Studies on Synthesis of Achiral and Chiral Amides, Amines, Allenes and on Electron Transfer Reactions

A Thesis

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

HARISH VAGALA

SCHOOL OF CHEMISTRY

UNIVERSITY OF HYDERABAD

HYDERABAD-500046

INDIA

December 2018

Dedicated to

My Family Members

School of Chemistry
University of Hyderabad
Central University P.O.
Hyderabad 500046
Telangana, India

DECLARATION

I, **HARISH VAGALA** hereby declare that this thesis entitled "**Studies on Synthesis of Achiral and Chiral Amides, Amines, Allenes and on Electron Transfer Reactions**" submitted by me under the guidance and supervision of **Professor M. Periasamy** is a bonafide research work which is also free from plagiarism. I also declare that it has not been submitted previously in part or in full to this University or any other University or Institution for the award of any degree or diploma. I hereby agree that my thesis can deposit in TURNITIN.

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CERTIFICATE

This is to certify that the thesis entitled "**Studies on Synthesis of Achiral and Chiral Amides, Amines, Allenes and on Electron Transfer Reactions**" submitted by **Mr. HARISH VAGALA** bearing registration number **11CHPH21** in partial fulfillment of the requirements for award of Doctor of Philosophy in the School of Chemistry is a bonafide work carried out by him under my supervision and guidance.

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Parts of this thesis have been published in the following publications:

1. **Harish, V**.; Periasamy, M. *Tetrahedron: Asymmetry* **2017**, *28*, 180.

He has also made presentations in the following conferences:

1. Poster presentation in the *Chemfest 2017* (annual in-house symposium) held at School of Chemistry, University of Hyderabad, INDIA, March-**2017**.
2. Oral presentation in the *Chemfest 2018* (annual in-house symposium) held at School of Chemistry, University of Hyderabad, INDIA, March-**2018**.
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Further the student has passed the following courses towards fulfillment of coursework requirement for Ph.D.:

	Course	Title	Credits	Pass/Fail
1.	CY-801	Research Proposal	3	Pass
2.	CY-805	Instrumental Methods A	3	Pass
3.	CY-806	Instrumental Methods B	3	Pass
4.	CY-840	Spectroscopic and other Physical Methods	3	Pass

Hyderabad
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Prof. M. Periasamy
(Thesis Supervisor)

Dean
School of Chemistry
University of Hyderabad
Hyderabad 500 046
INDIA

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Harish Vagala

Contents

Chapter 3

Electron Transfer Reactions using Amine, Amide Donors and *p*-Chloranil Acceptor

Abbreviations

$[\alpha]_D^{25}$	specific rotation at 25 °C, λ = 589 nm
Ac	acetyl
anhyd.	anhydrous
aq.	aqueous
Ar	aryl
Bn	benzyl
Boc	*tert*-butoxycarbonyl
9-BBN	9-borabicyclononane
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	1,1'-bi-2-naphthol
bp	boiling point
bs	broad singlet (spectral)
Bu	butyl
Bz	benzoyl
^{t}Bu	tertiarybutyl
c-hex	cyclo hexyl
cat.	catalytic
Cbz	benzyloxycarbonyl
cm^{-1}	wavenumber(s)
conf.	configuration
CSA	10-camphorsulfonic acid
DABCO	1,4-diazabicyclo[2.2.2]octane
DCM	dichloromethane
dd	doublet of doublet
de	diastereomeric excess
DEAD	diethyl azodicarboxylate
DEPT	distortionless enhancement by polarization transfer
DIPEA	*N*,*N*-diisopropylethylamine
DMAP	4-(*N*,*N*-dimethylamino)pyridine

DMF	dimethylformamide
DMSO	dimethyl sulfoxide
dr	diastereomeric ratio
ee	enantiomeric excess
EI	electron impact (in mass spectrometry)
equiv.	equivalent
ESI-MS	electronspray ionization mass spectrometry
Et	ethyl
h	hour(s)
HMPA	hexamethylphosphoramide
HPLC	high-performance liquid chromatography
i	iso
IPA	2-propanol
IR	infrared
O^iPr	isopropyloxy
J	coupling constant (in NMR spectroscopy)
KHMDS	potassium hexamethyldisilazide
LAH	lithium aluminium hydride
LDA	lithium diisopropylamide
LiHMDS	lithium hexamethyldisilazide
liq.	liquid
lit.	literature
LVT	low valent titanium
m	multiplet (spectral)
M	moles/liter
Me	methyl
MHz	megahertz
min.	minute(s)
mp	melting point
MS	mass spectrum
Ms	methanesulfonyl

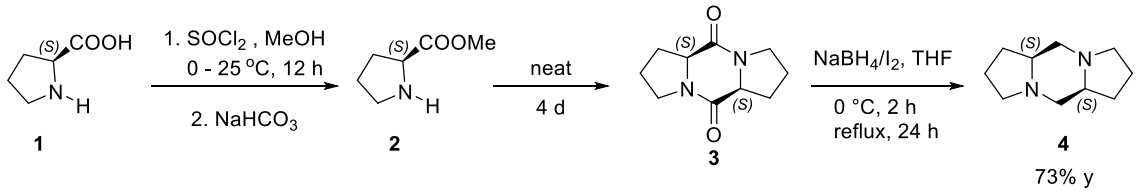
M.S.	molecular sieves
MSA	methanesulfonic acid
NMR	nuclear magnetic resonance
Nu	nucleophile
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
PMHS	polymethylhydrosiloxane
ppm	parts per million (spectral)
^{i}Pr	isopropyl
^{i}PrBA	isopropylbenzamide
psig	pounds per square inch gauge
PTSA	*p*-toluenesulfonic acid
Py	pyridine
q	quartet
rt	room temperature
s	singlet
sec	secondary
t	tertiary
t	triplet
TASF	tris(dimethylamino)sulfonium difluorotrimethylsilicate
TBAI	tetrabutylammonium iodide
TBSCl	tertiarybutyldimethylsilylchloride
Tf	trifluoromethanesulfonyl
TFA	trifluoroacetic acid
TfOH	triflic acid
THF	tetrahydrofuran
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
TMS	tetramethylsilane
Ts	toluenesulfonyl
Uv	ultraviolet
y	yield

Abstract

This thesis entitled "**Studies on Synthesis of Achiral and Chiral Amides, Amines, Allenes and on Electron Transfer Reactions**" comprises of three chapters. Each chapter is subdivided into four sections namely **Introduction**, **Results and Discussion**, **Conclusions** and **Experimental Section** along with **References**. The work described in this thesis is exploratory in nature

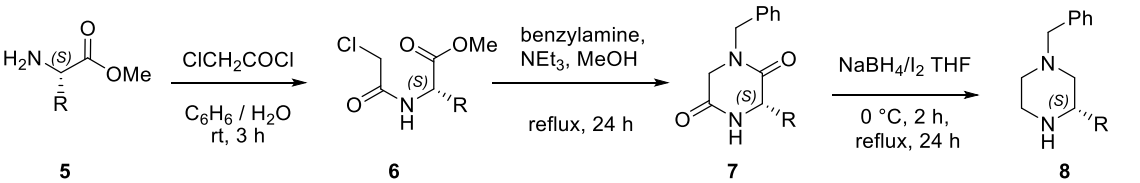
The first chapter describes studies on the synthesis of chiral amine derivatives using L-proline **1** and other amino acids. We have observed that the reduction of the readily accessible chiral (5a*S*,10a*S*)-octahydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-dione **3** gave the optically pure (5a*S*,10a*S*)-decahydrodipyrrolo[1,2-a:1',2'-d]pyrazine **4** in 73% yield using the $NaBH_4/I_2$ reagent system which generates diborane and H_3B:THF *in situ* in THF solvent at 0 ^oC (Scheme 1).

Scheme 1

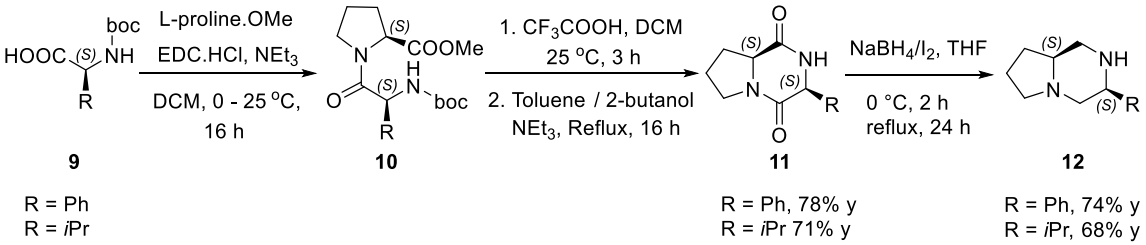


Also, the piperazine derivatives **8** were prepared *via* diketopiperazines **7** starting from the amino acids L-proline **1**, L-alanine **5a** and L-phenyl alanine **5b** (Scheme 2)

Scheme 2

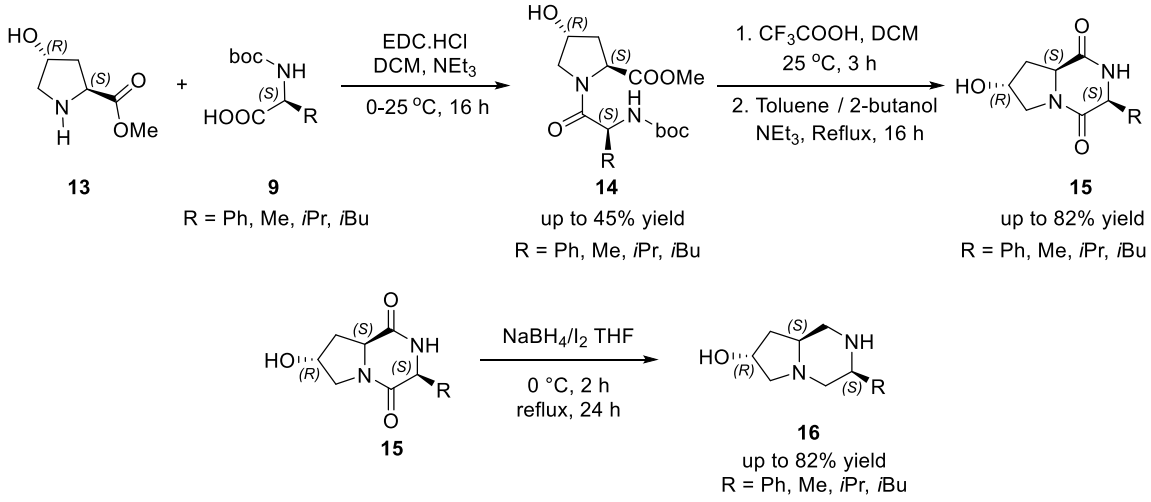


Scheme 2 (Continued)



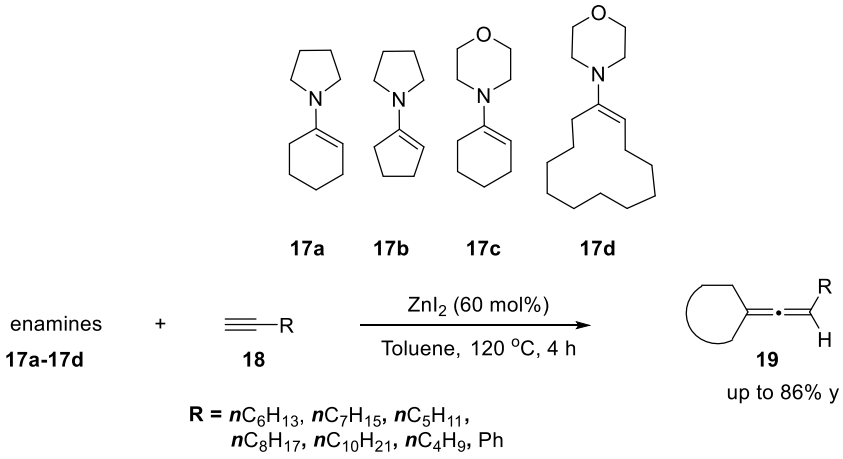
We have also synthesized the 4-hydroxyproline based chiral piperazines **16** using other amino acid derivatives *via* the corresponding diketopiperazines **15** (Scheme 3)

Scheme 3



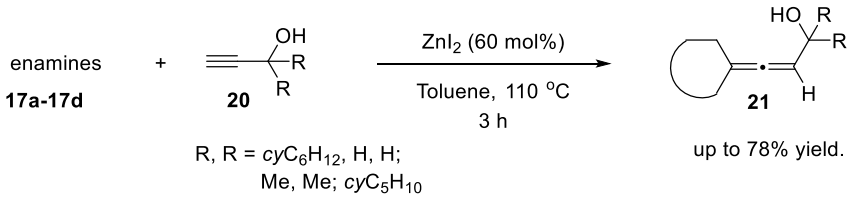
In Chapter 2, efforts were undertaken towards the ZnI_2 promoted conversion of enamines **17a-17d** to cycloalkyl allenes **19** in toluene at 120 °C (Scheme 4)

Scheme 4



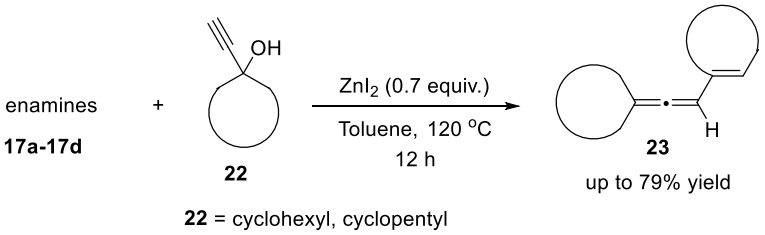
We have also examined the ZnI_2 promoted reaction of 1-alkynols **20** with enamines **17a-17d**. The corresponding allenol derivatives **21** were obtained in up to 78% yield (Scheme 5).

Scheme 5



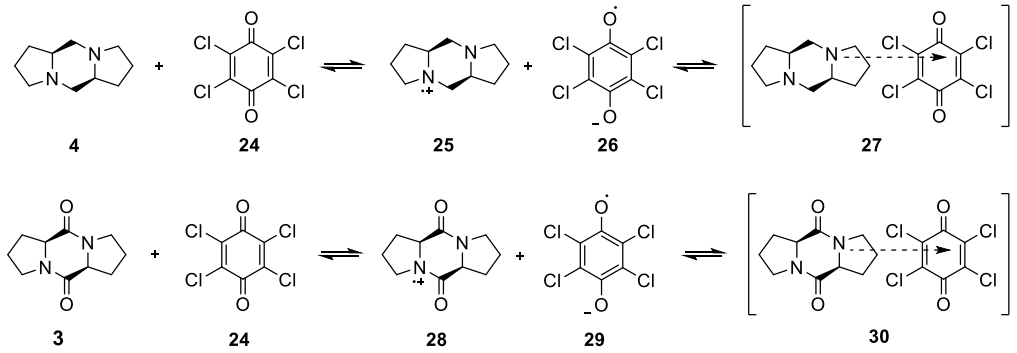
We have observed that the vinylic allenes **23** can be readily synthesized by tuning of the reaction condition using 70 mol% of ZnI_2 in toluene (Scheme 6).

Scheme 6



In the third chapter, studies undertaken on the electron transfer reactions of *p*-chloranil **24** with piperazine derivative **4** and the diketopiperazine derivative **3** prepared in chapter 1. The paramagnetic intermediates formed in the reaction in PC/DCM solvent were detected by epr spectral analysis (Scheme 7).

Scheme 7



Also, we have constructed organic electrochemical cells based on electron transfer reactions of amine **4**, amide **3** donors and *p*-chloranil **24**. We have also constructed the cells using isopropyl amide derivatives **31a-c** and **32a-d**. In these cells, the *p*-benzoquinone **33**, sulfone **36** and phthalimide derivatives **34** and **35** were used as electron transporters (Figure 1).

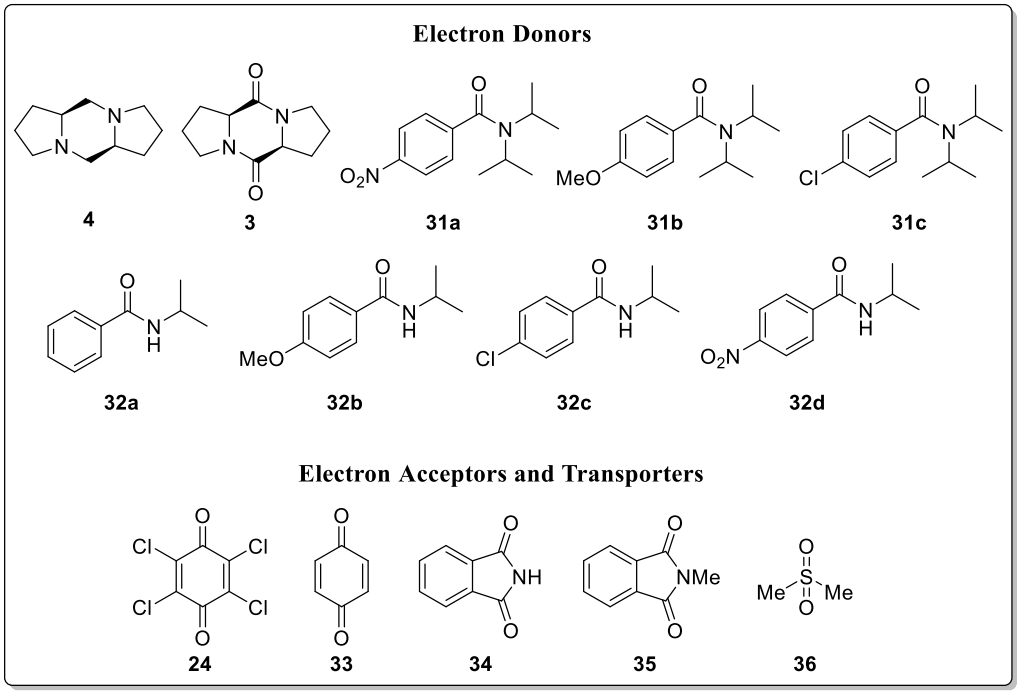


Figure 1

We have examined the performance of these electrochemical cells by measuring current (I) and voltage (V) characteristics, at the temperatures 28 ^{o}C, 35 ^{o}C and 40 ^{o}C with regular time intervals.

