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Lanthanide Chloride Catalyzed Imino Diels−Alder Reaction. One-Pot Synthesis of Pyrano[3,2-*c*]- and Furo[3,2-*c*]quinolines

Yun Ma, Changtao Qian,* Meihua Xie,[†] and Jie Sun

Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China, and Institute of Organic Chemistry, Anhui Normal University, Wuhu 241000, Anhui, China

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Introduction

Tetrahydroquinoline derivatives are an important class of natural products and exhibit biological activities in various field[1], such as psychotropic,[2] antiallergenic,[3] antiinflammatory,[4] and estronegic activity.[5] In addition, pyranoquinoline derivatives are used as potential pharmaceuticals.[6] It is therefore not surprising that many synthetic methods have been developed for these compounds.[7] Among them, the aza-Diels−Alder reaction between *N*-arylimines and nucleophilic olefins is probably one of the most powerful synthetic tools for constructing N-containing six-membered heterocyclic compounds. Since the pioneering work of Povarov,[8] $BF_3{\cdot}OEt_2$ has been the most commonly used catalyst for this reaction. Transition metal complexes such as $Co_2(CO)_8$ and $Ni(CO)_4$[9] are also found to be effective. Recently, $InCl_3$ and others begin to find their use in this reaction too.[10,11] All of the methods mentioned above require lengthy procedures to prepare the starting materials. To our knowledge, many imines are hygroscopic, unstable at high temperature, difficult to purify by distillation or column chromatography, and thus lack efficiency. Therefore, developing simple and efficient synthetic methods for preparing this type of compound becomes more and more important.

For such reactions, not only effective catalysts but also simple and convenient procedures are needed. Lanthanide chlorides, which are simple, low-cost, and commercially available reagents, have been used as effective catalysts in organic synthesis such as the cycloaddition of epoxides to isocyanates,[12] thioacetalization[13] and nucleophilic substitution,[14] as well as some other reactions.[15] Here, we describe an efficient one-pot aza-Diels−Alder type reaction between the imine (formed in situ from benzaldehyde and amines) and dihydropyran or dihydrofuran catalyzed by lanthanide chloride to afford pyrano[3,2-*c*]- or furo[3,2-*c*]quinolines in high yields.

Results and Discussion

Benzylideneaniline was treated with 3,4-dihydro-2*H*-pyran in the presence of a catalytic amount of $GdCl_3$ (20 mol %) in acetonitrile at room temperature. The reaction proceeded smoothly to afford the corresponding pyrano[3,2-*c*]quinoline in 88% yield. The product was obtained as a mixture of cis and trans isomers in a ratio of 34:66, but no other isomer could be detected. It shows that $GdCl_3$ did effectively catalyze the imino Diels−Alder reaction.

It is desirable from a synthetic point of view that imines, generated in situ from aldehydes and amines, immediately react with dihydropyran to afford pyrano[3,2-*c*]quinolines in an one-pot way without the need of preformation of the imines. It was found that the reaction of benzaldehyde, aniline, and 3,4-dihydro-2*H*-pyran was efficiently catalyzed by $GdCl_3$ in the presence of 4 Å molecular sieves or $MgSO_4$ under mild conditions (Scheme 1). The reaction is instantaneous and produces the pyrano[3,2-*c*]quinolines (stereoisomers **II** and **III**) as expected. Among the lanthanide chlorides screened, gadolinium chloride exhibited superior catalytic activity, while the yield of the adduct was lower for other lanthanide chlorides. The reaction did not occur in the presence of $MgSO_4$ without any lanthnide chlorides even after 12 h. Various solvents were used in the model reaction with $GdCl_3$ (20 mol %) as a catalyst; the results are summarized in Table 1. Acetonitrile was the best solvent among those tested, such as dichloromethane, tetrahydrofuran, ether, toluene, and hexane.

[†] Anhui Normal University.

[*] Corresponding author. Phone: 86-21-64163300. FAX: 86-21-64166128. E-mail: qianct@pub.sioc.ac.cn.

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Scheme 1

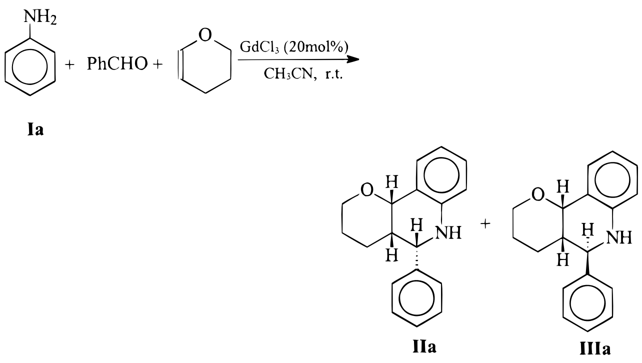


Table 1. Effect of Metal Salts and Solvents on the Reaction of Benzaldehyde, Aniline, and 3,4-Dihydro-2*H*-pyran

entry	solvent	catalyst[a]	additive	yield (%)[b]
1	CH_3CN	None	$MgSO_4$	no reaction
2	CH_3CN	$LaCl_3$	$MgSO_4$	35
3	CH_3CN	$SmCl_3$	$MgSO_4$	20
4	CH_3CN	$CeCl_3$	$MgSO_4$	25
5	CH_3CN	$NdCl_3$	$MgSO_4$	38
6	CH_3CN	$YbCl_3$	$MgSO_4$	69
7	CH_3CN	$GdCl_3$	$MgSO_4$	86
8	CH_3CN	$GdCl_3$	4 Å MS	84
9	toluene	$GdCl_3$	$MgSO_4$	trace
10	hexane	$GdCl_3$	$MgSO_4$	no reaction
11	THF	$GdCl_3$	$MgSO_4$	22
12	CH_2Cl_2	$GdCl_3$	$MgSO_4$	40
13	Et_2O	$GdCl_3$	$MgSO_4$	37

[a] 20 mol % of $LnCl_3$ was used. [b] Isolated yield.

Table 2. One−Pot Synthesis of Pyrano[3,2-*c*]quinolines from Aldehydes Catalyzed by $GdCl_3$[a]

entry	substrate (amine)	R^1	R^2	R^3	time (min)	product[b] ratio of **II**:**III**	overall yield (%)
1	**Ia**	H	H	H	30	33:67	86
2	**Ib**	H	H	Cl	45	42:58	70
3	**Ic**	H	Cl	H	30	47:53	75
4	**Id**	H	H	CH_3	45	39:61	80
5	**Ie**	H	H	OH	90	35:65	60
6	**If**	H	OCH_3	H	30	23:77	81
7	**Ig**	Cl	H	H	45		78
8	**Ih**	Cl	Cl	H	45		68

[a] 20 mol % of $GdCl_3$ was used. [b] The ratio is based on isolation by chromatography.

