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Syntheses, biological evaluation and photophysical studies of novel 1,2,3-triazole linked azo dyes†

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We have reported synthesis of two novel series of 1,2,3-triazole linked azo dyes using 4-hydroxy-5-methyl-2*H*-pyran-2-one and sesamol as coupling components in view of the increasing resistance to existing antimicrobial drugs and the need for new antioxidant agents and fluorescent materials. All newly synthesized compounds were evaluated for antibacterial activity, antifungal activity, antioxidant activity and photophysical properties. Antimicrobial activity was evaluated against six microbial strains. Compound **6a** was found to be the most potent antibacterial and antifungal agent, while other compounds showed good to moderate antimicrobial activity. Antioxidant activity was evaluated using DPPH free radical scavenging assay and nitric oxide radical scavenging assay. Compound **6b** was found to be **5** fold more potent than standard antioxidant BHT. Other compounds showed good antioxidant activity. Photophysical properties of all compounds were also investigated in detail.

1. Introduction

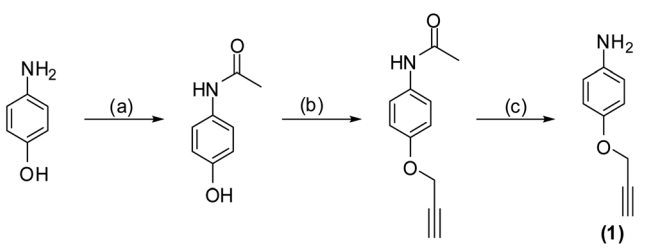
Azo compounds constitute one of the most important chemical classes of organic compounds owing to their diverse applications in various fields such as dying textile fibers, organic synthesis, lasers, liquid crystalline displays, and electro-optical devices. Azo compounds also exhibit biological properties including antibacterial activity,[1–3] pesticidal activities,[4] antiseptic[5] and antiprotozoal properties. There has been lot of research on the synthesis, spectroscopic properties and applications of these dyes in recent years.[6–11] 1,2,3-Triazoles also possess a number of desirable features in the context of medicinal chemistry and industrial applications. They are stable to acidic/basic hydrolysis, reductive/oxidative conditions, and resistant to metabolic degradation. Several members of the 1,2,3-triazole family have shown interesting biological properties, such as antiallergic,[12–14] antibacterial,[15] anti HIV activity,[16] antitumor,[17] cytotoxicity,[18] and as glycosidase inhibitors.[19] Triazoles have also found applications in herbicides, fungicides, and dyes.[20]

Multi-drug resistant bacteria and opportunistic mycoses are becoming increasingly common and are responsible for morbidity and mortality.[21] Although, several new antimicrobial agents have been reported, the problem of drug resistance continues with newly discovered antimicrobial entities. Therefore development of more potent and effective antimicrobial agents is important to overcome the emerging multi-drug resistance strains of bacteria and fungi.[22,23] In recent years, there have been several attempts to prepare novel conjugates having more than one active pharmacophores. We have attempted synthesis of some novel conjugates of 1,2,3-triazoles and azo groups as antimicrobial agents.

2. Results and discussion

2.1 Chemistry

In this work, we have reported the synthesis of two novel series of 1,2,3-triazole linked azo dyes using 4-hydroxy-5-methyl-2*H*-pyran-2-one and sesamol as enol coupling components The antimicrobial activity, antioxidant activity and photophysical properties of these 1,2,3-triazoles linked dyes have also been reported.



Scheme 1 *Reagents and reaction conditions*: (a) acetic anhydride (1.1 eq.), water, 60 °C, 20 min; (b) propargyl bromide (1.1 eq.), K_2CO_3 (2.5 eq.), DMF, 80 °C, 4 h; (c) HCl (36%), ethanol, 60 °C, 3 h.

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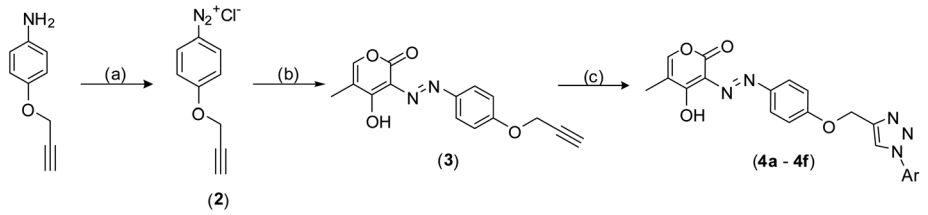


Scheme 2 *Reagents and conditions*: (a) HCl–water (1 : 1), $NaNO_2$ (1 eq.), 0 °C, 15 min; (b) aq. NaOH (12.5 eq.), 4-hydroxy-5-methyl-2*H*-pyran-2-one (1 eq.), 0 °C, 45 min; (c) THF–water (60 : 40), ArN_3 (1 eq.), $CuSO_4 \cdot 5H_2O$ (10 mol%), sodium ascorbate (20 mol%), 60 °C, 3–4 h.

The two novel series of 1,2,3-triazole linked azo dyes (**4a–4f**) and (**6a–6i**) were synthesized as depicted in Scheme 2 and 4, respectively. 4-(Prop-2-ynyloxy)aniline (**1**), which required to initiate the synthesis of desired azo dyes, was prepared from *p*-aminophenol involving[24,25] three step procedure as shown in Scheme 1. Reaction of *p*-aminophenol with acetic anhydride in water at 60 °C gave (4-hydroxyphenyl)acetamide, which on reaction with propargyl bromide in presence of K_2CO_3 in DMF and on subsequent deprotection with HCl yielded 4-(prop-2-ynyloxy)aniline (**1**) in high yield (Scheme 1).

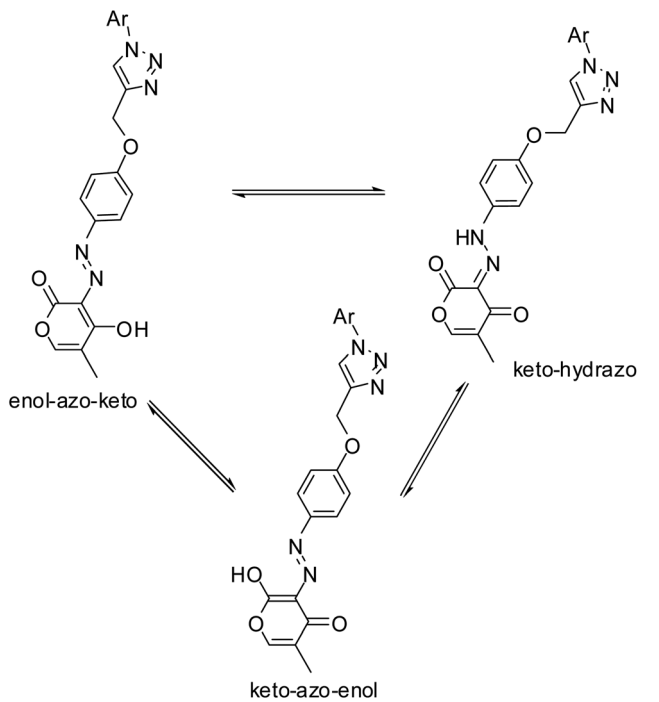
The triazole linked azo dyes (**4a–4f**) were then synthesized by a three step procedure using 4-hydroxy-5-methyl-2*H*-pyran-2-one as a enol coupling component (Scheme 2). The diazotization of (**1**) followed by its coupling with 4-hydroxy-5methyl-2*H*-pyran-2-one in basic solution at 0 °C led to the formation of 4-hydroxy-5-methyl-3-((4-(prop-2-ynyloxy)phenyl)diazenyl)-2*H*-pyran-2-one (**3**). The formation of **3** was confirmed by spectral analysis. IR spectra of compound **3** showed absorption band at 2121 cm^{-1} due to C–C triple bond stretching. ^1H NMR spectra of compound **3** showed a singlet at 4.71 ppm for OCH_2 and singlet at 2.21 for three methyl protons of 4-hydroxy-5-methyl-3-((4-(prop-2-ynyloxy)phenyl)diazenyl)-2*H*-pyran-2-one. The 1,3-dipolar cycloaddition reaction of **3** with various substituted aryl azides in THF–water (60 : 40, v/v) in the presence of $CuSO_4 \cdot 5H_2O$ (10 mol%) and sodium ascorbate (20 mol%) yielded the target compounds (**4a–4f**) in high yield as outlined in Table 1.

