Gold-Catalyzed Intermolecular Hydroamination of Allenes: First Example of the Use of an Aliphatic Amine in Hydroamination

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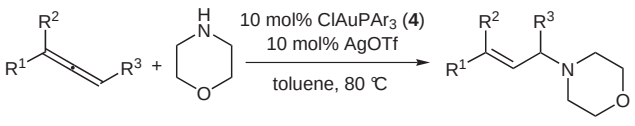
This paper is dedicated to Professor Miguel Yus on the occasion of his 60th birthday celebration.

Abstract: Treatment of allenes with morpholine in the presence of cationic gold(I) catalyst in toluene at 80 °C gave the corresponding allylic amines in good to moderate yields. To the best of our knowledge, this is the first example for carrying out the gold-catalyzed intermolecular hydroamination with an aliphatic amine.

Keywords: hydroamination, gold catalyst, aliphatic amine, allenes, gold–phosphine complex

The utility of gold complexes for homogeneous catalysis has been received much attention because of their soft carbophilic nature, which can activate unsaturated C–C bonds toward nucleophilic attack.[1] In the case of hydroamination, the formal addition of an N–H bond across an unsaturated C–C bond, the attack of a nitrogen nucleophile has been achieved not only to reactive alkynes[2] but also to less reactive allenes[3] and simple olefins[4] very recently. Despite much success to activate unsaturated C–C bonds, the nitrogen nucleophile has been limited in reactive sulfonamides, carbamates, and arylamines.[2–4] The intermolecular hydroamination with aliphatic amines is so far difficult, although the intramolecular version with aliphatic amines is known.[2a–e,2i,3a,e] Herein, we report that the intermolecular hydroamination of the allenes **1** with the aliphatic amine **2** (morpholine) takes place by using the cationic gold(I) catalysts **4** in toluene to give the corresponding allylic amines **3** in high to moderate yields (Equation 1). Furthermore, we uncovered that the steric effect rather than electronic effect of PAr_3 in **4** is important for enhancing the yield of **3** in this reaction.



1 2 3

Equation 1

It is known that the cationic gold(I)–phosphine system such as **4a**/AgOTf is an efficient catalyst for the addition of carbon,[3d,5] oxygen,[3d,6] and nitrogen[2–4,7] nucleophiles to C–C unsaturated bonds. It is noteworthy that the use of cationic gold(I)–phosphine catalysts such as **4h**/AgOTf and **4i**/AgOTf enables us to carry out the catalytic addition of less reactive nitrogen nucleophiles to allenes. This result suggests that pertinent steric crowding around the gold complexes is necessary to carry out the intermolecular hydroamination of allenes with the aliphatic amine.

In initial experiments, we examined $ClAuPPh_3$ **4a** activated by AgOTf for the intermolecular hydroamination of 4-methylphenylallene (**1a**) with morpholine (**2**). In the presence of 10 mol% of the in situ generated cationic gold(I)–phosphine catalyst, 1.2 equivalents of allene **1a**, and morpholine (**2**) in toluene, the reaction proceeded smoothly at 80 °C and the corresponding allylic amine **3a** was obtained in 64% yield after 12 hours (Table 1, entry 1). The reaction at 50 °C or at 120 °C gave **3a** in ca. 40% yield, and that at 100 °C gave **3a** in 60% yield. Other catalysts, such as AgOTf, CuOTf–benzene complex, $Cu(OTf)_2$, TfOH, and Au–halogen complexes, did not promote the hydroamination at all.[8,9] In the absence of AgOTf and by merely using **4a**, no reaction occurred, therefore we confirmed the efficiency of cationic gold species in this reaction.[10] As silver source, AgOTf shows the best reactivity. To improve the yield of **3a**, we applied $ClAuP(t\text{-}Bu)_2(o\text{-biphenyl})$ (**4b**),[3d,4c,f] which Widenhoefer and co-workers found as a very efficient catalyst for intramolecular hydroamination, however, a decrease in the yield was observed; the result of the intramolecular reaction is not necessarily applicable to the intermolecular version (Table 1, entry 2). Thus, we started to search for better catalysts in the present reaction system.

