Syntheses and reactions of α -benzotriazolylenamines: stable analogs of α -Chloroenamines

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Abstract

Synthetic routes to and utility of α-benzotriazolylenamines have been explored. α-Benzotriazolylenamines 3a-g, 4a-f and 5a,b were successfully synthesized (i) from *N*-(*trans*-buten-1-yl)-*N*-methylaniline (2) by reaction with 1-chloro-1*H*-1,2,3-benzotriazole, followed by base induced elimination of HCl and (ii) from amides 1a-g using benzotriazole, $POCl_3$ and NEt_3 in CH_3CN. The utility of 3a-g, 4a-f and 5a,b as stable alternatives to α-haloenamines was demonstrated by the successful reaction of *N*-[1-(2*H*-1,2,3-benzotriazol-2-yl)-2-methylprop-1-enyl]-*N*-methylaniline (5a) with phenylethynylzinc chloride to form *N*-methyl-*N*-[2-methyl-1-(2-phenylethynyl)-1-propenyl]aniline (7).

Keywords: α -Chloroenamines, α -benzotriazolylenamines, nucleophilic substitution, phenylethynylzinc chloride

Introduction

The chemistry of α-haloenamines has been investigated extensively since their initial discovery 70 years ago.[1] They are highly effective reagents for replacing an OH moiety with a halogen under mild conditions.[2a,b,c] α-Haloenamines have been utilized as coupling reagents[3a,b] and as precursors for α-aminovinyl Grignard reagents.[4a,b] Furthermore, they are versatile synthetic intermediates in the preparation of functionalized amides,[5a,b] enamines,[5a] 2-amino-1-azirines,[6] cyclobutenones,[7] cyclobutanones,[8] azetidinones[9] and numerous other classes of compounds.[10] Although the synthesis of α-haloenamines is reasonably easy, these compounds, especially α-

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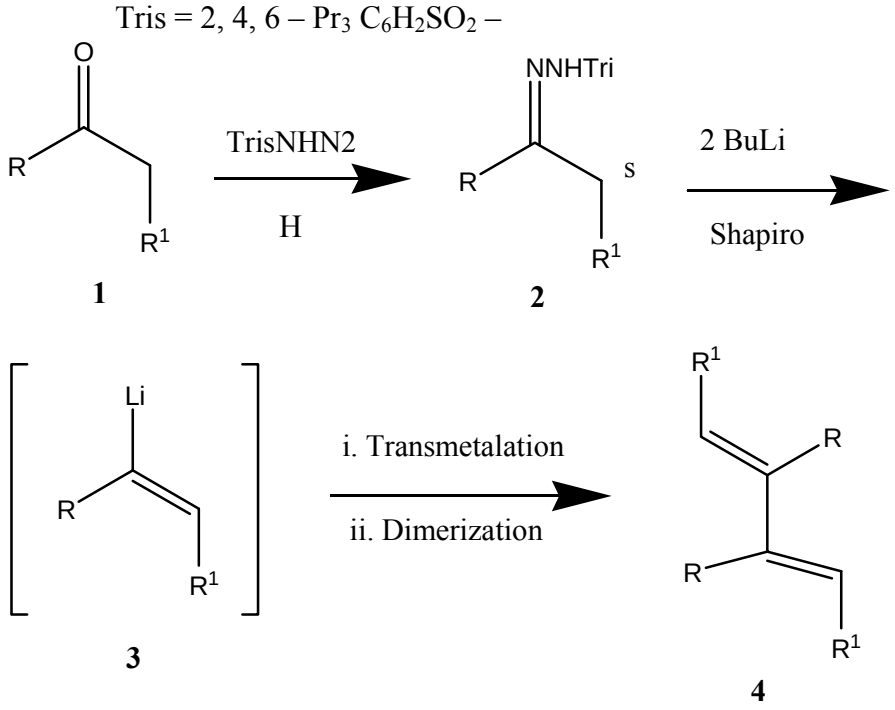
haloenamines with only one substituent at the 2-position, are unstable and require special handling and conditions for storage.[11]

Recently, α-triflyloxyenamines have been successfully synthesized and used in further transformations.[12a-d] Thus, there is an interest in enamines with leaving groups other than halogen in the α–position. The benzotriazolyl (Bt) moiety can behave similarly to halogen substituents, but benzotriazolyl derivatives are typically more stable and less reactive than their halogen analogs.[13] *N*-(α-Aminoalkyl)benzotriazoles are well-recognized synthetic intermediates that have been used in further reactions with nucleophiles.[14] In this context, our attention was drawn to the potential of α-benzotriazolylenamines.

Two previous publications from our group[15a,b] each describe a single example of α-benzotriazolylenamines (Scheme 1), but their chemistry was not further explored. In connection with the preparation of imidoylbenzotriazoles from aliphatic carboxylic acids,[15a] we previously showed that the action of BtH (4 equiv), $POCl_3$ (2 equiv) and NEt_3 (2 equiv) on benzamide at 0 °C gave benzonitrile in 87% yield. Under the same conditions, *N*-methyl-*N*-phenyloctanamide (1h) gave *N*-[1-(1*H*-1,2,3-benzotriazol-1-yl)-1-octenyl]-*N*-methylaniline (3h) in 70% yield. 1-(1*H*-1,2,3-Benzotriazol-1-yl)morpholino-2-methylpropene (3i) was synthesized in 37% yield from the sequential treatment of 1-morpholino-2-methyl-1-propene (2a) with 1-chloro-1*H*-1,2,3-benzotriazole and *tert*-BuOK at low temperature.[15b] The present study further explores the scope and limitations of α-benzotriazolylenamines as stable analogs of α-haloenamines.



Scheme 1

Results and Discussion

Preparation of Amides 1a-g. Amides 1a-g were synthesized in good to excellent yields by a procedure similar to the reaction reported by Human and Mills.[16] An attempt to make the amide from octanoic acid and carbazole failed, possibly due to the poor solubility of carbazole in the solvent system used.

