Articles

Cobalt(II)-Catalyzed Conversion of Allylic Alcohols/Acetates to Allylic Amides in the Presence of Nitriles

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Various secondary allylic alcohols or their acetates and tertiary allylic alcohols can be converted to the corresponding transposed allylic amides in the presence of a catalytic quantity of cobalt(II) chloride and acetic anhydride in acetonitrile. Tertiary alcohols undergo complete rearrangement whereas secondary ones afford a mixture of regioisomers. Moderate yields of amides are also obtained by reacting acrylonitrile with secondary alcohols in 1,2-dichloroethane. The presence of acetic anhydride or acetic acid is crucial to the formation of amides as the absence of the former affords no amides and the allylic alcohols are mainly recovered as regioisomeric mixtures. The regioselectivity during amide formation can be enhanced by using cobalt complexes **14**–**16** in acetic acid medium. Some preliminary studies indicate that these reactions are proceeding via an π-allyl complex or tight ion pair rather than a [3,3] sigmatropic rearrangement of acetamidate obtained in a Pinner reaction.

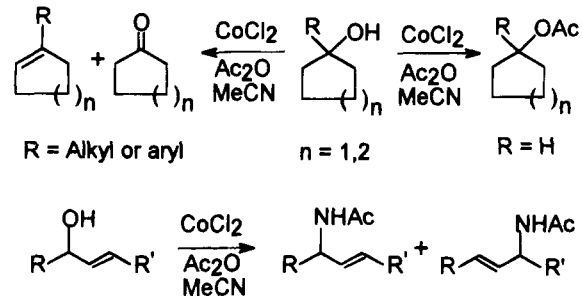
Introduction

A recent study from our group has indicated that cobalt(II) chloride is an efficient catalyst for the acetylation[1] of alcohols and thiols with acetic anhydride. The reactions are performed in acetonitrile medium in which primary and secondary alcohols undergo smooth acetylation whereas tertiary alcohols are esterified in poor yields (Scheme 1). The low propensity of tertiary alcohols for acetylation under these conditions was attributed to a process involving elimination and α-cleavage via an alkoxy radical. In a preliminary communication we have reported[2] that secondary and tertiary allylic alcohols also show very little tendency for esterification and instead they undergo facile conversion to the corresponding allylic amides[3] along with the small amounts of allylically rearranged acetates (Scheme 1). This paper describes a detailed investigation on this transformation and offers a plausible reaction mechanism.

Results and Discussion

We have already demonstrated that primary and secondary alcohols are efficiently acetylated with acetic anhydride in the presence of catalytic quantity of cobalt(II) chloride in acetonitrile at ambient temperature or at 80 °C. On the other hand, the secondary and tertiary

Scheme 1



allylic alcohols behaved quite differently under these conditions as they mainly afforded the corresponding allylic amides in moderate to good yields. Thus a variety of secondary allylic alcohols were transformed to the corresponding amides on heating with acetic anhydride in the presence of cobalt(II) chloride in acetonitrile medium (Table 1). These transformations were accompanied by small amount of (5–20%) corresponding allyl acetates as a mixture of regioisomers. The aromatic allylic alcohol **1a** underwent rearrangement to give the corresponding amide whereas the cinnamyl alcohol **1b** gave unrearranged amide as the main product (Table 1, entries 1 and 2). In both the cases some corresponding allyl acetate was also formed in addition to the allyl amides. Similarly, the diene alcohols **1c** and **1d** mainly afforded the unrearranged amides **2c** and **2d**, respectively, along with a small amount of the corresponding acetates (Table 1, entries 3 and 4). The aliphatic allylic alcohols **1e** and **1f** yielded a mixture of unrearranged and rearranged amides **2e**, **3e** and **2f**, **3f**, respectively (ratio determined by ^{1}H NMR). However, the rearranged amides were found to be the major product in these reactions (Table 1, entries 5 and 6). The acetylenic allylic alcohol **1g** was smoothly transformed to the corresponding rearranged amide **2g** exclusively (Table 1, entry 7). Interestingly, the optically pure anti carveol **1h** was converted to the corresponding amide **2h** mainly as a mixture of diastereomers, and the optical rotation of the

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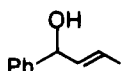
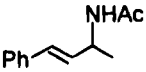
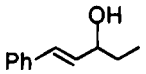
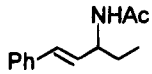
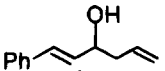
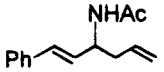
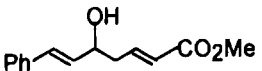
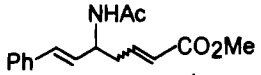
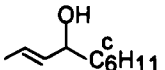
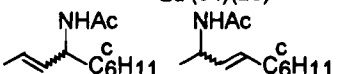
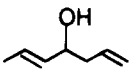
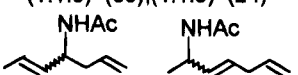
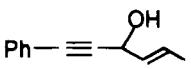
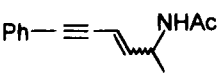
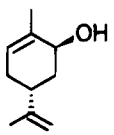
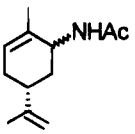
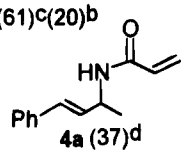
(1) (a) Iqbal, J.; Ahmad, S. *Tetrahedron Lett.* **1986**, *27*, 3791. (b) Ahmad, S.; Iqbal, J. *J. Chem. Soc., Chem. Commun.* **1987**, 114. (c) Iqbal, J.; Srivastava, R. R. *J. Org. Chem.* **1992**, *57*, 2001.

(2) Nayyar, N. K.; Reddy, M. M.; Iqbal, J. *Tetrahedron Lett.* **1991**, *32*, 6965.

(3) For some recent syntheses of allyl amides and amines see: (a) Sharpless, K. B.; Hori, T.; Truesdale, L. K.; Dietrich, C. L. *J. Am. Chem. Soc.* **1976**, *98*, 269. (b) Singer, S. P.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1448. (c) Kresze, G.; Munsterer, H. *J. Org. Chem.* **1983**, *48*, 3561, 5401. (d) Daleris, G.; Dunogues, J.; Gadras, A. *Tetrahedron* **1988**, *44*, 4243. (e) Helquist, P.; Connell, R. D.; Akermark, B. *J. Org. Chem.* **1989**, *54*, 3359. (f) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (g) Leblanc, Y.; Zamboni, R.; Bernstein, M. A. *J. Org. Chem.* **1991**, *56*, 1971.

