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Ferrocenylimidazoline palladacycles as efficient catalysts for the aza-Claisen rearrangement reaction of allylic imidates

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Chloride-bridged palladacycle dimers 1 have been evaluated as catalysts for the aza-Claisen rearrangement of allylic imidates 2 to the corresponding allyl amides 3. Cyclopalladated complexes 1b–e bearing electron-donating substituents on imidazoline ring were identified as being superior catalysts because excellent yields were obtained without using silver salts for activation. In addition, a correlation between substituents on the imidazoline ring and catalytic activity of palladacycles was established. The electron-deficient ligands and good solubility of catalysts in the reaction solution increase the catalytic activity.

Keywords: ferrocenylimidazoline; palladacycle; catalyst; aza-Claisen rearrangement reaction

Introduction

The aza-Claisen[3,3]-sigmatropic rearrangement offers convenient access to various allylic amides from the corresponding allylic alcohols[1] (shown in Scheme 1). Considerable efforts have been devoted to developing new and effective catalysts for this rearrangement. Complexes of soft metal salts, particularly those of palladium (II), can catalyze the rearrangement of allylic imidates and allow this transformation to be carried out at relatively low temperature, as exemplified by many recent reports.[2] Despite the large amount of work published, the palladium-catalyzed rearrangement reaction mediated by most previously reported catalysts suffers unavoidably from high catalyst loadings or long reaction times, which limit its large-scale application in industry.[3] Hence, exploring more efficient palladacycle catalysts is of current interest.

Transition metal (Cu, Ir, Pd or Ru) complexes of the ligands functioned with imidazoline have emerged as an attractive research area due to the modular character of the imidazoline ring and have proven to be highly active catalysts for a range of reactions.[4]

Recently, we demonstrated that ferrocenylimidazoline palladacycles **1** (shown in Fig. 1) act as phosphine-free catalysts to induce Suzuki reaction of aryl bromides with arylboronic acid at room temperature under aerobic conditions.[5] To further extend the scope of the application, we became interested in surveying their catalytic reactivity for the aza-Claisen rearrangement reaction of allylic imidates **2** (Scheme 2).

The investigated palladacycles, which do not require silver salt for activation, can efficiently initiate the rearrangement of a series of allylic imidates to the corresponding allylic amides with low catalyst loadings under mild conditions. In addition, the relationship between the electronic effects of substituents in the imidazoline moiety and catalytic activity of their corresponding cyclopalladated complexes is disclosed as well. To the best of our knowledge, this is the first effort to establish such a correlation with the family of ferrocenylimidazoline derivatives.

Results and Discussion

Allylic imidates **2a–e** were synthesized from allylic alcohol with *N*-aryl benzimidoyl chloride (shown in Scheme 2). Compound **2a** was chosen as the model substrate to optimize the reaction medium for ferrocenylimidazoline palladacycle **1b** (Fig. 1) catalyzed aza-Claisen rearrangement reactions. The results are summarized in Table 1. The reaction outcome turned out to be strongly dependent upon the solvents, and the optimal medium was CH_2Cl_2.

We tested the reactivity of palladacycle dimers **1a**–**g** in the rearrangement reaction of allylic *N*-(4-methylphenyl) benzimidate **2a** by fixing the catalyst loading at 1 mol%. The results are given in Table 2. According to the mechanism of cyclization-induced rearrangement catalysis introduced by Overman (Scheme 3),[6] the soft electrophiles,[7] palladium complexes with electron-deficient groups, are more favorable for an attack on a 'soft' carbon–carbon double bond than those with an electron-rich groups. However, the results clearly show that catalysts **1b–e** (Table 2, entries 2–5, 90–99% yields) bearing electron-donating substituents in imidazoline ring give better yields than **1a** (55%, Table 2, entry 1), **1f** (86%, Table 2, entry 6) and **1g** (45%, Table 2, entry 8), which have electron-withdrawing substituents. The results obtained are not consistent with the conclusion from Overman.

