Electronic Supplementary Material (ESI) for RSC Advances.

Ru/C: A Simple heterogeneous catalyst for the amination of azoles under ligand free conditions

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Contents

General Information:

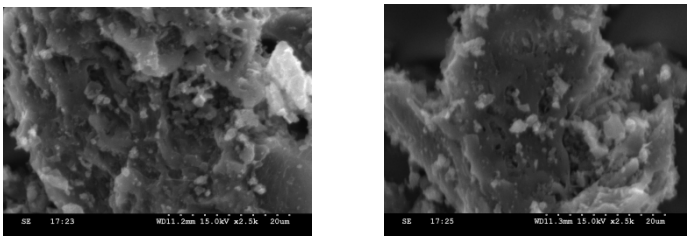
^{1}H NMR and ^{13}C NMR (Avance 300, Innova 400 MHz and Brucker Gemini 200 MHz) spectra were recorded in $CDCl_3$. Chemical shifts (δ) were reported in ppm, and spin-spin coupling constants (*J*) were in Hz. Melting points were determined on a Fischer-Johns melting point apparatus. IR and MS were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer and Finnegan MAT 1020 mass spectrometer operating at 70 eV.

General experimental procedure for amination of 2-halo azoles:

The reaction was carried in a 25 mL round bottom flask equipped with magnetic stir bar charged with 2-halo azoles(1 mmol), formamides / amines/cyanamides / N,N-DMF di-alkyl acetal(2 mL), LitBuo (1.0 mmol) and Ru/C (20 mg) catalyst. The resulting reaction mixture was stirred at 80 ^{o}C for 8h. The reaction progress was monitored by TLC. After the reaction, Ru/C was separated by centrifugation and the solvent was evaporated and the crude product was purified by column chromatography. The identity and purity of the product was confirmed by ^{1}H NMR, ^{13} C NMR and ESI-MS.

Recycling of the catalyst:

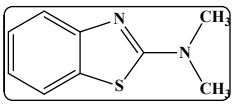
After the reaction was complete, the reaction mixture was allowed to cool, and Ru/C was removed by centrifugation. After each cycle, the catalyst was recovered by simple centrifugation, washing with ethyl acetate followed by acetone and then drying in vacuo. The recovered Ru/C was used directly in the next cycle. The native and used Ru/C were analyzed by SEM analysis. It was observed from the SEM studies that the used Ru/C was intact in size and shape even after four cycles compared to the native catalyst.



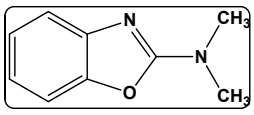
(a) (b)

Figure 2. SEM images of (a) native Ru/C (b) after four cycles Ru/C

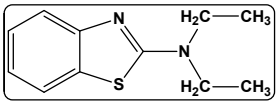
Spectroscopic Data:



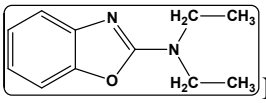
N,N-dimethylbenzo[d]thiazol-2-amine(3a)::^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60-7.55 (m, 2H), 7.32-7.25 (m, 1H), 7.07-7.02 (m, 1H), 3.19 (s, 6H); ^{13}C NMR (75 MHz,$CDCl_3$):168.7, 153.2, 131.1, 130.0, 127.9, 125.9, 120.7, 118.7, 40.1. ESI- MS: *m/z* 179 [M+1].



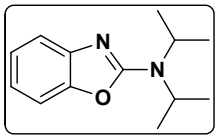
N,N-dimethylbenzo[d]oxazol-2-amine(3b):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35(d, *J* =7.7Hz, 1H), 7.23 (d, *J* =7.9Hz, 1H), 7.15 - 7.12 (m, 1H), 7.0-6.97 (m, 1H), 3.18 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.0, 148.9, 143.6, 123.8, 120.2, 115.9, 108.5, 37.6; ESI-MS: *m/z* 163 [M+1].



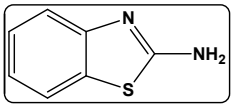
N,N-diethylbenzo[d]thiazol-2-amine(3c):^{1}H NMR (300 MHz, $CDCl_3$): δ7.53 (t, *J* = 8.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.01 – 6.96 (m, 1H), 3.48 – 3.42 (m, 4H), 1.19 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ166.8, 152.9,130.2, 125.3, 120.2, 120.1, 118.1, 44.9, 12.4; ESI- MS: *m/z* 207 [M+1].



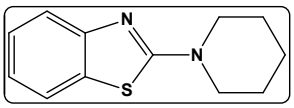
N,N-diethylbenzo[d]oxazol-2-amine(3d)[1]:^{1}H NMR (300 MHz, $CDCl_3$): δ7.35 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 1H), 3.55 (q, *J* = 7.1 Hz, 5H), 1.25 (t, *J* = 7.1 Hz, 8H); ESI- MS: *m/z* 191[M+1].



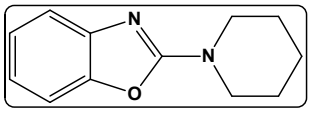
N,N-diisopropylbenzo[d]oxazol-2-amine(3f):^{1}H NMR (300 MHz, $CDCl_3$): δ7.35 (d, J = 7.7 Hz, 1H), 7.25 (d, J = 7.5 Hz, 1H), 7.13 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 4.28 - 4.15 (m, 2H), 1.38 (d, J = 6.9 Hz, 12H);^{13}C NMR (75 MHz, $CDCl_3$): δ162.2, 148.4, 142.8, 123.5, 119.5, 115.4, 108.2, 47.5, 20.7; ESI- MS: *m/z* 219[M+1].



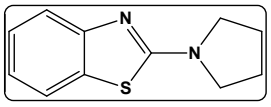
benzo[d]thiazol-2-amine(3g): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.93 Hz, 1H), 7.496 (d, *J* = 7.93 Hz, 1H), 7.32 - 7.26 (m, 1H), 7.14 -7.08 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ166.6, 151.4, 130.9, 125.9, 122.1, 120.8, 118.6; ESI- MS: *m/z* 151[M+1].



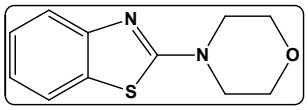
2-(piperidin-1-yl)benzo[d]thiazole(3i): ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 19.3, 7.9 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 3.59-3.58 (m, 4H), 1.68 (S, 6H); ^{13}C NMR (75 MHz, $CDCl_3$):δ168.8, 152.8, 125.7, 120.9, 120.4, 118.6, 49.5, 24.1, 25.2;ESI- MS: *m/z* 219[M+1].



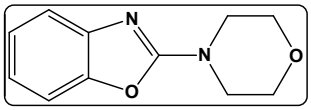
2-(piperidin-1-yl)benzo[d]oxazole(3j):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 15.8, 7.5 Hz, 2H 2H), 7.22 (t,*J* = 7.5 Hz, 1H) 7.03 - 6.96 (m, 1H), 3.59 - 3.51 (m, 4H), 1.69 (S, 6H);^{13}C NMR (75 MHz, $CDCl_3$): δ161.7, 148.2, 142.0, 123.9, 122.0, 120.4, 115.5, 109.8, 108.5, 46.5, 25.0, 23.7; ESI- MS: *m/z* 203[M+1].



2-**(pyrrolidin-1-yl)benzo[d]thiazole(3k)[2]:**^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 (dd, J = 8.3, 4.9 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.06 – 7.02 (m, 1H), 3.58 (t, J = 6.6 Hz, 2H), 2.09 – 2.05 (m, 2H).; ESI- MS: *m/z* 205[M+1].

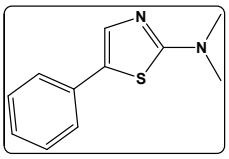


4-(benzo[d]thiazol-2-yl)morpholine(3m):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33 -7.28 (m, 1H), 7.21 - 7.18 (m, 1H), 7.14 - 7.08 (m, 1H), 7.0 - 6.94 (m, 1H) 3.77 - 3.71 (m, 4H) 3.65 - 3.62 (m, 4H) ;^{13}C NMR (75 MHz, $CDCl_3$): δ168.9, 152.3, 126.0, 121.6, 120.7, 119.2,66.1,48.4;ESI- MS: *m/z* 221[M+1].

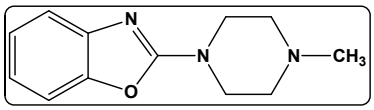


2-morpholinobenzo[d]oxazole(3n):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.32 - 7.28 (m, 1H), 7.12 - 7.07 (m, 1H),3.83 -

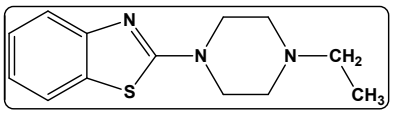
3.81 (m, 4H), 3.62 - 3.60(m, 4H);^{13}C NMR (75 MHz, $CDCl_3$): δ161.1, 148.1, 124.3 123.5, 121.2, 108.8, 116.0, 65.9, 45.7;ESI- MS: *m/z* 205[M+1].



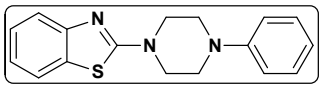
N,N-dimethyl-5-phenylthiazol-2-amine(3o):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 7.5 Hz, 2H), 7.23 - 7.08 (m, 3H), 6.52(s, 1H), 2.90(s, 6H);^{13}C NMR (75 MHz, $CDCl_3$): δ151.8, 135.0, 128.2, 127.2, 125.8, 100.7, 39.8;ESI- MS: *m/z* 205[M+1].



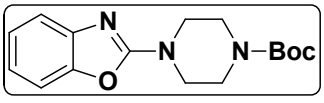
2-(4-methylpiperazin-1-yl)benzo[d]oxazole(5m)[3]:^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58 - 7.47 (m, 2H), 7.27 (t, J = 7.7 Hz, 1H), 7.05 (t, J = 7.7 Hz, 1H), 3.63 (t, J = 4.9 Hz, 4H), 2.49 (t, J = 4.9 Hz, 4H), 2.31 (s, 3H); ESI- MS: *m/z* 286[M+1].