Table 1 Synthesis of triazole linked azo dyes (**4a–4f**) and (**6a–6f**)

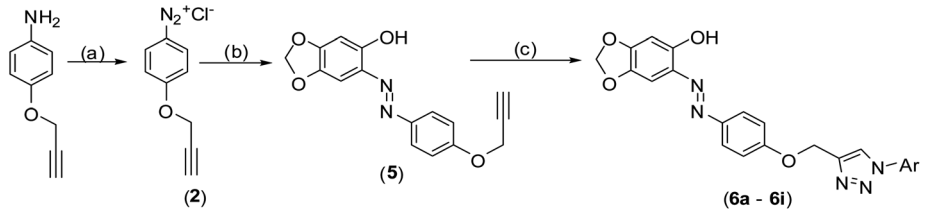
Entry	Ar	Product	Yield (%)	log S^a	*c* log P^a
1	4-$MeOC_6H_4$	**4a**	86	−4.45	1.25
2	C_6H_5	**4b**	82	−4.43	1.35
3	3-$MeOC_6H_4$	**4c**	85	−4.45	1.25
4	4-FC_6H_4	**4d**	86	−4.75	1.41
5	Napthyl	**4e**	84	−6.04	2.53
6	4-BrC_6H_4	**4f**	85	−5.27	2.05
7	4-$MeOC_6H_4$	**6a**	90	−5.63	3.95
8	C_6H_5	**6b**	89	−5.61	4.06
9	4-MeC_6H_4	**6c**	91	−5.96	4.37
10	4-FC_6H_4	**6d**	93	−5.93	4.11
11	Napthyl	**6e**	88	−7.24	5.93
12	4-$NO_2C_6H_4$	**6f**	92	−6.07	3.93
13	4-F-3-ClC_6H_3	**6g**	87	−6.66	4.73
14	4-BrC_6H_4	**6h**	91	−6.45	4.75
15	3-$MeOC_6H_4$	**6i**	93	−5.63	3.95

[a] *c* log *P* and solubility (log *S*) values were calculated using OSIRIS property explorer software.

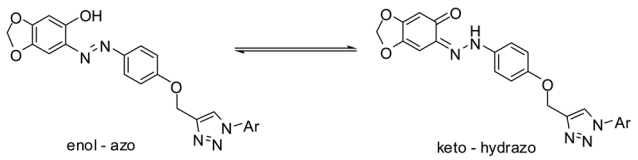
The formation of **4a–4f** was confirmed by IR, ^1H NMR, ^{13}C NMR and mass spectral analysis. Dyes **4a–4f** can exist in a three tautomeric forms as shown in Scheme 3. The IR spectra of dyes **4a–4f** did not show any absorption band for hydroxyl group. However, it showed a weak absorption band in the range of 3147–3140 cm^{-1}, assigned to imino group and two carbonyl absorption band in the range of 1736–1655 cm^{-1}. The data suggests that these dyes exist in a hydrazo–keto form in the solid state. Further evidence for this assignment is provided by the observation that the hydroxyazo OH proton resonates 3–5 ppm lower then NH proton. Hence, the OH proton resonance signal of enol forms is expected to be in region of 9–12 ppm.[26,27] In fact, the ^1H NMR spectra of dyes **4a–4f** showed a signal in the range of 16.52–16.58 ppm and no signal in range of 9–12 ppm. This signal undoubtedly corresponds to the hydrazone NH proton resonance related to keto–hydrazo form. Further support for this structure is provided by ^{13}C spectra. In ^{13}C spectra, carbon attached to –OH in keto–enol form is expected to give signal above 190 ppm, but in ^{13}C spectra of compounds **4a–4f** signal at 180 ppm is observed which is corresponding to carbon (C=N–NH–) associated with keto–hydrazo form.



Scheme 3 Tautomeric forms for azo dyes (**4a–4f**).



Scheme 4 *Reagents and conditions*: (a) HCl–water (1 : 1), $NaNO_2$ (1 eq.), 0 °C, 15 min; (b) aq. NaOH (12.5 eq.), sesamol (1 eq.), 0 °C, 30 min; (c) THF–water, ArN_3 (1 eq.), $CuSO_4 \cdot 5H_2O$ (10 mol%), sodium ascorbate (20 mol%), 60 °C, 1–2 h.



Scheme 5 Tautomeric forms for azo dyes (**6a–6i**).

Another series of novel 1,2,3-triazole linked azo dyes (**6a–6i**) was synthesized by using sesamol as an enol coupling component (Scheme 4). The coupling reaction of diazotized propargylated derivative (**2**) with sesamol under basic conditions at 0 °C afforded pure 6-((4-(prop-2-ynyloxy)phenyl)diazenyl)benzo-[*d*][1,3]dioxol-5-ol (**5**) in 92% yield. The formation of **5** was confirmed by spectral analysis. IR spectra of compound **5** showed broad absorption band at 3421 cm^{-1} due to OH group and carbon–carbon triple bond stretching at 2115 cm^{-1}. ^1H NMR spectra of compound **5** showed a singlet at 6.39 ppm because of the aromatic proton ortho to hydroxyl group over sesamol moiety, another aromatic proton of sesamol ring ortho to azo group merged with four other aromatic protons. Finally, 1,3-dipolar addition reaction of **5** with various substituted aryl azides in presence of $CuSO_4 \cdot 5H_2O$ (10 mol%) and sodium ascorbate (20 mol%) yielded the targeted compounds (**6a–6i**) in high yields (Table 1). The structures of compounds **6a–6i** were confirmed by spectral analysis.

Dyes **6a–6i** can exist in keto–hydrazo and enol–azo tautomeric forms as shown in Scheme 5. The IR spectra of dyes **6a–6i** showed broad absorption band at 3422–3446 cm^{-1} for hydroxyl group and did not show any absorption band for carbonyl group which indicates that these dyes exist in a enol–azo tautomeric form. ^1H NMR spectra of compound **6a–6i** showed singlet in range of 11.85–11.78 ppm, corresponding to OH group related to azo–enol tautomeric form. Further ^{13}C NMR spectra of dyes **6a–6i** did not show any signal in the range of 170–180 ppm for carbonyl carbon atom. All this data confirms that these dyes exist in an enol–azo tautomeric form predominantly due to aromatization of the ring (Scheme 5).

All these compounds **4a–4f** and **6a–6f** were then subjected to antimicrobial activity, antioxidant activity and photophysical studies.

3. Biological evaluation

The physico-chemical properties such as lipophilicity (*c* log *P*) of a molecule play an important role in deciding its drug-likeness as high *c* log *P* values may cause poor absorption or permeation across cell membrane which resulted in a lower biological activity of a molecule.[28] Similarly aqueous solubility (log *S*) of a compound significantly affects its absorption and distribution characteristics, hence low solubility generally results in lower biological activity. The lipophilicity (*c* log *P*) and solubility (log *S*) values of all newly synthesized compounds were calculated using OSIRIS property explorer software and are summarized in Table 1. It can be seen from Table 1 that all compounds showed good lipophilicity (*c* log *P*) and aqueous solubility (log *S*) values.

3.1 Antimicrobial activity

Total six microbial strains, two Gram-positive bacteria (*Staphylococcus aureus* MTCC 96 and *Bacillus subtilis* MTCC 121); two Gram-negative bacteria (*Escherichia coli* MTCC 1652 and *Pseudomonas aeruginosa* MTCC 741) and two fungi, *Aspergillus niger* and *A. flavus*, were selected for evaluation of antimicrobial activity of all compounds under study. Standard antibacterial drug ciprofloxacin and antifungal drug fluconazole was used as positive control.

3.1.1 Antibacterial activity. Triazole linked azo compounds **4a–4f** and **6a–6i** showed variable antimicrobial activity, against Gram positive (*Staphylococcus aureus*, *Bacillus subtilis*) and Gram negative (*Escherichia coli*) bacteria as shown in Table 2. However, none of the compounds showed activity against *Pseudomonas aeruginosa* bacteria. Compounds **4a–4f** containing pyran moiety showed zone inhibition in the range of 22.6–14.3 mm against *Staphylococcus aureus*, 23.6–16.6 mm against *Bacillus subtilis* and 16.6 mm to 14.6 mm against *Escherichia coli*. Compounds **4d** and **4f** however, did not exhibit activity against Gram negative *Escherichia coli* bacteria. Compound **4a** with a methoxy group at *para* position of aromatic ring was found to be most effective against Gram positive *Staphylococcus aureus* and Gram negative *Escherichia coli* bacteria with zone inhibition diameter of 22.6 mm and 16.6 mm respectively. Compound **4b** was found to be most effective against Gram positive *Bacillus subtilis* bacteria with zone inhibition of 23.6 mm, while compound **4a** showed zone inhibition of 23.3 mm. Other compounds showed moderate inhibition against both Gram positive and Gram negative bacteria. Compounds **6a–6i** having sesamol moiety also showed variable antibacterial (Table 2). Compounds **6a–6i** showed zone inhibition in the range of 23.3 mm to 14.3 mm against Gram positive *Staphylococcus aureus*, 24.6 mm to 14.3 mm against Gram positive *Bacillus subtilis* and 16.3 mm to 14.3 mm against

Table 2 Antibacterial activity of compounds (**4a–4f**, **6a–6i**)[a]

Product	Diameter of growth of inhibition zone[b] (mm)			
	Staphylococcus aureus	*Bacillus Subtilis*	*Escherichia coli*	*Pseudomonas aeruginosa*
4a	22.6	23.3	16.6	—
4b	22.3	23.6	15.3	—
4c	21.3	22.6	15.6	—
4d	14.3	16.6	—	—
4e	15.6	17.3	14.6	—
4f	15.6	16.6	—	—
6a	**23.3**	**24.6**	**16.3**	—
6b	19.6	21.3	14.6	—
6c	15.3	17.6	14.6	
6d	14.3	15.6	—	—
6e	14.6	15.6	—	—
6f	13.6	14.3	—	—
6g	14.3	15.3	—	—
6h	14.3	16.3	—	—
6i	16.3	18.3	14.3	—
Ciprofloxacin[c]	26.6	24.0	25.0	22.0
Sesamol	19.5	21.0	14.7	—
4-Hydroxy-5-methyl-2*H*-pyran-2-one	12.1	13.9	—	—
Amino triazole[d]	14.0	14.1	—	—

[a] —: no activity. [b] Values, including diameter of the well (8 mm), are means of three replicates. [c] Anti-bacterial drug. [d] 4-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline.

