Synthesis of some new oxazolinyl/thiazolinyl/imidazolinyl- benzoxazoles, benzothiazoles and benzimidazoles

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A new class of oxazolinyl/thiazolinyl/imidazolinyl-benzoxazoles/benzothiazoles/benzimidazoles have been prepared by exploiting the respective heterocyclic sulfonyl acetic acid methyl ester functionality with different nucleophiles using samarium(III) chloride.

Keywords: Oxazoline, thiazoline, imidazoline, samarium(III) chloride, cyclocondensation

Theazole derivatives particularly oxazolines, thiazolines and imidazolines are frequently found in biologically active natural products and pharmaceuticals. The oxazole ring is endowed with various activities such as hypoglycemic, analgesic, anti-inflammatory and antibacterial. A number of reliable preparative methods are known in the literature which includes cyclodehydration of carboxylic acids and $\beta$-amino alcohol, treatment of $\beta$-hydroxyamide with suitable cyclization reagents such as thionyl chloride, phosphorotris-(1,2,4)-triazolide, Mitsunobu conditions (DEAD/PPh$_3$) and phosphorous mediated Appel reaction conditions. Some thiazoline derivatives present interesting activities such as anti-HIV, anticancer, cell division inhibition, anti-bacterial, radioprotective and pheromone activities. The most commonly used synthetic approaches to thiazolines are cyclodehydration of $\beta$-hydroxythio amides under Mitsunobu conditions, condensation of 2-aminothiols with nitriles, carboxylic acids, esters, iminoethers, iminotriflates etc. Medicinal properties of imidazole derivatives include anticancer, antimicrobial and antioxidant. In fact clinically useful drugs such as miconazole, econazole and oxiconazole having imidazole moiety exhibit strong antifungal activity. There are several methods for the synthesis of 2-imidazolines from carboxylic acids, esters, nitriles, orthoesters, hydroximoylchlorides, hydroxy amides, etc. Thus, the potent biological activity and the prevalence of azoles in both natural products and pharmaceuticals has created significant interest in the synthesis of these heterocycles.

Results and Discussion

The synthetic pathway to achieve the target heterocycles is depicted in Scheme I. The synthetic intermediates 2-(chloromethyl)benzoxazole 1 and 2-(chloromethyl)benzothiazole 2 were obtained by the irradiation of 2-aminophenol/2-anthrothiophenol and chloroacetyl chloride for 10 min at a power of 500 W. However, 2-(chloromethyl)-1H-benzimidazole 3 was prepared by treating o-phenylenediamine with chloroacetic acid in the presence of 5N HCl. The reaction of 1, 2 and 3 with thioglycolic acid in the presence of sodium hydroxide in methanol resulted in 2-((benzoxazol-2-yl)methylthio)acetic acid 4, 2-((benzothiazol-2-yl)methylthio)acetic acid 5 and 2-((1H-benzimidazol-2-yl)methylthio)acetic acid 6. Oxidation of the latter compounds with hydrogen peroxide gave 2-((benzoxazol-2-yl)methylsulfonyl)-acetic acid 7, 2-((benzothiazol-2-yl)methylsulfonyl)-acetic acid 8 and 2-((1H-benzimidazol-2-yl)methylsulfonyl)-acetic acid 9. The IR spectra of 7, 8 and 9 displayed absorption bands at 1139-1154 and 1347-1356 (SO$_2$), 1567-1576 (C=N), 1682-1690 (C=O) and 3338-3347 cm$^{-1}$ (OH). Besides, the compound 9 showed a broad absorption band at 3321 cm$^{-1}$ (NH). The $^1$H NMR spectra of 7, 8 and 9 presented two sharp singlets at $\delta$ 4.28, 4.31, 4.26 and 5.31, 5.32, 4.95 due to methylene protons present between carboxylic acid and sulfonyl group and heterocyclic ring and sulfonyl group, respectively. Besides, a broad singlet was observed at 10.43, 10.56, 10.41 in these compounds due to OH. The compound 9 exhibited another broad singlet at 11.28 due to NH of benzimidazole. The signals of highly acidic protons disappeared when D$_2$O was added. The $^{13}$C NMR spectra of 7, 8 and 9 displayed signals at $\delta$ 51.8 (SO$_2$CH$_3$), 56.3, 56.6, 56.1 (CH$_2$SO$_2$), 160.9, 169.8, 150.1 (C-2) and 169.4, 170.7, 168.1 (CO$_2$H).

