SHORT PAPER

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Hypervalent iodine in synthesis 73: a new stereoselective synthesis of 1-(1-alkenyl) benzotriazoles by the reaction of alkenyl(phenyl)iodonium salts with benzotriazole†

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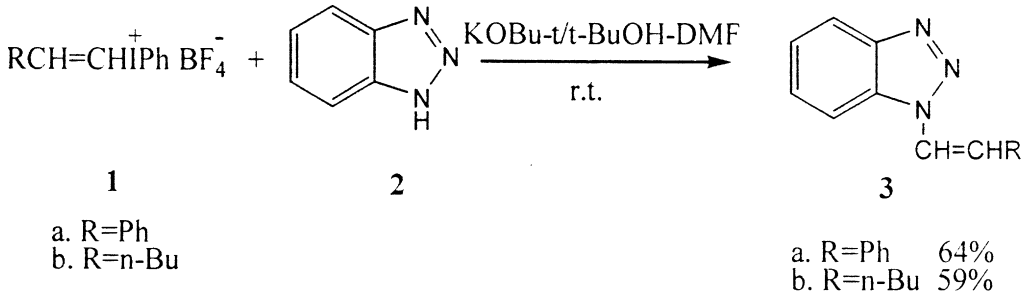
We report the preparation of 1-(1-alkenyl)benzotriazoles from alkenyl (phenyl)iodonium salts and benzotriazole. The reaction offers a simple and convenient route for the stereoselective synthesis of 1-(1-alkenyl)benzotriazoles. In addition, present method is particularly efficient for preparing 1-(1-alkenyl)benzotriazoles with amino-, acyl- and alkoxycarbonyl substituents, which were difficult to prepare by conventional methods.

Keywords: hypervalent iodine, 1-(1-alkenyl)benzotriazoles

1-(1-Alkenyl)benzotriazoles have been widely used in the preparation of pyrrolo[2,3-d]pyrimidines,[1] carbazoles[2,3] and indoles.[4-6] This versatility has also made them key intermediates in the synthesis of natural products.[7-9] There are several method for the synthesis of 1-(1-alkenyl)benzotriazoles. Previously the most general method for the preparation of 1-(1-alkenyl)benzotriazoles was developed by Rees and Torr[10] and involved the dehydrohalogenation of the product from the reaction of 1-chlorobenzotriazole and an olefin. But unfortunately, this mild and simple method always yielded a mixture of 1-(1-alkenyl)- and 2-(1-alkenyl)benzotriazoles, in which the latter predominated. Later, Marky *et al.*[11] developed an alternative method which involved the preparation of 1-allylbenzotriazoles by the alkylation of benzotriazole with allyl bromide and the subsequent base-catalysed isomerisation to 1-(1-alkenyl)benzotriazoles. The scope of this methodology was limited by the range of allyl halides available and furthermore the reaction leads to a mixture of *E*- and *Z*-isomers. The nucleophilic addition of benzotriazole anion to ethyl propiolate represents a further method for the synthesis of 1-(1-alkenyl)benzotriazoles.[6] A markedly improved method for the synthesis of 1-(1-alkenyl)benzotriazoles was reported by Katritzky *et al.*[12-14] It involved a Wittig reaction between the 1-(benzotriazolylmethyl)triphenylphosphonium chloride and a range of aldehydes. The stereoselectivity of this methodology(*trans* adduct isolated exclusivly) was offset by the modest yields obtained in all but one case. Finally the availability of 1-(1-alkenyl)benzotriazoles was extended considerably by the use of 1-(1-trimethylsilylalkyl)benzotriazoles in Peterson olefinations.[15] The synthesis of 1-(1-alkenyl)benzotriazoles is of current interest.[16,17] We now wish to report a simple and convenient method for the synthesis of 1-(1-alkenyl)benzotriazoles by the nucleophilic substitution reaction of benzotriazole anion and vinyl(phenyl)iodonium salts.

