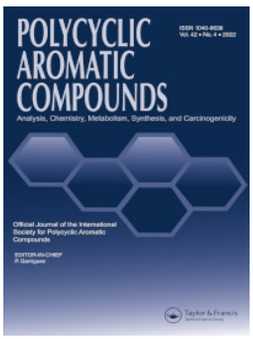

Polycyclic Aromatic Compounds

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gpol20

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To cite this article: Yuvaraj P. Sarnikar, Yogesh D. Mane, Smita S. Patil, Santosh M. Surwase, Radhakrishnan M. Tigote & Bhimrao C. Khade (2022): $(C_6F_5)_3B$ Catalyzed One-Pot Synthesis of Benzo[b]Cyclopenta[e][1,4]Oxazin-2(1H)-One and Thiazin-2(1H)-One Derivatives from Furan-2-yl(Phenyl)Methanol and 2-Aminophenol/Thiophenol, Polycyclic Aromatic Compounds, DOI: 10.1080/10406638.2022.2089173

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ABSTRACT

An efficient $(C_6F_5)_3B$ catalyzed method has been developed for the synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one and thiazin-2(1H)-one derivatives from furan-2-yl(phenyl)methanol (**1**) and 2-aminophenol/thiophenol (**2**) under reflux in acetonitrile. This reaction proceeds through an aza-Piancatelli rearrangement/Michael reaction in one-pot. This strategy provides a facile and rapid access to benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one and thiazin-2(1H)-one derivatives (**3a-l**) in good to high yields under mild conditions. Several advantages, such as simple reaction procedure, low catalyst loading, broad substrate scope, easy product isolation, high functional group tolerance, and short reaction time make this strategy more attractive.

ARTICLE HISTORY
Received 28 February 2022
Accepted 29 May 2022

KEYWORDS
Benzo[b][1,4]oxazine; Benzo[b][1,4]thiazine; Tris(pentafluorophenyl)Borane (BCF); Piancatelli rearrangement

Introduction

Benzo[b][1,4]oxazine/thiazine is the most prevalent heterocycle unit found in many biologically potent molecules.[1] They exhibit aldose reductase inhibitory activity[2] and potential therapeutic properties.[3] In particular substituted Benzo[b][1,4]oxazines exhibit a plethora of bioactivities[4–8] including antitumor, antiviral, antimycobacterial, antidiabetic, anti-inflammatory, anti-candidaalbicans, antifungal, antagonism to progesterone, kinase inhibitory, hypolipidaemic and CNS depressant. Benzo[b][1,4]oxazine/thiazine skeleton is a fascinating key structural motif in many drug molecules (Figure 1). Hence, the development of efficient synthetic methodologies for the synthesis of benzo[b][1,4]oxazine/thiazine is of great importance in the scientific domain.

Although benzo[b][1,4]oxazines/thiazines are bioactive, very few synthetic methods have been reported for the synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one.[9] In 2012, Reddy et al disclosed $In(OTf)_3$ catalyzed one pot synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one from furan-2-yl(phenyl)methanol and 2-aminophenol/thiophenol.[10]

Although above reported synthetic approach is significant, it makes use of $In(OTf)_3$ which is hygroscopic and irritating to eyes, skin and respiratory system. Considering the limitations of

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Supplemental data for this article can be accessed online at https://doi.org/10.1080/10406638.2022.2089173.

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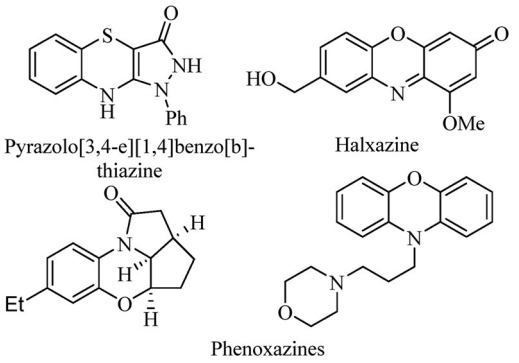


