Synthesis A. Lu et al. Paper

Tin-Mediated One-Pot Synthesis of α,α-Disubstituted Homoallylic Hydrazides from Ketones, Acylhydrazines and Allyl Bromide

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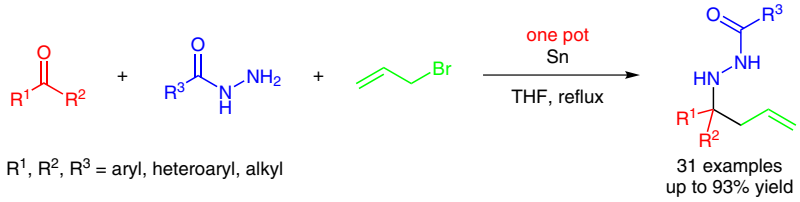


Received: 22.07.2015
Accepted after revision: 30.09.2015
Published online: 04.11.2015
DOI: 10.1055/s-0035-1560803; Art ID: ss-2015-h0449-op

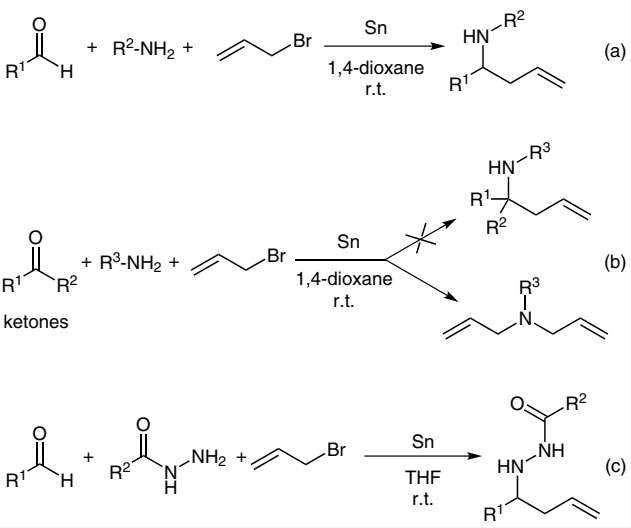
Abstract An efficient multicomponent one-pot reaction was developed for the synthesis of α,α-disubstituted homoallylic hydrazides by treating ketones, acylhydrazines and allyl bromide with tin powder in tetrahydrofuran under reflux. The reaction proceeds smoothly without any catalyst under mild conditions to give the corresponding products in high yields.

Key words tin powder, one pot, allylation, ketones, α,α-disubstituted homoallylic hydrazides

Homoallylic amines are versatile building blocks for nitrogen-containing compounds or related natural products, which are usually biologically active.[1–3] They can also be easily transformed into a variety of other valuable functional groups.[4–6] Thus, many synthetic processes have been developed for their synthesis.[7–9] Among these methods, nucleophilic addition of allylmetal reagents to the C=N bond of imines or their analogues is an effective and widely used method.[10–12] However, α-deprotonation usually takes place exclusively over the addition reactions when typical strong nucleophiles such as allyllithium or allylmagnesium reagents react with 'enolizable' base-sensitive imines or their derivatives. Low-reactive allylboronate, allylsilane and allylic stannane reagents have been successfully used for the preparation of homoallylic amines in high yields. Allylindium reagents are particularly interesting for this purpose as they display low basicity, high chemoselectivity and low toxicity.[10,13] However, Lewis acids or transition-metal catalysts are often needed in this transformation. As for α,α-disubstituted homoallylic amines, their synthesis is known to be difficult. To date, there have been a few reports on the synthesis of these compounds based on the addition of allylsilanes[14–17] or allylboronates[18] to ketimines or their analogues. The indium-induced three-component allylation reaction of ketones, acylhydrazine and allyl bromide was recently reported to give the corresponding α,α-disubstituted homoallylic hydrazides in high yields.[19]

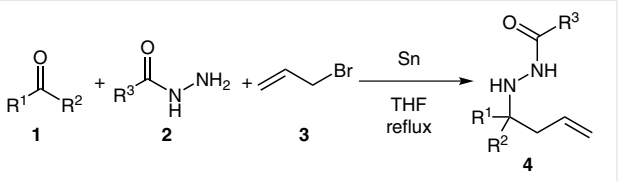
Organotin compounds[13,20] have received much attention and have been applied extensively in organic synthesis due to their stability toward heat, hydrolysis and oxidation, their tolerance to functional groups, and their high selectivity. Allylic stannanes, especially allyltributyltin, have been widely used to synthesize homoallylic amines.[21–23] However, most stannanes are very toxic and need to be prepared beforehand by means of other organometallic compounds such as magnesium, sodium and aluminum derivatives.[24] Moreover, in conventional allylation using allyltributyltin, only the allyl group is delivered into the product, with the tributyltin group usually being discarded as waste after the reaction; removal of the R_3Sn residue from the reaction mixture is required to obtain pure products. Thus, when allyltributyltin is used as a nucleophile, the process is not atom economic nor environmentally benign. To overcome this drawback, tin-powder-promoted allylation processes have been used as an alternative method.[13,25–27] In this process, the toxic allylic stannanes are replaced by tin powder and allyl bromide, and the amount of the organic moiety is much reduced.

Because of some advantages of tin-metal-promoted reactions, we are interested in tin-promoted organic reactions, and have found that tin-mediated one-pot allylation of aldehydes, amines and allyl bromide gives the homoallylic amines chemoselectively without the formation of homoallylic alcohols from allylation of the aldehydes or allylic amines from allylation of the amines (Scheme 1, a).[28] However, this method cannot be applied to ketones; if ketones are used instead of aldehydes under the same conditions, allylation of the amines to give allylic amines is the major reaction (Scheme 1, b).



