SILICA SUPPORTED PERCHLORIC ACID: AN EFFICIENT AND RECYCLABLE CATALYST FOR SYNTHESIS OF BENZIMIDAZOLO[2,3-*b*]QUINAZOLINONES

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Keywords: 2-Aminobenzimidazole; benzimidazolo[2,3-*b*]quinazolinones; heterogeneous catalyst; perchloric acid; silica.

Synthesis of benzimidazolo[2,3-*b*]quinazolinone derivatives has been reported in excellent yields by using silica-supported perchloric acid ($HClO_4$-SiO_2) as a mild and reusable heterogeneous catalyst. The procedure is simple, environmentally benign and has the advantage of high atom economy. Furthermore, the catalyst can be recovered and reused several times efficiently without substantial loss of catalytic activity.

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INTRODUCTION

Heterogeneous catalysis is an interesting area of research from an industrial point of view. It has the advantages of thermal stability, high selectivity, better activity, ease of separation, recyclability and long life.[1-4] Solid acid catalysts play an important role in organic transformations due to many advantages such as simplicity in handling, decreased reactor corrosion problems and more environmentally safe disposal of the catalyst.[5-7] Quinazolinones and their derivatives have been reported to possess interesting pharmacological activities, such as antibacterial,[8-9] antihypertension,[10] antihistaminic,[11] analgesic, anti-inflammatory,[12] anticancer,[13] and anti-HIV.[14] Moreover, a variety of quinazolinones derivatives with different biological activities were synthesized by medicinal chemistry researchers. These derivatives also have a long history of applications in agrochemicals and the pharmaceutical industry as herbicides and active pharmaceuticals. Awareness about environmental hazards in chemical industries becomes a significant concern due to the generation of waste products that leads to the development of environment-friendly synthetic processes. Heterocyclic compounds constitute comprehensive examples in pharmaceutical and chemical industries. Because of their potent physiological properties, they resulted in numerous applications.[15]

Several methods have been reported for the synthesis of substituted benzimidazolo-quinazolinones. The most common method is the reaction of substituted aldehydes with 2-aminobenzimidazole and dimedone using various basic and acidic catalysts under reflux conditions,[15-16] ionic liquids[17] and heteropolyacids.[18]

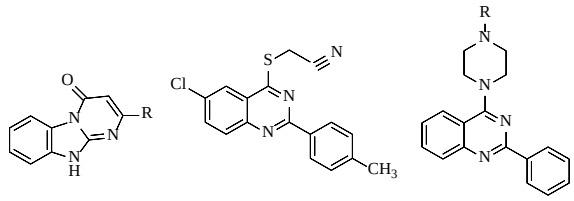
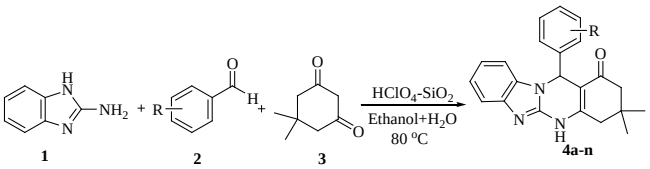


Figure 1. Biologically important quinazolines

All these methods are associated with several limitations such as the use of metal catalysts, harsh reaction conditions, tedious experimental procedure, low yields, prolonged reaction time and use of costly and moisture-sensitive catalyst. Hence, there is a need to develop a rapid, efficient and environmentally benign synthetic procedure for the synthesis of benzimidazole[2,3-*b*]quinazolinone derivatives.

In continuation of previous studies on silica-supported perchloric acid[19-21] herein, we developed an efficient and environment-friendly method for the synthesis of quinazolinone derivatives by the condensation of substituted aldehydes, 2-aminobenzimidazole, and dimedone using silica-supported perchloric acid as a heterogeneous catalyst (Scheme 1).



Scheme 1. Synthesis of benzimidazolo[2,3-*b*]quinazolinones

EXPERIMENTAL

Preparation of $HClO_4$-SiO_2 catalyst:

Aqueous perchloric acid (70 %, 1.8g, 12.5 mmol) was added to a suspension of SiO_2 (230-400 mesh, 23.7 g) in

ether (70 ml). The mixture was concentrated and the residue was heated at 100 °C for 72 h under vacuum to give $HClO_4$-SiO_2 (0.5 mmol g^{-1}) as free-flowing powder.[22]

General procedure: synthesis of 3,3-dimethyl-12-phenyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-one

Silica supported perchloric acid (10 wt.%) was added to a mixture of 2-aminobenzimidazole (1 mmol), aldehyde (1 mmol) and dimedone (1) mmol in 1:1 ethanol: water (5 mL). The reaction mixture was stirred at 80 °C for 20-40 minutes. After completion of the reaction, as monitored by TLC, the reaction mass was filtered. The filtrate was heated to remove the solvent. Separated solid was washed with water and dried under reduced pressure. Furthermore, the separated catalyst was dried and reused.

