J. Chem. Sci. Vol. 126, No. 4, July 2014, pp. 1081–1089.

Convenient synthesis of naphthopyrans using montmorillonite K-10 as heterogeneous catalyst

RAHMAN HOSSEINZADEH[a,*], MARYAM MOHADJERANI[b], MOHAMMAD JAVAD ARDESTANIAN[a], MOHAMMAD REZA NAIMI-JAMAL[c] and ZAHRA LASEMI[d]

[a]Faculty of Chemistry, Department of Organic Chemistry, University of Mazandaran, Babolsar, Iran
[b]Department of Molecular and Cell Biology, Faculty of Basic Sciences, University of Mazandaran, Babolsar, Iran
[c]Department of Chemistry, Iran University of Science & Technology, Naarmak, 16846-11367 Tehran, Iran
[d]Department of Chemistry, Firoozkooh Branch, Islamic Azad University, Firoozkooh, Iran
e-mail: r.hosseinzadeh@umz.ac.ir

MS received 23 December 2013; revised 14 March 2014; accepted 9 April 2014

Abstract. A simple and mild procedure for the synthesis of different naphthopyrans providing high yields in a short reaction time was reported. The reaction of propargylic alcohols with α- or β-naphthol and dihydroxy naphthalenes in the presence of montmorillonite K-10 was studied. This reaction afforded high yields of the corresponding naphthopyrans. In addition, a number of new phenylene and biphenylen-linked bisnaphthopyrans were synthesized providing excellent yields via the one-pot reaction of bis-propargyl alcohols with β-naphthol.

Keywords. Naphthopyran; propargylic alcohols; naphthol; montmorillonite K-10.

1. Introduction

Naphthopyrans, also known as benzochromenes are widely found in nature.[1] These compounds have been shown to have a wide range of significant biological and pharmacological properties, such as cancer chemopreventive activity,[2] and anti-viral activity against the hepatitis B virus.[3] These compounds are also interesting substances due to their photochromic properties.[4] This photochromic behaviour is the result of a photoinduced reversible opening of the pyran ring that converts the colorless form (the 'closed form') into a highly conjugated coloured form (the 'open form') (scheme 1). Therefore, naphthopyran derivatives have a wide variety of applications such as ophthalmic plastic lenses, solar protective glasses, electronic display systems, optical switches, and temporary or permanent memories.[5]

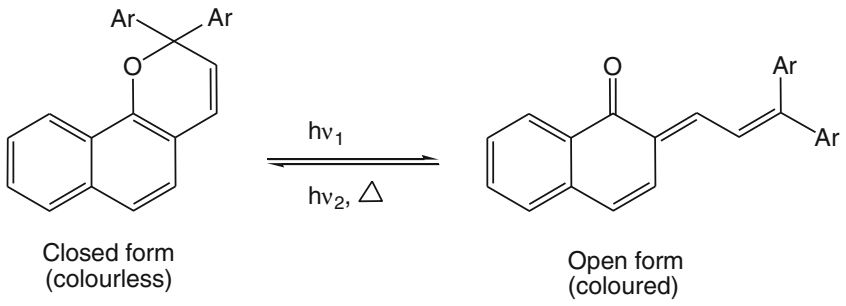
Several synthetic approaches to naphthopyrans have been reported. These methods include the catalyzed condensation of naphthols with propargylic alcohol by *p*-toluenesulfonic acid in solid phase,[6] acidic alumina in toluene,[7] *p*-toluenesulfonic acid in the presence of $(MeO)_3CH$ as a dehydrating agent,[8] and by indiumtrichloride tetrahydrate under solvent-free ball-milling conditions.[9] As in other methods, multistep strategies initiating from chromanones,[10] via Grignard reactions on benzocoumarins followed by dehydration[11] and reaction of 1-bromonaphthalene-2-ol with 3-methylbut-2-enal over organolithium[12] have been reported. In addition, cycloaddition of naphthol to α, β-unsaturated aldehydes in refluxing pyridine[13] or catalyzed by ethylenediamine diacetate[14] have also been reported. However, there is still a demand for general methods that can efficiently provide naphthopyran rings with various substituents.

The present study reports a very smooth procedure for the synthesis of different naphthopyrans containing phenyl, ferrocenyl and fluorenyl substituents by using montmorillonite K-10 as a suitable catalyst (scheme 2).

2. Experimental

Melting points were determined with a Stuart Scientific SMP1, or an Electrothermal 9100 apparatus and are uncorrected. Infrared (IR) spectra were recorded with a Bruker Vector 22 FT-IR spectrometer using potassium bromide pellets. 400 MHz ^{1}H NMR and 100 MHz ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometer and 500 MHz ^{1}H NMR and 125 MHz ^{13}C NMR spectra were recorded on a Bruker Avance DRX

*For correspondence



Scheme 1. Photochromic reaction of naphthopyrans.

500 spectrometer. The chemical shifts are reported in ppm (δ-scale) relative to internal TMS and coupling constants are reported in Hertz (Hz). CHN analyses were done with a CHN Elemental Analyzer LECO 600. The progress of the reactions was checked by thin-layer chromatography (TLC). Silica gel (70–230 mesh) was used for column chromatography.

