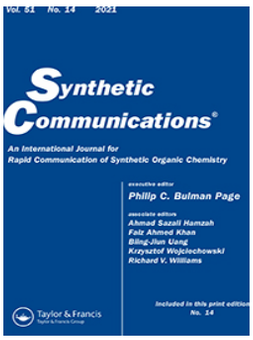

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Synthetic Communications

An International Journal for Rapid Communication of Synthetic Organic Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lsyc20

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To cite this article: Huu-Phuoc Le, Cong-Thang Duong, Xuan-Triet Nguyen & Thi Xuan Thi Luu (2021) Microwave accelerated the solvent-free synthesis of 4-aryl-3,4-dihydrocoumarin via the tandem reaction of cinnamic acids with phenols catalyzed by Amberlyst 15 resin, Synthetic Communications, 51:14, 2187-2203, DOI: 10.1080/00397911.2021.1925918

To link to this article: https://doi.org/10.1080/00397911.2021.1925918

Published online: 25 Jun 2021.

SYNTHETIC COMMUNICATIONS®
2021, VOL. 51, NO. 14, 2187–2203
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Microwave accelerated the solvent-free synthesis of 4-aryl-3,4-dihydrocoumarin via the tandem reaction of cinnamic acids with phenols catalyzed by Amberlyst 15 resin

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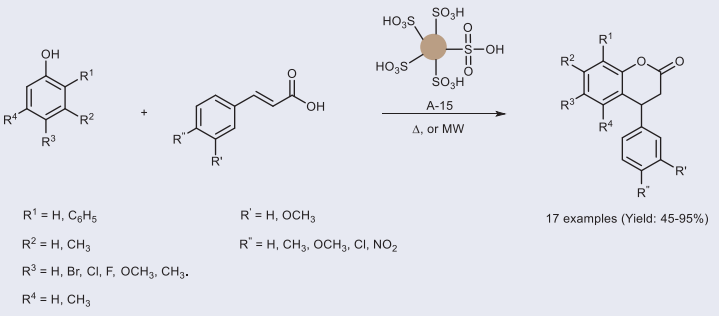
ABSTRACT

Amberlyst 15 resin supported the tandem reaction of cinnamic acids with phenols under solvent-free reaction condition has been introduced to afford 4-aryl-3,4-dihydrocoumarin (neoflavanone) derivatives. The efficiency of solid acidic sulfonic resin (A-15) has been illustrated in two reaction activation methods such as microwave irradiation and conventional heating. The important roles of Amberlyst 15 have been emphasized strongly through the high yields of 4-aryl-3,4-dihydrocoumarin in the shorter time under the assistance of microwave irradiation than of conventional heating, and its high recovery and reusability for six catalyst runs. The original catalyst as well as the recycled catalyst were characterized by XRD and FE-SEM to study the correlation of the surface of reused catalyst and its recyclability.

GRAPHICAL ABSTRACT



ARTICLE HISTORY
Received 20 January 2021

KEYWORDS
Amberlyst 15; 4-aryl-3,4-dihydrocoumarin; cinnamic acid; microwave irradiation; tandem reaction

Introduction

Coumarins (A) are one of the most well-known natural compounds presenting in plenty of plants.[1–6] Their biological activities have been stated in anti-inflammatory,[7] anti-oxidant,[7,8] anticoagulant,[9] anticancer,[9] and more. Consequently, a wide range of organic compounds based on coumarin structure has been efficiently synthesized,

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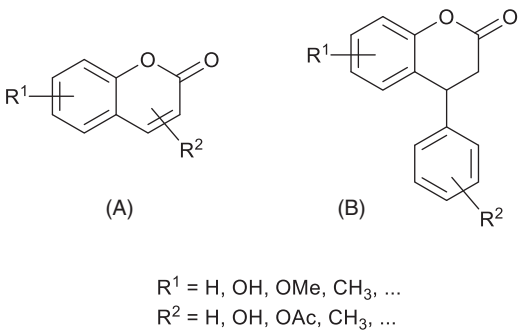
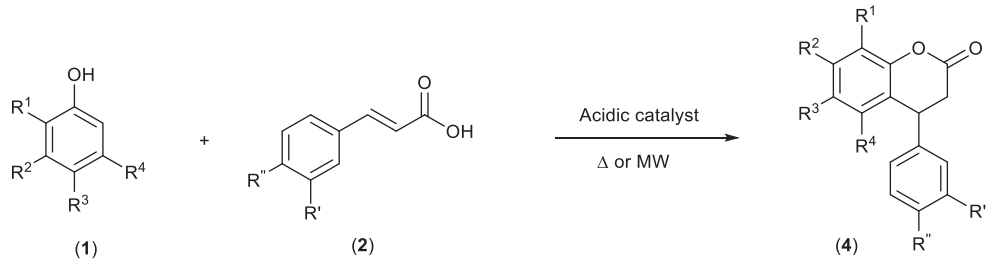


Figure 1. The structure of courmarin (A) and 4-aryl-3,4-dihydrocourmarin (B, called neoflavanone).

especially 4-aryl-3,4-dihydrocoumarin as known as neoflavanone (B) (Figure 1). This system embraced a distinct spot where the neoflavanone has played an important role as an agent for bactericidal, molluscicidal, insecticidal, anti-inflammatory, anti-fungal,[10] immunomodulatory, antioxidant,[11] antiherpetic agent affecting on aldose reductase and protein kinases.[12,13] Especially, 6-methyl-4-phenyl-3,4-dihydrocoumarin was a common reagent to synthesis tolterodine tartrate, a compound to treat overactive urinary bladder syndrome.[14]

