Ring-Opening Rearrangements of 2-(Benzotriazol-1-yl) Enamines and a Novel Synthesis of 2,4-Diarylquinazoline

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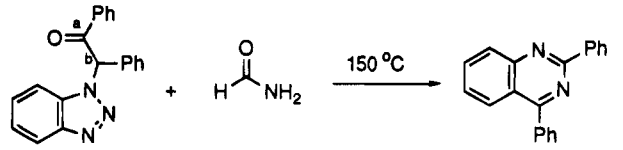
2-(Benzotriazol-1-yl) enamines (readily available from lithiated 1-(arylmethyl) benzotriazole and nitriles) undergo facile rearrangement into 2,4-diarylquinazolines. A plausible mechanism for this novel rearrangement is proposed and supported.

Quinazoline derivatives are of considerable importance as inhibitors, bactericides, ectoparasiticides, dyes, and fluorescent whitening agents.[1–6] Several methods to synthesize 2,4-diarylquinazolines are available, and the most general is the Meerwein cyclization.[7] A more specific cyclization reported by Bischler[8] involves acylation of a 2-aminoacylbenzene followed by heating (200 °C) with ammonia in a sealed tube. An alternate preparation of quinazolines by Bergman[9] utilized anthranilonitriles, but these starting materials are difficult to obtain.

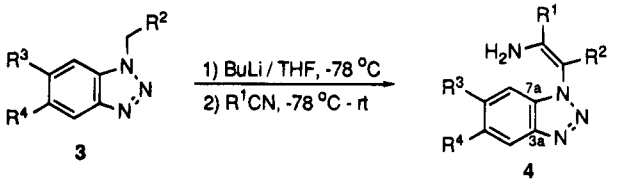
The benzotriazole ring is highly stable to acids and bases, to oxidation and reduction, and to heat. The classical Graebe–Ulmann pyrolytic conversions of 1-arylbenzotriazoles into carbazoles with loss of nitrogen require temperatures of 360 °C.[10,11] 1-Butyl-, 1-allyl-, 1-benzyl-, and 1-phenethylbenzotriazoles ring open and lose nitrogen at 400 °C to give the corresponding N-substituted anilines in yields of 4–18%.[12] Substituted benzotriazoles, on photolysis, extrude nitrogen to form diradicals which then cyclize to form carbazoles.[13–15] In our laboratory, we have observed opening of the benzotriazole ring in benzotriazol-1-yl alkyl carbanions α to the benzotriazol-1-yl group, with subsequent loss of nitrogen forming *o*-lithiated aniline imine.[16–18] Grignard reactions of 1-(α-alkoxyalkyl)benzotriazoles can also lead to opening of the benzotriazole rings.[19] We now report a new type of rearrangement, involving benzotriazole ring opening, which leads to the formation of quinazoline derivatives.

Scheme 1



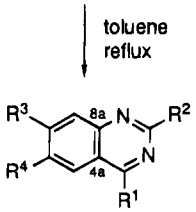
1 2a

Scheme 2



3 4

	R^1	R^2	R^3	R^4
a	Ph	Ph	H	H
b	*p*-MeC_6H_4	Ph	H	H
c	Ph	*p*-MeC_6H_4	H	H
d	*p*-BrC_6H_4	Ph	H	H
e	Ph	Ph	Me	Me
f	*p*-$MeOC_6H_4$	Ph	H	H
g	Ph	*p*-$MeOC_6H_4$	H	H



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Results and Discussion

2-(Benzotriazol-1-yl)-1,2-diphenylethanone (**1**) and formamide react at 150 °C to give 2,4-diphenylquinazoline (**2a**) (50%) instead of the expected 4,5-diphenylimidazole.[20,21] The identity of product **2a** was confirmed by NMR spectra, CHN analysis, mp, HRMS, and comparison with the literature data.[9] In the conversion **1** → **2a** the

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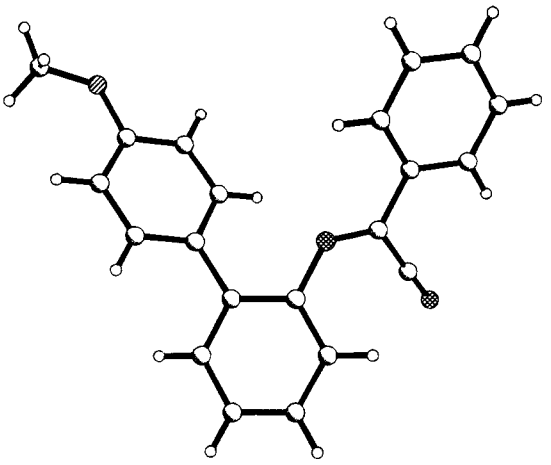

Figure 1. Perspective view of the X-ray structure of the iminonitrile **11f**.

