Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting information

Reduced graphene oxide-zinc Sulfide (RGO-ZnS) nanocomposite: A new and appropriate photocatalyst for oxidative cyclization of benzylamines to benzazoles under visible-light irradiation

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Supporting Information

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EXPERIMENTAL

General

Chemical materials were purchased from Merck, Fluka, Aldrich, and Acros chemical companies. All solvents were distilled, dried, and purified by usual standard procedures. Progress of reactions was followed by TLC using silica gel polygrams SIL G/UV 254 plates. Products were purified by column chromatography on Merck Kiesel gel (70–230 mesh) or recrystallization from appropriate solvents and identified by their melting point, ^{1}H NMR, FT-IR, and CHNS analyzer subsequently.

Melting points were determined by Buchi Melting Point B-545 electrical melting point apparatus. NMR spectra were recorded on a Bruker Avance DPX 250 MHz spectrophotometer in $CDCl_3$ or DMSO-d_6 using tetramethylsilane (TMS) as an internal reference and chemical shifts were reported in ppm relative to TMS. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained using a Shimadzu FT-IR 8300 spectrophotometer. Elemental analysis was performed using Thermofinigan Flash EA-1112 CHN rapid elemental analyzer.

The catalyst was characterized by UV, ICP, XRD, TEM, SEM, and BET as well as the characterization methods above. ZnS loading and leaching tests were carried out with an ICP analyzer (Varian, vista-pro). XRD spectra were taken on a Bruker AXS D8-advance X-ray diffractometer Kα radiation (γ = 1.5418). SEM images were obtained on HITACHI S-4160 and HRTEM images were obtained on a Philips EM208 transmission electron microscope with an accelerating voltage of 100 kV. UV–vis diffuse reflectance spectrum was performed with a Shimadzu UV-2450 spectrophotometer. BET surface area, pore-volume, and Barret–Joyner–Halenda (BJH) pore size distribution based on nitrogen adsorption-desorption isotherms were determined with a Micromeritics ASSP 2020 equipment. UV-vis absorption spectra were obtained using a UV−visible spectrophotometer (Alpha-1106/1506). Irradiation light was under 15 W compact fluorescent lamp (CFL), 15 W blue LED, 15 W green LED and 15 W red LED.

General Procedure for the Preparation of Graphene oxide [1]

Utilizing a magnetic stirrer, we oxidized graphite by mixing H_2SO_4:H_3PO_4 (320:80 mL), graphite flakes, and $KMnO_4$ (18 g). All materials were slowly added to the one-pot mixture, and the mixture was stirred for 3 days to allow the graphite to oxidize. After that, the color of the mixture turned into a dark brown color as the mixture was being stirred. The oxidation process was stopped later by adding H_2O_2 solution, which caused the mixture to change to a bright yellow color, indicating a high oxidation level. After forming the graphite oxide, it was washed three times with an aqueous solution of HCl and repeatedly with deionized water until the pH was between 4 and 5. The washing procedure consisted of centrifugation with a centrifugal force of 5,000 g followed by simple decantation of the supernatant. The graphite oxide was exfoliated during the washing process, causing the graphene solution to thicken, leading to GO gel formation.

General Procedure for the Preparation of ZnS [2]

The synthesis of ZnS nanoparticles has begun with the preparation of a 10 mL aqueous solution of 0.15 M $ZnCl_2$. Subsequently, 20 mL of 0.10 M Na_2S solution was added drop by drop to the mixture and kept stirring at room temperature for 4 h, which allows the formation of ZnS nanoparticles.

General Procedure for the Preparation of RGO-ZnS [2]

Typically, different ratios of GR in RGO-ZnS nanocomposites were synthesized in the following manner. After dispersing GO completely in 50 mL of deionized water by ultrasonication, 10 mL of 0.15 M $ZnCl_2$ solution was added to this suspension as well as heating this suspension to 333 K with magnetic stirring in an oil bath for 2 hours. By electrostatic attraction, the positively charged Zn^{2+} can adsorb onto the negatively charged GO surface. Subsequently, for allowing the growth of ZnS nanoparticles, 20 mL of 0.10 M Na_2S solution was added dropwise and stirred continuously for 4 h. Next, the mixture was transferred to a 100 mL reflux balloon and kept at 403 K for 12 h, which allowed sufficient reduction of GO to RGO. Next, the products were cooled to room temperature and recovered by filtration, washed by water, and fully dried at 333 K in an oven to obtain the final RGO-ZnS nanocomposites with different weights addition ratios of RGO, namely, 1, 5, and 10% RGO-ZnS nanocomposites.

General procedure for the synthesis of 2-phenyl-1*H*benzo[d]imidazole from amine as a precursor

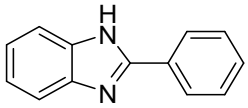
To a solution, *o*-phenylenediamine (1 mmol) in 5 ml of ethanol (96%) was added 1 mmol of benzylamine and irradiated by visible light (Irradiation light was under 15 W CFL, 15 W blue LED, 15 W green LED and 15 W red LED) for 24 h. After completion of the reaction (as monitored by thin-layer chromatography (TLC)), and separation of catalyst by centrifuge, the solvent was removed, and then 20 mL H_2O was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water (3×15 mL) and dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. Purification by silica gel column chromatography (70–230 mesh) using hexane-EtOAc as eluent to get pure products.

General procedure for the synthesis of 2-phenyl-1*H*benzo[d]imidazole from aldehyde as a precursor

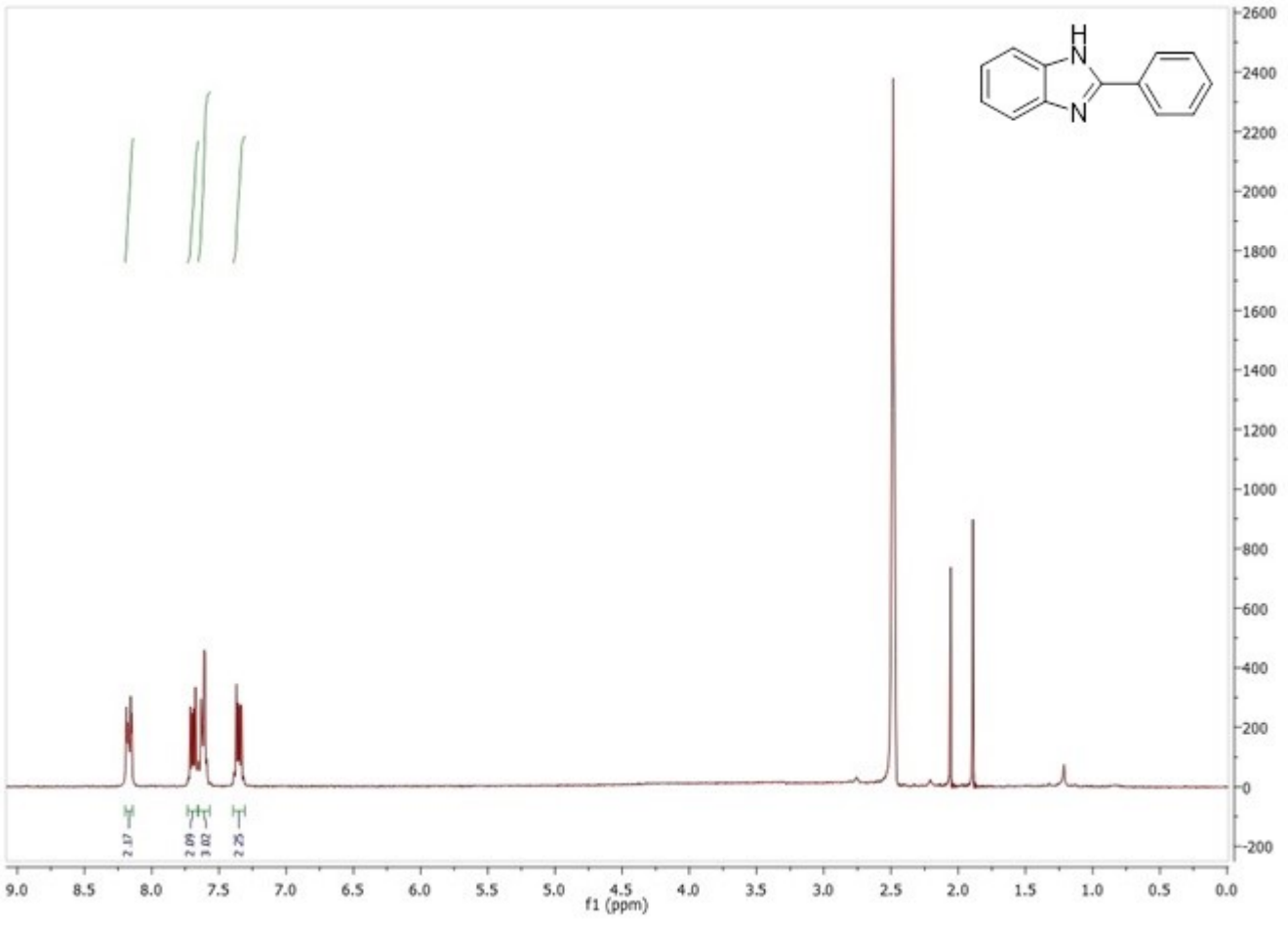
To a mixture of o-phenylenediamine (OPD) (1 mmol.) in 5 mL of ethanol (96%) was added 1 equiv of benzaldehyde and irradiated by visible light (Irradiation light was under 15 W CFL, 15 W blue LED, 15 W green LED and 15 W red LED) for 24 h. After completion of the reaction (as monitored by TLC), and separation of catalyst by centrifuge, the solvent was removed, and then 20 mL H_2O was added and the mixture was extracted with ethyl acetate. The organic phase was washed with water (3×15 mL) and dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. Purification by silica gel column chromatography (70–230 mesh) using hexane-EtOAc (10:2) as eluent to get pure products.

Physical and Spectral Data

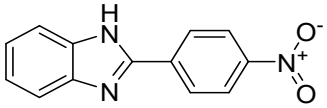
2-Phenyl-1*H*-benzimidazole



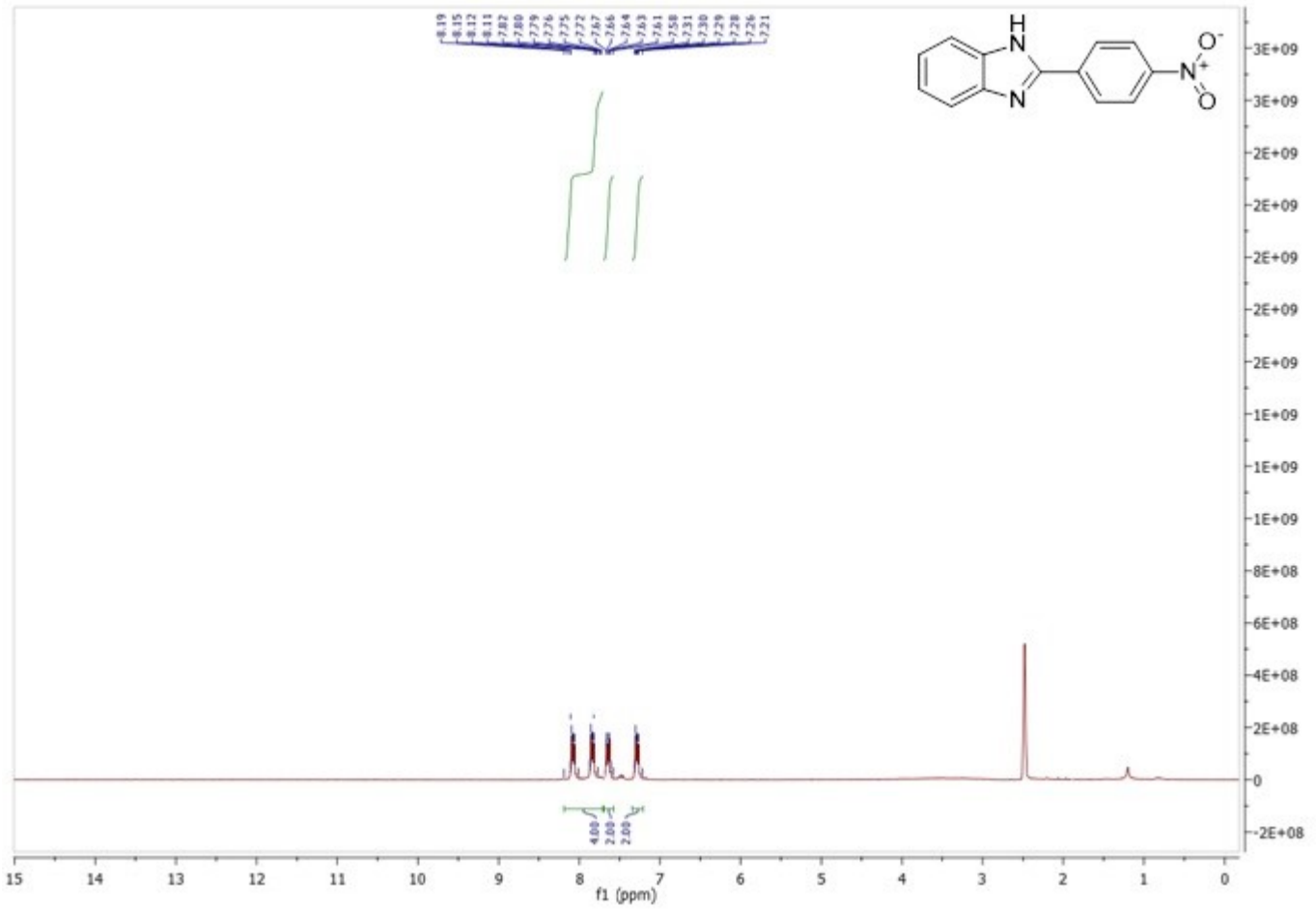
White solid; mp: 290–292°C; (Lit. [3] mp 292°C). IR (KBr): 1620 (C=N), 3440 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.33-7.37 (m, 2 H), 7.60-7.71 (m, 5 H), 8.20 (d, J = 2.50 Hz, 2H), 12.34 (br-s, 1 H). Anal. Calcd for $C_{13}H_{10}N_2$ (194.235): C, 80.39; H, 5.19; N, 14.42. Found: C, 80.33; H, 5.25; N, 14.39.



