EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201201757

A Mild and Efficient Three–Component Synthesis of Secondary and Tertiary Homoallylic Hydrazides

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Keywords: Multicomponent reactions / Allylation / Aldehydes / Ketones / Chemoselectivity / Hydrazides

A three-component reaction that involved a carbonyl compound, benzoylhydrazine, allyl bromide, and indium in the presence of readily available $Zn(ClO_4)_2 \cdot 6H_2O$ was developed for the syntheses of secondary and tertiary homoallylic hydrazides. Excellent chemoselectivities and diastereoselectivities were observed. Aldehydes as well as acyclic and cyclic ketones were well-suited to the reaction conditions and provided secondary and tertiary homoallylic hydrazides in excellent yields.

Introduction

Homoallylic amines are valuable building blocks for the syntheses of natural products and biologically active compounds, as the C=C bond and amine moieties can be further transformed into various functional groups.[1] The addition of allylmetals to C=N bonds is a general synthetic strategy for the formation of homoallylic amines.[2–6] Among the various reported methods for the preparation of homoallylic amines, one-pot three-component reactions that involve carbonyl compounds, nitrogen nucleophiles, and allylmetal reagents are attractive.[7] Despite their wide scope, these protocols are limited to the syntheses of secondary homoallylic amine derivatives and are not suitable for the preparation of tertiary homoallylic amine derivatives. For these compounds, a few examples of procedures that employ allylsilanes[8] and allylboronates[9] as nucleophiles have been reported.

Indium-mediated reactions for the synthesis of homoallylic amines are particularly interesting, as the indium metal has low toxicity and a high tolerance to moisture and air.[10] The one-pot addition of allylindium reagents to hydrazones, which are derived from ketones, for the purpose of synthesizing tertiary homoallylic amine derivatives has not yet been reported.[11] Herein, we wish to report the first one-pot three-component α-aminoallylation of carbonyl compounds with benzoylhydrazine, allyl bromide, and indium in the presence of $Zn(ClO_4)_2 \cdot 6H_2O$ to afford protected secondary and tertiary homoallylic amines under mild reaction conditions.

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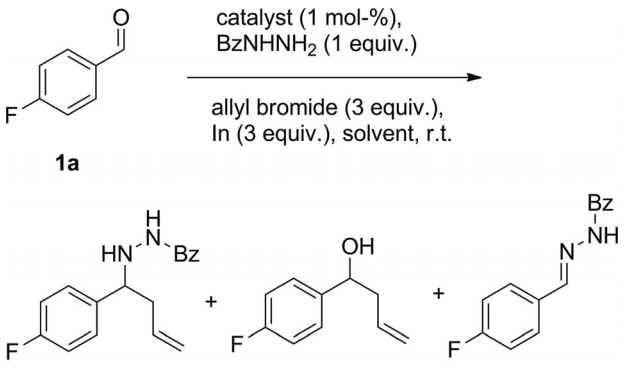
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201201757.

Results and Discussion

4-Fluorobenzaldehyde (**1a**) was chosen as a model aldehyde. First, a one-pot three-component reaction that involved **1a**, benzoylhydrazine, allyl bromide, and indium in MeOH at room temperature was performed (see Table 1, Entry 1). The reaction afforded the homoallylic amine derivative **2a** along with homoallylic alcohol **3a**. Because carbonyl groups are generally more reactive than hydrazones towards allylindium reagents, the first challenge was to achieve chemoselectivity from the allylindium species for the C=N bond over the C=O bond.[12] To our delight, when the low-cost, readily available Lewis acid $Zn(ClO_4)_2 \cdot 6H_2O$ was used, the reaction afforded **2a** in 95% yield without the accompanying homoallylic alcohol **3a** within 3 h at room temperature (see Table 1, Entry 2). The efficiencies of different additives were screened by treating **1a**, benzoylhydrazine, allyl bromide, and indium with 1 mol-% of an additive in MeOH at room temperature. Additives such as $MgBr_2$, $Sc(OTf)_3$ (Tf = trifluoromethylsulfonyl), and $Yb(OTf)_3$ promoted the reaction to produce the homoallylic amine derivative **2a** exclusively in high yields (see Table 1, Entries 3–5). With $In(OTf)_3$, $Mg(ClO_4)_2$, and $ZnCl_2$, the reaction afforded **2a** along with some **3a** (see Table 1, Entries 6–8). $SnCl_2 \cdot 2H_2O$ and $TiCl_3$ led to mixtures of **2a**, **3a**, and **4a**, which indicated that **4a** was not completely converted into **2a**, even after 24 h under the reaction conditions (see Table 1, Entries 9 and 10). A further survey of the reaction conditions showed that polar solvents such as MeOH, MeCN, and EtOAc were optimal (see Table 1, Entries 2, 11, and 12). After prolonged reaction times, nonpolar solvents such as toluene, chloroform, and 1,2-dichloroethane afforded **4a** as the major product (see Table 1, Entries 15–17). In terms of cost, efficiency, and reaction times, methanol was the solvent of choice. The reactions depended on the nature of the Lewis acids, which implied that the In(III) species that was generated in situ was

less effective than when Lewis acids were employed (see Table 1, Entry 1 vs. 2–8).

Table 1. Screening reaction conditions for the synthesis of **2a**.

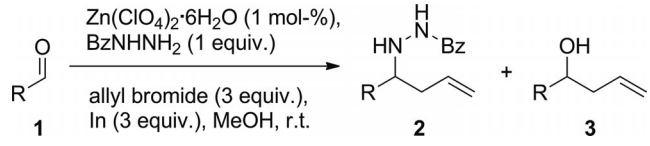


Entry	Catalyst	Time [h]	Solvent	% **2a**[a]	% **3a**[a]	% **4a**[a]
1	none	6	MeOH	60	35	0
2	$Zn(ClO_4)_2·6H_2O$	3	MeOH	95	0	0
3	$MgBr_2$	3	MeOH	94	0	0
4	$Sc(OTf)_3$	4	MeOH	93	0	0
5	$Yb(OTf)_3$	4	MeOH	92	0	0
6	$In(OTf)_3$	4	MeOH	89	4	0
7	$Mg(ClO_4)_2$	4	MeOH	74	17	0
8	$ZnCl_2$	4	MeOH	73	19	0
9	$SnCl_2·2H_2O$	24	MeOH	43	9	41
10	$TiCl_3$	24	MeOH	32	11	49
11	$Zn(ClO_4)_2·6H_2O$	4	CH_3CN	95	0	0
12	$Zn(ClO_4)_2·6H_2O$	20	EtOAc	94	0	0
13	$Zn(ClO_4)_2·6H_2O$	10	THF	84	11	0
14	$Zn(ClO_4)_2·6H_2O$	4	CH_2Cl_2	54	39	0
15	$Zn(ClO_4)_2·6H_2O$	24	toluene	9	0	83
16	$Zn(ClO_4)_2·6H_2O$	24	$CHCl_3$	13	5	76
17	$Zn(ClO_4)_2·6H_2O$	24	$(CH_2Cl)_2$	11	0	83

[a] Isolated yield.

With optimized reaction conditions on hand, we investigated the generality and scope of the synthetic method by using a range of aromatic and aliphatic aldehydes. The results are summarized in Table 2. A general trend was observed for different aromatic and aliphatic aldehydes. Reactions with benzaldehyde and *p*-ethylbenzaldehyde provided the corresponding homoallylic amine derivatives in excellent yields and with high chemoselectivities (see Table 2, Entries 1 and 2). Aromatic aldehydes with strong electron-donating groups gave the desired products in poor yields and with poor chemoselectivities. With aromatic aldehydes that were substituted with –OH and –OMe groups, the reaction produced mixtures of the homoallylic amine derivative and homoallylic alcohol in a ratio of approximately 6:4 (see Table 2, Entries 3 and 4). In the case of *N*,*N*′-dimethylaniline, the corresponding homoallylic alcohol was obtained as the major product instead of the homoallylic amine derivative (see Table 2, Entry 5). The reaction with aromatic aldehydes that were substituted with an electron-withdrawing group proceeded smoothly to afford the corresponding homoallylic amine derivatives exclusively in high yields (see Table 2, Entries 6–12). Aromatic aldehydes with an electron-withdrawing group at the sterically hindered *ortho* position also produced the corresponding protected homoallylic amine derivatives in excellent yields (see Table 2, Entries 6 and 7). Furthermore, the reactions with aliphatic aldehydes provided the desired product in excellent yields (see Table 2, Entries 13–16). These results imply that the carbonyl group in the substrate becomes a stronger Lewis base by changing from an electron-poor aromatic substrate to an electron-rich aromatic substrate. Thus, the catalyst may bind to the aldehyde, which then increases the rate of reaction with the allylindium instead of the formation of hydrazones. The reaction of organometallic compounds with hydrazones, which are derived from aliphatic aldehydes with an α-hydrogen, can be complicated because of the formation of enamines. Interestingly, the unsaturated aldehyde cinnamaldehyde gave low chemoselectivity with exclusive 1,2-addition to provide the homoallylic amine derivative in 56% yield along with the homoallylic alcohol in 35% yield (see Table 2, Entry 17).

