Supplementary Material (ESI) for Green Chemistry

Supporting Information

An Economically and Environmentally Sustainable Synthesis of 2-Aminobenzothiazoles and 2-Aminobenzoxazoles Promoted by Water

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1. General details

Melting points were measured by a Kofler micromelting point apparatus and were uncorrected. Flash chromatographic purification of products was performed on silica gel (200-300 mesh). Thin-layer chromatography was visualized with UV light (254 and 365 nm). ^{1}H and ^{13}C NMR spectra were determined on a Bruker AC 400 spectrometer as $CDCl_3$ or DMSO-d_6 solutions. Chemical shifts were expressed in parts per million (δ) downfield from the internal standard tetramethylsilane and were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants J were given in Hz. Mass spectra were obtained in API mode using a Waters Acquity SQ HPLC-mass spectrometer. The HRMS (High-Resolution Mass Spectra) were performed on a JEOL HX 110A spectrometer.

2. Synthetic methods

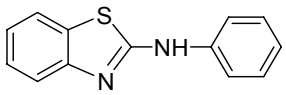
A typical procedure for the synthesis of 3a

A mixture of phenyl isothiocyanate (**1a**, 1 mmol) and 2-aminothiophenol (**2a**, 1 mmol) in water (2 mL) was stirred at 80 ºC. Upon completion, the reaction mixture was cooled to rt. The crude product was collected by suction. Higher purity of product could be achieved by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as eluent to give **3a** as colorless solid. **3b**-**3s** were obtained in a similar manner.

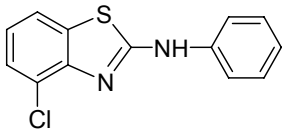
A typical procedure for the synthesis of 5a

A mixture of phenyl isothiocyanate (**1a**, 1 mmol), 2-aminophenol (**4a**, 1 mmol) and $FeCl_3 \cdot 6H_2O$ (0.2 mmol) in water (2 mL) was stirred at 80 ºC. Upon completion as indicated by TLC, the reaction mixture was cooled to rt. The crude product was collected by suction, which was further purified by column chromatography on silica gel using petroleum ether/ethyl acetate (20:1) as eluent to give **5a** as colorless solid. **5b**-**5o** were obtained in a similar manner.

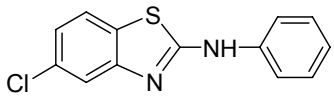
3. Spectroscopic characterization data



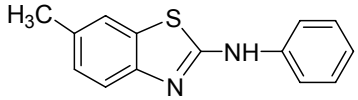
***N*-Phenylbenzo[*d*]thiazol-2-amine (3a):** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14- 7.19 (m, 2H, ArH), 7.34 (td, 1H, *J*1 = 8.0 Hz, *J*2 = 0.8 Hz, ArH), 7.41 (t, 2H, *J* = 8.0 Hz, ArH), 7.50-7.52 (m, 2 H, ArH), 7.59-7.65 (m, 2H, ArH), 8.44 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 119.26, 120.41, 120.85, 122.34, 124.42, 126.12, 129.56, 129.80, 139.91, 151.32, 164.97. MS: m/z 227 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{11}N_2S$: 227.0643 $[M+H]^+$, found: 227.0645.



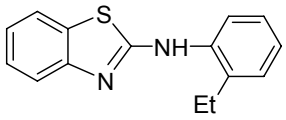
4-Chloro-*N*-phenylbenzo[*d*]thiazol-2-amine (3b): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.03 (t, 1H, *J* = 7.2 Hz, ArH), 7.09 (t, 1H, *J* = 7.6 Hz, ArH), 7.35-7.39 (m, 3H, ArH), 7.73 (d, 1H, *J* = 7.6 Hz, ArH), 7.83 (d, 2H, *J* = 8.0Hz, ArH), 10.73 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 118.51, 120.37, 122.98, 123.20, 123.29, 126.34, 129.48, 131.82, 140.79, 149.28, 162.79. MS: m/z 261 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}ClN_2S$: 261.0253 $[M+H]^+$, found: 261.0259.



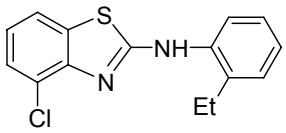
5-Chloro-*N*-phenylbenzo[*d*]thiazol-2-amine (3c): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.13 (dd, 1H, *J*1 = 8.4 Hz, *J*2 = 2.0 Hz, ArH), 7.20 (t, 1H, *J* = 7.4 Hz, ArH), 7.42 (t, 2H, *J* = 8.0 Hz, ArH), 7.48-7.51 (m, 2H, ArH), 7.53 (s, 1H, ArH), 7.58 (d, 1H, *J* = 2.0 Hz, ArH), 8.07 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO) δ: 118.47, 119.07, 122.43, 122.77, 122.88, 129.23, 129.45, 130.99, 140.72, 153.77, 163.79. MS: m/z 261 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}ClN_2S$: 261.0253 $[M+H]^+$, found: 261.0255.



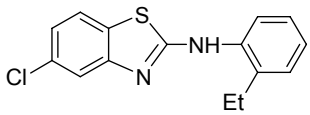
6-Methyl-*N*-phenylbenzo[*d*]thiazol-2-amine (3d): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.42 (s, 3H, CH_3), 7.14 (t, 2H, J = 7.4 Hz, ArH), 7.40 (t, 2H, J = 8.0 Hz, ArH), 7.44 (s, 1H, ArH), 7.48-7.52 (m, 3H, J = 8.2 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.27, 118.97, 119.91, 120.83, 124.06, 127.34, 129.49, 129.96, 132.26, 139.95, 149.19, 163.73. MS: m/z 241 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{13}N_2S$: 241.0799 $[M+H]^+$, found: 241.0793.



