Synthesis of Indeno[1,2-*b*]benzofurans using TPAB as Highly Efficient and Recoverable Catalyst

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ABSTRACT

Herein we report the synthesis of some novel indeno[1,2-*b*]benzofuran derivatives by reaction of ninhydrin with cyclic 1,3-dicarbonyl compounds including cyclopentane-1,3-dione, cyclohexane-1,3-dione, dimedone, 4,4-dimethylcyclohexane-1,3-dione, meldrum's acid, barbituric acid, thiobarbituric acid, 1,3-dimethylbarbituric acid and indane-1,3-dione. We also used tetrapropylammonium bromide (TPAB) as an organocatalyst.

KEYWORDS

Cyclic 1,3-dicarbonyl compounds, ninhydrin, indeno[1,2-*b*]benzofurans, TPAB.

1. Introduction

The synthesis of indeno[1,2-*b*]benzofurans through the reaction of ninhydrin with 1,3-diketones, aryl aldehydes and malononitrile has been carried out under different reaction conditions. Numerous types of reagents, like AcOH,[1] I_2/MeOH,[2] BF_3-OEt_2,[3] EtOH/US[4] are known for their catalyzing effect on this reaction. In spite of acceptable results obtained from the above-mentioned methods, their usage is limited by some disadvantages such as high cost, low yields of product, high reaction temperatures and the use of some less than desirable solvents.

The indeno[1,2-*b*]benzofurans are important heterocyclic compounds due to their wide range of pharmaceutical and biological activities, such as their anti-microbial, anti-oxidant, analgesic and anti-inflammatory properties.[1,5]

Tetrapropylammonium bromide (TPAB) is a readily available, and inexpensive chemical and one of the most commonly utilized phase-transfer catalysts (PTC) with numerous applications in diverse catalytic processes, including for instance in the synthesis of ZSM-type zeolites.[6]

Following our previous research work involving the synthesis of novel heterocyclic compounds,[7] we report here the production of some new indeno[1,2-*b*]benzofuran derivatives in excellent yield and relatively short reaction times, through the reaction of ninhydrin with cyclic 1,3-dicarbonyl compounds, using TPAB as a recyclable catalyst.

2. Experimental

The chemicals used in the current research were purchased from Acros and Merck companies. FTIR spectra were recorded with a Thermo Nicolet (Nexus 670) instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 300 and 75 MHz in $CDCl_3$ or DMSO-d_6 as solvents and using TMS as the internal standard. Mass spectra were recorded on a Varian Matt 311 spectrometer. Melting points were determined with an Electrothermal 9200 apparatus. Elemental analyses were performed using a Leco Analyzer 932.

General Procedure for the Synthesis of Products 3a–i

A mixture of ninhydrin (**1**, 1 mmol) and cyclic 1,3-dicarbonyl compounds **2a–i** (1 mmol) was heated in the presence of TPAB (20 mol%) in dichloromethane (2 mL) under reflux for an appropriate time (Scheme 1). The reaction progress was investigated by TLC using CH_2Cl_2/hexane/methanol, 15:15:1. After completion of the reaction, the solvent was removed under reduced pressure and the obtained precipitate was filtered and washed with H_2O/EtOH (1:2), resulting to the desired products **3a–i** in good yields of 87–98 %.

Recovery of TPAB

In the separation of products **3a–i**, after extraction of filtrate with $CHCl_3$, the aqueous layer was separated and evaporation of water gave TPAB, which may be used for reusability process.

4*a*,9*a*-Dihydroxy-2,3,4*a*,9*a*-tetrahydrocyclopenta[*b*]indeno[2,1-*d*]furan-1,9-dione (3a): This compound was obtained from cyclopentane-1,3-dione, time reaction 26 min, white powder, yield 87 %; m.p. 159–161 °C; FT-IR ν_{max}: 3494, 2926, 2563, 1749, 1714, 1604, 1545, 1370, 1291, 1142, 954, 848, 768, 717, 640, 581, 476, 426 cm^{-1}; δ_H: 7.98 (4H, bs, Ar), 3.61 (2H, bs, 2×OH), 2.38 (4H, bs, 2×CH_2); δ_C: 194.7, 191.5, 158.6, 143.2, 142.1, 141.3, 130.8, 127.8, 126.6, 119.3, 115.7, 72.2, 36.1, 29.3; *m*/*z*: 259 $[M+1]^+$ (95), 258 $[M]^+$ (100), 242 (46), 230 (95), 173 (39), 134 (28), 105 (62), 104 (57), 77 (42), 76 (38). Found: C, 65.12; H, 3.90 %. Calc. for $C_{14}H_{10}O_5$ (258); C, 65.29; H, 3.80 %.

4*b*,9*b*-Dihydroxy-6,7,8,9*b*-tetrahydro-9*H*-indeno[1,2-*b*]benzofuran-9,10(4*bH*)-dione (3b): This compound was obtained from cyclohexane-1,3-dione, time reaction 20 min, yellow needles, yield 93 %; m.p. 165–168 °C [lit.,[1] 174 °C].

4*b*,9*b*-Dihydroxy-7,7-dimethyl-6,7,8,9*b*-tetrahydro-9*H*-indeno[1,2-*b*]benzofuran-9,10(4*bH*)-dione (3c): This compound was obtained from dimedone, time reaction 25 min, white needles, yield 98 %; m.p. 198–200 °C [lit.,[4] 210 °C].

4*b*,9*b*-Dihydroxy-6,6-dimethyl-6,7,8,9*b*-tetrahydro-9*H*-indeno[1,2-*b*]benzofuran-9,10(4*bH*)-dione (3d): This compound was obtained from 4,4-dimethylcyclohexane-1,3-dione, time reaction 25 min, white powder, yield 97 %; m.p. 152–154 °C; FT-IR ν_{max}: 3389, 3253, 3096, 2941, 2880, 2679, 2495, 2360, 1711, 1660,

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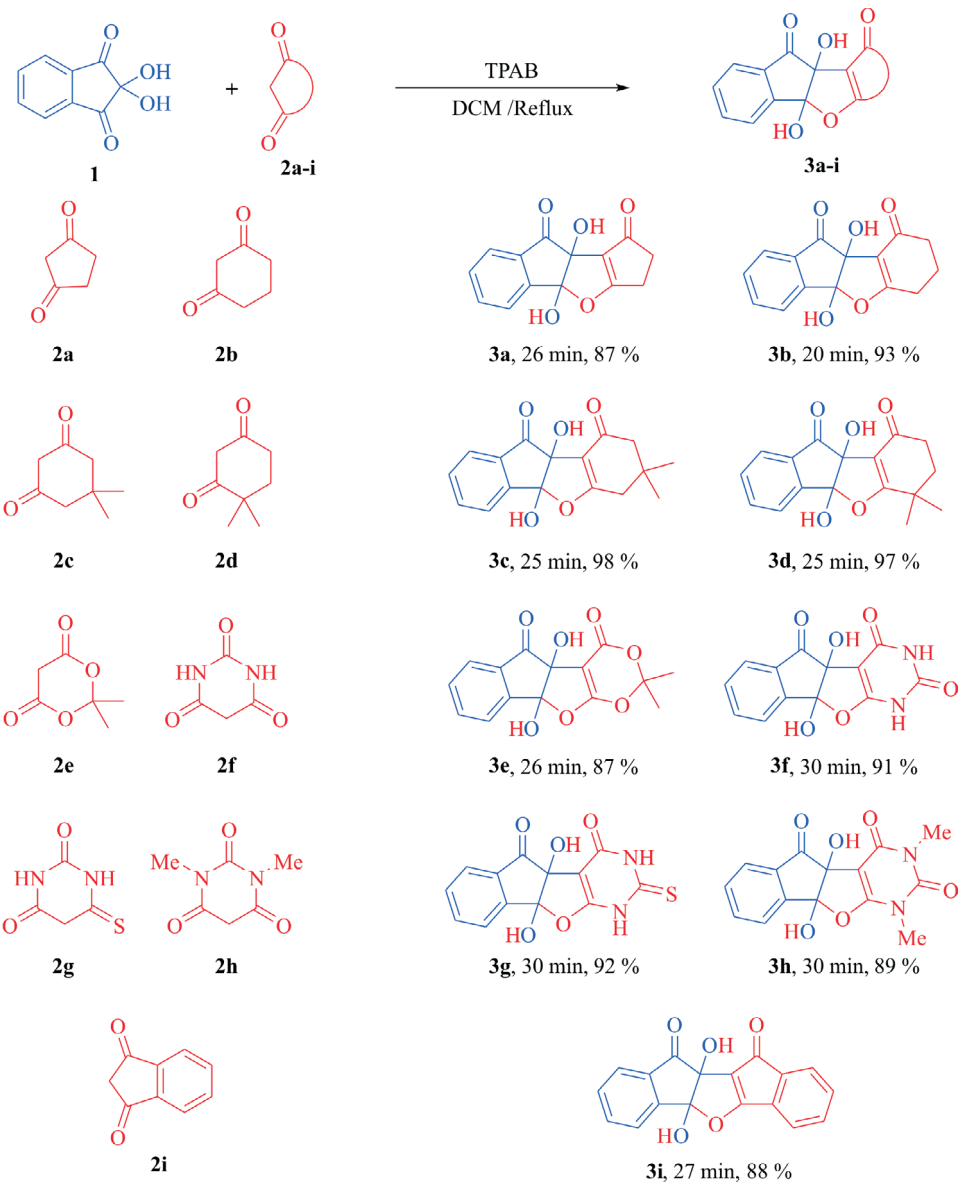


Scheme 1
Synthesis of indeno[1,2-*b*]benzofurans **3a–i.**

1609, 1469, 1392, 1330, 1294, 1263, 1178, 1158, 1066, 1006, 949, 920, 881, 852, 778, 668, 577, 520, 499, 448 cm^{-1}; δ_H: 7.90–7.88 (2H, m, Ar), 7.74–7.65 (2H, m, Ar), 5.51 (2H, bs, 2×OH), 2.26 (2H, bs, CH_2), 1.27 (2H, bs, CH_2), 1.03 (6H, s, 2×CH_3) ppm; δ_C: 196.1, 196.0, 163.5, 149.4, 148.0, 132.6, 121.7, 117.9, 116.2, 115.2, 109.7, 72.7, 45.5, 34.7, 23.4, 22.4 ppm; *m*/*z*: 301 $[M+1]^+$ (19), 300 $[M]^+$ (85), 243 (18), 226 (22), 202 (46), 167 (45), 146 (19), 134 (23), 104 (42), 83 (100), 55 (15). Found: C, 67.99; H, 5.37 %. Calc. for $C_{16}H_{16}O_5$ (300); C, 67.82; H, 5.47 %.

4*b*,9*b*-Dihydroxy-2,2-dimethyl-4*b*,9*b*-dihydro-4*H*,5*H*-indeno [2′,1′:4,5]furo[2,3-*d*][1,3]dioxine-4,5-dione (3e): This compound was obtained from Meldrum's acid, time reaction 26 min, white powder, yield 87 %; m.p. 110–113 °C; FT-IR ν_{max}: 3434, 3254, 2974, 1727, 1605, 1463, 1389, 1342, 1223, 1097, 976, 764, 654 cm^{-1}; δ_H: 7.28–7.15 (4H, m, Ar), 5.33 (2H, bs, 2×OH), 1.44 (6H, s, 2×CH_3) ppm; δ_C: 202.2, 192.7, 167.4, 162.3, 144.5, 140.5, 134.3, 131.7, 129.4, 122.0, 113.7, 86.0, 80.1, 24.6 ppm; *m*/*z*: 304 $[M]^+$ (4), 290 (15), 202 (10), 167 (25), 149 (68), 125 (19), 114 (100), 97 (39), 86 (40), 71 (51), 57 (67). Found: C, 59.22; H, 3.98 %. Calc. for $C_{15}H_{12}O_7$ (304); C, 59.40; H, 3.76 %.

4*b*,9*b*-Dihydroxy-4*b*,9*b*-dihydro-2*H*-indeno[2′,1′:4,5]furo [2,3-*d*] pyrimidine-2,4,5(1*H*,3*H*)-trione (3f): This compound was obtained from barbituric acid, time reaction 30 min, yellow solid, yield 91 %; m.p. 165–167 °C; FT-IR ν_{max}: 3607, 3456, 3175, 2970, 1697, 1583, 1471, 1370, 1247, 1182, 1045, 1009, 970, 852, 772, 730, 639, 580, 525, 424 cm^{-1}; δ_H: 9.43 (2H, bs, 2×NH), 7.91–7.85 (4H, m, Ar), 3.37 (2H, bs, 2×OH) ppm; δ_C: 204.9, 203.0, 202.9, 165.6, 152.2, 137.0, 134.7, 132.6, 124.3, 122.0, 119.3, 87.3, 79.6 ppm; *m*/*z*: 288 $[M]^+$ (13), 271 (4), 229 (17), 211 (4), 186 (4), 143 (20), 128 (14), 114 (100), 104 (45), 86 (38), 76 (38), 50 (8). Found: C, 54.18; H, 2.80; N, 9.72 %. Calc. for $C_{13}H_8N_2O_6$ (288); C, 54.00; H, 2.92; N, 9.61 %.

