A New Method of Synthesis for Propargylic Amines and Ethers via Benzotriazole Derivatives Using Sodium Dialkynyldiethylaluminates

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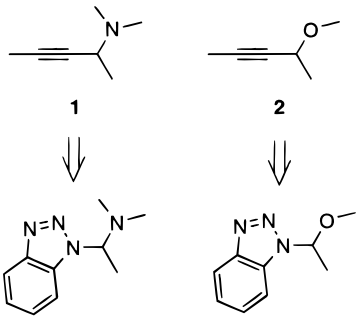
1-(α-Aminoalkyl)benzotriazoles react with sodium dialkynyldiethylaluminates to give propargylic amines in excellent yields, including unsubstituted *N*,*N*-dialkyl propargylamines, which are difficult to obtain from lithium acetylide. The reaction of α-benzotriazolyl alkyl ethers and sodium dialkynyldiethylaluminate in the presence of zinc iodide also gives propargylic ethers in excellent yields. Unsubstituted propargyl ethers are prepared via the desilylation of trimethylsilylpropargyl ethers.

N,*N*-Dialkyl-2-alkynamines **1** (tertiary propargylic amines), compounds of great pharmaceutical interest, can be prepared in good yields by the reaction of 1-(dialkylaminomethyl)benzotriazoles **3** with lithium alkynides.[1] Similarly, propargylic ethers **2** were prepared in good yields by reacting α-(benzotriazolyl)alkyl ethers **4** with alkynyl Grignard reagents.[2,3]

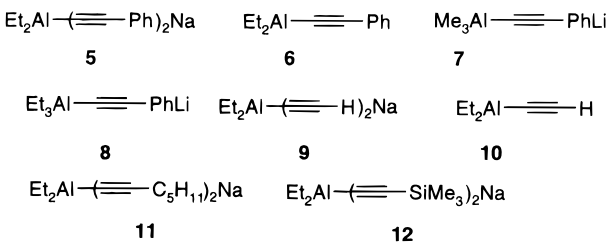


1 **2** **3** **4**

Recently, alkynylalkylaluminates **5**, **7**, **9**, **11**, and **12** have been shown by one of our groups to present a higher chemoselectivity than lithium alkynides in the alkynylation of carbonyl compounds.[4−6]

The present work represents a unification of the two methodologies mentioned above. We now report that the good leaving properties of benzotriazole[7] and the chemoselectivity of alkynylaluminates are combined in advantageous reactions of 1-(α-aminoalkyl)benzotriazoles **13** and

Aluminum Alkynylating Reagents (AAA)



5 **6** **7** **8** **9** **10** **11** **12**

16a−**j** and α-benzotriazolyl alkyl ethers **20a**−**g** with sodium dialkynyldiethylaluminates **5**, **9**, **11**, and **12** to give the corresponding propargylic amines **14a**,**b** and **17a**−**j** and ethers **21a**−**k**.

Results and Discussion

Synthesis of Propargylic Amines 14a,b and 17a−**j.** As shown in Table 1, 1-(*N*-methyl-*N*-phenylaminomethyl)benzotriazole (**13**) reacted with alkynylalkylaluminates **5** and **7**−**9** and alkynylalkylaluminum **6** and **10** to give compounds **14a**,**b** in yields reaching 94% and quantitative, respectively. Some aspects regarding the selectivity of reagents **5**−**10** need to be emphasized: (i) Both trimethylphenylethynylaluminate (**7**) (entry 3) and triethylphenylethynylaluminate (**8**) (entry 4) reacted with **13** to give 80% of the expected phenylethynyl derivative **14a** and *N*-ethyl-*N*-methylaniline or *N*-methyl-*N*-propylaniline (20% in both entries), which arose from a competitive reaction with the alkyl group. This is in agreement with the observation that compound **13** readily reacted with trimethylaluminum to give *N*-ethyl-*N*-methylaniline (100% by GC analysis). (ii) At room temperature, the reaction of compound **13** with aluminate **9** (entry 5) gave only 40% of the expected product **14b**. When the reaction was performed under reflux for 1 h, the conversion of **13** into the corresponding *N*-methyl-*N*-propynylaniline (**14b**) was 75%, but the product was contaminated with 1,4-bis(*N*-methyl-*N*-phenylamino)-2-butyne (**15**) (25%, entry 6). The amount of byproduct **15** decreased to 5% when using an excess of reagent **9** (entry 7).

