**Electronic Supplementary Information**

# Control of Selectivity in the Preparation of 2-Substituted Benzoazoles by Adjusting the Surface Hydrophobicity in Two Solid-Based Sulfonic Acid Catalyst

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1. **Experimental Procedure:**

### 1.1. Preparation of SBA-15-Pr$SO_3H$ (1b) and its characterizations

The synthesis of SBA-15-PrSH was achieved using the procedure described by Stucky and co-workers.[10h] This procedure involved a synthetic strategy based on the co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS) in the presence of Pluronic P123 as the structure directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw ¼ 5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83 g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6 g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhlet apparatus for 24 h. Conversion of thiol group of the catalyst to sulfonic acid moieties was accomplished using hydrogen peroxide. Typically, 0.3 g of solid material was suspended in 10 g of aqueous 30 wt% $H_2O_2$. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M $H_2SO_4$ solution for 2 h, washed several times with water and ethanol, and dried at 60 °C under vacuum overnight to give the corresponding SBA-15-Pr$SO_3H$.

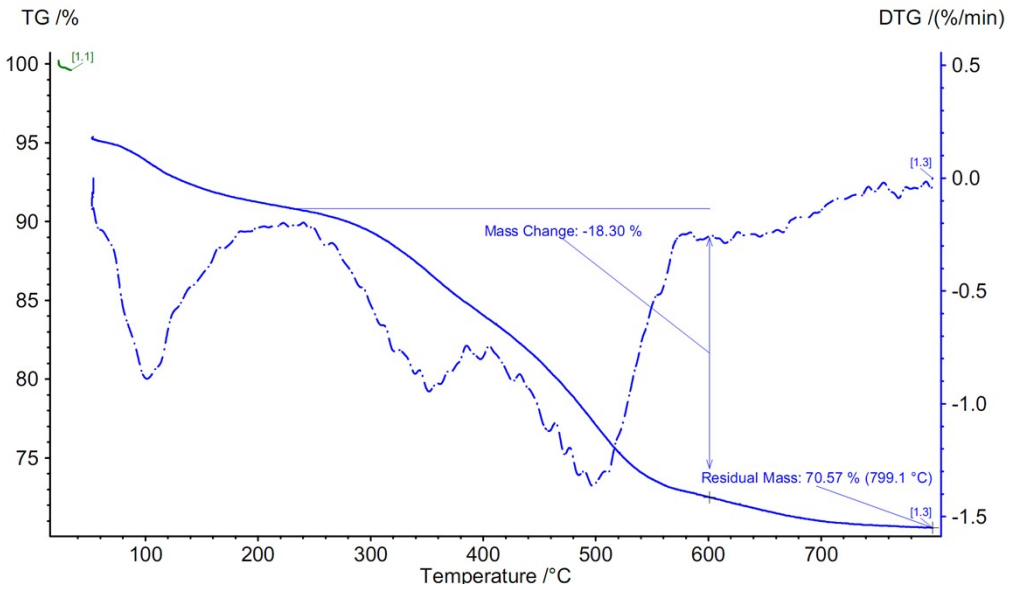



**Figure S1.** TGA and DTG diagram for SBA-15-Pr$SO_3H$

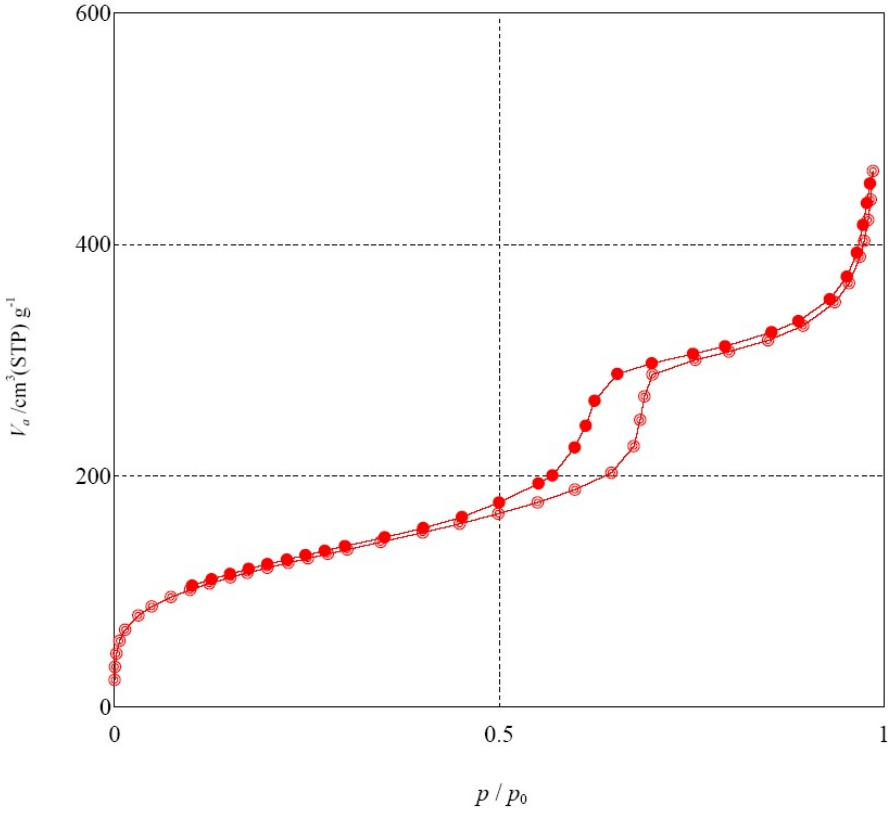



**Figure S2.** Nitrogen adsorption-desorption isotherm for SBA-15-Pr$SO_3H$

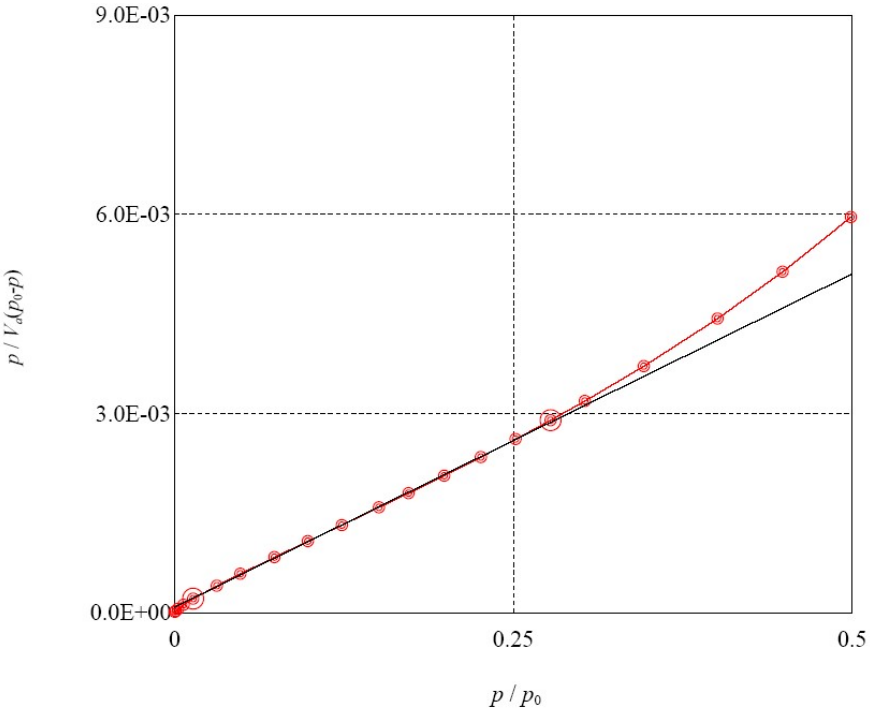



**Figure S3.** BET diagram for SBA-15-PrSO$_3$H

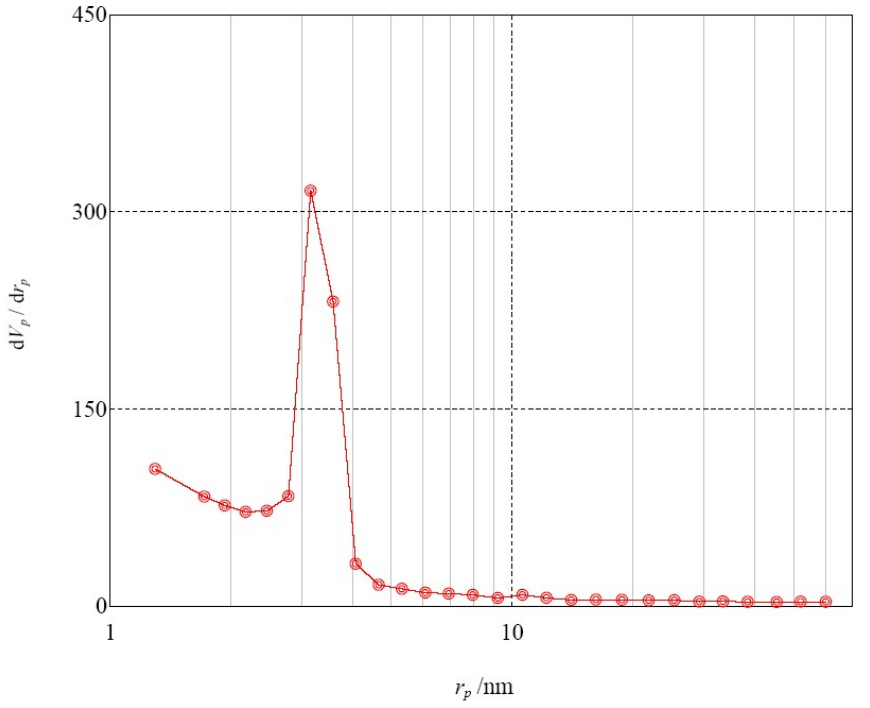



**Figure S4.** BJH average pore diameter diagram for SBA-15-PrSO$_3$H

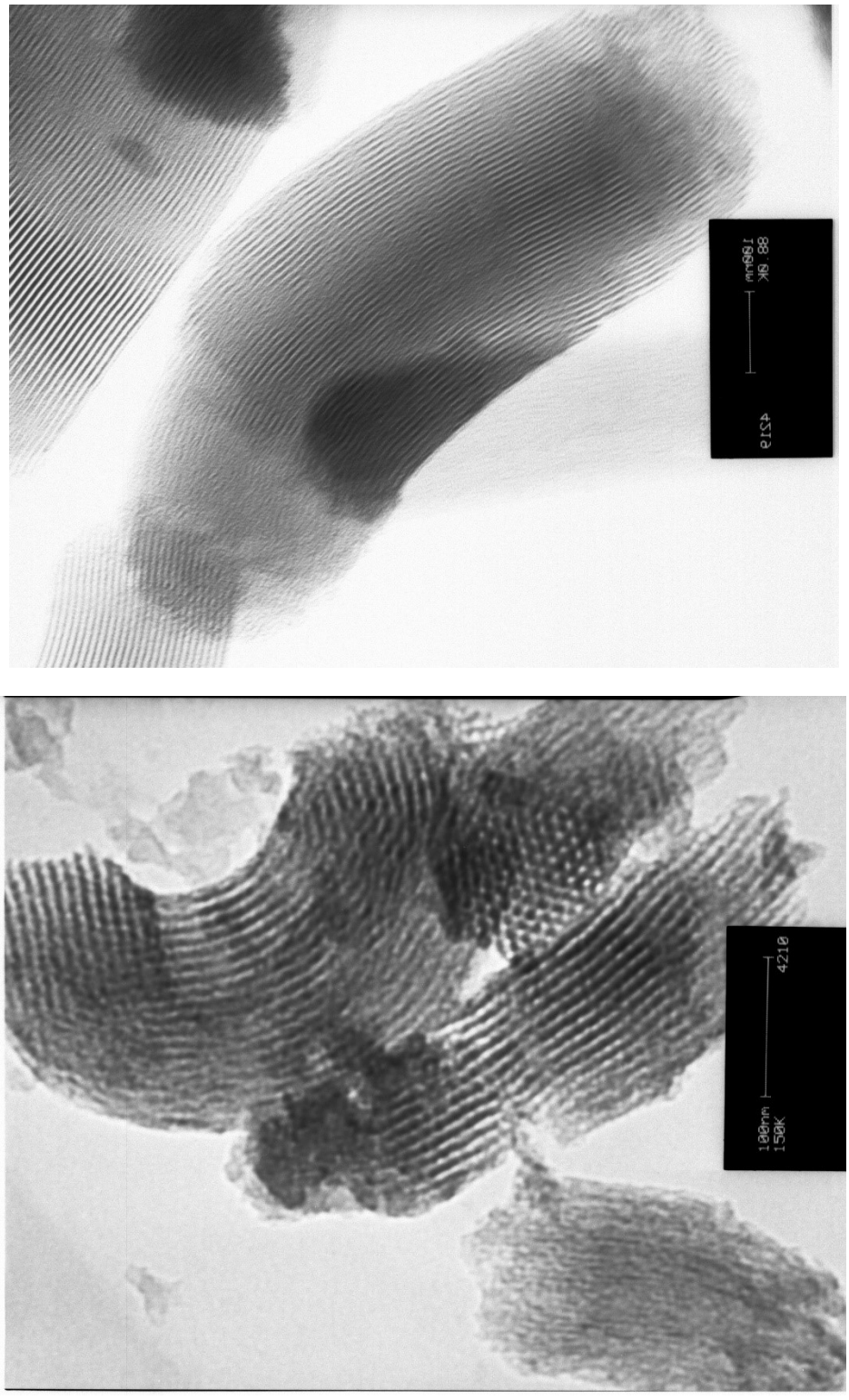
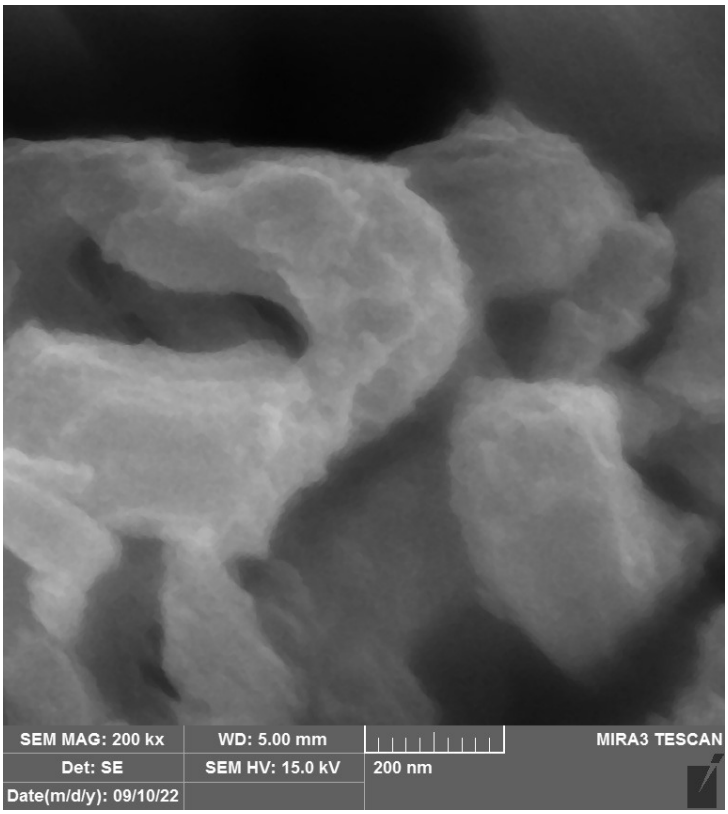



**Figure S5.** TEM images of SBA-15-Pr$SO_3H$



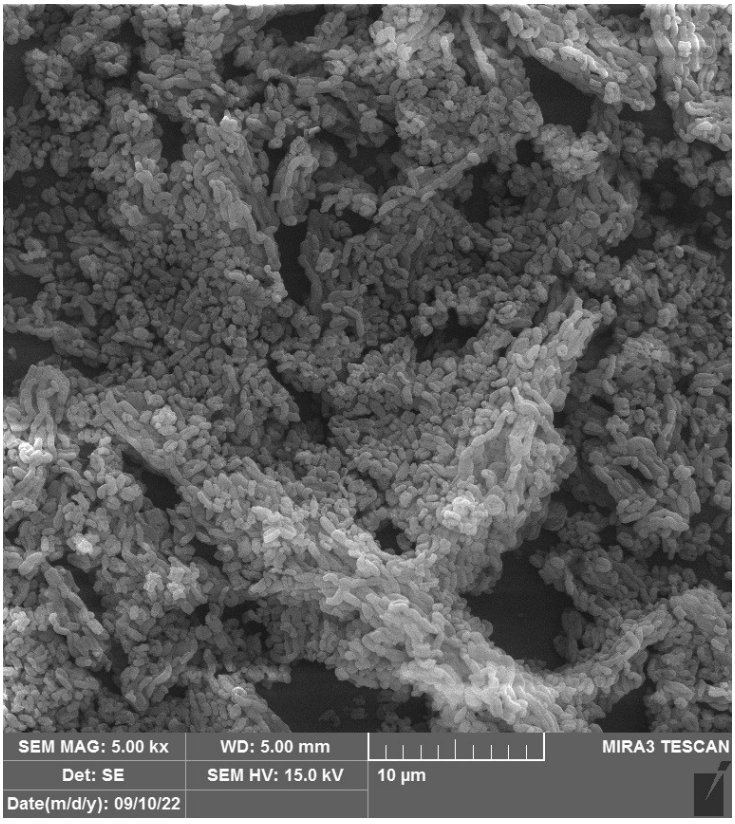




**Figure S6.** SEM images of SBA-15-Pr$SO_3H$

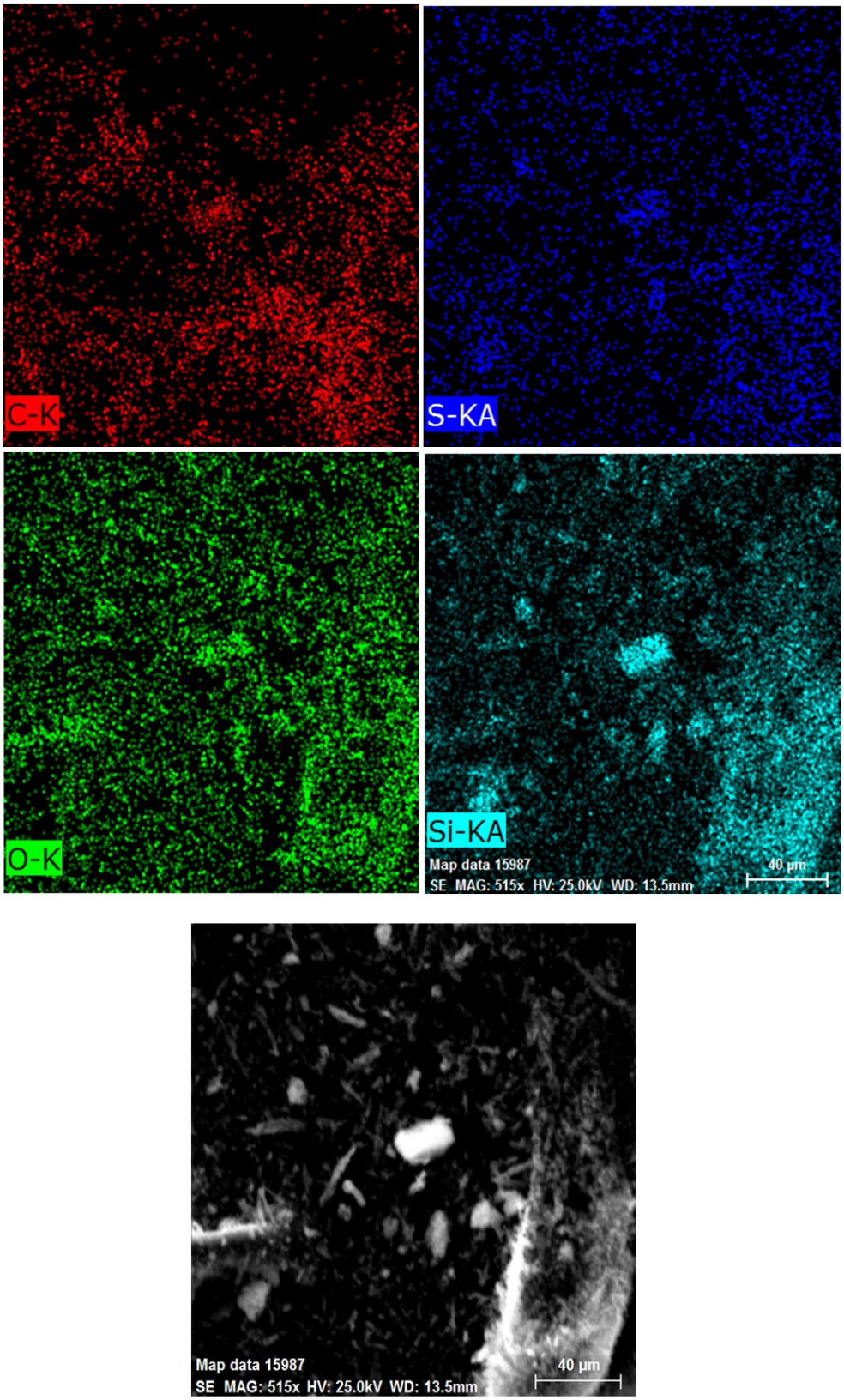
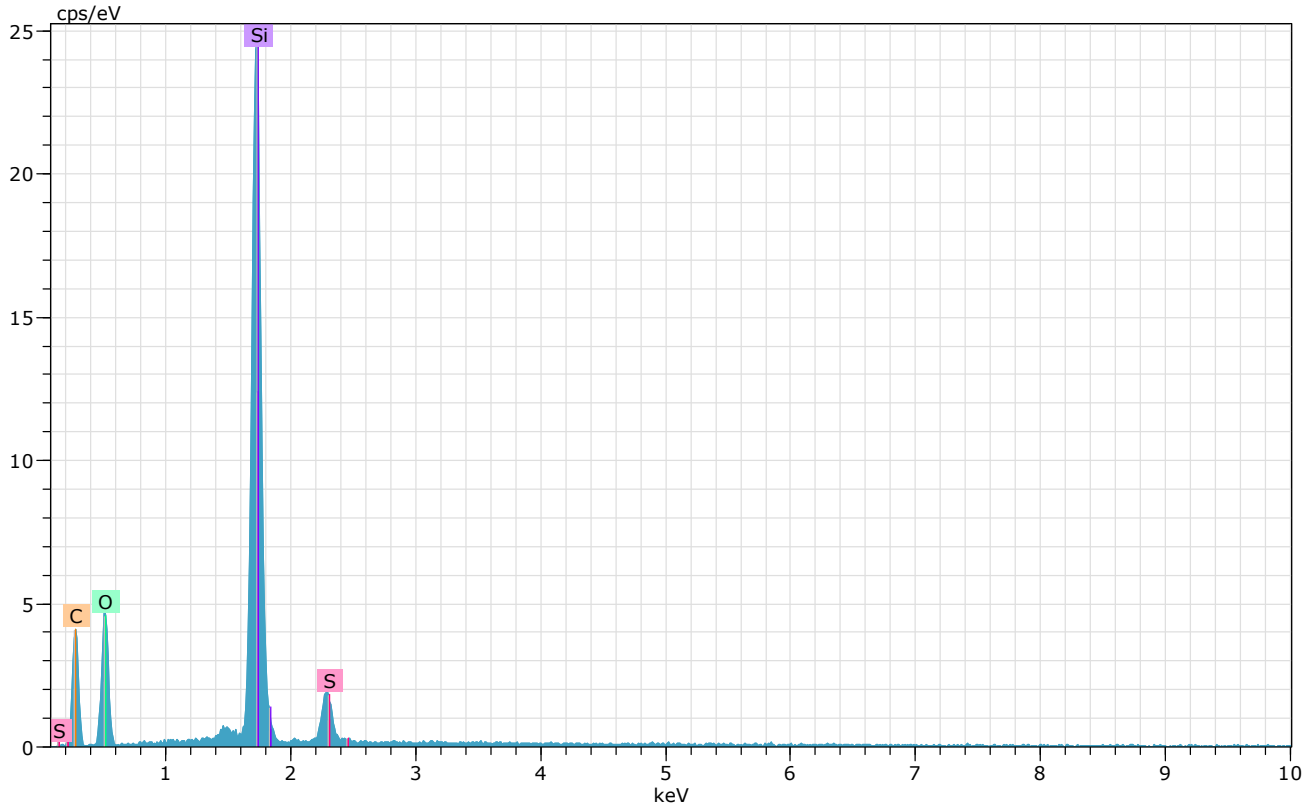



**Figure S7.** EDX mapping images of SBA-15-Pr$SO_3H$




SBA-15-PrSO$_3$H
Objects 614 HV:25.0kV Puls th.:4.83kcps

| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error (1 Sigma) [wt.%] |
|---|---|---|---|---|---|---|
| C | 6 | K-series | 46.73 | 44.22 | 55.89 | 8.40 |
| O | 8 | K-series | 36.59 | 34.62 | 32.85 | 6.25 |
| Si | 14 | K-series | 19.77 | 18.71 | 10.11 | 0.91 |
| S | 16 | K-series | 2.58 | 2.44 | 1.16 | 0.15 |
| | | Total: | 105.67 | 100.00 | 100.00 | |

**Figure S8.** EDS spectrum of the SBA-15-PrSO$_3$H

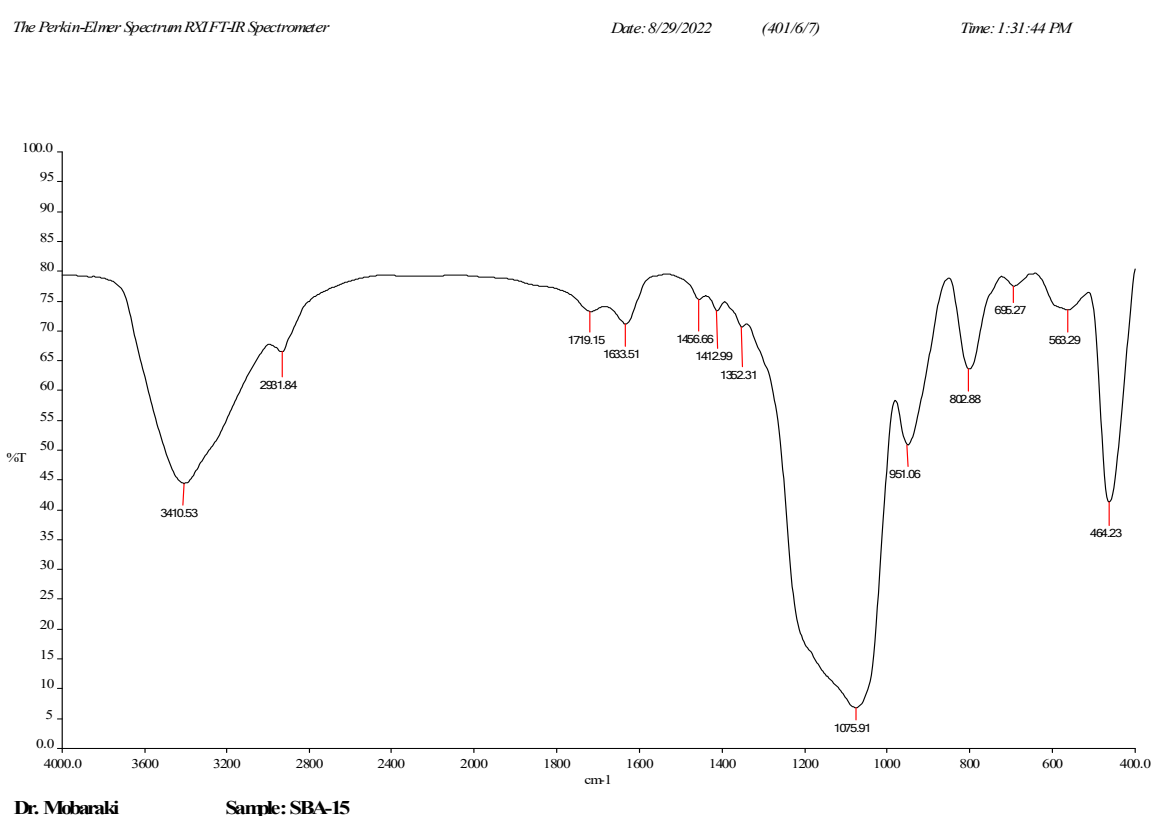



**Figure S9.** FT-IR spectrum of the SBA-15-Pr$SO_3H$

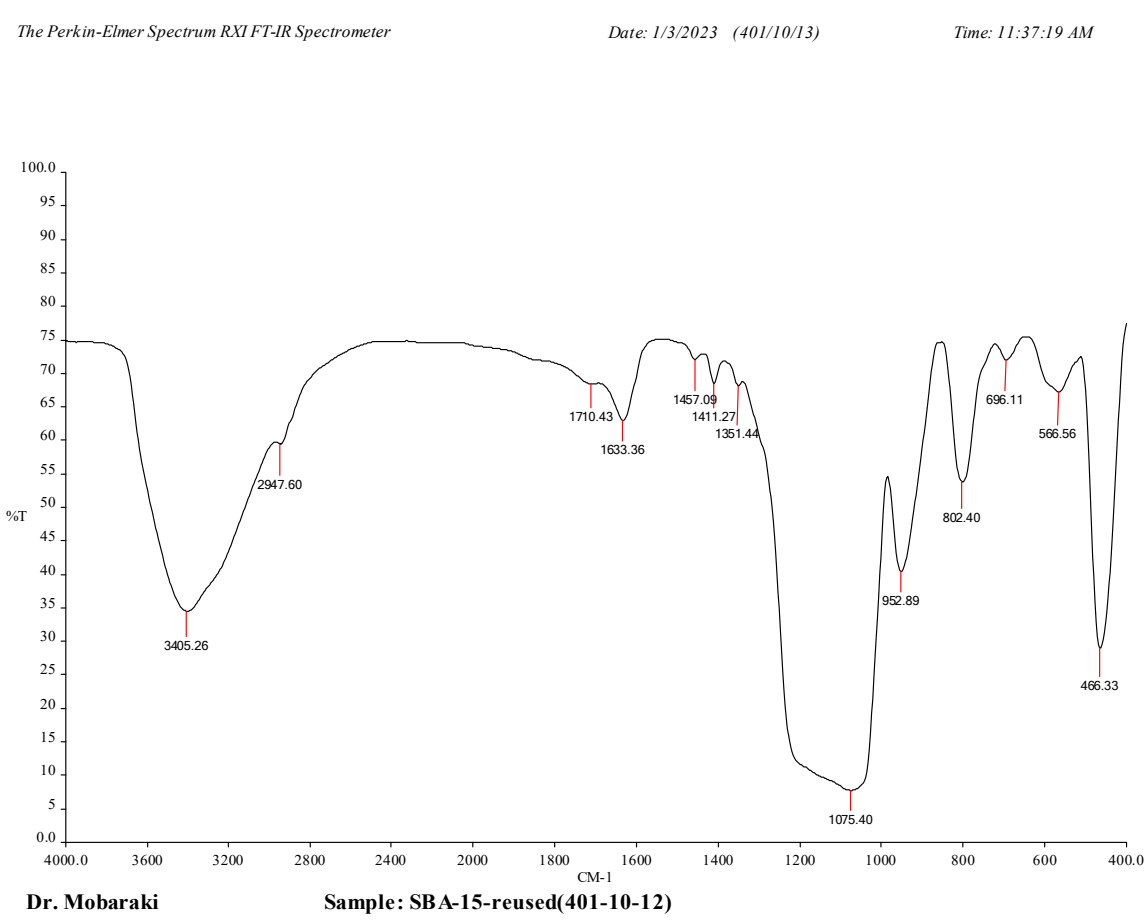



**Figure S10.** FT-IR spectrum of the Reused SBA-15-Pr$SO_3H$

### 1.2. Preparation of Et-PMO-Me-Pr$SO_3$H (1a) and its Characterizations

Organosulfonic acid-functionalized periodic mesoporous organosilicas Et-PMO-Me-Pr$SO_3$H was synthesized by a modification according to the methods of Hamoudi and co-workers.[12] In a typical preparation procedure, 0.66 g of Pluronic P123($EO_{20}PO_{70}EO_{20}$) was dissolved in 70 ml of HCl (2M) solution with stirring at room temperature. After addition and agitation of 2.77 g 1,2-bis(triethoxysilyl)-ethane (BTEE) for 3 h at 35 °C as a backbone of PMO, 0.478 g of thiol precursor 3-mercaptopropylmethyldimethoxysilane (MPMDS) was added and stirred for about 24 h at 35 °C. White precipitates were obtained after aging the mixture at 85 °C for 24 h under static conditions. The solid was recovered by filtration, washing (by deionized water) and dried at room temperature for 24 h. The residual block copolymer was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h. Conversion of thiol groups of catalyst to sulfonic acid moieties was accomplished by hydrogen peroxide. Typically, 0.2 g of solid hydrophobic material was suspended in 8 g of aqueous 30 wt% $H_2O_2$. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with deionized water and ethanol. Finally the wet material was suspended in 0.1M $H_2SO_4$ solution for 2 h and then was washed several times with deionized water until neutral *p*H and dried at 60 °C under vacuum overnight to give the corresponding Et-PMO-Me-Pr$SO_3$H (**1a**).

