Samarium(III) Triflate as an Efficient and Reusable Catalyst for Facile Synthesis of Benzoxazoles and Benzothiazoles in Aqueous Medium

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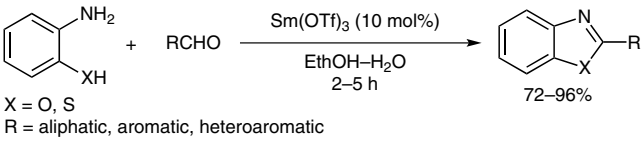
Abstract: A simple, green, and efficient method is presented for the synthesis of benzoxazoles and benzothiazoles from reaction of *o*-aminophenols, *o*-aminothiophenols, and aliphatic or aromatic aldehydes using samarium triflate as a reusable acid catalyst under mild reaction conditions in aqueous medium.

Key words: benzoxazoles, benzothiazoles, samarium triflate

Benzoxazoles and benzothiazoles have attracted considerable attention due to their biological properties.[1–10] The most commonly used synthetic approach involves condensation of *o*-aminothiophenols or *o*-aminophenols with aldehydes,[9,11] although carboxylic acids,[12] alcohols,[13] and acid chlorides[14] have been utilized. However, most of the traditional synthetic methods suffer from drawbacks such as the need for strongly acidic conditions and high temperatures,[15a–d] long reaction times,[15e,f] and significant amounts of catalyst or toxic solvents.[15g,h] Heterogeneous Lewis acid catalysis has attracted considerable attention[16] but, although a wide range of Lewis acids has been developed, most of them are used only under strictly anhydrous conditions.[17] Recently, with the objective of developing environmentally benign reaction conditions and media for organic reactions with excellent efficiency and selectivity, water has been shown to be a useful solvent for certain Lewis acids.[18] For instance, $In(OTf)_3$, $Yb(OTf)_3$, $Bi(OTf)_3$, $Sc(OTf)_3$, $Sm(OTf)_3$, and other metal triflates have been found to be water-tolerant, reusable Lewis acids catalysts and have received considerable interest for condensation reactions[17,19] and other organic transformations.[20–22]

In continuation of our interest in the synthesis of fused heterocyclic compounds,[23] we report herein the use of samarium triflate[24] as a water-tolerant Lewis acid catalyst for the synthesis of 2-substituted benzoxazoles and benzothiazoles by the condensation of *o*-aminophenols or *o*-aminothiophenols with aldehydes in aqueous ethanol as shown in Scheme 1.

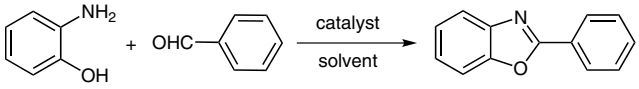
Initially, the samarium triflate catalyzed reaction between equimolar quantities of *o*-aminophenol and benzaldehyde was selected as a model reaction for optimization under different concentrations and using different solvents as summarized in Table 1. Samarium triflate (10 mol%) was found to be best suited for reaction in an ethanol–water (2:2) mixture at 60 °C compared to solvents such MeCN, dioxane, or toluene (Table 1, entry 7).



Scheme 1 Samarium triflate [$Sm(OTf)_3$] catalyzed synthesis of 2-substituted benzoxazoles and benzothiazoles

After optimization, we extended the study to various *o*-aminophenols and *o*-aminothiophenols with a range of aliphatic, aromatic, and heteroaromatic aldehydes. In general, most of reactions proceeded very smoothly to give the corresponding 2-substituted benzoxazoles and benzothizoles in moderate to excellent yields and aldehydes containing a range of sensitive functional groups were acceptable under these conditions. As a general trend, electron-deficient aldehydes gave better yields in shorter reaction times as compared to electron-rich aldehydes (Table 2).

Table 1 Optimization of Reaction Conditions for the Synthesis of 2-Phenylbenzoxazole[a]



Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)[b]
1	–	EtOH	12	25
2	ZnO (5)	EtOH–H_2O (2:2)	5	45
3	In_2O_3 (5)	EtOH–H_2O (2:2)	5	67
4	$Sm(OTf)_3$ (5)	EtOH	2	62
5	$Sm(OTf)_3$ (2)	EtOH–H_2O (2:2)	6	76
6	$Sm(OTf)_3$ (5)	EtOH–H_2O (2:2)	2	85
7	$Sm(OTf)_3$ (10)	EtOH–H_2O (2:2)	2	92
8	$Sm(OTf)_3$ (5)	MeCN	5	53
9	$Sm(OTf)_3$ (5)	dioxane	5	57
10	$Sm(OTf)_3$ (5)	toluene	5	60
11	$Sm(OTf)_3$ (10)	toluene	5	82

[a] Stirring at 50–60 °C.
[b] Isolated yield.