4*b*,9*b*-Dihydroxy-2-thioxo-2,3,4*b*,9*b*-tetrahydro-4*H*-indeno [2′,1′:4,5]furo[2,3-d]pyrimidine-4,5(1*H*)-dione (3g): This compound was obtained from thiobarbituric acid, time reaction 30 min, white needle, yield 92 %; m.p. 190–192 °C; FT-IR ν_{max}: 3585, 3515, 3070, 2969, 2879, 1712, 1590, 1528, 1433, 1378, 1289, 1248, 1194, 1014, 971, 889, 848, 771, 724, 626, 533 cm^{-1}; δ_H: 10.89 (2H, s, 2×NH), 7.92–7.87 (4H, m, Ar), 3.65 (2H, bs, 2×OH) ppm;

δ_C: 202.1, 174.5, 163.8, 147.3, 137.3, 135.0, 129.0, 126.9, 124.4, 122.1, 116.4, 97.1, 85.4 ppm; *m/z*: 304 $[M]^+$ (5), 290 (6), 186 (3), 160 (3), 144 (34), 132 (28), 114 (100), 104 (78), 86 (35), 72 (33), 76 (75), 59 (8). Found: C, 51.32; H, 2.65; N, 9.21 %, Calc. for $C_{13}H_8N_2O_5S$ (304); C, 51.43 %, H, 2.52, N, 9.35 %.

4*b*,9*b*-Dihydroxy-1,3-dimethyl-4*b*,9*b*-dihydro-2*H*-indeno[2′,1′:4,5]furo[2,3-*d*]pyrimidine-2,4,5(1*H*,3*H*)-trione (3h): This compound was obtained from 1,3-dimethylbarbituric acid, time reaction 30 min, yellow solid, yield 89 %; m.p. 128–130 °C; FT-IR ν_{max}: 3366, 2959, 2859, 1669, 1455, 1382, 1263, 1157, 1102, 990, 924, 884, 747, 623, 493 cm^{-1}; δ_H: 8.07–8.05 (2H, m, Ar), 7.93–7.90 (2H, m, Ar), 4.99 (1H, s, OH), 4.43 (1H, s, OH), 3.30 (6H, s, 2×CH_3) ppm; δ_C: 198.5, 197.4, 197.3, 150.2, 138.0, 135.7, 132.1, 131.6, 124.6, 122.3, 111.6, 94.1, 83.2, 26.5, 25.2 ppm; *m/z*: 316 $[M]^+$ (5), 300 (5), 186 (6), 156 (41), 132 (38), 104 (100), 76 (91), 50 (8). Found: C, 56.97; H, 3.82; N, 8.86 %. Calc. for $C_{15}H_{12}N_2O_6$ (316); C, 56.88; H, 3.96; N, 8.71 %.

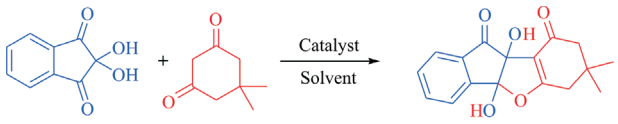
4*b*,10*b*-Dihydroxy-4*b*,10*b*-dihydrodiindeno[1,2-*b*:2′,1′-*d*]furan-10,11-dione (3i): This compound was obtained from indane-1,3-dione, time reaction 27 min, white powder, yield 88 %; m.p. 179–181 °C; FT-IR ν_{max}: 3418, 3081, 2906, 1707, 1587, 1464, 1344, 1265, 1155, 1083, 940, 887, 797, 755, 603, 443 cm^{-1}; δ_H: 7.95 (4H, m, Ar), 7.70–7.51 (4H, m, Ar), 4.99 (2H, bs, 2×OH) ppm; δ_C: 199.8, 197.2, 169.2, 167.8, 147.4, 141.2, 140.5, 138.6, 128.4, 128.1, 122.0, 120.8, 113.7, 113.0, 107.0, 105.5, 90.0, 72.6 ppm; *m/z*: 306 $[M]^+$ (3), 305 (8), 290 (30), 276 (16), 263 (15), 233 (16), 205 (10), 189 (18), 176 (25), 145 (14), 104 (100), 90 (9), 76 (58). Found: C, 70.59; H, 3.29 %. Calc. for $C_{18}H_{10}O_5$ (306); C, 70.81; H, 3.39 %.

3. Results and Discussion

The synthesis of the heterocyclic compounds started with arylglyoxals as core and used TPAB as an efficient organocatalyst with acceptable results.[8] As part of the project to develop catalytic applications of TPAB in synthesis of various heterocyclic compounds, it was found that the reaction of ninhydrin (**1**) with cyclic 1,3-dicarbonyl compounds **2a–i** using TPAB (20 mol%) in dichloromethane under reflux conditions, afforded indeno [1,2-*b*]benzofuran derivatives **3a–i** in excellent yield (Scheme 1).

In a preliminary study, the reaction was conducted without any catalyst, as a result, no product was obtained even after 24 h under reflux conditions (Table 1, entry 1). To determine the optimized reaction conditions for the synthesis of indeno [1,2-*b*] benzofurans, the reaction of ninhydrin (**1**, 1 mmol) with dimedone (**2c**, 1 mmol) was chosen as a model reaction to produce compound **3c**, and its behaviour was examined in the presence of several potential catalysts such as TPAB for phase transfer, *p*-TSA as acid source, L-cysteine and L-proline as zwiterions and sodium alginate as a salt, with different molar ratios and various solvents at room temperature ranging to reflux. To find out the appropriate solvent, for the reaction, model reaction was repeated in various solvents such as H_2O, acetone, CH_2Cl_2 and EtOH. Reaction in water or dichloromethane in the absence of any catalyst at room temperature or under reflux condition gave no product (Table 1, entry 1). After evaluating a number of different conditions (see Table), the optimum yield (98 %) was obtained when TPAB was used as catalyst, CH_2Cl_2 as solvent, 25 min of reaction time and under reflux conditions (Table 1, entry 21). To peruse the amount of catalyst in our trial reaction, the procedure was optimized using different molar concentrations of TPAB. To this end, an excellent yield of adduct **3c** was obtained using 20 mol%. On the contrary, lower quantities of the catalyst gave moderate yields of the product at longer reaction times (results not shown). Furthermore, using larger amounts of TPAB was not effective in terms of yields and resulted in large amounts of the starting materials

Table 1 Model reaction for the synthesis of compound **3c**[a].



1 **2c** **3c**

Entry	Solvent	Catalyst (20 mol%)	Temperature/°C	Time/min	Yield[b]/%
1	H_2O or CH_2Cl_2	No catalyst	RT-Reflux	24 h	–
2	H_2O	*p*-TSA	RT -Reflux	24 h	–
3	H_2O	Alginate sodium	RT -Reflux	24 h	–
4	H_2O	*L*-cysteine	RT -Reflux	24 h	–
5	H_2O	*L*-proline	RT -Reflux	24 h	–
6	H_2O	TPAB	RT -Reflux	24 h	–
7	EtOH	*p*-TSA	RT-Reflux	24 h	–
8	EtOH	Alginate sodium	RT-Reflux	24 h	–
9	EtOH	*L*-cysteine	RT-Reflux	24 h	–
10	EtOH	*L*-proline	RT-Reflux	24 h	–
11	EtOH	TPAB	RT-Reflux	24 h	Trace
12	Acetone	*p*-TSA	RT-Reflux	24 h	–
13	Acetone	Alginate sodium	RT-Reflux	24 h	–
14	Acetone	*L*-cysteine	RT-Reflux	24 h	–
15	Acetone	*L*-proline	RT-Reflux	24 h	–
16	Acetone	TPAB	RT-Reflux	24 h	Trace
17	CH_2Cl_2	*p*-TSA	RT-Reflux	24 h	–
18	CH_2Cl_2	Alginate sodium	RT-Reflux	24 h	–
19	CH_2Cl_2	*L*-cysteine	RT-Reflux	24 h	–
20	CH_2Cl_2	*L*-proline	RT-Reflux	24 h	–
21	**CH_2Cl_2**	**TPAB**	**Reflux**	**25**	**98**

[a] The reaction conditions: ninhydrin (1 mmol), dimedone (1 mmol), catalyst (20 mol%), solvent (2 mL), temperature reflux.
[b] Isolated yield. The bold type (entry 21) refers to the best reaction conditions.
'–' indicates no reaction.

remaining unconverted. The respective results of the investigations are displayed in Table 1.

Based on our survey and optimization of the reaction conditions, the generality and the scope of the organocatalyst in the synthesis process of **3a–i** were assessed by reaction of ninhydrin (**1**) with different cyclic 1,3-dicarbonyl compounds **2a–i** (Scheme 1). As depicted in Scheme 1, the desired compounds were obtained in excellent yields and short reaction times from all of the reactions. Formation of the indeno[1,2-*b*]benzofurans system were confirmed by studying FT-IR, ^{1}H-NMR, ^{13}C-NMR, mass spectral data and microanalysis, beside comparison of the obtained spectral data of known compounds with those reported in the literature.

In terms of spectroscopic characterization, the ^{1}H NMR spectrum of product **3d** showed a characteristic broad singlet at δ = 5.51 ppm attributable to the OH groups, which was exchanged by D_2O. Aromatic protons appeared as multiplet at δ = ~7.65–7.90 ppm, methylene groups gave broad singlets at δ = 2.26 and 1.27 ppm, and methyl groups displayed a singlet at δ = 1.03 ppm. The ^{13}C NMR spectrum showed 16 peaks for all the different carbons as expected. Moreover, the FT-IR (KBr) spectrum of **3d**, showed the characteristic absorptions bands at 1711 and 1660 cm^{-1} due to the vibrations of different carbonyl groups, and its mass spectrum showed the molecular ion at *m*/*z* 300 and a peak at *m*/*z* 83 with 100 % abundance as base peak.

The recyclability of TPAB was also investigated for the synthesis of **3c**. In this respect, the catalyst was recovered and reused more than four times for obtaining 4*b*,9*b*-dihydroxy-8,8-dimethyl-4*b*,8,9,9*b*-tetrahydro-7*H*-indeno[1,2-*b*]benzofuran-6,10-dione (**3c**). No significant loss of catalytic efficiency was observed (Fig. 1).

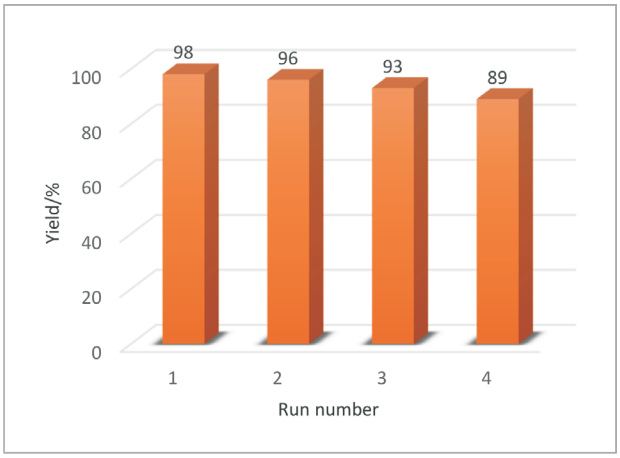


Figure 1 Reusability of TPAB for the synthesis of **3c**.

4. Conclusions

In conclusion, a highly efficient and easy procedure was reported for the synthesis of a new series of indeno[2,1-*b*]benzofuran derivatives **3a–i** in excellent yields, by reaction of ninhydrin and cyclic 1,3-dicarbonyl compounds using 20 mol% TPAB as an organocatalyst in CH_2Cl_2 as solvent. The reasonable reaction times, simple work-up, high yields and recoverability of the catalyst are the main merits of this procedure. The final obtained products are suitable for the synthesis of a series of polycyclic heterocycles that may show potential antimicrobial and inhibitory properties.[1]

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Supplementary Material

Supplementary information is provided in the online supplement.

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Supplementary Information

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4a,9a-Dihydroxy-2,3,4a,9a-tetrahydrocyclopenta[*b*]indeno[2,1-*d*]furan-1,9-dione (3a)

Fig. S1. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **3a**.

