

Supporting Information

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

Guangkai Yao,^{a,c} Bing-Feng Wang,^{a,b} Shuai Yang,^{a,c} Zhi-Xiang Zhang,^{a,c} Han-Hong Xu,^{a,c*} and Ri-Yuan Tang^{a,b*}

^a Key Laboratory of Natural Pesticide and Chemical Biology, Ministry of Education, South China Agricultural University, Guangzhou510642, China;

^b Department of Applied Chemistry, College of Materials and Energy, South China Agricultural University, Guangzhou510642, China;

^c State Key Laboratory for Conservation and Utilization of Subtropical Agro-Bioresources, South China Agricultural University, Guangzhou 510642, China;

* Correspondence: rytang@scau.edu.cn (R-Y.T.); hhxu@scau.edu.cn (H-H.X.); Tel.: +86-20-8528-5127(H-H.X.)

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(A) General information

All reagents were obtained from commercial sources and used as received. All reactions were carried out with flame-dried glassware using standard Schlenk techniques under an atmosphere of nitrogen. ^1H and ^{13}C NMR spectra were measured on a Bruker Avance 500 instrument (500 MHz for ^1H , 126 MHz for ^{13}C NMR spectroscopy) using CDCl_3 and $\text{DMSO}-d_6$ as the solvent and calibrated using residual deuterated solvents as an internal reference (CDCl_3 : δ 7.26 ppm for ^1H NMR, δ 77.16 ppm for ^{13}C NMR; $\text{DMSO}-d_6$: δ 2.50 ppm for ^1H 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

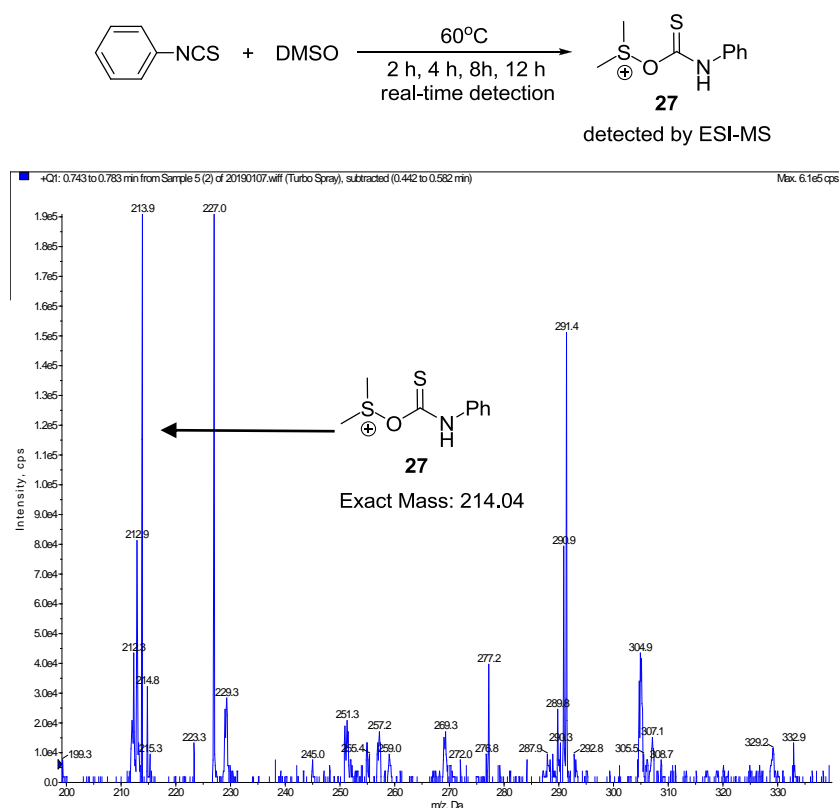


Figure S1. The real-time ESI-MS detection for intermediate A

(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.

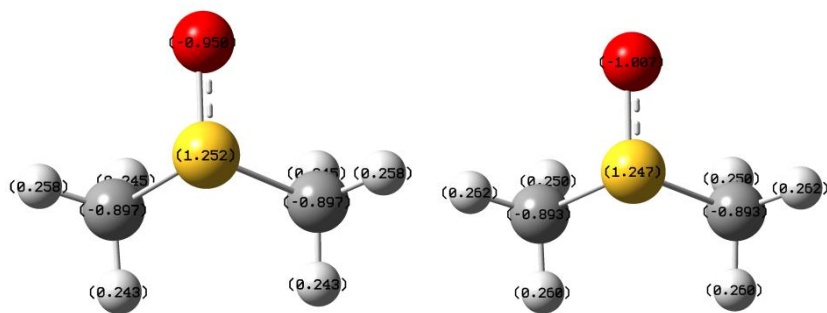


Figure S2. NBO charges of DMSO (Left: gas, Right: DMSO solvent)

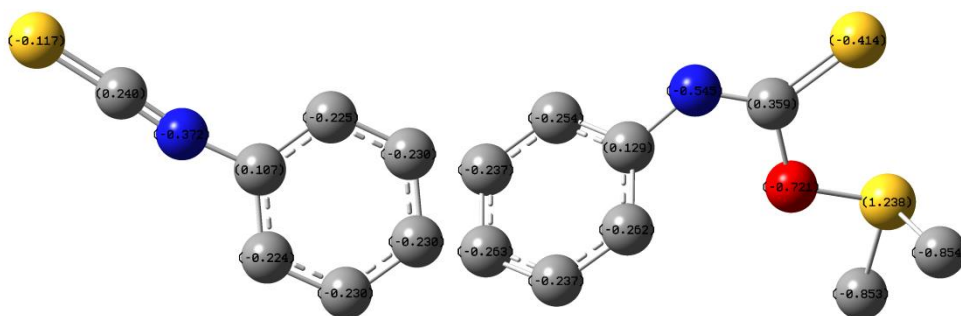
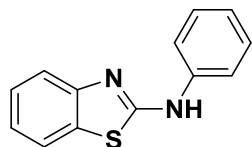


Figure S3. NBO charge of PhNCS and compound A

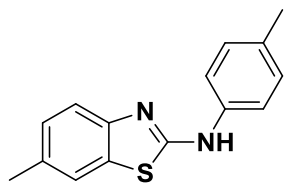
(D) Analytical data for 2-10 and 12-23

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



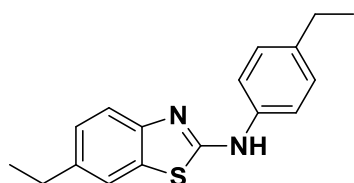
White solid. (37 mg, 82% yield). M.P.: 158-159 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.42 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.24 – 7.11 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 165.1, 151.3, 140.00, 129.8, 129.6, 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]



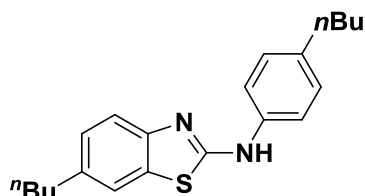
White solid. (39 mg, 76% yield). M.P.: 154-157 °C. ^1H NMR (500 MHz, CDCl_3) δ 9.33 (br, 1H), 7.47 – 7.39 (m, 2H), 7.37 (dd, $J = 8.0$ Hz, 2H), 7.21 (d, $J = 7.8$ Hz, 2H), 7.11 (d, $J = 8.1$ Hz, 1H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.2, 149.3, 137.6, 134.2, 131.8, 130.0, 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)



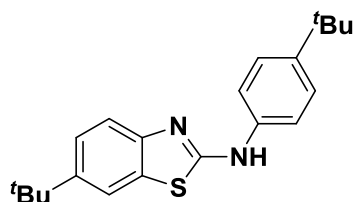
Yellow solid. (44 mg, 78% yield). M.P.: 137-139 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.28 (s, 1H), 7.68 (d, $J = 8.5$ Hz, 2H), 7.60 (s, 1H), 7.49 (d, $J = 8.2$ Hz, 1H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.15 (dd, $J = 8.3$, 1.8 Hz, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 2.60 – 2.53 (m, 2H), 1.19 (dt, $J = 15.4$, 7.6 Hz, 6H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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 $\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 283.1263, found 283.1272.

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



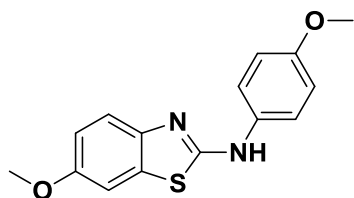
Yellow oil. (55 mg, 81% yield). ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.27 (s, 1H), 7.65 (d, $J = 8.5$ Hz, 2H), 7.57 (s, 1H), 7.46 (d, $J = 8.1$ Hz, 1H), 7.15 (d, $J = 8.2$ Hz, 2H), 7.12 (dd, $J = 8.2$, 1.7 Hz, 1H), 2.61 (t, $J = 7.7$ Hz, 2H), 2.53 (d, $J = 6.7$ Hz, 2H), 1.63 – 1.44 (m, 4H), 1.36 – 1.24 (m, 4H), 0.89 (td, $J = 7.5$, 1.3 Hz, 6H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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 $\text{C}_{21}\text{H}_{27}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 339.1889, found 339.1873.

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



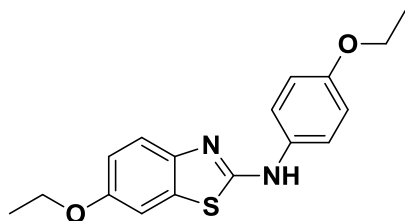
White solid. (57 mg, 84% yield). M.P.: 177-179 °C. ^1H NMR (500 MHz, CDCl_3) δ 9.02 (br, 1H), 7.64 (s, 1H), 7.52 (d, $J = 8.5$ Hz, 1H), 7.42 (s, 4H), 7.40 – 7.35 (m, 1H), 1.37 (d, $J = 8.1$ Hz, 18H). ^{13}C NMR (126 MHz, CDCl_3) δ 164.9, 149.2, 147.3, 145.6, 137.5, 129.9, 126.4, 123.8, 120.1, 120.1, 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 $\text{C}_{21}\text{H}_{26}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 339.1890, found 339.1891.

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



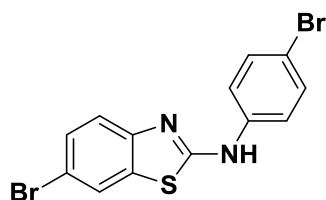
Yellow solid. (43 mg, 75% yield). M.P.: 157-159 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.09 (s, 1H), 7.71 – 7.60 (m, 2H), 7.45 (d, $J = 8.7$ Hz, 1H), 7.40 (d, $J = 2.7$ Hz, 1H), 6.96 – 6.92 (m, 2H), 6.90 (dd, $J = 8.8, 2.7$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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 $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{S}$ [$\text{M}+\text{H}$] $^+$: calcd. 287.0849, found 287.0851.

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



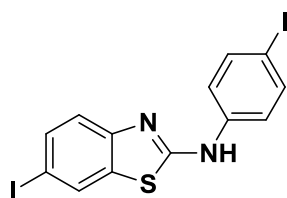
Yellow solid. (48 mg, 77% yield). M.P.: 146-148 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.08 (s, 1H), 7.65 (d, $J = 9.0$ Hz, 2H), 7.44 (d, $J = 8.8$ Hz, 1H), 7.38 (d, $J = 2.6$ Hz, 1H), 6.97 – 6.90 (m, 2H), 6.88 (dd, $J = 8.7, 2.6$ Hz, 1H), 4.01 (dq, $J = 15.7, 7.0$ Hz, 4H), 1.33 (q, $J = 6.7$ Hz, 6H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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)



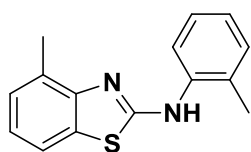
Yellow solid. (29 mg, 38% yield). M.P.: 225-227 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.72 (s, 1H), 8.08 (d, $J = 2.0$ Hz, 1H), 7.75 (d, $J = 8.9$ Hz, 2H), 7.56-7.52 (d, $J = 8.9$ Hz, 3H), 7.47 (dd, $J = 8.6, 2.1$ Hz, 1H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 162.5, 151.6, 140.2, 132.7, 132.3, 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 ($\text{M}^+ + 2$, 100), 382 (M^+ , 100);

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



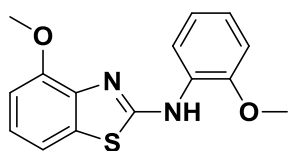
Yellow solid. (32 mg, 34% yield). M.P.: 230-231 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.67 (s, 1H), 8.20 (d, $J = 1.8$ Hz, 1H), 7.73 – 7.65 (m, 2H), 7.65 – 7.57 (m, 3H), 7.40 (d, $J = 8.4$ Hz, 1H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 162.2, 152.0, 140.6, 138.0, 135.0, 133.0, 129.7, 121.7, 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 $\text{C}_{13}\text{H}_9\text{I}_2\text{N}_2\text{S}$ ($\text{M} + \text{H}^+$): calcd. 478.8570, found 478.8564.

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



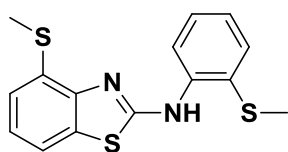
Yellow solid. (42 mg, 82% yield). M.P.: 131-133 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.65 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 1H), 7.54 (d, $J = 7.7$ Hz, 1H), 7.25 (td, $J = 7.6, 5.9$ Hz, 2H), 7.15 – 7.06 (m, 2H), 7.00 (t, $J = 7.6$ Hz, 1H), 2.48 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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]



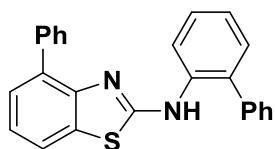
White solid. (36 mg, 63% yield). M.P.: 147-148 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.07 (br, 1H), 7.99 – 7.89 (m, 1H), 7.29 (d, $J = 7.4$ Hz, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.10 – 7.01 (m, 2H), 6.98 – 6.89 (m, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 4.03 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 161.7, 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)



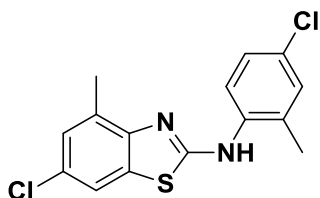
Yellow oil. (49 mg, 77% yield). ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 9.88 (s, 1H), 7.89 – 7.64 (m, 1H), 7.51 (dd, $J = 6.8, 2.1$ Hz, 1H), 7.39 (dd, $J = 6.9, 2.4$ Hz, 1H), 7.30 – 7.21 (m, 2H), 7.15 – 7.02 (m, 2H), 2.46 (d, $J = 5.0$ Hz, 3H), 2.42 (d, $J = 5.0$ Hz, 3H). ^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) 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 $\text{C}_{15}\text{H}_{15}\text{N}_2\text{S}_3$ ($\text{M}+\text{H}^+$): calcd. 319.0383, found 319.0375.

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



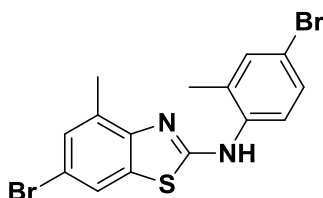
Gray oil. (63 mg, 83% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.23 (dd, $J = 8.2, 1.1$ Hz, 1H), 7.88 (dd, $J = 8.2, 1.3$ Hz, 2H), 7.64 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.54 – 7.46 (m, 5H), 7.46 – 7.37 (m, 5H), 7.34 (dd, $J = 7.6, 1.7$ Hz, 1H), 7.30 – 7.27 (m, 1H), 7.24 (td, $J = 7.5, 1.2$ Hz, 1H). ^{13}C NMR (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 $\text{C}_{25}\text{H}_{19}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 379.1263, found 379.1271.

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



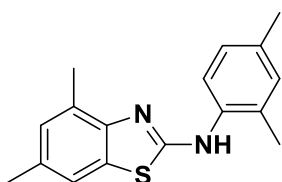
Yellow solid. (43 mg, 67% yield). M.P.: 189-191 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.78 (s, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.34 (d, J = 2.3 Hz, 1H), 7.29 (dd, J = 8.7, 2.5 Hz, 1H), 7.17 (d, J = 2.1 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) 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 $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 323.0171, found 323.0172.

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



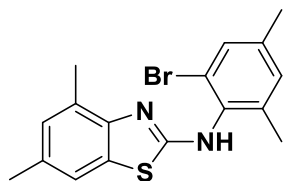
White solid. (54 mg, 66% yield). M.P.: 202-204 °C. ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.77 (s, 1H), 7.98 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 2.3 Hz, 1H), 7.47 (d, J = 2.5 Hz, 1H), 7.43 – 7.36 (m, 1H), 7.30 (d, J = 2.2 Hz, 1H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 163.8, 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 $\text{C}_{15}\text{H}_{12}\text{Br}_2\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 409.9088, found 409.9092.

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



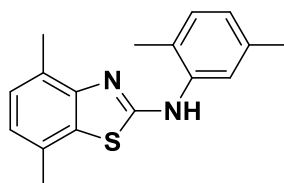
Gray solid. (27 mg, 47% yield). M.P.: 190-192 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.71 (br, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.20 (d, J = 1.6 Hz, 1H), 7.11 – 7.03 (m, 2H), 6.94 (s, 1H), 2.48 (s, 3H), 2.35 (d, J = 1.6 Hz, 6H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 165.8, 148.8, 136.1, 135.9, 132.4, 131.9, 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 $\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}$ ($\text{M}+\text{H}^+$): calcd. 283.1263, found 283.1268.