Recently our research interest is in the chemistry of hypervalent iodine compounds. Because of an excellent leaving group ability of a phenyliodonyl moiety, vinyl(phenyl)iodonium salts undergo nucleophilic vinyl substitutions under mild conditions, thus providing a useful route for the synthesis of various kinds of olefins.[18] In an extension of this investigation we have examined the reaction of vinyl(phenyl)iodonium salts with benzotriazole as a simple and convenient route for the stereoselective synthesis of 1-(1-alkenyl)benzotriazoles.

First, we selected (*E*)-(β-phenylvinyl)phenyliodonium tetrafluoroborate(**1a**)[19] and (*E*)-(β-n-butylvinyl)phenyliodonium tetrafluoroborate(**1b**)[19] as representatives of vinyl(phenyl)iodonium salts for investigating their reactivity with benzotriazole. We found that in the presence of potassium *tert*-butoxide the reaction of vinyl(phenyl)iodonium salts(**1**) with benzotriazole(**2**) readly occurred in *t*-BuOH-DMF at room temperature to afford the 1-(1-alkenyl)benzotriazoles(**3**) (Scheme 1).



Scheme 1

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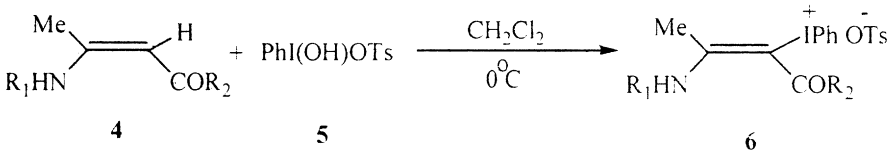
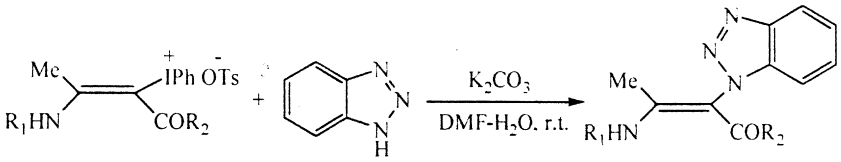
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*



4 5 6

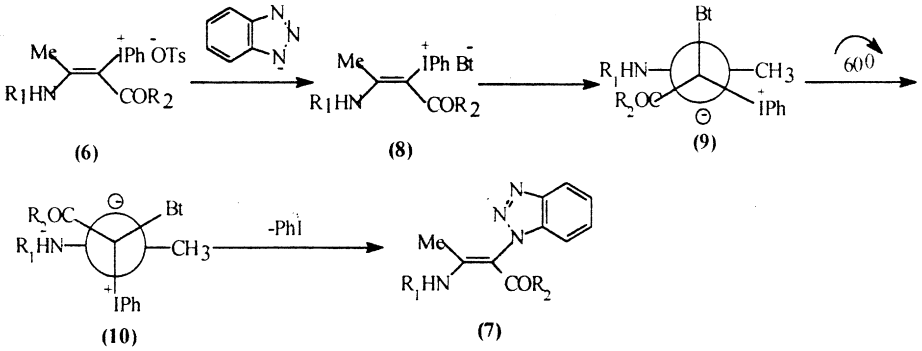
a: R_1=$PhCH_2$; R_2=OEt; yield. 60%
b: R_1=CH_3 ; R_2=OEt ; yield. 63%
c: R_1=p-ClC_6H_4; R_2=OEt ; yield.55%
d: R_1=$PhCH_2$; R_2=CH_3; yield.51%
e: R_1=$PhCH_2$; R_2=Ph ; yield. 68%
f: R_1=CH_3 ; R_2=CH_3 ; yield. 57%

Scheme 2



6 2 7

Scheme 3



(6) (8) (9) (10) (7)

Scheme 4

The products(**3**) were characterised by microanalyses, IR, ^{1}H NMR and MS.