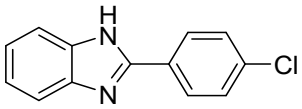
2-(4-Nitrophenyl)-1H-benzimidazole



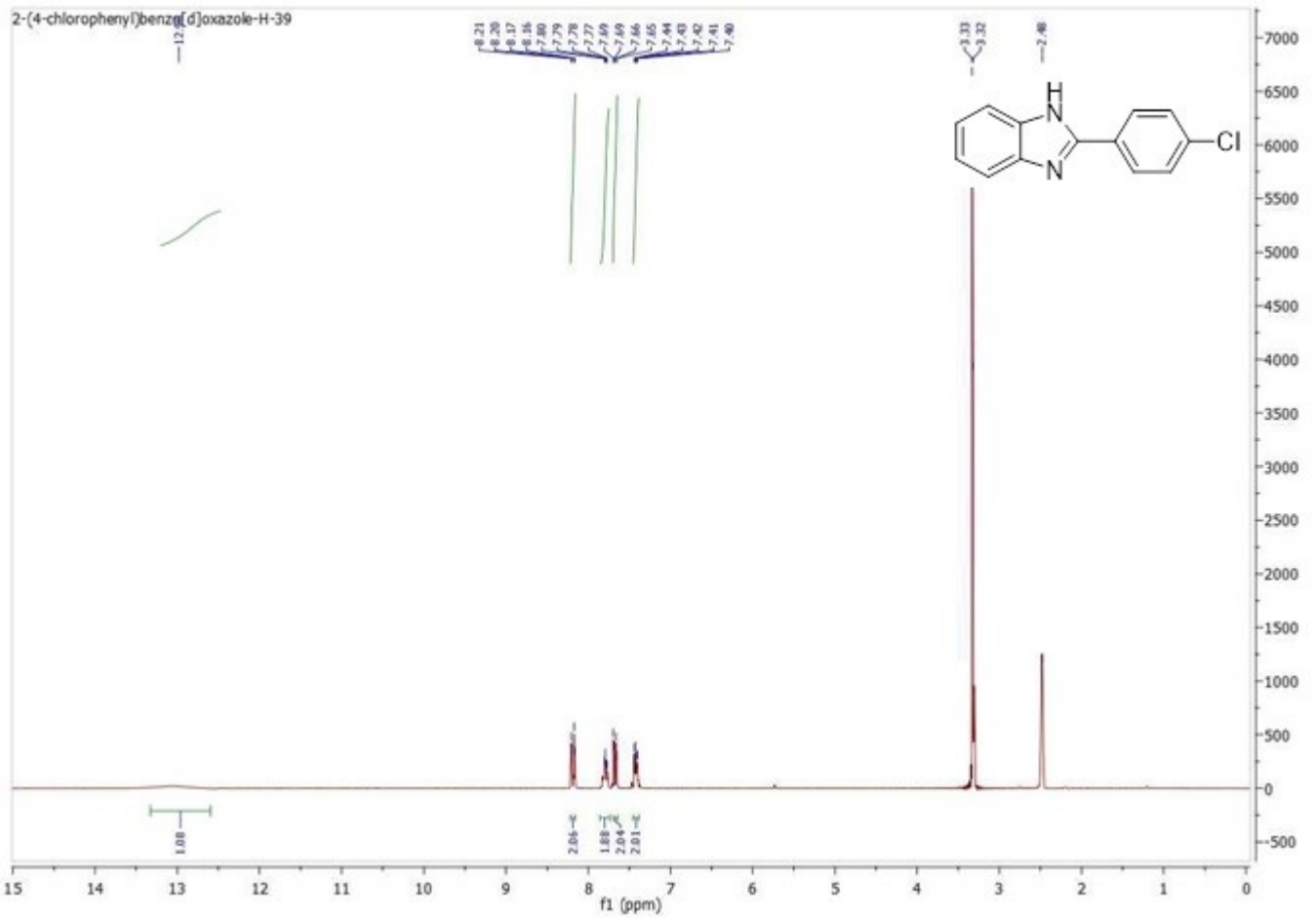
Yellow solid; mp: 312-314°C; (Lit. [3] mp 316 °C). IR (KBr): 1340, 1515 (NO_2)1620 (C=N), 3421 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.21-7.31 (m, 2H), 7.58-7.67 (m, 2H), 7.72-8.19 (m, 4H). Anal. Calcd for $C_{13}H_9N_3O_2$ (239.232): C, 65.27; H, 3.79; N, 17.56. Found: C, 65.20; H, 3.85; N, 17.50.



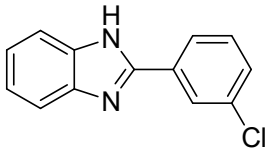
2-(4-Chlorophenyl)-1*H*-benzimidazole



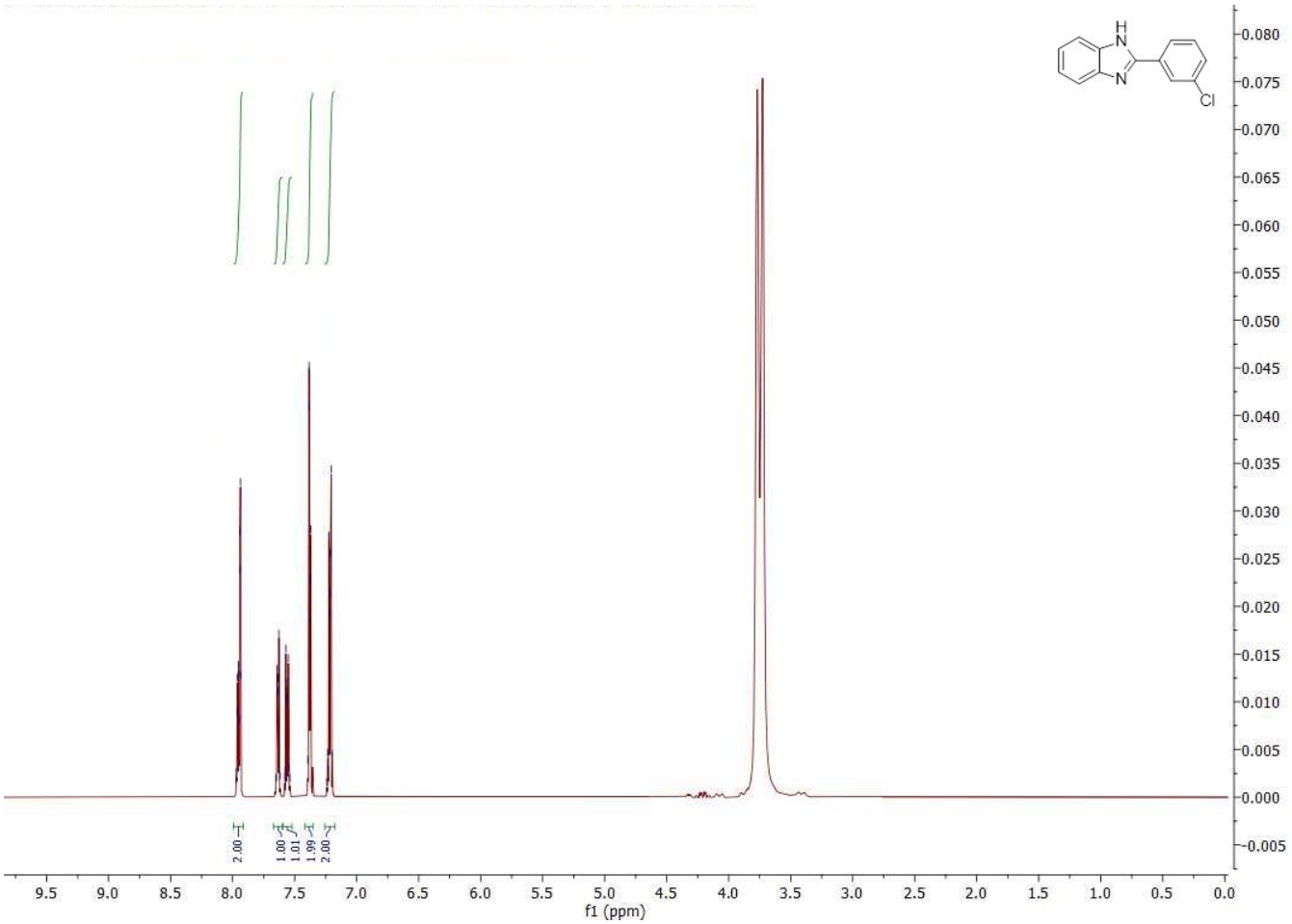
White solid; mp: 292°C; (Lit. [3] mp 290-292°C). IR (KBr): 1620 (C=N), 3445 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.40-7.44 (m, 2 H), 7.65-7.80 (m, 4 H), 8.16-8.21 (d, J = 2.50 Hz, 2H), 12.99 (br-s, 1 H). Anal.Calcd for $C_{13}H_9ClN_2$ (228.681): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.25; H, 3.95; N, 12.34.



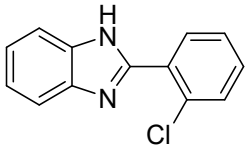
2-(3-Chlorophenyl)-1*H*-benzimidazole



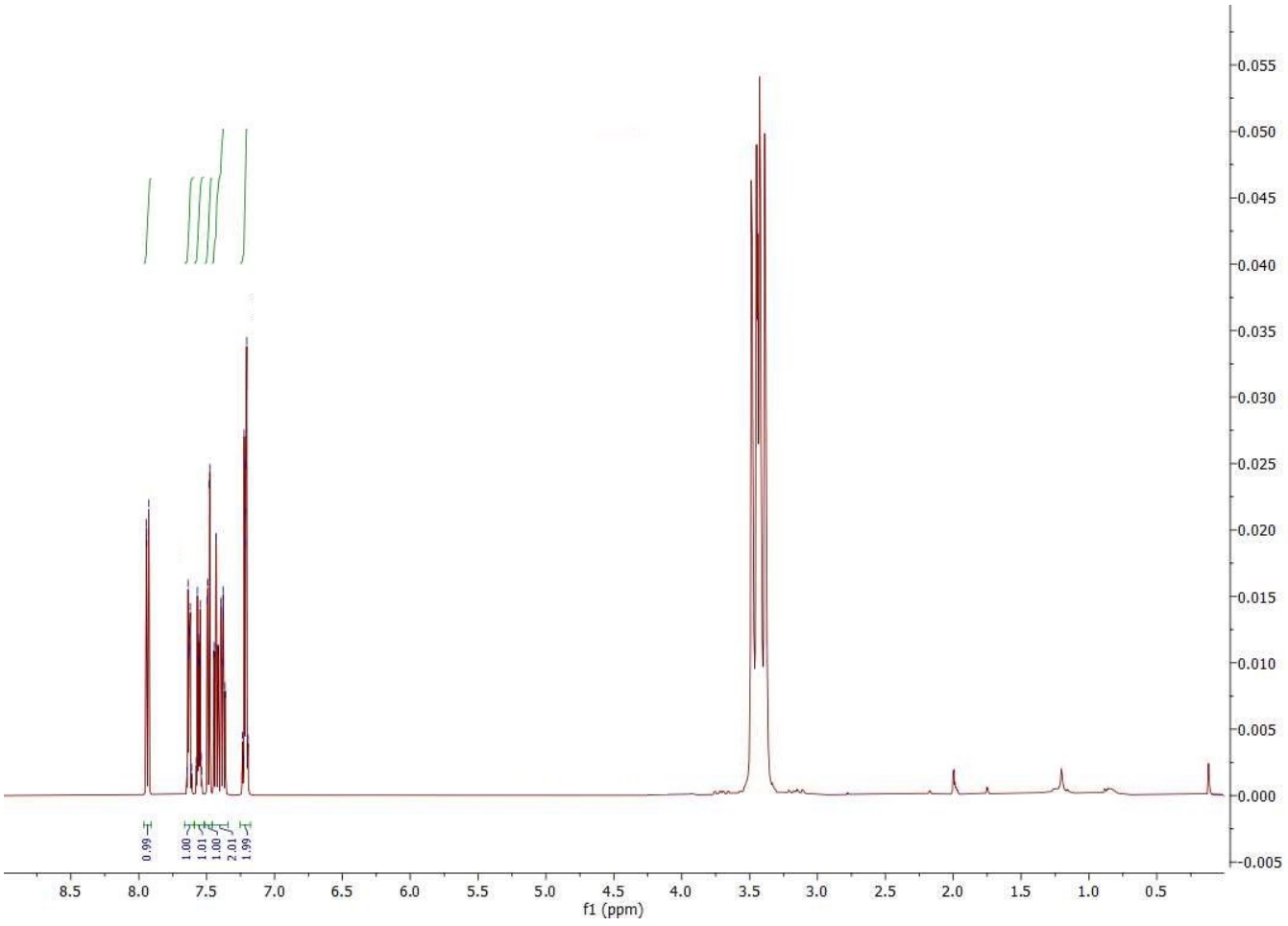
White solid; mp: 230-232°C; (Lit. [3] mp230-232°C). IR (KBr): 1625 (C=N), 3445 (NH) cm^{-1}. . ^1H NMR (DMSO-d_6, 250 MHz): δ 7.21 (m, 2H), 7.49-7.64 (m, 4H), 8.13 (dd, ^1J = 6.65 Hz, ^2J = 1.80 Hz, 1H), 8.21 (s, 1H), 13.04 (br-s, 1H). Anal.Calcd for $C_{13}H_9ClN_2$ (228.681): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.20; H, 4.02; N, 12.21.



