Generalization of the Benzotriazole-Mediated Introduction of *N*-Substituents into Amides

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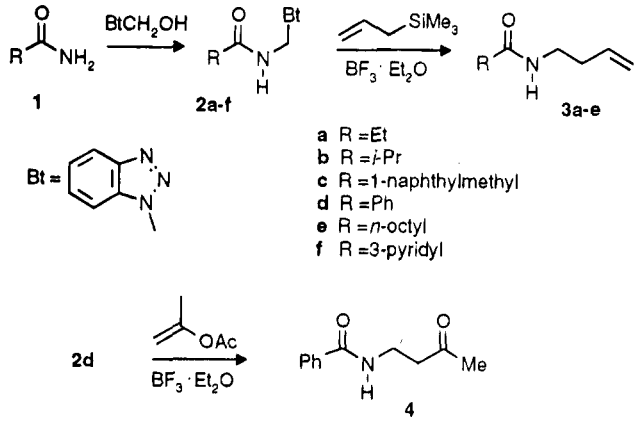
N-(Benzotriazol-1-ylmethyl) amides **2**, easily available by condensation of $BtCH_2OH$ with amides, are used for the preparation of a variety of *N*-substituted amides such as the homoallyl, 1,3-butadienyl, and 2,2-diphenylcyclopropyl derivatives by displacement of the benzotriazole group under different conditions.

Introduction

Over the past 25 years, there has been continuous interest in α-amidoalkylation and the many methods and reagents investigated have been reviewed.[1,2] In the past, *N*-(α-alkoxyalkyl) amides **5** were the most widely used precursors of *N*-acyliminium ions due to their stability.[3] More recently, *N*-(α-benzotriazol-1-ylalkyl) amides **2**, which are also quite stable and easily available by condensation of amides with aldehydes and benzotriazole, have been reported to be still more convenient amidoalkylation reagents.[4] During the past five years, benzotriazole methodology has been elaborated by our group for the α-amidoalkylation of a wide variety of nucleophilic substrates.[3,5–7]

A newly published study by the Hoffman group revealed efficient access to *N*-(α-isopropoxyalkyl) amides by ionization–rearrangement reactions of *N*-triflyloxy amides.[8,9] The method was shown to be quite tolerant of structural diversity, as follows from the wide range of sensitive functional groups incorporated; however, the triflyloxy method failed when a secondary or benzylic carbon was placed adjacent to the nitrogen.[9] Earlier, the benzotriazole method had been used for the preparation of *N*-(α-alkoxyalkyl) amides,[10] especially for the elaboration of *N*-benzyl substituents in amides derived from aryl carboxylic acids. Hoffman[9] pointed out that while "this method appears to be generally superior to the traditional methods... the structural limits of this method remain to be defined". No limitations are to be expected for extension of the benzotriazole methodology to the preparation of various types of *N*-alkyl amides of aliphatic acids; additionally, the stability of the benzotriazole intermediates **2** allows their direct use in α-amidoalkylation, without the need for the intermediate formation of *N*-(α-alkoxyalkyl) amides **5**. The present research has now generalized the benzotriazole method and extended it to the preparation of *N*-(homoallyl) amides and to the introduction of other *N*-unsaturated substituents into the amides, with the presentation of general routes for the elaboration of *N*-unsaturated substituents.

Scheme 1



Results and Discussion

N-(Benzotriazol-1-ylmethyl) amides **2a–f** were easily prepared by reaction of 1-(hydroxymethyl)benzotriazole with the appropriate amide in refluxing acetic acid according to the previously described method (Scheme 1).[11] The primary amides of a variety of aliphatic acids, both long and short chain, were used, and all gave the expected stable products **2** in good yield (Table 1). In addition, products **2c** and **2f** derived from naphthylacetamide and nicotinamide, respectively, indicate the generality of substituents. The availability of the starting materials, simplicity of the reaction conditions, and facile purification by crystallization from ethanol make *N*-(benzotriazol-1-ylmethyl) amides the most convenient amidoalkylation reagents yet reported.