Several amines were examined, and the results are listed in Table 2. In all cases, the three-component one-pot reaction proceeded smoothly to give the corresponding pyrano[3,2-*c*]quinolines which could be separated by column chromatography in most cases (Scheme 2).

The structures of compounds **II** and **III** were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analyses. There are strong NH stretching band at 3200−3450 cm^{-1} in the IR spectra. The most diagnostic parameter for structural assignment is the scalar coupling constant between protons H-4a and H-5. In the isomer **IIa** the coupling constant J(4a, 5) = 5.6 Hz is significantly smaller and typical for a gauche conformation. This orientation is present in both conformers of the configuration having cis orientation of the pyran ring and phenyl group. As expected for this configuration, reciprocal H−HCOSY (Figure 1) interaction was observed among protons H-4a, H-5, and H-10b. In the isomer **IIIa**, the J(4a, 5) = 10.8 Hz is relevant and indicative of the antireciprocal orientation of protons H-5 and H-4a. This orientation is only possible when the pyran ring and phenyl group are on opposite sides of the quinoline ring of **IIIa**. The H−HCOSY analysis confirms this structural assignment for **IIIa**: a strong reciprocal interaction is found between H-4a and H-10b, a weak one between protons H-4a and H-5, but none between protons H-10b and H-5, all in accord with a trans configuration.

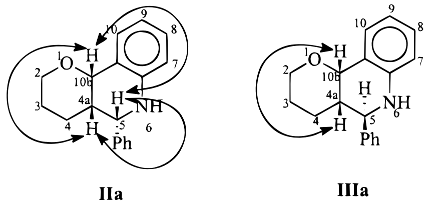
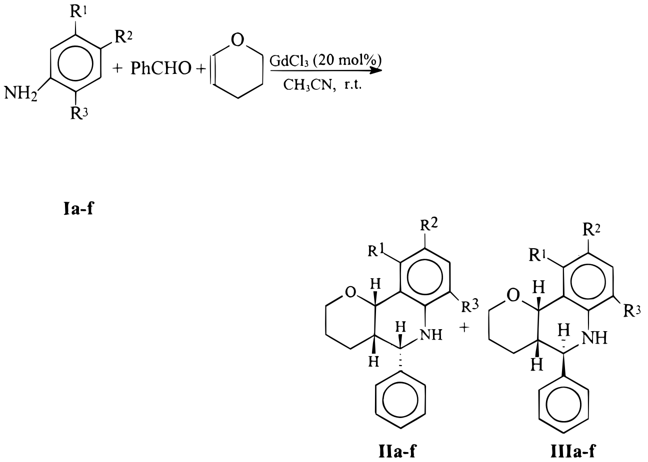


Figure 1. H−H cross-peaks observed in H−HCOSY spectra (in $CDCl_3$) of **IIa** and **IIIa**.

Scheme 2

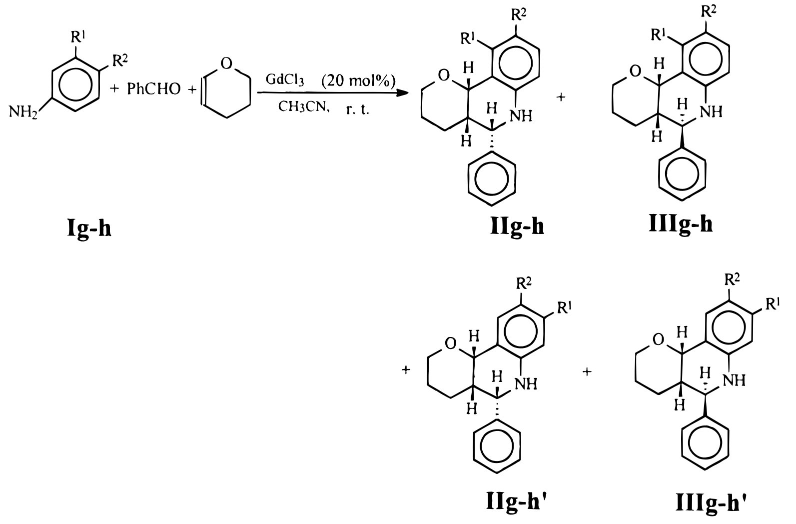


The reaction of aldehyde, *m*-chloroaniline, and dihydropyran gave a mixture of four isomers, **IIg**, **IIg′**, **IIIg**, and **IIIg′**, with a ratio of 17:15:61:7, which was determined by ^{1}H NMR in 78% combined yield. Unfortunately, the four isomers could not be separated as pure compounds by column chromatography. In addition, the reaction of 3,4-dichloroaniline with aldehyde and dihydropyran also produced **IIh**, **IIh′**, **IIIh**, and **IIIh′** in a ratio of 1:18: 21:60 with an overall yield of 80% (Scheme 3).

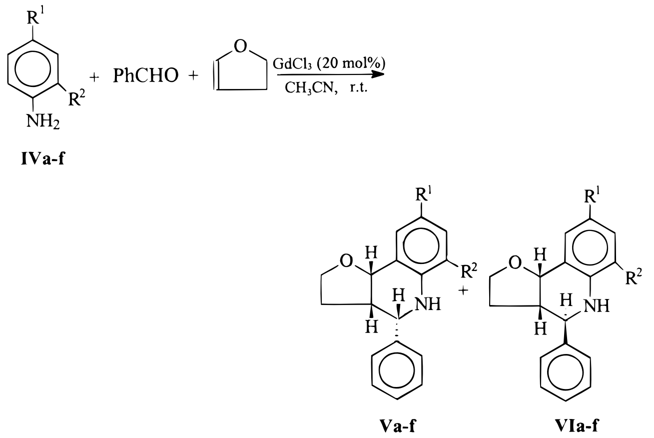
Further, we examined the reactivity of dihydrofuran with aldehyde and anilines catalyzed by $GdCl_3$. Thus, according to our method a catalytic amount of gadolinium chloride (20 mol %) and anhydrous $MgSO_4$ was treated at room temperature with a benzaldehyde and aniline in acetonitrile, followed by addition of 3,4-dihydrofuran to afford furo[3,2-*c*]quinolines **Va** and **VIa** in a ratio of 35:65 in an overall yield of 88% (Scheme 4). Therefore, dihydrofuran exhibited analogous behavior to that of dihydropyran. Similar results were obtained with other aldehyde and amines. The results are listed in Table 3. The structures of compounds **V** and **VI** were characterized by IR, ^{1}H NMR, ^{13}C NMR, MS, and elemental analyses.