Comparison of the efficiency of various $ClAuPAr_3$ catalysts in the hydroamination is summarized in Table 1. The catalysts bearing an electron-donating or electron-withdrawing group at *para* position (*p*-OMe **4c** and *p*-CF_3 **4d**) show reactivity comparable to $ClAuPPh_3$ (**4a**), indicating that the influence of electronic effect upon the chemical yield is not so strong (Table 1, entries 3 and 4). Next, we introduced heteroatom-containing groups at *ortho* position (*o*-OMe **4e**, *o*-OH **4f**, and *o*-pyridyl **4g**) with aim to know the influence of coordination of those heteroatoms to the gold center.[11] The complex **4e** gave the product in 63% yield comparable to **4a** (Table 1, entry 5), however, the reaction using **4f** and **4g** resulted in low yields (27% and 30%: Table 1, entries 6 and 7). This pyridyl complex **4g** is widely used as a precursor for various gold complexes, and it is known by X-ray crystal structure analysis that

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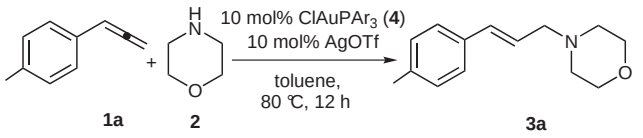
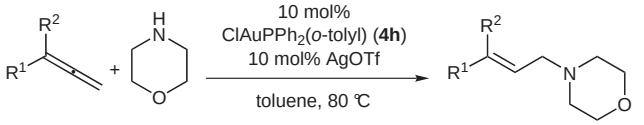
Table 1 Au(I)-Catalyzed Hydroamination of Allene **1a** with Various Au(I) Complexes[a]



Entry	PR_3		Yield (%)[b]
1	PPh_3	**4a**	64
2	P(*t*-Bu)$_2$(*o*-biphenyl)	**4b**	51
3	PPh_2(*p*-anisyl)	**4c**	62
4	PPh_2(*p*-$C_6H_4CF_3$)	**4d**	63
5	PPh_2(*o*-anisyl)	**4e**	63
6	PPh_2(*o*-C_6H_4OH)	**4f**	27
7	PPh_2(*o*-pyridyl)	**4g**	30
8	PPh_2(*o*-tolyl)	**4h**	83
9	PPh (*o*-tolyl)$_2$	**4i**	79
10	P(*o*-tolyl)$_3$	**4j**	32

[a] All the reactions were stopped after 12 h.
[b] Yield of isolated product.

Table 2 Au(I)-Catalyzed Hydroamination of Allenes **1a–f**,**h** Using Catalyst **4h**

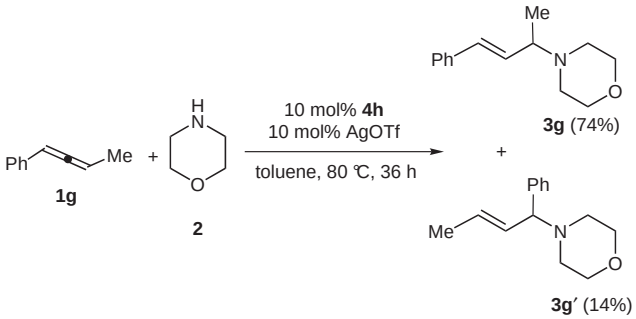


Entry	R^1	R^2		Time (h)	Yield (%)[a]
1	4-MeC_6H_4	H	**1a**	12	83
2	Ph	H	**1b**	24	66
3	Bn	H	**1c**	12	56
4	*n*-Oct	H	**1d**	9	46
5	Cy	H	**1e**	12	39
6	*t*-Bu	H	**1f**	24[b]	4
7	Ph	Me	**1h**	12	17[c]

