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Efficient Microwave Access to Polysubstituted Amidines from Imidoylbenzotriazoles

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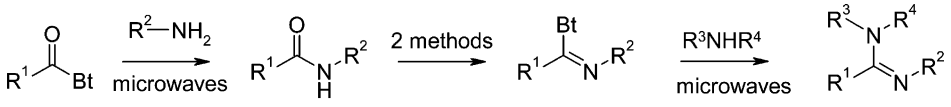

(Bt = 1-benzotriazolyl)

Microwave reactions of primary and secondary amines with imidoylbenzotriazoles **6a**−**w** gave diversely substituted amidines **7a**−**Aa** in 76−94% yields. Convenient preparations of a variety of amides **5a**−**Ab** (87−96%) and imidoylbenzotriazoles **6a**−**w** (56−95%) have also been developed using microwave irradiation under mild conditions and short reaction times. These results demonstrate further the advantages of microwave synthesis and introduce a new application of imidoylbenzotriazoles in the preparation of polysubstituted amidines.

Introduction

The synthesis of amidines has received much attention as a result of their biological properties[1a−e] and applications in heterocyclic synthesis.[1f,g] Literature methods include the preparation of (i) *N*-monosubstituted amidines by (a) addition of Grignard or organolithium reagents to carbodiimides or cyanoamides, followed by hydrolysis, and in this approach, a C−C bond is formed;[2a] (b) heating hydrazones in the presence of $NaNH_2$;[2b] (c) addition of the anions of urea and amines to nitriles;[2c] and (d) addition of amines to nitriles in the presence of $AlCl_3$;[2d,e] (ii) *N*,*N*-disubstituted amidines by the reaction of secondary amines with imidic ester salts derived from nitriles in which one C−N bond is formed; (iii) *N*,*N*′-disubstituted amidines by the reaction of two moles of an amine with *ortho*-esters, acetals, or thioesters, in which both the C−N bonds are formed, and (iv) *N*,*N*′-disubstituted and *N*,*N*,*N*′-trisubstituted amidines by imidoylation of amines with imidoyl chlorides (**1**),[2f−h] imidate fluoroborates (**2**),[2i] iminium triflates (**3**),[2j] or iminium sulfonates (**4**[2k]; Scheme 1).

Imidoyl chlorides (**1**) are generally prepared in situ by treatment of the corresponding amides with phosgene, thiophosgene, oxalyl chloride, phosphorus penta- and trihalides, thionyl chloride, sulfuryl chloride, and halogens.[3a] Chlorides **1** are labile toward hydrolysis, and with amines at elevated temperatures, side reactions have been reported if α-CH groups are present in the imidoyl chlorides.[3b] Many amidines can be obtained in one step by heating the monosubstituted amide with amine and phosphorus pentachloride; in some cases, the imidoyl chloride has to be isolated.[2g] Iminium triflates and imidate

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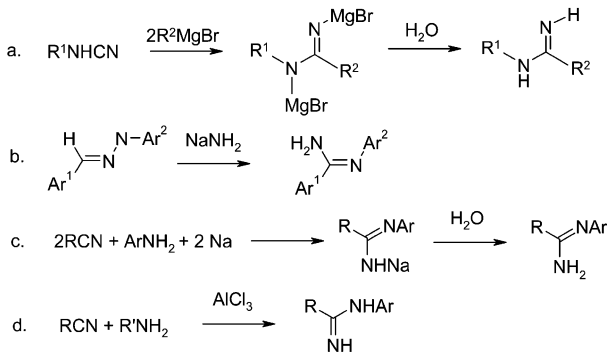
SCHEME 1