The X-ray analysis of compound **IIIh** and **VIb** was achieved in order to confirm their molecular structure as shown in Figures 2 and 3. The results clearly demonstrate that compound **IIIh** is cis[16] and **VIb** is the trans configuration,[17] which are in agreement with ^{1}H NMR analysis.

Scheme 3



Scheme 4



It can be concluded that gadolinium chloride is an efficient catalyst both in the reaction of imines with dihydropyran or dihydrofuran and in the one-pot reaction of aldehydes, amines, and dihydropyran or dihydrofuran to afford dihydropyrano[3,2-*c*]- or furo[3,2-*c*]quinolines in high yields under mild conditions. Further synthetic application of these reactions is now in progress.

Experimental Section

General. CH_3CN was distilled from CaH_2 under Ar. ^1H NMR and ^{13}C NMR spectra were recorded at 300 or 400 MHz in $CDCl_3$ using TMS as internal standard. ^{13}C NMR spectral measurements were performed at 75.4 MHz using $CDCl_3$ as an internal standard. IR spectra were obtained on FTS-185 as neat films. Mass spectra were determined on a Finigan 8230 mass spectrometer. Benzylideneaniline was prepared from aniline and benzaldehyde.[18]

Table 3. One−Pot Synthesis of Furo[3,2-*c*]quinolines from Aldehyde Catalyzed by $GdCl_3$[a]

entry	substrate (amine)	R^2	R^1	time (min)	product[b] ratio of **V**:**VI**	overall yield (%)
1	**IVa**	H	H	30	35:65	88
2	**IVb**	H	OCH_3	30	45:55	80
3	**IVc**	CH_3	H	30	25:75	74
4	**IVd**	OH	H	60	48:52	67
5	**IVe**	H	Cl	30	38:62	68
6	**IVf**	H	NO_2	120	40:60[c]	61

[a] 20 mol % of $GdCl_3$ was used. [b] The ratio is based on isolation by chromatography. [c] The ratio is determined by ^1H NMR.

Reaction of Benzylideneaniline with 3,4-Dihydro-2*H*-pyran. $GdCl_3$ (0.2 mmol), benzylideneaniline (1.0 mmol), and 3,4-dihydro-2*H*-pyran (1.4 mmol) were mixed in 5 mL of acetonitrile, the mixture was stirred for 30 min at room temperature, water was added, and the product was extracted with EtOAc. The organic layer was dried with anhydrous Na_2SO_4 and evaporated to give the crude product. Analytically pure products

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(16) For compound **IIIh**: $C_{18}H_{17}Cl_2NO$, $M = 334.24$, triclinic, space group $P1$ (No. 2), crystal dimensions 0.2 × 0.2 × 0.3 mm, colorless prismatic crystal, $a = 9.534(1)$ Å, $b = 11.2904(8)$ Å, $\alpha = 93.730(8)°$, $\beta = 107.215(8)°$, $\gamma = 71.441(7)°$, $\mu = 787.4(1)°A^3$ by least-squares refinement using the setting angles of 16 carefully centered reflections in the range of $18.29 < 2\theta < 24.56°$, $Z = 2$, $D_c = 1.41$ g cm^{-3}, $F(000) = 3348.00$. Data collection and processing: Rigaku AFC7R diffractometer, graphite monochromatic Mo−Kα radiation ($\lambda = 0.71069$ Å), μ(Mo−Kα) = 4.12 cm^{-1}, 2257 reflections measured, maximum 2θ value of 49.9°, 2097 unique reflections measured ($R_{int} = 0.023$), 1645 of these with $I > 2.00\sigma(I)$ used in refinement. The data were corrected for horizon and polarization effects. The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards increased by 1.1%. A linear correction factor was applied to the data to account for this phenomenon. Structure solution of refinement: The structure was solved by direct methods using SHELXS-86 expanded using a Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 1464 observed reflections of 199 variable parameters. Refinement converged at a final $R = 0.034$ and $R_w = 0.043$. Max/min peaks in final difference map, 0.36/−0.22. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corp.

(17) For compound **VIb**: $C_{18}H_{19}NO_2$, M = 281.35, triclinic, space group $P1$ (No. 2), crystal dimensions 0.2 × 0.2 × 0.3 mm, colorless prismatic crystal, $a = 9.387(1)$ Å, $b = 11.442(2)$ Å, $\alpha = 91.73(2)°$, $\beta = 101.62(1)°$, $\gamma = 79.83(1)°$, $\mu = 728.5(2)°A^3$, by least-squares refinement using the setting angles of 16 carefully centered reflections in the range of $18.87 < 2\theta < 21.6°$, $Z = 2$, $D_c = 1.283$ g cm^{-3}, $F(000) = 300.00$. Data collection and processing: Rigaku AFC7R diffractometer, graphite monochromatic Mo−Kα radiation ($\lambda = 0.71069$ Å), μ(Mo−Kα) = 0.83 cm^{-1}, 2736 reflections measured, maximum 2θ value 50.0°, 2564 unique reflections measured ($R_{int} = 0.018$), 1891 of these with $I > 2.00\sigma(I)$ used in refinement. The data were corrected for horizon and polarization effects. A correction for secondary extinction was applied (coefficient = $3.23461\times10^{0.6}$). The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standards increased by 1.1%. A linear correction factor was applied to the data to account for this phenomenon. Structure solution of refinement: The structure was solved by direct methods using SHELXS-86 of expanded using a Fourier technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 1891 observed reflections of 267 variable parameters. Refinement converged at a final $R = 0.036$ and $R_w = 0.043$. Max/min peaks in final difference map 0.2/−0.12. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