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



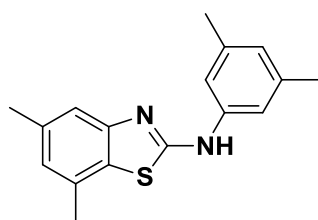
Yellow solid. (9 mg, 13% yield). M.P.: 229-230 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 2.0 Hz, 1H), 7.17 (s, 1H), 7.07 (s, 1H), 6.91 (s, 1H), 2.39 (s, 3H), 2.35 (d, *J* = 4.5 Hz, 6H), 2.33 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 167.2, 149.0, 139.6, 139.2, 134.8, 131.7, 131.4, 131.3, 130.4, 128.3, 128.1, 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 C₁₇H₁₇BrN₂S (M+H⁺): calcd. 361.0369, found 361.0373.

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



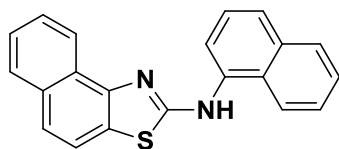
Gray solid. (40 mg, 71% yield). M.P.: 139-141 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.50 (s, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 7.03 (dd, *J* = 7.8, 2.2 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 2.53 (s, 3H), 2.40 (s, 6H), 2.32 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 165.8, 150.4, 138.2, 137.0, 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 C₁₇H₁₈N₂S (M+H⁺): calcd. 283.1264, found 283.1266.

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



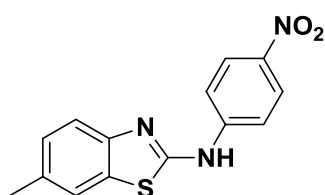
White solid. (48 mg, 85% yield). M.P.: 187-189 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.24 (s, 1H), 7.12 (s, 2H), 6.81 (d, *J* = 11.2 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 2.36 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 165.2, 151.3, 140.0, 139.3, 136.0, 130.4, 127.0, 126.1, 124.1, 118.3, 118.2, 117.2, 21.4, 21.4, 21.1. IR (ATR, cm⁻¹): 2916, 2851, 1581, 1471, 840, 741. LRMS (EI, 70 Ev) *m/z* (%): 282 (M⁺, 100). HRMS (ESI) for C₁₇H₁₈N₂S (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 °C. ^1H 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 °C. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) 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, $\text{DMSO}-d_6$) 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).

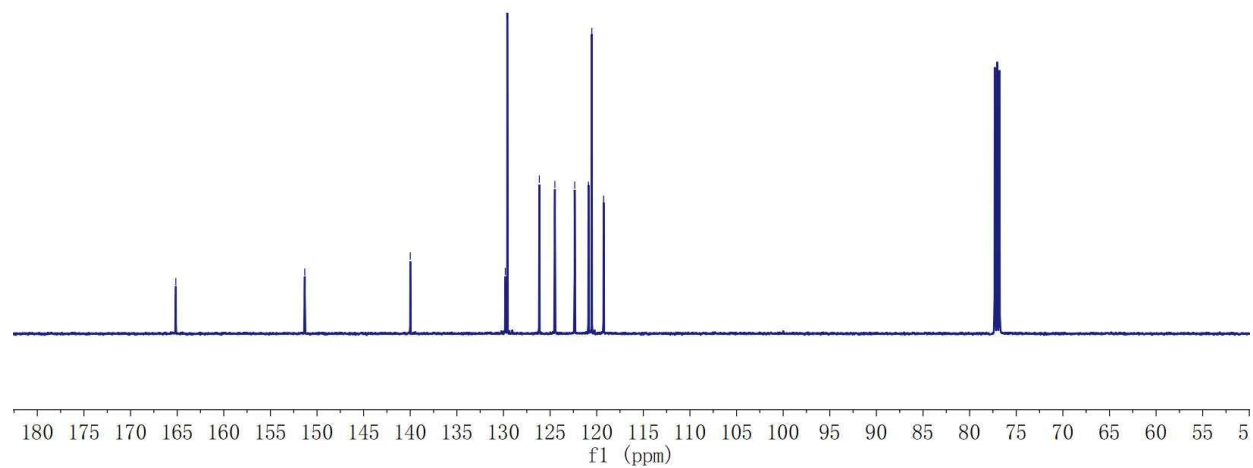
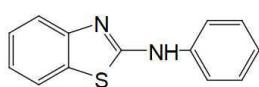
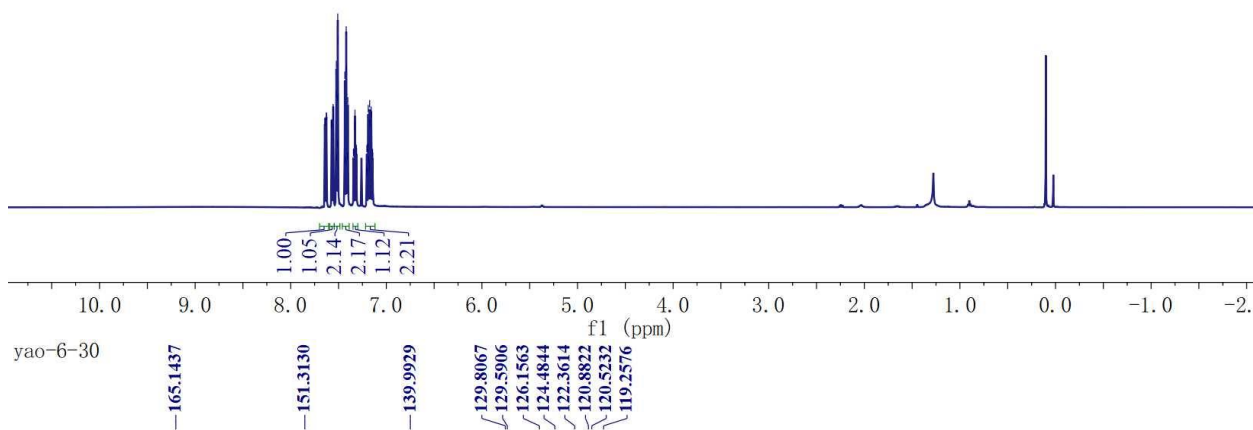
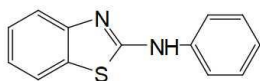
(E) Reference

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(F) Spectra

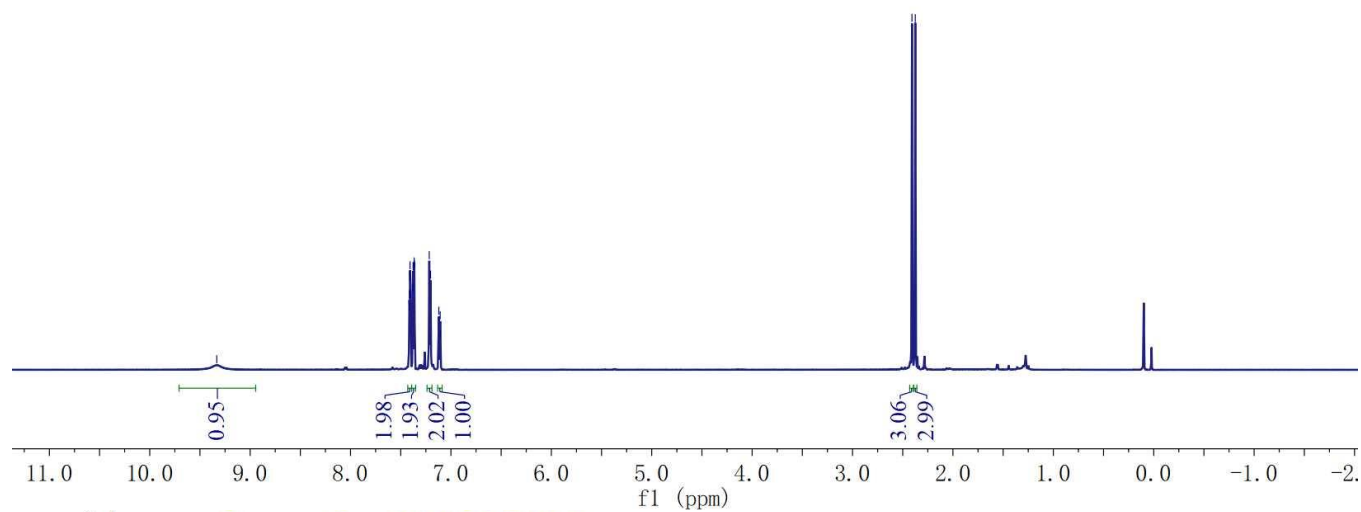
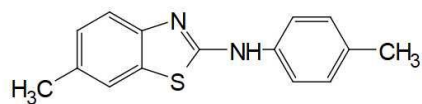
N-Phenylbenzo[*d*]thiazol-2-amine (2)

7.6433
7.6412
7.6278
7.6254
7.5729
7.5705
7.5565
7.5542
7.5255
7.5228
7.5189
7.5122
7.5103
7.5081
7.5059
7.4345
7.4303
7.4198
7.4174
7.4064
7.4028
7.3443
7.3418
7.3296
7.3280
7.3135
7.3110
7.2064
7.2040
7.2016
7.1918
7.1893
7.1866
7.1770
7.1744
7.1719
7.1590
7.1567
7.1438
7.1415

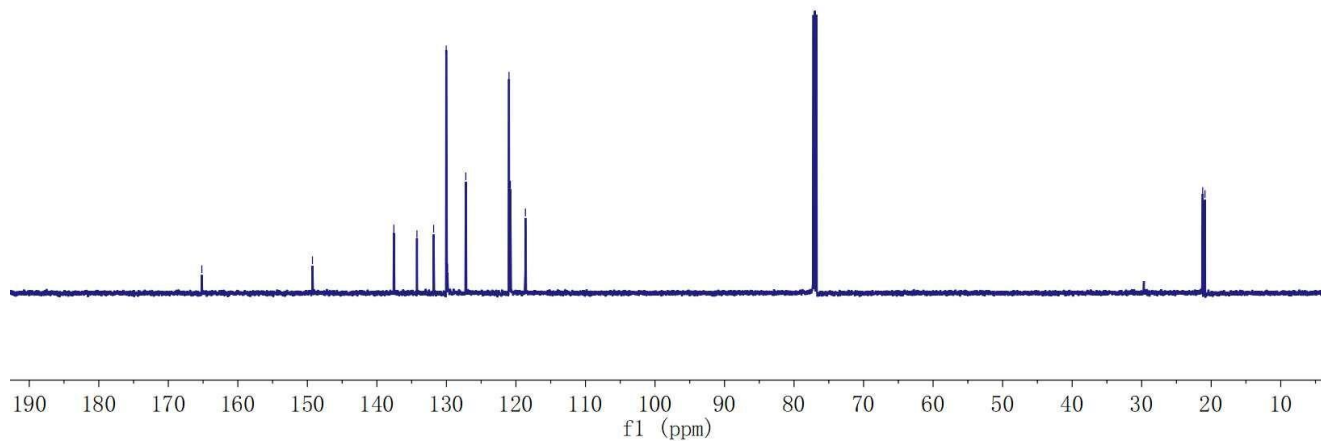
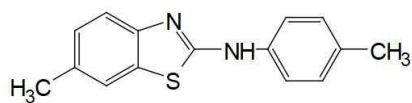


6-Methyl-N-p-tolylbenzo[d]thiazol-2-amine (3)

yao-7-1-a



yao-7-1-a



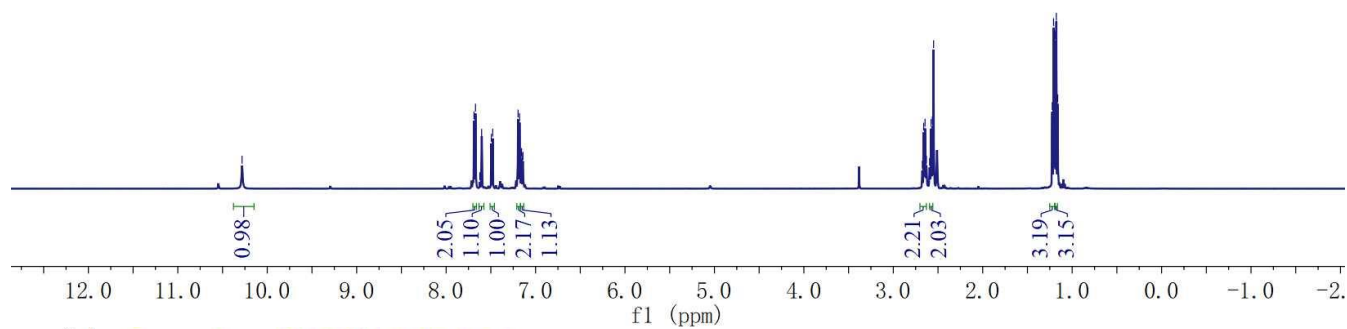
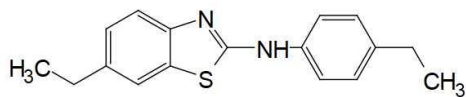
6-Ethyl-N-(4-ethylphenyl)benzo[d]thiazol-2-amine (4)

yao-7-1-c

10.2814

7.6885
7.6715
7.6233
7.6029
7.4951
7.4787
7.1956
7.1788
7.1608
7.1572
7.1442
7.1406

2.6751
2.6599
2.6448
2.6295
2.5935
2.5781
2.5631
2.5493
1.2229
1.2078
1.1922
1.1766
1.1615



yao-7-1-c

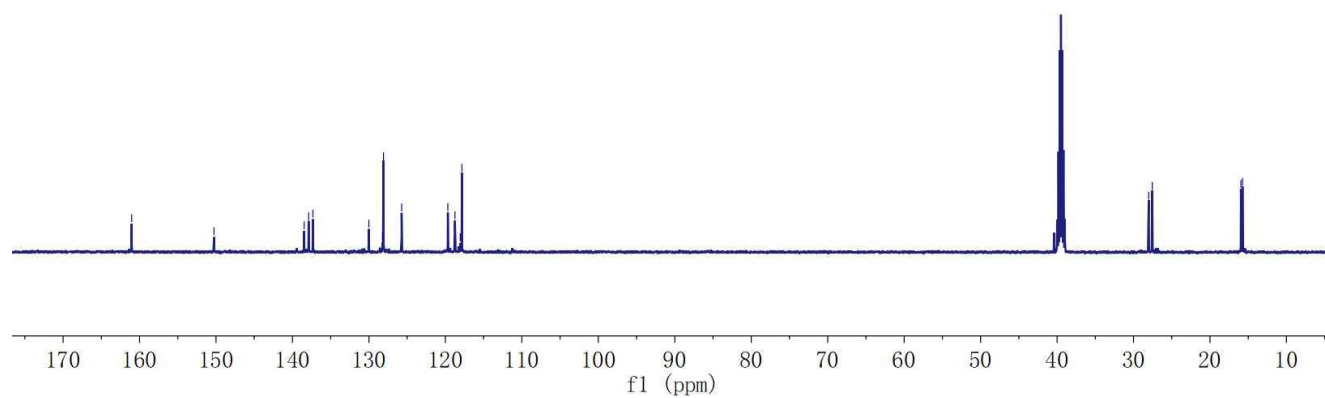
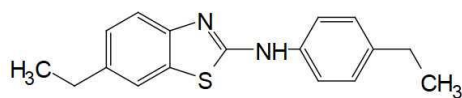
161.0320

150.2612

138.4822
137.8847
137.5239
130.0088
128.2137
128.0978
125.7283
119.6798
118.7506
118.0633
117.8392

