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SYNTHESIS AND CHARACTERIZATION OF 3-(4-ARYL-5*H*-6,7,-DIHYDROCYCLOPENTA[B]PYRIDIN-2-YL), 3-(4-ARYL-5,6,7,8-TETRAHYDROQUINOLIN-2-YL) AND 3-(5-HYDROXY-BIPHENYL-3-YL) COUMARINS USING PIPERIDINE AS A CATALYST

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Abstract: A series of the synthesis of various 3-(4-aryl-5*H*-6,7-dihydro cyclopenta[b]pyridin-2-yl) and 3-(4-aryl-5,6,7,8-tetrahydroquinolin-2-yl)coumarins using piperidine as a catalyst. The cyclopenta [b]pyridine and tetrahydroquinoline nuclei of these compounds have been built up by utilizing Krohnke's reaction.

Keywords: synthesis, coumrine, piperidine as catalyst, spectral analysis

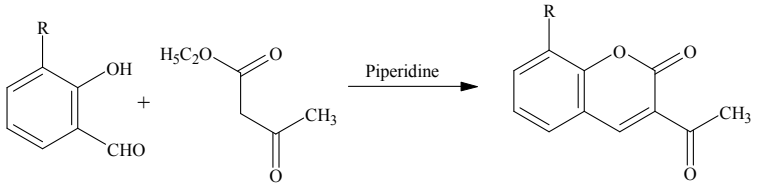
1. Introduction

The survey of the literature reveals that a very large number of coumarin derivatives containing heterocyclic moieties are used in drugs and dyes. A large number of coumarin derivatives having heterocyclic moieties like benzimidazole, triazole, diazole, thiadiazole, oxadiazole, quinazoline, diazine etc. As substituent groups either in the lactone ring or in the benzene ring of coumarin is used as dyes or fluorescent whitening agents [I-VII]. Similarly variety of coumarin derivatives having nucleus like pyridine, indole, imidazole, thiazole, and triazole as substituent groups possesses important biological activities [VIII -X]. Thus, incorporation of another heterocyclic moiety in coumarin nucleus either as substituent or as a fused component changes the properties of parent coumarins and converts them into more useful derivatives.

Among the heterocyclic substituted coumarins, pyridyl substituted coumarins have a special importance due to their diverse physiological actions. A number of coumarin derivatives having pyridine substituted mainly at 3- or 4- position of the coumarin possess CNS depressant activity. R.B.Moffett synthesized number of 3-pyridyl and 4-pyridyl coumarins using modified Pechmann, Knoevenagel and Perkin reactions of pyridine acetic acid or pyridoyl acetic acid with substituted salicylaldehyde [XI -XV].

2. Experimental

2.1 Preparation of 3-acetyl coumarin and 8-methoxy 3-acetyl coumarin.



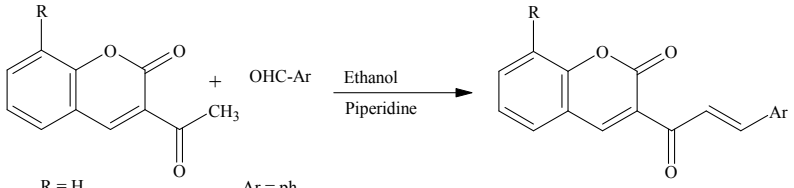
a) R=H , b) R=OCH_3

In a 100ml round bottom flask, a mixture of appropriate salicylaldehyde (0.1 mole), ethyl acetoacetate (0.1 mole) and 3-4 drops of piperidine was stirred for 10 minutes at room temperature. It was then heated for 30 minutes in water bath. A yellow solid obtained was taken out and washed with cold ether. It was recrystallized from chloroform-hexane.

a) 3-Acetyl coumarin: Yield: 65%, m.p: 119 ^oC.

b) 8-Methoxy-3-acetyl coumarin: Yield: 62%, m.p:174 ^oC.

