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Tandem synthesis of novel 4-(azidocarbonyl)phenylazide from 3-(4-hydrazinocarbonyl)phenylsydnone and its chemoselective 1,3 dipolar cycloaddition reaction and Curtius rearrangement

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Abstract: The 4-(azidocarbonyl)phenylazide **3** obtained from 4-(hydrazinocarbonyl) phenylsydnone **1** by tandem hydrolysis – diazotisation, is used as the key intermediate for the chemoselective one-pot 1,3- dipolar cycloaddition reaction with dimethylacetylene dicarboxylate (DMAD) along with Curtius rearrangement affording the carbamates **5a-c** and the isocyanate **6.** These compounds were further used as building blocks for the triheterocyclic carbamates **9a-c** and **10a-c** and 4- triazolophenylaryl ureas **7a-f.** The ethyl carbamate derivative **5a** exhibited antibacterial inhibition selectively against B.subtilis almost one and half times more than Norfloxacin while compounds **5a, 7b and 10c** were as active as Griseofulvin against *A.flavus*

Keywords: 4-(Hydrazinocarbonyl)phenylsydnone; 4-(Azidocarbonyl)phenylazide; Curtius rearrangement; 1,3-dipolar cycloaddition.

1. Introduction

Sydnone ring is readily cleaved by hydrochloric acid under mild conditions to generate excellent yields of monosubstituted hydrazines.[1] We have earlier demonstrated the synthetic utility of this simple, efficient and inexpensive route in one-pot synthesis of a variety of 1,2-diaza-five-membered heterocyclic systems.[2-4] Extending this acid hydrolysis to 3-(4-hydrazinocarbonyl)phenylsydnone **1** we were able to obtain the 4-(hydrazinocarbonyl) phenylhydrazine **2** which was used as a versatile synthon for some novel bismesoionic compounds. [5]

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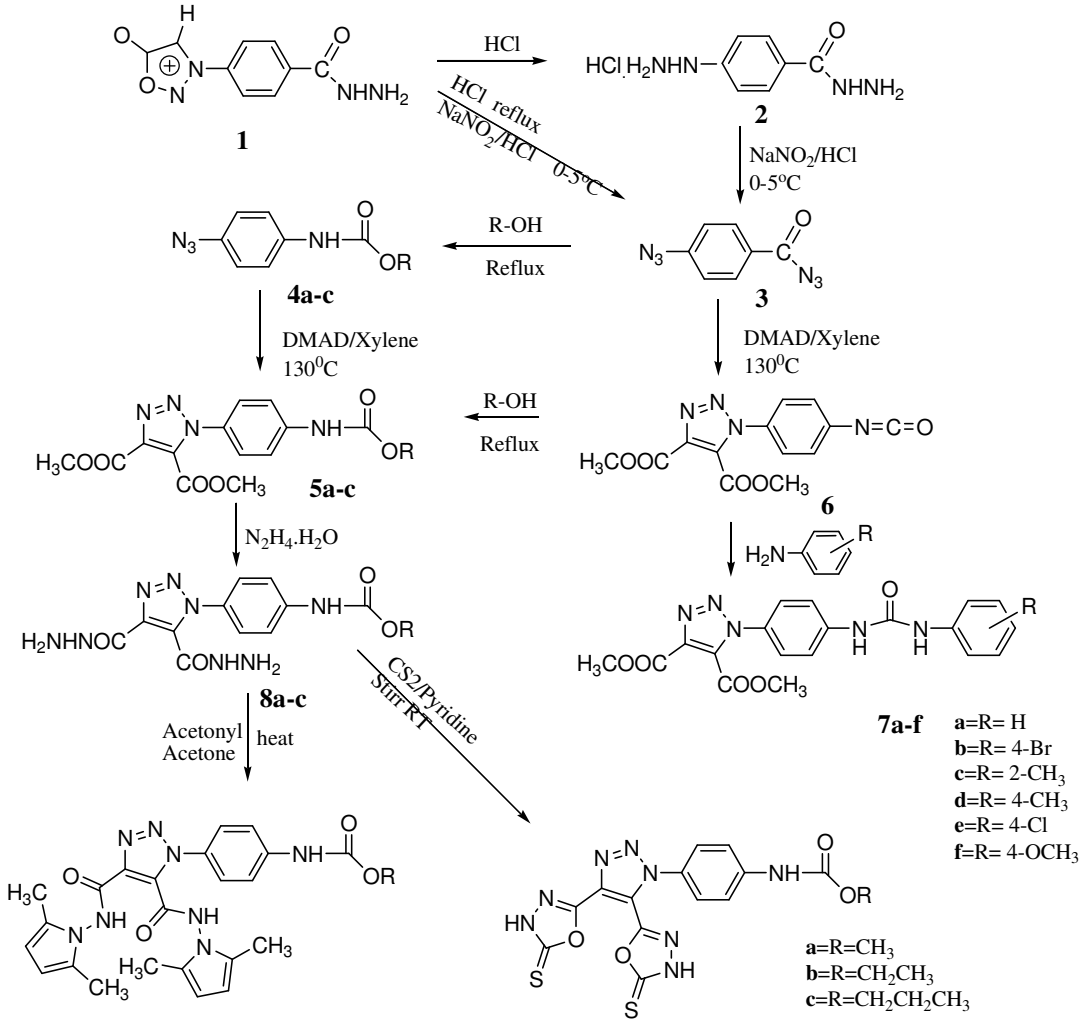
In this paper we report further synthetic utility of the bifunctional compound **1** for the one-pot synthesis of a new and novel bis azide – 4-(azidocarbonyl)phenyl azide **3.** This compound which appears to be a synthetic challenge by other methods, has been used as a pivotal intermediate for building different heterocycles coupled with functional groups like isocyanate, urea and carbamate. 1,3-Dipolar cycloaddition with DMAD and Curtius rearrangement reaction have been carried out on compound **3** to obtain the desired molecules.