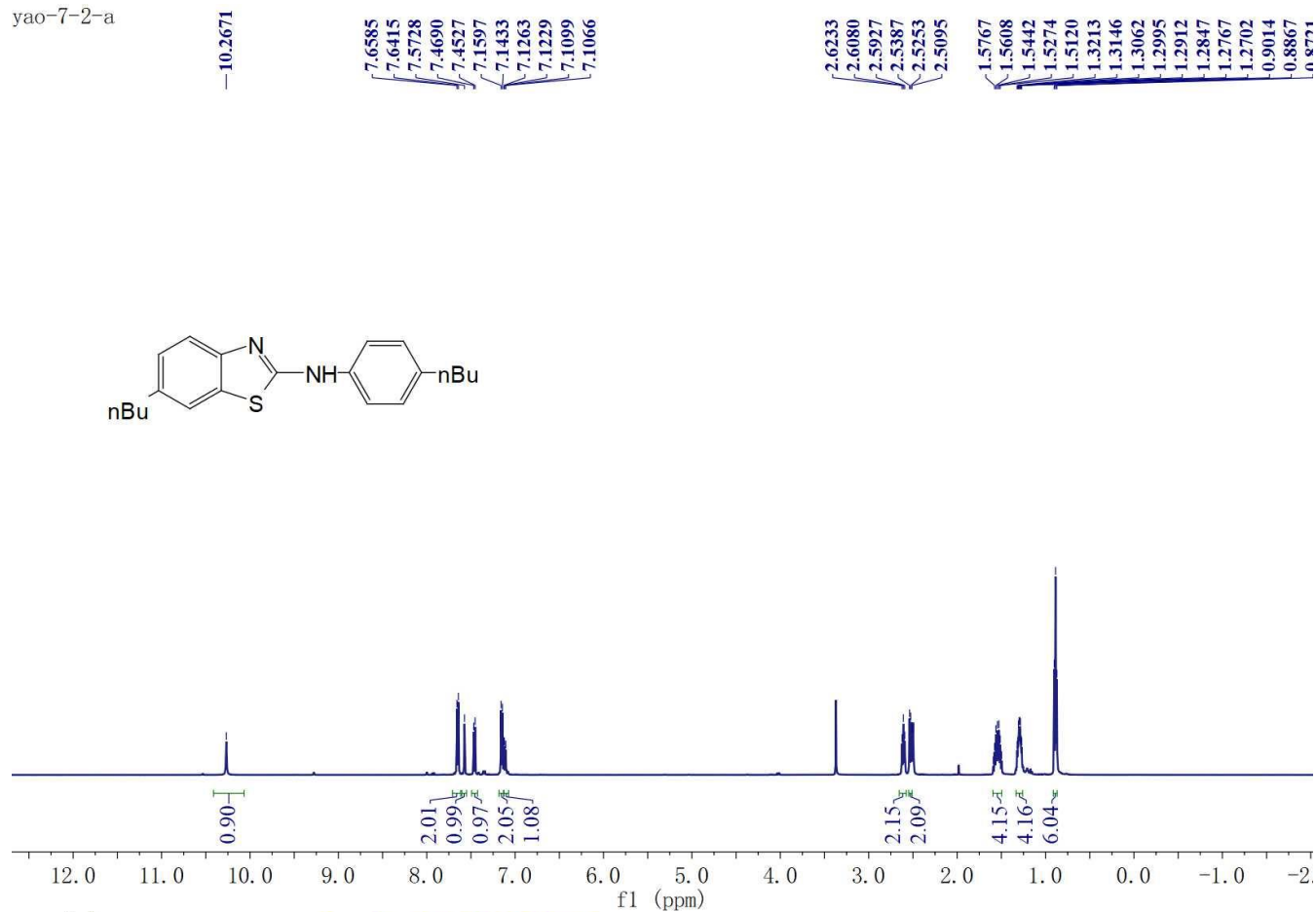
28.0129
27.5516

15.9575
15.7406

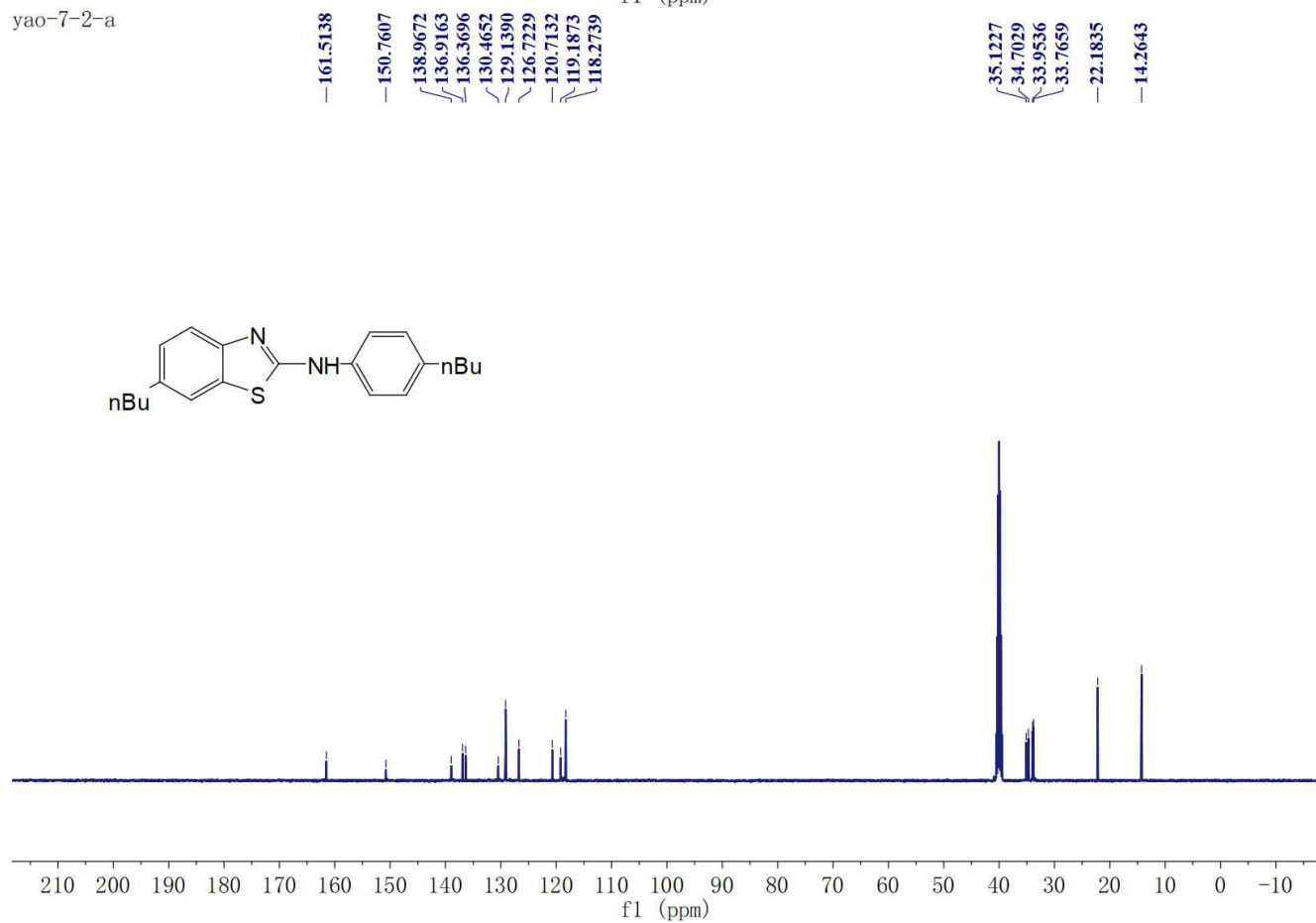


6-Butyl-N-(4-butylphenyl)benzo[d]thiazol-2-amine (5)

yao-7-2-a

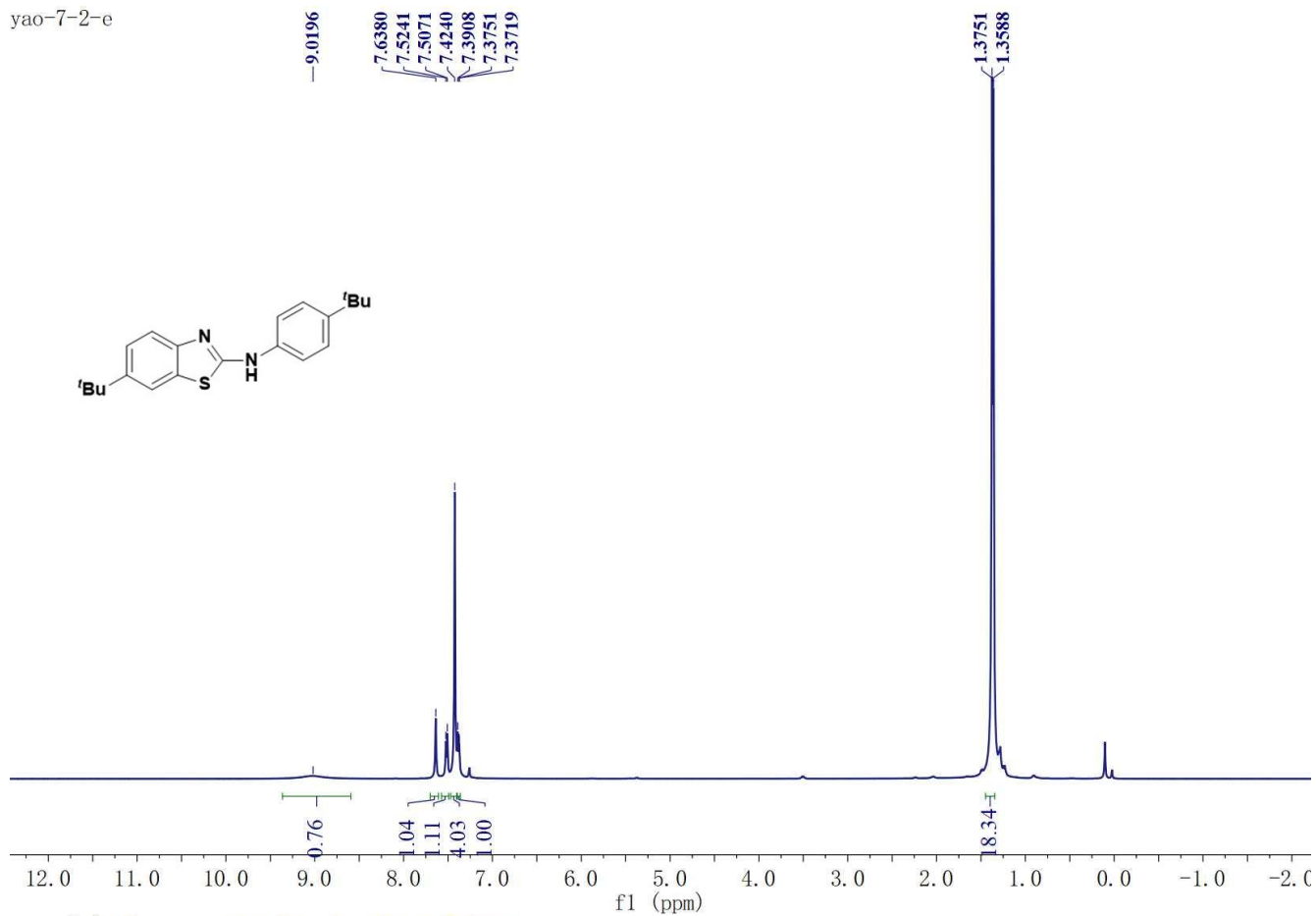


yao-7-2-a

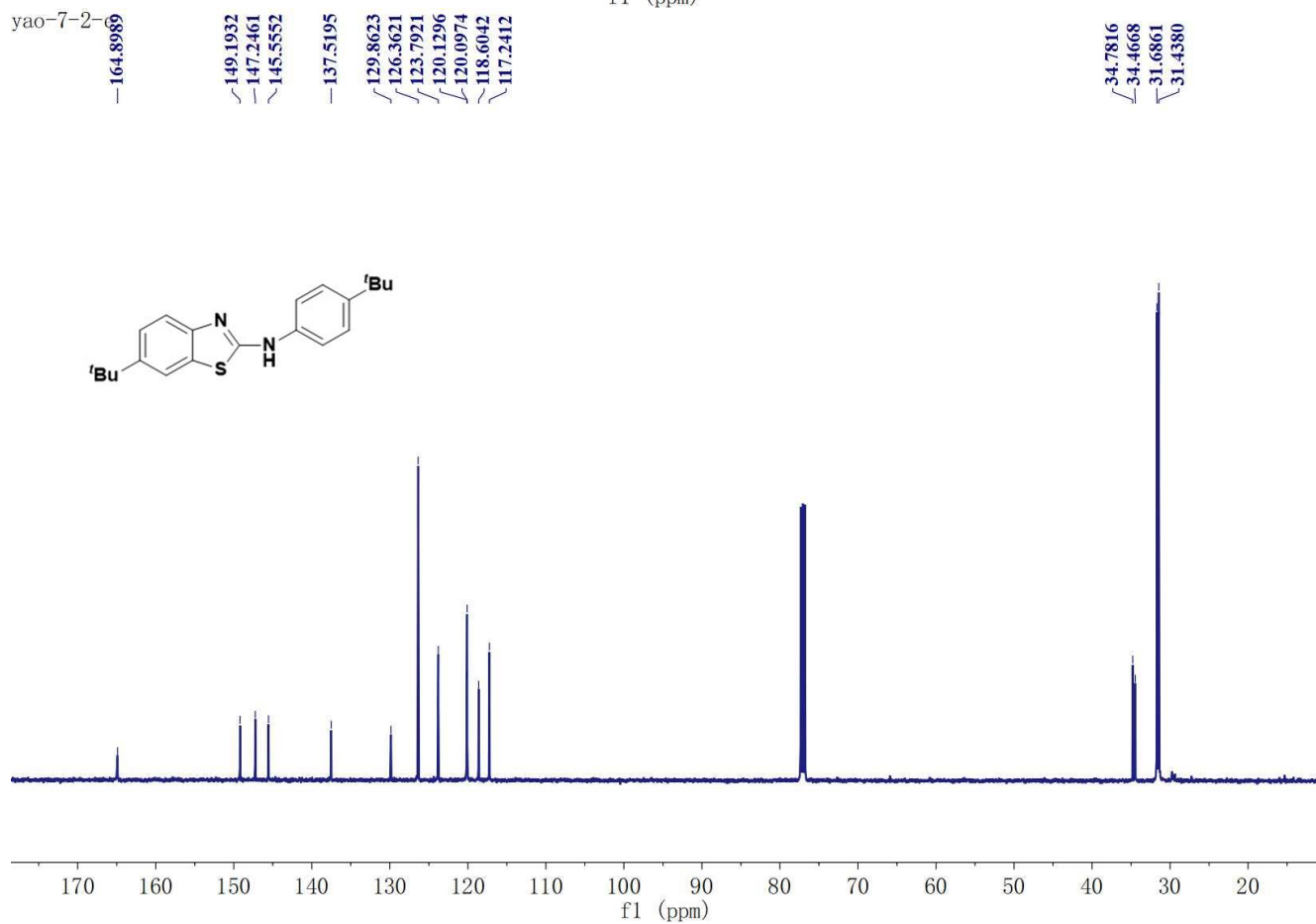


6-(tert-Butyl)-N-[4-(tert-butyl)phenyl]benzo[d]thiazol-2-amine (6)