(i) *N*-Monosubstituted amidines



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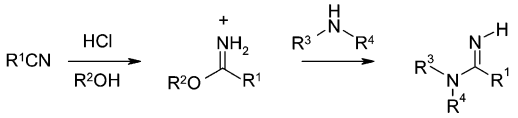
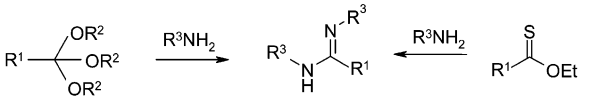
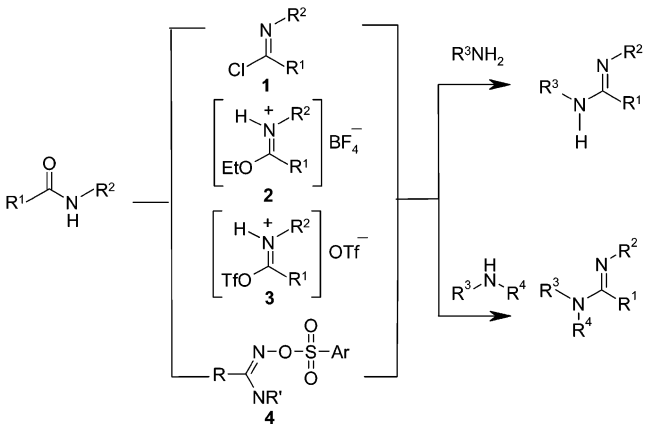


(iii) *N*,*N*′-Disubstituted amidines



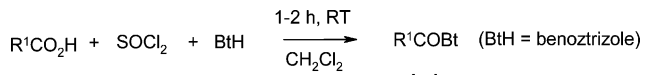
(iv) *N*,*N*′-Disubstituted and *N*,*N*,*N*′-trisubstituted amidines



fluoroborates require handling under inert atmosphere and cannot be isolated or purified.[2j]

Imidoylbenzotriazoles are stable and useful substitutes for imidoyl chlorides[4a−c] and have been reported as versatile reagents for the synthesis of enaminones[4d] and *N*-substituted *β*-enamino acid derivatives.[4e] We now apply imidoylbenzotriazoles under microwave irradiation in a mild and general procedure for the direct synthesis of *N*,*N*′-disubstituted and *N*,*N*,*N*′-trisubstituted amidines. The present work also includes the development of microwave synthesis of amides from *N*-acylbenzotriazoles and an easy access to imidoylbenzotriazoles by a one-pot reaction of an amide, thionyl chloride (or oxalyl chloride), and benzotriazole. Microwave heating has

TABLE 1. Preparation of *N*-Acylbenzotriazoles



4a-l

entry	R^1	product (yield %)[a]	mp (°C)	lit. mp (°C)
1	phenethyl	**4a** (89)	62−64	63−64[8]
2	*n*-hexyl	**4b** (92)	48−50	50−52[9]
3	2-thienyl	**4c** (93)	172−173	173−175[7]
4	*p*-nitrophenyl	**4d** (91)	191−193	192−193[10]
5	2-furyl	**4e** (92)	170−172	171−173[8]
6	Bn	**4f** (89)	63−65	65−66[8]
7	*p*-methoxyphenyl	**4g** (92)	109−111	102−103[11]
8	Ph	**4h** (96)	110−112	112[12]
9	*p*-tolyl	**4i** (95)	122−124	123−124[10]
10	Me	**4j** (96)	50−52	49−51[13]
11	phenylethenyl	**4k** (96)	149−150	151−152[7]
12	cyclohexyl	**4l** (85)	85−88	94−96[9]

[a] Isolated yield.

emerged as a powerful technique to promote a variety of chemical reactions,[5a−g] and the use of a single-mode cavity[5a] microwave synthesizer ensures reproducibility, safety, reduced pollution, and simplicity in processing and handling.[6a,b]

Results and Discussion

Preparation of *N*-Acylbenzotriazoles. *N*-Acylbenzotriazoles **4a**−**l** (Table 1) were prepared from the corresponding carboxylic acids by treatment with benzotriazole and thionyl chloride by a modification of a one-step general procedure.[7] Reducing the amount of benzotriazole from 4 equiv[7] to 3 equiv gives similar yields and simplifies the workup procedure.

Preparation of Amides. *N*-Acylbenzotriazoles have been used to prepare primary, secondary, and tertiary amides, but some of the reactions under conventional conditions require several hours (4−5 h) for completion.[8] We have now developed microwave conditions that produced the desired secondary amides by the reactions of a variety of primary amines with readily available *N*-acylbenzotriazoles. Thus, amides **5a**−**Ab** were obtained in 87−96% yields in 10 min at a reaction temperature of 80 °C and a microwave irradiation power of 80 W (Table 2). Microwave reactions were performed in a 50 mL round-bottomed flask equipped with a reflux condenser. Single-mode microwave irradiation was used at a fixed temperature, pressure, and irradiation power during the reaction time using an automatic power control.