The results presented in this thesis are discussed considering mechanisms involved in these transformations and comparison with literature reports.

Note: Scheme numbers and compound numbers given in this abstract are different from those given in the chapters.

Chapter 1

Enantiomerically Pure Chiral Piperazines via $NaBH_4/I_2$ Reduction of Cyclic Amides

1.1 Introduction

1.1.1 Importance of piperazines

The piperazine moiety is present in several drugs and also plays a key role in medicinal chemistry. A wide range of activities, such as anti-allergenic, antibacterial, anti-anxiety, anti-emetic, antimigraine and platelet anti-aggregatory activity showed by these pipearazine derivatives.[1,2] Gootz *et al*[3] tested several substituted piperazine derivatives **1-7** in a DNA cleavage assay with calf thymus topoisomerase II and observed that the methyl group in the C-7 piperazine ring influenced potency against the mammalian enzyme (Figure 1).

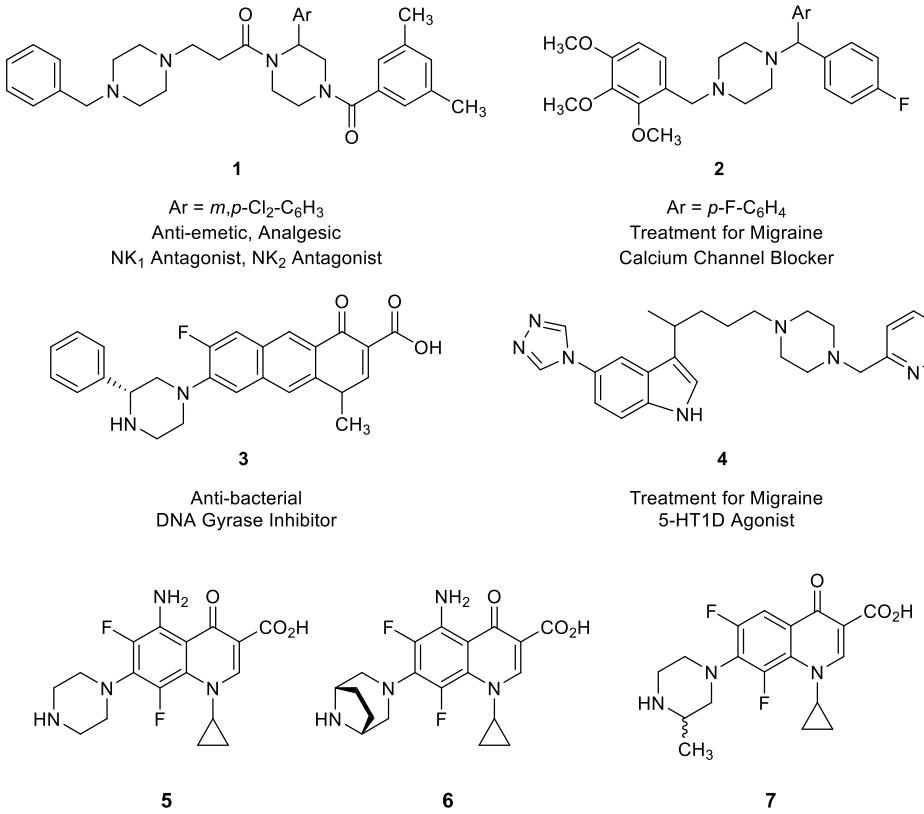
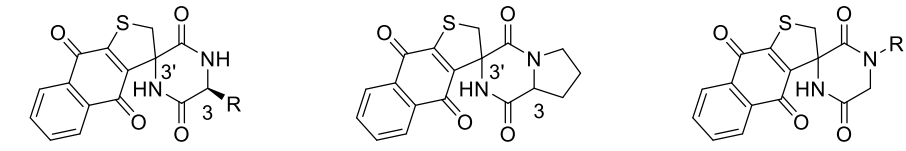


Figure 1

2,5-Diketopiperazines are the smallest cyclic peptides which can be prepared by the cyclization of two α-amino acids. The diketopiperazine motif is common in many natural products and in pharmacologically active compounds with a wide range of biological activities.[4] The chiral diketopiperazine and chiral piperazines are present in several biologically active compounds.[5] The 2, 5-diketopiperazine is also present in several the naturally occurring peptide antibiotics.[6]

2,5-Diketopiperazines have been used as DNA binding agents to overcome multidrug resistance of quinone-based anticancer agents.[7] DNA binding agents show selective cytotoxic activity and are commonly used as therapeutics for the treatment of cancer. The spirodiketopiperazines were found to be potential anticancer agents related to the doxorubicin and mitoxantrone with equivalent cytotoxic activity.[7] Among these spiro compounds, the (3S, 3′R) isomers **8-10** have cytotoxic potency greater than of doxorubicin against human breast and colon arcinoma cell lines. The (3R, 3′S) isomer of spirodiketopiperazine **9** is the most potent in both the cell lines. Substituents on nitrogen in compound **10** have the most potent of these derivatives, with a cytotoxic activity comparable to doxorubicin (Figure 2).[7]



8
R = CH_2SH (3*S*,3'*R*)
R = $CH_2CH_2SCH_3$ (3*S*,3'*R*)

9
(3*S*,3'*R*)
(3*R*,3'S)

10
R = $CH_2CH_2NMe_2$
R = $CH_2CH_2N(CH_2)_5$

Figure 2

The tryprostatin derivatives have attracted attention as potential anticancer drugs. For example, the tryprostatin B **12** is a mammalian cell-cycle inhibitor and

tryprostatin A **11** is an inhibitor of the multidrug-resistance protein (BCRP/ABCG2) in breast cancer treatment.[8] Cyclic dipeptide cycloserine dimer **14** is active against mycobacterium tuberculosis. Cairomycin B is active against gram-positive bacteria.[9] Also, the highly complex fused ring systems such as avrainvillamide, bicyclomycin are active against multidrug-resistant bacteria and gramnegative bacteria, respectively (Figure 3).

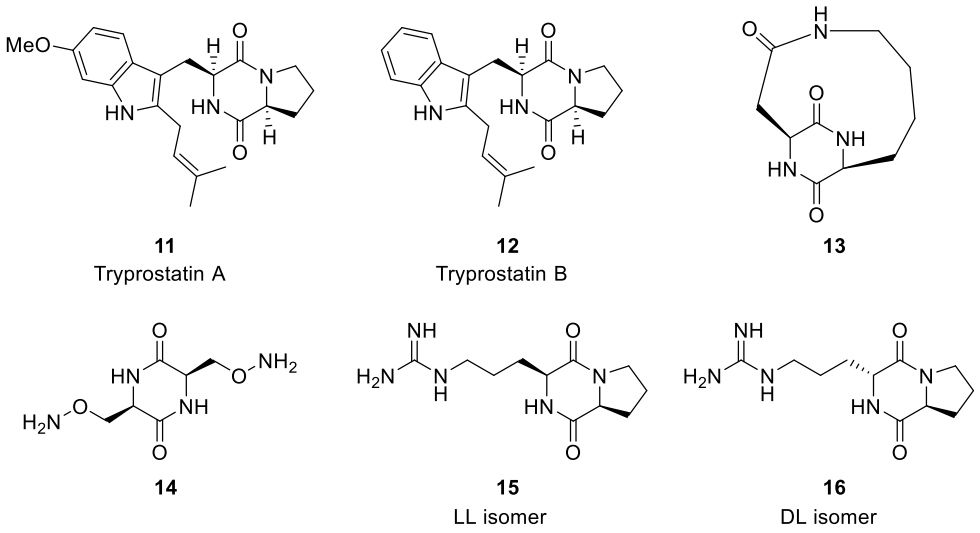
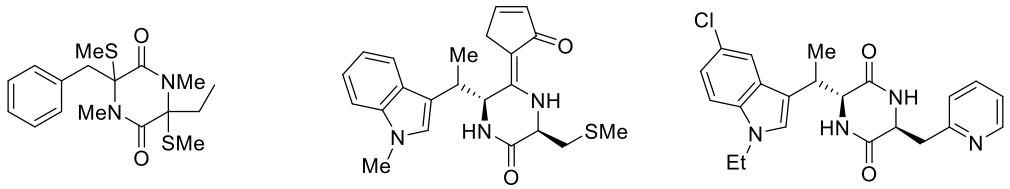


Figure 3

The chitinase inhibitor LL isomer **15** has comparable enzyme activity against chitinase from *bacillus* sp and its DL isomer **16** isomer was much less active. Also, a similar pattern of activity was found against the yeast *S. cerevisiae*[10] (Figure 3). The bis(methylthio)-2,5-diketopiperazine FR106969 **17** and oxocyclo pentylidene-2,5-diketopiperazine FR900452 **18** have showed high inhibitory potency against platelet activating factor induced rabbit platelet aggregation.[11] The diketopiperazine derivative **19** has also shown highly potent rabbit platelet aggregation (IC_{50} = 36 nM) (Figure 4).



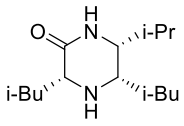
17 **18** **19**

Figure 4

1.1.2 Natural products containing diketopiperazines

Kim *et al*[12] reported the isolation of novel bioactive alkaloid from the leaves extract of *Arum palaestinum* Boiss. The alkylated piperazine skeleton piperazirum (3,5-diisobutyl-6-isopropyl-piperazin-2-one) **20** showed a significant cytotoxicitic activity against cultured tumor cell lines *in vitro*. Tadalafil **21** is a commercially available drug containing unnatural amino acid D-tryptophan and have been used for the treatment of erectile dysfunction (Figure 5).[13]

Mycocyclosin **22** is a diketopiperazine natural product isolated from *M. tuberculosis*. with close resemblance to the other natural products herquline A **23** and herquline B **24**.[14] Several complex fungal metabolites have the cyclo(L-Trp, L-Pro) skeleton of **25** such as brevianamides **26-27**, fumitremorgins **31**, spirotryprostatin A **28**, and cyclotryprostatin derivatives A-D **29-33**.[15] The diketopiperazine derivatives are annulated **29-33** or spiroannulated **26, 28** containing an extra bridging structure leads to increase the conformational rigidity and they possess higher in selectivity toward target proteins (Figure 5).[16]



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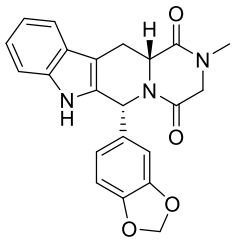
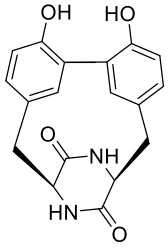


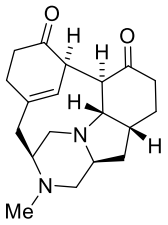
Tadalafil

21



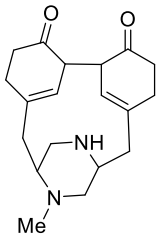
mycocyclosin

22



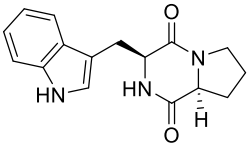
herquline A

23



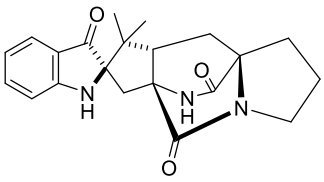
herquline B

24



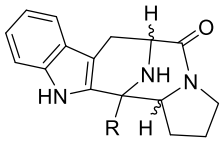
brevianamide F

25



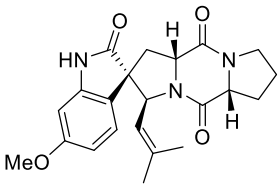
brevianamide A

26



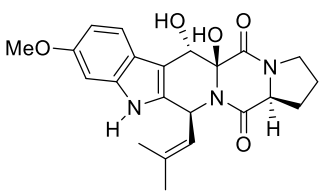
brevianamide F analogues

27



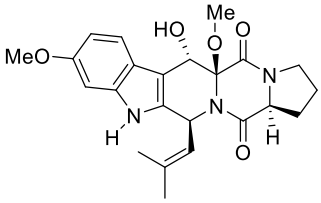
Spirotryprostatin A

28



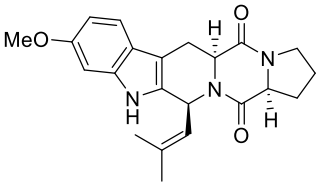
cyclotryprostatin A

29



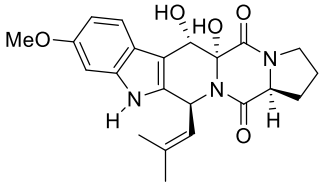
cyclotryprostatin B

30



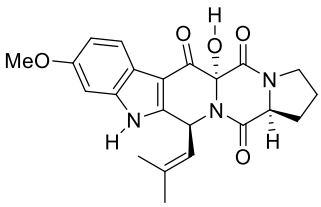
fumitremorgin C

31



cyclotryprostatin C

32



cyclotryprostatin D

33

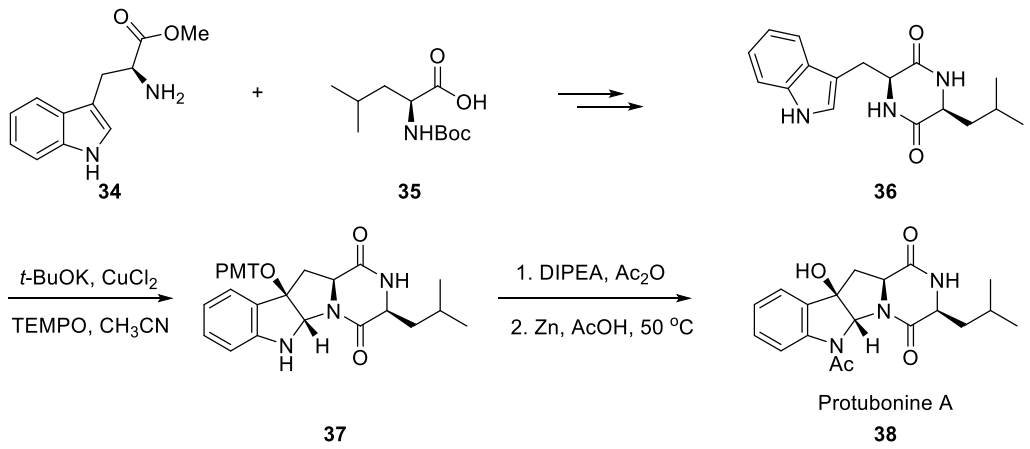
Figure 5

Brevianamide F **27** analogues possess human breast cancer resistance protein inhibitor activity and demethoxyfumitremorgin C has anticancer activity (Figure 5).[17]

Synthesis of alkaloid derivative Protubonine A

A method for the synthesis of 3-hydroxypyrroloindoline alkaloid derivative protubonine A **38** from the corresponding diketopiperazine **36** via copper-catalyzed annulations under aerobic reaction conditions was reported (Scheme 1).[18]

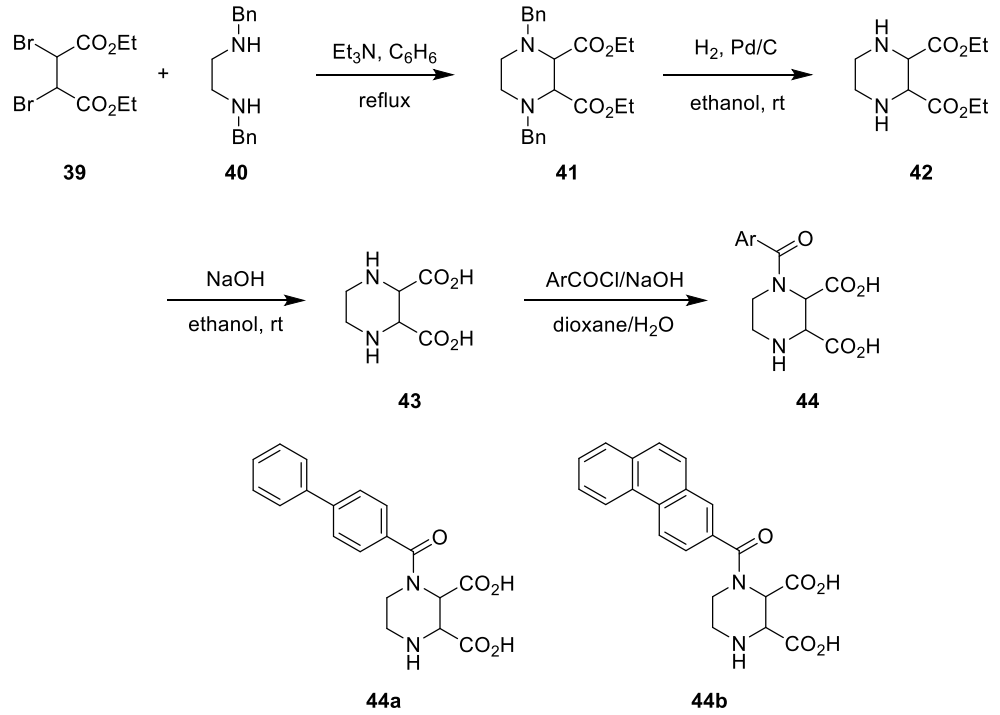
Scheme 1



Synthesis of 2,3-dicarboxylic acid substituted piperazines

N-Substituted piperazine-2,3-dicarboxylic acid derivatives were found to be active NMDA antagonists (Scheme 2). The compound **44a** displayed an unusual selectivity with relative affinity for NR2C and NR2D vs NR2A and NR2B. The phenanthrenyl-2-carbonyl derivative **44b** has higher affinity (scheme 2).[19]

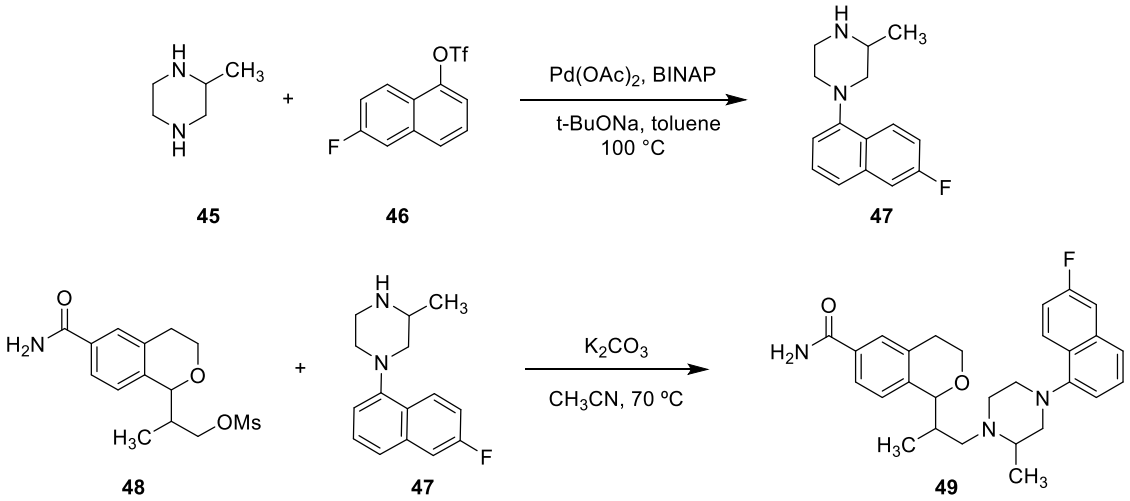
Scheme 2



Synthesis of naphthyl substituted piperazines

In a recent study by Bueno *et al*,[20] 1-naphthyl and 2-naphthyl piperazines **47** and **49** were shown to be good 5-HT1D/SRI pharmacophores (Scheme 3).