yao-7-2-e

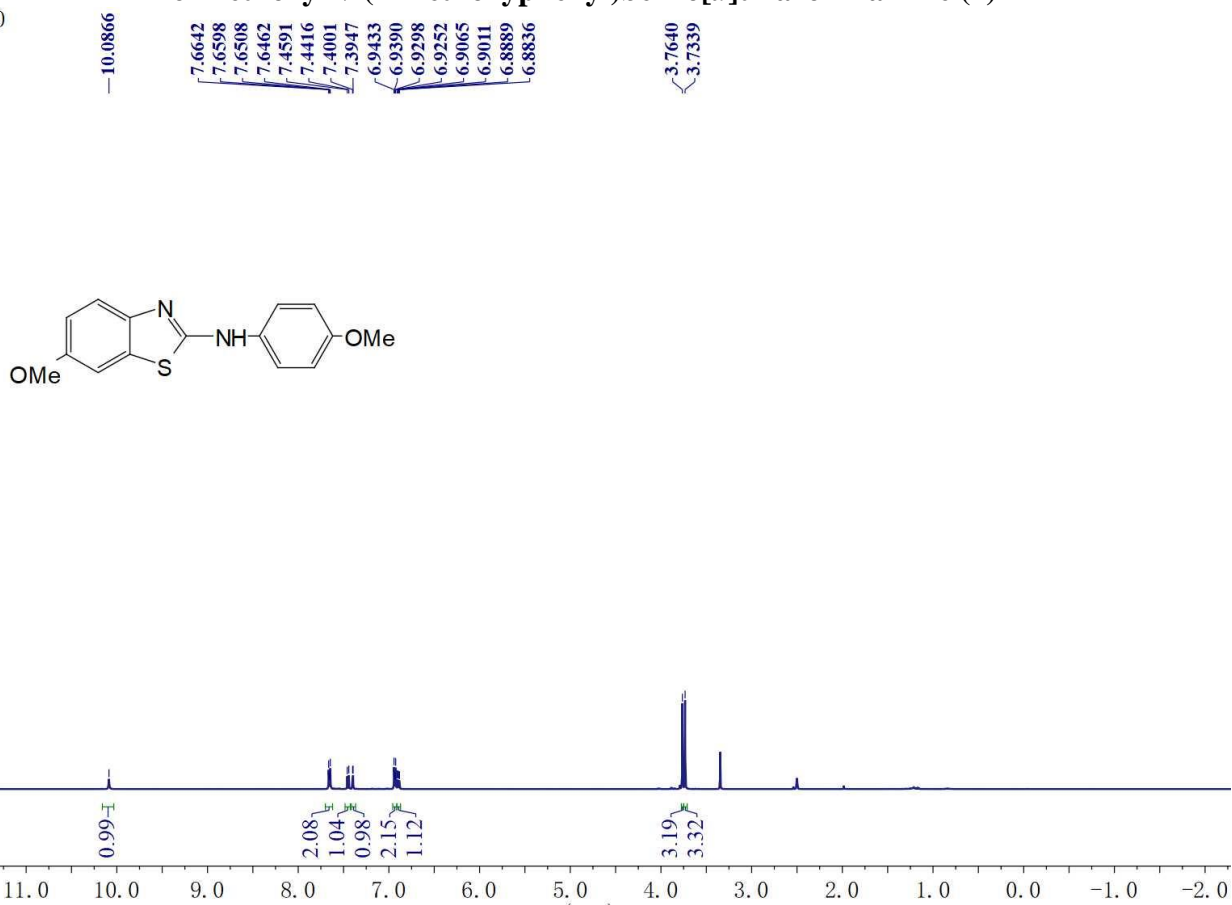


yao-7-2-f

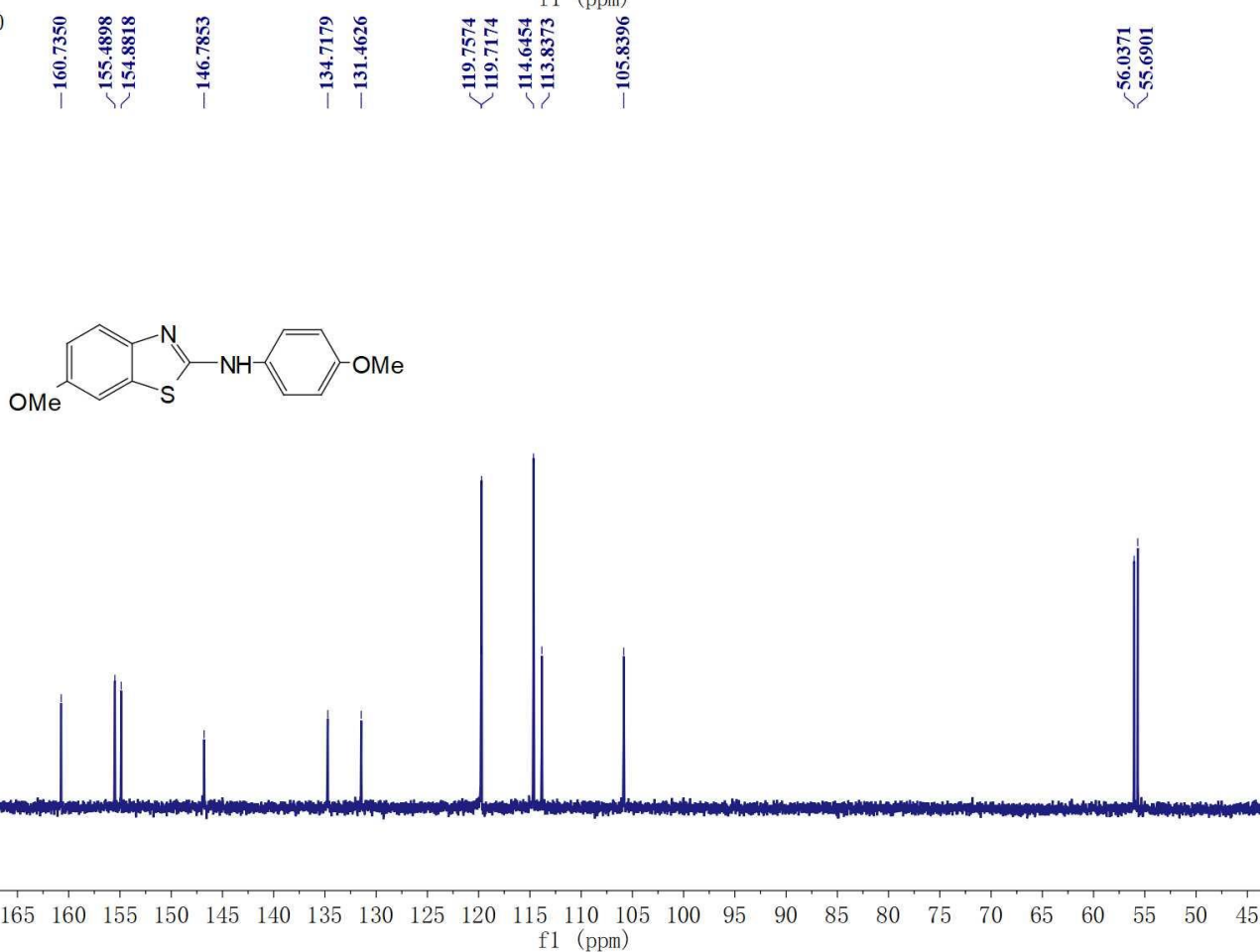


6-Methoxy-N-(4-methoxyphenyl)benzo[d]thiazol-2-amine (7)

yao-8-30



yao-8-30



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

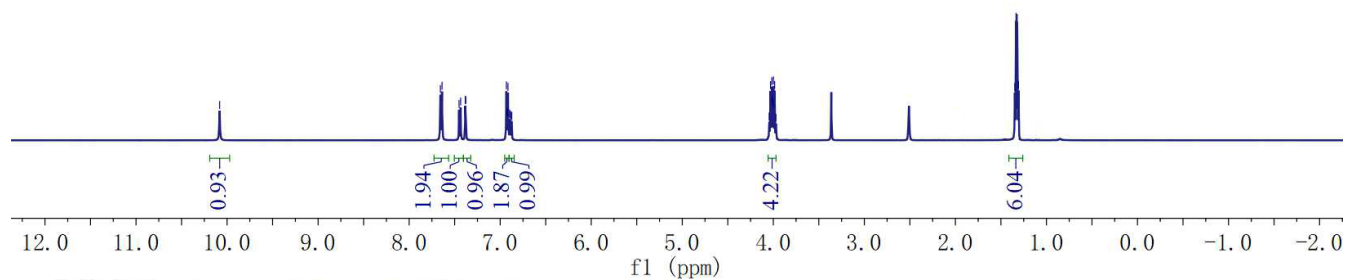
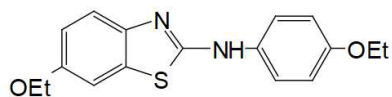
yao-7-15-b

10.0814

7.6567
7.6388
7.4519
7.4343
7.3838
7.3785
6.9321
6.9277
6.9186
6.9141
6.8958
6.8906
6.8785
6.8732

4.0444
4.0423
4.0303
4.0165
4.0132
4.0027
3.9991
3.9852
3.9713

1.3474
1.3339
1.3209
1.3074



yao-7-

160.1884
154.1922
153.6183

146.2322

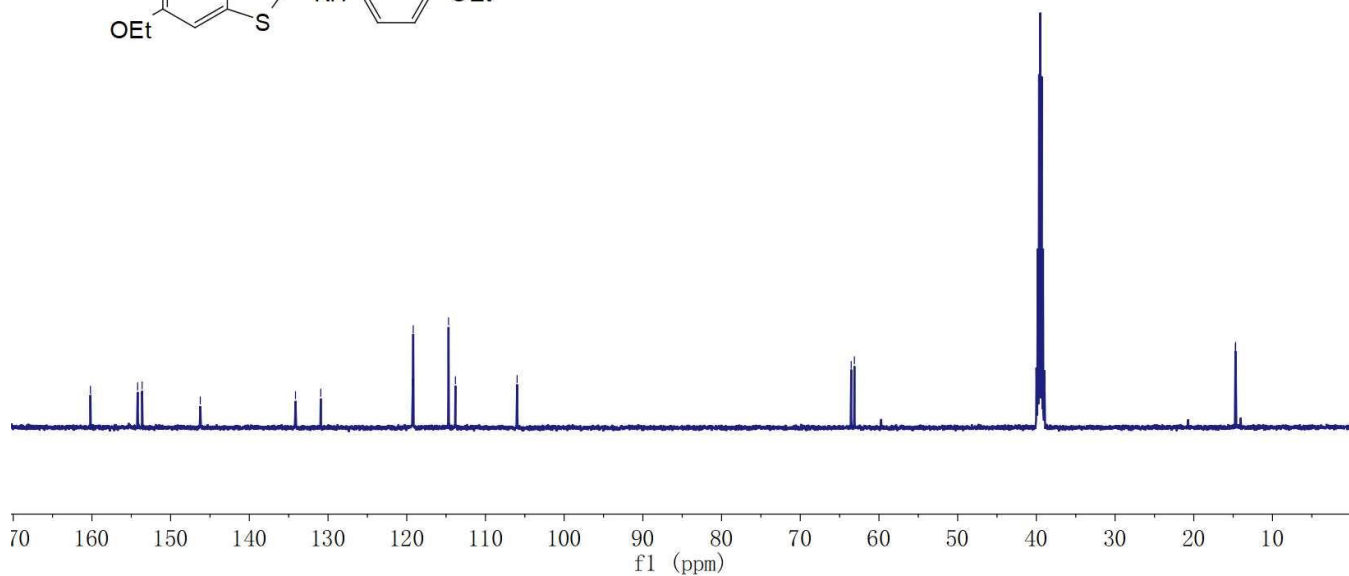
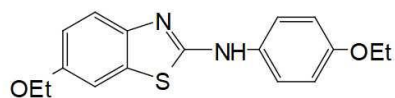
134.1340
130.9288

119.2389
119.1775
114.6875
113.8143

105.9760

63.5309
63.1220

14.7075
14.6842

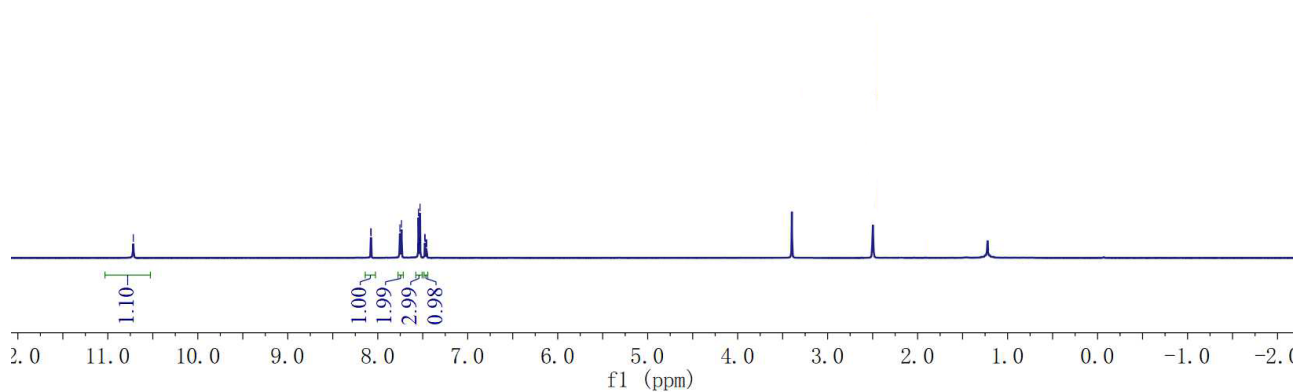
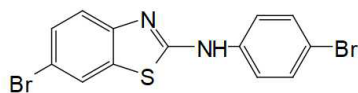


6-Bromo-N-(4-bromophenyl)benzo[d]thiazol-2-amine (9)

yao-7-6-a

10.7168

8.0775
8.0735
7.7540
7.7363
7.5545
7.5474
7.5347
7.5298
7.4777
7.4735
7.4605
7.4564



yao-7-6-a

162.4764

151.6365

140.1661

132.7221

132.2861

129.4157

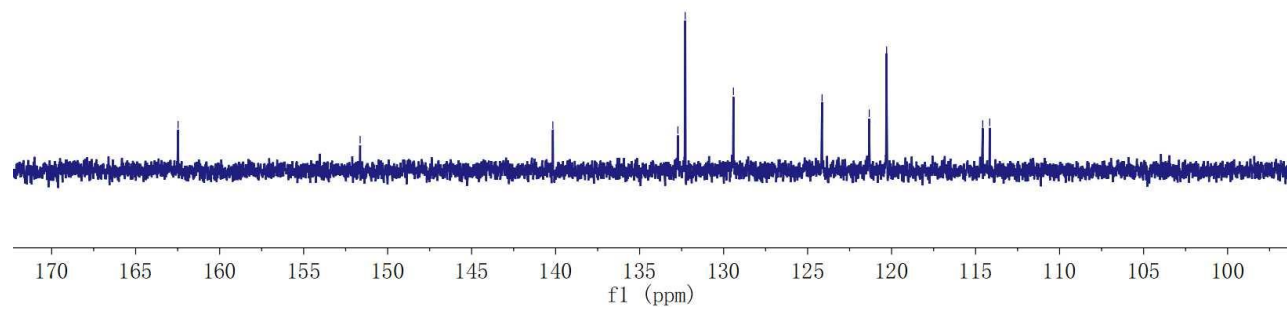
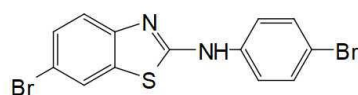
124.1406

121.3310

120.2994

114.5765

114.1601

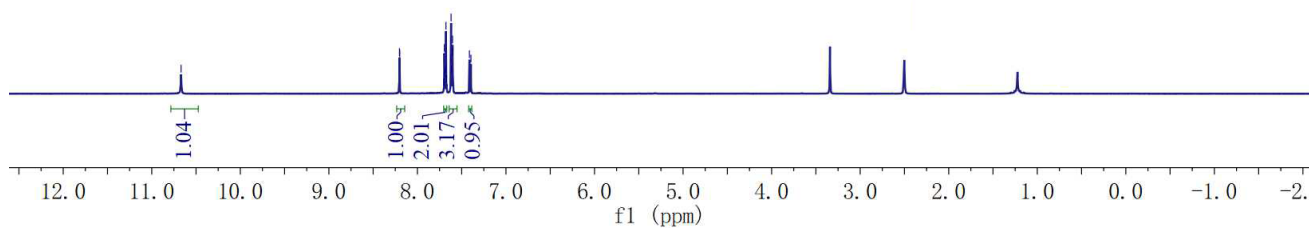
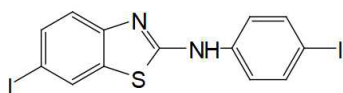


6-Iodo-N-(4-iodophenyl)benzo[d]thiazol-2-amine (10)

yao-7-6-e

10.6689

8.2030
8.1994
7.7009
7.6952
7.6911
7.6818
7.6775
7.6719
7.6240
7.6200
7.6155
7.6070
7.6029
7.4126
7.3958



yao-7-6-e

162.1803

151.9728

140.5802

138.0135

134.9969

133.0174

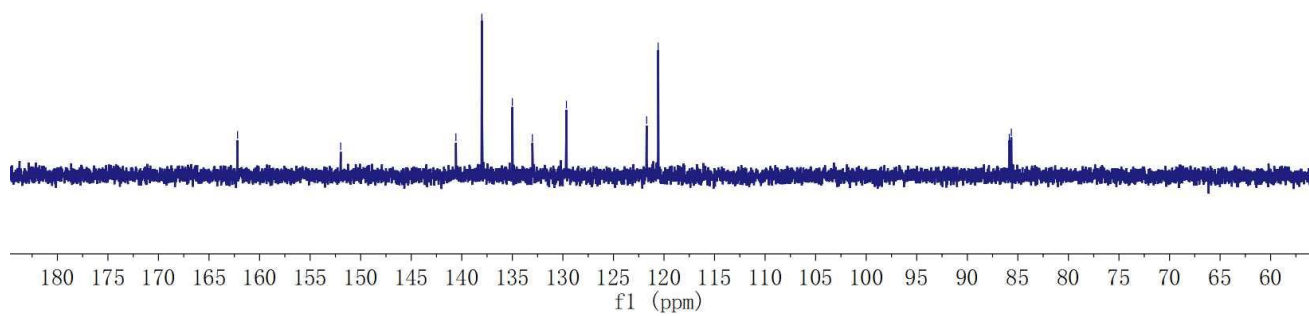
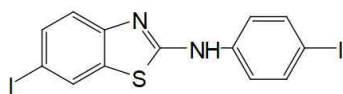
129.6530

121.7133

120.5776

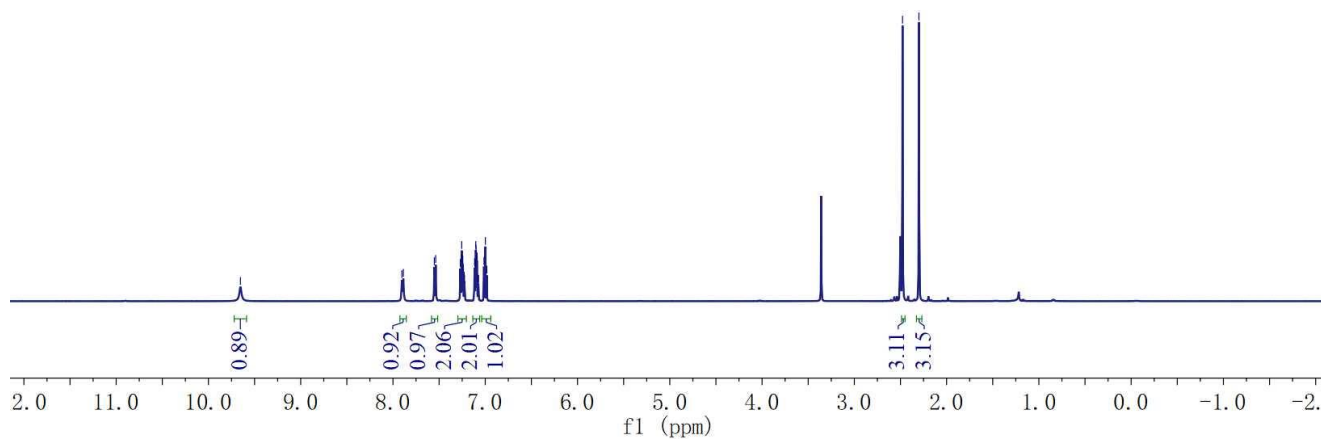
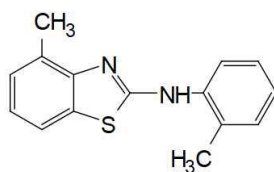
85.8495

