N-Butyllithium-Mediated Reactions of 1-(2-Azidoarylmethyl)-1*H*-benzotriazoles with Alkyl Halides

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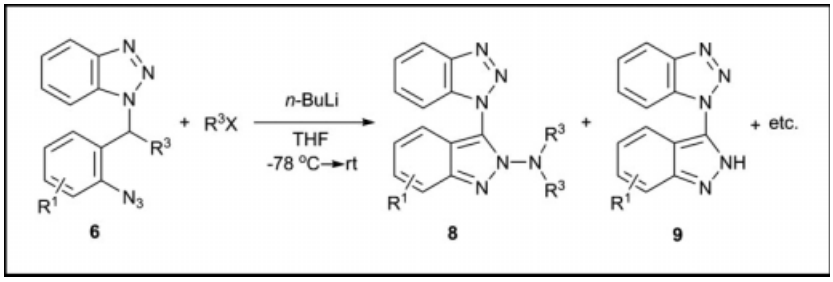

Treatment of 1-(2-azidoarylmethyl)-1*H*-benzotriazoles (**6**) with *n*-BuLi (2.5 equiv.) in THF at −78°C, followed by an addition of alkyl halides such as allyl, benzyl, and ethyl bromides with stirring for 2 h at room temperature afforded 2-(dialkylamino)-3-(benzotriazol-1-yl)-2*H*-indazoles (**8**), 3-(benzotriazol-1-yl)-2*H*-indazoles (**9**), 2-[(benzotriazol-1-yl)methyl]arylamine (**10**), and 2-[(benzotriazol-1-yl)(alkyl) methyl]arylamine (**11**).

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INTRODUCTION

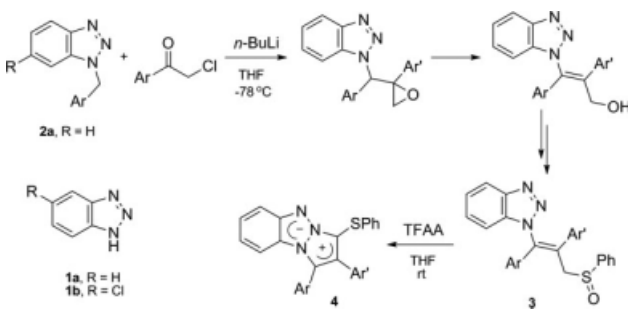
Benzotriazole has received a great amount of attention over the last three decades owing to the potential utility as a synthetic auxiliary for the synthesis of a diverse class of organic compounds [1]. Recently, we reported the reactions of 3-(benzotriazol-1-yl)-2,3-disubstituted propenyl phenyl sulfoxides **3** [2], prepared from 1-(arylmethyl)-1*H*-benzotriazoles **2a** and 1-aryl-2-chloroethanone in five steps, with trifluoroacetic anhydride (TFAA) yielding triazapentalenes **4** *via* a Pummerer-type intramolecular nucleophilic attack of N-2 of the benzotriazole moiety [2a] (Scheme 1).

In connection with the exploration of the synthetic utility of **1**, the introduction of an alkyl group at the benzylic position of 1-(2-azidoarylmethyl)-1*H*-benzotriazoles **6** (R^2 = 2-N_3) was attempted simply because the azido group may be utilized as a precursor for generation of nitrene [3]. Nitrene is known as a useful reactive species for the synthesis of nitrogen-containing heterocyclic compounds *via* insertion or addition reactions. One can envisage the reaction of a benzylic carbanion, generated from compounds **6** by a strong base, with alkyl halides. However, a problem to be encountered with this methodology is to overcome the possible reaction of the azido group with the strong base. A search through the literature showed that simple alkyl azides reacted with both Grignard reagents in diethyl ether at 0°C or alkyllithiums in *n*-pentane to give alkyltriazenes [4]. The latter reactions in ether did not occur. The reaction leading to triazenes was sensitive to the solvents. Furthermore, to the best of our knowledge, there has been no report on the reactions of aryl azides with both Grignard reagents and alkyllithiums. Compounds **6** are insoluble in *n*-pentane at room temperature. Consequently, it was necessary to obtain information on the reactivity of aryl azides including **6** toward various bases. The results obtained from our examination are described herein.

RESULTS AND DISCUSSION

2-Azidobenzyl bromides **5** (R^2 = 2-N_3, X = Br), precursors of 1-(2-azidoarylmethyl)-1*H*-benzotriazoles **6a-b**, **6d-e**, and **6g**, were prepared by diazotization of *o*-toluidine derivatives, followed by bromination of the methyl group using NBS in the presence of benzoyl peroxide [5b]. On the other hand, 2-azidobenzyl chloride **5** (R^2 = 2-N_3, X = Cl), precursors of compounds **6c** and **6f**, were prepared by diazotization of 2-aminobenzyl alcohols, followed by chlorination using $SOCl_2$ in CH_2Cl_2. Treatment of **5** with benzotriazoles **1a-b** in the presence of NaOEt in absolute ethanol [6] gave a mixture of **6** and 2-(2-azidoarylmethyl)-2*H*-benzotriazoles **7** which were separated by chromatography (Scheme 2).

Scheme 1



Yields of compounds **6** and **7** are summarized in Table 1.

Treatment of **6a** with *n*-BuLi (1.1 equiv.) in THF at −78°C, followed by addition of allyl bromide (1.1 equiv.) with stirring for 1 h did not reveal any new spots except for those of the starting materials on TLC. However, after being stirred at room temperature for 2 h, TLC of the reaction mixture showed four spots including that corresponding to **6a** (R_f = 0.71, EtOAc:*n*-hexane = 1:4). Chromatography of the reaction mixture (silica gel, 70–230 mesh) gave two 2*H*-indazole derivatives **8a** (R = R^1 = H) (25%), **9a** (R = R^1 = H) (21%), 2-[(benzotriazol-1-yl)methyl]phenylamine (**10a**) (R = R^1 = H) (25%) and 2-[1-(benzotriazol-1-yl)-3-butenyl]phenylamine (**11a**) (R = R^1 = H) (0%) together with unreacted **6a** (24%) containing a minute amount of 1-[(2-azidophenyl)(allyl)methyl]-1*H*-benzotriazole (**12a**) (Scheme 3). The yield of each product was variable depending on the concentrations of *n*-BuLi and allyl bromide. The results are summarized in Table 2.

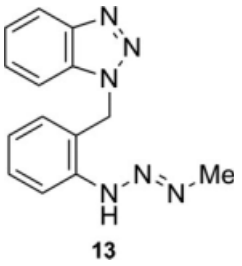
Table 2 shows that compounds **9a** and **10a** were formed without allyl bromide and a considerable amount of **6a** (40%) remained unreacted when 1.0 molar equiv. of *n*-BuLi was employed (entry 1). The result is inconsistent with the formation of dialkyltriazenes from analogous reactions involving simple alkyl azides and alkyllithiums in *n*-pentane [4a]. However, the reaction of **6a** with MeMgBr in THF for 1 h at 0°C, and subsequently at room temperature for 2 h, gave methyltriazene **13** (91%) as expected. The ^{1}H NMR (300 MHz, $CDCl_3$) spectrum showed a singlet at 3.24 ppm, corresponding to the structure of **13**.

Table 1

Yields of compounds **6** and **7**.

Compd	R	R^1	R^2	X	Compd	Yield[a] (%) **6**	**7**
1a	H	H	2-N_3	Br	**a**	50	19
1a	H	5-MeO	2-N_3	Br	**b**	44	19
1a	H	3-Me	2-N_3	Cl	**c**	55	16
1a	H	5-Br	2-N_3	Br	**d**	47	22
1a	H	4-Cl	2-N_3	Br	**e**	51	26
1a	H	5-Cl	2-N_3	Cl	**f**	48	23
1a	H	5-NO_2	2-N_3	Br	**g**	42	18
1a	H	H	4-N_3	Br	**h**	47	20
1b	Cl	H	2-N_3	Br	**i**	44[b]	19

[a] Isolated yields.
[b] Total yield of 1-(2-azidobenzyl)-5-chloro-1*H*-benzotriazole (**6i′**) and 1-(2-azidobenzyl)-6-chloro-1*H*-benzotriazole (**6i**).



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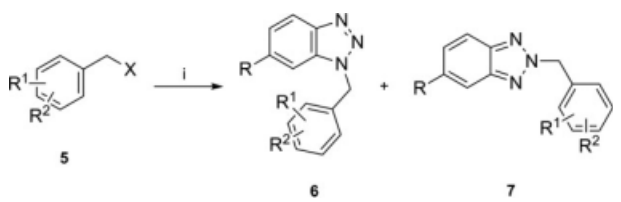
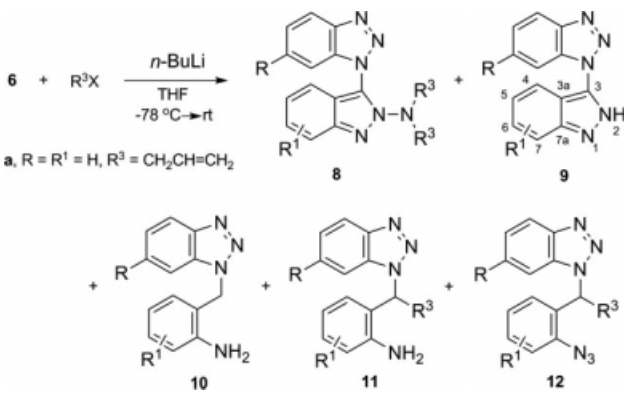
On addition of allyl bromide (1.1 equiv.), compound **8a** was obtained in 20% yield at the expense of **6a** and **10a** (entry 2). The amounts of recovered **6a** as well as **8a** were decreased somewhat by two-fold increase of the concentration of *n*-BuLi only (entry 3). When the concentrations of *n*-BuLi and allyl bromide were increased two-fold, respectively (entry 4), the yield of **8a** increased to 38% at the expense of **9a** and **6a**. However, further increase in the concentration of *n*-BuLi (4.0 equiv.) while maintaining the same concentration of

Scheme 2. Reagents and conditions: For X = Br, (i) **1a** (or **1b**), NaOEt, absolute EtOH, rt, 12 h; For X = Cl, (i) **1a**, NaOEt, absolute EtOH, reflux, 5 h.



5 **6** **7**

Scheme 3



8 **9** **10** **11** **12**

Table 2

Yields of compounds **8a**-**11a** at the different concentrations of *n*-BuLi and allyl bromide when [**6a**] = 1.40 mmol.

Entry	*n*-BuLi (equiv.)	Allyl bromide (equiv.)	Yield[a] (%)				
			8a	**9a**	**10a**	**11a**	Unreacted (**6a**)
1	1.0	0	0	24	37	0	40
2	1.1	1.1	20	21	25	0	24[b]
3	2.0	1.1	15	17	28	0	18[b]
4	2.5	2.2	38	15	5	18	13[b]
5	4.0	2.2	39	13	0	25	5[b]

[a] Isolated yields.
[b] Yields on the basis of the ^{1}H NMR intensities of a mixture of **6a** and **12a**.

allyl bromide (2.2 equiv.), did not affect the yields of **8a** and **9a** but only reduced the amount of unreacted **6a** by 5% (entry 5). Finally, the amount of unreacted **6a** decreased with increase in the concentration of *n*-BuLi and yet the yield of **8a** did not exceed 39%. In addition, the yields of **9a** were not much affected by altering the concentrations of either *n*-BuLi or allyl bromide.

Since the yields of compound **11a** increased with the concentrations of *n*-BuLi and allyl bromide (entries 4 and 5) and the sum of the yields of **10a** and **11a** appeared nearly constant, **10a**, prepared independently from **6a** and $NaBH_4$ [7], was treated with allyl bromide (2.5 and 3.0 equiv.) in the presence of *n*-BuLi (2.5 and 3.0 equiv.) in THF for 1 h at 0°C, and subsequently at room temperature for 2 h to observe if compound **11a** is formed *via* compound **10a**. From the reactions were obtained **11a** (0 and 3%), allyl[2-{(benzotriazol-1-yl)methyl}phenyl]amine (**14**) (38 and 16%), diallyl[2-{(benzotriazol-1-yl)methyl}phenyl]amine (**15**) (33 and 41%), and allyl[2-{1-(benzotriazol-1-yl)-3-butenyl}phenyl]-amine (**16**) (5 and 17%), respectively (Scheme 4). Compounds **14**–**16** were not detected in the reaction of **6a** under similar conditions but compound **11a** was observed (Scheme 4).

The result indicates that a small portion of compound **11a** may be formed *via* **10a**. For optimization of the reaction conditions, the reactions of **6a** (1.25 mmol) with allyl bromide were carried out in the presence of various bases under the same foregoing conditions. The results are summarized in Table 3.

Table 3 showed that not only a considerable amount of **6a** was used up to give unidentifiable mixtures but also a large quantity of unreacted **6a** was recovered. Consequently, *n*-BuLi was employed as a base for reactions of other compounds **6**. Yields of **8**–**11** and unreacted **6** are summarized in Table 4.

The structure of **8** was determined on the basis of the X-ray crystal structure of **8g** (Fig. 1).

The structures of **9** were determined on the basis of spectroscopic and analytical data. In particular, the HMBC spectrum of **9a** shows that the N2-H proton correlates with C3a and C7a carbon atoms, which clearly indicates that the compound is 2*H*-indazole derivative [8] rather than 1*H*-indazole derivative.

To obtain mechanistic information, **6h** was subjected to the same foregoing conditions (Scheme 5). From the reaction were obtained allylated compound **19** (4%) and amino compound **20** (45%) together with unreacted **6h** (28%). The result indicated that reduction of the azido group yielding amino group occurs readily compared with allylation at the benzylic position.