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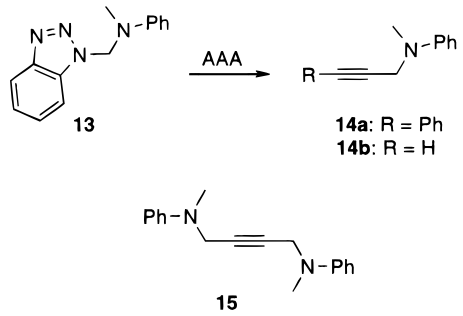
Table 1. Reactions of the Benzotriazole Derivative 13 with Various Aluminum Alkynylating Reagents (AAA) To Give Propargylamines 14a,b

entry	product	AAA (equiv)	temp (°C)	time (h)	yield (%)[a]
1	**14a**	**5**[b] (1.1)	20	1	100
2	**14a**	**6**[c] (1.1)	20	1	100
3	**14a**	**7**[d] (1.1)	20	1	80[h]
4	**14a**	**8**[e] (1.1)	20	1	80[i]
5	**14b**	**9**[f] (2.0)	20	24	40
6	**14b**	**9** (1.1)	reflux	1	75[j]
7	**14b**	**9** (4.0)	reflux	1	94[k]
8	**14b**	**10**[g] (1.1)	reflux	1	85[l]

[a] GC results. [b] 0.50 M solution of compound **5** was prepared by adding PhC≡CH to Et_2AlH_2Na (in toluene). [c] 0.25 M solution of compound **6** (hexane−THF 1:1) was prepared by adding Et_2AlCl (in hexane) to PhC≡CLi (in hexane−THF). [d] 0.33 M solution of compound **7** (toluene−hexanes−ether 3:2:5) solution was prepared by adding Me_3Al (in toluene) to PhC≡CLi (in hexanes−ether).[e] 0.25 M solution of compound **8** (toluene−hexanes−ether 3:2:5) was prepared by adding Et_3Al (in toluene) to PhC≡CLi (in hexanes−ether). [f] 0.25 M solution of compound **9** (toluene−THF 3:1) was prepared by adding HC≡CH gas to Et_2AlH_2Na (in toluene−THF). [g] 0.33 M solution of compound **10** (toluene−hexane 2:1) was prepared by adding HC≡CNa to Et_2AlCl (in hexane). [h] *N*-Ethyl-*N*-methylaniline (20%) was observed. [i] *N*-Methyl-*N*-propylaniline (20%) was observed. [j] 1,4-Bis(*N*-methyl-*N*-phenylamino)-2-butyne (**15**, 25%) was observed. [k] Compound **15** (5%) was observed. [l] Compound **15** (l−3%) and *N*-methyl-*N*-propylaniline (10%) were observed.



As reflected in Table 1, diethylphenylethynylaluminum (**6**) (entry 2) showed essentially quantitative conversion. However, it has been previously reported that alkynylaluminum reagents present poor chemoselectivity for carbonyl compounds and can react with other functional groups, such as halides and epoxides.[8−10] Consequently, despite the good yields listed in entry 2, we chose the more chemoselective sodium dialkynyldiethylaluminates **5**, **9**, and **11** as alkynylation reagents for reactions with benzotriazole derivatives **13** and **16a**−**j**.

