A New Conjugated Addition of Trialkyl Phosphites and Alkylidenephosphoranes to 3-ω-Azideoacetyl Coumarin Synthesis of Some 1,2,3,4-Triazaphospholes, Triazoles, and Azido-Coumarin Derivatives

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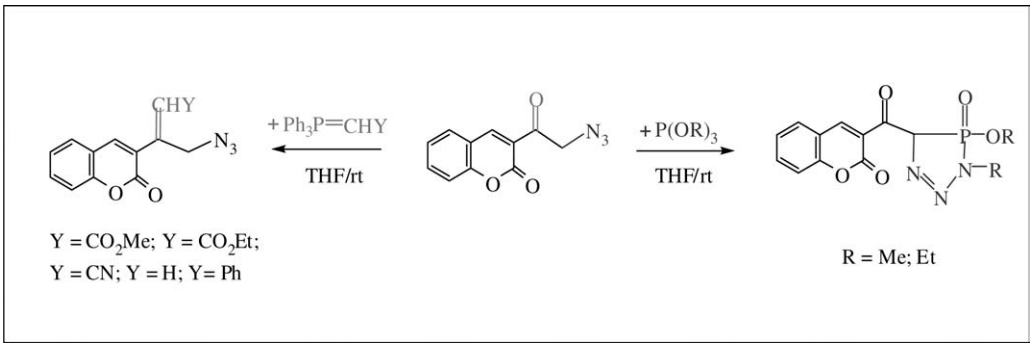

A new and efficient conjugate addition of trimethyl and triethyl phosphites to 3-ω-azidoacetylcoumarin **(1)** has been studied. The reaction proceeded smoothly at r.t. furnishing 1,2,3,4-triazaphosphole coumarin derivatives **4a,b** in ~75% yields. Linear substituted triazoles **10a,b** were also obtained from the reactions of **1** with α-keto ylides, acetyl- and benzoylmethylene triphenylphosphoranes. Contrary to these results, Wittig reaction was occurred when **1** was allowed to react with α-alkoxycarbonylmethylene- and cyanomethylenetriphenylphosphoranes **7c–e** as well as with methylidene- and benzylidenetriphenylphosphoranes **8a,b** resulting in the formation of the corresponding olefins either as an intermediate **14b** or as final products **11a–c**.

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INTRODUCTION

A considerable number of naturally occurring coumarins such as Muttalongin, Usthol, and 2,3-Auraptin were found to have strong antimicrobial and anticancer activities [1]. Also, coumarin dyes recently have found great interests because of their high potential in dye laser to achieve tunable blue-green light and are also used in enzyme determination; photobiological energy transfer processes fluorescent probe technique; and fluorescence whiteners in detergent products [2].

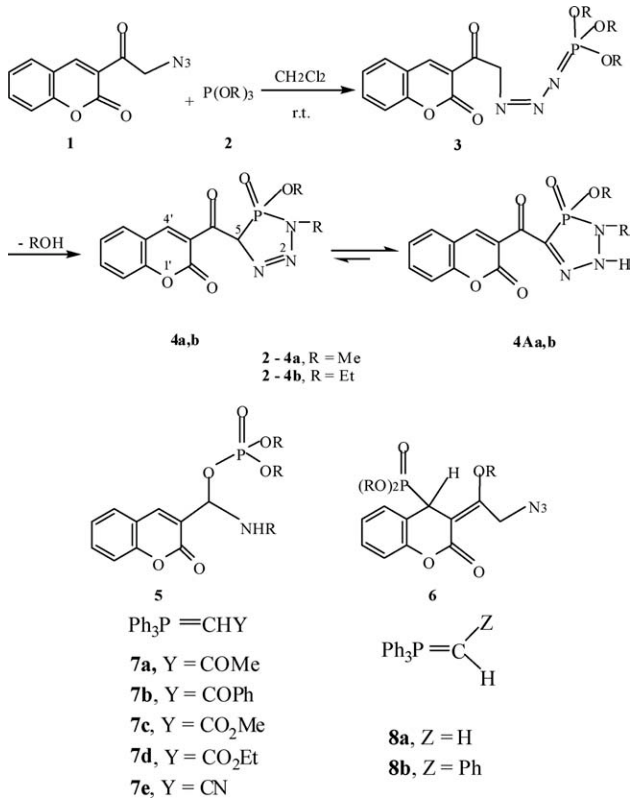
In continuation with our research program directed toward the utility of trivalent and pentavalent phosphorus reagents in synthesis of pharmaceuticals [3–12], we extend our precedent work on coumarins and relevant phosphor derivatives [13,14] to elaborate more novel coumarin derivatives of expecting pharmacological potenc. The methodology involved application of trialkyl phosphites and alkylidenephosphoranes to 3-azidoacetylcoumarin (**1**).

