A simple and straightforward strategy for expedient access to benzoxazoles using chemically engineered 2D magnetic graphene oxide nanosheets as an eco-compatible catalyst

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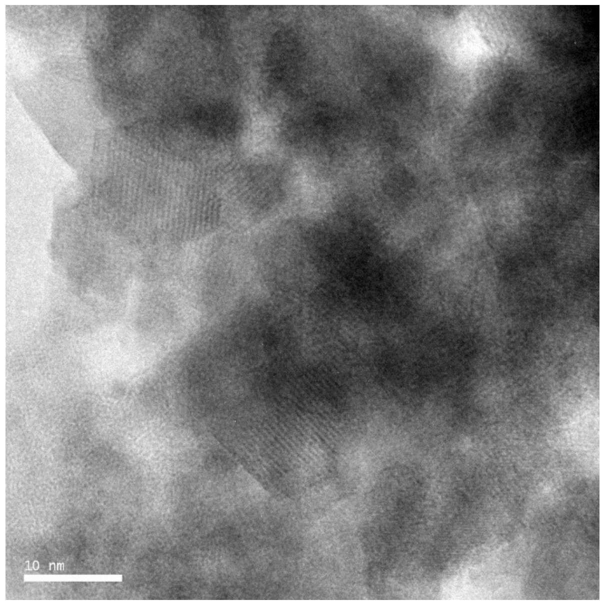


Figure S1. Lattice fringes of magnetite nanoparticles

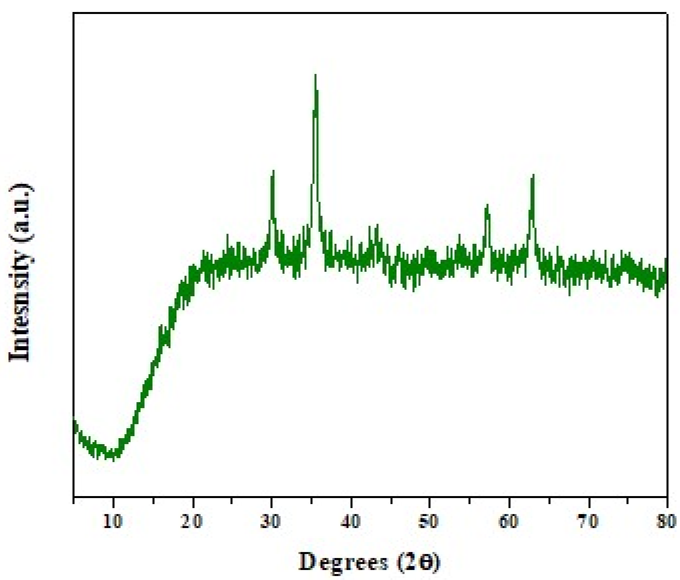


Figure S2. Powder XRD of MGO (Fe_3O_4-GO).