Scheme 3

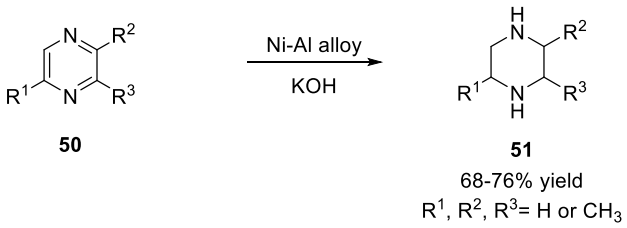


The presence of methyl group at 3rd position in the piperazine ring improves the affinity and also *S* isomer shows relatively better activity (Scheme 3).

Synthesis piperazines by reduction of pyrazines

Lunn *et al*[21] reported the synthesis of different substituted piperazine derivatives **51** by the reduction of pyrazines **50** using Ni/Al alloy in KOH solution (Scheme 4).

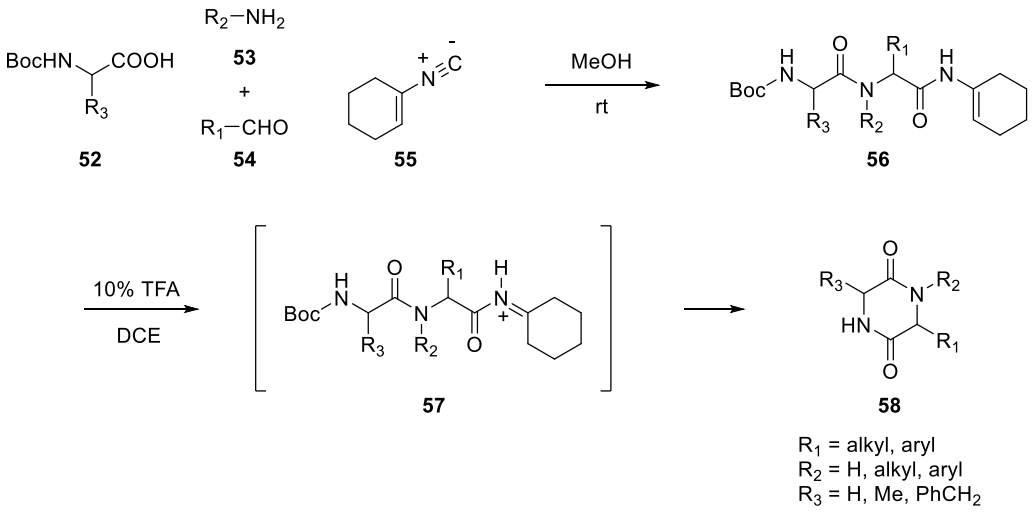
Scheme 4



1.1.3 Methods for synthesis diketopiperazines

A methodology using the boc-protected amino acid, cyclohexenyl isonitrile in Ugi reaction was reported for the synthesis of racemic 2,5-diketopiperazine **58** from transient activated N-acyliminium ion, generated *in situ* form dipeptide **56** (scheme 5).[22]

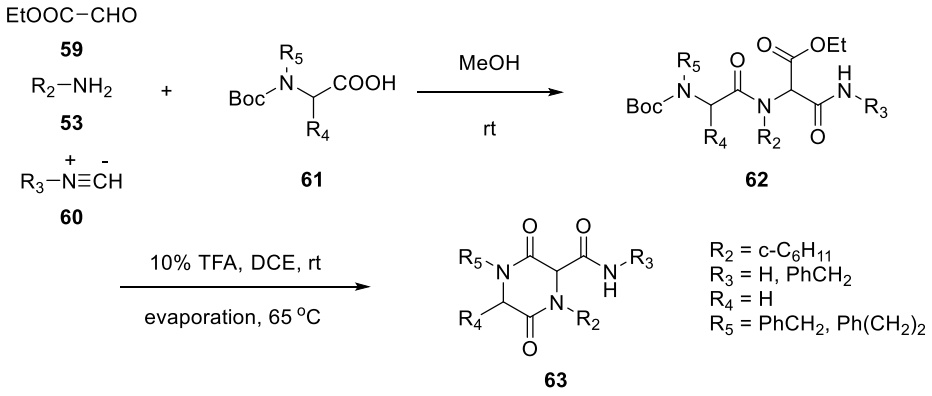
Scheme 5



N-4 Carboxamide Template

Also, a similar methodology using Ugi reaction condition was reported for the synthesis of 2,5-diketopiperazine carboxamide template **63** from the corresponding peptide derivatives **62** (scheme 6).[23]

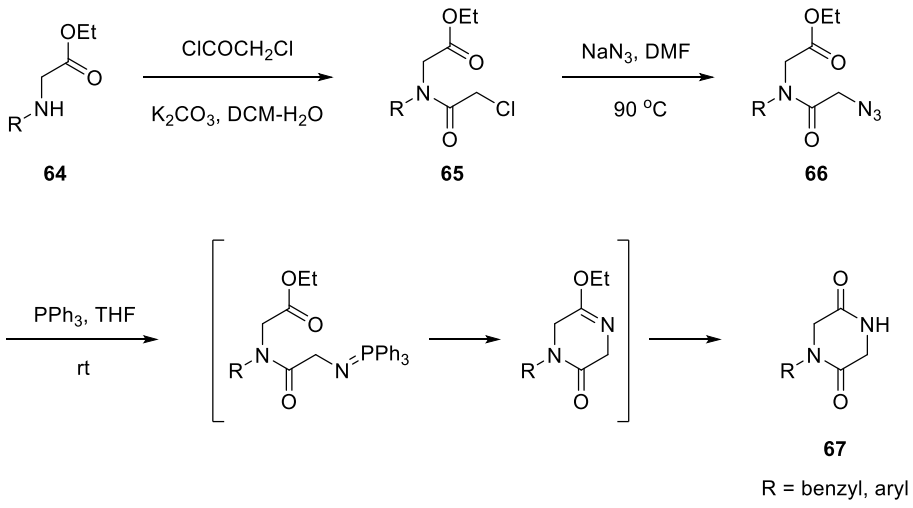
Scheme 6



Aza-Wittig Cyclization

An intramolecular Aza-Wittig reaction for the synthesis of N-substituted 2,5-diketopiperazines was reported using amine **64** *via* iminophosphorane and imino ether intermidiates, generated *in situ* from the azide derivative **66** (scheme 7).[24]

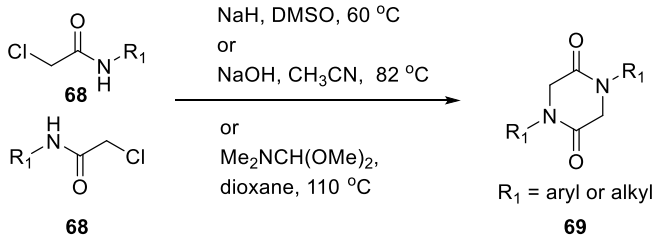
Scheme 7



Cyclization *via* Chloroacetamides

One pot synthesis of symmetrical 1,4-disubstituted-2,5-diketopiperazines **69** was reported using α-haloacyl derivatives **68** of amino acids in the presence of base (Scheme 8).[25]

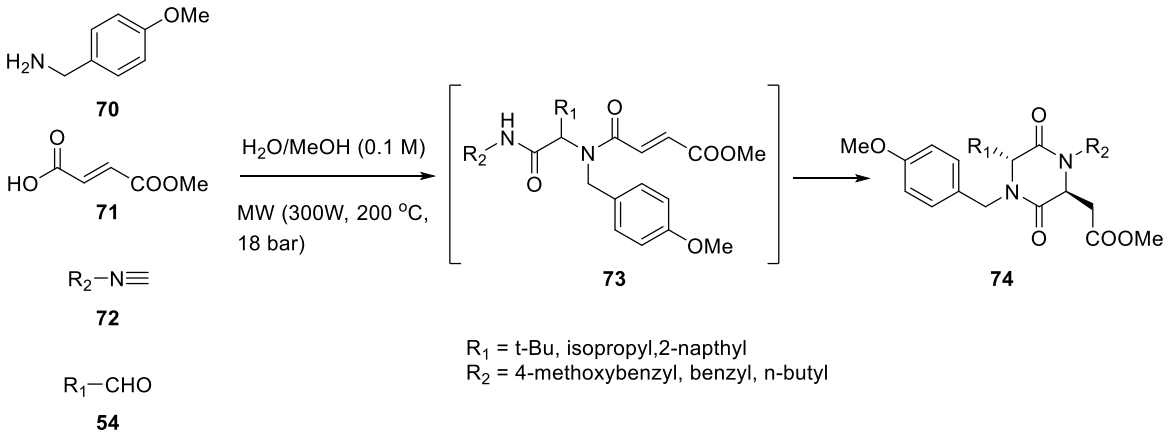
Scheme 8



Cyclization *via* Michael Addition

N,N'-Disubstituted diketopiperazine derivatives **74** were also obtained using four components *via* Michael addition reaction under microwave (300W, 200 °C, 18 bar) condition (Scheme 9).[26]

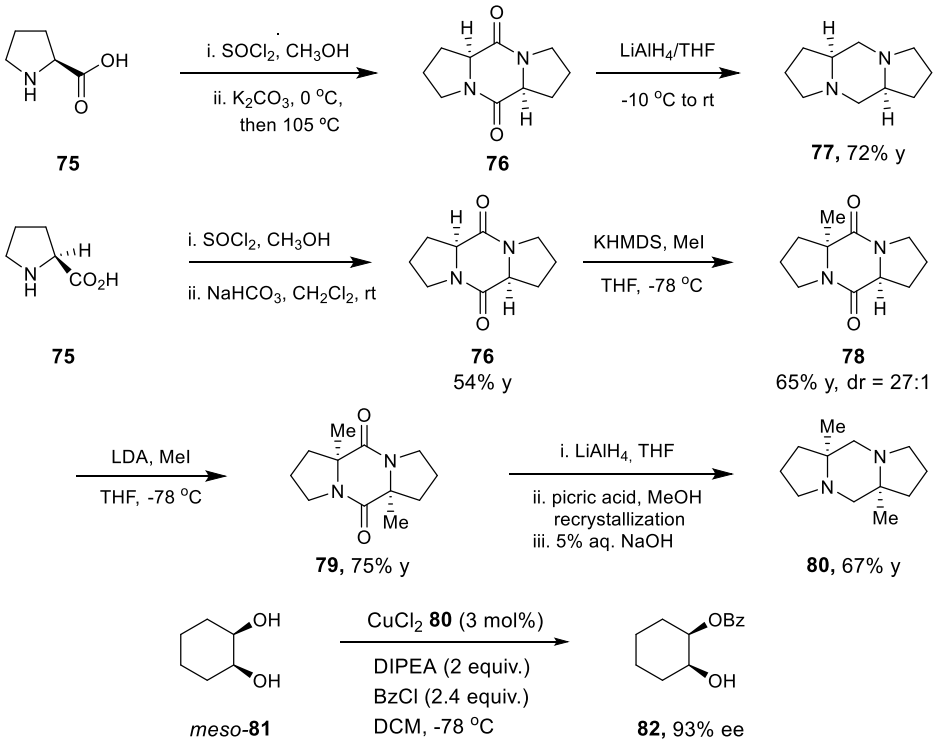
Scheme 9



Synthesis of chiral piperazines

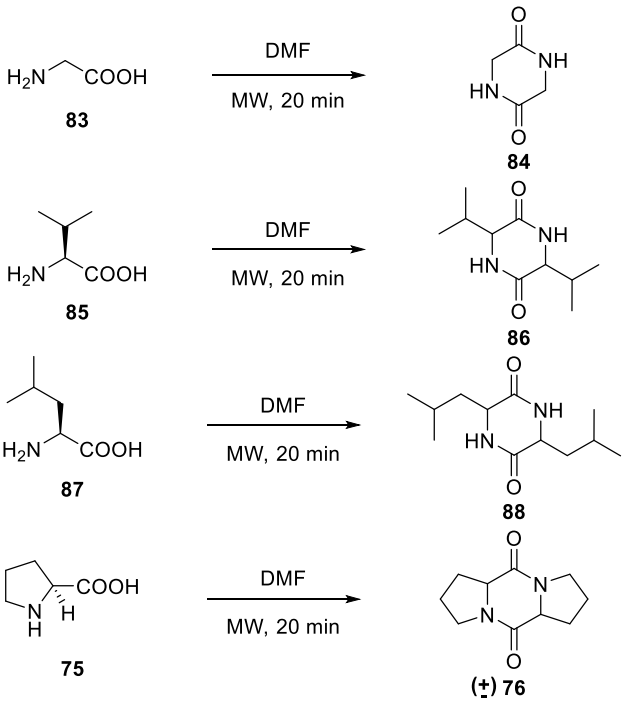
Shirai *et al*[27] reported the synthesis of L-proline based C_2-symmetric chiral diketopiperazine **76** using naturally occurring chiral L-proline **75** (Chart 1).

Chart 1



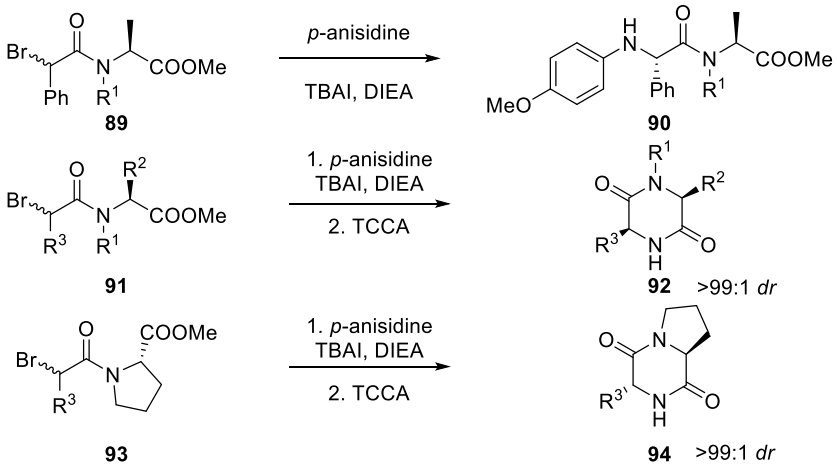
The chiral diketopiperazine **76** was reduced using LAH in THF to give chiral piperazine **77** in good yield. The compound **76** further converted to dimethyl substituted piperazine (*S,S*)-**80** and found to be an effective ligand for copper-catalyzed asymmetric acylation of *meso*-1,2-diols **81**. Very recently, self condensation of L-amino acids were reported under microwave irradiation in DMF solvent. In this condition, acyclic amino acid based chiral diketopiperazines were obtained. Whereas, cyclic amino acid L-proline diketopiperazine **76** was obtained only as a racemic mixture (Chart 2).[28]

Chart 2



Asymmetric synthesis of 3,4,6-trisubstituted 2,5-diketopiperazine derivatives **92** and proline based diketopiperazines were developed by using α-bromo acetamides **91** and *p*-anisidine (Scheme 10).[29]

Scheme 10



Methods for the synthesis of amino acid based diketopiperazines using two different amino acid derivatives were reported (Chart 3).[30]

