Aluminium Chloride-Catalyzed Intermolecular *vs* Intramolecular Friedel-Crafts Reaction of Acrylanilides and 3-Chloropropanamides

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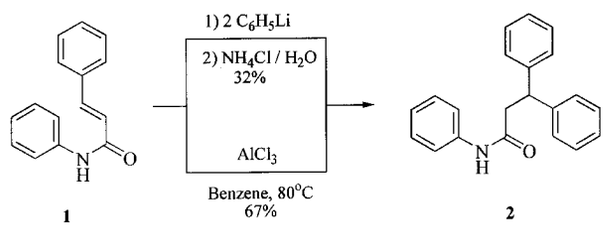
3-Phenylpropionanilide (**4a**) is obtained in a yield of 89% from acrylanilide by the treatment with $AlCl_3$ / benzene, compared with a yield of 39% by the 1,4-conjugate addition of phenyllithium. The formation of **4a** indicated that an intermolecular Friedel-Crafts reaction occurred, rather than the relatively more facile intramolecular ring cyclization, and provided a more efficient route than a conjugate addition of phenyllithium for the preparation of 3-phenylpropionanilide and its derivatives. Although the methoxy group is an activator of the nucleophilic substitution, introduction of a methoxy substituent at *N*-phenyl did not increase the competitive capability of the intramolecular cyclization because of $AlCl_3$-catalyzed demethylation to form the $ArOAlCl_2$ complex which decreased the availability of the π-electron in the *N*-phenyl aromatic system.

INTRODUCTION

The conjugate addition of organometallic reagents to unsaturated carbonyl compounds constitutes an important class of carbon-carbon bond forming reactions. Although reactive nucleophiles such as alkyllithium reagents usually undergo conjugate addition with α,β-unsaturated amides, several drawbacks have been observed such as large excesses of organometallic reagents are required, enolization of α,β-unsaturated amide to form deconjugated isomer, and poor yields due to the formation of dimers.[1-3] In 1980, Baldwin et al. described the conjugate addition of organolithium to α,β-unsaturated anilides.[2] The *n*- and *t*-butyllithium additions gave satisfying yields with a range of 82-94%, but the yield obtained for phenyllithium additions were only 0-48%. In the course of our investigation on hydroxy-2(1*H*)-quinolinones as key precursors for the preparation of potential cardiovascular agents,[4-8] we have synthesized 3,3-diphenylpropionanilide (**2**) from cinnamanilide (**1**) in $AlCl_3$ / benzene via Lewis acid catalyzed intermolecular Friedel-Crafts reaction (Scheme I).[6] The reaction proceeded smoothly and a 67% yield of **2** was obtained, compared with a yield of 32% from the conjugate addition of phenyllithium.[2] To study the scope and the limitations of this type of reaction, acrylanilide (**3a**, $R_1 = R_2 = H$),[9] 3,3-dimethylacrylanilide (**3b**, $R_1 = H$, $R_2 = Me$),[10] and its derivatives (**3c-i**),[11-13] *N*-phenyl-3-chloropropanamide (**8a**, $R_1 = H$)[9] and its derivatives (**8c-f**)[14-17] were prepared as starting materials. Their treatment with $AlCl_3$ / benzene and $AlCl_3$ / chlorobenzene is described.

Scheme I

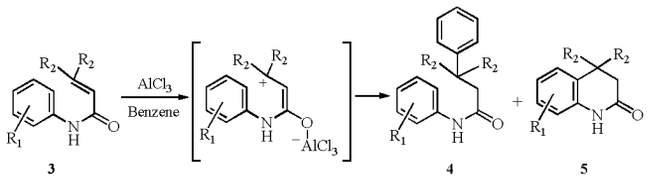


RESULTS AND DISCUSSION

Treatment of **3a** with $AlCl_3$ / benzene at 80°C gave 3-phenylpropionanilide (**4a**) as a sole product in 89% yield (Table 1, entry *a*), compared with a yield of 39% from the conjugate addition of phenyllithium.[2] The intermolecular Friedel-Crafts reaction of **3a** occurred rather than the relatively more facile intramolecular ring cyclization. However, reaction of 3,3-dimethylacrylanilide with $AlCl_3$ / benzene under the same reaction conditions gave exclusively 3,4-dihydro-4,4-dimethyl-2(1*H*)-quinolinone (**5b**, $R_2 = Me$, $R_4 = H$), an intramolecular ring cyclization product, in a 94% yield (entry *b*). A more steric hindered carbonium intermediate (entry *b*) seems to favor the intramolecular cyclization while a less hindered intermediate (entry *a*) tends to undergo intermolecular addition. Treatment of either *N*-(2-methoxyphenyl)-3-methyl-2-butenamide or its *N*-(3-methoxyphenyl)-analogue in benzene with aluminum chloride at 80°C gave a

Dedicated to the memory of the late Pro Ta-shue Chou (

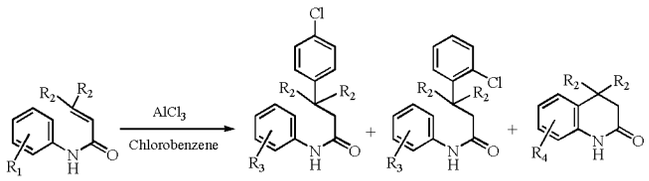
Table 1. Friedel-Crafts Reaction of Arylanilides in Aluminium Chloride / Benzene



