Unusual Anisotropic Effects from 1,3-Dipolar Cycloadducts of 4-Azidomethyl Coumarins

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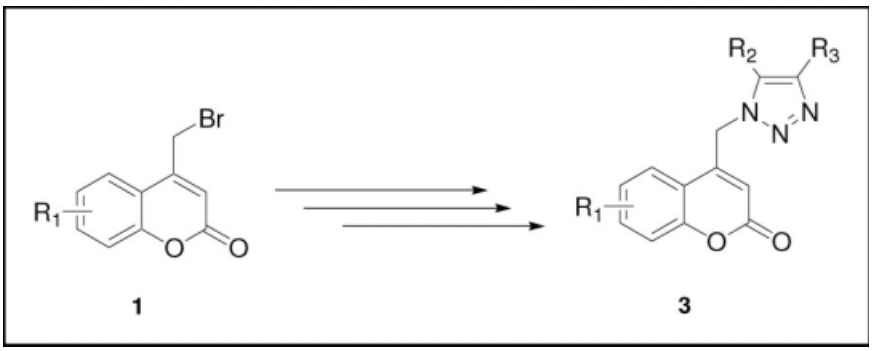

4-Bromomethylcoumarins (**1**) reacted with sodium azide in aqueous acetone to give 4-azidomethylcoumarins (**2**), which underwent 1,3-dipolar cycloaddition with acetylenic dipolarophiles to give triazoles (**3**). These triazoles (**3**) have been found to exhibit interesting variations in the chemical shifts of C_3—H and C_4-methylene protons. Protonation studies indicate that the shielding effect of the C_3—H of coumarin is due to π-electrons of the triazole ring, further supported by diffraction and computational studies.

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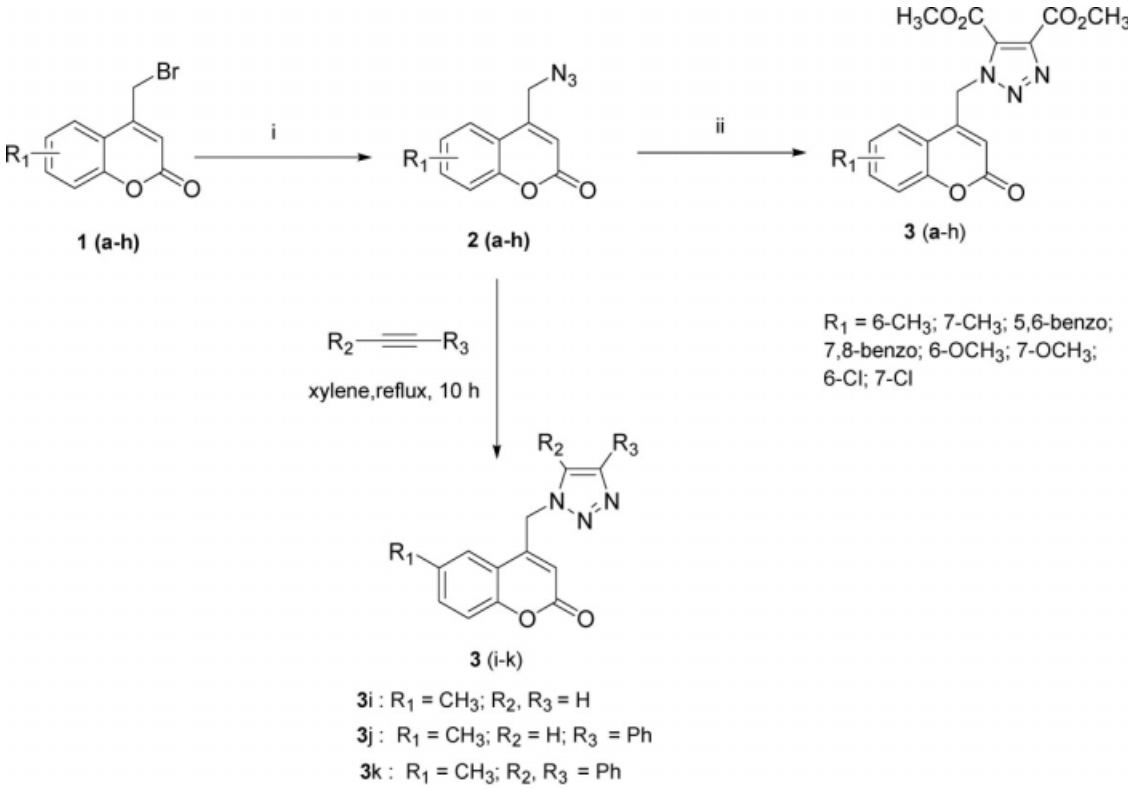
INTRODUCTION

