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Aryl chromanes-Novel methodology via base catalyzed ether rearrangements

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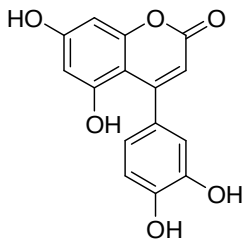
ABSTRACT

A new methodology for the preparation of 4-Aryl chromans is developed via Wittig rearrangement on ethers.

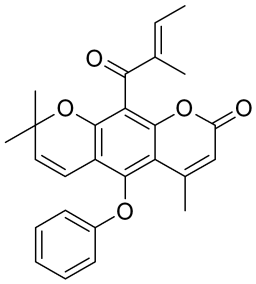
Keywords: Aryl Chroman, ether rearrangement, dehydration, hydrogenation.

INTRODUCTION

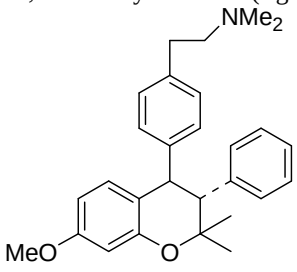
4-Aryl coumarins (neoflavones) are known to exhibit several important biological activities[1-2], such as anti tumor[3], anti-malarial[4], cytotoxic[5], anti-bacterial[6], anti-inflammatory[7], anti-HIV[8], anti-diabetic[9], anti-viral[10], anti-protozoal[11], and SERM. They are widely distributed as natural products, as the family members of flavonoids in Clusiaceae, Fabaceae, Rutaceae, Rubiaceae, Passifloraceae, Asteraceae, and Thelyteridaceae(fig 1).



Coutaregenin(Antidiabetic)



Apetatolide (Antitumour activity)



Levormeloxifene (saheli)
(SERM activity)

Fig –I. Biologically active chromane derivatives

The reported methods for the preparation of 4-arylcoumarins are based on the palladium-catalyzed Suzuki-type coupling reaction or Stille coupling reaction using organoboron[12], organotin[13], organobismuth[14], organozinc[15], organoindium[16], as organo metallic reagents with aryl triflate, halogen, phosphonate, tosylate or N, N-dimethyl carbonate as aryl electrophilic reagents. Recently rhodium [17], nickel [18], palladium [19], copper [20], catalysts were reported for Suzuki-Miyaura coupling, Negishi type coupling, and Heck coupling for the synthesis 4-arylcoumarins,

The other older procedures involved Pechmann or Perkin reaction [21], recently RCM methodology is also described for Aryl chromanes [22].

During our study of witting rearrangement on ethers [23] to prepare t- alcohols (fig-II) prompted us to study the same on cyclic ether.

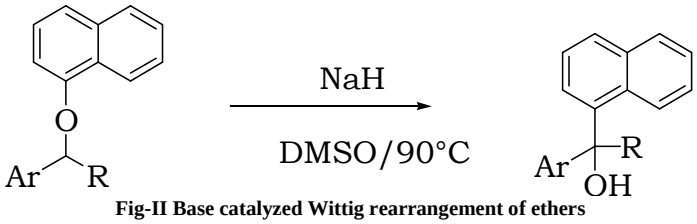
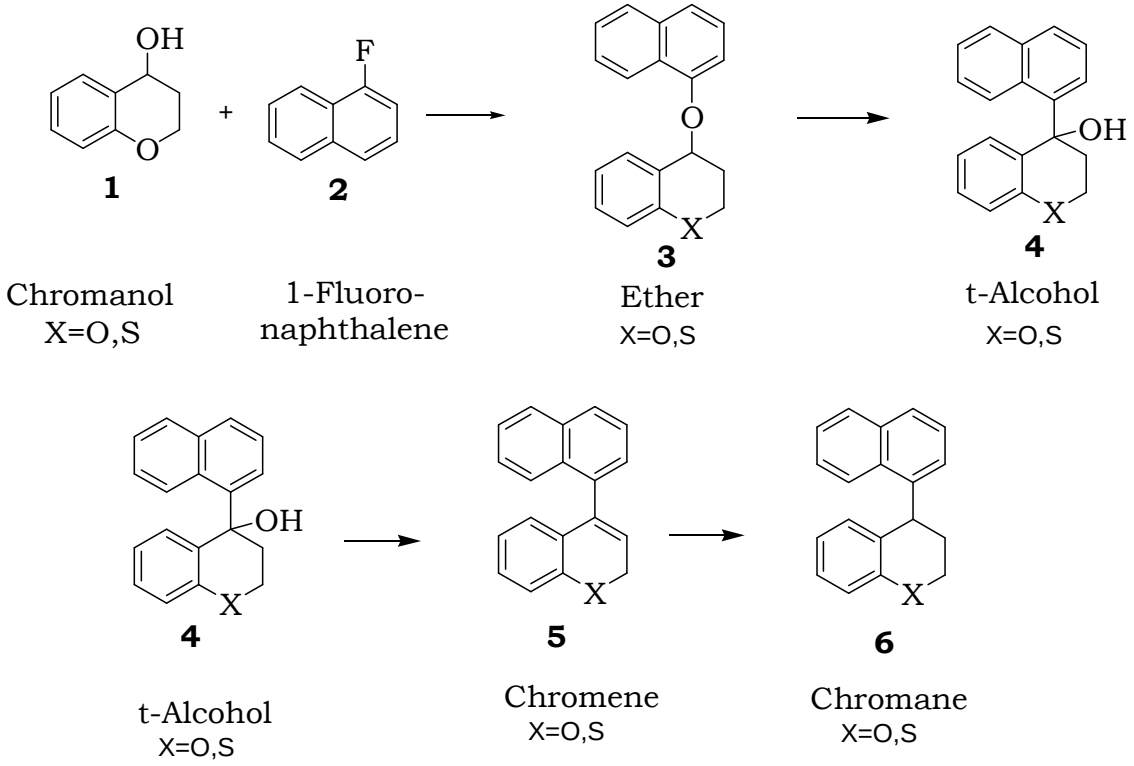


Fig-II Base catalyzed Wittig rearrangement of ethers

The success of base catalyzed Witting rearrangement method proved to be a good method for 4-Napthalen 1-yl chroman(scheme-1)and 4-Napthalen 1-yl- thiochromans



Scheme-1. Preparation of Chromanes

MATERIALS AND METHODS

All solvents were used as commercial anhydrous grade without further purification. 1H (400MHz) and 13C (100MHz) NMR spectra were recorded by using a Bruker 400 Spectrometer with TMS as internal standard. IR spectra were recorded on a PerkinElmer Spectrum 100 FTIR Spectrophotometer as KBr pellets or with the neat products. Mass spectra were recorded on a API 2000 LC-MS/MS-Applied bio-Systems MDS Sciex spectrometer. Microanalysis was performed on a Perkin Elmer-240CHN elemental analyzer. Analytical TLC was conducted on E-Merck 60F254 aluminum-packed plates of silica gel (0.2mm). Developed plates were visualized by using UV light or in an iodine chamber.

Typical procedures and Spectral Characterizations for ethers

To a solution of dimethyl sulfoxide (3 Vol), sodium hydride (60%) (99.0 mmoles) was added alcohol (66.0 mmoles) and fluoro compound (99.0 mmoles) at 25-30°C, then reaction mass heated to 70-80°C, maintained for 4-5 hours, and allowed to cool slowly to 25-30 °C, then dichloromethane 10 Vol and chilled water 10Vol were added, Reaction mixture stirred for 15 minutes, and the layers were separated. The aqueous was extracted again with dichloromethane (2 x 5 Vol). Combined organic layers were washed with water (2 x 5 Vol), dried over anhydrous sodium sulfate and concentrated at 35-40°C to get ether product.