***N*-(2-Ethylphenyl)benzo[*d*]thiazol-2-amine (3e):** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.12 (t, 3H, J = 7.2 Hz, CH_3), 2.65 (q, 2H, J = 7.2 Hz, CH_2), 7.06 (t, 1H, J = 7.2 Hz, ArH), 7.14 (t, 1H, J = 7.2 Hz, ArH), 7.21-7.28 (m, 3H, ArH), 7.43 (d, 1H, J = 8.0 Hz, ArH), 7.69-7.72 (m, 2H, ArH), 9.63 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 14.85, 24.32, 118.92, 121.41, 122.03, 124.97, 125.85, 126.13, 126.98, 129.47, 130.66, 137.76, 138.63, 152.42, 165.36. MS: m/z 255 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{15}N_2S$: 255.0956 $[M+H]^+$, found: 255.0960.

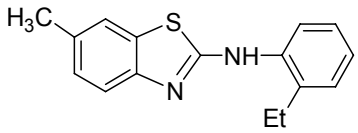


4-Chloro-*N*-(2-ethylphenyl)benzo[*d*]thiazol-2-amine (3f): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.19 (t, 3H, J = 7.2 Hz, CH_3), 2.69 (q, 2H, J = 7.2 Hz, CH_2), 7.00 (t, 1H, J = 8.0Hz, ArH), 7.26-7.35 (m, 4H, ArH), 7.42 (d, 1H, J = 8.0 Hz, ArH), 7.52-7.54 (m, 1H, ArH), 8.42 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.52, 24.46, 119.27, 122.30, 123.25, 125.71, 126.21, 127.27, 127.66, 129.64, 131.32, 137.55, 139.68, 149.02, 168.65. MS: m/z 289 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{14}ClN_2S$: 289.0566 $[M+H]^+$, found: 289.0572.

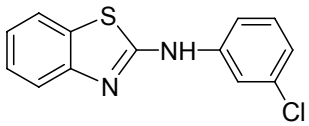


5-Chloro-*N*-(2-ethylphenyl)benzo[*d*]thiazol-2-amine (3g): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.23 (t, 3H, J = 7.2 Hz, CH_3), 2.78 (q, 2H, J = 7.2 Hz, CH_2), 7.04 (d, 1H, J = 8.4 Hz, ArH), 7.22 (s, 1H, ArH), 7.34-7.42 (m, 4H, ArH), 7.57-7.59 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.66,

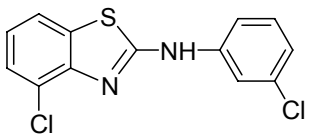
24.59, 118.39, 121.50, 121.89, 126.15, 127.40, 127.86, 128.15, 129.76, 131.86, 137.43, 139.96, 152.75, 170.29. MS: m/z 289 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{14}ClN_2S$: 289.0566 $[M+H]^+$, found: 289.0570.



6-Methyl-*N*-(2-ethylphenyl)benzo[*d*]thiazol-2-amine (3h): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (t, 3H, *J* = 7.2 Hz, CH_3), 2.38 (s, 3H, CH_3), 2.73 (q, 2H, *J* = 7.2 Hz, CH_2), 7.08 (d, 1H, *J* = 8.0 Hz, ArH), 7.24-7.36 (m, 5H, ArH), 7.62 (d, 1H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.46, 21.21, 24.51, 118.39, 120.86, 124.87, 126.72, 127.16, 127.18, 129.46, 130.14, 131.71, 137.79, 138.58, 149.50, 166.87. MS: m/z 269 $[M+H]^+$. HRMS (FAB) Calcd for $C_{16}H_{17}N_2S$: 269.1112 $[M+H]^+$, found: 269.1107.

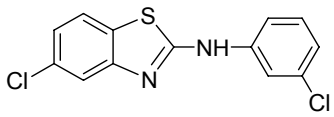


***N*-(3-Chlorophenyl)benzo[*d*]thiazol-2-amine (3i):** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.47 (d, 1H, *J* = 7.6 Hz, ArH), 7.17 (t, 1H, *J* = 7.2 Hz, ArH), 7.31-7.38 (m, 2H, ArH), 7.60 (d, 1H, *J* = 8.0 Hz, ArH), 7.63 (d, 1H, *J* = 8.0 Hz, ArH), 7.82 (d, 1H, *J* = 8.0 Hz, ArH), 8.03 (s, 1H, ArH), 10.63 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 116.57, 117.41, 119.97, 121.60, 122.01, 123.09, 126.43, 130.40, 131.05, 133.81, 142.35, 152.21, 161.63. MS: m/z 261 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}ClN_2S$: 261.0253 $[M+H]^+$, found: 261.0250.

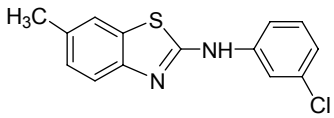


4-Chloro-*N*-(3-chlorophenyl)benzo[*d*]thiazol-2-amine (3j): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.08 (d, 1H, *J* = 7.6 Hz, ArH), 7.15 (t, 1H, *J* = 7.6Hz, ArH), 7.36-7.43 (m, 2H, ArH), 7.60 (d, 1H, *J* = 8.0 Hz, ArH), 7.79 (d, 1H, *J* = 8.0 Hz, ArH), 8.11 (s, 1H, ArH), 10.87 (br s, 1H, NH); ^{13}C NMR

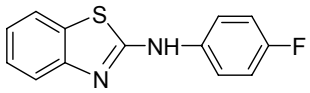
(100 MHz, DMSO-d_6) δ: 116.72, 117.83, 120.59, 122.42, 123.42, 123.77, 126.45, 131.04, 131.84, 133.90, 142.06, 148.95, 162.31. MS: m/z 295 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9Cl_2N_2S$: 294.9863 $[M+H]^+$, found: 294.9871.