2.1 *General procedure for the preparation of propargyl alcohols (**2**)*

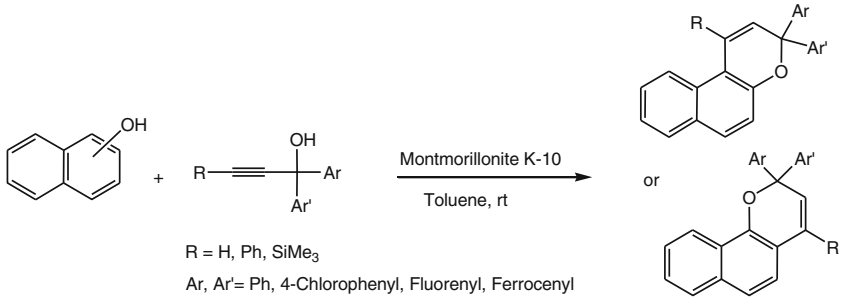
To a stirred solution of an acetylenic compound (32 mmol) in dry ether (50 mL) was gradually added a solution of 1.7 M *n*-BuLi in hexane (18 mL, 30 mmol) during 0.5 h at -10°C under argon. Stirring was continued for 1 h at the same temperature. The resulting acetylide solution was added dropwise to a stirred solution of a ketone (28 mmol) in dry ether (100 mL) at −10°C under argon. The reaction mixture was then allowed to warm up to room temperature. After completion of the reaction as monitored by TLC, water (50 mL) was added and the reaction mixture was extracted with ether (3 × 30 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration, the solution was concentrated under reduced pressure and the residue was recrystallized from *n*-hexane/dichloromethane to yield the desired propargyl alcohol (**2**).

2.1a *1,1,3-Triphenylprop-2-yn-1-ol (**2c**)*: Yield: 84%; M.p. 79–81°C;[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69–7.72 (*m*, 4H), 7.52–7.55 (*m*, 2H), 7.28–7.40 (*m*, 9H), 2.89 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.00, 131.79, 128.70, 128.34, 128.33, 127.76, 126.06, 122.41, 91.68, 87.25, 74.85.

2.1b *1-Ferrocenyl-1,3-diphenylprop-2-yn-1-ol (**2e**)*: Yield: 78%; M.p. 86–88°C;[18] IR (KBr): 3520, 2205, 1510, 1450, 1300 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):δ 7.71 (*d*, J = 8.4 Hz, 2H), 7.60 (*br d*, J = 6.0 Hz, 2H), 7.31–7.42 (*m*, 6H), 4.55 (*br s*, 1H), 4.43 (*br s*, 1H), 4.37 (*s*, 5H), 4.29 (*br s*, 1H), 4.23 (*br s*, 1H), 3.21 (*s*, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.50, 132.14, 128.96, 128.85, 128.50, 128.06, 126.03, 123.24, 97.70, 85.41, 72.27, 69.42, 68.97, 68.78,65.63.

2.1c *9-(2-(Trimethylsilyl)ethynyl)-9H-fluoren-9-ol (**2f**)*: Yield: 80%; M.p. 120–122°C;[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (*d*, J = 7.2 Hz, 2H), 7.60 (*d*, J = 7.2 Hz, 2H), 7.32–7.41 (*m*, 4H), 2.50 (*s*, 1H), 0.17 (*s*, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.06, 139.19, 129.63, 128.55, 124.33, 120.137, 104.82, 88.34, 75.05, -0.16.

2.1d *9-(2-Phenylethynyl)-9H-fluoren-9-ol (**2h**)*: Yield: 85%; Oil;^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (*d*, J = 8.0 Hz, 2H) 7.66 (*d*, J = 8.0 Hz, 2H), 7.38–7.49



Scheme 2. Synthesis of naphthopyrans using propargylic alcohols and naphthols in the presence of montmorillonite K-10 as catalyst.

(*m*, 6H), 7.28–7.33 (*m*, 3H), 2.94 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.23, 139.11, 132.00, 129.74, 128.66, 128.58, 128.24, 124.49, 122.43, 120.29, 89.10, 83.19, 75.24.

2.1e *1,4-Bis(2-bromo-9-hydroxy-9H-fluorene-9-yl)-ethynyl-benzen (**4**)*: 2 eq 2-Bromofluorenone reacted with 1 eq corresponding acetylide. Yield: 90%; M.p. 254–256°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (*d*, *J* = 1.6 Hz, 2H), 7.74 (*dd* , *J* = 8.0, 1.2 Hz, 2H), 7.60 (*d*, *J* = 7.2 Hz, 2H), 7.48–7.55 (*m*, 4H), 7.35–7.44 (*m*, 6H), 7.26 (*s*, 2H), 2.70 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 148.82, 146.72, 138.08, 138.04, 132.84, 131.79, 129.99, 129.02, 127.89, 124.42, 122.40, 122.16, 121.61, 120.34, 90.13, 83.12, 74.96. Anal. calcd for $C_{36}H_{20}O_2Br_2$: C, 67.10; H, 3.13; found: C, 66.52; H, 3.05.

2.1f *4,4'-Bis(2-bromo-9-hydroxy-9H-fluorene-9-yl) -ethynyl-biphenyl (**5**)*: 2 eq 2-Bromofluorenone reacted with 1 eq coresponding acetylide. Yield: 77%; M.p. 266–268°C; ^{1}H NMR (400 MHz, acetone-d_6): δ = 7.93 (*d*, *J* = 1.2 Hz, 2H) 7.80 (*d*, *J* = 6.8 Hz, 2H), 7.75 (*d*, *J* = 8.0 Hz, 2H), 7.55–7.67 (*m*, 6H), 7.42–7.51 (*m*, 10H), 2.86 (*s*, 2H). ^{13}C NMR (100 MHz, acetone-d_6): δ = 150.72, 148.20, 140.26, 138.60, 138.22, 132.57, 132.53, 129.81, 129.13, 127.97, 127.10, 124.86, 122.29, 122.14, 121.57, 120.67, 91.17, 82.36, 74.76. Anal. calcd for $C_{42}H_{24}O_2Br_2$: C, 70.02; H, 3.36; found: C, 69.60; H, 3.28.