Although there exist plentiful examples of the direct conversion of an azido group to an amino group [9], *n*-BuLi-mediated the same type of conversion has seldom appeared in the literature [10]. We have found that treatment of simple aryl azides with *n*-BuLi (2.0 equiv.) under the same foregoing conditions gave arylamine as

Scheme 4

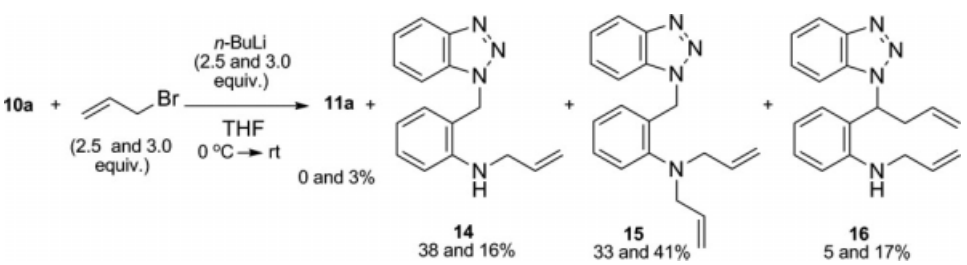


Table 3

Yields of compounds **8a**, **9a**, **10a**, and unreacted **6a**.

Base (equiv.)	Condition[a]	Yield[b] (%) 8a	9a	10a	6a
tert-BuLi (1.5)	[c]			[g]	
NaH (1.5)	[d]	0	0	trace	82
$NaNH_2$ (1.5)	[c]	0	0	0	75
n-BuLi (1.5)	[c,e]	15	12	25	21
$KN(SiMe_3)_2$ (1.5)	[c]	5	0	0	81
LDA (1.5)	[c,f]	6	8	15	41
LDA (1.2)	[c]	9	15	13	33

[a] Allyl bromide (1.5 equiv.) was used.
[b] Isolated yields.
[c] −78°C (1 h) → rt (2 h), THF.
[d] rt (5 h), THF.
[e] *n*-BuLi, followed by *tert*-BuOK (1.0 equiv.) was added.
[f] LDA, followed by TMEDA (1.0 equiv.) was added.
[g] Unidentifiable complex mixture.

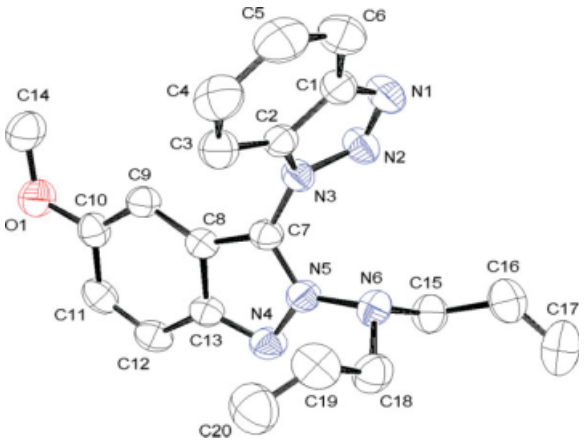


Figure 1. ORTEP drawing of **8g**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

major compounds (Scheme 6). Product yields are summarized in Table 5.

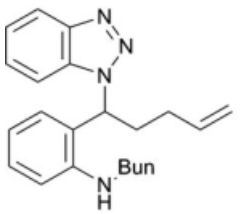
The formation of **19** coupled with **12c** as minor product indicates that alkylation at the benzylic position occurs under the conditions where the azido group is intact. Of course, compounds analogous to **8** and **9** cannot be formed from the reaction of **6h**. Interestingly, the reaction of **6a** with a mixture of an equal

Table 4

Yields of compounds **8a**, **9a**, **10a**, and unreacted **6a**.

Reactant		Product, Yield[a] (%)					
Compd (R)	R^3	Compd	**8** (R^1)	**9** (R^1)	**10** (R^1)	**11** (R^1)	**6** (R^1)
6a (H)	$CH_2CH{=}CH_2$	**a**	38 (H)	14 (H)	2 (H)	19 (H)	3 (H)
6a (H)	Et	**b**	25 (H)	13 (H)	21 (H)	0 (H)	trace (H)
6a (H)	$CH_2CH_2CH{=}CH_2$	**c**	0 (0)[b] (H)	16 (21)[b] (H)	20 (14)[b] (H)	4 (0)[b,c]	0 (4)[b] (H)
6a (H)	Bn	**d**	31 (H)	16 (H)	5 (H)	6 (H)	4 (H)
6a (H)	*n*-Bu	**e**	0 (H)	18 (H)	0 (H)	13[d] (H)	0 (H)
6a (H)	*tert*-Bu	**f**	0 (H)	21 (H)	14 (H)	0 (H)	31 (H)
6b (H)	$CH_2CH{=}CH_2$	**g**	24 (5-MeO)	19 (5-MeO)	8 (4-MeO)	3[e] (4-MeO)	3 (5-MeO)
6c (H)	$CH_2CH{=}CH_2$	**h**	34 (7-Me)	13 (7-Me)	10 (6-Me)	5[e] (6-Me)	trace (3-Me)
6d (H)	$CH_2CH{=}CH_2$	**i**	26 (5-Br)	14 (5-Br)	7 (4-Br)	4[e] (4-Br)	2 (5-Br)
6e (H)	$CH_2CH{=}CH_2$	**j**	26 (6-Cl)	16 (6-Cl)	5 (5-Cl)	6[e] (5-Cl)	2 (4-Cl)
6f (H)	$CH_2CH{=}CH_2$	**k**	28 (5-Cl)	17 (5-Cl)	2 (4-Cl)	8[e] (4-Cl)	4 (5-Cl)
6g (H)	$CH_2CH{=}CH_2$				[f]		
6i (Cl)	$CH_2CH{=}CH_2$	**l**	30 (H)	12 (H)	6 (H)	0 (H)	2 (H)

[a] Isolated yields.
[b] All data were obtained when alkyl bromides (X = Br) were used. Number in the parenthesis represents yields when iodide was used.
[c] When $CH_2{=}CHCH_2CH_2Br$ was used, compounds **12c** (R = R^1 = H, R^3 = $CH_2CH_2CH{=}CH_2$) and **17** were additionally isolated in 18 and 3% yields, respectively, whereas only **12c** was additionally isolated in 13% yield when $CH_2{=}CHCH_2CH_2I$ was used.
[d] When *n*-BuBr was used, compound **18** was additionally isolated in 11% yield.
[e] Yields calculated on the basis of the intensities of the ^1H NMR spectra of a mixture of **10** and **11**.
[f] Unidentifiable complex mixtures were obtained when R^1 = 5-NO_2.



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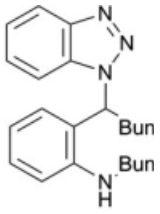

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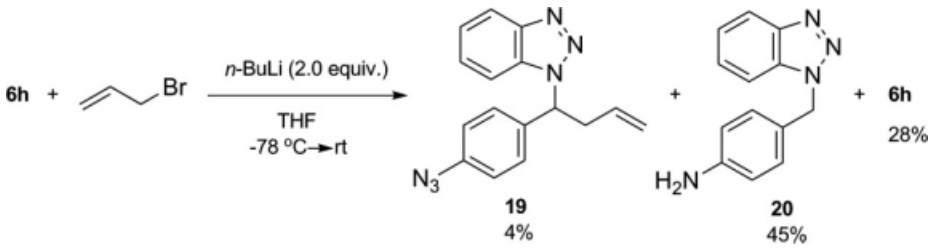
Scheme 5



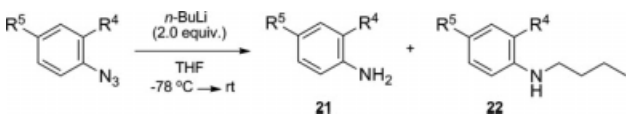
molar amount of allyl bromide (1.2 equiv.) and benzyl bromide (1.2 equiv.) under the same foregoing conditions showed four spots on TLC (silica gel, EtOAc:*n*-hexane = 1:4), corresponding to **8d** ($R_f = 0.79$), a mixture of **8a** and **23** ($R_f = 0.70$), **9a** ($R_f = 0.42$), and **10a** ($R_f = 0.27$) along with a weak spot having a long tail (Scheme 7).

An attempt at separation of the mixture of **8a** and **23** was unsuccessful. However, FAB MS shows mass number (*m*/*z*) 331 ($M^+ + 1$) and 381 ($M^+ + 1$), corresponding to the molecular weight of **8a** and **23** plus one, respectively. The formation of **23** suggests that the R^3 of compounds **8** is introduced in a stepwise manner.

The formation of compound **8a** may be initiated by deprotonation of benzylic hydrogen to give a carbanion **24**, followed by an intramolecular nucleophilic attack of the carbanion on the tetravalent nitrogen atom of an azido group, leading to a five-membered intermediate **25** with a negative charge on each nitrogen atom (Scheme 8).

Monoalkylation of **25** gives 1,3-dipolar intermediate **26a**, which is stabilized by a resonance form **26b**. Subsequent allylation, followed by deprotonation would give **8a**. In the meantime, a nucleophilic attack of *n*-butyl carbanion on an azido group gives 1-*n*-butyl-3-phenyltriazene **27a** [4], which may be stabilized by a resonance form **27b**. Intramolecular proton transfer of **27a** would generate a carbanion **28**. Protonation of **28**, followed by decomposition would give **10a** or **17** [11]. Alternatively, compounds **10a** and **17** can be formed from intermediate **27** *via* the same protonation and decomposition processes. In contrast, intramolecular nucleophilic attack of the benzylic carbanion **29**, a tautomer of **28**, on the trivalent nitrogen concomitant with displacing the *n*-butylamide ion would lead to **30**, a tautomer of **9a** and **31**. However, we obtained **9a** as a single compound. It has been reported that 1*H*-indazoles are thermodynamically more stable than 2*H*-indazoles [12] and that the equilibrium position between tautomers is dependent on the solvent polarity. However, molecular mechanics calculations show that **8g** ($E = 35.75$ kcal/mol) is more stable than its 1*H*-isomer ($E = 38.54$ kcal/mol) by 2.79 kcal/mol [13]. Similarly, 2*H*-indazole **9a** ($E = 29.75$ kcal/mol) is more stable than its 1*H*-indazole isomer ($E = 33.70$ kcal/mol) by 3.95 kcal/mol. This tendency is consistent with the experimental results. Further study is necessary to delineate why 2*H*-**8** and 2*H*-**9** are more stable than 1*H*-**8** and 1*H*-**9**, respectively. A nucleophilic attack of the carbanion **24** on allyl bromide would give **12a**, analogous to **19**. A similar reaction of **12a** as shown in the formation of **10a** from **27a** would give **11a**.

Scheme 6



CONCLUSION

In summary, when 1-(2-azidoarylmethyl)-1*H*-benzotriazoles (**6**) was treated with *n*-BuLi in THF at −78°C, followed by an addition of alkyl halides, *i.e.*, allyl, benzyl, ethyl bromides, TLC did not exhibit any new spots. On the other hand, four new spots corresponding to 2*H*-indazole derivatives **8** and **9**, which to the best of our knowledge had not been previously reported in the reactions of azido compounds, together with some weak spots, were observed at room temperature. Compounds **8** are envisaged to be formed by a nucleophilic attack of benzylic carbanion on the azido group, followed by displacement of halides twice in stepwise manner by the S_N2 mechanism. Compounds **9** would be formed by a nucleophilic attack of benzylic carbanion on triazenes. The formation of compounds **10** and **11** may be

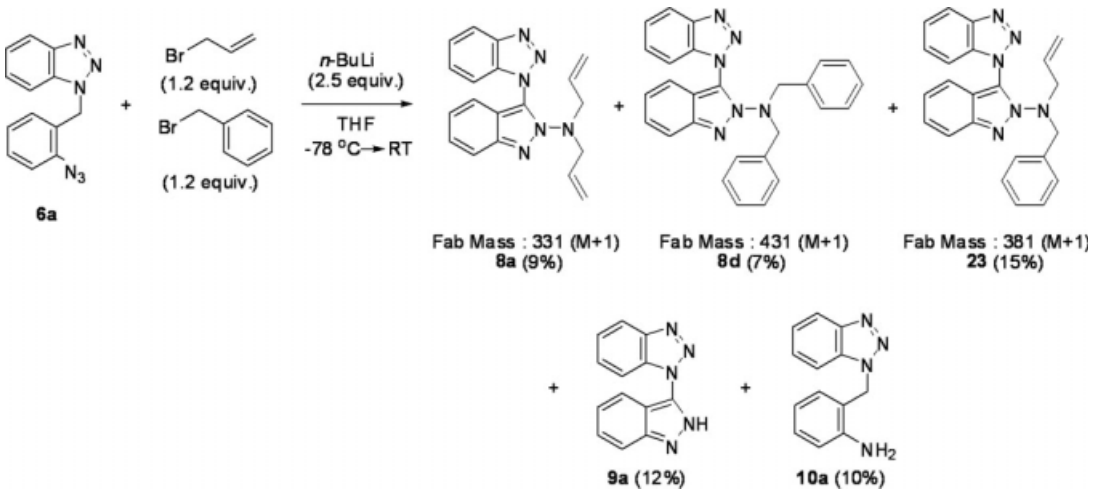
Table 5

Yields of compounds **21** and **22**.