[a] Yield of isolated product.
[b] The reaction was stopped after 24 h.
[c] Combined yield of the isolated stereoisomeric mixture. The *E*:*Z* ratio was about 5:4 (determined by ^{1}H NMR spectroscopy).

there is no coordination of the nitrogen atom to the gold center.[12] However, as far as we know, the information on coordination was obtained on neutral gold complexes. There is no knowledge on the cationic system [AgOTf/ $ClAuPPh_2$(*o*-pyridyl)], and it seems that coordination of the pyridyl nitrogen to gold presumably occurs judging from the dramatic decrease in the yield. It is clear that the approach using coordination effect leads to negative results. At last, we investigated the steric effect by introducing Me group at *ortho* position. The use of the monomethylated complex **4h** and dimethylated complex **4i** enhanced the yield of **3a** up to 83%[16] and 79%, respectively (Table 1, entries 8 and 9). On the other hand, the trimethylated analogue **4j** gave the product only in 32% yield (Table 1, entry 10). These results suggest that adjustment of the steric environment around gold center is a key to enhancing the yield of the intermolecular hydroamination. It should be noted that the *o*-anisyl derivative **4e** gave a similar yield as **4a**, but the *o*-tolyl derivative **4h**[14,15] afforded a much higher yield.

The scope of the hydroamination under the optimized conditions is summarized in Table 2. Aryl allenes **1a**, **1b**, and **1g** are proved to be good substrates for the hydroamination (Table 2, entries 1, 2, and 7). The aliphatic allenes **1c**, **1d**, and **1e** gave the corresponding products in moderate yields (Table 2, entries 3–5), but the sterically bulky aliphatic allene **1f** exhibited extremely low reactivity[13] (Table 2, entry 6). We also investigated the reactivities of disubstituted allenes. The 1,3-disubstituted allene **1g** showed reactivity comparable to the monosubstituted allene (Scheme 1) and gave a small amount of the regioisomer **3g′**. In our previous report, the $AuBr_3$-catalyzed hydroamination of a disubstituted allene with arylamines gave an excellent regioselectivity without producing a regioisomer.[3b] The 1,1-substituted allene **1h** gave the product as an unseparable stereoisomeric mixture in low yield (Table 2, entry 7). The *E*:*Z* ratio was about 5:4, determined by NOE experiments of the products.



Scheme 1 Reaction of 1,3-disubstituted allene

In conclusion, we have succeeded in running the gold(I)-catalyzed intermolecular hydroamination with an *aliphatic amine*, and found that the control of steric environment around gold center by using appropriate phosphine ligands is a key for making it feasible to carry out such aliphatic hydroamination. We are currently studying the detailed mechanism of this reaction and searching gold complexes, which enable the hydroamination with more simple aliphatic amines.

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(8) We examined the following complexes, but all attempts resulted in failure: AuCl, $AuCl_3$, $AuBr_3$, AuI, Au(CO)Cl, $NaAuCl_4 \cdot 2H_2O$. It is known that the hydroamination of olefins with tosylamides is accelerated by TfOH,[9] so we examined the TfOH-catalyzed (10 mol%) hydroamination of **1a** with **2** in toluene at 80 °C. However, the desired product (allylic amine) was not obtained at all. The allene **1a** was decomposed gradually in the presence of TfOH at 80 °C, and only 30% of **1a** was recovered after 12 h. It is clear that the present hydroamination is catalyzed by the gold complexes.

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(10) In order to know whether the cationic gold species really participate in the present hydroamination or not, we prepared the cationic gold species $[(MeCN)AuPPh_2(o\text{-tolyl})]^+ {}^-OTf$ according to the Echavarren's method and used it for the hydroamination of **1a**. The product **3a** was obtained in 71% yield, indicating that the cationic gold complex was a catalytic species. See: Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Buñuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 6146.

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(13) This reaction could not be checked by TLC nor GC-MS, because of its low boiling point (ca. 80 °C). Thus, reactions were stopped at 24 h.