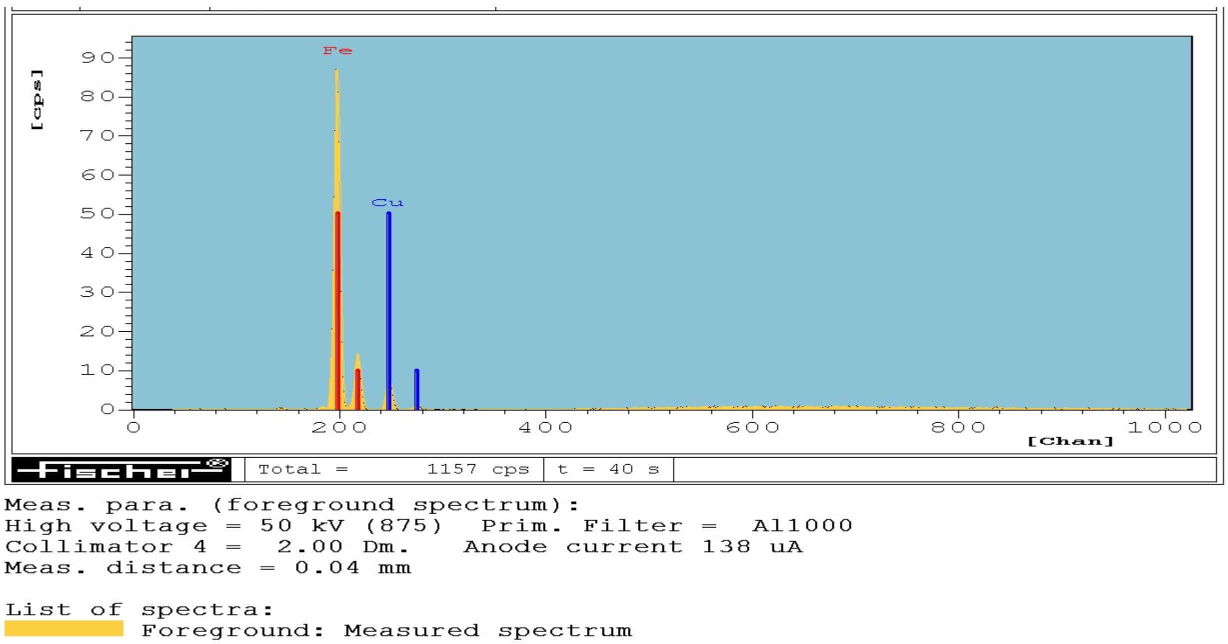


Figure S3. ED-XRF of final nanocatalyst (Cu@DHA@APTES@MGO).

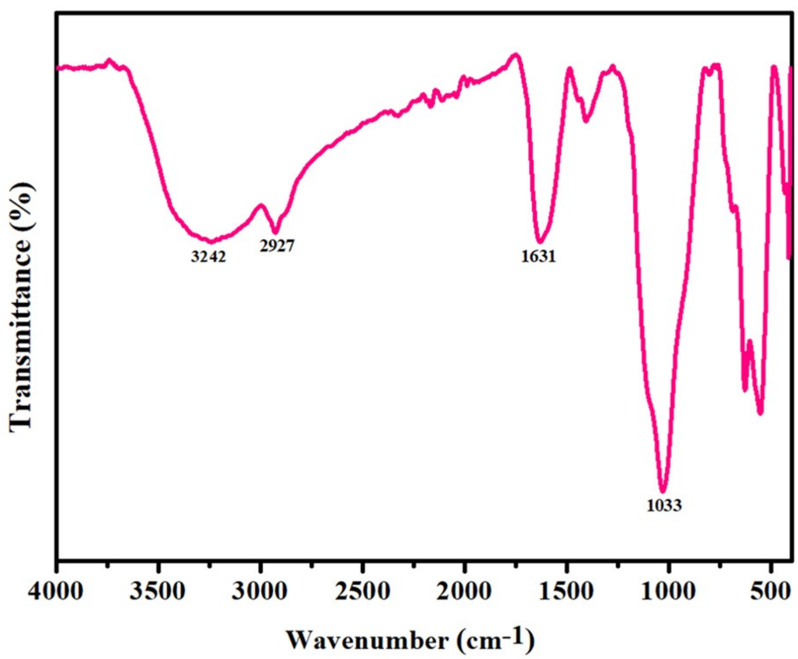


Figure S4. FT-IR of recovered catalyst.

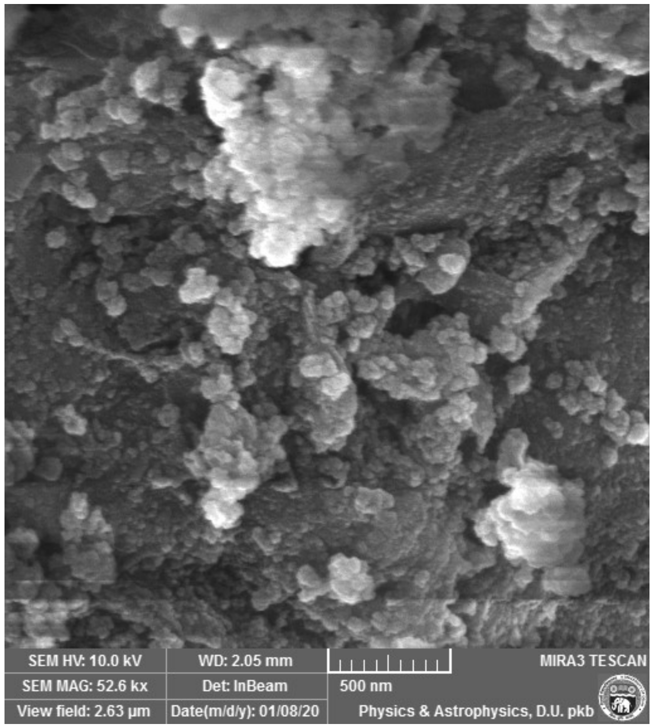
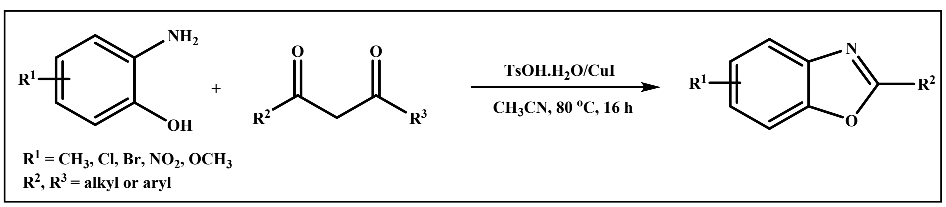


Figure S5. FESEM of recovered catalyst.