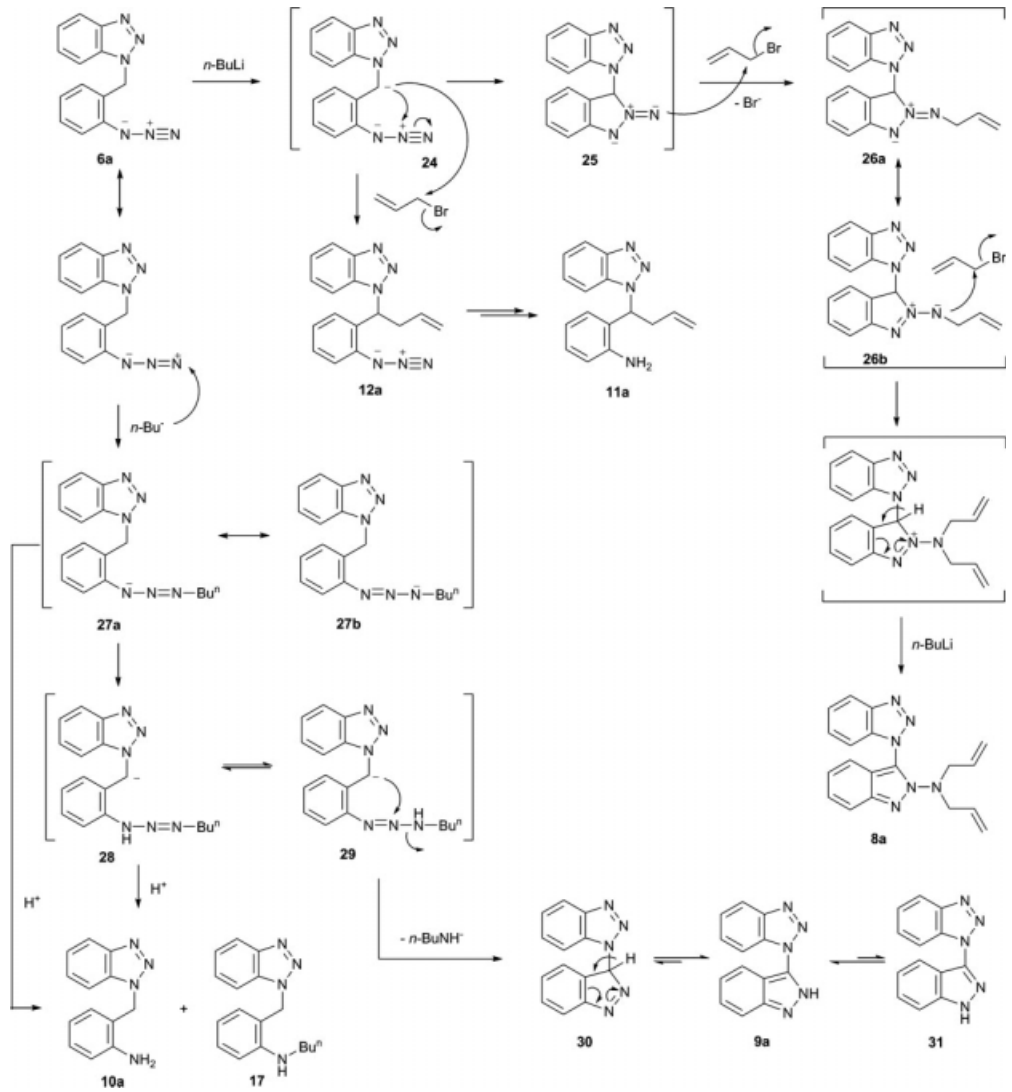
Compd	R^4	R^5	Yield[a] (%) **21**	Yield[a] (%) **22**
a	H	Me	69	8
b	Me	H	76	6
c	Et	H	69	8
d	Bz	H	72	7

[a] Isolated yields.

Scheme 7. Reaction of **6a** with the mixture of an equal molar amount of allyl bromide and benzyl bromide.



Scheme 8. Proposed mechanism of formation to the compounds **8**, **9**, **10**, **11**, and **17**.



explained in terms of decomposition of triazene, which has been reported in the literature [5].

EXPERIMENTAL

The ^{1}H NMR spectra was recorded at 300 MHz, unless otherwise stated in $CDCl_3$ solution containing tetramethylsilane as internal standard: *J* values are given in hertz (Hz). The ^{13}C NMR spectra were recorded at 75 MHz, unless otherwise stated in $CDCl_3$ solution. IR spectra were recorded in KBr or thin-film samples on KBr plates. Mass spectra were obtained by electron impact at 70 eV. Elemental analyses were determined by the National Center for Inter-University Research Facilities, Seoul National University. Column chromatography was performed using silica gel (Merck, 70-230 mesh ASTM). Mps were determined on a Fisher–Johns melting-point apparatus and are uncorrected.

General procedure for the synthesis of 2-azidoarylmethyl halides 5

2-Azidoarylmethyl bromides 5a-b, 5d-e, and 5g-h. To a stirred solution of arylamine (32.80 mmol) in concentrated H_2SO_4 (6 mL) was added $NaNO_2$ (39.36 mmol) at 0°C. The mixture was stirred for 30 min, followed by addition of NaN_3 (55.76 mmol), which was additionally stirred for 24 h. Work-up according to the literature procedure [5a] gave substituted 2-azidotoluenes. A mixture of 2-azidotoluene, *N*-bromosuccinimide (NBS) (1.05 equiv.) and benzoyl peroxide (0.05 equiv.) in benzene (60 mL) was heated at reflux for 24 h [5b]. Usual work-up of the reaction mixture gave **5a-b** (73, 87%), **5d-e** (79, 64%), and **5g** (89%), respectively. Similarly, 4-azidobenzyl bromide (**5h**) was prepared from 4-azidotoluene in 90% yield.

2-Azidoarylmethyl chlorides 5c and 5f. To a stirred solution of substituted 2-aminoarylmethyl alcohols (32.80 mmol) in concentrated H_2SO_4 (6 mL) was added $NaNO_2$ (39.36 mmol) at 0°C for 30 min, followed by addition of NaN_3 (55.76 mmol). The mixture was additionally stirred for 24 h, followed by usual work-up gave substituted 2-azidoarylmethyl alcohol. Treatment of 2-azidoarylmethyl alcohols with thionyl chloride [5c] (1.2 equiv.) at 0°C for 3 h gave **5c** (63%) and **5f** (62%).

General procedure for the synthesis of 1-(2-azidoarylmethyl)-1*H*-benzotriazoles 6 and 2-(2-azidoarylmethyl)-2*H*-benzotriazoles 7. To a stirred solution of sodium (5.65–8.82 mmol) in absolute ethanol (20 mL) was added a solution of benzotriazole (**1a**) (5.38–8.40 mmol) in absolute ethanol (30 mL). The mixture was stirred for 20 min, followed by addition of **5** (5.65–8.82 mmol), which was heated for 3.5 h at reflux. Work-up according to the literature procedure [6] gave compounds **6** and **7**. Yields are listed in Table 1.

1-(2-Azidophenylmethyl)-1H-benzotriazole 6a. Mp 97–99°C (from EtOAc–*n*-hexane) (Found: C, 62.3; H, 3.95; N, 33.7. Calc. for $C_{13}H_{10}N_6$: C, 62.4; H, 4.0; N, 33.6%); ν_{max} (KBr)/cm^{-1} 3040, 2944, 2112, 1572, 1480, 1441, 1302, 1278, 1216, 1152, 1073, 752, 739, and 523; ^{1}H NMR δ 5.83 (2H, s, CH_2), 7.05–7.16 (2H, m, ArH), 7.22 (1H, d, *J* 8.0, ArH), 7.34–7.41 (2H, m, ArH), 7.46 (1H, dd, *J* 8.3 and 1.0, ArH), 7.53 (1H, d, *J* 7.2, ArH) and 8.08 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 47.4, 110.2, 118.7, 120.4, 124.3, 125.6, 126.3, 126.4, 127.8, 130.3, 133.3, 138.3, and 146.5.

2-(2-Azidophenylmethyl)-2H-benzotriazole 7a. Mp 114–116°C (from EtOAc–*n*-hexane) (Found: C, 62.35; H, 3.9; N, 33.7. Calc. for $C_{13}H_{10}N_6$: C, 62.4; H, 4.0; N, 33.6%); ν_{max} (KBr)/cm^{-1} 3056, 2936, 2104, 1577, 1489, 1444, 1283, 1158, 1084, 851, 745, and 530; ^{1}H NMR δ 5.86 (2H, s, CH_2), 7.05 (1H, t, *J* 7.5, ArH), 7.12 (1H, d, *J* 7.5, ArH), 7.21 (1H, d, *J* 7.6, ArH), 7.28 (1H, d, *J* 7.7, ArH), 7.33 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.86 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 55.6, 118.6, 118.7, 125.4, 126.2, 126.8, 130.4, 130.9, 138.7, and 144.7.

1-[(2-Azido-5-methoxy)phenylmethyl]-1H-benzotriazole 6b. Mp 89–91°C (from EtOAc–*n*-hexane) (Found: C, 56.1; H, 4.3; N, 30.1. Calc. for $C_{14}H_{12}N_6O$: C, 56.0; H, 4.3; N, 30.0%); ν_{max} (KBr)/cm^{-1} 3056, 2930, 2824, 2108, 1603, 1494, 1446, 1424, 1281, 1236, 1155, 1078, 1032, 811, 744, and 521; ^{1}H NMR δ 3.67 (3H, s, OCH_3), 5.77 (2H, s, CH_2), 6.67 (1H, d, *J* 2.8, 1H, ArH), 6.88 (1H, dd, *J* 8.8 and 2.8, ArH), 7.12 (1H, d, *J* 8.8, ArH), 7.36 (1H, t, *J* 7.1, ArH), 7.45 (1H, t, *J* 6.8, ArH), 7.55 (1H, d, *J* 8.3, ArH), and 8.06 (1H, *J* 8.3 Hz, ArH); ^{13}C NMR δ 47.3, 56.0, 110.3, 115.4, 116.0, 119.8, 120.4, 124.4, 127.4, 127.9, 130.4, 133.2, 146.5, and 157.4.

2-[(2-Azido-5-methoxy)phenylmethyl]-2H-benzotriazole 7b. Mp 102–104°C (from EtOAc–*n*-hexane) (Found: C, 56.2; H, 4.3; N, 29.9. Calc. for $C_{14}H_{12}N_6O$: C, 56.0; H, 4.3; N, 30.0%); ν_{max} (KBr)/cm^{-1} 3048, 2936, 2824, 2112, 1603, 1556, 1489, 1454, 1424, 1281, 1236, 1161, 1030, 841, 746, 624, and 521; ^{1}H NMR δ 3.71 (3H, s, OCH_3), 5.85 (2H, s, CH_2), 6.79 (1H, d, *J* 2.9, ArH), 6.90 (1H, dd, *J* 8.8 and 2.9, ArH), 7.11 (1H, d, *J* 8.8, ArH), 7.37 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.88 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 55.6, 56.0, 115.9, 116.2, 118.6, 119.8, 126.9, 127.1, 131.0, 144.9, and 157.3.

1-[(2-Azido-3-methyl)phenylmethyl]-1H-benzotriazole 6c. Mp 54–56°C (from EtOAc–*n*-hexane) (Found: C, 63.55; H, 4.5; N, 31.9. Calc. for $C_{14}H_{12}N_6$: C, 63.6; H, 4.6; N, 31.8%); ν_{max} (KBr)/cm^{-1} 3048, 2936, 2104, 1606, 1585, 1454, 1427, 1340, 1286, 1220, 1153, 1084, 774, 740, and 520; ^{1}H NMR δ 2.42 (3H, s, CH_3), 5.86 (2H, s, CH_2), 6.91 (1H, d, *J* 7.1, ArH), 6.99 (1H, t, *J* 7.6, ArH), 7.10 (1H, d, *J* 7.4, ArH), 7.32 (1H, dt, *J* 1.3 and 6.7, ArH), 7.37–7.49 (2H, m, ArH), and 8.04 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 18.3, 48.6, 110.1, 120.3, 124.3, 126.7, 127.7, 127.8, 128.8, 132.3, 133.3, 133.5, 136.5, and 146.5.

2-[(2-Azido-3-methyl)phenylmethyl]-2H-benzotriazole 7c. Viscous liquid (Found: C, 63.5; H, 4.5; N, 31.95. Calc. for $C_{14}H_{12}N_6$: C, 63.6; H, 4.6; N, 31.8%); ν_{max} (KBr)/cm^{-1} 3040, 2948, 2110, 1607, 1585, 1454, 1420, 1342, 1286, 1221, 1150, 1084, 845, 746, and 521; ^{1}H NMR δ 2.48 (3H, s, CH_3), 5.99 (2H, s, CH_2), 7.06–7.11 (2H, m, ArH), 7.15–7.19 (1H, m, ArH), 7.38 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.89 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 18.5, 56.9, 118.6, 126.7, 126.8, 128.5, 128.8, 132.5, 133.6, 137.2, and 145.0.

1-[(2-Azido-5-bromo)phenylmethyl]-1H-benzotriazole 6d. Mp 84–86°C (from EtOAc–*n*-hexane) (Found: C, 47.3; H, 2.8; N, 25.45. Calc. for $C_{13}H_9BrN_6$: C, 47.4; H, 2.8; N, 25.5%); ν_{max} (KBr)/cm^{-1} 3056, 2948, 2110, 1574, 1482, 1441, 1302, 1288, 1217, 1154, 1073, 752, 740, and 521; ^{1}H NMR δ 5.77 (2H, s, CH_2), 7.09 (1H. d, *J* 8.5, ArH), 7.27 (1H, d, $J = 2.1$, ArH), 7.37–7.43 (1H, m, ArH), 7.46–7.56 (3H, m, ArH), and 8.10 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 46.8, 109.9, 118.5, 120.3, 120.6, 124.5, 128.1, 133.2, 133.3, 137.5, and 146.5.

2-[(2-Azido-5-bromo)phenylmethyl]-2H-benzotriazole 7d. Mp 94–96°C (from EtOAc–*n*-hexane) (Found: C, 47.25; H, 2.9; N, 25.5. Calc. for $C_{13}H_9BrN_6$: C, 47.4; H, 2.8; N, 25.5%); ν_{max}

(KBr)/cm^{-1} 3056, 2942, 2110, 1575, 1480, 1444, 1302, 1289, 1218, 1156, 1074, 754, 739, and 521; ^{1}H NMR δ 5.85 (2H, s, CH_2), 7.09 (1H. d, *J* 8.6, ArH), 7.38 (1H, d, *J* = 2.2, ArH), 7.42 (2H, dd, 6.6 and 3.1, ArH), 7.50 (1H, dd, 8.5 and 2.2, ArH), and 7.90 (2H, dd, 6.6 and 3.1, ArH); ^{13}C NMR δ 55.1, 118.3, 118.6, 120.3, 127.1, 127.9, 133.5, 133.7, 138.0, and 145.0.

