J. Braz. Chem. Soc., Vol. 22, No. 7, 1236-1240, 2011.
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0103 - 5053 $6.00+0.00

Article

$Zr(HSO_4)_4$ as an Efficient Catalyst for the Preparation of 10-Aryl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-diones under Solvent-Free Conditions

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A condensação de três componentes "one pot" de 3,4-metilenodioxifenol, aldeídos aromáticos, e ácido 1,3-dimetilbarbitúrico, eficientemente promovida na presença de $Zr(HSO_4)_4$, livre de solvente, produziu 10-aril-6,8-dimetil-6,10-diidro-5-oxa-6,8-diazaantra[2,3-*d*][1,3]dioxol-7,9-dionas. O método oferece diversas vantagens incluindo a simplicidade, facilidade e limpeza do procedimento extrativo, tempos de reação relativamente curtos e bons a altos rendimentos dos produtos.

A one-pot three-component condensation of 3,4-methylenedioxyphenol, aromatic aldehydes, and 1,3-dimethylbarbituric acid, efficiently promoted in the presence of $Zr(HSO_4)_4$ under solvent-free conditions, produced 10-aryl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3] dioxole-7,9-diones. The method offers several advantages including simple, easy and clean work-up procedure, relatively short reaction times and good to high yields of the products.

Keywords: benzo[1,3]dioxoles, 3,4-methylenedioxyphenol, $Zr(HSO_4)_4$, solvent-free

Introduction

Benzo[1,3]dioxoles constitute a major class of naturally occurring compounds,[1] and interest in their chemistry continues unabated because of their wide range of biological and therapeutic properties such as spasm,[2] synergistic,[3] antitumour,[4] antimicrobial,[4] anti-proliferative,[5] antioxidant,[1,6] anti-inflammatory,[6] anti-HIV,[7] antineoplastic and antiviral activities.[8] Considering the above reports, the development of new and simple synthetic methods for the efficient preparation of new benzo[1,3]dioxoles is therefore an interesting challenge.

Pyrano[2,3-*d*]pyrimidines and chromeno[2,3-*d*] pyrimidines are two 'privileged medicinal scaffolds' which are used for the development of pharmaceutical agents of various applications. Compounds with these motifs show a wide range of pharmacological activities such as antiviral,[9] antimicrobial,[10] antifungal,[11] anticonvulsant and analgesic activities.[12] Moreover, they are also useful reagents in organic synthesis, for example, 5-deaza-10-oxaflavin has the ability to oxidize alcohols to the corresponding carbonyl compounds.[13]

In recent years, metal hydrogen sulfates have been used as efficient reagents in organic chemistry.[14] A broad range of reactions including deprotection, oxidation, C–C, C–N and C–O bond formation and cleavage took place in the presence of these reagents under mild and heterogeneous conditions. In addition, stability, cheapness, ability to produce highly efficient products in a short time and in many cases reusability are among other important advantages of these reagents.

We herein report that $Zr(HSO_4)_4$ efficiently catalyzes the one-pot syntheses of 10-aryl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-diones by condensation of 3,4-methylenedioxyphenol, aromatic aldehydes, and 1,3-dimethylbarbituric acid under solvent-free conditions (Scheme 1).

Results and Discussion

Initially, we conducted the reaction of 3,4-methylenedioxyphenol, benzaldehyde, and 1,3-dimethylbarbituric acid in the presence of various metal hydrogen sulfates such

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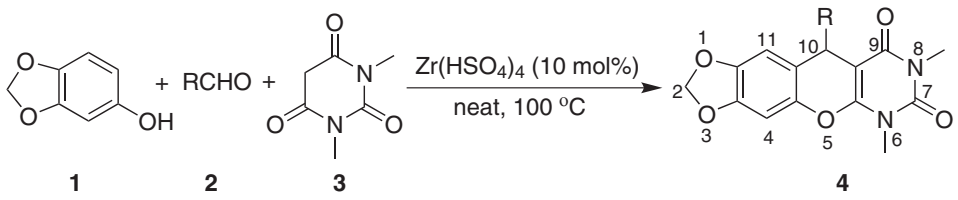


Scheme 1.

as $NaHSO_4$, $Mg(HSO_4)_2$, $Fe(HSO_4)_3$, $Zr(HSO_4)_4$, $Al(HSO_4)_3$ separately at 100 °C under solvent-free conditions. The corresponding 10-phenyl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-dione was formed in 49, 65, 58, 89 and 79% yield (Table 1). $Zr(HSO_4)_4$ was thus selected as the most effective catalyst to carry out this reaction.

Table 1. Synthesis of 10-phenyl-6,8-dimethyl-6,10- dihydro-5-oxa-6,8-diazaanthra[2,3-*d*] [1,3]dioxole-7,9-dione using metal hydrogen sulfates[a]

Entry	Metal hydrogen sulfates	time / min	Yield / (%)[b]
1	-	120	0
2	$NaHSO_4$	90	49
3	$Mg(HSO_4)_2$	60	65
4	$Fe(HSO_4)_3$	90	58
5	$Zr(HSO_4)_4$	45	89
6	$Al(HSO_4)_3$	45	79

[a]Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); 1,3-dimethylbarbituric acid (1 mmol); metal hydrogen sulfates (0.1 mmol); neat; 100 °C. [b]Isolated yield.

Next, to optimize the amount of catalyst and the reaction temperature, the reaction of 3,4-methylenedioxyphenol, benzaldehyde and 1,3-dimethylbarbituric acid was studied under solvent-free conditions in the presence of $Zr(HSO_4)_4$ at different temperatures. The results are summarized in Table 2, and showed that the reaction using 10 mol% $Zr(HSO_4)_4$ at 100 °C proceeded in highest yield.

With this optimized procedure in hand, the scope of application of this three-component reaction was examined using different aldehydes as staring materials. As seen from Table 3, aromatic aldehydes having electron-donating as well as electron-withdrawing groups were uniformly transformed into the corresponding 10-aryl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra [2,3-*d*][1,3]dioxole-7,9-diones in high to excellent yields within 60 min. Substituents on the aromatic ring had no obvious effect on yield or reaction time under the above optimal conditions (Table 3). All of the products **4a**-**4i** exhibited a singlet in their ^1H spectra at δ 4.98-5.58 ppm for H-10, two doublets at δ 5.90-5.98 ppm for $-OCH_2O-$ and two singlets at δ 6.44-6.71 ppm for H-4 and H-11. A distinguishing peak at δ 38.2-39.2 ppm for C-10 in their ^{13}C nuclear magnetic resonance (NMR) spectra, and two distinguishing peak at δ 97.9-98.4 ppm for C-4, 11.

Table 2. Synthesis of 10-phenyl-6,8-dimethyl-6,10- dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-dione under various conditions[a]

Entry	$Zr(HSO_4)_4$	Temperature / °C	time / min	Yield / (%)[b]
1	0	100	120	0
2	1	100	90	34
3	5	100	60	66
4	10	25	120	0
5	10	50	120	30
6	10	90	60	73
7	10	100	45	89
8	10	110	45	88
9	10	120	45	88
10	15	90	60	72
11	15	100	45	86
12	20	100	45	86

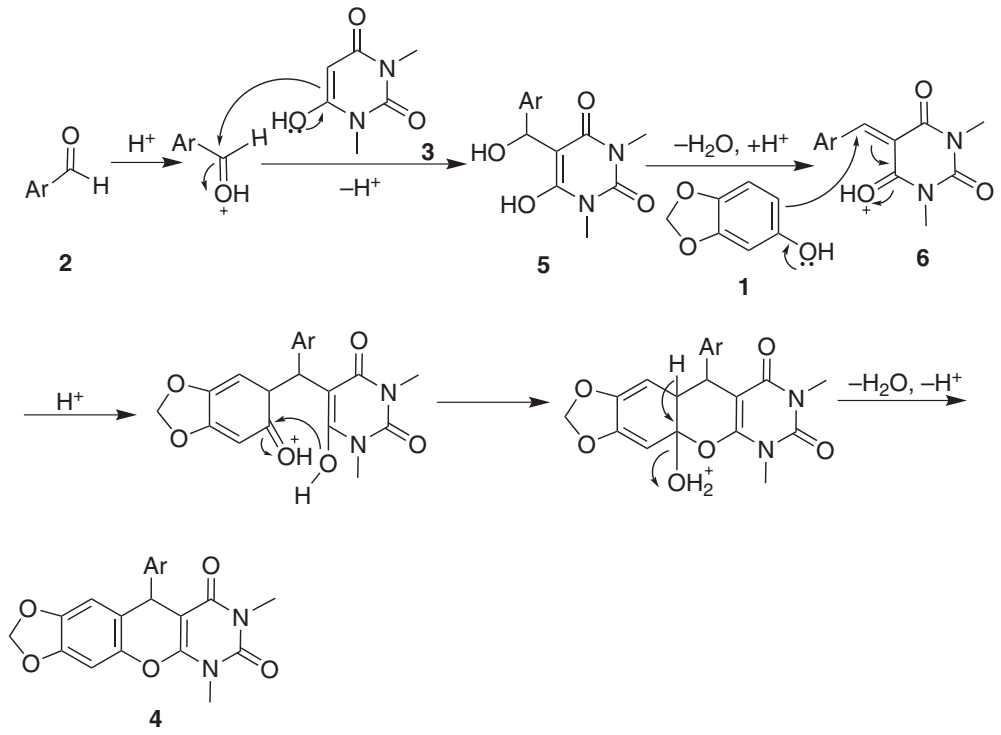
[a]Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); benzaldehyde (1 mmol); 1,3-dimethylbarbituric acid (1 mmol); neat. [b]Isolated yield.

Table 3. Preparation of 10-aryl-6,8-dimethyl-6,10- dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-diones[a]

Entry	R	time / min	Product	Yield / (%)[b]
1	C_6H_5	45	**4a**	89
2	4-Cl-C_6H_4	40	**4b**	91
3	4-F-C_6H_4	35	**4c**	87
4	4-Me-C_6H_4	60	**4d**	82
5	4-NO_2-C_6H_4	35	**4e**	93
6	3-NO_2-C_6H_4	40	**4f**	89
7	2,4-Cl_2-C_6H_3	50	**4g**	87
8	3,4-Cl_2-C_6H_3	50	**4h**	88
9	2-Cl-C_6H_4	40	**4i**	90

[a]Reaction conditions: 3,4-methylenedioxyphenol (1 mmol); aldehyde (1 mmol); 1,3-dimethylbarbituric acid (1 mmol); $Zr(HSO_4)_4$ (0.1 mmol); 100 °C; neat. [b]Isolated yield.

