Supporting Information

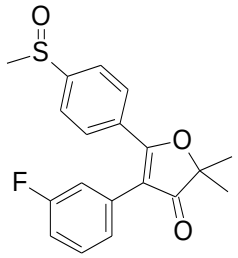
$NaNO_2$/HCl/TBAB catalyst: A controlled aerobic oxidation of sulfide substrate in the preparation of Polmocoxib intermediate under mild conditions

Macchindra B. Kadam [1,3], Deepak B. Nale [2], Dattatray N.Thorat [3], Venkateswara Rao Vallu [3], Bollikonda Satyanarayana [3], Padi Pratap Reddy [3] and Sayujjata R. Vaidya* [1]

	Table of content	Page No.

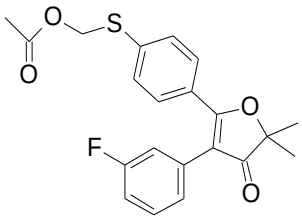
A) Spectral data of synthesized compounds:

Stage-1A*:* 4-(3-fluorophenyl)-5-[4-(methanesulfinyl)phenyl]-2,2-dimethylfuran-3(2*H*)-one



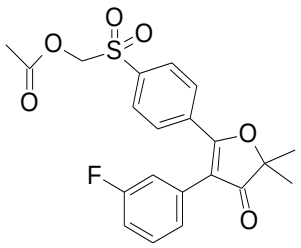
Off-white solid powder; IR (ATR) **(Fig. S1)**: 2931. 80, 1687.71, 1620.21, 1496.76, 1454.33, 1193.94, 1103.28, 1051.20 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz) **(Fig. S2)**: δ 7.80-7.72 (m, 4H), 7.47-7.40(m,1H), 7.23-7.05(m,3H), 2.80(S,3H), 1.50(S,6H) ppm; ^{13}C NMR (DMSO-*d6*, 75 MHz) **(Fig. S3)**: δ 203.85, 176.88, 163.70, 160.47, 150.58, 132.03, 131.16, 130.62, 128.73, 125.46, 124.05, 116.12, 114.67, 112.73, 42.88 and 22.84 ppm; MS **(Fig. S4)**: m/z 345 [M+H].

Stage-1B: ({4-[3-(3-fluorophenyl)-5,5-dimethyl-4-oxo-4,5-dihydrofuran-2-yl] phenyl} sulfanyl) methyl acetate



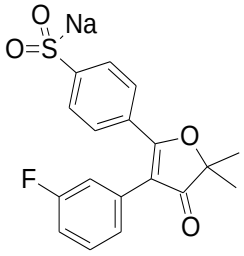
Light reddish coloured residue; IR (ATR) **(Fig. S5)**: 3082.25, 3001.24, 1784.15, 1749.44, 1550.77, 1498.69, 1454.33, 1151.50, 1078.21 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz) **(Fig. S6)**: δ 7.56-7.50 (m, 4H), 7.49-7.39(m, 1H), 7.21-7.17(m,1H), 7.16-7.01(m,2H), 5.58(S,2H), 2.05(S,3H), 1.48(S,6H) ppm; ^{13}C NMR (DMSO-*d6*, 75 MHz) **(Fig. S7)**: δ 203.65, 177.19, 169.82, 163.71, 160.48, 140.19, 132.40, 130.58, 128.63, 127.52, 125.52, 116.16, 114.54, 111.83, 64.88, 22.89 & 20.63 ppm; MS **(Fig. S8)**: m/z 387 [M+H].

Stage-1C: {4-[3-(3-fluorophenyl)-5,5-dimethyl-4-oxo-4,5-dihydrofuran-2-yl]benzene-1-sulfonyl}methyl acetate



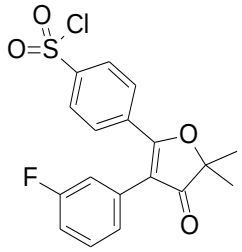
White solid powder; IR (ATR) **(Fig. S9)**: 3020.53, 2962.33, 1759.08, 1683.86, 1627.92, 1610.56, 1367.53, 1350.02, 1085.92 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz,) **(Fig. S10)**: δ 8.03-8.00(d, J=9,2H), 7.84-7.81 (d, J=9,2H), 7.47-7.39(m,1H), 7.23-7.16(m,1H), 7.13-7.12 (m,1H), 7.10-7.03(m,1H), 5.46(S,2H), 2.51(S,3H), 1.51(S,6H) ppm; ^{13}C NMR (DMSO-*d6*, 75 MHz) **(Fig. S11)**: δ 203.92, 176.09, 168.21, 163.70, 160.47, 139.38, 134.76, 131.56, 130.68, 129.14, 125.39, 116.05, 114.86, 113.71, 87.53, 75.25 & 22.80 ppm; MS **(Fig. S12)**: m/z 419 [M+H].

Stage-1: sodium 4-[3-(3-fluorophenyl)-5,5-dimethyl-4-oxo-4,5-dihydrofuran-2-yl]benzene-1-sulfinate



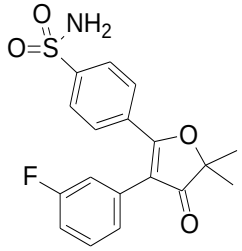
White solid powder; IR (ATR) **(Fig. S13)**: 1649.14, 1614.42,1 454.33, 1303.88, 1294.24, 1105.21, 941.26 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz,) **(Fig. S14)**: δ 7.523 (4H, S), 7.44 -7.37 (1H,m), 7.28-7.22 (1H,m), 7.10-7.09(1H,m), 7.068-7.01(1H,m), 1.48 (S,6H) ppm; ^{13}C NMR (DMSO-*d6*, 75 MHz) **(Fig. S15)**: δ 203.72, 178.52, 163.93, 60.44, 137.33, 132.52, 130.47, 128.89, 125.43, 124.58, 116.03, 114.38, 111.65, 86.93 & 22.94 ppm; MS **(Fig. S16)**: m/z 369 [M+H].

Stage-2A: 4-[3-(3-fluorophenyl)-5,5-dimethyl-4-oxo-4,5-dihydrofuran-2-yl]benzene-1-sulfonyl chloride



Yellow solid powder; IR (ATR) **(Fig. S17)**: 3088.03, 3045.60, 2931.80, 1932.67, 1649.14,1 429.25, 1307.74, 1111.0 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz,) **(Fig. S18)**: δ 8.06-8.03(d, J=9,2H), 7.91-7.88 (d J=9, 2H), 7.41-7.34 (m,1H), 7.12-7.03 (m ,3H), 1.48 (S,6H) ppm; ^{13}C NMR (DMSO-*d6*, 75 MHz) **(Fig. S19)**: δ 204.88, 175.01, 164.83, 161.56, 146.41, 136.27, 131.13, 130.84, 129.74, 127.31, 125.29, 116.74, 115.28, 88.12 & 23.48 ppm; MS **(Fig. S20)**: m/z 381 [M+H].

Stage-2: 4-[3-(3-fluorophenyl)-5,5-dimethyl-4-oxo-4,5-dihydrofuran-2-yl]benzene-1-sulfonamide / Polmocoxib



White to yellow powder; IR (ATR) **(Fig. S21)**: 2983.88, 2939.52, 1643.35, 1612.49, 1460.11, 1359.82, 1294.24, 1116.78, 948.98 cm^{-1}; ^{1}H NMR (DMSO-*d6*, 300 MHz,) **(Fig. S22)**: δ 7.91-7.88 (d, J=9,2H), 7.86-7.83(m, 2H), 7.72-7.69(m,2H), 7.43-7.35 (m,1H), 7.17-7.10 (m,1H), 7.05 -7.00 (m,2H), 1.51 (S,6H) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz) **(Fig. S23)**: δ 203.85, 176.82, 163.71, 160.48, 146.86, 132.24, 131.84, 130.63, 128.83, 126.03, 125.41, 116.08, 114.72, 87.38 & 22.86 ppm; MS **(Fig. S24)**: m/z 362 [M+H].

