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FULL PAPER

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Efficient synthesis of multiply substituted furans using BF@Propyl/dopamine/Pd as a green catalyst

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One of the commonly used methods to synthesize furans is the three-component reaction among aromatic aldehyde, arylamine, and acetylenedicarboxylate. The main advantages of this work are easy reaction work-up, short reaction time, high yield and easy recyclability, reusability of the catalyst. And also basalt fiber applications are surely innovative in many industrial and economic fields, because of its good mechanical, chemical and thermal performances.

KEYWORDS

basalt fibers, dimethyl acetylenedicarboxylate, furan, green, palladium

1 | INTRODUCTION

The catalyst support must have good surface cohesion to coat the various reagents and be chemically stable to the reactive environment.[1,2]

The usage of basalt fibers (BFs) as ceramic supports has significant potential in terms of cost and approachability of crude materials. Basalt is a natural material that exists in volcanic stones obtained from frozen lava.[3–5]

The form BFs is similar to glasslike filaments 4.5 to 7 cm in length and 1.5 to 6 μm in diameter. They are thermally stable to melting up to 950 °C, keep resistance to mechanical deformation up to 700 °C, and possesses high chemical stability. The basalt fiber consists of several metal oxides, such as those of Na, K, Ca, Mg, Al, Si, Fe, and Ti.[5] By chemical compositions analysis, it can be seen that SiO_2 is the major constituent and Al_2O_3 is the second constituent.[4,6–8]

The development and increasing application of basalt fibers are due to its useful properties such as high modulus and strength also remarkable heat resistance and notable vibration isolators. The growing use of basalt fiber brought up the question if basalt fiber is dangerous to health. Basalt looks to be harmless, as a result of different morphology and surface properties prevent any carcinogenic or poisonousness effects, which are shown by asbestos instead.[3,9,10]

In the last few years, the synthesis of *N*-heterocycles because of varied biological and pharmaceutical usages has been increasingly studied.[11–13]

Furan and its end product, obtained from synthetic in addition to natural resources, have attracted much attention with extensive varieties of medicine usages.[14,15]

These skeletons display several biological activities such as antimicrobial,[16–19] antifungal,[20] anti-inflammatory,[21,22] anticancer[23,24] and anti-viral HIV-1[25] activities.

Moreover, furans show pervasive synthetic building blocks capable of experiencing a range of transformations such as cycloaddition reactions that proceed with dearomatization of the furan moiety, resulting in the quick creation of molecular complexity.[26–28]

Some strategies have been devised to access furans bearing different substitution patterns, such as the Feist-Benary condensation of β-dicarbonyl derivatives with α-substituted ketones[29,30] For this vast variety of sufficiency and usability, different methods toward replaced furans have been extended, which involve the use of Pd $(Ph_3P)_2Cl_2$,[19] Al $(HSO_4)_3$,[25] Iron (III) chloride[31] and lactic acid.[32] Other approaches suffer from one of the following problems: low yields, long reaction times, waste pollution, harsh reaction conditions, and tiresome work-up.

The current study concentrates on the usage of basalt fibers as stable, inert, eco-friendly catalyst for synthesis of

furan byproducts with yield improved and reduce reaction period (Scheme 1).

2 | EXPERIMENTAL

2.1 | General information and methods

All chemicals were purchased from commercial suppliers (Merck and Fluka companies). Proton Nuclear Magnetic Resonance NMR (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were entered on Bruker BioSpin GmbH 400 MHz FT NMR spectrometers. Infrared (IR) spectra were taken using a Shimadzu 435-U-04 FT spectrophotometer from KBr tablets. IR data are represented as the frequency of absorption (cm^{-1}). Melting points were measured on a BUCHI 510 apparatus in open capillary tubes. Scanning electron microscopy (SEM) was fulfilled med on EM3200 instrument operated at 30 kV accelerating voltage. The structure of the new BF@Propyl/dopamine/Pd was characterized using XRD, IR, SEM, EDX and TGA analysis. Energy dispersive X-ray (EDX) and Scanning electron microscopy (SEM) analysis of the prepared catalyst was fulfilled on a FESEM-SIGM (Germany) instrument. Thermo-gravimetric analysis (TGA) was accomplished on a DUPONT 951 TA Instruments.[33]

2.2 | Preparation of surface modification of BF

Before the linkage an organic/inorganic coverage (propyl/dopamine/nanoparticle Pd) on the basalt fiber, crude basalt fibers were washed with acetone and dried under vacuum for 1 hr to remove the agent on the level and then behaved with piranha solution (H_2SO_4:H_2O_2 (*v*/v) =7:3) at 90 °C for 1 hr to produce more active silanol groups on the BF surface. Afterward, the basalt fibers prepared from the previous step were combined with 1 M HCl solution at 40 °C for 1 hr. Finally, it was washed with deionized water and dried in an oven at 100 °C.[34]

2.3 | Preparation of BF@propyl

Basalt fiber (1 g) synthesized in the previous step was added to a flask containing 50 ml of toluene was added. Then (3-chloropropyl)triethoxysilane (2.0 ml) was added and the mixture was refluxed at 110 °C with constant stirring conditions for 24 hr. After the reaction time was completed, the reaction mixture (BF@Propyl) was collected and separated by centrifugation, then washed with toluene and ethanol for several times. Finally, the resulting functionalized BF@Propyl was dried at 80 °C.