2.2 *General procedure for the preparation of propargylic alcohols containing terminal acetylenic group (**2, R=H**)*

Trimethylsilylethynyl alcohols (23.4 mmol) were reacted with K_2CO_3(19.35 g, 140.28 mmol) in MeOH (90 mL) and THF (90 mL). After completion of the reaction, the solvent was evaporated and water (100 mL) and ethyl acetate (100 mL) were added to the residue. After separation of the organic layer, the solvent was evaporated to give a solid, which was crystallized from *n*-hexane/dichloromethane to obtain the propargylic alcohols **2**.

2.2a *1, 1-Diphenylprop-2-yn-1-ol (**2a**)*: Yield: 80%; Oil;[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.61 (*m*, 4H), 7.30–7.34 (*m*, 4H), 7.23–7.29 (*m*, 2H), 3.02 (*s*, 1H), 2.87 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.43, 128.27, 127.82, 126.01, 86.45, 75.92, 75.52.

2.2b *1-(4-Chlorophenyl)-1-phenylprop-2-yn-1-ol (**2b**)*: Yield: 75%; Oil;[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60–7.63 (*m*, 2H), 7.55–7.58 (*m*, 2H), 7.31–7.39 (*m*, 5H), 3.11 (*s*, 1H), 2.91 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.05, 143.05, 133.75, 128.46, 128.44, 128.12, 127.51, 125.93, 85.96, 75.92, 73.85.

2.2c *1-Ferrocenyl-1-phenylprop-2-yn-1-ol (**2d**)*: Yield: 78%; M.p. 90–92°C;[18] IR (KBr): 3520, 3250, 2350, 1518, 1350, 1100 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 ((*pseudo br s*, 2H,(7.26–7.32 (*m*, 3H), 4.48 (*br s*, 1H), 4.18–4.32 (*m*, 8H), 3.19 (*s*, 1H), 2.81 (*s*, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.83, 128.10,127.74, 125.55, 96.67, 86.87, 71.24, 69.11, 68.55, 68.35, 65.18.

2.2d *9-Ethynyl-9H-fluoren-9-ol (**2g**)*: Yield: 83%; M.p. 107–109°C;[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (*dd*, *J* = 8.8, 0.8 Hz, 2H), 7.64 (*dd*, *J* = 8.8, 0.8 Hz, 2H), 7.44 (*dt*, *J* = 9.2, 1.6 Hz, 2H), 7.38 (*dt*, *J* = 9.2, 1.5 Hz, 2H), 2.60 (*s*, 1H), 2.50 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 146.60, 139.13, 129.89, 128.66, 124.27, 120.28, 83.85, 74.59, 71.41.

2.3 *General procedure for the preparation of naphthopyrans*

A mixture of a propargylic alcohol (1.0 mmol), β-naphthol (1.0 mmol), and montmorillonite K-10 (0.4 g) in toluene (10 mL) was reacted at room temperature. After the disappearance of the starting materials (monitored by TLC), ethyl acetate (20 mL) was added and the reaction mixture was filtered. The filtrate was then transferred into a separatory funnel, and washed with water (50 mL). The organic phase was dried over anhydrous Na_2SO_4 and filtered and the solvent was evaporated in a rotary evaporator. The crude product was purified by passing it over a column of silica gel, using a mixture of n-hexane and ethyl acetate as the eluent (4:1). All known products were characterized by comparison of their physical and spectroscopic data with those in literature.

2.3a *3,3-Diphenyl-[3H]-naphtho[2,1-b]pyran (**3a**)*: Yield: 97%; M.p. 161–163°C;[6] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (*d*, *J* = 8.4 Hz, 1H), 7.74 (*d*, *J* = 8.0 Hz, 1H), 7.68 (*d*, *J* = 8.8 Hz, 1H), 7.47–7.53 (*m*, 5H), 7.25–7.36 (*m*, 8H), 7.23 (*d*, *J* = 9.2 Hz, 1H), 6.30 (*d*, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.56, 144.86, 129.83, 129.35, 128.52, 128.10,

127.72, 127.53, 127.02, 126.62, 123.61, 121.33, 119.54, 118.36, 114.00, 82.55.

2.3b *3-(4-Chlorophenyl)-3-phenyl-[3H]-naphtho [2,1-b]pyran (**3b**)*: Yield: 85%; M.p. 157–159°C;[22] IR (KBr): 3476, 3386, 2926, 1631, 1451, 812, 759, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (*d*, *J* = 8.4 Hz, 1H), 7.74 (*d*, *J* = 8.0 Hz, 1H), 7.69 (*d*, *J* = 8.8 Hz, 1H), 7.43–7.50 (*m*, 5H), 7.26–7.37 (*m*, 7H), 7.20 (*d*, *J* = 8.8 Hz, 1H), 6.24 (*d*, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.34, 144.42, 143.36, 133.47, 130.02, 129.76, 129.40, 128.55,128.52, 128.27, 128.22, 127.71, 127.21, 126.90,126.75, 123.76, 121.31, 119.96, 118.23, 114.00, 82.09.