B) Characterization spectra of synthesized compounds:

Stage 1A:

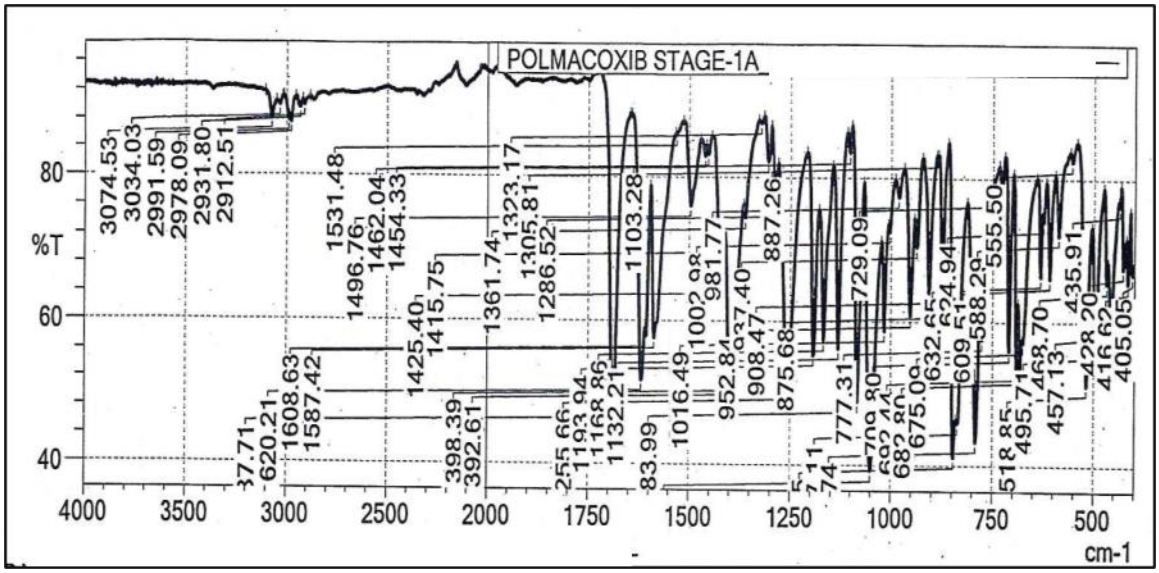


Fig. S1

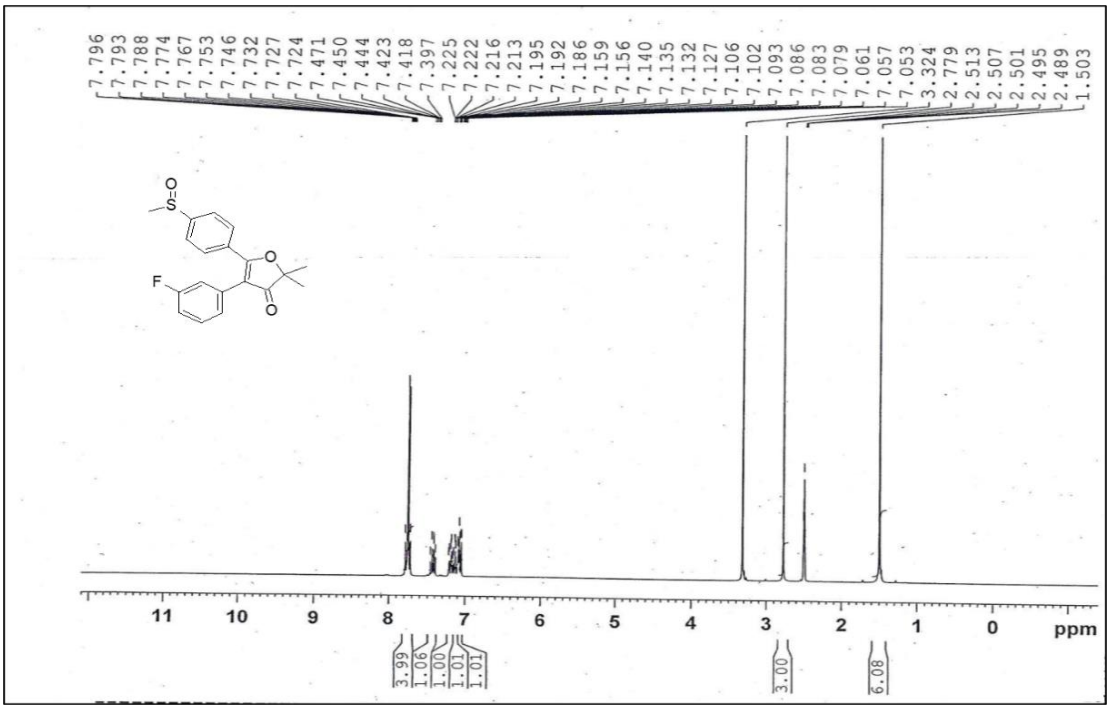


Fig. S2

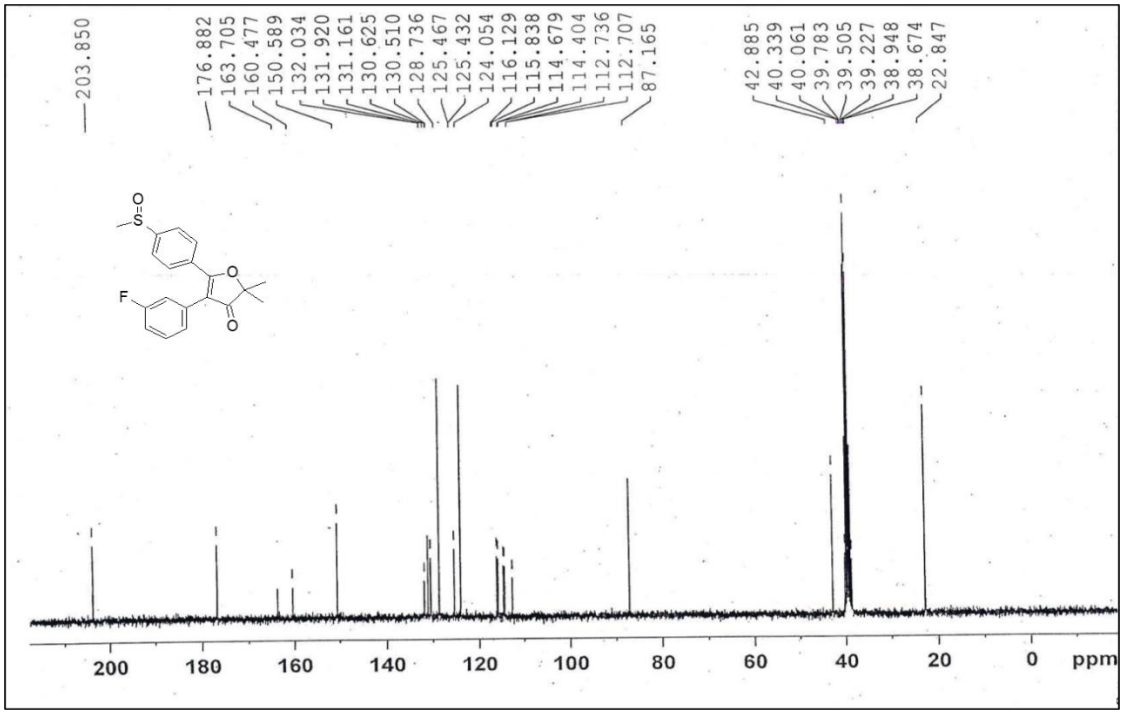

203.850
176.882
163.705
160.477
150.589
132.034
131.920
131.161
130.625
130.510
128.736
125.467
125.432
124.054
116.129
115.838
114.679
114.404
112.736
112.707
87.165
42.885
40.339
40.061
39.783
39.505
39.227
38.948
38.674
22.847
200
180
160
140
120
100
80
60
40
20
0
ppm

Fig. S3

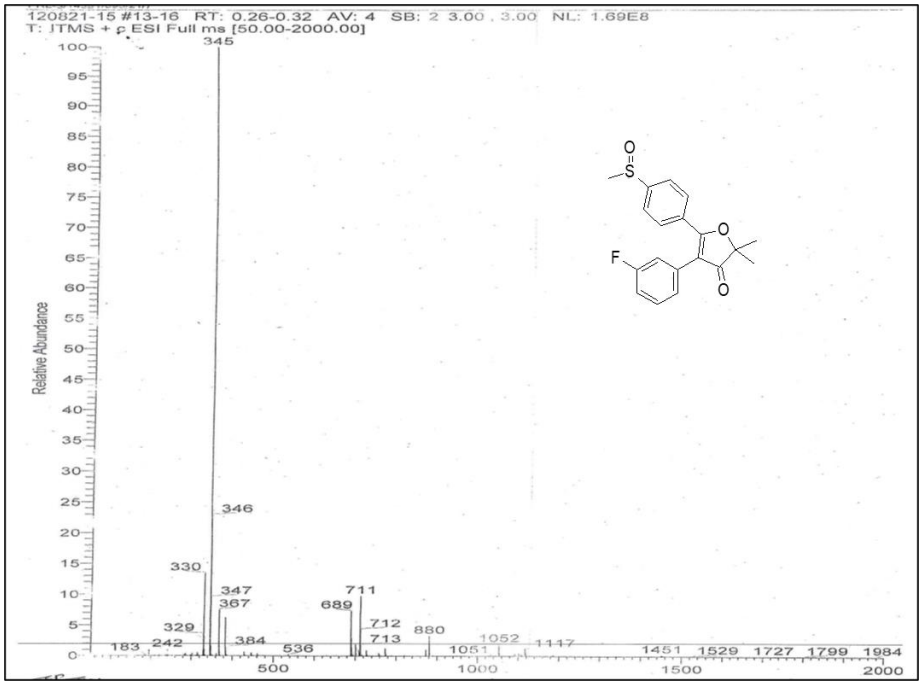

120821-15 #13-16 RT: 0.26-0.32 AV: 4 SB: 2 3.00 , 3.00 NL: 1.69E8
T: ITMS + c ESI Full ms [50.00-2000.00]
Relative Abundance
345
346
330
347
367
329
384
536
711
689
712
713
880
183
242
1052
1117
1451
1529
1727
1799
1984
500
1000
1500
2000