SCHEME 1 General synthesis of furans

2.4 | Preparation of BF@propyl/dopamine

BF@Propyl (1 g) was added to 50 ml of toluene and was dispersed using an ultrasonic bath for 20 min. Subsequently, 2-(3,4-dihydroxyphenyl)ethyleneamine (dopamine; 3 g) was added and refluxing for 24 hr. After this time, the basalt fiber coated with dopamine was synthesized and separated by filter paper. In the separation and purification step, the precipitate was washed with toluene and then water, then dried at 100 °C.

2.5 | Preparation of BF@propyl/dopamine/Pd

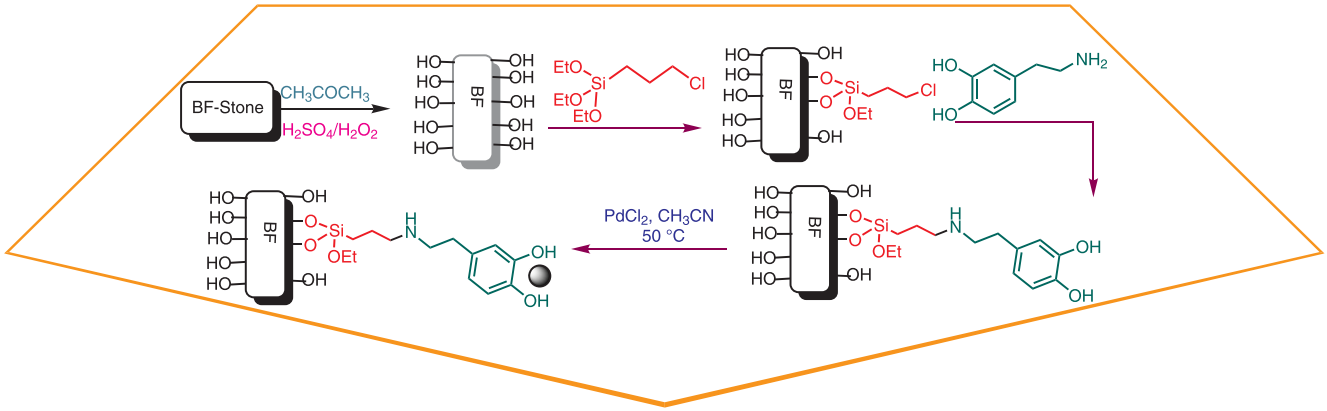
$PdCl_2$ (1 mmol) (dissolved in 10 ml of acetonitrile) to 0.5 g BF@Propyl/dopamine (dispersed in acetonitrile using an ultrasonic bath for 15 min) added. The reaction mixture was stirred at 90 °C for 24 hr. The precipitate was washed with acetone and then dried at 50 °C for 18 hr (Scheme 2).[35]

2.6 | General procedure for the synthesis of furans

Aromatic aldehyde (1.0 mmol), aryl amine (1.0 mmol), acetylenedicarboxylate (1.0 mmol) and 0.06 g BF@Propyl/dopamine/Pd nanocatalyst in EtOH (5 ml) was heated at 80 °C. After the completion of the reaction as indicated by the TLC (*n*-hexane/acetone 10:2), the reaction mixture was cooled to room temperature and filtered to eliminate the catalyst. The crude product washed with ethanol and purified by hot ethanol. The products were characterized using physical and spectroscopic (IR, NMR, MS) data. (Supporting Information 1-3).

2.7 | Evaluation of palladium removal from BF@propyl/dopamine/Pd catalyst surface in furan synthesis

Methyl-5-oxo-2-phenyl-4-(phenylamino)-2,-5-dihydrofuran-3-carboxylate derivative (4a) was selected



SCHEME 2 BF@Propyl/dopamine/Pd structure

as the sample for this test. After 50 per cent reaction progress (35 min), the reaction was stopped and the catalyst was separated from the reaction mixture by centrifugation. The reaction mixture was placed under the same conditions for 30 min after separation of the catalyst and no significant progress was observed in the reaction process. The results of this test showed that palladium nanoparticles were not released in the reaction medium and remained on the surface of the catalyst and as well as the catalyst was very stable in contrast to moisture, air and reaction conditions.[36]

2.8 | Analytical data of the selected products

2.8.1 | Methyl 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate 4a

Light yellow solid; M.p. 186–189 °C; FT-IR (KBr): ῡ (cm^{-1}) 3262, 3210, 2958, 1702, 1681, 1499, 1383, 1234, 1136; ^{1}H NMR (DMSO-d_6, 500 MHz): δ_H (ppm) 3.57 (s, 3H, OCH_3), 6.05 (s, 1H, CH), 7.07 (m, 1H, Ar-H), 7.23 (m, 7H, Ar-H), 7.54 (m, 2H, Ar-H), 11.73 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 51.0, 60.4, 111.9, 122.4, 127.6, 128.1, 128.6, 136.2, 136.4, 152.5, 162.4, 169.3; MS (m/z): 309.1 (M^+, 100%), 277.0, 250.1, 222.1, 189.1, 158.0, 130.1, 102.1, 77.1, 51.1.