Chart 3

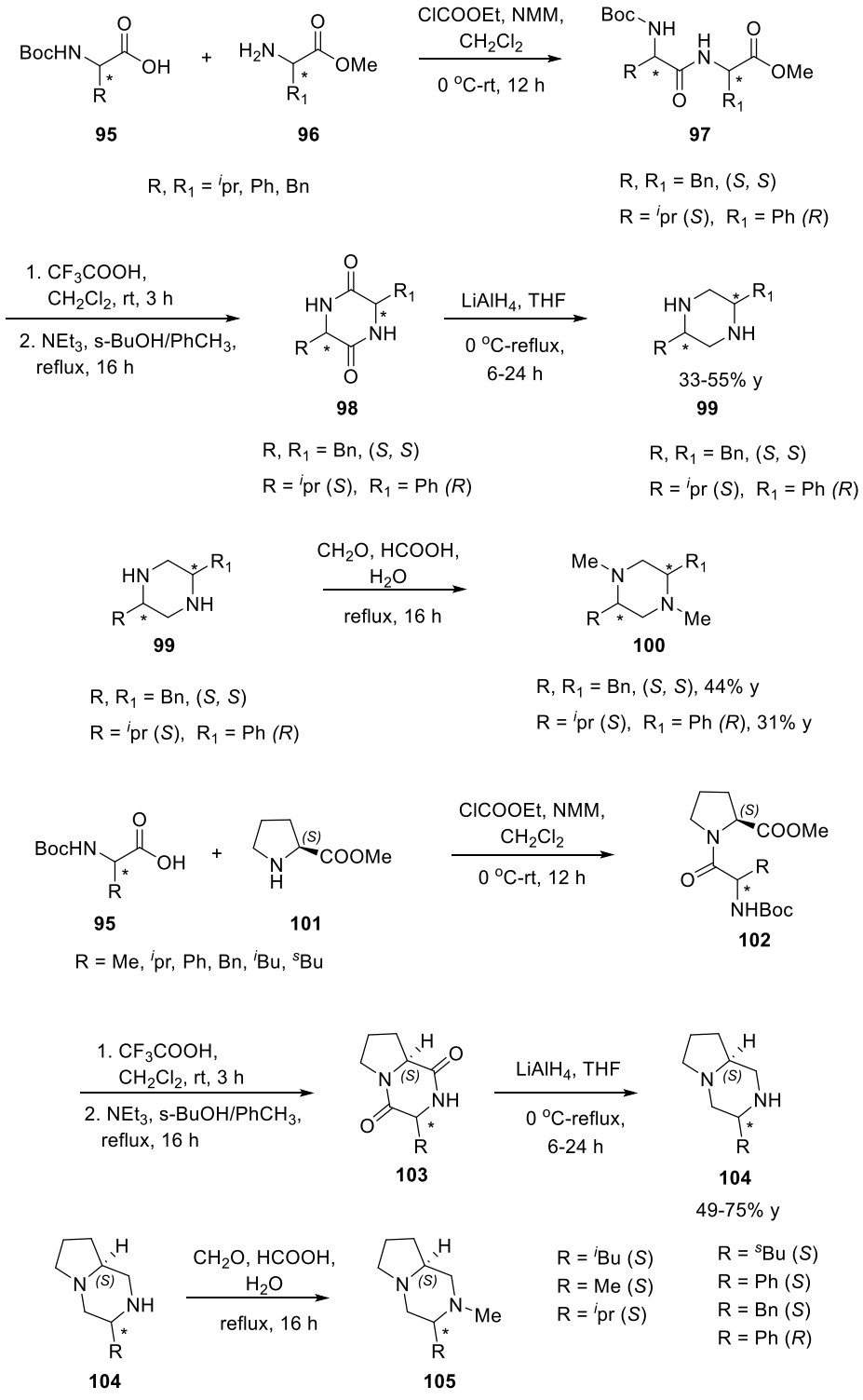
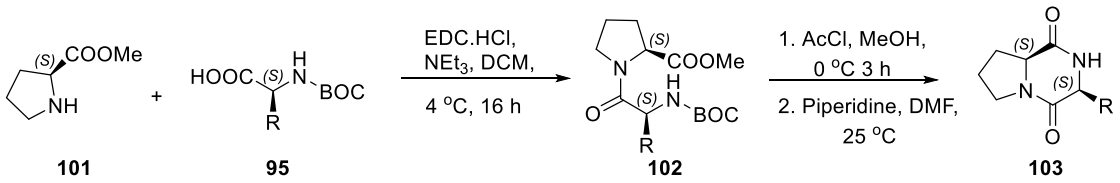


Chart 3 (Continued)

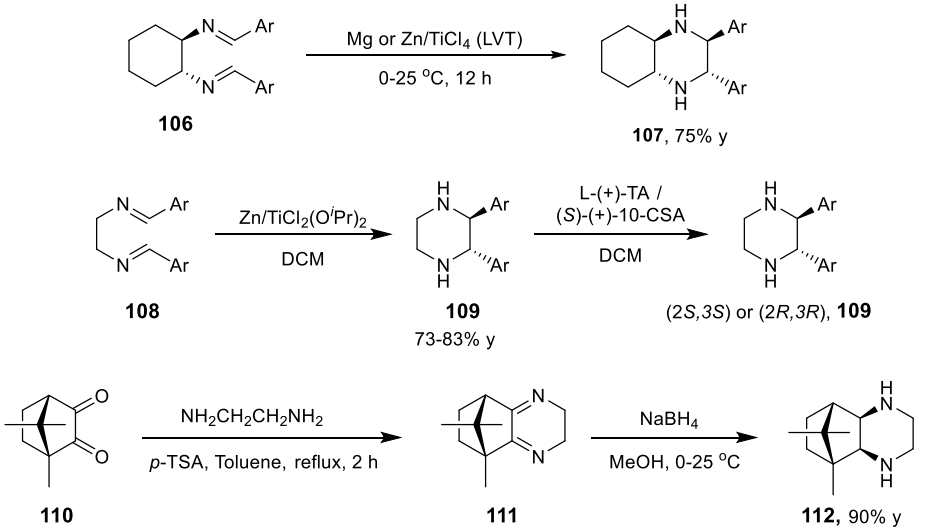


Further, reduction of diketopiperazines derivatives **98**, **103** using $LiAlH_4$ to obtain chiral piperazines **99**, **104** were reported (Chart 3).[30]

1.1.4 Previous methods for chiral amine synthesis reported from this laboratory.

Convenient methods were developed in this laboratory for the synthesis of several chiral piperazine derivatives **107**, **109** and **112** using simple, readily available starting materials.[31-33] For example, diastereomerically pure 3,4-disubstituted-2,5-diazabicyclo [4.4.0] decanes **107** and (±)-*trans*-2,3-diarylpiperazines **109** were prepared in 73-86% yields by intramolecular reductive coupling of diimines using the $Zn/TiCl_4$ and $Zn/Ti(O^iPr)_2Cl_2$ reagent systems (Chart 4).[31,32]

Chart 4



Also, synthesis of chiral piperazine using from D-(-)-camphorquinone **110** *via* condensation followed by $NaBH_4$ reduction was developed (Chart 4).[33]

Simple and convenient methods were also developed in this laboratory to reduce various types of organic functional groups such as carboxylic acid **117** and **119**, oxime **125** and amide **129** using the easy to handle $NaBH_4/I_2$ reagent system in THF solvent (Chart 5).[34]

Chart 5

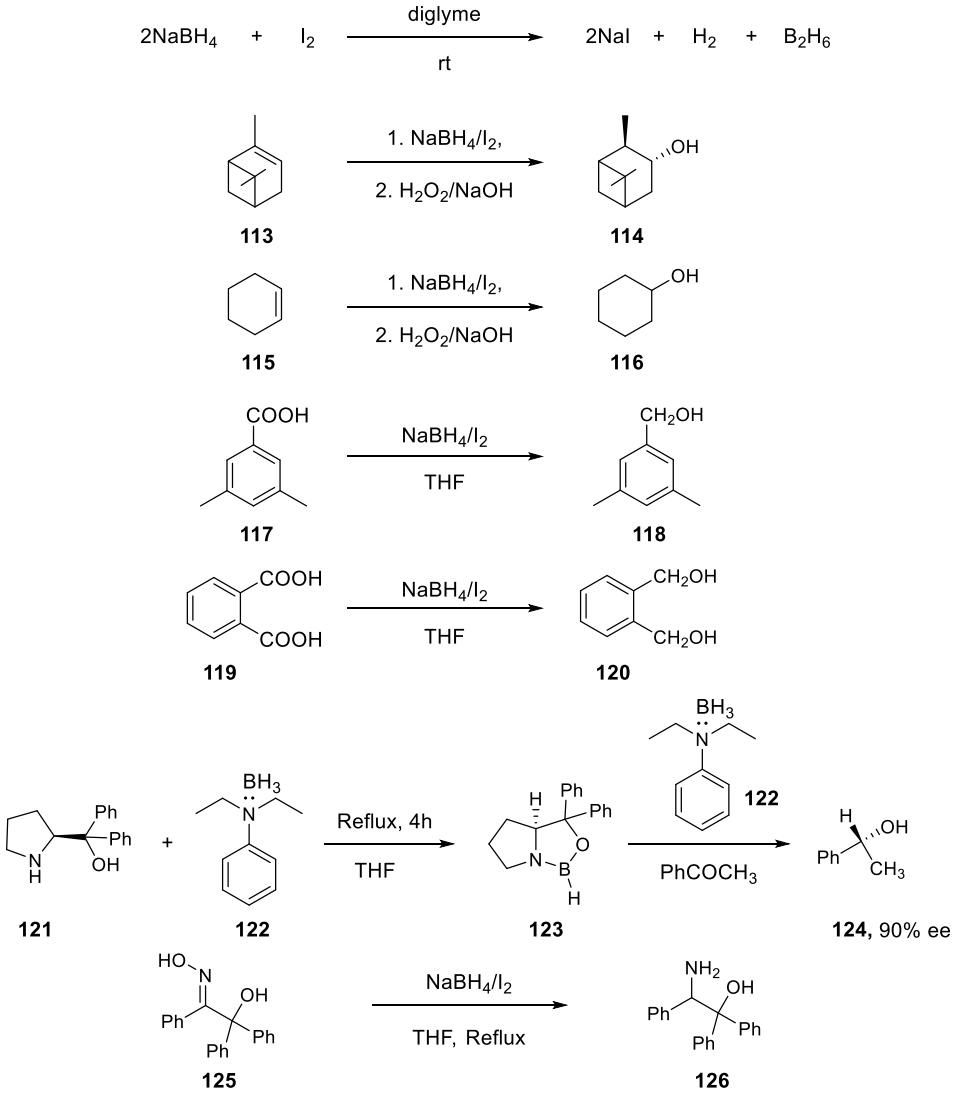
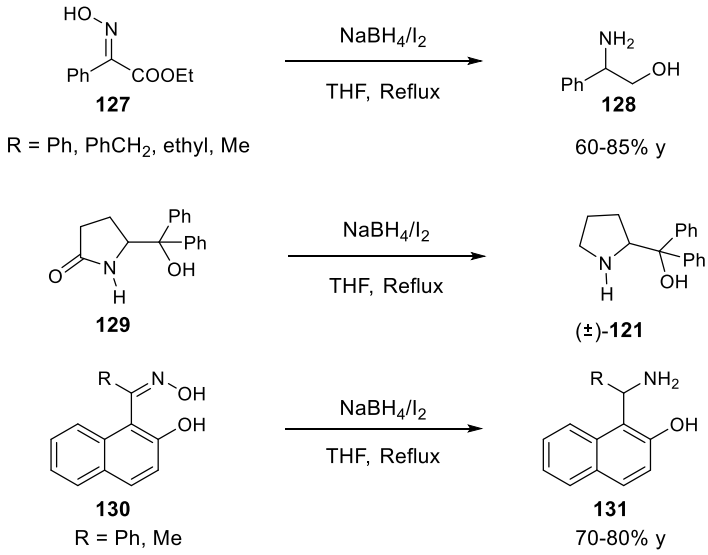
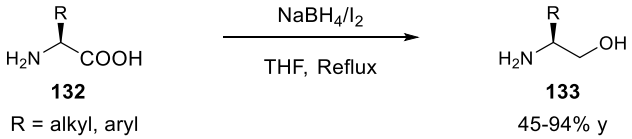


Chart 5 (Continued)



Meyers and coworkers[35] examined the reduction of amino acids **132** using the $NaBH_4/I_2$ reagent system, previously developed in this laboratory (Scheme).[36] It is of interest to note that no racemization occurs in the reduction of amino acids **132** using the $NaBH_4/I_2$ reagent system. The results indicate that it is an excellent reagent system for the conversion of amino acids to amino alcohols **133** (Scheme 11). The $NaBH_4/I_2$ reagent system is safe, simple and inexpensive. Hence, it is useful, especially in the large-scale synthesis of chiral amino alcohols (Scheme 11).[35]

Scheme 11



As outlined in this section, chiral diketopiperazines and piperazine derivatives are interesting compounds with significant biological importance. Hence, the development of a method to readily access piperazine derivatives from inexpensive starting materials would be desirable. Therefore, we turned our attention towards the

synthesis of chiral amines *via* the reduction of chiral diamides prepared using naturally occurring amino acids. We have also undertaken efforts toward the synthesis of chiral 4-hydroxy L-proline based diketopiperazines and reduction using the simple and easy to handle $NaBH_4/I_2$ reagent system. The results are described in the next section.

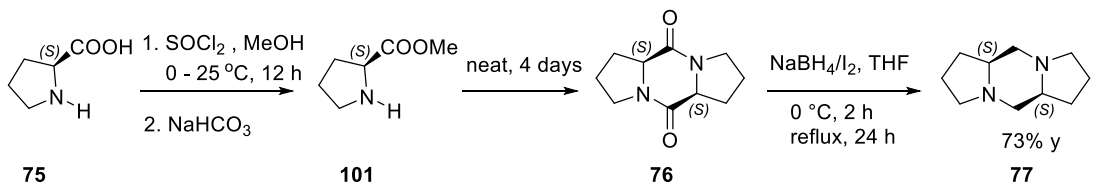
1.2 Results and Discussion

As outlined in the introductory section, the chiral (5a*R*,10a*S*)-decahydrodipyrrolo[1,2-a:1',2'-d]pyrazine **77** was prepared by $LiAlH_4$,[27] $Zn/TiCl_4$, $F_3B{:}OEt_2/NaBH_4$ reductions.[27-32] The LAH is hazardous and flammable upon exposure to air during synthetic operations, while the $F_3B{:}OEt_2$ and $TiCl_4$ systems are highly hygroscopic in nature and hence are not suitable for larger scale processes. Therefore, we have decided to develop methods to synthesize various chiral piperazine derivatives by following methods developed in this laboratory.

1.2.1 Synthesis of chiral L-proline based chiral piperazine

The required chiral (5a*S*,10a*S*)-octahydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-dione **76** was prepared in large quantity by following a well established protocol[27] through self condensation of L-proline methyl ester in neat condition. We have observed that the reduction of the readily accessible chiral (5a*S*,10a*S*)-octahydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-dione **76** gave the optically pure (5a*S*,10a*S*)-decahydrodipyrrolo[1,2-a:1',2'-d]pyrazine **77** in 73% yield using the $NaBH_4/I_2$ reagent system which generated borane *in situ* in THF solvent at 0 °C (Scheme 12).

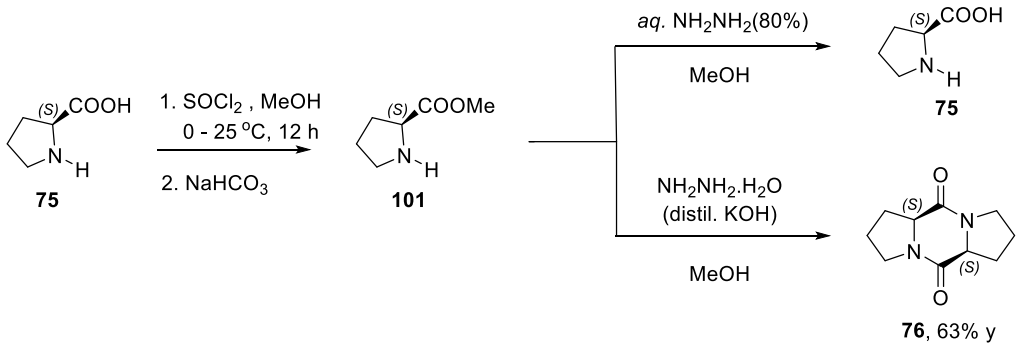
Scheme 12



75 **101** **76** **77**

The chiral (5a*S*,10a*S*)-octahydrodipyrrolo[1,2-a:1',2'-d]pyrazine-5,10-dione **76** can also prepared by the reaction of L-proline methyl ester **101**with aqueous hydrazine solution (distilled over KOH pellets) in methanol as solvent.[37] Whereas in the case of aqueous NH_2NH_2(80 %) and proline ester **101**, only L-proline resumed rather than the expected diketopiperazine **76** (Scheme 13).[37]

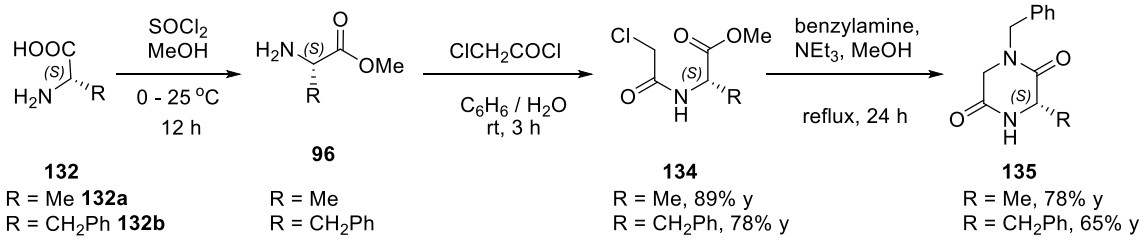
Scheme 13



1.2.2 Synthesis of chiral piperazines containing acyclic chiral amino acids

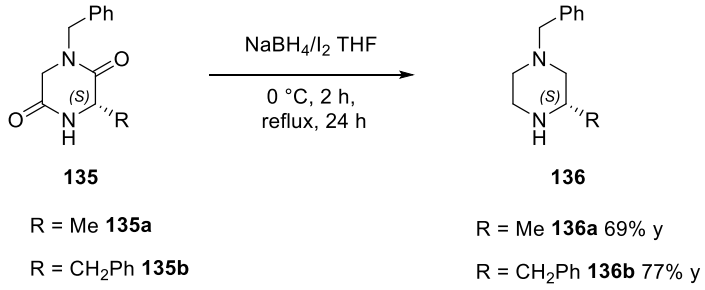
Previously, Wu *et al*[38] reported a general method for the synthesis of mono benzylated chiral piperazines from the commercially available amino acids. The chiral L-amino acid **132** on reaction with $SOCl_2$ in methanol solvent gave the amino acid methyl ester **96**. Subsequent, reaction with chloroacetyl chloride in a mixture of water and benzene followed by cyclization using benzylamine and triethylamine as base gave the corresponding diketopiperazine in good yields (Scheme 14).