RESULTS AND DISCUSSION

The azide **1** reacted smoothly with trimethyl- **2a** and triethyl phosphite **2b** in absolute methylene chloride at room temperature and yielded, in each case, the tautomeric structure **4a,b** ⇌ **4Aa,b** in ≈ 75% yield. Compound **4** can be viewed as derived from ring closure of the phosphazide 3, initially formed [15,16] with concomitant extrusion of the appropriate alcohol moiety. Further rearrangement through alkyl group shift led to the triazaphosphole products **4a,b** (Scheme 1).

Compounds **4a**,**b** showed ^{31}P-NMR chemical shifts around δ 11.4 ppm confirming the presence of N—P—C linkage in a phosphole moiety and readily eliminate any formation of phosphates for which a signal at $\delta p = \pm$ 2–4 ppm would be expected. The IR spectrum of **4a** revealed the presence of absorption bands at 1722 (C=O, lactone), 1633 (C=O, acetyl), 1265 (P=O, free), and at 1055 (P—O—CH_3) cm^{-1}. Moreover, the strong azide frequency present in the IR spectrum of **1** at 2093 cm^{-1} was absent in the IR spectra of **4**. In the

Scheme 1



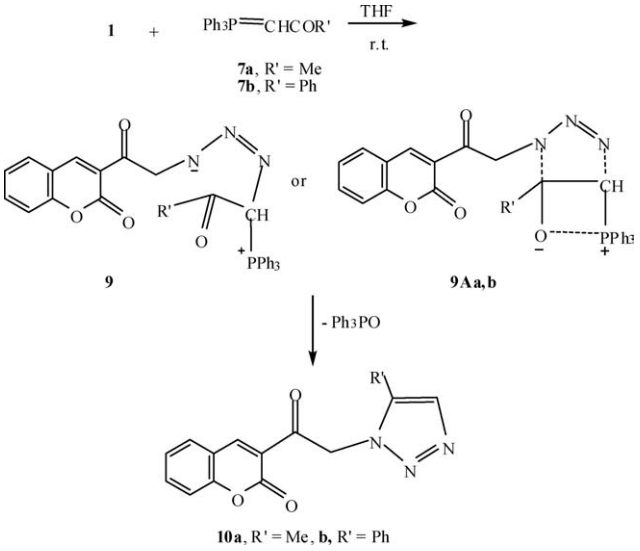
^{1}H-NMR [17] spectrum of **4a** ($CDCl_3$), the 4'-H of coumarin was observed as a singlet at δ 8.68 ppm. A doublet (3H, $^3J_{P\text{-}H} = 8.8$ Hz) was observed at δ 3.66 due to OCH_3 protons attached to the phosphorus atom. A doublet (3H, $^3J_{P\text{-}H} = 8.3$ Hz) was observed at δ 3.27 assigned to the CH_3 protons linked to the 3-N in the triazaphosphole ring. The singlet due to the methylene protons linked to the azide group present in the pmr spectrum of **1** at δ 4.73 ppm was absent in the spectrum of **4a**. Instead, a doublet (1H, $^2J_{P\text{-}H} = 23.4$ Hz) was displayed at δ 5.16 due to 5-H (**4a**). Remarkably, the structure **4Aa** (Scheme 1) cannot be overlooked since a weak broad signal was displayed at 3339 cm^{-1} in the IR spectrum assigned to an NH group; this signal appeared at δ 11.42 (br) in its pmr spectrum. It is noteworthy that the position of N-(H) hydrogen atom in triazoles such as structure **4** has been the subject of contradictory discussion [18] . Furthermore, the ^{31}P-NMR chemical shifts; the presence of 5-H as a doublet of high coupling constant and 4'-H coumarin singlet, and the lack of a singlet due to the methylene group in the pmr spectrum, as well as the absence of the azido group in its ir spectrum, confirm the assigned structures **4** ⇌ **4A** and rule out other alternative structures like **5** and **6.**

Next, the study has been extended to investigate the interaction of the azide compound **1** with three types of stabilized Wittig reagents: i- α-ketomethylene-**7a**,**b**, ii- alkoxycarbonyl-methylene-**7c**,**d**, iii- cyanomethylene-triphenylphosphorane **7e**; and two active ylides: i- methylidene- **(8a)** and benzylidenetriphenylphosphorane (**8b**).