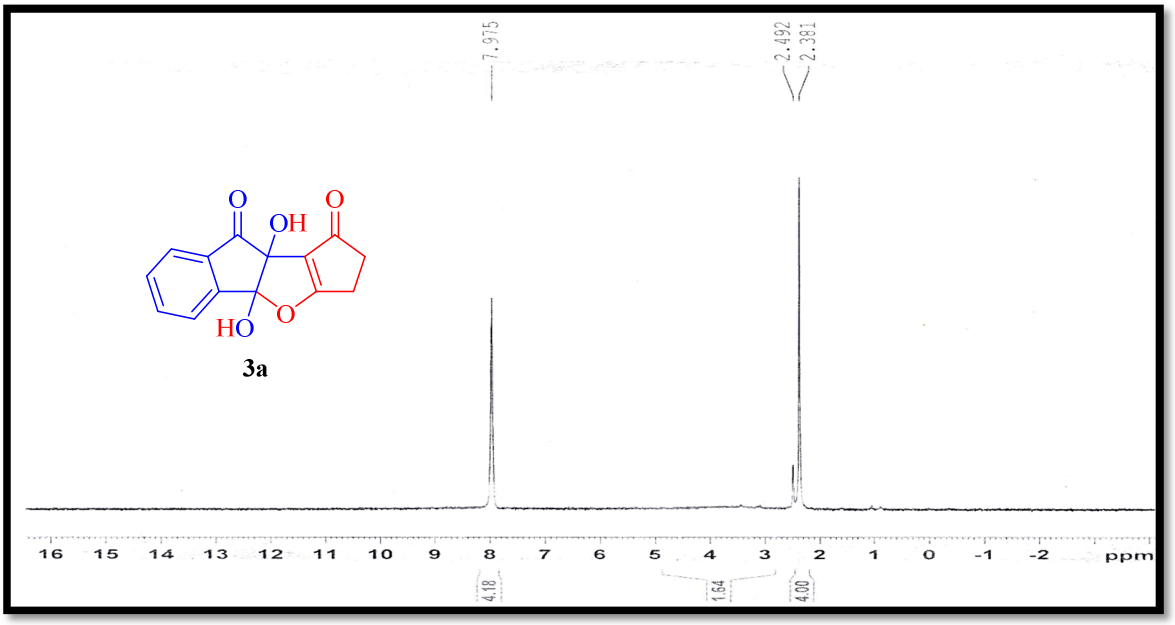


Fig. S2. ^{13}C NMR spectrum (75.5 MHz, DMSO-d_6) of compound **3a.**

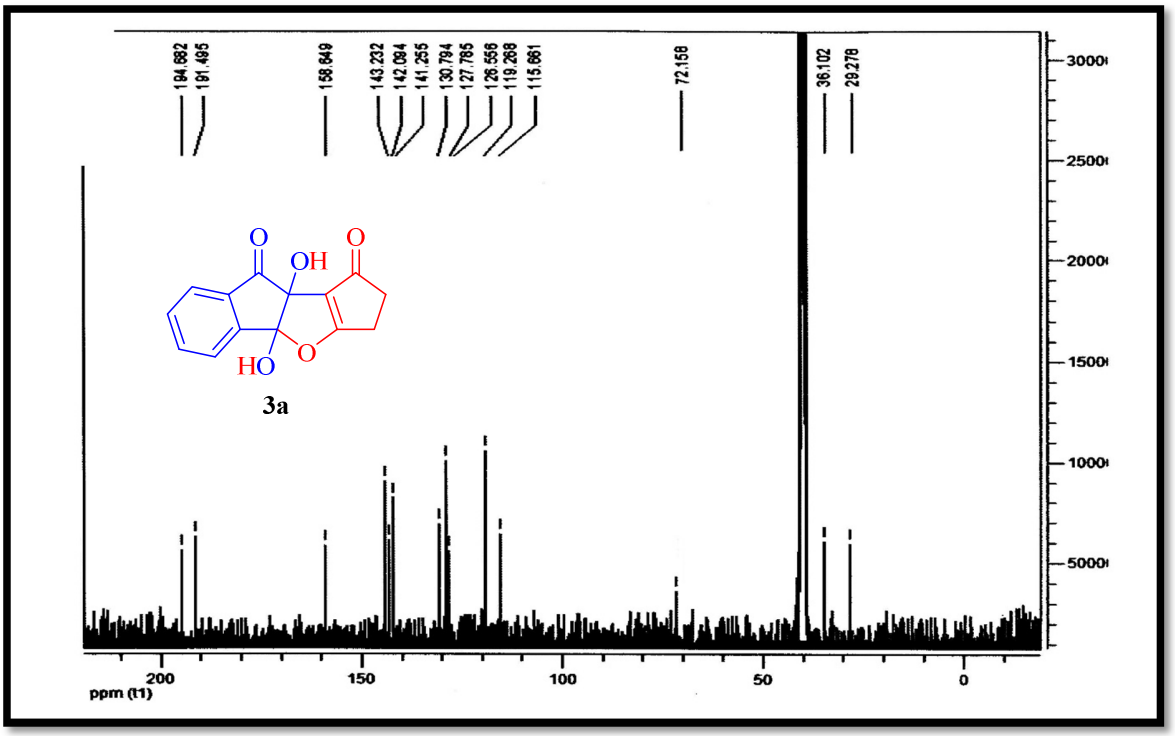


Fig. S3. IR spectrum (KBr) of compound **3a**.

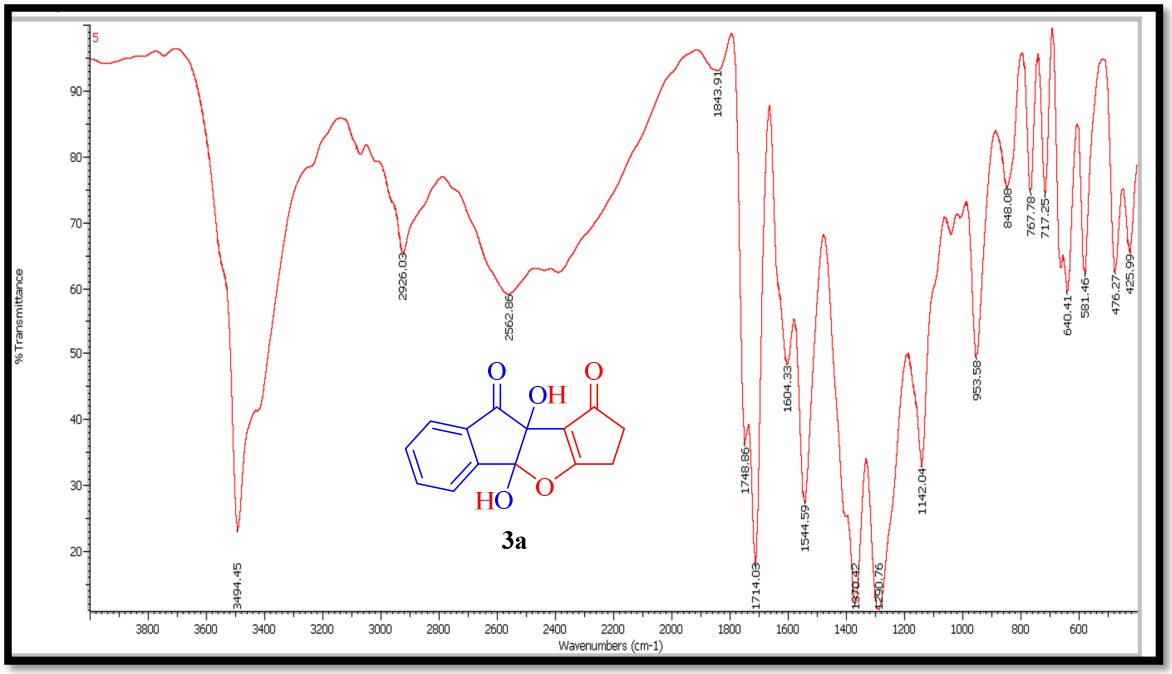
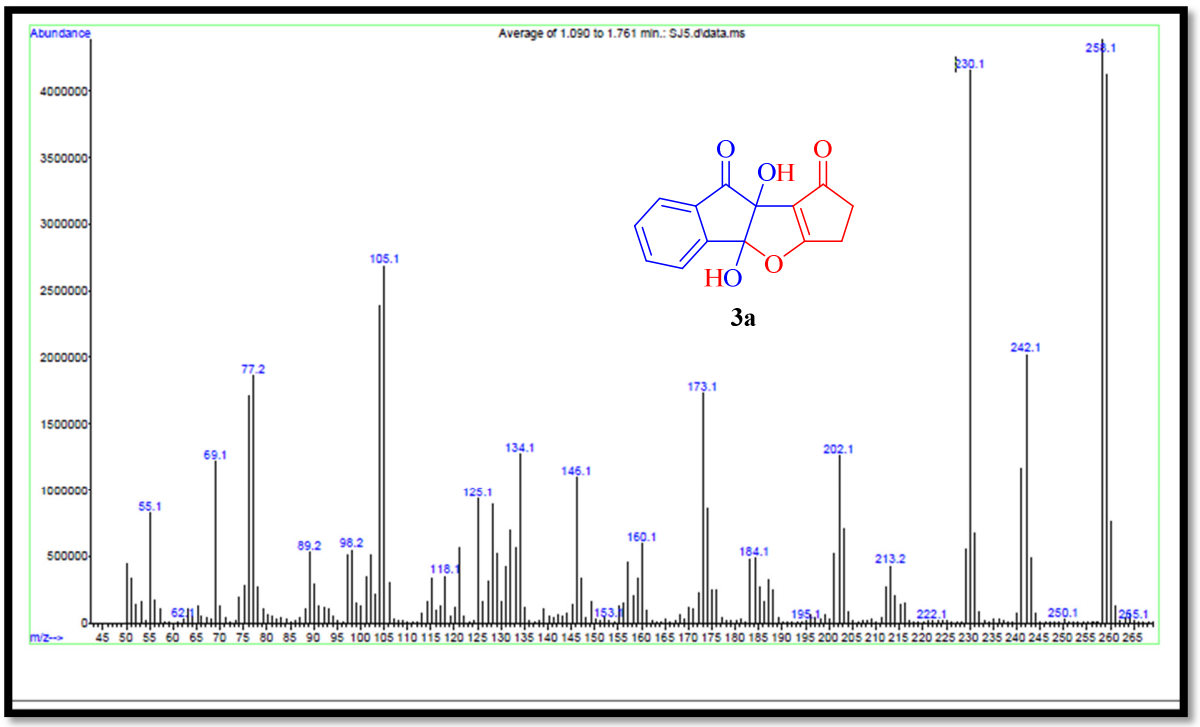


Fig. S4. Mass spectrum of compound **3a**.



4b,9b-Dihydroxy-6,6-dimethyl-6,7,8,9b-tetrahydro-9*H*-indeno[1,2-*b*]benzofuran-9,10(4*bH*)-dione (3d)