It is known that the reaction of (*E*)-(β-phenylvinyl(phenyl)iodonium tetrafluoroborate(**1a**) with nucleophilic reagents is a stereospecific reaction and that retention of configurations is observed.[18] However, a different result with complete inversion of configuration was obtained for the reaction of (**1b**), probably via an S_N2 transition state.[20] Our result is consistent with previous reports.[20] The configuration of the products(**3**) were assigned using ^{1}H NMR spectroscopy: the vinylic protons of *E*-isomer showed a *J* value of 14.5Hz in contrast with 8.4Hz for those of the *Z*-isomer.[21]

Next, the applicability of this reaction to the fuctionalised vinyl(phenyl)iodonium salts was investigated. More recently, Papoutsis *et al.*[22] reported that the reaction of methyl 3-aminocrotonate with [hydroxy(tosyloxy)iodo]benzene at 0°C readily gave the stable tosylate of methyl *E*-2-phenyliodonio-3-aminocrotonate. Following this procedure, we prepared several fuctionalized vinyl(phenyl)iodonium salts(**6**) (Scheme 2).

Because of the ease of vinylic substitutions of amino substituted vinyl(phenyl)iodonium salts,[22] we found that the reaction of vinyl(phenyl)iodonium salts **6(a–f)** with benzotriazole(**2**) readily occurred in the presence of potassium carbonate. In fact, simple stirring of (**6**)with (**2**) and K_2CO_3 in DMF–H_2O at room temperature for 6 hours gave, after workup and isolation, the desired 1-(1-alkenyl)benzotriazoles(**7**) in good yields (Scheme 3). The results are summarised in the Table 1.

The products(**7**) were characterised by microanalyses, IR, ^{1}H NMR and MS.

In order to confirm the configuration of products(**7**), a single-crystal X-ray structure of product **7a** was determined as representative. This showed it is *E*-isomer (Fig. 1)

Table 1 Synthesis of 1-(1-alkenyl)benzotriazoles **7a–f**

Entry	R_1	R_2	Product	Yield/%
a	$PhCH_2$	EtO	(*E*)-**7a**	80
b	CH_3	EtO	(*E*)-**7b**	94
c	p-ClC_6H_4	EtO	(*E*)-**7c**	68
d	$PhCH_2$	CH_3	(*E*)-**7d**	73
e	$PhCH_2$	Ph	(*E*)-**7e**	87
f	CH_3	CH_3	(*E*)-**7f**	67

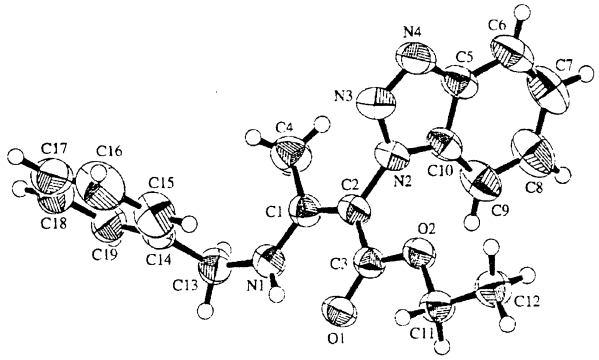


Fig.1 X-ray crystal structure for **7a**.

A multi-step addition-elimination mechanism, shown in Scheme 4, is compatible with the retention of stereochemistry in the nucleophilic vinylic substitutions of **6** with **2**. A β-benzylamino group of **6** makes it possible for a perpendicular attack of the benzotriazole anion to the π* orbital, which produces an α-benzylamino-stablised carbanion 9. The internal 60° rotation of **9**, followed by reductive elimination of the strongly electron-withdrawing supernucleofuge, the phenyliodonio group, would give 1-(1-alkenyl)benzotriazoles **7** steroselectively. Negative hyperconjugation between the supernucleofuge and the carbanionic electron pair in 9 accounts for the preference of the 60° rotation. Similarly, the presence of a β-phenyl substituent would facilitate the nucleophilic vinylic substitutions via a multi-step addition–elimination route, as was observed in the reaction of **1a**. Furthermore, the trisubstitution of the vinyl(phenyl)iodonium salts makes the S_N2 type transition state very difficult, because of the severe steric repulsion. Alternatively, ligand coupling on the iodine(III) of **8** will directly produce **7**.[25]