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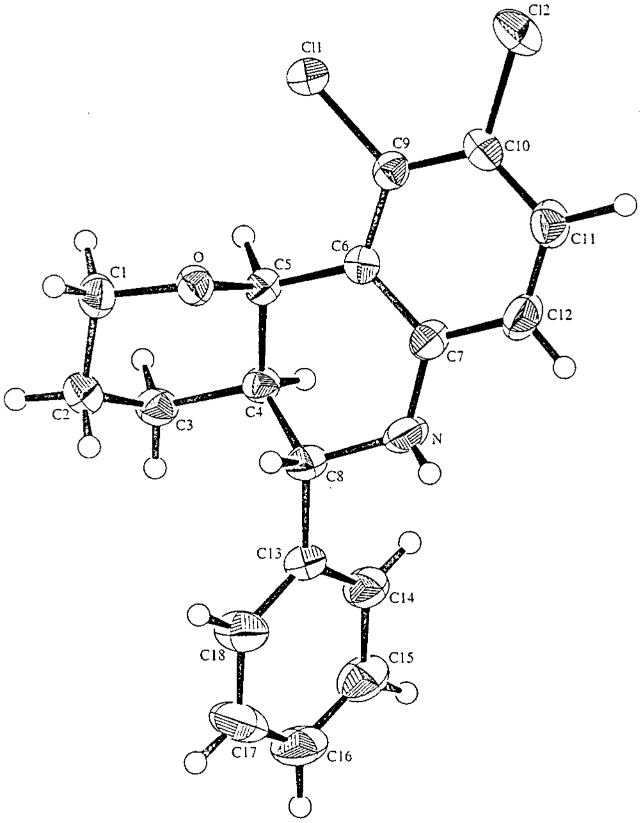

Figure 2. X-ray molecular structure of **IIIh** with the atom numbering scheme.

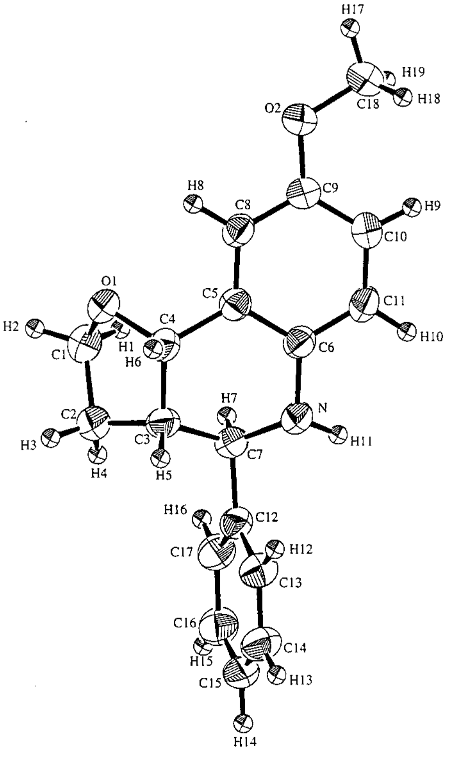

Figure 3. X-ray molecular structure of **VIb** with the atom numbering scheme.

(**IIa** and **IIIa**) were then obtained by column chromatography in 86% yield.

IIa: mp 130−132 °C (lit.[7] mp 128.8−131 °C); ^{1}H NMR δ 7.43−7.25 (6H, m), 7.03 (1H, tt, J = 7.6, 0.7 Hz), 6.77 (1H, td, J = 7.6, 1.0 Hz), 6.58 (1H, dd, J = 7.8, 0.9 Hz), 5.31 (1H, d, J = 5.6 Hz), 4.68 (1H, d, J = 2.6 Hz), 3.58−3.85 (3H, m), 2.15 (1H, m), 1.50−1.25 (4H, m); ^{13}C NMR δ 145.2, 141.2, 128.4, 128.1, 127.7, 127.6, 126.9, 120.0, 118.4, 114.5, 72.8, 60.7, 59.4, 39.0, 25.5, 18.1; IR (KBr) 3313 cm^{-1}; MS (m/e) 265 (M$^+$, 41), 206 (100). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.52; H, 7.16; N, 5.28. Found: C, 81.28; H, 7.23; N, 5.32.

IIIa: viscous oil; ^{1}H NMR δ 7.42−7.36 (5H, m), 7.25 (1H, dd, J = 7.1, 0.5 Hz), 7.07 (1H, td, J = 7.0, 1.3 Hz), 6.70 (1H, td, J = 7.0, 1.1 Hz), 6.51 (1H, dd, J = 7.1, 1.0 Hz), 4.72 (1H, d, J = 10.8 Hz), 4.39 (1H, d, J = 2.7 Hz), 4.08 (2H, m), 3.71 (1H, td, J = 11.6, 2.5 Hz), 2.11 (1H, m), 1.83 (1H, m), 1.66 (1H, m), 1.48 (1H, m), 1.25 (1H, m); ^{13}C NMR δ 144.7, 142.3, 130.9, 129.3, 128.6, 127.9, 127.8, 120.7, 117.4, 114.2, 74.5, 68.5, 54.9, 38.9, 24.1, 22.1; IR (KBr) 3373 cm^{-1}; MS (m/e) 265 (M$^+$, 42), 206 (100). HRMS calcd for $C_{18}H_{19}NO$: 265.1471. Found: 265.1431.

A Typical Procedure for One-Pot Reaction of Benzaldehyde, Aniline, and 3, 4-Dihydro-2*H*-pyran. To a suspension of $GdCl_3$ (0.2 mmol) and 4 Å molecular sieves or $MgSO_4$ (125 mg) were added an aldehyde (1.0 mmol) in CH_3CN (0.5 mL) and aniline (1.1 mmol) in CH_3CN (0.5 mL) at room temperature. The mixture was stirred for 10 min at room temperature. Then 3,4-dihydro-2*H*-pyran (1.4 mmol) was added. The mixture was further stirred for 30 min and it was then filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was chromatographied on silica gel to afford the pure products (**IIa** and **IIIa**) in 86% yield.

The following compounds were prepared similarly.

IIb: mp 154−156 °C; ^{1}H NMR δ 7.39−7.29 (6H, m),7.12 (1H, d, J = 7.6 Hz), 6.65 (1H, t, J = 7.6 Hz), 5.29 (1H, d, J = 5.4 Hz), 4.68 (1H, d, J = 2.3 Hz), 4.41 (1H, br, s), 3.55 (1H, m), 3.33 (1H, m), 2.12 (1H, m), 1.50−1.41 (2H, m), 1.20 (2H, m); IR (KBr) 3306 cm^{-1}; MS (m/e) 299 (M$^+$, 46), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01; N, 4.67. Found: C, 71.35; H, 6.00; N, 4.85.