Scheme 1 Homoallylation of aldehydes

Since it is known that *N*-acylhydrazones often serve as imine equivalents which can react with various nucleophiles,[29] we used acylhydrazines in our laboratory to replace the amines in the reaction. The one-pot reaction of aldehydes, acylhydrazines, allyl bromide and tin occurred smoothly to give the corresponding homoallylic hydrazides, as expected (Scheme 1, c).[30] Literature reports indicate that aldehyde-derived hydrazones are smoothly allylated with different allylation reagents, such as allyltin,[31] allylsilane[32] and allylindium[33] reagents. In contrast, allylations of sterically hindered ketone-derived hydrazones have been scarcely reported. In 2001, Kobayashi and co-workers reported the allylation of ketone-derived hydrazones using allyltrichlorosilane.[34] In 2008, the same research group disclosed another allylation method for ketone-derived hydrazones which uses pinacolyl allylboronate with indium(I) iodide catalysis.[35] Recently, Lee and Jang reported an indium-promoted three-component allylation of ketone-derived hydrazones generated in situ in the presence of a catalytic amount of zinc perchlorate hexahydrate.[19] Based on our previous research work, the allylation of ketone-derived hydrazones generated in situ was explored. To our delight, when ketones were reacted with acylhydrazines, allyl bromide and tin, the α,α-disubstituted homoallylic hydrazides could be obtained in high yields. Herein, we report a facile one-pot synthesis of α,α-disubstituted homoallylic hydrazides from ketones, acylhydrazines and allyl bromide promoted by tin powder (Scheme 2). It offers a convenient, inexpensive and efficient method for the formation of α,α-disubstituted homoallylic hydrazides, which can be easily converted into the corresponding homoallylic amines by N–N bond cleavage.[34]



Scheme 2 Homoallylation of ketones

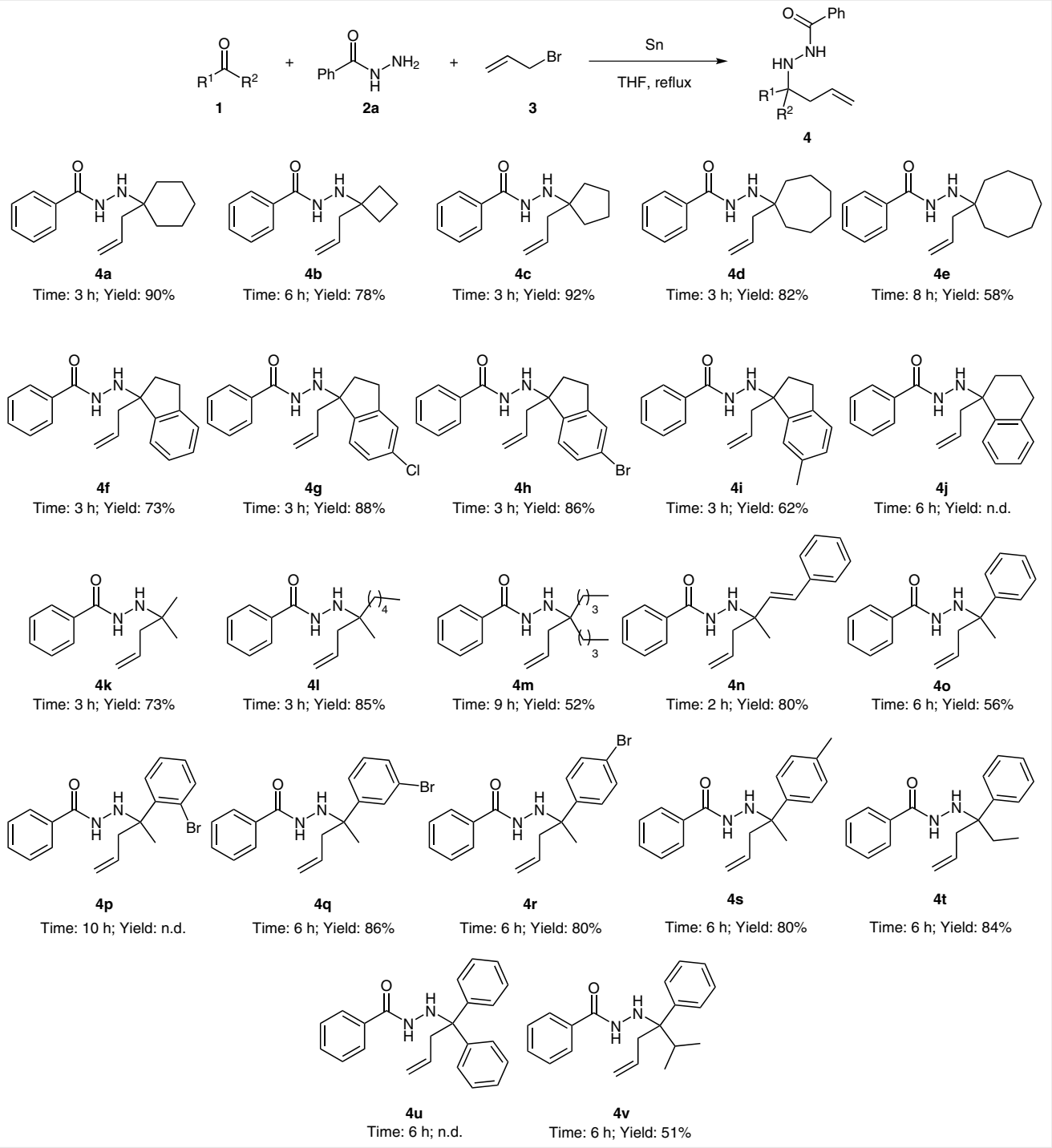
We first investigated the one-pot reaction of cyclohexanone (**1a**), benzoylhydrazine (**2a**), allyl bromide (**3**) and tin powder in tetrahydrofuran at room temperature. After 24 hours, the desired product **4a** was obtained in 65% yield. Considering ketimines are less reactive than aldimines, we carried out the same reaction under reflux. To our delight, the yield of **4a** increased to 90% and the reaction time was dramatically decreased to three hours (Scheme 3).

Various ketones were then examined in the reaction, and the results are summarized in Scheme 3. Various aliphatic cyclic ketones gave the products in good to excellent yields (**4a**–**e**). Indanones also produced the products in high yields (**4f**–**i**), but no target product **4j** was detected when 1-tetralone was used in the reaction. Further investigation indicated that the corresponding hydrazone was formed in 23% yield from 1-tetralone and benzoylhydrazine, but could not react further with allyl bromide and tin. Reaction with acyclic aliphatic ketones occurred smoothly to give the corresponding products in good yields (**4k**–**n**). It is worth noting that sterically hindered nonan-5-one gave product **4m** in reasonable yield, a result which has not been observed in other metal-promoted reactions. Furthermore, the α,β-unsaturated ketone showed exclusive 1,2-addition (product **4n**). As for the aromatic ketones, most gave the products in high yields; even the sterically more hindered ketone 2-methyl-1-phenylpropan-1-one provided a 61% yield of product **4v**. However, ketones with two phenyl rings attached to the carbonyl group such as benzophenone did not afford the allylic product (**4u**). The electronic properties of substituents on the phenyl ring of aromatic ketones had little effect on the reaction, but their position on the phenyl ring had a great influence on the results. For example, *m*-bromoacetophenone and *p*-bromoacetophenone provided the products **4q** and **4r** in high yields, but *o*-bromoacetophenone did not give the product **4p**. This may be due to steric hindrance. In any event, the results in Scheme 3 display a broad substrate scope for ketones.