4-(Naphthalen-1-yloxy)-chroman (3a): Yield (78%), Solid M.P-70.8-73.8°C. IR (In KBr):3051.5, 2879.42, 1626.0, 1578.41, 1397, 1267.75 cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.31 (d, 1H, *J* = 8.21 Hz), 7.89 (d, 1H, *J* = 7.98 Hz), 7.57 (m, 6H), 7.12 (d, 1H, *J* = 7.35 Hz), 7.04 (d, 1H, *J* = 7.8 Hz), 7.0 (d, 1H, *J* = 4.1 Hz), 5.61 (t, 1H, *J* = 5.8 Hz), 4.50 (m, 2H), 2.47 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 155.30, 153.14, 134.89, 130.93, 130.10, 127.54, 126.60, 125.79, 125.41, 122.46, 121.27, 120.94, 120.62, 118.12, 117.15, 106.14, 69.24, 62.44, 27.57 ppm;

6-Methyl-4-(naphthalen-1-yloxy)-chroman (3b): Yield (75%), Solid M.P-72-74.2°C. IR (In KBr):3051.8, 2923.11, 1594.8, 1578.57, 1396.43, 1264.02, 1092.05, 1060.94, 771.84cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.38 (d, 1H, *J* = 8.28 Hz), 7.91 (d, 1H, *J* = 8.0 Hz), 7.59 (m, 4H), 7.27 (t, 2H, *J* = 8.72 Hz), 7.14 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 7.59 Hz), 5.64 (t, 1H, *J* = 4.04 Hz), 4.44 (m, 1H), 4.94 (m, 1H), 2.71 (m, 1H), 2.34 (s, 3H), 2.29 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 155.24, 138.67, 133.68, 132.14, 131.64, 130.38, 129.76, 127.62, 127.00, 126.97, 126.96, 126.61, 125.49, 124.58, 123.6, 110.0, 73.95, 67.57, 22.87, 20.92ppm;

6-Ethyl-4-(naphthalen-1-yloxy)-chroman (3c): Yield (76%), Solid M.P-78.1-80.0°C.. IR (In KBr):3055.8, 2935.11, 1598.8, 1588.57, 1386.43, 1264.02, 1092.05, 1060.94, 771.84cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.38 (d, 1H, *J* = 8.28 Hz), 7.91 (d, 1H, *J* = 8.0 Hz), 7.59 (m, 4H), 7.27 (t, 2H, *J* = 8.72 Hz), 7.14 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 7.59 Hz), 5.64 (t, 1H, *J* = 4.04 Hz), 3.44 (m, 1H), 2.94 (m, 1H), 2.71 (m, 1H), 2.34 (s, 3H), 2.29 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 153.24, 134.97, 133.98, 132.14, 131.64, 130.38, 129.76, 127.62, 126.85, 126.77, 126.66, 125.91, 125.49, 122.57, 121.0, 107.0, 72.95, 27.57, 25.5, 22.87, 20.92ppm.

6-Chloro-4-(naphthalen-1-yloxy)-chroman (3d): Yield (70%), Solid M.P-103.3-104.5°C. IR (In KBr):3055.12, 288.43, 1578.7, 1483.2, 139.66, 1265.46, 1095.46, 1095.9, 772.21cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.24 (d, 1H, *J* = 8.25 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.53 (t, 2H, *J* = 7.86 Hz), 7.46 (t, 2H, *J* = 7.64 Hz), 7.36 (s, 1H), 7.28 (d, 1H *J* = 8.5 Hz), 7.04 (d, 1H, *J* = 7.46 Hz), 6.92 (d, 1H, *J* = 8.77 Hz), 5.52 (t, 1H, J = 5.86), 4.42 (m, 2H), 1.47 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 153.76, 152.68, 134.77, 130.11, 129.95, 127.45, 126.53, 126.37, 125.57, 125.39, 1255.18, 122.51, 122.16, 121.0, 118.47, 106.58, 68.17, 62.48, 27.13ppm.

[**6-Fluoro-4-(naphthalen-1-yloxy)-chroman (3e):** Yield (72%), Solid M.P-101-102.3°C.. IR (In KBr):3053.12, 2884.34, 1578.26, 1483.7, 1396.66, 1265.46, 1095.9, 772.21cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.26 (d, 1H, *J* = 8.25 Hz), 7.86 (d, 1H, *J* = 8.0 Hz), 7.41 (m, 4H), 7.0 (s, 1H), 7.03 (d, 1H, *J* = 3.07 Hz), 7.0 (s, 1H), 6.94 (d, 1H, *J* = 4.75 Hz), 5.55 (t, 1H, *J* = 3.6 Hz), 4.39 (m, 2H), 2.31 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 157.86, 155.49, 152.80, 151.20, 134.78, 127.46, 126.54, 125.60, 125.40, 122.18, 122.06, 121.99, 121.07, 118.0, 117.0, 116.8, 116.25, 116.0, 106.6, 69.0, 62.5, 27.31ppm.

2,2-Dimethyl-4-(naphthalen-1-yloxy)-chroman (3f): Yield (81%), Solid M.P-108-110.2°C. (In KBr):3033.3, 2977.14, 1688.8, 1455.8, 1305.7, 1118.9, 895.8, 765.17cm^{-1}. ^1H NMR ($CDCl_3$, 400MHz) δ = 8.29 (d, 1H, *J* = 8.2 Hz), 7.86 (d, 1H *J* = 8.12 Hz), 7.50 (s, 1H7.52 (d, 1H, *J* = 7.7 Hz), 7.48 (d, 1H, *J* = 3.75 Hz), 7.45 (t, 1H, *J* = 4.4 Hz), 7.31 (t, 1H, *J* = 7.54 Hz), 7.04 (d, 1H, *J* = 7.46 Hz), 7.0 (d, 1H, *J* = 7.44 Hz), 6.94 (d, 1H *J* = 8.36 Hz), 5.71 (t, 1H, *J* = 5.78 Hz), 2.4 (m 2H), 1.51 (s, 3H), 1.46 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 152.68, 144.52, 134.59, 129.52, 129.45, 129.31, 128.99, 128.54, 126.0, 125.55, 125.38, 125.12, 125.03, 124.93, 120.82, 117.58, 75.0, 70.8, 47.68, 30.66, 26.64ppm.

4-(Naphthalen-1-yloxy)-thiochroman (3g): Yield (82%), Yellow color liquid. IR (Neat):3053.2, 2924.55, 1577.18, 1396.18, 1235.54, 1091.85 cm^{-1}. . ^1H NMR ($CDCl_3$, 400MHz) δ= 8.25 (d, 1H, *J* = 8.26 Hz), 7.82 (d, 1H, *J* = 8.0 Hz), 7.50 (m, 5H), 7.23 (t, 2H, *J* = 6.64 Hz), 7.0 (d, 2H, *J* = 7.30 Hz), 5.61 (t, 1H, *J* = 5.7 Hz), 3.40 (m, 1H), 2.94 (m, 1H), 2.68 (m, 1H), 2.31 (m, 1H)ppm; cm^{-1}. 1H NMR (CDCl3, 400MHz) δ = 153.29, 135.04, 134.11, 132.44, 131.0, 128.83, 127.73, 127.0, 126.8, 126.76, 126.0, 125.62, 124.40, 122.60, 121.17, 107.32, 73.0, 73.0, 27.49, 22.49 ppm.

6-Methyl-4-(naphthalen-1-yloxy)-thiochroman (3h): Yield (83%), Solid M.P-66.2-68.0°C. IR (In KBr):3051.8, 2923.11, 1594.8, 1578.57, 1396.43, 1264.02, 1092.05, 1060.94, 771.84cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =8.38 (d, 1H, *J* = 8.28 Hz), 7.91 (d, 1H, *J* = 8.0 Hz), 7.59 (m, 4H), 7.27 (t, 2H, *J* = 8.72 Hz), 7.14 (d, 1H, *J* = 8.4 Hz), 7.11 (d, 1H, *J* = 7.59 Hz), 5.64 (t, 1H, *J* = 4.04 Hz), 3.44 (m, 1H), 2.94 (m, 1H), 2.71 (m, 1H), 2.34 (s, 3H), 2.29 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 153.24, 134.97, 133.98, 132.14, 131.64, 130.38, 129.76, 127.62, 126.85, 126.77, 126.66, 125.91, 125.49, 122.57, 121.0, 107.0, 72.95, 27.57, 22.87, 20.92 ppm.

6,8-Dimethyl-4-(naphthalen-1-yloxy)-thiochroman (3i): Yield (80%), Solid M.P-78.2-80.0C. IR (In KBr): 3052.8, 2925.11, 1584.8, 1588.57, 1496.43, 1264.02, 1092.05, 1070.94, 771.84cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.40 (d, 1H, *J* = 8.30 Hz), 7.92 (d, 1H, *J* = 8.0 Hz), 7.60 (t, 2H, *J* = 8.28 Hz), 7.54 (t, 2H, *J* = 7.72 Hz), 7.18 (s, 1H), 7.14 (d, 1H, *J* = 7.52 Hz), 7.09 (s, 1H), 5.6 (t, 1H, *J* = 3.33 Hz), 3.49 (m, 1H), 3.0 (m, 1H), 2.76 (m, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 2.29 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 153.26, 135.0, 134.66, 133.15, 132.0, 131.21, 129.90, 129.48, 127.63, 126.66, 125.59, 125.47, 122.64, 120.94, 106.98, 73.3, 27.17, 22.31, 20.87, 20.11ppm.