2.2 Preparation of 1-[2(*H*)-1-benzopyran-3-yl]-3-aryl-prop-2-en-1-ones and 1-[8-methoxy-2(*H*)-1-benzopyran-3-yl]-3-aryl-prop-2-en-1-ones(Coumarinchalcones)(1a-l).



R = H
R = OCH_3

Ar = ph
Ar = p-CH_3-ph
Ar = p-OCH_3-ph
Ar = p-NO_2-ph
Ar = 3,4-di-OCH_3-ph
Ar = styryl

(1a-l)

In a 100 ml round bottom flask, appropriate 3-acetyl coumarin (0.01 mole) and appropriate aromatic aldehyde (0.015 mole) were taken in 50 ml of ethanol. Catalytic amount of piperidine (1.0 ml) was added and the reaction mixture was stirred for 10 minutes at room temperature. The reaction mixture was then refluxed on water bath for 4 hours. It was allowed to come to room temperature. A solid product separated out was filtered off, washed with cold ethanol and dried. It was recrystallized from ethanol.

Compound 1a: 3-cinnamoyl-2*H*-chromen-2-one

Yield: 65%; m.p.: 157-159 ºC; IR: λ_{max} 1601 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1725 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1623 cm^{-1} (aromatic C=C stretching), 3032 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4;H,5.0;N,4.1; Found C, 81.6;H, 4.8; N, 4.0; NMR,3.5δ (3H, singlet,protons at C_6), 7.5-8.5δ (10*H*, multiplet, 8 aromatic protons and two -CH=CH- protons merged), 8.5δ (1H, singlet, C_4-H).

Compound1b: 8-methoxy-3-(3-(p-tolyl)acryloyl)-2*H*-chromen-2-one

Yield: 62%; m.p.: 232-34 ºC; IR: λ_{max} 1617cm^{-1} (>C=O stretching of α, β unsaturated ketone),1714 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1252 cm^{-1}(C-O-C stretching of methoxyl group), 1612 cm^{-1} (aromatic C=C stretching), 3042 cm^{-1} (aromatic C-H stretching);Mol. Formula: $C_{20}H_{16}O_4$ calculated C, 74.99; H,5.03; O,19.98; Found C, 74.50;H, 4.8; O, 19.30; NMR, 3.7 and 3.6δ (6*H*, two singlet, two-OCH_3), 6.7-7.8δ (9*H*, multiplet, 7 aromatic protons and two -CH=CH- protons merged), 8.65δ (1*H*, singlet C_4-H).

Compound 1c: 3-(3-(4-methoxyphenyl)acryloyl)-2*H*-chromen-2-one

Yield:67%; m.p.:78-80 ºC; IR: λ_{max} 1620 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1711 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1253 cm^{-1}(C-O-C stretching of methoxyl group), 1614 cm^{-1} (aromatic C=C stretching), 3045 cm^{-1}(aromatic C-H stretching);Mol. Formula: $C_{19}H_{14}O_4$ calculated C, 74.50; H,4.61; O,20.89; Found C, 74.26; H, 4.8; O, 20.33; NMR, 3.6 and 3.8δ (6*H*, two singlet), 6.5-8.2δ (7*H*, multiplet, two-OCH_3 7 aromatic protons and two -CH=CH- protons merged), 8.62δ (1*H*, singlet C_4-H).

Compound 1d: 8-methoxy-3-(3-(4-nitrophenyl)acryloyl)-2*H*-chromen-2-one

Yield: 58%; m.p.:167-168 ºC; IR: ν_{max} 1610 cm^{-1}(>C=O stretching of α, β unsaturated ketone),1360 cm^{-1} (C-NO_2 stretching), 1720 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1615 cm^{-1} (aromatic C=C stretching), 3030 cm^{-1}(aromatic C-H stretching).Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4; H,5.0; N,4.1; Found C, 81.6;H, 4.8; N, 4.0; NMR: 3.9δ (3H, singlet,-OCH_3), 6.9-8.1δ (9H, multiplet, 7 aromatic protons and two -CH=CH- protons merged), 8.7δ (1*H*, singlet, C_4-H).

