SYNTHESIS OF *N*-(ARYLPROP-2-EN-1-YL)BENZOTRIAZOLES BY THE HECK REACTION

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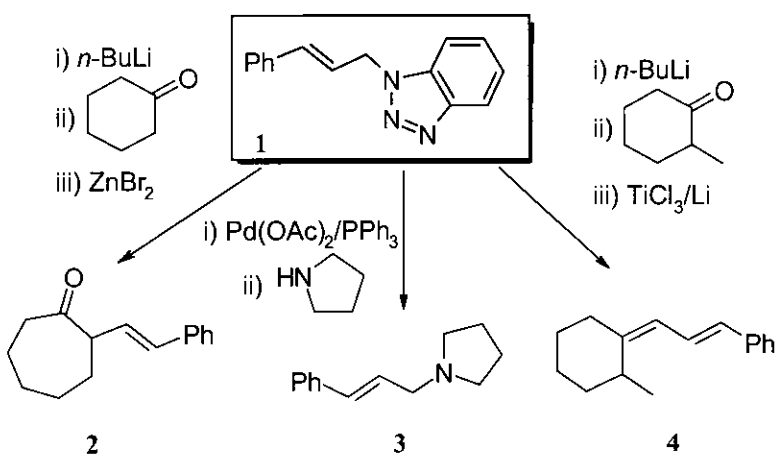
Abstract ___ Various substituted 1-prop-2-en-1-ylbenzotriazoles react with aryl halides under Heck reaction conditions to give the corresponding alkenylbenzotriazole derivatives (**10a-m**). These are useful synthons for the preparation of dienes, β,γ-unsaturated ketones, alcohols and amines.

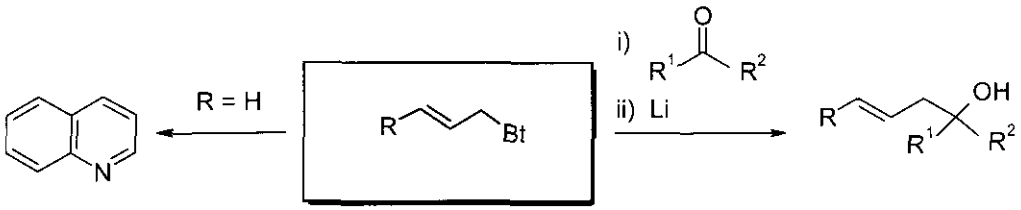
INTRODUCTION

N-Phenylprop-2-en-1-ylbenzotriazole (**1**) has recently been developed as a versatile organic synthon: **1** can be converted into (i) β,γ-unsaturated ketones (**2**) by deprotonation with butyllithium followed by treatment with a carbonyl compound and $ZnBr_2$,[1] (ii) dienes (**4**) by consecutive deprotonation, treatment with a carbonyl compound and reductive elimination of a benzotriazole group and a hydroxy group using low valent titanium catalysis,[2] or (iii) phenylprop-2-en-1-ylamines (**3**) by Pd catalyzed substitution of the benzotriazole moiety.[3]



Scheme 1 (in subsequent Schemes the benzotriazole residue is represented by "Bt")

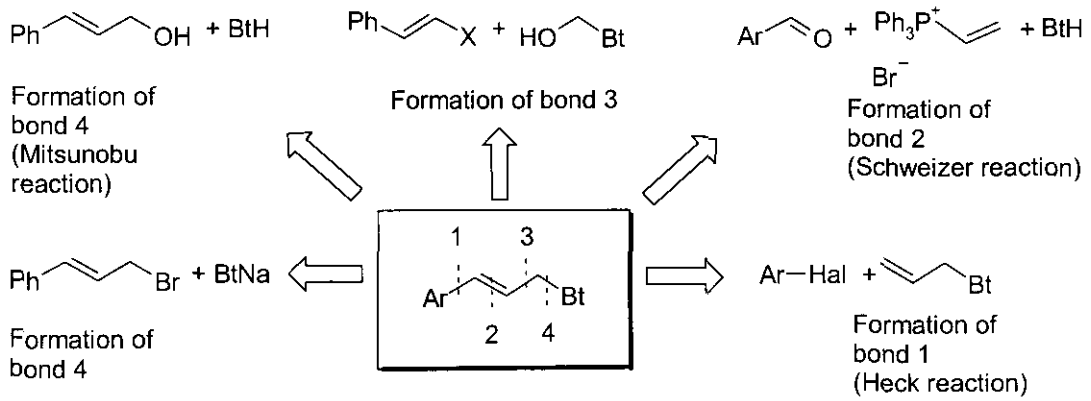
Known reactions of *N*-prop-2-en-1-ylbenzotriazoles (**5**), including conversion to quinolines (**6**)[4] by an extrusion of nitrogen from the benzotriazole moiety and synthesis of β,γ-unsaturated alcohols (**7**),[5,6] also represent further potential synthetic applications for *N*-phenylprop-2-en-1-ylbenzotriazoles (Scheme 2).