The plausible mechanism of the reaction is shown in Scheme 2. It is conceivable that $Zr(HSO_4)_4$ catalyzes the formation of a carbocation in a reversible reaction with the aromatic aldehyde. The higher reactivity of the carbocation



Scheme 2.

compared with the carbonyl species is utilized to facilitate Knoevenagel condensation between arylaldehyde **2** and 1,3-dimethylbarbituric acid **3** via intermediate **5**, and after dehydration olefin **6** is produced. Subsequent Michael-type addition of **1** to the olefin followed by cyclization and dehydration affords the corresponding products **4a**-**4i**.

Conclusions

In conclusion, we have developed a highly efficient methodology for the three-component reaction of 3,4-methylenedioxyphenol, aromatic aldehydes, and 1,3-dimethylbarbituric acid catalyzed by safe $Zr(HSO_4)_4$, furnishing a class of 10-aryl-6,8-dimethyl-6,10- dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9- diones in high yield. This method is advantageous in terms of simplicity and mildness, and could find wide application in synthesis of complex benzo[1,3]dioxole-containing compounds.

Experimental

IR spectra were determined on a FTS-40 infrared spectrometer; NMR spectra were determined on a Bruker AV-400 instrument at room temperature using TMS as internal standard; coupling constants (*J*) were measured in Hz. Elemental analysis were performed by a Vario-III elemental analyzer; mass spectra were taken on a Macro mass spectrometer (Waters) by electro-spray method (ES); melting points were determined on a XT-4 binocular microscope and were uncorrected; commercially available reagents were used without further purification.

*General procedure for the preparation of **4***

A mixture of 3,4-methylenedioxyphenol (1 mmol), aldehyde (1 mmol), 1,3-dimethylbarbituric acid (1 mmol) and $Zr(HSO_4)_4$ (0.1 mmol) was heated at 100 °C for an appropriate time (TLC). After completion, the reaction mixture was washed with water (15 mL) and the residue was recrystallized to afford the pure product **4**.

*10-Phenyl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (**4a**)*

White powder, mp 245-246 °C; IR (KBr) ν_{max}/cm^{-1}: 3076, 2972, 2899, 1703, 1667, 1659, 1482, 1432, 1211, 1139, 1031, 929, 878, 826, 745, 702, 572, 517, 421; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26-7.16 (m, 5H, ArH), 6.68 (s, 1H, ArH), 6.52 (s, 1H, ArH), 5.95 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.91 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.03 (s, 1H, CH), 3.55 (s, 3H, CH_3), 3.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 152.6, 150.7, 147.2, 145.6, 145.1, 143.1, 128.6, 127.8, 127.7, 126.9, 116.8, 108.2, 101.8, 98.0, 90.0, 39.2, 29.0, 28.1; MS (ESI): *m/z* 365 $[M+H]^+$; Anal. calc. for $C_{20}H_{16}N_2O_5$: C 65.93, H 4.43, N 7.69; found: C 65.90, H 4.48, N 7.74.

*10-(4-Chlorophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4b***)*

White powder, mp 254-255 °C; IR (KBr) ν_{max}/cm^{-1}: 3089, 2958, 2872, 1701, 1667, 1660, 1478, 1434, 1214, 1142, 1088, 1036, 1015, 975, 934, 854, 772, 751, 571, 521, 421; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (d, 2H, *J* 6.4 Hz, ArH), 7.18 (d, 2H, *J* 6.8 Hz, ArH), 6.67 (s, 1H, ArH), 6.47 (s, 1H, ArH), 5.97 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.92 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.00 (s, 1H, CH), 3.54 (s, 3H, CH_3), 3.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 152.6, 150.6, 147.4, 145.7, 143.6, 143.0, 132.7, 129.3, 128.8, 128.7, 116.1, 108.0, 101.9, 98.1, 89.6, 38.6, 29.0, 28.1; MS (ESI): *m/z* 399 $[M+H]^+$; Anal. calc. for $C_{20}H_{15}ClN_2O_5$: C 60.23, H 3.79, N 8.89; found: C 60.19, H 3.85, N 8.95.

10-(4-Fluorophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione **(4c***)*

White powder, mp 253-254 °C; IR (KBr) ν_{max}/cm^{-1}: 3079, 2962, 2859, 1707, 1667, 1648, 1522, 1436, 1353, 1212, 1142, 1031, 977, 930, 864, 817, 751, 703, 570, 516, 422; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22-7.19 (m, 2H, ArH), 6.95-6.91 (m, 2H, ArH), 6.67 (s, 1H, ArH), 6.48 (s, 1H, ArH), 5.96 (d, 1H, *J* 1.2 Hz, OCH_2O), 5.92 (d, 1H, *J* 1.2 Hz, OCH_2O), 5.01 (s, 1H, CH), 3.54 (s, 3H, CH_3), 3.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 152.5, 150.6, 147.3, 145.6, 143.0, 140.9, 129.4, 116.5, 115.4, 115.2, 108.1, 101.9, 98.0, 89.8, 38.4, 29.0, 28.1; MS (ESI): *m/z* 383 $[M+H]^+$; Anal. calc. for $C_{20}H_{15}FN_2O_5$: C 62.83, H 3.95, N 7.33; found: C 62.90, H 3.89, N 7.40.

*10-(4-Methylphenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4d***)*

White powder, mp 248-249 °C; IR (KBr) ν_{max}/cm^{-1}: 3078, 2956, 2870, 1708, 1671, 1644, 1478, 1434, 1211, 1140, 1032, 930, 930, 790, 572, 519, 421; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.14 (d, 2H, *J* 8.0 Hz, ArH), 7.07 (d, 2H, *J* 8.0 Hz, ArH), 6.67 (s, 1H, ArH), 6.52 (s, 1H, ArH), 5.95 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.90 (d, 1H, *J* 0.8 Hz, OCH_2O), 4.99 (s, 1H, CH), 3.54 (s, 3H, CH_3), 3.28 (s, 3H, CH_3), 2.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 152.5, 150.7, 147.1, 145.5, 143.0, 142.3, 136.5, 129.3, 129.2, 127.7, 127.6, 117.0, 108.2, 101.8, 98.0, 90.1, 38.8, 29.0, 28.1, 21.0; MS (ESI): *m/z* 379 $[M+H]^+$; Anal. calc. for $C_{21}H_{18}N_2O_5$: C 66.66, H 4.79, N 7.40; found: C 66.70, H 4.69, N 7.49.

*10-(4-Nitrophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4e***)*

White powder, mp 259-260 °C; IR (KBr) ν_{max}/cm^{-1}: 3089, 2991, 2881, 1706, 1668, 1650, 1522, 1437, 1395, 1352, 1213, 1143, 1032, 978, 929, 863, 816, 752, 570, 517, 423; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (d, 2H, *J* 8.8 Hz, ArH), 7.43 (d, 2H, *J* 8.4 Hz, ArH), 6.71 (s, 1H, ArH), 6.44 (s, 1H, ArH), 5.98 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.95 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.15 (s, 1H, CH), 3.56 (s, 3H, CH_3), 3.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 152.8, 152.1, 150.5, 147.8, 146.8, 145.9, 143.1, 128.9, 123.9, 114.9, 107.9, 102.1, 98.3, 88.8, 39.1, 29.1, 28.1; MS (ESI): *m/z* 410 $[M+H]^+$; Anal. calc. for $C_{20}H_{15}N_3O_7$: C 58.68, H 3.69, N 10.27; found: C 58.60, H 3.72, N 10.20.

*10-(3-Nitrophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4f***)*

White powder, mp 262-263 °C; IR (KBr) ν_{max}/cm^{-1}: 3052, 2944, 2852, 1701, 1666, 1659, 1529, 1504, 1486, 1436, 1351, 1224, 1171, 1038, 934, 871, 737, 717; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05-8.03 (m, 1H, ArH), 8.00-7.98 (m, 1H, ArH), 7.72 (d, 1H, *J* 7.6 Hz, ArH), 7.46 (t, 1H, *J* 7.6 Hz, ArH), 6.71 (s, 1H, ArH), 6.44 (s, 1H, ArH), 5.98 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.94 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.15 (s, 1H, CH), 3.57 (s, 3H, CH_3), 3.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 152.8, 150.5, 148.5, 147.8, 147.1, 145.9, 143.0, 134.5, 129.3, 122.9, 115.0, 107.9, 102.1, 98.4, 88.8, 39.1, 29.1, 28.1; MS (ESI): *m/z* 410 $[M+H]^+$; Anal. calc. for $C_{20}H_{15}N_3O_7$: C 58.68, H 3.69, N 10.27; found: C 58.72, H 3.75, N 10.22.

*10-(3,4-Dichlorophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4g***)*

White powder, mp 247-248 °C; IR (KBr) ν_{max}/cm^{-1}: 3092, 2972, 2861, 1682, 1588, 1561, 1426, 1383, 1318, 1250, 1112, 1036, 934, 868, 762, 562; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.33 (d, 1H, *J* 8.0 Hz, ArH), 7.26-7.25 (m, 1H, ArH), 7.15 (dd, 1H, *J* 2.0, 8.0 Hz, ArH), 6.68 (s, 1H, ArH), 6.45 (s, 1H, ArH), 5.98 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.94 (d, 1H, *J* 0.8 Hz, OCH_2O), 4.98 (s, 1H, CH), 3.55 (s, 3H, CH_3), 3.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.8, 152.7, 150.6, 147.6, 145.8, 145.3, 143.0, 132.6, 131.0, 130.4, 129.8, 127.5, 115.4, 107.9, 102.0, 98.2, 89.0, 38.5, 29.1, 28.1; MS (ESI): *m/z* 433 $[M+H]^+$; Anal. calc. for $C_{20}H_{14}Cl_2N_3O_7$: C 55.45, H 3.26, N 6.47; found: C 55.50, H 3.20, N 6.50.

*10-(2,4-Dichlorophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4h***)*

White powder, mp 277-278 °C; IR (KBr) ν_{max}/cm^{-1}: 3082, 2979, 2870, 1700, 1667, 1641, 1480, 1433, 1395, 1219, 1148, 1037, 934, 878, 794, 755, 594; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.36 (d, 1H, *J* 2.0 Hz, ArH), 7.14-7.12 (m, 2H, ArH), 6.63 (s, 1H, ArH), 6.55 (s, 1H, ArH), 5.96 (d, 1H, *J* 1.6 Hz, OCH_2O), 5.92 (d, 1H, *J* 1.6 Hz, OCH_2O), 5.52 (s, 1H, CH), 3.57 (s, 3H, CH_3), 3.27 (s, 3H,

CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.7, 153.1, 150.7, 147.4, 145.6, 142.7, 141.0, 133.5, 133.2, 131.2, 129.7, 127.6, 115.1, 107.5, 101.9, 98.0, 88.2, 38.6, 29.1, 28.1; MS (ESI): *m/z* 433 $[M+H]^+$; Anal. calc. for $C_{20}H_{14}Cl_2N_3O_7$: C 55.45, H 3.26, N 6.47; found: C 55.38, H 3.24, N 6.52.