Figure 1. Biologically active Benzo[b][1,4]oxazines and thiazines.

above reported methods, a safe, efficient, affordable and environmentally benign strategy for the synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one is highly desirable. To the best of knowledge, no $B(C_6F_5)_3$ catalyzed synthetic methodology has ever been reported for the synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one by using furan-2-yl(phenyl)methanol and 2-aminophenol/thiophenol. Moderate Lewis acidic nature of Tris(pentafluorophenyl)Borane (BCF) facilitates it's usage in organic synthesis. In recent times, BCF has evolved as a mild, nontoxic, environmentally benign, moisture-tolerant, air-stable, heat-stable, inherently electrophilic, moderate and versatile Lewis acid imparting high chemo-, region- and stereoselectivity in many organic transformation.[11–18] Low catalytic loading and moisture-tolerance, makes BCF superior acid catalyst than traditional Lewis acids. In this paper, we report facile and convenient $B(C_6F_5)_3$ catalyzed synthetic method for the synthesis of a series of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one derivatives from furan-2-yl(phenyl)methanol and 2-aminophenol/thiophenol in acetonitrile as a solvent.

Materials and methods

General information

Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. Melting points were determined in open capillary tubes and are uncorrected. Formation of the compounds was checked by TLC on silicagel-G plates of 0.5 mm thickness and spots were located by iodine and UV light. All compounds were purified by recrystallization/silicagel (100-200 mesh) gravity column with suitable organic solvents. Mass spectra were recorded on Shimadzu GC-MS-QP-2010 model using direct inlet probe technique. ^{1}H NMR and ^{13}C NMR were recorded in $CDCl_3$ and DMSO-d_6 solution on a Bruker Ac 300 or 500 MHz spectrometer. The results are in agreement with the assigned structures. Satisfactory microanalysis was obtained on Flash EA1112 CHN analyzer.

General procedures for synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one and thiazin-2(1H)-one (3a-l)

A mixture of furan-2-yl(phenyl)methanol (**1**, 1.2 mmol), 2-aminophenol (**2**, 1 mmol) in acetonitrile (4 mL) and $(C_6F_5)_3B$ (10 mol%) was refluxed for a specified time required to complete the reaction. After complete conversion, as indicated by TLC, the reaction was stopped by adding water and the reaction mass was extracted with EtOAc twice. Product containing EtOAc was washed with saturated aqueous NaCl solution and water was removed by adding solid anhydrous sodium sulfate. Solvent was removed on vacuum, and crude reaction mixture was purified on

column chromatography by using silica gel with ethyl acetate-hexane in the ratio 3:7 to obtain benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-ones and thiazin-2(1H)-ones derivatives (**3a-l**).

7-Chloro-1-phenyl-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3a). White solid, 82% Yield, mp 136-138 ^{0}C; IR (cm^{-1}) 3394, 2920, 2098, 1738, 1598, 1495, 1275, 1119, 1015, 745; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.36 (t, $J = 7.9$ Hz,2H), 7.30 (t, $J = 7.2$ Hz,1H),7.08 (d, $J = 7.2$ Hz, 2H), 6.82 (d, $J = 8.7$ Hz, 1H), 6.64 (dd, $J = 7.9$, 2.4 Hz, 1H), 6.56 (d, $J = 2.4$ Hz, 1H) ,4.62(t, $J = 3.9$ Hz, 1H),4.26-4.10 (brs, 1H), 4.08-4.00(m, 1H) 3.47 (d, $J = 10.3$ Hz, 1H), 2.92 (d, $J = 19.1$, Hz, 1H), 2.72 (dd, $J = 19.1$, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.1, 140.6, 135.4, 131.1, 129.1, 128.8, 127.7, 127.1, 118.4, 118.2, 114.5, 70.5, 58.5, 58.2, 45.4; MS (ESI): m/z: 298 $[M+1]^+$; Anal. Calc. For $C_{17}H_{14}ClNO_2$: C, 68.11%, H, 4.70%, N, 4.67%; Found: C, 68.04%, H, 4.59%, N, 4.60%.

