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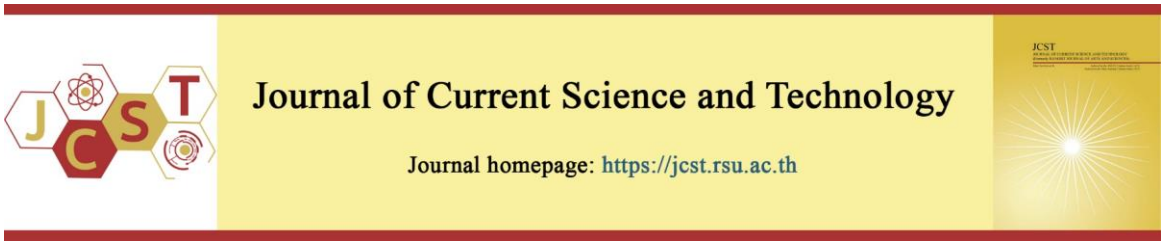

N-Aroylbenzimidazoles as efficient new reagents for a greener esterification reaction under solvent-free conditions

Baramee Phungpis* and Kanokkan Worawut

Faculty of Natural Resources, Rajamangala University of Technology Isan Sakonnakhon Campus, Sakonnakhon 47160, Thailand

*Corresponding author; E-mail: Barameephungpis@yahoo.com

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Abstract

Due to the increasing demand for green technology and its numerous advantages over conventional methodologies, this work has received interest for the development of a facile and efficient method for the synthesis of esters using benzimidazole chemistry. *N*-aroylbenzimidazole derivatives **2a-d** synthesized herein were found to be highly active acylation reagents, readily leading to high-yielding syntheses of ester products under solvent-free conditions without the need for a catalyst. A wide variety of esterification reactions between alcohols **1a-e** and *N*-aroylbenzimidazoles **2a-d** were carried out by grinding the mixtures, which were converted to their ester products **3a-t** in a simple synthetic procedure with yields in the range of 84% to 96% and recovery of the by-product benzimidazole (**4**) (80-93%). Compound **4** can be reused for the preparation of *N*-aroylbenzimidazoles **2a-d** without significant loss of efficiency. The advantages of this current methodology are the simple procedure; the absence of hazardous organic solvents; catalyst- and solvent-free conditions with high yields, low reaction temperatures, and short reaction times; and eco-friendly reactions generating no waste and allowing reagents to be recovered and reused.

Keywords: *N-aroylbenzimidazoles; aroylation reagent; esterification; grinding.*

1. Introduction

A general assumption regarding to organic reactions is that they are always performed in a solvent medium. Many conventional chemical processes use large amounts of toxic and volatile organic solvents (VOS) (Li, Pal, & Kannan, 2021; Safaei-Ghomi, & Ghasemzadeh, 2012; Gautam, & Chourasia, 2012; Nazari, & Shabanian, 2014). Different types of solvents, such as halogenated ones (*e.g.*, 1,1,2-trichloroethylene [TCE], methylene chloride [MC], perchloroethylene [PCE], 1-bromopropane, etc.) and other, chemical solvents, such as methanol, acetone, ethyl acetate, benzene, toluene, etc., have been widely used regardless of the environmental and health concerns that they pose.

A solid-state reaction also called a dry media or solventless reaction, is performed in the absence of a solvent (Marvaniya, Modi, & Sen, 2011). The drive for the development of solventless reactions in chemistry is due to several factors: the reactions are environmentally friendly because a solvent is not required, the removal of a solvent after a reaction has gone to completion (ultimately, the purification step) is not necessary, the reaction rate is high due to greater availability of the reactants, and low costs are involved (solvent costs are reduced). For this reason, the replacement of hazardous reaction solvents is one of the main goals of green chemistry (Asachenko, 2020; Sekhar et al., 2013; Karthikeyan, Kumar, Jagadeesh, & Bhagat, 2012).

During the past decade, chemists have developed effective methodologies for the synthesis of organic compounds, and many reactions have been carried out under green conditions. A variety of reactions, which have traditionally been conducted in solvent media, can now be carried out more profitably under solvent-free conditions. Dry media organic reactions have been used to synthesize various important compounds, such as halo-1,2,3-triazoles (Ageshina et al., 2019), *N*-substituted 3,4-diphenylpyrroles (Zeng, Xu, Yu, & Zhang, 2017), 1,4-disubstituted 5-halo-1,2,3-triazoles (Gribanov et al., 2017), and the dithienopyrrole series (Förtsch, S., & Bäuerle, 2017), and have been applied in different reactions, such as the Buchwald-Hartwig amination reaction (Gribanov et al., 2019), stannylation (Gribanov et al., 2018), copper-catalyzed azide-alkyne cycloadditions (CuAAC) (Hatit, Seath, Watson, & Burley, 2017), the copper-catalyzed *O*-methylation of carboxylic acids (Jia et al., 2016), etc. Different studies have recently reported on efficient reactions under solvent-free conditions (Heravi, Hamidi, Karimi, & Amouchi, 2018; Kazemi et al., 2018; Mohamadpour & Feilizadeh, 2021). Heravi et al. (2018) reported an efficient method and good yield for the ring-opening of epoxides with nitrogen heterocycles (indole and imidazole) using a heterogeneous catalyst called Caro's acid-silica gel (CA-SiO_2) in a solvent-free system. The solventless methodology also provides an efficient, simple, and clean route for multicomponent reactions such as the synthesis of polyhydroquinoline derivatives via the Hantzsch reaction of aldehydes, a β-diketone, a β-keto ester, and ammonium acetate using cerium (IV) sulfate tetrahydrate as a catalyst (Kazemi et al., 2018) and the preparation of xanthene derivatives using formic acid as a bio-based catalyst (Mohamadpour & Feilizadeh, 2021). However, these reactions have required relatively moderate to high temperatures for successful synthesis.

