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An efficient synthesis of benzofuro derivatives using active methylene group at platinum electrode

Narendra Kumar, Laxmi Kant Sharma, Abhishek Upadhayay, Rahul Dubey, R. K. P. Singh*

Electrochemical Laboratory of Green Synthesis
Department of Chemistry, University of Allahabad, Allahabad – 211002, U. P., India.

ABSTRACT

An efficient, facile route has been disclosed for synthesis of benzofuro derivatives by electrochemical oxidation of catechol at platinum electrode in the presence of active methylene group. Electro-organic synthesis has been performed in an undivided cell at ambient conditions. The products have been characterized by FTIR, ^{1}HNMR, ^{13}CNMR and mechanism was deduced by voltammetric studies.

Key Words: Anodic oxidation, Catechol, Michael addition, Controlled Potential Electrolysis (CPE), Cyclic voltammetry

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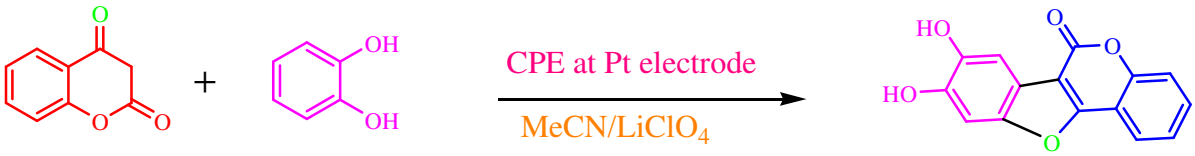
INTRODUCTION

An eco-friendly approach has been developed for the synthesis of benzofuro from catechol and chromene-2,4-dione derivatives. These are important class of biologically active compounds used in medicinal chemistry as an antifungal, antioxidant, anticarcinogenic, antibacterial agents [1-6] and HIV inhibitors [7-9]. They show a variety of applications in photography, dyeing fur, rubber and plastic industry [10] and also play an important role in mammalian metabolism. Therefore, the catechol derivatives are a promising group of compounds, which may lead to the discovery of selective acting biodegradable agrochemicals having high human, animal and plant compatibility [11].

The importance of catechol derivatives has prompted us to synthesize benzofuro moiety by electrochemical oxidation of catechol in presence of various active methylene groups. Construction of aromatic carbon-heteroatom bond is one of the most important challenging process in synthetic organic chemistry. A variety of benzofuro derivatives have been investigated as estrogenic receptor legends [12-14], receptor antagonists [15,16], selective legends for the dopamine D_3 receptor subtype [17], metalloproteinase-13 inhibitors [18] and antifungal agents [19]. Synthesis of benzofuro derivatives using electrochemical method provides a clean route to the formation of anion and cation species from neutral organic molecules with minimum side products. Conventional methods are based on chemical reactions in absolute

organic solvents such as benzene in both synthesis and work up processes, under inert atmosphere conditions, with low atom economy [20].

In the present protocol we report the electrochemical synthesis of benzofuro derivatives via anodic oxidation of catechol with various active methylene groups serving as nucleophiles using cyclic voltammetery and preparative electrolysis methods. Electrochemically generated reactive *o*-benzoquinone can be used to trigger a number of interesting reactions. Typically, the electro generated *o*-benzoquinone serves as a electrophile [21-23], trapped with a number of active methylene groups and undergo successively Michael type of conjugated addition reaction to synthesize a variety of benzofuro derivatives. In this technique electron act as sole reagent for oxidation or reduction without toxic chemicals and reagents [24, 25]. The present work led to the progress of a facile and environmentally benign strategy with high atom economy and excellent purity, in a simple beaker type cell. These results further demonstrate the versatility of the electrochemically synthesized benzofuro derivatives and their biological importance.



Scheme 1: Anodic oxidation of catechol in the presence of active methylene group

MATERIALS AND METHOD

Instrument and Reagents

Cyclic voltammetery was performed using ALSCH instruments electrochemical analyzer Model 600A with a traditional three electrode system. All experiments were carried out in a conventional electrochemical cell containing platinum working as well as the counter electrodes and a saturated calomel electrode (SCE) as reference electrode. IR spectra were registered with a Shimadzu 8201 PC spectrometer on KBr pellets. ^{1}HNMR (400 *MHz)* and ^{13}CNMR (100*MHz*) spectra were recorded with a Bruker DRX 400 spectrometer in DMSO. Chemical shifts are reported in ppm downfield from TMS as internal reference. Mass spectra (EI, ionizing voltage 70 eV) were determined using a Thermofisher ITQ- 900 DIP/GC-MS mass-selective detector. Elemental analyses were performed on a Perkin-Elmer model 240-B analyzer. IR spectra were measured using Bruker Alpha ATR spectrometer; samples were dissolved in $CHCl_3$. Chemicals used in reaction were reagent-grade, from Merck and Loba chemic. These chemicals were used without further purification. Water used for the experiment was double-distilled. All experiment were carried out in acetonitrile solution in presence of $LiClO_4$ as an electrolyte. All Chemicals used in reaction were reagent grade from E-Merck and Loba chemical. These chemicals were used without further purification. Water used for the experiment was double-distilled.