7-Chloro-1-(4-fluorophenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3 b). White solid, 78% Yield, mp 140-142 ^{0}C; IR (cm^{-1}) 3402, 3016, 2922, 1745, 1606, 1495, 1384, 1281, 1160, 1083, 990, 879, 754; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.02 (d, $J = 6.8$ Hz, 4H), 6.76 (d, $J = 9.1$ Hz, 1H), 6.62 (dd, $J = 8.3$, 2.3 Hz, 1H), 6.55 (d, $J = 2.3$ Hz, 1H), 4.54 (t, $J = 3.0$ Hz, 1H), 4.51-4.24 (brs, 1H), 3.99 (dd, $J = 10.5$, 3.0 Hz, 1H), 3.42 (d, $J = 10.5$ Hz, 1H) , 2.86 (d, $J = 19.6$ Hz, 1H), 2.66 (dd, $J = 18.8$, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.2, 163.8, 160.5, 140.5, 131.0, 130.4, 130.3, 127.1, 118.3, 118.2, 116.1, 115.8, 114.5, 70.3, 58.3, 57.5, 45.2; MS (ESI): m/z: 318 $[M+1]^+$; Anal. Calc. For $C_{17}H_{13}ClNO_2F$: C, 68.34%, H, 4.38%, N, 4.68%; Found: C, 68.29%, H, 4.32%, N, 4.58%.

6-Methyl-1-phenyl-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3c). White solid, 75% Yield, mp 163-165 ^{0}C; IR (cm^{-1}) 3390, 3053, 2915, 2857, 1753, 1642, 1527, 1463, 1295, 1241, 1121, 1038, 759; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.55 (dd, $J = 6.0$, 2.3 Hz, 1H), 7.44-7.34 (m, 2H), 7.32-7.25 (m, 2H), 7.05 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.82-6.65 (m, 2H), 4.72-4.65 (m, 1H), 4.35 (t, $J = 3.0$ Hz, 1H), 3.76 (dd, $J = 11.3$, 3.0 Hz, 1H), 3.34(d, $J = 10.5$ Hz, 1H), 2.84-2.75 (m, 1H), 2.64 (dd, $J = 18.8$, 4.5 Hz, 1H), 2.25 (s,3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.3, 161.7, 142.9, 137.8, 136.3, 135.6, 129.5, 128.9, 128.8, 127.7, 122.9, 117.9, 116.5, 69.7, 56.9, 56.6, 46.1,20.3; MS (ESI): m/z: 280 $[M+1]^+$; Anal. Calc. For $C_{18}H_{17}O_2N$: C, 77.39%, H, 6.13%, N, 5.01%; Found: C, 77.33%, H, 6.04%, N, 4.91%.

1-(4-Fuorophenyl)-6-methyl-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3d). White solid, 76% Yield, mp 140-142 ^{0}C; IR (cm^{-1}) 3396, 2923, 2855, 1741, 1597, 1509, 1293,1229 1155, 1020, 808, 758; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.06 (d, $J = 6.9$ Hz, 4H), 6.74 (s, 1H), 6.66 (d, $J = 7.9$ Hz, 1H), 6.54 (d, $J = 7.9$ Hz, 1H), 4.66 (t, $J = 2.9$ Hz, 1H), 3.98 (d, $J = 7.9$ Hz, 1H), 3.50 (d, $J = 10.8$ Hz, 1H) , 2.91 (d, $J = 19.8$ Hz, 1H), 2.67 (dd, $J = 19.8$, 4.9 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.6, 163.9, 131.2, 130.4, 130.3, 128.7, 123.1, 117.6, 116.0, 115.8, 115.2, 70.4, 58.8, 56.9, 45.4, 20.6; MS (ESI): m/z: 298 $[M+1]^+$; Anal. Calc. For $C_{18}H_{16}FO_2N$: C, 72.71%, H, 5.42%, N, 4.71%; Found: C, 72.65%, H, 5.39%, N, 4.63%.