The two azido groups of compound **3** exhibit chemoselectivity towards 1,3-Dipolar cycloaddition and Curtius rearrangement reactions. The arylazido and the acylazido groups differ in their chemical properties. Only the arylazides undergo facile 1 ,3-Dipolar cycloaddition with DMAD while Curtius rearrangement with alcohols requires the acylazido functionality. This is due to the lower temperature required for the rearrangement as compared to the cycloaddition reaction. However, we observed both the reactions occurring simultaneously in a single step at higher temperature.

Azides are considered as very important compounds due to both their industrial as well as biological applications. Azides are also used as synthons for many biologically active nitrogen containing heterocycles such as carbazoles, furoxans, azepines, triazolines, triazoles[6], tetrazoles[7], aziridines[8]. Azide derivatives are used in rubber vulcanization, polymer crosslinking, foaming of plastics and as dyes, pharmaceutical pesticides and herbicides[9]. One of the more useful synthetic applications of alky and aryl azides is the facile preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition reactions with acetylenic compounds[10]. A number of 1,2,3-triazole derivatives have found diverse use in synthetic, medicinal and photographic chemistry, and as agrochemicals, optical brightening agents and corrosion retardants[11].

2. Results and discussion.

3-(4-Hydrazinocarbonyl)phenylsydnone (**1)** was hydrolysed by warming with hydrochloric acid to obtain the bis bydrazine - 4-(hydrazine carbonyl) phenylhydrazine hydrochloride (**2).** This was then diazotized with aq.sodium nitrite solution at 0 ^{o}C to afford the bis azide – 4-(azidocarbonyl)phenyl azide (**3)** .This compound was also obtained in a single-pot reaction by warming compound 1 with hydrochloric acid followed by insitu diazotization as above. The acylazido group of the bisazide (**3)** selectively underwent Curtius rearrangement on heating with methyl, ethyl and propyl alcohols to give the corresponding 4-(azido)phenylcarbamates **4a-c.** Reaction with n-butyl and higher alcohols led to decomposition due to their high boiling points. These azido carbamates on reaction with DMAD gave the cycloadduct products - 4-[(dimethyl-1*H*-[1,2,3]-triazole-1yl)-4,5-dicarboxylate]phenyl carbamates **5a-c.** On the other hand, reaction of the bisazide (**3)** with DMAD at 120^{o}C resulted in an unusual one-pot cycloaddition and also rearrangement to afford the 4-[(dimethyl-1*H*-[1,2,3]-triazole-1yl)-4,5-dicarboxylate]phenyl isocyanate **(6).** This reaction appears to be a rare combination of two reactions in a single- pot as cycloaddition reactions do not take place in the thermal Curtius rearrangements[12] .This isocyanate on reaction with aromatic amines yielded the corresponding ureas – N-aryl-N'-[dimethyl-*1H* –[1,2,3]-triazole-4,5-dicarboxylate-1-yl]ureas (**7a-f).**The 4-triazolophenyl carbamates (**5a-c)** on reaction with hydrazine hydrate yielded the corresponding bishydrazides **(8a-c)** which on cyclisation with acetonyl acetone and CS_2 in pyridine gave the the triheterocyclic compounds - 4-[4,5-bis(2,5-dimethylpyrrole-1-yl-carbamoyl)-[1,2,3]triazole-1-yl]phenyl carbamates **(9a-c)** and 4-[4,5-bis(5-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-yl)-[1,2,3]triazole-1-yl] phenylcarbamates **(10a-c)** respectively. The carbamate group remained intact when heated in aqueous conditions. Attempts to build similar heterocyclic rings on the 4-triazolophenylureas **7a-f** were unsuccessful because of their resistance towards hydrazine hydrate which could be due to their poor solubility**.**