2.8.2 | Methyl 5-oxo-2-phenyl-4-(*p*-tolylamino)-2,5-dihydrofuran-3-carboxylate 4b

White solid; M.p. 185–187 °C; FT-IR (KBr): ῡ (cm^{-1}) 3231, 3064, 2955, 1706, 1680, 1515, 1467, 1382, 1201, 1038; ^{1}H NMR (500 MHz, DMSO-d_6) δ_H (ppm): 2.17 (s, 3H, CH_3), 3.58 (s, 3H, OCH_3), 6.00 (s, 1H, CH), 7.06 (m, 2H, Ar-H), 7.20–7.49 (m, 7H, Ar-H), 11.70 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-*d6*): δ_C (ppm) 20.3, 51.0, 60.6, 111.7, 122.5, 127.6, 128.2, 129.0, 129.1, 136.2, 133.7, 134.6, 136.5, 152.6, 162.4, 163.7; MS (m/z): 323.1 (M^+), 291.1, 264.1, 236.1, 214.0, 189.1, 158.0, 130.0 (100%), 102.0, 77.0, 51.1.

2.8.3 | Methyl 2-(4-fluorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate 4c

White solid; M.p. 186–188 °C; FT-IR (KBr) ῡ (cm^{-1}): 3171, 2955, 1685, 1600, 1510, 1379, 1231, 1003; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 3.57 (s, 3H, OCH_3), 6.09 (s, 1H, CH), 7.02 (m, 3H, Ar-H), 7.28 (m, 4H, Ar-H), 7.54 (m, 2H, Ar-H), 11.64 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 59.7, 60.0, 111.6, 115.1, 122.5, 122.6, 125.5, 128.6, 129.7, 132.6, 136.0, 152.6, 160.5, 162.4, 163.8; MS (m/z): 327.1 (M^+, 100%), 295.0, 268.1, 240.1, 207.0, 170.1, 148.0, 120.0, 99.2, 77.1, 51.1.

2.8.4 | Methyl 2-(2-chlorophenyl)-5-oxo-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate 4d

White solid; M.p. 214–216 °C; FT-IR (KBr) ῡ (cm^{-1}): 3302, 3066, 2958, 1719, 1687, 1658, 1499, 1367, 1257, 1189, 1131; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 3.56 (s, 3H, OCH_3), 6.41 (s, 1H, CH), 7.03 (m, 1H, Ar-H),7.15–7.29 (m, 5H, Ar-H), 7.44 (m, 3H, Ar-H), 11.89 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 51.0, 56.6, 111.5, 122.3, 128.7, 129.3, 133.9, 134.4, 136.0, 153.3, 162.2, 164.0; MS (m/z): 343.1 (M^+, 100%), 311.1, 284.1, 248.1, 214.1, 192.0, 164.1, 136.0, 101.1, 77.1, 51.1.

2.8.5 | Methyl 2-(2-chlorophenyl)-5-oxo-4-(*p*-tolylamino)-2,5-dihydrofuran-3-carboxylate 4e

White solid; M.p. 206–209 °C; FT-IR (KBr): ῡ (cm^{-1}): 3212, 2949, 1713, 1675, 1514, 1381, 1292, 1230, 1197, 1135; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 2.25 (s, 3H, CH_3), 3.74 (s, 3H, OCH_3), 6.42 (s, 1H, CH), 6.98–7.10 (m, 5H, Ar-H), 7.38 (m, 3H, Ar-H), 9.13 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 20.9, 52.1, 56.7, 121.8, 126.9, 127.4, 129.6,129.8 132.7, 133.3, 134.9, 135.8, 156.8, 162.7, 165.1; MS (m/z): 357.3 (M^+, 100%), 325.3, 290.3, 262.3, 228.3, 192.2, 164.2, 133.3, 91.3, 65.2, 41.3.

2.8.6 | Methyl 2-(2-chlorophenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydrofuran-3-carboxylate 4f

White solid; M.p. 192–194 °C; FT-IR (KBr): ῡ (cm^{-1}): 3177, 2955, 1709, 1679, 1514, 1391, 1252, 1137, 1000; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H (ppm) 3.73 (s, 6H, OCH_3), 6.38 (s, 1H, CH), 6.79–6.81 (m, 2H, Ar-H), 6.97 (m, 1H, Ar-H), 7.16 (m, 2H, Ar-H), 7.27–7.38 (m, 3H, Ar-H), 9.07 (s, 1H, NH); ^{13}C NMR (75 MHz, $CDCl_3$): δ_C (ppm) 54.4, 56.2, 56.8, 113.5, 114.9, 122.8, 124.0, 124.6, 126.5, 127.6, 128.8, 130.7, 132.6, 157.1, 162.5, 165.2; MS (m/z): 373 (M^+), 341, 306, 278, 245, 230, 210, 192, 178, 164, 149 (100%), 134, 115, 101, 83, 69, 55, 41.

2.8.7 | Methyl 2-(2-bromophenyl)-5-oxo-4-(*p*-tolylamino)-2,5-dihydrofuran-3-carboxylate 4 g

White solid; M.p. 205–208 °C; FT-IR (KBr): ῡ (cm^{-1}): 3354, 2912, 1690, 1538, 1514, 1383, 1242, 1154, 1029; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 2.18 (s, 3H, CH_3), 3.37 (s, 3H, OCH_3), 6.18 (s, 1H, CH), 6.81 (s, 1H, NH), 7.05 (m, 4H, Ar-H),7.33 (m, 2H, Ar-H), 7.45 (m, 1H, Ar-H); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 20.4, 50.0, 59.0, 122.0, 125.0, 127.3, 129.0, 129.1, 132.2, 134.4, 165.9, 167.5, 168.8; MS (m/z): 401 (M^+), 387.2 (100%), 340.2, 293.1, 227.2, 189.2, 149.1, 95.1, 43.1.