IIIb: mp 109−101 °C ; ^{1}H NMR δ 7.39−7.27 (5H, m), 7.15 (2H, m), 6.64 (1H, t, J = 7.7 Hz), 4.66 (1H, d, J = 10.7 Hz), 4.58 (1H, br, s), 4.34 (1H, d, J = 2.7 Hz), 4.04 (1H, dt, J = 10.0, 2.1 Hz), 3.66 (1H, td, J = 10.8, 2.6 Hz), 2.01 (1H, m), 1.85 (1H, m), 1.63 (1H, m), 1.48 (1H, m), 1.30 (1H, m); ^{13}C NMR δ 141.9 141.0, 129.7, 129.3, 129.2, 128.8, 128.1, 127.8, 121.9, 118.1, 117.0, 74.4, 68.6, 54.9, 38.8, 24.0, 22.1; IR (KBr) 3384 cm^{-1}; MS (m/e) 301 (M + 2, 14), 299 (M$^+$, 38), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01; N, 4.67. Found: C, 72.10; H, 5.99; N, 4.85.

IIc: mp 170−172 °C; ^{1}H NMR δ 7.39−7.32 (6H, m), 7.01 (1H, dd, J = 8.2, 0.7 Hz), 6.50 (1H, d, J = 8.0 Hz), 5.25 (1H, d, J = 5.5 Hz), 4.60 (1H, d, J = 2.5 Hz), 3.85 (1H, br), 3.60 (1H, m), 3.41 (1H, m), 2.13 (1H, m), 1.51 (3H, m), 1.25 (1H, m); ^{13}C NMR δ 143.7, 140.7, 128.5, 128.1, 127.7, 127.3, 126.8, 123.1, 121.7, 115.6, 72.5, 60.8, 59.3, 38.6, 25.3, 18.1; IR (KBr) 3370 cm^{-1}; MS (m/e) 301 (M+2, 33), 299 (M$^+$, 99), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01, N; 4.67. Found: C, 72.02; H, 6.01; N, 4.78.

IIIc: mp 125−126 °C; ^{1}H NMR δ 7.39−7.30 (5H, m), 7.19 (1H, d, J = 2.3 Hz), 7.01 (1H, dd, J = 8.0, 1.9 Hz), 6.41 (1H, d, J = 8.1 Hz), 4.63 (1H, d, J = 10.6 Hz), 4.30 (1H, d, J = 2.8 Hz), 4.02 (2H, m), 3.66 (1H, td, J = 15.0, 3.0 Hz), 2.01 (1H, m), 1.75 (1H, m), 1.62 (1H, m), 1.45 (1H, m), 1.27(1H, m); ^{13}C NMR δ 143.3, 142.0, 130.4, 129.2, 128.7, 128.0, 127.7, 121.9, 121.8, 115.3, 74.0, 68.5, 55.0, 38.7, 24.0, 22.1; IR (KBr) 3298 cm^{-1}; MS (m/e) 301 (M+2, 19), 299 (M$^+$, 58), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01; N, 4.67. Found: C, 72.12; H, 6.02; N, 4.81.

IId: mp 143−144 °C; ^{1}H NMR δ 7.48−7.32 (6H, m), 7.03 (1H, dd, J = 7.5, 0.6 Hz), 6.75 (1H, t, J = 7.5 Hz), 5.37 (1H, d, J = 5.5 Hz), 4.71 (1H, d, J = 2.4 Hz), 3.85−3.34 (3H, m), 2.15 (4H, s), 1.32−1.29 (4H, m); ^{13}C NMR δ 143.3, 141.5, 129.2, 128.5, 127.6, 126.9, 125.5, 121.6, 119.5, 117.8, 73.0, 60.7, 59.3, 38.8, 25.5, 18.1, 17.5; IR (KBr) 3338 cm^{-1}; MS (m/e) 279 (M$^+$, 62), 220 (100). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.73; H, 7.52; N, 5.01. Found: C, 81.33; H, 7.63; N, 5.02.

IIId: mp 130−132 °C; ^{1}H NMR δ 7.48−7.44 (2H, m), 7.42−7.39 (2H, m), 7.33−7.31 (1H, m), 7.12 (1H, dd, J = 7.5, 1.2 Hz), 7.03 (1H, dd, J = 7.5, 0.6 Hz), 6.66 (1H, t, J = 7.5 Hz), 4.77 (1H, d, J = 9.9 Hz), 4.40 (1H, d, J = 2.7 Hz), 4.11 (1H, dt, J = 12.3, 2.3 Hz), 3.90 (1H, br), 3.73 (1H, td, J = 11.7, 2.5 Hz), 2.11 (1H, m), 2.07 (3H, s), 1.87 (1H, m), 1.69 (1H, m), 1.49 (1H, m), 1.32

(1H, m); ^{13}C NMR δ 142.8, 142.7, 130.3, 128.9, 128.7, 128.0, 127.9, 121.2, 120.2, 117.0, 74.9, 68.7, 55.0, 38.9, 24.2, 22.1, 17.3; IR (KBr) 3389 cm^{-1}; MS (*m*/*e*) 279 (M$^+$, 40), 220 (100). HRMS calcd for $C_{19}H_{21}NO$: C, 81.73; H, 7.52; N, 5.01. Found: C, 81.70; H, 7.65; N, 5.13.

IIe: mp 218−219 °C; ^{1}H NMR δ 7.41−7.20 (6H, m), 7.01 (1H, t, J = 3.8 Hz), 6.60 (2H, t, J = 3.0 Hz), 5.30 (1H, d, J = 5.2 Hz), 4.75 (1H, br), 4.62 (1H, m), 3.54 (1H, dt, J = 9.8, 2.1 Hz), 3.37 (1H, td, J = 11.2, 2.5 Hz), 2.11 (1H, m), 1.52−1.25 (4H, m); ^{13}C NMR δ 142.0, 141.2, 134.3, 128.4, 127.5, 126.9, 121.2, 120.0, 117.3, 113.3, 77.2, 73.0, 60.9, 59.1, 38.9, 25.4, 18.1; IR (KBr) 3397, 3238 cm^{-1}; MS (*m*/*e*) 281 (M$^+$, 100). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.87; H, 6.76; N, 4.98. Found: C, 76.93; H, 6.75; N 5.15.