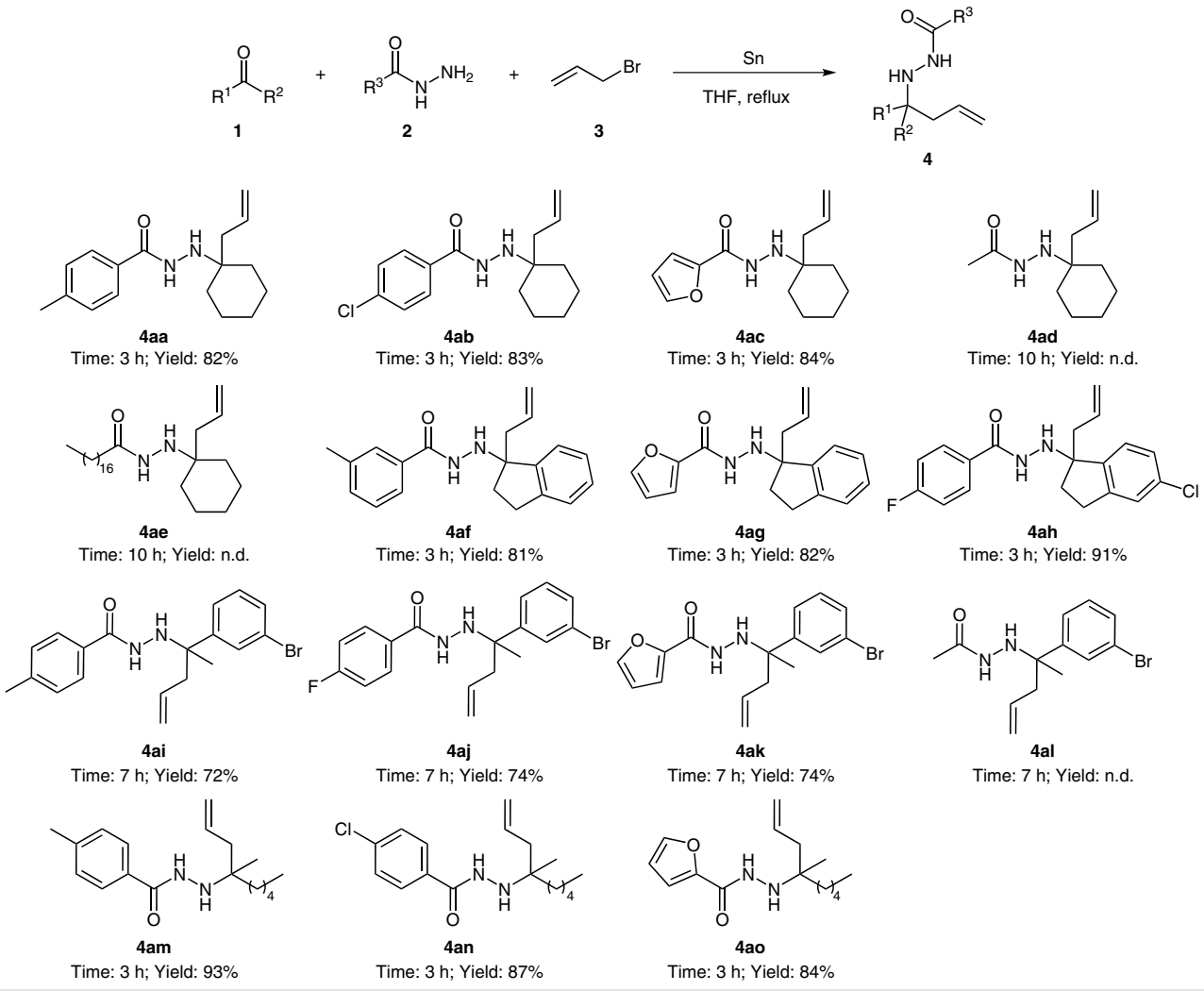
To test the generality of acylhydrazines, different acylhydrazines were reacted with different ketones in the presence of allyl bromide and tin powder under the above reaction conditions (Scheme 4). The reactions of various aromatic acylhydrazines with various ketones gave the desired products in excellent yields. However, the desired products **4ad**, **4ae** and **4al** were not obtained when aliphatic acylhydrazines were used in the reaction.

Further, to test the possibility of N–N bond cleavage in homoallylic hydrazides, compound **4s** was reacted with samarium(II) iodide in tetrahydrofuran at room temperature for two hours. The corresponding homoallylic amine **5** was obtained in 85% yield (Scheme 5).

To investigate the mechanism of the reaction, some control experiments were conducted to determine the reaction rate between the different reactants (Scheme 6). Firstly, *p*-

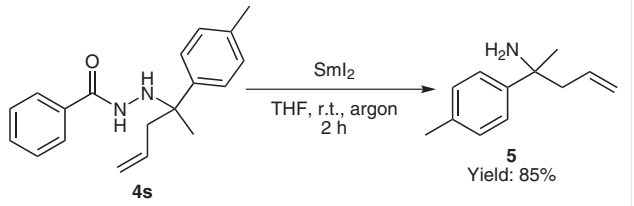


Scheme 3 One-pot reaction of various ketones with benzoylhydrazine. *Reagents and conditions*: ketone **1** (1 mmol), benzoylhydrazine (**2a**; 1.5 mmol), allyl bromide (**3**; 2.0 mmol), Sn powder (2.5 mmol), THF (5 mL), reflux, 3–10 h; isolated yields are shown; n.d. = not detected.



