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Original article

Poly(4-vinylpyridine): As a green, efficient and commercial available basic catalyst for the synthesis of chromene derivatives

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ABSTRACT

Poly(4-vinylpyridine) is reported as a green, commercial available and efficient basic recyclable catalyst for the synthesis of chromene derivatives. This catalyst can be easily recovered by simple filtration and recycled up to 5 consecutive runs without any loss of its efficiency.

1. Introduction

Numerous reactions such as isomerizations, alkylations, condensations, additions, and cyclizations were carried out industrially by using liquid bases catalysts [1]. The replacement of liquid bases by cleaner catalytic alternatives is quite necessary in the view of being environmentally benign. Solid base catalysts have many advantages over liquid bases. They are noncorrosive, environmentally benign and present fewer disposal problems while allowing easier separation and recovery of the products, catalysts and the solvent. Thus, solid base catalysis is one of the economically and ecologically important field. Catalysis and the replacement of liquid bases with heterogeneous catalysts are becoming more and more important in the chemical industry. Many solid basic catalysts have been studied, including ion-exchange resins [2], modified silicas such as xonotlite [3], hydrotalcite [4], sepioloites [5], and supports with surface oxynitrides [6]. Pyridine was used as a polar, basic, low-reactive solvent for example in Knoevenagel condensations. It is especially suitable for dehalogenation, where it acts as the base for the elimination reaction and bonds the resulting hydrogen halide to form a pyridinium salt. In esterifications and acylations, pyridine activates the carboxylic acid halides or anhydrides. Pyridine was also used as a liquid base in condensation reaction [7]. Nevertheless, pyridine is a highly flammable and highly toxic compound and can be absorbed through the skin mucous membranes. Therefore replacement of the pyridine with the corresponding cleaner solid alternatives, possessing desirable characteristics such as being nonstoichiometric, non-corrosive and reusable, is necessary in view of being environmentally benign. Poly(4-vinylpyridine) (PVPy) has been used as the support for the numerous reagents and catalysts in many organic reaction transformations. Cross-linked poly(4-vinylpyridine) as an insoluble polymer has remarkable properties and attracted much attention. It undergoes facile functionalization and has a large proportion of functional groups which showed good accessibility. Moreover, it is non-hygroscopic, prepared readily and is available commercially. Also it is easy to filter and swells in many organic solvents. The cross-linked PVPy by divinylbenzene (DVB) was used most often because of its commercial availability, its stability, reasonably high loading capacity, good swelling characteristics and good physicochemical structure [8]. However, to the best of the our knowledge, there is no report which utilizes poly(4-vinylpyridine) as a solid basic catalyst in the organic synthesis. Chromene derivatives are an important class of compounds that received significant attention from many pharmaceutical and organic chemists because of the broad spectrum of their biological and pharmaceutical properties such as antisterility and anticancer agents [9]. Moreover, these compounds can also be employed as cosmetics and pigments [10]. Therefore, various synthetic procedures have been developed for the preparation of chromene derivatives [11–25]. Herein we wish to report the applicability of

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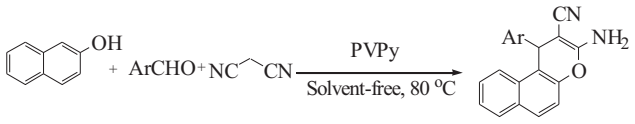

Scheme 1. Synthesis of chromene derivatives catalyzed by PVPy.

poly(4-vinylpyridine) as a green, commercial available and efficient basic recyclable catalyst for the synthesis of chromene derivatives *via* the one-pot three-component condensation of β-naphthol with aromatic aldehydes and malononitrile (Scheme 1).

2. Experimental

General: All products were characterized by comparison of their spectroscopic data (^{1}H NMR, IR) and physical properties with those reported in the literature. Chemicals were purchased from Fluka, Merck, and Aldrich Chemical. Yields refer to isolated pure products.

General procedure for the synthesis of chromene derivatives: A mixture of β-naphthol (1 mmol), malononitrile (1 mmol), aldehyde (1 mmol) and PVPy (0.1 g) was heated in an oil bath (80 °C) for the appropriate times as shown on Table 1. After completion of the reaction (monitored by TLC), the resulting mixture was cooled, ethylacetate (10 mL) was added and the catalyst was recovered by filtration to be reused subsequently. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol affords the pure products in high yields.