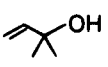
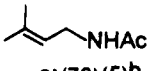
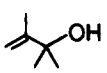
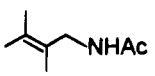
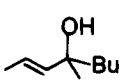
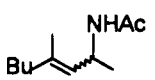
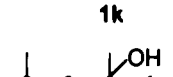
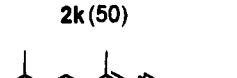
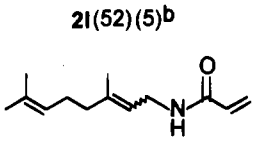
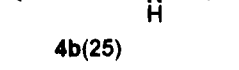
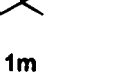
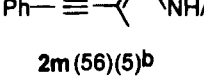
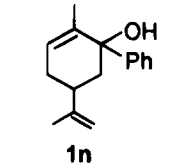
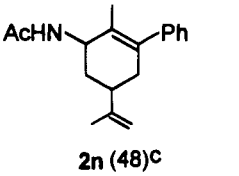
0022-3263/95/1960-2670$09.00/0

Table 1. Cobalt(II) Chloride-Catalyzed Synthesis of Allylic Amides from Secondary Allylic Alcohols and Nitriles

Entry	Alcohol	Products (%Yield)[a]
1	 **1a**	 **2a** (57)(5)[b]
2	 **1b**	 **2b**(64)(10)[b]
3	 **1c**	 **2c** (57)(14)[b]
4	 **1d**	 **2d** (34)(26)[b]
5	 **1e**	 **2e** **3e** (1:1.5)[e](69),(1:1.5)[e](24)[b]
6	 **1f**	 **2f** **3f** (1:1.5)[e](67),(1:1.5)[e](10)[b]
7	 **1g**	 **2g** (54)(25)[b]
8	 **1h**	 **2h** (61)[c](20)[b]
9	**1a**	 **4a** (37)[d]

[a] Isolated yield. [b] Yield of corresponding acetates. [c] Amide was obtained as a mixture of diastereomers from optically pure *anti*-carveol. [d] This reaction was performed with acrylonitrile in DCE. [e] The ratio of regioisomers was determined by ^{1}H-NMR of the crude reaction mixture.

Table 2. Cobalt(II) Chloride-Catalyzed Synthesis of Allylic Amides from Tertiary Allylic Alcohols and Nitriles

Entry	Alcohol	Products (Yield %)[a]
1	 **1i**	 **2i**(70)(5)[b]
2	 **1j**	 **2j**(66)(8)[b]
3	 **1k**	 **2k** (50)
4	 **1l**	 **2l**(52)(5)[b]
5	**1l**	 **4b**(25)
6	**1m**	 **2m** (56)(5)[b]
7	 **1n**	 **2n** (48)[c]
8	 **1o**	 **2o** (55)[c](20)[b]

[a] Isolated yield. [b] Yield of corresponding acetates. [c] Obtained as a mixture of diastereomers.

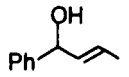
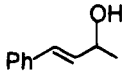
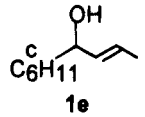
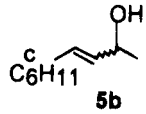
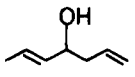
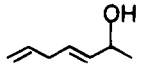
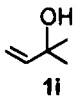
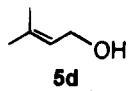
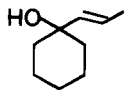
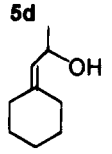
latter indicated it to be a racemic compound. The formation of allylic amides can also be achieved by using nitriles other than acetonitrile; however, the reaction with the former were conducted in 1,2-dichloroethane (DCE). Thus alcohol **1a** was converted to the corresponding acrylic amide **4a** with acrylonitrile in DCE in moderate yields (Table 1, entry 9).

The reaction with tertiary alcohols leads to an exclusive formation of allylically rearranged amides in good yields. The formation of the corresponding acetate is also observed under these conditions. Thus a variety of tertiary alcohols **1i**, **1j**, and **1k** were converted to the corresponding rearranged amides in good yields (Table 2, entries 1–3). Linalool **11** was completely transformed to the corresponding rearranged amide **21** and **4b** with acetonitrile and acrylonitrile, respectively, in moderate to good yields (Table 2, entry 4 and 5). However, the reaction with acrylonitrile also yielded polymeric material. The acetylenic tertiary allylic alcohol **1m** gave the rearranged amide **2m** as the major product. The tertiary alcohols **1n** and **1o**, derived from carvone, were converted to a mixture of diastereomers of the corresponding amide **2n** and **2o**, respectively (Table 2, entries 7 and 8). However, alcohol **1o** also yielded the corresponding allylically rearranged acetate in moderate yield.

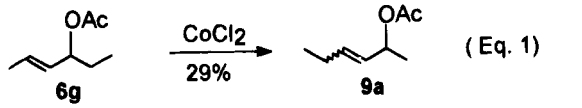
It is interesting to note that the absence of acetic anhydride inhibits the formation of amide, and the allylic alcohols are instead converted to a mixture of regioisomers (Table 3). The amide formation can also be achieved from the corresponding allyl acetate in the presence of catalytic amount of cobalt(II) chloride and acetic acid (Table 4). This protocol provides a relatively higher yield of amide; however, there is no improvement in the regioselectivity as evidenced by comparing the results of alcohol **1e** (Table 1) and acetate **6e** (Table 4). On the other hand, the allyl acetates afforded a mixture of regioisomers in the absence of acetic acid as indicated[4]

(4) For palladium-catalyzed rearrangements of allylic acetates see: (a) Overman, L. E.; Knoll, F. M. *Tetrahedron Lett.* **1979**, 321. (b) Trost, B. M.; Verhoeven, T. R.; Fortunak, J. M. *Tetrahedron Lett.* **1979**, 2301. (c) Grieco, P. A.; Tetsuo, T.; Shannon, L. B.; Hideo, T. *J. Am. Chem. Soc.* **1980**, *102*, 7587.

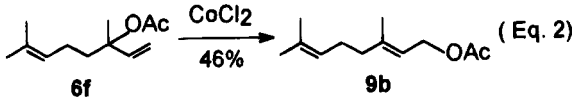
Table 3. Cobalt(II) Chloride-Catalyzed Isomerization of Allylic Alcohols

Entry	Alcohol	Product	% Of isomerisation[a,b]
1	 1a	 5a	(90)
2	 1e	 5b	(45)
3	 1f	 5c	(40)
4	 1i	 5d	(67)
5	 1p	 5e	(85)

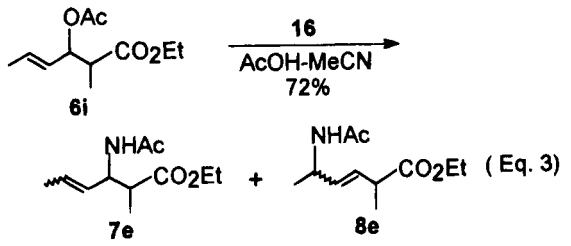
[a] Deduced from the ^{1}H-NMR of the crude reaction mixture. [b] Alcohols were heated at 80 °C for 10–12 h in the presence of catalytic amount of $CoCl_2$.



