



Faculty of Resource Science and Technology

**Bis-2'-hydroxychalcone and its Complexes as Potential Dye Sensitizer for
Dye-sensitized Solar Cell Application**

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Bis-2'-hydroxychalcone and its Complexes as Potential Dye Sensitizer for Dye-sensitized Solar Cell Application.

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A thesis submitted

In fulfilment of the requirements for the degree of Master of Science

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DECLARATION

I declare the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. It is original and is the result of my work, unless otherwise indicated or acknowledged as reference work. The thesis has not been accepted for any degree and is not concurrently submitted in candidature for any other degree.

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ABSTRACT

In this study, the power conversion efficiency of bis-chalcone derivatives and its complexes as the dye sensitizer in dye-sensitized solar cell had been determined. A total of 6 compounds of bis-chalcone derivatives, namely, compound **1A**, **1B**, **2A**, **2B**, **3A** and **3B** had been synthesized by the Claisen-Schmidt condensation reaction. Two compounds, compound **1B** and compound **2B** were further proceeded to the complexation with *cis*-dichlorotetrakis(dimethylsulfoxide) ruthenium(II) precursor to yield the complex **CX1** and complex **CX2**. The molecular structure of the synthesized compounds and complexes were characterized and confirmed by the fourier transform infrared spectrophotometer, proton and carbon nuclear magnetic resonance spectrometer, UV-visible spectrophotometer and CHN analysis. Finally, all of the synthesized materials were applied as the dye sensitizer in the dye-sensitized solar cell and the power conversion efficiency was measured using the San Ei XES-40S1 Solar Simulator under monochromatic light of air mass 1.5 global (AM 1.5G) with the incident light intensity of 100 mW/cm². Results showed that compound **1B** afforded the highest power conversion efficiency of 0.05 % due to the good dye absorption towards the TiO₂ semiconductor with the fill factor value of 51.60 % recorded. On the other hand, both ruthenium complexes of **CX1** and **CX2** showed very low power conversion efficiency value of 2.79×10^{-3} % and 1.68×10^{-3} %, respectively. This may have resulted from the symmetrical molecular framework of the ruthenium complex, which hindered the electron transfer towards the TiO₂ semiconductor. Therefore, the intermediate compound **1C** can be served as the future prospects to further modify the molecular framework of bis-chalcone derivatives.

Keywords: bis-chalcone derivatives, ruthenium complex, dye sensitizer, dye-sensitized solar cell, power conversion efficiency

Bis-2'-hidroksilkalkon serta Kompleksnya terhadap Potensi Aplikasi Sebagai Pewarna Sensitasi dalam Sel Solar Terpeka Pewarna

ABSTRAK

Dalam kajian ini, kecekapan penukaran tenaga bagi terbitan bis-kalkon dan kompleksnya sebagai pewarna sensitasi dalam sel solar terpeka perwarna telah dicapai. Sejumlah 6 sebatian terbitan bis-kalkon antaranya sebatian **1A**, **1B**, **2A**, **2B**, **3A** dan **3B** telah disediakan melalui tindak balas kondensasi Claisen-Schmidt. Selepas itu, dua sebatian iaitu sebatian **1B** dan sebatian **2B** yang dihasilkan dilanjutkan untuk pengkompleksan dengan cis-diklorotetrakis (dimetilsulfusid)rutenium(II) untuk menghasilkan kompleks **CX1** dan **CX2**. Kesemua sebatian yang disintesis telah dicirikan dengan menggunakan kaedah spektroskopi seperti inframerah, resonans magnet nukleus, ultralembayung dan analisis CHN. Akhir sekali, kesemua sebatian dan kompleks telah diaplikasikan sebagai perwana foton dalam sel solar terpeka pewarna manakala kecekapan penukaran tenaga telah diukur dengan menggunakan alat San Ei XES-40S1 Suria Simulasi di bawah cahaya monokromatik bersamaan dengan jisim udara 1.5 global (JU 1.5G) dalam tenaga cahaya insiden sebanyak 100 mW/cm^2 . Data menunjukkan sebatian **1B** mencatatkan kecekapan penukaran tenaga yang tertinggi iaitu 0.05 % disebabkan penyerapannya yang baik pada semikonduktor TiO_2 dengan faktor pengisian sebanyak 51.60 %. Manakala, kompleks **CX1** dan **CX2** menunjukkan kecekapan penukaran tenaga yang amat rendah iaitu $2.79 \times 10^{-3} \%$ dan $1.68 \times 10^{-3} \%$, masing-masingnya. Ini kerana struktur molekul kompleks ruthenium yang simetri menjejaskan pemindahan elektron ke arah semikonduktor TiO_2 . Oleh itu, sebatian **1C** telah dihasilkan sebagai kajian masa depan untuk mengubah struktur molekul terbitan bis-kalkon.

Kata kunci: terbitan bis-kalkon, kompleks ruthenium, pewarna sensitasi, sel suria bercirikan perwarna sensitasi, kecekapan penukaran tenaga

TABLE OF CONTENTS

	Page
DECLARATION	i
ACKNOWLEDGEMENT	ii
ABSTRACT	iv
ABSTRAK	v
TABLE OF CONTENTS	vi
LIST OF TABLES	xii
LIST OF FIGURES	xiii
LIST OF SCHEMES	xix
LIST OF ABBREVIATIONS	xxi
CHAPTER 1: INTRODUCTION	1
1.1 Solar energy as the alternative resource	1
1.2 Overview of photovoltaic technologies.....	2
1.3 General principle of dye-sensitized solar cell (DSSC).....	7
1.4 General properties of dye sensitizers	9
1.5 General background on flavonoids	10
1.6 Introduction to chalcone family	12
1.7 Problem Statement and objectives of study	14
1.8 Scope of the thesis.....	15

CHAPTER 2: LITERATURE REVIEW	16
2.1 Composition of DSSC and its roles in solar conversion efficiency	16
2.1.1 Transparent conductive oxide (TCO) coated film.....	16
2.1.2 The semiconductor titanium dioxide (TiO ₂)	17
2.1.3 Dye sensitizer	18
2.1.4 Redox Electrolyte	22
2.1.5 Counter electrode	24
2.1.6 DSSC assembling and its performance evaluation	24
2.2 Synthesis pathway of chalcone and its derivatives	27
2.2.1 Claisen-Schmidt condensation reaction	27
2.2.1 (a) Acid catalytic reaction pathway	28
2.2.1 (b) Basic catalytic reaction pathway	30
2.2.2 Suzuki-Miyaura reaction	31
2.2.3 Grinding technique	33
2.2.4 Sonocatalysis and thermally activated reactions	34
2.2.5 Microwave-assisted technique	35
2.3 Application of chalcone and its derivatives towards society	36
2.3.1 Biological potential of chalcone and its derivatives.....	36
2.3.2 Electronic potential of chalcone and its derivatives.....	40
2.4 Review on 2'-hydroxychalcone complex synthesis and analysis	45
2.5 Application of 2'-hydroxychalcone complexes	50

CHAPTER 3: METHODOLOGY	53
3.1 Materials, Chemicals and reagents	53
3.1.1 (a) Materials, chemicals and reagents used for bis-chalcone synthesis	53
3.1.1 (b) Materials, chemicals and reagents used for complex synthesis.....	53
3.1.1 (c) Materials and chemicals used in fabrication of DSSC	54
3.2 Procedure.....	54
3.2.1 Synthesis of bis-chalcone	54
3.2.1.1 Preparation of Series 1 bis-chalcone	54
3.2.1.2 Preparation of Series 2 bis-chalcone	58
3.2.1.3 Preparation of bis-chalcone (Series 3)	60
3.2.1.4 Characterization	62
3.2.2 Synthesis of metal(II) complexes	63
3.2.2.1 Preparation of <i>cis</i> -dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, PC1	63
3.2.2.2 Complexation of bis-2'-hydroxychalcone derivatives with PC1	64
3.2.2.3 Characterization	68
3.2.3 Fabrication of dye-sensitized solar cell (DSSC)	68
3.2.3.1 Preparation of TiO ₂ working electrode	69
3.2.3.2 Preparation of standard dye (N3) solution	69
3.2.3.3 Preparation of bis-chalcone compounds and ruthenium complexes as dye-sensitizer....	70
3.2.3.4 Preparation of Pt counter electrode.....	70

3.2.3.5	Composition of electrolyte	71
3.2.3.6	Preparation of dye-sensitized working electrode.....	71
3.2.3.7	Sealing of dye-sensitized solar cell.....	72
3.2.3.8	Characterization.....	72
CHAPTER 4: RESULTS AND DISCUSSION.....		74
4.1	Results and discussion on synthesized bis-chalcone compounds	74
4.1.1	Working mechanism on synthesis of bis-chalcone derivatives.....	74
4.1.2	Strategy in bis-chalcone synthesis and work up.....	76
4.1.3	Spectroscopic data of Series 1 bis-chalcone	80
4.1.3.1	(2 <i>E</i> , 2' <i>E</i>)-3-3'-(1,4-phenylene)bis(1-phenylprop-2-en-1-one), 1A	80
4.1.3.2	(2 <i>E</i> , 2' <i>E</i>)-3-3'-(1-4-phenylene)bis(1-(2-hydroxy phenyl) prop-2- en-1-one), 1B	82
4.1.3.3	(<i>E</i>)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl) benzaldehyde, 1C	84
4.1.4	Spectroscopic data of Series 2 bis-chalcone	86
4.1.4.1	(2 <i>E</i> , 2' <i>E</i>)-3,3'-(1,3-phenylene)bis(1-phenylprop-2-en-1-one), 2A	86
4.1.4.2	(2 <i>E</i> , 2' <i>E</i>)-3-3'-(1,3-phenylene)bis[1-(2'-hydroxyphenyl) prop-2-en-1-one], 2B	88
4.1.5	Spectroscopic data of Series 3 bis-chalcone	90
4.1.5.1	(2 <i>E</i> , 2' <i>E</i>)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-phenylprop-2-en-1-one), 3A	90

4.1.5.2	(2 <i>E</i> , 2' <i>E</i>)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-[2'-hydroxyphenyl] prop-2-en-1-one), 3B	92
4.1.6	Spectroscopic analysis of bis-chalcone series	94
4.1.6.1	FT-IR spectra analysis	94
4.1.6.2	Nuclear Magnetic Resonance (NMR) spectroscopy analysis.....	96
4.1.6.3	UV-visible spectroscopy analysis.....	100
4.2	Results and discussion of complexation between bis-2'-hydroxychalcone (1B and 2B) and ruthenium precursor, PC1	102
4.2.1	Synthesis method and work up strategies	102
4.2.2	Cis-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, PC1	105
4.2.3	1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1	106
4.2.4	1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2	110
4.2.5	Spectroscopy analysis of ruthenium complexes.....	113
4.2.5.1	FT-IR spectra analysis of CX1 and CX2	113
4.2.5.2	NMR spectra analysis of CX1 and CX2	115
4.2.5.3	UV-visible analysis.....	118
4.3	Results and discussion on the application of synthesized bis-chalcone and complexes in DSSC.....	119
4.3.1	Morphology of titanium dioxide (TiO ₂) on FTO glass	119

4.3.2	Application of bis-chalcone derivatives towards solar cell efficiency.....	122
4.3.3	Electrochemistry study of compound 1B	126
4.3.4	Application of complex CX1 and CX2 in solar cell efficiency	127
CHAPTER 5: CONCLUSION AND SUGGESTION FOR FUTURE WORK.....		131
5.1	Conclusion on the overall project.....	131
5.2	Suggestion for future work.....	132
REFERENCES.....		135
APPENDICES... ..		155

LIST OF TABLES

	Page
Table 4.1	92
Table 4.2	94
Table 4.3	96
Table 4.4	97
Table 4.5	109
Table 4.6	111
Table 4.7	111
Table 4.8	114
Table 4.9	119
Table 4.10	124

LIST OF FIGURES

		Page
Figure 1.1	Schematic illustration of CPV solar cell with InGaP/InGaAs/Ge triple-junction	3
Figure 1.2	Cross-section view of mono and multicrystalline silicon solar cell	4
Figure 1.3	Structure of the 1st generation single junction p-i-n amorphous Si thin film solar cell	5
Figure 1.4	Basic structure of dye sensitized solar cell	6
Figure 1.5	Best research cell efficiencies obtained from NREL (Retrieved from https://www.nrel.gov/pv/)	7
Figure 1.6	Typical structure of flavonoid	10
Figure 1.7	Structure of some selected flavonoids	10
Figure 1.8	General molecular structure of chalcone	12
Figure 1.9	Complex coordination of 2'-hydroxychalcone with metals ion	12
Figure 2.1	General structure of <i>cis</i> -bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium (II) complex (N3 dye)	19
Figure 2.2	Molecular structure of donor- π -bridge acceptor zinc porphyrin	19
Figure 2.3	Molecular structure of boron chalconate complex	20

Figure 2.4	Molecular structure of terthiophene organic dye sensitizer	21
Figure 2.5	<i>J/V</i> measurement of typical DSSC	25
Figure 2.6	Structure of licochalcone A (12) and 4-methylamino-3',4'-dimethoxychalcone (13)	37
Figure 2.7	Structure of 3-indolyl-1-phenylpropenone derivatives	38
Figure 2.8	Structure of 4,4'-dihydroxychalcone	38
Figure 2.9	Structure of synthesized DMMC with high SHG efficiency	40
Figure 2.10	Structure of synthesized substituted bis-chalcone	41
Figure 2.11	Bis-chalcone compound with high emission property	43
Figure 2.12	Structures of metal(II) complexes with substituted 2'-hydroxychalcones	45
Figure 2.13	Boron complexes derived from hydroxychalcone derivatives	50
Figure 3.1	Proposed molecular structure of compound 1A (a) and compound 1B (b)	53
Figure 3.2	Proposed molecular structure of compound 1C (c) and compound 1D (d)	54
Figure 3.3	Proposed molecular structure of compound 2A (e) and 2B (f)	56
Figure 3.4	Proposed molecular structure of compound 3A (g) and 3B (h)	58

Figure 3.5	Molecular structure of <i>cis</i> - dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, PC1	61
Figure 3.6	Proposed molecular structure of complex CX1 (i) and CX2 (j)	63
Figure 3.7	Schematic structure of DSSC	66
Figure 3.8	Electron beams evaporation technique	68
Figure 4.1	FT-IR spectrum of compound 1A	77
Figure 4.2	¹ H NMR spectrum of compound 1A	78
Figure 4.3	¹³ C NMR spectrum of compound 1A	78
Figure 4.4	UV-visible spectrum of compound 1A	79
Figure 4.5	FT-IR spectrum of compound 1B	79
Figure 4.6	¹ H NMR spectrum of compound 1B	80
Figure 4.7	¹³ C NMR spectrum of compound 1B	80
Figure 4.8	UV-visible spectrum of compound 1B	81
Figure 4.9	FT-IR spectrum of compound 1C	81
Figure 4.10	¹ H NMR spectrum of compound 1C	82
Figure 4.11	¹³ C NMR spectrum of compound 1C	82
Figure 4.12	UV-visible spectrum of compound 1C	83
Figure 4.13	FT-IR spectrum of compound 2A	83

Figure 4.14	^1H NMR spectrum of compound 2A	84
Figure 4.15	^{13}C NMR spectrum of compound 2A	84
Figure 4.16	UV-visible spectrum of compound 2A	85
Figure 4.17	FT-IR spectrum of compound 2B	85
Figure 4.18	^1H NMR spectrum of compound 2B	86
Figure 4.19	^{13}C NMR spectrum of compound 2B	86
Figure 4.20	UV-visible spectrum of compound 2B	87
Figure 4.21	FT-IR spectrum of compound 3A	87
Figure 4.22	^1H NMR spectrum of compound 3A	88
Figure 4.23	^{13}C NMR spectrum of compound 3A	88
Figure 4.24	UV-visible spectrum of compound 3A	89
Figure 4.25	FT-IR spectrum of compound 3B	89
Figure 4.26	^1H NMR spectrum of compound 3B	90
Figure 4.27	^{13}C NMR spectrum of compound 3B	90
Figure 4.28	UV-visible spectrum of compound 3B	91
Figure 4.29	FT-IR of ruthenium precursor PC1	102
Figure 4.30	^1H NMR spectrum of ruthenium precursor PC1	102

Figure 4.31	^{13}C NMR spectrum of ruthenium precursor PC1	103
Figure 4.32	FT-IR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1	103
Figure 4.33	^1H NMR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1 [(a) Downfield; (b) Upfield]	104
Figure 4.34	^{13}C NMR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1 [(a) Downfield; (b) Upfield]	105
Figure 4.35	UV-visible spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1	106
Figure 4.36	FT-IR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2	106
Figure 4.37	^1H NMR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2 [(a) Downfield; (b) Upfield]	107
Figure 4.38	^{13}C NMR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2 [(a) Downfield; (b) Upfield]	108
Figure 4.39	UV-visible spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2	109

Figure 4.40	SEM image of TiO ₂ surface morphology on FTO glass	117
Figure 4.41	Molecular structure of synthesized bis-chalcone derivatives	118
Figure 4.42	<i>J/V</i> measurement of bis-chalcone compounds (without –OH substituent, compounds 1A , 2A , and 3A , left); (with –OH substituent, compounds 1B , 2B and 3B , right)	122
Figure 4.43	Cyclic Voltammogram of compound 1B in DCM/0.1 M [NBu ₄]PF ₆ at 0.05 V s ⁻¹ scan rate	123
Figure 4.44	Molecular structure of CX1 and CX2	124
Figure 4.45	<i>J/V</i> measurement of standard N3 dye (left) and synthetic dye of ruthenium complexes (right)	125
Figure 5.1	Proposed bis-chalcone molecular structure for future work	128
Figure 5.2	Proposed ruthenium complex with the bis-chalcone moiety	130

LIST OF SCHEMES

	Page
Scheme 1.1 General idea on the mechanism of the DSSC	8
Scheme 2.1 Synthesis of 2,5-dihydroxy substituted chalcone with SOCl ₂	26
Scheme 2.2 Synthesis pathway of chalcone based on acid catalytic reaction	28
Scheme 2.3 Synthesis pathway of base catalytic Claisen-Schmidt condensation reaction	30
Scheme 2.4 Suzuki-Miyaura reaction of chalcone synthesis	31
Scheme 2.5 Synthesis of chalcone through grinding technique	32
Scheme 2.6 Synthesis of <i>meta</i> -chalcone compound <i>via</i> grinding technique	33
Scheme 2.7 Synthesis of 4'-hydroxy and 4'-carboxyl chalcone <i>via</i> ultrasonic irradiation	34
Scheme 2.8 Synthesis of chalcone <i>via</i> microwave-assisted technique	34
Scheme 2.9 Synthesis pathway of chalcone derivatives as anti-oxidant agents	36
Scheme 2.10 The synthesis pathway of poly(aryl ether chalcone)	40
Scheme 2.11 Schematic diagram of interaction between PDAC and PVA	42
Scheme 2.12 Square planar geometry of 2'-hydroxychalcone complex	44
Scheme 2.13 Different conformation of 2'-hydroxychalcone ruthenium complex	46

Scheme 2.14	Schematic diagram of ruthenium(II) complex	47
Scheme 2.15	Synthesis of bis-2'-hydroxychalcone with ruthenium (II) precursor	48
Scheme 4.1	Claisen-Schmidt condensation mechanism of bis-chalcone derivatives	72

LIST OF ABBREVIATIONS

SOCl ₂	Thionyl chloride
HCl	Hydrochloric acid
AlCl ₃	Aluminium chloride
NaOH	Sodium hydroxide
KOH	Potassium hydroxide
Ba(OH) ₂	Barium hydroxide
Pd(PPh ₃) ₄	Tetrakis(triphenylphosphine)palladium(0)
Cs ₂ CO ₃	Caesium carbonate
K	Kelvin
K ₂ CO ₃	Potassium carbonate
Nrf2-AREs	nucleus factor erythroid 2 p45-related factor 2
H ₂ O ₂	Hydrogen peroxide
iNOS	Nitric oxide synthase
MTT	dimethyl thiazolyl diphenyl tetrazolium
NLO	nonlinear optical
D	Donor
A	Acceptor

SHG	second harmonic generation
DMMC	1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one
PMMA	Poly(methyl methacrylate)
PDAC	1-phenyl-3-(4-dimethoxyaminophenyl) prop-2-en-1-one
PVA	poly(vinyl alcohol)
DSSC	dye-sensitized solar cell
TiO ₂	Titanium dioxide
FF	fill factor
TLC	thin layer chromatography
NMR	Nuclear magnetic resonance
CDCl ₃	Deuterated chloroform
DMSO-d ₆	Deuterated dimethylsulfoxide
IR	Infrared spectra
KBr	Potassium bromide
Et ₃ N	triethylamine
DCM/ CH ₂ Cl ₂	Dichloromethane
DMF	Dimethylformamide

J	Coupling constant
Δ	Chemical shift in part per million
-C=O	Carbonyl
-OH	Hydroxyl
C=C	Alkene
-OCH ₃	Methoxy
Hz	Hertz
ppm	Part per million
-CHO	Aldehyde
¹ H	Proton
¹³ C	Carbon
N.A	Not available
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
N	Non-bonding
ICT	Intermolecular charge transfer
MLCT	Metal to ligand charge transfer

S	Singlet
D	Doublet
T	Triplet
CPV	Concentrator photovoltaic system
c-Si	wafer-based monocrystalline
PV	Photovoltaic
TCO	Transparent conductive oxide
ITO	Indium tin oxide
FTO	Fluorine doped indium tin oxide
I/T_3	Iodide/ triiodide
ZnO	Zinc oxide
PCE	Power conversion efficiency
PC61BM	[6,6]phenyl-C61-butyric acid methyl ester
DMHImI	1,2-dimethyl-3-hexylimidazolium iodide
TBP	tert-butylpyridine
LiI	lithium iodide
KI	potassium iodide

TPAI	tetrapropylammonium iodide
Pt	Platinum
AM	Air mass
DMPII	1,2-dimethyl-3-propylimidazolium
MPN	3-methoxypropionitrile
<i>J_{sc}</i>	short circuit current
<i>V_{oc}</i>	open circuit voltage
SEM	Scanning electron microscope

CHAPTER 1

INTRODUCTION

1.1 Solar energy as the alternative resource

Energy can be defined as the source of power that is utilized either from physical or chemical resource to provide human daily necessities such as electricity and fuels (Hornby, 2000). According to the Global Energy Statistical Yearbook (2017), about 80 % of the energy consumption used in year 2016 was generated from fossil fuels such as natural gas, crude oil and coal. In Malaysia, the electricity and fuels are mainly produced from these resources and the amount of energy consumption would increase 3 times greater by year 2030 as the human population and economic growth are increasing year by year (Gan & Li, 2008).

As reported by Begum *et al.* (2015), the power sector comprised of electricity that run by fossil fuels is the main reason for the rise of CO₂ emissions, which resulted up to 60 % of the greenhouse gas effects. As the consequences, global warming and climate change are well observed all around the world. Besides, in concerning the fact that fossil fuels are non-renewable resources which would take millions of years to regenerate (“National Geographic,” 2018), the depletion of these resources is indeed inevitable. Therefore, scientists have developed several green technologies to reduce the CO₂ emissions as well as to decrease the dependency on the usage of non-renewable energy. This can be achieved by switching to the use of renewable energy such as bio-fuels, solar, wind and hydrothermal energy.

According to the current trend, solar energy has grown much attention to researchers from all over the world due to the sustainability and availability of sunlight throughout the years. For past few decades, solar applications have been widely commercialized into electronic appliances such as in solar powered traffic lights, solar battery charger, water dispenser and more (Hou *et al.*, 2004; Khaehintung & Sirisuk, 2007; Prabucki, 2007). Theoretically, the

electrical energy generated is mainly derived from the chemical energy that adsorbed the photon of the sunlight, which excites the systems to produce the electrons that circulate around the cell. This phenomenon is typically known as the photovoltaic effect where it was first discovered by a French physicist named Alexandre Edmond Becquerel in year 1839 (Chaar *et al.*, 2011). Since then, this noble discovery had gained interest of many scientists, which they further reveal the theory and apply it into various applications. As known for today, solar cells are constructed based on this photovoltaic principle.

1.2 Overview of photovoltaic technologies

Typically, solar cell can be categories into four different types of photovoltaic technologies namely concentrator photovoltaic system, wafer-based crystalline silicon, thin-film technologies and emerging technologies.

With no doubt, concentrator photovoltaic system (CPV) solar cell is well known with its high solar conversion efficiency, which incorporated with the multijunction inorganic layers such as GaInP/GaInAs/Ge triple-junction (Figure 1.1) and mostly used for the space applications (Nishioka *et al.*, 2006). The triple-junctions create a wide band gap within the system, allowing more incident lights to be adsorbed rather than lost during the interconnection of the sub-cells (Yamaguchi *et al.*, 2006). In addition, concentrating optics such as Fresnel lenses and mirrors are used in order to maximize and concentrate the sunlight intake into the cells (Philipps *et al.*, 2015). Nevertheless, the drawback of CPV type solar cell is the increase in temperature during the light-concentrating operations, which causes the decrease in the V_{oc} values due to its temperature dependence characteristic and indirectly reduces the overall conversion efficiency of the solar cell (Araki *et al.*, 2002). For this reason, Nishioka *et al.* (2006) had conducted a research on the effect of increasing the light concentration ratios at 25 °C in CPV solar cell. Surprisingly, they found that there was a significant improvement on

the V_{oc} values observed when the concentration ratio increased with the conversion efficiency of 37% recorded, thus overcome the reduction of the V_{oc} during the increased of temperature (Nishioka *et al.*, 2006).

Ag eletrode	
n-GaAs Contact	
AR Coating	
n-AlInP window	InGaP top cell (1.82 eV)
n-InGaP emitter	
p-InGap base	
p-AlInP BSF	
p-AlGaAs/n-InGaP	Tunnel-junction
n-InGaP window	InGaAs middle cell (1.40 eV)
n-InGaAs emitter	
p-InGaAs base	
p-InGaP BSF	
p-GaAs/n-GaAs	Tunnel-junction
n-InGaAs buffer	Buffer- layer
InGaP 1st layer	
n-Ge	Ge bottom cell (0.65 eV)
p-Ge	
Ag electrode	

Figure 1.1: Schematic illustration of CPV solar cell with InGaP/InGaAs/Ge triple-junction

Moving on, wafer-based monocrystalline (c-Si) and multicrystalline silicon (mc-Si) PV solar cells have been reported with the highest commercial production in the PV market industry as compare to the other types of the photovoltaic technologies (Saga, 2010). This is because the raw material, silicon is one of the most abundant resources available on Earth and with its electronic bandgap of 1.1 eV, it is ideal to be used as the semiconductor in PV system. In short, the monocrystalline silicon PV solar cells are manufactured from the single crystal silicon ingot that grow *via* Czohralski (CZ) process, while multicrystalline silicon PV solar cells are made by melting the silicon crystal into the crucible, solidifying and forming into

multicrystalline silicon ingot, which are then sliced into thin wafers (Saga, 2010; Chaar *et al.*, 2011). Figure 1.2 shows the typical cross-section of the solar cell. According to the review made by Polman *et al.* (2016), the current average cell efficiency of mono and multicrystalline silicon is at 25% and 21%, respectively. Indeed, multicrystalline silicon solar cell has consistently achieved lower conversion efficiency than the monocrystalline silicon solar cell due to the low silicon purity used, but the advantages of this PV technology is the reduction in manufacturing cost, reduce the chance in metal contamination and also decrease the defect in its crystal structure (Manna & Mahajan, 2007).

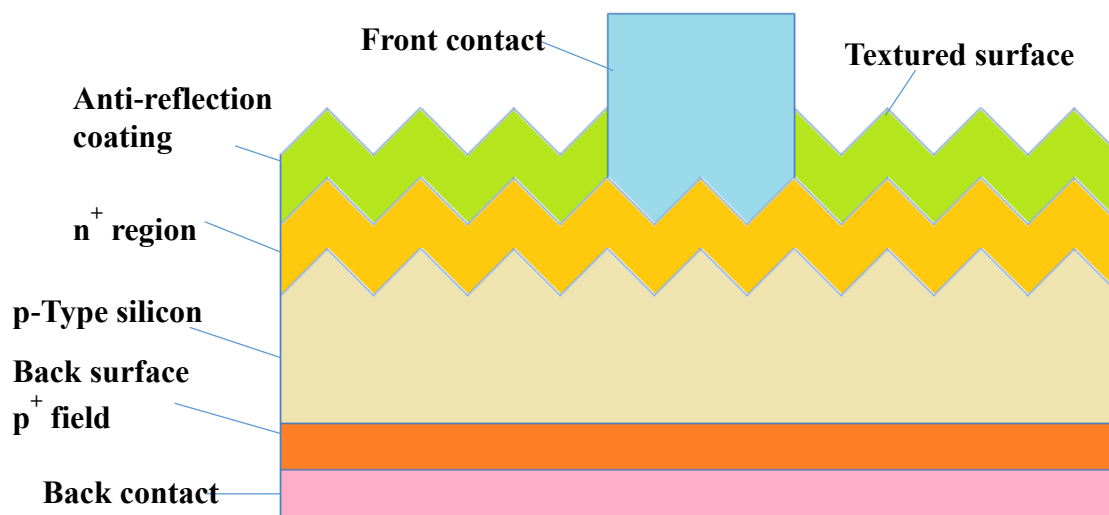


Figure 1.2: Cross-section view of mono and multicrystalline silicon solar cell

In order to further cut-down the production cost by reducing the raw materials used, scientist invented a thinner PV module and hence the thin film solar cells are introduced into the PV market. For instance, the first discovery of this fabrication technique is on the single junction n-i-p amorphous silicon thin film solar cell (Figure 1.3), which incorporated with the photosensitive material in micrometre (μm) thickness such as transparent conductive oxide (TCO) on the inexpensive substrate i.e. plastic, glass or even stainless steel (Chu, 2011). Unlike the wafer-based mono and multicrystalline silicon solar cell, the conversion efficiency

of this a-Si thin film PV solar cell degrades gradually under the sun irradiation and stabilized at 4-8 % (Chaar *et al.*, 2011). This is due to the increase of recombination current resulted from the alteration in hydrogenated amorphous silicon during the long exposure of sunlight or commonly known as the Staebler-Wronski effect, thus reduce the conversion efficiency (Kolodziej, 2004). Therefore, the developments of micromorph silicon thin-film which consist of multi-crystalline junctions have been performed in order to create a wider band gap for better sustainability in absorbing the incident light and increase the efficiency (Meir *et al.*, 1998; Bu *et al.*, 2015). Besides that, the enhancement in knowledge and technology has consistently allow scientists to find new pathway in fabricating higher conversion efficiency with cost-effective thin film solar cells, such as the substitution of the a-Si into copper indium selenide (CIS) or copper indium gallium selenide (CIGS). (Repins *et al.*, 2008).

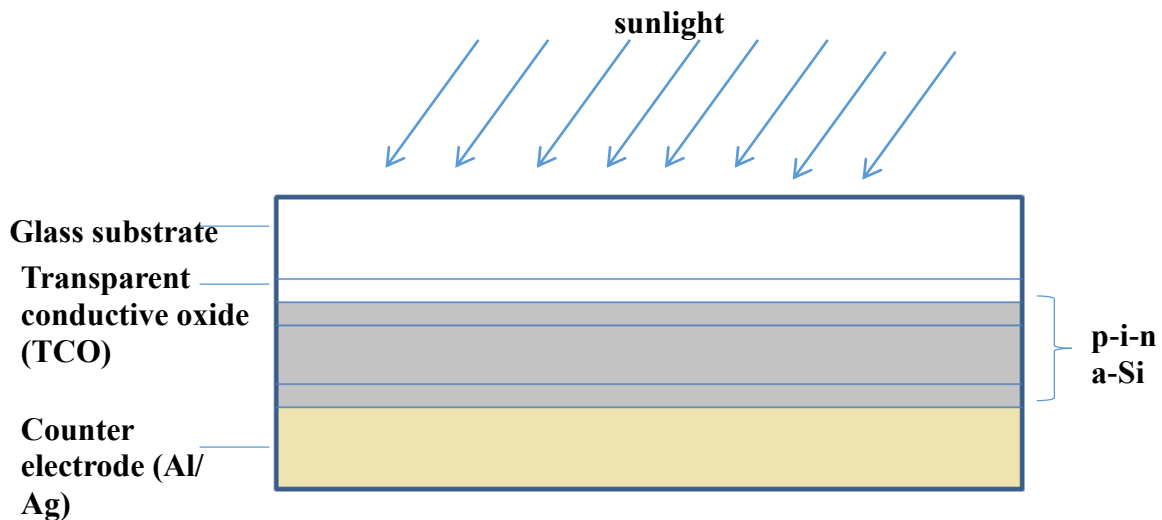


Figure 1.3: Structure of the 1st generation single junction p-i-n amorphous Si thin film solar cell

Meanwhile, in the advancement of scientific instrumentations and research publications available, photovoltaic technologies have come into progression where emerging technologies are getting more interest by researchers due to the inexpensive materials used and the ability

to tune the molecular structure for better conversion efficiency. As for example, dye sensitizer solar cell (DSSC) which consists of organic or inorganic compounds have gained the popularity among the university researchers, as it can be readily made in the laboratory into the organic or inorganic based thin film solar cell. Practically, π -conjugated organic molecules and polymers with donors and acceptors substituent are chosen for the role as dye sensitizer credited to their ability in optical excitations, charge injection and charge transfer during the illumination of light (Braun *et al.*, 2009). Herein, Figure 1.4 shows the basic structure of DSSC thin film solar cell.

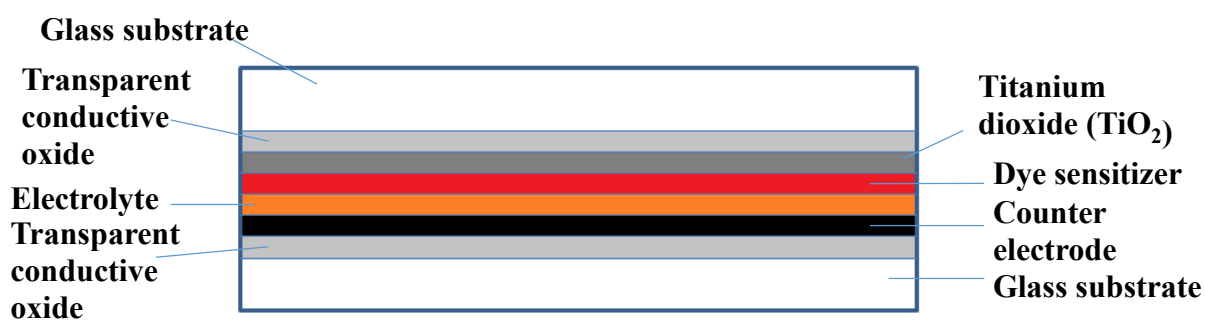


Figure 1.4: Basic structure of dye sensitized solar cell

To date, the opportunities to discover and modify the DSSC into high power conversion efficiency solar cell are relatively competitive due to its low-cost production, flexibility in selection of materials and also known to be the latest generation in the PV market industry. According to the chronological chart obtained from the National Renewable Energy Laboratory (NREL) as shown in Figure 1.5, the study on the first photovoltaic solar cell namely the amorphous silicon type solar cell had been started since 1976 (National Renewable Energy Laboratory, 2017). However, it is clearly seen that the multijunction photovoltaic cells have overtaken other PV cells with the best PCE throughout the time frame which currently could reach up to 44.6 %. On the other hand, dye sensitized solar cell had been introduced to the market in the year 1991 and steadily making its progression with the

highest PCE recorded at 12 % in the year 2012. As the matter of facts, this emerging PV type solar cell is a low cost photovoltaic device and is considerably having a young history as compared to the other PV solar cell (O'Regan & Grätzel, 1991). Hence, the scope of research for dye sensitized solar cell is still vast for researchers to optimize and improve the PCE of the PV cell in the near future.

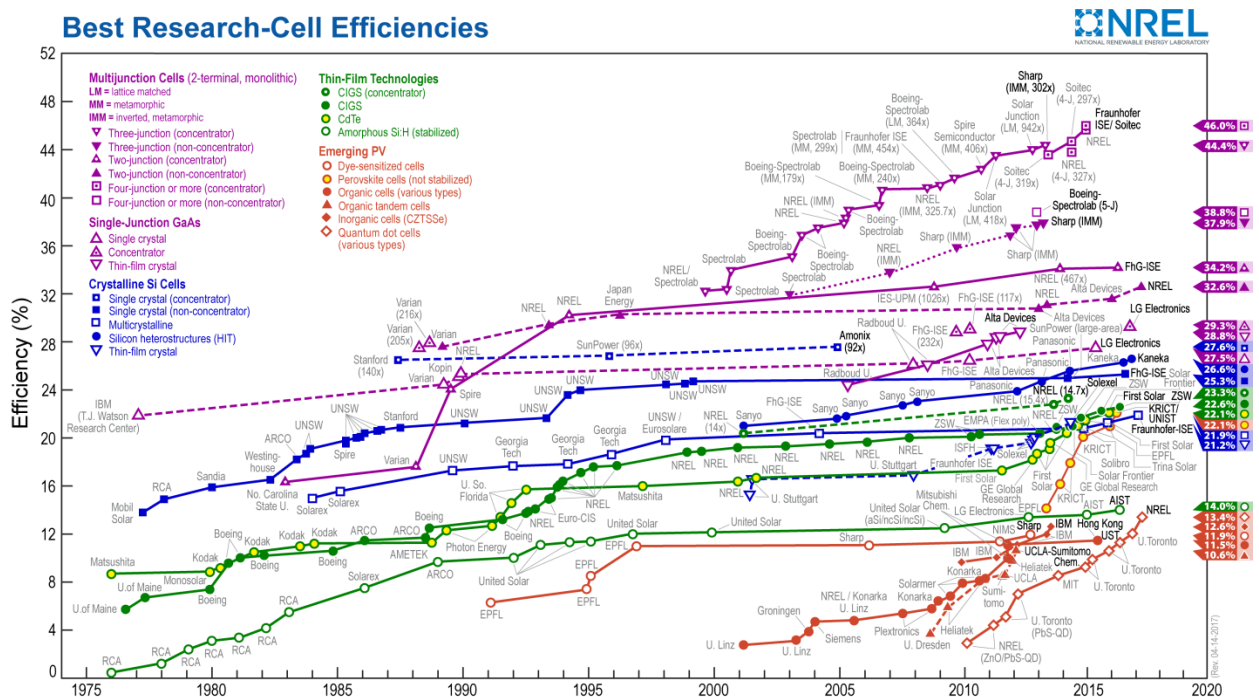
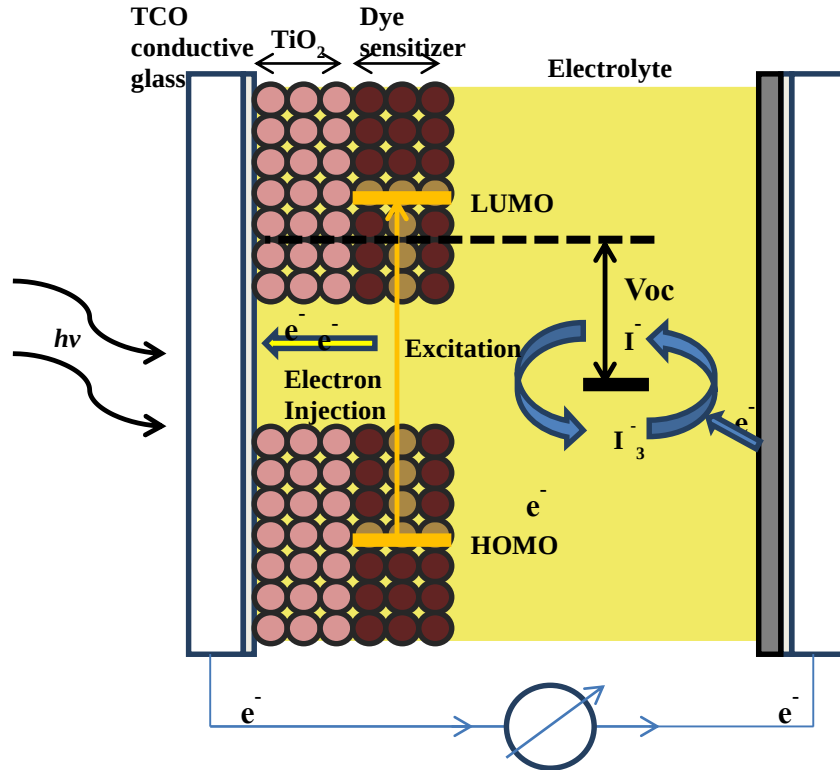


Figure 1.5: Best research cell efficiencies obtained from NREL (Retrieved from <https://www.nrel.gov/pv/>)

1.3 General principle of dye-sensitized solar cell (DSSC)

The earliest development of dye-sensitized solar cell (DSSC) was performed by O'Regan and Grätzel in year 1991 with the overall power conversion efficiency of 7.1 % to 7.9 % under solar light simulation (O'Regan & Grätzel, 1991). In contrast with other conventional photovoltaic solar cell, the role of light absorption and charge carrier transport in DSSC are separated by the semiconductor layer and the dye sensitizer layer, respectively (Grätzel,

2003). Scheme 1.1 shows the illustration of the DSSC followed by the explanation on its mechanism.



Scheme 1.1: General idea on the mechanism of the DSSC

During the illumination of light towards the transparent conductive oxide TCO (ITO/FTO) conductive glass, the photon is absorbed by the dye sensitizer and oxidized, causing the electron in the highest occupied molecular orbital (HOMO) of the dye sensitizer to excite and move towards the anti-bonding orbital or the lowest unoccupied molecular orbital (LUMO) (Hara & Arakawa, 2003). Next, the excited electron is injected into the conduction band of the semiconductor layer, namely the mesoporous TiO₂, which then received by the TCO conductive glass and transfer the electron to the counter electrode (cathode) through the external circuit (Grätzel, 2003; Hara & Arakawa, 2003; Nazeeruddin *et al.*, 2011; Carrem *et al.*, 2014).

From the counter electrode, the electron is received by the redox electrolyte such as potassium triiodide (I_3^-), thus reduces it into the iodide (I^-) (Grätzel, 2003). Due to its redox properties, I^- is further oxidized back into its initial form of I_3^- and releases an electron into the system, which then diffuses back to the oxidized dye sensitizer at the photoanode to refill the electron into the HOMO orbital (Hara & Arakawa, 2003). Hence, the process is repeated and this resulted a continuous electron flows in DSSC and produces current with condition that continuous light is present (Grätzel, 2003; Hara & Arakawa, 2003; Nazeeruddin *et al.*, 2011; Carrem *et al.*, 2014). In this thesis, the component of the DSSC that we were focusing on is the dye sensitizer.

1.4 General properties of dye sensitizers

The ability of the dye sensitizer to absorb light efficiently is mainly depending on its molecular absorption spectrum (Nazeeruddin *et al.*, 2011), which means the ability of dye sensitizer to absorb wavelength ranging from ultraviolet region to near red-infrared region is likely to be able to absorb more incident lights. As the advancement of scientific knowledge continue and the availability of starting materials, the tuning of the dye molecules to a desired absorption spectrum is possible to be carried out. One way of increasing the absorption spectrum of the dye molecule is by introducing π -conjugation into the molecular structure (Pavia *et al.*, 2001). Besides, the introduction of different substituents to the molecular structure also possible to enhance the molecular absorption spectrum (Chambon *et al.*, 2013). From all the natural compounds available, flavonoids are one of the candidates that worth to study on the potential as dye sensitizers due to their unique characteristic such as variety in color and also the presence of π -conjugation system in the molecular structure. The availability of starting materials to synthesize specific flavonoid also allow more study to be conducted, extensively.

1.5 General background on flavonoids

Flavonoids are a kind of natural products which can be found in most of the plants (Ferreyra *et al.*, 2012). They comprise a general backbone structure of $C_6-C_3-C_6$ and could be categorized based on the different attachment of B-phenyl ring bonded to the oxo-heterocyclic C-ring (Figure 1.6). They are namely flavonoids (2-phenylbenzopyrans) **1**, isoflavonoids (3-benzopyrans) **2**, and the neoflavonoids (4-benzopyrans) **3** (Marais *et al.*, 2006).

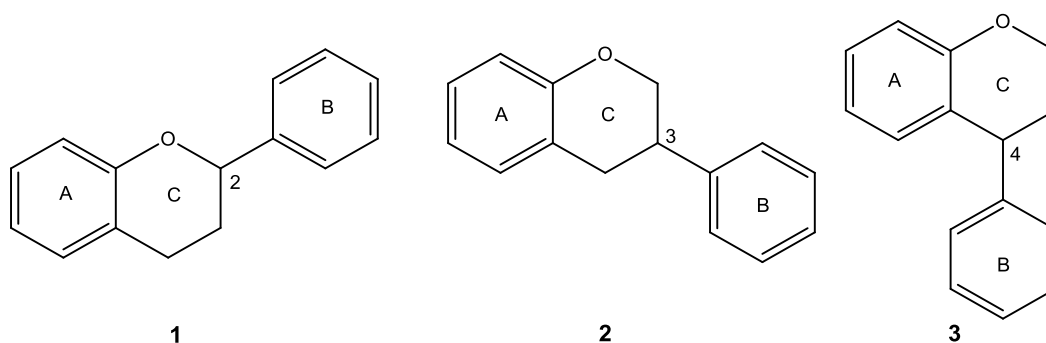


Figure 1.6: Typical structure of flavonoid (Marais *et al.*, 2006)

In addition, flavonoids could be further distributed into other subgroups depending on the degree of oxidation and substituent present in the heterocyclic C-ring as shown in the Figure 1.7. Some common examples are flavonol **4**, anthocyanidin **5**, isoflavone **6**, isoflavanol **7**, 4-arylcoumarin **8**, neoflavene **9** and more (Ferreyra *et al.*, 2012; Marais *et al.*, 2006).

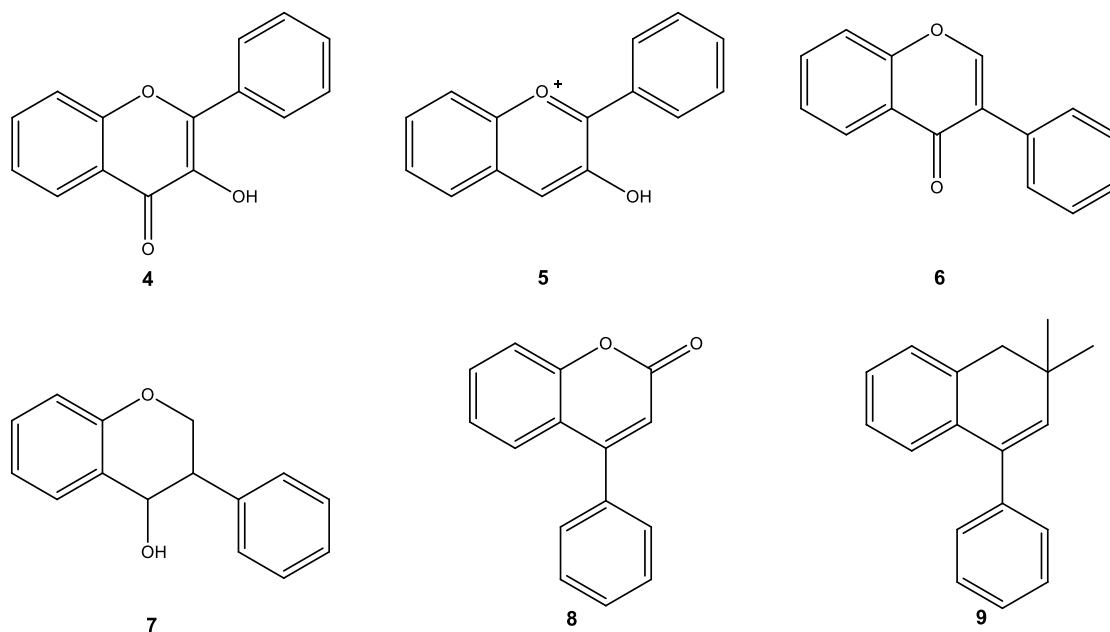


Figure 1.7: Structure of some selected flavonoids (Ferreyra *et al.*, 2012; Marais *et al.*, 2006)

Typically, flavonoids give the plants pigments in distinctive color, which helps in attracting the pollinators to pollinate the pollen grains from plants to plants (Bradshaw & Schemske, 2003). Besides that, flavonoids are well known with their biological function in plants such as UV photoprotection, protection against photo-oxidation, regulate the internal plant cell physiology and stress protection against the surrounding environment (Feild *et al.*, 2001; Winkel-Shirley, 2001; Mandal *et al.*, 2010; Ferreyra *et al.*, 2012). On top of that, the use of flavonoid as natural dye which obtained from plants such as rosella, blue pea and other plant extracts to the application in DSSC has been reported (Hao *et al.*, 2006; Wongcharee *et al.*, 2007). On the other hand, one of the flavonoid derivatives that have gained the attention of most researchers is the 1,3-diphenyl-2-propen-1-one or commonly known as chalcone, which was named by Kostanecki and Tampar in year 1899 for their novel discovery (Parmar *et al.*, 1980).