Esterification of the acid functionality in 7, 8 and 9 with methanol and conc. H$_2$SO$_4$ produced methyl 2-((benzoxazol-2-yl)methylsulfonyl)acetate 10, methyl...
2-((benzothiazol-2-yl)-methylsulfonyl)acetate 11 and methyl 2-((1H-benzimidazol-2-yl)methylsulfonyl)acetate 12. The absence of absorption bands corresponding to acid moieties and the presence of a strong band ≈ 1730 cm\(^{-1}\) for ester group in the IR spectra of 10, 11 and 12 confirmed their formation.

The \(^1\)H NMR spectra of 10, 11 and 12 exhibited three sharp singlets at δ 4.30, 4.33, 4.29, 4.98, 5.34, 4.96 and 3.75, 3.71, 3.74 due to methylene protons present between sulfonyl and carbomethoxy group, heterocyclic ring and sulfonyl group and methoxy protons of carbomethoxy group, respectively. In addition, compound 12 exhibited another broad singlet at δ 11.38 for NH of benzimidazole. The \(^1\)C NMR spectra of 10, 11 and 12 showed signals at δ 52.3, 53.4, 51.9 (SO\(_2\)CH\(_2\)), 52.5, 53.8, 52.3 (OCH\(_3\)), 56.5, 56.9, 56.4 (CH\(_2\)SO\(_2\)), 159.8, 170.9, 157.2 (C-2') and 164.5, 164.8, 164.1 (CO\(_2\)Me).

The cyclocondensation of 10, 11 and 12 with 2-aminoethanol and n-butyllithium complexed with a suspension of 5-10% molar equivalent of anhydrous samarium(III) chloride in toluene resulted in 2-(((4',5'-dihydrooxazol-2'-yl)methylsulfonyl)methyl)benzoxazole 13, 2-(((4',5'-dihydrooxazol-2'-yl)methylsulfonyl)methyl)benzothiazole 14 and 2-(((4',5'-dihydro-oxazol-2'-yl)methylsulfonyl)methyl)-1H-benzimidazole 15. The IR spectra of 13, 14 and 15 displayed absorption bands at 1140-1153 and 1322-1330 and 1580-1600 cm\(^{-1}\) due to SO\(_2\) and C=N. Besides, compound 15 exhibited another band at δ 3328 cm\(^{-1}\) due to NH. The \(^1\)H NMR spectra of 13, 14 and 15 exhibited two singlets at δ 4.92, 5.02, 4.96 and 4.32, 4.35, 4.31 due to methylene protons. The signal at downfield region was assigned to the methylene protons present between benzofused heterocyclic and sulfonyl group. Besides, two triplets were observed at δ 3.50, 3.45, 3.49 and 3.69, 3.62, 3.60 which were assigned to C-4' and C-5'-H. The compound 15 exhibited another broad singlet at 11.49 due to NH of benzimidazole which disappeared on deuteration. The \(^1\)C NMR spectra of 13, 14 and 15 showed signals at δ 52.8, 51.7, 50.7 (C-4'), 53.6, 52.3, 50.9 (SO\(_2\)CH\(_2\)), 55.5, 54.8, 54.9 (CH\(_2\)SO\(_2\)), 60.4, 61.7, 61.1 (C-5'), 162.0, 163.1, 162.8 (C-2') and 164.5, 166.2, 155.7 (C-2).