1-(4-Fluorophenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3e). White solid, 83% Yield, mp 138-140 ^{0}C; IR (cm^{-1}) 3433, 3026, 2918, 1739, 1603, 1305, 1216, 1119, 838, 732; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.06 (d, $J = 6.8$ Hz, 4H), 6.94-6.81 (m, 2H), 6.75 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.65 (dd, $J = 7.5$, 1.5 Hz, 1H), 4.64 (t, $J = 3.8$ Hz, 1H), 4.20-4.08 (brs, 1H) , 4.04 (d, $J = 10.6$ Hz, 1H), 3.55 (d, $J = 10.5$ Hz, 1H) , 2.93 (d, $J = 18.1$ Hz, 1H), 2.71 (dd, $J = 18.8$, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.4, 163.7, 160.4, 142.2, 131.2, 130.5, 130.5, 129.8, 122.4, 118.6, 117.1, 116.2, 115.6, 115.4, 70.1, 58.6, 57.4, 45.4; MS (ESI): m/z: 284 $[M+1]^+$;

Anal. Calc. For $C_{17}H_{16}FO_2N$: C, 71.56%, H, 5.65%, N, 4.91%; Found: C, 71.51%, H, 5.60%, N, 4.87%.

2-(2,4-Dichloro-benzyloxymethyl)-2-imidazol-1-ylmethyl-indan-1-one (3f). White solid, 84% Yield, mp 127-129 ^{0}C; IR (cm^{-1}) 3385, 2925, 2853, 1744, 1606, 1250, 1126, 1029, 757; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.01 (d, $J = 8.7$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 6.78 (d, $J = 8.5$ Hz, 1H), 6.70-6.60 (m, 1H), 6.58 (d, $J = 2.3$ Hz, 1H), 4.60 (t, $J = 3.7$ Hz, 1H), 4.42-4.12 (brs, 1H) , 3.99 (dd, $J = 10.$ 7, 3.0 Hz, 1H), 3.79 (s, 3H) , 3.41 (d, $J = 10.5$ Hz, 1H), 2.87 (d, $J = 19.1$ Hz, 1H), 2.68 (dd, $J = 19.1$, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.5, 163.7, 160.4, 144.2, 131.2, 130.5, 130.5, 129.8, 122.4, 118.6, 117.1, 116.2, 115.6, 115.4, 70.1, 58.6, 57.4, 44.4; MS (ESI): m/z: 330 $[M+1]^+$; Anal. Calc. For $C_{18}H_{16}ClO_3N$: C, 65.55%, H, 4.89%, N, 4.24%; Found: C, 65.52%, H, 4.80%, N, 4.20%.

1-(4-Methoxyphenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3 g). White solid, 90% Yield, mp 119-121 ^{0}C; IR (cm^{-1}) 3385, 2922, 2841, 1738, 1608, 1249, 1026, 826, 748; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.04 (d, $J = 9.1$ Hz, 2H), 6.94-6.82 (m, 4H), 6.74 (dd, $J = 7.5$, 1.5 Hz, 1H), 6.62 (dd, $J = 7.5$, 1.5 Hz, 1H), 4.64(t, $J = 3.7$ Hz, 1H),4.02 (dd, $J = 10.5$, 2.3 Hz, 1H), 3.82 (s, 3H) , 3.46 (d, $J = 10.5$ Hz, 1H), 2.88 (d, $J = 18.8$, Hz, 1H), 2.67 (dd, $J = 18.8$, 4.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.0, 158.8, 142.2, 130.2, 129.8, 127.4, 122.5, 118.5, 117.2, 115.2, 114.2, 70.4, 58.7, 57.4 55.1, 45.4; MS (ESI): m/z: 297 $[M+1]^+$; Anal. Calc. For $C_{18}H_{17}O_3N$: C, 73.20%, H, 5.80%, N, 4.74%; Found: C, 73.10%, H, 5.71%, N, 4.68%.