Esters, occurring widely in nature, are carboxylic acid derivatives found in essential oils and fruits and are commonly used as fragrances. Esters can be prepared by various methods essentially from alcohols and carboxylic acids or their derivatives such as acid chlorides and acid anhydrides (Otera, 2003) (Figure 1). Previous studies have commonly used Brønsted acids, such as HCl, H_3BO_3/H_2SO_4, H_2SO_5, DBSA, etc., to catalyze the esterification of carboxylic acids with alcohols (Rodriguez, Nomen, Spur, & Godfroid, 1998; Lawrence, 1971; Nishihara, & Kubota, 1986; Manabe, Sun, & Kobayashi, 2001; Manabe, Iimura, Sun, & Kobayashi, 2002; Jing, Li, Han, & Chu, 2008).

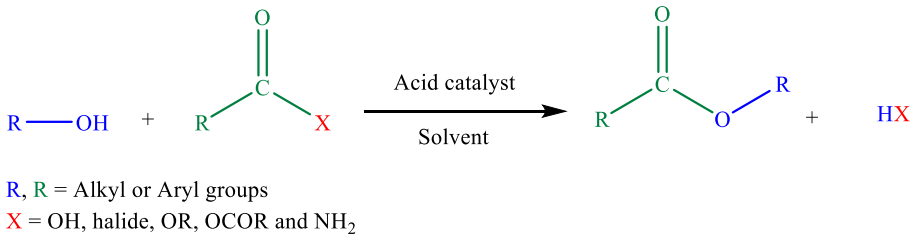


Figure 1 The original preparation of esters

During the past few years, a limited number of new studies have reported the synthesis of ester derivatives, such as the palladium-catalyzed benzylation of carboxylic acids (Liu et al., 2013); the copper-catalyzed oxidation of benzylic alcohols (Zhu, & Wei, 2013); and a catalyst-free protocol for the direct oxidative esterification of alcohols and aldehydes, with the reaction proceeding smoothly under mild conditions to produce high yields of products within a short time. (Rajbongshi, Sarma, & Phukan, 2014).

Over half a century ago, the acylation of alcohols was noted as one of the most important steps involved in esterification by treatment with carboxylic acids – mainly their derivatives including a large group of acyl chlorides or anhydrides – and in the presence of organic bases, such as triethylamine and pyridine, the reagents also lead to the formation of esters (Höfle, Steglich, & Vorbrüggen, 1978). To date, only a few reports have described efficient acylation in the preparation of esters – and example is the acylation of alcohols with acid anhydrides in the presence of the classical DMAP-catalyst under solvent-free conditions to give the corresponding esters in high yields (Sakakura et al., 2007). Very recently, carbonylimidazole derivatives have been found to be highly active acylating reagents for esterification

in the presence of pyridinium salts, giveing good yields of esters under mild conditions (Heller, Fu, & Sarpong, 2012) – in addition, this method enables the preparation of esters from *N*-acylimidazoles, also demonstrated to be effective *O*-acylating agents.

We have recently reported the success of using *N*-heterocyclic carbene generated from an ionic liquid (1-butyl-3-methylimidazolium bromide) as a catalyst for the cross-coupling between *N*-aroylbenzotriazoles and aromatic aldehydes (Phungpis, & Hahnvajanawong, 2021a), and *N*-aroylbenzotriazoles as efficient reagents for *O*-aroylation in the absence of organic solvent (Phungpis, & Hahnvajanawong, 2021b). Benzimidazoles are a class of compounds that have shown significant pharmaceutical activity (Asif, 2019); in this work, however, we have focused on their utilization as starting materials for the synthesis of acylating agents. Therefore, in continuation of our interest in the employment of *N*-aroylbenzimidazoles (**2**) as acylation agents, herein, we have reported their use as new and highly efficient acylating reagents for esterification by simple grinding in a mortar at room temperature under catalyst- and solvent-free conditions and with short reaction times (Figure 2). The substrate scope has also been investigated. Moreover, the by-product benzimidazole (**4**) can be readily recovered and reused as the substrate for the preparation of **2**. Therefore, no waste is generated from the aroylation.

2. Objectives

This work aimed to study the efficiency of *N*-benzoyl-1H-benzimidazoles as new acylating agents for esterification reactions and to investigate yields of ester products from the reaction between *N*-benzoyl-1H-benzimidazoles and alcohols under solvent-free conditions.

3. Materials and methods

All chemicals and reagents used in this study were of analytical grade and were used as purchased. Melting points were determined with a Sanyo Gallenkamp apparatus. IR spectra were recorded on a Shimadzu spectrometer. Spectra of solids were measured using KBr pellets. ^{1}H NMR and ^{13}C NMR data were obtained in $CDCl_3$ with TMS as the internal standard, using a VARIAN MERCURY plus spectrometer (400 MHz).

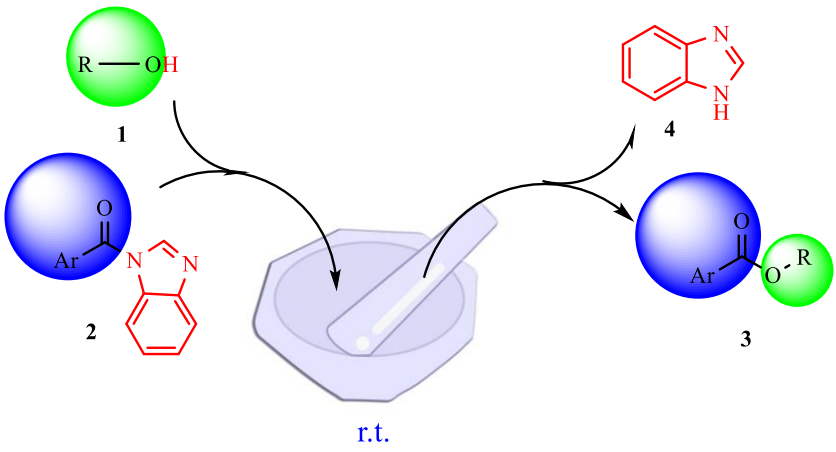
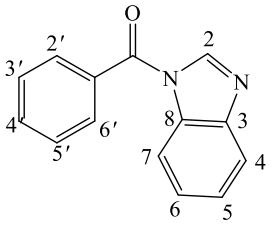


Figure 2 Aroylation reaction between alcohols (**1**) and *N*-aroylbenzimidazoles (**2**) to afford ester products (**3**)

