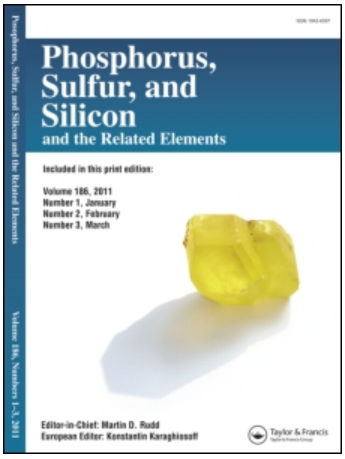

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Tetrachlorosilane–Zinc Chloride as a New Potent Binary Reagent for One-Pot, Three-Component Synthesis of Mannich-Type Products

Doria S. Badawy,[1] Ebrahim Abdel-Galil,[1] Ezzat M. Kandeel,[1] Wahid M. Basyouni,[2] and Tamer K. Khatab[2]
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*A combination of tetrachlorosilane and zinc chloride in dichloromethane as an efficient and ambient binary reagent to promote a one-pot amidoalkylation reaction of enolizable ketones, aromatic aldehydes with acetonitriles, or benzonitrile have been developed. The newly synthesized β-acetamidoketones **3** and β-benzamidoketones **5** were obtained in good yields.*

Keywords β-Acylaminoeketones; amidoalkylation; binary reagent; multicomponent; naphthyl; tetrachlorosilane

INTRODUCTION

Multicomponent condensation reactions (MCRs) represent efficient methods of rapidly increasing molecular complexity in a modular fashion,[1] from early examples, such as the Strecker,[2] Hantsch,[3] and Mannich[4] reactions to more recent reports.[1,5–11] MCRs are important for the achievement of high levels of diversity, as they allow more than two building blocks to be combined in practical, time-saving, one-pot operations, giving rise to complex structures by simultaneous formation of two or more bonds, according to the domino principle.[1]

Also, MCRs contribute to the requirements of an environmentally friendly process by reducing the number of synthetic steps, energy consumption, and waste production. Researchers have transformed this powerful technology into one of the most efficient and economic tools for

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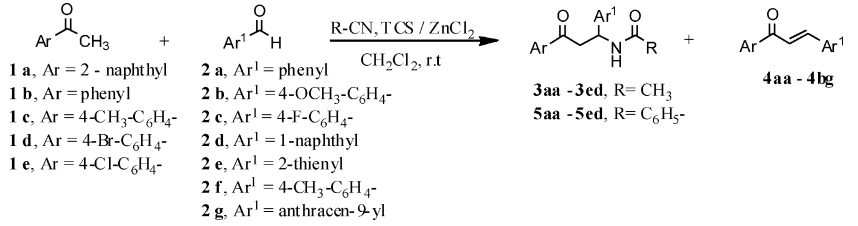
combinatorial and parallel synthesis.[1,5] Due to their inherently simple experimental procedures and their one-pot character, they are perfectly suited for automated synthesis. Thus, MCRs play an important role in combinatorial chemistry because of their ability to synthesize a small drug-like molecule in a few steps and usually in a one-pot operation.[12] Another typical benefit from these reactions is simplified purification, because all of the reagents are incorporated into the final product.

Acetamido- or amino-ketone derivatives are important for their biological and pharmaceutical properties,[13] and in the preparation of antibiotic drugs such as nikkomycine or neopolyoxines.[14] The best known route for the synthesis of this class of compounds is the Dakin–West reaction,[15a] which involves the condensation of an amino acid with acetic anhydride in the presence of a base.[15b] Recently, other synthetic methods have been used for the formation of β-acetamidoketones through the multicomponent condensation of aryl aldehydes, enolizable ketones, and acetyl chlorides in acetonitrile in the presence of Lewis or Br¨nsted acid catalysts such as $CoCl_2$,[16,17] Montmorillonite K-10 clay,[18] silica sulfuric acid,[19] $BiCl_3$ generated from BiOCl,[20] $ZrOCl_2.8H_2O$,[21] heteropoly acid,[22] sulfuric acid absorbed on silica gel,[23] $Sc(OTf)_3$,[24] silica supported $H_3PW_{12}O_4$,[25] $Fe(HSO_4)_3$,[26] Nafion-H,[27] $NaHSO_4{\cdot}H_2O$,[28] and iron(III) chloride.[29]

RESULTS AND DISCUSSION

In recent years, tetrachlorosilane[30] (TCS) and its reagents in combination with ethanol,[31] sodium iodide,[32] sodium azide,[33] *N*-bromosuccinimide,[34] potassium cyanide,[35] and zinc chloride [36] have gained much interest in organic synthesis. Since zinc chloride is a commercially available, low-cost, and eco-environmentally reagent, we report in this article a mild and efficient method for the preparation of β-acylamino ketones by one-pot three-component reactions of enolizable ketones **1a–e**, aromatic aldehydes **2a–g**, and acetonitrile or benzonitrile in the presence of TCS/$ZnCl_2$ as a binary reagent at room temperature (Scheme 1).