2.3c *1,3,3-Triphenyl-[3H]-naphtho[2,1-b]pyran (**3c**)*: Yield: 98%; M.p. 210–212°C;[23] ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (*d*, *J* = 8.0 Hz, 1H), 7.73 (*d*, *J* = 8.0 Hz, 1H), 7.62 (*d*, *J*= 8.0 Hz, 4H), 7.41 (*t*, *J* = 4.5 Hz, 6H), 7.30–7.36 (*m*, 4H), 7.22–7.27 (*m*, 3H), 7.16 (*d*, *J* = 6.8 Hz, 1H), 7.05–7.08 (*m*, 1H), 6.27 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 152.56, 144.48, 141.29, 137.18, 130.85, 130.26, 129.80, 129.40, 128.46, 128.37,128.02, 127.64, 127.49, 127.10, 126.48, 125.03, 123.14, 118.75, 116.57, 82.12.

2.3d *3-(Ferrocenyl)-3-phenyl-[3H]-naphtho[2,1-b]pyran (**3d**)*: Yield: 95%; M.p. 145–147°C;[4d] ^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (*d*, *J* = 11.2 Hz, 1H), 7.69–7.76 (*m*, 2H), 7.56 (*d*, *J* = 10.0 Hz, 2H), 7.36–7.49 (*m*, 1H), 7.19-7.34 (*m*, 6H), 6.43 (*d*, *J* = 13.1 Hz, 1H), 4.41 (*s*, 1H), 4.26 (*s*, 2H), 4.16 (*s*, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.11, 145.35, 129.87, 129.71, 129.25, 128.56, 127.73, 127.33, 127.08, 126.61, 125.98, 123.47, 121.25, 118.23, 113.58, 95.22, 80.04, 69.26, 68.86, 68.28, 66.86.

2.3e *3-(Ferrocenyl)-1,3-diphenyl-[3H]-naphtho[2,1-b]pyran (**3e**)*: Yield: 70%; M.p. 193–195°C; IR (KBr): 3070, 2928, 2859, 1626, 952, 844, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68–7.74 (*m*, 5H), 7.34–7.42 (*m*, 5H), 7.23–7.27 (*m*, 2H), 7.17–7.20 (*m*, 2H), 6.98–7.07 (*m*, 2H), 6.51 (*s*, 1H), 4.15–4.23 (*m*, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.06, 143.67, 141.67, 136.31, 130.62, 130.15, 129.85, 129.08, 128.58, 128.36,128.08, 127.56, 127.46, 127.38, 126.55, 126.45, 124.97, 123.02, 118.72, 116.44, 95.45, 79.53, 69.62, 68.87, 68.80, 67.79, 67.63. Anal. calcd for $C_{35}H_{26}FeO$: C, 81.08; H, 5.06; found: C, 81.06; H, 5.07.

2.3f *1'-Trimethylsilyl-spiro[9H-fluorene-9,3'-[3'H]-naphtho[2,1-b]pyran] (**3f**)*: Yield: 66%; M.p. 171–173°C; IR (KBr): 3070, 2927, 1626, 1074, 952, 844, 745, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.22 (*d*, *J* = 8.4 Hz, 1H), 7.84 (*d*, *J* = 8.0 Hz, 1H), 7.68 (*dd*, *J* = 10.8, 3.6 Hz, 3H), 7.54 (*tt*, *J* = 8.4, 1.4 Hz, 1H), 7.38–7.45 (*m*, 5H), 7.16–7.20 (*m*, 3H), 6.32 (*s*, 1H), 0.34 (*s*, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.26, 146.36, 139.69, 137.69, 136.10, 131.08, 130.10, 129.79, 129.20, 128.62, 128.31, 125.36, 125.28, 125.02, 123.63, 120.65, 120.01, 119.25, 83.53, 1.45. Anal. calcd for $C_{28}H_{24}SiO$: C, 82.96; H, 5.97; found: C, 82.94; H, 5.99.

2.3g *Spiro[9H-fluorene-9,3'-[3'H]-naphtho[2,1-b] pyran] (**3g**)*: Yield: 70%; M.p. 200–203°C;[6] ^1H NMR (400 MHz, $CDCl_3$):δ 8.11 (*d*, *J* = 8.0 Hz, 1H), 7.82 (*d*, *J* = 8.0 Hz, 1H), 7.68–7.70 (*m*, 3H), 7.55–7.59 (*m*, 3H), 7.48 (*d*, *J* = 12.0 Hz, 1H), 7.39–7.45 (*m*, 3H),7.24–7.28 (*m*, 2H), 7.07 (*d*, *J* = 8.0 Hz, 1H), 5.74 (*d*, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.10, 147.49, 139.03, 129.93, 129.82, 129.47, 128.67, 128.37, 126.74, 125.21, 124.87, 123.66, 121.16, 120.27, 120.11, 118.40, 112.98, 85.50.

2.3h *1'-Phenyl-spiro[9H-fluorene-9,3'-[3'H]-naphtho [2,1-b]pyran] (**3h**)*: Yield: 75%; M.p. 243–245°C;[9,24] IR (KBr): 3053, 2925, 1623, 1447, 1240, 1000, 820, 740 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$):δ 7.83 (*d*, *J* = 8.0 Hz, 1H), 7.79 (*d*, *J* = 8.8 Hz, 1H), 7.70 (*d*, *J* = 6.8 Hz, 2H), 7.49 (*d*, *J* = 8.0 Hz, 2H), 7.40–7.44 (*m*, 2H), 7.36-7.39 (*m*, 3H), 7.33–7.35 (*m*, 2H), 7.28–7.32 (*m*, 2H), 7.24 (*d*, *J* = 8.0 Hz, 1H), 7.14–7.20 (*m*, 3H), 5.97 (*s*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.58, 146.39, 141.24, 139.61, 138.22, 130.65, 130.58, 129.96, 129.79, 128.63, 128.51, 128.32, 127.90, 127.63, 126.45, 126.14, 125.29, 125.18, 123.38, 120.08, 118.97, 116.49, 84.48.