3.1 General procedure for the preparation of *N*-aroylbenzimidazoles 2

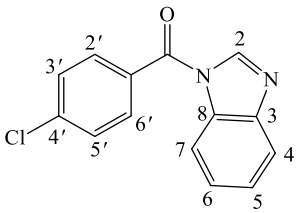
Benzimidazole (**4**) (1.0 mmol), potassium carbonate K_2CO_3 (2.0 mmol), and an appropriate acid halide (**5**) (1.2 mmol) were ground together with a pestle and mortar at room temperature for 0.5 to 1.5 hours. After completion of the reaction, as indicated by thin-layer chromatography (TLC; 50% dichloromethane/hexane), the reaction mixture was extracted with dichloromethane (3 × 30 mL). The extracts were dried (anh. Na_2SO_4) and concentrated at reduced pressure. The residue was purified by PLC (50% dichloromethane/hexane) to give the *N*-aroylbenzimidazoles **2a-d** – these are listed as follows with their physical and spectral data.

***N*-Benzoyl-1H-benzimidazole (2a)**



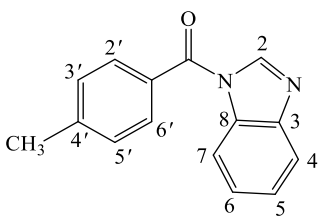
White solid (Yield 93%); R_f = 0.56 (50% dichloromethane/hexane); m.p. 113-114 °C; IR (KBr); ν_{max} 3151, 3066, 2994, 2818, 1696, and 1592 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.47 (1H, s, 2-*H*), 8.00 (1H, d, *J* = 8.8 Hz, 7-*H*), 7.77 (1H, d, *J* = 8.8 Hz, 4-H), 7.68-7.73 (3H, m, 2′-*H*, 4′-*H* and 6′-*H*), 7.53 (2H, t, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 7.14 (1H, t, *J* = 8.0 Hz, 5-*H*) and 7.07 (1H, t, *J* = 8.0 Hz, 6-*H*); ^{13}C NMR ($CDCl_3$): δ 110.6, 120.0, 122.5, 123.0, 128.5, 128.6, 128.9, 132.5, 135.5, 141.2, 143.6 and 165.2

***N*-(4-Chlorobenzoyl)-1H-benzimidazole (2b)**



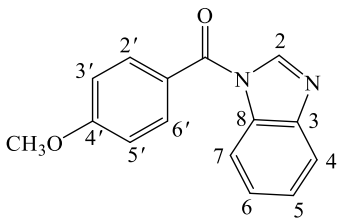
White solid (Yield 97%); R_f = 0.54 (50% dichloromethane/hexane); m.p. 128-130 °C; IR (KBr); ν_{max} 3201, 3077, 2989, 2833, 1689, and 1599 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.46 (1H, s, 2-*H*), 8.10 (1H, d, *J* = 8.8 Hz, 7-*H*), 7.77 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.53 (1H, d, *J* = 8.4 Hz, 4-*H*), 7.54 (2H, t, *J* = 8.8 Hz, 3′-*H* and 5′-*H*), 7.14 (1H, t, *J* = 8.4 Hz, 5-*H*) and 7.07 (1H, t, *J* = 8.4 Hz, 6-*H*); ^{13}C NMR ($CDCl_3$): δ 109.9, 118.4, 128.1 128.2, 128.3, 128.7, 131.2, 133.7, 136.1, 141.2, 143.4 and 164.9

***N*-(4-Methylbenzoyl)-1H-benzimidazole (2c)**



White solid (Yield 90%); R_f = 0.52 (50% dichloromethane/hexane); m.p. 142-144 °C; IR (KBr); ν_{max} 3179, 3100, 2978, 2857, 1692, and 1597 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.48 (1H, s, 2-*H*), 8.00 (1H, d, *J* = 8.4 Hz, 7-*H*), 7.93 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*), 7.77 (1H, d, *J* = 8.4 Hz, 4-*H*), 7.16 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.11 (1H, t, *J* = 8.0 Hz, 5-*H*), 7.08 (1H, t, *J* = 8.0 Hz, 6-*H*) and 2.37 (3H, s, ArCH_3); ^{13}C NMR ($CDCl_3$): δ 21.3, 109.9, 118.5, 128.0 128.2, 128.3, 129.1, 131.2, 136.1, 141.2, 141.5, 143.5 and 164.9

***N*-(4-Methoxybenzoyl)-1H-benzimidazole (2d)**

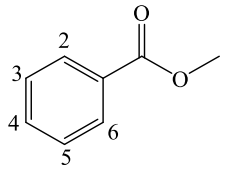


White solid (Yield 88%); R_f = 0.51 (50% dichloromethane/hexane); m.p. 158-160 °C; IR (KBr); ν_{max} 3229, 3112, 2979, 2880, 1690, and 1600 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.46 (1H, s, 2-*H*), 8.03 (1H, d, *J* = 8.0 Hz, 7-*H*), 7.99 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.76 (1H, d, *J* = 8.4 Hz, 4-*H*), 7.13 (1H, t, *J* = 8.0 Hz, 5-*H*), 7.06 (1H, t, *J* = 8.0 Hz, 6-*H*), 7.03 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), and 3.87 (3H, s, ArOCH_3); ^{13}C NMR ($CDCl_3$): δ 56.0, 109.7, 114.3, 118.7, 128.1 128.2, 129.6, 131.2, 136.1, 141.2, 143.4, 159.8 and 165.4

3.2 General procedure for aroylation reaction between alcohols 1a-e and *N*-aroylbenzimidazoles 2a-d by grinding with a pestle and mortar

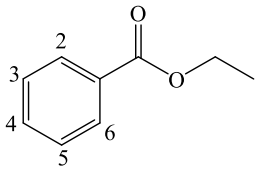
The mixture of the corresponding alcohols (2.0 mmol) and *N*-aroylbenzimidazoles (1.0 mmol) were ground together with a pestle and mortar at room temperature for 1.5 to 3.0 hours. The completion of the reactions were monitored by TLC in hexane : dichloromethane (1:1) solvent systems. The resulting mixture were purified by preparative thin-layer chromatography (silica gel, elution with 50% dichloromethane/hexane) yielding the desired ester compounds **3a-t** and benzimidazole (**4**) – compounds **3a-t** are listed as follows with their physical and spectral data.

