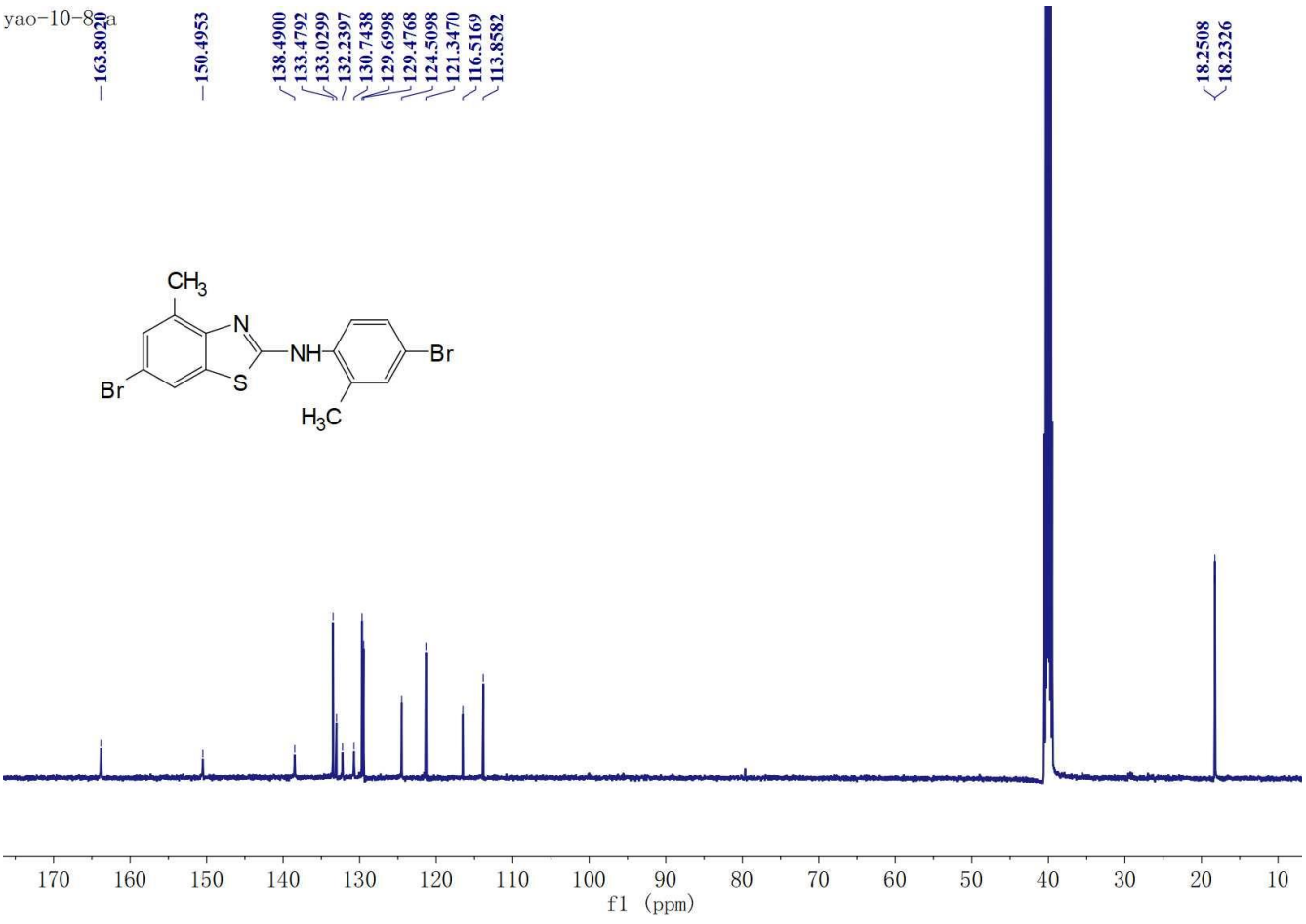
6-Chloro-*N*-(4-chloro-2-methylphenyl)-4-methylbenzo[*d*]thiazol-2-amine (16)