3 4 5

Entry	R_1	R_2	R_3	R_4	Yeild (%)	Ratio (**4/5**)
a	H	H	H	-	89	1/0
b	H	Me	-	H	94	0/1
c	2-OMe	Me	2-OH	8-OH	66	2.7/1
d	3-OMe	Me	3-OH	7-OH	93	2.6/1
e	4-OMe	Me	4-OH	-	90	1/0
f	4-OH	Me	4-OH	6-OH	88	3.6/1
g	4-Cl	Me	4-Cl	6-Cl	99	1.3/1
h	$4\text{-}NO_2$	Me	$4\text{-}NO_2$	-	93	1/0
i	4-Me	Me	-	6-Me	82	0/1

Table 2. Friedel-Crafts Reaction of Arylanilides in Aluminium Chloride / Chlorobenzene



3 6 7 5

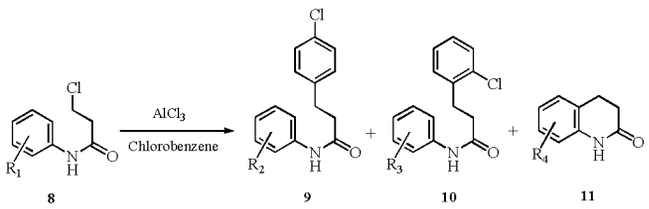
Entry	R_1	R_2	R_3	R_4	Yeild (%)	Ratio (**6/7/5**)
a	H	H	H	-	66	2/1/0
b	H	Me	-	H	93	0/0/1
c	2-OMe	Me	2-OH	8-OH	99	4/0/1
d	3-OMe	Me	-	7-OH	79	0/0/1
e	4-OMe	Me	-	6-OH	84	0/0/1
f	4-OH	Me	-	6-OH	62	0/0/1
g	4-Cl	Me	4-Cl	6-Cl	95	1/0/7.6
h	$4\text{-}NO_2$	Me	$4\text{-}NO_2$	-	76	1/0/0
i	4-Me	Me	-	6-Me	91	0/0/1

mixture of addition and cyclization products in favor of intermolecular addition reaction (entries *c* and *d*). However, the *N*-(4-methoxyphenyl) counterpart gave exclusively the intermolecular addition product of *N*-(4-hydroxyphenyl)-3-methyl-3-phenylbutanamide (entry *e*). This is unusual because the methoxy is an electron-donating group which should accelerate the intramolecular cyclization. Both 4-hydroxy derivative (entry *f*) and 4-chloro derivative (entry *g*) tend to favor the intermolecular addition in a ratio of 3.6:1 and 1.3:1, respectively. The 4-nitro derivative (entry *h*), however, gave only the intermolecular addition product due to strong electron-withdrawing capacity of nitro group. In contrast, 4-methyl derivative (entry *i*) gave exclusively the intramolecular cyclization product due to the electron-donating capacity of the methyl group.

Except for entries *b* and *i*, all the above competitive reactions are in favor of intermolecular Friedel-Crafts addition in which benzene functions as a nucleophilic moiety. The next question was, if benzene was replaced with a less nucleophilic solvent such as chlorobenzene, will the intermolecular addition still predominate? Thus, **3a** was treated with $AlCl_3$ / chlorobenzene at 120 °C, 3-(4-chlorophenyl)-propionanilide (**6a**) and 3-(2-chlorophenyl)-propionanilide (**7a**) were obtained in a ratio of 2 to 1 indicating that only the intermolecular addition occurred (Table 2, entry *a*). Again, the intramolecular cyclization product of **5b** was obtained by treating **3b** with $AlCl_3$ / chlorobenzene. Although treatment of **3c** with $AlCl_3$ / chlorobenzene gave a mixture of addition and cyclization products in favor of intermolecular addition reaction, both **3d** and **3e** proceeded via the intramolecular cyclization pathway and gave exclusively cyclization products of **5d** and **5e**, respectively. However, **3g** gave a mixture of **6g** and **5g** in a ratio of 1:7.6 due to the electron-withdrawing effect of the 4-chloro substituent. Accordingly, 4-nitro derivative **3h** gave exclusively the intermolecular addition product of **6h** while the 4-methyl derivative **3i** gave exclusively the intramolecular cyclization product of **5i**.

By comparison of entries *b* and *c* from Tables 1 and 2, the methoxy substituent tends to decrease the competitive capability of the intramolecular Friedel-Crafts cyclization. This is unusual because the methoxy group is considered as an activator and therefore, should enhance the nucleophilic capability of the *N*-phenyl aromatic ring. To further confirm the influence of methoxy substituent with respect to the intermolecular addition vs intramolecular cyclization, a typical Friedel-Crafts alkylation was initiated by treating *N*-phenyl-3-chloropropanamide **8a** and its derivatives (**8c-f**)[14-17] with $AlCl_3$ / chlorobenzene (Table 3). The results indicated that when 8a was treated with $AlCl_3$ / chlorobenzene, both cyclization (**11a**) and addition (**9a** and **10a**) products were obtained in favor of the intramolecular cyclization. Introduction of a methoxy substituent at *N*-phenyl (**8c-e**) did not enhance the competitive capability of the intramolecular cyclization. In contrast, it decreased the competition of the *N*-phenyl and therefore, the intermolecular addition of chlorobenzene became predominate (Table 3, entries *c-e*). This unusual result could be due to $AlCl_3$-catalyzed demethylation to form the $ArOAlCl_2$ complex which decreased the availability of the π-electron in the *N*-phenyl aromatic system. Treatment of

Table 3. Friedel-Crafts Reaction of *N*-Phenyl-3-chloropropanamide in Aluminium Chloride / Chloroenzene