When the azide **1** was treated with acetylmethylene-**7a** or benzoylmethylenetriphenyl-phosphorane (**7b**) in tetrahydrofuran (THF) at room temperature for 24 h, 1,2,3-triazoloactyl-coumarins **10a**,**b** were formed in ∼74% yield. Triphenylphosphine oxide (TPPO) was also isolated from the reaction medium. The triazole structure **10** was deduced from analytical and spectroscopic data. In the IR spectrum of **10a,** the lactone carbonyl was observed at 1721 and that of the 3-acetyl carbonyl group observed at 1685 cm^{-1}. In its ^{1}H-NMR, the protons of methylene group were observed downfield as a singlet at δ 5.37 ppm.

As depicted in Scheme 2, a 1,3-dipolar addition of the azide **1** on the P=C bond of the ylide **7a,b** followed by elimination of TPPO from the cyclic intermediate **9** afforded *N*-1-substituted-5-methyl (or 5-phenyl)-1,2,3-triazoles **10a**,**b** [19–23] . The formation of the triazoles from treating **1** with **7a**,**b** adequately demonstrates the regiochemistry [23] of the reaction that leads to the exclusive formation of 1,5- instead of 1,4-disubstituted triazoles. Furthermore, the formation of **10** through either a two step addition, *via* the intermediate **9**, or a

Scheme 2

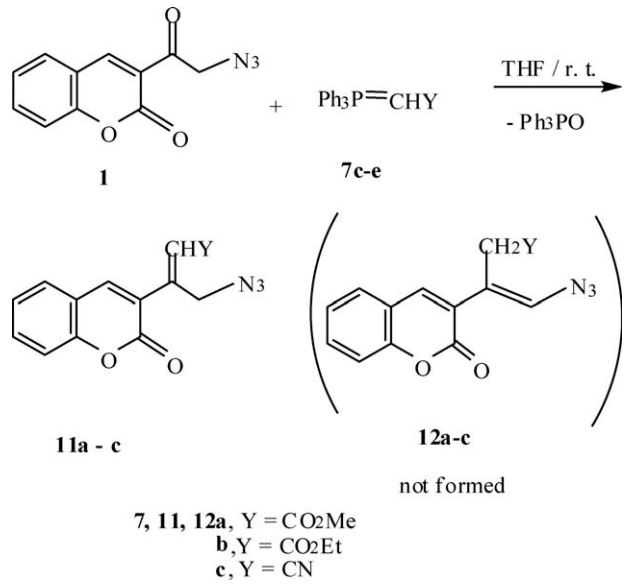


concerted cycloaddition, *via* the transition state **9A**, is consistent with the observed result.

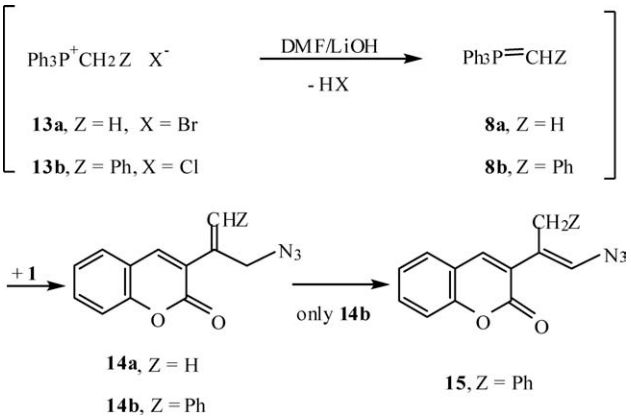
In the contrary to the behavior of trialkyl phosphites and α-keto ylides, the reactions of **1** with α-alkoxy carbonyl- and α-cyanomethylenetriphenylphosphoranes **(7c–e)**, performed under similar conditions, followed the Wittig reaction, gave coumarin-azido-derivatives **11a–c** in ≈70% yields. Compounds **11a–c** were obtained as *Z*-isomers predominantly based of spectroscopic data and due to steric demand of the transition states to form the oxaphosphetane **9A** (Scheme 3) [24–27] .

The spectroscopic data of compounds **11a-c** are in agreement with the assigned structure. In the EI mass

Scheme 3



Scheme 4



spectra, they showed the molecular ion peaks (M^+ %) that displayed the expected fragmentations of the corresponding spectrum. The most characteristic signals in their ^{1}H-NMR spectra are those of the methylene (CH_2N_3) and the methinic (=CHY) protons, which appeared as a doublet and a triplet each with $^4J_{H\text{-}H}$ = 1.6 Hz at δ 4.44–4.23 and 6.08–6.28, respectively. The presence of (=CHY) and (CH_2N_3) moieties were also attested by signals at δc 112-98, and 55–52 ppm in ^{13}C-NMR spectra. These recorded data for the methine (=CH) and the methylene protons could readily eliminate structure like **12**, which would predict a doublet at ∼3.5 and a triplet at ∼7.3 ppm.