6 **5** **7**

Scheme 2

The present work was aimed at developing the synthesis of useful synthons (**1**). Possible routes to compound (**1**) are shown in Scheme 3. The formation of the C-N bond (bond 4, Scheme 3) is a familiar route; however, alkylations of sodium benzotriazole with substituted phenylprop-2-en-1-yl bromides[7] are limited by the accessibility of the corresponding phenylprop-2-en-1-yl halides and the formation of mixtures of benzotriazol-1-yl (Bt-1) and benzotriazol-2-yl (Bt-2) isomers. The preparation of *N*-phenylprop-2-en-1-ylbenzotriazole from phenylprop-2-en-1-yl alcohol by the Mitsunobu reaction[8] has similar limitations. The well-known synthesis of allylamines by the Schweizer method (formation of bond 2, Scheme 3) frequently forms mixtures of geometric isomers[9] and requires separation of triphenylphosphine oxide. Furthermore, this method, as well as the formation of bond 3 (Scheme 3) of phenylprop-2-en-1-yl derivatives starting from substituted styrene, formaldehyde and an amine,[10] has not previously been performed using benzotriazole as the amine component. The Heck reaction (formation of bond 1, Scheme 3), one of the most general methods to obtain aryl substituted olefins in good yields by Pd catalyzed coupling of olefins with aryl halides, could provide an additional general and versatile pathway to *N*-alkenylbenzotriazoles.[11-13]

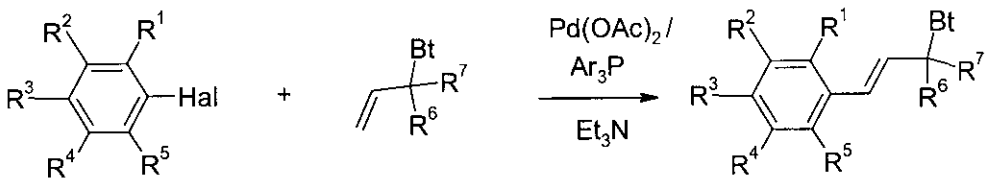


Scheme 3

RESULTS AND DISCUSSION

In continuation of our study on the synthetic utility of benzotriazole derivatives, we found that aryl halides couple with alkenylbenzotriazoles to afford the expected *E*-products in high yields. Thus iodoarenes (**8a-c**) coupled with *N*-prop-2-en-1-ylbenzotriazole derivatives (**9a-e**) in the presence of palladium acetate, triphenylphosphine and triethylamine to produce the corresponding new benzotriazole derivatives (**10a-g**) in high isolated yields (Scheme 4, Table 1). ^{1}H NMR and GC-MS spectra of the crude product indicated the presence of *trans* isomers only. Coupling of *N*-prop-2-en-1-ylbenzotriazole (**9a**) was successfully extended using catalysis by tris(*o*-tolyl)phosphine to various aromatic bromides, such as 1-bromo-4-methylnaphthalene (**8f**), 9-bromoanthracene (**8h**) and 9-bromophenanthrene (**8g**) (Scheme 4, Table 1) to give products (**10j-l**) in moderate yields. A higher ratio of phosphine to palladium acetate and longer reaction time were used in these cases.

The coupling reaction of *N*-prop-2-en-1-ylbenzotriazole (**9**) is applicable for aryl halides (**8**) with different R^3 substituents ($R^1 = R^2 = R^4 = R^5 = H$). Good preparative yields were obtained whether a methyl, methoxy or bromo substituent was present in the substrate (**8**). However, the utilization of arene (**8d**) with a strong electron-withdrawing cyano group required a longer reaction time and an additional amount of catalyst. An attempt to obtain (4-nitrophenyl)prop-2-en-1-ylbenzotriazole (**10i**) failed.

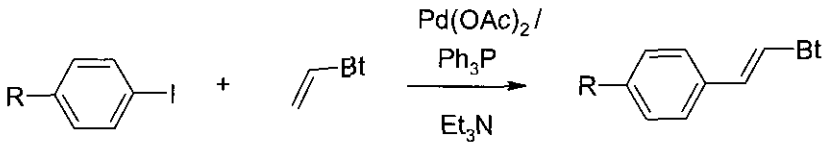


8 **9** **10**

Scheme 4

Reaction conditions for coupling *N*-prop-2-en-1-ylbenzotriazole (**9**) are more severe then those previously described for olefins: [see[11] for review] *e.g.* coupling **9a** with 4-iodotoluene (**8a**) required 20 hours compared to 5-5.5 hours for the reaction of allyl alcohols.[14] Our results are in accordance with a hypothesis that a neutral catalyst-aryl halide complex is formed during the reaction; such a complex would react faster with electron poor olefins containing a strong π-acceptor and poor σ-donor substituents.[15] A decrease in the reactivity of *N*-prop-2-en-1-ylbenzotriazole may be explained by the weaker activation effect of the benzotriazole moiety, which is separated from the olefin bond by the methylene group. For comparison, we investigated *N*-vinylbenzotriazole (**11**) in the Heck reaction. An

olefinic bond directly attached to the electron-withdrawing benzotriazole group is more reactive, so that **11** coupled with 4-iodoarenes (**8a,b**) at shorter reaction times to yield **12a,b** (Scheme 5).