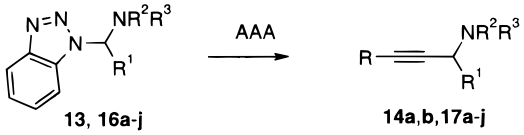
As shown in Table 2, compounds **5** and **11** reacted with benzotriazole derivatives **13** and **16a**−**j** to furnish the corresponding propargylic amines **14a**, **17a**−**c**, **17e**, **17g**, **17h**, and **17j** in good to excellent yields (78−94%) at room temperature. The reaction of aluminate **9** with benzotriazole derivatives **13**, **16d**, **16f**, and **16i** were complete in 1 h under reflux (see also Table 1) and gave the corresponding unsubstituted *N*,*N*-dialkylpropargylamines (compounds 1**4b**, **17d**, **17f**, and **17i**), in yields ranging from 60% to 82%.

The effect of changing the solvent was studied for the reaction of benzotriazole derivative **16e**. When the reaction was carried out in toluene, the propargylic amine **17e** was obtained in only 40% yield. The yield improved to 78% when the reaction was run in a mixture of toluene: THF (3:1). When the yields are compared to those of the reactions of benzotriazole derivatives with the corresponding lithium alkynides,[1] the yields are higher when aluminate **5** is used (e.g., preparation of **17g** previously reported in 33% yield was now achieved in 96% yield). Compounds **13** and **16i** also gave better yields in toluene−THF (3:1) (see Table 2).

Table 2. Propargylamines Synthesized by the Alkynylation of Benzotriazole Derivatives 13 and 16a−j with Various Sodium Dialkynyldiethylaluminates (AAA)[a]

product	R^1	NR^2R^3	AAA	R	conditions	yield (%)[b]
14a	H	$NPhCH_3$	**5**	Ph	rt, 3 h	91
14b	H	$NPhCH_3$	**9**	H	reflux, 1 h	81[c]
17a	H	$N(CH_2CH_3)_2$	**5**	Ph	rt, 3 h	94
17b	H	$N(CH_2CH_3)_2$	**11**	C_5H_{11}	rt, 3 h	90
17c	H	$N(CH_2CH_2)_2O$	**5**	Ph	rt, 3 h	90
17d	H	$N((CH_2)_7CH_3)_2$	**9**	H	reflux, 1 h	75
17e	Ph	$NPhCH_3$	**5**	Ph	rt, 3 h	78[c,d]
17f	Ph	$NPhCH_3$	**9**	H	reflux, 1 h	60
17g	Ph	$N(CH_2CH_2)_2O$	**5**	Ph	rt, 3 h	96
17h	Ph	$N(CH2CH_2)_2O$	**11**	C_5H_{11}	rt, 3 h	94
17i	Ph	$N(CH_2CH_2)_2O$	**9**	H	reflux, 1 h	82[c]
17j	CH_3	NPhH	**5**	Ph	reflux, 3 h	80

[a] The appropriate benzotriazole derivative (5 mmol) was reacted with the corresponding sodium dialkynyldiethylaluminate (5.5 mmol) in toluene. [b] Isolated yields. [c] Toluene−THF (3:1). [d] A 40% yield was obtained in toluene.



Sodium dialkynyldiethylaluminates have appeared to be highly chemoselective reagents, as reported in our previous communication.[4] The above-mentioned reagents do not affect other functional groups such as epoxides, esters, amides, and nitriles, if the reactions are performed at 0 °C. Halides were also found to be inert even at room temperature. We have thus studied the chemoselectivity of aluminate **5** by carrying out some competitive reactions. This reagent reacted selectively with 1-(*N*-methyl-*N*-phenylaminomethyl)benzotriazole (**13**) in the presence of 1,2-decene oxide (**18**) or octyl iodide with an excellent selectivity even at room temperature, whereas alkynylaluminum **6** showed a poor selectivity.