2-(4-ethylpiperazin-1-yl)benzo[d]thiazole(5n):^{1}H NMR (300 MHz, $CDCl_3$): δ7.60 - 7.54 (m, 2H), 7.29 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H),3.66 (t, J = 5.0 Hz, 4H), 2.57 (t, J = 4.6 Hz, 4H), 2.50 - 2.45 (m, 2H), 1.12 (t, J = 7.1 Hz, 3H); ESI- MS: *m/z* 248 [M+1].



2-(4-phenylpiperazin-1-yl)benzo[d]thiazole(5p):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 - 7.29 (m, 1H), 7.27 - 7.18(m, 3H), 7.17 - 7.11(m, 1H), 7.01 - 6.83(m, 1H), 3.85 (t, J = 5.2 Hz, 4H), 3.28 (t, J = 5.2 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ161.8, 150.8, 148.6, 142.5, 129.2, 124.0, 120.9, 120.8, 116.9, 116.2, 108.7, 49.1, 45.5; ESI- MS: *m/z* 296[M+1].



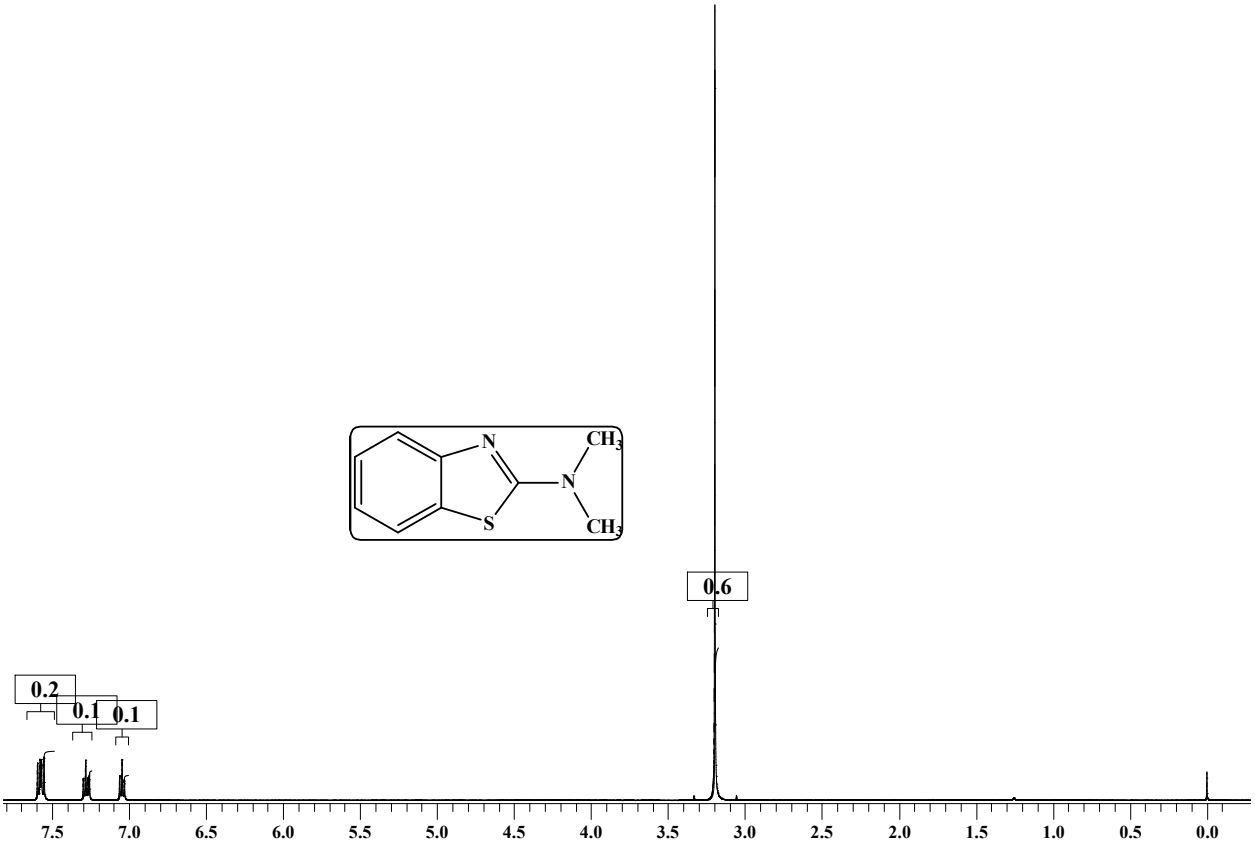
tert-butyl4-(benzo[d]oxazol-2-yl)piperazine-1-carboxylate(5v):^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 1H),7.17 (t, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 3.56 (d, *J* = 7.5 Hz, 8H), 1.49 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ161.7, 154.3, 148.5, 142.6, 123.9, 120.7, 116.2, 108.6, 80.1, 45.2, 28.1; ESI- MS: *m/z* 304 [M+1].

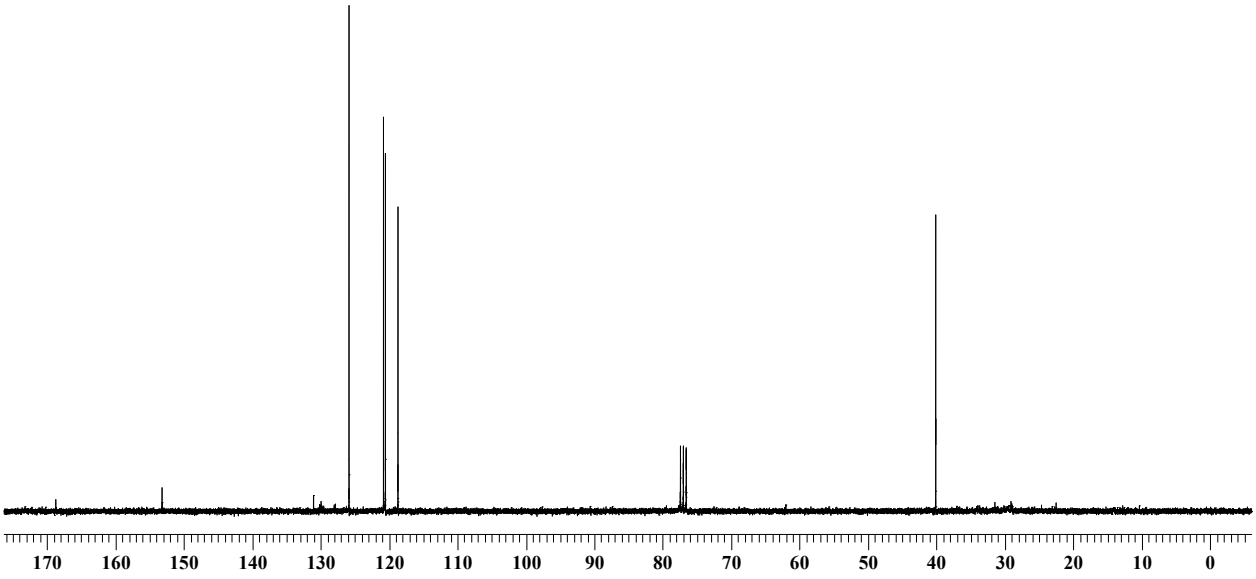
References:

1. J. Wang, J. T. Hou, J. Wen, J. Zhang, X.Q. Yu. *Chem.Commun.* 2011, **47**, 3652.
2. S. K. Verma, B. N. Acharya, M. P. Kaushik. *Org.Biomol.Chem.* 2011, **9**, 1324.
3. Y. S. Wagh, D. N. Sawant, B. M. Bhanage. *Tetrahedron Letters.* 2012, **53**, 3482.

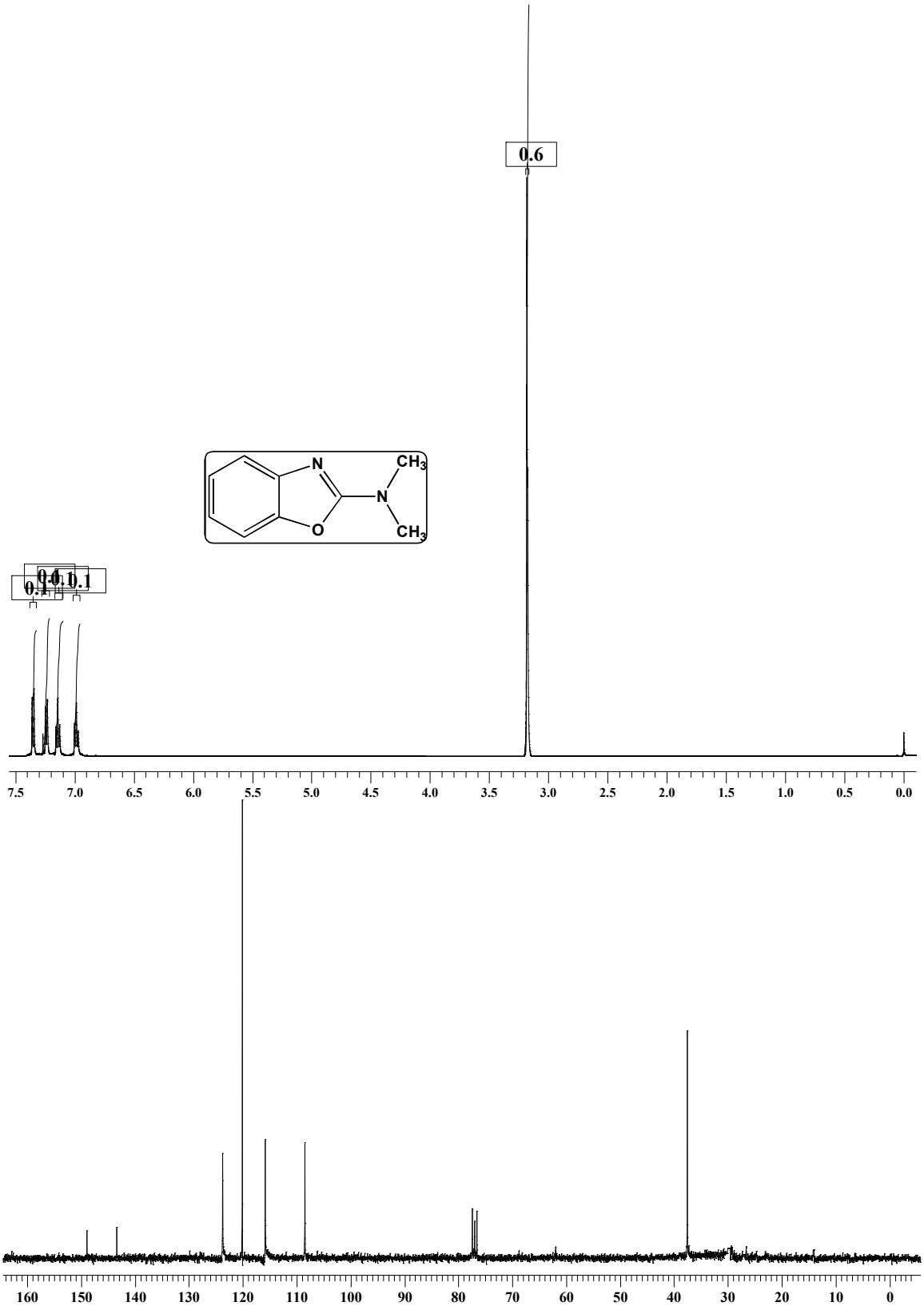
Copies of ^{1}H NMR and ^{13}C NMR of Compounds:

N,N-dimethylbenzo[d]thiazol-2-amine (3a):

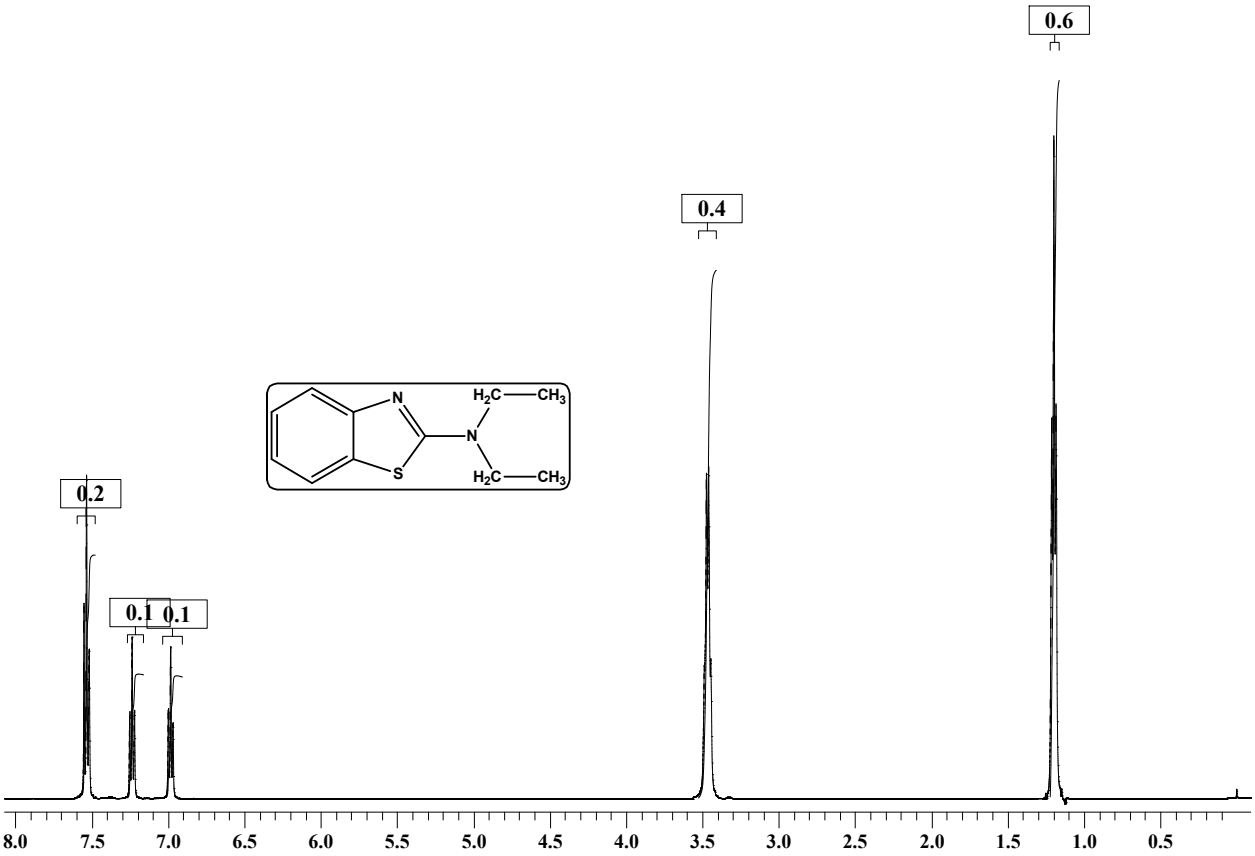


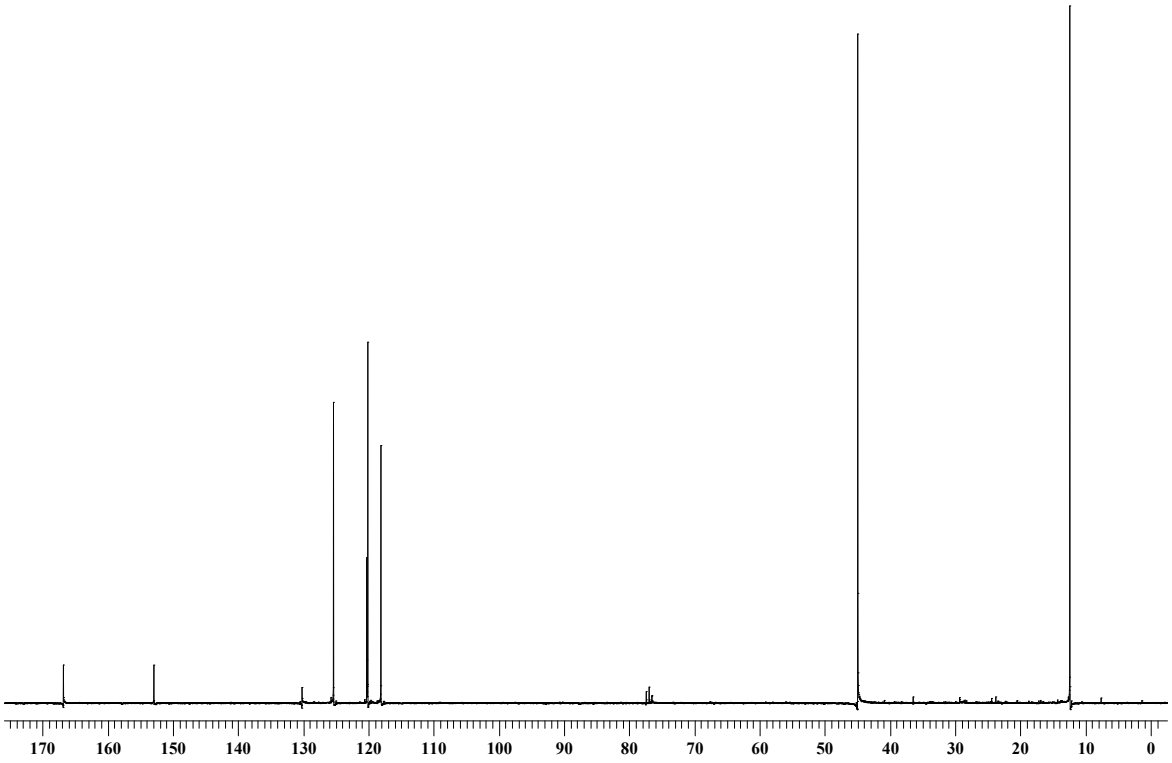


N,N-dimethylbenzo[d]oxazol-2-amine(3b):

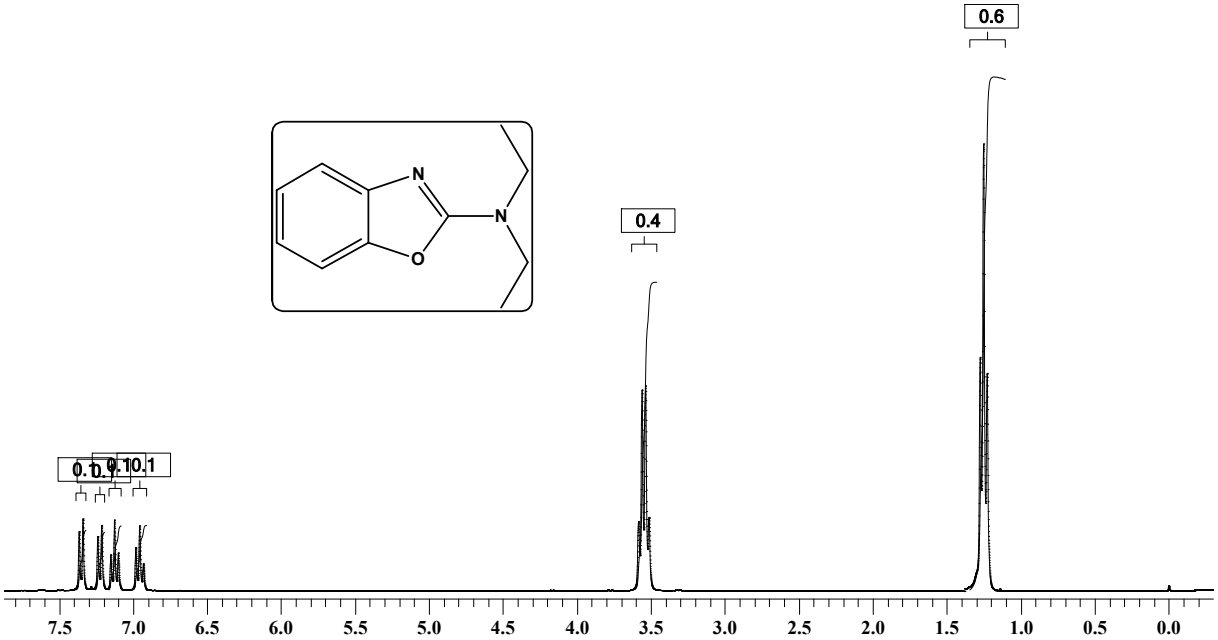


N,N-diethylbenzo[d]oxazol-2-amine(3c):

