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Synthesis of *N*-protected allylic amines from allyl ethers

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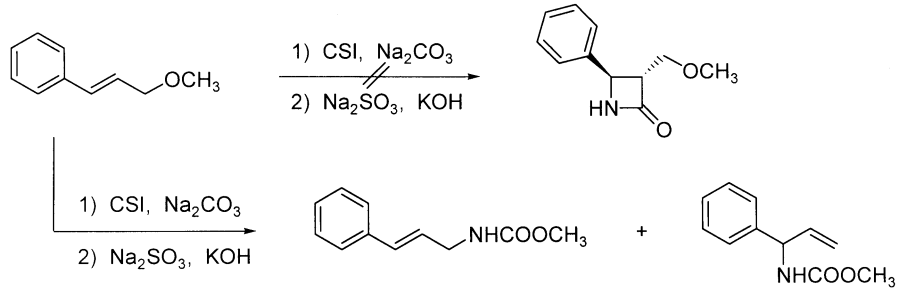
Abstract—A synthetic method for *N*-protected allylic amines from allyl ethers using chlorosulfonyl isocyanate (CSI) is presented. The reaction of 4-phenylbut-2-enyl methyl ether (**1i**) with CSI afforded methyl *N*-(1-benzylallyl)carbamate (**2i**) and methyl *N*-(4-phenylbut-2-enyl)carbamate (**3i**) in a 1:1.1 ratio. On the other hand, 1-benzylallyl methyl ether (**1k**) afforded the same products in a 4.6:1 ratio. The reactions of 1,4-diphenylbut-2-enyl methyl ether (**1p**) and (1-benzylcinnamyl) methyl ether (**1q**) with CSI gave only one product, methyl *N*-(1-benzylcinnamyl)carbamate (**2p**), due to the steric hindrance of the phenyl ring and the formation of a stable conjugated product. We also examined the reactions of diene ethers (**4**) with CSI.

1. Introduction

The synthesis of allylic amines has been an area of intense research in synthetic and industrial fields, because of their important roles in organic synthesis as fundamental building blocks and their occurrence in a number of natural products. General methods for the synthesis of these compounds can be divided into two large categories; nucleophilic allylic substitution and direct allylic amination.[1] Of these two methods, the former has been used widely and efficiently so far, including metal-catalyzed nucleophilic substitutions. Examples include the Mitsunobu reaction of allyl alcohols,[2] the thermal [3,3]-sigmatropic rearrangement of allylic trichloroacetimidates,[3] the Gabriel amination of allyl halides,[4] and palladium-,[5] copper-,[6] iron-,[7] rhodium-[8] catalyzed allylic aminations. The direct allylic amination methods involve the nitrene addition[9] and the ene reaction[10] of diimido and aza compounds. Besides the reactions mentioned above, indirect approaches have been developed, such as the rearrangement of aziridines[11] and the reduction of α,β-unsaturated imines and oximes.[12]

According to their structure, allylic amines are classified into internal and terminal types. The internal allylic amines are of practical value, because they can be transformed into a range of products, such as α- and β-amino acids, by functionalization, reduction, or oxidation of the double bond.[13] Considerable attention has been focused on the development of methods for the preparation of internal allylic amines,[14] which allow the facile incorporation of functional groups and structural variability.

Recently we reported a novel synthetic method for *N*-allylcarbamates from cinnamyl alkyl ethers, using chlorosulfonyl isocyanate (CSI).[15] To date, CSI has been used in the [2+2] cycloaddition reactions of various substituted alkenes, especially enol ethers, to synthesize the β-lactam moiety of carbapenem antibiotics and β-amino acids.[16] Recently, chiral enol ethers have been used as the precursors of chiral β-lactam compounds and chiral β-amino acids.[17] As part of a program aimed at producing various amino acids to be used as versatile building blocks, benzyl cinnamyl ether was reacted with CSI to obtain a β-lactam with a



Scheme 1.

Keywords: chlorosulfonyl isocyanate; allylic amine; *N*-allylcarbamate; allyl ether.
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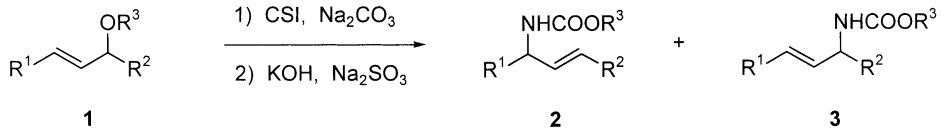


1 2 3

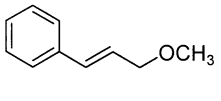
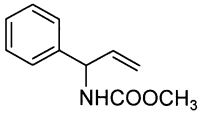
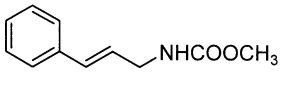
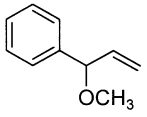
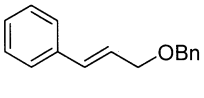
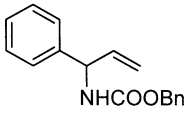
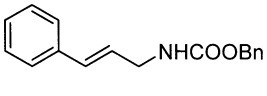
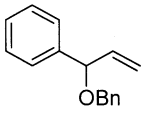
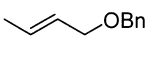
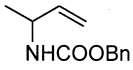
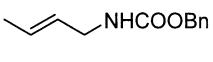
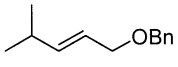
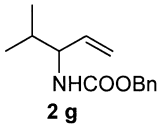
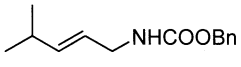
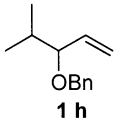
Scheme 2.

benzyloxy methyl moiety, which can be readily converted to the acid moiety.

However, instead of obtaining the expected β-lactam products arising from the formal [2+2] annulation, the corresponding *N*-allylcarbamates were obtained as the sole products (Scheme 1). Early examples of *N*-allylcarbamate formation using CSI were reported by several groups, in which the reactions of unsaturated oxiranes or acetal moieties in sugars with CSI were studied.[18] Similar results of the conversion of tertiary or allyl alcohols to the corresponding amines using CSI were also reported.[19]

In connection with these studies, we now report the results of the regioselective *N*-protected allylic amination of various allyl ethers. Especially, we tried to increase the

Table 1. Conversions of allyl ethers to the corresponding *N*-protected allylic amines with CSI