Compound 1e: 3-(3-(3,4-dimethoxyphenyl)acryloyl)-2*H*-chromen-2-one

Yield:55%; m.p.:161-162 ºC; IR: λ_{max} 1604 cm^{-1} (>C=O stretching of α, β unsaturated ketone),1253 cm^{-1} (C-O-C stretching of methoxyl group), 1726 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1632 cm^{-1} (aromatic C=C stretching), 3057 cm^{-1}(aromatic C-H stretching); Mol. Formula: $C_{20}H_{16}O_5$ calculated C, 71.42.4; H,4.80; O,23.78; Found C, 71.11; H, 4.9; O, 24.21; NMR, 3.8 and 3.8δ (9*H*, two singlet), 6.2-8.1δ (8*H*, multiplet, 6 aromatic protons and two -CH=CH- protons merged), 8.8δ (1*H*, singlet, C_4-H).

Compound 1f: 8-methoxy-3-((2E, 4E)-5-phenylpenta-2, 4-dienoyl)-2*H*-chromen-2-one

Yield: 60 %; m.p.:148-149 ºC; IR: λ_{max} 1615 cm^{-1} (>C=O stretching of α, β unsaturated ketone),1715 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1250 cm^{-1} (C-O-Cstretching of methoxyl group), 1605 cm^{-1} (aromatic C=C stretching), 3045 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4; H,5.0; N,4.1; Found C, 81.6; H, 4.8; N, 4.0; NMR 3.9δ (3*H*, singlet,-OCH_3), 6.9-7.9δ (12*H*, multiplet, 8 aromatic protons and 4H of two -CH=CH- protons merged), 8.60δ (1*H*, singlet, C_4-H).

Compound 1g: 3-(3-(p-tolyl) acryloyl)-2*H*-chromen-2-one

Yield: 60%; m.p.:159-160 ºC; IR: λ_{max} 1613 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1720 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1256 cm^{-1}(C-O-C stretching of methoxyl group), 1618 cm^{-1} (aromatic C=C stretching), 3043 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{19}H_{14}O_3$ calculated C, 78.61; H,4.86; O,16.53; Found C, 78.98; H, 4.24; O, 16.75; NMR, 3.5 and 3.7δ (6*H*, two singlet), 6.2-7.5δ (7*H*, multiplet, two-OCH_3, 7 aromatic protons and two -CH=CH- protons merged), 8.69δ (1*H*, singlet C_4-H).

Compound 1h: 8-methoxy-3-(3-phenylpropanoyl)-2*H*-chromen-2-one

Yield: 60%; m.p.:148-149 ºC; IR: λ_{max} 1605 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1720 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1620 cm^{-1} (aromatic C=C stretching), 3035 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4;H,5.0;N,4.1; Found C, 81.6;H, 4.8; N, 4.0; NMR, 3.9δ (3H, singlet,-OCH_3), 7.0-8.0δ (10*H*, multiplet, 8 aromatic protons and two -CH=CH- protons merged), 8.7δ (1H, singlet, C_4-H).

Compound 1i: 3-(3-(4-nitrophenyl)acryloyl)-2*H*-chromen-2-one

Yield: 56%; m.p.: 152-153 ºC; IR: ν_{max} 1615 cm^{-1}(>C=O stretching of α, β unsaturated ketone), 1365 cm^{-1} (C-NO_2 stretching), 1715 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1612 cm^{-1} (aromatic C=C stretching), 3024 cm^{-1}(aromatic C-H stretching).Mol. Formula: $C_{18}H_{11}NO_5$ calculated C, 67.29; H,3.45; N,4.36; O,24.90; Found C, 68.11;H, 3.68; N, 4.38;O,25.07; NMR: 4.2δ (3H, singlet,protons at C_6), 6.7-8.0δ (9H, multiplet, 7 aromatic protons and two -CH=CH- protons merged), 8.9δ (1H, singlet, C_4-H).