1-[(2-Azido-4-chloro)phenylmethyl]-1H-benzotriazole 6e. Mp 72–74°C (from EtOAc–*n*-hexane) (Found: C, 54.9; H, 3.1; N, 29.4. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3048, 2952, 2112, 1572, 1480, 1444, 1302, 1278, 1210, 1160, 1074, 756, and 516; ^{1}H NMR δ 5.77 (2H, s, CH_2), 7.06 (2H, s, ArH), 7.20 (1H, s, ArH), 7.37–7.42 (1H, m, ArH), 7.45–7.54 (2H, m, ArH), and 8.08 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 46.8, 110.0, 118.9, 120.5, 124.5, 124.8, 125.9, 128.0, 131.4, 133.2, 135.9, 139.6, and 146.5.

2-[(2-Azido-4-chloro)phenylmethyl]-2H-benzotriazole 7e. Mp 80–82°C (from EtOAc–*n*-hexane) (Found: C, 54.8; H, 3.15; N, 29.3. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3048, 2947, 2112, 1575, 1489, 1441, 1302, 1268, 1211, 1160, 1084, 756, 642, and 516; ^{1}H NMR δ 5.85 (2H, s, CH_2), 7.10 (1H, dd, *J* 8.2 and 1.9, ArH), 7.20 (1H, d, *J* 1.9, ArH), 7.21 (1H, d, *J* 8.2, ArH), 7.41 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.88 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 55.1, 118.5, 119.0, 124.6, 125.8, 127.0, 123.1, 136.2, 140.1, and 145.0.

1-[(2-Azido-5-chloro)phenylmethyl]-1H-benzotriazole 6f. Mp 97–99°C (from EtOAc–*n*-hexane) (Found: C, 54.7; H, 3.2; N, 29.6. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3052, 2952, 2829, 2110, 1576, 1442, 1306, 1281, 1224, 1156, 1077, 904, 742, and 520; ^{1}H NMR δ 5.77 (2H, s, CH_2), 7.11 (1H, s, ArH), 7.15 (1H, dd, *J* 8.6 and 2.7, ArH), 7.32–7.43 (2H, m, ArH), 7.47–7.54 (2H, m, ArH), and 8.09 (1H, d, *J* 7.7, ArH); ^{13}C NMR δ 46.9, 109.9, 119.9, 120.6, 124.5, 128.0, 128.1, 130.2, 130.4, 131.1, 133.2, 136.9, and 146.5.

2-[(2-Azido-5-chloro)phenylmethyl]-2H-benzotriazole 7f. Mp 113–115°C (from EtOAc–*n*-hexane) (Found: C, 54.8; H, 3.1; N, 29.65. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3054, 2952, 2828, 2112, 1580, 1444, 1307, 1281, 1224, 1156, 1078, 905, 746, and 516; ^{1}H NMR δ 5.82 (2H, s, CH_2), 7.06 (1H, d, *J* 8.6, ArH), 7.19 (1H, d, *J* 2.4, ArH), 7.28 (1H, dd, *J* 8.6 and 2.4, ArH), 7.36 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.87 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 55.1, 118.6, 119.9, 127.0, 127.7, 130.4, 130.7, 130.8, 137.3, and 145.0.

1-[(2-Azido-5-nitro)phenylmethyl]-1H-benzotriazole 6g. Mp 144–146°C (from EtOAc–*n*-hexane) (Found: C, 52.9; H, 3.1; N, 10.7. Calc. for $C_{13}H_9N_7O_2$: C, 52.85; H, 3.1; N, 10.8%); ν_{max} (KBr)/cm^{-1} 3064, 3024, 2112, 1603, 1574, 1504, 1476, 1331, 1281, 1214, 1148, 1081, 824, 768, 736, and 526; ^{1}H NMR δ 5.84 (2H, s, CH_2), 7.34 (1H, d, *J* 8.8, ArH), 7.37–7.43 (1H, m, ArH), 7.48–7.56 (2H, m, ArH), 8.03 (1H, d, *J* 2.5, ArH), 8.09 (1H, d, *J* 8.3, ArH), and 8.24 (1H, dd, *J* 8.8 and 2.6, ArH); ^{13}C NMR δ 46.9, 109.6, 119.2, 120.7, 124.7, 125.8, 126.0, 127.5, 128.3, 133.2, 145.0, 145.1, and 146.4.

2-[(2-Azido-5-nitro)phenylmethyl]-2H-benzotriazole 7g. Mp 171–173°C (from EtOAc–*n*-hexane) (Found: C, 53.0; H, 3.2; N, 10.7. Calc. for $C_{13}H_9N_7O_2$: C, 52.85; H, 3.1; N, 10.8%); ν_{max} (KBr)/cm^{-1} 3058, 3026, 2112, 1605, 1578, 1506, 1476, 1334, 1280, 1148, 1080, 824, 768, 624, and 526; ^{1}H NMR δ 5.94 (2H, s, CH_2), 7.34 (1H, d, *J* 8.8, ArH), 7.42 (2H, dd, *J* 6.6 and 3.1, ArH), 7.88 (2H, dd, 6.6 and 3.1, ArH), 8.17 (1H, d, *J* 2.5, ArH), and 8.28 (1H, dd, *J* 8.8 and 2.5, ArH); ^{13}C NMR δ 55.0, 118.6, 119.2, 125.9, 126.7, 127.1, 127.2, 144.9, 145.1, and 145.4.

1-(4-Azidophenylmethyl)-1H-benzotriazole 6h. Mp 90–92°C (from EtOAc–*n*-hexane) (Found: C, 62.5; H, 4.0; N, 33.7. Calc. for $C_{13}H_{10}N_6$: C, 62.4; H, 4.0; N, 33.6%); ν_{max} (KBr)/cm^{-1} 3048, 2944, 2112, 1600, 1571, 1494, 1438, 1297, 1214, 1147, 1081, 822, 776, 758, 740, and 524; ^{1}H NMR δ 5.83 (2H, s, CH_2), 7.00 (2H, d, *J* 8.5, ArH), 7.29 (2H, d, *J* 8.5, ArH), 7.33–7.46 (3H, m, ArH), and 8.08 (1H, d, *J* 9.0, ArH); ^{13}C NMR δ 52.0, 109.9, 120.0, 120.6, 124.4, 127.9, 129.6, 131.8, 133.1, 140.8, and 146.8.

2-(4-Azidophenylmethyl)-2H-benzotriazole 7h. Mp 108–110°C (from EtOAc–*n*-hexane) (Found: C, 62.45; H, 3.9; N, 33.7. Calc. for $C_{13}H_{10}N_6$: C, 62.4; H, 4.0; N, 33.6%); ν_{max} (KBr)/cm^{-1} 3048, 2924, 2110, 1601, 1573, 1495, 1438, 1280, 1210, 1147, 1081, 822, 774, 740, and 518; ^{1}H NMR δ 5.87 (2H, s, CH_2), 7.01 (2H, d, *J* 8.4, ArH), 7.30 (2H, d, *J* 8.4, ArH), 7.38 (2H, dd, *J* 6.6 and 3.1, ArH), and 7.89 (2H, dd, *J* 6.6 and 3.1, ArH); ^{13}C NMR δ 58.4, 111.4, 120.2, 124.5, 126.6, 130.3, 138.7, and 146.1.

Reaction of 5-chlorobenzotriazole (1b) with 2-azidobenzyl bromide (5a). In accordance with the aforementioned general procedure, **5a** (1770 mg, 8.34 mmol) was added to a mixture of **1b** (1220 mg, 7.94 mmol) and Na (183 mg, 8.34 mmol) in absolute ethanol (50 mL). The mixture was stirred for 12 h at room temperature. After removal of the solvent *in vacuo*, the residue was chromatographed on a silica gel (3.0 × 15 cm^2) using a mixture of EtOAc and *n*-hexane (1:5) to give 2-(2-azidophenylmethyl)-2*H*-(5-chlorobenzotriazole) (**7i**) (407 mg, 18%), a mixture of 1-(2-azidophenylmethyl)-6-chloro-1*H*-benzotriazole (**6i**) and 1-(2-azidophenylmethyl)-5-chloro-1*H*-benzotriazole (**6i′**) (995 mg, 44%) and unreacted **1b**. The mixture of **6i** and **6i′** (1:1 based on the ^{1}H NMR signal of CH_2) was separated by the repeated recrystallization using a mixture of EtOAc and *n*-hexane (1:15) to give **6i** and **6i′** as solids.

6i. Mp 77–79°C (from EtOAc–*n*-hexane) (Found: C, 54.7; H, 3.1; N, 29.5. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3056, 2952, 2848, 2112, 1575, 1481, 1440, 1302, 1278, 1206, 1155, 1074, 740, and 518; ^{1}H NMR δ 5.78 (2H, s, CH_2), 7.07–7.17 (2H, m, ArH), 7.27 (1H, d, *J* 8.0, ArH), 7.33 (1H, dd, *J* 8.7 and 1.5, ArH), 7.40 (1H, td, *J* 7.5 and 2.0, ArH), 7.53 (1H, d, *J* 1.7, ArH), and 7.99 (1H, d, *J* 8.8, ArH); ^{13}C NMR δ 47.6, 110.1, 118.8, 121.4, 125.6, 125.7, 125.8, 130.4, 130.6, 133.9, 134.3, 138.4, and 145.1.

6i′. Mp 116–118°C (from EtOAc–*n*-hexane) (Found: C, 54.9; H, 3.0; N, 29.4. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3048, 2954, 2110, 1572, 1488, 1444, 1302, 1278, 1201, 1160, 1074, 756, 642, and 516; ^{1}H NMR δ 5.80 (2H, s, CH_2), 7.10–7.18 (2H, m, ArH), 7.22 (1H, d, *J* 7.9, ArH), 7.39 (1H, d, *J* 1.4, ArH), 7.42 (1H, d, *J* 1.7, ArH), 7.46 (1H, s, ArH), and 8.04 (1H, d, *J* 1.7, ArH); ^{13}C NMR δ 47.7, 111.3, 118.8, 119.7, 125.7, 128.8, 130.3, 130.4, 130.5, 130.6, 131.9, 138.4, and 147.1.

7i. Mp 102–104°C (from EtOAc–*n*-hexane) (Found: C, 54.9; H, 3.1; N, 29.3. Calc. for $C_{13}H_9ClN_6$: C, 54.8; H, 3.2; N, 29.5%); ν_{max} (KBr)/cm^{-1} 3050, 2952, 2112, 1574, 1480, 1441, 1308, 1280, 1200, 1157, 1065, 756, 648, and 520; ^{1}H NMR δ 5.88 (2H, s, CH_2), 7.14 (1H, td, *J* 7.7 and 1.5, ArH), 7.34 (1H,

dd, *J* 9.1 and 1.9, ArH), 7.42 (1H, td, *J* 8.0 and 1.5, ArH), 7.82 (1H, d, *J* 1.9, ArH), and 7.88 (1H, d, *J* 1.6, ArH); ^{13}C NMR δ 55.9, 117.6, 118.8, 119.8, 125.5, 125.7, 128.4, 130.7, 131.0, 132.7, 138.9, 143.4, and 145.2.

General procedure for the reactions of 6 with alkyl halides in the presence of *n*-BuLi. To a solution of **6** (1.80 mmol) in THF (40 mL) at –78°C were added *n*-BuLi (2.5*M* in *n*-hexane, 4.50 mmol) and alkyl halide (4.50 mmol), which was stirred for 1 h. The mixture was additionally stirred for 2 h at room temperature, quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined extract was dried over $MgSO_4$. Evaporation of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel (2.5 × 13 cm^2) using a mixture of EtOAc and *n*-hexane (1:6) to give 2-(*N*,*N*-dialkylamino)-3-(benzotriazol-1-yl)-2*H*-indazoles **8**, 3-(benzotriazol-1-yl)-2*H*-indazole **9**, 2-[(benzotriazol-1-yl)methyl]arylamines **10**, 2-[(benzotriazol-1-yl)(alkyl)methyl]arylamines **11**, and unreacted **6**.

Reaction of 6a with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (350 mg, 1.40 mmol), allyl bromide (423 mg, 3.50 mmol), and *n*-BuLi (3.50 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-diallylamino)-3-(benzotriazol-1-yl)-2*H*-indazole (**8a**) (176 mg, 38%), 3-(benzotriazol-1-yl)-2*H*-indazole (**9a**) (46 mg, 14%), 2-[(benzotriazol-1-yl)methyl]phenylamine (**10a**) (6 mg, 2%), 2-[1-(benzotriazol-1-yl)-3-butenyl]-phenylamine (**11a**) (70 mg, 19%), and unreacted **6a** (11 mg, 3%).

8a. Mp 89–91°C (from *n*-hexane) (Found: C, 68.95; H, 5.5; N, 25.4. Calc. for $C_{19}H_{18}N_6$: C, 69.1; H, 5.5; N, 25.4%); ν_{max} (KBr)/cm^{-1} 3056, 2912, 2848, 1630, 1601, 1555, 1523, 1440, 1398, 1371, 1280, 1227, 1200, 1166, 1033, 990, 924, 836, 740, and 516; ^{1}H NMR δ 3.86 (4H, d, *J* 6.6, CH_2), 4.96 (2H, *J* 17.4, $=CH_2$), 5.01 (2H, d, *J* 24.7, $=CH_2$), 5.49–5.65 (2H, m, =CH), 7.08–7.16 (1H, m, ArH), 7.23–7.31 (2H, m, ArH), 7.33–7.41 (1H, m, ArH), 7.43–7.57 (2H, m, ArH), 7.79 (1H, d, *J* 8.9, ArH), and 8.20 (1H, d, *J* 7.9, ArH); ^{13}C NMR δ 60.8, 110.4, 115.7, 118.7, 118.8, 120.5, 120.7, 124.3, 125.0, 127.4, 129.1, 132.8, 135.1, 145.4, and 145.7.