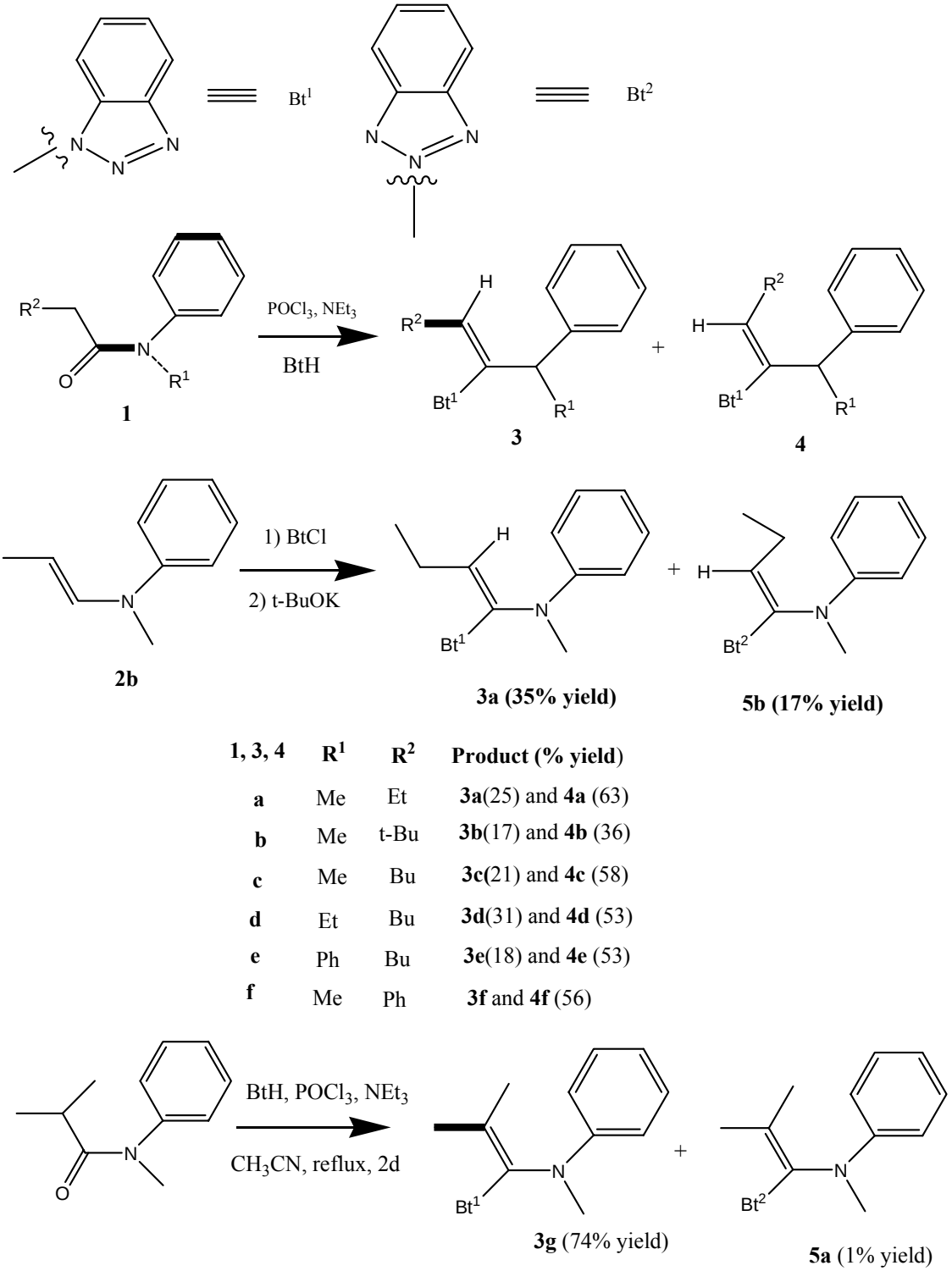
Table 1. Physical Properties for Compounds 1a-g

Entry	Literature mp or bp	Observed	Reference
1a	141-142 °C/17 mm	102-105 °C/2.1 mm	17a
1b	-	128-132 °C/2.0 mm	17b
1c	-	136-140 /2.0 mm	17c
1f	127-128 °C/0.3 mm	146-149 °C/2.0 mm	17d
1g	79 °C	81 °C	17e

Amides 1a,b,c,f,g[17a-e](Table 1) have been previously described; their proton and carbon-13 NMR spectra and boiling and melting points were consistent with those reported in the literature and with the proposed structure. *N*-Ethyl-*N*-phenylhexanamide (1d) and *N*,*N*-diphenylhexanamide (1e) gave satisfactory elemental analyses and NMR spectra.

Preparation of enamine 2b. Syntheses of enamines formally derived from an aliphatic aldehyde unbranched in the 2-position and an *N*-alkylaniline are rare (for reviews on enamines see[18a,b]). Elimination of dimethylammonium bromide, as used in the synthesis of *N*-methyl-*N*-vinylaniline from trimethyl-[(2-(*N*-methylanilino)ethyl]ammonium bromide,[19] is limited by the isomerization which converts *N*-allyl-*N*-methylaniline into *N*-methyl-*N*-(1-propenyl)aniline.[20] We synthesized enamine 2b by the reaction of BtH, butyraldehyde (1 equiv) and *N*-methylaniline (1 equiv).[21]

Preparation of α-benzotriazolylenamines 3a-g, 4a-f and 5a,b. We have now explored and extended the reaction of BtH and $POCl_3$ with an amide for the synthesis of α-benzotriazolylenamines. In a typical procedure, BtH (4 equiv), $POCl_3$ (2 equiv), NEt_3 (2 equiv) and the tertiary amide 1 (5 mmol) were sequentially added dropwise as solutions in CH_3CN into a nitrogen-blanketed round-bottomed flask at rt (Scheme 2). Disappearance of the amide was monitored by TLC or GC. The reactions which afforded Bt-enamines 3a,c,d and 4a,c,d were performed over 14 h at rt, but refluxing was required for the synthesis of Bt-enamines 3g, 5a (2 d), 3e,f, 4e,f (3 d) and 3b, 4b (10 d). The reaction was worked-up as described in the experimental section once no amide was left in the reaction mixture.