Table 2. Synthesis of secondary homoallylic amine derivatives from various aldehydes.

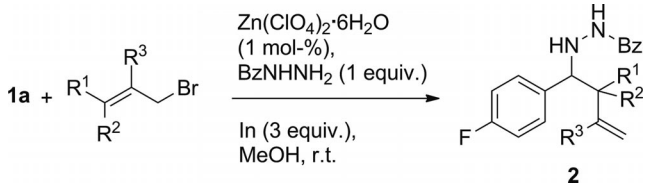


Entry	**1**, R	Time [h]	Product	% Yield[a]
1	**1b**, C_6H_5	4	**2b**	95
2	**1c**, *p*-Et-C_6H_4	4	**2c**	97
3	**1d**, *p*-MeO-C_6H_4	4	**2d** (**3b**)	56 (34)
4	**1e**, *p*-HO-C_6H_4	4	**2e** (**3c**)	53 (41)
5	**1f**, *p*-$(Me)_2N$-C_6H_4	6	**2f** (**3d**)	7 (85)
6	**1g**, *o*-Br-C_6H_4	3	**2g**	94
7	**1h**, *o*-F-C_6H_4	3	**2h**	96
8	**1i**, *m*-F-C_6H_4	3	**2i**	95
9	**1j**, *o*-Cl-C_6H_4	4	**2j**	94
10	**1k**, *m*-Cl-C_6H_4	4	**2k**	94
11	**1l**, *p*-Cl-C_6H_4	4	**2l**	95
12	**1m**, *p*-NO_2-C_6H_4	4	**2m**	92
13	**1n**, $PhCH_2CH_2$	4	**2n**	95
14	**1o**, heptyl	4	**2o**	95
15	**1p**, *i*Pr	4	**2p**	95
16	**1q**, cyclohexyl	4	**2q**	93
17	**1r**, (*E*)-cinnamyl	6	**2r** (**3e**)	56 (35)

[a] Isolated yield.

Reactions of **1a** with methallyl bromide, crotyl bromide, cinnamyl bromide, and prenyl bromide were also investigated, and the results are summarized in Table 3. A selectivity for γ-addition and a high chemoselectivity were observed (see Table 3, Entries 1–5). An excellent selectivity for *anti* addition was observed with cinnamyl bromide (see Table 3, Entry 3). As expected, the γ-addition reaction with sterically hindered prenyl bromide did not go to completion, even after 48 h (see Table 3, Entry 4). Using a large excess amount of prenyl bromide and indium resulted in a shorter reaction time, and the product was produced in excellent yield (see Table 3, Entry 5).

Table 3. Reaction of **1a** with various allyl bromides.

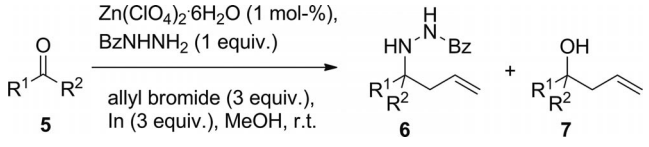


Entry	R^1	R^2	R^3	Time [h]	Product	% Yield[a]
1	H	H	CH_3	4	**2s**	93
2[b]	CH_3	H	H	4	**2t**	95
3[c]	Ph	H	H	6	**2u**	92
4	CH_3	CH_3	H	48	**2v** (**4a**)	81 (12)
5[d]	CH_3	CH_3	H	6	**2v**	94

[a] Isolated yield. [b] Diastereomeric ratio (*anti*/*syn*, 77:23) was obtained by ^{1}H NMR spectroscopic analysis.[13] [c] Diastereomeric ratio (*anti*/*syn*, 99:1) was obtained by ^{1}H NMR spectroscopic analysis. [d] Employed 6 equiv. of prenyl bromide and indium.

Next, we extended this method to the synthesis of tertiary homoallylic amine derivatives by starting from ketones. It was previously reported that the one-pot allylation of hydrazones, which are derived from ketones with allylindium reagents, was unachievable even at 60 °C.[6a] The reactivities of ketones were examined under the present reaction conditions, and the results are summarized in Table 4. Interestingly, the one-pot three-component reaction that involved **5a**, benzoylhydrazine, allyl bromide, and indium in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ proceeded smoothly even at room temperature to provide the corresponding tertiary homoallylic amine derivative **6a** in 94% yield (see Table 4, Entry 1). Other acyclic ketones such as **5b** and **5c** also led to the desired products **6b** and **6c**, respectively, in excellent yields (see Table 4, Entries 2 and 3). An extension of this methodology to cyclic ketones **5d**, **5e**, and **5f** resulted in the corresponding tertiary homoallylic amine derivatives in high yields (see Table 4, Entries 4–6). However, the reactions with aromatic ketones and α,β-unsaturated ketones afforded the homoallylic alcohols **7** exclusively (see Table 4, Entries 7–9) and none of the desired tertiary homoallylic amine derivatives.

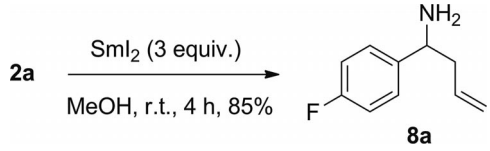
Table 4. Synthesis of tertiary homoallylic amine derivatives from various ketones.



Entry	**5**	R^1, R^2	Time [h]	Product	% Yield[a]
1	**5a**	CH_3CH_2, CH_3	4	**6a**	94
2	**5b**	$CH_3(CH_2)_6$, CH_3	4	**6b**	92
3	**5c**	$PhCH_2CH_2$, CH_3	4	**6c**	90
4	**5d**	$-(CH_2)_4-$	4	**6d**	92
5	**5e**	$-(CH_2)_5-$	4	**6e**	95
6	**5f**	$-(CH_2)_{11}-$	4	**6f**	92
7	**5g**	C_6H_5, CH_3	5	**7a**	96
8	**5h**	*p*-F-C_6H_4, CH_3	5	**7b**	95
9	**5i**	(*E*)-cinnamyl, CH_3	5	**7c**	94

[a] Isolated yield.

Amine **8a** was obtained in 85% yield through the N–N bond cleavage of compound **2a**. This reaction was carried out by treating **2a** with SmI_2 in MeOH at room temperature as shown in Scheme 1.[1a]



Scheme 1. N–N bond cleavage of **2a**.

Conclusions

In summary, an efficient one-pot, three-component reaction was developed for the synthesis of secondary and tertiary homoallylic amine derivatives by treating aldehydes and ketones, respectively, with benzoylhydrazine, allyl bromide, and indium in the presence of readily available $Zn(ClO_4)_2{\cdot}6H_2O$. The reaction was general for aldehydes as well as acyclic and cyclic ketones, which provided tertiary homoallylic amine derivatives, whereas aromatic ketones afforded homoallylic alcohols.

Experimental Section

General Methods: Unless otherwise specified, the chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed using silica gel (230–400 mesh, Merck). TLC was performed on glass sheets precoated with silica gel (Kieselgel 60 PF_{254}, Merck). The melting points were measured with a Fisher-Johns melting point apparatus. The ^{1}H and ^{13}C NMR spectroscopic data were recorded with a Bruker 400 NMR spectrometer that operated at 400 MHz for ^{1}H and 100 MHz for ^{13}C nuclei. The spectra were internally referenced to residual protio solvent signals. Chemical shifts were reported in parts per million (ppm). IR spectra were recorded with a Perkin–Elmer 16 PC FTIR spectrometer. Microanalyses were performed with a CE instrument EA1110 elemental analyzer.

Typical Procedure for the One-Pot Synthesis of Homoallylic Amine Derivatives: A solution of aldehyde or ketone (1.47 mmol), benzoylhydrazine (200 mg, 1.47 mmol), allyl bromide (533 mg, 2.19 mmol), and indium powder (506 mg, 2.19 mmol) in the presence of $Zn(ClO_4)_2{\cdot}6H_2O$ (6 mg, 1.47×10^{-2} mmol) in MeOH (7 mL) was stirred at room temperature until the reaction went to completion. The solvent was then removed, and the residue was diluted with CH_2Cl_2. The resulting solution was washed with 1 M HCl, saturated aqueous $NaHCO_3$ solution, and brine. The organic layer was dried with anhydrous $MgSO_4$ and then was evaporated under reduced pressure. The resulting residue was purified by silica gel column chromatography to afford the product.