(14) **General Procedure for Preparation of Catalysts**
These complexes were prepared following a literature procedure, and characterized by comparison of the NMR data with literature values, except for **4c**, **4d**, and **4h**. A solution of SMe_2 (1.2 mL, 16 mmol) in MeOH (6 mL) was added to a solution of $NaAuCl_4 \cdot 2H_2O$ (2.19 g, 5.5 mmol) in MeOH (30 mL) with minimum light exposure. The white precipitate was recovered by filtration, washed (MeOH, Et_2O, and pentane), and dried under vacuum. Then, $[AuCl(SMe_2)]$ was obtained in 99% yield (1.60 g) and used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.73 (s, 6 H). A solution of diphenyl(*o*-tolyl)phosphine (0.589 g, 2 mmol) in acetone (50 mL) was added to a solution of $[AuCl(SMe_2)]$ (0.553 g) in acetone (150 mL). The mixture was stirred for 2 h and concentrated, recrystallized from toluene, and dried under vacuum; $[AuClPPh_2(o\text{-Me-}C_6H_4)]$(**4h**) was obtained in 83% (0.83 g). See: Brandys, M.-C.; Jennings, M. C.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **2000**, 4601.

(15) $ClAuPPh_2(o\text{-}MeOC_6H_4)$(**4c**): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.71 (3 H, s), 6.82 (1 H, ddd, *J* = 13.2, 7.8, 1.8 Hz), 6.97 (1 H, dd, *J* = 8.4, 5.1 Hz), 6.93–6.97 (1 H, m), 7.42–7.47 (4 H, m), 7.49–7.57 (7 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 55.9, 111.6 [d, $J(^{13}C–^{31}P)$ = 4.1 Hz], 116.4 [d, $J(^{13}C–^{31}P)$ = 57.0 Hz], 121.1 [d, $J(^{13}C–^{31}P)$ = 10.8 Hz], 128.4,

128.9 [d, $J(^{13}C–^{31}P)$ = 11.6 Hz], 131.5 [d, $J(^{13}C–^{31}P)$ = 2.5 Hz], 133.9 [d, $J(^{13}C–^{31}P)$ = 1.7 Hz], 134.0 [d, $J(^{13}C–^{31}P)$ = 14.9 Hz], 134.2 [d, $J(^{13}C–^{31}P)$ = 7.5 Hz], 160.7 [d, $J(^{13}C–^{31}P)$ = 5.0 Hz]. ^{31}P NMR (121.5 Hz, $CDCl_3$): δ = 25.0. IR (neat, ATR): 1584, 1572, 1473, 1459, 1435, 1278, 1247, 1101, 1011, 764, 747 cm^{-1}. Anal. Calcd for $C_{19}H_{17}AuClOP$: C, 43.49; H, 3.27; Cl, 6.76. Found: C, 43.62; H, 3.32; Cl, 6.75. ESI-HRMS: *m/z* calcd for $C_{19}H_{17}AuClOP$ [M + Na]: 547.0263; found: 547.0267.

$ClAuPPh_2$(*p*-$F_3CC_6H_4$) (**4d**): ^1H NMR (600 MHz, $CDCl_3$): δ = 7.48–7.60 (10 H, m), 7.64 (2 H, dd, *J* = 12.6, 7.8 Hz), 7.72 (2 H, dd, *J* = 7.8, 1.5 Hz). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 121.4 [d, $J(^{13}C–^{31}P)$ = 1.2 Hz], 126.0 [dq, $J(^{13}C–^{31}P)$ = 11.8 Hz, $J(^{13}C–^{19}F)$ = 3.7 Hz], 126.7 [q, $J(^{13}C–^{19}F)$ = 81.3 Hz], 128.0, 129.5 [d, $J(^{13}C–^{31}P)$ = 11.8 Hz], 132.4 [d, $J(^{13}C–^{31}P)$ = 2.5 Hz], 134.2 [d, $J(^{13}C–^{31}P)$ = 8.8 Hz], 134.3 [d, $J(^{13}C–^{31}P)$ = 14.3 Hz]. ^{31}P NMR (121.5 Hz, $CDCl_3$): δ = 33.3. IR (neat, ATR): 1436, 1395, 1322, 1125, 1103, 1061, 1014, 838, 748, 708 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{19}H_{14}AuClF_3P$ [M + Na]: 585.0031; found: 585.0032.

