Iridium Complex-Catalyzed Allylic Amination of Allylic Esters

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Received May 15, 2001

Abstract: Iridium complex-catalyzed allylic amination of allylic carbonates was studied. The solvent strongly affected the catalytic activity. The use of a polar solvent such as EtOH is essential for obtaining the products in high yield. The reaction of (*E*)-3-substituted-2-propenyl carbonate and 1-substituted-2-propenyl carbonate with pyrrolidine in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (P/Ir = 2) gave a branch amine with up to 99% selectivity. Both secondary and primary amines could be used for this reaction. When a primary amine was used, selective monoallylation occurred. No diallylation product was obtained. The reaction of 1,1-disubstituted-2-propenyl acetate with amines exclusively gave an α,α-disubstituted allylic amine. This reaction provides an alternative route to the addition of an organometallic reagent to ketimines for the preparation of such amines. The reaction of (*Z*)-3-substituted-2-propenyl carbonate with amines gave (*Z*)-linear amines with up to 100% selectivity. In all cases, no (*E*)-linear amine was obtained. The selectivities described here have not been achieved in similar palladium complex-catalyzed reactions.

Introduction

There have been dramatic improvements recently in methods for organic synthesis. Many of these improvements have been achieved by the catalytic and stoichiometric application of transition metal complexes.[1] These can be used to catalyze several selective transformations that would be either difficult or impossible by conventional methodologies. Transition metal complex-catalyzed carbon−nitrogen bond formation is particularly important for the synthesis of nitrogen-containing natural products. Of the methods recently reported, the palladium complex-catalyzed amination of arenes[2] has become an indispensable tool for the synthesis of aminoarenes and *N*-heterocycles, which are difficult to prepare by traditional methods.

Another important variant for transition metal complex-catalyzed carbon−nitrogen bond formation is allylic amination.[3] Nucleophilic attack by an amine to a π-allyl intermediate generated from an allylic substrate gives an allylic amine, which is an important synthetic intermediate.[4] For example, oxidation of the carbon−carbon double bond gives α- or β-amino acids.[5] Palladium complexes are general and versatile catalysts for allylic amination.[6,7] When a π-allyl palladium intermediate is terminally monosubstituted, the amine generally attacks at the unsubstituted allylic terminus to give an (*E*)-linear allylic amine (Scheme 1).[8] Recently, ruthenium,[9a,b] rhodium,[9c,d] iron,[9e] and nickel[9f,g] complexes have served as catalysts for allylic amina-

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(1) (a) Tsuji, J. *Transition Metal Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: Chichester, 2000. (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*, 2nd ed.; University Science Books: Mill Valley, 1999. (c) *Transition Metal Catalyzed Reactions*; Murahashi, S.-I., Davies, S. G., Eds.; Blackwell Science: Oxford, 1999. (d) *Transition Metals for Organic Synthesis*; Beller, M., Bolm, C., Eds.; Wiley-VCH: New York, 1998.

(2) (a) Wolfe, J. P.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1144. (b) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158. (c) Stauffer, S. R.; Lee, S.; Stambuli, J. P.; Hauck, S. I.; Hartwig, J. F. *Org. Lett.* **2000**, *2*, 1423. (d) Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417. (e) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575. (f) Bei, X.; Uno, T.; Norris, J.; Turner, H. W.; Weinberg, W. H.; Guram, A. S.; Petersen, J. L. *Organometallics* **1999**, *18*, 1840. (g) Huang, J.; Grasa, G.; Nolan, S. P. *Org. Lett.* **1999**, *1*, 1307. (h) Wolfe, J. P.; Wagaw, S.; Marcoux, J. F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. (i) Hartwig, J. F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2047. (j) Frost, C. G.; Mendonça, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2615.

(3) Johansen, M.; Jørgensen, K. A. *Chem. Rev.* **1998**, *98*, 1689.

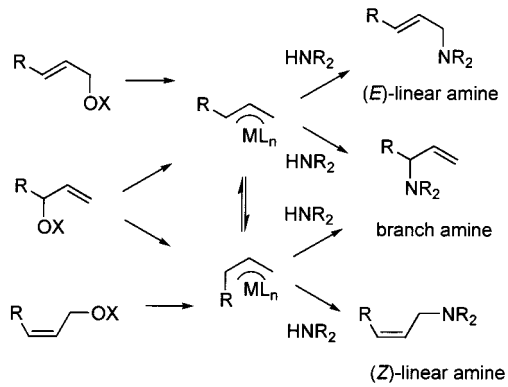
(4) (a) Johnson, T. A.; Curtis, M. D.; Beak, P. *J. Am. Chem. Soc.* **2001**, *123*, 1004. (b) Jun, C.-H.; Lee, H.; Park, J.-B.; Lee, D.-Y. *Org. Lett.* **1999**, *1*, 2161. (c) Mori, M.; Sakakibara, N.; Kinoshita, A. *J. Org. Chem.* **1998**, *63*, 6082. (d) Magnus, P.; Lacour, J.; Coldham, I.; Mugrage, B.; Bauta, W. B. *Tetrahedron* **1995**, *51*, 11087. (e) Vedejs, E.; Gringras, M. *J. Am. Chem. Soc.* **1994**, *116*, 579. (f) Albeck, A.; Persky, R. *J. Org. Chem.* **1994**, *59*, 653. (g) Burgess, K.; Liu, L. T.; Pal, B. *J. Org. Chem.* **1993**, *58*, 4758. (h) Gonda, J.; Helland, A.-C.; Ernst, B.; Belluš, D. *Synthesis* **1993**, 729. (i) Burgess, K.; Ohlmeyer, M. J. *J. Org. Chem.* **1991**, *56*, 1027. (j) Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. *J. Org. Chem.* **1987**, *52*, 1487.

(5) (a) Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301. (b) Bower, J. F.; Jumnah, R.; Williams, A. C.; Williams, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1411.

(6) (a) Martijn, W. van L.; Diederen, J. J. H.; Elsevier, C. J. *Adv. Synth. Catal.* **2001**, *343*, 255. (b) Katritzky, A. R.; Yao, J.; Yang, B. *J. Org. Chem.* **1999**, *64*, 6066. (c) Olivo, H. F.; Yu, J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 391. (d) Kapeller, H.; Marschener, C.; Weissenbacher, M.; Griengl, H. *Tetrahedron* **1998**, *54*, 1439. (e) Sirisoma, N. S.; Woster, P. M *Tetrahedron Lett.* **1998**, *39*, 1489. (f) Gatti, R. G. P.; Larsson, A. L. E.; Bäckvall, J.-E. *J. Chem. Soc., Perkin Trans. 1* **1997**, 577. (g) Larsson, A. L. E.; Gatti, R. G. P.; Bäckvall, J.-E. *J. Chem. Soc., Perkin Trans. 1* **1997**, 2873. (h) Flegelová, Z.; Pátek, M. *J. Org. Chem.* **1996**, *61*, 6735. (i) Larock, R. C.; Tu, C. *Tetrahedron* **1995**, *51*, 6635. (j) Hutchins, R. O.; Wei, J.; Rao, S. J. *J. Org. Chem.* **1994**, *59*, 4007. (k) Garro-Helion, F.; Merzouk, A.; Guibé, F. *J. Org. Chem.* **1993**, *58*, 6109. (l) Genêt, J.-P.; Thorimbert, S.; Touzin, A.-M. *Tetrahedron Lett.* **1993**, *34*, 1159. (m) Tsuda, T.; Kiyoi, T.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 3388. (n) Trost, B. M.; Scanlan, T. S. *J. Am. Chem. Soc.* **1989**, *111*, 4988. (o) Tsuda, T.; Horii, Y.; Nakagawa, Y.; Ishida, T.; Saegusa, T. *J. Org. Chem.* **1989**, *54*, 977. (p) Nikaido, M.; Aslanian, R.; Scavo, F.; Helquist, P.; Åkermark, B.; Bäckvall, J.-E. *J. Org. Chem.* **1984**, *49*, 4738. (q) Bäckvall, J.-E.; Nordberg, R. E.; Zetterberg, K.; Åkermark, B. *Organometallics* **1983**, *2*, 1625. (r) Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769. (s) Godleski, S. A.; Heacock, D. J.; Meinhart, J. D.; Wallendeal, S. V. *J. Org. Chem.* **1983**, *48*, 2101. (t) Åkermark, B.; Åkermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* **1981**, *103*, 3037. (u) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1980**, *45*, 2741. (v) Stakem, F. G.; Heck, R. F. *J. Org. Chem.* **1980**, *45*, 3584.

10.1021/ja0112036 CCC: $20.00
Published on Web 09/11/2001

Scheme 1

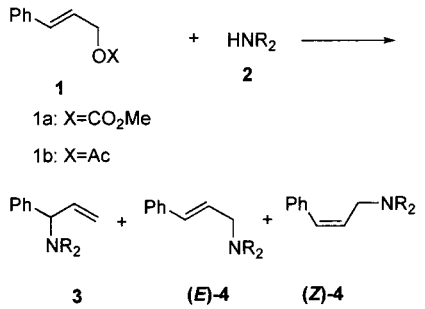


tion. The selectivity of allylic amination changes with the use of other transition metal complexes.

We first reported that an iridium complex was an efficient catalyst for allylic alkylation.[10] The regio- and stereoselectivities of iridium complex-catalyzed allylic alkylation are quite different from those of palladium complex-catalyzed allylic alkylation, and therefore, an iridium catalyst provides a useful complement to a palladium catalyst. We report here the details of the extension of this chemistry to the iridium complex-catalyzed allylic amination of allylic esters.

Results

Allylic Amination of (*E*)-3-Aryl-2-propenyl Carbonates and 1-Aryl-2-propenyl Carbonates. Fine tuning of the regio-, stereo-, and enantioselectivity of allylic substitution through the selection of a central metal or the design of a ligand has been extensively studied. The solvent should strongly influence such selectivities by stabilizing π-allyl metal intermediates or the transition state of the reaction.[11] We observed that the solvent strongly affects iridium complex-catalyzed allylic amination. The results are summarized in Table 1. The reaction of (*E*)-3-phenyl-2-propenyl carbonate (**1a**) with 3 equiv of piperidine (**2a**) in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ (Ir atom 4 mol %) and $P(OPh)_3$ (P/Ir = 2) gave **3a** and (*E*)-**4a** (eq



1). EtOH and MeOH gave good results (entries 1 and 2). Branch amine **3a** was obtained in high yield with high selectivity. The reaction under refluxing acetone gave the products in decreased yield (entry 4). Although THF is a common solvent for palladium complex-catalyzed allylic substitution, reactions in THF or dioxane gave products in low yields (entries 8 and 9). The $E_T(30)$ value is a well-known measure of solvent polarity.[12] Solvents with $E_T(30)$ values above 40 gave the products in good yield (entries 1−7). A polar solvent clearly enhances the reaction of **1a** with piperidine (**2a**). It is important to note that no (*Z*)-**4a** was obtained in any of the cases.