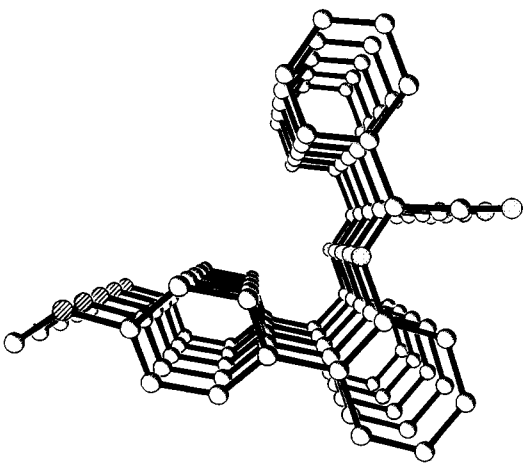

Figure 2. Molecular packing of **11f** approximately perpendicular to the α axis.

benzotriazole does not act in its usual role as a leaving group.[22] Rather, the mechanism must involve opening of the benzotriazole ring evidently followed by cleavage of the bond between carbon a and carbon b in **1** (Scheme 1).

A likely intermediate in this reaction appeared to be 1,2-diphenyl-2-(benzotriazol-1-yl)ethenamine (**4a**). Enamine **4a** was readily prepared from lithiated 1-benzylbenzotriazole and benzonitrile. Indeed, refluxing **4a** in toluene for 2 days gave the same product **2a**. A series of further 1,2-diaryl-2-(benzotriazol-1-yl)ethenamines **4b–g** similarly gave the corresponding quinazolines **2b–g** (Scheme 2); however, attempts to synthesize 1-alkyl-2-(benzotriazol-1-yl)enthenamines from 1-benzylbenzotriazole and nitriles bearing acidic α-protons, such as acetonitrile, were unsuccessful.

The transformation of **4** → **2** depicted in Scheme 2 is completely regiospecific. Thus, when 2-(benzotriazol-1-yl)-1-(*p*-methylphenyl)-2-phenylethenamine (**4b**) was refluxed in toluene for 2 days, only 2-phenyl-4-(*p*-methylphenyl)quinazoline (**2b**) was obtained. Moreover, heating 2-(benzotriazol-1-yl)-1-phenyl-2-(*p*-methylphenyl)-ethenamine (**4c**) gave only 2-(*p*-methylphenyl)-4-phenylquinazoline (**2c**). Obviously, the aryl group at the

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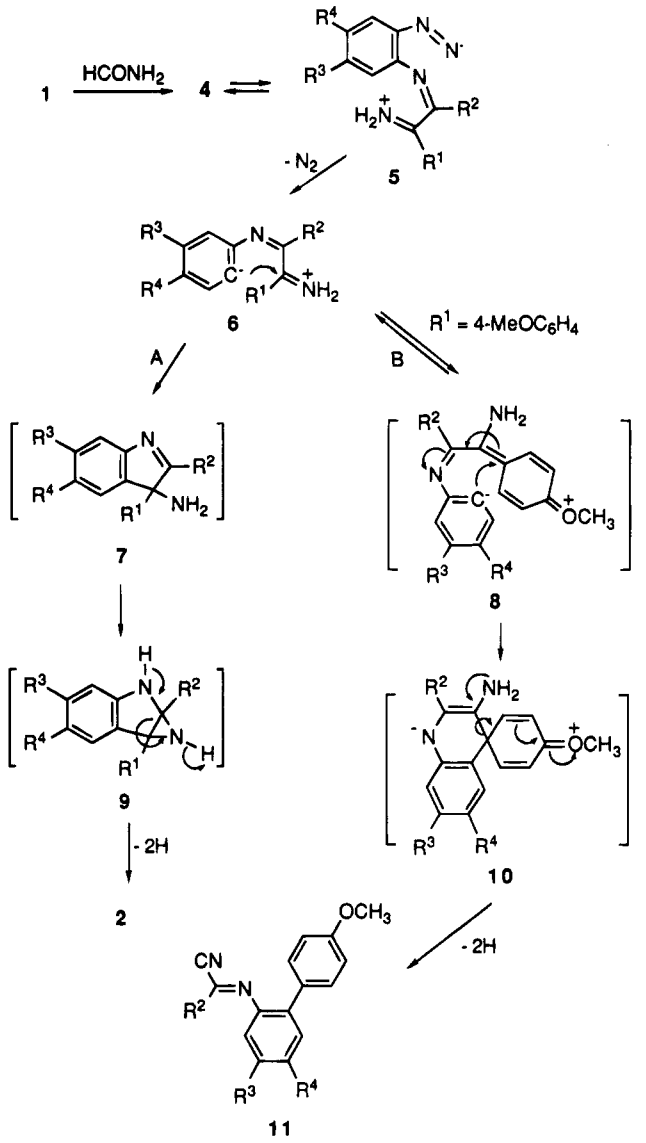
Scheme 3