In similar competitive reactions in the presence of ethyl benzoate or benzonitrile, compound **13** was completely transformed into the propargylic amine 1**4a** in 3 h at room temperature; however, ethyl benzoate or benzonitrile also reacted with the alkynylation reagents **5** to some extent (10% and 20%, respectively).

Synthesis of Propargylic Ethers 21a−k. The model used for establishing the reaction conditions for the synthesis of propargylic ethers was the alkynylation of benzotriazolylmethyl octyl ether (**20a**) (Table 3). The desired propargylic product was not detected (entries 1 and 2), presumably due to the lower reactivity of benzotriazolylalkyl ethers compared to those of the corresponding amino derivatives.[11] Nevertheless, good yields were

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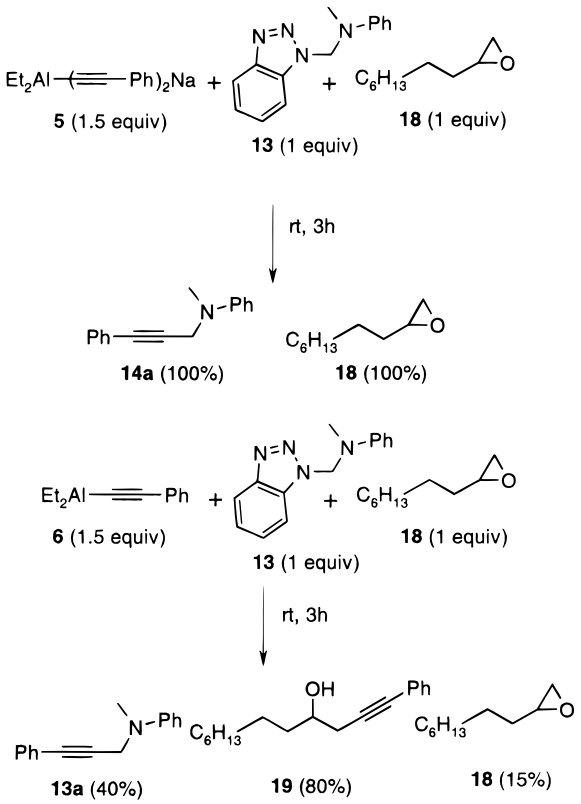
Table 3. Reactions of Benzotriazolylmethyl Octyl Ether (20a) with Metal Alkynides in the Presence of Metal Halides To Afford Phenylpropargyl Ether (21a)[a]

no.	AAA (equiv)	catalyst (equiv)	solvent[b]	time (h)	yield (%)[c]
1	**5** (4.0)	none	Tol:Et_2O (4:1)	3	0
2	**5** (4.0)	$BF_3{\cdot}OEt_2$ (3.0)	Tol	3	0
3	**5** (4.0)	ZnI_2 (3.0)	Tol:Et_2O (2:1)	1	11
4	**5** (4.0)	ZnI_2 (3.0)	Tol:Et_2O (4:1)	3	100
5	**5** (4.0)	ZnI_2 (1.0)	Tol:Et_2O (4:1)	6	17
6	**5** (4.0)	ZnI_2 (0.5)	Tol:Et_2O (4:1)	6	3
7	**5** (1.1)	ZnI_2 (1.1)	Tol:Et_2O (4:1)	6	100
8	**5** (1.1)	ZnI_2 (2.0)	Tol:Et_2O (4:1)	1	100
9	**5** (1.1)	$ZnBr_2$ (2.0)	Tol:Et_2O (4:1)	6	85
10	**5** (1.1)	$ZnCl_2$ (2.0)	Tol:Et_2O (4:1)	6	70
11	PhC≡CLi (2.0)	none	Tol:Et_2O (4:1)	1	36
12	PhC≡CLi (1.1)	ZnI_2 (1.1)	Tol:Et_2O (4:1)	3	23

[a] Benzotriazolylmethyl octyl ether (**20a**) (2 mmol) was reacted with sodium diethyldiphenylethynylaluminate (**5**) in the presence of zinc halide and in the appropriate solvent under reflux. [b] Tol = toluene, refluxing temperatures were found to be 56 °C for Tol:Et_2O (1:1), 67 °C for Tol:Et_2O (2:1), and 81 °C for Tol:Et_2O (4:1). [c] GC results.



obtained when the reactions were carried out in the presence of zinc iodide (entries 4, 7, and 8), using as solvent a mixture of toluene and ether (4:1) at reflux.