9a. Mp 219–220°C (CH_2Cl_2–*n*-hexane) (Found: C, 66.3; H, 3.8; N, 29.8. Calc. for $C_{13}H_9N_5$: C, 66.4; H, 3.9; N, 29.8%); ν_{max} (KBr)/cm^{-1} 3136, 3040, 2928, 2880, 1609, 1523, 1488, 1436, 1385, 1342, 1273, 1244, 1166, 1094, 1003, 984, 918, 892, and 737; ^{1}H NMR δ (DMSO) 7.34 (1H, t, *J* 7.8, ArH), 7.52–7.62 (2H, m, ArH), 7.66–7.79 (2H, m, ArH), 8.25 (2H, d, *J* 8.3, ArH), 8.37 (1H, d, *J* 8.4, ArH), and 13.6 (1H, s, NH); ^{13}C NMR δ (DMSO) 111.8, 113.7, 115.0, 120.5, 121.8, 122.9, 126.2, 128.8, 130.0, 132.1, 140.3, 142.1, and 145.9.

10a. Mp 111–113°C (from EtOAc–*n*-hexane) (Found: C, 69.5; H, 5.3; N, 25.05. Calc. for $C_{13}H_{12}N_4$: C, 69.6; H, 5.4; N, 25.0%); ν_{max} (KBr)/cm^{-1} 3352, 3232, 3056, 2912, 1627, 1601, 1577, 1488, 1446, 1299, 1262, 1219, 1152, 1006, 740, and 521; ^{1}H NMR δ 4.32 (2H, s, NH_2), 5.74 (2H, s, CH_2), 6.67 (1H, d, *J* 7.9, ArH), 6.77 (1H, t, *J* 7.5, ArH), 7.14 (1H, t, *J* 7.8, ArH), 7.29–7.36 (2H, m, ArH), 7.42 (1H, t, *J* 6.8, ArH), 7.53 (1H, d, *J* 8.3, ArH), and 8.04 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 50.6, 110.4, 117.2, 118.7, 118.9, 120.4, 124.5, 126.3, 128.0, 130.7, 131.1, 133.1, and 146.5.

11a. Viscous liquid (Found: C, 72.6; H, 6.0; N, 21.35. Calc. for $C_{16}H_{16}N_4$: C, 72.7; H, 6.1; N, 21.2%); ν_{max} (film)/cm^{-1} 3432, 3344, 3224, 3056, 2920, 1624, 1486, 1446, 1304, 1265, 1228, 1153, 996, 918, 740, and 520; ^{1}H NMR δ 3.24–3.31 (1H, m, CH_2), 3.40–3.51 (1H, m, CH_2), 4.02 (2H, s, NH_2), 5.02 (1H, d, *J* 14.3, $=CH_2$), 5.07 (1H, d, *J* 20.6, $=CH_2$), 5.68–5.82 (1H, m, =CH), 6.09 (1H, dd, *J* 9.2 and 6.5, CH), 6.65 (1H, d, *J* 8.0, ArH), 6.84 (1H, t, *J* = 7.6, ArH), 7.14 (1H, dt, *J* 1.4 and 7.7, ArH), 7.28–7.39 (2H, m, ArH), 7.41–7.48 (2H, m, ArH), and 8.05 (1H, d, *J* = 7.4, ArH); ^{13}C NMR δ 36.5, 60.8, 110.8, 117.6, 118.8, 119.2, 120.5, 124.4, 127.7, 128.0, 130.1, 132.6, 133.6, 145.8, and 147.0.

Reaction of 6a with ethyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (500 mg, 2.00 mmol), ethyl bromide (545 mg, 5.00 mmol), and *n*-BuLi (5.00 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-diethylamino)-3-(benzotriazol-1-yl)-2*H*-indazole (**8b**) (153 mg, 25%), **9a** (66 mg, 13%), and **10a** (94 mg, 21%).

8b. Viscous liquid (Found: C, 66.7; H, 6.1; N, 27.25. Calc. for $C_{17}H_{18}N_6$: C, 66.65; H, 5.9; N, 27.4%); ν_{max} (film)/cm^{-1} 3048, 2960, 2856, 1606, 1526, 1444, 1371, 1275, 1206, 1081, 1038, 1000, 966, 938, and 739; ^{1}H NMR δ 0.83 (6H, t, *J* 7.1, CH_3), 3.27 (4H, d, *J* 6.2, CH_2), 7.15–7.21 (1H, m, ArH), 7.30 (2H, d, *J* 8.5, ArH), 7.42–7.56 (3H, m, ArH), 7.83 (1H, d, *J* 8.9, ArH), and 8.23 (1H, d, *J* 7.8, ArH); ^{13}C NMR δ (DMSO) 12.6, 52.7, 110.1, 115.9, 118.6, 118,8, 120.8, 124.3, 124.9, 127.5, 129.2, 135.3, 145.6, and 145.7.

Reaction of 6a with 4-bromo-1-butene. In accordance with the aforementioned general procedure, a mixture of **6a** (400 mg, 1.60 mmol), 4-bromo-1-butene (540 mg, 4.00 mmol), and *n*-BuLi (4.00 mmol) was stirred for 1 h at −78°C and 2 h at room temperature. Chromatography of the reaction mixture gave **9a** (31 mg, 16%), **10a** (72 mg, 20%), 2-[1-(benzotriazol-1-yl)-4-pentenyl]phenylamine (**11c**) (18 mg, 4%), 1-[1-(2-azidophenyl)-4-pentenyl]-1*H*-benzotriazole (**12c**) (88 mg, 18%), [2-{1-(benzotriazol-1-yl)-4-pentenyl}phenyl]butylamine (**17**) (14 mg, 3%).

11c. Viscous liquid (Found: C, 73.6; H, 6.4; N, 19.9. Calc. for $C_{17}H_{18}N_4$: C, 73.35; H, 6.5; N, 20.1%); ν_{max} (film)/cm^{-1} 3434, 3226, 3048, 2924, 1604, 1487, 1441, 1308, 1272, 1220, 1154, 996, 740, and 520; ^{1}H NMR δ 1.97–2.21 (2H, m, $CHCH_2CH_2$), 1.38–1.50 (1H, m, $CHCH_2CH_2$), 2.89–3.01 (1H, m, $CHCH_2CH_2$), 4.95 (1H, d, *J* 17.1, $=CH_2$), 5.03 (1H, d, *J* 10.1, $=CH_2$), 5.76–5.89 (1H, m, =CH), 6.20 (1H, dd, *J* 9.4 and 5.7, CH), 7.10 (1H, dt, *J* 1.0 and 7.3, ArH), 7.18 (1H, dd, *J* 8.0 and 1.0, ArH), 7.25–7.38 (2H, m, ArH), 7.42–7.51 (2H, m, ArH), 7.57 (1H, d, *J* 8.3, ArH), and 8.07 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 30.9, 34.3, 56.1, 110.2, 116.5, 118.4, 120.3, 124.4, 125.9, 127.6, 128.6, 129.9, 131.1, 133.7, 137.1, 137.4, and 146.2.

12c. Viscous liquid (Found: C, 67.2; H, 5.2; N, 27.4. Calc. for $C_{17}H_{16}N_6$: C, 67.1; H, 5.3; N, 27.6%); ν_{max} (film)/cm^{-1} 3056, 2928, 2848, 2112, 1675, 1632, 1601, 1483, 1443, 1264, 1211, 1153, 1070, 993, 910, 743, 696, and 523; ^{1}H NMR δ 2.03–2.15 (2H, m, $CHCH_2CH_2$), 2.50–2.62 (1H, m, $CHCH_2CH_2$), 2.88–3.01 (1H, m, $CHCH_2CH_2$), 4.98 (1H, d, *J* 17.0, $=CH_2$), 5.04 (1H, d, *J* 10.2, $=CH_2$), 5.75–5.91 (2H, m, =CH and CH), 7.25–7.40 (7H, m, ArH), and 8.07 (1H, d, *J* 8.0, ArH); ^{13}C NMR δ 30.9, 34.3, 63.0, 110.2, 116.7, 120.4, 124.3, 127.3, 127.6, 128.7, 129.3, 133.3, 137.2, 139.6, and 146.6.

17. Viscous liquid (Found: C, 75.5; H, 7.65; N, 16.8. Calc. for $C_{21}H_{26}N_4$: C, 75.4; H, 7.8; N, 16.75%); ν_{max} (film)/cm^{-1} 3264, 3056, 2936, 2856, 1630, 1603, 1475, 1440, 1392, 1198,

993, 910, 740, and 518; ^{1}H NMR δ 1.03 (3H, t, *J* 7.3, CH_3), 1.45–1.57 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.69–1.72 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.01–2.14 (2H, m, $CHCH_2CH_2$), 2.48–2.59 (1H, m, $CHCH_2CH_2$), 2.91–3.06 (1H, m, $CHCH_2CH_2$), 3.76 (2H, t, *J* 7.1, NCH_2), 4.93 (1H, d, *J* 17.7, $=CH_2$), 4.98 (1H, d, *J* 10.5, $=CH_2$), 5.73–5.90 (2H, m, =CH and CH), 6.82 (1H, t, *J* = 7.2, NH), 7.13 (1H, t, *J* 6.9, ArH), 7.23 (1H, t, *J* 7.4, ArH), 7.29–7.51 (5H, m, ArH), and 8.06 (1H, d, *J* 7.7, ArH); ^{13}C NMR δ 14.3, 20.9, 31.1, 33.0, 34.5, 44.6, 56.3, 110.6, 116.1, 120.1, 124.3, 127.0, 127.2, 127.3, 128.0, 129.0, 129.4, 133.8, 137.7, and 146.3.

Reaction of 6a with 4-iodo-1-butene. In accordance with the aforementioned general procedure, a mixture of **6a** (350 mg, 1.40 mmol), 4-iodo-1-butene (644 mg, 3.50 mmol), and *n*-BuLi (3.50 mmol) was stirred for 1 h at −78°C and 2 h at room temperature. Chromatography of the reaction mixture gave **9a** (68 mg, 21%), **10a** (44 mg, 14%), **12c** (55 mg, 13%), and unreacted **6a** (14 mg, 4%).

Reaction of 6a with benzyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (320 mg, 1.28 mmol), benzyl bromide (547 mg, 3.20 mmol), and *n*-BuLi (3.20 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-2*H*-indazole (**8d**) (171 mg, 31%), **9a** (48 mg, 16%), **10a** (14 mg, 5%), 2-[{1-(benzotriazol-1-yl)-2-phenyl}ethyl]phenylamine (**11d**) (24 mg, 6%), and unreacted **6a** (13 mg, 4%).

8d. Mp 115–117°C (from EtOAc–*n*-hexane) (Found: C, 75.25; H, 5.0; N, 19.6. Calc. for $C_{27}H_{22}N_6$: C, 75.3; H, 5.15; N, 19.5%); ν_{max} (KBr)/cm^{-1} 3040, 2912, 2848, 1628, 1595, 1555, 1524, 1486, 1446, 1396, 1372, 1278, 1227, 1198, 1166, 1030, 904, 739, 694, and 520; ^{1}H NMR δ 4.49 (4H, s, CH_2), 6.52 (1H, d, *J* 8.3, ArH), 6.99–7.21 (11H, m, ArH), 7.29–7.36 (2H, m, ArH), 7.41–7.47 (2H, m, ArH), 7.89 (1H, d, *J* 8.9, ArH), 8.22 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 61.5, 110.4, 114.9, 118.7, 118.8, 120.3, 124.1, 124.8, 127.5, 128.2, 128.7, 129.6, 134.5, 136.2, 145.4, and 145.5.

11d. Viscous liquid (mixed with **10a**); ^{1}H NMR δ 4.28 (2H, s, NH_2), 4.50 (2H, d, *J* 5.0, CH_2), 6.18 (1H, dd, *J* 8.2 and 4.9, CH), 6.53 (1H, d, *J* 8.3, ArH), 7.09–7.46 (10H, m, ArH), 8.06 (1H, d, *J* 8.3, ArH), and 8.43 (1H, d, *J* 8.3, ArH).

Reaction of 6a with *n*-butyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (350 mg, 1.40 mmol), *n*-butyl bromide (480 mg, 3.50 mmol), and *n*-BuLi (3.50 mmol) was stirred. Chromatography of the reaction mixture gave **9a** (59 mg, 18%), 2-[1-(benzotriazol-1-yl)pentyl]phenylamine (**11e**) (51 mg, 13%), [2-{1-(benzotriazol-1-yl)pentyl}phenyl]butylamine (**18**) (50 mg, 11%).

11e. Viscous liquid (Found: C, 72.6; H, 7.3; N, 19.9. Calc. for $C_{17}H_{20}N_4$: C, 72.8; H, 7.2; N, 20.0%); ν_{max} (film)/cm^{-1} 3048, 2928, 2856, 1600, 1577, 1483, 1448, 1368, 1264, 1214, 1155, 774, 739, 694, and 518; ^{1}H NMR δ 0.89 (3H, t, *J* 7.2, CH_3), 1.24–1.37 (4H, m, $CH_2CH_2CH_2CH_3$), 2.45–2.56 (1H, m, $CHCH_2$), 2.74–2.87 (1H, m, $CHCH_2$), 4.05 (2H, s, NH_2), 5.80 (1H, dd, *J* 9.0 and 6.5, CH), 7.29–7.40 (7H, m, ArH), and 8.07 (d, *J* 8.0, ArH); ^{13}C NMR δ 14.3, 22.7, 29.2, 34.9, 64.2, 110.3, 120.4, 124.3, 126.3, 127.3, 127.5, 128.6, 128.8, 129.3, 133.2, 139.8, and 146.6.