2-position in quinazolines **2a–g** is derived from **3**, whereas the aryl group at the 4-position is derived from the nitrile.

In only one case was a significant byproduct formed: 1-(*p*-methoxyphenyl)-2-(benzotriazol-1-yl)-2-phenylethenamine (**4f**) under the same conditions gave 10% of iminonitrile **11f** along with 30% of the expected quinazoline **2f**. By contrast, heating 1-phenyl-2-(benzotriazol-1-yl)-2-(*p*-methoxyphenyl)ethenamine (**4g**) in toluene led only to the isolation of **2g** (67%). The structure of **11f** was determined by single crystal X-ray crystallography using a sample recrystallized from ethyl acetate.[28] Figure 1 shows a perspective view of the crystal structure of iminonitrile **11f** which has bonding geometry similar to that of structurally related compounds.[23–26] The NCCN plane is close to coplanar with the attached phenyl ring but inclined to the attached biphenyl ring at an angle of 49.8°. The angle between the planes of the two

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Table 1. Preparation of Quinazoline Derivatives 2, Enamines 4, and Iminonitrile 11f

									analysis/HRMS					
									found			required		
compd	R^1	R^2	R^3	R^4	reaction temp (°C)	t (h)	yield (%)	mp (°C)	C	H	N	C	H	N
2a	Ph	Ph	H	H	150[a]	6	50	117–119[9]	84.96	5.01	9.83	85.08	5.00	9.92
					111[b]	45	64		282.1103			282.1157		
2b	*p*-MePh	Ph	H	H	111[b]	90	74	130.5–131.5	85.00	5.43	9.38	85.11	5.44	9.45
2c	Ph	*p*-MePh	H	H	111[b]	120	61	167–168	84.95	5.39	9.35	85.11	5.44	9.45
2d	*p*-BrPh	Ph	H	H	111[b]	120	73	155–157	66.35	3.58	7.67	66.50	3.63	7.75
2e	Ph	Ph	Me	Me	111[b]	30	57	195–196	84.86	5.81	8.91	85.13	5.85	9.02
2f	*p*-MeOPh	Ph	H	H	111[b]	120	30	131–132.5	80.81	5.16	8.96	80.75	5.16	8.97
2g	Ph	*p*-MeOPh	H	H	111[b]	24	67	157–159	81.14	5.19	8.63	80.75	5.16	8.97
4a	Ph	Ph	H	H	rt	20	35.3	181.5–182.5	77.20	5.19	18.12	76.89	5.17	17.94
4b	*p*-MePh	Ph	H	H	rt	45	51	163–164	77.30	5.54	17.25	77.28	5.56	17.17
4c	Ph	*p*-MePh	H	H	rt	50	38.4	156–158	77.11	5.53	17.07	77.28	5.56	17.17
4d	*p*-BrPh	Ph	H	H	rt	30	53.7	184–185.5	61.24	3.80	14.21	61.39	3.86	14.32
4e	Ph	Ph	Me	Me	rt	20	42	168–170	77.37	5.90	16.45	77.62	5.92	16.46
4f	*p*-MeOPh	Ph	H	H	67	15	41	192–193.5	73.38	5.27	16.27	73.67	5.30	16.36
4g	Ph	*p*-MeOPh	H	H	rt	20	56	198.5–200	73.51	5.24	16.34	73.67	5.30	16.36
11f	*p*-MeOPh	Ph	H	H	111[b]	120	10	106–108						

[a] Reaction of 2-(benzotriazol-1-yl)benzylphenone with formamide (method A). [b] Heating of 1,2-diaryl-2-(benzotriazol-1-yl) enamine (method B).