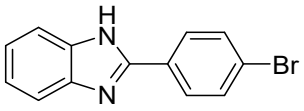
2-(2-Chlorophenyl)-1*H*-benzimidazole



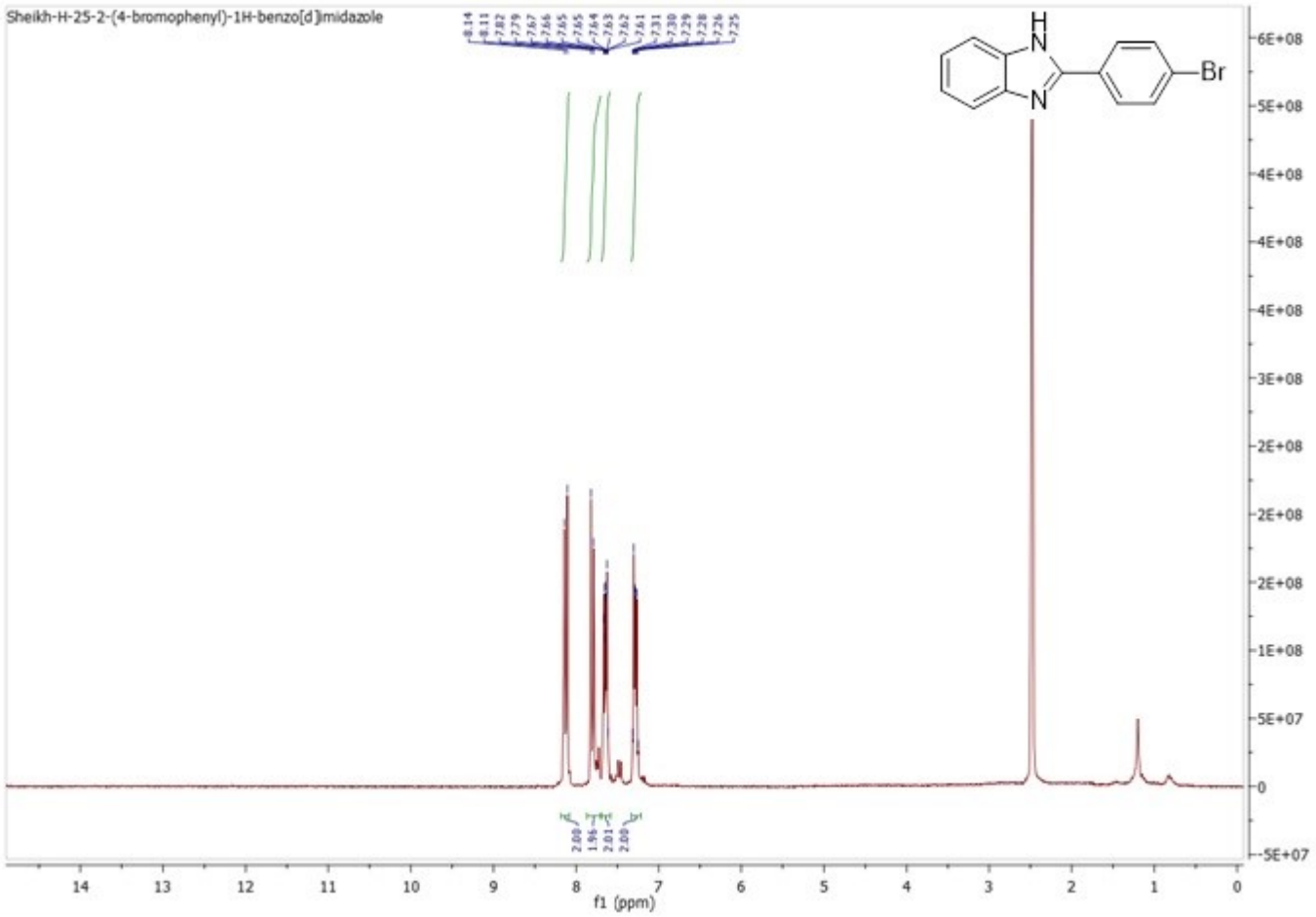
White solid; mp: 233–234°C; (Lit. [3] mp 234°C). IR (KBr): 1620 (C=N), 3445 (NH) cm^{-1}. ^1H NMR (DMSO-*d6*, 250 MHz): δ 7.20-7.24 (m, 2H), 7.48-7.51 (m, 2H), 7.54-7.68 (m, 3H), 7.89-7.93 (m, 1H), 12.74 (br-s, 1H). Anal. Calcd for $C_{13}H_9ClN_2$ (228.681): C, 68.28; H, 3.97; N, 12.25. Found: C, 68.22; H, 4.09; N, 12.20.



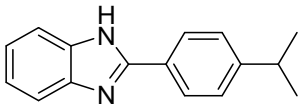
2-(4-Bromophenyl)-1*H*-benzo[d]imidazole



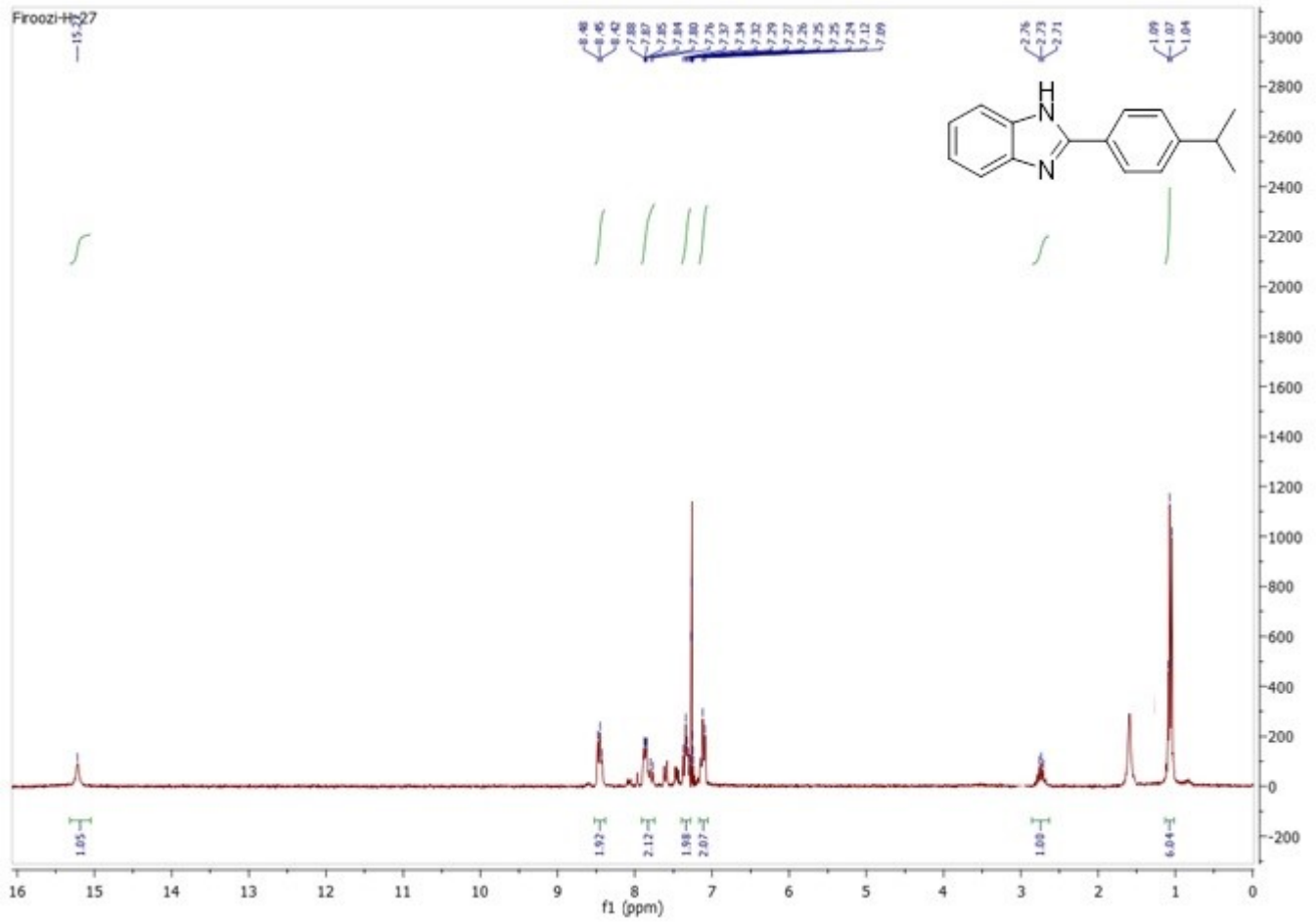
White solid; mp: 292–293°C; (Lit. [3] mp 292 °C). IR (KBr): 1626 (C=N), 3445 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 7.25-7.31 (m, 2 H), 7.61-7.67 (m, 2 H), 7.80 (d, J = 7.50 Hz, 2H), 8.13 (d, J = 7.50 Hz, 2H). Anal. Calcd for $C_{13}H_9BrN_2$ (273.133): C, 57.17; H, 3.32; Br, 29.25; N, 10.26. Found: C, 57.15; H, 3.30; Br, 29.27; N, 10.30.



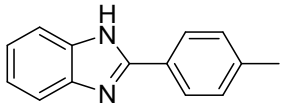
2-(4-Isopropylphenyl)-1*H*-benzimidazole



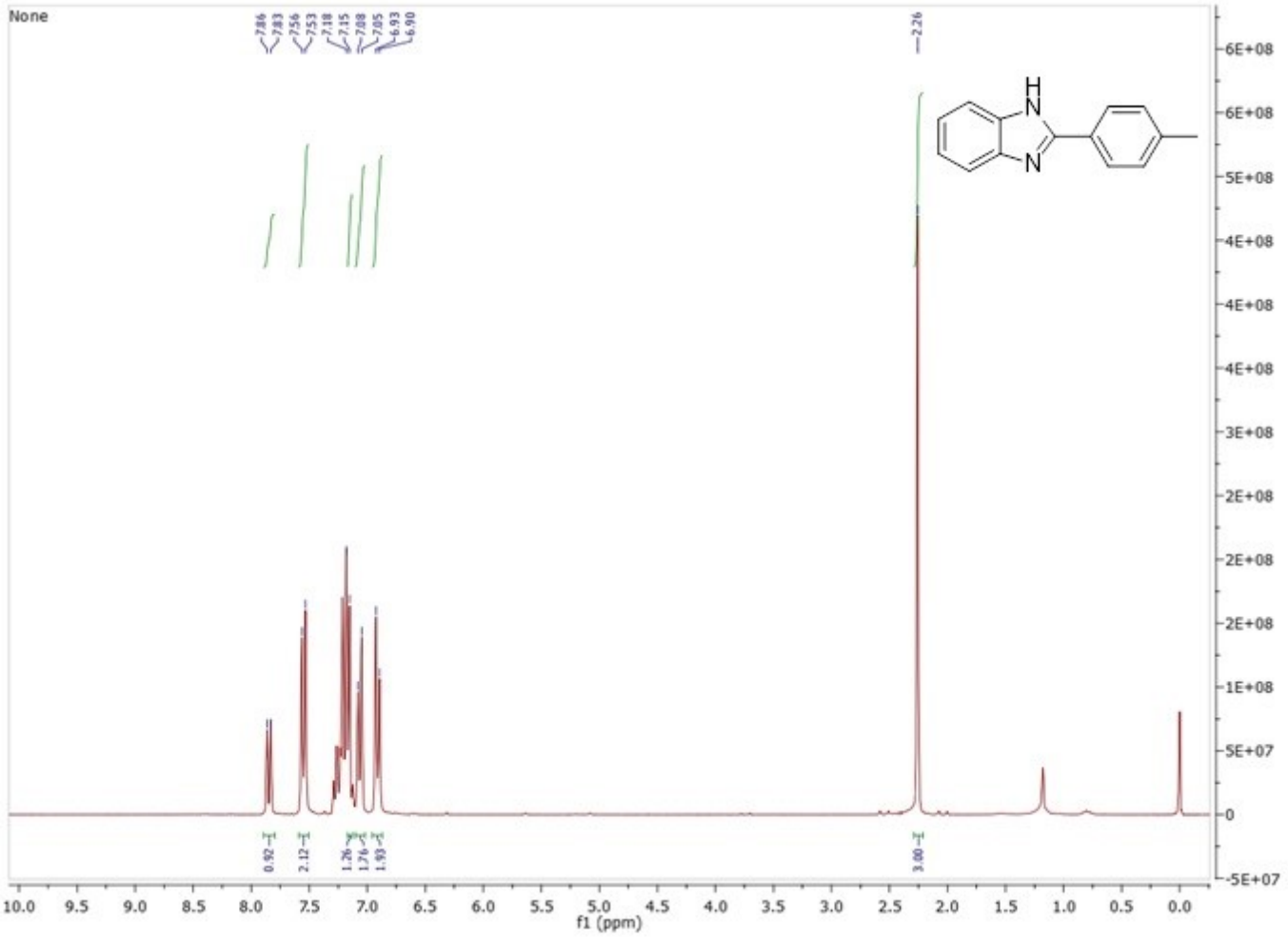
White solid; mp: 250-251°C; (Lit. [3] mp 250-251 °C). IR (KBr): 1620 (C=N), 3425 (NH) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 1.07 (d, *J* = 7.5 Hz, 6H), 2.71-2.75 (m, 1H), 7.9-7.14 (m, 2H), 7.24-7.37 (m, 2H), 7.76- 7.88 (m, 2H), 8.45 (d, *J* = 7.5 Hz, 2H), 15.22 (br-s, 1H). Anal. Calcd for $C_{16}H_{16}N_2$ (236.316): C, 81.32; H, 6.82; N, 11.85. Found: C, 81.29; H, 6.86; N, 11.79.