Preparation of Imidoylbenzotriazoles. Reported procedures for the preparation of imidoylbenzotriazoles include (i) the reaction of secondary amides with benzotriazole and $POCl_3$ in the presence of triethylamine;[4a] (ii) the reaction of oximes with 1-(*p*-toluenesulfonyl)benzotriazole;[36a] (iii) the reaction of sulfinyldibenzotriazole with secondary amides;[4b] (iv) the reaction

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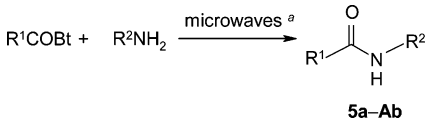
TABLE 2. Microwave Preparation of Secondary Amides 5a−Ab Using *N*-Acylbenzotriazoles

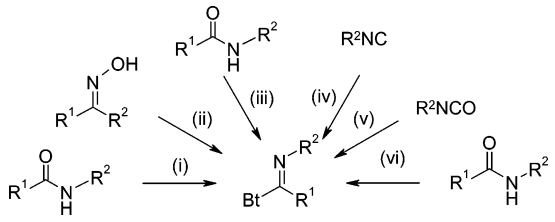


entry	R^1	R^2	product[b] (yield %)	mp (°C)	lit. mp (°C)
1	cyclohexyl	*p*-tolyl	**5a** (96)	154−156	144.7−145[14]
2	Ph	2-pyridyl	**5b** (91)	77−78	82[15]
3	Bn	Bn	**5c** (90)	115−117	117−118[16]
4	Bn	*p*-tolyl	**5d** (91)	133−135	135−137[17]
5	phenethyl	*p*-tolyl	**5e** (92)	127−129	129−130[18]
6	*p*-chlorophenyl	*p*-tolyl	**5f** (91)	206−209	213-215[19]
7	*p*-methoxyphenyl	Bn	**5g** (89)	128−130	128−129[20]
8	*p*-nitrophenyl	Bn	**5h** (96)	136−137	141−142[21]
9	2-furyl	*p*-tolyl	**5i** (96)	108−110	109−110[22]
10	*n*-hexyl	*p*-tolyl	**5j** (93)	77−79	78−79[23]
11	Ph	2-furylmethyl	**5k** (90)	96−98	99−100[24]
12	2-furyl	cyclohexyl	**5l** (94)	106−107	110−111[22]
13	*p*-tolyl	*p*-tolyl	**5m** (91)	158−160	158−160[19]
14	phenethyl	Bn	**5n** (93)	80−82	82−83[25]
15	Ph	*p*-methoxyphenyl	**5o** (88)	156−157	157−158[22]
16	*p*-nitrophenyl	Ph	**5p** (95)	206−208	211[26]
17	*p*-tolyl	*n*-butyl	**5q** (92)	52−54	48−53[27]
18	2-thienyl	*p*-tolyl	**5r** (89)	103−105	104−105[28]
19	2-thienyl	Bn	**5s** (92)	116−118	119−120[29]
20	2-thienyl	2-furylmethyl	**5t** (92)	100−102	novel
21	2-indolyl	Bn	**5u** (93)	218−220	220[29]
22	Ph	Bn	**5v** (92)	101−103	105−106[30]
23	$-C_6H_4-$	Bn	**5w** (92)	262−264	264−266[21]
24	$-C_6H_4-$	*n*-butyl	**5x** (92)	230−232	233−234[31]
25	Me	*p*-tolyl	**5y** (93)	150−152	153[32]
26	$-CH_2CH_2-$	Ph	**5z** (94)	250−252	254[33]
27	phenylethenyl	*p*-tolyl	**5Aa** (87)	156−158	159[34]
28	phenylethenyl	Bn	**5Ab** (92)	107−109	107−110[35]

[a] Reaction conditions: MW, 80 W; temp., 80 °C; reaction time, 10 min; solvent, $CHCl_3$. [b] Isolated yield.