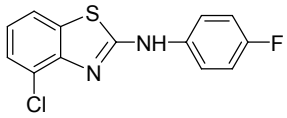
5-Chloro-*N*-(3-chlorophenyl)benzo[*d*]thiazol-2-amine (3k): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.23 (d, 1H, *J* = 8.0 Hz, ArH), 6.34 (d, 1H, *J* = 8.0 Hz, ArH), 6.50 (t, 1H, *J* = 8.0 Hz, ArH), 6.74 (d, 1H, *J* = 8.0 Hz, ArH), 6.81 (s, 1H, ArH), 6.85 (d, 1H, *J* = 8.0 Hz, ArH), 7.15 (s, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 116.32, 117.63, 119.15, 121.83, 122.08, 122.45, 128.93, 130.21, 131.25, 134.01, 141.67, 153.29, 163.18. MS: m/z 295 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9Cl_2N_2S$: 294.9863 $[M+H]^+$, found: 294.9869.



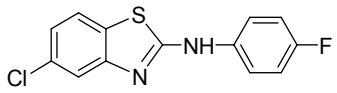
6-Methyl-*N*-(3-chlorophenyl)benzo[*d*]thiazol-2-amine (3l): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.34(s, 3H, CH_3), 7.02 (d, 1H, *J* = 7.6 Hz, ArH), 7.12 (d, 1H, *J* = 8.0 Hz, ArH), 7.34 (t, 1H, *J* = 8.0 Hz, ArH), 7.51 (d, 1H, *J* = 8.0 Hz, ArH), 7.56-7.58 (m, 2H, ArH), 8.04 (s, 1H, ArH), 10.54 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.27, 116.44, 117.28, 119.62, 121.40, 121.83, 127.53, 130.46, 131.00, 132.43, 133.80, 142.46, 150.10, 160.83. MS: m/z 275 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}ClN_2S$: 275.041 $[M+H]^+$, found: 275.0414.



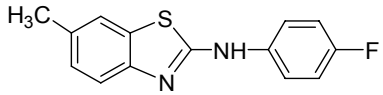
***N*-(4-Fluorophenyl)benzo[*d*]thiazol-2-amine (3m):** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.13 (t, 1H, *J* = 7.6 Hz, ArH), 7.19 (t, 2H, *J* = 8.8 Hz, ArH), 7.30 (t, 1H, *J* = 7.6 Hz, ArH), 7.57 (d, 1H, *J* = 7.6 Hz, ArH), 7.77-7.81 (m, 3H, ArH), 10.49 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 115.85, 116.07, 119.60, 119.76, 119.83, 121.48, 122.71, 126.31, 130.39, 137.55, 152.45, 156.57, 162.06. MS: m/z 245 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}FN_2S$: 245.0549 $[M+H]^+$, found: 245.0544.



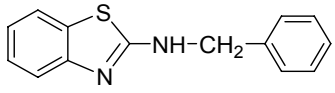
4-Chloro-*N*-(4-fluorophenyl)benzo[*d*]thiazol-2-amine (3n): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03 (t, 1H, *J* = 7.6 Hz, ArH), 7.06-7.10 (m, 2H, ArH), 7.30 (d, 1H, *J* = 8.0 Hz, ArH), 7.39-7.44 (m, 2H, ArH), 7.46 (s, 1H, ArH), 9.36 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 116.28, 116.50, 119.33, 122.71, 123.43, 124.51, 124.59, 126.40, 130.91, 135.91, 135.94, 148.65, 159.51, 161.59, 167.25. MS: m/z 279 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9ClFN_2S$: 279.0159 $[M+H]^+$, found: 279.0163.



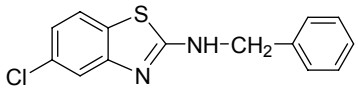
5-Chloro-*N*-(4-fluorophenyl)benzo[*d*]thiazol-2-amine (3o): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.13-7.20 (m, 3H, ArH), 7.57 (d, 1H, *J* = 2.0 Hz, ArH), 7.74-7.78 (m, 3H, ArH), 10.61 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 107.05, 115.89, 116.11, 119.02, 120.16, 120.24, 122.45, 122.75, 129.18, 131.02, 137.14, 153.65, 156.82, 159.20, 163.88. MS: m/z 279 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9ClFN_2S$: 279.0159 $[M+H]^+$, found: 279.0161.



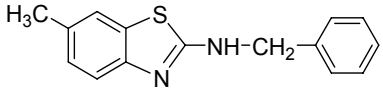
6-Methyl-*N*-(4-fluorophenyl)benzo[*d*]thiazol-2-amine (3p): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.32 (s, 3H, CH_3), 7.10 (d, 1H, *J* = 8.4 Hz, ArH), 7.17 (t, 2H, *J* = 8.8 Hz, ArH), 7.45 (d, 1H, *J* = 8.0 Hz, ArH), 7.55 (s, 1H, ArH), 7.76-7.80 (m, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.25, 115.80, 116.02, 119.26, 119.60, 119.67, 121.32, 127.38, 130.44, 131.99, 137.65, 150.34, 156.47, 158.84, 161.26. MS: m/z 259 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}FN_2S$: 259.0705 $[M+H]^+$, found: 259.0708.