Characteristics of products:

8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one 4(a):

M.P. 310°C, $C_{15}H_8O_5$, Mol. Wt. 268; FTIR (KBr) (λmax cm^{-1}) 3350, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.45 (1H, s, Ar-H), 7.19 (1H, m, Ar-

H), 7.13 (1H, d, Ar-H), 7.13 (1H, m, Ar-H) 6.8 (1H, s, Ar-H), 6.7 (1H, s, Ar-, 5.00 (2H, broad, OH); ^{13}CNMR (100 MHz, DMSO): δ 169.8, 152.2, 151.7, 151.2, 147.2, 145.8, 129.2, 127.9, 126.1, 122.1, 122.0, 115.8, 107.3, 99.5.

3,8,9-trihydroxy-6H-benzofuro-[3,2-c]chromen-6-one 4(b):

M.P 325°C, C15H8O6, Mol. Wt. 284; FTIR (KBr) (λmax cm^{-1}) 3350, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 7.28 (1H, d, Ar-H) , 6.80 (1H, s, Ar-H), 6.70 (1H, s, Ar-H), 6.60 (1H, d, Ar-H) 6.60 (1H, s, Ar-H), 5.00 (3H, broad, OH); ^{13}CNMR (100 MHz, DMSO): δ 158.9, 152.6, 152.2 151.7, 147.2, 145.8, 129.3, 115.8, 114.6, 113.6, 109.8, 107.8, 99.2.

8,9-dihydroxy-3-methyl-6H-benzofuro[3,2-c]chromen-6-one 4(c):

M.P. 318ºC, C16H11O5, Mol. Wt. 282; FTIR (KBr) (λmax, cm^{-1}), 3350, 2925, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 7.33 (1H, d, Ar-H), 6.93 (1H, s, Ar-H), 6.93 (1H, d, Ar-H), 6.80 (1H, s, Ar-H) 6.70 (1H, s, Ar-H), 5.00 (2H, br, OH); 2.35 (3H, s, CH_3); ^{13}CNMR (100 MHz, DMSO): δ 169.8, 152.2, 151.7, 151.1, 147.2, 145.8, 138.8, 127.8, 126.4, 120.9, 119.0, 115.8, 109.8, 107.4, 99.1, 24.7.

8,9-dihydroxy-3-methoxy-6H-benzofuro-[3,2-c]chromen-6-one 4(d):

M.P. 326ºC, C16H10O6, Mol. Wt. 298; FTIR (KBr) (λmax cm^{-1}): 3350, 2950, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 7.34 (1H, d, Ar-H), 6.8 (1H, s, Ar-H), 6.7 (1H, s, Ar-H), 6.64 (1H, d, Ar-H) 6.64 (1H, s, Ar-H), 5.00 (2H, br, OH); 3.73 (3H, s, CH_3); ^{13}CNMR (100 MHz, DMSO) δ 169.8, 161.1, 152.2, 151.7, 147.2, 145.8, 128.9, 111.6, 115.8, 114.3, 109.8, 108.2, 107.5, 99.4, 55.9.

2-chloro-8,9-dihydroxy-6H-benzofuro-[3,2-c]chromen-6-one 4(e):

M.P. 335°C, C15H7O5Cl Mol. Wt. 303; FTIR (KBr) (λmax cm^{-1}): 3300, 2925,1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085, 770; ^{1}HNMR (400 MHz, DMSO): δ 7.46 (1H, s, Ar-H), 7.2 (1H, d, Ar-H), 7.07 (1H, d, Ar-H), 6.8 (1H, s, Ar-H), 6.75 (1H, s, Ar-H) 5.00 (2H, br, OH); ^{13}CNMR (100 MHz, DMSO): δ 169.8, 152.2, 151.7, 149.3, 145.8, 131.6, 129.3, 127.8, 123.5, 123.4, 115.8, 109.4, 107.9, 99.2.

3,8,9-trihydroxy-4-methyl-6H-benzofuro-[3,2-c]chromen-6-one 4(f):

M.P. 342°C, $C_{16}H_{10}O_6$, Mol. Wt. 301; FTIR (KBr) (λmax cm^{-1}): 3350, 2925, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 7.09 (1H, d, Ar-H), 6.8 (1H, s, Ar-H), 6.75 (1H, s, Ar-H), 6.48 (1H, d, Ar-H), 5.05 (3H, s, OH), 2.35 (3H, s, CH_3); ^{13}CNMR (100 MHz, DMSO): δ 169.8, 156.6, 153.7, 152.2, 151.7, 147.2, 145.8, 126.3, 121.2, 115.8, 114.5, 113.1, 109.0, 107.2, 99.7.

3-chloro-8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one 4(g):

M.P. 338ºC, $C15H7Cl_5O5$, Mol. Wt. 302; FTIR (KBr) (λmax cm^{-1}): 3300, 2925, 1700, 1640,

1470, 1350, 1270, 1240, 1200, 1085, 770; ^{1}HNMR (400 MHz, DMSO): δ 7.39 (1H, d, Ar-H) , 7.14 (1H, s, Ar-H), 7.14 (1H, d, Ar-H), 6.8 (1H, s, Ar-H), 6.7 (1H, s, Ar-H) 5.00 (2H, br, OH); ^{13}CNMR(100MHz,DMSO): δ 169.8, 152.6, 152.2, 151.7, 147.2, 145.8, 134.7, 129.3, 126.2, 122.9, 120.1, 115.2, 109, 107.1, 99.6.