In conclusion, the preparation of 1-(1-alkenyl)benzotriazoles from alkenyl(phenyl)iodonium salts by the reaction with benzotriazole has been established. The reaction offers a simple and convenient route for the stereoselective synthesis of 1-(1-alkenyl)benzotriazoles. In addition, the present method is particularly efficient for preparing 1-(1-alkenyl)benzotriazoles with amino-, acyl- and alkoxycarbonyl substituents, which were difficult to prepare by conventional methods.

Experimental

Melting points. were measured on a X_4-Data microscope melting point apparatus and are uncorrected. Microanalyses were obtained using Carlo-Erba Ea-1100. IR spectra were recorded with a VECTOR spectrometer (Bruker). ^{1}H NMR spectra were recorded in $CDCl_3$ solution on a AVANCE DMX400 spectrometer (Bruker) at 400MHz and chemical shifts are reported in ppm downfield from tetramethylsilane. Mass spectra were obtained by electron impact at 70eV (HP5989B).

General procedure for the synthesis of **6:** Ph(OH)OTs (0.74g,2mmol) was added to a solution of 4-(benzylamino)pent-3-en-2-one (0.378g,2mmol) in CH_2Cl_2 (5ml) and the suspension was stirred for 1 hour under 0°C. The resulting solution was concentrated to half of its volume and the iodonium salt, *(E)-3-phenyliodonio-4-benzylaminopent-3-en-2-one tosylate* **(6d)** was precipitated upon the addition of diethyl ether, 0.575g(51%). M.p. 182–184°C; IR(KBr): 3200–3100cm^{-1}, 1665cm^{-1}, 1280cm^{-1}, 1180cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.12–8.20 (m,14H), 4.04(d,2H,*J*=6.0Hz), 3.36(s,3H), 2.51(s,3H), 2.30(s,3H); MS: 314(0.37), 204(3.38), 172(49.42), 155(4.26), 127(2.23), 106(100), 91(72.14), 77(27.18), 43(53.64); Anal. Calcd for $C_{25}H_{26}NO_4IS$: C,53.29; H,4.65; N,2.49. Found: C,53.56; H,4.38; N,2.75.

Ethyl E-2-phenyliodonio-3-benzylamino-crotonate tosylate **(6a):** M.p. 90–92°C(lit.[22] 90–92°C); IR(KBr): 3260–3100cm^{-1}, 1615cm^{-1}, 1285cm^{-1}, 1180cm^{-1}; ^{1}H NMR($CDCl_3$): δ 6.92–8.02 (m,15H), 4.54(q,2H,*J*=6.2Hz), 3.43(d,2H,*J*=7.2Hz), 4.06(d,2H,*J*=6.0Hz), 2.53(s,3H), 2.29(s,3H), 1.12(t,3H,*J*=6.0Hz); MS: 344(6.13), 234(45.34), 204(19.42), 155(58.98), 139(68.22), 127(8.12), 91(100), 77(38.35).

Ethyl E-2-phenyliodonio-3-methylamino-crotonate tosylate **(6b):** M.p. 108–110°C; IR(KBr): 3260–3100cm^{-1}, 1690cm^{-1}, 1225cm^{-1}, 1175cm^{-1}, 1060cm^{-1}; ^{1}H NMR($CDCl_3$): δ 6.90–7.85 (m,9H), 4.02(q,2H,*J*=6.2Hz), 3.43(d,3H,*J*=6.0Hz), 2.41(s,3H), 2.27(s,3H), 1.08(t,3H,*J*=6.2Hz); MS: 268(3.66), 234(3.53), 204(5.03), 172(33.01), 155(19.43), 139(58.26), 127(7.68), 91(100), 77(21.12); Anal. Calcd for $C_{20}H_{24}NO_5IS$: C,46.43; H,4.68; N,2.71. Found: C,46.05; H,4.36; N,2.43.