of isonitriles with *N*-(aminoalkyl)benzotriazoles in the presence of $BF_3.Et_2O$;[36b] (v) the reaction of *N*-acylbenzotriazoles with isocyanates;[36c] and (vi) the reaction of secondary amides with 1-chlorobenzotriazole in the presence of triphenylphosphine[4e] (Scheme 2). In a modification of method (i), we have found that the reaction of secondary amides (1 equiv), $SOCl_2$ (2 equiv), and benzotriazole (4 equiv) at 80 °C and 80 W irradiation power for 10 min gives imidoylbenzotriazoles **6b**−**e**,**i**−**l**,**n**−**r**,**u**−**w** (with R^1 = aryl group) in 78−95% yields (Table 3). Imidoylbenzotriazoles **6a**,**f**−**h**,**m**,**s**,**t** (with R^1 = aliphatic group) were prepared in 56−75% yields by the reaction of amides (1 equiv),

SCHEME 2



(i) BtH, $POCl_3/Et_3N$; (ii) BtTs; (iii) Bt_2SO; (iv) BtR^1, $BF_3{\cdot}Et_2O$; (v) R^1COBt; (vi) BtCl, PPh_3.

$(COCl)_2$ (1 equiv), and benzotriazole (2 equiv) in the presence of pyridine. All compounds were fully characterized by ^1H and ^{13}C NMR spectroscopy and by either elemental analysis or comparison of melting point with literature data.

Preparation of Amidines. Microwave reactions of imidoylbenzotriazoles **6** with amines were performed in sealed heavy-

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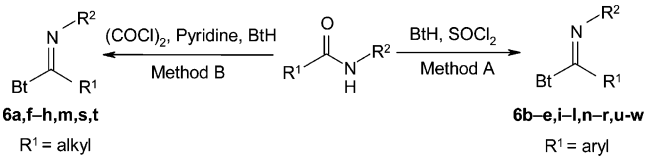
TABLE 3. Preparation of Imidoylbenzotriazoles 6a−w



entry	R^1	R^2	product[a] (yield %)	mp (°C)	lit. mp (°C)
1	Me	Ph	**6a** (75)	106−108	108[4a]
2	Ph	Ph	**6b** (88)	129−131	132−133[4e]
3	*p*-tolyl	*p*-tolyl	**6c** (82)	138−140	novel
4	2-furyl	*p*-tolyl	**6d** (84)	120−123	novel
5	Ph	*p*-methoxyphenyl	**6e** (82)	100−103	104−105[4e]
6	Me	*p*-tolyl	**6f** (65)	113−115	115[4a]
7	Bn	*p*-tolyl	**6g** (62)	124−126	123−125[4d]
8	Bn	Bn	**6h** (56)	oil	oil[4d]
9	Ph	Bn	**6i** (93)	108−110	108[4b]
10	*p*-chlorophenyl	*p*-tolyl	**6j** (90)	118−120	novel
11	*p*-$MeOC_6H_4$	Bn	**6k** (78)	115−118	novel
12	Ph	2-furylmethyl	**6l** (84)	oil	novel
13	*n*-hexyl	*p*-tolyl	**6m** (57)	oil	novel
14	2-furyl	cyclohexyl	**6n** (95)	oil	novel
15	*p*-nitrophenyl	Bn	**6o** (86)	117−119	novel
16	*p*-nitrophenyl	Ph	**6p** (88)	183−185	novel
17	*p*-tolyl	*n*-butyl	**6q** (84)	oil	novel
18	2-thienyl	*p*-tolyl	**6r** (91)	133−135	novel
19	phenethyl	Bn	**6s** (57)	77−79	novel
20	phenethyl	*p*-tolyl	**6t** (64)	116−118	novel
21	2-thienyl	Bn	**6u** (83)	oil	novel
22	2-thienyl	2-furylmethyl	**6v** (81)	oil	novel
23	phenylethenyl	*p*-tolyl	**6w** (65)	oil	novel

[a] Isolated yield.