1.6 Introduction to chalcone family

Chalcone could be found in most of the edible or medicinal plants and is categorized as a minor flavonoid group due to its small quantity presence. This compound is crucial as it acts as an intermediate of many heterocyclic compounds such as open chain flavonoids and isoflavonoids (Rahman, 2011).

Despite having the same molecular backbone structure as the typical flavonoid, chalcone has an open chain α,β - conjugated keto-enol group instead of the heterocyclic C- ring, with 2 phenyl ring attached at both side (Ravichandran *et al.*, 2013). The presence of this unsaturated α,β - conjugated group enable the molecule to exists either in *cis* (*Z*) or *trans* (*E*) conformation. Nevertheless, chalcone with *trans*-conformation is thermodynamically favoured due to the much stable conjugated π electron system within the compound (Muller, 2012). Figure 1.8 shows the general molecular structure of chalcone with *cis* **10** and *trans* **11** conformation, respectively. Furthermore, the α,β - conjugated double bonds of chalcone also plays a role in the delocalization of π electron, allowing the electron to transfer within the structure. According to Shin *et al.* (2001), the double bond between α,β carbon shows a partial double bond character while the double bond in carbonyl shows a single bond character, which are affected by the electron delocalization along the conjugated moiety that jump from one energy level to the other at the π orbital.

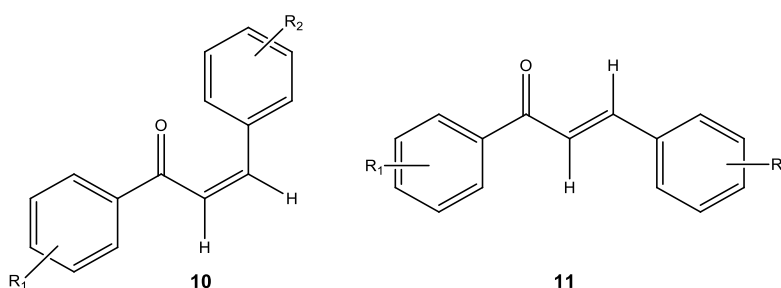


Figure 1.8: General molecular structure of chalcone (Muller, 2012)

On the other hand, chalcone with hydroxyl group attached at *ortho* position of the phenyl rings has the potential to react with the metal salts to form complexes. This could have happened due to formation of coordination bond of metal ion with the carbonyl group and hydroxyl group of the chalcone. For instance, Palaniandavar and Natarajan (1980) reported the synthesis of cobalt(II), nickel(II) and copper(II) complexes with 2'-hydroxychalcone derivatives in (O, O) coordination mode (Figure 1.9).

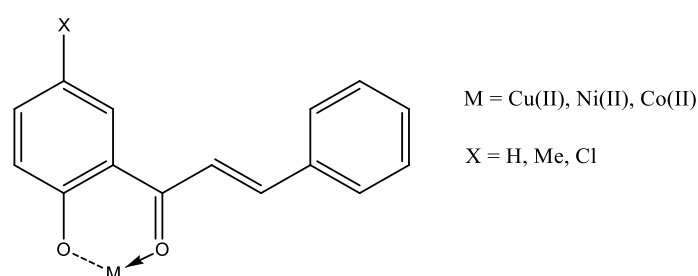


Figure 1.9: Complex coordination of 2'-hydroxychalcone with metals ion (Palaniandavar & Natarajan, 1980)

In the prospect view of inorganic chemistry, incorporation of organic compounds to a metal centre is to tune the electronic properties and improve the biological activities of the complex (Reyes *et al.*, 2006; Muthukumar *et al.*, 2007; Gaur & Mishra, 2013). Looking into the field of DSSC, the complex dyes for example ruthenium-based dye has been used in the DSSC for few decades due to its high chemical stability and able to sensitize the TiO₂ up to 700 nm (Desilvestro *et al.*, 2014). Therefore, we incorporated the bis-2'-hydroxychalcone series to the metal (II) salts with (O,O) coordination mode to create the complex dye sensitizers for DSSC application.

1.7 Problem Statement and objectives of study

Currently, most of the research conducted on the chalcone derivatives were mono-based, where only one α,β -conjugated keto group ($-\text{CH}=\text{CH}-\text{CO}-$) present in the molecular structure. Despite the studies on the bis-chalcone with two α,β -conjugated keto groups in the structure have also been found, yet limited studies regarding the bis-chalcone derivatives were reported. Moreover, the lack of studies in the complexation of bis-chalcone derivatives with transition metals was seen. By far, none of the scientific paper discusses on the use of bis-chalcone derivatives and their complexes as a dye sensitizer in dye sensitized solar cells (DSSC) application. In fact, chalcone has the continuous π -conjugation system in the molecular structure that could facilitate the electron transfers, which shows similar characteristic to that of the common dye sensitizer used in DSSC. Hence, the curiosity began by asking; What is the power conversion efficiency that could be obtained from bis-chalcone compounds as the dye sensitizer? What is the outcome after introducing the different substituents and metals towards the power conversion efficiency of DSSC? How does the molecular structure of the bis-chalcone affects the electron transfers in DSSC? Due to lack of information given from the previous studies to answer above matters, thus this research was conducted.

Therefore, the objectives of this thesis are:

- i. to synthesize the bis-chalcone compounds with different substituents and complexes for the use as a synthetic dye sensitizer
- ii. to determine the power conversion efficiency of each of the synthesized bis-chalcone compounds and complexes in DSSC
- iii. to find out and discuss on the molecular structure of the synthesized compounds and complexes that give the best power conversion efficiency

1.8 Scope of the thesis

Generally, the thesis is divided into five chapters in order to present the works of this project. The first two chapters are the General Introduction and Literature Review. Meanwhile, the third chapter is about the Methodology of the bis-2'-hydroxychalcone compounds, their complexes followed by the procedure in fabricating the DSSC. Chapter 4 focuses into the Results and Discussion that have been conducted for the entire project. Lastly, Chapter 5 is the Conclusion and suggestion for future work for this thesis.

CHAPTER 2

LITERATURE REVIEW

2.1 Composition of DSSC and its roles in solar conversion efficiency

Based on the general understanding in the principle of DSSC described earlier in the Chapter 1 (Section 1.3), it is clearly seen that each of the composition in the DSSC has its unique role in assuring the whole system to function effectively. Besides that, the choice of materials used in DSSC also greatly influence the solar conversion efficiency. Hence, it is important to have the fundamental knowledge regarding the materials and the current progress on the innovation made in order to obtain the maximum conversion efficiency, which are explained further in the next sub-sections. The major components in DSSC are the transparent conductive oxide (TCO) coated film, semiconductor titanium dioxide (TiO_2), dye sensitizer, redox electrolyte and counter electrode.

2.1.1 Transparent conductive oxide (TCO) coated film

The transparent conductive oxide (TCO) such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) are very common substrate used in the optoelectronic devices application, for instance in the DSSC (Bach *et al.*, 1998). Normally, these transparent conductive films are coated *via* the spray pyrolysis deposition technique (Kawashima *et al.*, 2003). In order to obtain high solar conversion efficiency, it is required that the conductive film is remained in high transparency with low sheet resistance (Hara & Arakawa, 2003). However, the sheet resistance for ITO increases during the calcination process of mesoporous TiO_2 at 450 °C, resulted in the reduction in photoelectric conversion efficiency (Kawashima *et al.*, 2003). Hence, FTO is commonly selected as the conductive films for the fabrication of DSSC due to its characteristics to withstand higher temperature.

On top of that, Kawashima and coworkers (2003) had performed the deposition of FTO/ITO double-layered transparent conductive oxide on a glass substrate. With others parameters kept in constant, they found out that the efficiency of ITO DSSC and FTO/ITO DSSC generated was 2.1 % and 3.7 %, respectively. This is due to the decrease in the TCO substrate resistance and also the increase in heat resistance, thus resulted higher conversion efficiency (Kawashima *et al.*, 2003).

2.1.2 The semiconductor titanium dioxide (TiO₂)

Under conventional photovoltaic solar cell, the semiconductor materials used such as single positive and negative type silicon (*p*- and *n* -Si), Gallium Arsenide (*p*- and *n* -GaAs,) Indium Phosphide (*p*- and *n*-InP), and Cadmium Sulfide (*n*-CdS) have taken in two functions simultaneously, that are as the light absorbance and the charge carrier transport (Grätzel, 2003). Nevertheless, these materials are unsuitable to be used in the DSSC fabrication due to the photo-corrosion of the electrode by the electrolyte solution under the prolonged irradiation of sunlight (Hara & Arakawa, 2003). Therefore, the oxide semiconductor materials such as Titanium dioxide (TiO₂), Zinc oxide (ZnO) or Tin dioxide (SnO₂) are chosen for its good stability property under redox electrolyte and light irradiation. Yet, due to the relatively wide band gap presence in the oxide semiconductors for charge carrier transport purposes, they are unable to absorb the visible light. Hence, photosensitizer is necessary to take in the role of absorbing the visible light. For an effective cell performance, it is important to take note that creating a large surface area of TiO₂ photo-electrodes could enhance the absorption of dye sensitizer and increase the light-harvesting efficiency, thereby increase the overall cell performance (Hara & Arakawa, 2003).

In addition, the light scattering property of TiO₂ had also been studied extensively as research showed that it resulted in better dye absorption which improved the incident photon current

efficiency (IPCE) of the DSSC (Ferber & Luther, 1998; Zhu *et al.*, 2007; Chen *et al.*, 2009). Based on the light scattering simulations conducted by Ferber and Luther (1998), they predicted that with the mixture of small particles TiO_2 of 20 nm diameter and the large particles TiO_2 ranging from 250 – 300 nm diameter, the power conversion efficiency (PCE) would increase. This is because the small particles of the TiO_2 increase the surface area whereas the large particles of TiO_2 promote the light scattering effect, thus improved the dye absorption towards the TiO_2 surface (Ferber & Luther, 1998).

Moreover, Chen and coworkers (2009) had reported the synthesis the TiO_2 beads with a diameter of (830 ± 40) nm using the sol-gel and solvothermal processes for the fabrication of the DSSC working electrode. Over the surface of these TiO_2 beads, nanocrystals $((14.5 \pm 0.5))$ and pores (~ 13.8 nm) were observed, thus creating the crystalline mesoporous TiO_2 . Based on their findings, the overall conversion efficiency of the DSSC with the mesoporous TiO_2 beads recorded 7.20 %, while only 5.66 % conversion efficiency was observed for the DSSC that incorporated with the standard Degussa P25 TiO_2 . This interesting result is due to the ability of the mesoporous TiO_2 beads to promote the light scattering efficiently and enhance the dye absorption, thereby increase the current density which resulted a high photon-to-current conversion efficiency (Chen *et al.*, 2009).

2.1.3 Dye sensitizer

Undeniably, dye sensitizer plays a vital role in determining the overall conversion efficiency of the DSSC. As known, the excitation of the dye sensitizer (D) is initiated with the absorption of photon (Eq. 2.1). The excited dye sensitizer D^* at the LUMO will then oxidized to release an electron and injected into the conduction band of TiO_2 semiconductor (Eq. 2.2). At the same time, the recombination of the injected electron with the oxidized dye sensitizer may occur (Eq. 2.3), resulting in the backward current and eventually affects the overall

efficiency (Nazeeruddin *et al.*, 2011). According to Xuhui *et al.* (2014), one of the reasons for the recombination to happen is due to the large surface area of the mesoporous TiO₂, despite it facilitates in the dye sensitizer absorption.



In order to synthesize the best dye sensitizer for high solar conversion efficiency in the DSSC, there are few criteria that should take into consideration. Firstly, the sensitizer should be able to absorb most of the visible light and near infrared region. In addition, the molecular structure of the sensitizer should have the substituents that could anchor firmly to the TiO₂ surface, for example the carboxylate or the phosphonate group. Besides, the energy level of the LUMO in the excited sensitizer should be complementary with the conduction band of the semiconductor oxide at the lower bound in order to reduce the energy loss during the electron transfer. Moreover, the molecules should be possessing high redox potential for the effective electron regeneration to return to the original state after excitation (Grätzel, 2003).

By far, the most well-known sensitizer used commercially is the *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium(II) complex or commonly known as the N3 dye (Figure 2.1). This is due to its ability to absorb the visible light ranging from 400 to 800 nm which corresponded to the metal-to ligand charge transfer (MLCT) transition (Hara & Arakawa, 2003, Vallejo *et al.*, 2011). Besides that, the carboxylate groups presence in the N3 dye sensitizer allows it to anchor firmly on the semiconductor TiO₂ via the formation of bidentate coordination and ester linkages, while the (-NCS) groups play a role in absorbing the visible light. Moreover, several ruthenium complexes with appropriate substituents show the power

conversion efficiency of 7 to 11 % (Grätzel, 2003; Zeng, *et al.*, 2009; Balasingam *et al.*, 2012; Chang *et al.*, 2013).

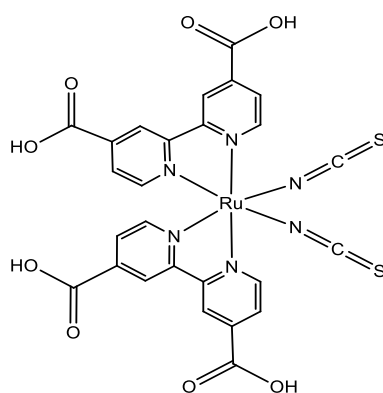


Figure 2.1: General structure of *cis*-bis(4,4'-dicarboxy-2,2'-bipyridine)dithiocyanato ruthenium (II) complex (N3 dye) (Grätzel, 2003)

Besides that, Bessho *et al.* (2010) had synthesized the inorganic donor- π -bridge-acceptor zinc porphyrin dye as sensitizer which demonstrated the power conversion efficiency of up to 11% with iodide/triiodide as the redox electrolyte. From the molecular structure as shown in Figure 2.2, the electron acceptor characteristic of ethynylbenzoic acid moiety enable it to stick on the semiconductor surface, while the diarylamine group attached to the porphyrin ring serves as the electron donor, producing the push-pull effect within the system (Bessho *et al.*, 2010).

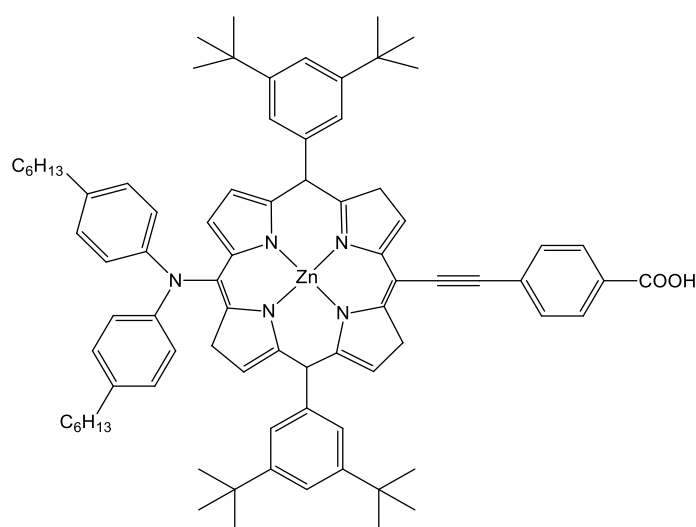


Figure 2.2: Molecular structure of donor- π -bridge acceptor zinc porphyrin (Bessho *et al.*, 2010)

In addition, Chambon *et al.* (2013) had reported the boron complex of 2'-hydroxychalcone with triphenylamine terminal (Figure 2.3). The introduction of triphenylamine terminal as the electron donor unit at one end while the difluorodioxaborine rings as the electron acceptor at another end had created the push-pull effect within the molecule, which broaden the UV absorption band to far-red region. With this feature observed, the complex was used as the dye sensitizer and blended with the [6,6]phenyl-C61-butyric acid methyl ester (PC₆₁BM), thereby displayed the power conversion efficiency of 1.13 % (Chambon *et al.*, 2013).

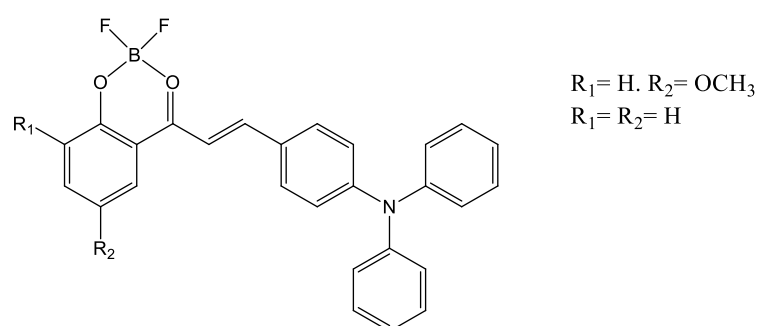


Figure 2.3: Molecular structure of boron chalconate complex (Chambon *et al.*, 2013)

Apart from the inorganic dye sensitizer, the studies on the organic dye sensitizer have also been performed, extensively. In terms of economical and environmental point of view, the cost of production for organic sensitizer is relatively cheaper, less complicated procedures require and typically harmless towards the environment as compared to the inorganic sensitizer (Ito, 2011). Generally, organic compounds do not possess any of the MLCT due to absence of the metal ions, but they do have the intermolecular charge transfer (ICT) to assist in the electron transfer.

In order to tune such properties, the presence of donor-acceptor substituents and π -conjugated system are essential in the molecular structure in order to generate the push-pull effect (Hagberg *et al.*, 2007; Zhang *et al.*, 2009). Besides, increasing the π -conjugated moieties could reduce the energy gap between the HOMO and LUMO of the organic dye sensitizer,

thus increase the lifetimes of the excited state and enhance the electron injection process (Hagberg *et al.*, 2007).

Nonetheless, the drawback of organic dye sensitizer is the aggregation of the organic compound on the TiO₂ semiconductor surface, therefore decreasing the rate of electron injection into the TiO₂ which resulted from the self-quenching of the organic dye (Liu *et al.*, 1997). Despite the disadvantage, Choi *et al.* (2008) had resolved the issue by introducing the nonplanar bis-methylamino moiety for overcoming the degradation caused by light irradiation; terthiophene unit to enhance the interface between dye and electrolyte; and cyanoacrylic acid moiety which acts as the electron acceptor and anchoring group into an organic framework (Figure 2.4). As a result, the compound demonstrated a visible light absorption ranging from 400-610 nm, yielding an overall conversion efficiency of 8.60 %.

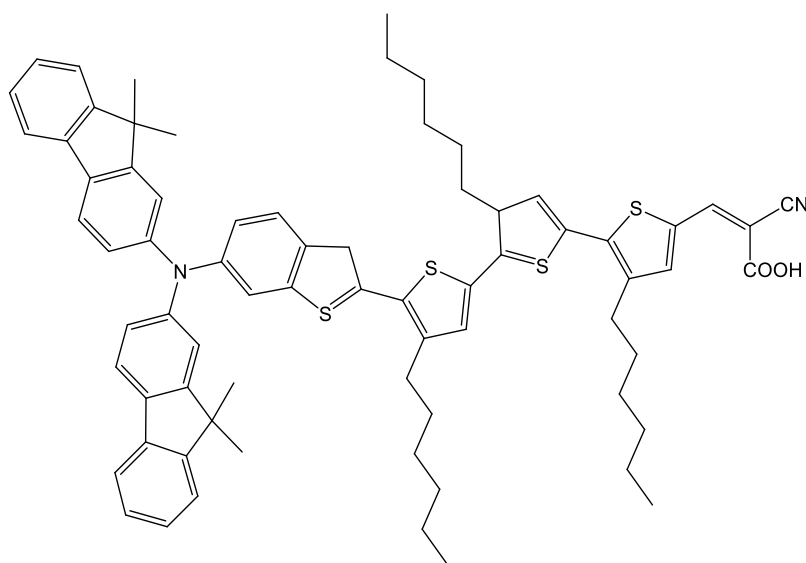
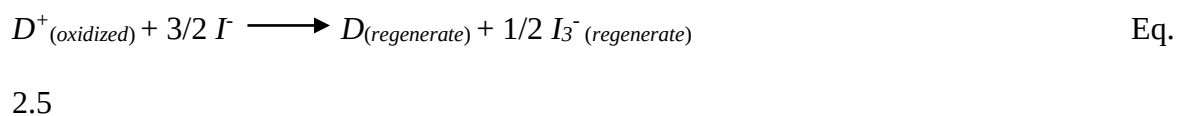


Figure 2.4: Molecular structure of terthiophene organic dye sensitizer (Choi *et al.*, 2008)

2.1.4 Redox Electrolyte

By now, the increasing numbers of different redox electrolytes for DSSC have been well documented (Choi *et al.*, 2008; Wu *et al.*, 2008; Bessho *et al.*, 2010; Careem *et al.*, 2014;

Buraidah, *et al.*, 2017). Typically, the most common type that used in the DSSC is the iodide/triiodide due to its good redox potential at the affordable price. As informed, the triiodide is reduced to iodide when the injected electron is released into the redox mediator from the counter electrode (Eq. 2.4). Eventually, the iodide is then diffused into the oxidized dye sensitizer, thus replenish the dye and the triiodide (Eq. 2.5). Yet, the charge of interception or commonly known as the dark current may occur (Eq. 2.6), where the injected electron is directed towards the redox couple without channeling through the external circuit, thus reduce the current flow (Nazeeruddin *et al.*, 2011).



Even though the iodide/triiodide redox mediator has been widely used, there are disadvantages to this redox couple such as the corrosion to the electrode and high volatility under the light irradiation which makes them unsuitable for the long term applications. Hence, more innovations have been made to counter this problem. For example, the introduction of the mixture redox mediator composed of 1,2-dimethyl-3-hexylimidazolium iodide (DMHImI), lithium iodide (LiI), iodine and tert-butylpyridine (TBP) in acetonitrile has been reported to enhance the open circuit voltage (Barbé *et al.*, 1997, Choi *et al.*, 2008). According to the Papageorgiou *et al.* (1996), the presence of DMHImI is able to reduce the resistance of the electrolyte solution, thus improve the DSSC performance. On top of that, the addition of TBP can suppress the charge of interception of the injected electrons to the I_3^- , hence more

electron flows through the external circuit and resulted a higher open circuit voltage (Huang *et al.*, 1996).

Besides that, Careem *et al.* (2014) had synthesized the polyvinyl alcohol gel polymer electrolyte which consists of the double salts, namely the potassium iodide (KI) and tetrapropylammonium iodide (TPAI). The comparisons of the conversion efficiency were made between the single salt KI and the double salts in N3 dye by the Careem and coworkers (2014), with 2.64 % and 3.12 % conversion recorded. This is due to the mixed cations effect that allows better electron injection into the TiO₂ conduction band, leading to higher efficiency.

2.1.5 Counter electrode

Last but not least, the counter electrode is the last composition that built up a DSSC. Usually, platinum (Pt) is coated onto the TCO substrate to create the light reflection effect that could improve the photocurrent properties. Moreover, Papageorgiou *et al.* (1996) had introduced the formation of Pt colloids on the TCO substrate in order to increase the electrocatalytic activity and facilitate the reduction of the triiodide ions to iodide. Besides, the fill factor of the solar cell is also depending mainly on the Pt counter electrode, thus the overall conversion efficiency is well dependence on the efficiency of the counter electrode to release the electron back to electrolyte medium (Hara & Arakawa, 2003).

2.1.6 DSSC assembling and its performance evaluation

Commonly, the PV performance of the DSSC can be measured under unsealed condition, where two binder clips were used to fasten the TiO₂ electrode containing dye sensitizer and few drops of electrolyte with the counter electrode. However, this method is not favourable for long term stability due to the loss of electrolyte to the surrounding, resulting in a decrease

of efficiency over time. Therefore, the low melting point Surlyn dupont polymer film is used in between the two electrodes to seal the cell firmly and increase the shelf life of the DSSC (Hara & Arakawa, 2003).

For supplementary information, several parameters are come across during the performance evaluation of DSSC, namely the open circuit voltage (V_{oc}), solar circuit current density (J_{sc}), short circuit current (I_{sc}), fill-factor (FF), incident photon to current efficiency (IPCE), power of incident light (P_{in}) and power conversion efficiency (PCE). In this context, V_{oc} corresponds to the energy difference between the redox mediator and the TiO_2 semiconductor under the light illumination. Therefore, factors such as semiconductor surface morphology, the rate of redox couple recovery and the recombination process of dye sensitizer would significantly influence the V_{oc} value (Grätzel, 2003). On the other hand, the I_{sc} value is directly proportional to the area of the solar cell and the solar circuit current density as shown in Eq. 2.7. The value increases with the increase in light intensity.

$$I_{sc} = J_{sc} \times \text{cell area (cm}^2\text{)} \quad \text{Eq. 2.7}$$

Another important unit to pay attention is the FF value which measures the ideality of the solar cell device. Generally, the value can be generated manually based on the ratio of the known maximum photocurrent (I_{max}) and max photovoltage (V_{max}) to the I_{sc} and V_{oc} (Eq. 2.8).

$$\begin{aligned} \text{FF} &= (I_{max} \times V_{max}) / (I_{sc} \times V_{oc}) \\ &= P_{max} / (I_{sc} \times V_{oc}) \end{aligned} \quad \text{Eq. 2.8}$$

Meanwhile, IPCE is the efficiency measurement in percent value that determines the effectiveness of the electron generated and detected in the external circuit under incident

photons at a given wavelength (λ) (Eq. 2.9). Thus, the ability of the dye sensitizer to harvest light, the rate of electron injection to the TiO₂ semiconductor and the electron distribution at counter electrode are the several factors that could significantly affects the IPCE (Grätzel, 2003).

$$\text{IPCE} = (1240 \times J_{sc}) / (\lambda \times P_{in}) \quad \text{Eq. 2.9}$$

Lastly, PCE is the data that signify the overall conversion efficiency of the fabricated device, which corresponds to the ratio of J_{sc} , V_{oc} and FF to the power of incident light (P_{in}) (Eq. 2.10). Herein, Figure 2.5 shows the general J/V measurement curve of DSSC. Some informations such as J_{sc} , J_{max} , P_{max} , V_{max} and V_{oc} can be obtained directly from the J/V measurement curve (Grätzel, 2003).

$$\text{PCE}, \eta = (J_{sc} \times V_{oc} \times \text{FF}) / P_{in} \quad \text{Eq. 2.10}$$

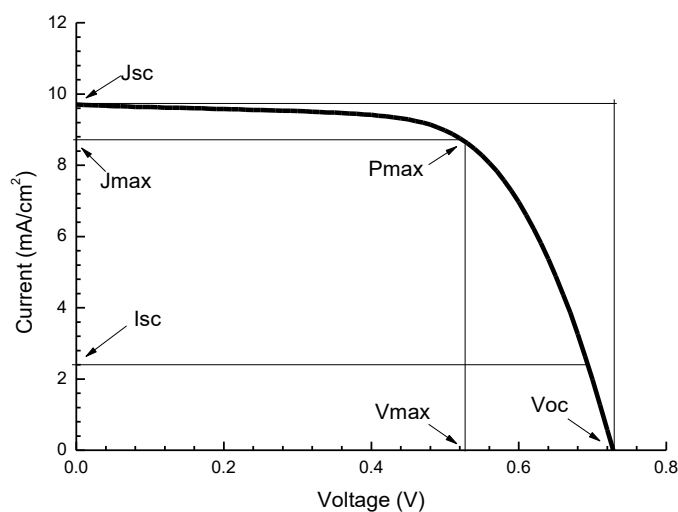


Figure 2.5: J/V measurement of typical DSSC

To sum up, each of the components in DSSC plays an important role for determining the solar power conversion efficiency. In this project, bis-chalcone compounds and complexes had been selected to run as a dye sensitizer in DSSC due to the presence of α , β -conjugated

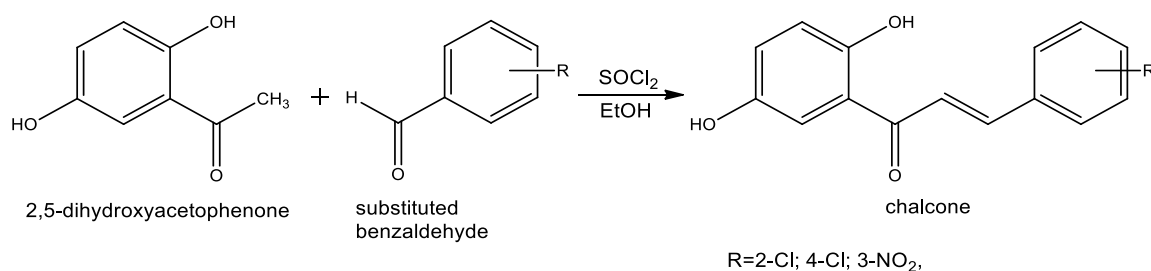
system, which can facilitate the electron transfer within the molecular structure. As known, chalcone can be synthesized in various methods and was discussed further in the next section.

2.2 Synthesis pathway of chalcone and its derivatives

Chalcone can be synthesized in the laboratory with various experimental methods due to the availability of the starting materials and advancement in scientific instrumentation. Among them, Claisen-Schmidt condensation reaction is the most known procedure used to synthesize chalcone and its derivatives (Nielson *et al.*, 2004; Go *et al.*, 2005; Sashidhara *et al.*, 2009). Moreover, other alternative methods which yield the same products also have been reported such as Suzuki reaction (Haddach & McCarthy, 1999; Eddarir *et al.*, 2003; Ren & Meng, 2008), microwave assisted technique (Srivastava, 2008; Abdel-Aziz *et al.*, 2011; Ahmad & Bano, 2011), solvent free techniques such as sonochemical and thermally activated reactions (Perozo-Rondón *et al.*, 2006; Saravanamurugan *et al.*, 2005) and grinding technique (Krishna & Rani, 2003; Zangade *et al.*, 2011).

2.2.1 Claisen-Schmidt condensation reaction

Claisen-Schmidt condensation reaction is the most typical and straight forward method used to synthesize the chalcone compound and also its derivatives. The basic mechanism of chalcone synthesis is by reacting the appropriate substituted benzaldehyde with the substituted acetophenone in either acid or basic catalytic condition (Nielsen *et al.*, 2004). For instance, Jayapal *et al.*, (2010) synthesized the 2,5-dihydroxy substituted chalcones from 2,5-dihydroxyacetophenone with different substituted benzaldehyde in the presence of thionyl chloride (SOCl₂) and absolute ethanol with excellent yields of more than 80% for every synthesized derivative (Scheme 2.1).



Scheme 2.1: Synthesis of 2,5-dihydroxy substituted chalcone with SOCl₂ (Jayapal *et al.*, 2010)

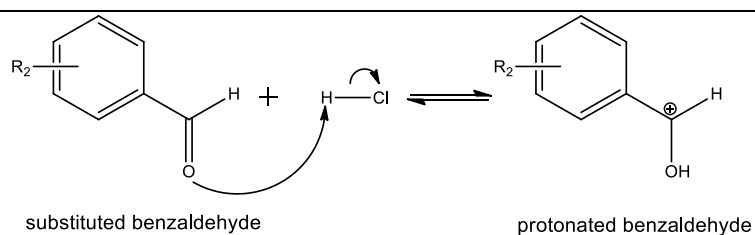
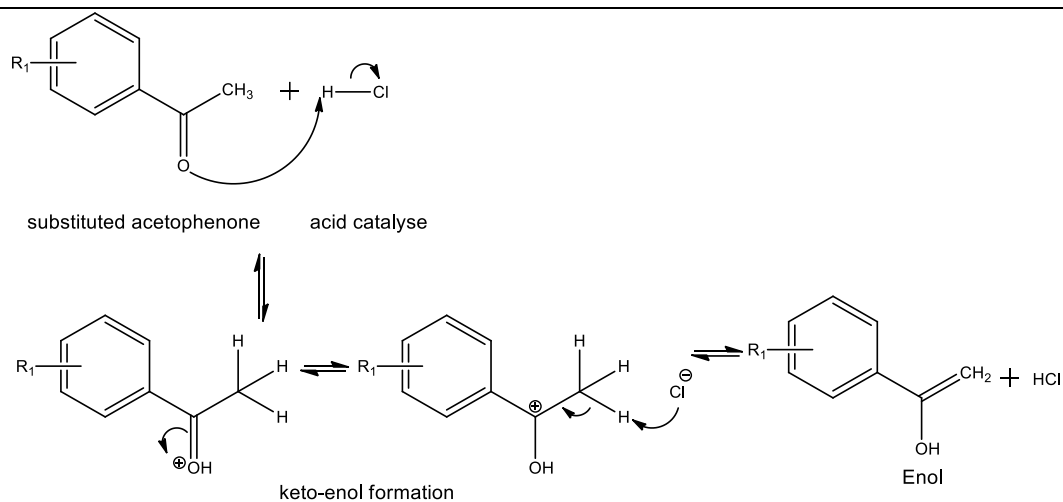
2.2.1 (a) Acid catalytic reaction pathway

The mechanism of the acid catalytic reaction is described according to Patil *et al.*, (2009). This process requires the use of acidic reagents such as hydrochloric acid (HCl), SOCl₂ or aluminium chloride (AlCl₃) in order to promote the formation of electrophile at the beginning stage (Scheme 2.2). During the exposure of the reactants in aqueous acidic condition, the electron deficient hydrogen ion is attacked by the nucleophile carbonyl group present either in the substituted acetophenone or substituted benzaldehyde, thus forming the intermediate carbocation. Simultaneously, the acidic α hydrogen in acetophenone would further attacked by the anion such as chlorine ion, causing the electron transfer and form another intermediate known as enol. Generally, the formation of carbocation to enol compound is called the keto-enol formation, where it is a reversible process. On the other hand, since aldehyde does not have the acidic α hydrogen, the intermediate remains as carbocation (Scheme 2.2).

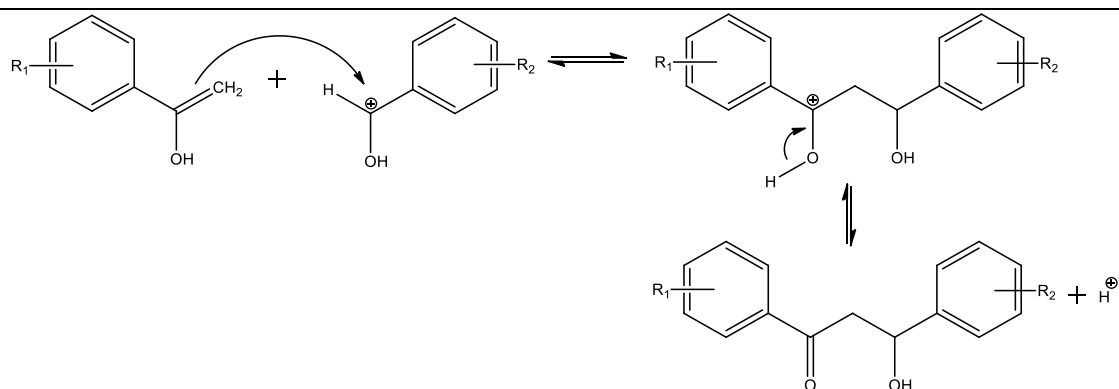
The next stage involves in the addition of enol to the protonated carbonyl compound. The enol acts as a nucleophile attacks the electron deficient carbonyl group, forming the aldol compound and a hydrogen ion. The hydrogen ion formed earlier would then temporary attach to the β hydroxyl group, forming another cat-ion. At the final stage, α hydrogen is been

removed by the anion, causing the electron transfers to the α,β bond and a water molecule is removed.

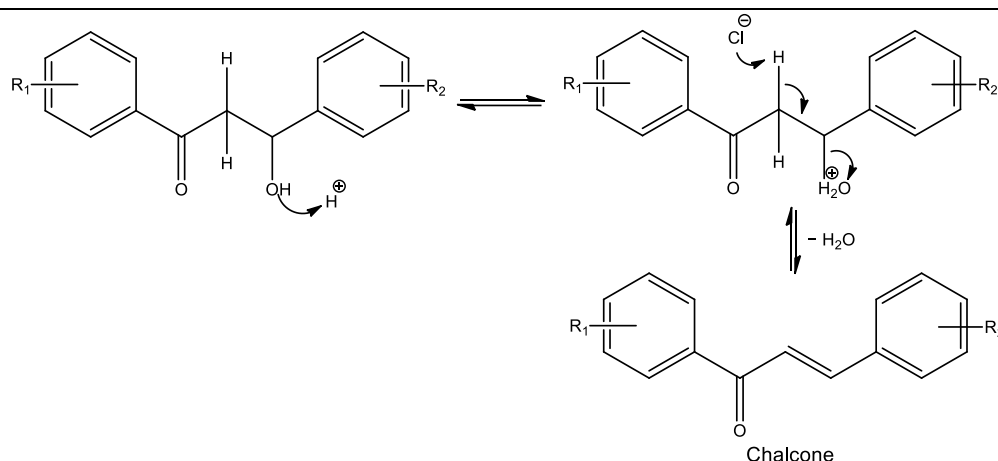
Stage 1: Formation of Enol



Stage 2: Addition of Enol



Stage 3: Electron transfer and dehydration process



Scheme 2.2: Synthesis pathway of chalcone based on acid catalytic reaction (Patil *et al.*, 2009)

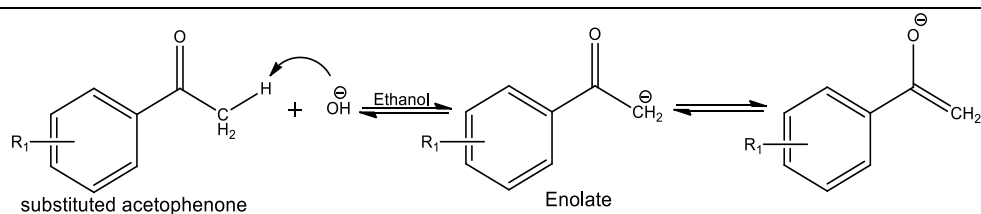
2.2.1 (b) Basic catalytic reaction pathway

In contrast with the acid catalytic reaction's mechanism, basic catalytic reaction pathway forms anion intermediate rather than cation intermediate (Scheme 2.3). Some common base reagents used are sodium hydroxide (NaOH), potassium hydroxide (KOH) and barium hydroxide $\text{Ba}(\text{OH})_2$ (Cheng *et al.*, 2000). At the beginning of the reaction, the acidic α hydrogen of the substituted acetophenone prompt to be attack by the hydroxide ion, causing the hydrogen to leave and form an anion compound known as enolate. In this case, the substituted benzaldehyde would not take part in the deprotonation since there is no α hydrogen present (Scheme 2.3).

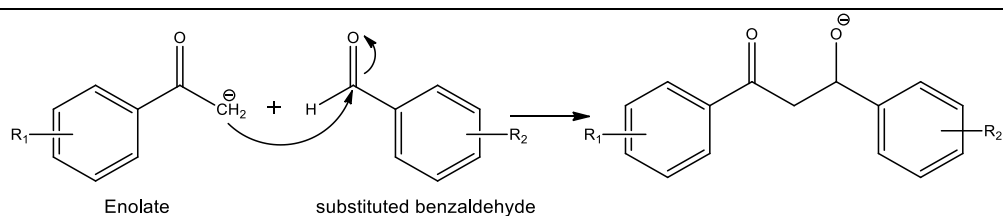
Next, nucleophilic addition takes place where the highly reactive enolate nucleophile attacks the carbon of the carbonyl group in the substituted benzaldehyde, producing the intermediate alkoxide. The alkoxide would then undergo protonation by taking a hydrogen ion from the water molecule and form β hydroxyl aldol compound. Lastly, the acidic α hydrogen is taken away by the hydroxide ion and electron transfer occur, causing the β hydroxyl to leave. Thus,

the α,β double bond is formed after the rearrangement of electron and a stable chalcone compound is produced (Scheme 2.3).

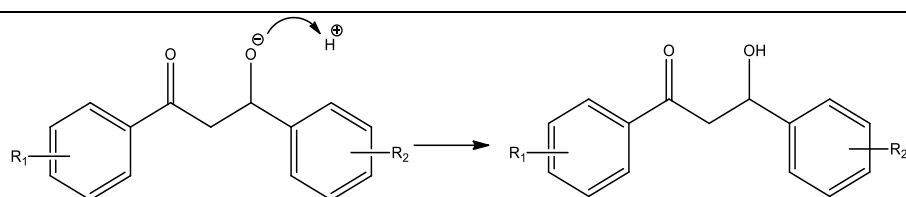
Step 1: Formation of Enolate



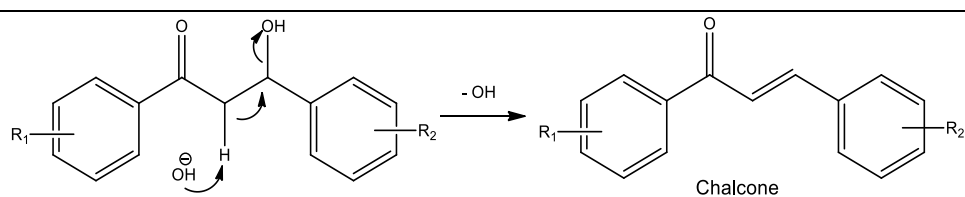
Step 2: Addition of Enolate



Step 3: Protonation



Step 4: Dehydration

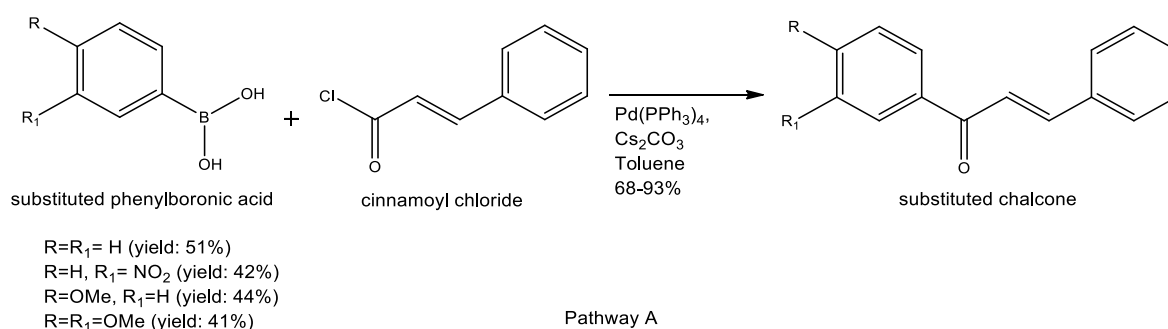


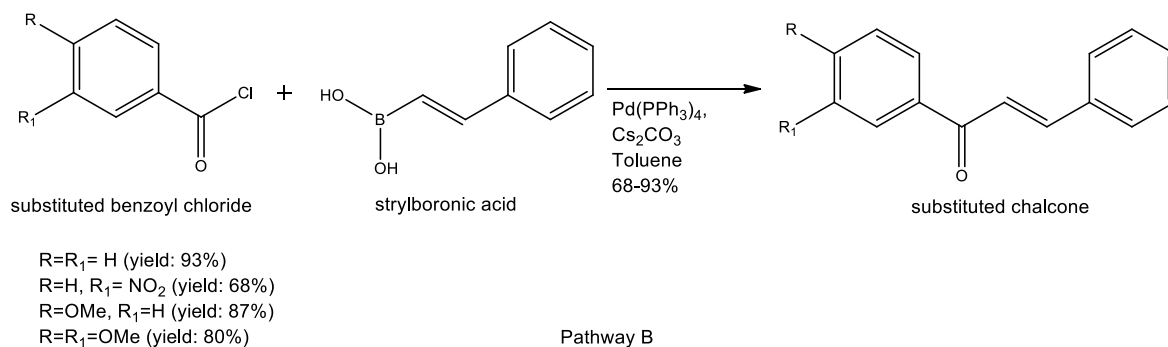
Scheme 2.3: Synthesis pathway of base catalytic Claisen-Schmidt condensation reaction (Cheng *et al.*, 2000)

2.2.2 Suzuki-Miyaura reaction

Suzuki-Miyaura reaction is a mechanism or a process that named over the founder, Akira Suzuki, who discovered the cross-coupling reaction between the aryl or vinyl substituted

boronic acid with the alkenyl or alkynyl halide in the presence of palladium complex catalyst (Miyaura *et al.*, 1979). Few decades later, Haddach and McCarthy (1999) reviewed and modified the method by substituting the starting materials into substituted phenylboronic acid and cinnamoyl chloride, respectively, with the presence of anhydrous toluene, tetrakis(triphenylphosphine)palladium(0) $[Pd(PPh_3)_4]$ and cesium carbonate (Cs_2CO_3), in order to synthesize the chalcone compound. They labelled this reaction as a pathway A. Afterwards, they further modified the reaction under the same reaction condition by coupling the substituted benzoyl chloride with the styrylboronic acid, which labelled as pathway B. Interestingly, pathway B showed much higher yield compared to the traditional Suzuki reaction as in pathway A with the percentage yield up to 93% and 51%, respectively (Scheme 2.4) (Haddach & McCarthy, 1999). According to Eddarir *et al.* (2003), the reason for the higher yield in pathway B is mainly due to the less side products produced at the end of the reaction. Nevertheless, the major concern of this synthetic pathway is the catalyst $[Pd(PPh_3)_4]$. Once the reaction started, the catalyst would be hardly separated from the mixture and the purification of the desired product would take much longer time to complete. Furthermore, if improper chemical waste management happens, the leaching of catalyst into the environment may cause hazardous effect as the phosphine ligands presence in the catalysts are naturally toxic (Ren & Meng, 2008).

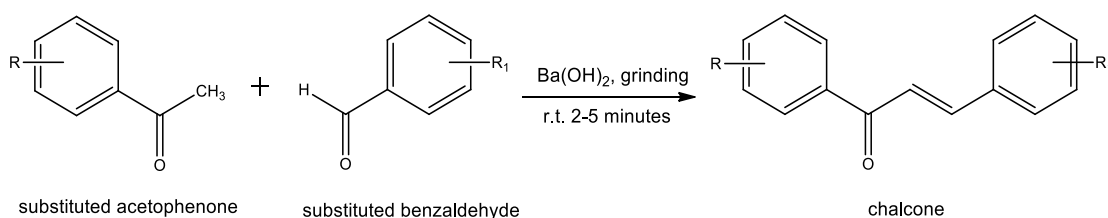




Scheme 2.4: Suzuki-Miyaura reaction of chalcone synthesis (Haddach & McCarthy, 1999)

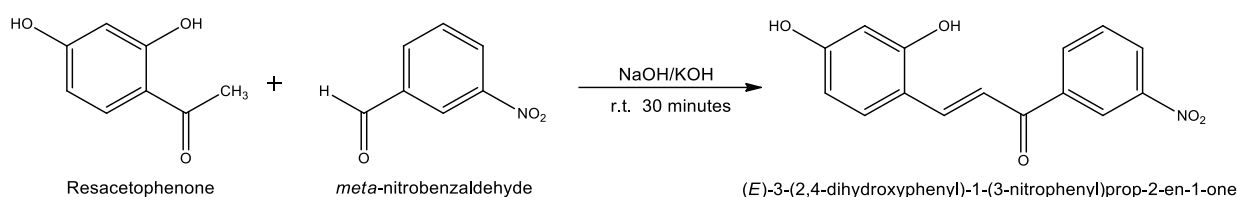
2.2.3 Grinding technique

Previously, chalcone synthesis used up immense amount of organic solvents either during the reaction or after workup process such as purification and isolation. These solvents used are normally volatile and could be harmful to human health under long exposure. Hence, scientists have discovered a greener approach of chalcone synthesis which known as the grinding technique. Generally, this method generates a local heat through grinding of the mixture by using mortar and pestle, which initiate the forward reaction (Shyam *et al.*, 2012). For example, Kumar *et al.*, (2008) had synthesized a series of chalcones by grinding the mixture of different substituted acetophenone, aryl aldehydes and anhydrous barium hydroxide for 2-5 minutes under solvent-free condition (Scheme 2.5). According to their finding, the used of anhydrous barium hydroxide as the catalyst had proven to increase the yield of the product in a shorter time to 83-92% (Kumar *et al.*, 2008).



Scheme 2.5: Synthesis of chalcone through grinding technique (Kumar *et al.*, 2008)

On the other hand, Shyam *et al.*, (2012) had also synthesized the chalcone derivatives by using similar grinding method but with different catalyst as compared to the earlier reported literature. As stated in their methodology, one equivalent molar amount of resacetophenone (or 2,5-dihydroxyacetophenone) and *ortho*, *para*, *meta* substituted benzaldehyde were grinded continuously with pestle at room temperature, followed by the addition of equivalent amount of NaOH or KOH and the mixture were grinded for another 30 minutes. The precipitate was then poured into the cold water and neutralized with hydrochloric acid (HCl) before recrystallized it *via* acetic acid. Based on the collected data, the *meta*-nitro substituted chalcone derivative showed the highest yield obtained with 76% recorded (Scheme 2.6) (Shyam *et al.*, 2012).