Gram negative *Escherichia coli* bacteria. Compound **6d**, **6e**, **6f**, **6g** and **6h** did not exhibit activity against Gram negative *Escherichia coli* bacteria. Compound **6a** with methoxy group at *para* position of aromatic ring was found to be most effective against *Staphylococcus aureus*, *Bacillus subtilis* and *Escherichia coli* with zone inhibition of 23.3 mm, 24.6 mm and 16.6 mm, respectively. Other compounds showed moderate antibacterial activity (Table 2).

Minimum inhibitory concentration (MIC) of all compounds (**4a–4f, 6a–6i**) was also measured against Gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and Gram-negative bacteria (*Escherichia coli*) as shown in Table 3. Among compounds having pyran moiety (**4a–4f**), compounds **4a**, **4b** and **4c** showed lowest MIC of 32 μg mL^{-1} against Gram positive bacteria (*Staphylococcus aureus* and *Bacillus subtilis*) and 128 μg mL^{-1} against Gram-negative *Escherichia coli* bacteria. While among compounds having sesamol moiety (**6a–6i**), compound **6a** was found to most effective against all three strains with lowest MIC of 32 μg mL^{-1}, 16 μg mL^{-1} and 126 μg mL^{-1} against Gram positive *Staphylococcus aureus*, *Bacillus subtilis* and Gram negative *Escherichia coli* bacteria, respectively. Other compounds showed MIC in the range of 32 μg mL^{-1} to 256 μg mL^{-1} in comparison of standard drug ciprofloxacin. It can be inferred from structure activity relationship (SAR) of compounds **4a–4f** and **6a–6i** that compounds **4d**, **4f**, **6d**, **6g** and **6h** having halogen substituent over aromatic ring did not exhibit activity against Gram negative *Escherichia coli* bacteria, while presence of substituent like OMe, Me or H over aromatic ring enhances the antibacterial activity.

Table 3 Minimum inhibitory concentration (MIC) (in μg mL^{-1}) of compounds (**4a–4f**, **6a–6i**)

Product	*Staphylococcus aureus*	*Bacillus Subtilis*	*Escherichia coli*
4a	32	32	128
4b	32	32	128
4c	32	32	128
4d	256	128	nt
4e	128	128	256
4f	128	128	nt
6a	**32**	**16**	**128**
6b	64	32	256
6c	128	128	256
6d	256	128	nt
6e	256	128	nt
6f	256	256	nt
6g	256	128	nt
6h	256	128	nt
6i	128	64	256
Ciprofloxacin[a]	6.25	6.25	6.25
Sesamol	64	32	256
4-Hydroxy-5-methyl-2*H*-pyran-2-one	512	256	—
Amino triazole[b]	256	256	—

[a] Anti-bacterial drug, nt – not tested. [b] 4-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline, —: no activity.

3.1.2 Antifungal activity. Antifungal activity of all compounds (**4a–4f, 6a–6i**) was evaluated against *Aspergillus niger* and *Aspergillus flavus*. All compounds showed moderate to good antifungal activity against both strains (Table 4). Compound **4a**

Table 4 Antifungal activity of compounds (**4a–4f**, **6a–6i**) through poisoned food method

Product	Mycelial growth inhibition (%)	
	Aspergillus niger	*Aspergillus flavus*
4a	51.1	53.3
4b	48.8	51.1
4c	50	55.5
4d	37.7	43.3
4e	35.5	42.2
4f	37.7	43.3
6a	53.3	57.7
6b	52.2	56.6
6c	41.1	45.5
6d	43.3	46.6
6e	37.7	44.4
6f	48.8	45.8
6g	42.2	45.5
6h	35.5	38.8
6i	41.1	43.3
Fluconazole[a]	81.1	77.7
Sesamol	47.6	45.2
4-Hydroxy-5-methyl-2*H*-pyran-2-one	30.8	34.2
Amino triazole[b]	35.1	36.3

[a] Standard antifungal drug. [b] 4-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline.

having pyran moiety and 4-OMe substituent over aromatic ring showed highest 51.1% mycelial growth inhibition against *Aspergillus niger* while compound **4c** showed 55.5% mycelial growth inhibition against *Aspergillus flavus*. Compound **4c** showed 50% Mycelial growth inhibition against *Aspergillus niger*, whereas compounds **4a** and **4b** showed more than 50% inhibition of mycelial growth against *Aspergillus flavus*. Compound **6a** with sesamol moiety and 4-OMe substituent over aromatic ring showed highest inhibition of mycelial growth against *Aspergillus niger* (53.3%) and *Aspergillus. flavus* (57.7%). While compound **6b** showed more than 50% inhibition of mycelial growth against *Aspergillus niger* and *Aspergillus flavus*.

For comparison of the antimicrobial activity of all compounds with their precursors the amino triazole namely, 4-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline, which is a part of the parent molecule **6a** reported to posses highest antimicrobial activity was prepared by the reaction of 4-(prop-2-ynyloxy)aniline with 1-azido-4-methoxybenzene in THF–water (60 : 40, v/v) in the presence of $CuSO_4 \cdot 5H_2O$ (10 mol%) and sodium ascorbate (20 mol%) at 60 °C. This has been included in Experimental section. Antibacterial and antifungal activity of all compounds (**4a–4f**, **6a–6i**) was compared with their coupling components like sesamol, 4-hydroxy-5-methyl-2*H*-pyran-2-one and amino triazole *i.e.* 4-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline. As shown in Tables 2 and 4 all compounds showed better antimicrobial activity as compared to 4-hydroxy-5-methyl-2*H*-pyran-2-one and amino triazole. Compounds **4a**, **4b**, **4c**, **6a** and **6b** showed better antibacterial activity as compared to sesamol against *S. aureus* and *B. subtilis* bacteria, while compounds **4a**, **4b**, **4c** and **6a** showed better antibacterial activity as compared to sesamol against *E. coli* bacteria. Further compounds **4a**, **4b**, **4c**, **6a**, **6b** and **6f** showed better antifungal activity as compared to sesamol against *A. niger*, while compounds **4a**, **4b**, **4c**, **6a**, **6b**, **6c**, **6d**, **6f** and **6g** showed better antifungal activity as compared to sesamol against *A. flavus*.

3.2 Antioxidant activity

In vitro antioxidant activity of all compounds was measured against 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical and nitric oxide radical according to literature procedures.[29] The results of antioxidant activity are listed in Table 5. Synthetic antioxidant butylated hydroxytoulene (BHT) was used as positive control.

3.2.1 DPPH Free radical scavenging activity. DPPH radical scavenging activity evaluation is a rapid and convenient assay for screening the antioxidant activities of compounds. It can be observed from Table 5 that compounds **4a–4f** showed good DPPH radical scavenging activity compared to synthetic commercial antioxidant BHT with IC_{50} values ranging from 375.65 μM to 1717.42 μM using DPPH assay. Compound **4f** showed lowest IC_{50} value of 375.65 μM. Compounds **6a–6i** also showed good to excellent DPPH radical scavenging activity compared to standard BHT with IC_{50} values ranging from 10.32 to 70.63 μM. Compound **6b** was found to be **5** fold more potent than BHT with IC_{50} value of 10.32 μM, whereas compounds **6e**, **6i**, **6d**, **6a**, **6c**, **6h**, **6f**, **6h** showed better DPPH radical scavenging activity with IC_{50} values of 18.25, 25.96, 30.22, 33.29, 34.22, 36.01, 44.51 μM respectively, compared to standard BHT.

Table 5 Radical scavenging activities of compounds **4a–4f** and **6a–6i**

Product	DPPH radical scavenging activity (IC_{50} μM)	Nitric oxide radical scavenging activity (IC_{50} μM)
4a	695.32	1025.75
4b	1717.42	967.29
4c	574.38	748.56
4d	1365.30	1231.52
4e	221.984	866.99
4f	375.65	659.34
6a	33.29	1105.25
6b	10.35	875.52
6c	34.22	399.87
6d	30.22	5066.49
6e	18.35	1146.65
6f	36.01	932.23
6g	70.63	1437.58
6h	44.51	309.88
6i	25.96	586.68
BHT[a]	50.18	366.34
Sesamol	35.50	215.10
4-Hydroxy-5-methyl-2*H*-pyran-2-one	120.40	950.23
Amino triazole[b]	—	—

[a] Standard antioxidant. [b] 4-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-methoxy)aniline.

