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ORIGINAL ARTICLE

Phosphoric acid supported on alumina: A useful and effective heterogeneous catalyst in the preparation of α-amidoalkyl-β-naphthols, α-carbamato-alkyl-β–naphthols, and 2-arylbenzothiazoles

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KEYWORDS

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α-Amidoalkyl-β-naphthols;
α-Carbamato-alkyl-β–naphthols;
2-Arylbenzothiazoles;
Heterogeneous catalyst

Abstract Phosphoric acid supported on alumina (H_3PO_4/Al_2O_3) is found to be an efficient catalyst for the three-component condensation reaction of β-naphthol, aromatic aldehydes and amides or carbamates to afford the corresponding α-amidoalkyl-β-naphthols, α-carbamato-alkyl-β-naphthols under solvent-free conditions. In addition, the preparation of 2-arylbenzothiazoles from the reaction of aromatic aldehydes and 2-aminothiophenol was described under mild and solvent-free conditions. The remarkable features of these catalytic procedures are high conversions, shorter reaction times, cleaner reaction, simple experimental, and work-up procedures. Phosphoric acid supported on alumina as catalyst can be reused several times without significant loss of its catalytic activity.

1. Introduction

The development of cleaner technologies is a major subject in green chemistry (Kumar et al., 2011; Paul et al., 2009). Among the several aspects of green chemistry, the use of heterogeneous catalysts and replacement of volatile organic solvents with solvent-free reaction medium are of greatest concern (Rothenberg, 2008). Heterogeneous organic reactions and solvent-free reactions have many advantages such as: reduced pollution, low costs, simplicity in process, ease handling of catalyst, cleaner reactions, easier work up, decreasing corrosive problems, and reduced reaction times (Ballini, 2009). The development of efficient and environmentally benign chemical processes or methodologies for widely used heterogeneous recyclable catalyst under solvent-free conditions are one of the major challenges for chemists in organic synthesis (Almahy, 2011). Meanwhile, the use of solvent-free method gains importance from a view point of green chemistry (Kumar et al., 2011).

Phosphoric acid supported Alumina was prepared for the first time by Araujo et al. by the mixing of alumina with phosphoric acid (Araujo et al., 2006). This heterogeneous catalyst

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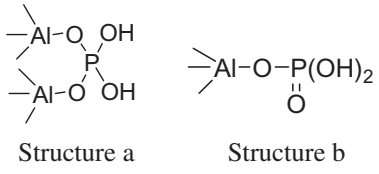
was characterized and catalytic evaluation of oleic acid conversion to biofuels and biolubricant was studied (Araujo et al., 2006). The best catalytic performance was achieved with this catalyst which shows highest surface area alumina impregnated with H_3PO_4, and it allied high total acidity with a large quantity of mesopores (Araujo et al., 2006). According to the ^{31}P-NMR data, two structures for the catalyst were suggested: structure a) different phosphorous and aluminum interactions in bridging structures (Dixon, 1989), and structure b) linear phosphorous and aluminum bonding (Dixon, 1989) (Scheme 1).

The second research on application of H_3PO_4/Al_2O_3 was performed by Zarei et al. who reported thioacetalization and transthioacetalization using catalytic amount of H_3PO_4/Al_2O_3 under microwave irradiation (Zarei et al., 2009). Thus, only a few works were applied on this catalyst.

In continuation of our research on the solid heterogeneous acidic catalysts (Shaterian et al., 2012a,b), we wish to describe a new protocol for the rapid synthesis of α-amidoalkyl-β-naphthols and α-carbamato-alkyl-β–naphthols by employing three-component reactions of β-naphthol with aromatic aldehydes and amide or carbamate with a catalytic amount of H_3PO_4/Al_2O_3 (50% w/w) as a reusable heterogeneous catalyst under thermal solvent-free conditions (Scheme 2). In addition, the application of the mentioned catalyst in the preparation of 2-arylbenzothiazoles from aromatic aldehydes and 2-aminothiophenol at room temperature under solvent-free conditions was described (Scheme 3).

2. Experimental

All reagents were purchased from Merck and Sigma–Aldrich and used without further purification. H_3PO_4/Al_2O_3 (50%w/w) was prepared according to the reported procedure (Zarei et al., 2009). All yields refer to isolated products after purification. Products were characterized by comparing physical data with authentic samples and spectroscopic data (IR and NMR). The NMR spectra were recorded on a Bruker Avance DPX 500 MHz instrument. The spectra were measured in DMSO relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on Silica–gel polygram SILG/UV 254 plates.



Scheme 1 The structure of Phosphoric acid supported on alumina.

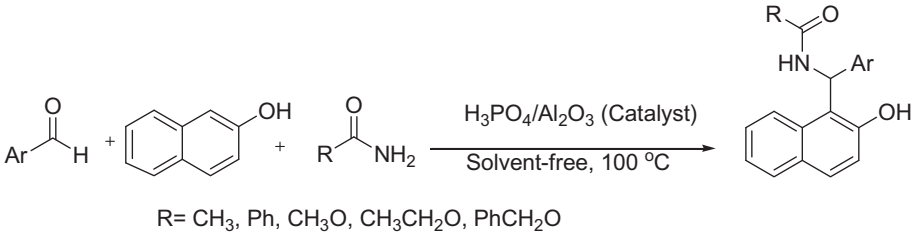
2.1. General procedure for the synthesis of α-amidoalkyl-β-naphthol and α-carbamato-alkyl-β–naphthol derivatives

A stirred mixture of arylaldehydes (10 mmol), β-naphthol (10 mmol), amide or carbamat (12 mmol), and H_3PO_4/Al_2O_3 (50%w/w, 1.2 g) was reacted in an oil bath at 100 °C for the appropriated times (Tables 3 and 4). Completion of the reaction was indicated by TLC. After completion of the reaction, it was cooled to room temperature and the crude solid product was solved in ethylacetate, and filtered for separation of the catalyst. The catalyst was washed four times with ethyl acetate (4 × 5 ml), and then recovered catalyst was dried in an oven at 100 °C for 3 h. The filtered organic solution was concentrated. The solid product was purified by recrystallization procedure in aqueous EtOH (15%).