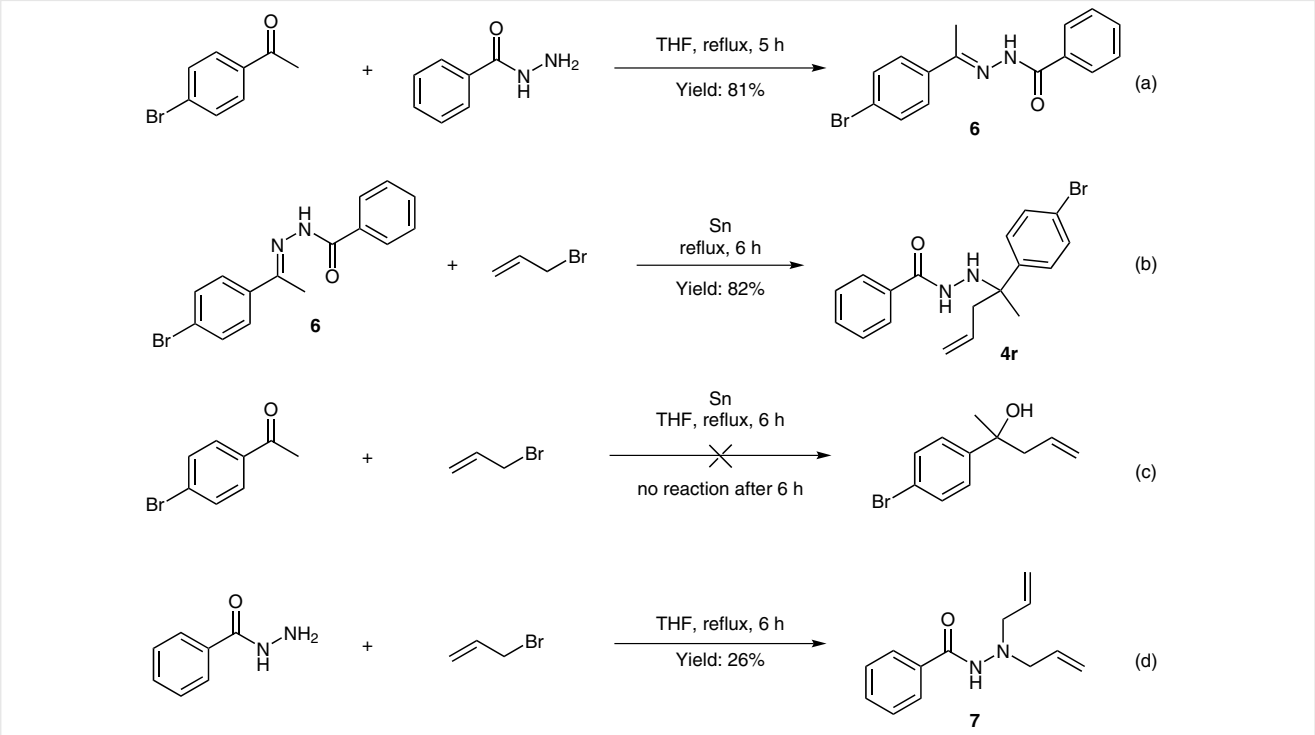
Scheme 4 One-pot reaction of various ketones with various acylhydrazines. *Reagents and conditions*: ketone **1** (1 mmol), acylhydrazine **2** (1.5 mmol), allyl bromide (**3**; 2.0 mmol), Sn powder (2.5 mmol), THF (5 mL), reflux, 3–10 h; isolated yields are shown; n.d. = not detected.

bromoacetophenone was refluxed in tetrahydrofuran with benzoylhydrazine. It was obvious from TLC that the reaction occurred after 30 minutes to give the corresponding hydrazone **6**, and the yield reached 81% after five hours (Scheme 6, a). Hydrazone **6** reacted with allyl bromide and tin powder under standard reaction conditions to give the corresponding homoallylic hydrazide **4r** in 82% yield (Scheme 6, b). Secondly, when *p*-bromoacetophenone was stirred with allyl bromide and tin powder in tetrahydrofuran under reflux for six hours, no reaction was observed (Scheme 6, c). Finally, the reaction between benzoylhydrazine and allyl bromide under the same conditions gave double allylated product **7** in 26% yield (Scheme 6, d), with 48% recovery of benzoylhydrazine. Apparently, the fastest reaction between the reactants is the formation of acylhydrazone from the ketone and the hydrazine.

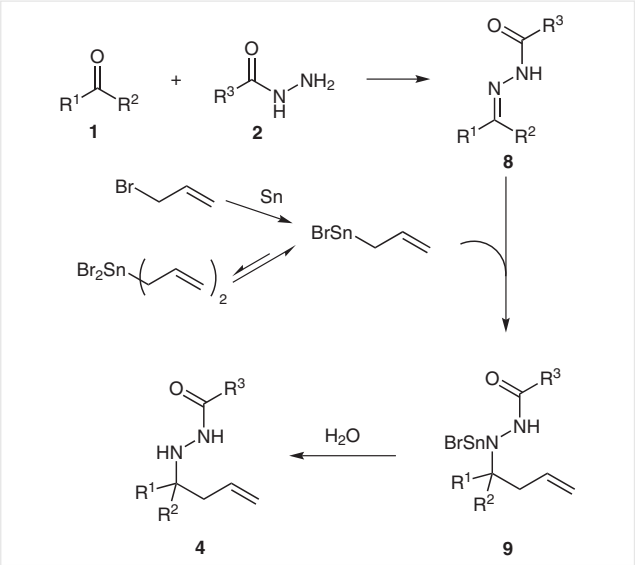


Scheme 5 N–N Bond cleavage in homoallylic hydrazide **4s**

Based on the above experimental results and the literature,[27,36] the proposed reaction mechanism is as follows (Scheme 7): ketone **1** reacts with acylhydrazine **2** to form acylhydrazone **8**, which then reacts with allyltin bromide to give intermediate **9**. Then, hydrolysis of intermediate **9** produces the corresponding product **4**.



Scheme 6 Control experiments



Scheme 7 Proposed reaction mechanism

In conclusion, we have developed an effective tin-mediated one-pot reaction for the synthesis of α,α-disubstituted homoallylic hydrazides from ketones, acylhydrazines and allyl bromide. This approach tolerates a broad substrate scope, including sterically hindered ketones. Compared with reactions using other metals, this tin-promoted process has the following features: catalyst free, operational simplicity, high yields and avoidance of the preparation of allyltin reagents beforehand. It offers a novel method for the synthesis of α,α-disubstituted homoallylic amines.

All reactions were performed under an atmosphere of dry nitrogen gas. Flash chromatography was performed using silica gel 60 (230–400 mesh). IR spectra were obtained using an Alpha Centauri FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker APEX II Fourier transform ion cyclotron resonance mass spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, on a Varian Mercury 400 plus spectrometer or at 600 MHz and 150 MHz, respectively, on an Agilent DD2-600 spectrometer. Chemical shifts are reported as δ values (ppm) relative to TMS for ^{1}H NMR and chloroform for ^{13}C NMR data. Melting points were determined on a Beijing Taike X-4 apparatus and are uncorrected. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques.