8,9-dihydroxy-4-methyl-6H-benzofuro[3,2-c]chromen-6-one 4(h):

M.P. 321ºC, $C_{16}H_{11}O_5$ Mol. Wt. 283, FTIR (KBr) (λmax cm^{-1}): 3350, 2925, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 7.26 (1H, d, Ar-H), 7.01 (1H, m, Ar-H), 6.99 (1H, d, Ar-H), 6.8 (1H, s, Ar-H), 6.7 (1H, s, Ar-H), 5.0 (2H, br. OH), 2.35 (3H, s, CH_3); ^{13}CNMR (100 MHz, DMSO) δ 169.8, 152.3, 152.2, 151.7, 147.2, 145.8, 132.3, 129.5, 126.0, 124.9, 121.9, 115.8, 109.8, 107.5, 99.4, 14.2.

1,8,9-trihydroxy-3-methoxy-6H-benzofuro-[3,2-c]chromen-6-one 4(i):

M.P. 348°C, $C_{16}H_{10}O_7$, Mol. Wt. 314; FTIR (KBr) (λmax cm^{-1}): 3350, 3310, 2845, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO): δ 6.8 (1H, s, Ar-H), 6.7 (1H, s, Ar-H), 6.2 (1H, s, Ar-H), 6.11 (1H, s, Ar-H), 5.05 (3H, s, OH), 3.73 (3H, s, CH_3); ^{13}CNMR (100 MHz, DMSO): δ 169.8, 156.7, 153.6, 152.2, 151.7, 147.2, 145.8, 115.8, 114.5, 113.1, 109.8, 107.5, 100.8, 99.3, 55.9 .

3-chloro-8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one 4(j):

M.P. 343ºC, $C_{15}H_7ClO_6$, Mol. Wt. 302; FTIR (KBr) (λmax cm^{-1}): 3300, 3200, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085, 800; ^{1}HNMR (400 MHz, DMSO): δ 6.8 (1H, s, Ar-H), 6.7 (2H, s, ArH) 6.61 (1H, s, Ar-H), 5.0 (3H, br OH); ^{13}CNMR (100MHz, DMSO)δ 169.8, 157.1, 154.0, 152.2, 151.7, 147.2, 145.8, 136.1, 118.9, 115.8, 115.5, 114.0, 109, 107.8, 99.2.

8,9-dihydroxy-2-4-dimethyl-6H-benzofuro[3,2-c]chromen-6-one 4(k):

M.P. 329ºC, $C_{17}H_{12}O_5$, Mol. Wt. 296; FTIR (KBr) (λmax, cm^{-1}) 3350, 2925, 2915, 1700, 1640, 1470, 1350, 1270, 1240, 1200, 1085; ^{1}HNMR (400 MHz, DMSO):δ 7.06 (1H, s, Ar-H), 6.8 (1H, s, Ar-H), 6.79 (1H, s, Ar-H), 6.7 (1H, s, Ar-H) 5.00 (2H, br, OH); 2.35 (6H, s, CH_3); ^{13}CNMR (100 MHz, DMSO):δ 169.8, 152.2, 151.7, 149.3, 147.2, 145.8, 135.6, 131.3, 127.8, 121.8, 115.8, 109.8, 107.2, 99.8, 24.2, 14.6.

RESULT AND DISCUSSIONS

In the course of our studies towards the synthesis of benzofuro derivatives, we have reported the highly effective electrochemical technique for the oxidative conversion of catechol into *o*-benzoquinone in the presence of active methylene groups. Herein our interest is establishing a convenient, practical and general methodology for a variety of biologically active benzofuro derivatives. In general, the efficiency of electrooxidation process can be enhanced by using a suitable solvent, supporting electrolyte and increasing the concentration of the intermediate.

After screening several solvents/supporting electrolyte, we found that $CH_3CN/LiClO_4$ promoted the Michael addition followed by intramolecular cyclization of benzoquinone with active

methylene groups to the corresponding benzofuro derivative in excellent yield with short reaction time (Table 1, Entry 4). DMF/LiClO4, DMF/NaClO4, MeCN/NaClO4, AcOH/LiClO4, AcOH/NaClO4, MeOH/LiClO4 and MeOH/NaClO4 gave compound 4a in moderate yield (60-70%) (Table 1, Entries 1, 2, 5, 7, 8, 10, 11) while DMF/Bu4BrN, MeCN/ Bu4BrN, AcOH/Bu4BrN, MeOH/Bu4BrN, DCM/$LiClO_4$ and DCM/Bu_4BrN provided compound 4a in lower yield (Table 1, Entries 3, 6, 9, 12, 13, 14).

Substrate (1a) was selected as a model substrate and $LiClO_4$ as a supporting electrolyte. Both were dissolved in MeCN at room temperature. After electrolysis product (4a) was synthesize with complete consumption of the starting material in two hours. No significant byproducts were detected by TLC, ^{1}HNMR and ^{13}CNMR spectroscopy.

Cyclic Voltammetric study of catechol:

Cyclic voltammetry of 1mM solution of catechol (1a) were recorded in acetonitrile solution containing $LiClO_4$ as supporting electrolyte at an ambient temperature. The experiment was carried out using a three electrode cell as working and counter electrode. The potential of the working electrode was measured vs. saturated calomel electrode as reference electrode at scan rate of 0.01 Vs^{-1}. The results of the voltammetric experiments show two anodic peaks which correspond to transformation of catechol (1a) to *o*-benzoquinone (2a) by two electron process and exhibited no reduction peak. The result suggested that the electro oxidation involves a transformation of 1a to 1b within a two electron oxidation process (Figure 1).

