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Synthesis of Acetanilide's Tertiary Amide Derivatives via Secondary Amines Acylation

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Abstract

This study aims to synthesize derivatives of acetanilide that can be used to find out novel therapeutic effects through a series of tertiary amide molecules which were obtained using, as a first step, the reactions between benzenamine (aniline) and other different molecules which are ketone and aldehyde (benzaldehyde, benzophenone, acetophenone, butanone and acetone). These optimized reactions were performed to produce imines, which were subsequently reduced to secondary amines through using $NaBH_4$ at 0°C for 12 h. In the second stage, the acylation of these amines was carried out using acetic acid as a solvent and anhydride acetic at 80°C for 30 minutes to yield the desired tertiary amide derivatives of acetanilide. These synthesized molecules were attained in good yields and were characterized using Infrared (IR), Nuclear Magnetic Resonance (NMR) 1H, 13C, and High-performance liquid chromatography-mass spectrometry (HPLC-MS) techniques.

Keywords: Derivatives of Acetanilide, aniline, secondary amine, synthesis, tertiary amine

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1. Introduction

In recent years, the exploration of novel therapeutic agents has become significant in the field of medicinal chemistry. Recent research has highlighted the significance of acetanilide derivatives in drug development. Studies [1-3] showcase the diverse pharmacological activities of acetanilide derivatives. These derivatives exhibit multifaceted properties and have interesting chemical reactivity and biological activities since acetanilide has served as a fundamental component in the design and synthesis of various pharmaceutical products and, thus, has been discovered as an analgesic agent under the trade name of Antifebrin [4]. Furthemore, Acetanilide derivatives have demonstrated diverse pharmacological and biological activities, including anesthetic [5] antimicrobial [6] antiinflammatory [7] antitumor [8] anthelmintic [9], analgesic [10,11] antifungal, and antibacterial[12,13]. Additionally, the acetaminophen derivative of acetanilide has been used to treat a variety of acute painful conditions, such as dental pain [14,15], headaches [16], osteoarthritic pain [17], musculoskeletal pain [18], and back pain [19]. It has also been used to manage postoperative discomfort [20]. This has prompted researchers to delve into the synthesis of new compounds with enhanced biological properties. The synthesis and exploration of tertiary amide molecules have emerged as a cutting-edge research area due to their potential therapeutic effects. Various studies have explored the diverse synthetic applications of tertiary amides in various fields, especially medicinal chemistry. Recently, there has been frequent utilization of the tertiary amide fragment in the design of novel pharmaceutical cancer drugs aimed at enhancing their biological and therapeutic potency [21]. Moreover, [22] present, for the first time, a series of novel tertiary amide derivatives identified as Neddylation pathway activators, and explore their structure-activity relationships.

The objective of the current study is to provide a detailed understanding of the chemical structures of these molecules, which is crucial for evaluating their potential bioactivity. This aims to facilitate the introduction of structural modifications that may enhance their therapeutic properties. It focuses on a systematic approach to synthesizing unique tertiary amide derivatives, which are

introduced, for the first time, as derivatives of acetanilide, as demonstrated in figure 1.

2. Materials and methods

So as to carry out the synthesis of tertiary amide derivatives of acetanilide, two reaction methods were followed. The initial step involved reactions between aniline 1 and various molecules, including ketones and aldehydes such as benzaldehyde, benzophenone, acetophenone, butanone and acetoneusing EtOH as a solvent. Subsequently, these molecules were heated under magnetic stirring at 110 °C for 6 h. These reactions resulted in the formation of imines 2, 3, 4, 5 and 6 followed by the reduction of these imines through using $NaBH_4$at 0°C for 30min to yield secondary amines 2a, 3a, 4a, 5a and 6a, as shown in figure 2. The optimized results indicate that all the preceding amines were pale yellow, oily liquids. The same method was employed to derive other secondary amines from the work previously conducted in a prior study [23]. The amines were purified by crystallizing their hydrochloride, which were obtained through treatment with 2M HCl. The subsequent stage of the synthesis, as shown in figure 3, involved the acetylation of these secondary amines, using acetic acid as a solvant and acetic anhydride. Then, they were heated under magnetic stirring at 80°C for 30 minutes. These reactions resulted in the generation of tertiary amides derivatives of acetanilide, in which 2b and 3b were white and solid with melting point Pf (3b) = 130°C and Pf (2b) = 84°C, respectively. However, 4b, 5b, and 6b were light brown and oily liquids.