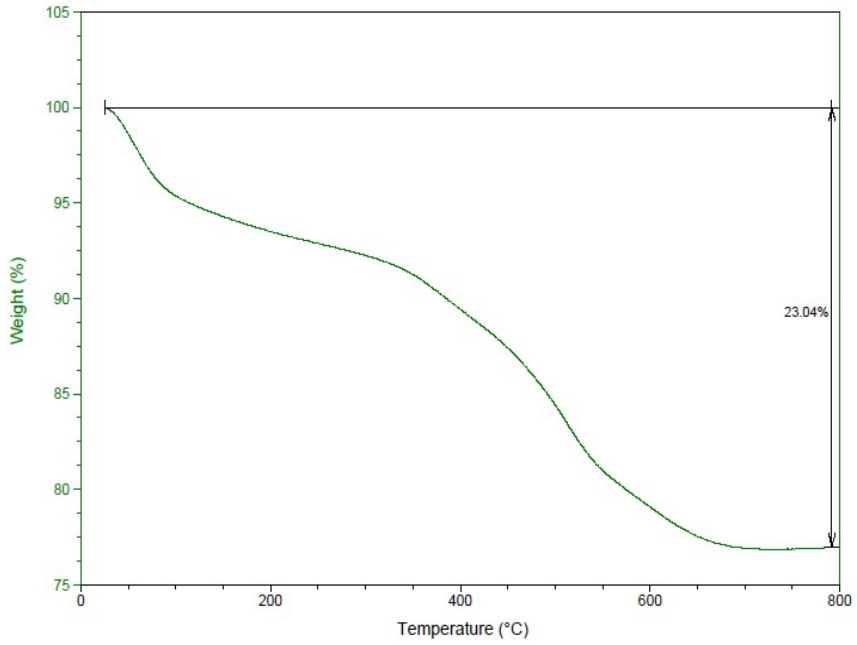



**Figure S11.** TGA diagram for Et-PMO-Me-Pr$SO_3$H

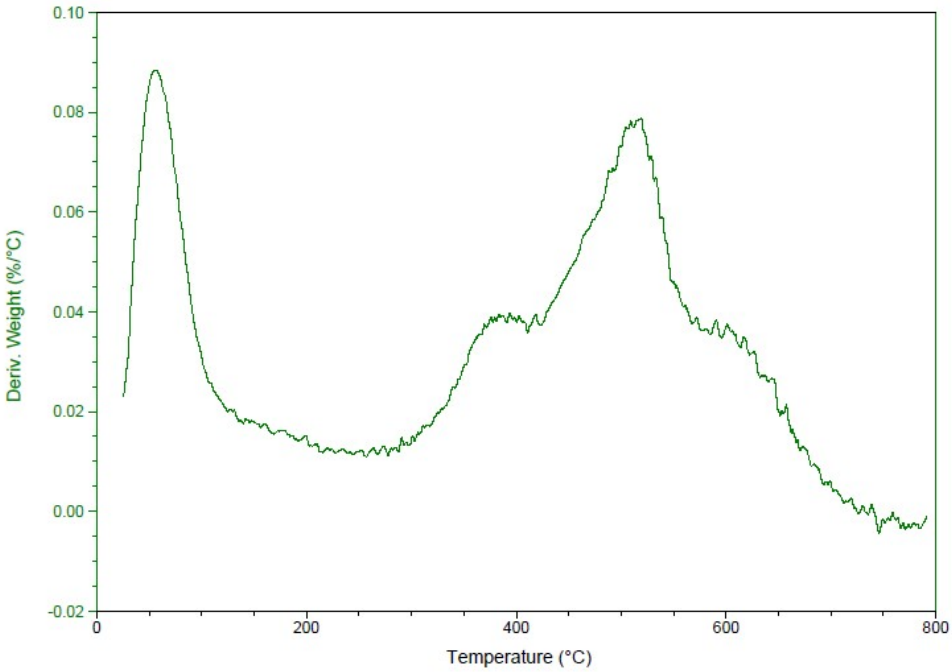



**Figure S12.** DTA diagram for Et-PMO-Me-Pr$SO_3$H

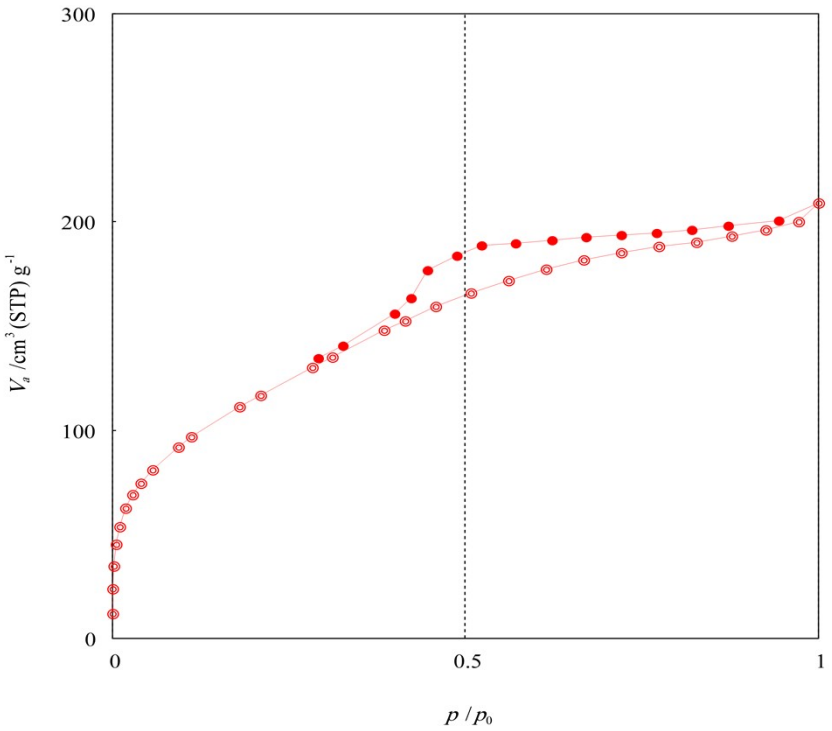



**Figure S13.** Nitrogen adsorption-desorption isotherm for Et-PMO-Me-Pr$SO_3$H

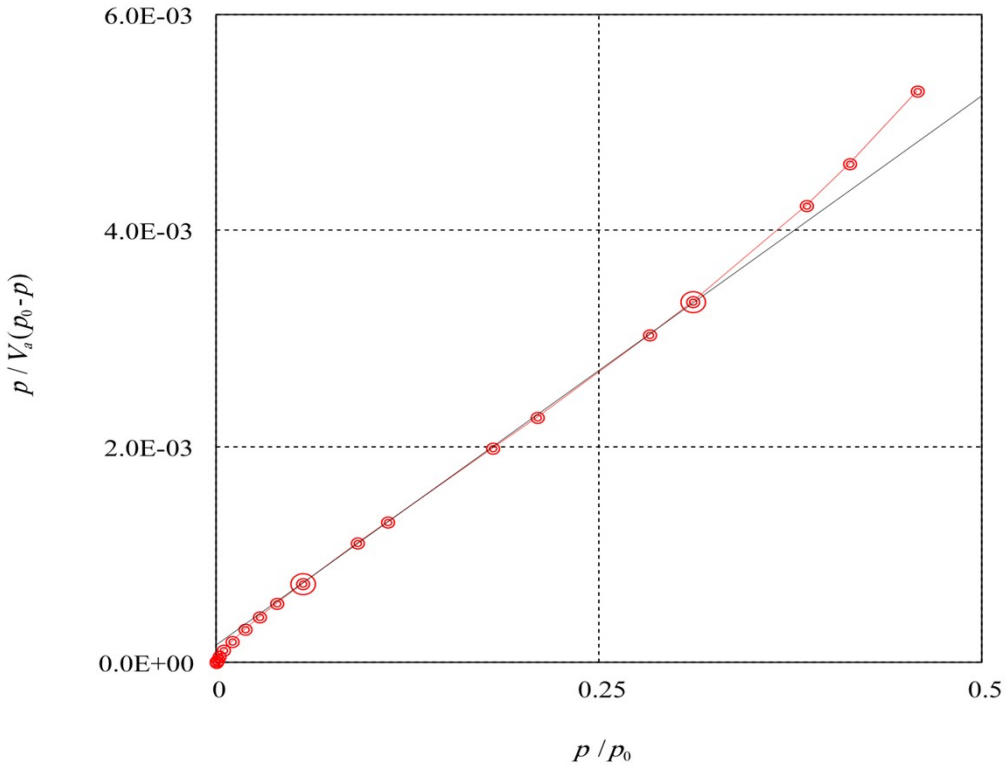



**Figure S14.** BET diagram for Et-PMO-Me-Pr$SO_3$H

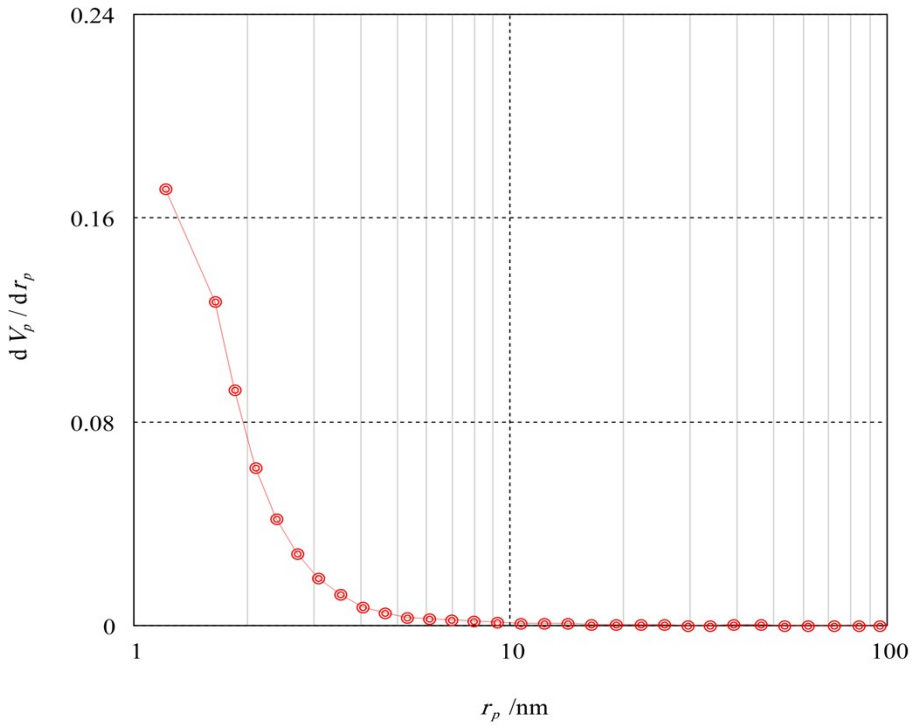



**Figure S15.** BJH average pore diameter diagram for Et-PMO-Me-Pr$SO_3$H

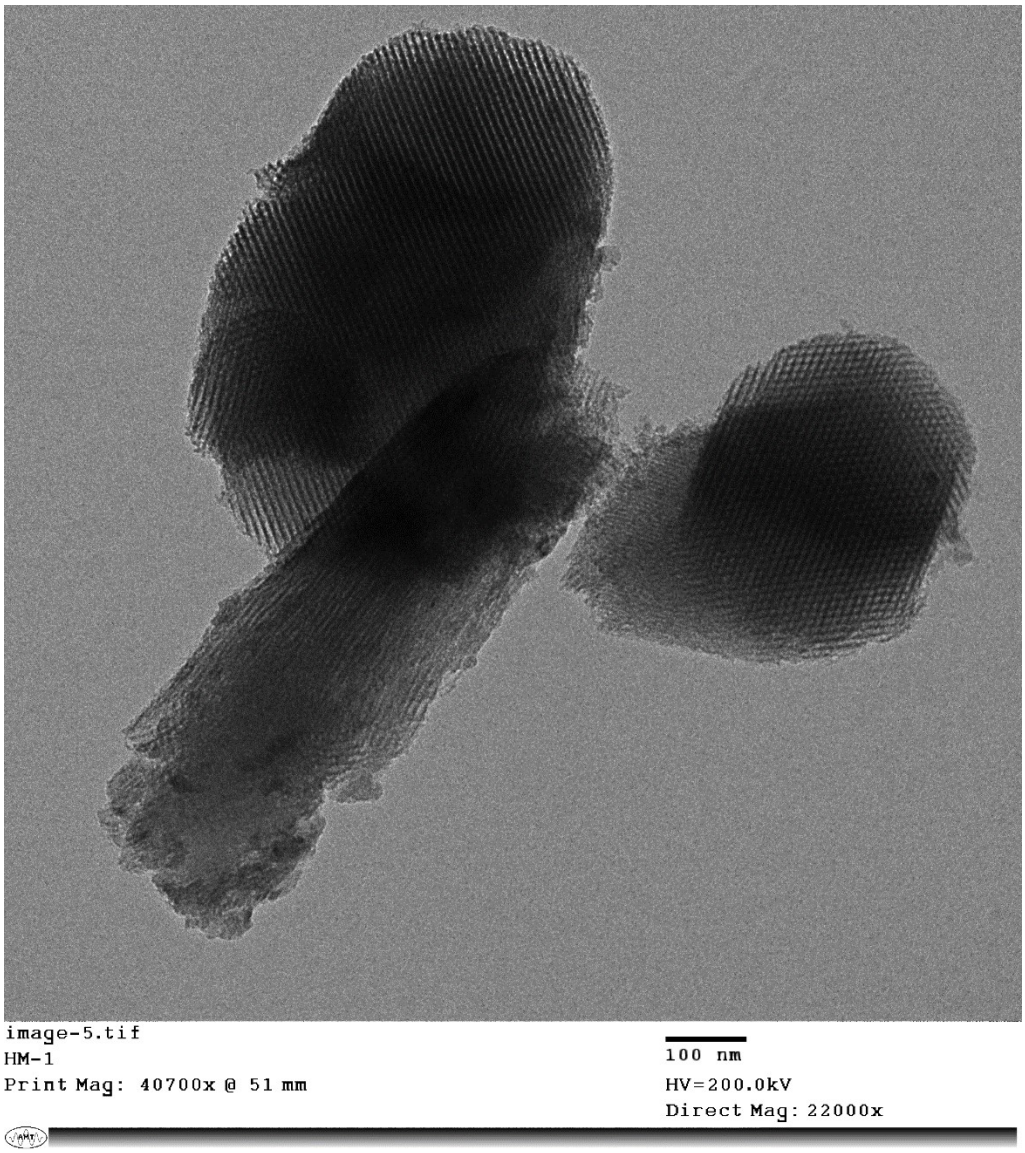



**Figure S16.** TEM image of Et-PMO-Me-Pr$SO_3$H

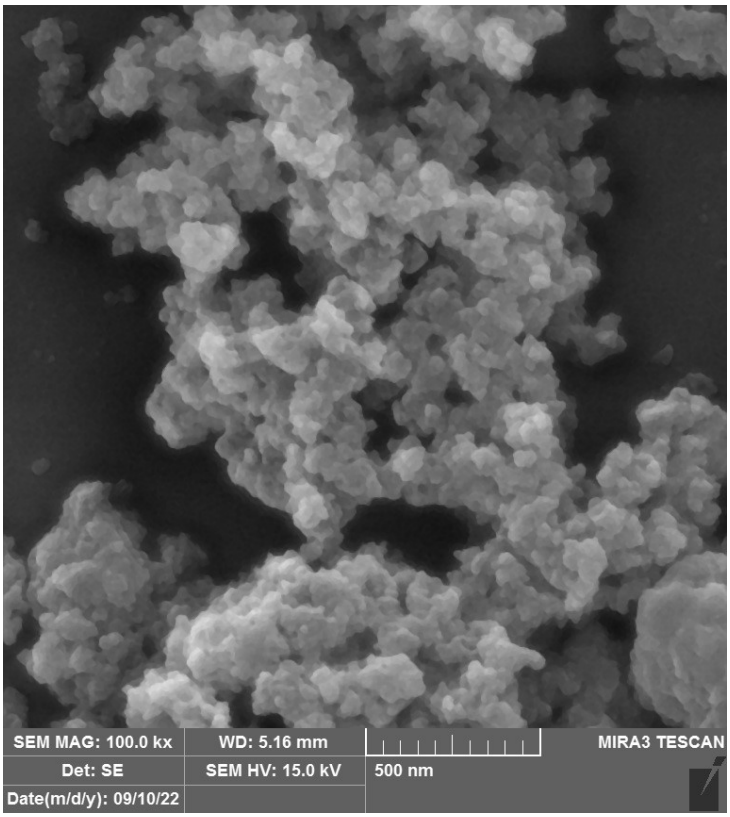



**Figure S17.** SEM images of the Et-PMO-Me-Pr$SO_3$H

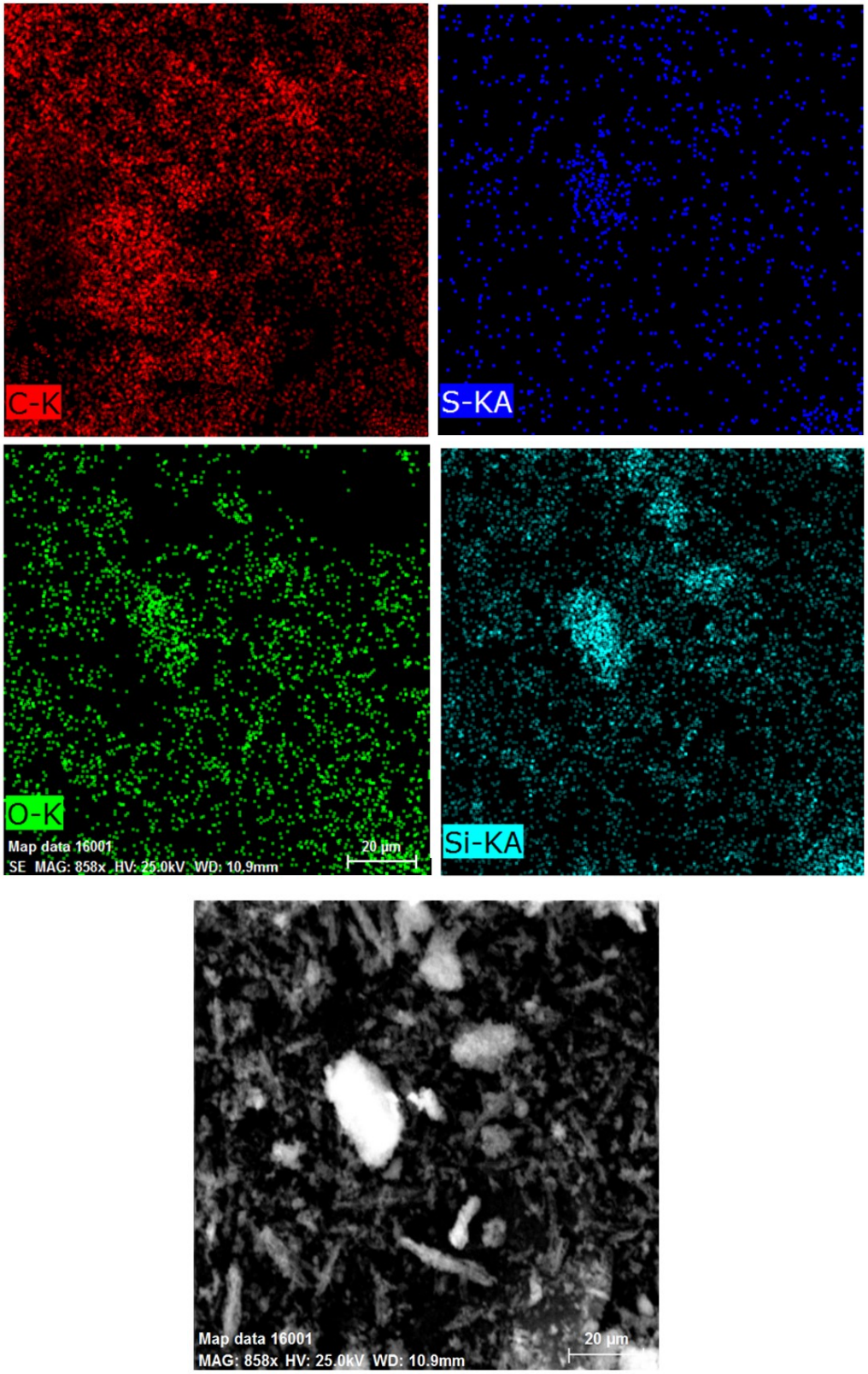
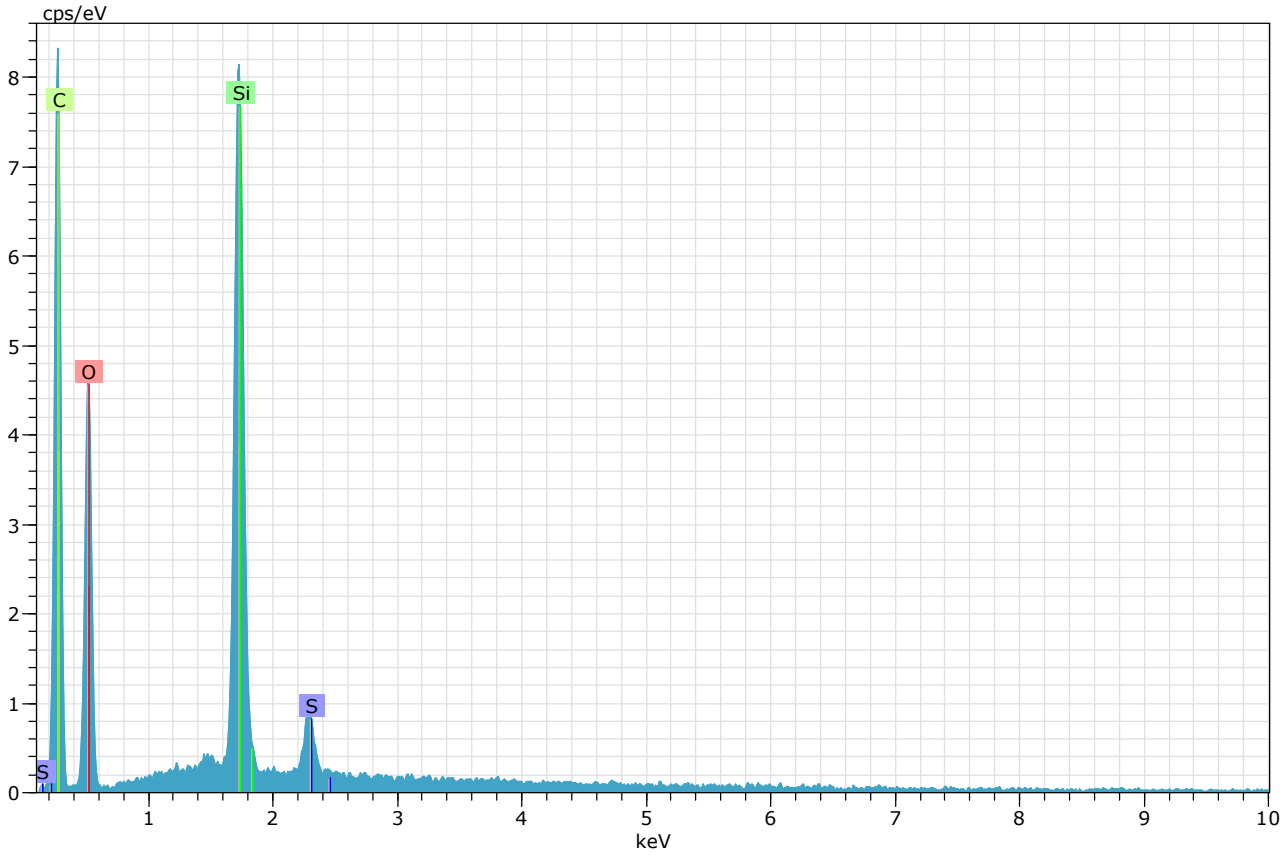



**Figure S18.** EDX mapping images of the Et-PMO-Me-Pr$SO_3H$




Et-PMO-Me-PrSO$_3$H
Objects 6141 HV:25.0kV Puls th.:3.21kcps

| El | AN | Series | unn. C [wt.%] | norm. C [wt.%] | Atom. C [at.%] | Error (1 Sigma) [wt.%] |
|---|---|---|---|---|---|---|
| C | 6 | K-series | 54.82 | 54.82 | 63.54 | 7.93 |
| O | 8 | K-series | 37.75 | 37.75 | 32.84 | 5.93 |
| Si | 14 | K-series | 6.40 | 6.40 | 3.17 | 0.32 |
| S | 16 | K-series | 1.03 | 1.03 | 0.45 | 0.08 |
| Total: | | | 100.00 | 100.00 | 100.00 | |