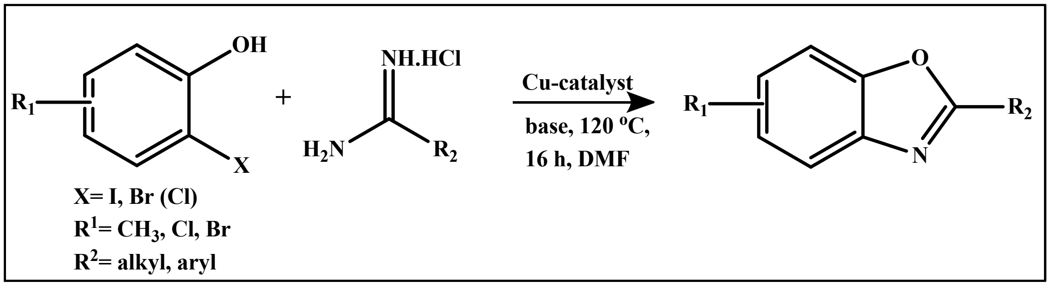
Comparison of method for the synthesis of benzoxazoles with literature precedents

Mayo *et al.* for the first time introduced the novel pathway for cyclization of 2-aminophenols and β-diketones for obtaining relatively large number of benzoxazole scaffolds (scheme S1). 2-aminophenol and 2,4-pentanedione were employed as test substrates using p-toluenesulphonnic acid as co-catalyst and copper iodide (CuI) as catalyst.[1]



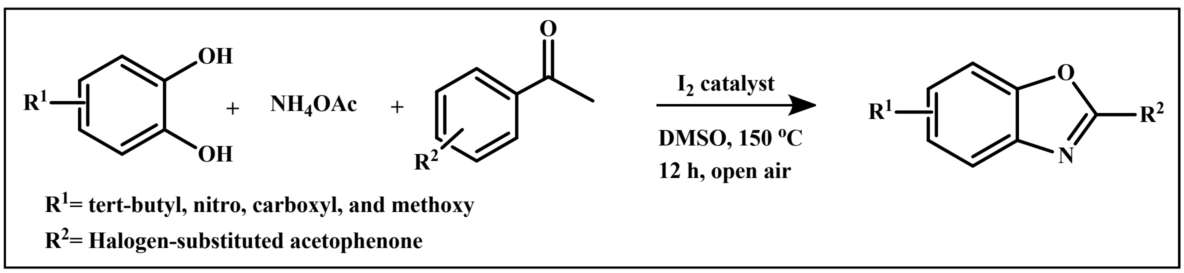
Scheme S1 Synthesis of benzoxazoles from 2-aminophenols and β-Diketones by using CuI as catalyst and p-TsOH as co-catalyst.

Another approach used for the synthesis of benzoxazoles and its derivatives reported by Tiwari and his colleagues was copper catalyzed tandem cyclization of 2-halophenols with amidines. This reaction was carried out in basic medium using KOH as base and DMF as solvent at 120 °C for 16 h (scheme S2).[2]



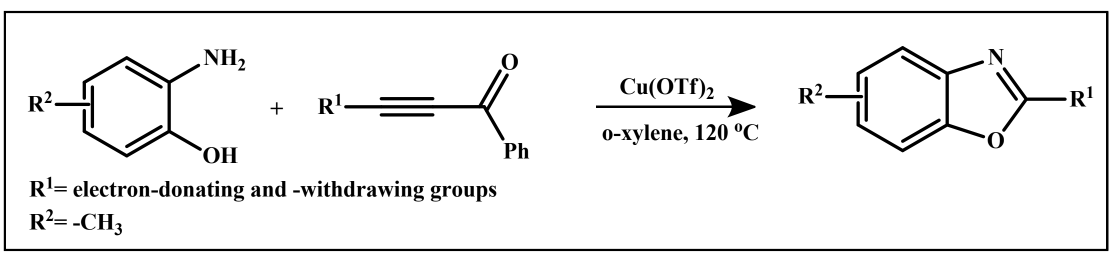
Scheme S2 Synthesis of benzoxazoles from2-halophenols with amidines using CuI as catalyst.