3.2.2 Nitric oxide radical scavenging activity. Nitric oxide (NO) is an important chemical mediator generated by endothelial cells, macrophages, neurons, *etc.* and is involved in the regulation of various physiological processes. Excess concentration of NO is associated with several diseases. Oxygen reacts with the excess nitric oxide to generate nitrite and peroxynitrite anions, which act as free radicals.[30] All compounds showed good to moderate nitric oxide radical scavenging activity as shown in Table 5. Compounds **4a–4f** showed moderate antioxidant activity against nitric oxide radical with IC_{50} values ranging from 659.34 μM to 1231.52 μM compared to BHT with IC_{50} value of 366.34 μM. Compounds **6a–6i** showed good antioxidant activity with IC_{50} values ranging from 309.88 μM to 5066.49 μM. Compound **6h** showed IC_{50} value of 366.34 μM which is lower than standard BHT. The higher antioxidant activity of compounds **6a–6i** could be due to the formation of stable sesamolyl free radical.

Antioxidant activity of all synthesized compounds (**4a–4f**, **6a–6i**) was also compared with their precursors as shown in Table 5. It can be seen from Table 5 that amino triazole did not show antioxidant activity, while compounds **6a**, **6b**, **6c**, **6d**, **6e** and **6i** showed better DPPH antioxidant activity as compare to sesamol, whereas compounds **6a–6i** showed better DPPH antioxidant activity as compare to 4-hydroxy-5-methyl-2*H*-pyran-2-one. The nitric oxide radical scavenging activity of all compounds was found to be lower as compared with sesamol, while compounds **4c**, **4e**, **4f**, **6b**, **6c**, **6f**, **6h** and **6i** showed better nitric oxide radical scavenging activity as compare to 4-hydroxy-5-methyl-2*H*-pyran-2-one.

Table 6 Photophysical data of compounds **4a–4f** and **6a–6i** in chloroform (1×10^{-5} M)

Product	λ_{max} (nm)	$\varepsilon \times 10^5$ (L mol^{-1} cm^{-1})	λ_{em} (nm)	Stoke shift ($\Delta\nu$) cm^{-1}
4a	441	0.49	537	4054
4b	442	0.79	543	4208
4c	441	0.70	542	4225
4d	442	0.31	542	4174
4e	359	0.11, 0.02	517	3180
4f	365, 442	0.10, 0.13	539	4072
6a	342, 447, 530 s	0.60, 0.88, 0.48	593	5508
6b	341, 448,527 s	0.72, 0.95, 054	571	4808
6c	341, 448, 526 s	0.64, 0.93, 0.49	572	4839
6d	339, 447, 529 s	0.55, 0.78, 0.44	570	4918
6e	338, 448, 529 s	0.57, 0.81, 0.43	577	4990
6f	339, 445, 530 s	0.58, 0.81, 0.43	572	4989
6g	339, 444, 529 s	0.49, 0.68, 0.41	583	5370
6h	342, 453, 529 s	0.35, 0.48, 0.29	575	4684
6i	345, 451, 530 s	0.39, 0.50, 0.30	587	5137

4. Photophysical studies

Development of new fluorescent materials is an active area of research because of their wide applications in different areas of research such as telecommunications, optical computing, optical storage, fluorescent probes and fluorescent chemosensors for biologically important metal ions.[31] Thus in view of importance of novel fluorescent materials and their photophysical properties like absorption and emission characteristics, we decided to explore the photophysical properties of all newly synthesized compounds.

4.1 Absorption and emission characteristics

The spectral characteristics of the all compounds such as absorption maxima (λ_{max}), emission maxima (λ_{em}) and extinction coefficient (ε) were measured in chloroform and are presented in Table 6. Compounds **4a–4d** showed single absorption band in the region of 441–442 nm, while compounds **4e** and **4f** showed two absorption bands in the region of 359–362 nm and 442–444 nm, which suggest that compounds **4e** and **4f** exist in two tautomeric forms in chloroform. Compounds **6a–6i** showed three absorption bands, band I in the region of 338–345 nm, band II in the region of 444–453 nm and one shoulder absorption band in the region of 526–530 nm (Fig. 1).

The fluorescence spectrum of all compounds (**4a–4f** and **6a–6i**) was measured in chloroform (Fig. 2). All compounds showed fluorescence even in the presence of azo group which is known to quench the fluorescence intensity, this may be due to the presence of azo group in conjugation with aromatic substituent's which resulted in a partial quenching of fluorescence and hence all compounds showed a weak fluorescence in

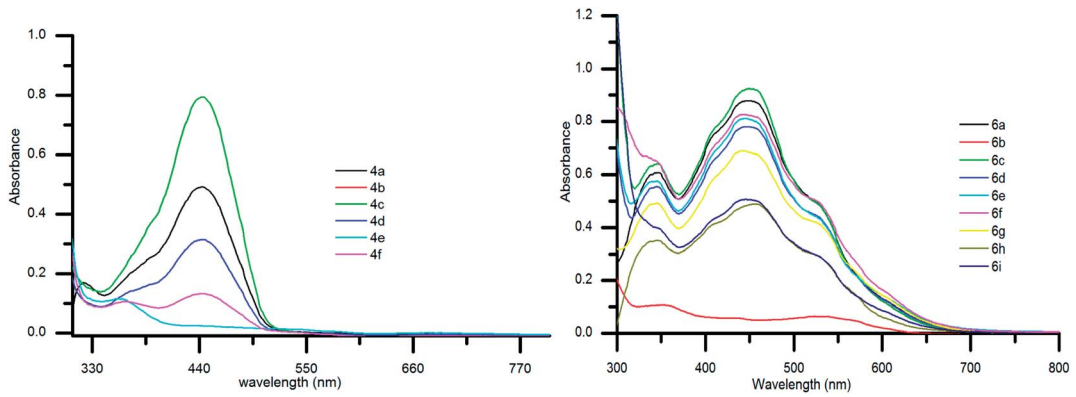


Fig. 1 Absorption spectra of compounds **4a–4f** and **6a–6i** in chloroform (1×10^{-5} M).

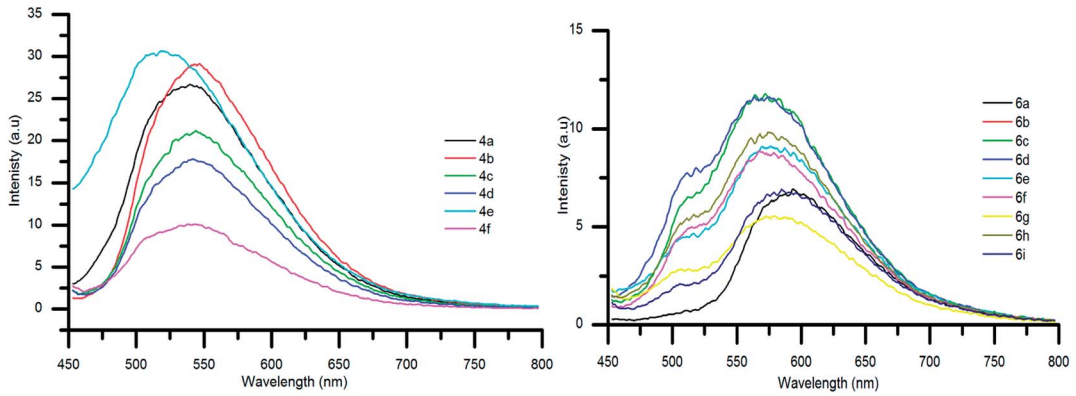


Fig. 2 Emission spectra of compounds **4a–4f** and **6a–6i** in chloroform (1×10^{-5} M).

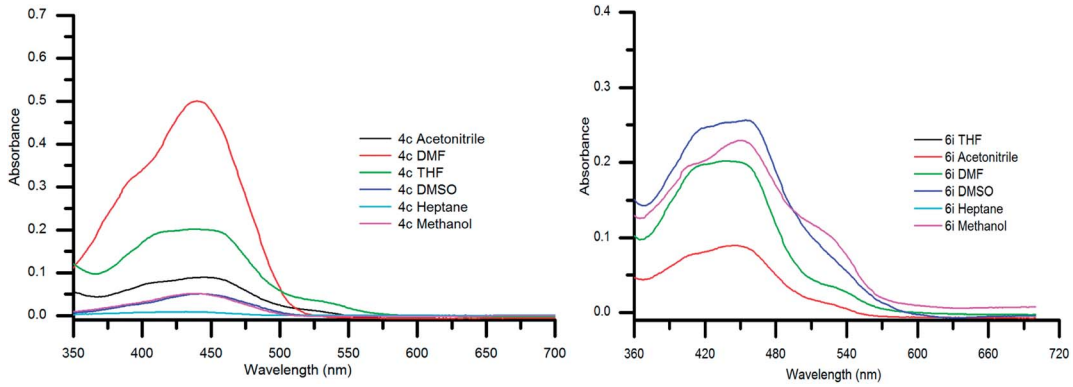


Fig. 3 Absorption characteristics of compound **4c** and **6i** in various solvents (1×10^{-5} M).