**Figure S19.** EDS spectrum of the Et-PMO-Me-PrSO$_3$H

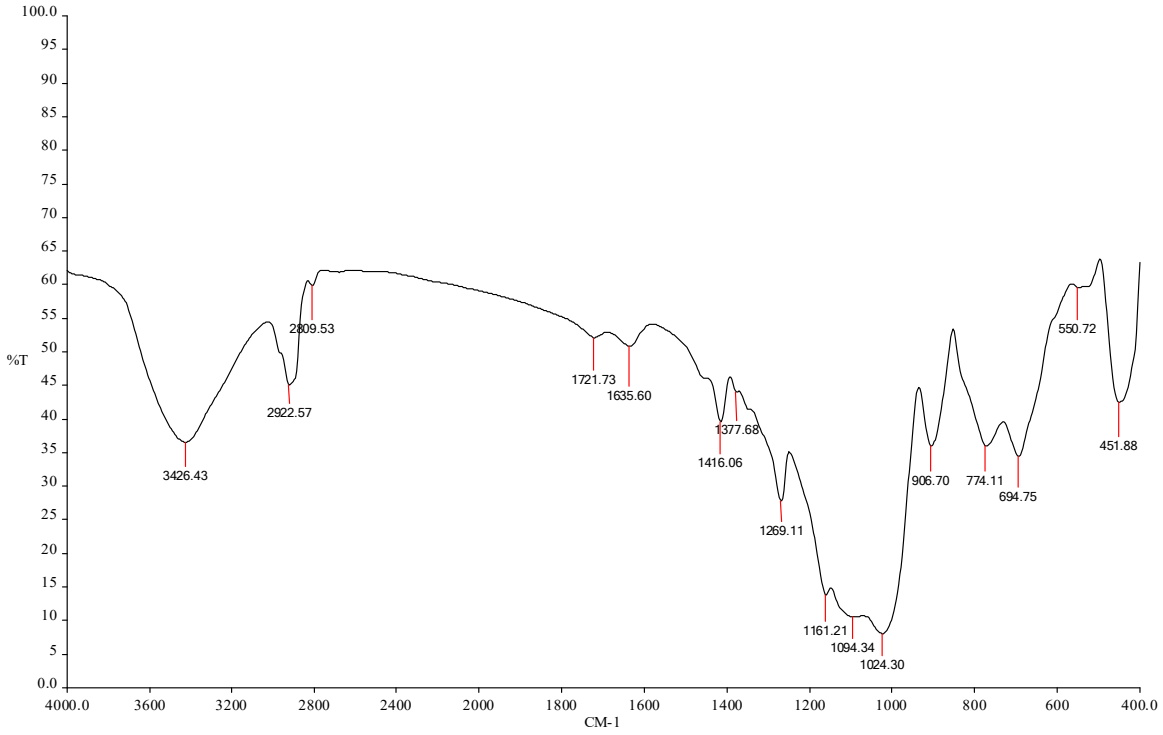



**Figure S20.** FT-IR spectrum of the Et-PMO-Me-Pr$SO_3H$

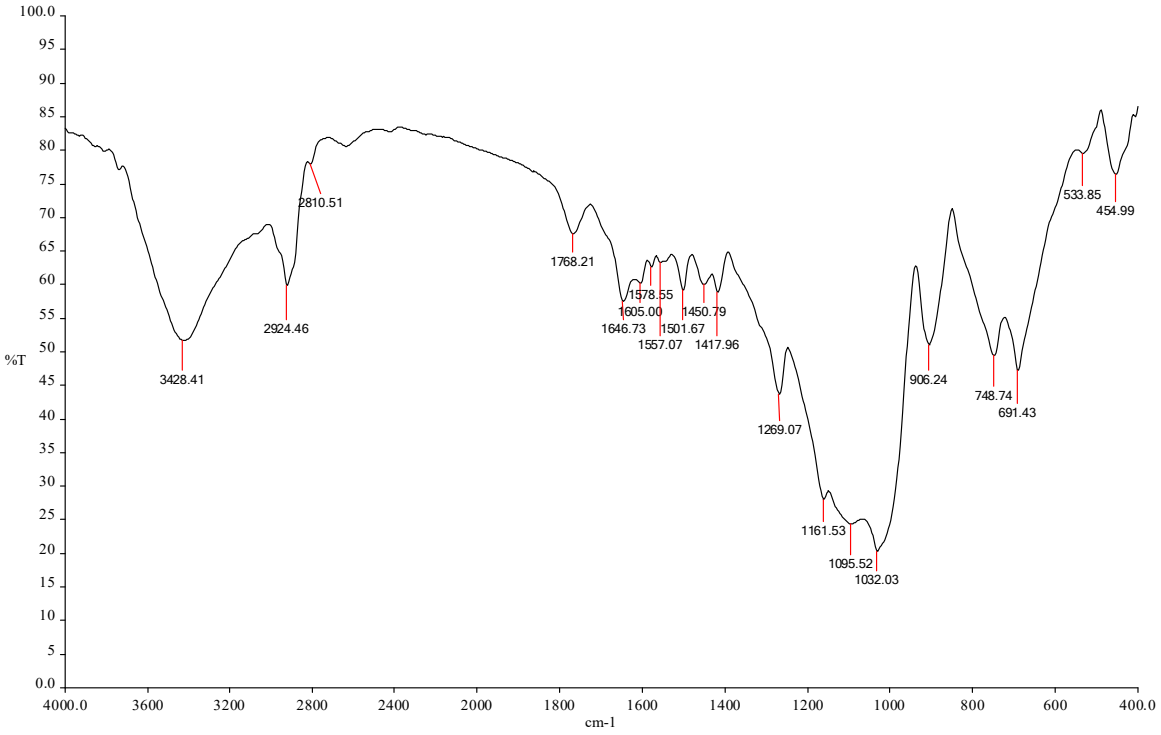



**Figure S21.** FT-IR spectrum of the reused Et-PMO-Me-Pr$SO_3$H

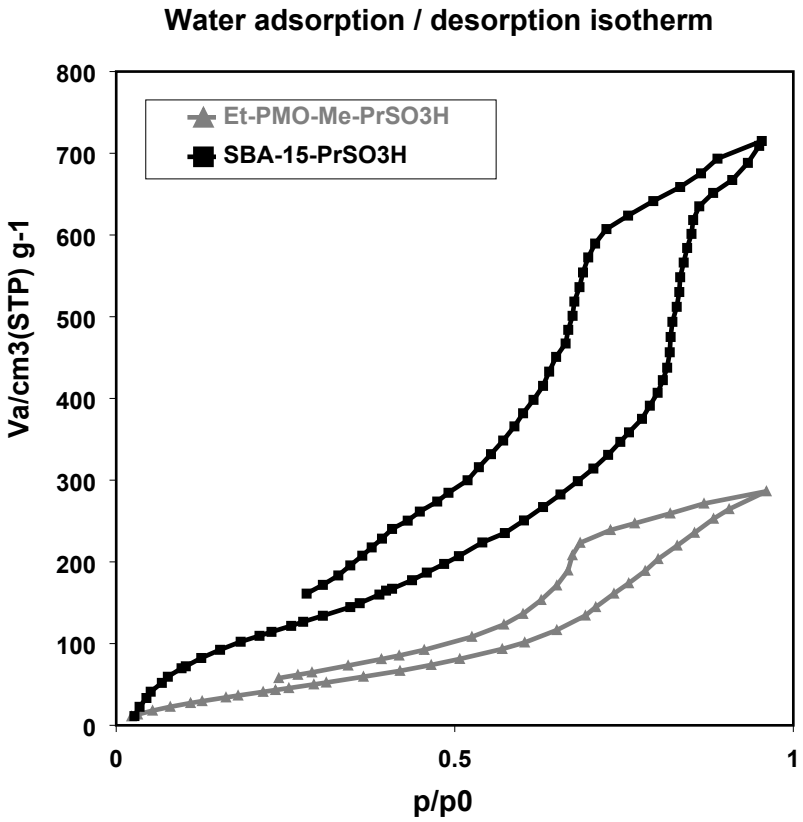



**Figure S22.** Water adsorption-desorption isotherms of Hydrophilic ordered mesoporous silica (OMS) based sulfonic acid (**1b**) and hydrophobic ethane-bridges PMO based sulfonic acid (**1a**) solids.

### 1.3. General procedure for the one-pot preparation of 2-aminobenzothiazoles

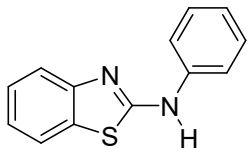
A mixture of 2-aminothiophenol (2 mmol), isothiocyanate (2 mmol), were stirred at 100 °C for an appropriate time in solvent and catalyst-free condition (Table 2). The progress and completion of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated with acetone by filtration to obtain the crude product. The crude products were recrystallized in ethylacetate and n-hexane mixture or acetone dependence to utilized isothiocyanate or subjected to silica gel column chromatography in order to further purification if it is necessary.

### 1.4. General procedure for the one-pot preparation of 2-substituted benzoxazole derivatives

A mixture of 2-aminophenol or 2-aminoaniline (2 mmol), isothiocyanate (2 mmol), and catalysts (0.3 mol%) were stirred at 100 °C for an appropriate time in solvent-free condition (Table 4). The progress and completion of the reaction was monitored by TLC. After the completion of the reaction, the catalyst was separated with acetone by filtration to obtain the crude product. The crude products were recrystallized in ethylacetate and n-hexane mixture or acetone dependence to utilized isothiocyanate or subjected to silica gel column chromatography in order to further purification if it is necessary.

## 2. Spectral data for Table 3 and 5:

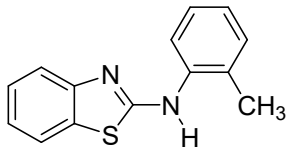
### 1. *N*-Phenylbenzo[*d*]thiazol-2-amine



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$= 9.18(br, 1H, exchangeable with $D_2O$), 7.66-7.68(d, $J$=8.0 Hz,1H), 7.54-7.59(m, 3H), 7.43-7.47(t, $J$=7.6 Hz, 2H), 7.33-7.38(t, $J$=7.6 Hz, 1H), 7.17-7.24(qui, $J$=7.2 Hz, 2H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ =165.4, 151.2, 140.0, 129.7, 129.6, 126.2, 124.5, 122.4, 120.9, 120.6, 119.2; IR(KBr) ν.cm$^{-1}$: 3452.5, 3232.8, 3185.5, 3126.0, 3055.3, 2997.4, 2942.1, 2853.2, 1622.0, 1563.9, 1497.5, 1455.8, 1322.6, 1260.3, 1235.3, 1218.0, 1223.8, 747.4, 713.4, 588.3.

Boiling point: 164.3-166.8 °C

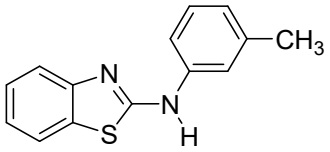
### 2. *N*-o-Tolylbenzo[*d*]thiazol-2-amine



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$= 9.18(br, 1H, exchangeable with $D_2O$), 7.66-7.68(d, $J$ = 7.6 Hz,1H), 7.59-7.61(d, $J$ = 7.6 Hz, 1H), 7.34-7.39(m, 3H), 7.27-7.31(t, $J$ = 7.6 Hz, 2H), 7.11-7.14(t, $J$ = 7.6 Hz, 1H), 2.43(s, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ =168.4, 151.6, 138.4, 133.3, 131.4, 130.0, 127.3, 126.9, 126.1, 125.1, 121.9, 120.9, 118.6, 18.0; IR (KBr) ν.cm$^{-1}$: 3186.2, 3127.3, 3064.3, 3019.1, 2858.6, 1613.9, 1566.4, 1450.9, 1323.5, 1263.5, 1112.0, 1047.1, 1017.9, 925.6, 847.7, 752.8, 691.8, 599.4, 498.4, 429.9.

Boiling point: 129.2-131.3 °C

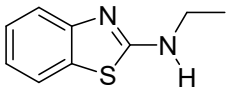
**3. *N*-m-Tolylbenzo[*d*]thiazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$= 7.66-7.68(d, $J$ = 7.6 Hz,1H), 7.59-7.61(d, $J$ = 7.6 Hz, 1H), 7.29-7.40(m, 4H), 7.19-7.23(t, $J$ = 7.6 Hz, 1H), 7.03-7.04(d, $J$ = 4.4 Hz, 1H), 2.41(s, 3H); $^{1}$H-NMR (400 MHz; $D_2O$): $\delta_H$= 7.66-7.68(d, $J$ = 7.6 Hz, 1H), 7.59-7.61(d, $J$ = 7.6 Hz, 1H), 7.29-7.40(m, 4H), 7.19-7.23(t, $J$ = 7.6 Hz, 1H), 7.03-7.04(d, $J$ = 4.4 Hz, 1H), 2.41(s, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ =165.6, 150.2, 139.7, 139.6, 129.5, 129.1, 126.3, 125.6, 122.5, 121.3, 121.0, 118.8, 117.6, 21.5; IR (KBr) ν.cm$^{-1}$ : 3454.8, 3232.3, 3189.9, 3134.5, 3052.8, 2925.9, 1621.5, 1571.7, 1481.8, 1450.1, 1322.6, 1243.4, 1161.4, 1025.3, 879.0, 745.3, 714.2, 674.3, 597.9, 530.7.

Boiling point: 126.2-128.5 °C

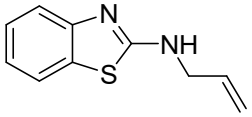
**4. *N*-Ethylbenzo[*d*]thiazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$= 7.62-7.64(d, $J$ = 8.0 Hz, 1H), 7.55-7.57(d, $J$ = 8.0 Hz, 1H), 7.33-7.36(t, $J$ = 8.0 Hz, 1H), 7.12-7.16(t, $J$ = 8.4 Hz, 1H), 6.01(br, 1H, exchangeable with $D_2O$), 3.48-3.53(q, $J$ = 8.4 Hz, 2H), 1.35-1.39(t, $J$ = 7.2 Hz, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ =167.5, 151.6, 129.9, 126.1, 121.6, 120.9, 118.6, 40.4, 14.8; IR (KBr) ν.cm$^{-1}$ : 3408.9, 3229.4, 3053.6, 2971.6, 2926.6, 2305.2, 1607.9, 1554.5, 1449.1, 1386.9, 1346.7, 1263.7, 1215.2, 1093.4, 865.4, 800.9, 749.6, 461.0.

Boiling point: 66.3-68.4 °C

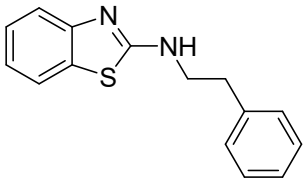
**5. *N*-Allylbenzo[*d*]thiazol-2-amine**



$^1$H-NMR (400 MHz; *$CDCl_3$*): $\delta_H$= 7.61-7.63(d, *J* = 7.6 Hz, 1H), 7.54-7.56(d, *J* = 8.0 Hz, 1H), 7.31-7.35(t, *J* = 7.6 Hz, 1H), 7.10-7.14(t, *J* = 7.6 Hz, 1H), 5.95-6.05(m, 1H), 5.37-5.41(d, *J* = 17.2 Hz, 1H), 5.25-5.28(d, J = 10.4 Hz, 1H), 4.08-4.10(d, *J* = 5.2 Hz, 2H); $^1$H-NMR (400 MHz; *$D_2O$*): $\delta_H$= 7.61-7.63(d, *J* = 7.6 Hz, 1H), 7.54-7.56(d, *J* = 8.0 Hz, 1H), 7.31-7.35(t, *J* = 7.6 Hz, 1H), 7.10-7.14(t, *J* = 7.6 Hz, 1H), 5.95-6.05(m, 1H), 5.37-5.41(d, *J* = 17.2 Hz, 1H), 5.25-5.28(d, *J* = 10.4 Hz, 1H), 4.08-4.10(d, *J* = 5.2 Hz, 2H); $^{13}$C-NMR (100.6 MHz, *$CDCl_3$*): $\delta_C$ = 167.7, 152.0, 133.4, 130.2, 126.0, 121.6, 120.9, 118.8, 117.4, 47.8; IR (KBr) ν.cm$^{-1}$ : 3447.8, 3190.2, 3056.1, 2964.7, 2896.8, 2235.4, 1607.6, 1541.4, 1439.4, 1338.4, 1267.0, 1222.0, 1095.0, 1021.8, 910.7, 864.5, 805.0, 748.6, 624.5, 554.8.

Boiling point: 82.3-84.9 °C

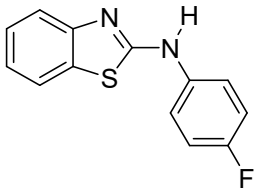
**6. *N*-Phenethylbenzo[*d*]thiazol-2-amine**



$^1$H-NMR (400 MHz; *$CDCl_3$*): $\delta_H$ = 7.62-7.64(d, *J* = 7.6 Hz, 1H), 7.53-7.55(d, *J* = 8.0 Hz, 1H), 7.31-7.37(m, 3H), 7.25-7.29(t, *J* = 6.0 Hz, 3H), 7.11-7.15(t, *J* = 7.6 Hz, 1H), 6.17(br, 1H, exchangeable with *$D_2O$*), 3.69-3.73(t, *J* = 6.8 Hz, 2H), 3.01-3.05(t, *J* = 6.8 Hz, 2H); $^{13}$C-NMR (100.6 MHz, *$CDCl_3$*): $\delta_C$ = 167.6, 152.4, 138.4, 130.3, 128.9, 128.8, 126.7, 126.0, 121.5, 120.9, 118.8, 46.7, 35.6; IR (KBr) ν.cm$^{-1}$ : 3455.2, 3233.6, 3194.6, 3093.2, 2909.4, 1622.2, 1568.2, 1480.8, 1440.8, 1348.3, 1264.3, 1182.6, 1109.4, 1010.0, 880.5, 749.2, 696.0, 657.1, 531.6, 493.3.

Boiling point: 153.3-155.8 °C

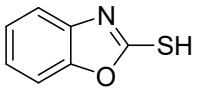
**7. *N*-(4-fluorophenyl)benzo[*d*]thiazol-2-amine**




$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$=10.53(br, 1H, exchangeable with $D_2O$), 7.80-7.85(m, 3H), 7.60-7.62(d, $J$ = 8.0 Hz, 1H), 7.31-7.35(t, $J$ = 7.6 Hz, 1H), 7.14-7.24(m, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ = 162.1, 157.8 (d, $J_{C\text{-}F}$ = 239.4 Hz), 152.4, 137.6 (d, $J_{C\text{-}F}$ = 1.0 Hz), 130.4, 126.4, 122.8, 121.5, 119.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 119.6, 116.0 (d, $J_{C\text{-}F}$ = 22.1 Hz); IR (KBr) ν.cm$^{-1}$ : 3449.6, 3194.5, 3136.0, 3048.7, 2909.7, 1627.4, 1568.7, 1508.1, 1449.7, 1327.1, 1277.4, 1215.8, 1094.8, 1017.6, 919.6, 834.3, 790.7, 736.2, 668.2, 581.1.

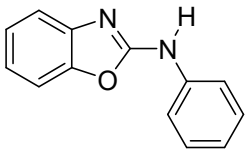
Boiling point: 204.5-206.7 °C

**1. Benzo[*d*]oxazole-2-thiol**



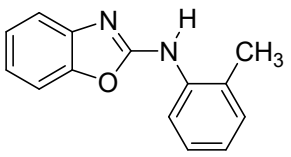

$^{1}$H-NMR (400 MHz; *DMSO*): $\delta_H$= 13.87(br, 1H, exchangeable with $D_2O$), 7.50-7.52(m, 1H), 7.24-7.32(m, 3H); $^{13}$C-NMR (100.6 MHz, *DMSO*): $\delta_C$ = 180.6, 148.6, 131.6, 125.6, 124.3, 110.9, 110.9; IR (KBr) ν.cm$^{-1}$ : 3343.2, 2922.2, 1614.0, 1556.3, 1504.2, 1443.3, 1268.9, 1126.9, 1089.4, 926.4, 805.3, 744.0, 646.8.
Boiling point: 197.6-199.8 °C

**2. *N*-Phenylbenzo[*d*]oxazol-2-amine**




$^{1}$H-NMR (400 MHz; *DMSO*): $\delta_H$ = 10.63(br, 1H, exchangeable with $D_2O$), 7.78-7.80(d, *J* = 8.0 Hz, 2H), 7.46-7.50(t, *J* = 6.8 Hz, 2H), 7.36-7.40(t, *J* = 7.6 Hz, 2H), 7.21-7.25(td, *J* = 7.6 Hz, *J* = 0.8 Hz, 1H), 7.11-7.15(td, *J* = 8.0 Hz, *J* = 0.8 Hz, 1H), 7.02-7.06(t, *J* = 7.6 Hz, 1H); $^{13}$C-NMR (100.6 MHz, *DMSO*): $\delta_C$ =158.5, 147.5, 142.9, 139.2, 129.4, 124.5, 122.6, 122.1, 118.0, 117.0, 109.4; IR (KBr) ν.cm$^{-1}$ : 3381.1, 3165.2, 3034.6, 2961.9, 1938.0, 1867.6, 1654.3, 1571.7, 1490.9, 1364.4, 1229.9, 1159.2, 1094.2, 1018.2, 888.4, 805.4, 737.3, 685.5, 497.5.
Boiling point: 181.5-183.7 °C

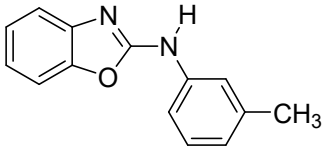
**3.** ***N*-o-Tolylbenzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; *DMSO*): $\delta_H$= 9.69(br, 1H, exchangeable with $D_2O$), 7.82-7.84(d, *J* = 8.4 Hz, 1H), 7.45-7.47(d, *J* = 8.0 Hz, 1H), 7.36-7.38(d, *J* = 7.6 Hz, 1H), 7.25-7.26(m, 2H), 7.17-7.21(t, *J* = 7.6 Hz, 1H), 7.07-7.11(t, *J* = 7.2 Hz, 2H), 2.31(s, 3H); $^{13}$C-NMR (100.6 MHz, *DMSO*): $\delta_C$ = 160.0, 147.9, 143.0, 137.0, 131.0, 130.7, 126.9, 124.9, 124.4, 123.1, 121.7, 116.8, 109.3, 18.3; IR (KBr) ν.cm$^{-1}$ : 3446.6, 3025.8, 2962.1, 2862.2, 2357.8, 1661.5, 1585.8, 1460.3, 1348.7, 1236.5, 1177.3, 1104.1, 1011.2, 964.9, 799.3, 732.1, 465.2.

Boiling point: 145.0-147.2 °C

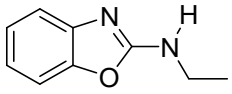
**4.** ***N*-m-Tolylbenzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; *CDCl$_3$*): $\delta_H$ = 7.49-7.53(d, *J* = 6.4 Hz, 1H), 7.40-7.46(t, *J* = 7.6Hz, 3H), 7.31-7.34(t, *J* = 12.8 Hz, 2H), 7.21-7.23(t, *J* = 8.0 Hz, 1H), 6.88-6.89(d, *J* = 6.8 Hz, 1H), 5.92(br, 1H, exchangeable with $D_2O$), 2.43(s, 3H); $^{13}$C-NMR (100.6 MHz, *CDCl$_3$*): $\delta_C$ = 159.0, 147.9, 141.8, 139.3, 137.9, 129.2, 124.4, 124.3, 121.7, 119.5, 116.7, 115.9, 109.3, 21.6; IR (KBr) ν.cm$^{-1}$ : 3449.2, 3171.3, 3042.2, 2962.8, 1652.6, 1577.3, 1497.9, 1459.6, 1346.7, 1244.3, 1173.4, 1096.6, 1015.0, 927.3, 865.9, 805.1, 738.3, 681.6, 640.9, 431.1.

Boiling point: 148.2-150.1 °C

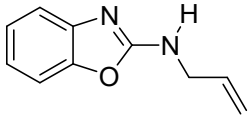
**5.** ***N*-Ethylbenzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$= 7.37-7.39(d, *J*=7.6 Hz, 1H), 7.26-7.28(d, *J* = 8.8 Hz, 1H), 7.17-7.21(t, *J* = 7.6 Hz, 1H), 7.04-7.08(t, *J* = 7.6 Hz, 1H), 5.65(s, 1H, exchangeable with $D_2O$), 3.54-3.59(q, *J* = 7.2 Hz, 2H), 1.33-1.37(t, *J* = 7.2 Hz, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ = 161.9, 148.3, 142.4, 124.0, 120.9, 116.0, 108.8, 38.0, 15.2; IR (KBr) ν.cm$^{-1}$ : 3457.0, 3159.6, 3052.8, 2963.6, 2878.3, 1695.9, 1578.9, 1459.5, 1333.4, 1245.8, 1144.8, 1097.9, 1056.9, 1012.5, 968.6, 807.5, 736.3, 578.6.

Boiling point: 93.7-95.2 °C

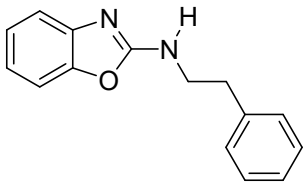
**6.** ***N*-Allylbenzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$ = 7.37-7.39(d, *J* = 8.0 Hz, 1H), 7.27-7.29(d, *J* = 6.4 Hz, 1H), 7.17-7.21(t, *J* = 7.6 Hz, 1H), 7.04-7.08(t, *J* = 7.6 Hz, 1H), 6.03(s, 1H, exchangeable with $D_2O$), 5.97-6.07(m, 1H), 5.34-5.38(dd, *J* = 17.2 Hz, *J* = 1.2 Hz, 1H), 5.23-5.26(dd, *J* = 10.4 Hz, *J* = 1.2 Hz, 1H), 4.14-4.16(d, *J* = 5.6 Hz, 2H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ =161.9, 148.4, 142.4, 133.8, 124.0, 120.9, 116.9, 116.2, 108.9, 45.4; IR (KBr) ν.cm$^{-1}$ : 3450.8, 3157.6, 3058.8, 2965.7, 2915.8, 1665.3, 1582.2, 1488.8, 1459.9, 1344.4, 1247.2, 1177.3, 1096.2, 1030.3, 910.9, 804.2, 740.8, 688.2, 644.4.

Boiling point: 71.9-73.3 °C

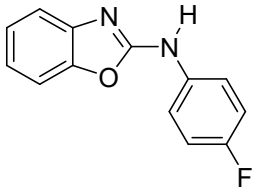
**7.** ***N*-Phenethylbenzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$ = 8.04-8.07(t, $J$ = 5.6 Hz, 1H, exchangeable with $D_2O$), 7.26-7.34(m, 6H), 7.21-7.23(tt, $J$ = 1.6 Hz, $J$ = 6.8 Hz, 1H), 7.09-7.13(td, $J$ = 7.6 Hz, $J$ = 0.8 Hz, 1H), 6.96-7.00(td, $J$ = 7.6 Hz, $J$ = 1.2 Hz, 1H), 3.52-3.57(q, $J$ = 6.8 Hz, 2H), 2.91-2.94(t, $J$ = 7.2 Hz, 1H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ = 162.7, 148.5, 143.8, 139.6, 129.2, 128.3, 126.6, 124.0, 120.5, 115.9, 108.9, 44.2, 35.3; IR (KBr) ν.cm$^{-1}$ : 3302.0, 3198.3, 3151.9, 3060.5, 2949.9, 1664.7, 1580.7, 1458.3, 1342.6, 1244.8, 1199.3, 1149.6, 1097.6, 1005.5, 959.8, 908.9, 846.8, 741.0, 694.8, 574.8.

Boiling point: 100.8-102.4 °C

**8.** ***N*-(4-Fluorophenyl)benzo[*d*]oxazol-2-amine**



$^{1}$H-NMR (400 MHz; $CDCl_3$): $\delta_H$ = 8.96(s, 1H, exchangeable with $D_2O$), 7.57-7.60(q, $J$ = 4.4 Hz, 2H), 7.46-7.48(d, $J$ = 8.0 Hz, 1H), 7.38-7.40(d, $J$ = 8.0 Hz, 1H), 7.25-7.29(t, $J$ = 7.2 Hz, 1H), 7.14-7.18(m, 3H); $^{13}$C-NMR (100.6 MHz, $CDCl_3$): $\delta_C$ = 160.3, 158.4 (d, $J_{C-F}$ = 99.6 Hz), 147.8, 141.6, 135.2, 133.8, 124.7 (d, $J_{C-F}$ = 54.3 Hz), 121.9, 120.6 (d, $J_{C-F}$ = 8.0 Hz), 116.4 (d, $J_{C-F}$ = 53.3 Hz), 115.9; IR (KBr) ν.cm$^{-1}$ : 3452.7, 3171.9, 3042.5, 2956.7, 1655.8, 1580.8, 1502.9, 1459.1, 1356.0, 1251.9, 1216.9, 1157.3, 1095.4, 969.1, 820.3, 742.3, 627.5, 587.4, 505.6.