8 9 10 11

Entry	R_1	R_2	R_3	R_4	Yeild (%)	Ratio (**9/10/11**)
a	H	H	H	H	86	1/1.8/4.3
c	2-OMe	2-OH	2-OH	-	79	1/1.9/0
d	3-OMe	3-OH	3-OH	7-OH	76	9/9/1
e	4-OMe	4-OH	4-OH	6-OH	89	11/11/1
f	4-Me	4-Me	4-Me	6-Me	90	1/1.4/7.6

N-(4-methylphenyl)-3-chloropropanamide **8f** with $AlCl_3$ / chlorobenzene gave both addition products (**9f** and **10f**) and cyclization product **11f** in favor of the latter, indicating the electron-donating methyl substituent which was free of complex formation does improve the nucleophilic capability of the *N*-phenyl aromatic ring and therefore, the intramolecular cyclization product **11f** became predominant (Table 3, entry *f*).

EXPERIMENTAL SECTION

TLC: precoated (0.2 mm) silica gel 60 F-254 plates from EM Laboratories, Inc.; detection by UV light (254 nm). Mp Electrothermal IA-9000 micromelting-point apparatus; uncorrected. ^{1}H- and ^{13}C-NMR spectra: Varian-Gemini-200 spectrometer, δ in ppm with Me_4Si as an internal standard. Elemental analyses were carried out on a Heraeus CHN-O-Rapid elemental analyzer and results were within +/- 0.4% of calculated values.

Acrylanilide (3a)

To a stirred solution of aniline (1.86 g, 20 mmol), K_2CO_3 (4.15 g, 30 mmol), H_2O (40 mL), and acetone (20 mL) was added dropwise acryloyl chloride (2.26 g, 25 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h (monitored by TLC) and then poured into ice-water (100 mL). The resulting precipitate was collected and crystallized from hexane / Et_2O (1:1) to give **3** (2.80 g, 95 %), mp 103-104 °C, Lit.[9] mp 101-103 °C; ^{1}H NMR ($CDCl_3$): δ 5.71 (dd, *J* = 2.4 and 9.3 Hz, 1H), 6.29 (dd, *J* = 9.3 and 16.9 Hz, 1H), 6.42 (dd, *J* = 2.4 and 16.9 Hz, 1H), 7.07-7.61 (m, 5H), 8.05 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 120.22, 124.53, 127.61, 128.94, 131.25, 137.78, 163.93.

General Procedure for the Preparation of *N*-phenyl-3-methyl-2-butenamide and *N*-(methoxyphenyl)-3-methyl-2-butenamide (3b-i)

To a stirred solution of aniline (1.86 g, 20 mmol) or methoxyaniline (2.46 g, 20 mmol), K_2CO_3 (4.15 g, 30 mmol), H_2O (40 mL), and acetone (20 mL) was added dropwise 3,3-dimethylacryloyl chloride (2.96 g, 25 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h (monitored by TLC) and then poured into ice-water (100 mL). The resulting precipitate was collected and crystallized from a specified solvent to give **3b-i**.

N-Phenyl-3-methyl-2-butenamide (3b)

Yield: 92 %; mp 129-130 °C (hexane / Et_2O 10:1), Lit.[10] mp 129-130 °C. ^{1}H NMR ($CDCl_3$): δ 1.88 (d, *J* = 1.1 Hz, 3H), 2.21 (d, *J* = 1.3 Hz, 3H), 5.72 (m, 1H), 7.03-7.55 (m, 5H), 7.29 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.92, 27.30, 118.64, 119.79, 123.93, 128.87, 138.22, 153.22, 165.11.

N-(2-Methoxyphenyl)-3-methyl-2-butenamide (3c)

Yield: 95 %; mp 63-64 °C (CH_2Cl_2 / Et_2O 1:1), Lit.[11] mp 65 °C. ^{1}H NMR ($CDCl_3$): δ 1.90 (d, *J* = 1.3 Hz, 3H), 2.22 (d, *J* = 1.3 Hz, 3H), 3.87 (s, 3H), 5.76 (m, 1H), 6.84-8.46 (m, 4H), 7.69 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.85, 27.31, 55.62, 109.80, 119.13, 119.61, 121.06, 123.23, 128.06, 147.72, 152.65, 164.85.

N-(3-Methoxyphenyl)-3-methyl-2-butenamide (3d)

Yield: 92 %; mp 112-113 °C (CH_2Cl_2 / Et_2O 1:1), ^{1}H NMR ($CDCl_3$): δ 1.88 (d, *J* = 1.3 Hz, 3H), 2.21 (d, *J* = 1.3 Hz, 3H), 3.79 (s, 3H), 5.71 (m, 1H), 6.61-7.23 (m, 4H), 7.34 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.96, 27.36, 55.27, 105.25, 109.97, 111.82, 118.63, 129.55, 139.49, 153.49, 160.11, 165.06. Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82; Found: C, 69.90; H, 7.42; N, 6.81.

N-(4-Methoxyphenyl)-3-methyl-2-butenamide (3e)

Yield: 93 %; mp 88-89 °C (CH_2Cl_2 / Et_2O 1:1), Lit.[11] mp 90 °C. ^{1}H NMR ($CDCl_3$): δ 1.87 (d, *J* = 1.1 Hz, 3H), 2.20 (d, *J* = 1.2 Hz, 3H), 3.77 (s, 3H), 5.69 (m, 1H), 6.81-7.45 (m, 4H), 7.27 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.87, 27.28, 55.43, 114.04, 118.68, 121.63, 131.34, 152.60, 156.15, 164.99 (C=O).

