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KF/CP NPS promoted synthesis of lactones through the reaction of OH-acids with activated acetylenes

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Abstract: The reaction between propiolate and various OH-acids such as phenol, 1-naphthol, 2-naphthol, 8-hydroxyquinoline, 1,6-dihydroxynaphthalene, cathechol, hydroquinone, or resorcinol in the presence of catalytic amounts of KF/Clinoptilolite nanoparticles leads to lactone derivatives in good yields.

Keywords: Propiolate, Phenol, 1-naphthol, 2-naphthol, 8-hydroxyquinoline, 1,6-dihydroxynaphthalene.

Introduction

The lactones are an important structure unit in natural products and intermediates in organic synthesis. There has been considerable work on the synthesis of these compounds due to the discovery of many naturally occurring cytotoxic or antitumor agents. Although this ring system has been the objective of synthestic projects in a number of laboratories [1-3], the number of basically different approaches is not large. Multicomponent reactions are very significant in organic synthesis because of the creation of carbon-carbon and carbon-hetero atom bonds in one pot [4-6]. Some advantages of these reactions include easy and clean procedures, producing of high yield bond formation, consuming of low time and energy, and low costs are among [7]. On the past few years, chemists have been informed about the environmental conditions and performing the reaction in green conditions.

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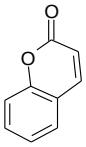
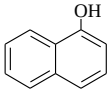
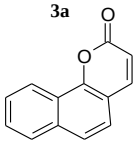
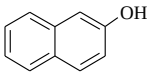
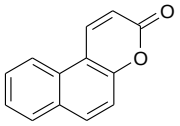
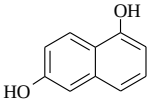
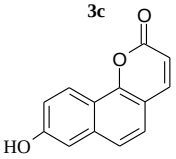
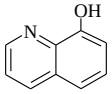
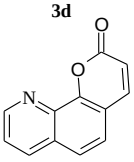
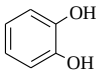
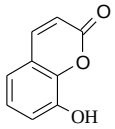
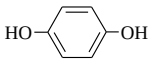
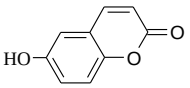
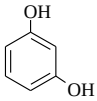
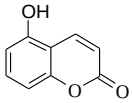
Therefore, they are attempted to expand new synthetic procedures, reaction conditions, and employing of materials that decrease the dangers to persons and the environment. Organic solvents are hazardous because they are frequently volatile liquids and employed alot. Therefore, in recent years, performing organic reactions under solvent-free conditions is interest because of high yields, easy separation of product and catalyst, low costs, mild reaction conditions and low pollution [8-10]. Chemistry of heterocyclic compounds has been studied in several subjects such as natural products, biologically active agrochemicals, pharmaceutical agents and organic materials [11]. KF/CP that is used as a new natural and economical solid base synthesized from putting Potassium fluoride on clinoptilolite as a new natural and inexpensive solid base system [12-20]. Clinoptilolite is a natural zeolite with a high internal surface area. It is precious because of its high replacing capability for cations mainly for K+. Therefore, more free fluoride anions act as good base. In contrast, the preparation of clinoptilolite (KF/CP) is very easy without the need for any pre-activation [21-23]. Herein

We now report a synthesis of lactone derivatives **3** through the reaction of propiolate with naphtholes in the presence of catalytic amount of KF/CP NPs. Our results are summarized in Table **1**.

Table 1. Reaction of propiolate with phenols in the presence of KF/CP NPs

Entry	Starting materials	Product	Yield (%)
1	 **1a**	 **3a**	**93**
2	 **1b**	 **3b**	**94**
3	 **1c**	 **3c**	**90**
4	 **1d**	 **3d**	**85**
5	 **1e**	 **3e**	**86**
6	 **1f**	 **3f**	**80**
7	 **1g**	 **3g**	**88**
8	 **1h**	 **2h**	**84**