1, 3, 4	R^1	R^2	Product (% yield)
a	Me	Et	**3a**(25) and **4a** (63)
b	Me	t-Bu	**3b**(17) and **4b** (36)
c	Me	Bu	**3c**(21) and **4c** (58)
d	Et	Bu	**3d**(31) and **4d** (53)
e	Ph	Bu	**3e**(18) and **4e** (53)
f	Me	Ph	**3f** and **4f** (56)

Scheme 2

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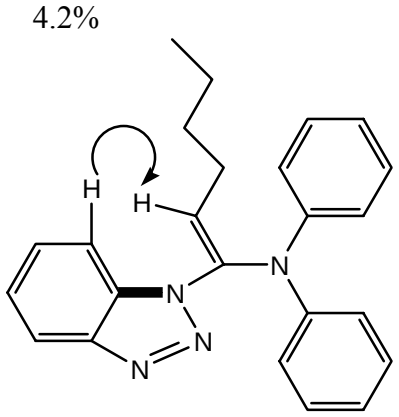
The desired α-benzotriazolylenamines 3 and 4 were typically isolated as separated *Z* 3a-e and *E* 4a-e isomers in good combined yields (53-88%). Exceptionally, *N*-[1-(1*H*-1,2,3-benzotriazol-1-yl)-2-methylprop-1-enyl]-*N*-methylaniline (3g, 74%) can only exist as one *E/Z* isomer and *N*-[1-(1*H*-1,2,3-benzotriazol-1-yl)-2-phenyleth-2-enyl]-*N*-methylaniline (3f/4f, 56%) was isolated as an *E/Z* mixture (about 10:1) by flash column chromatography. Traces of what could have been Bt^2 isomers 5 were detected in the MS of the crude reaction mixture obtained from each amide 1a-g. However, Bt-enamine 5a was the only Bt^2 isomer isolated using this method, this being from the reaction mixture of *N*,2-dimethyl-*N*-phenylpropanamide (1g). Enamine 5a proved to be remarkably stable even after two months' storage at ambient conditions.

In a reinvestigation of the synthesis of α-benzotriazolylenamines from enamines, we found that when *N*-(*trans*-1-butenyl)-*N*-methylaniline (2b) was sequentially reacted with 1-chloro-1*H*-1,2,3-benzotriazole[25] and *t*-BuOK in Et_2O at –38 °C (CH_3CN-CO_2 bath) a 52% yield of a 2:1 mixture of *N*-[(*Z*)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-butenyl]-*N*-methylaniline (3a) and *N*-[(*E*)-1-(2*H*-1,2,3-benzotriazol-2-yl)-1-butenyl]-*N*-methylaniline (5b) isomers was obtained (Scheme 2). α-Benzotriazolylenamine isomers 3a and 5b were isolated as separate compounds by silica gel, flash column chromatography. Further exploration of this method was not pursued because the amide method gave superior yields.

Structure elucidation of α -benzotriazolylenamines 3a-g, 4a-f and 5a,b. α -Benzotriazolylenamines 3a-g, 4a-f and 5a,b were all characterized by elemental analysis and by their ^1H and ^{13}C NMR spectra. For example, *N*-[(*Z*)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-butenyl]-*N*-methylaniline (3a) showed the expected carbon resonances for the Bt^1 moiety [δ_C 145.4 (C3a), 132.7 (C7a), 127.9 (C6), 124.0 (C5), 121.0 (C4) and 110.8 (C7)], the *N*-phenyl group [δ_C 146.8 (C1), 129.0 (C2), 119.9 (C4) and 117.8 (C3)], the double bond [137.0 (C) and 119.2 (CH)], the *N*-CH_3 (δ_C 38.8) and the alkyl group [δ_C 20.5 (CH_2) and 14.3 (CH_3)]. Similarly, the proton resonances for both the benzotriazolyl and *N*-monosubstituted-phenyl moieties in the aromatic region, a one-proton triplet (δ_H 5.52 ppm, J = 7.6 Hz) in the olefinic region, and an *N*-CH_3 singlet (d $_H$ 3.10 ppm), a CH_2 multiplet (δ_H 2.13-2.03 ppm) and a CH_3 triplet (δ_H 1.04, J = 7.6 Hz) in the aliphatic region were observed. The fact that there was coupling between the CH_2 of the ethyl group (d $_H$ 2.13-2.03 ppm) and the vinylic proton (δ_H 5.52 ppm) of Bt-enamine 3a and that this coupling was absent in *N*-[(*Z*)-1-(1*H*-1,2,3-benzotriazol-1-yl)-3,3-dimethyl-1-butenyl]-*N*-methylaniline (3b) is evidence that the vinylic proton is attached to the same carbon of the double bond as the alkyl fragment derived from the acid portion of the amide.

When C2 has an attached proton as in Bt-enamines 3a-f, 4a-f and 5b, both α-Bt^1- and α-Bt^2-enamines could exist as either *E* or *Z* isomers. Stereochemistry of the Bt^1 compounds was assigned based on the fact that irradiation of the C7 proton of the Bt^1 moiety (δ_H 7.74 ppm) of *N*-[(*E*)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-hexenyl]-*N*-phenylaniline (4e) gave a small (4.2%)

positive NOE for the vinylic proton (δ_H 5.94 ppm), establishing a cisoid relationship between these two groups in this compound (Figure 1). For the Bt[1] isomers (Table 2), the vinylic proton consistently appeared at either δ_H ~6.0 ppm for the *E* or δ_H ~5.5 ppm corresponding to the *Z* isomer for each pair of products from an amide. Due to this consistency in the chemical shifts of the two isomers, and the fact that the stereochemistry of Bt-enamine 4e (δ_H 5.94 ppm) was confirmed as *E* by an NOE experiment, it was concluded that all such Bt[1] isomers with δ_H ~6.0 ppm 4a-e had *E* stereochemistry and those with δ_H ~5.5 ppm 3a-e had *Z* stereochemistry.



4e

Figure 1

Table 2. [1]H NMR Data for Vinylic Protons of Bt-enamines 3a-e, 4a-e

Z-Bt-enamine	C=C*H* (δ_H ppm) [multiplicity]	E-Bt-enamine	C=C*H* (δ_H ppm) [multiplicity]
3a	5.52 [t]	4a	5.98 [t]
3b	5.62 [s]	4b	6.01 [s]
3c	5.53 [t]	4c	5.99 [t]
3d	5.56 [t]	4d	6.01 [t]
3e	5.57 [t]	4e	5.94 [t]