$ClAuPPh_2$(*o*-MeC_6H_4) (**4h**): ^1H NMR (600 MHz, $CDCl_3$): δ = 2.53 (3 H, s), 6.74 (1 H, ddd, *J* = 12.7, 7.7, 1.2 Hz), 7.18 (1 H, dd, *J* = 7.5, 7.5 Hz), 7.29–7.33 (1 H, m), 7.43 (1 H, ddd, *J* = 7.5, 7.5, 1.4 Hz), 7.46–7.51 (4 H, m), 7.53–7.60 (6 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 22.6 [d, $J(^{13}C–^{31}P)$ = 12.2 Hz], 126.3 [d, $J(^{13}C–^{31}P)$ = 10.0 Hz], 126.8 [d, $J(^{13}C–^{31}P)$ = 60.2 Hz], 128.0 [d, $J(^{13}C–^{31}P)$ = 63.8 Hz], 129.4 [d, $J(^{13}C–^{31}P)$ = 12.2 Hz], 131.8 [d, $J(^{13}C–^{31}P)$ = 2.2 Hz], 132.0 [d, $J(^{13}C–^{31}P)$ = 9.3 Hz], 132.1 [d, $J(^{13}C–^{31}P)$ = 2.2 Hz], 133.0 [d, $J(^{13}C–^{31}P)$ = 8.6 Hz], 134.5 [d, $J(^{13}C–^{31}P)$ = 14.3 Hz], 142.0 [d, $J(^{13}C–^{31}P)$ = 12.2 Hz]. ^{31}P NMR (121.5 Hz, $CDCl_3$): δ = 32.1. IR (neat, ATR): 1589, 1479, 1436, 1101, 997, 804, 751, 714 cm^{-1}. Anal. Calcd for $C_{19}H_{17}AuClP$: C, 44.86; H, 3.37; Cl, 6.97. Found: C, 45.00; H, 3.60; Cl, 6.93. ESI-HRMS: *m/z* calcd for $C_{19}H_{17}AuClP$ [M + Na]: 531.0314; Found: 531.0314.

^1H, ^{13}C, and ^{31}P NMR chemical shifts are reported relative to $CDCl_3$ and 85% H_3PO_4.

(16) **General Procedure for Hydroamination of Allenes**

To a suspension of [$AuClPPh_2$(*o*-tolyl)] (25.4 mg, 0.05 mmol) in toluene (0.5 mL) was added morpholine (43.7 mg, 0.502 mmol). To the reaction mixture was added 4-methylphenylallene (**1a**, 79.3 mg, 0.6 mmol) and the resulting mixture was stirred at 80 °C under an Ar atmosphere. The reaction mixture was colorless and heterogeneous at the beginning, but it turned yellow to brown as the reaction progressed. After the reaction was completed (12 h), the reaction mixture was filtered through short Florisil® gel pad with EtOAc as an eluent and the resulting filtered solution was concentrated. The product was purified by column chromatography (basic silica gel, hexane–EtOAc = 100:1 to 10:1) to give **3a** in 83% yield (90.8 mg).

(17) (*E*)-4-(3-*p*-Tolylallyl)morpholine (**3a**): ^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (3 H, s), 2.40–2.59 (4 H, m), 3.12 (2 H, dd, *J* = 6.8, 1.3 Hz), 3.72 (4 H, dd, *J* = 4.7, 4.7 Hz), 6.18 (1 H, dt, *J* = 15.8, 6.8 Hz), 6.48 (1 H, d, *J* = 15.8 Hz), 7.10 (2 H, d, *J* = 8.1 Hz), 7.25 (2 H, d, *J* = 8.1 Hz). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 21.2, 53.7, 61.5, 67.0, 124.9, 126.2, 129.3, 133.3, 134.0, 137.4. IR (neat): 1712, 1512, 1452, 1116, 1006, 968, 869, 809, 776 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_{19}NO$ [M^+]: 217.1462; found: 217.1464.