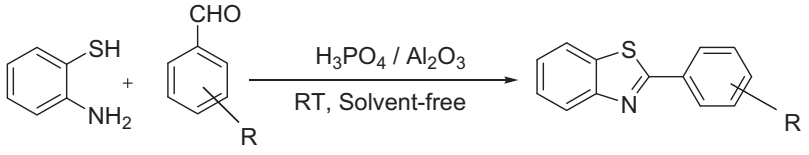
All the products were characterized by the comparison of their spectroscopic and physical data with the authentic samples (Almahy, 2011; Ansari et al., 2010; Jafari and Moghanian, 2012; Shaterian et al., 2012a,b; Dabiri et al., 2007).The spectral data for some selected products are given below:

2.1.1. N-(1-(2-hydroxynaphthalen-1-yl)-3-henylpropyl)acetamide (Table 3, Entry 17)

Mp: 185–186 °C: ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.85 (s, 3H), 2.07–2.12 (m, 1H), 2.33–2.37 (m, 1H), 2.43–2.49 (m, 1H), 2.65–2.69 (m, 1H), 5.77–5.81 (m, 1H), 7.13–7.17 (m,



Scheme 2 Synthesis of α-amidoalkyl-β- naphthols and α-carbamato-alkyl-β–naphthols.



Scheme 3 Synthesis of 2-arylbenzothiazoles.

Table 1 Optimization of temperature in the reaction of β-naphthol, benzaldehyde, acetamide in the presence of H_3PO_4/Al_2O_3 (120 mg) as catalyst under solvent-free conditions at different temperatures.

Entry	Temperature (°C)	Time (min)	Yield (%)[a]
1	60	150	58
2	80	115	62
3	90	62	73
4	100	40	85
5	110	38	86
6	120	37	85

[a] Yields refer to the isolated pure products.

Table 2 Optimization of amount of H_3PO_4/Al_2O_3 as the catalyst in the reaction of β-naphthol, benzaldehyde and acetamide under solvent-free conditions.

Entry	Catalyst (mg)	Time (min)	Yield (%)[a]
1	70	105	55
2	80	92	64
3	90	83	70
4	100	66	74
5	120	40	85
6	130	35	76
7	140	32	73

[a] Yields refer to the isolated pure products.

4H), 7.22–7.26 (m, 3H), 7.37 (t, J = 7.6 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.99 (brd, J = 8.2 Hz, 1H), 8.10 (brs, 1H), 9.87 (s,1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 22.7, 32.5, 35.6, 45.7, 118.6, 119.6, 122.2, 122.3, 122.5, 125.6, 126.0, 128.1 (2C), 128.2 (2C), 128.3, 128.4, 132.2, 141.8, 153.0, 168.5 ppm; IR (KBr, cm^{-1}): 3421, 3230, 2922, 1638, 1516, 1438, 1334, 810, 741.

2.1.2. Methyl(4-cyanophenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 3, Entry 18)

Mp: 233–234 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.57 (s, 3H), 6.89 (d, J = 8.3 Hz, 1H), 7.18 (d, J = 8.8 Hz, 1H), 7.27 (t, J = 7.38 Hz, 1H), 7.38 (t, J = 9.2 Hz, 3H), 7.71 (d, J = 1.4 Hz, 2H), 7.73–7.79 (m, 3H), 7.83 (brs, 1H), 10.17 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 50.3, 51.7, 109.0, 117.9, 118.3, 118.8, 122.6, 122.7, 126.7, 126.9 (2C), 128.3, 128.6, 129.7, 131.9, 132.0 (2C), 148.4, 153.0, 156.6 ppm; IR (KBr, cm^{-1}): 3417, 3171, 2227, 1678, 1629, 1607, 1516, 1439, 1327, 1277, 1234, 1199, 1137, 1066, 1040, 956, 855, 832, 806, 745.

2.1.3. Methyl(3-methoxyphenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 4, Entry 19)

Mp: 180–182 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 3.56 (s, 3H), 3.65 (s, 3H), 6.73–6.77 (m, 2H), 6.80–6.83 (m, 2H), 7.15 (t, J = 8.9 Hz, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.38 (brt, J = 7.1 Hz, 1H), 7.67 (brs, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 7.95 Hz, 1H), 7.90 (brs, 1H), 10.09 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 50.3, 51.6, 54.8, 111.0, 112.4, 118.4, 118.8, 122.4, 122.9, 126.4, 128.3, 128.5, 129.1, 129.2, 129.3, 132.0, 144.0, 152.8, 156.5, 159.1 ppm; IR (KBr, cm^{-1}): 3421, 3353, 1689, 1600, 1516, 1489, 1330, 1274, 1241, 1164, 1049, 1035, 812, 779, 742.

2.1.4. Ethyl(4-nitrophenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 4, Entry 20)

Mp: 222–223 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.15 (t, J = 6.9, 3H), 3.96–4.05 (m, 2H), 6.83 (d, J = 8.5 Hz, 1H), 7.19–7.22 (m, 3H), 7.27 (t, J = 7.3 Hz,1H), 7.32 (d, J = 8.6 Hz, 2H), 7.39 (brt, J = 7.1 Hz, 1H), 7.62 (brs, 1H), 7.75–7.80 (m, 2H),7.88 (brs, 1H),10.14 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.6, 49.7, 60.1, 118.4, 118.5, 122.5, 122.8, 126.6, 127.8, 128.0 (2C), 128.3 (2C), 128.5, 129.4, 130.9, 131.9, 141.5, 152.8, 156.1 ppm; IR (KBr, cm^{-1}): 3429, 3185, 3067, 2978, 1685, 1516, 1349, 1267, 1236, 1146, 1070, 1049, 852, 821, 708.

2.1.5. Ethyl(4-chlorophenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 4, Entry 21)

Mp: 220–221 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.16 (t, J = 6.8 Hz, 3H), 3.98–4.07 (m, 2H), 6.93 (d, J = 8.2 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 7.28 (t, J = 7.3 Hz, 1H), 7.40 (brt, J = 7.3 Hz, 1H), 7.45 (d, J = 8.5 Hz, 2H), 7.76–7.82 (m, 3H), 7.89 (brs, 1H), 8.14 (d, J = 8.7 Hz, 2H), 10.19 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.5, 50.0, 60.3, 118.0, 118.3, 122.6, 122.7, 123.3 (2C), 126.8, 127.1(2C), 128.3, 128.6, 129.8, 131.8, 146.0, 150.7, 153.0, 156.2; IR (KBr, cm^{-1}): 3423, 3187, 1678, 1628, 1578, 1516, 1489, 1477, 1329, 1274, 1231, 1171, 1144, 1088, 1069, 1001, 940, 814, 751.