The reaction of phenol (**1a**) with propiolate in the presence of catalytic amount of KF/CP NPs at room temperature under solvent-free conditions lead to the fused lactone derivative **3a** in 93% yield (see Table 1). No other compound was obtained from the residue by column chromatography. The structure of the product was deduced from its elemental analyses and its IR, ^{1}H NMR, ^{13}C NMR, and mass spectral data.The ^{1}H NMR spectrum of **3a** exhibited one singlets identified as olefinic (δ = 7.01 ppm) protons along with multiplets (δ = 6.65, 7.23, 7.31, and 7.48 ppm) for the aromatic protons. The ^{13}C NMR spectrum of **3a** showed eleven distinct resonances in agreement with the proposed structure.The first step in these reactions is optimization of the reaction conditions. For this reason, we selected the reaction between phenol **1**, methyl propiolate **2a** as a model. For achieving to the best conditions for generating of lactone derivative **3a**, we changed solvent, catalyst, amount of catalyst and temperature until the best outcome is achieved. The reaction was tested without a catalyst and showed these reactions have very low yield without catalyst. A number of catalysts for example CM-ZnO, CuO-NPs, KF/CP-NPs, ZnO-NPs and TiO_2-NPs were tested for achieving to the best catalyst (Table 2).

Also, some solvents such as CH_2Cl_2, CH_3CN, H_2O, toluene and solvent-free conditions was examined for selecting the best solvent for these reactions. Different temperatures were tested for the model reaction and the results are shown in the Table **2**.

As shown in the Table **2**, in the solvent-free conditions, product have high yield than other solvents. In the CH_3CN and toluene, product have similar yield than to solvent-free conditions but both of two solvents are organic and toxic.

Table 2: Effect of solvent, catalyst and temperature on the formation of compound **4a**

Entry	Catalyst	Solvent	Temp.	Yield (%)
1	KF/CP (NPs)	CH_3CN	50	78
2	KF/CP (NPs)	CH_3CN	80	80
3	KF/CP (NPs)	Solvent-free	r.t.	80
4	**KF/CP (NPs)**	**Solvent-free**	**50**	**90**
5	KF/CP (NPs)	Solvent-free	80	92
6	ZnO-NPs	H_2O	r.t.	35
7	ZnO-NPs	H_2O	50	47
8	ZnO-NPs	CH_3CN	50	65
9	ZnO-NPs	Solvent-free	r.t.	58
10	**ZnO-NPs**	**Solvent-free**	**50**	**75**
11	ZnO-NPs	Solvent-free	80	78
12	TiO_2-NPs	toluene	50	68
13	TiO_2-NPs	CH_3CN	50	75
14	**TiO_2-NPs**	**Solvent-free**	**50**	**80**
15	TiO_2-NPs	Solvent-free	80	80

16	Fe_3O_4-MNPs	H_2O	50	65
17	Fe_3O_4-MNPs	CH_3CN	50	78
18	Fe_3O_4-MNPs	toluene	50	75
19	**Fe_3O_4-MNPs**	**Solvent-free**	**50**	**82**
20	**CuO-NPs**	**Solvent-free**	**50**	**70**
21	CuO-NPs	Solvent-free	80	70

Between the catalyst, KF/CP NPs is the best catalyst for these reactions. KF/CP-NPs are basic catalyst that prepared very easily according to the reported article. The morphology of synthesized the KF/CP-NPs were carried out by scanning electron microscopy images (SEM) Figure 1.

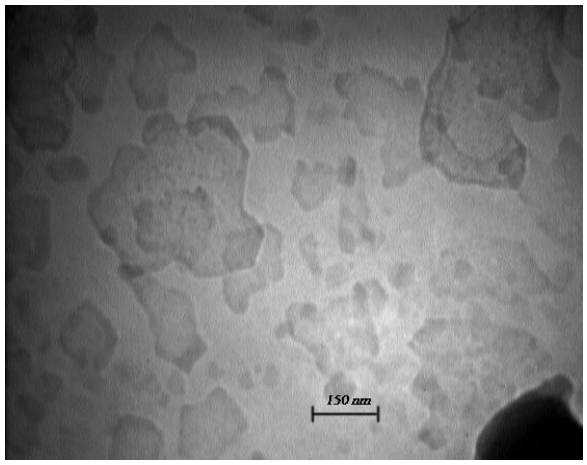


Fig. 1. SEM image of KF/CP NPs[24]

X-ray diffraction patterns (XRD) was used for calculating of the size of prepared KF/CP-NPs (Figure 2). The average crystallite size (D) for KF/CP-NPs was calculated based on peak with the strongest intensity using the Debye–Scherrer's equation ($D=K\lambda/\beta cos\theta$); where D is the grain size, □ is full-width at half-maximum or half-width (FWHM) in radians and h is the position of the maximum of diffraction peak, *K* is the so-called shape factor (0.89), □ is Bragg's diffraction angle and □ is the X-ray wavelength used (1.5406 A˚ for CuK_α). Particles size of KF/CP has been found to be 41 nm.