Further extension of this study to other ylides, application of methylidene- **(8a)** and benzylidene-triphenylphosphorane **(8b)** to **1** was investigated. When dimethylformamide (DMF) solution of an equivalent amounts of **1** and **8a**, prepared in situ from its bromide salt **13a**, in the presence of aqueous LiOH was stirred at rt for 12 h, the reaction afforded the Wittig product **14a** (80%), on the basis of comparable spectroscopic arguments (Scheme 4).

On the other hand, the reaction of **1** with slight excess (10%) of **8b** (prepared in situ from its chloride salts, **13b**) under the same conditions gave the benzylvinyl derivative **15** (84%), which is an isomer of the Wittig product **14b** (Scheme 4).

In summary, the condensation of trialkyl phosphites and alkylidenephosphoranes (resonance-stabilized- and active ylides) with 3-azidoacetylcoumarin resulted in an interesting spectrum of the reactivity. Furtherward, the structural products (**4a**,**b**, **10a**,**b**, **11a–c**, **14a**, and **15**) obtained from the four studied reactions, however, indicated two positions in **1** that are susceptible to nucleophilic attack by the phosphorus reagents. The first position relates to an attack at the azide group; this addition was observed by trialkyl phosphites and α-keto

ylides, which afforded, via 1:3-dipolar intermediates, 1,2,3,4-triazaphosphole and triazolylacetyl-coumarin derivatives, respectively. The second site of attack is concerned with the attack of the ylides **7c–e** and **8a**,**b** at the acetyl carbonyl carbon group, which led to the respective olefins.

Finally, the synthesized heterocyclic phosphole system **4a**,**b** that included a phosphorus linked to a nitrogen atom are of great interest because this system is common to a diverse array of important biological molecules.

EXPERIMENTAL

General: Melting points were determined with open capillary tube on an Electrothermal (variable heater) melting point apparatus and were uncorrected. IR spectra were recorded on a Perkin–Elmer spectrophotometer model 297 using KBr disc. NMR spectra were measured with a JEOL E.C.A-500 MHz (^{13}C: 125.7 MHz, ^{1}H: 500 MHz, ^{31}P: 202.4 MHz) spectrometer. ^{31}P-NMR spectra were recorded with H_3PO_4 (85%) as external reference. ^{1}H- and ^{13}C-NMR spectra were recorded with trimethylsilane as internal standard in $CDCl_3$ or DMSO-d^6. Chemical shifts (δ) are given in ppm. The mass spectra were performed at 70 eV on an MS-50 Kratos (A.E.I.) spectrometer provided with a data system. The appropriate precautions in handling moisture-sensitive compounds were observed. Materials and reagents were purchased from Aldrich Company. The substrate, 3-azidoacetycoumarin **1** was prepared according to the reported method [15] .

Reaction of 3-azidoacetylcoumarin (1) withtrialkylphosphites 2a,b. Preparation of compounds 4a and 4b. To a solution of 0.8 g (3.5 mmol) of the azide **1** in 25 mL of absolute CH_2Cl_2 at 0°C, 3.5 mmol of freshly distilled trimethyl- **2a** or triethyl phosphite **2b** were added dropwise with stirring. After the addition was complete, the reaction mixture was stirred at room temperature for 6 h, and the solvent was evaporated to dryness. The residue was washed several times with light petroleum (40–60°C) and crystallized from the proper solvent to give **4a** or **4b**, respectively.