Methyl benzoate (3a)



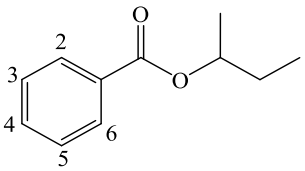
Yellow liquid (Yield 96%); R_f = 0.68 (50% dichloromethane/hexane); IR (neat): ν_{max} 3430, 3054, 2992, 2840, 1720, 1603, 1585, 1451, 1367, 1270 and 715 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.03 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.52 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.40 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*) and 3.87 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$): δ 52.1, 128.3, 130.1, 132.8, 133.3 and 167.1

Ethyl benzoate (3b)



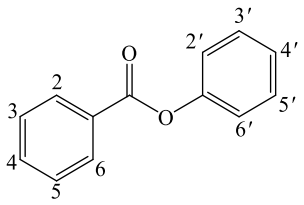
Yellow liquid (Yield 95%); R_f = 0.67 (50% dichloromethane/hexane); IR (neat): ν_{max} 3430, 3062, 2983, 2939, 1716, 1605, 1453, 1366, 1270 and 719 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.05 (2H, d, *J* = 8.0 Hz, 2-*H* and 6-*H*), 7.52 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.42 (2H, t, *J* = 8.0 Hz, 3-*H* and 5-*H*), 4.37 (2H, q, *J* = 7.2 Hz, OCH_2CH_3) and 1.38 (1H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 14.3, 60.9, 128.3, 129.5, 130.5, 132.7 and 166.7

***sec*-Butyl benzoate (3c)**



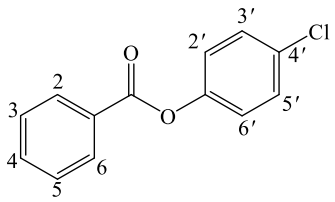
Yellow liquid (Yield 92%); R_f = 0.65 (50% dichloromethane/hexane); IR (neat): ν_{max} 3064, 2974, 2937, 2879, 1716, 1602, 1451, 1379, 1276 and 711 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.05 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.55 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.42 (2H, t, *J* = 8.0 Hz, 3-*H* and 5-*H*), 5.07-5.12 (1H, m, $OCH(CH_3)CH_2CH_3$), 1.69-1.72 (2H, m, $OCH(CH_3)CH_2CH_3$), 1.33 (3H, d, *J* = 6.3 Hz, $OCH(CH_3)CH_2CH_3$) and 0.97 (3H, t, *J* = 7.5 Hz, $OCH(CH_3)CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 9.7, 19.5, 28.9, 72.8, 128.2, 129.5, 130.9, 132.6 and 166.2

Phenyl benzoate (3d)



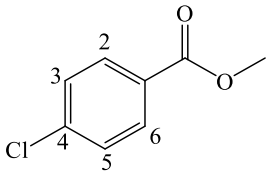
Yellow liquid (Yield 90%); R_f = 0.66 (50% dichloromethane/hexane); IR (neat): ν_{max} 3058, 1731, 1596, 1487, 1450, 1262, 1062 and 751 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.24 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.64 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.52 (2H, t, *J* = 8.4 Hz, 3-*H* and 5-*H*), 7.42 (2H, t, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 7.28 (1H, t, *J* = 7.6 Hz, 4′-*H*) and 7.22 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*); ^{13}C NMR ($CDCl_3$): δ 121.7, 125.9, 128.6, 129.5, 129.6, 130.2, 133.6, 150.9 and 165.2

4-Chlorophenyl benzoate (3e)



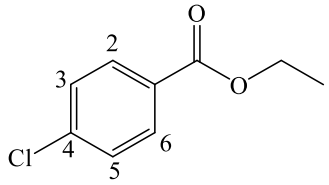
Yellow liquid (Yield 91%); R_f = 0.64 (50% dichloromethane/hexane); IR (neat): ν_{max} 3063, 1734, 1600, 1490, 1285, 1219, 1061 and 861 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.19 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.65 (1H, t, *J* = 7.6 Hz, 4-*H*), 7.52 (2H, t, *J* = 7.8 Hz, 3-*H* and 5-*H*), 7.40 (2H, d, *J* = 8.8 Hz, 3′-*H* and 5′-*H*) and 7.17 (2H, t, *J* = 8.8 Hz, 2′-*H* and 6′-*H*); ^{13}C NMR ($CDCl_3$): δ 123.1, 128.6, 129.2, 129.5, 130.2, 131.3, 133.8, 149.4 and 164.9

Methyl 4-chlorobenzoate (3f)



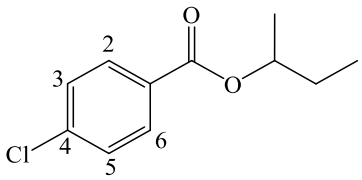
Yellow liquid (Yield 94%); R_f = 0.65 (50% dichloromethane/hexane); IR (neat): ν_{max} 3330, 3065, 2979, 2842, 1723, 1600, 1581, 1449, 1355, 1268 and 723 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.76 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.55 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 3.83 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$): δ 52.2, 128.7, 129.5, 131.3, 133.7 and 166.1

Ethyl 4-chlorobenzoate (3g)



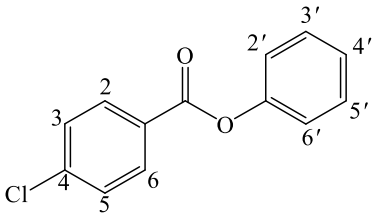
Yellow liquid (Yield 93%); R_f = 0.67 (50% dichloromethane/hexane); IR (neat): ν_{max} 3391, 3043, 2977, 2912, 1718, 1599, 1463, 1359, 1281 and 745 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.77 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.56 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 4.26 (2H, q, *J* = 7.2 Hz, OCH_2CH_3) and 1.24 (1H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 14.2, 61.2, 128.7, 129.5, 131.3, 133.7 and 166.2