2.1.6. Ethyl(phenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 4, Entry 22)

Mp: 203–204 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.17 (t, J = 6.9 Hz, 3H), 4.04 (q, J = 7.4, 2H), 6.89 (brd, J = 9.8 Hz, 1H), 7.15–7.19 (m, 1H), 7.24 (d, J = 9.2 Hz, 1H), 7.26 (t, J = 4.6 Hz, 4H), 7.29 (d, J = 7.5 Hz, 1H), 7.41 (brt, J = 7.8 Hz, 1H), 7.56 (brs, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1H), 10.13 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.5, 50.3, 60.0, 118.4, 18.9, 122.4, 122.8, 125.9 (2C), 126.2, 126.5, 128.0(2C), 128.3, 128.5, 129.2, 132.0, 142.4, 152.8, 156.0 ppm; IR (KBr, cm^{-1}):3424, 3169, 3033, 2993, 1672, 1518, 1437, 1331, 1272, 1042, 939, 814, 742, 695.

2.1.7. Ethyl(2,4-dimethoxyphenyl)(2-hydroxynaphthtalen-1-yl)methylcarbamate (Table 4, Entry 23)

Mp: 217–218 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.15 (t, J = 7.0 Hz, 3H), 3.57 (s, 3H), 3.66 (s, 3H), 4.00 (q, J = 7.2 Hz, 2H), 6.73–675 (m, 1H), 6.81 (d, J = 7.7 Hz, 1H), 7.04 (d, J = 9.3 Hz, 1H), 7.18 (d, J = 8.6 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 7.42 (brs, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 8.25 (d, J = 8.7 Hz, 1H), 10.06 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.5, 18.5, 55.2, 55.9, 56.0, 59.8, 111.5, 111.9, 115.3, 118.6, 118.8, 122.3, 123.2, 125.9, 128.1, 128.2, 128.8, 131.4, 132.2, 150.5, 152.8, 152.9, 155.4 ppm; IR (KBr, cm^{-1}):3425, 3226, 2997, 1678, 1515, 1498, 1317, 1275, 1210, 1148, 1026, 794, 749.

Table 3 Three-component synthesis of α-amidoalkyl-β-naphthol drivatives through direct condensation of β-naphthol, aldehyde and amides (molar ratio: 1/1/1.2) catalyzed by H_3PO_4/Al_2O_3 (120 mg) under solvent free conditions at 100 °C.

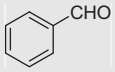
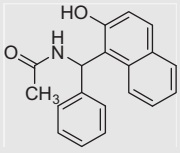
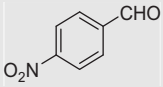
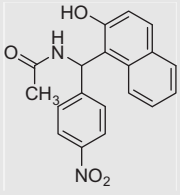
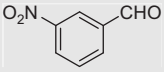
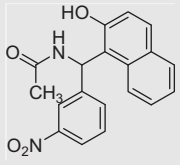
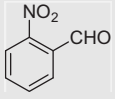
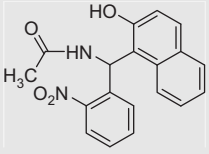
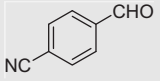
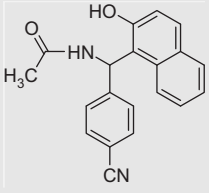
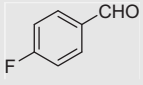
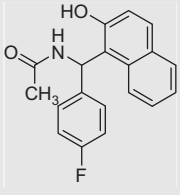
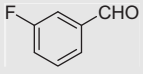
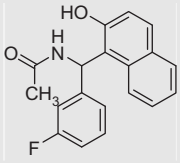
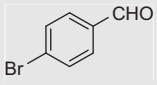
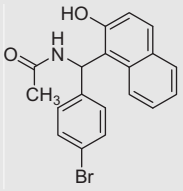
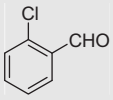
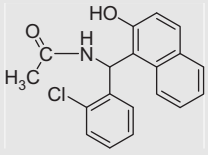
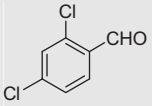
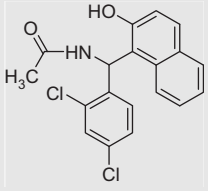
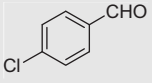
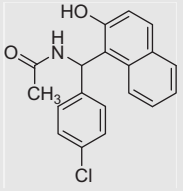
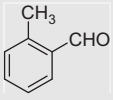
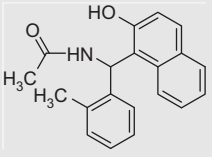
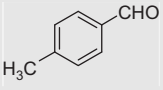
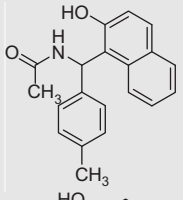
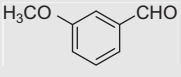
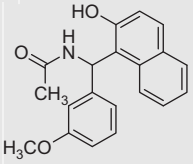
Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
1			40	85	242–243	[245–246] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
2			33	82	242–243	[248–250] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
3			42	78	242–243	[241–242] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
4			35	80	180–182	[179–182] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
5			40	76	262–263	[261–262] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
6			45	75	239–240	[230–232] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
7			43	73	248–249	[248–249] Sharghi et al. (2012) and Shaterian et al. (2012a,b)

Table 3 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
8			55	79	229–231	[227–226] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
9			40	83	212–213	[213–215] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
10			47	84	205–206	[201–203] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
11			60	85	229–230	[223–225] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
12			80	72	230–231	[199–202] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
13			90	70	215–216	[222–223] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
14			55	72	215–216	[201–204] Sharghi et al. (2012) and Shaterian et al. (2012a,b)

(*continued on next page*)

Table 3 (*Continued*)