Although the uncommon occurrence of 4-aryl-3,4-dihydrocoumarin in nature has been accounted for, there are a great number of neoflavanone derivatives found in *Aloe vera*,[11] fern *Pityrogramma Calomelanos*,[15,16] fern *Pityrogramma Tartarea*,[17] and *Prunus mahaleb*.[18] Due to rarely natural existence, several synthetic works of 4-aryl-3,4-dihydrocoumarin framework have been developed with various categories of reactions, for instance the chiral hydrogenation of 4-arylcoumarins,[19] the direct oxidative cyclization of 3-arylpropionic acids using phenyliodine(III) bis(trifluoroacetate) or oxone as an oxidant,[20] the three-component reaction of 2-hydroxybenzaldehydes, Meldrum's acid and isocyanides,[21] the annulation reactions of phenols with 5-alkylidene Meldrum's acids catalyzed by $Yb(OTf)_3$,[22] aluminum chloride mediated the reaction of acrylonitrile with phenol or the *para*-substituted phenols,[23] aluminum chloride catalyzed the coupling of α-hydroxyketene-*S*,*S*-acetals with phenols or naphthol,[24] the domino conjugate addition-cyclization between arylboroxines and *ortho*-hydroxycinnamate catalyzed by $[Rh(OH)(cod)]_2$,[25] alkenyl carbene chromium(0) complexes reacting with ketene acetals,[26] Friedel-Crafts alkylation-cycloaddition between *tert*-butyl 3-hydroxyl-3-(2-hydroxyphenyl)propanoate and arenes catalyzed by $HClO_4$,[27] the inverse-electron-demand hetero-Diels–Alder reaction with *ortho*-quinone methides and oxazolones catalyzed by Sc(III)-complex[28] or organocatalyst,[29] the cycloaddition *ortho*-quinone methides and 3-nitro-3,4-dihydrocoumarin with organocatalyst,[30] the [4 + 2] annulation of *ortho*-hydroxy benzhydryl alcohols with oxazolones under phosphoric acid catalyst,[31] carbene and acid combination accelerated the cycloaddition of α-chloro aldehyde and *ortho*-hydroxy benzhydryl amine,[32] the α-addition/transesterification reaction with butenolides and 2-(1-tosylalkyl)phenols under alkaline condition catalyzed by organocatalyst[33], the 1,6-addition/transesterification of α-isocyanoacetates and *para*-quinone methides catalyzed by organocatalyst[34] and the tandem reaction of cinnamic acid/cinnamate and phenols regarded as the most popular synthetic pathway of 4-aryl-3,4-dihydrocoumarins. In this route, numerous catalysts such as $FeCl_3$,[35]



R^1 = H, C_6H_5

R^2 = H, CH_3

R^3 = H, Br, Cl, F, OCH_3, CH_3.

R^4 = H, CH_3

R' = H, OCH_3

R'' = H, CH_3, OCH_3, Cl, NO_2

Scheme 1. Solvent-free synthesis of 4-aryl-3,4-dihydrocourmarin via the tandem reaction of cinnamic acids with phenols.

trifluoroacetic acid (TFA),[36,37] *p*-toluenesulfonic acid (*p*-TSA),[38,39] I_2,[40,41] Mont K10,[42,43] silica-supported Wells-Dawson heteropoly acid ($H_6P_2W_{18}O_{62}.24H_2O$),[44] Preyssler heteropolyacid ($H_{14}P_5NaW_{30}O_{110}$),[45] $BF_3{\cdot}Et_2O$,[46] H-Y zeolite,[47] and ionic liquid [H-MNP][HSO_4] have been investigated.[48]

With the large and useful applications of 4-aryl-3,4-dihydroxycourmarin group and our ambitiousness for reaction improvement based on the principles of green chemistry, we found the interest to synthesize 4-aryl-3,4-dihydroxycoumarin derivatives via the solvent-free reaction of cinnamic acids with phenols catalyzed by Amberlyst-15 under the microwave irradiation with high demand for the efficient and eco-friendly method, preferably recyclable and reusable catalyst (Scheme 1). Amberlyst-15 is a macro reticular polystyrene based ion exchange resin with strongly acidic sulfonic group. It has been used as a green and solid acidic catalyst due to safe to use, easy to handle, easy storage, quick removal of catalyst at the reaction work up with high recyclability and reusability in several organic reactions, for instance, the esterification of simple alcohols and carboxylic acid, the transesterification, the condensation, halogenation, Friedel–Crafts reaction, Michael addition reaction, aza-Michael addition reaction, opening epoxide ring reaction, multicomponent reaction, etc.[49–51]