Fig. S5. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3d.**

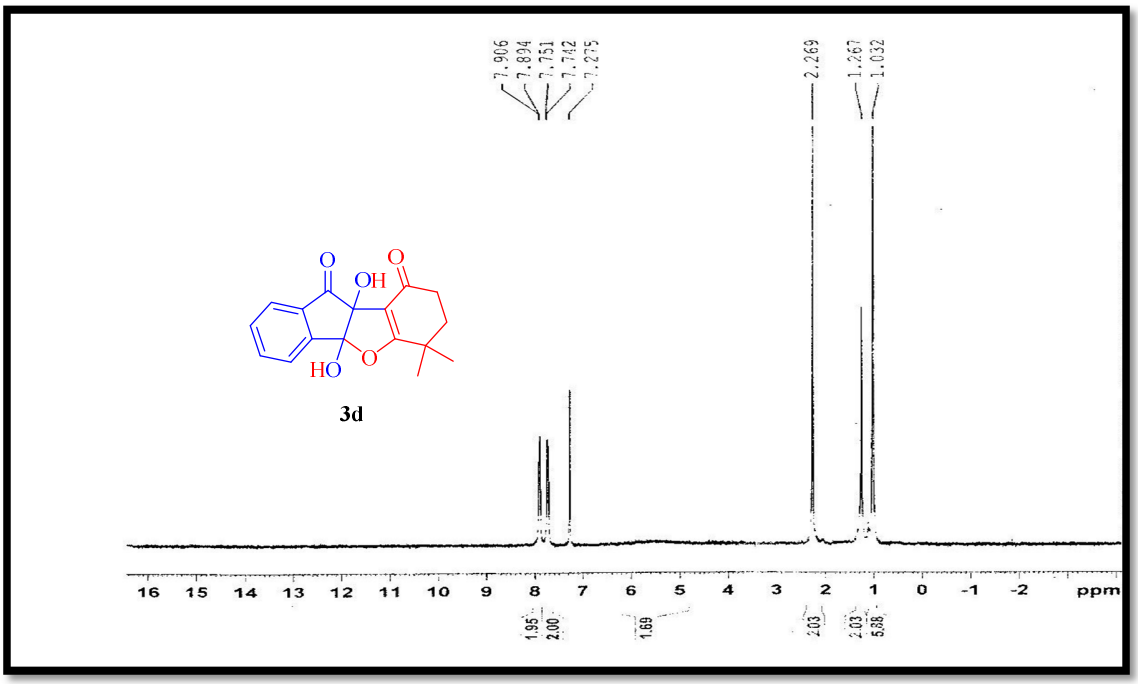


Fig. S6. ^{13}C NMR spectrum (75.5 MHz, $CDCl_3$) of compound **3d.**

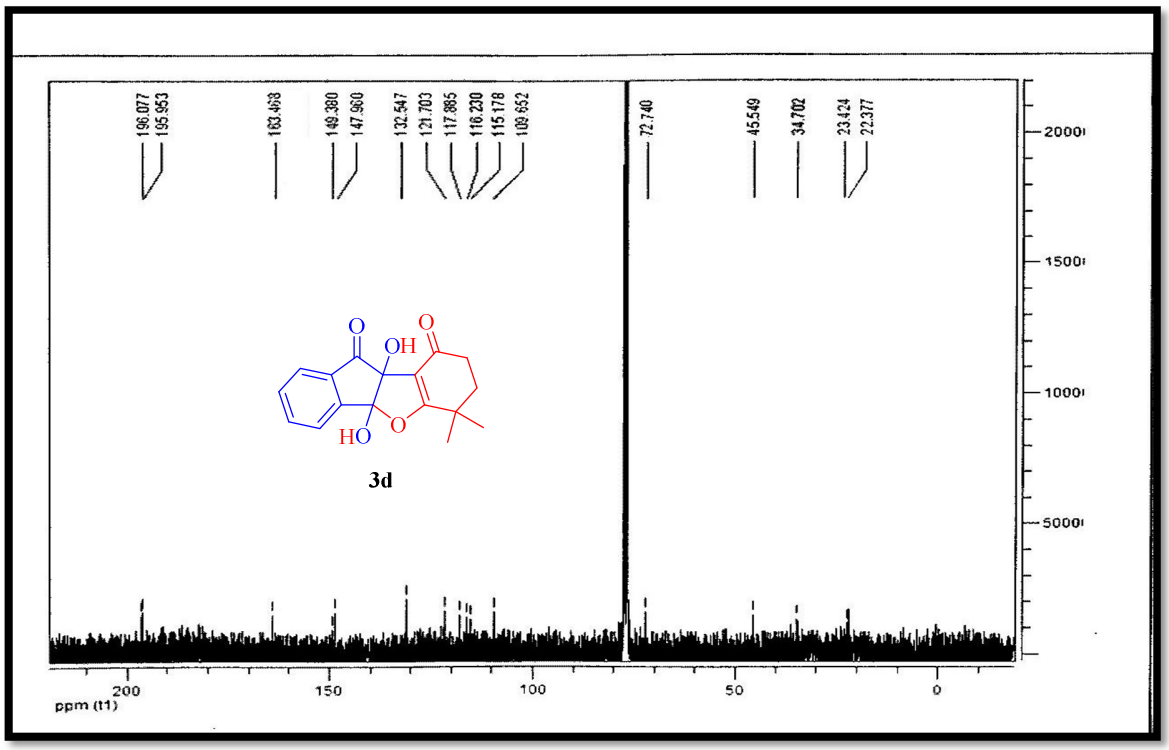


Fig. S7. IR spectrum (KBr) of compound **3d.**

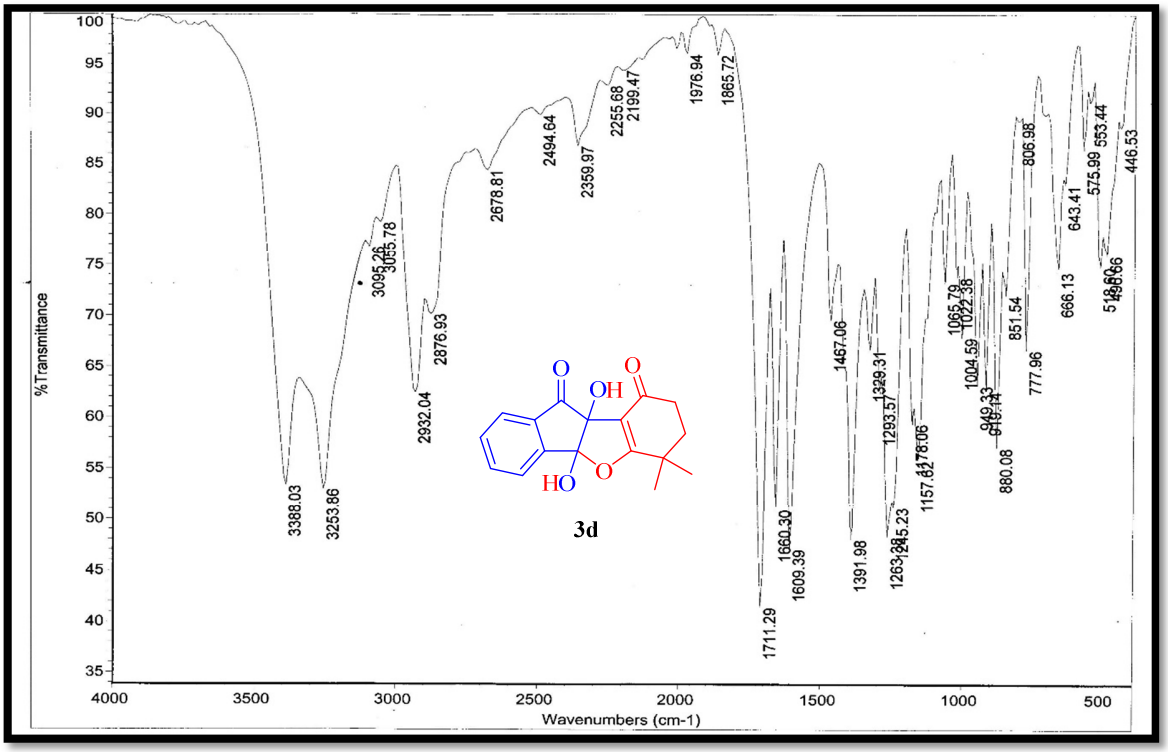
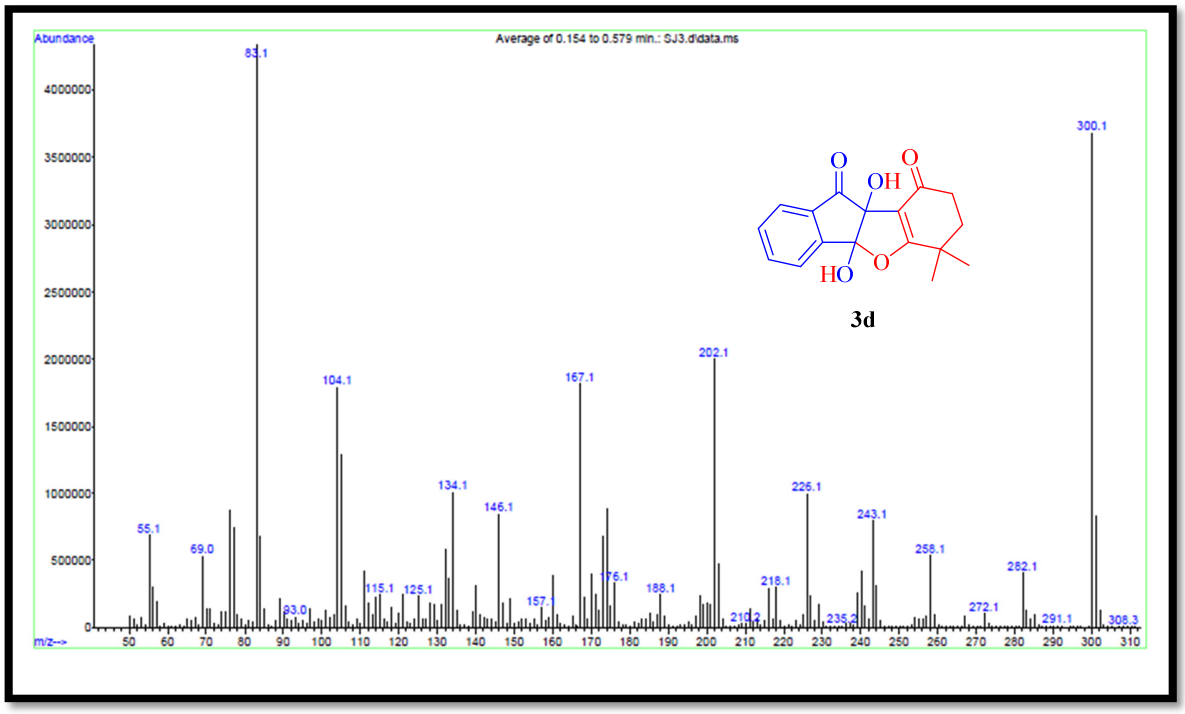


Fig. S8. Mass spectrum of compound **3d.**



4b,9b-Dihydroxy-2,2-dimethyl-4b,9b-dihydro-4*H*,5*H*-indeno[2',1':4,5]furo[2,3-*d*][1,3]dioxine-4,5-dione (3e)