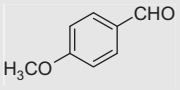
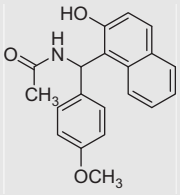
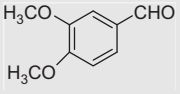
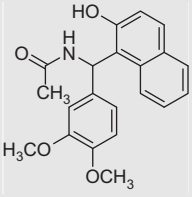
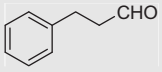
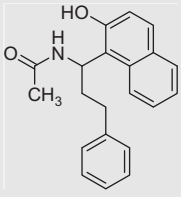
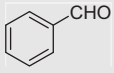
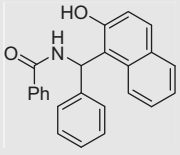
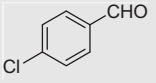
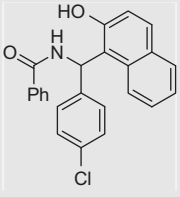
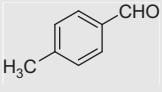
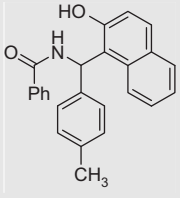
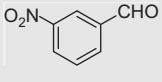
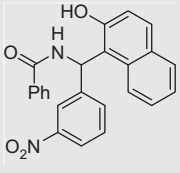
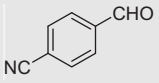
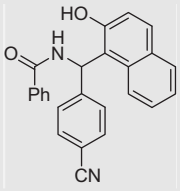
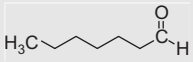
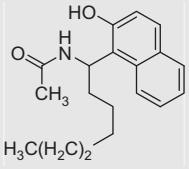
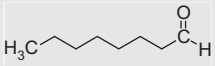
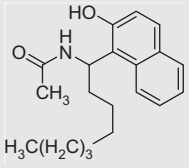
Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
15			100	70	180–182	[183–185] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
16			95	70	235–236	[235–237] Sharghi et al. (2012) and Shaterian et al. (2012a,b)
17			160	60	185–186	[185–186] Shaterian et al., 2012a,b
18			30	81	234–235	[233–235] Mahdavinia et al. (2008)
19			40	85	227–229	[225–227] Mahdavinia et al. (2008)
20			45	75	177–179	[175–177] Mahdavinia et al. (2008)
21			20	79	215–217	[216–217] Mahdavinia et al. (2008)

Table 3 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
22			25	74	176–177	[176–178] Mahdavinia et al. (2008)
23			24 h	–	–	–
24			24 h	–	–	–

[a] Yields refer to the isolated pure products. All the products were characterized by comparison of their spectroscopic and physical data with the authentic samples (Sharghi et al., 2012; Shaterian et al., 2012a,b; Mahdavinia et al., 2008). The reaction was carried out under thermal solvent-free conditions in an oil bath at 100 °C.

2.1.8. Benzyl(4-cyanophenyl)(2-hydroxynaphthalen-1-yl)methylcarbamate(Table 4, Entry 24)

Mp: 202–203 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 5.08 (d, J = 12.3 Hz, 1H), 5.13 (d, J = 12.6 Hz, 1H), 6.98 (d, J = 8.2 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.28–7.44 (m, 9H), 7.74 (d, J = 8.3 Hz, 2H), 7.77–7.83 (m, 2H), 7.93(brs, 2H), 10.20 (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): δ = 50.3, 65.8, 109.1, 117.9, 118.3, 118.8, 122.5, 122.7, 126.7 (2C), 126.9, 127.6, 127.7, 128.2 (2C), 128.3 (2C), 128.6, 129.7, 131.9 (2C), 132.0, 136.8, 148.3, 153.0, 156.1 ppm; IR (KBr, cm^{-1}): 3424, 3204, 2231, 1678, 1509, 1439, 1320, 1273, 1067, 943, 857, 814, 746, 700.

2.2. General procedure for the synthesis of 2-arylbenzothiazoles catalyzed with H_3PO_4/Al_2O_3

To a stirred solution of aldehyde (10 mmol) and 2-aminothiophenol (10 mmol) was added H_3PO_4/Al_2O_3 (1 g) and the mixture was stirred at room temperature for the time specified in Table 6. The reaction was followed by TLC (*n*-Hexane–EtOAc, 9:1). After completion of the reaction (checked by TLC), the reaction mixture was solved using ethylacetate and filtered to separate the catalyst. It was washed well with ethylacetate (2 × 5 ml) and then dried at 100 °C for 2 h before being further used. Then, the filtered solution was evaporated and purified by passing through a short pad column of silica gel using *n*-hexane as eluent (2 × 20 ml). Evaporation of the solvent under reduced pressure gave pure product(s) (Table 6). The desired pure product(s) was characterized by comparison of their physical data with those of known compounds (Nalage et al., 2010; Sharghi et al., 2012; Yelwande et al., 2012; Sadek et al., 2012; Bahrami et al., 2009).

2.3. Selected spectral data

2.3.1. 2-(3-Nitrophenyl)-1,3-benzothiazole(Table 6, Entry 6)

M.p. 184–186 °C; IR (ν max, KBr, cm^{-1}): 3080, 3033, 1612, 1577; ^{1}H-NMR: δ 7.54 (t, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.88 (t, J = 8.0 Hz, 1H), 8.16 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 8.0 Hz, 1H, Ar-H), 8.41 (d, J = 8.0 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.84 (s, 1H).

2.3.2. 2-(3,4-Dimethoxyphenyl)-1,3-benzothiazole(Table 6, Entry 10)

M.p. 130–132 °C; IR (ν max, KBr, cm^{-1}): 3078, 3053, 2962, 2835, 1600; ^{1}H-NMR: δ = 3.85 (s, 3H), 3.89 (s, 3H), 7.11 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 7.8 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.60–7.66 (m, 2H), 8.02–8.09 (m, 1H), 8.10 (d, J = 8.4 Hz, 1H).

3. Results and siscussion

To study the effect of catalyst loading and temperature on the three component condensation reactions for the synthesis of *N*-[phenyl-(2-hydroxy-naphthalen-1-yl)-methyl]acetamide from benzaldehyde, 2-naphthol, acetamide (molar ratio

Table 4 Preparation of α-carbamato-alkyl-β–naphthols catalyzed by H_3PO_4/Al_2O_3 (120 mg) under solvent-free conditions at 100 °C.