Our initial study was performed on the reaction between 2-acetylnaphthalene (**1a**), benzaldehyde (**2a**), and acetonitrile in the presence of TCS/$ZnCl_2$ in dichloromethane at room temperature. The progress of the reaction was monitored by TLC. To our delight, the desired reaction products, *N*-(3-naphth-2-yl)-3-oxo-1-phenylpropyl)acetamide (**3aa**) and 1-naphth-2-yl-3-phenylprop-2-en-1-one (**4aa**), were obtained in (80%) and (10%), respectively. Then, the



SCHEME 1

reaction was carried out under various conditions as shown in Table I. When the ratio of TCS/$ZnCl_2$ was increased to 15 mmol, *N*-(3-(naphth-2-yl)-3-oxo-1-phenylpropyl)acetamide (**3aa**) was obtained in 80% yield within 20 h; when 5 mmol of TCS/$ZnCl_2$ was used, **3aa** was obtained in 51% yield after a prolonged reaction time. In addition, the reaction was found to be solvent-dependent. It proceeded smoothly in chloroform or acetonitrile with a relatively longer reaction time than in dichloromethane, but it failed in diethyl ether or tetrahydrofuran. Therefore, dichloromethane was proven to be the best solvent and was selected for the following investigation.

The scope of the reaction of 2-acetylnaphthalene (**1a**) with various aromatic aldehydes **2b–2e** containing both electron-donating **2b** and electron-withdrawing **2c** substituents was investigated under the same experimental conditions. We have found that the corresponding β-acetamidoketones are produced in good yields (Table II, entries 2 and 3). Similarly, polynuclear and heterocyclic aldehydes such as 1-naphthaldehyde (**2d**) and thiophene-2-carbaldehyde (**2e**) also react under the same experimental conditions and provided the desired

TABLE I Experimental Results of TCS/$ZnCl_2$-Mediated Amidoalkylation Reaction of 2-Acetylnaphthalene (1a), Benzaldehyde (2a), and Acetonitrile Under Normal Conditions

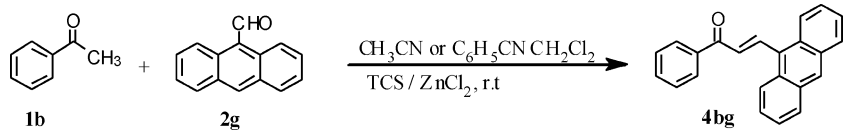
Entry	**1a** (mmol)	**2a** (mmol)	TCS/$ZnCl_2$	Solvent	Time (h)	Yield (%) **3aa**
1	5	5	5	CH_2Cl_2	20	51
2	5	5	10	CH_2Cl_2	20	59
3	5	5	15	CH_2Cl_2	20	80
4	5	5	15	$CHCl_3$	25	49
5	5	5	15	CH_3CN	45	50
6	5	5	15	$(C_2H_5)_2O$	50	—
7	5	5	15	THF	50	—

TABLE II TCS/$ZnCl_2$-Catalyzed Multicomponent Reaction of Enolizable Ketones, Aromatic Aldehydes, and Acetonitrile or Benzonitrile in CH_2Cl_2 at Room Temperature

Entry	Ketones	Aldehydes	Time (h)	Products (yield)	
1	**1a**	**2a**	20	**3aa** (80)	**4aa** (10)
2	**1a**	**2b**	15	**3ab** (75)	**4ab** (15)
3	**1a**	**2c**	18	**3ac** (75)	**4ac** (20)
4	**1a**	**2d**	30	**3ad** (45)	**4ad** (50)
5	**1a**	**2e**	16	**3ae** (70)	**4ae** (20)
6	**1b**	**2d**	20	**3bd** (75)	**4bd** (18)
7	**1c**	**2d**	16	**3cd** (78)	**4cd** (12)
8	**1d**	**2d**	22	**3dd** (76)	**4dd** (15)
9	**1e**	**2d**	19	**3ed** (77)	**4ed** (16)
10	**1a**	**2a**	22	**5aa** (70)	**4aa** (20)
11	**1a**	**2c**	17	**5ac** (70)	**4ac** (25)
12	**1a**	**2e**	22	**5ae** (60)	**4ae** (30)
13	**1a**	**2f**	20	**5af** (78)	**4af** (14)
14	**1b**	**2d**	22	**5bd** (72)	**4bd** (18)
15	**1c**	**2d**	20	**5cd** (75)	**4cd** (15)
16	**1d**	**2d**	24	**5dd** (70)	**4dd** (20)
17	**1e**	**2d**	18	**5ed** (75)	**4ed** (15)
18	**1b**	**2g**	40	**5bg** (0)	**4bg** (80)