Compounds **2a–e** reacted with allyltrimethylsilane in the presence of a Lewis acid (Scheme 1) slowly upon refluxing in methylene chloride (7 days for completion) or chloroform (3 days), but completely in 24 h under reflux in 1,1,2-trichloroethane, to give *N*-homoallyl amides **3a–e** in good yields (56–85%, Table 1) by displacement of the benzotriazole group. The yield is essentially independent of the solvent used, though the reaction

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Table 1. Preparation of Compounds 2–5, 7, and 8

cpd no.	R (R^1)	yield (%)	mp (°C) or bp/mmHg	molecular formula	calcd C	calcd H	calcd N	found C	found H	found N
2a	Et	63	112–113	$C_{10}H_{12}N_4O$	58.79	5.93	27.44	58.62	5.85	27.71
2b	*i*-Pr	79	109–111	$C_{11}H_{14}N_4O$	60.52	6.47	25.68	60.39	6.49	26.04
2c	(1-naphthyl)methyl	77	183–184	$C_{19}H_{16}N_4O$	72.12	5.10	17.72	72.24	5.13	17.84
2e	*n*-octyl	57	82–83	$C_{16}H_{24}N_4O$	66.62	8.39	19.44	66.32	8.44	19.74
2f	3-pyridyl	69	181–182	$C_{13}H_{11}N_5O$	61.64	4.38	27.66	61.75	4.34	28.05
3a	Et	72	110–120/0.3	$C_7H_{13}NO$	66.09	10.31	11.02	66.35	10.66	10.94
3b	*i*-Pr	56	80/0.2	$C_8H_{15}NO$	68.03	10.71	9.92	67.66	10.67	10.30
3c	(1-naphthyl)methyl	57	96–97	$C_{16}H_{17}NO$	80.29	7.16	5.86	80.32	7.22	5.87
3d	Ph	64	130/0.5[a]	$C_{11}H_{13}NO$	75.39	7.48	8.00	75.18	7.57	7.93
3e	*n*-octyl	85	145/0.4	$C_{13}H_{25}NO$	73.87	11.93	6.63	73.61	12.09	6.49
4	–	33	78[b]	$C_{19}H_{16}NO_2$	69.08	6.86	7.33	68.95	6.94	7.52
5a	Et	94	78/0.25	$C_7H_{15}NO_2$	57.89	10.42	9.65	57.64	10.64	9.63
5b	*i*-Pr	76	80/0.3	$C_7H_{15}NO_2$	57.89	10.42	9.65	57.78	10.72	9.64
5c	3-pyridyl	89	59–60	$C_{10}H_{14}N_2O_2$	61.82	7.27	14.43	61.74	7.26	14.50
7	–	92[c]	125–126[d]	$C_{11}H_{11}NO$[d]	76.26	6.41	8.09	75.90	6.41	8.06
			amorph[c]	$C_{11}H_{11}NO$[c]	76.26	6.41	8.09	76.09	6.40	8.04
8	–	70	158–159[e]	$C_{22}H_{19}NO$	84.31	6.11	4.47	83.92	6.07	4.54

[a] Literature[15] bp 99–100 °C/0.08 mmHg. [b] Literature[16] mp 78 °C. [c] Mixture of *Z*- and *E*-isomers. [d] *E*-isomer. [e] Literature[13] mp 156–158 °C.

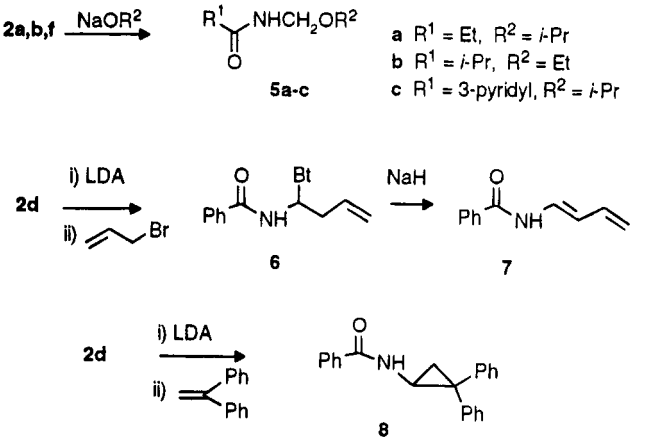
mixture darkens upon long periods of refluxing; $BF_3{\cdot}Et_2O$ gave better results as the Lewis acid rather than $TiCl_4$. The mechanism probably involves slow formation of an acyliminium ion which is then immediately trapped by allyltrimethylsilane.