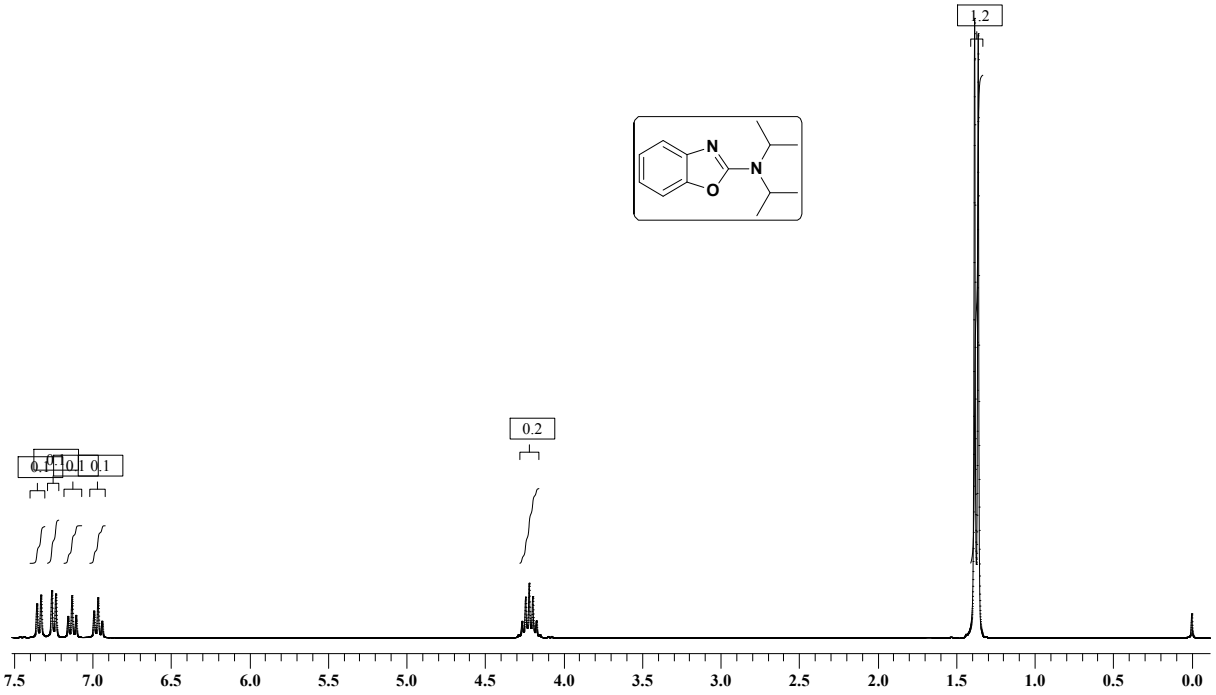


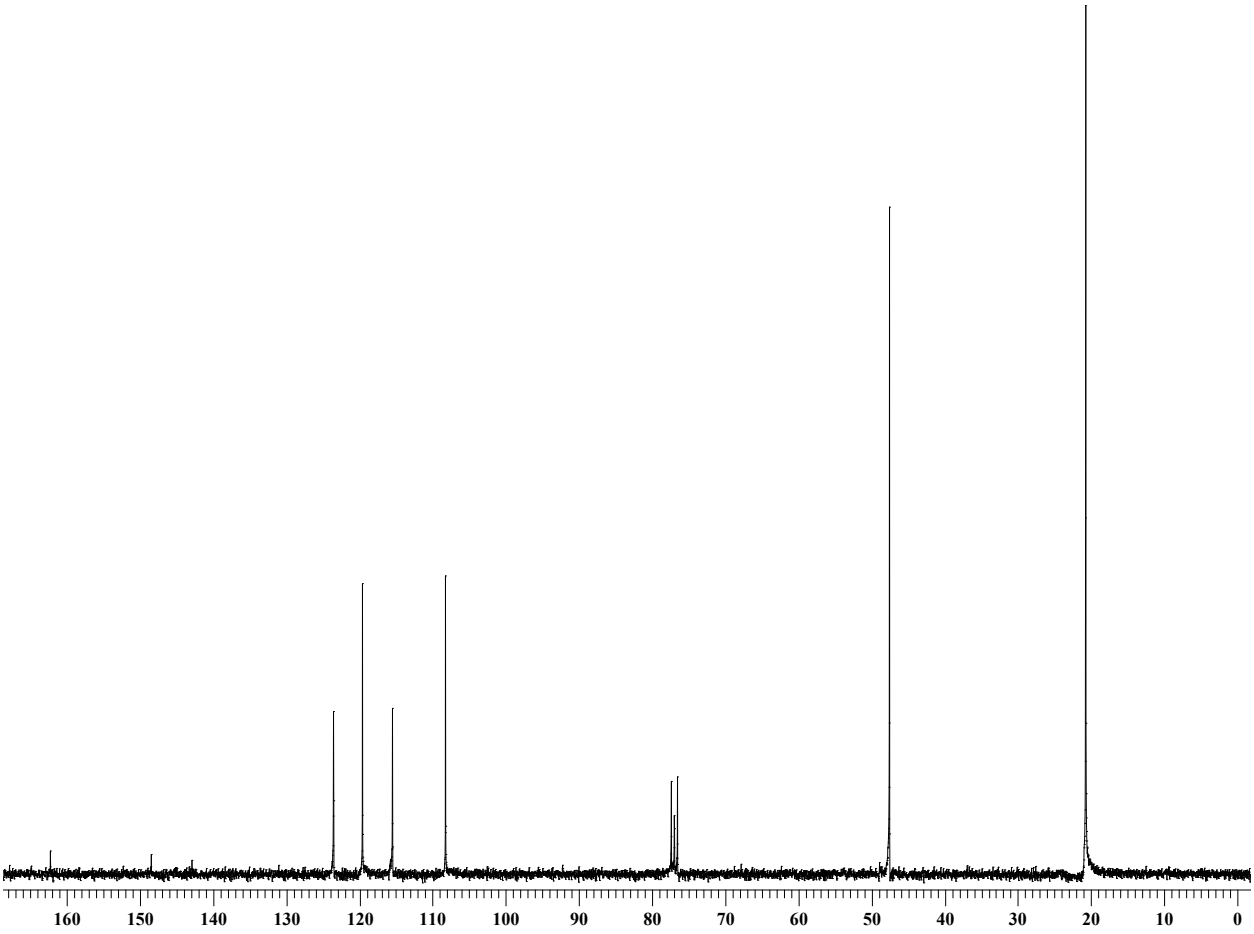


N,N-diethylbenzo[d]oxazol-2-amine(3d):

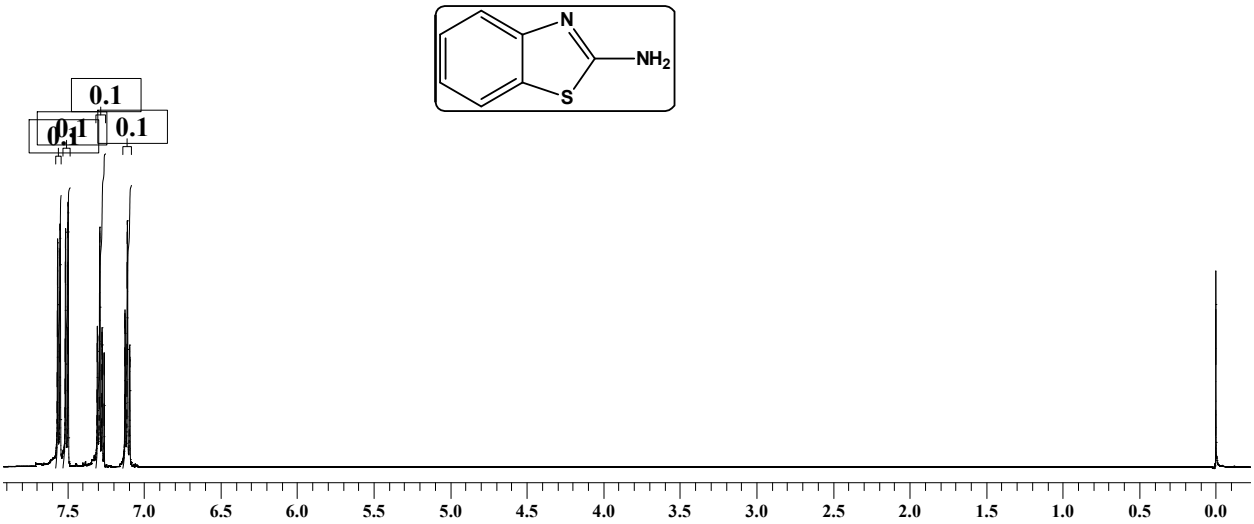


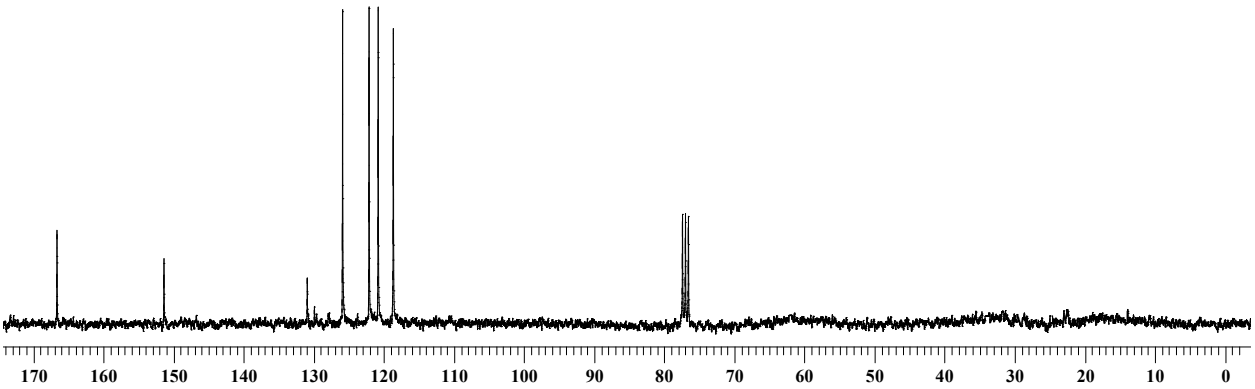
N,N-diisopropylbenzo[d]oxazol-2-amine(3f):