85.6476

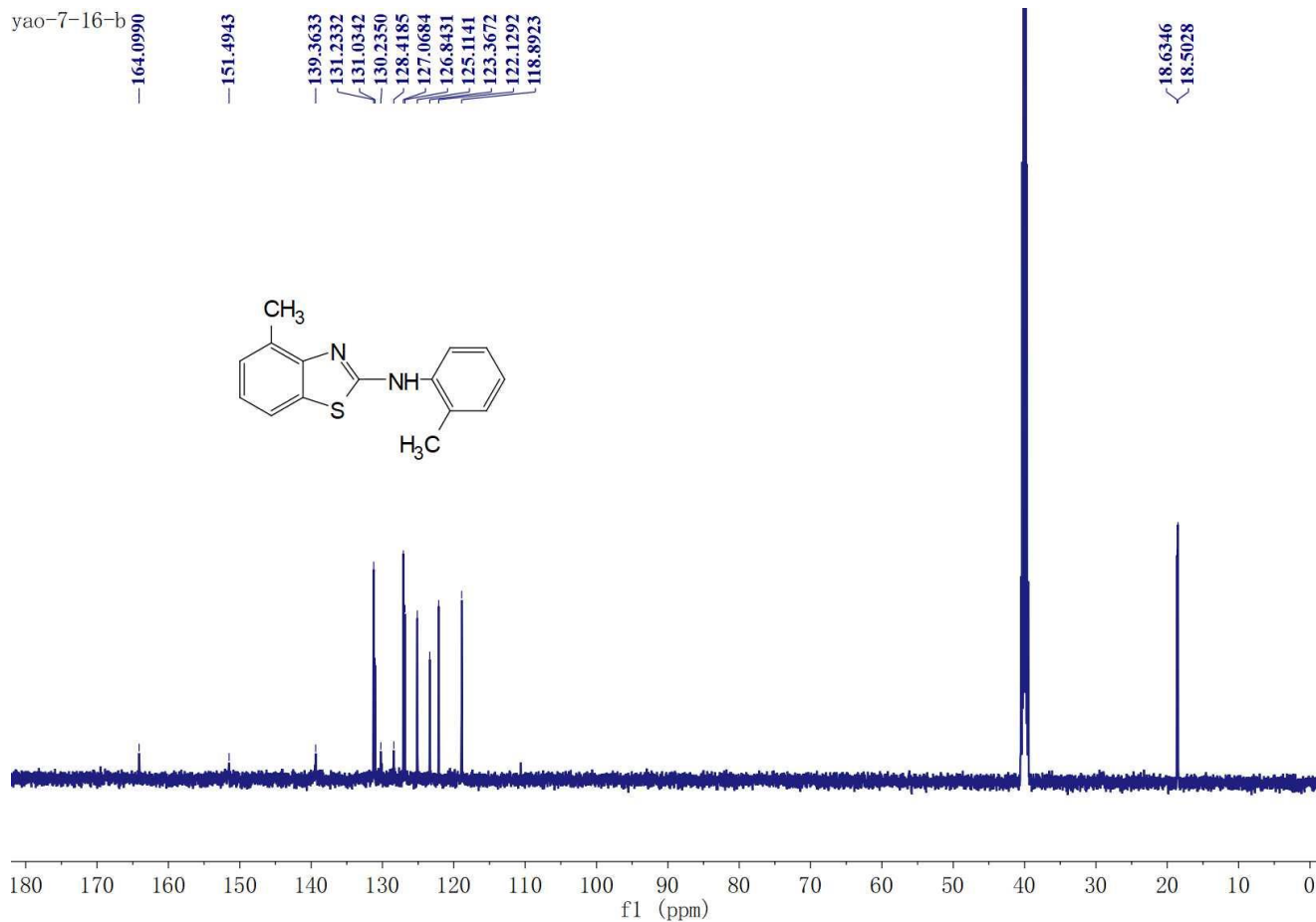
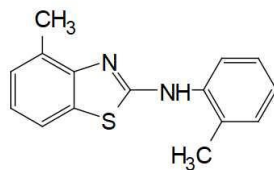


4-Methyl-N-(*o*-tolyl)benzo[*d*]thiazol-2-amine (12)

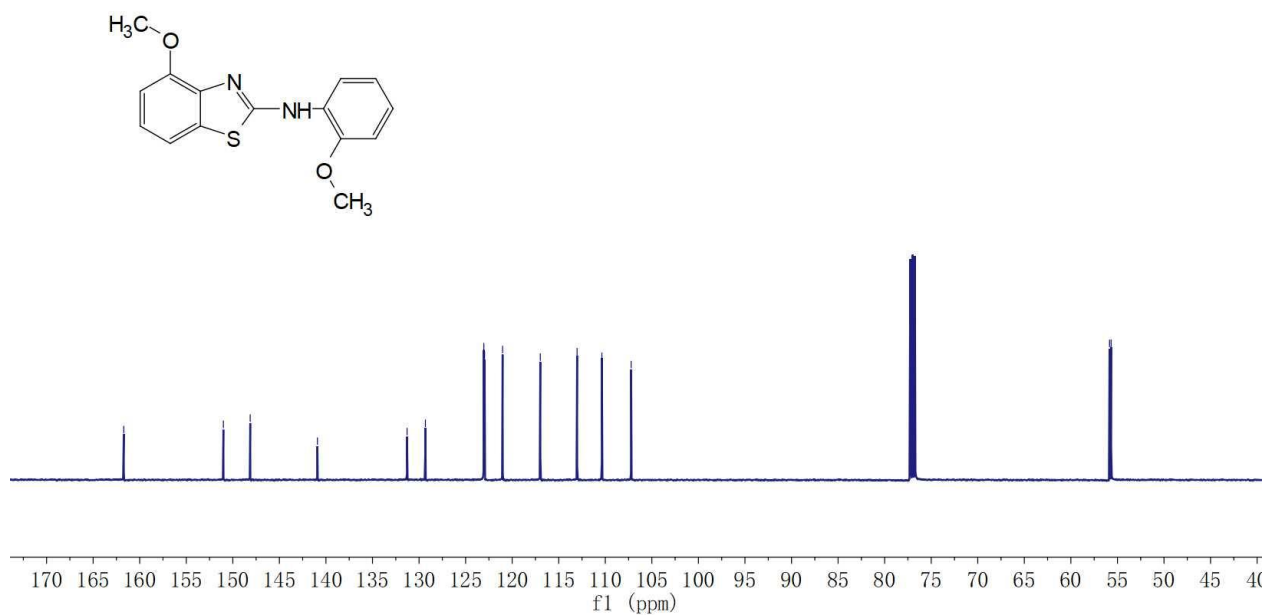
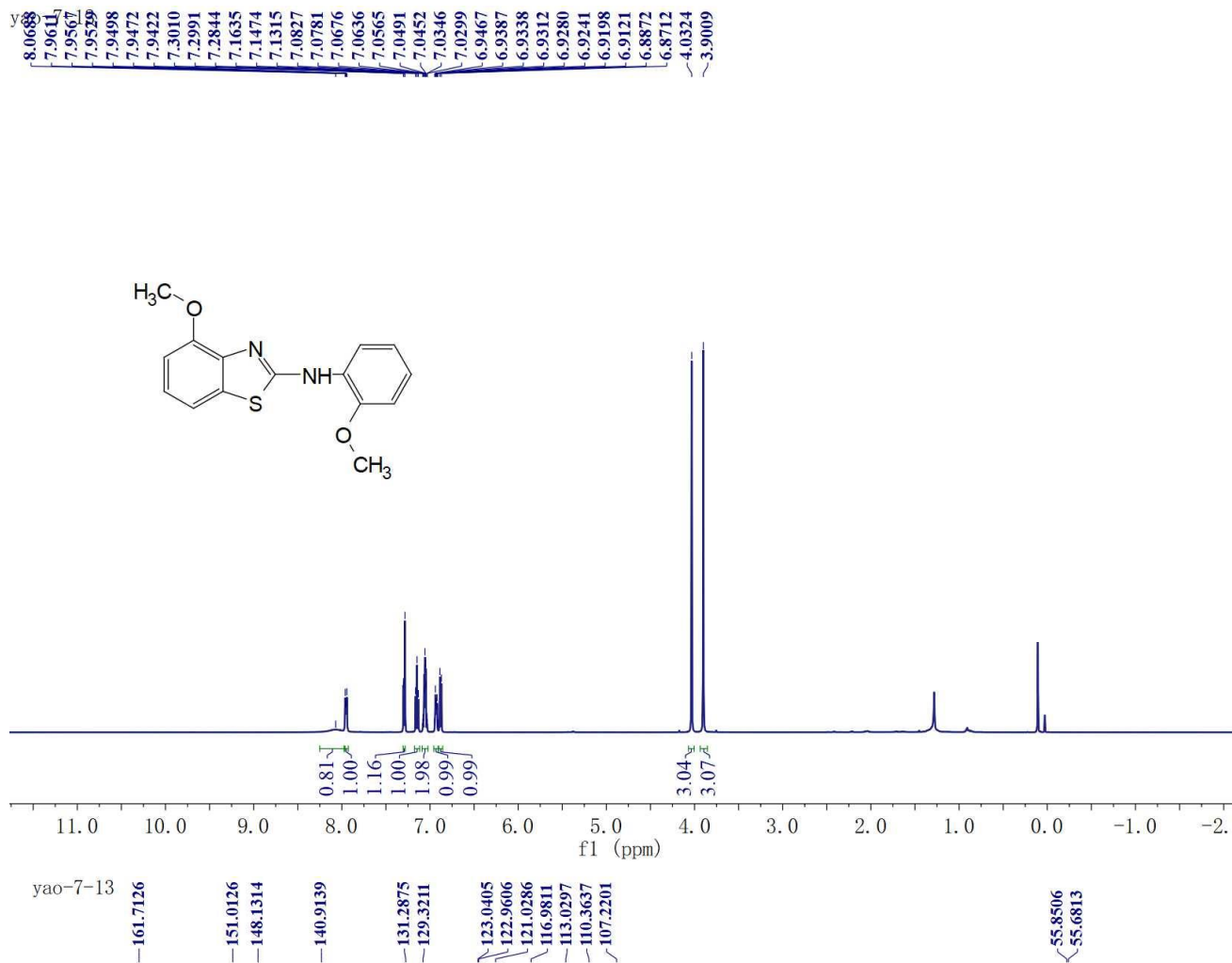
yao-7-16-b



yao-7-16-b

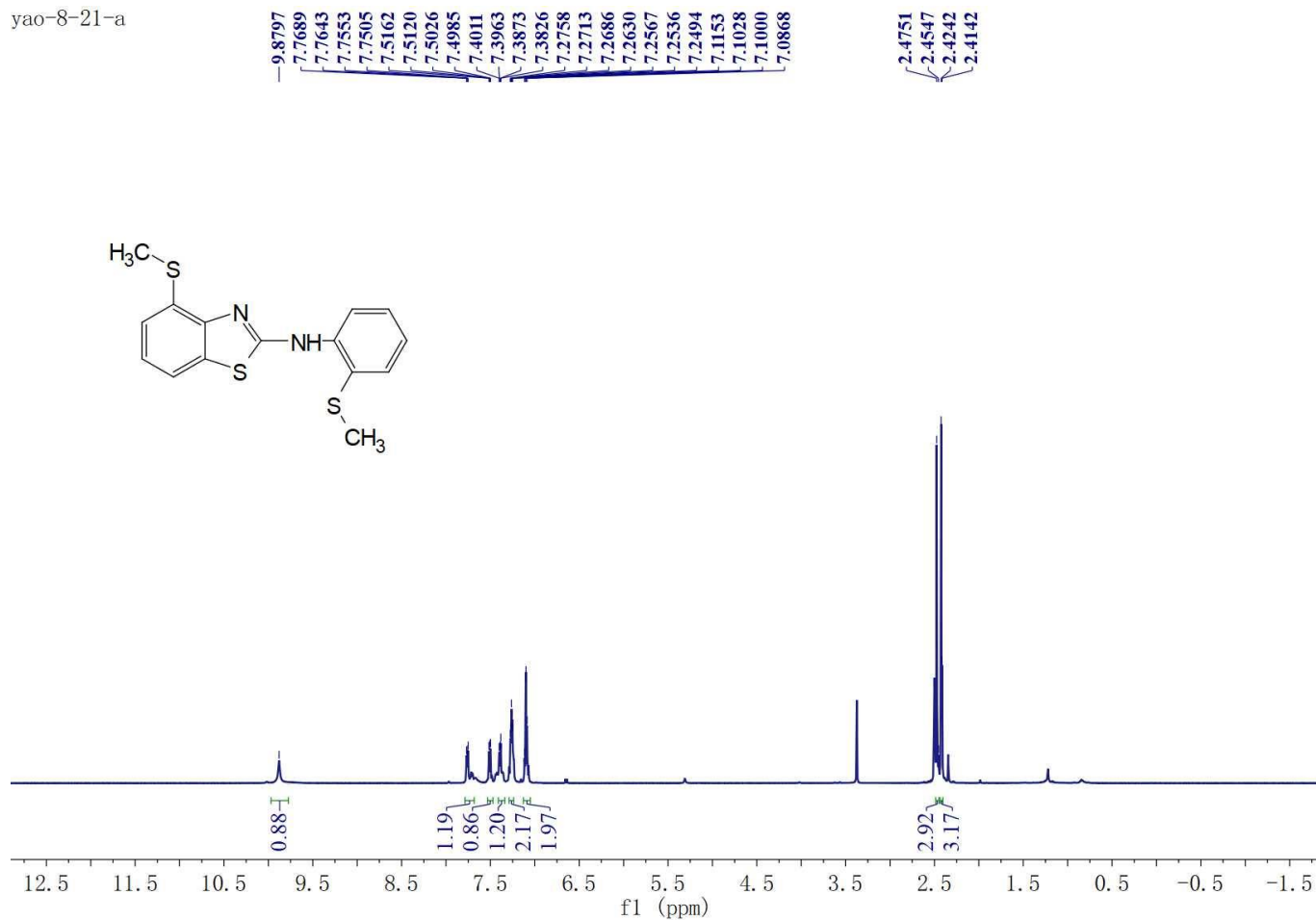


4-Methoxy-N-(2-methoxyphenyl)benzo[d]thiazol-2-amine (13)