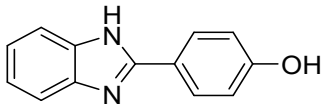
2-(4-Methylphenyl)-1*H*-benzimidazole



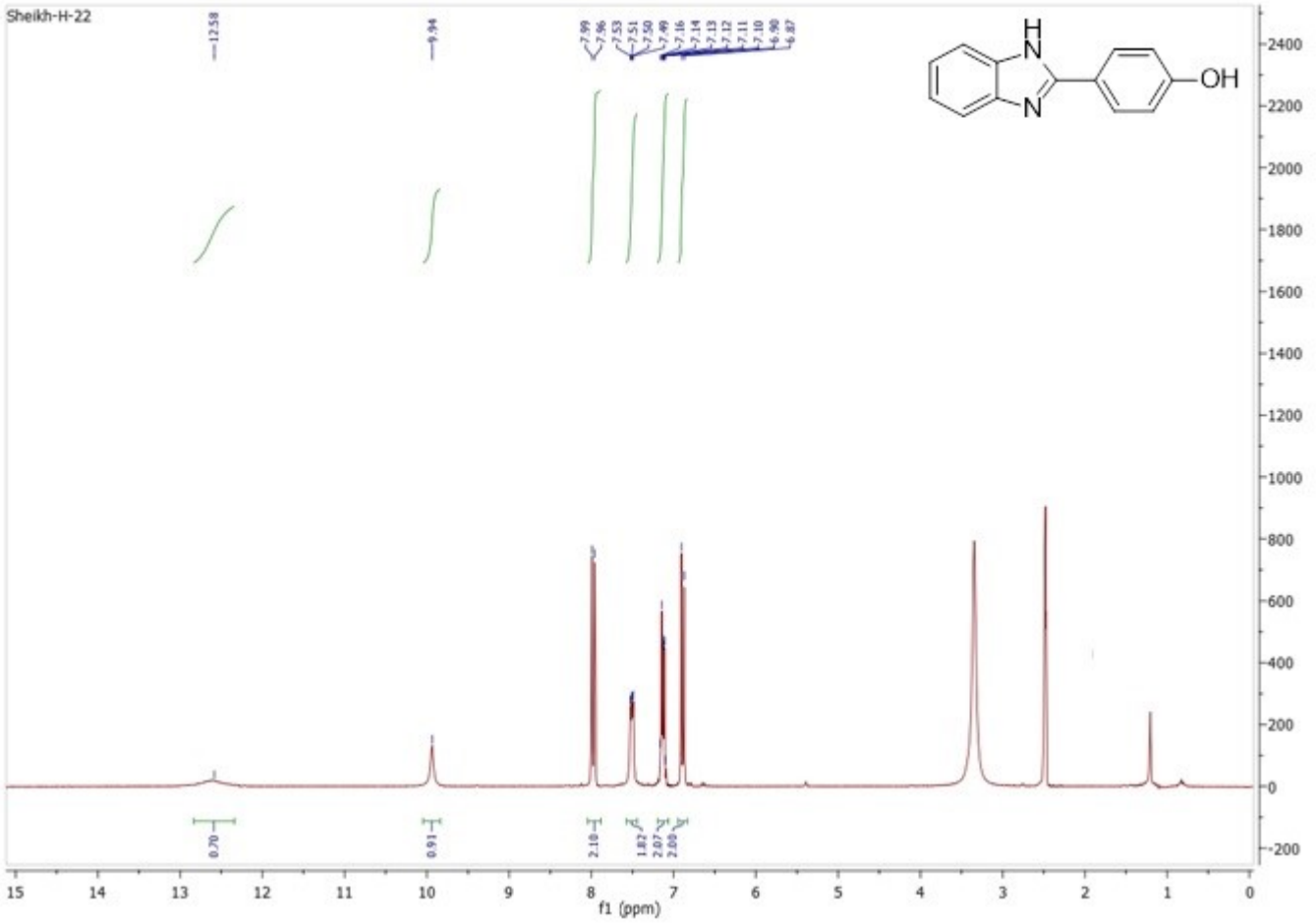
White solid; mp: 270-272°C; (Lit. [3]mp 270-272°C). IR (KBr):1620 (C=N), 3649 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 2.25 (s, 3H), 6.91 (d, J = 7.50 Hz, 2H), 7.06 (d, J = 7.50 Hz, 2H), 7.55 (d, J = 7.50 Hz, 2H), 7.84 (d, J = 7.50 Hz, 2H). Anal. Calcd for $C_{14}H_{12}N_2$ (208.262): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.79; H, 5.80; N, 13.40.



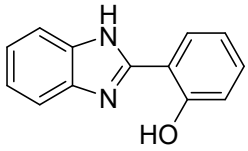
4-(1*H*-Benzo[d]imidazol-2-yl)phenol



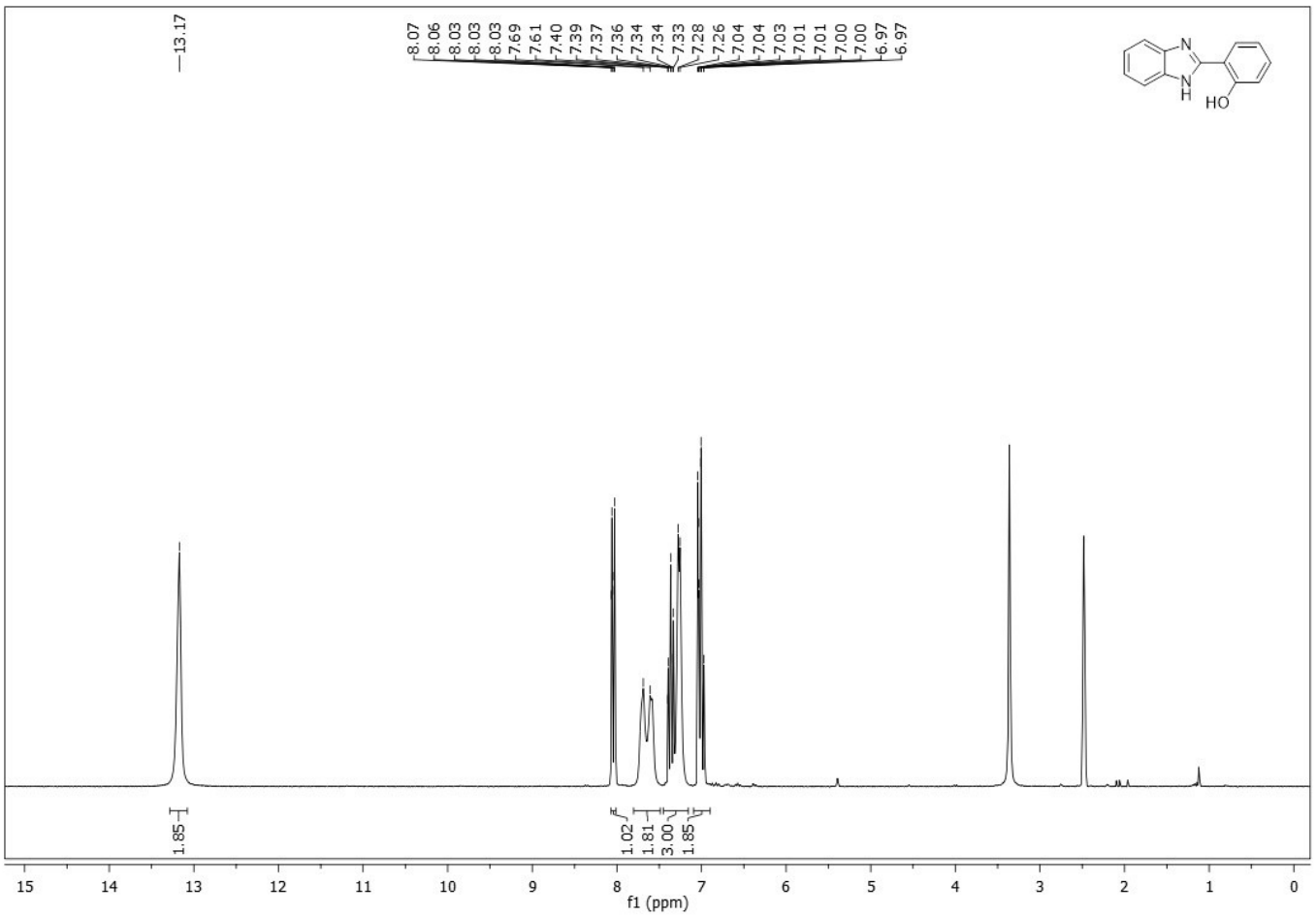
Pale yellow solid; mp: 254°C; (Lit. [3] mp 254-255 °C) IR (KBr): 1620 (C=N), 3250 (OH, NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 6.93 (dd, ^1J = 8.50 Hz, ^2J = 1.25 Hz, 2H), 7.10-7.16 (m, 2H), 7.49-7.53 (m, 2H), 7.98 (d, J = 7.50 Hz, 2H), 9.94 (s, 1H), 12.58 (br-s, 1H). Anal. Calcd for $C_{13}H_{10}N_2O$ (210.234): C, 74.27; H, 4.79; N, 13.33. Found: C, 74.20; H, 4.80; N, 13.33.



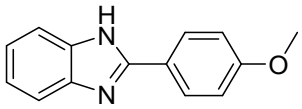
2-(1*H*-Benzimidazol-2-yl)phenol



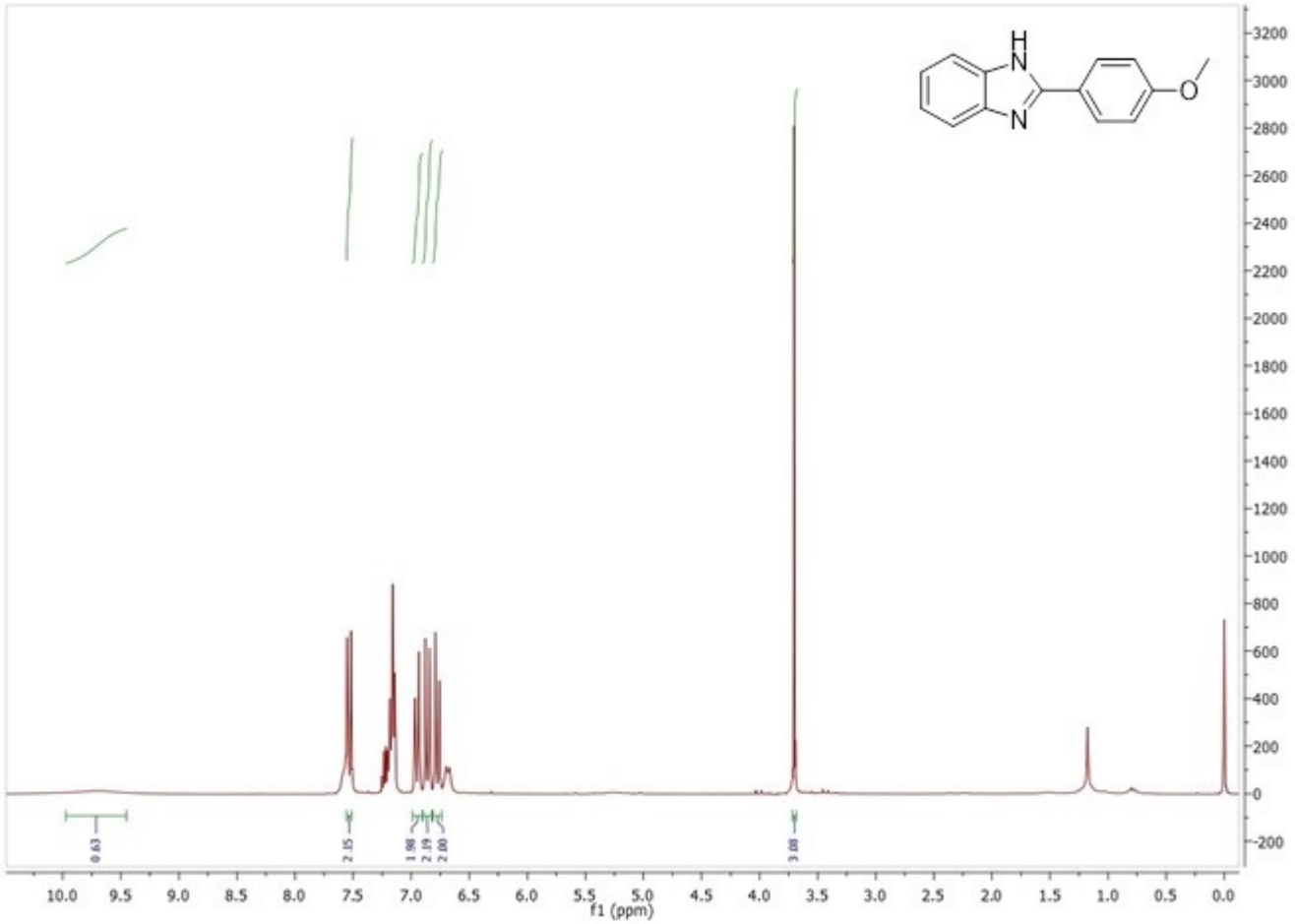
Yellow solid; mp: 240-242°C; (mp 242 °C). IR (KBr): 1620 (C=N), 3240 (OH, NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 6.97-7.04 (m, 2H), 7.25-7.45 (m, 3H), 7.63-7.67 (m, 2H), 8.02 (d, J = 7.80 Hz, 1H), 13.07 (s, 2H). Anal. Calcd for C_{13} $H_{10}N_2O$ (210.234): C, 74.27; H, 4.79; N, 13.33. Found: C, 74.21; H, 4.83; N, 13.32.