Fig. S4

Stage 1B:

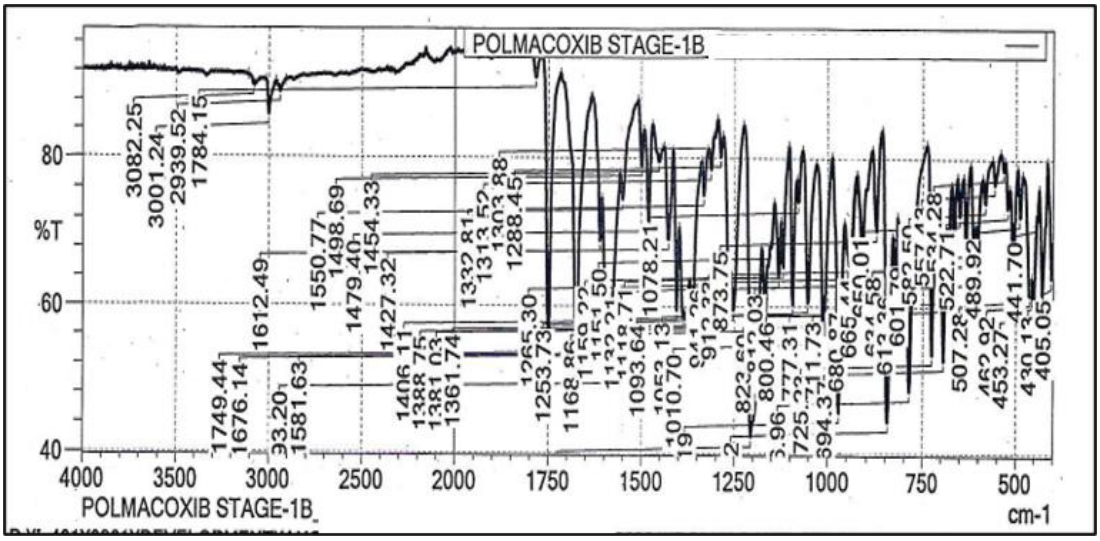


Fig. S5

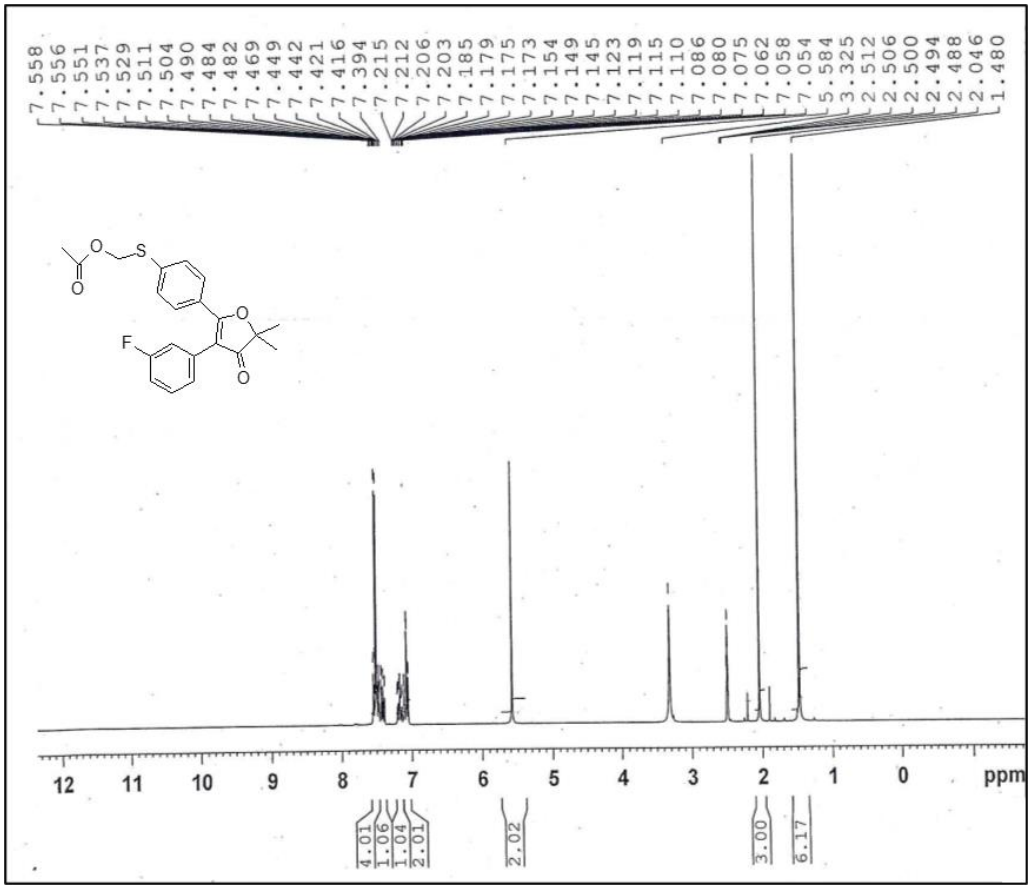


Fig. S6

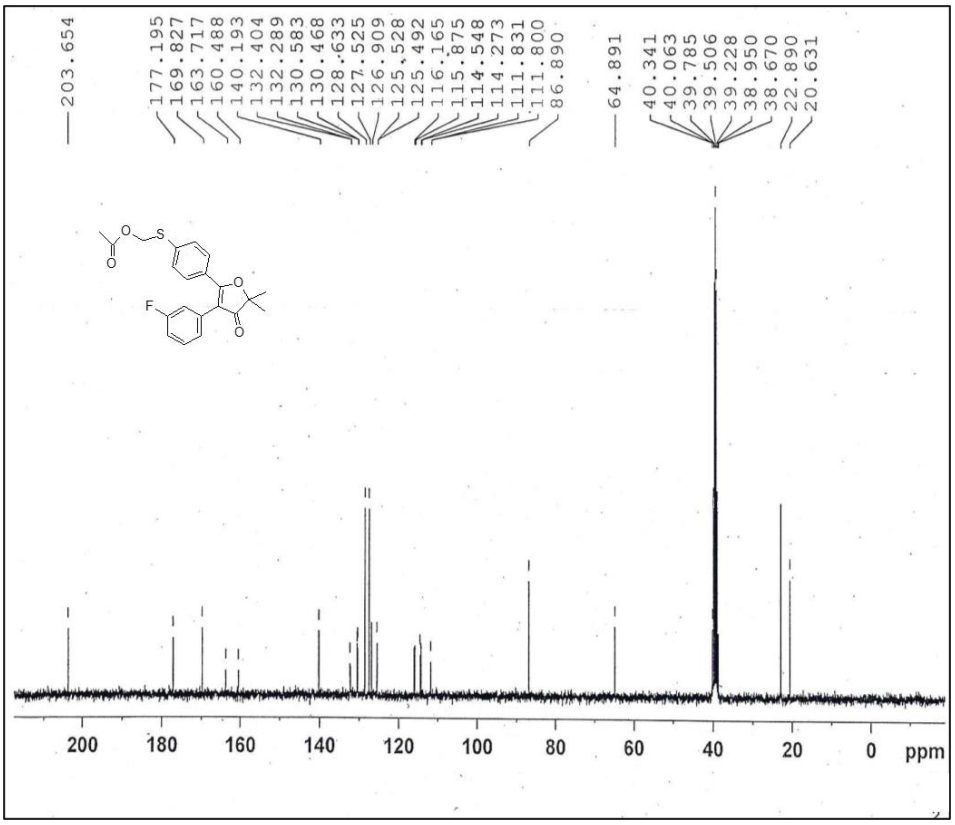

203.654
177.195
169.827
163.717
160.488
140.193
132.404
132.289
130.583
130.468
128.633
127.525
126.909
125.528
125.492
116.165
115.875
114.548
114.273
111.831
111.800
86.890
64.891
40.341
40.063
39.785
39.506
39.228
38.950
38.670
22.890
20.631
200
180
160
140
120
100
80
60
40
20
0
ppm