Organic azides are an important class of 1,3-dipoles, which have been recently recognized as crucial functional groups in click chemistry [1]. The exergonic reaction of azides with acetylenic dipolarophiles has resulted in one of the best synthetic routes to 1,2,3-triazoles [2]. This single-step transformation has been investigated for its regioselectivity in aqueous systems [3], in ionic liquids [4], in copper (I) catalysis [5], and by the solid-phase approach [6]. In view of the wide range of biological activities of 1,2,3-triazoles [7,8] and in continuation of our study on biologically active and fluorescent 4-substituted coumarins [9,10], it was thought of substantial intellectual appeal to link the 1,2,3-triazole moiety at the allylic position with respect to the biogenetically important C_3—C_4 double bond of coumarin. There are very few reports on pyranone-substituted 1,3 dipoles except for the reactions of coumarin 4-nitrile oxides [11].

RESULTS AND DISCUSSION

The required dipolar azide intermediates (**2**) were synthesized by the reaction of sodium azide with various 4-bromomethylcoumarins (**1**) [12] in aqueous acetone at room temperature and were quite stable even above 100°C. The first acetylenic dipolarophile used in this investigation was dimethylacetylenedicarboxylate (DMAD), giving rise to triazolomethylcoumarins (**3**) in refluxing xylene (Scheme 1). In the ^{1}H NMR spectrum of the azide, (**2a**, R_1 = 6-CH_3) as expected, the C_4—CH_2 protons linked to the azido group were observed at 4.57 ppm and the C_3—H of coumarin, appeared as a singlet at 6.52 ppm. The ^{1}H NMR of DMAD adduct **3a** showed two interesting features such as (i) C_4—CH_2 protons showed a downfield shift and were observed at 6.05 ppm when compared with 4.56 ppm observed in the case of 4-anilinomethylcoumarins or 5.20 ppm observed in the case of 4-phenoxymethylcoumarins. (ii) The C_3—H of coumarin in the DMAD

Scheme 1. Synthesis of triazolomethylcoumarins from click chemistry.



adduct experienced an upfield shift and was observed as a singlet at 5.60 ppm, as against 6.60–6.70 ppm in the case of both 4-anilinomethyl or 4-phenoxymethyl coumarins [13,14]. To the best of our knowledge, there is only one report in the literature on this type of shielding effect of coumarin C_3—H in 7-methoxy-4-platinomethylcoumarin complex coordinated with 1,10-phenanthroline [15]. This rare type of shielding effect of coumarin C_3—H and simultaneous pronounced deshielding of the C_4-methylene protons were due to the triazole on the C_4—CH_2 group, which has been consistently observed in all the cycloaddition adducts of the azides and DMAD (Table 1). It is interesting to note that benzylic azides have also been reported to undergo similar dipolar cycloaddition reaction [16], but no effects on the chemical shifts of the *ortho* protons have been observed. The chemical shift for the methylene protons in *p*-hydroxybenzyl azide and DMAD adduct is around 5.60 ppm, whereas the aromatic *ortho* protons were found to resonate at 7.11 ppm [17].

Table 1

Chemical shift values of C_4—CH_2 and C_3—H in azides (**2**) and cycloadducts (**3**) ($CDCl_3$).

		C_4—CH_2		C_3—H	
Entry	R	Azide (**2**)	DMAD adduct (**3**)	Azide (**2**)	DMAD adduct (**3**)
a	6-CH_3	4.57	6.05	6.52	5.60
b	7-CH_3	4.56	6.03	6.47	5.67
c	5,6-benzo	4.96	6.54	6.71	5.46
d	7,8-benzo	4.63	6.10	6.57	5.78
e	6-OCH_3	4.57	6.01	6.53	5.80
f	7-OCH_3	4.61	6.08	6.53	5.89
g	6-Cl	4.55	6.01	6.58	5.77
h	7-Cl	4.54	6.06	6.56	5.81