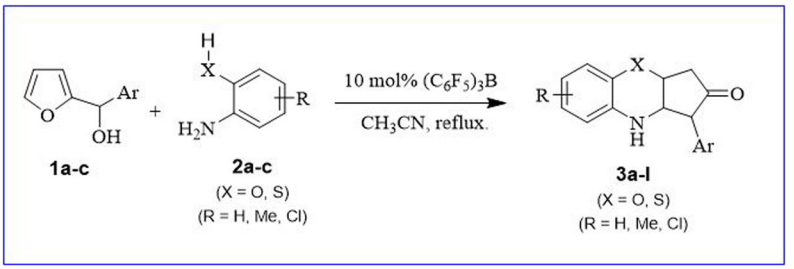
1-(4-Methoxyphenyl)-6-methyl-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4] oxazin2(1H)-one (3 h). White solid, 80% Yield, mp 127-129 ^{0}C; IR (cm^{-1}) 3396, 3014, 2925, 1745, 1612, 1512, 1460, 1297, 1251, 1124, 1024, 757; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.97 (d, $J = 8.8$ Hz, 2H), 6.87 (d, $J = 7.7$ Hz, 2H), 6.68 (s, 1H), 6.65 (d, $J = 7.7$ Hz, 1H), 6.48 (d, $J = 8.8$ Hz, 1H), 4.58 (t, $J = 3.1$ Hz, 1H), 3.94 (dd, $J = 11.0$, 2.2 Hz, 1H), 3.78 (s, 3H) , 3.43 (d, $J = 10.7$ Hz, 1H), 2.84 (d, $J = 18.7$ Hz, 1H), 2.63 (dd, $J = 18.7$, 4.4 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.1, 159.0, 142.1, 134.1, 129.8, 128.6, 127.6, 127.3, 122.9, 117.6, 115.4, 114.5, 70.6, 58.7, 56.9, 55.4, 45.5, 20.5; MS (ESI): m/z: 310 $[M+1]^+$; Anal. Calc. For $C_{19}H_{19}O_3N$: C, 73.76%, H, 6.19%, N, 4.52%; Found: C, 73.69%, H, 6.13%, N, 4.48%.

7-Chloro-1-(3,4,5-trimethoxyphenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3i). White solid, 89% Yield, mp 169-171 ^{0}C; IR (cm^{-1}) 3346, 2930, 2836,1744, 1593, 1500, 1456, 1419, 1297, 1387, 1343, 1244, 1123, 997, 910, 876, 728; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.80 (d, $J = 8.8$ Hz, 1H), 6.62 (d, $J = 7.7$ Hz, 2H), 6.20 (s, 2H), 4.30 (d, $J = 7.7$ Hz, 2H), 4.0 (d, $J = 8.8$ Hz, 1H), 3.80 (s, 9H), 3.4 (d, $J = 11.0$, 1H), 2.9 (d, $J = 11.0$, 3H) , 2.7 (d, $J = 10.7$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.3, 153.4, 140.5, 137.2, 131.5, 131.0, 127.1, 118.0, 117.8, 114.2, 105.7, 70.3, 60.6, 58.7, 58.2, 55.9, 45.2; MS (ESI): m/z: 390 $[M+Na]^+$; Anal. Calc. For $C_{20}H_{20}ClO_5N$: C, 61.61%, H, 5.17%, N, 3.59%; Found: C, 61.52%, H, 5.10%, N, 3.53%.

1-(3,4,5-Trimethoxyphenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (3j). White solid, 85% Yield, mp 174-176 ^{0}C; IR (cm^{-1}) 3382, 2935, 2839, 2250, 1744, 1701, 1588, 1502, 1485, 1419, 1310, 1247, 1126, 1002, 911, 833, 734, 647; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.02-6.88 (m, 4H), 6.52(s, 2H), 4.8 (brs, 1H), 4.55-4.46 (m, 1H), 4.10-4.02 (m, 1H) , 3.82 (s, 9H), 3.61-3.53 (m, 1H), 2.84 (d, $J = 18.7$ Hz, 1H), 2.63 (dd, $J = 18.7$, 4.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.7, 155.6, 142.1, 137.4 122.5, 118.7, 117.3, 115.1, 105.8, 104.7, 70.2, 60.7, 58.6, 58.5, 56.1, 51.1, 45.5, 44.7; MS (ESI): m/z: 378 $[M+1]^+$; Anal. Calc. For $C_{20}H_{21}O_5N$: C, 67.59%, H, 5.95%, N, 3.94%; Found: C, 67.53%, H, 5.89%, N, 3.87%.