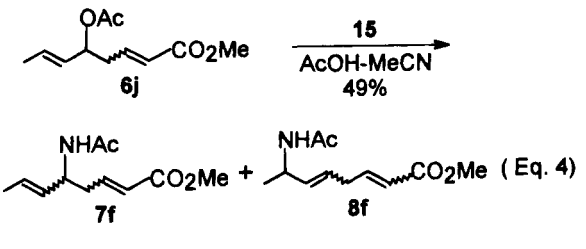
(Eq. 1)



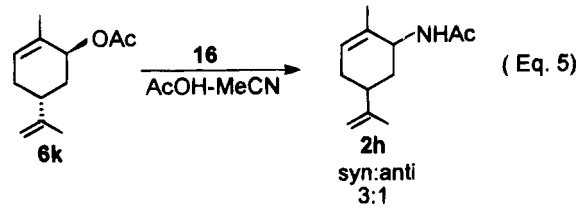
(Eq. 2)



(Eq. 3)

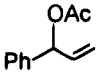
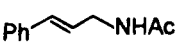
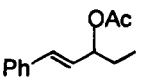
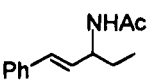
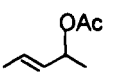
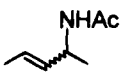
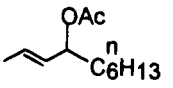
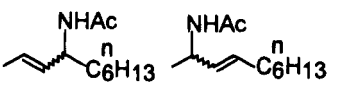
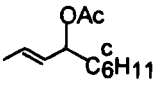
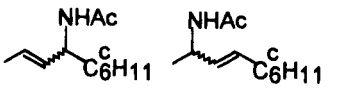
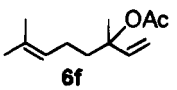


(Eq. 4)



(Eq. 5)

Table 4. Cobalt(II) Chloride-Catalyzed Synthesis of Allylic Amides from Secondary and Tertiary Allylic Acetates and Nitriles

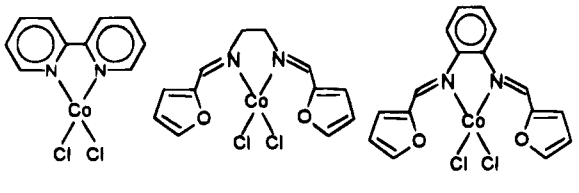
Entry	Acetate	Product (% Yield)[a,b]
1	 6a	 7a (70)
2	 6b	 2b (76)
3	 6c	 7b (84)
4	 6d	 7c 8c (1:2)[c] (70)
5	 6e	 2e 3e (1:1.5)[c] (78)
6	 6f	2l (73)

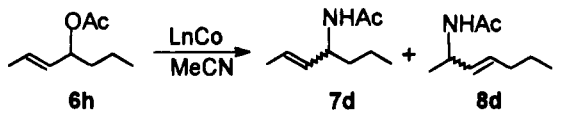
[a] Isolated yield. [b] The acetates were heated (80 °C) in acetonitrile in the presence of catalytic amount of anhydrous $CoCl_2$ and acetic acid. [c] The ratio of regioisomers were determined by ^{1}H-NMR of crude reaction mixture.

by the partial rearrangement of **6g** and **6f** to the corresponding regioisomers **9a** and **9b**, respectively (eqs 1 and 2).

In order to achieve the high regioselectivity during amide formation, we have prepared cobalt complexes **14**–**16** bearing bipyridyl and *N,N'*-difurfurylideneethylenediamine and *N,N*-difurfurylidenephenylenediamine ligands. The reaction using these catalysts in acetonitrile did not give good chemical yields; however, by changing the reaction medium to acetic acid the results were quite rewarding. The reaction in the presence of catalysts **14** and **15** provided high chemical yields but with no significant improvement in the regioselectivity (Table 5, entries 1–6). However, catalyst **16** proved very efficient in providing high yield and enhanced regioselectivity during this reaction (Table 5, entries 7 and 8). It is worth mentioning that the amide formation with catalysts **14**–**16** in acetonitrile as reaction medium proceeds in low yields. On the other hand, $CoCl_2$ catalyzes this reaction in acetic acid in moderate yield. The reaction time is increased considerably in this medium (Table 5, entry 2). Catalyst **15** and **16** have proven to be useful during the conversion of acetate **6i** and **6j** to the corresponding amide as a mixture of geometrical and regioisomers (ratio determined by ^{1}H NMR) in good yield (eqs 3 and 4). Interestingly, these acetates (i.e. **6i** and **6j**) failed to react under catalysis by cobalt chloride. Similarly the optically pure *trans*-carvyl acetate **6k** was transformed in the presence of catalyst **16** to the corresponding amide **2h**

Table 5. Regiochemical Studies on the Amidation of Allyl Acetate 6h in the Presence of Different Cobalt Catalysts in Acetic Acid

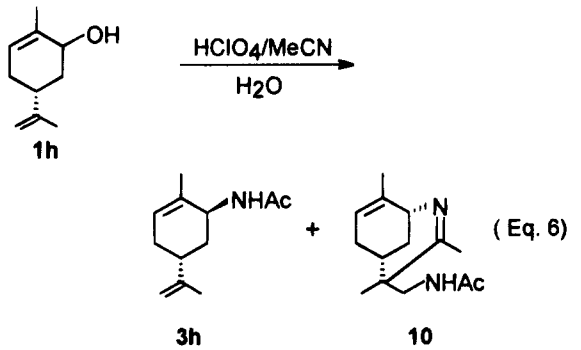




Entry	Catalyst	Solvent	Time (h)	Products[a] (ratio) 7d : 8d	Yield (%)[b,c]
1	$CoCl_2$	MeCN	20	1:1.5	51
2	$CoCl_2$	AcOH	32	1:2	41
3	14	MeCN	22	1:1	47
4	14	AcOH	16	1:1	71
5	15	MeCN	25	1:1	68
6	15	AcOH	16	1:1.5	76
7	16	MeCN	32	1:1.5	50
8	16	AcOH	16	1:4	81

[a] Ratio determined from ^{1}H-NMR of the crude reaction mixture. [b] Isolated yield. [c] Amides are obtained as a mixture of geometrical isomers.

as a 3:1 mixture of (determined by ^{1}H-NMR of the crude mixture) racemic diastereomers in which *syn*-amide was found to be the major product (eq 5). The reaction with carveol **1h** or its acetate **6k** indicates that these transformations are not proceeding via Ritter reaction as it would require the formation of a free carbocation which may lead to the bicylic product **10** as reported[5] earlier (eq 6). Thus absence of any bicyclic product in our reaction clearly indicates that a free allyl cation is not involved in the cobalt-catalyzed reaction.