Boiling point: 185.2-187.3 °C

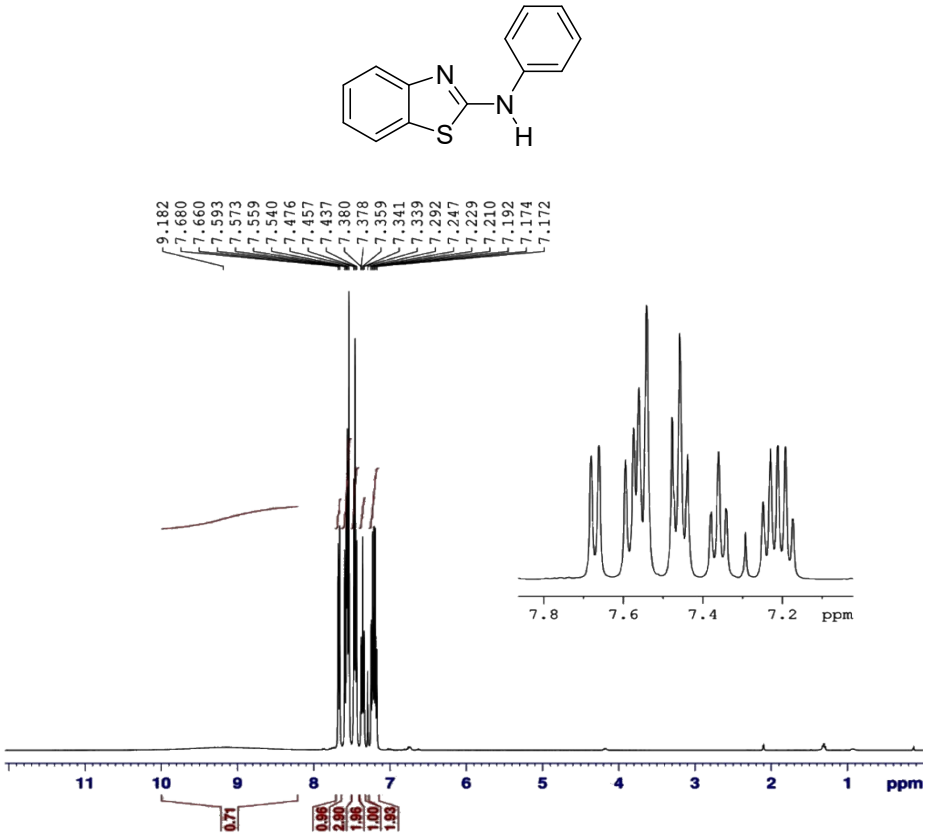



**Figure S23.** $^{1}$H-NMR spectrum of *N*-phenylbenzo[d]thiazol-2-amine in $CDCl_3$

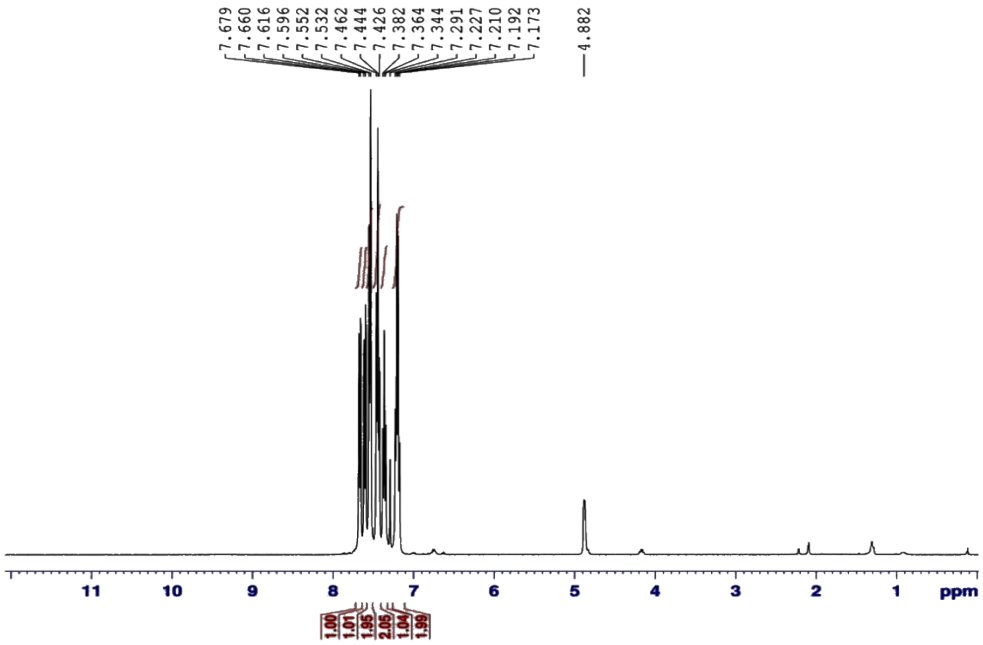



**Figure S24.** $^{1}$H-NMR spectrum of *N*-phenylbenzo[d]thiazol-2-amine in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