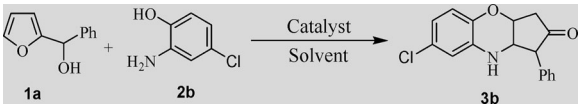
1-(4-Fluorophenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]thiazin-2(1H)-one (3k). White solid, 85% Yield, mp 140-141 ^{0}C; IR (cm^{-1}) 3476, 2937, 2834, 1758, 1542, 1539, 1364, 1215, 1137, 1043, 854, 728; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.28 (d, $J = 1.3$ Hz, 4H), 7.21 (d, $J = 6.7$ Hz, 4H), 7.04 (t, $J = 7.1$ Hz, 1H), 6.60 (t, $J = 7.4$ Hz, 1H), 6.43 (d, $J = 7.6$ Hz, 1H), 4.22 (brs, 1H), 4.20-4.14 (m, 1H) , 3.71 (t, $J = 5.6$ Hz, 1H), 3.62 (d, $J = 10.2$ Hz, 1H) , 2.58 (d, $J = 19.2$ Hz, 1H), 2.46 (dd, $J = 19.2$, 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 216.6, 164.3, 168.3, 147.6, 132.5, 131.3, 130.6, 128.8, 125.1, 119.4, 117.4, 116.2, 114.2, 113.4, 58.2, 57.5, 43.2, 36.4; MS (ESI): m/z: 300 $[M+1]^{+}$; Anal. Calc. For $C_{17}H_{14}FSNO$: C, 68.20%, H, 4.71%, N, 4.67%; Found: C, 68.12%, H, 4.64%, N, 4.61%.

1-(4-Methoxyphenyl)-3,3a,9,9a-tetrahydrobenzo[b]cyclopenta[e][1,4]thiazin-2(1H)-one (3l). White solid, 85% Yield, mp 118-120 ^{0}C; IR (cm^{-1}) 3372, 2946, 2854, 1774, 1558, 1467, 1262, 1146, 1038, 746; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.32 (d, $J = 7.4$ Hz, 1H), 7.14 (d, $J = 8.3$ Hz, 2H) 6.76 (t, $J = 8.4$ Hz, 1H), 6.68 (d, $J = 8.2$ Hz, 1H), 6.54 (t, $J = 7.4$ Hz, 1H), 6.36 (d, $J = 8.2$ Hz, 1H), 4.18 (brs, 1H), 4.14-4.10 (m, 1H), 3.67 (s, 3H) , 3.48 (m, 1H), 3.40 (d, $J = 10.1$ Hz, 1H), 2.62 (dd, $J = 18.1$, 6.4 Hz, 1H), 2.41 (d, $J = 18.1$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 216.6, 162.7, 141.2, 131.4, 127.7, 125.3, 121.2, 117.6, 116.8, 114.3, 113.2, 68.6, 55.3, 56.6, 55.6, 44.1; MS (ESI): m/z: 310 $[M+1]^{+}$; Anal. Calc. For $C_{18}H_{17}SNO_2$: C, 69.42%, H, 5.50%, N, 4.49%; Found: C, 69.35%, H, 5.41%, N, 4.43%.