*10-(2-Chlorophenyl)-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-d][1,3]dioxole-7,9-dione (***4i***)*

White powder, mp 233-234 °C; IR (KBr) ν_{max}/cm^{-1}: 3082, 2965, 2858, 1701, 1663, 1520, 1435, 1361, 1281, 1118, 1036, 936, 736, 427; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, 1H, *J* 7.6 Hz, ArH), 7.17-7.12 (m, 3H, ArH), 6.63 (s, 1H, ArH), 6.61 (s, 1H, ArH), 5.95 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.90 (d, 1H, *J* 0.8 Hz, OCH_2O), 5.58 (s, 1H, CH), 3.57 (s, 3H, CH_3), 3.27 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ161.7, 153.1, 150.8, 147.3, 145.5, 142.7, 142.3, 132.8, 130.3, 130.0, 128.1, 127.2, 115.7, 107.7, 101.8, 97.9, 88.7, 38.2, 29.1, 28.1; MS (ESI): *m/z* 399 $[M+H]^+$; Anal. calc. for $C_{20}H_{15}ClN_2O_5$: C 60.23, H 3.79, N 8.89; found: C 60.22, H 3.80, N 8.92.

Supplementary Information

The spectroscopic ^1H NMR, ^{13}C NMR, and IR data of **4a**-**4i** are provided as supplementary information and available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

We are pleased to acknowledge the financial support from Xinxiang Medical University.

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Submitted: October 25, 2010
Published online: February 24, 2011

J. Braz. Chem. Soc., Vol. 22, No. 7, S1-S14, 2011.
Printed in Brazil - ©2011 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

$Zr(HSO_4)_4$ as an Efficient Catalyst for the Preparation of 10-Aryl-6,8-dimethyl-6,10-dihydro-5-oxa-6,8-diazaanthra[2,3-*d*][1,3]dioxole-7,9-diones under Solvent-Free Conditions

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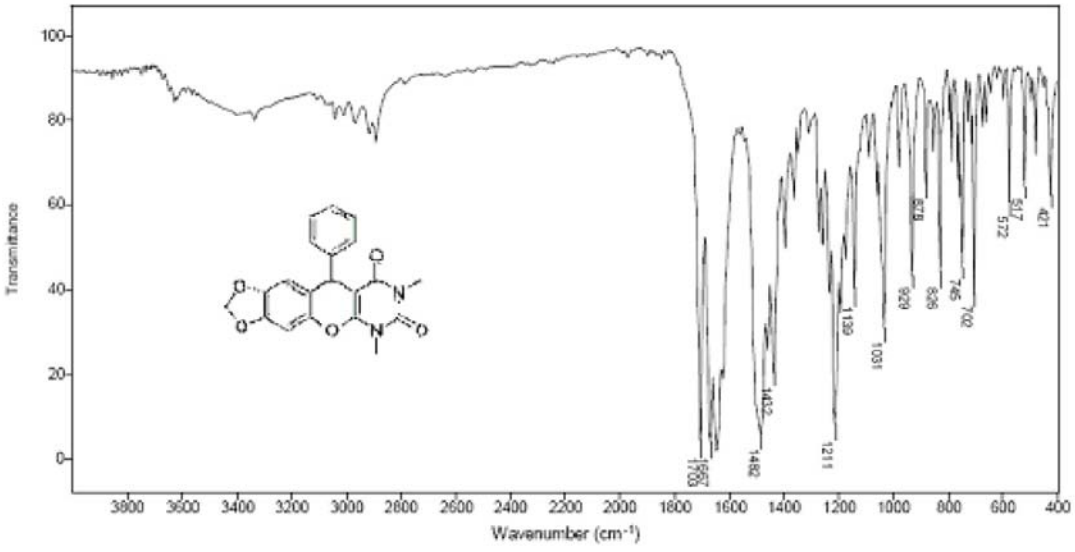

Figure S1. IR (KBr) of **4a**.

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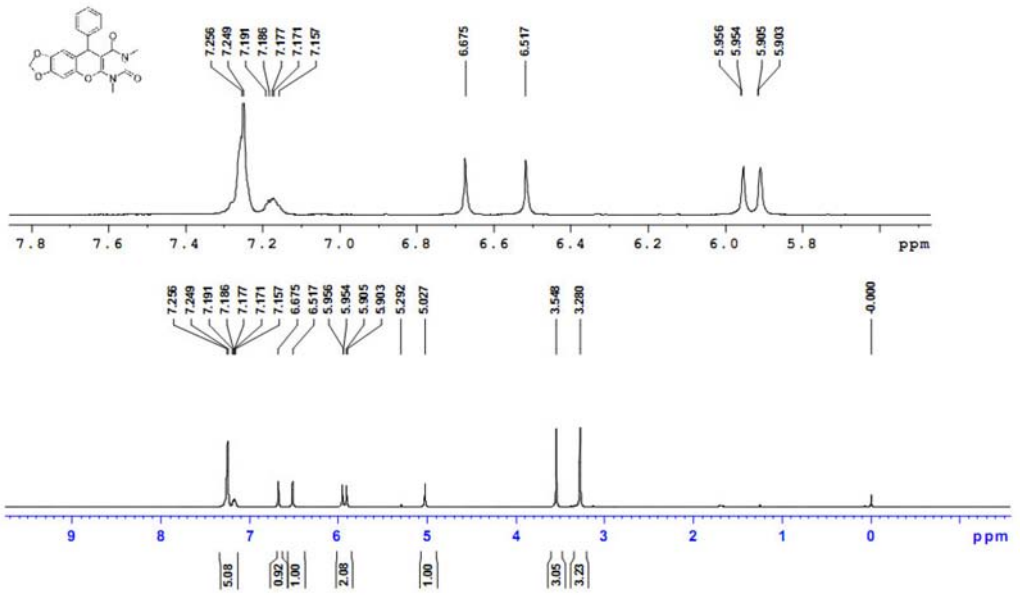

Figure S2. ^{1}H NMR of **4a** (400 MHz, $CDCl_3$).

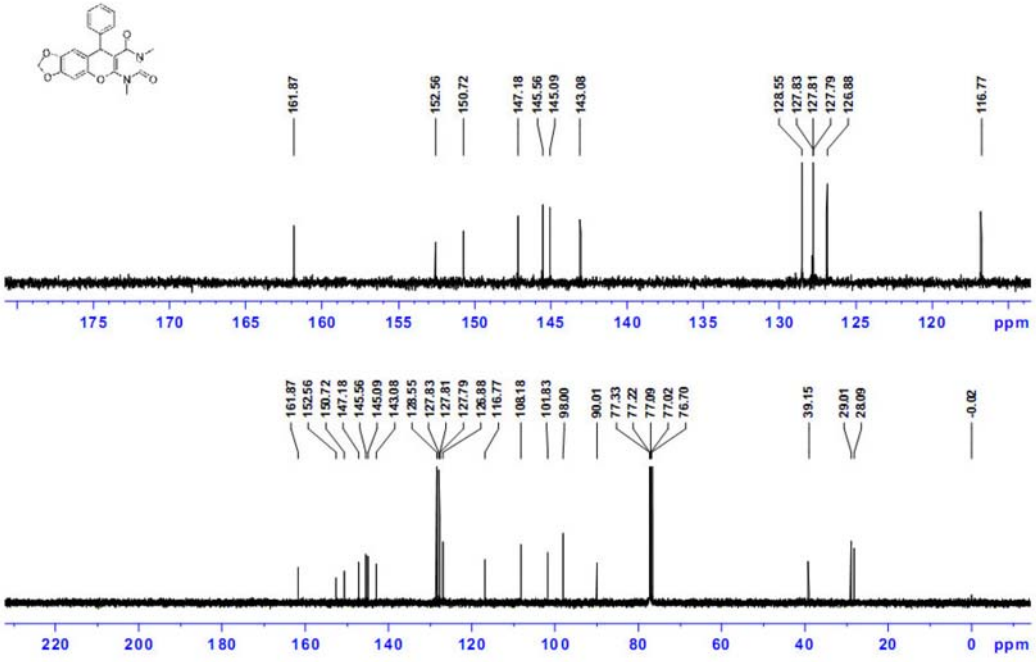

Figure S3. ^{13}C NMR of **4a** (100 MHz, $CDCl_3$).