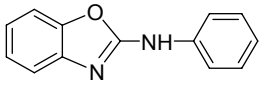
***N*-Benzylbenzo[*d*]thiazol-2-amine (3q):** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.58 (d, 2H, J = 5.6 Hz, CH_2), 7.00 (t, 1H, J = 7.6 Hz, ArH), 712-7.38 (m, 7H, ArH), 7.65 (d, 1H, J = 7.6 Hz, ArH), 8.49 (t, 1H, J = 5.6 Hz, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 47.63, 118.53, 121.37, 121.40, 125.97, 127.46, 127.81, 128.81, 130.84, 139.37, 152.88, 166.66. MS: m/z 241 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{13}N_2S$: 241.0799 $[M+H]^+$, found: 241.0798.



5-Chloro-*N*-benzylbenzo[*d*]thiazol-2-amine (3r): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.58 (d, 2H, J = 5.6 Hz, CH_2), 7.03 (dd, 1H, $J1$ = 8.4 Hz, $J2$ = 2.0 Hz), 7.22-7.39 (m, 6H, ArH), 7.66 (d, 1H, J = 8.8 Hz, ArH), 8.69 (t, 1H, J = 5.6 Hz, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 47.69, 117.95, 121.08, 122.63, 127.55, 127.85, 128.85, 129.64, 130.70, 139.02, 154.16, 168.30. MS: m/z 275 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}ClN_2S$: 275.041 $[M+H]^+$, found: 275.0406.

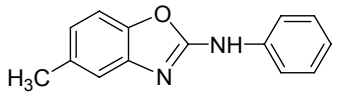


6-Methyl-*N*-benzylbenzo[*d*]thiazol-2-amine (3s): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H, CH_3), 4.61 (s, 2H, CH_2), 7.07 (d, 1H, J = 8.0 Hz, ArH), 7.26-7.41 (m, 7H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.20, 49.39, 118.46, 120.89, 127.13, 127.66, 127.80, 128.78, 130.38, 131.40, 137.53, 149.90, 166.86. MS: m/z 255 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{15}N_2S$: 255.0956 $[M+H]^+$, found: 255.0953.

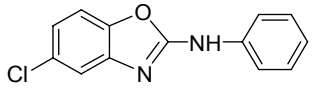


***N*-Phenylbenzo[*d*]oxazol-2-amine (5a):** ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.02 (t, 1H, J = 7.2 Hz, ArH), 7.11 (t, 1H, J = 7.2 Hz, ArH), 7.20 (t, 1H, J = 7.2 Hz, ArH), 7.36 (t, 2H, J = 8.0 Hz, ArH), 7.45 (t, 2H, J = 8.4 Hz, ArH), 7.75 (d, 2H, J = 8.0 Hz, ArH), 10.56 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 109.35, 117.03, 118.03, 122.07, 122.54, 124.41, 129.38, 139.17, 142.87, 147.44, 158.43. MS: m/z 211 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{11}N_2O$: 211.0871 $[M+H]^+$, found:

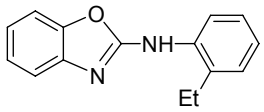
211.0874.



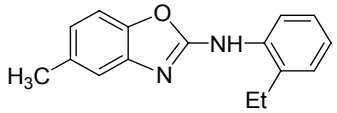
5-Methyl-*N*-phenylbenzo[*d*]oxazol-2-amine (5b): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.34 (s, 3H, CH_3), 6.90 (d, 1H, J = 7.6 Hz, ArH), 7.00 (t, 1H, J = 7.6Hz, ArH), 7.24 (s, 1H, ArH), 7.30-7.37 (m, 3H, ArH), 7.75 (d, 2H, J = 8.0 Hz, ArH), 10.54 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.50, 108.72, 117.32, 117.94, 122.43, 122.65, 129.38, 133.54, 139.23, 143.02, 145.57, 158.52. MS: m/z 225 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{13}N_2O$: 225.1028 $[M+H]^+$, found: 225.1033.



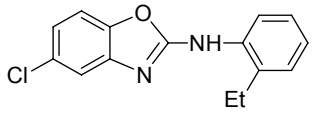
5-Chloro-*N*-phenylbenzo[*d*]oxazol-2-amine (5c): ^{1}H NMR (400 MHz, DMSO- d_6) δ: 7.03 (t, 1H, J = 7.6 Hz, ArH), 7.11 (dd, 1H, $J1$ = 8.4 Hz, $J2$ = 2.0 Hz, ArH), 7.35 (t, 2H, J = 7.6 Hz, ArH), 7.48 (d, 2H, J = 8.8 Hz, ArH), 7.72 (d, 2H, J = 8.0 Hz, ArH), 10.75 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 110.47, 116.73, 118.26, 121.71, 122.92, 128.60, 129.44, 138.77, 144.49, 146.30, 159.55. MS: m/z 245 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}ClN_2O$: 245.0482 $[M+H]^+$, found: 245.0490.



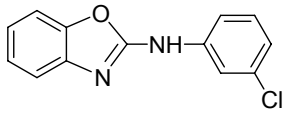
***N*-(2-Ethylphenyl)benzo[*d*]oxazol-2-amine (5d):** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28 (t, 3H, J = 7.6Hz, CH_3), 2.73 (q, 2H, J = 7.6 Hz, CH_2), 7.09-7.34 (m, 6H, ArH), 7.42 (d, 1H, J = 8.0 Hz, ArH), 7.98 (d, 1H, J = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.95, 24.29, 109.03, 117.01, 121.65, 121.79, 124.17, 124.86, 127.08, 128.80, 134.31, 135.25, 142.43, 148.00, 159.23. MS: m/z 239 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{15}N_2O$: 239.1184 $[M+H]^+$, found: 239.1180.