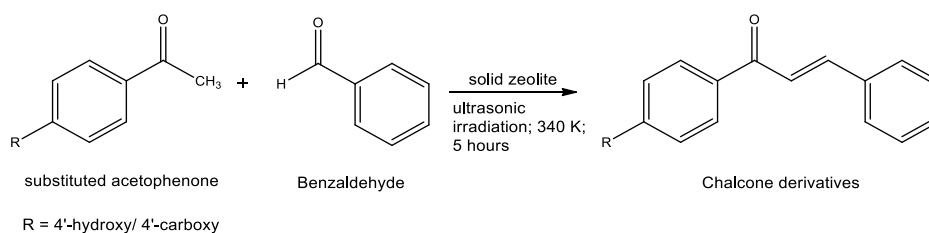


Scheme 2.6: Synthesis of *meta*-chalcone compound *via* grinding technique (Shyam *et al.*, 2012)

2.2.4 Sonocatalysis and thermally activated reactions

Apart from using the homogeneous acid or base catalyst *via* Claisen-Schmidt condensation reaction, another green alternative used to catalyse the reaction is by using the heterogeneous solid catalyst under no solvent condition. As reported by Perozo-Rondón *et al.*, (2006), the attempt on using zeolites as heterogeneous catalyst in the combination with ultrasonic irradiation had shown remarkable results in chalcone synthesis. Based on their experimental procedure, the equimolar amount of benzaldehyde with substituted acetophenones (4'-

hydroxy and 4'-carboxy) were mixed in a flask and was suspended into the ultrasonic water bath at 303, 323 and 343 K, respectively, under solvent free condition. Zeolite was then introduced into the mixture and the reactions were run for approximately 5 hours (Scheme 2.7). Another set of experiment which used the conventional heating method was conducted under same procedure and condition as the ultrasonic induced reaction in order to compare the conversion yield of both reactions. Through their findings, Perozo-Rondón and coworker deduced that the ultrasonic irradiation at 343 K was shown to have the highest conversion percentage yield up to 45% (4'-hydroxy) and 65% (4'-carboxy) compared to the conventional heating method which only yield around 20% and 35%, respectively (Perozo-Rondón *et al.*, 2006).



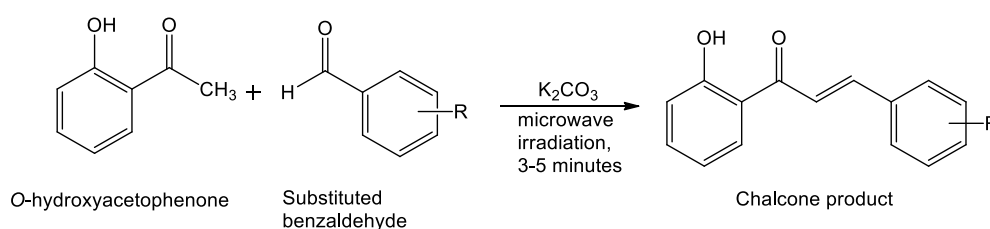
Scheme 2.7: Synthesis of 4'-hydroxy and 4'-carboxyl chalcone *via* ultrasonic irradiation

(Perozo-Rondón *et al.*, 2006)

2.2.5 Microwave-assisted technique

Moreover, another eco-friendly method used to synthesise the chalcone derivatives *via* modified Claisen-Schmidt condensation reaction is through microwave irradiation. Similar to the ultrasonic irradiation, the purpose of microwave-assisted technique was mainly to speed up the rate of reaction and reduced or free from the used of organic solvent during the reaction. For example, Srivastava (2008) had synthesized the chalcone derivatives by reacting *O*-hydroxy acetophenone with substituted benzaldehyde in the presence of anhydrous potassium carbonate (K_2CO_3) (Scheme 2.8). Thick paste was formed upon mixing and it was

then undergoing microwave irradiation for 3-5 minutes. The mixture content was dissolved in ethanol while the remaining solid precipitate was filtered off and the filtrate was left to yield the chalcone product in 80-90 % conversion yield. Based on the physical data that had been tabulated by Srivastava (2008), the microwave-assisted technique had drastically reduced the reaction time to about 200 times quicker and also shown to have better yield conversion as compared to the conventional synthesis method.



Scheme 2.8: Synthesis of chalcone *via* microwave-assisted technique (Srivastava, 2008)

2.3 Application of chalcone and its derivatives towards society

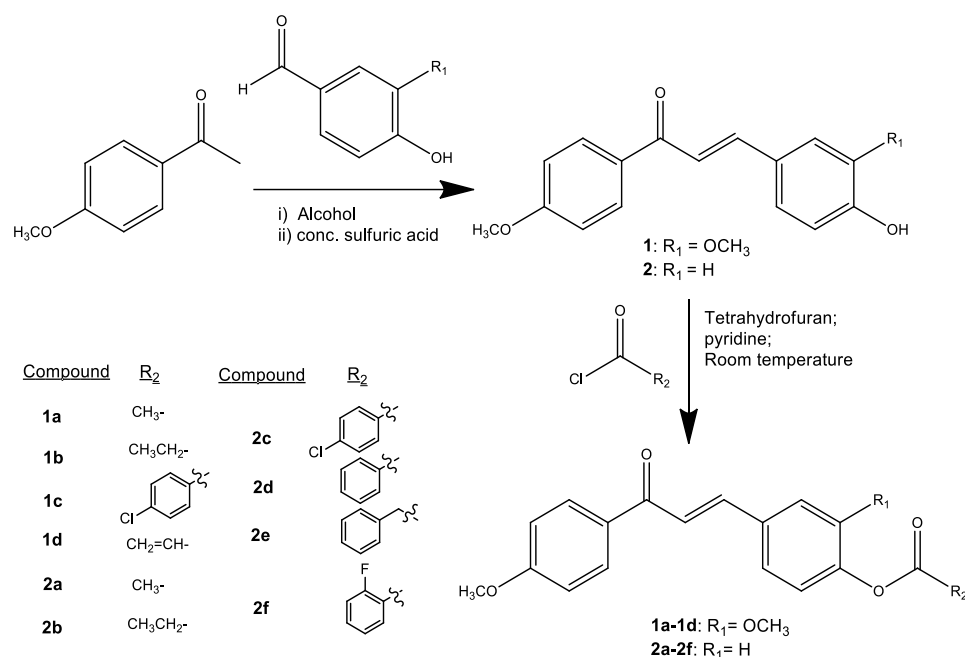
The success in synthesizing different kind of chalcone derivatives have brought scientists to further explore into its purposes and contributions towards mankind. Without a doubt, plenty of publications have been published decades ago on the application of chalcone in medicinal chemistry. In addition, it was also reported to have the potential application in electronic fields. Hence, the next sub-sections would reveal several scientific works done by previous researchers in chalcone and its derivatives' applications.

2.3.1 Biological potential of chalcone and its derivatives

It has been proven that chalcone shows numerous pharmacological properties such as anti-malarial (Awasthi *et al.*, 2009), anti-cancer, anti-microbial (Prasad *et al.*, 2008), anti-oxidant, anti-bacterial (Asiri & Khan, 2011), anti-inflammatory and antitumor (Rahman, 2011). From these works, it can be summarized that the degree of inhibition activity mainly depends on

two reasons: the substituent groups present in the aromatic rings and the presence of α,β -conjugated keto-enol group (Modzelewska *et al.*, 2006). Based on the physiochemical properties of chalcones, the introduction of substituent groups in the phenyl rings are responsible for the planarity and stability of the chalcone structure, which in turns affects the bonds of α,β - conjugated keto-enol group that significantly plays a role in the biological activity (Go *et al.*, 2005).

For instance, chalcone and its derivatives have been reported to have anti-oxidant property due to their ability to activate the nuclear factor erythroid 2 p45-related factor 2 anti-oxidant responsive elements (Nrf2-AREs) that contributes to the reduction of oxidative stress induced by the reactive oxygen species (Ishii *et al.*, 2000). In addition, Wu *et al.*, (2014) also published on the synthetic chalcones with potent anti-oxidant ability on H₂O₂-induced apoptosis in PC12 cells. Chalcone with the methoxyl group at meta-position and the presence of short fatty chains in acyl group gave the best anti-oxidant effects (Scheme 2.9). This is because the presence of electron donating substituents such as methoxyl and short fatty chains group in the phenyl ring of chalcone compounds protect the PC12 cells from oxidative stress-induced neuronal cell death prior to the Nrf2-AREs activation (Wu *et al.*, 2014).



Scheme 2.9: Synthesis pathway of chalcone derivatives as anti-oxidant agents (Wu *et al.*, 2014)

Besides, researches on the anti-infective activities such as anti-leishmanial, anti-malarial, anti-fungal and anti-bacterial of chalcone and its derivatives have been well documented (Chen *et al.*, 2001; Go *et al.*, 2004; López *et al.*, 2001; Tsukiyama *et al.*, 2002). For example, licochalcone A (**12**) as shown in Figure 2.1 had been proven to show the bacteriostatic effects against the Gram-positive and Gram-negative bacteria (Tsukiyama *et al.*, 2002; Friis-Møller *et al.*, 2002). The unsaturated α,β -conjugated ketone present in the chalcone structure was found to be responsible for the bactericidal effects, due to its ability to undergo conjugated addition with the essential protein (Nowakowska, 2007). Moreover, the hydroxyl group present at the *para* position in the ring B of the licochalcone A also shows an important role in against the bacteria *Staphylococcus aureus* as the removal of this functional group completely eliminates the inhibition activity (Nielsen *et al.*, 2004).

On top of that, Licochalcone A also possesses the anti-leishmanial effect due to its ability to alter the respiratory chain, function and ultrastructure of mitochondria of the parasites. (Zhai

et al., 1999; Chen *et al.*, 2001). Besides, the biological activity of this compound against the malaria infection such as *Plasmodium falciparum* was reported effective through the inhibition of its respiratory chain (Chen *et al.*, 1994; Mi-ichi *et al.*, 2005). As reviewed from the work conducted by Mi-ichi *et al.* (2005), the *bc*₁ complex (ubiquinol-cytochrom *c* reductase) and complex II, namely, succinate ubiquinone reductase of *Plasmodium falciparum* had been inhibited. Hence, the respiratory chain of the malaria was affected and eventually unable to grow. On the other hand, the anti-inflammatory property of 4-methylamino-3',4'-dimethoxychalcone (**13**) (Figure 2.6) has been proven to effectively inhibit the iNOS protein overexpression which commonly induced the formation of nitric oxide that contributes to the inflammation (Herencia *et al.*, 2001).

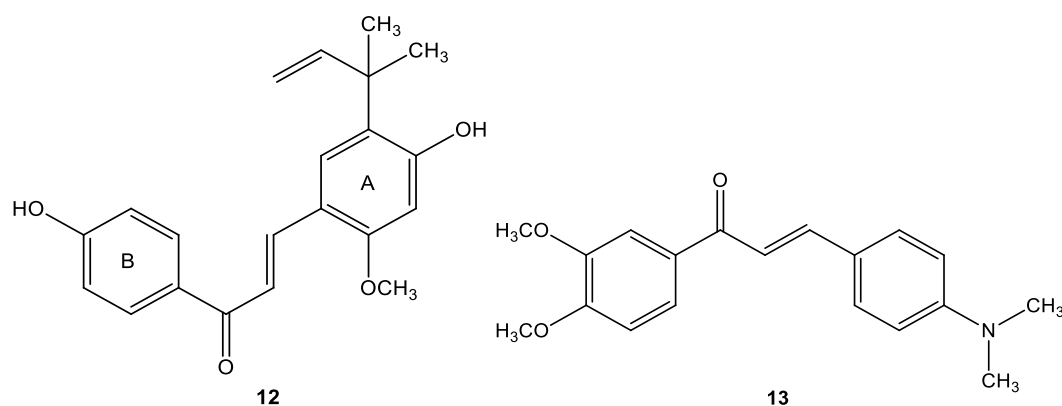


Figure 2.6: Structure of licochalcone A (**12**) and 4-methylamino-3',4'-dimethoxychalcone (**13**) (Herencia *et al.*, 2001).

For the past few years, indole chalcone has become the interest among the scientists for its potential application as an anti-cancer drug. Two series of indoyl chalcones with different substituents were synthesized and assayed for their cytotoxicity properties against human cancer cell lines (Kumar *et al.*, 2010). Showing that the addition of another methoxy substituent in A ring (**14** and **15**) (Figure 2.7) significantly enhanced the cytotoxicity effects

towards cancer cell studied. Furthermore, the substitution of methoxy group at position 3' and 5' in A ring is greatly influence in its inhibition potency and cytotoxicity Valdmeri *et al.* (2012).

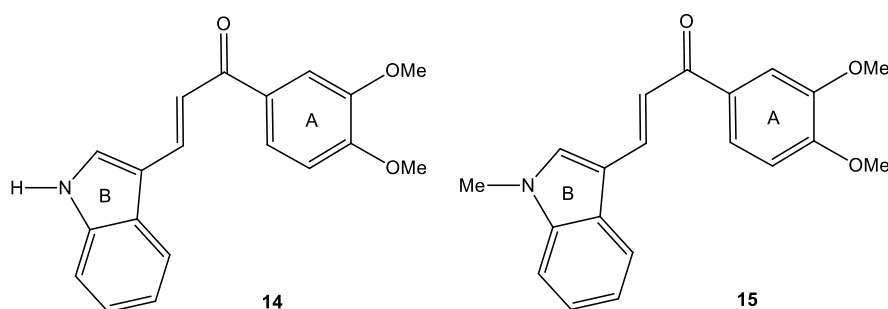


Figure 2.7: Structure of 3-indolyl-1-phenylpropenone derivatives (Valdmeri *et al.*, 2012)

Research has also been conducted on the bis-chalcone compound on the growth inhibition of T47D breast cancer cell line (Mahmoodi *et al.*, 2014). MTT assay conducted in the aforementioned study showed that a synthetic 4,4'-dihydroxychalcone or scientifically known as [(2*E*, 2'*E*)-3,3'-(1,4-phenylene)bis(1-(4-hydroxyphenyl) prop2-en-1one)] (Figure 2.8) has shown to effectively inhibit the proliferation of T47D breast cancer cell line in a manner of concentration and time-dependent cells growth inhibition.

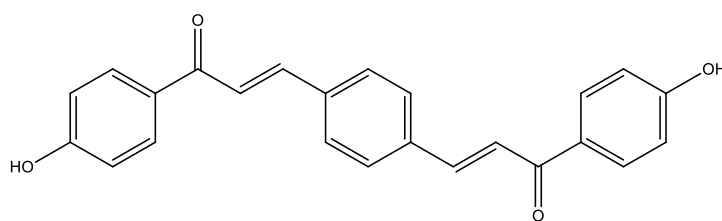


Figure 2.8: Structure of 4,4'-dihydroxychalcone (Mahmoodi *et al.*, 2014)

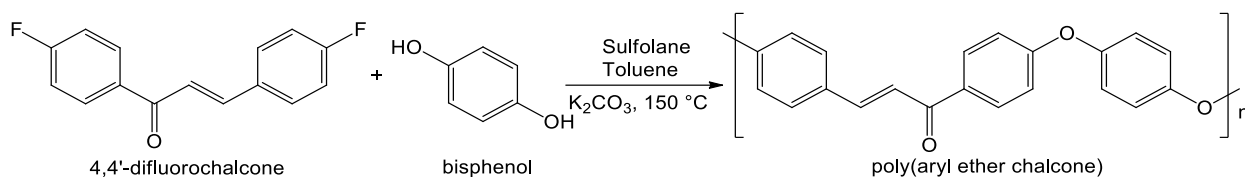
2.3.2 Electronic potential of chalcone and its derivatives

The molecular structure of chalcone has gained much attention among the researchers in nonlinear optical (NLO) applications. The highlight towards this group of compound is mainly because of the presence of π -conjugated system between the two phenyl rings, which

is essential for the effective nonlinear optical response (Indira *et al.*, 2002). Besides, the ability to modify and tune the substituents of chalcone derivatives offer a wide range of possible designs. For example, the creation of acceptor-donor-acceptor (A-D-A), donor-acceptor-donor (D-A-D), donor- π -acceptor (D- π -A) or donor- π -donor (D- π -D) types of molecular structure could further enhance the effect of the nonlinear optics properties (Reinhardt *et al.*, 1998; Kiran *et al.*, 2014). In addition, these molecular designs have also resulted strong two photon absorption (TPA) that have been observed in most of the chalcone derivatives which plays a vital role in photonics field of studies (Poornesh *et al.*, 2008).

Despite the fact that chalcone derivatives exhibit excellent molecular structure design, they cannot be applied directly in photonic device applications due to the tendency of undergoing degradation or bleaching when the molecule exposes to the strong optical signals (Shettigar *et al.*, 2006; Poornesh *et al.*, 2008). Therefore, scientists incorporated the organic compound into the polymer matrix to improve its physical and chemical stability and at the meantime retain its NLO properties (Tao *et al.*, 1996; Shettigar *et al.*, 2006; Poornesh *et al.*, 2009; Kumar *et al.*, 2016).

As early as in year 1996, Tao and coworkers had reported the second harmonic generation (SHG) of poly(aryl ether chalcone) from the monomer of 4,4'-difluorochalcone for the NLO application. Based on their discussion, the purpose of selecting fluorine as the substituent is mainly because it acts as a better leaving group which can easily been replaced with other electron-withdrawing group and for instance, difluoro has been replaced with diphenoxide to form the poly(aryl ether chalcone)s (Scheme 2.10). In addition, P- and S-polarized SH light are observed in the synthesized polymer which indicates the presence of SHG interaction and thus could be the potential candidates for the NLO applications (Tao *et al.*, 1996).



Scheme 2.10: The synthesis pathway of poly(aryl ether chalcone) (Tao *et al.*, 1996)

To add on, the SHG of chalcone named 1-(4-methoxyphenyl)-3-(3,4-dimethoxyphenyl)-2-propen-1-one (DMMC, Figure 2.9) had been studied by Shettigar *et al.* (2006). The single crystal of DMMC was grown in the acetone solvent *via* slow evaporation technique at ambient temperature. Based on their analysis, the crystal exhibit good transparency range with the UV cutoff at 430 nm. The crystal was grounded into microcrystalline powder for SHG test and a wavelength of 532 nm was detected by the photomultiplier tube which then was converted into the electrical signal. As compared with the standard urea crystal powder, they claimed that the SHG efficiency of the DMMC was 15 times higher than the standard. Hence, they deduced that the presence of high SHG efficiency and good transparency range in DMMC may contribute in the NLO applications (Shettigar *et al.*, 2006).

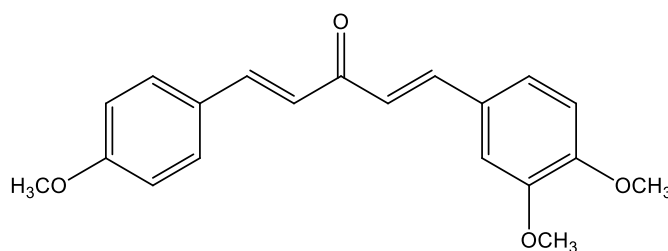


Figure 2.9: Structure of synthesized DMMC with high SHG efficiency (Shettigar *et al.*, 2006)

Meanwhile, Poornesh *et al.* (2009) had also conducted the experiments on the nonlinear optical studies in PMMA doping but with different bis-chalcone derivatives (Figure 2.10). Along the way, they realized that the introduction of better electron donating group as the substituent would significantly increase the nonlinear optical response due to the strong π -

electron delocalization. Similarly, two-photon absorption is observed and is a promising material for the optoelectronic applications.

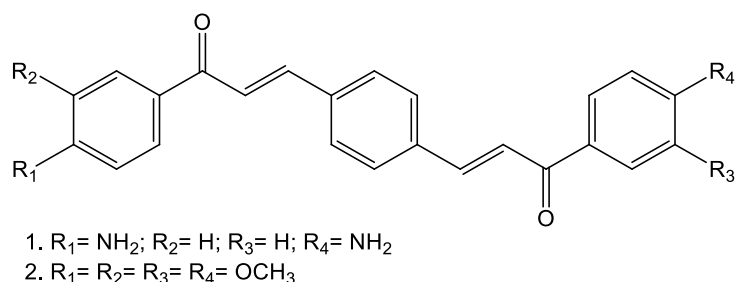
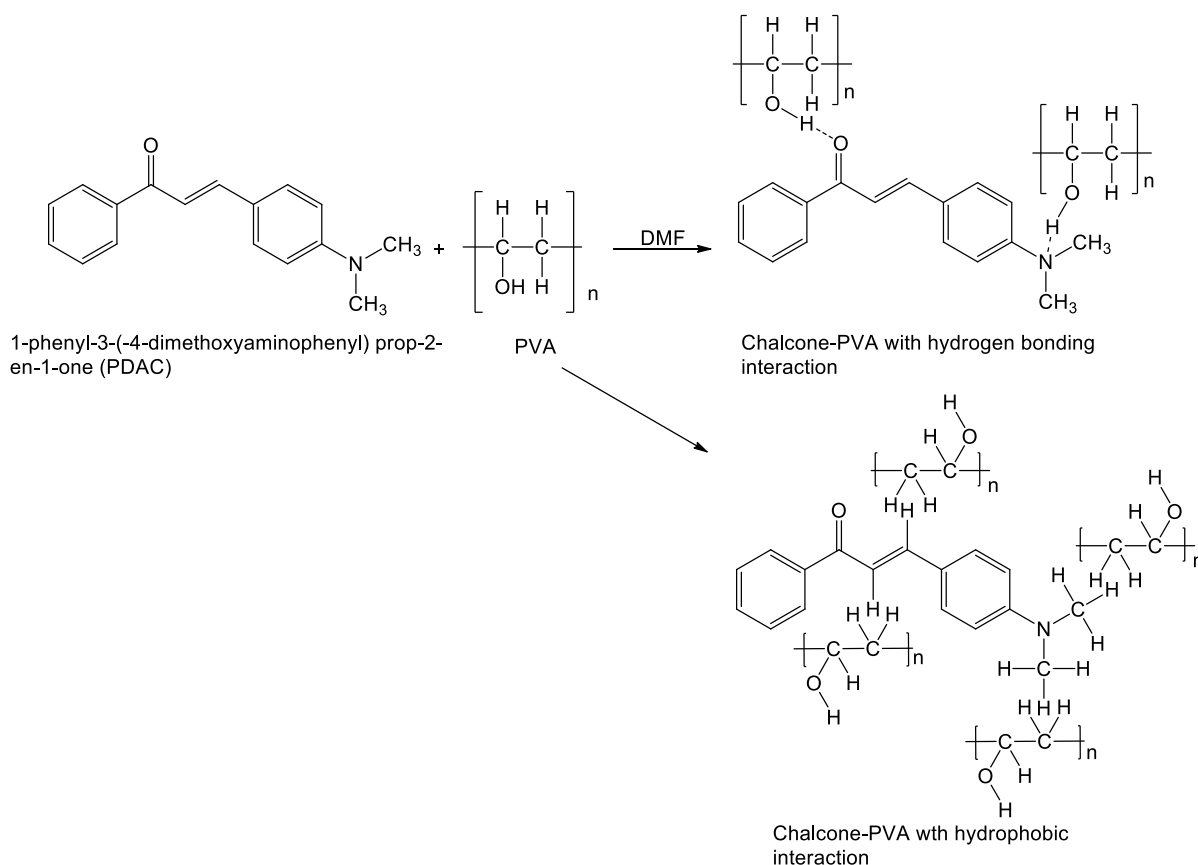


Figure 2.10: Structure of synthesized substituted bis-chalcone (Poornesh *et al.*, 2009)

Another work had been published regarding the study on the nonlinear optical response of 1-phenyl-3-(4-dimethoxyaminophenyl) prop-2-en-1-one (PDAC) which doped into the poly(vinyl alcohol) (PVA) (Scheme 2.11) (Kumar *et al.*, 2016). The mixing of these two compounds had led to a compact structure designs and thus enhances its physical and chemical properties. Two major interactions were observed which is the hydrogen bonding formed between the oxygen carbonyl group and nitrogen group with the hydroxyl of the PVA; and the hydrophobic interaction between the hydrogen of the carbon-carbon group, as illustrated in Scheme 2.3. This causes the UV-vis absorption spectrum of the polymer shifted to the visible region due to the presence of charge transfer along the moieties. Furthermore, they found out this chalcone doped-PVA exhibit high third order nonlinear optical susceptibility (Kumar *et al.*, 2016).



Scheme 2.11: Schematic diagram of interaction between PDAC and PVA (Kumar *et al.*, 2016)

The photophysical properties of chalcone derivatives had also been reported by chalcone application in electronic field (Tay *et al.*, 2016). From their findings, the introduction of methoxy substituents at the central phenyl ring of bis-chalcone (Figure 2.11) had significantly improved the emission efficiency with quantum yield of 0.57 in DCM solution. In addition, the λ_{max} emission of this particular compound was directly proportional to solvent polarity due to the solvatochromism effect. Nevertheless, the presence of hydroxyl substituent at *ortho* position at each end of phenyl ring reduced the emission effect due to the quenching caused by intramolecular hydrogen bond.

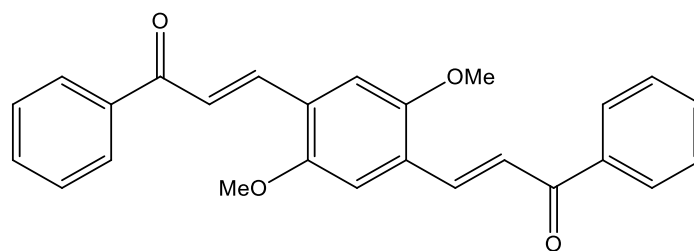


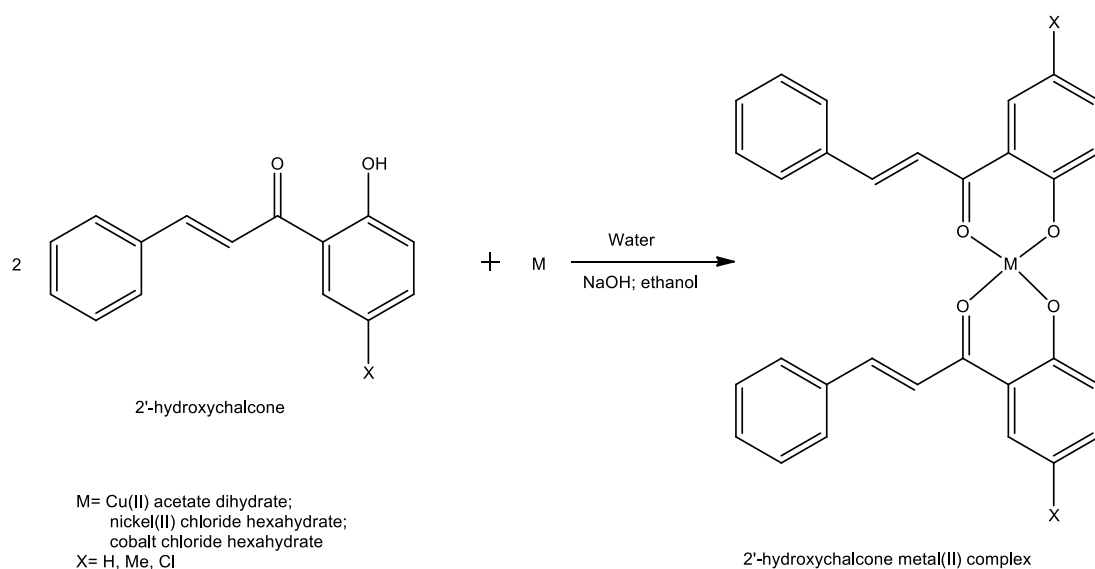
Figure 2.11: Bis-chalcone compound with high emission property (Tay *et al.*, 2016)

2.4 Review on 2'-hydroxychalcone complex synthesis and analysis

In inorganic chemistry field, IR, NMR and UV-vis spectroscopy are the most convenient method to observe the occurrence of complexation. For example, under (O, O) coordination as shown in Figure 1.4 (Chapter 1), the most obvious changes in the IR spectroscopy are the disappearance of OH stretching band at around 3200 cm^{-1} and the shifting of C=O frequency to a lower frequency due to the back bonding from metal center. Moreover, the absorption bands of $\pi \rightarrow \pi^*$ for the C=C aromatic transition and $n \rightarrow \pi^*$ for the C=O transition in the UV-vis spectroscopy also show some changes after the 2'-hydroxychalcone bind to a metal center. Due to ease of complexation of 2'-hydroxychalcone to a metal centre, vast publications have been found over the past decades in order to gain insight the changes of electronic properties and biological activities of chalcone complexes. Thus, the complexation of 2'-hydroxychalcone with different metals as well as their spectroscopic data are going to be discussed in the coming section.

The synthesis of 2'-hydroxychalcone metal complexes has been well established due to the stability of (O,O) coordination with the metal center in forming a chelating ring. Typically, most of the metal to ligand ratios used during the complexation was in 1 to 2 ratio. For example, in the complexation reaction conducted by Palaniandavar and Natarajan (1980), the respective metal salts namely copper(II) acetate dihydrate, nickel(II) chloride hexahydrate and

cobalt(II) chloride hexahydrate was reacted respectively with 2'-hydroxychalcone derivatives in the metal to ligand ratio of 1:2 under basic condition. From their electronic spectra analysis, all of the synthesized complexes were found to be in low-spin square planar geometry (Scheme 2.12).



Scheme 2.12: Square planar geometry of 2'-hydroxychalcone complex (Palaniandavar & Natarajan, 1980)

The formation of complexes had resulted the decreased in $\nu(\text{C}=\text{O})$ stretching frequency by 13-5 cm^{-1} as compared to the free ligand 2'-hydroxychalcone in their IR spectra. This is due to the delocalization of electron along the π -conjugated system (Hendrickson *et al.*, 1970). Meanwhile, the new absorption band presents at around 600 -500 cm^{-1} was attributed to metal-sensitive peak of M-O bond (Percy & Thornton, 1973).

Later, Rao *et al.* (1988) published the complexation of substituted 2'-hydroxychalcone with cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II). Based on the infrared spectra analysis, the oxygen atom of carbonyl and hydroxyl has participated in the coordination with the metal ions, respectively. In fact, the complex showed different geometries based on the

properties of metal centre and its corresponding ligand (Figure 2.12). For Cu(II) and Ni(II) metal ions, square planar complex was resulted [Figure 2.12(a)], whereas for Group XII elements such as Zn(II) and Cd(II), the complex present as tetrahedral geometry [Figure 2.12(b)]. In addition, the authors also proposed six-coordinated octahedral complex for a 2'-hydroxychalcone with pyridine ring as shown Figure 2.12(c). The metal ions involved in this six-coordinated complex were Co(II) and Ni(II).

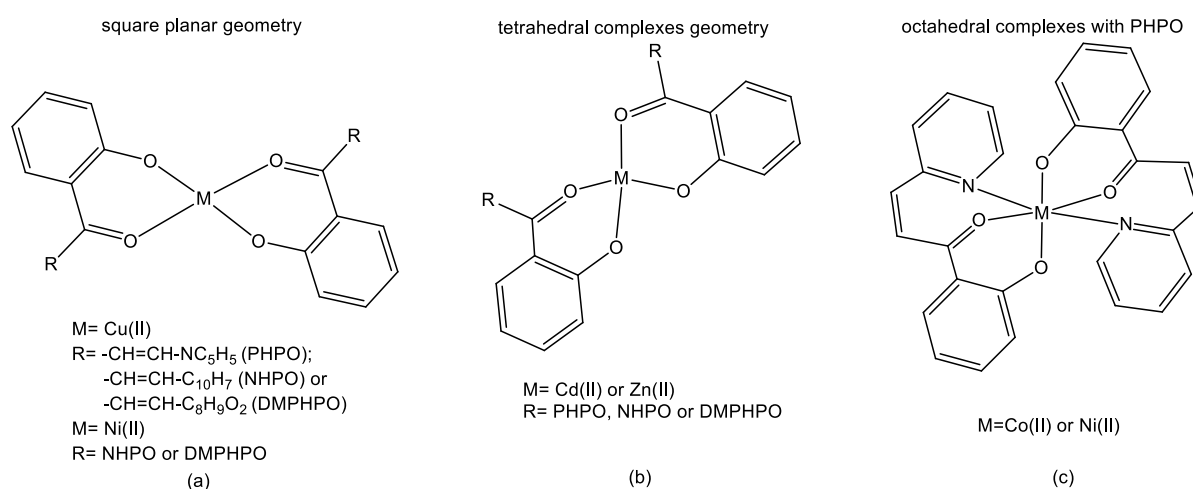
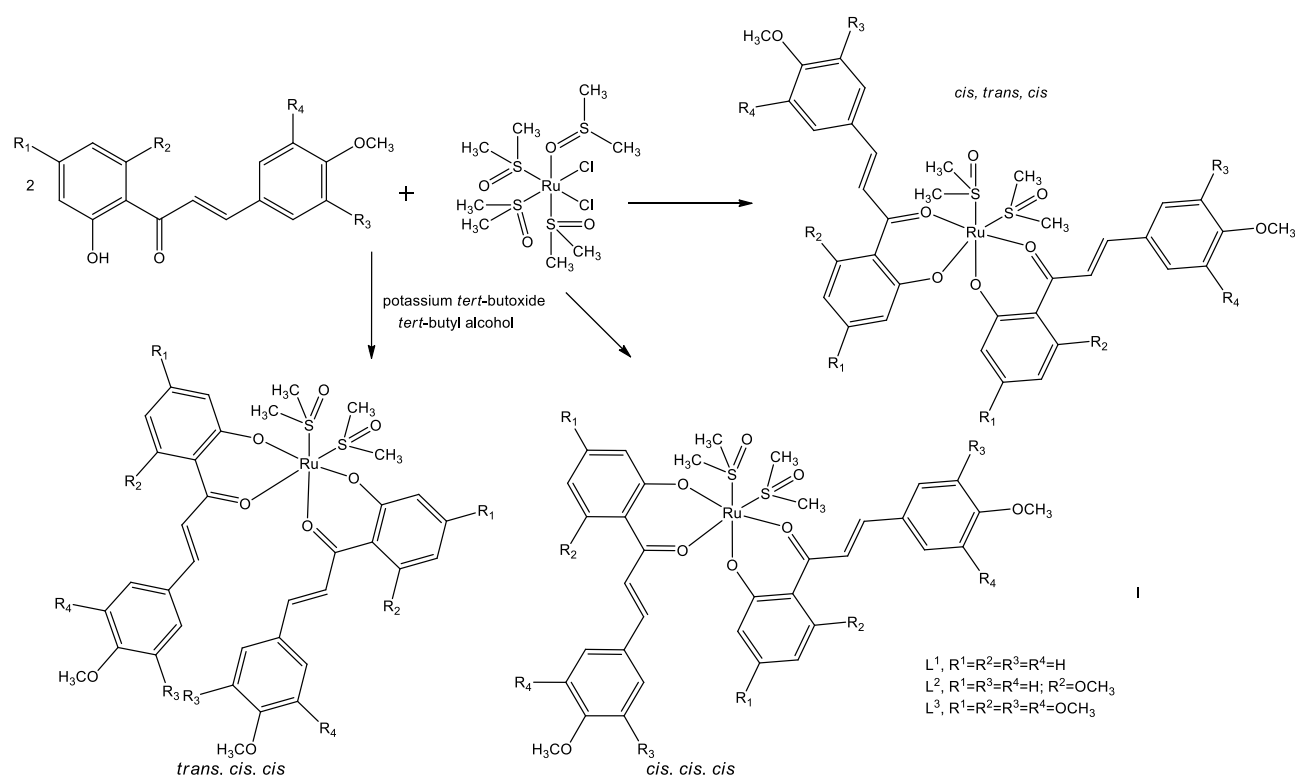


Figure 2.12: Structures of metal(II) complexes with substituted 2'-hydroxychalcones (Rao *et al.*, 1988)

Meanwhile, the chalcone complexation of ruthenium(II) has also been studied extensively. Silva *et al.* (1999) reported the synthesis and characterization of ruthenium complexes of substituted 2'-hydroxychalcones. The substituted 2'-hydroxychalcone was reacted to *cis*-[RuCl₂(DMSO)₄] in 2:1 ratio under inert and continuously refluxed for 2 to 6 days. The crude product was passed through a column chromatography 8:2 CHCl₃-acetone ratio in order to separate the three complex mixtures as shown in Scheme 2.13. Based on the ¹H and ¹³C NMR spectroscopy reported (Silva *et al.* 1999), the absence of free DMSO signal in ¹³C at 40.1 ppm in CDCl₃ indicated no O-bonded DMSO ligand was observed; while the appearance of high

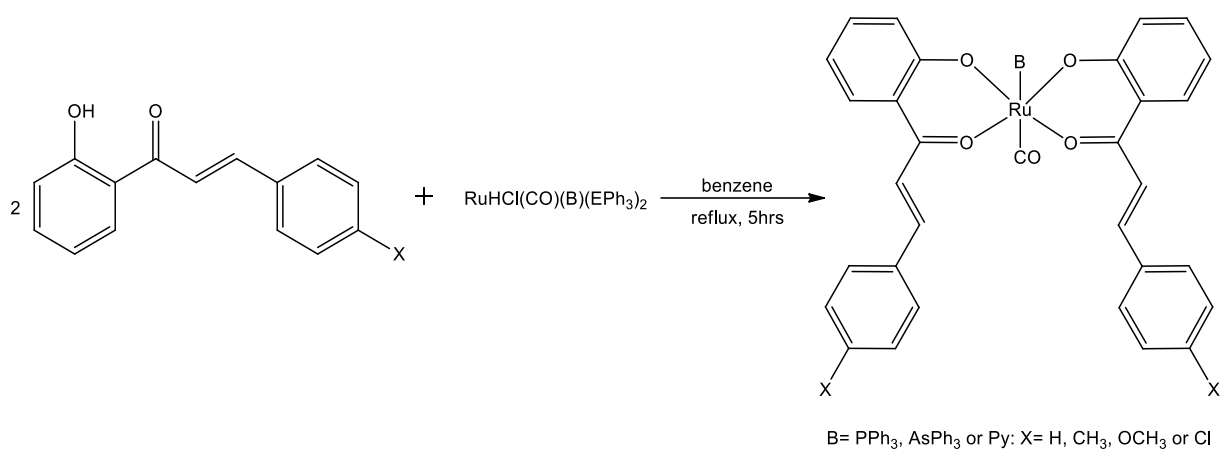
carbon resonance at 42.3-44.7 ppm indicated all the DMSO ligands were present as S-bonded to the ruthenium metal center. The spectrum was further supported with the equal intensity signals at the region of 2.97- 3.35 ppm in the ^1H NMR, which corresponded to the S-bonded DMSO as illustrated in the Scheme 2.13.



Scheme 2.13: Different conformation of 2'-hydroxychalcone ruthenium complex (Silva *et al.* 1999)

Several years later, Muthukumar and co-workers (2007) had developed the reactions of ruthenium(II) precursors and 2'-hydroxychalcone substituents in 1:2 stoichiometry ratio. Generally, the complex of $[\text{RuHCl}(\text{CO})(\text{B})(\text{EPh}_3)]$, where $\text{B} = \text{EPh}_3$ or pyridine; $\text{E} =$ phosphine (P) or As, was reacted with appropriate chalcone in 1:2 ratio and the mixture was refluxed for 5 hours (Scheme 2.14). The solvent was then removed and small amount of petroleum ether (60-80 $^\circ\text{C}$) was added to separate the desired product. Crystallization was

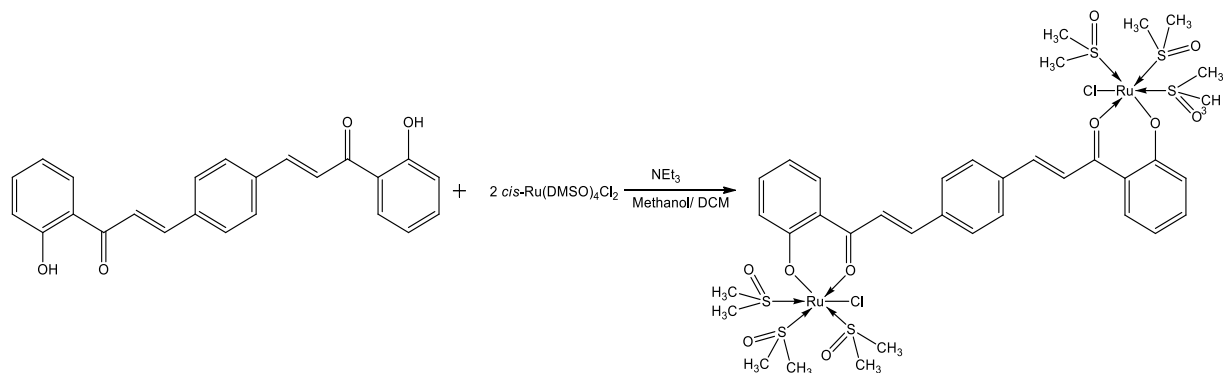
performed under CH_2Cl_2 and petroleum ether mixture (Muthukumar *et al.*, 2007). The significant change in IR frequency of $\text{C}=\text{O}$ stretching by reducing $20\text{-}30\text{ cm}^{-1}$ from 1640 cm^{-1} in α,β -conjugated keto moiety indicated the oxygen atom from $\text{C}=\text{O}$ coordinated to ruthenium metal center in the structure. On the other hand, the disappearance of OH stretching frequency at $3400\text{-}3600\text{ cm}^{-1}$ in the IR spectra of the complexes also revealed that the hydroxyl oxygen bound to the ruthenium metal center through deprotonation.



Scheme 2.14: Schematic diagram of ruthenium(II) complex (Muthukumar *et al.*, 2007)

As the research progressed, Gaur and Mishra (2013) had synthesized the bis-2'-hydroxychalcone complex with the ruthenium precursor namely $[\text{RuCl}_2(\text{DMSO-S})_3(\text{DMSO-O})]$. According to the procedure claimed, bis-2'-hydroxychalcone was reacted with the ruthenium precursor in mild basic solution at room temperature for 24 hours. The final product was extracted from dichloromethane (DCM) to give the red crystalline complex. (Scheme 2.15) (Gaur & Mishra, 2013). From the IR spectrum, the formation of coordination between the carbonyl oxygen and Ru(II) metal ion resulted the down shift of $\nu(\text{C}=\text{O})$ of ruthenium complex to 1614 cm^{-1} (Hendrickson *et al.*, 1970; Dharmaraj & Natarajan, 1997). As in UV visible spectroscopy analysis, the peaks at λ_{max} 377 and 511 nm were attributed to

the intra-ligand transition and metal to ligand charge transfer (MLCT) transition, correspondingly.



Scheme 2.15: Synthesis of bis-2'-hydroxychalcone with ruthenium (II) precursor (Gaur & Mishra, 2013)

To sum up, all the chalcone complexes showed significant changes in infrared, NMR and UV visible spectra. For instance, the deprotonation of –OH functional group were proved to be success in the IR and ^1H NMR data due to the disappearance of the respective peak. The formation of coordination bond between oxygen of carbonyl group and metal ion resulted in decrease of C=O frequency in IR spectra. Besides that, the new peak observed in the region of $600 - 400\text{ cm}^{-1}$ was signified as the M-L bond. Last but not least, the MLCT transition was observed in the complex UV spectra due to the different electronic environments presence around the metal centre.

2.5 Application of 2'-hydroxychalcone complexes

Chalcone based complexes have attracted significant attention of researchers due to their potential application electronic fields and biological activities. Indeed, the study of chalcone complexes on the biological activities had been well documented compared to those in electronic properties. For example, antiviral activity of Cu(II), Ni(II) and Zn(II) complexes

with substituted chalcones had been reported (Mallikarjun, 2004). Besides that, Muthukumar *et al.* (2007) had studied the biological activity on the 2'-hydroxychalconate complex of ruthenium(II). Moreover, Rachmale (2012) had discovered the antimicrobial activity of chalcone-based copper complexes.

Interestingly, all of the results obtained from the above authors brought to the same conclusion, where the inhibition of viral or bacterial growth on targeted cell were shown positive when tested with the synthesized complexes and were found to be more toxic than their respective ligands. The main reason for this phenomenon was due to the presence of metal chelation, which reduces the metal ion's polarity resulted by the partial sharing of the positive charge with the donor groups in conjunction with π -electron delocalization around the chelate ring (Tweedy, 1964; Malhotra *et al.*, 1993). Hence, this characteristic of metal complexes enhances the lipophilic activity of the metal ion, which favored the breakdown of the permeability barrier of the virus cell, thus inhibited the normal cell growth process (Mallikarjun, 2004; Muthukumar *et al.*, 2007; Rachmale, 2012).

Besides, the study on Topoisomerase I inhibition from *Escherichia coli* by using the synthesized bis-2'-hydroxychalcone complex of ruthenium(II) which had been conducted by Gaur and Mishra (2013) has found that, the IC₅₀ values to inhibit the Topoisomerase I in the presence of bis-2'-hydroxychalcone ruthenium complex was found to be 87 μ M. Moreover, Gaur and Mishra (2013) had also did an application on the effects of bis-2'-hydroxychalcone ruthenium complex towards DNA cleavage. They concluded that the complex has the tendency to bind with the minor groove of DNA.

Apart from the application in biological activities, Reyes *et al.* (2006) had reported the potential application of boron complexes derived from hydroxychalcones in nonlinear optics

(NLO) application. The authors were well aware of the π -conjugated system presence in the molecular structure of hydroxychalcone while boron atom is undoubtedly shows excellent electron acceptor (Yuan *et al.*, 1990). Hence, the idea of incorporate the boron atom into *para*-donor substituted hydroxychalcones were came into mind in order to create a ‘push-pull’ boron complexes for a better electron delocalization within the molecules. Herein, Figure 2.13 showed a series of boron complexes synthesized by Reyes and coworkers (2006) with ‘push-pull’ effect as the potential candidates in NLO applications.

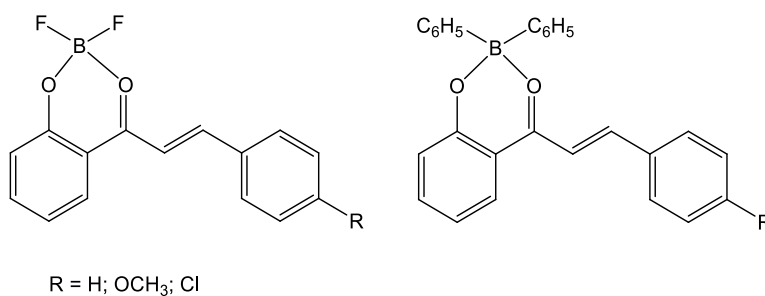


Figure 2.13: Boron complexes derived from hydroxychalcone derivatives (Reyes *et al.*, 2006)

CHAPTER 3

METHODOLOGY

3.1 Materials, Chemicals and reagents

3.1.1 (a) Materials, chemicals and reagents used for bis-chalcone synthesis

The chemicals required for the synthesis of compound 1-6 were used as purchased without any further purification, namely, acetophenone (BDH Laboratory Supplies), 2'-hydroxyacetophenone (MERCK), 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (ALDRICH), isophthalaldehyde (MERCK), terephthalaldehyde (ALDRICH) and potassium hydroxide (R&M Chemicals) Meanwhile, the reagents used were ethanol, methanol, tetrahydrofuran, dichloromethane, hexane, triethylamine (Et₃N) and distilled water. Ethanol was purified and dried under reflux system with the presence of magnesium granular and iodine. After the solution changed to colourless, the dried ethanol was collected by normal distillation.

3.1.1 (b) Materials, chemicals and reagents used for complex synthesis

All the chemicals used as received without further purification. The chemicals used for metal(II) complex synthesis were ruthenium(III) trichloride hydrate (Precious Metal Online), copper(II) chloride (J. T. Baker), nickel(II) chloride hexahydrate (Hamburg Chemical GmbH), bis-2'-hydroxychalcone derivatives (compound **1B** and **2B**) and silica gel. On the other hand, the solvents used were ethanol, methanol, acetone, sodium hydroxide (NaOH), dichloromethane (DCM), dimethylsulfoxide (DMSO) and chloroform (CHCl₃).

3.1.1 (c) **Materials and chemicals used in fabrication of DSSC**

The study of solar cell fabrication and efficiency test was under the collaboration with Prof. Tsai Jenn-Kai in the National Formosa University, Taiwan. Hence, all the materials were obtained and supplied directly from the respective university. The materials used for fabrication were FTO glasses, ITO glass, surlyn dupont 60 μm , microscopic slide and film coater (5 μm , 10 μm , 15 μm and 20 μm). The dyes which were tested in this section were those bis-chalcone compounds and their complexes which have been synthesized and characterized. Chemicals were mainly TiO_2 P25 (UR-ITIT001-500G), silver paste and the redox electrolyte while the reagents were acetone, methanol and deionized water and *tert*-butylalcohol. The cyclic voltamogram was carried out in 0.1 M TBAPF6 ($E^\circ = -1.686$ V; glassy carbon electrode; Pt wire counter, aqueous reference, scan rate = 0.05 Vs⁻¹) in Universiti Malaysia Terengganu.

3.2 **Procedure**

3.2.1 **Synthesis of bis-chalcone**

All of the synthesis method used was based on Claisen Schmidt condensation reaction at room temperature. Three series of bis-chalcone compounds with different R-substituent were synthesized and the procedure was described in the next sub-section. The procedures were referred to the previous work conducted by Tiong (2014).

3.2.1.1 **Preparation of Series 1 bis-chalcone**

The compound of R-acetophenone ($R = \text{H}$, 2'-OH) (2 equivalent moles) was dissolved into 40 mL of ethanol solution, respectively. 5 mL of 20% KOH solution was added slowly into the mixture and stirred for 10 minutes. Terephthalaldehyde (0.01 mol, 1.34 g) was then added and the reaction was stirred for 4 hours. Upon completion, the mixture was poured into 100 mL of cold distilled water, followed by the addition of HCl (3.0M). The precipitate formed was

filtered and washed with ethanol and distilled water several times and dried in room temperature. The dry mass of the precipitate was weighed and then crystallized with THF solvent. Figure 3.1 showed the proposed molecular structure of the Series 1 compound, where (a) referred to the compound **1A** and (b) referred to compound **1B**.