Scheme 1. Synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one and thiazin-2(1H)-one Derivatives (**3a-l**)

Table 1. Screening of reaction conditions.[a]



Entry.	Catalyst (10 mol %)	Solvent	Time (hr)	Yield (%)[b]
1	–	CH_3CN	6 h	–
2	$CeCl_3.7H_2O$	CH_3CN	4 h	42
3	$InBr_3$	CH_3CN	4 h	60
4	$InCl_3$	CH_3CN	4 h	55
5	Fe_3O_4	CH_3CN	3 h	32
6	$NbCl_5$	CH_3CN	3 h	–
6	$HClO_4$-SiO_2	CH_3CN	4 h	30
7	H_2SO_4-SiO_2	CH_3CN	4 h	30
8	Fe_3O_4-SiO_2	CH_3CN	4 h	25
9	$(C_6F_5)_3B$	CH_3CN	2 h	90
10	$(C_6F_5)_3B$	Toluene	4 h	45
11	$(C_6F_5)_3B$	THF	4 h	40
12	$(C_6F_5)_3B$	DCM	4 h	45

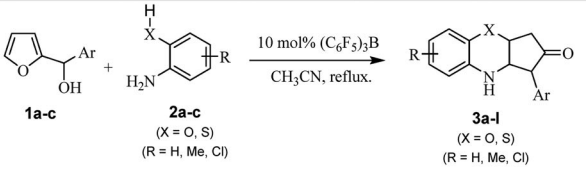
[a] Reaction conditions; 1a (1.2 mmol), 2 b (1 mmol), catalyst (10 mol%), solvent (4 ml), under reflux; [b] Isolated yields

Results and discussion

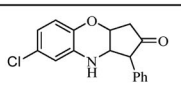
The required starting substrate furan-2-yl(phenyl)methanol (**1a**) was prepared by using the procedures mentioned in the literature.[19] We first attempted the reaction of furan-2-yl(phenyl)methanol (**1a**) with 2-amino-4-chlorophenol (**2a**) in the presence of 10 mol% $(C_6F_5)_3B$ in acetonitrile (Scheme 1). To our delight, the reaction proceeded smoothly at reflux to furnish the desired product benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one (**3a**) in 86% yield. To optimize reaction conditions, above reaction was carried out by changing different reaction parameters such as catalysts, solvents, molar ratio of reactants and temperature. Among the various used catalysts such as $InCl_3$, $InBr_3$, $HClO_4$-SiO_2, H_2SO_4-SiO_2, Fe_3O_4-SiO_2, $CeCl_3.7H_2O$, $NbCl_5$, Fe_3O_4, Fe_3O_4-SiO_2 and $(C_6F_5)_3B$, 10 mole% of $(C_6F_5)_3B$ was found to give best results in CH_3CN under reflux in 2-4 hrs (Table 1). Furthermore, none of the benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one was detected in the absence of $(C_6F_5)_3B$ catalyst under reflux in CH_3CN (entry 9, Table 1). Next we examined the effect of various solvents such as 1,1-dichloromethane, tetrahydrofuran, toluene and acetonitrile. Among these solvents, acetonitrile was found to give the best results (entry 9, Table 1). Hence, 10 mol% of $(C_6F_5)_3B$ in acetonitrile is efficient for this

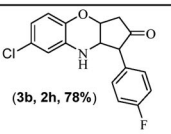
Table 2. Substrate scope for synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/ thiazin-2(1H)-one.[a]

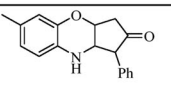
Substrate scope for synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/ thiazin-2(1H)-one [a]

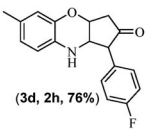


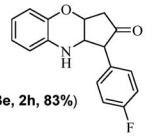
1a-c **2a-c** (X = O, S) (R = H, Me, Cl) **3a-l** (X = O, S) (R = H, Me, Cl)

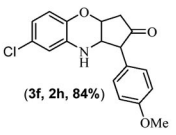

(3a, 2h, 92%)

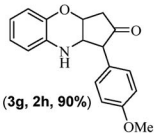

(3b, 2h, 78%)

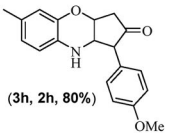

(3c, 2h, 75%)

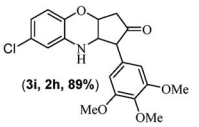

(3d, 2h, 76%)