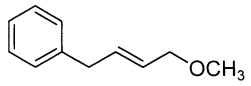
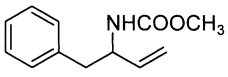
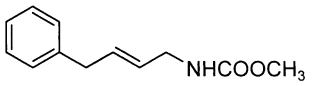
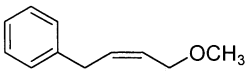
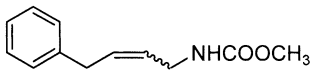
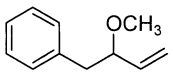
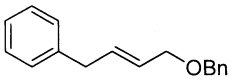
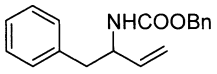
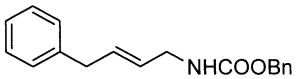
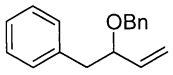
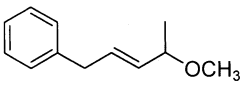
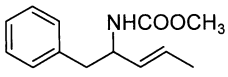
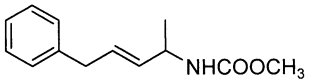
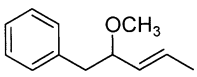
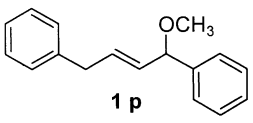
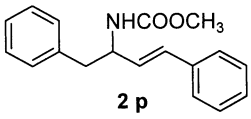
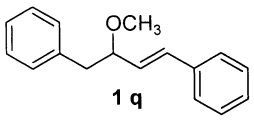
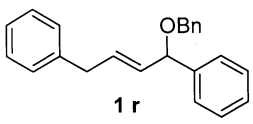
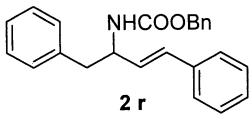
	Allyl ethers	Allylic amines	Yield (%)[a] ratio
1	 **1 a**	 **2 a** +  **3 a**	88 1 : 2.7
2	 **1 b**	**2 a** + **3 a**	87 1 : 2.6
3	 **1 c**	 **2 c** +  **3 c**	90 1 : 8.4
4	 **1 d**	**2 c** + **3 c**	89 1 : 7.4
5	 **1 e**	 **2 e** +  **3 e**	72 1 : 1[b]
6	 **1 f**	**2 e** + **3 e**	77 3.2 : 1[b]
7	 **1 g**	 **2 g** +  **3 g**	60 1 : 2.2
8	 **1 h**	**2 g** + **3 g**	81 1 : 1

All reactions were carried out at 20°C.

[a] Isolated yield of pure material.

[b] Isomer ratio determined from the ^{1}H NMR spectrum of the mixture after column chromatography.

Table 2. Conversions of allyl ethers to the corresponding *N*-protected allylic amines with CSI

	Allyl ethers	Allylic amines			Yield (%)[a] ratio
9	 **1 i**	 **2 i**	+	 **3 i**	70 1 : 1.1
10	 **1 j**	**2 i**	+	 **3 j**	56 1 : 1.4 cis:trans=11.6:1[b]
11	 **1 k**	**2 i**	+	**3 i**	72 4.6 : 1
12	 **1 l**	 **2 l**	+	 **3 l**	61 1 : 2.2
13	 **1 m**	**2 l**	+	**3 l**	55 6.3 : 1
14	 **1 n**	 **2 n**	+	 **3 n**	78 1 : 3.1
15	 **1 o**	**2 n**	+	**3 n**	88 3.2 : 1
16	 **1 p**	 **2 p**			65
17	 **1 q**	**2 p**			72
18	 **1 r**	 **2 r**			70

All reactions were carried out at 20°C, except for entries 12–16 (−78°C).
[a] Isolated yield of pure material.
[b] Isomer ratio determined from the ^{1}H NMR spectrum of the mixture after column chromatography.

formation of internal allylic amines in the reaction of various allyl ethers with CSI. We also report the results of the CSI reaction with diene ethers.

2. Results and discussion

Our initial studies examined the reaction of regioisomeric allyl ethers (**1**) with CSI to afford an internal allylic amine (**2**) and a terminal one (**3**) (Scheme 2).[20]

Our previous report (entries 1 and 2) showed that the CSI reaction of cinnamyl methyl ether (**1a**)[21] produced the terminal allylic amine as major product (1:2.7 ratio), and 1-phenylallyl methyl ether (**1b**)[22] yielded a similar result to **1a** (1:2.6 ratio). In the cases of cinnamyl benzyl ether (**1c**)[23] and 1-phenylallyl benzyl ether (**1d**), the results were similar to that obtained in the methyl case, except for the decrease of the internal allylic amine due to the steric hindrance of the benzyl group (entries 3 and 4). However, entries 5–8 reveal that the substitution mainly occurred where the alkoxy moiety was attached, to afford the corresponding allylic amines. The results are summarized in Table 1.

In the cases of entries 1–4, the identical, stable allylic cation may be formed from **1a**–**1d** to afford the similar ratio of

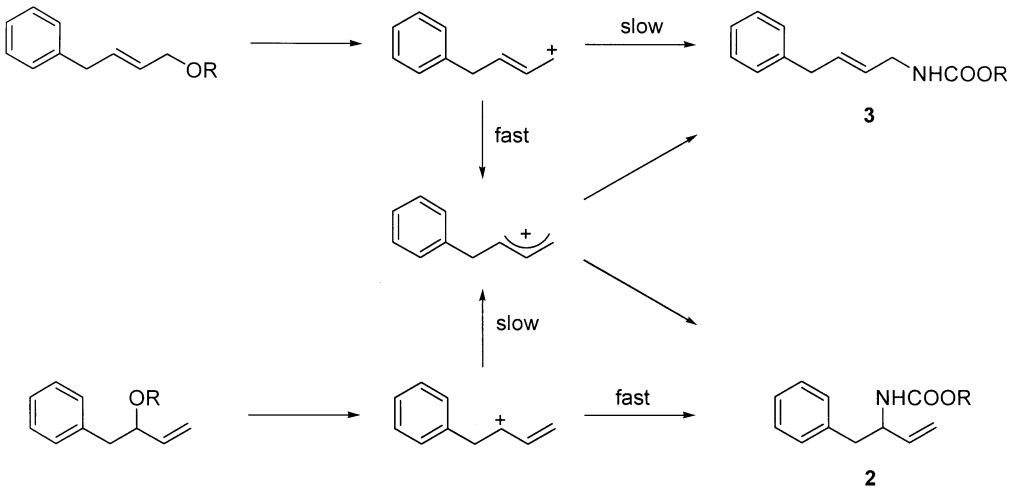


Figure 1.

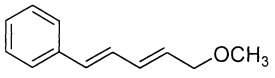
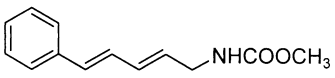
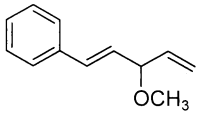
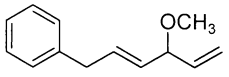
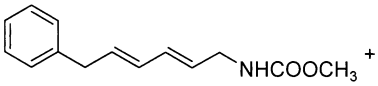
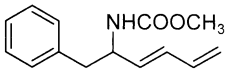
allylic amines such as entries 1 and 2 and entries 3 and 4, in which the ratio was controlled by the steric effect of the phenyl ring to give the terminal one as the main product. However, in the cases of entries 5 and 6 and entries 7 and 8, each isomer of the allyl ethers gave a different ratio of allylic amines. These results were rather intriguing, since it implied that these reactions were not proceeding through the same allylic carbocation intermediate.