Compound 1j: 8-methoxy-3-(3-(4-methoxyphenyl)acryloyl)-2*H*-chromen-2-one

Yield: 65%; m.p.:151-152 ºC; IR: λ_{max} 1619 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1715 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1250 cm^{-1}(C-O-C stretching of methoxyl group), 1610 cm^{-1} (aromatic C=C stretching), 3040 cm^{-1} (aromatic C-H stretching). Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4; H,5.0; N,4.1; Found C, 81.6;H, 4.8; N, 4.0; NMR, 3.8 and 3.9δ (6*H*, two singlet, two-OCH_3), 6.8-8.0δ (9*H*, multiplet, 7 aromatic protons and two -CH=CH- protons merged), 8.62δ (1*H*, singlet C_4-H).

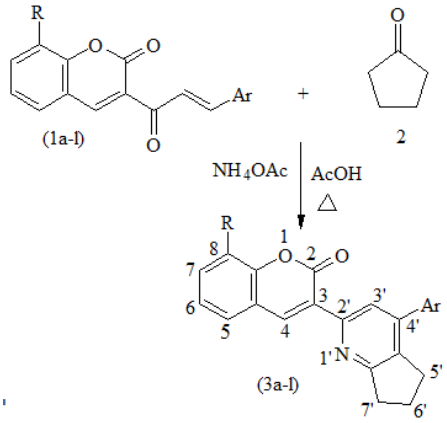
Compound 1k: 3-cinnamoyl-2*H*-chromen-2-one

Yield: 69%; m.p.:169-70 ºC; IR: λ_{max} 1612 cm^{-1} (>C=O stretching of α, β unsaturated ketone), 1712 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1254 cm^{-1}(C-O-Cstretching of methoxyl group), 1608 cm^{-1} (aromatic C=C stretching), 3047 cm^{-1} (aromatic C-H stretching);Mol. Formula: $C_{18}H_{12}O_3$ calculated C, 78.25; H,4.38; O,17.37; Found C, 78.26; H, 4.28; O, 17.56; NMR 4.2δ (3*H*, singlet), 6.7-7.8δ (12*H*, multiplet, 8 aromatic protons and 4H of two -CH=CH- protons merged), 8.66δ (1H, singlet, C_4-H).

Compound 1l: 3-(3-(3,4-dimethoxyphenyl)acryloyl)-8-methoxy-2*H*-chromen-2-one

Yield: 58%; m.p.:165-166 ºC; IR: λ_{max} 1609 cm^{-1} ((>C=O stretching of α, β unsaturated ketone), 1250 cm^{-1} (C-O-C stretching of methoxyl group), 1720 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1630 cm^{-1} (aromatic C=C stretching), 3055 cm^{-1}(aromatic C-H stretching); Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4; H,5.0; N,4.1; Found C, 81.6; H, 4.8; N, 4.0; NMR, 3.8 and 3.9δ (9*H*, two singlet, three-OCH_3), 6.4-8.3δ (8*H*, multiplet, 6 aromatic protons and two -CH=CH- protons merged), 8.6δ (1*H*, singlet, C_4-H).

2.3 Synthesis of 3-(4-aryl-5H-6,7-dihydrocyclopenta[*b*]pyridin-2-yl) coumarins. (3a-l).



a: R= H , Ar=Ph
b: R= OCH_3, Ar=p-CH_3-Ph
c: R= H, Ar=p-OCH_3-Ph
d: R= OCH_3, Ar=p-NO_2-Ph
e: R= H, Ar=3,4-di-OCH_3-Ph
f: R= OCH_3, Ar=styryl
g: R= H, Ar=p-CH_3-Ph
h: R= OCH_3, Ar=Ph
i: R= H, Ar=p-NO_2-Ph
j: R= OCH_3, Ar=p-OCH_3-Ph
k: R= H, Ar=styryl
l: R= OCH_3, Ar=3,4-di-OCH_3