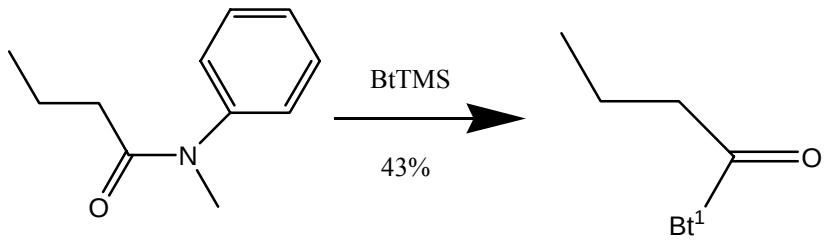
Stability of α-Benzotriazolylenamines 3a-g, 4a-f and 5a,b. *N*-[(*E*)-1-(2*H*-1,2,3-Benzotriazol-2-yl)-1-butenyl]-*N*-methylaniline (5b) isomerized upon storage. After 1 month in $CDCl_3$, the [1]H NMR of a sample of Bt-enamine 5b, which initially displayed one triplet for the vinylic proton at δ_H 6.62 ppm, displayed three triplets at d $_H$ 6.62, 5.70 and 5.52 ppm. The signal at δ_H 5.52 ppm was assigned to the *Z*-Bt[1] isomer 3a, indicating that the Bt[2] compounds can isomerize into the

Bt^1 isomers. Since the Bt^1 compounds with the more shielded vinylic signals (δ_H ~6.0 ppm) had *E* stereochemistry while the others (δ_H ~5.5 ppm) had *Z* stereochemistry, Bt^2-enamine 5b (δ_H 6.62 ppm) was assigned *E* stereochemistry and the signal at δ_H 5.70 ppm was assigned to the vinylic proton of the corresponding *Z*-(Bt^2) isomer. The *E* and *Z* isomers derived from the Bt^2-enamine 5b could not be separated. *N*-[1-(2*H*-1,2,3-Benzotriazol-2-yl)-2-methyl-1-propenyl]-*N*-methylaniline (5a) was characterized by elemental analysis and ^1H and ^{13}C NMR spectroscopy. Its NMR spectra were similar to those of Bt-enamine 3g, except for the expected differences between Bt^2 and Bt^1 compounds.

It is shown by NMR spectra of the pure samples that the Bt^1 isomeric pairs 3 and 4 did not interconvert under ambient conditions either neat or in solution. Additionally, Bt-enamines 3a-g, 4a-f and 5a did not decompose under acidic ($POCl_3$) reaction conditions, basic (saturated aqueous K_2CO_3) work-up or silica gel column chromatography. a -Benzotriazolylenamines 3a and 5b, which were made by reaction of enamine 2b with BtCl, were stable to the basic reaction conditions (*t*-BuOK) and silica gel column chromatography.

Limitations to the Preparation of a -Benzotriazolylenamines 3 and 4 from Amides 1. Although the synthesis of α-benzotriazolylenamines tolerated alkyl (1a-e,g) and aryl (1f) groups as well as linear (1a,c-e) and branched (1b,g) groups on the acid portion of an amide, the amine portion of the amide had to be a tertiary aniline derivative. Thus, *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylpropionamide and 1-acetylpiperidine did not yield any a -benzotriazolylenamine. The use of other acetamides (*N*-methylacetanilide and *N*-phenylacetanilide) also failed to give any desired α-benzotriazolylenamine. Starting amide was recovered when CH_2Cl_2 or THF was used as solvent instead of CH_3CN.

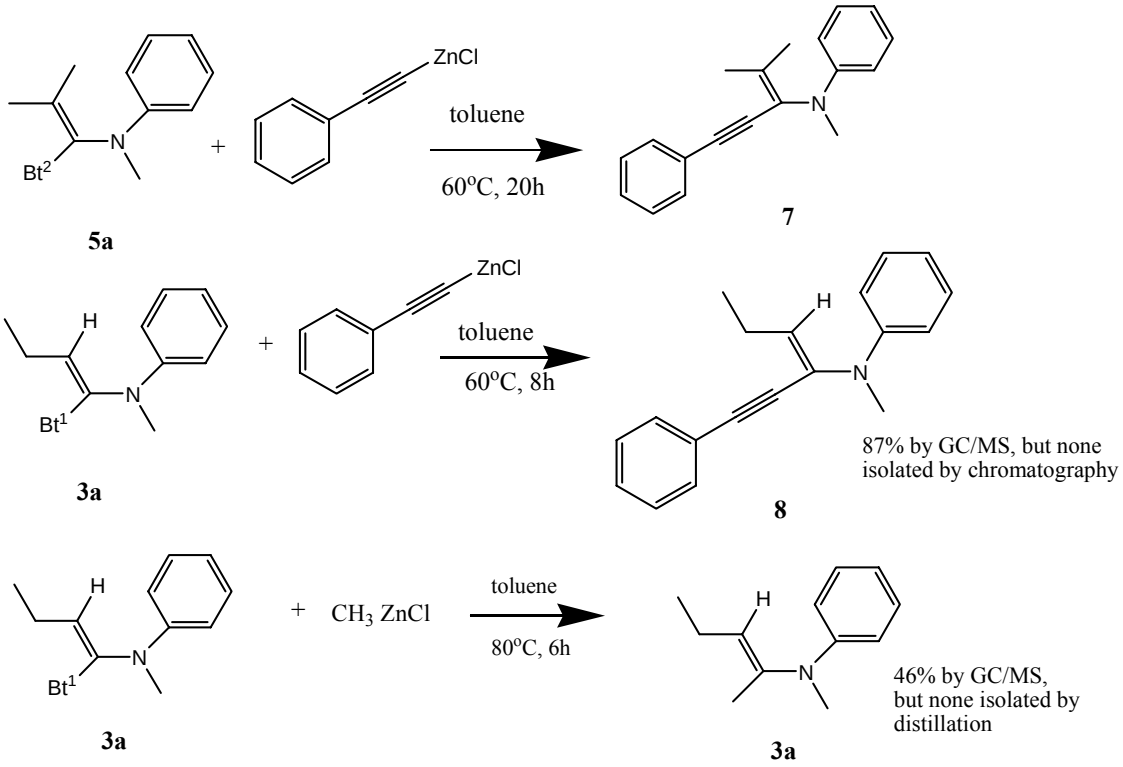
Furthermore, the use of 1-(trimethylsilyl)-1*H*-1,2,3-benzotriazole[26] instead of BtH in the reaction of *N*-methyl-*N*-phenylbutanamide (1a) under optimized conditions produced the transamination product 1-(1*H*-1,2,3-benzotriazol-1-yl)butan-1-one (6) (Scheme 3)[27] in 43% yield as the major product without any α-benzotriazolylenamine being detected by GC/MS of the crude reaction mixture.