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3. Conclusion

We have introduced a very simple route for the synthesis of a novel bisazide containing the aryl- and acylazido groups which would serve as a versatile synthon for chemoselective reactions. We consider the one-pot 1,3-dipolar cycloaddition and Curtius reactions affording compound **6**, as the highlight of our synthetic work, as it appeared to us that such 1,3-dipolar cycloaddition accompanied by other reactions simultaneously in a single step, would be a rare example. Addition reactions do not take place in the thermal Curtius rearrangements[12].

4. Antimicrobial Activity

The antimicrobial activity was done against two pathogenic bacteria – *Bacillus subtilis* and *S.aureus* and *Asperigillus niger* and *Asperigillus flavus* as the fungal strains by cup-plate method. The reference drugs used were Norfloxacin and Griseofulvin respectively. The activity for the samples and the reference drugs was assayed under identical conditions at 50μg concentration in DMSO as the

control. The zone of inhibition was measured in mm. Compound **4a** exhibited growth inhibition against *B.Subtilis* equal to that of the reference drug. Amongst the carbamates, the ethyl derivative **5b** was almost one and half times more active than Norfloxacin against *B. Subtilis*, while the corresponding hydrazides **8a-c** were less active. The triheterocyclic carbamates **9a-c** and **10a-c** showed moderate antibacterial activity against both the microbes used. All the phenylcarbamates **5a-c** exhibited fungal growth inhibition against *A.niger* slightly more than that of reference drug used. (Table 1).

Table 1. Antimicrobial screening results

Compound	R	Antibacterial		Antifungal	
		B.subtilis Zone of inhibition **(mm)**	**S.aureus** Zone of inhibition **(mm)**	**A.niger** Zone of inhibition **(mm)**	**A.flavus** Zone of inhibition **(mm)**
4a	CH_3	**31**	15	13	11
5b	CH_2CH_3	**44**	17	11	10
7a	CH_3	19	16	17	**19**
7b	CH_2CH_3	23	19	18	**20**
7c	$CH_2CH_2CH_3$	17	-	18	**20**
8b	CH_2CH_3	23	18	18	**20**
10a	H	-	22	12	10
10b	**4-Br**	23	18	**19**	11
10c	2-CH3	25	14	**20**	11
10d	4-CH3	24	**15**	**19**	13
10e	4-Cl	27	17	**18**	12
10f	4-OCH3	28	14	13	12
Norfloxacin		**29**	**24**	**-**	**-**
Griseofulvin		**-**	**-**	**18**	**20**

5. Experimental

IR spectra were recorded on Nicolet-Impact 410 FT-IR spectrophotometer in KBr pellets. ^{1}H-NMR and ^{13}C-NMRspectra were recorded on Brucker 300MHz FT-NMR spectrometer in $CDCl_3$/DMSO-d_6 with TMS as an internal standard. Mass spectra were analyzed by EIMS technique on a Autospec Mass Spectrometer. Elemental analysis was obtained on Heraus CHN rapid analyzer. Purity of the compounds was checked by TLC on Silica Gel plate.

4-(Azidocarbonyl) phenyl azide[13] **(3): Method 1** 3-(p-Hydrazinocarbonyl) phenylsydnone **(1)** (0.01m) was refluxed with conc.HCl (10 mL) on a water-bath for 1 hr. The reaction mixture was then cooled and a solution of sodium nitrite (0.02 m) was added dropwise at 0-5^{0}C. After the complete addition of sodium nitrite solution, the reaction mixture was stirred at room temperature for 2hr. The pale yellow azide separated, was filtered and washed with water.

Method 2 To a stirred solution of 3-(p-hydrazinocarbonyl)phenylhydrazine hydrochloride **(2)** (0.01m) in 25% HCl, a solution of sodium nitrite was added dropwise at 0-5^{0}C.The compound was isolated as above. Yield: 80%, m.p. 96-98 ^{0}C. FT-IR: ν_{cm-1}) 2108 (br, N_3), 1681(C=O); ^{1}H-NMR ($CDCl_3$):δ 7.0

(d,2H, J= 8Hz), 8.5 (d,2H, J= 8Hz). MS :m/z 188 (M^+), 160, 146, 118, 104, 90,7 7. Anal. Calcd. for $C_7H_4N_6O$: C, 44.68; H, 2.12; N, 44.68. Found: C, 44.60; H, 2.06; N, 44.62.