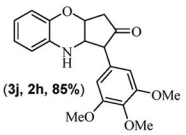

(3e, 2h, 83%)

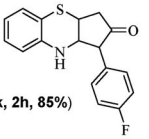

(3f, 2h, 84%)

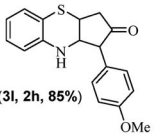

(3g, 2h, 90%)


(3h, 2h, 80%)

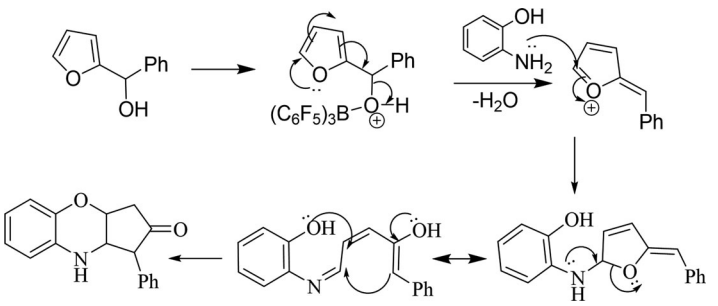

(3i, 2h, 89%)


(3j, 2h, 85%)


(3k, 2h, 85%)


(3l, 2h, 85%)

[a] All products were purified by column chromatography to determine the yield and characterized by ^1H & ^{13}C NMR, IR and mass spectroscopy



Scheme 2. Mechanism for $(C_6F_5)_3B$ catalyzed synthesis of **3a-l**

conversion. Under the above optimized reaction conditions, we examined the scope of $(C_6F_5)_3B$ catalyzed synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one from substituted furan-2-yl(phenyl)methanol (**1 b-c**) and substituted 2-aminophenol/thiophenol (**2 b-c**) and the results are shown below (Table 2).

We studied the reactivity of various 2-aminophenols/thiophenols with furan-2-yl(aryl)methanol derivatives. The scope of the reaction is illustrated with respect to various substrates and the results are summarized in Table 2. From Table 2 it is cleared that halogenated 2-aminophenols took shorter reaction time and gave comparatively higher yields than methyl-substituted 2-aminophenols. This may be due to the lower reactivity of 2-aminophenol than 2-aminothiophenol.

All the synthesized benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one derivatives (**3a-l**) were characterized by spectral analysis (^{1}H-NMR,^{13}C-NMR, and Mass) and are in full agreement with the proposed structures. The spectroscopic and analytical data of reported compounds were in good agreement with those in the literature.[10]

Based on the previous reports, a plausible reaction pathway for the synthesis of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one derivatives is shown in Scheme 2. The reaction is expected to proceed *via* the formation of oxocarbenium ion from furan-2-yl(phenyl)methanol, likely after activation through $(C_6F_5)_3B$. This is followed by attack of 2-aminophenol resulting in the formation of aminal. An acid catalyzed rearrangement of aminal followed by oxa Michael reaction respectively would give the desired product (Scheme 2).

Conclusion

We have developed a straightforward method for the synthesis of pharmacologically effective benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-one/thiazin-2(1H)-one scaffolds by the $(C_6F_5)_3B$ catalyzed tandem aza-Piancatelli/Michael reaction between furan-2-yl(phenyl)methanols and 2-aminophenols/2-aminothiophenols. This method is simple and convenient to prepare a wide range of benzo[b]cyclopenta[e][1,4]oxazin-2(1H)-ones/thiazin-2(1H)-ones in good to high yields in one step. The present protocol demonstrates several key advantages such as short reaction times, high functionality group tolerance and use of nontoxic solid acid catalyst.

Acknowledgment

The authors are grateful to the Department of Postgraduate Studies and Research in Chemistry, Dnyanopasak College, Parbhani and Shri Chhatrapati Shivaji College, Omerga, India, Dayanand Science College, Latur for providing laboratory facilities and Indian Institute of Chemical Technology, Hyderabad for spectral analysis.

Disclosure statement

No potential conflict of interest was reported by the authors.

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