Further studies examined the reaction of 4-phenylbut-2-enyl methyl ether (**1i**) and its derivatives with CSI. The results are summarized in Table 2.

Treatment of 4-phenylbut-2-enyl methyl ether (**1i**) with CSI furnished methyl *N*-(1-benzylallyl)carbamate (**2i**) and methyl *N*-(4-phenylbut-2-enyl)carbamate (**3i**) as a 1:1.1 mixture of regioisomers, in which the formation of the internal isomer was slightly increased as compared to the case of **1a**, due to the reduced steric hindrance (entry 9). Also, the *cis*-primary allyl ether (**1j**) afforded a 1:1.4 mixture of regioisomers and a 11.6:1 mixture of geometric isomers in favor of the *cis*-terminal allylic amine (**3j**) (entry 10). However, the isomeric secondary allyl ether (**1k**),[22] under the same reaction conditions, gave an inversed product ratio (4.6:1) in favor of the internal allylic amine (**2i**), similar to the case of entry 6 (entry 11). With the benzyl ethers, the results were quite similar to that obtained in the methyl case, except for the increase in the ratio (entries 12 and 13).

One plausible mechanism for these regioselective allylic aminations is shown in Fig. 1. As soon as the unstable primary allylic carbocation is formed from the terminal ether **1i**, it is rapidly converted to the stable allylic carbocation hybrid, and then slightly more **3i** than **2i** is formed, according to the steric hindrance. In the case of the internal ether **1k**, on the other hand, the stable secondary allylic carbocation is formed and is rapidly attacked by the nucleophile, instead of being converted to the hybrid to form the more substituted allylic amine. Namely, the nucleophilic

Table 3. Conversions of diene ethers to the corresponding *N*-protected allylic amines with CSI

	Diene ethers	Allylic amines	Yield (%)[a] ratio
19	 **4 a**	 **5 a**	64
20	 **4 b**	**5 a**	48
21	 **4 c**	 **5 c** +  **6 c**	84 1 : 2.4

All reactions were carried out at −78°C.
[a] Isolated yield of pure material.

attack rapidly occurs where the alkoxy moiety was attached, before the formation of the allylic carbocation hybrid.

In order to improve the isomer ratio of the internal allylic amine, we introduced the phenyl ring at the allylic position in the same direction as that of the alkoxy moiety. The reactions of 1,4-diphenylbut-2-enyl methyl ether (**1p**)[24] and 1-benzylcinnamyl methyl ether (**1q**) with CSI gave only one product, methyl *N*-(1-benzylcinnamyl)carbamate (**2p**), due to the steric hindrance of the phenyl ring and the formation of a stable conjugated product (entries 16 and 17). In the benzyl ether case (**1r**), the results were also quite similar to that obtained in the methyl ether case (entry 18). No product derived from an attack at the benzylic position was observed.

We also examined the reaction of diene ethers (**4**) with CSI. The results are summarized in Table 3. The treatment of the terminal diene ether **4a** and the internal diene ether **4b** with CSI afforded only the terminal allylic amine **5a**, due to the steric hindrance of the phenyl ring and the stability of the product (conjugation of diene), as in entries 16 and 18 (entries 19 and 20). However, the reaction of **4c** with CSI afforded **5c** and **6c** as a 1:2.4 mixture of regioisomers (entry 21). In the cases of entries 20 and 21, no product derived from an attack on the position where the alkoxy moiety was attached was observed due to avoidance of the destruction of the conjugated diene.

From the results in Tables 1–3, it appears that the regioselectivity of these reactions by the attack of the nucleophile (N^- moiety of CSI) profoundly depends upon the substitution patterns and the positions of the alkoxy moiety.

3. Conclusion

We have demonstrated that the reactions of various allyl ethers with CSI afforded regioselective *N*-protective allylic amines via the stable allylic carbocation and the allylic rearrangement in one pot. We also found that steric and electronic factors affect the regioselectivity, in terms of the ratios of internal and terminal allylic amines. We are actively pursuing further applications of these reactions, including a more refined definition of its reaction mechanism with an eye toward stereoselectivity.

4. Experimental

4.1. General

Commercially available reagents were used without additional purification, unless otherwise stated. All anhydrous solvents were distilled over CaH_2 or P_2O_5 or Na/benzophenone prior to reaction. All reactions were performed under an inert atmosphere of nitrogen or argon. Melting points were measured on a Gallenkamp melting point apparatus and were not corrected. Nuclear magnetic resonance spectra (^1H and ^{13}C NMR) were recorded on a Varian Unity Inova 500 MHz spectrometer for $CDCl_3$ solutions and chemical shifts are reported as parts per million (ppm) relative to, respectively, residual $CHCl_3$ δ_H (7.26 ppm) and $CDCl_3$ δ_C (77.0 ppm) as internal standards. Resonance patterns are reported with the notations s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). In addition, the notation br is used to indicate a broad signal. Coupling constants (*J*) are reported in Hertz (Hz). IR spectra were recorded on a Nicolet 205 Infrared spectrophotometer and are reported as cm^{-1}. Thin layer chromatography was carried out using plates coated with Kieselgel $60F_{254}$ (Merck). For flash column chromatography, E. Merck Kieselgel 60 (230–400 mesh) was used. Elemental analyses were performed with an the EA 1110 analyzer, and high-resolution mass spectra (HRMS) were recorded on a JEOL, JMS-AX505WA spectrometer using the chemical ionization (CI) method.

4.2. General procedure for preparation of methyl ether

To a solution of alcohol (5 mmol) in THF (20 ml) was added NaH (7.5 mmol, 60% in mineral oil) and methyl iodide (7.5 mmol). The reaction mixture was stirred at 45–50°C for 1 h under N_2, quenched with H_2O (20 ml), then extracted with EtOAc (20 ml). The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc) to afford methyl ether.

4.2.1. (*E*)-1-Methoxy-4-phenylbut-2-ene (1i). (*E*)-4-Phenylbut-2-en-1-ol[25] was converted to (*E*)-1-methoxy-4-phenylbut-2-ene **1i** as a colorless oil in 82% yield. ^1H NMR (500 MHz, $CDCl_3$):δ 3.34 (s, 3H), 3.41 (dd, 2H, J=6.5, 1 Hz), 3.92 (dd, 2H, J=7, 1 Hz), 5.64 (ddt, 1H, J=14, 7, 1 Hz), 5.88 (ddt, 1H, J=14, 6.5, 1 Hz), 7.20–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$):δ 39.45, 58.56, 73.70, 126.81, 128.32, 129.15, 129.30, 133.80, 140.69; IR (neat):2926, 2897, 1603, 1495, 1463, 1382, 1196, 1119, 1091 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{14}O$+H $(M+H)^+$ 163.1123. Found: 163.1128.