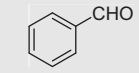
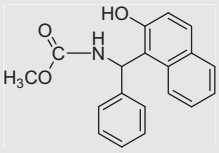
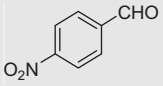
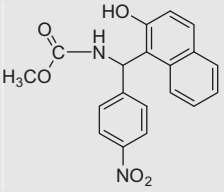
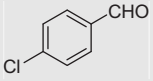
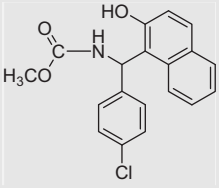
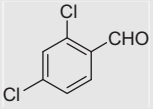
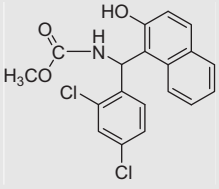
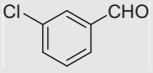
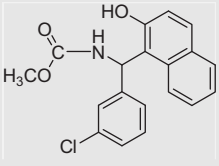
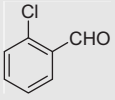
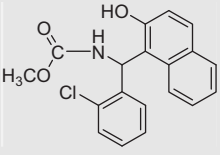
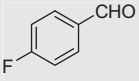
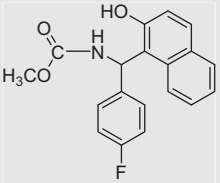
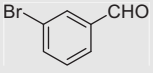
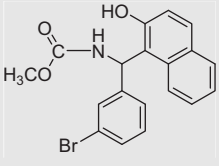
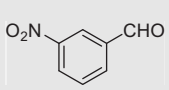
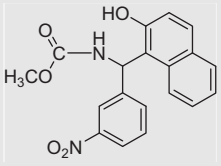
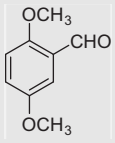
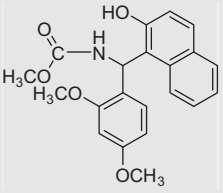
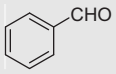
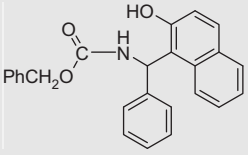
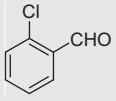
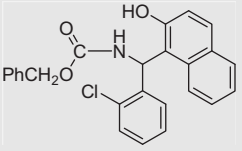
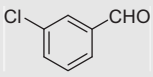
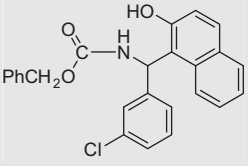
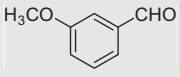
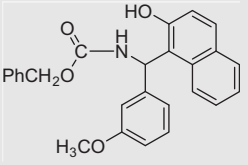
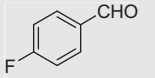
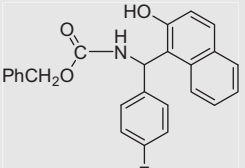
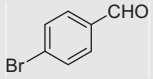
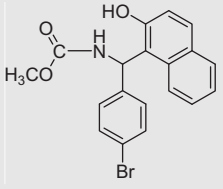
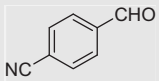
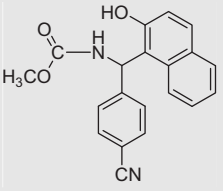
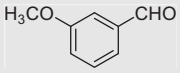
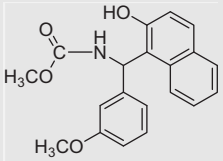
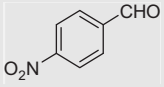
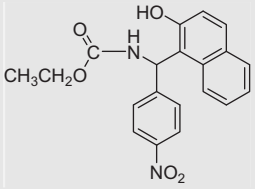
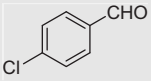
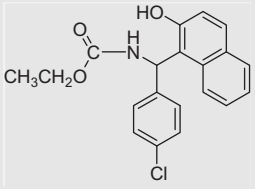
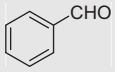
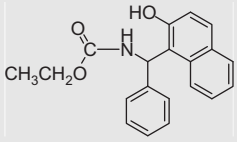
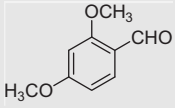
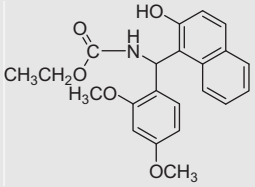
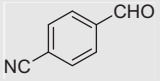
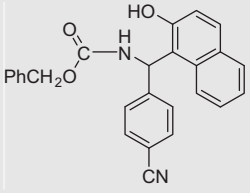
Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
1			55	78	215–217	[217–218] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
2			47	75	207–208	[205–207] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
3			47	70	200–202	[198–200] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
4			45	80	192dec	[192dec] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
5			47	76	198–200	[196–198] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
6			50	70	183–185	[182–184] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
7			47	77	204–205	[202–204] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
8			47	70	194–195	[193–195] Dabiri et al. (2007) and Shaterian et al. (2012a,b)

Table 4 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
9			45	82	254dec	[252dec] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
10			63	70	216dec	[215dec] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
11			60	82	180–181	[179–180] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
12			55	80	163–165	[163–165] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
13			55	85	203dec	[203dec] Dabiri et al. (2007) and Shaterian et al. (2012a,b)
14			70	70	184–185	[182–184]Dabiri et al. (2007) and Shaterian et al. (2012a,b)
15			60	65	185–186	[185–186]Dabiri et al. (2007) and Shaterian et al. (2012a,b)
16			47	68	196–198	[195–197]Dabiri et al. (2007) and Shaterian et al. (2012a,b)
17			50	70	233–234	[233–234] Shaterian et al., 2012a,b

(*continued on next page*)

Table 4 (*Continued*)

Entry	Substrate	Product	Time (min)	Yield (%)[a]	Melting points (°C)	
					Found	Lit. [Ref.]
18			63	68	180–182	[180–182] Shaterian et al., 2012a,b
19			47	80	222–223	[222–223] Shaterian et al., 2012a,b
20			50	83	220–221	[220–221] Shaterian et al., 2012a,b
21			55	78	203–204	[203–204] Shaterian et al., 2012a,b
22			67	72	217–218	[217–218] Shaterian et al., 2012a,b
23			60	68	202–203	[202–203] Shaterian et al., 2012a,b

[a] Yields refer to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ^{1}H and ^{13}C NMR) with those of known compounds. (Dabiri et al., 2007; Shaterian et al., 2012a,b The reaction was carried out under thermal solvent-free conditions in an oil bath at 100 °C.