2.8.8 | Methyl 2-(2-bromophenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydrofuran-3-carboxylate 4 h

White solid; M.p. 185–187 °C; FT-IR (KBr): ῡ (cm^{-1}): 3194, 2952, 1713, 1676, 1513, 1458, 1382, 1252, 1181, 1028; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 3.54 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 6.27 (s, 1H, CH), 6.83 (m, 3H, NH, Ar-H), 7.09 (m, 1H, Ar-H),7.29 (m, 3H, Ar-H), 7.48 (m, 2H, Ar-H); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 51.0, 55.1, 57.0, 111.2, 113.8, 124.4, 128.8, 129.3, 134.0, 134.4, 153.5, 157.0, 162.2, 163.8; MS (m/z): 417.1 (M^+), 387.0, 340.0, 306.1, 278.1, 247.1, 210.1, 180.0, 149.1 (100%), 101.0, 75.1, 43.1.

2.8.9 | Methyl 2-(2-nitrophenyl)-5-oxo-4-(*p*-tolylamino)-2,5-dihydrofuran-3-carboxylate 4i

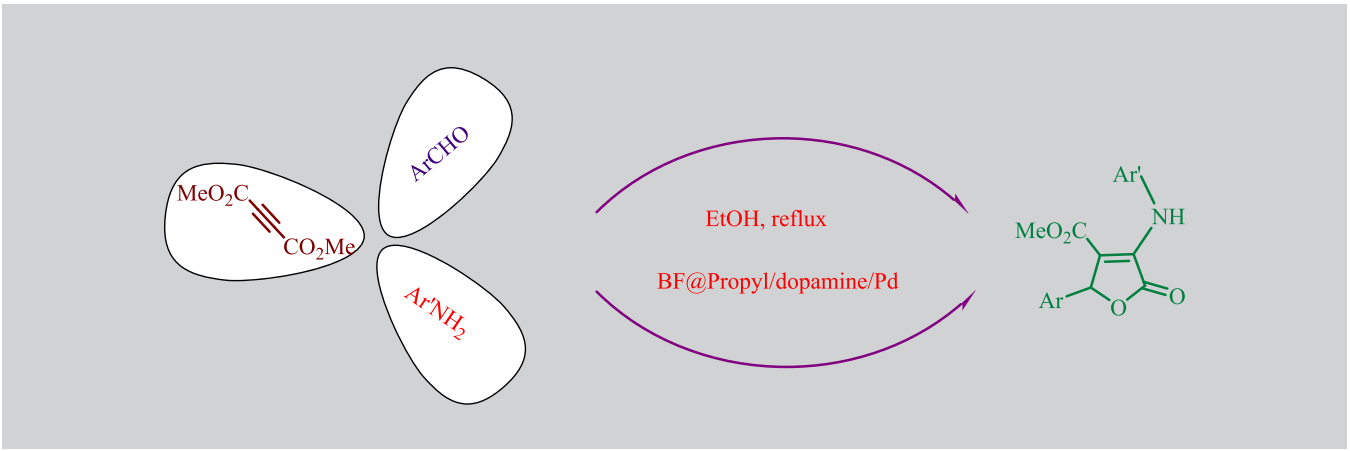
White solid; M.p. 198–201 °C; FT-IR (KBr): ῡ (cm^{-1}): 3177, 3064, 2955, 1710, 1684, 1639, 1526, 1385, 1201, 1105, 1038; ^{1}H NMR (500 MHz, DMSO-d_6): δ_H (ppm) 2.19 (s, 3H, CH_3), 3.50 (s, 3H, OCH_3), 6.77 (s, 1H, CH), 7.12 (m, 3H, Ar-H), 7.51 (m, 4H, Ar-H),7.86 (m, 1H, Ar-H), 11.98 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ_C (ppm) 20.1, 50.9, 54.4, 111.0, 122.0, 122.1, 124.6, 127.3, 129.3, 131.0, 133.6, 135.0, 150.1, 153.6, 156.9, 162.2, 164.2; MS (m/z): 368.1 (M^+), 345.1, 322.1, 277.1, 247.1, 207.1 (100%), 175.1, 134.1, 91.1, 65.1, 41.1.

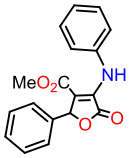
TABLE 1 Optimization of reaction conditions[a]

Entry	Catalyst (g)	Solvent	Temperature (°C)	Time (min)	Yield (%)[b]
1	0.05	-	110	720	15
2	0.05	H_2O/EtOH	100	1440	20
3	0.05	CH_3CN	Reflux	720	40
4	0.05	EtOH	Reflux	65	82
5	0.06	EtOH	Reflux	65	86

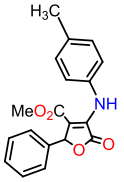
[a]Reaction conditions: benzaldehyde (1 mmol), aniline (1 mmol), dimethyl acetylenedicarboxylate (1 mmol), catalyst, solvent (5 mL).
[b]Isolated yield.