1a **6**

Scheme 3

Reaction of α-Benzotriazolylenamines 3a and 5a with Organozinc Reagents. Similarly to the displacement of chloride from *N*-(1-chloro-2-methylpropyl)piperidine by phenylmagnesium bromide (70% yield),[5a] *N*-[1-(2*H*-1,2,3-benzotriazol-2-yl)-2-methylprop-1-enyl]-*N*-methylaniline (5a) readily underwent nucleophilic substitution of the benzotriazolyl moiety by phenylethynylzinc chloride, and was thereby converted in 76% yield into *N*-methyl-*N*-[2-methyl-1-(2-phenylethynyl)-1-propenyl]aniline (7) (Scheme 4). Enamine 7 was characterized by NMR spectroscopy. The ^{1}H NMR showed a 10-proton integration in the aromatic region, a 3-proton singlet at δ_H 3.01 typical for an *N*-CH_3 group and two 3-proton singlets further upfield [δ_H 2.07 and 1.73 ppm] which correspond to the vinylic methyl groups. The ^{13}C NMR showed signals that reaffirmed those from the ^{1}H NMR spectrum in addition to two quaternary signals expected from the presence of the triple bond (δ_C 90.7, 86.0 ppm); no signals characteristic of a benzotriazolyl group were detected.



Scheme4

Mass spectral examination of reactions of 2-unsubstituted-1-(benzotriazol-1-yl)enamines with other organozinc reagents (Scheme 4) showed species with m/e appropriate to the expected products 8 and 9. Unlike enamine 7, compounds 8 and 9 proved to be isolated by silica gel flash

column chromatography or distillation. In fact such enamines are known to be quite reactive and tend to undergo self-condensation at even moderate temperatures (over 60 °C).[29] More specifically, the reaction of *N*-[(*Z*)-1-(1*H*-1,2,3-benzotriazol-1-yl)-1-butenyl]-*N*-methylaniline (3a) with phenylethynylzinc chloride (2 equiv) in toluene at 60 °C for 8 h gave an 87% GC/MS yield (excluding organozinc dimer) of m/e = 261, but no compounds were isolated by silica gel chromatography. When methylzinc chloride (2 equiv) was reacted with Bt-enamine 3a (5 mmol) at 60 °C for 2 d in toluene, GC/MS showed only unreacted starting material. The same reaction gave a 46% GC/MS yield of m/e = 165 after 6 h at 80 °C, but no expected product was isolated by vacuum distillation.

Conclusions

In conclusion, the earlier work in this group[15a,b] on the synthesis of α-benzotriazolylenamines was further developed in order to ascertain the scope and limitations of these syntheses and to demonstrate the potential utility of α-benzotriazolylenamines as stable analogs to α-chloroenamines. A variety of α-(benzotriazol-1-yl)enamines 3a-g, 4a-f and 5a were easily prepared as separated E and Z isomers, except for the mixture of Bt-enamines 3f/4f, in good overall yields from amides 1a-g by the action of BtH, $POCl_3$ and NEt_3. The amides 1a-g were readily synthesized in excellent purity from reactions of acids with aniline derivatives by the action of $SOCl_2$ and pyridine. Additionally, *N*-[(*E*)-1-(2*H*-1,2,3-benzotriazol-2-yl)-1-butenyl]-*N*-methylaniline (5b) was synthesized along with *N*-[(*Z*)-1-(1*H*-1,2,3-benzo-triazol-1-yl)-1-butenyl]-*N*-methylaniline (3a) in moderate yield by reaction of *N*-(*trans*-1-butenyl)-*N*-methylaniline (2b) with 1-chloro-1*H*-1,2,3-benzotriazole and *t*-BuOK. The utility of these stable compounds was demonstrated by the nucleophilic substitution of the benzotriazolyl moiety from Bt-enamine 5a by phenylethynylzinc chloride to form *N*-methyl-*N*-[2-methyl-1-(2-phenylethynyl)-1-propenyl]aniline(7).

Experimental Section

General Procedures. All melting points were measured on a hot-stage microscope and are uncorrected. NMR experiments were conducted with a Varian VXR-300 NMR spectrometer at 75 MHz for ^{13}C and 300 MHz for ^{1}H spectra. Samples were dissolved in $CDCl_3$ with the internal reference being TMS (δ_H = 0.00 ppm) for ^{1}H spectra and the solvent (δ_C = 77.0 ppm) for ^{13}C spectra. Elemental analyses were performed on a Carlo Erba-1106 elemental analyzer. Prior to

use, CH_3CN was distilled from CaH_2, Et_2O and THF were distilled from Na/benzophenone and toluene was distilled from Na. Column chromatography was carried out using silica gel (230-400 mesh, Fisher). All other chemicals were obtained from commercial sources and were not further purified. Reactions were carried out under dry nitrogen with magnetic stirring.

***N*-(*trans*-1-Butenyl)-*N*-methylaniline (2b)** was prepared by the literature method in 18% yield.[lit.[21] bp 48-51 °C/0.1 mm] 1-Chloro-1*H*-1,2,3-benzotriazole [lit.[25] mp 104-106 °C], 1-(trimethylsilyl)-1*H*-1,2,3-benzotriazole [lit.[27] bp 100-102 °C/ 1.5 mm] and 1-[(4-methylphenyl)sulfonyl]-1*H*-1,2,3-benzotriazole [lit.[29] mp 135 °C] were prepared in accordance with the literature methods. 1-(1*H*-1,2,3-Benzotriazol-1-yl)butan-1-one (6) has been made previously.[lit.[27] mp 62-63 °C]

Preparation of amides 1a-g

All amides were synthesized in good yields using the procedure of Human and Mills, which delivers pure compounds.[16] Pyridine (20 or 50 mmol) was added to a Et_2O solution of an aliphatic acid (1 equiv). After 5 min in an ice water bath, $SOCl_2$ (1 equiv) was added dropwise to the reaction vessel. After 5 min, a mixture of pyridine (1 equiv) and aniline derivative (1 equiv) was then added dropwise to the reaction vessel. The ice bath was removed, and the mixture stirred for 2 h at rt. Successive washes with 2 N $HCl_{(aq)}$ (3 x 100 mL), 10% $NaOH_{(aq)}$ (3 x 50 mL) and brine (50 mL) gave, after reduced-pressure removal of volatiles, analytically pure product. Syntheses of *N*-methyl-*N*-phenylbutanamide (1a),[17a] *N*,3,3-trimethyl-*N*-phenylbutanamide (1b),[17b] *N*-methyl-*N*-phenylhexanamide (1c),[17c] *N*-methyl-*N*,2-diphenylacetamide (1f)[17d] and *N*,2-dimethyl-*N*-phenylpropanamide (1g)[17e] by alternative methods have been reported (Table 1).