***N′*-[1-(4-Fluorophenyl)but-3-enyl]benzohydrazide (2a):**[6b] Colorless oil (397 mg, 95% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3275, 1643, 1604, 1224 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37–2.52 (m, 2 H, $–CH_2–$), 4.13 (t, J = 6.8 Hz, 1 H, –CH), 5.08 (dd, J = 18.6 Hz, J = 11.2 Hz, 2 H, $=CH_2$), 5.20 (d, J = 5.3 Hz, 1 H, NH), 5.69–5.80 (m, 1 H, –CH=), 6.99 (t, J = 8.6 Hz, 2 H, Ar), 7.30 (m, 4 H, Ar), 7.45 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.61 (d, J = 7.6 Hz, 2 H, Ar), 7.98 (d, J = 6.3 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 162.2 ($J_{C,F}$ = 240 Hz), 137.3, 134.3, 132.8, 131.9, 129.4, 129.3, 128.6, 127.0, 118.1, 115.3 ($J_{C,F}$ = 21 Hz), 63.2, 40.3 ppm.

***N′*-(1-Phenylbut-3-enyl)benzohydrazide (2b):**[6b] White solid (371 mg, 95% yield); m.p. 98–99 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3300, 1635, 1578, 1314 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39–2.51 (m, 2 H, $–CH_2–$), 4.13 (td, J = 3.0 Hz, J = 2.1 Hz, 1 H, –CH), 5.05 (d, J = 10.1 Hz, 1 H, $=CH_2$), 5.10 (dd, J = 17.1 Hz, J = 1.3 Hz, 1 H, $=CH_2$), 5.23 (dd, J = 6.7 Hz, J = 2.3 Hz, 1 H, NH), 5.71–5.81 (m, 1 H, –CH=), 7.23–7.34 (m, 7 H, Ar), 7.41 (td, J = 2.7 Hz, J = 1.1 Hz, 1 H, Ar), 7.58 (d, J = 7.0 Hz, 2 H, Ar), 8.07 (d, J = 6.6 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 141.4, 134.3, 132.7, 131.5, 128.4, 128.3, 127.6, 127.5, 126.8, 117.7, 63.7, 40.0 ppm.

***N′*-[1-(4-Ethylphenyl)but-3-enyl]benzohydrazide (2c):**[6b] White solid (419 mg, 97% yield); m.p. 63–64 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3272, 1641 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (t, J = 3.0 Hz, J = 2.1 Hz, 3 H, $–CH_3$), 2.41–2.54 (m, 2 H, $–CH_2–$), 2.61 (d, J = 7.6 Hz, 2 H, $–CH_2–$), 4.11 (t, J = 7.0 Hz, 1 H, –CH), 5.06 (d, J = 10.0 Hz, 1 H, $=CH_2$), 5.13 (dd, J = 17.1 Hz, J = 1.2 Hz, 1 H, $=CH_2$), 5.24 (s, 1 H, NH), 5.75–5.80 (m, 1 H, –CH=), 7.14 (d, J = 8.0 Hz, 2 H, Ar), 7.25 (d, J = 8.0 Hz, 2 H, Ar), 7.31 (dd, J = 7.8 Hz, J = 7.4 Hz, 2 H, Ar), 7.42 (dd, J = 7.5 Hz, J = 7.3 Hz, 1 H, Ar), 7.59 (d, J = 7.2 Hz, 2 H, Ar), 7.81 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 143.5, 138.8, 134.8, 133.0, 131.7, 128.5, 128.0, 127.8, 127.1, 117.7, 63.7, 40.2, 28.5, 15.5 ppm.

***N′*-[1-(4-Methoxyphenyl)but-3-enyl]benzohydrazide (2d):**[6b] White solid (244 mg, 56% yield); m.p. 167–168 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3271, 1640, 1613, 1248 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41–2.55 (m, 2 H, $–CH_2–$), 3.78 (s, 3 H, $–CH_3$), 4.10 (td, J = 7.2 Hz, J = 1.8 Hz, 1 H, –CH), 5.08 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.14 (d, J = 17.1 Hz, 1 H, $=CH_2$), 5.22 (dd, J = 6.8 Hz, J = 2.0 Hz, 1 H, NH), 5.77–5.83 (m, 1 H, –CH=), 6.86 (d, J = 8.8 Hz, 2 H, Ar), 7.27 (d, J = 8.8 Hz, 2 H, Ar), 7.35 (t, J = 7.7 Hz, 2 H, Ar), 7.46 (t, J = 7.4 Hz, 1 H, Ar), 7.59 (d, J = 7.3 Hz, 2 H, Ar), 7.68 (d, J = 6.8 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 159.0, 134.7, 133.5, 133.0, 132.7, 128.9, 128.5, 127.0, 117.7, 113.8, 63.3, 55.2, 40.1 ppm.

***N′*-[1-(4-Hydroxyphenyl)but-3-enyl]benzohydrazide (2e):**[6b] Off-white solid (110 mg, 53% yield); m.p. 88–90 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3236, 1627, 1596, 1252 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41–2.54 (m, 2 H, $–CH_2–$), 4.07 (dd, J = 7.2 Hz, J = 6.8 Hz, 1 H, –CH), 5.06 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.12 (d, J = 17.1 Hz, 1 H, $=CH_2$), 5.26 (br. s, 1 H, NH), 5.72–5.82 (m, 1 H, –CH=), 6.82 (d, J = 8.0 Hz, 2 H, Ar), 7.19 (d, J = 8.4 Hz, 2 H, Ar), 7.35 (dd, J = 8.0 Hz, J = 7.6 Hz, 2 H, Ar), 7.46 (t, J = 7.2 Hz, 1 H, Ar), 7.59 (d, J = 7.6 Hz, 2 H, Ar), 7.72 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 155.2, 134.6, 133.7, 132.9 131.8, 129.0, 128.7, 126.8, 118.0, 115.4, 63.5, 40.4 ppm.

***N′*-{1-[4-(Dimethylamino)phenyl]but-3-enyl}benzohydrazide (2f):**[5a] Colorless oil (32 mg, 7% yield); R_f = 0.7 (EtOAc/hexane, 3:7). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46–2.57 (m, 2 H, $–CH_2–$), 2.96 (s, 6 H, $–CH_3$), 4.07 (t, J = 7.0 Hz, 1 H, –CH), 5.12 (d, J = 10.1 Hz, 1 H, $=CH_2$), 5.20 (dd, J = 17.2 Hz, J = 1.4 Hz, 1 H, $=CH_2$), 5.26 (d, J = 6.4 Hz, 1 H, NH), 5.80–5.91 (m, 1 H, –CH=), 6.73 (d, J = 8.8 Hz, 2 H, Ar), 7.31 (m, 2 H, Ar), 7.32 (d, J = 6.4 Hz, 1 H, NH), 7.38 (dd, J = 7.8 Hz, J = 7.4 Hz, 2 H, Ar), 7.47 (dd, J = 7.5 Hz, J = 7.3 Hz, 1 H, Ar), 7.60 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 150.2, 135.0, 133.1, 131.7, 129.2, 128.6, 128.5, 117.7, 112.6, 63.4, 40.6, 40.3 ppm.

***N′*-[1-(2-Bromophenyl)but-3-enyl]benzohydrazide (2g):**[6b] White solid (477 mg, 94% yield); m.p. 76–77 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3070, 1633, 1602, 1315 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.35–2.55 (m, 2 H, $–CH_2–$), 4.71 (t, J = 5.9 Hz, 1 H, –CH), 5.09 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.14 (dd, J = 17.1 Hz, J = 1.2 Hz, 1 H, $=CH_2$), 5.28 (dd, J = 6.4 Hz, J = 2.1 Hz, 1 H, NH), 5.81–5.92 (m, 1 H, –CH=), 7.05 (td, J = 7.8 Hz, J = 1.6 Hz, 1 H, Ar), 7.27 (t, J = 7.7 Hz, 3 H, Ar), 7.39 (t, J = 13.8 Hz, 1 H, Ar), 7.48 (dd, J = 8.0 Hz, J = 1.1 Hz, 1 H, Ar), 7.60 (d, J = 7.1 Hz, 2 H, Ar), 7.64 (dd, J = 7.8 Hz, J = 1.6 Hz, 1 H, Ar), 8.16 (d, J = 6.4 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4, 140.7, 134.1, 133.0, 132.8, 131.7, 128.8, 128.5, 127.7, 127.0, 124.6, 118.4, 62.1, 39.3 ppm.