Fig. S9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3e.**

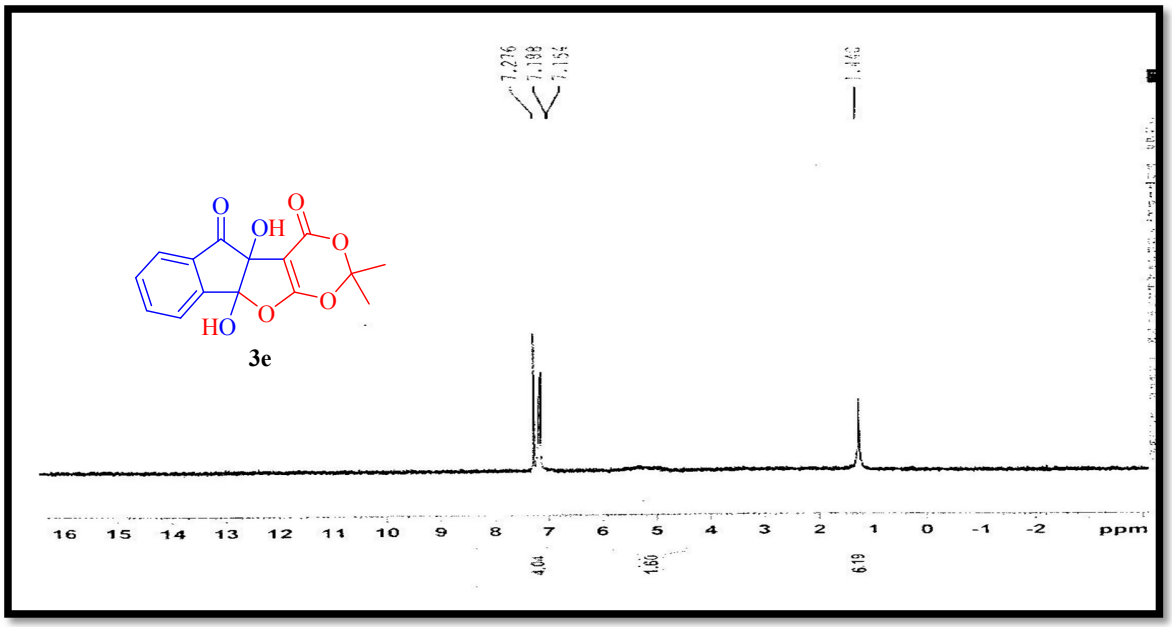


Fig. S10. ^{13}C NMR spectrum (75.5 MHz, $CDCl_3$) of compound **3e.**

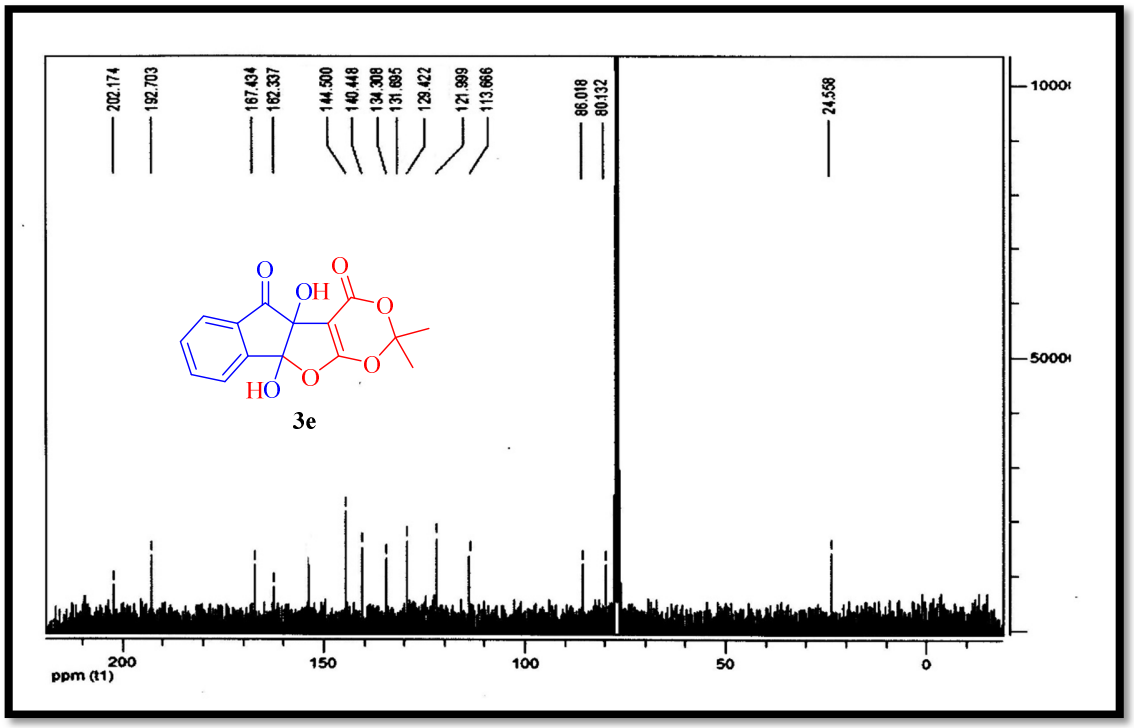


Fig. S11. IR spectrum (KBr) of compound **3e.**

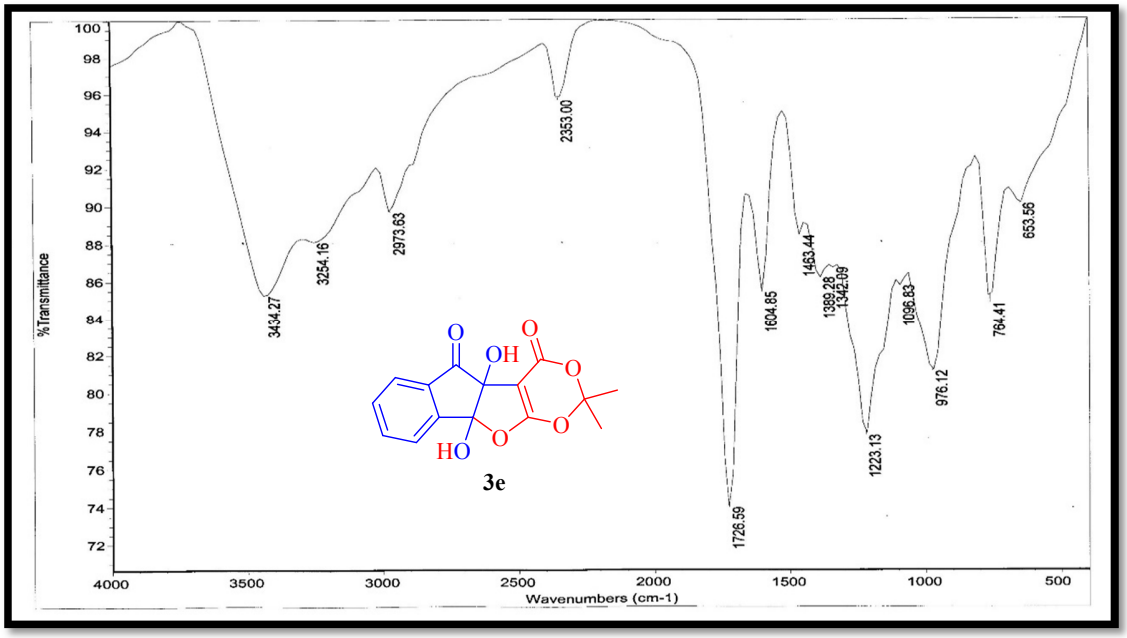
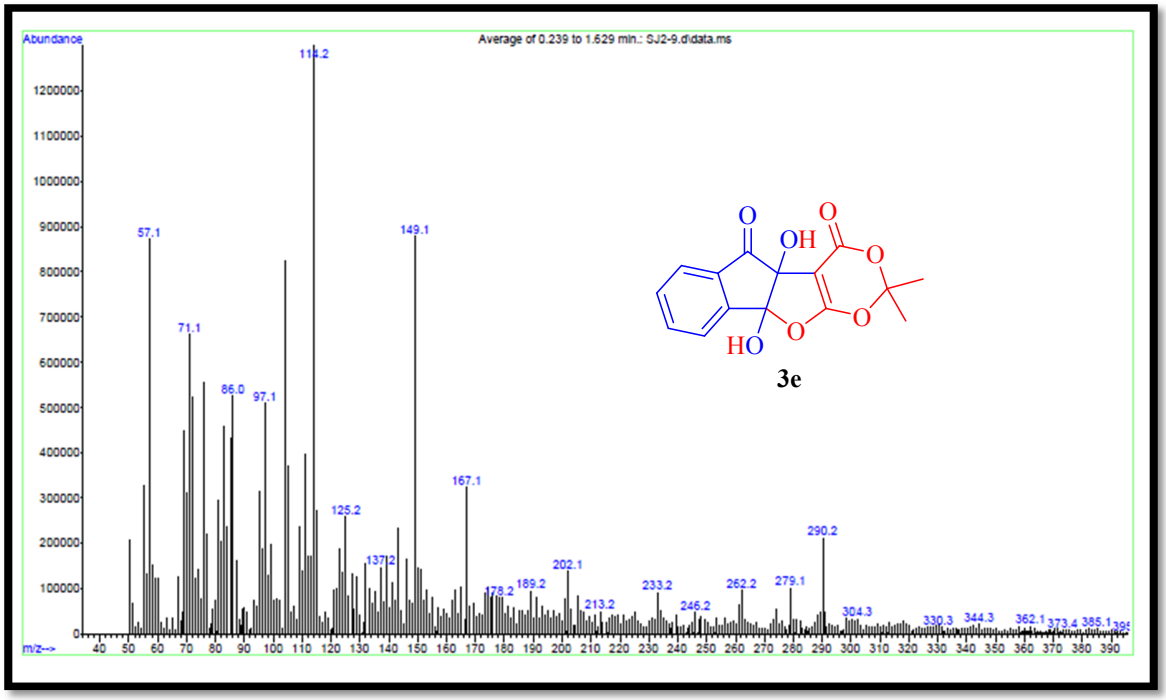


Fig. S12. Mass spectrum of compound **3e**.



4b,9b-Dihydroxy-4b,9b-dihydro-2*H*-indeno[2',1':4,5]furo[2,3-*d*]pyrimidine-2,4,5(1*H*,3*H*)-trione (3f):