3-[(4-Methoxy-3-methyl-4-oxido-4,5-dihydro-3*>H-*1,2,3,4-triazaphosphol-5-yl)-carbonyl]-2*H-*chomen-2-one (4a). This was obtained as straw yellow needles, 863 mg (77%); mp 170–172°C (cyclohexane); IR: ν_{max} NH 3339 (**4Aa**), 2C=O 1722, 1633, P=O, free 1265, 1055 (P—O—C) cm^{-1}; ^{1}H-NMR (DMSO^6): δ 3.27 (d, $^{3}J_{P\text{-}H}$ = 8.3 Hz, 3H, NC*H*$_3$), 3.66 (d, $^{3}J_{P\text{-}H}$ = 8.8 Hz, 3H, POC*H*$_3$), 5.16 (d, $^{2}J_{P\text{-}H}$ = 23.4 Hz, 1H, 5-*H*, **4a**), 7.32 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.52 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 8.68 (s, 1H, 4'-*H*), 11.42 ppm (br, 1H, N*H*, **4Aa**); ^{13}C-NMR (DMSO^6): δ 177.4 (d, $^{2}J_{P\text{-}C}$ = 5.8 Hz, *C*=O), 158.8 (*C*=O, lactone), 153.3 (9'-*C*), 147.7 (4'*C*), 134.3, 131.5, 126.4, 118.7, 116.2 (7'-*C*, 8'*C*, 5'-*C*, 6'-*C*, 10'-*C*), 133 (d, $^{1}J_{P\text{-}C}$ = 139 Hz, 5-C-P, **4Aa**), 120.2 (d, $^{3}J_{P\text{-}C}$ = 4.4 Hz, 3'-*C*), 65.3 (d, $^{1}J_{P\text{-}C}$ = 141 Hz, 5-*C*-P), 55.1 (d, $^{2}J_{P\text{-}C}$ = 7.5 Hz, POCH$_3$), 28.8 ppm (d,$^{2}J_{P\text{-}C}$ = 7 Hz, N-*C*H$_3$); ^{31}P-NMR (DMSO^6): δ 11.4 ppm; ms: *m*/*z* (EI): 323 [M$^+$ + 2, 80 %], 321 [M$^+$, 100%], 306 (16), 291 (31), 252 (83), 228 (33), 227 (24), 213 (19), 188 (18), 173(43), 170 (10), 77 (18). Anal. Calcd. for $C_{13}H_{12}N_3O_5P$ (321.2): C, 48.61; H, 3.77; N, 13.08; P, 9.64. Found: C, 48.68; H, 3.82; N, 13.15; P, 9.59.

3-[(4-Ethoxy-3-ethyl-4-oxido-4,5-dihydro-3*H-*1,2,3,4-triazaphosphol-5-yl)-carbonyl]-2*H-*chromen-2-one (4b) This was obtained as yellow needles, 0.9 g (74%); mp 132–134°C (cyclohexane); IR: ν_{max} NH 3384 (**4Ab**), 2C=O 1722, 1638, P=O, free 1258, 1088 (P—O—C) cm^{-1}; ^{1}H-NMR (DMSO^6): δ 1.03–1.31 (2dt (m), 6H, NC.C*H*$_3$ and POC.C*H*$_3$), 3.99 (dq, $^{3}J_{H\text{-}H}$ = 6.4, $^{3}J_{P\text{-}H}$ = 4.8 Hz, 2H, NC*H*$_2$), 4.09 (dq, $^{3}J_{H\text{-}H}$ = 6.4, $^{3}J_{P\text{-}H}$ = 4.8 Hz, 2H, POC*H*$_2$), 5.09 (d, $^{2}J_{P\text{-}H}$ = 23.4 Hz, 1H, 5-*H*, **4b**), 7.35 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'*H* and 7'*H*), 7.57 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'*H* and 8'*H*), 8.64 (s, 1H, 4'*H*), 11.14 ppm (br, 1H, N*H*, **4Ab**); ^{13}C-NMR (DMSO^6): δ 177.6 (d, $^{2}J_{P\text{-}C}$ = 5.8 Hz, *C*=O), 158.8 (*C*=O, lactone), 154.7 (9'-*C*), 147.8 (4'*C*), 134.7, 130.6, 126.4, 118.3, 117.6 (7'-C, 8'-C, 5'-*C*, 6'-*C*, 10'-*C*), 136 (d, $^{1}J_{P\text{-}C}$ =139 Hz, 5-C-P, **4Ab**), 120.4 (d, $^{3}J_{P\text{-}C}$ = 4.4 Hz, 3'-*C*), 67.4 (d, $^{1}J_{P\text{-}C}$ = 144 Hz, 5-*C*-P), 62.5 (d, $^{2}J_{P\text{-}C}$ = 7.5 Hz, POC*H*$_2$), 44.1(d, $^{2}J_{P\text{-}C}$ = 7 Hz, N-*C*H$_2$), 19.6 (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz, POC.*C*H$_3$), 14.4 ppm (d, $^{3}J_{P\text{-}C}$ = 5.8 Hz,, N—C.*C*H$_3$); ^{31}P-NMR (DMSO^6): δ 10.8 ppm; ms: *m*/*z* (ei): 351 [m+ + 2, 26%], 349 (74) [m+], 320 (17), 291 (37), 263(100), 252 (71), 227 (83), 213 (20), 188 (13), 173(53), 170 (15), 77 (18); Anal. Calcd. for $C_{15}H_{16}N_3O_5P$ (349.3): C, 51.58; H, 4.62; N, 12.03; P, 8.87. Found: C, 51.65; H, 4.57; N, 12.11; P, 8.91.