N-(4-Hydroxyphenyl)-3-methyl-2-butenamide (3f)

Yield: 42 %; mp 194-195 °C (CH_2Cl_2 / Et_2O 1:1), Lit.[12]

mp 194-197 °C; ^{1}H NMR (DMSO-d_6): δ 1.84 (s, 3H), 2.13 (s, 3H), 5.81 (m, 1H), 6.65-7.41 (m, 4H), 9.15 (s, 1H), 9.65 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 19.38, 26.97, 115.01, 119.38, 120.79, 131.20, 149.97, 153.07, 164.12 (C=O).

_N_-(4-Chlorophenyl)-3-methyl-2-butenamide (3g)

Yield: 87 %; mp 121-122 °C (CH_2Cl_2 / Et_2O 1:1), Lit.[11] mp 122 °C; ^{1}H NMR ($CDCl_3$): δ 1.89 (d, J = 1.2 Hz, 3H), 2.21 (d, J = 1.2 Hz, 3H), 5.69 (m, 1H), 7.23-7.49 (m, 4H), 7.27 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 19.98, 27.39, 118.29, 120.94, 121.32, 128.88, 136.80, 154.13, 164.94 (C=O).

_N_-(4-Nitrophenyl)-3-methyl-2-butenamide (3h)

Yield: 70 %; mp 129-130 °C (CH_2Cl_2 / Et_2O 1:1), ^{1}H NMR ($CDCl_3$): δ 1.94 (d, J = 1.3 Hz, 3H), 2.25 (d, J = 1.3 Hz, 3H), 5.76 (m, 1H), 7.72-8.22 (m, 4H), 7.57 (br s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.20, 27.61, 117.80, 118.80, 125.06, 143.14, 144.36, 156.66, 164.91 (C=O). Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72; Found: C, 59.69; H, 5.49; N, 12.58.

_N_-(4-Methyphenyl)-3-methyl-2-butenamide (3i)

Yield: 79 %; mp 106-107 °C (CH_2Cl_2 / Et_2O 1:1), Lit.[13] mp 106-107 °C; ^{1}H NMR ($CDCl_3$): δ 1.88 (s, 3H), 2.21(d, J = 1.6 Hz, 3H), 2.30 (d, J = 1.6 Hz, 3H), 5.70 (m, 1H), 7.09-7.42 (m, 4H), 7.15 (br s, 1H). 13C NMR (CDCl3): d 19.90, 20.81, 27.30, 118.73, 119.80, 129.38, 133.52, 135.63, 152.88, 164.95 (C=O).

3-Phenylpropionanilide (4a)

$AlCl_3$ (6.4 g, 48 mmol) was added portionwise to a suspension of **3a** (1.18 g, 8 mmol) in benzene (50 mL) at 0 °C. The reaction mixture was gradually warmed to 80 °C and then stirred for 6h (monitored by TLC). The mixture was poured into ice-water (100 mL) and extracted with CH_2Cl_2 (3 × 60 mL). The CH_2Cl_2 extracts were combined and washed with water, dried (Na_2SO_4), and evaporated to give a residual solid which was purified by column chromatography on silica gel with hexane / CH_2Cl_2 (1:1) as an eluent and then crystallized from hexane / Et_2O (1:1) to give **4a** (1.60 g, 89 %). mp 96-97 °C. Lit.[18] mp 98 °C. ^{1}H NMR ($CDCl_3$): δ 2.64 (t, J = 8.0 Hz, 2H), 3.04 (t, J = 8.0 Hz, 2H), 7.08-7.45 (m, 10H). ^{13}C NMR ($CDCl_3$): δ 31.53, 39.40, 119.93, 124.27, 126.35, 128.36, 128.60, 128.92, 137.69, 140.59, 170.40.

The same procedures were used to convert each of the compounds **3b-i** to the respective **4b-i** and/or **5b-i**.

3,4-Dihydro-4,4-dimethyl-2(1*H*)-quinolinone (5b)

Yield: 94 %; m.p. 114-115°C (hexane / Et_2O 1:1), Lit.[19] m.p. 116°C; ^{1}H NMR ($CDCl_3$): δ 1.34 (s, 6H), 2.50 (s, 2H), 6.87-7.30 (m, 4H), 9.44 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 27.64, 33.87, 45.23, 115.89, 123.55, 124.36, 127.46, 132.38, 135.80, 171.45.

_N_-(2-Hydroxyphenyl)-3-methyl-3-phenylbutanamide (4c) and 3,4-Dihydro-8-hydroxy-4,4-dimethyl-2(1*H*)-quinolinone (5c)

4c: 48 % yield; mp 118-119 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.43 (s, 6H), 2.72 (s, 2H), 6.70-7.57 (m, 9H), 9.06 (br s, 1H), 9.62 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.61, 37.27, 49.23, 115.90, 118.88, 122.19, 124.59, 125.47, 125.56, 126.27, 127.94, 147.83, 148.96, 169.98. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20; Found: C, 75.85; H, 7.11; N, 5.12.

5c: 18 % yield; mp 174-175 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.20 (s, 6H), 2.33 (s, 2H), 6.69-6.83 (m, 3H), 8.76 (br s, 1H), 9.69 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 27.19, 33.69, 45.08, 113.44, 114.62, 122.55, 124.48, 133.33, 143.89, 168.61. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32; Found: C, 68.99; H, 6.94; N, 7.23.

