Regioselective and Stereoselective Addition of Tetrazole Derivatives to Electron-poor Acetylenic Esters in the Presence of Triphenylphosphine

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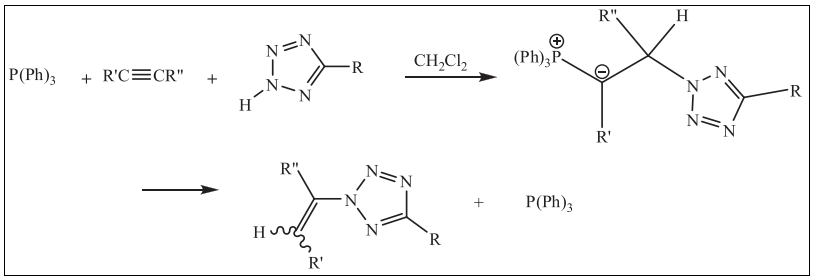

Protonation of the highly reactive 1:1 intermediates produced in the reaction between triphenylphosphine and acetylenic esters by tetrazole derivatives leads to the formation of vinyltriphenylphosphonium salts. The cation of these salts undergoes an addition reaction with the counter anion in CH_2Cl_2 at room temperature to yield the corresponding stabilized phosphorus ylides. Elimination of triphenylphosphine from the stabilized phosphorus ylides leads to the corresponding electron-poor *N*-vinyl tetrazoles in fairly high yields. Structures of *N*-vinyl tetrazoles were determined by IR, ^{1}H NMR, ^{13}C NMR and single crystal X-ray structure analyses. The reaction is fairly regioselective and stereoselective.

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INTRODUCTION

Tetrazole derivates are well known not only as compounds with a high level of biological activity but also as precursors to a variety of nitrogen containing heterocycles [1–8]. Various procedures have been developed for their syntheses. Tetrazoles have a wide range of applications in materials as specialty explosives and information recording systems, in pharmaceuticals as lipophilic spacers and carboxylic acid surrogates, and in coordination chemistry as ligands [9]. They form stable complexes with metals [10–12]. These compounds are useful as oxidizers and effective agents for regulating plant growth. Tetrazole derivatives have also fungicidal, antiviral (including HIV) antimicrobial, antiinflammatory, antilipemic, anticancer, antihypertensive and antiallergic activity [13]. 5-Substituted tetrazoles that contain a free N–H bond are also frequently referred to as tetrazolic acids, and exist as a nearly 1:1 ratio of 1H- and 2H-tautomeric forms [14]. The free N–H bond of tetrazoles makes them acidic molecules because of the ability of the moiety to stabilize a negative charge by electron delocalization. Tetrazolate anionic species are more reactive than the corresponding neutral species toward a variety of electrophiles and alkylating agents [15–20].

Organophosphorus compounds have been extensively used in organic synthesis as useful reagents and as important ligands in a number of transition metal catalysts [21]. *N*-additions of nucleophiles to the vinyl group of vinylic phosphonium salts leading to the formation of new alkylidenephosphoranes have attracted much attention as a very convenient and synthetically useful method in organic synthesis [22]. Phosphorus ylides are a special type of zwitterions, which bear a strongly nucleophilic, electron-rich carbanionlike function adjacent to a phosphonium center. The electron distribution around the P^+–C^- bond and its consequent chemical implications have been probed and assessed through theoretical, spectroscopic and crystallographic investigations [22]. The nucleophilicity at the ylidic carbon is a factor of essential mechanistic importance in the use of phosphorus ylides as Wittig reagents. These are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity [23]. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually obtained from a phosphine and an alkyl halide. Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins and in other ways [24]. The phosphonium salts are most often converted to the ylide by treatment with a strong base, although weaker bases can be used if the salt is acidic enough.

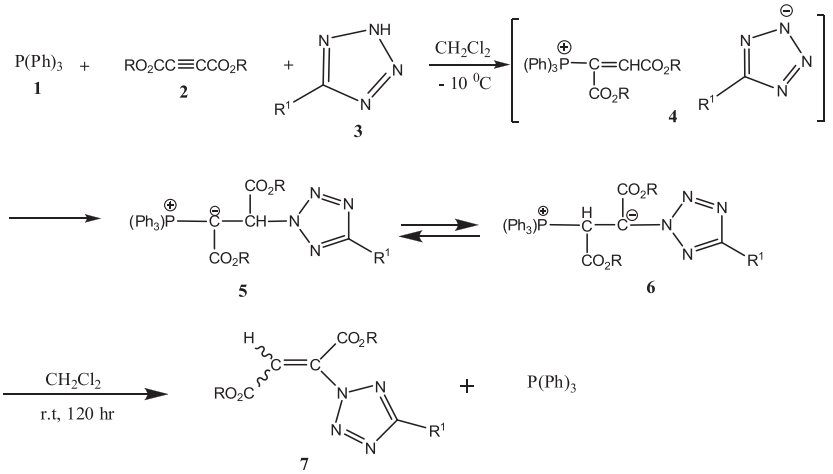
Acetylenic esters are reactive systems and take part in many chemical syntheses. The compounds act almost as Michael acceptors in organic reactions [25–36]. In recent years, there has been an increasing interest in the applications of acetylenic esters in multicomponent synthesis, especially for preparing stabilized phosphorus ylides [25–36].Recently, we have established a one-pot method for the synthesis of organophosphorus compounds [37–40]. In this article, we attempt to describe the regioselective and stereoselective preparation of electron-poor *N*-vinyl tetrazoles from the acetylenic esters and 5-benzyl-2*H*-tetrazole in the presence of triphenylphosphine in fairly good yields.