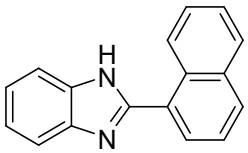
2-(4-Methoxyphenyl)-1*H*-benzimidazole



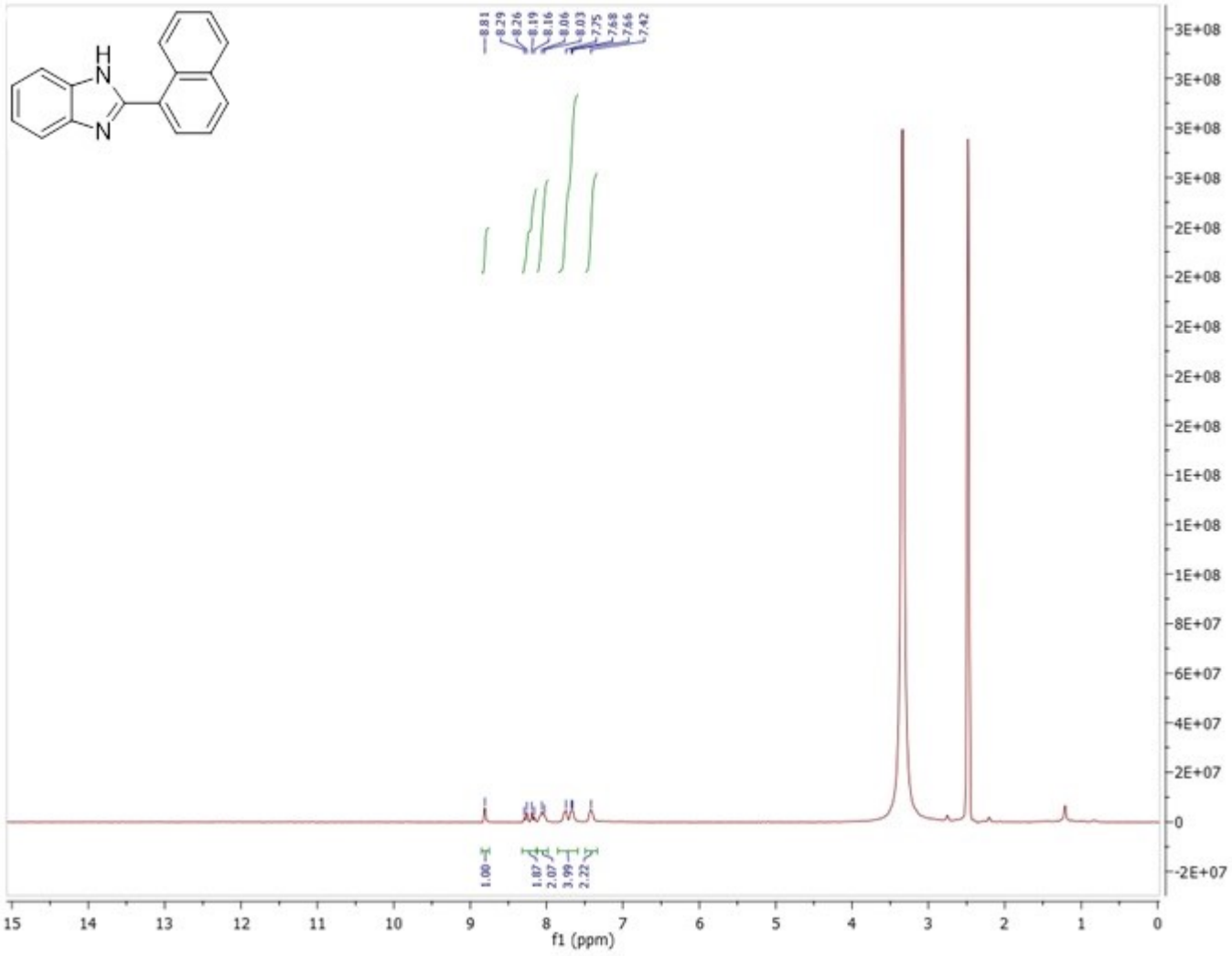
White solid; mp: 223°C; (Lit. [3] mp 222-225°C). IR (KBr): 1615 (C=N), 3430 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 3.70 (s, 3 H), 6.77 (d, J = 10 Hz, 2H), 6.86 (d, J=10 Hz, 2H), 6.95 (d, J = 10.00 Hz, 2H), 7.53 (d, J = 7.5 Hz, 2H), 9.68 (br-s, 1H). Anal. Calcd for $C_{14}H_{12}N_2O$ (224.261): C, 74.98; H, 5.39; N, 12.49. Found: C, 74.90; H, 5.40; N, 12.50.



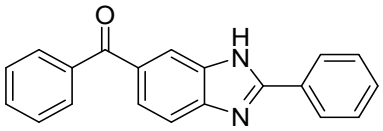
2-(Naphthalen-1-yl)-1*H*-benzo[d]imidazole



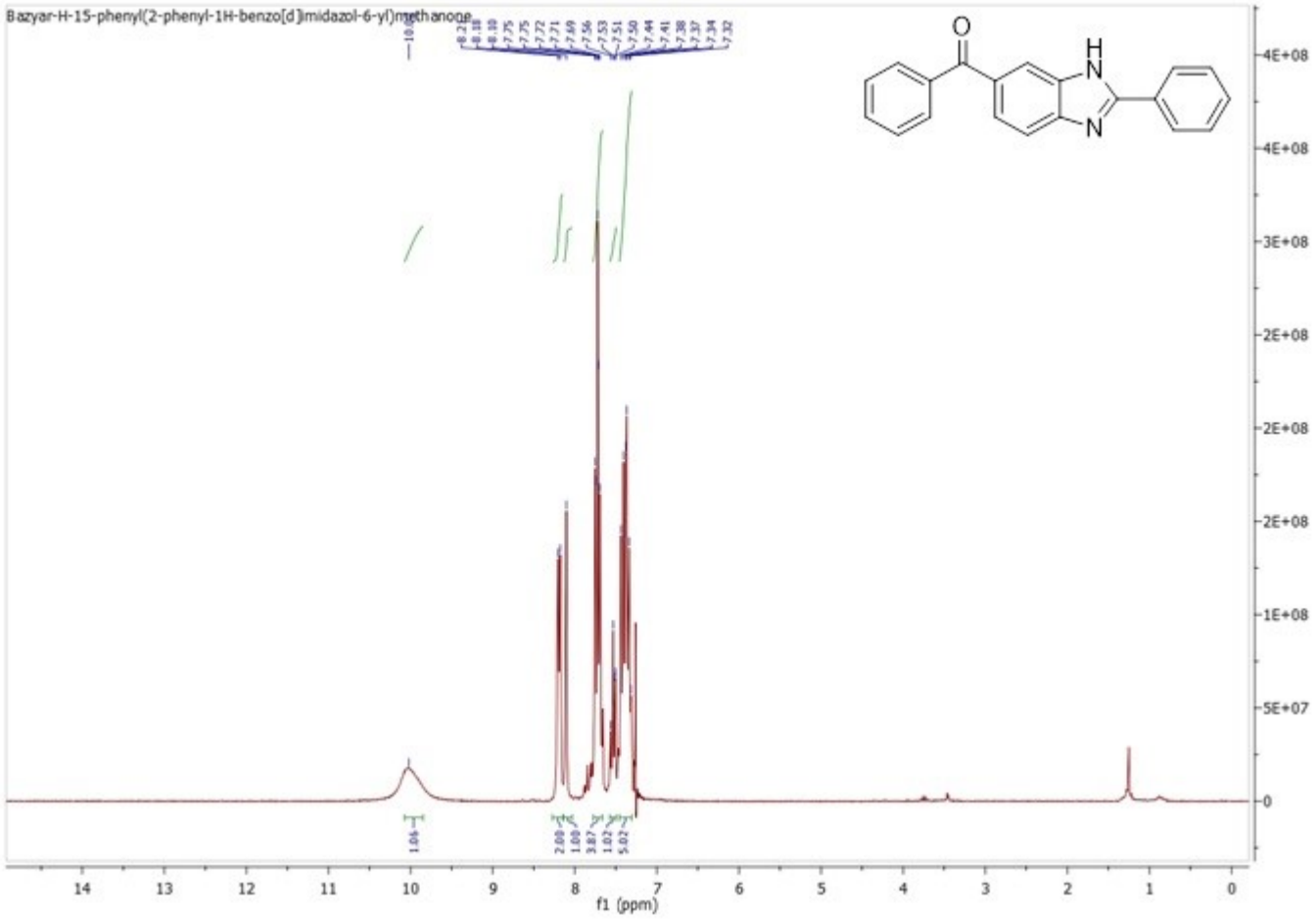
Color less powder; mp: 218°C; (Lit. [3] 218 °C). IR (KBr): 1620 (C=N), 3440 (NH) cm^{-1}. ^1H NMR ($CDCl_3$, 250 $MHz_)$ δ: 7.34-7.41 (m, 2H,), 7.65-7.83 (m, 4H). 8.02-8.29 (m, 4H), 8.81 (br-s, 1H). Anal. Calced for $C_{17}H_{12}N_2$ (244.10): C, 83.58; H, 4.95; N, 11.47. Found: C, 83.52; H, 4.99; N, 11.46.



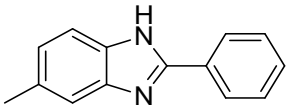
Phenyl(2-phenyl-1*H*-benzimidazol-5-yl)methanone



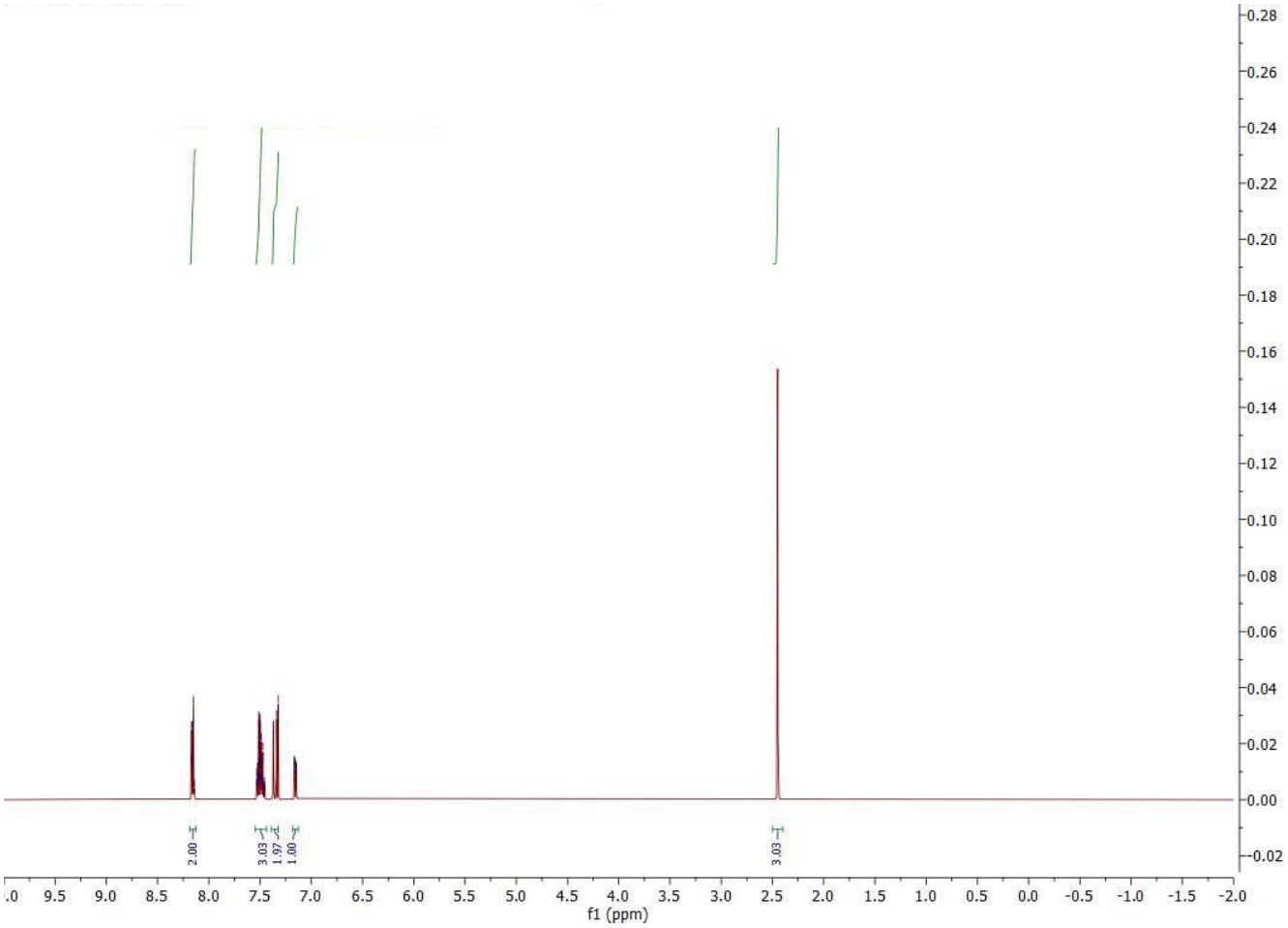
Pale yellow solid; mp: 221-222°C; (Lit. [3] mp 221-221.5 °C). IR (KBr): 1612 (C=N), 1643 (C=O), 3244 (NH) cm^{-1}. . ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.32-8.10 (m, 11H), 8.20 (d, *J* = 7.50 Hz, 2H), 10.02 (br-s, 1H). Anal. Calcd for $C_{20}H_{14}N_2O$ (298.343): C, 80.52; H, 4.73; N, 9.39. Found: C, 80.59; H, 4.75; N, 9.27.