walled Pyrex tubes or 50 mL round-bottomed flasks under controlled conditions in a safe and reproducible procedure. Optimization of the microwave reaction conditions was carried out on the condensation of *N*-[(*E*)-1-(1*H*-1,2,3-benzotriazol-1-yl)ethylidene]aniline (**6a**) and morpholine in the presence of acetic acid, for which different combinations of temperature, time and, irradiation power were studied to achieve the optimum chemical yield at the lowest reaction temperature. It was found that the microwave reaction of **6a** and morpholine at 120 °C and 120 W irradiation power for 10 min gave 76% yield of 4-[(*E*)-1-methyl-2-phenylethenyl]morpholine (**7a**). However, the presence of acetic acid in the reaction mixture resulted in the formation of amide side products by the acetylation of amines, and the H_2O that was generated reacted with imidoylbenzotriazoles to give the corresponding amides. To avoid this, we used either (i) a catalytic amount (20% in moles) of Lewis acid ($AlCl_3$) or (ii) the hydrochloride salts of amines at 80 °C and 80 W irradiation power for 10 min. Using the optimized microwave reaction conditions, we prepared a variety of polysubstituted amidines **7a**−**Aa** in 76−94% yields (Table 4). These results illustrate the general applicability of this method for the preparation of amidines under mild conditions (80−120 °C) and short reaction times (10 min). Imidoylbenzotriazoles are stable crystalline solids that can be purified and stored at room temperature; their use also avoids side reactions, toxic reagents, and special handling procedures involved with imidoyl chlorides, iminium triflates, and imidate fluoroborates.[3a]

Summary

In summary, we have developed a new general method for the synthesis of polysubstituted amidines from imidoylbenzotriazoles using microwaves under mild reaction conditions and short reaction times. New microwave reaction conditions for the preparation of amides and imidoylbenzotriazoles provide efficient methods for access to these synthetic intermediates.

Experimental Section

Melting points are uncorrected. Reactions under microwave irradiation were conducted in heavy-walled Pyrex tubes sealed with aluminum crimp caps fitted with a silicon septum or in round-bottomed flasks equipped with a reflux condenser. Microwave heating was carried out with a single-mode cavity Discover Microwave Synthesizer (CEM Corporation, NC), producing continuous irradiation at 2450 MHz. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$ (with TMS for ^{1}H and chloroform-*d* for ^{13}C as the internal reference), unless specified otherwise.

1-(3-Phenylpropanoyl)-1*H*-1,2,3-benzotriazole (4a). Thionyl chloride (4.00 mL, 55 mmol) and benzotriazole (18.45 g, 155 mmol) in methylene chloride (100 mL) were added dropwise to hydrocinnamic acid (7.51 g, 50 mmol) in methylene chloride (100 mL). A white solid precipitated within 5 min. The reaction mixture was stirred for 1 h. The precipitated white solid was filtered off, and

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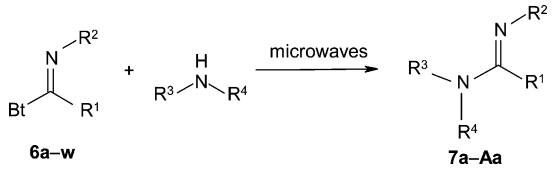
TABLE 4. Preparation of Amidines 7A−Aa from Imidoylbenzotriazoles 6a−w