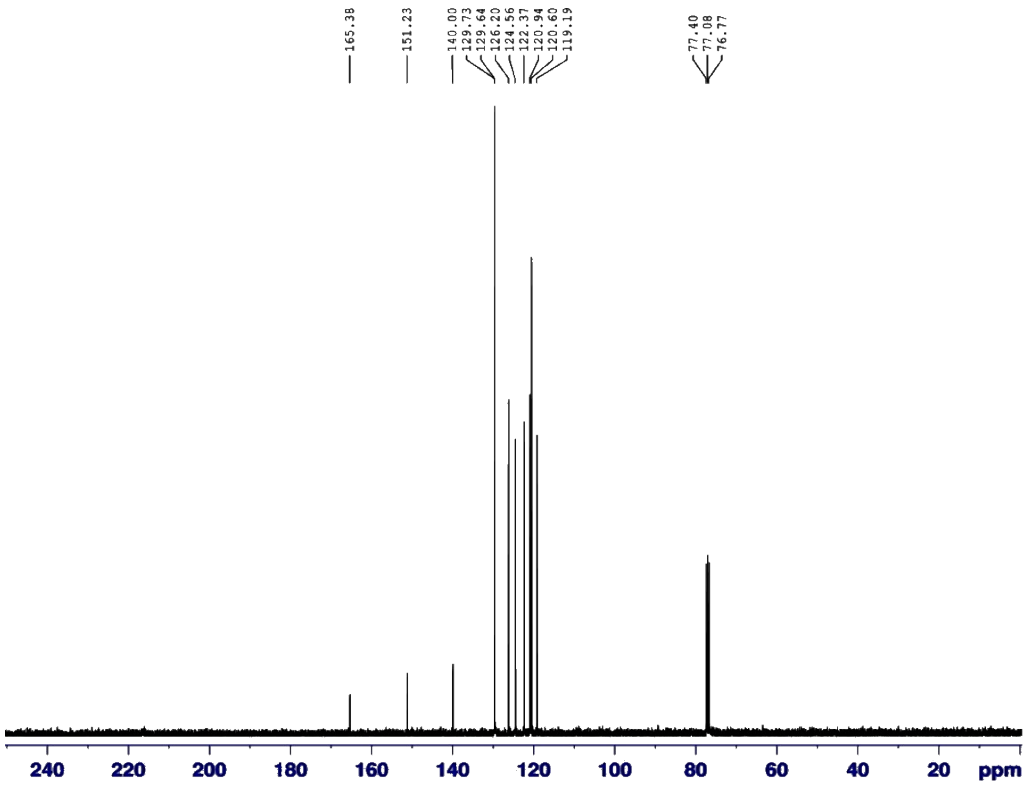



**Figure S25.** $^{13}$C-NMR spectrum of *N*-phenylbenzo[d]thiazol-2-amine in $CDCl_3$

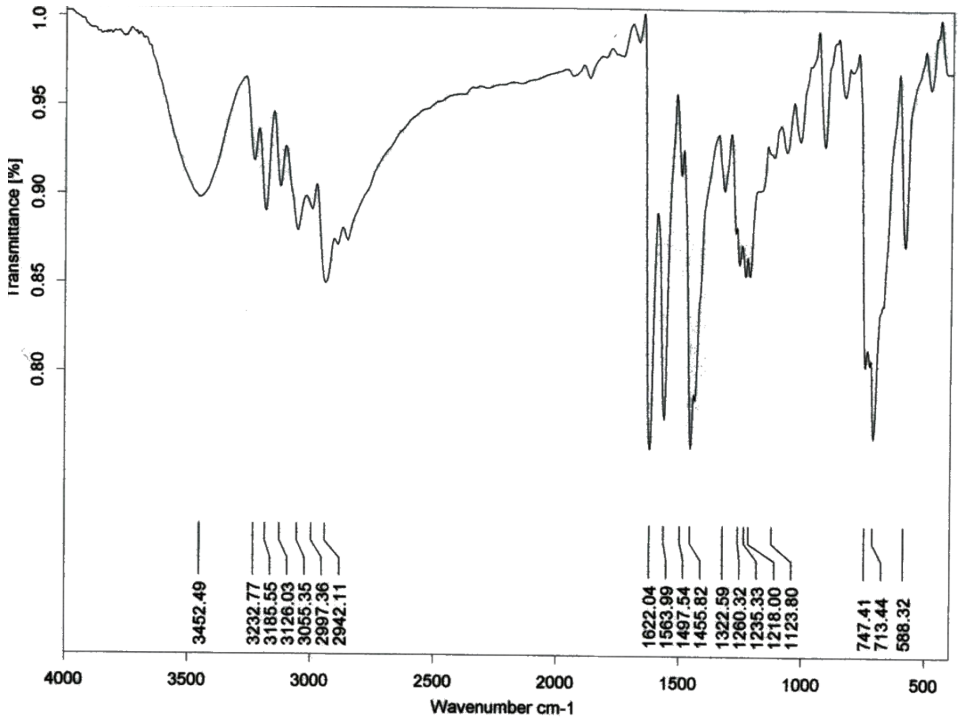



**Figure S26.** IR (KBr discs) spectrum of *N*-phenylbenzo[d]thiazol-2-amine

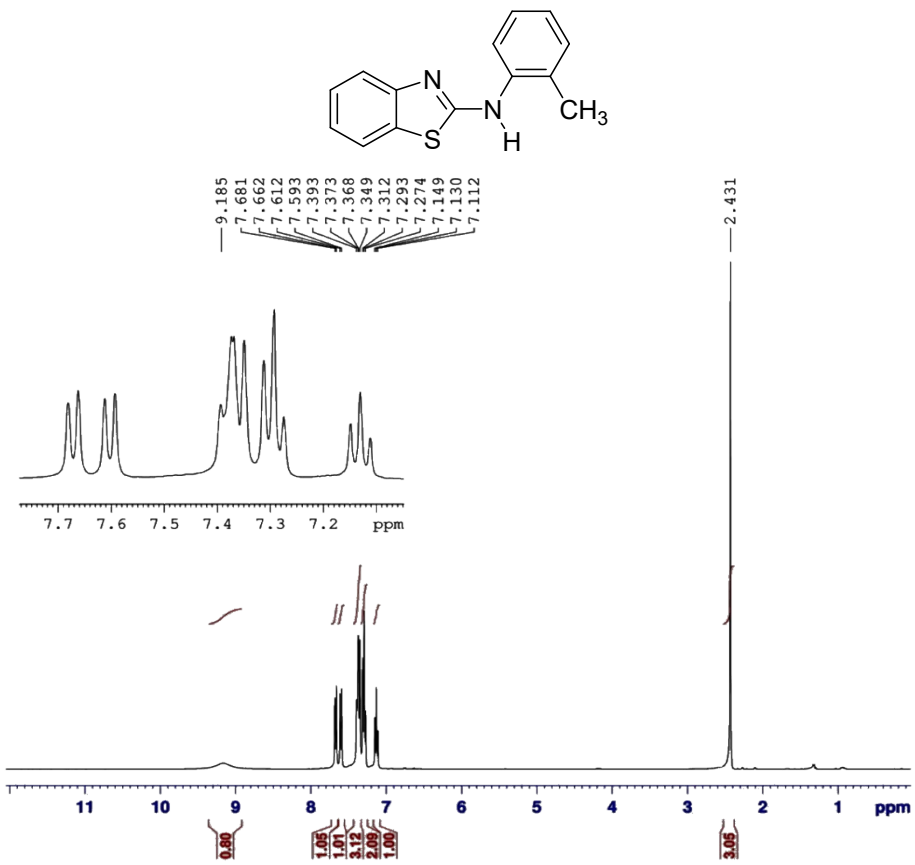



**Figure S27.** $^{1}$H-NMR spectrum of *N-o-tolylbenzo[d]thiazol-2-amine* in $CDCl_3$

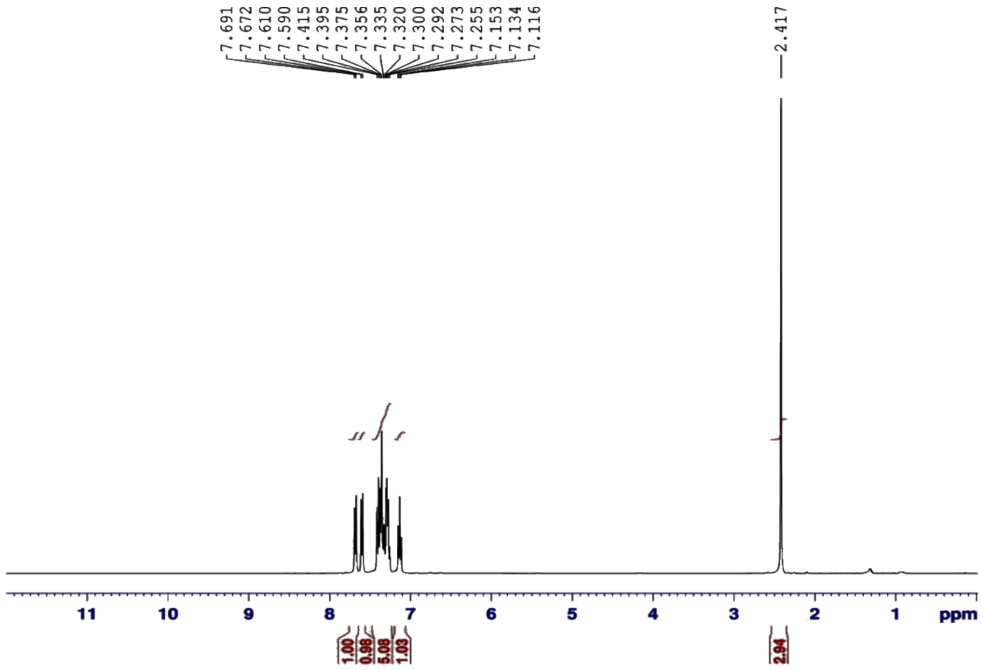



**Figure S28.** $^{1}$H-NMR spectrum of *N-o-tolylbenzo[d]thiazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

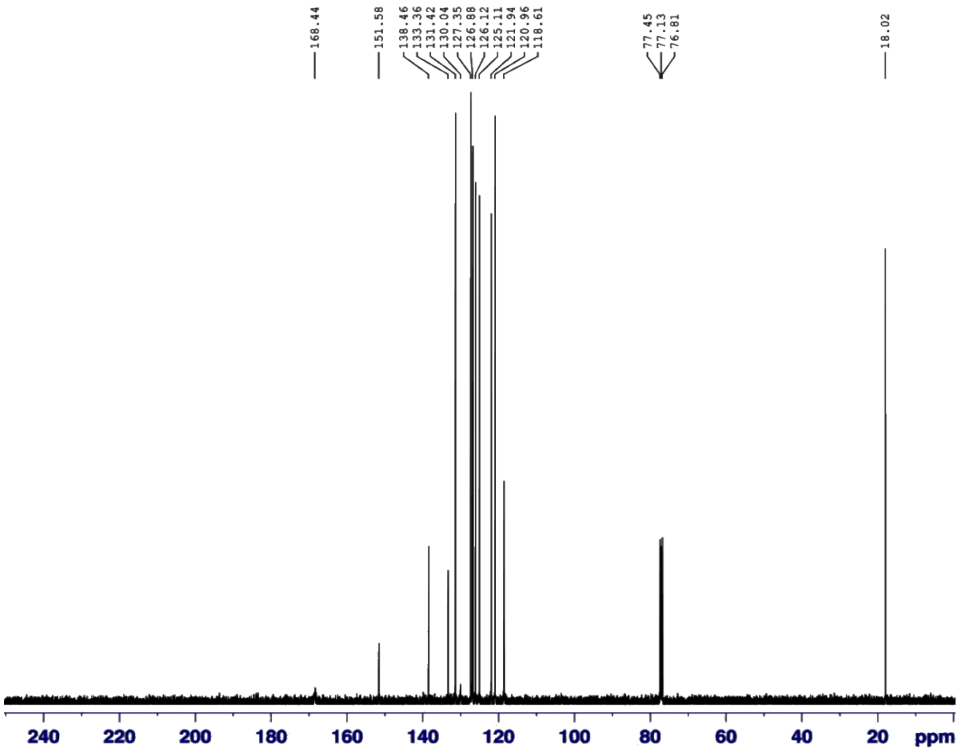



**Figure S29.** $^{13}$C-NMR spectrum of *N-o-tolylbenzo[d]thiazol-2-amine* in $CDCl_3$

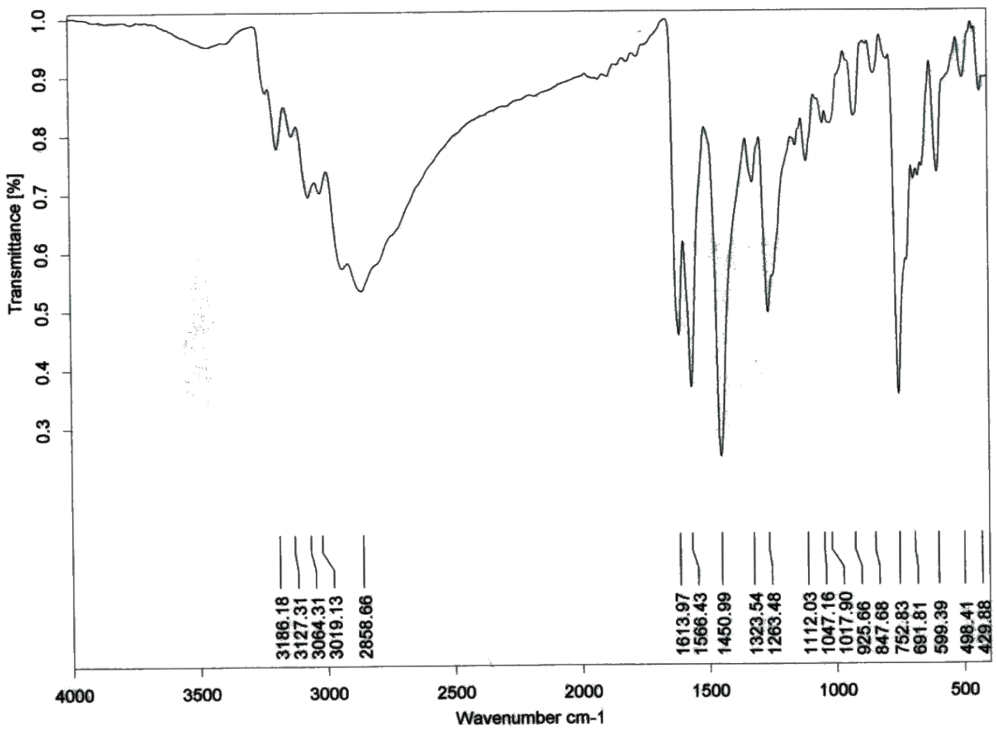



**Figure S30.** IR (KBr discs) spectrum of *N-o-tolylbenzo[d]thiazol-2-amine*

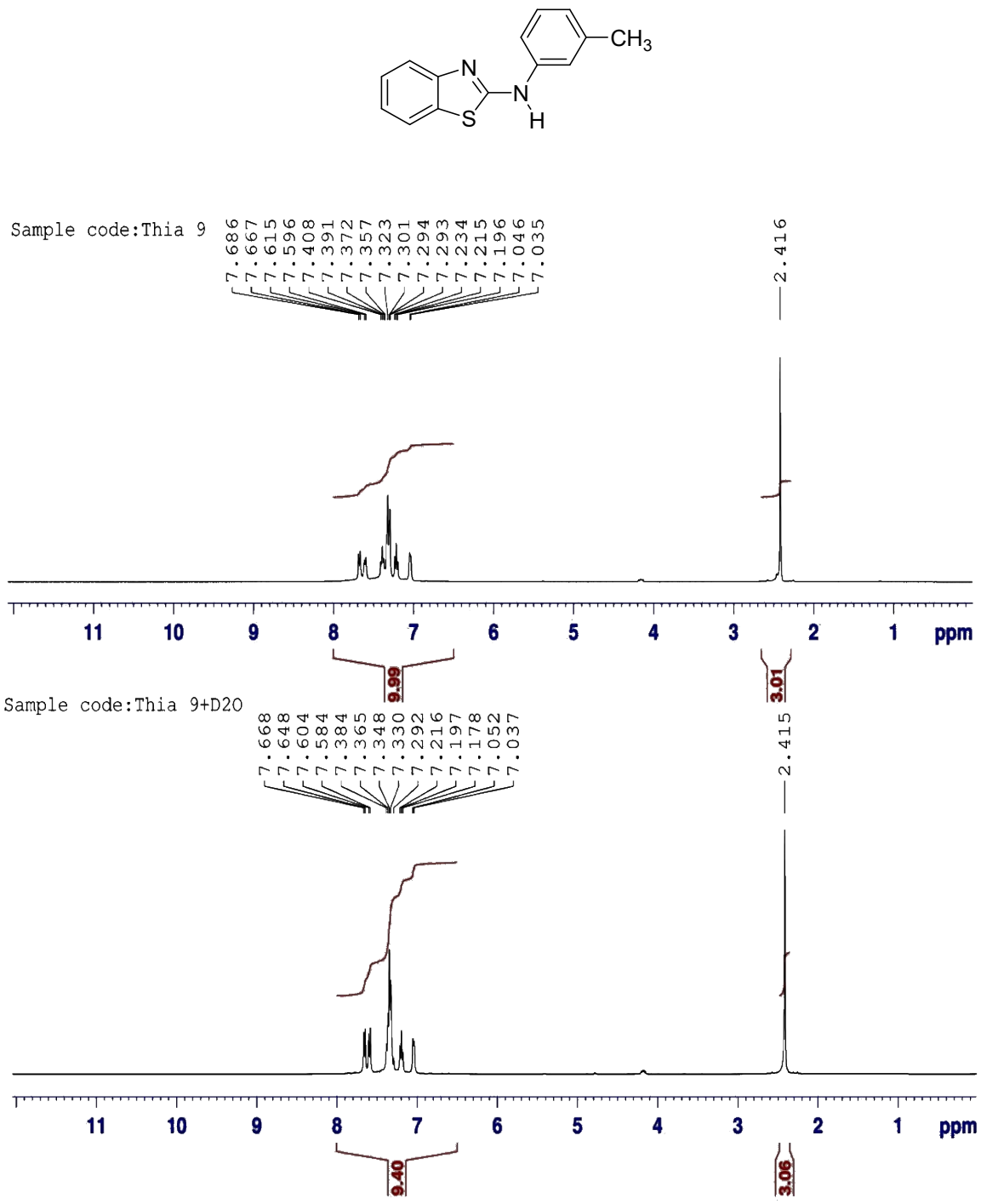



**Figure S31.** $^{1}$H-NMR spectrum of *N-m-tolylbenzo[d]thiazol-2-amine* in $CDCl_3$

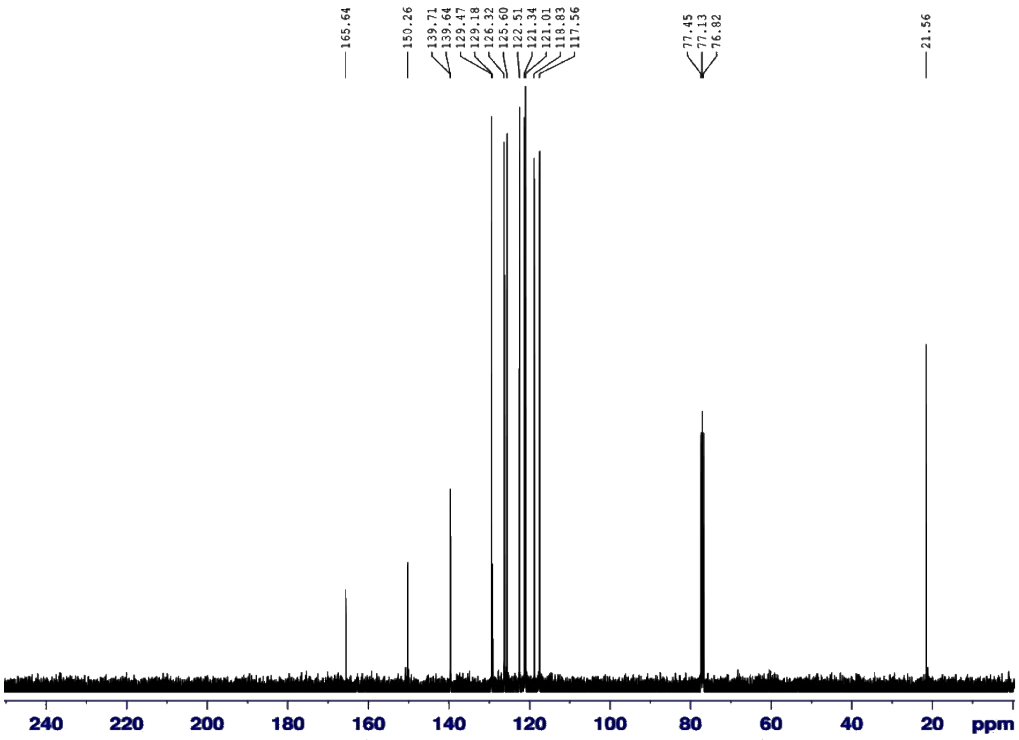



**Figure S32.** $^{13}$C-NMR spectrum of *N-m-tolylbenzo[d]thiazol-2-amine* in $CDCl_3$

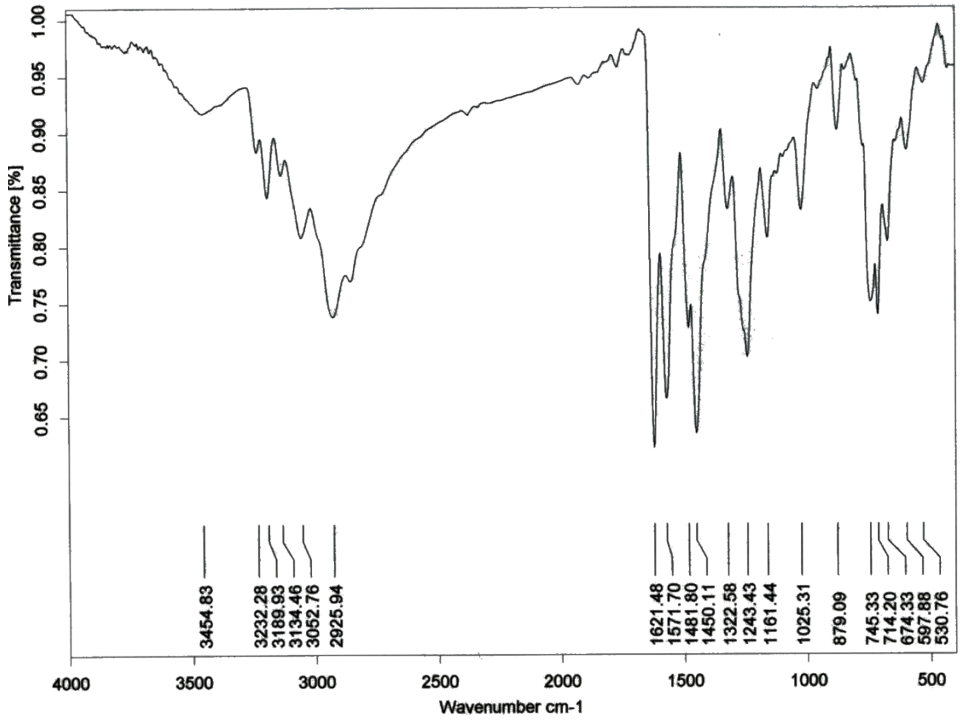



**Figure S33.** IR (KBr discs) spectrum of *N-m-tolylbenzo[d]thiazol-2-amine*

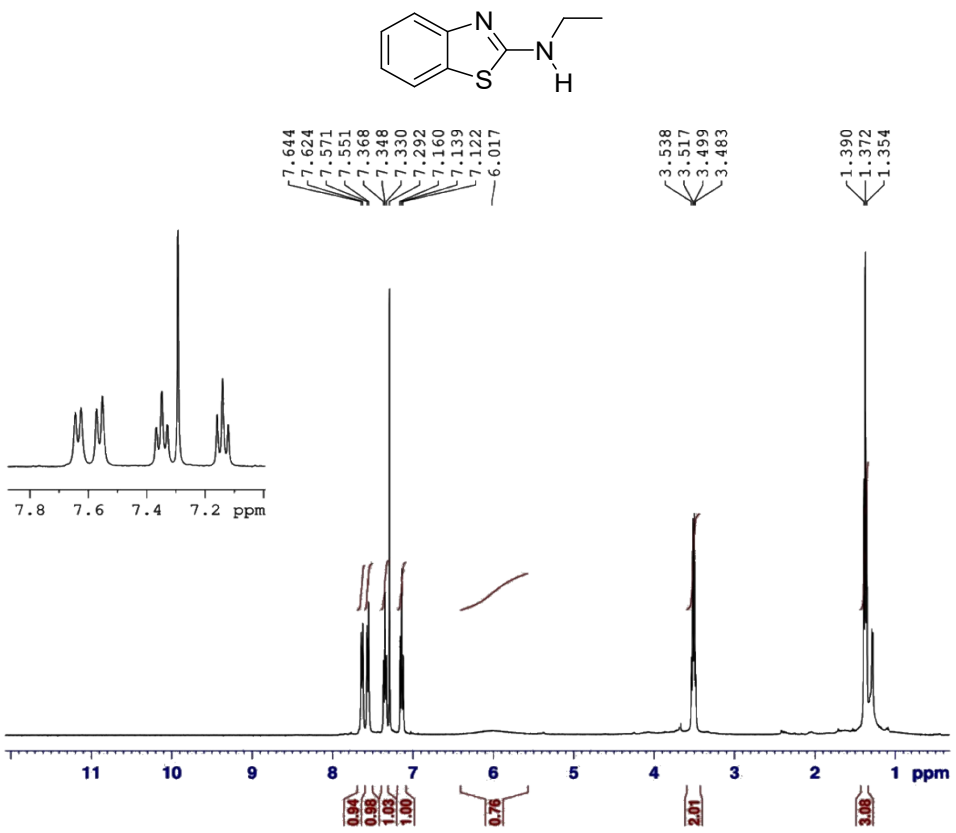



**Figure S34.** $^{1}$H-NMR spectrum of *N-ethylbenzo[d]thiazol-2-amine* in $CDCl_3$

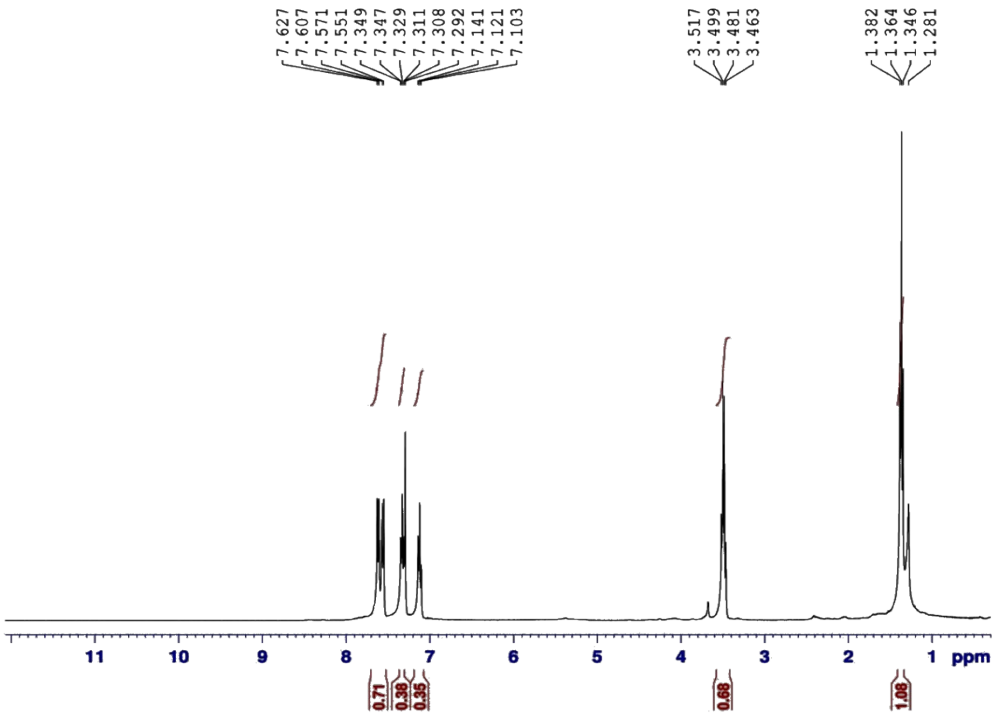



**Figure S35.** $^{1}$H-NMR spectrum of *N-ethylbenzo[d]thiazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

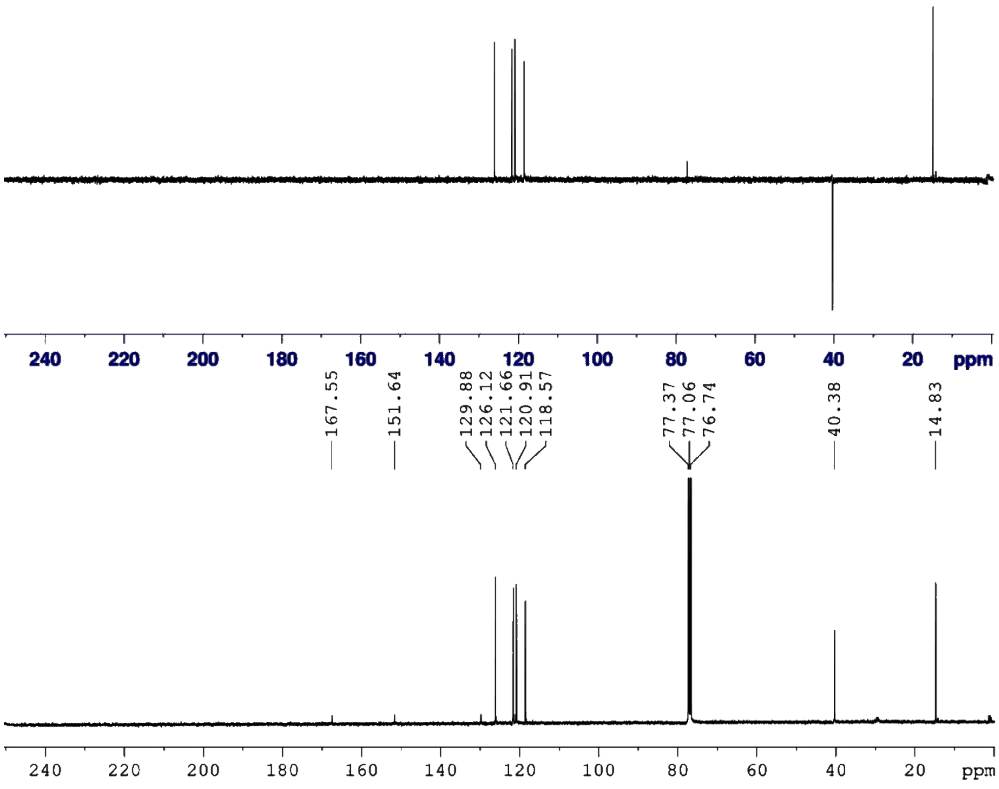