3. Results and Discussions

3.1.Synthesis of N-(1, 1-diphenylmethy) benzenamine, 2a (General Procedure)

The procedure involved dissolving 2 grams (21.5 mmol) of aniline in 30 mL of ethanol and introducing 4.3 grams (23.65 mmol) of benzophenone to the solution. The mixture heated up to boiling (bath temperature: 110 ºC). After 6 hours, the reaction mixture was cooled using an ice bath, and 0.368 grams (9.72 mmol) of NaBH4 were added. It was allowed to react for 12 hours. The ethanol was evaporated, and 15 mL of water, solid KOH until the pH exceeded 10, and solid NaCl were introduced. The resulting mixture was subjected to ether extraction, and the ethereal phase was washed with a saturated NaCl solution and H_2O. After drying over anhydrous Na2SO4, the ether was filtered and evaporated, yielding 5 grams (90% yield) of 2a. 40 mL of 2M HCl at an elevated temperature was introduced to 5 grams of 2a. The crystalline hydrochloride was infiltrated and rinsed with H_2O. Ultimately, 4 grams (constituting 80% yield) of 2a hydrochloride was acquired. To produce the free amine 2a, 4 grams (15.5 mmol) of the hydrochloride form of 2a were gradually introduced into 50 mL of 2M KOH while stirring, and the reaction continued for 3 hours. Subsequently, solid NaCl was added, and the mixture was extracted with ether. The organic phase was then allowed to dry over anhydrous Na_2SO_4, which was infiltrated, and the ether was evaporated, resulting in 3.5 grams (87.5% yield) of 2a. Other secondary amines, namely 3a, 4a, 5a, and 6a, were synthesized using the same procedure as that used for 2a.

HPLC-MS: 259.13034**,** IR (ν_{max}, cm^{-1}): 3371, 3028, 1618, 1497, 1215, 744,698,, ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 5.82 (1H, s, CH), 6.67-6.79 (5H, m, N-ArH), 7.15-7.39 (10H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 76.32 (CH), 115.34-129.40 (15xCH, Ar), 143.95(C,2C_{ipso}), 146.28 (C, C_{ipso}).

3.2. Synthesis of N-(1-phenylethyl) benzenamine 3a

Compund 3a was synthesized using the same procedure as that used for 2a. Initially, 2 grams (21.5 mmol) of aniline were dissolved in 30mL of ethanol. Subsequently, 2.83 grams (23.56 mmol) of acetophenone were added to the mixture. This process resulted in the formation of 3.98 grams (94% yield) of 3a.

HPLC-MS: 197.11488**,** IR (ν_{max}, cm^{-1}): 3341, 3031, 1619, 1449, 1203, 749, 691, , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 1.48 (3H, d, CH_3), 4.89 (1H, q, CH), 6.68-6.79 (5H, m, N-ArH), 7.15-7.36 (5H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 25.26 (CH_3), 70.50 (CH), 115.34-129.39 (10xCH, Ar), 145.91(C,C_{ipso}), 146.15 (C, C_{ipso}).

3.3. Synthesis of N-(1-metylpropyl) benezenamine, 4a

Compund 4a was synthesized using the same procedure as that used for 2a**.** Initially, 2 grams (21.5 mmol) of aniline were dissolved in 30mL of ethanol. Subsequently, 1.7 grams (23.56 mmol) of butanone were added to the mixture. This process resulted in the formation of 3.1 grams (96% yield) of 4a.

HPLC-MS: 149.11519**,** IR (ν_{max}, cm^{-1}): 3019, 1214, 745, 668 , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 0.96 (3H, t, CH_3), 1.76 (3H, d, CH_3), 1.47 (1H, m, CH_2), 1.59 (1H, m, CH_2), 3.4 (1H, m, CH), 6.60-7.17 (5H, m, N-ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 10.45 (CH_3), 20.25 (CH_3), 29.66 (CH_2), 50.09 (CH), 113.4-129.36 (5xCH, Ar),147.53 (C, C_{ipso}).

3.4. Synthesis of N-(1-metylethyl) benzenamine, 5a

Compund 5a was synthesized using the same procedure as that used for 2a**.** Initially, 2 grams (21, 5 mmol) of aniline were dissolved in 30mL of ethanol. Subsequently, 1.36 grams (23.56 mmol) of acetone were added to the mixture. This process resulted in the formation of 2.8 grams (96% yield) of 5a.