Fig. S7

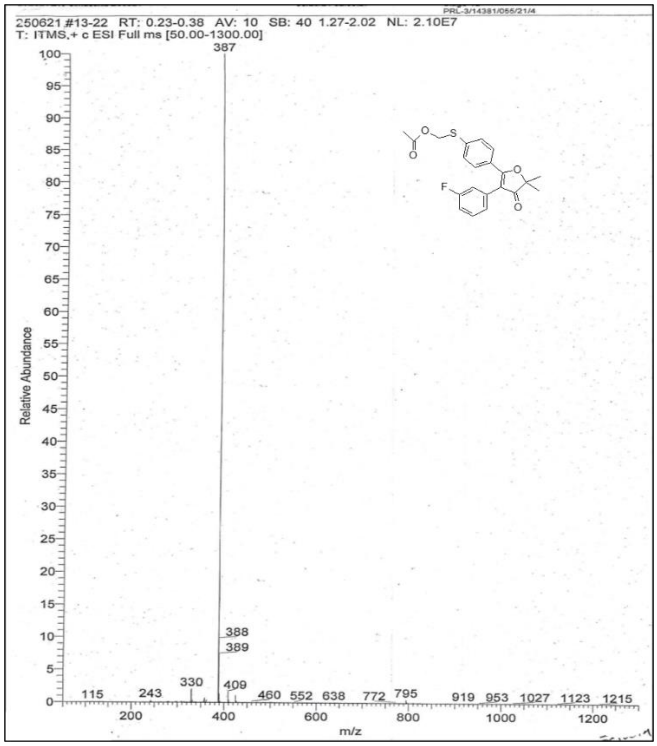

250621 #13-22 RT: 0.23-0.38 AV: 10 SB: 40 1.27-2.02 NL: 2.10E7
T: ITMS + c ESI Full ms [50.00-1300.00]
387
388
389
409
Relative Abundance
m/z

Fig. S8

Stage 1C:

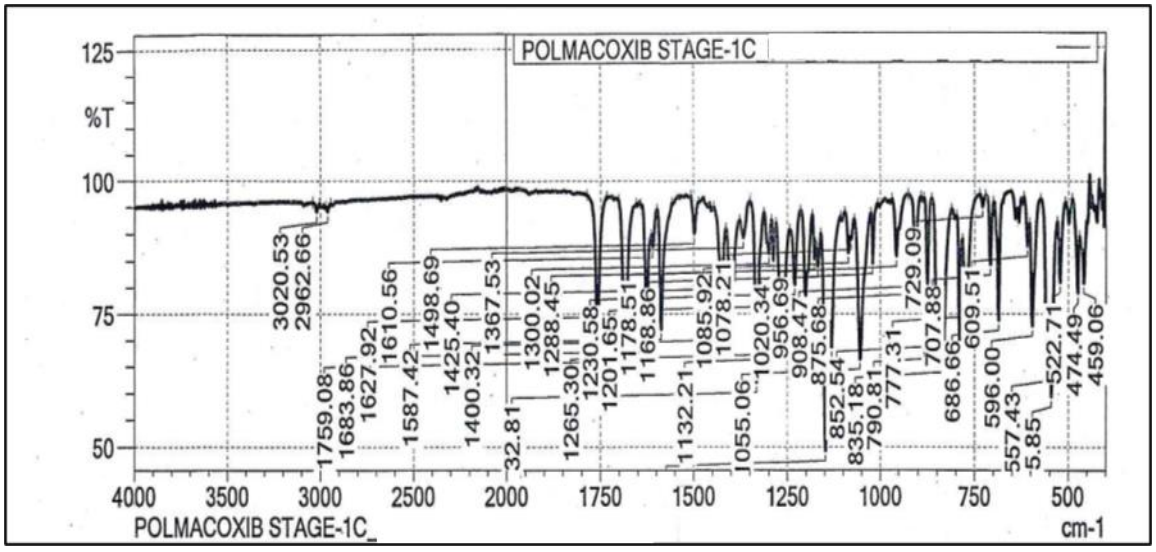


Fig. S9

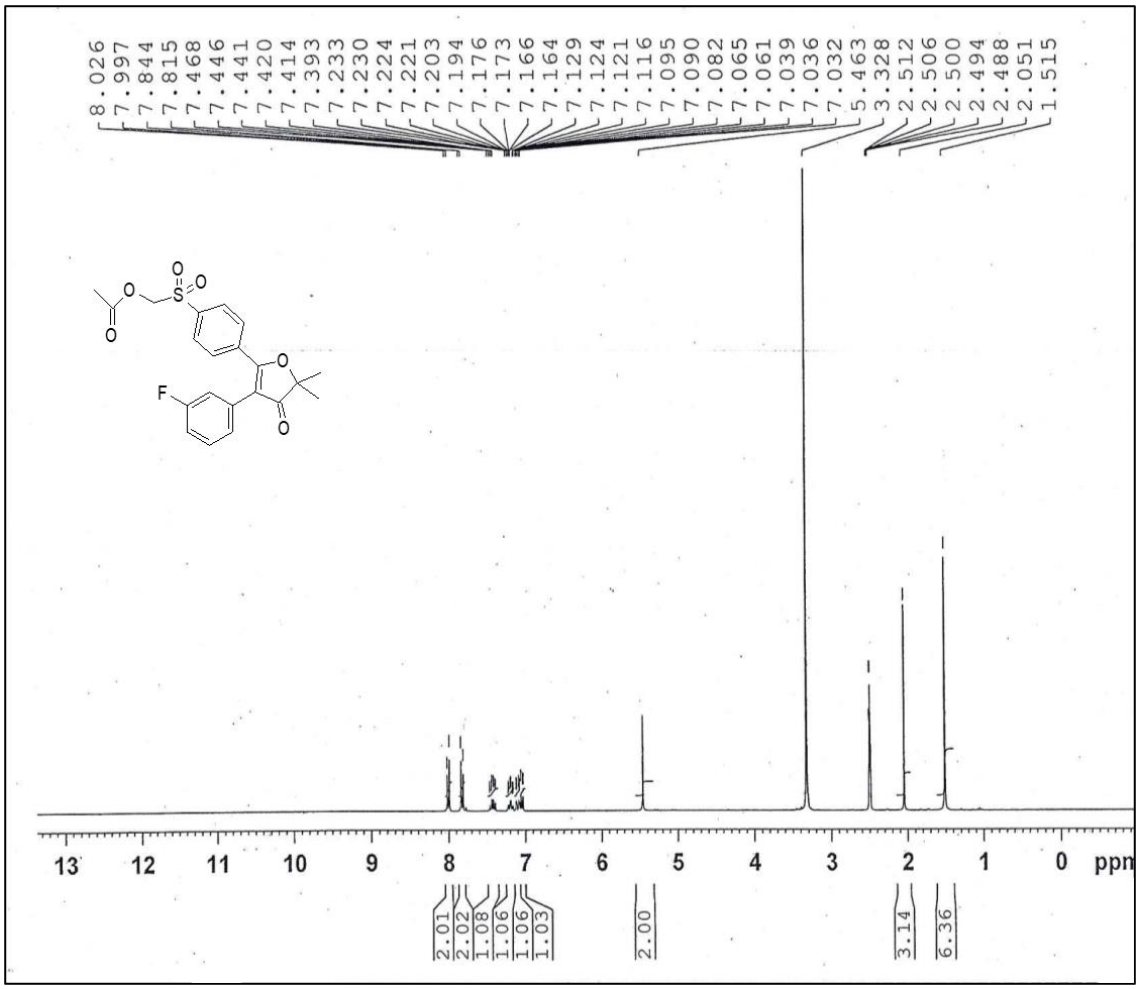


Fig. S10

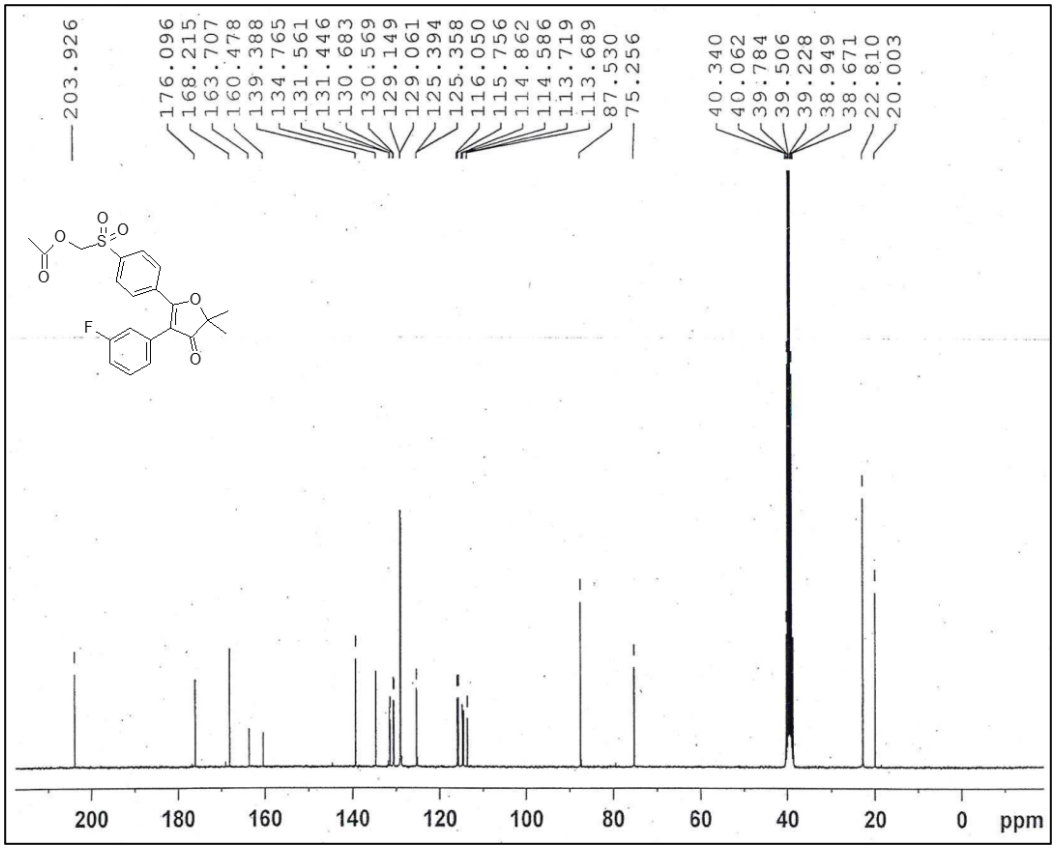


Fig. S11

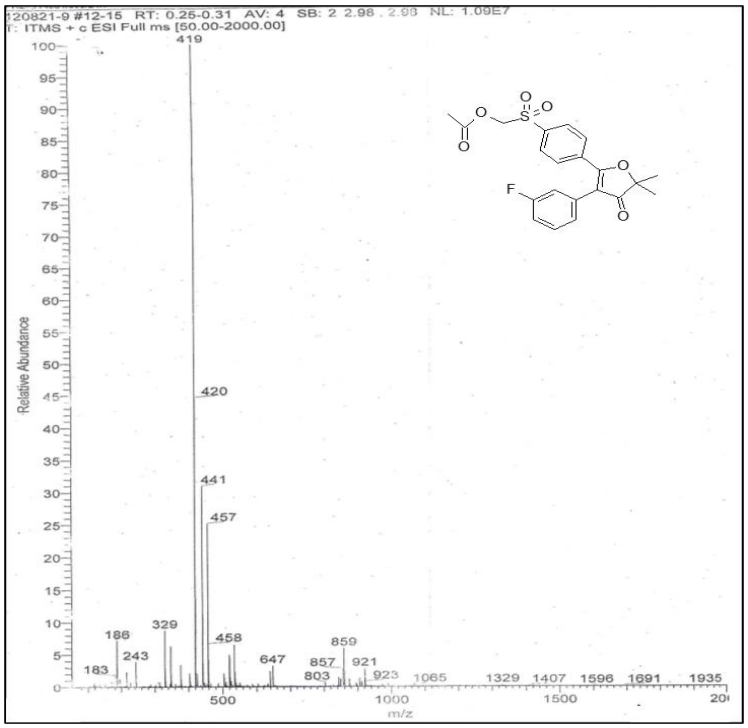


Fig. S12

Stage 1:

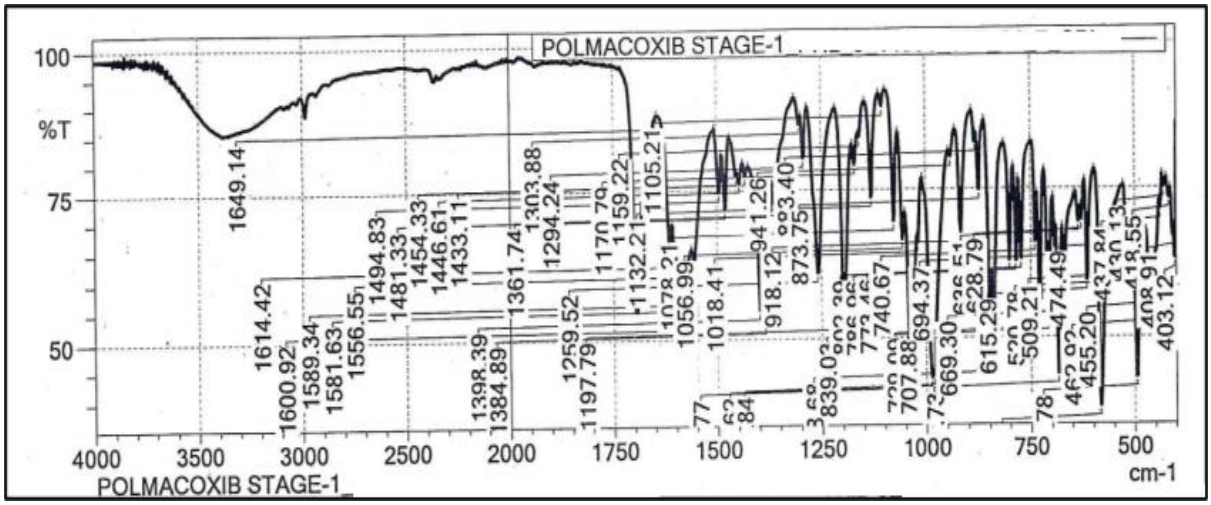


Fig. S13

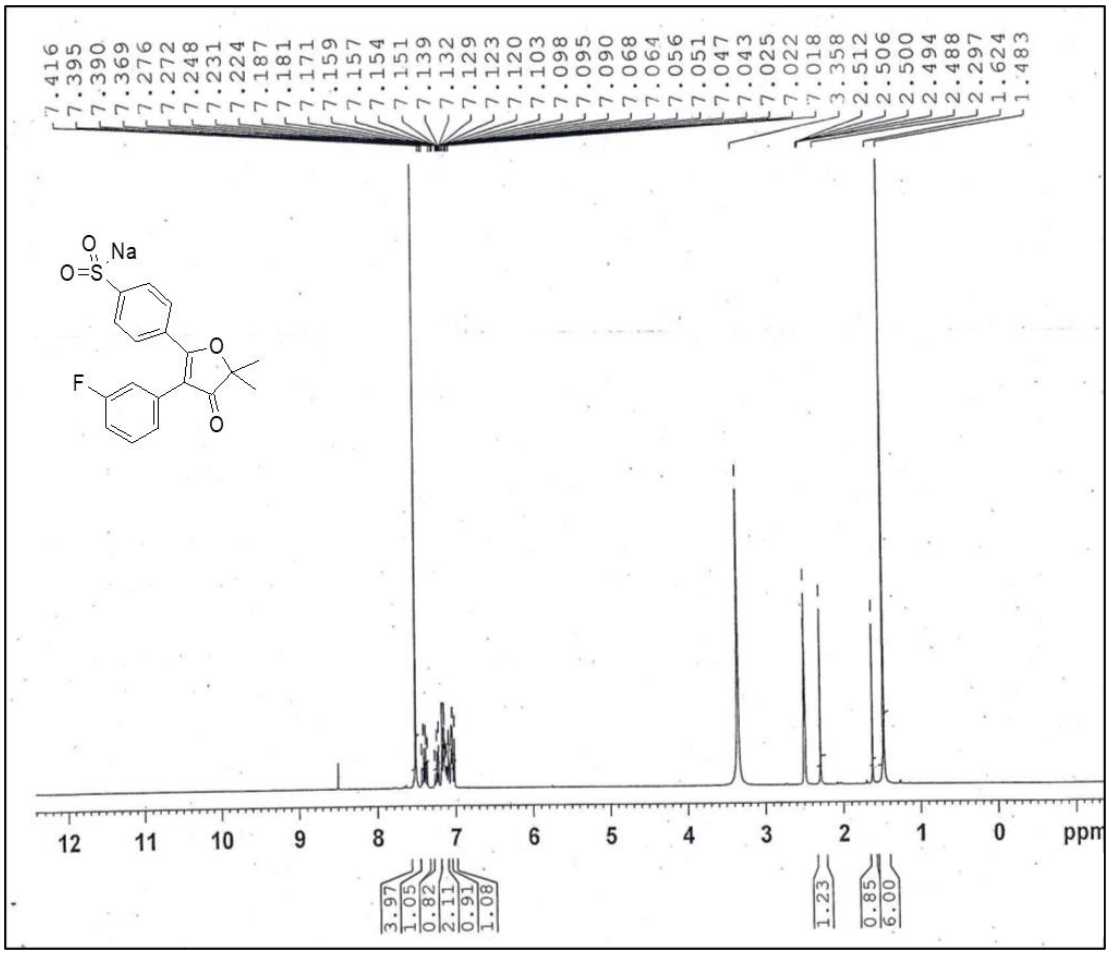


Fig. S14

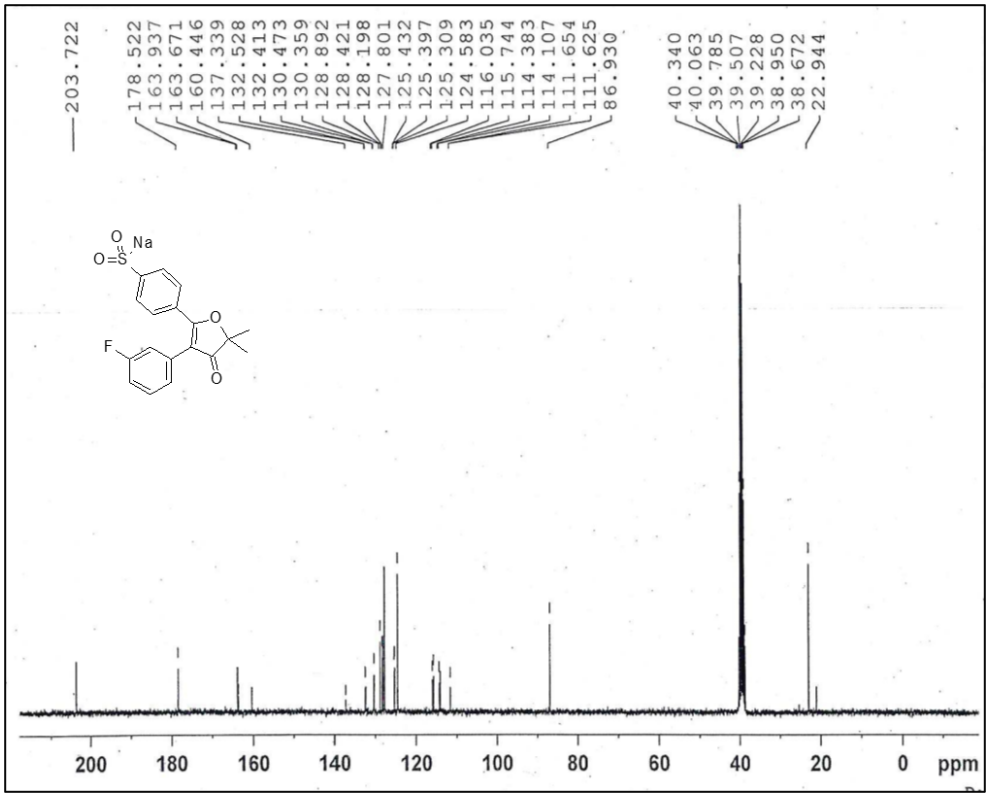


Fig. S15

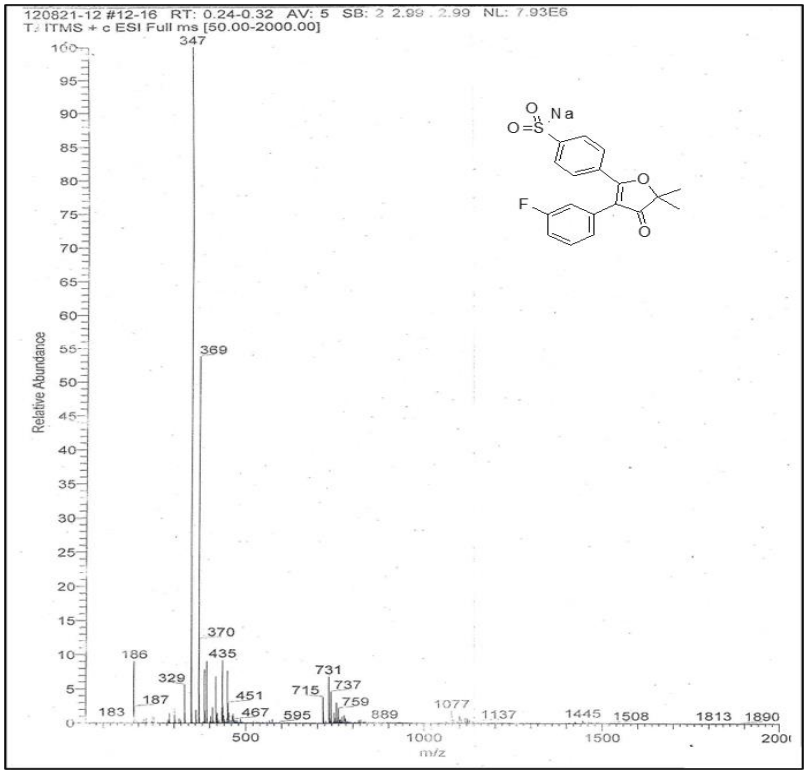


Fig. S16

Stage 2A:

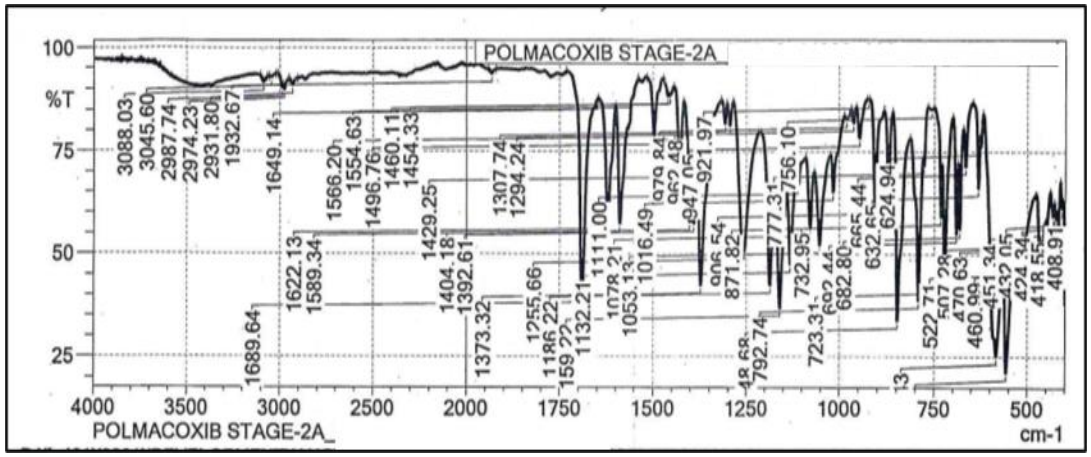


Fig. S17

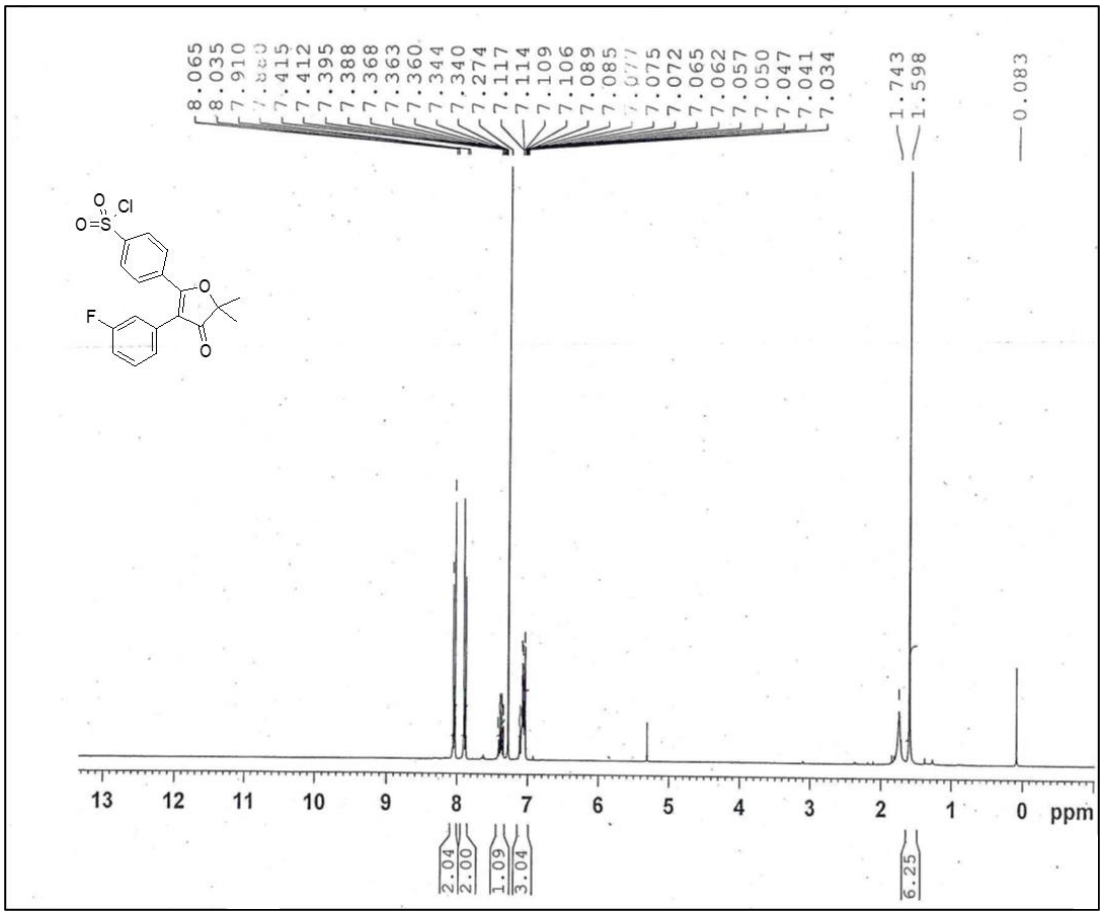


Fig. S18

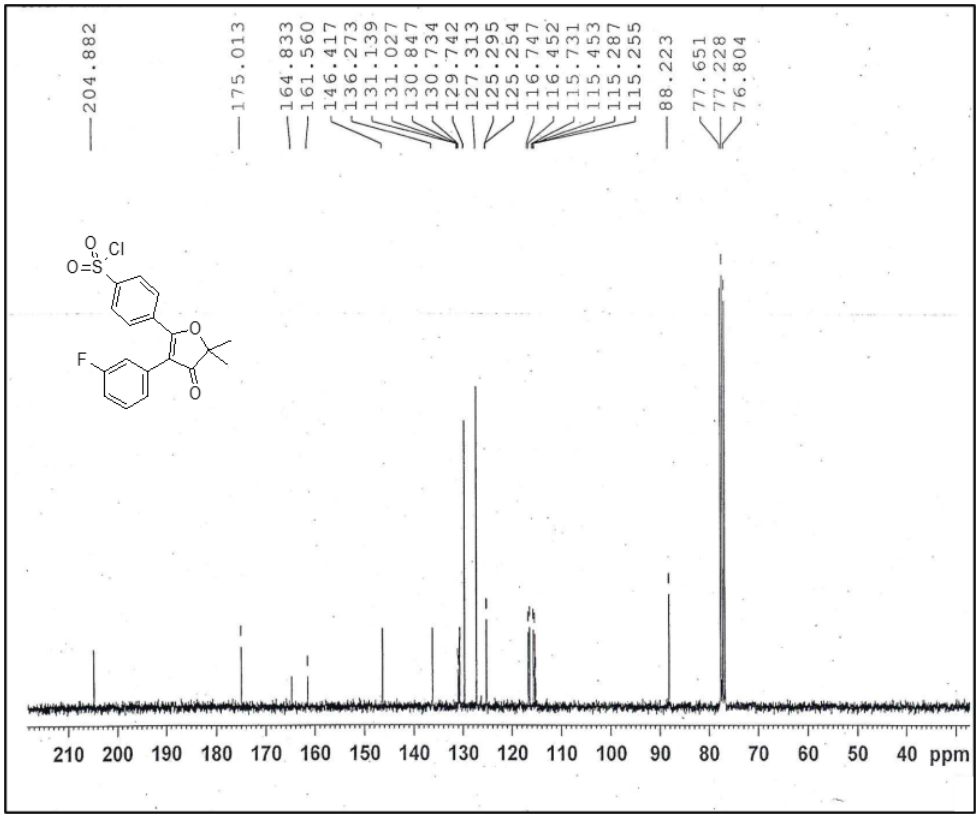


Fig. S19

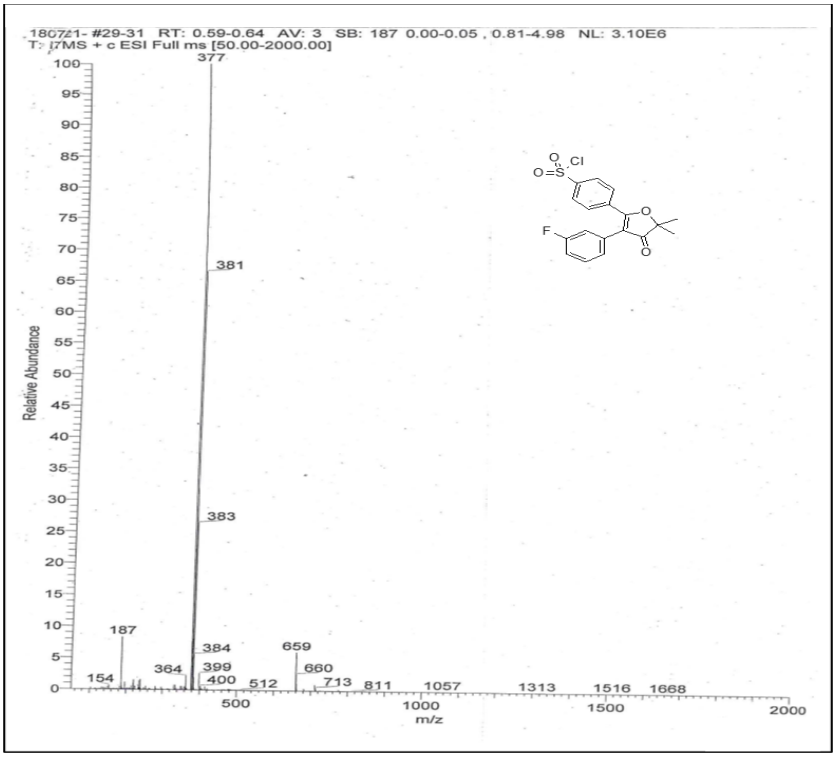


Fig. S20

Stage 2:

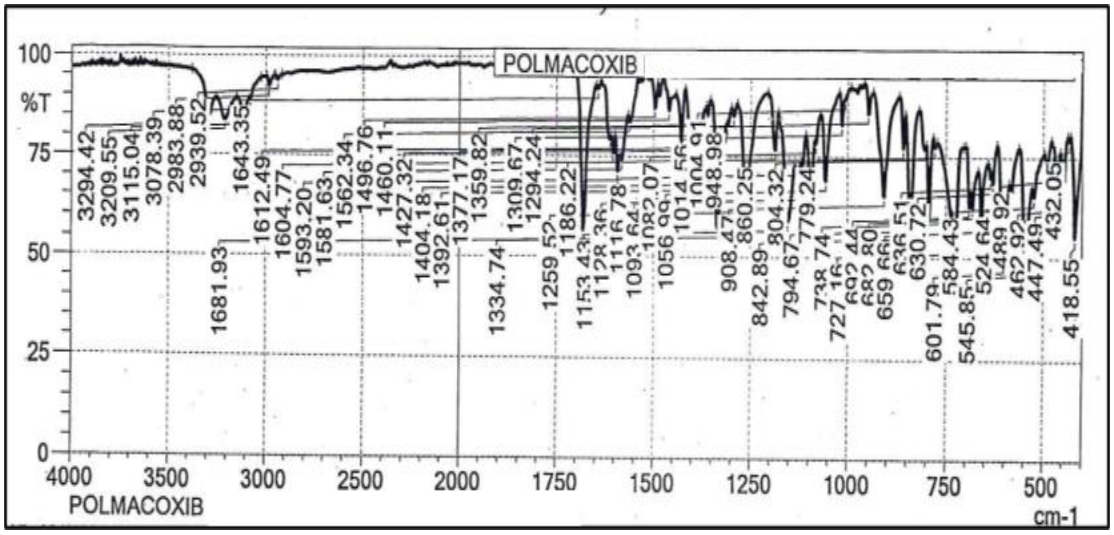


Fig. S21

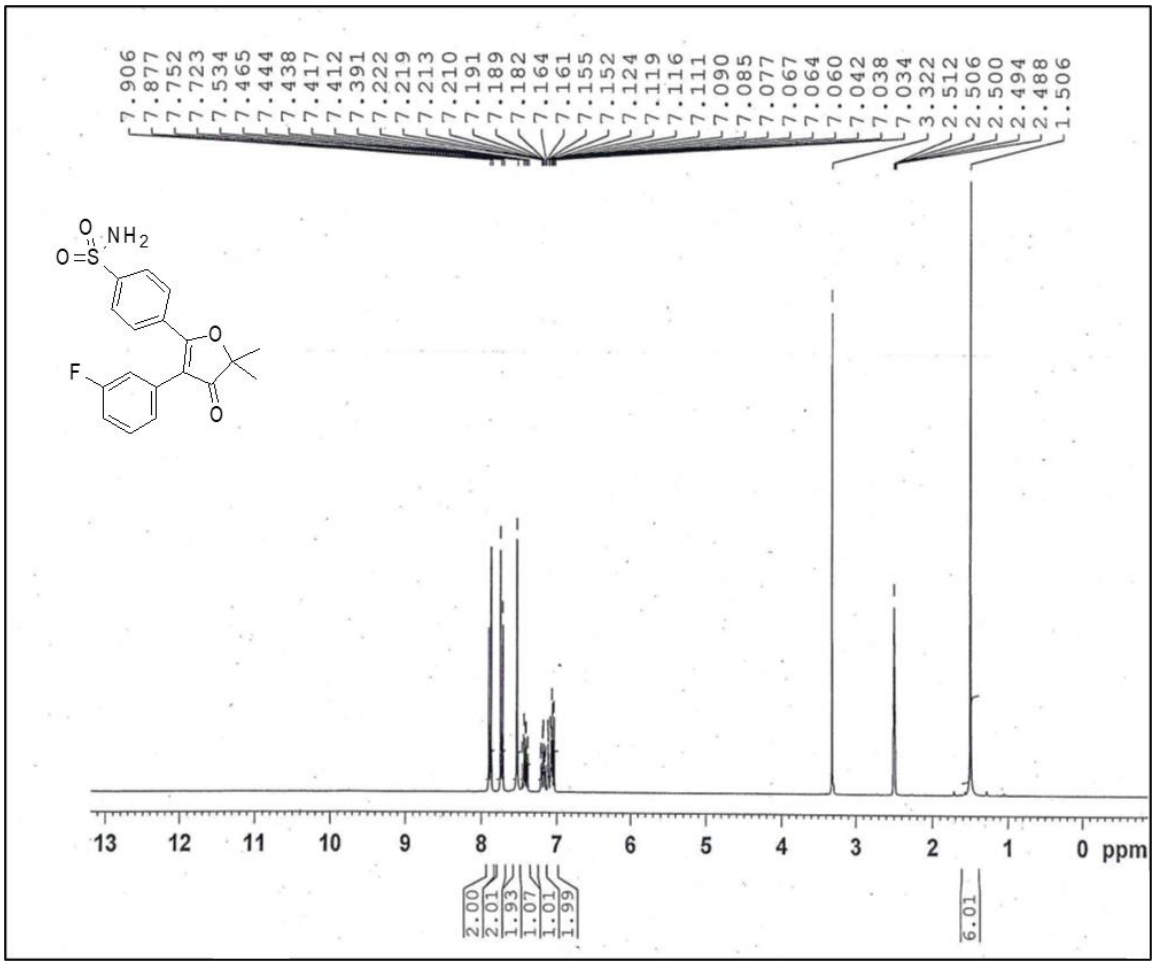


Fig. S22

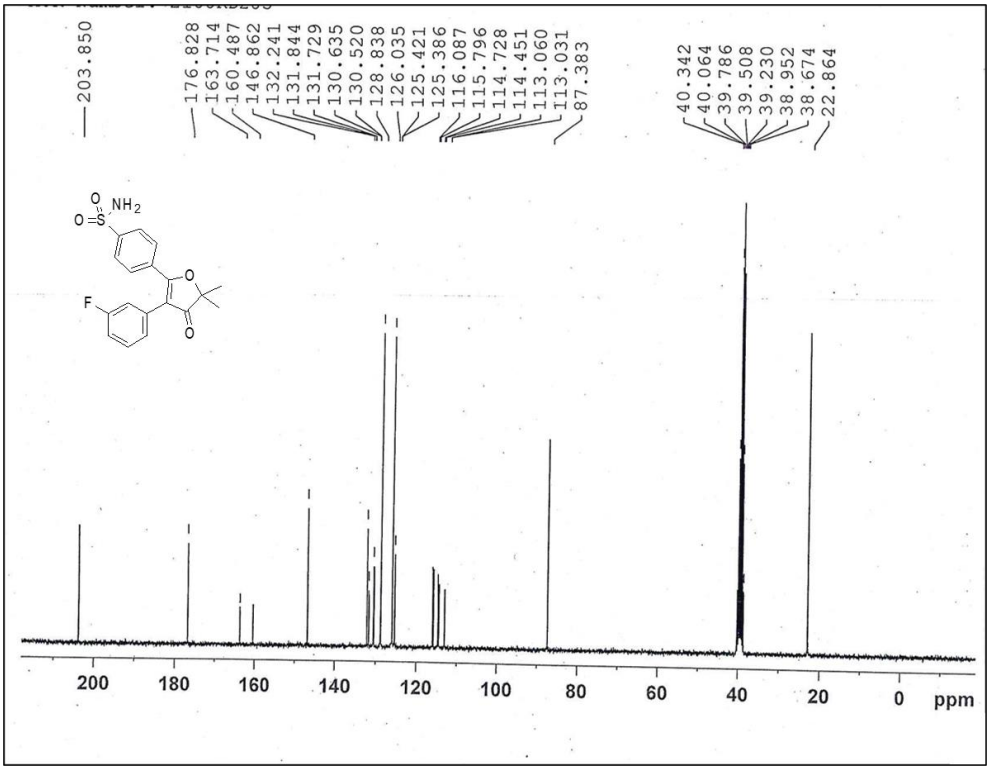


Fig. S23

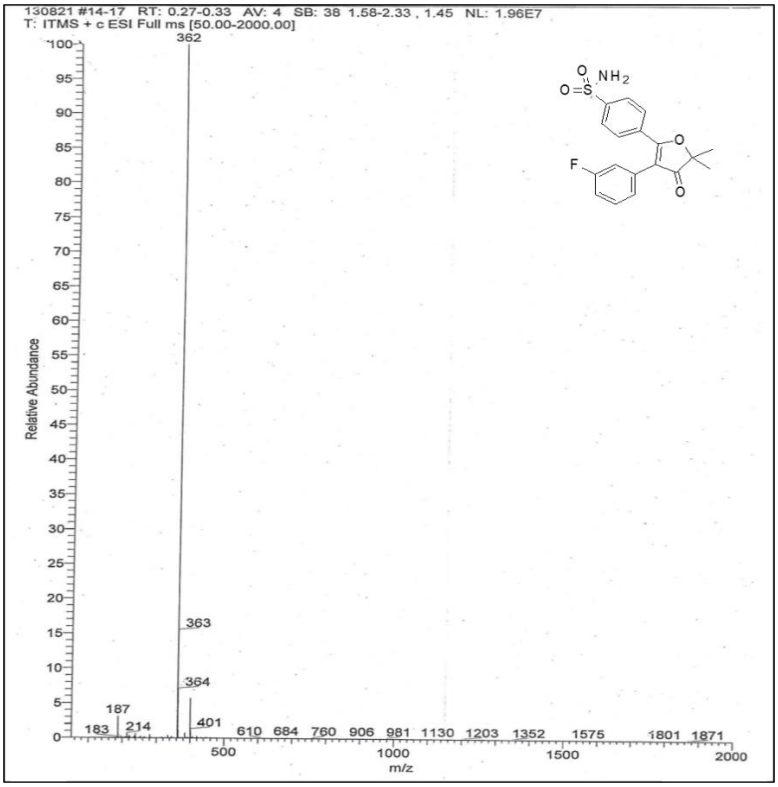


Fig. S24