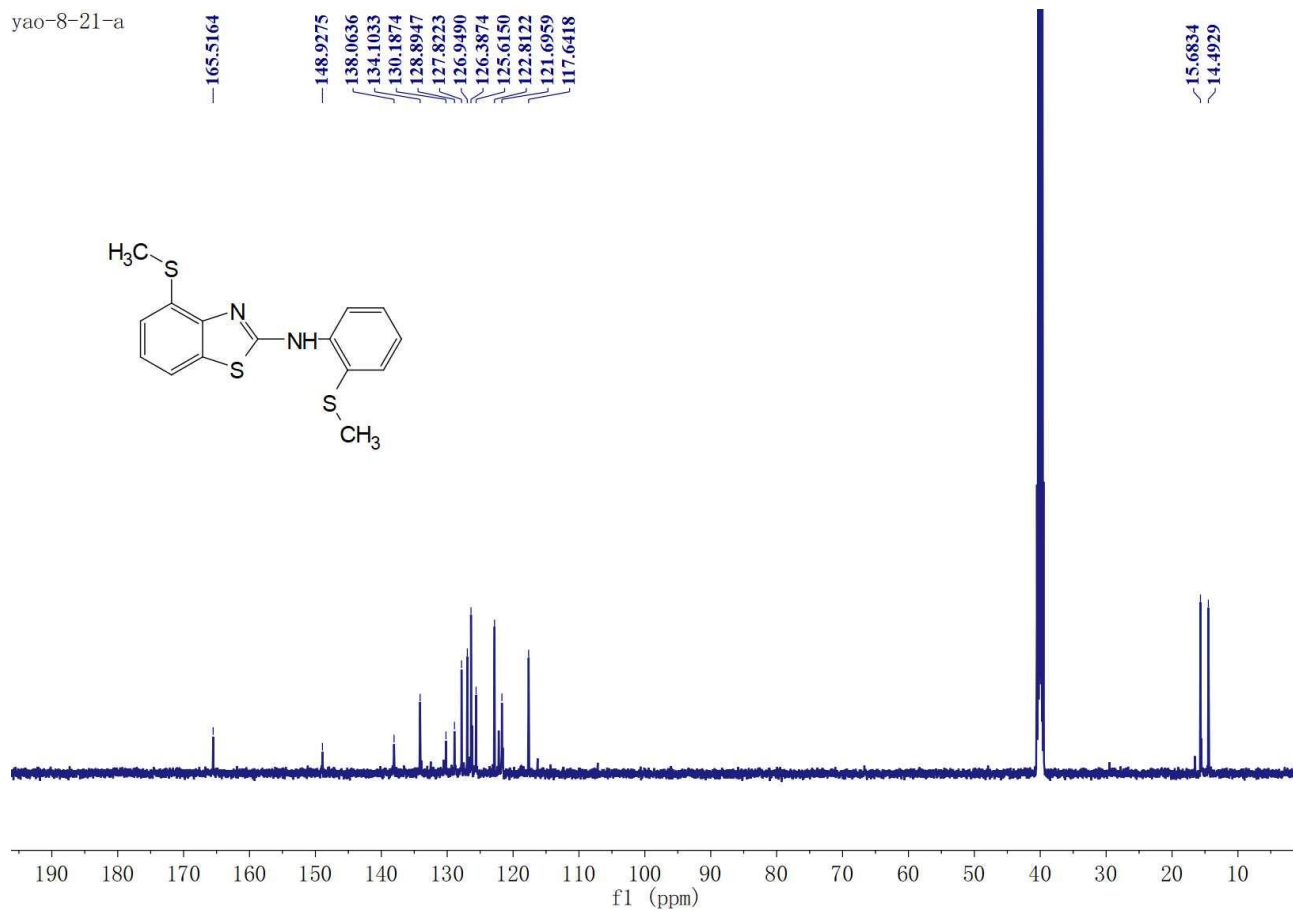


4-(Methylthio)-*N*-(3-(methylthio)phenyl)benzo[*d*]thiazol-2-amine (14)

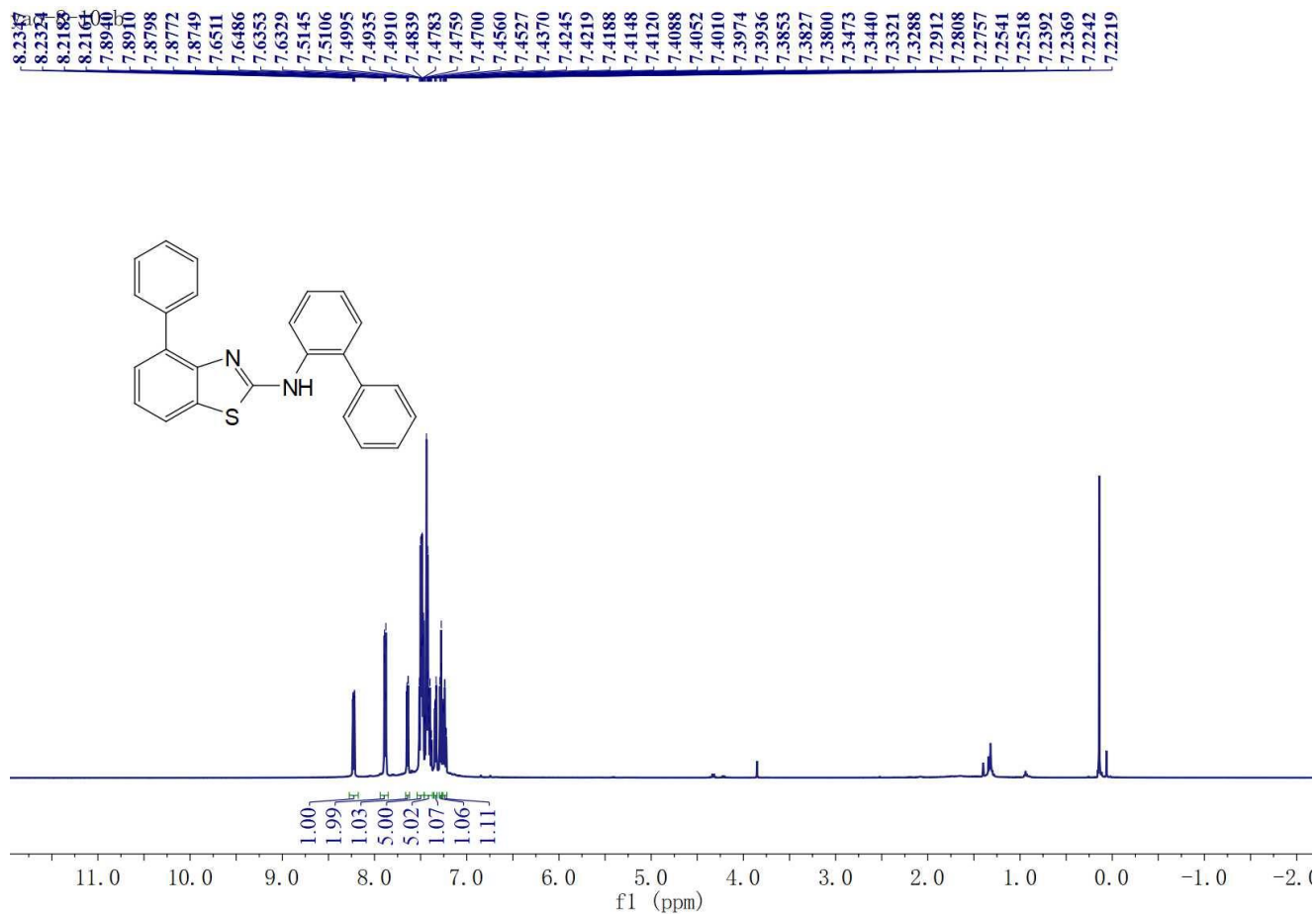
yao-8-21-a



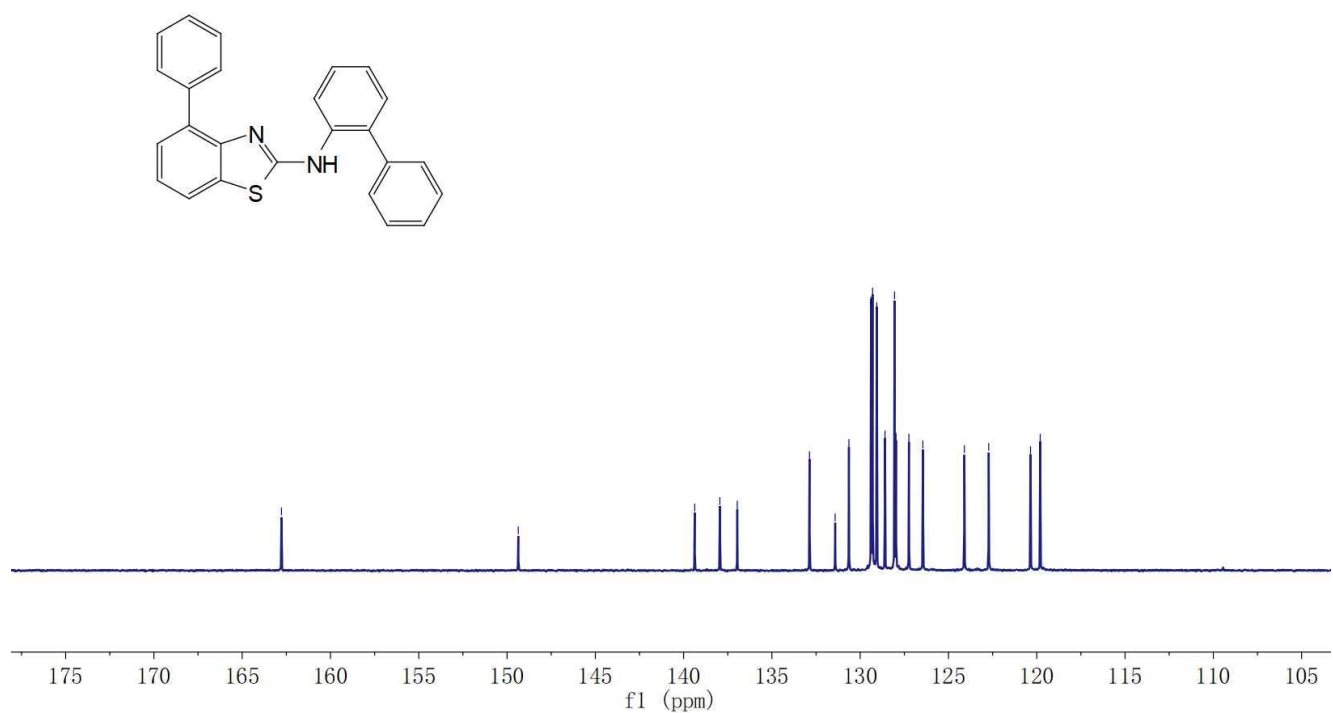
yao-8-21-a



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

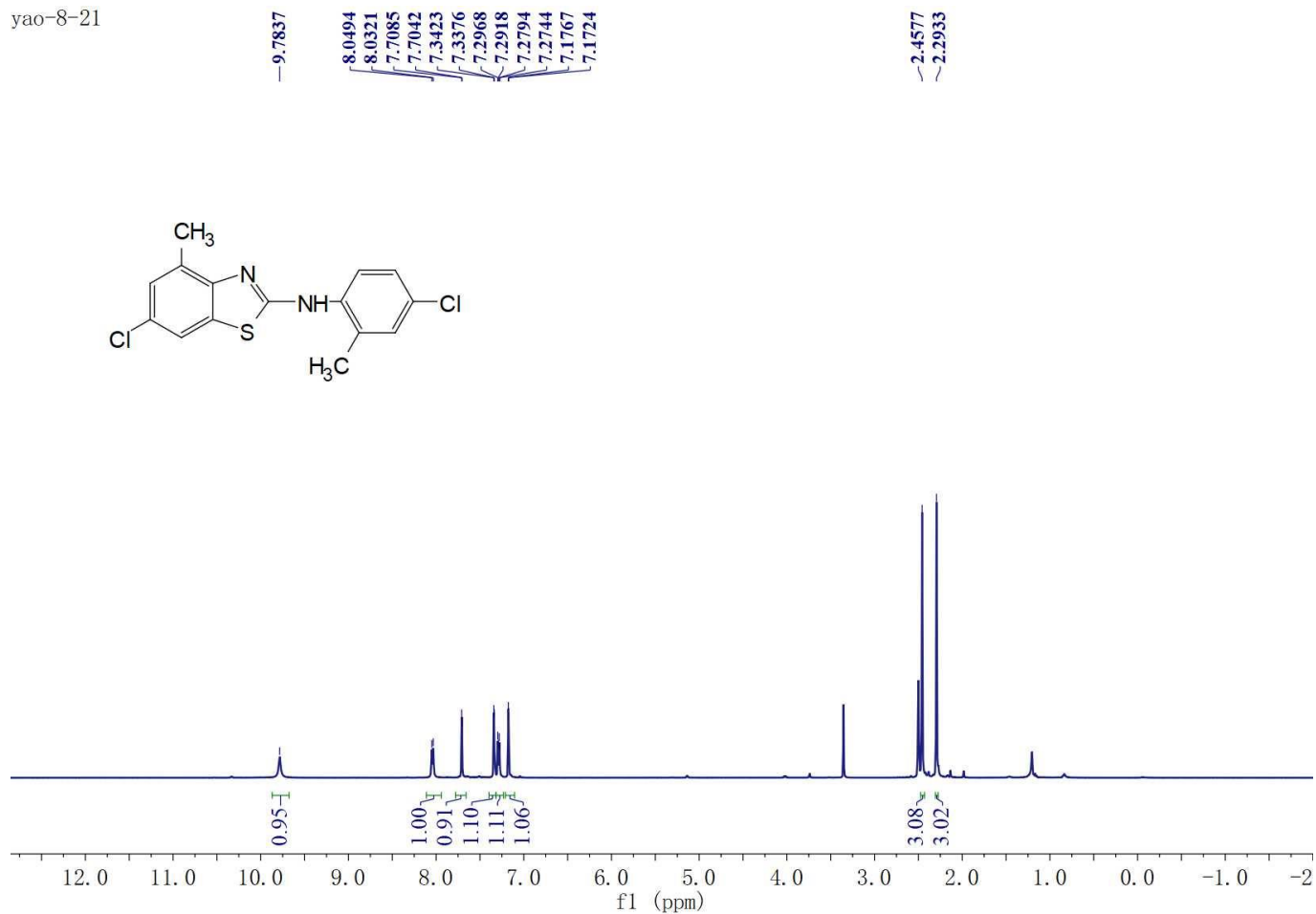


yao-8-10-b

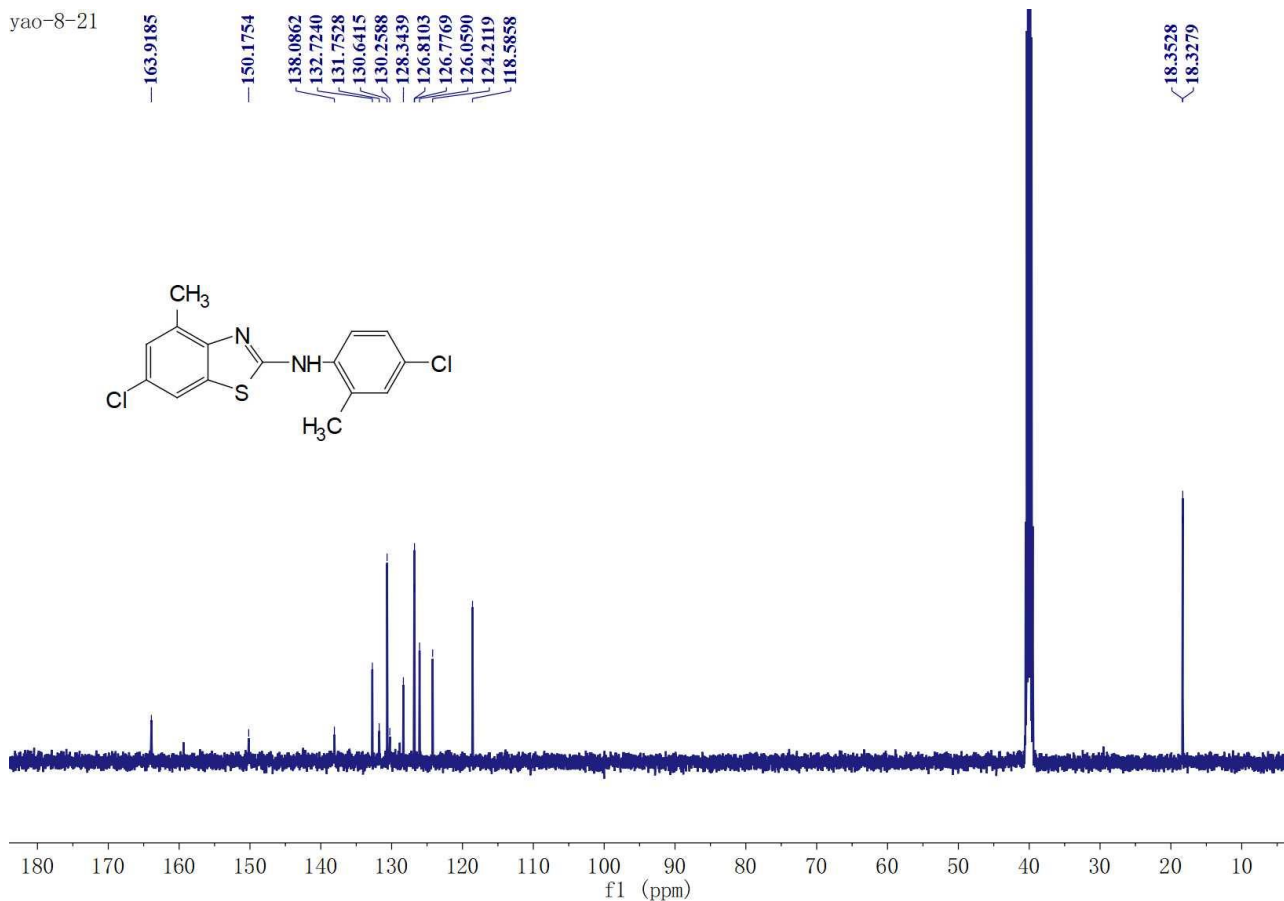


6-Chloro-N-(4-chloro-2-methylphenyl)-4-methylbenzo[d]thiazol-2-amine (16)

yao-8-21



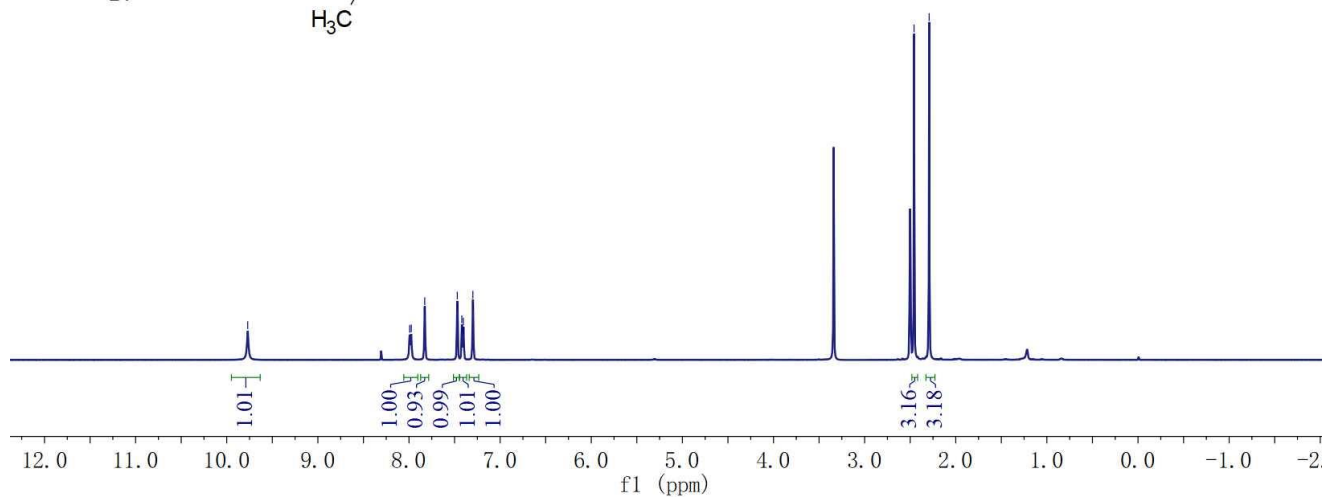
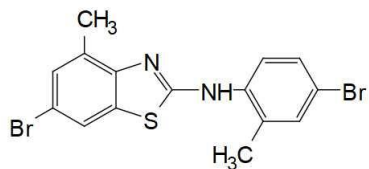
yao-8-21