***sec*-Butyl 4-chlorobenzoate (3h)**



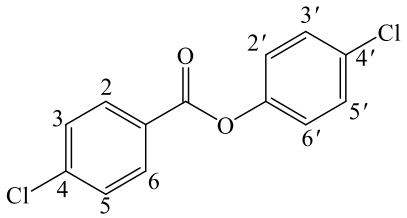
Yellow liquid (Yield 93%); R_f = 0.63 (50% dichloromethane/hexane); IR (neat): ν_{max} 3033, 2956, 2937, 2859, 1719, 1601, 1476, 1351, 1280 and 719 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.58 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.56 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 4.80-4.89 (1H, m, $OCH(CH_3)CH_2CH_3$), 1.64-1.67 (2H, m, $OCH(CH_3)CH_2CH_3$), 1.42 (3H, d, *J* = 6.9 Hz, $OCH(CH_3)CH_2CH_3$) and 0.94 (3H, t, *J* = 7.2 Hz, $OCH(CH_3)CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 9.9, 20.8, 29.5, 72.8, 128.7, 129.5, 131.3, 133.7 and 165.8

Phenyl 4-chlorobenzoate (3i)



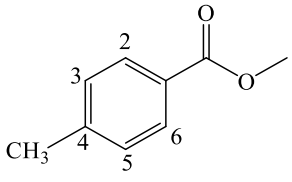
Yellow liquid (Yield 91%); R_f = 0.62 (50% dichloromethane/hexane); IR (neat): ν_{max} 3061, 1729, 1599, 1481, 1461, 1274, 1111 and 747 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.77 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.57 (2H, t, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.47 (2H, t, *J* = 7.6 Hz, 3′-*H* and 5′-*H*), 7.29 (2H, d, *J* = 8.8 Hz, 2′-*H* and 6′-*H*) and 7.28 (1H, t, *J* = 7.6 Hz, 4′-*H*); ^{13}C NMR ($CDCl_3$): δ 116.7, 127.8, 128.7, 129.4, 129.5, 131.3, 133.7, 150.6 and 164.2

4-Chlorophenyl 4-chlorobenzoate (3j)



Yellow liquid (Yield 96%); R_f = 0.64 (50% dichloromethane/hexane); IR (neat): ν_{max} 3041, 2983, 1730, 1597, 1490, 1264, 1120, 1058 and 754 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.77 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.56 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 7.50 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*) and 7.23 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*); ^{13}C NMR ($CDCl_3$): δ 120.0, 128.7, 129.3, 129.5, 131.3, 133.6, 133.7, 150.6 and 164.2

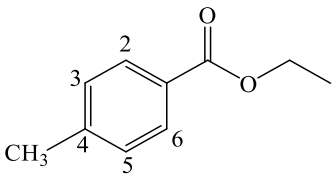
Methyl 4-methylbenzoate (3k)



Yellow liquid (Yield 89%); R_f = 0.61 (50% dichloromethane/hexane); IR (neat): ν_{max} 3346, 3039, 2970, 2851, 1721, 1602, 1579, 1453, 1342, 1277 and 732 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.92 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.15 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 3.81 (3H, s, OCH_3) and 2.32 (3H, s,

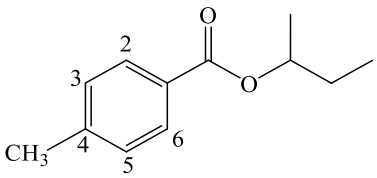
COArC*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 21.3, 52.2, 129.1, 129.5, 129.6, 141.5 and 166.1

Ethyl 4-methylbenzoate (3l)



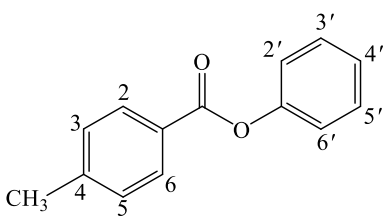
Yellow liquid (Yield 89%); R_f = 0.65 (50% dichloromethane/hexane); IR (neat): ν_{max} 3378, 3033, 2965, 2934, 1725, 1599, 1443, 1342, 1261 and 755 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.92 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.12 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 4.12 (2H, q, *J* = 7.3 Hz, OC*H*$_2$CH$_3$), 2.33 (3H, s, COArC*H*$_3$) and 1.23 (1H, t, *J* = 7.2 Hz, OCH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 14.2, 21.3, 61.2, 129.1, 129.5, 129.6, 141.5 and 166.2

***sec*-Butyl 4-methylbenzoate (3m)**



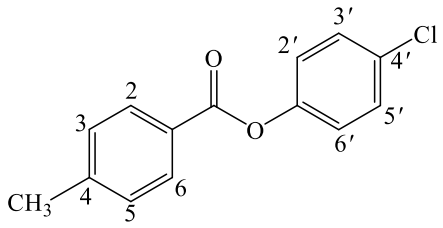
Yellow liquid (Yield 87%); R_f = 0.67 (50% dichloromethane/hexane); IR (neat): ν_{max} 3052, 2961, 2932, 2832, 1721, 1601, 1444, 1361, 1259 and 747 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.92 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.15 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 4.81-4.87 (1H, m, OC*H*(CH$_3$)CH$_2$CH$_3$), 2.31 (3H, s, COArC*H*$_3$), 1.63-1.67 (2H, m, OCH(CH$_3$)C*H*$_2$CH$_3$), 1.42 (3H, d, *J* = 6.8 Hz, OCH(C*H*$_3$)CH$_2$CH$_3$) and 0.94 (3H, t, *J* = 7.3 Hz, OCH(CH$_3$)CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 9.9, 20.8, 21.3, 29.5, 72.8, 129.1, 129.5, 129.6, 141.5 and 165.8

Phenyl 4-methylbenzoate (3n)



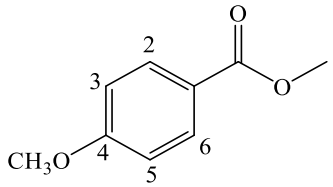
Yellow liquid (Yield 85%); R_f = 0.60 (50% dichloromethane/hexane); IR (neat): ν_{max} 3027, 1728, 1600, 1471, 1351, 1255, 1121 and 717 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.91 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.47 (2H, t, *J* = 7.8 Hz, 3′-*H* and 5′-*H*), 7.28 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.27 (1H, t, *J* = 7.6 Hz, 4′-*H*), 7.18 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 2.33 (3H, s, COArC*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 21.3, 116.7, 127.8, 129.1, 129.4, 129.5, 129.6, 141.5, 150.6 and 164.2