Table 2. ^{1}H NMR Data of Compounds 2 (δ, ppm; J, Hz)

	quinazoline				
compd	H5	H6	H7	H8	other signals
2a	7.85 (d, J = 9.0)	8.14 (t, J = 9.0)	8.14 (t, J = 9.0)	7.84 (d, J = 9.0)	7.50–7.54 (m, 4H), 7.58–7.61 (m, 3H), 7.88 (m, 1H), 8.70 (m, 2H)
2b	7.50 (d, J = 9.0)	8.13 (m)	8.12 (m)	7.49 (d, J = 9.0)	2.48 (s, 3H), 7.38, 7.78 (AB, 4H, J = 8.0), 7.50 (m, 2H), 7.83 (m, 1H), 8.70 (m, 2H)
2c	7.89 (d, J = 9.0)	8.13 (t, J = 9.0)	8.12 (t, J = 9.0)	7.88 (d, J = 9.0)	2.44 (s, 3H), 7.33, 8.58 (AB, 4H, J = 8.0), 7.53 (m, 2H), 7.59 (m, 2H), 7.86 (m, 1H)
2d	7.55 (m)	8.06 (m)	8.16 (m)	7.53 (m)	7.50 (m, 2H), 7.74, 7.76 (AB, 4H, J = 8.5), 7.89 (m, 1H), 8.66 (m, 2H)
2e	7.83 (s)			7.92 (s)	2.40 (s, 3H), 2.49 (s, 3H), 7.49 (m, 3H), 7.57 (m, 3H), 7.86 (m, 2H), 8.65 (m, 2H)
2f	7.52 (d, J = 8.5)	8.15 (t, J = 8.5)	8.15 (t, J = 8.5)	7.53 (d, J = 8.5)	3.92 (s, 3H), 7.12, 7.89 (AB, 4H, J = 8.0), 7.54 (m, 2H), 7.85 (m, 1H), 8.68 (m, 2H)
2g	7.85 (m)	8.09 (t, J = 8.5)	8.09 (t, J = 8.5)	7.48 (m)	3.88 (s, 3H), 7.03, 8.15 (AB, 4H, J = 8.0), 7.58 (m, 2H), 7.88 (m, 2H)

Table 3. ^{13}C NMR Data of Compounds 2 (δ, ppm)

	quinazoline								
compd	C_2	C_4	C_5	C_6	C_7	C_8	C_{8a}	C_{4a}	other carbons
2a	168.3	160.3	129.1	129.9	133.5	130.5	152.0	121.7	127.0, 128.5, 128.6, 130.2, 137.7, 138.2
2b	168.3	160.2	129.1	129.2	133.6	130.4	152.1	121.8	21.8, 126.8, 128.4, 128.5, 128.7, 130.1, 134.8, 138.2, 140.0
2c	168.2	160.3	129.1	129.2	133.4	129.9	152.0	121.6	21.6, 126.7, 127.0, 128.5, 128.6, 130.2, 135.5, 137.7, 140.7
2d	167.1	160.2	128.6	129.3	133.7	130.6	152.1	121.4	124.6, 126.5, 127.2, 128.6, 131.7, 131.8, 136.5, 138.0
2e	167.0	159.6	129.7	137.2	144.5	130.1	151.1	120.3	20.64, 20.30, 125.9, 128.5, 130.8, 138.0, 138.4
2f	167.7	160.1	126.8	129.1	133.3	130.4	152.0	121.6	55.4, 114.0, 127.0, 128.5, 128.6, 130.1, 131.8, 138.3, 161.2
2g	168.1	160.0	126.5	128.9	133.4	129.8	152.1	121.4	55.3, 113.9, 127.0, 128.5, 130.1, 130.3, 131.0, 137.8, 161.8

biphenyl rings is 41.8°. Despite these significant deviations from planarity the molecules exhibit close intermolecular associations wherein they stack in layers with each of the phenyl rings closely associated with its partners in the adjacent unit cells. This results in channels of phenyl rings approximately perpendicular to the short α axis of the unit cell (Figure 2). The distances between the planes of the stacked phenyl rings vary between 3.38 and 3.74 Å.