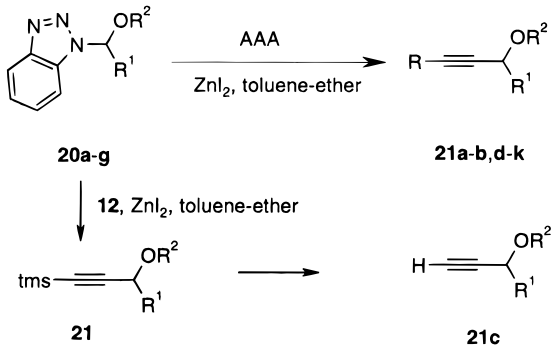
The optimum conditions were established when 2 equiv of zinc iodide was used in toluene−diethyl ether (4:1) at reflux (entries 7 and 8). In similar conditions, the alkynylation of ether **20a** with lithium phenylacetylide (entries 11 and 12) gave significantly lower yields than with aluminate **5**.

Reactions of aluminates **5** and **11** with alkoxyalkylbenzotriazoles **20a**−**g** were examined in the presence of zinc iodide, under the conditions established above (Table 4). However, the reactivity of the benzotriazole derivatives depended significantly on the type of substituent R^1 (H, alkyl, or aryl) and on the reaction temperature. Optimum reaction temperatures were achieved by using

Table 4. Propargyl Ethers Obtained by the Alkynylation of Benzotriazole Derivatives 20a−k with Sodium Dialkynyldiethylaluminates in the Presence of Zinc Iodide[a]

product/ reactant	R^1	R^2	R	AAA	solvent[b]	yield (%)[c]
21a/20a	H	C_8H_{17}	Ph	**5**	Tol:Et_2O (4:1)	97
21b/20a	H	C_8H_{17}	C_5H_{11}	**11**	Tol:Et_2O (4:1)	93
21c/20a	H	C_8H_{17}	H	**12**	Tol:Et_2O (4:1)	90[d]
21d/20b	H	$CH(CH_3)_2$	Ph	**5**	Tol:Et_2O (4:1)	90
21e/20c	H	$C(CH_3)_3$	Ph	**5**	Tol:Et_2O (4:1)	87
21f/20d	C_3H_7	CH_2CH_3	Ph	**5**	Tol:Et_2O (2:1)	82
21g/20e	$CH_2(CH_2)_2CH_2$		Ph	**5**	Tol:Et_2O (2:1)	98
21h/20e	$CH_2(CH_2)_2CH_2$		TMS	**12**	Tol:Et_2O (2:1)	77
21i/20f	Ph	CH_3	Ph	**5**	Tol:Et_2O (1:1)	91
21j/20g	PhC≡C	CH_2CH_3	Ph	**5**	Tol:Et_2O (1:1)	97
21k/20g	PhC≡C	CH_2CH_3	TMS	**12**	Tol:Et_2O (1:1)	83

[a] The benzotriazole derivative (2 mmol) was reacted with the appropriate sodium dialkynyldiethylaluminate (2.2 mmol, 1.1 equiv) in the presence of zinc iodide (4 mmol, 2.0 equiv) under reflux for 1 h. [b] Tol = toluene. [c] Isolated yields. [d] Desilylation of the corresponding trimethylsilylpropargyl octyl ether gave propargyl octyl ether (**21c**).



as solvent a mixture of toluene/ether in the following ratios: (4:1) for R^1 = H (compounds **21a**−**e**), (2:1) for R^1 = alkyl (compounds **21f**−**h**), and (1:1) for R^1 = aryl and phenylacetyl (compounds **21i**−**k**).

