JOC Article

Stereoselective Synthesis of Both *syn*- and *anti*-*N*-*tert*-Alkylamines Using Highly Stereospecific Crotylation of Ketone-Derived Acylhydrazones with Crotyltrichlorosilanes

Chikako Ogawa, Masaharu Sugiura, and Shū Kobayashi*

Graduate School of Pharmaceutical Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

skobayas@mol.f.u-tokyo.ac.jp

Received April 25, 2002

Crotyltrichlorosilanes reacted with *ketone-derived N*-benzoylhydrazones in DMF without any catalyst. This is the first example of highly stereospecific crotylation of *ketimine analogues* leading to both *syn*- and *anti*-*N*′-*tert*-alkyl-*N*-benzoylhydrazines. Different reactivities between (*Z*)- and (*E*)-crotylsilanes in terms of yields and selectivities were observed. A kinetic study with both geometrically pure (*Z*)- and (*E*)-crotylsilanes was performed. These reactions are most likely to proceed via a cyclic chairlike transition state where the aromatic group of hydrazones takes an axial position. Both diastereomers of allylation products can be converted to the corresponding α,α-disubstituted homoallylic amines without epimerization.

Introduction

Aldimines and their *aldehyde-derived* analogues such as hydrazones and oximes are currently recognized as useful prochiral electrophiles for the construction of a stereogenic carbon center alpha to a nitrogen atom due to their relatively high reactivity.[1,2] On the other hand, *ketimines* and their *ketone-derived* analogues have been less utilized because of the low productivity caused by steric hindrance and side reactions such as isomerization of the imine form to an enamine form. Furthermore, stereochemical control of their electrophilic reactions is difficult since the discrimination of their prochiral faces would be harder than that of the aldehyde counterparts. As for allylation of these electrophiles, for example, stereospecific crotylation is unprecedented,[3] though there are several reports on synthesis of *N*-*tert*-alkylamines based on addition of allylmetal reagents to ketimines.[4,5] In this context, we have recently found that allyltrichlorosilanes smoothly reacted with *aldehyde*- or *ketone-derived N*-benzoylhydrazones in DMF without the use of any catalyst to afford the corresponding homoallylic benzoylhydrazines.[6] Moreover, crotylation of these *aldehyde-derived* hydrazones with (*E*)- and (*Z*)-crotyltrichlorosilanes[7,8] provided *syn* and *anti* adducts with high stereospecificity. As a further extension of this study, we describe herein the first examples of highly stereospecific crotylation of *ketone-derived N*-benzoylhydrazones leading to both *syn*- and *anti*-*N*′-*tert*-alkyl-*N*-benzoylhydrazines which can be converted to the corresponding α,α-disubstituted homoallylic amines.

(1) For comprehensive discussions on the functional group transformations of imines and their *N*-substituted derivatives, see: *Comprehensive Organic Functional Group Transformations*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Pattenden, G., Volume Ed.; Pergamon, Oxford, UK, 1995; Vol. 3, pp 403−490.

(2) For general reviews on organic synthesis utilizing imines and their *N*-substituted derivatives as electrophiles, see: (a) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, UK, 1991; Vol. 2, pp 893−1109. (b) Bloch, R. *Chem. Rev.* **1998**, *98*, 1407−1438. (c) Enders, D.; Reinhold, U. *Tetrahedron: Asymmetry* **1997**, *8*, 1895−1946. (d) For a recent review on Mannich reactions, see: Arend, M.; Westermann, B.; Risch, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 1044−1070. (e) For a recent review on catalytic enantioselective additions to imines, see: Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069−1094.

(3) For reviews on addition of allylmetals to C=O and C=N double bonds, see; (a) Yamamoto, Y.; Asano, N. *Chem. Rev.* **1993**, *93*, 2207−2293. (b) Denmark, S. E.; Almstead, N. G. In *Modern Carbonyl Chemistry*; Otera, J., Ed.; Wiley-VHC: Weinheim, Germany, 2000; Chapter 10.

(4) For recent examples of addition of allylmetals to ketimines or their analogues, see: (a) Hilt, G.; Smolko, K. I.; Waloch, C. *Tetrahedron Lett.* **2002**, *43*, 1437−1439 (*N*-phenylimines/indium). (b) Kumar, H. M. S.; Anjaneyulu, S.; Reddy, E. J.; Yadav, J. S. *Tetrahedron Lett.* **2000**, *41*, 9311−9314 (*N*-tosylhydrazones/indium). (c) Nicolaou, K. C.; Rodríguez, R. M.; Mitchell, H. J.; Suzuki, H.; Fylaktakidou, K. C.; Baudoin, O.; van Delft. F. L. *Chem. Eur. J.* **2000**, *6*, 3095−3115 (*O*-benzyloximes/magnesium). (d) Steining, A. G.; Spero, D. M. *J. Org. Chem.* **1999**, *64*, 2406−2410 (chiral *N*-alkylimines/magnesium). (e) Cogan, D. A.; Liu, G.; Ellman, J. *Tetrahedron* **1999**, *55*, 8883−8904 (chiral *N*-sulfinylimines/magnesium). (f) Kobayashi, S.; Sugita, K.; Oyamada, H. *Synlett* **1999**, 138−140 (a *N*-acylhydrazone/tin). (g) Wang, D.-K.; Dai, L.-X.; Hou, X.-L.; Zhang, Y. *Tetrahedron Lett.* **1996**, *37*, 4187−4188 (*N*-benzylimines/magnesium or zinc). (h) Wang, J.; Zhang, Y.; Bao, W. *Synth. Commun.* **1996**, *26*, 2473−2477 (a *N*-phenylimine/samarium).

(5) Crotylations of ketimines and related compounds have been precedented, though their diastereoselectivities were low, see: (a) Barbot, F.; Miginiac, L. *Synth. Commun.* **1997**, *27*, 2601−2614. (b) Felix, C.; Laurent, A.; Lesniak, S.; Mison, P. *J. Chem. Res. (S)* **1991**, 32−33. (c) Epifani, E.; Florio, S.; Ingrosso, G.; Babudri, F. *Tetrahedron* **1989**, *45*, 2075−2082. (d) Epifani, E.; Florio, S.; Ingrosso, G.; Sgarra, R.; Stasi, F. *Tetrahedron* **1987**, *43*, 2769−2778. (e) Chaabouni, R.; Laurent, A.; Marquet, B. *Tetrahedron* **1980**, *36*, 877−885.

(6) (a) Kobayashi, S.; Hirabayashi, R. *J. Am. Chem. Soc.* **1999**, *121*, 6942−6943. (b) Hirabayashi, R.; Ogawa, C.; Sugiura, M.; Kobayashi, S. *J. Am. Chem. Soc.* **2001**, *123*, 9493−9499.