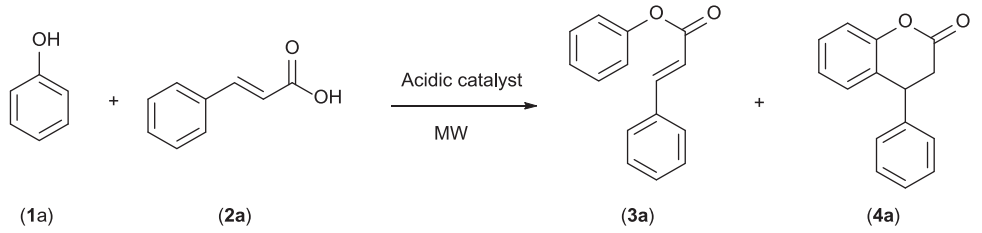
Result and discussion

To test our strategy, several categories of acidic catalysts, e.g. traditional Lewis acid (zinc chloride), Brønsted acid (*p*-toluenesulfonic acid, *p*-TSA), acidic solid support (montmorillonite K-10), acidic ionic liquid 1-methyl-3-(4-sulfobutyl)imidazolium hydrogen sulfate [$(HSO_3)^4C_4C_1Im]HSO_4$) and acidic polymer (Amberlyst 15 resin, A-15) were selected incidentally for the reaction of cinnamic acid with phenol at the beginning of this work as in Table 1. Among the used catalysts, 1-methyl-3-(4-sulfobutyl)imidazolium hydrogen sulfate was regarded as less efficient than zinc chloride, Mont K-10 and *p*-TSA; while A-15 resin was stood out as the most efficient catalyst owing to better yield of desired product obtained 65% (Entry 5, Table 1) under microwave irradiation at 120 °C for 5 minutes.

With our experiences on the esterification,[52] the factor on reaction temperature of the esterification mediated by A-15 firstly selected in the range from 80 to 130 °C was investigated under the microwave irradiation (Figure 2). The results in Figure 2 showed that increasing the reaction temperature led to increasing the product selectivity as well as the reaction yield. Finally, the highest product selectivity and yield of desired product alternately achieved 100 and 69% at 130 °C.

In the further investigation, the molar ratios of cinnamic acid, phenol and the amount of A-15 were paid attention owing to their considerable influences on the optimized reaction condition as in Figures 3 and 4. Consequently, increasing the amount of phenol from 1.5 to 2.0 mmol or the amount of A-15 from 0.1 to 0.2 g led to the increasing of desired product significantly; however, the excess amount of A-15 (used over

Table 1. Nature of catalyst influenced on the formation of 4-aryl-3,4-dihydrocourmarin.[a]



(1a) (2a) (3a) (4a)

Entry	Catalyst (g)	Yield (%)[b] (3a)	(4a)
1	$ZnCl_2$ (0.17)	1	32
2	Mont K10 (0.4)	<1	26
3	*p*-TSA (0.22)	2	48
4	$[(HSO_3)^4C_4C_1Im]HSO_4$ (0.6)	3.5	4
5	Amberlyst 15 (0.2)	7	65

[a]The reaction of cinnamic acid (1.5 mmol) with phenol (1.5 mmol) was performed under microwave irradiation at 120°C for 5 min.
[b]Yield was calculated based on GC/MS analyses.

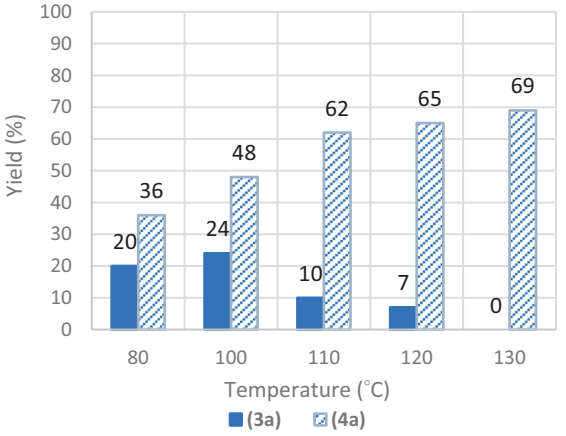


Figure 2. Influence of temperature on the tandem reaction of cinnamic acid (1.5 mmol) with phenol (1.5 mmol) catalyzed by A-15 (0.2 g) under microwave irradiation for 5 minutes.

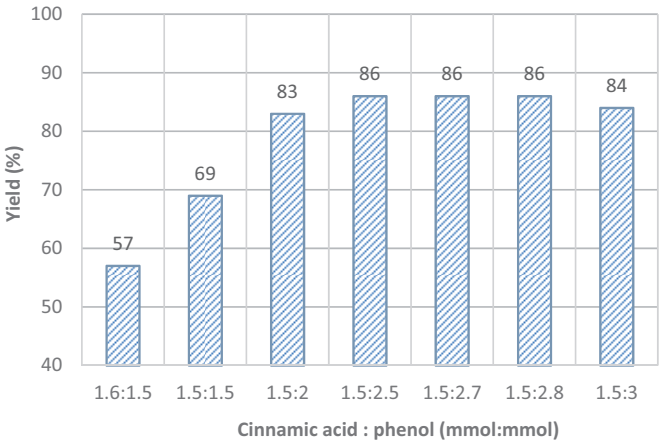


Figure 3. The influence of molar ratio between cinnamic acid and phenol on the yield of 4-aryl-3,4-dihydrocourmarin formed from the tandem reaction catalyzed by A-15 (0.2 g) under microwave irradiationat 130°C for 5 minutes.