Ethyl E-2-phenyliodonio-3-(4-chlorobenzyl)amino-crotonate tosylate **(6c):** M.p. 178–180°C; IR(KBr): 3180–3100cm^{-1}, 1705cm^{-1}, 1300cm^{-1}, 1185cm^{-1}, 1065cm^{-1}; ^{1}H NMR($CDCl_3$): δ 6.92–7.11(m,2H), 7.28–7.59(m,11H), 3.88(q,2H,*J*=6.6Hz), 3.11(s,3H), 2.33(s,3H), 1.16(t,3H,*J*=6.6Hz); MS: 368(0.42), 236(0.46), 204(13.17), 172(24.01), 155(1.85), 127(100), 111(1.41), 113(0.49), 91(34.49), 77(5.95); Anal. Calcd for $C_{25}H_{25}ClNO_5IS$: C,48.91; H,4.10; N,2.28. Found: C,49.37; H,3.88; N,2.65.

(E)-2-phenyliodonio-3-benzylamino-1-phenylbut-2-en-1-one tosylate **(6e):** M.p. 199–201°C; IR(KBr): 3320–3210cm^{-1}, 1610cm^{-1}, 1320cm^{-1}, 1140cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.02–7.65 (m,19H), 4.60(d,2H,*J*=6.0Hz), 3.20(s,3H), 2.29(s,3H), 2.03(s,3H); MS: 376(0.47), 204(1.03), 172(2.13), 155(1.62), 127(2.40), 106(37.06), 105(38.60), 91(100), 77(33.59); Anal. Calcd for $C_{30}H_{28}NO_4IS$: C,57.60; H,4.51; N,2.24. Found: C,57.98; H,4.26; N,2.60.

(E)-3-phenyliodonio-4-methylaminopent-3-en-2-one tosylate **(6f):** M.p. 210–212°C; IR(KBr): 3320–3190cm^{-1}, 1670cm^{-1}, 1220cm^{-1}, 1120cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.13–7.90 (m,9H), 3.47(d,3H,*J*=6.0Hz), 2.45(s,3H), 2.23(s,3H); MS: 300(0.97), 204(3.66), 172(37.89), 155(5.88), 139(13.76), 127(1.52), 91(83.20), 77(18.25), 43(100); Anal. Calcd for $C_{24}H_{24}NO_4IS$: C,52.47; H,4.40; N,2.55. Found: C,52.81; H,4.78; N,2.86.

General procedure for the synthesis of **3a** *and* **3b:** To a solution of benzotriazole (0.19g,1 mmol) and BuOK(0.22g)/BuOH(5ml) in DMF(5ml) was added a solution of **1a** (0.394g,1mmol) in DMF(10ml), and the mixture was stirred for 24 hours at room temperature. Then water (40 ml) was added to the reaction mixture, and it was extracted with CH_2Cl_2 (10 ml×2). The extracts were dried (Na_2SO_4) and evaporated to dryness. The residue was purified by column chromatography on silica gel using a mixture of cyclohexane-ethyl acetate (4:1) as the eluent to give 0.14g (64%) of *(E)-1-(1-styryl)benzotriazole***(3a)** as a white powder. M.p. 113–115°C; IR(KBr): 3020cm^{-1}, 1656cm^{-1}, 1650cm^{-1}, 1647cm^{-1}, 1635cm^{-1}, 1255cm^{-1}, 740cm^{-1}; ^{1}H NMR($CDCl_3$): δ 8.92 (d,1H,*J*=14.5Hz), 8.54(d,1H,*J*=14.5Hz), 7.20–7.62 (m,9H); MS: 221 (M^+,34.31), 103(100); Anal. Calcd for $C_{14}H_{11}N_3$: C,76.00; H,5.01; N,18.99. Found: C,76.37; H,4.80; N,19.32.