The effect of the ratio of $P(OPh)_3$ to Ir on the reaction was examined by reacting **1a** with piperidine (**2a**). The results are summarized in Table 2. Reactions at P/Ir ratios of 1 and 2 gave **3a** in high selectivity (entries 2 and 3). A different selectivity was observed at a P/Ir ratio of 3. Linear amine (*E*)-**4a** was obtained as a major product in 89% selectivity (entry 4). On the basis of our previous study,[10b,d] a catalytically active species is considered to be a monophosphite species. The reaction with a P/Ir ratio of 3 would form a bisphosphite species as a major catalytically active species. Increasing the steric bulkiness of

Table 1. Solvent Effect on the Reaction of **1a** with **2a**[a]

entry	solvent	$E_T(30)$[b]	conditions	yield[c]/%	ratio[d] **3a**/**4a** (*E*/*Z*)
1	EtOH	51.9	50 °C 3 h	95	95/5 (100/0)
2	MeOH	55.4	50 °C 3 h	84	92/8 (100/0)
3	*i*-PrOH	48.4	50 °C 3 h	99	83/17 (100/0)
4	acetone	42.4	reflux 17 h	71	96/4 (100/0)
5	$MeNO_2$	46.3	50 °C 12 h	89	68/32 (100/0)
6	MeCN	45.6	50 °C 7 h	83	89/11 (100/0)
7	CH_2Cl_2	40.7	reflux 22 h	90	80/20 (100/0)
8	THF	37.4	50 °C 23 h	25	89/11 (100/0)
9	dioxane	36.0	50 °C 22 h	39	91/9 (100/0)
10	Et_3N	32.1	50 °C 23 h	34	80/20 (100/0)
11	AcOEt	38.1	reflux 22 h	45	91/9 (100/0)
12	benzene	34.3	reflux 16 h	58	85/15 (100/0)

[a] A mixture of **1a** (2 mmol), piperidine (**2a**) (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and solvent (4.4 mL) was stirred under argon. [b] Reference 12. [c] Isolated yield. [d] Ratios determined by GLC and NMR.

(7) For enantioselective allylic amination, see: (a) Reference 5. (b) Evans, D. A.; Campos, K. R.; Tedrow, J. S.; Michael, F. E.; Gangé, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 7905. (c) Selvakumar, K.; Valentini, M.; Wörle, M.; Pregosin, P. S.; Albinati, A. *Organometallics* **1999**, *18*, 1207. (d) Constantieux, T.; Brunel, J.-M.; Labende, A.; Buono, G. *Synlett* **1998**, 49. (e) Burckhardt, U.; Baumann, M.; Trabesinger, G.; Gramlich, V.; Togni, A. *Organometallics* **1997**, *16*, 5252. (f) Sudo, A.; Saigo, K. *J. Org. Chem.* **1997**, *62*, 5508. (g) Togni, A.; Burckhardt, U.; Gramlich, V.; Pregosin, P. S.; Salzmann, R. *J. Am. Chem. Soc.* **1996**, *118*, 1031. (h) Blöchl, P. E.; Togni, A. *Organometallics* **1996**, *15*, 4125. (i) von Matt, P.; Loiseleur, O.; Koch, G.; Pfaltz, A.; Lefeber, C.; Feucht, T.; Helmchen, G. *Tetrahedron: Asymmetry* **1994**, *5*, 573.

(8) (a) Katritzky, A. R.; Yao, J.; Denisko, O. V. *J. Org. Chem.* **2000**, *65*, 8063. (b) Delbecq, F.; Lapouge, C. *Organometallics* **2000**, *19*, 2716. (c) Kuhn, O.; Mayr, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 343. (d) Yang, S.-C.; Hung, C.-W. *J. Org. Chem.* **1999**, *64*, 5000. (e) Yang, S.-C.; Chung, W.-H. *Tetrahedron Lett.* **1999**, *40*, 953. (f) Katritzky, A. R.; Yao, J.; Qi, M. *J. Org. Chem.* **1998**, *63*, 5232. (g) Santos, D. S.; Tong, Y.; Quignard, F.; Choplin, A.; Sinou, D.; Dutasta, J. P. *Organometallics* **1998**, *17*, 78. (h) Kling, R.; Sinou, D.; Pozzi, G.; Choplin, A.; Quignard, F.; Busch, S.; Kainz, S.; Koch, D.; Leitner, W. *Tetrahedron Lett.* **1998**, *39*, 9439. (i) Bergbreiter, D. E.; Liu, Y.-S. *Tetrahedron Lett.* **1997**, *38*, 7843. (j) Audoire-Lemaire, S.; Savignac, M.; Pourcelot, G.; Genêt, J.-P.; Bernard, J.-M. *J. Mol. Catal. A* **1997**, *116*, 247. (k) Masuyama, Y.; Kagawa, M.; Kurusu, Y. *Chem. Lett.* **1995**, 1121. (l) Blart, E.; Genêt, J. P.; Safi, M.; Savignac, M.; Sinou, D. *Tetrahedron* **1994**, *50*, 505. (m) Hayashi, T.; Kishi, K.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* **1990**, *31*, 1743. (n) Bergbreiter, D. E.; Weatherford, D. A. *J. Org. Chem.* **1989**, *54*, 2726. (o) Connell, R. D.; Rein, T.; Åkermark, B.; Helquist, P. *J. Org. Chem.* **1988**, *53*, 3845. (p) Åkermark, B.; Vitagliano, A. *Organometallics*, **1985**, *4*, 1275. (q) Trost, B. M.; Keinan, E. *J. Org. Chem.* **1979**, *44*, 3451. (r) Takahashi, K.; Miyake, A.; Hata, G. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 230.

(9) For Ru, see: (a) Morisaki, Y.; Kondo, T.; Mitsudo, T. *Organometallics* **1999**, *18*, 4742. (b) Kondo, T.; Ono, H.; Satake, N.; Mitsudo, T.; Watanabe, Y. *Organometallics* **1995**, *14*, 1945. For Rh, see: (c) Evans, P. A.; Robinson, J. E.; Nelson, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 6761. (d) Evans, P. A.; Robinson, J. E. *Org. Lett.* **1999**, *1*, 1929. For Fe, see: (e) Enders, E.; Finkam, M. *Synlett* **1993**, 401. For Ni, see: (f) Bricout, H.; Carpentier, J.-F.; Mortreux, A. *Tetrahedron* **1998**, *54*, 1073. (g) Bricout, H.; Carpentier, J.-F.; Mortreux, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1863.

(10) (a) Takeuchi, R.; Kashio, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 263. (b) Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998**, *120*, 8647. (c) Takeuchi, R.; Tanabe, K. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 1975. (d) Takeuchi, R. *Polyhedron* **2000**, *19*, 557.

(11) Solvents affected the regio- and enantioselectivity of palladium complex-catalyzed allylic substitution. See: Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1999**, *121*, 4545.

(12) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319.

Table 2. Effect of the Ratio of P/Ir[a]

entry	P/Ir	time/h	yield[b]/%	ratio[c] **3a**/**4a** (*E*/*Z*)
1	0	3	78	77/23 (100/0)
2	1	2	89	92/8 (100/0)
3	2	2	84	92/8 (100/0)
4	3	9	75	11/89 (100/0)

[a] A mixture of **1a** (2 mmol), piperidine (**2a**) (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$, and EtOH (4.4 mL) was stirred under refluxing conditions. [b] Isolated yield. [c] Determined by GLC and NMR.

Table 3. Reaction of **1a** with **2**[a]

entry	amine **2**	time/h	product	yield[b]/%	ratio[c] **3**/**4** (*E*/*Z*)
1	**2b**, pyrrolidine	3	**3b**, **4b**	95	96/4 (100/0)
2	**2c**, morpholine	2	**3c**, **4c**	92	92/8 (100/0)
3	**2d**, cyclopentylamine	2	**3d**, **4d**	93	96/4 (100/0)
4	**2e**, *n*-butylamine	5	**3e**, **4e**	79	95/5 (100/0)
5	**2f**, diethylamine	3	**3f**, **4f**	75	65/35 (100/0)
6	**2g**, *tert*-butylamine	2	**3g**, **4g**	92	81/19 (100/0)
7	**2h**, benzylamine	7	**3h**, **4h**	89	96/4 (100/0)

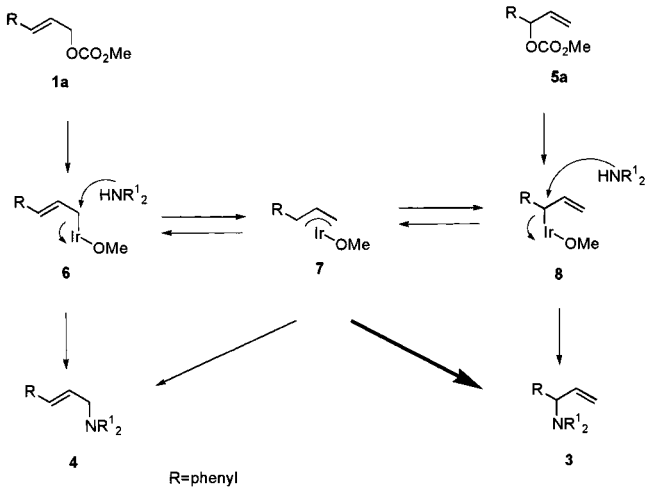
[a] A mixture of **1a** (2 mmol), amine (**2**) (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and EtOH (4.4 mL) was stirred under reflux. [b] Isolated yield. [c] Ratios determined by GLC and NMR.

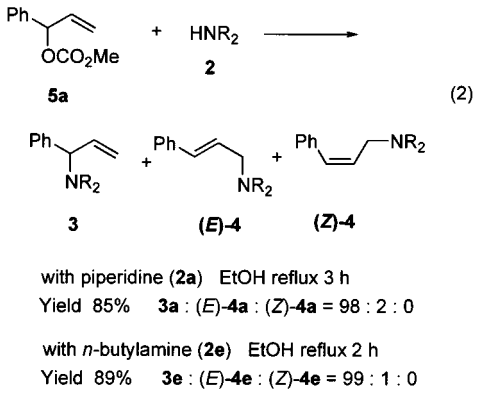
this species would lead an amine to the unsubstituted allylic terminus to give linear amine (*E*)-**4a**.

Carbonate **1a** reacted with 3 equiv of amine (**2**) under refluxing EtOH to give **3** and (*E*)-**4** as an inseparable mixture. The results are summarized in Table 3. In all cases, no (*Z*)-**4** was obtained. Both secondary and primary amines could be used. The yields were generally good, but the selectivities depended on the amine used. The reactions of **1a** with pyrrolidine (**2b**), morpholine (**2c**), cyclopentylamine (**2d**), *n*-butylamine (**2e**), and benzylamine (**2h**) gave **3b**−**e**,**h** in selectivities of 92−96% (entries 1−4 and 7). Reactions with primary amines (**2d**,**e**,**g**,**h**) gave monoallylation products exclusively. It is well-known that palladium complex-catalyzed allylic amination with a primary amine gives a monoallylation product and a considerable amount of a diallylation product.[8e,f,l,q] For example, the reaction of **1b** with 2 equiv of *n*-butylamine (**2e**) has been reported to give a monoallylation product in 80% yield and a diallylation product in 11% yield.[8l] An iridium complex has an advantage over a palladium complex with regard to the control of monoallylation and diallylation, in that no diallylation product was obtained. Diethylamine (**2f**) gave a lower selectivity for **3** than cyclic secondary amines (**2a**−**c**). The selectivity of **3f** was 65% (entry 5). The basicities of these amines are almost the same (piperidine, $pK_a = 11.1$; *N*,*N*′-diethylamine, $pK_a = 10.8$).[13] The difference in selectivity is likely due to the steric effect of amines. The cone angle is generally used to measure the steric bulk of a ligand. The cone angle of diethylamine (125°) is slightly larger than that of piperidine (121°).[14] To examine whether this small difference in the cone angle affects the regioselectivity, we examined the reaction with *tert*-butylamine (**2g**), which has a cone angle of 123°.[14] The reaction with *tert*-butylamine (**2g**) gave an 81:19 mixture of **3g** and (*E*)-**4g** in 92% yield (entry 6). The selectivity of **3** decreased as the steric bulk of the amine increased (piperidine > *tert*-butylamine > diethylamine).