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

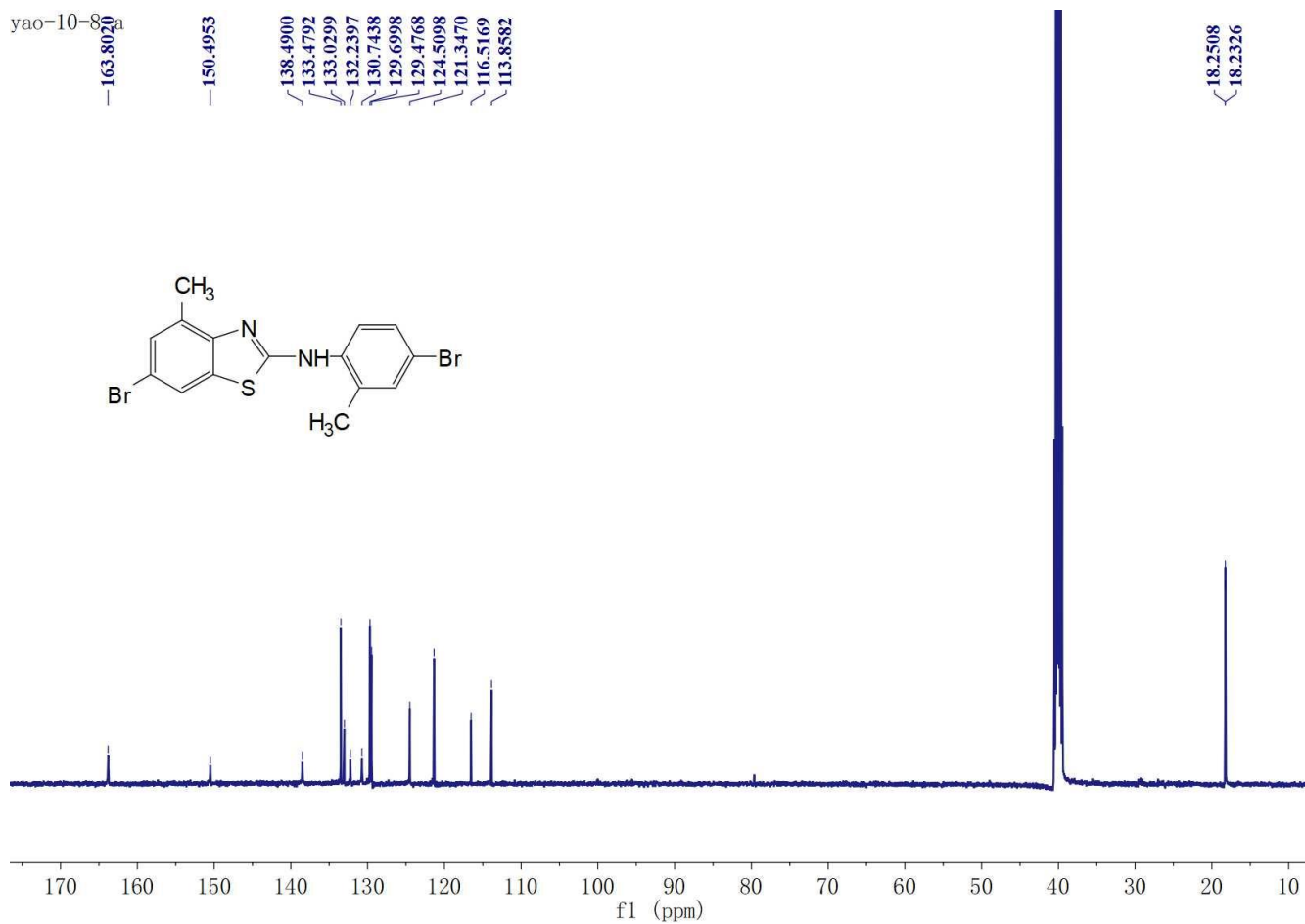
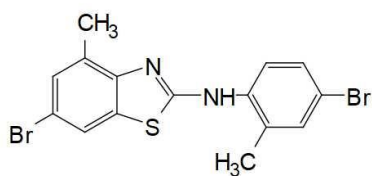
yao-10-8-a

9.7697
7.9926
7.9754
7.8275
7.8230
7.4705
7.4655
7.4205
7.4152
7.4034
7.3983
7.2988
7.2943
2.4576
2.2919



yao-10-8-a

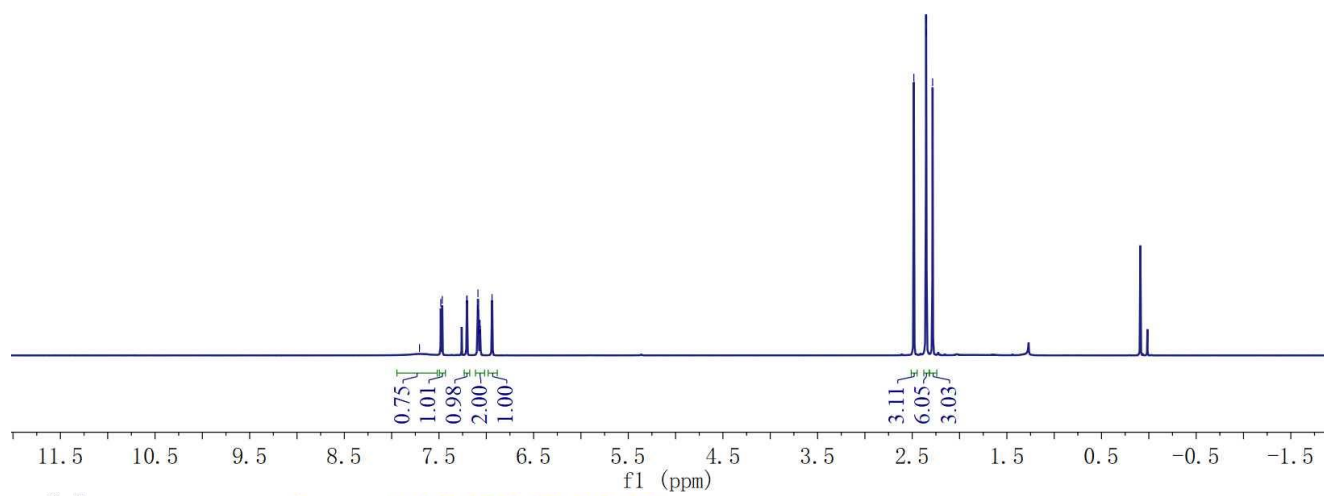
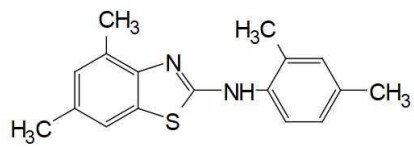
163.8020
150.4953
138.4900
133.4792
133.0299
132.2397
130.7438
129.6998
129.4768
124.5098
121.3470
116.5169
113.8582
18.2508
18.2326



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

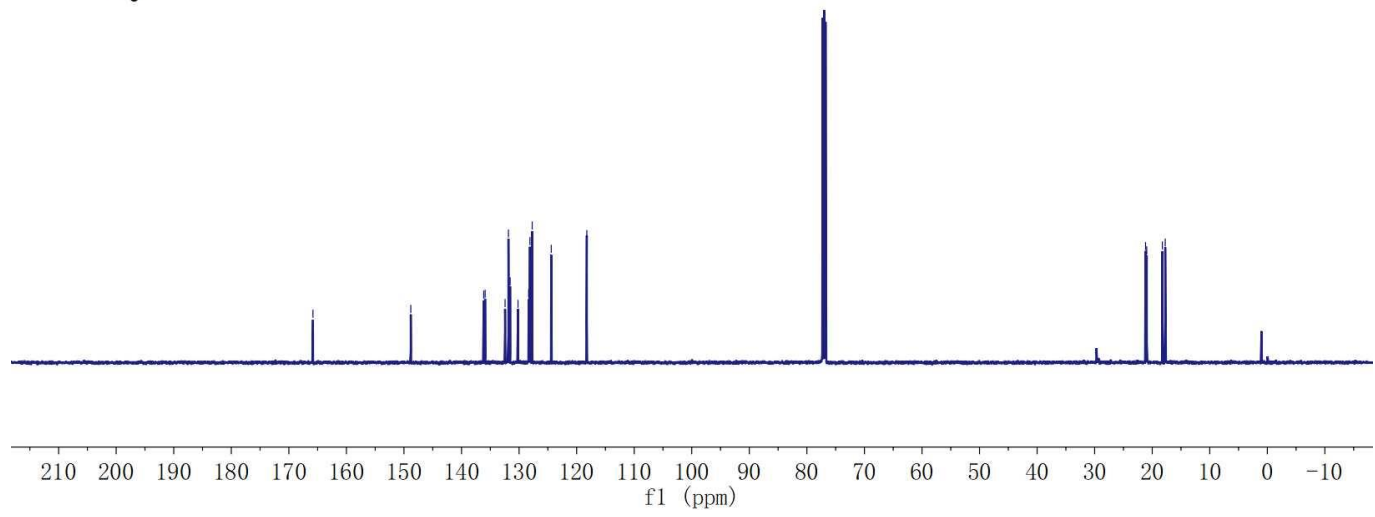
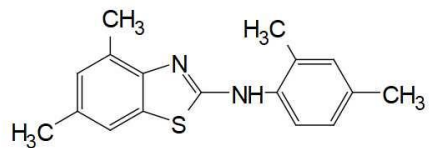
yao-8-6-c

7.7059
7.4809
7.4653
7.2061
7.2030
7.0919
7.0882
7.0820
7.0779
7.0663
7.0622
6.9394
2.4826
2.3537
2.3505
2.2846



yao-8-6-c

165.8137
148.8151
136.1410
135.8984
132.4328
131.8474
131.5550
130.1829
128.3345
128.1137
127.7242
124.4168
118.2361
21.1519
20.9494
18.2378
17.7396

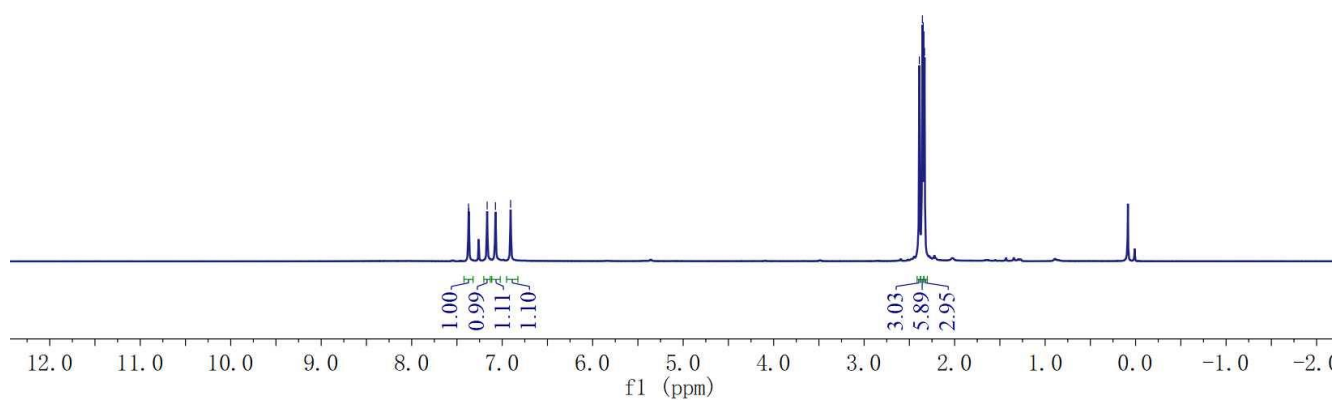
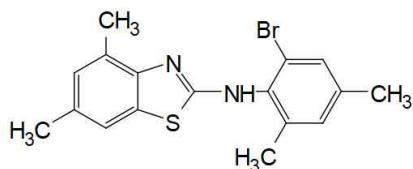


N-(2-Bromo-4,6-dimethylphenyl)-4,6-dimethylbenzo[d]thiazol-2-amine (19)

yao-9-26-a

7.3717
7.3678
7.1661
7.0743
6.9068

2.3898
2.3560
2.3471
2.3325

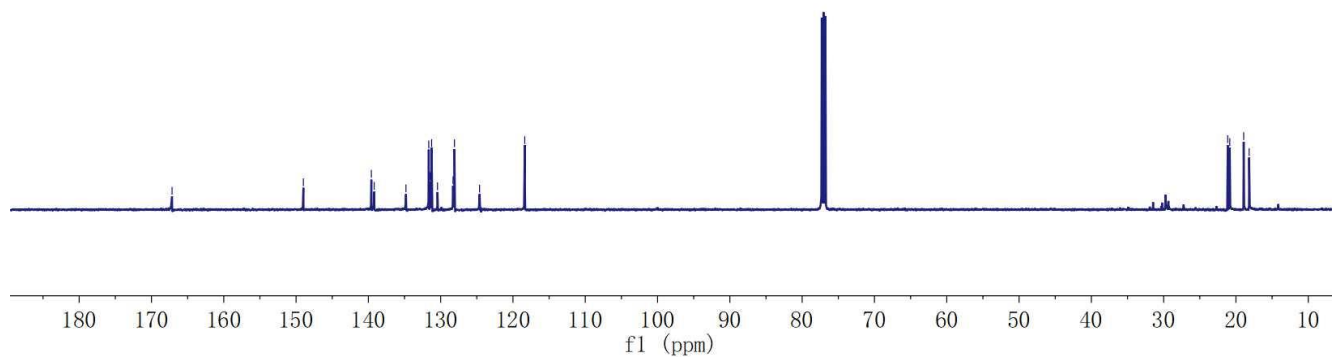
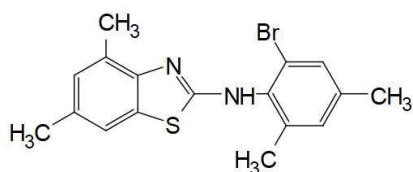