TABLE 2 Synthesis of furan derivatives using BF@Propyl/dopamine/Pd as a green catalyst[a]

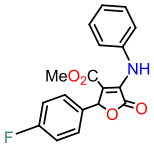




4a (00:65 min, 86%)

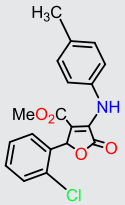


4b (00:55 min, 87%)

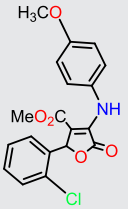


4c (00:55 min, 85%)

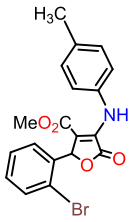
4d (00:65 min, 88%)



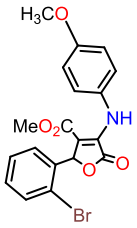
4e (00:60 min, 89%)



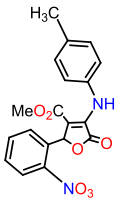
4f (00:65 min, 90%)



4g (00:75 min, 75%)



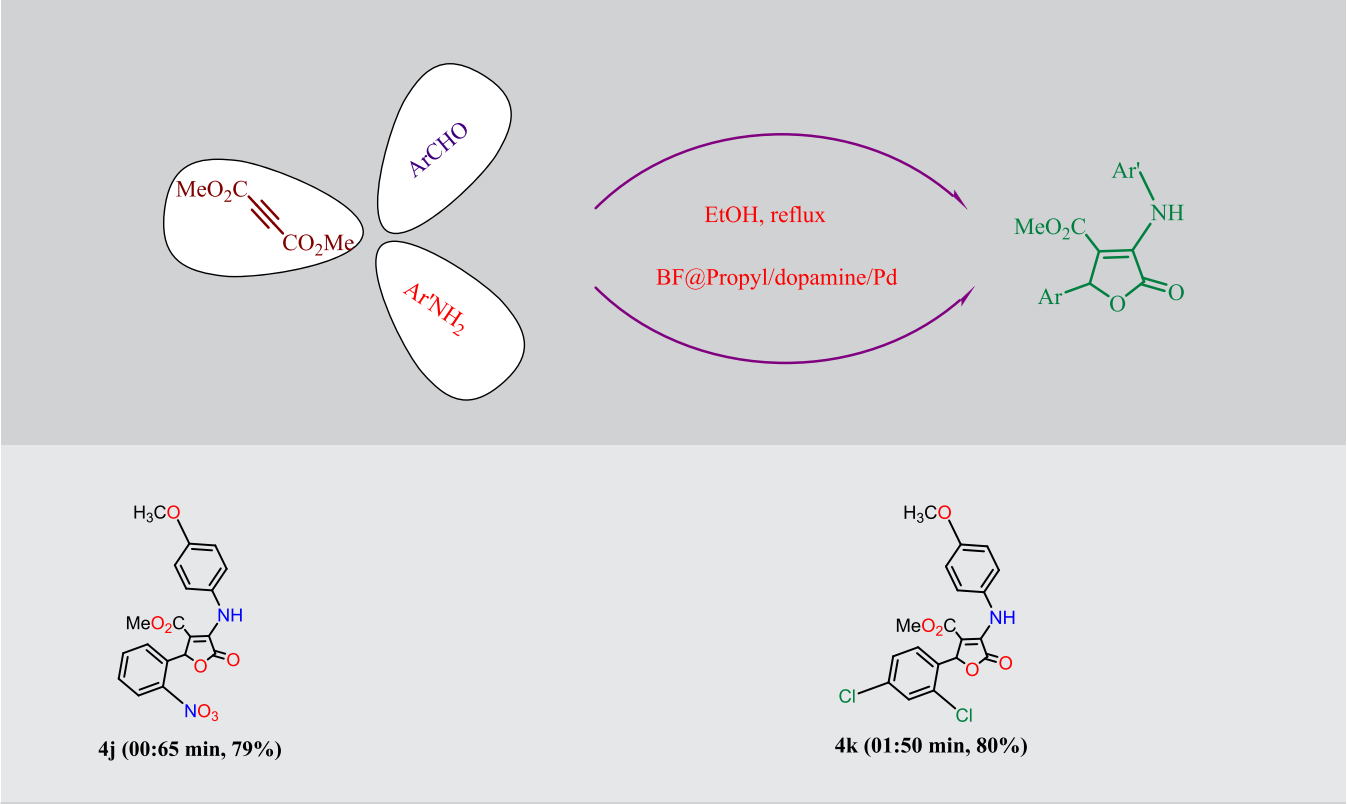
4h (00:80 min, 86%)



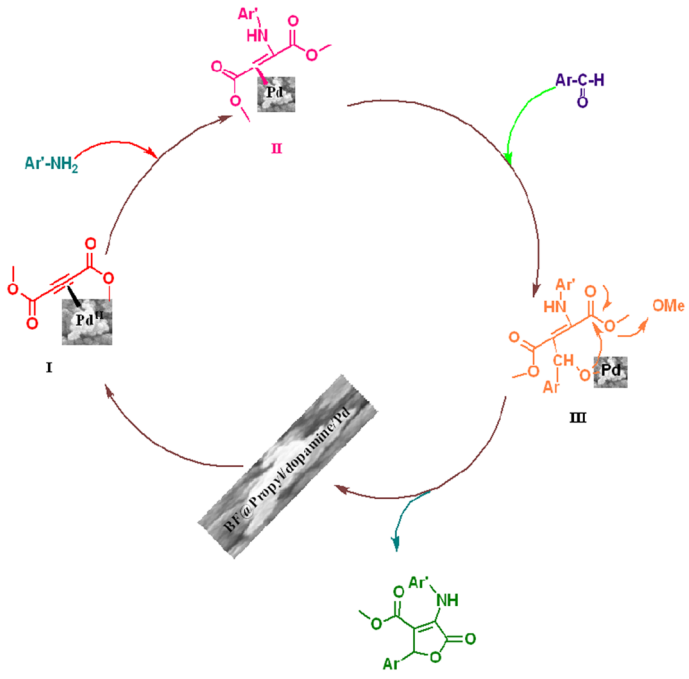
4i (00:80 min, 85%)

(Continues)

TABLE 2 (Continued)



[a]Reaction conditions: benzaldehyde (1 mmol), aniline (1 mmol), dimethyl acetylenedicarboxylate (1 mmol), BF@Propyl/dopamine/Pd (0.06 g), EtOH (5 ml), reflux.