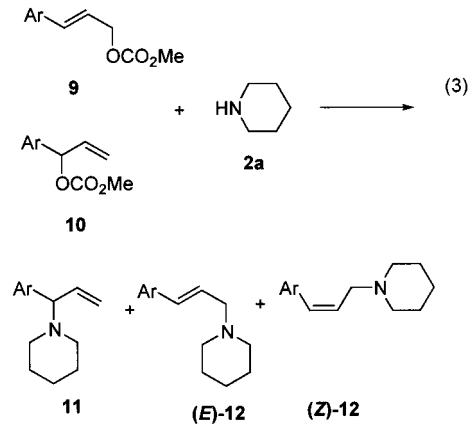
1-Phenyl-2-propenyl carbonate (**5a**), which is a regioisomeric carbonate of **1a**, reacted with both a secondary amine and a primary amine to give branch amine **3** (eq 2). These results strongly suggest the intermediacy of a π-allyl iridium complex.

Scheme 2





Iridium complex-catalyzed allylic alkylations of (*E*)-3-monosubstituted-2-propenyl acetates and 1-monosubstituted-2-propenyl acetates gave the same product distribution.[10] This allylic amination gave a slightly different product distribution. Carbonate **5a** gave a higher selectivity of **3** than **1a**. Considering that the S_N2 substitution of the σ-allyl iridium intermediate with an amine is a minor reaction path reasonably explained this difference. A plausible mechanism is outlined in Scheme 2. The major reaction path of both reactions gives **3** and a small amount of **4**. The minor reaction path of the reaction of **1a** and **5a** gives a different product. S_N2 substitution of σ-allyl iridium intermediate **6** with an amine gives **4**, whereas the same reaction of **8** with an amine gives **3**. As a consequence, the reaction of **5a** is more selective for **3** than that of **1a**.



(13) *Lange's Handbook of Chemistry*, 13th ed.; Dean, J. A., Ed.; McGraw-Hill: New York, 1985; section 5.

(14) For cone angle of amines, see: Seligson, A. L.; Trogler, W. C. *J. Am. Chem. Soc*. **1991**, *113*, 2520.

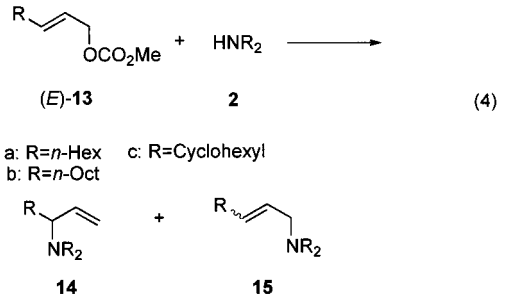
Table 4. Reaction of **9** and **10** with **2a**[a]

entry	substrate	time/h	products	yield[b]/%	ratio[c] **11**/**12** (*E*/*Z*)
1	**9a**, Ar = 4-methylphenyl	2	**11a**, **12a**	80	94/6 (100/0)
2	**10a**, Ar = 4-methylphenyl	3	**11a**, **12a**	85	99/1 (100/0)
3	**9b**, Ar = 4-fluorophenyl	3	**11b**, **12b**	91	95/5 (100/0)
4	**10b**, Ar = 4-fluorophenyl	6	**11b**, **12b**	83	99/1 (100/0)
5	**9c**, Ar = 2-thienyl	2	**11c**, **12c**	89	95/5 (100/0)
6	**10c**, Ar = 2-thienyl	6	**11c**, **12c**	80	97/3 (100/0)

[a] A mixture of **9** or **10** (2 mmol), piperidine (**2a**) (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and EtOH (4.4 mL) was stirred under reflux. [b] Isolated yield. [c] Ratios determined by GLC and NMR.

Allylic amination of (*E*)-3-aryl-2-propenyl carbonate (**9**) and 1-aryl-2-propenyl carbonate (**10**) was examined (eq 3). The results are summarized in Table 4. The nature of the aryl group did not affect the yield and the selectivity.

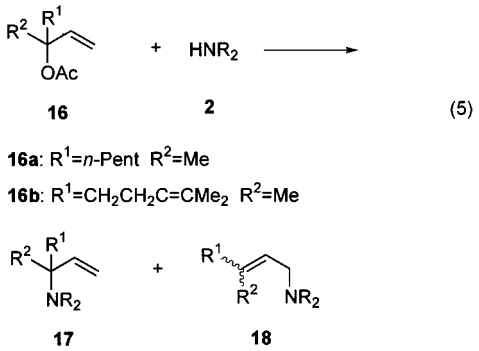
Allylic Amination of (*E*)-2-Alkenyl Carbonates. Allylic amination of (*E*)-2-alkenyl carbonate ((*E*)-**13**) was less regioselective for the branch amine (**14**) than that of (*E*)-3-aryl-2-propenyl carbonate (eq 4). The results are summarized in Table 5. The yields of the products were generally good. The choice



of catalyst and solvent was important for obtaining a branch amine in high selectivity. The reaction of (*E*)-**13a** with pyrrolidine (**2b**) using $[Ir(COD)OMe]_2$ under refluxing acetone gave **14ab** in 85% selectivity (entry 2). MeCN was also a good solvent and gave **14ab** in 84% selectivity (entry 3). Because piperidine (**2a**) is more sterically demanding than pyrrolidine (**2b**),[14] the reaction with piperidine (**2a**) decreased the selectivity of the branch amine (**14aa**) slightly (entry 4). Cyclopentylamine (**2d**), *n*-butylamine (**2e**), and aniline (**2i**) gave better selectivity of the branch amine than pyrrolidine (**2b**). Branch amines **14ad**, **14ae**, and **14ai** were obtained in selectivies of 92−95% (entries 5−7). It is noteworthy that the diallylation of a primary amine was not observed.

Oxidative addition of (*E*)-2-alkenyl carbonate gives a 1-alkyl π-allyl iridium intermediate. Because an alkyl group is more electron-donating than an aryl group,[15] an allylic terminus substituted with an alkyl group is less electron-deficient than that substituted with an aryl group. Thus, the amination of a 1-alkyl π-allyl iridium intermediate is less regioselective for the branch amine than that of a 1-aryl π-allyl iridium intermediate.

Allylic Amination of 1,1-Disubstituted-2-propenyl Acetates. Acetate **1b** was less reactive than carbonate **1a**. The reaction of **1a** with 3 equiv of piperidine (**2a**) was complete under refluxing EtOH for 2 h. On the other hand, the reaction of **1b** with piperidine (**2a**) under the same reaction conditions was complete in 9 h to give a 90:10 mixture of **3a** and (*E*)-**4a** in 80% yield. 1-Phenyl-2-propenyl acetate (**5b**), which is a regioisomeric acetate of **1b**, showed a reactivity comparable to that of carbonate **1a**. Acetate **5b** reacted with piperidine (**2a**) under refluxing EtOH for 3 h to give a 98:2 mixture of **3a** and (*E*)-**4a** in 88% yield.[16] This result prompted us to examine the allylic amination of 1,1-disubstituted-2-propenyl acetate (**16**) (eq 5). Allylic amination at the disubstituted allylic terminus would give an α,α-disubstituted allylic amine. A general route to such amines is the addition of organometallic reagents to ketimines and their iminium salts.[17] However, when ketimines have an α-hydrogen, the addition of organometallic reagents to an imine carbon is problematic, because α-deprotonation competes with the addition reaction.[18] A more widely applicable method for the synthesis of an α,α-disubstituted allylic amine is needed. Regioselective allylic amination at the disubstituted allylic terminus should be a useful alternative route.



Allylic amination of 1,1-disubstituted-2-propenyl acetates (**16**) was examined. The results are summarized in Table 6. 1-Methyl-1-(*n*-pentyl)-2-propenyl acetate (**16a**) smoothly reacted with piperidine (**2a**) under refluxing EtOH for 4 h to give **17aa** as a single product in 76% yield (entry 1). The reaction occurred with perfect regioselectivity at the disubstituted allylic terminus. No **18aa** was obtained. The use of EtOH was essential for this reaction. The same reaction under refluxing dioxane for 24 h gave no amination product, with the recovery of **16a** in a quantitative yield. Similarly, acetate **16a** reacted with pyrrolidine (**2b**) and aniline (**2i**) to give **17ab** and **17ai** exclusively in yields of 70 and 77%, respectively (entries 2 and 4). The reaction of **16a** with *n*-butylamine (**2e**) gave **17ae** exclusively, in a somewhat decreased yield compared to the yields of **17aa**, **17ab**, and **17ai** (entry 3). Linalyl acetate (**16b**) reacted with piperidine (**2a**) to give **17b** exclusively in 76% yield (entry 4). $Pd(PPh_3)_4$-catalyzed allylic amination of 1,1-disubstituted allylic nitro compounds with piperidine (**2a**) has been reported to give both an (*E*)-linear allylic amine and an α,α-

(15) The group electronegativity of an aryl group is bigger than that of an alkyl group. See: Inamoto, N.; Masuda, S. *Chem. Lett*. **1982**, 1003.

(16) The steric effect of the alkene in the allylic system affects the coordination of a transition metal complex prior to oxidative addition. Because of this effect, acetate **5b**, a terminal alkene, is more reactive than acetate **1b**, an internal alkene.

(17) (a) Cogan, D. A.; Ellman, J. A. *J. Am. Chem. Soc*. **1999**, *121*, 268. (b) Spero, D. M.; Kapadia, S. R. *J. Org. Chem*. **1997**, *62*, 5537. (c) Ciganek, E. *J. Org. Chem*. **1992**, *57*, 4521.

(18) (a) Whitesell, J. K.; Whitesell, M. A. *J. Org. Chem*. **1977**, *42*, 377. (b) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc*. **1963**, *85*, 2178. (c) In the reaction of the *N*-cyclohexylimine of 2-methylcyclohexanone with *n*-butyllithium, it has been reported that selective α-deprotonation occurs. See: Hosomi, A.; Araki, Y.; Sakurai, H. *J. Am. Chem. Soc*. **1982**, *104*, 2081.

Table 5. Reaction of **13** with **2**[a]

entry	substrate	amine	catalyst	solvent	conditions	product	yield[b]/%	ratio[c] **14**/**15** (*E*/*Z*)
1	**13a**, R = *n*-hexyl	**2b**, pyrrolidine	$[Ir(COD)Cl]_2$	EtOH	reflux 3 h	**14ab**, **15ab**	85	65/35 (100/0)
2	**13a**, R = *n*-hexyl	**2b**, pyrrolidine	$[Ir(COD)OMe]_2$	acetone	reflux 2 h	**14ab**, **15ab**	94	85/15 (100/0)
3	**13a**, R = *n*-hexyl	**2b**, pyrrolidine	$[Ir(COD)OMe]_2$	MeCN	reflux 4 h	**14ab**, **15ab**	86	84/16 (100/0)
4	**13a**, R = *n*-hexyl	**2a**, piperidine	$[Ir(COD)OMe]_2$	acetone	reflux 3 h	**14aa**, **15aa**	87	81/19 (100/0)
5[d]	**13a**, R = *n*-hexyl	**2d**, cyclopentylamine	$[Ir(COD)OMe]_2$	MeCN	reflux 24 h	**14ad**, **15ad**	76	92/8 (100/0)
6[d]	**13a**, R = *n*-hexyl	**2e**, *n*-butylamine	$[Ir(COD)OMe]_2$	MeCN	reflux 24 h	**14ae**, **15ae**	70	95/5 (100/0)
7[e]	**13a**, R = *n*-hexyl	**2i,** aniline	$[Ir(COD)OMe]_2$	EtOH	reflux 2 h	**14ai**, **15ai**	95	93/7 (100/0)
8	**13b**, R = *n*-octyl	**2b**, pyrrolidine	$[Ir(COD)OMe]_2$	MeCN	reflux 3 h	**14bb**, **15bb**	92	86/14 (100/0)
9	**13c**, R = cyclohexyl	**2b**, pyrrolidine	$[Ir(COD)OMe]_2$	acetone	reflux 3 h	**14cb**, **15cb**	85	84/16 (100/0)
10[f]	**13c**, R = cyclohexyl	**2i,** aniline	$[Ir(COD)OMe]_2$	EtOH	reflux 47 h	**14ci**, **15ci**	96	91/9 (100/0)

[a] A mixture of **13** (2 mmol), **2** (6 mmol), Ir complex (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and solvent (4.4 mL) was stirred under argon. [b] Isolated yield. [c] Ratios determined by GLC and NMR. [d] Compound **2** (12 mmol), $[Ir(COD)OMe]_2$ (0.08 mmol), $P(OPh)_3$ (0.32 mmol), solvent (4.0 mL). [e] Aniline (**2i)** (3 mmol), $[Ir(COD)OMe]_2$ (0.02 mmol), $P(OPh)_3$ (0.08 mmol), EtOH (4.0 mL). [f] Aniline (**2i)** (4 mmol).