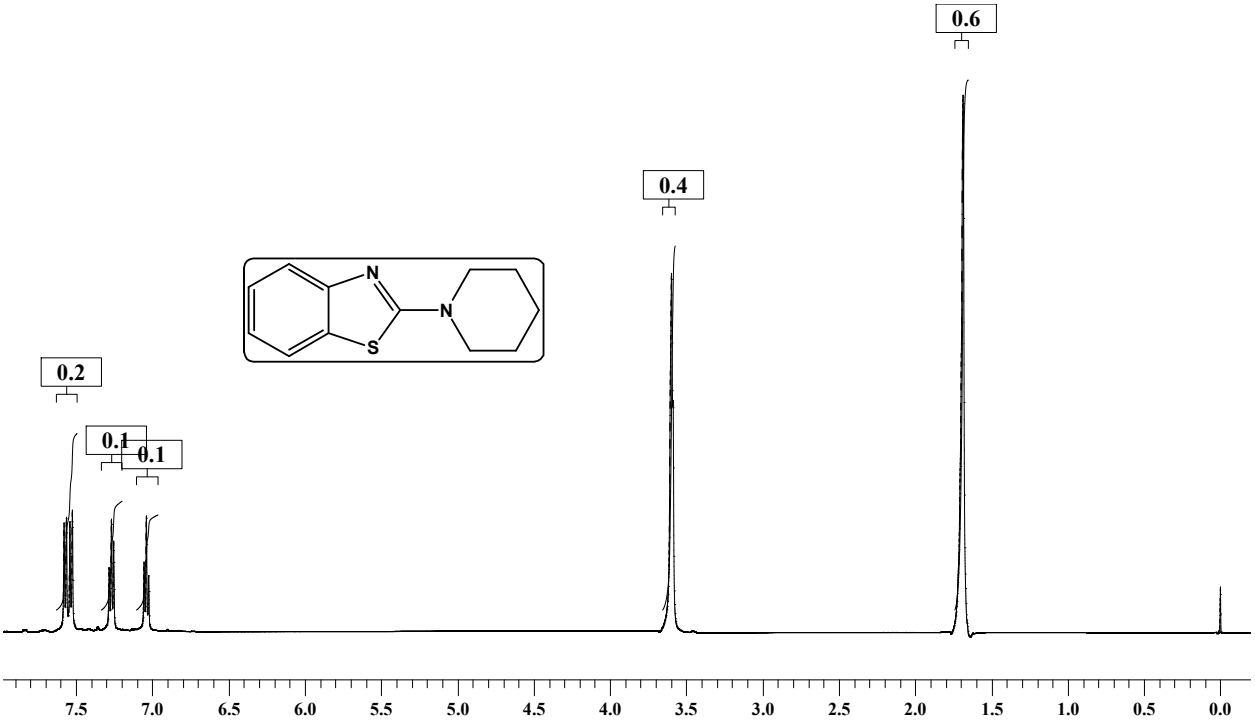


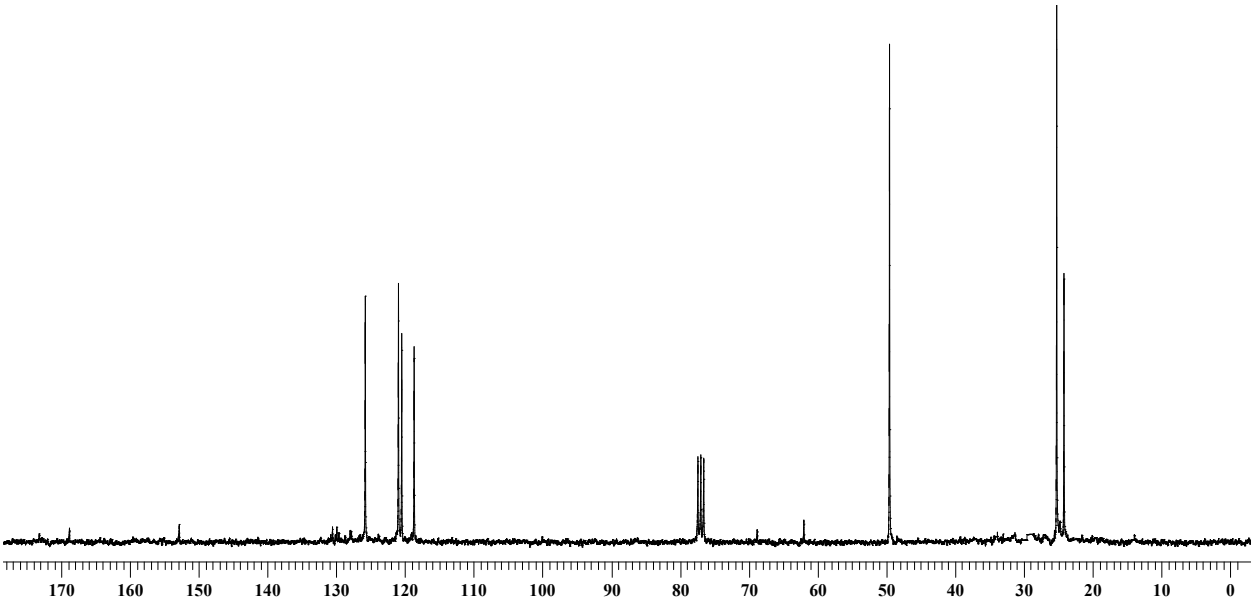
benzo[d]thiazol-2-amine(3g):