Fig. S13. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **3f.**

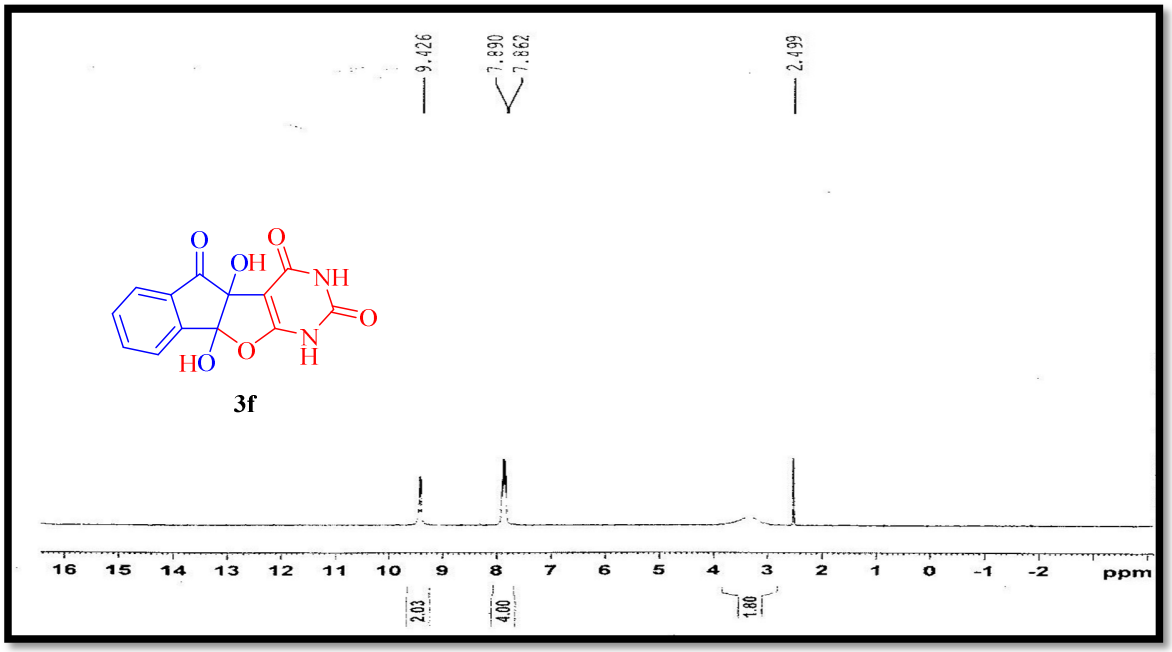


Fig. S14. ^{13}C NMR spectrum (75.5 MHz, DMSO-d_6) of compound **3f.**

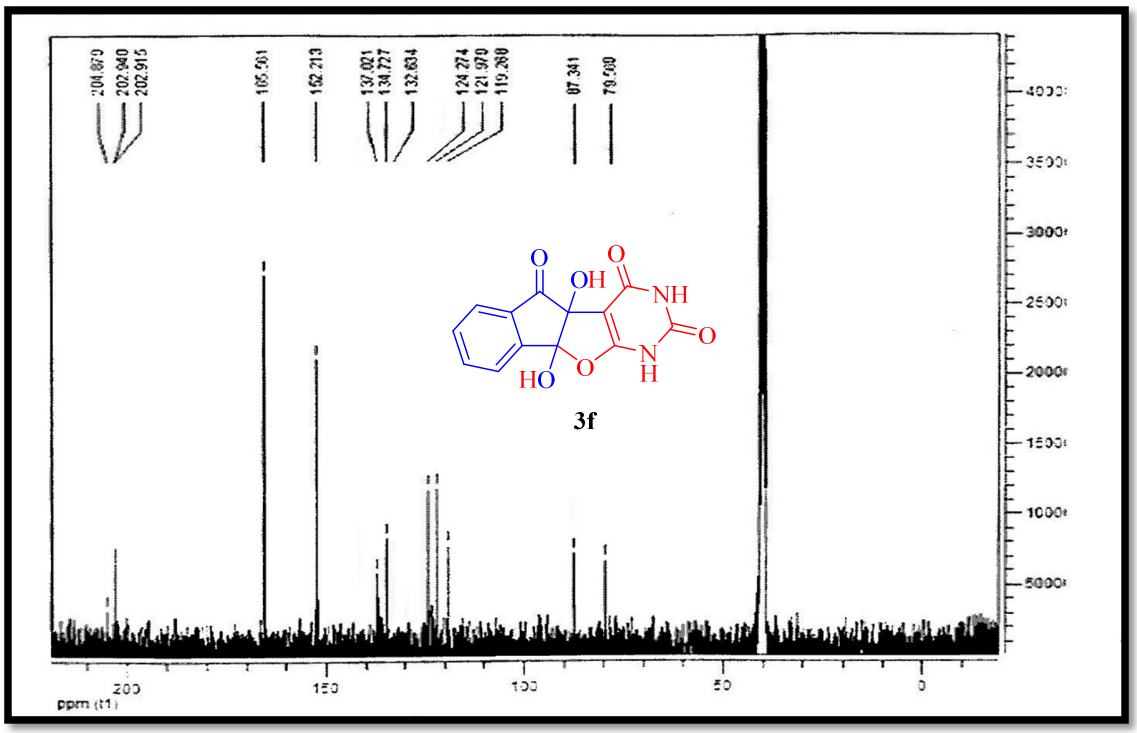


Fig. S15. IR spectrum (KBr) of compound **3f.**

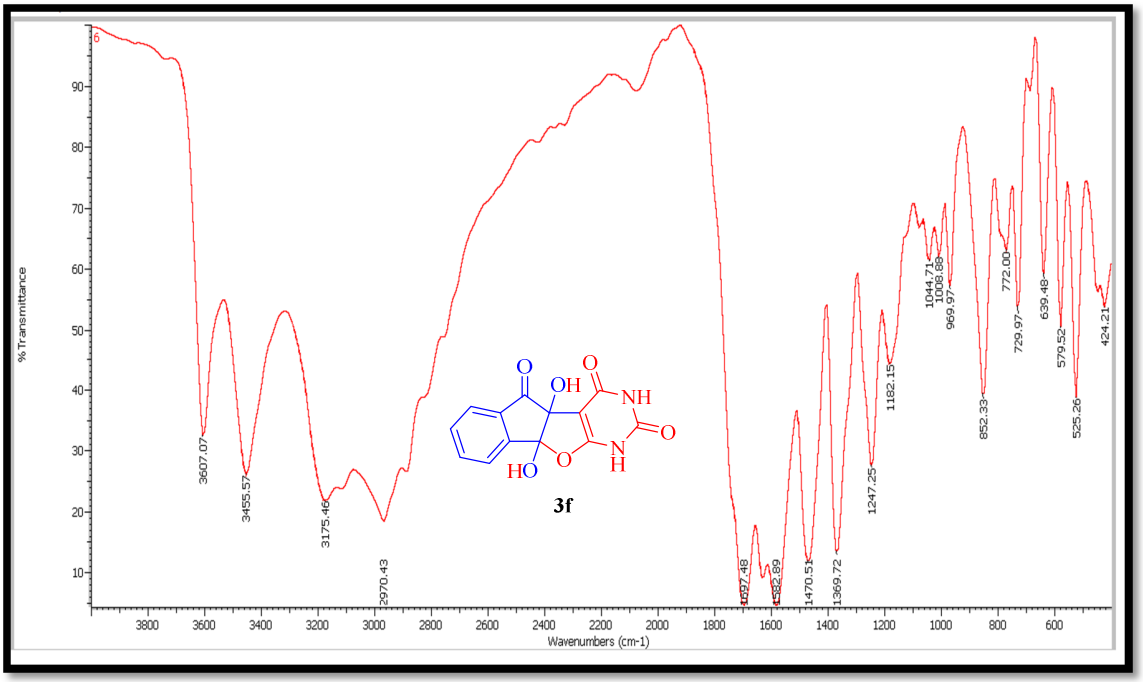
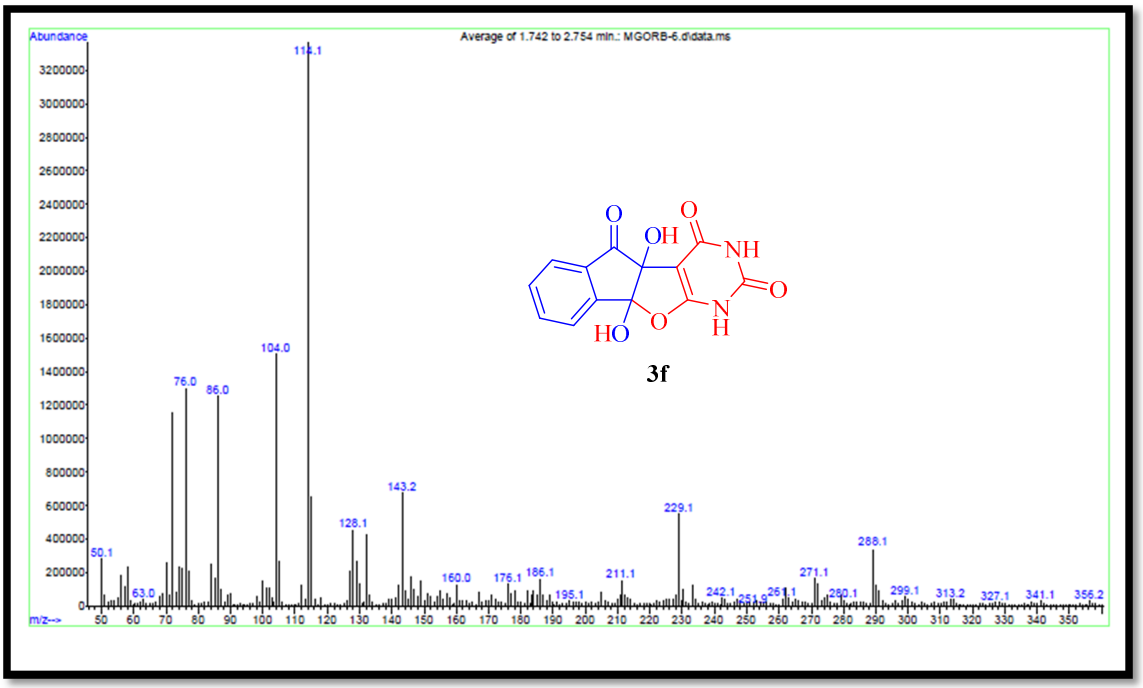


Fig. S16. Mass spectrum of compound **3f.**



4b,9b-Dihydroxy-2-thioxo-2,3,4b,9b-tetrahydro-4*H*-indeno[2',1':4,5]furo[2,3-*d*]pyrimidine-4,5(1*H*)-dione (3g)