2.3i *1,4-Bis(spiro[2-bromo-9H-fluorene-9,3'-[3'H]-naphtho[2,1-b] pyran-3-yl]) benzene (**6**)*: Yield: 97%; M.p. 297°C (dec); IR (KBr): 3053, 1620, 1450, 1231, 1007, 815, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.84 (*d*, *J* = 8.0 Hz, 2H), 7.79 (*d*, *J* = 8.8 Hz, 2H), 7.69 (*br s*, 2H), 7.65 (*d*, *J* = 7.6 Hz, 2H), 7.50–7.56 (*m*, 6H), 7.33-7.42 (*m*, 12H), 7.21 (*d*, *J* = 8.8 Hz, 2H), 7.14 (*tt*, *J* = 7.2, 1.3 Hz, 2H), 5.93 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.23, 148.61, 145.84, 140.49, 138.77, 138.35, 138.10, 133.07, 131.01, 130.67, 130.17, 129.70, 128.76, 128.69, 128.61, 128.08, 126.48, 125.33, 125.25, 125.14,123.57, 121.88, 121.41,120.17,

Table 1. Optimization of catalyst and solvent.[a]

Entry	Catalyst	Amount of catalyst (g)	Solvent	Yield (%) of the **3a**
1	*p*-Toluenesulfonic acid	0.4	-	60
2	Amberlyst 15	0.4	-	76
3	Montmorillonite K-10	0.4	-	80
4	Montmorillonite KSF	0.4	-	78
5	Silica gel	0.4	-	Trace
6	Alumina	0.4	-	Trace
7	$(NH_4)_{10}H_2(W_2O_7)_6.xH_2O$	0.4	-	Trace
8	$H_3PW_{12}O_{40}$	0.4	-	30
9	Montmorillonite K-10	0.4	DMSO	Trace
10	Montmorillonite K-10	0.4	THF	Trace
11	Montmorillonite K-10	0.4	CH_3CN	30
12	Montmorillonite K-10	0.4	CH_2Cl_2	70
13	Montmorillonite K-10	0.4	*n*-Hexane	75
14	Montmorillonite K-10	0.4	Toluene	97
15	-	-	Toluene	-
16	Montmorillonite K-10	0.2	Toluene	85
17	Montmorillonite K-10	1.2	Toluene	98

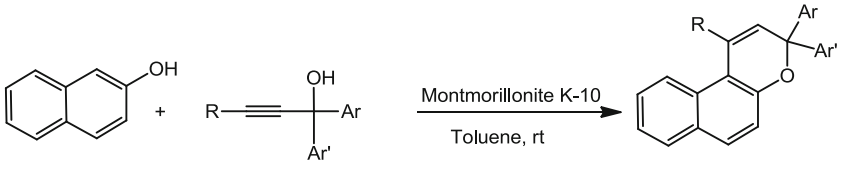
[a]Reaction condition: 1 mmol β-naphtol (**1a**) and 1 mmol 1,1-diphenyl-2-propyn-1-ol (**2a**) were reacted at room temperature for 35 min.

118.76, 116.00, 84.27. Anal. calcd for $C_{56}H_{32}Br_2O_2$: C, 75.01; H, 3.60; found: C, 75.03; H, 3.58.

2.3j *4,4'-Bis(spiro[2-bromo-9H-fluorene-9,3'-[3'H]-naphtho[2,1-b] pyran-3-yl])biphenyl (**7**)*: Yield: 95%; M.p. 249°C (dec); IR (KBr): 3048, 1674, 1621, 1235, 1007, 955, 817, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.79-7.84 (*m*, 4H), 7.65–7.68 (m, 7H),7.56 (*d*, *J* = 0.8 Hz, 4H), 7.32–7.42 (*m*, 12H), 7.13–7.23 (*m*, 7H), 5.95 (*s*, 2H). Anal. calcd for $C_{62}H_{36}Br_2O_2$: C, 76.55; H, 3.73; found: C, 76.59; H, 3.70.

2.3k *2,2-Diphenyl-[2H]-naphtho[2,1-b]pyran (**11**)*: Yield: 60%; Oil;[14] ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (*d*, *J* = 8.4 Hz, 1H), 7.74 (*d*, *J* = 8.4 Hz, 1H), 7.53–7.56 (*m*, 4H), 7.43–7.51 (*m*, 2H), 7.28–7.37 (*m*, 6H), 7.26 (*t*, *J* = 2.4 Hz, 1H), 7.18 (*d*, *J* = 8.0 Hz, 1H), 6.76 (*d*, *J* = 9.6 Hz, 1H), 6.22 (*d*, *J* = 9.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 147.74, 145.20, 134.67, 128.15, 127.65, 127.47, 127.28, 126.86, 126.29, 125.56, 124.71, 124.53, 123.86, 122.02, 120.48, 115.44, 83.19.