On the other hand, the cyclocondensation of 10, 11 and 12 with 2-aminoethanethiol produced 2-(((4',5'-dihydrothiazol-2'-yl)methylsulfonyl)methyl)benzoxazole 16, 2-(((4',5'-dihydrothiazol-2'-yl)methylsulfonyl)methyl)benzothiazole 17 and 2-(((4',5'-dihydrothiazol-2'-yl)-methylsulfonyl)methyl)-1H-benzimidazole 18. The IR spectra of these compounds presented absorption bands at 1138-1151 and 1320-1348 (SO\(_2\)), 1585-1600 cm\(^{-1}\) (C=N). The compound 18 showed
Another absorption band at 3327 cm\(^{-1}\) (NH). The \(^1\)H NMR spectra of 16, 17 and 18 displayed two singlets at \(\delta\) 4.25, 4.27, 4.19 and 5.03, 5.08, 4.91 for two methylene protons and two triplets at \(\delta\) 4.38, 4.20, 4.41 and 3.52, 3.48, 3.44 for \(\text{C}_4\)-H and \(\text{C}_5\)-H, respectively. In addition to these, compound 18 displayed a broad singlet at \(\delta\) 11.28 for NH of benzimidazole. The \(^{13}\)C NMR spectra of 16, 17 and 18 showed signals at \(\delta\) 37.7, 38.8, 38.1 (C-5’), 52.7, 53.8, 52.1 (\(\text{SO}_2\text{CH}_2\)), 61.6, 61.9, 61.7 (\(\text{CH}_2\text{SO}_2\)), 62.3, 60.9, 61.2 (C-4’), 165.2, 168.3, 156.7 (C-2) and 172.8, 173.5, 174.1 (C-2’) besides the signals of aromatic carbons. Adopting similar methodology, the compounds 2-(((4’,5’-dihydro-1’H-imidazol-2’-yl)-methylsulfonyl)methyl)-benzoxazole 19, 2-(((4’,5’-dihydro-1’H-imidazol-2’-yl)methyl)sulfonylmethyl)-benzothiazole 20 and 2-(((4’,5’-dihydro-1’H-imidazol-2’-yl)methylsulfonylmethyl)-1H-benzimidazole 21 were prepared from \(10\/11\/12\) and 1,2-ethanediame in the presence of \(n\)-butyllithium and samarium(III) chloride. The IR spectra of 19, 20 and 21 exhibited absorption bands at 1132-1144 and 1325-1329 (\(\text{SO}_2\)), 1590-1610 (C=N) and 3326-3340 cm\(^{-1}\) (NH). The \(^1\)H NMR spectra of 19, 20 and 21 showed two singlets at \(\delta\) 4.36, 4.39, 4.31 and 5.06, 5.10, 4.99 for methylene protons \(\text{SO}_2\text{CH}_2\) and \(\text{CH}_2\text{SO}_2\), respectively. The imidazoline ring protons, \(\text{C}_4\)-H and \(\text{C}_5\)-H of 19, 20 and 21 displayed a singlet at \(\delta\) 3.63, 3.65, 3.58. Besides, compound 21 showed a broad singlet at \(\delta\) 11.67 due to NH of benzimidazole. The signals of NH in these compounds disappeared when D\(_2\)O was added. The \(^{13}\)C NMR spectra of 19, 20 and 21 displayed signals at \(\delta\) 51.6, 52.8, 52.3 (C-4’ & C-5’), 52.7, 53.9, 52.5 (\(\text{SO}_2\text{CH}_2\)), 62.1, 62.3, 61.6 (\(\text{CH}_2\text{SO}_2\)), 157.3, 155.4, 154.7 (C-2’) and 168.9, 169.1, 155.2 (C-2).