6a–w **7a–Aa**

entry	R^1	R^2	R^3	R^4	product[a] (yield %)	mp (°C)	lit. mp (°C)
1	Me	Ph	$-(CH_2)_2O(CH_2)_2-$		**7a** (76)[b]	80−82	82[37]
2	Me	Ph	Et	Et	**7b** (88)[b,c]	102−104	novel[f]
3	Me	Ph	Bn	H	**7c** (77)[b,c]	88−90	novel[f]
4	Me	Ph	*p*-tolyl	H	**7d** (89)[b]	87−89	90[38]
5	Ph	Ph	Et	Et	**7e** (87)[d]	oil	oil[39]
6	Ph	Ph	$-(CH_2)_2O(CH_2)_2-$		**7f** (90)[d]	85−87	85[37]
7	Ph	Ph	*p*-tolyl	H	**7g** (91)[e]	130−132	133−135[40]
8	4-$MeOC_6H_4$	Bn	*p*-tolyl	H	**7h** (91)[e]	115−117	novel
9	4-$MeOC_6H_4$	Bn	$-(CH_2)_2O(CH_2)_2-$		**7i** (88)[d]	oil	novel
10	Bn	*p*-tolyl	*p*-tolyl	H	**7j** (94)[e]	89−91	novel
11	Bn	*p*-tolyl	$-(CH_2)_2O(CH_2)_2-$		**7k** (88)[d]	104−106	novel
12	2-thienyl	*p*-tolyl	*p*-tolyl	H	**7l** (88)[e]	121−123	novel
13	2-thienyl	*p*-tolyl	$-(CH_2)_2O(CH_2)_2-$		**7m** (92)[d]	109−111	novel
14	2-furyl	*p*-tolyl	*p*-tolyl	H	**7n** (90)[e]	120−122	novel
15	2-furyl	*p*-tolyl	$-(CH_2)_2O(CH_2)_2-$		**7o** (89)[d]	94−96	novel
16	4-$O_2NC_6H_4$	Bn	*p*-tolyl	H	**7p** (92)[e]	121−123	novel
17	Me	*p*-tolyl	*p*-tolyl	H	**7q** (91)[e]	118−120	119−120[41]
18	Ph	Bn	*p*-tolyl	H	**7r** (87)[e]	114−116	127−127.5[42]
19	2-furyl	cyclohexyl	*p*-tolyl	H	**7s** (85)[e]	oil	novel
20	phenethyl	*p*-tolyl	Ph	Me	**7t** (91)[d]	89−91	novel
21	4-ClC_6H_4	*p*-tolyl	Ph	Me	**7u** (90)[d]	123−125	novel
22	Me	Ph	*n*-Bu	H	**7v** (92)[c]	oil	novel[f]
23	Ph	Ph	*n*-Bu	H	**7w** (91)[d]	95−97	novel
24	Me	Ph	$BnCHCO_2Me$	H	**7x** (90)[b,c]	55−57	novel
25	Me	*p*- tolyl	$-(CH_2)_2O(CH_2)_2-$		**7y** (92)[d]	67−68	novel
26	4-$O_2NC_6H_4$	Ph	cyclohexyl	H	**7z** (90)[d]	142−144	novel
27	4-$O_2NC_6H_4$	Ph	*p*-tolyl	H	**7Aa** (91)[c]	127−129	138[43]

[a] Isolated yield. [b] Reaction conditions: solvent, HOAc; MW, 120 W; temperature, 120 °C; reaction time, 10 min. [c] Obtained as an acetic acid salt. [d] Reaction conditions: $AlCl_3$ (catalytic amount); solvent, $CHCl_3$; MW, 80 W; temperature, 80 °C; reaction time, 10 min. [e] Reaction conditions: HCl salt of amine used; solvent, $CHCl_3$; MW, 80 W; temperature, 80 °C; reaction time, 10 min. [f] Amidines have been reported in the literature in other forms other than acetic acid salts.

the solvent was removed in vacuo to obtain the crude product, which was purified by recrystallization from chloroform/hexane to obtain colorless needles: mp 62−64 °C (lit.[8] 63−64 °C); yield, 89% (11.17 g); ^{1}H NMR δ 3.21 (t, J = 7.7 Hz, 2H), 3.73 (t, J = 7.7 Hz, 2H), 7.17−7.23 (m, 1H), 7.25−7.30 (m, 4H), 7.44 (t, J = 7.6 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 30.0, 36.9, 114.2, 119.9, 125.9, 126.4, 128.3, 128.5, 130.2, 130.9, 139.7, 145.9, 171.4.

***N*-(4-Methylphenyl)cyclohexanecarboxamide (5a).** 1-(Cyclohexylcarbonyl)-1*H*-1,2,3-benzotriazole (2.29 g, 10 mmol) and amine (1.12 g, 10.5 mmol) in chloroform (10 mL) were exposed to microwave irradiation (80 W) for 10 min at a temperature of 80 °C. The reaction mixture was diluted with chloroform (20 mL). The reaction mixture was washed by concentrated sodium carbonate solution (20 mL, twice) and brine (20 mL). The organic layer was dried over magnesium sulfate. After filtration, $CHCl_3$ was removed under reduced pressure to yield the crude product, which was further purified by recrystallization from chloroform/hexanes to obtain colorless plates: mp 154−156 °C (lit.[14] 144.7−145 °C); yield, 96% (2.08 g); ^{1}H NMR δ 1.24−1.35 (m, 2H), 1.46−1.58 (m, 2H), 1.69 (m, 1H), 1.80−1.83 (m, 2H), 1.91−1.93 (m, 2H), 2.16−2.25 (m, 1H), 2.30 (s, 3H), 7.09 (d, J = 8.1 Hz, 2H), 7.35 (br s, 1H), 7.40 (d, J = 8.1 Hz, 3H); ^{13}C NMR δ (1 signal is hidden) 20.7, 25.6, 29.6, 46.4, 119.9, 129.3, 133.6, 135.5, 174.3.