***N*-Ethyl-*N*-phenylhexanamide (1d).** Colorless oil, 74%; ^{1}H NMR δ_H 7.45-7.32 (m, 3H), 7.16 (d, 2H, J = 7.4 Hz), 3.76 (q, 2H, J = 7.1 Hz), 2.02 (t, 2H, J = 7.7 Hz), 1.62-1.52 (m, 2H), 1.26-1.03 (m, 7H), 0.82 (t, 3H, J = 7.2 Hz); ^{13}C NMR δ_C 172.1, 142.1, 129.2, 128.0, 127.4, 43.5, 33.9, 31.0, 24.8, 21.9, 13.4, 12.6. Anal. Calcd for $C_{14}H_{21}NO$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.38; H, 9.92; N, 6.61.

***N*,*N*-Diphenylhexanamide (1e).** White rods (EtOAc), mp 42-44 °C, 81%; ^{1}H NMR δ_H 7.42-7.14 (m, 10H), 2.25 (t, 2H, J = 7.4 Hz), 1.73-1.58 (m, 2H), 1.32-1.16 (m, 4H), 0.85 (t, 3H, J = 6.5 Hz); ^{13}C NMR δ_C 173.2, 142.8, 129.1, 130.5-124.8/br, 35.1, 31.2, 25.1, 22.2, 13.8. Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.86; H, 8.23; N, 5.25.

Preparation of 3a and 5b by the reaction of *N*-(1-butenyl)-*N*-methylaniline (2b) with 1-Chloro-1*H*-1,2,3-benzotriazole. To a 250 mL schlenk flask with magnetic stirrer and rubber septum was added enamine 2b (5 mmol, 0.81 g) under an argon atmosphere. Diethyl ether was added (100 mL), and the reaction vessel was placed in an CH_3CN/CO_2 bath (-38 °C). After 30 min a solution of 1-chloro-1*H*-1,2,3-benzotriazole (5 mmol, 0.77 g) in Et_2O (30 mL) was added

dropwise. After 2 h at the same temperature, a solution of *t*-BuOK (5.5 mmol, 0.61 g) in THF (30 mL) was added dropwise. After 30 min the bath was removed, and the reaction was stirred at rt for 4 h. Water (30 mL) was added, and the layers were separated. The aqueous layer was extracted with Et_2O (2 x 20 mL). The combined organic solutions were washed with brine, dried over anhydrous Na_2SO_4 and filtered. The products were isolated by silica gel, flash column chromatography (10:1 pentane:Et_2O).

***N*-[(*Z*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-butenyl]-*N*-methylaniline (3a).** Yellow oil, 35%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.2 Hz), 7.52 (d, 1H, *J* = 8.2 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.33 (t, 1H, *J* = 7.5 Hz), 7.18 (t, 2H, *J* = 7.8 Hz), 7.07 (d, 2H, *J* = 8.0 Hz), 6.84 (t, 1H, *J* = 7.3 Hz), 5.52 (t, 1H, *J* = 7.6 Hz), 3.10 (s, 3H), 2.13-2.03 (m, 2H), 1.04 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR δ_C 146.8, 145.4, 137.0, 132.7, 129.0, 127.9, 124.0, 121.0, 119.9, 119.2, 117.8, 110.8, 38.8, 20.5, 14.3. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.15; H, 6.68; N, 20.02. Compound 3a was also prepared from amide 1a in 25% yield.

***N*-[(*E*)-1-(2*H*-1,2,3-Benzotriazol-2-yl)-1-butenyl]-*N*-methylaniline (5b).** Yellow rods (EtOAc), mp 64-66 °C, 17%; ^{1}H NMR δ_H 7.82 (dd, 2H, *J* = 6.6, 3.0 Hz), 7.32 (dd, 2H, *J* = 6.6, 3.3 Hz), 7.19 (t, 2H, *J* = 7.8 Hz), 6.84 (d, 2H, *J* = 8.4 Hz), 6.77 (t, 1H, *J* = 7.3 Hz), 6.62 (t, 1H, *J* = 7.5 Hz), 3.32 (s, 3H), 2.33-2.23 (m, 2H), 1.13 (t, 3H, *J* = 7.6 Hz); ^{13}C NMR δ_C 146.5, 144.4, 140.1, 129.1, 126.7, 125.0, 118.7, 118.3, 113.0, 38.4, 20.4, 13.3. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.14; H, 6.67; N, 20.07.

General procedure for the synthesis of α-Benzotriazolylenamines 3a-g, 4a-f and 5a

A pressure equalized dropping funnel was placed on a 250 mL round bottom flask containing a magnetic stirrer, BtH (20 mmol, 2.38 g) and a nitrogen inlet. Acetonitrile was added to the round bottom flask (10 mL) and to the dropping funnel (7 mL). The vessel was heated gently until the BtH dissolved, and then cooled to rt. Phosphorus oxychloride (10 mmol, 0.925 mL) was added to the dropping funnel, the contents of which were gently swirled and then added dropwise to the reaction vessel. The dropping funnel was rinsed with CH_3CN (7 mL) and then filled with the same. Triethylamine (10 mmol, 1.01 g) was added to the dropping funnel, the contents of that were swirled and then added dropwise to the vessel. After 15 min a solution of amide 1 (5 mmol) in CH_3CN (3 mL) was added in one portion, and the dropping funnel replaced with a water-jacketed condenser topped with a nitrogen inlet. Complete reaction, as determined by GC or TLC analysis, sometimes required refluxing. Volatile compounds were removed under reduced-pressure using a rotary evaporator. The resulting oil was dissolved in $CHCl_3$ (100 mL). Saturated, aqueous K_2CO_3 (200 mL) was added, and the mixture swirled. After 30 min the mixture was filtered through a medium sintered funnel under reduced pressure (water aspirator). The layers were separated, and the aqueous layer extracted with $CHCl_3$ (50 mL). The combined

organic solutions were dried over anhydrous Na_2SO_4, filtered and had the solvent removed by rotary evaporation. The residue was purified by silica gel, flash column chromatography using a pentane/Et_2O mixture as eluent.