4.2.2. (*Z*)-1-Methoxy-4-phenylbut-2-ene (1j). (*Z*)-4-Phenylbut-2-en-1-ol[25] was converted to (*Z*)-1-methoxy-4-phenylbut-2-ene **1j** as a colorless oil in 78% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 3.38 (s, 3H), 3.45 (d, 2H, J=7.5 Hz), 4.09 (d, 2H, J=6.5 Hz), 5.70 (dt, 1H, J=9, 6.5 Hz), 5.78 (dt, 1H, J=9, 7.5 Hz), 7.19–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 34.51, 58.78, 68.79, 126.79, 127.68, 129.05, 129.21, 132.47, 140.92; IR (neat): 2916, 1627, 1455, 1351, 1101 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{14}O$+H $(M+H)^+$ 163.1123. Found: 163.1126.

4.2.3. 2-Methoxy-5-phenylpent-3-ene (1n). 5-Phenylpent-3-en-2-ol[26] was converted to 2-methoxy-5-phenylpent-3-ene **1n** as a colorless oil in 87% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (d, 3H, J=6 Hz), 3.27 (s, 3H), 3.39 (d, 2H, J=6.5 Hz), 3.73 (dq, 1H, J=6.5, 6 Hz), 5.44 (dd, 1H, J=15.5, 6.5 Hz), 5.79 (dt, 1H, J=15.5, 6.5 Hz), 7.19–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.08, 39.38, 56.53, 78.54, 126.80, 129.15, 129.23, 132.24, 133.90, 140.89; IR (neat): 2929, 1654, 1605, 1452, 1354, 1188, 1097 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{16}O$–H $(M-H)^+$ 175.1123. Found: 175.1126.

4.2.4. 1-Phenyl-2-methoxypent-3-ene (1o). 1-Phenylpent-3-en-2-ol[27] was converted to 1-phenyl-2-methoxypent-3-

ene **1o** as a colorless oil in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.66 (dd, 3H, J=6.5, 1.5 Hz), 2.72 (dd, 1H, J=14, 6.5 Hz), 2.88 (dd, 1H, J=14, 7 Hz), 3.21 (s, 3H), 3.68 (ddd, 1H, J=7, 6.5, 1 Hz), 5.31 (ddd, 1H, J=15, 6.5, 1.5 Hz), 5.53 (ddq, 1H, J=15, 6.5, 1 Hz), 7.15–7.26 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.37, 43.06, 56.73, 84.05, 126.72, 128.77, 129.77, 130.24, 131.78, 139.34, 140.89; IR (neat): 2929, 1721, 1603, 1455, 1351, 1098 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{16}O$–H $(M-H)^+$ 175.1123. Found: 175.1126.

4.2.5. 1,4-Diphenyl-2-methoxybut-3-ene (1q). 1,4-Diphenylbut-3-en-2-ol[28] was converted to 1,4-diphenyl-2-methoxybut-3-ene **1q** as a colorless oil in 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.89 (dd, 1H, J=14, 6 Hz), 3.04 (dd, 1H, J=14, 7 Hz), 3.30 (s, 3H), 3.97 (ddd, 1H, J=7.5, 7, 6 Hz), 6.12 (dd, 1H, J=16, 7.5 Hz), 6.49 (d, 1H, J=16 Hz), 7.21–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.22, 57.23, 84.08, 126.93, 127.21, 128.43, 128.92, 129.30, 130.29, 133.18, 137.27, 138.93; IR (neat): 3037, 2928, 1700, 1609, 1460, 1337, 1093 cm^{-1}; HRMS (CI) Calcd for $C_{17}H_{18}O$–H $(M-H)^+$ 237.1280. Found: 237.1278.

4.2.6. 1-Methoxy-5-phenylpenta-2,4-diene (4a). *5-Phenylpenta-2,4-dien-1-ol*. To a solution of ethyl 5-phenylpenta-2,4-dienoate[29] (7 mmol) in benzene (20 ml) was added DIBAL-H (14 mmol, 1.5 M in toluene) at 0°C under N_2. The reaction mixture was stirred at room temperature for 1 h, and 1N HCl (50 ml) was added at 0°C. The reaction mixture was stirred at 0°C for 1 h, then extracted with ether (20 ml). The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc=3:1) to afford 5-phenylpenta-2,4-dien-1-ol as a white solid in 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.58–1.69 (br, 1H), 4.25 (d, 2H, J=6 Hz), 5.96 (dt, 1H, J=15, 6 Hz), 6.42 (dd, 1H, J=15, 11 Hz), 6.57 (d, 1H, J=15.5 Hz), 6.81 (dd, 1H, J=15.5, 11 Hz), 7.22–7.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 64.13, 127.10, 128.34, 128.85, 129.33, 132.33, 133.20, 133.49, 137.82; IR (CH_2Cl_2): 3334, 3023, 2926, 1671, 1619, 1449, 1395, 1267, 1125, 1083 cm^{-1}; mp: 67–69°C; Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.44; H, 7.49.

1-Methoxy-5-phenylpenta-2,4-diene (**4a**). 5-Phenylpenta-2,4-dien-1-ol was converted to 1-methoxy-5-phenylpenta-2,4-diene **4a** as a colorless oil in 94.3% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.40 (s, 3H), 4.05 (dd, 2H, J=6, 1 Hz), 5.91 (dt, 1H, J=15.5, 6 Hz), 6.46 (ddd, 1H, J=15.5, 11, 1 Hz), 6.59 (d, 1H, J=16 Hz), 6.83 (dd, 1H, J=16, 11 Hz), 7.25–7.45 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 58.69, 73.53, 127.15, 128.34, 128.98, 129.36, 130.75, 133.45, 133.64, 137.90; IR (neat): 3012, 2913, 1701, 1603, 1460, 1331, 1109 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{14}O$+H $(M+H)^+$ 175.1123. Found: 175.1133.