**Experimental Section**

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The homogeneity of the compounds was checked by TLC (silica gel H, BDH, ethyl acetate-hexane, 1:3). The IR spectra were recorded on a Thermo Nicolet IR 200 FT-IR spectrometer as KBr pellets and the wave numbers were given in cm\(^{-1}\). The \(^1\)H NMR spectra were recorded in CDCl\(_3\)/DMSO-\(d_6\) on a Jeol JNM \(\lambda\)-400 MHz machine. The \(^{13}\)C NMR spectra were recorded in CDCl\(_3\)/DMSO-\(d_6\) on a Jeol JNM spectrometer operating at 100 MHz. All chemical shifts are reported in \(\delta\) (ppm) using TMS as an internal standard. The microanalyses were performed on Perkin-Elmer 240C elemental analyzer. The compounds 2-((chloromethyl)benzoxazole 1, 2-(chloromethyl)benzothiazole 2 and 2-(chloromethyl)-1H-benzimidazole 3 were prepared by the literature procedure.\(^{31,32}\)

**General method for the preparation of 2-((benzoazol-2-yl)methylthio)acetic acid, 4 (Ref 33) / 2-((benzothiazol-2-yl)methylthio)acetic acid, 5/2-((1H-benzimidazol-2-yl)methylthio)acetic acid, 6 (Ref 34)**

To a solution of sodium hydroxide (0.001 mol) in methanol (10 mL) mercaptoacetic acid (0.01 mol) was added slowly. After complete addition 2-(chloromethyl)benzoxazole 1/2-(chloromethyl)benzothiazole 2/2-(chloromethyl)-1H-benzimidazole 3 (0.01 mol) was added portionwise. The reaction mixture was refluxed for 20-24 hr, cooled and poured into crushed ice containing conc. HCl. The separated solid was filtered and dried. The resultant compound was purified by recrystallization from water.
General method for the preparation of 2-((benzoxazol-2-yl)methylsulfonyl)acetic acid, 7/2-
((benzothiazol-2-yl)methylsulfonyl)acetic acid, 8/2-
((1H-benzimidazol-2-yl)methyl-sulfonyl)acetic acid, 9

An ice-cold solution of 2-((benzoxazol-2-yl)methylthio)acetic acid 4/2-((benzothiazol-2-
yl)methylthio)acetic acid 5/2-((1H-benzimidazol-2-yl)methylthio)acetic acid 6 (0.01 mol) in glacial acetic acid (30 mL) was treated with 30% hydrogen peroxide (20 mL) in portions. The contents were allowed to attain laboratory temperature and then refluxed for 3 hr. The reaction mixture was cooled and acetic acid was removed in vacuo. The residual portion was poured onto crushed ice and the product obtained was collected by filtration. It was washed with cold water and dried. The crude compound was purified by recrystallization from water.

2-((Benzoxazol-2-yl)sulfonyl)acetic acid, 7: White solid, yield 85%, m.p. 199-201°C. IR (KBr): 1150, 1351 (SO₂), 1570 (C=N), 1685 (C=O), 3341 (OH) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 4.28 (s, 2H, SO₂-CH₂), 5.31 (s, 2H, CH₂SO₂), 7.26-7.52 (m, 4H, Ar-H), 10.43 (bs, 1H, OH); ¹³C NMR (100 MHz, DMSO-d₆): δ 52.1 (SO₂-CH₂), 56.3 (CH₂SO₂), 117.3 (Ar-C), 120.8 (Ar-C), 125.3 (Ar-C), 126.1 (Ar-C), 141.2 (Ar-C), 147.8 (Ar-C), 160.9 (C=O), 169.4 (COOH). Anal. Calcd for C₁₀H₁₀NO₂S (255.26): C, 47.05; H, 3.55; N, 5.49. Found: C, 47.18; H, 3.62; N, 5.56%.

2-((Benzothiazol-2-yl)sulfonyl)acetic acid, 8: White solid, yield 80%, m.p. 178-80°C. IR (KBr): 1154, 1356 (SO₂), 1576 (C=N), 1690 (C=O), 3347 (OH) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 4.31 (s, 2H, SO₂-CH₂), 5.32 (s, 2H, CH₂SO₂), 7.30-7.58 (m, 4H, Ar-H), 10.56 (bs, 1H, OH); ¹³C NMR (100 MHz, DMSO-d₆): δ 53.3 (SO₂-CH₂), 56.6 (CH₂SO₂), 121.9 (Ar-C), 122.4 (Ar-C), 125.5 (Ar-C), 125.8 (Ar-C), 135.3 (Ar-C), 151.1 (Ar-C), 169.8 (C=O), 170.7 (COOH). Anal. Calcd for C₁₀H₈NO₃S₂ (271.32): C, 44.27; H, 3.34; N, 5.16. Found: C, 44.39; H, 3.40; N, 5.25%.