Scheme 14



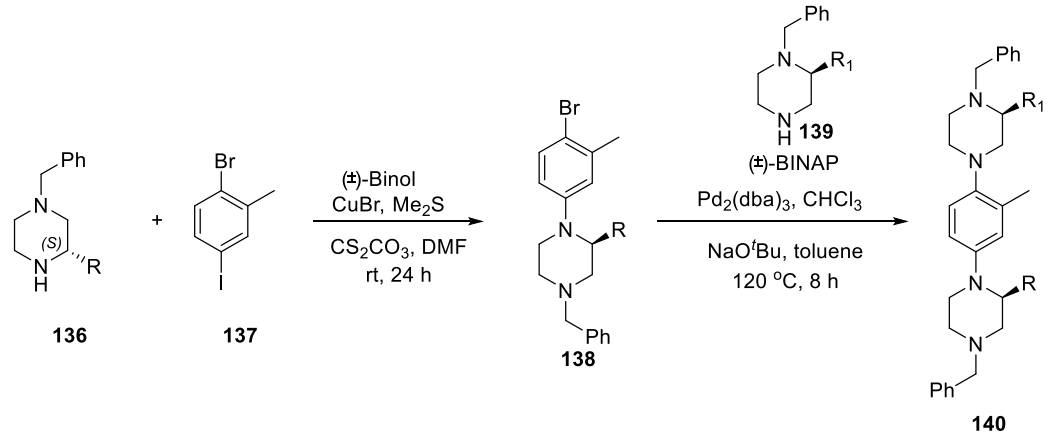
We have observed that the diketopiperazine derivatives **135** prepared following a previously reported reaction sequence (Scheme 15)[38] upon reduction using $NaBH_4/I_2$ in anhydrous THF gave the corresponding piperazine derivatives **136** in good yields. Thus, the optically pure piperazine derivatives (*S*)-1-benzyl-3-methylpiperazine **136a**, (*S*)-1,3-dibenzylpiperazine **136b**, were obtained in 69% and 77% yields, respectively (Scheme 15).

Scheme 15



Recently, Konig *et al*[39] reported a method for the synthesis of chiral terphenyl-type peptide helix mimetics **140** by using chiral monobenzyl piperazines **136** and 2-bromo-5-iodo toluene (Scheme 16) The terphenyl structure has proven to be an ideal scaffold mimicking side-chain functionalities of peptidic α-helices.

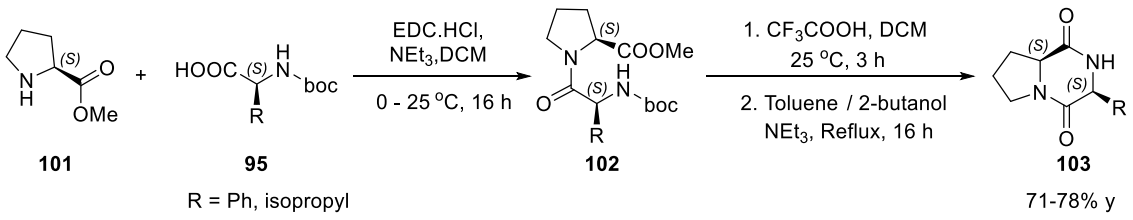
Scheme 16



1.2.3 Synthesis of chiral piperazines containing two amino acids

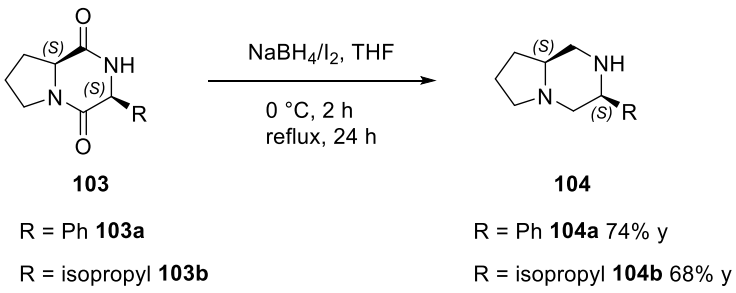
The L-proline based diketopiperazine derivatives **103** are readily accessible in 71-78% yields following a slightly modified synthetic protocol.[30,40] The reaction of L-proline methyl ester and N-boc protected acyclic amino acid **95** using 3-(ethyliminomethyleneamino)-*N*,*N*-dimethylpropan-1-amine hydrochloride (EDC.HCl) as a coupling agent in DCM solvent in the presence of base NEt_3 gave the corresponding amide **102**. The amide **102** upon further reaction with trifluoroacetic acid and cyclization afforded the diketopiperazines **103** (Scheme 17).

Scheme 17



We have observed that these compounds **103** are also converted to the corresponding enatiomerically pure piperazine derivatives **104** in 68-74% yields by the $NaBH_4/I_2$ reduction in THF solvent. Thus, the optically pure piperazine derivatives (3*S*,8a*S*)-3-phenyloctahydropyrrolo[1,2-*a*]pyrazine **104a**, (3*S*,8a*S*)-3-Isopropyl octahydropyrrolo[1,2-*a*]pyrazine **104b**, were obtained 74% and 68% yields, respectively (Scheme 18).

Scheme 18



1.2.4 Synthesis of chiral piperazines containing 4-hydroxy L-proline

We extended this synthetic sequence for the synthesis of optically pure piperazine derivatives **142** by the reduction of the corresponding 4-hydroxyproline based diketopiperazines **141** prepared using the enantiomerically pure hydroxyproline **143** (Figure 6).

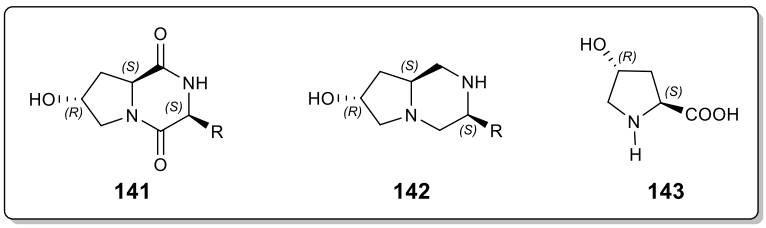
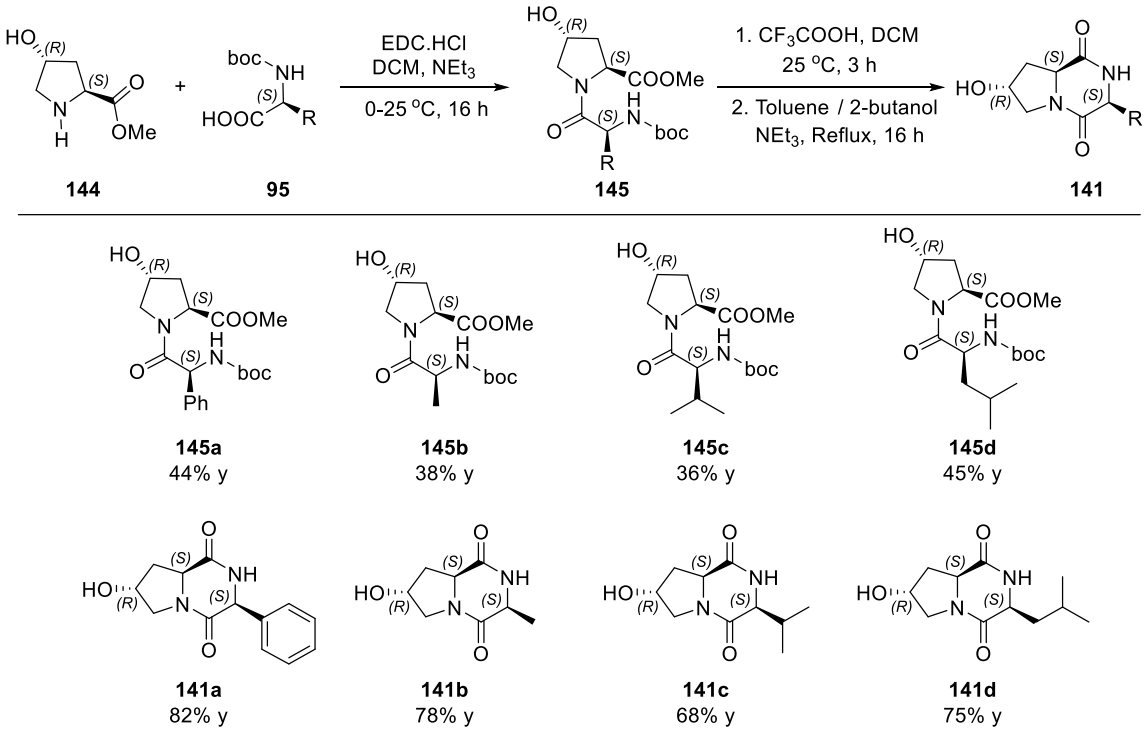


Figure 6

The (2*S*, 4*R*)-methyl 4-hydroxypyrrolidine-2-carboxylate **144** was prepared from 4-hyrdroxyproline **143** using $SOCl_2$ in methanol (Table 1). The resulting (2*S*, 4*R*)-methyl 4-hydroxypyrrolidine-2-carboxylate **144** was reacted with N-boc protected amino acid derivatives **95** and 3-(ethyliminomethyleneamino)-*N*,*N*-dimethylpropan-1-amine hydrochloride (EDC.HCl) as a coupling agent in DCM solvent in the presence of NEt_3 to prepare the compounds **145** which after CF_3COOH treatment and cyclization afforded the diketopiperazine derivatives **141**. The results are summarized in Table 1.

Table 1. Synthesis of diketopiperazine derivatives using two amino acid derivatives **144** and **95**.[a-d]



[a] For first step, all the reactions were carried out with ester **144** (15 mmol), acid (15 mmol), NEt_3 (15 mmol) DCM (100 mL) for 16 h at 0 °C to room temperature. [b]Isolated yields of **145**, and **141**. [c]The products were characterized by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR).

Whereas the (2'*S*,4'*R*)-methyl1'-((*S*)-2-*tert*-butoxycarbonyl)amino)-2-phenylacetyl)-4'-hydroxypyrrolidine-2'-carboxylate **145a** in 44 % yield, the product (**145b)** (2'*S*,4'*R*)-methyl1'-((*S*)-2-*tert*-butoxy carbonyl) amino) propanoyl)-4'-hydroxy pyrrolidine-2'-carboxylate product was obtained 38% yield following this method. Also, the N-boc valine **95c** N-boc leucine **95d** derived products **145c**, **145d** were obtained in 36%, and 45%, respectively. These N-boc amide derivatives **145a-145d** were converted to the corresponding diketo derivatives **141a-141d** by deprotection using with trifluoroacetic acid followed by cyclization in the presence of triethylamine in refluxing toluene/2-butanol in 82%, 78%, 68% and 75%, respectively.

The (3*S*,7*R*,8a*S*)-7-Hydroxy-3-isopropylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione **141c** was crystallized from methanol to obtain crystals suitable for X-ray structural analysis. The ORTEP diagram of the (3*S*,7*R*,8a*S*)-7-Hydroxy-3-isopropylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione **141c** is shown in Figure 7. The crystal structure data of the compound **141c** is summarized in Table 2.

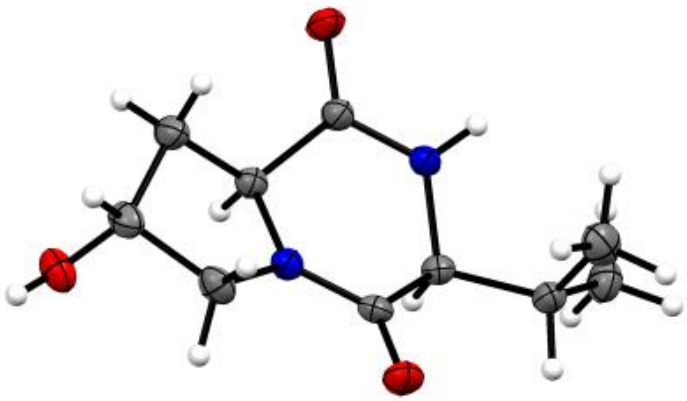
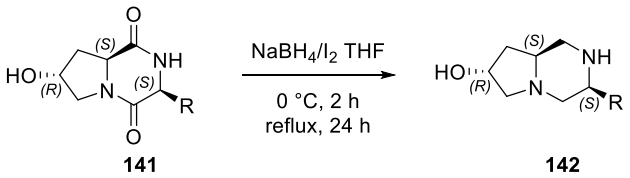


Figure 7. ORTEP representation of the crystal structure of diketopiperazine **141c** (Thermal ellipsoids are drawn at 50% probability).

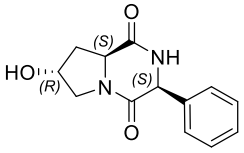
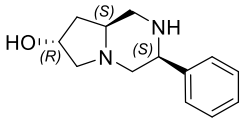
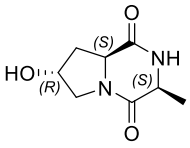
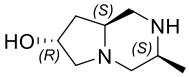
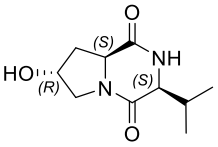
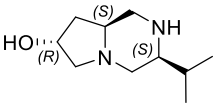
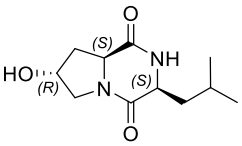
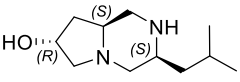
Table 2. Crystal data and structure refinement for compound 141c.

Identification code	**141c**	
Empirical formula	C_{10} H_{16} N_2 O_3	
Formula weight	212.25	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.3814(7) Å	α= 90°.
	b = 10.2308(7) Å	β= 90°.
	c = 11.2657(8) Å	γ= 90°.
Volume	1081.27(13) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	456	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.69 to 26.40°.	
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14	
Reflections collected	10981	
Independent reflections	2167 [R(int) = 0.0305]	
Completeness to theta = 26.40°	97.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2167 / 0 / 142	
Goodness-of-fit on F^2	1.199	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1037	
R indices (all data)	R1 = 0.0454, wR2 = 0.1038	
Absolute structure parameter	0.3(02)	
Largest diff. peak and hole	0.177 and -0.219 $e.Å^{-3}$	

Table 3. Reduction of diketopiperazine to piperazine [a-c]



141 **142**

S.No	Substrate	Product	Yield[b] (%)
1	 **141a**	 **142a**	79
2	 **141b**	 **142b**	73
3	 **141c**	 **142c**	66
4	 **141d**	 **142d**	70

[a]All the reactions were carried out with DKP **141** (3 mmol), $NaBH_4$ (15 mmol), I_2 (7 mmol) THF (15 mL) for 24 h at 0 °C to reflux. [b]Isolated yields of **142**. [c]The products were characterized by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and HRMS).

The hydroxy proline based chiral diketopiperazine derivatives **141** are readily reduced to optically pure piperazine derivatives **142** using the easy to handle sodium borohydride-iodine reagent system in anhydrous THF solvent (Table 3). Whereas the optically pure (3*S*,7*R*,8a*S*)-3-phenyloctahydropyrrolo[1,2-*a*]pyrazine-7-ol **142a** was obtained in 79% yield, the derivatives **142b**, **142c** and **142d** were obtained in 73 %, 66 % and 70 % yields, respectively (Table 3).

We have utilized the diketopiperazine **76** and the corresponding piperazine **77** in the electron transfer reactions with *p*-chloranil. These results are described in Chapter 3. We have also carried out studies on the ZnI_2 promoted conversion of enamines to allenes. These results are described in chapter 2.

1.3 Conclusions

We have developed a convenient method for the synthesis of enantiomerically pure diketopiperazine derivatives. The method described for the reduction of diketopiperazine derivatives involves a simple, inexpensive and easy to handle $NaBH_4/I_2$ reagent system in THF as the solvent and compares favourably with reported methods using lithium aluminum hydride (LAH), $NaBH_4/F_3B{:}OEt_2$ and $NaBH_4$-$TiCl_4$ reagent systems. The LAH is hazardous and flammable upon exposure to air during synthetic operations, while the $F_3B{:}OEt_2$ and $TiCl_4$ systems are highly hygroscopic in nature and hence are not suitable for larger scale processes.

The methods developed using the $NaBH_4/I_2$ reagent system give comparable results when the reductions were carried out on a 50–100 mmol scale. Hence, the methods described herein are useful for the preparation of enantiomerically pure piperazine derivatives for application in asymmetric organic synthesis. Recently, some pyrrolidine derivatives derived from 4-hydroxyproline were reported to exhibit potent inhibitory activity against influenza A neuraminidase.[41] Therefore, the synthetic methods described also have potential for further exploitation in medicinal chemistry.

1.4. Experimental Section

1.4.1. General Information

Sodium borohydride ($NaBH_4$) was purchased from SRL and used as received. Iodine purchased from E-Merck (India) was used as received. Amino acids were purchased from SRL were used as received. The melting points reported in this literature are uncorrected and were determined using a superfit capillary point apparatus. IR spectra were recorded on a FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance-400 MHz and 500 MHz Spectrometer with chloroform-d, Methanol-d and dimethylsulfoxide as solvents and TMS as reference. Optical rotations were measured in an AUTOPOL-IV digital polarimeter (readability $\pm 0.001^{\circ}$).