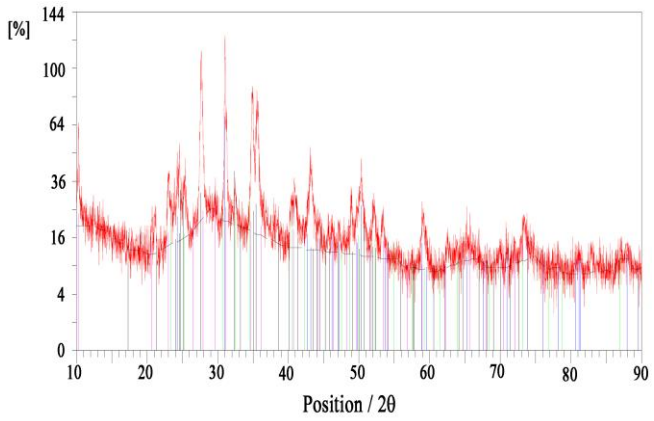


Fig. 2. XRD spectra of KF/CP NPs [24]

The amount of catalyst is changed from 10 to 25%. When the amount of catalyst is increased from 10 to 25%, the yield of reaction didn't show any considerable increase. Consequently, 10% (w/w) KF/CP-NPs was selected as optimum amount. According to results, the optimum condition for formation of compound **3a** are 10 mol% KF/CP-NPs as a catalyst, 50^{o}C temperature and solvent-free conditions. These conditions are tested for other reactions that are shown in Table**1**.

The reusability is one of the significant properties of this catalyst. After the reaction was complete, ethyl acetate is poured in the mixture of reactions and catalyst is separated by filteration. The catalyst was then washed with ethyl acetate, air-dried, and employed directly under the same conditions without further purification. It was shown that the catalyst could be employed for five runs without considerable decreasing in the yield of product and its catalytic activity (Table 3).

Table 3: Reuse of KF/CP-NPs for the Synthesis of **3a**

	Cycle				
	1	2	3	4	5
Yield (%)	90	90	90	87	87

Conclusion

In summary, the reaction between propiolate and phenols in the presence of catalytic amounts of KF/CP NPs leads to fused lactone derivatives in excellent yields. The presented one-pot reaction carries the advantage that not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification.

Experimental

M.p.: *Electrothermal-9100* apparatus; uncorrected. IR Spectra: *Shimadzu IR-460* spectrometer. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectra: Bruker DRX-500 AVANCE instrument; in $CDCl_3$ at 500.1, 125.7, and 202.4 MHz, resp.; δ in ppm, *J* in Hz. EI-MS (70 eV): Finnigan-MAT-8430 mass spectrometer, in *m/z*. Elemental analyses (C, H, N) were performed with a Heraeus CHN-O-Rapid analyzer.

All chemicals were obtained from *Fluka* and were used without further purification. Alkylisatins were prepared according to the literature procedure [20].

*Typical procedure for the synthesis of **3a**:*

To a stirred solution of **1a** (0.19 g, 2 mmol) and propiolate **2a** (0.28 g, 2 mmol) in 10 mL dry ether was added drop wise 0.02 g KF/CP NPs (10 mol%) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the residue was separated by silica gel column chromatography (Merck 230-400 mesh) using *n*-hexane-EtOAc (4:1) as eluent to give **3a**.

*Compound **3a**:*

Yellow oil; yield 0.38 g, 93%. IR (KBr) (ν_{max}/cm^{-1}): 1735 and 1650 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.72 (3 H, s, OMe), 6.65 (1 H, d, $^{3}J_{HH}$ =7.9 Hz, CH), 7.01 (1 H, s, CH), 7.23 (1 H, dd, $^{3}J_{HH}$ = 7.9 Hz, $^{3}J_{HH}$ = 7.5 Hz, CH), 7.31(1 H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 7.5 Hz, CH), 7.48 (1 H, d, $^{3}J_{HH}$ =7.8 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 52.6 (OCH_3), 111.2 (CH), 122.1 (CH), 123.1 (CH), 123.5 (C), 124.3 (CH), 130.6 (CH), 138.2 (C), 153.5 (C), 165.3 (C=O), 166.5 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 204 (M^+, 12), 189 (17), 160 (47), 145 (73), 144 (36), 132 (100), 91 (14), 76 (68), 59 (42). Anal. Calcd for $C_{11}H_8O_4$ (204.2): C, 64.71; H, 3.95%. Found: C, 65.18; H, 3.99%.