To study the mechanism of the reaction **4** → **2**, we carried out a crossover reaction of 2-(benzotriazol-1-yl)-1-(*p*-methylphenyl)-2-phenylethenamine (**4b**) with benzonitrile. The only product obtained was 2-phenyl-4-(*p*-methylphenyl)quinazoline (**2b**), indicating that the rearrangement of **4** to **2** does not involve reverse scission of **4** back into **3** and R^1CN. Refluxing 2-(5,6-dimethylbenzotriazol-1-yl)-1,2-diphenylethenamine (**4e**) in toluene gave only 2,4-diphenyl-6,7-dimethylquinazoline (**2e**), thus demonstrating that the carbon at the 4a-position of the quinazoline ring is derived from the 3a-position of the benzotriazole ring (Scheme 2).

The intramolecular process of Scheme 3 is proposed for the mechanism of this thermolytic rearrangement. In the first step, the amino group of enamines **4** facilitates the opening of the triazole ring to form an intermediate betaine **5**. As mentioned above, we have previously reported[17,18] that if a carbanion center is directly connected to the benzotriazol-1-yl group, the normally resistant triazole ring of benzotriazole is susceptible to being opened. We therefore postulate that ring opening of benzotriazole may occur in derivatives which bear electron-rich groups adjacent to the benzotriazole moiety. Betaine **5** loses nitrogen to form intermediate **6**, which undergoes rapid intramolecular ring closure to form the five-membered ring of **7** (route A). Attack of the imine carbon by the amino group of **7** gives the three-membered ring intermediate **9** which undergoes ring expansion to give the six-membered ring followed by aromatization to

Table 4. ^{1}H NMR Data of Compounds 4 (δ, ppm; J, Hz)

	benzotriazole					
compd	H4	H5	H6	H7	NH_2(2H)	other signals
4a	8.12 (m)	7.24 (m)	7.35 (m)	7.37 (m)	3.95 (s)	6.77 (m, 2H), 6.97 (m, 3H), 7.36 (m, 3H), 7.55 (m, 2H)
4b	8.10 (m)	7.25 (m)	7.35 (m)	7.37 (m)	3.89 (s)	2.36 (s, 3H), 6.78 (m, 2H), 7.00 (m, 3H), 7.14, 7.41 (AB, 4H, J = 8.0)
4c	8.09 (m)	7.24 (m)	7.35 (m)	7.37 (m)	3.90 (s)	2.20 (s, 3H), 6.67, 6.82 (AB, 4H, J = 8.0), 7.35 (m, 3H), 7.55 (m, 2H)
4d	8.11 (m)	7.17 (m)	7.36 (m)	7.37 (m)	3.95 (s)	6.80 (m, 2H), 7.05 (m, 3H), 7.39, 7.46 (AB, 4H, J = 8.0)
4e	7.82 (s)			7.32 (s)	3.88 (s)	2.30 (s, 3H), 2.39 (s, 3H), 6.75 (m, 2H), 7.01 (m, 3H), 7.45 (m, 3H), 7.54 (m, 2H)
4f	8.09 (m)	7.24 (m)	7.33 (m)	7.35 (m)	3.86 (s)	3.78 (s, 3H), 6.79 (m, 2H), 6.99 (m, 3H), 6.83, 7.44 (AB, 4H, J = 8.8)
4g	8.11 (m)	7.22 (m)	7.35 (m)	7.35 (m)	3.87 (s)	3.68 (s, 3H), 6.57, 6.75 (AB, 4H, J = 9.0), 7.35 (m, 3H), 7.52 (m, 2H)

Table 5. ^{13}C NMR Data of Compounds 4 (δ, ppm)

	benzotriazole						enamine		
compd	C_4	C_5	C_6	C_7	C_{3a}	C_7	C_1	C_2	other carbons
4a	119.2	127.7	124.0	111.1	145.8	132.2	136.2	107.8	126.0, 127.9, 128.6, 128.7, 129.2, 136.6, 143.5
4b	119.2	127.6	124.0	110.9	145.8	133.4	136.4	107.8	21.33, 125.9, 127.9, 128.6, 129.1, 129.4, 133.6, 139.2, 143.5
4c	119.8	127.6	124.0	111.0	145.8	133.3	136.8	107.9	20.90, 127.6, 128.6, 129.0, 129.2, 133.3, 135.7, 142.8
4d	120.0	127.8	124.2	110.9	145.8	133.2	135.8	108.2	126.5, 128.2, 128.9, 130.9, 131.9, 132.6, 135.6, 142.0
4e	119.0	138.0	133.0	111.1	145.0	132.2	136.4	107.8	125.9, 127.3, 127.8, 128.5, 128.6, 129.2, 136.8, 143.4
4f	119.9	127.4	124.0	110.9	145.8	133.4	136.6	107.2	55.30, 114.1, 125.8, 127.9, 128.6, 128.7, 130.6, 134.8, 160.3
4g	119.9	127.6	124.1	111.1	145.8	133.3	136.2	107.8	55.10, 113.5, 128.6, 128.8, 128.9