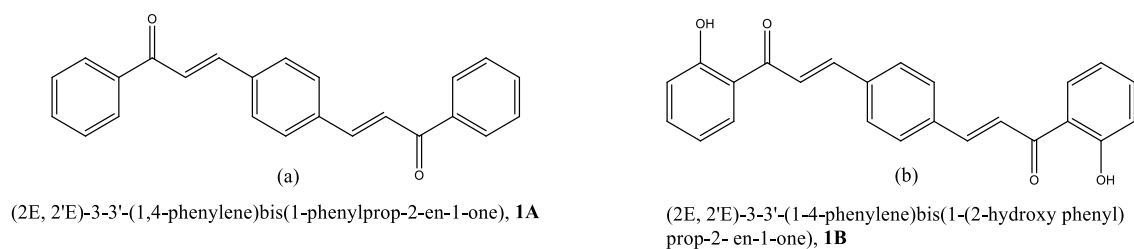


Figure 3.1: Proposed molecular structure of compound **1A** (a) and compound **1B** (b)

An attempt to synthesize the donor-acceptor bis-chalcone consisting *ortho*-OH at one terminal phenyl ring and *para*-NO₂ at another terminal phenyl ring had also been carried out in this series. In this case, the intermediate compound of (*E*)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl)benzaldehyde (**1C**) (Figure 3. 2 (c)) was pre-synthesized with the following procedure.

The compound of 2'-hydroxyacetophenone (1 equivalent amount) was dissolved in 20 mL ethanol solution with the presence of triethylamine (Et₃N) (1 equivalent amount) and the solution was stirred for 10 minutes. Terephthalaldehyde (0.01 mol, 1.34 g) was then added into the mixture and the reaction was stirred vigorously for 24 hours. The precipitate formed was filtered and washed several times with distilled water and ethanol. The filtrate was re-stirred for overnight in order to obtain more precipitate and this process was repeated until no further precipitate formed in the filtrate. After that, it was dried under room temperature and the solid precipitate was recrystallized *via* slow diffusion method of DCM and hexane.

Next, 4-nitroacetophenone (1 equivalent amount) was dissolved into 20 mL ethanol and then, 5 mL of 10% KOH was added slowly. The mixture was allowed to react for 10 minutes. The synthesized intermediate compound (0.20g, 0.0007 mol) was added into the solution and the reaction was stirred for 4 hours. The mixture was poured into cold distilled water and 3.0 M HCl was added to neutralize the mixture. The precipitate formed was filtered and washed several times with ethanol and distilled water. The precipitate was air dried and weighed, followed by slow diffusion crystallization *via* DCM with hexane. Unfortunately, no crystal was formed. The proposed molecular structure was shown in Figure 3.2 (d) as compound **1D**.

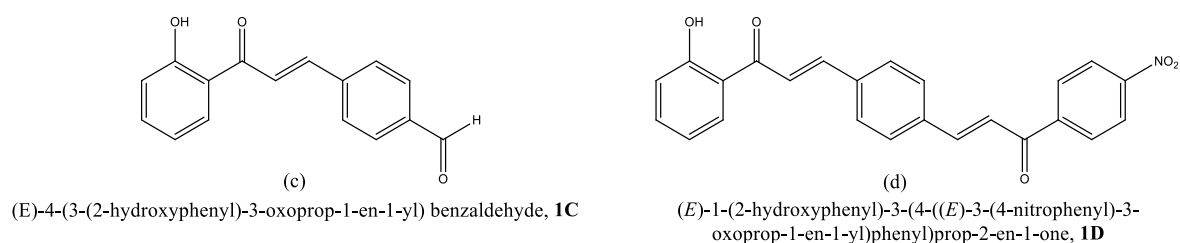
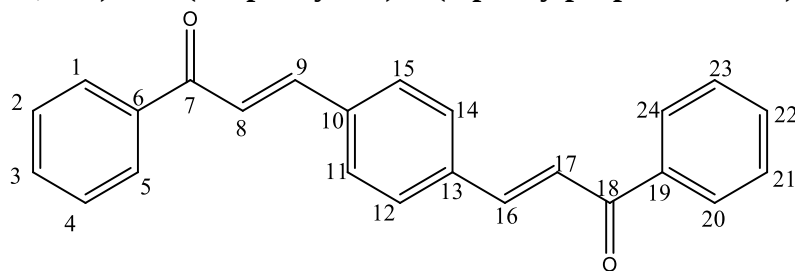


Figure 3.2: Proposed molecular structure of compound **1C** (c) and compound **1D** (d)

3.2.1.1 (a) (2E, 2'E)-3-3'-(1,4-phenylene)bis(1-phenylprop-2-en-1-one), **1A**

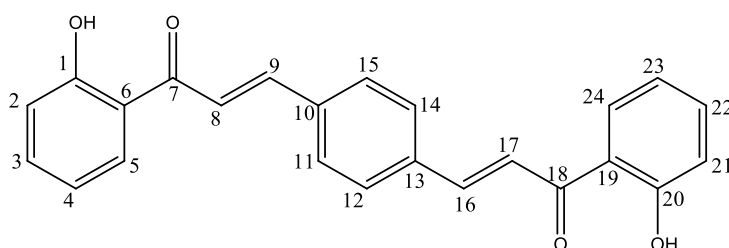


Acetophenone (2.40 g, 0.02 mol). Pale yellow crystal. Yield: 2.58 g, 76%. IR (KBr, cm^{-1}) ν : 1655 (carbonyl group -C=O stretch), 1607 (aliphatic -C=C- stretch), 1577 and 1446 (aromatic -C=C- stretch). ^1H NMR (500 MHz, CDCl_3) δ H: 8.03 (d, 4H, J = 8 Hz, H-1, 5, 20, 24), 7.80 (d, 2H, J = 16 Hz, H-8, 17), 7.69 (s, 4H, H-11, 12, 14, 15), 7.58 (d, 2H, J = 16 Hz, H- 9, 16), 7.60 (t, 2H, J = 7 Hz, H-3, 22), 7.52 (t, 4H, J = 8 Hz, H-2, 4, 21, 23). ^{13}C NMR (125 MHz, DMSO-d_6) δ C: 190.39 (C-7, 18), 143.68 (C-9, 16), 138.18 (C-6, 19), 137.01 (C-

10, 13), 133.09 (C-3, 22), 129.10 (C-2, 4, 21, 23), 128.83 (C-11, 12, 14, 15), 128.66 (C-1, 5, 20, 24), 123.18 (C-8, 17). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 277 (π to π^*) and 353 (n to π^*). Anal. Calcd. For $\text{C}_{24}\text{H}_{18}\text{O}_2$: C, 85.18; H, 5.36; O, 9.46. Found: C, 85.23; H, 5.37; O, 9.40.

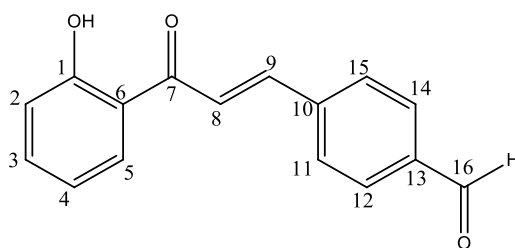
3.2.1.1 (b) (2*E*, 2'*E*)-3-3'-(1-4-phenylene)bis(1-(2-hydroxy phenyl) prop-2-en-1-one),

1B



2'-hydroxyacetophenone (2.72 g, 0.02 mol). Yellow crystal. Yield: 1.62 g, 44%. IR (KBr, cm^{-1}) ν : 3441 (-OH), 1640 (carbonyl group -C=O stretch), 1572 (aliphatic -C=C- stretch), 1489 (aromatic -C=C- stretch). ^1H NMR (500 MHz, CDCl_3) δ H: 12.75 (s, 2H, OH), 7.95 (d, 2H, J = 8 Hz, H-2, 21), 7.93 (d, 2H, J = 15 Hz, H-8, 17), 7.74 (s, 4H, H-11, 12, 14, 15), 7.72 (d, 2H, J = 15 Hz, H-9, 16), 7.53 (t, 2H, J = 8 Hz, H-4, 23), 7.05 (d, 2H, J = 8 Hz, H-5, 24), 6.97 (t, 2H, J = 8 Hz, H-3, 22). ^{13}C NMR (125 MHz, CDCl_3) δ C: 193.58 (C-7, 18), 163.81 (C-1, 20), 144.20 (C-9, 16), 137.02 (C-3, 22), 136.81 (C-10, 13), 129.79 (C-5, 24), 129.38 (C-11, 12, 14, 15), 121.52 (C-4, 23), 120.10 (C-6, 19), 119.11 (C-8, 17), 118.89 (C-2, 21). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 280 (π to π^*) and 369 (n to π^*). Anal Calcd. for $\text{C}_{24}\text{H}_{18}\text{O}_4$: C, 77.82; H, 4.90; O, 17.28. Found: C, 79.13; H, 4.50; O, 16.37.

3.2.1.1 (c) (E)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl) benzaldehyde, 1C



2'-hydroxyacetophenone (1.36 g, 0.01 mol). Yellow solid. Yield: 0.453 g, 34%. IR (KBr, cm^{-1}) ν : 3453 (-OH), 1695 (carbonyl group CHO stretch), 1639 (carbonyl group -C=O stretch), 1604 (aliphatic -C=C- stretch), 1567 (aromatic -C=C- stretch). ^1H NMR (500 MHz, CDCl_3) δ H: 12.67 (s, 1H, OH), 10.06 (s, 1H, CHO), 7.96 (d, 1H, $J = 8$ Hz, H-2), 7.93 (d, 1H, $J = 16$ Hz, H-8), 7.92 (d, 2H, $J = 8$ Hz, H-12, 14), 7.82 (d, 2H, $J = 8$ Hz, H-11, 15), 7.77 (d, 1H, $J = 16$ Hz, H-9), 7.53 (t, 1H, $J = 8$ Hz, H-4), 7.05 (d, 1H, $J = 8$ Hz, H-5), 6.97 (t, 1H, $J = 8$ Hz, H-3). ^{13}C NMR (125 MHz, CDCl_3) δ C: 193.58 (C-7), 192.95 (C-16), 161.80 (C-1), 142.99 (C-9), 140.18 (C-10), 137.31 (C-13), 136.73 (C-3), 131.15 (C-5), 130.10 (C-12, 14), 129.79 (C-11, 15), 125.12 (C-4), 121.12 (C-6), 119.51 (C-8), 117.91 (C-2). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 320, 363. Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{O}_3$: C, 76.18; H, 4.79; O, 19.03. Found: C, 73.89; H, 4.58; O, 21.53.

3.2.1.2 Preparation of Series 2 bis-chalcone

The compound of R-acetophenone ($\text{R} = \text{H}$, 2'-OH) (2 equivalent amount) was added into 20 mL of ethanol and followed by 5 mL of 20% KOH solution was added into the solution. The mixture was stirred for around 10 minutes. Isoterephthalaldehyde (0.0015 mol, 0.20 g) was then mixed into the solution and the reaction was stirred for another 5 hours. Upon completion, the mixture was poured into 50 mL ice cold water and transferred to the separatory funnel. The solution was extracted with 50 mL dichloromethane (4 times) and the solvent was evaporated in order to obtain the solid precipitate. Finally, the precipitate was washed with ethanol and air dried followed by recrystallization with DCM. Figure 3.3 (e) and (f) were the proposed molecular structure of the Series 2 namely compound **2A** and **2B**, respectively.

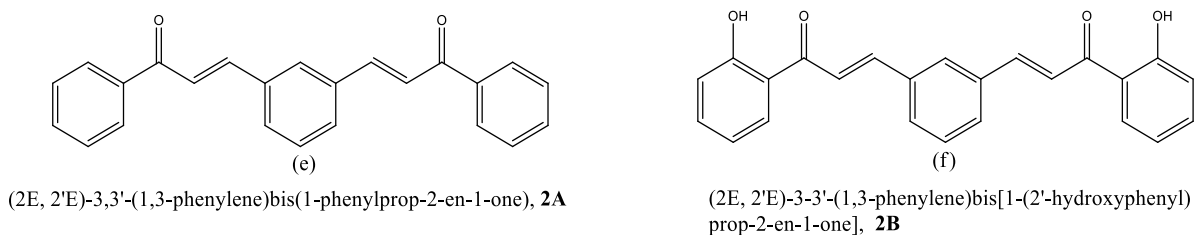
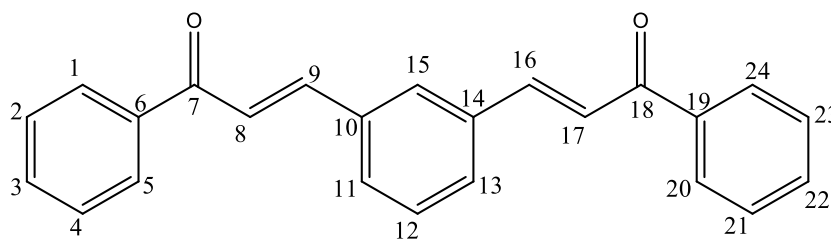


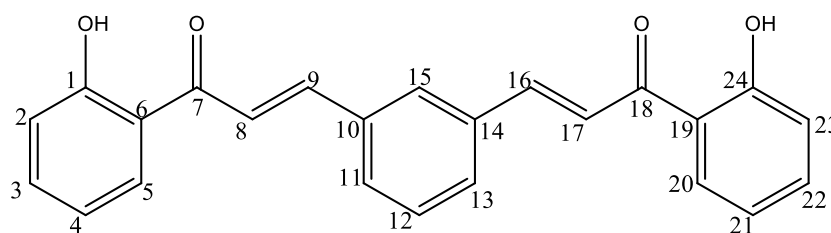
Figure 3.3: Proposed molecular structure of compound **2A** (e) and **2B** (f)

3.2.1.2 (a) (2E, 2'E)-3,3'-(1,3-phenylene)bis(1-phenylprop-2-en-1-one), **2A**



Acetophenone (0.360 g, 0.003 mol). White solid. Yield: 0.53 g, 95%. IR (KBr, cm^{-1}) ν : 1663 (carbonyl group $\text{C}=\text{O}$ stretch), 1607 (aliphatic $\text{C}=\text{C}$ stretch), 1578 (aromatic $\text{C}=\text{C}$ stretch). ^1H NMR (500 MHz, CDCl_3) δ H: 8.05 (d, 4H, $J = 8$ Hz, H-1, 5, 20, 24), 7.89 (s, 1H, H-15), 7.84 (d, 2H, $J = 16$ Hz, H-8, 17), 7.69 (d, 2H, $J = 8$ Hz, H-11, 13), 7.59 (d, 2H, $J = 16$ Hz, H-9, 17), 7.62 (t, 2H, $J = 8$ Hz, H-3, 22), 7.53 (m, 5H, H-2, 4, 12, 21, 23). ^{13}C -NMR (125 MHz, CDCl_3) δ C: 190.5 (C-7, 18), 143.9 (C-9, 16), 138.1 (C-6, 19), 135.8 (C-10, 14), 133.1 (C-3, 22), 130.3 (C-11, 13), 129.7 (C-12), 128.8 (C-2, 4, 21, 23), 128.7 (C-1, 5, 20, 24), 128.4 (C-8, 17) and 123.1. UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 261 (π to π^*) and 307 n to π^* . Anal Calcd. for $\text{C}_{24}\text{H}_{18}\text{O}_2$: C, 85.18; H, 5.36; O, 9.46. Found: C, 85.62; H, 5.43; O, 8.95.

3.2.1.2 (b) (2E, 2'E)-3,3'-(1,3-phenylene)bis[1-(2'-hydroxyphenyl) prop-2-en-1-one], **2B**



2'-Hydroxyacetophenone (0.408 g, 0.003 mol). Yellow solid. Yield: 0.161 g, 27%. IR (KBr, cm^{-1}) ν : 3436 (OH), 1640 (carbonyl group C=O stretch), 1578 (aliphatic C=C stretch), 1488 (aromatic C=C stretch). ^1H NMR (500 MHz, CDCl_3) δ H: 12.74 (s, 2H, OH), 7.96 (d, 2H, overlapped, H-2, 23), 7.95 (d, 2H, $J = 15$ Hz, H-8, 17), 7.91 (s, 1H, H-15), 7.74 (d, 2H, overlapped, H-11, 13), 7.72 (d, 2H, $J = 15$ Hz, H-9, 16), 7.53 (t, 3H, $J = 8$ Hz, H-4, 12, 21), 7.05 (d, 2H, $J = 8$ Hz, H-5, 20), 6.98 (t, 2H, $J = 8$ Hz, H-3, 22). ^{13}C NMR (125 MHz, CDCl_3) δ C: 193.64 (C-7, 18), 163.78 (C-1, 24), 144.44 (C-9, 16), 136.80 (C-10, 14), 135.67 (C-3, 22), 130.61 (C-5, 20), 129.84 (C-11, 13), 128.96 (C-12), 121.42 (C-4, 6, 19, 21), 120.06 (C-15), 119.13 (C-8, 17) and 118.87 (C-2,23). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 315 (π to π^*) and 360 (n to π^*). Anal Calcd. for $\text{C}_{24}\text{H}_{18}\text{O}_4$: C, 77.82; H, 4.90; O, 17.28. Found: C, 77.84; H, 4.95; O, 17.21.

3.2.1.3 Preparation of bis-chalcone (Series 3)

The reaction procedures were similar to those which as described in bis-chalcone series 2, however, terephthalaldehyde was replaced by 2,5-dimethoxybenzene-1,4-dicarboxaldehyde (0.001 mol, 0.20 g). Upon completion, the mixture was poured into 50 mL cold distilled water and 3.0 M HCl was used to neutralize the compound. The precipitate was filtered, washed several times with water with ethanol and allowed to dry. Finally, the precipitate was crystallized with hot DMF as a single solvent crystallization. Herein, Figure 3.4 represented the proposed molecular structure of Series 3 compounds that were named as compound **3A** (g) and **3B** (h).

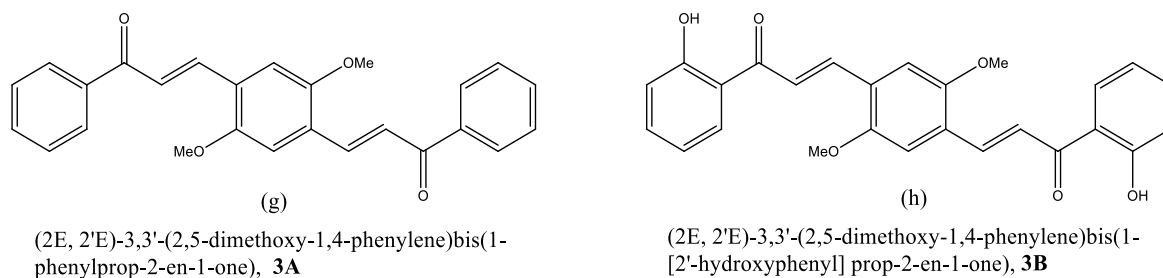
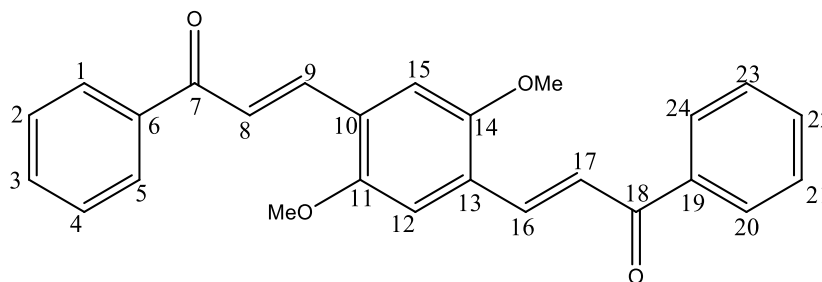


Figure 3.4: Proposed molecular structure of compound **3A** (g) and **3B** (h)

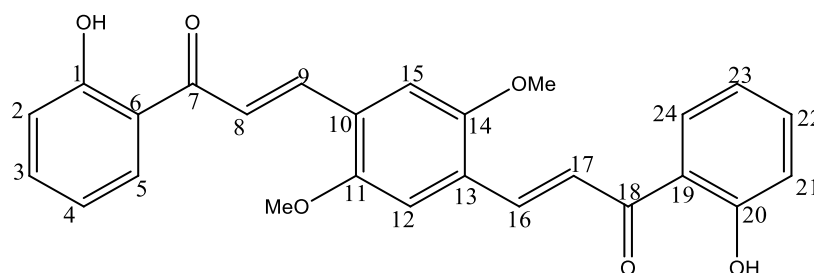
3.2.1.3 (a) (2E, 2'E)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-phenylprop-2-en-1-one), 3A



Acetophenone (0.25 g, 2.1 mmol). Yellow solid. Yield: 0.34 g, 85%. IR (KBr, cm^{-1}) ν : 1655 (C=O stretching of $-\text{COCH}$), 1587 (aliphatic $-\text{C}=\text{C}$ stretch), 1572 (aromatic $-\text{C}=\text{C}$ stretch), 1186 (OCH_3). ^1H NMR (500 MHz, CDCl_3) δ H: 8.06 (d, 2H, $J = 16$ Hz, H-8, 17), 8.03 (d, 4H, $J = 8$ Hz, 1, 5, 20, 24), 7.66 (d, 2H, $J = 15$ Hz, H-9, 16), 7.60 (t, 2H, $J = 8$ Hz, H-3, 22), 7.52 (t, 4H, $J = 8$ Hz, H-2, 4, 21, 23), 7.17 (s, 2H, H-12, 15), 3.95 (s, 6H, OCH_3). ^{13}C NMR (125 MHz, CDCl_3) δ C: 191.18 (C-7, 18), 153.21 (C-11, 14), 139.67 (C-9, 16), 138.44 (C-6, 19), 132.91 (C-3, 22), 128.77 (C-2, 4, 21, 23), 128.73 (C-1, 5, 20, 24), 126.84 (C-10, 13), 124.28 (C-8, 17), 111.85 (C-12, 15), 56.34 ($-\text{OCH}_3$). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 269 (π to π^*), 335 (n

to π^*) and 423 (ICT). Anal Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57; O, 16.06. Found: C, 77.75; H, 5.54; O, 16.71.

3.2.1.3 (b) (2E, 2'E)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-[2'-hydroxyphenyl] prop-2-en-1-one), 3B



2'-hydroxyacetophenone (0.28 g, 2 mmol). Red solid. Yield: 0.18 g, 42%. IR (KBr, cm^{-1}), ν : 3450 (OH), 1632 ($-C=O$ stretching of $-COCH$), 1560 (aliphatic $-C=C$ stretch), 1487 (aromatic $-C=C$ stretch), 1196 (OCH_3). ^1H NMR (500 MHz, $CDCl_3$) δ H: 12.86 (s, 2H, OH), 8.18 (d, 2H, $J = 15$ Hz, H-8, 17), 7.94 (d, 2H, $J = 8$ Hz, H-2, 21), 7.85 (d, 2H, $J = 16$ Hz, H-9, 16), 7.52 (t, 2H, $J = 8$ Hz, H-4, 23), 7.18 (s, 2H, H-12, 15), 7.06 (d, 2H, $J = 8$ Hz, H-5, 24), 6.98 (t, 2H, $J = 7$ Hz, H-3, 22), 3.98 (s, 6H, OCH_3). ^{13}C NMR (125 MHz, $DMSO-d_6$): δ C: 193.62 (C-7, 18), 161.91 (C-1, 20), 152.84 (C-11, 14), 138.14 (C-9, 16), 136.49 (C-3, 22), 130.80 (C-5, 24), 126.58 (C-10, 13), 122.96 (C-6, 19), 120.81 (C-4, 23), 119.18 (C-8, 17), 117.80 (C-2, 21), 111.20 (C-12, 15) and 56.67 ($-OCH_3$). UV-Vis (DCM) (λ_{max}/nm): 273 (π to π^*), 346 (n to π^*) and 436 (ICT). Anal Calcd for $C_{26}H_{22}O_6$: C, 72.55; H, 5.15; O, 22.30. Found: C, 70.94; H, 5.18; O, 23.88.

3.2.1.4 Characterization

Each of the compounds was undergone a preliminary test *via* thin layer chromatography (TLC) to check for the completion of the reaction and the purity of the product based on the spot observed. The infrared spectra (IR) were conducted in KBr disc in the wavelength region

from 400 to 4000 cm^{-1} using Thermo Scientific Nicolet iS10 FTIR spectrophotometer. The proton (^1H , 500 MHz) and carbon (^{13}C , 125 MHz) NMR spectra were obtained from the Jeol 500 MHz FT-NMR spectrometer. Deuterated solvent namely chloroform-d (CDCl_3) and dimethyl sulfoxide-d₆ (DMSO-d_6) were used as the NMR solvent with the solvent peak at 7.26 and 2.5 ppm, respectively, which set as the reference peak for each of the spectrum. The UV-vis absorption spectra were recorded using a Jasco V-630 Ultraviolet spectrophotometer under absorption range of 200-500 nm by dissolving the compounds in DCM solvent. The purity of the compounds was reconfirmed by using the CHN analyzer.

3.2.2 Synthesis of metal(II) complexes

3.2.2.1 Preparation of *cis*-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, **PC1**

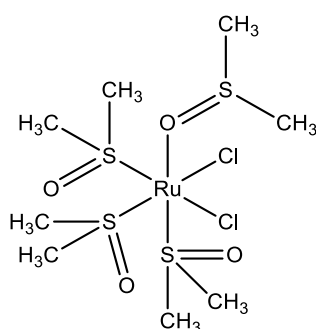


Figure 3.5: Molecular structure of *cis*-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, **PC1**

Figure 3.5 shows the molecular structure of ruthenium precursor, **PC1**. The synthetic method of ruthenium(II) precursor was in accordance to the method reported by Bratsos and Alessio (2010). Ruthenium(III) trichloride n-hydrate (1 g, 3.83 mmol, n = 3) was dissolved partially in 25 mL ethanol and refluxed for 3 hours at 78 °C. The colour of the solution observed changed from dark brown to deep green over the period of time. The ethanol was removed totally *via*

rotary evaporator and oily dark green residue was formed. It was then added with 4 mL of DMSO and the mixture was refluxed for another 2 hours at 150 °C. During the first minute of the reaction, the solution changed from dark green to bright orange, indicating the formation of intermediate compound. After approximately 1 hour, yellow solid precipitate was observed. Upon completion of the reaction, the solution was allowed to cool to room temperature. 60 mL of acetone was added into the solution and the mixture was kept aside for one day. The bright yellow microcrystalline solid formed was filtered and washed several times with cold acetone. Finally, it was dried *in vacuo*. Yellow solid. Yield: 1.38 g, 75%. IR (KBr, cm^{-1}) ν : 3014 (C-H stretch), 1106 (DMSO, S-bonded stretch), 927 (DMSO, O-bonded stretch), 426 (Ru-S stretch). ^1H NMR (500 MHz, D_2O) δ : 3.43 (s, 6H, S-bonded $(\text{CH}_3)_2$), 3.41 (s, 6H, S-bonded $(\text{CH}_3)_2$), 3.33 (s, 6H, S-bonded $(\text{CH}_3)_2$), 2.70 (s, 6H, O-bonded $(\text{CH}_3)_2$). ^{13}C NMR (125 MHz, D_2O , δ ppm) C: 46.89 (DMSO, S-bonded), 46.66 (DMSO, S-bonded), 45.86 (DMSO, S-bonded), 45.27 (DMSO, S-bonded), 44.82 (DMSO, S-bonded), 44.48 (DMSO, S-bonded), 38.81 (DMSO, O-bonded). Anal Calcd. for $\text{C}_8\text{H}_{24}\text{Cl}_2\text{O}_4\text{RuS}_4$: C, 19.83; H, 4.99. Found: C, 18.83; H, 4.60.

3.2.2.2 Complexation of bis-2'-hydroxychalcone derivatives with PC1

The synthetic method was referring to the method which has been reported by Gaur & Mishra (2013) with minor modification. The general procedures are as described below.

The compound of bis-2'-hydroxychalcone namely compound **1B** and **2B** (0.185 g, 0.5 mmol) was partially dissolved in 25 mL of methanol and were sonicated for 10-15 minutes. 0.040 g, 1.0 mmol of NaOH was added into the solution containing compound **1B** and stirred for 10 minutes. For the compound **2B**, 1mL of triethylamine (Et_3N) was used instead of NaOH. At the meantime, the precursor **PC 1** (0.484 g, 1.0 mmol) was dissolved in 25 mL of methanol and sonicated for 20 minutes. Then, both solutions were mixed together by adding the

precursor solution into the bis-2'-hydroxychalcone dropwise and the mixture was stirred at room temperature for 24 hours. The colour of the solution changed from orange to deep red gradually.

The undissolved precipitate was filtered using filter funnel and the dark red filtrate was diluted with 100 mL of cold water followed by extraction using DCM. The solvent was removed to yield the dark red precipitate. The purity of the precipitate was determined by conducting TLC analysis. The excess unreacted bis-2'-hydroxychalcone was removed via column chromatography by using CHCl_3 as the eluent, then followed by the mixture of CHCl_3 with ethanol (1:1) to elute out the desired complex namely **CX1** (Figure 3.6 (i)) (**PC1** with ligand **1B**) and **CX2** (Figure 3.6 (j)) (**PC1** with ligand **2B**). An additional step was applied for the separation of complex **CX1** in column chromatography, where the mixture of CHCl_3 and acetone in 1:1 ratio were used to elute the side product before proceeded to CHCl_3 and ethanol (1:1) solvent mixture. Complexation of compound **3B** with **PC1** was not available due to the poor solubility of the compound **3B** in basic methanol solution. Besides, the starting materials to synthesized compound **3B** were limited, which the amount was only adequate for characterization purposes and also the application as dye sensitizer in DSSC.

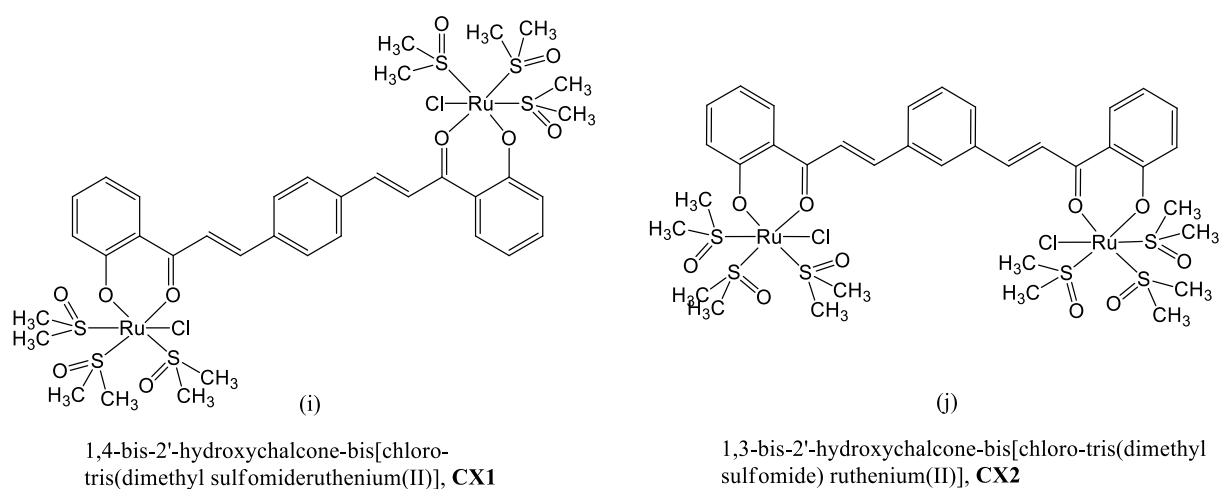
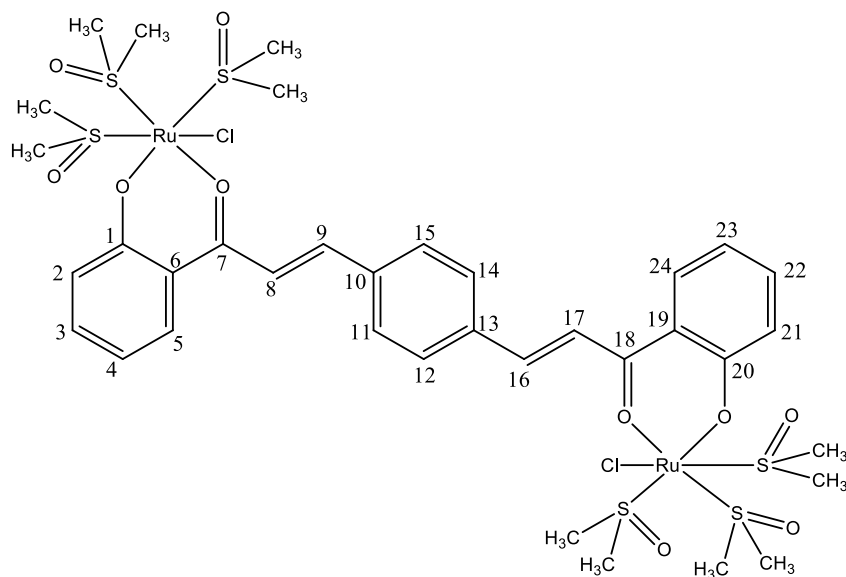


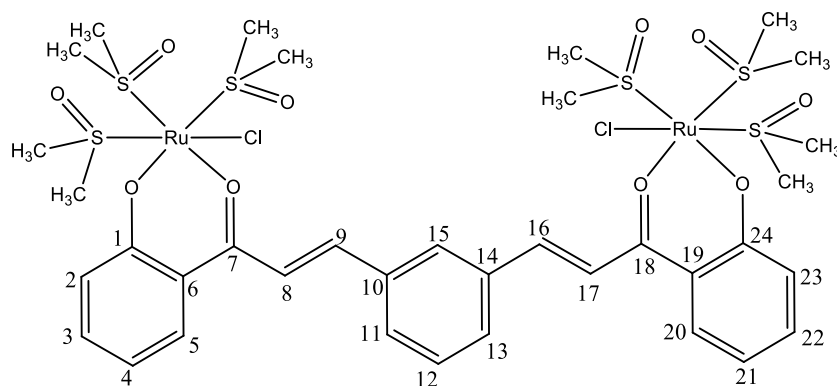
Figure 3.6: Proposed molecular structure of complex CX1 (i) and CX2 (j)

3.2.2.2 (a) 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxideruthenium (II)], CX1



Red solid. Yield: 0.033 g, 22%. IR (KBr, cm^{-1}) ν : 1622 (carbonyl group -C=O stretch), 1542 (aliphatic -C=C- stretch), 1507-1462 (aromatic -C=C- stretch), 1112 (S=O stretch, S-bonded), 423 (Ru-S stretch). ^1H NMR (500 MHz, CDCl_3 , δ ppm) H: 7.77 (d, $J = 8$ Hz, 2H, H-2, 21), 7.68 (d, $J = 15$ Hz, 2H, H-8, 17), 7.61 (s, 4H, H-11, 12, 14, 15), 7.53 (d, 2H, $J = 15$ Hz, H-9, 16), 7.33 (t, $J = 8$ Hz, 2H, H-4, 23), 6.97 (d, $J = 8$ Hz, 2H, H-5, 24), 6.57 (t, $J = 8$ Hz, 2H, H-3, 22), 3.57, 3.47, 3.46, 3.45, 3.38, 3.10 (s, 36H, DMSO, S-bonded). ^{13}C NMR (125 MHz, CDCl_3 , δ ppm) C: 188.60 (C-7, 18), 171.91 (C-1, 20), 142.26 (C-9, 16), 137.10 (C-3, 22), 136.96 (C-10, 13), 132.28 (C-5, 24), 128.98 (C-11, 12, 14, 15), 125.86 (C-4, 23), 125.72 (C-6, 19), 121.78 (C-8, 17), 115.51 (C-2, 21), 47.67 (DMSO, S-bonded), 46.78 (DMSO, S-bonded), 46.29 (DMSO, S-bonded), 44.88 (DMSO, S-bonded), 44.32 (DMSO, S-bonded), 43.08 (DMSO, S-bonded). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 245, 310, 372 and 494. Anal Calcd for $\text{C}_{36}\text{H}_{52}\text{Cl}_2\text{O}_{10}\text{Ru}_2\text{S}_6$: C, 38.95; H, 4.72. Found: C, 40.00; H, 5.20.

3.2.2.2 (b) 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium (II)], CX2



Red solid. Yield: 0.241 g, 43%. IR (KBr, cm^{-1}) ν : 3449 (free $-\text{OH}$), 1628 (carbonyl group - $\text{C}=\text{O}$ stretch), 1548 (aliphatic $-\text{C}=\text{C}-$ stretch), 1510 and 1460 (aromatic $-\text{C}=\text{C}-$ stretch), 1109 ($\text{S}=\text{O}$ stretch, S-bonded), 423 (Ru-S stretch). ^1H NMR (500 MHz, CDCl_3 , δ ppm) H: 7.78 (d, $J = 8$ Hz, 2H, H-2, 23), 7.69 (s, 1H, H-15), 7.66 (d, $J = 15$ Hz, 2H, H-8, 17), 7.62 (d, $J = 8$ Hz, 2H, H-11, 13), 7.53 (d, $J = 15$ Hz, 2H, H-9, 16), 7.47 (t, $J = 8$ Hz, 1H, H-12) 7.35 (d, $J = 8$ Hz, 2H, H-4, 21), 6.97 (d, $J = 8$ Hz, 2H, H-5, 20), 6.58 (t, $J = 8$ Hz, 2H, H-3, 22), 3.57 (DMSO, S-bonded), 3.47 (DMSO, S-bonded), 3.46 (DMSO, S-bonded), 3.45 (DMSO, S-bonded), 3.38 (DMSO, S-bonded), 3.10 (DMSO, S-bonded). ^{13}C NMR (125 MHz, CDCl_3 , δ ppm) C: 188.84 (C-7, 18), 171.84 (C-1, 24), 142.25 (C-9, 16), 136.98 (C-10, 14), 136.15 (C-3, 22), 132.46 (C-5, 20), 129.87 (C-12), 129.71 (C-11, 13), 128.20 (C-15), 125.94 (C-4, 21), 125.81 (C-6, 19), 121.70 (C-8, 17), 115.51 (C-2, 23), 47.67 (DMSO, S-bonded), 46.77 (DMSO, S-bonded), 46.37 (DMSO, S-bonded), 44.28 (DMSO, S-bonded), 43.02 (DMSO, S-bonded). UV-Vis (DCM) ($\lambda_{\text{max}}/\text{nm}$): 253, 328, 374 and 490. Anal Calcd. for $\text{C}_{36}\text{H}_{52}\text{Cl}_2\text{O}_{10}\text{Ru}_2\text{S}_6$: C, 38.95; H, 4.72. Found: C, 38.19; H, 4.92.

3.2.2.3 Characterization

The infrared (IR) spectra were recorded in KBr disc in the wavelength region from 400 to 4000 cm^{-1} using Thermo Scientific Nicolet iS10 FTIR spectrophotometer. The proton (^1H , 500 MHz) and carbon (^{13}C , 125 MHz) NMR spectra were obtained from JEOL 500 MHz FT-NMR spectrometer. Deuterated NMR solvents namely D_2O , and CDCl_3 with the standard solvent reference peak at 4.79 and 7.26, respectively, were used to dissolve the selected sample. The UV-visible data of the complexes were analyzed via UV-1800 Shimadzu UV spectrophotometer while the the respective spectra were plotted using the Origin8 software. The purity of the complexes was confirmed by the percentage of the carbon and hydrogen obtained from CHN analyzer in comparison with the calculated carbon and hydrogen percentage.

3.2.3 Fabrication of dye-sensitized solar cell (DSSC)

The fabrication method of DSSC was based the method as reported in literature (Tsai *et al.*, 2013) with slight modification. Figure 3.7 (k) shows the typical assembly of DSSC and Figure 3.7 (l) shows the complete assembly DSSC. In this DSSC, the FTO glass coated with layers of TiO_2 is the working electrode whereas the ITO glass coated with Platinum acts as the counter electrode. The preparation procedures of each individual component as described in the following sub-sections.

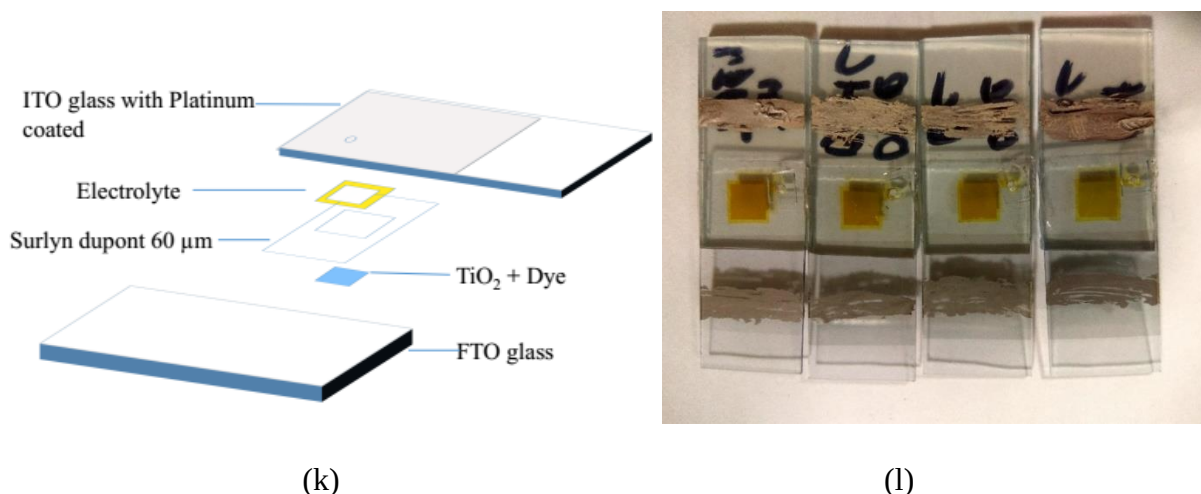


Figure 3.7: Schematic structure of DSSC

3.2.3.1 Preparation of TiO₂ working electrode

Titanium oxide (TiO₂) P25 (5 g) was transferred into a mixture of 30 mL of *tert*-butylalcohol and 15 mL of deionized water in a beaker. It was stirred for overnight to homogenize the paste.

FTO glass (1.5 cm x 3.0 cm) was used in the fabrication. The glass was sonicated with acetone, followed by methanol and deionized water. It was dried at 45 °C for about 10 minutes. Upon completion, it was treated under UV light for 30 minutes. The treated FTO glass was directly used for the TiO₂ coating by using the doctor blade technique. The TiO₂ coating was started from the thickness of 5 μm, followed by 10, 15, 20, 35, 40, 45 and lastly 50 μm. Each coat was kept for 60 minutes' interval gap. The excess TiO₂ was scraped out using microscopic slide to create a dimension of 0.5 cm x 0.5 cm as a working electrode. The film was treated to 150 °C for 90 minutes and annealed to 450 °C for 30 minutes.

3.2.3.2 Preparation of standard dye (N3) solution

The standard dark red dye namely N3 (0.0223 g, 0.03 mmol) was dissolved into a mixture of 50 mL acetonitrile and 50 mL *tert*-butylalcohol in a beaker. Lights were off during the

preparation due to light sensitive of N3. The mixture was capped and sonicated for about 30 minutes. The beaker was covered with aluminium foil to avoid direct light contact.

3.2.3.3 Preparation of bis-chalcone compounds and ruthenium complexes as dye-sensitizer

The respective bis-chalcone compounds and the ruthenium complexes (0.03 mmol) was dissolved into 5 mL of acetonitrile and 5 mL of tertbutylalcohol in a glass vial. The mixture was capped and sonicated for 30 minutes.

3.2.3.4 Preparation of Pt counter electrode

Electron beams evaporation technique (Figure 3.8) was used to coat Pt counter electrode. This technique involves the use of electricity to generate the electron beams in a high pressure vacuum chamber of about 7.5×10^{-5} Torr (10^{-2} Pa) and control of magnetic field to deflect the beams by 180° or 270° onto the evaporation material. The kinetic energy produced from the electricity drove the generated electron beams and upon contact to the evaporation material, they were converted into thermal energy that produces heat to melt or sublimate it. Once sufficient heat and pressure were reached, the vapour evaporated upwards and formed a thin layer film on the substrate that is attached onto the substrate dome.

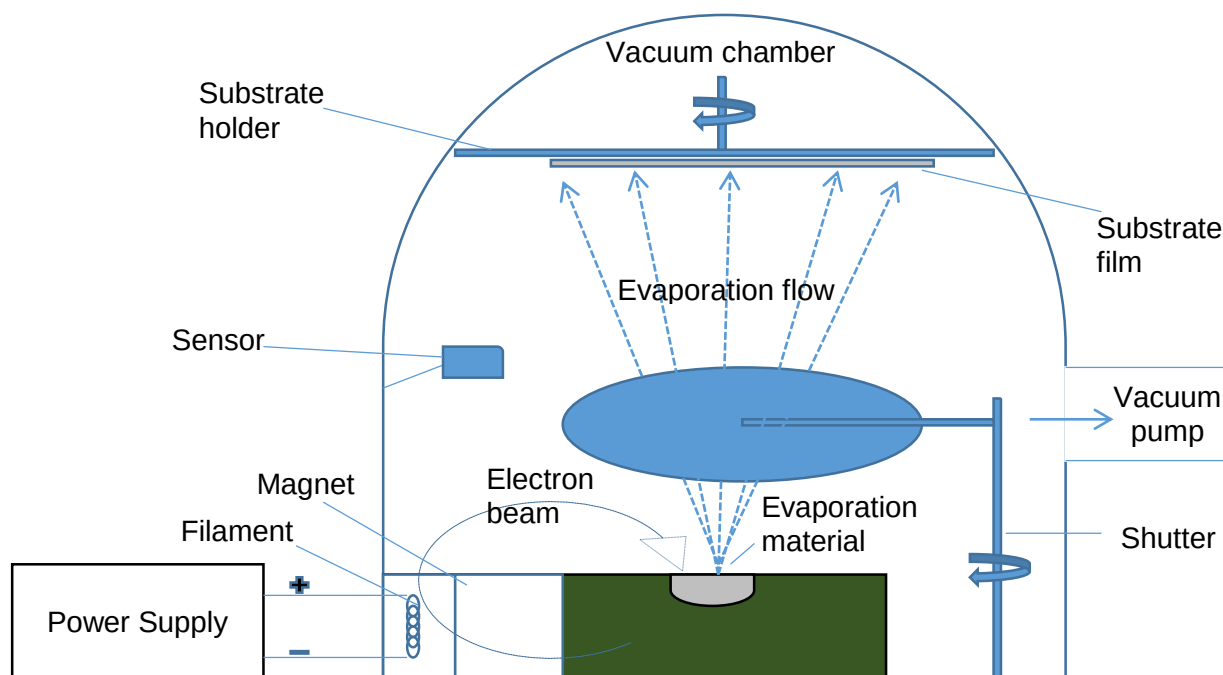


Figure 3.8: Electron beams evaporation technique

3.2.3.5 Composition of electrolyte

The electrolyte was purchased by the National Formosa University. Its composition consists of 0.05 mol iodine (I_2), 0.5 mol lithium iodide (LiI), 0.5 mol 4-tertbutylpyridine (4-TBP) and 1 mol 1,2-dimethyl-3-propylimidazolium (DMPII) in 15 mL 3-methoxypropionitrile (MPN).

3.2.3.6 Preparation of dye-sensitized working electrode

The TiO_2 working electrode was immersed into the N3 dye in a dark room and put into the oven at 45 °C for 120 minutes. Upon completion, the film was taken out and dipped into the acetonitrile solution for few times. It was allowed to air dried.

For the bis-chalcone organic dye, the prepared TiO_2 working electrode was immersed into the respective bis-chalcone compound and put into the oven at 45 °C for overnight. Upon completion, the film was taken out and was allowed to air dried. Meanwhile, similar procedure was performed on the inorganic ruthenium complexes namely CX1 and CX2.

3.2.3.7 Sealing of dye-sensitized solar cell

The working electrode and counter electrode were sealed using the surlyn 60 μm . Electrolyte was injected into the small drilled hole. The hole was sealed with another piece of small glass using the surlyn 60 μm . Silver paste was applied on both of the conductive side. The DSSC was ready to be tested.

3.2.3.8 Characterization

The coated TiO_2 morphology was observed using the Jeol Hitachi S4800-l Field Emission Scanning Electron Microscopy. The Platinum counter electrode was prepared *via* electron beam evaporation technique by using ULVAC HPS-510S machine. The fabricated DSSC was illuminated under San Ei XES-40S1 Solar Simulator under monochromatic light of air mass 1.5 global (AM 1.5G) with the incident light intensity of 100 mW/cm^2 . The J/V measurement of the solar cell efficiency was recorded using the Keithley 2400 and the data was plotted *via* Origin8 software.