Aluminates **5** and **11** were found to be good alkynylating reagents for **20a** and produced **21a** and **21b** in yields of 97% and 93%, respectively, while aluminate **9** gave the expected products in less than 50%. Consequently, unsubstituted derivatives could not be obtained starting from aluminate **9**, but this problem was overcome by using the trimethylsilyl-substituted analogue **12**. The trimethylsilylpropargyl octyl ether obtained quantitatively from benzotriazole derivative **20a** and reagent **12** was treated without prior isolation with KOH and methanol for 30 min at room temperature[12] to give propargyl octyl ether (**21c**) in 90% yield. Bulky isopropoxy or *tert*-butoxy groups (as in compounds **20b**,**c**) did not affect the reaction, and their corresponding phenylpropargyl ether derivatives **21d**,**e** were obtained in yields of 90% and 87%, respectively. For compounds **20a**−**c**, the classical treatment with Grignard reagents did not lead to the expected ethers.[11] Therefore, this system of sodium dialkynyldiethylaluminates−zinc iodide becomes a valuable alternative for the preparation of propargylic ethers with R^1 = H.

An excellent yield of 2-phenylethynyltetrahydropyran (**21g**, 98%) was obtained in the reaction of 2-(benzotriazol-1-yl)tetrahydropyran with aluminate **5**, higher than that previously reported for phenylethynylmagnesium

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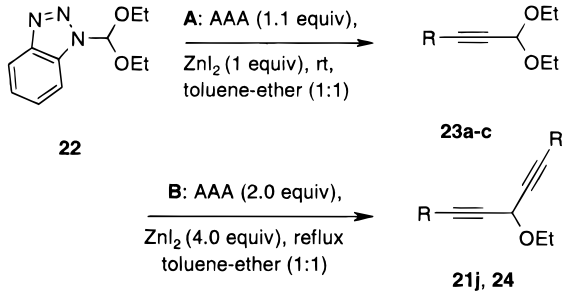
Table 5. Reactions of (Benzotriazol-1-yl)diethoxymethane (22) with Sodium Dialkynyldiethylaluminates ($Et_2Al(C{\equiv}CR)_2Na$) in the Presence of Zinc Iodide

R	AAA	conditions[a]	product	yield (%)[b]
Ph	**5**	**A**	**23a**	95
Ph	**5**	**B**	**21j**	85
C_5H_{11}	**11**	**A**	**23b**	89
$(CH_3)_3Si$	**12**	**A**	**23c**	90
$(CH_3)_3Si$	**12**	**B**	**24**	75

[a] Benzotriazole derivative **22** (2.0 mmol) was reacted for 1 h with the appropriate aluminate (**A**, 2.2 mmol, 1.1 equiv; **B**, 4.0 mmol, 2.0 equiv) in the presence of zinc iodide (**A**, 2.0 mmol, 1.0 equiv; **B**, 8.0 mmol, 4.0 equiv) at room temperature (**A**) or under reflux (**B**), both in toluene−ether (1:1). [b] Isolated yields.

iodide (84%)[3] and comparable to the reaction of 2-phenylsulfonyltetrahydropyran with phenylethynylzinc (97%).[13,14]



An interesting example is represented by the alkynylation of (benzotriazol-1-yl)diethoxymethane (**22**) with sodium dialkynyldiethylaluminates **5**, **11,** and **12** in the presence of zinc iodide under two different reaction conditions, marked **A** and **B** in Table 5.

(i) Under conditions **A**, the benzotriazole derivative **22** was treated with 1.1 equiv of the appropriate aluminate and 1 equiv of zinc iodide at room temperature, to afford propargylic aldehyde acetals **23a**−**c** as unique compounds (89−95%).