produce quinazoline **2** (Scheme 3); transformations similar to that of **9** to **2** have been found in the literature.[27] When R^1 is an electron-donating group, intermediate **6** can evidently also rearrange *via* route B. The intramolecular nucleophilic attack shown in **8** generates a new six-membered ring intermediate **10** which aromatizes to form **11**.

These mechanisms can explain two facts: firstly, when benzonitrile has a strong electron-donor on the phenyl ring, e.g., **4f**, route A is very slow. Accordingly, the yield of **2f** was low and part of starting material **4f** was transformed into compound **11f**. Second, the observed rapid rearrangement of **4g** to **2g** is the result of the carbanion in intermediate **6** being more active due to the strong electron-donor R^2 group.

In conclusion, the presence of an electron donating group adjacent to the benzotriazol-1-yl moiety makes the triazole ring susceptible to ring opening on heating. The present method describes a new rearrangement of 2-(benzotriazol-1-yl)ethenamines and the synthesis of quinazoline derivatives from 2-(benzotriazol-1-yl)-1,2-diaryl enamines.

Experimental Section

General. Melting points were determined with a Kofler hot stage apparatus without correction. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ with TMS or $CDCl_3$ as the internal reference. High-resolution mass spectra were measured on a Kratos/AE1-MS 30 mass spectrometer. Microanalysis were performed on a Carbo Erba 1106 elemental analyzer. THF was distilled from sodium/benzophenone prior to use. Lithiation reactions were carried out under the protection of dry nitrogen. All glassware was oven dried. All moisture-sensitive reagents were transferred by means of predried syringes.

General Procedure for the Preparation of Quinazoline Derivatives 2a–g and 11f. Method A. A mixture of 1,2-diphenyl-2-(benzotriazol-1-yl)ethanone (**1**) (1 mmol) and an excess of formamide was heated at 150 °C for several hours. The excess formamide was removed *in vacuo* and the residue purified by chromatography on a silica gel column (eluent: hexane:ethyl acetate = 8:1) to yield **2a**.

Method B. A solution of 1,2-diaryl-2-(benzotriazol-1-yl) enamine **4a–g** (1 mmol) in toluene (10 mL) was refluxed for the appropriate time. The solvent was removed *in vacuo* and the residue purified by chromatography on a silica gel column (eluent:hexane/ethyl acetate) to yield **2a–g** and **11f**.

N-[2-(*p*-Methoxyphenyl)phenyl]-2-cyanobenzylimine (**11f**): ^{1}H NMR δ 3.79 (s, 3 H), 7.12 (d, 1 H, J = 8.0 Hz), 7.31, 6.88 (AB, 4 H, J = 8.5 Hz), 7.38 (t, 2 H, J = 7.8 Hz), 7.45–7.58 (m, 4 H), 8.01 (d, 2 H, J = 8.1 Hz); ^{13}C NMR δ 55.20, 111.0, 113.4, 118.9, 127.5, 127.7, 128.2, 129.0, 130.5, 130.9, 131.0, 132.7, 133.0, 134.0, 140.1, 146.7, 158.8 (see Tables 1–3).

General Procedure for the Preparation of 1,2-Diaryl-2-(benzotriazol-1-yl) Enamines 4a–g. To a solution of the (α-arylbenzotriazol-1-yl)methane **3** (10.0 mmol) in THF (50 mL) at −78 °C was added *n*-BuLi (4.4mL, 2.5M, 11 mmol). The solution was kept at this temperature for 2 h, and then arylnitrile was added at −78 °C. The resulting solution was allowed to warm slowly to room temperature. **4f** was refluxed in THF for the appropriate time. The solution was poured into water (20 mL) and extracted with ethyl acetate (3 × 30 mL), and the combined extracts were dried with $MgSO_4$. The solvent was removed *in vacuo* and the residue purified by chromatography on a silica gel column (eluent:hexane/ethyl acetate) (see Tables 1, 4, and 5).

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(28) The author has deposited atomic coordinates for **11f** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.