IIIe: mp 190−191 °C; ^{1}H NMR δ 7.47−7.36 (6H, m), 6.88 (1H, dd, J = 7.1, 0.8 Hz), 6.65 (2H, m), 4.73(1H, d, J = 10.6 Hz), 4.44 (1H, d, J = 2.5 Hz),4.30 (1H, br), 4.11 (1H, dt, J = 8.8, 2.0 Hz), 3.73 (1H, td, J = 8.9, 2.4 Hz), 2.14 (1H, m), 1.83 (1H, m), 1.67 (1H, m), 1.51 (1H, m), 1.33 (1H, m); ^{13}C NMR δ 142.3, 141.8, 134.2, 129.2, 129.0, 128.8, 128.3, 127.9, 123.3, 121.8, 116.7, 114.4, 74.3, 68.7, 54.7, 39.0, 24.2, 22.1; IR (KBr) 3390, 3372 cm^{-1}; MS (*m*/*e*) 281 (M$^+$, 94), 222 (100). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.87; H, 6.76; N, 4.98. Found: C, 77.10; H, 6.86; N, 5.11

IIf: mp 144−146 °C (lit.[7] 144−146 °C); ^{1}H NMR δ 7.44−7.26 (5H, m),7.02 (1H, d, J = 2.8 Hz), 6.75 (1H, dd, J = 8.7, 2.8 Hz), 6.60 (1H, d, J = 8.7 Hz), 5.30 (1H, d, J = 5.3 Hz), 4.60 (1H, d, J = 1.9 Hz), 3.75 (3H, s), 3.55 (1H, m), 3.33(1H, m), 3.85−3.12 (1H, br), 2.08 (1H, m), 1.48−1.24 (4H, m); IR (KBr) 3401 cm^{-1}; MS (*m*/*e*) 295 (M$^+$, 100). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.30; H, 7.11; N, 4.74. Found: C, 77.12; H, 7.25; N 4.95.

IIIf: mp 98−100 °C; ^{1}H NMR δ 7.37−7.27 (5H, m), 6.79 (1H, d, J = 2.8 Hz), 6.65 (1H, dd, J = 8.4, 2.8 Hz), 6.45 (1H, d, J = 8.4 Hz), 4.60 (1H, d, J = 10.4 Hz), 4.31(1H, d, J = 2.8 Hz), 4.04 (1H, m), 3.70 (3H, s), 3.64 (1H, m), 2.05 (1H, m), 1.75 (1H, m) 1.61 (1H, m), 1.43 (1H, m), 1.25 (1H, m); ^{13}C NMR δ 152.0, 142.4, 139.0, 128.6, 127.8, 121.4, 116.9, 115.5, 114.9, 74.6, 68.5, 55.9, 55.3, 39.0, 24.2, 22.1. IR (KBr) 3373 cm^{-1}; MS (*m*/*e*) 295 (M$^+$, 100). Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.30; H, 7.11; N 4.74. Found: C, 77.48; H, 7.23; N, 4.92.

IIg and IIg′: ^{1}H NMR δ 7.38−7.27 (11H, m), 7.00 (1H, t, J = 7.9 Hz), 6.75 (2H, t, J = 7.7 Hz), 6.58 (1H, d, J = 1.8 Hz), 6.50 (1H, d, J = 7.9 Hz), 5.26 (1H, d, J = 5.6 Hz), 5.05 (1H, d, J = 4.7 Hz), 4.67 (1H, d, J = 2.5 Hz), 4.52 (1H, d, J = 4.4 Hz), 3.76−4.30 (1H, b r), 3.34−3.65 (5H, m), 2.35 (1H, m), 2.14 (1H, m), 1.78 (2H, m), 1.49 (3H, m), 1.28 (3H, m); IR (KBr) 3356 cm^{-1}; MS (*m*/*e*) 301 (M$^+$ + 2, 13), 299 (M$^+$, 38), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01; N, 4.67. Found: C, 71.94; H, 6.12; N, 4.69.

IIIg and IIIg′: ^{1}H NMR δ 7.44−7.32 (10H, m), 7.11 (1H, m), 6.94 (1H, t, J = 8.0 Hz), 6.73 (1H, d, J = 8.0 Hz), 6.67 (1H, d, J = 8.0 Hz), 6.39 (1H, s), 6.46 (1H, t, J = 8.1 Hz), 4.76 (3H, m), 4.39 (1H, d, J = 2.5 Hz), 4.18 (2H, dd, J = 12.0, 4.5 Hz), 4.60−3.80 (2H, br), 3.75 (2H, td, J = 12.1, 2.3 Hz), 2.02−1.87 (4H, m), 1.80 (2H, m), 1.67 (2H, m), 1.49 (2H, m), 1.28 (2H, m); ^{13}C NMR δ (**IIIg**) 146.2, 141.8, 136.1, 129.8, 128.7, 128.1, 127.9, 118.0, 117.9, 112.8, 72.0, 69.0, 54.2, 38.8, 23.9, 21.8; IR (KBr) 3388 cm^{-1}; MS (*m*/*e*) 301 (M + 2, 13), 299 (M$^+$, 38), 240 (100). Anal. Calcd for $C_{18}H_{18}ClNO$: C, 72.15; H, 6.01; N, 4.67. Found: C, 71.73; H, 5.99; N, 4.78.

IIh and IIh′: ^{1}H NMR δ 7.53−7.16 (10H, m), 7.08 (1H, d, J = 8.9 Hz), 6.84 (1H, s), 6.61 (1H, s), 6.35 (1H, d, J = 8.9 Hz), 5.15 (1H, d, J = 5.1 Hz), 4.91 (1H, d, J = 4.5 Hz), 4.59 (1H, d, J = 4.2 Hz), 4.40 (1H, d, J = 4.8 Hz), 4.20 (2H, br), 3.45 (4H, m), 2.30 (2H, m), 1.84−1.40 (4H, m), 1.27 (2H, m), 0.88 (2H, m); IR (KBr) 3402 cm^{-1}; MS (*m*/*e*) 335 (M$^+$ + 2, 25), 333 (M$^+$, 39), 274 (100). HRMS calcd for $C_{18}H_{17}Cl_2NO$: 333.0680. Found: 333.0750.