products (Table II, entries 4 and 5) easily. To demonstrate the versatility of this binary reagent (TCS/$ZnCl_2$)-catalyzed, multicomponent reactions, a variety of acetophenone derivatives **1b–1e** were reacted with 1-naphthaldehyde (**2d**) and acetonitrile in the presence of TCS/$ZnCl_2$ under the same experimental conditions to provide the corresponding β-acetamidoketones (Table II, entries 6–9) in good yields. Next, the preparative utility and generality of this one-pot, multicomponent reaction were extended by replacing acetonitrile with benzonitrile. Thus, under the optimized reaction conditions, when a variety of aromatic aldehydes **2a–f** were treated with 2-acetylnaphthalene (**1a**) or acetophenone derivatives **1b–e** and benzonitrile in the presence of TCS/$ZnCl_2$, the corresponding β-benzamidoketones **5aa–5ed** were obtained in good yields (Table II, entries 10–17).

Interestingly, as shown in Scheme 2, during the course of our study, we have noticed that when anthracene-9-carbaldehyde (**2g**) is treated with acetophenone (**1b**) and acetonitrile or benzonitrile under the same experimental conditions, it gives only the aldol condensations product **4bg** instead of the expected β-acylaminoketones **3bg**, **5bg** (Table II, entry 18). Although the exact explanation of this anomaly is yet to be determined, the formation of the aldol condensation as the sole product

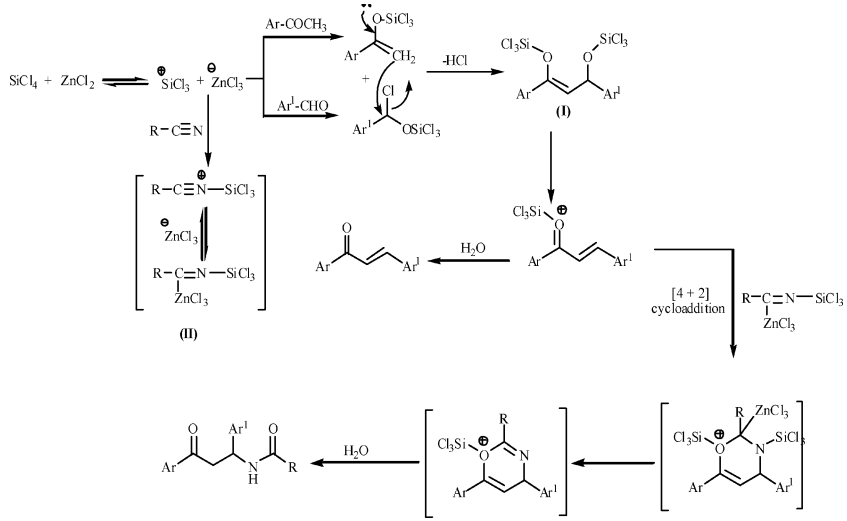


SCHEME 2

seems to be due to the steric hindrance of the bulky anthracenyl group. It is noteworthy to mention that no reaction was observed in the absence of either tetrachlorosilane (TCS) or zinc chloride. All these products were fully characterized through spectral and elemental analysis.

Next we turned our attention to a study of the mechanistic aspect of this one-pot three component reaction. A plausible mechanism for the present reaction proceeds as depicted in Scheme 3 through addition of stiochiometric Cl_3Si^+-$^-ZnCl_3$[37]-like species generated in situ from the reaction of TCS and $ZnCl_2$ in 1:1 molar ratio to the carbonyl group of the aldehydes and enolizable ketones, as well as to the cyano group of the nitrile led to the formation of intermediate **I** and **II**,[38–40] respectively.

In conclusion, we have developed a new synthetic methodology using a cheap, readily available, and efficient TCS/$ZnCl_2$ binary reagent for the one-pot synthesis of β-acetamidoketone derivatives **3** and β-benzamidoketone derivatives **5**. In addition, a thorough but not extensive investigation on the mechanistic aspect of this one-pot, three-component reaction in this article was performed.



SCHEME 3

EXPERIMENTAL

Melting points are uncorrected. Microanalyses were carried out by the Microanalytical Laboratory, National Research Center, Cairo, Egypt. Infrared spectra (KBr-disc) were recorded using a Jasco FT/IR-300E spectrometer. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ using Varian Mercury 300 MHz and Varian Gemini 200 MHz with chemical shifts using TMS as standard solvent. Mass spectra were recorded on a GC/MS Finnigan SSQ 7000 spectrometer. All reactions were carried out under atmospheric conditions at room temperature. Tetrachlorosilane (TCS) was obtained from commercial sources. Anhydrous zinc chloride was used as obtained from Aldrich. The solvents were distilled and dried before use. Reactions were monitored by TLC on 0.25 mm Merck Silica gel sheets (60 GF 354) (4 × 2 cm), and the spots were detected with UV light.