RESULTS AND DISCUSSION

Reactions are known in which an α,β-unsaturated carbonyl compound is produced from phosphonium salts [25]. Thus, the compound **5** may result from initial addition of triphenylphosphine **1** to the acetylenic esters **2** and concomitant protonation of the 1:1 adducts by the tetrazole derivatives **3** to form the corresponding triphenylphosphonium salts **4**. Addition of the anion in **4** to the vinyltriphenylphosphonium cation leads to the formation of the stabilized phosphorus ylides **5** (Scheme 1) that undergoes intramolecular proton transfer leading to formation of sterically congested electron-poor *N*-vinyl tetrazoles **7** via zwitterionic intermediate **6** (Scheme 1). In this reaction, triphenylphosphine acts as a catalyst. TLC indicated formation of *N*-vinyl tetrazoles **7** in CH_2Cl_2 at room temperature. The mechanism of the reaction outlined earlier has not been established experimentally. However, a possible explanation [29] is proposed in Scheme 1.

The structures of products **7** were proved by their IR, ^{1}H NMR and ^{13}C NMR spectral data (see the Experimental section). The NMR spectra indicated that solutions of compound **7a**, **7c**, and **7d** ($CDCl_3$ as solvent) contain *Z* stereoisomer as only product. It may be a result from thermodynamic stability of *Z* stereoisomer relative to *E* stereoisomer. The steric and electronic effects in the stereoisomers can be conducted *E*/*Z* equilibrium toward *Z* stereoisomer in the presence of PPh_3 as a nucleophilic catalyst (via addition to electron-poor C=C of **7a**, **7c**, and **7d**). The ^{1}H NMR spectrum of the *Z* stereoisomer of **7a** exhibited five signals readily recognized as arising from OMe groups ($\delta = 3.84$, s and $\delta = 4.04$, s), CH_2 ($\delta = 4.31$, s), =CH ($\delta = 6.90$, s), and aromatic moieties ($\delta = 7.23$–7.34, m). The ^{13}C NMR spectrum of the *Z* stereoisomer showed 12 distinct resonances according to expectation. Partial assignment of these resonances is given in the Experimental section. The NMR spectra indicated that solution of compound **7b** ($CDCl_3$ as solvent) contains *E* and *Z* stereoisomers. Relative population of *E* and *Z* isomers was determined via their ^{1}H NMR spectra (%*E* = 50.25, %*Z* = 49.75). The ^{1}H and ^{13}C NMR spectra of compound **7b** are similar to those of **7a**, except for the ester group, which exhibits characteristic signals with appropriate chemical shifts (see Spectral Analysis section). The ^{1}H NMR spectrum of the *Z* stereoisomer of **7c** exhibited four signals readily recognized as arising from OMe groups ($\delta = 3.87$, s and $\delta = 4.09$, s), =CH ($\delta = 7.01$, s), and aromatic moieties ($\delta = 7.26$–8.22, m). The ^{13}C NMR spectrum of the *Z* stereoisomer showed 11 distinct resonances according to expectation. Partial assignment of these resonances is given in the Experimental section. The ^{1}H and ^{13}C NMR spectra of compound **7d** are similar to those of **7c**, except for the ester group, which exhibits characteristic signals with appropriate chemical shifts (see Spectral Analysis section).

Scheme 1. Synthesis of electron-poor *N*-vinyl tetrazoles **7a-d** from triphenylphosphine 1, dialkyl acetylene dicarboxylate **2** and tetrazole derivatives **3**.



7a :R^1= $PhCH_2$, R= Me ; **7b** :R^1= $PhCH_2$, R= Et; **7c**: R^1= Ph, R=Me ; 7d: R^1= Ph, R=Et

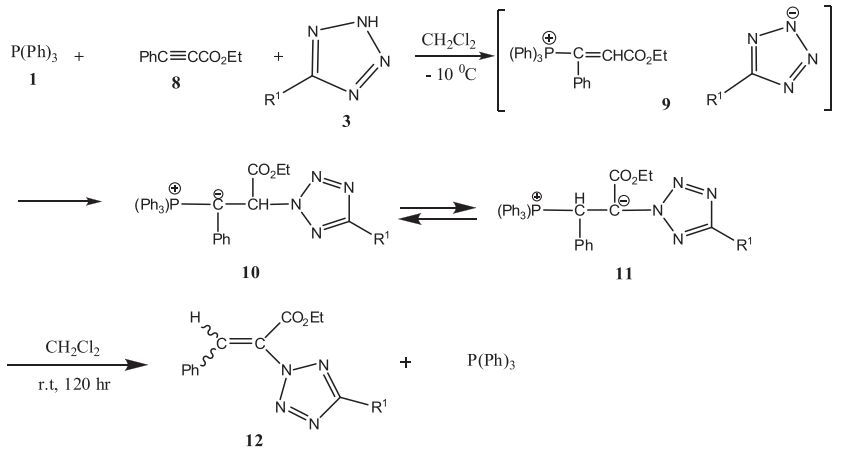
We have also used ethyl phenyl acetylenecarboxylate **8** (Scheme 2) instead of alkyl acetylenecarboxylate **2** in this reaction. The stabilized phosphorus ylides **10** may result from initial addition of triphenylphosphine **1** to the acetylenic ester **8** and concomitant protonation of the 1:1 adduct, followed by attack of the NH-acid anion **9** on the vinyltriphenylphosphonium cation to form the phosphorane **10** (Scheme 2). In this reaction, triphenylphosphine acts as a catalyst. TLC indicated formation of the *N*-vinyl tetrazoles **12a-c** in CH_2Cl_2. The mechanism of the reaction outlined earlier has not been established experimentally. However, a possible explanation [29] is proposed in Scheme 2. The NMR spectra indicated that solution of compound **12a** ($CDCl_3$ as solvent) contains *E* stereoisomer as major product, which may result from easier formation of *E* isomer than *Z* isomer. It may be a result from thermodynamic stability of *E* stereoisomer relative to *Z* stereoisomer. The steric and electronic effects in the stereoisomers **12** can be conducted *E/Z* equilibrium toward *E* stereoisomer in the presence of PPh_3 as a nucleophilic catalyst (via addition to electron-poor C=C of **12**). Relative population of *E* and *Z* isomers was determined via their ^{1}H NMR spectra (%*E* = 63.13, % *Z* = 36.87). The ^{1}H NMR spectrum of the *E* stereoisomer of **12a** exhibited five signals readily recognized as arising from OCH_2 group (δ = 4.33, q), OMe (δ = 3.88, s), CH_3 (δ = 1.31, t), =CH (δ = 7.28, s), and aromatic moieties (δ = 6.87–8.19, m). The ^{13}C NMR spectrum of the *E* stereoisomer showed 15 distinct resonances according to expectation. Partial assignment of these resonances is given in the Experimental section. The ^{1}H and ^{13}C NMR signals of the minor stereoisomer *Z* are similar to those of the major stereoisomer (see Spectral Analysis section). The ^{1}H NMR and ^{13}C NMR spectra of compounds **12b-c** are similar to those of **12a**, except for the aromatic substituent on the tetrazole ring, which exhibits characteristic signals with appropriate chemical shifts (see Spectral Analysis section). Structure of **12c** was determined by single crystal X-ray structure analysis.