***N′*-[1-(2-Fluorophenyl)but-3-enyl]benzohydrazide (2h):** Colorless oil (401 mg, 96% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3282, 1634, 1603, 1229 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.53 (t, J = 7.3 Hz, 2 H, $–CH_2–$), 4.55 (td, J = 12.4 Hz, J = 6.8 Hz, 1 H, –CH), 5.09 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.14 (dd, J = 17.1 Hz, J = 1.3 Hz, 1 H, $=CH_2$), 5.26 (dd, J = 6.7 Hz, J = 2.8 Hz, 1 H, NH), 5.78–5.88 (m, 1 H, –CH=), 7.01 (dd, J = 9.6 Hz, J = 9.0 Hz, 1 H, Ar), 7.13 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.20–7.26 (m, 1 H, Ar), 7.34 (dd, J = 7.8 Hz, J = 7.4 Hz, 2 H, Ar), 7.45 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.52 (td, J = 7.4 Hz, J = 1.5 Hz, 1 H, Ar), 7.61 (d, J = 7.5 Hz, 2 H, Ar), 7.80 (d, J = 6.6 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 161.2 ($J_{C,F}$ = 240 Hz), 160.0, 134.2, 132.8, 131.8, 129.0, 128.9, 128.6, 128.5, 126.9, 124.3, 118.2, 115.6 ($J_{C,F}$ = 22 Hz), 57.1, 39.0 ppm. $C_{17}H_{17}FN_2O$ (284.33): calcd. C 71.81, H 6.03, N 9.85; found C 71.90, H 6.08, N 9.70.

***N′*-[1-(3-Fluorophenyl)but-3-enyl]benzohydrazide (2i):** White solid (397 mg, 95% yield); m.p. 55–56 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3294, 1632 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.38–2.51 (m, 2 H, $–CH_2–$), 4.16 (t, J = 6.5 Hz, 1 H, –CH), 5.08 (d, J = 10.5 Hz, 1 H, $=CH_2$), 5.12 (d, J = 18.9 Hz, 1 H, $=CH_2$), 5.21 (dd, J = 6.5 Hz, J = 1.8 Hz, 1 H, NH), 5.72–5.82 (m, 1 H, –CH=), 6.93 (td, J = 8.4 Hz, J = 2.5 Hz, 1 H, Ar), 7.12 (dd, J = 8.1 Hz, J = 7.1 Hz, 1 H, Ar), 7.25 (dd, J = 7.8 Hz, J = 5.7 Hz, 1 H, Ar), 7.33 (dd, J = 7.7 Hz, J = 7.6 Hz, 2 H, Ar), 7.44 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.61 (d, J = 7.8 Hz, 2 H, Ar), 8.03 (d, J = 6.5 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 163.0 ($J_{C,F}$ = 240 Hz), 144.6, 144.5, 134.1, 132.7, 131.8, 130.0, 130.0, 129.9, 128.6, 127.0, 123.6, 118.2, 114.5 ($J_{C,F}$ = 21 Hz), 114.4 ($J_{C,F}$ = 21 Hz), 114.3, 63.5, 40.3 ppm. $C_{17}H_{17}FN_2O$ (284.33): calcd. C 71.81, H 6.03, N 9.85; found C 71.78, H 6.11, N 9.80.

***N′*-[1-(2–Chlorophenyl)but-3-enyl]benzohydrazide (2j):** White solid (414 mg, 94% yield); m.p. 80–81 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3260, 1627 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37–2.55 (m, 2 H, $–CH_2–$), 4.75 (t, J = 7.6 Hz, 1 H, –CH), 5.08 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.13 (d, J = 17.2 Hz, 1 H, $=CH_2$), 5.28 (dd, J = 6.5 Hz, J = 2.3 Hz, 1 H, NH), 5.79–5.90 (m, 1 H, –CH=), 7.13 (td, J = 7.6 Hz, J = 1.2 Hz, 1 H, Ar), 7.20–7.30 (m, 4 H, Ar), 7.39 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.64 (d, J = 7.7 Hz, 1 H, Ar), 7.60 (d, J = 7.4 Hz, 2 H, Ar), 8.20 (d, J = 6.5 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 139.2, 134.2, 134.1, 132.8, 131.7, 129.7, 128.6, 128.4, 128.2, 127.1, 126.9,

118.3 59.6, 39.2 ppm. $C_{17}H_{17}ClN_2O$ (300.79): calcd. C 67.88, H 5.70, N 9.31; found C 67.85, H 5.76, N 9.28.

***N′*-[1-(3–Chlorophenyl)but-3-enyl]benzohydrazide (2k):**[6b] Off-white solid (414 mg, 94% yield); m.p. 65–66 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3286, 1631, 1601, 1313 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39–2.52 (m, 2 H, $–CH_2–$), 4.14 (t, J = 6.5 Hz, 1 H, –CH), 5.10 (d, J = 10.6 Hz, 1 H, $=CH_2$), 5.14 (d, J = 18.2 Hz, 1 H, $=CH_2$), 5.20 (d, J = 6.5 Hz, 1 H, NH), 5.73–5.83 (m, 1 H, –CH=), 7.21–7.24 (m, 3 H, Ar), 7.32–7.47 (m, 4 H, Ar), 7.60 (d, J = 7.8 Hz, 2 H, Ar), 7.82 (d, J = 6.5 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 144.0, 134.4, 134.0, 132.7, 131.8, 129.7, 128.6, 127.8, 127.8, 127.0, 126.2, 118.3, 63.5, 40.3 ppm.

***N′*-[1-(4–Chlorophenyl)but-3-enyl]benzohydrazide (2l):**[6b] White solid (419 mg, 95% yield); m.p. 114–115 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3269, 1643, 1313 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.39–2.52 (m, 2 H, $–CH_2–$), 4.15 (dd, J = 7.2 Hz, J = 6.8 Hz, 1 H, –CH), 5.10 (d, J = 8.7 Hz, 1 H, $=CH_2$), 5.14 (d, J = 17.8 Hz, 1 H, $=CH_2$), 5.20 (d, J = 5.4 Hz, 1 H, NH), 5.73–5.83 (m, 1 H, –CH=), 7.29 (m, 4 H, Ar), 7.36 (dd, J = 8.0 Hz, J = 7.6 Hz, 2 H, Ar), 7.42 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.58 (d, J = 7.6 Hz, 2 H, Ar), 7.64 (d, J = 6.0 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 140.2, 134.1, 133.3, 132.8, 131.9, 129.1, 128.7, 128.6, 127.0, 118.3, 63.3, 40.3 ppm.

***N′*-[1-(4-Nitrophenyl)but-3-enyl]benzohydrazide (2m):**[6b] Yellow oil (420 mg, 92% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3299, 1631, 1515, 1341 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44–2.57 (m, 2 H, $–CH_2–$), 4.35 (dd, J = 7.2 Hz, J = 6.4 Hz, 1 H, –CH), 5.16 (d, J = 10.1 Hz, 1 H, $=CH_2$), 5.18 (dd, J = 10.2 Hz, J = 1.4 Hz, 1 H, $=CH_2$), 5.23 (d, J = 6.3 Hz, 1 H, NH), 5.77–5.87 (m, 1 H, –CH=), 7.37–7.43 (m, 3 H, Ar), 7.49 (dt, J = 7.5 Hz, J = 1.1 Hz, 1 H, Ar), 7.56–7.61 (m, 4 H, Ar), 8.20 (d, J = 8.7 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 149.6, 147.4, 133.3, 132.4, 132.1, 128.7, 128.6, 126.9, 123.8, 119.0, 63.4, 40.4 ppm.

***N′*-(1-Phenylhex-5-en-3-yl)benzohydrazide (2n):**[6b] Colorless oil (398 mg, 92% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3281, 1639, 1602, 1313 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.69–1.85 (m, 2 H, $–CH_2–$), 2.19–2.34 (m, 2 H, $–CH_2–$), 2.64–2.76 (m, 2 H, $–CH_2–$), 3.04–3.10 (m, 1 H, –CH), 4.91–5.08 (m, 1 H, NH), 5.09 (d, J = 9.6 Hz, 1 H, $=CH_2$), 5.13 (dd, J = 17.0 Hz, J = 1.3 Hz, 1 H, $=CH_2$), 5.81–5.91 (m, 1 H, –CH=), 7.13–7.19 (m, 3 H, Ar), 7.24 (dd, J = 7.6 Hz, J = 2.4 Hz, 2 H, Ar), 7.36 (dd, J = 8.0 Hz, J = 7.2 Hz, 2 H, Ar), 7.46 (dd, J = 7.6 Hz, J = 7.2 Hz, 1 H, Ar), 7.71 (d, J = 7.2 Hz, 2 H, Ar), 8.12 (s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 142.2, 135.3, 133.0, 131.8, 128.7, 128.5, 128.4, 127.1, 125.9, 117.6, 59.2, 37.4, 34.3, 32.0 ppm.