General Procedure

In a dry, two-necked, round-bottomed flask equipped with a rubber septa, a magnetic stirring bar, and a dry condenser, a mixture of ketone (5 mmol), aldehyde (5 mmol), nitrile (5 mmol), and anhydrous $ZnCl_2$ (15 mmol) in CH_2Cl_2 (20 mL) was allowed to stir with exclusion of moisture at room temperature for 5 min, then tetrachlorosilane (15 mmol) was added, and the reaction mixture was stirred for the specified time, poured onto ice cold water (100 mL), neutralized by Na_2CO_3, extracted with $CHCl_3$ (3 × 30 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by chromatographic methods to obtain the products.

N-*(3-(Naphth-2-yl)-3-oxo-1-phenylpropyl)acetamide (3aa)*

Mp 166°C R_f 0.42 (pet.ether:ethylacetate 1:1): IR (KBr) ν (cm^{-1}): 3340 (NH), 3065 (CH, Ar), 2926–2850 (CH_3, CH_2, CH), 1666 (CO), 1645 (CONH), 1600 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.08 (s, 3H, CH_3), 3.45–3.62 (dd, 1H, J = 16, 6.5, H_Z, $\underline{CH_2}CH$), 3.72–3.80 (dd, 1H, J = 16, 5.5 H_Z, $\underline{CH_2}CH$), 6.31–6.40 (m, 1H, $CH_2\underline{CH}$), 7.30–8.20 (m, 13H, ArH + NH) MS: (m/z,%) 317 (M^+, 6), 274 (M^+—$COCH_3$, 100), 258 (M^+-$NHCOCH_3$, 25), 155 ($C_{10}H_7CO$, 40), 127 (naphthyl $C_{10}H_7$, 55). Anal. Calcd. for $C_{21}H_{19}NO_2$ (317.38): C, 79.47, H, 6.03, N, 4.41. Found: C, 79.33, H, 6.00, N, 4.62%.

1-(Naphth-2-yl)-3-phenylprop-2-en-1-one (4aa)

Mp 83°C (lit[45], mp 85–86°C).

N-*(1-(4-Methoxyphenyl)-3-(naphth-2-yl)-3-oxopropyl)acetamide (3ab)*

Mp 110°C R_f 0.35 (pet.ether:ethylacetate 1:1): IR (KBr) ν (cm^{-1}): 3306 (NH), 3080 (CH, Ar), 2921–2830 (CH_3, CH_2, CH), 1680 (CO), 1652 (CONH), 1600, 1541 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.08 (s, 3H, CH_3), 3.57–3.66 (dd, 1H, J = 16.5, 6 H_Z, $\underline{CH_2}CH$), 3.85 (s, 3H, -OCH_3), 4.78–4.86 (dd, 1H, J = 16.5, 5 H_Z, $\underline{CH_2}CH$), 6.38 (m, 1H, $CH_2\underline{CH}$), 8.15–7.16(m, 12H, ArH + NH), MS: (m/z,%) 347 (M^+, 15), 304 (M^+-$COCH_3$, 5), 288 (M^+- NH_2COPh, 15), 181 (M^+-CH_2COnaphthyl, 100), 155 (M^+—COnaphthyl, 30). Anal. Calcd for $C_{22}H_{21}NO_3$ (347.41): C, 76.06, H, 6.09, N, 4.03. Found: C, 76.00, H, 5.95, N, 3.97%.

*1-(Naphth-2-yl)-3-*p*-methoxyphenylprop-2-en-1-one (4ab)*

Mp 96°C (lit[42], mp 95–97°C).

N-*(1-(4-Fluorophenyl)-3-(naphth-2-yl)-3-oxopropyl)acetamide (3ac)*

Mp 160°C R_f 0.40 (pet.ether:ethylacetate 1:1): IR (KBr) ν (cm^{-1}): 3286 (NH), 3064 (CH, Ar), 2920–2900 (CH_3, CH_2, CH), 1681 (CO), 1644 (CONH), 1548 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 1.99 (s, 3H, CH_3), 3.49–3.50 (dd, 1H, J = 16, 6 H_Z, $\underline{CH_2}CH$), 3.82–3.83 (dd, 1H, J = 16, 5 H_Z, $\underline{CH_2}CH$), 5.52–5.54 (m, 1H, $CH_2\underline{CH}$), 7.82–8.37 (m, 12H, ArH + NH). ^{13}C NMR: δ (ppm) 198.52 (C=O), 169.55 (CONH), 130.15–123.42 (16 Aromatic carbon atoms), 49.37 (CHNH), 43.00 (CO), 23.50 (CH_3). MS: (m/z,%) 335 (M^+, 15), 292 (M^+ -$COCH_3$, 40), 180 (M^+- COnaphthyl, 10), 155 (COnaphthyl, 100), 127 (naphthyl, 40). Anal. Calcd. for $C_{21}H_{18}FNO_2$ (335.37): C, 75.21, H, 5.41, F, 5.66, N, 4.18. Found: C, 75.12, H, 5.35, N, 4.05%.