Fig. S17. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **3g.**

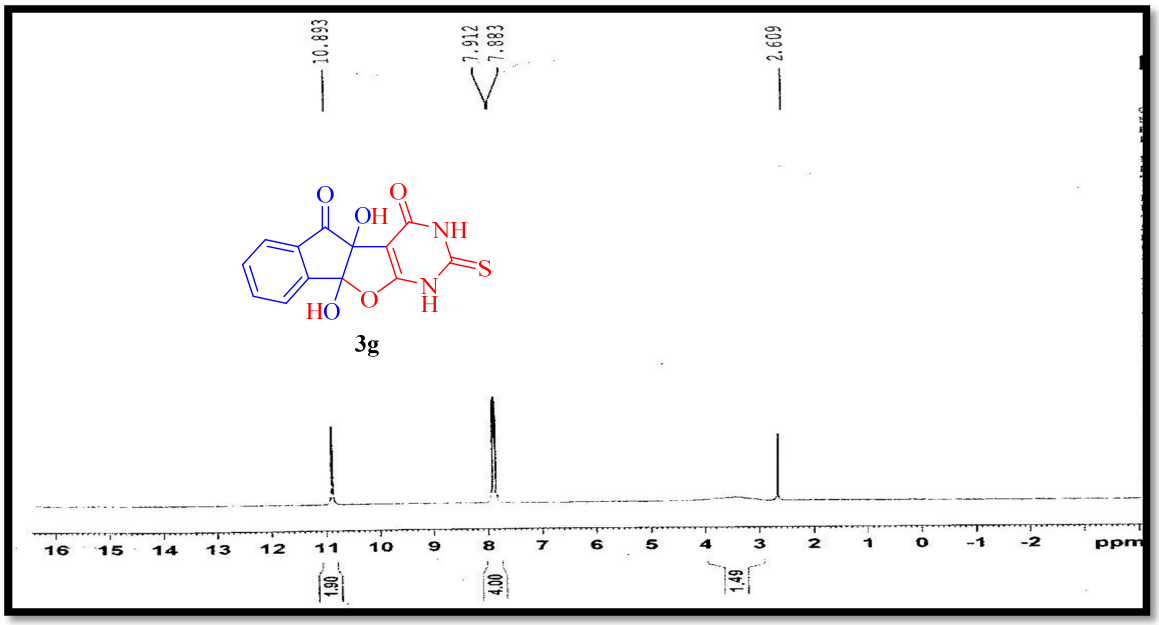


Fig. S18. ^{13}C NMR spectrum (75.5 MHz, DMSO-d_6) of compound **3g.**

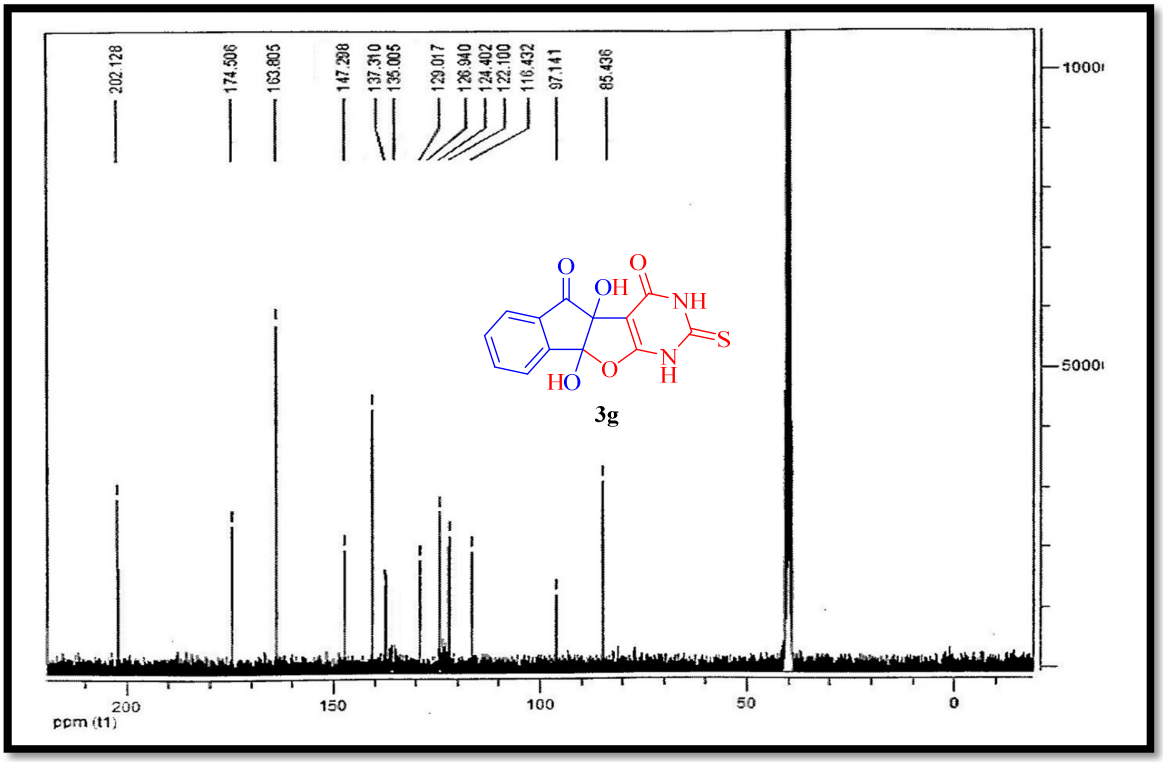


Fig. S19. IR spectrum (KBr) of compound **3g.**

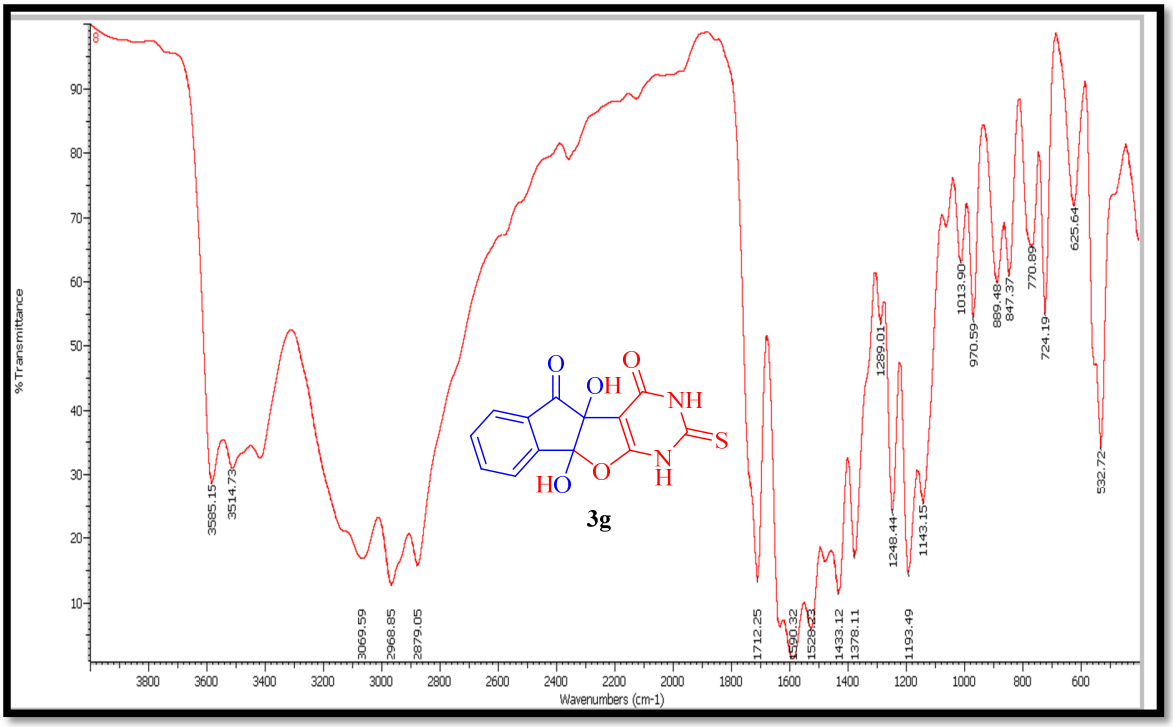
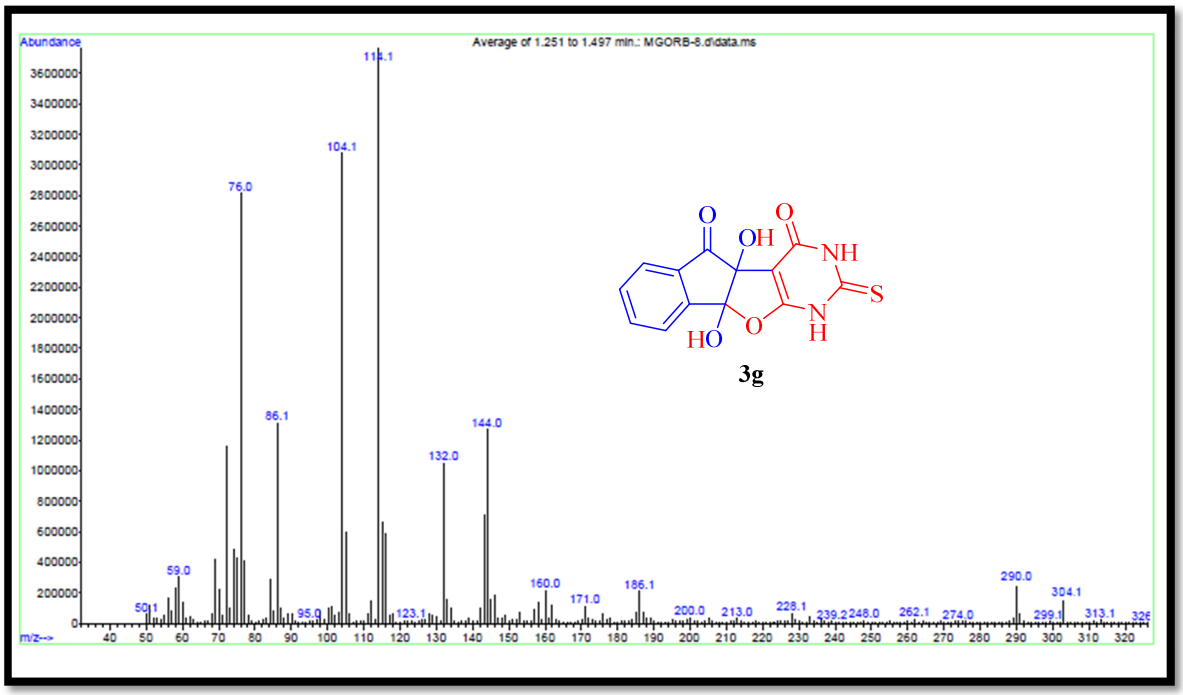


Fig. S20. Mass spectrum of compound **3g.**



4b,9b-Dihydroxy-1,3-dimethyl-4b,9b-dihydro-2*H*-indeno[2',1':4,5]furo[2,3-*d*]pyrimidine-2,4,5(1*H*,3*H*)-trione (3h)

Fig. S21. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **3h.**

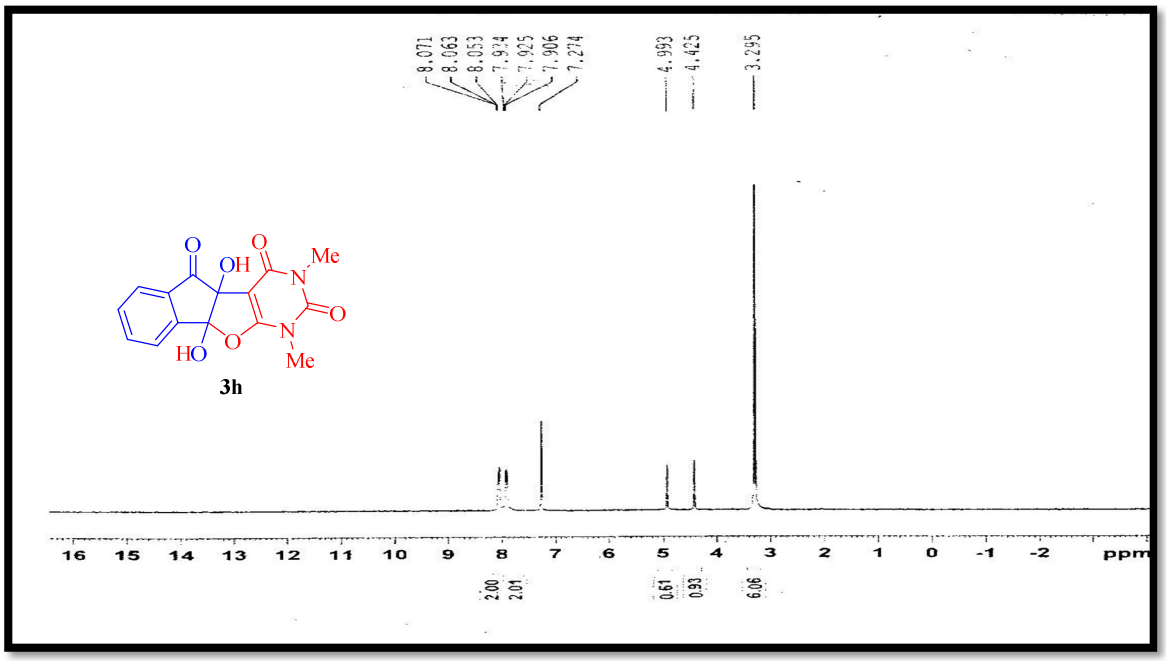


Fig. S22. ^{13}C NMR spectrum (75.5 MHz, $CDCl_3$) of compound **3h.**

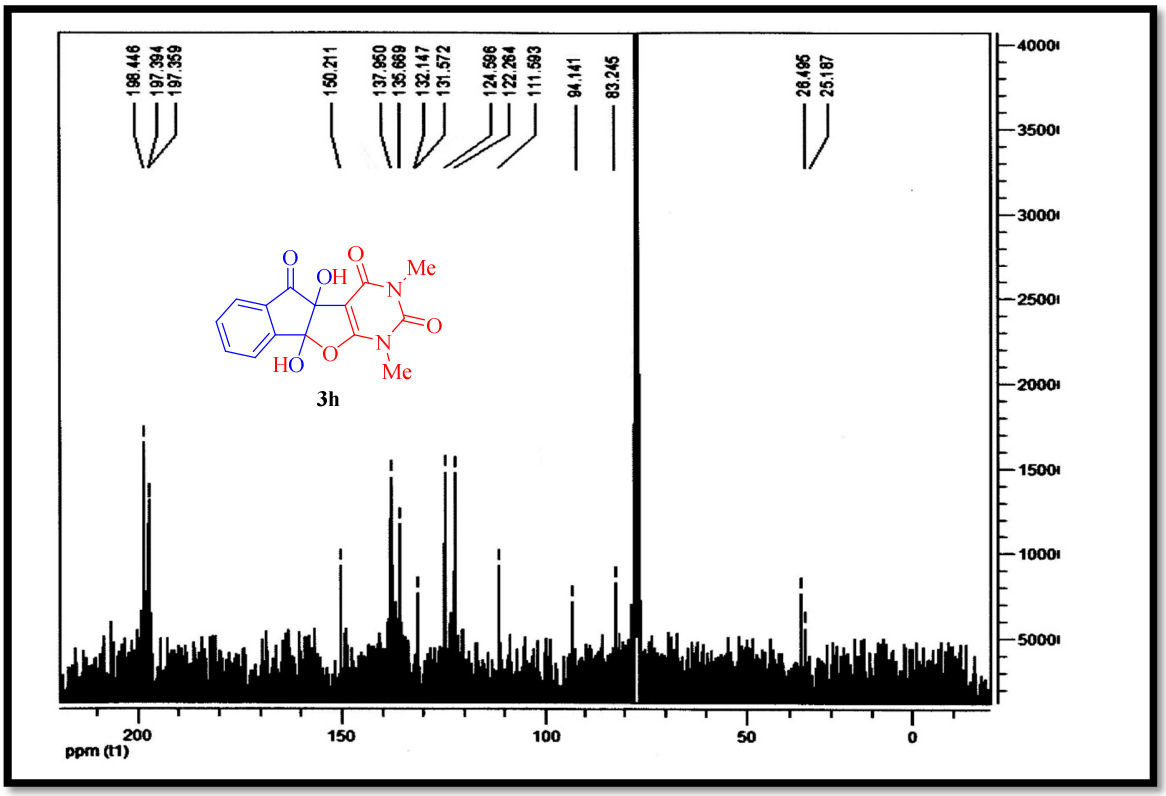


Fig. S23. IR spectrum (KBr) of compound **3h.**

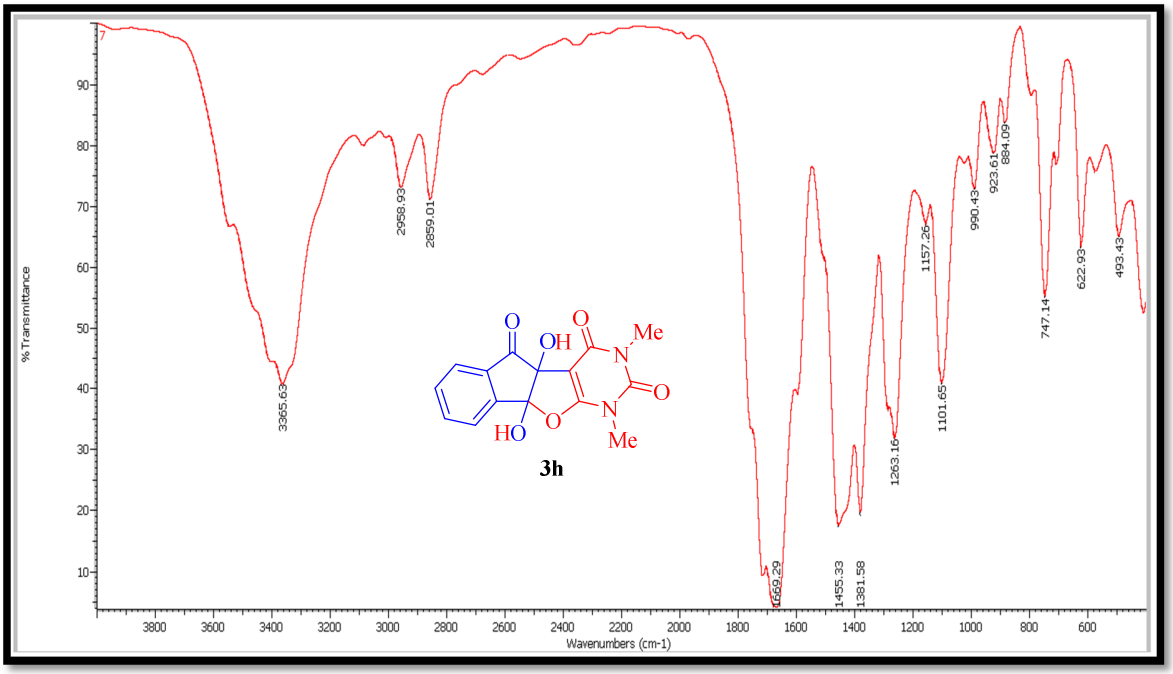
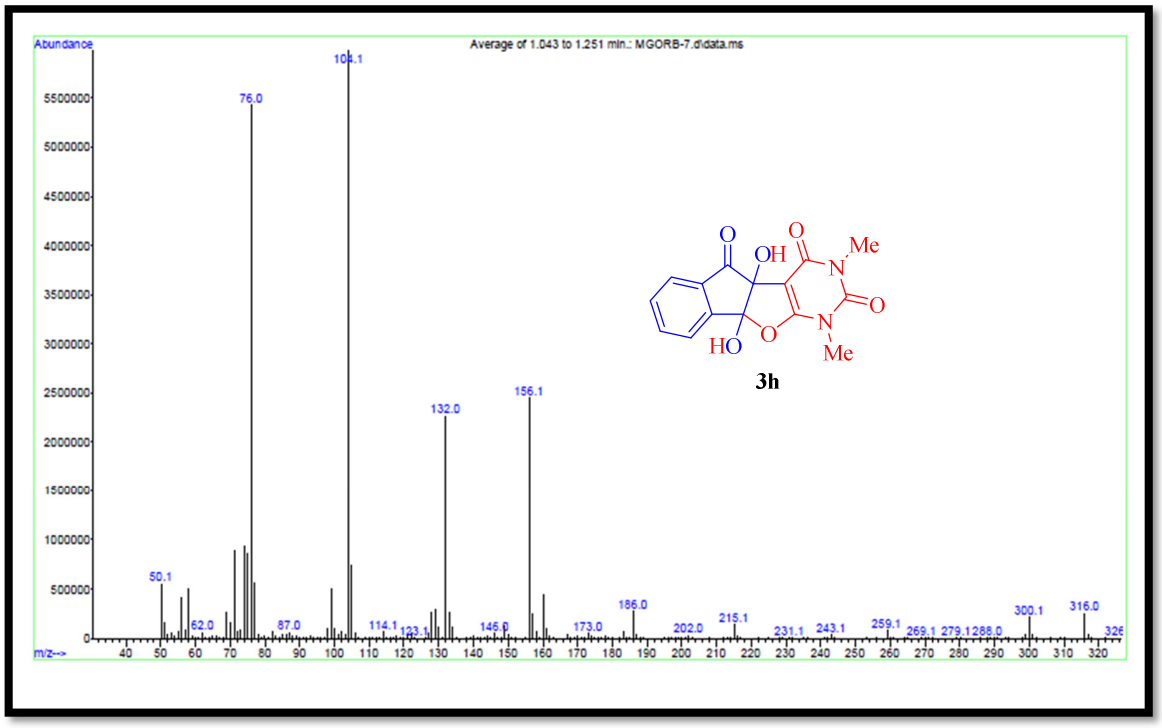