2,2-Dimethyl-4-phenoxy-chroman (8f): Yield (68%), Solid M.P-85.2-88.0°C.IR (In KBr): 3055.3, 2988.14, 1678.8, 1466.8,, 1482.7, 1252.9, 922.8, 751.17cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.42 (d, 1H, *J* = 7.57 Hz), 7.36 (t, 1H, *J* = 7.74 Hz), 7.28 (d, 1H, *J* = 7.82 Hz), 7.24 (d, 1H, *J* = 7.47 Hz), 7.05 (t, 3H, *J* = 8.35 Hz), 6.96 (t, 1H *J* = 7.46 Hz), 6.88 (d, 1H, *J* = 8.16 Hz), 5.47 (t, 1H, *J* = 5.88 Hz), 2.25 (m, 2H), 1.46(s, 3H), 1.40(s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ=154.04, 145.04, 129.77, 128.74, 128.55, 127.70, 126.57, 124.54, 119.8, 117.24, 74.51, 43.54, 39.92, 29.96, 24.24ppm.

4-Phenoxy-thiochroman (8g): Yield (64%), Solid M.P-75.1-79.8°C. IR (In KBr):3059.21, 2952.61, 1594.22, 1481.62, 1225.10, 1031.51, 921.43, 748.19cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.37 (m, 3H), 7.23 (d, 2H, *J* = 6.2 Hz), 7.08 (m, 4H), 5.39 (t, 1H, *J* = 5.68 Hz), 3.39 (m, 1H), 3.25 (m, 1H), 2.90(m, 1H), 2.61 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ=157.26, 133.72, 132.0, 130.7, 129.6, 128.5, 126.7, 124.11, 121.31, 116.6, 72.20, 27.15, 22.67

6-Methyl-4-phenoxy-thiochroman (8h): Yield (69%), Solid M.P-84.2-87.2°C. IR (In KBr):3015.2, 2927.9, 1593.52, 1482.01, 1291.61, 1222.3, 1041.5, 924.28, 749.98cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.38 (t, 2H, *J* = 7.73 Hz), 7.28 (s,1H), 7.17 (t, 1H, *J* = 8.0 Hz), 7.07 (d, 4H, *J* = 6.55 Hz), 5.36(t, 1H, *J* = 5.85 Hz), 3.34 (m, 1H), 2.80 (m, 1H), 2.60 (m, 1H), 2.30 (s, 3H), 2.20 (m, 1H)ppm;^{13}C NMR ($CDCl_3$, 100MHz) δ= 159.25, 138.51, 136.01, 133.56, 133.00, 130.62, 130.55, 129.24, 121.36, 116.56, 72.95, 26.81, 21.68, 20.88, 20.65, 19.84ppm.

6,8-Dimethyl-4-phenoxy-thiochroman (8i): Yield (66%), Solid M.P-78.9-81.4°C. IR (In KBr):3055, 2966.56, 1582.19, 1483.40, 1222.47, 1014.63, 772.3cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.40 (t, 3H, *J* = 7.94 Hz), 7.08 (d, 2H, *J* = 8.14 Hz), 7.04 (d, 2H, *J* = 10.0 Hz), 5.41 (t, 1H, *J* = 5.61 Hz), 3.37 (m, 1H), 2.92(m, 1H), 2.63 (m, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 2.17 (m, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ= 157.25, 134.51, 133.01, 131.56, 131.00, 129.62, 129.55, 129.24, 121.36, 116.56, 72.95, 26.81, 21.68, 20.65, 19.84ppm.

Typical procedures and Spectral Characterizations for t-alcohol

A solution of Ether (21.0 mmoles) in dimethyl sulfoxide (2 Vol) was added to solution of dimethyl sulfoxide(3 Vol) and sodium hydride(65.0 mmoles) over a period of 15 minutes at RT. reaction mixture was heated to 75-80°C, maintained for 2-3 hours and allowed to cool to RT.Then 10 Vol of chilled water and10 Vol of dichloromethane were added slowly and the reaction mixture was stirred for 15 minutes and the layers were separated. The aqueous layer was extracted again with dichloromethane (2 x 5 Vol). combined organic layers were washed with water (2 x 5 Vol) and organic layer dried over sodium sulfate and concentrated at 35-40°C to get t-alcohol product.

4-Naphthalen-1-yl-chroman-4-ol (4a): Yield (70%), Solid M.P-125-126.8°C. IR (In KBr): 3246, 2878.09, 1580, 1489.6, 1228.33, 1022.05, 772.78 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.80 (m, 3H), 7.53 (t, 2H, *J* = 3.8 Hz), 7.36 (d, 1H, *J* = 7.6 Hz), 7.25 (d, 1H, *J* = 7.6 Hz), 7.15 (t, 1H, *J* = 5.6 Hz), 6.92 (d, 1H, *J* = 7.72 Hz), 6.76 (s, 1H), 6.71 (d, 1H, *J* = 7.22 Hz), 6.1 (s, 1H), 4.4 (t, 1H, *J* = 5.4 Hz), 4.2 (t, 1H, *J* =5.4), 3.3 (d, 1H, *J*= 3 Hz), 2.0 (d, 1H, *J* =7.4 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ=154.2, 143.0, 134.6, 129.9, 129.5, 129.4, 129.3, 129.0, 128.6, 126.0, 125.8, 125.4, 125.17, 125.13, 120.8, 116.9, 70.3, 63.3, 37.5ppm.

6-Methyl-4-naphthalen-1-yl-chroman-4-ol (4b): Yield (80%), Solid M.P-123.1-126.4°C. IR (In KBr):3541.2, 2930.9, 1498.7, 1223.8, 778.98cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.09 (d, 1H, *J* = 5.4 Hz), 7.86 (t, 2H, *J* = 7.26 Hz), 7.54 (t, 2H, *J* = 7.65 Hz), 7.39 (t, 1H, *J* = 7.40 Hz), 7.26 (t, 1h *J* = 8.11 Hz), 7.03 (d, 1H, *J* = 8.1 Hz), 6.92 (d,

1H, *J* = 8.2 Hz), 6.66 (s, 1H), 4.51 (q, 1H), 4.33 (q, 1H), 2.94 (m, 1H), 2.36 (s, 1H), 2.09 (m, 4H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =152.13, 143.09, 134.56, 129.71, 129.58, 129.29, 129.19, 128.55, 126.0, 125.69, 125.44, 125.17, 125.15, 116.77, 70.31, 63.19, 37.71, 20.53ppm.

6-Ethyl-4-naphthalen-1-yl-chroman-4-ol (4c): Yield (72%), Solid M.P-130.1-132.0°C. IR (In KBr):3569.9, 2960.4, 1494.4, 1258.6 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.0 (s 1H), 7.8 (t, 2H, *J* = 7.19 Hz), 7.6 (s 1H), 7.5 (t, 1H, *J* = 7.6 Hz), 7.41 (t, 2H, *J* = 7.32 Hz), 7.29 (t, 1H, *J* = 7.45 Hz), 7.10 (d, 1H, *J* = 8.2 Hz), 6.99 (d, 1H *J* = 8.3 Hz), 6.73 (s 1H), 4.5 (t, 1H, *J* =10.8 Hz), 4.3 (d, 1H, *J* =10.8 Hz), 2.9 (m, 1H), 2.6 (s 1H), 2.13 (q 2H), 1.6 (q, 1H), 1.01 (t, 3H, *J* =7.2 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =71.6, 63.4, 37.1, 27.8, 15.71, 152.2, 141.5, 137.1, 134.5, 129.5, 129.0, 128.9, 128.7, 128.6, 127.0, 125.9, 125.3, 125.2, 124.9, 124.8, 117.2ppm.

6-Chloro-4-naphthalen-1-yl-chroman-4-ol (4d): Yield (60%), Solid M.P-136.12-141.0°C. IR (In KBr):3274.9, 1479.5, 1258.5, 1023.44cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.92 (m, 2H), 7.55 (m, 2H), 7.41 (t, 1H, *J* = 7.38 Hz), 7.31 (d, 1H, *J* = 7.7 Hz)7.22 (q, 1H), 6.98 (d, 1H, *J* = 8.76 Hz) 6.77 (s, 1H), 6.33 (s, 1H) 4.22 (m, 1H), 4.21 (m, 1H), 2.75 (m, 1H), 2.03 (q, 1H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =153.1, 142.0, 134.6, 131.7, 129.4, 129.3, 129.0, 128.9, 128.5, 125.9, 125.7, 125.4, 125.3, 125.2, 124.2, 119.0, 36.9, 63.4, 70.5ppm.