***N′*-(Undec-1-en-4-yl)benzohydrazide (2o):**[6b] Colorless oil (402 mg, 95% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3282, 1634, 1603, 1314 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (dd, 3 H, $–CH_3$), 1.27–1.51 (m, 12 H, $–CH_2–$), 2.16–2.31 (m, 2 H, $–CH_2–$), 2.99–3.03 (m, 1 H, –CH), 5.01 (br. s, 1 H, NH), 5.10 (d, J = 9.2 Hz, 1 H, $=CH_2$), 5.13 (dd, J = 17.8 Hz, J = 1.7 Hz, 1 H, $=CH_2$), 5.83–5.94 (m, 1 H, –CH=), 7.42 (dt, J = 7.7 Hz, J = 1.6 Hz, 2 H, Ar), 7.50 (dt, J = 7.6 Hz, J = 7.6 Hz, 1 H, Ar), 7.75 (d, J = 7.0 Hz, 2 H, Ar), 8.02 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 135.2, 132.7, 131.4, 128.2, 126.8, 116.8, 59.2, 37.2, 32.3, 31.5, 29.6 29.0, 25.5, 22.4, 13.8 ppm.

***N′*-(2-Methylhex-5-en-3-yl)benzohydrazide (2p):**[5a] White solid (324 mg, 95% yield); m.p. 75–76 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3232, 1630 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (dd, J = 6.9 Hz, J = 3.9 Hz, 6 H, $–CH_3$), 1.85–1.93 (m, 1 H, –CH–), 2.07–2.15 (m, 1 H, $–CH_2–$), 2.24–2.30 (m, 1 H, $–CH_2–$), 2.86–2.89 (m, 1 H, –CH–), 4.98 (dd, J = 6.3 Hz, J = 2.5 Hz, 1 H, NH), 5.10 (d, J = 10.1 Hz, 1 H, $=CH_2$), 5.16 (dd, J = 17.1 Hz, J = 1.3 Hz, 1 H, $=CH_2$), 5.86–5.97 (m, 1 H, –CH=), 7.40 (dd, J = 7.7 Hz, J = 7.2 Hz, 2 H, Ar), 7.46–7.50 (m, 1 H, Ar), 7.75 (d, J = 7.1 Hz, 2 H, Ar), 8.02 (d, J = 6.1 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 136.4, 133.0, 131.7, 128.6, 126.9, 117.0, 64.4, 33.8, 29.4, 18.7, 17.6 ppm.

***N′*-(1–Cyclohexylbut-3-enyl)benzohydrazide (2q):**[5a] White solid (372 mg, 93% yield); m.p. 115–116 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3301, 1626, 1546, 1311 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.04–1.27 (m, 5 H, $–CH_2–$), 1.48–1.55 (m, 1 H, –CH–), 1.65–1.81 (m, 5 H, $–CH_2–$), 2.12–2.19 (m, 1 H, $–CH_2–$), 2.27–2.33 (m, 1 H, $–CH_2–$), 2.82–2.86 (m, 1 H, –CH), 4.99 (br. s, 1 H, NH), 5.09 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.13 (dd, J = 17.2 Hz, J = 1.2 Hz, 1 H, $=CH_2$), 5.86–5.96 (m, 1 H, –CH=), 7.39 (dd, J = 7.6 Hz, J = 7.2 Hz, 2 H, Ar), 7.48 (dd, J = 7.4 Hz, J = 7.3 Hz, 1 H, Ar), 7.75 (d, J = 7.2 Hz, 2 H, Ar), 8.07 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 136.6, 133.0, 131.6, 128.5, 127.0, 116.8, 64.3, 40.0, 34.6, 29.1, 28.5, 26.7, 26.6 ppm.

***(E)*-*N′*-(1-Phenylhexa-1,5-dien-3-yl)benzohydrazide (2r):**[5a] Off-white solid (240 mg, 56% yield); m.p. 83–84 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3247, 1630, 1602, 1333 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (t, J = 6.8 Hz, 2 H, $–CH_2–$), 3.72–3.77 (m, 1 H, –CH), 5.10 (dd, J = 6.8 Hz, J = 2.3 Hz, 1 H, NH), 5.15 (d, J = 10.2 Hz, 1 H, $=CH_2$), 5.21 (dd, J = 17.1 Hz, J = 1.5 Hz, 1 H, $=CH_2$), 5.85–5.95 (m, 1 H, –CH=), 6.12 (dd, J = 15.9 Hz, J = 8.5 Hz, 1 H, –CH=), 6.56 (d, J = 15.9 Hz, 1 H, –CH=), 7.24 (dd, J = 7.1 Hz, J = 6.9 Hz, 1 H, Ar), 7.31 (t, J = 7.4 Hz, 2 H, Ar), 7.39 (dd, J = 13.4 Hz, J = 7.5 Hz, 4 H, Ar), 7.47–7.50 (m, 1 H, Ar), 7.67–7.72 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 136.7, 134.4, 133.1, 133.0 128.7, 127.7, 127.1, 126.5, 118.0, 62.6, 38.4 ppm.

***N′*-[1-(4-Fluorophenyl)-3-methylbut-3-enyl]benzohydrazide (2s):** White solid (416 mg, 95% yield); m.p. 118–119 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3286, 1628, 1603, 1219 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, $–CH_3$), 2.27–2.32 (m, 1 H, $–CH_2–$), 2.44–2.50 (m, 1 H, $–CH_2–$), 4.27–4.31 (ddd, J = 8.88 Hz, J = 5.4 Hz, J = 1.8 Hz, 1 H, –CH–), 4.88 (d, J = 6.4 Hz, 2 H, $=CH_2$), 5.21 (dd, J = 6.8 Hz, J = 2.0 Hz, 1 H, NH), 6.99 (dd, J = 8.8 Hz, J = 8.4 Hz, 2 H, Ar), 7.31–7.36 (m, 4 H, Ar), 7.43–7.56 (m, 1 H, Ar), 7.57 (d, J = 7.2 Hz, 2 H, Ar), 7.70 (d, J = 6.4 Hz, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 163.4 ($J_{C,F}$ = 240 Hz), 142.0, 137.9, 132.9, 131.8, 129.2, 128.6, 126.9, 115.4 ($J_{C,F}$ = 22 Hz), 61.0, 45.0, 22.1 ppm. $C_{18}H_{19}FN_2O$ (298.36): calcd. C 72.46, H 6.42, N 9.39; found C 72.09, H 6.47, N 9.31.

***N′*-[1-(4-Fluorophenyl)-2-methylbut-3-enyl]benzohydrazide (2t):**[13] A mixture of diastereomers (*anti*/*syn*, 77:23) and a white solid (407 mg, 93% yield); m.p. 124–125 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3280, 1632, 1220 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.76 (d, J = 6.8 Hz, 2.3 H, $–CH_3$), 1.04 (d, J = 6.8 Hz, 0.7 H, $–CH_3$), 2.35–2.45 (m, 0.8 H, –CH–), 2.57–2.45 (m, 0.2 H, –CH–), 3.81 (d, J = 9.5 Hz, 0.8 H, –CH–), 4.06 (d, J = 5.6 Hz, 0.2 H, –CH–), 4.96–5.02 (m, 0.5 H, $=CH_2$), 5.18–5.28 (m, 1.5 H, $=CH_2$), 5.32 (d, J = 6.0 Hz, 1 H, NH), 5.72–5.80 (m, 0.2 H, =CH–), 5.85–5.94 (m, 0.8 H, =CH–), 6.95–7.01 (m, 2 H, Ar), 7.27–7.34 (m, 4 H, Ar), 7.42–7.46 (m, 1 H, Ar), 7.53–7.57 (m, 2 H, Ar), 7.67 (d, J = 6.1 Hz, 0.8 H, NH), 7.82 (d, J = 5.5 Hz, 0.2 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 167.2, 162.2 ($J_{C,F}$ = 240 Hz), 141.2, 139.7, 136.5, 132.9, 132.8, 131.7, 130.1,

130.0, 128.6, 126.7, 126.9, 116.7, 115.2 ($J_{C,F}$ = 22 Hz), 115.0 ($J_{C,F}$ = 21 Hz), 68.1, 67.9, 44.0, 41.9, 17.7, 15.6 ppm.