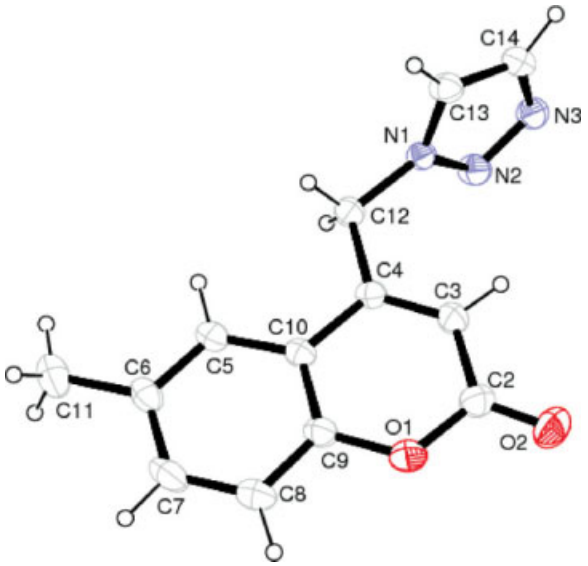


Figure 1. ORTEP diagram of triazole adduct **3i**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effect of substituents. The possible role played by the two ester groups in this observation was verified by using other dipolarophiles such as acetylene, phenylacetylene, and diphenylacetylene in this reaction with azide **2a** (Fig. 1). This led to the formation of adducts **3i**, **3j**, and **3k**, respectively (Scheme 1). In all these cases, similar trend has been observed. Hence, the origin of this effect lies in the triazole ring rather than the substituents.

Temperature effect. To understand the nature of this phenomenon, we recorded the temperature-dependent NMR for one of the DMAD adducts (**3a)** at various temperatures. Up to a temperature of 393 K, there was a regular decrease in the chemical shift values of C_4-methylene protons from 6.1790 to 6.1090 δ ppm. The C_3—H protons showed a slight increase from 5.638 to 5.790 ppm (Table 2). This behavior indicated the absence of any intramolecular hydrogen bonding between C_3—H and triazole nitrogen *via* a six-membered ring.

Table 2

Temperature dependence of chemical shifts of C4—CH_2 and C3—H of (**3a**) in DMSO-d_6.

	Chemical shifts (δ ppm)	
Temperature (K)	C_4—CH_2	C_3—H
303.1	6.1790	5.638
313.1	6.1710	5.654
323.1	6.1645	5.670
333.1	6.1565	5.689
343.1	6.1475	5.706
353.1	6.1405	5.725
373.1	6.1245	5.758
393.1	6.1090	5.790

Protonation behavior. Qualitative protonation studies were performed by adding two drops of trifluoroacetic acid (CF_3CO_2H) in $CDCl_3$, which resulted in significant changes in the chemical shifts of C_3—H and C_4—CH_2 protons. In the case of **3a,** the C_3—H proton was further shifted downfield to 6.01 ppm from 5.60 ppm and C_4—CH_2 protons were also deshielded to 6.30 ppm from 6.05 ppm. This trend was observed for all the substituted cycloadducts (**3**) (Table 3). In the case of acetylene adduct **3i**, the trend was also similar, whereas the C_4—CH_2 protons showed downfield shift from 5.77 to 6.16 ppm and the C_3—H from 5.94 to 6.41 ppm. Probable structures of the protonated species **5** and **6** (Scheme 2) indicate that N_1 of the triazole ring can be quaternized and inductively withdraw the electron density at C_4—CH_2, which would cause deshielding effect.

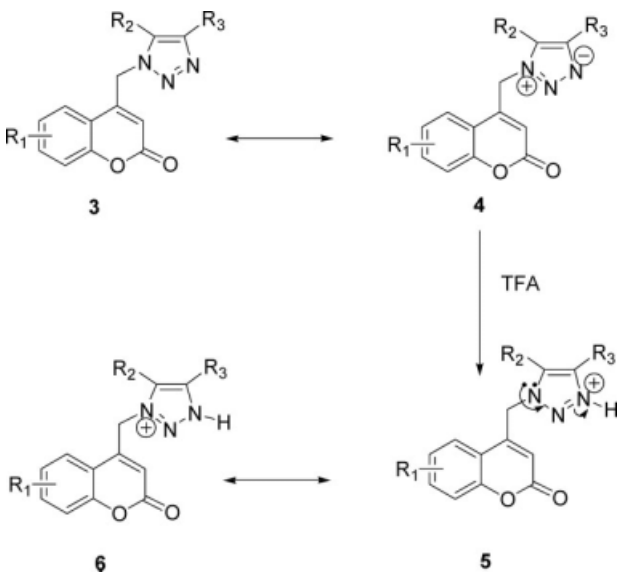
However, the simultaneous deshielding effect of C_3—H under this condition strongly supports an argument that the C_3—H proton falls in the shielding zone of the triazole moiety, which is perturbed due to protonation. Further, the higher deshielding of the methylene protons was observed, which can also be explained in

Table 3

Chemical shifts of C4—CH_2 and C3—H upon protonation ($CDCl_3$ + TFA) in DMAD adducts (**3a–3h**).