The spectral and analytical data for the known compounds are as follows:

Table 1, entry 1: IR (KBr, cm^{-1}): ν_{max} 3420, 3340, 3150, 2190, 1640, 1580, 1000–1300, 690, 710. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.32 (s, 1H), 7.04 (s, 2H, NH_2), 7.13–7.28 (m, 5H), 7.35–7.46 (m, 3H), 7.84–7.95 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.51, 58.38, 116.16, 117.27, 121.04, 124.10, 125.40, 127.08, 127.48, 127.55, 128.94, 129.19, 129.97, 130.65, 131.30, 146.21, 147.32, 160.20.

Table 1, entry 2: IR (KBr, cm^{-1}): ν_{max} 3400, 3300, 3200, 2900, 2200, 1645, 1550, 1350, 1400, 1300–1000. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.62(s, 1H, CH), 7.15 (s, 2H, NH_2), 7.37 (d, 1H, J = 8.9Hz, Ar), 7.41–7.47 (m, 2H, Ar), 7.56 (t, 1H, J = 7.8 Hz, Ar), 7.68 (d, 1H, J = 7.7 Hz, Ar), 7.85 (d, 1H, J = 8.2 Hz, Ar), 7.94 (d, 1H, J = 7.6 Hz, Ar), 7.97 (d, 1H, J = 8.9 Hz, Ar), 8.02 (d, 1H, J = 8.07 Hz, Ar), 8.09 (s,1H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 57.81, 115.46, 117.75, 121.05, 122.17, 122.73, 124.35, 126.02, 128.29, 129.47, 130.77, 130.94, 131.34, 131.74, 134.58, 147.83, 148.756, 148.85, 160.83.

Table 1, entry 3: IR (KBr, cm^{-1}): ν_{max} 3430, 3325, 2190, 1650, 1610, 1582, 1540, 1502, 1340, 1244, 1200, 1070, 810. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.45 (s, 1H, CH), 7.20 (s, 2H, NH_2). 7.36–7.52 (m, 3H, Ar), 7.69–8.03 (m, 2H, Ar), 7.98 (d, 1H, J = 9.2 Hz, Ar), 7.44 (d, 2H, Ar), 8.15(d, 2H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.53, 60.27, 116.45, 117.47, 121.17, 124.24, 125.49, 127.48, 127.62, 129.05, 129.82, 129.99, 130.74, 131.42, 136.23, 143.37, 147.33, 160.38.

Table 1, entry 5: IR (KBr, cm^{-1}): ν_{max} 3450, 3300, 2200, 1640, 1400, 1300–1000. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.37 (s, 1H, CH), 7.09 (s, 2H, NH_2), 7.21 (d, 2H, J = 8.4 Hz, Ar), 7.31–7.37 (m, 3H, Ar), 7.40–7.47 (m, 2H, Ar), 7.81 (d, 1H, J = 8.0 Hz, Ar), 7.90–7.96 (m, 2H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.85 (CH), 57.90 (CN), 115.63, 117.29, 120.87, 124.02, 125.47, 127.65, 128.99, 129.18, 129.33, 130.17, 130.53, 131.31, 131.67, 132.60, 145.16, 147.29, 160.21.

Table 1, entry 7: IR (KBr, cm^{-1}): ν_{max} 3416, 3323, 3194, 3051, 2193, 1641, 1591, 1485, 1410, 1234, 1080, 1012, 819, 736. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.23(s, 1H, CH), 4.64 (s, 2H, NH_2), 7.07 (d, 2H, J = 8.4 Hz), 7.27 (d, 2H, J = 6.3 Hz), 7.45–7.40 (m, 3H), 7.63 (d, 1H, J = 6.4 Hz), 7.84(d, 2H, J = 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.8, 57.4, 115.5, 117.3, 120.2, 120.6, 124.0, 125.5, 127.7, 129.0, 129.7, 130.2, 130.5, 131.3, 132.1, 145.6, 147.3, 160.2.

Table 1
Synthesis of chromene derivatives catalyzed by PVPy.