***N*-[1-(1*H*-1,2,3-Benzotriazol-1-yl)ethylidene]aniline (6a).** To a solution of acetanilide (0.68 g, 5.0 mmol) in methylene chloride (20 mL) was added dropwise at 0 °C pyridine (0.45 mL, 5.5 mmol), followed by oxalyl chloride (0.48 mL, 5.5 mmol) in methylene chloride (20 mL). Gas evolution was observed during the process. After the addition, the reaction was continued for 15 min, then benzotriazole (1.25 g, 10.5 mmol) was added in one portion to the reaction flask. The ice bath was removed to allow the reaction to continue at room temperature, and the reaction was monitored by TLC. The precipitated white solid was filtered off, and sodium bicarbonate solution (saturated) was added to dilute the reaction mixture. Aqueous workup gave a crude product that was purified by column chromatography on basic alumina, using hexanes/EtOAc (8:1) as eluent to give colorless needles (from chloroform/hexanes): mp 106−108 °C (lit.[4a] 108 °C); yield, 75% (0.89 g); ^{1}H NMR δ 2.75 (s, 3H), 6.95 (d, J = 7.5 Hz, 2H), 7.19 (t, J = 7.3 Hz, 1H), 7.40−7.50 (m, 3H), 7.60 (t, J = 7.6 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 8.54 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 16.3, 115.7, 119.8, 120.2, 124.3, 125.4, 129.2, 129.2, 131.3, 146.6, 147.4, 154.0.

1-[Phenyl(phenylimino)methyl]-1*H*-benzotriazole (6b). Thionyl chloride (0.77 mL, 10.5 mmol) and benzotriazole (2.44 g, 20.5 mmol) were dissolved in chloroform (10 mL) in a 50 mL round-bottomed flask, and then benzanilide (0.99 g, 5 mmol) was added to the flask. The reaction mixture was exposed to microwave irradiation for 10 min at 80 °C and 80 W. The precipitated solid was filtered off, and aqueous workup gave a crude product that was purified by column chromatography on basic alumina, using hexanes/EtOAc (8:1) as eluent to give yellow needles (from chloroform/hexanes): mp 129−131 °C (lit.[4e] 132−133 °C); yield, 88% (1.31 g); ^{1}H NMR δ 6.84 (d, J = 7.4 Hz, 2H), 7.02 (t, J = 7.4 Hz, 1H), 7.23 (t, J = 7.8 Hz, 2H), 7.35−7.42 (m, 5H), 7.49 (t, J = 7.6 Hz, 1H), 7.61 (t, J = 7.3 Hz, 1H), 8.15 (d, J = 8.2 Hz,

1H), 8.48 (d, J = 8.4 Hz, 1H); ^{13}C NMR δ 115.3, 119.9, 121.4, 124.1, 125.5, 128.1, 128.8, 129.2, 130.1, 130.2, 130.3, 132.0, 146.4, 146.9, 153.7.

***N*,*N*-Diethyl-*N*′-phenylbenzenecarboximidamide (7e).**[39] 1-[Phenyl(phenylimino)methyl]-1*H*-benzotriazole (0.149 g, 0.5 mmol) was dissolved in chloroform (1 mL) in a 10 mL microwave reaction tube. Aluminum chloride (0.014 g, 0.1 mmol) was added to the tube, followed by diethylamine (0.073 g, 1 mmol). The tube containing the reaction mixture was sealed with an aluminum crimp cap fitted with a silicon septum and then exposed to microwave irradiation (80 W) for 10 min at 80 °C. The reaction mixture was diluted with chloroform (20 mL). Aqueous workup gave a residue that was purified by column chromatography on basic alumina using hexanes/EtOAc (8:1) as eluent to give a colorless oil: yield, 87% (0.110 g); ^{1}H NMR δ 1.17 (br s, 6H), 3.35 (br s, 4H), 6.53 (d, J = 7.5 Hz, 2H), 6.68 (t, J = 7.3 Hz, 1H), 6.96 (t, J = 7.7 Hz, 2H), 7.07−7.10 (m, 2H), 7.18−7.23 (m, 3H); ^{13}C NMR δ 13.4, 41.8, 120.7, 123.0, 127.9, 128.0, 128.6, 134.3, 151.7, 159.6.