2-((1H-Benzimidazol-2-yl)methylsulfonyl)acetic acid, 9: White solid, yield 89%, m.p. 192-94°C. IR (KBr): 1139, 1347 (SO₂), 1567 (C=N), 1682 (C=O), 3321 (NH), 3338 (OH) cm⁻¹; ¹H NMR (400 MHz, DMSO-d₆): δ 4.26 (s, 2H, SO₂-CH₂), 4.95 (s, 2H, CH₂SO₂), 7.33-7.61 (m, 4H, Ar-H), 10.41 (bs, 1H, OH) 11.28 (bs, 1H, NH); ¹³C NMR (100 MHz, DMSO-d₆): δ 51.8 (SO₂-CH₂), 56.1 (CH₂SO₂), 117.7 (Ar-C), 121.6 (Ar-C), 128.1 (Ar-C), 128.6 (Ar-C), 137.8 (Ar-C), 138.4 (Ar-C), 150.1 (C=O), 168.1 (COOH). Anal. Calcd for C₁₀H₈NO₃S₂ (254.27): C, 47.24; H, 3.96; N, 11.02. Found: C, 47.10; H, 4.05; N, 11.14%.

General method for the preparation of methyl 2-((benzoxazol-2-yl)methylsulfonyl)acetate, 10/methyl 2-((benzothiazol-2-yl)methylsulfonyl)acetate, 11/methyl 2-((1H-benzimidazol-2-yl)methylsulfonyl)acetate, 12

A mixture of 2-((benzoxazol-2-yl)sulfonyl)acetic acid 7/2-((benzothiazol-2-yl)sulfonyl)acetic acid 8/2-((1H-benzimidazol-2-yl)sulfonyl)acetic acid 9 (0.01 mol), methanol (10 mL) and conc. H₂SO₄ (1.5 mL) was refluxed on a steam bath for 4-5 hr. The contents of the flask were cooled and poured onto crushed ice. The crude product was purified by recrystallization from methanol.
27°C. IR (KBr): 1159, 1354 (SO$_2$), 1573 (C=N), 1729 (C=O), 3325 (NH) cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.74 (s, 3H, OCH$_3$), 4.29 (s, 2H, SO$_2$-CH$_2$), 4.96 (s, 2H, CH$_2$SO$_2$), 7.45-7.70 (m, 4H, Ar-H), 11.38 (bs, 1H, NH); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 51.9 (SO$_2$-CH$_3$), 52.3 (OCH$_3$), 56.4 (CH$_2$SO$_2$), 117.4 (Ar-C), 117.8 (Ar-C), 128.6 (Ar-C), 128.8 (Ar-C), 138.5 (Ar-C), 138.8 (Ar-C), 157.2 (C-2), 164.1 (CO$_2$Me). Anal. Calcd for C$_{11}$H$_2$N$_2$O$_5$S (268.29): C, 49.33; H, 4.46; N, 10.44. Found: C, 49.32; H, 4.51; N, 10.32%.