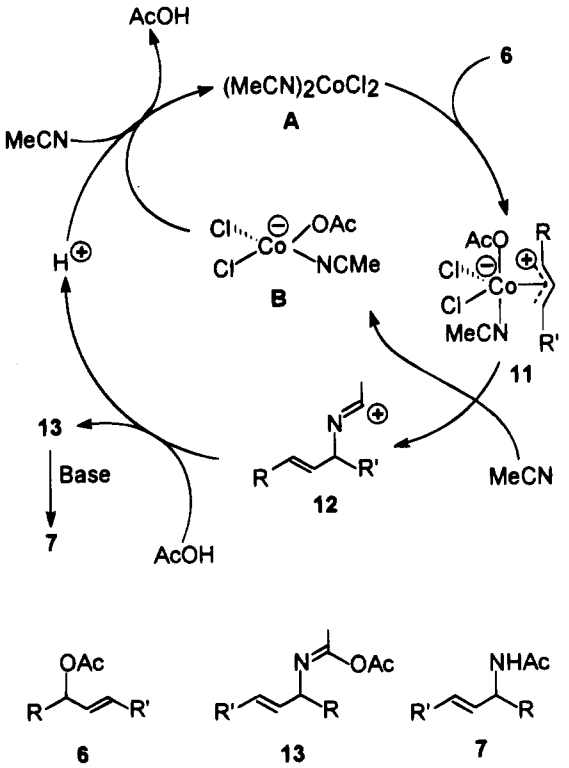


(Eq. 6)

The absence of amides during the rearrangement of allyl alcohols or acetates clearly reveals that acetic anhydride or acetic acid is playing a crucial role during the formation of amides. The formation of rearranged amides suggests that the reaction is proceeding via an π-allyl complex which can be obtained from the corresponding allyl acetate. Thus, initially the allyl alcohols may undergo cobalt(II) chloride-catalyzed acylation[1] with

(5) Kabore, I. Z.; Khuong-Huu, Q.; Pancrazi, A. *Tetrahedron* **1978**, *34*, 2815.

Scheme 2



acetic anhydride to give the allyl acetate **6** which may afford a cobalt π-allyl complex or a tight ion pair **11** on interaction[6] with cobalt(II) (Scheme 2). The absence of any products arising out of elimination and the exclusive formation of the rearranged amides from tertiary alcohols indicate it to be a tight ion pair rather than a solvent[7]-stabilized free allyl cation. An intermolecular attack of acetonitrile to the allyl ligand **11** will provide the cation **12** which may be attacked by acetic acid to give the imidate ester **13** and the latter affords the amide **7** during the workup with base (Scheme 2). The presence of small amount of rearranged and unrearranged acetates from the corresponding alcohols may be arising due to the recombination of the ion pair **11**. Similarly, the absence of acetic anhydride or acetic acid causes the formation of the regioisomer of acetate **6** by reversible elimination–addition of the acetate via **11**. Alternatively, the amide formation may be proceeding via allylic acetamidate[8] as the formation of the latter in a Pinner reaction[9] and its subsequent [3,3]-sigmatropic rearrangement could be catalyzed by cobalt(II). However, Pinner reaction can be ruled out in the present case as our preliminary studies have indicated that aqueous acidic workup affords no significant amount of acetate from alcohol in the presence of catalytic cobalt chloride and acetic acid in acetonitrile. The latter observation clearly indicates that imidates are not being formed under these conditions and it is also worth noting that [3,3]-sigmatropic rearrangement of imidates will only yield transposed allyl amides rather than a mixture of regioisomers. Moreover, the rear-

(6) (a) We have proposed a cobalt π-allyl complex from allyl acetate and cobalt(II) chloride: Bhatia, B.; Reddy, M. M.; Iqbal, J. *Tetrahedron Lett.* **1993**, *34*, 6301. (b) Maikap, G. C.; Reddy, M. M.; Mukhopadhyay, M.; Bhatia, B.; Iqbal, J. *Tetrahedron* **1994**, *50*, 9145. (c) Cobalt(II) chloride also catalyzes the acetylation of alcohols with acetic acid.

(7) For a similar study involving palladium complex see: Trost, B. M.; Strege, P. E. *J. Am. Chem. Soc.* **1977**, *99*, 1649.

(8) For thermal or metal-catalyzed rearrangements of allylic imidates see: Overman, L. E. *Acc. Chem. Res.* **1980**, *13*, 218.

(9) For Pinner reaction see: Compagnon, P. L.; Miocque, M. *Ann. Chim.* (Paris) **1970**, *5*, 23–27.

rangement of allylic alcohols or acetates in the absence of acetic anhydride or acetic acid also gives an indication that a tight ion pair or cobalt π-allyl complex are readily formed under these conditions. Also the formation of amides from both allyl alcohols and acetates under the aegis of acetic acid and/or acetic anhydride clearly reveals that the reaction is proceeding via allyl acetate. Our recent studies on the cobalt(II) chloride-catalyzed allylation of 1,3-dicarbonyl compounds with allyl acetate also strongly suggests[6] the intermediacy of a tight ion pair or π-allyl complex in these reactions.

The reaction pathway for this transformation may have some resemblence with that of the Ritter reaction.[10] *However, regioselectivity in the amide formation from tertiary alcohol appears to be different from what would be expected under classical Ritter conditions. The latter observation also suggests that the free allyl cation is unlikely to be the intermediate in cobalt(II)-catalyzed amide formation from allyl alcohol and/or acetate and acetonitrile.*

In conclusion, the cobalt(II) chloride-catalyzed formation of allylic amides from allylic alcohols or acetates and nitriles constitutes a novel methodology which can be of wide applicability in organic synthesis. The reported reaction can be performed under nearly neutral conditions and thus this route provides a viable alternative to palladium-catalyzed synthesis of protected allylic amines which requires a strong hindered base as a source of nitrogen. Some preliminary studies involving catalyst **14–16** in acetic acid has indicated that the regioselectivity in the amide formation may be enhanced by a change of catalyst and reaction medium. We are currently pursuing studies to firmly address the stereo- and regiochemical aspect of this reaction.

Experimental Section

Materials and Methods. Acetonitrile, THF, aldehydes, alkyl halides, and acetic anhydride were purified[11] by standard procedures. $CoCl_2$ was purchased from LOBA India Ltd., Bombay, and dried at 100 °C for 3–4 h before use. Column chromatography was performed by using ACME TLC silica gel. ^{1}H-NMR spectra were recorded at 60, 80, and 200 MHz in $CDCl_3$ or CCl_4. All known compounds were characterized by comparing with literature data.