4-(Azido)phenylcarbamates (4a-c): A suspension of 4-(azidocarbonyl) phenyl azide **(3)** (0.01m) in alcohol (15 mL) was refluxed on a steam bath for 3 hrs. The reaction mixture was concentrated and then diluted with water. The product separated was collected and recrystallised from ethanol to get brown needles:
4a. Yield: 87%, m.p. 139-141 ^{0}C. IR (KBr): 3310 (br, NH), 2108 (br, N_3), 1681 cm^{-1} (C=O); ^{1}H-NMR (300MHz,$CDCl_3$) (δ /ppm) :7.44 (d ,2H, Ar-H, *J*=8.3Hz), 7.01 (d ,2H, Ar-H *J*=8.3Hz),6.63 (s,1H, NH), 3.75 (s,3H,OCH_3)..Anal. Calcd. for $C_8H_8N_4O_2$: C, 50.00; H, 4.16; N, 29.16. Found: C, 49.94; H, 4.07; N, 29.23. **4b.**Yield: 89%, m.p. 133-135 ^{0}C. IR (KBr): 3314 (br NH), 2119 (br N_3), 1692 cm^{-1} (C=O); ^{1}H-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 7.38 (d , 2H, Ar-H, *J*=8.1Hz)), 6.96 (d ,2H, Ar-H, *J*=8.1Hz)), 6.71 (s,1H, NH), 4.25 (q,2H,CH_2 J=5Hz), 1.30 (t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300MHz,$CDCl_3$) (δ /ppm) : 15.5, 55.8, 121.5(two carbons), 127.1(two carbons), 136.2, 146.3, 169.3; Anal. Calcd. for $C_9H_{10}N_4O_2$: C, 52.42; H, 4.85; N, 27.18. Found: C, 52.34; H, 4.77; N, 27.13. **4c.**Yield: 81%, m.p. 123-125 ^{0}C. IR (KBr): 3334 (br NH), 2103 (br N_3), 1696 cm^{-1}(C=O) ; ^{1}H-NMR (300MHz,$CDCl_3$) (δ /ppm) : 7.27 (d ,2H, Ar-H, *J*=8.4), 6.86 (d ,2H, Ar-H *J*=8.4), 6.74 (s,1H, NH), 4.10 (t, 2H, CH_2 J=4.5Hz), 1.65 (m, 2H, CH_2 CH_3),0.95 (t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300 MHz,$CDCl_3$) (δ /ppm) : 15.5, 25.4, 60.8, 122.0(two carbons), 127.0(two carbons), 136.2, 146.3, 169.3; Anal. Calcd. for $C_{10}H_{12}N_4O_2$: C, 54.54; H, 5.45; N, 25.45. Found: C, 54.48; H, 5.37; N, 25.36.