4.2.7. 1-Phenyl-3-methoxypenta-1,4-diene (4b). 1-Phenylpenta-1,4-dien-3-ol[30] was converted to 1-phenyl-3-methoxypenta-1,4-diene **4b** as a pale yellow oil in 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (s, 3H), 4.27 (dd, 1H, J=7, 6.5 Hz), 5.28 (dd, 1H, J=10.5, 1.5 Hz), 5.33 (dd, 1H, J=17.5, 1.5 Hz), 5.89 (ddd, 1H, J=17.5, 10.5, 6.5 Hz), 6.17 (dd, 1H, J=15.5, 7 Hz), 6.62 (d, 1H, J=15.5 Hz), 7.25–7.44 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 27.05, 56.75, 83.88, 117.60, 127.27, 128.49, 129.29, 129.47, 132.74, 137.32, 138.30; IR (neat): 2939, 2845, 1709, 1617, 1448, 1307, 1179, 1085 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{14}O$+H $(M+H)^+$ 175.1123. Found: 175.1120.

4.2.8. 3-Methoxy-6-phenylhexa-1,4-diene (4c). *6-Phenylhexa-1,4-dien-3-ol*. To a solution of 4-phenylbut-2-enal[31] (7 mmol) in THF (14 ml) was added vinylmagnesium bromide (8.4 mmol, 1.0 M in THF) at −78°C under N_2. The reaction mixture was stirred at 0–5°C for 1 h, quenched with saturated NH_4Cl (20 ml) aqueous solution, then extracted with ether (20 ml). The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc=6:1) to afford 6-phenylhexa-1,4-dien-3-ol as a pale yellow oil in 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.40 (d, 2H, J=6.5 Hz), 4.63 (dd, 1H, J=6.5, 6.5 Hz), 5.15 (dd, 1H, J=10.5, 1.5 Hz), 5.28 (dd, 1H, J=17, 1.5 Hz), 5.60 (dd, 1H, J=15.5, 6.5 Hz), 5.88 (dt, 1H, J=15.5, 6.5 Hz), 5.93 (ddd, 1H, J=17, 10.5, 6.5 Hz), 7.19–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.35, 74.30, 115.71, 126.88, 129.18, 129.30, 131.89, 133.07, 140.30, 140.59; IR (neat): 3354, 3032, 2898, 1623, 1424, 1272, 1097 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{14}O$–H $(M-H)^+$ 173.0967. Found: 173.0963.

3-Methoxy-6-phenylhexa-1,4-diene (**4c**). 6-Phenylhexa-1,4-dien-3-ol was converted to 3-methoxy-6-phenylhexa-1,4-diene **4c** as a pale yellow oil in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.33 (s, 3H), 3.43 (d, 2H, J=6.5 Hz), 4.09 (dd, 1H, J=7, 7 Hz), 5.21 (dd, 1H, J=9.5, 1.5 Hz), 5.26 (dd, 1H, J=17, 1.5 Hz), 5.52 (dd, 1H, J=15, 7 Hz), 5.83 (ddd, 1H, J=17, 9.5, 7 Hz), 5.87 (dt, 1H, J=15, 6.5 Hz), 7.20–7.33 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.49, 56.56, 83.66, 117.25, 126.84, 129.17, 129.31, 131.39, 133.13, 138.57, 140.68; IR (neat): 2929, 1703, 1607, 1441, 1304, 1091 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{16}O$+H $(M+H)^+$ 189.1279. Found: 189.1279.

4.3. General procedure for preparation of benzyl ether

To a solution of alcohol (5 mmol) in THF (28 ml) and DMF (7 ml) was added NaH (7.5 mmol, 60% in mineral oil) and benzyl bromide (7.5 mmol). The reaction mixture was stirred at room temperature for 15 h under N_2, quenched with H_2O (20 ml), then extracted with EtOAc (20 ml). The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc) to afford benzyl ether.

4.3.1. 1-Benzyloxy-1-phenylprop-2-ene (1d). 1-Phenylprop-2en-1-ol[32] was converted to 1-benzyloxy-1-phenylprop-2-ene **1d** as a colorless oil in 71% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.54 (s, 2H), 4.85 (s, 1H, J=6.5 Hz), 5.25 (dd, 1H, J=10.5, 1.5 Hz), 5.32 (dd, 1H, J=17, 1.5 Hz), 5.99 (ddd, 1H, J=17, 10.5, 6.5 Hz), 7.29–7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 70.78, 82.71, 117.15, 127.70, 128.22, 128.40, 129.08, 129.14, 129.21, 139.19, 139.61, 141.69; IR (neat): 2925, 2836, 1631,

1451, 1356, 1196, 1090 cm^{-1}; HRMS (CI) Calcd for $C_{16}H_{16}O$–H $(M-H)^+$ 223.1123. Found: 223.1126.

4.3.2. (*E*)-1-Benzyloxybut-2-ene (1e). (*E*)-Crotyl alcohol was converted to (*E*)-1-benzyloxybut-2-ene **1e** as a colorless oil in 59% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.77 (dd, 3H, *J*=6.5, 1.5 Hz), 4.01 (dd, 2H, *J*=6, 1.5 Hz), 4.55 (s, 2H), 5.69 (dtq, 1H, *J*=15.5, 6, 1.5 Hz), 5.78 (dtq, 1H, *J*=15.5, 6.5, 1.5 Hz), 7.31–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.58, 71.66, 72.66, 128.28, 128.32, 128.52, 129.10, 130.39, 139.22; IR (neat): 2926, 2858, 1602, 1452, 1363, 1291, 1233, 1091 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{14}O$–H $(M-H)^+$ 161.0967. Found: 161.0963.

4.3.3. 2-Benzyloxybut-3-ene (1f). But-3-en-2-ol was converted to 2-benzyloxybut-3-ene **1f** as a colorless oil in 50% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.32 (d, 3H, *J*=6.5 Hz), 3.94 (dq, 1H, *J*=6.5, 6.5 Hz), 4.42 (d, 1H, *J*=12 Hz), 4.60 (d, 1H, *J*=12 Hz), 5.24 (dd, 1H, *J*=10.5, 1 Hz), 5.26 (dd, 1H, *J*=17, 1 Hz), 5.83 (ddd, 1H, *J*=17, 10.5, 6.5 Hz), 7.28–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.13, 70.67, 76.95, 116.85, 128.23, 128.51, 129.13, 139.52, 140.97; IR (neat): 3044, 2919, 1711, 1619, 1453, 1362, 1256, 1086 cm^{-1}; HRMS (CI) Calcd for $C_{11}H_{14}O$–H $(M-H)^+$ 161.0967. Found: 161.0969.

4.3.4. 1-Benzyloxy-4-methylpent-2-ene (1g). 4-Methylpent-2-en-1-ol[33] was converted to 1-benzyloxy-4-methylpent-2-ene **1g** as a colorless oil in 66% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 1.01 (d, 3H, *J*=7 Hz), 1.02 (d, 3H, *J*=7 Hz), 2.33 (dq, 1H, *J*=7, 6.5 Hz), 3.99 (d, 2H, *J*=6.5 Hz), 4.52 (s, 2H), 5.57 (dt, 1H, *J*=16.5, 6.5 Hz), 5.70 (dd, 1H, *J*=16.5, 6.5 Hz), 7.29–7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.92, 31.51, 71.79, 72.62, 123.92, 128.24, 128.55, 129.07, 139.18, 142.51; IR (neat): 2945, 2867, 1621, 1456, 1363, 1091 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{18}O$–H $(M-H)^+$ 189.1280. Found: 189.1282.