The J/V measurement was recorded using the Keithley 2400 source meter with illuminating monochromatic light of air mass 1.5 global (AM 1.5G) with the incident light intensity of 100 mW/cm^2 . The working dimension for the solar cell was set at 0.25 cm^2 . The J/V measurement graph of solar circuit current density (J_{sc} , mAcm^{-2}) against voltage (V) was plotted using the Origin8 Pro SR4 software. The power conversion efficiency of the solar cell can be calculated using the equation as shown in Eq 3.1 below:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \quad \text{Eq. 3.1}$$

where

J_{sc} = solar circuit current density (mA/cm²)

V_{oc} = open circuit photovoltage (V)

FF = fill factor (%)

P_{in} = incident light intensity (100 mW/cm²)

η = power conversion efficiency (%)

CHAPTER 4

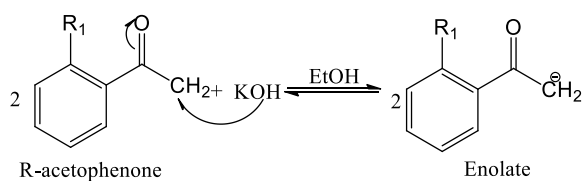
RESULTS AND DISCUSSION

4.1 Results and discussion on synthesized bis-chalcone compounds

4.1.1 Working mechanism on synthesis of bis-chalcone derivatives

The Claisen Schmidt condensation mechanism of the bis-chalcone derivative is illustrated in Scheme 4.1. Initially, the hydroxide ion of the base solution such as KOH attacks the acidic α -hydrogen of the R-substituted acetophenone to form enolate. Next, the enolates attack the carbonyl group of each side that present in the R-substituted terephthalaldehyde or isophthalaldehyde. This causes the two electrons from the carbonyl double bond to transfer to the oxygen atom and form alkoxide. In the neutralization process with HCl, the alkoxide deprotonates the acid and produced the hydroxide ions to generate the aldol product. For the following step, the hydroxide ions in the solution attack the acidic α -hydrogens and form the nucleophile enolate ions. Lastly, protons transfer and removal of hydroxyl groups take place to form the conjugated α,β -unsaturated carbonyl system.

Step 1: Formation of enolate



Series 1

1A: $R_1 = \text{H}$, $R_2 = \text{H}$

1B: $R_1 = \text{OH}$, $R_2 = \text{H}$

Series 2

2A: $R_1 = \text{H}$

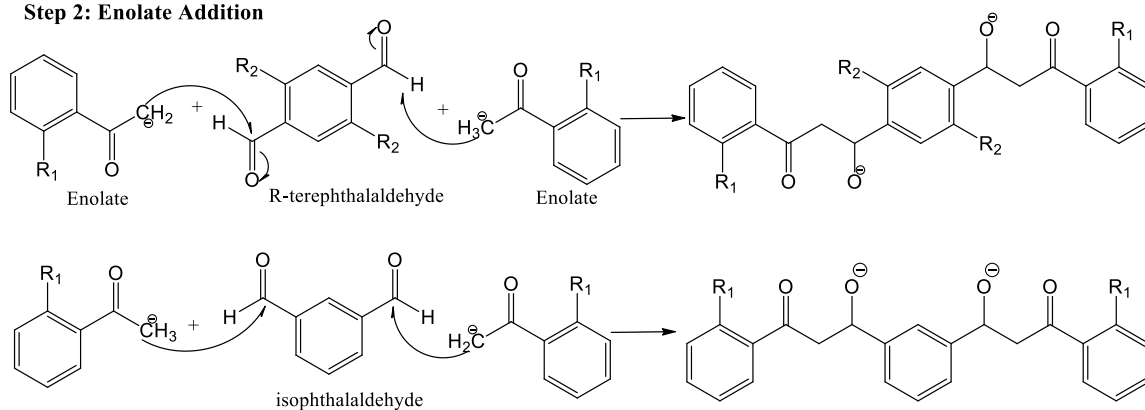
2B: $R_1 = \text{OH}$

Series 3

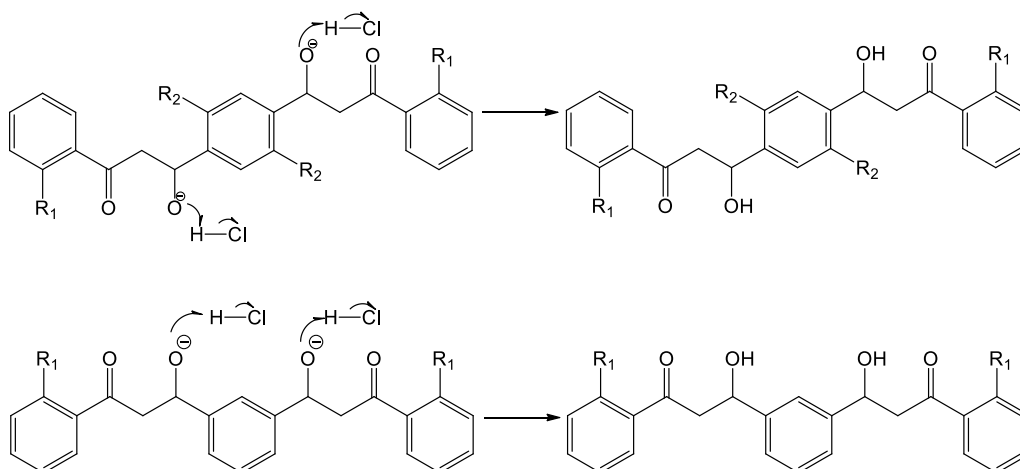
3A: $R_1 = \text{H}$, $R_2 = \text{OMe}$

3B: $R_1 = \text{OH}$, $R_2 = \text{OMe}$

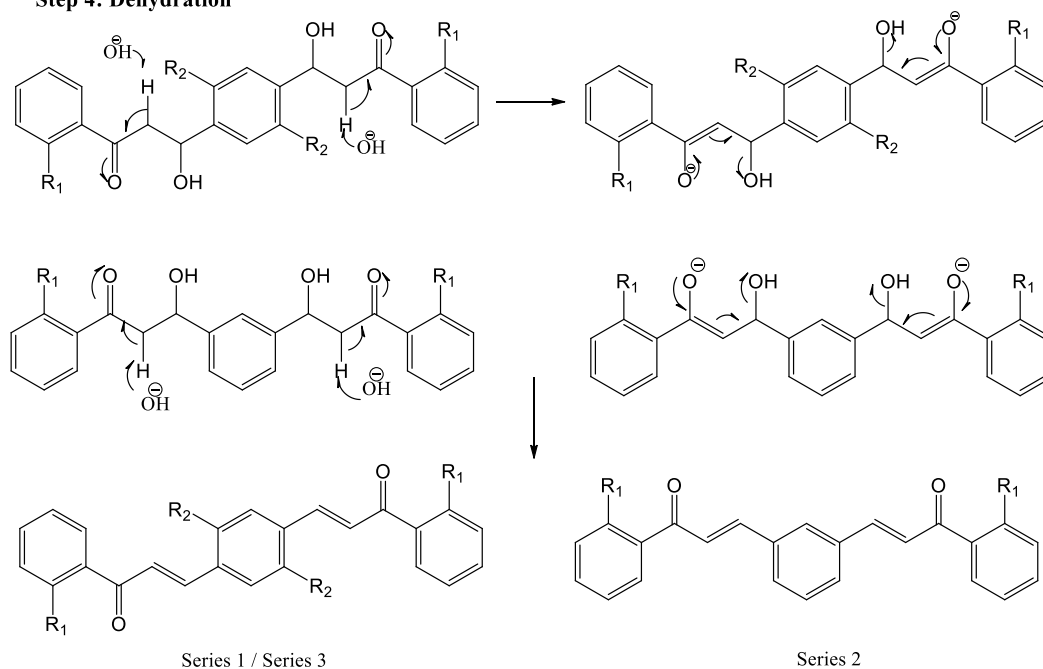
Step 2: Enolate Addition



Step 3: Neutralization/Protonation



Step 4: Dehydration



Scheme 4.1: Claisen-Schmidt condensation mechanism of bis-chalcone derivatives

4.1.2 Strategy in bis-chalcone synthesis and work up

In general, three series of bis-chalcone derivatives have been successfully synthesized through Claisen-Schmidt condensation reaction at room temperature. Despite the fact that the method used was similar, the work up procedures to obtain the pure compounds differed to each other. Some issues that have been identified were the substituents presence and the chemical structure of the bis-chalcone compounds. Based on the experimental experience, the synthesis of parent compounds (i.e. R = H) for every series did not encounter any major problems in obtaining pure products. However, for the bis-2'-hydroxychalcone derivatives, problems such as black oily gel, coagulation of precipitate and failure in recrystallization were commonly observed along the experimental work up. Hence, the discussion on the synthesis and work up in this section are emphasizing more in bis-2'-hydroxychalcone derivatives.

In series 1, the path to synthesize **1B** was relatively easier compared to the other two derivatives. The reactants involved in the reaction were namely 2'-hydroxyacetophenone and terephthalaldehyde with the aid of KOH solution in ethanol at room temperature. The precipitate was obtained in high yield (78%) after neutralized with 3.0 M HCl. Nevertheless, it is advisable to dilute the mixture with cold water before conduct the neutralization process in order to prevent the coagulation of the precipitate. Besides, neutralization commonly known to be exothermic reaction which generates heat and this could be one of the causes that promote the coagulation during the process and thus forming gel-like precipitate. The precipitate was washed thoroughly with distilled water and ethanol to get rid of the excess salts and other impurities.

When the precipitate was spotted on the thin layer chromatography (TLC) plate and eluted with DCM as the mobile phase, three spots were observed under the short wavelength of 254 nm, indicating the formation of desired product with the by-products remained. As reported

by Pinto *et al.*, (2003), the by-products seen under the TLC was formed due to the Cannizzarro reaction during the synthesis duration, where the terephthalaldehyde undergo redox disproportionation in the presence of strong base and produced the carboxylate acid and alcohol. After several trials, the precipitate was able to be purified via single solvent recrystallization method using either the THF or DMF in an intermediate yield.

Unfortunately, the attempt on the synthesis of donor-acceptor bis-chalcone (compound **1D**) was failed due to the unstable reaction and purification. Nevertheless, it is worth to mention that the intermediate compound **1C** was synthesized by reacting 2'-hydroxyacetophenone with terephthalaldehyde in 1:1 mole ratio in order to obtain mono-substituted chalcone. The reaction was carried out in weak base (i.e. triethylamine) instead of strong base in ethanolic solution. The used of strong base such as NaOH and KOH would result in more by-products due to its high reactivity. The synthesis duration for this compound required at least 24 hours to yield the yellow precipitate. The precipitate was filtered and the filtrate was stirred again in order to yield more yellow precipitate. In contrast with the work up of **1B**, the neutralization step of compound **1C** could be omitted completely since only weak base was used. In fact, triethylamine salt is very soluble in water, thus the precipitate was washed thoroughly with distilled water and dried. The pure compound **1C** was obtained by repetitive recrystallization with DCM.

On the other hand, the series 2 bis-chalcone namely **2B** was successfully synthesized despite the multiple fail attempts. As comparison with the **1B**, the difference in molecular structure is mainly the substituent of the aldehyde at the *meta* and *para* position, respectively. From the experience gained, the formation of **2B** is relatively heat sensitive, less reactive and unstable. Few strategies have been tried out in obtaining the best yield. Basically, strategy 1 was similar to the previous series, but a higher concentration of KOH was recommended to deprotonate

the 2'-hydroxyacetophenone due to the less reactive *meta* site. Furthermore, the addition of cold water to dilute the mixture before neutralized with HCl was necessary because it easily coagulated into oily gel precipitate at room temperature due to the exothermic reaction during the process. The precipitate was washed several times with distilled water and ethanol before proceed to the crystallization in order to remove the excess salts and impurities. Surprisingly, the solubility of the precipitate is readily dissolved in DCM, THF and DMF at room temperature, but the attempts for recrystallization was not successful. Instead of forming the crystal or pure compound, the gel precipitate was obtained frequently. This may due to the high solubility of the precipitate at room temperature in a minimum volume of solvent, which makes the by-products formed through the Cannizarro reaction to precipitate out with the desired product (Pinto *et al.*, 2003).

For this reason, strategy 2 was performed by using the column chromatography technique in order to separate out the desired compound. The mobile phase used was the DCM solvent and the yellow solution was collected every three minutes due to the close RF distance between the desired compound and the by-products. From the results obtained, the first yellow compound that eluted out was the compound **2B**, which formed crystal directly upon drying up. However, the yield obtained was very low (< 10%) indeed.

Therefore, the attempt of using the extraction method was carried out. Unexpectedly, the pure yield obtained seems to be much better compared to the first two strategies. Instead of neutralized with HCl after the dilution with cold water as mentioned in strategy 1, the mixture was straight away extracted with DCM and allowed to stand for 30 minutes before separated out in order to allow the yellow mixture to diffuse from water and ethanol mixture into the DCM layer. The DCM was then evaporated out totally and the TLC analysis was performed to the yellow precipitate formed. From the analysis, only one spot was observed in the TLC

plate under short UV wavelength at 254 nm. The precipitate was recrystallized with minimum amount of DCM and the pure yield obtained was around 27%.

Meanwhile, the structure of bis-chalcone derivatives in series 3 are likely similar with the series 1 but with the additional of 2 methoxy groups present at the central phenyl ring. As for the work up of **3B**, the purification of the precipitate was performed by washing with ethanol several times to get rid of the by-products. The attempts of crystallized the precipitate using hot DCM and THF were impure as seen in the NMR data. Hence, hot DMF was chosen due to its high boiling point and low volatility which enable the slow formation of crystal within the solvent at room temperature. However, the solubility of the crystal in deuterated chloroform and dimethylsulfoxide was hardly soluble which causes the difficulty of obtaining signals in the NMR spectra especially for the carbon-13 NMR.

Interestingly, among all the series, **3A** exhibits the luminescence property with strong emission at 506 nm due to presence of the methoxy groups at the central phenyl ring (Tiong, 2014). Moreover, according to Tay *et al.* (2016) research, the solvatochromism study showed that the used of higher solvent polarity would cause an bathochromical shift to a lower energy in the UV spectrum. This is due to the interaction of dipole moment between the polar solvent molecules and **3A** is relatively larger than in non-polar solvent, hence, the excited molecule is stabilized in polar solvent rather than non-polar solvent (Han *et al.*, 2003). Conversely, compound **3B** does not show any luminescence under UV radiation. Indeed, none of the bis-chalcone derivatives containing hydroxyl substituent exhibited luminescent property. This is due to the fact that the excited energy loses through the intramolecular torsional motions and *cis-trans* isomerization in the α ,-unsaturated ketone moiety (Fayed & Awad, 2004; Wei *et al.*, 2011).

From the above detailed explanation, all the compounds were obtained successfully except for compound **1D**, where the attempt to get pure crystal was not succeeded. The spectroscopic data for each series of bis-chalcone compounds, namely Series 1 (**1A**, **1B** and **1C**), Series 2 (**2A** and **2B**) and Series 3 (**3A** and **3B**) were arranged in the order of IR, NMR and UV-visible.

4.1.3 Spectroscopic data of Series 1 bis-chalcone

4.1.3.1 (2E, 2'E)-3-3'-(1,4-phenylene)bis(1-phenylprop-2-en-1-one), **1A**

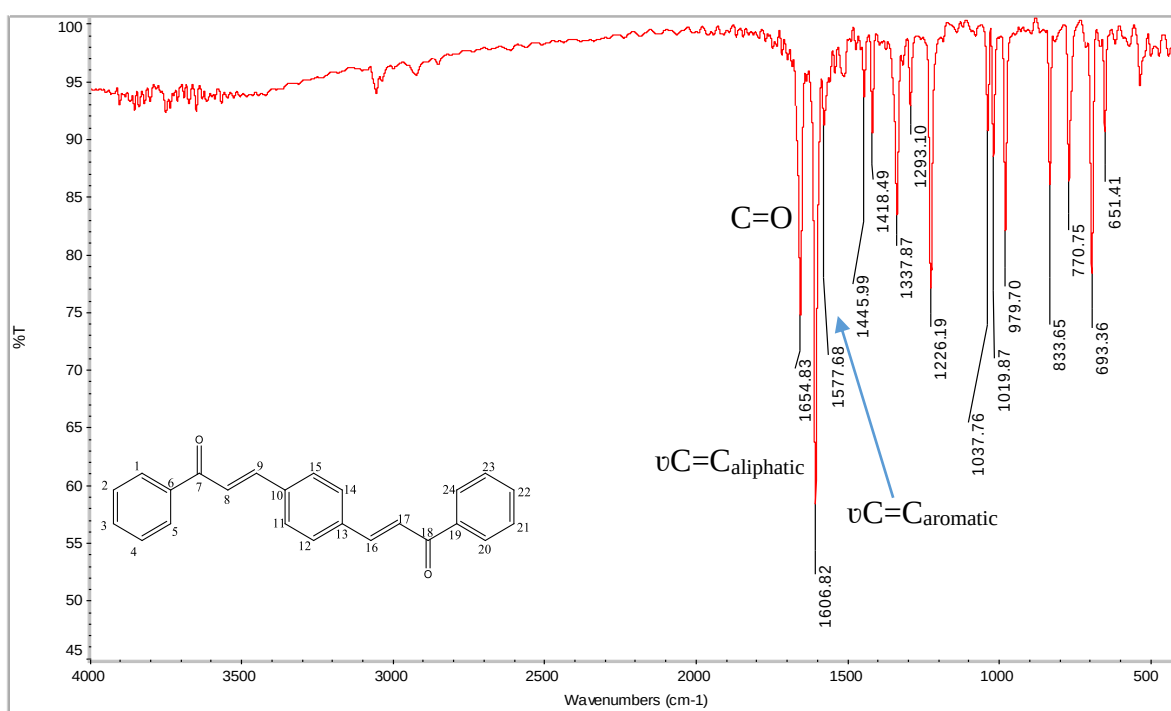


Figure 4.1: FT-IR spectrum of compound **1A**

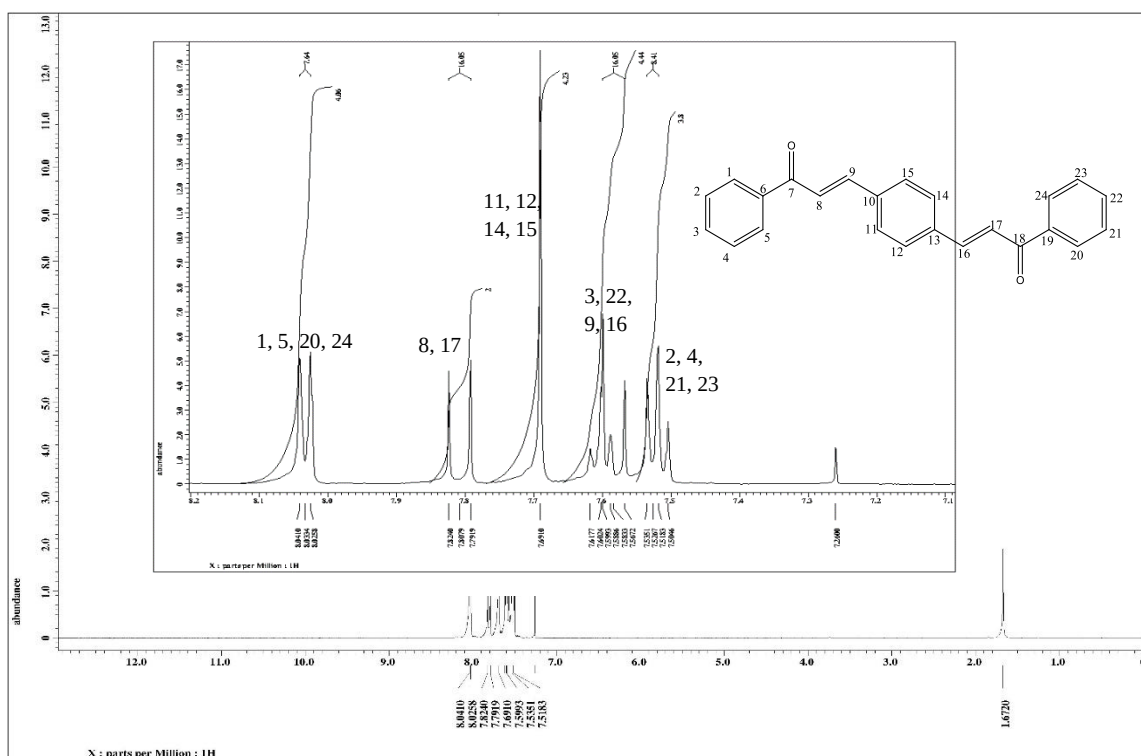


Figure 4.2: ^1H NMR spectrum of compound 1A

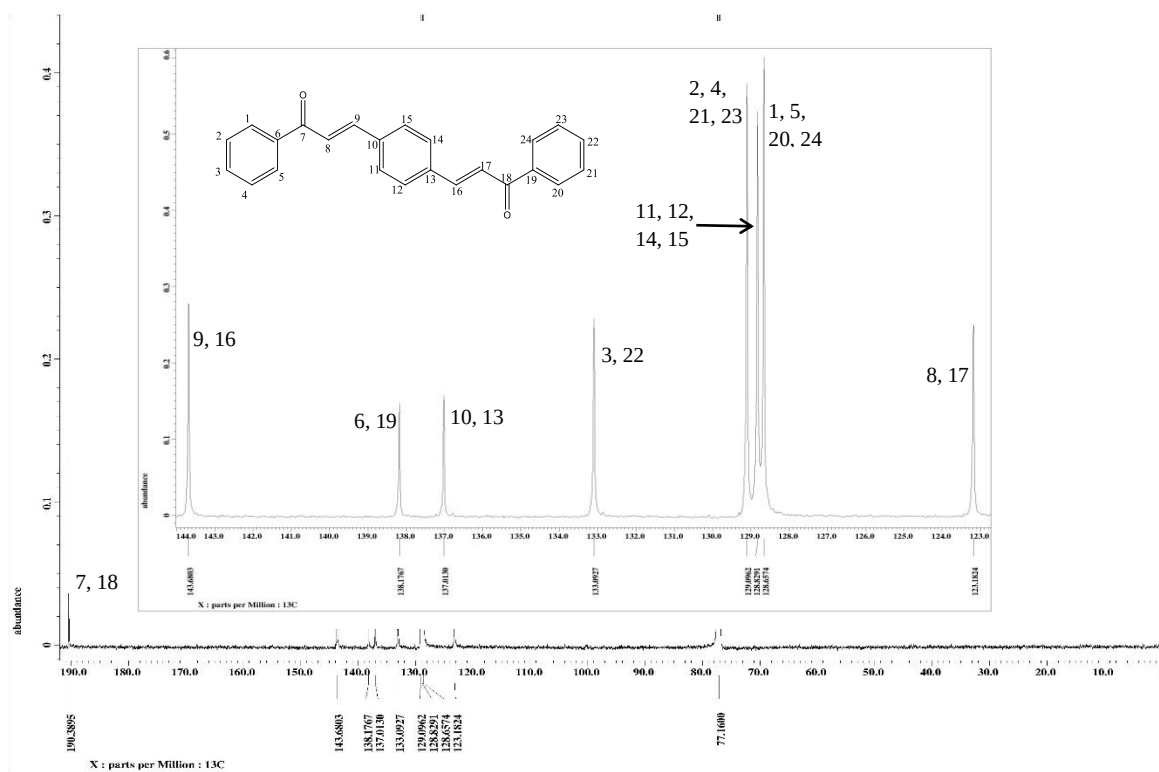


Figure 4.3: ^{13}C NMR spectrum of compound 1A

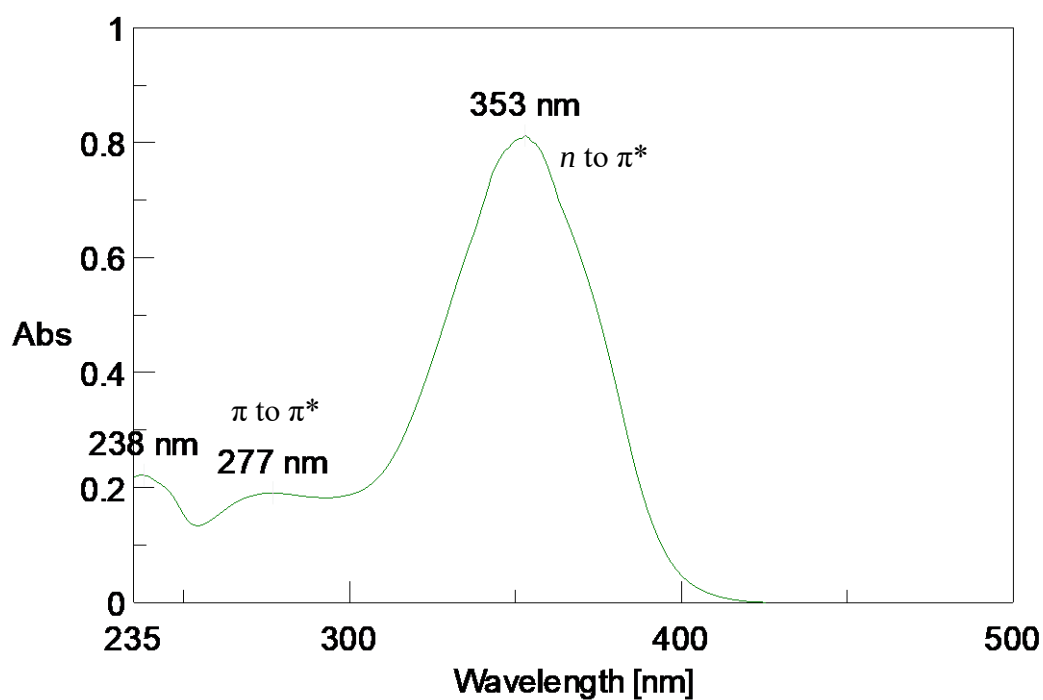


Figure 4.4: UV-visible spectrum of compound 1A

4.1.3.2 (2E, 2'E)-3-3'-(1-4-phenylene)bis(1-(2-hydroxy phenyl) prop-2-en-1-one),
1B

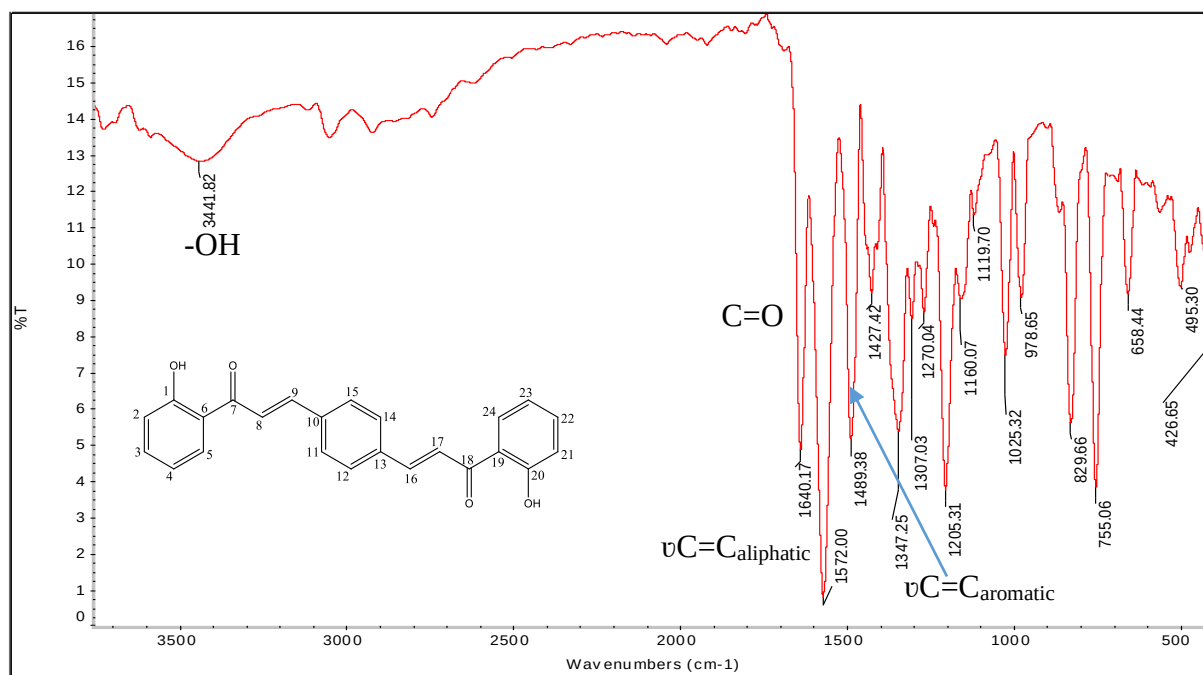


Figure 4.5: FT-IR spectrum of compound 1B

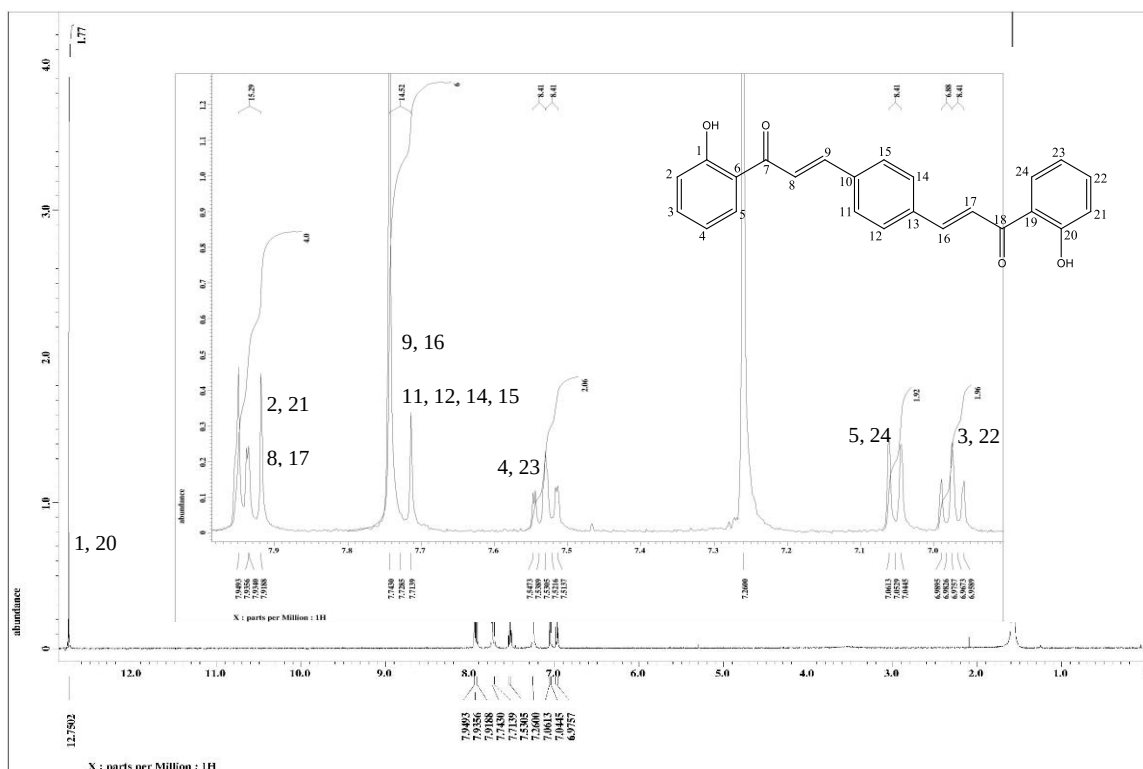


Figure 4.6: ¹H NMR spectrum of compound 1B

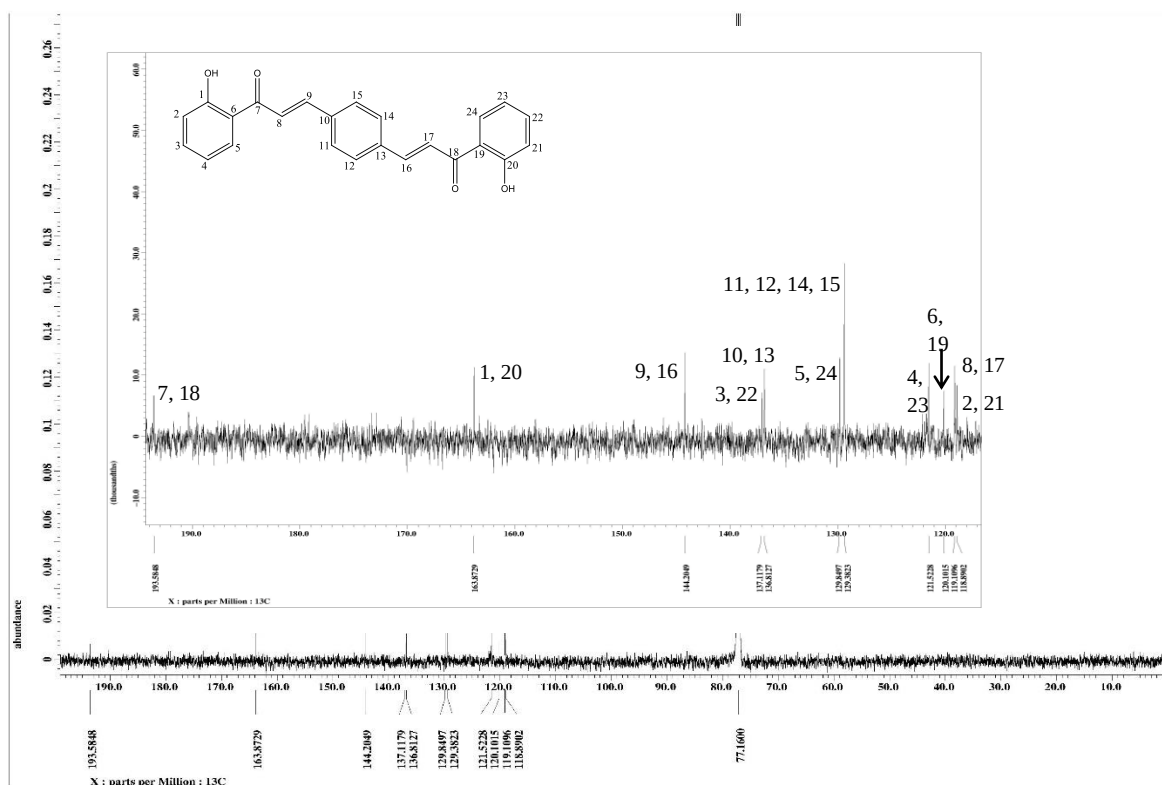


Figure 4.7: ¹³C NMR spectrum of compound 1B

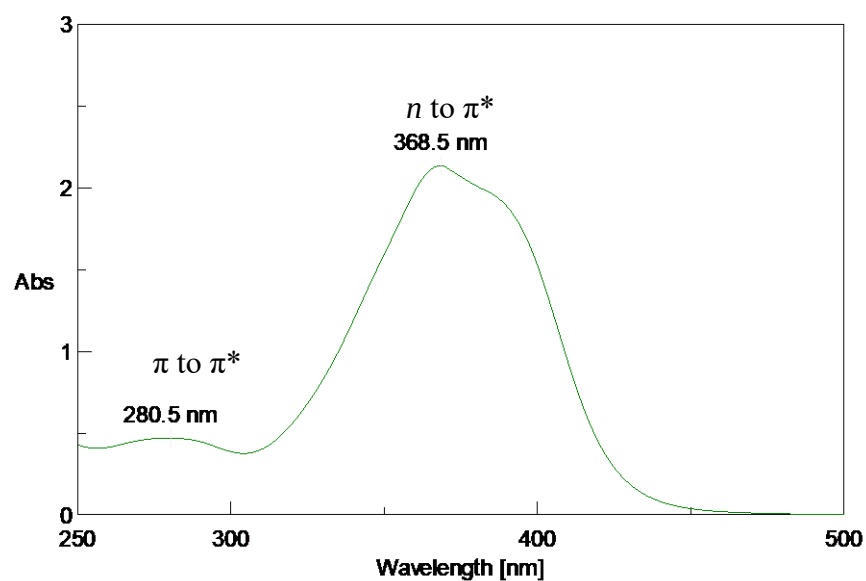


Figure 4.8: UV-visible spectrum of compound **1B**

4.1.3.3 (E)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl) benzaldehyde, **1C**

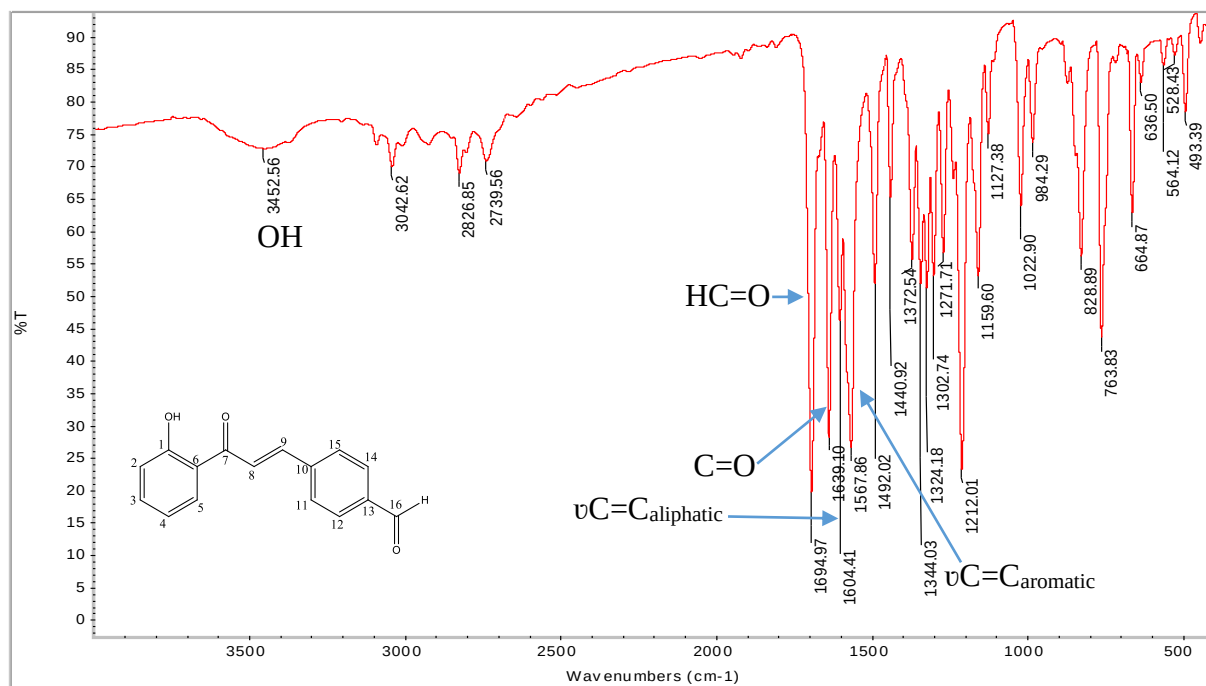


Figure 4.9: FT-IR spectrum of compound **1C**

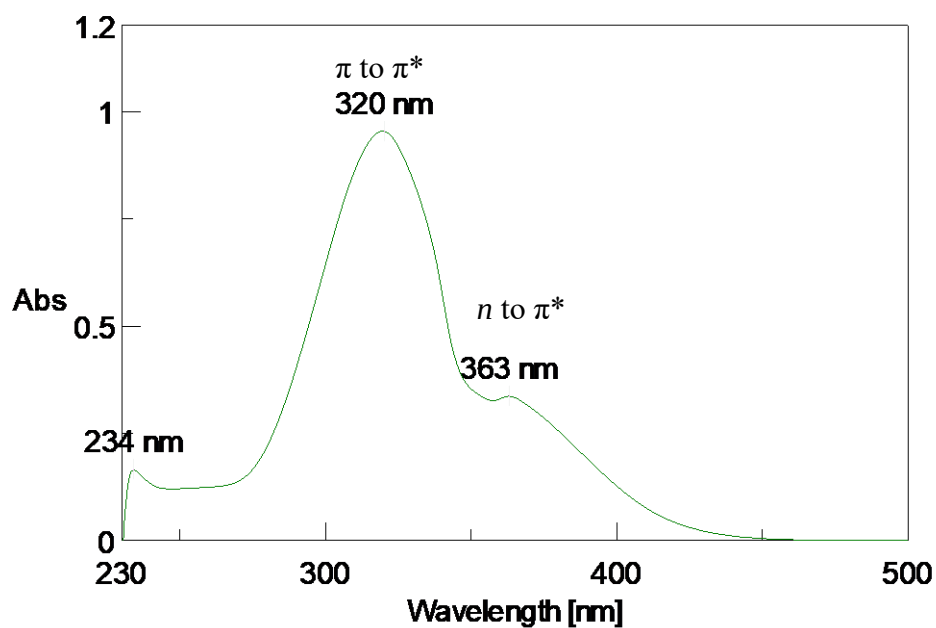


Figure 4.12: UV-visible spectrum of compound 1C

4.1.4 Spectroscopic data of Series 2 bis-chalcone

4.1.4.1 (2E, 2'E)-3,3'-(1,3-phenylene)bis(1-phenylprop-2-en-1-one), 2A

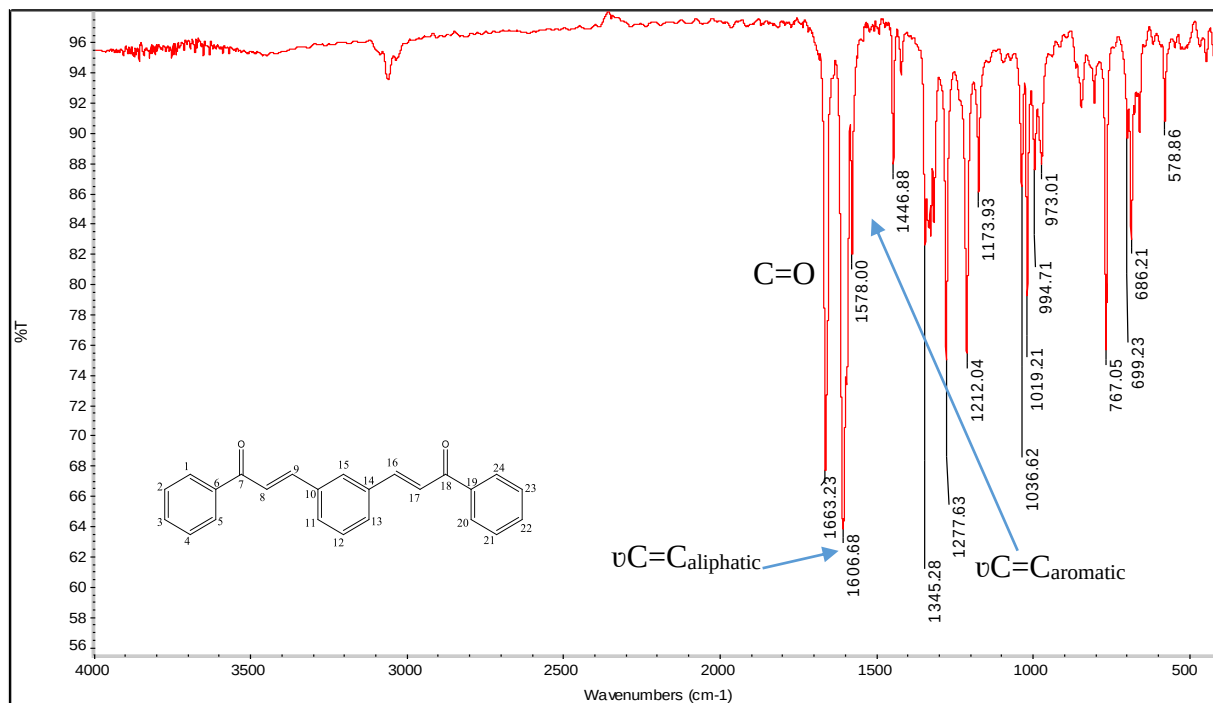


Figure 4.13: FT-IR spectrum of compound 2A

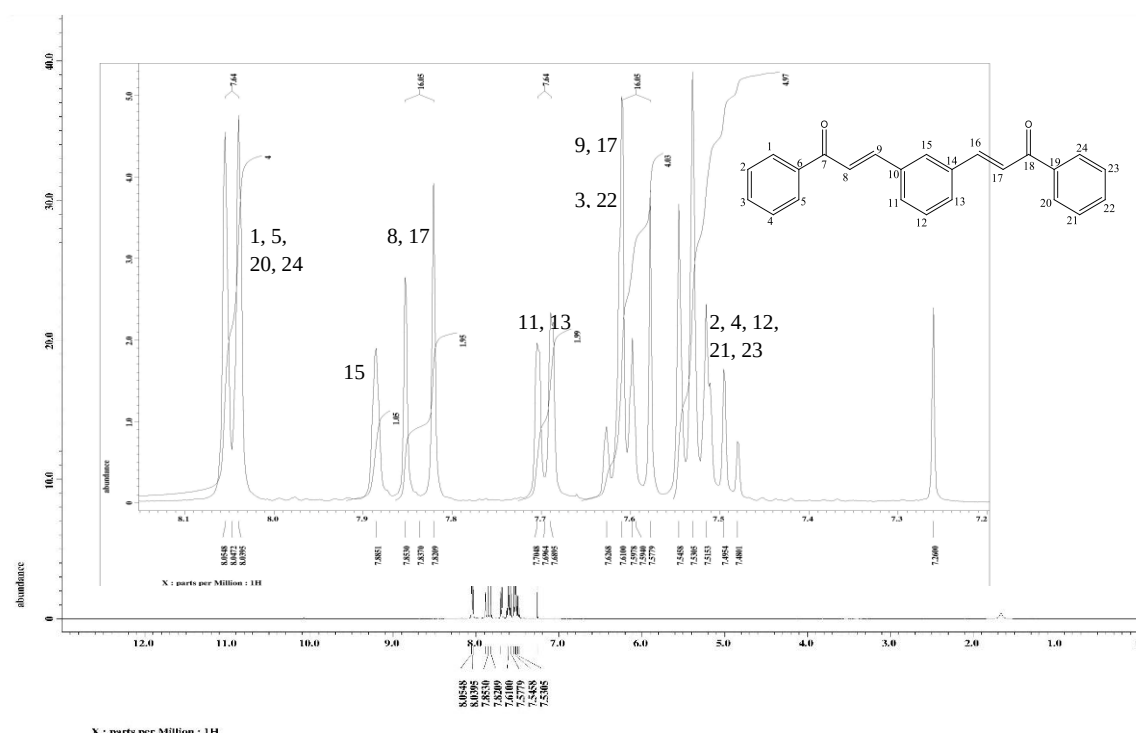


Figure 4.14: ¹H NMR spectrum of compound 2A

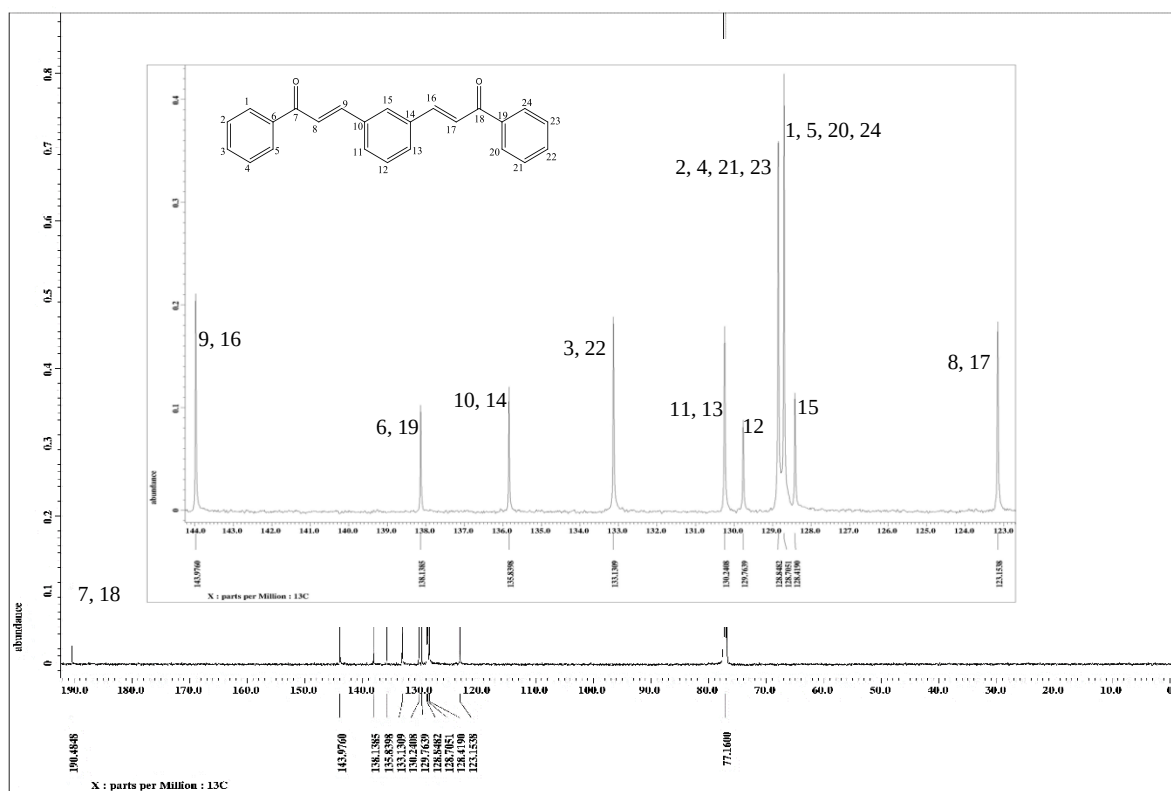


Figure 4.15: ¹³C NMR spectrum of compound 2A

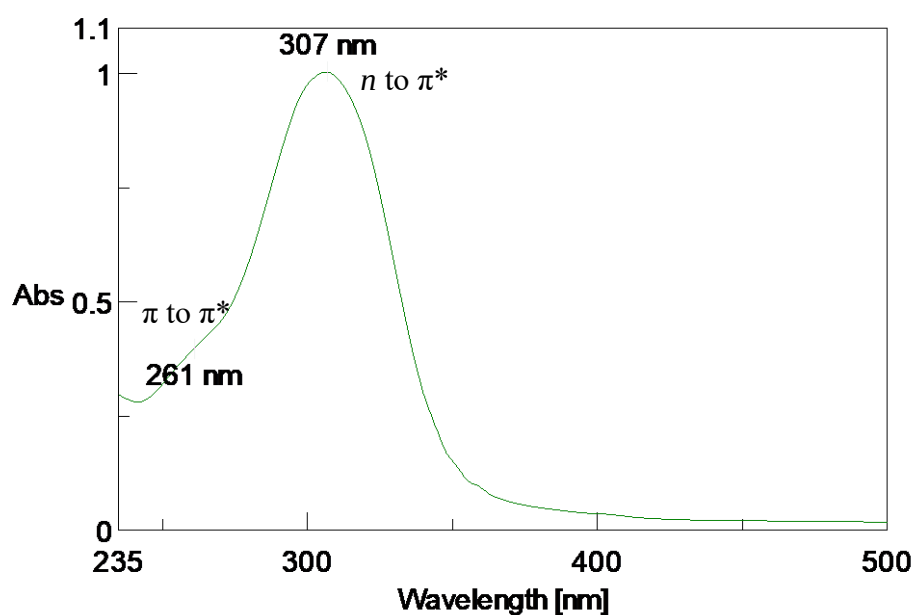


Figure 4.16: UV-visible spectrum of compound 2A

4.1.4.2 (2E, 2'E)-3-3'-(1,3-phenylene)bis[1-(2'-hydroxyphenyl) prop-2-en-1-one],
2B