Reaction of 1 withketomethylenetriphenyphosphoranes7a,b. Preparation of compounds 10a and 10b. A mixture of azide **1** (0.8 g, 3.5 mmol) and acetyl- **7a** (1.3 g, 3.5 mmol) or benzoylmethylenetriphenylphosphorane **(7b)** (1.1 g, 3.5 mmol) in 30 mL of dry tetrahydrofuran (THF) was stirred at rt for 24 h. After removing the solvent, the residue was chromatographed on silica gel to afford the triazoles **10a** or **10b**. Triphenylphosphine oxide (Ph_3PO) was also isolated.

3-[(5-Methyl-1*H-*1,2,3-triazol-1-yl)acetyl]-2*H-*chromen-2-one (10a). This was obtained as yellow crystals, 705 mg (75%); mp 158–160°C (MeCN); IR: ν_{max} 2C=O 1721, 1685 cm^{-1}; ^{1}H-NMR (DMSO^6): δ 2.38 (d, $J_{H\text{-}H}$ = 2.3 Hz, 3H, 5-C.C*H*$_3$), 5.37 (s, 2H, C(O)C*H*$_2$), 7.34 (d, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.55 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 7.58 (q, $J_{H\text{-}H}$ = 2.3 Hz, 1H, 4-*H*), 8.65 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 187.4 (*C*=O, acetyl), 161.2 (2'-*C*=O), 154.7 (9'-*C*), 148.7 (4'-*C*), 142.8 (5-*C*), 138.3 (4-*C*), 134.3, 131.5, 126.4, 118.7, 114.2 (7'-C, 8'-*C*, 5'-*C*, 6'-*C*, 10'-*C*), 121.6 (3'-*C*), 53.8 (*C*H$_2$, acetyl), 13.3 ppm (5-C—*C*H$_3$); ms: *m*/*z* (EI): 270 (27) [M$^+$ + 1], 269 (22) [M$^+$], 254 (26), 237 (100), 188 (63), 172 (53), 170 (15), 145 (18), 77 (16). Anal. Calcd. for $C_{14}H_{11}N_3O_3$ (269.3): C, 62.45; H, 4.12; N, 15.61. Found: C, 62.52; H, 4.06; N, 15.64.

3-[(5-Phenyl-1*H-*1,2,3-triazol-1-yl)acetyl]-2*H-*chromen-2-one (10b). This was obtained as yellow crystals, 855 mg (74%); mp 186–188°C (MeCN); IR: ν_{max} 2C=O 1720, 1680 m^{-1}; ^{1}H-NMR (DMSO^6): δ 5.27 (s, 2H, C(O)C*H*$_2$), 7.24–7.37 (m, 3H, *H*-Ph and *H*-Ar), 7.46–7.66 (m, 6H, *H*-Ph and *H*-Ar), 8.02 (s, 1H, 4-*H*), 8.53 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 186.7, 160.4 (2*C*=O), 154.7 (9'-*C*), 148.7 (4'-*C*), 142.8 (5-*C*),)134.3 (4-*C*), 131.5, 130.5, 129.2, 126.4, 125.7, 123.6, 123.1, 122.6, 118.7, 114.2 (*C*-Ph and *C*-Ar), 121.6 (3'-*C*), 53.8 (*C*H$_2$, acetyl); ms: *m*/*z* (EI): 333 (36) [M$^+$ +2], 331(100) [M$^+$], 303 (92), 289 (78), 288 (51), (26), 237 (100), 188 (63), 172 (53), 170 (15), 145 (18), 77 (14). Anal. Calcd. for $C_{19}H_{13}N_3O_3$ (331.3): C, 68.88; H, 3.95; N, 12.68. Found: C, 68.85; H, 4.01; N, 12.62.

Reaction of 1 with alkylidenetriphenyphosphoranes 7c–e.Preparation of compounds 11a, 11b, and 11c. A mixture of the azide **1** (0.8 g, 3.5 mmol) and 3.5 mmol of methoxycarbonyl- **(7c)**, ethoxycarbonyl- **(7d),** or cyanomethylenetriphenylphosphorane (**7e**) in 30 mL THF was stirred at r.t. for 24 h. After removing the solvent, the residue was chromatographed on silica gel to afford **11a**, **11b,** or **11c**, respectively. Ph_3PO was also isolated.