4-Chlorophenyl 4-methylbenzoate (3o)



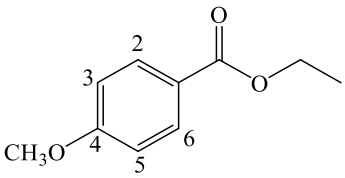
Yellow liquid (Yield 88%); R_f = 0.59 (50% dichloromethane/hexane); IR (neat): ν_{max} 3028, 2977, 1731, 1599, 1480, 1254, 1142, 1076 and 761 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.91 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.50 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.23 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.12 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 2.32 (3H, s, COArC*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 21.3, 120.0, 129.1, 129.3, 129.5, 129.6, 133.7, 141.5, 150.6 and 164.3

Methyl 4-methoxybenzoate (3p)



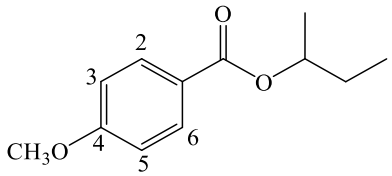
Yellow liquid (Yield 86%); R_f = 0.66 (50% dichloromethane/hexane); IR (neat): ν_{max} 3069, 2958, 2839, 1723, 1601, 1589, 1464, 1355, 1258 and 741 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.99 (2H, d, *J* = 8.4 Hz, 2-*H* and 6-*H*), 7.06 (2H, d, *J* = 8.4 Hz, 3-*H* and 5-*H*), 3.84 (3H, s, ArOC*H*$_3$) and 3.83 (3H, s, OC*H*$_3$); ^{13}C NMR ($CDCl_3$): δ 52.2, 56.0, 114.3, 129.5, 131.6, 159.8 and 166.2

Ethyl 4-methoxybenzoate (3q)



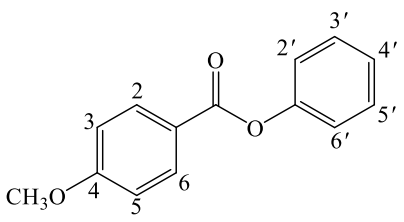
Yellow liquid (Yield 85%); R_f = 0.64 (50% dichloromethane/hexane); IR (neat): ν_{max} 3318, 3040, 2965, 2946, 1721, 1594, 1453, 1361, 1242 and 738 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.98 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.06 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 4.25 (2H, q, *J* = 7.2 Hz, OCH_2CH_3), 3.84 (3H, s, $COArOCH_3$), and 1.24 (1H, t, *J* = 7.2 Hz, OCH_2CH_3); ^{13}C NMR ($CDCl_3$): δ 14.2, 56.0, 61.2, 114.3, 129.5, 131.6, 159.8 and 166.2

***sec*-Butyl 4-methoxybenzoate (3r)**



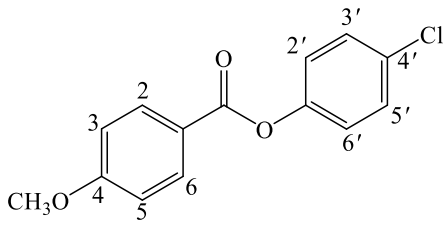
Yellow liquid (Yield 84%); R_f = 0.62 (50% dichloromethane/hexane); IR (neat): ν_{max} 3048, 2974, 2841, 1719, 1600, 1452, 1350, 1263 and 740 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.00 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.07 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*), 4.81-4.85 (1H, m, $OCH(CH_3)CH_2CH_3$), 3.84 (3H, s, $COArCH_3$), 1.64-1.68 (2H, m, $OCH(CH_3)CH_2CH_3$), 1.42 (3H, d, *J* = 6.9 Hz, $OCH(CH_3)CH_2CH_3$) and 0.95 (3H, t, *J* = 7.2 Hz, $OCH(CH_3)CH_2CH_3$); ^{13}C NMR ($CDCl_3$): δ 9.8, 20.9, 29.5, 56.0, 72.7, 114.3, 129.5, 131.6, 159.8 and 165.9

Phenyl 4-methoxybenzoate (3s)



Yellow liquid (Yield 92%); R_f = 0.60 (50% dichloromethane/hexane); IR (neat): ν_{max} 3034, 1725, 1603, 1482, 1364, 1260, 1146 and 739 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.01 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.47 (2H, t, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.28 (1H, t, *J* = 7.6 Hz, 4′-*H*), 7.29 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.07 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 3.84 (3H, s, $COArCH_3$); ^{13}C NMR ($CDCl_3$): δ 56.0, 114.3, 116.7, 127.8, 129.4, 129.5, 131.6, 150.6, 159.8 and 164.4

4-Chlorophenyl 4-methoxybenzoatev (3t)



Yellow liquid (Yield 92%); R_f = 0.58 (50% dichloromethane/hexane); IR (neat): ν_{max} 3043, 2969, 1728, 1593, 1489, 1246, 1139, 1054 and 745 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.05 (2H, d, *J* = 8.8 Hz, 2-*H* and 6-*H*), 7.51 (2H, d, *J* = 8.4 Hz, 3′-*H* and 5′-*H*), 7.23 (2H, d, *J* = 8.4 Hz, 2′-*H* and 6′-*H*), 7.07 (2H, d, *J* = 8.8 Hz, 3-*H* and 5-*H*) and 3.84 (3H, s, $COArOCH_3$); ^{13}C NMR ($CDCl_3$): δ 56.0, 114.3, 120.0, 129.3, 129.5, 131.6, 133.7, 150.6, 159.8 and 164.4

4. Results and discussion

Our strategy began with the preparation of the acylating reagent compounds of *N*-aroylbenzimidazoles **2a**-**d** from the reaction of the corresponding mixture of acid halides (**5**) (1.2 mmol) with benzimidazole (**4**) (1.0 mmol) and K_2CO_3 (2.0 mmol) by grinding the mixture in a mortar under solvent-free conditions, following a similar process that we have previously reported in the literature (Phungpis, Hahnvajanawong, & Theramongkol, 2016). The reaction procedure was completed within 0.5 to 1.5 hours to afford the desired *N*-aroylbenzimidazoles **2a**-**d** in good to excellent yields (88-97%), as shown in Figure 3.