_N_-(3-Hydroxyphenyl)-3-methyl-3-phenylbutanamide (4d) and 3,4-Dihydro-7-hydroxy-4,4-dimethyl-2(1*H*)-quinolinone (5d)

4d: 67 % yield; mp 183-184 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.41 (s, 6H), 2.59 (s, 2H), 6.39-7.43 (m, 9H), 9.28 (br s, 1H), 9.58 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.55, 37.26, 49.56, 106.35, 109.92, 110.11, 125.41, 125.55, 127.94, 129.17, 140.13, 149.20, 157.47, 169.24. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20; Found: C, 75.70; H, 7.12; N, 5.11.

5d: 26 % yield; mp 224-225 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.16 (s, 6H), 2.27 (s, 2H), 6.32-7.05 (m, 3H), 9.30 (br s, 1H), 9.98 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 27.67, 32.90, 45.46, 102.55, 109.33, 122.73, 125.02, 137.73, 156.43, 169.71. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32; Found: C, 68.81; H, 6.92; N, 7.29.

_N_-(4-Hydroxyphenyl)-3-methyl-3-phenylbutanamide (4e)

Yield: 90 %; mp 200-201 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.41 (s, 6H), 2.54 (s, 2H), 6.62-7.44 (m, 9H), 9.15 (br s, 1H), 9.45 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.59, 37.28, 49.47, 114.93, 121.11, 125.45, 125.56, 127.96, 130.80, 149.29, 153.20, 168.70. Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20; Found: C, 75.64; H, 7.11; N, 5.25.

3,4-Dihydro-6-hydroxy-4,4-dimethyl-2(1*H*)-quinolinone (5f)

Yield: 19%; mp 223-224 °C (Et_2O). ^{1}H NMR (DMSO-d_6): δ 1.18 (s, 6H), 2.27 (s, 2H), 6.52-6.70 (m, 3H), 9.04 (br s,

1H), 9.86 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 27.20, 33.52, 44.93, 111.06, 113.46, 116.28, 128.87, 133.38, 152.85, 168.72. Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32; Found: C, 69.09; H, 6.87; N, 7.21.

_N_-(4-Chlorophenyl)-3-methyl-3-phenylbutanamide (4g) and 6-Chloro-3,4-dihydro-4,4-dimethyl-2(1_H_)-quinolinone (5g)

4g: 56 % yield; mp 148-149 °C (Et_2O). ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 6H), 2.67 (s, 2H), 6.95-7.48 (m, 9H), 6.24 (s, 1H); ^{13}C NMR ($CDCl_3$): δ 28.74, 37.75, 53.13, 120.71, 125.85, 126.69, 128.71, 128.97, 136.04, 147.51, 169.16. Anal. Calcd for $C_{17}H_{18}ClNO$: C, 70.86; H, 6.30; N, 4.87; Found: C, 70.86; H, 6.29; N, 4.83.

5g: 43 % yield; mp 187-188 °C (Et_2O). ^{1}H NMR (DMSO-d_6): δ 1.22 (s, 6H), 2.35 (s, 2H), 6.87-7.30 (m, 3H), 10.24 (br s, 1H); ^{13}C NMR (DMSO-d_6): d 26.94, 33.76, 44.38, 116.94, 124.29, 126.17, 126.98, 134.27, 135.93, 169.11. Anal. Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77; N, 6.68; Found: C, 62.92; H, 5.81; N, 6.62.

_N_-(4-Notrophenyl)-3-methyl-3-phenylbutanamide (4h)

Yield: 93 %; mp 105-106 °C (hexane). ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 6H), 2.74 (s, 2H), 7.14-8.09 (m, 9H), 6.49 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 28.73, 37.85, 53.38, 118.66, 124.86, 125.87, 126.96, 129.17, 143.21, 147.20, 169.56. Anal. Calcd for $C_{17}H_{18}N_2O_3$: C, 68.44; H, 6.08; N, 9.39; Found: C, 68.07; H, 6.00; N, 9.46.

3,4-Dihydro-4,4,6-trimethyl-2(1_H_)-quinolinone (5i)

Yield: 82 %; mp 160-161 °C (Et_2O), Lit.[19] m.p. 157 °C (H_2O); ^{1}H NMR (DMSO-d_6): δ 1.20 (s, 6H), 2.24 (s, 3H), 2.30 (s, 2H), 6.73-7.08 (m, 3H), 10.03 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 20.63, 27.29, 33.45, 45.05, 115.32, 124.71, 127.47, 131.22, 131.97, 134.44, 169.17. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40; Found: C, 76.15; H, 8.01; N, 7.38.

3-(4-Chlorophenyl)-propionanilide (6a) and 3-(2-Chlorophenyl)-propionanilide (7a)

$AlCl_3$ (6.4 g, 48 mmol) was added portionwise to a suspension of **3a** (1.18 g, 8 mmol) in chlorobenzene (50 mL) at 0 °C. The reaction mixture was gradually warmed to 120 °C and then stirred for 6h (monitored by TLC). The mixture was poured into ice-water (100 mL) and extracted with CH_2Cl_2 (3 × 60 mL). The dichloromethane extracts were combined and washed with water, dried (Na_2SO_4), and evaporated to give a residual solid which was purified by column chromatography on silica gel with hexane / CH_2Cl_2 (1:1) as an eluent and then crystallized from hexane / Et_2O (1:1) to give **6a** (0.92 g, 44 %) and **7a** (0.45 g, 22 %). **6a**: mp 158-159 °C. ^{1}H NMR ($CDCl_3$): δ 2.61 (t, J = 7.9 Hz, 2H), 3.00 (t, J = 7.8 Hz, 2H), 7.12-7.42 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 30.74, 39.13, 119.95, 124.42, 128.67, 128.98, 129.74, 132.10, 137.59, 139.08, 170.00. Anal. Calcd for $C_{15}H_{14}ClNO$: C, 69.37; H, 5.43; N, 5.39; Found: C, 69.23; H, 5.51; N, 5.39.