4.3.5. 1-Benzyloxy-4-phenylbut-2-ene (1l). 4-Phenylbut-2-en-1-ol[25] was converted to 1-benzyloxy-4-phenylbut-2-ene **1l** as a colorless oil in 71% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 3.45 (d, 2H, *J*=7 Hz), 4.06 (d, 2H, *J*=6 Hz), 4.56 (s, 2H), 5.73 (dt, 1H, *J*=16.5, 6 Hz), 5.95 (dt, 1H, *J*=16.5, 7 Hz), 7.23–7.44 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.59, 71.43, 72.81, 126.96, 127.52, 128.48, 128.67, 129.22, 129.34, 129.49, 134.01, 139.05, 140.79; IR (neat): 3039, 2875, 1683, 1609, 1454, 1354, 1086 cm^{-1}; HRMS (CI) Calcd for $C_{17}H_{18}O$+H $(M+H)^+$ 239.1436. Found: 239.1440.

4.3.6. 1-Phenyl-2-benzyloxybut-3-ene (1m). 1-Phenylbut-3-en-2-ol[34] was converted to 1-phenyl-2-benzyloxybut-3-ene **1m** as a colorless oil in 95% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 2.83 (dd, 1H, *J*=14, 6 Hz), 2.99 (dd, 1H, *J*=14, 7 Hz), 3.99 (ddd, 1H, *J*=7, 6.5, 6 Hz), 4.35 (d, 1H, *J*=12 Hz), 4.50 (d, 1H, *J*=12 Hz), 5.21 (dd, 1H, *J*=10, 1 Hz), 5.23 (dd, 1H, *J*=16.5, 1 Hz), 5.80 (ddd, 1H, *J*=16.5, 10, 6.5 Hz), 7.20–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.07, 70.93, 82.15, 118.14, 126.87, 128.05, 128.27, 128.81, 128.97, 130.42, 139.09, 139.30; IR (neat): 2909, 2879, 1606, 1449, 1334, 1212, 1081 cm^{-1}; HRMS (CI) Calcd for $C_{17}H_{18}O$+H $(M+H)^+$ 239.1436. Found: 239.1440.

4.3.7. 1,4-Diphenyl-1-benzyloxybut-2-ene (1r). *1,4-Diphenylbut-2-en-1-ol*. To a solution of 4-phenylbut-2-enal[31] (7 mmol) in ether (14 ml) was added phenylmagnesium bromide (8.4 mmol, 3.0 M in ether) at −78°C under N_2. The reaction mixture was stirred at 0–5°C for 1 h, quenched with saturated NH_4Cl (20 ml) aqueous solution, then extracted with ether (20 ml). The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc=6:1) to afford 1,4-diphenylbut-2-en-1-ol as a white solid in 90% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 2.19–2.25 (br, 1H), 3.44 (d, 2H, *J*=6.5 Hz), 5.21 (d, 1H, *J*=6 Hz), 5.78 (dd, 1H, *J*=15, 6 Hz), 5.85 (dt, 1H, *J*=15, 6.5 Hz), 7.22–7.42 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.36, 75.64, 126.93, 126.99, 128.34, 129.25, 129.27, 129.35, 131.64, 134.41, 140.70, 143.88; IR (CH_2Cl_2): 3355, 3029, 2899, 1602, 1494, 1452, 1195, 1006 cm^{-1}; mp: 40–41°C; Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.67; H, 7.22.

1,4-Diphenyl-1-benzyloxybut-2-ene (**1r**). 1,4-Diphenylbut-2-en-1-ol was converted to 1,4-diphenyl-1-benzyloxybut-2-ene **1r** as a colorless oil in 68% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 3.41 (d, 2H, *J*=6.5 Hz), 4.52 (d, 2H, *J*=5 Hz), 4.84 (d, 1H, *J*=7 Hz), 5.74 (dd, 1H, *J*=16, 7 Hz), 5.85 (dt, 1H, *J*=16, 6.5 Hz), 7.17–7.39 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.43, 70.67, 82.17, 126.81, 127.61, 128.17, 128.25, 128.43, 129.05, 129.15, 129.29, 132.71, 132.96, 139.19, 140.72, 142.17; IR (neat): 3030, 2864, 1695, 1602, 1495, 1452, 1311, 1203, 1067 cm^{-1}; HRMS (CI) Calcd for $C_{23}H_{22}O$–H $(M-H)^+$ 313.1593. Found: 313.1598.

4.4. General procedure for reaction of allyl ether with chlorosulfonyl isocyanate (CSI)

A suspension of Na_2CO_3 (6.75 mmol) in anhydrous CH_2Cl_2 (12 ml) was adjusted to 20°C or −78°C, then CSI (4.5 mmol) and allyl ether (3 mmol) was added under N_2. The reaction mixture was stirred at 20°C or −78°C. quenched with H_2O (10 ml) when the reaction was completed (TLC monitoring), then extracted with EtOAc (10 ml×2). The organic layer was added to an aqueous solution of Na_2SO_3 (25%) and KOH (10%), and the reaction mixture was stirred at room temperature overnight. The organic layer was washed with H_2O and brine, dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (*n*-Hex/EtOAc) to afford *N*-protected allylic amine.

4.4.1. Benzyl *N*-(1-phenylallyl)carbamate (2c). White solid; ^1H NMR (500 MHz, $CDCl_3$): δ 5.12 (s, 2H), 5.15 (dd, 1H, *J*=5.5, 5 Hz), 5.24 (dd, 1H, *J*=9.5, 1.5 Hz), 5.25 (dd, 1H, *J*=18, 1.5 Hz), 5.33–5.40 (br, 1H), 6.01 (ddd, 1H, *J*=18, 9.5, 5.5 Hz), 7.21–7.38 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 57.81, 67.65, 116.54, 126.79, 127.74, 128.42, 128.87, 129.23, 129.46, 137.06, 138.27, 141.32, 156.25; IR (CH_2Cl_2): 3322, 3045, 2934, 1707, 1515, 1242, 1042 cm^{-1}; mp: 46–47°C; HRMS (CI) Calcd for $C_{17}H_{17}NO_2$+H $(M+H)^+$ 268.1337. Found: 268.1343.