HPLC-MS: 135.08031**,** IR (ν_{max}, cm^{-1}): 3019, 2926, 1734, 1215, 667 , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 1.04(6H, d, 2xCH_3), 5.01 (1H, m, CH), 7.09-7.34 (5H, m, N-ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 21.08 (CH_3), 21.09 (CH_3), 45.92 (CH), 128.4-130.26 (5xCH, Ar), 139.24 (C, C_{ipso}).

3.5. Synthesis of N-(-1-phenylmethyl)benzenamine, 6a

Compound 6a was synthesized using the same procedure as that used for 2a**.** Initially, 2 grams (21, 5 mmol) of aniline were dissolved in 30mL of ethanol. Subsequently, 2.49 grams (23.56 mmol) of benzaldeyde were added to the

mixture. This process resulted in the formation of 3.69 grams (94% yield) of 6a.

HPLC-MS: 183.09932**,** IR (ν_{max}, cm^{-1}): 3060, 2925, 1626, 1214, 749, 691 , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 4.34 (2H, s, CH_2), 6.65-6.75 (5H, m, N-ArH), 7.18-7.39 (5H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 48.48 (CH_2), 113.05-129.36 (10xCH, Ar), 139.47 (C, C_{ipso}).148.14 (C, C_{ipso}).

3.6. Synthesis of N-phenyl-N-1, 1-diphenylmethyl acetamide, 2b (General Procedure)

The reaction involved dissolving 3 grams (11.6 mmol) of N-(1,1-diphenylmethy) benzenamine, 2a, in 10 mL of ethanoic acid and adding 5 mL of acetic anhydride drop by drop. The solution reached boiling point (80 ºC bath temperature). After 30 minutes, 10 mL of cold water was added, and the reaction mixture was cooled using an ice bath. Ether was used to extract the reaction mixture, and the ethereal phase was washed with H_2O and a saturated NaCl solution. The resulting mixture was dried over anhydrous Na_2SO_4, and after filtering and evaporating the ether, 1.95 grams (56% yield) of 2b was obtained.

Other tertiary amides, namely 3b, 4b, 5b, and 6b, were synthesized using the same procedure as that used for 2b.

HPLC-MS: 302.19003**,** IR (ν_{max}, cm^{-1}): 3301, 3019, 1665, 1441, 1215, 745,698, , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 2.15 (3H, s, CH_3), 5.84 (1H, s, CH), 7.27-7.39 (15H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 24.72 (CH_3), 76.34 (CH), 119.34-129.40 (15xCH, Ar), 137.92 (C, C_{ipso}),143.95(C,C_{ipso}), 168.38(C, C_{ipso}).

3.7. Synthesis of N-phenyl-N-1-phenylethyl acetamide, 3b

Compound 3b was synthesized using the same procedure as that used for 2b. Initially, 3 grams (15.23 mmol) of N-(1-phenylethyl) benzenamine (3a) were dissolved in 10 mL of ethanoic acid. Subsequently, 5 mL of acetic anhydride was added dropwise to the mixture. This process resulted in the formation of 2.07 grams (57% yield) of compound 3b.

HPLC-MS: 239.0175**,** IR (ν_{max}, cm^{-1}): 3301, 3012, 1665, 1498, 1216, 747,698, , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 1.49 (3H, d, CH_3), 2.15 (3H, s, CH_3), 4.90 (1H, s, CH), 7.07-7.49 (10H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 24.70 (CH_3), 25.26 (CH_3), 70.52 (CH), 119.9-128.40 (10xCH, Ar), 137.93 (C, C_{ipso}),145.82(C,C_{ipso}), 145.82(C, C_{ipso}). 168.47(C, C_{ipso}).

3.8. Synthesis of N-phenyl-N-1-methypropylacetamide, 4b

Compund 4b was synthesized using the same procedure as that used for 2b. Initially, 3 grams (20.13 mmol) of N-(1-methypropyl) benzenamine (4a) were dissolved in 10mL of ethanoic acid. Subsequently, 5 mL of acetic anhydride was added dropwise to the mixture. This process resulted in the formation of 2.11grams (55% yield) of compound 4b.

HPLC-MS: 191.774**,** IR (ν_{max}, cm^{-1}): 3062, 2962, 1651, 1390, 767, 601, ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 0.95 (3H, t, CH_3), 1.01 (3H, d, CH_3), 1.24 (1H, m, CH_2), 1.47 (1H, m, CH_2), 1.73 (3H, s, CH_3), 4.78 (1H, m, CH), 7.09-7.40 (5H, m, N-ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 11.44 (CH_3), 18.86 (CH_3), 23.65 (CH_3), 27.98 (CH_2), 51.78 (CH), 128.2-129.3 (5xCH, Ar), 139.61 (C, C_{ipso}), 140.4 (C, C_{ipso}).