It was previously demonstrated that the benzotriazole group in *N*-(α-benzotriazol-1-ylalkyl) amides can be displaced by organozinc reagents to give tertiary (both alkyl and aryl) amides in modest to good (30–64%) yields.[6] We have now found that treatment of **2a** or **2d** with allylzinc bromide under the same conditions gives the corresponding *N*-homoallyl amides **3a** and **3d** in 44 and 41% yields, respectively, significantly lower than those achieved using allylsilane. The use of allyl Grignard reagent gave only a 36% yield of compound **3a**. Thus, the optimum conditions for the introduction of a homoallyl group into amides involve acyliminium ion formation as the result of benzotriazole displacement by heating the amidoalkylation reagents **2** in the presence of a Lewis acid, followed by trapping with allyltrimethylsilane. Other reagents can also be employed for acyliminium trapping, as represented by the successful preparation of compound **4** (Scheme 1, Table 1).

We have also prepared the "classical" amidoalkylation reagents **5a–c** (alkoxy as the leaving group) from alkylamides **1a,b,f** via the *N*-(benzotriazol-1-ylmethyl) amides **2a,b,f**, which react readily with sodium alkoxides to give the expected products **5a–c** in excellent yields (Scheme 2, Table 1). Since amidoalkylations via compounds **2** require temperatures of 110–115 °C, reagents **5a–c** are of value for the amidoalkylation of sensitive substrates; their importance in natural product chemistry and industrial synthesis has been discussed.[10]

Recent work has demonstrated that not only can nucleophiles be trapped by acyliminium ions, but that also a variety of electrophiles, such as alkyl halides, ketones, or esters can be introduced using the benzotriazole amidoalkylation method.[12] This is achieved by deprotonation of the methylene (methine) group between the amide nitrogen and the benzotriazole group and subsequent quenching of the resultant anion with electrophiles. The benzotriazole group is later displaced with Grignard reagents, thiols, or alcohols, thus dramatically increasing the number of amides with functional groups available. According to this concept, compound **6** was

Scheme 2



prepared by the reaction **2d→6** as described earlier.[12] Treatment of **6** with sodium hydride in refluxing toluene caused elimination of a benzotriazole molecule (Scheme 2) to give *N*-butadienyl amide **7** in excellent yield (Table 1). Benzotriazole was removed from the reaction mixture by washing with sodium carbonate to yield crude **7** as a mixture of *Z*- and *E*-isomers. The major component, the *E*-isomer, was separated by fractional crystallization and fully characterized (Tables 1–3). The *Z*-isomer was characterized by comparison of the spectral data for the pure *E*-isomer and the *Z,E*-mixture (Tables 2, 3) and by elemental analysis of the *Z,E*-mixture (Table 1).

Lithiation of **2d** and trapping with 1,1-diphenylethylene as the electrophile gave *N*-cyclopropyl-substituted benzamide **8** in 70% yield (Scheme 2, Table 1). The only previously known preparation of **8** was a four-step procedure starting from 2,2-diphenylcyclopropanecarboxylic acid.[13] Presumably the mechanism **2d→8** involves Michael addition of the anion derived from **2d** to the double bond of 1,1-diphenylethylene followed by intramolecular displacement of the benzotriazole group by the γ-carbanionic center.[14]

The structures of all of the new products were proven by CHN analysis and by comparison of their NMR

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Table 2. ^{1}H NMR Spectral Data of Compounds 2–5, 7, and 8