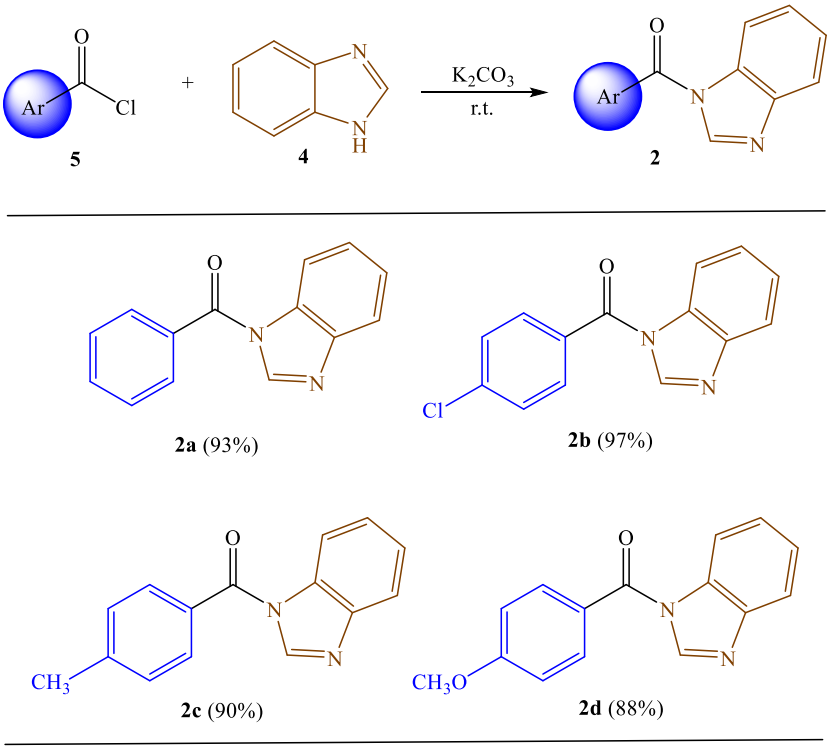


Figure 3 Preparation of *N*-aroylbenzimidazoles **2a-d**

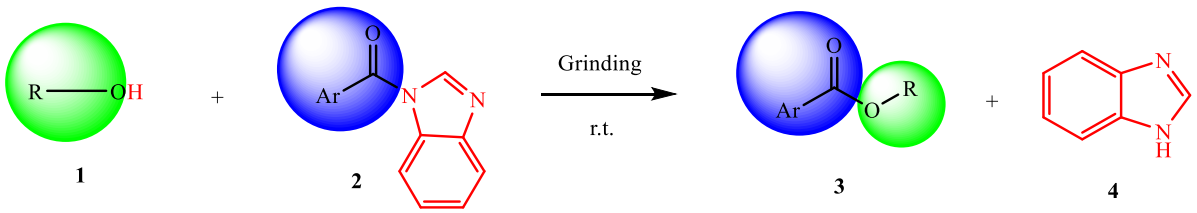
After their synthesis, *N*-aroylbenzimidazoles **2a-d** were used as acylating reagents with different alcohols by grinding the mixtures at room temperature in the absence of an organic solvent (Table 1), following a similar process as in our previous work (Phungpis, & Hahnvajanawong, 2021b) for the synthesis of esters with the help of *N*-aroylbenzotriazole derivatives.

Experimentally, it was found that primary and secondary alcohols (*e.g.*, methanol [**1a**], ethanol [**1b**], and sec-butyl alcohol [**1c**]) and aromatic alcohols such as phenol (**1d**) and 4-chlorophenol (**1e**), gave very good yields of ester products **3a-j** for the cross-coupling reactions with *N*-aroylbenzimidazoles **2a** and **2b** (Table 1; entries 1 to 10). In the dry media reaction between the corresponding alcohols **1a-e** and *N*-aroylbenzimidazoles **2c-d**, the electron-donating substituents on the aromatic ring of **2c-d** slightly decreased the yields of the ester products **3k-t** and slightly increased the reaction times (Table-1; entries 11 to 20).

Therefore, considering all the experimental results, all of ester products **3a-t** can be obtained in high yields within a few hours by grinding a mixture of corresponding *N*-aroylbenzimidazoles (**2**) and alcohols (**1**) at room temperature under solvent-free conditions. In addition to very satisfactory yields of ester products (**3**) (84-96%), **4** (80-93%) was obtained as a by-product (Table 1; entries 1 to 20) and can be reused as the substrate for the preparation of *N*-aroylbenzimidazole derivatives **2a-d**

In summary, we have established a simple and efficient experimental method for the synthesis of esters using benzimidazole chemistry. *N*-benzoyl-1H-benzimidazole (**2a**), *N*-(4-chlorobenzoyl)-1H-benzimidazole (**2b**), *N*-(4-methylbenzoyl)-1H-benzimidazole (**2c**), and *N*-(4-methoxybenzoyl)-1H-benzimidazole (**2d**) were synthesized and used for the high-yielding synthesis of esters **3a-t** under solvent-free conditions, where the by-product **4** can be reused in preparing **2a-d**.