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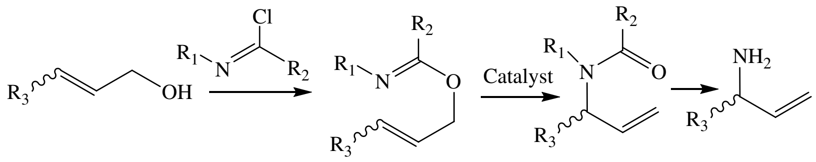
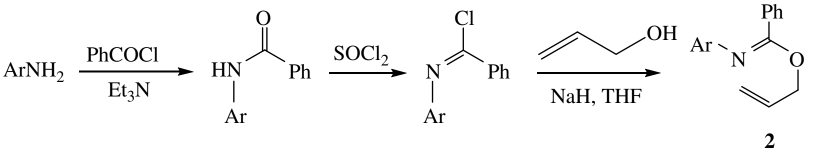
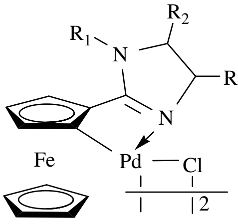


Scheme 1. Preparation of allylic amides from the corresponding allylic alcohols .



Ar = p-$CH_3C_6H_4$(**a**); p-$OCH_3C_6H_4$(**b**); p-ClC_6H_4(**c**); m-Cl(**d**); p-$NO_2C_6H_4$(**e**)

Scheme 2. Synthesis of Allylic imidates **2a-e**.



1a: R_1=H	R_2=Ph
1b: R_1=Benzyl	R_2=H
1c: R_1=n-C_5H_{11}	R_2=H
1d: R_1=n-C_8H_{17}	R_2=H
1e: R_1=n-$C_{14}H_{29}$	R_2=H
1f: R_1=Acetyl	R_2=Ph
1g: R_1=Acetyl	R_2=H

Figure 1. Structures of compounds **1**.

To provide a correlation between the variation of substituents on the imidazoline ring and the catalytic activity of the corresponding cyclopalladated complexes without silver salts for activation, we extended the scope of substrates **2** (aryl substituents are from methyl group to nitro group) catalyzed by the palladacycle dimers **1a–g** at 1 mol% catalyst loading. The results are summarized in Table 3.

For all substrates tested the results show that the catalysts **1b–e** gave higher yields than **1a,1f** and **1g** (Table 3). The solubility of complexes **1b–e** in common organic solvent is superior to that of **1a,1f** and **1g**, which possess similar solubility in dichloromethane. In addition, acetyl at 1-N and two benzyl groups at C-4 and C-5 lower the electronic density of complex **1f** on the imidazoline ring. Complex **1f** gave noticeably higher yields of the desired products compared with catalysts **1a** and **1g** (entries 6 in Tables 2 and 3), which is consistent with the observation reported from Overman *et al.*[8] Therefore, the results imply that the electronic properties of substituents in the imidazoline moiety are important factors in the catalytic properties of palladacycle dimers and strong electron-withdrawing substituents are favored for the aza-Claisen rearrangement reaction. On the other hand, the solubility of catalyst may also play a crucial role.

To investigate the influence of *N*-aryl groups on allylic imidates, different *N*-aryl allylic imidates **2** were examined. The results obtained are given in Table 2 and 3. It is evident that **2a** and **2b**, which have an electron-donating group in *N*-aryl ring, were rearranged to the corresponding allylic amides **3a** and **3b** in good to excellent yields in the presence of complexes **1b–e**. When allylic imidiates such as **2c** and **2d** were employed as substrates, the desired products were obtained in low to moderate yields. Meanwhile, changing aryl substituents from methoxyl (**2b**) to nitro (**2e**) resulted in obvious decreases in yields. Presumably, the electron-donating group on the *N*-aryl ring stabilizes the cyclization-induced transition state **III** (Scheme 3). Fortunately, we were pleased to find that less active substrate **2e** could be efficiently rearranged to the corresponding allylic amides **3e** in excellent isolated yields (>94%) catalyzed by complex **1b**. The results reveal that the nature of substrate seems to be predominant in the arrangement reaction.