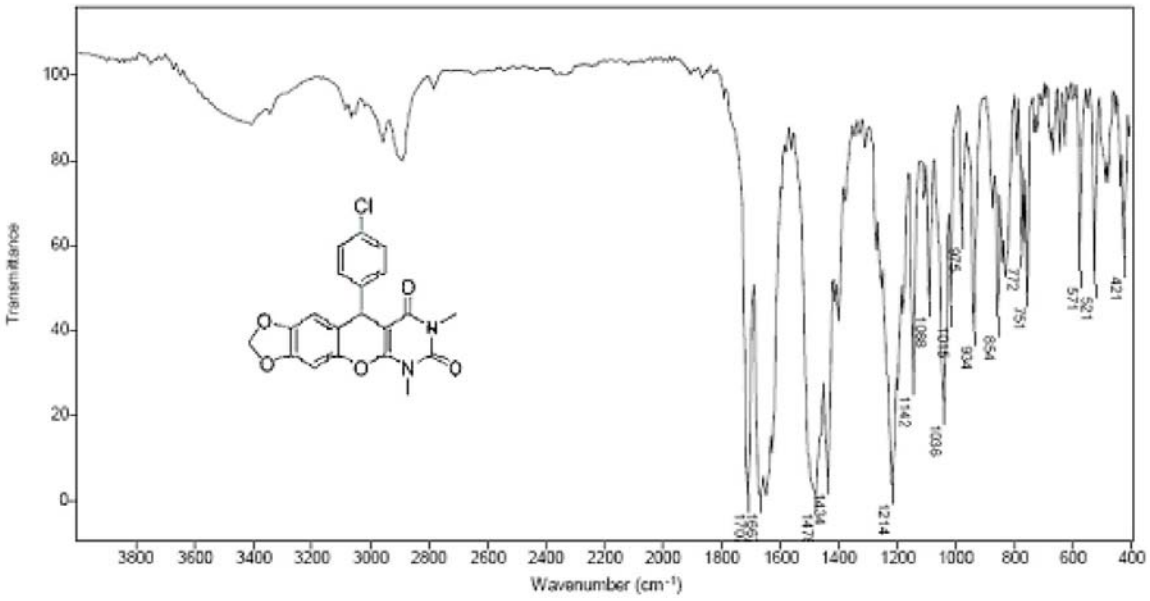

Figure S4. IR (KBr) of **4b.**

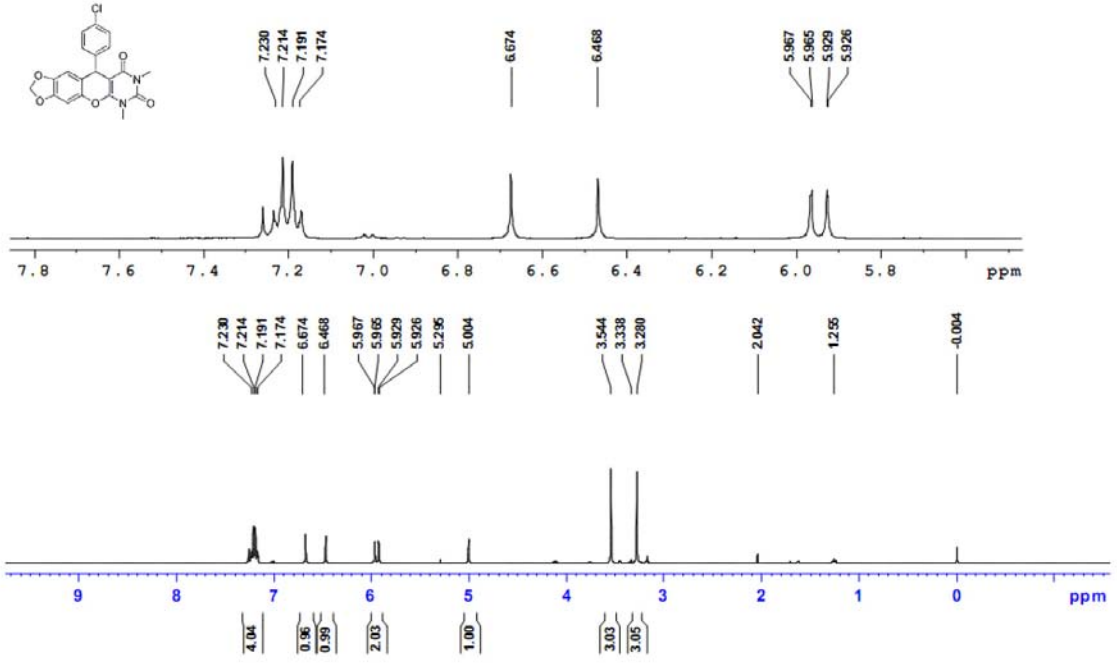

Figure S5. ^{1}H NMR of **4b** (400 MHz, $CDCl_3$).

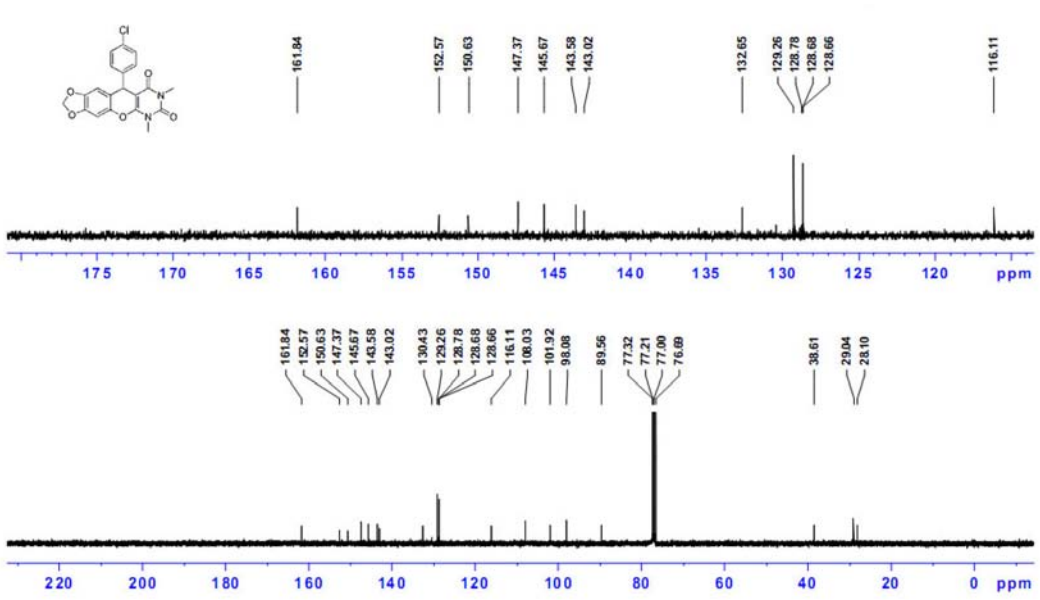

Figure S6. ^{13}C NMR of **4b** (100 MHz, $CDCl_3$).

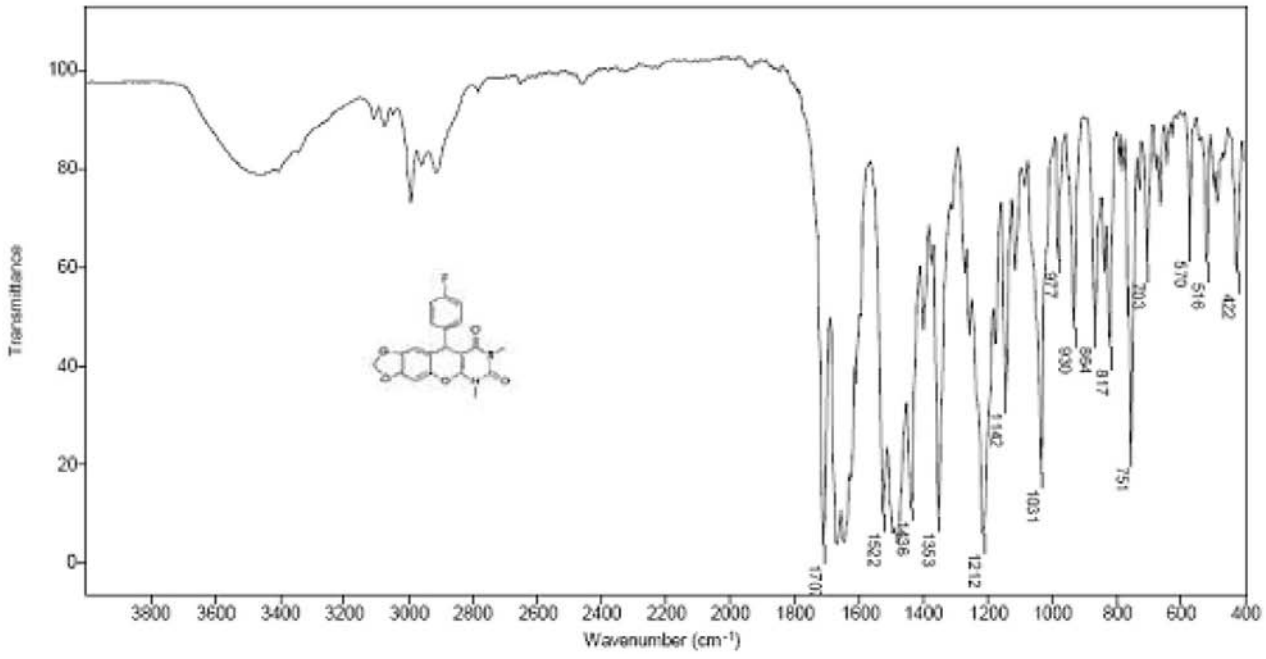

Figure S7. IR (KBr) of **4c**.

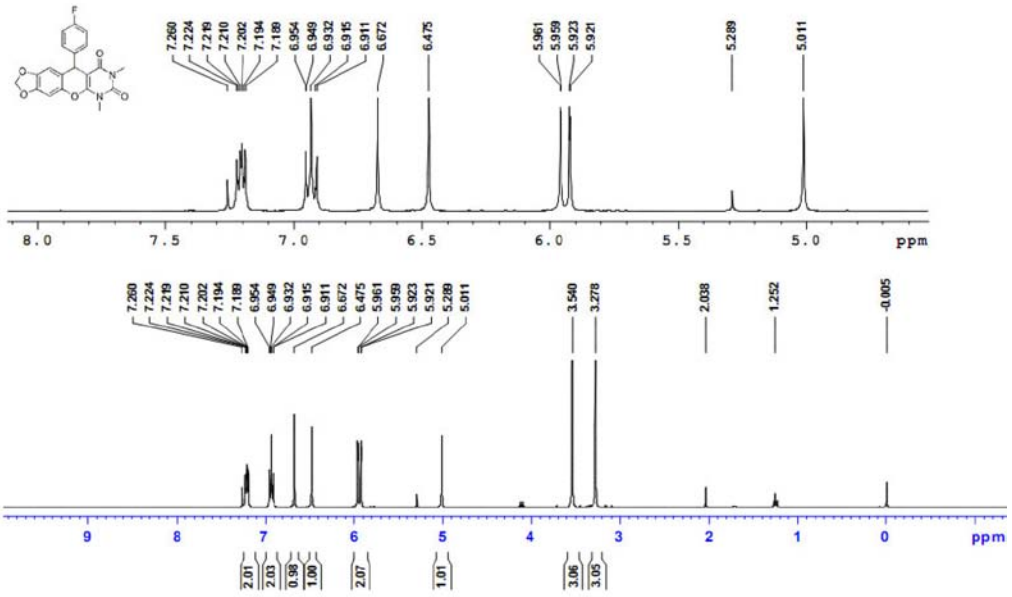

Figure S8. ^{1}H NMR of **4c** (400 MHz, $CDCl_3$).

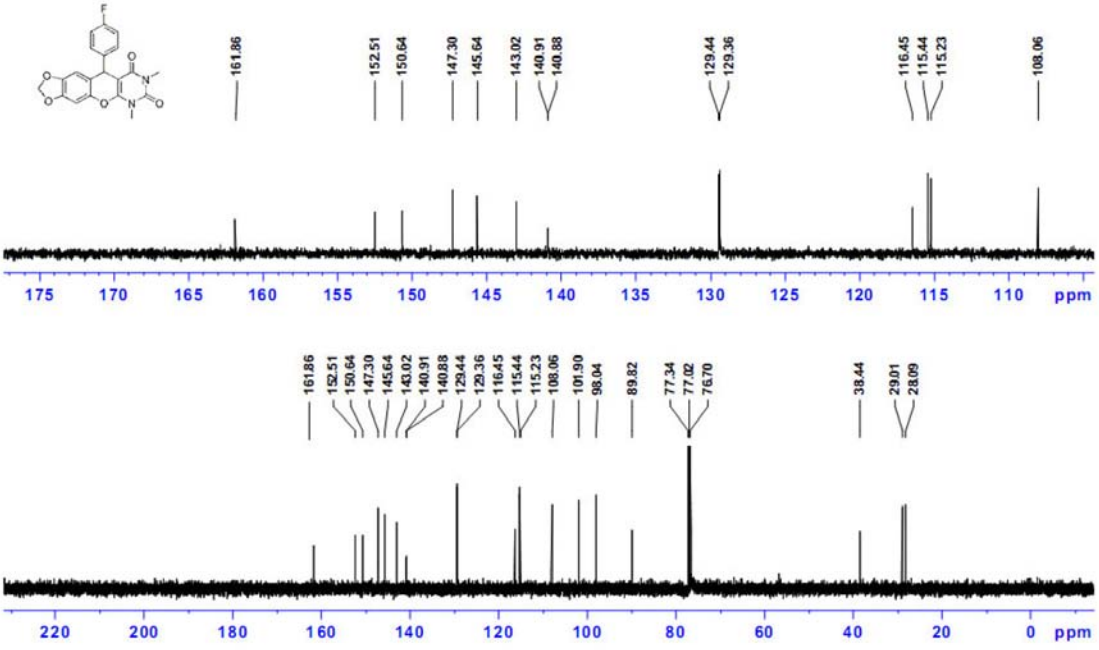

Figure S9. ^{13}C NMR of **4c** (100 MHz, $CDCl_3$).