Entry	Aldehyde	Time (min)	Yield (%)[a]	Mp (°C)[b]
1	C_6H_5CHO	10	93	274–276
2	3-$O_2NC_6H_4CHO$	8	89	233–235
3	4-$O_2NC_6H_4CHO$	5	93	186–187
4	2-ClC_6H_4CHO	12	93	258–260
5	4-ClC_6H_4CHO	10	90	205–206
6	2,4-ClC_6H_3CHO	8	93	214–216
7	4-BrC_6H_4CHO	15	89	242–244
8	4-$MeOC_6H_4CHO$	30	87	217–218
9	3,4-$MeOC_6H_3CHO$	40	89	210–211
10	4-CNC_6H_4CHO	12	89	258–259
11	4-FC_6H_4CHO	15	88	233–234
12	4-MeC_6H_4CHO	20	88	270–272
13	4-HOC_6H_4CHO	45	86	246–248
14	4-$MeCONHC_6H_4CHO$	20	89	253–255[c]
15	4-Cl-3-$O_2NC_6H_3CHO$	10	92	201–202[c]

[a] Isolated yield.
[b] Products were characterized by comparison of their spectroscopic data (NMR and IR) and melting points with those reported in the literature [13,15,19].
[c] New compounds.

Table 1, entry 9: IR (KBr, cm^{-1}): ν_{max} 3450, 3300, 2200, 1640, 1400, 1300, 1000. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.72 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 5.58 (s, 1H, CH), 7.20 (s, 2H, NH_2), 7.37 (d, 1H, J = 9.2 Hz, Ar), 7.43–7.51 (m, 3H), 7.68 (d, 1H, J = 8 Hz, Ar), 7.85 (d, 1H, J = 8.0 Hz, Ar), 7.94–8.00 (m, 3H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.35, 56.45, 56.92, 57.90, 114.49, 117.39, 120.51, 123.72, 123.80, 124.21, 125.64, 127.95, 129.10, 130.30, 130.60, 131.30, 132.65, 132.86, 147.12, 147.37, 148.00, 160.41.

Table 1, entry 10: IR (KBr, cm^{-1}): ν_{max} 3462, 3356, 2200, 2190, 1654, 1589. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.43 (s, 1H, CH), 7.16 (s, 2H, 9.5. 7.24–7.41 (m, 3H, Ar), 7.58–7.86 (m, 2H, Ar), 7.88 (d, 1H, J = 9.2 Hz, Ar), 7.42 (d, 2H, J = 8.0 Hz Ar), 8.12 (d, 2H, J = 8.0 Hz, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 38.50, 60.22, 113.74, 116.40, 117.40, 121.10, 124.20, 125.45, 127.44, 127.57, 129.02, 129.79, 129.95, 130.72, 131.39, 136.20, 143.35, 147.30, 160.30

Table 1, entry 12: IR (KBr, cm^{-1}): ν_{max} 3310, 3410, 3050, 2190, 1640, 1580, 1400, 1000–1300, 810. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.19 (s, 3H, CH_3), 5.26 (s, 1H, CH), 6.99 (s, 2H, NH_2), 7.04–7.10 (m, 4H), 7.33 (d, 1H J = 8 Hz, Ar), 7.39–7.46 (m, 2H), 7.83 (d, 1H, J = 8.0 Hz) 7.90–7.94 (t, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.02, 38.22, 58.51, 116.27, 117.26, 121.06, 124.14, 125.35, 127.38, 127.50, 128.92, 129.72, 129.88, 130.66, 131.29, 136.16, 143.30, 147.24, 160.09.

The spectral and analytical data for the new compounds are as follows:

Table 1, entry 14: White solid, mp: 253–255 °C; IR (KBr, cm^{-1}): ν_{max} 3400, 3300, 2200, 1650, 1600–1400, 1320, 1100, 810. ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.99 (s, 3H, Me), 5.24 (s, 1H, CH), 6.98 (s, 2H, NH_2), 7.11 (d, 2H, J = 8.4 Hz, Ar), 7.34 (d, 1H, J = 8.8 Hz, Ar), 7.40–7.45 (m, 4H, Ar), 7.83 (d, 1H, J = 8.0 Hz, Ar), 7.90–7.95 (m, 2H, Ar), 9.89 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ 24.34(Me), 38.05, 58.36, 116.15, 117.29, 119.83, 121.04, 124.15, 125.38, 127.51, 127.76, 128.93, 129.90, 130.65, 131.28, 138.24, 140.86, 147.18, 160.01, 168.60. Elem. Anal. Found: C, 74.41; H, 4.79 N, 11.88 (calculated for $C_{22}H_{17}O_2$ N_3: C, 74.35; H, 4.82; N, 11.82).