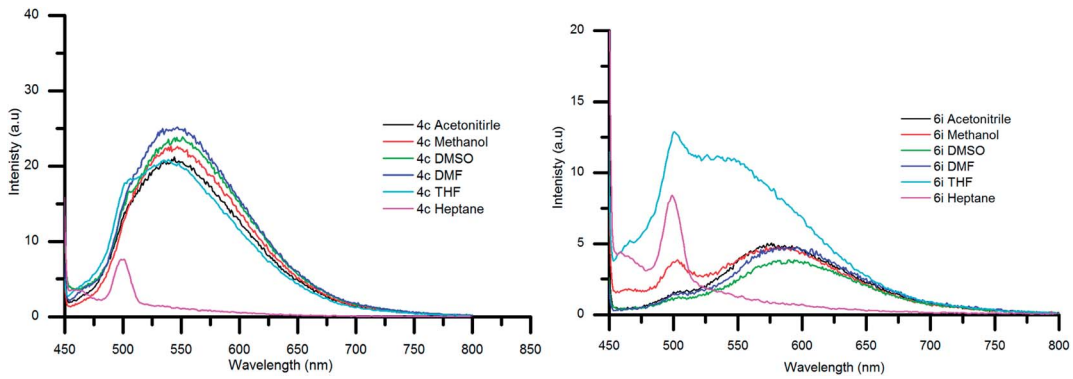


Fig. 4 Emission characteristics of compound **4c** and **6i** in various solvents (1×10^{-5} M).

solution. All compound showed almost similar fluorescence spectra. Compounds **4a–4f** showed emission in the range of 517–543 nm while compounds **6a–6i** showed emission in the range of 570–593 nm. A fluorescence excitation wavelength of 435 nm was used for all compounds.

4.2 Effect of solvent polarity on absorption and emission spectra

The effect of solvent polarities on photophysical properties was investigated by studying the absorption and emission characteristics of triazole linked azo dyes **4c** and **6i** in six different solvents of varying polarity. Effects of solvent polarity on absorption and emission spectra of these dyes are shown in Fig. 3 and 4, respectively and summarized in Table 7. It is very obvious from Table 7 that compounds **4c** and **6i** showed bathochromically shifted absorption and emission maxima in polar solvents like methanol and THF relative to non-polar heptane.

Stokes shift was calculated as the difference between absorption and emission maxima obtained from the spectra on the wavenumber scale. There is a significant increase in stoke shift with increasing polarity from non-polar heptane to polar solvents for compounds **4c** and **6i.**

Solvent dependent spectral shift was investigated using Lippert–Mataga plot[31] to comprehend the polarity effect on compounds **4c** and **6i.** Lippert–Mataga plot describes the effect

Table 7 Effect of solvent polarity on photophysical properties of compound **4c** and **6i**

	4c				**6i**			
Solvents	λ_{max} (nm)	$\varepsilon \times 10^5$ (L mol^{-1} cm^{-1})	λ_{emi} (nm)	Stoke shift $\Delta\lambda$ (cm^{-1})	λ_{max} (nm)	$\varepsilon \times 10^5$ (L mol^{-1} cm^{-1})	λ_{emi} (nm)	Stoke shift $\Delta\lambda$ (nm)
MeOH	438	0.05	542	4381	449	0.22	581	5060
DMF	440	0.5	543	4311	438	0.20	588	5824
ACN	435	0.8	540	4470	444	0.09	581	5311
DMSO	441	0.05	546	4360	448	0.25	591	5401
THF	442	0.08	539	4072	445	0.21	538	3884
Heptane	432	0.02	498	3068	436	0.06	499	2895

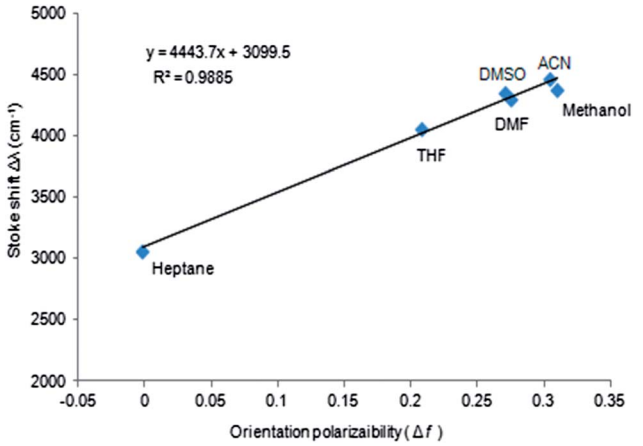


Fig. 5 Lippert–Mataga plot for compound **4c**.

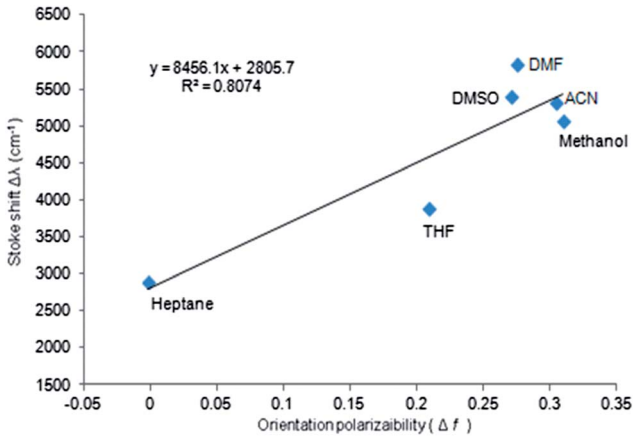


Fig. 6 Lippert–Mataga plot for compound **6i**.

of solvent polarity on the stoke shift of molecule and can be obtained by plotting stoke shift *vs.* orientation polarizaibility, which is a result of both the mobility of electrons in the solvent and dipole moment of solvent. The Lippert–Mataga plot for compounds **4c** and **6i** (Fig. 5 and 6) shows good linear relationship (correlation factor $R^2 = 0.9885$ and 0.8074 for **4c** and **6i**, respectively), suggesting that the dipole–dipole interaction and dipole-induced dipole interactions between the solute and solvent are mainly responsible for the solvent-dependent fluorescence shift.

4.3 Effect of base and acid on absorption spectra and emission spectra

The effect of addition of base and acid on the absorption of compounds **4c** and **6i** was investigated by addition of 0.1 mL of base (potassium hydroxide, 0.1 M) and 0.1 mL of acid (hydrochloric acid, 0.1 M) to 1 mL solution of compounds **4c** and **6i** in acetonitrile. The absorption spectra of compounds **4c** and **6i** was sensitive to addition of base (potassium hydroxide, 0.1 M). Compound **4c** showed an hypochromic shift from λ_{abs} at 433 nm to λ_{abs} at 371 nm (shift of 62 nm) on the addition of

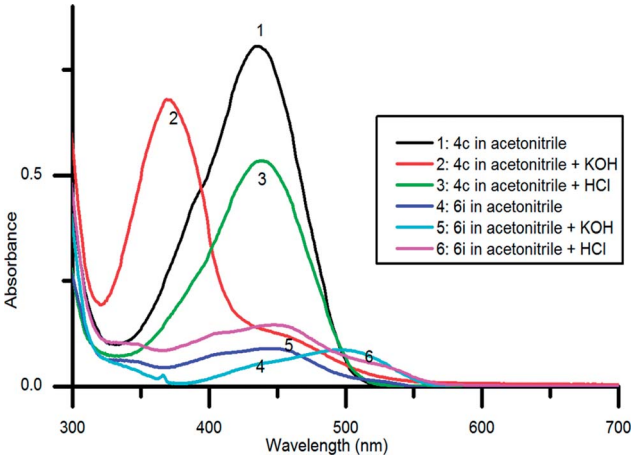


Fig. 7 Absorption spectra of compounds **4c** and **6i** in acidic and basic solutions (1×10^{-5} M).

0.1 mL of base (Fig. 7). However, compound **6i** showed bathochromic shift on addition of base from λ_{abs} at 439 nm to λ_{abs} 494 nm (bathochromic shift of 55 nm) (Fig. 7). However, addition of 0.1 mL acid (HCl 0.1 M) to **4c** and **6i** in acetonitrile resulted in bathochromic shift. Compounds **4c** and **6i** showed same bathochromic shift of 5 nm on addition of acid (Fig. 7). These results indicate that tautomeric forms of compound **4c** and **6i** in acetonitrile changed to another tautomeric form on addition of acid or base.