The synthetic startegy employed by Aboonajmi and co-workers used coupling of catechols, ammonium acetate and alkenes/alkynes/ketones for the synthesis of benzoxazoles and its derivatives (scheme S3).[3] Authors also synthesized desired products by using different styrenes and phenylacetylenes.



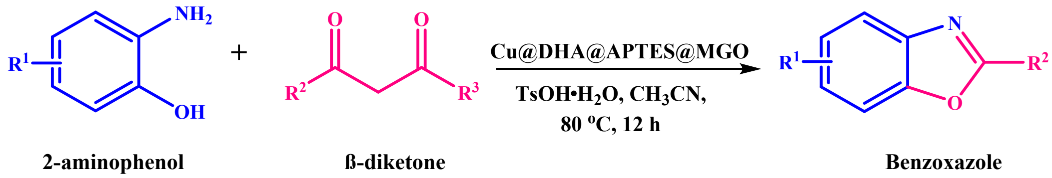
Scheme S3 Use of different ketone sources and catechols in the benzoxazole synthesis using I_2 as catalyst.

Hydroamination of alkynones with 2-aminophenols catalyzed by $Cu(OTf)_2$ was reported by Oshimoto and team in which authors have produced a wide variety of benzoxazoles derivatives with good yield.[4]



Scheme S4 ortho-C–H functionalization of phenols with nitroalkanes to synthesize benzoxazoles.

A variety of methods have been reported in literature for the synthesis of benzoxazoles and we have compared few methods with out present protocol. Unfortunately, methodologies used in literature precedents involved the utilization of homogeneous catalytic system, high reaction temperatures and harsh solvents which hinder their commercial applicability due to the problems associated with separation and recovery of catalyst. In the present work, we reported a magnetically retrievable graphene oxide based copper nanocatalytic system that has been exploited for the synthesis of benzoxazoles *via* cyclization of 2-aminophenols and β-diketones with excellent conversion percentage.