(ii) Under conditions **B**, the benzotriazole derivative **22** was heated at reflux with 2 equiv of the appropriate aluminate and 4 equiv of zinc iodide to give derivatives **21j** and **24** in 85% and 75% yields, respectively.

In conclusion, the use of sodium dialkynyldiethylaluminates as alkynylating reagents in the reaction with benzotriazole derivatives is a good alternative to the classical methods and not only displays good yields and selectivity in the synthesis of propargylic amines and ethers but also shows an excellent chemoselectivity when other functional groups such as epoxides, halides, esters, and nitriles are present. Propargyl aldehyde acetals **23a**−**c** obtained from (benzotriazol-1-yl)diethoxymethane (**22**) are useful starting materials for the generation of α,β-unsaturated ethers, γ-lactones, pyrroles, and functionalized alkynyl ketones via various propargyl ethyl ether intermediates.[15−17] Since this benzotriazole derivative is readily available, the synthesis of propargylalkyl ethers by desilylation of compounds of type **23c** and **24** is straightforward and would certainly find many applications.

Experimental Section

General Comments. Sodium diethyldihydroaluminate (Et_2AlH_2Na) was purchased from Aldrich. Benzotriazole derivatives **13**, **16a**−**j,** and **20a**−**g** were obtained by procedures already described in the literature.[7]

Preparation of $Et_2Al(C{\equiv}CPh)_2Na$ (5). Into a 150 mL flask under nitrogen were introduced at room temperature a solution of Et_2AlH_2Na in toluene (1.54 M, 19.4 mL, 30 mmol) and toluene (33.9 mL). Phenylacetylene (6.7 mL, 61.5 mmol) was added with vigorous stirring, which was continued for an additional 3 h, until the evolution of hydrogen ceased. The solution thus prepared was 0.5 M in alkynide **5**.

Preparation of $Et_2Al(C{\equiv}CH)_2Na$ (9). Into a 150 mL flask under nitrogen were introduced at room temperature a solution of Et_2AlH_2Na in toluene (1.54 M, 19.4 mL, 30 mmol) and toluene (40.6 mL). The solution was maintained at 0 °C, and acetylene gas (99% purity) was introduced with vigorous stirring. The solution was stirred for 40 min under a flow of acetylene; then the solution was stirred at room temperature for an additional 1 h. The solution thus prepared was 0.5 M in alkynide **9**.

General Procedure for the Preparation of Propargylamines 14a,b and 17a−**j.** The alkynylation of 1-(*N*-methyl-*N*-phenylaminomethyl)benzotriazole (**13**) is representative. To a solution of aluminate **5** in toluene (0.5 M, 5.5 mmol, 11 mL) was added a solution of 1-(*N*-methyl-*N*-phenylaminomethyl)-benzotriazole (**13**) (0.5 M, 5 mmol, 10 mL) in toluene at room temperature. After 3 h, the reaction mixture was hydrolyzed with saturated NH_4Cl (25 mL) and the product was extracted with ethyl acetate (25 mL). The ethyl acetate layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was subjected to column chromatography on a silica gel column (eluent: hexanes/EtOAc, 95:5) to give 1.01 g (91%) of *N*-methyl-*N*-phenyl-3-phenylpropyn-2-ylamine (**14a**): ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 3 H), 4.27 (s, 2 H), 6.80−7.50 (m, 10 H); IR (neat) 3061, 2957, 2361, 1599, 1504; GCMS *m/z* (relative intensity) (EI, 70 eV) 221 (M^+, 95), 77 (16), 104 (14), 115 (100), 116 (11), 144 (20), 220 (88). Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.90; H, 6.92; N, 6.15.