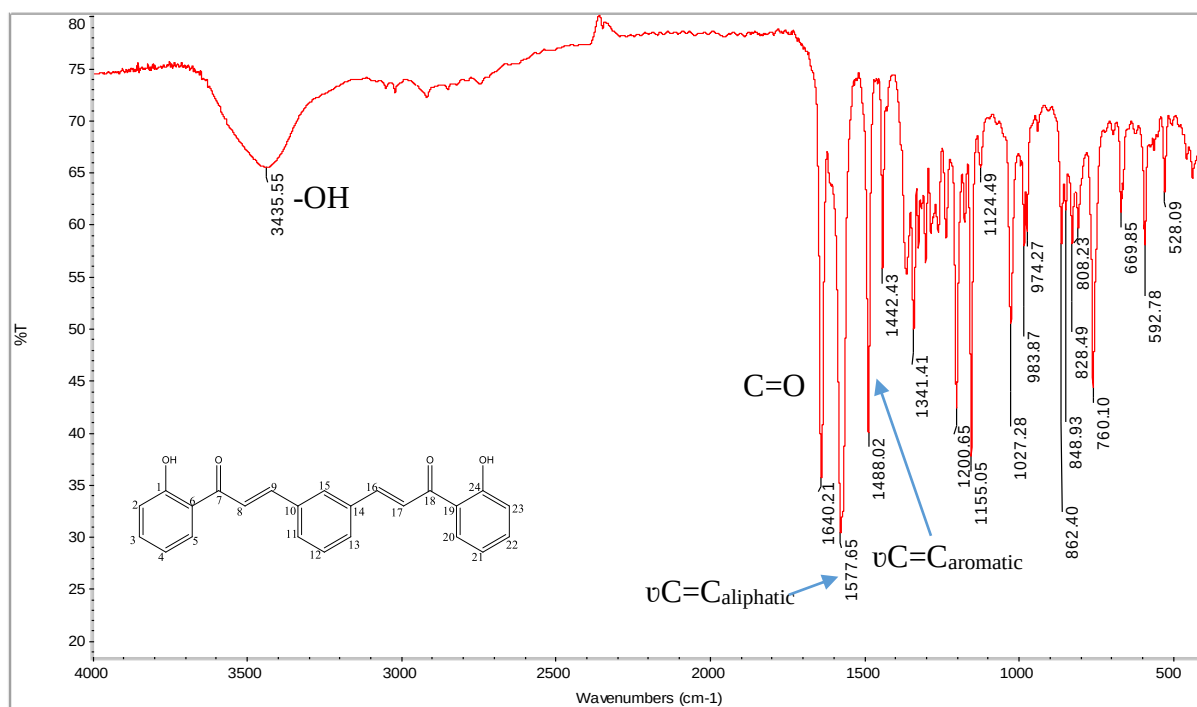


Figure 4.17: FT-IR spectrum of compound 2B

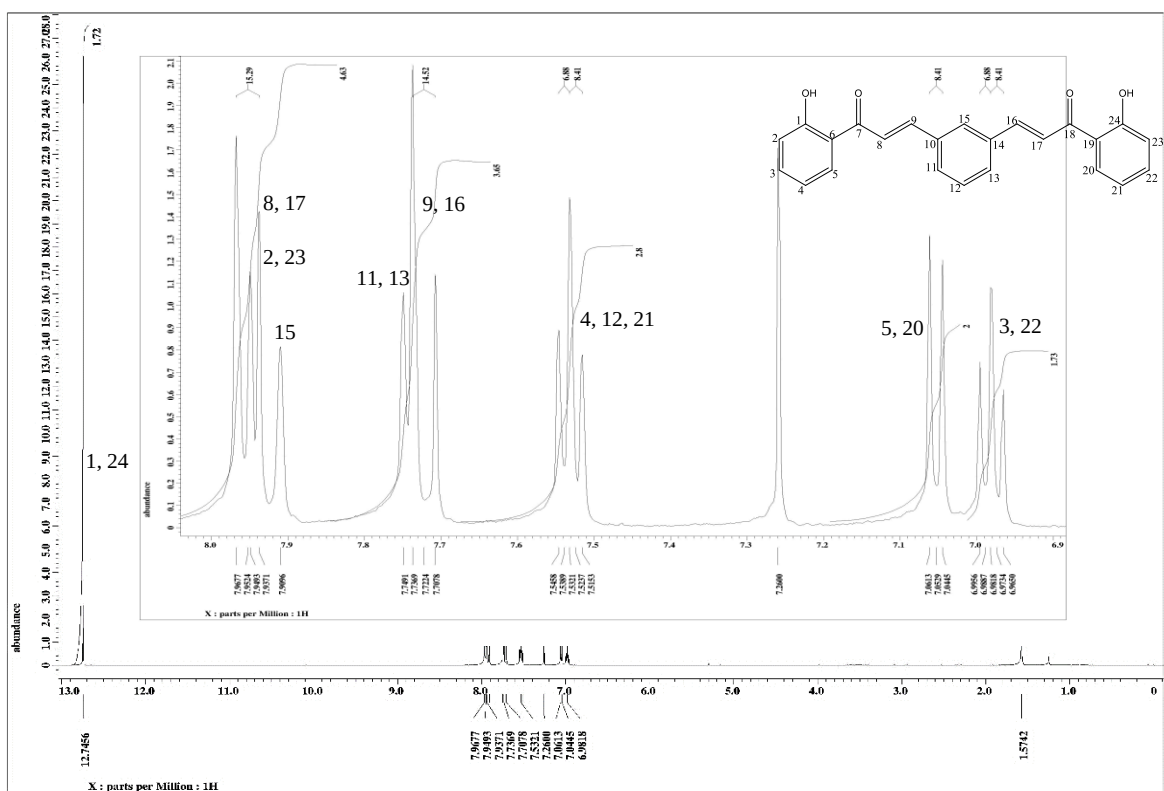


Figure 4.18: ^1H NMR spectrum of compound **2B**

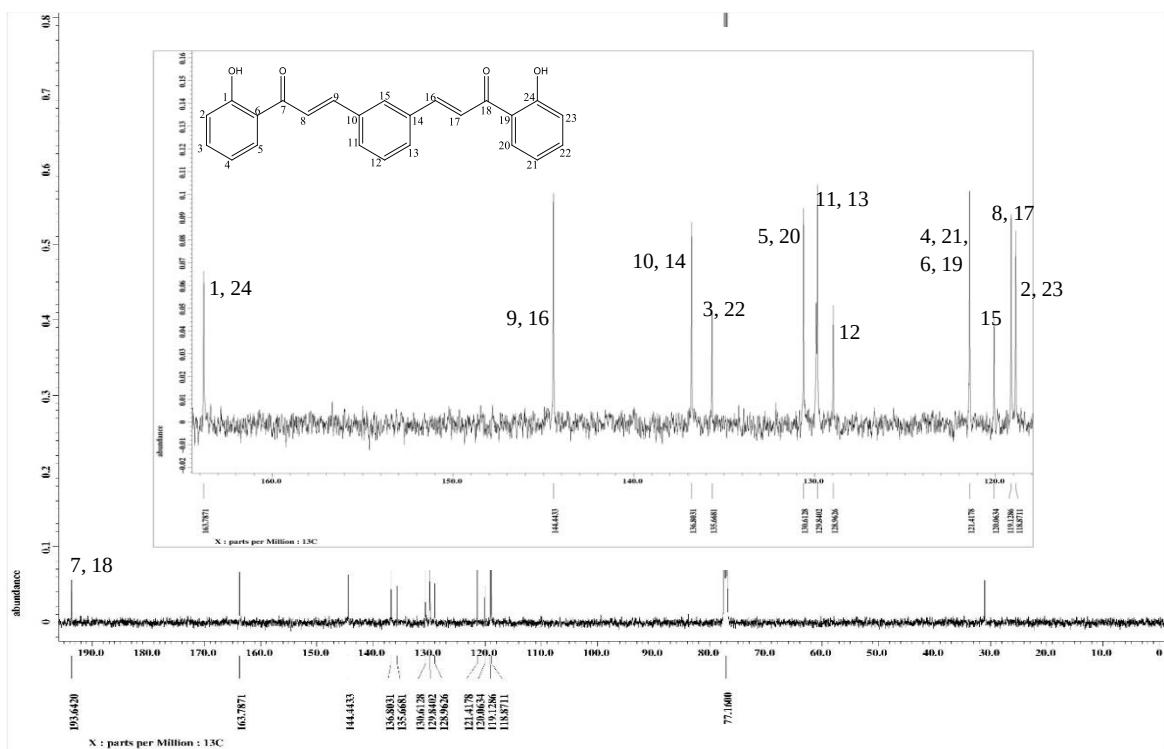


Figure 4.19: ^{13}C NMR spectrum of compound **2B**

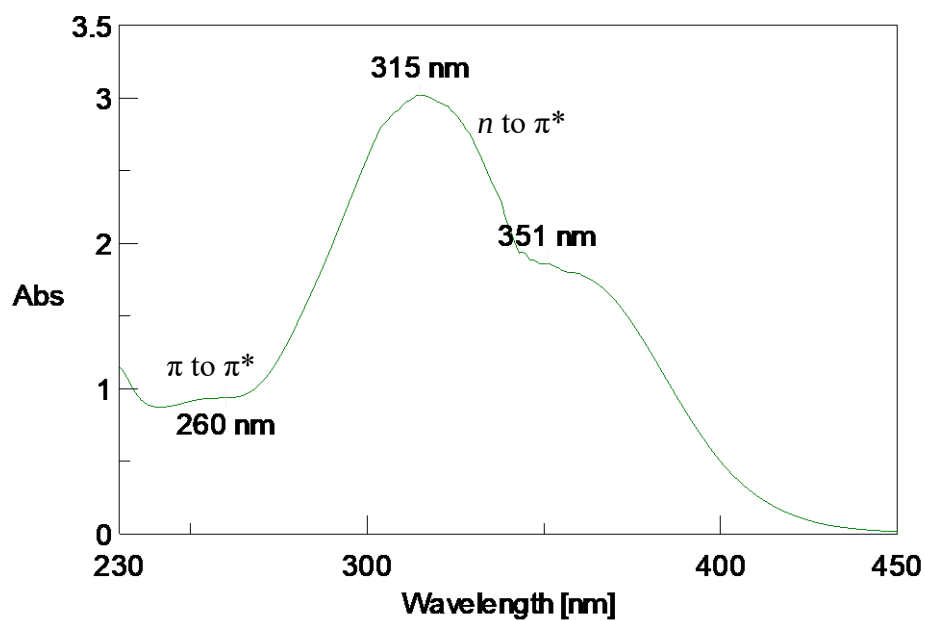


Figure 4.20: UV-visible spectrum of compound 2B

4.1.5 Spectroscopic data of Series 3 bis-chalcone

4.1.5.1 (2E, 2'E)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-phenylprop-2-en-1-one), 3A

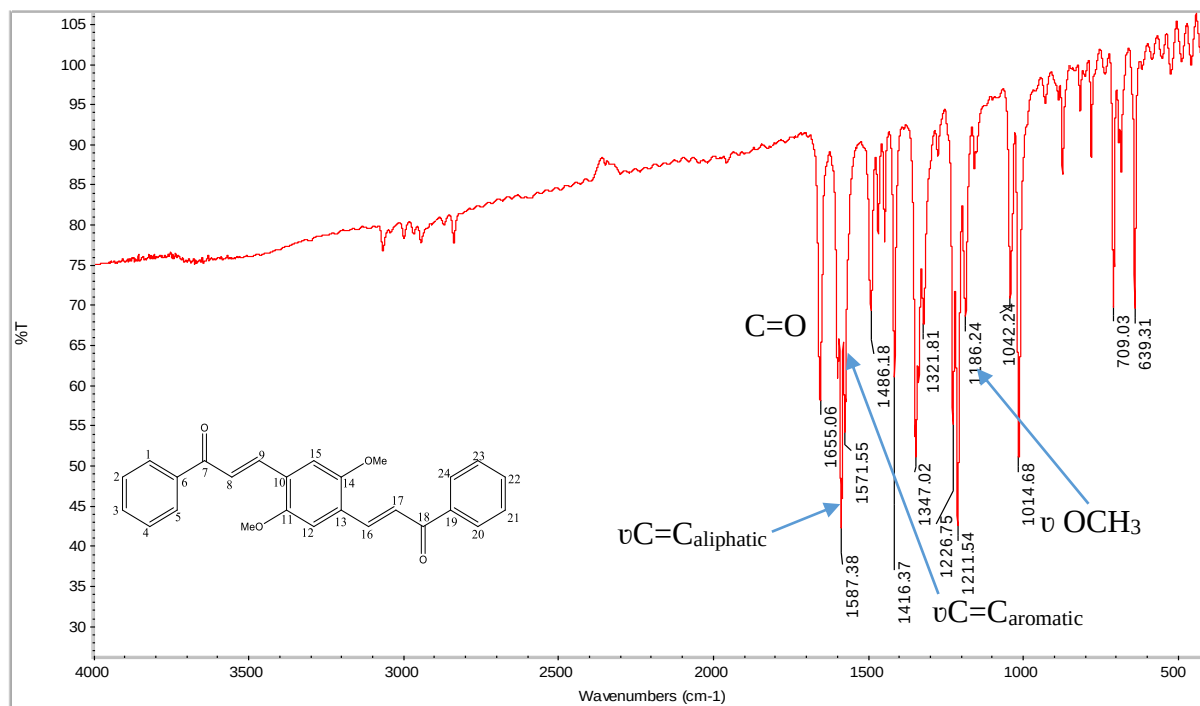
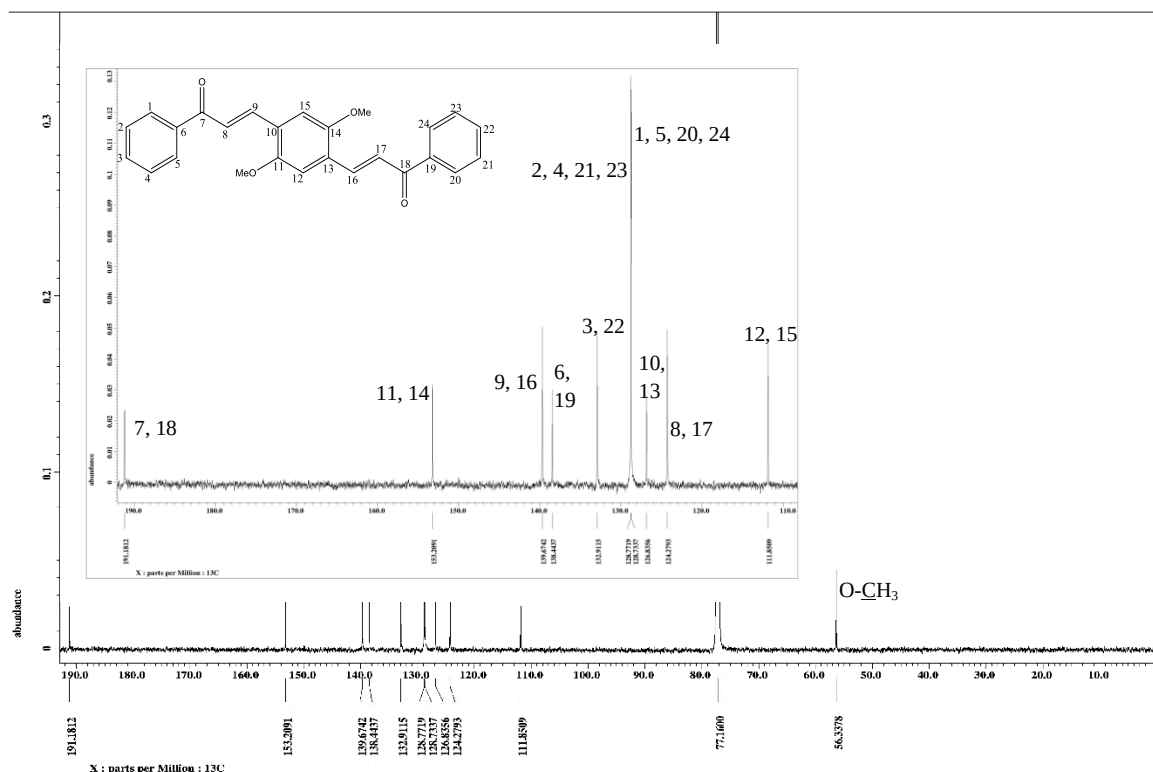
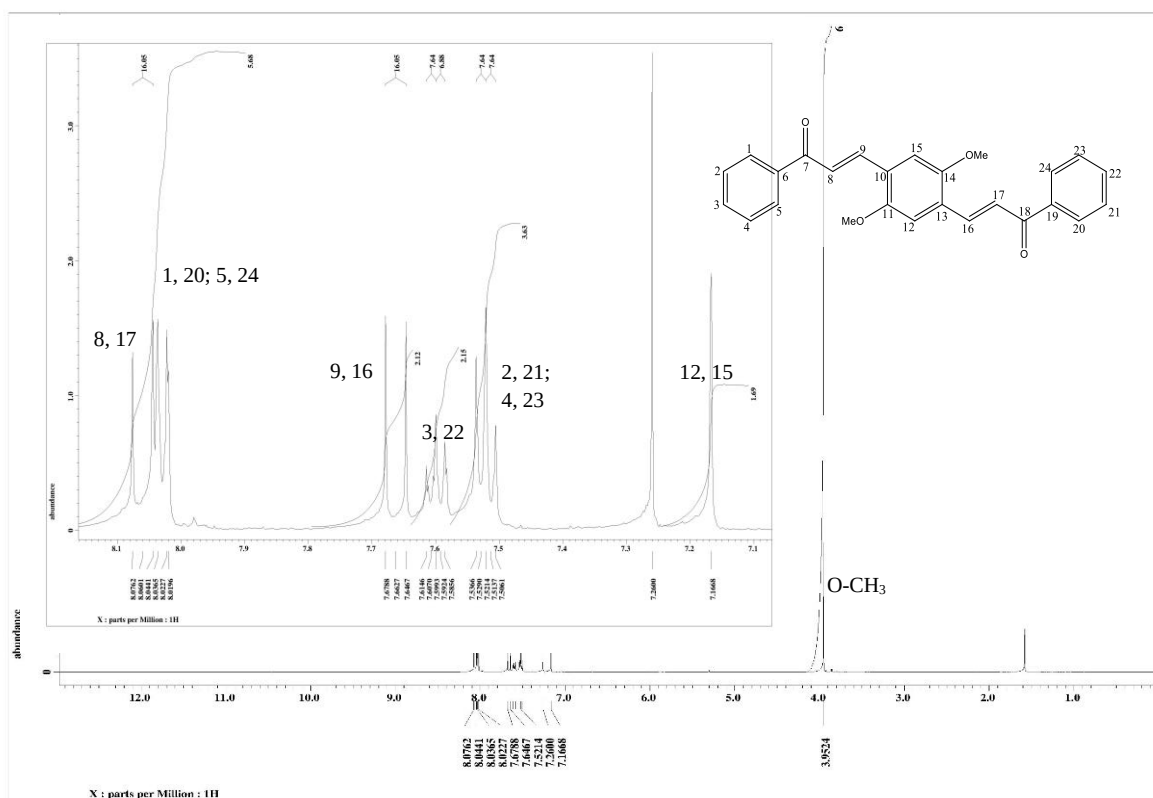


Figure 4.21: FT-IR spectrum of compound 3A



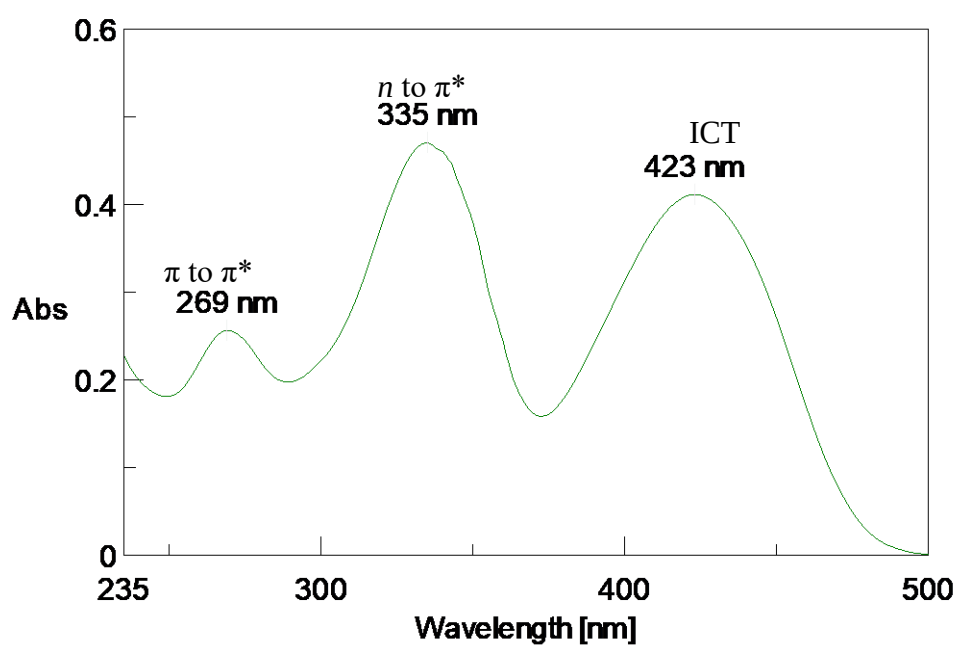


Figure 4.24: UV-visible spectrum of compound 3A

4.1.5.2 (2E, 2'E)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(1-[2'-hydroxyphenyl] prop-2-en-1-one), 3B

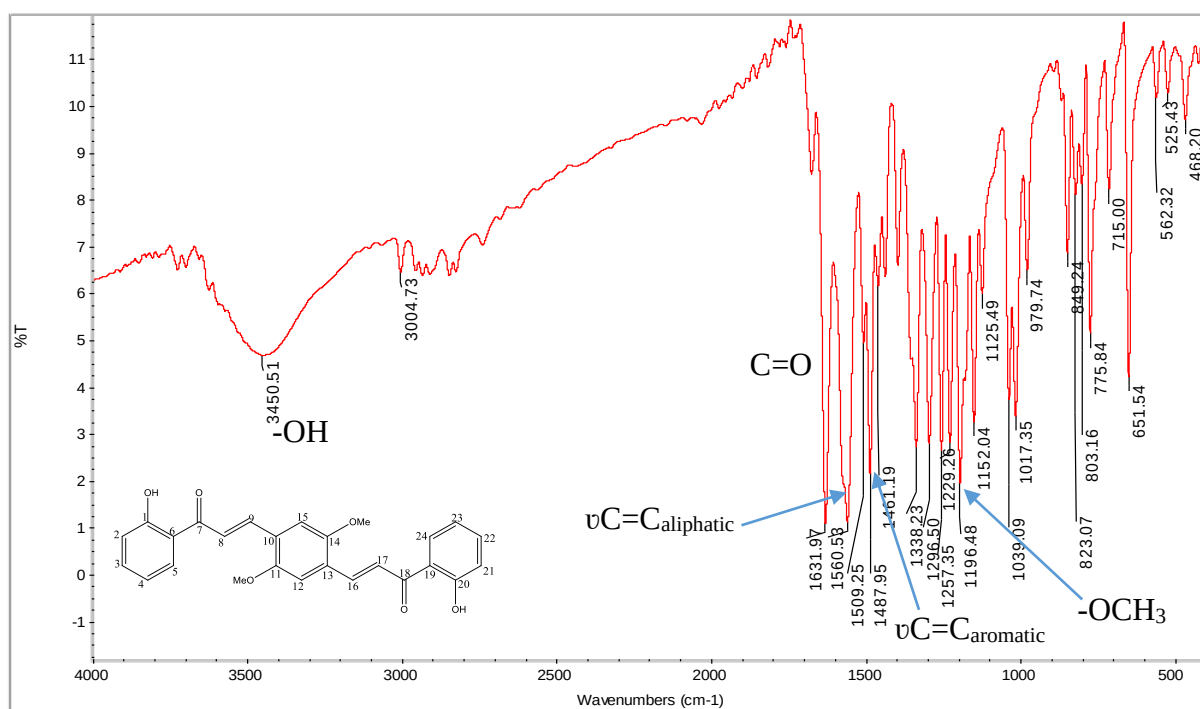


Figure 4.25: FT-IR spectrum of compound 3B

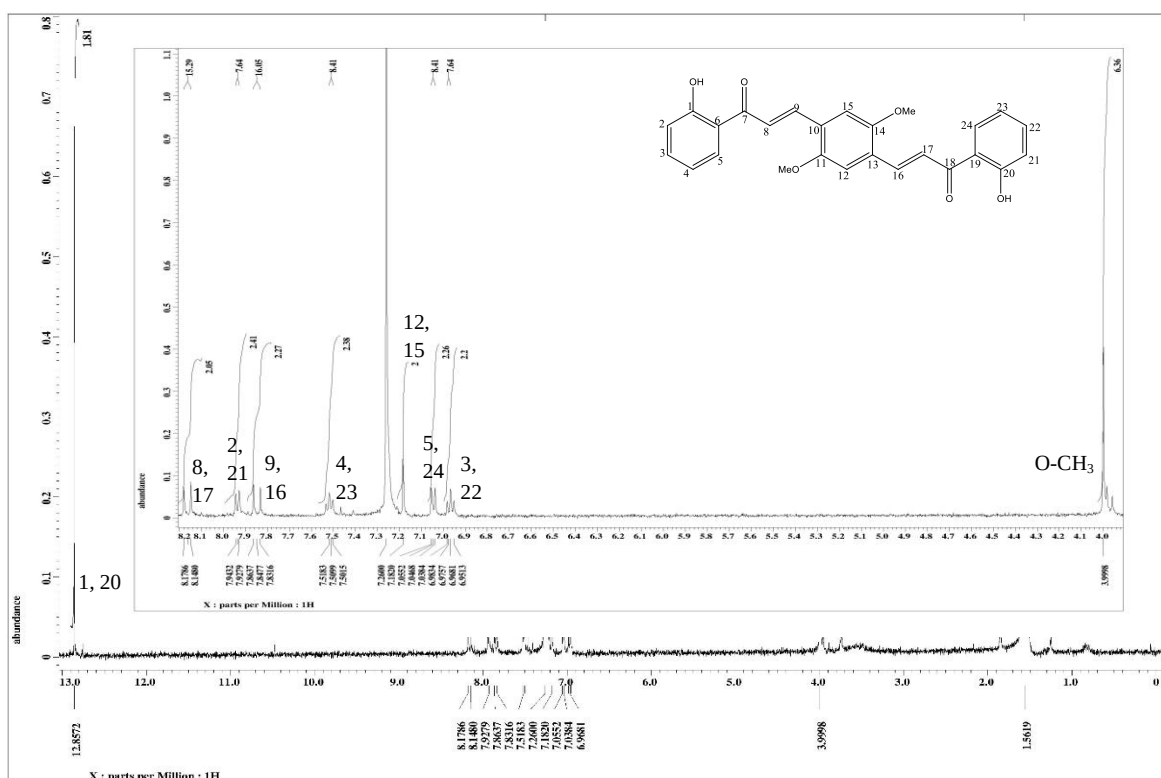


Figure 4.26: ^1H NMR spectrum of compound 3B

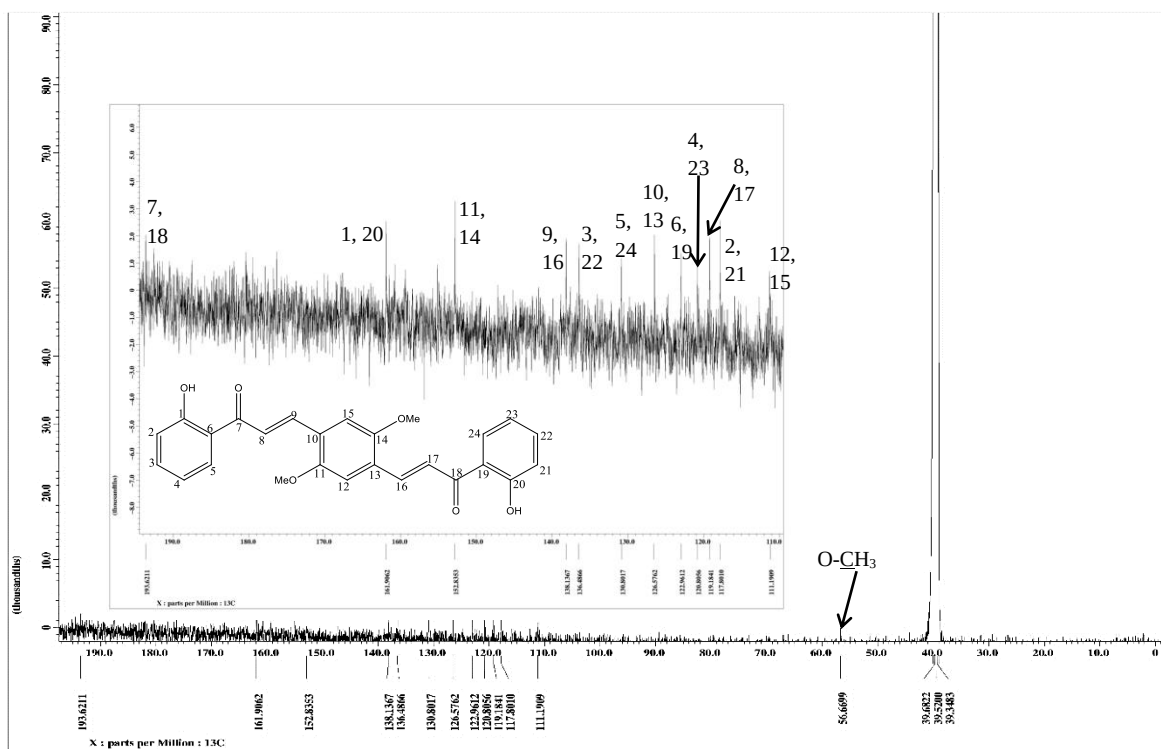


Figure 4.27: ^{13}C NMR spectrum of compound 3B

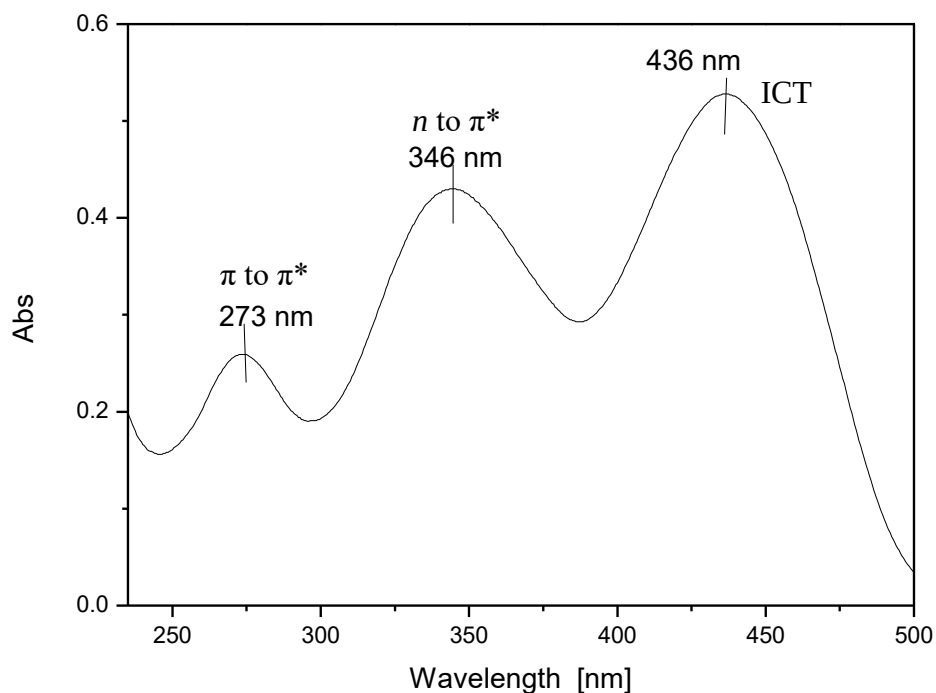


Figure 4.28: UV-visible spectrum of compound **3B**

4.1.6 Spectroscopic analysis of bis-chalcone series

4.1.6.1 FT-IR spectra analysis

Typically, all of the IR spectra were obtained from the grinding of the KBr crystal with the respective bis-chalcone compound in the detection range of 400-4000 cm^{-1} , respectively. Table 3.1 shows the summary of the significant IR band based on the functional group of the compound series. All of the IR spectra can be found in the above section as following orders: Compound **1A** (Figure 4.1), **1B** (Figure 4.5), **1C** (Figure 4.9), **2A** (Figure 4.13), **2B** (Figure 4.17), **3A** (Figure 4.21) and **3B** (Figure 4.25).

Table 4.1: Selected IR data of bis-chalcone derivatives

Functional group (cm ⁻¹) Compound	ν OH	ν C=O	ν C=C _{aliphatic}	ν C=C _{aromatic}	ν OCH ₃
1A	NA	1655	1606	1577 & 1446	NA
1B	3442	1640	1572	1489 & 1427	NA
1C	3453	1695 & 1639	1604	1567 & 1492	NA
2A	NA	1663	1607	1578 & 1447	NA
2B	3436	1640	1578	1488 & 1442	NA
3A	NA	1655	1587	1572 & 1491	1185
3B	3450	1632	1560	1487 & 1461	1196

* NA = Not Available

As summarized in Table 4.1, the absorption frequency of hydroxyl substituent is only shown in **1B**, **1C**, **2B** and **3B** at the range of 3430-3460 cm⁻¹, but not in **1A**, **2A** and **3A** due to the absence of the respective functional group. The lower absorption frequency of -OH group as compared to the free -OH stretching absorption band of phenol which commonly appears at 3610 cm⁻¹ is mainly because the formation of intramolecular hydrogen bonding between the carbonyl and hydroxyl group has weakened the O-H bond, thus shifting to the lower energy. Moreover, the most important information that could be retrieved from the FTIR spectra was the C=O stretching vibration in the range of 1660-1630 cm⁻¹. The absorption frequency observed was lowered than the typical C=O bond located at 1720-1708 cm⁻¹ due to the delocalization of π electrons which cause by the conjugation effect of α,β -C=C-C=O functional group. Besides, the formation of intramolecular hydrogen bond between -OH and C=O also contributes to the reduction of absorption frequency of C=O stretching vibration (Pavia *et al.*, 2001). In addition, the presence of α,β -conjugation systems does influenced the absorption frequency of C=C aliphatic of the synthesized compounds to detect at a lower frequency ranging from 1610-1550 cm⁻¹, accordingly, where free alkene group were commonly observed at 1660-1600 cm⁻¹ (Pavia *et al.*, 2001). As in **1C** (Figure 4.9), two intense

absorption frequency of C=O stretching were observed at 1695 cm^{-1} and 1639 cm^{-1} , indicating the presence of C=O stretching of aldehyde group and the C=O stretching of the α,β -C=C-C=O group, respectively, thus proving that one side of the terephthalaldehyde was not reacted with 2'-hydroxyacetophenone (Cheng *et al.*, 2000).

According to the textbook edited by Pavia *et al.*, (2001), the aromatic C=C stretching vibration normally occurs in pairs at $1600\text{--}1475\text{ cm}^{-1}$, but the recorded data was lower than expected value, suggesting that the delocalization of electrons happens along the molecular structure. On the other hand, only **3A** and **3B** show the absorption band at 1196 and 1185 cm^{-1} , which indicated the presence of -OCH₃ stretching vibration.

4.1.6.2 Nuclear Magnetic Resonance (NMR) spectroscopy analysis

As for the general information, the solvent reference peak for CDCl₃ in proton NMR and carbon NMR is recorded at 7.26 ppm and 77.16 ppm, respectively. On the other hand, solvent peak for DMSO-d₆ is presented at 2.50 ppm and 35.2 ppm in proton and carbon NMR, correspondingly. All the synthesized bis-chalcone compounds were dissolved in CDCl₃ prior for proton NMR analysis. The coupling constant was calculated by multiplying the differences of two peaks to 500 MHz. The ¹H NMR spectrum for each of the compound was presented in Section 4.1.1, 4.1.2 and 4.1.3 and were arranged as follow: Compound **1A** (Figure 4.2), **1B** (Figure 4.6), **1C** (Figure 4.10), **2A** (Figure 4.14), **2B** (Figure 4.18), **3A** (Figure 4.22) and **3B** (Figure 4.26). Table 4.2 showed the sum up of all important signals of the respective compound in ¹H NMR spectrum.

Table 4.2: ¹H NMR data of bis-chalcone derivatives

Peak (ppm) Compound	δ OH	δ α-H	δ β-H	δ H _{aromatic}	δ OCH ₃	δ CHO
1A	NA	7.80	7.58	7.69	NA	NA
1B	12.75	7.93	7.72	7.74	NA	NA
1C	12.67	7.93	7.77	7.92 & 7.82	NA	10.05
2A	NA	7.84	7.59	7.84	NA	NA
2B	12.74	7.95	7.72	7.91	NA	NA
3A	NA	8.06	7.66	7.17	3.95	NA
3B	12.86	8.16	7.84	7.18	3.99	NA

* NA = Not Available

From Table 4.2, there was a trend observed throughout the compounds, where the proton resonances for the compounds substituted with –OH such as **1B**, **1C**, **2B** and **3B** were slightly shifted to downfield as compared with their respective parent compounds with no other substituents, namely **1A**, **2A** and **3A**. This is because the influence of electronegative –OH substituent as an electron-withdrawing group reduces the valence electron density around the protons of the attached carbon, in conjunction with the delocalization of electron within molecular structure itself, thus the signals observed were shifted to the downfield region (Pavia *et al.*, 2001). In addition, based on the calculated coupling constant for the α and β protons, the values shown were in between 15-16 Hz which lies in the range of the *trans* coupling constants from 15-18 Hz (Pavia *et al.*, 2001). Therefore, all of the synthesized bis-chalcone compounds are presented as *trans*-conformation structure.

Furthermore, the chemical shift for α-H is commonly observed at the downfield as compared with the β-H because α-H is bonded next to the electron deficient carbonyl group, which causes the α-H deshielded. On the other hand, the most significant aromatic signals are the protons shown at the central phenyl ring in the molecular structure. For instance, since the molecular structure of Series 1 (**1A** and **1B**) and Series 3 (**3A** and **3B**) are symmetrical, the aromatic protons at the central phenyl ring are existed as a singlet which attributed to four

protons in Series 1 and two protons in Series 3, respectively. In contrast, the significant difference of bis-chalcone in Series 3 as compared to other series is the presence of methoxy substituents at the central phenyl ring which gives a singlet at the region of 3-4 ppm with the integration of six protons. Meanwhile, one of the hydrogen at the central phenyl ring of Series 2 (**2A** and **2B**) bis-chalcone shows only one proton for the singlet signal due to its *meta* position. Moreover, as for the particular phenyl ring mentioned earlier, the central phenyl ring of compound **1C** gives two doublets at 7.92 and 7.82 ppm due to its unsymmetrical structure. In ^1H NMR spectrum of compound **1C**, the singlet with one proton located at 10 ppm is corresponded to the signal of unreacted aldehyde group (CHO). In addition, the information such as presence of singlet; one proton resonance from $-\text{OH}$ group at 12.67 ppm along with the doublet signal of one proton resonance integrated at 7.93 and 7.77 ppm with J coupling constant of 16 Hz, which representing the proton of α,β -conjugated $\text{C}=\text{C}$, have proven the formation of one sided chalcone compound was indeed successful.

In the ^{13}C spectroscopy evidence, all the ^{13}C spectra obtained for each of the compound were correlated to its' respective carbon number as shown in the spectrum: Compound **1A** (Figure 4.3), **1B** (Figure 4.7), **1C** (Figure 4.11), **2A** (Figure 4.15), **2B** (Figure 4.19), **3A** (Figure 4.23) and **3B** (Figure 4.27). Typically, the carbon assignments were arranged based on the closeness of the actual value to the calculated value in the spectrum. The carbon shift was calculated in accordance to the base value and the total increment of the substituents that were related to the respective carbon atom (Pavia *et al.*, 2001). Appendix 1.1 and Appendix 1.2 showed the Table of ^{13}C substituent increments for alkene (vinyl) carbon and benzene rings, which used as a references for ^{13}C peaks assignment. For the information, all of the carbon spectra were recorded using the CDCl_3 as the standard reference, except for the compound **3B**, which was recorded in $\text{DMSO}-d_6$. This is because the solubility of compound **3B** in CDCl_3 was poor,

resulting no signal shown in ^{13}C NMR spectrum. Despite the low intensity of carbon peaks observed, the signals were referred to the previous work conducted by Tiong (2014), in order to justify the weak signals shown. Table 4.3 below recorded some significant peaks used to justify the molecular structure of the compound.

Table 4.3: ^{13}C NMR data of bis-chalcone derivatives

Peak (ppm) Compound	$\delta \text{C=O}$	δCHO	$\delta \text{C-OH}$	$\delta \text{C-OCH}_3$	$\delta \alpha \text{C=C}$	$\delta \text{C=C}\beta$	δOCH_3
1A	190.39	N.A.	N.A.	N.A.	123.18	143.68	N.A.
1B	193.58	N.A.	163.87	N.A.	119.11	144.20	N.A.
1C	193.51	192.95	161.80	N.A.	119.51	142.99	N.A.
2A	190.48	N.A.	N.A.	N.A.	123.15	143.98	N.A.
2B	193.64	N.A.	163.79	N.A.	119.13	144.44	N.A.
3A	191.18	N.A.	N.A.	153.21	124.28	139.67	56.34
3B	193.62	N.A.	161.90	152.84	119.18	138.14	56.67

*N.A.: Not available

From the tabulated data as shown above, the carbon resonance signal for the carbonyl group of all the synthesized compounds were appeared at the downfield region, which positioned at 190 to 194 ppm. As noticed, the compound **1B**, **1C**, **2B** and **3B** have higher $\delta \text{C=O}$ signal recorded as compared to compound **1A**, **2A** and **2B**. This is due to the presence of intramolecular forces formed between the hydrogen of the hydroxyl group and the oxygen of the carbonyl group, which indirectly caused the C=O to be deshielded (Tiong, 2014). Furthermore, only carbon that attached to the hydroxyl group for compound **1B**, **1C**, **2B** and **3B** showed carbon resonances at around 160 ppm.

On the other hand, compounds **3A** and **3B** showed two distinctive carbon peaks observed at 150 ppm and 56 ppm that corresponded to the carbon resonance of C-OCH_3 and OCH_3 , respectively. Meanwhile, the aliphatic ethylene α and β -carbon resonance of the chalcone derivatives were reported at the region of 119-124 ppm and 138-145 ppm, accordingly (Tiong, 2014). Among all the bis-chalcone derivatives, only compound **1C** showed it

individual carbon peak at 191 ppm, which signified the presence of -CHO carbon. Besides, the presence of C-OH peak at 163 ppm in the ^{13}C spectrum convinced the molecular structure of **1C** to be one-sided chalcone.

4.1.6.3 UV-visible spectroscopy analysis

The UV-visible spectroscopy analysis of the bis-chalcone derivatives were examined using the Jasco V-630 Ultraviolet Spectrophotometer under absorption range of 200-500 nm. All the compounds were analyzed by dissolving the samples in the DCM solvent and the data was shown in the earlier section: Compound **1A** (Figure 4.4), **1B** (Figure 4.8), **1C** (Figure 4.12), **2A** (Figure 4.16), **2B** (Figure 4.20), **3A** (Figure 4.24) and **3B** (Figure 4.28). The absorption bands were summarized in Table 4.4.

Table 4.4: UV-visible absorption data of bis-chalcone derivatives

Compound	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)	Intramolecular charge transfer (ICT) (nm)
1A	277	353	N.A.
1B	280	369	N.A.
1C	320	363	N.A.
2A	261	307	N.A.
2B	260	315 & 351	N.A.
3A	269	335	423
3B	273	346	436

N.A.: Not Available

The $\pi \rightarrow \pi^*$ transition of the aromatic C=C delocalization for each of the compound was recorded at the region of 260-280 nm, except compound **1C** which was at 320 nm. By analyzing the molecular structure, the presence of α,β -conjugated systems reduced the energy gap between the HOMO and LUMO in the molecular orbital, thus a higher absorption wavelength was recorded than the typical $\pi \rightarrow \pi^*$ transition of aromatic C=C which commonly observed at the range of 220-250 nm (Tiong, 2014). On the other hand, the reason behind the increase in absorption wavelength of $\pi \rightarrow \pi^*$ transition in compound **1C** was due to the push-

pull effect between the hydroxyl and the aldehyde functional group in conjunction with α,β -conjugated system, which may significantly reduce the HOMO and LUMO energy gap (Bures, 2014).

Furthermore, the presence of C=O in the organic molecules resulted another UV absorption band appeared at 300 – 380 nm that corresponded to the $n \rightarrow \pi^*$ transition. Since the energy level of the non-bonding orbital (n) is higher than the π bonding orbital, the energy gap in between the non-bonding orbital and π^* orbital becomes smaller and hence higher absorption wavelength was recorded. Meanwhile, compounds **3A** (Figure 4.24) and **3B** (Figure 4.28) showed the additional absorption peak at visible region of 450 nm was representing the intramolecular charge transfer (ICT) (Allen *et al.*, 1987). The presence of ICT band in bis-chalcones **3A** and **3B** is due to the presence of methoxy group at the central phenyl ring. The electron-donating nature of the methoxy group push the π electrons from central phenyl ring towards the side rings through the C=C-C=O moiety resulted the additional ICT absorption band at 450 nm region (Allen *et al.*, 1987; Tay *et al.*, 2016).

Herein, this concluded the characterization of all the synthesized bis-chalcone compounds. The molecular structure of compounds **1A**, **1B**, **1C**, **2A**, **2B**, **3A** and **3B** were confirmed through the spectroscopic analysis by using FT-IR, ^1H NMR, ^{13}C NMR and UV-visible spectroscopy. The purity of the compounds was determined from the CHN analysis, where all the carbon and hydrogen percentage was in accordance to the calculated value.

4.2 Results and discussion of complexation between bis-2'-hydroxychalcone (**1B** and **2B**) and ruthenium precursor, **PC1**

4.2.1 Synthesis method and work up strategies

In the beginning of the project, a series of complexation between metal(II) namely copper, nickel and zinc with respective compounds **1B** and **2B** were attempted to synthesize in 2:1 metal to ligand ratio. The synthesis was conducted through direct reaction between metal(II) salt with ligand **1B** or **2B**. Unfortunately, all of the metal(II) complexes were insoluble in organic solvents such as DCM, CHCl_3 , DMF and even DMSO, which caused us not able to fully characterized the complexes especially using NMR spectroscopy. This problem led us to search for alternative method. From the literature search, the ruthenium-DMSO complex which was reported by Gaur and Mishra (2013) has drawn our attention due to its' good solubility in organic solvents.