7a: mp 102-103 °C. Lit.[20] mp 99-101 °C. ^{1}H NMR ($CDCl_3$): δ 2.66 (t, J = 8.1 Hz, 2H), 3.15 (t, J = 8.0 Hz, 2H), 7.08-7.47 (m, 9H). ^{13}C NMR ($CDCl_3$): δ 29.47, 37.26, 119.97, 124.30, 127.02, 127.91, 128.92, 129.53, 130.77, 133.78, 137.68, 138.11, 170.12.

The same procedures were used to convert each of the compounds **3b-i** to the respective **6b-i**, **7b-i**, and/or **5b-i**.

_N_-(2-Hydroxyphenyl)-3-(4-chlorophenyl)-3-methylbutanamide (6c)

Yield: 63 %; mp 128-129 °C (hexane / EtOAc: 10/1). ^{1}H NMR ($CDCl_3$): δ 1.49 (s, 6H), 2.69 (s, 2H), 6.44-7.41 (m, 8H), 6.90 (s, 1H), 8.63 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 28.75, 37.73, 51.65, 119.73, 120.36, 121.89, 125.26, 127.18, 127.24, 128.95, 132.56, 145.77, 148.61, 171.15. Anal. Calcd for $C_{17}H_{18}ClNO_2$: C, 67.22; H, 5.97; N, 4.61; Found: C, 67.21; H, 6.06; N, 4.65.

3,4-Dihydro-6-hydroxy-4,4-dimethyl-2(1_H_)-quinolinone (5e)

Yield: 84 %; mp 220-221 °C (CH_2Cl_2). ^{1}H NMR (DMSO-d_6): δ 1.17 (s, 6H), 2.26 (s, 2H), 6.51-6.70 (m, 3H), 9.07 (br s, 1H), 9.86 (br s, 1H). ^{13}C NMR (DMSO-d_6): δ 27.25, 33.58, 44.97, 111.14, 113.53, 116.36, 128.90, 133.48, 152.92, 168.86. Anal. Calcd for $C_{11}H_{13}NO_2$ 0.125 H_2O: C, 68.29; H, 6.90; N, 7.24; Found: C, 68.31; H, 6.88; N, 7.24.

_N_-(4-Chlorophenyl)-3-(4-chlorophenyl)-3-methylbutanamide (6g), _N_-(4-Chlorophenyl)-3-(2-chlorophenyl)-3-methylbutanamide (7g) and 6-Chloro-3,4-Dihydro-4,4-dimethyl-2(1_H_)-quinolinone (5g)

6g and **7g** (0.35 g, 11 % yield). ^{1}H NMR ($CDCl_3$): δ 1.48 (s, 6H), 1.49 (s, 6H), 2.62 (s, 4H), 7.08-7.41 (m, 16H), 6.44 (s, 1H), 6.48 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 28.62, 28.74, 37.55, 37.88, 52.49, 52.58, 120.91, 121.00, 123.98, 126.21, 126.72, 127.24, 128.80, 128.87, 129.20, 130.00, 132.39, 134.79, 135.90, 135.95, 146.26, 150.05, 168.82. Anal. Calcd for $C_{17}H_{17}Cl_2NO$: C, 63.37; H, 5.32; N, 4.35; Found: C, 63.33; H, 5.31; N, 4.30. **5g** (1.76 g, 84 % yield).

_N_-(2-Nitrophenyl)-3-(4-chlorophenyl)-3-methylbutanamide (6h)

Yield: 76 %; mp 146-147 °C (hexane). ^{1}H NMR ($CDCl_3$): δ 1.50 (s, 6H), 2.69 (s, 2H), 7.27-8.14 (m, 8H), 6.74

(s, 1H). ^{13}C NMR ($CDCl_3$): δ 28.73, 37.63, 52.72, 118.79, 124.96, 127.21, 128.94, 132.60, 143.17, 143.40, 145.93, 169.21. Anal. Calcd for $C_{17}H_{17}ClN_2O_3$: C, 61.36; H, 5.15; N, 8.42; Found: C, 61.23; H, 5.04; N, 8.31.

General Procedure for the preparation of *N*-Phenyl-3-chloropropanamide (8a), *N*-(Methoxyphenyl)-3-chloropropanamide (8c-e) and *N*-(Methyphenyl)-3-chloropropanamide (8f)

To a stirred solution of aniline (1.86 g, 20 mmol) or methoxyaniline (2.46 g, 20 mmol) or 4-methylaniline (2.14 g, 20 mmol), K_2CO_3 (4.15 g, 30 mmol), H_2O (40 mL), and acetone (20 mL) was added dropwise 3-chloropropioyl chloride (3.18 g, 25 mmol) at 0 °C. The mixture was stirred at 0 °C for 1 h (monitored by TLC) and then poured into ice-water (100 mL). The resulting precipitate was collected and crystallized from CH_2Cl_2 / Et_2O 1:1 to give **8a-f**. **8a**: 98 % yield. mp 115-116 °C. Lit.[9] mp 115-117 °C. ^{1}H NMR ($CDCl^3$): δ 2.79 (t, J = 6.4 Hz, 2H), 3.85 (t, J = 6.4 Hz, 2H), 7.07-7.53 (m, 5H), 7.76 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 39.88, 40.36, 120.23, 124.69, 128.99, 137.41, 167.98.