SCHEME 3 Proposed mechanism for formation of furans

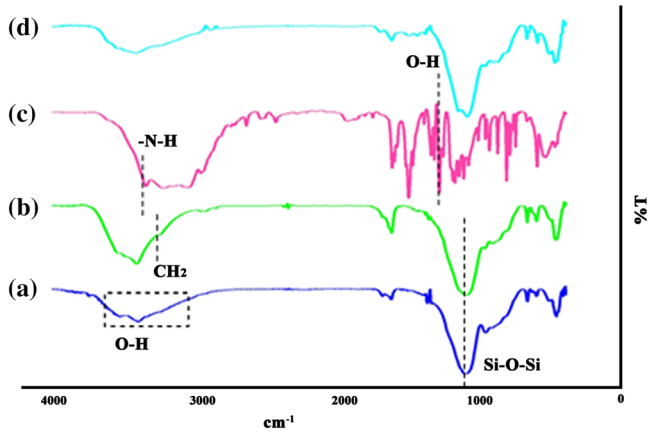


FIGURE 1 FT-IR spectra: a) BF; b) BF@Propyl; c) BF@Propyl/dopamine; d) BF@Propyl/dopamine/Pd 97x67mm (300 x 300 DPI)

2.8.10 | Methyl 4-((4-methoxyphenyl) amino)-2-(2-nitrophenyl)-5-oxo-2,5-dihydrofuran-3-carboxylate 4j

White solid; M.p. 204–207 °C; FT-IR (KBr): ῡ (cm^{-1}): 3428, 3189, 2955, 1712, 1676, 1534, 1514, 1460, 1386, 1255, 1183, 1031; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 3.51 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 6.74 (s, 1H, CH), 6.90 (m, 2H, Ar-H), 7.29 (m, 1H, Ar-H), 7.53 (m, 4H, Ar-H), 7.86 (m, 1H, Ar-H), 12.11 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (ppm) 51.2, 54.7, 55.1, 111.0, 114.0, 124.1, 124.6, 127.4, 128.9, 129.2, 130.9, 133.6, 150.2, 153.5, 157.0, 162.2, 164.1; MS (m/z): 384.1 (M^+), 352.1, 327.1, 300.1, 263.1, 235.1, 207.1, 175.0, 149.1 (100%), 122.1, 77.1, 51.1.

2.8.11 | Methyl 2-(2,4-dichlorophenyl)-4-((4-methoxyphenyl)amino)-5-oxo-2,5-dihydrofuran-3-carboxylate 4 k

White solid; M.p. 230–235 °C; FT-IR (KBr): ῡ (cm^{-1}): 3327, 2954, 2834, 1720, 1686, 1655, 1512, 1434, 1374, 1314, 1247, 1125, 1038; ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 3.57 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 6.69 (s, 1H, CH), 6.89 (m, 2H, Ar-H), 7.22 (m, 2H, Ar-H), 7.34 (m, 2H, Ar-H), 7.43 (m, 1H, Ar-H), 11.91 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ_H (ppm) 51.1, 55.1, 57.9, 107.5, 114.0, 124.1, 128.7, 128.9, 129.6, 130.5, 133.6, 137.5, 155.0, 157.1, 162.4, 164.3; MS (m/z): 407.0 (M^+), 375.0, 340.0, 312.0, 279.0, 244.1, 198.0, 149.1 (100%), 122.1, 83.0, 47.0.

3 | RESULT AND DISCUSSION

In continuing our work on the use of catalysts,[32–37] herein, we focus on further improvement of the catalytic efficiency and the development of new catalyst with high activity. Therefore, this promising procedure was investigated for the synthesis of furans.

Firstly, we raised the reaction effectiveness by using BF@Propyl/dopamine/Pd as a catalyst in different solvents (Table 1, entries 1–4). Therefore, ethanol showed to be the best solvent that afforded the product in 82% yield (Table 1, entry 4). Then, we studied the influence of catalyst loading on the model reaction (Table 1, entries 4–7). The results revealed that a rise in catalyst loading (0.06 g) increases the yield of the product (Table 1, entry 5). Meanwhile, in the case of increasing the catalyst loading to 0.1 g, noticeable change was not detected in the product yield (Table 1, entry 6). On the other hand, a reduction in catalyst loading (0.025 g) reduces the product yield to 45% (Table 1, entry 7). Accordingly, a catalyst loading of 0.06 g of BF@Propyl/dopamine/Pd catalyst in ethanol at reflux condition for 65 min was the best reaction conditions for the synthesis of 5-oxo-2-phenyl-4-(phenylamino)-2,5-dihydrofuran-3-carboxylate (4a) (Table 1, entry 5).