8a,b **11** **12a,b**

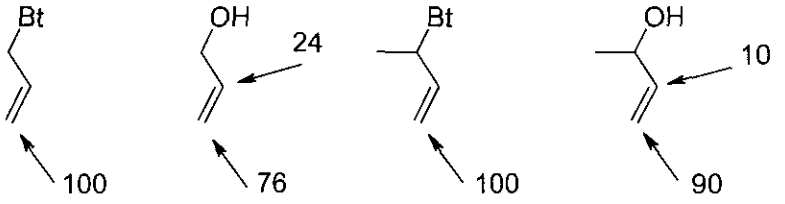
a: R = Me, **b:** R = OMe

Scheme 5

Table 1. Reaction conditions and yields of *N*-(3-arylprop-2-en-1-yl)benzotriazoles (**10**)

	8							9		Catalyst	Mol	Time,	Product	Yield,
	R^1	R^2	R^3	R^4	R^5	Hal		R^6	R^7		% : %	h	**10**	%
8a	H	H	Me	H	H	I	**9a**	H	H	$Pd(OAc)_2/Ph_3P$	1 : 2	20	**10a**	90
8b	H	H	OMe	H	H	I	**9a**	H	H	$Pd(OAc)_2/Ph_3P$	1 : 2	20	**10b**	94
8c	H	H	Br	H	H	I	**9a**	H	H	$Pd(OAc)_2$/ -	1 : 0	20	**10c**	81
8a	H	H	Me	H	H	I	**9b**	Me	H	$Pd(OAc)_2/Ph_3P$	1 : 2	20	**10d**	87
8a	H	H	Me	H	H	I	**9c**	Et	H	$Pd(OAc)_2/Ph_3P$	1 : 2	20	**10e**	83
8a	H	H	Me	H	H	I	**9d**	Bu	H	$Pd(OAc)_2/Ph_3P$	1 : 2	30	**10f**	76
8a	H	H	Me	H	H	I	**9e**	Bu	Bu	$Pd(OAc)_2/Ph_3P$	1 : 2	40	**10g**	70
8d	H	H	CN	H	H	Br	**9a**	H	H	$Pd(OAc)_2/(o\text{-tol})_3P$	2 : 4	72	**10h**	25
8e	H	H	NO_2	H	H	Br	**9a**	H	H	$Pd(OAc)_2/(o\text{-tol})_3P$	2 : 4	160	**10i**	0
8f	$-(CH)_4-$		Me	H	H	Br	**9a**	H	H	$Pd(OAc)_2/(o\text{-tol})_3P$	2 : 4	72	**10j**	45
8g	$-(CH)_4-$		$-(CH)_4-$		H	Br	**9a**	H	H	$Pd(OAc)_2/(o\text{-tol})_3P$	2 : 4	72	**10k**	46
8h	$-(CH)_4-$		H	$-(CH)_4-$		Br	**9a**	H	H	$Pd(OAc)_2/(o\text{-tol})_3P$	2 : 4	72	**10l**	51

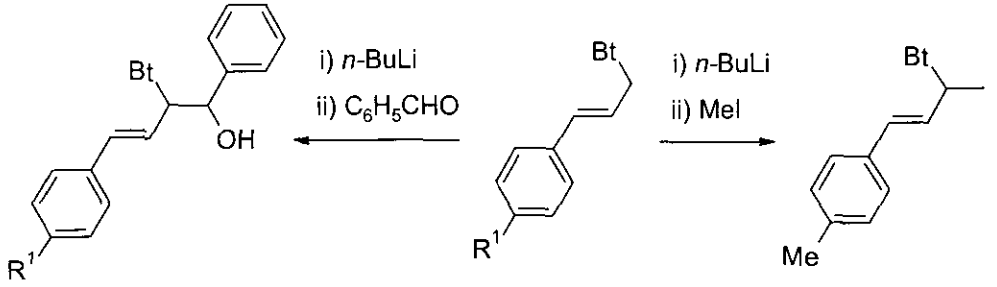
Unlike allylic tertiary amines[11] no double-bond migration was observed in the coupling products (**10**). In contrast to allyl alcohols,[11] for all cases starting from *N*-prop-2-en-1-ylbenzotriazoles (**9a-d**) we observed only the formation of the linear products (**10**), which are a result of coupling the aryl group with the less substituted carbon of the allyl fragment (Scheme 6). Substitution at the allylic carbon of the starting prop-2-en-1-ylbenzotriazole (**9**) did not affect the coupling reaction. Alkyl substituted compounds (**10d-g**) were obtained in good yields by coupling the corresponding prop-2-en-1-ylbenzotriazoles (**9b-e**) with 4-iodotoluene (**8a**); the 3-alkyl substituent did not change the regioselectivity of the coupling (Scheme 6). Exclusive terminal coupling was observed for **9b-e** in contrast to reports for similar allyl alcohols, for which the substitution with a methyl group leads to the formation of 10% internal coupling product.[15] Two *n*-butyl substituents slightly decreased the reactivity of compound (**9e**) in comparison with the less substituted compounds, so the reaction time in this case was twice as long as that for compounds (**9a-c**).