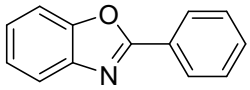
5-Methyl-2-phenyl-1H-benzimidazole



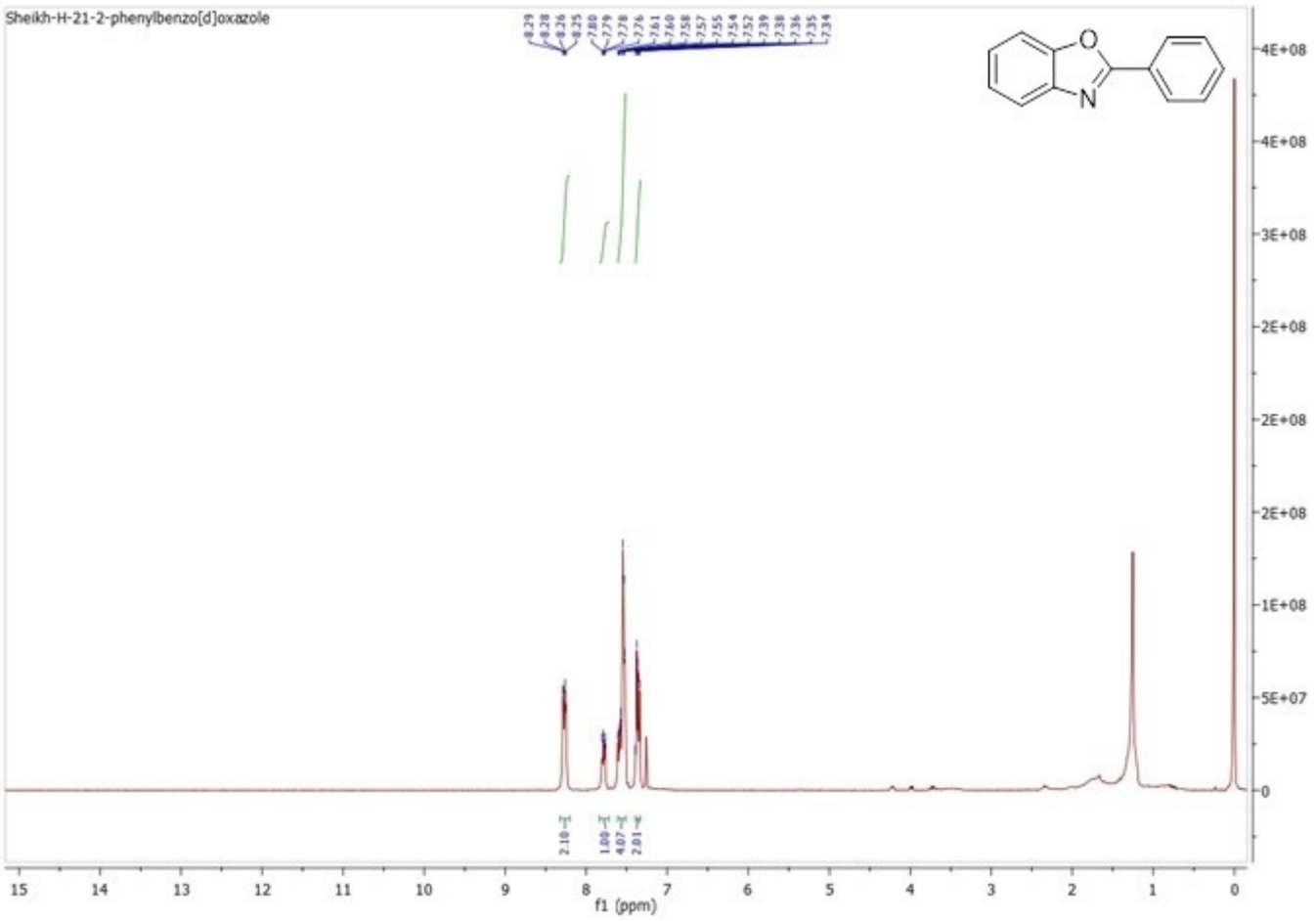
White solid; mp: 242-243°C; (Lit. [3] mp 242-143 °C). IR (KBr): 1620 (C=N), 3444 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 2.35 (s, 3H), 7.00 (d, *J*=8.10 Hz, 1H), 7.36- 7.55 (m, 5H), 8.14(d, *J*=7.65 Hz, 2H), 12.75 (br-s, 1H). Anal. Calcd for $C_{14}H_{12}N_2$ (208.10): C, 80.74; H, 5.81; N, 13.45. Found: C, 80.74; H, 5.80; N, 13.44.



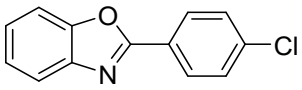
2-phenylbenzo[d]oxazole



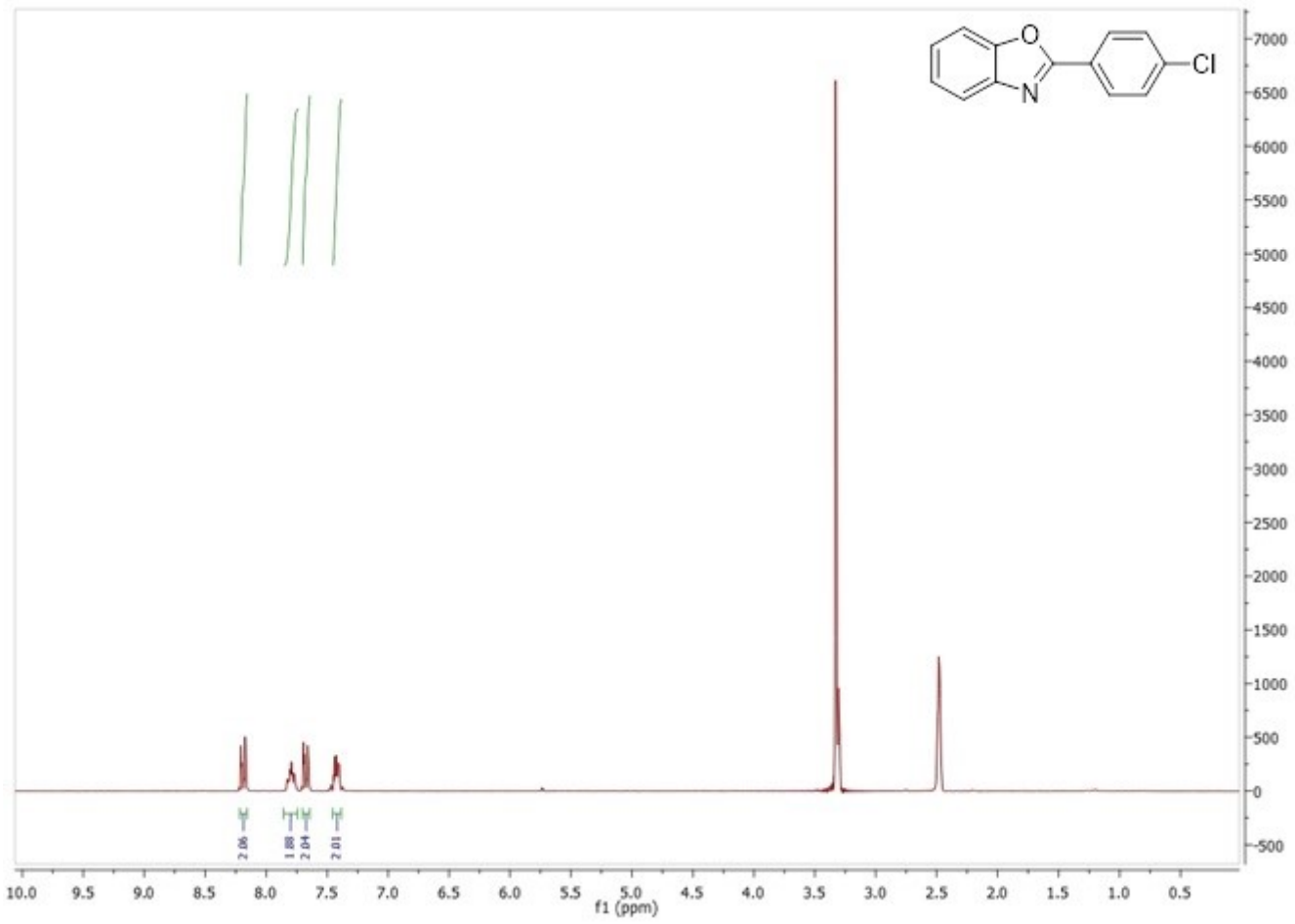
Light brown solid; m.p= 95 °C; (Lit. [4] mp 95-97 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.34-7.39 (m, 2H), 7.52-7.61 (m, 4H), 7.76-7.80 (m, 1H), 8.25-8.29 (m, 2H). Anal. Calcd for $C_{13}H_9NO$ (195.07): C, 79.98; H, 4.65; N, 7.17. Found: C, 79.95; H, 4.67; N, 7.16.



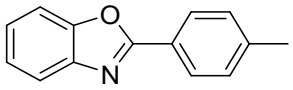
2-(4-Chlorophenyl)benzo[d]oxazole



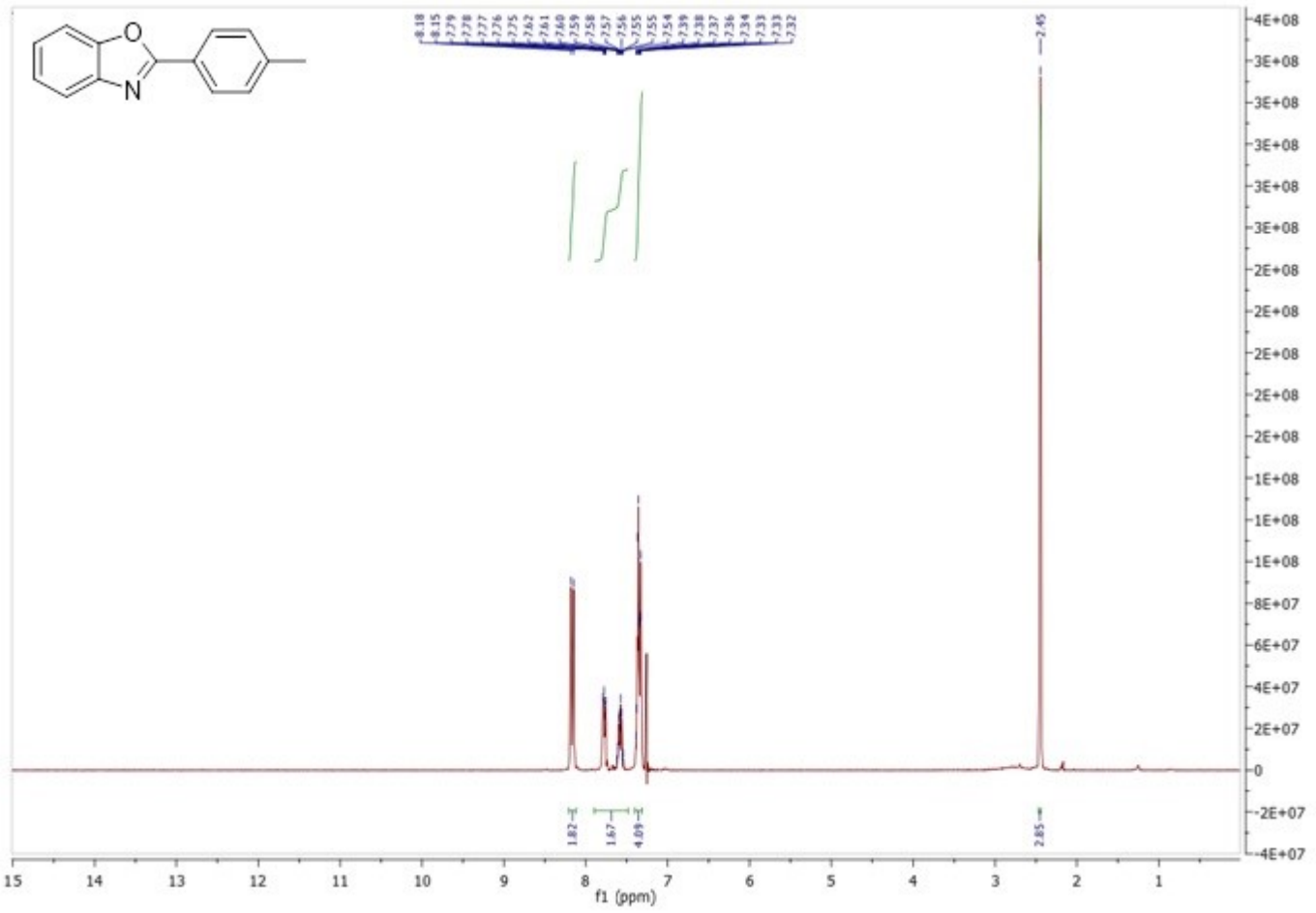
Light brown solid; m.p= 144-146°C (Lit. [4] mp 144-145 °C). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.36-7.40 (m, 2H), 7.52-7.61 (m, 2H), 7.57-7.6 (m, 1H), 7.76-7.80 (m, 1H), 8.19-8.22 (m, 2H). Anal.Calcd for$C_{13}H_8ClNO$ (229.03): C, 67.99; H, 3.51; N, 6.10. Found: C, 67.89; H, 3.53; N, 6.09.