In a 100 ml round bottom flask equipped with a magnetic stirrer, cyclopentanone (2) (0.006 mole) in glacial acetic acid (15ml) was taken. To this ammonium acetate (0.06 mole) was added with stirring at room temperature. Then a solution of appropriate coumarin chalcone (1a-l)

(0.006 mole) in glacial acetic acid (15ml) was added with stirring at room temperature during 15 minutes. The reaction mixture was further stirred for 1 hour and then refluxed for 22 hours at 140 ^{o}C. It was then allowed to come to room temperature and was poured into ice-cold water. A sticky mass was separated out which was then extracted with chloroform (3x30 ml). The chloroform layer was then washed with 5% $NaHCO_3$ and then with water. It was then dried over anhydrous sodium sulphate. The chloroform was removed under reduced pressure. The gummy residue was obtained, which upon column chromatography using silica gel and ethyl acetate-pet. Ether (60:80) (4:6) as an eluent gave compounds (3a-l). The compounds thus obtained were recrystallized from chloroform-hexane.

Compound3a: **3-(4-phenyl-6, 7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one**

Yield: 53 %; m.p.:232-34 ºC;IR: λ_{max} 1725 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1610 cm^{-1} and 1440 cm^{-1}(aromatic C=C and C=N stretching), 2945 cm^{-1} (aliphatic C-H stretching), 3035 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{23}H_{17}NO_2$ calculated C, 81.4; H,5.0; N,4.1; Found C, 81.6;H, 4.8; N, 4.0;); NMR: 2.0-2.6δ (2*H*, multiplet, protons at C_6'), 3.0-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 6.6-8.5δ (11*H*, multiplet, 10 aromatic protons + C_4H).

Compound3b: **8-methoxy-3-(4-(methyl (phenyl) phosphanyl)-6, 7-dihydro-5*H*-cyclopenta[b] pyridine-2-yl)-2*H*-chromen-2-one**;

Yield: 63 %; m.p.:239-40 ºC; IR: λ_{max} 1720 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1635 cm^{-1} and 1425 cm^{-1}(aromatic C=C and C=N stretching), 1245 cm^{-1} (C-O-C stretching), 2930 cm^{-1} (aliphatic C-H stretching), 3010 cm^{-1} (aromati C-H stretching). Mol. Formula: $C_{25}H_{21}NO_3$ calculated C, 78.3;H, 5.5;N,3.6; Found C,78.5;H,5.3; N, 3.7; NMR: 1.9-2.6δ (5*H*, multiplet, two protons at C_6' and aromatic methyl proton signals merged), 2.9-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.9δ (3*H*, singlet,-OCH_3), 6.8-8.8δ (9H, multiplet, 8 aromatic protons +C_4-H).

Compound3c: 8-methoxy-3-(4-(methyl (phenyl) phosphanyl)- 6,7- dihydro -5*H*-cyclopenta [b]pyridin-2-yl)- 2*H*-chromen -2-one

Yield: 58 %; m.p.:228-29 ºC; IR:λ_{max} 1715 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1600 cm^{-1} and 1430 cm^{-1} (aromatic C=C and C=N stretching), 1255 cm^{-1} (C-O-C stretching), 2955 cm^{-1} (aliphatic C-H stretching), 3030 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{24}H_{19}NO_3$ calculated C, 78.0; H,5.1; N,3.7; Found C,78,1; H,5.2; N,3.5; NMR: 2.0-2.6δ (2*H*, multiplet, protons at C_6'), 3.0-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.8δ (3*H*, singlet, -OCH_3), 6.6-8.7δ (10*H*, multiplet, 9 aromatic protons + C_4-H).