α,α-Disubstituted Homoallylic Hydrazides 4; General Procedure

A solution of a ketone **1** (1.0 mmol), an acylhydrazine[37] **2** (1.5 mmol), allyl bromide (**3**; 2.0 mmol) and Sn powder (2.5 mmol) in THF (5 mL) was stirred under reflux for 3–10 h (monitored by TLC). Then, the reaction mixture was quenched with saturated aq NH_4Cl (10 mL). The organic layer was separated, and the aqueous phase was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether–EtOAc) to afford the desired product.

***N'*-(1-Allylcyclohexyl)benzohydrazide (4a)**[36]

Yield: 232.5 mg (90%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 7.34 (s, 1 H), 6.09–5.96 (m, 1 H), 5.20–5.00 (m, 3 H), 2.28 (d, *J* = 7.2 Hz, 2 H), 1.67 (d, *J* = 4.8 Hz, 2 H), 1.61–1.36 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 134.8, 133.0, 131.6, 128.6, 126.7, 117.4, 58.9, 41.5, 31.6, 25.7, 21.9.

***N'*-(1-Allylcyclobutyl)benzohydrazide (4b)**

Yield: 180.1 mg (78%); colorless syrup.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.4 Hz, 3 H), 7.49 (t, *J* = 7.2 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 2 H), 5.96–5.91 (m, 1 H), 5.16 (t, *J* = 14.4 Hz, 3 H), 2.40 (d, *J* = 7.2 Hz, 2 H), 2.09–2.04 (m, 2 H), 1.84 (t, *J* = 9.6 Hz, 2 H), 1.76–1.63 (m, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 167.5, 134.2, 132.8, 131.8, 128.7, 126.9, 117.9, 62.5, 41.7, 30.1, 13.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}N_2O$: 231.1492; found: 231.1493.

***N'*-(1-Allylcyclopentyl)benzohydrazide (4c)**[36]

Yield: 224.0 mg (92%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.70 (m, 3 H), 7.49 (t, *J* = 7.2 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 6.04–5.91 (m, 1 H), 5.21–4.75 (m, 3 H), 2.32 (d, *J* = 7.2 Hz, 2 H), 1.83–1.48 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 135.4, 132.8, 131.6, 128.5, 126.8, 117.4, 69.0, 42.8, 35.0, 24.4.

***N'*-(1-Allylcycloheptyl)benzohydrazide (4d)**

Yield: 223.0 mg (82%); white solid; mp 67–68 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.2 Hz, 2 H), 7.54–7.38 (m, 4 H), 6.10–5.98 (m, 1 H), 5.20–5.00 (m, 3 H), 2.23 (d, *J* = 7.2 Hz, 2 H), 1.70–1.38 (m, 12 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 135.4, 132.9, 131.6, 128.6, 126.7, 117.3, 62.8, 43.8, 36.6, 30.7, 22.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{25}N_2O$: 273.1961; found: 273.1965.

***N'*-(1-Allylcyclooctyl)benzohydrazide (4e)**

Yield: 166.8 mg (58%); colorless syrup.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.2 Hz, 2 H), 7.47 (t, *J* = 6.6 Hz, 1 H), 7.40 (t, *J* = 7.2 Hz, 2 H), 7.32 (s, 1 H), 6.07–6.00 (m, 1 H), 5.15–5.10 (m, 2 H), 5.05 (s, 1 H), 2.20 (d, *J* = 7.2 Hz, 2 H), 1.73–1.69 (m, 2 H), 1.63 (s, 5 H), 1.54–1.51 (m, 4 H), 1.45–1.42 (m, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.6, 135.5, 133.0, 131.6, 128.6 126.7, 117.1, 62.1, 42.3, 31.9, 28.4, 25.3, 22.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{27}N_2O$: 287.2118; found: 287.2115.

***N'*-(1-Allyl-2,3-dihydro-1*H*-inden-1-yl)benzohydrazide (4f)**

Yield: 213.2 mg (73%); white solid; mp 89–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.6 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.37 (t, *J* = 7.6 Hz, 3 H), 7.25 (s, 4 H), 5.88–5.75 (m, 1 H), 5.42 (s, 1 H), 5.21–5.09 (m, 2 H), 3.04–2.93 (m, 1 H), 2.90–2.79 (m, 1 H), 2.67–2.54 (m, 2 H), 2.24–2.09 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 144.4, 144.3, 133.7, 132.7, 131.6, 128.6, 128.1, 126.7, 126.4, 125.0, 123.6, 118.7, 72.0, 42.6, 33.8, 30.0.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{20}N_2NaO$: 315.1468; found: 315.1473.

***N'*-(1-Allyl-5-chloro-2,3-dihydro-1*H*-inden-1-yl)benzohydrazide (4g)**

Yield: 287.0 mg (88%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.6 Hz, 2 H), 7.48 (t, *J* = 7.2 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.35–7.24 (m, 2 H), 7.19 (d, *J* = 8.0 Hz, 2 H), 5.82–5.71 (m, 1 H), 5.41 (s, 1 H), 5.17–5.11 (m, 2 H), 2.99–2.89 (m, 1 H), 2.86–2.75 (m, 1 H), 2.62–2.51 (m, 2 H), 2.21–2.10 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 146.2, 143.0, 133.8, 133.3, 132.5, 132.4, 131.8, 128.6, 126.7, 125.2, 124.8, 118.9, 71.6, 42.6, 33.9, 29.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}ClN_2NaO$: 349.1078; found: 349.1080.

***N'*-(1-Allyl-5-bromo-2,3-dihydro-1*H*-inden-1-yl)benzohydrazide (4h)**

Yield: 319.0 mg (86%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (s, 2 H), 7.53–7.18 (m, 7 H), 5.84–5.70 (m, 1 H), 5.42 (s, 1 H), 5.18–5.14 (m, 2 H), 3.01–2.89 (m, 1 H), 2.88–2.76 (m, 1 H), 2.57 (s, 2 H), 2.16 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 146.6, 143.5, 133.2, 132.5, 131.8, 129.6, 128.6, 128.2, 126.7, 125.2, 122.0, 119.0, 71.7, 42.6, 33.8, 29.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{19}BrN_2NaO$: 393.0573; found: 393.0585.