4-Cinnamylmorpholine (**3b**): ^1H NMR (300 MHz, $CDCl_3$): δ = 2.45 (4 H, dd, *J* = 4.6, 4.6 Hz), 3.10 (2 H, dd, *J* = 6.8, 1.3 Hz), 3.68 (4 H, dd, *J* = 4.6, 4.6 Hz), 6.19 (1 H, dt, *J* = 15.8, 6.8 Hz), 6.47 (1 H, d, *J* = 15.8 Hz), 7.11–7.38 (5 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 53.7, 61.5, 66.9, 125.8, 126.3, 127.6, 128.6, 133.5, 136.7. IR (neat): 1598, 1496, 1451, 1277, 1115, 1006, 966, 868, 741 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{13}H_{17}NO$ [M^+]: 203.1305; found: 203.1308.

(*E*)-4-(4-Phenylbut-2-enyl)morpholine (**3c**): ^1H NMR (300 MHz, $CDCl_3$): δ = 2.30–2.54 (4 H, m), 2.95 (2 H, dd, *J* = 6.6, 0.9 Hz), 3.36 (2 H, d, *J* = 6.6 Hz), 3.70 (4 H, dd, *J* = 4.8, 4.8 Hz), 5.54 (1 H, dtt, *J* = 15.2, 6.6, 1.3 Hz), 5.76 (1 H, dtt, *J* = 15.2, 6.6, 1.3 Hz), 7.11–7.23 (3 H, m), 7.23–7.33 (2 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 38.9, 53.5, 61.1, 67.0, 126.1, 127.3, 128.4, 128.5, 133.4, 140.2. IR (neat): 1603, 1495, 1453, 1116, 1003, 975, 865, 745 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_{19}NO$ [M^+]: 217.1462; found: 217.1464.

(*E*)-4-(Undec-2-enyl)morpholine (**3d**): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.81 (3 H, t, *J* = 6.6 Hz), 1.03–1.43 (12 H, m), 1.95 (2 H, dt, *J* = 7.0, 6.6 Hz), 2.26–2.48 (4 H, m), 2.86 (2 H, d, *J* = 6.6 Hz), 3.65 (4 H, dd, *J* = 4.6, 4.6 Hz), 5.39 (1 H, dt, *J* = 15.2, 6.6 Hz), 5.54 (1 H, dt, *J* = 15.2, 6.6 Hz). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 14.1, 22.7, 29.2, 29.2, 29.3, 29.4, 31.9, 32.3, 53.5, 61.4, 67.0, 125.6, 135.3. IR (neat): 1720, 1454, 1004, 972, 867 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{15}H_{29}NO$ [M^+]: 239.2244; found: 239.2246.

(*E*)-4-(3-Cyclohexylallyl)morpholine (**3e**): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.98–1.31 (5 H, m), 1.55–1.85 (5 H, m), 1.85–2.03 (1 H, m), 2.34–2.55 (4 H, m), 2.93 (2 H, d, *J* = 6.8 Hz), 3.71 (4 H, dd, *J* = 4.7, 4.7 Hz), 5.40 (1 H, dtd, *J* = 15.4, 6.6, 0.9 Hz), 5.55 (1 H, dd, *J* = 15.4, 6.6 Hz). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 26.0, 26.1, 32.9, 40.5, 53.5, 61.5, 67.0, 123.0, 141.1. IR (neat): 1718, 1449, 1118, 1005, 971, 866 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{13}H_{23}NO$ [M^+]: 209.1775; found: 209.1779.