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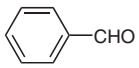
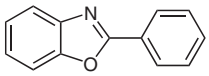
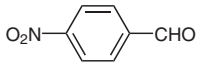
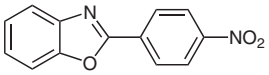
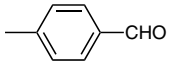
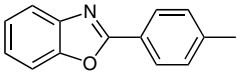
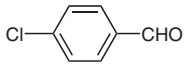
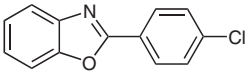
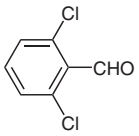
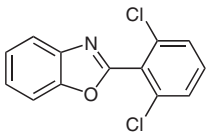
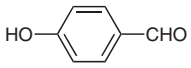
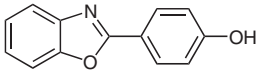
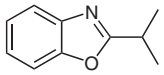
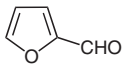
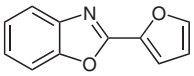
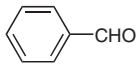
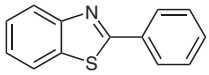
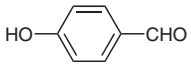
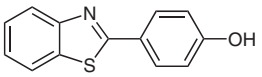
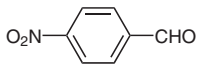
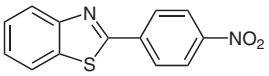
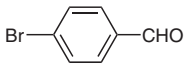
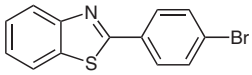
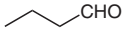
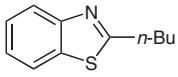
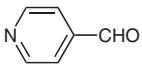
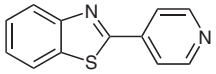
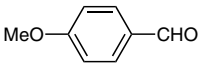
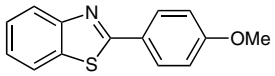
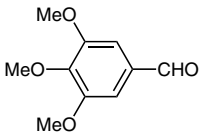
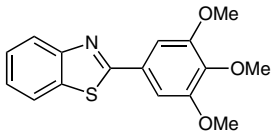
After completion of the reaction, the catalyst was removed by simple filtration and washed with ethanol. The catalyst was then dried at 100 °C for one hour and could

Table 2 $Sm(OTf)_3$-Catalyzed Synthesis of 2-Substituted Benzoxazoles and Benzothiazoles[a]

Entry	Aldehyde	Product	Time (h)	Yield (%)[b]
1			2	92
2			3	94
3			4	85
4			3.5	96
5			4	95
6			3.5	82
7			4.5	74
8			3	89
9			2	89
10			4	75
11			3.5	92
12			4	94
13			5	72
14			4.5	87
15			3.5	82
16			6	78

[a] Reaction conditions: aldehyde (1 mmol), *o*-aminophenol/*o*-aminothiophenol (1 mmol), $Sm(OTf)_3$ (10 mol%), EtOH–H_2O (4:2 mL), stirring at 50–60 °C.
[b] Isolated yield.

Table 3 Catalyst Reusability Study for the Reaction of Benzaldehyde with *o*-Aminophenol[a]

Entry	Yield (%)[b]	Catalyst recovery (%)
1	92	94
2	90	92
3	88	90
4	86	88

[a] Reaction conditions: benzaldehyde (1 mmol), *o*-aminophenol (1 mmol), $Sm(OTf)_3$ (10 mol%), EtOH–H_2O (2:2 mL), 50–60 °C.
[b] Isolated yield.

be reused. It was found that the catalytic activities of the recovered catalyst were almost the same as that of fresh catalyst over several runs (Table 3).

In conclusion, a simple and efficient method has been developed for the synthesis of 2-substituted benzoxazoles and benzothiazoles by using samarium triflate as a water-tolerant, recyclable Lewis acid catalyst in aqueous ethanol.