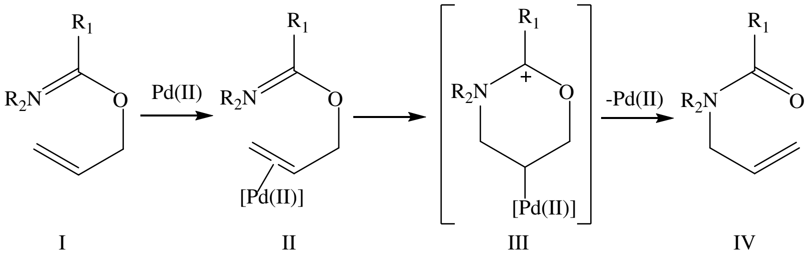
Conclusions

In summary, a series of ferrocenylimidazoline palladacycles were found to serve as effective catalysts for the aza-Claisen rearrangement of various allylic imidates. These catalytic rearrangements occur at room temperature (25 °C) with 1mol% catalyst loading without the use of silver salts for activation. The electronic properties of substituents on the imidazoline moiety and the solubility of chloride-bridged palladacycle dimers significantly affect the catalytic activity of ferrocenylimidazoline palladacycles. The electron-deficient ligand and good solubility of catalysts in the reaction solution are efficient in increasing the catalytic activity. In addition, the effect of the nature of the substrates should also be taken into account. This study is significant since it provides more insight into the understanding of the role of the 'tenability' of imidazoline moiety in the catalytic process. Further studies on the application of these palladacycles in organic synthesis, especially in asymmetric catalysis, are in progress.

Experimental

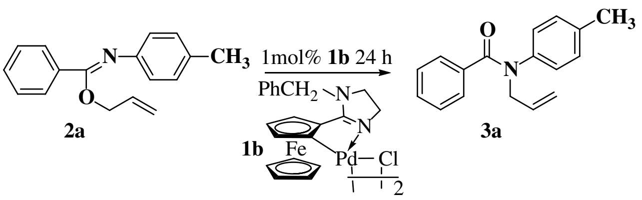
General

Tetrahydrofuran (Tianjin no. 1 Chemical Reagent Factory, AR) and diethyl ether (Tianjin no. 1 Chemical Reagent Factory, AR) were purified freshly by distillation from sodium/benzophenone. Dichloromethane (Tianjin no. 1 Chemical Reagent Factory, AR) was distilled from calcium hydride (Aldrich, 90–95%) under nitrogen. Melting points were measured on a WC-1 microscopic apparatus and uncorrected. Elemental analyses were determined with a PE-2400 II apparatus. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument using $CDCl_3$ as the solvent and TMS (0.00 ppm) as the internal reference. ^1H spectra were collected at 400 MHz using a 6000 Hz spectral width, a relaxation delay of 3 s,



Scheme 3. The mechanism of cyclization-induced rearrangement.

Table 1. Aza-Claisen rearrangement of allylic *N*-(4-methylphenyl)benzimidate **2a** to allyl *N*-(4-methylphenyl)benzamide **3a** at room temperature: study of the reaction solvents[a]



Entry	Solvent	Temperature (°C)	Yield (%)[b]
1	$ClCH_2CH_2Cl$	25	57
2	$ClCH_2CH_2Cl$	50	80
3	THF	25	64
4	THF	60	84
5	CH_2Cl_2	25	90

[a] Reaction conditions: 1 equiv. of **2a**, 2 ml of solvent, 1 mol% of **1b**, 24 h.
[b] Isolated yields, average of two runs.