1:1:1.2), in the presence of H_3PO_4/Al_2O_3, as catalyst was selected as a model under solvent-free conditions (Table 1). The reaction was carried out with different amount of H_3PO_4/Al_2O_3 (50% w/w) as catalyst, and at different temperatures (Tables 1 and 2). As it was shown in Table 1, 120 mg of the catalyst at 100 °C afforded the corresponding product in 40 min with 85% of yield (Table 1 and 2). However, the reaction rate accelerates in 110 and 120 °C, but the yield increases slightly (1–2%).

A further increase in the catalyst (130, 140 mg) causes the reaction performed at the short reaction times (35, 32 min), but decreases the yield of the product (Table 2).

Using these optimized reaction conditions (120 mg) of H_3PO_4/Al_2O_3 (50% w/w) at 100 °C, under solvent-free conditions, the scope and efficiency of the reaction were explored for the synthesis of a wide variety of substituted α-amidoalkyl-β-naphthols using various aldehydes, β-naphthol, and amides. The results are summarized in Table 3.

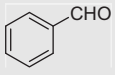
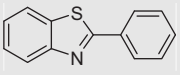
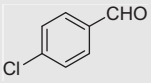
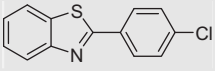
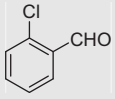
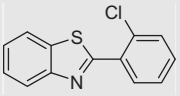
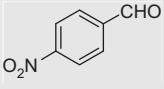
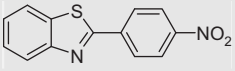
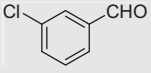
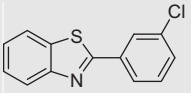
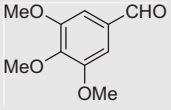
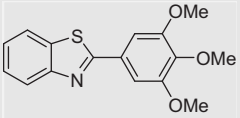
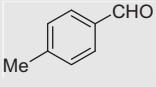
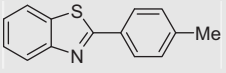
In all the cases the corresponding α-amidoalkyl-β-naphthols were obtained in good to excellent yields. However, with aromatic aldehydes with electron-withdrawing groups as substrates, the reaction time is shorter than those with electron-donating groups. Though *meta*- and *para*-substituted aromatic aldehydes gave good results, *ortho*-substituted aromatic aldehyde (*o*-methylbenzaldehyde) gave corresponding products in shorter time than other positions because of the steric effects that decrease electron-donation to center of reaction in *ortho*-quinone methides (*o*-QMs) as a highly reactive and

Table 5 Comparison results of H_3PO_4/Al_2O_3 with $Ce(SO_4)_2$, I_2, Montmorillonite k_{10} clay, $K_5CoW_{12}O_{40}{\cdot}3H_2O$, $H_3Mo_{12}O_{40}P$, $Fe(HSO_4)_3$, $KHSO_4$ in the synthesis of α-amidoalkyl-β-naphthols.

Entry	Catalyst	Amount of Catalyst	Conditions	Time	Yield (%)
1	$Ce(SO_4)_2$	(1 mol %)	Reflux in acetonitrile	36 h	72
2	I_2	(5 mol %)	Solvent-free	5.5 h	85
3	$H_3Mo_{12}O_{40}P$	(6.6 mol %)	Reflux in Ethyl acetate	3.5 h	95
4	$K_5CoW_{12}O_{40}{\cdot}3H_2O$	(0.01 g)	Solvent-free	2 h	90
5	Montmorillonite K_{10} clay	(0.1 g)	Solvent-free	1.5 h	89
6	$Fe(HSO_4)_3$	(5 mol %)	Solvent-free	65 min	83
7	KHSO4	(15 mol %)	Solvent-free	1 h	90
8	H_3PO_4/Al_20_3	(120 mg)	Solvent-free	40 min	85 (present work)

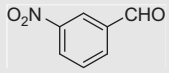
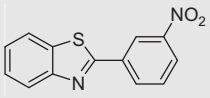
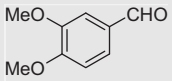
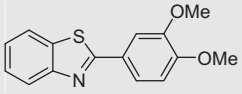
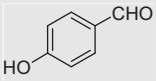
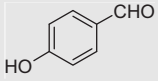
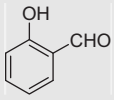
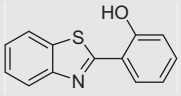
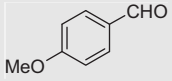
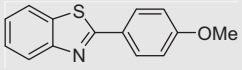
[a]Based on the reaction of β-naphthol, benzaldehyde and acetamide.

Table 6 Synthesis of 2-arylbenzothiazole derivatives through direct condensation of aryl aldehyde and 2-aminothiophenol (molar ratio: 1.0/1.0) catalyzed by H_3PO_4/Al_2O_3 (0.1 g) under solvent free conditions at room temperatures.

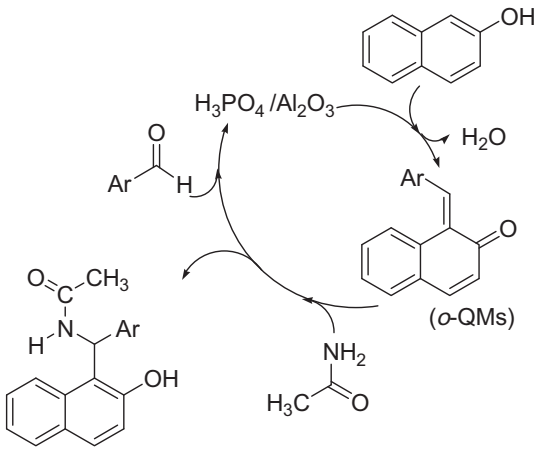
Entry	R	Product	Time (min)	Yield (%)[a]	Melting points (°C) Found m. p. Lit. m.p. [Ref.]
1			10	92	113–114 [112–113]Ref 20
2			20	89	116–118 [116–118] Sadek et al., 2012
3			25	87	84–85 [82–84] Ansari et al., 2010
4			10	90	224–225 [224–225] Sadek et al., 2012
5			20	92	95–96 [95–97] Ansari et al., 2010
6			40	85	130–132 [130–131] Ansari et al., 2010
7			20	84	87–89 [84–86] Sadek et al., 2012

(*continued on next page*)

Table 6 (*Continued*)

Entry	R	Product	Time (min)	Yield (%)[a]	Melting points (°C) Found m. p. Lit. m.p. [Ref.]
8			10	88	184–186 [184–186] Sadek et al., 2012
9			30	87	130–132 [130–132] Sadek et al., 2012
10			50	84	230–232 [227–229] Ansari et al., 2010
11			45	87	121–122 [123–124] Ansari et al., 2010
12			25	90	127–128 [126–128] Sadek et al., 2012

[a] Yields refer to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ^{1}H and ^{13}C NMR) with those of known compounds. (Ansari et al., 2010; Sadek et al., 2012) The reaction was carried out under thermal solvent-free conditions in an oil bath at 100 °C.