yao-9-26-a

167.1540

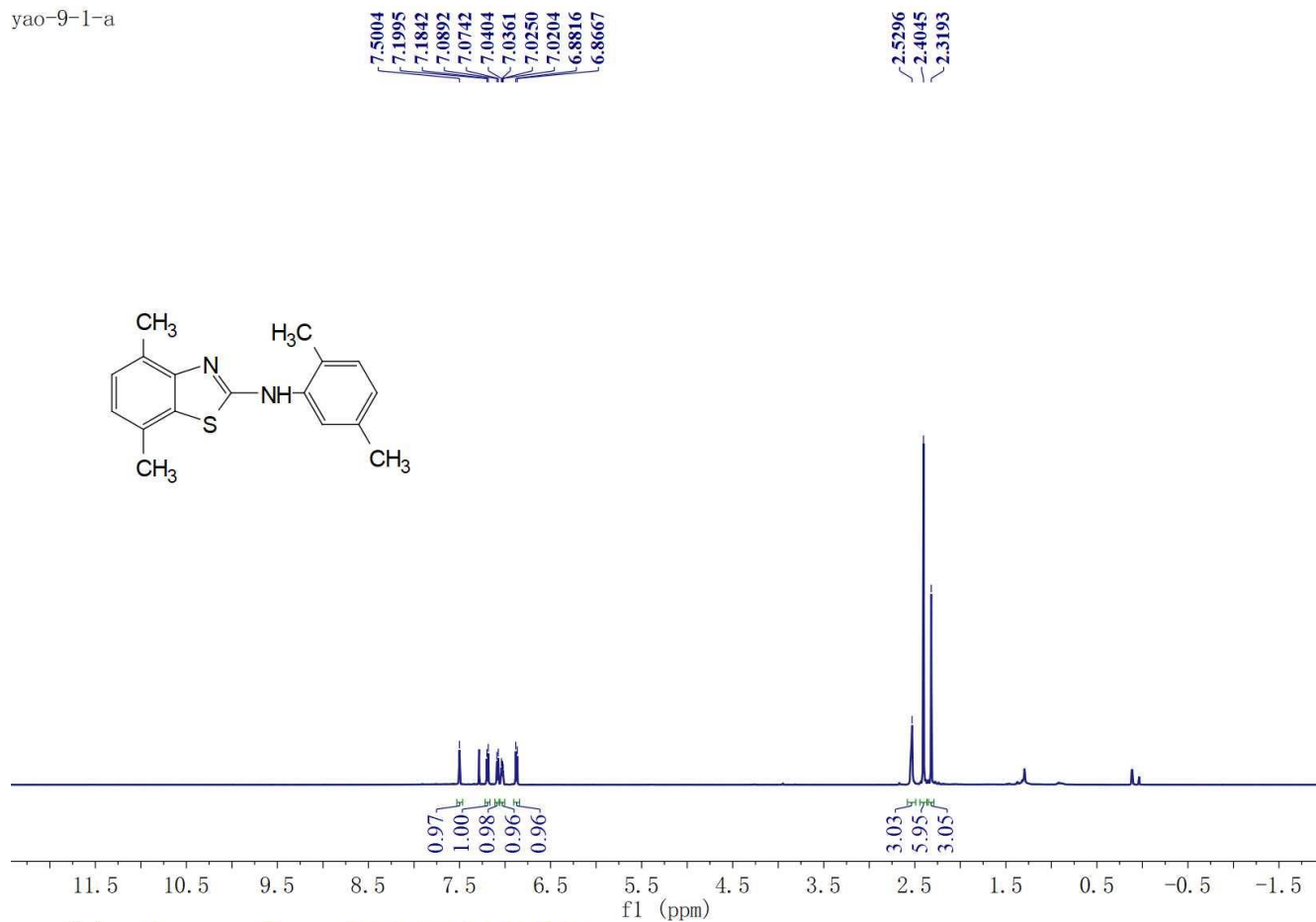
148.9896
139.5885
139.1949
134.8005
131.6497
131.4317
131.2492
130.4391
128.2907
128.0917
124.6197
118.3689

21.1400
20.8570
18.9322
18.1753

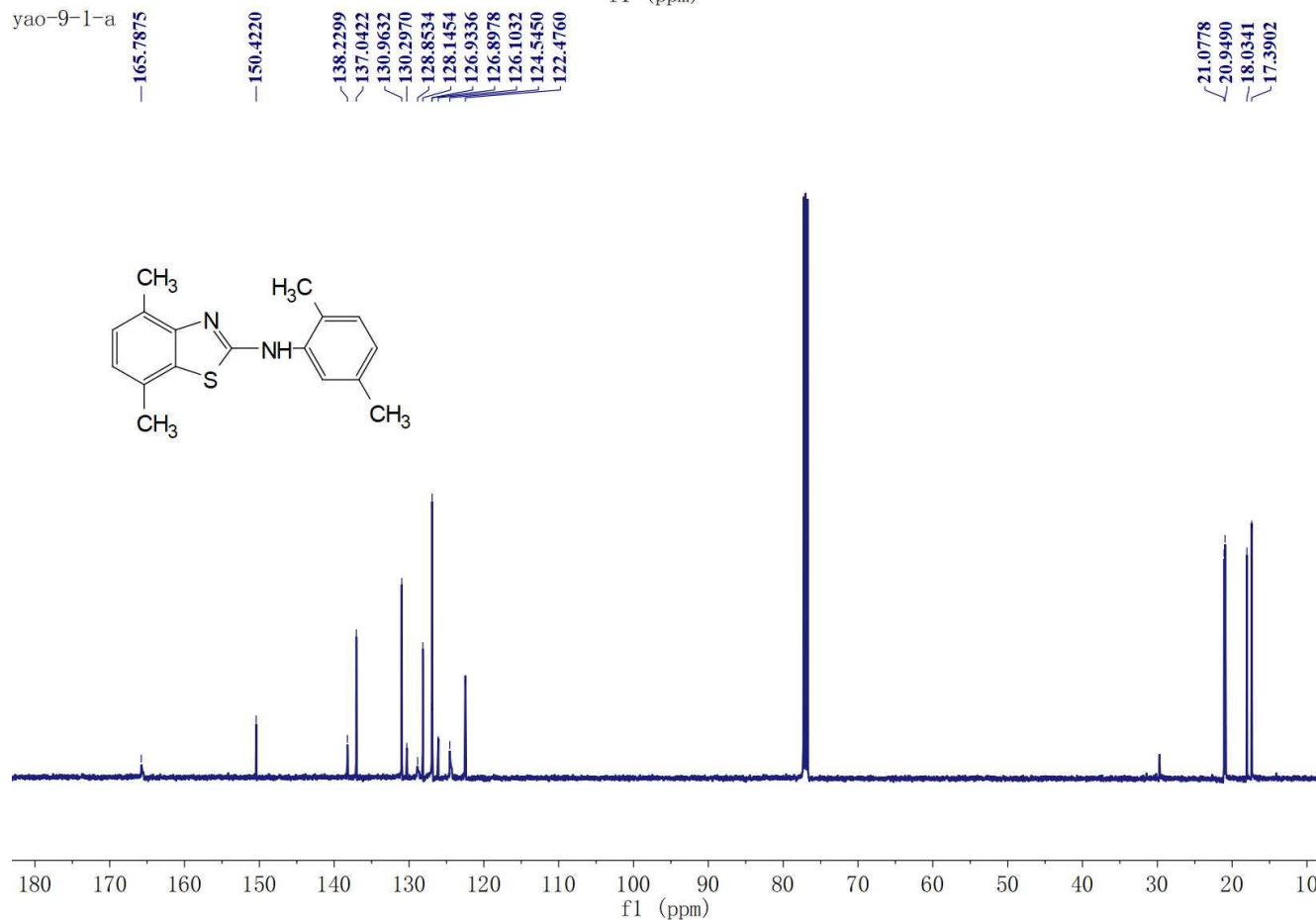


N-(2,5-dimethylphenyl)-4,7-dimethylbenzo[d]thiazol-2-amine (20)

yao-9-1-a



yao-9-1-a

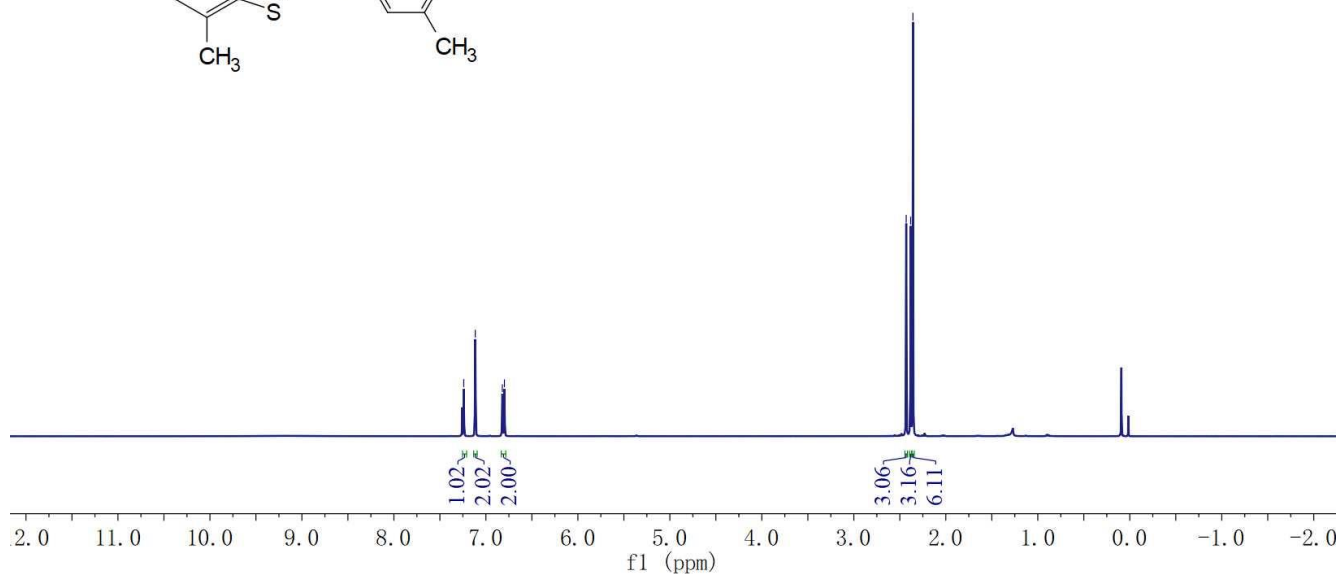
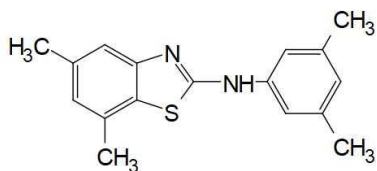


N-(2,5-dimethylphenyl)-4,7-dimethylbenzo[d]thiazol-2-amine (21)

yao-9-1-b

7.2406
7.1156
6.8212
6.7988

2.4305
2.3823
2.3576



yao-9-1-b

165.1615

151.3276

140.0221

139.2668

135.9898

130.3804

126.9863

126.0792

124.1122

118.2513

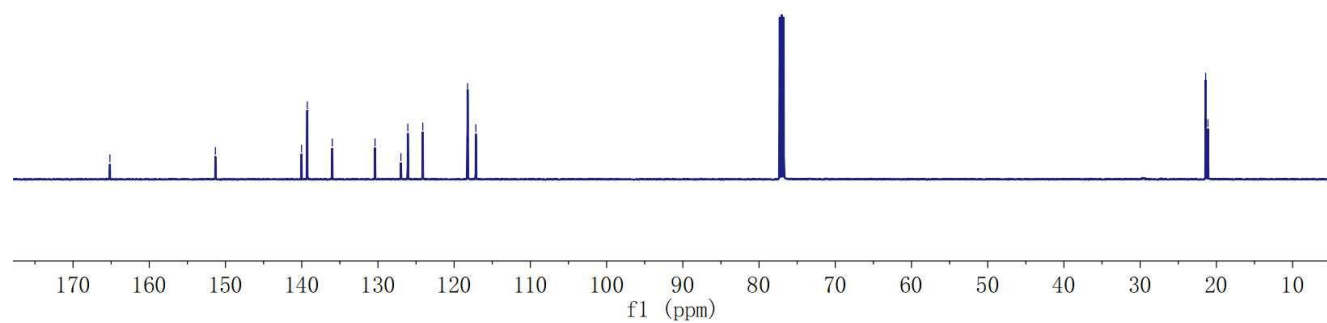
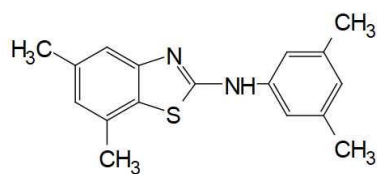
118.2359

117.1583

21.4298

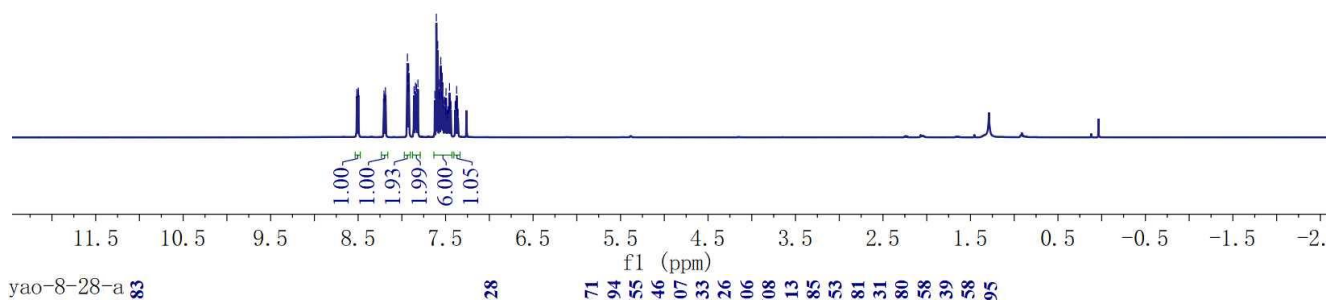
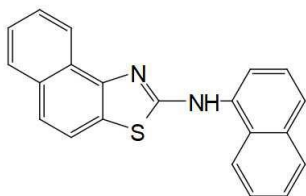
21.4041

21.1062



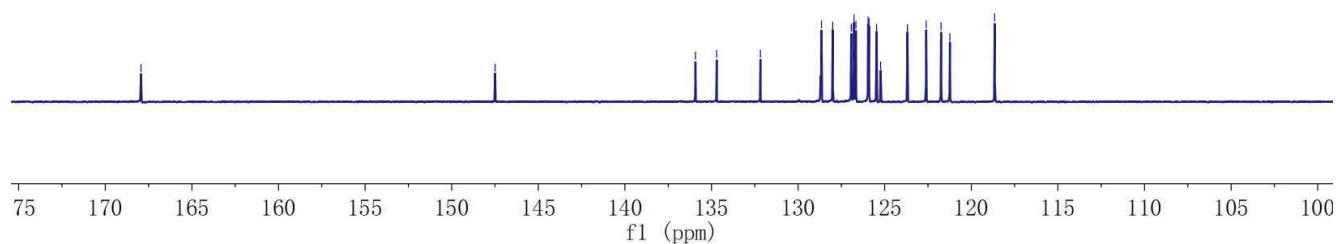
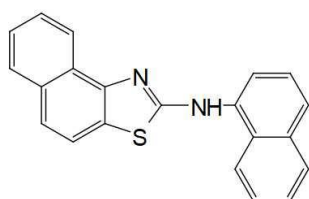
***N*-(Naphthalen-1-yl)naphtho[1,2-*d*]thiazol-2-amine (22)**

8.5145
8.5127
8.4989
8.4952
8.2007
8.2021
8.1878
8.1853
7.9388
7.9364
7.9333
7.9242
7.9215
7.9174
7.8607
7.8443
7.8330
7.8163
7.6232
7.6059
7.5900
7.5728
7.5698
7.5548
7.5531
7.5434
7.5408
7.5383
7.5273
7.5245
7.5124
7.5093
7.4988
7.4956
7.4928
7.4819
7.4791
7.4715
7.4688
7.4578
7.4550
7.4523
7.4413
7.4386
7.3904
7.3878
7.3766
7.3739
7.3711
7.3601
7.3575



yao-8-28-a

167.9383
147.4928
135.9271
134.6994
132.1755
128.6946
128.6507
128.0033
126.9326
126.7906
126.7708
126.6613
125.9585
125.9053
125.4681
125.2331
123.6880
122.6058
121.7439
121.2358
118.6495

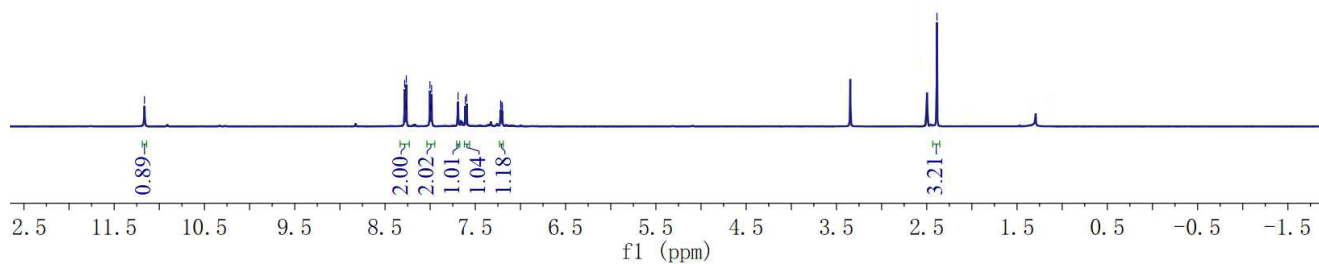
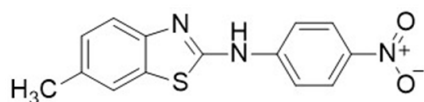


6-Methyl-N-(4-nitrophenyl)benzo[d]thiazol-2-amine (23)

yao-9-20-b
-11.1643

8.2824
8.2681
8.2640
8.0023
7.9979
7.9880
7.9838
7.6908
7.6114
7.5950
7.2198
7.2164
7.2033
7.1998

-2.3868



yao-9-20
-159.8113

-149.3328
-146.4807
-140.7520
-132.6622
-130.3694
-129.5317
-127.3399
-125.4226
-121.1401
-119.6670
-116.9826

-20.8935