1.4.2. General procedure for the preparation of L-proline diketopiperazine 76

We have prepared **76** following reported procedure.[8] To a suspension of L-proline (10 mmol) in methanol (50 mL) was added thionyl chloride (15 mmol) dropwise at ice cold bath. This solution was allowed to r.t. and stirred for 12 h. The solvent was evaporated under reduced pressure, to give HCl salt of L proline methyl ester. The HCl salt was dissolved in CH_2Cl_2 (100 mL), then neutralized with sodium hydrogen carbonate. The residue was removed by filtration and the solvent was evaporated under reduced pressure. Then the neat was stirred at r.t. for 4 days. The filtrate was dissolved in CH_2Cl_2 and washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification by recrystallization from ethyl acetate provided the diketopiperazine as colorless needles.

1.4.3. General procedure for preparation of diketopiperazines 135

We have prepared compound **135** following reported procedure.[9] To a suspension of L-amino acid **132** (10 mmol) in CH_3OH (50 mL) cooled in an ice-salt bath, $SOCl_2$ (40 mmol) was added drop-wise. The resulting mixture was stirred for an additional 6 h at room temparature. The solution was concentrated to dryness, and without any further purification, the residue was dissolved in water (4 mL) and cooled in ice-salt bath. To the solution, $NaHCO_3$ (20 mmol) was added in one portion, and then the solution of chloroacetyl chloride (10 mmol) in benzene (15 mL) was added dropwise. The reaction mixture was stirred for an additional 3 h at rt. The aqueous layer was extracted twice with ethyl acetate (30 mL), and the combined organic phases were dried over anhydrous Na_2SO_4. After evoparation of solvents, crude product was purified using column chromatography. Then we moved further to a solution of benzylamine (10 mmol) in CH_3OH (10 mL) was added dropwise over 1.5 h to a solution of compound **134** and TEA (10 mmol) in CH_3OH (10 mL) and refluxed for 20 h, the pale yellow solution was cooled to r.t. and concentrated, and the residue was dissolved in 30 mL CH_2Cl_2. The organic phase was washed with 20 mL of 5% aqueous citric acid, 20 mL of saturated aqueous $NaHCO_3$, and 20 mL of brine, and dried over Na_2SO_4.

1.4.4. General procedure for preparation of diketopiperazines 103

Diketo piperazine derivatives **103** were prepared using slightly modified reported procedure.[30,40] (see general procedure **3** and **4**)

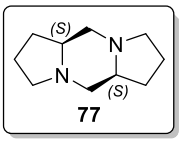
Preparation of L-proline methyl ester **101**: To a suspension of L-proline **75** (10 mmol) in methanol (50 mL) was added thionyl chloride (15 mmol) dropwise at ice cold

bath. This solution was allowed to warm to r.t. and stirred for 12 h. The solvent was evaporated under reduced pressure, to give HCl salt of L proline methyl ester.

1.4.5. General procedure for reduction using sodium borohydride-iodine reagent system

An oven dried three necked reaction flask was cooled under nitrogen atmosphere and placed stirring bar. Diketopiperazine (3 mmol) was dissolved in of freshly distilled THF(10 mL) and $NaBH_4$ (15 mmol) added at 0 °C. A solution of iodine (7 mmol) in freshly distilled THF (5 mL) was introduced drop wise during 30 min via side neck of the reaction flask and allowed to stir for 2 h and refluxed for 24 h. The reaction was brought to room temperature and quenched with methanol (the residue was carefully poured into the methanol containing ice cold beaker slowly) and the solvents were evaporated. The residue obtained after evaporation, was refluxed with 5 N KOH (10 mL) for 6 h and resultant mono protected piperazine was extracted with DCM (2 X 30 mL) dried over anhydrous Na_2SO_4. The combined organic extract was evaporated and chromatographed on basic Al_2O_3 column using 50:50 hexane and ethyl acetate as eluent.

1.4.6. Preparation of (5a*S*,10a*S*)-decahydrodipyrrolo[1,2-a:1',2'-d]pyrazine



77

Yield **:** 0.363 g (73%); pale yellow liquid

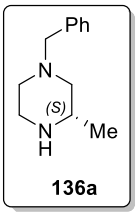
$[\alpha]_D^{25}$: -8.2 (c 0.27, $CHCl_3$)

IR (neat) : 2772, 1463, 1345, 1267, 1035, 937, 880 cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$) 2.91-2.85 (m, 2H), 2.65-2.63 (m, 4H), 2.52-2.46 (m, 4H), 1.91-1.60 (m, 8H).

^{13}C NMR : (100 MHz, ppm, $CDCl_3$):61.1, 54.3, 53.1, 26.6, 21.7

1.4.7. Preparation of (*S*)-1-Benzyl-3-methylpiperazine



136a

Yield : 0.393 g (69%); pale yellow liquid

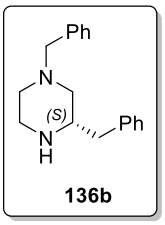
[α]D^{25} : -7.3 (c 0.15, $CHCl_3$)

IR (neat) : 2925, 2806, 1435, 1138, 1055, 735, 699 cm^{-1};

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 7.34-7.29 (m, 5H), 3.51 (s, 2H), 2.96-2.88 (m, 2H), 2.80-2.77 (m, 2H), 2.05-1.99 (m, 2H), 1.68 (t, *J* = 10.4, 2H) 1.03 (d, *J* = 6.3, 3H).

^{13}C NMR : (125 MHz, ppm, $CDCl_3$): 138.0, 129.2, 128.2, 127.0, 63.4, 61.3, 53.6, 50.5, 45.9, 20.0.

1.4.8. Preparation of (*S*)-1,3-Dibenzylpiperazine



136b

Yield : 0.582 g (77%); pale yellow liquid

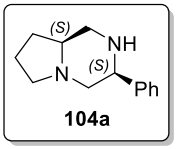
[α]D^{25} : -1.5 (c 0.49, $CHCl_3$)

IR (neat) : 2930, 2812, 1479, 1443, 1314, 1117, 1055 cm^{-1}

^{1}H NMR : (500 MHz, ppm, $CDCl_3$) 7.35 (d, *J* = 4.3, 4H), 7.33-7.28 (m, 3H), 7.24-7.21 (m, 3H), 3.60-3.56 (m, 2H), 3.03-3.01 (m, 1H), 2.93-2.81 (m, 3H), 2.79-2.72 (m, 2H), 2.60-2.54 (m, 1H), 2.15-2.10 (m, 1H), 1.93 (t, *J* = 10.2, 1H)

^{13}C NMR : (125 MHz, ppm, $CDCl_3$) 138.0, 129.2, 128.2, 127.0, 63.4, 61.3, 53.6, 50.5, 45.9, 20.0. 138.6, 138.1, 129.2, 129.2, 128.5, 128.2, 127.0, 126.4, 63.4, 59.8, 56.3, 53.5, 45.8, 40.9.

1.4.9. Preparation of (3*S*,8a*S*)-3-Phenyloctahydropyrrolo[1,2-*a*]pyrazine



104a

Yield : 0.448 g (74%); light brown liquid

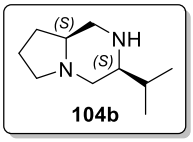
[α]D^{25} : 8.6 (c 0.14, $CHCl_3$)

IR (neat) : 2951, 2786, 1598, 1438, 1030, 761, 689 cm^{-1}

^{1}H NMR : (500 MHz, ppm, $CDCl_3$) 7.50 (d, *J* = 7.3, 2H), 7.33-7.30 (m, 2H), 7.26-7.23 (m, 1H), 3.98-3.96 (dd, *J* = 3.4, *J* = 6.4, 1H), 3.19-3.16 (dd, *J* = 3.4, *J* = 12.0, 1H), 2.94-2.88 (m, 3H), 2.70-2.68 (dd, *J* = 3.5, *J* = 11.1, 1H), 2.62-2.58 (m, 2H), 1.93-1.72 (m, 4H)

^{13}C NMR : (125 MHz, ppm, $CDCl_3$): 142.8, 128.2, 127.4, 127.0, 60.9, 57.1, 55.4, 54.3, 45.9, 25.5, 25.2

1.4.10. Preparation of (3*S*,8a*S*)-3-Isopropyloctahydropyrrolo[1,2-*a*]pyrazine



104b

Yield : 0.342 g (68%); light brown liquid

$[\alpha]_D^{25}$: -6.4 (c 0.22, $CHCl_3$)

IR (neat) : 2956, 2781, 1458, 1288, 1066, 761 cm^{-1}

^{1}H NMR : (500 MHz, ppm, $CDCl_3$) 2.94-2.91 (m, 1H), 2.89-2.86 (m, 1H), 2.82-2.79 (dd, *J* = 4.1, *J* = 11.0, 1H), 2.70-2.69 (dd, *J* = 7.7, *J* = 11.8, 1H), 2.33-2.29 (m, 2H), 2.27-2.22 (m, 2H), 2.14-2.09 (m, 1H), 2.05-2.01 (m, 1H), 1.82-1.77 (m, 1H), 1.71-1.60 (m, 2H), 1.49-1.43 (m, 1H), 0.91 (d, *J* = 6.7, 3H), 0.87 (d, *J* = 6.6, 3H)

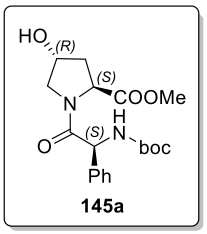
^{13}C NMR : (125 MHz, ppm, $CDCl_3$): 62.6, 59.4, 54.5, 53.4, 45.9, 27.4, 26.5, 20.9, 20.3, 19.6

1.4.11. General procedure for the preparation of amide derivatives

(*S*)-*N*-Boc amino acid **95** (20 mmol) was dissolved in CH_2Cl_2 (50 mL) at 0 °C, (*S*)-amino ester **144** (20 mmol) and Et_3N (20 mmol) were added, followed by 3-(Ethyliminomethyleneamino)-*N*,*N*-dimethylpropan-1-amine hydrochloride (EDC.HCl) (20 mmol). The reaction mixture was stirred for 16 h at 0 °C to room temperature then washed with 1 M citric acid (25 mL) 2 N. $NaHCO_3$ (25 mL) dried with Na_2SO_4 filtered

and evaporated to dryness to give gummy type compound. The crude product was further purified by column chromatography on silica gel (100-200 mesh) using 50:50 hexane and ethyl acetate.

1.4.12. Preparation of (2'*S*,4'*R*)-Methyl 1'-((*S*)-2-*tert*-butoxycarbonyl)amino)-2-phenylacetyl)-4'-hydroxypyrrolidine-2'-carboxylate



145a

Yield : 2.401 g (44%); colorless liquid

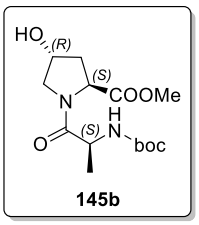
$[\alpha]_D^{25}$: 52.6 (c 0.16, EtOH)

IR (neat) : 3416, 2977, 1753, 1711, 1644, 1438, 1365, 1169, 709 cm^{-1}

^{1}H NMR : (500 MHz, ppm, $CDCl_3$): 7.43-7.34 (m, 5H), 5.86 (d, *J* = 7.7, 1H), 5.42 (d, *J* = 7.6, 1H), 4.67 (t, *J* = 8.1, 1H), 4.40 (s, 1H), 3.73 (s, 3H), 3.64-3.62 (m, 1H), 3.17-3.13 (m, 1H), 2.32-2.27 (m, 1H), 1.95-1.89 (m, 1H), 1.40 (s, 9H).

^{13}C NMR : (125 MHz, ppm, $CDCl_3$): 172.3, 169.1, 155.4, 136.4, 128.9, 128.4, 128.3, 80.0, 70.2, 58.1, 56.6, 55.1, 52.2, 37.4, 28.3.

1.4.13. Preparation of (2'*S*,4'*R*)-Methyl1'-((*S*)-2-*tert*-butoxycarbonyl)amino) propanoyl)-4'-hydroxypyrrolidine-2'-carboxylate



145b

Yield : 2.476 g (38%); colorless liquid

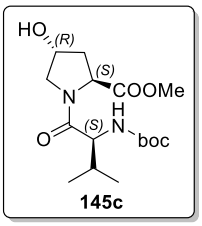
$[\alpha]_D^{25}$: -84.2 (c 0.28, EtOH)

IR (neat) : 3369, 2977, 2930, 1742, 1686, 1634, 1531, 1458, 1159 cm^{-1}

^{1}H NMR : (500 MHz, ppm, $CDCl_3$): 5.53-5.49 (m, 1H), 4.59-4.55 (m, 1H), 4.48 (s, 1H), 4.39-4.36 (m, 1H), 4.13-4.12 (m, 1H), 3.75-3.72 (m, 1H), 3.67 (s, 3H), 3.64-3.60 (m, 1H), 2.30-2.25 (m, 1H), 1.99 (s, 1H), 1.36 (s, 9H), 1.27 (d, *J* = 6.8, 3H)

^{13}C NMR : (125 MHz, ppm, $CDCl_3$): 172.5, 172.0, 155.4, 79.8, 70.0, 57.7, 54.9, 52.2, 47.8, 37.3, 28.9, 17.8.

1.4.14. Preparation of (2'*S*,4'*R*)-Methyl 1'-((*S*)-2-*tert*-butoxycarbonyl)amino)-3-methylbutanoyl)-4'-hydroxypyrrolidine-2'-carboxylate



145c

Yield : 2.470 g (36%); colorless liquid

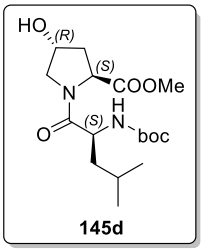
$[\alpha]_D^{25}$: -79.5 (c 0.28, EtOH)

IR (neat) : 3390, 2961, 1737, 1691, 1629, 1520, 1365, 1169, 875. cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 5.37 (d, *J* = 8.7, 1H), 4.61 (t, *J* = 8.3, 1H), 4.48 (s, 1H), 4.19-4.15 (m, 1H), 3.93-3.86 (m, 2H), 3.68 (s, 3H), 2.33-2.27 (m, 3H), 2.00-1.95 (m, 2H), 1.38 (s, 9H), 1.24-1.22 (m, 1H), 0.98 (d, *J* = 6.7, 3H), 0.89 (d, *J* = 6.7, 3H)

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 172.6, 171.5, 156.2, 79.8, 69.9, 57.7, 57.0, 55.4, 52.1, 37.4, 30.9, 28.3, 19.2, 17.3

1.4.15. Preparation of (2'*S*,4'*R*)-Methyl 1'-((*S*)-2-*tert*-butoxycarbonyl)amino)-4-methylpentanoyl)-4'-hydroxypyrrolidine-2'-carboxylate



145d

Yield : 3.22 g (45%); colorless liquid

$[\alpha]_D^{25}$: -58.3 (c 0.27, EtOH)

IR (neat) : 3344, 2961, 2868, 1753, 1701, 1649, 1520, 1427, 1092 cm^{-1}

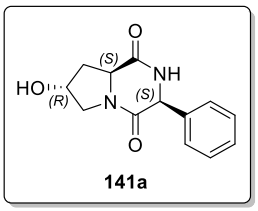
^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 5.17 (d, *J* = 8.4, 1H), 4.72-4.68 (m, 1H), 4.56 (s, 1H), 4.45-4.39 (m, 1H), 4.09 (d, *J* = 11.2, 1H), 3.75 (s, 3H), 3.69-3.67 (m, 1H), 3.07 (s, 1H), 2.41-2.36 (m, 1H), 2.05-1.98 (m, 1H), 1.812 (s, 3H), 1.43 (s, 9H), 1.00-0.96 (m, 6H).

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 172.6, 172.1, 156.0, 79.8, 70.1, 57.6, 54.9, 52.2, 50.4, 41.5, 37.4, 28.3, 24.5, 23.2, 21.9

1.4.16. Preparation of General procedure for the preparation of diketopiperazine derivatives

A solution of amide **145** (5 mmol) in dry CH_2Cl_2 (20 mL) was treated with trifluoroacetic acid (0.4 mL) at rt for 3 h. Solvent was then evaporated and the reaction mixture was dissolved in 2-butanol:toluene (1:2 mL) followed by addition of triethylamine (5 mmol). The mixture was allowed to reflux for 16 h. After the evaporation of solvent, diketopiperazine **141** precipitated as a white solid, which was further purified by column chromatography on silica gel (100-200 mesh) using 90:10 ethyl acetate and methanol.

1.4.17. Preparation of (3*S*,7*R*,8a*S*)-7-hydroxy-3-phenylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione



141a

Yield : 1.00 g (82%); White solid

M.P. : 228-230 ˚C

[α]D^{25} : -57.9 (c 0.1, EtOH)

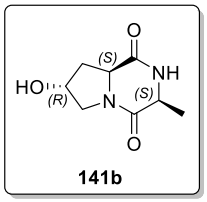
IR (KBr) : 3321, 3240, 2925, 1665, 1634, 1433, 973, 720 cm^{-1}

^{1}H NMR : (500 MHz, ppm, DMSO-d_6): 8.41 (s, 1H), 7.37-7.32 (m, 2H), 7.25 (d, *J* = 7.2, 2H), 5.24 (s, 1H), 5.15 (s, 1H), 4.51-4.47 (m, 1H), 4.33 (s, 1H), 3.59-3.56 (m, 1H), 3.23 (d, *J* = 12.5, 1H), 2.50-2.49 (m, 1H), 2.14-2.10 (m, 1H), 2.02-1.97 (m, 1H)

^{13}C NMR : (125 MHz, ppm, DMSO-d_6) 170.2, 165.4, 137.2, 129.3, 128.4, 128.3, 67.3, 60.2, 57.6, 54.6, 37.8

HRMS : (ESI): calcd for $C_{13}H_{14}N_2O_3$: 247.1082 m/z $[M+H]^+$; found 247.1083.