8c: 94 % yield; mp 68-69 °C. Lit.[14] mp 68 °C. ^{1}H NMR ($CDCl_3$): δ 2.85 (t, J = 6.6 Hz, 2H), 3.88 (t, J = 6.6 Hz, 2H), 3.88 (s, 3H), 6.85-8.39 (m, 4H), 7.88 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 39.78, 40.74, 55.67, 109.94, 119.86, 121.06, 123.96, 127.27, 147.74, 167.35.

8d: 95 % yield; mp 91-92 °C. Lit.[15] mp 95 °C. ^{1}H NMR ($CDCl_3$): δ 2.80 (t, J = 6.4 Hz, 2H), 3.87 (t, J = 6.4 Hz, 2H), 3.79 (s, 3H), 6.66-7.29 (m, 4H), 7.54 (br s, NH). ^{13}C NMR ($CDCl_3$): δ 39.79, 40.50, 55.29, 105.81, 110.52, 112.13, 129.69, 138.62, 160.15, 167.80.

8e: 95 % yield; mp 120-121 °C. Lit.[16] mp 121-122 °C. ^{1}H NMR ($CDCl_3$): δ 2.77 (t, J = 6.4 Hz, 2H), 3.86 (t, J = 6.4 Hz, 2H), 3.78 (s, 3H), 6.82-7.42 (m, 4H), 7.61 (br s, NH); ^{13}C NMR ($CDCl_3$): δ 40.01, 40.20, 55.44, 114.11, 122.16, 130.46, 156.65, 167.76.

8f: 95 % yield; mp 118-119 °C, Lit.[17] mp 120 °C; ^{1}H NMR ($CDCl_3$): δ 2.31 (s, 3H), 2.78 (t, J = 6.4 Hz, 2H), 3.86 (t, J = 6.4 Hz, 2H), 7.09-7.41 (m, 4H), 7.50 (s, NH). ^{13}C NMR ($CDCl_3$): δ 20.84, 39.94, 40.41, 120.24, 129.49, 134.36, 134.84, 167.69. Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.77; H, 6.12; N, 7.09; Found: C, 61.00; H, 6.22; N, 7.12.

3-(4-Chlorophenyl)propionanilide (9a = 6a), 3-(2-Chlorophenyl)propionanilide (10a = 7a), and 3,4-Dihydro-2(1*H*)-quinolinone (11a)

$AlCl_3$ (4.0 g, 30 mmol) was added portionwise to a suspension of **8a** (0.92 g, 5 mmol) in chlorobenzene (50 mL) at 0 °C. The reaction mixture was gradually warmed to 120 °C and then stirred for 6h (monitored by TLC). The mixture was poured into ice-water (100 mL) and extracted with CH_2Cl_2 (3 × 60 mL). The CH_2Cl_2 extracts were combined and washed with H_2O, dried (Na_2SO_4), and evaporated to give a residual solid which was purified by column chromatography on silica gel with hexane / EtOAc (1:1) as an eluent and then crystallized from hexane / Et2O (1:1) to give **9a** (0.16 g, 12 %), **10a** (0.28 g, 22%), and **11a** (0.39 g, 52%). **11a**: mp 165-166 °C, Lit.[21] mp 167-168 °C; ^{1}H NMR (DMSO-d_6): δ 2.43 (t, J = 8.2 Hz, 2H), 2.86 (t, J = 8.2 Hz, 2H), 6.82-7.17 (m, 4H), 10.05 (br s, 1H); ^{13}C NMR (DMSO-d_6): δ 24.77, 30.42, 114.96, 121.87, 123.50, 127.03, 127.68, 138.27, 170.18.

The same procedures were used to convert each of the compounds **8c-f** to the respective **9c-f**, **10c-f** and/or **11c-f**.

***N*-(2-Hydroxyphenyl)-3-(4-chlorophenyl)propanamide (9c) and *N*-(2-Hydroxyphenyl)-3-(2-chlorophenyl)propanamide (10c)**

9c: 27 % yield; mp 135-136 °C, ^{1}H NMR (DMSO-d_6): δ 2.70 (t, J = 7.6 Hz, 2H), 2.90 (t, J = 7.6 Hz, 2H), 6.71-7.72 (m, 8H), 9.25 (s, 1H), 9.71 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 30.26, 37.21, 115.78, 118.94, 122.28, 124.58, 126.26, 128.16, 130.20, 130.52, 140.19, 147.80 (arom. C), 170.74. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 65.33; H, 5.18; N, 5.03.

10c: 52 % yield; mp 155-156 °C. ^{1}H NMR (DMSO-d_6): δ 2.73 (t, J = 8.0 Hz, 2H), 3.01 (t, J = 8.0 Hz, 2H), 6.73-7.70 (m, 8H), 9.30 (s, 1H), 9.70 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.61, 35.46, 115.78, 118.92, 122.38, 124.61, 126.21, 127.22, 127.95, 129.16, 130.50, 132.90, 138.40, 147.85, 170.51. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 64.96; H, 5.32; N, 4.91.