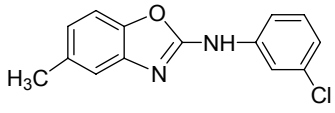
5-Methyl-*N*-(2-ethylphenyl)benzo[*d*]oxazol-2-amine (5e): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.28 (t, 3H, *J* = 7.6Hz, CH_3), 2.72 (q, 2H, *J* = 7.6 Hz, CH_2), 6.91 (d, 1H, *J* = 8.4 Hz, ArH), 7.14-7.34, (m, 5H, ArH), 7.97 (d, 1H, *J* = 8.0 Hz, ArH),; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.92, 21.53, 24.28, 108.39, 117.35, 121.64, 122.36, 124.72, 127.05, 128.75, 133.88, 134.15, 135.34, 142.51, 146.15, 159.31. MS: m/z 253 $[M+H]^+$. HRMS (FAB) Calcd for $C_{16}H_{17}N_2O$: 253.1341 $[M+H]^+$, found: 253.1346.



5-Chloro-*N*-(2-ethylphenyl)benzo[*d*]oxazol-2-amine (5f): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.27 (t, 3H, *J* = 7.6 Hz, CH_3), 2.72 (q, 2H, *J* = 7.6 Hz, CH_2), 7.05 (dd, 1H, *J1* = 8.4 Hz, *J*2 = 2.0 Hz, ArH), 7.18-7.35 (m, 5H, ArH), 7.87 (d, 1H, *J* = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.01, 24.29, 109.62, 116.95, 121.52, 122.43, 125.48, 127.08, 128.93, 129.56, 134.78, 135.06, 143.67, 146.61, 160.40. MS: m/z 273 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{14}ClN_2O$: 273.0795 $[M+H]^+$, found: 273.0801.

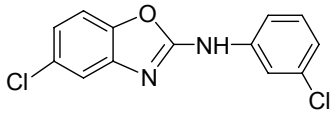


***N*-(3-Chlorophenyl)benzo[*d*]oxazol-2-amine (5g):** ^{1}H NMR (400 MHz, DMSO- d_6) δ: 7.07 (d, 1H, *J* = 7.2 Hz, ArH), 7.14 (t, 1H, *J* = 7.6 Hz, ArH), 7.22 (t, 1H, *J* = 7.6 Hz, ArH), 7.38 (t, 1H, *J* = 8.0 Hz, ArH), 7.49 (d, 2H, *J* = 7.6 Hz, ArH), 7.60 (d, 1H, *J* = 7.6 Hz, ArH), 7.96 (s, 1H, ARH), 10.85 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 109.52, 116.53, 117.27, 117.34, 122.17, 122.47, 124.56, 131.05, 133.88, 140.64, 142.50, 147.37, 157.91. MS: m/z 245 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}ClN_2O$: 245.0482 $[M+H]^+$, found: 245.0489.

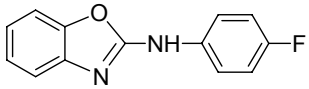


5-Methyl-*N*-(3-chlorophenyl)benzo[*d*]oxazol-2-amine (5h): ^{1}H NMR (400 MHz, DMSO- d_6) δ: 1.60 (s, 3H, CH_3), 6.16 (d, 1H, *J* = 7.2 Hz, ArH), 6.24 (d, 1H, *J* = 7.2 Hz, ArH), 6.44-6.54 (m, 3H,

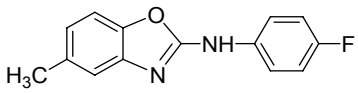
ArH), 6.73 (d, 1H, *J* = 7.6 Hz, ArH), 7.12 (s, 1H, ArH); ^{13}C NMR (100 MHz, DMSO- d_6) δ: 19.52, 107.34, 115.14, 116.24, 116.47, 121.12, 121.86, 129.29, 132.96, 133.45, 139.43, 141.57, 144.82, 157.28. MS: m/z 259 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}ClN_2O$: 259.0638 $[M+H]^+$, found: 259.0645.



5-Chloro-*N*-(3-chlorophenyl)benzo[*d*]oxazol-2-amine (5i): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 6.91-6.93 (m, 1H, ArH), 6.99 (dd, 1H, *J*1 = 8.8 Hz, *J*2 = 2.0 Hz, ArH), 7.17-7.23 (m, 2H, ArH), 7.31 (d, 1H, *J* = 1.6 Hz, ArH), 7.38-7.40 (m, 1H, ArH), 7.77 (s, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 109.46, 116.00, 116.50, 117.36, 121.55, 122.16, 128.92, 129.96, 134.15, 139.69, 143.73, 146.10, 158.89. MS: m/z 279 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9Cl_2N_2O$: 279.0092 $[M+H]^+$, found: 279.0099.

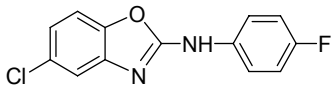


***N*-(4-Fluorophenyl)benzo[*d*]oxazol-2-amine (5j):** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07-7.15 (m, 3H, ArH), 7.24 (t, 1H, *J* = 7.6 Hz, ArH), 7.35 (d, 1H, *J* = 8.0 Hz, ArH), 7.44 (d, 1H, *J* = 8.0Hz, ArH), 7.54-7.57 (m, 2H, ArH), 9.02 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 109.22, 115.89, 116.11, 116.70, 120.50, 120.58, 121.79, 124.39, 133.95, 141.82, 147.85, 158.85. MS: m/z 229 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_{10}FN_2O$: 229.0777 $[M+H]^+$, found: 229.0770.