4-(Dimethyl-1H-[1,2,3]-triazole-4,5-dicarboxylate-1-yl)phenylcarbamates (5a-c): A mixture of 4-(azidocarbonyl) phenyl azide **(3)** (0.002 mole) in dry xylene and dimethylacetylenedicarboxylate DMAD (0.002 mole) was refluxed at 130^{0}C for 5 hr and then cooled. The separated solid was filtered and recrystallised from ethanol.
5a. Yield: 80%, m.p. 171-173 ^{0}C. IR (KBr): 3310 (br NH), 1734 (C=O), 1719(C=O), 1700 cm^{-1}(C=O); ^{1}H-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 7.69 (d ,2H, Ar-H, *J*=8.1Hz), 7.54 (d ,2H, Ar-H, *J*=8.1Hz), 7.23 (s,1H, NH), 4.03 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3). Anal. Calcd. for $C_{14}H_{14}N_4O_6$: C, 50.29; H, 4.19; N, 16.76. Found: C, 50.24; H, 4.12; N, 16.73. **5b.**Yield: 82%, m.p. 179-181 ^{0}C. IR (KBr): 3310 (br NH), 1738 (C=O), 1720 (C=O),1696 cm^{-1}(C=O); ^{1}H-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 7.61 (d ,2H, Ar-H, *J*=8.4Hz), 7.45 (d ,2H, Ar-H, *J*=8.4Hz), 7.20 (s,1H, NH), 4.27 (t, 2H, CH_2 J=5Hz), 4.00 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3),1.31 (t, 3H, CH_3 J=5Hz), ^{13}C-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 15.0, 53.0, 54.8, 61.60, 119.5(two carbons), 125.5(two carbons), 130.2, 132.8, 138.5, 141.5, 154.10, 159.8, 160.5; Anal. Calcd. for $C_{15}H_{16}N_4O_6$: C, 51.72; H, 4.59; N, 16.09. Found: C, 51.64; H, 4.52; N, 16.03. **5c.**Yield: 77%, m.p. 166-167 ^{0}C. IR (KBr): 3333 (br NH), 1744 (C=O), 1700 cm^{-1}(C=O); ^{1}H-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 7.55 (d ,2H, Ar-H, *J*=8.2Hz), 7.37 (d ,2H, Ar-H, *J*=8.2Hz), 7.11 (s,1H, NH), 4.34 (t, 2H, CH_2 J=4.5Hz), 3.99 (s, 3H, OCH_3), 3.91 (s, 3H, OCH_3), 1.63 (m, 2H, CH_2 CH_3),0.99 (t, 3H, CH_3 J=4.5Hz); ^{13}C-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 12.5, 23.0, 53.0, 54.1, 61.60,119.0, 125.5(two carbons), 130.2, 132.5,138.0, 141.5,154.0, 159.5, 160.5; Anal. Calcd. for $C_{16}H_{18}N_4O_6$: C, 53.03; H, 4.97; N, 15.46. Found: C, 52.94; H, 4.92; N, 15.39.

4-(Dimethyl-1H-[1,2,3]-triazole-4,5-dicarboxylate)phenylisocyanate 6: A mixture of 4-(azidocarbonyl) phenyl azide **(3)** (0.002 mole) in dry xylene and dimethylacetylene dicarboxylate DMAD (0.002 mole) was refluxed at 130^{0}C for 5 hr and then cooled. The separated solid was filtered and used for the further reactions. Yield: 81%, m.p. 132-134 ^{0}C. IR (KBr): 1743(C=O), 1700(C=O), 1606(C=O), 1452(C=N); ^{1}H-NMR (300 MHz,$CDCl_3$) (δ /ppm) : 8.33 (d ,2H, Ar-H J=8.5Hz), 7.69 (d ,2H, Ar-H J=8.5Hz), 4.03(s,3H,OCH_3), 3.96(s,3H,OCH_3); ^{13}C-NMR(300 MHz,$CDCl_3$) (δ /ppm) : 53.0, 53.6, 119.5(two carbons), 124.5(two carbons), 128.0, 129.0, 135.5, 140.6, 142.0, 160.0, 161.0; Anal. Calcd. for $C_{13}H_{10}N_4O_5$: C, 51.65; H, 3.31; N, 18.54. Found: C, 51.60; H, 3.24; N, 18.47.

N-Aryl-N'-(dimethyl-1H-[1,2,3]-triazole-4,5-dicarboxylate-1-yl)phenylureas (7a-f):