Similarly, the other derivatives were also synthesized using the same method (Table 1**)**. Spectral data of the synthesized compounds is mentioned below:

3,3-Dimethyl-12-phenyl-1,2,3,4,5,12-hexahydrobenzo[4,5]-imidazo[2,1-*b*]quinazolin-1-one (4a)

M.p. 270-280 °C; IR (KBr): 3350, 2920, 1640, 1620, 1610,1565 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δH= 1.06 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 2.04 (s, 2H, CH_2), 2.30 (s, 2H, CH_2), 6.41 (s, 1H, CH), 6.93-7.38 (m, 9H, Ar-H), 11.12 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(2,4-dichlorophenyl)-1,2,3,4,5,12-hexahydro-benzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4b)

M.p. 315-330 °C; IR (KBr): 3085, 2930, 1615, 1520 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δ H = 1.0 (s, 3H, CH_3), 1.08 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 2.35 (s, 2H, CH_2), 6.90 (s, 1H, CH), 7.25-8.10 (m, 4H, Ar-H), 7.25-8.10 (m, 2H, Ar-H), 8.15 (s, 1H, Ar-H), 911.31 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-bromophenyl)-1,2,3,4,5,12-hexahydroben-zo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4c)

M.p. 295-300 °C; IR (KBr): 3420, 2920, 1640, 1610, 1530 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ H = 0.90 (s,3H, CH_3), 1.05 (s, 3H, CH_3), 2.00 (s, 2H, CH_2), 2.20 (s, 2H, CH_2), 6.42 (s,1H, CH), 6.98-7.88 (m, 8H, Ar-H), 11.00 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-nitrophenyl)-1,2,3,4,5,12-hexahydroben-zo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4d)

M.p. 290-300 °C; IR (KBr): 2869, 1681, 1612, 1518 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δ H = 0.85 (s,3H, CH_3), 1.6 (s, 3H, CH_3), 2.20 (s, 2H, CH_2), 2.28 (s, 2H, CH_2), 6.60 (s, 1H, CH), 7.04-810 (m, 8H, Ar-H), 11.90 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-flurophenyl)-1,2,3,4,5,12-hexahydroben-zo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4e)

M.p.285-295 °C; IR (KBr): 3020, 2915, 1645, 1580, 1330 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ H=1.04 (s,3H, CH_3), 1.07 (s, 3H, CH_3), 2.20 (s, 2H, CH_2), 2.04 (s, 2H, CH_2), 6.49 (s, 1H,CH), 6.90-7.90 (m, 8H, Ar-H), 10.90 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-chlorophenyl)-1,2,3,4,5,12-hexahydroben-zo[4,5]imidazo [2,1-*b*]quinazolin-1-one (4f)

M.p. 285-295 °C; IR (KBr): ν_{max} = 3465, 2945, 1670, 1619, 1560, 1566 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ H = 1.06 (s,3H, CH_3), 1.11 (s, 3H, CH_3), 2.03 (s, 2H, CH_2), 2.40 (s, 2H, CH_2), 6.56 (s, 1H, CH), 6.94-7.53 (m, 8H, Ar-H), 11.27 (s, 1H, NH) ppm**.**

3,3-Dimethyl-12-(2,4,6-methoxyphenyl)-1,2,3,4,5,12-hexahyd-robenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4g)

M.p. 292-302 °C; IR (KBr): 3210, 2969, 1690, 1590, 1312, 1258 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δ H = 1.09 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 2.11 (s, 2H, CH_2), 2.49 (s, 2H, CH_2), 3.69 (s, 3H, OCH_3), 3.75 (s, 6H, OCH_3), 6.30 (s, 1H, CH), 6.55 (s, 2H, Ar-H), 6.73-7.42 (m,4H, Ar-H), 11.01 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-methoxyphenyl)-1,2,3,4,5,12-hexahydro-benzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4h)