		C_4—CH_2		C_3—H	
Compound	R	$CDCl_3$	$CDCl_3$ + TFA	$CDCl_3$	$CDCl_3$ + TFA
3a	6-CH_3	6.05	6.30	5.60	6.01
3b	7-CH_3	6.03	6.21	5.67	5.94
3c	5,6-benzo	6.54	6.73	5.46	5.87
3d	7,8-benzo	6.10	6.33	5.78	6.06
3e	6-OCH_3	6.01	6.21	5.85	6.09
3f	7-OCH_3	6.08	6.29	5.89	6.02
3g	6-Cl	5.94	6.19	5.77	6.16
3h	7-Cl	6.06	6.17	5.81	6.00

Scheme 2. Schematic representation of protonation behavior.



terms of enhanced contribution of the dipolar form **4** to the ground-state resonance of compound **3**.

Diffraction studies. We have performed a single crystal analysis of the acetylene adduct **3i**. The ORTEP diagram (Fig. 1) clearly shows that the planar triazole ring is oriented at an angle of 78.88° with respect to the coumarin ring. This supports our argument that the shielding of the C_3—H is due to the triazole ring and not because of any substituents.

Computational support. We have also performed the geometry optimization of the triazoles **3a** and **3k** molecules, which are shown in the Figure 2 using the Gaussian 03 program [18]. The minimization was performed according to the density functional theory at the B3LYP method with standard Gaussian split-valence 6-31G (d,p) basis set. The two structures clearly revealed the relative orientations of the triazole ring with respect to the C_3 proton of the coumarin (Fig. 2). The anisotropic effect observed on the C_3—H of coumarin is due to the angularly oriented triazole ring, the π-electron cloud of which will have a shielding effect.

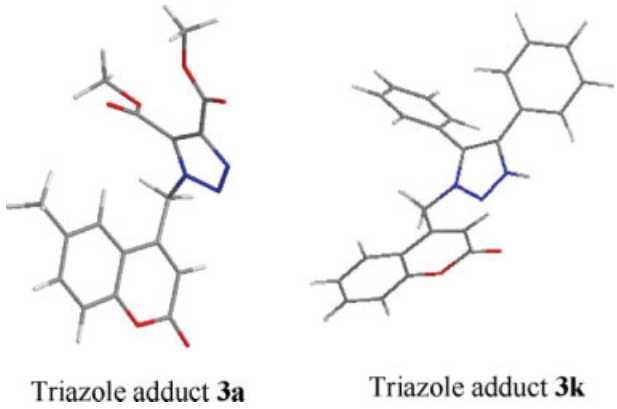


Figure 2. Optimized geometries of compounds **3a** and **3k**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

The unusual anisotropic effects observed in the 4-triazolomethyl coumarins synthesized from 4-azidomethyl-coumarins **2** and a variety of acetylenic dipolarophiles are due to the angularly oriented triazole, which has been shown by NMR, X-ray diffraction, and computational studies.

Table 4

Synthesis of 4-azidomethyl-chromen-2-ones **(2a–2h)**and 1-(2-oxo-*2H*-chromen-4-ylmethyl)-*1H*-[1,2,3]triazoles **(3a–3k).**

Entry	Product	R_1	R_2	R_3	Melting point (°C)	Yield (%)
1	**2a**	6-CH_3	–	–	110	63
2	**2b**	7-CH_3	–	–	104	60
3	**2c**	5,6-Benzo	–	–	146	65
4	**2d**	7,8-Benzo	–	–	131	64
5	**2e**	6-OCH_3	–	–	106	62
6	**2f**	7-OCH_3	–	–	92	59
7	**2g**	6-Cl	–	–	118	66
8	**2h**	7-Cl	–	–	102	65
9	**3a**	6-CH_3	$COOCH_3$	$COOCH_3$	192	76
10	**3b**	7-CH_3	$COOCH_3$	$COOCH_3$	151	75
11	**3c**	5,6-Benzo	$COOCH_3$	$COOCH_3$	180	78
12	**3d**	7,8-Benzo	$COOCH_3$	$COOCH_3$	226	79
13	**3e**	6-OCH_3	$COOCH_3$	$COOCH_3$	194	70
14	**3f**	7-OCH_3	$COOCH_3$	$COOCH_3$	182	69
15	**3g**	6-Cl	$COOCH_3$	$COOCH_3$	209	72
16	**3h**	7-Cl	$COOCH_3$	$COOCH_3$	194	70
17	**3i**	6-CH_3	H	H	199	69
18	**3j**	6-CH_3	H	Ph	168	71
19	**3k**	6-CH_3	Ph	Ph	170	67