3.9. Synthesis of N-phenyl-N-1-methyethylacetamide, 5b

Compund 5b was synthesized using the same procedure as that used for 2b. Initially, 2 grams (14.81 mmol) of **N-(1-Methylethyl) benzenamine** (5a) were dissolved in 7mL of ethanoic acid. Subsequently, 3.5 mL of acetic anhydride was added dropwise to the mixture. This process resulted in the formation of 1.08 grams (54% yield) of 5b.

HPLC-MS: 177.00119**,** IR (ν_{max}, cm^{-1}): 2951, 2932, 1647, 1391, 1118, 749 , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 1.04(6H, d, 2xCH_3), 1.73(3H, s, CH_3), 5.01 (1H, m, CH), 7.08-7.42 (5H, m, N-ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 21.08 (CH_3), 21.09 (CH_3), 23.56 (CH_3), 45.93 (CH), 128.4-130.26 (5xCH, Ar), 139.48 (C, C_{ipso}), 170.23 (C, C_{ipso}).

3.10. Synthesis of N-phenyl-N-1-phenymethythylacetamide, 6b

Compund 6b was synthesized using the same procedure as that used for 2b. Initially, 3 grams (16.39 mmol) of N-phenyl benzyl amine (6a) were dissolved in 10mL of ethanoic acid. Subsequently, 5 mL of acetic anhydride was added dropwise to the mixture. This process resulted in the formation of 2.06g (56% yield) of 6b.

HPLC-MS: 225.13799**,** IR (ν_{max}, cm^{-1}): 3062, 3030, 1654, 1494, 1273, 716, 695 , ^{1}H NMR δ (ppm) (500MHz, $CDCl_3$): 1.88 (3H, s, CH_3), 4.87 (2H, s, CH_2), 6.65-6.75 (5H, m, N-ArH), 6.96-7.31 (5H, m, ArH), ^{13}C NMR δ (ppm) (50MHz, $CDCl_3$): 22.80 (CH_3), 52.93 (CH_2), 127.43-129.62 (10xCH, Ar), 137.50 (C, C_{ipso}), 142.90 (C, C_{ipso}), 170.60 (C, C_{ipso}).