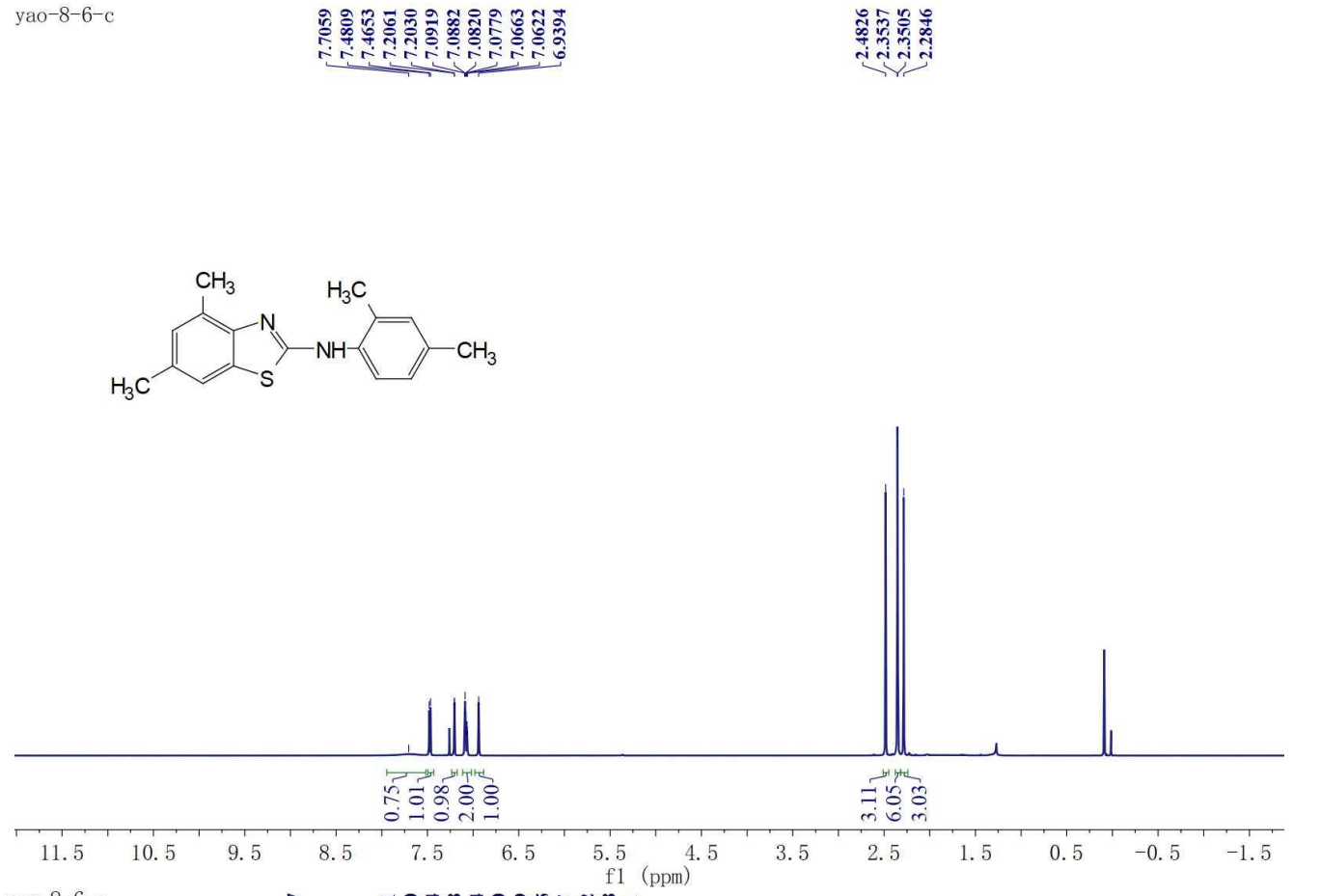


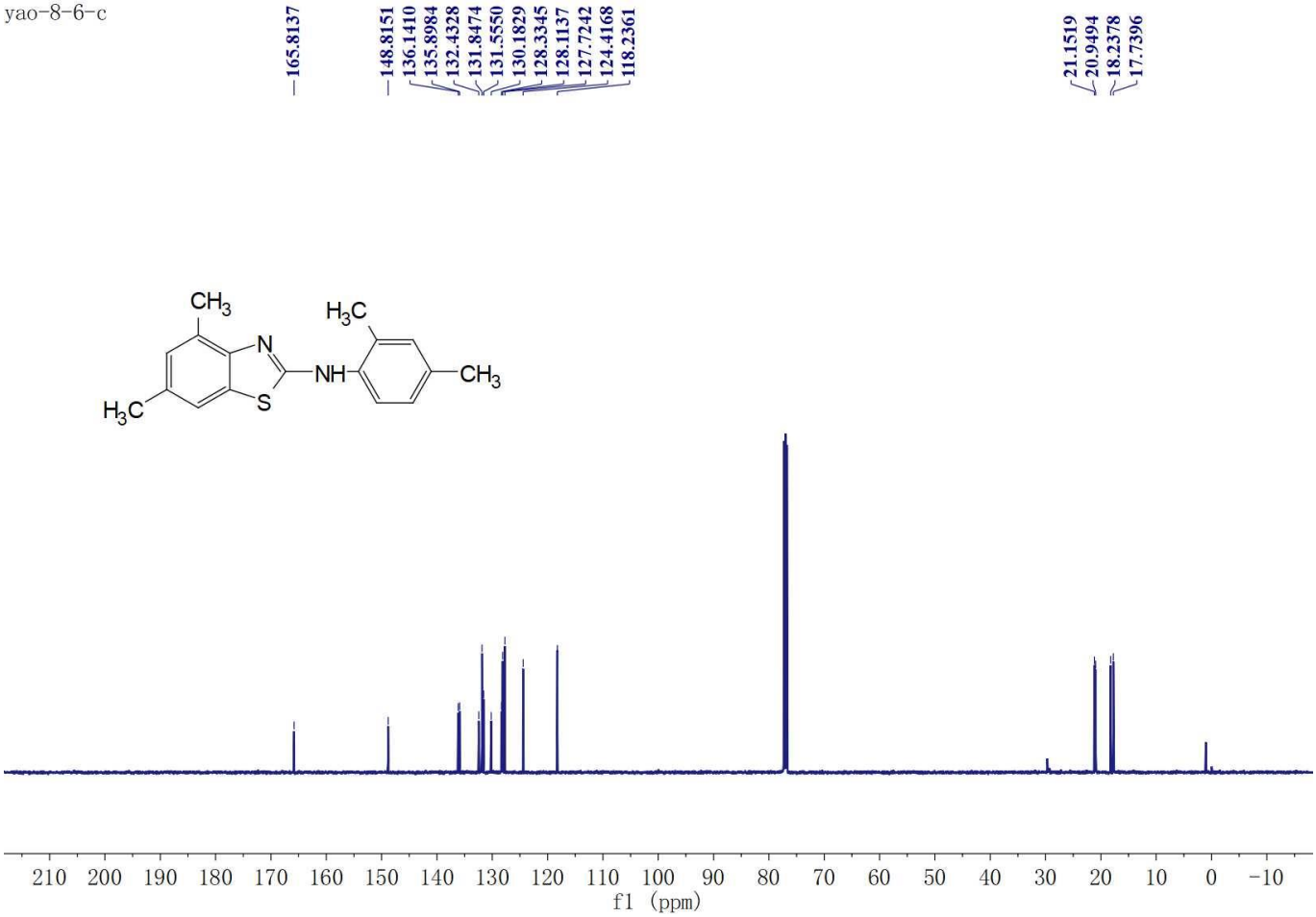
6-Bromo-*N*-(4-bromo-2-methylphenyl)-4-methylbenzo[*d*]thiazol-2-amine (17)