Regioselectivity of the coupling reaction of *N*-prop-2-en-1-ylbenzotriazoles compared with allyl alcohols[11]

Scheme 6

Substitution at the carbon α to the benzotriazole residue in products (**10d-g**) can also be achieved from **10a-c** by successive lithiation / treatment with electrophile, as was demonstrated for example (**10d**) (Scheme 7). The introduction of an electron-donor substituent in the *para*-position of the aromatic ring does not change the ability of compounds (**10**) to form the carbanion. Thus compounds (**13a,b**) were obtained in high yields by the sequential treatment of **10a,b** with *n*-BuLi and benzaldehyde (Scheme 7).

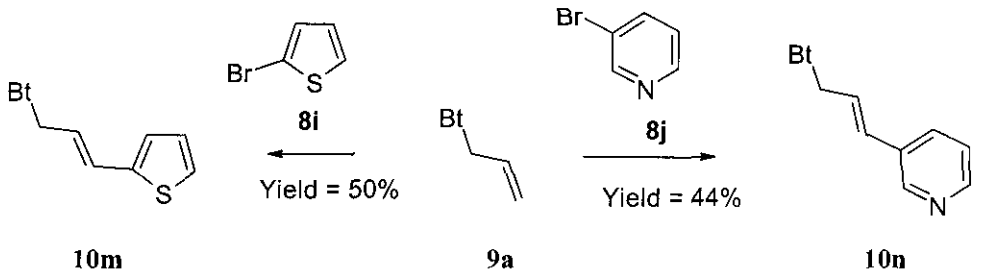


13a,b **10a,b** **10d**

a: R^1 = Me, **b:** R^1 = OMe

Scheme 7

Attempts to use electron-poor **8j** and electron-rich **8i** heteroaromatic bromides (Scheme 8) in the reaction with *N*-prop-2-en-1-ylbenzotriazole (**9a**) under standard conditions failed even after 160 hours of reflux in acetonitrile. Preparatively useful yields of compounds (**10m,n** (50% and 44%, respectively)) were achieved by heating in DMF at 100 °C for 72 hours in the presence of 2% (mol) palladium acetate[11] (Scheme 8).



Conditions: DMF, 100 °C, 72 h, $Pd(Ac)_2$ (2% mol), $(o\text{-}Tol)_3P$ (4% mol)

Scheme 8

CONCLUSIONS

We have utilized a Heck method for the arylation of alkenes to obtain diverse *N*-(3-arylprop-2-en-1-yl)benzotriazoles (**10a-m**) in moderate to good yields. This easy preparation of *N*-(3-arylprop-2-en-1-yl)benzotriazole synthons opens new synthetic possibilities.

EXPERIMENTAL

General. Melting points were determined on a Koefler hot stage apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively in $CDCl_3$ referenced to Me_4Si for the ^1H spectra and $CDCl_3$ for the ^{13}C spectra. Tetrahydrofuran (THF) was distilled under nitrogen from sodium-benzophenone immediately before use. All reactions with moisture-sensitive compounds were carried out in a dry nitrogen atmosphere. *N*-Prop-2-en-1-ylbenzotriazoles (**9a-e**) were prepared according to previously reported procedures.[6,7] Aryl halides (**8a-j**) were used as obtained from commercial sources.

General Procedure for the Synthesis of Arylalkenylbenzotriazoles (10a-l): A mixture of aryl halide (**8**) (10 mmol), alkenylbenzotriazole (**9**) (12.5 mmol), palladium acetate (0.1-0.2 mmol) (see Table 1), triphenylphosphine (0.2-0.4 mmol) (see Table 1), triethylamine (5 mL) and acetonitrile (4 mL) was

introduced to a heavy-walled pyrex tube. The tube was flushed with argon, capped and heated at 110 °C for 20 h. On cooling, the mixture was poured onto ether (300 mL) and stirred. The precipitate (triethylammonium iodide and metallic Pd) was filtered off and washed with ether (3 x 10 mL). The combined organic solution was evaporated *in vacuo* and the residue was crystallized from ether/hexane (1:3) or purified by column chromatography on silica gel using hexane/ethyl acetate (3:1) as eluent. No triphenylphosphine was used in the synthesis of **10c**.