4.4.2. Benzyl *N*-(3-phenylprop-2-enyl)carbamate (3c). White solid; ^1H NMR (500 MHz, $CDCl_3$): δ 3.99 (dd, 2H,

J=6, 4.5 Hz), 4.88–4.97 (br, 1H), 5.15 (s, 2H), 6.17 (dt, 1H, J=16, 6 Hz), 6.53 (d, 1H, J=16 Hz), 7.23–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.88, 67.54, 126.52, 127.11, 128.41, 128.85, 129.10, 129.25, 129.29, 132.49, 137.25, 156.98; IR (KBr): 3319, 2832, 1686, 1543, 1451, 1261, 1248, 1138 cm^{-1}; mp: 62–63°C; Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.52; H, 6.46; N, 5.22.

4.4.3. Benzyl *N*-(1-methylallyl)carbamate (2e) and benzyl *N*-(but-2-enyl)carbamate (3e). *Benzyl N-(1-methylallyl)carbamate* (**2e**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24 (d, 3H, J=6.5 Hz), 4.27–4.35 (br, 1H), 4.72–4.79 (br, 1H), 5.10 (dd, 1H, J=10, 1 Hz), 5.11 (s, 2H), 5.17 (dd, 1H, J=17, 1 Hz), 5.84 (ddd, 1H, J=17, 10, 5 Hz), 7.30–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.35, 49.39, 67.36, 114.72, 128.64, 128.81, 129.23, 137.26, 140.40, 159.30.

Benzyl N-(but-2-enyl)carbamate (**3e**). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.68 (d, 3H, J=6.5 Hz), 3.74 (dd, 2H, J=5.5, 5.5 Hz), 4.75–4.85 (br, 1H), 5.11 (s, 2H), 5.48 (dt, 1H, J=16, 5.5 Hz), 5.61 (dq, 1H, J=16, 6.5 Hz), 7.30–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.36, 43.71, 67.36, 127.85, 128.64, 128.74, 128.81, 129.23, 140.48, 156.92; IR (neat): 3410, 3331, 3033, 2971, 2937, 1729, 1769, 1691, 1531, 1454, 1334, 1293, 1241, 1134, 1053 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1178.

4.4.4. Benzyl *N*-(1-isopropylallyl)carbamate (2g). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (d, 3H, J=6.5 Hz), 0.90 (d, 3H, J=6.5 Hz), 1.81 (dq, 1H, J=6.5, 6.5 Hz), 4.04–4.11 (br, 1H), 4.70–4.78 (br, 1H), 5.11 (s, 2H), 5.14 (dd, 1H, J=10, 1.5 Hz), 5.16 (dd, 1H, J=17, 1.5 Hz), 5.75 (ddd, 1H, J=17, 10, 6 Hz), 7.31–7.37 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 18.71, 19.38, 32.88, 59.33, 67.45, 116.21, 128.86, 129.26, 137.26, 137.64, 156.73; IR (CH_2Cl_2): 3327, 3049, 2942, 1707, 1517, 1246, 1081, 1016 cm^{-1}; mp: 48–50°C; Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 72.31; H, 8.22; N, 5.89.

4.4.5. Benzyl *N*-(4-methylpent-2-enyl)carbamate (3g). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 (d, 3H, J=7 Hz), 0.99 (d, 3H, J=7 Hz), 2.27 (dq, 1H, J=7, 6.5 Hz), 3.76 (dd, 2H, J=6, 5.5 Hz), 4.73–4.82 (br, 1H), 5.11 (s, 2H), 5.41 (dt, 1H, J=15.5, 6.5 Hz), 5.59 (dd, 1H, J=15.5, 6.5 Hz), 7.30–7.38 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.93, 31.39, 43.76, 67.37, 123.62, 128.61, 128.84, 129.22, 137.31, 141.11, 156.78; IR (neat): 3334, 2947, 1707, 1524, 1349, 1246, 1126, 1025 cm^{-1}; HRMS (CI) Calcd for $C_{14}H_{19}NO_2$+H $(M+H)^+$ 234.1484. Found: 234.1492.

4.4.6. Methyl *N*-(1-benzylallyl)carbamate (2i). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.86 (d, 2H, J=6.5 Hz), 3.66 (s, 3H), 4.40–4.48 (br, 1H), 4.57–4.65 (br, 1H), 5.11 (dd, 1H, J=10.5, 1.5 Hz), 5.12 (dd, 1H, J=17, 1.5 Hz), 5.81 (ddd, 1H, J=17, 10.5, 5.5 Hz), 7.18–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.06, 52.83, 54.62, 115.72, 127.33, 129.11, 130.21, 137.77, 138.45, 157.01; IR (nujol): 3330, 2954, 2861, 1693, 1539, 1459, 1376, 1255 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1182.

4.4.7. (*E*)-Methyl *N*-(4-phenylbut-2-enyl)carbamate (3i). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.36 (d, 2H, J=6.5 Hz), 3.73 (s, 3H), 3.78 (dd, 2H, J=6, 4.5 Hz), 4.70–4.78 (br, 1H), 5.54 (dt, 1H, J=15, 6 Hz), 5.77 (dt, 1H, J=15, 6.5 Hz), 7.16–7.31 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.30, 43.48, 52.82, 126.87, 128.22, 129.18, 129.24, 132.34, 140.64, 157.58; IR (nujol): 3352, 2954, 2850, 1696, 1515, 1463, 1377, 1260, 1234, 1055 cm^{-1}; mp: 60–61°C; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1182.

4.4.8. (*Z*)-Methyl *N*-(4-phenylbut-2-enyl)carbamate (3j). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.46 (d, 2H, J=7.5 Hz), 3.69 (s, 3H), 3.95 (dd, 2H, J=6.5, 4.5 Hz), 4.82–4.90 (br, 1H), 5.55 (dt, 1H, J=10.5, 6.5 Hz), 5.75 (dt, 1H, J=10.5, 7.5 Hz), 7.18–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 34.24, 38.81, 52.87, 126.85, 127.28, 129.01, 129.26, 132.19, 140.82, 157.72; IR (CH_2Cl_2): 3323, 3035, 2969, 1701, 1634, 1457, 1265, 1031 cm^{-1}; HRMS (CI) Calcd for $C_{12}H_{15}NO_2$+H $(M+H)^+$ 206.1181. Found: 206.1185.

4.4.9. Benzyl *N*-(1-benzylallyl)carbamate (2l). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88 (d, 2H, J=5.5 Hz), 4.50–4.58 (br, 1H), 4.76–4.85 (br, 1H), 5.10 (s, 2H), 5.13 (dd, 1H, J=10.5, 1.5 Hz), 5.15 (dd, 1H, J=16.5, 1.5 Hz), 5.82 (ddd, 1H, J=16.5, 10.5, 5.5 Hz), 7.18–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.03, 54.74, 67.40, 115.79, 127.34, 128.82, 128.94, 129.13, 129.24, 130.25, 137.24, 137.82, 138.43, 156.39; IR (CH_2Cl_2): 3326, 3031, 2927, 1700, 1629, 1504, 1454, 1335, 1246, 1077 cm^{-1}; mp: 67–70°C; HRMS (CI) Calcd for $C_{18}H_{19}NO_2$+H $(M+H)^+$ 282.1494. Found: 282.1491.