3-(4-Fluorophenyl)-1-(naphth-2-yl)prop-2-en-1-one (4ac)

Mp 150°C (lit[41], mp 150–152°C).

N-*(1-(Naphth-1-yl)-3-(naphth-2-yl)-3-oxopropyl)acetamide (3ad)*

Mp 198–195°C R_f 0.35 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3303 (NH), 3032–3061 (CH, Ar), 2900 (CH_3, CH_2, CH), 1685 (CO), 1636 (CONH), 1600, 1586 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 1.99 (s, 3H, CH_3), 3.82–3.94 (dd, 1H, J = 16, 6 H_Z, $\underline{CH_2}CH$), 4.13–4.20 (dd, 1H, J = 16, 5 H_Z, $\underline{CH_2}CH$), 6.58–6.72 (m, 1H, $CH_2\underline{CH}$)), 7.28–8.38 (m, 15H, ArH + NH). MS: (m/z,%) 367 (M^+, 5), 324 (M^+-$COCH_3$, 15), 308 (M^+-NH_2COCH_3, 30), 212 (M^+-COnaphthyl, 45), 155 (COnaphthyl, 100).

Anal. Calcd. for $C_{25}H_{21}NO_2$ (367.44): C, 81.72, H, 5.76, N, 3.81. Found: C, 81.70, H, 5.74, N, 3.79%.

3-(Naphth-1-yl)-1-(naphth-2-yl)prop-2-en-1-one (4ad)

Mp 158°C (lit[43], m- 156–158°C).

N-*(3-(Naphth-2-yl)-3-oxo-1-(2-thienyl)propyl)acetamide (3ae)*

Mp 148°C R_f 0.4 (pet.ether:ethylacetate 1:1): IR (KBr) ν (cm^{-1}): 3288 (NH), 3065 (CH, Ar), 2950–2850 (CH_3, CH_2, CH), 1685 (aliphatic- CO), 1642 (CONH), 1600, 1550 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.08 (s, 3H, CH_3), 3.43–3.48 (dd, 1H, J = 16.5, 6.5, H_Z, $\underline{CH_2}CH$), 3.52–3.58 (dd, 1H J = 16.5, 4.8 H_Z, $\underline{CH_2}CH$), 5.23–5.28 (m, 1H, $CH_2\underline{CH}$), 6.96–8.12 (m, 11H, ArH + NH). MS: (m/z,%) 323 (M^+, 10), 280 (M^+-$COCH_3$, 45), 264 (M^+- NH_2COCH_3, 60), 168 (M^+- CO naphthyl ion, 15), 155 (COnaphthyl ion, 100). Anal. Calcd. for $C_{19}H_{17}NO_2S$ (323.41): C, 70.56, H, 5.30, N, 4.33, S, 9.91. Found: C, 70.42, H, 5.25, N, 4.30, S, 9.77%.

1-(Naphth-2-yl)-3-(2-thienyl)prop-2-en-1-one (4ae)

Mp 83°C (lit[45], mp 85–86°C).

N-*(1-(Naphth-1-yl)-3-oxo-3-phenylpropyl)acetamide (3bd)*

Mp 180°C R_f 0.42 (pet.ether : ethyl acetate 1:1). IR (KBr) ν (cm^{-1}): 3341 (NH), 3064 (CH, Ar), 2922–2850 (CH_3, CH_2, CH), 1669 (CO), 1649 (CONH), 1605 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.00 (s, 3H, CH_3), 3.45–3.62 (dd, 1H, J = 17, 6.5 H_Z, $\underline{CH_2}CH$), 3.72–3.80 (dd, 1H, J = 16.9, 5.5 H_Z, $\underline{CH_2}CH$), 6.31–6.40 (m, 1H, $CH_2\underline{CH}$), 7.32–8.21 (m, 13H, ArH + NH). MS: (m/z,%) 317 (M^+, 45), 274 (M^+—$COCH_3$, 85), 258 (M^+-$NHCOCH_3$, 35), 212 (M^+—COPh, 15), 156 (naphthylamine ion, 100), 105 (COPh, 95). Anal. Calcd. for $C_{21}H_{19}NO_2$ (317.38): C, 79.47, H, 6.03, N, 4.41. Found: C, 79.35, H, 6.00, N, 4.66%.

3-(Naphth-1-yl)-1-phenylprop-2-en-1-one (4bd)

Mp 87°C (lit[47], mp 88–89°C).