Scheme 4 The suggested mechanism for preparation of α-amidoalkyl-β-naphthol derivatives.

ephemeral intermediate. Interestingly, 3-phenylpropinaldehyde also gave the desired product in excellent yield. On the other hand, reactions with *n*-heptaldehyde and *n*-octanaldehyde provided corresponding α-amidoalkyl-β-naphthols with < 10% yields, the reactions did not complete after 24 h and almost 90% of aldehydes were intact without the formation of aldol condensation products (Table 3, entries 23, 24). We also use benzamide instead of acetamide in the above mentioned reaction (Table 3, entries 18–22), the α-benzamidoalkyl-β-naphthol derivates were obtained in excellent yield with short reaction times.

The suggested mechanism is described in Scheme 4. As reported in literature, (Selvam and Perumal, 2006) the reaction of β-naphthol with aromatic aldehydes in the presence of acid catalyst is known to give *ortho*-quinone methides (*o*-QMs) as a highly reactive and ephemeral intermediate. The same *o*-QMs, generated *in situ*, have been reacted with acetamide to form α-amidoalkyl-β-naphthol derivatives (Scheme 4). A reasonable explanation for this result can be given by considering the nucleophilic addition to (*o*-QMs) intermediate favorable *via* conjugate addition on α, β-unsaturated carbonyl group that aromatizes naphthalene ring of this intermediate. The electron withdrawing groups (EWD) substituted on benzaldehyde in (*o*-QMs) intermediate increase the rate of 1,4-nucleophilic addition reaction because alkene LUMO is at lower energy in the neighboring withdrawing groups than electron donating groups (EDG) (Shaterian et al., 2012a,b).The reactions of aliphatic aldehydes (Table 3, entry 23,24) instead of aromatic aldehydes were not completed and give the desired products with low yield as well as the known catalysts, such as $K_5CoW_{12}O_{40}{\cdot}3H_2O$ (Nagarapu et al., 2007) p-TSA (Khodaei et al., 2006) Sulfamic acid (Nagawade and Shinde, 2007) and cation-exchange resins (Sachin et al., 2007) probably due to less stability of *o*-quinonemethide intermediate (*o*-QMs) from aliphatic aldehydes.

Table 7 Comparison result of H_3PO_4/Al_2O_3 with $Cu(OAc)_2$/MCM-41, bakers' yeast, H_2O_2/CAN, silica sulfuric acid and P_2O_5 in the synthesis of 2-phenylbenzo[d]thiazole.

Entry	Catalyst	Conditions	Amount of Catalyst	Time (min)	Yield (%)[a]
1	$Cu(OAc)_2$/MCM-41	Solvent free, RT, ultrasound	0.05 g	20 min	95
2	Bakers' yeast	Solvent (DCM), RT	0.25 g	24 h	75
3	H_2O_2/CAN system	Solvent free, 50 °C	30% H_2O_2 (4 mmol)$NH_4Ce(NO_2)_6$ (0.1 mmol)	13 min	97
4	Silica sulfuric acid	Solvent free, MW	0.1 g	12 min	90
5	P_2O_5	Solvent (Methanol), RT	0.1 mmol	3.2 h	89
6	Glyserol	RT	10 ml	30 min	92
7	SnO_2/SiO_2	EtOH/H_2O (Reflux)	0.1 g	70 min	93
8	H_3PO_4/Al_2O_3	Solvent free, RT	0.1 g (50% w/w)	10 min	92 (present work)

[a] Yields refer to the isolated pure products.

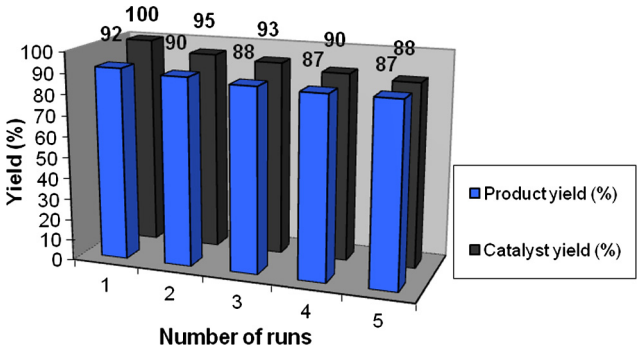


Figure 1 The investigation of the recycling of H_3PO_4/Al_2O_3.

In continuation of our research, we try to prepare α-carbamato-alkyl-β–naphthols in a one-pot and three component reaction using benzaldehydes, β-naphthol and carbomates in the presence of H_3PO_4/Al_2O_3 (120 mg) as catalyst under solvent-free conditions at 100 °C. We extended our study with different aromatic aldehydes to prepare a series of α-carbamato-alkyl-β–naphthols. Table 4 summarized some of these results.

In order to show the accessibility of the present work in comparison with the reported results in the literature such as $Ce(SO_4)_2$ (Selvam and Perumal, 2006), I_2 (Nagarapu et al., 2007), $H_3Mo_{12}O_{40}P$ (Jiang et al., 2008) Montmorillonite k_{10} clay (Kantevari et al., 2007) $K_5CoW_{12}O_{40}.3H_2O$ (Shaterian et al., 2008a,b), $Fe(HSO_4)_3$ (Shaterian et al., 2008a,b) and $KHSO_4$ (Almahy, 2011). We summarized some of the results for the preparation of α-amidoalkyl-β-naphthols in Table 5, which shows that H_3PO_4/Al_2O_3 is the most efficient catalyst with respect to the reaction time and temperature and exhibits broad applicability in terms of yield.

In addition, we applied the mentioned catalyst in condensation reaction of aromatic aldehydes with 2-aminothiophenol under solvent-free conditions at room temperature (Scheme 3). Similarly, we generally described optimization procedure, the reaction of benzaldehyde and 2-aminothiophenol was selected as model reaction. The reaction was carried out in the presence different amount of catalyst (0.002, 0.05, 0.1, 0.2, 0.3 g) at ambient and solvent-free conditions. The best results were obtained with the amount of the catalyst (0.1 g). Using these optimized reaction conditions 0.1 g of H_3PO_4/Al_2O_3, the scope and efficiency of the reaction were explored for the synthesis of 2-arylbenzothiazoles at room temperature (Table 6).