cmp no.	NH	R	*N*-substituent
2a	9.29 (t, 6.5)	1.00 (t, 7.6, 3H); 2.19 (q, 7.6, 2H)	6.06 (d, 6.5, 2H); 7.43 (m, 1H); 7.60 (m, 1H); 8.00 (d, 8.3, 1H); 8.07 (d, 8.3, 1H)
2b[a]	9.23 (t, 6.5)	0.99 (d , 6.9, 6H); 2.41 (sept, 6.9, 1H)	6.02 (d, 6.5, 2H); 7.42 (dt, 8.4, 0.9, 1H); 7.58 (dt, 8.4, 0.9, 1H); 7.95 (dd, 8.4, 0.9, 1H); 8.05 (dd, 8.4, 0.9, 1H)
2c[a]	9.66 (t, 6.4)	3.99 (s, 2H); 6.07 (d, 6.4, 2H); 7.33–7.53 (m, 6H); 7.81 (m, 1H); 7.88–7.93 (m, 3H); 8.06 (d, 8.3, 1H)[b]	
2e	7.70 (t, 6,7)	0.84 (t, 7.0, 3H); 1.18–1.22 (m, 10H); 1.62 (m, 2H); 2.28 (t, 7.5, 2H)	6.11 (d, 6.8, 2H); 7.37 (ddd, 8.3, 7.0, 1.0, 1H); 7.50 (ddd, 8.3, 7.0, 1.0, 1H); 7.94 (dd, 8.3, 0.9, 1H); 7.98 (dd, 8.3, 0.9, 1H)
2f	10.16 (t, 6.3)	7.54 (dd, 8.0, 4.8, 1H); 8.27 (ddd, 8.0, 2.2, 1.8, 1H); 8.76 (dd, 4.8, 1.4, 1H); 9.09 (d, 2.2, 1H)	6.28 (d, 6.3, 2H); 7.44 (dt, 7.9, 1.1, 1H); 7.62 (dt, 7.9, 1.0, 1H); 8.08 (dd, 8.2, 0.8, 1H); 8.09 (dd, 8.3, 1.0, 1H)
3a	5.84 (bs)	1.07 (t, 7.6, 3H); 2.13 (q, 7.6, 2H)	2.19 (ddt, 13.6, 6.8, 1.3, 2H); 3.25 (dt, 6.8, 5.8, 2H); 4.98–5.06 (m, 2H); 5.69 (ddt, 13.6, 10.2, 6.8, 1H)
3b	6.01 (bs)	1.14 (d, 6.9, 6H); 2.38 (sept, 6.9, 1H)	2.23–2.32 (m, 2H); 3.31 (dd, 12.6, 6.8, 2H); 5.05–5.12 (m, 2H); 5.70–5.84 (m, 1H)
3c	5.63 (bs)	4.04 (s, 2H); 7.36–7.44 (m, 2H); 7.46–7.54 (m, 2H); 7.79 (d, 7.5, 1H); 7.84 (m, 1H); 7.94 (m, 1H)	2.03 (ddt, 13.5, 6.8, 1.2, 2H); 3.22 (dt, 6.6, 6.0, 2H); 4.63 (ddd, 17.1, 3.2, 1.5, 1H); 4.75 (ddt, 10.2, 1.9, 1.0, 1H); 5.47 (ddt, 17.1, 10.2, 6.9, 1H)
3d	6.92 (bs)	7.29–7.30 (m, 2H); 7.42–7.48 (m, 1H); 7.77 (dd, 8.3, 1.4, 2H)	2.34 (ddt, 13.7, 6.9, 1.3, 2H); 3.47 (dt, 6.9, 5.8, 2H); 5.04–5.13 (m, 2H); 5.79 (ddt, 13.6, 10.2, 6.8, 1H)
3e	6.09 (bs)	0.87 (t, 6.5, 3H); 1.27 (m, 10H); 1.62 (m, 2H); 2.18 (t, 7.5, 2H)	2.21–2.30 (m, 2H); 3.32 (dd, 12.6, 6.8, 2H); 5.05–5.13 (m, 2H); 5.77 (m, 1H)
4	6.99 (bs)	7.28–7.51 (m, 3H); 7.73–7.77 (m, 2H)	2.16 (s, 3H); 2.79 (dist t, 5.8, 5.5, 2H); 3.67 (dd, 6.0, 5.5, 2H)
5a	6.82 (bs)	1.16 (t, 7.6, 3H); 2.26 (q, 7.6, 2H)	1.17 (d, 6.1, 6H); 3.79 (sept, 6.1, 1H); 4.74 (d, 6.7, 2H)
5b	6.93 (bs)	1.17 (d, 6.9, 6H); 2.44 (sept, 6.9, 1H)	1.19 (t, 7.0, 3H); 3.54 (q, 7.0, 2H); 4.73 (d, 6.7, 2H)
5c	7.41 (bs)	7.41 (ddd, 8.0, 4.9, 0.8, 1H); 8.18 (ddd, 8.0, 2.2, 1.7, 1H); 8.74 (dd, 4.9, 1.7, 1H); 9.05 (dd, 2.3, 0.8, 1H)	1.21 (d, 6.1, 6H); 3.89 (septet, 6.1, 1H); 4.98 (d, 6.6, 2H)
7[c]	8.00 (m)	7.45 (m, 2H); 7.52 (m, 1H); 7.81 (m, 2H)	5.01 (dd, 10.2, 0.8, 1H); 5.12 (dd, 16.2, 0.8, 1H); 5.99 (dd, 14.1, 10.7, 1H); 6.36 (ddd, 16.9, 10.7, 10.2, 1H); 7.22 (dd, 14.1, 10.9, 1H)
7[d]	8.53 (d, 10.0)	7.35–7.55 (m, 3H); 7.75–7.85 (m, 2H)	5.11 (dd, 11.1, 0.8, 1H); 5.26 (dd, 16.6, 0.8, 1H); 5.52 (dd, 10.6, 9.7, 1H); 6.59 (ddt, 16.6, 10.3, 1.0, 1H); 6.91 (t, 10.0, 1H)
8	5.92 (d, 4.6)	1.62–1.74 (m, 2H); 3.83 (dt, 7.8, 5.2, 1H); 7.14–7.31 (m, 8H); 7.37–7.45 (m, 7H)[b]	