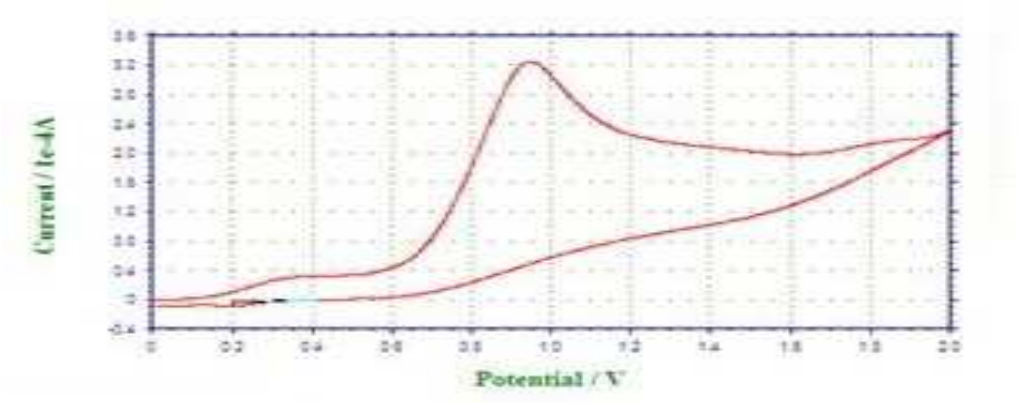


Figure 1: Cyclic voltammetry of catechol (**1a**) in absence of nucleophiles at scan rate 0.01 m/s at potential range 1.0 - 2.0V.

Figure 2 shows the cyclic voltammogram obtained for a 1mM solution of (**1a**) in the presence of 1mM carbon nucleophile. The voltammogram exhibits various anodic peaks between 0.9-2.0V versus SCE respectively. These Peaks corresponds to oxidation of the product, polymer in low yield. On the other hand, high concentration of electrolyte and nucleophiles favors the proposed mechanism for the formation of benzofuro derivatives**.**

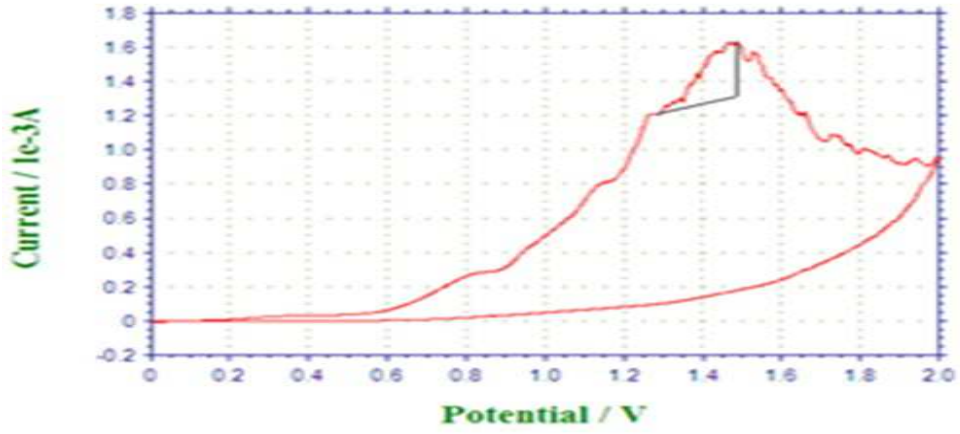
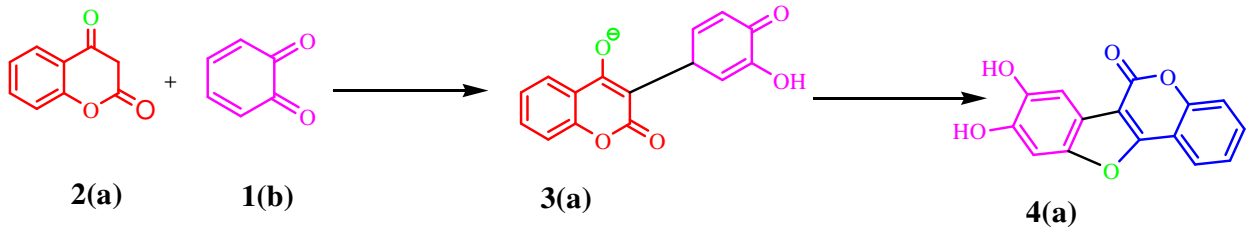


Figure 2: Oxidation of catechol (**1a**) in presence of carbon nucleophile.