18. Viscous liquid (Found: C, 67.2; H, 5.2; N, 27.4. Calc. for $C_{21}H_{28}N_4$: C, 67.1; H, 5.3; N, 27.6%); ν_{max} (film)/cm^{-1} 3385, 3056, 2928, 2850, 1601, 1578, 1473, 1446, 1392, 1193, 1153, 1086, 774, 740, and 521; ^{1}H NMR δ 0.88 (3H, t, *J* 6.8, $CHCH_2CH_2CH_2CH_3$), 1.02 (3H, t, *J* 7.3, $NCH_2CH_2CH_2CH_3$), 1.27–1.44 (4H, m, $CHCH_2CH_2CH_2CH_3$), 1.45–1.56 (2H, m, $NCH_2CH_2CH_2CH_3$), 1.69–180 (2H, m, $NCH_2CH_2CH_2CH_3$), 2.40–2.51 (1H, m, $CHCH_2CH_2CH_2CH_3$), 2.77–2.90 (1H, m, $CHCH_2CH_2CH_2CH_3$), 3.76 (2H, dt, *J* 3.4 and 7.0, NCH_2), 6.72 (1H, t, *J* 6.9, NH), 7.12 (1H, dt, *J* 1.1 and 7.4, ArH), 7.24 (1H, dt, *J* 1.4 and 7.9, ArH), 7.31–7.49 (5H, m, ArH), and 8.05 (1H, d, *J* 7.3, ArH); ^{13}C NMR δ 14.2, 14.3, 20.7, 22.7, 29.2, 32.1, 35.1, 44.0, 57.3, 110.5, 117.2, 120.1, 124.1, 127.0, 127.1, 127.3, 128.9, 133.8, and 146.3.

Reaction of 6a with *tert*-butyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (350 mg, 1.40 mmol), *tert*-butyl bromide (480 mg, 3.50 mmol), and *n*-BuLi (3.50 mmol) was stirred. Chromatography of the reaction mixture gave **9a** (69 mg, 21%), **10a** (60 mg, 14%), and unreacted **6a** (109 mg, 31%).

Reaction of 6b with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6b** (400 mg, 1.43 mmol), allyl bromide (432 mg, 3.58 mmol), and *n*-BuLi (3.58 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-5-methoxy-2*H*-indazole (**8g**) (124 mg, 24%), 3-(benzotriazol-1-yl)-5-methoxy-2*H*-indazole (**9g**) (72 mg, 19%), [2-(benzotriazol-1-yl)methyl-4-methoxy]phenylamine (**10g**) (29 mg. 8%), [2-{1-(benzotriazol-1-yl)-3-butenyl}-4-methoxy]phenylamine (**11g**) (13 mg, 3%), and unreacted **6b** (12 mg, 3%).

8g. Mp 151–153°C (from EtOAc–*n*-hexane) (Found: C, 66.7; H, 5.5; N, 23.3. Calc. for $C_{20}H_{20}N_6O$: C, 66.65; H, 5.6; N, 23.3%); ν_{max} (KBr)/cm^{-1} 3064, 2936, 2848, 1638, 1600, 1558, 1499, 1446, 1278, 1212, 1036, 926, 809, 742, and 521; ^{1}H NMR δ 3.69 (3H, s, OCH_3), 3.83 (4H, d, *J* 7.6, CH_2), 4.99 (2H, d, *J* 10.1, $=CH_2$), 5.04 (2H, d, *J* 17.2, $=CH_2$), 5.47–5.62 (2H, m, =CH), 6.43 (1H, d, *J* 2.2, ArH), 7.09 (1H, dd, *J* 9.4, 2.4, ArH), 7.32 (1H, d, *J* 6.7, ArH), 7.46–7.59 (2H, m, ArH), 7.69 (1H, d, *J* 9.4, ArH), and 8.23 (1H, d, *J* 8.1, ArH); ^{13}C NMR δ 55.8, 60.8, 110.5, 116.0, 120.3, 120.4, 120.8, 122.7, 124.9, 126.3, 128.9, 132.9, 135.2, 141.9, and 145.7.

Crystal data for 8g. $C_{20}H_{20}N_6O$, *M* = 360.42, triclinic, *a* = 8.009(3), *b* = 8.019(2), *c* = 14.760(8) Å, α = 81.91(5), β = 82.16(4), γ = 96.01(3)°, *U* = 928.5(7) Å^3, *T* = 293(2) K, space group *P*-1, *Z* = 2, μ(Mo-K$_\alpha$) = 0.085 mm^{-1}, λ = 0.71070 Å, 3266 reflections measured, 3265 unique (R_{int} = 0.0029) which were used in all calculations. The final $wR(F^2)$ was 0.1110. CCDC 212914.

9g. Mp 234–236°C (from CH_2Cl_2–*n*-hexane) (Found: C, 63.4; H, 4.0; N, 26.3. Calc. for $C_{14}H_{11}N_5O$: C, 63.4; H, 4.2; N, 26.4%); ν_{max} (KBr)/cm^{-1} 3130, 3048, 2928, 1632, 1609, 1525, 1478, 1431, 1386, 1344, 1273, 1167, 1094, 984, 918, 892, and 740; ^{1}H NMR δ (DMSO) 3.85 (3H, s, OCH_3), 7.19 (1H, dd, *J* 9.1 and 2.2, ArH), 7.54–7.63 (3H, m, ArH), 7.73 (1H, t, *J* 7.3, ArH), 8.24 (1H, d, *J* 8.3, ArH), 8.32 (1H, d, *J* 8.3, ArH), and 13.5 (1H, s, NH); ^{13}C NMR δ (DMSO) 56.3, 100.0, 113.0, 113.7, 115.2, 120.4, 121.2, 126.1, 129.9, 132.1, 138.0, 139.7, 145.8, and 155.9.

10g. Viscous liquid (mixed with **11g**); ^{1}H NMR δ 3.65 (3H, s, OCH_3), 4.29 (2H, s, NH_2), 5.78 (2H, s, CH_2), 6.65 (1H, d, *J* 2.9, ArH), 6.84 (1H, d, *J* 8.9, ArH), 7.31–7.58 (4H, m, ArH), and 8.08 (1H, d, *J* 8.3, ArH).

11g. Viscous liquid (mixed with **10g**); ^{1}H NMR δ 3.20–3.29 (1H, m, CH_2), 3.36–3.48 (1H, m, CH_2), 3.62 (3H, s, OCH_3), 4.10 (2H, s, NH_2), 5.04 (1H, d, *J* 11.7, $=CH_2$), 5.11 (1H, d, *J* 19.1, $=CH_2$), 5.61–5.77 (1H, m, =CH), 6.10 (1H, dd, *J* 9.3

and 6.1, CH), 6.58 (1H, d, *J* 8.8, ArH), 7.10–7.59 (m, 5H, ArH), and 8.11 (1H, d, *J* 8.2, ArH).

Reaction of 1-[(2-azido-3-methyl)phenylmethyl]benzotriazole (6c) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6c** (350 mg, 1.32 mmol), allyl bromide (399 mg, 3.30 mmol), and *n*-BuLi (3.30 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-7-methyl-2*H*-indazole (**8h**) (168 mg, 34%), 3-(benzotriazol-1-yl)-7-methyl-2*H*-indazole (**9h**) (43 mg, 13%), [2-(benzotriazol-1-yl)methyl-6-methyl]phenylamine (**10h**) (32 mg, 10%), [2-{1-(benzotriazol-1-yl)-3-butenyl}-6-methyl]phenylamine (**11h**) (18 mg, 5%).

8h. Mp 123–125°C (from EtOAc–*n*-hexane) (Found: C, 69.6; H, 5.9; N, 24.5. Calc. for $C_{20}H_{20}N_6$: C, 69.75; H, 5.85; N, 24.4%); ν_{max} (KBr)/cm^{-1} 3056, 2904, 2840, 1627, 1604, 1547, 1505, 1443, 1371, 1280, 1233, 1168, 1038, 990, 924, 864, 747, and 521; ^{1}H NMR δ 2.71 (3H, s, CH_3), 3.89 (4H, d, *J* 6.6, CH_2), 4.97 (2H, d, *J* 10.1, $=CH_2$), 5.05 (2H, d, *J* 17.1, $=CH_2$), 5.52–5.66 (2H, m, =CH), 7.01–7.17 (3H, m, ArH), 7.31 (1H, d, *J* 7.8, ArH), 7.47–7.58 (2H, m, ArH), and 8.22 (1H, d, *J* 7.9, ArH); ^{13}C NMR δ 17.2, 60.7, 110.5, 115.6, 116.0, 120.2, 120.7, 124.5, 124.9, 126.2, 128.9, 129.0, 133.1, 135.2, 145.6, and 145.7.

9h. Mp 210–212°C (from CH_2Cl_2–*n*-hexane) (Found: C, 67.6; H, 4.6; N, 28.0. Calc. for $C_{14}H_{11}N_5$: C, 67.5; H, 4.45; N, 28.1%); ν_{max} (KBr)/cm^{-1} 3144, 3056, 2928, 1606, 1516, 1440, 1344, 1270, 1246, 1176, 1153, 1097, 1035, 852, 779, 737, and 521; ^{1}H NMR δ (DMSO) 2.61 (3H, s, CH_3), 7.23 (1H, t, *J* 7.9, ArH), 7.32 (1H, d, *J* 6.8, ArH), 7.58 (1H, t, *J* 7.9, ArH), 7.76 (1H, t, *J* 7.8, ArH), 8.05 (1H, d, *J* 8.1, ArH), 8.25 (1H, d, *J* 8.3, ArH), 8.35 (1H, d, *J* 8.3, ArH), and 13.7 (1H, s, NH); ^{13}C NMR δ (DMSO) 17.4, 113.7, 114.9, 119.1, 120.5, 121.7, 123.2, 126.1, 128.4, 130.0, 132.1, 140.5, 142.2, and 145.9.

10h. Viscous liquid (mixed with **11h**); ^{1}H NMR δ 2.14 (3H, s, CH_3), 4.28 (2H, s, NH_2), 5.79 (2H, s, CH_2), 6.73 (1H, t, *J* 7.5, ArH), 7.08 (1H, d, *J* 7.2, ArH), 7.24–7.61 (4H, m, ArH), and 8.06 (1H, d, *J* 8.3, ArH).

11h. Viscous liquid (mixed with **10h**); ^{1}H NMR δ 2.19 (3H, s, CH_3), 4.06 (2H, s, NH_2), 3.21–3.30 (1H, m, CH_2), 3.39–3.50 (1H, m, CH_2), 5.04 (1H, d, *J* 11.3, $=CH_2$), 5.11 (1H, d, *J* 18.7, $=CH_2$), 5.65–5.79 (1H, m, =CH), 6.10 (1H, dd, *J* 9.2 and 6.5, CH), 6.72 (1H, t, *J* 7.5, ArH), 7.07 (1H, d, *J* 7.6, ArH), 7.18–7.54 (4H, m, ArH), and 8.05 (1H, d, *J* 8.3, ArH).

Reaction of 1-[(2-azido-5-bromo)phenylmethyl]benzotriazole (6d) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6d** (300 mg, 0.91 mmol), allyl bromide (276 mg, 2.28 mmol), and *n*-BuLi (2.28 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-5-bromo- 2*H*-indazole (**8i**) (97 mg, 26%), 3-(benzotriazol-1-yl)-5-bromo-2*H*- indazole (**9i**) (40 mg, 14%), [2-(benzotriazol-1-yl) methyl-4-bromo]phenylamine (**10i**) (19 mg, 7%), [2-{1-(benzotriazol-1-yl)-3-butenyl}-4-bromo]phenylamine (**11i**) (12 mg, 4%), and unreacted **6d** (6 mg, 2%).

8i. Viscous liquid (Found: C, 55.6; H, 4.35, N, 20.0. Calc. for $C_{19}H_{17}BrN_6$: C, 55.8; H, 4.2; N, 20.5%); ν_{max} (film)/cm^{-1} 3064, 2936, 2856, 1632, 1603, 1582, 1558, 1516, 1444, 1384, 1278, 1196, 1092, 990, 924, 739, and 518; ^{1}H NMR δ 3.85 (4H, d, *J* 6.8, CH_2), 4.99 (2H, d, *J* 10.8, $=CH_2$), 5.04 (2H, d, *J* 17.7, $=CH_2$), 5.50–5.65 (2H, m, =CH), 7.27–7.35 (2H, m, ArH), 7.48 (1H, s, ArH), 7.52 (1H, d, *J* 7.7, ArH), 7.57 (1H, d, *J* = 8.8, ArH), and 8.23 (1H, d, *J* 8.1, ArH); ^{13}C NMR δ 60.8, 110.2, 116.8, 118.0, 120.6, 120.7, 120.8, 120.9, 124.6, 129.3, 131.3, 132.6, 135.0, 143.7, and 145.7.

9i. Mp 260–262°C (from CH_2Cl_2–*n*-hexane) (Found: C, 49.6; H, 2.6; N, 22.35. Calc. for $C_{13}H_8BrN_5$: C, 49.7; H, 2.6; N, 22.3%); ν_{max} (KBr)/cm^{-1} 3140, 3056, 2930, 2889, 1612, 1541, 146, 1381, 1339, 1241, 1165, 1089, 984, 918, 892, 737, and 642; ^{1}H NMR δ (DMSO) 7.59 (1H, t, *J* 7.4, ArH), 7.66–7.72 (2H, m, ArH), 7.77 (1H, t, *J* 7.3, ArH), 8.26 (1H, d, *J* 8.3, ArH), 8.36 (1H, d, *J* 8.3, ArH), 8.42 (1H, s, ArH), and 13.8 (1H, s, NH); ^{13}C NMR δ (DMSO) 113.7, 114.0, 115.0, 116.3, 120.6, 124.0, 126.3, 130.2, 131.6, 131.9, 140.8, and 145.9.