2.3l *3,3,9,9-Tetraphenyl-3H,9H-naphtho[2,1-b:6,5-b']dipyran (**12**)*: Yield: 70%; M.p. 228–230°C;[6] ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.55 (*m*, 10H), 7.32–7.36 (*m*, 8H), 7.25–7.29 (*m*, 4H), 7.17 (*d*, *J* = 9.6 Hz, 2H), 7.08 (*d*, *J* = 8.4 Hz, 2H), 6.10 (*d*, *J* = 9.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.81, 144.65, 130.96, 129.01, 128.03, 127.53,



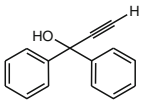
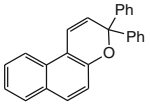
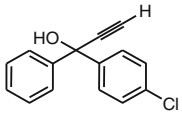
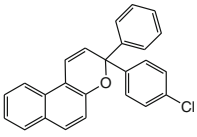
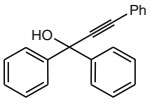
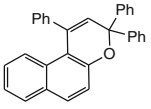
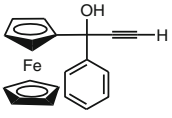
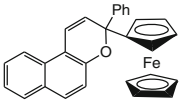
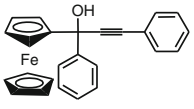
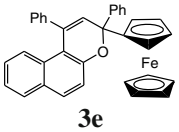
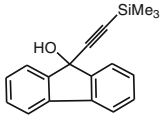
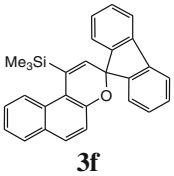
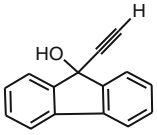
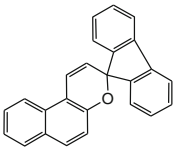
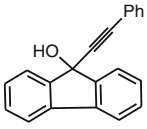
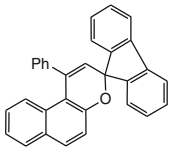
2a: Ar= Ar'= Ph, R= H
2b: Ar= Ph, Ar'= 4-Chlorophenyl, R= H
2c: Ar= Ar'= R= Ph
2d: Ar= Ferrocenyl, Ar'= Ph, R= H
2e: Ar= Ferrocenyl, Ar'= R= Ph
2f: Ar= Ar'= Fluorenyl, R= TMS
2g: Ar= Ar'= Fluorenyl, R= H
2h: Ar= Ar'= Fluorenyl, R= Ph

Scheme 3. Reaction of propargylic alcohols with β-naphthol catalyzed by montmorillonite K-10 in toluene at room temperature.

127.10, 125.71, 124.88, 124.16, 115.90, 114.75, 82.14.

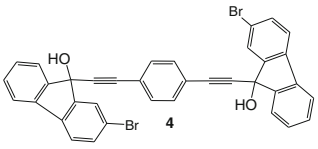
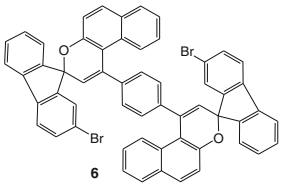
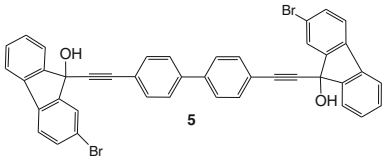
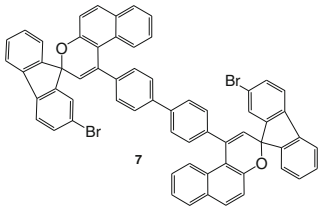
2.3m *1,3,3,6,6,8-Hexaphenyl-3H,6H-naphtho[2,1-b:3, 4-b']dipyran (**13**)*: Yield: 98%; M.p. 250°C; IR (KBr): 3049, 1955, 1615, 1398, 1260, 1191, 1116, 1000, 957 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.65–7.68 (*m*, 8H), 7.25–7.33 (*m*, 22H), 7.03-7.06 (*m*, 2H), 6.73–6.76 (*m*, 2H), 6.24 (*s*, 2H). ^{13}C NMR (100 MHz, $CDCl_3$):δ 144.59, 143.95, 141.27, 137.01, 129.38, 128.45, 128.13, 128.05, 127.60, 127.40, 127.03, 126.82, 125.86, 122.30, 118.80, 82.08. Anal. calcd for $C_{52}H_{36}O_2$: C, 90.14; H, 5.24; found: C, 90.15; H, 5.26.

Table 2. Cycloaddition reactions of propargylic alcohols with β-naphthol (**1**) catalyzed by montmorillonite K-10.

Entry	Propargylic alcohols	Products	Time (min)	Yield (%)[a]
1	 **2a**	 **3a**	45	97
2	 **2b**	 **3b**	120	85
3	 **2c**	 **3c**	30	98
4	 **2d**	 **3d**	30	95
5	 **2e**	 **3e**	120	70
6	 **2f**	 **3f**	120	66
7	 **2g**	 **3g**	120	70
8	 **2h**	 **3h**	120	75

[a]Yields refer to isolated products.

Table 3. Synthesis of some new bis-naphthopyrans by the reaction of bis-acethylenes **4** and **5** with β-naphthol catalyzed by montmorillonite K-10.

Entry	Propargylic alcohol	Naphthopyran	Time (min)	Yield (%)[a]	M.p. (°C)
1	 **4**	 **6**	45	97	297(dec.)
2	 **5**	 **7**	45	95	249(dec.)

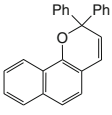
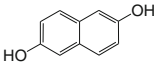
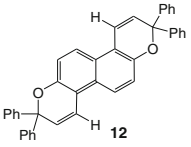
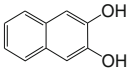
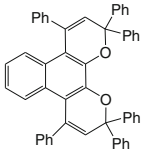
[a] Yields refer to isolated products.