General method for the preparation of 2-(((4',5'-dihydrooxazol-2'-yl)methylsulfonyl)methyl)benzoazole, 13
To a flask charged with anhydrous samarium(III) chloride (0.001 mol) and dry toluene (20 mL), 2-aminoethanol (0.02 mol) was added followed by n-butyllithium (0.02 mol) at 0°C. The reaction mixture was stirred at 0°C for 15 min and heated to reflux. Then, methyl 2-(((benzothiazol-2-yl)methylsulfonyl)acetate 10/methyl 2-(((benzothiazol-2-yl)methylsulfonfonyl)acetate 11/methyl 2-((1H-benzimidazol-2-yl)methylsulfonfonyl)acetate 12 (0.01 mol) was added to the contents and continued refluxion for an additional period of 6-8 hr. The suspension was cooled to RT and filtered. The filtrate was extracted with chloroform, washed with water followed by brine solution. The solvent was removed in vacuo. The solid obtained was purified by column chromatography (ethyl acetate-hexane,1:3).

2-(((4',5'-Dihydrooxazol-2'-yl)methylsulfonfonyl)-methyl)benzoxazole, 13: White solid, yield 68%, m.p. 159-61°C. IR (KBr): 1143, 1326 (SO$_2$), 1585 (C=N) cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.50 (t, 2H, C$_5$H, $J$ = 7.7 Hz), 3.69 (t, 2H, C$_5$H, $J$ = 7.7 Hz), 4.32 (s, 2H, SO$_2$-CH$_2$), 4.92 (s, 2H, CH$_2$SO$_2$), 7.18-7.36 (m, 4H, Ar-H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta$ 52.8 (C-4'), 53.6 (SO$_2$-CH$_3$), 55.5 (CH$_3$-SO$_2$), 60.4 (C-5'), 118.1 (Ar-C), 121.5 (Ar-C), 122.9 (Ar-C), 125.2 (Ar-C), 139.6 (Ar-C), 149.6 (Ar-C), 162.0 (C-2'), 164.5 (C-2'). Anal. Calcd for C$_{11}$H$_2$N$_2$O$_5$S (279.31): C, 51.60; H, 4.69; N, 15.04. Found: C, 51.73; H, 4.75; N, 15.17%.

General method for the preparation of 2-(((4',5'-dihydrothiazol-2'-yl)methylsulfonfonyl)-methyl)benzoazole, 16
To a flask charged with anhydrous samarium(III) chloride (0.001 mol) and dry toluene (10 mL), 2-aminoethanethiol (0.02 mol) was added followed by n-butyllithium (0.022 mol) at 0°C. The reaction mixture was stirred at 0°C for 15 min and heated to reflux. Then, methyl 2-(((benzothiazol-2-yl)methylsulfonyl)acetate 10/methyl 2-((benzothiazol-2-yl)methylsulfonfonyl)acetate 11/methyl 2-((1H-benzimidazol-2-yl)methylsulfonfonyl)acetate 12 (0.01 mol) was added to the contents and continued refluxion for an additional period of 8-10 hr. The suspension was cooled to RT and filtered. The filtrate was extracted with chloroform, washed with water followed by brine solution. The solvent was removed in vacuo. The solid obtained was purified by column chromatography (hexan-ethyl acetate,3:1).

2-(((4',5'-Dihydrothiazol-2'-yl)methylsulfonfonyl)-methyl)benzoazole, 16: White solid, yield 65%, m.p. 165-67°C. IR (KBr): 1142, 1321 (SO$_2$), 1587 (C=N) cm$^{-1}$; $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 3.52 (t, 2H, C$_5$H, $J$ = 7.7 Hz), 4.25 (s, 2H, SO$_2$-CH$_2$), 4.38
(t, 2H, C\textsubscript{5}-H, J = 7.5 Hz), 5.03 (s, 2H, CH\textsubscript{2}-SO\textsubscript{2}), 7.58-8.14 (m, 4H, Ar-H); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}); δ 37.7 (C-5'), 52.7 (SO\textsubscript{2}-CH\textsubscript{2}), 61.6 (CH\textsubscript{2}-SO\textsubscript{2}), 62.3 (C-4'), 118.4 (Ar-C), 122.8 (Ar-C), 126.3 (Ar-C), 126.8 (Ar-C), 142.1 (Ar-C), 148.7 (Ar-C), 165.2 (C-2), 172.8 (C-2'). Anal. Calcld for Ar-C, 126.8 (Ar-C), 142.1 (Ar-C), 148.7 (Ar-C), 165.2 (C-2), 172.8 (C-2').