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(24) **General Procedure**
To a mixture of the requisite *o*-aminophenol/*o*-aminothiophenol (1 mmol) and aldehyde (1 mmol) in EtOH–H_2O (2:2 mL), samarium triflate catalyst (10 mol%) was added, and the resulting mixture was stirred at 60 °C. After completion of the reaction, as monitored by TLC, the mixture was diluted with H_2O–EtOAc (1:1, 10 mL) and catalyst recovered by filtration. The filtrate was extracted with Et_2O (2 × 10 mL) and dried with anhydrous Na_2SO_4. After filtration and evaporation of solvent, the crude product was recrystallized from EtOAc or MeOH. All the structures were confirmed by their analytical data and comparison with literature data.[25–30]
Spectroscopic Data for Selected Compounds
2-Phenylbenzo[*d*]oxazole (Table 2 Entry 1)
Mp 100–102 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.39 (m, 2 H), 7.57 (m, 3 H), 7.64 (m, 1 H), 7.80 (m, 1 H), 8.29 (m, 2 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 110.6, 119.9, 124.5, 125.1, 127.3, 127.5, 128.9, 131.5, 142.2, 150.8, 163.0. IR (KBr): 740, 1171, 1355, 1511, 1640, 3100 cm^{-1}. MS (EI): *m*/*z* = 195.1 [M$^+$].
2-(4-Methylphenyl)benzo[*d*]oxazole (Table 2 Entry 3)
Mp 114–116 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.45 (s, 3 H), 7.36 (d, 2 H, *J* = 8.1 Hz), 7.41 (t, 1 H, *J* = 8.4 Hz), 7.51 (t, 1 H, *J* = 8.4 Hz), 7.96 (d, 1 H, *J* = 8.0 Hz), 8.00–8.06 (m, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 21.2, 121.6, 122.9, 125.0, 126.2, 127.3, 129.7, 131.0, 135.0, 141.6, 154.2, 168.0. IR (KBr): 760, 1186, 1409, 1590, 1621, 2968 cm^{-1}. MS (EI): *m*/*z* = 209.07 [M$^+$].
2-(4-Chlorophenyl)benzo[*d*]oxazole (Table 2 Entry 4)
Mp 147–149 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.44 (t, 1 H, *J* = 7.6 Hz), 7.50–7.56 (m, 3 H), 7.98 (d, 1 H, *J* = 8.1 Hz), 8.05–8.09 (m, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 121.7, 123.2, 125.4, 126.5, 128.7, 129.2, 132.2, 135.1, 136.8, 154.1, 166.5. IR (KBr): 775, 1175, 1371, 1640, 2980 cm^{-1}. MS (EI): *m*/*z* = 229 [M$^+$] and 231 [M + 2].
2-(4-Nitrophenyl)benzo[*d*]thiazole (Table 2 Entry 11)
Mp 225–227 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.51 (t, 1 H, *J* = 7.5 Hz), 7.60 (t, 1 H, *J* = 7.6 Hz), 8.01 (d, 1 H, *J* = 7.8 Hz), 8.16 (d, 1 H, *J* = 8.1 Hz), 8.36 (q, 4 H, *J* = 9.4 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 121.9, 123.8, 124.4, 126.1, 126.8, 128.2, 135.6, 139.2, 149.0, 154.1, 165.0. IR (KBr): 807, 1169, 1370, 1556, 1690, 3056 cm^{-1}. MS (EI): *m*/*z* = 256.0 [M$^+$].
2-(Pyridin-4-yl)benzo[*d*]thiazole (Table 2 Entry 14)
Mp 130–132 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.44–7.50 (m, 2 H), 7.57 (t, 1 H, *J* = 8.1 Hz), 8.01 (d, 1 H, *J* = 7.9 Hz), 8.13 (d, 1 H, *J* = 8.2 Hz), 8.40 (dt, 1 H, *J* = 8.0, 1.7 Hz), 8.73 (dd, 1 H, *J* = 4.8z, 1.7 Hz). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 121.8, 123.3, 123.8, 125.6, 129.6, 134.4, 135.1, 148.5, 154.0, 164.7. IR (KBr): 690, 1150, 1400, 1653, 2360, 2905 cm^{-1}. MS (EI): *m*/*z* = 212.03 [M$^+$].
2-(4-Methoxyphenyl)benzo[*d*]thiazole (Table 2 Entry 15)
Mp 122–124 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.89 (s, 3 H), 7.02 (d, 2 H, *J* = 8.4 Hz), 7.39 (t, 1 H, *J* = 7.2 Hz), 7.51 (t, 1 H, *J* = 7.2 Hz), 7.94 (d, 1 H, *J* = 7.8 Hz), 8.06 (m, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 55.4, 114.3, 121.6, 122.7, 124.8, 126.2, 126.4, 129.0, 135.0, 154.3, 162.0, 167.7. IR (KBr): 781, 1170, 1450, 1597, 1650, 3010 cm^{-1}. MS (EI): *m*/*z* = 241 [M$^+$].
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