10i. Viscous liquid (mixed with **11i**); ^{1}H NMR δ 4.32 (2H, br, NH_2), 5.77 (2H, s, CH_2), 7.10–7.62 (6H, m, ArH), and 8.11 (1H, d, *J* 8.3, ArH).

11i. Viscous liquid (mixed with **10i**); ^{1}H NMR δ 3.21–3.30 (1H, m, CH_2), 3.35–3.49 (1H, m, CH_2), 4.25 (2H, br, NH_2), 5.01 (1H, d, *J* 10.8, $=CH_2$), 5.07 (1H, d, *J* 18.2, $=CH_2$), 5.65–5.81 (1H, m, =CH), 6.60 (1H, dd, *J* 9.1 and 6.0, CH), 7.10–7.62 (6H, m, ArH), and 8.17 (1H, d, *J* 8.2, ArH).

Reaction of 1-[(2-azido-4-chloro)phenylmethyl]benzotriazole (6e) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6e** (480 mg, 1.69 mmol), allyl bromide (512 mg, 4.23 mmol), and *n*-BuLi (4.23 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-6-chloro-2*H*-indazole (**8j**) (160 mg, 26%), 3-(benzotriazol-1-yl)-6-chloro-2*H*-indazole (**9j**) (73 mg, 16%), [2-(benzotriazol-1-yl)methyl-5-chloro]phenylamine (**10j**) (22 mg, 5%), [2-{1-(benzotriazol-1-yl)-3-butenyl}-5-chloro]phenylamine (**11j**) (30 mg, 6%), and unreacted **6e** (10 mg, 2%).

8j. Mp 80–82°C (from CH_2Cl_2–*n*-hexane) (Found: C, 62.5; H, 4.6; N, 23.2. Calc. for $C_{19}H_{17}ClN_6$: C, 62.55; H, 4.7; N, 23.0%); ν_{max} (KBr)/cm^{-1} 3064, 2908, 2848, 1630, 1608, 1518, 1473, 1443, 1374, 1280, 1195, 1163, 1043, 992, 928, 851, 744, and 520; ^{1}H NMR δ 3.85 (4H, d, *J* 6.7, CH_2), 4.98 (2H, d, *J* 10.1, $=CH_2$), 5.04 (2H, d, *J* 17.1, $=CH_2$), 5.48–5.62 (2H, m, =CH), 7.12 (1H, dd, *J* 8.9, 1.7, ArH), 7.22–7.31 (2H, m, ArH), 7.48–7.60 (2H, m, ArH), 7.80 (1H, d, *J* 1.3, ArH), and 8.23 (1H, d, *J* 8.1, ArH); ^{13}C NMR δ 60.8, 110.3, 114.0, 117.8, 120.1, 120.7, 120.9, 125.1, 125.8, 125.9, 129.3, 132.6, 133.6, 135.0, 145.4, and 145.7.

9j. Mp 172–174°C (from CH_2Cl_2–*n*-hexane) (Found: C, 57.8; H, 3.1; N, 26.1. Calc. for $C_{13}H_8ClN_5$: C, 57.9; H, 3.0; N, 26.0%); ν_{max} (KBr)/cm^{-1} 3156, 3052, 2908, 2850, 1639, 1608, 1523, 1478, 1436, 1375, 1278, 1244, 1196, 1049, 984, 918, 852, 738, and 516; ^{1}H NMR δ (DMSO) 7.35 (1H, d, *J* = 8.7, ArH), 7.59 (1H, t, *J* 7.8, ArH), 7.75 (1H, d, *J* 7.6, ArH), 7.79 (1H, s, ArH), 8.25 (1H, d, *J* 5.9, ArH), 8.28 (1H, d, *J* 6.3, ArH), 8.36 (1H, d, *J* 8.4, ArH), and 13.7 (1H, s, NH); ^{13}C NMR δ (DMSO) 111.3, 113.7, 120.5, 123.6, 123.7, 126.2, 126.3, 130.2, 131.9, 133.8, 142.3, and 145.9

10j. Viscous liquid (mixed with **11j**); ^{1}H NMR δ 4.27 (2H, s, NH_2), 5.77 (2H, s, CH_2), 7.06 (1H, d, *J* 8.5, ArH), 7.21–7.42 (4H, m, ArH), 7.48 (1H, s, ArH), and 8.06 (1H, d, *J* 7.9, ArH).

11j. Viscous liquid (mixed with **10j**); ^{1}H NMR δ 3.19–3.30 (1H, m, CH_2), 3.35–3.49 (1H, m, CH_2), 4.17 (2H, s, NH_2), 5.01 (1H, d, *J* 10.7, $=CH_2$), 5.06 (1H, d, *J* 18.9, $=CH_2$), 5.63–5.80 (1H, m, =CH), 6.02 (1H, dd, *J* 9.1 and 6.6, CH), 6.64 (1H, d, *J* 2.0, ArH), 6.78 (1H, dd, *J* 8.3 and 2.0, ArH), 7.31–7.43 (4H, m, ArH), and 8.04 (1H, d, *J* 7.7, ArH).

Reaction of 1-[(2-azido-5-chloro)phenylmethyl]benzotriazole (6f) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6f** (350 mg, 1.23 mmol), allyl bromide (377 mg, 3.08 mmol), and *n*-BuLi (3.08 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-dibenzylamino)-3-(benzotriazol-1-yl)-5-chloro-2*H*-indazole (**8k**) (126 mg, 28%), 3-(benzotriazol-1-yl)-5-chloro-2*H*-indazole (**9k**) (56 mg, 17%), [2-(benzotriazol-1-yl)methyl-4-chloro]phenylamine (**10k**) (6 mg, 2%), [2-{1-(benzotriazol-1-yl)-3-butenyl}-4-chloro]phenylamine (**11k**) (29 mg, 8%), and unreacted **6f** (14 mg, 4%).

8k. Mp 102–104°C (from CH_2Cl_2–*n*-hexane) (Found: C, 62.6; H, 4.8; N, 22.9. Calc. for $C_{19}H_{17}ClN_6$: C, 62.55; H, 4.7; N, 23.0%); ν_{max} (KBr)/cm^{-1} 3053, 2910, 2848, 1627, 1600, 1520, 1445, 1380, 1284, 1159, 1045, 996, 924, 849, 742, and 521; ^{1}H NMR δ 3.85 (4H, d, *J* 6.7, CH_2), 4.99 (2H, d, *J* = 12.7, =CH_2), 5.04 (2H, d, *J* 18.0, =CH_2), 5.48–5.63 (2H, m, =CH), 7.27–7.36 (3H, m, ArH), 7.46–7.61 (2H, m, ArH), 7.75 (1H, d, *J* 9.1, ArH), and 8.23 (1H, d, *J* 8.1, ArH); ^{13}C NMR δ 110.2, 116.1, 117.4, 120.5, 120.7, 120.9, 125.1, 129.0, 129.3, 130.2, 132.6, 135.2, 143.7, and 145.7.

9k. Mp 198–200°C (from CH_2Cl_2–*n*-hexane) (Found: C, 57.8; H, 2.9; N, 26.0. Calc. for $C_{13}H_8ClN_5$: C, 57.9; H, 3.0; N, 26.0%); ν_{max} (KBr)/cm^{-1} 3144, 3054, 2918, 2838, 1630, 1609, 1523, 1450, 1385, 1340, 1278, 1167, 1039, 994, 928, 837, 737, and 516; ^{1}H NMR δ (DMSO) 7.55 (1H, t, *J* 2.6, ArH), 7.58 (1H, d, *J* 2.2, ArH), 7.75 (2H, d, *J* 9.1, ArH), 8.25 (1H, d, *J* 5.7, ArH), 8.26 (1H, d, *J* 4.3, ArH), 8.36 (1H, d, *J* 8.3, ArH), and 13.8 (1H, s, NH); ^{13}C NMR δ (DMSO) 111.7, 113.5, 121.0, 123.7, 123.8, 126.5, 126.6, 130.1, 132.0, 133.9, 142.5, and 145.9.

10k. Viscous liquid (mixed with **11k**); ^{1}H NMR δ 4.35 (2H, s, NH_2), 5.70 (2H, s, CH_2), 6.61 (1H, d, *J* 8.5, ArH), 7.11 (1H, d, *J* 8.4, ArH), 7.28–7.54 (4H, m, ArH), and 8.12 (1H, d, *J* 8.1, ArH).

11k. Viscous liquid (mixed with **10k**); ^{1}H NMR δ 3.21–3.29 (1H, m, CH_2), 3.39–3.50 (1H, m, CH_2), 4.05 (2H, s, NH_2), 5.02 (1H, d, *J* 11.6, =CH_2), 5.08 (1H, d, *J* 17.1, =CH_2), 5.66–5.81 (1H, m, =CH), 6.01 (1H, dd, *J* 9.2 and 6.1, CH), 6.58 (1H, d, *J* 8.6, ArH), 7.09 (1H, d, *J* 8.5, ArH), 7.31–7.59 (4H, m, ArH), and 8.06 (1H, d, *J* 8.2, ArH).

Reaction of 1-[(2-azido-5-nitro)phenylmethyl]benzotriazole (6g) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6g** (300 mg, 1.02 mmol), allyl bromide (308 mg, 2.55 mmol), and *n*-BuLi (2.55 mmol) was stirred to give very complex mixtures, which were unidentifiable.

Reaction of 1-(4-azidophenylmethyl)benzotriazole (6h) with allyl bromide. In accordance with the aforementioned general procedure, **6h** (500 mg, 2.00 mmol) was treated with *n*-BuLi (4.00 mmol), followed by addition of allyl bromide (484 mg, 4.00 mmol). Chromatography of the reaction mixture gave 1-[{(4-azidophenyl)(allyl)}methyl]-1*H*-benzotriazole (**19**) (23 mg, 4%), 4-[(benzotriazol-1-yl)methyl]phenylamine (**20**) (202 mg, 45%), and unreacted **6h** (140 mg, 28%).

19. Viscous liquid (Found: C, 66.4; H, 4.8; N, 29.0. Calc. for $C_{16}H_{14}N_4$: C, 66.2; H, 4.9; N, 28.95%); ν_{max} (film)/cm^{-1} 3056, 2920, 2848, 2112, 1683, 1595, 1500, 1443, 1276, 1224, 1155, 1064, 992, 916, 824, 744, and 529; ^{1}H NMR δ 3.17–3.28 (1H, m, CH_2), 3.46–3.58 (1H, m, CH_2), 5.04 (1H, d, *J* 10.2, =CH_2), 5.13 (d, *J* 18.4, =CH_2), 5.65–5.77 (1H, m, =CH), 5.83 (1H, dd, *J* 8.8, 6.7, CH), 7.00 (2H, d, *J* 8.6, ArH), 7.34–7.50 (5H, m, ArH), and 8.07 (1H, d, *J* 7.8, ArH).

20. Mp 128–130°C (from EtOAc–*n*-hexane) (Found: C, 69.7; H, 5.3; N, 25.1. Calc. for $C_{13}H_{12}N_4$: C, 69.6; H, 5.4; N, 25.0%); ν_{max} (KBr)/cm^{-1} 3448, 3336, 3040, 2920, 1611, 1507, 1436, 1283, 1216, 1176, 1126, 1076, 830, 776, 736, and 518; ^{1}H NMR δ 3.76 (2H, s, NH_2), 5.73 (2H, s, CH_2), 6.61 (2H, d, *J* 8.4, ArH), 7.13 (2H, d, *J* 10.1, ArH), 7.33–7.42 (3H, m, ArH), and 8.04 (1H, d, *J* 8.1, ArH); ^{13}C NMR δ 52.6, 110.4, 115.6, 120.3, 124.2, 124.6, 127.6, 129.5, 133.4, 146.7, and 147.2.

Reaction of 1-(2-azidophenylmethyl)-6-chloro-1*H*-benzotriazole (6i) with allyl bromide. In accordance with the aforementioned general procedure, a mixture of **6i** (199 mg, 0.70 mmol), allyl bromide (212 mg, 1.75 mmol), and *n*-BuLi (1.75 mmol) was stirred. Chromatography of the reaction mixture gave 2-(*N*,*N*-diallylamino)-3-(6-chlorobenzotriazol-1-yl)-2*H*-indazole (**8l**) (77 mg, 30%), 3-(6-chlorobenzotriazol-1-yl)-2*H*-indazole (**9l**) (23 mg, 12%), 2-[(6-chlorobenzotriazol-1-yl)methyl]-phenylamine (**10l**) (11 mg, 6%), and unreacted **6i** (4 mg, 2%).

8l. Viscous liquid (Found: C, 62.6; H, 4.6; N, 23.15. Calc. for $C_{19}H_{17}ClN_6$: C, 62.55; H, 4.7; N, 23.0%); ν_{max} (film)/cm^{-1} 3056, 2906, 2865, 1631, 1608, 1518, 1473, 1444, 1374, 1280, 1166, 1043, 992, 928, 851, 744, and 522; ^{1}H NMR δ 3.87 (4H, d, *J* 6.3, CH_2), 5.01 (2H, d, *J* 9.0, =CH_2), 5.06 (2H, d, *J* 15.9, =CH_2), 5.49–5.64 (2H, m, =CH), 7.22 (1H, d, *J* 6.7, ArH), 7.29–7.34 (2H, m, ArH), 7.42–7.49 (2H, m, ArH), 7.82 (1H, d, *J* 8.9, ArH), and 8.15 (1H, d, *J* 8.8, ArH); ^{13}C NMR δ 60.9, 110.5, 115.7, 118.5, 118.9, 120.8, 121.7, 124.6, 126.2, 127.6, 132.7, 135.7, 144.3 and 145.4.