*(Z)-1-(1-hexenyl)benzotriazole***(3b):** M.p. 83°C; IR(KBr): 3020cm^{-1}, 1684cm^{-1}, 1653cm^{-1}, 1647cm^{-1}, 1636cm^{-1}, 1457cm^{-1}, 1265 cm^{-1}, 940 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 8.04 (d,1H,*J*=8.4Hz), 7.88(d,1H,*J*=8.4Hz), 7.39–7.54 (m,4H), 2.98(t,2H), 2.62(m,4H), 1.25(t,3H); MS: 201 (M^+,18.10), 57(100); Anal. Calcd for $C_{12}H_{15}N_3$: C,71.61; H,7.51; N,20.88. Found: C,72.28; H,7.26; N,21.23.

General procedure for the synthesis of **7a–7f:** To a solution of benzotriazole (0.19g,1mmol) and K_2CO_3 (0.2g) in DMF(2ml)-H_2O(2ml) was added a solution of **6a** (0.593g,1mmol) in DMF(8ml)-H_2O(8ml), and the mixture was stirred for 6 hours at room temperature. Then waver (30 ml) was added to the reaction mixture, and it was extracted with Et_2O (10ml×2). The extracts were dried (Na_2SO_4) and evaporated to dryness. The residue was purified by column chromatography on silica gel using a mixture of cyclohexane–ethyl acetate (4:1) as the eluent to give 0.27g (80%) of *(E)-1-[1-ethoxycarbonyl-2-(N-benzylamino)-1-propenyl]benzotriazole***(7a)** as a white powder. M.p. 62–64°C; IR(KBr): 3200–3130cm^{-1}, 1655cm^{-1}, 1280 cm^{-1}, 1170 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.21–7.98 (m,9H), 4.50 (d,2H,*J*=5.7Hz), 3.95 (q,2H,*J*=7.1Hz), 1.56 (s,3H), 0.92 (t,3H,*J*=7.1Hz); ^{13}C NMR($CDCl_3$,100MHz): δ 167.31, 162.84, 145.46, 137.17, 135.53, 129.08, 127.89, 127.54, 126.94, 123.67, 119.85, 110.08, 94.34, 59.65, 47.50, 14.44, 14.22; MS: 336 (M^+,1.07), 291 (1.61), 279 (37.52), 155 (1.40), 118 (1.50), 105 (4.45), 91 (100), 57 (12.91), 43 (21.82); Anal. Calcd for $C_{19}H_{20}N_4O_2$: C,67.84; H,5.99; N,16.66. Found: C,67.48; H,5.96; N,17.03.

(E)-1-[1-ethoxycarbonyl-2-(N-methylamino)-1-propenyl]benzotriazole **(7b):** M.p. 76–78°C; IR(KBr): 3200–3100cm^{-1}, 1680cm^{-1}, 1225 cm^{-1}, 1110 cm^{-1}; 1H NMR($CDCl_3$): δ 7.10–8.00 (m,4H), 3.84 (q,2H,*J*=7.2Hz), 3.02 (d,3H,*J*=6.0Hz), 1.49 (s,3H), 0.91

(t,3H,*J*=7.2Hz); MS: 260 (M^+,1.17), 215 (2.76), 203 (23.12), 142 (7.80), 118 (5.76), 43(100); Anal. Calcd for $C_{13}H_{16}N_4O_2$: C,59.99; H,6.20; N,21.52. Found: C, 60.36; H,5.88; N,21.21.

(E)-1-[1-ethoxycarbonyl-2-(N-(4-chlorobenzyl)amino)-1-propenyl]benzotriazole **(7c):** M.p. 132–134°C; IR(KBr): 3180–3100cm^{-1}, 1640cm^{-1}, 1280 cm^{-1}, 1150 cm^{-1}; 1H NMR(CDCl3): d6.50–6.70 (m,2H), 6.90–7.10(m,2H), 7.45–7.80(m,4H), 3.85 (q,2H,*J*=7.2Hz), 2.75 (s,3H), 1.10 (t,3H,*J*=7.2Hz); MS: 358 (M^+,0.37), 356 (M^+,1.07), 313 (1.29), 311(3.87), 240 (1.76), 238(5.31), 125(19.30), 123(58.00), 118 (2.81), 76(100); Anal. Calcd for $C_{18}H_{17}ClN_4O_2$: C,60.58; H,4.80; N,15.73. Found: C,60.87; H,5.14; N,15.40.