6-Fluoro-4-naphthalen-1-yl-chroman-4-ol (4e): Yield (62%), Solid M.P-141.9-144.1°C. IR (In KBr):3497.6, 2884.8, 1488.1, 1258.6, 774.8cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.91 (q, 2H), 7.6 (s 1H), 7.54 (t, 1H, *J* = 7.71 Hz), 7.39 (s, 1H, *J* = 7.54 Hz), 7.30 (t, 1H, *J* =7.66 Hz), 7.02 (m,2H), 6.55 (m, 1H), 6.32 (s, 1H), 4.41 (t, 1H *J* = 9.9 Hz), 4.20 (t, 1H, *J* = 5.3 Hz), 2.75 (d, 1H), 2.05 (d, 1H, *J* = 14.3 V)ppm ; ^{13}C NMR ($CDCl_3$, 100MHz) δ =157.5, 155.2, 150.5, 142.28, 131.2, 129.4, 128.8, 125.9, 125.8, 125.67, 125.29, 125.17, 118.4, 115.7, 114.7, 70.5, 63.4, 36.9ppm.

2, 2-Dimethyl-4-naphthalen-1-yl-chroman-4-ol (4f): Yield (85%), Solid M.P-123.0-127.5°C. IR (In KBr):3458.31, 2974.59, 1933.5, 1581.7, 1137.7, 749.2cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = (d, 1H, *J* = 8.01 Hz), 7.86 (m, 2H,), 7.5 (t, 2H, *J* = 7.71 Hz), 7.31 (t, 1H, J = 7.59 Hz), 7.20 (t, 1H, *J* = 7.45 Hz), 7.12 (t, 1H, *J* = 7.02 Hz, 6.93 (d, 1H, *J* = 8.10 Hz), 6.83 (d, 1H, *J* = 7.41 Hz), 6.69 (t, 1H, *J* = 7.32 Hz), 5.80 (s, 1H), 2.65 (d, 1H, *J* = 14.64 Hz), 2.17 (d, 1H, *J* = 14.6 Hz), 1.54 (s, 3H), 1.33 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =152.68, 144.52, 134.53, 129.52, 129.45, 129.31, 128.99, 125.55, 125.38, 125.12, 125.0, 124.90, 120.8, 118.21, 117.58, 75.08, 70.82, 47.68, 30.66, 26.64ppm.

4-Naphthalen-1-yl-thiochroman-4-ol (4g): Yield (78%), Solid M.P-138.12-141.8°C. IR (In KBr):3460.78, 2923.5, 1054.8, 778.50cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =8.08 (d, 1H, *J* = 7.08), 7.88 (m, 2H), 7.56 (t, 1H, *J* =7.70), 7.46 (d, 1H, *J* = 8.50), 7.33(d, 1H, *J* = 7.50), 7.23 (t, 2H, *J* = 8.11), 7.07 (q, 1H), 6.81 (q, 2H), 6.09 (s,1H), 3.49 (m, 1H), 2.81 (m, 2h), 2.20 (dd, 1H, J_1 = 2.46, J_2 =8.0)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =143.9, 139.9, 134.5, 132.48, 130.41, 129.42, 129.25, 128.46, 127.62, 126.78, 125.98, 125.48, 125.32, 125.10, 124.81, 124.74, 72.32, 38.60, 23.03ppm.

6-Methyl-4-naphthalen-1-yl-thiochroman-4-ol (4h): Yield (82), Solid M.P-109.1-113.2°C. IR (In KBr):3504.4, 2915.7, 1475.0, 1056.7 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =8.0 (d, 1H, *J* = 7.08 Hz), 7.8 (m, 2H), 7.56 (t, 1H, *J* = 7.7 Hz), 7.4, (d, 1H, *J* = 8.50 Hz) 7.35 (t, 1H, *J* = 7.5 Hz), 7.25 (t, 1H, *J* =7.7 Hz), 7.12 (d, 1H, *J* = 8.0 Hz), 6.9 (d, 1H, *J* = 7.1 Hz), 6.6 (s, 1H), 6.0 (s, 1H), 3.4 (q, 1H), 2.7 (m, 2H), 2.1 (m, 1H), 1.9 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =144.05, 139.93, 134.53, 133.55, 130.61, 129.45, 129.24, 129.00, 128.58, 18.43, 126.79, 126.03, 125.50, 125.32, 125.12, 124.77, 72.4, 38.4, 23.0, 20.8ppm.

6, 8-Dimethyl-4-naphthalen-1-yl-thiochroman-4-ol (4i): Yield (78%), Solid M.P-178.12-179.8°C. IR (In KBr):35072.2, 2917.6, 1060.18, 775.06cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.04 (d, 1H, *J* = 4.71 Hz), 7.85 (m, 2H), 7.54 (t, 2h *J* = 7.19 Hz), 7.34 (t, 1H, *J* = 6.57 Hz), 7.22 (t 1H, *J* =6.71 Hz), 6.84 (s, 1H), 6.57 (s, 1H), 6.0 (s, 1H), 3.40 (d, 2H, *J* =13.7 Hz), 3.42 (d, 1H, *J* = 11.80 Hz), 2.73 (t, 1H, *J* = 12.9 Hz), 2.25 (s, 3H)1.88 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =144.38, 139.85, 134.5, 133.6, 129.83, 129.52, 129.19, 128.61, 128.34, 128.31, 126.08, 125.45, 125.31, 125.09, 124.71, 72.70, 37.90, 22.74, 20.72, 20.24ppm.

2,2-Dimethyl-4-phenyl-chroman-4-ol (9f): Yield (71%), Yellow color liquid. IR (Neat):3252.2, 2971.52, 1576.95, 14825.66, 1252.66, 751.28cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.39 (m, 3H), 7.32 (d, 1H, *J* = 6.93 Hz), 7.27 (d, 1H, *J* = 7.16 Hz), 7.16 (d, 1H, *J* = 5.65 Hz), 6.92 (d, 1H, *J* = 8.0 Hz), 6.81 (m, 2H), 2.01 (s, 1H), 2.13 (m, 2H), 1.52 (s,

3H), 1.43 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 154.04, 145.0, 129.77, 128.7, 128.55, 127.7, 126.57, 124.54, 119.81, 117.24, 74.51, 43.54, 39.92, 29.96, 24.24ppm.

4-Phenyl-thiochroman-4-ol (9g): Yield (69%), Yellow color liquid. IR (Neat):3448.79, 2927.4, 1590.8, 1431.5, 1216.59, 1032.57, 757.19cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.34 (m, 4H), 7.31 (q, 1H), 7.21 (d, 1H, *J* = 7.21 Hz), 7.16 (d, 1H, *J* = 7.22 Hz), 7.11 (d, 1H, *J* = 7.8 Hz), 6.99 (t, 1H, *J* = 6.8 Hz), 3.22 (q, 1H), 2.77 (q, 1H), 2.68 (s, 1H), 2.41 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =147.22, 138.60, 133.85, 129.59, 127.98, 127.87, 127.0, 126.45, 126.25, 124.36, 73.85, 39.51, 23.0ppm.

6-Methyl-4-phenyl-thiochroman-4-ol (9h): Yield (66%), Yellow color liquid. IR (Neat):3028.51, 2878.88, 1640.31, 1468.70, 1072.7, 701.42cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.35 (m, 5H,), 7.11 (d, 1H, *J* = 7.99 Hz), 7.0 (s, 1H), 6.97 (d, 1H, *J* = 6.99 Hz), 3.21 (m, 1H), 2.77 (m, 1H), 2.50 (s, 1H), 2.41 (m, 2H), 2.18 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =147.29, 138.41, 134.0, 130.21, 129.86, 128.95, 127.96, 127.01, 126.38, 126.26, 73.90, 39.92, 23.0, 20.8ppm.

6, 8-Dimethyl-4-phenyl-thiochroman-4-ol (9i): Yield (70%), Solid M.P-79.8-83.2°C. IR (Neat):3296.08, 2928.59, 1378.25, 1045.82, 703.0 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.37 (m,5H), 6.93 (s 1H), 6.83 (s, 1H), 3.20 (m 2H), 2.80 (m, 2H), 2.46 (s, 1H), 2.39 (m, 2H), 2.32 (s, 3H), 2.16 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =147.70, 138.52, 134.11, 132.95, 130.31, 129.79, 127.90, 127.90, 127.49, 126.91, 126.25, 74.22, 39.59, 22.76, 20.7, 20.16ppm.

Typical procedures and Spectral Characterizations for Chromenes (dehydration)

To a solution of t-alcohol (18.0 mmoles) in toluene (7 Vol) was added p-toluene sulfonic acid (PTSA,3.0 mmoles) at RT. Reaction mixture was heated to 80-85°C and maintained for 3-4 hours. Allowed to RT and then 10 Vol of water was added, the reaction mixture stirred for 15 minutes and the layers were separated. The aqueous layer again extracted with toluene (2 x 5 Vol) and combined organic layers were washed with water (2 x 10 Vol) . Organic layer was dried over anhydrous sodium sulfate and concentrated at 50-60°C to get chromene product.