2-(((4',5'-Dihydro-1'-H-imidazol-2'-yl)methyl)sulfonyl)-methyl)benzothiazole, 19: White solid, yield 70%, m.p. 166-68°C. IR (KBr): 1142, 1328 (SO\textsubscript{2}), 1607 (C=N), 3335 (NH) cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}); δ 3.63 (s, 4H, C\textsubscript{5}-H & C\textsubscript{6}-H), 4.36 (s, 2H, SO\textsubscript{2}-CH\textsubscript{2}), 5.06 (s, 2H, CH\textsubscript{2}-SO\textsubscript{2}), 5.05 (s, 1H, NH), 7.41-7.56 (m, 4H, Ar-H); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}); δ 51.6 (C-4' & C-5'), 52.7 (SO\textsubscript{2}-CH\textsubscript{2}), 118.7 (Ar-C), 122.5 (Ar-C), 122.9 (Ar-C), 127.1 (Ar-C), 142.4 (Ar-C), 149.2 (Ar-C), 157.3 (C-2'), 168.9 (C-2').

The contents and continued refluxion for an additional period of 5-7 hr. The suspension was cooled to RT and filtered. The filtrate was extracted with chloroform, washed with water followed by brine solution. The solvent was removed in vacuo. The solid obtained was purified by column chromatography (hexane-ethyl acetate, 3:1).

2-(((4',5'-Dihydro-1'-H-imidazol-2'-yl)methyl)sulfonyl)-methyl)benzothiazole, 20: White solid, yield 66%, m.p. 162-64°C. IR (KBr): 1144, 1329 (SO\textsubscript{2}), 1610 (C=N), 3340 (NH) cm\textsuperscript{-1}; \textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}); δ 3.65 (s, 4H, C\textsubscript{5}-H & C\textsubscript{6}-H), 4.39 (s, 2H, SO\textsubscript{2}-CH\textsubscript{2}), 5.08 (s, 1H, NH), 5.10 (s, 2H, CH\textsubscript{2}-SO\textsubscript{2}), 7.43-7.62 (m, 4H, Ar-H); \textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}); δ 52.8 (C-4' & C-5'), 53.9 (SO\textsubscript{2}-CH\textsubscript{2}), 62.1 (CH\textsubscript{2}-SO\textsubscript{2}), 123.4 (Ar-C), 123.7 (Ar-C), 127.1 (Ar-C), 142.4 (Ar-C), 149.2 (Ar-C), 157.3 (C-2'), 169.1 (C-2').

General method for the preparation of 2-(((4',5'-dihydro-1'-H-imidazol-2'-yl)methyl)sulfonyl)-benzothiazole, 19/2-(((4',5'-dihydro-1'-H-imidazol-2'-yl)methyl)sulfonyl)-benzothiazole, 20/2-(((4',5'-dihydro-1'-H-imidazol-2'-yl)methyl)sulfonyl)-methyl)-1H-benzimidazole, 21

To a flask charged with anhydrous samarium(III) chloride (0.001 mol) and dry toluene (10 mL), 1,2-ethanediame (0.02 mol) was added followed by n-butyllithium (0.022 mol) at 0°C. The reaction mixture was stirred at 0°C for 15 min and heated to reflux. Then, methyl 2-((benzothiazol-2-yl)methyl)sulfonyl)acetate 10/methyl 2-((benzothiazol-2-yl)methyl)sulfonyl)acetate 11/methyl 2-((1H-benzimidazol-2-yl)methyl)sulfonyl)acetate 12 (0.01 mol) was added to

NOTES

A new class of oxazolinyl/thiazolinyl/imidazolinyl-benzoxazoles/benzothiazoles/benzimidazoles were prepared by exploiting the respective heterocyclic
sulfonyl acetic acid methyl ester functionality with different nucleophiles using samarium(III) chloride.

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**References**