*Compound **3b**:*

Brown crystals, mp 176-178 °C, yield 0.48 g, 94%. IR (KBr) (ν_{max}/cm^{-1}): 1715 and 1616 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.02 (3 H, s, OMe), 6.94 (1 H, s, CH), 7.59 (1 H, dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 6.9 Hz, CH), 7.62 (1 H, dd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 5.1 Hz CH), 7.63 (1 H, d, $^{3}J_{HH}$ = 5.1 Hz, CH), 7.81 (1 H, d, $^{3}J_{HH}$ = 6.3 Hz, CH), 8.10 (1 H, d, $^{3}J_{HH}$ = 6.9 Hz, CH), 8.46 (1 H, d, $^{3}J_{HH}$ = 6.3 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 53.2 (OCH_3), 111.4 (CH), 118.2 (C), 121.7 (CH), 122.5 (CH), 122.9 (C), 124.5 (CH), 127.2 (CH), 127.6 (CH), 129.2 (CH), 134.8 (C), 143.2 (C), 151.7 (C-O), 159.9 (C=O), 164.5 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 5), 251 (22), 223 (100), 195 (38), 135 (56), 113 (84), 109 (54), 55 (78). Anal. Calcd for $C_{15}H_{10}O_4$ (254.2): C, 70.86; H, 3.96%. Found: C, 70.40; H, 3.81%.

*Compound **3c**:*

Green powder, mp 113-115 °C, yield 0.46 g, 90%. IR (KBr) (ν_{max}/cm^{-1}): 1724 and 1620 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.06 (3 H, s, OMe), 6.59 (1 H, s, CH), 7.46 (1 H, d, $^{3}J_{HH}$ = 8.1 Hz, CH), 7.55 (1H, dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HH}$ = 6.1 Hz, CH), 7.64 (1 H, dd, $^{3}J_{HH}$ = 7.2 Hz, $^{3}J_{HH}$ = 8.1 Hz, CH), 7.77 (1 H, d, $^{3}J_{HH}$ = 8.4 Hz, CH), 7.92 (1 H, d, $^{3}J_{HH}$ = 6.1 Hz, CH), 8.02 (1 H, d, $^{3}J_{HH}$ = 8.4 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 53.5 (OCH_3), 110.1 (CH), 115.5 (CH), 117.3 (CH), 123.3 (C), 126.1 (CH), 127.9 (CH), 128.1 (CH), 129.4 (C), 130.9 (C), 134.6 (CH), 145.9 (C), 154.9 (C), 159.5 (C=O), 167.8 (C=O) ppm. MS (EI, 70 eV): *m/z* (%) = 254 (M^+, 10), 251 (45), 223 (100), 135 (50), 113 (84), 109 (65), 55 (75). Anal. Calcd for $C_{15}H_{10}O_4$ (254.2): C, 70.86; H, 3.96%. Found: C, 70.39; H, 3.82%.

*Compound **3d**:*

Orange powder, mp 187-189 °C, yield 0.46 g, 85%. IR (KBr) (ν_{max}/cm^{-1}): 3435 (OH), 1712 and 1617 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.89 (3 H, s, OMe), 6.67 (1 H, s, CH), 7.27 (1 H, d, $^{4}J_{HH}$ = 3.2 Hz, CH), 7.29 (1 H, dd, $^{3}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 3.2 Hz, CH), 7.50 (1 H, d, $^{3}J_{HH}$ = 8.5 Hz, CH), 7.96 (1 H, d, $^{3}J_{HH}$ = 8.7 Hz, CH), 8.45 (1 H, d, $^{3}J_{HH}$ = 8.5 Hz, CH), 9.34 (1 H, s, OH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 52.6 (OCH_3), 111.3 (CH), 114.2 (C), 114.4 (CH), 120.5 (CH), 121.9 (C), 123.0 (CH), 124.7 (CH), 124.9 (CH), 124.9 (C), 134.9 (C), 139.7 (C), 151.7 (C), 159.9 (C=O), 164.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 270 (M^+, 20), 242 (100), 239 (26), 211 (78), 155 (100), 126 (42), 77 (26). Anal. Calcd for $C_{15}H_{10}O_5$ (270.2): C, 66.67; H, 3.73%. Found: C, 66.91; H, 3.65%.