Crystal structure of 12c. The crystal of **12c** is built up from molecules shown in Figure 1. The summary of the experimental details is given in Table 1. The overall structure of **12c** is similar to that observed in the related compounds described by us previously and deposited at the Cambridge Structural Database [41]. Like in these compounds, two planes (with the atoms N(1) and C(4) being common) may be distinguished in the molecule of **12c**: the ethyl (2*Z*)-2-amino-3-phenylacrylate moiety (forming plane 1 with r. m. s. deviation of fitted atoms = 0.08 Å) and the rest of the molecule (plane 2 with r.m. s. = 0.19 Å). The dihedral angle between the least-squares planes 1 and 2, amounting to 88.4(1)°, reveals that the two planes are almost perpendicular to each other. However, it has to be noted that the two rings within the plane 2 (tetrazolyl and C(13) ~ C(18) phenyl) are slightly twisted with each other, which is reflected in the N(2)–C(12)–C(13)–C(14) torsion angle of −18.0(2)°. Moreover, some deviation from the planarity of the fragment defined here as plane 1, that is, slight twist of the C(6)–C(11) phenyl ring, is revealed by the value of the C(4)–C(5)–C(6)–C(7) torsion angle of −6.4(2)°. This was previously observed in most of the *Z* geometrical isomers of similar structures reported so far [41].

As it was observed for the analogs of **12c** [41], the molecule adopts *Z* geometry with respect to the double bond C(4)–C(5), which is reflected in the value of the torsion angle N(1)–C(4)–C(5)–C(6) of −3.5(2)° (Table 2). The carbonyl atom O(1) of the ester group is in *antiperiplanar* conformation in relation to the vinyl atom C(5) [O(1)–C (3)–C(4)–C(5) torsion angle of 176.6(1)°], as also found for most of the structurally related compounds [41].

The weak intramolecular hydrogen interactions: C(5)–H(5)–O(2) and C(7)–H(7)–N(1), also observed before [41], give rise

Scheme 2. Synthesis of electron-poor *N*-vinyl tetrazoles **12a-c** from triphenylphosphine 1, ethyl phenyl acetylenecarboxylate **8**, and tetrazole derivatives **3**.



12a :R^1 = *p*-CH_3O-Ph ; **12b** :R^1 = $PhCH_2$; **12c**: R^1 = Ph

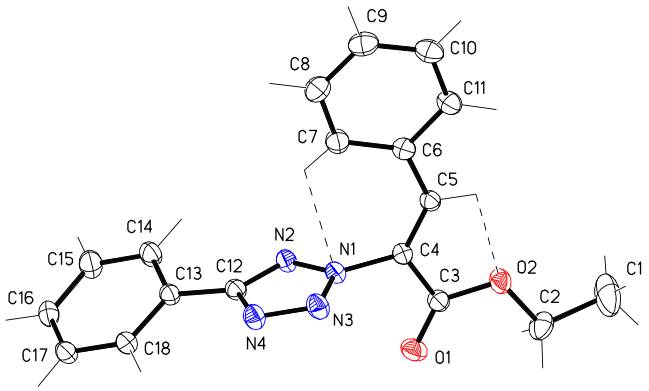


Figure 1. Molecular structure of compound **12c**, showing the X-ray atom-numbering scheme and intramolecular C–H–O/N hydrogen bonds forming S(5) and S(6) motifs, respectively (dashed lines). Displacement ellipsoids represent the 50% probability level. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1

Crystallographic data of compound **12c**

Crystallized from	CH_2Cl_2/petroleum ether	μ [mm^{-1}]	0.088
Empirical formula	$C_{18}H_{16}N_4O_2$	$F(000)$ [e]	336
M_r	320.35	Scan type	ω and φ
Crystal color, habit	colorless, block	Index range	$-10 \le h \le 8$
Crystal dimensions [mm]	$0.35 \times 0.28 \times 0.22$		$-15 \le k \le 15$
Radiation type, λ [Å]	Mo$K\alpha$, 0.71073		$-12 \le l \le 15$
Temperature [K]	120(2)	Measured reflections	7080
Crystal system	triclinic	Independent reflections	4348
Space group	$P\bar{1}$	Reflections with $I > 2\sigma(I)$	3406
Z	2	R_{int}	0.020
θ Range [°]	4.77–29.99	Refinement on	F^2
a [Å]	7.207(2)	Data, restraints, parameters	4348, 0, 281
b [Å]	11.102(3)	R ($F_o^2 > 2\sigma(F_o^2)$)	$R_1 = 0.040$[a]
c [Å]	11.372(3)		$wR_2 = 0.113$ [a]
α [°]	64.94(3)	R (all data)	$R_1 = 0.052$
β [°]	89.78(3)		$wR_2 = 0.121$
γ [°]	86.86(3)	Goodness-of-fit = S	1.12
V [Å^3]	822.8(4)	Weighting parameter a/b	0.0778/0.0
D_x (calc.) [g cm^{-3}]	1.293	$\Delta\rho$ (max; min) [e Å^{-3}]	0.31; −0.21

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \sqrt{\sum\left[w\left(F_o^2 - F_c^2\right)^2\right]/\sum\left[w\left(F_o^2\right)^2\right]}$. Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 2

Selected interatomic distances [Å], valence angles [°], and torsion angles [°] of **12c**.