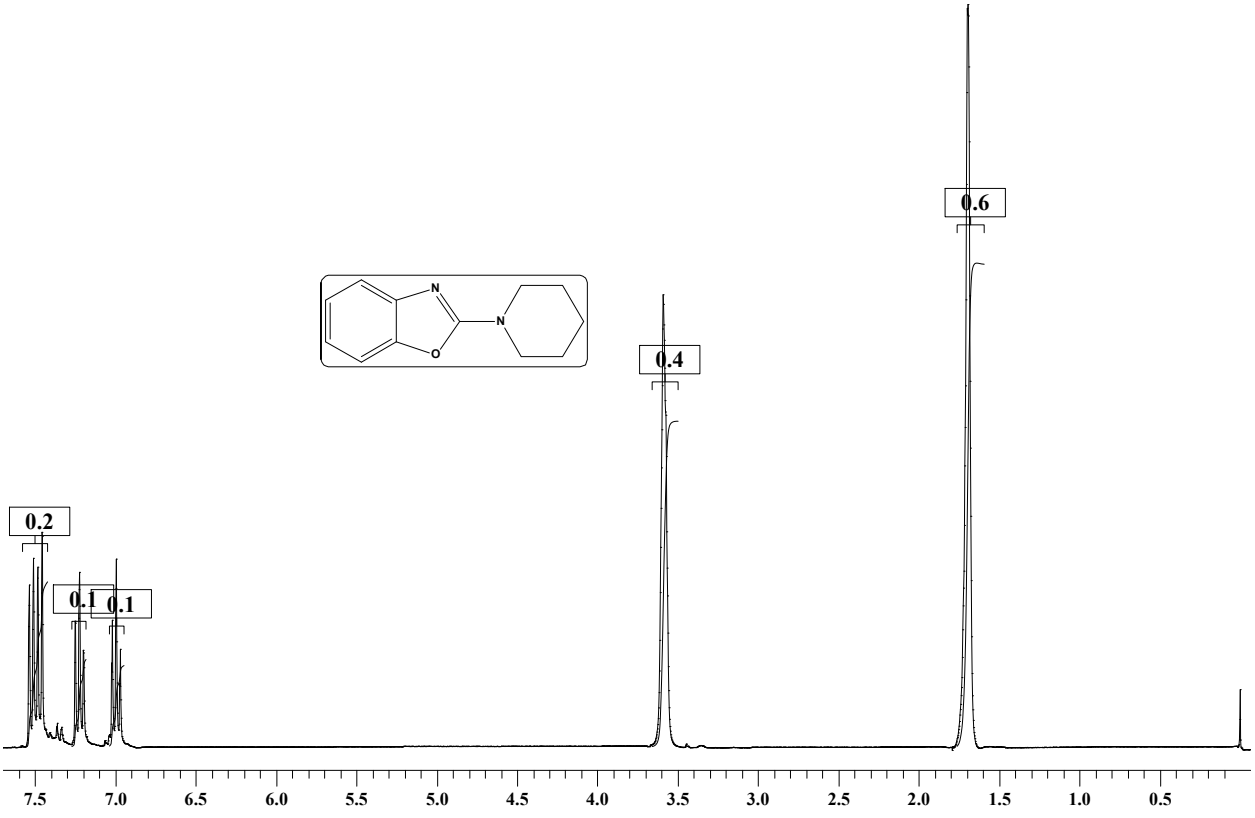


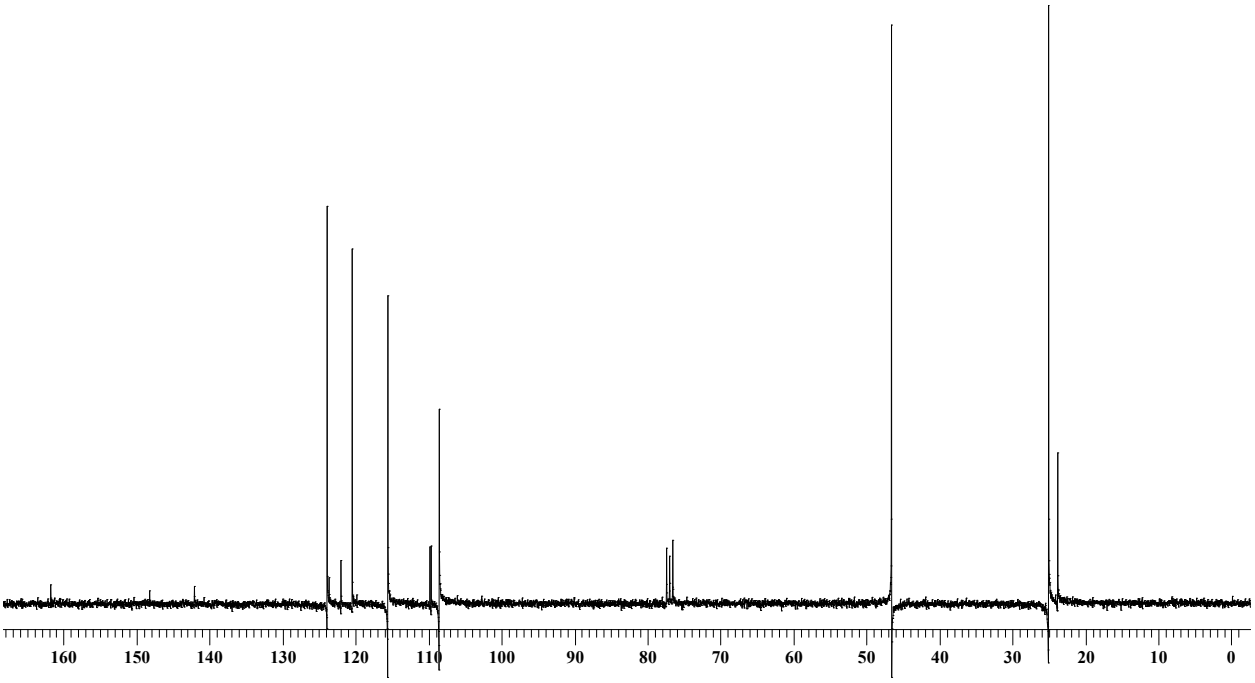
4-(benzo[d]thiazol-2-yl)morpholine(3i):



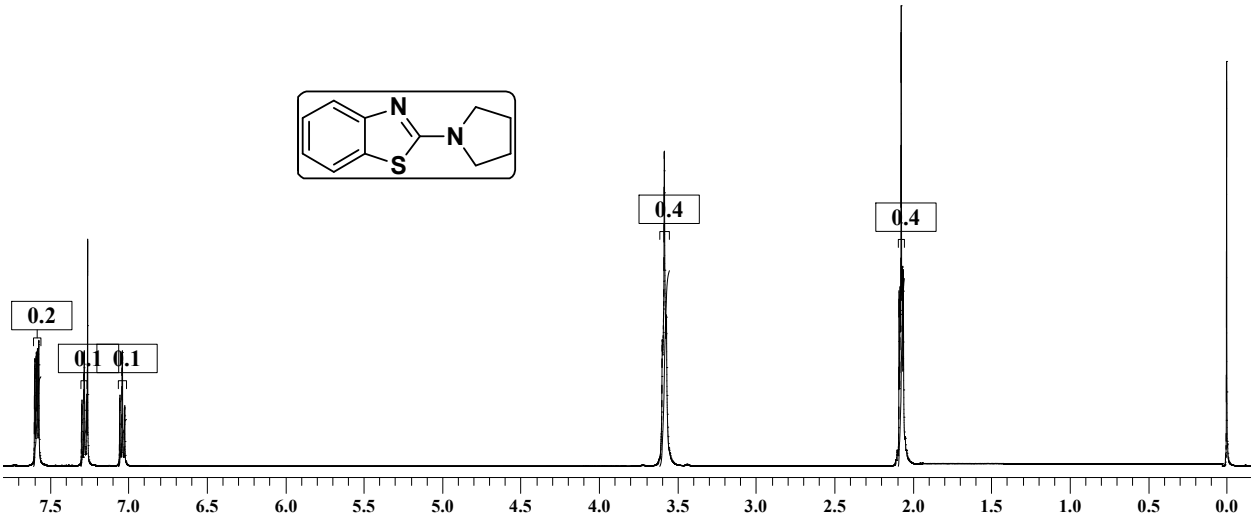


2-(piperidin-1-yl)benzo[d]oxazole(3j):

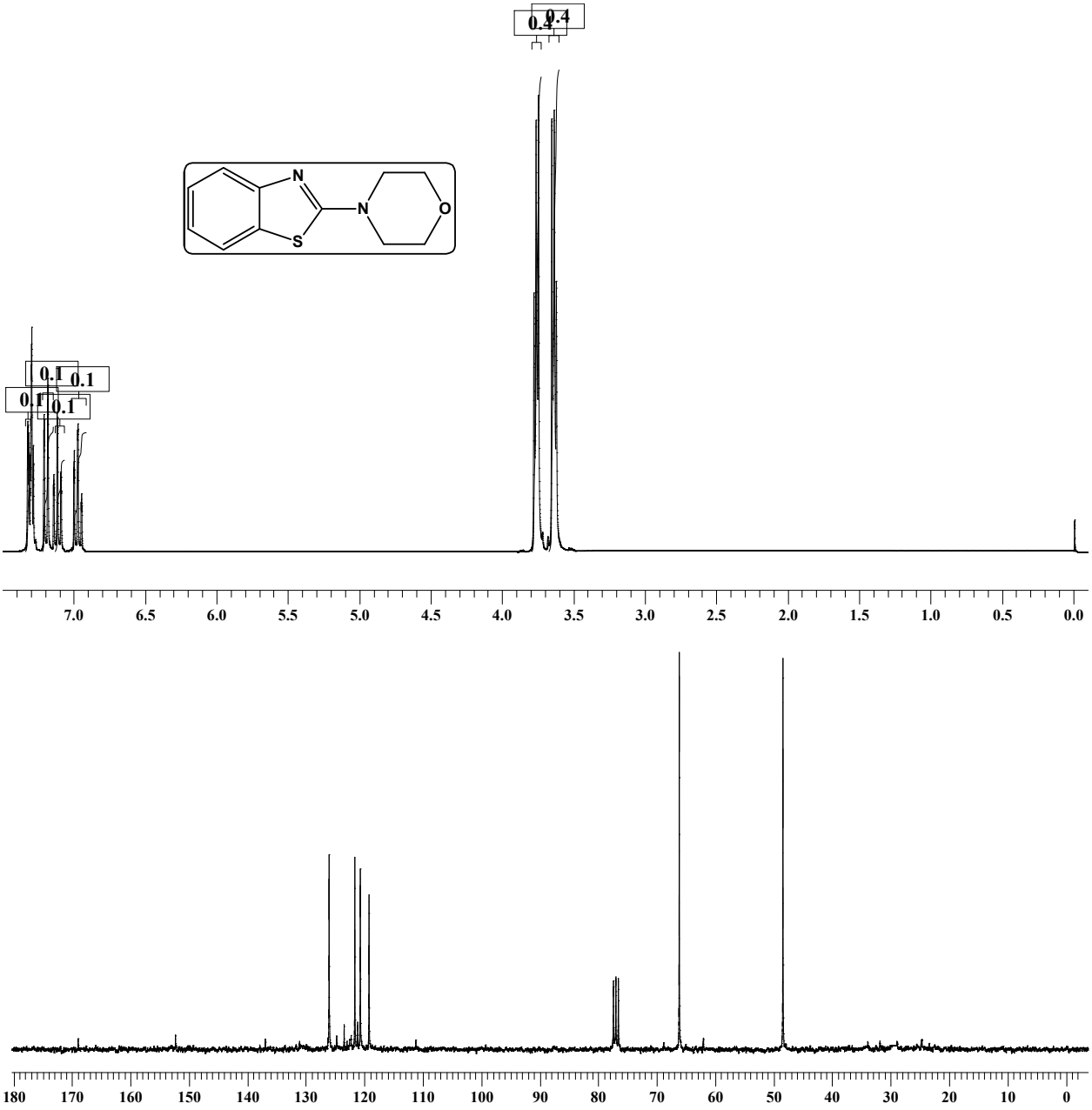




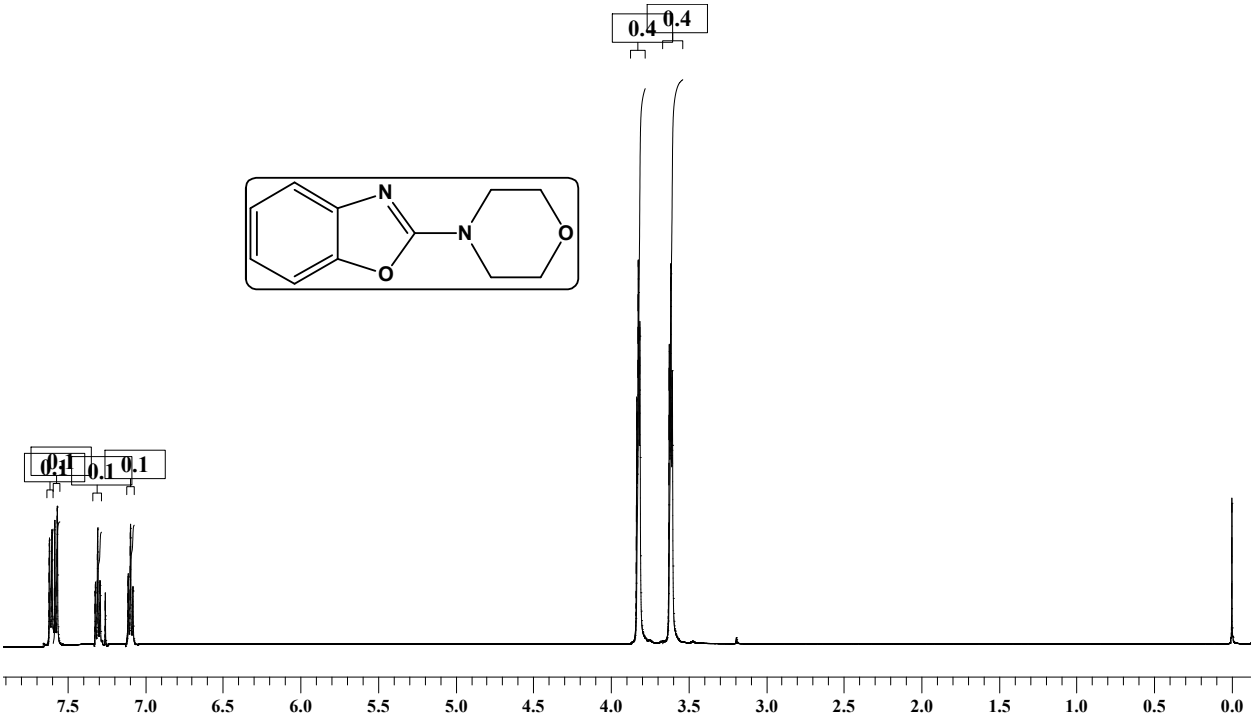
2-(pyrrolidin-1-yl)benzo[d]thiazole(3k):