Table 6. Reaction of **16** with **2**[a]

entry	substrate	amine	time/h	yield[b]/%	product	ratio[c]
1	**16a**, R^1 = *n*-pentyl, R^2 = Me	**2a**, piperidine	4	76	**17aa**, **18aa**	100/0
2	**16a**, R^1 = *n*-pentyl, R^2 = Me	**2b**, pyrrolidine	4	70	**17ab**, **18ab**	100/0
3	**16a**, R^1 = *n*-pentyl, R^2 = Me	**2e**, *n*-butylamine	16	59	**17ae**, **18ae**	100/0
4	**16a**, R^1 = *n*-pentyl, R^2 = Me	**2i**, aniline	11	77	**17ai**, **18ai**	100/0
5	**16b**, $R^1 = Me_2C{=}CHCH_2CH_2$, R^2 = Me	**2a**, piperidine	4	76	**17b**, **18b**	100/0

[a] A mixture of **16** (2 mmol), amine (**2**) (6 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol) and EtOH (4.4 mL) was stirred under reflux. [b] Isolated yield. [c] Determined by GLC and NMR.

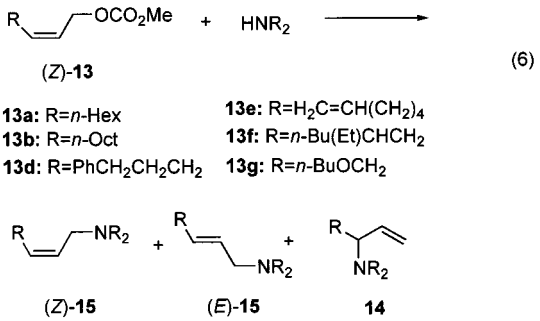
disubstituted allylic amine.[19] The selectivity of an α,α-disubstituted allylic amine was moderate. Only iridium complex-catalyzed allylic amination gave an α,α-disubstituted allylic amine as a single product.

Allylic Amination of (*Z*)-2-Alkenyl Carbonates.[20] Allylic amination of (*Z*)-2-alkenyl carbonate ((*Z*)-**13a**) was examined (eq 6). Palladium complex-catalyzed allylic amination of (*Z*)-2-alkenyl acetate gave (*E*)-linear allylic amine,[8q] because the anti π-allyl palladium intermediate easily isomerized to a syn π-allyl palladium intermediate[21] prior to nucleophilic attack by an amine. The retention of *Z* stereochemistry in the palladium complex-catalyzed allylic substitution of (*Z*)-2-alkenyl esters has been difficult to achieve. Limited examples have been reported,[22] and these have had to be carried out at −78 °C to retain *Z* stereochemistry. We previously reported that iridium complex-catalyzed allylic alkylation of (*Z*)-2-hexenyl acetate gave a (*Z*)-linear product in 70% selectivity.[10b] Extending this methodology, we have achieved the first complete retention of *Z* stereochemistry in allylic amination. The reaction of (*Z*)-2-nonenyl carbonate ((*Z*)-**13a**) with piperidine (**2a**) was carried out in various solvents. The results are summarized in Table 7. The solvent of choice was $MeNO_2$. The reaction under refluxing $MeNO_2$ gave products in 91% yield (entry 1). The selectivity of (*Z*)-**15aa** was 91%. No (*E*)-**15aa** was obtained. The reaction at 50 °C increased the selectivity of (*Z*)-**15aa** up to 94% (entry 2). Decreasing the amount of piperidine (**2a**) decreased the yield of the products (entry 3). The use of EtOH gave products in 93% yield, but the selectivity of (*Z*)-**15aa** decreased to 88% (entry 4). The reaction in acetone required a longer reaction time (entry 5). THF and CH_2Cl_2 were less efficient than $MeNO_2$ (entries 6 and 7).

Table 7. Solvent Effect on the Reaction of (*Z*)-**13a** with **2a**[a]

entry	solvent	conditions	yield[b]/%	ratio[c](*Z*)-**15aa**/(*E*)-**15aa**/**14aa**
1	$MeNO_2$	reflux 3 h	91	91/0/9
2	$MeNO_2$	50 °C 16 h	87	94/0/6
3[d]	$MeNO_2$	50 °C 16 h	73	93/0/7
4	EtOH	reflux 2 h	93	88/0/12
5	acetone	reflux 47 h	82	91/0/9
6	THF	reflux 24 h	14	92/0/8
7	CH_2Cl_2	reflux 24 h	65	93/0/7

[a] A mixture of (*Z*)-**13a** (2 mmol), piperidine (**2a**) (10 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and solvent (4.1 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC and NMR. [d] Piperidine (**2a**) (6 mmol).



The reaction of (*Z*)-**13a** with various amines (**2**) in $MeNO_2$ was examined. The results are summarized in Table 8. Allylic amines (*Z*)-**15aa**−**ac**,**ae**,**af** were obtained in selectivities of 79−97%. No (*E*)-isomer was obtained in any of the cases. The structure of the amine strongly affected the yield of the products. The reaction of (*Z*)-**13a** with a secondary amine gave the corresponding product in good yield (entries 1−3 and 5). In contrast to the results obtained with secondary amines, the reaction of (*Z*)-**13a** with *n*-butylamine (**2e**) had a decreased yield

(19) (a) Tamura, R.; Hegedus, L. S. *J. Am. Chem. Soc*. **1982**, *104*, 3727. (b) Tamura, R.; Kai, Y.; Kakihana, M.; Hayashi, K.; Tsuji, M.; Nakamura, T.; Oda, D. *J. Org. Chem*. **1986**, *51*, 4375.

(20) A preliminary work described here, see: Takeuchi, R.; Shiga, N. *Org. Lett*. **1999**, *1*, 265.

(21) (a) Sjögren, M.; Hansson, S.; Norrby, P.; Åkermark, B.; Cucciolito, M. E.; Vitagliano, A. *Organometallics* **1992**, *11*, 3954. (b) Åkermark, B.; Hansson, S.; Vitagliano, A. *J. Am. Chem. Soc*. **1990**, *112*, 4587. (c) Faller, J. W.; Mattina, M. *Inorg. Chem*. **1972**, *11*, 1296. (d) Faller, J. W.; Thomsen, M. E.; Mattina, M. J. *J. Am. Chem. Soc*. **1971**, *93*, 2642.

(22) (a) Kazmaier, U.; Zumpe, F. L. *Angew. Chem., Int. Ed. Engl*. **2000**, *39*, 802. (b) Hutzinger, M. W.; Oehlschlager, A. C. *J. Org. Chem*. **1991**, *56*, 2918.

Table 8. Reaction of (*Z*)-**13** with **2**[a]

entry	substrate	amine	conditions	product	yield/%[b]	ratio[c] (*Z*)-**15**/(*E*)-**15**/ **14**
1	(*Z*)-**13a**, R = *n*-hexyl	**2a**, piperidine	50 °C 16 h	**15aa**, **14aa**	87	94/0/6
2	(*Z*)-**13a**, R = *n*-hexyl	**2b**, pyrrolidine	50 °C 3 h	**15ab**, **14ab**	80	94/0/6
3	(*Z*)-**13a**, R = *n*-hexyl	**2c**, morpholine	50 °C 25 h	**15ac**, **14ac**	80	88/0/12
4[d]	(*Z*)-**13a**, R = *n*-hexyl	**2e**, *n*-butylamine	50 °C 20 h	**15ae**, **14ae**	56	79/0/21
5	(*Z*)-**13a**, R = *n*-hexyl	**2f**, diethylamine	50 °C 21 h	**15af**, **14af**	69	97/0/3
6	(*Z*)-**13b**, R = *n*-octyl	**2a,** piperidine	50 °C 22 h	**15ba**, **14ba**	86	94/0/6
7	(*Z*)-**13d**, R = $Ph(CH_2)_3$	**2a,** piperidine	50 °C 18 h	**15d**, **14d**	89	92/0/8
8[e]	(*Z*)-**13e**, R = $H_2C{=}CH(CH_2)_4$	**2a,** piperidine	50 °C 3 h	**15e**, **14e**	89	100/0/0
9[e]	(*Z*)-**13f**, R = *n*-BuEtCHCH_2	**2a**, piperidine	50 °C 5 h	**15f**, **14f**	70	100/0/0
10	(*Z*)-**13g**, R = *n*-BuOCH_2	**2a,** piperidine	50 °C 7 h	**15g**, **14g**	95	99/0/1

[a] A mixture of (*Z*)-**13** (2 mmol), amine (**2**) (10 mmol), $[Ir(COD)Cl]_2$ (0.04 mmol), $P(OPh)_3$ (0.16 mmol), and $MeNO_2$ (4.1 mL) was stirred under argon. [b] Isolated yield. [c] Determined by GLC and NMR. [d] $[Ir(COD)Cl]_2$ (0.08 mmol), $P(OPh)_3$ (0.32 mmol). [e] Piperidine (**2a**) (5 mL) was used as a solvent.

(entry 4). A rather bulky amine is necessary to obtain (*Z*)-**15** in high yield.[23]

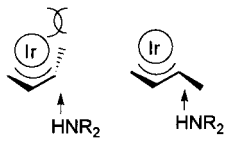
As shown in Table 8, (*Z*)-**13b**,**d**−**g** were successfully reacted with piperidine to give (*Z*)-**15ba**,**d**−**g** with selectivities of 92−100% (entries 6−10). No (*E*)-isomer was obtained. Terminal alkene and alkoxy functionalities were tolerated in the allylic amination (entries 8 and 10). Allylic amine (*Z*)-**15g** was obtained with 99% selectivity (entry 10).

Discussion

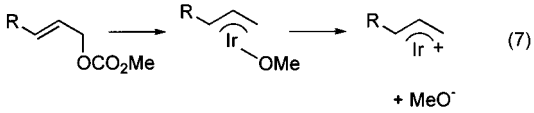
Regioselectivity. The electron-withdrawing property of $P(OPh)_3$ plays a crucial role in the high selectivity of a branch amine. On the basis of a previous study,[10b,d] a π-allyl iridium intermediate is considered to be a monophosphite species in which $P(OPh)_3$ coordinates with the metal trans to the substituted allylic terminus. The carbonium ion character of the substituted allylic terminus enhanced by the electron-withdrawing property of $P(OPh)_3$ directs an amine to this position to give a branch amine.