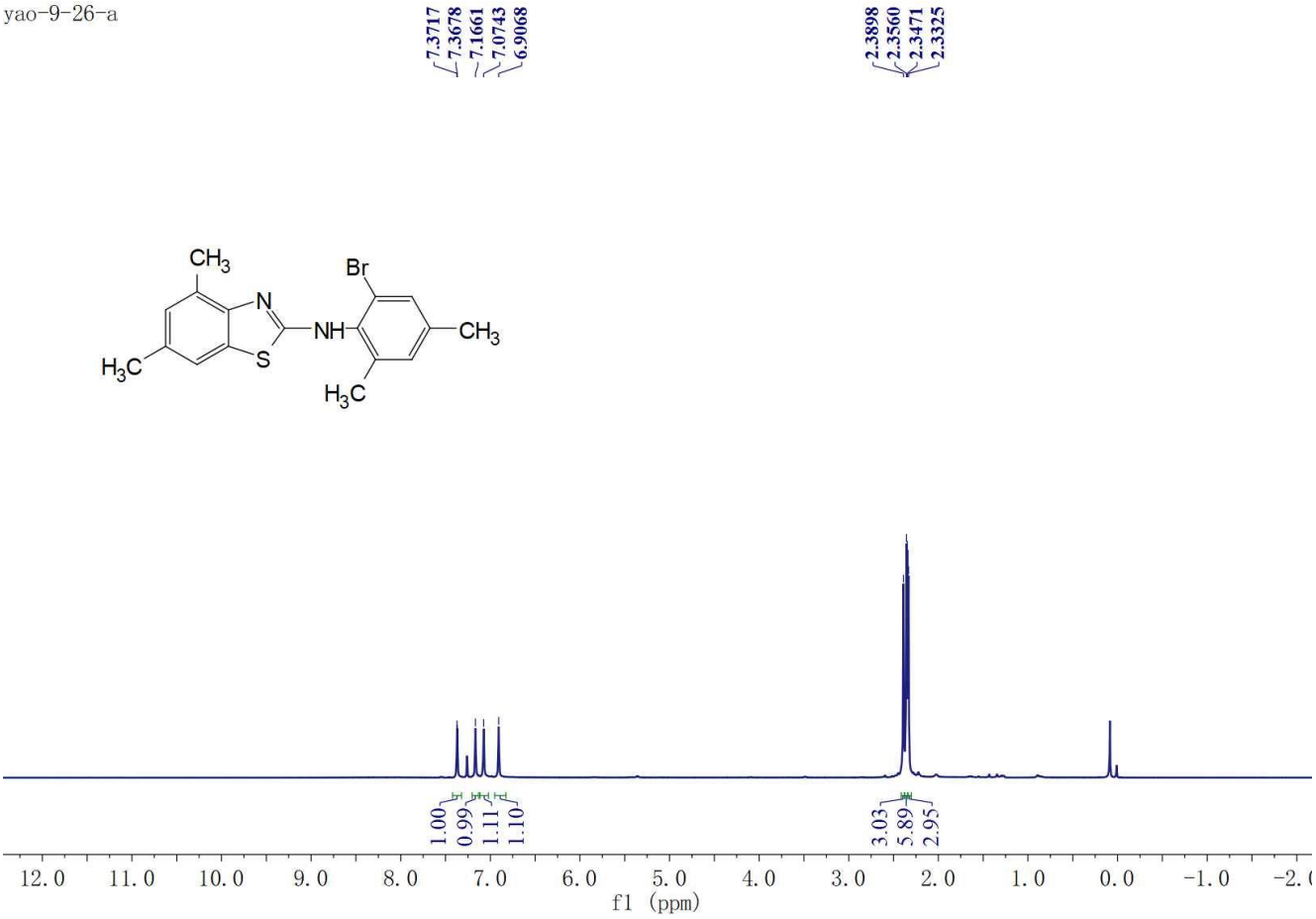


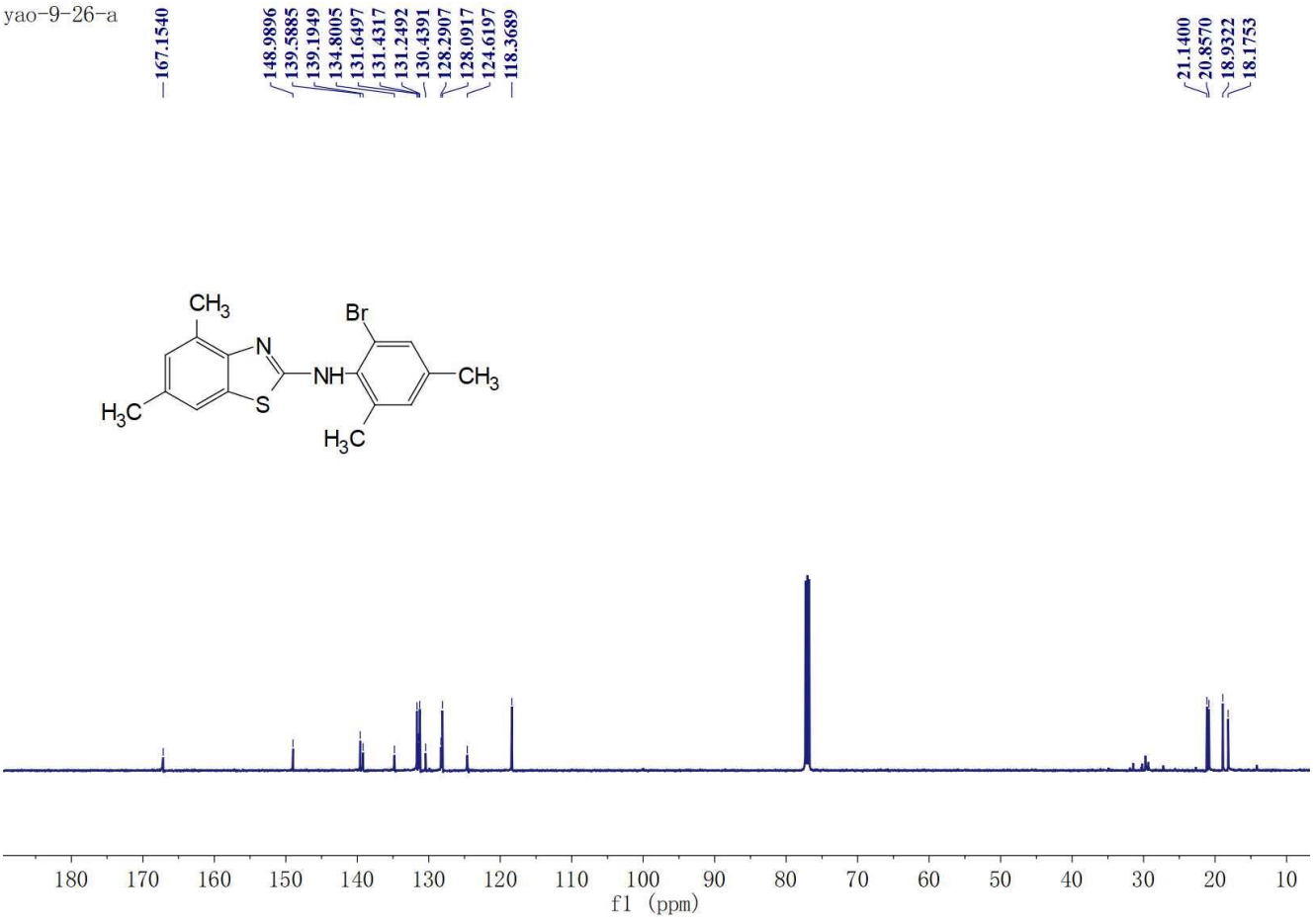
N-(2,4-dimethylphenyl)-4,6-dimethylbenzo[*d*]thiazol-2-amine (18)