The effect of acid and base on emission spectra of compound **4c** and **6i** in acetonitrile was also investigated (Fig. 8). Addition of 0.1 mL of acid (HCl, 0.1 M) did not affect the emission spectra of compound **4c**. Whereas addition of 0.1 mL of base (KOH, 0.1 M) resulted in a large blue shift of 40 nm. The large shift could be due to change in tautomeric form on addition of base. Emission spectra of **6i** was insensitive to addition of acid and base and showed only slight red shift of 9 nm and 7 nm on addition of base and acid, respectively.

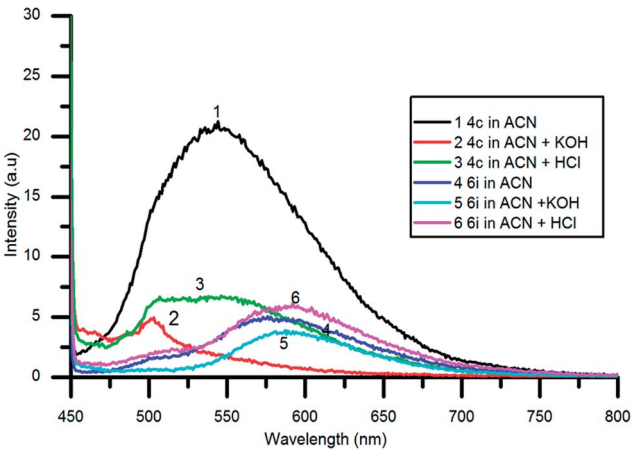


Fig. 8 Emission spectra of compounds **4c** and **6i** in acidic and basic solutions (1×10^{-5} M).

5. Conclusion

In conclusion, we have synthesized two novel series of 1,2,3-triazole linked azo dyes, **4a–4f** and **6a–6i** using 4-hydroxy-5-methyl-2*H*-pyran-2-one and sesamol as coupling components. All newly synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and HRMS analysis. Spectral study suggests that azo compound **4a–4f** exists in keto–hydrazo tautomeric form, while compound **6a–6i** containing sesamol moiety exists in enol–azo tautomeric form. All compounds were evaluated for antibacterial activity against Gram positive as well as Gram negative bacteria. Compound **6a** was found to be most potent against both Gram positive (*Staphylococcus aureus*, *Bacillus subtilis*) and Gram negative (*Escherichia coli*) bacteria. Other compounds showed moderate antibacterial activity. Antifungal activity of all compounds was also evaluated against *Aspergillus niger* and *Aspergillus. flavus*. Compound **6a** was found to be most effective against both fungal strains with 53.3% and 57.7% inhibition of mycelial growth against *Aspergillus niger* and *Aspergillus. flavus*, respectively. Thus it can be concluded that compound **6a** showed good antibacterial and antifungal activity among all the compounds. Antioxidant activity of all compounds was measured using DPPH free radical assay and nitric oxide radical scavenging assay. All compounds showed good DPPH radical scavenging activity and good to moderate nitric oxide radical scavenging activity. Compounds having sesamol moiety (**6a–6i**) showed higher antioxidant activity compared to compounds with pyran moiety (**4a–4i**). In DPPH assay, compound **6b** was found to be **5** fold more potent than standard antioxidant BHT, while compounds **6e**, **6i**, **6d**, **6a**, **6c**, **6h**, **6f**, **6h** showed better DPPH radical scavenging activity than BHT. Compound **6h** also showed good nitric oxide radical scavenging activity with IC_{50} value lower than BHT. Photophysical properties of all the compounds were also studied. All compounds showed fluorescence in solution. Effect of solvent polarity on absorption and emission spectra of compound **4c** and **6i** was investigated. It was observed that fluorescence spectra depends on solvent polarity and showed good correlation to Lippert–Mataga plot. Effect of addition of acid and base on absorption and emission spectra has also been reported.

6. Experimental

All chemicals were purchased from Sigma-Aldrich and Spectrochem and were used as received. Silica gel 60 F_{254} (precoated aluminium plates) from Merck were used to monitor reaction progress. IR (KBr) spectra were recorded on Perkin Elmer FTIR spectrophotometer and the values are expressed as ν_{max} cm^{-1}. The NMR (^{1}H and ^{13}C) spectra were recorded on Jeol JNM ECX-400P at 400 MHz and 100 MHz, respectively. The chemical shift values are recorded on δ scale and the coupling constants (J) are in Hertz. The high resolution mass spectra were recorded on an Agilent 6520 – QTOF LCMS having ESI source in positive mode. Ultraviolet-visible (UV-Vis) absorption spectra were recorded on Analytikjena specord 250 spectrophotometer. The fluorescence spectra were measured at Cary Eclipse Fluorescence spectrophotometer.

6.1 General procedure for the synthesis of 4-hydroxy-5-methyl-3-((4-(prop-2-ynyloxy)phenyl)diazenyl)-2*H*-pyran-2-one (3)

4-(Prop-2-ynyloxy)aniline (0.01 mol) was dissolved in a mixture of water and conc. hydrochloric acid (4 mL, ratio 1 : 1) and the solution was cooled to 0–5 °C. Sodium nitrite (0.01 mol) was added slowly with vigorous stirring and reaction mixture was stirred for about 20 min. Solution of 4-hydroxy-2-methyl-5*H*-pyran-2-one (0.01 mol) in water (10 mL) containing sodium hydroxide (0.125 mol) was then added slowly to the reaction mixture with stirring at 0–5 °C. The reaction mixture was stirred at this temperature for another 2 h. After completion of reaction as monitored by TLC using ethyl acetate–petroleum ether, 60 : 40, v/v as eluent, reaction mixture was diluted with water (20 mL) and the precipitate formed were filtered at pump, washed with water and recrystallized from ethanol to afford pure 4-hydroxy-5-methyl-3-((4-(prop-2-ynyloxy)phenyl)diazenyl)-2*H*-pyran-2-one (3) in 86% yield.

Red solid, M.p.: 145 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.57 (s, 1H, N=NH), 7.58 (d, 2H, J = 7.32 Hz, ArH) 7.04–6.97 (m, 3H, ArH), 4.71 (s, 2H, OCH_2), 2.53 (s, 1H, CH), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.4, 56.1, 75.4, 76.1, 106.7, 114.7, 115.4, 115.7, 116.1, 119.5, 129.5, 166.2, 185.2; IR (ν_{max} cm^{-1}, film): = 3291, 2121, 1728, 1641, 1508, 1219; HRMS (ESI) $[M + H]^+$ calcd for $C_{15}H_{12}N_2O_4$: 285.0840, found: 285.0760.

6.2 General procedure for the synthesis of 1,2,3-triazole linked azo dyes (4a–4f)

A mixture of 4-hydroxy-5-methyl-3-((4-(prop-2-ynyloxy)phenyl) diazenyl)-2*H*-pyran-2-one **3** (1 mmol), substituted aryl azide (1 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol%), sodium ascorbate (20 mol%) and 10 mL of THF–water (60 : 40, v/v) was placed in a 50 mL round-bottomed flask. The reaction mixture was stirred at 60 °C for 3–4 h. The progress of reaction was monitored by TLC using ethyl acetate–petroleum ether (60 : 40, v/v) as eluent. After completion of the reaction as indicated by TLC, water (20 mL) was added to the reaction mixture. The precipitate formed was collected by filtration at pump and washed with water. The crude product was purified by flash column chromatography over silica gel (230–400 mesh) using ethyl acetate–petroleum ether as eluent to afford pure products (**4a–4f**).

4-Hydroxy-3-((4-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-methoxy)phenyl)diazenyl)-5-methyl-2*H*-pyran-2-one (4a). Brown solid, M.p.: 149 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.58 (s, 1H, N=NH), 7.96 (s, 1H, triazolyl-H), 7.62–7.60 (m, 4H, ArH), 7.09–6.99 (m. 5H, ArH), 5.30 (s, 2H, OCH_2), 3.85 (s, 3H, CH_3), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 166.2, 160.0, 159.9, 158.3, 143.8, 134.5, 130.2, 122.2, 121.3, 121.2, 119.6, 115.9, 114.7, 107.5, 62.2, 55.6, 20.4; IR (ν_{max} cm^{-1}, film): = 3142, 1715, 1650, 1603, 1504, 1437, 1221; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{19}N_5O_5$: 434.1454, found: 434.1381.

4-Hydroxy-5-methyl-3-((4-((1-phenyl-1*H*-1,2,3-triazol-4-yl)-methoxy)phenyl)diazenyl)-2*H*-pyran-2-one (4b). Brown solid, M.p.: 239 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.58 (s, 1H, N=NH), 8.04 (s, 1H, triazolyl-H) 7.72 (d, 2H, J = 7.36 Hz, ArH), 7.58–6.43 (m. 6H, ArH), 7.08 (d, 2H, J = 7.32 Hz, ArH), 5.31 (s, 2H, OCH_2), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7,

166.2, 161.6, 160.0, 159.1, 142.8, 136.8, 134.6, 129.8, 129.0, 124.9, 121.0, 120.6, 119.7, 119.6, 115.97, 107.5, 62.2, 20.2; IR (ν_{max} cm^{-1}, film): = 3140, 3071, 2926, 1734, 1655, 1604, 1519, 1405, 1250; HRMS (ESI) $[M + H]^+$ calcd for $C_{21}H_{17}N_5O_4$: 404.1354, found: 404.1285.