Bond lengths			
N(1)–N(2)	1.333(2)	N(4)–C(12)	1.361(2)
N(1)–N(3)	1.336(2)	C(3)–C(4)	1.492(2)
N(3)–N(4)	1.318(2)	C(4)–C(5)	1.337(2)
N(1)–C(4)	1.437(2)	C(5)–C(6)	1.464(2)
N(2)–C(12)	1.338(2)		
Valence angles			
N(2)–N(1)–N(3)	114.14(8)	N(1)–N(3)–N(4)	105.59(8)
N(2)–N(1)–C(4)	123.60(8)	N(3)–N(4)–C(12)	106.78(8)
N(3)–N(1)–C(4)	122.16(8)	C(4)–C(5)–C(6)	132.01(9)
N(1)–N(2)–C(12)	101.62(8)		
Torsion angles			
C(3)–O(2)–C(2)–C(1)	−178.7(2)	O(2)–C(3)–C(4)–C(5)	−3.0(2)
C(2)–O(2)–C(3)–C(4)	175.5(1)	N(1)–C(4)–C(5)–C(6)	−3.5(2)
N(2)–N(1)–C(4)–C(5)	100.6(2)	C(4)–C(5)–C(6)–C(7)	−6.4(2)
O(2)–C(3)–C(4)–N(1)	179.0(1)	N(2)–C(12)–C(13)–C(14)	−18.0(2)

to five-membered *S*(5) and six-membered *S*(6) motifs, respectively (Fig. 1, Table 3). Both of them are formed in plane 1 and stabilize the molecular structure of the compound. Besides, atom H(7) is involved in intramolecular C(7)–H(7)–π[*Cg*(1)] interaction with tetrazolyl ring (see Table 3 for details).

The crystal packing of **12c** is dominated by weak C–H⊙⊙⊙O/N/π contacts with the atom O(1) playing the main accepting role (Table 3). The molecules in the crystal are joined to each other by C(9)–H(9)⊙⊙⊙O(1)^{i} bonds to form infinite chains along the *b* axis (Fig. 2), almost identical to these observed in the ethyl (*Z*)-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-phenyl-2-propenoate crystal [42]. The adjacent chains interact with each other via C(15)–H(15)⊙⊙⊙N(4)^{ii} contacts, giving rise to layers parallel to (001) plane. The neighboring layers are connected to each other through centrosymmetric bifurcated C(16)–H(16)⊙⊙⊙O(1)^{iii}, C(17)–H(17)⊙⊙⊙O(1)^{iii} bonds resulting in three-dimensional network of hydrogen contacts in the crystal of **12c**. Additional stabilization of the crystal packing is provided by the centrosymmetric weak C–H⊙⊙⊙π interactions.

We have also used alkyl acetylenecarboxylates **13** (Scheme 3) instead of dialkyl acetylenedicarboxylate **2** in this reaction. The stabilized phosphorus ylides **15** may result from initial addition of triphenylphosphine **1** to the acetylenic esters **13** and concomitant protonation of the 1:1 adduct, followed by attack of the NH-acid anion **14** on the vinyltriphenylphosphonium cation to form the phosphorane **15** (Scheme 3). In this reaction, triphenylphosphine acts as a catalyst. TLC indicated formation of the *N*-vinyl tetrazoles **17a-d** in CH_2Cl_2. The mechanism of the reaction outlined earlier has not been established experimentally. However, a possible explanation [29] is proposed in Scheme 3.

The NMR spectra indicated that solutions of compound **17a–d** ($CDCl_3$ as solvent) contain *E* stereoisomer as only product. The ^{1}H NMR spectrum of the *E* stereoisomer of **17a** exhibited six signals readily recognized as arising from OMe groups (δ = 3.87, s and δ = 3.88, s), =CH (δ = 6.89, d, $^3J_{HH}$ = 14.0 Hz), –NCH = (δ = 8.45, d, $^3J_{HH}$ = 14.0 Hz) and aromatic moieties (δ = 7.03, d, 2 H, $^3J_{HH}$ = 8.75 Hz; 8.14, d, 2 H, $^3J_{HH}$ = 8.75 Hz). The ^{13}C NMR spectrum of the *E* stereoisomer showed 10 distinct resonances according to expectation. Partial assignment of these resonances is given in the Experimental section. The ^{1}H and ^{13}C NMR spectra of compounds **17b-d** are similar to those of **17a**, except for the ester group, which exhibits characteristic signals with appropriate chemical shifts (see Spectral Analysis Section).

Table 3

Geometry of proposed C–H⊙⊙⊙O/N/π close contacts for **12c**.

D–H⊙⊙⊙A	D–H [Å]	H⊙⊙⊙A [Å]	D⊙⊙⊙A [Å]	D–H⊙⊙⊙A [°]
C(5)–H(5)⊙⊙⊙O(2)	0.96(2)	2.36(2)	2.730(2)	102(1)
C(7)–H(7)⊙⊙⊙N(1)	0.94(2)	2.49(2)	3.072(2)	120(1)
C(9)–H(9)⊙⊙⊙O(1)^{i}	0.98(2)	2.50(2)	3.429(2)	160(1)
C(15)–H(15)⊙⊙⊙N(4)^{ii}	1.00(2)	2.60(2)	3.418(2)	139(2)
C(16)–H(16)⊙⊙⊙O(1)^{iii}	1.00(2)	2.65(2)	3.284(2)	121(1)
C(17)–H(17)⊙⊙⊙O(1)^{iii}	0.95(2)	2.60(2)	3.251(2)	126(1)
C(7)–H(7) ⊙⊙⊙*Cg*(1)	0.94(2)	2.66(2)	3.456(2)	142(2)
C(2)–H(2B) ⊙⊙⊙*Cg*(2)^{iv}	0.99(2)	2.98(2)	3.856(2)	149(2)

Symmetry codes: (*i*) *x*, *y*−1, *z*; (*ii*) *x*−1, *y*, *z*; (*iii*) −*x*, −*y*+1, −*z*−1; (*iv*) −*x*+1, −*y*, −*z*;

Cg(1) and *Cg*(2) are the centroids of the tetrazolyl N(1)–N(2) and phenyl C(6)–C(11) rings, respectively.