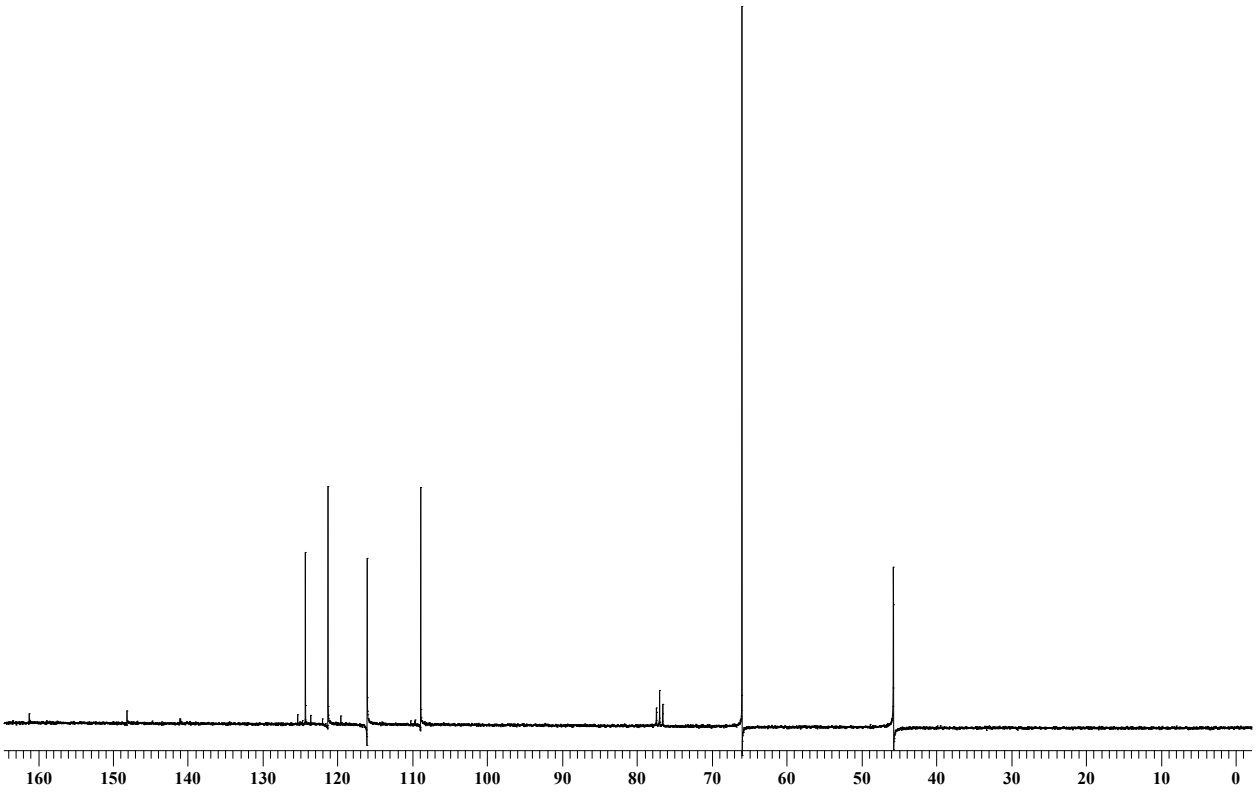


4-(benzo[d]thiazol-2-yl)morpholine(3m):

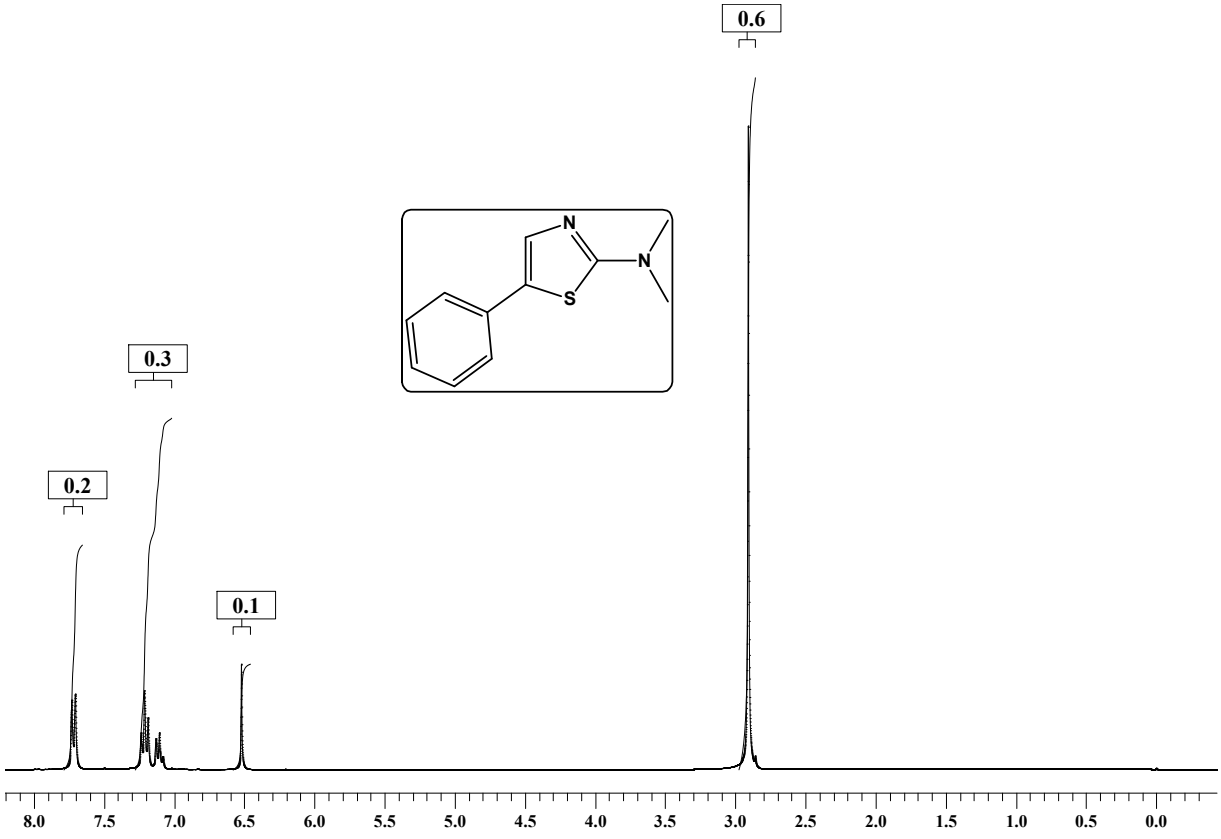


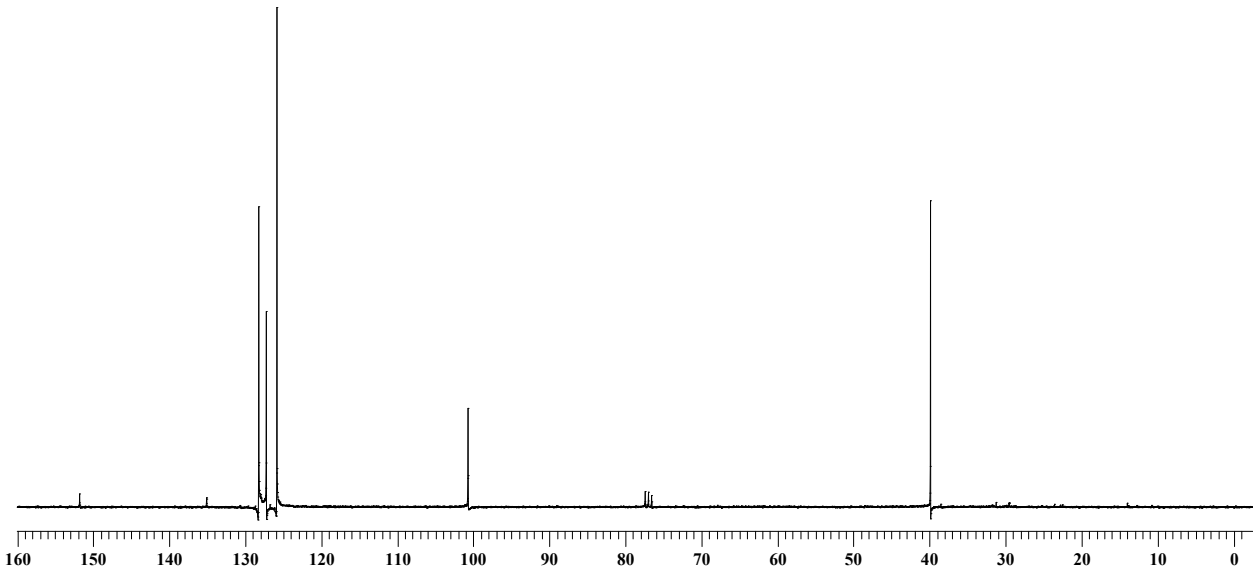
2-morpholinobenzo[d]oxazole(3n):