IIIh: mp 198−200 °C; ^{1}H NMR δ 7.36−7.21(5H, m), 7.08 (1H, d, J = 9.1 Hz,), 6.30 (1H, d, J = 9.1 Hz, 8 Hz), 4.66 (2H, m), 4.10 (1H, dd, J = 18, 4.5 Hz), 3.85 (1H, br), 3.65 (1H, td, J = 12.2, 2.5 Hz), 1.90 (1H, m), 1.82 (1H, m), 1.61 (1H, m), 1.41 (1H, m), 1.26 (1H, m); ^{13}C NMR δ 144.6, 141.3, 134.0, 130.3, 128.8, 128.3, 127.9, 120.0, 113.7, 72.5, 69.1, 54.0, 38.6, 23.8, 21.8; IR (KBr) 3378 cm^{-1}; MS (*m*/*e*) 335 (M + 2, 17), 333 (M$^+$, 26), 274 (100). HRMS calcd for $C_{18}H_{17}Cl_2NO$: 333.0680. Found: 333.0750

IIIh′: ^{1}H NMR δ 7.31 (5H, m), 7.18 (1H, s), 6.56 (1H, s), 4.55 (1H, d, J = 10.0 Hz), 4.25 (1H, d, J = 2.6 Hz), 4.00 (1H, d, J = 11.0 Hz), 3.62 (1H, td, J = 11.0, 2.6 Hz), 1.96 (1H, m), 1.75 (1H, m), 1.55 (1H, m), 1.46−1.25 (2H, m); IR (KBr) 3380 cm^{-1}; MS (*m*/*e*) 335 (M$^+$ + 2, 26), 333 (M$^+$, 40), 274 (100). HRMS calcd for $C_{18}H_{17}Cl_2NO$: 333.0680. Found: 333.0642.

A Typical Procedure for One-Pot Reaction of Benzaldehyde, Amine, and 2, 3-Dihydrofuran. To a suspension of $GdCl_3$ (0.2 mmol) and 4 Å molecular sieves or $MgSO_4$ (125 mg) were added an aldehyde (1.0 mmol) in CH_3CN (0.5 mL) and an amine (1.1 mmol) in CH_3CN (0.5 mL) at room temperature. The mixture was stirred for 10 min at room temperature. Then 2,3-dihydrofuran (1.4 mmol) was added. The mixture was further stirred for 30−120 min and then filtered through a short plug of silica gel. After evaporation of the filtrate, the residue was chromatographed on silica gel to afford the pure products (**V** and **VI)** in 61−88% yield.

Va: mp 117−118 °C (lit.[7] mp 95 °C); ^{1}H NMR δ 7.47−7.26 (6H, m), 7.08 (1H, td, J = 7.8, 1.5 Hz), 6.80 (1H, td, J = 7.8, 1.1 Hz) 6.59 (1H, dd, J = 7.8, 1.0 Hz), 5.26 (1H, d, J = 8.0 Hz), 4.69 (1H, d, J = 3.0 Hz), 3.77 (3H, m), 2.75 (1H, m), 2.19 (1H, m), 1.50 (1H, m); ^{13}C NMR δ 144.9, 142.2, 130.1, 128.6, 128.3, 127.6, 126.5, 122.7, 119.2, 114.9, 75.9, 66.8, 57.5, 45.8, 24.7; IR (KBr) 3348 cm^{-1}; MS (*m*/*e*) 251 (M$^+$, 85), 206 (100). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.28; H, 6.77; N, 5.58. Found: C, 80.88; H, 6.65; N, 5.29.

VIa: viscous oil; ^{1}H NMR δ 7.46−7.24 (6H, m), 7.12 (1H, td, J = 7.7, 1.1 Hz), 6.79 (1H, td, J = 7.8, 0.9 Hz), 6.62 (1H, d, J = 8.0 Hz), 4.59 (1H, d, J = 5.1 Hz), 4.08 (1H, m), 3.85 (3H, m), 2.45 (1H, m), 2.01 (1H, m), 1.72 (1H, m); ^{13}C NMR δ 145.3, 141.7, 131.1, 128.8, 128.6, 128.2, 128.0, 120.0, 118.2, 114.6, 76.1, 65.0, 57.6, 43.3, 28.7; IR (KBr) 3327 cm^{-1}; MS (*m*/*e*) 251 (M$^+$, 68), 206 (100). HRMS calcd for $C_{17}H_{17}NO$: 251.1299. Found: 251.1409.

Vb: mp 132−133 °C; ^{1}H NMR δ 7.46−7.25 (5H, m), 6.96 (1H, d, J = 2.8 Hz), 6.73 (1H, dd, J = 8.6, 2.8 Hz), 6.52 (1H, d, J = 8.7 Hz), 5.23 (1H, d, J = 8.0 Hz), 4.64 (1H, d, J = 2.9 Hz), 3.77 (3H, s), 3.52−3.80 (3H, m), 2.75 (1H, m), 2.20 (1H, m), 1.52 (1H, m); ^{13}C NMR δ 153.1, 142.4, 139.0, 128.6, 127.6, 126.5, 123.5, 116.2, 115.8, 113.8, 76.3, 66.9, 57.9, 55.7, 45.9, 24.5; IR (KBr) 3300 cm^{-1}; MS (*m*/*e*) 282 (M$^+$ + 1, 29), 281 (100). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.87; H, 6.76; N, 4.98. Found: C, 76.80; H, 6.77; N, 5.06.

VIb: mp 94−96 °C; ^{1}H NMR δ 7.46−7.39 (5H, m), 6.99 (1H, d, J = 2.8 Hz), 6.80 (1H, dd, J = 8.1, 2.8 Hz), 6.61 (1H, d, J = 8.1 Hz), 4.63 (1H, d, J = 5.3 Hz), 4.06 (1H, m), 3.78 (3H, s), 3.87−3.73 (2H, m), 2.49 (1H, br), 2.01 (1H, m), 1.70 (1H, m), 1.20 (1H, m); IR (KBr) 3298 cm^{-1}; MS (*m*/*e*) 282 (M$^+$ + 1, 3), 220 (100). Anal. Calcd for $C_{18}H_{19}NO_2$: C 76.87; H, 6.76; N, 4.98. Found: C, 77.02; H, 6.85; N, 5.17.

Vc: mp 102−103 °C; ^{1}HNMR δ 7.51−7.33 (5H, m), 7.25 (1H, d, J = 6.6 Hz), 6.99 (1H, d, J = 6.6 Hz), 6.77 (1H, t, J = 7.5 Hz), 5.32 (1H, d, J = 8.0 Hz), 4.70 (1H, d, J = 3.0 Hz), 3.80−3.66 (3H, m), 2.79 (1H, m), 2.20 (1H, m), 2.14 (3H, s), 1.46 (1H, m); ^{13}C NMR δ 143.1, 142.5, 129.4, 128.7, 127.9, 127.7, 126.6, 122.2, 121.8, 118.4, 76.2, 66.7, 57.3, 45.6, 24.6, 17.2; IR (KBr) 3322 cm^{-1}; MS (*m*/*e*) 265 (M$^+$, 100). HRMS calcd for$C_{18}H_{19}NO$: 265.1457. Found: 265.1467.