(7) For preparation of (*E*)-crotyltrichlorosilane, see: (a) Nystrom. R. F.; Grown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197−1199. (b) Hatch, L. F.; Nesbitt, S. S. *J. Am. Chem. Soc.* **1950**, *72*, 727−730. (c) Young, W. G.; Andrews, L. J. *J. Am. Chem. Soc.* **1944**, *66*, 421−425. (d) Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 1099−1102 (>99% *E*).

(8) For preparation of (*Z*)-crotyltrichlorosilane, see: Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143−2146.

10.1021/jo0258599 CCC: $22.00
Published on Web 06/27/2002

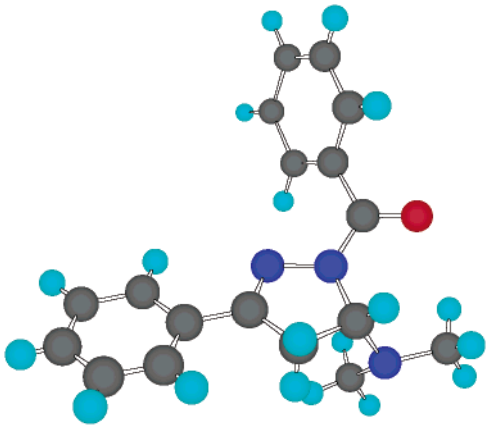
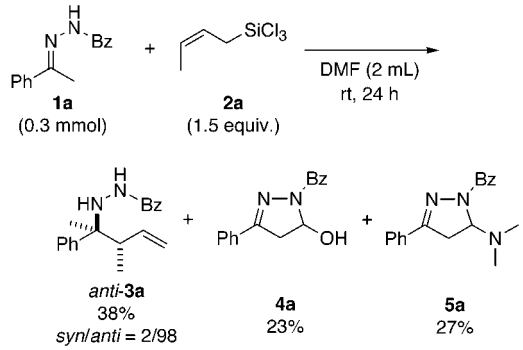


FIGURE 1. The structure of **5a**.

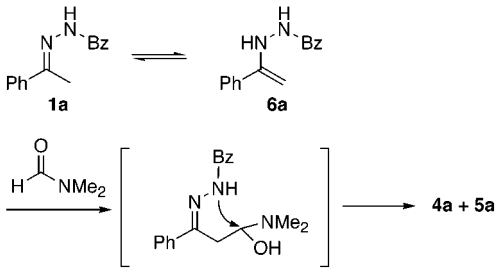
SCHEME 1. Preliminary Result



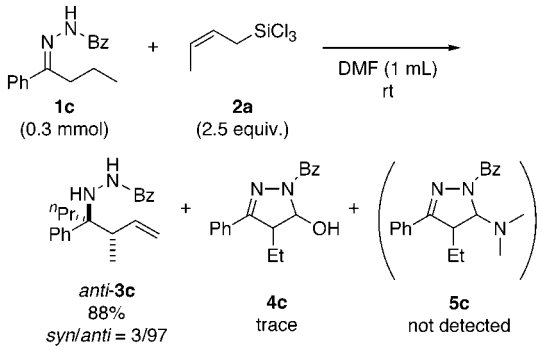
Results and Discussion

At the outset, we investigated crotylation of acetophenone-derived benzoylhydrazone **1a** with (*Z*)-crotyltrichlorosilane (**2a**) by simply mixing these compounds in DMF at ambient temperature (Scheme 1). Compared with crotylation of the *benzaldehyde*-derived hydrazone, which we reported,[6] the reaction was found to be sluggish and provided the adduct **3a** in lower yield (38%) even after prolonged reaction time, although high diastereoselectivity for the formation of **3a** (*syn*/*anti* = 2/98) was observed. The stereochemical assignment was made after converting to the corresponding *N*-tosylhomoallylamine derivative (vide infra). While the main reason for the lower reactivity of **1a** toward **2a** would be steric bulkiness due to the methyl group of **1a**, careful isolation of byproducts revealed that dihydropyrazole derivatives **4a** and **5a** were unexpectedly formed. The structure of **5a** was unequivocally established on the basis of its X-ray crystallography (Figure 1).[9] It is likely that the nucleophilic addition of enamine **6a**, the tautomeric isomer of **1a**, to DMF followed by dehydrative or deaminative cyclization formed these dihydropyrazoles presumably under Lewis acid catalysis of the trichlorosilane (Scheme 2).[10,11]

SCHEME 2. Formation of Dihydropyrazoles 4a and 5a



SCHEME 3. Crotylation of 1c with *Z*-Crotyltrichlorosilane



To diminish the formation of the dihydropyrazoles, we attempted to use other solvents such as HMPA or DMA, or to increase the reaction temperature to accelerate the desired reaction. However, no significant improvement was observed. As another approach to address this issue, introduction of bulkier substituents on the hydrazone carbon, that is, use of butyrophenone-derived benzoylhydrazones **1c**, was next investigated. After optimization of the reaction conditions for **1c** including the amount of reagent, concentration of the substrates, and the quenching method, it was revealed that use of slight excess amounts of **2a** (2.5 equiv) in a higher concentration (0.3 mmol of **1c** in 1.0 mL of DMF) provided the adduct **3c** in excellent yield with high diastereoselectivity (Scheme 3).

Under the conditions optimized for **1c**, reactions of various aromatic ketone-derived benzoylhydrazones **1a**−**l** with (*Z*)- and (*E*)-crotyltricholorosilanes (**2a** and **2b**) were next investigated (Table 1). Remarkably, the reactions proceeded smoothly in most cases to afford the corresponding *N*′-*tert*-alkyl-*N*-benzoylhydrazines in good yields. Following are the characteristic features of this reaction: (1) high levels of stereospecificity were obtained, i.e., the (*Z*)-crotyltrichlorosilane (**2a**) provided *anti* adducts, while the (*E*)-counterpart gave *syn* adducts with high selectivities; (2) in most cases, the (*Z*)-crotylsilane provided better yields and selectivities than the (*E*)-crotylsilane; and (3) both electron-withdrawing (NO_2, Cl, or Br) and -donating (Me or Et) substituents on the aromatic ring are tolerated in this reaction.

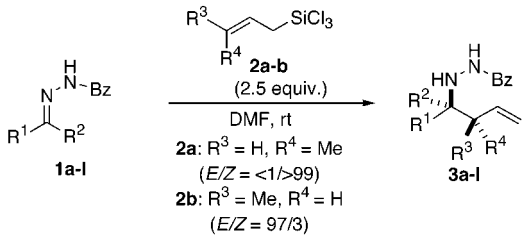
To clarify the difference in reactivity between (*Z*)- and (*E*)-crotylsilanes toward benzoylhydrazones, we performed a kinetic study on the crotylation of **1c** (Figure 2). Higher reactivity of the (*Z*)-crotylsilane was clearly shown, and hence the geometric purity of **2** significantly affected the reaction rate. In crotylation with an excess amount of (*E*)-crotylsilane (97% *E*), the contaminated

(9) See Supporting Information.