EXPERIMENTAL

Melting points were determined by open capillary method and are uncorrected. The elemental analysis was performed using Heraus CHN rapid analyzer. Analytical TLC was performed on Merck precoated 60 F_{254} silica gel plates. IR spectra (KBr disc) were recorded on a Nicolet-5700 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The chemical shifts are expressed in δ ppm scale down field from tetramethylsilane and proton signals are indicated as s = singlet, d = doublet, t = triplet and m = multiplet. EI 70 EV and AUTOSPEC electron impact mass spectrometer was used to record mass spectra.

Preparation of substituted 4-bromomethylcoumarins (1a–1h). The required substituted 4-bromomethylcoumarins **1** [14] have been synthesized by the Pechmann cyclization of various phenols with 4-bromoethylacetoacetate.

General procedure for the preparation of 4-azidomethylchromen-2-ones (2a–2h). 4-Bromo-methylcoumarin **1** (0.01 mol) was taken in acetone (20 mL) in a round bottom flask. To this, sodium azide (0.012 mol) in 3 mL of water was added dropwise with stirring. The stirring was continued for 10 h (reaction was monitored by TLC). Then, the reaction mixture was poured to ice cold water. The separated solid was filtered and recrystallized using suitable solvent (Table 4).

4-Azidomethyl-6-methyl-chromen-2-one (2a). Colorless solid (ethanol), mp. 110°C, yield 63%; IR (KBr, ν in cm^{-1}): 1722 (lactone C=O), 2109 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 2.44 (s, 3H, C6—CH_3), 4.57 (s, 2H, CH2—N_3), 6.52 (s, 1H, C3—H), 7.30 (s, 1H, C5—H), 7.32 (d, 1H, C7—H, J = 7.9 Hz), 7.40 (d, 1H, C8—H, J = 8.3 Hz); LCMS *m/z*: 216 [M + 1]. Anal. Calcd. for $C_{11}H_9N_3O_2$; C, 61.39; H, 4.22; N, 19.53; Found: C, 61.36; H, 4.10; N, 19.51.

4-Azidomethyl-7-methyl-chromen-2-one (2b). Colorless solid (petroleum ether + benzene), mp. 104°C, yield 60%; IR (KBr, ν in cm^{-1}): 1732 (lactone C=O), 2098 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 2.47 (s, 3H, C7—CH_3), 4.56 (s, 2H, CH2—N_3), 6.47 (s, 1H, C3—H), 7.27 (s, 1H, C8—H), 7.13 (d, 1H, C6—H, J = 8.0 Hz), 7.41 (d, 1H, C5—H, J = 8.0 Hz); LCMS *m/z*: 216 [M + 1]. Anal. Calcd. for $C_{11}H_9N_3O_2$; C, 61.39; H, 4.22; N, 19.53; Found: C, 61.32; H, 4.08; N, 19.47.

1-Azidomethyl-benzo[f]chromen-3-one (2c). Colorless solid (ethanol), mp. 146°C, yield 65%; IR (KBr, ν in cm^{-1}): 1727 (lactone C=O), 2099 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 4.96 (s, 2H, CH2—N_3), 6.71 (s, 1H, C3—H), 7.50 (d, 1H, Ar—H, J = 8.8 Hz), 7.58 (t, 1H, Ar—H, J = 6.6 Hz), 7.69 (t, 1H, Ar—H, J = 6.6 Hz), 7.94 (d, 1H, C7—H, J = 8.1 Hz), 8.02 (d, 1H, Ar—H, J = 8.9 Hz), 8.25 (d, 1H, C8—H, J = 8.0 Hz). Anal. Calcd. for $C_{14}H_9N_3O_2$; C, 66.93; H, 3.61; N, 16.73; Found: C, 66.90; H, 3.54; N, 16.70.

4-Azidomethyl-benzo[h]chromen-2-one (2d). Colorless solid (ethanol), mp. 131°C, yield 64%; IR (KBr, ν in cm^{-1}): 1716 (lactone C=O), 2115 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 4.63 (s, 2H, CH2—N_3), 6.57 (s, 1H, C3—H), 7.26–8.54 (m, 6H, Ar—H). Anal. Calcd. for $C_{14}H_9N_3O_2$; C, 66.93; H, 3.61; N, 16.73; Found: C, 66.87; H, 3.53; N, 16.66.