Synthesis of Catalysts. The synthesis of catalysts **14–16** was achieved by reacting preheated (100 °C) $CoCl_2$ and the ligands (i.e., bipyridyl, *N,N'*-difurfurylidenethylenediamine and *N,N*-difurfurylidenephenylenediamine). The reactions were performed under N_2 by mixing the stoichiometric amount of $CoCl_2$ and ligand at ambient temperature in dry acetonitrile. The complexes can be isolated as crystalline solids from gummy residues on trituration with petroleum ether or diethyl ether.

The crystalline complexes **14–16** were characterized by their UV-vis spectra. The complexes have a typical absorption pattern between 600–700 nm, which implies that they are tetrahedral.

Synthesis of Ligands. *N,N'*-Difurfurylideneethylenediamine. To a solution of ethylenediamine (3 g, 0.05 mol) in dry methanol (25 mL) was added furfural (9.6 g, 0.1 mol) and the reaction mixture was stirred at rt for 2 h. The solvent was evaporated in vacuo, and the residue was washed with petroleum ether to afford the ligand (67%): ^{1}H NMR ($CDCl_3$) δ 7.9 (s, 2H), 7.2 (d, J = 6.5 Hz, 2H), 6.5 (d, J = 6.5 Hz, 2H), 6.2 (m, 2H), 3.6 (s, 4H).

***N,N*-Difurfurylidenephenylenediamine.** The ligand was prepared by the above method with *o*-diaminobenzene (5.4 g, 0.05 mol) and furfural (9.6 g, 0.1 mol): ^{1}H NMR ($CDCl_3$) δ 7.6 (s, 2H), 7.2 (d, J = 6.5 Hz, 2H), 7.0 (m, 4H), 6.5 (d, J = 6.5 Hz, 2H), 6.2 (m, 2H).

Preparation of Catalyst 14. To a solution of bipyridyl (1.56 g, 0.01 mol) in dry acetonitrile (25 mL) under N_2 was added dry $CoCl_2$ (1.3 g, 0.01 mol), and the reaction mixture was stirred for 12 h at rt (25 °C). The solvent was evaporated in vacuo, and the residue was triturated with petroleum ether and recrystallized from CH_2Cl_2 to give a crystalline solid (49%): MS (FAB) m/z (relative intensity) 286 (1) [M^+], 250 (100). Anal. Calcd for $C_{10}H_8N_2CoCl_2$: C, 42.00; H, 2.79; N, 9.79. Found: C, 42.09; H, 2.71; N, 9.83.

Preparation of Catalyst 15. To a solution of *N,N'*-difurfurylideneethylenediamine (7 g, 0.032 mol) in dry acetonitrile (25 mL) under N_2 was added dry $CoCl_2$ (4.16 g, 0.032 mol), and the solution was allowed to stir for 12 h at rt. The solvent was evaporated in vacuo, and the residue was washed with petroleum ether and recrystallized from CH_2Cl_2 to give a green crystalline solid (51%): MS(FAB) m/z (relative intensity) 346 (1) [M^+], 310 (100). Anal. Calcd for $C_{12}H_{12}N_2O_2CoCl_2$: C, 41.65, H, 3.47; N, 8.09. Found: C, 41.56; H, 3.52; N, 7.99.

Preparation of Catalyst 16. To a solution of *N,N*-difurfurylidenephenylenediamine (2.64 g, 0.01 mol) in dry acetonitrile (25 mL) under N_2 was added dry $CoCl_2$ (1.3 g, 0.01 mol). The mixture was stirred at rt. Finally, the solvent was evaporated in vacuo, and the residue was washed with petroleum ether and recrystallized from CH_2Cl_2 to give a green crystalline solid (53%): MS(FAB) m/z (relative intensity) 394 (1) [M^+], 365 (48). Anal. Calcd for $C_{16}H_{12}N_2O_2CoCl_2$: C, 48.77; H, 3.04; N, 7.10. Found: C, 48.69; H, 2.99; N, 7.17.

General Procedure for the Synthesis of Allylic Alcohols. Alcohols were either obtained commercially or were prepared by $NaBH_4$ reduction or by Grignard reaction with the corresponding carbonyl compounds. *syn*- and *anti*-carveol were prepared by $NaBH_4$ reduction of carvone.

Preparation of Alcohols 1m and 1o. To a solution of phenylacetylene (1 equiv) in dry THF (25 mL) was added n-butyllithium (1.2 equiv) at ~−20 °C. The reaction mixture was stirred for 0.5 h at this temperature and then stirred at rt for 0.5 h. A THF solution of aldehyde or ketone (1.5 equiv) was added dropwise to the reaction mixture at 0 °C, and the mixture was stirred for 1 h and then warmed to ~50 °C. The reaction mixture was quenched with saturated NH_4Cl solution and extracted with ethyl acetate (3 × 50 mL). The organic layer was washed with saturated NH_4Cl solution and brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave a gum which was purified by column chromatography on silica gel (1:9 EtOAc:petroleum ether).

Alcohol 1m: yield 75%, ^{1}H-NMR (CCl_4) δ 7.1 (s, 5H), 5.5–6.1 (m, 2H), 2.2 (s, 1H), 1.7 (d, J = 7 Hz, 3H), 1.4 (s, 3H); IR (thin film) 3380, 3080, 2200 cm^{-1}.

Alcohol 1o: yield 70%; ^{1}H-NMR (CCl_4) δ 7.0 (s, 5H), 5.3 (br s, 1H), 4.6 (m, 2H), 1.8–2.3 (m, 5H), 1.7 (s, 6H); IR (thin film) 3400, 3060, 2200 cm^{-1}.

Representative Procedure for the Synthesis of Allylic Acetates. Ethyl 3-Acetoxy-2-methylhex-4-enoate (6i). Crotonaldehyde (9 mmol) and ethyl bromopropionate (7.5 mmol) was dissolved in a mixture of 10 mL of dry ether and 40 mL of dry benzene. Part of this solution (5 mL) was mixed with dry Zn powder (0.58 g) and heated on a water bath. When the reaction had begun, the remainder of the solution was added dropwise over the reaction mixture. Finally, the reaction mixture was refluxed for 30 min on a water bath and then cooled in a ice-bath followed by addition of cold 10% H_2SO_4 (50 mL) with vigorous stirring. The organic layer was extracted with benzene (3 × 50 mL), and this extract was successively washed with 5% H_2SO_4 (2 × 20 mL), 10% aqueous $NaHCO_3$ (25 mL), and water (2 × 25 mL). Drying (Na_2SO_4) and evaporation of the solvent gave the crude alcohol which was acylated with acetic anhydride and triethylamine in the presence of DMAP to give the corresponding acetate **6i** (66%) after purification by column chromatography: ^{1}H NMR ($CDCl_3$)

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δ 5.1–5.5 (m, 2H), 4.0 (q, J = 6.8 Hz, 2H), 2.5 (t, J = 6.8 Hz, 1H), 2.0 (m, 1H), 1.85 (s, 3H), 1.65 (d, J = 6.5 Hz, 3H), 1.1 (t, J = 6.5 Hz, 3H), 0.9 (d, J = 7 Hz, 3H).