(10) This dihydropyrazole formation from *N*-acylhydrazones with DMF is unprecedented. Lewis acid-catalyzed reactions of hydrazones with such electrophiles are now under investigations.

(11) It has been reported that chlorosilanes (weak Lewis acids) served as effective enantioselective Lewis acid catalysts in the presence of chiral Lewis bases, see: Denmark, S. E.; Wynn, T. *J. Am. Chem. Soc.* **2001**, *123*, 6199−6200.

TABLE 1. Crotylation of Various *Ketone-Derived* Benzoylhydrazones



entry	R^1	R^2	2	time/h	3	yield/%	*syn*/*anti*
1	Ph	Me (**1a**)	**2a**	24	**3a**	52	2/98
2			**2b**	24	**3a**	46	92/8
3	Ph	Et (**1b**)	**2a**	24	**3b**	65	<1/>99
4			**2b**	24	**3b**	61	86/14
5	Ph	*n*-Pr (**1c**)	**2a**	12	**3c**	88	3/97
6			**2b**	24	**3c**	78	87/13
7	Ph	*n*-Bu (**1d**)	**2a**	24	**3d**	63	1/99
8			**2b**	24	**3d**	60	90/10
9	*β*-Nap	Me (**1e**)	**2a**	24	**3e**	37	2/98
10			**2b**	24	**3e**	49	93/7
11	*m*-NO_2Ph	Me (**1f**)	**2a**	24	**3f**	49	7/93
12			**2b**	24	**3f**	47	93/7
13	*p*-BrPh	Me (**1g**)	**2a**	24	**3g**	38	6/94
14			**2b**	24	**3g**	50	95/5
15	*p*-ClPh	Et (**1h**)	**2a**	36	**3h**	63	<1/>99
16			**2b**	24	**3h**	59	92/8
17	*p*-ClPh	*n*-Pr (**1i**)	**2a**	36	**3i**	77	<1/>99
18			**2b**	36	**3i**	68	91/9
19	*p*-MePh	Et (**1j**)	**2a**	24	**3j**	66	3/97
20			**2b**	36	**3j**	54	92/8
21	*p*-MePh	*n*-Pr (**1k**)	**2a**	29	**3k**	74	<1/>99
22			**2b**	29	**3k**	58	93/7
23	*p*-EtPh	Et (**1l**)	**2a**	24	**3l**	55	<1/>99
24			**2b**	36	**3l**	49	92/8

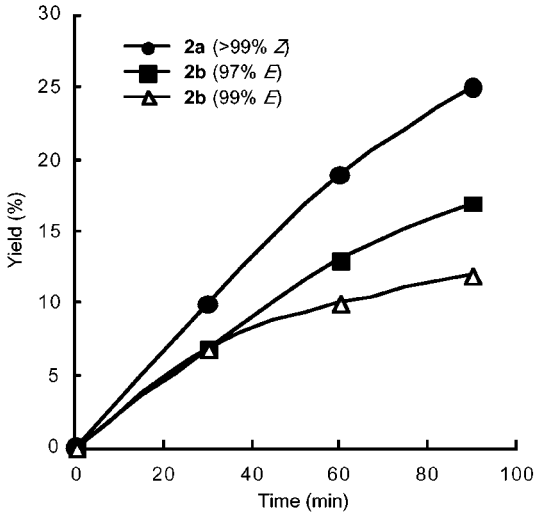


FIGURE 2. Plots of yield of **3c** versus time for the crotylation of **1c** with **2a** or **2b**.

Z-isomer reacted preferentially over the (*E*)-crotylsilane at the initial stage of the reaction giving lower selectivities. The stereoselectivity of the reaction is most likely explained by assuming a chairlike transition structure where the nitrogen atom and the benzoyl carbonyl group coordinate to the silicon atom.[12] The *E*-geometry of the ketone-derived benzoylhydrazone[13] put the aromatic R^1 group at an axial direction on the basis of reactions of aldehyde-derived benzoylhydrazones (Figure 3).[6] In this transition state for crotylation, *anti-periplaner* orientation of the methyl group of the (*Z*)-crotylsilane against the aromatic R^1 would be more sterically favored than *syn-clinal* orientation of the methyl group of the (*E*)-crotylsilane. Consequently, (*Z*)-crotylsilane reacted with ketone-derived benzoylhydrazone faster than (*E*)-crotylsilane.

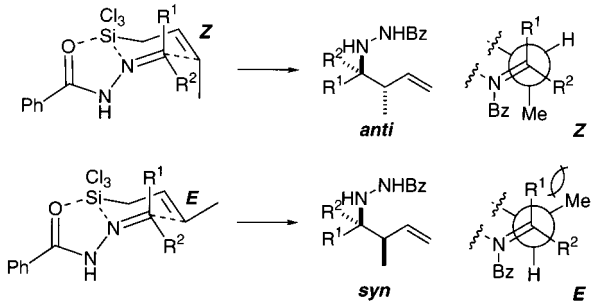
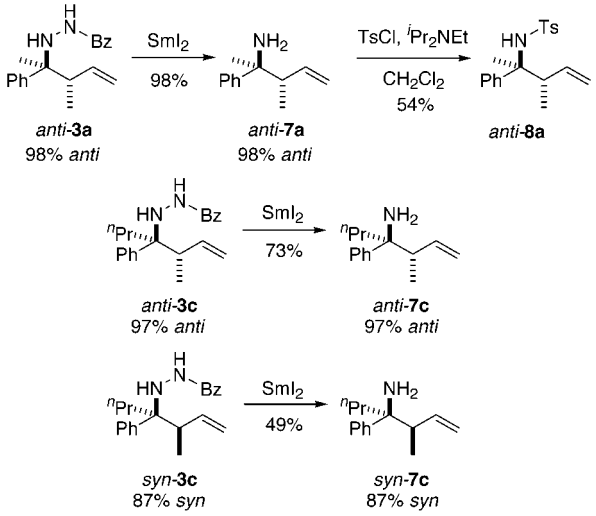


FIGURE 3. Assumed transition states of crotylation.

SCHEME 4. Transformation of 3a and 3c to Homoallylic Primary Amines



Conversion of Products to the Corresponding α,α-Disubstituted Homoallylic Primary Amines and Assignment of Relative Configuration. Benzoylhydrazine *anti*-**3a** was converted to the corresponding α,α-disubstituted homoallylic primary amines *anti*-**7a** by treatment of excess amounts of SmI_2 (Scheme 4).[14] The relative configuration of *anti*-**7a** was assigned by X-ray diffraction analysis after converting to tosylamide **8a** (Figure 4).[9] The relative configurations of other products were tentatively assigned on the basis of the analogy. In

(12) For a related discussion on the mechanism of allylation of aldehydes with allyltrichlorosilanes, see: Denmark, S. E.; Fu, J. *J. Am. Chem. Soc.* **2000**, *122*, 12021−12022.