Compound3d: **8- methoxy-3-(4-(methyl(phenyl) phosphanyl) -6,7-dihydro-5cyclopenta[b] pyridin-2-yl)- 2*H*-chromen-2 -one**

Yield: 55 %; m.p.:230-31 ºC; IR:λ_{max} 1705 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1615 cm^{-1} and 1425 cm^{-1} (aromatic C=C and C=N stretching), 1350 cm^{-1} (C-NO_2 stretching), 1245 cm^{-1}(C-O-C stretching), 2925 cm^{-1} (aliphatic C-H stretching), 3060 cm^{-1} (aromatic C-H stretching);Mol. Formula: $C_{24}H_{18}N_2O_5$ calculated C, 69.5; H,4.3; N,6.7; Found C, 69.7; H,4.; N, 6.9; NMR: 1.8-2.5δ (2*H*, multiplet, protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.8δ (3*H*, singlet, -OCH_3), 6.8-8.6δ (9*H*, multiplet, 8aromatic protons + C_4-H).

Compound3e: **3-(4-(3, 4-dimethoxyphenyl)-6, 7-dihydro-5*H*cyclopenta[b]pyridin-2-yl)-2*H*-chromen -2-one**

Yield: 61 %; m.p.:202-04 ºC; IR:λ_{max} 710 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1630 cm^{-1} and 1440 cm^{-1} (aromatic C=C and C=N stretching), 1255 cm^{-1} (C-O-Cstretching), 2945 cm^{-1} (aliphatic C-H stretching), 3050 cm^{-1}(aromatic C-H stretching); Mol. Formula: $C_{25}H_{21}NO_4$ calculated C, 75.1; H,5.3; N,3.5; Found C,75.8;H, 5.4; N, 3.3; NMR:1.8-2.6δ (2*H*, multiplet,

protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.8 δ (6*H*, singlet, two-OCH_3), 6.7- 8.6 δ (9*H*, multiplet, 8 aromatic protons +C_4-H).

Compound3f:8-methoxy-3-(4-styryl-6,7-dihydro- 5H-cyclopenta[b]pyridine -2-yl)-2H-chromen- 2-one

Yield: 60 %; m.p.:233-34 ºC; IR: λ_{max} 1720 cm^{-1}(δ-lactone, carbonyl of coumarin), 1615 cm^{-1} and 1435 cm^{-1} (aromatic C=C and C=N stretching), 1240 cm^{-1}(C-O-C stretching), 2955 cm^{-1} (aliphatic C-H stretching), 3035 cm^{-1}(aromatic C-H stretching); Mol. Formula: $C_{26}H_{21}NO_3$ calculated C, 78.9; H,5.3; N,3.5; Found C,78.8; H,5.5; N, 3.4; NMR,1.8-2.5δ (2*H*, multiplet, protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.8(3*H*, singlet,-OCH_3), 6.6- 8.8 δ (12*H*, multiplet, 9 aromatic protons + C_4-H and -CH=CH- merged).

Compound 3g: **3-(4-(p-tolyl)-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one**

Yield: 54 %; m.p.:223-24 ºC; IR: λ_{max} 1715 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1635 cm^{-1} and 1425 cm^{-1} (aromatic C=C and C=N stretching), 2935 cm^{-1} (aliphatic C-H stretching), 3045 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{24}H_{19}NO_2$ calculated C,81.5; H,5.4; N,3.9; Found C, 81.7;H, 5.2; N, 3.9; NMR,1.8-2.6δ (5*H*, multiplet, two protons at C_6' and aromatic methyl signals merged), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 6.8- 8.6δ (10*H*, multiplet, 9 aromatic protons + C_4-H).

Compound3h:**8-methoxy-3-(4-phenyl-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one**

Yield: 58 %; m.p.:238-40 ºC; IR: λ_{max} 1735 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1620 cm^{-1} and 1445 cm^{-1}(aromatic C=C and C=N stretching), 1250 cm^{-1} (C-O-C stretching), 2945 cm^{-1} (aliphatic C-H stretching), 3060 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{24}H_{19}NO_3$ calculated C, 78.0; H,5.1; N,3.7; Found C, 78.1;H, 5.3; N, 3.5; NMR ,1.8-2.5δ (2*H*, multiplet, protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.9 δ (3*H*, singlet, -OCH_3), 6.8-8.7δ (10*H*,multiplet, 9 aromatic protons + C_4-H).