***N'*-(1-Allyl-6-methyl-2,3-dihydro-1*H*-inden-1-yl)benzohydrazide (4i)**

Yield: 189.8 mg (62%); yellow solid; mp 86–87 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (s, 2 H), 7.52–7.34 (m, 3 H), 7.28–7.04 (m, 4 H), 5.90–5.75 (m, 1 H), 5.41 (s, 1 H), 5.24–5.10 (m, 2 H), 2.99–2.87 (m, 1 H), 2.85–2.74 (m, 1 H), 2.69–2.52 (m, 2 H), 2.37 (s, 3 H), 2.25–2.08 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 144.5, 141.4, 136.1, 133.8, 132.8, 131.6, 129.1, 128.6, 126.7, 124.7, 124.1, 118.6, 71.9, 42.8, 33.9, 29.7, 21.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{22}N_2NaO$: 329.1624; found: 329.1631.

***N'*-(2-Methylpent-4-en-2-yl)benzohydrazide (4k)**[19]

Yield: 159.2 mg (73%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.72 (m, 2 H), 7.52 (t, *J* = 7.2 Hz, 2 H), 7.44 (t, *J* = 7.2 Hz, 2 H), 5.99–5.86 (m, 1 H), 5.19–5.10 (m, 3 H), 2.22 (d, *J* = 7.2 Hz, 2 H), 1.12 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.2, 134.5, 132.9, 131.7, 128.6, 126.8, 117.8, 57.6, 44.8, 25.0.

***N'*-(4-Methylnon-1-en-4-yl)benzohydrazide (4l)**

Yield: 232.8 mg (85%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.2 Hz, 2 H), 7.37 (s, 1 H), 7.23 (d, *J* = 7.2 Hz, 2 H), 5.99–5.87 (m, 1 H), 5.16–4.96 (m, 3 H), 2.34 (s,

3 H), 2.22 (dd, *J* = 7.0, 2.9 Hz, 2 H), 1.49–1.20 (m, 8 H), 1.08 (s, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 134.6, 132.9, 131.6, 128.5, 126.7, 117.5, 59.6, 42.5, 37.7, 32.4, 23.2, 22.7, 22.5, 21.4, 14.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{27}N_2O$: 275.2118; found: 275.2122.

***N*′-(5-Allylnonan-5-yl)benzohydrazide (4m)**

Yield: 157.0 mg (52%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 7.6 Hz, 2 H), 7.51–7.44 (m, 3 H), 7.18 (s, 1 H), 6.05–5.94 (m, 1 H), 5.17 (s, 1 H), 5.12 (d, *J* = 6.4 Hz, 2 H), 2.23 (d, *J* = 6.8 Hz, 2 H), 1.41–1.32 (m, 12 H), 0.93 (d, *J* = 6.4 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5, 135.0, 133.1, 131.6, 128.7, 126.7, 117.4, 61.5, 40.7, 34.8, 25.4, 23.4, 14.1.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{31}N_2O$: 303.2431; found: 303.2429.

***N*′-((*E*)-3-Methyl-1-phenylhexa-1,5-dien-3-yl)benzohydrazide (4n)**

Yield: 245.0 mg (80%); yellow solid; mp 120–122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 7.2 Hz, 2 H), 7.56–7.44 (m, 2 H), 7.42–7.34 (m, 4 H), 7.30 (t, *J* = 7.5 Hz, 2 H), 7.23 (t, *J* = 7.2 Hz, 1 H), 6.51 (d, *J* = 16.4 Hz, 1 H), 6.27 (d, *J* = 16.4 Hz, 1 H), 5.97–5.84 (m, 1 H), 5.48–5.10 (m, 3 H), 2.49–2.37 (m, 2 H), 1.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 136.9, 134.1, 133.6, 132.9, 131.6, 129.8, 128.6, 128.5, 127.5, 126.7, 126.4, 118.5, 61.2, 44.0, 22.2.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{22}N_2NaO$: 329.1624; found: 329.1625.

***N*′-(2-Phenylpent-4-en-2-yl)benzohydrazide (4o)**[38]

Yield: 156.5 mg (56%); white solid; mp 93–94 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 12.0, 7.8 Hz, 4 H), 7.46 (t, *J* = 7.2 Hz, 1 H), 7.38 (q, *J* = 7.6 Hz, 4 H), 7.33–7.25 (m, 1 H), 7.16 (s, 1 H), 5.74–5.62 (m, 1 H), 5.44 (s, 1 H), 5.14–5.05 (m, 2 H), 2.66–2.57 (m, 1 H), 2.55–2.47 (m, 1 H), 1.55 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 144.3, 133.5, 132.8, 131.6, 128.6, 128.4, 127.0, 126.7, 126.4, 118.5, 62.4, 46.1, 22.7.

***N*′-(2-(3-Bromophenyl)pent-4-en-2-yl)benzohydrazide (4q)**

Yield: 308.8 mg (86%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.60 (s, 2 H), 7.51–7.18 (m, 7 H), 5.71–5.57 (m, 1 H), 5.42 (s, 1 H), 5.09 (d, *J* = 12.4 Hz, 2 H), 2.61–2.41 (m, 2 H), 1.52 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 147.1, 133.0, 132.6, 131.7, 130.1, 129.9, 129.8, 128.6, 126.7, 125.2, 122.8, 119.0, 62.4, 46.1, 22.5.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{20}BrN_2O$: 359.0754; found: 359.0765.

***N*′-(2-(4-Bromophenyl)pent-4-en-2-yl)benzohydrazide (4r)**[32d]

Yield: 287.3 mg (80%); white solid; mp 100–101 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 7.6 Hz, 2 H), 7.52–7.34 (m, 7 H), 7.21 (s, 1 H), 5.70–5.57 (m, 1 H), 5.41 (s, 1 H), 5.12–5.04 (m, 2 H), 2.57–2.47 (m, 2 H), 1.52 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 143.5, 133.0, 132.6, 131.7, 131.5, 128.6, 128.4, 126.7, 121.1, 118.9, 62.3, 46.0, 22.5.