4.4.10. Benzyl *N*-(4-phenylbut-2-enyl)carbamate (3l). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.37 (d, 2H, J=7 Hz), 3.81 (dd, 2H, J=6.5, 4.5 Hz), 4.78–4.87 (br, 1H), 5.17 (s, 2H), 5.56 (dt, 1H, J=15, 6.5 Hz), 5.77 (dt, 1H, J=15, 7 Hz), 7.17–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.30, 43.53, 67.45, 126.89, 127.35, 128.09, 128.84, 129.20, 129.26, 129.30, 132.51, 137.24, 140.62, 156.90; IR (CH_2Cl_2): 3332, 3042, 2925, 1706, 1521, 1434, 1251, 1114, 1017 cm^{-1}; mp: 85–88°C; Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98. Found: C, 76.93; H, 6.78; N, 4.80.

4.4.11. Methyl *N*-(1-methyl-4-phenylbut-2-enyl)carbamate (3n). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (d, 3H, J=6.5 Hz), 3.37 (d, 2H, J=6.5 Hz), 3.67 (s, 3H), 4.24–4.33 (br, 1H), 4.61–4.70 (br, 1H), 5.50 (dd, 1H, J=15.5, 5.5 Hz), 5.77 (dt, 1H, J=15.5, 6.5 Hz), 7.17–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.87, 39.26, 48.72, 52.71, 126.82, 129.15, 129.25, 133.70, 140.78, 157.50; IR (neat): 3326, 2963, 1707, 1522, 1419, 1339, 1245, 1075 cm^{-1}; HRMS (CI) Calcd for $C_{13}H_{17}NO_2$+H $(M+H)^+$ 220.1337. Found: 220.1340.

4.4.12. Methyl *N*-(1-benzyl-3-phenylprop-2-enyl)carbamate (2p). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.96 (d, 2H, J=6.5 Hz), 3.68 (s, 3H), 4.61–4.70 (br, 1H), 4.71–4.80 (br, 1H), 6.15 (dd, 1H, J=16, 6 Hz), 6.47 (dd, 1H,

J=16, 1 Hz), 7.21–7.39 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.49, 52.92, 54.39, 127.13, 127.39, 128.34, 129.20, 129.26, 130.26, 130.30, 131.07, 137.32, 137.73, 156.99; IR (CH_2Cl_2): 3318, 3027, 1691, 1638, 1537, 1493, 1448, 1321, 1264, 1061 cm^{-1}; mp: 113–115°C; HRMS (CI) Calcd for $C_{18}H_{19}NO_2$+H $(M+H)^+$ 282.1494. Found: 282.1492.

4.4.13. Benzyl *N*-(1-benzyl-3-phenylprop-2-enyl)carbamate (2r). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.97 (d, 2H, J=6.5 Hz), 4.62–4.70 (br, 1H), 4.77–4.87 (br, 1H), 5.10 (s, 2H), 6.14 (dd, 1H, J=16, 6 Hz), 6.47 (d, 1H, J=16 Hz), 7.20–7.34 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.47, 54.46, 67.47, 127.13, 127.39, 128.34, 128.83, 129.20, 129.25, 129.94, 130.27, 131.24, 137.17, 137.29, 137.68, 156.32; IR (CH_2Cl_2): 3324, 3029, 1693, 1531, 1496, 1451, 1256, 1049 cm^{-1}; mp: 102–104°C; Anal. Calcd for $C_{24}H_{23}NO_2$: C, 80.64; H, 6.49; N, 3.92. Found: C, 80.62; H, 6.52; N, 3.79.

4.4.14. Methyl *N*-(5-phenylpenta-2,4-dienyl)carbamate (5a). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (s, 3H), 3.86–3.95 (br, 1H), 4.75–4.83 (br, 1H), 5.80 (dt, 1H, J=15.5, 6 Hz), 6.34 (dd, 1H, J=15.5, 10.5 Hz), 6.53 (d, 1H, J=15.5 Hz), 6.76 (dd, 1H, J=15.5, 10.5 Hz), 7.21–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 43.57, 52.95, 127.07, 128.31, 128.65, 129.32, 130.53, 132.80, 133.35, 137.78, 157.60; IR (CH_2Cl_2): 3332, 2831, 1695, 1541, 1449, 1279, 1125, 1049 cm^{-1}; mp: 78–80°C; HRMS (CI) Calcd for $C_{13}H_{15}NO_2$+H $(M+H)^+$ 218.1181. Found: 218.1174.

4.4.15. Methyl *N*-(6-phenylhexa-2,4-dienyl)carbamate (5c). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.42 (d, 2H, J=7 Hz), 3.68 (s, 3H), 3.81 (dd, 2H, J=6.5, 5 Hz), 4.73–4.80 (br, 1H), 5.60 (dt, 1H, J=15, 6.5 Hz), 5.82 (dt, 1H, J=15, 7 Hz), 6.07 (dd, 1H, J=15, 10 Hz), 6.16 (dd, 1H, J=15, 10 Hz), 7.17–7.32 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 39.65, 43.45, 52.88, 126.85, 128.52, 129.17, 129.28, 131.10, 132.52, 134.06, 140.69, 157.61; IR (neat): 3340, 3017, 2936, 1708, 1526, 1447, 1257, 1004 cm^{-1}; HRMS (CI) Calcd for $C_{14}H_{17}NO_2$+H $(M+H)^+$ 232.1337. Found: 232.1339.

4.4.16. Methyl *N*-(1-benzylpenta-2,4-dienyl)carbamate (6c). White solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (d, 2H, J=6.5 Hz), 3.63 (s, 3H), 4.51–4.59 (br, 1H), 4.75–4.85 (br, 1H), 5.07 (dd, 1H, J=10, 1.5 Hz), 5.18 (dd, 1H, J=17, 1.5 Hz), 5.65 (dd, 1H, J=15, 6 Hz), 6.13 (dd, 1H, J=15, 6 Hz), 6.30 (ddd, 1H, J=17, 10, 6 Hz), 7.21–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.26, 52.83, 53.95, 118.25, 127.28, 129.21, 130.26, 131.90, 134.05, 136.86, 137.80, 156.98; IR (CH_2Cl_2): 3324, 3029, 2949, 1728, 1692, 1604, 1535, 1452, 1355, 1258 cm^{-1}; mp: 30–31°C; HRMS (CI) Calcd for $C_{14}H_{17}NO_2$+H $(M+H)^+$ 232.1337. Found: 232.1329.

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