Regarding the optimized reaction conditions, we investigated these conditions for aromatic aldehydes and amines bearing either electron-withdrawing or electron-donating substituents and aromatic amines with dimethyl acetylenedicarboxylate (Scheme 1). The cases in Table 2 obvious that the catalysis progressed well for a wider variety of aryl aldehydes and aromatic

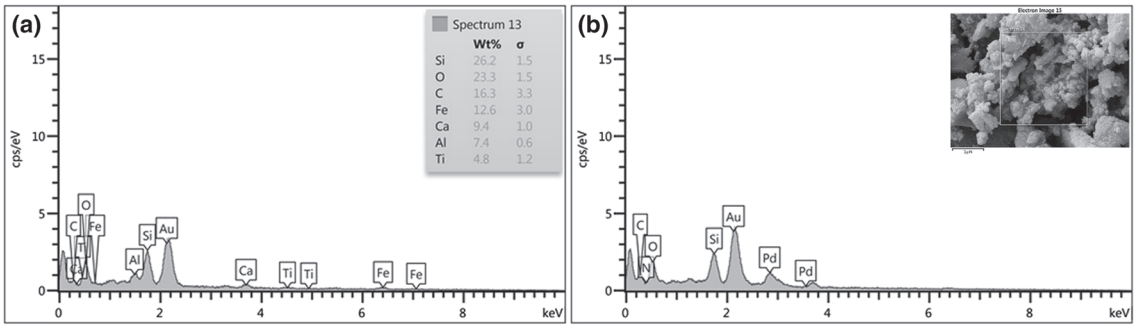


FIGURE 2 EDX spectrum: a) BF; b) BF@Propyl/dopamine/Pd

amines, given that the corresponding furan to be in high yields.

We have suggested a plausible mechanism for the synthesis of furan derivatives in the presence of BF@Propyl/dopamine/Pd as a green catalyst (Scheme 3).

TABLE 3 Atomic compositions of BF and BF@Propyl/dopamine/Pd particles determined by EDX

Samples/ Elements	BF (Atomic%)	BF@Propyl/ dopamine/Pd (%)
C	16.3	1.9
O	23.3	22.6
Fe	12.6	trace
Ti	4.8	trace
Al	7.4	trace
Ca	9.4	trace
Si	26.2	24
Pd	-	51.5

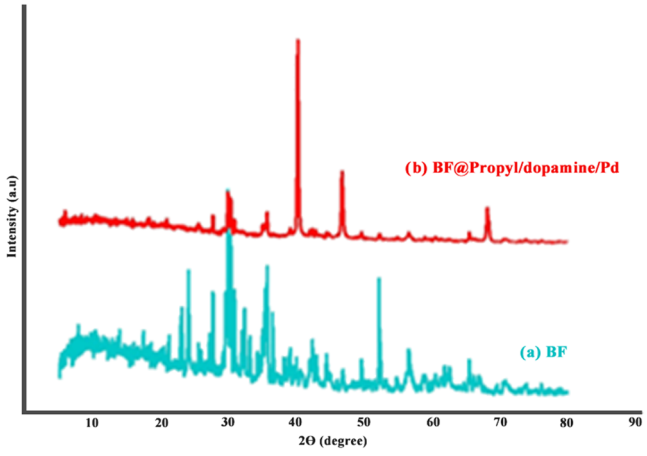


FIGURE 3 XRD patterns: a) BF; b) BF@Propyl/dopamine/Pd

Primary, dimethyl acetylenedicarboxylate, which is activated by palladium (intermediate I), is attacked by amines and intermediate II is formed. Subsequently, aldehyde and intermediate II reacted together and resulted in the intermediate III, then the intramolecular ringing reaction occurred with the oxygen attack to the carbonyl group and the exit of the OMe molecule and finally the product formed.

The results of the IR spectrum of the catalyst (BF@Propyl/dopamine/Pd) are shown in Figure 1. From the spectrum of BF (a), the characteristic peaks of O-H at about 3000–3650 cm^{-1} were observed, and the absorption peak at about 1120 cm^{-1} was connected with Si-O-Si groups. The spectrum (b) corresponds to BF@$(CH_2)_3$-Cl. The peak in the region 2959 cm^{-1} is related to the methylene groups, which represented the successful reaction of (3-chloropropyl)triethoxysilane with a basalt fiber substrate. In spectrum c, N-H peaks appear in the region of 3350 cm^{-1}, besides, wide absorption peak at 1350–2750 cm^{-1} is related to the -OH groups. Another absorption band at 1344 cm^{-1} and 1358 cm^{-1} are related to the C-N and C-O groups of dopamine, respectively, and indicate a successful reaction of dopamine with BF@$(CH_2)_3$-Cl.

The decrease in peak intensity (d) in the 3350 cm^{-1} region denoted that the BF@Propyl/dopamine/Pd coating had been successfully appended onto the BF surface.

Figure 2 (a,b) is a spectrum of EDX basalt fiber (BF) and catalyst (BF@Propyl/dopamine/Pd). Figure 2 (a) shows the presence of O, C, Fe, Ca, Al, Ti and Si elements on the basalt fiber substrate. Also, in Table 3 exhibits a composition of 26.2 atomic% Si, 9.4% Ca, 4.8% Ti, 12.6% Fe, and 7.4% Al, which confirmed that the basalt fibers contains diverse metal oxides.