4-Naphthalen-1-yl-2H-chromene (5a): Yield (75%), Solid M.P-121.0-123.5°C. IR (In KBr):2845.11, 1484.8, 1225.44, 754.768cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.96 (d, 2H, *J* = 8.1 Hz), 7.66 (d, 1H, *J* = 8.3 Hz), 7.56 (t, 2H, *J* =7.60 Hz), 7.48 (d, 2H, *J* = 7.5 Hz), 7.46 (t, 2H, *J* = 6.36 Hz), 7.09 (s, 1H), 6.89 (d, 1H, *J* = 7.96), 6.63 (s, 1H), 6.32 (d, 1H, *J* = 7.34 Hz), 5.91 (t, 1H, *J* = 3.45 Hz) 4.99 (d, 1H, *J* = 3.9 Hz), 4.93 (d, 1H, *J* = 3.2 Hz ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 153.84, 135.85, 134.61, 133.52, 131.64, 129.64, 128.64, 128.49, 127.19, 126.54, 126.35, 126.0, 125.77, 125.67, 124.3, 123.14, 121.52, 116.26, 65.37ppm.

6-Methyl-4-naphthalen-1-yl-2H-chromene (5b): Yield (78%), Yellow color liquid. IR (Neat):3013.45, 1505.6, 1491.8, 1215.7, 758.6cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.95 (d, 2H, *J* = 7.70 Hz), 7.90 (d, 1H, *J* = 8.44 Hz), 6.99 (d, 1H, *J* = 8.0 Hz), 6.91 (d, 1H, *J* = 8.13 Hz), 6.41 (s, 1H), 5.89 (t, 1H, *J* = 3.60 Hz), 5.03 (m, 2H), 2.06 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 151.69, 136.22, 135.71, 133.53, 132.05, 130.50, 129.70, 128.16, 128.10, 126.93, 126.32, 126.13, 126.02, 125.89, 125.47, 124.18, 122.08, 115.72, 65.46, 20.51ppm.

6-Ethyl-4-naphthalen-1-yl-2H-chromene (5c): Yield (65%), Yellow color liquid. IR (Neat):2962.8, 1738.2, 1489.9, 1229.7, 779.3cm$^{-1;}$ ^{1}H NMR ($CDCl_3$, 400MHz) δ= 7.98(t, 3H, *J* = 9.71 Hz), 7.62 (m, 4H), 7.07 (dd, 1H, J_1 = 1.79 Hz, J_2 = 1.79 Hz), 6.99 (d, 1H, *J* = 8.14 Hz), 6.50 (d, 1H, *J* = 1.38 Hz), 5.92 (t, 1H, *J* = 3.68 Hz), 5.04 (m, 2H), 2.42 (q, 2H), 1.11 (t, 3H, *J* = 8.50 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =151.94, 137.13, 136.30, 135.87, 133.59, 132.09, 128.49, 128.20, 128.17, 127.0, 126.24, 125.9, 125.93, 125.52, 125.4, 124.22, 122.0, 115.85, 65.5, 28.0, 15.83ppm.

6-Chloro-4-naphthalen-1-yl-2H-chromene (5d): Yield (68%), Yellow color liquid. IR (Neat):2924.61, 1481.82, 1231.27, 779.80cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.93 (d, 2H, J = 8.02 Hz), 7.69 (d, 1H, *J* = 8.27 Hz), 7.51 (m, 2H), 7.39 (m, 2H), 7.09(d, 1H, *J* = 2.0 Hz), 6.90 (d, 1H, *J* = 8.49 Hz)6.29 (s, 1H), 5.93 (d, 1H, *J* = 2.89 Hz), 5.04 (dd, J_1 = 3.54 Hz, J_2 = 3.52 Hz), 4.94 (dd, 1H, J_1 = 2.75 Hz, J_2 = 2.73 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 152.68, 134.98, 134.96, 133.58, 131.49, 129.13, 128.79, 128.74, 127.29, 126.71, 126.43, 126.01, 125.88, 125.51, 125.24, 124.80, 124.63, 118.04, 65.68ppm.

6-Fluoro-4-naphthalen-1-yl-2H-chromene (5e): Yield (72%), Yellow color liquid. IR (Neat):283.16, 1582.3, 1486.8, 1200.2, 950.0, 781.4cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.93 (d, 2H, *J* = 8.02 Hz, 7.81 (d, 1H, *J* = 8.32 Hz), 7.56 (m, 2H), 7.45 (m, 2H), 6.90 (m, 2H), 6.29 (t, 1H, *J* = 4.54 Hz), 5.95 (t, 1H, *J* = 3.93 Hz), 5.0 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =158.55, 156.18, 149.72, 149.70, 135.30, 135.16, 131.71, 128.46, 128.27, 126.95, 126.19, 125.99, 125.79, 125.44, 125.42, 123.0, 116.78, 116.7, 115.4, 115.16, 112.49, 112.25, 65.55ppm.

2,2-Dimethyl-4-naphthalen-1-yl-2H-chromene (5f): Yield (78%), Yellow color liquid. IR (Neat):2975.68, 1934.89, 1602.07, 1453.57, 1152.79, 761.29cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.90 (t, 2H, *J* = 7.80 Hz), 7.80 (d, 1H, *J* = 8.37 Hz), 7.53 (m, 2H), 7.42 (m, 2H), 7.12 (t, 1H *J* = 7.21 Hz), 6.92 (d, 1H, *J* = 8.0 Hz), 6.66 (t, 1H, *J* = 7.39 Hz), 6.53 (d, 1H, *J* = 7.2), 5.70 (s, 1H), 1.63 (s, 3H), 1.57 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =152.66, 136.14, 133.58, 133.38, 132.19, 130.69, 129.28, 128.27, 128.15, 127.03, 126.09, 126.06, 125.93, 125.55, 123.07, 120.72, 166.6, 76.11, 28.23, 27.72ppm.

4-Naphthalen-1-yl-2H-thiochromene (5g): Yield (72%), Solid M.P-125.0-126.5°C. IR (In KBr):2894.23, 1465.93, 1159.5, 779.69cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.92 (d, 2H, *J* = 8.17 Hz), 7.54 (m, 3H), 7.37 (m, 3H), 7.06 (t, 1H, *J* = 7.12 Hz), 6.80 (t, 1H, *J* = 6.5 Hz), 6.4 (d, 1H, *J* = 7.72 Hz), 6.0 (t, 1H, *J* = 2.85 Hz), 3.67 (dd, 1H, J_1 = 4.29 Hz, J_2 = 4.31 Hz), 3.50(dd, 1H, J_1 = 4.50 Hz, J_2 = 6.50)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =139.16, 138.26, 134.64, 133.56, 132.26, 131.77, 128.59, 128.34, 128.19, 127.78, 127.55, 127.30, 126.47, 126.0, 125.92, 125.83, 123.95, 24.68ppm.

6-Methyl-4-naphthalen-1-yl-2H-thiochromene (5h): Yield (71%), Solid M.P-93.5-95.8°C. IR (In KBr):2875.0, 1463.8, 1343.2, 783.95cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.94 (d, 2h, *J* = 8.36 Hz), 7.57 (t, 1H, *J* = 7.61 Hz), 7.48 (t, 2H, *J* = 7.51 Hz), 7.39 (t, 2H, *J* = 7.39 Hz), 7.27 (d, 1H, *J* = 7.84 Hz), 6.94 (d, 1H, *J* = 7.64 Hz), 6.28(s, 1H), 6.08 (t, 1H, *J* = 3.09 Hz), 3.64 (m, 2H), 1.91 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =139.22, 138.35, 135.02, 134.68, 133.56, 131.85,128.92, 128.81, 128.57, 128.29, 127.73, 127.65, 127.49, 126.44, 126.21, 125.97, 125.84, 124.20, 124.76, 20.78ppm.

6,8-Dimethyl-4-naphthalen-1-yl-2H-thiochromene (5i): Yield (78%), Solid M.P-140.0-141.5°C. IR (In KBr):2862.87, 1376.18, 782.56cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ=7.94 (d, 2H, *J* = 8.36 Hz), 7.57 (t, 1H, *J* = 7.61 Hz), 7.48 (t, 2h, *J* = 7.51 Hz), 7.39 (t, 2H, *J* = 7.39 Hz), 7.27(d, 1H, *J* = 7.84 Hz), 6.94(d, 1H, *J* = 7.64 Hz), 6.28(s,1H), 6.08(t, 1H, *J* = 3.09 Hz), 3.64 (m, 2H), 1.94(s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =139.22, 138.35, 134.68, 133.85, 128.92, 128.57, 128.29, 127.73, 127.65, 127.49, 126.44, 126.21, 125.97, 125.84, 124.20, 24.76, 20.78ppm.