4-(Dimethyl-1H-[1,2,3]-triazole-4,5-dicarboxylate)phenylisocyanate **(5)** (0.01m) and aromaticamines (0.01m) were refluxed in anhydrous toluene (15 mL) for 4 hrs at 120^{0}C. Thecrystallineproduct that separated was collected and washed with petroleum ether.
7a.Yield: 68%, m.p. 186-188 ^{0}C. IR (KBr): 3351, (br NH), 1742 cm^{-1} (br, C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) **:** 8.60 (br s,2H, NH), 7.57- 7.27 (m ,8H, Ar-H), 3.89 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) **:** 53.0, 54.0, 120.0(two carbons), 122.5(two carbons), 125.5(two carbons), 129.5(two carbons), 130.5, 132.5, 135.0, 140.0, 141.0, 142.0, 156.5, 160.0,162.5; Anal. Calcd. for $C_{19}H_{17}N_5O_5$: C, 57.72; H, 4.40; N, 17.72. Found: C, 57.67; H, 4.26; N, 17.67. **7b**.Yield: 70%, m.p. 178-180 ^{0}C. IR (KBr): 3345,(br NH), 1740 cm^{-1}(br, C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) **:** 8.72 (br s,2H,NH),7.50- 7.20 (m ,8H, Ar-H), 3.93 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 52.5, 53.5, 119.0, 121.5(two carbons), 123.6(two carbons), 128.6, 129.2, 130.1, 130.8, 132.5, 140.2, 140.8, 158.0, 162.5, 164.0; Anal. Calcd. for $C_{19}H_{16}BrN_5O_5$: C, 57.72; H, 4.40; N, 17.72. Found: C, 57.67; H, 4.26; N, 17.67. **7c**.Yield: 66%, m.p. 192-194 ^{0}C. IR (KBr): 3340, (br NH), 1736 cm^{-1}(br, C=O); ^{1}H-NMR (300 MHZ,DMSO-d_6) (δ /ppm) : 9.24 (br s,2H, NH), 7.68- 7.39 (m ,8H, Ar-H), 3.92 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 21.3, 53.5, 55.0, 118.5(two carbons), 122.0(two carbons), 124.5(two carbons), 129.7, 130.5, 130.5, 133.0, 135.5, 136.8, 140.5, 143.5, 157.0, 162.4, 162.8; Anal. Calcd. for $C_{20}H_{19}N_5O_5$: C, 58.67; H, 4.65; N, 17.11. Found: C, 58.63; H, 4.58; N, 17.06. **7d**.Yield: 70%, m.p. 168-170 ^{0}C. IR ν $_{cm-1}$: 3350, (br NH), 1742 (br, C=O); ^{1}H-NMR (DMSO-d_6) (δ /ppm) : 8.95(br s,2H, NH), 7.58- 7.33 (m ,8H, Ar-H), 3.84 (s, 3H, OCH_3), 3.77(s, 3H, OCH_3), 2.21 (s, 3H, CH_3); ^{13}C-NMR($CDCl_3$) (δ /ppm) : 24.3, 53.5, 55.0, 118.5(two carbons), 122.0(two carbons), 124.5(two carbons), 129.7(two carbons), 130.5, 133.0, 135.5, 136.8, 140.5, 143.5, 157.0, 162.4, 162.8; Anal. Calcd. for $C_{20}H_{19}N_5O_5$: C, 58.67; H, 4.65; N, 17.11. Found: C, 58.61; H, 4.60; N, 17.05. **7e**.Yield: 68%, m.p. 173-175 ^{0}C. IR (KBr): 3351, (br NH), 1740 cm^{-1}(br, C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) : 8.62 (br s,2H, NH), 7.57- 7.27 (m ,8H, Ar-H), 3.89 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 53.5, 55.0, 118.5(two carbons), 122.6(two carbons), 124.7(two carbons), 129.7, 130.9, 131.4, 132.6, 135.2, 137.2, 140.6, 143.5, 157.4, 159.0, 163.3; Anal. Calcd. for $C_{19}H_{16}ClN_5O_5$: C, 53.02; H, 3.72; N, 16.27. Found: C, 52.97; H, 3.67; N, 16.21. **7f**.Yield: 66%, m.p. 192-194 ^{0}C. IR (KBr): 3333, (br NH), 1736 cm^{-1} (br, C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) : 9.20 (br s,2H, NH), 7.69- 7.50 (m ,8H, Ar-H), 4.09 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 53.5, 55.0, 56.8, 118.7, 121.5(two carbons), 125.4, 127.5(two carbons), 131.8(two carbons), 132.7(two carbons), 135.6, 137.5, 141.5, 144.0, 160.0, 164.0; Anal. Calcd. for $C_{20}H_{19}N_5O_6$: C, 56.47; H, 4.47; N, 16.47. Found: C, 56.41; H, 4.42; N, 16.43.

4-[4,5-Bis (hydrazinocarbonyl)-[1,2,3]-triazole-1-yl]phenylcarbamates (8a-c): To a solution of compounds (**7a-c**) (0.001 mol) in 10 mL of ethanol, hydrazine hydrate (99-100%, 0.001 mol) was added and the reaction mixture refluxed for 5 hours. The white solid separated on cooling was filtered, washed with water and recrystallised from ethanol/DMF. **8a.**Yield: 68%, m.p. 222-224 ^{0}C. IR (KBr): 3310, 3216 (br NH), 1692 (C=O), 1683(C=O),1668 cm^{-1}(C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) : 9.46 (br,2H, NH), 7.70 (s,1H, NH of carbamate), 7.57(d ,2H, Ar-H J=8.5), 7.14 (d ,2H, Ar-H J=8.5), 3.66 (s, 3H, OCH_3); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 50.5, 122.0(two carbons), 128.5, 139.4(two carbons), 135.6, 137.0, 141.5, 144.0, 157.5, 164.5; Anal. Calcd. for $C_{12}H_{14}N_8O_4$: C, 43.11; H, 4.19; N, 33.53. Found: C, 43.04; H, 4.12; N, 33.47. **8b.**Yield: 70%, m.p. 198-200 ^{0}C. IR (KBr): 3318, 3225 (br NH), 1690 cm^{-1}(C=O), 1681(C=O),1665 cm^{-1} (C=O), ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) : 9.57 (br,2H, NH), 7.76 (s,1H, NH of carbamate), 7.62(d ,2H, Ar-H J=8.5Hz), 7.24 (d ,2H, Ar-H J=8.5Hz), 4.15 (t, 2H, CH_2 J=4.5Hz), 1.26 (t, 3H, CH_3 J=4.5Hz); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 14.5, 50.5, 122.0(two carbons), 128.5, 139.4(two carbons), 135.6, 137.0, 141.5, 144.0, 157.5, 164.5; Anal. Calcd. for $C_{13}H_{16}N_8O_4$: C, 44.82; H, 4.59; N, 32.18. Found: C, 44.78; H, 4.52; N, 32.07. **8c.**Yield: 66%, m.p. 212-214 ^{0}C. IR (KBr)::3333,3224 (br NH), 1680 (C=O), 1665 cm^{-1} (C=O); ^{1}H-NMR (300 Hz,DMSO-d_6) (δ /ppm) : 9.40 (br,2H, NH), 7.55 -