Table 1. Synthesis of esters (**3a-t**) from the reaction between *N*-aroylbenzimidazoles (**2a-d**) and different alcohols by grinding



1 **2** **3** **4**

Entry	R	Ar	Time (h)	Yield of **3** (%)	Yield of **4** (%)
1	CH_3 (**1a**)	C_6H_5 (**2a**)	1.5	96 (**3a**)	93
2	C_2H_5 (**1b**)	C_6H_5 (**2a**)	1.5	95 (**3b**)	92
3	$CH_3CH_2(CH_3)CH$ (**1c**)	C_6H_5 (**2a**)	2.0	92 (**3c**)	89
4	C_6H_5 (**1d**)	C_6H_5 (**2a**)	2.0	90 (**3d**)	87
5	4-ClC_6H_4 (**1e**)	C_6H_5 (**2a**)	1.5	91 (**3e**)	89
6	CH_3 (**1a**)	4-ClC_6H_4 (**2b**)	1.5	94 (**3f**)	91
7	C_2H_5 (**1b**)	4-ClC_6H_4 (**2b**)	1.5	93 (**3g**)	90
8	$CH_3CH_2(CH_3)CH$ (**1c**)	4-ClC_6H_4 (**2b**)	2.0	93 (**3h**)	89
9	C_6H_5 (**1d**)	4-ClC_6H_4 (**2b**)	2.0	91 (**3i**)	88
10	4-ClC_6H_4 (**1e**)	4-ClC_6H_4 (**2b**)	1.5	96 (**3j**)	92
11	CH_3 (**1a**)	4-MeC_6H_4 (**2c**)	2.0	89 (**3k**)	87
12	C_2H_5 (**1b**)	4-MeC_6H_4 (**2c**)	2.0	89 (**3l**)	86
13	$CH_3CH_2(CH_3)CH$ (**1c**)	4-MeC_6H_4 (**2c**)	2.5	87(**3m**)	84
14	C_6H_5 (**1d**)	4-MeC_6H_4 (**2c**)	2.5	85 (**3n**)	84
15	4-ClC_6H_4 (**1e**)	4-MeC_6H_4 (**2c**)	2.0	88 (**3o**)	85
16	CH_3 (**1a**)	4-$MeOC_6H_4$ (**2d**)	2.5	86 (**3p**)	83
17	C_2H_5 (**1b**)	4-$MeOC_6H_4$ (**2d**)	2.5	85 (**3q**)	82
18	$CH_3CH_2(CH_3)CH$ (**1c**)	4-$MeOC_6H_4$ (**2d**)	3.0	84 (**3r**)	80
19	C_6H_5 (**1d**)	4-$MeOC_6H_4$ (**2d**)	3.0	92 (**3s**)	89
20	4-ClC_6H_4 (**1e**)	4-$MeOC_6H_4$ (**2d**)	2.5	92 (**3t**)	90

Moreover, it can be seen that the *N*-aroylbenzimidazole derivatives **2a-d**, providing esters in excellent yields (84-96%) are not inferior in efficiency as acylating reagents in esterification reactions in comparison with *N*-aroylbenzotriazole derivatives (70-93% yield), referenced in our previous work (Phungpis, & Hahnvajanawong, 2021b). As such, both benzimidazoles and benzotriazoles can be used as effective reagents for the preparation of very efficient acylating reagents (*N*-aroylbenzimidazoles and *N*-aroylbenzotriazoles) for esterification reactions. However, an *N*-aroylbenzimidazole in this work showed greater efficiency in the case of the reaction of **2a** with aliphatic alcohols (92-96% yield) as compared with *N*-benzoylbenzotriazole (70-78% yield). This is likely due to the steric effect of the alkyl groups of aliphatic alcohols.

We proposed a mechanism (Figure 4) to understand the acylation of alcohols **1** by treatment with activated *N*-aroylbenzimidazoles derivatives **2**. Nucleophilic addition of **1** to **2** produces the adduct, Intermediate I, which, through a 1,4-proton transfer, leads to Intermediate II. Elimination of the benzimidazole ring generates the ester products **3a-t** and by-product **4**; the latter can be consistently recovered and reused as the substrate for the preparation of **2**.

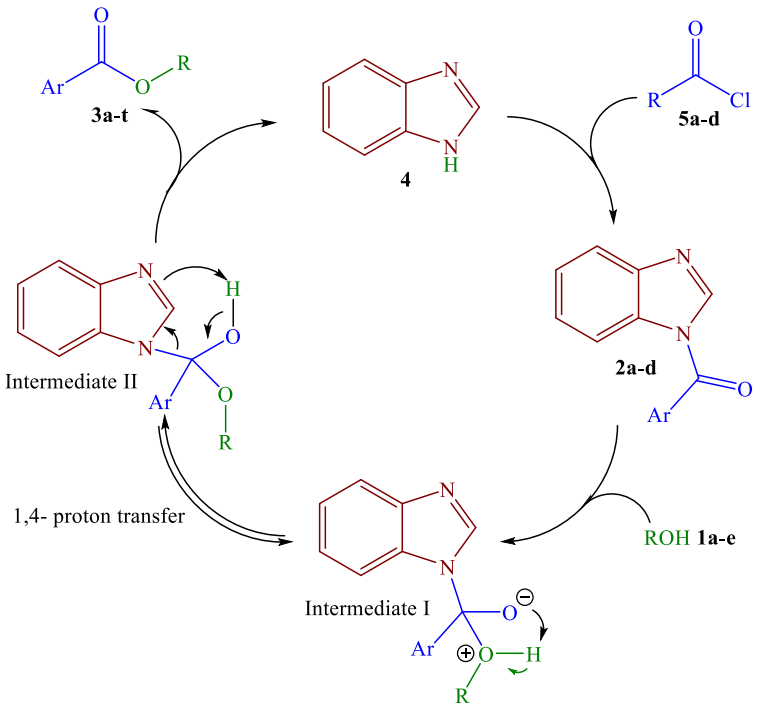


Figure 4. Proposed mechanism of the formation of ester products **3a-t** of the acylation reaction between *N*-aroylbenzimidazoles **2a-d** and alcohols **1a-e**

5. Conclusion

A mild and selective method for esterification using *N*-aroylbenzimidazole derivatives **2a-d** was developed, grinding the derivatives with alcohols (**1**) under solvent-free conditions. All reactions gave high yields of the corresponding esters **3** (84-96%) and benzimidazole **4** (80-93%) within 1.5 to 3.0 hours. Compound **4** can be consistently recovered and reused as the substrate for the preparation of the *N*-aroylbenzimidazoles derivatives **2a-d**. Electron-donating substituents on the aromatic ring of *N*-aroylbenzimidazoles **2c** and **2d** (*i.e.*, methyl and methoxy groups), caused a slight reduction in the yields and a slight increase in the reaction times.

7. Acknowledgements

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8. References

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