2,2-Dimethyl-4-phenyl-2H-chromene (10f): Yield (70%), Solid M.P-63.9-64.9°C. IR (In KBr):2970.33, 1598.58, 1448.83, 1267.80, 1140.66, 703.43cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.46 (m, 5H), 7.25 (t, 1H *J* = 7.27 Hz), 7.11 (d, 1H, *J* = 7.49 Hz), 6.99 (d, 1H, *J* = 7.96 Hz), 6.91 (t, 1H *J* = 7.49 Hz), 5.69 (s, 1H), 1.58 (s, 3H), 1.56 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =153.54, 138.41, 134.81, 129.20, 128.73, 128.31, 127.66, 125.57, 122.32, 120.53, 116.87, 75.70, 27.63, 27.62ppm.

4-Phenyl-2H-thiochromene (10g): Yield (70%), Solid M.P-63.5-65.8°C. IR (In KBr):2871.0, 1435.0, 820.24, 774.56cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.39 (q, 4H), 7.29, (2H, q), 7.16 (m, 1H), 7.0(t, 2H, *J* = 9.7 Hz), 6.07 (t, 1H, *J* = 5.06 Hz), 3.47 (d, 2H, *J* = 5.64 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =141.54, 140.8, 134.31, 133.75, 129.02, 128.21, 128.0, 127.67, 127.54, 125.34, 120.94, 25.23ppm.

6-Methyl-4-phenyl-2H-thiochromene (10h): Yield (69%), Yellow color liquid. IR (Neat):2879.20, 1469.21, 1072.57, 810.68, 762.73cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.38 (m,3H), 7.30 (m, 3H), 6.99 (d, 1H, *J* = 7.6 Hz), 6.85 (s, 1H), 6.08 (t, 1H, *J* = 5.30 Hz), 3.40 (d, 2H, *J* = 5.45 Hz), 2.21 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =141.57, 140.90, 134.99, 130.09, 128.98, 128.77, 128.56,128.45, 128.16, 127.44, 121.50, 25.29, 21.03ppm.

6,8-Dimethyl-4-phenyl-2H-thiochromene (10i): Yield (71%), Yellow color liquid. IR (Neat):2919.89, 1622.76, 1443.49, 1670.44, 761.5, 700.53cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.47 (t 3H, *J* = 6.35 Hz), 7.36 (d, 2H, *J* = 7.2 Hz), 6.97 (s, 1H), 6.80 (s, 1H), 6.11 (t, 1H, *J* = 5.60 Hz), 3.46 (d, 2H, *J* = 5.56 Hz), 2.45 (s, 3H), 2.45 (s, 3H), 2.24 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =25.29, 26.31, 122.64, 128.54, 129.65, 128.16, 128.45, 128.88, 128.98, 131.9, 134.8, 141.9, 142.56ppm.

Typical procedures and Spectral Characterizations for Chromanes. (Hydrogenation)
To a solution of Chromene (7.7 mmoles) and Methanol (15.0 Vol) added Pd/C (10%,400mg,20%w/w) in an Autoclave Vessel under nitrogen condition and heated to 40-50°C with 4-5 Kg of Hydrogen pressure. Reaction mixture maintained for 2-3 hours. And allowed to cool to RT and reaction mixture unloaded under nitrogen condition. Pd/C filtered up on hyflo bed and washed with methanol (3.0 Vol) Filtrate concentrated at 45-50°C to get Chromane product.

4-Naphthalen-1-yl-chroman (6a): Yield (78%), Solid M.P-127.3-128.5°C. IR (In KBr):2881.44, 1487.13, 1241.8, 1219.6, 1052.2, 761.80cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.97 (t, 1H, *J* = 4.52 Hz), 7.81 (d, 1H, *J* = 8.1 Hz), 7.65 (s, 1H), 7.57 (m, 2H), 7.41 (t, 1H, *J* = 7.6 Hz), 7.14 (t, 1H *J* = 4.16 Hz), 6.91 (d, 1H, *J* = 8.10 Hz), 6.88 (d, 1H, *J* = 8.20 Hz), 6.78 (d, 2H, *J* = 4.26 Hz), 5.05 (t, 1H, *J* = 5.25 Hz), 4.18 (m, 2H), 2.49 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =155.39, 141.79, 134.0, 131.0, 130.15, 129.23, 128.0, 127.56, 126.6, 126.3, 125.3, 124.8, 123.76, 120.64, 116.83, 63.29, 39.23, 39.23, 29.67ppm.

6-Ethyl-4-naphthalen-1-yl-chroman (6c): Yield (82%), Yellow color liquid. IR (Neat):2962.0, 1585.22, 1496.86, 1227.1, 756.8cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.29 (d, 1H, *J* = 7.53 Hz), 8.02 (d, 1H, *J* = 7.78 Hz), 7.85 (d, 1H, *J* = 8.0 Hz), 7.68 (m, 2H), 7.47 (t, 1H, *J* = 7.58 Hz), 7.16 (d, 2H, *J* = 7.26 Hz), 7.0 (d, 1H, *J* = 8.27 Hz), 6.88 (s, 1H), 5.0 (t, 1H, *J* = 7.0 Hz), 4.27 (m, 2H), 2.61 (q, 2H), 2.27 (m, 2H), 1.26 (t, 3H, *J* = 7.44 Hz)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 153.64, 141.74, 136.26, 134.0, 131.0, 130.0, 129.20, 127.65, 127.53, 127.14, 126.26, 125.63, 125.32, 123.78, 123.14, 116.66, 63.05, 53.40, 30.36, 22.84, 15.89ppm.

4-Naphthalen-1-yl-thiochroman (6g): Yield (81%), Solid M.P-143.6-145.0°C. IR (In KBr):2920.93, 1593.3, 1433.8, 1059.46, 789.0cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ= 8.23 (d, 1H, *J* = 8.11 Hz), 7.97 (d, 1h, *J* = 7.74 Hz), 7.81 (d, 1H, *J* = 8.06 Hz), 7.62 (m, 2H), 7.43 (t, 1H, *J* = 7.55 Hz), 7.32 (d, 1H, *J* = 7.80 Hz), 7.19 (t, 1H, *J* = 8.10 Hz), 7.04(m, 3H), 5.10(t,1H, *J* = 7.5 Hz), 2.98 (m, 2H), 2.61 (m, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =140.48, 135.71, 134.03, 133.83, 131.37, 130.76, 129.0, 128.0, 127.75, 127.12, 126.87, 126.41, 126.16, 125.49, 125.32, 124.11, 123.25, 40.19, 28.85, 23.56ppm.

6-Methyl-4-naphthalen-1-yl-thiochroman (6h): Yield (82%), Solid M.P-114.5-116.0°C. IR (In KBr):2918.47, 1594.75, 1479.55, 1250.42, 1074.8, 783.5cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 8.25 (d, 1H, *J* = 8.19 Hz), 7.98 (d, 1H, *J* = 7.77 Hz), 7.81 (d, 1H, *J* = 8.03 Hz), 7.65 (m, 2H), 7.44 (t, 1H, *J* = 7.57 Hz), 7.23 (d, 1H, *J* = 7.90 Hz), 7.0 (d, 1H, *J* = 7.24 Hz), 6.83 (s, 1H), 5.09 (t, 1H, *J* = 7.81 Hz), 2.98 (m, 2H), 260 (m, 2H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 100MHz) δ = 140.64, 135.40, 134.02, 133.64, 132.04, 130.74, 129.09, 127.93, 127.84, 127.04, 126.25, 126.17, 125.48, 125.32, 123.19, 1.04, 28.95, 23.33, 20.71.

6,8-Dimethyl-4-naphthalen-1-yl-thiochroman (6i): Yield (88%), Solid M.P-126.5-128.9°C. IR (In KBr):2923.0, 1462.88, 1432.7, 1062.6, 799.0, 782.6cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =8.27 (d, 1H, *J* = 8.34 Hz), 7.97 (d, 1H, *J* = 7.88 Hz), 7.80 (d, 1H, *J* = 8.12 Hz), 7.65 (m, 2H), 7.43 (t, 1H, *J* = 7.65 Hz), 7.0 (d, 1H, *J* = 7.0 Hz), 6.90 (s, 1H), 6.73 (s, 1H), 5.15 (t, 1H, *J* = 3.88 Hz), 2.93 (m, 2H), 2.5 (m, 2H), 2.38 (s, 3H), 2.21 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =140.84, 135.3, 134.05, 134.03, 132.78, 130.73, 129.79, 129.77, 129.39, 129.11, 127.90, 126.98, 126.17, 125.47, 125.34, 123.21, 40.32, 28.48, 23.33, 20.59, 20.07ppm.