Methyl (2Z)-4-azido-3-(2-oxo-2H-chromen-3-yl)but-2-enoate (11a). This was obtained as yellow crystals, 657 mg (66%); mp 165–167°C ($CHCl_3$); IR: ν_{max} C-N_3 2112, C=O (lactone) 1721, C=O (ester)1713, C=C (exocyclic) 1611 cm^{-1}; ^{1}H-NMR (DMSO^6): δ 3.73 (s, 3H, OC*H*$_3$), 4.23 (d, $^4J_{H\text{-}H}$ = 1.6 Hz, 2H, H_2C-N_3), 6.28 [t, $^4J_{H\text{-}H}$ = 1.6 Hz, 1H, =C*H*C(O)], 7.34 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.56 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 8.45 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 162.5, 161.8 (2*C*=O), 153.7 (9'-*C*), 146.7 (3'-C—*C*=), 141.7 (4'-*C*), 133.3, 126.4, 125.6, 118.7, 114.2 (7'-C, 8'-*C*, 5'-*C*, 6'-*C*, 10'-*C*), 113.2 (3'-*C*), 112.8 [=*C*HC(O)], 56.5 (H_2C-N_3), 52.6 ppm (O*C*H$_3$, ester); ms: *m/z* (EI): 286 (9) [M^+ + 1], 285 (17) [M^+], 254 (11), 243 (100), 225 (32), 198 (28), 171 (43), 170 (19), 142 (10), 114 (8). Anal. Calcd for $C_{14}H_{11}N_3O_4$ (285.3): C, 58.95; H, 3.89; N, 14.73. Found: C, 59.01; H, 3.84; N, 14.67.

Ethyl (2Z)-4-azido-3-(2-oxo-2H-chromen-3-yl)but-2-enoate (11b). This was obtained as yellow leaflets, 710 mg (68%); mp 128–130°C (cyclohexane); IR: ν_{max} N_3 2102, C=O (lactone) 1720, C=O (ester) 1714, C=C (exocyclic) 1608 cm^{-1}; ^{1}H-NMR (DMSO^6): δ 1.23 (t, 3H, $J_{H\text{-}H}$ = 6.8 Hz, OC.C*H*$_3$), 4.08 (q, $J_{H\text{-}H}$ = 6.8 Hz, 2H, O*CH*$_2$, ester), 4.39 [d, 2H, $^4J_{H\text{-}H}$ = 1.8 Hz, H_2C—N], 6.08 [t, $^4J_{H\text{-}H}$ = 1.8 Hz, 1H, =C*H*C(O)], 7.34 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.56 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 8.42 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 163.2, 162.6 (2*C*=O), 152.8 (9'-*C*), 145.6 (3'-C—*C*=), 140.1 (4'-*C*), 132.7, 127.1, 125.8, 118.8, 114.2 (7'-C, 8'-*C*, 5'-*C*, 6'-*C*, 10'-*C*), 113.7 (3'-*C*), 112.6 [=*C*HC(O)], 62.6 (O*C*H$_2$, 56.5 (H_2C—N_3), 15.6 ppm (OC.*C*H$_3$); ms: *m/z* (EI): 300 (11) [M^++1], 299 (22) [M^+], 257 (100), 242 (18), 225 (35), 198 (25), 171 (16), 142 (10), 114 (8); Anal. Calcd for $C_{15}H_{13}N_3O_4$ (299.2): C, 60.20; H, 4.38; N, 14.04. Found: C, 60.27; H, 4.43; N, 14.13.

(2Z)-4-Azido-3-(2-oxo-2H-chromen-3-yl)but-2-enenitrile (11c). This was obtained as yellow leaflets, 669 mg (76%); mp 148–150°C (EtOH); IR: ν_{max} CN 2216, N_3 2102, C=O (lactone) 1721, C=C (exocyclic) 1607 cm^{-1}; ^{1}H-NMR (DMSO^6): δ 4.44 (d, $^4J_{H\text{-}H}$ = 2.1 Hz, 2H, H_2C-N_3), 6.26 (t, $^4J_{H\text{-}H}$ = 2.1 Hz, 1H, =C*H*CN), 7.33 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.55 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 8.45 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 161.2 (*C*=O), 154.7 (9'-*C*), 148.6 (*C*=C—CN), 139.7 (4'-*C*), 132.3, 130.5, 126.4, 118.7, 114.2 (7'-C, 8'-*C*, 5'-*C*, 6'-*C*, 10'-*C*), 120.4 (3'-*C*), 115.6 (*C*N), 98.6 (=*C*HCN), 52.3 ppm (H_2C—N_3); ms: *m/z* (EI): 253 (11) [M^++1], 252 (16) [M^+], 224 (77), 210 (48), 197 (100), 169 (85), 140 (42), 114 (13); Anal. Calcd for $C_{13}H_8N_4O_2$ (252.2): C, 61.90; H, 3.20; N, 22.21. Found: C, 61.96; H, 3.24; N, 22.16.