Table 2. Palladacycles **1a–g** catalyzed aza-Claisen rearrangement reaction of allylic imidates **2a**[a]

Entry	Substrate	Catalyst	Product	Time (h)	Yield (%)[b]
1	**2a**	**1a**	**3a**	24	55
2	**2a**	**1b**	**3a**	24	90
3	**2a**	**1c**	**3a**	24	98
4	**2a**	**1d**	**3a**	24	99
5	**2a**	**1e**	**3a**	24	99
6	**2a**	**1f**	**3a**	24	86
7	**2a**	**1g**	**3a**	24	45

[a] Reaction conditions: 1 equiv. of **2a**, 2 ml of CH_2Cl_2, 1 mol% of **1**, at room temperature.
[b] Isolated yields, average of two runs.

32k data points and a pulse width of 38°. ^{13}C NMR spectra were collected at 100 MHz using a 25 kHz spectra width, a relaxation delay of 3 s, 32k data points and a pulse width of 40°. IR spectra were collected on a Bruker VECTOR22 spectrophotometer using KBr pellet in the 4000–400 cm^{-1} region.

Materials

The *N*-*p*-tolyl-benzimidoyl chloride,[9] *N*-(*p*-methoxylphenyl)-benzimidoyl chloride,[9] *N*-(*p*-chlorophenyl)-benzimidoyl chloride,[10] *N*-(*m*-chlorophenyl)-benzimidoyl chloride,[9] *N*-(*p*-nitrophenyl)-benzimidoyl chloride[11] and ferrocenylimidazoline palladacycles **1a–f**[5] were prepared according to the reported procedures. Unless noted, all other chemicals were commercial products and used without further purification.

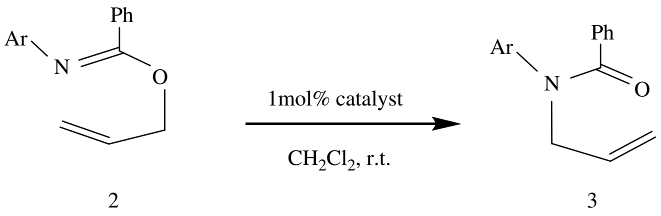
General procedure for synthesis of allylic imidates 2 is given as described for 2a

A solution of allyl alcohol (174 mg, 3mmol) in dry THF (10 ml) was added to a suspension of NaH (150 mg, 3.75mmol, 60% in mineral oil) in dry THF (10 ml) under nitrogen. The mixture was stirred for 20 min at room temperature and then refluxed for 2 h. The mixture was cooled to room temperature and treated with a solution of *N*-*p*-tolyl-benzimidoyl chloride (687 mg, 3 mmol) in dry THF (10 ml). The mixture was stirred overnight and a small amount of water was added. The mixture was extracted with Et_2O (4 × 15 ml) and the combined organic layer was washed with H_2O (2 × 10 ml) and brine (20 ml) and dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvent gave an oily residue, which was purified by column chromatography (diethyl ether : petroleum ether, 60–90 °C, 1 : 3) to give the product **2a** (624 mg, 82%).

*Characterization for allyl N-p-tolylbenzimidate (**2a**)*

Pale yellow oil. Yield: 82%. IR (KBr pellet): 3024, 2923, 1660, 1603, 1506, 1448, 1264, 1112, 977, 927, 824, 778, 697 cm^{-1}. ^{1}H NMR ($CDCl_3$, ppm): δ = 7.31 (m, 2H, C_6H_5), 7.23 (m, 1H, C_6H_5), 7.15

Table 3. Palladacycles **1a–g** catalyzed aza-Claisen rearrangement reaction of allylic imidates **2b–e**[a]



Ar = *p*-$CH_3OC_6H_4$(**b**); *p*-ClC_6H_4(**c**); *m*-ClC_6H_4(**d**); *p*-$NO_2C_6H_4$(**e**)