***N*-(3-Hydroxyphenyl)-3-(4-chlorophenyl)propanamide (9d), *N*-(3-Hydroxyphenyl)-3-(2-chlorophenyl)propanamide (10d) and 3,4-Dihydro-7-hydroxy-2(1*H*)-quinolinone (11d)**

9d: 34 % yield; mp 177-178 °C. ^{1}H NMR (DMSO-d_6): δ 2.59 (t, J = 8.0 Hz, 2H), 2.89 (t, J = 8.0 Hz, 2H), 6.41-7.34 (m, 8H), 9.34 (s, 1H), 9.76 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 30.06, 37.69, 106.26, 109.83, 110.18, 128.18, 129.27, 130.15, 130.52, 140.17, 140.24, 157.54, 170.01. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 64.95; H, 5.17; N, 5.06.

10d: 38 % yield; mp 134-135 °C. ^{1}H NMR (DMSO-d_6): δ 2.61 (t, J = 8.1 Hz, 2H), 3.00 (t, J = 8.1 Hz, 2H), 6.40-7.45 (m, 8H), 9.33 (s, 1H), 9.79 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.51, 35.91, 106.26, 109.83, 110.18, 127.25, 127.99, 129.20, 129.26, 130.52, 132.90, 138.46, 140.16, 157.54, 169.78. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 65.60; H, 5.25; N, 5.00.

11d: 4 % yield; mp 232-233 °C. Lit.[22] mp 230 °C. ^{1}H NMR (DMSO-d_6): δ 2.38 (t, J = 7.2 Hz, 2H), 2.72 (t, J = 7.2 Hz, 2H), 6.28-6.92 (m, 3H), 9.24 (s, 1H), 9.92 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 24.01, 30.90, 102.29, 108.77, 113.69, 128.25, 139.01, 156.43, 170.29.

***N*-(4-Hydroxyphenyl)-3-(4-chlorophenyl)propanamide (9e), *N*-(4-Hydroxyphenyl)-3-(2-chlorophenyl)propanamide (10e) and 3,4-Dihydro-6-hydroxy-2(1*H*)-quinolinone (11e)**

9e: 43 % yield; mp 179-180 °C. ^{1}H NMR (DMSO-d_6): δ 2.55 (t, J = 7.6 Hz, 2H), 2.88 (t, J = 7.6 Hz, 2H), 6.66-7.34 (m, 8H), 9.14 (s, 1H), 9.63 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 30.19, 37.49, 114.98, 120.89, 128.17, 130.13, 130.50, 130.82, 140.31, 153.17, 169.37. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 65.36; H, 5.20; N, 5.06.

10e: 42 % yield; mp 141-142 °C. ^{1}H NMR (DMSO-d_6): δ 2.57 (t, J = 8.2 Hz, 2H), 3.00 (t, J = 8.2 Hz, 2H), 6.65-7.41 (m, 8H), 9.14 (s, 1H), 9.66 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 28.64, 35.72, 114.97, 120.88, 127.24, 127.96, 129.18, 130.51, 130.80, 132.87, 138.52, 153.16, 169.15. Anal. Calcd for $C_{15}H_{14}ClNO_2$: C, 65.34; H, 5.12; N, 5.08; Found: C, 65.34; H, 5.24; N, 5.06.

11e: 4 % yield; mp 233-234 °C. Lit.[20] mp 237-238 °C. ^{1}H NMR (DMSO-d_6): δ 2.36 (t, J = 7.9 Hz, 2H), 2.76 (t, J = 7.9 Hz, 2H), 6.50-6.68 (m, 3H), 9.00 (s, 1H), 9.79 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 25.07, 30.44, 113.40, 114.53, 115.79, 124.72, 130.25, 152.32, 169.60.

***N*-(4-Methylphenyl)-3-(4-chlorophenyl)propanamide (9f), *N*-(4-Methylphenyl)-3-(2-chlorophenyl)propanamide (10f) and 3,4-Dihydro-6-methyl-2(*1H*)-quinolinone (11f)**

9f: 11 % yield; mp 130-131 °C. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H), 2.60 (t, J = 7.3 Hz, 2H), 3.00 (t, J = 7.3 Hz, 2H), 7.07-7.34 (m, 8H), 7.26 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.83, 30.82, 39.13, 120.10, 128.65, 129.46, 129.76, 132.07, 134.09, 135.02, 139.16, 169.92. Anal. Calcd for $C_{16}H_{16}ClNO$: C, 70.20; H, 5.89; N, 5.12; Found: C, 69.90; H, 5.96; N, 5.16.

10f: 8 % yield; mp 141-142 °C. ^{1}H NMR ($CDCl_3$): δ 2.30 (s, 3H), 2.65 (t, J = 7.2 Hz, 2H), 3.16 (t, J = 7.2 Hz, 2H), 7.08-7.36 (m, 8H), 7.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 20.82, 29.55, 37.29, 120.06, 127.04, 127.91, 129.43, 129.55, 130.83, 133.80, 133.97, 135.10, 138.19, 169.94. Anal. Calcd for $C_{16}H_{16}ClNO$: C, 70.20; H, 5.89; N, 5.12; Found: C, 70.12; H, 5.85; N, 5.13.

11f: 61 % yield; mp 133-134 °C. Lit.[23] mp 136-136.5 °C; ^{1}H NMR (DMSO-d_6): δ 2.21 (s, 3H), 2.41 (t, J = 7.2 Hz, 2H), 2.81 (t, J = 7.2 Hz, 2H), 6.72-6.96 (m, 3H), 9.97 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 20.30, 24.79, 30.48, 114.85, 123.39, 127.37, 128.24, 130.68, 135.81, 170.06. Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69; Found: C, 74.51; H, 6.94; N, 8.64.

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Intermolecular Friedel-Crafts addition; Intramolecular Friedel-Crafts cyclization; 3-Phenylpropionanilide; 3-Chloropropanamide.

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