Allylic amination of (*Z*)-2-alkenyl carbonate gave a (*Z*)-linear amine. When an amine approached the substituted allylic terminus of an anti π-allyl iridium intermediate, the substituent and iridium moiety are close together to increase the steric repulsion (Scheme 3). Thus, the transition state of the amination at the substituted allylic terminus of an anti π-allyl iridium intermediate is less stable than that of a syn π-allyl iridium intermediate. Therefore, amination of an anti π-allyl iridium intermediate preferentially occurs at the unsubstituted allylic terminus to give a (*Z*)-linear allylic amine.

Scheme 3



Mechanistic Consideration of the Solvent Effect. In this allylic amination, the use of a polar solvent such as EtOH is essential to obtain a product in high yield. This effect of a polar solvent may be explained as follows. A neutral π-allyl Ir intermediate formed by oxidative addition of an allylic carbonate can dissociate methoxide with the aid of a polar solvent to give a cationic π-allyl Ir intermediate (eq 7).[24] Because a cationic π-allyl intermediate is more reactive to a nucleophile than a neutral π-allyl intermediate, the reaction in a polar solvent increases the yield of an amination product. If this hypothesis is correct, methoxide will be formed by the dissociation from a neutral π-allyl Ir intermediate. Thus, allylic alkylation with diethyl malonate[25] in EtOH may give an alkylation product without using a base. To probe this hypothesis, we examined the reaction of **1a** with diethyl malonate in the presence of a catalytic amount of $[Ir(COD)Cl]_2$ and $P(OPh)_3$ (Ir atom 4 mol %, P/Ir = 2) under refluxing EtOH for 24 h. No alkylation product was obtained. The starting material was recovered in quantitative yield. This result strongly suggests that a π-allyl Ir intermediate is neutral and does not dissociate methoxide.



(7)

When the substrate and nucleophile in an S_N2 reaction are both neutral, the charge density in the transition state is greater than that of the initial reactants. A polar solvent can stabilize the transition state to enhance an S_N2 reaction.[26] It is well-known that oxidative addition to a low-valent transition metal complex proceeds via an S_N2-type mechanism.[27] Oxidative addition to an Ir (+1) complex in a polar solvent has been reported to be enhanced by stabilization of the transition state.[28] Because of this solvent effect, oxidative addition in this reaction might be enhanced. Furthermore, a polar solvent plays an important role in the nucleophilic attack by an amine to a π-allyl Ir intermediate. As described above, a π-allyl Ir intermediate generated in this reaction is a neutral species. The transition state of the nucleophilic attack is more polar than the initial reactants. As a consequence, the nucleophilic attack by an amine to a π-allyl Ir intermediate is also enhanced by a polar solvent. Thus, this allylic amination in a polar solvent is enhanced to give an amination product in high yield.

Comparison with Ruthenium, Rhodium, and Nickel Complex-Catalyzed Allylic Amination. A ruthenium complex

(23) The decrease in the yield of (*Z*)-**15** may be ascribed to the side reaction where carbonate (*Z*)-**13a** undergoes nucleophilic attack of an amine to the carbonyl carbon.

(24) It has been reported that a cationic rhodium complex was formed in a polar solvent such as alcohol or $MeNO_2$ by the dissociation of an anionic ligand from a neutral rhodium complex. See: Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

(25) Pd complex-catalyzed allylic alkylation under neutral conditions is well-known. See: (a) Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, T.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523. (b) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140.

(26) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Germany, 1988; p 137.

(27) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, 1987; p 306. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, 2001; p 156. (c) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*, 2nd ed.; Wiley-VCH: 1997; p 158.

(28) (a) Wilson, M. R.; Liu, H.; Prock, A.; Giering, W. P. *Organometallics* **1993**, *12*, 2044. (b) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511.

has been reported to give a branch amine predominantly. Ruthenium complex-catalyzed allylic amination of (*E*)-**1a** with piperidine (**2a**) gave **3a** in 84% selectivity.[9b] Similarly, rhodium complex-catalyzed allylic amination of 1-(*n*-propyl)-2-propenyl carbonate gave a branch amine in high selectivity.[9c,d] In the rhodium case, lithium *N*-tosyl amide was used as a nucleophile to obtain products in high yield. The use of an amine gives a modest yield of products. Although the ruthenium complex and the rhodium complex favor the formation of a branch amine, the iridium complex shows branch amine selectivity better or comparable to those of the ruthenium complex and the rhodium complex. On the other hand, the regioselectivity of nickel complex-catalyzed allylic amination is similar to that of palladium complex-catalyzed allylic amination. A nickel complex has been reported to give a linear amine predominantly.[9f]

In conclusion, we have realized highly selective allylic amination by using an iridium complex as a catalyst. The selectivities described here have not been achieved in previous studies with palladium. Iridium complex-catalyzed allylic amination represents a new method for the synthesis of various allylic amines.

Experimental Section

Materials. All reagents and solvents were dried and purified before use by the usual procedures. Allylic esters were prepared by the reaction of the corresponding alcohols with acetyl chloride, acetic anhydride, or methyl chloroformate. Linalyl acetate was purchased. (*E*)-3-Phenyl-2-propen-1-ol, (*E*)-2-nonen-1-ol, (*E*)-2-undecen-1-ol, (*Z*)-2-nonen-1-ol, and (*Z*)-2-buten-1,4-diol were purchased. 1-Phenyl-2-propen-1-ol, 1-(4-methylphenyl)-2-propen-1-ol, 1-(4-fluorophenyl)-2-propen-1-ol, and 1-(2-thienyl)-2-propen-1-ol were prepared by the reaction of vinylmagnesium bromide with the corresponding aldehyde. 3-Methyl-1-octen-3-ol was prepared by the reaction of vinylmagnesium bromide with 2-heptanone. (*Z*)-2-Nonen-1-ol, (*Z*)-2-undecen-1-ol, (*Z*)-6-phenyl-2-hexen-1-ol, (*Z*)-2,8-nonadien-1-ol, (*Z*)-5-ethyl-2-nonen-1-ol, and (*Z*)-3-phenyl-2-propen-1-ol were prepared by the hydrogenation of the corresponding 2-alkyn-1-ol. (*Z*)-2-Nonyn-1-ol, (*Z*)-2-undecyn-1-ol, and (*Z*)-6-phenyl-2-hexyn-1-ol were prepared by the reaction of 1-alkynyllithium with paraformaldehyde.[29] (*Z*)-2-Nonyn-8-en-1-ol and (*Z*)-5-ethyl-2-nonyn-1-ol were prepared by the reaction of dilithiated propargyl alcohol with the corresponding alkyl bromide in liquid ammonia.[30] (*Z*)-4-Butoxy-2-buten-1-ol was prepared by the reaction of monosodio-(*Z*)-2-buten-1,4-diol with 1-iodobutane. $[Ir(COD)Cl]_2$,[31] $[Ir(COD)_2]BF_4$,[32] and $[Ir(COD)OMe]_2$[33] were prepared according to the published method. Lindlar catalyst was purchased from Wako chemicals. Amines, 4-methylbenzaldehyde, 4-fluorobenzaldehyde, 2-thiophenaldehyde, cyclohexanecarboxaldehyde, triethyl phosphonoacetate, and DIBALH (diisobutylaluminum hydride) were purchased.

General Methods. ^{1}H NMR and ^{13}C NMR spectra were measured on a JEOL EX-270 spectrometer or a Bruker AVANCE−400 spectrometer using Me_4Si as an internal standard. Samples were dissolved in $CDCl_3$ or benzene-d_6 solutions. GC analyses were performed on a Shimadzu GC-14A by using 3 mm × 2 m glass columns packed with either 5% PEG-HT on 60/80 mesh chromosorb w AW-DMCS, 5% PEG-HT + 1% KOH on 60/80 mesh uniport HP, or 5% OV-17 on 60/80 mesh chromosorb w AW-DMCS. Column chromatography was carried out on 70−230 mesh silica gel (Merck, Silica Gel 60). Elemental analyses were performed at the Microanalytical Center of Kyoto University.

(*E*)-3-(4-Methylphenyl)-2-propen-1-ol. To a THF (60 mL) solution of 4-methylbenzaldehyde (4.806 g, 40 mmol) and triethyl phosphonoacetate (8.968 g, 40 mmol) was added an ethanol (20 mL) solution of sodium ethoxide (prepared from 60 mmol of Na) at −30 °C. The reaction mixture was stirred for 4 h at room temperature. Water was added, and the mixture was extracted with ether. The ether solution was dried over $MgSO_4$ and evaporated in vacuo. Distillation of the residue gave ethyl 3-(4-methylphenyl)-2-propenoate (6.088 g, 32 mmol). To 0.95 M diisobutylaluminum hydride in *n*-hexane (68 mL) was added dropwise 3-(4-methylphenyl)-2-propenoate (6.088 g, 32 mmol). The mixture was stirred at −78 °C for 2 h. The cooling bath was removed, and the mixture was allowed to warm to room temperature. The mixture was poured into water, and the aqueous layer was extracted with ether. The combined organic layers were dried with $MgSO_4$. The solvent was evaporated in vacuo. Column chromatography (*n*-hexane/AcOEt = 90/10) of the residue gave (*E*)-3-(4-methylphenyl)-2-propen-1-ol, yield 4.078 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (br, 1H), 2.32 (s, 3H), 4.26 (dd, J = 5.8, 1.4 Hz, 2H), 6.27 (dt, J = 15.9, 5.8 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 63.6, 126.3 (2C), 127.4, 129.2 (2C), 131.0, 133.8, 137.4.

(*E*)-3-(4-Fluorophenyl)-2-propen-1-ol was prepared similarly to give (*E*)-3-(4-methylphenyl)-2-propen-1-ol from 4-fluorobenzaldehyde and triethyl phosphonoacetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (br, 1H), 4.28 (d, J = 5.6 Hz, 2H), 6.24 (dt, J = 15.9, 5.6 Hz, 1H), 6.54 (d, J = 15.9 Hz, 1H), 6.98 (t, J = 8.7 Hz, 2H), 7.30 (dd, J = 8.7, 5.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.3, 115.4 (d, J_{C-F} = 21.6 Hz, 2C), 127.9 (d, J_{C-F} = 8.0 Hz, 2C), 128.2 (d, J_{C-F} = 1.7 Hz), 129.8, 132.8 (d, J_{C-F} = 3.2 Hz), 162.2 (d, J_{C-F} = 246.8 Hz).

(*E*)-3-(2-Thienyl)-2-propen-1-ol was prepared similarly to give (*E*)-3-(4-methylphenyl)-2-propen-1-ol from 2-thiophenaldehyde and triethyl phosphonoacetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (br, 1H), 4.21 (d, J = 5.7 Hz, 2H), 6.15 (dt, J = 15.7, 5.7 Hz, 1H), 6.69 (d, J = 15.7 Hz, 1H), 6.91−6.94 (m, 2H), 7.12−7.13 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 63.0, 124.0, 124.2, 125.6, 127.2, 128.1, 141.7.

(*E*)-3-Cyclohexyl-2-propen-1-ol. To a solution of NaH (1.056 g, 44 mmol) in dimethoxyethane (80 mL) was added triethyl phosphonoacetate (10.761 g, 48 mmol) dropwise at 0 °C. The mixture was stirred at 0 °C for 30 min, and the mixture was gradually warmed to room temperature. Cyclohexanecarboxaldehyde (4.487 g, 40 mmol) was added, and the resulting mixture was stirred at room temperature for 3 h. Water was added, and the mixture was extracted with ether. The ether solution was dried with $MgSO_4$ and evaporated in vacuo. Column chromatography (*n*-hexane/AcOEt = 98/2) of the residue gave ethyl (*E*)-3-cyclohexyl-2-propenoate, yield 5.249 g (72%). Medium-pressure column chromatography of this mixture gave pure (*E*)-3-cyclohexyl-2-propenoate. Reduction of (*E*)-3-cyclohexyl-2-propenoate by DIBALH gave (*E*)-3-cyclohexyl-2-propen-1-ol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02−1.32 (m, 5H), 1.62−1.79 (m, 6H), 1.93−2.00 (m, 1H), 4.07 (d, J = 5.0 Hz, 2H), 5.57 (dt, J = 15.6, 5.0 Hz, 1H), 5.64 (dd, J = 15.6, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9 (2C), 26.1, 32.7 (2C), 40.2, 63.8, 126.3, 139.0.