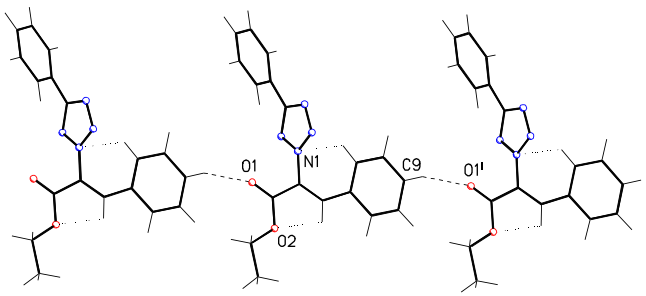
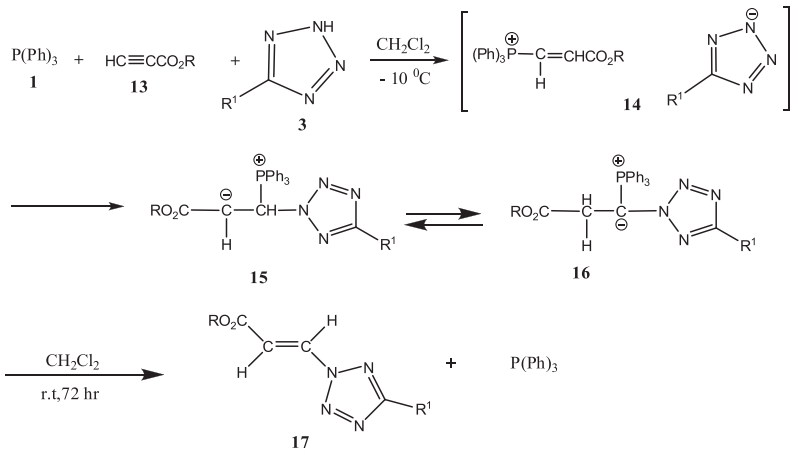


Figure 2. A fragment of infinite chains formed along the *b* axis in the crystal of **12c** with adjacent molecules joined by C(9)–H(9)⊙⊙⊙O(1)^{i} hydrogen bonds (dashed lines). Intramolecular C–H⊙⊙⊙O/N close contacts are shown with dotted lines. Symmetry codes are given in Table 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 3. Synthesis of electron-poor *N*-vinyl tetrazoles **17a-d** from triphenylphosphine1, alkyl acetylenecarboxylate **13**, and tetrazole derivatives **3**.

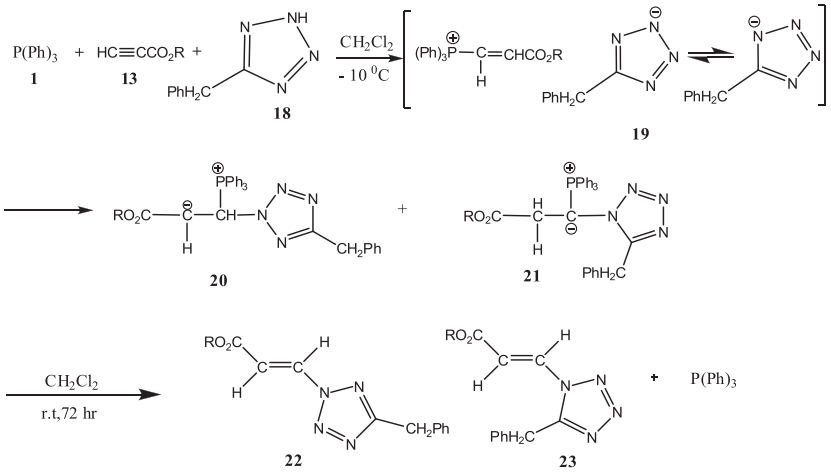


17a: $R^1 = p$-CH_3O-Ph, R=Me ; **17b**: $R^1 = p$-CH_3O-Ph, R=Et; **17c**: R^1= Ph, R=Me ; 17d: R^1= Ph, R=Et

We have also used alkyl acetylenecarboxylates **13** (Scheme 4) instead of dialkyl acetylenedicarboxylate **2** and 5-benzyl-2*H*-tetrazol in this reaction. The stabilized phosphorus ylides **20** and **21** may result from initial addition of triphenylphosphine **1** to the acetylenic esters **13** and concomitant protonation of the 1:1 adduct, followed by attack of the NH-acid anion **19** on the vinyltriphenylphosphonium cation to form the phosphorane **20** and **21** (Scheme 4). In this reaction, triphenylphosphine acts as a catalyst. TLC indicated formation of the *N*-vinyl tetrazoles **22** and **23** in CH_2Cl_2. The mechanism of the reaction outlined earlier has not been established experimentally. However, a possible explanation [29] is proposed in Scheme 4. The formation of tautomeric forms of **22** and **23** may be a result from the reduction of steric hindrance (benzyl group is less steric than aryl group and H group is less steric than CO_2R group) in their formation in comparison with the formation of compounds **7**, **12,** and **17** (Schemes 1–4).

The NMR spectra indicated that solutions of compound **22a-b** and **23a-b** ($CDCl_3$ as solvent) contain *E* isomer of 2H-tautomeric form as major product, which may result from the easy tautomerism of 1H- and 2H-tautomeric forms. Relative population of *E* isomers of 1H- and 2H-tautomeric forms were determined via their ^{1}H NMR spectra (**22a**: *%E* = 58, **23a:** *%E* = 42; **22b**: *%E* = 60, **23b:** *% E* = 40). The structure of products **22a-b** and **23a-b** was proved by their IR, ^{1}H NMR and ^{13}C NMR spectral data (see the Experimental section).

Scheme 4. Synthesis of electron-poor *N*-vinyl tetrazoles **22a-b** and **23a-b** from triphenylphosphine **1**, alkyl acetylenecarboxylate **13** and 5-benzyl-2*H*-tetrazol **18**.