***N*′-(2-(*p*-Tolyl)pent-4-en-2-yl)benzohydrazide (4s)**

Yield: 235.0 mg (80%); white solid; mp 114–115 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 7.8 Hz, 2 H), 7.44–7.43 (m, 3 H), 7.36–7.32 (m, 3 H), 7.18 (d, *J* = 8.4 Hz, 2 H), 5.71–5.64 (m, 1 H), 5.41 (br s, 1 H), 5.10–5.05 (m, 2 H), 2.61 (dd, *J* = 13.8, 6.6 Hz, 1 H), 2.51 (dd, *J* = 13.8, 7.8 Hz, 1 H), 2.35 (s, 3 H), 1.53 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 166.5, 141.2, 136.6, 133.7, 132.9, 131.6, 129.2, 128.6, 126.8, 126.4, 118.4, 62.2, 46.0, 22.8, 21.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{23}N_2O$: 295.1805; found: 295.1806.

***N*′-(3-Phenylhex-5-en-3-yl)benzohydrazide (4t)**[32d]

Yield: 247.0 mg (84%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61–7.23 (m, 10 H), 7.13 (s, 1 H), 5.91–5.80 (m, 1 H), 5.55 (d, *J* = 6.4 Hz, 1 H), 5.16–5.04 (m, 2 H), 2.66 (d, *J* = 7.2 Hz, 2 H), 1.94–1.77 (m, 2 H), 0.82 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 142.8, 134.0, 132.8, 131.5, 128.5, 128.4, 126.9, 126.6, 126.5, 117.9, 65.0, 40.3, 29.2, 7.8.

***N*′-(2-Methyl-3-phenylhex-5-en-3-yl)benzohydrazide (4v)**

Yield: 157.0 mg (51%); colorless syrup.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.2 Hz, 2 H), 7.52 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.2 Hz, 1 H), 7.40–7.35 (m, 4 H), 7.28 (t, *J* = 7.2 Hz, 1 H), 7.23 (d, *J* = 7.8 Hz, 1 H), 6.07–6.00 (m, 1 H), 5.67 (d, *J* = 8.4 Hz, 1 H), 5.20 (d, *J* = 16.8 Hz, 1 H), 5.10 (d, *J* = 10.8 Hz, 1 H), 2.91–2.80 (m, 2 H), 2.06–2.00 (m, 1 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.85 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.2, 140.5, 134.9, 133.0, 131.5, 128.6, 128.1, 127.7, 126.7, 126.6, 117.8, 67.6, 38.6, 35.2, 17.7, 17.2.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{20}H_{25}N_2O$: 309.1961; found: 309.1969.

***N*′-(1-Allylcyclohexyl)-4-methylbenzohydrazide (4aa)**

Yield: 223.0 mg (82%); white solid; mp 104–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.40 (s, 1 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 6.07–5.95 (m, 1 H), 5.27–4.86 (m, 3 H), 2.39 (s, 3 H), 2.26 (d, *J* = 7.4 Hz, 2 H), 1.73–1.59 (m, 2 H), 1.58–1.35 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 142.0, 134.8, 130.1, 129.2, 126.7, 117.3, 58.8, 41.4, 33.6, 25.7, 21.9, 21.4.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{25}N_2O$: 273.1961; found: 273.1959.

***N*′-(1-Allylcyclohexyl)-4-chlorobenzohydrazide (4ab)**

Yield: 242.8 mg (83%); white solid; mp 113–115 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 8.4 Hz, 2 H), 7.50 (s, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 6.06–5.93 (m, 1 H), 5.24–4.89 (m, 3 H), 2.26 (d, *J* = 7.2 Hz, 2 H), 1.71–1.59 (m, 2 H), 1.55–1.36 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 137.8, 134.7, 131.3, 128.8, 128.2, 117.4, 58.9, 41.4, 33.6, 25.7, 21.9.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{22}ClN_2O$: 293.1415; found: 293.1420.

***N*′-(1-Allylcyclohexyl)furan-2-carbohydrazide (4ac)**

Yield: 208.0 mg (84%); white solid; mp 76–77 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1 H), 7.45 (d, *J* = 0.7 Hz, 1 H), 7.11 (d, *J* = 3.2 Hz, 1 H), 6.51 (dd, *J* = 3.4, 1.7 Hz, 1 H), 6.06–5.93 (m, 1 H), 5.19–5.10 (m, 2 H), 4.92 (s, 1 H), 2.25 (d, *J* = 7.4 Hz, 2 H), 1.73–1.60 (m, 2 H), 1.54–1.37 (m, 8 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 146.8, 143.9, 134.4, 117.5, 114.3, 112.0, 58.9, 41.2, 33.5, 25.7, 21.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}N_2O_2$: 249.1598; found: 249.1605.

N′-(1-Allyl-2,3-dihydro-1*H*-inden-1-yl)-3-methylbenzohydrazide (4af)

Yield: 248.0 mg (81%); yellow syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (s, 1 H), 7.38–7.18 (m, 8 H), 5.87–5.74 (m, 1 H), 5.40 (br s, 1 H), 5.18–5.10 (m, 2 H), 3.03–2.93 (m, 1 H), 2.88–2.79 (m, 1 H), 2.67–2.54 (m, 2 H), 2.34 (s, 3 H), 2.23–2.08 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 144.4, 144.3, 138.4, 133.7, 132.7, 132.3, 128.4, 128.1, 127.5, 126.4, 125.0, 123.6, 123.5, 118.5, 72.0, 42.6, 33.8, 30.0, 21.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{22}N_2NaO$: 329.1624; found: 329.1621.

N′-(1-Allyl-2,3-dihydro-1*H*-inden-1-yl)furan-2-carbohydrazide (4ag)

Yield: 231.5 mg (82%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (s, 1 H), 7.38–7.32 (m, 2 H), 7.28–7.20 (m, 3 H), 7.07 (d, *J* = 3.2 Hz, 1 H), 6.46 (dd, *J* = 3.2, 1.6 Hz, 1 H), 5.85–5.73 (m, 1 H), 5.34–5.07 (m, 3 H), 3.03–2.91 (m, 1 H), 2.88–2.78 (m, 1 H), 2.65–2.53 (m, 2 H), 2.22–2.08 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 146.5, 144.3, 144.2, 144.0, 133.6, 128.1, 126.4, 125.0, 123.5, 118.6, 114.5, 111.9, 72.0, 42.5, 33.9, 29.9.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{18}N_2NaO_2$: 305.1260; found: 305.1257.