3. Results and discussion

In a model reaction, 1 mmol (0.144 g) β-naphthol (**1a**), 1 mmol (0.208 g) 1,1-diphenyl-2-propyn-1-ol (**2a**), and 0.4 g of a Lewis acid catalyst were ground together for 10 min at room temperature. Different Lewis acids such as *p*-toluenesulfonic acid, amberlyst 15, montmorillonite K-10, montmorillonite KSF, silica gel, alumina, $(NH_4)_{10}H_2(W_2O_7)_6.xH_2O$ and tungstophosphoric acid were investigated. The yields of the products have been summarized in table 1 (entries 1-8). According to these results, montmorillonite K-10 was chosen for this reaction due to its ease of use, availability and low cost and high yield of the product. The model reaction was also repeated in 10 mL of different solvents as shown in table 1 (entries 9-14). A dramatic increase in the yield of **3a** was observed when toluene was taken as reaction media (table 1, entry 14). The amount of the catalyst was also investigated as shown in table 1 (entries 14-17). As it is shown, 0.4 g catalyst for 1.0 mmol of **2a** is sufficient to provide an excellent yield of **3a.** The reaction did not take place in the absence of catalyst (table 1, entry 15).

According to these results, the optimal reaction conditions were chosen as 1.0 mmol of propargylic alcohols, 1.0 mmol of β-naphthol, 0.4 g montmorillonite K-10 stirred in toluene at room temperature (scheme 3).

Table 4. Cycloaddition reactions of propargylic alcohols with α-naphthol and dihydroxy naphthalens catalyzed by montmorillonite K-10.

Entry	Naphthol	Propargyl alcohol	Naphthopyran	Time (min)	Yield (%)[a]	M.p. (°C)
1	 **8**	**2a**	 **11**	120	60	Oil
2	 **9**	**2a**	 **12**	120	70	228-230
3	 **10**	**2c**	 **13**	30	98	250

[a] Yields refer to isolated products.

Table 5. Recycling studies of reaction between β-naphtol (**1a**) and 1,1-diphenyl-2-propyn-1-ol (**2a**) in the presence of montmorillonite K-10 to give product **3a**.

Entry	Cycle	Time (min)	Yield (%)[a]
1	fresh	45	97
2	1	45	95
3	2	45	92
4	3	45	90

[a]Yields refer to isolated products.

Under optimized conditions, the substrate scope was subsequently investigated. The results have been listed in table 2. Both terminal and internal alkynes reacted with β-naphthol smoothly and provided the desired products in excellent yields (table 2, entries 1-3).

It is known that the photochromic properties of the 2*H*-chromenes can be greatly influenced by the nature of the substituents located in the 2-position.[15] Previous works have shown that, for example, when a ferrocenyl group replaces a phenyl group in the 2-position, the photochromic properties are modified.[4d] In order to synthesize benzochromenes substituted by the ferrocenyl group in the 2-position, propargylic alcohols having ferrocenyl group (**2d** and **2e**) were reacted with β-naphthol under optimal conditions to yield the corresponding products **3d** and **3e** in substantial yields (table 2, entries 4-5). Propargylic alcohols bearing fluorenyl moieties (**2f-h**) have also afforded the desired naphthopyran products in good yields (table 2 entries 6-8).

Recently, some interesting results have been obtained on bi-photochromic molecules with two naphthopyrans sharing an aromatic ring linked through the two pyran ring sp^3-C atoms. These molecules have showed a very significant bathochromic shift of the maximum wavelength of absorption of the open form and high colourabilities due to the extension of *p*-conjugation and the opening of both photochromic systems.[16] In order to synthesize a number of new bi-photochromic molecules containing conjugated spacers, bis-propargyl alcohols **4** and **5** were synthesized and reacted with β-naphthol in the presence of montmorillonite K-10. The yields of new naphtopyrans **6** and **7** were excellent as tabulated in table 3.

The reaction of propargylic alcohols with dihydroxynaphthalenes **8**-**10** also provided high yields of the corresponding naphthopyrans **11**-**13** (table 4).

Another interesting feature of this method is that the catalyst can be recovered at the end of the reaction and can be used several times without losing its activity. To recover the catalyst, after completion of the reaction, the mixture was filtered and catalyst was washed with EtOH. After activating the catalyst at 100°C, it was used for further reaction. This process was repeated for three cycles and the yield of product **3a** did not change significantly (table 5).

In order to show the merits and drawbacks of this catalyst, some of our results were compared with other catalysts reported in literature (table 6). As shown in table 6, naphthopyrans **3a**, **3c** and **3g** can be prepared at room temperature and in a short reaction time with excellent yields according to our procedure.

4. Conclusion

The present study presents a practical method for the efficient cyclizations of propargylic alcohols with naphthols catalyzed by montmorillonite K-10 in good to high yields. The advantages of this method includes mild reaction conditions, high yields, short reaction times, easy work-up procedures, and ease of recovering and reusing of the catalyst, which make it a useful method for the preparation of naphthopyrans.

Table 6. Comparison of montmorillonite K-10 with other catalysts for the synthesis of **3a**, **3c** and **3 g**.

Entry	Naphthopyran	Catalyst	Reaction Conditions	Time (h)	Yield (%)	Ref
1	**3a**	Montmorillonite K-10	PhMe /rt	0.75	97	-
2	**3a**	*p*-TsOH/Silica gel	rt	1	56	6
3	**3a**	PPTS/$(MeO)_3CH$	$ClCH_2CH_2Cl$	-	92	8
4	**3c**	Montmorillonite K-10	PhMe /rt	0.5	98	–
5	**3c**	TsOH	Dry PhMe/N_2/rt	2	89	23
6	**3c**	Pentafluorophenyl boronic acid /4 Å MS	CH_2Cl_2/rt	16	97	24
7	**3c**	$InCl_3.4H_2O$	Ball milling at 30 Hz/rt	1	97	9
8	**3g**	Montmorillonite K-10	PhMe /rt	2	70	-
9	**3g**	TsOH	Dry PhMe/N_2/rt	2	44	23
10	**3g**	*p*-TsOH	Dry CH_2Cl_2/rt	2	50	25

Acknowledgements

Financial support of this work from the Research Council of University of Mazandaran is gratefully acknowledged.