**Figure S36.** $^{13}$C-NMR and Dept 135 spectra of *N-ethylbenzo[d]thiazol-2-amine* in $CDCl_3$

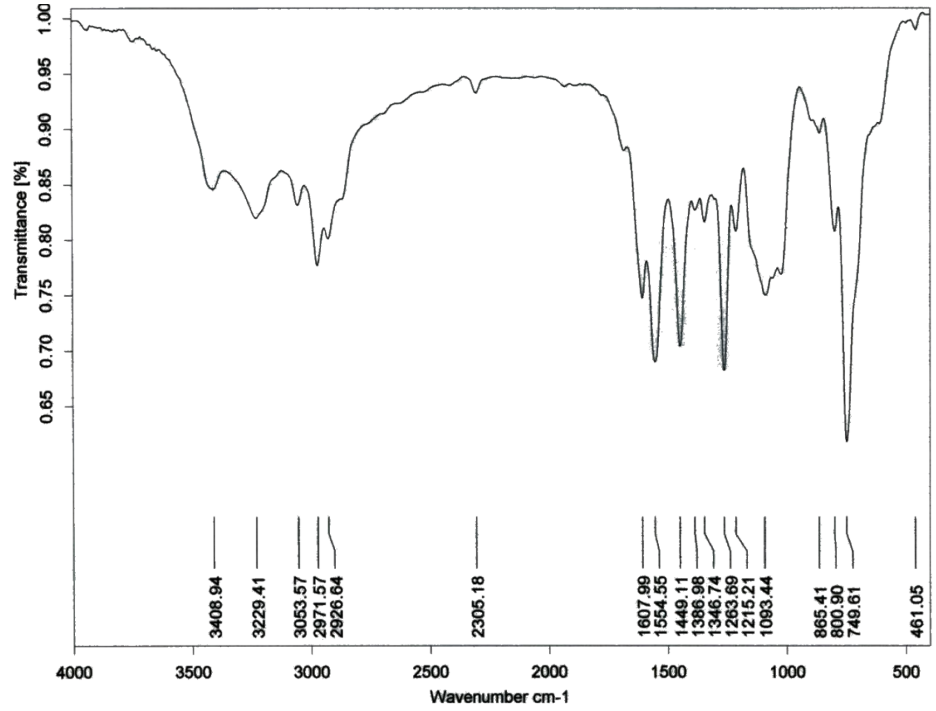



**Figure S37.** IR (KBr discs) spectrum of *N-ethylbenzo[d]thiazol-2-amine*

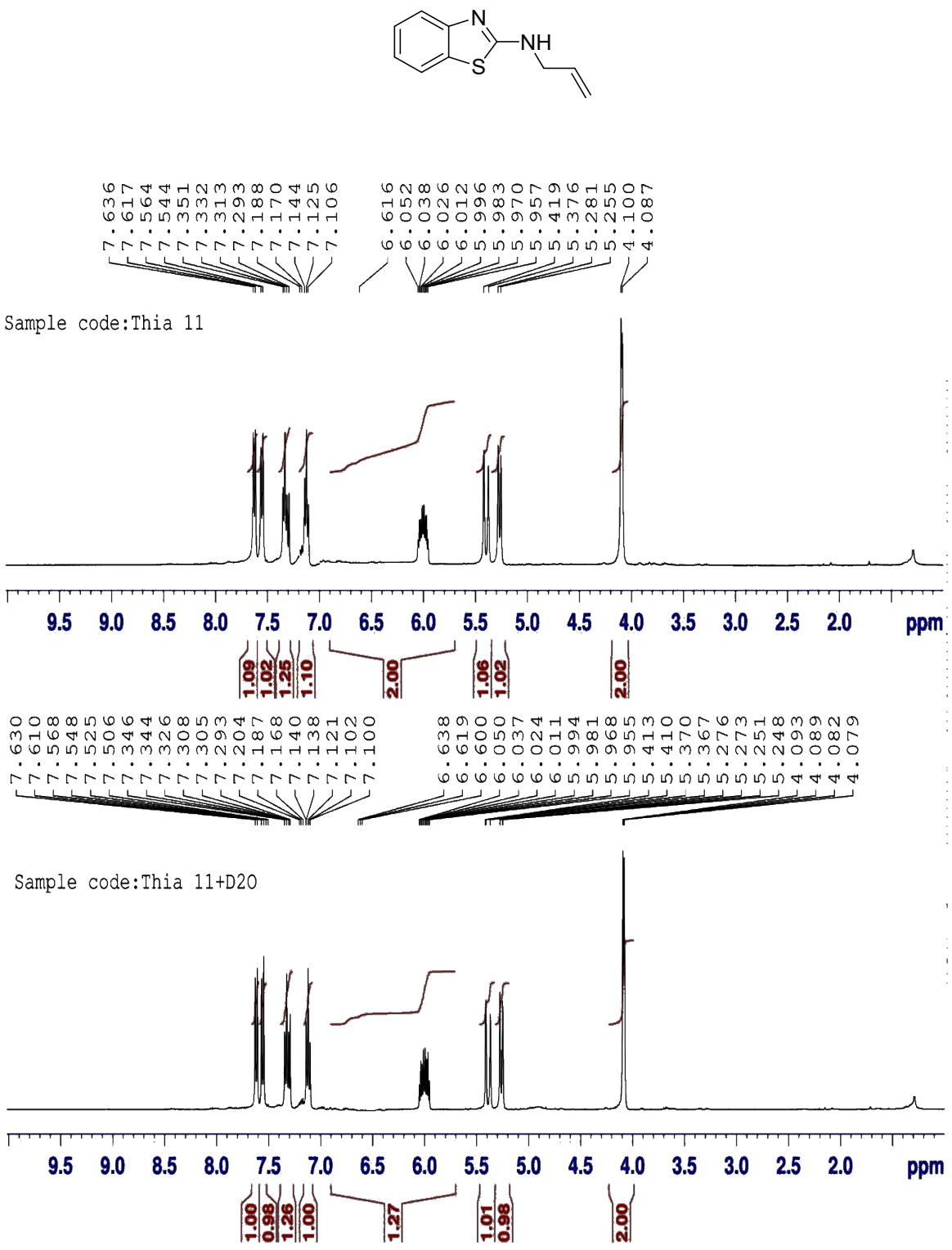



**Figure S38.** $^{1}$H-NMR spectra of *N-allylbenzo[d]thiazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

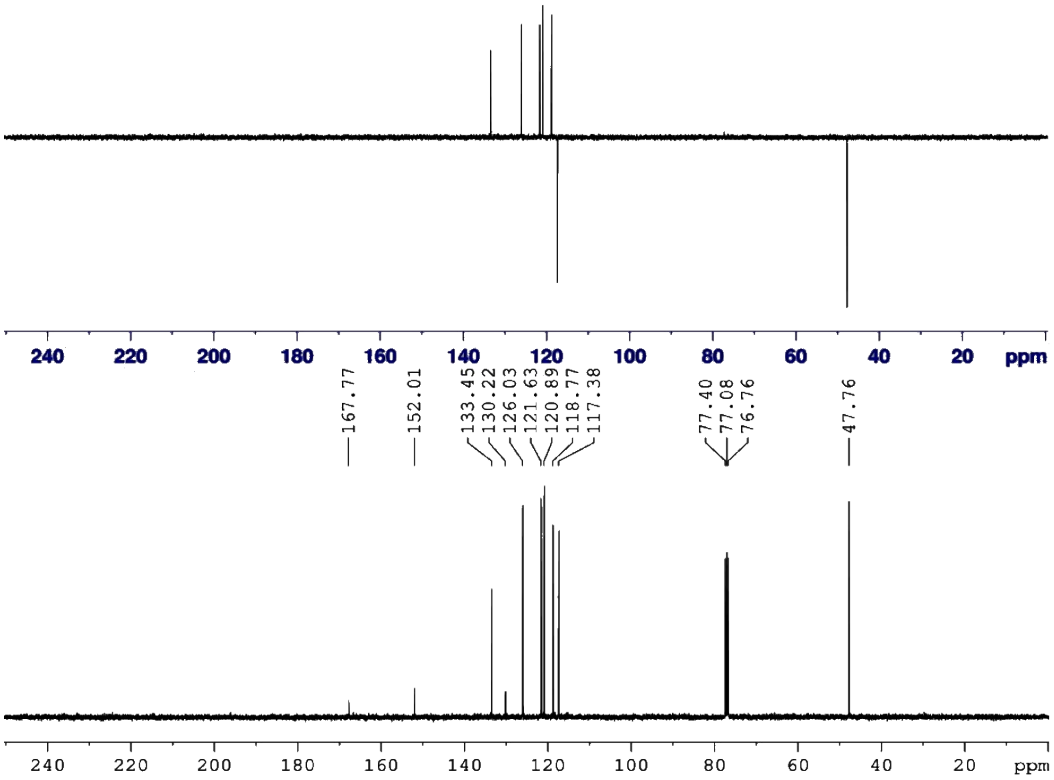



**Figure S39.** $^{13}$C-NMR and Dept 135 spectra of *N-allylbenzo[d]thiazol-2-amine* in $CDCl_3$

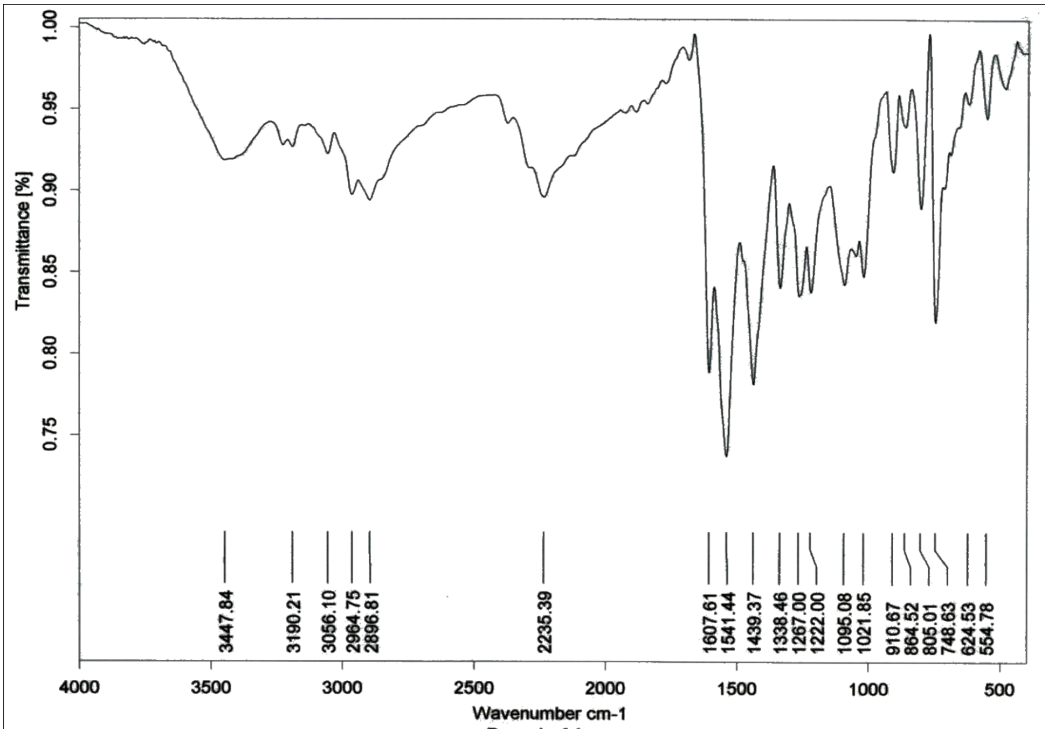



**Figure S40.** IR (KBr discs) spectrum of *N-allylbenzo[d]thiazol-2-amine*

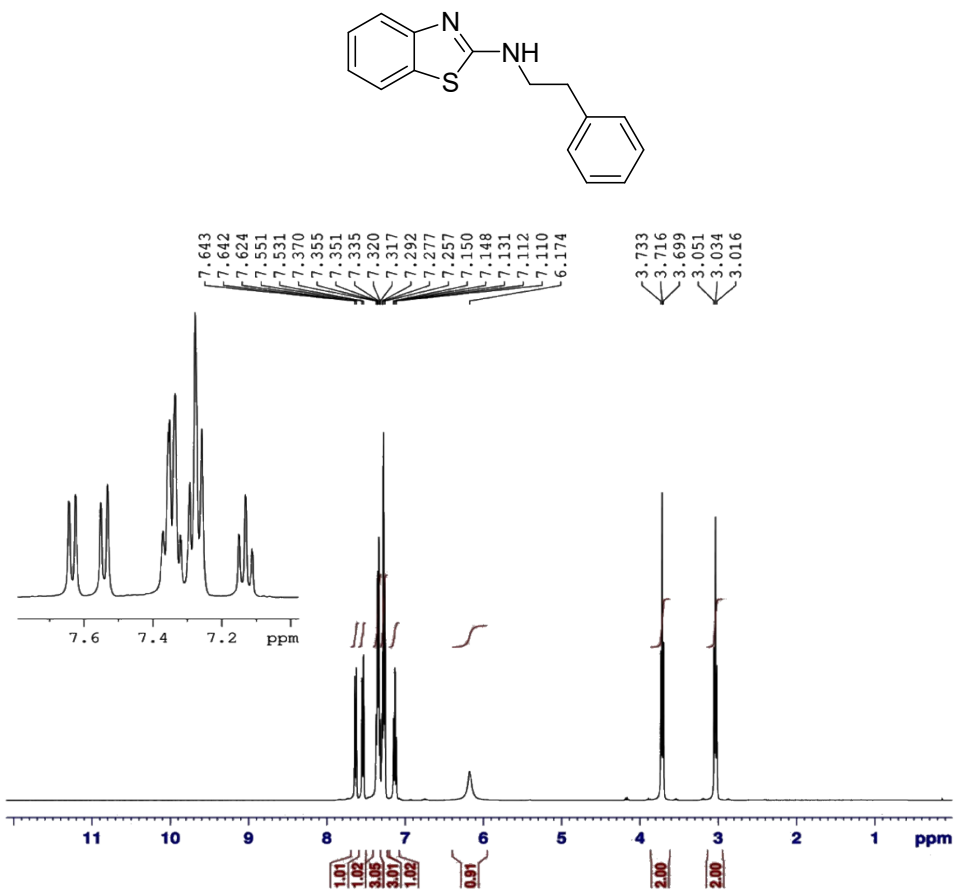



**Figure S41.** $^{1}$H-NMR spectrum of *N-phenethylbenzo[d]thiazol-2-amine* in $CDCl_3$

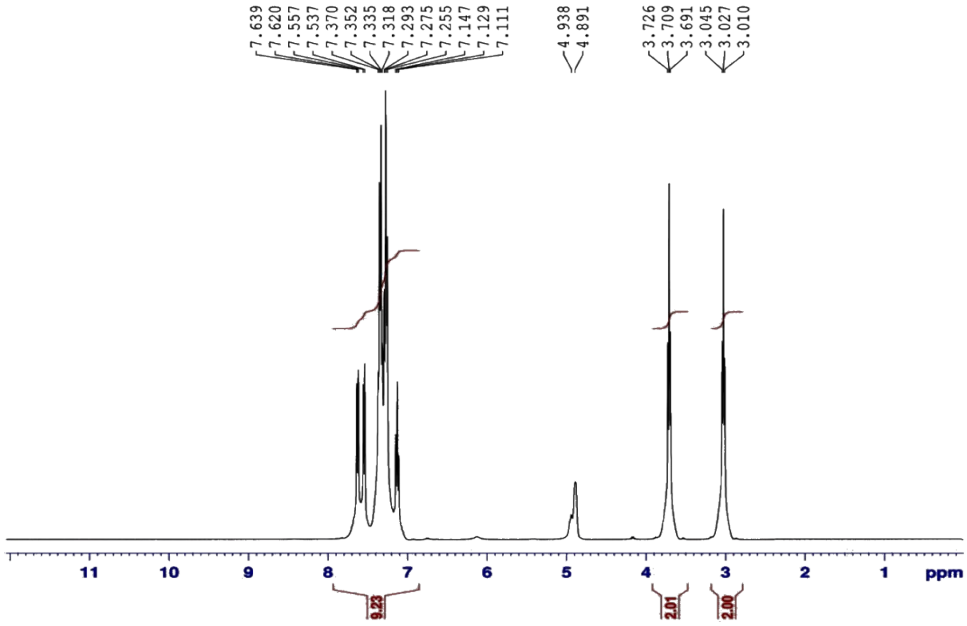



**Figure S42.** $^{1}$H-NMR spectrum of *N-phenethylbenzo[d]thiazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

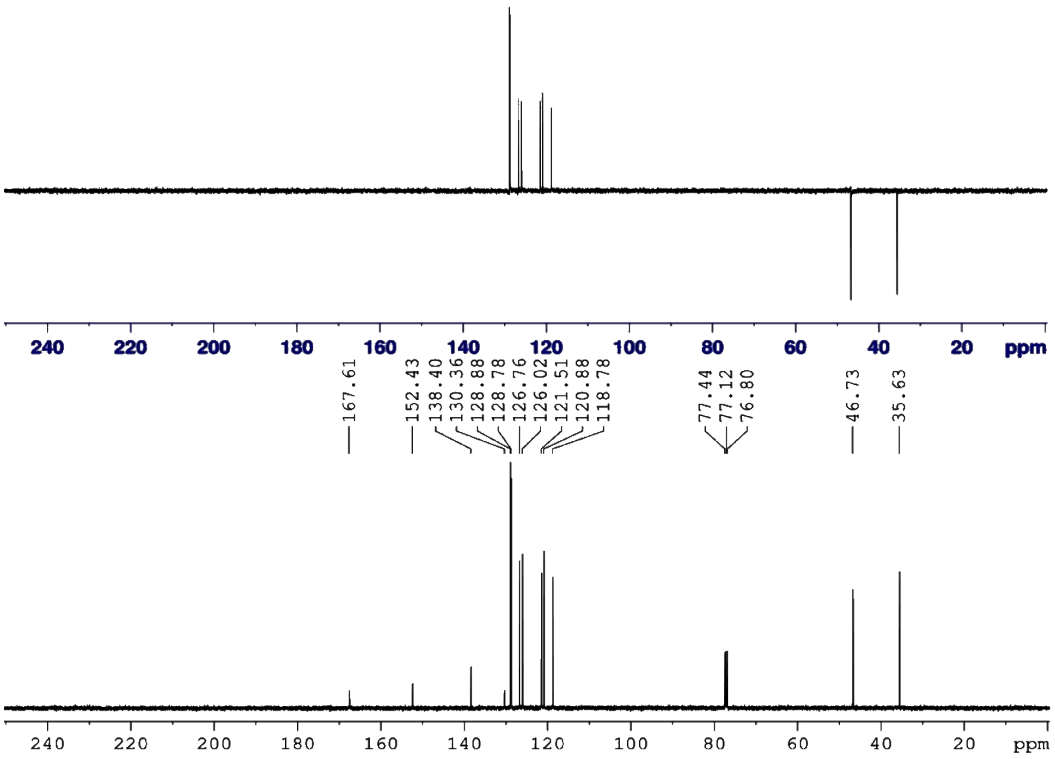



**Figure S43.** $^{13}$C-NMR and Dept 135 spectra of *N-phenethylbenzo[d]thiazol-2-amine* in $CDCl_3$

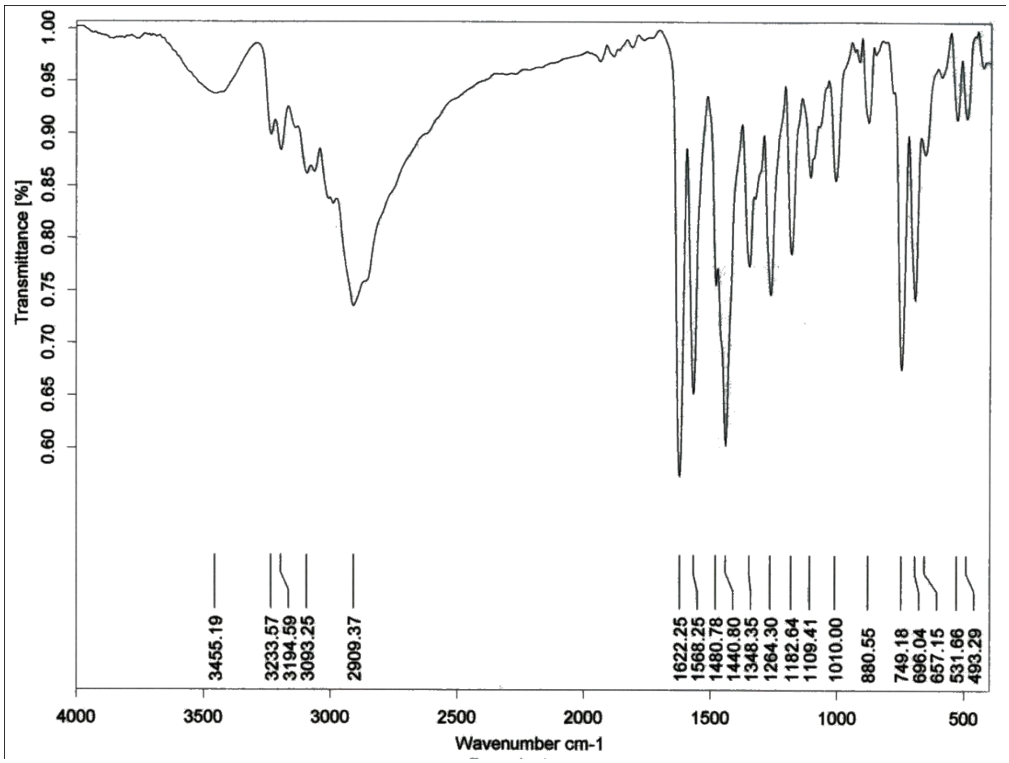



**Figure S44.** IR (KBr discs) spectrum of *N-phenethylbenzo[d]thiazol-2-amine*

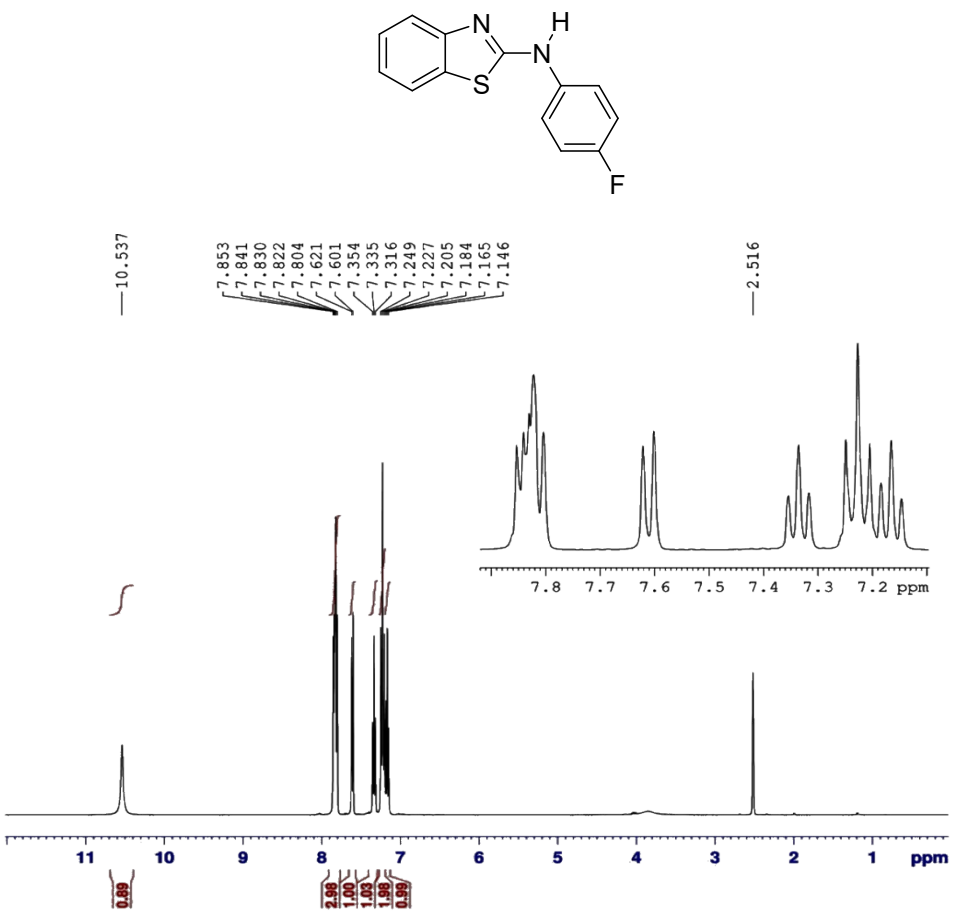



**Figure S45.** $^{1}$H-NMR spectrum of *N-(4-fluorophenyl)benzo[d]thiazol-2-amine* in $CDCl_3$

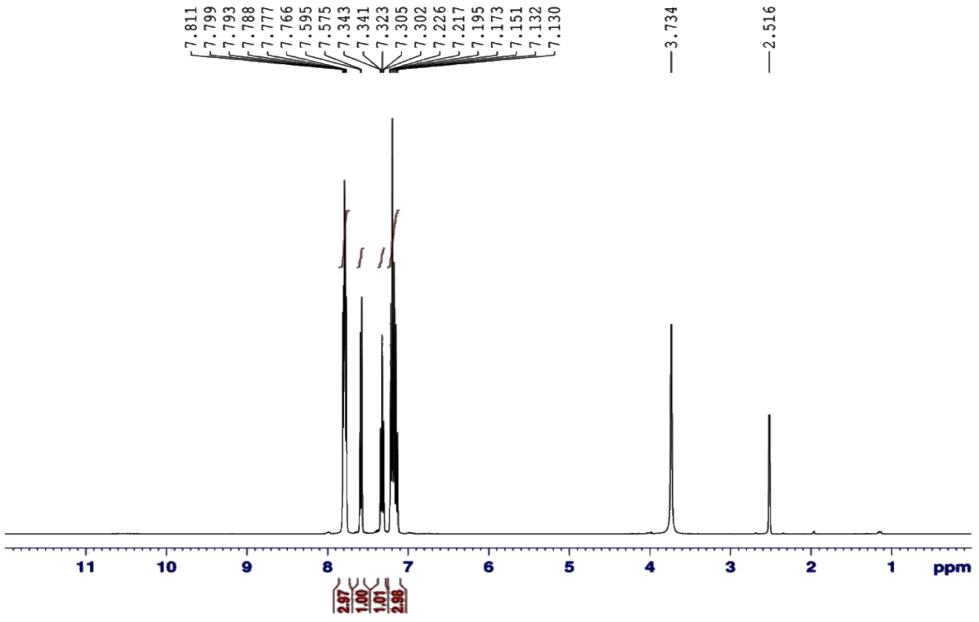



**Figure S46.** $^{1}$H-NMR spectrum of *N-(4-fluorophenyl)benzo[d]thiazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