Reaction of 1 with phosphonium salts 13a,b. Preparation of 14a and 15. A dimethylformamide (DMF) solution of 3.5 mmol methyltriphenylphosphonium bromide **13a** (or benzyltriphenylphosphonium chloride, **13b**) and the azide **1** (0.8 g, 3.5 mmol) was treated with aqueous LiOH. The reaction mixture was stirred at r.t. for 24 h. The product mixture was concentrated to 10 mL, diluted with 30 mL of dist H_2O, acidified with conc. HCl, and then extracted with two portions of ethyl acetate. The AcOEt extracts were combined and washed with 50 mL of dist H_2O and dried, and the solvents were evaporated to dryness. The residue was purified by column chromatography with *n*-hexane /AcOEt) as the eluents, whereupon compounds **14a** and **15**, were obtained. Ph_3PO was also isolated.

3-[1-(Azidomethyl)vinyl]-2H-chromen-2-one (14a). This was obtained as yellow leaflets, 635 mg (80%); mp 173–175°C (acetone); IR: ν_{max} C—N_3 2106, C=O (lactone) 1720, C=C (exocyclic) 1618 cm^{-1}; ^{1}H-NMR (DMSO^6): δ 4.02 (t, $J_{H\text{-}H}$ = 2.2 Hz, 2H, H_2CN_3), 5.45, 5.66 (2t(br), 2 × 1H, =CH_2), 7.28 (t, $J_{H\text{-}H}$ = 7.4 Hz, 2H, 6'-*H* and 7'-*H*), 7.54 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H, 5'-*H* and 8'-*H*), 8.43 ppm (s, 1H, 4'-*H*); ^{13}C-NMR (DMSO^6): δ 156.2 (2'-*C*=O), 154.2 (9'-*C*), 139.7 (*C*=CH_2), 132.3, 129.5, 128.4, 126.4, 118.7, 117.2 (7'-C, 4'-*C*, 5'-*C*, 6'-*C*, 8'-*C*, 10'-*C*), 120.4 (3'-*C*), 114.2 (C=*C*H_2), 60.2 ppm (H_2C—N_3); ms: *m/z* (EI): 228 (11) [M^++1], 227 (16) [M^+], 185 (44), 167 (48), 149 (100), 99 (65), 77 (28); Anal. Calcd for $C_{12}H_9N_3O_2$ (227.2): C, 63.43; H, 3.99; N, 18.49. Found: C, 63.51; H, 3.96; N, 18.43.

3-[(E,Z)-2-Azido-1-benzylvinyl]-2H-chromen-2-one (15). This was obtained as yellow leaflets, 890 mg (84%); mp 198–200°C ($CHCl_3$, mixture of isomers *E* and *Z*, 50:50); IR: ν_{max} C—N_3 2108, C=O (lactone) 1721, C=C (exocyclic) 1617 cm^{-1}; ^{1}H-NMR (DMSO^6): *E* isomer: δ 3.38 (d, 2H, $J_{H\text{-}H}$ = 2.1 Hz, CH_2), 7.18 (t, $J_{H\text{-}H}$ = 2.1 Hz, 1H, =C*H*N_3), 7.24–7.38 (m, 3H, *H*-Ph and *H*-Ar, *E, Z*), 7.45–7.67 (m, 6H, *H*-Ph and *H*-Ar, *E, Z*), 8.46, 8.54 ppm (2s, 2 × 1H, 4'-*H, E, Z*); *Z* isomer: δ 3.47 (d, 2H, $J_{H\text{-}H}$ = 2.2 Hz, CH_2), 7.23 (t, $J_{H\text{-}H}$ = 2.2 Hz, 1H, =C*H*N_3); ms: *m/z* (EI): 304 (13) [M^++1], 303 (21) [M^+], 275 (100), 256 (77), 210 (21), 149 (44), 137 (36), 111 (13), 77 (58); Anal. Calcd for $C_{18}H_{13}N_3O_2$ (303.3): C, 71.28; H, 4.32; N, 13.85. Found: C, 71.33; H, 4.37; N, 13.90.

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