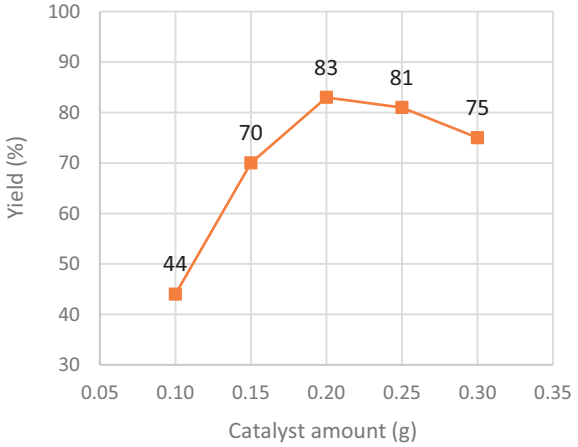
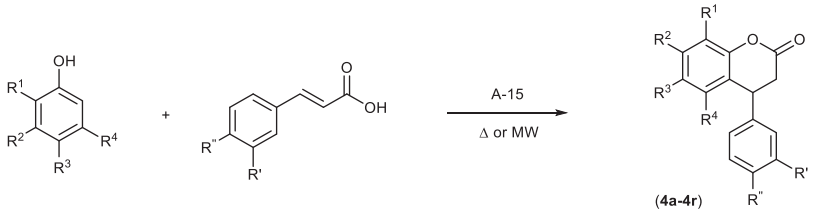


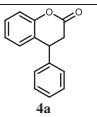
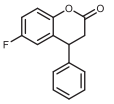
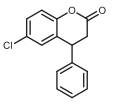
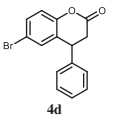
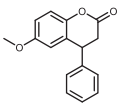
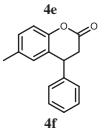
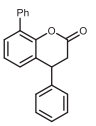
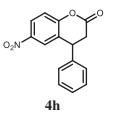
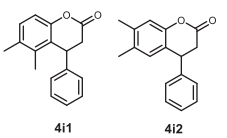
Figure 4. Influence of catalytic amount on the tandem reaction of cinnamic acid (1.5 mmol) with phenol (2.0 mmol) catalyzed by A-15 under microwave irradiation at 130°C for 7 minutes.

0.2 g) could cause the obstacles for reactant interactions leading to the decreasing of product yield. Therefore, the optimized amount of reagents for the excellent formation of 4-aryl-3,4-dihydrocourmarin were achieved at the amount of phenol (2.0 mmol), cinnamic acid (1.5 mmol) and A-15 (0.2 g). In order to increase the reaction conversion as well as the yield of reaction, the reaction time was also tested for each minute from 5 minutes up to longer time at 130 °C under microwave irradiation. Finally, the maximum yield of 4-aryl-3,4-dihydrocourmarine via the tandem reaction was up to 83% at the optimized reaction time, seven minutes (Entry 1, Table 2).

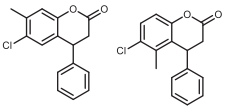
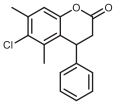
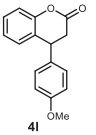
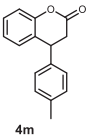
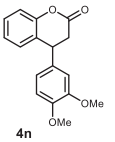
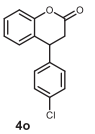
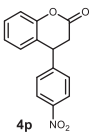
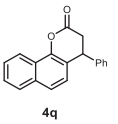
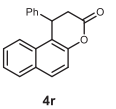
In order to understand the influences of substituents linked aromatic rings of phenols and cinnamic acids, altogether twelve phenols, six cinnamic acids and two naphthols were subjected for further series of experiments by fixing the optimized conditions consisting of reaction temperature, the molar ratio of reagents and the amount of catalyst and only

Table 2. The optimized yields of 4-aryl-3,4-dihydrocourmarin derivatives from the hydroarylation catalyzed by Amberlyst 15 under two activation methods.[a]



Entry	R^1	R^2	R^3	R^4	$R^{'}$	$R^{''}$	Product	Isolated yield (%)(Time)[b] Method A[c]	Method B[d]
1	H	H	H	H	H	H	 **4a**	83 (7)	81 (1.5)
2	H	H	F	H	H	H	 **4b**	92 (17)	83 (2.0)
3	H	H	Cl	H	H	H	 **4c**	90 (25)	81 (2.0)
4	H	H	Br	H	H	H	 **4d**	87 (25)	80 (2.5)
5	H	H	OCH_3	H	H	H	 **4e**	88 (18)	82 (3.0)
6	H	H	CH_3	H	H	H	 **4f**	76 (15)	76 (2.0)
7	C_6H_5	H	H	H	H	H	 **4g**	47 (18)	40 (9.0)
8	H	H	NO_2	H	H	H	 **4h**	27[e] (17)	25[e] (8.0)
9	H	CH_3	CH_3	H	H	H	 **4i1** **4i2** (72 : 28)[f]	94 (13)	95 (4.0)

(*continued*)

10	H	CH_3	Cl	H	H	H	 4j1 4j2 (71 : 29)[f]	94 (36)	92 (3.5)
11	H	CH_3	Cl	CH_3	H	H	 4k	93 (12)	91 (4.0)
12	H	H	H	H	H	OCH_3	 4l	93 (7)	90 (3.0)
13	H	H	H	H	H	CH_3	 4m	95 (7)	89 (3.0)
14	H	H	H	H	OCH_3	OCH_3	 4n	89 (11)	78 (5.0)
15	H	H	H	H	H	Cl	 4o	92 (25)	89 (8.0)
16	H	H	H	H	H	NO_2	 4p	0 (20)	0 (8.0)
17					H	H	 4q	85 (18)	80 (8.0)
18					H	H	 4r	95 (19)	92 (9.0)

[a]The reactions were performed with the amount of cinnamic acid derivatives (1.5 mmol), phenols (2.0 mmol) and Amberlyst 15 (0.2 g) at temperature 130 °C. [b]Reaction time in minutes for method A and in hours for method B. [c]Method A: the reaction mixture was assisted by microwave irradiation.[d]Method B: the reaction mixture was assisted by conventional heating. [e]Yields were calculated based on the GC/MS analyses. [f]Ratio of isomers were reported based on the GC/MS analysis results.

varying a period of appreciate time for each substance tended to reach a noteworthy yield under two activation methods: microwave irradiation and conventional heating (Table 2).