M.p. 280-290 °C; IR (KBr): 3243, 2961, 1680, 1641, 1612, 1589, 1566, 1258 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ H =1.03 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.06-2.15 (m, 2H, CH_2), 2.25-250 (m, 2H, CH_2), 3.66 (s, 3H, OCH_3), 6.35 (s, 1H, H-12), 6.73-7.42 (m, 8H, Ar-H), 11.01 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(2,4-methoxyphenyl)-1,2,3,4,5,12-hexa-hydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4i)

M.p. 250-260 °C; IR (KBr): 3085, 2925, 1600, 1575 1262 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δ H =1.06 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.90 (s, 2H, CH_2), 2.45 (s 2H, CH_2), 3.72 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.20 (s, 1H, CH), 6.54-7.44 (m, 3H, Ar-H), 6.58 (t, 1H, Ar-H), 7.44 (d, 1H, Ar-H), 7.00-7.50 (m, 4H, Ar-H), 11.21 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-hydroxyphenyl)-1,2,3,4,5,12-hexahyd-robenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4j)

M.p. 270-275 °C; IR (KBr): 3469, 2962, 1574, 1264 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz):δ H = 1.06 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 2.04 (s, 2H, CH_2), 2.43 (s, 2H, CH_2), 6.19 (s, 1H, CH), 6.60-7.35 (m, 8H, Ar-H), 8-9.32 (s, 1H, OH), 11.01 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(3-hydroxyphenyl)-1,2,3,4,5,12-hexahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4k)

M.p.287-292 °C; IR (KBr): 3090, 2950, 1572, 1249 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δ H =1.07 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 1.95 (s, 2H, CH_2), 2.50 (s, 2H, CH_2), 6.23 (s, 1H, CH), 6.69-7.00 (m, 3H, Ar–H), 7.10 (t, J = 7.90, Hz, 1H, Ar-H), 7.52 (d, J = 5.69, Hz, 1H, Ar-H), 7.30-7.70 (m, 4H, Ar-H), 9.20 (s, 1H, OH), 11.30 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(4-methylphenyl)-1,2,3,4,5,12-hexahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4l)

M.p. 260-270 °C; IR (KBr): 3085, 2930, 1570, 1253 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz):δ H = 1.10 (s,3H, CH_3), 1.12 (s, 3H, CH_3), 2.15 (s, 2H, CH_2), 2.40 (s, 2H, CH_2), 2.70 (s, 3H, CH_3), 6.35(s, 1H, H-12), 6.60-7.35 (m, 8H, Ar-H), 11.01 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(2-nitrophenyl)-1,2,3,4,5,12-hexahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4m)

M.p.275-280 °C; IR (KBr): 3400, 2995, 1589, 1320 1258, 749 cm^{-1}; ^{1}H NMR (DMSO-d_6, 300 MHz): δ H = 1.07 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 2.70 (s, 2H, CH_2), 6.45 (s, 1H, CH), 7.05 (d, 1H, Ar-H), 7.20-7.35 (m, 1H, Ar-H), 7.15-7.44 (m, 1H, Ar-H), 7.15-7.44 (m, 1H, Ar-H), 7.44 (d, J = 8.15 Hz, 1H, Ar-H), 7.50-7.90 (m, 4H, Ar-H), 11.29 (s, 1H, NH) ppm.

3,3-Dimethyl-12-(2-methoxyphenyl)-1,2,3,4,5,12-hexahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1-one (4n)

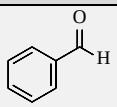
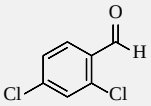
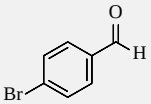
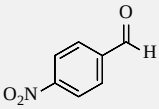
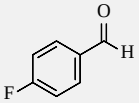
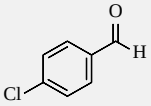
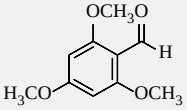
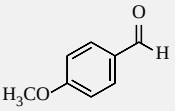
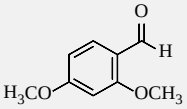
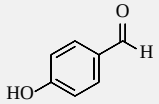
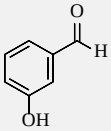
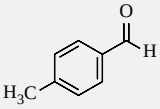
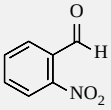
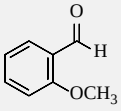
M.p. 245-255 °C; IR (KBr): 3089, 2895, 1590, 1248, 740 cm^{-1}; ^{1}H-NMR (DMSO-d_6, 300 MHz): δH=1.09 (s,3H, CH_3), 1.14 (s, 3H, CH_3), 1.99 (s, 2H, CH_2), 2.45 (s, 2H, CH_2), 3.72 (s, 3H, OCH_3), 6.29 (s, 1H, CH), 6.90-7.44 (m, 4H, Ar-H), 7.15-7.64 (m, 4H, Ar-H), 11.27 (s, 1H, NH) ppm.