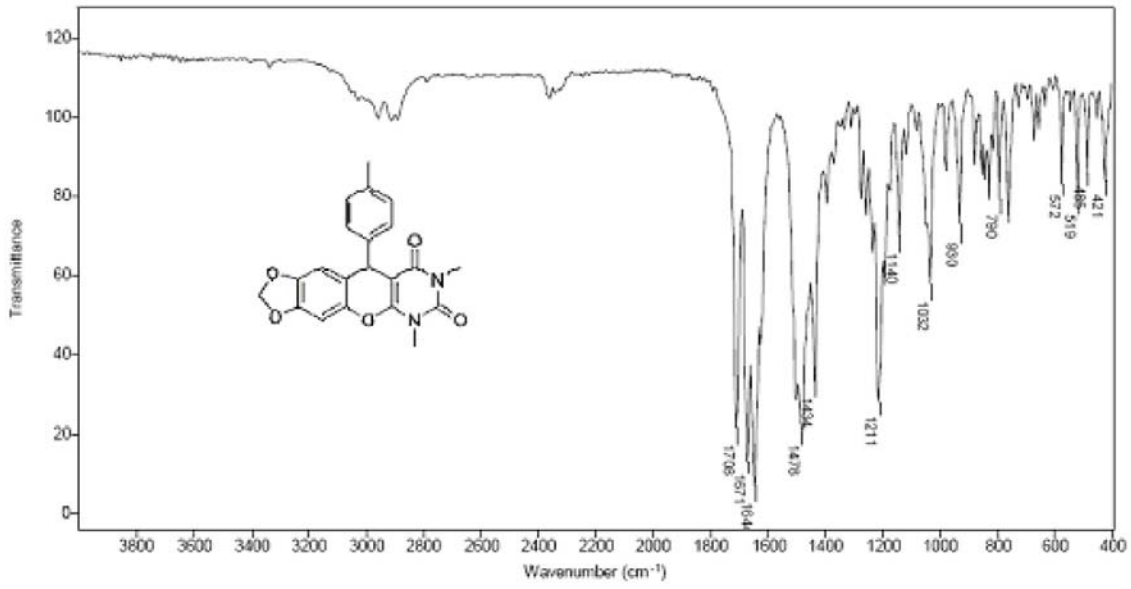

Figure S10. IR (KBr) of **4d.**

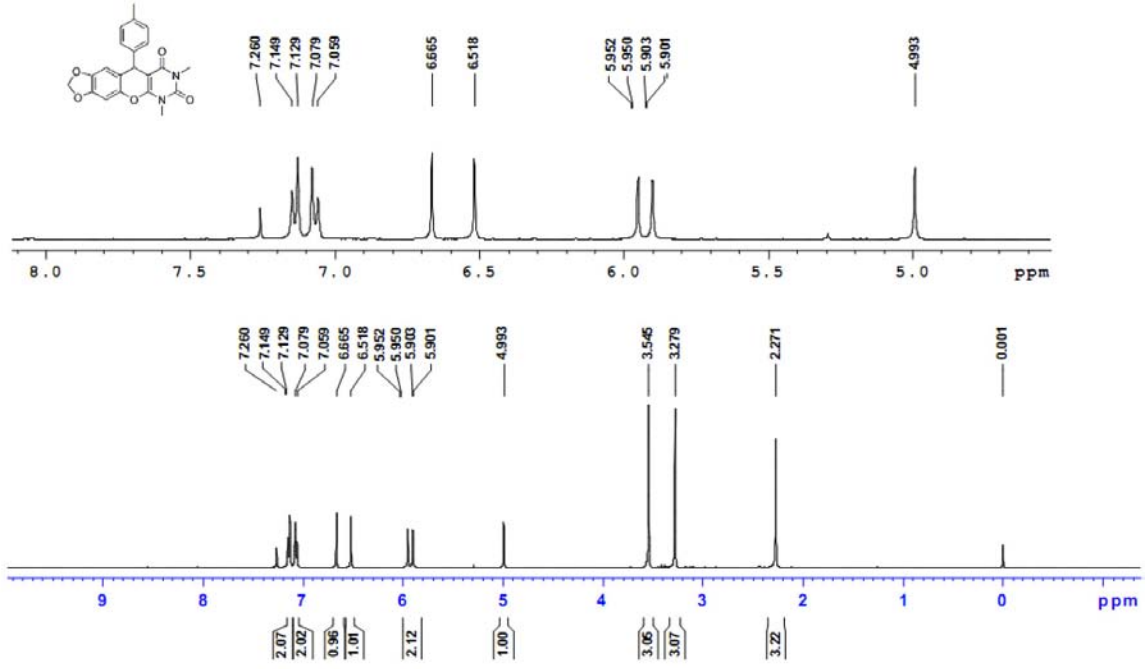

Figure S11. ^{1}H NMR of **4d** (400 MHz, $CDCl_3$).

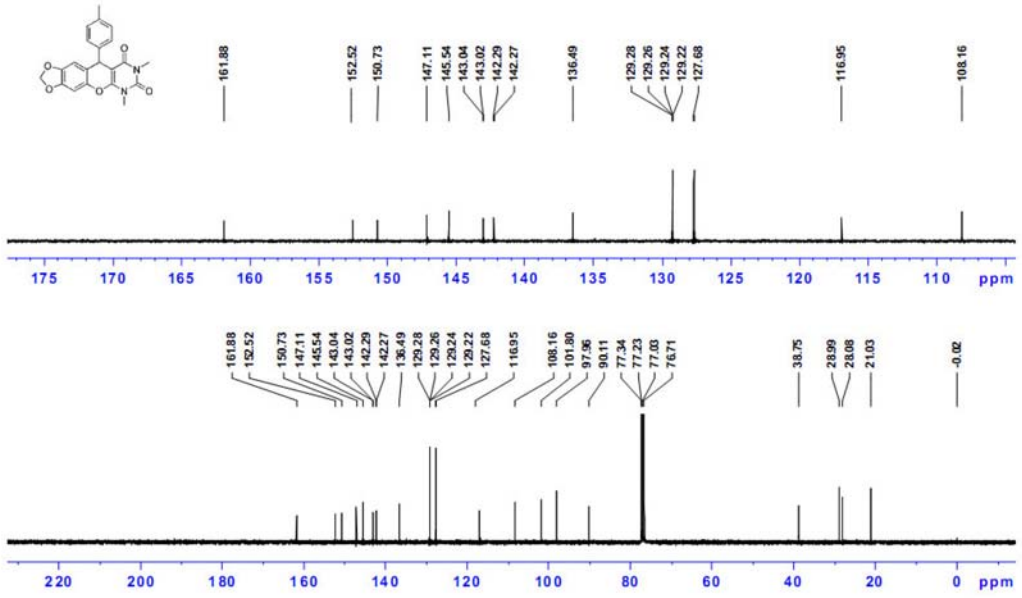

Figure S12. ^{13}C NMR of **4d** (100 MHz, $CDCl_3$).

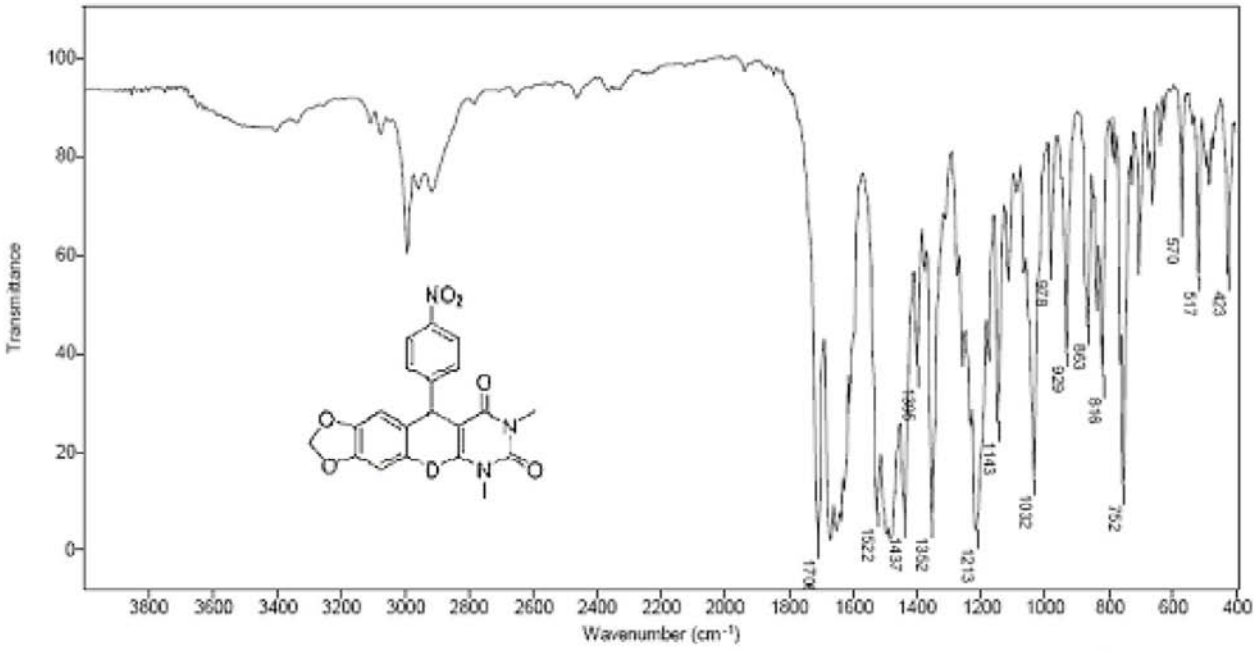

Figure S13 IR (KBr) of **4e**.