Entry	Substrate	Catalyst	Product	Time (h)	Yield (%)[b]
1	**2b**	**1a**	**3b**	24	63
2	**2b**	**1b**	**3b**	24	96
3	**2b**	**1c**	**3b**	24	99
4	**2b**	**1d**	**3b**	24	99
5	**2b**	**1e**	**3b**	24	99
6	**2b**	**1f**	**3b**	24	90
7	**2b**	**1g**	**3b**	24	51
8	**2c**	**1a**	**3c**	24	31
9	**2c**	**1b**	**3c**	24	45
10	**2c**	**1c**	**3c**	24	52
11	**2c**	**1d**	**3c**	24	56
12	**2c**	**1e**	**3c**	24	68
13	**2c**	**1f**	**3c**	24	31
14	**2c**	**1g**	**3c**	24	20
15	**2c**	**1c**	**3c**	24	52
16	**2d**	**1a**	**3d**	24	30
17	**2d**	**1b**	**3d**	24	73
18	**2d**	**1c**	**3d**	24	54
19	**2d**	**1d**	**3d**	24	65
20	**2d**	**1e**	**3d**	24	50
21	**2d**	**1f**	**3d**	24	35
22	**2d**	**1g**	**3d**	24	27
24	**2e**	**1a**	**3e**	72	19
25	**2e**	**1b**	**3e**	24	94
26	**2e**	**1c**	**3e**	24	21
27	**2e**	**1d**	**3e**	24	22
28	**2e**	**1e**	**3e**	72	22
29	**2e**	**1f**	**3e**	72	14

[a] Reaction conditions: 1 equiv. of **2**, 2 ml of CH_2Cl_2, 1 mol% of **1**, at room temperature.
[b] Isolated yields, average of two runs.

(m, 2H, C_6H_5), 6.93 (m, 2H, C_6H_4), 6.59 (m, 2H, C_6H_4), 6.11 (m, 1H, =CH), 5.40m, 5.23m (2H, $=CH_2$), 4.84 (m, 2H, CH_2O), 2.20 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 157.8$ (C=N), 145.5, 133.1, 131.3, 129.6, 129.3, 129.2, 127.7, 121.3 (C_{Ar}), 131.6 (CH=), 117.3 ($CH_2=$), 66.9 (CH_2O), 20.6 (CH_3). Anal. calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.53; H, 6.47; N, 5.39%.

*Characterization for allyl N-p-methoxylphenylbenzimidate (**2b**)*

Pale yellow oil. Yield: 77%. IR (KBr pellet): 1657, 3031, 1601, 1501, 1112, 979, 926 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm): $\delta = 7.29$ (m, 3H, C_6H_5), 7.22 (2H, m, C_6H_5), 6.72(2H, m, C_6H_4), 6.63 (2H, m, C_6H_4), 6.14m, 5.43m (2H, $=CH_2$), 5.27 (1H, m, $=CH_2$), 4.85 (2H, m, CH_2O), 3.73 (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 158.4$ (C=N), 155.3, 141.5, 131.4, 129.7, 129.3, 128.1, 122.5, 114.2 (C_{Ar}), 133.2 (CH=), 117.5 ($CH_2=$), 67.1 (CH_2O), 55.4 (OCH_3). Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.52; H, 6.17; N, 5.49%.

*Characterization for allyl N-p-chlorophenylbenzimidate (**2c**)*

Pale yellow oil. Yield: 62%. IR (KBr pellet): 3084, 3028, 2925, 2854, 1659, 1595, 1487, 1448, 1275, 1114, 975, 927, 834, 778, 697 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.32$ (m, 3H, C_6H_5), 7.26 (m, 2H, C_6H_5), 7.12 (m, 2H, C_6H_4), 6.64 (m, 2H, C_6H_4), 6.13 (m, 1H, =CH), 5.44m, 5.29m (2H, $=CH_2$), 4.86 (m, 2H, CH_2O). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 158.7$ (C=N), 146.9, 130.8, 130.1, 129.2, 128.9, 128.0, 127.8, 122.9 (C_{Ar}), 132.8 (CH=), 117.7 ($CH_2=$), 67.3 (CH_2O). Anal. calcd for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.44; H, 5.03; N, 5.07%.