Fig. S24. Mass spectrum of compound **3h.**



4b,10b-Dihydroxy-4*b*,10*b*-dihydrodiindeno[1,2-b:2',1'-*d*]furan-10,11-dione (3i)

Fig. S25. ^{1}H NMR spectrum (300 MHz, DMSO-d_6) of compound **3i.**

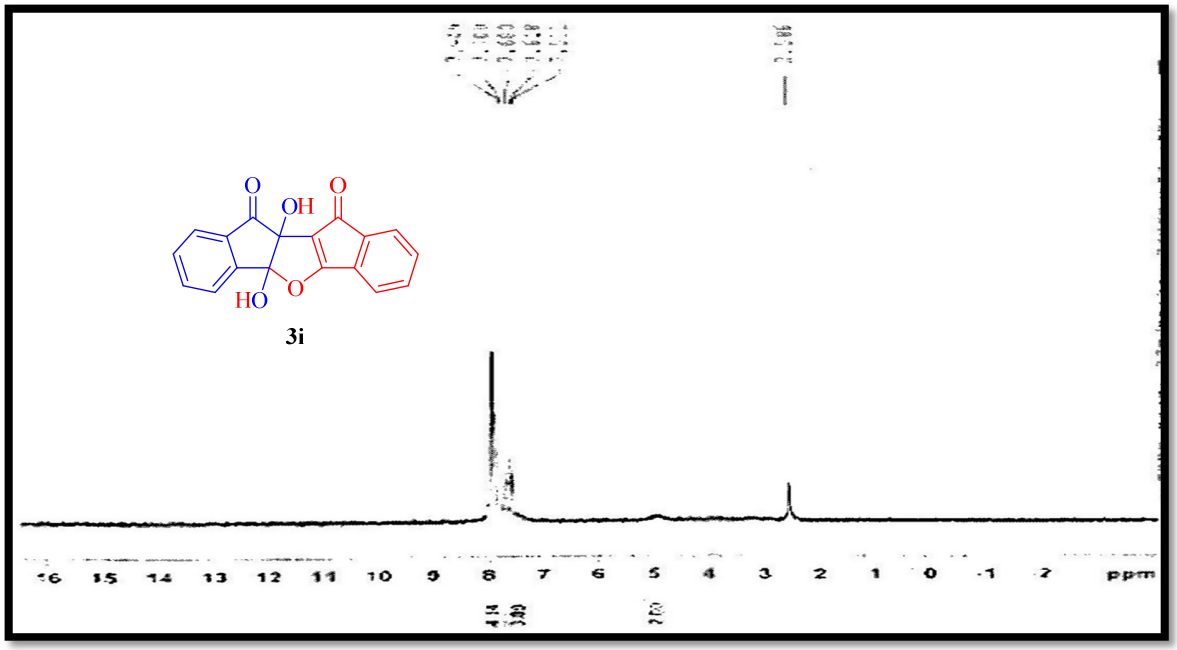


Fig. S26. ^{13}C NMR spectrum (75.5 MHz, DMSO-d_6) of compound **3i.**

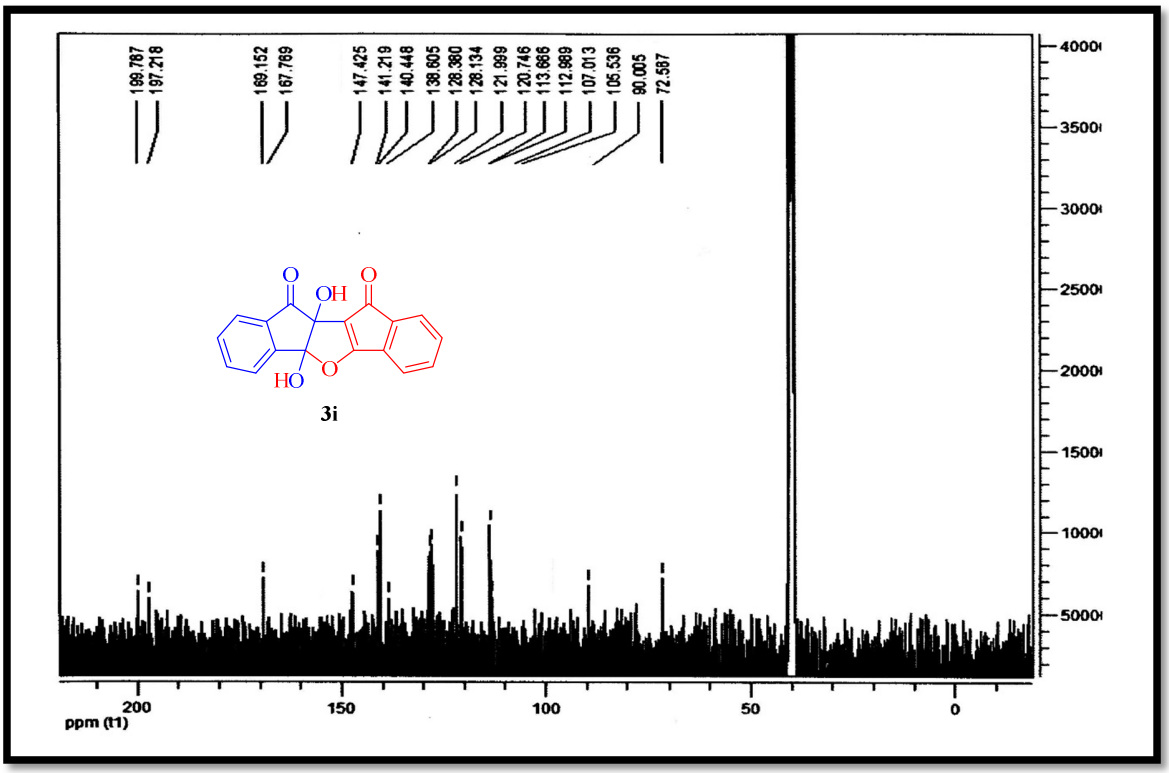
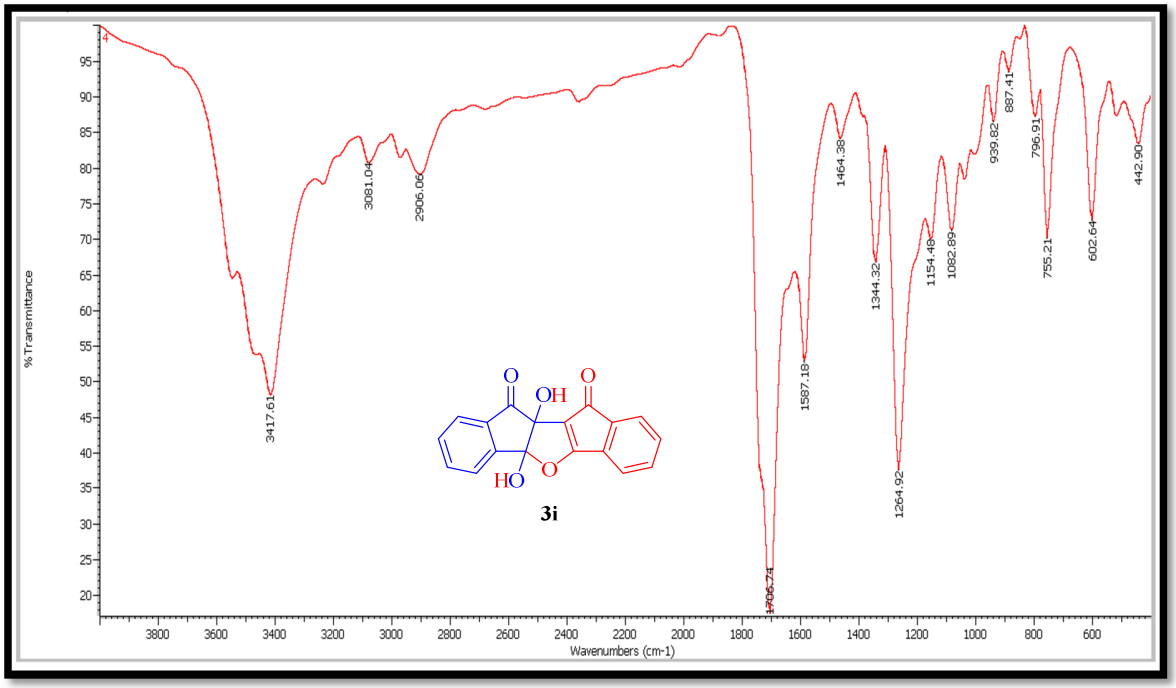
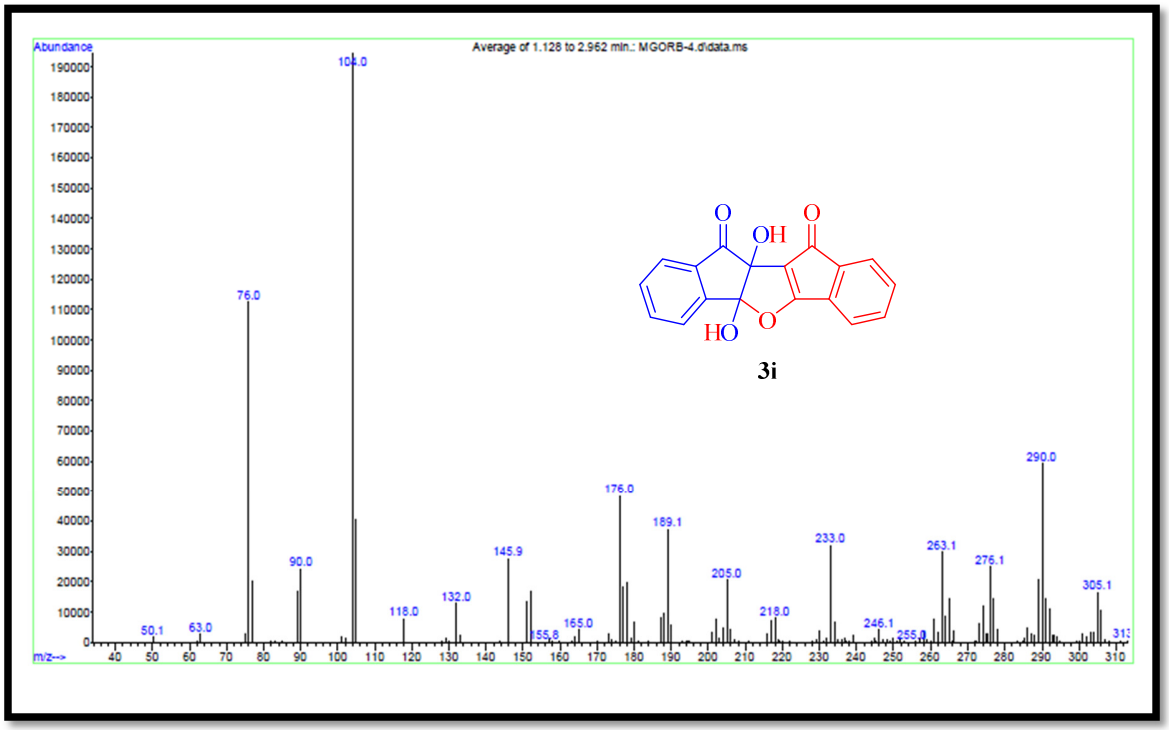


Fig. S27. IR spectrum (KBr) of compound **3i.**



3i

Fig. S28. Mass spectrum of compound **3i.**



3i