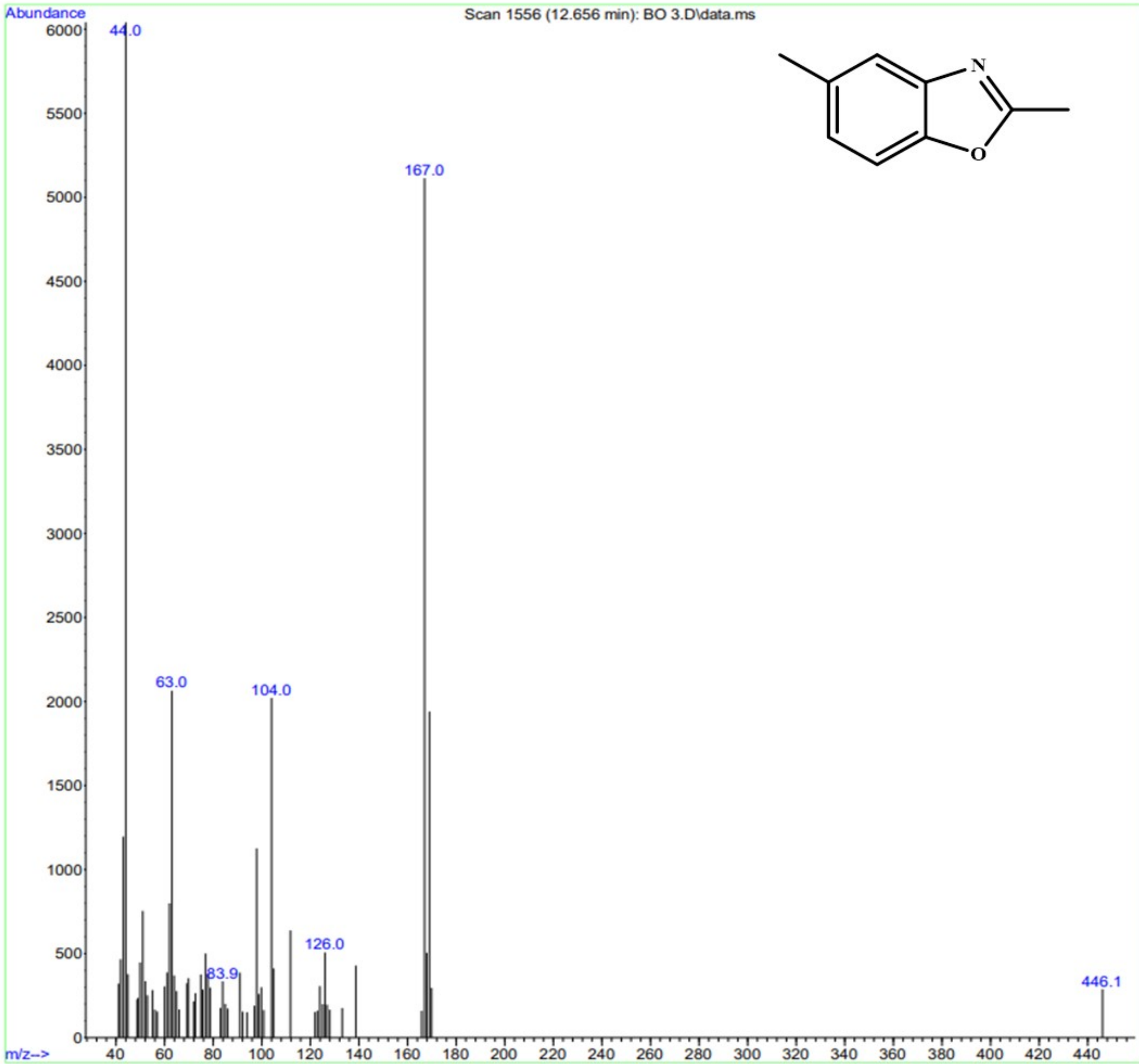


Scheme S5 Synthesis of benzoxazoles from 2-aminophenols and β-Diketones Cu@DHA@APTES@MGO nanocatalyst.