***N*-[(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-butenyl]-*N*-methylaniline (4a).** Rt, 14 h, eluent 10:1, white prisms (EtOAc), mp 76-77 °C, 55%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.0 Hz), 7.42-7.21 (m, 6H), 6.93 (d, 2H, *J* = 8.2 Hz), 6.82 (t, 1H, *J* = 7.1 Hz), 5.98 (t, 1H, *J* = 7.4 Hz), 3.11 (s, 3H), 2.20-2.09 (m, 2H), 1.09 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR δ_C 145.8, 145.6, 135.6, 131.7, 129.2, 127.9, 123.9, 121.9, 119.8, 119.1, 113.6, 110.6, 36.8, 20.3, 13.2. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.13; H, 6.76; N, 20.33.

***N*-[(*Z*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-dimethyl-1-butenyl]-*N*-methylaniline (3b).** Reflux, 10 d, eluent 6:1, yellow rods (EtOAc), mp 81-84 °C, 17%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.2 Hz), 7.53 (d, 1H, *J* = 8.2 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.33 (t, 1H, *J* = 7.4 Hz), 7.23 (t, 2H, *J* = 8.1 Hz), 7.14 (d, 2H, *J* = 8.2 Hz), 6.86 (t, 1H, *J* = 7.2 Hz), 5.62 (s, 1H), 2.96 (s, 3H), 0.92 (s, 9H); ^{13}C NMR δ_C 147.1, 145.5, 134.6, 133.4, 130.5, 129.0, 128.0, 124.1, 120.6, 119.9, 117.5, 110.5, 37.9, 32.8, 30.1. Anal. Calcd for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.58; H, 7.60; N, 18.67.

***N*-[(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3,3-dimethyl-1-butenyl]-*N*-methylaniline (4b).** Reflux, 10 d, eluent 6:1, yellow oil, 36%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.0 Hz), 7.47-7.28 (m, 3H), 7.20 (t, 2H, *J* = 7.7 Hz), 6.87 (d, 2H, *J* = 8.2 Hz), 6.78 (t, 1H, *J* = 7.1 Hz), 6.01 (s, 1H), 3.23 (s, 3H), 1.21 (s, 9H); ^{13}C NMR δ_C 146.6, 145.8, 133.8, 132.6, 132.2, 129.1, 127.9, 123.9, 120.0, 118.9, 113.6, 110.6, 39.1, 33.2, 29.5. Anal. Calcd for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.28; H, 7.53; N, 18.67.

***N*-[(*Z*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-methylaniline (3c).** Rt, 14 h, eluent 8:1, yellow oil, 21%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.2 Hz), 7.52 (d, 1H, *J* = 8.2 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.33 (t, 1H, *J* = 7.5 Hz), 7.18 (t, 2H, *J* = 7.6 Hz), 7.06 (d, 2H, *J* = 8.2 Hz), 6.84 (t, 1H, *J* = 7.2 Hz), 5.53 (t, 1H, *J* = 7.6 Hz), 3.10 (s, 3H), 2.07 (q, 2H, *J* = 7.3 Hz), 1.40-1.21 (m, 4H), 0.81 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR δ_C 146.8, 145.4, 137.3, 132.7, 129.0, 127.9, 124.0, 120.9, 119.9, 117.9, 117.8, 110.8, 38.8, 31.7, 26.7, 22.2, 13.8. Anal. Calcd for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.19; H, 7.48; N, 18.60.

***N*-[(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-methylaniline (4c).** Rt, 14 h, eluent 8:1, yellow oil, 58%; ^{1}H NMR δ_H 8.01 (d, 1H, *J* = 8.0 Hz), 7.42-7.20 (m, 5H), 6.92 (d, 2H, *J* = 7.8 Hz), 6.81 (t, 1H, *J* = 7.2 Hz), 5.99 (t, 1H, *J* = 7.3 Hz), 3.12 (s, 3H), 2.13 (q, 2H, *J* = 7.2 Hz), 1.56-1.30 (m, 4H), 0.88 (t, 3H, *J* = 6.9 Hz); ^{13}C NMR δ_C 145.7, 145.6, 135.9, 131.6, 129.1, 127.8, 123.8, 120.5, 119.7, 119.0, 113.5, 110.6, 36.8, 30.6, 26.4, 22.1, 13.6. Anal. Calcd for $C_{19}H_{22}N_4$: C, 74.48; H, 7.24; N, 18.28. Found: C, 74.29; H, 7.48; N, 18.61.

***N*-[(*Z*)-1-1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-ethylaniline (3d).** Rt, 14 h, eluent 10:1, yellow oil, 31%; ^{1}H NMR δ_H 8.02 (d, 1H, *J* = 8.2 Hz), 7.55 (d, 1H, *J* = 8.2 Hz), 7.42 (t, 1H, *J* = 7.3 Hz), 7.33 (t, 1H, *J* = 7.5 Hz), 7.18 (t, 2H, J=7.1 Hz), 7.09 (d, 2H, J=7.1 Hz), 6.83 (t, 1H, *J* = 7.2 Hz), 5.56 (t, 1H, *J* =7.6 Hz), 3.44 (q, 2H, *J* = 7.1 Hz), 2.09-2.02 (m, 2H), 1.44-1.34 (m, 2H), 1.33-1.16 (m, 5H), 0.81 (t, 3H, *J* = 7.3 Hz); ^{13}C NMR δ_C 145.7, 145.4, 136.0, 132.7, 129.1, 127.8, 124.0, 120.7, 119.8, 118.5, 118.2, 110.8, 44.5, 31.7, 26.8, 22.2, 13.7, 12.4. Anal. Calcd for $C_{20}H_{24}N_4$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.76; H, 7.82; N, 17.87.

***N*-[(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-ethylaniline (4d).** Rt, 14 h, eluent 10:1, yellow oil, 53%; ^{1}H NMR δ_H 8.06 (dd, 1H, *J* = 7.0, 1.9 Hz), 7.45-7.26 (m, 5H), 7.03 (d, 2H, *J* = 8.0 Hz), 6.86 (t, 1H, *J* = 7.3 Hz), 6.01 (t, 1H, *J* = 7.3 Hz), 3.33 (q, 2H, *J* = 7.1 Hz), 2.07 (q, 2H, *J* = 7.3 Hz), 1.50-1.31 (m, 4H), 1.21 (t, 3H, *J* = 7.0 Hz), 0.87 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR δ_C 145.9, 145.4, 134.4, 131.9, 129.4, 127.9, 124.0, 121.9, 119.9, 119.0, 114.1, 111.1, 111.0, 42.7, 30.6, 26.9, 22.4, 13.8, 12.6. Anal. Calcd for $C_{20}H_{24}N_4$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.91; H, 7.22; N, 17.72.