The results also illustrated that the scope of phenol derivatives was applied for the tandem reaction in a wide range of substituents from the electron donating groups to

Table 3. Comparison of previous methods for the synthesis of 3,4-dihydrocoumarin from the reaction of cinnamic acids and phenols promoted by several catalysts.

Catalyst (g)	Catalyst cost (USD) For 100 gram[b]	Catalyst cost (USD) For experiment	Method (°C)	Solvent	Time (h)	Reusability (run times)	Yield[g] (%)	Ref.
$FeCl_3$ (0.24)	44.50	0.11	Stirring (rt.)	CH_2Cl_2	6 – 12	None	54–85	[35]
TFA (1 mL)	89.80[c]	0.90	Δ (100)	–	16 – 72	None	54–99	[36]
TFA (1 mL)	89.80[c]	0.90	Stirring (rt.)	–	24	None	20–100	[37]
p-PSA (0.86)	34.30	0.29	Δ (125)	–	3	None	67–99[h]	[38]
p-PSA (0.25)	34.30	0.08	Δ (140)	–	4	None	20–83	[39]
I_2 (0.33)	91.90	0.30	Δ (130)	–	1 – 4	None	60–85	[40]
I_2 (0.33)	91.90	0.30	Δ (130)	–	1 – 4	None	50–85	[41]
Mont K10 (1.0)	30.70	0.31	M.W (160)	PhCl	5[f]	3	19–81	[42]
Mont K10 (2.0)	30.70	0.61	M.W (640[e])	–	10[f]	None	65–69	[43]
SiO_2@ $H_6P_2W_{18}O_{62}$ (0.44)	–	–	M.W (110)	–	5–15[f]	None	56–82	[44]a
$H_{14}P_5NaW_{30}O_{110}$ (0.037)	–	–	Δ (130)	–	2	4	61–77	[45]a
$BF_3{\cdot}Et_2O$ (2.5 mL)	38.00[c]	0.95	Stirring (rt.)	–	4 – 12	None	54–75	[46]
H-Y Zeolite (1.0)	–	–	Δ (110)	CH_3Ph	4	None	68–82	[47]a
[H-NMP][HSO_4] (0.59)	–	–	Δ (120)	–	2 – 5	None	82–95	[48]a
Amberlyst 15 (0.2)	106.00[d]	0.85	M.W (130)	–	7–25[f]	6	47–95	Our work

[a]Synthesized catalysts which could not be estimated their economic potential.
[b]The price was consulted in www.sigmaaldrich.com.
[c]Price 100 mL; [d]Price 250 gram; [e]Watt; [f]Minutes; [g]Isolated yield; [h]GC yield.

the electron withdrawing groups. Owing to the acidity of phenol, the nucleophilic addition of phenol into carbon atom of C = O bond of carboxylic acid often occurs difficultly. Therefore, the electron donating groups on phenolic ring via inductive effect or resonance effect have certainly caused the reaction transformation toward the advantages; for instances, the halogen substitutents (e.g. fluoro, chloro and bromo) as well as methoxy group with electron releasing resonance increased the yields of products, especially under microwave irradiation (Entry 2–5, Table 2). Similarly, several electron-donating substituents in phenolic ring accounted for a bit higher yield than the yield obtained from one electron-donating substituent (Entry 6,9–11, Table 2). Exceptionally, although the presence of phenyl group located in the *ortho* position of phenolic ring caused electron-donating inductive and resonance, a steric hindrance has influenced predominately on the decrease of the desired product unexpectedly (Entry 7, Table 2). Moreover, strong electron withdrawing group in phenolic ring as nitro substituent increases the acidity and decreases the nucleophilicity of phenol group remarkably, consequently the formation of 6-nitro-4-phenyl-3,4-dihydrocoumarin slowly occurred with low product selectivity and low yield detected by thin layer chromatography and gas chromatography-mass spectrometry (Entry 8, Table 2). Furthermore, the effects of substituents in aromatic ring of cinnamic acids have been studied. Subsequently, nitro group in aromatic ring of cinnamic acid also affected on reaction toward a disadvantage (Entry 16, Table 2), while the electron donating groups as methyl or methoxy promoted the better conversion (Entry 12–14, Table 2).

Additionally, in Table 2, the first series of reactions were performed under microwave irradiation at 130 °C (Method A) and the next series were carried out under conventional heating (Method B). Consequently, the yields of the products were not achieved much different in both above methods, however the reaction time was reduced remarkably. Microwave irradiation is proved that it is useful for the fast and homogeneous

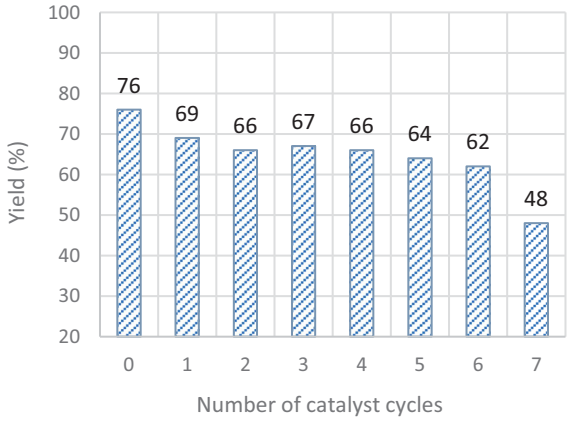


Figure 5. Reusability of Amberlyst (0.2 g) used for the tandem reaction of cinnamic acid (1.5 mmol) with *p*-cresol (2.0 mmol) under microwave irradiation at 130°C for 15 minutes.