7.37 (m ,4H, Ar-H, 1H, NH), 4.30 (t, 2H, CH_2 J=5Hz), 1.60 (m, 2H, CH_2CH_3),0.89 (t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 14.5, 21.5, 50.5, 122.0(two carbons), 128.5, 139.4(two carbons), 135.6, 137.0, 141.5, 144.0, 157.5, 164.5; Anal. Calcd. for $C_{14}H_{18}N_8O_4$: C, 46.40 H, 4.97; N, 30.93. Found: C, 46.34; H, 4.92; N, 30.89.

4-[4,5-Bis(2,5-dimethylpyrrole-1-yl-carbamoyl)-[1,2,3]triazole-1-yl]phenyl carbamates (9a-c):

To a suspension of compounds (**8a-c**) (0.001 mol) in ethanol (15mL) was added acetonyl acetone (0.002 mol) and glacial acetic acid (0.5mL) and the reaction mixture heated on a boiling water bath for 6 hrs. The reaction mixture was concentrated to half of its original volume and poured into crushed ice. The separated solid was filtered, washed with water, dried and crystallized from benzene-pet ether as white compound.

9a. Yield: 68%, m.p. 174-176 ^{0}C. IR (KBr): 3308, (br NH), 1683 cm^{-1}(br,C=O); ^{1}H-NMR (300MHz,DMSO-d_6) (δ /ppm) : 10.00 (s,1H, NH), 9.92 (s,1H, NH), 7.72-7.54 (m ,4H, Ar-H, 1H, NH), 5.68 (s,2H, Pyrrole), 5.55 (s,2H, Pyrrole), 3.75 (s, 3H, OCH_3), 2.01 (s, 6H, CH_3 of Pyrrole), 1.72 (s, 6H, CH_3 of Pyrrole); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 18.8, 19.4, 20.0, 21.0, 53.0,110.5(two carbons),110.9,124.5, 129.5(two carbons),131.4, 132.9, 133.6(two carbons), 139.5, 140.2, 145.0, 149.5, 159.4, 176.6, 167.2,169.0; Anal. Calcd. for $C_{24}H_{26}N_8O_4$: C, 58.77; H, 5.30; N, 22.85. Found: C, 58.70; H, 5.34; N, 22.81. **9b.**Yield: 65%, m.p. 163-165 ^{0}C. IR (KBr): 3318, (br NH), 1680 cm^{-1}(br,C=O); ^{1}H-NMR (300MHz,DMSO-d_6) (δ /ppm) : 10.04 (s,1H, NH), 9.98 (s,1H, NH), 7.68-7.54 (m ,4H, Ar-H, 1H, NH), 5.70 (s,2H, Pyrrole), 5.59 (s,2H, Pyrrole), 4.15 (q, 2H, CH_2 J=5Hz), 2.05 (s, 6H, CH_3 of Pyrrole), 1.78 (s, 6H, CH_3 of Pyrrole),1.31(t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 14.7, 19.2, 19.9, 21.0, 21.5, 53.0, 110.6(two carbons),110.9,124.5, 129.7(two carbons),131.4, 132.9, 133.6(two carbons), 139.5, 140.2, 145.0, 149.5, 159.4, 176.6, 167.2,169.0; Anal. Calcd. for $C_{25}H_{28}N_8O_4$: C, 59.52; H, 5.55; N, 22.22. Found: C, 59.46; H, 5.47; N, 22.17. **9c.**Yield: 61%, m.p. 157-159 ^{0}C. IR (KBr): 3311, (br NH), 1684 cm^{-1}(br,C=O); ^{1}H-NMR (300MHz,DMSO-d_6) (δ /ppm) : 10.00 (s,1H, NH), 9.93 (s,1H, NH), 7.74-7.50 (m ,4H, Ar-H, 1H, NH), 5.65 (s,2H, Pyrrole), 5.49 (s,2H, Pyrrole), 4.15 (q, 2H, CH_2 J=4.5Hz), 2.05 (s, 6H, CH_3 of Pyrrole), 1.78 (s, 6H, CH_3 of Pyrrole), 1.60 (m, 2H, CH_2 CH_3),0.89 (t, 3H, CH_3 J=4.5); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 16.7, 19.2, 20.0, 21.0, 21.5, 23.2, 53.0, 110.6(two carbons),110.9,124.5, 129.7(two carbons),131.4, 132.9, 133.6(two carbons), 139.5, 140.2, 145.0, 149.5, 159.4, 176.6, 167.2,169.0; Anal. Calcd. for $C_{26}H_{30}N_8O_4$: C, 60.23; H, 5.79; N, 21.62. Found: C, 60.17; H, 5.72; N, 21.57.