22a: R=Me 22b: R=Et; 23a: R=Me 23b: R=Et

CONCLUSIONS

In conclusion, we have developed a convenient, one-pot regioselective and stereoselective method for preparing electron-poor *N*-vinyl tetrazoles (**7a–c** and **12a–b**) utilizing *in situ* generation of the phosphonium salts. Other aspects of this process are under investigation.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu IR-460 spectrometer (Shimadzu, Kyoto, Japan). ^{1}H and ^{13}C NMR spectra were measured with a Bruker Spectrospin spectrometer at 250 and 62.5 MHz, respectively.

Synthesis of tetrazole derivatives. Twenty millimolar benzonitrile derivatives, 15 mL of water, 1.56 g sodium azide, and 1.632 g zinc chloride were added to a three-necked 50 mL round bottomed flask. The reaction solution was refluxed for 24 h with vigorous stirring. After the mixture was cooled to room temperature, the pH value was adjusted to 1.0 with concentrated HCl, and the solution was stirred for 30 min to form a solid precipitate. The new precipitate was then filtered, washed with 1 *M*/L HCl, and dried in a drying oven at 90°C overnight to give 5-benzyl-2*H*-tetrazole as a white powder; the crude product was recrystallized in ethanol (60% yield).

General procedure for the preparation of electron-poor *N*-vinyl tetrazoles. To a magnetically stirred solution of triphenylphosphine (0.262 g, 1 m*M*) and tetraazol derivatives (1 m*M*) in dichloromethane (5 mL) was added dropwise a mixture of acetylenic esters (1 m*M*) in dichloromethane (2 mL) at −10°C over 15 min. The mixture was allowed to warm up to room temperature and stirred for 72–120 h at room temperature. The solvent was removed under reduced pressure, and the viscous residue was purified by flash column chromatography (silica gel; petroleum ether–ethyl acetate). The solvent was removed under reduced pressure, and the products were obtained. The characterization data of the compounds are given in the following.

Dimethyl (Z)-2-(5-benzyl-2H-1,2,3,4-tetraazol-2-yl)-2-butenedioate (7a). Viscous colorless oil, yield 62%. IR (KBr): 3038.46, 2946.15, 1746.15, 1661.54, 1446.15 cm^{-1}. - ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.84 (s, 3 H, CH_3 of OMe), 4.04 (s, 3 H, CH_3 of OMe), 4.31 (s, 2 H, CH_2), 6.90 (s, 1 H, C=CH), 7.23–7.34 (m, 5 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.71, 53.93 (CH_3 of OMe), 31.76 (CH_2), 111.63, 127.23 (2CH), 128.80, 128.86 (4CH), 135.49, 139.22, 161.49 (3C), 163.87, 165.29 (CO of ester). $C_{14}H_{14}N_4O_4$ (302.10).

Diethyl (E, Z)-2-(5-benzyl-2H-1,2,3,4-tetraazol-2-yl)-2-butenedioate (7b). Viscous colorless oil, yield 60%. IR (KBr): 3092.31, 2938.46, 1730.77, 1661.54, 1407.69 cm^{-1}. **for *E***: ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 1.40 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.26 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.51 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.30 (s, 2 H, CH_2), 6.23 (s, 1 H, C=CH), 7.23–7.73 (m, 5 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.75, 14.00 (CH_3 of OEt), 63.40, 61.78 (CH_2 of OEt), 31.78 (CH_2), 111.97, 129.78 (2CH), 128.86, 128.77 (4CH), 135.56, 139.31, 160.16 (3C), 163.33, 166.41 (CO of ester). **for *Z***: ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 1.40 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.26 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.51 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.30 (s, 2 H, CH_2), 6.88 (s, 1 H, C=CH), 7.23–7.73 (m, 5 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.75, 14.00 (CH_3 of OEt), 61.78, 61.22 (CH_2 of OEt), 30.09 (CH_2), 111.97, 127.19 (2CH), 128.86, 128.77 (4CH), 135.56, 139.31, 160.16 (3C), 165.24, 166.41 (CO of ester).

Dimethyl (Z)-2-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-butenedioate (7c). White solid, m.p. 86°C, yield 70%. IR (KBr): 3076.92, 2961.54, 1730.77, 1653.85, 1453.85 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.87 (s, 3 H, CH_3 of OMe), 4.09 (s, 3 H, CH_3 of OMe), 7.01 (s, 1 H, C=CH), 7.26–8.22 (m, 5 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.73, 53.95 (CH_3 of OMe), 111.56, 131.35 (2CH), 127.43, 129.06 (4CH), 125.89, 139.44, 160.70 (3C), 163.92, 165.69 (CO of ester). $C_{13}H_{12}N_4O_4$ (288.09).

Diethyl (Z)-2-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-butenedioate (7d). Viscous colorless oil, yield 67%. IR (KBr): 3184.62, 2930.77, 1730.77, 1661.54, 1469.23 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.34 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 1.44 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.31 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.55 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 6.98 (s, 1 H, C=CH), 7.51–8.2 (m, 5 H, arom CH).^{13}C NMR (62.5 MHz, $CDCl_3$): δ 13.83, 14.08 (CH_3 of OEt), 61.87, 63.50 (CH_2 of OEt), 111.78, 131.32 (2CH), 127.37, 129.07 (4CH), 125.94, 139.45, 160.25 (3C), 163.44, 167.78 (CO of ester). $C_{15}H_{16}N_4O_4$ (316.12).