Table 1, entry 15: Yellow solid, mp: 201–202 °C; IR (KBr, cm^{-1}): ν_{max} 3400, 3300, 2200, 1640, 1550, 1350, 1300– 1000, 800– 740. ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.58(s, 1H, CH), 7.20 (s, 2H, NH_2), 7.37 (d, 1H, J = 9.2 Hz, Ar), 7.43–7.51 (m, 3H), 7.68 (d, 1H, J = 8 Hz, Ar), 7.85 (d, 1H, J = 8.0 Hz, Ar), 7.94–8.00 (m, 3H, Ar). ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.37, 56.95, 114.52, 11.41, 120.54, 123.74, 123.84, 124.24, 125.66, 127.97, 129.13, 130.34, 130.65, 131.34, 132.69, 132.91, 147.17, 147.42, 148.03, 160.44. Elem. Anal. Found:

Table 2
Recyclability study of PVPy.

Run	1	2	3	4	5	6
Time(min)	10	10	15	20	30	45
Yield (%)[a]	93	93	91	91	90	90

[a] Isolated yield.

C, 63.65; H, 3.24 N, 11.14 (calculated for $C_{20}H_{12}O_3N_3Cl$:C, 63.58; H, 3.20; N, 11.12).

3. Results and discussion

At first, for the optimization of the reaction conditions, the reaction of benzaldehyde, β-naphthol and malononitrile was investigated as a model and its behavior was studied under various conditions. The best results were achieved by carrying out the reaction of benzaldehyde, β-naphthol and malononitrile (with 1:1:1 mol ratio) in the presence of 0.1 g of PVPy at 80 °C for 10 min under solvent-free conditions (Table 1, entry 1). Using these optimized conditions, the reaction of various aromatic aldehydes, containing electron-donating and electron-withdrawing groups, was explored. All the products were cleanly isolated with simple filtration and evaporation of the solvent. The solid products were easily recrystallized from hot ethanol and were obtained in good to high yields during the short reaction times. All the known products were identified by comparison of the melting points and the analytical data (IR, NMR) of those reported for authentic samples. A distinct characterization of the present method, illustrated in this work, is the formation of corresponding products without by-product.

It is also noteworthy that PVPy does not suffer from extensive mechanical degradation after running. When using a heterogeneous catalyst, the key point is the recyclability of the catalyst. In order to exhibit the recyclability of the PVPy, the reaction of benzaldehyde, β-naphthol and malononitrile was selected again as a model. After reaction completion, the PVPy was washed with ethylacetate, dried and stored for another consecutive reaction run. This process was repeated for five runs and no appreciable yield decrease was observed. Almost consistent activity was observed over five runs and desired products were obtained in high yields after 1–5 runs, respectively (Table 2). Finally, in order to evaluate the efficiency and superiority of our method, we began to run the reaction between benzaldehyde, β-naphthol and malononitrile in the presence of pyridine at the same conditions. The obtained results showed that solid base catalyst (PVPy) has an advantage over pyridine in term of high reactivity and easily recyclable. PVPy is very cheap, easy to handle and can be recovered simply by filtration. It can be reused in the next runs without significant yield decrease of the products. Further, PVPy makes the chromenes synthesis eco-friendly, with the possibility of scale-up to an environmentally benign and clean technology.

4. Conclusion

In conclusion, we have developed a mild, simple and green procedure for the one-pot synthesis of chromene derivatives using recyclable PVPy under solvent-free conditions. PVPy as a commercial available basic catalyst can promote the yields over 5 runs. Moreover, high yields of the products, short reaction times, recyclability of the reagent, solvent-free nature of the reaction, ease of work-up and clean procedure, will make the present method an efficient and important addition to the present methodologies for the synthesis of chromene derivatives.

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