***N*-[(*Z*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-phenylaniline (3e).** Reflux, 3 d, eluent 6:1, yellow oil, 18%; ^{1}H NMR δ_H 7.95 (d, 1H, *J* = 8.2 Hz), 7.77 (d, 1H, *J* = 8.2 Hz), 7.44 (t, 1H, *J* = 7.6 Hz), 7.28 (t, 1H, *J* = 8.2 Hz), 7.22-7.14 (m, 9H), 6.96-6.91 (m, 2H), 5.57 (t, 1H, *J* = 7.7 Hz), 2.15 (q, 2H, *J* = 7.4 Hz), 1.42-1.34 (m, 2H), 1.28-1.19 (m, 2H), 0.80 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR δ_C 145.2, 136.4, 132.5, 129.1, 127.9, 124.0, 123.3, 122.9, 120.6, 119.9, 110.7, 31.4, 26.9, 22.2, 13.7. Anal. Calcd for $C_{24}H_{24}N_4$: C, 78.23; H, 6.56; N, 15.20. Found: C, 77.96; H, 6.89; N, 15.37.

***N*-[(*E*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-1-hexenyl]-*N*-phenylaniline (4e).** Reflux, 3 d, eluent 6:1, white rods (ethyl acetate), mp 94-96 °C, 53%; ^{1}H NMR δ_H 7.92 (d, 1H, *J* = 8.2 Hz), 7.74 (d, 1H, *J* = 8.5 Hz), 7.37 (t, 1H, *J* = 7.6 Hz), 7.28-7.17 (m, 9H), 6.94 (t, 2H, *J* = 7.0 Hz), 5.94 (t, 1H, *J* = 7.4 Hz), 2.05 (q, 2H, *J* = 7.2 Hz), 1.43-1.23 (m, 4H), 0.82 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR δ_C 145.7, 143.9, 134.9, 131.8, 129.2, 127.8, 123.9, 123.0, 121.3, 120.4, 119.8, 110.8, 30.4, 26.4, 22.3, 13.7. Anal. Calcd for $C_{24}H_{24}N_4$: C, 78.23; H, 6.56; N, 15.20. Found: C, 77.91; H, 6.59; N, 15.39.

***N*-[1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-phenylethenyl]-*N*-methylaniline (3f and 4f).** Reflux, 3 d, eluent 6:1, viscous yellow oil, 56%; signals given for major isomer only ^{1}H NMR δ_H 8.04 (d, 1H, *J* = 8.2 Hz), 7.49 (d, 1H, *J* = 8.2 Hz), 7.44-7.11 (m, 9H), 6.92 (d, 2H, *J* = 8.2 Hz), 6.80-6.76 (m, 2H), 3.30 (s, 3H); ^{13}C NMR δ_C 146.0, 144.5, 136.0, 133.6, 132.1, 129.3, 128.6, 128.2, 128.0, 127.3, 124.3, 120.3, 120.2, 116.9, 114.9, 110.8, 38.1. Anal. Calcd for $C_{21}H_{18}N_4$: N, 17.17. Found: N, 17.31.

***N*-[1-(1*H*-1,2,3-Benzotriazol-1-yl)-2-methyl-1-propenyl]-*N*-methylaniline (3g).** Reflux, 2 d, eluent 4:1, colorless rhomboids (EtOAc), mp 106-107 °C, 74%; ^{1}H NMR δ_H 8.05 (d, 1H, *J* = 7.8

Hz), 7.40-7.24 (m, 5H), 6.92 (d, 2H, *J* = 8.2 Hz), 6.82 (t, 1H, *J* = 7.2 Hz), 3.01 (s, 3H), 1.85 (s, 3H), 1.72 (s, 3H); ^{13}C NMR δ_C 146.3, 145.3, 133.0, 130.4, 129.3, 129.2, 127.9, 123.9, 119.9, 118.6, 113.3, 110.6, 36.3, 19.9, 19.7. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.40; H, 6.74; N, 20.29.

***N*-[1-(2*H*-1,2,3-Benzotriazol-2-yl)-2-methyl-1-propenyl]-*N*-methylaniline (5a).** Reflux, 2 d, eluent 4:1, yellow oil, 1%; ^{1}H NMR δ_H 7.86 (dd, 2H, *J* = 6.5, 3.0 Hz), 7.35 (dd, 2H, *J* = 6.6, 3.0 Hz), 7.25-7.19 (m, 2H), 6.92 (d, 2H, *J* = 8.2 Hz), 6.76 (t, 1H, *J* = 7.2 Hz), 3.20 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H); ^{13}C NMR δ_C 146.5, 143.9, 135.6, 131.1, 129.1, 126.6, 118.5, 118.4, 113.3, 37.6, 19.8, 19.5. Anal. Calcd for $C_{17}H_{18}N_4$: C, 73.35; H, 6.52; N, 20.13. Found: C, 73.57; H, 6.70; N, 20.29.

***N*-Methyl-*N*-[2-methyl-1-(2-phenylethynyl)-1-propenyl]aniline (7).** To a solution of *N*-[1-(2*H*-1,2,3-benzotriazol-2-yl)-2-methyl-1-propenyl]-*N*-methylaniline (5a) (4 mmol) in toluene (40 mL) under a nitrogen atmosphere was added a solution made from phenylethynylmagnesium bromide (4.4 mL, 1.0 M in THF) and $ZnCl_2$ (4.4 mL, 1.0 M in Et_2O). The mixture was heated to 60 °C for 20 h. The reaction was quenched with an aqueous saturated K_2CO_3 solution (20 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organics were dried over anhydrous Na_2SO_4, filtered and had the volatiles removed by rotary evaporation. The title compound was obtained in 76% yield as a red oil by silica gel, flash column chromatography using pentane as eluent; ^{1}H NMR δ_H 7.33-7.29 (m, 2H), 7.24-7.15 (m, 5H), 6.75-6.71 (m, 3H), 3.01 (s, 3H), 2.07 (s, 3H), 1.73 (s, 3H); ^{13}C NMR δ_C 147.9, 141.4, 131.3, 128.8, 128.0, 127.7, 123.3, 122.6, 117.2, 113.0, 90.7, 86.0, 37.2, 21.4, 18.9. Anal. Calcd for $C_{19}H_{19}N$: N, 5.36. Found: N, 5.27.

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