Ethyl(E,Z)-2-[5-(4-methoxyphenyl)-2H-1,2,3,4-tetraazol-2-yl]-3-phenyl-2-propenoate (12a). Viscous colorless oil, yield 65%. IR (KBr): 3069.23, 2923.08, 1730.77, 1653.85, 1469.23 cm^{-1}. **for *E***: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.31 (t, 3H, $^3J_{HH}$ = 7.25 Hz, CH_3 of OEt), 3.88 (s, 3 H, CH_3 of OMe), 4.33 (q, 2H, $^3J_{HH}$ = 7.25 Hz, CH_2 of OEt), 7.28 (s, 1 H, C=CH), 6.87–8.19 (m, 9 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.20 (CH_3 of OEt), 62.37 (CH_2 Of OEt), 55.42 (CH_3 of OMe), 128.17, 128.96, 129.41, 130.43 (8CH); 114.34, 131.53 (2CH); 161.54, 151.00, 141.28, 119.48, 130.69 (5C), 162.80 (CO of ester). **for *Z***: ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.37 (t, 3H, $^3J_{HH}$ = 7.25 Hz, CH_3 of OEt), 3.88 (s, 3 H, CH_3 of OMe), 4.44 (q, 2H, $^3J_{HH}$ = 7.25 Hz, CH_2 of OEt), 8.07 (s, 1 H, C=CH), 6.87–8.19 (m, 9 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.20 (CH_3 of OEt), 61.79 (CH_2 of OEt), 55.42 (CH_3 of OMe), 128.69, 129.10, 129.48,

130.37 (8CH); 114.34, 131.78 (2CH); 161.06, 151.00, 142.12, 125.6, 136.12 (5C), 165.50 (CO of ester). $C_{19}H_{18}N_4O_3$ (350.14).

Ethyl (Z)-2-(5-benzyl-2H-1,2,3,4-tetraazol-2-yl)-3-phenyl-2-propenoate (12b). Viscous colorless oil, yield 70%. IR (KBr): 3030.77, 2984.62, 1738.46, 1646.15, 1453.85 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.23 (t, 3 H, $^3J_{HH}$ = 7.25 Hz, CH_3 of OEt), 4.24 (q, 2 H, $^3J_{HH}$ = 7.25 Hz, CH_2 of OEt), 4.35 (s, 2 H, CH_2), 8.09 (s, 1 H, C=CH), 6.68–7.29 (m, 10 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.02 (CH_3 of OEt), 62.50 (CH_2 Of OEt), 31.77 (CH_2), 128.64, 128.69, 128.97, 130.18 (8CH), 126.93, 142.16, 131.71 (3CH), 125.56, 130.27, 136.70, 162.20 (4C), 166.28 (CO of ester). $C_{19}H_{18}N_4O_2$ (334.14).

Preparation of single crystals of ethyl-(Z)-3-phenyl-2-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (12c). Colorless single crystals of ethyl-(*Z*)-3-phenyl-2-(5-phenyl-2*H*-1,2,3,4-tetraazol-2-yl)-2-propenoate were obtained from slow evaporation of its dichloromethane/light petroleum ether (1:3) solution (20–25°C). The colorless single crystals were filtered off, washed with a cold mixture of dichloromethane/light petroleum ether (1:3) and dried at room temperature.

Ethyl (Z)-3-phenyl-2-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (12c). White solid, m.p. 96°C, yield 77%. IR (KBr): 3061.54, 2976.92, 1723.08, 1653.85, 1453.85 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.29 (t, 3 H, $^3J_{HH}$ = 7.25 Hz, CH_3 of OEt), 4.33 (q, 2 H, $^3J_{HH}$ = 7.25 Hz, CH_2 of OEt), 8.17 (s, 1 H, C=CH), 6.88 (d, 2 H, $^3J_{HH}$ = 7.75 Hz arom. CH); 7.34 (d of d, 2 H, $^3J_{HH}$ = 7.75 Hz, $^3J_{HH}$ = 7.25 Hz, arom. CH), 7.25 (t, 1 H, $^3J_{HH}$ = 7.25 Hz, arom. CH), 7.50–8.27 (m, 5 H, arom. CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.10 (CH_3 of OEt), 62.56 (CH_2 of OEt), 127.15, 128.97, 129.11, 130.33 (8CH), 130.68, 130.33, 131.81 (3CH), 125.58, 126.96, 142.18, 162.29 (4C), 165.6 (CO of ester). $C_{18}H_{16}N_4O_2$ (320.13).

Methyl (E)-3-[5-(4-methoxyphenyl)-2H-1,2,3,4-tetraazol-2-yl]-2-propenoate (17a). White solid, m.p. 119°C, yield 78%. IR (KBr): 3076.92, 2923.08, 1730.77, 1661.54, 1476.92 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 3.87 (s, 3 H, CH_3 of OMe), 3.88 (s, 3 H, CH_3 of OMe), 6.89 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 8.45 (d,1 H, $^3J_{HH}$ = 14 Hz, CH=CH), 7.03 (d, 2 H, $^3J_{HH}$ = 8.75 Hz, arom CH), 8.14 (d, 2 H, $^3J_{HH}$ = 8.75 Hz, arom CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.41, 55.42 (CH_3 of OMe), 114.46, 128.92 (4CH), 112.92, 135.36 (2CH), 118.64, 161.92,165.32 (3C), 165.62 (CO of ester). $C_{12}H_{12}N_4O_3$ (260.09).

Ethyl (E)-3-[5-(4-methoxyphenyl)-2H-1,2,3,4-tetraazol-2-yl]-2-propenoate (17b). White solid, m.p. 93°C, yield 77%. IR (KBr): 3107.69, 2930.77, 1738.46, 1615.38, 1484.62 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.37 (t, 3 H, $^3J_{HH}$ = 7.00 Hz, CH_3 of OEt), 3.88 (s, 3 H, CH_3 of OMe), 4.32 (q, 2 H, $^3J_{HH}$ = 7.00 Hz, CH_2 of OEt), 6.89 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 8.39 (d, 1 H, $^3J_{HH}$ = 14 Hz, CH=CH), 7.03 (d, 2 H, $^3J_{HH}$ = 9 Hz, arom CH), 8.14 (d, 2 H, $^3J_{HH}$ = 9 Hz, arom CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.22 (CH_3 of OEt), 55.43 (CH_3 of OMe), 61.43 (CH_2 of OEt), 114.47, 128.91 (4CH), 113.44, 135.18 (2CH), 118.68, 161.91,164.86 (3C), 165.59 (CO of ester). $C_{13}H_{14}N_4O_3$ (274.11).