Allylic Amination of Allylic Esters. A typical procedure is described (Table 1, entry 1). A mixture of methyl (*E*)-3-phenyl-2-propenyl carbonate, **1a**, (384 mg, 2.0 mmol), triphenyl phosphite (49.6 mg, 0.16 mmol), $[Ir(COD)Cl]_2$ (26.9 mg, 0.04 mmol), piperidine (511 mg, 6.0 mmol), and EtOH (4.4 mL) was stirred under refluxing EtOH for 2 h under an Ar atmosphere. The progress of the reaction was monitored by GLC. After **1a** was consumed, the reaction mixture was diluted with ether. The ethereal solution was extracted with 6 M HCl. Combined acidic layers were neutralized with NaOH and extracted with ether. The organic layer was dried with $MgSO_4$ and filtered. After evaporation of the solvent, the residue was purified by column chromatography (*n*-hexane/ethyl acetate (70/30)) to give **3a** and (*E*)-**4a** (338 mg; yield 84%).

1-[(*E*)-3-Phenyl-2-propenyl]pyrrolidine ((*E*)-4b). Compound (*E*)-**4b** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **3b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.27 (d, J = 6.7 Hz, 2H), 6.33 (dt, J = 15.8, 6.7 Hz, 1H), 6.54 (d, J = 15.8 Hz, 1H).

***N*-(1-Phenyl-2-propenyl)cyclopentylamine (3d).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24−1.88 (m, 9H), 3.03 (quintet, J = 7.0 Hz, 1H), 4.24 (d, J = 7.1 Hz, 1H), 5.08 (dd, J = 10.2, 1.1 Hz, 1H), 5.18 (dd, J

(29) Brandsma, L. *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988; p 81.

(30) Ref 29, p 57.

(31) Crabtree, R. H.; Quirk, J. M.; Felkin, H.; Fillebeen-Khan, T. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 407.

(32) Schenck, T. G.; Downs, J. M.; Milne, C. R. C.; Mackenzie, P.; Boucher, H.; Whealan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.

(33) Uson, R.; Oro, L. A.; Cabeza, J. A. *Inorg. Synth.* **1985**, *23*, 128.

= 17.2, 1.1 Hz, 1H), 5.93 (ddd, J = 17.2, 10.2, 7.1 Hz, 1H), 7.22−7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9 (2C), 33.2, 33.4, 57.1, 64.5, 114.6, 127.0, 127.3 (2C), 128.4 (2C), 141.5, 143.3. Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.23; H, 9.41; N, 6.93.

***N*-[(*E*)-3-Phenyl-2-propenyl]cyclopentylamine ((*E*)-4d):** Compound (*E*)-**4d** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **3d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (dd, J = 6.4, 1.4 Hz, 2H), 6.32 (dt, J = 15.8, 6.4 Hz, 1H), 6.52 (d, J = 15.8 Hz, 1H).

***N*-(1-Phenyl-2-propenyl)-*n*-butylamine (3e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.34 (sextet, J = 7.3 Hz, 2H), 1.40 (br, 1H), 1.47 (quintet, J = 7.3 Hz, 2H), 2.49 (dt, J = 11.4, 7.3 Hz, 1H), 2.59 (dt, J = 11.4, 7.3 Hz, 1H), 4.17 (d, J = 7.1 Hz, 1H), 5.08 (dd, J = 10.2, 1.5 Hz, 1H), 5.19 (dd, J = 17.1, 1.5 Hz, 1H), 5.92 (ddd, J = 17.1, 10.2, 7.1 Hz, 1H), 7.21−7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 20.9, 32.8, 47.8, 66.7, 115.1, 127.5, 127.6 (2C), 128.9 (2C), 141.7, 143.6. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.19; H, 9.94; N, 7.26.

(1-Phenyl-2-propenyl)diethylamine (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (t, J = 7.1 Hz, 6H), 2.55 (q, J = 7.1 Hz, 2H), 2.57 (q, J = 7.1 Hz, 2H), 4.13 (d, J = 8.9 Hz, 1H), 5.12 (dd, J = 10.1, 1.3 Hz, 1H), 5.18 (dd, J = 17.1, 1.3 Hz, 1H), 5.95 (ddd, J = 17.1, 10.1, 8.9 Hz, 1H), 7.19−7.39 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5 (2C), 42.8 (2C), 69.4, 116.0, 126.8, 127.8 (2C), 128.3 (2C), 139.5, 143.0. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.36; H, 10.36; N, 7.23.

***N*-(1-Phenyl-2-propenyl)-*t*-butylamine (3g).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 9H), 1.31 (s, 1H), 4.40 (d, J = 6.9 Hz, 1H), 4.99 (dt, J = 10.1, 1.5 Hz, 1H), 5.10 (dt, J = 17.1, 1.5 Hz, 1H), 5.98 (ddd, J = 17.1, 10.1, 6.9 Hz, 1H), 7.17−7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.6 (3C), 52.0, 60.9, 114.0, 127.1, 127.7 (2C), 128.8 (2C), 144.1, 146.8. Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.34; H, 10.35; N, 7.30.

***N*-(1-Phenyl-2-propenyl)benzylamine (3h).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (s, 1H), 3.72 (d, J = 4.1 Hz, 2H), 4.22 (d, J = 7.1 Hz, 1H), 5.11 (dd, J = 10.2, 1.5 Hz, 1H), 5.22 (dd, J = 17.1, 1.5 Hz, 1H), 5.94 (ddd, J = 17.1, 10.2, 7.1 Hz, 1H), 7.22−7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.3, 65.1, 115.1, 126.9, 127.2, 127.3 (2C), 128.1 (2C), 128.4 (2C), 128.5 (2C), 140.5, 141.0, 142.8. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 85.79; H, 7.50; N, 6.26.

***N*-[(*E*)-3-Phenyl-2-propenyl]benzylamine ((*E*)-4h).** Compound (*E*)-**4h** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **3h**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.31 (dt, J = 15.9, 6.3 Hz, 1H), 6.53 (d, J = 15.9 Hz, 1H).

1-[1-(4-Methylphenyl)-2-propenyl]piperidine (11a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37−1.43 (m, 2H), 1.54 (quintet, J = 5.6 Hz, 4H), 2.26−2.40 (m, 7H), 3.61 (d, J = 8.6 Hz, 1H), 5.05 (dd, J = 10.1, 1.7 Hz, 1H), 5.15 (dd, J = 17.1, 1.7 Hz, 1H), 5.94 (ddd, J = 17.1, 10.1, 8.6 Hz, 1H), 7.10−7.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 24.7, 26.2 (2C), 52.4 (2C), 75.1, 115.5, 127.8 (2C), 129.1 (2C), 136.4, 139.4, 140.6. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.49; H, 9.98; N, 6.22.

1-[(*E*)-3-(4-Methylphenyl)-2-propenyl]piperidine ((*E*)-12a). Compound (*E*)-**12a** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **11a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10 (dd, J = 6.7, 1.2 Hz, 2H), 6.24 (dt, J = 15.8, 6.7 Hz, 1H), 6.46 (d, J = 15.8 Hz, 1H).

1-[1-(4-Fluorophenyl)-2-propenyl]piperidine (11b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38−1.44 (m, 2H), 1.54 (quintet, J = 5.5 Hz, 4H), 2.24−2.29 (m, 2H), 2.39−2.40 (m, 2H), 3.65 (d, J = 8.6 Hz, 1H), 5.08 (dd, J = 10.1, 1.7 Hz, 1H), 5.16 (dd, J = 17.1, 1.7 Hz, 1H), 5.90 (ddd, J = 17.1, 10.1, 8.6 Hz, 1H), 6.95−7.01 (m, 2H), 7.25−7.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 26.0 (2C), 52.3 (2C), 74.4, 115.1 (d, J_{C-F} = 21.0 Hz, 2C), 116.0, 129.3 (d, J_{C-F} = 7.8 Hz, 2C), 138.1 (d, J_{C-F} = 3.1 Hz), 140.1, 161.8 (d, J_{C-F} = 244.7 Hz). Anal. Calcd for $C_{14}H_{18}FN$: C, 76.68; H, 8.27; F, 8.66; N, 6.39. Found: C, 76.66; H, 8.44; F, 8.95; N, 6.10.

***N*-[(*E*)-3-(4-Fluorophenyl)-2-propenyl]piperidine ((*E*)-12b).** Compound (*E*)-**12b** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **11b**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (dt, J = 15.8, 6.8 Hz, 1H), 6.45 (d, J = 15.8 Hz, 1H).

1-[1-(2-Thienyl)-2-propenyl]piperidine (11c). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38−1.44 (m, 2H), 1.56 (quintet, J = 5.6 Hz, 4H), 2.38 (quintet, J = 5.6 Hz, 2H), 2.49 (quintet, J = 5.6 Hz, 2H), 4.10 (d, J = 8.3 Hz, 1H), 5.20 (dd, J = 10.5, 0.9 Hz, 1H), 5.21 (dd, J = 16.7, 0.9 Hz, 1H), 5.99 (ddd, J = 16.7, 10.5, 8.3 Hz, 1H), 6.86 (dd, J = 3.5, 0.9 Hz, 1H), 6.93 (dd, J = 5.1, 3.5 Hz, 1H), 7.21 (dd, J = 5.1, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 26.2 (2C), 51.5 (2C), 69.5, 117.2, 124.4, 124.5, 126.3, 137.9, 146.5. Anal. Calcd for $C_{12}H_{17}NS$: C, 69.51; H, 8.26; N, 6.76; S, 15.47. Found: C, 69.46; H, 8.13; N, 6.65; S, 15.69.

***N*-[(*E*)-3-(2-Thienyl)-2-propenyl]piperidine ((*E*)-12c).** Compound (*E*)-**12c** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **11c**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (d, J = 6.9 Hz, 2H), 6.13 (dt, J = 15.6, 6.9 Hz, 1H), 6.61 (d, J = 15.6 Hz, 1H).

1-[1-(*n*-Hexyl)-2-propenyl]piperidine (14aa). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.19−1.27 (m, 8H), 1.36−1.43 (m, 4H), 1.45−1.63 (m, 4H), 2.26−2.40 (m, 2H), 2.49−2.54 (m, 2H), 2.68 (td, J = 8.9, 4.3 Hz, 1H), 5.02 (dd, J = 16.5, 2.0 Hz, 1H), 5.13 (dd, J = 10.3, 2.0 Hz, 1H), 5.68 (ddd, J = 16.5, 10.3, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 24.9, 26.4 (2C), 26.6, 29.4, 31.8, 31.9, 50.7 (2C), 69.2, 116.8, 138.1. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.02; H, 13.08; N, 6.60.

1-[(*E*)-2-Noneyl]piperidine ((*E*)-15aa). Compound (*E*)-**15aa** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14aa**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (d, J = 5.9 Hz, 2H), 5.49 (dt, J = 15.3, 6.3 Hz, 1H), 5.56 (dt, J = 15.3, 5.9 Hz, 1H).