N-*(1-(Naphth-1-yl)-3-oxo-3-*p*-tolylpropyl)acetamide (3cd)*

Mp 134–136°C R_f 0.42 (pet.ether:ethylacetate 1:1).IR (KBr) ν (cm^{-1}): 3304 (NH), 3090, 3059 (CH, Ar), 2920–2850 (CH_3, CH_2, CH), 1684 (CO), 1650 (CONH), 1607, 1557 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.05 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.57–3.66 (dd, 1H, J = 17, 6.5 H_Z, $\underline{CH_2}CH$), 3.78–3.86 (dd, 1H, J = 17, 5 H_Z, $\underline{CH_2}CH$), 6.30–6.42 (m, 1H, $CH_2\underline{CH}$), 7.16–8.15 (m, 12H, ArH + NH), ^{13}C NMR: δ (ppm) 198.10 (C=O), 169.30 (CONH), 144.32–123.03 (16 Aromatic carbon atoms), 46.28 (CHNH),

42.37 (CO), 23.26, 21.67 two (CH_3). MS: (m/z,%) 331 (M^+, 5), 288 (M^+-$COCH_3$, 35), 272 (M^+- NH_2COCH_3, 30), 212 (M^+—COtolyl, 8), 119 (COtolyl, 100). Anal. Calcd. for $C_{22}H_{21}NO_2$ (331.41): C, 79.73, H, 6.39, N, 4.23. Found: C, 79.70, H, 6.20, N, 4.10%.

*3-(Naphth-1-yl)-1-*p*-tolylprop-2-en-1-one (4cd)*

Mp 85°C (lit[44], mp 84–86°C).

N-*(3-(4-Bromophenyl)-1-(naphth-1-yl)-3-oxopropyl)acetamide (3dd)*

Mp 125–126°C R_f 0.36 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3311 (NH), 3061 (CH, Ar), 2920–2850 (CH_3, CH_2, CH), 1688 (CO), 1649 (CONH), 1584 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.08 (s, 3H, CH_3), 3.59–3.70 (dd, 1H, $J = 16.8$, 6 H_Z, $\underline{CH_2}CH$), 3.85–3.90 (dd, 1H, $J = 16.8$, 5 H_Z, $\underline{CH_2}CH$), 6.31–6.42 (m, 1H, $CH_2\underline{CH}$), 7.28–8.18 (m, 12H, ArH + NH). MS: (m/z,%) 397 (M^++2, 8), 395 (M^+, 10), 352 (M^+-$COCH_3$, 30), 336 (M^+—$NCOCH_3$, 20), 198 (M^+-*p*-(Br)COPh, 95),156 (naphthylamine ion, 100). Anal. Calcd. for $C_{21}H_{18}BrNO_2$ (396.28): C, 63.65, H, 4.58, Br, 20.16, N, 3.53. Found: C, 63.60, H, 4.45, Br, 20.10, N, 3.43%.

1-(4-Bromophenyl)-3-(naphth-1-yl)prop-2-en-1-one (4dd)

Mp 107°C (lit[46], mp 108–110°C).

N-*(3-(4-Chlorophenyl)-1-(naphth-1-yl)-3-oxopropyl)acetamide (3ed)*

Mp 128–130°C R_f 0.38 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3300 (NH), 3060 (CH, Ar), 2900–2850 (CH_3, CH_2, CH), 1665 (aliphatic-CO), 1630 (CONH), 1590 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.1 (s, 3H, CH_3), 3.62–3.75 (dd, 1H, $J = 16.5$, 6 H_Z, $\underline{CH_2}CH$), 3.85–3.92 (dd, 1H, $J = 16.5$, 5 H_Z, $\underline{CH_2}CH$), 6.30–6.40 (m, 1H, $CH_2\underline{CH}$), 7.33–8.18 (m, 12H, ArH + NH). M.S: (m/z,%) 353 (M^++2, 25), 351 (M^+, 90), 308 (M^+-$COCH_3$, 100), 292 (M^+-NH_2COCH_3, 40), 212 (M^+—*p*-(Cl)COPh, 10), 198 (M^+- *p*-(Cl)PhCOCH$_2$, 20), 169(M^+- (*p*-(Cl)COPh+$COCH_3$), 35), 138 (*p*-(Cl)COPh, 38). Anal. Calcd. for $C_{21}H_{18}ClNO_2$ (351.83): C, 71.69, H, 5.16, Cl, 10.08, N, 3.98. Found: C, 71.66, H, 5.15, Cl, 10.02, N, 3.95%.

1-(4-Chlorophenyl)-3-(naphth-1-yl)prop-2-en-1-one (4ed)

Mp 100°C (lit[46], mp 99–100°C).

N-*(3-(Naphth-2-yl)-3-oxo-1-phenylpropyl)benzamide (5aa)*

Mp 143°C R_f 0.45 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3310 (NH), 3060 (CH, Ar), 2910–2850 (CH_2, CH), 1690 (CO), 1632 (CONH),

1599 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.71–3.79 (dd, 1H, J = 16.5, 6.6 H_Z, $\underline{CH_2}CH$), 3.95–4.02 (dd, 1H, J = 16.5, 4.8 H_Z, $\underline{CH_2}CH$), 6.58–6.59 (m, 1H, $CH_2\underline{CH}$), 7.24–8.24 (m, 18H, ArH + NH), MS: (m/z,%) 379 (M^+, 12), 274 (M^+- COPh, 100), 257(M^+- NH_2COPh, 70), 155 (COnaphthyl, 35), 105 (COPh, 45). Anal. Calcd. for $C_{26}H_{21}NO_2$ (379.45): C, 82.30, H, 5.58, N, 3.69. Found: C, 82.23, H, 5.52, N, 3.60%.