*Compound **3e**:*

Pale yellow crystals, mp 155-157 °C, yield 0.44 g, 86%. IR (KBr) (ν_{max}/cm^{-1}): 1714 and 1619 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.91 (3 H, s, OMe), 7.2 (1 H, s, CH), 7.35 (1 H, d, $^3J_{HH}$ = 8.5 Hz, CH), 7.45 (1 H, dd, $^3J_{HH}$ =8.5 Hz, $^3J_{HH}$ = 6.7 Hz, CH), 7.50 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH), 8.15 (1 H, d, $^3J_{HH}$ = 6.7 Hz, CH), 8.78 (1 H, d, $^3J_{HH}$ = 7.2 Hz, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 52.8 (OCH_3), 112.7 (CH), 116.9 (C), 117.6 (CH), 122.1 (CH), 127.9 (C), 129.4 (C), 136.1 (CH), 137.95 (C), 148.2 (CH), 148.2 (CH), 150.4 (C), 159.5 (C=O), 164.4 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 255 (M^+, 5), 224 (100), 195 (45), 128 (65), 109 (54), 77 (24), 59 (78), 31 (52). Anal. Calcd for $C_{14}H_9NO_4$ (255.2): C, 65.88; H, 3.55%. Found: C, 65.50; H, 3.46%.

*Compound **3f**:*

Brown oil, yield 0.35 g, 80%. IR (KBr) (ν_{max}/cm^{-1}): 3440 (OH), 1739 and 1645 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 3.78 (3 H, s, OMe), 6.30 (1 H, br s, OH), 6.68 (1 H, d, $^3J_{HH}$ =8.3 Hz, CH), 6.89 (1 H, s, CH), 7.20 (1 H, dd, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 7.4 Hz, CH), 7.48 (1 H, d, $^3J_{HH}$ =7.4 Hz, CH) ppm. ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 53.4 (OCH_3), 104.8 (CH), 109.5 (CH), 120.7 (CH), 123.0 (C), 125.3 (CH), 129.6 (C) 131.9 (C) 146.9 (C), 163.9 (C=O), 166.5 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 220 (M^+, 15), 189 (100), 160 (45), 119 (80), 31 (100), 60 (25), 77 (10). Anal. Calcd for $C_{11}H_8O_5$ (220.2): C, 60.01; H, 3.66%. Found: C, 60.41; H, 3.50%.

*Compound **3g**:*

Yellow powder, mp 117-119 °C, yield 0.39 g, 88%. IR (KBr) (ν_{max}/cm^{-1}): 3440 (OH), 1712 and 1640 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.78 (3 H, s, OMe), 6.67 (1 H, d, $^3J_{HH}$ = 6.5 Hz, CH), 6.79 (1 H, dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 4.4 Hz CH), 6.82 (1 H, d, $^4J_{HH}$ = 4.4 Hz, CH), 6.95 (1 H, s, CH), 7.71 (1 H, br s, OH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 114.3 (CH), 116.5 (CH), 118.3 (C), 127.9 (CH), 129.4 (C), 150.5 (C), 151.1 (CH), 154.3 (C), 163.3 (C=O), 168.1 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 220 (M^+, 10), 189 (100), 160 (26), 119 (78), 31 (100), 60 (42), 77 (26). Anal. Calcd for $C_{11}H_8O_5$ (220.2): C, 60.01; H, 3.66%. Found: C, 60.54; H, 3.54%.

*Compound **3h**:*

Yellow oil; yield 0.32 g, 84%. IR (KBr) (ν_{max}/cm^{-1}): 1694 and 1596 (C=O). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.32 (1 H, d, $^3J_{HH}$ = 6.2 Hz, CH), 6.35 (1 H, dd, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.2 Hz, CH), 6.34 (1 H, d, $^3J_{HH}$ = 6.6 Hz, CH), 6.98 (1 H, s, CH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 103.4 (CH), 107.5 (CH), 117.6 (CH), 122.1 (C), 125.3 (C), 130.6 (CH), 137.9 (C), 146.9 (C), 159.3 (C=O), 167.7 (C=O) ppm. MS (EI, 70 eV): *m*/*z* (%) = 188 (M^+, 15), 119 (85), 69 (45), 77 (26), 45 (100). Anal. Calcd for $C_{10}H_4O_4$ (188.1): C, 63.84; H, 2.14%. Found: C, 63.53; H, 2.26%.

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