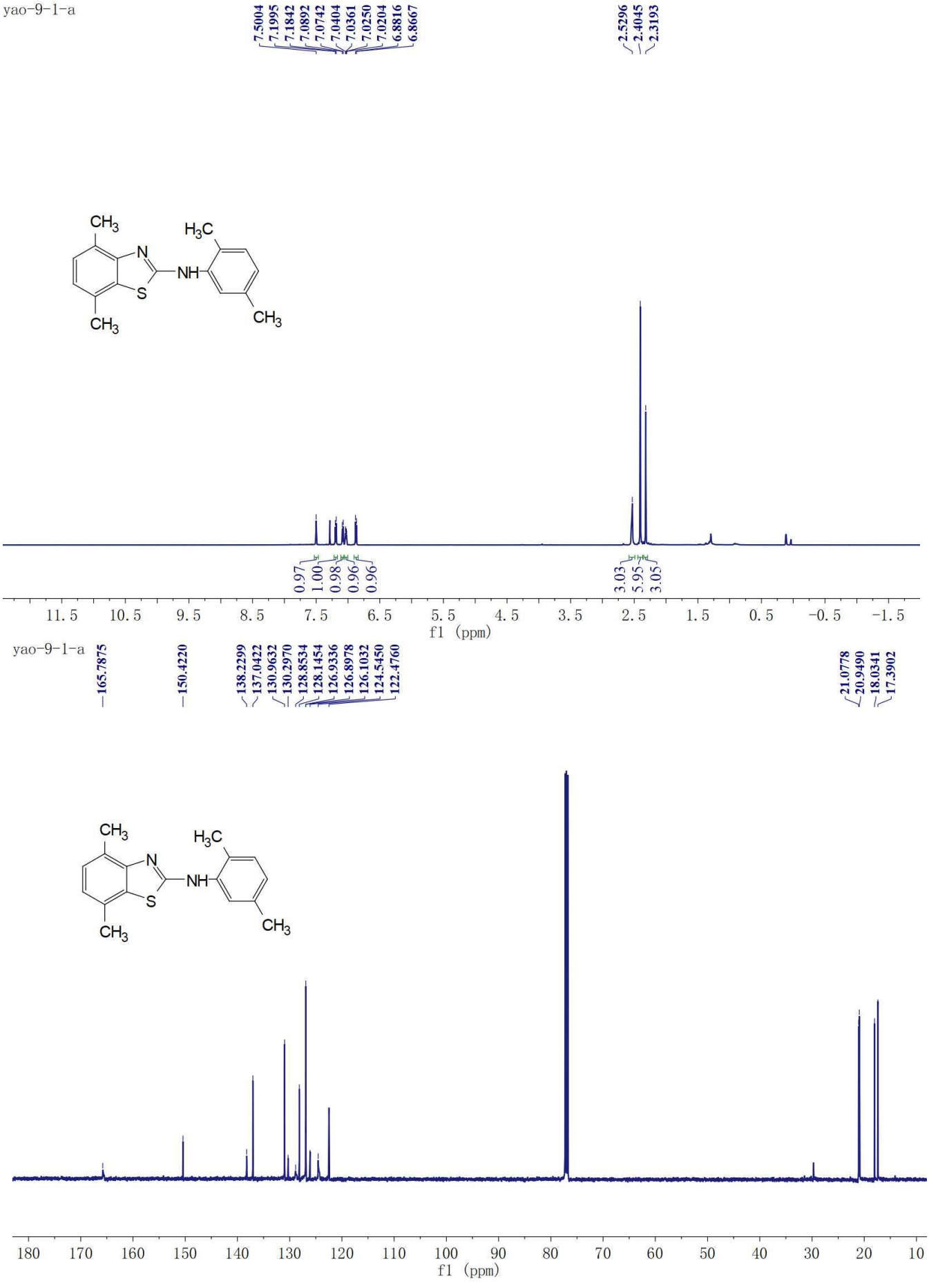


N-(2-Bromo-4,6-dimethylphenyl)-4,6-dimethylbenzo[*d*]thiazol-2-amine (19)