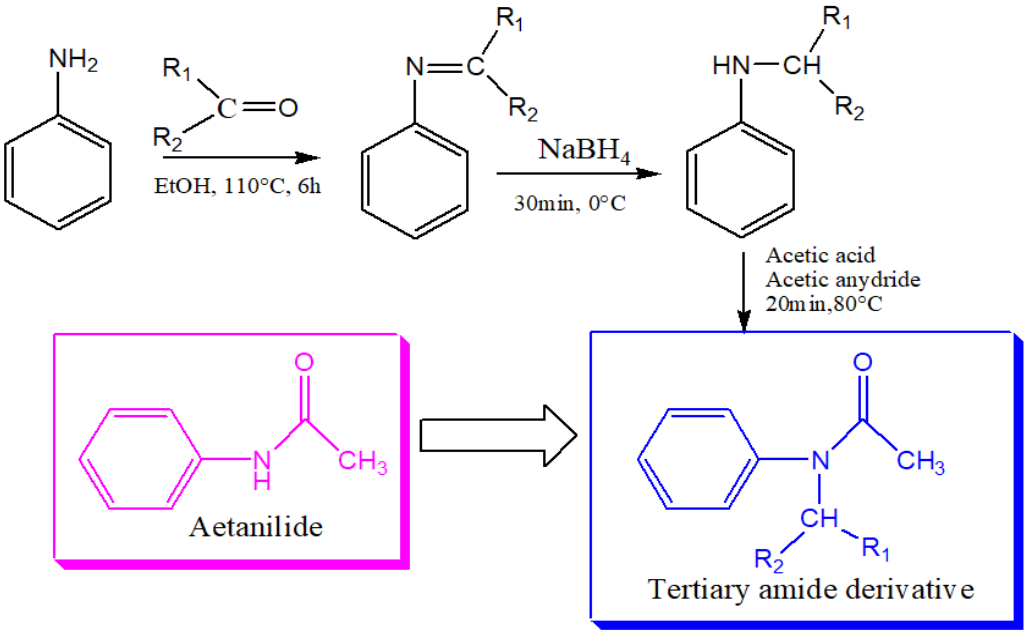

Fig. 1. General Scheme of Acetanilide's Tertiary Amide Derivatives

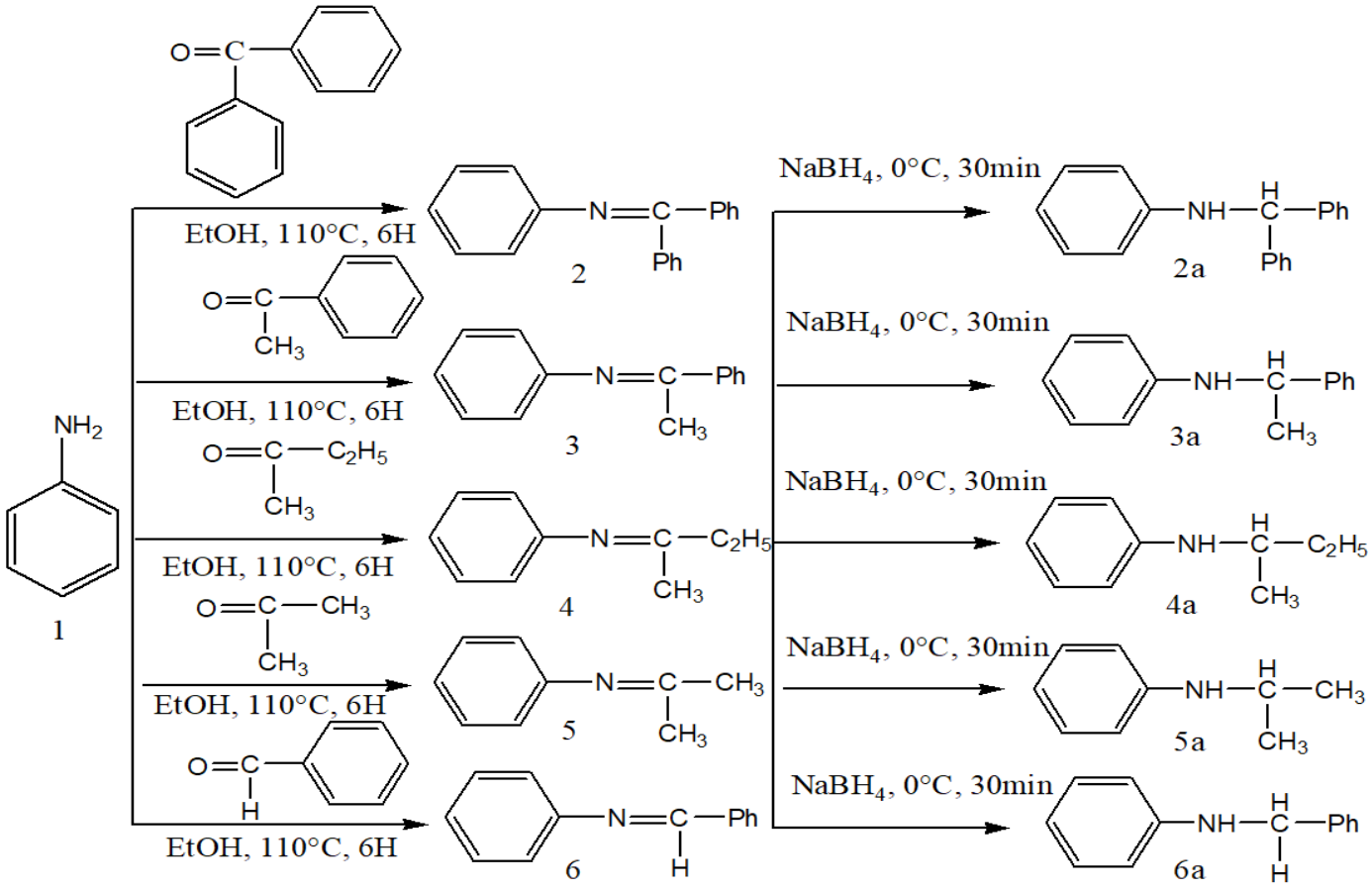

Fig. 2. Synthesis of secondary amines from aniline and different ketone and aldehyde