RESULTS AND DISCUSSION

We developed a new method for the synthesis of benzimidazolo[2,3-*b*]quinazolinone derivatives in good yields by using $HClO_4$-SiO_2 as a mild and reusable heterogeneous catalyst in water:ethanol (1:1) solvent. The procedure is environment-friendly, operationally simple and thus has the advantage of high atom economy. Furthermore, the catalyst can be recovered and reused several times efficiently without substantial loss of activity. We also studied the reaction in aqueous medium only, but the reaction proceeded very slowly and the product formation was also very poor. When we used ethanol:water (1:1) solvent system, the reaction proceeded faster with a high yield of the corresponding product.

The effect of temperature on yield of the product **4a** was studied by carrying the reactions at different temperatures (30, 55, 80 and 100 °C) as shown in Table 2. By raising the reaction temperature from room temperature to 100 °C gradually, the yield of reactions was found to be increased.

Table 1. Synthesis of 3,3-dimethyl-12-(un)substituted phenyl-3,4,5,12-tetrahydrobenzo[4,5]imidazo[2,1-*b*]quinazolin-1(2*H*)-ones using silica supported perchloric acid.

Entry	Aldehydes (2)	Products (4)	Time (min)	Yield (%)
1		**4a**	30	85
2		**4b**	30	90
3		**4c**	40	85
4		**4d**	20	80
5		**4e**	25	75
6		**4f**	25	90
7		**4g**	30	80
8		**4h**	20	90
9		**4i**	25	90
10		**4j**	35	75
11		**4k**	30	90
12		**4l**	20	90
13		**4m**	25	90
14		**4n**	20	90

Reaction conditions: Aldehyde (1.0 mmol), dimedone (1.0 mmol), 2-aminobenzimidazole (1.0 mmol), $HClO_4$–SiO_2 (10 wt%) 20-40 min reflux.

At 80 ˚C temperature, the reaction completed in 25 minutes affording 90 % of product yield. Similarly, increasing the reaction temperature to 100 ºC does not affect the yield of the product significantly. Thus, we confirmed that 80 ºC was the optimum temperature for the transformation. Under these optimized conditions, various aldehydes were reacted with dimedone and aminobenzimidazoles, whose results are summarized in Table 1.

Table 2. Effect of temperature on the preparation of 3,3-dimethyl-12-phenyl-1,2,3,4,5,12-hexahydrobenzo[4,5]-imidazo[2,1-*b*]quinazolin-1-one (**4a**)

Entry	Temp., ºC	Time, min	Yield, %[@]
1	30	240	40
2	50	60	70
3	80	25	90
4	100	25	90

[@]Reactions performed in case of 4-chlorobenzaldehyde

Reusability of the catalyst

Solid silica-based perchloric acid works under heterogeneous conditions. It is an inexpensive and non-hazardous solid acid catalyst which can be easily handled and separated from the reaction mixture by simple filtration. The recovered catalyst was reused thrice for consecutive runs with a minimum variation of yields of the products. After completion of the reaction, the catalyst was filtered, thoroughly washed with ethanol and dried at 100 ºC for 2 hr and reused for subsequent runs (Table 3). This reusability demonstrates the high stability and turnover of solid silica-based perchloric acid under operating conditions.

Table 3.-Reusability of catalyst for the synthesis of 3,3-dimethyl-12-phenyl-1,2,3,4,5,12-hexahydrobenzo[4,5]-imidazo[2,1-*b*]quinazolin-1-one (**4a**)

Entry	Number of recycling	Time, min	Yield, %[@]
1	Fresh	40	90
2	First	45	88
3	Second time	60	88
4	Third time	70	85

[@]Yields in case of 4-chlorobenzaldehyde

CONCLUSION

A convenient method has been developed by the reaction of 2-aminobenzimidazole, dimedone and aldehyde catalyzed by the silica-supported perchloric acid catalyst. Use of inexpensive and reusable catalyst, enhanced reaction rates, readily available starting materials, high yield and easy purification of the products are the key features of this method.

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