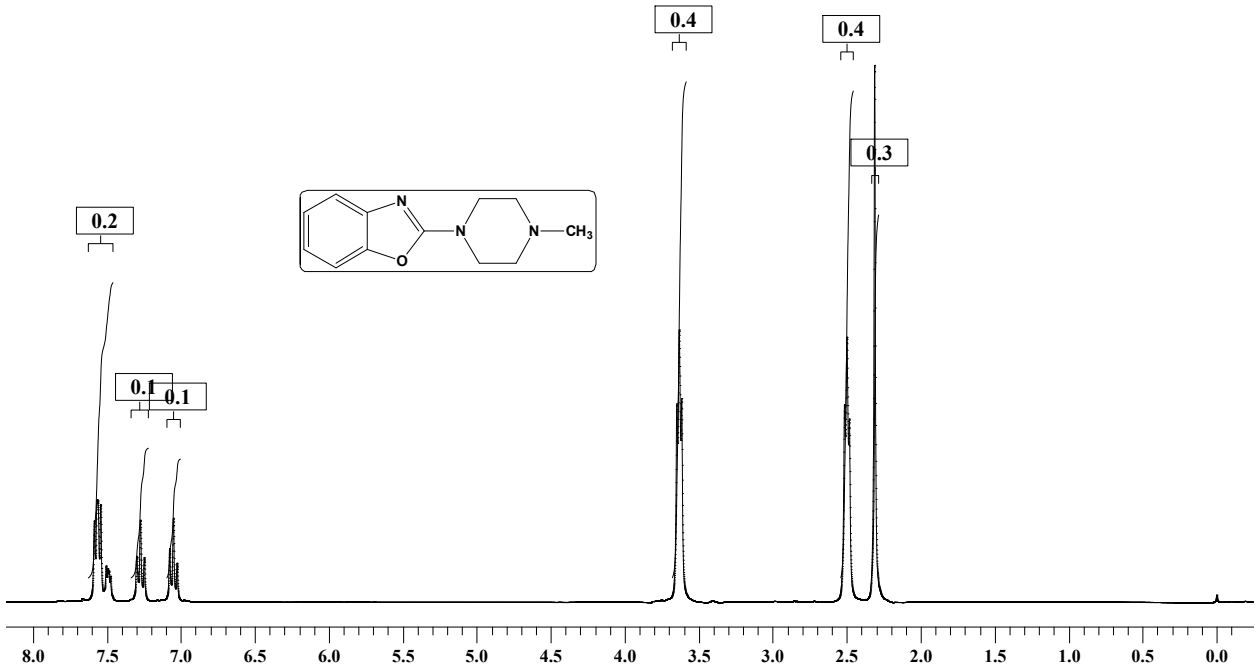


N,N-dimethyl-5-phenylthiazol-2-amine(3o):

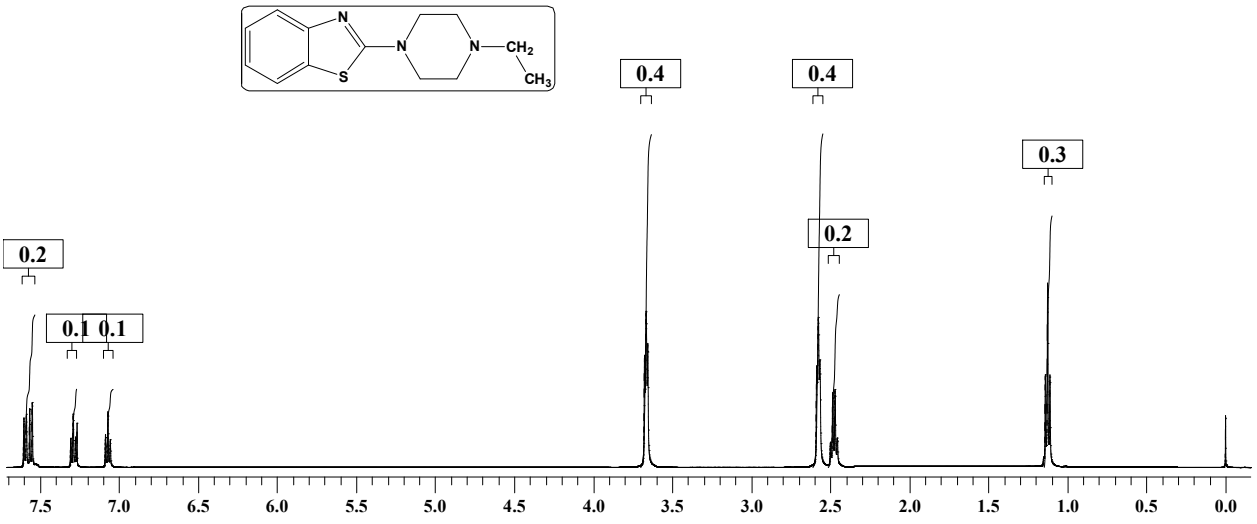




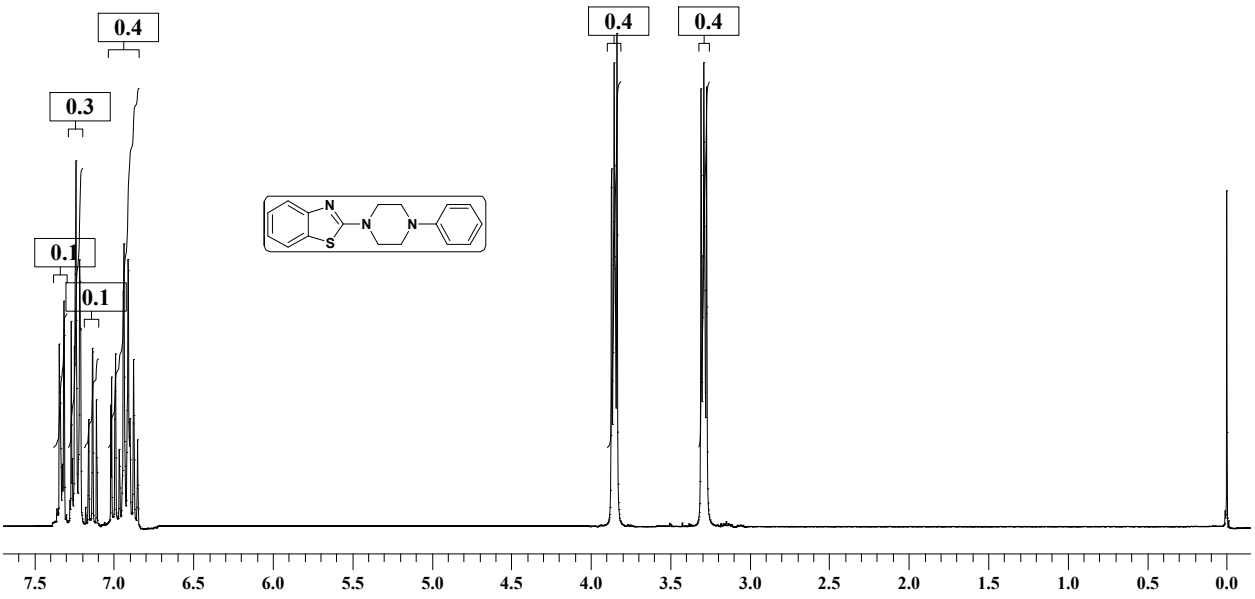
2-(4-methylpiperazin-1-yl)benzo[d]oxazole(5m):

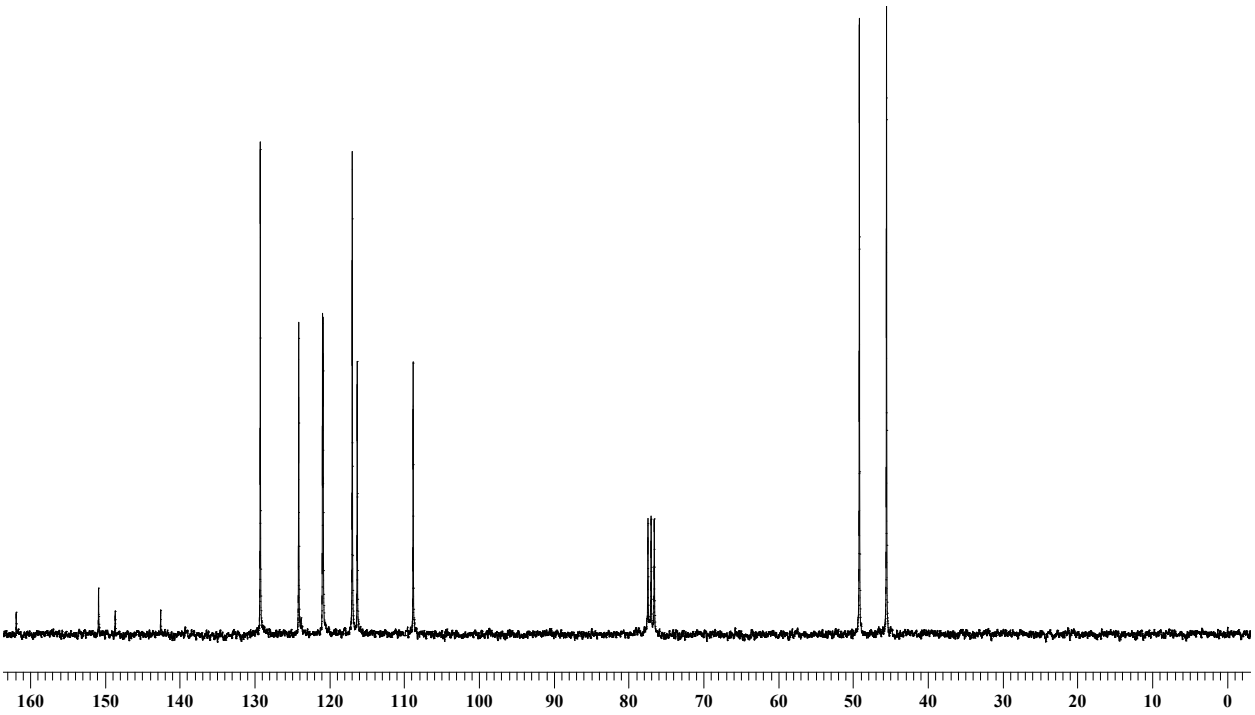


2-(4-ethylpiperazin-1-yl)benzo[d]thiazole(5n):



2-(4-phenylpiperazin-1-yl)benzo[d]thiazole(5p):





tert-butyl 4-(benzo[d]oxazol-2-yl)piperazine-1-carboxylate(5v):