Methyl 5-Acetoxyocta-2,6-dienoate (6j): yield 57%; ^{1}H NMR ($CDCl_3$) δ 6.7–6.9 (m, 1H), 5.05–6.32 (m, 4H), 3.6 (s, 3H), 2.35 (m, 2H), 1.95 (s, 3H), 1.75 (d, J = 8 Hz, 3H).

General Procedure for Cobalt-Catalyzed Isomerization of Allylic Alcohols. Allyl alcohol (5 mmol) and $CoCl_2$ (5 mol %) were heated in acetonitrile (30 mL) at 80 °C for 10–12 h. Removal of acetonitrile gave a residue which was dissolved in ether, and the organic layer was washed successively with a saturated solution of $NaHCO_3$ and water. Drying ($MgSO_4$) and evaporation of solvent gave a residue which was purified by column chromatography to yield the regioisomeric mixture of allyl alcohols. The ratio were determined from the integral of the methyl signals in ^{1}H-NMR.

General Procedure for the Synthesis of Allylic Amides. Allylic alcohol (10 mmol) and acetic anhydride (12 mmol) were added to a solution of $CoCl_2$ (5 mol %) in dry acetonitrile (~120 mL). The reaction mixture was heated at 80 °C for 15–20 h, and the progress of the reaction was monitored by TLC. Removal of the solvent yielded a residue which was dissolved in ethyl acetate (~50 mL), and the organic layer was washed successively with saturated sodium bicarbonate solution (5 × 20 mL), water (3 × 20 mL), and brine (1 × 30 mL). Drying (Na_2SO_4) and evaporation of the solvent yielded a residue which was subjected to column chromatography to afford allylic amides in good yields.

The reaction with allylic acetates was carried out as described above by heating a mixture of allylic acetate (10 mmol), acetic acid (5 mol%), and $CoCl_2$ (5 mol %) at 80 °C for 25–35 h.

The reaction of allylic acetates was also carried out in acetic acid (~25 mL) with acetonitrile (2 equiv) in the presence of catalytic amount of **14**, **15**, or **16** complex at 90 °C for 12–16 h. Removal of acetic acid gave a residue which was dissolved in ether and washed with saturated solution of $NaHCO_3$ (~50 mL) to neutralize acetic acid. The usual workup and column chromatography (SiO_2) afforded the product.

3-Acetamido-1-phenylbut-1-ene (2a): yield 57% (0.6 g); mp 91 °C; ^{1}H-NMR (CCl_4) δ 7.0 (bs, 6H), 6.25 (d, J = 16.5 Hz, 1H) 5.9 (dd, J = 16.5, 6.8 Hz, 1H), 4.7–4.3 (m, 1H), 1.85 (s, 3H), 1.2 (d, J = 8 Hz, 3H); IR (KBr) 3280, 3080, 1630 cm^{-1}. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.19; H, 7.93. Found: C, 76.26; H, 7.97.

3-Acetamido-1-phenylpent-1-ene (2b): yield 64% (0.69 g); mp 115 °C; ^{1}H-NMR (CCl_4) δ 7.1 (s, 5H), 6.56 (d, J = 16.5 Hz, 1H), 5.85 (dd, J = 16.5, 6.8 Hz, 1H), 4.4 (m, 1H), 1.9 (s, 3H), 1.5 (m, 2H), 0.9 (t, J = 7.8 Hz, 3H); IR (KBr) 3300, 3080–3030, 1630 cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO$: C, 76.84; H, 8.37. Found: C, 76.95; H, 8.42.

3-Acetamido-1-phenylhexa-1,5-diene (2c): yield 57% (0.70 g); mp 95 °C; ^{1}H-NMR (CCl_4) δ 7.1 (s, 5H), 6.58 (d, J = 16.8 Hz, 1H), 5.76 (dd, J = 16.8, 7.2 Hz, 1H), 5.21 (m, 1H), 4.95 (m, 2H), 4.42 (m, 1H), 2.25 (t, J = 7.8 Hz, 2H), 1.85 (s, 3H); IR (CCl_4) 3300, 3080, 1640 cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO$: C, 78.14; 7.90. Found: C, 78.25; H, 7.89.

Methyl 5-Acetamido-7-phenylhepta-2,6-dienoate (2d): yield 34% (0.27 g); ^{1}H-NMR (CCl_4) δ 6.95–7.26 (m, 6H), 6.42 (d, J = 16.8 Hz, 1H), 5.25–5.43 (m, 2H), 4.50 (m, 1H), 3.52 (s, 3H), 2.88 (m, 2H), 1.85 (s, 3H); IR (thin film) 3280, 3040, 1720, 1640 cm^{-1}. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.33; H, 6.96. Found: C, 70.42; H, 6.93.

4-Acetamido-4-cyclohexylbut-2-ene (2e): yield 26% (0.20 g); ^{1}H-NMR (CCl_4) δ 7.2 (br d, 1H), 5.48 (m, 2H), 4.25 (m, 1H), 2.03 (m, 1H), 1.95 (s, 3H), 1.85 (d, J = 7.2 Hz, 3H), 1.12–1.68 (m, 10H); IR (thin film) 3310, 3090, 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.84; H, 10.77. Found: C, 73.98; H, 10.82.

3-Acetamido-1-cyclohexylbut-1-ene (3e): yield 43% (0.35 g); ^{1}H-NMR (CCl_4) δ 7.2 (br d, 1H), 5.36 (m, 2H), 4.30 (m, 1H), 2.12 (m, 1H), 1.86 (s, 3H), 1.18–1.59 (m, 10H), 1.15 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 20.85, 23.44, 26.02, 26.14, 32.89, 40.30, 46.44, 53.58, 70.36, 128.57, 136.63, 169.33; IR (CCl_4) 3310, 3090, 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.79; H, 10.80. Found: C, 73.82; H, 10.92.

4-Acetamidohepta-1,5-diene (2f): yield 27% (0.37 g); ^{1}H-NMR (CCl_4) δ 7.15 (br d, 1H), 5.25–5.71 (m, 3H), 4.95 (m, 2H), 4.3 (m, 1H), 2.25 (t, J = 7.8 Hz, 2H), 1.89 (s, 3H), 1.76 (d, J = 7.8 Hz, 3H); IR (KBr) 3300, 3080, 1640 cm^{-1}. Anal. Calcd for $C_9H_{15}NO$: C, 70.58; H, 9.80. Found: C, 70.66; H, 9.92.