1-[(*E*)-3-(4-Methylphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10a**): Yield 2.39 g (90%), mp 80-81 °C. ^{1}H-NMR δ: 8.04 (d, *J* = 8.2 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 7.2 Hz, *J* = 8.2 Hz, 1H), 7.31 (dd, *J* = 7.2 Hz, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.29 (dt, *J* = 15.8 Hz, *J* = 6.0 Hz, 1H), 5.36 (d, *J* = 6.0 Hz, 2H), 2.28 (s, 3H). ^{13}C-NMR δ: 146.0, 138.1, 134.1, 132.7, 132.6, 129.1 (2C), 127.1, 126.3 (2C), 123.7, 120.9, 119.7, 109.6, 50.4, 21.0. *Anal.* Calcd for $C_{16}H_{15}N_3$: C, 77.07; H, 6.08; N, 16.86. Found: C, 77.39; H, 6.25; N, 17.11.

1-[(*E*)-3-(4-Methoxyphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10b**): Yield 2.50 g (94%), mp 89-90 °C. ^{1}H-NMR δ: 8.05 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.48-7.28 (m, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.27 (dt, *J* = 15.9 Hz, *J* = 6.3 Hz, 1H), 5.36 (d, *J* = 6.3 Hz, 2H), 3.74 (3H, s). ^{13}C-NMR δ: 159.5, 146.0, 133.7, 132.7, 128.1, 127.7 (2C), 127.1, 123.7, 119.7, 119.6, 113.8 (2C), 109.7, 55.0, 50.5. *Anal.* Calcd for $C_{16}H_{15}N_3O$: C, 72.43; H, 5.71; N, 15.84. Found: C, 72.00; H, 5.75; N, 15.87.

1-[(*E*)-3-(4-Bromophenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10c**): Yield 2.55 g (81%), mp 115-116 °C. ^{1}H-NMR δ: 8.08 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 7.50 - 7.30 (m, 4H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 16.0 Hz, 1H), 6.38 (dt, *J* = 15.9 Hz, *J* = 6 Hz, 1H), 5.42 (d, *J* = 6.0 Hz, 2H). ^{13}C-NMR δ: 146.2, 134.5, 133.0, 132.8, 131.7 (2C), 128.1 (2C), 127.4, 123.9, 123.0, 122.2, 120.0, 109.5, 50.2. *Anal.* Calcd for $C_{15}H_{12}N_3Br$: C, 57.34; H, 3.86; N, 13.38. Found: C, 56.97; H, 4.08; N 13.21.

1-[(*E*)-1-Methyl-3-(4-methylphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10d**): Yield 2.3 g (87%), mp 80-81 °C. ^{1}H-NMR δ: 8.06 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.45 - 7.27 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.63 - 6.38 (m, 2H), 5.75 - 5.55 (m, 1H), 2.29 (s, 3H), 1.93 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR δ: 146.2, 137.9, 132.7, 132.0, 131.9, 129.1 (2C), 126.8, 126.7, 126.3 (2C), 123.6, 119.8, 110.1, 57.3, 21.0, 20.0. *Anal.* Calcd for $C_{17}H_{17}N_3$: C, 77.53; H, 6.52; N, 15.96. Found: C, 77.44; H, 6.89; N, 16.12.

1-[(*E*)-1-Ethyl-3-(4-methylphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10e**): Yield 2.30 g (83%), oil. ^{1}H-NMR δ: 8.07 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.41 (dd, *J* = 7.1 Hz, *J* = 8.2 Hz, 1H), 7.34 (dd, *J* = 7.1 Hz, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.60 - 6.40 (m, 2H),

5.38 (m, 1H), 2.50 - 2.20 (m, 2H), 2.28 (s, 3H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C-NMR δ: 146.1, 137.9, 132.8, 132.7, 132.3, 129.1 (2C), 126.9, 126.3 (2C), 125.6, 123.7, 119.8, 109.9, 63.7, 27.5, 21.0, 10.6. *Anal.* Calcd for $C_{18}H_{19}N_3$: C, 77.94; H, 6.92. Found: C, 77.67; H, 7.05.

1-[(*E*)-1-Butyl-3-(4-methylphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10f**)**:** Yield 2.32 g (76%), oil. ^{1}H-NMR δ: 8.07 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.50-6.90 (m, 6H), 6.63-6.42 (m, 2H), 5.55-5.40 (m, 1H), 2.50-2.30 (m, 2H), 2.28 (s, 3H), 1.55-1.10 (m, 4H), 0.84 (t, J = 7.9 Hz, 3H). ^{13}C-NMR δ: 146.0, 137.8, 132.8, 132.5, 132.2, 129.1 (2C), 126.8, 126.3 (2C), 125.9, 123.6, 119.8, 109.9, 62.1, 33.8, 28.0, 22.0, 20.9, 13.6. HRMS: Calcd for $C_{20}H_{24}N_3$: 306.1970 (M+1). Found: 306.1966.