4-Azidomethyl-6-methoxy-chromen-2-one (2e). Colorless solid (petroleum ether), mp. 106°C, yield 62%; IR (KBr, ν in cm^{-1}): 1710 (lactone C=O), 2115 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, C6—OCH_3), 4.57 (s, 2H, CH2—N_3), 6.53 (s, 1H, C3—H), 6.96 (d, 1H, C7—H, J = 8.1 Hz), 7.26 (d, 1H, C8—H, J = 8.1 Hz), 7.40 (s, 1H, C5—H). Anal. Calcd. for $C_{11}H_9N_3O_3$; C, 57.14; H, 3.92; N, 18.17; Found: C, 57.11; H, 3.83; N, 18.06.

4-Azidomethyl-7-methoxy-chromen-2-one (2f). Colorless solid (petroleum ether), mp. 92°C, yield 59%; IR (KBr, ν in cm^{-1}): 1712 (lactone C=O), 2116 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H, C7—OCH_3), 4.61 (s, 2H, CH2—N_3), 6.53 (s, 1H, C3—H), 6.55–7.44 (m, 3H, Ar—H). Anal. Calcd. for $C_{11}H_9N_3O_3$; C, 57.14; H, 3.92; N, 18.17; Found: C, 57.09; H, 3.86; N, 18.02.

4-Azidomethyl-6-chloro-chromen-2-one (2g). Colorless solid (petroleum ether), mp. 118°C, yield 66%; IR (KBr, ν in cm^{-1}): 1720 (lactone C=O), 2121 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 4.55 (s, 2H, CH2—N_3), 6.58 (s, 1H, C3—H), 7.32 (d, 1H, C7—H, J = 8.2 Hz), 7.54 (d, 1H, C8—H, J = 8.2 Hz), 7.70 (s, 1H, C5—H); LCMS *m/z*: 237 [M + 2]. Anal. Calcd. for $C_{10}H_6ClN_3O_2$; C, 50.97; H, 2.57; N, 15.05; Found: C, 50.82; H, 2.54; N, 15.01.

4-Azidomethyl-7-chloro-chromen-2-one (2h). Colorless solid (petroleum ether), mp. 102°C, yield 65%; IR (KBr, ν in cm^{-1}): 1710 (lactone C=O), 2120 (N_3); ^1H NMR (300 MHz, $CDCl_3$): δ 4.54 (s, 2H, CH2—N_3), 6.56 (s, 1H, C3—H), 7.21 (d, 1H, C6—H, J = 8.1 Hz), 7.41 (s, 1H, C8—H), 7.71 (d, 1H, C5—H, J = 7.9 Hz). Anal. Calcd. for $C_{10}H_6ClN_3O_2$; C, 50.97; H, 2.57; N, 15.05; Found: C, 50.91; H, 2.52; N, 15.00.

General procedure for the preparation of 1-(2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3a–3h). Mixture of 4-azidomethylcoumarin **2** (0.01 mol) and DMAD (0.01 mol) was taken in a dry xylene (5 mL) in a round bottom flask. The mixture was refluxed in an oil bath at 130°C under dry conditions for 8 h (reaction was monitored by TLC) and then cooled. The separated solid was collected by filtration and recrystallized using suitable solvent.

1-(6-Methyl-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3a). Colorless solid (ethanol), mp. 192°C, yield 76%; IR (KBr, ν in cm^{-1}): 1722 (lactone C=O), 1722 (ester C=O); ^1H NMR (300 MHz, $CDCl_3$): δ 2.46 (s, 3H, C6—CH_3), 3.95 (s, 3H, —$COOCH_3$), 4.02 (s, 3H, —$COOCH_3$), 5.60 (s, 1H, C3—H), 6.05 (s, 2H, C4—CH_2), 7.36 (d, 1H, C7—H, J = 8.4 Hz), 7.51 (d, 1H, C8—H, J = 8.4 Hz), 7.67 (s, 1H, C5—H); ^{13}C NMR (75 MHz, $CDCl_3$): 22, 50, 53, 54, 114, 117, 118, 124, 130, 134, 135, 141, 148, 152, 158, 161, 162; LCMS *m/z*: 358 [M + 1]. Anal. Calcd. for $C_{17}H_{15}N_3O_6$; C, 57.14; H, 4.23; N, 11.76; Found: C, 57.18; H, 4.17; N, 11.69.