References

1. (a) Costa S M O, Lemos T L G, Pessoa O D L, Pessoa C, Montenegro R C and Braz-Filho R 2001 *J. Nat. Prod.* **64** 792; (b) Singh R, Geetanjali G, Chauhan, S M S 2004 *Chem. Biodiv.* **1** 1241; (c) Visentin S, Rolando B, Di Stilo A, Fruttero R, Novara M, Carrbone E, Roussel C, Vanthuyne N and Gasco A 2004 *J. Med. Chem.* **47** 2688
2. Itoigawa M, Ito C, Tan H T W, Okuda M, Tokuda H, Nishino H and Furukawa H 2001 *Cancer Lett.* **174** 135
3. (a) Kawasaki Y, Goda Y and Yoshihira K 1992 *Chem. Pharm. Bull.* **40** 1504; (b) Marec F, Kollarova I and Jegorov A 2001 *Planta. Med.* **67** 127; (c) Ho L K, Don M J, Chen H C, Yeh S F and Chen J M 1996 *J. Nat. Prod.* **59** 330; d) Chung M I, Jou S J, Cheng H C, Lin C N, Ko F N and Teng C M 1994 *J. Nat. Prod.* **57** 313
4. (a) Nakatsuji S 2004 *Chem. Soc. Rev.* **33** 348; (b) Ushakov E N, Nazarov V B, Fedorova O A, Gromov S P, Chebunkova A V, Alfimov M V and Barigelletti F 2003 *J. Phys. Org. Chem.* **16** 306; (c) Hannesschlager P and Brun P 2000 *Appl. Organomet. Chem.* **14** 371; (d) Anguille S, Brun P, Guglielmetti R, Strokach Y P, Ignatin A A, Barachevsky V A and Alfimov M V 2001 *J. Chem. Soc., Perkin Trans* **2** 639
5. (a) Van Gemert B 2000 *Mol. Cryst. Liq. Cryst.* **344** 57; (b) Van Gemert, B. 1999 In *Organic Photochromic and Thermochromic Compounds* J C Crano, R J Guglielmetti (eds.) (New York: Kluwer Academic-Plenum) vol. 1 Chapter 3 pp. 111
6. Tanaka K, Aoki H, Hosomi H and Ohba S 2000 *Org. Lett.* **2** 2133
7. Gabbut C D, Heron B M and Instone A C 2006 *Tetrahedron* **62** 737
8. Zhao W and Carreira E M 2003 *Org. Lett.* **5** 4153
9. Dong Y W, Wang G W and Wang L 2008 *Tetrahedron* **64** 10148
10. Gabbutt C D, Hartley D J, Hepworth J D, Heron B M, Kanjia M and Rahman M 1994 *Tetrahedron* **50** 2507
11. Cottam J and Livingstone R 1965 *J. Chem. Soc.* 6646
12. Talley J J 1983 *Synthesis* 845
13. (a) North J T, Kronenthal D R, Pullockaran A J, Real S D and Chen H Y 1995 *J. Org. Chem.* **60** 3397; (b) Tiabi M and Zamarlik H 1991 *Tetrahedron Lett.* **32** 7251; (c) Calderon-Higginson C, Crombie L, Redshaw S D and Whiting D A 2000 *J. Chem. Soc., Perkin. Trans.* **1** 2491; (d) Lamcharfi E, Menguy L and Zamarlik H 1993 *Synth. Commun.* **23** 3019
14. Lee Y R and Kim Y M 2007 *Helv. Chim. Acta.* **90** 2401
15. (a) Van Gemert B, Bergomi M and Knowles D 1994 *Mol. Cryst. Liq. Cryst.* **246** 67; (b) Anguille S, Brun P and Guglielmetti R 1998 *Heterocycl Commun.* **4** 63
16. (a) Zhao W and Carreira E M 2002 *J. Am. Chem. Soc.* **124** 1582; (b) Zhao W and Carreira E M 2003 U.S. Patent 0078441A1; (c) Coelho P J, Salvador M A, Heron B M and Carvalho L M 2005 *Tetrahedron* **61** 11730
17. Wei L M, Wei L L, Pan W B and Wu M J 2005 *Synlett* **14** 2219
18. Asgari S 2008 M.Sc. Thesis, University of Mazandaran, Babolsar, Iran
19. Dunn J A, Hunks W J, Ruffolo R, Rigby S S, Brook M A and McGlinchey M J 1999 *Organometallics* **18** 3372
20. Saikachi H and Kitagawa T 1969 *Yakugaku Zasshi.* **89** 1626
21. Shapiro S L, Soloway H and Freedman L 1955 *J. Am. Chem. Soc.* **77** 4874
22. Guo K and Chen Y 2009 *Mol. Cryst. Liqu. Cryst.* **501** 62
23. Pozzo J L, Samat A, Guglielmetti R, Dubest R and Aubard J 1997 *Helv. Chim. Acta.* **80** 725
24. McCubbin J A, Nassar C and Krokhin O V 2011 *Synthesis* 3152
25. Demadrille R, Rabourdin A, Campredon M and Giusti G 2004 *J. Photochem. Photobiol. A: Chem.* **168** 143