4-Hydroxy-3-((4-((1-(3-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)-methoxy)phenyl)diazenyl)-5-methyl-2*H*-pyran-2-one (4c). Brown solid, M.p.: 173 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.58 (s, 1H, N═NH), 8.03 (s, 1H, triazolyl-H), 7.58 (d, 2H, J = 9.16 Hz, ArH), 7.41–7.32 (m, 4H, ArH), 7.08 (d, 2H, J = 7.32 Hz, ArH), 6.96 (d, 2H, J = 7.32 Hz, ArH), 5.30 (s, 2H, OCH_2), 3.86 (s, 3H, CH_3), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 166.2, 160.5, 159.9, 158.3, 144.0, 137.8, 134.6, 134.08, 130.5, 121.1, 119.6, 115.9, 114.8, 114.7, 112.4, 107.5, 62.2, 55.6, 20.4; IR (ν_{max} cm^{-1}, film): = 3140, 3071, 2926, 1736, 1655, 1609, 1507, 1406, 1219; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{19}N_5O_5$: 434.1459, found: 434.1351.

3-((4-((1-(4-Fluorophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-phenyl)diazenyl)-4-hydroxy-5-methyl-2*H*-pyran-2-one (4d). Brown solid, M.p.: 218 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.52 (s, 1H, N═NH), 7.96 (s, 1H, triazolyl-H), 7.67–7.63 (m, 2H, ArH), 7.53 (d, 2H, J = 7.32 Hz, ArH), 7.19–7.14 (m, 3H, ArH), 7.03 (d, 2H, J = 9.2 Hz, ArH), 5.26 (s, 2H, OCH_2), 2.16 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 166.2, 161.2, 159.9, 158.3, 144.3, 134.6, 122.6, 122.5, 121.2, 119.6, 116.9, 116.6, 115.9, 107.4, 62.2, 20.4; IR (ν_{max} cm^{-1}, film): = 3147, 3064, 2925, 1735, 1654, 1602, 1403, 1217; HRMS (ESI) $[M + H]^+$ calcd for $C_{21}H_{16}FN_5O_4$: 422.1259, found: 422.1182.

4-Hydroxy-5-methyl-3-((4-((1-(naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl) diazenyl)-2*H*-pyran-2-one (4e). Brown solid, M.p.: 106 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.57 (s, 1H, N═NH), 8.01 (s, 1H, triazolyl-H), 7.70–7.56 (m, 7H, ArH), 7.24–7.08 (m, 5H, ArH), 5.30 (s, 2H, OCH_2), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.6, 166.2, 162.4160.0, 158.3, 142.7, 138.6, 134.6, 129.7, 128.9, 126.6, 126.0, 125.4, 125.0, 121.4, 120.9, 120.6, 119.7, 117.8, 115.9, 107.13, 61.6, 20.6; IR (ν_{max} cm^{-1}, film): = 3144, 3064, 2927, 1675, 1599, 1508; HRMS (ESI) $[M + H]^+$ calcd for $C_{25}H_{19}N_5O_4$: 454.1510, found: 454.1415.

3-((4-((1-(4-Bromophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl) diazenyl)-4-hydroxy-5-methyl-2*H*-pyran-2-one (4f). Brown solid, M.p.: 215 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 16.57 (s, 1H, N═NH), 8.03 (s, 1H, triazolyl-H), 7.64–7.56 (m, 7H, ArH), 7.07 (d, 2H, J = 9.16 Hz, ArH), 5.30 (s, 2H, OCH_2), 2.21 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7, 166.3, 163.8, 161.0, 158.2, 134.1, 134.8, 132.9, 128.2, 128.0, 127.1, 124.9, 123.6, 122.5, 121.9, 120.8, 119.6, 116.9, 115.9, 110.9, 107.4, 62.2, 29.6; IR (ν_{max} cm^{-1}, film): = 3140, 2925, 1735, 1653, 1604, 1508, 1402, 1296; HRMS (ESI) $[M + H]^+$ calcd for $C_{21}H_{16}BrN_5O_4$: 482.0459, found: 482.0389.

6.3 Procedure for synthesis of 6-((4-(prop-2-ynyloxy)phenyl)-diazenyl)benzo[*d*][1,3]dioxol-5-ol (5)

4-(Prop-2-ynyloxy)aniline (0.01 mol) was dissolved in a mixture of water and concentrated hydrochloric acid (4 mL, ratio 1 : 1) and solution was cooled to 0–5 °C. Sodium nitrite (0.01 mol) was added slowly with vigorous stirring and reaction mixture was stirred for about 20 min. Solution of sesamol (0.01 mol) in water (10 mL) containing sodium hydroxide (0.125 mol) was added slowly to the reaction mixture with stirring at 0–5 °C. The reaction mixture was stirred at this temperature for another 1 h. After completion of reaction as indicated by TLC using ethyl acetate–petroleum ether (60 : 40, v/v) as eluent, reaction mixture was diluted with water (20 mL) and the precipitate formed were filtered at pump, washed with water and recrystallized from ethanol to afford pure 6-((4-(prop-2-ynyloxy)phenyl)diazenyl)-benzo[*d*][1,3]dioxol-5-ol **(5)** in 92% yield.

Red solid, M.p.: 176 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 14.69 (s, 1H, OH), 7.68 (d, 2H, J = 9.2 Hz, ArH), 7.05–7.02 (m, 3H, ArH), 6.39 (s, 1H, ArH), 5.99 (s, 2H, OCH_2), 4.73 (s, 2H, OCH_2), 2.54 (s, 1H, CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3, 158.0, 142.8, 141.7, 131.7, 121.9, 115.6, 108.2, 100.0, 99.9, 98.9, 78.0, 75.6, 56.0; IR (ν_{max} cm^{-1}, film): = 3421, 3068, 2916, 2115, 1602, 1495, 1219; HRMS (ESI) $[M + H]^+$ calcd for $C_{16}H_{12}N_2O_4$: 297.0870, found: 297.0796.

6.4 General procedure for the synthesis of 1,2,3-triazole linked azo dyes (6a–6i)

A mixture of 6-((4-(prop-2-ynyloxy)phenyl)diazenyl)benzo[*d*][1,3]-dioxol-5-ol (5) (1 mmol), substituted aryl azide (1 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol%), sodium ascorbate (20 mol%) and 10 mL of THF–water (60 : 40, v/v) was placed in a 50 mL round-bottomed flask. The reaction mixture was stirred at 60 °C for 1–2 h. The progress of reaction was monitored by TLC using ethyl acetate–petroleum ether (70 : 30, v/v) as eluent. After completion of the reaction as observed by TLC, water (20 mL) was added to the reaction mixture. The precipitate formed was collected by filtration at pump and washed with water. The product so obtained, was recrystallized from ethanol to afford pure products in good yield (**6a–6i**).

6-((4-((1-(4-Methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-phenyl)diazenyl)benzo[*d*][1,3]dioxol-5-ol (6a). Dark red solid, M.p.: 290 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.85 (s, 1H, OH), 8.86 (s, 1H, triazolyl-H), 7.87–7.79 (m, 4H, ArH), 7.15–7.11 (m, 5H, ArH), 6.60 (s, 1H, ArH), 6.06 (s, 2H, OCH_2), 5.30 (s, 2H, OCH_2), 3.81 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 159.3, 154.5, 153.2, 152.1, 141.5, 132.1, 123.4, 123.3, 121.6, 120.0, 116.6, 115.3, 115.2, 114.7, 103.0, 100.5, 99.4, 61.3, 59.4; IR (ν_{max} cm^{-1}, KBr): = 3421, 3068, 2908, 1600, 1560, 1519, 1461, 1252; HRMS (ESI) $[M + H]^+$ calcd for $C_{23}H_{19}N_5O_5$: 446.1459, found: 446.1376.

6-((4-((1-Phenyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)diazenyl)-benzo[*d*][1,3]dioxol-5-ol (6b). Dark red solid, M.p.: 180 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.78 (s, 1H, OH), 8.83 (s, 1H, triazolyl-H), 7.78–7.75 (m, 4H, ArH), 7.43–7.06 (m, 6H, ArH), 6.48 (s, 1H, ArH), 5.94 (s, 2H, OCH_2), 5.17 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.5, 154.7, 152.3, 141.9, 136.5, 132.2, 130.0, 129.9, 128.9, 128.8, 123.5, 123.3, 123.2, 120.2, 115.4, 115.3, 102.2, 100.56, 98.4, 61.4; IR (ν_{max} cm^{-1}, KBr): = 3430, 3067, 2917, 1599, 1499, 1474, 1239; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{17}N_5O_4$: 416.4088, found: 416.4011.