*Characterization for allyl N-m-chlorophenylbenzimidate (**2d**)*

Pale yellow oil. Yield: 57%. IR (KBr): 3063, 2925, 2854, 1660, 1588, 1449, 1356, 1274, 1117, 1027, 975, 927, 868, 780, 697 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.28$ (m, 3H, C_6H_5), 7.18 (m, 2H, C_6H_5), 7.00 (m, 1H, C_6H_4), 6.90 (m, 1H, C_6H_4), 6.77 (m, 1H, C_6H_4), 6.56 (m, 1H, C_6H_4), 6.08 (m, 1H, =CH), 5.40m, 5.25m (2H, =CH_2), 4.83 (m, 2H, CH_2O). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 158.7$ (C=N), 149.7, 134.4, 130.4, 130.2, 129.9, 129.2, 128.1, 122.6, 121.8, 119.8 (C_{Ar}), 132.9 (CH=), 117.8 (CH_2=), 67.4 (CH_2-O). Anal. calcd for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.51; H, 4.92; N, 5.02%.

*Characterization for allyl N-p-nitrophenylbenzimidate (**2e**)*

Yellow solid. Yield: 44%. IR (KBr): 3057, 2920, 2852, 1638, 1586, 1502, 1446, 1334, 1270, 1126, 1102, 971, 924, 849, 755, 699 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.30$ (m, 5H, C_6H_5), 8.07 (m, 2H, C_6H_4), 6.79 (m, 2H, C_6H_4), 6.13 (m, 1H, =CH), 5.45m, 5.32m (2H, =CH_2), 4.87 (m, 2H, CH_2O). ^1H NMR ($CDCl_3$, ppm): $\delta = 8.08{-}8.06$ (m, 2H, ArH), 7.36–7.24 (m, 5H, ArH), 6.80–6.78 (m, 2H, ArH), 6.16–6.09 (m, 1H, CH), 5.48–5.43 (m, 1H, CH_2CH), 5.33–5.31 (m, 1H, CH_2CH), 4.87–4.86 (m, 2H, CH_2O). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 159.1$ (C=N), 154.9, 143.0, 130.8, 130.1, 129.2, 128.3, 125.1, 121.8 (C_{Ar}), 132.4 (CH=), 118.2 (CH_2=), 67.8 (CH_2O). Anal. calcd for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.23; H, 4.83; N, 9.75%.

Aza-Claisen rearrangement of allylic imidates 2 catalyzed with 1a–g

A general procedure was given for the aza-Claisen rearrangement of **2a** (Table 2, entry 1). To a solution of **2a** in dichloromethane (1 ml, 0.2 M), palladacycle **1a** (0.002 mmol) was added. The reaction mixture was stirred at room temperature for 24 h in the air. Then the crude reaction mixture was purified by column chromatography (diethyl ether : petroleum ether, 60–90 °C, 1 : 3) to give the product **3a**. The yields are found in Table 2.

*Characterization for N-allyl-N-p-tolylbenzamide (**3a**)*

Yellow solid. IR (KBr): 3024, 2923, 1660, 1506, 1448, 1353, 1264, 1112, 1029, 977, 927, 824, 778, 697 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.31$ (m, 2H, C_6H_5), 7.23 (m, 1H, C_6H_5), 6.98 (m, 2H, C_6H_5), 7.15 (m, 2H, C_6H_4), 6.90 (m, 2H, C_6H_4), 5.97 (m, 1H, =CH), 5.18 (m, 2H, =CH_2), 4.50 (m, 2H, NCH_2), 2.25 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 170.6$ (C=O), 141.3, 136.8, 136.5, 130.0, 129.9, 129.1, 128.1, 127.7 (C_{Ar}), 133.6 (CH=), 118.0 (CH_2=), 53.6 (CH_2–N), 21.3 (CH_3). Anal. calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.03; H, 6.68; N, 5.41%.