4-[4,5-Bis(5-thioxo-4,5-dihydro-[1,3,4]oxadiazol-2-yl)-[1,2,3]triazole-1-yl] phenylcarbamates (10a-c): A solution of compound (**8a-c**) (0.001 mol) in pyridine (10 mL) was treated with 5 mL of carbon disulfide and the solution stirred at room temperature for 36 hours. The cooled reaction mixture was poured on crushed ice and neutralized with hydrochloric acid. The solid obtained was filtered, washed with water and dried and recrystallised from dimethylformamide.

10a. Yield: 68%, m.p. 261-263 ^{0}C. IR (KBr): 3308, (br NH), 1690 cm^{-1}(C=O); ^{1}H-NMR (300 MHz,DMSO-d_6) (δ /ppm) : 9.94 (s,1H, NH), 9.86 (s,1H, NH), 7.65-7.54 (m ,4H, Ar-H, 1H, NH), 3.75 (s, 3H, OCH_3); ^{13}C-NMR((300 MHz,DMSO-d_6) (δ /ppm) : 50.8, 121.8(two carbons), 128.0, 130.0(two carbons), 139.2(two carbons),140.1, 144.3, 149.0, 155.0, 157.8, 160.0; Anal. Calcd. for $C_{14}H_{10}N_8O_4S_2$: C, 40.19; H, 2.39; N, 26.79. Found: C, 40.10; H, 2.34; N, 26.71. **10b.**Yield: 64%, m.p. 212-214 ^{0}C. IR (KBr): 3311 (br NH), 1694 (C=O); ^{1}H-NMR (300MHz,DMSO-d_6) (δ /ppm) : 9.83 (s,1H, NH), 9.73 (s,1H, NH), 7.61-7.45 (m ,4H, Ar-H, 1H, NH), 4.11 (q, 2H, CH_2 J=5Hz), 1.20 (t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 15.5, 54.8, 128.1(two carbons), 130.0(two carbons), 139.2(two carbons),140.1, 144.3, 149.0, 155.0, 157.8, 160.0; Anal. Calcd. for $C_{15}H_{12}N_8O_4S_2$: C, 41.66; H, 2.77; N, 25.92. Found: C, 41.60; H, 2.71; N, 25.71. **10c.**Yield: 66%, m.p. 253-255 ^{0}C. IR (KBr): 3301 (br NH), 1689 cm^{-1}(C=O); ^{1}H-NMR (300MHz,DMSO-d_6) (δ /ppm) : 9.78 (s,1H, NH), 9.63 (s,1H, NH), 7.71-7.50 (m ,4H, Ar-H, 1H, NH), 4.10 (t, 2H, CH_2 J=5Hz) 1.65 (m, 2H, CH_2CH_3),0.95 (t, 3H, CH_3 J=5Hz); ^{13}C-NMR(300MHz,DMSO-d_6) (δ /ppm) : 14.5, 21.5 68.2,

128.1(two carbons), 130.0(two carbons), 139.2(two carbons),140.1, 144.3, 149.0, 155.0, 157.8, 160.0; Anal. Calcd. for $C_{16}H_{14}N_8O_4S_2$: C, 43.04; H, 3.13; N, 25.11. Found: C, 42.95; H, 3.07; N, 25.04.

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