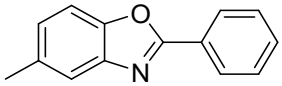
2-(4-Methylphenyl)-1*H*-benzimidazole



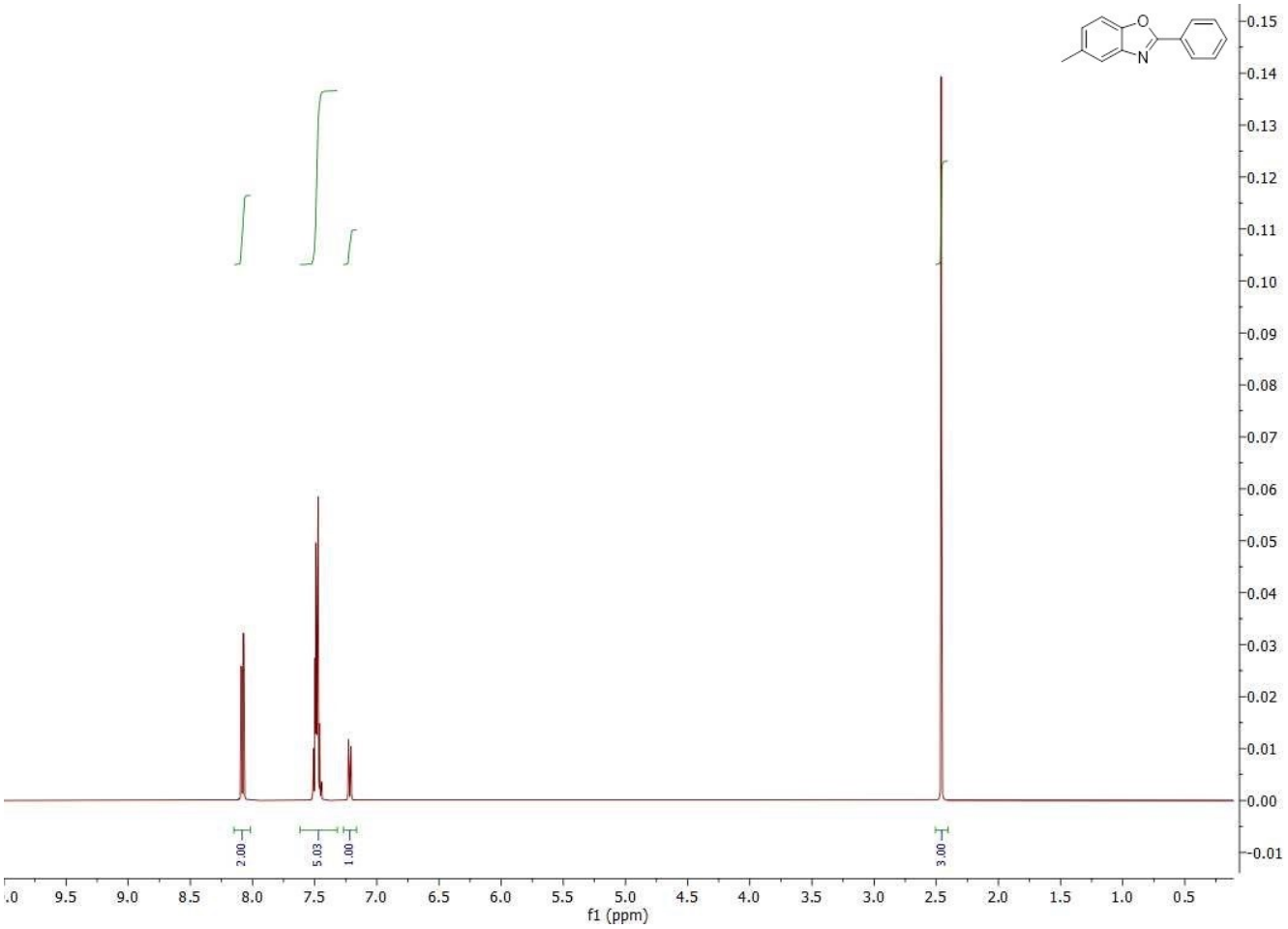
Light brown solid; m.p= 114-116 °C; (Lit. [4] mp 113-115). IR (KBr):1620 (C=N), 3649 (NH) cm^{-1}. ^1H NMR (DMSO-d_6, 250 MHz): δ 2.45 (s, 3H), 7.15-7.20 (m, 2H), 7.32-7.39 (m, 4H), 7.54-7.79 (m, 2H), 8.16 (d, *J*=7.50 Hz, 2H). Anal. Calcd for C14H11NO (209.08): C, 80.36; H, 5.30; N, 6.69.Found: C, 80.36; H, 5.28; N, 5.31.



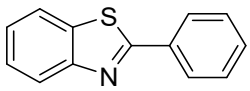
5-methyl-2-phenylbenzo[d]oxazole



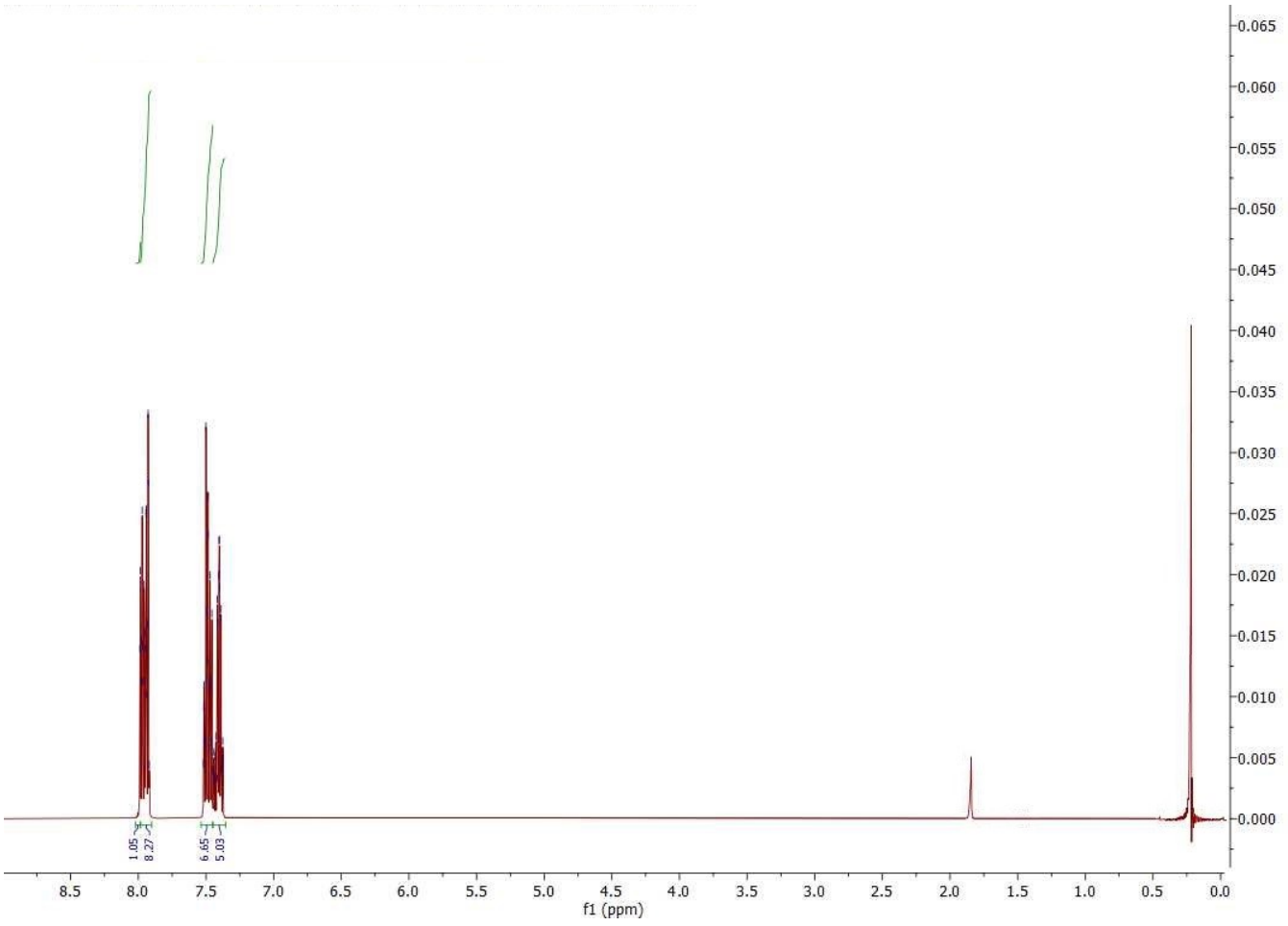
brown solid; m.p= 130-135 °C; (Lit. [4] mp 133-135). ^{1}H NMR (250 MHz) δ 3.35 (s, 3H), 7.23 (d, J = 8.10 Hz, 1H), 7.61 (m, 4H), 7.68 (d, J = 8.1 Hz, 1H), 8.19 (m, 2H)



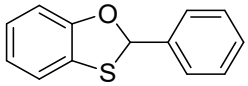
2-phenylbenzo[d]thiazole



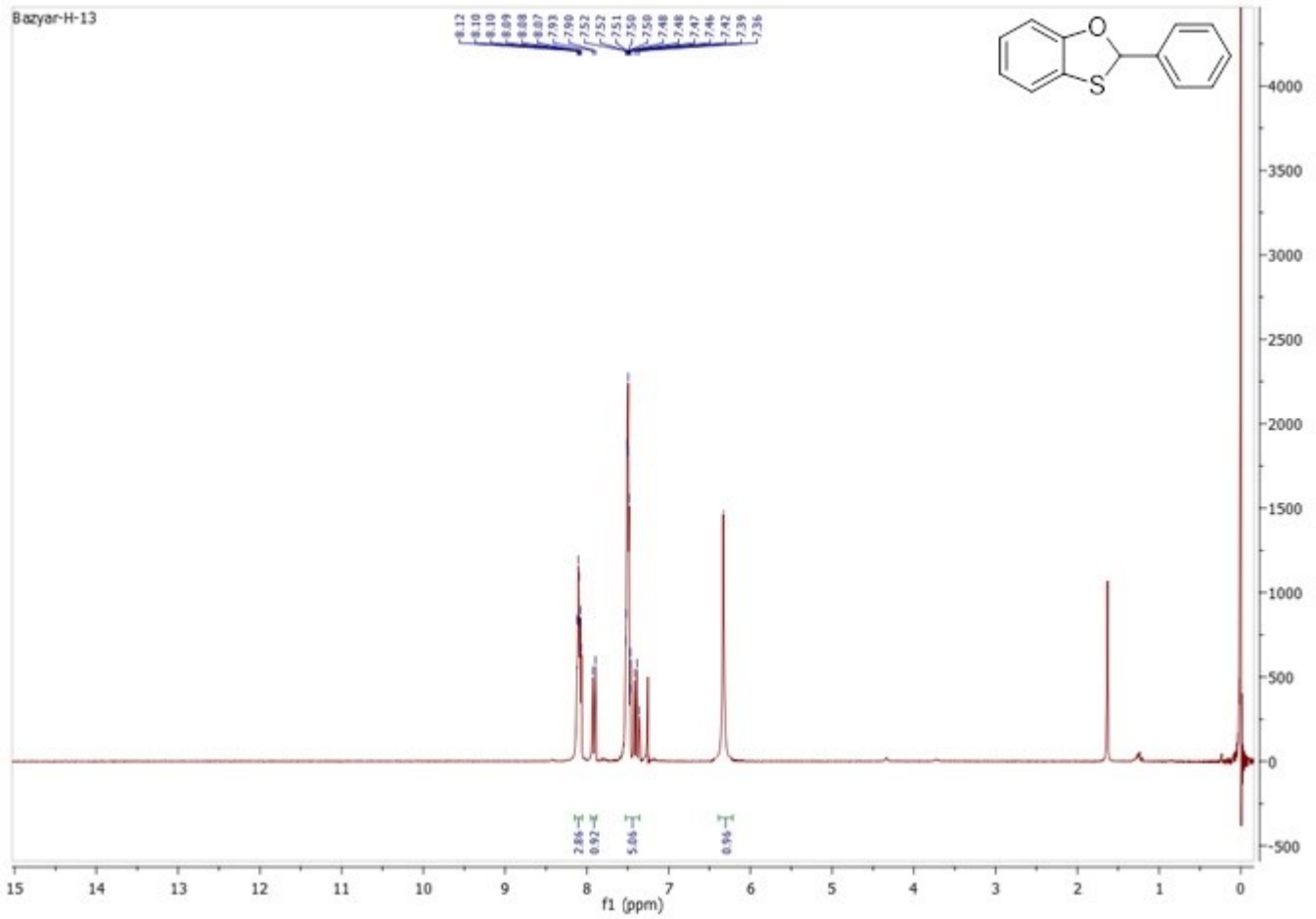
Color less solid; m.p= 114-116 °C; (Lit. [4] mp 113=115). ^{1}H NMR ($CDCl_3$, 250 MHz): δ 6.36 (s, 1H), 7.36-7.52 (m, 5 H), 8.91 (d, *J* = 7.5 Hz, 2H), 8.07-8.12 (m, 2H).