Mass spectra of synthesized amide products

Table 2 in the manuscript

ENTRY 2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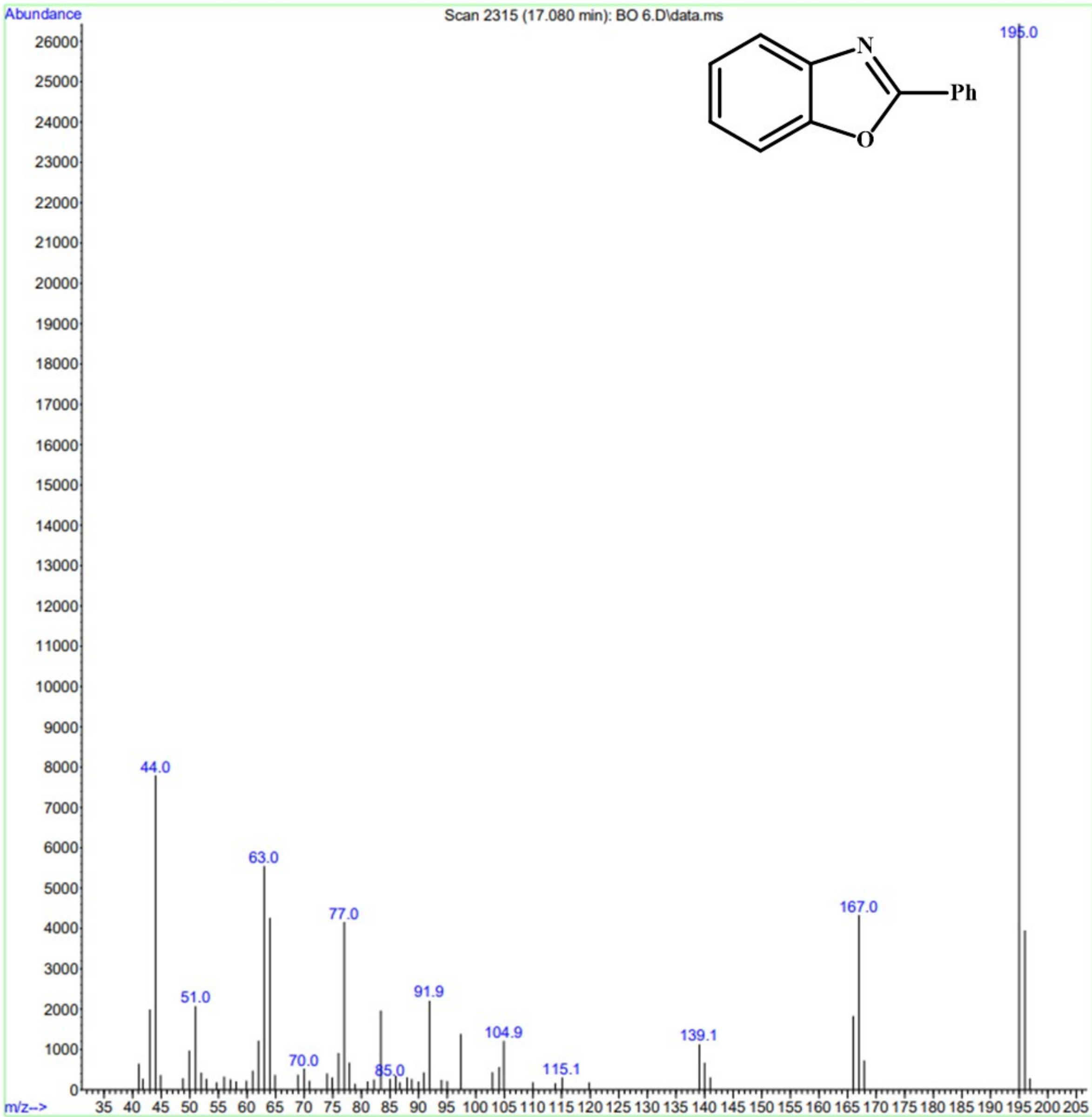
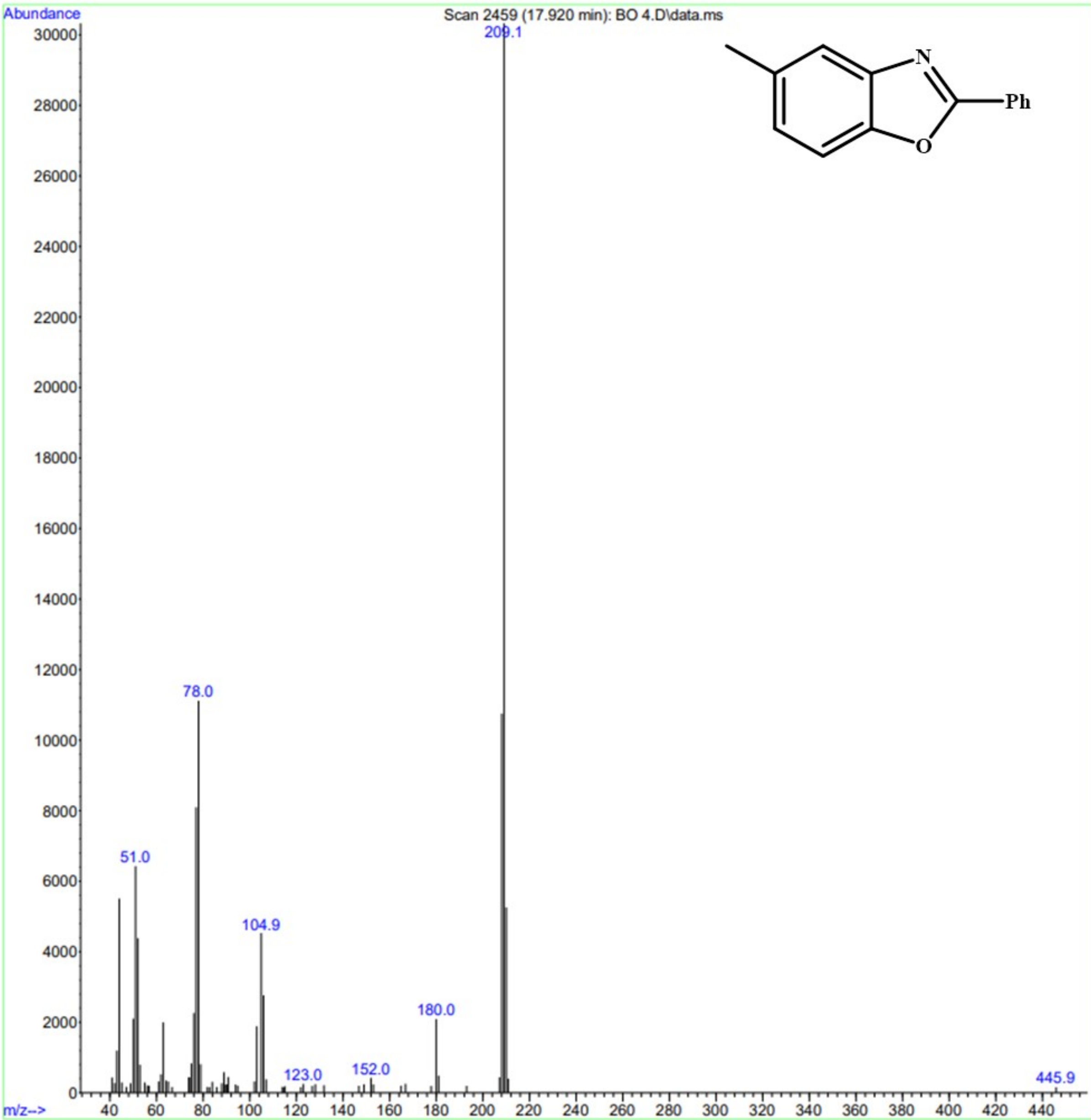
167.0
63.0
104.0
83.9
126.0
446.1
m/z-->
N
O