(*E*)-4-(4,4-Dimethylpent-2-enyl)morpholine (**3f**): ^1H NMR (300 MHz, $CDCl_3$): δ = 0.94 (9 H, s), 2.27–2.44 (4 H, m), 2.87 (2 H, dd, *J* = 6.8, 1.0 Hz), 3.66 (4 H, dd, *J* = 4.7, 4.7 Hz), 5.32 (1 H, dt, *J* = 15.6, 6.8 Hz), 5.56 (1 H, d, *J* = 15.6 Hz). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 29.6, 29.7, 53.5, 61.5, 67.0, 120.3, 146.2. IR (neat): 1732, 1454, 1260, 1119, 1005, 975, 868 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{11}H_{21}NO$ [M + H]: 184.1696; found: 184.1696.

(*E*)-4-(4-Phenylbut-3-en-2-yl)morpholine (**3g**): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (3 H, d, *J* = 6.6 Hz), 2.54 (4 H, dt, *J* = 4.8, 4.4 Hz), 3.00 (2 H, dq, *J* = 8.1, 6.6 Hz), 3.71 (4 H, dd, *J* = 4.4, 4.4 Hz), 6.15 (1 H, dt, *J* = 15.8, 8.1 Hz), 6.44 (1 H, d, *J* = 15.8 Hz), 7.14–7.42 (5 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 17.8, 50.8, 63.1, 67.2, 126.2, 127.5, 128.6, 131.2, 132.1, 136.9. IR (neat): 1600, 1494, 1447, 1265, 1116, 963, 864, 747 cm^{-1}. HRMS (EI): *m/z* calcd for $C_{14}H_{19}NO$ [M^+]: 217.1462; found: 217.1465.

(*E*)-4-(1-Phenylbut-2-enyl)morpholine (**3g′**): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.59 (3 H, dd, *J* = 6.0, 1.1 Hz), 2.15–2.31 (2 H, m), 2.33–2.56 (2 H, m), 3.48 (1 H, d, *J* = 8.6 Hz), 3.61 (4 H, dd, *J* = 4.4, 4.4 Hz), 5.45 (1 H, ddd, *J* = 15.0, 8.6, 1.1 Hz), 5.58 (1 H, dq, *J* = 15.0, 6.0 Hz), 7.11–7.31 (5 H, m). ^{13}C NMR (75.5 Hz, $CDCl_3$): δ = 17.8, 52.0, 67.2, 74.6, 127.0, 127.7, 127.9, 128.5, 132.7, 142.3. IR (neat): 1492, 1449, 1271, 1116, 1003, 967, 875, 755 cm^{-1}. ESI-HRMS: *m/z* calcd for $C_{14}H_{19}NO$ [M + H]: 218.1539; found: 218.1539.

4-(3-Phenylbut-2-enyl)morpholine (**3h**): inseparable stereoisomeric mixture. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.05 (*E*- and *Z*-3 H, s), 2.25–2.42 (*Z*-4 H, m), 2.44–2.60 (*E*-4 H, m), 2.91 (*Z*-2 H, d, *J* = 6.8 Hz), 3.17 (*E*-2 H, d, *J* = 6.8 Hz), 3.70 (*Z*-4 H, dd, *J* = 4.6, 4.6 Hz), 3.72 (*E*-4 H, dd, *J* = 4.6, 4.6 Hz), 5.55 (*Z*-1 H, td, *J* = 6.8, 1.3 Hz), 5.86 (*E*-1 H, td, *J* = 6.8, 1.3 Hz), 7.09–7.45 (*E*- and *Z*-5 H, m). NOE Experiment for **3h**: Two signals were observed by irradiation for Me peak (δ = 2.05 ppm); 0.52% for allyl-H peak of *E*-isomer (δ = 3.17 ppm) and 1.64% for vinyl-H peak of *Z*-isomer (δ = 5.55 ppm). From this experiment, we determined that the major product was *E*-isomer and the *E*:*Z* ratio was 5: 4.