1.4.18. Preparation of (3*S*,7*R*,8a*S*)-7-Hydroxy-3-methylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione



141b

Yield : 0.717 g (78%); White solid

M.P. : 228-230 ˚C

M.P : 198-201 ˚C

$[\alpha]_D^{25}$: -130.2 (c 0.09, EtOH)

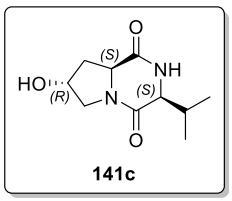
IR (KBr) : 3380, 3235, 1675, 1639, 1422, 1283, 1097, 957, 756 cm^{-1}

^{1}H NMR : (400 MHz, ppm, MeOH-d_4): 4.56-4.48 (m, 1H), 4.27-4.25 (m, 1H), 3.70-3.68 (m, 1H), 3.47-3.44 (m, 1H), 3.33 (s, 1H), 2.32-2.28 (m, 1H) 2.13-2.07 (m, 1H), 1.41 (d, *J* = 6, 3H).

^{13}C NMR : (100 MHz, ppm, MeOH-d_4): 171.4, 167.7, 67.7, 57.5, 53.8, 50.6, 36.8, 14.3

HRMS : (ESI): calcd for $C_8H_{12}N_2O_3$: 185.0926 m/z $[M+H]^+$; found 185.0925.

1.4.19. Preparation of (3*S*,7*R*,8a*S*)-7-Hydroxy-3-isopropylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione



141c

Yield : 0.669 g (68%); White solid

M.P : 196-198 ˚C

$[\alpha]_D^{25}$: -136.7 (c 0.08, EtOH)

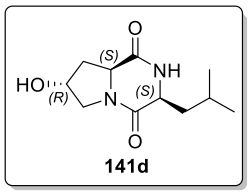
IR (KBr) : 3369, 3271, 2967, 2879, 1675, 1644, 1422, 1092, 740, 601 cm^{-1}

^{1}H NMR : (400 MHz, ppm, MeOH-d_4) : 4.52-4.48 (m, 2H), 4.10 (s, 1H), 3.76-3.72 (dd, *J* = 4.5, *J* = 12.9, 1H), 3.44 (d, *J* = 13, 1H), 2.53-2.50 (m, 1H), 2.33-2.28 (dd, *J* = 6.1, *J* = 13.1, 1H) 2.10-2.02 (m, 1H), 1.12 (d, *J* = 7.2, 3H), 0.96 (d, *J* = 6.9, 3H)

^{13}C NMR : (100 MHz, ppm, MeOH-d_4):171.5, 166.2, 67.5, 60.0, 56.9, 53.8, 37.2, 28.3, 17.5, 15.3

HRMS : (ESI): calcd for $C_{10}H_{16}N_2O_3$: 213.1239 m/z $[M+H]^+$; found 213.1237

1.4.20. Preparation of (3*S*,7*R*,8a*S*)-7-Hydroxy-3-isobutylhexahydropyrrolo[1,2-*a*]pyrazine-1,4-dione



141d

Yield : 0.847 g (75%); White solid

M.P. : 176-178 ˚C

[α]$_D^{25}$: -141.8 (c 0.07, EtOH)

IR (KBr) : 3447, 3276, 2941, 1686, 1670, 1618, 1433, 1097 cm^{-1}

^{1}H NMR : (400 MHz, ppm, MeOH-d_4): 4.56-4.48 (m, 2H), 4.19-4.18 (m, 1H), 3.70-3.66 (m, 1H), 3.47-3.44 (m, 1H), 3.33 (s, 1H), 2.32-2.27 (m, 1H) 2.14-2.07 (m, 1H), 1.95-1.92 (m, 2H), 1.55-1.51 (m, 1H), 0.99-0.98 (m, 6H)

^{13}C NMR : (100 MHz, ppm, MeOH-d_4): 171.6, 167.6, 67.7, 57.3, 53.7, 53.2, 37.9, 36.7, 24.4, 21.9, 20.8

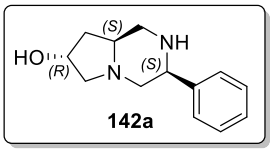
HRMS : (ESI): calcd for $C_{11}H_{18}N_2O_3$: 227.1395 m/z $[M+H]^+$; found 227.1395

1.4.21. General procedure for the Reduction of diketopiperazine derivatives

An oven dried three necked reaction flask was cooled under nitrogen atmosphere and placed stirring bar. Diketopiperazine **141**(3 mmol) was dissolved in of freshly distilled THF(10 mL) and $NaBH_4$ (15 mmol) added at 0 °C. A solution of iodine (7 mmol) in freshly distilled THF (5 mL) was introduced drop wise during 30

min via side neck of the reaction flask and allowed to stir for 2 h and refluxed for 24 h. The reaction was brought to room temperature and quenched with methanol (the residue was carefully poured into the methanol containing ice cold beaker slowly) and the solvents were evaporated. The residue obtained after evaporation, was refluxed with 5 N KOH (10 mL) for 6 h and resultant chiral piperazine **142** was extracted with DCM (2 X 30 mL) dried over anhydrous Na_2SO_4. The combined organic extract was evaporated and chromatographed on basic Al_2O_3 column using 50:50 hexane and ethyl acetate as eluent.

1.4.22. Preparation of (3*S*,7*R*,8a*S*)-3-phenyloctahydropyrrolo[1,2-*a*]pyrazine-7-ol



142a

Yield : 0.516 g (79%); light brown liquid

$[\alpha]_D^{25}$: 6.9 (c 0.19, EtOH)

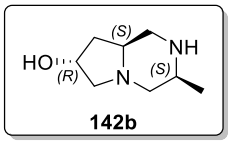
IR (neat) : 3282, 2925, 2843, 1453, 1309, 1092 cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 7.50 (d, *J* = 7.36, 2H), 7.36-7.27 (m, 3H), 4.57-4.53 (m, 1H), 4.02-3.99 (m, 1H), 3.65 (s, 1H), 3.33-3.29 (dd, *J* = 6.6, *J* = 11.2, 1H), 3.19-3.15 (dd, *J* = 3.3, *J* = 12.0, 1H), 3.06-3.02 (m, 1H), 2.93-2.88 (m, 2H), 2.84-2.80 (m, 1H), 2.63-2.59 (dd, *J* = 4.6, *J* = 11.2, 1H), 2.17-2.13 (m, 1H), 2.03 (s, 1H), 1.76-1.71 (dd, *J* = 6.0, *J* = 13.4, 1H)

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 142.5, 128.3, 127.5, 127.1, 69.7, 64.1, 59.2, 56.8, 55.9, 45.6, 37.4

HRMS : (ESI): calcd for $C_{13}H_{18}N_2O$: 219.1497 m/z $[M+H]^+$; found 219.1498.

1.4.23. Preparation of (3*S*,7*R*,8a*S*)-3-methyloctahydropyrrolo[1,2-*a*]pyrazine-7-ol



142b

Yield : 0.341 g (73%); light brown liquid

[α]D^{25} : -6.6 (c 0.26, EtOH)

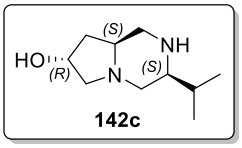
IR (neat) : 3375, 2930, 2858, 1551, 1463, 1102, 802, 673 cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 4.46-4.41 (m, 1H), 3.33-3.28 (s, 3H), 3.09-3.06 (m, 1H), 2.97-2.93 (dd, *J* = 3.1, *J* = 12.3, 1H), 2.78-2.72 (m, 1H), 2.58-2.54 (dd, *J* = 3.5, *J* = 10.9, 1H), 2.46-2.39 (m, 2H), 2.21-2.17 (dd, *J* = 5.3, *J* = 10.2, 1H), 1.87-1.79 (m, 1H), 1.64-1.59 (dd, *J* = 5.8, *J* = 13.0, 1H), 1.20 (d, *J* = 6.7, 3H)

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 68.8, 64.1, 60.6, 57.3, 47.8, 44.8, 38.3, 18.4

HRMS : (ESI): calcd for $C_8H_{16}N_2O$: 157.1341 m/z $[M+H]^+$; found 157.1346

1.4.24. Preparation of (3*S*,7*R*,8a*S*)-3-isopropyloctahydropyrrolo[1,2-*a*]pyrazine-7-ol



142c

Yield : 0.364 g (66%); light brown liquid

[α]D^{25} : -22.1 (c 0.10, EtOH)

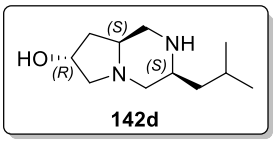
IR (neat) : 3395, 2920, 1567, 1097, 802, 673 cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 4.40-4.34 (m, 1H), 3.47 (s, 1H), 3.21-3.17 (m, 1H), 2.89-2.84 (m, 1H), 2.67-2.58 (m, 2H), 2.55-2.51 (m, 1H), 2.34-2.18 (m, 3H), 1.97-1.87 (m, 2H), 1.83-1.75 (m, 1H), 1.56-1.51 (dd, *J* = 5.9, *J* = 13.0, 1H), 0.85-0.79 (m, 6H)

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 68.8, 64.1, 60.0, 59.2, 53.1, 45.4, 37.9, 27.3, 20.0, 19.4.

HRMS : (ESI): calcd for $C_{10}H_{20}N_2O$: 185.1654 m/z $[M+H]^+$; found 185.1654.

1.4.25. Preparation of (3*S*,7*R*,8a*S*)-3-isobutyloctahydropyrrolo[1,2-*a*]pyrazine-7-ol



142d

Yield : 0.415 g (70%); light brown liquid

$[\alpha]_D^{25}$: -20.9 (c 0.11, EtOH)

IR (neat) : 3364, 2956, 2925, 1562, 1402, 1102, 870 cm^{-1}

^{1}H NMR : (400 MHz, ppm, $CDCl_3$): 4.41-4.36 (m, 1H), 3.49 (s, 1H), 3.27-3.22 (m, 1H), 2.92-2.88 (m, 2H), 2.67-2.62 (m, 1H), 2.57-2.53 (m, 1H), 2.46-2.37 (m, 1H), 2.19-2.15 (m, 1H), 1.98 (s, 1H), 1.82-1.73 (m, 1H), 1.61-1.48 (m, 3H), 1.33-1.28 (m, 1H), 0.86-0.83 (m, 6H)

^{13}C NMR : (100 MHz, ppm, $CDCl_3$): 68.6, 64.0, 60.4, 55.8, 50.2, 44.9, 40.4, 38.3, 24.8, 22.8, 22.3

HRMS : (ESI): calcd for $C_{11}H_{22}N_2O$: 199.1810 m/z $[M+H]^+$; found 199.1812.

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Chapter 2

ZnI_2 Promoted Conversion of Enamines and 1-Alkynes to Allenes

2.1 Introduction

2.1.1 Chiral allenic natural products

Chiral allenes are highly valuable synthons in organic synthesis. Occurrence of allenic structures in a variety of natural products and in pharmacologically active compounds have inspired immense interest among organic and medicinal chemists.[1] Pyrethrolone **1** is the first naturally occuring allene characterized by Staudinger and Ruzicka.[2] In the last few years, several natural products containing allene moiety **2-6** were isolated and some of them are shown in Figure 1.[3]

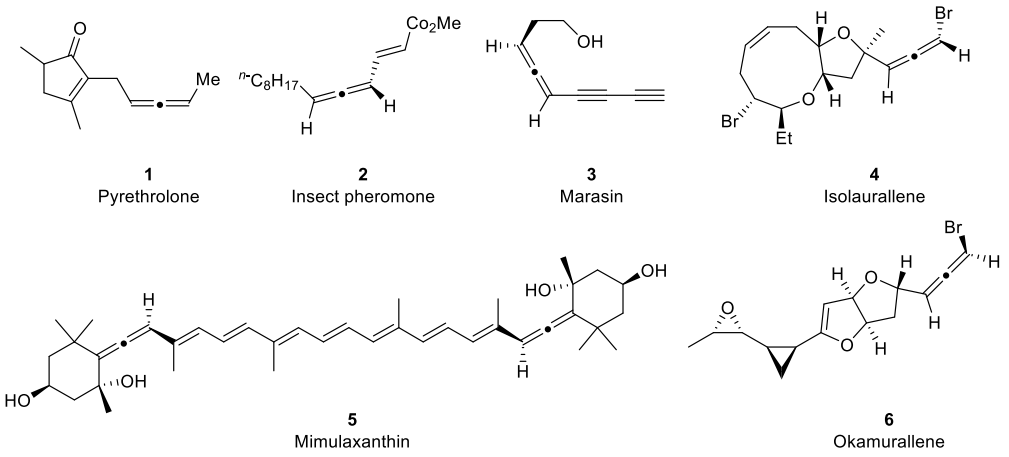


Figure 1

2.1.2 Biologically active chiral allenes

Allenic motifs not only occur in nature but also exhibit a wide range of biologically activities.[4,5] For example, the compounds scorodonin **7**, nemotin **8** and phomallenic acid A **9** have inhibiting effects on the growth of bacteria, yeasts and

filamentous fungi.[6] Other allenic derivatives which exhibit inhibiting effects are sterol biosynthesis inhibitor **10**, gastric acid inhibitor **11**, inhibitor of HIV **12**, hepatitis B replication inhibitor **13** and vitamin B_6-dependent decarboxylase inhibitor (suicide substrate) **14** (Figure 2).[7,8]