ENTRY 6



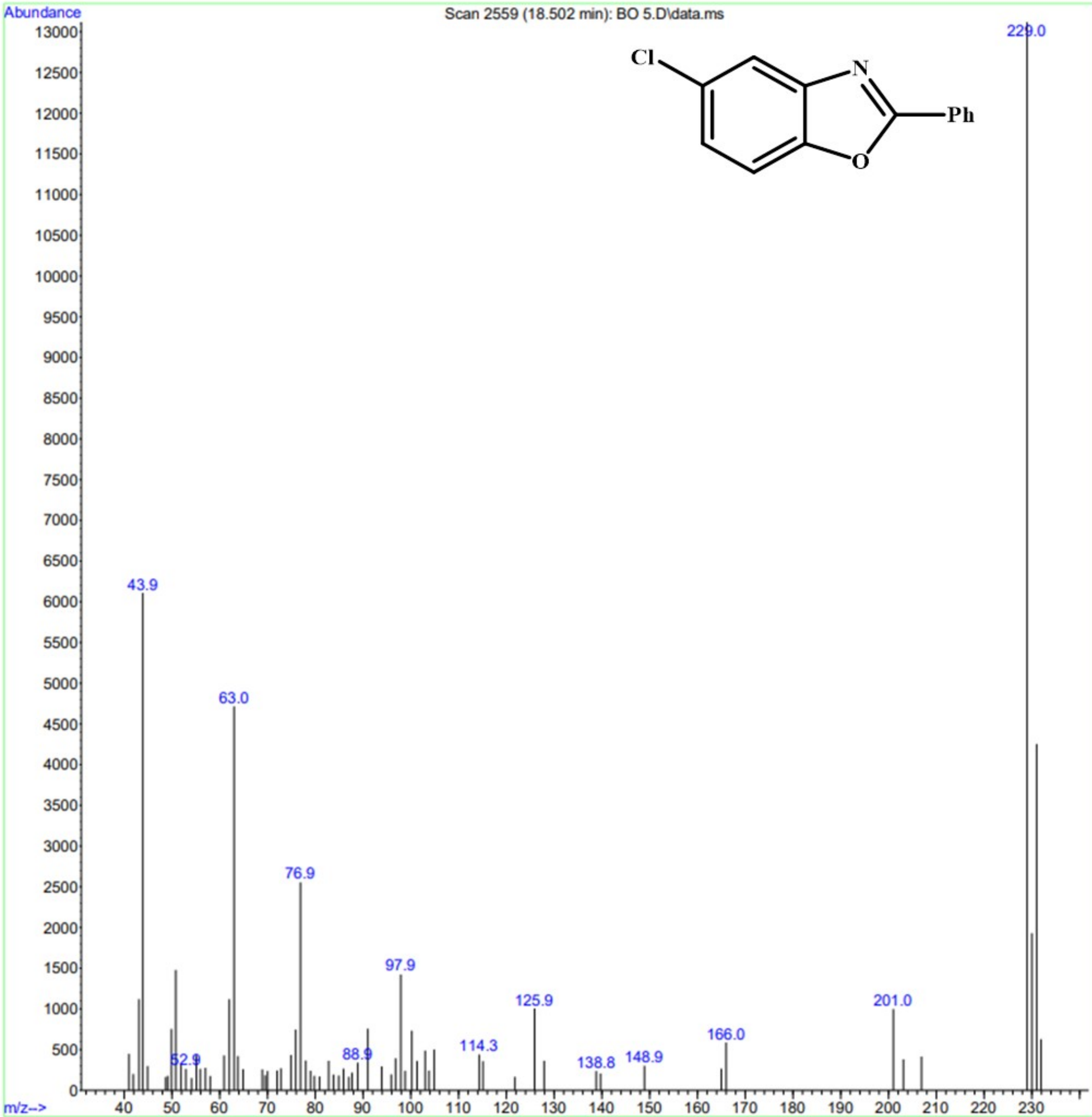
Abundance
Scan 2315 (17.080 min): BO 6.D\data.ms
N
O
Ph
195.0
44.0
63.0
77.0
167.0
51.0
91.9
104.9
70.0
85.0
115.1
139.1
m/z-->

ENTRY 7



Abundance
Scan 2459 (17.920 min): BO 4.D\data.ms
209.1
78.0
51.0
104.9
123.0
152.0
180.0
445.9
m/z-->
N
O
Ph