***N′*-[1-(4-Fluorophenyl)-2-phenylbut-3-enyl]benzohydrazide (2u):** Colorless oil (492 mg, 93% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3281, 1634, 1603, 1224 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.57–3.59 (dd, J = 9.5 Hz, J = 8.4 Hz, 1 H, –CH–), 4.49 (dd, J = 10.0 Hz, J = 1.7 Hz, 1 H, –CH–), 4.72 (d, J = 17.0 Hz, 1 H, =CH_2), 4.88 (d, J = 10.9 Hz, 1 H, =CH_2), 4.92 (dd, J = 6.7 Hz, J = 1.8 Hz, 1 H, NH), 5.70–5.79 (dt, J = 17.3 Hz, J = 2.3 Hz, 1 H, =CH), 7.01 (t, J = 8.6 Hz, 2 H, Ar), 7.14 (d, J = 6.6 Hz, 1 H, NH), 7.27–7.36 (m, 5 H, Ar), 7.38–7.44 (m, 7 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 162.3 ($J_{C,F}$ = 240 Hz), 140.3, 138.2, 136.1, 136.0, 132.7, 131.8, 130.3, 130.2, 129.0, 128.6, 127.4, 126.8, 116.8, 115.3 ($J_{C,F}$ = 21 Hz), 67.1, 56.1 ppm. $C_{23}H_{21}FN_2O$ (360.43): calcd. C 76.64, H 5.87, N 7.77; found C 76.32, H 6.01, N 7.58.

***N′*-[1-(4-Fluorophenyl)-2,2-dimethylbut-3-enyl]benzohydrazide (2v):** White solid (431 mg, 94% yield); m.p. 139–140 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3280, 1633, 1603, 1219 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.96 (s, 3 H, –CH_3), 1.02 (s, 3 H, –CH_3), 3.98 (d, 1 H, –CH–), 5.16 (dd, J = 17.4 Hz, J = 0.9 Hz, 1 H, =CH_2), 5.23 (dd, J = 10.7 Hz, J = 0.9 Hz, 1 H, =CH_2), 5.23 (dd, J = 10.7 Hz, J = 0.9 Hz, 1 H, NH), 6.11 (dd, J = 17.4 Hz, J = 10.7 Hz, 1 H, –CH=), 7.03 (t, J = 8.7 Hz, 2 H, Ar), 7.13 (d, J = 6.8 Hz, 1 H, NH), 7.32–7.38 (m, 4 H, Ar), 7.43–7.49 (m, 3 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 162.2 ($J_{C,F}$ = 240 Hz), 145.5, 134.6, 132.9, 131.7, 130.9, 130.8, 128.6, 126.8, 114.6 ($J_{C,F}$ = 21 Hz), 113.7, 71.1, 40.6, 26.5, 19.8 ppm. $C_{19}H_{21}FN_2O$ (312.39): calcd. C 73.05, H 6.78, N 8.97; found C 73.02, H 6.81, N 8.95.

1-(4-Fluorophenyl)but-3-en-1-ol (3a):[14] Colorless oil (55 mg, 39% yield); R_f = 0.3 (EtOAc/hexane, 3:7). ^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (td, J = 7.0 Hz, J = 1.0 Hz, 2 H, –CH_2–), 2.55 (d, J = 2.8 Hz, 1 H, OH), 4.64 (td, J = 6.4 Hz, J = 3.1 Hz, 1 H, –CH–), 5.08 (m, 1 H, =CH_2), 5.11–5.12 (m, 1 H, =CH_2), 5.18–5.79 (m, 1 H, =CH), 6.99 (t, J = 8.7 Hz, 2 H, Ar), 7.26 (dd, J = 8.5 Hz, J = 5.5 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2 ($J_{C,F}$ = 240 Hz), 139.6, 134.2, 127.5, 124.4, 118.6, 115.2 ($J_{C,F}$ = 21 Hz), 72.7, 43.9 ppm.

1-(4-Methoxyphenyl)but-3-en-1-ol (3b):[14] Colorless oil (89 mg, 34% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3401, 1612, 1604, 1513 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (d, J = 3.20 Hz, 1 H, OH), 2.47 (t, J = 6.8 Hz, 2 H, –CH_2–), 3.78 (s, 3 H, OCH_3), 4.64 (td, J = 6.48 Hz, J = 3.1 Hz, 1 H, –CH–), 5.09 (m, 2 H, =CH_2), 5.86–5.82 (m, 1 H, =CH), 6.86 (d, J = 8.8 Hz, 2 H, Ar), 7.25 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 136.2, 134.7, 127.1, 118.0, 113.8, 55.3, 43.7 ppm.

4-(1-Hydroxybut-3-enyl)phenol (3c):[15] Colorless oil (99 mg, 41% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3337, 1640, 1614, 1515, 1236 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41–2.52 (m, 2 H, –CH_2–), 2.95 (br. s, 1 H, OH), 4.61 (dd, J = 6.8 Hz, J = 6.4 Hz, 1 H, –CH–), 5.05–5.11 (m, 2 H, =CH_2), 5.66–5.76 (m, 1 H, =CH), 6.71 (d, J = 8.4 Hz, 2 H, Ar), 7.11 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 135.1, 134.4, 127.5, 118.4, 115.5, 73.6, 43.3 ppm.

1-[4-(Dimethylamino)phenyl]but-3-en-1-ol (3d):[16] Yellow oil (239 mg, 85% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 1615, 1521, 1348 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.36–2.43 (m, 1 H, –CH_2–), 2.54–2.62 (m, 2 H, –CH_2–), 2.94 (s, 6 H, OCH_3), 4.07 (dd, J = 6.1 Hz, J = 1.2 Hz, 1 H, –CH–), 5.00 (dq, J = 10.2 Hz, J = 1.0 Hz, 1 H, =CH_2), 5.05 (dq, J = 17.2 Hz, J = 1.6 Hz, 1 H, =CH_2), 5.74–5.80 (m, 1 H, =CH), 6.67 (d, J = 8.2 Hz, 2 H, Ar), 7.16 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.2, 135.4, 129.3, 127.8, 116.6, 112.4, 83.4, 56.3, 42.5, 40.6 ppm.

(*E*)-1-Phenylhexa-1,5-dien-3-ol (3e):[14] Colorless oil (217 mg, 85% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3368, 1641, 1599 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, J = 3.4 Hz, 1 H, -OH), 2.34–2.47 (m, 2 H, –CH_2–), 4.30 (m, 1 H, –CH–), 5.14 (d, J = 3.4 Hz, 1 H, =CH_2), 5.18 (dd, J = 12.4 Hz, J = 1.4 Hz, 1 H, =CH_2), 5.80–5.90 (m, 1 H, =CH), 6.23 (dd, J = 15.9 Hz, J = 6.3 Hz, 1 H, =CH), 6.59 (d, J = 15.9 Hz, 1 H, =CH), 7.23 (dd, J = 7.2 Hz, J = 6.8 Hz, 1 H, Ar), 7.30 (dd, J = 7.6 Hz, J = 7.2 Hz, 2 H, Ar), 7.37 (d, J = 7.6 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.7, 134.1, 131.6, 130.4, 128.6, 127.7, 126.5, 118.5, 71.7, 42.0 ppm.

***N′*-(3-Methylhex-5-en-3-yl)benzohydrazide (6a):** Colorless oil (160 mg, 94% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3282, 2969, 1635, 1603 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, J = 7.5 Hz, 3 H, –CH_3), 1.04 (s, 3 H, –CH_3), 1.39–1.53 (m, 2 H, –CH_2–), 2.14–2.27 (m, 2 H, –CH_2–), 4.87 (br. s, 1 H, –NH), 5.07 (s, 1 H, =CH_2), 5.10 (d, J = 5.8 Hz, 1 H, =CH_2), 5.85–5.96 (m, 1 H, =CH), 7.36 (t, J = 7.7 Hz, 2 H, Ar), 7.34 (t, J = 7.5 Hz, 1 H, Ar), 7.73 (d, J = 7.7 Hz, 2 H, Ar), 8.00 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 134.6, 133.0, 131.6, 128.5, 127.0, 117.6, 59.7, 42.1, 30.1, 22.3, 8.1 ppm. $C_{14}H_{20}N_2O$ (232.32): calcd. C 72.38, H 8.68, N 12.06; found C 71.86, H 8.80, N 11.84.

***N′*-(4-Methylundec-1-en-4-yl)benzohydrazide (6b):** Colorless oil (203 mg, 92% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3282, 2929, 1635, 1603 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, J = 6.9 Hz, 3 H, –CH_3), 1.08 (s, 3 H, –CH_3), 1.28–1.46 (m, 12 H, –CH_2–), 2.17–2.27 (m, 2 H, –CH_2–), 5.00 (br. s, 1 H, –NH), 5.10 (s, 1 H, =CH_2), 5.13 (d, J = 4.8 Hz, 1 H, =CH_2), 5.88–5.98 (m, 1 H, =CH), 7.42 (t, J = 7.7 Hz, 2 H, Ar), 7.34–7.51 (m, 2 H, Ar), 7.74 (d, J = 7.1 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 134.7, 133.0, 131.6, 128.6, 126.9, 117.6, 59.7, 42.6, 37.9, 31.8, 30.3, 29.3, 23.7, 22.8, 22.7, 14.1 ppm. $C_{19}H_{30}N_2O$ (302.46): calcd. C 75.45, H 10.00, N 9.26; found C 75.40, H 10.05, N 9.18.