[a] Solvent: DMSO-d_6. [b] R and *N*-substituent signals are overlapped. [c] *E*-isomer. [d] *Z*-Isomer (from NMR spectra of *Z*,*E*-mixture).

Table 3. ^{13}C NMR Spectral Data of Compounds 2–5, 7, and 8

cmp no.	C=O	R	*N*-substituent
2a	173.9	9.4, 28.2	51.0, 111.3, 119.0, 124.1, 127.4, 132.1, 145.3
2b[a]	177.1	19.2, 33.9	51.1, 111.2, 119.0, 124.1, 127.3, 132.0, 145.3
2c[a]	171.3	39.5, 124.0, 125.4, 127.3, 125.6, 125.9, 127.9, 128.4, 131.8, 131.9, 133.3	51.2, 111.3, 119.0, 124.1, 127.3, 132.1, 145.3
2e	174.0	14.0, 22.5, 25.2, 28.9, 29.0, 29.1, 31.6, 36.2	50.9, 111.1, 119.2, 124.3, 127.9, 132.3, 145.8
2f	165.6	123.5, 128.5, 135.2, 148.6, 152.6	51.6, 111.2, 119.0, 124.1, 127.5, 132.3, 145.3
3a	173.8	9.8, 29.6	33.7, 38.2, 116.9, 135.2
3b	176.9	19.5, 35.4	33.7, 38.1, 116.8, 135.2
3c	170.7	41.1, 123.2, 125.0, 125.6, 126.2, 127.8, 127.9, 128.2, 130.4, 131.5, 133.4	32.9, 37.8, 116.6, 134.1
3d	167.5	126.8, 128.2, 131.1, 134.5	33.6, 38.8, 116.9, 135.2
3e	173.7	14.3, 22.9, 26.1, 29.4, 29.5, 29.6, 32.1, 37.0	34.1, 38.7, 117.2, 135.6
4	167.3	126.8, 128.4, 131.4, 134.2	30.1, 34.5, 42.8, 208.6
5a	174.4	9.3, 29.4	22.1, 67.6, 69.0
5b	177.8	19.2, 35.3	14.9, 63.4, 69.5
5c	165.4	123.1, 129.3, 135.0, 147.6, 152.0	21.9, 67.9, 69.4
7[b]	164.4	127.1, 128.7, 132.1, 133.4	114.6, 114.8, 126.1, 134.5
7[c]	164.6	127.2, 128.5, 131.9, 133.5	111.6, 114.5, 117.1, 121.8
8	168.8	20.4, 35.2, 36.8, 126.5, 126.6, 127.1, 128.3, 128.4, 128.5, 128.7, 130.0, 131.3, 134.4, 139.8, 144.4[d]	

[a] Solvent: DMSO-d_6. [b] *E*-Isomer. [c] *Z*-Isomer (from NMR spectra of *Z*,*E*-mixture). [d] R and *N*-substituent signals are overlapped.

spectral data with similar literature spectra. For *N*-methylene groups, characteristic doublets were observed in the narrow range of 6.02–6.28 (compounds **2a–f**) or 4.73–4.98 ppm (compounds **5a–c**), with coupling constants within the range of 6.3–6.8 Hz. NH Groups were observed as triplets (compounds **2a–f**) or broad singlets (**3–5**). Signals for *N*-homoallyl groups were in agreement with the literature data.[9] Signals for the vinyl protons of the *N*-butadienyl group (compound **7**) were found at 5.01–7.22 ppm with characteristic couplings. *Z*,*E*-Configurations were assigned according to the higher values of J_{trans} (16–17 Hz) than J_{cis} (10–11 Hz).