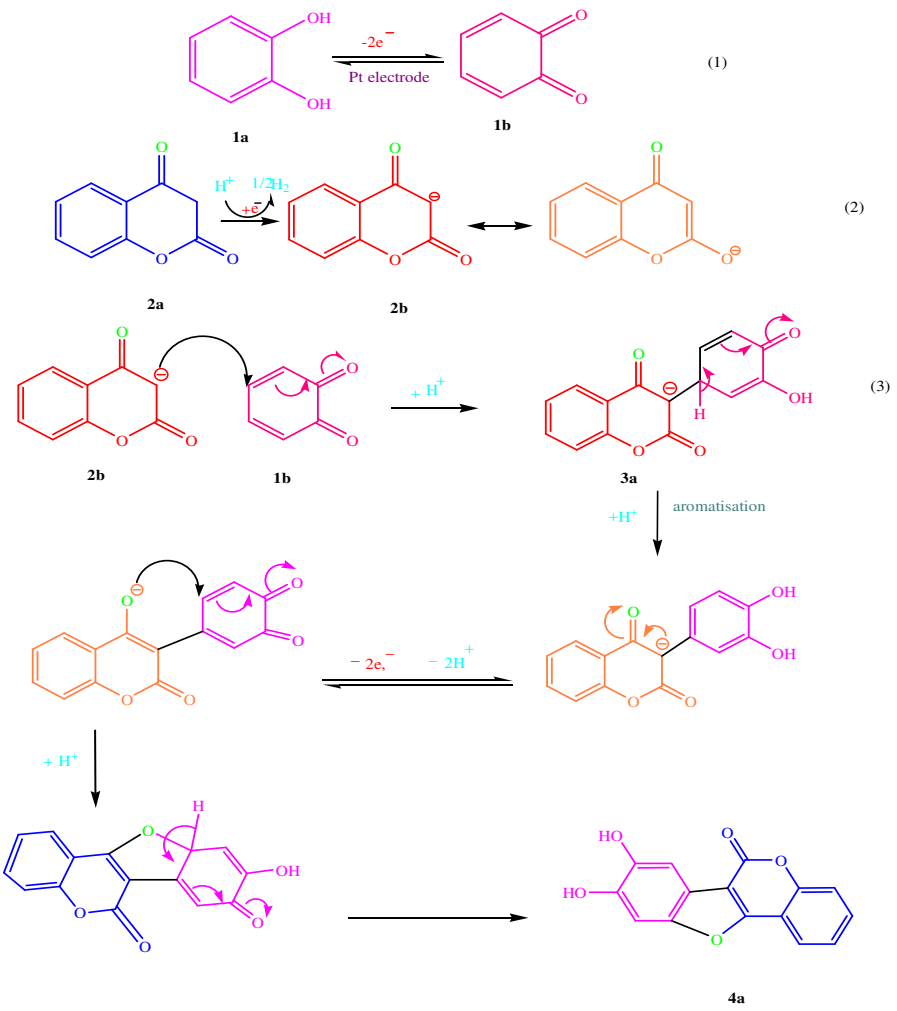
Controlled potential electrolysis (CPE) and electrochemical synthesis of products (4a-4k) Preparative scale electrolysis [19-25] were carried out in a 50mL undivided cell assembly of three platinum electrode of (flattened sheet of dimension 1.0 × 1.0 cm) as working as well as the auxiliary electrode and SCE [26-34] as reference electrode. In a typical procedure, 5mmol of catechol, 5mmol of active methylene group, $LiClO_4$ (0.8g, 0.1N) as an electrolyte was dissolved in acetonitrile solvent. The reaction mixture was electrolyzed under constant potential in an undivided cell equipped with a magnetic stirrer. After the electrolysis, the reaction mixture was extracted with chloroform. The $CHCl_3$ was evaporated under vacuum, brown colour product was obtained which was characterized by spectroscopy.

Reaction mechanism:

Adams *etal.* and Nematollahi *etal.*[35-47] described the anodic oxidation of catechol in the presence of different active methylene groups. The anodic oxidation of catechol (**1a**) leads to the formation of the corresponding *o*-benzoquinone (**1b**) by removal of two electrons. Electrochemically generated *o*-benzoquinone is highly reactive intermediate which undergo Michael type of conjugated addition with the eletrogenerated base of active methylene compounds (**2a**). The product formed undergoes intramoleular cyclization and aromatization to give the desired product (**4a**).



Scheme 2: Electro organic synthesis of benzofuro derivatives (**4a-4k**)



Scheme 3. Proposed mechanism for the anodic oxidation of catechol in presence of active methylene group.

IR and NMR Spectra of compound - 8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one **(4a)**:

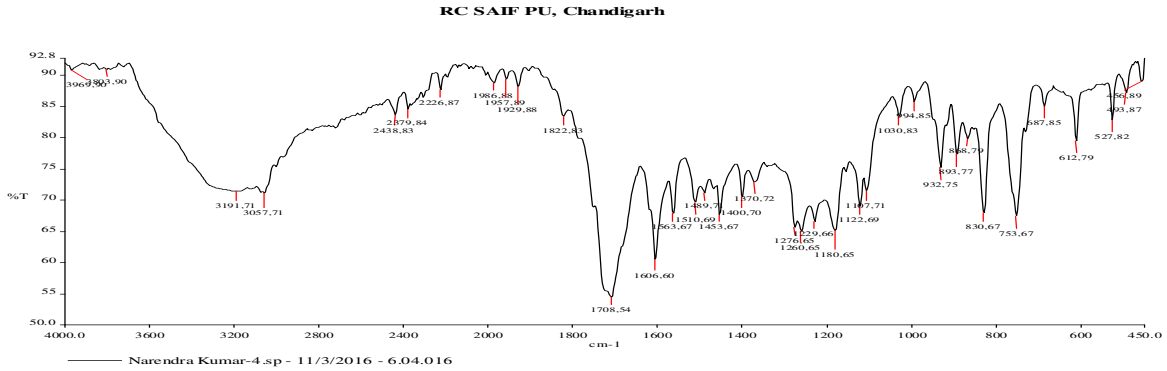


Figure 3: Infrared Spectrum of 8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one**(4a)**.