2, 2-Dimethyl-4-phenyl-chroman (11f): Yield (77%), Solid M.P-120.02-122.4°C. IR (In KBr):2971.52, 1576.95, 14825.66, 1252.66, 751.28cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.39 (m, 3H), 7.32 (d, 1H, *J* = 6.93 Hz), 7.27 (d, 1H, *J* = 7.16 Hz), 7.16 (d, 1H, *J* = 5.65 Hz), 6.92 (d, 1H, *J* = 8.0 Hz), 6.81 (m, 2H), 4.18 (t, 1H, *J* = 5.60 Hz), 2.13 (m, 2H), 1.52 (s, 3H), 1.43 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 154.04, 145.0, 129.77, 128.7, 128.55, 127.7, 126.57, 124.54, 119.81, 117.24, 74.51, 43.54, 39.92, 29.96, 24.24ppm.

4-Phenyl-thiochroman (11g): Yield (72%), Yellow color liquid. IR (Neat):2917.64, 1434.89, 1072.55, 744.47cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ =7.40 (t, 2H, *J* = 7.32 Hz), 7.32 (q, 2H), 7.20 (t, 3H, *J* = 6.60 Hz), 7.04 (m, 2H), 4.32 (t, 1H, *J* = 4.88 Hz), 3.0 (m, 2H), 2.42 (q, 2H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ = 145.11, 135.29, 133.54, 131.27, 128.57, 128.46, 126.89, 126.43, 126.39, 123.97, 44.18, 30.65, 23.46ppm.

6-Methyl-4-phenyl-thiochroman (11h): Yield (69%), Yellow color liquid. IR (Neat):2918.64, 1482.22, 1039.13, 808.4cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.38 (t, 2H, *J* = 7.25 Hz), 7.30 (t, 1H *J* = 7.19 Hz), 7.16 (d, 3H, *J* = 7.8 Hz), 7.0 (d, 1H, *J* = 7.75 Hz), 6.81 (s, 1H), 4.27 (t, 1H, *J* = 4.58 Hz), 3.0 (m, 2H), 2.39 (q, 2H), 2.25 (s, 3H)ppm; ^{13}C

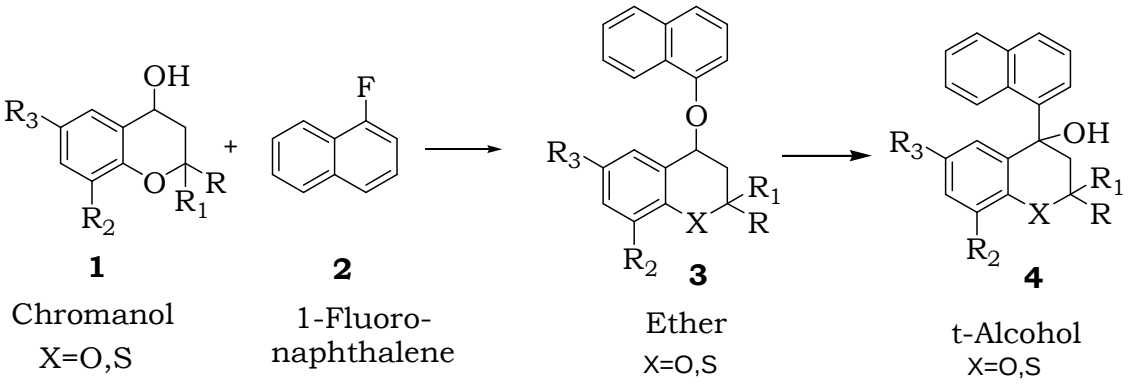
NMR ($CDCl_3$, 100MHz) δ = 145.23, 134.95, 133.44, 131.87, 129.83, 128.55, 128.39, 127.89, 126.29, 126.26, 44.09, 30.77, 23.20, 20.77ppm.

6, 8-Dimethyl-4-phenyl-thiochroman (11i): Yield (78%), Yellow color liquid. IR (Neat):2918.28, 1462.97, 1060.0, 702.14cm^{-1}. ^{1}H NMR ($CDCl_3$, 400MHz) δ = 7.37 (t, 2H, *J* = 7.29 Hz), 7.29 (t, 1H, *J* = 7.10 Hz), 7.15 (d, 2H, *J* = 7.38 Hz), 6.94 (s, 1H), 6.70 (s, 1H), 4.31 (t, 1H, *J* = 4.31 Hz), 2.99 (m, 2H), 2.37 (s, 3H), 2.35 (t, 2H, *J* = 4.73 Hz), 2.23 (s, 3H)ppm; ^{13}C NMR ($CDCl_3$, 100MHz) δ =145.45, 134.77, 134.04, 132.57, 129.57, 129.32, 129.30, 128.51, 128.33, 126.20, 30.26, 23.13, 20.61, 19.98ppm.

RESULTS AND DISCUSSION

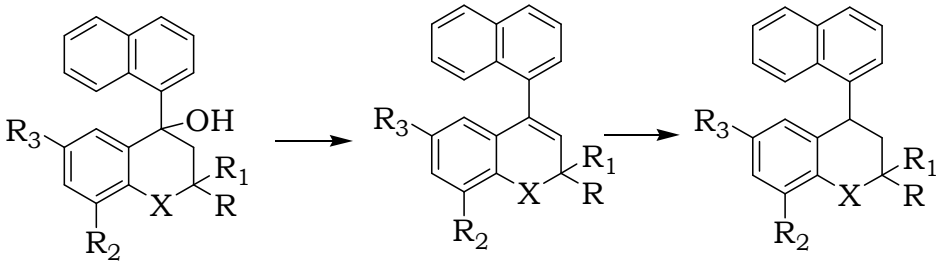
Base catalyzed witting rearrangement was carried out with NaH(60%) as a base and dehydration was carried out with para-toluene sulphonic acid (PTSA) in toluene reflux and the hydrogenation is carried out with Pd-C (10%) in methanol as solvent. All the t-alcohols, olefin compounds and chromans are characterized by spectral means. The following compounds are prepared to prove the generality of the reaction.

Table 1: t-alcohol (4-napthyl) preparation & characterization



Substrate						Ether **(3)**		Alcohol **(4)**	
Entry	X	R	R_1	R_2	R_3	Yield (%)	M.P(°C)	Yield (%)	M.P(°C)
a	O	H	H	H	H	78	70-73.8	70	125-126.8
b	O	H	H	H	CH_3	75	72-74.0	80	123.1-126.4
c	O	H	H	H	C_2H_5	76	78.1-80.0	72	131.2-132.0
d	O	H	H	H	Cl	70	103.-104.5	60	136.1-141.8
e	O	H	H	H	F	72	101-102.3	62	141.9-144.1
f	O	CH_3	CH_3	H	H	81	108-110.2	85	123.1-126.4
g	S	H	H	H	H	82	48.8-52.2	78	138.1-141.8
h	S	H	H	H	CH_3	83	66.2-68.0	82	109.1-113.2
i	S	H	H	CH_3	CH_3	80	78.2-80.0	78	178.1-179.7

Table 2: Chromanes (4-napthyl) preparation & characterization

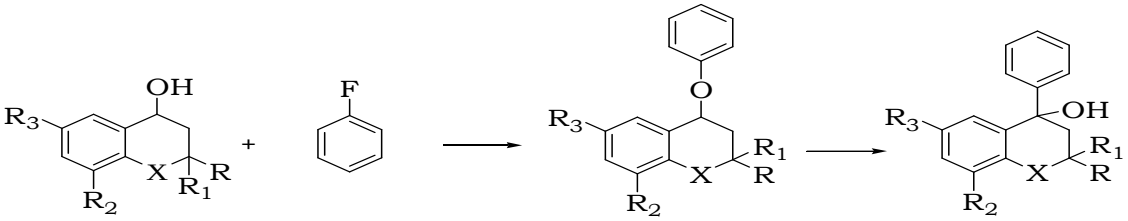


4 t-Alcohol X=O,S → **5** Chromene X=O,S → **6** Chromane X=O,S

Substrate						Chromene **(5)**		Chromane **(6)**	
Entry	X	R	R_1	R_2	R_3	Yield (%)	M.P(°C)/purity by HPLC	Yield (%)	M.P(°C)
a	O	H	H	H	H	75	121.6-123.8/ 98.75	78	127.3-128.5
b	O	H	H	H	CH_3	78	Liq/99.2	X	--
c	O	H	H	H	C_2H_5	65	Liq/98.77	82	Liq
d	O	H	H	H	Cl	68	Liq/98.62	X	--
e	O	H	H	H	F	72	Liq/99.4	X	--
f	O	CH_3	CH_3	H	H	78	Liq/99.0	X	--
g	S	H	H	H	H	72	125.8-126.9/ 98.65	81	143.6-145.0
h	S	H	H	H	CH_3	71	93.5-95.8/ 99.7	82	114.5-116.0
i	S	H	H	CH_3	CH_3	78	126.5-128.9/ 99.6	88	126.5-128.9