1-(Naphth-2-yl)-3-phenylprop-2-en-1-one (4aa)

Mp 142°C (lit[41], mp 142–143°C).

N-*(1-(4-Fluorophenyl)-3-(naphth-2-yl)-3-oxopropyl)benzamide (5ac)*

Mp 180°C R_f 0.43 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3275 (NH), 3080–3060 (CH, Ar), 2920–2880 (CH_2, CH), 1683 (-CH_2CO), 1643 (CONH), 1600, 1550 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.43–3.48 (dd, 1H, J = 16.8, 6.5 H_Z, $\underline{CH_2}CH$), 4.12–4.18 (dd, 1H, J = 16.8, 5 H_Z, $\underline{CH_2}CH$), 6.17–6.21 (m, 1H, $CH_2\underline{CH}$), 6.98–8.11 (m, 17H, ArH + NH). MS: (m/z,%) 397 (M^+, 5), 354 (M^+ -CONH, 30), 198 ($C_{10}H_7COCH_2CH_2N$, 24), 183 ($C_{10}H_7COCH_2CH_2$, 34), 170 ($C_{10}H_7COCH_2CH_3$, 63).156 ($C_{10}H_7CHO$, 100), 127 ($C_{10}H_7$, 23). Anal. Calcd. for $C_{26}H_{20}FNO_2$ (397.44): C, 78.57, H, 5.07, F, 4.78, N, 3.52. Found: C, 78.45, H, 4.98, N, 3.45%.

3-(4-Fluorophenyl)-1-(naphth-2-yl)prop-2-en-1-one (4ac)

Mp 150°C (lit[41], mp 150–152°C.

N-*(3-(Naphth-2-yl)-3-oxo-1-(2-thienyl)propyl)benzamide (5ae)*

Mp 145°C R_f 0.45 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3280 (NH), 3099, 3055 (CH, Ar), 2959 (CH_2, CH), 1685 (CO), 1642 (CONH), 1591 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.71–3.79 (dd, 1H, J = 17.2, 6.6 H_Z, $\underline{CH_2}CH$), 3.96–4.03 (dd, 1H, J = 17.2, 4.8 H_Z, $\underline{CH_2}CH$), 6.57–6.59 (m, 1H, $CH_2\underline{CH}$), 7.26–8.24 (m, 16H, ArH + NH). MS: (m/z,%) 385 (M^+, 3), 264 (M^+-NH_2COPh, 100), 230 (M^+- COnaphthyl, 12), 155 (COnaphthyl, 15), 127 (naphthyl, 35). Anal. Calcd. for $C_{24}H_{19}NO_2S$ (385.48): C, 74.78, H, 4.97, N, 3.63, S, 8.32. Found: C, 74.76, H, 4.94, N, 3.59, S, 8.29%.

1-(Naphth-2-yl)-3-(2-thienyl)prop-2-en-1-one (4ae)

Mp 83°C (lit[45], mp 85–86°C).

N-*(3-(Naphth-2-yl)-3-oxo-1*-p-*tolylpropyl)benzamide (5af)*

Mp 160°C R_f 0.46 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3287 (NH), 3055 (CH, Ar), 2967–2840 (CH_2, CH), 1679 (CO), 1643 (CONH), 1550 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.28 (s, 3H, CH_3), 3.60–3.75 (dd, 1H, J = 16.5, 6.6 H_Z, $\underline{CH_2}CH$), 3.90–4.00 (dd, 1H, J = 16.5, 4.8 H_Z, $\underline{CH_2}CH$), 6.40–6.48 (m, 1H, $CH_2\underline{CH}$), 7.28–8.35 (m, 17H, 16ArH+NH). MS: (m/z,%) 393 (M^+, 5), 288 (M^+- COPh, 18), 273 (M^+- NH_2COPh, 100), 155(COnaphthyl ion, 60), 105 (COPh, 80). Anal. Calcd for $C_{27}H_{23}NO_2$ (393.48): C, 82.42, H, 5.89, N, 3.56. Found: C, 82.41, H, 5.87, N, 3.53%.

*1-(Naphth-2-yl)-3-*p-*tolylprop-2-en-1-one (4af)*

Mp 105°C (lit[42], mp 105–107°C).