*Characterization for N-allyl-N-(p-methoxylphenyl)benzamide (**3b**)*

Yellow solid. IR (KBr): 3011, 1645, 1603, 971, 923 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.28$ (m, 2H, C_6H_5), 7.17 (m, 3H, C_6H_5), 6.92 (2H, m, C_6H_4), 6.70 (2H, m, C_6H_4), 5.96 (1H, m, =CH), 5.17 (2H, m, =CH_2), 4.47 (2H, m, NCH_2), 3.70 (3H, s, CH_3). $^{13}CNMR$ ($CDCl_3$, ppm): $\delta = 170.3$ (C=O), 157.9, 136.2, 133.2, 129.5, 128.8, 128.6, 127.9, 127.7 (C_{Ar}), 136.1 (CH=), 117.6 (CH_2=), 114.2, 55.3 (CH_3O), 53.3 (CH_2O). Anal. calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.68; H, 6.07; N, 5.37%.

*Characterization for N-allyl-N-(p-chlorophenyl)benzamide (**3c**)*

Yellow solid. IR (KBr): 3064, 2927, 1648, 1490, 1376, 1305, 1094, 1016, 923, 835, 789, 720, 645 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.30$ (m, 2H, C_6H_4), 7.24 (m, 1H, C_6H_5), 7.16 (m, 4H, C_6H_5 and C_6H_4), 6.96 (m, 2H, C_6H_5), 5.95 (m, 1H, =CH), 5.18 (m, 2H, =CH_2), 4.49 (m, 2H, NCH_2). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 170.1$ (C=O), 142.1, 135.5, 132.1, 129.9, 129.2, 128.7, 127.9 (C_{Ar}), 132.8 (CH=), 118.0 (CH_2=), 53.1 (CH_2-N). Anal. calcd for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.56; H, 5.34; N, 5.01%.

*Characterization for N-allyl-N-(m-chlorophenyl)benzamide (**3d**)*

Yellow solid. IR (KBr): 3068, 2927, 1650, 1583, 1477, 1373, 1302, 1084, 1031, 977, 923, 873, 786, 701 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 7.32$ (m, 2H, C_6H_5), 7.10 (m, 3H, C_6H_5), 7.26 (m, 1H, C_6H_4), 7.18 (m, 2H, C_6H_4), 6.86 (m, 1H, C_6H_4), 6.00 (m, 1H, =CH), 5.18 (m, 2H, =CH_2), 4.49 (m, 2H, NCH_2). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 170.3$ (C=O), 157.9, 135.4, 134.4, 132.8, 130.0, 128.6, 127.9, 127.2, 126.8, 125.9 (C_{Ar}), 129.4 (CH=), 114.1 (CH_2=), 55.3 (CH_2-N). Anal. calcd for $C_{16}H_{14}ClNO$: C, 70.72; H, 5.19; N, 5.15. Found: C, 70.39; H, 5.41; N, 5.31%.

*Characterization for N-allyl-N-(p-nitrophenyl)benzamide (**3e**)*

Yellow solid. IR (KBr): 3077, 2929, 2851, 1656, 1593, 1593, 1517, 1343, 1230, 1113, 917, 925, 854, 792, 706, 645 cm^{-1}. ^1H NMR ($CDCl_3$, ppm): $\delta = 8.07$ (m, 2H, C_6H_4), 7.24 (m, 2H, C_6H_4), 7.33 (m, 3H, C_6H_5), 7.17 (m, 2H, C_6H_5), 5.96 (m, 1H, =CH), 5.24 (m, 2H, =CH_2), 4.60 (m, 2H, NCH_2). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 170.2$ (C=O), 149.6, 145.1, 134.9, 130.7, 128.8, 128.2, 127.0, 124.5 (C_{Ar}), 132.6 (CH=), 118.2 (CH_2=), 52.9 (CH_2-N). Anal. calcd for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.33; H, 4.71; N, 9.78%.

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