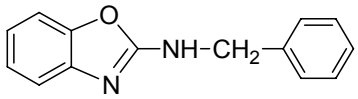


5-Methyl-*N*-(4-fluorophenyl)benzo[*d*]oxazol-2-amine (5k): ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.34 (s, 3H, CH_3), 6.90 (d, 1H, *J* = 8.0 Hz, ArH), 7.17-7.22 (m, 2H, ArH), 7.31 (d, 1H, *J* = 8.0 Hz, ArH), 7.72-7.76 (m, 2H, ArH), 10.56 (br s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.46, 108.73, 115.83, 116.06, 117.28, 119.46, 119.54, 122.67, 133.57, 135.53, 135.65, 142.89, 145.59, 156.66, 158.55. MS: m/z 243 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}FN_2O$: 243.0934 $[M+H]^+$,

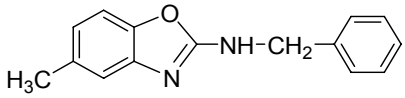
found: 243.0939.



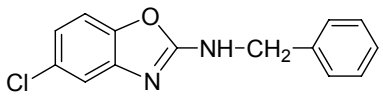
5-Chloro-*N*-(4-fluorophenyl)benzo[*d*]oxazol-2-amine (5l): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.08-7.12 (m, 3H, ArH), 7.21-7.23 (m, 1H, ArH), 7.43 (d, 1H, *J* = 1.6 Hz, ArH), 7.53-7.57 (m, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 110.47, 111.60, 115.91, 116.14, 116.68, 119.85, 119.93, 121.70, 123.90, 128.59, 135.19, 144.38, 146.31, 159.57. MS: m/z 263 $[M+H]^+$. HRMS (FAB) Calcd for $C_{13}H_9ClFN_2O$: 263.0387 $[M+H]^+$, found: 263.0381.



***N*-Benzylbenzo[*d*]oxazol-2-amine (5m):** ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.68 (s, 2H, CH_2), 6.79 (br s, 1H, NH), 7.03 (t, 1H, *J* = 7.6 Hz, ArH), 7.15 (t, 1H, *J* = 7.6 Hz, ArH), 7.20-7.42 (m, 8H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 46.93, 108.82, 116.17, 120.78, 123.96, 127.61, 127.75, 128.79, 137.86, 142.74, 148.46, 162.29. MS: m/z 225 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{13}N_2O$: 225.1028 $[M+H]^+$, found: 225.1025.



5-Methyl-*N*-benzylbenzo[*d*]oxazol-2-amine (5n): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.38 (s, 3H, CH_3), 4.67 (s, 2H, CH_2), 6.83 (d, 1H, *J* = 8.0 Hz, ArH), 6.90 (br s, 1H, NH), 7.11 (d, 2H, *J* = 8.0 Hz, ArH), 7.30-7.42 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 16.70, 42.14, 103.38, 111.73, 116.59, 122.92, 122.95, 124.01, 128.83, 133.19, 138.01, 141.81, 157.77. MS: m/z 239 $[M+H]^+$. HRMS (FAB) Calcd for $C_{15}H_{15}N_2O$: 239.1184 $[M+H]^+$, found: 239.1189.



5-Chloro-*N*-benzylbenzo[*d*]oxazol-2-amine (5o): ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.65 (s, 2H,

CH_2), 6.75 (br s, 1H, NH), 6.96-7.02 (m, 2H, ArH), 7.12 (d, 1H, J = 8.0 Hz, ArH), 7.35-7.38 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 46.95, 109.26, 116.09, 120.48, 127.75, 128.04, 128.89, 129.29, 137.36, 143.99, 146.96, 163.17. MS: m/z 259 $[M+H]^+$. HRMS (FAB) Calcd for $C_{14}H_{12}ClN_2O$: 259.0638 $[M+H]^+$, found: 259.0631.

4. Selected copies of ^{1}H and ^{13}C NMR spectra of 3 and 5

(1) ^{1}H and ^{13}C NMR spectra of *N*-phenylbenzo[*d*]thiazol-2-amine (3a)

(2) ^{1}H and ^{13}C NMR spectra of 4-chloro-*N*-(2-ethylphenyl)benzo[*d*]thiazol-2-amine (3f)

(3) ^{1}H and ^{13}C NMR spectra of 5-chloro-*N*-(3-chlorophenyl)benzo[*d*]thiazol-2-amine (3k)

(4) ^{1}H and ^{13}C NMR spectra of 6-methyl-*N*-(4-fluorophenyl)benzo[*d*]thiazol-2-amine (3p)

(5) ^{1}H and ^{13}C NMR spectra of *N*-benzylbenzo[*d*]thiazol-2-amine (3q)