N-*(1-(Naphth-1-yl)-3-oxo-3-phenylpropyl)benzamide (5bd)*

Mp 220°C R_f 0.46 (pet.ether: ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3318 (NH), 3060 (CH, Ar), 2912–2850 (CH_2, CH), 1691 (CO), 1632 (CONH), 1598 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.71–3.79 (dd, 1H, J = 16.8, 6.6 H_Z, $\underline{CH_2}CH$), 3.96–4.03 (dd, 1H, J = 17, 4.8 H_Z, $\underline{CH_2}CH$), 6.57–6.59 (m, 1H, $CH_2\underline{CH}$), 7.26–8.24 (m, 18H, ArH + NH). MS: (m/z,%) 379 (M^+, 18), 301 (M^+-Ph, 18), 273 (M^+- COPh, 25), 156 (naphthylamine ion, 10), 105 (COPh, 100), 77(Ph, 67). Anal. Calcd. for $C_{26}H_{21}NO_2$ (379.45): C, 82.30, H, 5.58, N, 3.69. Found: C, 82.26, H, 5.50, N, 3.61%.

3-(Naphth-1-yl)-1-phenylprop-2-en-1-one (4bd)

Mp 87°C (lit[47], mp 88–89°C).

N-*(1-(Naphth-1-yl)-3-oxo-3-*p-*tolylpropyl)benzamide (5cd)*

Mp 156°C R_f 0.44 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3329 (NH), 3062 (CH, Ar), 2956–2856 (CH_2, CH), 1676 (CO), 1629 (CONH), 1577 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 2.30 (s, 3H, CH_3), 3.65–3.79 (dd, 1H, J = 16.8, 6 H_Z, $\underline{CH_2}CH$), 4.11–4.22 (dd, 1H, J = 16.8, 5 H_Z, $\underline{CH_2}CH$), 6.55–6.65 (m, 1H, $CH_2\underline{CH}$), 7.22–8.00 (m, 17H, ArH + NH),. Anal. Calcd. for $C_{27}H_{23}NO_2$ (393.48): C, 82.42, H, 5.89, N, 3.56. Found: C, 82.40, H, 5.85, N, 3.50%.

*3-(Naphth-1-yl)-1-*p-*tolylprop-2-en-1-one (4cd)*

Mp 85°C (lit[44], mp 84–86°C).

N-*(3-(4-Bromophenyl)-1-(naphth-1-yl)-3-oxopropyl)benzamide (5dd)*

Mp 172–170°C R_f 0.40 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3297 (NH), 3085–3052 (CH, Ar), 2920–2880 (CH_2, CH), 1687 (CO), 1636 (CONH), 1582 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.78–3.89 (dd, 1H, J = 17, 6.5 H_Z, $\underline{CH_2}CH$), 4.00–4.18 (dd, 1H, J = 17, 5.5 H_Z, $\underline{CH_2}CH$), 6.40–6.52 (m, 1H, $CH_2\underline{CH}$), 7.30–8.35 (m, 17H, ArH + NH). MS: (m/z,%) 459 (M^++2, 9), 457 (M^+, 10), 352 (M^+- COPh, 15), 334 (M^+- NH_2COPh, 100), 182 (M^+-*p*-(Br)COPh, 35). Anal. Calcd. for $C_{26}H_{20}BrNO_2$ (458.35): C, 68.13, H, 4.40, Br, 17.43, N, 3.06. Found: C, 68.02, H, 4.32, Br, 17.35, N, 3.00%.

1-(4-Bromophenyl)-3-(naphth-1-yl)prop-2-en-1-one (4dd)

Mp 107°C (lit[46], mp 108–110°C).

N-*(3-(4-Chlorophenyl)-1-(naphth-1-yl)-3-oxopropyl)benzamide (5ed)*

Mp 205°C R_f 0.42 (pet.ether:ethylacetate 1:1). IR (KBr) ν (cm^{-1}): 3294 (NH), 3061 (CH, Ar), 2924–2855 (CH_2, CH), 1684 (CO), 1637 (CONH), 1586 (C=C, Ar). H NMR ($CDCl_3$): δ (ppm) 3.66–3.78 (dd, 1H, J = 16.5, 6 H_Z, $\underline{CH_2}CH$), 3.95–4.10 (dd, 1H, J = 16.5, 5 H_Z, $\underline{CH_2}CH$), 6.51–6.66 (m, 1H, $CH_2\underline{CH}$), 7.28–8.40 (m, 17H, ArH + NH). MS: (m/z,%) 413 (M^+, 0.27), 308 (M^+—PhCO, 100), 292 (M^+-NH_2COPh, 35), 155 (*p*-(Cl)C_6H_4-$COCH_3$, 50), 139(*p*-(Cl)C_6H_4-CO, 40), 127 (naphthyl, 15). Anal. Calcd. for $C_{26}H_{20}ClNO_2$ (413.9): C, 75.45, H, 4.87, Cl, 8.57, N, 3.38. Found: C, 75.42, H, 4.85, Cl, 8.52, N, 3.36%.

1-(4-Chlorophenyl)-3-(naphth-1-yl)prop-2-en-1-one (4ed)

Mp 100°C (lit[46], mp 99–100°C).

3-(Anthracen-9-yl)-1-phenylprop-2-en-1-one (4bg)

The general procedure yielded only chalcone, mp 125°C (lit[43], mp 124–125°C).

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