Methyl (E)-3-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (17c). White solid, m.p. 146°C, yield 75%. IR (KBr): 3100, 2923.08, 1730.77, 1653.85, 1461.54 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 3.88 (s, 3 H, CH_3 of OMe), 6.93 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.5–8.23 (m, 5 H, arom. CH), 8.42 (d,1 H, $^3J_{HH}$ = 14 Hz, CH=CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.46 (CH_3 of OMe), 113.38, 135.36, 131.22 (3CH), 127.32, 129.08 (4CH), 126.17, 165.22 (2C), 165.8 (CO of ester). $C_{11}H_{10}N_4O_2$ (230.08).

Ethyl (E)-3-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (17d). White solid, m.p. 128°C, yield 73%. IR (KBr): 3092.31, 2930.77, 1723.08, 1676.92, 1469.23 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.38 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.35 (q, 2 H, $^3J_{HH}$ =7.25, CH_2 of OEt), 6.94 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.51–8.23 (m, 5 H, arom. CH), 8.42 (d, 1 H, $^3J_{HH}$ = 14 Hz, CH=CH).^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.21 (CH_3 of OEt), 61.49 (CH_2 of OEt), 113.90, 135.17, 131.20 (3CH), 127.30, 129.08 (4CH), 126.21, 164.75 (2C), 165.71 (CO of ester). $C_{12}H_{12}N_4O_2$ (244.10).

Methyl (E)-3-(5-benzyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (22a). White solid, m.p. 75°C, Total yield 77%. IR (KBr): 3084.62, 2930.77, 1723.08, 1661.54, 1446.15 cm^{-1}. -^1H NMR (250 MHz, $CDCl_3$): δ 3.85 (s, 3 H, CH_3 of OMe), 4.30 (s, 2 H, CH_2), 6.83 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.25–7.72 (m, 5 H, arom CH), 8.33 (d,1 H, $^3J_{HH}$ = 14 Hz, CH=CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.39 (CH_3 of OMe), 31.83 (CH_2), 113.42, 127.20, 135.27 (3CH), 128.80, 128.87 (4CH), 135.72, 159.06 (2C), 165.13 (CO of ester). $C_{12}H_{12}N_4O_2$ (244.10).

Methyl (E)-3-(5-benzyl-1H-1,2,3,4-tetraazol-1-yl)-2-propenoate (23a). Viscous colorless oil, Total yield 77%. IR (KBr): 3038.46, 2930.77, 1730.77, 1661.54, 1438.46 cm^{-1}. -^1H NMR (250 MHz, $CDCl_3$): δ 3.81(s, 3 H, CH_3 of OMe), 4.42 (s, 2 H, CH_2), 6.81 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.02–7.46 (m, 5 H, arom CH), 7.78 (d,1 H, $^3J_{HH}$ = 14 Hz, CH=CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 52.42 (CH_3 of OMe), 29.37 (CH_2), 114.64, 128.10, 130.74 (3CH), 128.37, 129.41 (4CH), 153.3,136,11 (2C), 166.12 (CO of ester). $C_{12}H_{12}N_4O_2$ (244.10).

Ethyl (E)-3-(5-benzyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate (22b). Viscous colorless oil, Total yield 73%. IR (KBr): 3100, 2930.77, 1730.77, 1661.54, 1461.54 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.34 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.3 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.30 (s, 2 H, CH_2), 6.82 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.25–7.34 (m, 5 H, arom. CH), 8.32 (d, 1 H, $^3J_{HH}$ = 14 Hz, CH=CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.17 (CH_3 of OEt), 61.42 (CH_2 of OEt), 31.84 (CH_2), 113.92, 135.75,

127,19 (3CH), 128.79, 128.88 (4CH), 135.09, 164.67 (2C), 166.60 (CO of ester). $C_{13}H_{14}N_4O_2$ (258.11).

Ethyl (E)-3-(5-benzyl-1H-1,2,3,4-tetraazol-1-yl)-2-propenoate (23b). Viscous colorless oil, Total yield 73%. IR (KBr): 3100, 2930.77, 1723.08, 1661.54, 1453.85 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 1.31 (t, 3 H, $^3J_{HH}$ =7.25 Hz, CH_3 of OEt), 4.25 (q, 2 H, $^3J_{HH}$ =7.25 Hz, CH_2 of OEt), 4.38 (s, 2 H, CH_2), 6.78 (d, 1 H, $^3J_{HH}$ = 14 Hz, HC=CH), 7.08–7.50 (m, 5 H, arom. CH), 7.75 (d, 1 H, $^3J_{HH}$ = 14 Hz, CH=CH). ^{13}C NMR (62.5 MHz, $CDCl_3$): δ 14.10 (CH_3 of OEt), 61.47 (CH_2 of OEt), 30.89 (CH_2), 115.11, 130.57, 128,08 (3CH), 128.39, 129.39 (4CH), 132.92, 153.12 (2C), 164.5 (CO of ester). $C_{13}H_{14}N_4O_2$ (258.11).

X-ray crystal-structure determination of 12c (Table 1 and Fig. 1)[43]. The crystallographic measurement was performed on a κ-geometry *Xcalibur PX* automated four-circle diffractometer with graphite-monochromatized Mo*K*α radiation (λ 0.71073 Å). The data for the crystal were collected at 120(2) K by using the *Oxford-Cryosystems* cooler. A summary of the conditions for the data collection and the structure refinement parameters are given in Table 1. The data were corrected for *Lorentz* and polarization effects. Data collection, cell refinement, and data reduction and analysis were carried out with the *Xcalibur PX* software (*Oxford Diffractiod Ltd.*): CrysAlis CCD and CrysAlis RED, respectively [44]. The structure was solved by direct methods with the SHELXS-97 program [45] and refined by a full-matrix least-squares technique with SHELXL-97 [45] and anisotropic thermal parameters for non-H atoms. All H-atoms were found in different *Fourier* maps and were refined isotropically. Figures were made with the XP program [46].

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