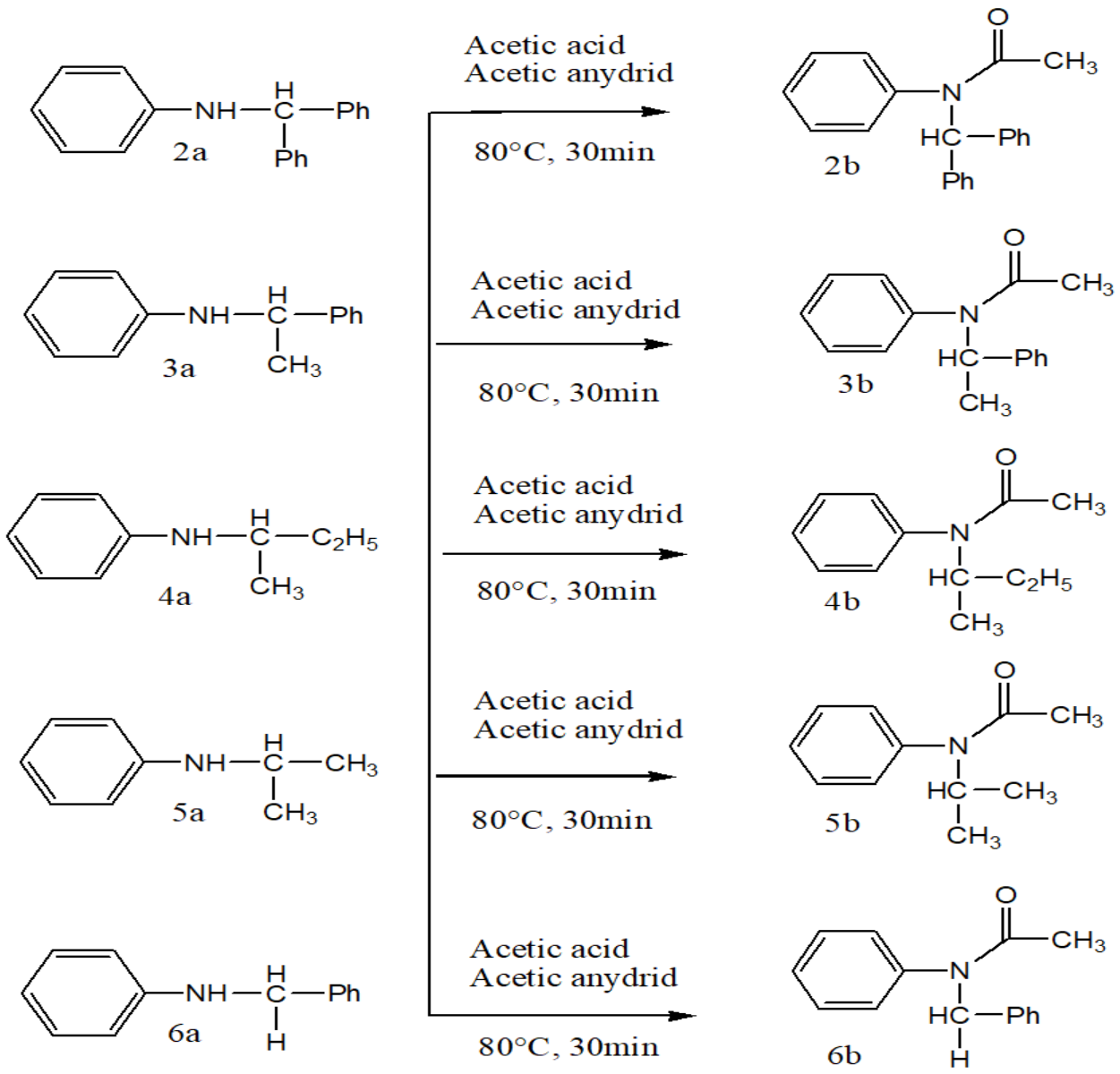

Fig.3. Synthesis of tertiary amides derivatives of acetanilide

4. Conclusions

To conclude, This synthetic strategy aims to generate diverse compounds. Each compound potentially possesses unique therapeutic effects. The synthesized molecules were characterized using analytical techniques such as infrared spectroscopy (IR), proton and carbon nuclear magnetic resonance spectroscopy (NMR 1H, C13), and high-performance liquid chromatography-mass spectrometry (HPLC-MS). The current study not only contributes to the generation of new knowledge regarding acetanilide derivatives but also lays the foundation for future studies seeking to uncover their therapeutic benefits. Successful synthesis of these derivatives would pave the way for further investigations into their pharmacological properties and biological activities.

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