9l. Mp 215–217°C (from CH_2Cl_2–*n*-hexane) (Found: C, 57.95; H, 3.1; N, 26.0. Calc. for $C_{13}H_8ClN_5$: C, 57.9; H, 3.0; N, 26.0%); ν_{max} (KBr)/cm^{-1} 3124, 3058, 2920, 2846, 1627, 1600, 1523, 1456, 1385, 1340, 1278, 1175, 1039, 994, 928, 837, 737, 694, and 516; ^{1}H NMR δ (DMSO) 7.35 (1H, dd, *J* 7.7 and 6.6, ArH), 7.56 (1H, dt, *J* 1.0 and 6.9, ArH), 7.61 (1H, dd, *J* 8.9 and 1.9, ArH), 7.70 (1H, d, *J* 8.5, ArH), 8.24 (1H, d, *J* 8.3, ArH), 8.29 (1H, d, *J* 8.8, ArH), 8.39 (1H, d, *J* 1.7, ArH), and 13.6 (s, 1H, NH); ^{13}C NMR δ (DMSO) 111.8, 113.3, 114.8, 121.7, 122.1, 123.1, 126.9, 128.9, 132.6, 134.9, 140.0, 142.1, and 144.6.

10l. Mp 87–89°C (from CH_2Cl_2–*n*-hexane) (Found: C, 60.5; H, 4.1; N, 21.6. Calc. for $C_{13}H_{11}ClN_4$: C, 60.35; H, 4.3; N, 21.7%); ν_{max} (KBr)/cm^{-1} 3348, 3231, 3042, 2950, 2856, 1601, 1580, 1441, 1281, 1154, 1072, 906, 742, and 521; ^{1}H NMR δ 4.29 (2H, s, NH_2), 5.77 (2H, s, CH_2), 7.10–7.19 (2H, m, ArH), 7.28 (1H, d, *J* 8.0, ArH), 7.31 (1H, d, *J* 8.7, ArH), 7.42–7.52 (2H, m, ArH), and 8.17 (1H, d, *J* 8.8, ArH); ^{13}C NMR δ 50.6, 110.1, 118.8, 121.4, 125.6, 125.7, 125.8, 130.4, 130.6, 133.9, 134.3, 138.4, and 145.1.

Reaction of 6a with a mixture of allyl bromide and benzyl bromide. In accordance with the aforementioned general procedure, a mixture of **6a** (330 mg, 1.32 mmol), allyl bromide (191 mg, 1.58 mmol), benzyl bromide (270 mg, 1.58 mmol), and *n*-BuLi (3.30 mmol) in THF was stirred for 1 h at −78°C to room temperature for 2 h. TLC (silica gel, EtOAc: *n*-hexane = 1:4) showed four major spots (R_f = 0.79, 0.70, 0.42, and 0.27). The mixture was chromatographed on a silica gel (2.5 × 13 cm^2). Elution with EtOAc and *n*-hexane (1:6) gave **8a** (40 mg, 7%), a mixture of compounds (114 mg), **9a** (37 mg, 12 %), and **10a** (29 mg, 10%). Separation of the mixture has been unsuccessful. However, the ^{1}H NMR spectrum of the mixture indicated that the mixture consisted of **8a** (39 mg, 9%) and 2-(*N*-allyl-*N*-benzylamino)-3-(benzotriazol-1-yl)-2*H*-indazole (**23**) (75 mg, 15%). FAB MS showed mass

number (*m*/*z*) 331 and 381, which corresponding to the molecular weights of **8a** plus 1 and **23** plus 1, respectively.

23. Viscous liquid (mixed with **8a**); ν_{max} (KBr)/cm^{-1} 3056, 2924, 2840, 1628, 1600, 1554, 1523, 1444, 1370, 1226, 1160, 990, 942, 830, 740, and 520; ^{1}H NMR δ 3.97 (1H, d, *J* 4.6, C*H*$_2$CH=CH$_2$), 4.09 (2H, s, C*H*$_2$Ph), 5.06 (1H, d, *J* 16.9, =CH$_2$), 5.14 (1H, d, *J* 17.2, =CH$_2$), 5.71–5.87 (1H, m, =CH), 6.77–6.97 (4H, m, ArH), 7.01–7.25 (3H, m, ArH), 7.30–7.51 (4H, m, ArH), 7.85 (1H, d, *J* 8.7, ArH), and 8.21 (1H, d, *J* 8.3, ArH); ^{13}C NMR δ 61.1, 61.6, 110.4, 118.7, 120.5, 124.2, 124.8, 127.5, 128.1, 128.6, 128.7, 128.9, 129.5, 129.6, 132.8, 134.7, 135.9, 145.4, and 145.5.

Reaction of 6a with allyl bromide in the presence of various bases. In accordance with the aforementioned general procedure, **6a** (200 mg, 1.25 mmol) was treated with bases such as *tert*-BuLi (1.88 mmol), $NaNH_2$ (1.88 mmol), $KN(SiMe_3)_2$ (1.88 mmol), LDA (1.88 mmol) followed by TMEDA (145 mg, 1.25 mmol), and *n*-BuLi (1.88 mmol) followed by *tert*-BuOK (140mg, 1.25 mmol) in THF (25 mL) for 1 h at −78°C and then 2 h at room temperature. The only exception was the reaction with NaH (1.88 mmol) for 5 h at room temperature. The reaction was quenched by addition of water (30 mL). The mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined extract was dried over $MgSO_4$. Chromatography (2.5 × 10 cm^2, EtOAc:*n*-hexane = 1:5) of the residue gave unreacted **6a** and **8a**-**10a**, depending on the bases. The results are summarized in Table 3.

General procedure for the reactions of simple aryl azides with *n*-BuLi. To a stirred solution of aryl azides (4.88 mmol) in THF (25 mL) for 1 h at −78°C was added *n*-BuLi (9.76 mmol). The mixture was stirred for 2 h at room temperature and worked up as usual. Chromatography of the residue using a mixture of EtOAc and *n*-hexane (1:10) gave alkyl aryl amines **22**, aryl amines **22**, and unreacted aryl azides.

Reaction with *p*-azidotoluene. In accordance with the aforementioned general procedure, *p*-azidotoluene (540 mg, 4.06 mmol) was treated with *n*-BuLi (8.12 mmol) to give *p*-toluidine (**21a**) (300 mg, 69%), *N*-butyl-*p*-toluidine [14] (**22a**) (53 mg, 8%) and unreacted *o*-azidotoluene (5 mg, 1%).

Reaction with *o*-azidotoluene. In accordance with the aforementioned general procedure, *o*-azidotoluene (650 mg, 4.88 mmol) was treated with *n*-BuLi (9.76 mmol) to give *o*-toluidine (**21b**) (397 mg, 76%), *N*-butyl-*o*-toluidine [14] (**22b**) (48 mg, 6%) and unreacted *o*-azidotoluene (13 mg, 2%).

Reaction with *o*-azidoethylbenzene. In accordance with the aforementioned general procedure, *o*-azidoethylbenzene (520 mg, 3.53 mmol) was treated with *n*-BuLi (7.06 mmol) to give *o*-ethylamine (**21c**) (295 mg, 69%) and *N*-butyl-2-ethylphenyl amine [15] (**22c**) (50 mg, 8%).

Reaction with 2-azidodiphenylmethane. In accordance with the aforementioned general procedure, 2-azidodiphenylmethane (500 mg, 2.39 mmol) was treated with *n*-BuLi (4.78 mmol) to give *o*-(*n*-butylamino)diphenylmethane [16] (**22d**) (40 mg, 7%) and 2-benzylaniline [17] (**21d**) (315 mg, 72%).

Reaction of 6a with methylmagnesium bromide. To a solution of methylmagnesium bromide (250 mg, 2.10 mmol) in THF (15 mL) at 0°C was added **6a** (350 mg, 1.40 mmol). The mixture was stirred for 1 h at 0°C and then at room temperature for 2 h. The mixture was worked up as usual and chromatographed on a silica gel (2.5 × 5 cm^2) using a mixture of EtOAc and *n*-hexane (1:1) to give 2-[(benzotriazol-1-yl)methyl]phenyl methyltriazene (**13**) (338 mg, 91%). Mp 133–135°C (from CH_2Cl_2–*n*-hexane) (Found: C, 63.0; H, 5.3; N, 31.65. Calc. for $C_{14}H_{14}N_6$: C, 63.1; H, 5.3; N, 31.6%); ν_{max} (KBr)/cm^{-1} 3263, 3066, 3003, 2954, 1431, 1371, 1220, 1077, 943, 746, 718, and 531; ^{1}H NMR δ 3.24 (3H, s, CH_3), 6.16 (2H, s, CH_2), 7.07–7.07 (2H, m, ArH), 7.25–7.38 (3H, m, ArH), 7.42–7.51 (2H, m, ArH), 8.05 (1H, d, *J* 7.1, ArH), and 8.36 (1H, s, NH); ^{13}C NMR δ 48.4, 110.7, 120.2, 124.2, 126.7, 127.5, 129.4, 129.6, 133.4, and 146.6.

Preparation of 1-(2-aminophenylmethyl)benzotriazole 10a. In accordance with the literature procedure [7], a solution of 1-(2-azidophenylmethyl)benzotriazole (**6a**) (250 mg, 1.00 mmol) in a mixture of THF (30 mL) and MeOH (0.3 mL) was treated with $NaBH_4$ (12 mg, 0.30 mmol). The mixture was heated at reflux for 2 h. Work-up gave **10a** (202 mg, 90%).

Reaction of 10a with allyl bromide in the presence of *n*-BuLi. To a stirred solution of **10a** (202 mg, 0.90 mmol) in THF (25 mL) at −78°C was added *n*-BuLi (2.25 mmol) and allyl bromide (272 mg, 2.25 mmol). After being stirred for 2 h at room temperature, the mixture was worked up as usual. Chromatography (2.5 × 13 cm^2) using a mixture of EtOAc and *n*-hexane (1:4) as an eluent gave allyl[2-{1-(benzotriazol-1-yl)-3-butenyl}-phenyl]amine (**16**) (14 mg, 5%), diallyl[2-{(benzotriazol-1-yl)methyl}phenyl]amine (**15**) (89 mg, 33%), allyl[2-{(benzotriazol-1-yl)methyl}phenyl]amine (**14**) (90 mg, 38%).

14. Viscous liquid (Found: C, 72.65; H, 5.9; N, 21.4. Calc. for $C_{16}H_{16}N_4$: C, 72.7; H, 6.1; N, 21.2%); ν_{max} (film)/cm^{-1} 3260, 3054, 2928, 2865, 1603, 1480, 1446, 1316, 1228, 1156, 994, 742, and 526; ^{1}H NMR δ 3.78 (2H, s, NCH_2), 4.95 (1H, s, NH), 5.14 (1H, d, *J* 11.8, =CH$_2$), 5.19 (1H, d, *J* 17.6, =CH$_2$), 5.78 (2H, s, CH_2), 5.83–5.98 (1H, m, =CH), 6.65 (1H, d, *J* 8.2, ArH), 6.76 (1H, t, *J* 7.4, ArH), 7.25 (1H, t, *J* 7.6, ArH), 7.32–7.46 (3H, m, ArH), 7.54 (1H, d, *J* 7.4, ArH), and 8.05 (1H, d, *J* 7.6, ArH); ^{13}C NMR δ 46.4, 51.1, 110.5, 112.2, 116.6, 117.1, 118.6, 120.5, 124.4, 127.9, 130.8, 131.2, 133.2, 135.0, 146.7, and 147.4.

15. Viscous liquid (Found: C, 75.2; H, 6.5; N, 18.25. Calc. for $C_{19}H_{20}N_4$: C, 75.0; H, 6.6; N, 18.4%); ν_{max} (film)/cm^{-1} 3056, 3001, 2948, 2920, 1608, 1511, 1490, 1442, 1248, 1110, 996, 910, 740, 694, and 516; ^{1}H NMR δ 3.65 (4H, d, *J* 6.3, NCH_2), 5.17 (2H, d, *J* 11.5, =CH$_2$), 5.23 (2H, d, *J* 17.2, =CH$_2$), 5.83–5.92 (2H, m, CH), 6.02 (2H, s, CH_2), 6.87 (1H, d, *J* 8.2, ArH), 7.01 (1H, t, *J* 7.4, ArH), 7.22–7.43 (6H, m, ArH), and 8.08 (1H, d, *J* 8.2, ArH).

16. Viscous liquid (Found: C, 74.9; H, 6.5; N, 18.6. Calc. for $C_{19}H_{20}N_4$: C, 75.0; H, 6.6; N, 18.4%); ν_{max} (film)/cm^{-1} 3271, 3048, 2920, 1624, 1489, 1445, 1300, 1256, 1221, 1154, 996, 740, and 521; ^{1}H NMR δ 3.25–3.34 (1H, m, CHC*H*$_2$CH=CH$_2$), 3.45–3.56 (1H, m, CHC*H*$_2$CH=CH$_2$), 3.69 (2H, s, NHC*H*$_2$CH=CH$_2$), 4.54 (1H, s, NH), 4.98–5.14 (4H, m, CHCH$_2$CH=C*H*$_2$ and NHCH$_2$CH=C*H*$_2$), 5.68–5.89 (2H, m, CHCH$_2$C*H*=CH$_2$ and NHCH$_2$C*H*=CH$_2$), 6.14 (1H, dd, *J* 9.4 and 6.2, CH), 6.63 (1H, d, *J* 8.2, ArH), 6.82 (1H, t, *J* 7.5, ArH), 7.23 (1H, t, *J* 8.4, ArH), 7.28–7.36 (2H, m, ArH), 7.42–7.46 (1H, m, ArH), 7.52 (1H, d, *J* 7.7, ArH), and 8.04 (1H, d, *J* 7.2, ArH); ^{13}C NMR δ 36.5, 46.4, 60.8, 110.9, 112.5, 116.5, 117.3, 119.1, 120.5, 121.1, 124.4, 127.7, 127.9, 130.3, 132.5, 133.7, 134.9, 146.8, and 147.1.

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