1-[(*Z*)-2-Nonenyl]piperidine ((*Z*)-15aa). ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (t, J = 7.0 Hz, 3H), 1.30−1.51 (m, 10H), 1.66 (quintet, J = 5.1 Hz, 4H), 2.19 (q, J = 7.1 Hz, 2H), 2.48 (t, J = 5.1 Hz, 4H), 3.09 (d, J = 6.7 Hz, 2H), 5.64 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.77 (dtt, J = 11.0, 6.7, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 24.3, 26.0 (2C), 27.4, 28.9, 29.5, 31.7, 54.5 (2C), 55.8, 126.3, 132.7. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.07; H, 13.01; N, 6.65.

1-[1-(*n*-Hexyl)-2-propenyl]pyrrolidine (14ab). ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (t, J = 6.8 Hz, 3H), 1.38−1.44 (m, 8H), 1.57−1.63 (m, 2H), 1.71−1.80 (m, 4H), 2.54−2.62 (m, 4H), 2.77 (td, J = 8.9, 4.3 Hz, 1H), 5.14 (dd, J = 10.2, 2.2 Hz, 1H), 5.17 (dd, J = 17.2, 2.2 Hz, 1H), 5.88 (ddd, J = 17.2, 10.2, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 14.3, 23.1, 23.8 (2C), 26.1, 30.0, 32.3, 34.5, 51.4 (2C), 68.4, 115.6, 140.9. Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 79.78; H, 13.10; N, 7.00.

1-[(*E*)-2-Noneyl]pyrrolidine ((*E*)-15ab). Compound (*E*)-**15ab** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14ab**. ^{1}H NMR (400 MHz, C_6D_6) δ 3.17 (d, J = 5.9 Hz, 2H), 5.73 (dt, J = 15.3, 6.3 Hz, 1H), 5.80 (dt, J = 15.3, 5.9 Hz, 1H).

1-[(*Z*)-2-Nonenyl]pyrrolidine ((*Z*)-15ab). ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (t, J = 6.8 Hz, 3H), 1.31−1.51 (m, 8H), 1.71−1.77 (m, 4H), 2.20 (q, J = 7.3 Hz, 2H), 2.54−2.63 (m, 4H), 3.26 (d, J = 6.7 Hz, 2H), 5.62 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.83 (dtt, J = 11.0, 6.7, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 23.0, 24.0 (2C), 27.9, 29.3, 30.0, 32.1, 52.9, 54.2 (2C), 128.4, 131.6. Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 80.01; H, 12.98; N, 7.14.

1-[(*Z*)-2-Nonenyl]morpholine ((*Z*)-15ac). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.89 (t, J = 6.9 Hz, 3H), 1.29−1.34 (m, 8H), 2.06 (q, J = 6.9 Hz, 2H), 2.44−2.55 (m, 4H), 3.01 (d, J = 6.4 Hz, 2H), 3.72 (t, J = 4.6 Hz, 4H), 5.44 (dt, J = 11.2, 6.9 Hz, 1H), 5.58 (dt, J = 11.2, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 27.5, 28.9, 29.5, 31.7, 53.6 (2C), 55.5, 67.0 (2C), 125.3, 133.8. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63; O, 7.57. Found: C, 74.13; H, 12.08; N, 6.80.

1-(1-*n*-Hexyl-2-propenyl)morpholine (14ac). Compound **14ac** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of (*Z*)-**15ac**. ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.07 (dd,

J = 16.3, 2.0 Hz, 1H), 5.18 (dd, J = 10.2, 2.0 Hz, 1H), 5.65 (ddd, J = 16.3, 10.2, 7.9 Hz, 1H).

***N*-(1-*n*-Hexyl-2-propenyl)cyclopentylamine (14ad).** ^{1}H NMR (400 MHz, C_6D_6) δ 0.88 (t, J = 7.1 Hz, 3H), 1.25−1.47 (m, 15 H), 1.62−1.82 (m, 4H), 2.96−3.00 (m, 1H), 3.13 (quintet, J = 6.5 Hz, 1H), 5.02 (dd, J = 10.1, 2.0 Hz, 1H), 5.04 (dd, J = 17.2, 2.0 Hz, 1H), 5.54 (ddd, J = 17.2, 10.1, 8.1 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 14.3, 23.0, 24.3 (2C), 26.3, 29.8, 32.3, 33.3, 34.5, 36.8, 57.0, 60.6, 114.4, 143.1. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.56; H, 13.16; N, 6.51.

***N*-[(*E*)-2-Nonenyl]cyclopentylamine ((*E*)-15ad).** Compound **(*E*)-15ad** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14ad**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.52 (dt, J = 15.3, 5.7 Hz, 1H), 5.58 (dt, J = 15.3, 5.2 Hz, 1H).

***N*-(1-*n*-Hexyl-2-propenyl)-*n*-butylamine (14ae).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.2 Hz, 6H), 1.25−1.45 (m, 15H), 2.44 (dt, J = 11.2, 6.6 Hz, 1H), 2.63 (dt, J = 11.2, 6.8 Hz, 1H), 2.91 (q, J = 7.9 Hz, 1H), 5.03 (dd, J = 10.2, 2.0 Hz, 1H), 5.06 (dd, J = 17.2, 2.0 Hz, 1H), 5.58 (ddd, J = 17.2, 10.2, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.24, 14.28, 20.9, 23.0, 26.3, 29.9, 32.2, 33.1, 36.4, 47.3, 62.4, 114.7, 142.9. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 78.96; H, 13.83; N, 7.09.

***N*-[(*E*)-2-Nonenyl]-*n*-butylamine ((*E*)-15ae).** Compound (*E*)-**15ae** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14ae**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (d, J = 5.8 Hz, 2H), 5.51 (dt, J = 15.4, 5.9 Hz, 1H), 5.58 (dt, J = 15.4, 5.8 Hz, 1H).

***N*-[(*Z*)-2-Nonenyl]-*n*-butylamine ((*Z*)-15ae).** ^{1}H NMR (400 MHz, C_6D_6) δ 0.97−1.03 (m, 6H), 1.36−1.53 (m, 13H), 2.17 (q, J = 7.3 Hz, 2H), 2.65 (t, J = 5.9 Hz, 2H), 3.37 (d, J = 6.6 Hz, 2H), 5.60 (dt, J = 10.9, 7.3 Hz, 1H), 5.68 (dt, J = 10.6, 6.6 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 13.9, 14.0, 20.5, 22.6, 27.4, 28.9, 29.6, 31.7, 32.2, 46.3, 49.2, 128.0, 131.9. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.11; H, 14.03; N, 7.01.

***N*-[(*Z*)-2-Nonenyl]diethylamine ((*Z*)-15af).** ^{1}H NMR (400 MHz, C_6D_6) δ 1.00 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 6H), 1.34−1.50 (m, 8H), 2.19 (q, J = 7.1 Hz, 2H), 2.59 (q, J = 7.1 Hz, 4H), 3.24 (d, J = 6.6 Hz, 2H), 5.63 (dtt, J = 11.0, 7.1, 1.6 Hz, 1H), 5.75 (dtt, J = 11.0, 6.6, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 12.5 (2C), 14.2, 23.0, 27.9, 29.3, 30.1, 32.1, 47.2 (2C), 50.3, 128.4, 132.1. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.14; H, 13.75; N, 7.12.

***N*-[1-(*n*-Hexyl)-2-propenyl]diethylamine (14af).** Compound **14af** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of (*Z*)-**15af**. ^{1}H NMR (400 MHz, C_6D_6) δ 5.11 (dd, J = 17.2, 2.1 Hz, 1H), 5.20 (dd, J = 10.4, 2.2 Hz, 1H), 5.81 (ddd, J = 17.2, 10.4, 6.9 Hz, 1H).

***N*-[1-(*n*-Hexyl)-2-propenyl]aniline (14ai).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.28−1.45 (m, 8H), 1.54−1.60 (m, 2H), 3.59 (br, 1H), 3.78 (q, J = 6.2 Hz, 1H), 5.10 (dd, J = 10.3, 1.3 Hz, 1H), 5.19 (d, J = 17.2, 1.3 Hz, 1H), 5.72 (ddd, J = 17.2, 10.3, 6.2 Hz, 1H), 6.56−6.69 (m, 3H), 7.11−7.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 25.9, 29.2, 31.7, 35.9, 55.9, 113.3 (2C), 114.9, 117.1, 129.1 (2C), 140.2, 147.7. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.63; H, 10.87; N, 6.27.

***N*-[(*E*)-2-Nonenyl]aniline ((*E*)-15ai).** Compound (*E*)-**15ai** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14ai**. ^{1}H NMR (400 MHz, C_6D_6) δ 5.38 (dt, J = 15.3, 5.7 Hz, 1H), 5.53 (dt, J = 15.3, 6.7 Hz, 1H).

1-[(*Z*)-2-Undecenyl]piperidine ((*Z*)-15ba). ^{1}H NMR (400 MHz, C_6D_6) δ 1.0 (t, J = 6.7 Hz, 3H), 1.39−1.48 (m, 14H), 1.66 (quintet, J = 5.7 Hz, 4H), 2.20 (q, J = 7.3 Hz, 2H), 2.48 (t, J = 5.1 Hz, 4H), 3.10 (d, J = 6.7 Hz, 2H), 5.64 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.77 (dtt, J = 11.0, 6.7, 1.5 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.1, 22.6, 24.4, 26.0 (2C), 27.4, 29.3 (2C), 29.4, 29.5, 31.8, 54.5 (2C), 55.9, 126.3, 132.8. Anal. Calcd for $C_{16}H_{31}N$: C, 80.94; H, 13.16; N, 5.90. Found: C, 80.81; H, 13.10; N, 5.74.

1-[1-(*n*-Octyl)-2-propenyl]piperidine (14ba). Compound **14ba** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of (*Z*)-**15ba**. ^{1}H NMR (400 MHz, C_6D_6) δ 5.13 (dd, J = 17.2, 2.2 Hz, 1H), 5.21 (dd, J = 10.3, 2.2 Hz, 1H), 5.84 (ddd, J = 17.2, 10.3, 6.9 Hz, 1H).

1-[1-(*n*-Octyl)-2-propenyl]pyrrolidine (14bb). ^{1}H NMR (400 MHz, C_6D_6) δ 0.86 (t, J = 7.1 Hz, 3H), 1.24−1.26 (m, 12H), 1.40−1.49 (m, 2H), 1.56−1.69 (m, 4H), 2.41−2.48 (m, 4H), 2.64 (td, J = 8.6, 4.4 Hz, 1H), 5.01 (dd, J = 10.2, 2.1 Hz, 1H), 5.04 (dd, J = 17.2, 2.1 Hz, 1H), 5.75 (ddd, J = 17.2, 10.2, 8.6 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 14.3, 23.1, 23.8 (2C), 26.2, 29.8, 30.1, 30.4, 32.3, 34.6, 51.4 (2C), 68.4, 115.6, 140.9. Anal. Calcd for $C_{15}H_{29}N$: C, 80.65; H, 13.08; N, 6.27. Found: C, 80.43; H, 13.36; N, 6.12.

1-[(*E*)-2-Undecenyl]pyrrolidine ((*E*)-15bb). Compound **(*E*)-15bb** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14bb**. ^{1}H NMR (400 MHz, C_6D_6) δ 3.03 (d, J = 5.3 Hz, 2H), 5.59 (dt, J = 15.4, 6.3 Hz, 1H), 5.66 (dt, J = 15.4, 5.3 Hz, 1H).

1-[1-Cyclohexyl-2-propenyl]pyrrolidine (14cb). ^{1}H NMR (400 MHz, C_6D_6) δ 0.91−1.31 (m, 4H), 1.50−1.77 (m, 10H), 1.98−2.00 (m, 1H), 2.42−2.47 (m, 5H), 5.00 (dd, J = 17.2, 2.3 Hz, 1H), 5.07 (dd, J = 10.3, 2.3 Hz, 1H), 5.73 (ddd, J = 17.2, 10.3, 9.3 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 23.7 (2C), 27.0, 27.1, 27.4, 28.5, 31.4, 40.9, 51.1 (2C), 73.4, 116.7, 138.1. Anal. Calcd for $C_{13}H_{23}N$: C, 80.76; H, 11.99; N, 7.25. Found: C, 80.99; H, 12.23; N, 7.17.