X-Hydrogenation did not proceed well b, d, e, f compounds gave multiple products on TLC

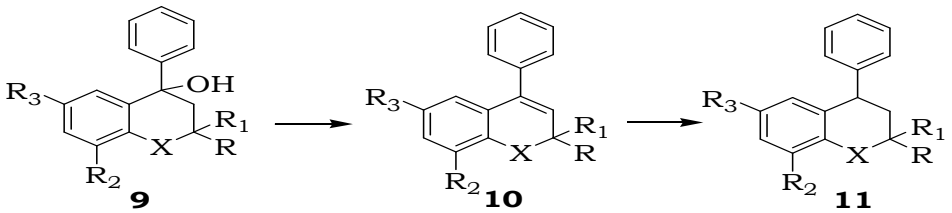
Table 3: t-Alcohol(4-Aryl) preparation & characterization



1 Chromanol + **7** Fluoro-benzene → **8** Ether X=O,S → **9** t-Alcohol X=O,S

Substrate						Ether **(8)**		Alcohol (9)	
Entry	X	R	R_1	R_2	R_3	Yield (%)	M.P(°C)	Yield (%)	M.P(°C)/ purity by HPLC
f	O	CH_3	CH_3	H	H	68	85.2-88.8	71	Liq/98.43
g	S	H	H	H	H	64	75.1-79.8	69	Liq/98.72
h	S	H	H	H	CH_3	69	84.2-87.0	66	Liq/99.65
i	S	H	H	CH_3	CH_3	66	78.9-81.4	70	Liq/99.0

Table 4: 4-Aryl chromanes preparation & characterization



Substrate						Chromene **(10)**		Chromane **(11)**	
Entry	X	R	R_1	R_2	R_3	Yield (%)	M.P(°C)/ purity by HPLC	Yield (%)	M.P(°C)/ purity by HPLC
f	O	CH_3	CH_3	H	H	70	Liq/99.7	77	Liq/99.76
g	S	H	H	H	H	72	Liq/98.9	72	Liq/99.54
h	S	H	H	H	CH_3	69	Liq/98.43	69	Liq/99.0
i	S	H	H	CH_3	CH_3	71	Liq/99.73	78	Liq/98.87

All ethers are prepared from 4-chromanols/thiochromanols and fluoro naphthalene/fluorobenzene under basic conditions. 4-chromanols/thiochromanols are prepared from 4-Chromanones/thiochromanones. All chromones / thiochromones are prepared by known methods.

CONCLUSION

In conclusion we prepared 4-Arylchromanes and thiochromans by Witting rearrangement method in good yields.

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REFERENCES

[1] MM Garazd, YL ,Garazd, VP Khilya.*chem.Nat.compd*.**2003**,39,54-121.
[2] M.M Garazd, YL Garazd, VP Khilya.*Khim.prir.soedin***.2003**,3947-82.
[3](a) T Taechowisan,Clu,Yshen, SJ Lumyong, SJ Canser.*Res.Ther*.**2007**,3,86-92. (b)M Itigwa,C Ito, H.T.W Tan, H,Kuchide, M,Tokude, H Nishino, H Furukawa. *CancerLetters.* **2001**, 169, 15-19.
[4]R Argotte Ramos, G,Ramirez.Avila, M.d.c Rodrignez Gutierrez, M Gonlez-Cortazar, Alvarez. L. *J.nat.prod.***2006**,69,1442-1444.
[5] (a)Sb combes, P Barbier, S Douillard, A McLeer-florin, VR Bourgarel-Ray, JT Pierson, AY Fedorov, JP Finet, J Boutonnat, V Peyrot. *J.Med.*chem. **2011,54**,3153-3162.(b)C Balilly,C Bal, P Barbier, S Combes, JP Finet, MP Hilderand, V Peyrot N Wattez. *J.Med.Chem* **2003**, 46, 5437-5444.
[6] T Taechowisan. *Microbiology*. 2**005**, 151, 1691-1695.
[7] T Taechowisan, C Lu, Y Shen, S Lumyong. *Food.Agr.Immunol*, **2007**, 18, 203-211
[8]T Pengsnparp, M Serit, SH Hughes, DD Soejarto, JM Pezzuto. *J. Nat. prod*, **1996**, 59, 839-842.
[9] R Korec, KH Sensch,T Zoukas *Arzneium.Forsch*, **2000**, 50, 122-128.
[10] MDP Queiroz *Patent WO* **98/25608, 1997.**
[11] JT Pierson, A Dumetrc, S Hutter, F Delmas, M Laget, JP Finet, N Azas S Combes *Eur. j.Med.Chem.* **2010**, 45, 864-869.
[12](a)GM Boland, DMX Donnelhy, JP Finet, MD Rea. *J.Chemsoc Perkin Trans*, 1, **1996**, 2591.(b)J Wn, L Zhang, HG Xia. *Tetrahedron Lett*.**2009**, 50, 2103-2105. (c)ML Yao, MZ Deng. *Heteroat Chem*. **2000**, 11, 380-382.(d)PY wong, WK Chow, KH Chung, CM So, CP Lau, FY Kwong. *Chem-commun*. **2011**, 47, 8328.
[13]MLN Rao, V Venkatesh, DN Jadhav . *EUR. J. Chem.***2010**, 3945-3955.
[14](a)J Wu, Y Liao, Z Yang. J.Org.Chem. 2001, 66, 3642-3645. (b)RD Rieke, S kim,H Tetrahedron Lett.2011,52, 3094-3096.
[15]W Gao, Y Luo, Q Ding, Y Peng, Wu,j.*Tetrahedron Lett*.**2010**, 51, 136-138.
[16](a)L Schio, F Chatreaux, M klich. *Tetrahedron Lett*. **2000**, 41, 1543-1547. (b)PG Ciattini, E Morera, G Ortat. *Synth Commun* **1995**, 25, 2883-2894.

[17](a)J Wu, L Zhang, K Gao, *Eur J. Org. Chem*. **2006**, 5260-5263. (b)J Wu, L Zhang, Y Luo. *Tetrahedron Lett*. **2006**, 47, 6747-6750.
[18](a)L Xu, BJ Li, ZH Wu, XY Lu, BT Guan, BQ Wang, KQ Zhao, Z Shi. *J. Org. Lett*. **2010**, 12, 884-887.(b)CH Xing, JR Lee, ZY Tang, JR Zheng, QS Hu, *Adv. Synth Catal*. **2011**, 353, 2051-2059.(c)JI Kuroda, K Inamoto, K HiroyoT. T Doi. Eur. *J. Org. Chem*. **2009**, 2251,-2261.(d)ZY Tang, QS Hu, *Adv. Synth. Catal*. **2004,** 346, 1635-1637.(e)J Wu, Z Yang. *J. Org. Chem*. **2001,** 66, 7875-7878.
[19]Y Li, Z Qi, H Wang, X Fu, C Duan. *J. Org. Chem*. **2012**, 77, 2053-2057.
[20]S Hajra, D Sinha. *J. Org. Chem*. **2011**, 76, 7334-7340.
[21](a)G Battistuzzi, S Cacchi, I De Salve, G Fabrizi, LM Parsi. Adv. *Synth. Catal***. 2005**, 347, 308-312.(b)Y Yamamoto, N Kirai. *Org. Lett*. **2008**, 10, 5513-5516.(c)Rac Leao, PDFD Moraes, MCBCPedro, PRR Costa. Synthesis 2011, 3692-3696.(d)J Sun, WX Ding, KY Zhang, Y Zou. *Chin. Chem. Lett*. **2011**, 22, 667-670.(e)C Jia, D Piao, J Oyamada, W Lu, T Kitumura, Y Fujiwara. Science. 2000, 287, 1992-1995.(f)MM Garazd, YL Garazd, VP Khilya. Chem. Nat. Compd. 2005, 41, 245-271.
[22]B Schmidt, S KRehl, SM Veronica. *Synthesis*. **2012**, 44, 1603-1613.
[23]VR Arava, SR Amasa, SR Bandatmakuru, MCS Subha Communicated to *J. Korean. Chem*. Soc (**2013)**