1-(7-Methyl-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3b). Colorless solid (benzene), mp. 151°C, yield 75%; IR (KBr, ν in cm^{-1}): 1722 (lactone C=O), 1754 (ester C=O); ^1H NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H, C7—CH_3), 3.94 (s, 3H, —$COOCH_3$), 4.01 (s, 3H, —$COOCH_3$), 5.67 (s, 1H, C3—H), 6.03 (s, 2H, C4—CH_2), 7.17 (d, 1H, C6—H, J = 7.2 Hz), 7.37 (s, 1H, C8—H), 7.57 (d, 1H, C5—H, J = 7.1 Hz); LCMS *m/z*: 358 [M + 1]. Anal. Calcd. for $C_{17}H_{15}N_3O_6$; C, 57.14; H, 4.23; N, 11.76; Found: C, 57.19; H, 4.16; N, 11.72.

1-(3-Oxo-3*H*-benzo[f]chromen-1-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3c). Colorless solid (ethanol), mp. 180°C, yield 78%; IR (KBr, ν in cm^{-1}): 1731 (lactone C=O), 1731 (ester C=O); ^1H NMR (300 MHz, $CDCl_3$): δ 3.85 (s, 3H, —$COOCH_3$), 4.03 (s, 3H, —$COOCH_3$),

5.46 (s, 1H, C3—H), 6.54 (s, 2H, C4—CH_2), 7.52 (d, 1H, J = 8.9 Hz), 7.62 (t, 1H, J = 7.3 Hz), 7.72 (t, 1H, J = 7.5 Hz), 8.00 (d, 1H, C7—H, J = 8.0 Hz), 8.07 (d, 1H, J = 8.9 Hz), 8.19 (d, 1H, C8—H, J = 8.0 Hz). Anal. Calcd. for $C_{20}H_{15}N_3O_6$; C, 61.07; H, 3.84; N, 10.68; Found: C, 61.01; H, 3.79; N, 10.60.

1-(2-Oxo-2*H*-benzo[*h*]chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3d). Colorless solid (ethanol + dioxane), mp. 226°C, yield 79%; IR (KBr, ν in cm^{-1}): 1711 (lactone C=O), 1738 (ester C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94 (s, 3H, —$COOCH_3$), 4.01 (s, 3H, —$COOCH_3$), 5.78 (s, 1H, C3—H), 6.10 (s, 2H, C4—CH_2), 7.20–8.54 (m, 6H, Ar—H). Anal. Calcd. for $C_{20}H_{15}N_3O_6$; C, 61.07; H, 3.84; N, 10.68; Found: C, 61.04; H, 3.80; N, 10.63.

1-(6-Methoxy-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3e). Colorless solid (ethanol + dioxane), mp. 194°C, yield 70%; IR (KBr, ν in cm^{-1}): 1720 (lactone C=O), 1744 (ester C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H, C6—OCH_3), 3.93 (s, 3H, —$COOCH_3$), 4.00 (s, 3H, —$COOCH_3$), 5.85 (s, 1H, C3—H), 6.01 (s, 2H, C4—CH_2), 7.16–7.34 (m, 3H, Ar—H). Anal. Calcd. for $C_{17}H_{15}N_3O_7$; C, 54.69; H, 4.05; N, 11.26; Found: C, 54.62; H, 4.17; N, 11.25.

1-(7-Methoxy-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3f). Colorless solid (ethanol + dioxane), mp. 182°C, yield 69%; IR (KBr, ν in cm^{-1}): 1722 (lactone C=O), 1742 (ester C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H, C7—OCH_3), 3.96 (s, 3H, —$COOCH_3$), 4.01 (s, 3H, —$COOCH_3$), 5.89 (s, 1H, C3—H), 6.08 (s, 2H, C4—CH_2), 7.21–7.92 (m, 3H, Ar—H). Anal. Calcd. for $C_{17}H_{15}N_3O_7$; C, 54.69; H, 4.05; N, 11.26; Found: C, 54.60; H, 4.13; N, 11.21.

1-(6-Chloro-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3g). Colorless solid (ethanol), mp. 209°C, yield 72%; IR (KBr, ν in cm^{-1}): 1726 (lactone C=O), 1726 (ester C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.96 (s, 3H, —$COOCH_3$), 4.02 (s, 3H, —$COOCH_3$), 5.77 (s, 1H, C3—H), 6.01 (s, 2H, C4—CH_2), 7.35 (d, 1H, C7—H, J = 8.8 Hz), 7.57 (d, 1H, C8—H, J = 8.7 Hz), 7.70 (s, 1H, C5—H); LCMS *m/z*: 379 [M + 2]. Anal. Calcd. for $C_{16}H_{12}ClN_3O_6$; C, 50.87; H, 3.20; N, 11.12; Found: C, 50.79; H, 3.15; N, 11.05.