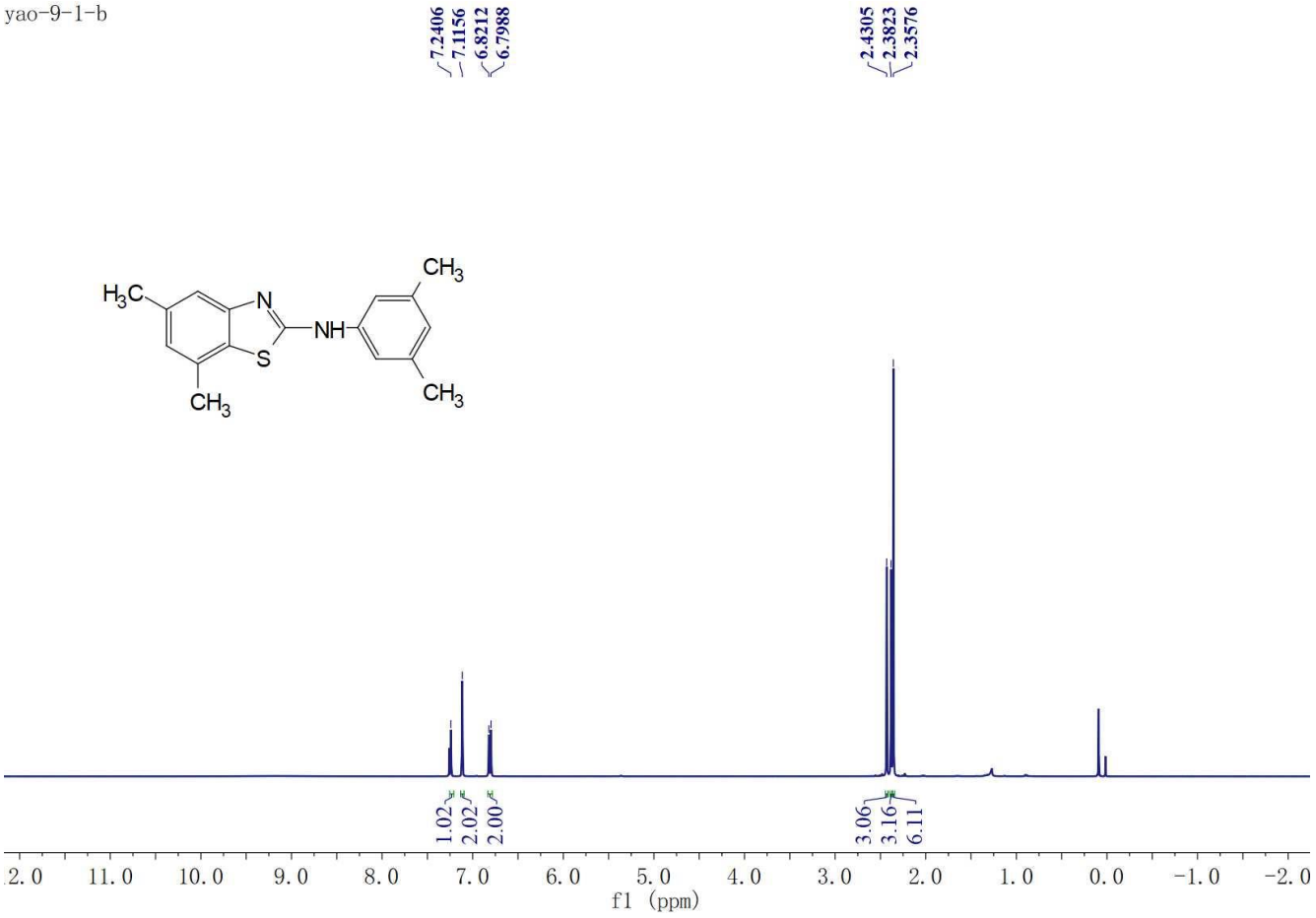


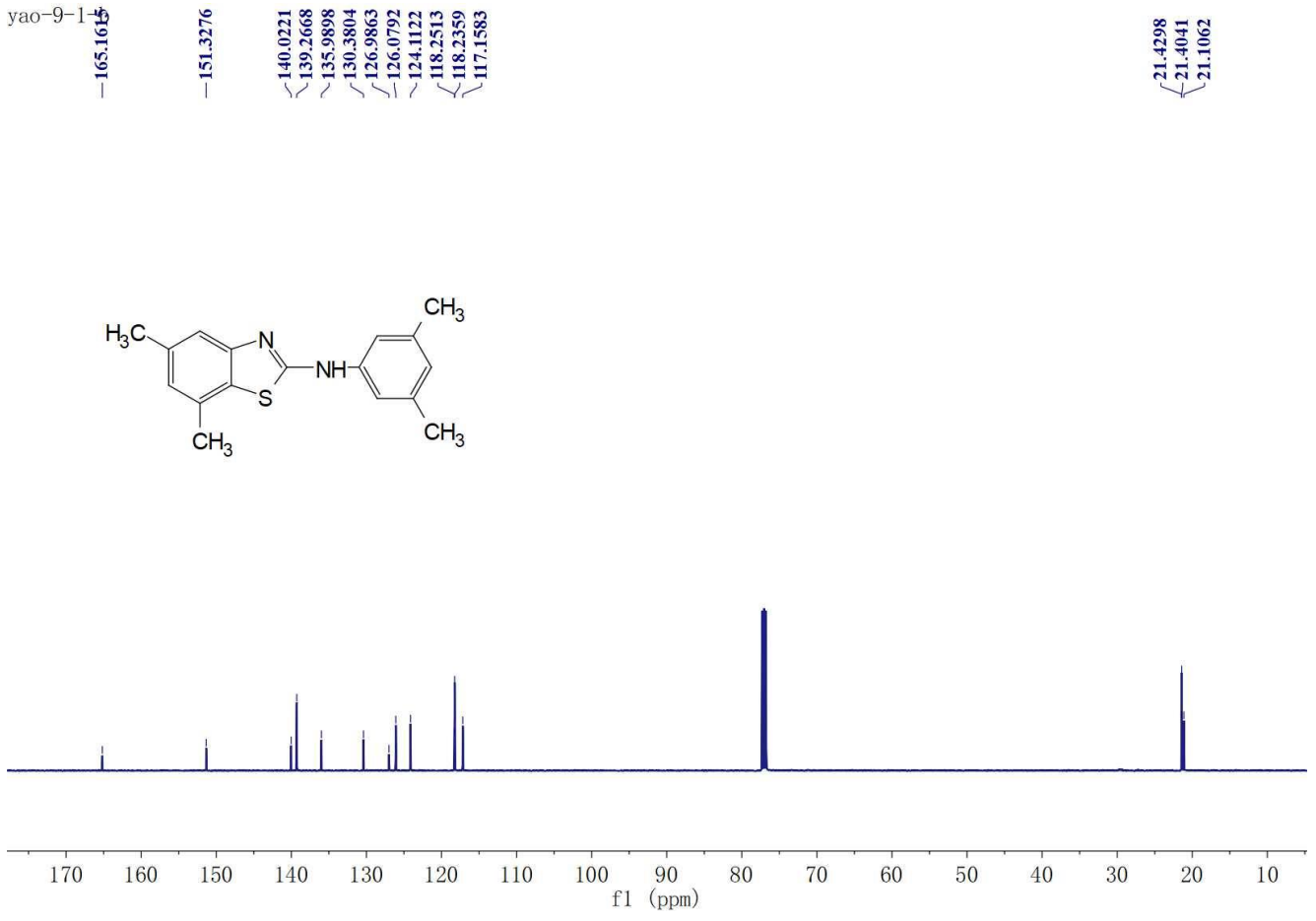


N-(2,5-dimethylphenyl)-4,7-dimethylbenzo[*d*]thiazol-2-amine (20)

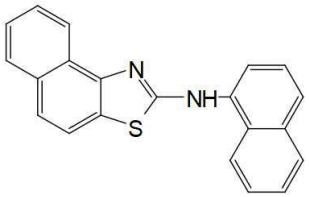


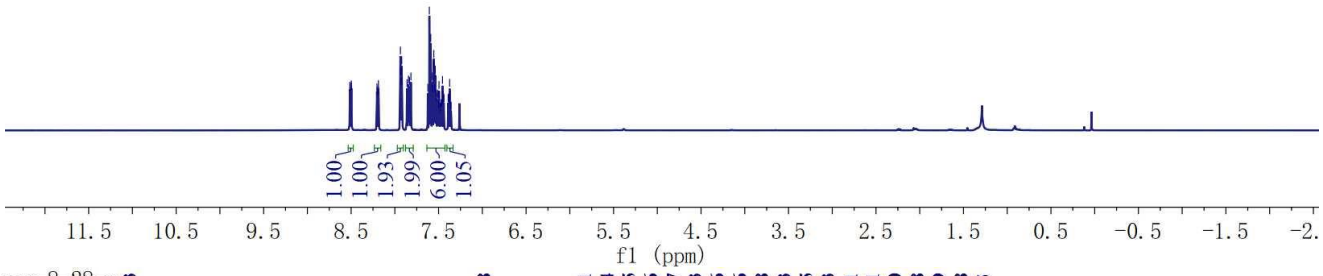