***N′*-(3-Methyl-1-phenylhex-5-en-3-yl)benzohydrazide (6c):** Colorless oil (204 mg, 90% yield); R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3281, 2974, 1634, 1603 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, –CH_3), 1.70–1.80 (m, 2 H, –CH_2–), 2.24–2.34 (m, 2 H, –CH_2–), 2.72 (t, 2 H, –CH_2–), 5.07 (br. s, 1 H, NH), 5.13 (s, 1 H, =CH_2), 5.16 (d, J = 7.2 Hz, 1 H, =CH_2), 5.90–6.00 (m, 1 H, =CH), 7.14–7.20 (m, 3 H, Ar), 7.26 (t, J = 7.4 Hz, 2 H, Ar), 7.39 (t, J = 7.8 Hz, 2 H, Ar), 7.44–7.49 (m, 2 H, Ar), 7.69 (d, J = 7.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 142.7, 134.4, 132.9, 131.7, 128.7, 128.5, 126.9, 125.8, 118.1, 59.7, 42.8, 39.8, 30.1, 23.0 ppm. $C_{20}H_{24}N_2O$ (308.42): calcd. C 77.89, H 7.84, N 9.08; found C 77.84, H 7.78, N 8.93.

***N′*-(1-Allylcyclopentyl)benzohydrazide (6d):** Off-yellow solid (165 mg, 92% yield); m.p. 69–70 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3304, 2955, 1630, 1578 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.50–1.75 (m, 8 H, –CH_2–), 2.31 (d, J = 7.2 Hz, 2 H, –CH_2–), 4.89 (br. s, 1 H, NH), 5.08 (s, 1 H, =CH_2), 5.12 (d, J = 8.0 Hz, 1 H, =CH_2), 5.93–6.01 (m, 1 H, =CH), 7.38 (t, J = 7.6 Hz, 2 H, Ar), 7.46 (t, J = 7.3 Hz, 1 H, Ar), 7.73 (d, J = 7.4 Hz, 2 H, Ar), 8.02 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 135.5, 132.9, 131.6, 128.6, 126.9, 117.5, 69.1, 42.8, 35.1, 24.5 ppm. $C_{15}H_{20}N_2O$ (244.34): calcd. C 73.74, H 8.25, N 11.47; found C 73.79, H 8.28, N 11.38.

***N′*-(1-Allylcyclohexyl)benzohydrazide (6e):** White solid (360 mg, 95% yield); m.p. 71–72 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat):

$\tilde{\nu}$ = 3300, 2929, 1637, 1578 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35–1.46 (m, 8 H, $–CH_2–$), 1.62 (d, J = 5.2 Hz, 2 H, $–CH_2–$), 2.22 (d, J = 7.3 Hz, 2 H, $–CH_2–$), 5.00 (br. s, 1 H, NH), 5.05 (s, 1 H, $=CH_2$), 5.09 (d, J = 5.1 Hz, 1 H, $=CH_2$), 5.91–6.02 (m, 1 H, =CH), 7.30 (t, J = 7.6 Hz, 2 H, Ar), 7.40 (t, J = 7.2 Hz, 1 H, Ar), 7.72 (d, J = 8.1 Hz, 2 H, Ar), 8.27 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 134.7, 133.0, 131.4, 128.4, 127.0, 117.3, 58.8, 41.1, 33.4, 25.7, 21.9 ppm. $C_{16}H_{22}N_2O$ (258.36): calcd. C 74.38, H 8.58, N 10.84; found C 74.28, H 8.67, N 10.95.

***N′*-(1-Allylcyclododecyl)benzohydrazide (6f):** White solid (239 mg, 95% yield); m.p. 95–96 °C. R_f = 0.7 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3260, 2939, 1667, 1579 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.37–1.55 (m, 22 H, $–CH_2–$), 2.19 (d, J = 7.2 Hz, 2 H, $–CH_2–$), 5.10–5.19 (m, 3 H, NH, $=CH_2$), 6.08–6.18 (m, 1 H, =CH), 7.32 (br. s, 1 H, NH), 7.43 (t, J = 7.7 Hz, 2 H, Ar), 7.50 (t, J = 7.2 Hz, 1 H, Ar), 7.72 (d, J = 7.1 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 135.5, 133.1, 131.6, 128.7, 126.8, 117.2, 62.3, 41.6, 31.1, 26.1, 22.7, 22.2, 19.1 ppm. $C_{22}H_{34}N_2O$ (342.52): calcd. C 77.14, H 10.01, N 8.18; found C 76.81, H 10.08, N 8.05.

2-Phenylpent-4-en-2-ol (7a): Colorless oil (228 mg, 96% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3435, 1639, 1602, 1446 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.49 (s, 3 H, $–CH_3$), 2.42–2.63 (m, 3 H, $–CH_2$-, OH), 5.02 (d, J = 0.9 Hz, 1 H, $=CH_2$), 5.06 (d, J = 8.1 Hz, 1 H, $=CH_2$), 5.55–5.65 (m, 1 H, =CH), 7.17 (t, J = 7.3 Hz, 1 H, Ar), 7.29 (t, J = 7.9 Hz, 2 H, Ar), 7.39 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 134.0, 128.2, 126.7, 125.0, 119.1, 73.8, 48.6, 29.7 ppm. $C_{11}H_{14}O$ (162.23): calcd. C 81.44, H 8.70; found C 80.95, H 8.57.

2-(4-Fluorophenyl)pent-4-en-2-ol (7b): Colorless oil (125 mg, 95% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3435, 1639, 1602, 1510 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 3 H, $–CH_3$), 2.45–2.50 (dd, J = 13.7 Hz, J = 8.2 Hz, 1 H, $–CH_2–$), 2.60–2.65 (dd, J = 13.8 Hz, J = 6.6 Hz, 1 H, $–CH_2–$), 5.10 (d, J = 12.2 Hz, 2 H, $=CH_2$), 5.55–5.66 (m, 1 H, =CH), 6.96–7.02 (m, 2 H, Ar), 7.36–7.41 (m, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 ($J_{C,F}$ = 243 Hz), 143.4, 133.5, 126.6, 119.6, 114.8 ($J_{C,F}$ = 21 Hz), 73.4, 48.6, 29.9 ppm. $C_{11}H_{13}FO$ (180.22): calcd. C 73.31, H 7.27; found C 73.63, H 7.08.

(*E*)-3-Methyl-1-phenylhexa-1,5-dien-3-ol (7c): Colorless oil (129 mg, 94% yield); R_f = 0.3 (EtOAc/hexane, 3:7). IR (neat): $\tilde{\nu}$ = 3401, 1639, 1598, 1494 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, $–CH_3$), 2.39–2.42 (m, 3 H, $–CH_2$-, OH), 5.09 (d, J = 5.2 Hz, 1 H, $=CH_2$), 5.13 (s, 1 H, $=CH_2$), 5.76–5.87 (m, 1 H, =CH), 6.25 (d, J = 16.1 Hz, 1 H, =CH), 6.56 (d, J = 16.1 Hz, 1 H, =CH), 7.16–7.20 (m, 1 H, Ar), 7.26 (t, J = 7.5 Hz, 2 H, Ar), 7.33 (d, J = 7.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 136.4, 133.8, 128.7, 127.5, 126.6, 119.1 72.5, 47.5, 27.9 ppm. $C_{13}H_{16}O$ (188.27): calcd. C 82.94, H 8.57; found C 82.73, H 8.18.

General Procedure for N–N Bond Cleavage of Hydrazides:[1a] Hydrazide (0.6 mmol) was dissolved in MeOH (1 mL) and treated with SmI_2 [0.1 M in tetrahydrofuran (THF), 18 mL, 1.8 mmol] at room temperature for 4 h under argon. After the reaction went to completion, the mixture was diluted with CH_2Cl_2. The resulting solution was washed with distilled water and then dried with anhydrous $MgSO_4$. After filtration and evaporation of the solvent, the residue was passed through a short silica gel column to obtain the product.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra.

Acknowledgments

This work was supported by the Korean Government (Korean Research Foundation Grant number KRF-2011-0021279).