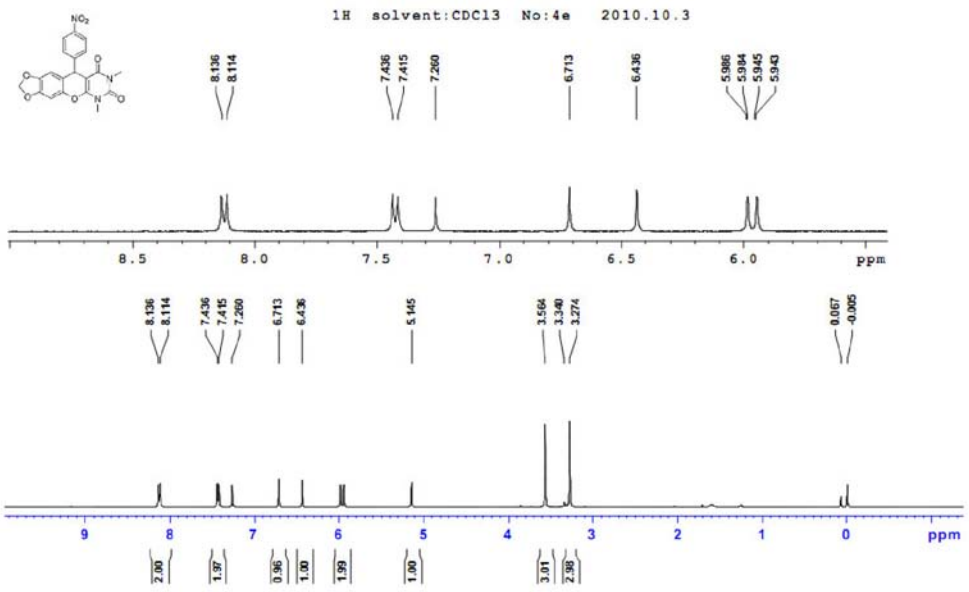

Figure S14. ^{1}H NMR of **4e** (400 MHz, $CDCl_3$).

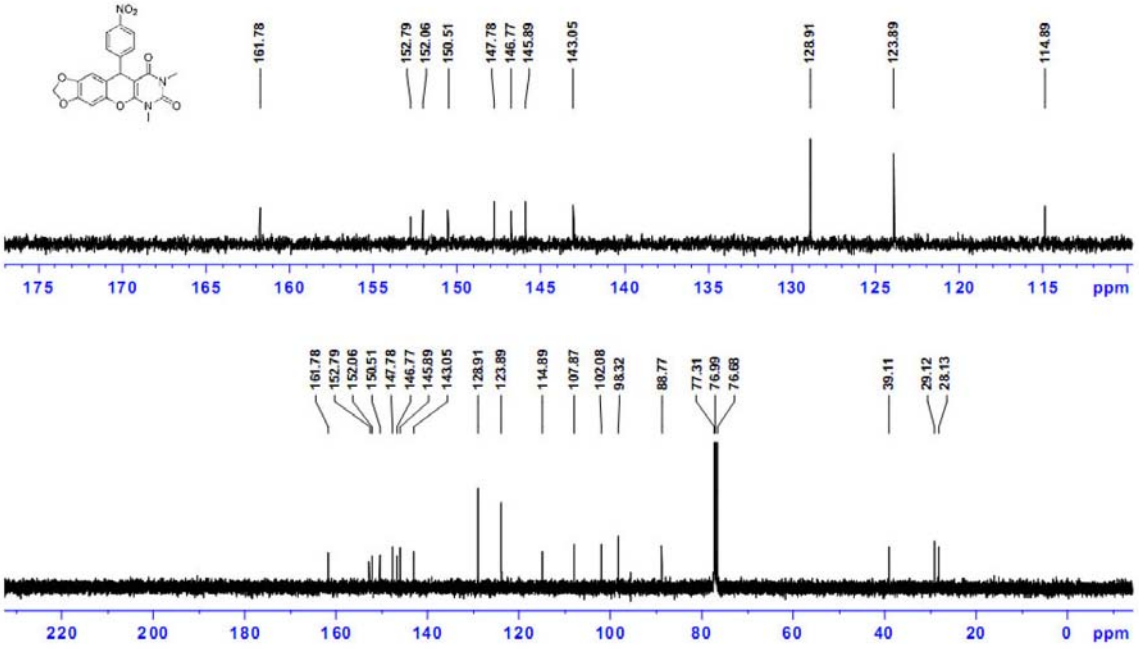

Figure S15. ^{13}C NMR of **4e** (100 MHz, $CDCl_3$).

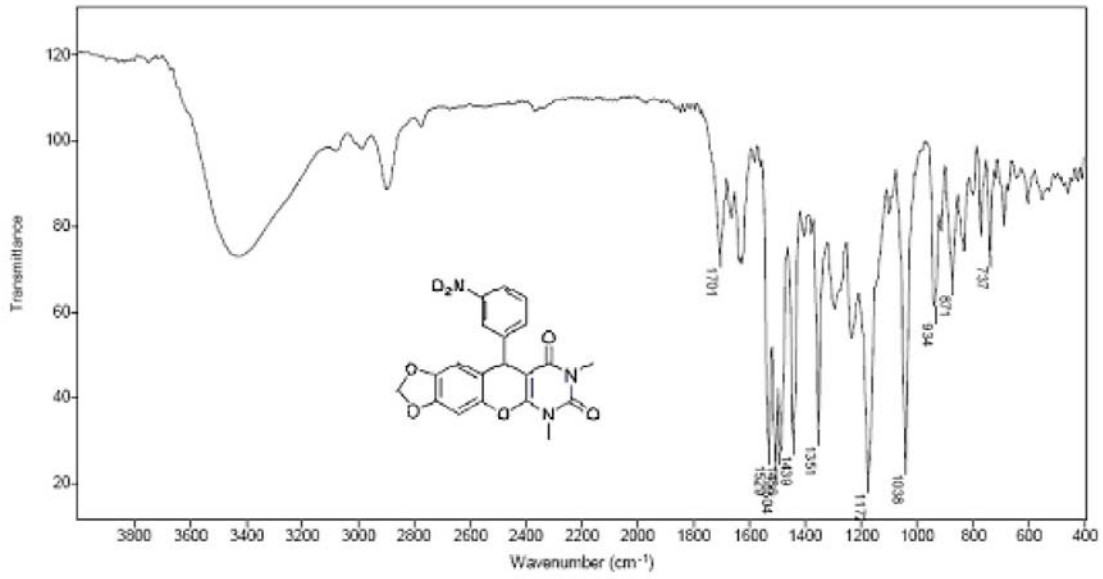

Figure S16. IR (KBr) of **4f.**

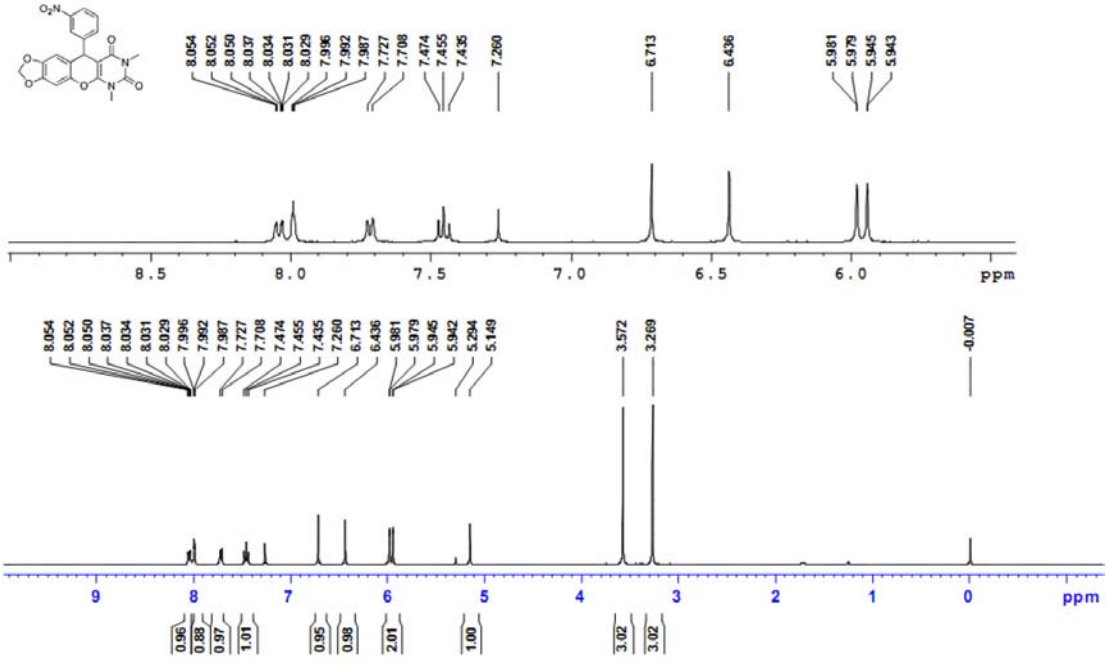

Figure S17. ^{1}H NMR of **4f** (400 MHz, $CDCl_3$).

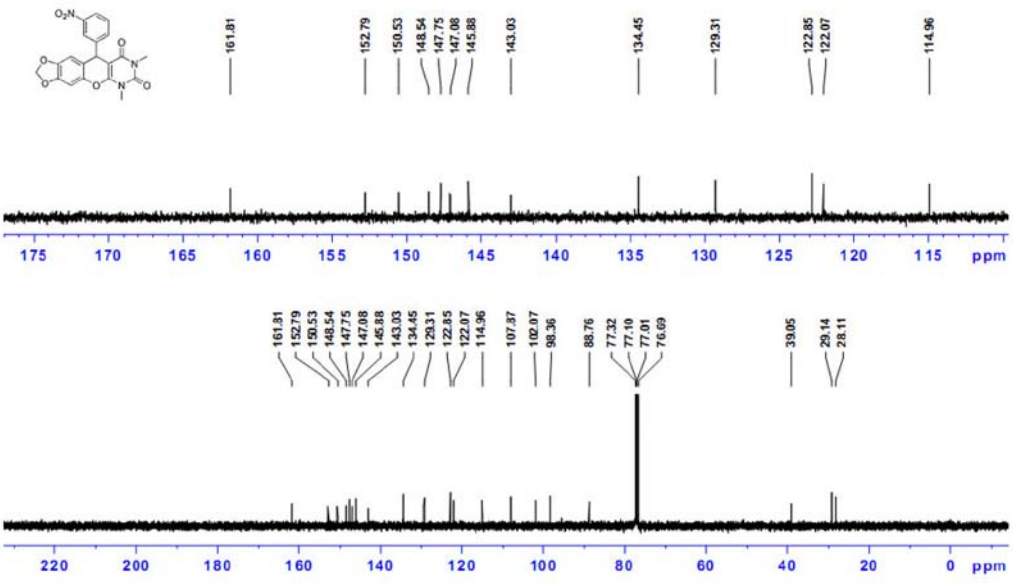

Figure S18. ^{13}C NMR of **4f** (100 MHz, $CDCl_3$).