According to the method reported by Gaur and Mishra (2013), the **CX1** complex was synthesized by using equivalent mole amount of Et_3N and extracted with DCM after the completion of the reaction to yield the complex. However, few attempts had been conducted using similar procedure but most of the compound **1B** were not fully dissolved in methanol. The reason behind this may due to the weak base nature of Et_3N that causes an incomplete deprotonation of the hydroxyl group in compound **1B**. Furthermore, the workup processes were even time consuming because there was mixture of compounds present in ^1H NMR spectrum.

Due to this reason, an equivalent mole of NaOH solution was used to replace Et_3N in order to improve the basicity and solubility of the compound **1B** in methanol solution. From the observation, the use of NaOH seemed to be much convincing because a dark red mixture

solution was obtained after stirring for 24 hours. This may have indicated that the reaction between the ruthenium precursor and compound **1B** was more reactive by using the NaOH solution. After 24 hours of stirring, the orange precipitate that contained in the dark red solution was filtered. Meanwhile, the attempt of stirring the mixture for more than one day was also performed, but the observation was similar as the previous set up. Hence, another set up was conducted by refluxing the mixture at 50 °C in the duration of 24 hours. As predicted, the undissolved precipitate seems to be decrease in yield and the solution was turning darker than that was stirring at the room temperature. However, this caused the precipitate extracted out from the DCM to be in black solid, which it was very hard to be purified. In the end, the initial method with stirring the mixture for 24 hours at room temperature was chosen.

Further investigation was performed for the obtained precipitate and the dark red filtrate. The dark red solution filtrate was extracted using DCM to yield the dark red precipitate. The purity of both solids was then checked with TLC. Yet, a red spot was remained stationary at the baseline of the TLC plate. After several attempts made, a red spot was separated from the baseline when eluted with CHCl₃-acetone solvent mixture while the other mixed solution of CHCl₃ and ethanol was found to be able to move the remaining spot. Hence, this method was applied into the column chromatography in a solvent mixture sequence of CHCl₃, CHCl₃-acetone and finally CHCl₃-ethanol to yield the desired complex at the isolated yield of 22%.

Meanwhile, by adopting the synthetic and workup method used for **CX1**, the novel complex of **CX2** was also successfully synthesized. In contrast to **CX1**, the solubility of compound **2B** was better in methanol containing excess of Et₃N (1 mL), thus most of the ligand and metal precursor were able to react during the reaction time. Interestingly, **CX2** complex was also found in the undissolved red precipitate, which was initially suspected as the unreacted ligand and metal precursor based on the TLC test. Unlike the **CX1** isolation, the undissolved

precipitate of **CX2** did not contain any by-product and could be easily separated using DCM and EtOH solvent mixture at 1:1 ratio.

On the other hand, the dark red filtrate was diluted with water and then extracted with DCM, which was then evaporated to obtain the dark red precipitate. Likewise, column chromatography was performed to remove unreacted compound **2B** which can be eluted using DCM in column chromatography. After eluted the unreacted **2B**, the complex **CX2** was then eluted *via* mixture of DCM and EtOH in 1:1 ratio. Unfortunately, based on the ^1H NMR spectrum obtained, there were some unwanted signals present with multiple proton signals observed. Hence, a slightly higher solvent polarity such as CHCl_3 in replaced with DCM was used and 1 red spot was moved along the TLC plate while another spot was remained stationary until CHCl_3 -EtOH solvent mixture was introduced. Therefore, this method was incorporated into column chromatography to yield the pure complex which was isolated using CHCl_3 -EtOH solvent mixture with the recovery yield of 43%.

As noticed, compound **3B** was not participated in the complexation with ruthenium precursor. This is because **3B** was not soluble in methanol solution with the presence of base. Moreover, due to the lack of starting materials available, the trials to synthesized complex with compound **3B** was very limited. In considering the above factors, compound **3B** was only used as dye sensitizer in DSSC application but not in complexation.

Herein, the complexation between respective compound **1B** and **2B** with ruthenium precursor **PC1** were successfully conducted to yield complex **CX1** and **CX2**. The spectroscopic results such as FT-IR, ^1H NMR, ^{13}C NMR and UV-visible of **CX1** and **CX2** were obtained and analyzed thoroughly to clarify the attained precursor and complexes, which were listed in 4.2.2, 4.2.3 and 4.2.4, respectively.

4.2.2 *Cis*-dichlorotetrakis(dimethylsulfoxide)ruthenium(II) precursor, PC1

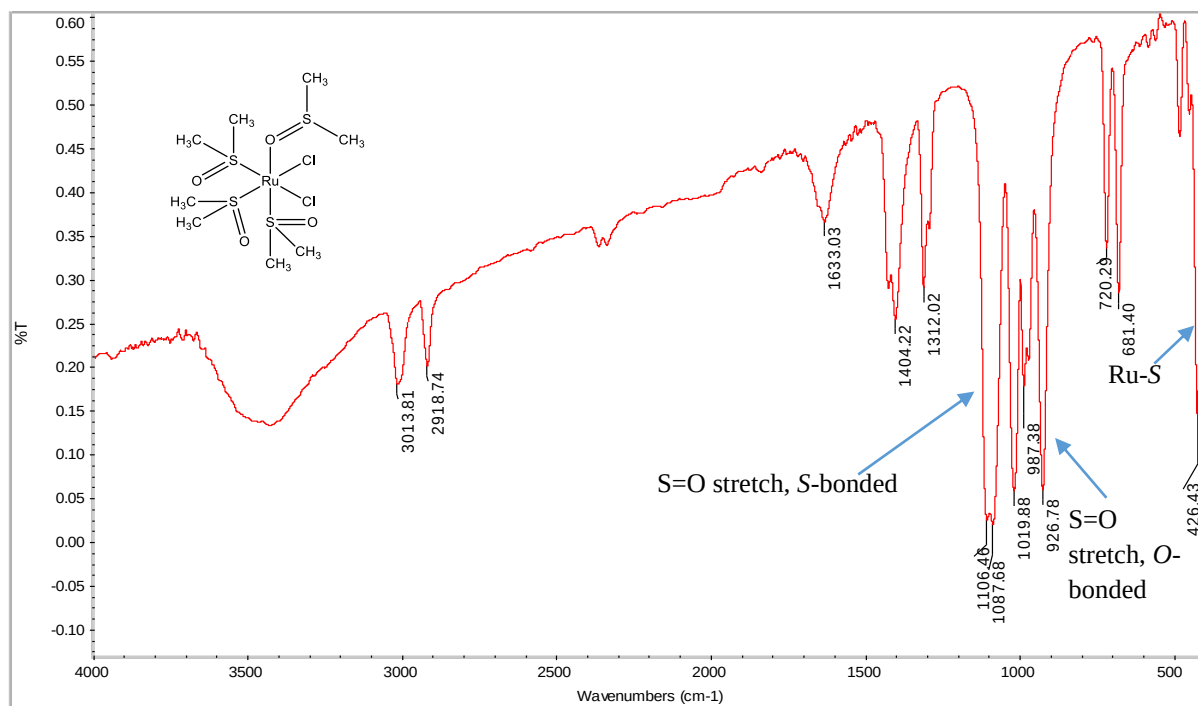


Figure 4.29: FT-IR of ruthenium precursor **PC1**

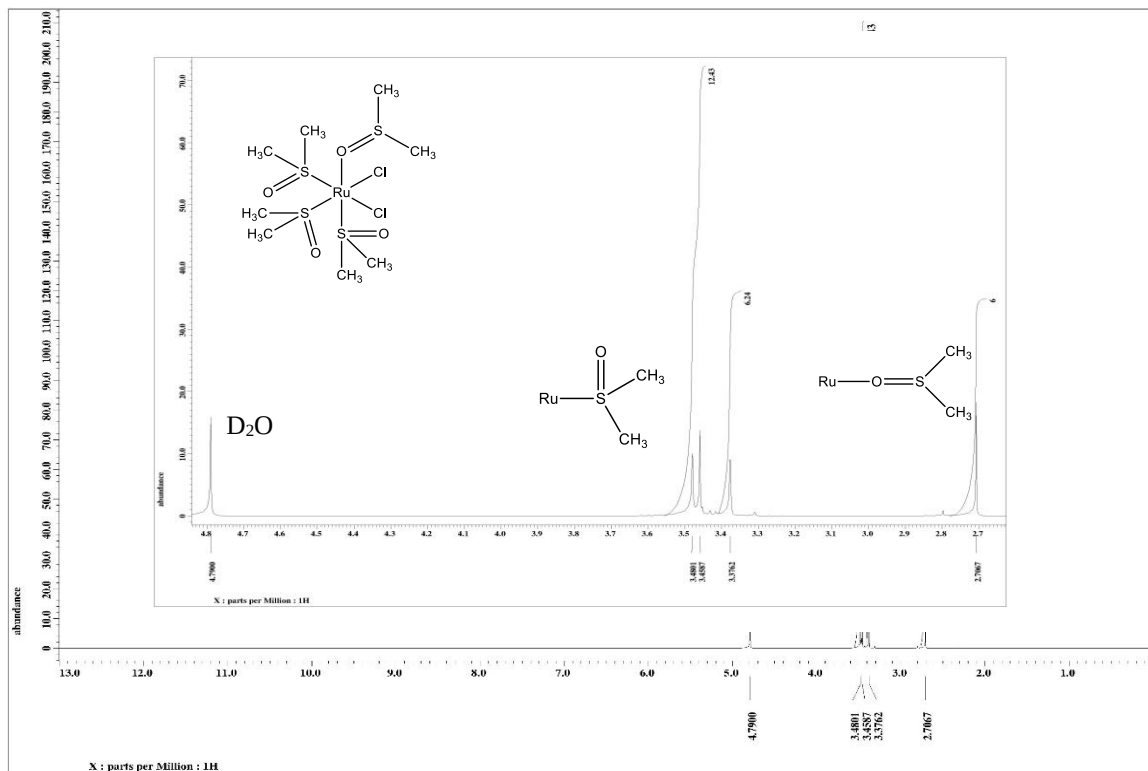


Figure 4.30: ^1H NMR spectrum of ruthenium precursor **PC1**

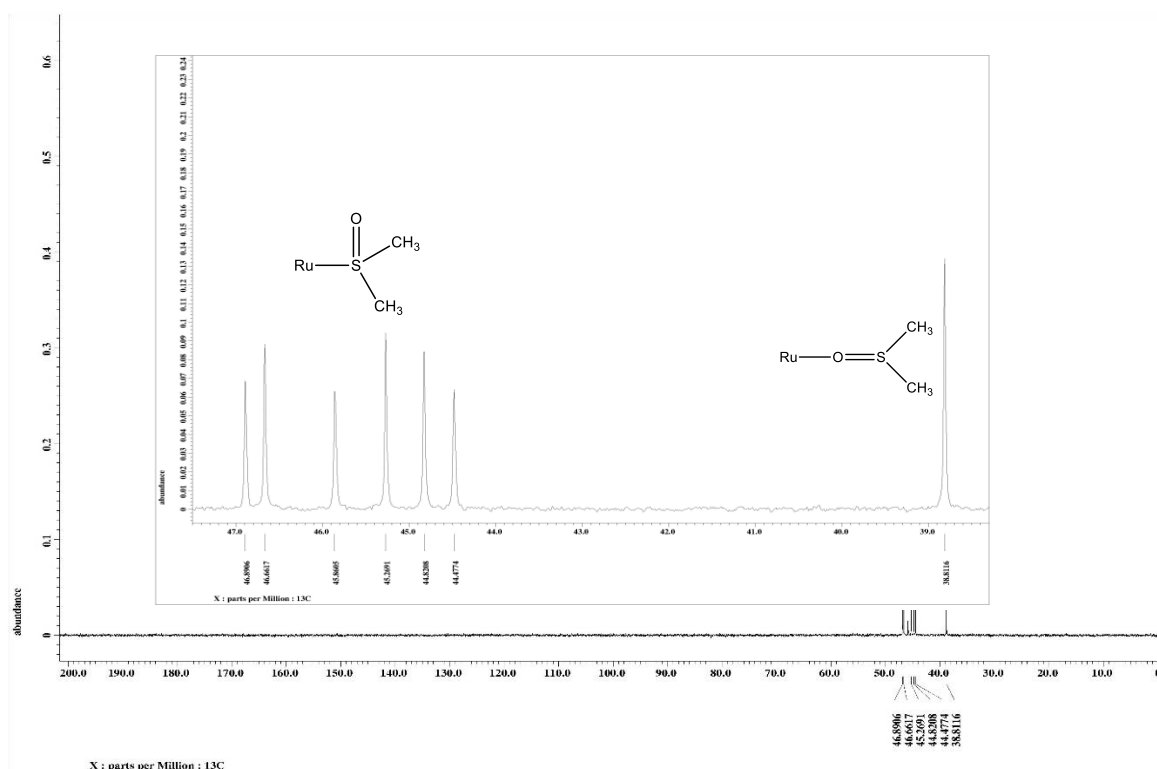


Figure 4.31: ^{13}C NMR spectrum of ruthenium precursor PC1

4.2.3 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxideruthenium(II)], CX1

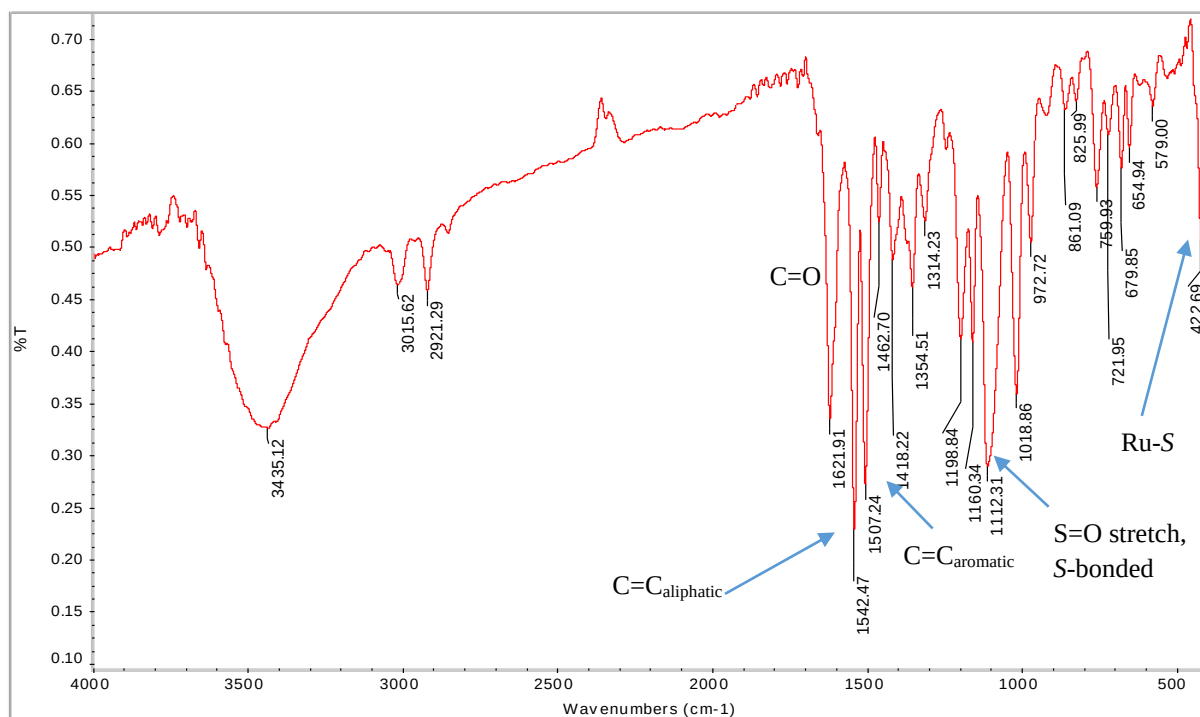


Figure 4.32: FT-IR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX1

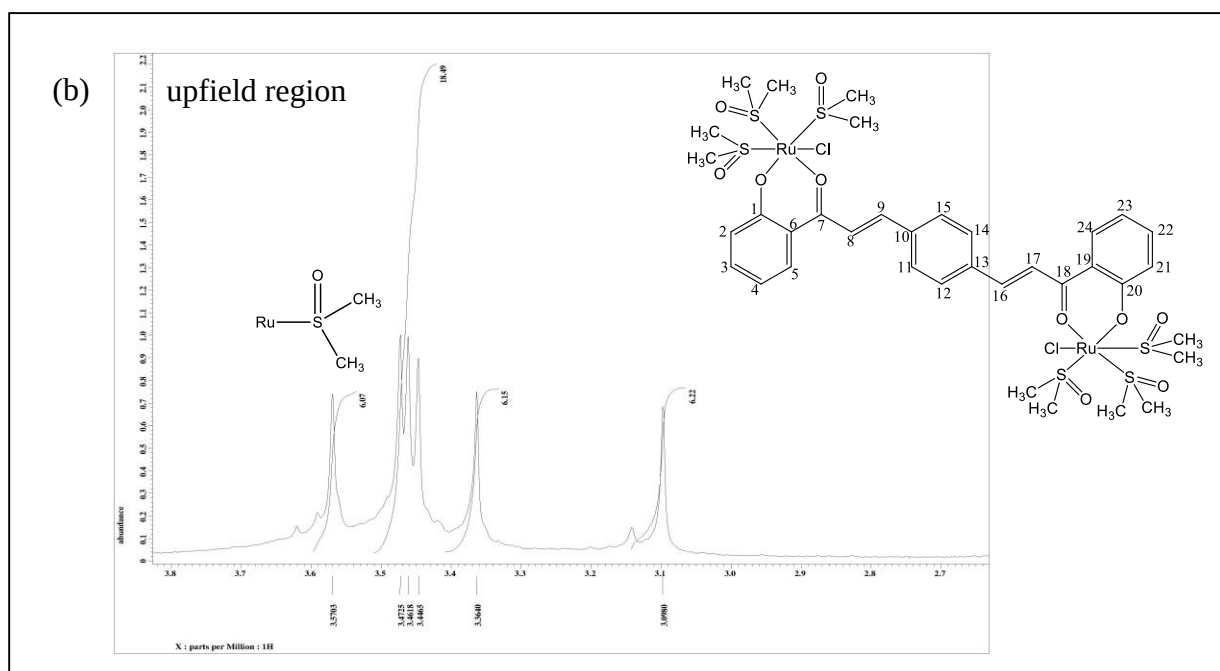
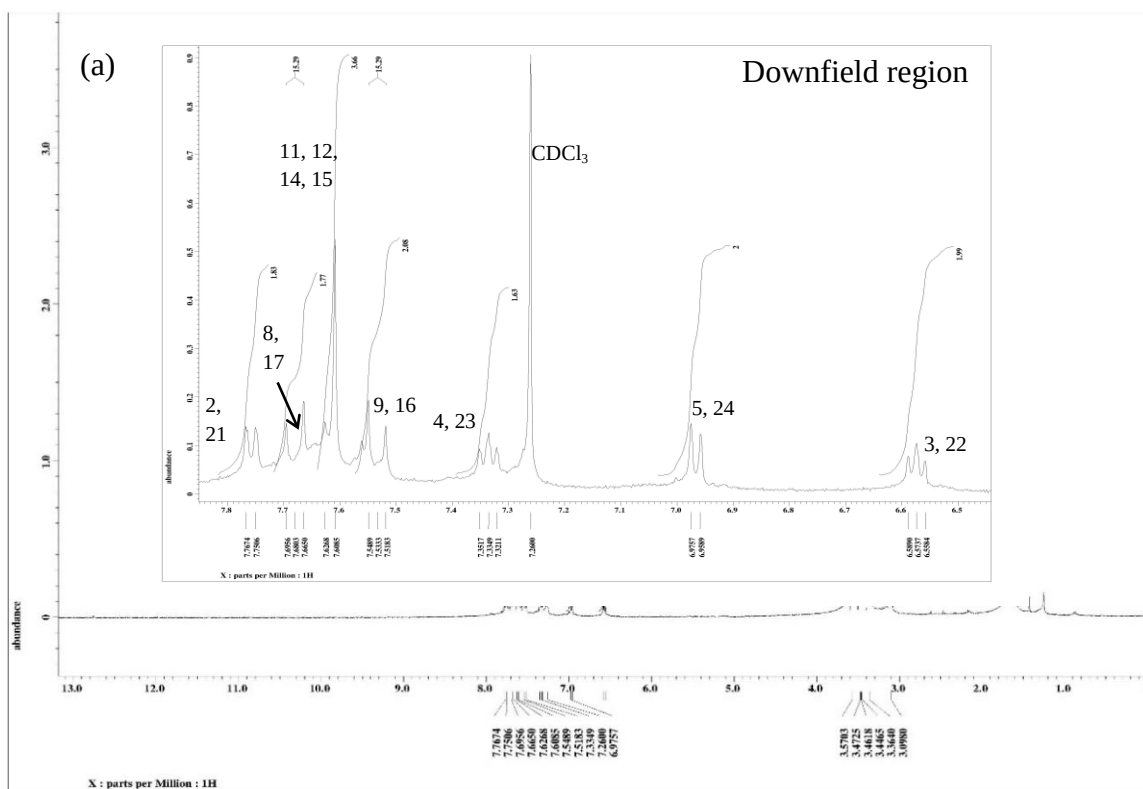
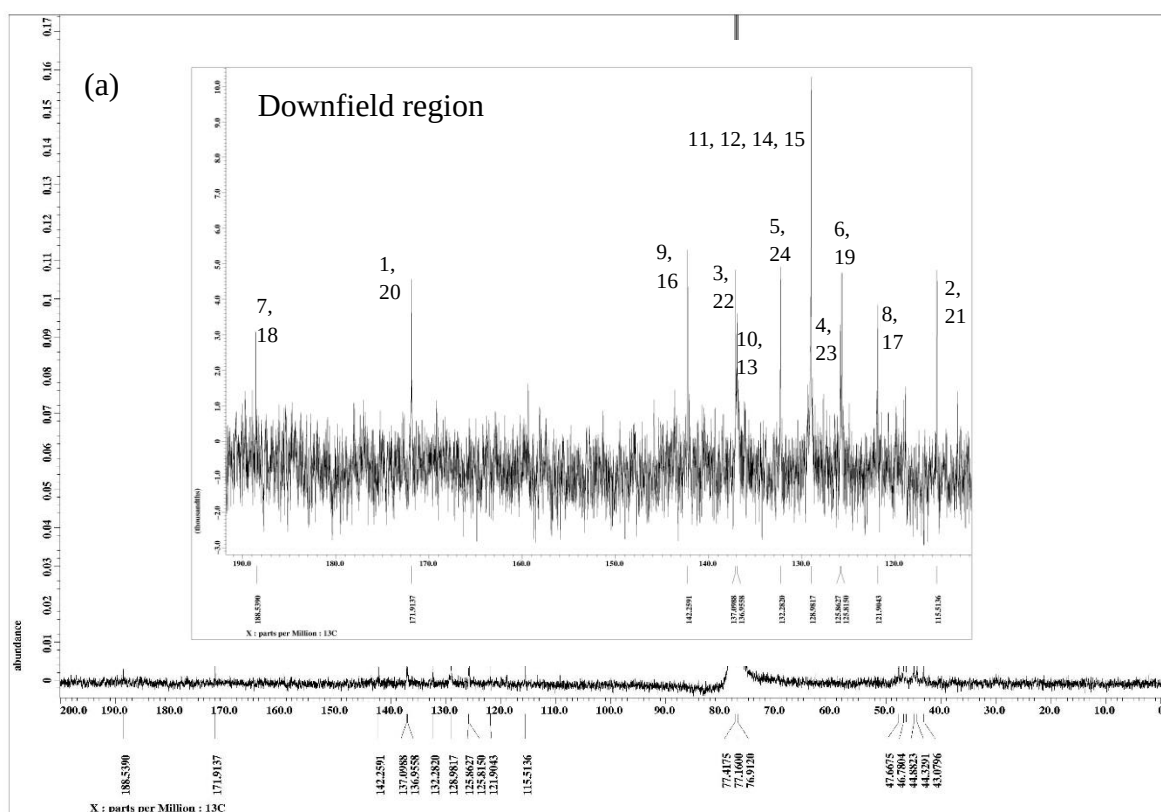


Figure 4.33: ^1H NMR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro- tris(dimethyl sulfoxide)ruthenium(II)], **CX1** [(a) Downfield; (b) Upfield]



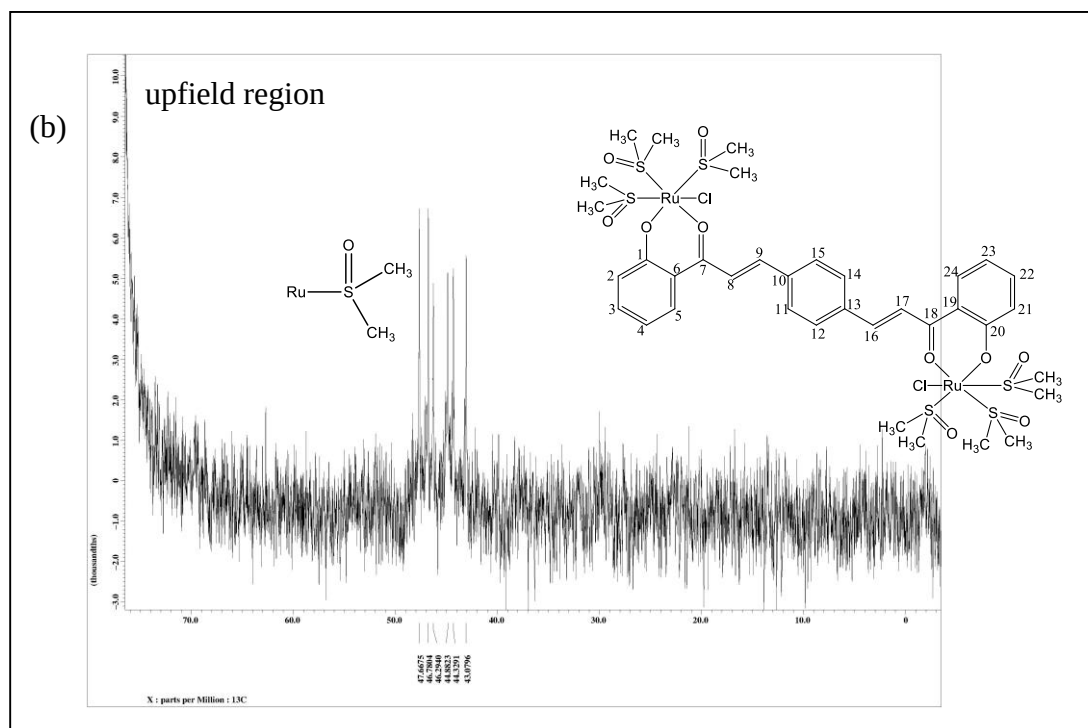


Figure 4.34: ^{13}C NMR spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], CX1 [(a) Downfield; (b) Upfield]

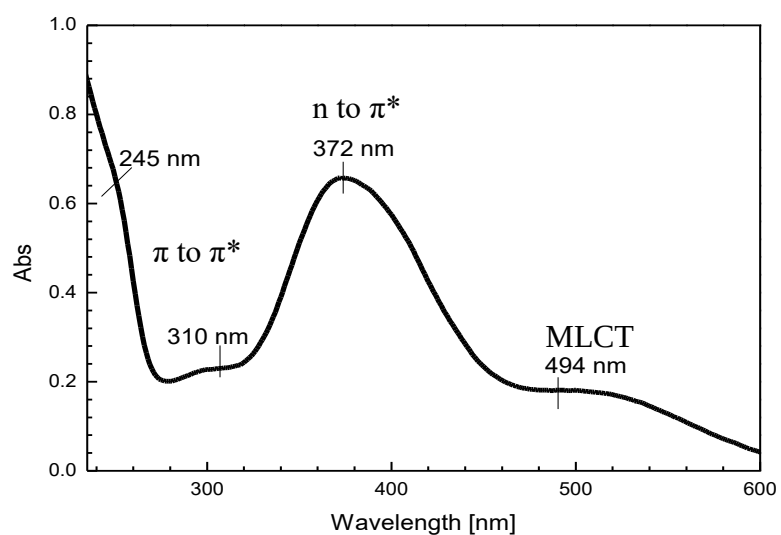


Figure 4.35: UV-visible spectrum of 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], CX1

4.2.4 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethylsulfoxide)ruthenium(II)], CX2

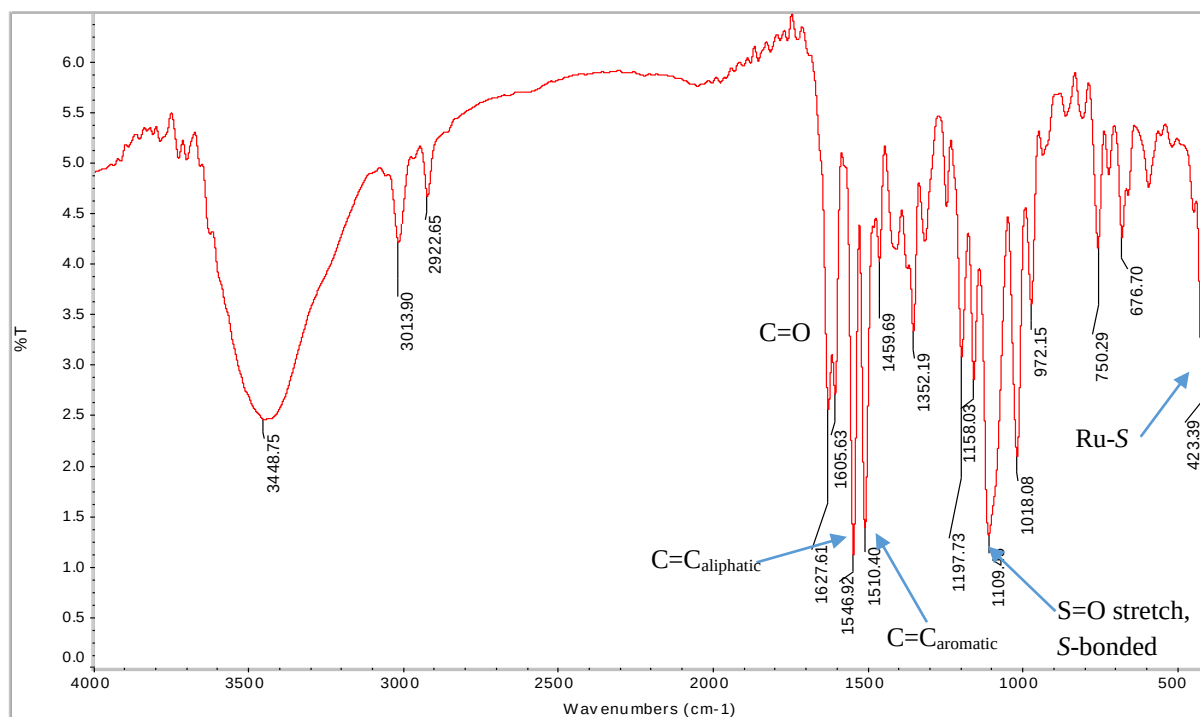


Figure 4.36: FT-IR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], CX2

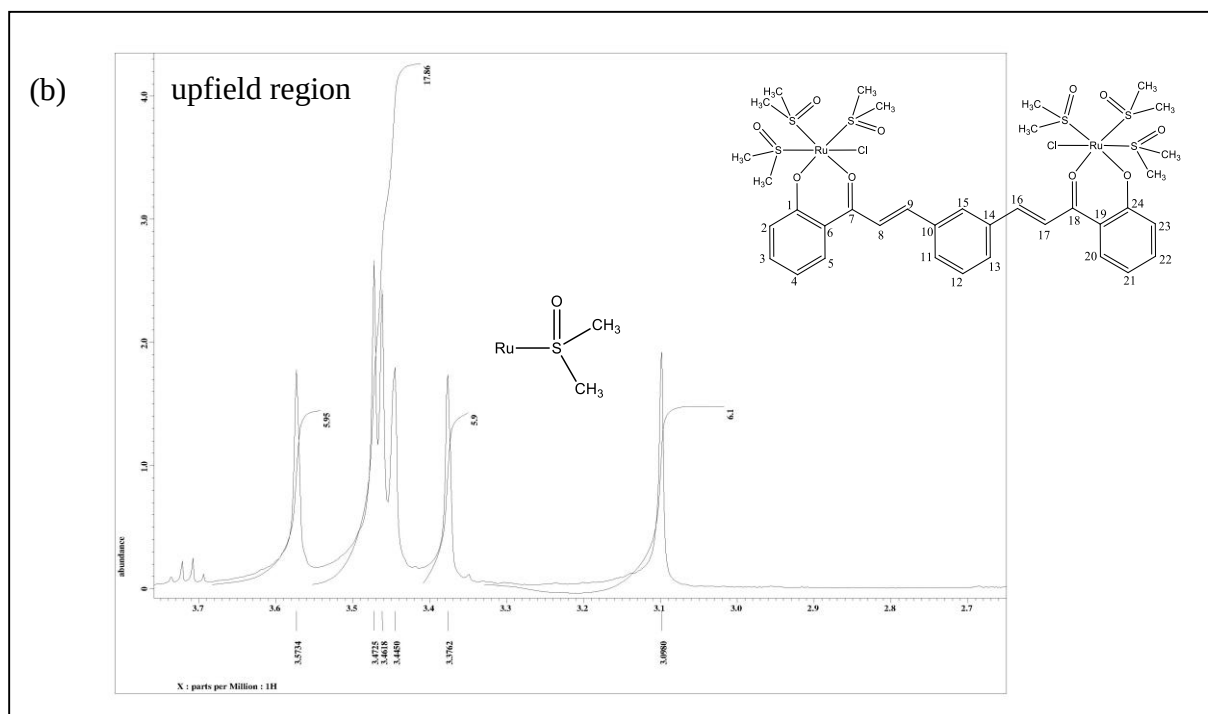
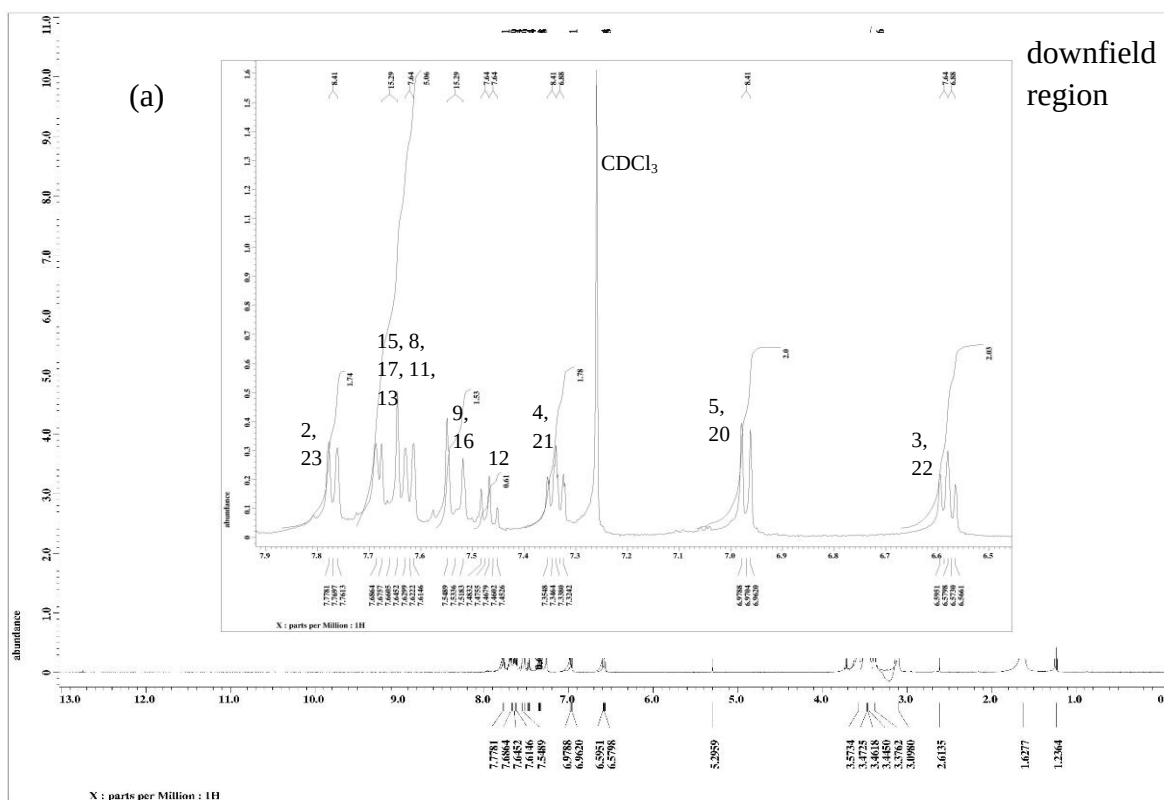


Figure 4.37: ¹H NMR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], CX2 [(a) Downfield; (b) Upfield]

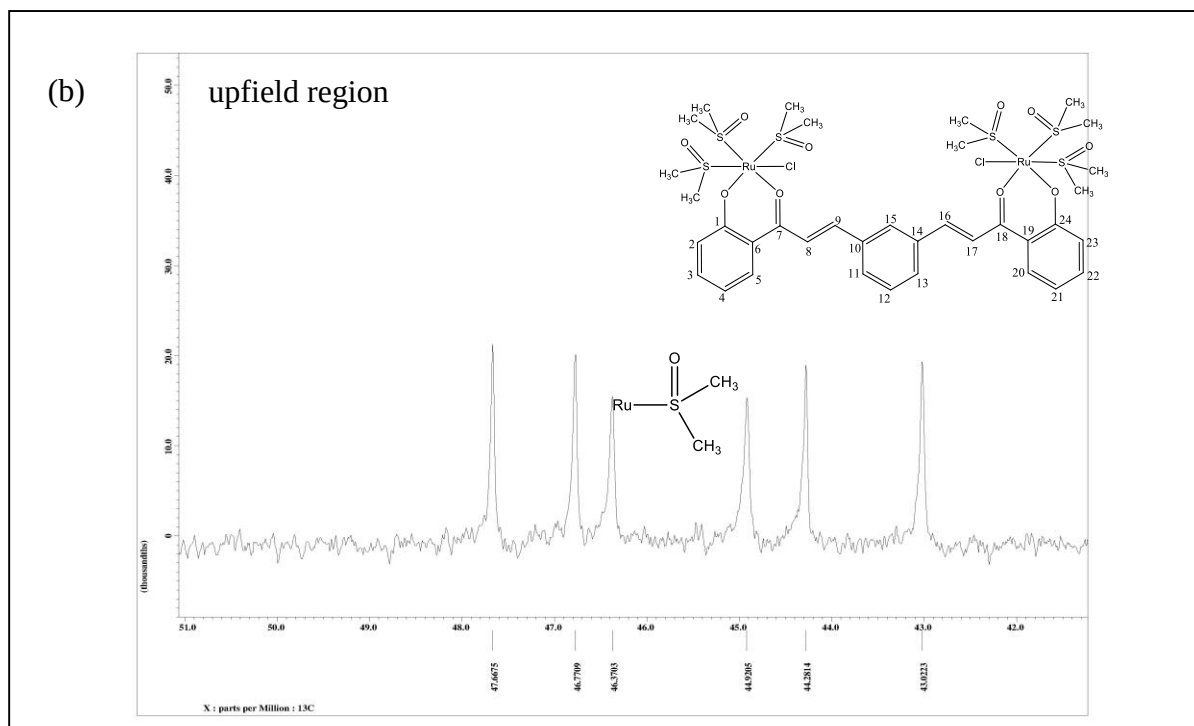
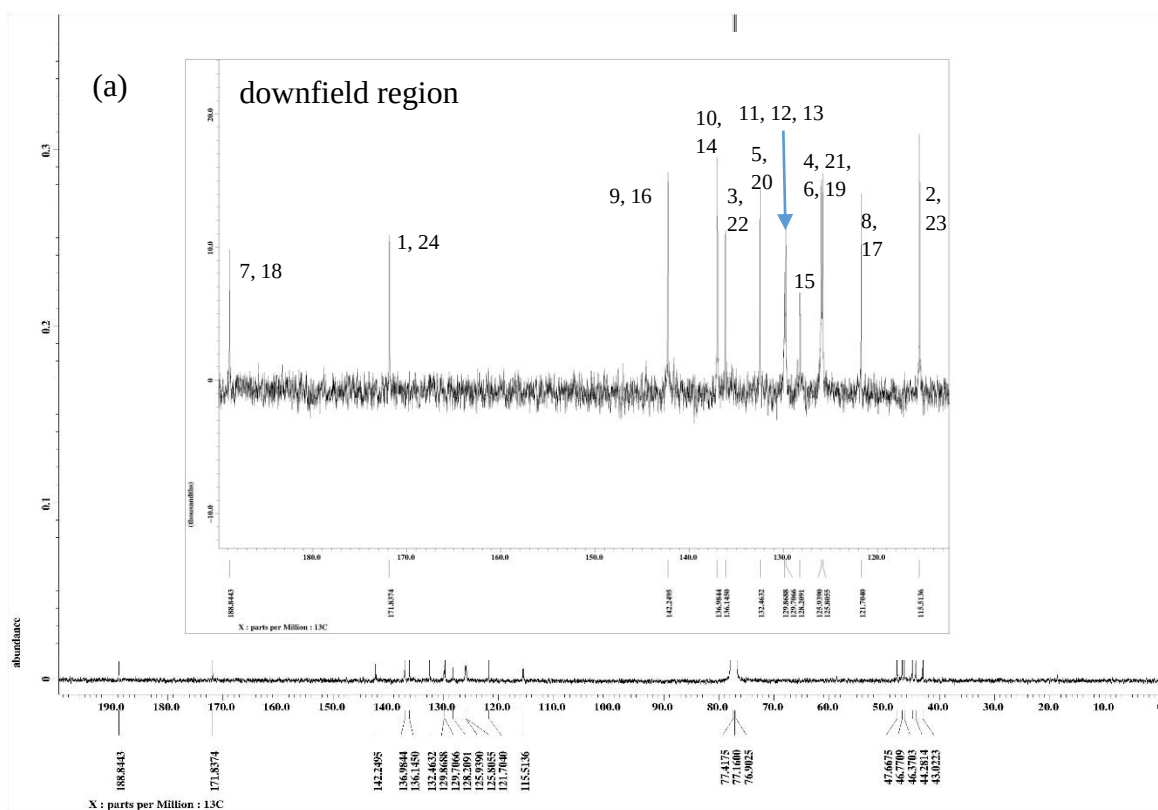


Figure 4.38: ^{13}C NMR spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], CX2 [(a) Downfield; (b) Upfield]

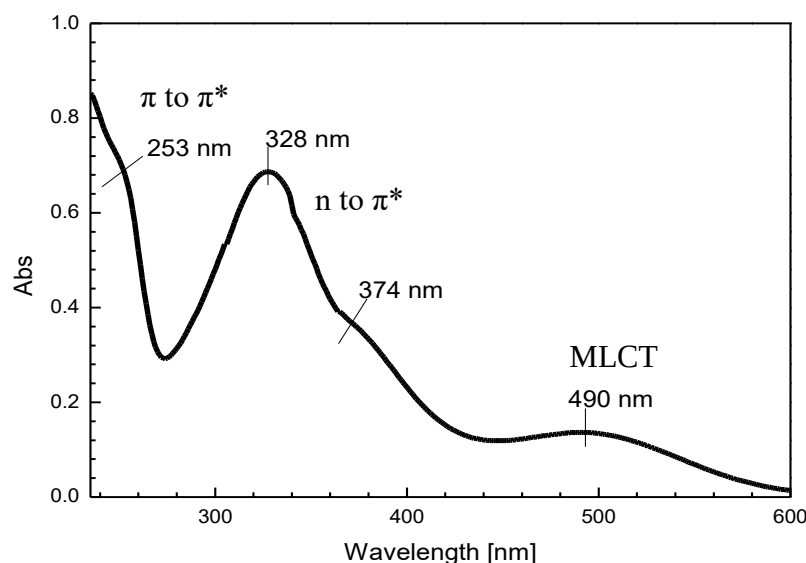


Figure 4.39: UV-visible spectrum of 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], **CX2**

4.2.5 Spectroscopy analysis of ruthenium complexes

4.2.5.1 FT-IR spectra analysis of CX1 and CX2

As aforementioned, IR spectroscopy is one of the methods which is usually used to determine the complexation of a reaction. The IR spectra of complexes of **CX1** and **CX2** were recorded using Thermo Scientific Nicolet iS10 FTIR spectrophotometer and the important IR signals in comparison to their free ligand are tabulated in Table 4.5.

Table 4.5: IR peak of bis-2'-hydroxychalcone ligands and ruthenium(II) complexes

Functional group (cm ⁻¹) Compound	ν OH	ν C=O	ν C=C _{aliphatic}	ν C=C _{aromatic}	ν S=O	ν Ru-S
1B	3442	1640	1572	1489 & 1427	N.A.	N. A.
CX1	3435	1622	1542	1507 & 1462	1112	423
2B	3455	1639	1574	1486 & 1440	N.A.	N. A.
CX2	3449	1628	1547	1510 & 1460	1109	423

Note: N.A. = not available

From the IR spectra in Figure 4.32 and 4.36, the high intensity of OH stretching vibration at 3400 cm^{-1} region presence spectrum was generally the signal from ethanol which was used to elute the complexes during the column chromatography procedure. For that reason, it is unable to draw a conclusion at this point to state either the proton of the -OH in the ligand **1B** and **2B** have been deprotonated based on the IR result. On the other hand, the absorption frequency of C=O showed dramatically reduced from $1640\text{-}1638\text{ cm}^{-1}$ in free ligands to 1622 and 1628 cm^{-1} in **CX1** and **CX2**, respectively. As reported earlier in the literature, the decreased of the absorption frequency was because of the electron back bonding from ruthenium metal center to the carbonyl group in bis-2'-hydroxychalcone (Hendrickson *et al.*, 1970; Dharmaraj & Natarajan, 1997). Moreover, this phenomenon also affected the stretching vibration of the aliphatic $\text{C}_\alpha=\text{C}_\beta$ of the ligand, causing it shifted to a lower frequency as compared with the free ligand **1B** and **2B**.

Meanwhile, the aromatic C=C stretching vibration was shown in the range of 1510 to 1420 cm^{-1} , which was corresponded to the information reported by Pavia *et al.* (2001). In **PC1** IR spectrum, two strong absorption peaks observed at 1106 cm^{-1} and 927 cm^{-1} were assigned for νSO stretching of DMSO-S and DMSO-O , accordingly (Bratsos & Alessio, 2010). On the other hand, the νSO stretching of DMSO-S in **CX1** and **CX2** were both visible at 1112 cm^{-1} and 1109 cm^{-1} , respectively but the νSO stretching of DMSO-O was not present in the both spectra. According to Bratsos and Alessio (2010), the range of νSO stretching in DMSO-O is from $890\text{-}950\text{ cm}^{-1}$. This indicated that the DMSO-O that bonded to the ruthenium had been dissociated during the complexation. Lastly, the prominent signal located at the finger print region of 423 cm^{-1} was representing the stretching band of the ruthenium metal ion and the sulphide of the DMSO (Gaur & Mishra, 2013).

4.2.5.2 NMR spectra analysis of CX1 and CX2

The NMR spectra of **CX1** and **CX2** were obtained in CDCl₃ using JEOL 500 MHz FT-NMR spectrometer. Table 4.6 showed the proton arrangement presented for the proposed complex **CX1** and compared to the free ligand **1B**. Alternatively, Table 4.7 showed the proton arrangement for the proposed complex **CX2** in comparison with the corresponded ligand **2B**.

Table 4.6: Comparison of ¹H NMR for 1,4-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], **CX1** and compound **1B**

Proton (H)	Integration Number	¹ H chemical shift (ppm)		Splitting	J (Hz)	Remarks
		1B	CX1			
1, 20	2	12.75	-	Singlet	-	-OH
2, 21	2	7.95	7.77	Doublet	8	Aromatic
8, 17	2	7.93	7.68	Doublet	15	α proton
11, 12, 14, 15	4	7.74	7.61	Singlet	-	Aromatic
9, 16	2	7.72	7.53	Doublet	15	β proton
4, 23	2	7.53	7.33	Triplet	8	Aromatic
-	-	7.26	7.26	Singlet	-	CDCl ₃
5, 24	2	7.05	6.97	Doublet	8	Aromatic
3, 22	2	6.97	6.57	Triplet	8	Aromatic
-	36	-	3.57-3.10	Singlet	-	DMSO-S (CH ₃)

Table 4.7: Comparison of ¹H NMR for 1,3-bis-2'-hydroxychalcone-bis[chloro-tris(dimethyl sulfoxide)ruthenium(II)], **CX2** and compound **2B**

Proton	Integration Number	¹ H Chemical shift (ppm)		Splitting	J(Hz)	Remarks
		2B	CX2			
1, 24	2	12.75	-	Singlet	-	-OH
2, 23	2	7.97	7.78	Doublet	8	Aromatic
15	1	7.91	7.69	singlet	-	Aromatic
8, 17	2	7.95	7.66	Doublet	15	α proton
11, 13	2	7.74	7.62	Doublet	8	Aromatic
9, 16	2	7.71	7.53	Doublet	15	β proton
12	1	7.53	7.47	Triplet	8	Aromatic
4, 21	2	7.53	7.35	Triplet	8	Aromatic
-	-	7.26	7.26	Singlet	-	CDCl ₃
5, 20	2	7.06	6.97	Doublet	8	Aromatic
3, 22	2	6.98	6.58	Triplet	8	Aromatic
-	36	-	3.57-3.10	Singlet	-	DMSO-S (CH ₃)

The ^1H NMR spectra of **CX1** and **CX2** can be found at Section 4.2.3 (Figure 4.33) and Section 4.2.4 (Figure 4.37), correspondingly. From the information given in the Table 4.6 and Table 4.7 above, all of the chemical resonance in **CX1** and **CX2** were apparently shifted to the upfield region. This may be due to the electropositive nature of the ruthenium metal which can increase the overall electron density of the molecule and resulting the whole molecule to be more shielded. It is worth to note that the singlet that is assigned to the OH proton at 12.75 ppm in compound **1B** and **2B** was completely disappeared after the complexation reaction with ruthenium precursor **PC1** with the formula of $[\text{RuCl}_2(\text{DMSO-S})_3(\text{DMSO-O})]$. This exciting result has confirmed that the ligand **1B** and **2B** were deprotonated to form bond with the ruthenium(II) metal ion during the complexation.