***N*′-Benzyl-4-methoxy-*N*-(4-methylphenyl)benzenecarboximidamide (7h).** *N*-[1*H*-1,2,3-Benzotriazol-1-yl(4-methoxyphenyl)-methylene]-*N*-benzylamine (0.171 g, 0.5 mmol), *p*-toluidine hydrochloride (0.144 g, 1.0 mmol), and chloroform (1 mL) were placed in a 10 mL microwave reaction tube. The tube containing the reaction mixture was sealed with an aluminum crimp cap fitted with a silicon septum and then exposed to microwave irradiation (80 W) for 10 min at 80 °C. The reaction mixture was diluted with chloroform (20 mL), and the insoluble portion was filtered off. Aqueous workup gave a residue that was purified by recrystallization from chloroform/hexanes to give white microcrystals: mp 115−117 °C; yield, 91% (0.150 g); ^{1}H NMR δ 2.21 (s, 3H), 3.74 (s, 3H), 4.67 (s, 2H), 6.58 (d, J = 7.4 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 7.0 Hz, 2H), 7.37 (t, J = 7.0 Hz, 2H), 7.44 (d, J = 7.1 Hz, 2H); ^{13}C NMR δ (3 signals are hidden) 20.7, 46.2, 55.2, 113.5, 122.8, 127.3, 128.1, 128.6, 129.0, 130.0, 139.1, 148.3, 159.9. Anal. Calcd for $C_{22}H_{22}N_2O$: C, 79.97; H, 6.71; N, 8.48. Found: C, 79.67; H, 7.07; N, 8.24.

***N*-Butyl-*N*′-phenylethanimidamide Acetate (7v).** *N*-[1-(1*H*-1,2,3-Benzotriazol-1-yl)ethylidene]aniline (0.118 g, 0.5 mmol), *n*-butylamine (0.073 g, 1 mmol), and acetic acid (1 mL) were placed in a 10 mL microwave reaction tube. The tube containing the reaction mixture was sealed with an aluminum crimp cap fitted with a silicon septum and then exposed to microwave irradiation (120 W) for 10 min at 120 °C. The reaction mixture was diluted with chloroform (20 mL). Aqueous workup gave a residue that was purified by column chromatography on basic alumina using methylene chloride/methanol (20:1) to give pale yellow needles (from chloroform/hexanes): mp 88−90 °C; yield, 92% (0.115 g); ^{1}H NMR δ 0.89 (t, J = 7.2 Hz, 3H), 1.25−1.37 (m, 2H), 1.44−1.51 (m, 2H), 1.96 (s, 3H), 2.15 (s, 3H), 3.20 (q, J = 6.8 Hz, 2H), 6.64 (br s, 1H) 7.06 (t, J = 7.3 Hz, 1H), 7.27 (t, J = 7.8 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 9.21 (br s, 1H); ^{13}C NMR δ 13.5, 19.8, 22.9, 24.0, 31.3, 39.2, 120.0, 123.8, 128.5, 138.3, 169.3, 170.5. Anal. Calcd for $C_{14}H_{22}N_2O_2$: C, 67.17; H, 8.86; N, 11.19. Found: C, 66.84; H, 8.86; N, 11.01.

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Supporting Information Available: General procedures for the preparation of *N*-acylbenzotriazoles **4a**−**l**, amides **5a**−**Ab**, imidoylbenzotriazoles **6a**−**w**, and amidines **7a**−**Aa** and characterization data for compounds **4b**−**l**, **5b**−**Ab**, **6c**−**w**, and **7a**−**d**,**f**,**g**,**i**−**u**,**w**−**Aa**. This material is available free of charge via the Internet at http://pubs.acs.org.

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