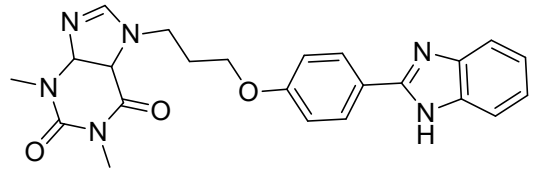
2-phenylbenzo[d][1,3]oxathiole



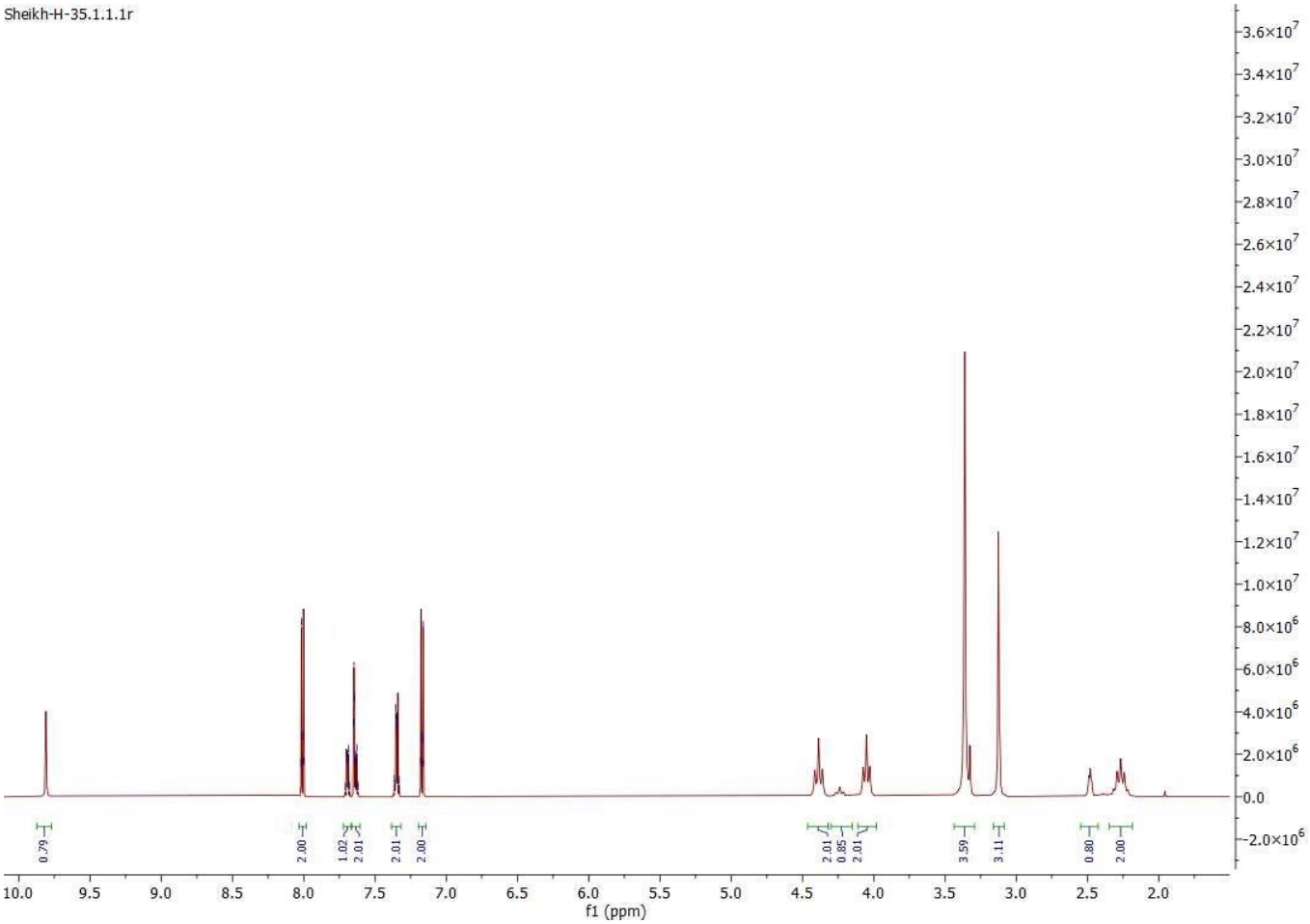
Purple solid; mp: 290–292°C; (Lit. mp 292°C). IR (KBr): 1120 (C-O), 1240 (C-S) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): δ 6.36 (s, 1H), 7.36-7.52 (m, 5 H), 8.91 (d, J = 7.5 Hz, 2H), 8.07-8.12 (m, 2H).



7-(3-(4-(1*H*-Benzo[d]imidazol-2-yl)phenoxy)propyl)-1,3-dimethyl-3,4,5,7-tetrahydro-1H-purine-2,6-dione



Purple solid; mp: 280–282°C. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 2.36 (qu, J = 6.25 Hz, 2H), 3.25 (s, 3H), 3.48 (s, 3H), 4.10 (t, J = 6.25 Hz, 2H), 4.50 (t, J = 6.25 Hz, 2H), 7.08 (d, J= 8.75 Hz, 2H), 7.22 (dd, ^{1}J = 6.00 Hz, ^{2}J = 3.00 Hz, 2H), 7.61 (dd, ^{1}J = 6.00 Hz, ^{2}J = 3.25 Hz, 2H), 8.12 (s, 1H), 8.15 (d, J = 2.25 Hz), 12.82 (br-s, 1H)



Tables and, Figures

Figure S1. Three types of catalysts in terms of ZnS content. Respectively from right to left RGO-ZnS1%, RGO5%-ZnS, and RGO10%-ZnS.

Figure S2. Three types of catalysts in terms of ZnS content. Respectively from right to left RGO-ZnS1%, RGO55-ZnS, and RGO10%-ZnS.

Surface Area	187.318 m^2/g
Pore Volume	0.260 cc/g
Pore Diameter Dv (d)	3.891 nm

Table S1. The specific surface area of RGO55-ZnS.

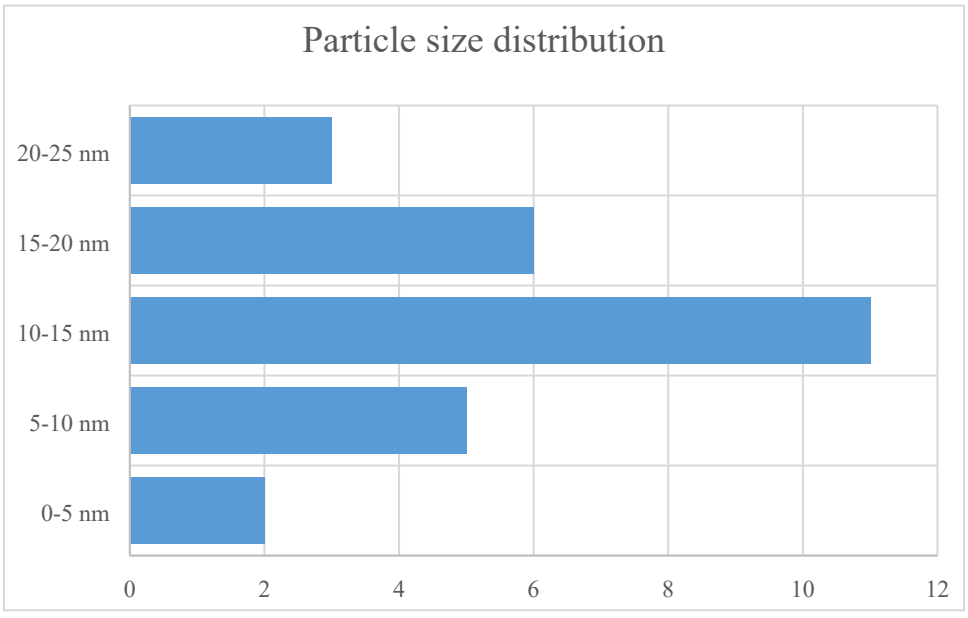


Table S2. Effect of common solvents on the model reaction.[a]

Entry	*Solvent 1 (mL)*	*Solvent 2 (mL)*	*Conversion (%)[b]*	*Yield of 3a (%)[c]*
1	MeCN (4)	EtOH 96% (2)	100	96
2[d]	MeCN (4)	EtOH 96% (2)	80	43
3	MeCN (2)	EtOH 96% (1)	83	43
4	H_2O (6)	-	60	0
5	DMF (6)	-	20	0
6	EtOAc (6)	-	0	0
7	CH_2Cl_2 (6)	-	20	0
8	Acetone (6)	-	0	0
9	THF (6)	-	0	0
10	H_2O (2)	EtOH 96% (4)	0	0
11	MeCN (4)	H_2O (2)	0	0
12	MeCN (6)	-	0	0
13	-	EtOH 96% (6)	0	0
14	-	-	0	0
15[e]	MeCN (4)	EtOH (2)	60	0
16f	MeCN (4)	EtOH (2)	70	43
17	MeCN (4)	MeOH (2)	64	0
18[g]	MeCN (4)	MeOH (2)	85	53
19[h]	MeCN (4)	MeOH (2)	68	43

*[a] Reaction conditions: 1 mmol of benzylamine **1a** and 1 mmol of ortho-Phenylenediamine **2a** in the presence of 3 mg RGO5%-ZnS at room temperature, 24 h, CFL White (15 W). [b] Predict by the amount of benzylamine. [c] Isolated Yields. [d] 0.5 mmol of benzylamine and 0.5 mmol of ortho-Phenylenediamine. [e] EtOH absolute. [f] EtOH 90%. [g] MeOH 95%. [h] MeOH 90%.*

Table S3. Effect of atmosphere on the model reaction.[a]

Entry	atmosphere	Conversion (%)[b]	Yield of 3a (%)[c]
1	O_2	95	92
2	Ar	10	0
3	air	45	30

[a]Reaction conditions: 1 mmol of benzylamine and 1 mmol of OPD in the presence of 3 mg RGO5%-ZnS at room temperature, CFL 15 W, 24 h. [b] Predicted by the amount of benzylamine. [c] Isolated yield.

Table S4. Optimization of catalyst type.[a]

Entry	Catalyst	Time (min)	Conversion	Yield 3a [%][b]
1	RGO1%-ZnS	120	97	98
2	RGO5%-ZnS	20	98	98
3	RGO10%-ZnS	20	98	98
4	-	300	0	0

[a] Reaction conditions: Benzaldehyde (1 mmol), OPD (1 mmol), MeOH, open to the air, irradiation under a 15 W blue LED at room temperature, 0.003 g of catalyst. [b] Yield were determined by TLC.

Table S5. Optimization of catalyst amount.[a]

Entry	*Amount of catalyst*	*Time (min)*	*Conversion (%)*	*Yield of 3a [%][b]*
1	0.001	70	98	98
2	0.003	20	98	98
3	0.004	20	98	98
4	0.01	100	98	98

[a] Reaction conditions: Benzaldehyd (1 mmol), OPD (1 mmol), RGO5%-ZnS, open to the air, irradiation under a 15 W blue LED at room temperature. [b] yield were determined by TLC.

Table S6. Effect of common solvents.[a]

Entry	*Solvent*	*Time (min)*	*Conversion (%)*	*Side product (%)*	*Yield of 3a [%] [b]*
1	EtOH	60	98	30	70
2	MeCN	60	97	50	50
3	DMF	60	Trace	Trace	Trace
4	EtOAc	60	20	0	0
5	H2O	60	Trace	Trace	Trace
6	CH_2Cl_2	60	20	0	Trace
7	THF	60	0	0	0
8	-	60	Trace	Trace	Trace
9	MeOH	20	98	0	98

[a] Reaction conditions: Benzaldehyde (1 mmol), OPD (1 mmol), RGO5%-ZnS (0.03 g), open to the air, irradiation under a 15 W blue LED at room temperature. [b] yields were determined by TLC.

References

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2. Y. Zhang, N. Zhang, Z.-R. Tang and Y.-J. Xu, Graphene transforms wide band gap ZnS to a visible light photocatalyst. The new role of graphene as a macromolecular photosensitizer, *Acs Nano*, 2012, **6**, 9777-9789.
3. H. Sharghi, M. Hosseini-Sarvari and F. Moeini, Copper-catalyzed one-pot synthesis of benzimidazole derivatives, *Canadian J. Chem.*, 2008, **86**, 1044-1051.
4. H. Naeimi, Z. Rouzegar and S. Rahmatinejad, Sonocatalyzed facile synthesis of 2-aryl benzoxazoles using MnO_2 nanoparticles as oxidant agent under mild conditions, *Synth. Comm.*, 2017, , 2087–209.