VIc: mp 92−94 °C; ^{1}H NMR δ 7.46−7.26 (6H, m), 6.99 (1H, d, J = 7.4 Hz), 6.72 (1H, t, J = 7.5 Hz), 4.55 (1H, d, J = 4.9 Hz), 4.02 (2H, m), 3.82 (2H, m), 2.43 (1H, m), 2.08 (3H, s), 1.92 (1H, m), 1.65 (1H, m); ^{13}C NMR δ 143.4, 142.0, 130.0, 129.1, 128.7, 128.4, 128.2, 121.7, 119.4, 117.8, 76.5, 65.1, 57.8, 43.2, 28.9, 17.2; IR (KBr) 3401 cm^{-1}; MS (*m*/*e*) 265 (M$^+$, 73), 220 (100). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.16; N, 5.28. Found: C, 81.63; H, 7.28; N, 5.43.

Vd: mp 188−189 °C; ^{1}H NMR δ 7.53−7.44 (2H, m), 7.38−7.26 (4H, m), 7.01 (1H, d, J = 8.4 Hz), 6.71 (2H, m), 5.31 (1H, d, J = 6.5 Hz), 4.80 (1H, br), 4.68 (1H, s), 3.79 (2H, m), 2.81 (1H, m), 2.25 (1H, m), 1.58 (1H, m); ^{13}C NMR δ (300 MHz in DMSO-d_6) 143.7, 143.6, 142.6, 134.2, 128.3, 127.1, 126.3, 122.8, 120.1, 117.4, 112.6, 112.5, 75.2, 65.7, 56.3, 45.0, 24.3; IR (KBr) 3385 cm^{-1}; MS (*m*/*e*) 267 (M$^+$, 100). HRMS calcd for $C_{17}H_{17}NO_2$: 267.1282. Found: 267.1512.

VId: mp 155−156 °C; ^{1}H NMR δ 7.61−7.25 (6H, m), 7.01 (1H, d, J = 8.0 Hz), 6.69 (2H, m), 4.65 (1H, d, J = 5.0 Hz), 4.07 (1H, m), 3.87 (2H, m), 4.10−3.50 (1H,br), 2.63 (1H, m), 2.04 (1H, m), 1.69 (1H, m); ^{13}C NMR δ 142.5, 141.7, 134.8, 128.7, 128.4, 128.2, 123.4, 121.2, 117.8, 114.1, 76.2, 65.3, 57.7, 43.4, 28.9. IR (KBr)

3397, 3193 cm^{-1}; MS (*m*/*e*) 267 (M$^+$, 83), 222 (100). HRMS calcd for $C_{17}H_{17}NO_2$: 267.1255. Found: 267.1295.

Ve: mp 153−155 °C; ^{1}H NMR δ 7 42−7.21 (6H, m), 6.98 (1H, dd, J = 8.50, 3.4 Hz), 6.48 (1H, d, J = 8.5 Hz), 5.16 (1H, d, J = 7.8 Hz), 4.63 (1H, d, J = 2.9 Hz), 3.80−3.64 (3H, m), 2.72 (1H, m), 2.14 (1H, m), 1.50 (1H, m); ^{13}C NMR δ 143.4, 141.9, 129.8, 128.8, 128.4, 127.9, 126.6, 124.2, 123.8, 116.2, 75.7, 67.0, 57.4, 45.5, 24.6; IR (KBr) 3342 cm^{-1}; MS (*m*/*e*) 285 (M$^+$, 100). Anal. Calcd for $C_{17}H_{16}ClNO$: C, 71.48; H, 5.60; N, 4.90. Found: C, 71.34; H, 5.58; N, 5.13.

VIe: mp 99−101 °C; ^{1}H NMR δ 7.39−7.28 (6H, m), 7.05 (1H, dd, J = 8.5, 2.4 Hz), 6.51 (1H, d, J = 8.5 Hz), 4.50(1H, d, J = 5.1 Hz), 3.89−4.25 (2H, m), 3.78 (2H, m), 2.43 (1H, m), 1.98 (1H, m), 1.68 (1H, m); ^{13}C NMR δ 144.0, 141.3, 130.8, 128.9, 128.8, 128.3, 128.2, 122.9, 121.6, 115.9, 75.7, 65.3, 57.8, 43.3, 28.8; IR (KBr) 3343 cm^{-1}; MS (*m*/*e*) 285 (M$^+$, 100). Anal. Calcd for $C_{17}H_{16}ClNO$: C, 71.48; H, 5.60; N, 4.90. Found C, 71.39; H, 5.63; N, 5.07.

Vf and VIf: ^{1}H NMR δ 8.31 (1H, d, J = 2.0 Hz), 8.30 (1H, d, J = 2.0 Hz), 8.04 (1H, dd, J = 8.0, 1.5 Hz), 8.00 (1H, dd, J = 8.0, 1.5 Hz), 7.75 (10H, m), 6.58 (1H, d, J = 9.0 Hz), 6.54 (1H, d, J = 9.0 Hz), 5.25 (1H, d, J = 7.5 Hz), 4.84 (1H, d, J = 3.2 Hz), 4.75 (1H, br), 4.60 (2H, d, J = 4.6 Hz), 4.10 (1H, m), 3.80−2.80 (4H, m), 2.80 (1H,m), 2.48 (1H, m), 2.10 (2H, m), 1.82 (1H, m), 1.64 (1H, m), 1.25 (1H, m); ^{13}C NMR δ 150.5, 149.8, 140.6, 140.2, 129.1, 129.0, 128.8, 128.5, 128.4, 128.2, 127.0, 126.4, 125.7, 124.9, 121.8, 118.7, 113.9, 113.8, 75.4, 74.8, 66.9, 65.2, 57.1, 56.5, 44.7, 42.5, 28.6, 24.7; IR (KBr) 3363 cm^{-1}; MS (*m*/*e*) 296 (M$^+$, 33), 251 (100). HRMS calcd for $C_{17}H_{16}N_2O_3$: 296.1165. Found: 296.1205.

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Supporting Information Available: ^{1}H NMR spectra of the compounds synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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