(13) The ^{1}H NMR analysis of **1a** in DMF-d_7 shows that it exists in geometrically pure form in the solution. For general discussions on the geometrical isomerism of azomethine compounds, see: Tennant, G. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, UK, 1979; Vol. 2, pp 396−398.

(14) Burk, M. J.; Feaster, J. *J. Am. Soc. Chem.* **1992**, *114*, 6266−6267.

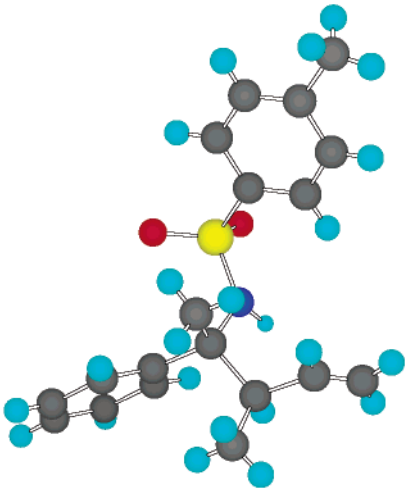


FIGURE 4. The structure of **8a**.

addition, both *anti*- and *syn*-hydrazines **3c** were successfully transformed to *anti*- and *syn*-homoallylic amines **7c**, respectively. This N−N bond cleavage proceeded smoothly without detectable epimerization.

Conclusions

In summary, we have demonstrated that crotylation of *ketone-derived* benzoylhydrazones with crotylsilanes proceeded in a highly stereospecific manner to afford both *syn*- and *anti*-*N*′-*tert*-alkyl-*N*-benzoylhydrazines. The N−N bonds of these products can be readily cleaved without epimerization. Thus, the overall sequence offers an unprecedented stereospecific synthesis of homoallylic *N*-*tert*-alkylamines.

Experimental Section

General Methods. Melting points are uncorrected. Tetramethylsilane (TMS) served as internal standard (δ 0) for ^{1}H NMR, and $CDCl_3$ was used as internal standard (δ 77.0) for ^{13}C NMR. Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography (PTLC) was carried out with Wakogel B-5F. Dimethylformamide was distilled from P_2O_5 and dried over MS 4A. All other solvents and chemical compounds were purified based on standard procedures.

Preparation of Benzoylhydrazones. Benzoylhydrazones were prepared by simply mixing benzoylhydrazine and ketones (1.05 equiv) in THF containing a catalytic amount of concentrated HCl at ambient temperature. After the solution was stirred for 8 h, the precipitates formed were filtered, and the crude materials were then recrystallized from MeOH.

Typical Experimental Procedure for the Reaction of a Benzoylhydrazone with Crotyltrichlorosilane. Crotyltrichlorosilane (0.75 mmol) was added dropwise to a solution of a benzoylhydrazone (0.3 mmol) in DMF (1.0 mL) at room temperature. The mixture was stirred for 24−36 h at the same temperature (checked by TLC), and then saturated aqueous NaOAc was added to quench the reaction. Immediately, the organic layer was extracted with ethyl acetate, and the aqueous layer was further extracted with the same solvent. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC to afford a crotylation adduct. The diastereomeric ratios of the products were determined by ^{1}H and ^{13}C NMR analyses.

***N*′-(1,2-Dimethyl-1-phenylbut-3-enyl)benzohydrazide (*anti*-3a):** Mp 131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, J = 7.0 Hz, 3H), 1.43 (s, 3H), 2.53 (qd, J = 6.8 Hz, 1H), 5.17 (apparent dd, J = 2.2, 10.2 Hz, 1H), 5.21 (apparent dd, J = 1.8, 17.1 Hz, 1H), 5.15−5.25 (br, 1H), 5.73−5.85 (m, 1H), 6.91 (br, 1H), 7.19−7.51 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 15.8, 17.1, 48.4, 64.8, 117.6, 126.6, 127.0, 127.2, 128.4, 128.6, 131.5, 132.8, 139.6, 143.9, 166.2. IR (KBr) 3271, 1648, 1452, 1319, 699 cm^{-1}. Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.58; H, 7.50; N, 9.46.

***N*′-(1,2-Dimethyl-1-phenylbut-3-enyl)benzohydrazide (*syn*-3a):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (d, J = 6.8 Hz, 3H), 1.53 (s, 3H), 2.61 (qd, J = 6.8 Hz, 1H), 4.97−5.02 (m, 2H), 5.64−5.76 (m, 1H), 5.76 (br, 1H), 7.09 (br, 1H), 7.26−7.57 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.7, 20.2, 47.3, 65.2, 115.5, 126.6, 126.9, 127.1, 128.2, 128.6, 131.6, 132.9, 139.6, 143.3, 166.3. IR (neat) 3304, 1625, 1243, 1004 cm^{-1}. Anal. Calcd for $C_{19}H_{22}N_2O$: C, 77.52; H, 7.53; N, 9.52. Found: C, 77.27; H, 7.59; N, 9.49.

***N*′-(1-Ethyl-2-methyl-1-phenylbut-3-enyl)benzohydrazide (*anti*-3b):** Mp 113 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 1.83−2.02 (m, 2H), 2.57 (qd, J = 7.0 Hz, 1H), 4.95−5.07 (m, 2H), 5.57 (ddd, J = 1.7, 7.0, 18.5 Hz, 1H), 5.60−5.63 (br, 1H), 7.05 (br, 1H), 7.08−7.55 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.8, 15.1, 26.3, 44.8, 67.0, 115.6, 126.6, 126.8, 127.7, 128.0, 128.6, 131.5, 133.0, 140.5, 140.8, 165.3. IR (neat) 3290, 1830, 1637, 1578, 1545, 1438, 1371, 924, 910 cm^{-1}. Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08. Found: C, 77.93; H, 7.98; N, 9.03.

***N*′-(1-Ethyl-2-methyl-1-phenylbut-3-enyl)benzohydrazide (*syn*-3b):** Mp 76−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, J = 6.9 Hz, 3H), 0.91 (t J = 7.3 Hz, 3H), 1.82−1.93 (m, 1H), 1.95−2.06 (m, 1H), 2.55 (qd, J = 6.9 Hz, 1H), 5.00−5.10 (m, 2H), 5.56 (brd, J = 6.8 Hz, 1H), 5.70−5.79 (m, 1H), 7.12 (brd, J = 5.6 Hz, 1H), 7.17−7.55 (m, 10H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 7.9, 15.7, 26.1, 44.8, 67.4, 114.9, 126.6, 126.7, 127.6, 128.0, 128.6, 131.5, 133.1, 140.4, 141.0, 165.6. Anal. Calcd for $C_{20}H_{24}N_2O$: C, 77.89; H, 7.84; N, 9.08, Found: C, 77.84; H, 7.89; N, 9.06.