N-(2,5-dimethylphenyl)-4,7-dimethylbenzo[*d*]thiazol-2-amine (21)

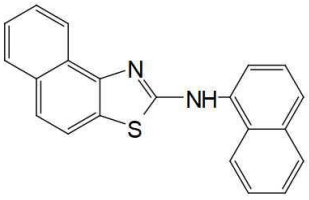


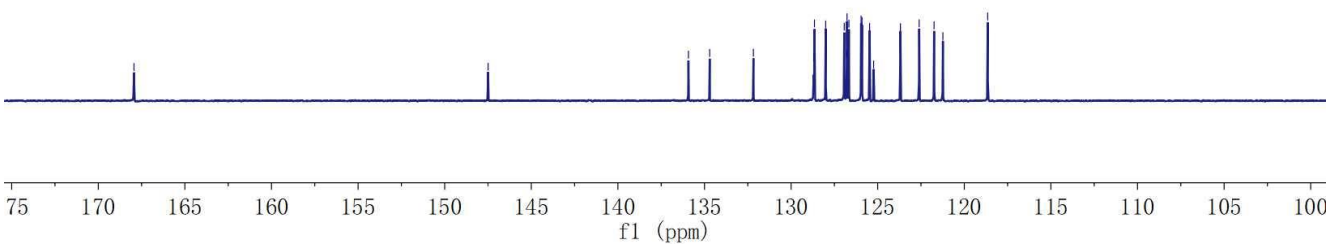


N-(Naphthalen-1-yl)naphtho[1,2-*d*]thiazol-2-amine (22)









6-Methyl-*N*-(4-nitrophenyl)benzo[*d*]thiazol-2-amine (23)