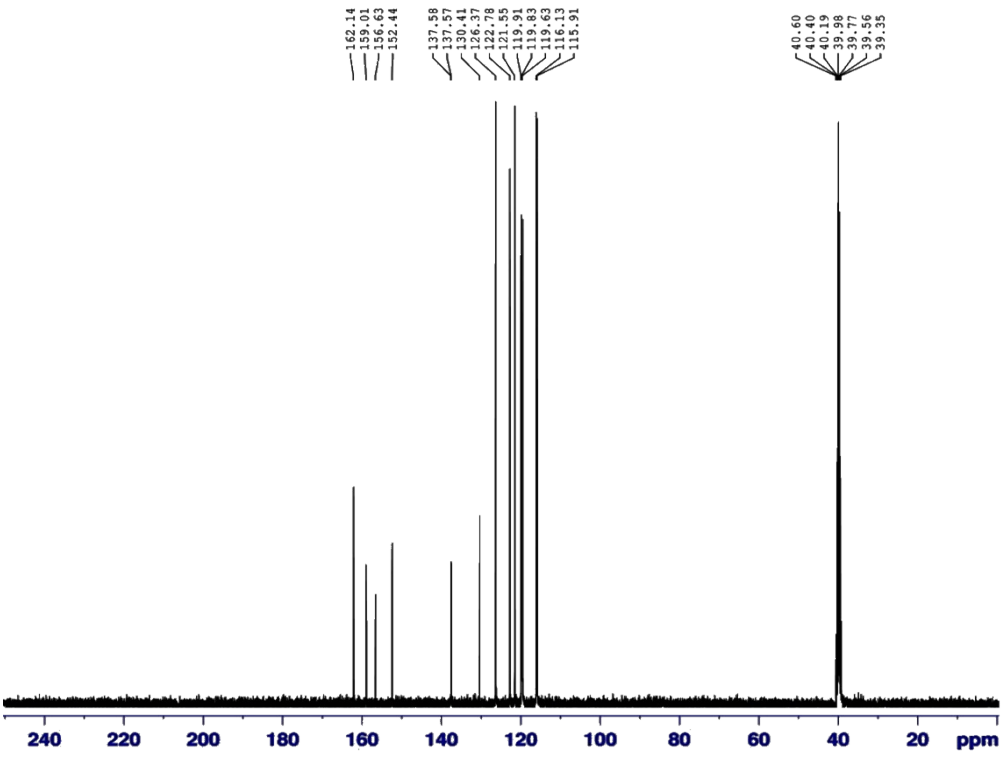



**Figure S47.** $^{13}$C-NMR spectrum of *N-(4-fluorophenyl)benzo[d]thiazol-2-amine* in $CDCl_3$

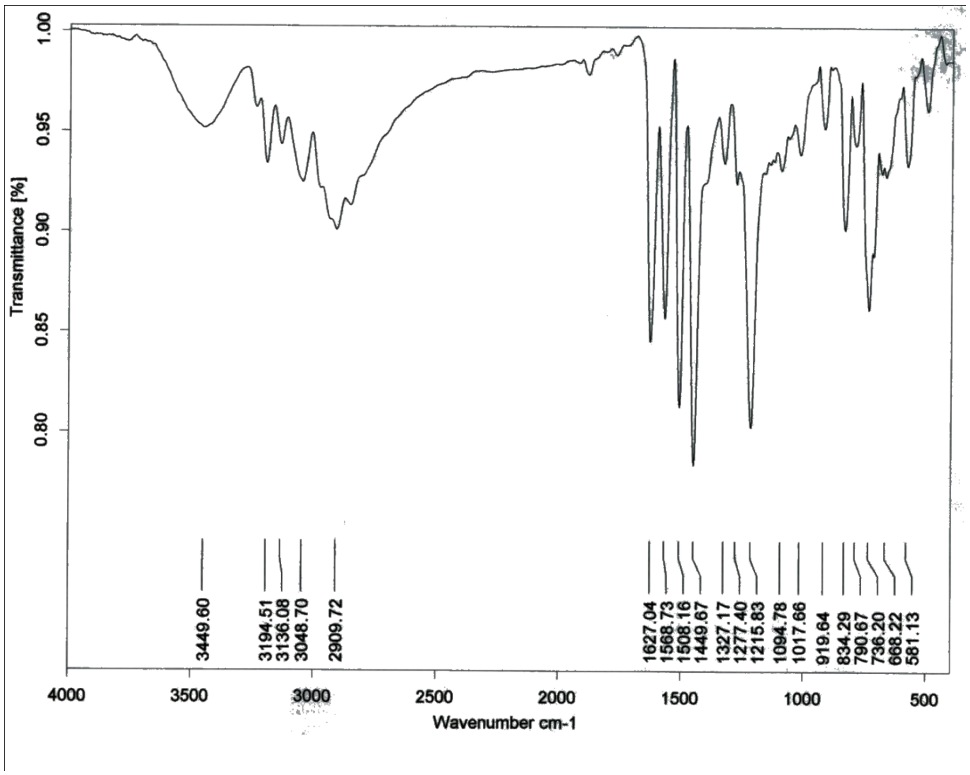



**Figure S48.** IR (KBr discs) spectrum of *N-(4-fluorophenyl)benzo[d]thiazol-2-amine*

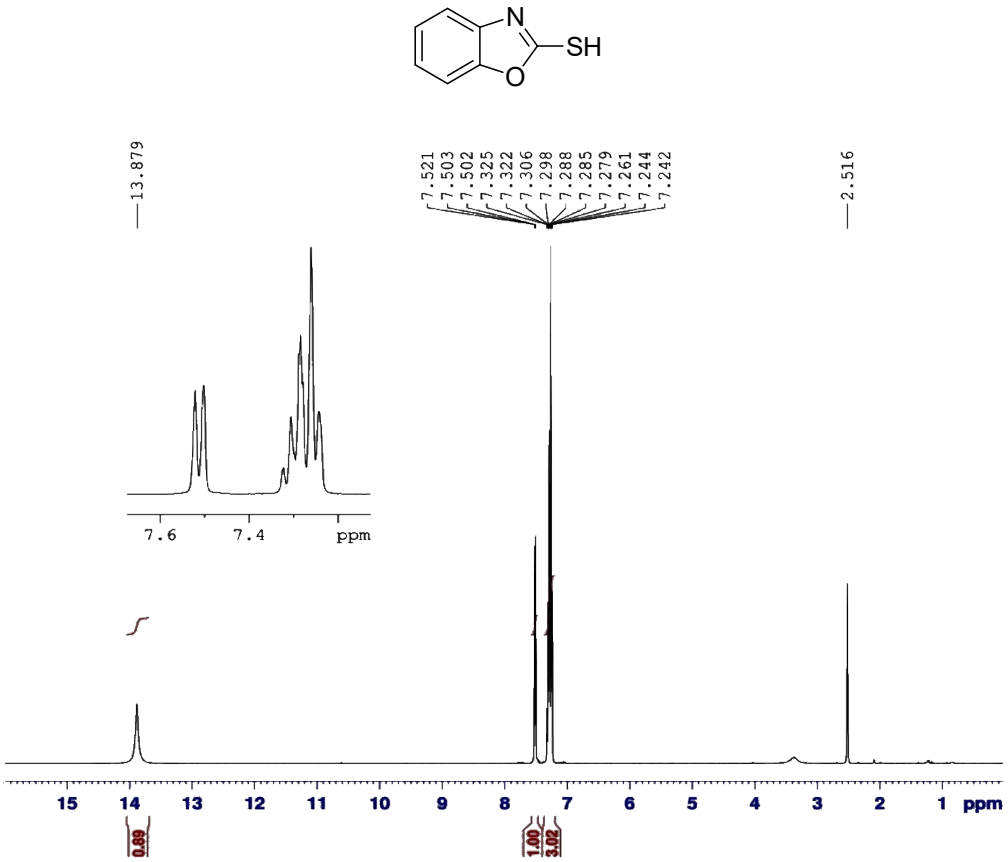



**Figure S49.** $^{1}$H-NMR spectrum of *2-mercaptobenzoxazole* in DMSO

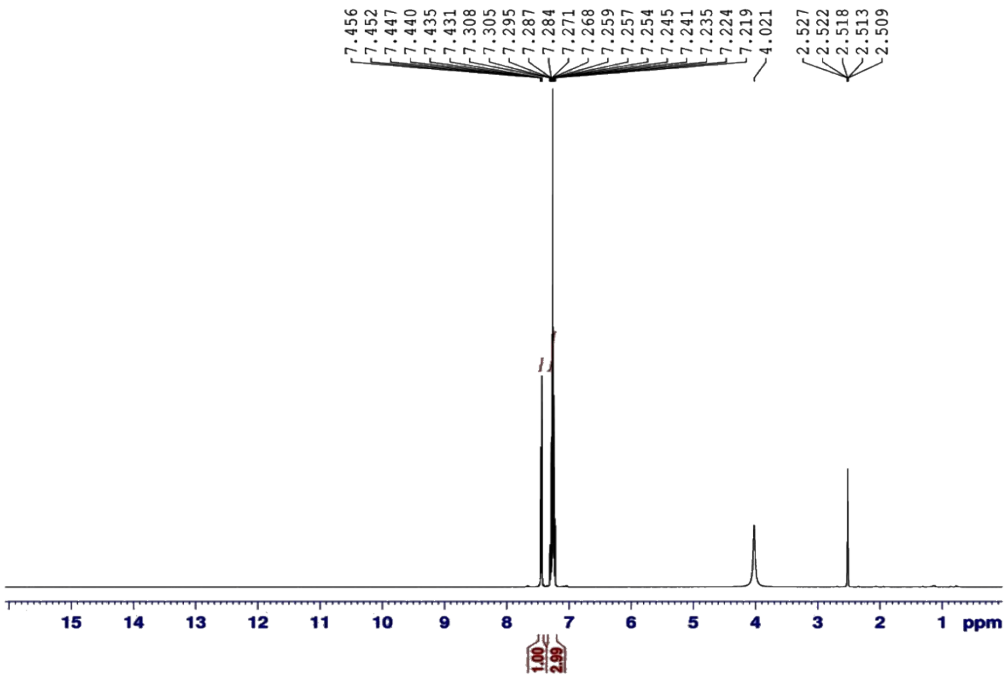



**Figure S50.** $^{1}$H-NMR spectrum of *2-mercaptobenzoxazole* in DMSO ($D_2O$ as exchanged solvent is used)

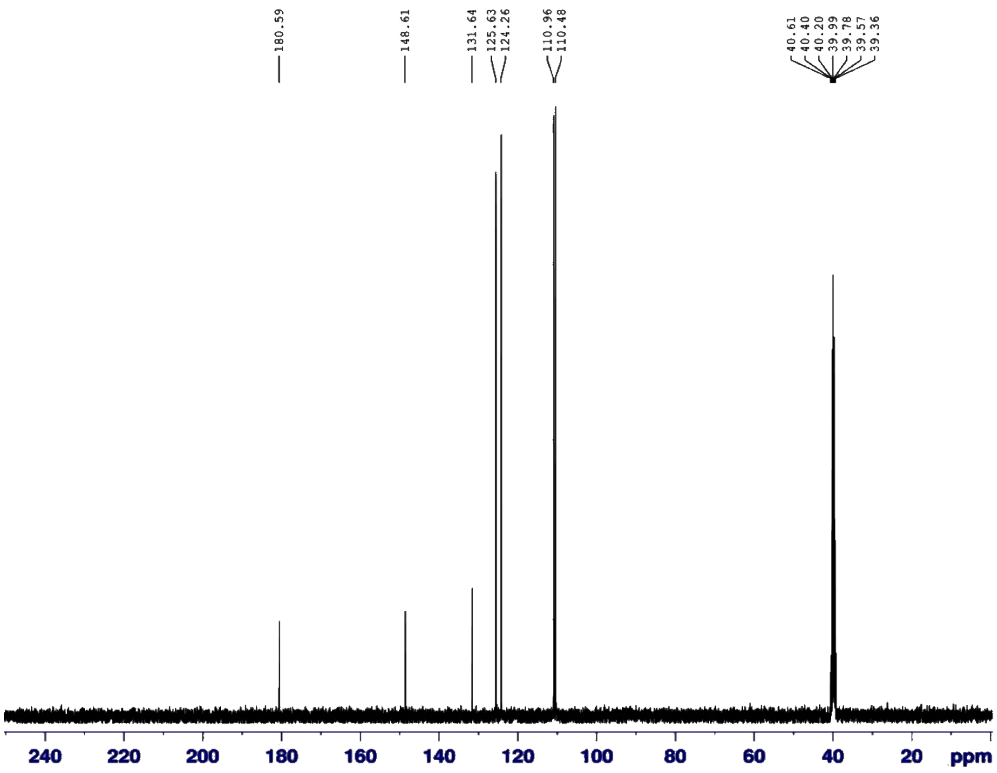



**Figure S51.** $^{13}$C-NMR spectrum of *2-mercaptobenzoxazole* in DMSO

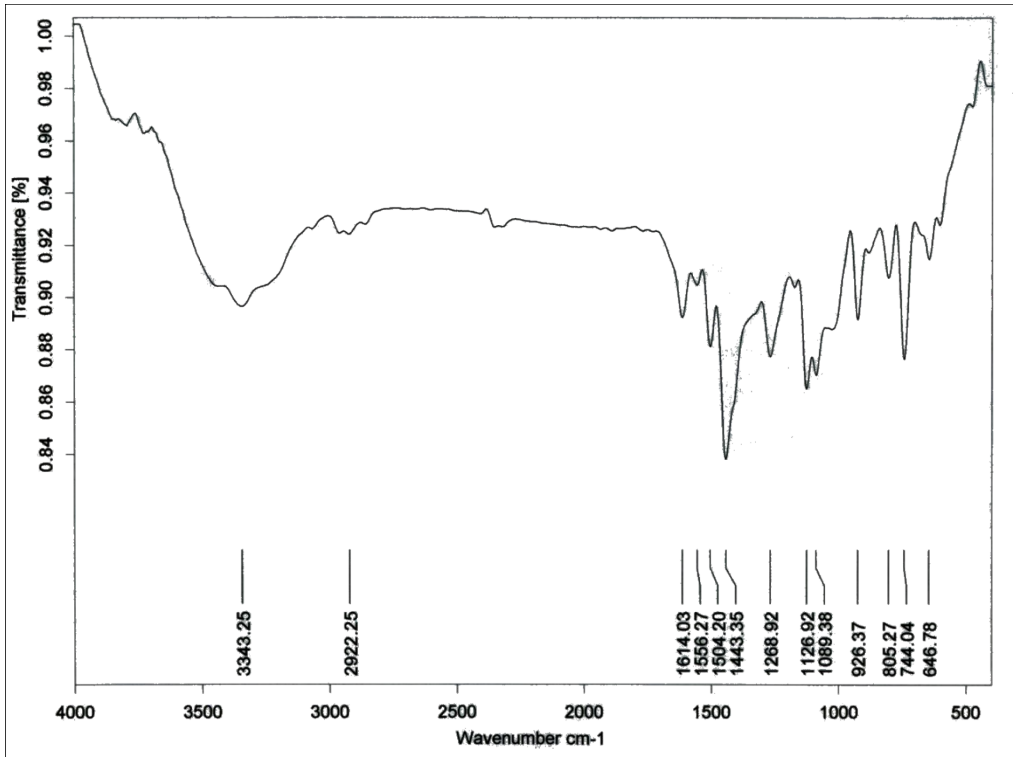



**Figure S52.** IR (KBr discs) spectrum of *2-mercaptobenzoxazole*

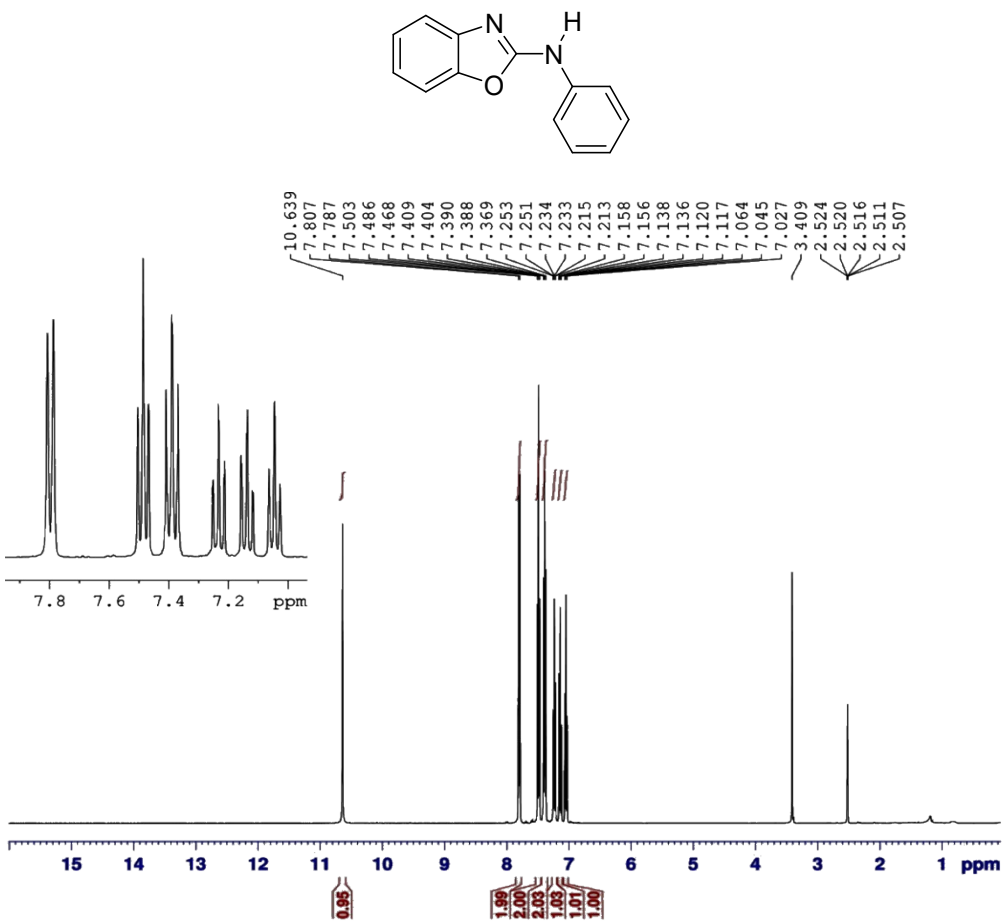



**Figure S53.** [1]H-NMR spectrum of *N-phenylbenzo[d]oxazol-2-amine* in DMSO

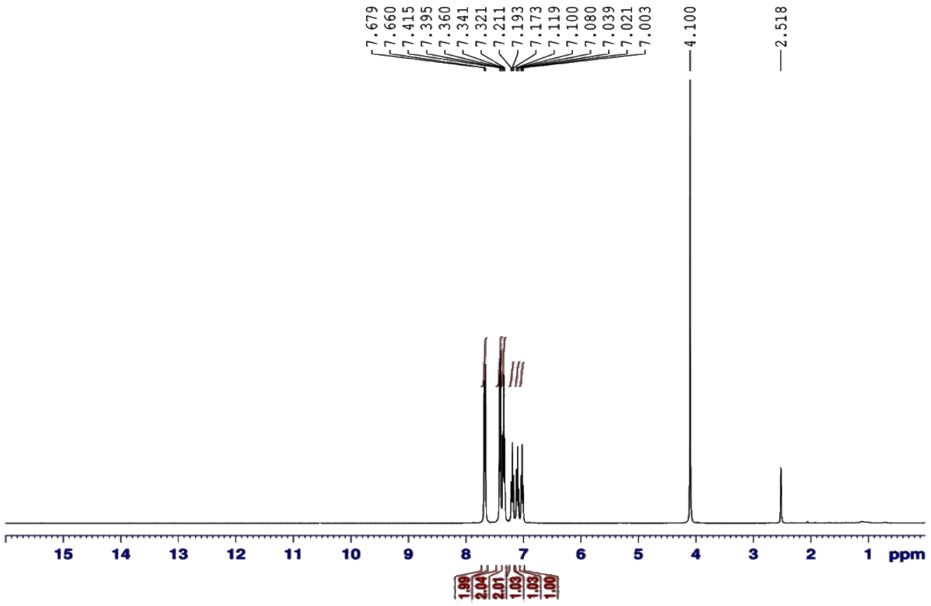



**Figure S54.** [1]H-NMR spectrum of *N-phenylbenzo[d]oxazol-2-amine* in DMSO ($D_2O$ as exchanged solvent is used)

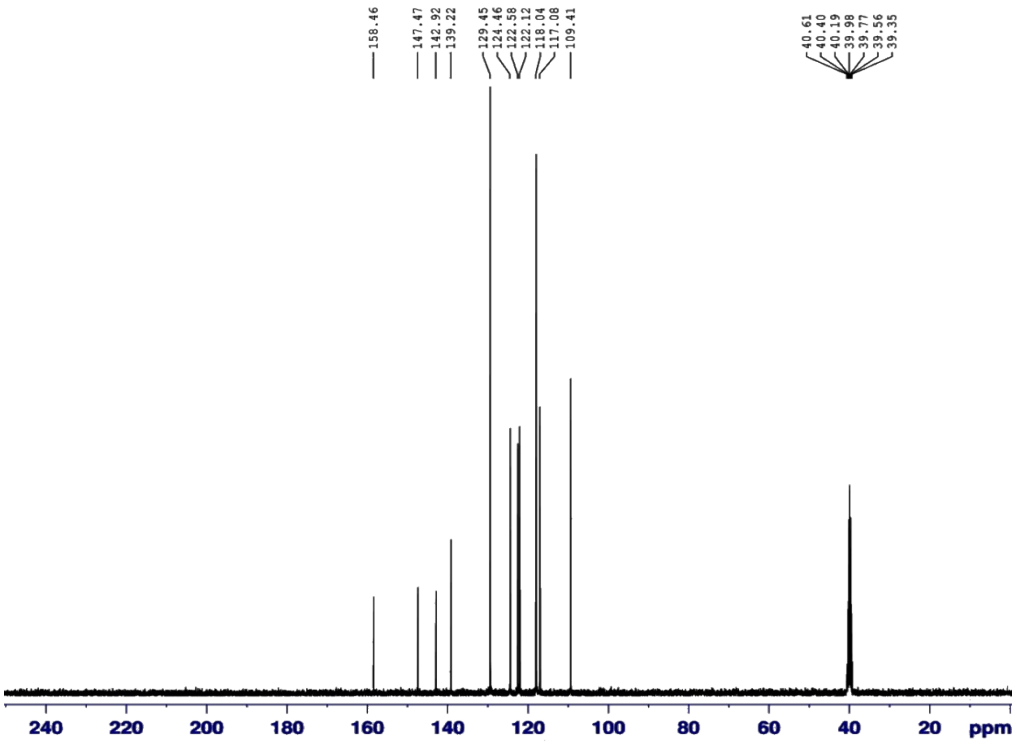



**Figure S55.** $^{13}$C-NMR spectrum of *N-phenylbenzo[d]oxazol-2-amine* in DMSO

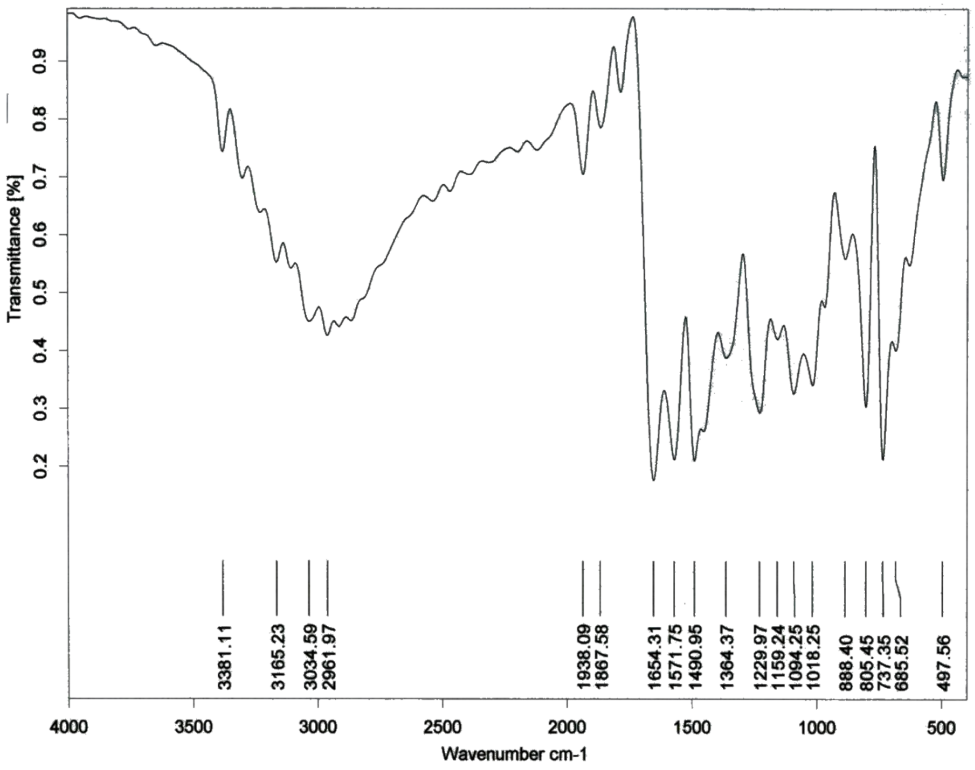



**Figure S56.** IR (KBr discs) spectrum of *N-phenylbenzo[d]oxazol-2-amine*

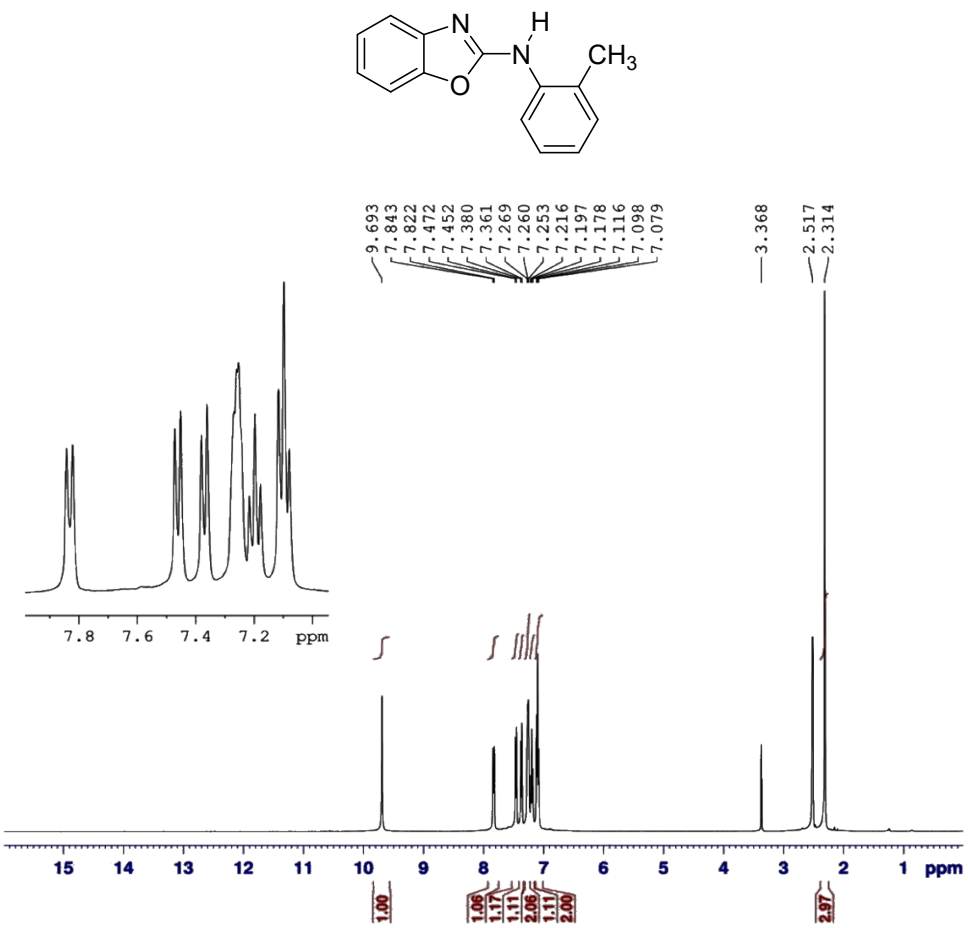



**Figure S57.** [1]H-NMR spectrum of *N-o-tolylbenzo[d]oxazol-2-amine* in DMSO

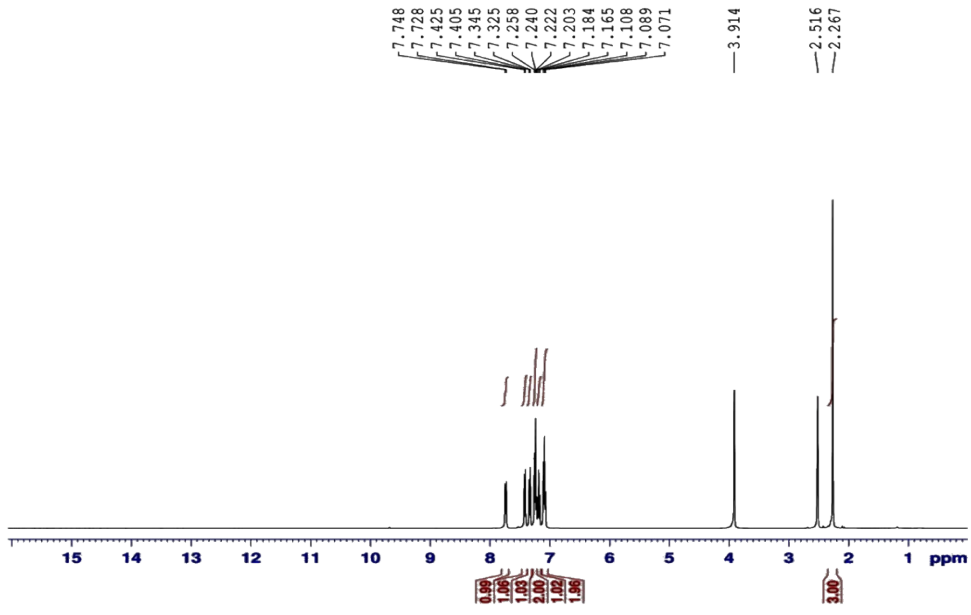



**Figure S58.** [1]H-NMR spectrum of *N-o-tolylbenzo[d]oxazol-2-amine* in DMSO ($D_2O$ as exchanged solvent is used)

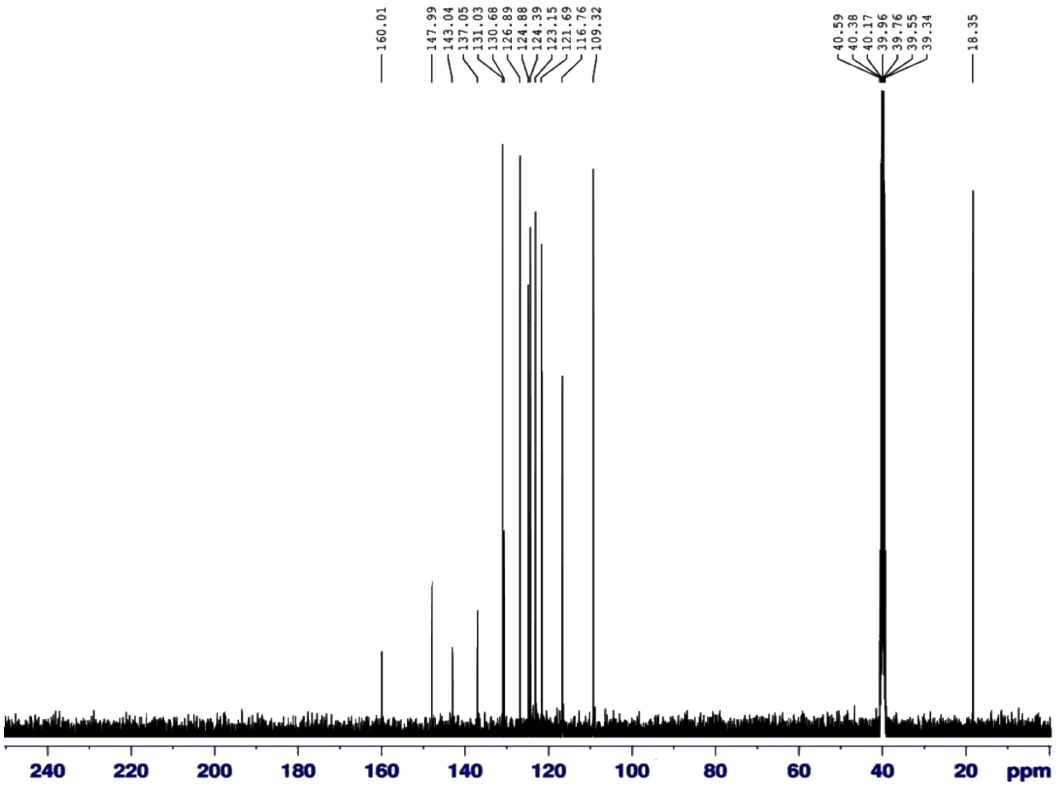



**Figure S59.** $^{13}$C-NMR spectrum of *N-o-tolylbenzo[d]oxazol-2-amine* in DMSO

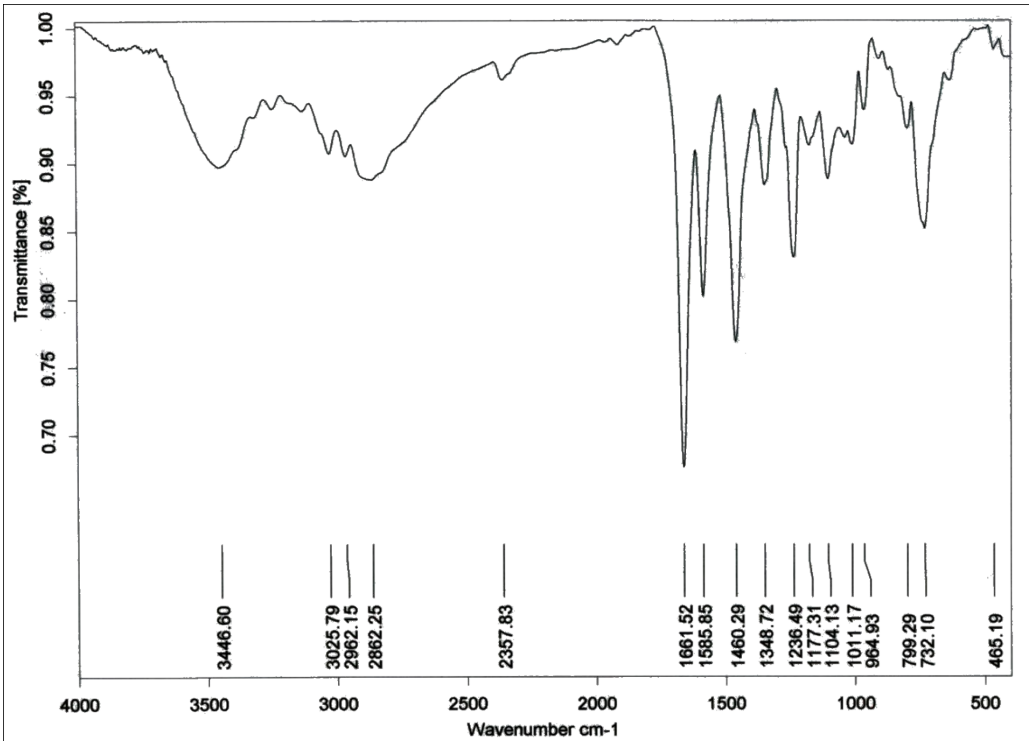



**Figure S60.** IR (KBr discs) spectrum of *N-o-tolylbenzo[d]oxazol-2-amine*

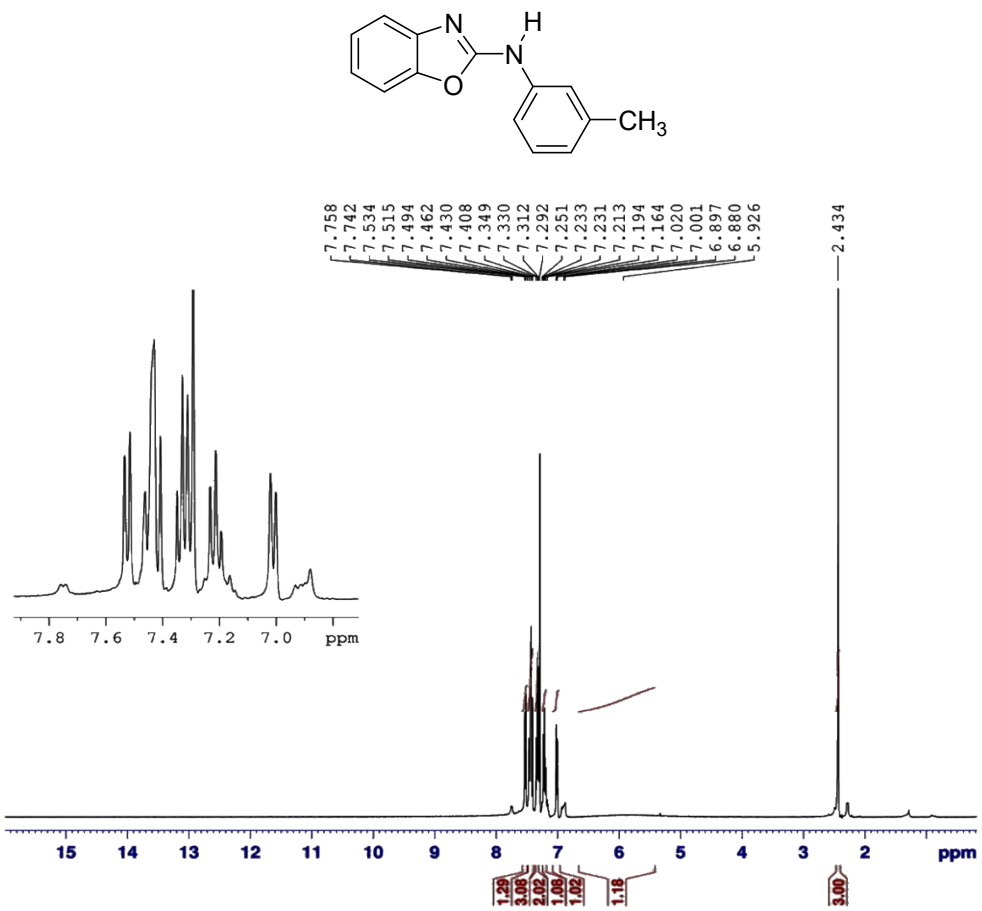



**Figure S61.** $^{1}$H-NMR spectrum of *N-m-tolylbenzo[d]oxazol-2-amine* in $CDCl_3$

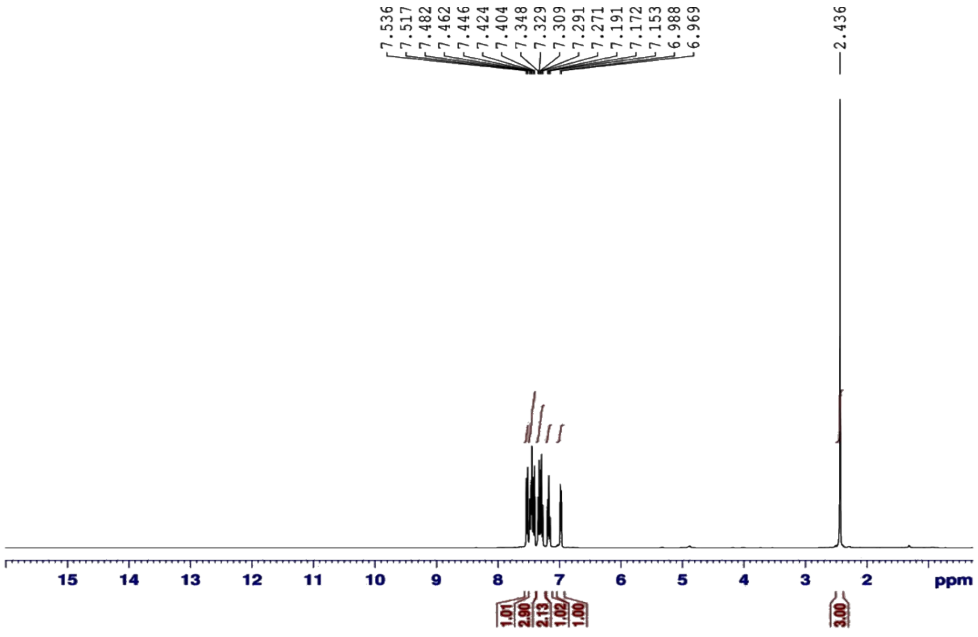



**Figure S62.** $^{1}$H-NMR spectrum of *N-m-tolylbenzo[d]oxazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

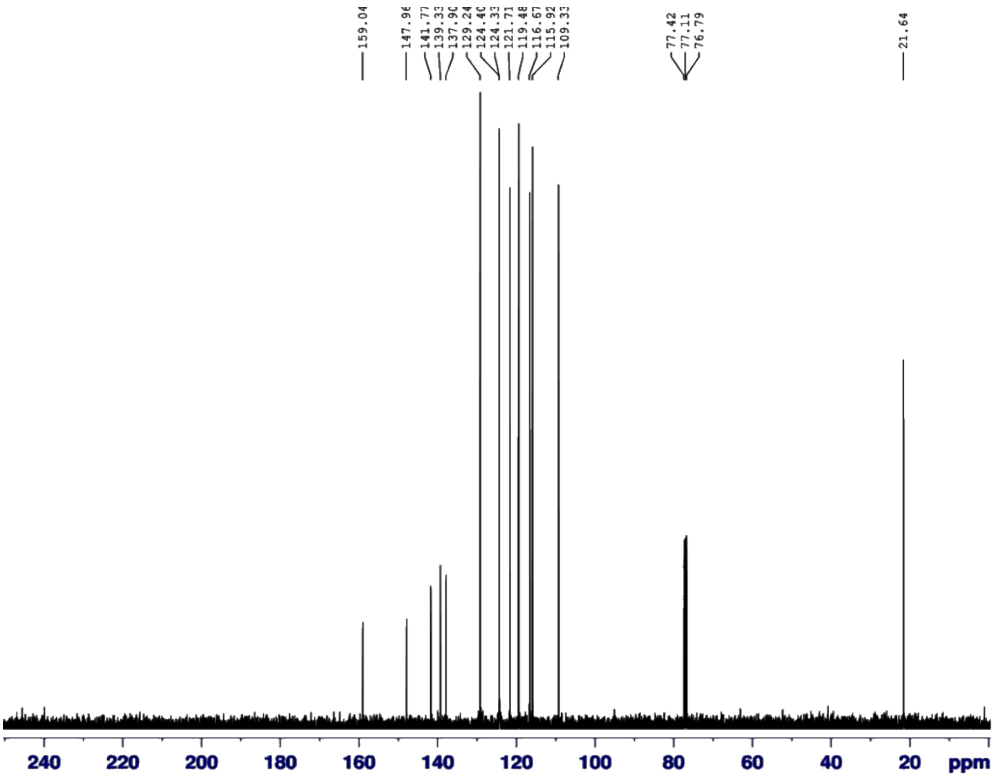



**Figure S63.** $^{13}$C-NMR spectrum of *N-m-tolylbenzo[d]oxazol-2-amine* in $CDCl_3$

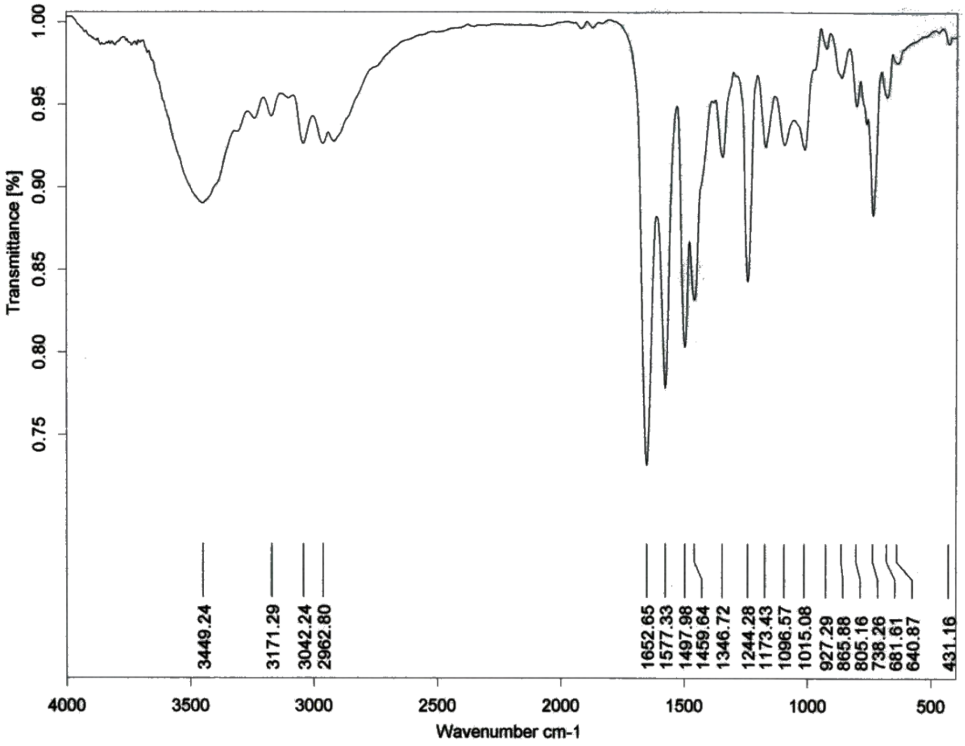