ENTRY 8


Abundance
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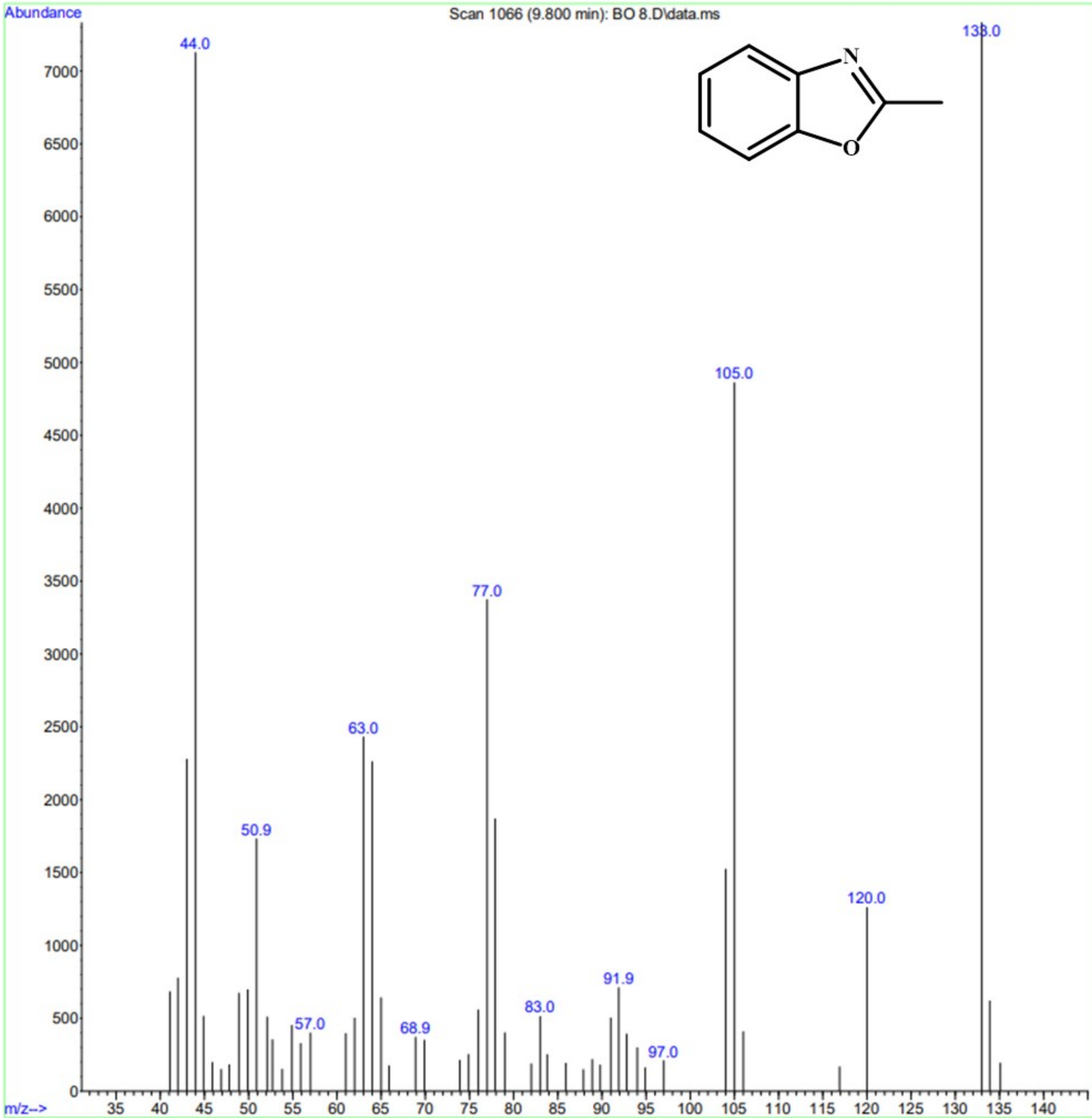
12000
11500
11000
10500
10000
9500
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
229.0
43.9
63.0
76.9
97.9
125.9
201.0
166.0
114.3
88.9
52.9
138.8
148.9
m/z-->
40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
Cl
N
O
Ph

ENTRY 10



References

1. M.S. Mayo, X. Yu, X. Zhou, X. Feng, Y. Yamamoto, M. Bao, *J. Org. Chem.* 2014, **79**, 6310-6314.

2. A. R. Tiwari, B. M. Bhanage, *Org. Biomol. Chem.*, 2016, **14**, 7920-7926.

3. J. Aboonajmi, F. Panahi, M. A. Hosseini, M. Aberi, H. Sharghi, *RSC adv.*, 2022, **12**, 20968-20972.

4. K. Oshimoto, H. Tsuji, M. Kawatsura, *Org. Biomol. Chem*, 2019 **17**, 4225-4229.