1-[(*E*)-3-Cyclohexyl-2-propenyl]pyrrolidine ((*E*)-15cb). Compound **(*E*)-15cb** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14cb**. ^{1}H NMR (400 MHz, C_6D_6) δ 3.06 (d, J = 5.4 Hz, 2H), 5.58 (dd, J = 15.8, 6.0 Hz, 1H), 5.65 (dt, J = 15.8, 5.4 Hz, 1H).

***N*-(1-Cyclohexyl-2-propenyl)aniline (14ci).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01−1.30 (m, 5H), 1.46−1.51 (m, 1H), 1.66−1.86 (m, 5H), 3.62−3.65 (m, 2H), 5.13 (d, J = 10.3, 1.6 Hz, 1H), 5.16 (dd, J = 17.0, 1.6 Hz, 1H), 5.71 (ddd, J = 17.0, 10.3, 6.6 Hz, 1H), 6.56−6.66 (m, 3H), 7.10−7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.27, 26.33, 26.5, 29.3, 29.4, 42.7, 61.0, 113.2 (2C), 115.7, 116.9, 129.1 (2C), 138.3, 147.9. Anal. Calcd for $C_{15}H_{21}N$: C, 83.67; H, 9.83; N, 6.50. Found: C, 83.39; H, 10.03; N, 6.54.

***N*-((*E*)-3-Cyclohexyl-2-propenyl)aniline ((*E*)-15ci).** Compound **(*E*)-15ci** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of **14ci**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (d, J = 5.8 Hz, 2H), 5.51 (dtd, J = 15.5, 5.8, 1.0 Hz, 1H), 5.64 (dd, J = 15.5, 6.5 Hz, 1H).

1-[(*Z*)-6-Phenyl-2-hexenyl]piperidine ((*Z*)-15d). ^{1}H NMR (400 MHz, C_6D_6) δ 1.32−1.38 (m, 2H), 1.54 (quintet, J = 5.6 Hz, 4H), 1.60 (quintet, J = 7.5 Hz, 2H), 2.03 (q, J = 7.3 Hz, 2H), 2.32 (br, 4H), 2.49 (t, J = 7.6 Hz, 2H), 2.91 (d, J = 6.7 Hz, 2H), 5.49 (dtt, J = 11.0, 7.3, 1.6 Hz, 1H), 5.67 (dtt, J = 11.0, 6.7, 1.6 Hz, 1H), 7.06−7.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.3, 25.9 (2C), 27.0, 31.2, 35.4, 54.5 (2C), 55.9, 125.7, 127.0, 128.2 (2C), 128.4 (2C), 132.2, 142.3. Anal. Calcd for $C_{17}H_{25}N$: C, 83.89; H, 10.35; N, 5.75. Found: C, 83.64; H, 10.65; N, 5.67.

1-[1-(3-Phenylpropyl)-2-propenyl]piperidine (14d). Compound **14d** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of (*Z*)-**15d**. ^{1}H NMR (400 MHz, C_6D_6) δ 4.96 (dd, J = 17.2, 2.1 Hz, 1H), 5.07 (dd, J = 10.3, 2.1 Hz, 1H).

1-[(*Z*)-2,8-Nonadienyl]piperidine ((*Z*)-15e). ^{1}H NMR (400 MHz, C_6D_6) δ 1.24−1.37 (m, 6H), 1.54 (quintet, J = 5.7 Hz, 4H), 1.93−2.04 (m, 4H), 2.34 (br, 4H), 2.95 (d, J = 6.7 Hz, 2H), 4.97 (ddt, J = 10.2, 2.0, 1.0 Hz, 1H), 5.02 (dq, J = 17.1, 2.0 Hz, 1H), 5.48 (dtt, J = 11.0, 7.3, 1.5 Hz, 1H), 5.65 (dtt, J = 11.0, 6.7, 1.5 Hz, 1H), 5.75 (ddt, J = 17.1, 10.2, 6.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 26.0 (2C), 27.3, 28.5, 29.0, 33.6, 54.5 (2C), 55.9, 114.3, 126.6, 132.5, 138.9. Anal. Calcd for $C_{14}H_{25}N$: C, 81.09; H, 12.15; N, 6.75. Found: C, 80.83; H, 12.42; N, 6.74.

1-[(*Z*)-5-Ethyl-2-nonenyl]piperidine ((*Z*)-15f). ^{1}H NMR (400 MHz, C_6D_6) δ 0.99 (t, J = 7.0 Hz, 3H), 1.02 (t, J = 6.7 Hz, 3H), 1.38−1.47 (m, 11H), 1.66 (quintet, J = 5.6 Hz, 4H), 2.18−2.20 (m, 2H), 2.49 (t, J = 5.2 Hz, 4H), 3.12 (d, J = 6.7 Hz, 2H), 5.65 (dtt, J = 11.1, 7.3, 1.6 Hz, 1H), 5.81 (dtt, J = 11.1, 6.7, 1.5 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 11.0, 14.1, 23.0, 24.4, 25.8, 26.0 (2C), 29.0, 31.1, 32.7, 39.5, 54.6 (2C), 56.1, 127.2, 131.4. Anal. Calcd for $C_{16}H_{31}N$: C, 80.94; H, 13.16; N, 5.90. Found: C, 80.99; H, 13.12; N, 5.84.

1-[(*Z*)-4-(*n*-Butoxy)-2-butenyl]piperidine ((*Z*)-15g). ^{1}H NMR (400 MHz, C_6D_6) δ 0.86 (t, J = 7.3 Hz, 3H), 1.29−1.42 (m, 4H), 1.47−1.58 (m, 6H), 2.28 (br, 4H), 2.88 (d, J = 6.6 Hz, 2H), 3.32 (t, J = 6.4 Hz, 2H), 4.00 (d, J = 6.1 Hz, 2H), 5.68 (dtt, J = 11.2, 6.6, 1.5 Hz, 1H), 5.78 (dtt, J = 11.2, 6.1, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 14.1, 19.8, 24.8, 26.4 (2C), 32.3, 54.8 (2C), 56.4, 66.9, 70.2, 129.3, 130.0. Anal. Calcd for $C_{13}H_{25}NO$: C, 73.88; H, 11.92; N, 6.63; O, 7.57. Found: C, 73.58; H, 11.91; N, 6.49.

1-(*n*-Butoxylmethyl-2-propenyl)piperidine (14g). Compound **14g** could not be isolated in a pure form. Partial ^{1}H NMR spectra were obtained from the mixture of (*Z*)-**15g**. ^{1}H NMR (400 MHz, C_6D_6) δ 5.16 (d, J = 9.8 Hz, 1H), 5.18 (d, J = 18.8 Hz, 1H), 5.88 (ddd, J = 18.8, 9.8, 7.3 Hz, 1H).

1-[1-Methyl-1-(*n*-pentyl)-2-propenyl]piperidine (17aa). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H), 1.01 (s, 3H), 1.20−1.32 (m, 6H), 1.39−1.45 (m, 4H), 1.53 (quintet, J = 5.7 Hz, 4H), 2.45 (t, J = 4.5 Hz, 4H), 4.96 (dd, J = 17.7, 1.5 Hz, 1H), 5.06 (dd, J = 10.9, 1.5 Hz, 1H), 5.80 (dd, J = 17.7, 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 16.4, 22.6, 23.5, 25.2, 27.0 (2C), 32.6, 39.2, 47.1 (2C), 60.9, 112.7, 145.5. Anal. Calcd for $C_{14}H_{27}N$: C, 80.31; H, 13.00; N, 6.69. Found: C, 80.42; H, 13.14; N, 6.56.

1-[1-Methyl-1-(*n*-pentyl)-2-propenyl]pyrrolidine (17ab). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.11 (s, 3H), 1.26−1.33 (m, 6H), 1.46−1.54 (m, 2H), 1.71−1.73 (m, 4H), 2.62 (br, 4H), 5.01 (dd, J = 17.7, 1.5 Hz, 1H), 5.12 (dd, J = 11.0, 1.5 Hz, 1H), 5.85 (dd, J = 17.7, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.2, 22.6, 23.76 (2C), 23.81, 32.6, 40.1, 45.7 (2C), 59.1, 113.7, 142.5. Anal. Calcd for $C_{13}H_{25}N$: C, 79.93; H, 12.90; N, 7.17. Found: C, 79.76; H, 13.12; N, 7.05.

***N*-[1-Methyl-1-(*n*-pentyl)-2-propenyl]-*n*-butylamine (17ae).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 7.2 Hz, 3H), 1.11 (s, 3H), 1.17−1.46 (m, 13H), 2.39−2.49 (m, 2H), 4.99 (dd, J = 17.6, 1.2 Hz, 1H), 5.05 (dd, J = 10.8, 1.2 Hz, 1H), 5.69 (dd, J = 17.6, 10.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0 (2C), 20.6, 22.6, 23.1, 23.4, 32.5, 33.1, 40.5, 42.1, 56.8, 112.4, 145.7. Anal. Calcd for $C_{13}H_{27}N$: C, 79.11; H, 13.79; N, 7.10. Found: C, 79.02; H, 13.86; N, 7.37.

***N*-[1-Methyl-1-(*n*-pentyl)-2-propenyl]aniline (17ai).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, J = 6.5 Hz, 3H), 1.21−1.37 (m, 9H), 1.43−1.59 (m, 1H), 1.65−1.72 (m, 1H), 3.64 (br, 1H), 5.14 (dd, J = 10.5, 1.1 Hz, 1H), 5.15 (dd, J = 17.8, 1.1 Hz, 1H), 5.94 (dd, J = 17.8, 10.5 Hz, 1H), 6.64−6.70 (m, 3H), 7.07−7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.6, 23.1, 24.4, 32.2, 41.6, 57.2, 113.4, 115.7 (2C), 117.3, 128.7 (2C), 145.5, 146.7. Anal. Calcd for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.44. Found: C, 82.60; H, 10.56; N, 6.36.

1-[1-Methyl-1-(3-methyl-2-butenyl)-2-propenyl]piperidine (17b). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 3H), 1.37−1.56 (m, 11H), 1.67 (s, 3H), 1.82−2.02 (m, 2H), 2.45 (br, 4H), 4.98 (dd, J = 17.7, 1.5 Hz, 1H), 5.07−5.08 (m, 1H), 5.08 (dd, J = 11.0, 1.5 Hz, 1H), 5.83 (dd, J = 17.7, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.5, 17.6, 22.6, 25.2, 25.7(2C), 27.0, 39.3, 47.1 (2C), 60.8, 112.9, 125.1, 131.0, 145.2. Anal. Calcd for $C_{15}H_{27}N$: C, 81.38; H, 12.29; N, 6.33. Found: C, 81.32; H, 12.43; N, 6.36.

Acknowledgment. Financial support by a Grant-in-Aid for Science Research (12650857) from the Ministry of Education, Culture, Sports, Science and Technology, a Research Grant from the Yokohama Academic Foundation, and a Research Grant from the Takamura Foundation is gratefully acknowledged. We thank Hodogaya Chemical Co., Ltd. for the gift of methyl chloroformate.

Supporting Information Available: Spectral data of known compounds (**3a**, (*E*)-**4a**, **3b**, **3c**, (*E*)-**4c, (*E*)-4e, (*E*)-4f, (*E*)-4g**) (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

JA0112036