***N*′-(2-Methyl-1-phenyl-1-propylbut-3-enyl)benzohydrazide (*anti*-3c):** Mp 97−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 1.23−1.41 (m, 2H), 1.76−1.82 (m, 1H), 1.85−1.93 (m, 1H), 2.57 (qd, J = 6.7 Hz, 1H), 4.98 (dd, J = 1.8, 10.3 Hz, 1H), 5.04 (brd, J = 17.8, 1H), 5.60 (ddd, J = 1.8, 10.3, 17.8, 1H), 5.57−5.64 (br, 1H), 6.97−7.09 (br, 1H), 7.16−7.60 (m, 10H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.8, 15.0, 16.6, 36.5, 45.3, 66.9, 115.6, 126.6, 126.8, 127.5, 128.0, 128.6, 131.5, 133.1, 140.5, 141.1, 165.3. IR (KBr) 3271, 3059, 1648, 1624, 1576, 1377, 1318, 1298, 1292, 1064, 924 cm^{-1}. Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 77.97; H, 8.22; N, 8.72.

***N*′-(2-Methyl-1-phenyl-1-propylbut-3-enyl)benzohydrazide (*syn*-3c):** Mp 124−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (t, J = 7.3 Hz, 3H), 0.89 (d, J = 7.0 Hz, 3H), 1.23−1.40 (m, 2H), 1.76−1.82 (m, 1H), 1.85−1.91 (m, 1H), 2.57 (qd, J = 7.0 Hz, 1H), 4.98 (dd, J = 1.8, 10.1 Hz, 1H), 5.04 (brd, J = 17.8 Hz, 1H), 5.61 (ddd, J = 1.8, 10.1, 17.8 Hz, 1H), 5.57−5.62 (br, 1H), 7.08 (br, 1H), 7.19−7.54 (m, 10H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 14.9, 15.0, 16.6, 36.5, 45.4, 67.0, 115.6, 126.6, 126.8, 127.6, 128.0, 128.7, 131.5, 133.1, 140.5, 141.2, 165.3. IR (KBr) 3303, 1624, 1577, 1553, 1431, 1314, 1153, 1066, 922, 785 cm^{-1}. Anal. Calcd for $C_{21}H_{26}N_2O$: C, 78.22; H, 8.13; N, 8.69. Found: C, 78.27; H, 8.17; N, 8.68.

***N*′-(1-Butyl-2-methyl-1-phenylbut-3-enyl)benzohydrazide (*anti*-3d):** Mp 90 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (t, J = 7.1 Hz, 3H), 0.96 (d, J = 7.2 Hz, 3H), 1.19−1.44 (m, 4H), 1.85−2.02 (m, 2H), 2.65 (qd, J = 7.2 Hz, 1H), 5.02−5.12 (m, 2H), 5.61−5.73 (m, 1H), 7.20 (br, 2H), 7.24−7.61 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.9, 15.0, 23.3, 25.2, 33.8, 45.2, 66.8, 115.6, 126.6, 126.7, 127.5, 128.0, 128.6, 131.4, 133.1, 140.5, 141.1, 165.3. IR (KBr) 3311, 3059, 1610, 1156, 1107

cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.60; H, 8.48; N, 8.27.

***N′*-(1-Butyl-2-methyl-1-phenylbut-3-enyl)benzohydrazide (*syn*-3d):** Mp 85 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3H), 0.81 (d, J = 7.0 Hz, 3H), 1.19−1.25 (m, 2H), 1.28−1.33 (m, 2H), 1.75−1.85 (m, 1H), 1.92−2.00 (m, 1H), 2.54 (qd, J = 7.0 Hz, 1H), 5.00 (apparent d, J = 10.3 Hz, 1H), 5.07 (apparent d, J = 17.1 Hz, 1H), 5.56 (br, 1H), 5.68−5.77 (m, 1H), 7.09 (br, 1H), 7.14−7.56 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.0, 15.7, 23.3, 25.3, 33.7, 45.2, 67.2, 115.0, 126.6, 126.7, 127.5, 128.0, 128.6, 131.4, 133.2, 140.8, 141.0, 165.5. IR (KBr) 3303, 1577, 1308, 923 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.51; H, 8.35; N, 8.29.

***N′*-(1,2-Dimethyl-1-naphthalen-2-ylbut-3-enyl)benzohydrazide (*anti*-3e):** Mp 149−150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (d, J = 7.1 Hz, 3H), 1.53 (s, 3H), 2.64 (qd, J = 7.1 Hz, 1H), 5.19−5.28 (m, 2H), 5.70 (brd, J = 8.5 Hz, 1H), 5.79−5.88 (m, 1H), 6.89 (brd, J = 8.1 Hz, 1H), 7.03−7.84 (m, 12H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 15.9, 16.7, 48.2, 64.9, 117.9, 125.1, 126.0, 126.1, 126.4, 126.6, 127.4, 128.16, 128.18, 128.5, 131.5, 132.4, 132.7, 133.2, 139.5, 141.6, 166.3. IR (KBr) 3266, 1625, 1546, 1508, 1449, 1227, 1201, 1135, 1119, 1019, 923 cm^{-1}. Anal. Calcd for $C_{23}H_{24}N_2O$: C, 80.20; H, 7.01; N, 8.13. Found: C, 80.16; H, 7.17; N, 8.11.

***N′*-(1,2-Dimethyl-1-naphthalen-2-ylbut-3-enyl)benzohydrazide (*syn*-3e):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.01 (d, J = 7.1 Hz, 3H), 1.56 (s, 3H), 2.62 (qd, J = 7.1 Hz), 4.87−4.93 (m, 2H), 5.56−5.68 (m, 1H), 7.06 (br, 2H), 7.16−7.89 (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.7, 20.0, 47.1, 65.3, 115.6, 125.3, 125.9, 126.0, 126.2, 126.6, 127.4, 127.9, 128.2, 128.5, 131.5, 132.3, 132.7, 133.1, 139.5, 141.0, 166.4. IR (KBr) 3290, 1637, 1449, 1131 cm^{-1}. HRMS calcd for $C_{23}H_{24}N_2O$ (M^+) 331.1889. Found 331.1894.

***N′*-[1,2-Dimethyl-1-(2-nitrophenyl)but-3-enyl]benzohydrazide (*anti*-3f):** Mp 141−142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (d, J = 6.8 Hz, 3H), 1.03 (s, 3H), 2.10 (qd, J = 7.1 Hz, 1H), 4.73−4.79 (m, 2H), 5.13 (br, 1H), 5.30 (ddd, J = 7.1, 10.0, 17.1 Hz, 1H), 6.64 (br, 1H), 6.74−7.91 (m, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 15.6, 17.1, 48.2, 64.8, 118.3, 122.1, 122.3, 126.7, 128.6, 129.2, 131.8, 132.8, 133.5, 138.7, 146.9, 148.4, 167.2. IR (KBr) 3288, 1635, 1529, 1456, 1351, 1315, 1107, 926, 914 cm^{-1}. Anal. Calcd for $C_{19}H_{21}N_3O_3$: C, 67.24; H, 6.24; N, 12.38. Found: C, 67.06; H, 6.43; N, 12.32.