6-Acetamidohepta-1,4-diene (3f): yield 40% (0.55 g); ^{1}H-NMR (CCl_4) δ 7.25 (br d, 1H), 5.18–5.68 (m, 3H), 5.85 (m, 2H), 4.37 (m 1H), 2.65 (m, 2H), 1.86 (s, 3H), 1.15 (d, J = 8 Hz, 3H); IR (KBr) 3310, 3080, 1640 cm^{-1}. Anal. Calcd for $C_9H_{15}NO$: C, 70.58, H, 9.80. Found: C, 70.67; H, 9.87.

5-Acetamido-1-phenylhex-3-en-1-yne (2g): yield 54% (0.40 g); mp 104–105 °C; ^{1}H-NMR ($CDCl_3$) δ 7.4 (m, 6H), 6.12–6.28 (m, 1H), 5.48–5.80 (m, 1H), 4.76 (m, 1H), 2.0 (s, 3H), 1.20 (d, J = 7.8 Hz, 3H); IR (KBr) 3280, 3080, 1630 cm^{-1}. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.08. Found: C, 78.96; H, 7.18.

3-Acetamido-5-isopropenyl-2-methylcyclohex-1-ene (2h): yield 61% (0.64 g); mp 56–58 °C; ^{1}H-NMR (CCl_4) δ 7.3 (br d, 1H), 5.48 (m, 1H), 4.68 (bs, 2H), 4.2 (m, 1H), 2.1–2.27 (m, 3H), 1.95 (s, 3H), 1.85 (s, 3H), 1.81 (s, 3H), 1.30–1.43 (m, 2H); IR (KBr) 3280, 3080, 1640 cm^{-1}. Anal. Calcd for $C_{12}H_{19}NO$: C, 74.61; H, 9.84. Found: C, 74.72; H, 9.97.

The compound **2h** was also prepared by reacting *trans*-carvyl acetate (**6k**) (1.7 g, 0.01 mol), acetonitrile (0.82 g, 0.02 mol), and catalyst **16** (~25 mg) in acetic acid (~25 mL) at 90 °C for 13 h. Usual workup followed by column chromatography afforded a 3:1 mixture of *syn*- and *anti*-amide **2h** (79%). The ^{1}H-NMR of *syn*- and *anti*-**2h** was consistent with the reported[5] spectrum.

3-(Prop-1′-enamido)-1-phenylbut-1-ene (4a): yield 37% (0.55 g); mp 108 °C; ^{1}H-NMR ($CDCl_3$) δ 7.3 (s, 5H), 5.95–6.88 (m, 4H), 5.7 (dd, J = 10, 3.7 Hz, 1H), 4.62 (m, 1H), 1.31 (d, J = 7.8 Hz, 3H); IR (KBr) 3280, 3060, 1645 cm^{-1}. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.61; H, 7.46. Found: C, 77.72; H, 7.52.

4-Acetamido-2-methylbut-2-ene (2i): yield 70% (0.62 g); ^{1}H-NMR (CCl_4) δ 7.1 (br d, 1H), 5.1 (t, J = 7.0 Hz, 1H), 3.7 (t, J = 7.0 Hz, 2H), 1.85 (s, 3H), 1.78 (s, 6H); IR (thin film) 3300, 3080, 1640 cm^{-1}. Anal. Calcd for $C_7H_{13}NO$: C, 66.14; H, 10.23. Found: C, 66.21; H, 10.36.

4-Acetamido-2,3-dimethylbut-2-ene (2j): yield 66% (0.55 g); ^{1}H-NMR (CCl_4) δ 7.2 (br d, 1H), 3.78 (d, J = 6.8 Hz, 2H), 1.9 (s, 3H), 1.83 (s, 3H), 1.79 (s, 3H), 1.72 (s, 3H); IR (thin film) 3300, 1640 cm^{-1}. Anal. Calcd for $C_8H_{15}NO$: C, 68.08; H, 10.63. Found: C, 68.17; H, 10.69.

4-Acetamido-4-methyloct-2-ene (2k): yield 50% (0.45 g); ^{1}H-NMR (CCl_4) δ 7.2 (d, J = 8.2 Hz, 1H), 5.45 (m, 1H), 4.52 (m, 1H), 2.18 (m, 2H), 1.85 (s, 3H), 1.78 (s, 3H), 1.25 (m, 4H), 1.21 (d, J = 7.2 Hz, 3H), 0.88 (t, J = 7.0 Hz, 3H); IR (thin film) 3280, 3080, 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NO$: C, 72.13; H, 11.47. Found: C, 72.17; H, 11.52.

8-Acetamido-2,6-dimethylocta-2,6-diene (21): yield 52% (0.78 g); ^{1}H-NMR (CCl_4) δ 7.2 (br d, 1H), 5.1–5.32 (m, 2H), 3.6 (m, 2H), 2.15 (m, 4H), 1.88 (s, 3H), 1.80 (s, 3H), 1.77 (s, 3H), 1.72 (s, 3H); IR (thin film) 3320, 3090, 1650 cm^{-1}. Anal. Calcd for $C_{12}H_{21}NO$: C, 73.84; H, 10.77. Found: C, 73.89; H, 10.82.

8-(Prop-1′-enamido)-2,6-dimethylocta-2,6-diene (4b): yield 25% (0.21 g); mp 104–106 °C; ^{1}H-NMR ($CDCl_3$) δ 7.2 (m, 1H), 6.1–6.22 (m, 2H), 5.31–5.62 (m, 3H), 3.42 (m, 2H), 1.85–2.12 (m, 4H), 1.82 (s, 3H), 1.78 (s, 3H), 1.75 (s, 3H). IR (KBr) 3260, 3060, 1640 cm^{-1}. Anal. Calcd for $C_{13}H_{21}NO$: C, 75.36; H, 10.14. Found: C, 75.42; H, 10.25.

5-Acetamido-3,5-dimethyl-1-phenylpent-3-en-1-yne (2m): yield 56% (0.44 g); ^{1}H-NMR (CCl_4) δ 7.1 (s, 5H), 5.5 (m, 1H), 4.7 (m, 1H), 1.85 (s, 3H), 1.8 (s, 3H), 1.15 (d, J = 8 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 21.10, 23.16, 46.05, 119.68, 123.11, 128.30, 129.93, 130.94, 131.56, 138.29, 141.85, 169.45; IR (KBr) 3300, 3060, 2100, 1640 cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.53. Found: C, 79.37; H, 7.63.