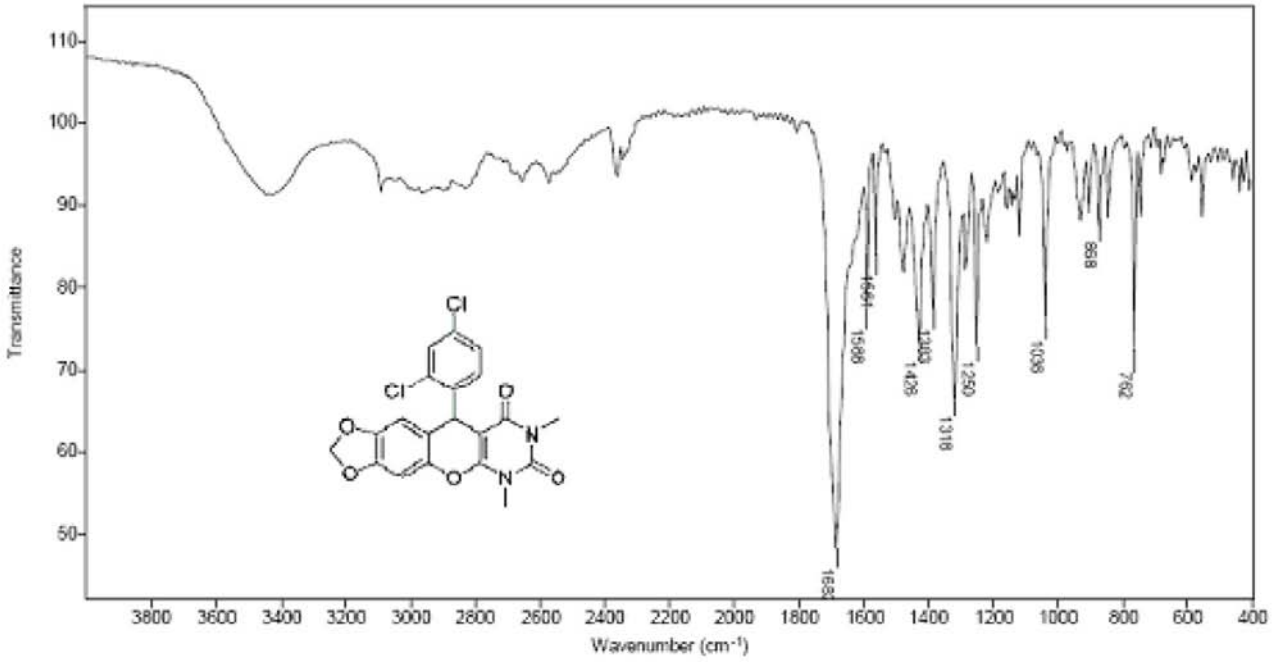

Figure S19. IR (KBr) of **4g.**

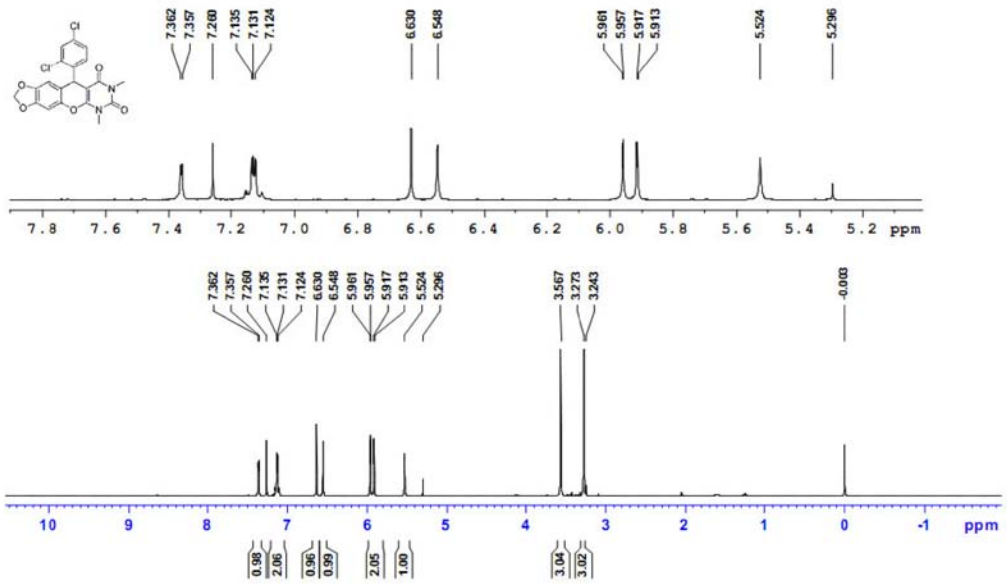

Figure S20. ^{1}H NMR of **4g** (400 MHz, $CDCl_3$).

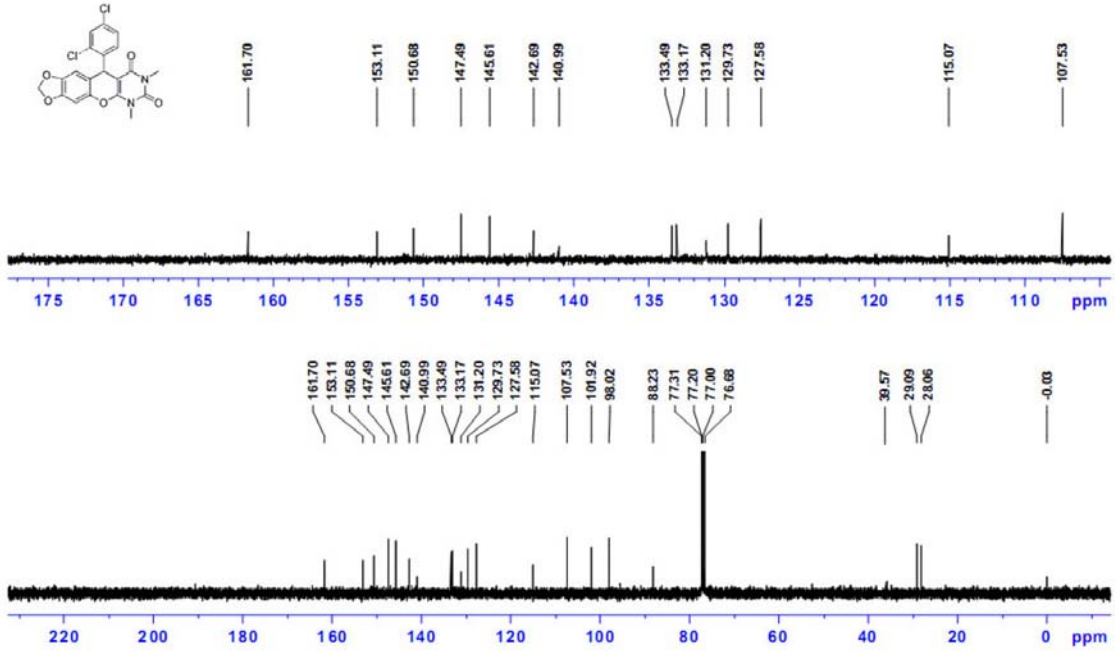

Figure S21. ^{13}C NMR of **4g** (100 MHz, $CDCl_3$).

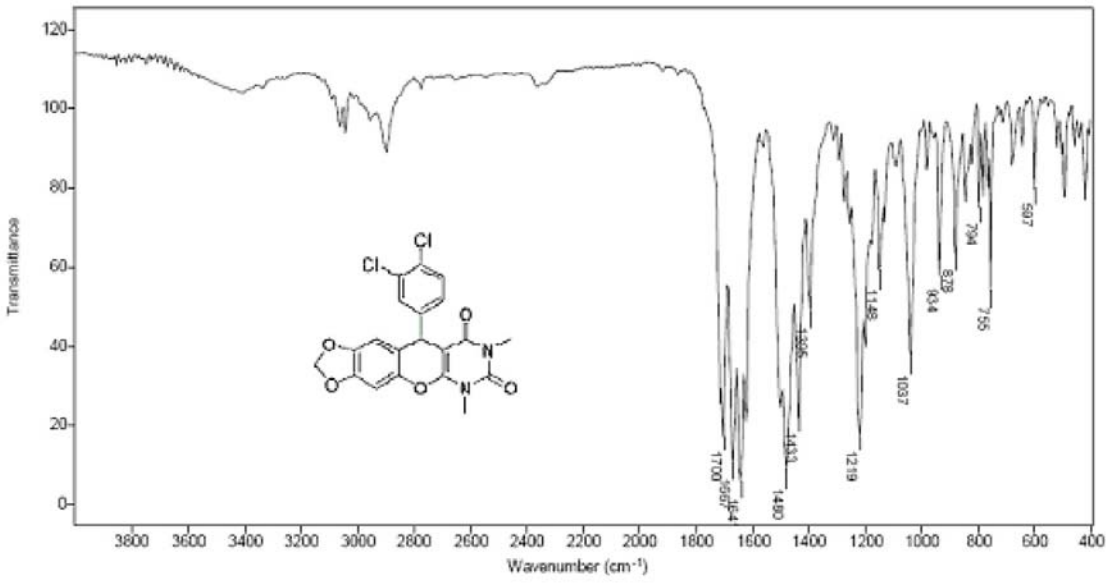

Figure S22. IR (KBr) of **4h.**

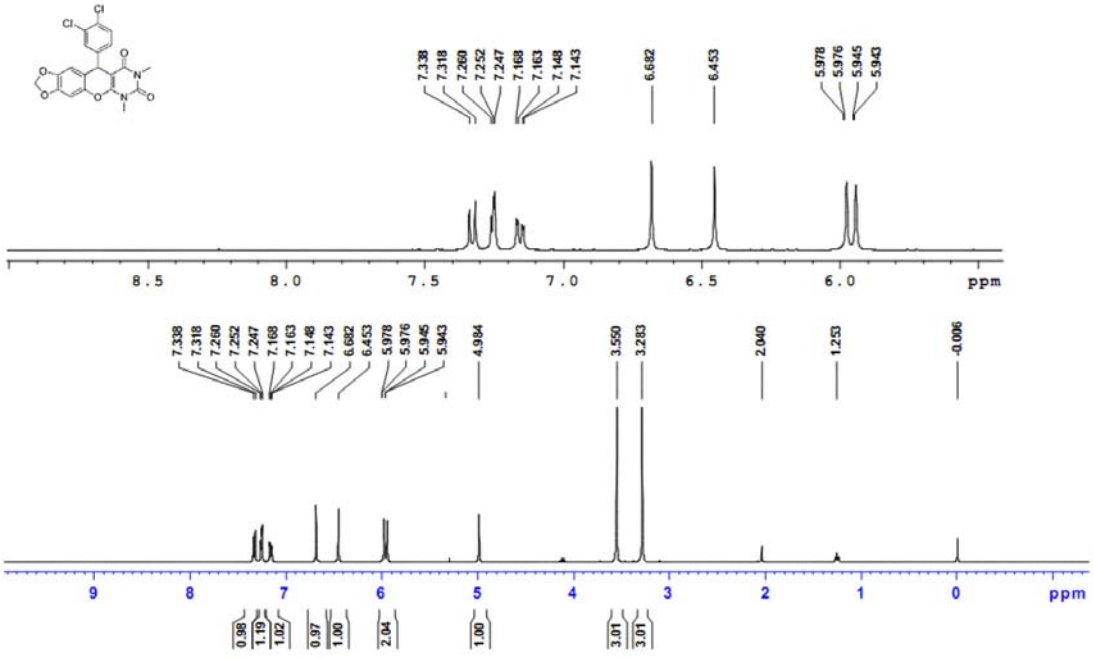

Figure S23. ^{1}H NMR of **4h** (400 MHz, $CDCl_3$).