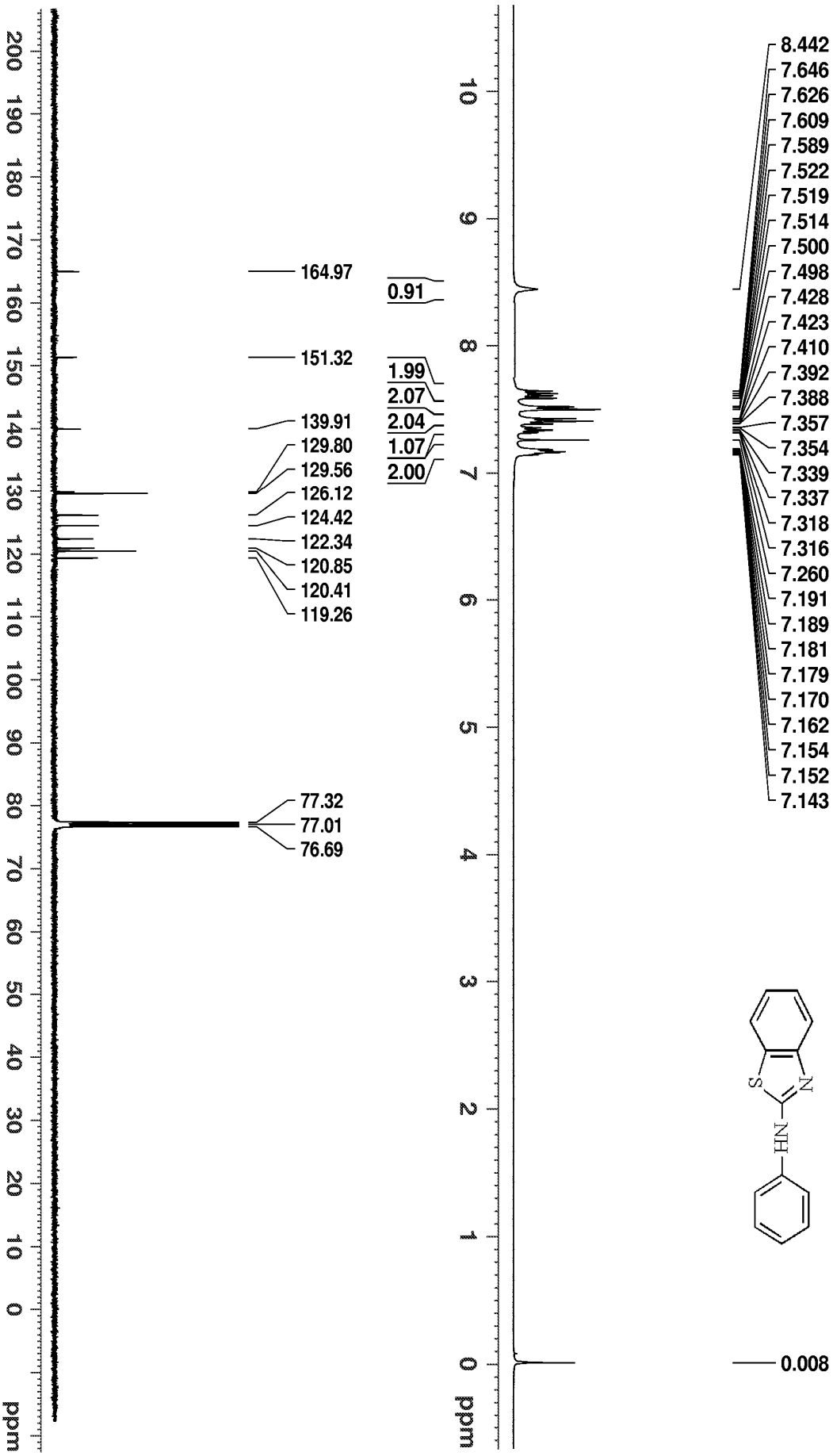
(6) ^{1}H and ^{13}C NMR spectra of *N*-phenylbenzo[*d*]oxazol-2-amine (5a)

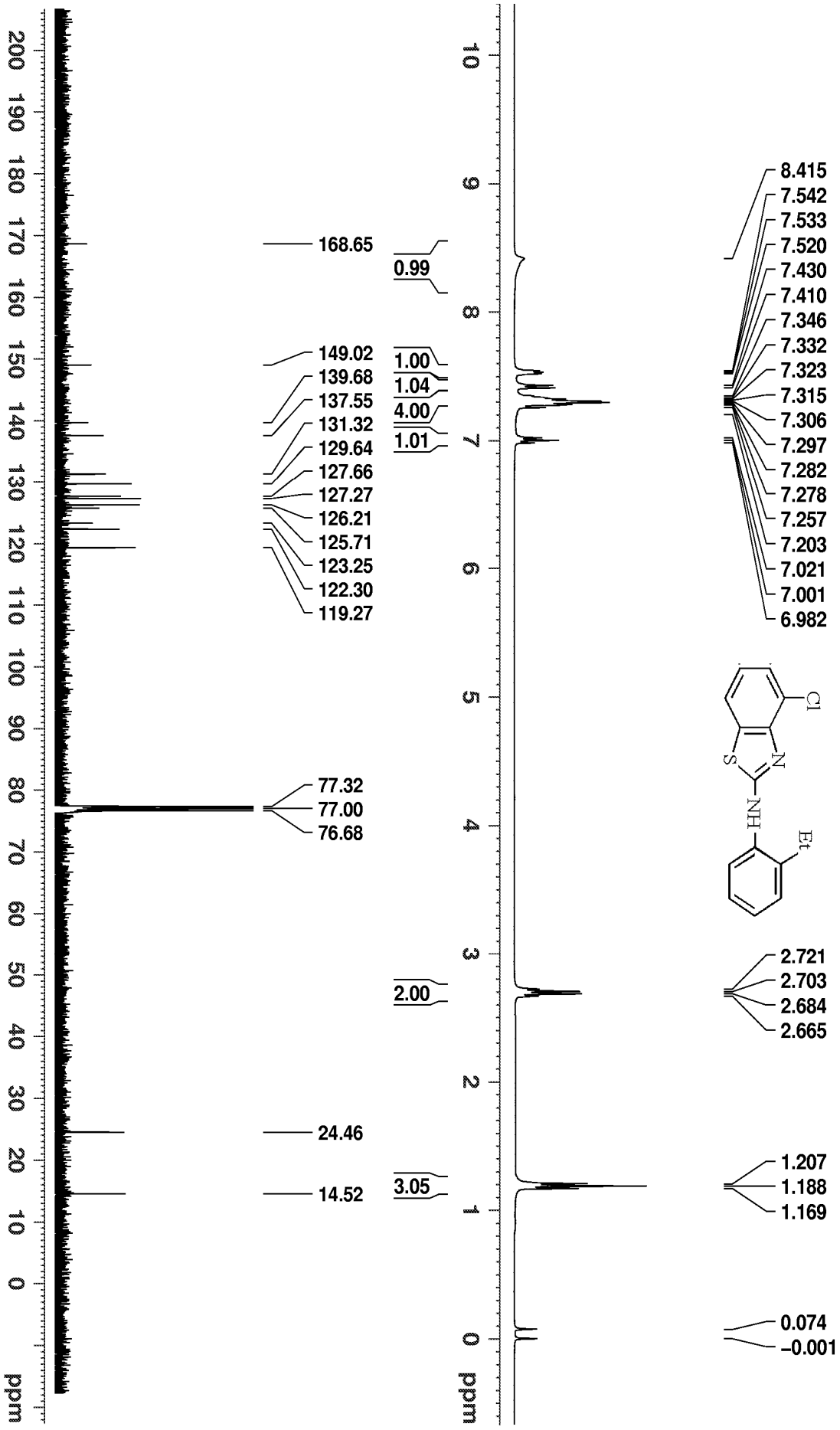
(7) ^{1}H and ^{13}C NMR spectra of 5-chloro-*N*-(2-ethylphenyl)benzo[*d*]oxazol-2-amine (5f)