[1] For recent applications of homoallylic amines, see: a) F. Piao, M. K. Mishra, D. O. Jang, *Tetrahedron* **2012**, *68*, 7050; b) M. Morgen, S. Bretzke, P. Li, D. Menche, *Org. Lett.* **2010**, *12*, 4494; c) E. Airiau, N. Girard, M. Pizzeti, J. Salvadori, M. Taddei, A. Mann, *J. Org. Chem.* **2010**, *75*, 8670; d) C. Denhez, J.-L. Vasse, D. Harakat, J. Szymoniak, *Tetrahedron: Asymmetry* **2007**, *18*, 424; e) J. E. Kropf, I. C. Meigh, M. W. P. Bebbington, S. M. Weinreb, *J. Org. Chem.* **2006**, *71*, 2046; f) M. K. Pandey, A. Bisai, A. Pandey, V. K. Singh, *Tetrahedron Lett.* **2005**, *46*, 5039.

[2] For reviews, see: a) S. Kobayashi, M. Sugiura, C. Ogawa, *Adv. Synth. Catal.* **2004**, *346*, 1023; b) C. O. Puentes, V. J. Kouznetsov, *J. Heterocycl. Chem.* **2002**, *39*, 595; c) S. Kobayashi, H. Ishitani, *Chem. Rev.* **1999**, *99*, 1069.

[3] For allylsilane, see: a) K. K. Pasunooti, M. L. Leow, S. Vedachalam, B. K. Gorityala, X.-W. Liu, *Tetrahedron Lett.* **2009**, *50*, 2979; b) G. Smitha, B. Miriyala, J. S. Williamson, *Synlett* **2005**, 839; c) P. Phukan, *J. Org. Chem.* **2004**, *69*, 4005; d) T. Ollevier, T. Ba, *Tetrahedron Lett.* **2003**, *44*, 9003; e) M. Billet, P. Klotz, A. Mann, *Tetrahedron Lett.* **2001**, *42*, 631; f) L. Niimi, K. Serita, S. Hiraoka, T. Yokozawa, *Tetrahedron Lett.* **2000**, *41*, 7075; g) S. J. Veenstra, P. Schmid, *Tetrahedron Lett.* **1997**, *38*, 997.

[4] For allyltin, see: a) A. V. Narsaiah, J. K. Kumar, P. Narsimha, *Synthesis* **2010**, 1609; b) P. Thirupathi, S. S. Kim, *Tetrahedron* **2009**, *65*, 5168; c) B. Das, K. Laxminarayana, B. Ravikanth, B. Ramarao, *Tetrahedron Lett.* **2006**, *47*, 9103; d) T. Akiyama, J. Iwai, Y. Onuma, H. Kagoshima, *Chem. Commun.* **1999**, 2191.

[5] For allylborane, see: a) U. Schneider, I.-H. Chen, S. Kobayashi, *Org. Lett.* **2008**, *10*, 737; b) S. Kobayashi, K. Hirano, M. Sugiura, *Chem. Commun.* **2005**, 104; c) M. Sugiura, K. Hirano, S. Kobayashi, *J. Am. Chem. Soc.* **2004**, *126*, 7182.

[6] For allylindium, see: a) J. C. González-Gómez, M. Medjahdi, F. Foubelo, M. Yus, *J. Org. Chem.* **2010**, *75*, 6308; b) S. J. Kim, D. O. Jang, *J. Am. Chem. Soc.* **2010**, *132*, 12168; c) D. Samanta, R. B. Kargbo, G. R. Cook, *J. Org. Chem.* **2009**, *74*, 7183; d) R. B. Kargbo, G. R. Cook, *Curr. Org. Chem.* **2007**, *11*, 1287; e) R. Kargbo, Y. Takahashi, S. Bhor, G. R. Cook, G. C. Lloyd-Jones, I. R. Shepperson, *J. Am. Chem. Soc.* **2007**, *129*, 3846; f) K. L. Tan, E. N. Jacobsen, *Angew. Chem.* **2007**, *119*, 1337; *Angew. Chem. Int. Ed.* **2007**, *46*, 1315; g) T. Vilaivan, C. Winotapan, V. Banphavivhit, T. Sinada, Y. Ohfune, *J. Org. Chem.* **2005**, *70*, 3464; h) F. Foubelo, M. Yus, *Tetrahedron: Asymmetry* **2004**, *15*, 3823; i) G. R. Cook, B. C. Maity, R. Kargbo, *Org. Lett.* **2004**, *6*, 1741; j) I. R. Cooper, R. Grigg, W. S. MacLachlan, V. Sridharan, M. Thornton-Pett, *Tetrahedron Lett.* **2003**, *44*, 403.

[7] a) A. J. von Wangelin, H. Neumann, D. Gördes, S. Klaus, D. Strübing, M. Beller, *Chem. Eur. J.* **2003**, *9*, 4286; b) A. Dömling, I. Ugi, *Angew. Chem.* **2000**, *112*, 3300; *Angew. Chem. Int. Ed.* **2000**, *39*, 3168.

[8] For allylsilanes, see: a) E. Prusov, M. E. Maier, *Tetrahedron* **2007**, *63*, 10486; b) Q.-Y. Song, B.-L. Yang, S.-K. Tian, *J. Org. Chem.* **2007**, *72*, 5407; c) N. R. Perl, J. L. Leighton, *Org. Lett.* **2007**, *9*, 3699; d) R. Berger, K. Duff, J. L. Leighton, *J. Am. Chem. Soc.* **2004**, *126*, 5686; e) C. Ogawa, M. Sugiura, S. Kobayashi, *J. Org. Chem.* **2002**, *67*, 5359.

[9] For allylboronates, see: a) S. Pramanik, P. Ghorai, *Chem. Commun.* **2012**, *48*, 1820; b) B. Dhudshia, J. Tiburcio, A. N. Thadani, *Chem. Commun.* **2005**, 5551.

[10] For reviews, see: a) Z.-L. Shen, S.-Y. Wang, Y.-K. Chok, Y.-H. Xu, T.-P. Loh, *Chem. Rev.* **2013**, *113*, 271; b) V. Nair, S. Ros, N. C. Jayan, B. S. Pillai, *Tetrahedron* **2004**, *60*, 1959; c) J. Podlech, T. C. Maier, *Synthesis* **2003**, 633; d) B. C. Ranu, *Eur. J.*

Org. Chem. **2000**, 2347; e) K. K. Chauhan, C. G. Frost, *J. Chem. Soc. Perkin Trans. 1* **2000**, 3015.

[11] For reactions with preformed imines at high temperature, see: J. A. Sirvent, F. F. Foubelo, M. Yus, *Chem. Commun.* **2012**, *48*, 2543.

[12] a) S. M. Capps, T. P. Clarke, J. P. H. Charmant, H. A. F. Hoppe, G. C. Lloyd-Jones, M. Murry, T. M. Peakman, R. A. Stentifold, K. E. Walsh, P. A. Worthington, *Eur. J. Org. Chem.* **2000**, 963; b) H. A. Hoppe, G. C. Lloyd-Jones, M. Murry, T. M. Peakman, K. E. Walsh, *Angew. Chem.* **1998**, *110*, 1653; *Angew. Chem. Int. Ed.* **1998**, *37*, 1545; c) S. Araki, H. Ito, N. Katsumura, Y. Butsugan, *J. Organomet. Chem.* **1989**, *369*, 291; d) S. Yamasaki, K. Fujii, R. Wada, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2002**, *124*, 6536; e) S. Kobayashi, S. Nagayama, *J. Am. Chem. Soc.* **1997**, *119*, 10049.

[13] S. Kobayashi, R. Hirabayashi, *J. Am. Chem. Soc.* **1999**, *121*, 6943.

[14] B. K. Bhuyan, A. J. Borah, K. K. Senapati, P. Phukan, *Tetrahedron Lett.* **2011**, *52*, 2649.

[15] Z. Du, T. Li, F. Wang, W. Zhou, J.-X. Wang, *Synth. Commun.* **2011**, *41*, 1664.

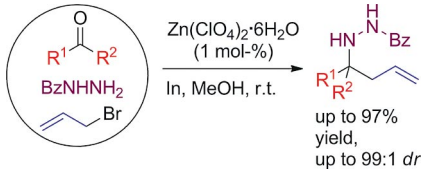
[16] S. E. Denmark, S. T. Nguyen, *Org. Lett.* **2009**, *11*, 781.

Received: December 29, 2012
Published Online: ■

EurJOC European Journal of Organic Chemistry

Multicomponent Reaction

A three-component reaction that involved a carbonyl compound, benzoylhydrazine, allyl bromide, and indium in the presence of readily available $Zn(ClO_4)_2 \cdot 6H_2O$ provided secondary and tertiary homoallylic hydrazides in high yields with excellent chemoselectivities and diastereoselectivies.



Keywords: Multicomponent reactions / Allylation / Aldehydes / Ketones / Chemoselectivity / Hydrazides