General Procedure for the Competitive Reaction with $Et_2Al(C{\equiv}CPh)_2Na$ (5). To a 0.5 M solution of aluminate **5** (1.5 mmol, 3 mL) in toluene at room temperature were added a solution 0.5 M of 1-(*N*-methyl-*N*-phenylaminomethyl)benzotriazole (**13**) and 1,2-decene oxide (**18**) (1 mmol, 2 mL) in toluene. After 3 h, the reaction mixture was hydrolyzed with saturated NH_4Cl (5 mL), and ethyl acetate (5 mL) was added. The organic layer was dried over anhydrous $MgSO_4$. GC analysis showed the formation of *N*-methyl-*N*-phenyl-3-phenylpropyn-2-ylamine (**14a**) (100% by GC), while 1,2-decene oxide (**18**) remained unreacted.

General Procedure for the Preparation of Propargylic Ethers 21a−**k**. The alkynylation of benzotriazolylmethyl octyl ether (**20a**) is representative. To a mixture of toluene (3.6 mL) and ether (4.0 mL) at room temperature were added zinc iodide (98% purity, 4.0 mmol, 1.28 g), a 0.5 M solution of $Et_2Al(C{\equiv}CPh)_2Na$ (2.2 mmol, 4.4 mL) in toluene, and a 0.25 M solution of benzotriazolylmethyl octyl ether (2.0 mmol, 8.0 mL) in toluene. After 1 h, the reaction mixture was hydrolyzed with saturated NH_4Cl (25 mL) and the product was extracted with ethyl acetate (25 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was subjected to column chromatography on a silica gel column (eluent: hexanes/EtOAc, 99:1) to give 0.472 g (97%) of phenylpropargyl octyl ether (**21a**): ^{1}H NMR ($CDCl_3$) δ 0.85−0.88 (m, 3 H), 1.28−1.64 (m, 12 H), 3.58 (t, 2 H, J = 6.6 Hz), 4.36 (s, 2 H), 7.30−7.47 (m, 5 H); IR (neat) 3059, 2928, 2235, 1099; GCMS *m/z* (relative intensity) (EI, 70

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eV) 244 (M^+, 1), 77 (4), 115 (100), 131 (17), 145 (29). Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.35; H, 9.89.

Propargyl Octyl Ether (21c). To a solution of zinc iodide (98% purity, 4.0 mmol, 1.28 g) in toluene (3.6 mL) and ether (4.0 mL) at reflux were added aluminate **12** (2.2 mmol, 4.4 mL as a 0.5 M solution in toluene) and benzotriazolylmethyl octyl ether as a solution in toluene (0.25 M, 2.0 mmol, 8.0 mL). After 1 h, the reaction mixture was hydrolyzed with saturated NH_4Cl (25 mL) and the product was extracted with ethyl acetate (25 mL). The ethyl acetate layer was concentrated under reduced pressure. The remaining liquid was stirred for 30 min at room temperature with a methanolic solution of KOH (0.4 g in 5 mL of methanol). Most of the methanol is then distilled off using a rotary evaporator. After addition of water (25 mL), the product was extracted in ether (25 mL), and the ethereal extract was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude residue was chromatographed on a silica gel column (eluent: hexanes/EtOAc, 99:1) to give 0.302 g (90%) of propargyl octyl ether (**21c**): ^{1}H NMR ($CDCl_3$) δ 0.85−0.90 (m, 3 H), 1.15−1.40 (m, 10 H), 1.50−1.69 (m, 2 H), 2.41 (s, 1 H), 3.48 (t, 2 H, J = 6.6 Hz), 4.13 (d, 2 H, J = 2.4 Hz); IR (neat) 2928, 2856, 2185, 1464, 1103; GCMS m/z (relative intensity) (EI, 70 eV) 168 (M^+, 1), 56 (49), 69 (100), 70 (46), 83 (46), 84 (47), 112 (16). Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.69; H, 11.61.

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Supporting Information Available: Characterization data for compounds **14b**, **17a**−**j**, **21b**, **21d**−**k**, **23a**−**c**, and **24** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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