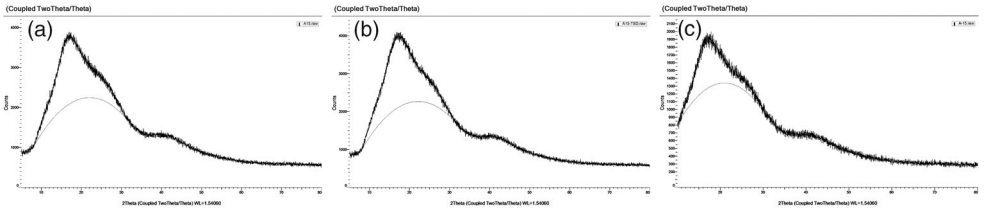


Figure 6. XRD patterns of (a) original Amberlyst 15 (**0A-15**), (b) first-cycled Amberlyst 15 (**1A-15**) and (c) sixth-cycled Amberlyst 15 (**6A-15**)

heating in any kind of reactions which need heating activation as the esterification.[53–55]

With advantages of Amberlyst-15 on enhanced reactivity and mildness, its recovery and reusability were paid attention to be examined following the straightforward work-up procedure and the optimized reaction conditions. The Amberlyst-15 particles collected after filtration from the previous reaction were washed with methanol (3 × 5 mL), and then impregnated with 0.1% aqueous solution of hydrochloric acid for two hours. Subsequently, Amberlyst-15 particles after filtration to remove the solution of hydrochloric acid were washed with methanol (3 × 5 mL) until pH = 5–6, dried at 100 °C for 3 hours, stored in desiccator overnight and obtained in 85% of recycled yield. The recycled Amberlyst-15 particles were used for the solvent-free tandem reaction between *p*-cresol and cinnamic acid under microwave irradiation at 130 °C for 15 minutes as that of the optimized experiment presented in Entry 6, Table 2. The catalytic efficiency of Amberlyst-15 did not decrease drastically even after six cycles of catalyst recovery and reuse (Figure 5).

The structures of recovered catalysts at the first and sixth recycle times were analyzed by X-Ray Diffraction (XRD) and Field Emission Scanning Electron Microscope (FE-SEM) in comparison with the structure of the fresh A-15 in terms of surface and activity. The positions and relative intensities in XRD images of the fresh catalyst (0 A-15),