(E)-1-[1-acetyl-2-(N-benzylamino)-1-propenyl]benzotriazole **(7d):** M.p. 76–78°C; IR(KBr): 3190–3100cm^{-1}, 1655cm^{-1}, 1280 cm^{-1}, 1130 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.20–7.80(m,9H), 4.32 (d,2H,*J*=6Hz), 2.33 (s,3H), 1.85 (s,3H); MS: 306 (M^+,0.82), 132(19.30), 123(18.43), 119 (1.51), 106(3.88), 91(100), 43(18.99); Anal. Calcd for $C_{18}H_{18}N_4O$: C,70.57; H,5.92; N,18.29. Found: C,70.27; H,5.83; N,17.96.

(E)-1-[1-benzoyl-2-(N-benzylamino)-1-propenyl]benzotriazole **(7e):** M.p. 124–126°C; IR(KBr): 3300–3200cm^{-1}, 1620cm^{-1}, 1280 cm^{-1}, 1190 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 11.46(br,1H), 6.83–7.30(m,14H), 4.50 (d,2H,*J*=5Hz), 2.23 (s,3H); MS: 354 (M^+,1.32), 119 (1.81), 105(100), 91(57.82); Anal. Calcd for $C_{22}H_{18}N_4O$: C,74.56; H,5.12; N,15.81. Found: C,74.88; H,4.81; N,16.25.

(E)-1-[1-acetyl-2-(N-methylamino)-1-propenyl]benzotriazole **(7f):** M.p. 96–98°C; IR(KBr): 3200–3100cm^{-1}, 1705cm^{-1}, 1250 cm^{-1}, 1120 cm^{-1}; ^{1}H NMR($CDCl_3$): δ 7.20–7.75(m,4H), 3.10 (d,3H,*J*=6Hz), 2.25 (s,3H), 2.05(s,3H); MS: 230 (M^+,2.13), 118 (3.85), 112(1.45), 43(100); Anal. Calcd for $C_{12}H_{14}N_4O$: C,62.16; H,6.13; N,24.33. Found: C,61.81; H,5.77; N,24.69.

X-Ray diffraction study: X-Ray structure determination of **7a** [$C_{19}H_{20}O_2N_4$]: Single crystals of compound **7a** were grown by slow evaporation of methanol. A crystal of size 0.20×0.20×0.30nm was used for data collection on an Rigaku AFC7R single crystal X-ray diffractometer using Mo–Kα radiation (λ=0.71069Å) and ω–2θ scan mode to a maximum θ range of 55.0°. M=336.39, monoclinic, space group *C*2/*c*, *a*=13.071(3), *b*=8.360(1), *c*=17.418(4) Å, β=109.01(2)0, *V*=1799.7(7) Å^3, *Z*=4, D_c=1.241g/cm^3.

The structure was solved by direct methods[23] and expanded using Fourier techniques[24]. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of fullmatrix least-squares refinement was based on 2395 observed reflections (I>2.50σ(I)) and 227 variable parameters and converged (largest parameter was 0.00 times esd) with unweighted and weighted agreement factors of:

$$R=\Sigma \| F_0 | - | F_c \| / \Sigma | F_0 | = 0.042$$

$$R_w=[\ \Sigma w(| F_0 | - | F_c |)^2 / \Sigma | F_0^2 |]^{1/2} = 0.051$$

The standard deviation of an observation of unit weight was 1.85. The weighting scheme was based on counting statistics and included a factor (P=0.030) to downweight the intense reflections. Plots of $\Sigma w(| F_0 | - | F_c |)^2$ versus $| F_0 |$, reflection order in data collection, sin θ/λ and various classes showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.15 and –0.15eÅ^{-3}, respectively.

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