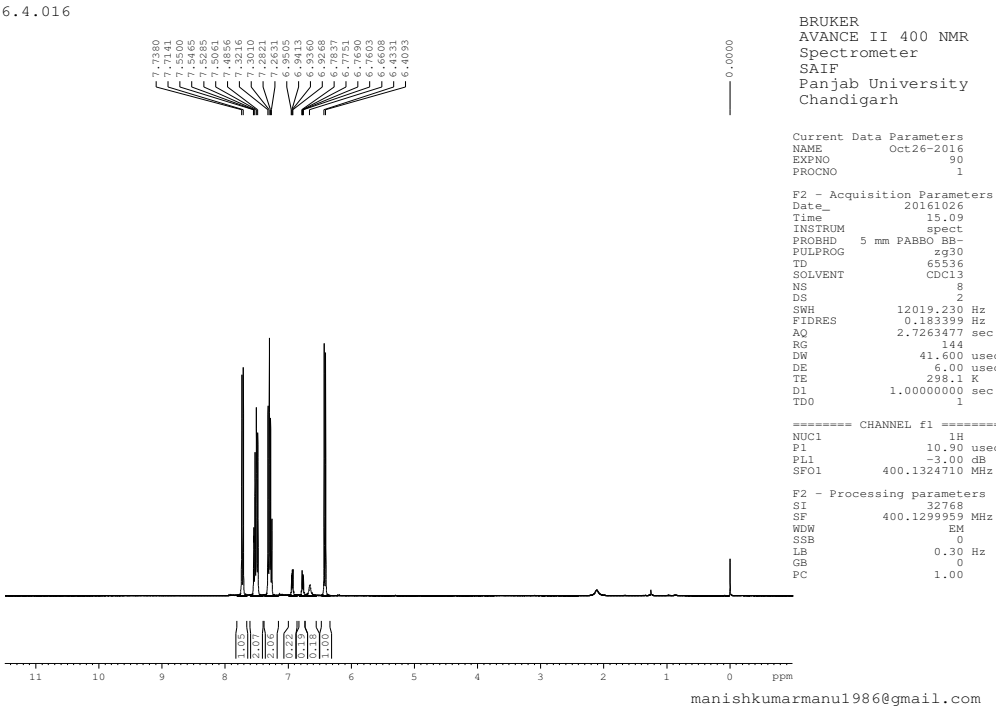


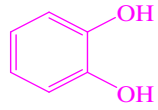
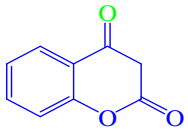
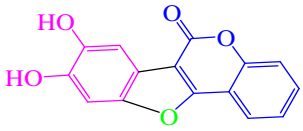
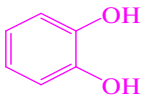
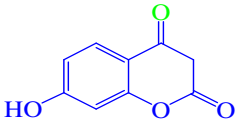
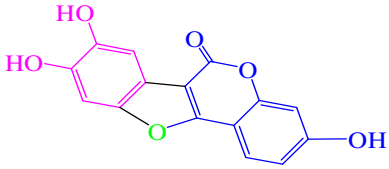
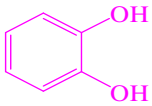
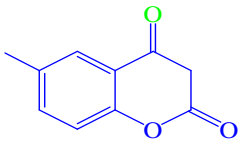
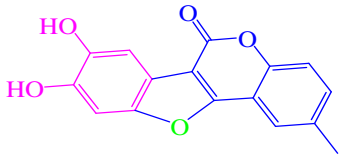
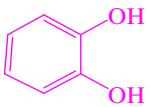
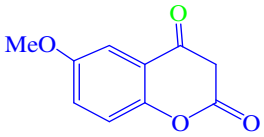
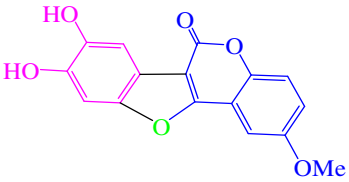
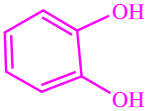
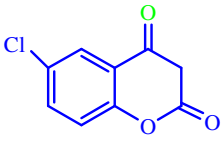
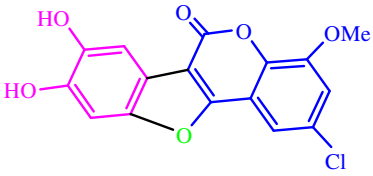
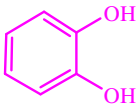
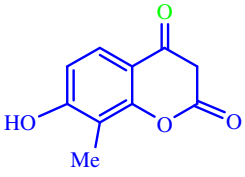
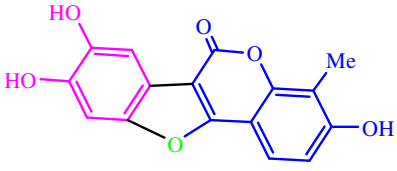
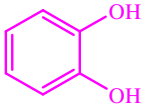
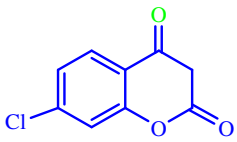
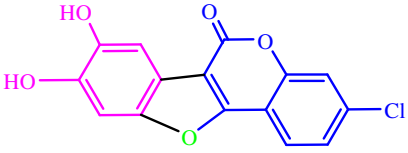
Figure 4: NMR spectrum of 8,9-dihydroxy-6H-benzofuro[3,2-c]chromen-6-one**(4a)**.