1-(7-Chloro-2-oxo-2*H*-chromen-4-ylmethyl)-1*H*-[1,2,3]triazole-4,5-dicaboxylic acid dimethyl ester (3h). Colorless solid (ethanol), mp. 194°C, yield 70%; IR (KBr, ν in cm^{-1}): 1721 (lactone C=O), 1754 (ester C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.90 (s, 3H, —$COOCH_3$), 4.04 (s, 3H, —$COOCH_3$), 5.81 (s, 1H, C3—H), 6.06 (s, 2H, C4—CH_2), 7.72–7.64 (m, 3H, Ar—H). Anal. Calcd. for $C_{16}H_{12}ClN_3O_6$; C, 50.87; H, 3.20; N, 11.12; Found: C, 50.75; H, 3.12; N, 11.09.

Preparation of 6-methyl-4-[1,2,3]triazol-1ylmethyl-chromen-2-one (3i). To the 4-azido-methylcoumarin **2a** (0.01 mol) in a dry xylene (15 mL), dry acetylene gas was passed for 30 min and then the flask was sealed and heated in an oil bath at 130°C for 10 h (reaction was monitored by TLC). The flask was cooled, and the separated solid was filtered and recrystallized from alcohol. Colorless solid (ethanol), mp. 199°C, yield 69%; IR (KBr, ν in cm^{-1}): 1720 (lactone C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, C6—CH_3), 5.77 (s, 2H, C4—CH_2), 5.94 (s, 1H, C3—H), 7.28 (d, 1H, C7—H, J = 8.7 Hz), 7.36 (s, 1H, C5—H), 7.40 (d, 1H, C8—H, J = 8.6 Hz), 7.66 (d, 1H, triazole), 7.82 (d, 1H, triazole); LCMS *m/z*: 242 [M + 1]. Anal. Calcd. for $C_{13}H_{11}N_3O_2$; C, 64.72; H, 4.60; N, 17.42; Found: C, 64.68; H, 4.58; N, 17.40.

Preparation of 6-methyl-4-(4-phenyl-[1,2,3]triazol-1-ylmethyl)-chromen-2-one (3j). Mixture of 4-azidomethylcoumarin **2a** (0.01 mol) and phenyl acetylene (0.01 mol) was taken in a dry xylene (5 mL) in a dry round bottom flask. The mixture was refluxed in an oil bath at 130°C under dry conditions for 10 h (reaction was monitored by TLC) and cooled. The separated solid was filtered and recrystallized from alcohol.Colorless solid (ethanol), mp. 168°C, yield 71%; IR (KBr, ν in cm^{-1}): 1738 (lactone C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H, C6—CH_3), 5.77 (s, 2H, C4—CH_2), 6.10 (s, 1H, C3—H), 7.28–7.84 (m, 9H, Ar—H); LCMS *m/z*: 318 [M + 1]. Anal. Calcd. for $C_{19}H_{15}N_3O_2$; C, 71.91; H, 4.76; N, 13.24; Found: C, 71.80; H, 4.72; N, 13.18.

Preparation of 4-(4,5-diphenyl-[1,2,3]triazol-1-ylmethyl)-6-methyl-chromen-2-one (3k). Mixture of 4-azidomethylcoumarin **2a** (0.01 mol) and diphenylacetylene (0.01 mol) was taken in a dry xylene (5 mL) in a dry round bottom flask. The mixture was refluxed in an oil bath at 130°C under dry conditions for 10 h (reaction was monitored by TLC) and cooled. The separated solid was filtered and recrystallized from alcohol.

Colorless solid (ethanol), mp. 170°C, yield 67%; IR (KBr, ν in cm^{-1}): 1732 (lactone C=O); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, C6—CH_3), 5.58 (s, 2H, C4—CH_2), 5.70 (s, 1H, C3—H), 7.24–7.58 (m, 13H, Ar—H); LCMS *m/z*: 394 [M + 1]. Anal. Calcd. for $C_{25}H_{19}N_3O_2$; C, 76.32; H, 4.87; N, 10.68; Found: C, 76.26; H, 4.84; N, 10.65.

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