Compound3i:**3-(4-(4-nitrophenyl)-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one**

Yield: 60 %; m.p.:234-35 ºC; IR:λ_{max} 1720 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1635 cm^{-1} and 1440 cm^{-1} (aromatic C=C and C=N stretching), 1345 cm^{-1}(C-NO_2 stretching), 2949 cm^{-1} (aliphatic C-H stretching), 3035 cm^{-1}(aromatic C-H stretching);Mol. Formula: $C_{23}H_{16}N_2O_4$ calculated C,71.8; H,4.2; N,7.2; Found C, 71.9; H,4.1; N,7.3; NMR, 1.8-2.5 δ (2*H*, multiplet, protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 6.8-8.6δ (10*H*, multiplet, 9 aromatic protons + C_4-H).

Compound 3j: **8-methoxy-3-(4-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one**

Yield: 75.1 %; m.p.:224-25 ºC; IR: λ_{max} 1710 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1625 cm^{-1} and 1425 cm^{-1} (aromatic C=C and C=N stretching), 1245 cm^{-1} (C-O-C stretching), 2930 cm^{-1} (aliphatic C-H stretching), 3055 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{25}H_{21}NO_4$ calculated C, 75.1; H,5.3; N,3.5; Found C, 75.0; H, 5.4; N, 3.3; NMR, 1.8-2.6 δ (2*H*, multiplet, protons at C6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5' and C_7'), 3.8 and 3.9 δ (6*H*, two singlet, two-OCH_3), 6.7 -8.6δ (9*H*, multiplet, 8 aromatic protons + C_4-H).

Compound 3k: 3-(4-styryl-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-2*H*-chromen-2-one

Yield:52 %; m.p.:224-25 ºC; IR:λ_{max} 1725 cm^{-1} (δ-lactone carbonyl stretching of coumarin), 1605 cm^{-1} and 1430 cm^{-1} (aromatic C=C and C=N stretching), 2930 cm^{-1} (aliphatic C-H stretching), 3045 cm^{-1} (aromatic C-H stretching);Mol. Formula: $C_{25}H_{19}NO_2$ calculated C, 82.1; H,5.2; N,3.8; Found C, 82.3; H, 5.0; N, 3.8; NMR: 1.8-2.6δ (2*H*, multiplet, protons at C_6'), 2.8-

3.6(4*H*, multiplet, protons at C_5' and C_7'), 6.5-8.6(13*H*, multiplet, 10 aromatic protons + C_4-H and -CH=CH protons merged).

Compound3l:3-(4-(3, 4-dimethoxyphenyl)-6,7-dihydro-5*H*-cyclopenta[b]pyridin-2-yl)-8-methoxy-2*H*-chromen-2-one

Yield: 57 %; m.p.:185-87ºC; IR: λ_{max} 1710 cm^{-1}(δ-lactone carbonyl stretching of coumarin), 1625 cm^{-1} and 1435 cm^{-1} (aromatic aromatic C=C and C=N stretching), 1240 cm^{-1} (C-O-C stretching), 2945 cm^{-1} (aliphatic C-H stretching), 3020 cm^{-1} (aromatic C-H stretching); Mol. Formula: $C_{26}H_{23}NO_5$ calculated C,72.7; H,5.4; N,3.2; Found C, 72.5; H,5.5; N, 3.3; NMR, 1.8 - 2.5δ (2*H*, multiplet, protons at C_6'), 2.8-3.6δ (4*H*, multiplet, protons at C_5'and C_7'), 3.8 and 3.9δ (9*H*, two singlet, three-OCH_3) 6.7- 8.5δ (8*H*, multiplet, 7 aromatic protons + C_4-H).