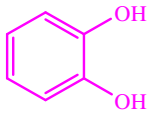
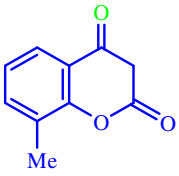
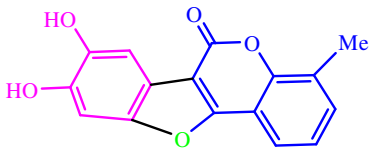
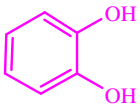
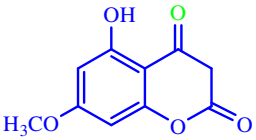
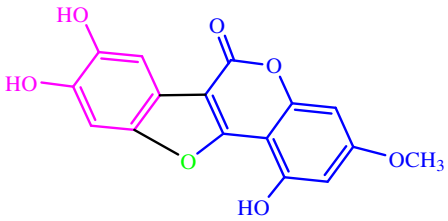
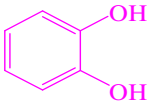
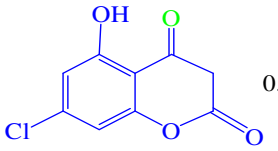
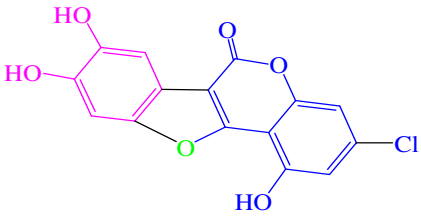
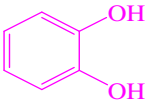
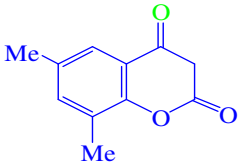
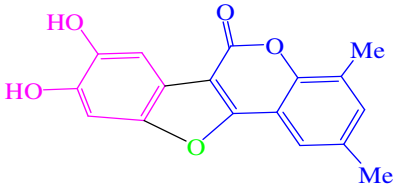
Table 1. Optimization of reaction conditions for the construction of benzofuro derivatives.

Entry	Solvent	Electrolyte	Time/Min.	Yield (%)
1	DMF	$LiClO_4$	232	62
2	DMF	$NaClO_4$	215	60
3	DMF	Bu_4BrN	241	51
4	MeCN	$LiClO_4$	195	90
5	MeCN	$NaClO_4$	205	70
6	MeCN	Bu_4BrN	247	48
7	AcOH	$LiClO_4$	251	67
8	AcOH	$NaClO_4$	240	68
9	AcOH	Bu_4BrN	253	59
10	MeOH	$LiClO_4$	218	70
11	MeOH	$NaClO_4$	225	68
12	MeOH	Bu_4BrN	221	47
13	DCM	$LiClO_4$	215	35
14	DCM	Bu_4BrN	232	29

Considering these preliminary observation, a series of benzofuro derivatives (**4a-4k**) were synthesized. These products were easily accessible in high yields from the corresponding *o*-benzoquinone with active methylene groups. All the reactions were completed within 4-5 hours. In our present protocol desired product was extracted from reaction mixture by simple solvent extraction method. The structures of isolated products (**4a-4k**) were deduced by means of FTIR, ^{1}HNMR and ^{13}CNMR spectroscopy.

Table 2. Electrochemical synthesis of products (**4a-4k**) under constant potential electrolysis.

Entry	Substrate (**1a**)	Nucleophile (**2a-2k**)	Anode Potential (Volts)	Current (mA)	Product (**4a-4k**)	Yield (%)
1.			1.10	37		87
2.			0.90	34		92
3.			0.80	28		86
4.			0.85	40		93
5.			0.90	43		86
6.			1.20	36		92
7.			1.00	32		84

8.			1.20	35		89
9.			1.10	28		65
10			0.90	24		78
11.			0.80	32		91

CONCLUSION

In conclusion, we have developed an efficient one pot methodology for benzofuro derivatives. This simple, mild and environmentally sustainable method gives easy access to the preparation of pharmaceutically important heterocyclic scaffold. Application of electricity in the place of use $LiClO_4$ as supporting electrolyte and high atom economy are attractive features of our work.

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REFERENCES

[1] L Manickavasagam; S Gupta; S Mishra; A Kumar; A Raghuvanshi; A Goel; DG Singh, K Jain; Biomed. Chrom. **2011**;25: 843; (b) J Malviya; SK Devi; H Singh; RKP Singh; JAC **2016**;4: 7.

[2] MZ Zhang; RR Zhang; JQ Wang; X Yu; YL Zhang; QQ Wang; WH Zhang; Eur. J. Med. Chem. **2016**;124: 10.

[3] M Rajabi; Z Hossaini; MA Khalilzadeh; S Datta; M Halder; SA Mousa; J Photochem Photobiol B **2015**;148: 66.

[4] A Shaabani; R Ghadari; S Ghasemi; M Pedarpour; AH Rezayan; A Sarvary; SW Ng; J COMB CHEM **2009**;11: 956.