***N′*-[1,2-Dimethyl-1-(2-nitrophenyl)but-3-enyl]benzohydrazide (*syn*-3f):** Mp 105−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (d, J = 6.8 Hz, 3H), 1.64 (s, 3H), 2.68 (qd, J = 6.8 Hz, 1H), 4.98−5.06 (m, 2H), 5.62 (ddd, J = 7.8, 10.3, 18.3 Hz, 1H), 7.35−7.61 (m, 8H), 7.87−7.81 (m, 1H), 7.35−7.61 (m, 1H), 8.35−8.36 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.7, 19.7, 30.2, 47.0, 65.3, 116.5, 122.0, 122.3, 126.7, 128.6, 128.9, 131.9, 133.5, 138.5, 146.2, 148.2, 167.4. IR (KBr) 3302, 1637, 1304, 909 cm^{-1}. Anal. Calcd for $C_{19}H_{21}N_3O_3$: C, 67.24; H, 6.24; N, 12.38. Found: C, 66.99; H, 6.30; N, 12.42.

***N′*-[1-(4-Bromophenyl)-1,2-dimethylbut-3-enyl]benzohydrazide (*anti*-3g):** Mp 130−131 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70 (d, J = 7.0 Hz, 3H), 1.40 (s, 3H), 2.51 (qd, J = 7.3 Hz, 1H), 5.17−5.26 (m, 2H), 5.75 (ddd, J = 7.3, 9.5, 17.1 Hz, 1H), 7.02 (br, 2H), 7.19−7.50 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 15.7, 16.9, 31.4, 48.2, 64.9, 118.2, 121.2, 126.7, 128.6, 129.1, 131.8, 132.4. IR (KBr) 3390, 3262, 1649, 1432, 1006 cm^{-1}. Anal. Calcd for $C_{19}H_{21}BrN_2O$: C, 61.13; H, 5.67; N, 7.50. Found: C, 60.88; H, 5.80; N, 7.41.

***N′*-[1-(4-Bromophenyl)-1,2-dimethylbut-3-enyl]benzohydrazide (*syn*-3 g):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (d, J = 6.8 Hz, 3H), 1.45 (s, 3H), 2.46−2.53 (m, 1H), 4.88−4.96 (m, 2H), 5.60 (ddd, J = 8.1, 10.5, 18.3 Hz, 1H), 5.56−5.61 (br, 1H), 7.00 (br, 1H), 7.29−7.55 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.7, 20.0, 47.2, 65.0, 115.9, 121.0, 126.7, 128.4, 128.7, 129.1, 131.3, 131.8, 139.2, 142.6, 166.7. IR (KBr) 3499, 3181, 1633, 1452, 1009 cm^{-1}. HRMS calcd for $C_{19}H_{21}N_2O$ (M^+) 372.0837. Found 372.0831.

***N′*-[1-(4-Chlorophenyl)-1-ethyl-2-methylbut-3-enyl]benzohydrazide (*anti*-3h):** Mp 94−95 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82−0.88 (m, 6H), 1.89 (qd, J = 1.4, 7.5 Hz, 2H), 2.54 (qd, J = 7.5 Hz, 1H), 4.96−5.04 (m, 2H), 5.37 (br, 1H), 5.52 (ddd, J = 8.4, 9.8, 18.5 Hz, 1H), 7.06 (br, 1H), 7.19−7.63 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.8, 14.9, 26.2, 44.6, 68.8, 115.9, 126.7, 128.1, 128.6, 129.2, 131.6, 132.7, 132.8, 139.3, 140.0, 165.7. IR (KBr) 3295, 1832, 1638, 1550, 1492, 1449, 1319, 1097, 1014, 911 cm^{-1}. Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 69.87; H, 6.91; N, 8.16.

***N′*-[1-(4-Chlorophenyl)-1-ethyl-2-methylbut-3-enyl]benzohydrazide (*syn*-3h):** Mp 149 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 0.88 (t, J = 7.3 Hz, 3H), 1.78−2.03 (m, 2H), 2.52 (qd, J = 7.7 Hz, 1H), 5.00−5.10 (m, 2H), 5.58 (br, 1H), 5.71 (ddd, J = 8.6, 10.1, 17.2 Hz, 1H), 7.13 (br, 1H), 7.25−7.56 (m, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 7.8, 15.7, 26.0, 44.8, 67.3, 115.2, 126.6, 128.1, 128.7, 129.2, 131.6, 132.7, 132.8, 139.0, 140.7, 165.8. IR (KBr) 3296, 1830, 1638, 1550, 1097, 1014, 911 cm^{-1}. Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 70.52; H, 7.10; N, 7.84.

***N′*-[1-(4-Chlorophenyl)-2-methyl-1-propylbut-3-enyl]benzohydrazide (*anti*-3i):** Mp 115−116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, J = 7.3 Hz, 3H), 0.85 (d, J = 6.8 Hz, 3H), 1.12−1.24 (m, 1H), 1.27−1.40 (m, 1H), 1.71−1.87 (m, 2H), 2.50−2.54 (m, 1H), 4.95−5.02 (m, 2H), 5.48−5.57 (m, 1H), 7.21−7.5 (m, 9H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 14.7, 14.8, 16.5, 36.3, 45.0, 66.6, 115.9, 126.6, 127.9, 128.5, 129.0, 131.5, 132.5, 132.8, 139.5, 140.0, 165.7. IR (KBr) 3324, 1614, 1575, 1496, 1428, 1370, 1313, 1153, 1093, 1071, 1026, 1012, 916 cm^{-1}. Anal. Calcd for $C_{21}H_{25}ClN_2O$: C, 70.67; H, 7.06; N, 7.85. Found: C, 70.52; H, 7.15; N, 7.81.

***N′*-[1-(4-Chlorophenyl)-2-methyl-1-propylbut-3-enyl]benzohydrazide (*syn*-3i):** Mp 141−143 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.79−0.86 (m, 6H), 1.15−1.44 (m, 2H), 1.66−1.79 (m, 1H), 1.84−1.95 (m, 1H), 2.52 (qd, J = 7.0 Hz, 1H), 4.99−5.03 (m, 2H), 5.09 (br, 1H), 5.66−5.78 (m, 1H), 7.13 (br, 1H), 7.18−7.56 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.7, 15.7, 16.6, 36.3, 45.2, 67.2, 115.2, 126.6, 128.0, 128.7, 129.1, 131.6, 132.7, 132.9, 139.3, 140.6, 165.8. IR (KBr) 3301, 1740, 1620, 1575, 1550, 1430, 1401, 1373, 1311, 1150, 1067, 1012, 922 cm^{-1}. Anal. Calcd for $C_{21}H_{25}ClN_2O$: C, 70.67; H, 7.06; N, 7.85. Found: C, 70.43; H, 7.23; N, 7.77.