1-[(*E*)-1,1-Dibutyl-3-(4-methylphenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10g**)**:** Yield 2.53 g (70%), oil. ^{1}H-NMR δ: 8.11-8.02 (m, 1H), 7.65-7.54 (m, 1H), 7.43-7.22 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 6.59-6.44 (m, 2H), 2.55-2.25 (m, 4H), 2.35 (s, 3H), 1.45-1.20 (m, 8H), 0.83 (t, J = 6.9 Hz, 6H). ^{13}C-NMR δ: 146.8, 140.5, 138.1, 133.4, 132.6, 131.1, 130.5, 129.4 (2C), 126.5 (3C), 123.4, 120.0, 112.5, 69.0, 37.0 (2C), 25.5 (2C), 22.8 (2C), 13.9 (2C). HRMS: Calcd for $C_{24}H_{32}N_3$: 362.2596 (M+1). Found: 362.2595.

4-[(*E*)-3-(1*H*-1,2,3-Benzotriazol-1-yl)-1-propenyl]benzonitrile (**10h**)**:** Yield 0.65 g (25%), mp 149-150 °C. ^{1}H-NMR δ: 8.08 (d, J = 8.2 Hz, 1H), 7.65-7.30 (m, 7H), 6.70-6.45 (m, 2H), 5.48 (d, J = 4.7 Hz, 2H). ^{13}C-NMR δ: 146.0, 139.9, 132.7, 132.3 (2C), 132.2, 127.5, 127.0 (2C), 126.2, 124.0, 120.0, 118.5, 111.4, 109.3, 49.8. *Anal.* Calcd for $C_{16}H_{12}N_4$: C, 73.82; H, 4.66; N, 21.53. Found: C, 73.64; H, 4.86; N, 21.64.

1-[(*E*)-3-(4-Nitrophenyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10i**)**:** only starting material was isolated by the general procedure after 160 h.

1-[(*E*)-3-(4-Methyl-1-naphthyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10j**)**:** Yield 1.35 g (45%), mp 120-121.5 °C. ^{1}H-NMR δ: 8.09 (d, J = 8.3 Hz, 1H), 8.05-7.92 (m, 2H), 7.62 (d, J = 8.2 Hz, 1H), 7.55-7.30 (m, 5H), 7.23 (d, J = 6.9 Hz, 1H), 6.37 (dt, J = 6.1 Hz, J = 15.4 Hz, 1H), 5.52 (d, J = 6.1 Hz, 2H), 2.65 (s, 3H). ^{13}C-NMR δ: 146.3, 135.1, 132.9, 132.5, 132.0, 131.6, 131.0, 127.3, 126.4, 125.9, 125.7, 124.7, 124.5, 123.9(2C), 120.1, 109.7, 50.8, 19.5 (one signal is missing). *Anal.* Calcd for $C_{20}H_{17}N_3$: C, 80.23; H, 5.74 N, 14.04. Found: C, 80.16; H, 5.76; N, 14.33.

1-[(*E*)-3-(9-Phenanthryl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10k**)**:** Yield 1.54 g (46%), mp 165-166.5 °C. ^{1}H-NMR δ: 8.67 (d, J = 7.7 Hz, 1H), 8.60 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.73 (s, 1H), 7.70-7.20 (m, 8H), 6.48 (m, 1H), 5.54 (d, J = 6.0 Hz, 2H). ^{13}C-NMR δ: 146.3, 133.0, 132.3, 131.4, 130.3 (3C), 130.1, 128.7,127.5, 126.8 (2C), 126.7, 126.6, 125.7, 125.3, 124.3, 124.0, 123.1, 122.5, 120.1, 109.7, 50.6. HRMS: Calcd for $C_{23}H_{18}N_3$: 336.1501 (M+1). Found: 336.1463.

1-[(*E*)-3-(9-Anthryl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10l**): Yield 1.70 g (51%), mp 135-136 °C. ^{1}H-NMR δ: 8.33 (s, 1H), 8.20-8.03 (m, 3H), 8.03-7.89 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.36-7.30 (m, 5H), 7.28 (d, *J* = 16.2 Hz, 1H), 6.25 (dt, *J* = 5.2 Hz, *J* = 16.2 Hz, 1H), 5.65 (d, *J* = 5.2 Hz, 2H). ^{13}C-NMR δ: 146.1, 132.8, 131.0 (2C), 130.6, 130.5, 130.3, 129.1 (2C), 128.5 (2C), 127.4, 126.8, 125.6 (2C), 125.2 (2C), 125.0 (2C), 123.9, 120.0, 109.4, 50.2. *Anal.* Calcd for $C_{23}H_{17}N_3$: C, 82.36; H, 5.12; N, 12.53. Found: C, 82.13; H, 5.15; N, 12.63.