To show the merit of the present work in comparison with reported results in the literature, we compared the results of H_3PO_4/Al_2O_3 with $Cu(OAc)_2$/MCM-41(Sadjadi and Sepehrian, 2011), bakers' yeast (Pratap et al., 2009), H_2O_2/CAN system (Bahrami et al., 2008), silica sulfuric acid (Niralwad et al., 2010), and P_2O_5 (Nalage et al., 2010), Glyserol (Sadek et al., 2012) and SnO_2/SiO_2 (Ansari et al., 2010) in the synthesis of 2-aminothiophenol. As shown in Table 7, H_3PO_4/Al_2O_3 can act as an effective catalyst with respect to reaction times, amount of the catalyst, and yields of the obtained products. Thus, the present protocol with H_3PO_4/Al_2O_3 catalyst is convincingly superior to some of the reported catalytic methods.

We also investigated the recycling of the catalyst under solvent-free conditions using a model reaction of benzaldehde, β-naphthol and acetamide. After completion of the reaction, the reaction was cooled to room temperature, and the crude solid product was dissolved in ethyl acetate. The mixture was filtered for separation of the catalyst. The catalyst was washed twice (4 × 5 ml) using ethylacetate. The recovered catalyst was dried in vacuum and was used as such for the subsequent catalytic runs. The catalytic system worked well up to four catalytic runs. Catalytic cycles with respect to 85% yield (Table 3, entry 1). The recovered catalyst was reused five times without any loss of its activities (Fig. 1).

4. Conclusion

We have developed a green and straightforward protocol for the synthesis of α-amidoalkyl-β-naphthols, α-carbamato-alkyl-β–naphthols and 2-arylbenzothiazoles using H_3PO_4/Al_2O_3 (50% w/w) as a catalytic medium under solvent-free conditions. This procedure provides several advantages such as cleaner reactions, easier workup, reduced reaction times, reusable catalyst, and eco-friendly promising strategy.

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References

Almahy, H.A.A., 2011. J. Appl. Sci. Res. 6, 464.
Ansari, S.A.M.K., Sangshetti, J.N., Nagnnath, D.D., Wakte, P.S., Shinde, D.B., 2010. Indian J. Chem. Technol. 17, 71.
Araujo, L.R.R.D., Scofield, C.F., Pastura, N.M.R., Gonzalez, W.D.A., 2006. Mater. Res. 9, 181.
Bahrami, K., Khodaei, M.M., Naali, F., 2009. Synlett 569.

Bahrami, K., Khodaei, M.M., Naali, F., 2008. J. Org. Chem. 73, 6835.
Ballini, R., 2009. Eco-Friendly Synthesis of Fine Chemicals. RSC Publications, Cambridge, UK.
Dabiri, M., Delbari, A.S., Bazgir, A.A., 2007. Hetrocycles 71, 543.
Dixon, K.R., 1989. Phosphorus to bismuth. In: Mason, J. (Ed.), Multinuclear NMR, second ed. Plenum Press, London.
Jafari, H., Moghanian, H., 2012. Lett. Org. Chem. 9, 273.
Jiang, W.-Q., An, L.-T., Zou, J.-P., 2008. Chin. J. Chem. 26, 1697.
Khodaei, M.M., Khosropour, A.R., Moghanian, H., 2006. Synlett 6, 916.
Kantevari, S., Vuppalapati, S.V.N., Nagarapu, L., 2007. Catal. Commun. 8, 1857.
Kumar, A., Tripathi, V.D., Kumar, P., 2011. Green Chem. 13, 51.
Mahdavinia, G.H., Bigdeli, M.A., Heravi, M.M., 2008. Chin. Chem. Lett. 19, 1171.
Nalage, S.V., Bhosale, S.V., Bhosale, D.S., Jadhav, W.N., 2010. Chin. Chem. Lett. 21, 790.
Nagawade, R.R., Shinde, D.B., 2007. Mendeleev Commun. 17, 299.
Nagarapu, L., Baseeruddin, M., Apuri, S., Kantevari, S., 2007. Catal. Commun. 8, 1729.
Niralwad, K.S., Shingate, B.B., Shingare, M.S., 2010. Bull. Korean Chem. Soc. 31, 981.
Paul, T.A., Irvin, J.L., Kathryn, E.P., 2009. Green Chemistry Education: Changing the Course of Chemistry. Oxford University press.
Pratap, U.R., Mali, J.R., Jawale, D.V., Mane, R.A., 2009. Tetrahedron Lett. 50, 1352.
Rothenberg, G., 2008. Catalysis* Concepts and Green Applications. Wiley-VCH, West Sussex, UK.
Sachin, B.P., Pankajkumar, R.S., Mandar, P.S., Shriniwas, D.S., 2007. Synth. Commun. 37, 1659.
Sadek, K.U., Mekheimer, R.A., Abdel Hameed, A.M., Elnahas, F., Elnagdi, M.H., 2012. Molecules 17, 6011.
Sadjadi, S., Sepehrian, H., 2011. Ultrason. Sonochem. 18, 480.
Selvam, N.P., Perumal, P.T., 2006. Tetrahedron Lett. 47, 7481.
Sharghi, H., Aberi, M., Doroodmand, M.M., 2012. J. Iran. Chem. Soc. 9, 189.
Shaterian, H.R., Hosseinian, A., Ghashang, M., 2008a. Tetrahedron Lett. 49, 5804.
Shaterian, H., Amirzadeh, A., Khorami, F., Ghashang, M., 2008b. Synth. commun. 38, 2983.
Shaterian, H.R., Azizi, K., Fahimi, N., 2012a. Chem. Sci. Trans. 1, 73.
Shaterian, H.R., Azizi, K., Fahimi, N., 2012b. Chem. Sci. Trans. 1, 85.
Yelwande, A.A., Navgire, M.E., Tayde, D.T., Arbad, B.R., Lande, M.K., 2012. Bull. Korean Chem. Soc. 33, 1856.
Zarei, A., Hajipour, A.R., Khazdooz, L., Mirjalili, B.F., Zahmatkesh, S.Fast., 2009. J. Mol. Catal. A: Chem. 301, 39.