N′-(1-Allyl-5-chloro-2,3-dihydro-1*H*-inden-1-yl)-4-fluorobenzohydrazide (4ah)

Yield: 313.5 mg (91%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 7.2, 5.6 Hz, 2 H), 7.38 (br s, 1 H), 7.30–7.15 (m, 3 H), 7.05 (t, *J* = 8.3 Hz, 2 H), 5.82–5.69 (m, 1 H), 5.36 (br s, 1 H), 5.17–5.11 (m, 2 H), 2.99–2.88 (m, 1 H), 2.86–2.75 (m, 1 H), 2.62–2.50 (m, 2 H), 2.22–2.08 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 163.6, 146.3 142.9, 133.9, 133.2, 129.1, 129.0, 128.6, 126.7, 125.2 ($J_{C,F}$ = 122.6 Hz), 119.0, 115.8 ($J_{C,F}$ = 62.7 Hz), 71.6, 42.6, 33.9, 29.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{18}ClFN_2NaO$: 367.0984; found: 367.0986.

N′-(2-(3-Bromophenyl)pent-4-en-2-yl)-4-methylbenzohydrazide (4ai)

Yield: 269.0 mg (72%); white solid; mp 82–83 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.55–7.37 (m, 4 H), 7.28–7.14 (m, 4 H), 5.70–5.57 (m, 1 H), 5.41 (s, 1 H), 5.13–5.04 (m, 2 H), 2.60–2.54 (m, 1 H), 2.49–2.44 (m, 1 H), 2.36 (s, 3 H), 1.51 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 147.1, 142.2, 133.0, 130.1, 129.9, 129.8, 129.7, 129.2, 126.7, 125.2, 122.7, 118.9, 62.3, 46.1, 22.4, 21.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{22}BrN_2O$: 373.0910; found: 373.0908.

N′-(2-(3-Bromophenyl)pent-4-en-2-yl)-4-fluorobenzohydrazide (4aj)

Yield: 279.5 mg (74%); white solid; mp 80–81 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (s, 1 H), 7.66–7.56 (m, 2 H), 7.50–7.32 (m, 3 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 7.03 (t, *J* = 8.0 Hz, 2 H), 5.69–5.56 (m, 1 H), 5.41 (br s, 1 H), 5.08 (d, *J* = 13.6 Hz, 2 H), 2.58–2.53 (m, 1 H), 2.49–2.44 (m, 1 H), 1.50 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 163.5, 147.0, 132.9, 130.2, 129.9, 129.8, 129.2 ($J_{C,F}$ = 25.7 Hz), 128.7, 125.2, 122.8, 119.0, 115.7 ($J_{C,F}$ = 62.7 Hz), 62.3, 46.0, 22.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}BrFN_2O$: 377.0659; found: 377.0672.

N′-(2-(3-Bromophenyl)pent-4-en-2-yl)furan-2-carbohydrazide (4ak)

Yield: 259.3 mg (74%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (s, 1 H), 7.50–7.32 (m, 4 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.09 (d, *J* = 3.2 Hz, 1 H), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1 H), 5.69–5.57 (m, 1 H), 5.26 (s, 1 H), 5.13–5.05 (m, 2 H), 2.60–2.51 (m, 1 H), 2.50–2.42 (m, 1 H), 1.52 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.5, 146.9, 146.4, 144.1, 132.8, 130.2, 130.0, 129.7, 125.2, 122.8, 119.0, 114.7, 112.0, 62.4, 46.0, 22.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}BrN_2O_2$: 349.0546; found: 349.0550.

4-Methyl-*N*′-(4-methylnon-1-en-4-yl)benzohydrazide (4am)

Yield: 267.6 mg (93%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 2 H), 7.37 (s, 1 H), 7.23 (d, *J* = 7.8 Hz, 2 H), 5.98–5.89 (m, 1 H), 5.18–4.85 (m, 3 H), 2.39 (s, 3 H), 2.27–2.16 (m, 2 H), 1.50–1.20 (m, 8 H), 1.08 (s, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 142.1, 134.8, 130.1, 129.3, 126.7, 117.5, 59.6, 42.6, 37.8, 32.5, 23.3, 22.8, 22.6, 21.4, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{29}N_2O$: 289.2274; found: 289.2279.

4-Chloro-*N*′-(4-methylnon-1-en-4-yl)benzohydrazide (4an)

Yield: 267.8 mg (87%); white solid; mp 68–69 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 8.4 Hz, 2 H), 7.50 (br s, 1 H), 7.39 (d, *J* = 8.4 Hz, 2 H), 5.93–5.86 (m, 1 H), 5.15–4.85 (m, 3 H), 2.27–2.15 (m, 2 H), 1.45–1.18 (m, 8 H), 1.07 (s, 3 H), 0.89 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 134.8, 133.0, 131.6, 128.6, 126.7, 117.4, 58.9, 42.6, 37.8, 32.5, 24.2, 22.8, 22.6, 14.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{26}ClN_2O$: 309.1728; found: 309.1733.

N′-(4-Methylnon-1-en-4-yl)furan-2-carbohydrazide (4ao)

Yield: 221.0 mg (84%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (s, 1 H), 7.45 (d, *J* = 0.8 Hz, 1 H), 7.12 (d, *J* = 3.2 Hz, 1 H), 6.51 (dd, *J* = 3.2, 1.6 Hz, 1 H), 5.99–5.85 (m, 1 H), 5.17–5.08 (m, 2 H), 4.87 (br s, 1 H), 2.27–2.15 (m, 2 H), 1.47–1.23 (m, 8 H), 1.08 (s, 3 H), 0.89 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8, 134.8, 133.0, 131.6, 128.6, 126.7, 117.4, 59.6, 42.4, 37.7, 32.5, 23.4, 22.8, 22.5, 19.0.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{25}N_2O_2$: 265.1911; found: 265.1917.

2-(*p*-Tolyl)pent-4-en-2-amine (5)

Yield: 50.0 mg (85%); colorless syrup.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 8.4 Hz, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 5.62–5.52 (m, 1 H), 5.09–5.03 (m, 2 H), 2.56 (dd, *J* = 13.6, 6.8 Hz, 1 H), 2.41 (dd, *J* = 13.6, 8.0 Hz, 1 H), 2.33 (s, 3 H), 1.75 (s, 2 H), 1.46 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.8, 135.9, 134.6, 129.1, 125.3, 118.7, 54.7, 49.8, 31.1, 21.1.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{18}N$: 176.1434; found: 176.1439.

Acknowledgment

We are thankful for financial support from the National Natural Science Foundation of China (Grant No. 21462037), Key Laboratory Polymer Materials of Gansu Province (Northwest Normal University), Bioactive Products Engineering Research Center for Gansu Distinctive Plants, and State Key Laboratory of Applied Organic Chemistry, Lanzhou University.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560803.

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