***N′*-(1-Ethyl-2-methyl-1-*p*-tolylbut-3-enyl)benzohydrazide (*anti*-3j):** Mp 111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3H), 0.89 (d, J = 6.8 Hz, 3H), 1.85−1.95 (m, 2H), 2.29 (s, 3H), 2.54 (qd, J = 7.2 Hz, 1H), 4.73 (dd, J = 1.8, 7.2 Hz, 1H), 5.02 (brd, J = 17.2 Hz, 1H), 5.51−5.63 (m, 1H), 7.09−7.81 (m, 11H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.8, 15.1, 20.9, 26.3, 44.8, 66.8, 115.4, 126.6, 127.6, 128.6, 128.8, 131.5, 133.1, 136.3, 137.7, 140.6, 165.1. IR (KBr) 3298, 3221, 1816, 1637, 1577, 1544, 1449, 1371, 1321, 1190, 1146, 1100, 1054, 1005, 947, 910 cm^{-1}. Anal. Calcd for $C_{21}H_{26}N_2O$: C,78.22; H, 8.13; N, 8.69. Found: C, 78.19; H, 8.31; N, 8.71.

***N′*-(1-Ethyl-2-methyl-1-*p*-tolylbut-3-enyl)benzohydrazide (*syn*-3j):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.59 (d, J = 7.0 Hz, 3H), 0.90 (t, J = 7.3 Hz, 3H), 1.77−1.90 (m, 1H), 1.92−2.05 (m, 1H), 2.28 (s, 3H), 2.54 (qd, J = 7.0, 7.5 Hz, 1H), 5.04 (dd, J = 1.5, 10.0 Hz, 2H), 5.73 (ddd, J = 1.5, 7.5, 10.0 Hz, 1H), 7.14 (br, 2H), 7.09−7.55 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.9, 15.8, 20.9, 26.1, 44.8, 67.2, 114.9, 126.6, 127.6, 128.6, 128.7, 131.5, 133.1, 136.3, 137.2, 141.2, 165.5. IR (KBr) 3292, 1638, 1308, 1003 cm^{-1}. HRMS calcd for $C_{21}H_{26}N_2O$ (M^+) 322.2045. Found 322.2059.

***N′*-(2-Methyl-1-propyl-1-*p*-tolylbut-3-enyl)benzohydrazide (*anti*-3k):** Mp 90−91 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (t, J = 7.3 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 1.21−1.41 (m, 2H), 1.67−1.91 (m, 2H), 2.28 (s, 3H), 2.55 (qd, J = 7.0 Hz, 1H), 4.96 (dd, J = 1.7, 10.2 Hz, 1H), 5.02 (brd, J = 17.2 Hz, 1H), 5.60 (ddd, J = 8.6, 10.2, 18.5 Hz, 1H), 7.09−7.11 (br, 2H), 7.18−7.54 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.9, 15.1, 16.6, 20.9, 36.5, 45.3, 66.7, 115.5, 126.6, 127.4, 128.6, 128.8,

131.4, 133.1, 136.3, 137.9, 140.6, 165.2. IR (KBr) 3290, 1957, 1918, 1833, 1621, 1550, 1512, 1191, 1109, 1056, 1025, 1007, 949, 916 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.27; H, 8.49; N, 8.23.

***N′*-(2-Methyl-1-propyl-1-*p*-tolylbut-3-enyl)benzohydrazide (*syn*-3k):** Mp 108 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (apparent t, J = 5.9 Hz, 6H), 1.29−1.40 (m, 2H), 1.63−1.77 (m, 1H), 1.82−1.95 (m, 1H), 2.27 (s, 3H), 2.53 (qd, J = 7.1 Hz, 1H), 5.00 (dd, J = 1.5, 10.2 Hz, 1H), 5.06 (brd, J = 17.1 Hz, 1H), 5.08 (br, 1H), 5.68−5.77 (m, 1H), 7.02 (br, 1H), 7.05−7.54 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.9, 15.8, 16.7, 20.9, 36.4, 45.3, 67.2, 115.0, 126.7, 127.5, 128.7, 128.8, 131.5, 133.2, 136.4, 137.6, 141.2, 165.6. IR (KBr) 3308, 1619, 1302, 1370, 1001 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.30; H, 8.49; N, 8.24.

***N′*-[1-Ethyl-1-(4-ethylphenyl)-2-methylbut-3-enyl]benzohydrazide (*anti*-3l):** Mp 110 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 0.87 (t, J = 7.5 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H), 1.18 (t, J = 7.7 Hz, 3H), 1.83−1.97 (m, 2H), 2.50−2.63 (m, 3H), 4.93−5.05 (m, 2H), 5.51−5.63 (m, 1H), 5.61 (br, 1H), 6.88 (br, 1H), 6.91−7.55 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.8, 15.1, 15.3, 26.3, 28.3, 44.8, 66.8, 115.4, 126.6, 127.5, 127.6, 128.6, 131.4, 133.1, 137.9, 140.6, 142.6, 165.1. IR (KBr) 3287, 3224, 3065, 1636, 1577, 1544, 1510, 1438, 1370, 1321, 1145, 1054, 1006, 910 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_2O$: C, 78.53; H, 8.39; N, 8.33. Found: C, 78.27; H, 8.49; N, 8.23.

***N′*-[1-Ethyl-1-(4-ethylphenyl)-2-methylbut-3-enyl]benzohydrazide (*syn*-3l):** ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (d, J = 7.0 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H), 1.28 (t, J = 7.7 Hz, 3H), 1.89−2.00 (m, 1H), 2.03−2.16 (m, 1H), 2.59−2.72 (m, 3H), 5.11 (dd, J = 1.5, 10.3 Hz, 1H), 5.18 (dd, J = 1.5, 17.2 Hz, 1H), 5.50 (br, 1H), 5.83 (ddd, J = 1.5, 10.3, 17.2 Hz, 1H), 7.20 (br, 1H), 7.21−7.65 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.9, 15.3, 15.8, 26.1, 28.2, 44.8, 67.4, 114.9, 126.7, 127.5, 127.6, 128.6, 131.5, 133.1, 137.4, 141.2, 142.6, 165.5. IR (KBr) 3380, 1660, 1310, 1004, 760 cm^{-1}. HRMS calcd for $C_{22}H_{28}N_2O$ (M^+) 336.2202. Found 336.2202.