The EDX peaks in Figure 2(b) confirms that the positioning of the palladium particles on the basalt fiber substrate. The EDX is only a surface analytical

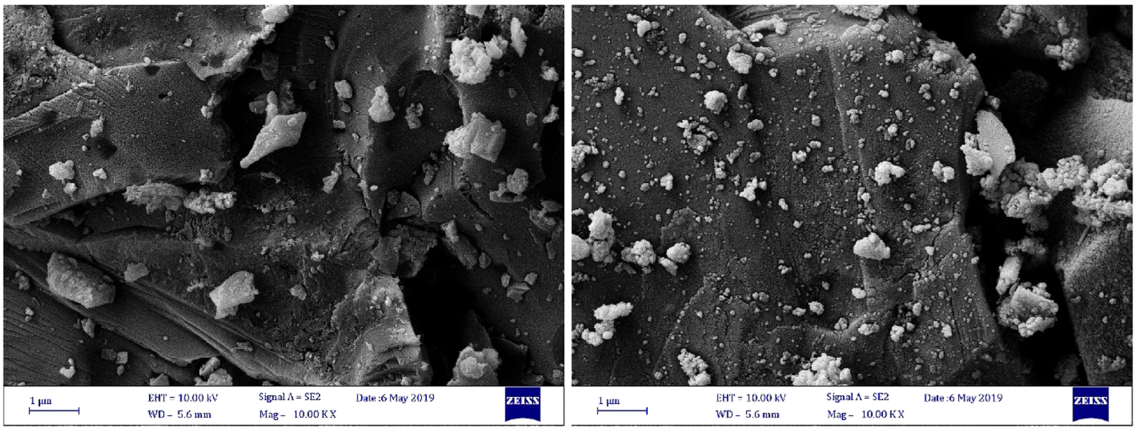


FIGURE 4 Morphology and particle size: a) BF; b) BF@Propyl/dopamine/Pd

procedure and, hence, the relative concentrations of the components may vary depending on the position of the surface.

Figure 3 presents the XRD patterns of the catalyst (BF@Propyl/dopamine/Pd). The corresponding XRD spectra have been investigated in the range of 2θ between 5–80 °C. The peaks at 2θ values of 40.0, 46.6 and 68.4 were related to palladium particles on the BF substrate.

Scanning electron microscopy (SEM) was used to obtain information on the surface morphology of the basalt fiber and the catalyst synthesized. In the SEM images of Figure 4(a), the basalt fiber shows plate shape. The observed tiny particles on the BF substrate show the presence of palladium particles (Figure 4(b)).

Thermal weight analysis (TGA) was performed to illustrate the thermal stability of the BF@Propyl/dopamine/Pd catalyst (Figure 5). The first weight loss occurs at temperatures below 100 °C, which may be related to the residual water and solvents used during catalyst synthesis. Subsequent weight loss was related to palladium removal and occurred in the temperature range of 100–145 °C. Propyl groups attached to the surface of the basalt fiber also decomposed in the temperature range of 150–100 °C. The temperature drops in the range of 450–350 °C is also related to dopamine. Finally, the last layer (basalt fiber) was decomposed in the temperature range of 470–600 °C. According to these results, the catalyst was stable to a very high-temperature range and has been shown to be attributed to the strong interaction of dopamine with the basalt fiber surface, which prevents the catalyst from decomposing rapidly at low temperatures.

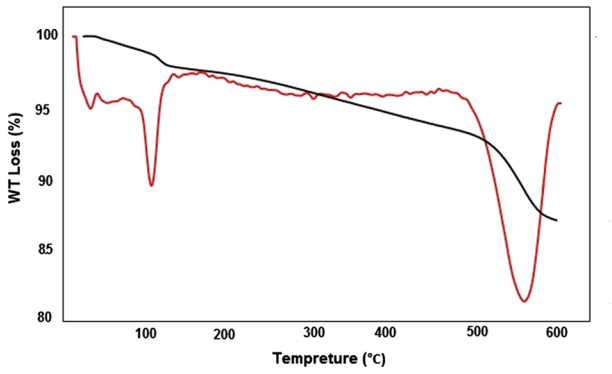


FIGURE 5 TGA curve of BF@Propyl/dopamine/Pd

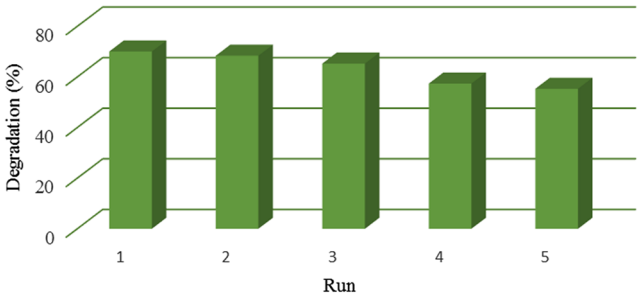


FIGURE 6 Recyclability test of BF@Propyl/dopamine/Pd

In this respect, the recovery and reusability of BF@Propyl/dopamine/Pd were inquired into the reaction of benzaldehyde (1.0 mmol), aniline (1.0 mmol), acetylenedicarboxylate (1.0 mmol) in EtOH under reflux conditions using 0.06 g of the catalyst. At the end of the experiment, BF@Propyl/dopamine/Pd was readily separated from the reaction mixture using a filter, washed several times with warm deionized water and acetone and dried at 100 °C. Then, the recovered catalyst was reused for a subsequent fresh batch of the reaction under similar conditions.

The BF@Propyl/dopamine/Pd can be reused up to the fifth cycle with a minor decrease in yield indicating its catalytic efficiency (see Figure 6).

4 | CONCLUSION

Basalt fiber can be considered as eco-friendly and non-hazardous materials. It is not a new material, but its applications are surely innovative in many industrial and economic fields, because of its good mechanical, chemical and thermal performances.

Basalt fiber as an eco-friendly catalyst has resulted in good to excellent yields of desired furan products.

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SUPPORTING INFORMATION

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