[5] S Prado; YL Janin; B Saint-Joanis; P Brodin; S Michel; M Koch; ST Cole; F Tillequin; PE Bost; Bioorg. Med. Chem. Lett. **2007**;15: 2177.

[6] M Adib; M Mahdavi; S Bagherzadeh; HR Bijanzadeh; Synlett **2009**;15: 2542.

[7] HM Li; C Zhou; CH Chen; RT Li; KH Lee; Helv. Chim. Acta **2015**;98: 1177.

[8] SA Galal; ASA El-All; MM Abdallah; HI El-Diwani; *Bioorg. Med. Chem.* **2009**;19: 2420.

[9] M Sairam; G Saidachary; BC Raju; *Tetrahedron Lett.* **2015**;56: 1338.

[10] MB Teimouri; F Mansouri; J COMB CHEM **2008**;10: 507.

[11] BD Parmar; TR Sutariya; GC Brahmbhatt; NJ Parmar; R Kant; VK Gupta; J. Org. Chem. **2016**;81: 4955.

[12] SS Hosseiny Davarani; D Nematollahi; M Shamsipur; NM Najafi; L Masoumi; S Ramyar; J. Org. Chem. **2006**;71: 2139.

[13] R Pratap; VJ Ram; Chem. Rev. **2014**;114: 10476.

[14] Y Dong; Q Shi; K Nakagawa-Goto; PC Wu; SL Morris-Natschke; A Brossi; KF Bastow; JY Lang; MC Hung; KH Lee; *Bioorg. Med. Chem.* **2010**;18: 803.

[15] C Hu; S Wang; Y Wang; E Huang; X Liu; D Li; U. S. Patent **2014**;8: 877.

[16] VJ Ram; P Srivastava; AS Saxena; J. Org. Chem. **2001**;66: 5333.

[17] AK Yadav; BK Singh; N Singh; RP Tripathi; Tetrahedron Lett. **2007**;48: 6628.

[18] A Manlove; MP Groziak; J. Heterocyclic Chem **2009**;21: 375.

[19] SA Hessein; MA El-Sharief; SY Abbas; HK Thabet; YA Ammar; Croat. chem. acta **2016**;89: 1.

[20] J Gong; Z Zhao; F Zhang; S Wu; G Yan; Y Quan; B Ma; Org. Lett. **2014**;16: 5524.

[21] FM Abdelrazek; P Metz; EK Farrag; Arch Pharm **2004**;337: 482.

[22] CC Zeng; FJ Liu; DW Ping; LM Hu; YL Cai; RG Zhong; Tetrahedron **2009**;65: 4505.

[23] N Majumdar; ND Paul; S Mandal; Bde Bruin; WD Wulff; ACS CATAL **2015**;5: 2329.

[24] A Jansen; A Taugerbeck; M Klasen-Memmer; G Bernatz; Furochroman derivatives, U. S. Patent **2010**;7: 678.

[25] J Fry Synthetic Organic Electrochemistry **1989**;352.

[26] LK Sharma; S Singh; RKP Singh; J. Indian Chem. Soc. **2011**;88: 155.

[27] LK Sharma; S Singh; RKP Singh; J. Indian Chem. Soc. **2011**;50: 110.

[28] LK Sharma; S Kumar; S Singh; RKP Singh; Electrokhimiya **2010**;46: 37.

[29] S Singh; LK Sharma; A Saraswat; RKP Singh; Mon. f. Chem. **2012**;143: 1427; (b) A

Upadhayay, LK Sharma, VK Singh, RKP Singh; Tetrahedron Lett. **2016**;58: 5599.

[30] (a) A Saraswat; LK Sharma; S Singh; IR Siddiqui; RKP Singh; Res. Chem. Intermed **2012**;49: 1287; (b) A Upadhayay; LK Sharma, VK Singh, R Dubey, N Kumar, R.K.P. Singh; Tetrahedron Lett. **2017**;58: 1245.

[31] D Nematollahi; M Rafiee; Green Chem. **2005**;7: 638.

[32] D Nematollahi; D Habibi; M Rahmati; M Rafiee; J. Org. Chem. **2004**;69: 2637.

[33] AR Fakhari; D Nematollahi; M Shamsipur; S Makarem; SSH Davarani; A Alizadeh; H. R Khavasi; Tetrahedron **2007**;63: 3894.

[34] SSH Davarani; D Nematollahi; M Shamsipur; NM Najahi; L Masoumi; S Ramyar J. Org. Chem. **2006**;71: 2139.

[35] D Nematollahi; M Alimoradi; S Waqif Husain; Electrochim. Acta. **2006**;51: 2620.

[36] D Nematollahi; MS Workentin; E Tammari; Chem. Commun. **2006**;15: 1631.

[37] SM Golabi; D Nematollahi; J. Electroanal.Chem. **1997**;420: 127.

[38] D Nematollahi; Z Forooghi; Tetrahedron **2002**;58: 4949.

[39] SM Golabi; D Nematollahi; J. Electroanal. Chem. **1997**;430: 141.

[40] D Nematollahi; D Habibi; J. Org. Chem. **2004**;69: 2637.

[41] D Nematollahi; M Rafiee; J. Electroanal. Chem. **2004**;566: 31.

[42] D Nematollahi; M Rafiee; Green. Chem. **2005**;7: 638.

[43] F Hartmer; SR Waldvogel; Chem. Commun. **2015**;51: 16346.