6-((4-((1-4-Tolyl-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)diazenyl)-benzo[*d*][1,3]dioxol-5-ol (6c). Dark red solid, M.p.: 185 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.84 (s, 1H, OH), 8.91 (s, 1H, triazolyl-H),

7.89–7.76 (m, 4H, ArH), 7.39 (d, 2H, J = 7.36 Hz, ArH), 7.22–7.16 (m, 3H, ArH), 6.60 (s, 1H, ArH), 6.06 (s, 2H, OCH_2), 5.31 (s, 2H, OCH_2), 2.36 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.4, 154.6, 152.0, 144.4, 141.7, 138.4, 134.3, 132.0, 130.0, 123.4, 122.9, 122.8, 120.0, 115.2, 102.0, 100.2, 98.3, 61.3, 20.5; IR (ν_{max} cm^{-1}, KBr): = 3412, 2918, 1603, 1507, 1474, 1251; HRMS (ESI) $[M + H]^+$ calcd for $C_{23}H_{19}N_5O_4$: 430.1510, found: 430.1436.

6-((4-((1-(4-Fluorophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-diazenyl)benzo[*d*][1,3]dioxol-5-ol (6d). Dark red solid, M.p.: 207 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.83 (s, 1H, OH), 8.95 (s, 1H, triazolyl-H), 7.95–7.88 (m, 4H, ArH), 7.45–7.16 (m, 5H, ArH), 6.60 (s, 1H, ArH), 6.06 (s, 2H, OCH_2), 5.32 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.4, 154.5, 152.1, 144.8, 141.6, 132.9, 132.1, 123.4, 123.2, 122.5, 122.4, 116.8, 116.6, 115.3, 102.0, 100.3, 98.3, 61.3; IR (ν_{max} cm^{-1}, KBr): = 3420, 3084, 2917, 1601, 1514, 1475, 1238; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{16}FN_5O_4$: 434.1259, found: 434.1175.

6-((4-((1-(Naphthalen-1-yl)-1*H*-1,2,3-triazol-4-yl)methoxy)-phenyl)diazenyl)benzo[*d*][1,3]dioxol-5-ol (6e). Dark red solid, M.p.: 212 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.82 (s, 1H, OH), 8.82 (s, 1H, triazolyl-H), 8.20–8.11 (m, 2H, ArH), 7.92–7.90 (m, 2H, ArH), 7.74–7.61 (m, 4H, ArH), 7.45 (d, 2H, J = 7.32 Hz, ArH), 7.27–7.17 (m, 3H, ArH), 6.61 (s, 1H, ArH), 6.07 (s, 2H, OCH_2), 5.39 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.3, 154.5, 152.1, 144.8, 141.6, 133.5, 133.0, 132.0, 130.2, 128.2, 127.9, 127.8, 127.4, 127.0, 125.3, 123.9, 123.4, 122.70, 121.7, 115.3, 102.0, 100.2, 98.3, 61.2; IR (ν_{max} cm^{-1}, KBr): = 3413, 3070, 2920, 1601, 1497, 1473, 1240; HRMS (ESI) $[M + H]^+$ calcd for $C_{26}H_{19}N_5O_4$: 466.1510, found: 466.1440.

6-((4-((1-(4-Nitrophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-diazenyl)benzo[*d*][1,3]dioxol-5-ol (6f). Dark red solid, M.p.: 239 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.81 (s, 1H, OH), 9.19 (s, 1H, triazolyl-H), 8.45 (d, 2H, J = 9.2 Hz, ArH), 8.24 (d, 2H, J = 7.36 Hz, ArH), 7.89 (d, 2H, J = 9.16 Hz, ArH), 7.23–7.16 (m, 3H, ArH), 6.60 (s, 1H, ArH), 6.07 (s, 2H, OCH_2), 5.36 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.2, 155.7, 154.6, 152.1, 146.7, 144.8, 141.7, 140.6, 132.2, 125.5, 123.5, 123.4, 120.7, 115.3, 102.0, 100.2, 98.3, 61.3; IR (ν_{max} cm^{-1}, KBr): = 3422, 3082, 2925, 1597, 1505, 1481, 1341, 1238; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{16}N_6O_6$: 461.1204, found: 461.1105.

6-((4-((1-(3-Chloro-4-fluorophenyl)-1*H*-1,2,3-triazol-4-yl)-methoxy)phenyl)diazenyl)benzo [*d*][1,3]dioxol-5-ol (6g). Dark red solid, M.p.: 183 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.47 (s, 1H, OH), 9.03 (s, 1H, triazolyl-H), 8.24 (d, 2H, J = 9.2 Hz, ArH), 7.99–7.88 (m, 3H, ArH), 7.71–7.66 (m, 1H, ArH), 7.22–7.16 (m, 3H, ArH), 6.61 (s, 1H, ArH), 6.07 (s, 2H, OCH_2), 5.33 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.4, 158.1, 154.6, 151.1, 144.8, 141.6, 133.5, 132.2, 123.4, 123.3, 122.0, 122.2, 122.4, 120.9, 118.1, 115.2, 101.9, 100.1, 98.3, 61.1; IR (ν_{max} cm^{-1}, KBr): = 3433, 3085, 2924, 1604, 1508, 1474, 1239; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{15}ClFN_5O_4$: 468.0870, found: 468.0765.

6-((4-((1-(4-Bromophenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)phenyl)-diazenyl)benzo[*d*][1,3]dioxol-5-ol (6h). Dark red solid, M.p.: 212 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.81 (s, 1H, OH), 9.00 (s, 1H, triazolyl-H), 7.87–7.78 (m, 7H, ArH), 7.21–7.15 (m, 2H, ArH), 6.60 (s, 1H, ArH), 6.06 (s, 2H, OCH_2), 5.32 (s, 2H, OCH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.2, 154.4, 152.0, 144.7, 140.5, 135.5, 134.2, 132.6, 131.9, 123.2, 122.8, 121.8, 118.5, 115.0, 101.9, 100.1, 98.2, 61.2; IR (ν_{max} cm^{-1}, KBr): = 3446, 3114, 2918, 1605, 1495, 1472, 1248; HRMS (ESI) $[M + H]^+$ calcd for $C_{22}H_{16}BrN_5O_4$: 494.0459, found: 494.0377.

6-((4-((1-(3,5-Dimethoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)-phenyl)diazenyl)benzo[*d*][1,3]dioxol-5-ol (6i). Dark red solid, M.p.: 167 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.81 (s, 1H, OH), 8.63 (s, 1H, triazolyl-H), 7.89 (d, 2H, J = 7.32 Hz, ArH), 7.24–7.09 (m, 6H, ArH), 6.60 (s, 1H, ArH), 6.06 (s, 2H, OCH_2), 5.31 (s, 2H, OCH_2), 3.79 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.3, 154.4, 153.0, 152.0, 149.3, 145.3, 144.7, 141.5, 132.0, 126.7, 125.6, 123.4, 115.6, 115.1, 114.1, 110.9, 110.3, 101.8, 98.2, 61.1, 56.3, 55.7; IR (ν_{max} cm^{-1}, KBr): = 3422, 2926, 1601, 1508, 1474, 1226; HRMS (ESI) $[M + H]^+$ calcd for $C_{24}H_{21}N_5O_6$: 476.1565, found: 476.1481.

Procedure for synthesis of amino triazole *i.e.* 4-((1-(4-methoxyphenyl)-1*H*-1,2,3-triazol-4-yl)methoxy)aniline. A mixture of 4-(prop-2-ynyloxy)aniline (1 mmol), 1-azido-4-methoxybenzene (1 mmol), $CuSO_4 \cdot 5H_2O$ (10 mol%), sodium ascorbate (20 mol%) and 10 mL of THF–water (60 : 40, v/v) was placed in a 50 mL round-bottomed flask. The reaction mixture was stirred at 60 °C for 2 h. The progress of reaction was monitored by TLC using ethyl acetate–petroleum ether (70 : 30, v/v) as eluent. After completion of the reaction as observed by TLC, water (20 mL) was added to the reaction mixture. The precipitate formed was collected by filtration at pump and washed with water. The product so obtained, was recrystallized from ethanol to afford amino triazole as brown solid in 87% yield.

Brown solid, M.p.: 120 °C, ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.50 (s, 1H, triazolyl-H), 7.93 (s, 1H, ArH), 7.38–7.08 (m, 6H, ArH), 6.78 (s, 2H, NH_2), 6.48 (s, 1H, ArH), 5.04 (s, 2H, OCH_2), 3.75 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.0, 153.3, 145.4, 126.6, 125.6, 125.3, 115.8, 113.9, 110.8, 61.5, 56.7, 55.8; IR (ν_{max} cm^{-1}, film): = 3416, 3349, 2932, 1606, 1510; MS (ESI) $[M + H]^+$ calcd for $C_{24}H_{21}N_5O_6$: 297.14, found: 297.12.

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