Preparation of 1-[(*E*)-2-(4-methylphenyl)ethenyl]-1*H*-1,2,3-benzotriazole (12a): Obtained by the general procedure for the preparation of **10a-l**, except that the mixture was heated for 12 h instead of 20h. Yield 2.02 g (86%), mp 148-149 °C (from ether/hexane 1:3). ^{1}H-NMR δ: 8.10 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 14.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.57 (dd, *J* = 7.1 Hz, *J* = 8.3 Hz, 1H), 7.49-7.36 (m, 4H), 7.28-7.16 (m, 2H), 2.38 (s, 3H). ^{13}C-NMR δ: 146.3, 138.5, 131.4, 129.7 (2C), 128.1, 126.5 (2C), 124.5, 121.2, 121.0, 120.3, 110.1, 21.3. *Anal.* Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.58; N, 17.86. Found: C, 76.32; H, 5.68; N, 17.98.

Preparation of 1-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1*H*-1,2,3-benzotriazole (12b): Obtained by the general procedure for the preparation of **10a-l**, except that the mixture was heated for 12 h instead of 20h, as a mixture with approximately 5-10% of the Bt-2 isomer. Yield 2.19 g (87%). ^{1}H-NMR (Bt-1 isomer) δ: 8.09 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 14.5 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.56 (dd, *J* = 7.2 Hz, *J* = 8.3 Hz, 1H), 7.49-7.34 (m, 4H), 7.00-6.83 (m, 2H), 3.84 (s, 3H). ^{13}C-NMR δ: 159.9, 146.2, 131.6, 130.4, 128.0, 127.8 (2C), 127.3, 124.5, 121.1, 120.3, 114.4 (2C), 110.0, 55.3. *Anal.* Calcd for $C_{15}H_{13}N_3O$: C, 71.69; H, 5.23; N, 16.73. Found: C, 72.05; H, 5.37; N, 16.42.

General Procedure for the Synthesis of Hetarylalkenylbenzotriazoles (10m,n): A mixture of hetaryl bromide (10 mmol), 1-prop-2-en-1-ylbenzotriazole (2.06 g, 13 mmol), triethylamine (5.0 mL, 36 mmol), palladium (II) acetate (0.045 g, 0.2 mmol), tris(*o*-tolyl)phosphine (0.122 g, 0.4 mmol) and DMF (10 mL) was prepared in a heavy-walled *pyrex* tube. The tube was flushed with argon, capped and heated at 100 °C for 72 h. To the cooled mixture was added water (100 mL) and ether (50 mL). The water layer was extracted with ether (2 x 50 mL), and the combined ether solution was washed with water, dried over magnesium sulfate and evaporated. The oily residue solidified overnight. The product was washed with cold ether (3 x 10 mL) and dried under vacuum to give pale-yellow plates.

1-[(*E*)-3-(2-Thienyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10m**): Yield 1.21 g (50%), mp 77-78.5 °C (from ether/hexane 1:3). ^{1}H-NMR δ: 8.08 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.47 (dd, *J* = 7.6 Hz, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 7.6 Hz, *J* = 8.2 Hz, 1H), 7.17 (d, *J* = 4.5 Hz, 1H), 7.00-6.85 (m, 2H), 6.77 (d, *J* = 15.7 Hz, 1H), 6.22 (dt, *J* = 6.3 Hz, *J* = 15.7 Hz, 1H), 5.40 (d, *J* = 6.3 Hz, 2H). ^{13}C-NMR δ:

146.2, 140.4, 132.8, 127.4 (3C), 126.8, 125.2, 123.9, 121.4, 120.0, 109.6, 50.2. *Anal.* Calcd for $C_{13}H_{11}N_3S$: C, 64.70; H, 4.60; N, 17.42. Found: C, 64.55; H, 4.49; N, 17.51.

1-[(*E*)-3-(4-Pyridinyl)prop-2-en-1-yl]-1*H*-1,2,3-benzotriazole (**10n**): The yield 1.05 g (44%), mp 87-89 °C (from ether/hexane 1:3). ^{1}H-NMR δ: 8.58 (s, 1H), 8.53-8.43 (m, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.49 (dt, J = 7.1 Hz, J = 7.7 Hz, 1H), 7.39 (dd, J = 7.4 Hz, J = 7.5 Hz, 1H), 7.25-7.18 (m, 1H), 6.63 (d, J = 16.2 Hz, 1H), 6.49 (dt, J = 5.5 Hz, J = 16.2 Hz, 1H), 5.47 (d, J = 5.5 Hz, 2H). ^{13}C-NMR δ: 149.3, 148.4, 146.2, 133.0, 132.8, 131.2, 130.6, 127.5, 124.6, 124.0, 123.4, 120.1, 109.4, 50.1. *Anal.* Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.13; N, 23.72. Found: C, 70.94; H, 5.14; N, 23.77.