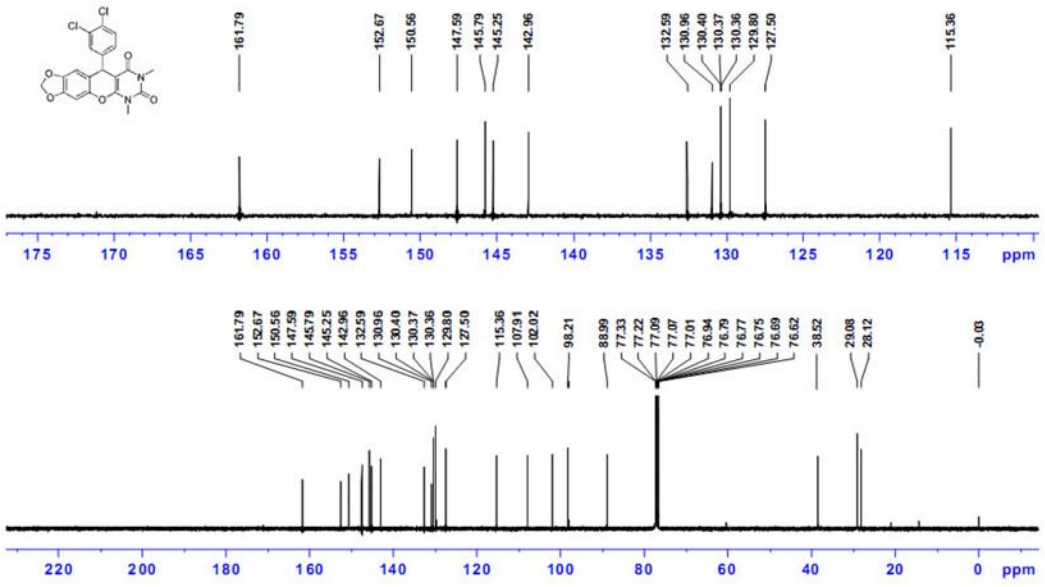

Figure S24. ^{13}C NMR of **4h** (100 MHz, $CDCl_3$).

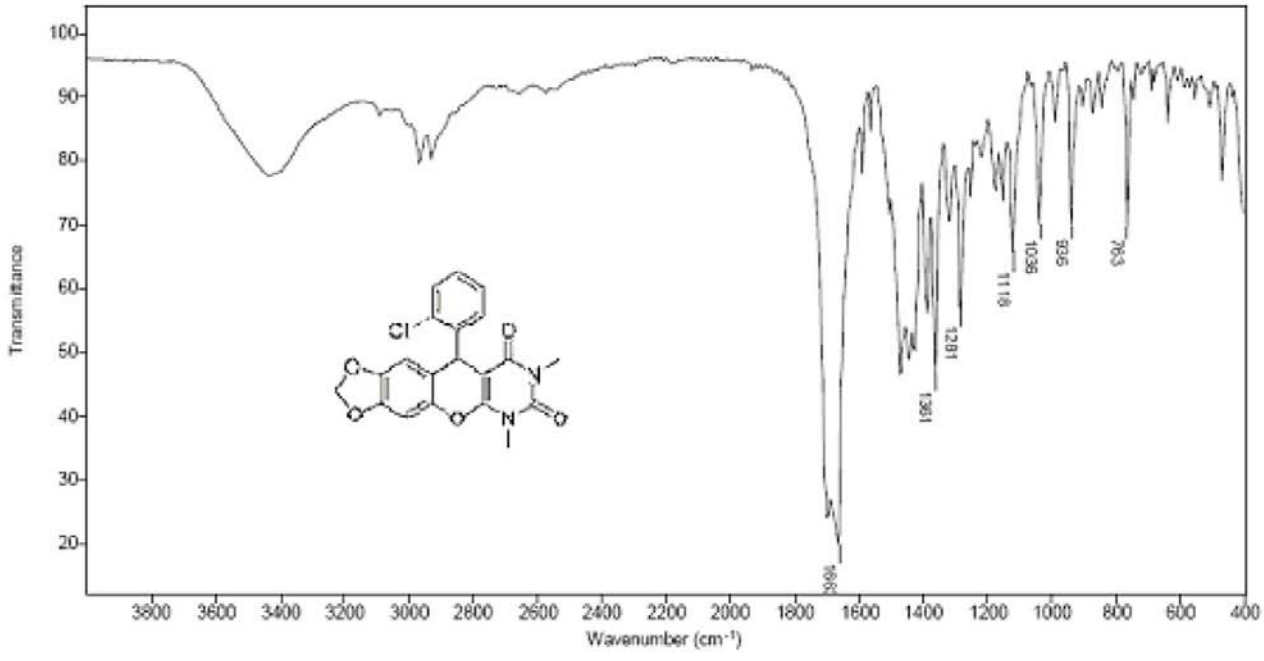

Figure S25. IR (KBr) of **4i**.

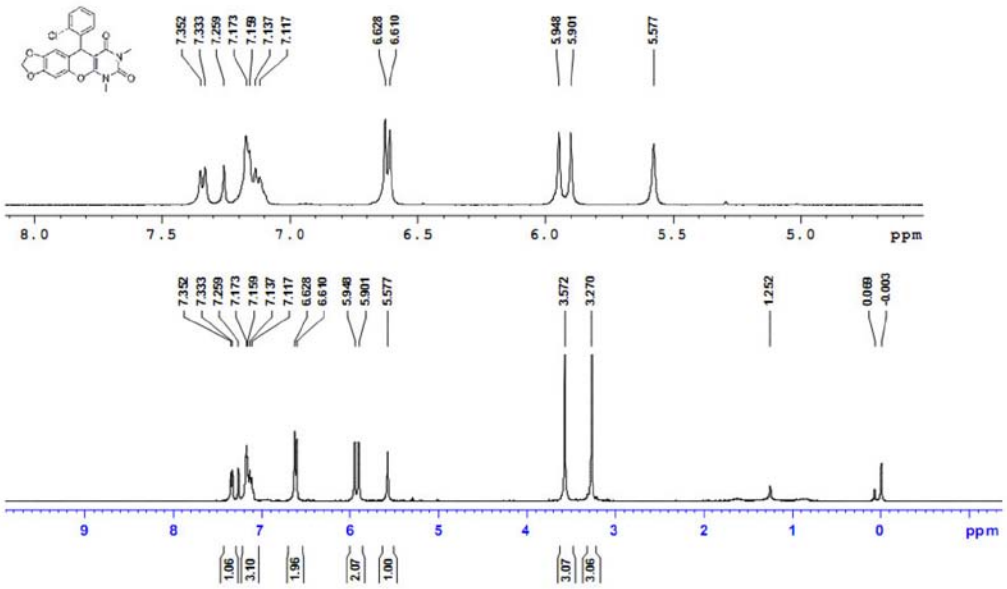

Figure S26. ^{1}H NMR of **4i** (400 MHz, $CDCl_3$).

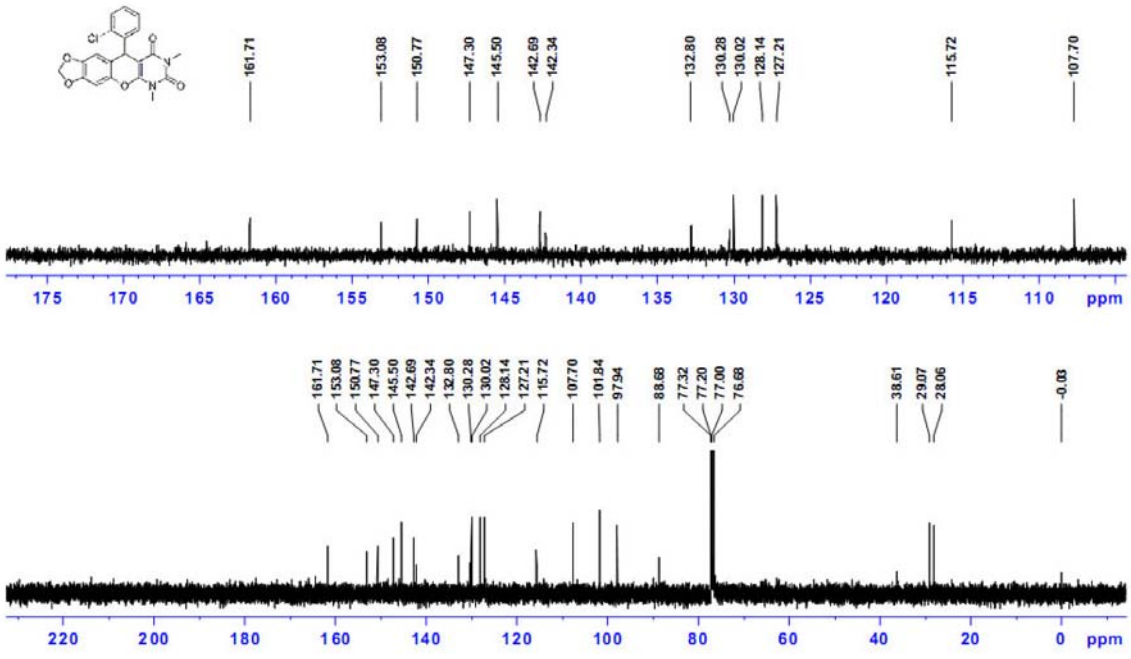

Figure S27. ^{13}C NMR of **4i** (100 MHz, $CDCl_3$).