**Figure S64.** IR (KBr discs) spectrum of *N-m-tolylbenzo[d]oxazol-2-amine*

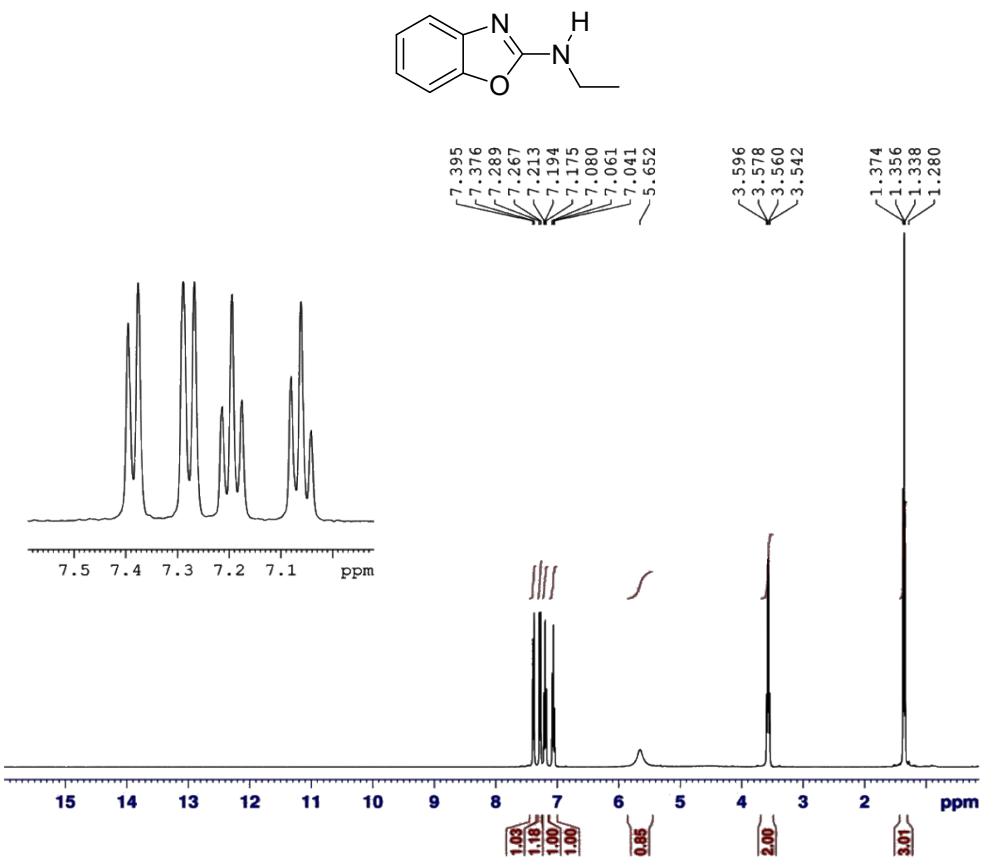



**Figure S65.** $^{1}$H-NMR spectrum of *N-ethylbenzo[d]oxazol-2-amine* in $CDCl_3$

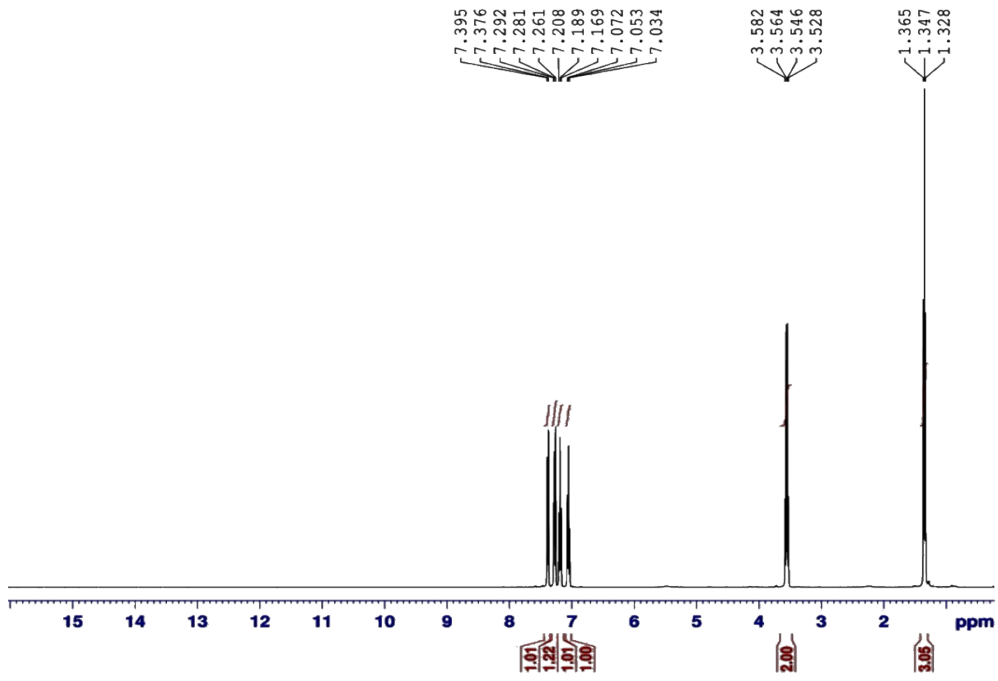



**Figure S66.** $^{1}$H-NMR spectrum of *N-ethylbenzo[d]oxazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

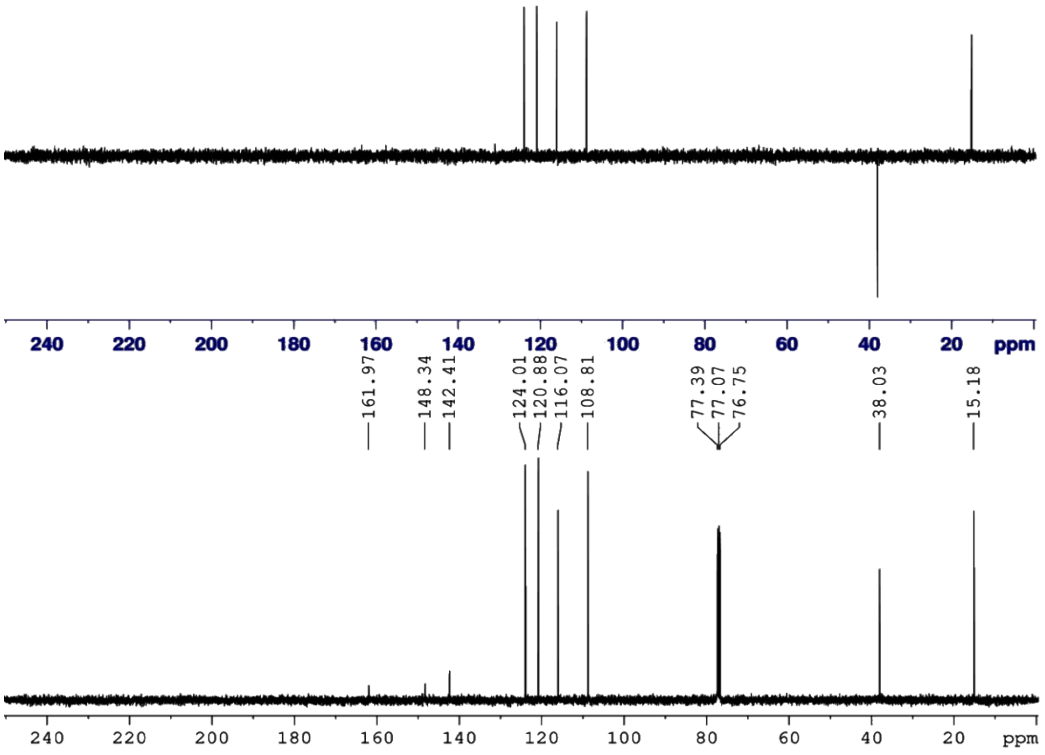



**Figure S67.** $^{13}$C-NMR and Dept 135 spectra of *N-ethylbenzo[d]oxazol-2-amine* in $CDCl_3$

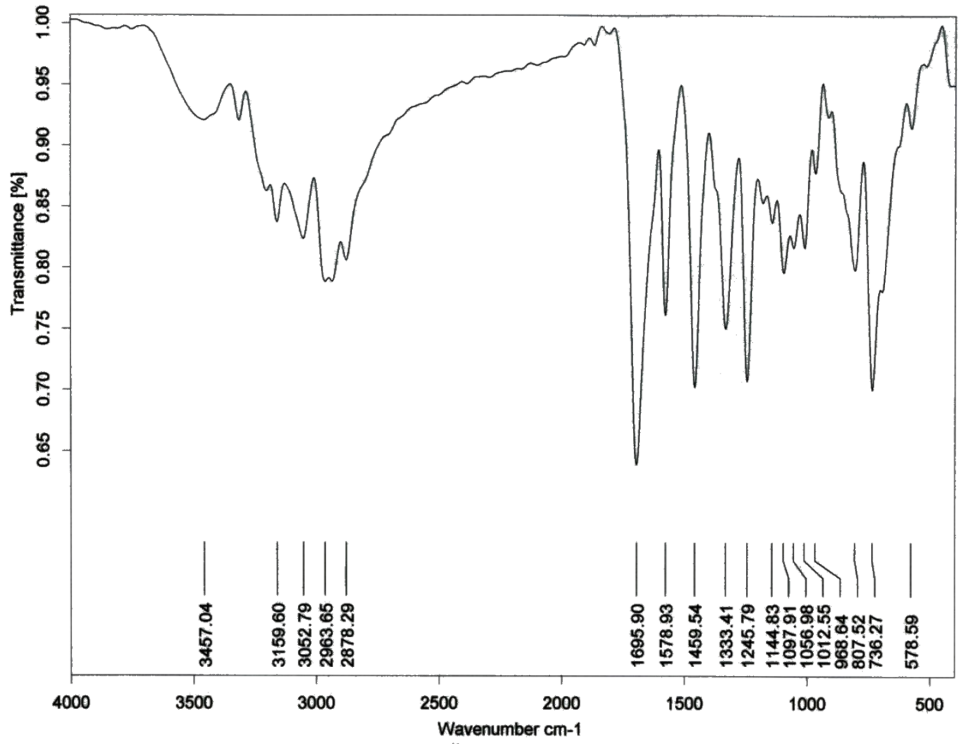



**Figure S68.** IR (KBr discs) spectrum of *N-ethylbenzo[d]oxazol-2-amine*

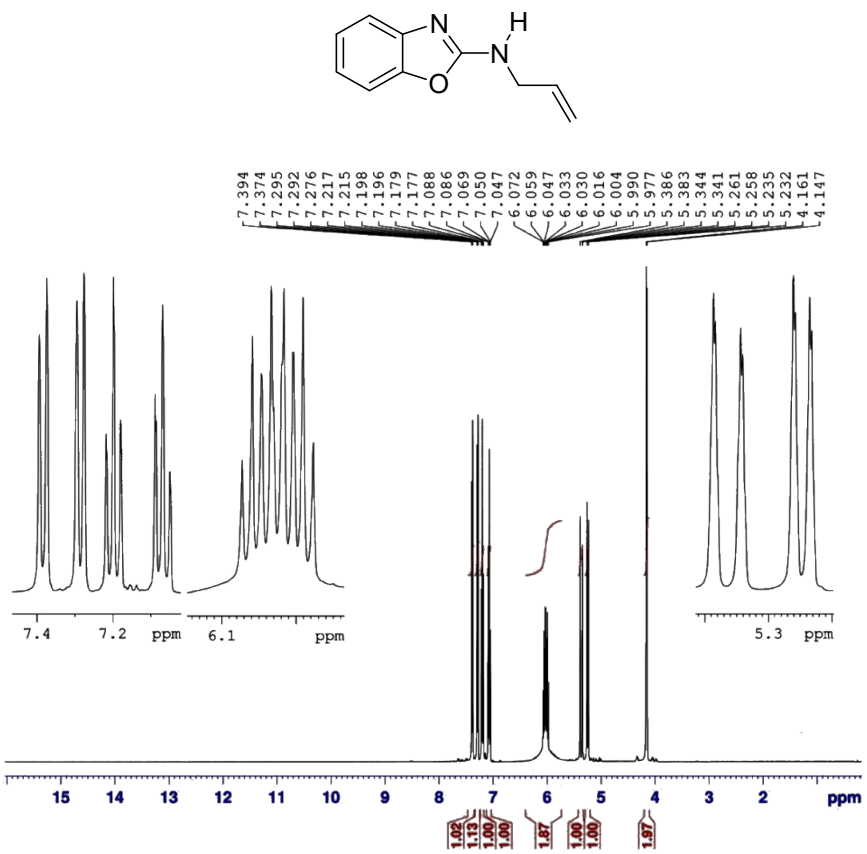


**Figure S69.** $^{1}$H-NMR spectrum of *N-allylbenzo[d]oxazol-2-amine* in $CDCl_3$

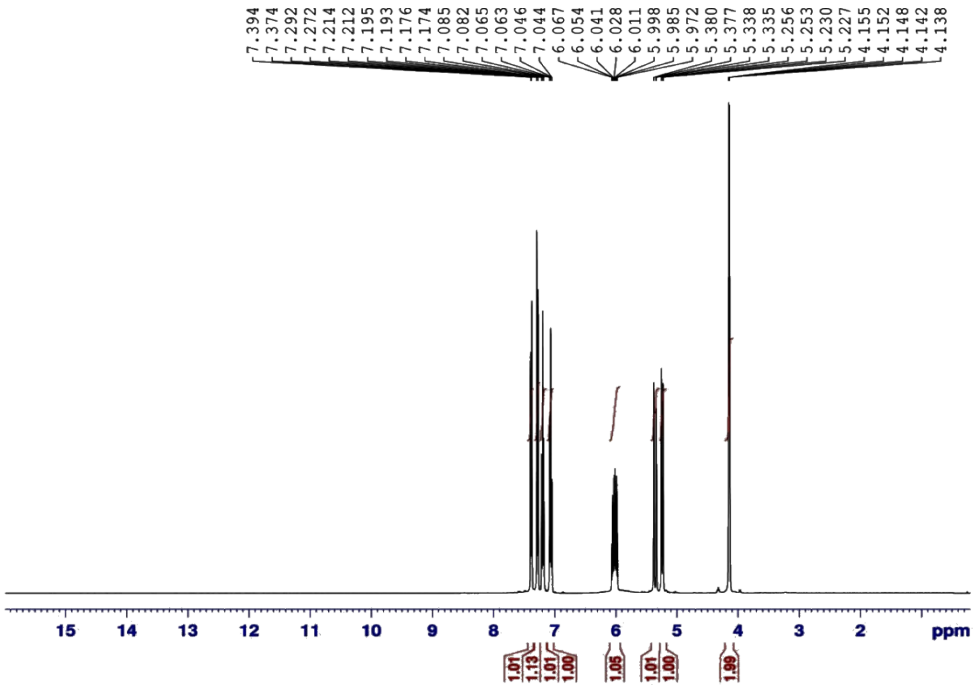


**Figure S70.** $^{1}$H-NMR spectrum of *N-allylbenzo[d]oxazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

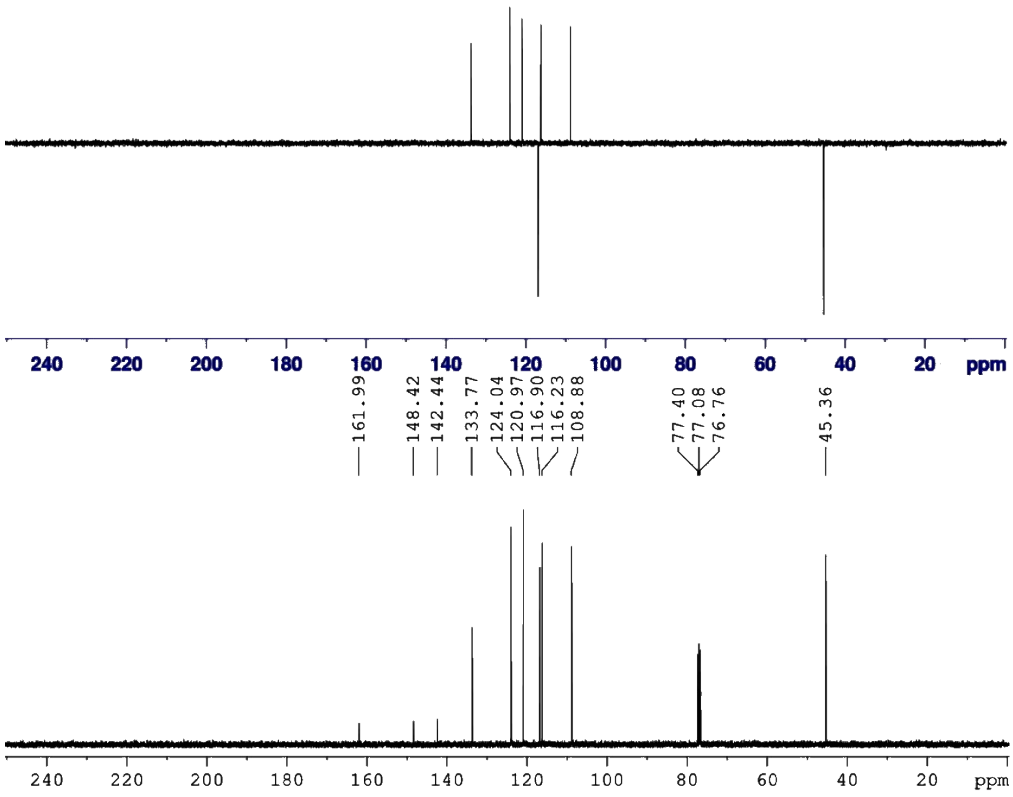



**Figure S71.** $^{13}$C-NMR and Dept 135 spectra of *N-allylbenzo[d]oxazol-2-amine* in $CDCl_3$

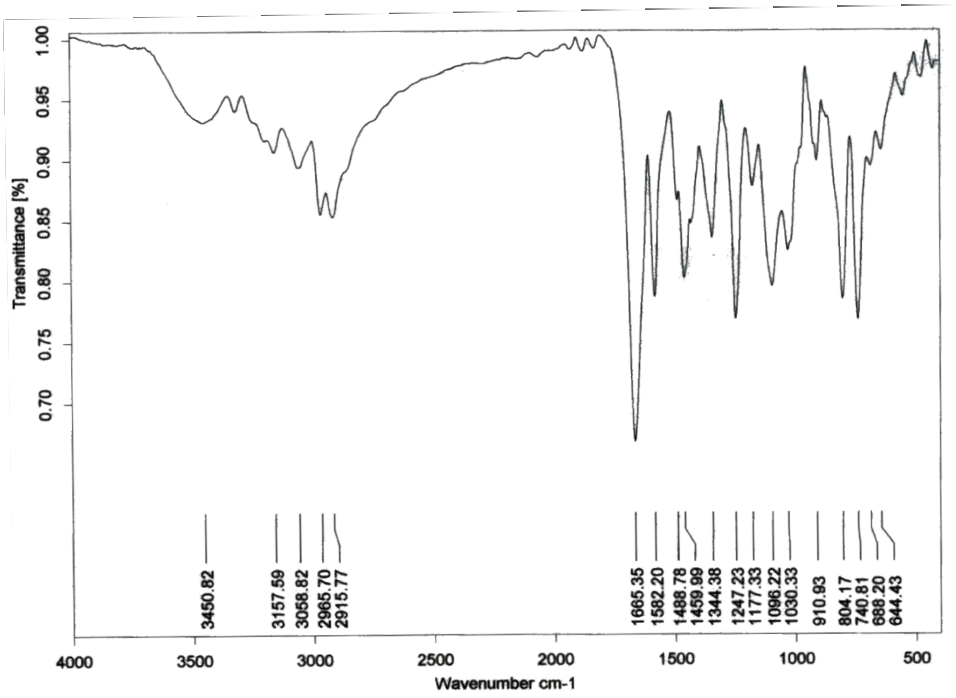



**Figure S72.** IR (KBr discs) spectrum of *N-allylbenzo[d]oxazol-2-amine*

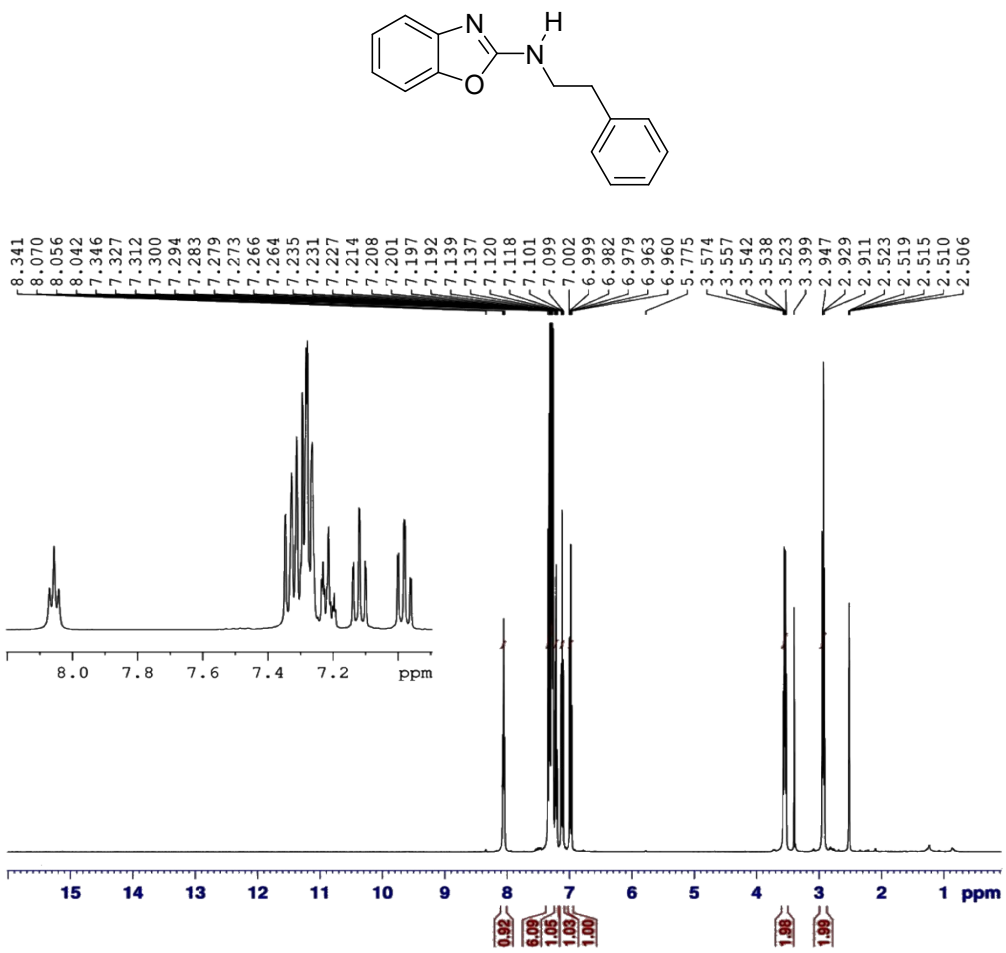


**Figure S73.** $^{1}$H-NMR spectrum of *N-phenethylbenzo[d]oxazol-2-amine* in $CDCl_3$

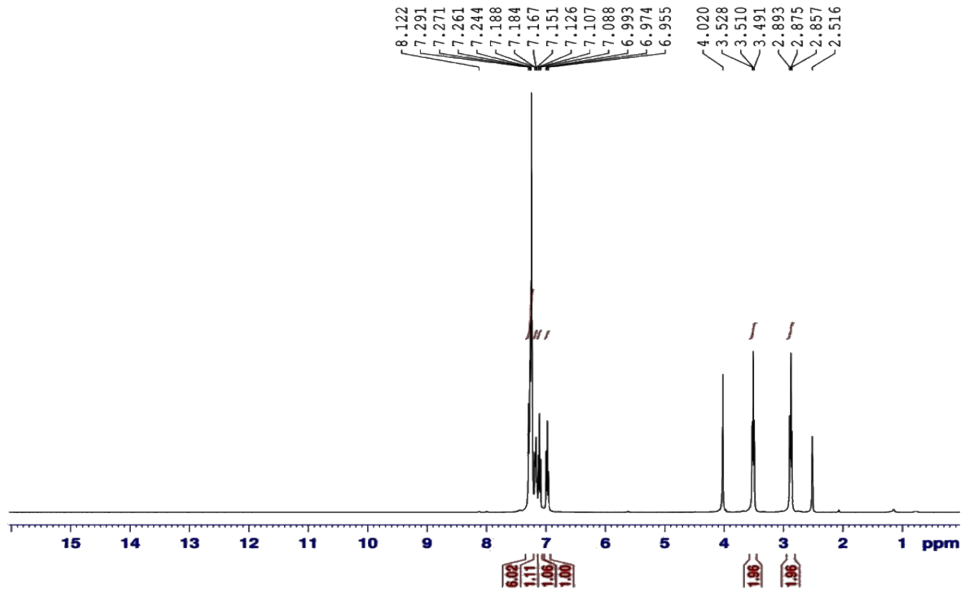


**Figure S74.** $^{1}$H-NMR spectrum of *N-phenethylbenzo[d]oxazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

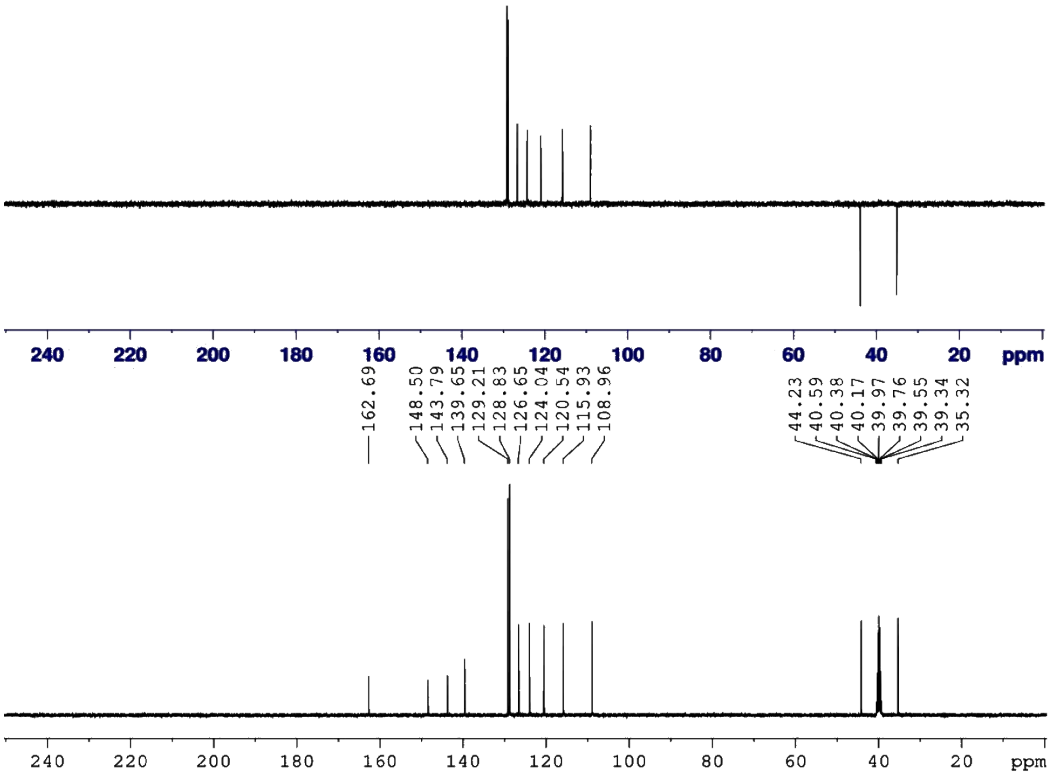



**Figure S75.** $^{13}$C-NMR and Dept 135 spectra of *N-phenethylbenzo[d]oxazol-2-amine* in $CDCl_3$

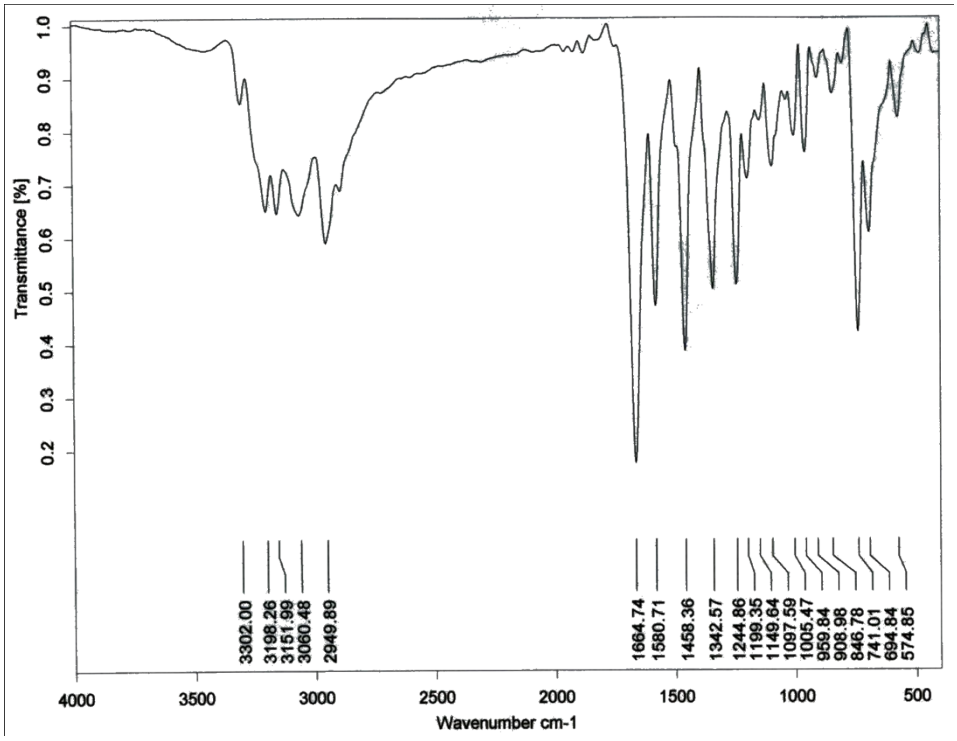



**Figure S76.** IR (KBr discs) spectrum of *N-phenethylbenzo[d]oxazol-2-amine*

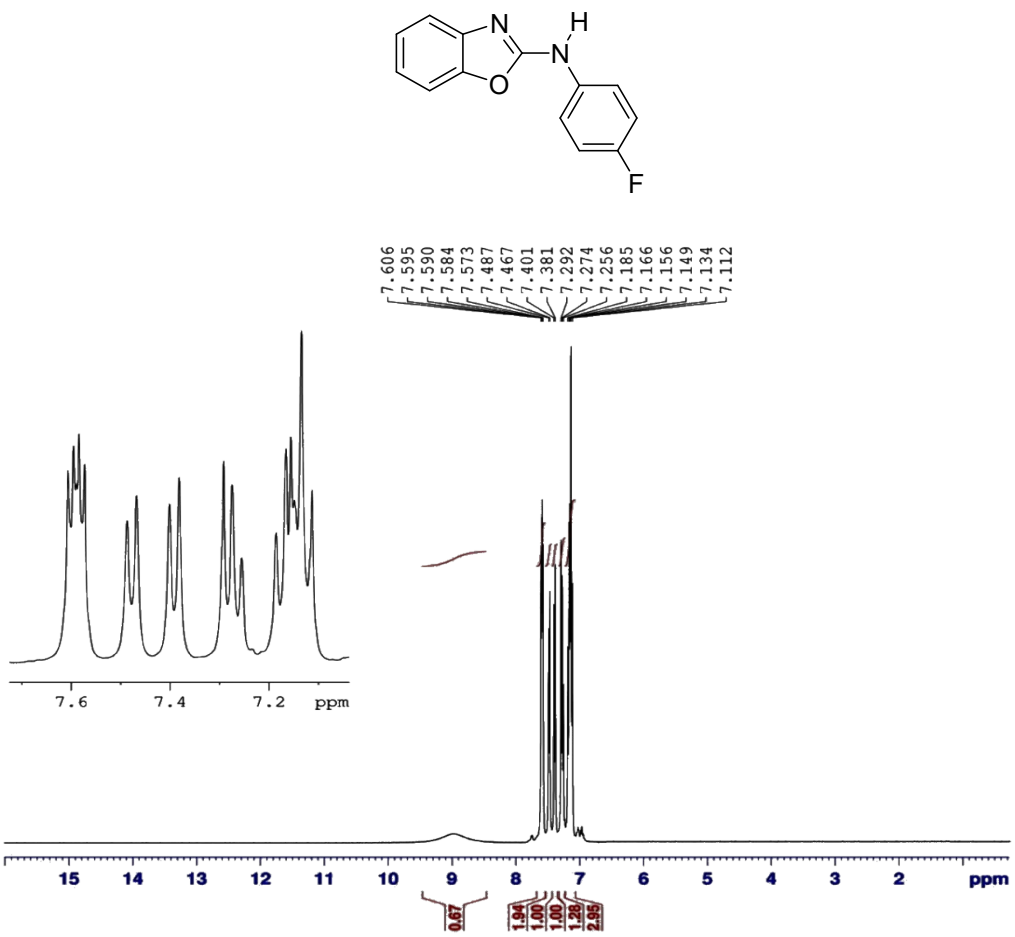



**Figure S77.** $^{1}$H-NMR spectrum of *N-(4-fluorophenyl)benzo[d]oxazol-2-amine* in $CDCl_3$

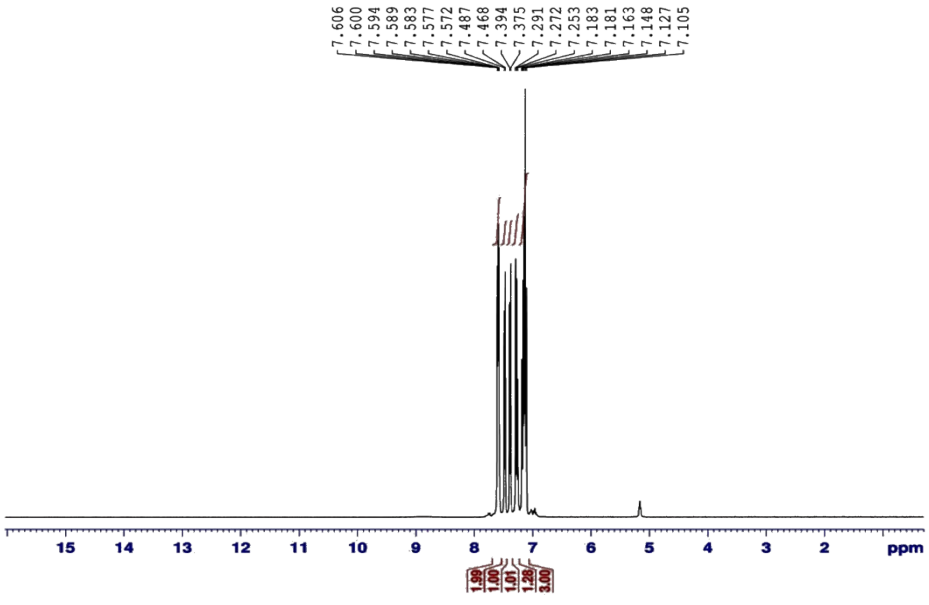



**Figure S78.** $^{1}$H-NMR spectrum of *N-(4-fluorophenyl)benzo[d]oxazol-2-amine* in $CDCl_3$ ($D_2O$ as exchanged solvent is used)

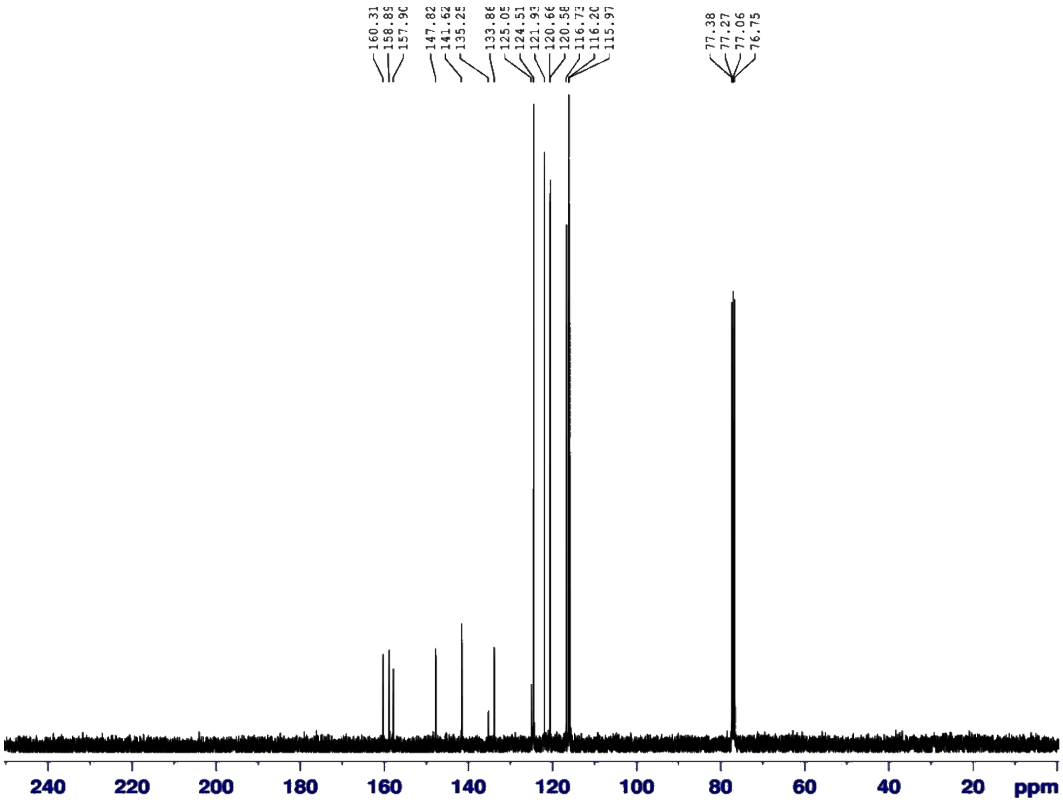



**Figure S79.** $^{13}$C-NMR spectrum of *N-(4-fluorophenyl)benzo[d]oxazol-2-amine* in $CDCl_3$

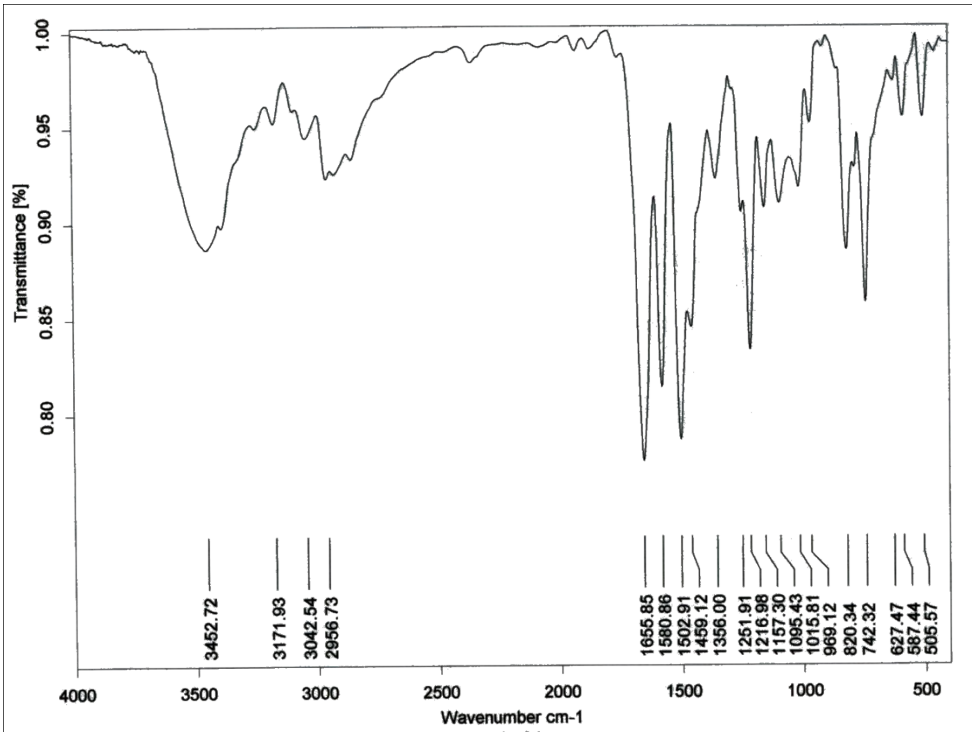



**Figure S80.** IR (KBr discs) spectrum of *N-(4-fluorophenyl)benzo[d]oxazol-2-amine*