This work has demonstrated the considerable versatility of the benzotriazole approach to amidoalkylation. As demonstrated, the benzotriazole group can be eliminated or displaced by a variety of methods, so that different types of *N*-unsaturated amides can be obtained from the same starting materials **2**. *N*-(Benzotriazol-1-ylmethyl) amides **2** are easily accessible from simple reagents, provide superior yields of amidoalkylation products and, in some cases, are the only reagents which can be used for the preparation of certain amides.

Experimental Section

Melting points were determined on a hot stage apparatus and are uncorrected. ^{1}H NMR spectra were obtained at 300 MHz, and ^{13}C NMR spectra were determined at 75 MHz. Chemical shifts are reported in ppm relative to TMS or $CDCl_3$.

Elemental analyses were carried out in this department. Column chromatography was performed on silica gel 60 (230–400 mesh) using EtOAc/hexane as the eluent, in most cases. Isopropenyl acetate, allyltrimethylsilane, allyl bromide, LDA, amides **1a–d,f**, 1,1-diphenylethylene, $BF_3{\cdot}Et_2O$, 1,1,2-trichloroethane, and benzotriazole were purchased from Aldrich, and amide **1e** was purchased from Pfaltz & Bauer and used as received. Compounds **2d**, mp 178–181 °C, lit.[11] mp 177–179 °C; **6** mp 143–144 °C, lit.[12] mp 144–145 °C; and $BtCH_2OH$, mp 148–151 °C, lit.[17] mp 148–151 °C were prepared as previously reported.

Preparation of *N*-(Benzotriazol-1-ylmethyl) Amides 2a–f. General Procedure. A mixture of $BtCH_2OH$ (14.9 g, 0.1 mol) and the appropriate amide (0.1 mol) in AcOH (50 mL) was refluxed for 4–6 h. The solvent was evaporated, and the residue was dissolved in chloroform. The resulting solution was washed with Na_2CO_3 (10%, 3 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was crystallized from ethanol (Table 1).

Preparation of *N*-(3-Butenyl) Amides 3a–e and *N*-(3-Oxobutyl)benzamide 4. General Procedure. A trapping reagent (allyltrimethylsilane or isopropenyl acetate, 20 mmol) was added to a solution of the appropriate *N*-(benzotriazol-1-ylmethyl) amide **2** (10 mmol) in 1,1,2-trichloroethane (20 mL) at rt followed by addition of $BF_3{\cdot}Et_2O$ (20 mmol). The mixture was slowly heated to reflux and stirred for 24 h. It was then cooled, diluted with chloroform (30 mL), washed with brine, followed by Na_2CO_3 (10%, 3 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled under reduced pressure (Table 1) or purified by chromatography (compounds **3c** and **4**).

Preparation of *N*-(Alkoxymethyl) Amides 5a–c. General Procedure. The *N*-(benzotriazol-1-ylmethyl) amide **2** (10 mmol) was added in one portion to a solution of sodium (0.28 g, 12 mmol) in the appropriate alcohol (30 mL) at rt. The mixture was stirred at rt overnight and poured into water (200 mL). The aqueous solution was extracted with chloroform (3 × 30 mL). The combined organic layers were washed with Na_2CO_3 (10%, 3 × 50 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was distilled under reduced pressure (Table 1).

Preparation of *N*-(1,3-Butadienyl)benzamide 7. Sodium hydride (30 mg, 1.25 mmol) was added to a solution of **6** (290 mg, 1 mmol) in toluene (10 mL) in one portion. The mixture was refluxed for 24 h. The solvent was evaporated, and the residue was dissolved in chloroform (20 mL). The resulting solution was washed with water (10 mL) and Na_2CO_3 (10%, 2 × 20 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was crystallized from EtOAc to yield pure *E*-isomer (60 mg, 34%). Concentration of the mother liquor afforded a mixture (100 mg, 58%) of both *Z*- and *E*-isomers (Table 1).

Preparation of *N*-(2,2-Diphenylcyclopropyl)benzamide 8. To a solution of **2d** (1.26 g, 5 mmol) in THF (30 mL) was added LDA (6.7 mL of a 1.5 *M* solution, 10 mmol) at −78 °C, and the mixture was stirred for 2 h. 1,1-Diphenylethylene (0.9 g, 5 mmol) was then added and stirring was continued for 14 h at −78 °C. Water (25 mL) was added and the resulting icy mixture was extracted with ether (3 × 50 mL). The combined organic layers were washed with water (30 mL), dried over $MgSO_4$, and concentrated in vacuo. The residue was crystallized from EtOAc (Table 1).

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