3. Result and discussion

The condensation of coumarin chalcones (1a-l) with cyclopentanone (2) under Krohnke's reaction condition proceeded smoothly and gave the expected (3a-l) in 52-63 % yield. The structures of all the compounds (3a-l) were confirmed by analytical and spectral data. Thus the reaction of coumarin chalcone (1c) with cyclopentanone (2) gave a compound (3c) as a white solid product.

The IR spectrum of compound (3c) showed a strong band at 1715 cm^{-1} which is due to carbonyl stretching of the lactone ring present in the coumarin nucleus. The bands observed at 1600 cm^{-1} and 1430 cm^{-1} can be assigned to aromatic C=C and C=N stretching vibrations respectively. The Compound showed bands at 1255 cm^{-1} and 1040 cm^{-1} which can be attributed to asymmetric and symmetric C-O-C stretching due to the methoxyl the group present in the phenyl ring attached at C_4'.Compound showed a medium band at 835 cm^{-1} which can be assigned to C-H banding vibration for p-disubstituted phenyl ring present at C_4'. The observed bands at 2955 cm^{-1} and 3030 cm^{-1} can be assigned to aliphatic C-H stretching of cyclopentane ring and aromatic C-H stretching respectively.

The PMR spectrum (60 MHz) of compound (3c) showed a multiplet between 2.0-2.6δ which is due to two protons present at C_6'. A multiplet observed between 3.0-3.6δ integrating for four protons is due to the protons attached at C_5' and C_7'. A methoxyl signal appeared as a singlet at 3.8δ. A multiplet observed between 6.8-8.7δ (10*H*) is due to nine aromatic protons and one C_4 proton of the coumarin nucleus.

The structure of 3c was further supported by high-resolution PMR (300MHz) and ^{13}C spectral data. The PMR (300MHz) spectrum of compound 3c multiplet centered at 2.29δ (2*H*) is due to two protons attached at C_6'.A triplet centered at 3.18δ integrating for two protons is due to protons attached at C_5'. A triplet centered at 3.48δ integrating for two protons is due to protons attached at C_7'. A methoxyl signal appeared at 3.84δ as a singlet. A multiplet observed between 6.90-8.61δ (10*H*) is due to nine aromatic protons and one C_4 proton of coumarin nucleus. The coumarin ring protons present at C_5, C_6, C_7, and C_8 positions forms AA'BB' spin system and therefore the aromatic region appears as a very complex multiplet and hence assignment of individual aromatic protons as well as C_4-H proton is not possible, however the spectrum shows two clear doublets centered at 6.91δ and 7.65δ which can be assigned as ortho coupled doublets for the protons of para-disubstituted phenyl ring attached at C_4'. The ^{13}C-spectrum of 3c A signal the appeared at 23.03δ is due to C_6'carbon. The C_5' and C_7' carbons signals appeared at 34.06δ and 35.08δ respectively. A signal that appeared at 55.56δ is for a carbon of –OCH_3 present in the compound. The signals appeared at 111.33, 113.44, 114.36, 117.66, 118.30, 124.32, 125.07, 127.40, 128.71, 129.59, 130.19, 131.07, 136.99, 139.77, 152.80 159.13, and 160.42δ

corresponding to seventeen carbons are due to aromatic carbons including C_3 and C_4 carbons. The most downfield signal that appeared at 163.57δ can be assigned to the carbonyl carbon of the δ-lactone ring of coumarin. In the absence of ^{13}C DEPT spectra, the assignment of primary, secondary and tertiary carbons was not possible.

Conclusion

Synthesis of various 3-[4-aryl-5H-6, 7, dihydro cyclopenta[b]pyridin-2-yl]coumarins have been carried out by reacting to various chalcones of 3-acetyl coumarins with cyclopentanone respectively in the presence of ammonium acetate and acetic acid. The synthesis involves Krohnke's mechanism for the formation of pyridine nucleus. All synthesized compounds were analyzed with physico-chemical methods and confirm its structural identity and high yields product. This strategy includes simple reagents and clean reaction conditions of non-pollution in environmentally benign solvents.

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