General Procedure for the Reaction of the Anions of 10a,b with Electrophiles: *n*-Butyllithium (3.8 mL, 5.5 mmol, 1.45 M solution in hexanes) was added to a solution of **10a,b** (5 mmol) in THF (40 mL) under argon at -78 °C, and the solution was stirred at this temperature for 1 h. Electrophile (5 mmol) in THF (10 mL) was added, and the mixture was stirred overnight. The reaction was quenched with a saturated ammonium chloride solution (20 mL). The organic layer was separated, and the aqueous one was extracted with ethyl acetate (3 x 15 mL). The combined organic extracts were dried over magnesium sulfate and filtered. The solvent was evaporated *in vacuo*, and the residue was crystallized. Yield of **12a,b** given for the mixture of diastereomers obtained in a 1:1 ratio. Analytical data given for diastereomer crystallized from diethyl ether.

1-[(E)-1-Methyl-3-(4-methylphenyl)prop-2-en-1-yl]-1H-1,2,3-benzotriazole (**10d**): Yield 1.01 g (77%), mp 80-81 °C (from ether/hexane 1:3). ^{1}H-NMR and ^{13}C-NMR spectra are identical with a sample obtained by the Heck method described above.

2-(Benzotriazol-1-yl)-1-phenyl-4-(4-methylphenyl)-3-buten-1-ol (**13a**): Yield 1.45 g (82% for two diastereomers), mp 123-125 °C (one diastereomer, from ether). ^{1}H-NMR δ: 7.98 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.47-7.18 (m, 7H), 7.09 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.40 (dd, J = 7.2 Hz, J = 16.0 Hz, 1H), 6.22 (d, J = 16.0 Hz, 1H), 5.66-5.50 (m, 2H), 3.66 (d, J = 4.6 Hz, OH), 2.28 (s, 3H). ^{13}C-NMR δ: 145.9, 139.9, 138.3, 134.6, 133.5, 132.8, 129.2 (2C), 128.5 (2C), 128.4, 127.4, 126.7 (2C), 126.5 (2C), 124.1, 122.5, 119.8, 110.0, 76.2, 68.0, 21.2. *Anal.* Calcd for $C_{23}H_{21}N_3O$: C, 77.71; H, 5.97; N, 11.82. Found: C, 77.36; H, 5.99; N, 12.01.

2-(Benzotriazol-1-yl)-1-phenyl-4-(4-methoxyphenyl)-3-buten-1-ol (**13b**): Yield 1.52 g (80% for two diastereomers), mp 122-124 °C (one diastereomer, from ether). ^{1}H-NMR δ: 7.94 (d, J = 8.3 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.46-7.20 (m, 7H), 7.12 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.33 (dd, J = 7.1

Hz, J = 15.9 Hz, 1H), 6.19 (d, J = 15.9 Hz, 1H), 5.66-5.50 (m, 2H), 3.84 (d, J = 4.7 Hz, OH), 3.74 (s, 3H). ^{13}C-NMR δ: 159.7, 145.5, 140.0, 134.1, 133.5, 128.5 (2C), 128.3, 127.8 (2C), 127.4, 126.7 (2C), 124.1, 121.3, 119.7, 113.9 (2C), 110.1, 76.2, 68.1, 55.2. *Anal.* Calcd for $C_{23}H_{21}N_3O_2$: C, 74.37; H, 5.71; N, 11.32. Found: C, 74.45; H, 5.92; N, 11.37.

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REFERENCES

1. A. R. Katritzky, D. Toader, and L. Xie, *J. Org. Chem.*, 1996, **61**, 7571.
2. A. R. Katritzky and J. Li, *J. Org. Chem.*, 1997, **62**, 238.
3. A. R. Katritzky, J. Yao, and M. Qi, *J. Org. Chem.*, 1998, **63**, 5232.
4. S. J. Barker, G. B. Jones, K. R. Randles, and R. C. Storr, *Tetrahedron Lett.*, 1988, **29**, 953.
5. A. R. Katritzky and M. Qi, *J. Org. Chem.*, 1997, **62**, 4116.
6. A. R. Katritzky, C. N. Fali, and M. Qi, *Tetrahedron Lett.*, 1998, **39**, 363.
7. A. R. Katritzky, J. Li, and N. Malhotra, *Liebigs Ann. Chem.*, 1992, 843.
8. A. R. Katritzky, D. C. Oniciu, and I. Ghiviriga, *Synth. Comm.*, 1997, **27**, 1613.
9. A. I. Meyers, J. P. Lawson, and D. R. Carver, *J. Org. Chem.*, 1981, **46**, 3119.
10. N. A. Petasis and I. Akritopoulou, *Tetrahedron Lett.*, 1993, **34**, 583.
11. R. F. Heck, *Org. React.*, 1982, **27**, 345.
12. A. de Meijere and F. E. Meyer, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2379.
13. R. F. Heck, *Acc. Chem. Res.*, 1979, **12**, 146.
14. J. B. Melpolder and R. F. Heck, *J. Org. Chem.*, 1976, **41**, 265.
15. W. Cabri and I. Candiani, *Acc. Chem. Res.*, 1995, **28**, 2.

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