3-Acetamido-5-isopropenyl-2-methyl-1-phenylcyclohex-1-ene (2n): yield 48% (0.94 g); mp 129 °C; ^{1}H-NMR (CCl_4) δ 6.98 (m, 6H), 4.82 (s, 2H), 4.31–4.41 (m, 1H), 1.91–2.12 (m, 3H), 1.82 (s, 3H), 1.79 (s, 3H), 1.68 (s, 3H), 1.55 (m, 2H); IR (KBr) 3300, 3080, 1630 cm^{-1}. Anal. Calcd for $C_{18}H_{23}NO$: C, 80.29; H, 8.55. Found: C, 80.24; H, 8.42.

3-Acetamido-5-isopropenyl-2-methyl-1-(2′-phenylethynyl)cyclohex-1-ene (2o): yield 55% (0.48 g); ^{1}H-NMR ($CDCl_3$) δ 7.15 (m, 6H), 4.71 (s, 2H), 4.5 (m, 1H), 1.90–2.1 (m, 3H), 1.85 (s, 3H), 1.80 (s, 6H), 1.46 (m, 2H); IR (KBr) 3300,

3080, 2200, 1640 cm^{-1}. Anal. Calcd for $C_{20}H_{23}NO$: C, 81.91; H, 7.85. Found: C, 81.81; H, 7.76.

3-Acetamido-1-phenylprop-1-ene (7a): yield 70% (1.2 g); ^{1}H-NMR (CCl_4) δ 7.1 (s, 5H), 6.57 (d, J = 16.8 Hz, 1H), 5.9 (m, 2H), 3.9 (t, J = 6.8 Hz, 2H), 1.85 (s, 3H); IR (CCl_4) 3280, 3080, 1630 cm^{-1}; MS (CI) m/z (relative intensity) 175 (12.2) [M^+], 176 (87.7), 193 (100).

4-Acetamidopent-2-ene (7b): yield 84% (0.9 g); ^{1}H-NMR (CCl_4) δ 7.15 (br d, 1H), 5.45 (m, 2H), 4.25 (m, 1H), 1.8 (s, 3H), 1.6 (d, J = 7.0 Hz, 3H), 1.2 (d, J = 7.8 Hz, 3H). IR (CCl_4) 3300, 3050, 1630 cm^{-1}.

4-Acetamidodec-2-ene (7c): yield 23% (0.22 g); ^{1}H-NMR (CCl_4) δ 6.3–5.9 (br d, 1H), 5.4 (m, 2H), 4.2 (m, 1H), 1.8 (s, 3H), 1.6 (d, J = 8.0 Hz, 3H), 1–1.30 (br s, 10H), 0.9 (t, J = 6.8 Hz, 3H); IR (CCl_4) 3300, 3050, 1630 cm^{-1}; MS (CI) m/z (relative intensity) 197 (100) [M^+].

2-Acetamidodec-3-ene (8c): yield 47% (0.46 g); ^{1}H-NMR δ 6.0–6.5 (br d, 1H), 5.4 (m, 2H), 4.2 (m, 1H), 1.85 (s, 3H), 1.15–1.4 (m, 13H), 0.95 (t, J = 6.8 Hz, 3H); IR (CCl_4) 3310, 3060, 1630 cm^{-1}; MS (CI) m/z (relative intensity) 197 (100) [M^+].

4-Acetamidohept-2-ene (7d). The reaction was performed with **6h** (0.01 mol, 1.56 g), acetonitrile (0.02 mol, 0.82 g), $CoCl_2$/Co-catalyst **14**, **15**, or **16** in acetic acid (25 mL) at 90 °C for 15 h. Usual workup followed by column chromatography afforded **7d**: ^{1}H-NMR ($CDCl_3$) δ 7.6 (br d, 1H), 5.2–5.4 (m, 2H), 4.2 (m, 1H), 1.9 (s, 3H), 1.65 (d, J = 5.8 Hz, 3H), 1.3 (m, 4H), 0.9 (t, J = 7 Hz, 3H); IR (thin film) 3330, 2985, 1635 cm^{-1}; MS (CI) m/z (relative intensity) 155 (100) [M^+].

2-Acetamidohept-3-ene (8d): ^{1}H-NMR ($CDCl_3$) δ 7.6 (br d, 1H), 5.2–5.4 (m, 2H), 4.2 (m, 1H), 2.2 (m, 2H), 1.9 (s, 3H), 1.4 (m, 2H), 1.1 (d, J = 7 Hz, 3H), 0.9 (t, J = 7 Hz, 3H); IR (thin film) 3330, 2985, 1635 cm^{-1}; MS (CI) m/z (relative intensity) 155 (100) [M^+].

Ethyl 3-Acetamido-2-methylhex-4-enoate (7e): ^{1}H-NMR δ 7.1 (br d, 1H), 5.2–5.75 (m, 2H), 4.05 (m, 3H), 2.5 (m, 1H), 1.7 (d, J = 6.8 Hz, 3H), 1.9 (s, 3H), 1.26 (d, J = 6.8 Hz, 3H), 1.1 (t, J = 6.5 Hz, 3H); IR (thin film) 3295, 2980, 1720, 1640 cm^{-1}; MS (CI) m/z (relative intensity) 155 (100).

Ethyl 5-acetamido-2-methylhex-3-enoate (8e): yield 26%; ^{1}H-NMR ($CDCl_3$) δ 7.2 (br d, 1H), 5.2–5.71 (m, 2H), 4.12 (m, 1H), 4.05 (q, J = 6.5 Hz, 2H), 2.41 (m, 1H), 2.05 (s, 3H), 1.25 (d, J = 6.8 Hz, 3H), 1.20 (d, J = 7 Hz, 3H), 1.05 (t, J = 7 Hz, 3H); IR (thin film) 3295, 2980, 1720, 1640 cm^{-1}; MS (CI) m/z (relative intensity) 155 (100).

Methyl 5-acetamido-2,6-octadienoate (7f): yield 21%; ^{1}H-NMR ($CDCl_3$) δ 7.20 (br d, 1H), 6.95 (m, 1H), 5.23–6.25 (m, 3H), 4.20 (m, 1H), 3.60 (s, 3H), 2.30 (m, 2H), 1.95 (s, 3H), 1.7 (d, J = 6.8 Hz, 3H); IR (thin film) 3400, 2980, 1720, 1640 cm^{-1}; MS (CI) m/z (relative intensity) 211 (100) [M^+].

Methyl 7-acetamido-2,5 octadienoate (8f): yield 28%; ^{1}H-NMR δ 7.2 (br d, 1H), 6.89 (m, 1H), 5.2–6.67 (m, 3H), 4.25 (m, 1H), 3.6 (s 3H), 2.52 (m, 2H), 2.0 (s, 3H), 1.21 (d, J = 7 Hz, 3H); IR (thin film) 3400, 2980, 1720, 1640 cm^{-1}. MS (CI) m/z (relative intensity) 211 (100) [M^+].

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