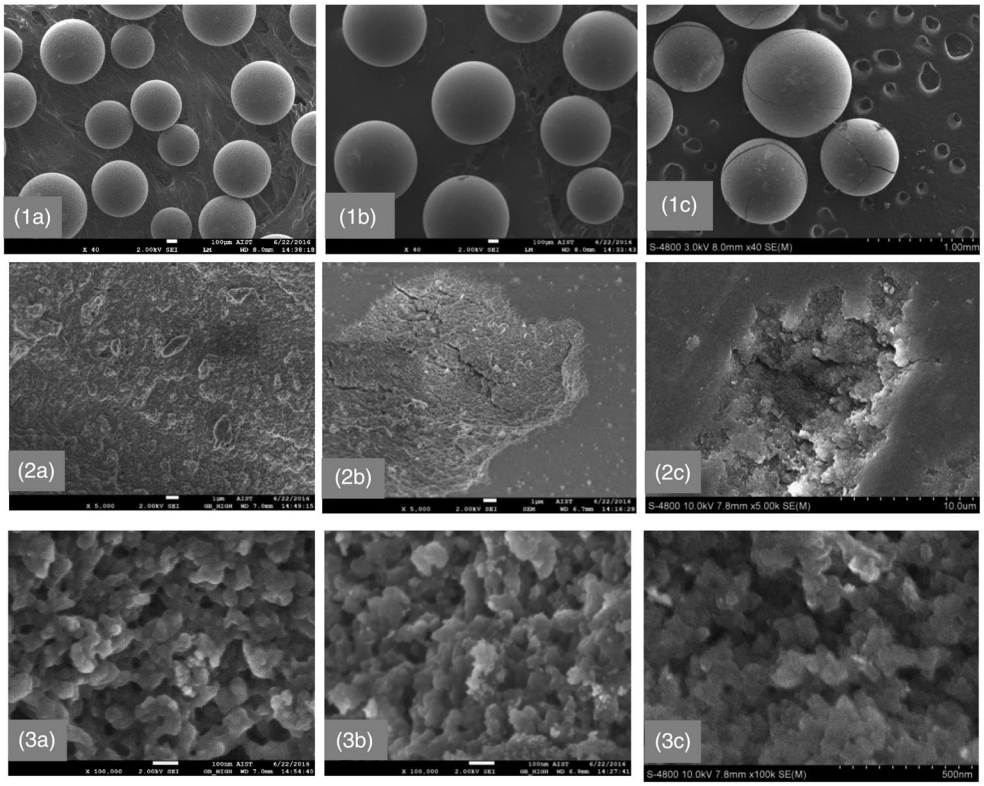
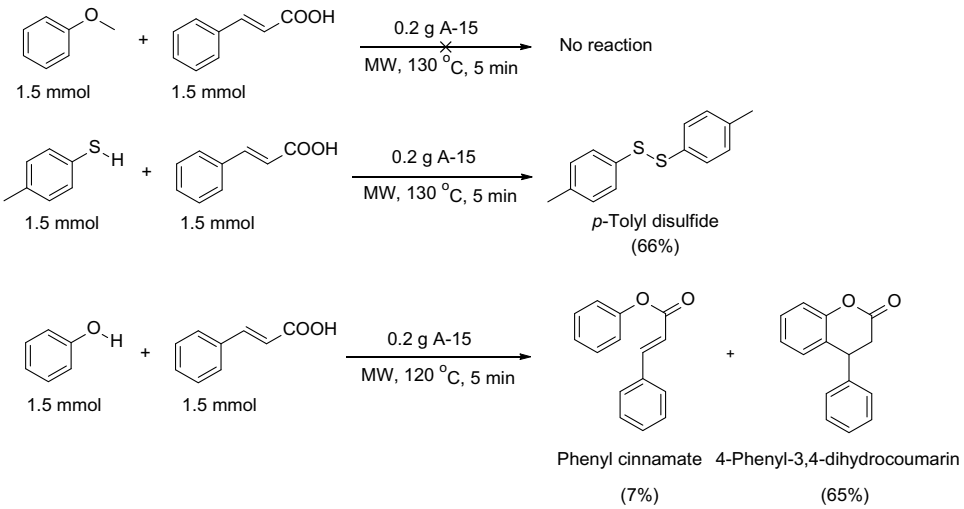
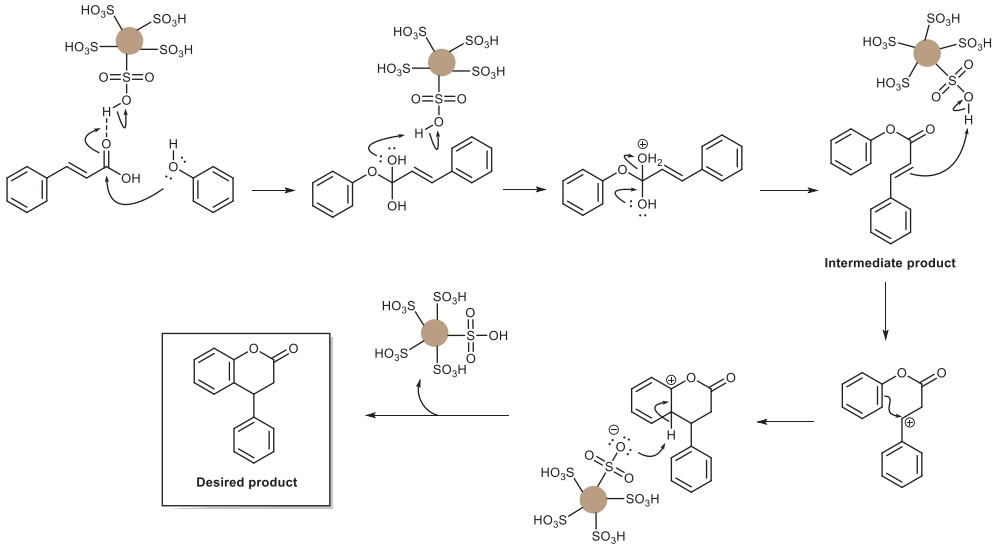


Figure 7. SEM images of catalyst Amberlyst 15 (a) original, (b) 1st cycle, (c) 6th cycle at the magnification of (1) 40 times, (2) 5,000 times, (3) 100,000 times.



Scheme 2. Several controlling experiments for reaction mechanism.



Scheme 3. Plausible mechanism of the reaction between cinnamic acid and phenol.

the first recycled catalyst (1 A-15) and the sixth-recycled catalyst (6 A-15) are all compatible. The XRD patterns of three samples have been similar in a broad and wide bottom of a peak to stand for amorphousness of Amberlyst 15 (Figure 6). As shown in Figure 7, the FE-SEM images at forty-time magnification illustrated that the original Amberlyst 15 were spherical shape particles with an average diameter in the range of 400–650 µm (1a, Figure 7); however, the resin particles with spherical shape after the first recycling became bigger in size varying within the range of 550–800 µm (1 b, Figure 7) and the spherical-shape particles after the sixth-time recycling were larger in the range of 600–900 µm with long cracks on the surface (1c, Figure 7). At the magnification of 5,000 times, three images showed the differences that the small and shallow cracks appeared on the surface of resin particles after the first recycle (2 b, Figure 7); while several rougher and deeper cracks were recognized on the surface of resin after the sixth recycle (2c, Figure 7). Undoubtedly, Amberlyst 15 particles were illustrated to be porous structure with multiple units linked homogeneously, however the porous structure of resin particles were found un-homogeneous gradually after the sixth recycle (3c, Figure 7). The cracks on the surface obviously demonstrated that the catalyst structure had been destructed after several times recycling, consequently the cohesion inside spherical-shaped particles was gradually collapsed to make the size of catalyst particle bigger.