As for the coupling constant, each of the doublets or triplets is calculated based on the difference between two reading multiply by 500 MHz (Pavia *et al.*, 2001). The coupling constant for both α and β protons in **CX1** and **CX2** are remained at 15 Hz, indicating the bis-chalcone analogue was still remained in *trans*-conformation. Meanwhile, in comparison the ^1H NMR spectrum between **CX1** and **CX2**, the only proton peaks that could differentiate both structures are the protons located at the central phenyl ring. For complex **CX1**, there are four identical protons signals (H-11, 12, 14 and 15) appears as a singlet at 7.61 ppm due to the same magnetic environment resulted from the *para* branching, while for complex **CX2**, the spectrum shows a doublet (H-11 and 13) at 7.62 ppm, a triplet (H-12) at 7.47 ppm and a singlet (H-15) at 7.69 ppm, which is indicating the *meta* branching of **CX2** as shown in the spectrum (Figure 4.37).

Furthermore, a total of 36 protons are successfully integrated at the region of 3.57 to 3.10 ppm, which corresponded to the total $-\text{CH}_3$ groups in DMSO molecules that attach to ruthenium(II) metal center. In the ruthenium precursor **PC1** (Figure 4.30), one of the DMSO

is bonded to ruthenium metal center through the oxygen atom, whereas the rest are bonded to ruthenium through sulfur atom. This can be confirmed from the ^1H NMR spectrum of ruthenium precursor **PC1** in which a singlet presents at 2.70 ppm due to the *O*-bonded DMSO molecule (Gaur & Mishra, 2013). Surprisingly, the *O*-bonded DMSO molecule was not observed in both complexes' ^1H NMR spectra as shown in Figure 4.33 and 4.37. This finding can further supported by the IR analysis of **CX1** (Figure 4.32) and **CX2** (Figure 4.36), where the disappearance of the $\nu\text{S=O}$ for DMSO-*O* at 890-950 cm^{-1} as reported in the previous section (Bratsos & Alessio, 2010). Hence, it was concluded that the *O*-bonded DMSO molecule had dissociated from ruthenium metal center during the complexation.

Apart from ^1H NMR analysis, ^{13}C NMR analysis had also been conducted for both of the complexes. Generally, the chemical shift of the carbon-13 NMR for both complexes were referring back to the carbon-13 NMR of their corresponding ligands. The number of carbon presence in the ligands were in accordance to that in the complexes, which were tabulated in the Appendix 1.3 and Appendix 1.4 for **CX1** and **CX2**, accordingly. From the ^{13}C NMR spectra of **CX1** and **CX2** complexes (Figure 4.34 and Figure 4.38), in which there are a total of six carbon resonances present at 47 to 43 ppm representing the six methyl carbons in each DMSO molecules in **CX1** and **CX2**. Again, the carbon peak for the *O*-bonded DMSO that previously located at 38.81 ppm in **PC1** was not seen in **CX1** and **CX2** spectra, proving that the DMSO-*O* had left during the complexation happened.

Lastly, although the structures of **CX1** and **CX2** have yet been confirmed using X-ray crystallography, with the evidences from IR and NMR spectroscopy, the proposed structure of **CX1** and **CX2** can be proposed as shown in Figure 3.6.

4.2.5.3 UV-visible analysis

Table 4.8 showed the UV-visible spectroscopy data of **CX1** and **CX2** complexes in comparison with their respective ligands **1B** and **2B**. For the information, the analysis was conducted using the UV-1800 Shimdazu UV spectrophotometer with DCM solvent as the baseline.

Table 4.8: UV-visible absorption data of **CX1** and **CX2** complex

Sample	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)	Metal to ligand charge transfer (MLCT)
1B	280	369	N.A.
CX1	245	310 and 372	494
2B	260	315 and 351	N.A.
CX2	253	328 and 374	490

N.A.: Not Available

As observed in Figure 4.35 and 4.39, a weak shoulder band was appeared in **CX1** and **CX2** at the region of 245 nm and 253 nm, respectively, representing the $\pi \rightarrow \pi^*$ transition of aromatic C=C (Tiong, 2014). From the observation, the $\pi \rightarrow \pi^*$ transition of the complexes showed a decrease in the UV wavelength which initially recorded at the region of 280 nm and 260 nm in compound **1B** and **2B**, correspondingly. This may due to the absence of push-pull effect within the α, β - π -conjugated system in the molecular structure as the hydroxyl group had been deprotonated in order to coordinate with the ruthenium metal centre that consists of only acceptor ligands such as DMSO and chlorine. Thus, this resulted the $\pi \rightarrow \pi^*$ transition of aromatic C=C to be seen at the normal wavelength as reported by (Tiong, 2014).

On the other hand, the peaks shown for **CX1** ($\lambda_{\max}$ 310 and 372 nm) and **CX2** ($\lambda_{\max}$ 328 and 374 nm) were assigned as the $n \rightarrow \pi^*$ transition. These absorption peaks were red shifted to a longer wavelength as compared to the $\lambda_{\max}$ of the corresponded ligands due to the backbonding of electron from the ruthenium metal centre to the π^* orbital of the C=O functional group, hence decrease the LUMO and HOMO energy gap. Moreover, the low spin

property of ruthenium(II) ion with d^6 electronic configuration caused the t_{2g} orbital to be fully filled. During the excited state, this electron in the t_{2g} orbital can be transfer to the t_{2g}^* orbital, which relatively interact with the low lying ligand π^* orbital. Hence, this phenomenon resulted the metal to ligand charge transfer or MLCT transition which can be seen at the region of λ 494 nm and 490 nm of the **CX1** and **CX2**, respectively (Gaur & Mishra, 2013).

As the conclusion, ruthenium complexes namely **CX1** and **CX2** were successfully synthesized and characterized thoroughly by using the spectroscopic analysis as discussed above. Purity of **CX1** and **CX2** was determined by comparing the percentage of calculated carbon and hydrogen with the analyzed data using CHN analyzer.

4.3 Results and discussion on the application of synthesized bis-chalcone and complexes in DSSC

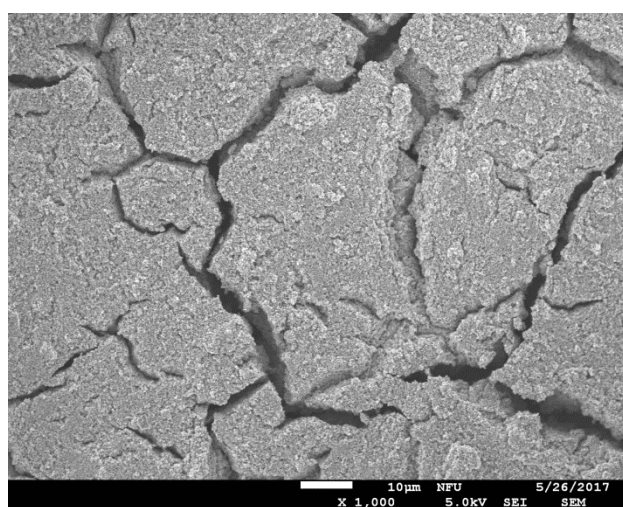
After completing the synthesis of bis-chalcone and ruthenium complexes, we applied them as the dye sensitizer for the use in DSSC and determined the power conversion efficiency. Before began, the morphology of the titanium dioxide (TiO_2) that coated on top of the FTO glass was observed under SEM to examine the coated surface and its thickness. Besides, another reason to conduct this analysis was to determine the consistency and the reliability of the results of power conversion efficiency obtained, implying that this variable was controlled.

4.3.1 Morphology of titanium dioxide (TiO_2) on FTO glass

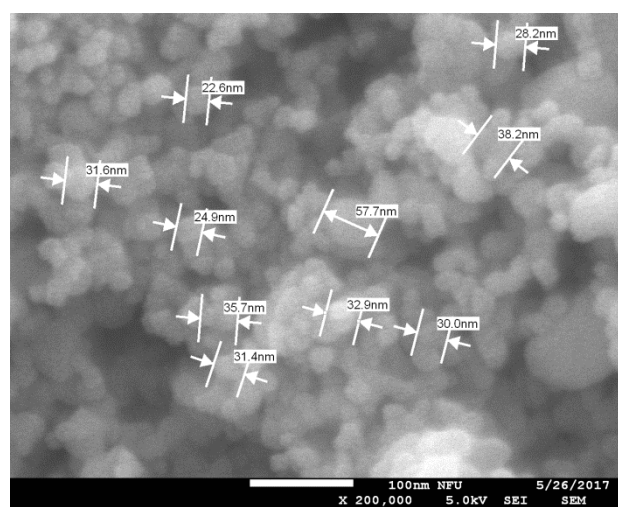
A total of up to 50 μm TiO_2 was coated on the FTO glass surface by using the designated film coater. After the TiO_2 was annealed to 450 $^{\circ}C$ and cooled to room temperature, the particular FTO glass was cut into 1 cm x 1 cm for the SEM analysis (Figure 4.40). From the Figure 4.40 (a), it was clearly seen that the surface of the TiO_2 was cracked after the solvent was dried

completely. This may due to the over coating process that resulted in an increase in TiO_2 thickness, thus showing the cracking scenario after the annealation. Nevertheless, less clumping of TiO_2 was appeared in the image, where the size of the TiO_2 was reduced to between 22.6 nm to 57.7 nm as shown in Figure 4.40 (b).

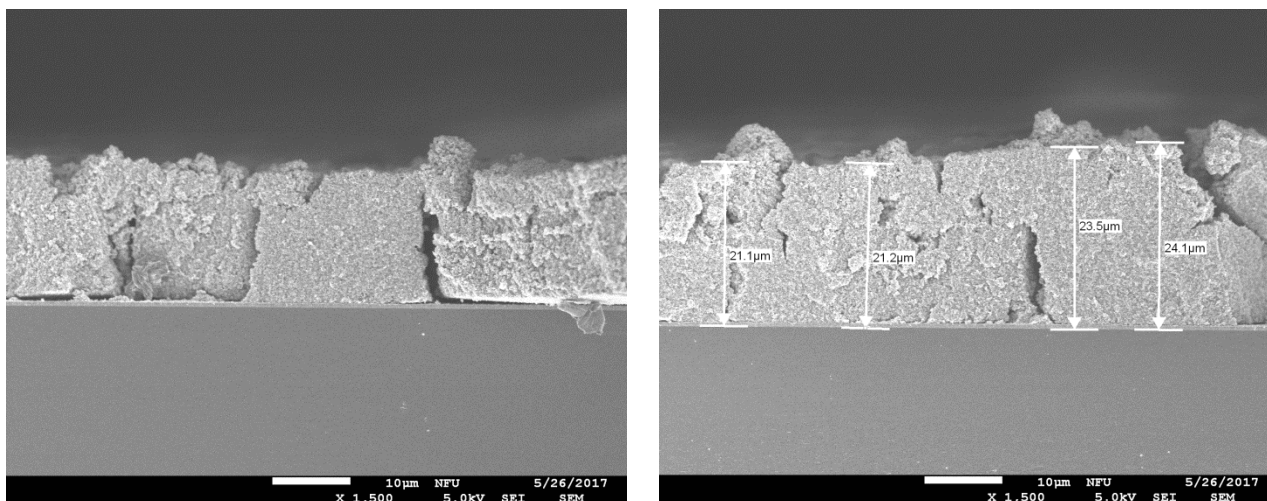
Besides, a cross-section view of TiO_2 layer was taken under 1500 times zoom. From the Figure 4.40 (c), some TiO_2 was seemed to be unattached onto the FTO glass surface after the heat treatment process. This observation probably because of the water, solvent and organic substances presence in the TiO_2 mixture was evaporated during the annealation, causing some of the TiO_2 to rise. In addition, this explanation could be further supported with the decreased in thickness of the TiO_2 to around 24 μm from the initial coating of 50 μm after annealed at high temperature Figure 4.40 (d).



a. Top view of TiO_2 at x1000 zoom



b. Top view of TiO_2 at x200000 zoom



c. Cross-section view of TiO_2 at x1500 zoom d. Cross-section view of TiO_2 at x1500 zoom

Figure 4.40: SEM image of TiO_2 surface morphology on FTO glass

Indeed, the TiO_2 surface morphology is one of the factors that influence the overall conversion efficiency of the dye sensitized solar cell. According to Sedghi and Miankushki (2015), some parameters such as the thickness of the TiO_2 semiconductor could affect the short circuit current (J_{sc}) and open circuit voltage (V_{oc}). From their experimental result, the optimum thickness of TiO_2 at $15.2 \mu\text{m}$ showed the highest J_{sc} and V_{oc} value, which in turn give the highest conversion efficiency. Beyond the thickness would increase the internal surface area and reduce the capabilities of TiO_2 in dye absorption (Sedghi & Miankushki, 2015). Furthermore, the incident light intensity that penetrate into the dye-sensitized TiO_2 layer also reduce as its thickness increase, resulting more charge point defects that cause electron loss and eventually reduce the J_{sc} value (Kao *et al.*, 2009; Sedghi & Miankushki, 2015). Subsequently, the open circuit photovoltage also been affected due to the electron dilution effect, where the electron density becomes lower as it passed through the depth of TiO_2 film, until a certain thickness that the electron density is insufficient to be transmitted across the thicker layer, thus decrease the V_{oc} value (Gómez & Salvador, 2005). Unfortunately, due to the time constraint, the optimization of the TiO_2 surface morphology

was unable to be performed. Nevertheless, three replicates of the DSSC fabrication using similar TiO₂ semiconductor thickness on the standard N3 dye showed an average conversion efficiency of 4.5 %. Hence, these results proved that the coating procedure was still reliable, despite the flaws seen under the SEM.

4.3.2 Application of bis-chalcone derivatives towards solar cell efficiency

Meanwhile, Figure 4.41 below showed the synthesized bis-chalcone derivatives that had been reported and discussed in Chapter 3 and Chapter 4. All of these compounds were applied as the dye sensitizer in the DSSC, respectively, where other compositions of the DSSC such as the thickness of TiO₂, the TCO glass substrate, redox electrolyte and counter electrode were kept in constant.

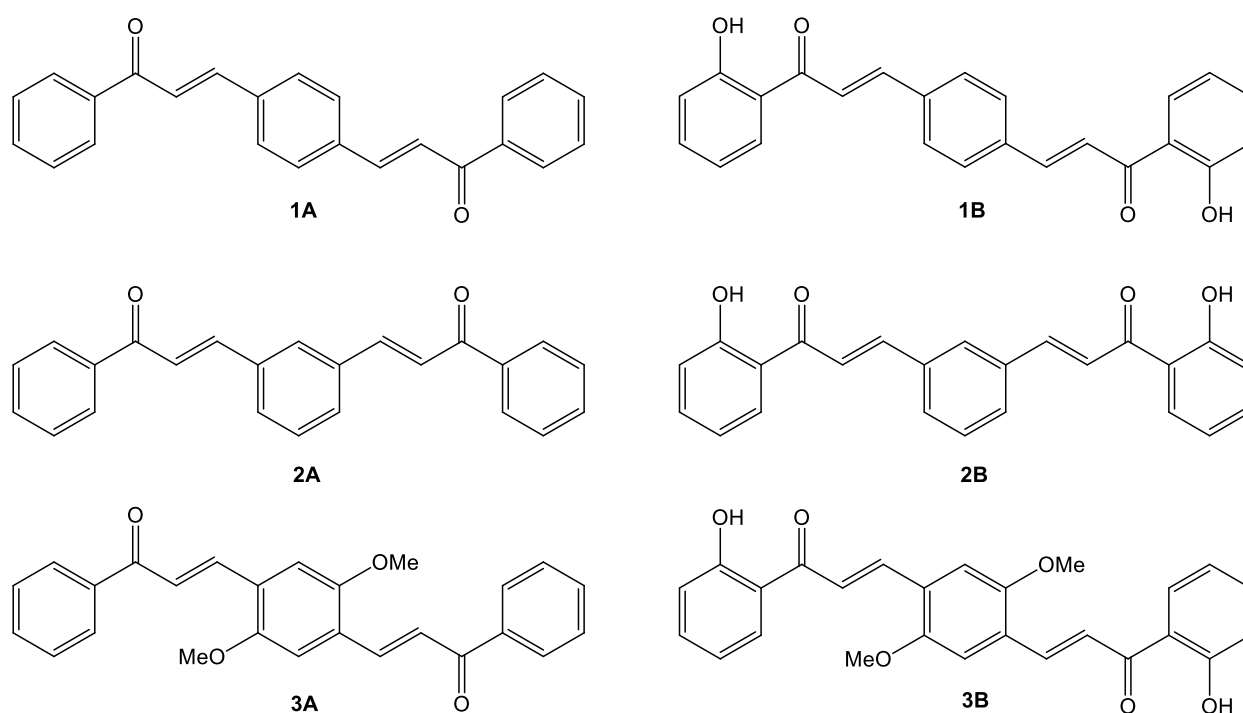


Figure 4.41: Molecular structure of synthesized bis-chalcone derivatives

The power conversion efficiencies of bis-chalcone derivatives recorded were summarized in Table 4.9. Meanwhile, Figure 4.42 shows the J/V measurement of the bis-chalcone series, which was divided into two categories, with and without –OH substituted compounds.

Table 4.9: Summary of power conversion efficiency of bis-chalcone compounds

Compound	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)
1A	0.41	0.14	50.65	0.034
1B	0.46	0.23	51.60	0.055
2A	0.36	0.14	41.62	0.021
2B	0.39	0.18	49.42	0.035
3A	0.44	0.15	48.57	0.032
3B	0.37	0.19	43.97	0.031

As known, the power conversion efficiency of bis-chalcone compounds can be calculated by using the equation stated below:

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

where

J_{sc} = solar circuit current density (mA/cm²)

V_{oc} = open circuit photovoltage (V)

FF = fill factor (%)

P_{in} = incident light intensity (100 mW/cm²)

η = power conversion efficiency (%)

Hence, the calculation for all the compounds which recorded in Table 4.9 were calculated as follows:

Compound **1A**

$$\begin{aligned} \eta &= \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \\ &= \frac{0.14 \text{ mA/cm}^2 \times 0.41 \text{ V} \times 50.65 \%}{100 \text{ mW/cm}^2} = 0.034 \% \end{aligned}$$

Compound **1B**

$$\begin{aligned} \eta &= \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \\ &= \frac{0.23 \text{ mA/cm}^2 \times 0.46 \text{ V} \times 51.60 \%}{100 \text{ mW/cm}^2} = 0.055 \% \end{aligned}$$

Compound **2A**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.14 \text{ mA/cm}^2 \times 0.36 \text{ V} \times 41.62 \%}{100 \text{ mW/cm}^2} = 0.021 \%$$

Compound **2B**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.18 \text{ mA/cm}^2 \times 0.39 \text{ V} \times 49.42 \%}{100 \text{ mW/cm}^2} = 0.035 \%$$

Compound **3A**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.15 \text{ mA/cm}^2 \times 0.44 \text{ V} \times 48.57 \%}{100 \text{ mW/cm}^2} = 0.032 \%$$

Compound **3B**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.19 \text{ mA/cm}^2 \times 0.37 \text{ V} \times 43.97 \%}{100 \text{ mW/cm}^2} = 0.031 \%$$

As shown in Table 4.9, compound **1B** showed the best solar conversion efficiency of 0.055 %, which is due to the good absorption of the compound **1B** dye to the TiO₂ layer, where yellow colour can be seen clearly dyed onto the surface. The result can be also supported by the fill factor (FF) value which gave up to 51.60 %. Fill factor is generally defined as the ideal of the device system work. Several factors that could affect the fill factor value include the thickness of TiO₂, the electrolyte, the resistance of the cell and also the conversion of photocurrent absorbed by the dye (Grätzel, 2000). Thus, the higher absorption of the dye sensitizer allowed more photon been absorbed, which resulted more photocurrent that could be transported to the nanocrystalline TiO₂ layer and increased the overall performance. In addition, the structure of compound **1B** consists of –OH substituent from one end to the other end that could acts as the donor or acceptor. Hence, this promotes the charge transfer to occur in the molecule and delivered the electron towards the TiO₂ semiconductor layer. In comparison with compound **1A**, the absence of –OH functional group in the molecule structure showed a significant effect towards the solar conversion efficiency with only 0.034 % recorded.

On the other hand, the presence of π -conjugation in the structure also plays vital role in solar conversion efficiency. This effect can be observed when we changed the substitution position of central phenyl ring from *para* (compound **1B**) to *meta*-position (compound **2B**). Compound **2B** showed 20 % lower solar conversion efficiency compared to the compound **1B**, which is 0.035 %, despite having the –OH substituted functional group. According to He and co-workers (2016), the π -conjugation effect in the molecule bonded by phenyl *meta*-branching point is destroyed, causing the electron-hole pair localized and electronic decoupling. Hence, this affects the overall performance of the dye-sensitizer to facilitate the electron to the semiconductor layer. Due to this reason, the conversion efficiency for compound **2A** is the lowest solar efficiency with only 0.021 %.

Compounds **3A** and **3B** were introduced with two methoxy groups attached at 2 and 5 positions of the central phenyl ring with *para*-branching point, respectively. The initial aim of introducing methoxy groups to the central phenyl ring of compounds **3A** and **3B** was to induce push-pull effect along the molecule. Interestingly, compound **3A** is highly luminescent with the λ emission centred at 505 nm and the Φ of 0.57 in DCM solution (Tay *et al.*, 2016). Indeed, compound **3A** also showed slightly higher conversion efficiency compared with compound **1A** and **2A**, where higher V_{oc} and J_{sc} values were recorded. However, compound **3B** which has both methoxy and hydroxyl substituent groups showed the least efficiency in comparison with compounds **1B** and **2B**. This may due to the poor solubility of the compound **3B** in the solvent system, where the crystal of compound **3B** was observed to reform on top of the TiO_2 surface. This caused the increase of the thickness in dye sensitizer layer and the direct contact towards counter electrode would results the increase of cell resistance and eventually affects the V_{oc} and J_{sc} value.

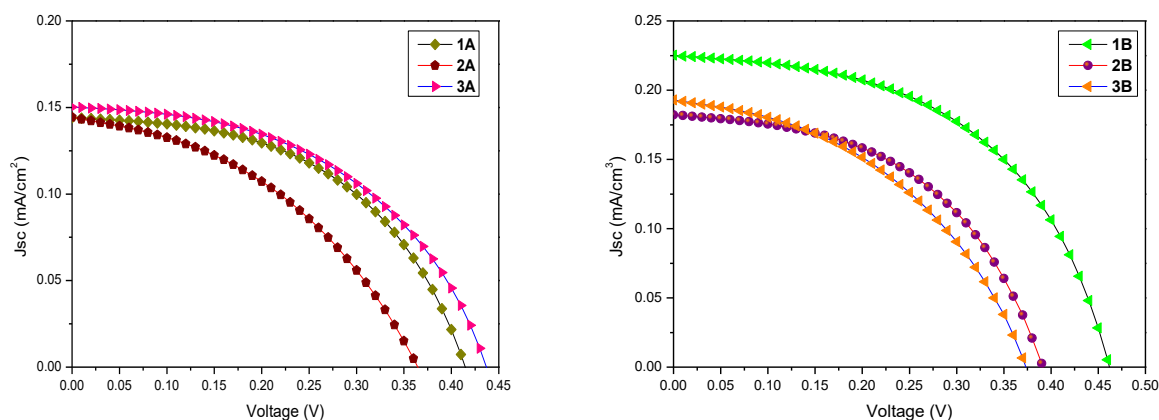


Figure 4.42: J/V measurement of bis-chalcone compounds (without $-\text{OH}$ substituent, compounds **1A**, **2A**, and **3A**, left); (with $-\text{OH}$ substituent, compounds **1B**, **2B** and **3B**, right)

4.3.3 Electrochemistry study of compound **1B**

Since compound **1B** exhibits the best PCE among the other derivatives, it is noteworthy to look into the electrochemical behavior of this compound by using the cyclic voltammetry analysis in order to determine its redox reaction (Figure 4.43). For the information, the cyclic voltammogram of **1B** was obtained by setting it at glassy carbon electrode and recorded in the DCM solution with 0.1 M $[\text{NBu}_4]\text{PF}_6$ as supporting electrolyte at 0.05 V s^{-1} scan rate. From the analysis, the cyclic voltammogram of **1B** showed a well-defined quasi-reversible reduction in the range of -0.5 V to -2.3 V . The quasi-reversibility of the reduction process is confirmed with the corresponding peak separation value between the cathodic peak potential ($E_{\text{pc}} = -1.58 \text{ V}$) and the two anodic peak potential ($E_{\text{pa}} = -1.79 \text{ V}$) and ($E_{\text{pa}} = -1.23 \text{ V}$) (Ilhan *et al.*, 2007). The existence of this cyclic voltammetry (CV) wave may be ascribed to the reduction of $\text{C}=\text{O}$ group and showed a mixed adsorptive and diffusive response for the system (Naik & Nandibewoor, 2012; Tavares *et al.*, 2013; Dhananjayulu *et al.*, 2014). These findings were supported by previous literatures describing on similar type of molecular frameworks

where they focused on proton coupled electron transfers leading to the reduction of the carbonyl bond to form the hydroxyl and hydrogenation of the vinylic bond (Naik & Nandibewoor, 2012; Tavares *et al.*, 2013). Hence, the presence of this redox potential in **1B** enables it to oxidize and reduce during the electron transfer process in DSSC.

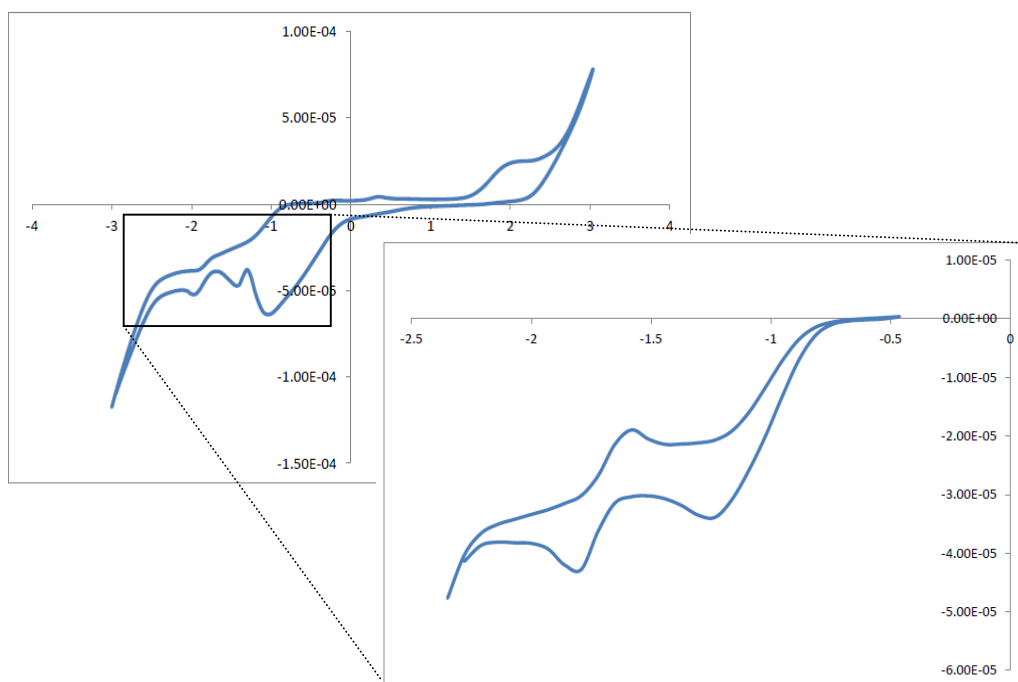


Figure 4.43: Cyclic Voltammogram of compound **1B** in DCM/0.1 M [NBu₄]PF₆ at 0.05 Vs⁻¹ scan rate

4.3.4 Application of complex CX1 and CX2 in solar cell efficiency

On the other hand, compounds **1B** and **2B** were reacted with [RuCl₂(DMSO-S)₃(DMSO-O)] precursor to obtain their respective ruthenium complex. The complexation procedures were adopted from the method as reported by Gaur and Mishra (2013) with minor modification which has been discussed extensively in Chapter 3 and Chapter 4 (Section 4.2). Thus, Figure 4.44 showed the molecular structure of **CX1** and **CX2** that had been synthesized.

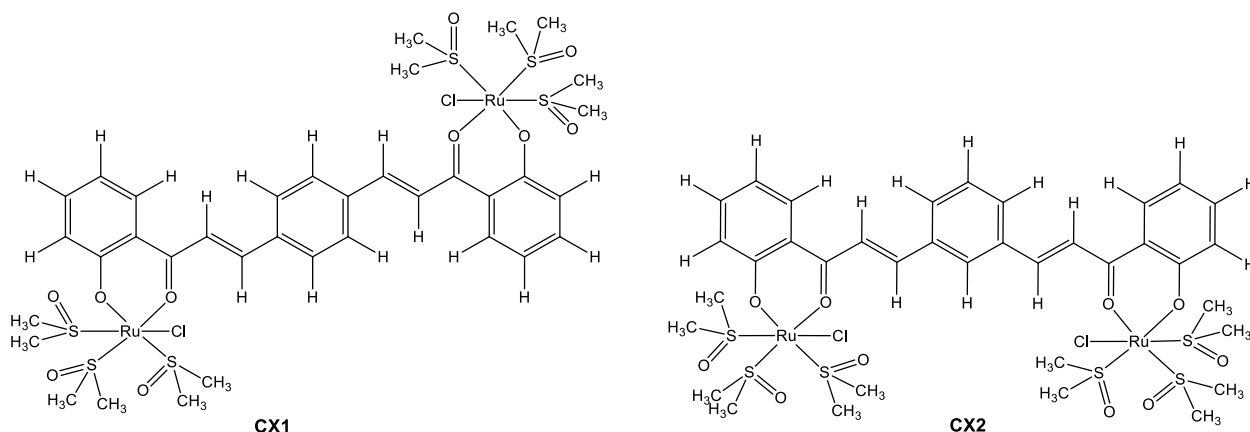


Figure 4.44: Molecular structure of **CX1** and **CX2**

Conversely, Table 4.10 showed the comparison of the power conversion efficiency between the standard N3 dye, the ruthenium complexes (**CX1** and **CX2**) and their respective ligands (**1B** and **2B**). Meanwhile, Figure 4.45 showed the J/V measurement of ruthenium complexes of **CX1** and **CX2** with ligand **1B** and **2B**, respectively.

Table 4.10: Summary of power conversion efficiency of ruthenium complexes with respective ligands

Compound/ complex	V_{oc} (V)	J_{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)
N3	0.71	10.05	64.05	4.570
CX1	0.08	0.13	28.30	2.943×10^{-3}
CX2	0.06	0.10	27.01	1.621×10^{-3}
1B	0.46	0.23	51.60	0.055
2B	0.39	0.18	49.42	0.035

Similarly, the power conversion efficiency of CX1 and CX2 were calculated as follows:

Complex **CX1**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.13 \text{ mA/cm}^2 \times 0.08 \text{ V} \times 28.30 \%}{100 \text{ mW/cm}^2} = 2.94 \times 10^{-3} \%$$

Complex **CX2**

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

$$= \frac{0.10 \frac{\text{mA}}{\text{cm}^2} \times 0.06 \text{ V} \times 27.01 \%}{100 \text{ mW/cm}^2} = 1.62 \times 10^{-3}$$

%

From the data shown in Table 4.10, the solar conversion efficiency of complex **CX1** and **CX2** as dye sensitizer recorded was only $2.94 \times 10^{-3} \%$ and $1.62 \times 10^{-3} \%$, respectively, which was 18 and 24 times lower in PCE value as compared to their respective ligand **1B** and **2B**, correspondingly. In fact, the molecular structure of the standard N3 dye also consists of ruthenium metal center, but with the conversion efficiency of up to 4.6 % recorded. Therefore, several factors may need to be taken into consideration for the low PCE results obtained in complex **CX1** and **CX2**.

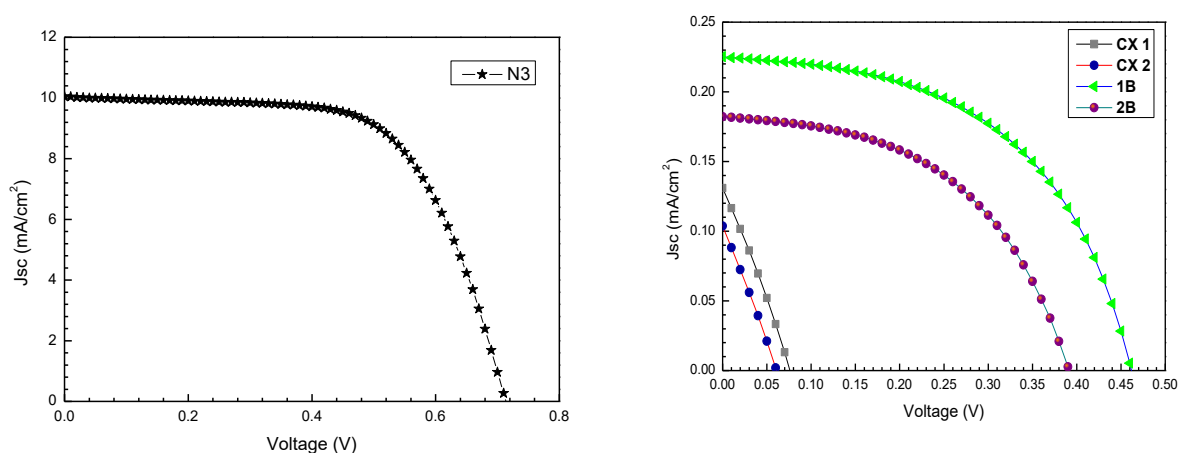


Figure 4.45: J/V measurement of standard N3 dye (left) and synthetic dye of ruthenium complexes (right)

Based on the inorganic dye sensitizer available in the market, most of them are consisted of single metal ion bonded to the highly conjugated compounds with strong donor and acceptor substituents present, for example the carboxylate group and NCS group that presence in the N3 dye itself. On the other hand, the **CX1** and **CX2** molecular structure showed two ruthenium metal ions bonded at (O,O) of each terminal of the ligand **1B** and **2B**,

correspondingly. Thereby, the formation of these complexes caused the disappearance of –OH donor substituents due to the deprotonation of the respective hydroxyl groups. Meanwhile, considering the fact that the DMSO substituents that attached at the ruthenium metal center are π -acceptors and with no donor substituents available at each terminal, this situation might have consequently disrupted the electron transfer within the molecular framework, despite the presence of two α , β - π -conjugated moieties in the bis-chalcone molecules.

As the results, no push-pull effect was seen in the complex **CX1** and **CX2** due to the absence of D- π -A molecular framework, thus creating a high resistance in the DSSC and caused the open circuit voltage and short circuit current to decrease, resulting in a low PCE value. Apart from that, the absorption of the **CX1** and **CX2** dyes to the TiO₂ semiconductor layer was relatively poor although the dye solution exhibits dark red in colour. This may be due to the absence of anchoring group such as carboxylate group to form bidentate ester linkage with the TiO₂ surface, hence hindered the process of electron injection into its conduction band (Grätzel, 2003). Therefore, a low fill-factor value was observed for both **CX1** and **CX2** with 28.30 % and 27.01 %, correspondingly, indicating the transportation of electron along the DSSC were not ideal.

In conclusion, as a role in dye sensitizer, compound **1B** afforded the best power conversion efficiency of 0.05 % in DSSC application among other bis-chalcone compound and complexes. This is due to the presence of –OH substituent from one end to the other end that could act as the donor or acceptor. Therefore, this promotes the charge transfer to occur within the molecule, thus electrons were delivered towards the TiO₂ semiconductor layer. On the other hand, ruthenium complexes **CX1** and **CX2** showed the low power conversion efficiency due to absence of push-pull effect in the molecular structure.

CHAPTER 5

CONCLUSION AND SUGGESTION FOR FUTURE WORK

5.1 Conclusion on the overall project

Three series of bis-chalcone had been successfully carried out by using the Claisen Schmidt condensation reaction namely compound **1A**, **1B**, **1C**, **2A**, **2B**, **3A** and **3B**. Each of them had been fully characterized with FT-IR, NMR, UV-visible spectroscopy and also CHN analysis. Similarly, two ruthenium complexes which derived from ligand **1B** and **2B** with ruthenium precursor **PC1** had been successfully obtained and characterized. The bis-chalcone derivatives and the ruthenium complexes were used as the dye sensitizer in DSSC and the power conversion efficiency were recorded. From the findings, compound **1B** showed the highest power conversion efficiency and fill factor with the value of 0.05 % and 51.60 %, respectively. On the other hand, both complex **CX1** and **CX2** showed much lower conversion efficiency than their respective ligand with only 2.79×10^{-3} % and 1.68×10^{-3} %, correspondingly. Besides, the fill factor of **CX1** and **CX2** recorded was only 28.30 % and 27.01 %, respectively. This concluded that the molecular structure of compound **1B** had the best design as a dye sensitizer for electron transfer in DSSC. Herein, the objectives for this research on determining the power conversion efficiency of bis-chalcone compounds and their complexes as dye sensitizer in DSSC had been achieved. The best molecular structure for the dye sensitizer had also been determined.

5.2 Suggestion for future work

Based on the results obtained in the DSSC application of bis-chalcone derivatives and its complexes, some useful information has been obtained. As proven in the results, bis-2'-hydroxychalcone or compound **1B** showed the best solar conversion efficiency of 0.05 %. This showed that the –OH substituents at each of the terminals resulted a minimal push-pull effect along the molecular structure. In order to further increase the push-pull effect within the molecular structure, it is necessary to enhance the light absorption wavelength of the bis-chalcone compounds to the visible region from 400 nm and above. By doing so, suitable substituents must be introduced for this purpose.

On the other hand, the reason for introducing the intermediate (E)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl)benzaldehyde (**1C**) was mainly to set up the platform for the modification of the molecular framework with other substituted acetophenone to recreate a new push-pull bis-chalcone compounds. Some recommendation of the molecular structure was shown in the Figure 5.1.

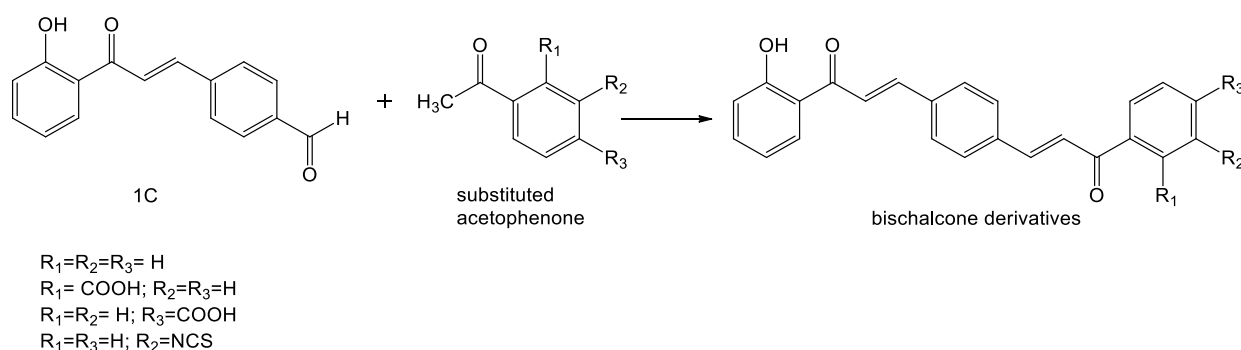


Figure 5.1: Proposed bis-chalcone molecular structure for future work

Generally, the idea of the proposed bis-chalcone molecular structure (Figure 5.1) is based on the molecular framework of N3 dye (Figure 2.1 in Chapter 2), which is a well-known dye sensitizer used in DSSC with consistently high power conversion efficiency. According to

Grätzel (2003), few criteria that need to be fulfilled by the role of dye sensitizer for high conversion efficiency are:

1. presence of substituents that can anchor firmly to the TiO₂ surface, i.e. carboxylate or phosphonate group
2. able to absorb most of the visible light to near infrared region
3. the energy level of LUMO in the excited sensitizer should well matched with the conduction band of the TiO₂ semiconductor at the lower bound
4. the designated molecule should possess high redox potential for the effective electron regeneration to return to the original state after excitation

Hence, by introducing the carboxylic group into the bis-chalcone molecular structure, it is believed that the absorption of the compounds to the TiO₂ will be improved. Besides, hydroxyl group is said to be able to act either as acceptor or donor substituent, thereby it can help in the light absorption. On the other hand, -NCS group plays huge role in absorbing visible light, thus it is worth to incorporated into the bis-chalcone moiety.

In fact, N3 dye is one of the dye sensitizer that bonded with the ruthenium metal centre. However, the conversion efficiency of the synthesized ruthenium complexes with bis-2'-hydroxychalcone were extremely low. It might due to the symmetrical molecular structure of the complexes which hindered the charge transfer which indirectly affected the electron injection to the TiO₂ semiconductor. For this reason, the importance of intermediate (*E*)-4-(3-(2-hydroxyphenyl)-3-oxoprop-1-en-1-yl)benzaldehyde (**1C**) come in placed. Figure 5.2 shows the possible molecular framework with ruthenium complex with bis-chalcone moiety for the future work. Apart from that, it is considerable to blend the synthesized compounds and complexes with polymer heterojunction such as [6,6]phenyl-C61-butyric acid methyl ester

(PC₆₁BM) as the active layer due to its ability to act as a charge transfer carrier and harvest the incident light (Yue *et al.*, 2009). To support the statement claimed, Chambon *et al.* (2013) had attempted the BF₂-hydroxychalcone complexes blended with the PC₆₁BM and significant improvement had been observed with the PCE of 1.13 % recorded.

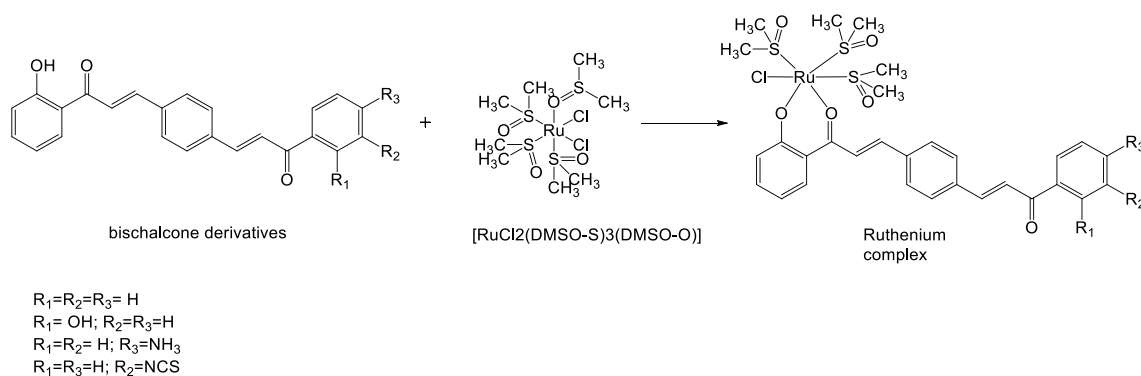


Figure 5.2: Proposed ruthenium complex with the bis-chalcone moiety

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APPENDICES

$ \begin{array}{c} \text{c} - \text{b} - \text{a} \quad \quad \text{a}' - \text{b}' - \text{c}' \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{C} = \text{C} \\ \quad \quad \quad \diagup \quad \diagdown \\ \quad \quad \quad \text{a} \quad \quad \text{a}' \end{array} $						
Substituent	a	b	c	a'	b'	c'
Carbon	10.6	7.2	-1.5	-7.9	-1.8	-1.5
-C ₆ H ₅	12	-	-	-11	-	-
-OR	29	2	-	-39	-1	-
-OCOR	18	-	-	-27	-	-
-COR	15	-	-	6	-	-
-COOH	4	-	-	9	-	-
-CN	-16	-	-	15	-	-
-Cl	3	-1	-	-6	2	-
-Br	-8	0	-	-1	2	-
-I	-38	-	-	7	-	-

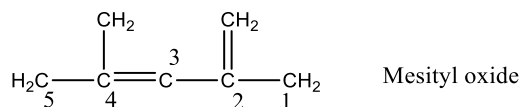
Appendix 1.1: ^{13}C substituent increments for alkene (vinyl) carbons (Pavia *et al.*, 2001)

* The symbol in the molecular structure represents:

- | | |
|-------------------|--------------------|
| i) $a = \alpha$ | iii) $a = \alpha'$ |
| ii) $b = \beta$ | iv) $b = \beta'$ |
| iii) $c = \gamma$ | v) $c = \gamma'$ |

* In the upper chains, if a group is in the β or γ position, the preceding atoms (α and/ or β) are assumed to be carbon atoms. Add these increments to the base value of ethylene (123.3ppm).

• Example



Actual value

$$\text{C3} = 123.3 + 15 - 7.9 - 7.9 = 122.5 \text{ ppm}$$

124.3 ppm

$$\text{C4} = 123.3 + 10.6 + 10.6 + 6 = 150.5 \text{ ppm}$$

154.6 ppm

Substituent Y	α (<i>ipso</i>)	o (<i>ortho</i>)	m (<i>meta</i>)	p (<i>para</i>)
-CH ₃	9.3	0.7	-0.1	-2.9
-CH ₂ CH ₃	15.6	-0.5	0	-2.6
-CH(CH ₂) ₂	20.1	-2.0	0	-2.5
-C(CH ₃) ₃	22.2	-3.4	-0.4	-3.1
-CH=CH ₂	9.1	-2.4	0.2	-0.5
—C $\equiv$ CH	-5.8	6.9	0.1	0.4
-C ₆ H ₅	12.1	-1.8	-0.1	-1.6
-CHO	8.2	1.2	0.6	5.8
-COCH ₃	7.8	-0.4	-0.4	2.8
-COC ₆ H ₅	9.1	1.5	-0.2	3.8
-COOH	2.9	1.3	0.4	4.3
-COOCH ₃	2.0	1.2	-0.1	4.8

-CN	-16.0	3.6	0.6	4.3
-NH ₂	19.2	-12.4	1.3	-9.5
-N(CH ₃) ₂	22.4	-15.7	0.8	-11.8
-NHCOCH ₃	11.1	-9.9	0.2	-5.6
NO ₂	19.6	-5.3	0.9	6.0
-OH	26.6	-12.7	1.6	-7.3
-OCH ₃	31.4	-14.4	1.0	-7.7
-OCOCH ₃	22.4	-7.1	-0.4	-3.2
-F	35.1	-14.3	0.9	-4.5
-Cl	6.4	0.2	1.0	-2.0
-Br	-5.4	3.4	2.2	-1.0
-I	-32.2	9.9	2.6	-7.3

Appendix 1.2: ¹³C substituent increments for benzene rings (Pavia *et al.*, 2001)

* Add these increments to the base value for benzene ring carbon (128.5 ppm)

Carbon (C)	¹³ C chemical shift (ppm)		Remarks
	1B	CX1	
7, 18	193.58	188.60	C=O
1, 20	163.81	171.91	Aromatic C-O
9, 16	144.20	142.26	-C=Cβ -
3, 22	137.02	137.10	Aromatic
10, 13	136.81	136.96	Aromatic
5, 24	129.79	132.28	Aromatic
11, 12, 14, 15	129.38	128.98	Aromatic
4, 23	121.52	125.86	Aromatic
6, 19	120.10	125.72	Aromatic
8, 17	119.11	121.78	-αC=C-
2, 21	118.89	115.51	Aromatic
-	-	47.67- 43.08	DMSO-S (CH ₃)

Appendix 1.3: ^{13}C chemical shift of ligand **1B** and complex **CX1**

Carbon (C)	^{13}C chemical shift (ppm)		Remarks
	2B	CX2	
7, 18	193.64	188.84	C=O
1, 24	163.78	171.84	Aromatic C-O
9, 16	144.44	142.25	-C=C β -
10, 14	136.80	136.98	Aromatic
3, 22	135.67	136.15	Aromatic
5, 20	130.61	132.46	Aromatic
11, 13	129.84	129.71	Aromatic
12	128.96	128.87	Aromatic
4, 21	121.42	125.94	Aromatic
6, 19	121.42	125.80	Aromatic
15	120.06	128.20	Aromatic
8, 17	119.13	121.70	- α C=C-
2, 23	118.87	115.51	Aromatic
-	-	47.67- 43.08	DMSO-S (CH ₃)

Appendix 1.4: ^{13}C chemical shift of ligand **2B** and complex **CX2**