(5-Hydroxy-3-phenyl-4,5-dihydro-pyrazol-1-yl)phenylmethanone (4a): Mp 128 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 3.11 (dd, 2.2, 18.1 Hz, 1H), 3.37 (dd, J = 7.0, 18.1 Hz, 1H), 4.39 (br, 1H), 6.31 (d, 7.0 Hz, 1H), 7.19−7.99 (m, 10H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 39.3, 81.6, 126.7, 127.8, 128.7, 130.3, 130.5, 131.2, 131.6, 133.2, 155.4, 168.0. IR (KBr) 3389, 1625, 1458, 1073, 693 cm^{-1}. HRMS calcd for $C_{16}H_{14}N_2O_2$ (M^+) 266.1055. Found 266.1059. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.89; H, 5.52; N, 10.41.

(5-Dimethylamino-3-phenyl-4,5-dihydropyrazol-1-yl)-phenylmethanone (5a): ^1H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 3.03 (dd, J = 2.4, 18.3 Hz, 1H), 3.38 (dd, J = 10.0, 18.3 Hz, 1H), 5.83 (dd, J = 2.4, 10.0 Hz, 1H), 7.39−7.52 (m, 6H), 7.69 (dd, J = 4.2, 7.7 Hz, 2H), 8.00 (dd, J = 1.8, 8.1 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 36.7, 40.3, 126.6, 127.0, 127.6, 128.3, 128.7, 130.0, 130.3, 130.8, 154.8, 168.7. IR (KBr) 1692, 1627, 1451, 1351 cm^{-1}. HRMS calcd for $C_{18}H_{19}N_3O$ (M^+) 293.1528. Found 293.1523. Crystals suitable for X-ray diffraction analysis were grown from a hexane/ethyl acetate solution. The crystallographic data of **5a** are given in the Supporting Information.

1,2-Dimethyl-1-phenylbut-3-enylamine (*anti*-7a): To a solution of *anti*-**3a** (126.6 mg, 0.43 mmol) in MeOH (3 mL) was added a SmI_2-THF solution (3.6 mmol) at −78 °C. The mixture was stirred for 24 h at the same temperature and then concentrated under reduced pressure to remove the solvents. The residue was extracted with 1 N HCl and the aqueous layers were washed with Et_2O, alkalified with 1 N aqueous NaOH, and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC to afford *anti*-**7a** (73.1 mg, 0.42 mmol, 98% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, J = 6.8 Hz, 3H), 1.37 (s, 3H), 1.45 (br, 2H), 2.46 (qd, J = 7.0 Hz, 1H), 4.96−5.00 (m, 2H), 5.56−5.62 (m, 1H), 7.12−7.40 (m, 5H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.5, 26.7, 49.0, 56.8, 115.9, 125.8, 126.1, 127.9, 140.3, 148.2. IR (KBr) 3425, 1628, 1124 cm^{-1}. HRMS calcd for $C_{12}H_{17}N$ (M^+) 175.1361. Found 175.1368.

2-Methyl-1-phenyl-1-propylbut-3-enylamine (*anti*-7a): According to the procedure for the preparation of *anti*-**7a**, the reaction of *anti*-**3c** (32.1 mg, 0.10 mmol) with SmI_2 (1 mmol) afforded *anti*-**7c** (14.9 mg, 0.07 mmol) in 73% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (t, J = 6.8 Hz, 3H), 0.72−0.91 (m, 2H), 0.94 (d, J = 6.9 Hz, 3H), 1.06−1.22 (m, 1H), 1.36 (br, 2H), 1.50−1.60 (m, 1H), 1.77−1.87 (m, 1H), 2.49 (qd, J = 6.9 Hz, 1H), 4.85−4.91 (m, 2H), 5.41−5.52 (m, 1H), 7.10−7.35 (m, 5H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 13.4, 14.6, 17.1, 42.6, 48.2, 59.7, 115.4, 125.8, 126.4, 127.7, 140.3. IR (KBr) 3306, 1632, 1384, 1123 cm^{-1}. HRMS calcd for $C_{14}H_{21}N$ (M^+) 203.1674. Found 203.1673.

2-Methyl-1-phenyl-1-propylbut-3-enylamine (*syn*-7c): According to the procedure for the preparation of *anti*-**7a**, the reaction of *syn*-**3c** (32.2 mg, 0.10 mmol) with SmI_2 (1 mmol) afforded *syn*-**7c** (10.0 mg, 0.05 mmol) in 49% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 0.77 (t, J = 7.1 Hz, 3H), 0.74−0.90 (m, 2H), 0.94 (d, J = 6.8 Hz, 3H), 1.09−1.21 (m, 1H), 1.33 (br 2H), 1.52−1.59 (m, 1H), 1.78−1.86 (m, 1H), 2.49 (qd, J = 6.8 Hz, 1H), 4.86−4.90 (m, 2H), 5.42−5.51 (m, 1H), 7.11−7.34 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 13.4, 14.6, 17.1, 42.6, 48.2, 59.7, 115.4, 125.8, 126.4, 127.7, 140.3. IR (KBr) 3055, 1639, 1421, 1265, 740 cm^{-1}. HRMS calcd for $C_{14}H_{21}N$ (M^+) 203.1674. Found 203.1672.

***N*-(1,2-Dimethyl-1-phenylbut-3-enyl)-4-methylbenzenesulfonamide (*anti*-8a):** To a solution of *anti*-**7a** (31.6 mg, 0.23 mmol) in CH_2Cl_2 (3.0 mL) was added diisopropylethylamine (0.26 mmol) and TsCl (0.26 mmol) at room temperature. The mixture was stirred for 6 h at the same temperature (checked by TLC), and then water was added to quench the reaction. After separation of the organic layer, the aqueous layer was further extracted with CH_2Cl_2. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC and by recrystallization from MeOH to afford crystalline *anti*-**8a** (31.8 mg, 0.10 mmol, 54% yield), which was suitable for the X-ray diffraction analysis. Mp 110 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 0.63 (d, J = 7.0 Hz, 3H), 1.58 (s, 3H), 2.29 (s, 3H), 2.39−2.49 (m, 1H), 5.03 (br, 1H), 5.13−5.19 (m, 2H), 5.57−5.69 (m, 1H), 6.70−7.40 (m, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 14.1, 20.1, 21.4, 50.1, 62.8, 118.5, 126.7, 126.7, 126.8, 127.7, 129.0, 138.9, 139.9, 142.4, 14.7. IR (KBr) 3312, 1320, 1223, 1157, 1000 cm^{-1}. Anal. Calcd for $C_{19}H_{22}N_2O$: C, 69.27; H, 7.04; N, 4.25. Found: C, 68.98; H, 7.04; N, 4.18. The crystallographic data of *anti*-**8a** are given in the Supporting Information.

Acknowledgment. This work was partially supported by CREST and SORST, Japan Science Technology Corporation, and a Grant-in-Aid for Scientific Research from Japan Society of the Promotion of Sciences.

Supporting Information Available: Lists of complete X-ray crystallographic data of **5a** and *anti*-**8a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0258599