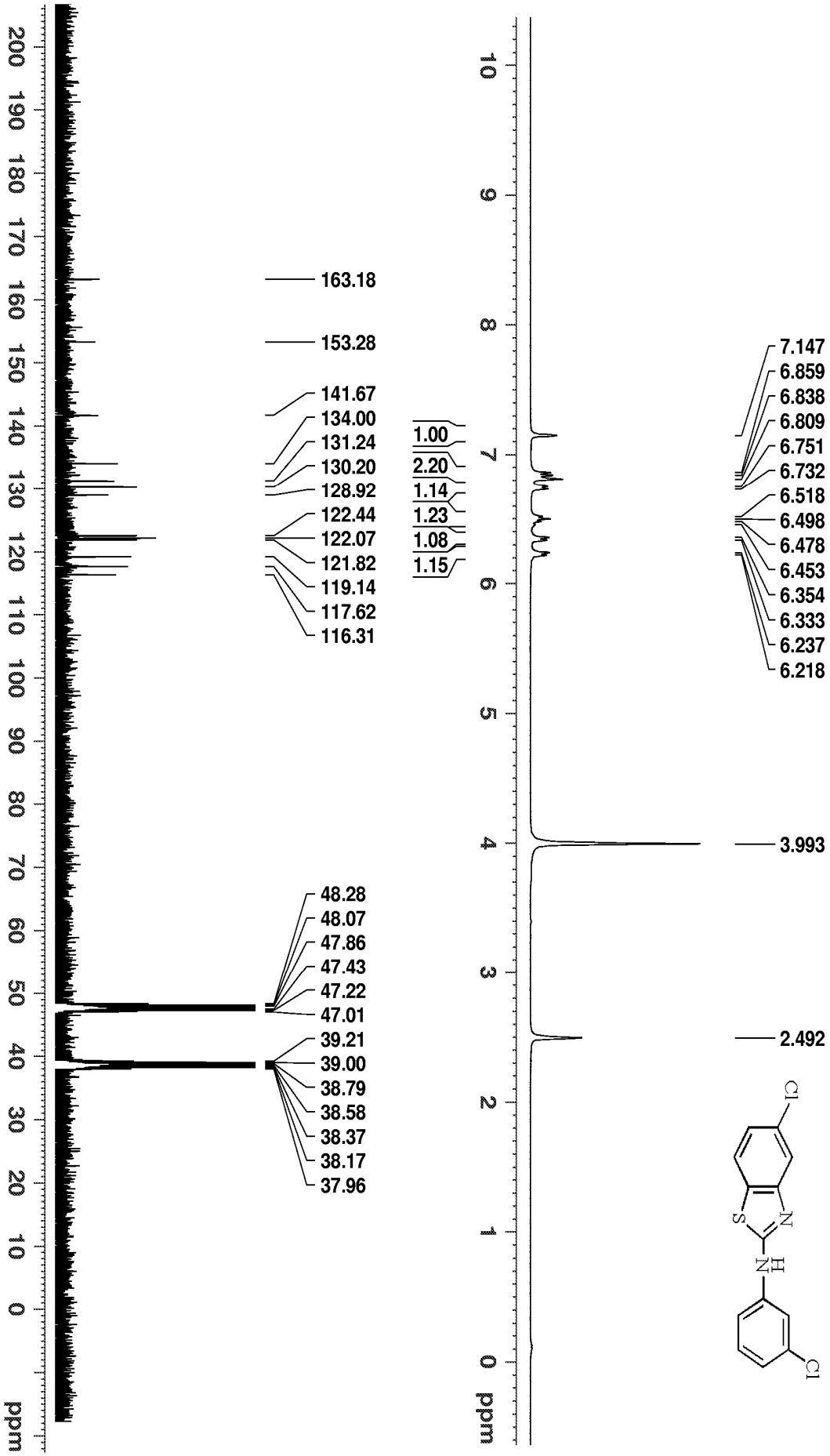
(8) ^{1}H and ^{13}C NMR spectra of 5-methyl-*N*-(3-chlorophenyl)benzo[*d*]oxazol-2-amine (5h)

(9) ^{1}H and ^{13}C NMR spectra of 5-methyl-*N*-(4-fluorophenyl)benzo[*d*]oxazol-2-amine (5k)

(10) ^{1}H and ^{13}C NMR spectra of *N*-benzylbenzo[*d*]oxazol-2-amine (5m)



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6.453
6.354
6.333
6.237
6.218
3.993
2.492
ppm
Cl
S
N
H
N
Cl