Based on previous investigations on the formation of 4-aryl-3,4-dihydrocoumarin from the reaction of cinnamic acids and phenols, the reaction mechanism was proposed in two pathways, either via the esterification followed by the hydroarylation or via the hydroarylation followed by the esterification.[36,37,40,48] Moreover, the products from the hydroarylation of cinnamic acids and anisole derivatives mediated by *p*-toluenesulfonic acid were obtained in high yields at 125 °C.[38] In order to understand the tandem reaction mechanism of cinnamic acids and phenols mediated by A-15, several reactions were investigated by performing the reaction of cinnamic acid and anisole or thiophenol catalyzed by A-15 as

described in Scheme 2. Consequently, either the hydroarylation or the esterification catalyzed by A-15 has not been occurred at 130 °C under the assistance of microwave irradiation for 5 minutes. While the experiments described in Figure 2 showed that the intermediate product, phenyl cinnamate was formed and obtained with low yield (7%).

The results of several controlling experiments illustrated that a possible mechanism for the tandem reaction of cinnamic acids and phenols catalyzed by A-15 under the assistance of microwave irradiation was proposed firstly via the esterification to produce phenyl cinnamate, and subsequently the hydroarylation to afford 4-phenyl-3,4-dihydrocoumarin as described in Scheme 3.

The introduced protocol for the synthesis of 4-aryl-3,4-dihydrocoumarin offers many advantages in terms of high product yield, green, efficient and economic catalyst, solvent-free and shorter reaction time under microwave irradiation, compared with the previous literature reported the syntheses with different reaction conditions as well as catalysts.

Conclusion

Comprehensive experiments on the solvent-free tandem reaction of cinnamic acids and phenols utilizing the solid acidic catalyst Amberlyst 15 resin under the assistance of microwave irradiation or conventional heating have made us to introduce and get down to some considerations. Microwave irradiation has efficiently activated the formation of 4-aryl-3,4-dihydrocoumarin derivatives with less time-consumption (in minutes) than conventional heating (in hours). Furthermore, Amberlyst 15 resin is eco-friendly, efficient and economic acidic catalyst for this solvent-free tandem reaction irradiated by means of microwave oven. The catalyst has been proved to successfully promote in a wide range of phenols and cinnamic acids with moderate to high yields of desired products. Interestingly, the structure and efficiency of the reused catalyst have not impacted the product yield even after several recycles.

Experimental

Chemicals and instrumentation

All commercially available chemicals used were from Aldrich Sigma/Acros and analyzed for authenticity and purity by GC/MS (gas chromatography/mass spectrometry) before being used. The melting point was determined by Büchi melting point. The microwave irradiation was performed by means of microwave oven CEM – Discover, the irradiation program was applied to get the most efficient reaction conditions. NMR spectra were recorded on a Brüker Advance DPX 500 MHz spectrometer at 500 MHz (^{1}H) and 125 MHz (^{13}C); deuterated solvent was purchased from Cambridge Isotope Laboratories Inc. ($CDCl_3$ and CD_3COCD_3). GC/MS Hewlett Packard 6890GC Series II with TX – DP5 column was employed to monitor reaction progress. HRMS-ESI (electrospray ionization) analyses were performed on a microTOF – QII (Brüker) with UV/Vis and MS detector, the heated capillary of ion trap mass spectrometer was set to 350 °C, reverse column ACE 3C18 (5 µm × 4.6 × 150 mm). The structure of Amberlyst 15 particles before and after usage were characterized by D2 Phaser – Brüker X-ray diffraction (XRD) (Cu K_α radiation,

scanning speed 0.02° min^{-1} from 5° to 70°) and were investigated about their dimension by means of S4800 HITACHI Scanning electron microscopy (SEM).

General procedure

The tandem reaction of cinnamic acid with phenol catalyzed by amberlyst-15 under microwave irradiation (method A)

Suitable amounts of cinnamic acid (1.5 mmol, 0.222 g), phenol (2.0 mmol, 0.188 g) and Amberlyst 15 (0.2 g) were added successively into the test tube ($\Phi = 10$ mm, h = 100 mm) placed into CEM oven. The irradiation program set up at 130 °C for 7 minutes was applied to the reaction mixture. After cooling, the product mixture was extracted with diethyl ether (4 × 15 mL) and filtrated by porous filter funnel to separate and collect the acidic catalyst A-15 for recycling. Subsequently, the filtrate was stirred magnetically with 10 mL of aqueous sodium hydroxide 5% (to remove all excess or unreacted cinnamic acid and phenol) and then washed with water until neutralization. Organic layer was dried by anhydrous sodium sulfate and removed solvent by rotary evaporation. The remaining crude product was analyzed by GC/MS to check the composition of crude product. The desired product was purified by silica gel column chromatography, and then was identified their structure by HRMS, ^{1}H and ^{13}C NMR spectroscopy.

The tandem reaction of cinnamic acid with phenol catalyzed by amberlyst-15 under conventional heating (method B)

A test tube ($\Phi = 10$ mm, h = 200 mm) containing a pertinent quantity of cinnamic acid (1.5 mmol, 0.222 g), phenol (2.0 mmol, 0.188 g) and Amberlyst 15 (0.2 g) was placed in an oil bath heated to the suitable temperature (130 °C) for 1.5 hours. After cooling, the reaction mixture was worked up as described in Method A.

Full spectral data of all compounds can be found in Supporting Information via the "Supplementary Content" section of this article's webpage.

Acknowledgement

We acknowledge Van Cong Le, Xuan-Huyen Thi Ngo, Thanh Van Tran, Hoai-Linh Thi Tran (Ho Chi Minh University of Science) and Prof. Fritz Duus (Roskilde University) for technical assistance and chemical support.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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