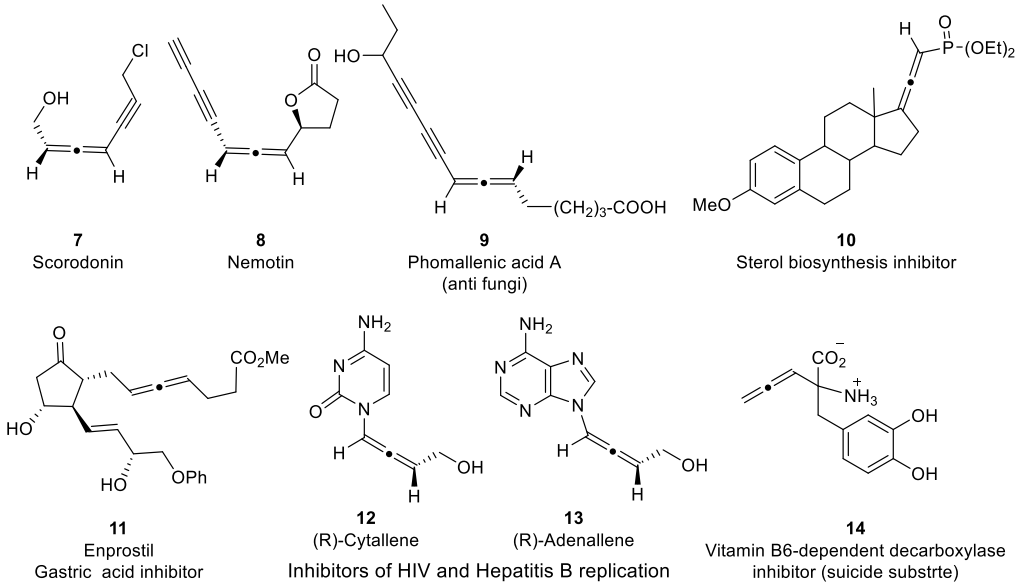


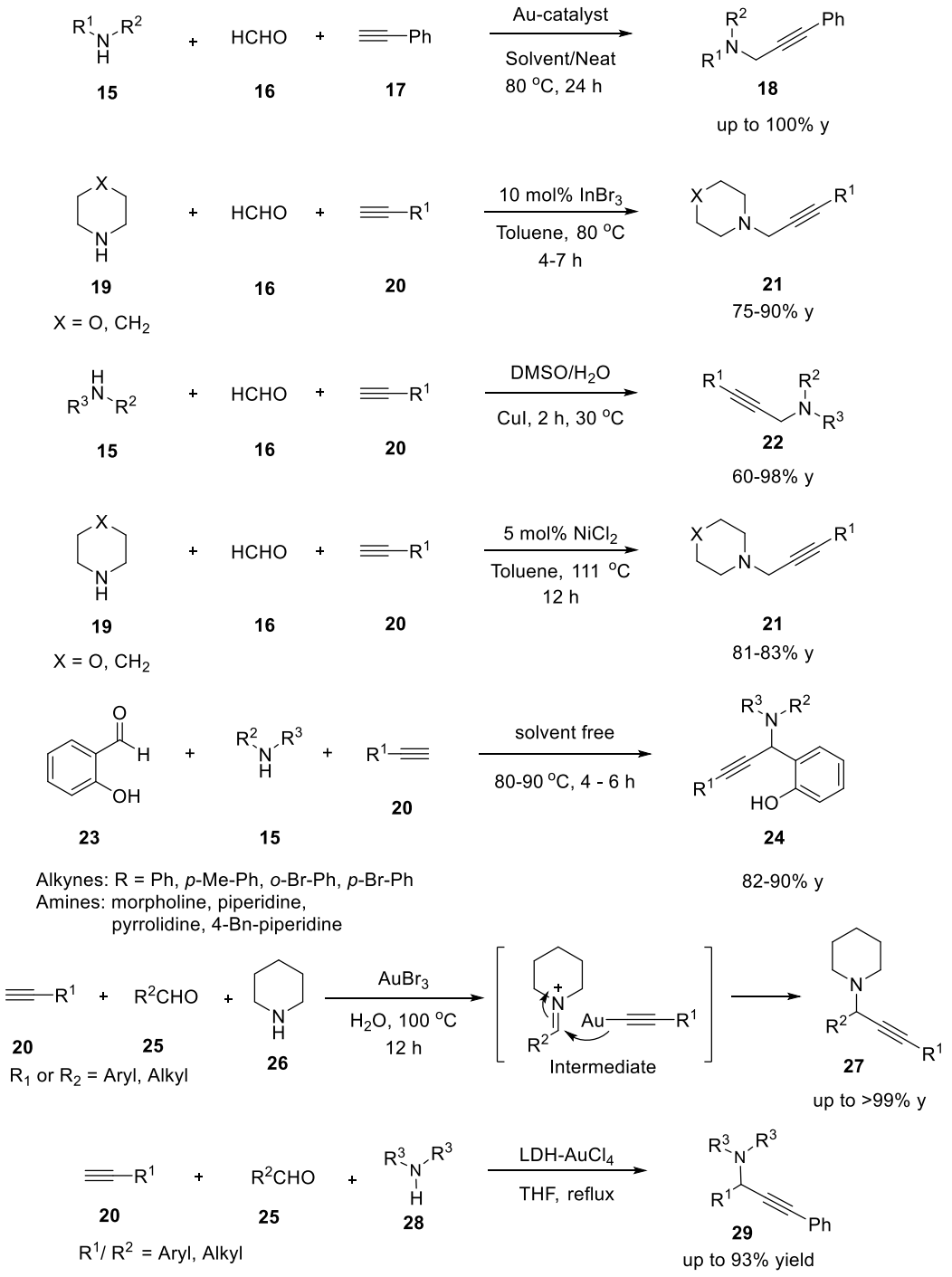
Figure 2

Methods for synthesis of propargylamines

2.1.3 Synthesis of propargylamines using aldehydes and 1-alkynes and secondary amines

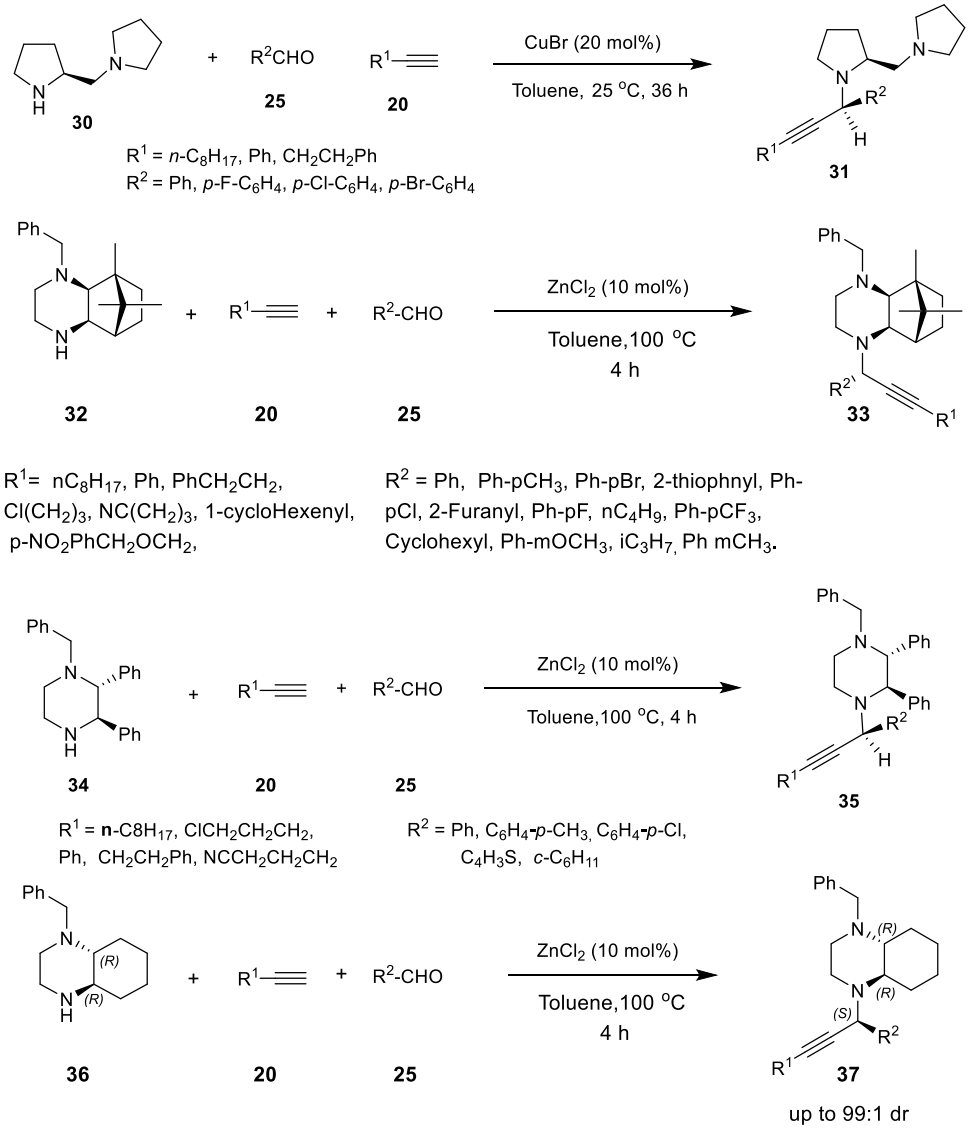
In recent years, there have been immense interest on the development of synthetic methods to obtain propargylamines. The propargylamines were readily prepared by using cyclic or acyclic secondary amines, aldehydes **16** and 1-alkynes **20** in the presence of catalysts (Chart 1).[9-21]

Chart 1



Methods were developed in this laboratory for the synthesis of the chiral proapargylamine derivatives **31**, **33**, **35**, and **3**7 using aldehydes, 1-alkynes and chiral amines in presence of copper or zinc halide catalysts (Chart 2).[22]

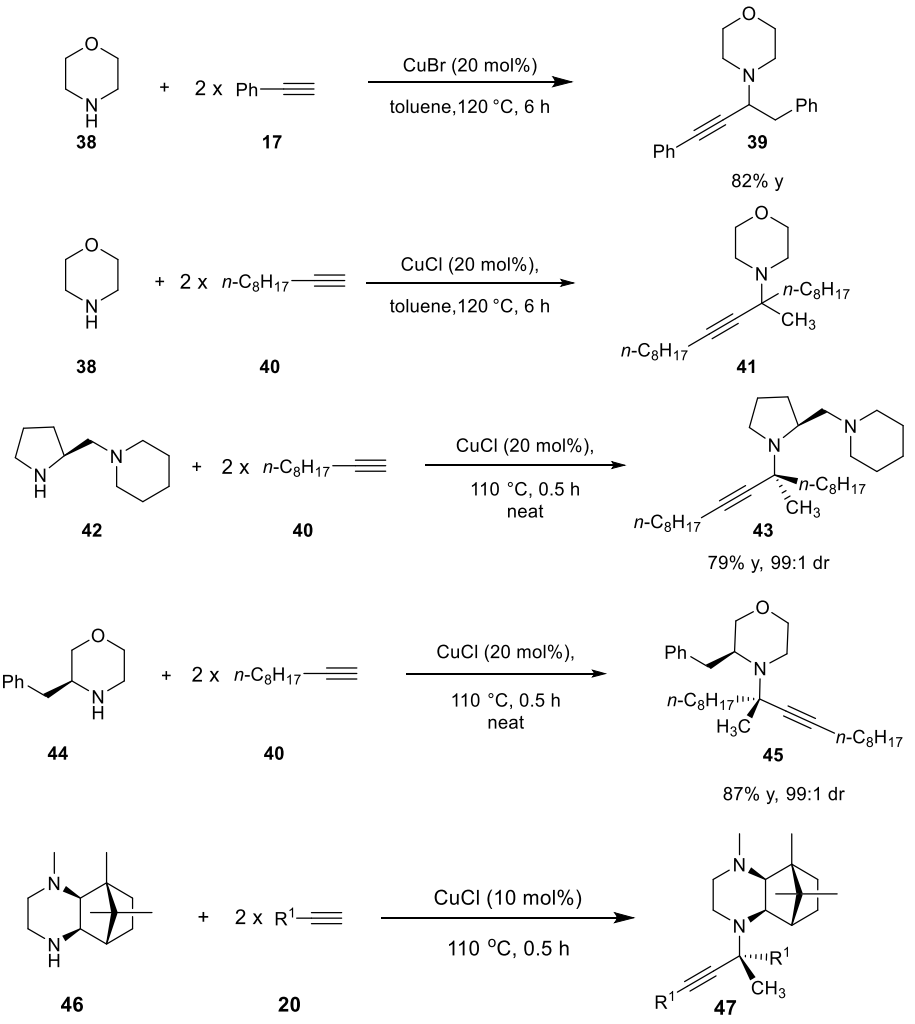
Chart 2



2.1.4 Synthesis of propargylamines using two 1-alkynes

Recently, methods were also developed in this laboratory for the synthesis of chiral and achiral tetrasubstituted propargylamines using amines and two 1- alkynes *via* hydroamination reaction in presence of CuCl (Chart 3).[23]

Chart 3

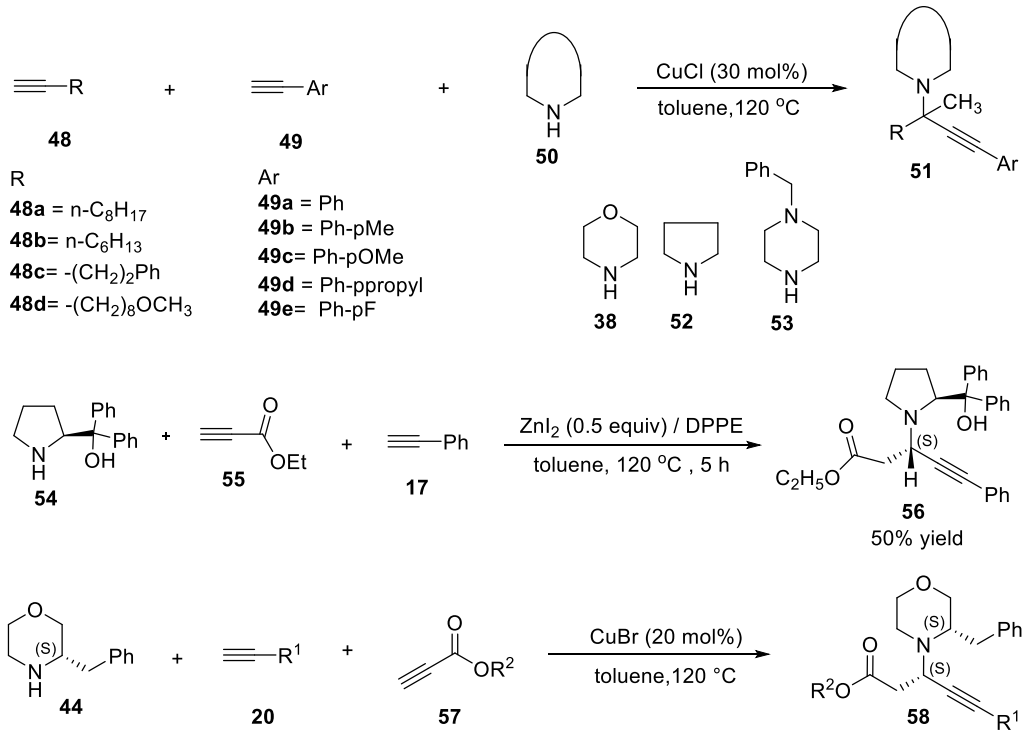


R^1

20a = n-C_8H_{17} **20b** = n-C_6H_{13} **20c** = n-C_5H_{11} **20d** = c-$C_5H_9CH_2$ **20e** = c-$C_6H_{11}CH_2$ **20f** = c-C_5H_9 **20g**= c-C_6H_{11} **20h** = Ph-$(CH_2)_2$ **20i** = Ph-$(CH2)_3$ **20j**= Ph-$(CH2)_4$ **20k** = CN-$(CH2)_3$- **20l** = MeO-$(CH2)_8$-

Very recently, methods were developed to access for tetrasubstituted propargylamines using two different alkynes and secondary amines. Also, propargylamino esters were synthesized using amine, ethyl propiolate and 1-alkynes in the presence of metal catalysts (Chart 4).[24-25]

Chart 4



2.1.5 Synthesis of propargylamines using ketones and 1-alkynes

Gold, CdI_2 catalyzed and CuX/Fe_3O_4 or $Ti(OEt)_4$ promoted synthesis of tetrasubstituted propargylamines were reported using amines, ketones and 1-alkynes (Chart 5).[26-31]

Chart 5

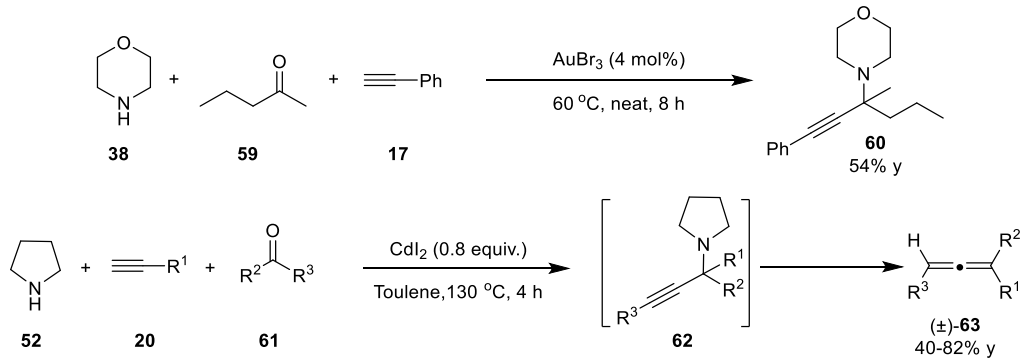
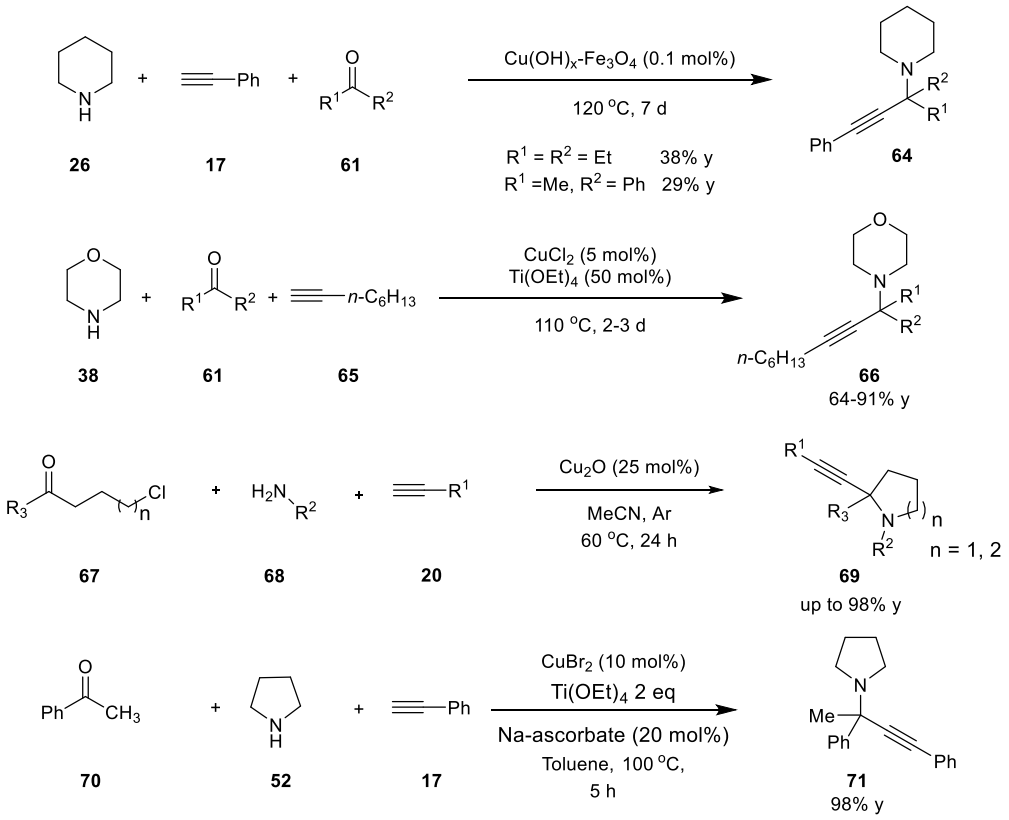


Chart 5(continued)



Very recently, methods were developed in this laboratory using secondary amines with unsaturated ketones and 1-alkynes in presence of copper salts to obtain the propargylamine derivatives *via* Michael addition reaction (Chart 6).[32]

Chart 6

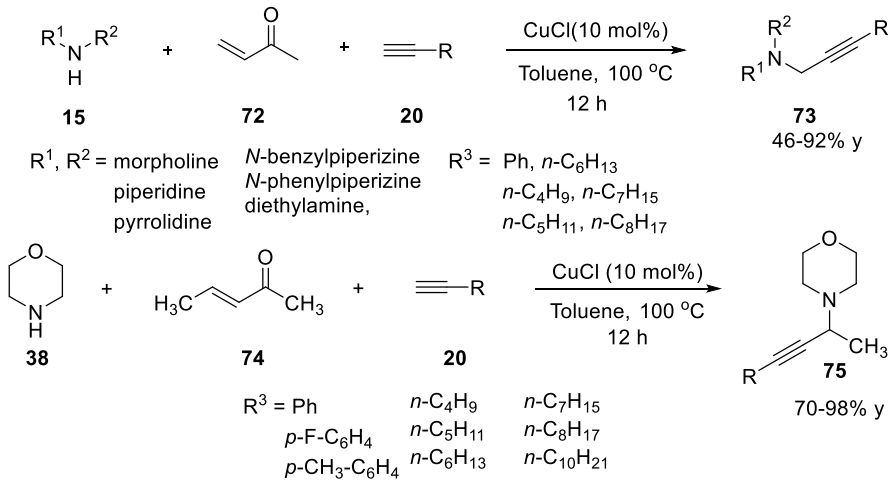
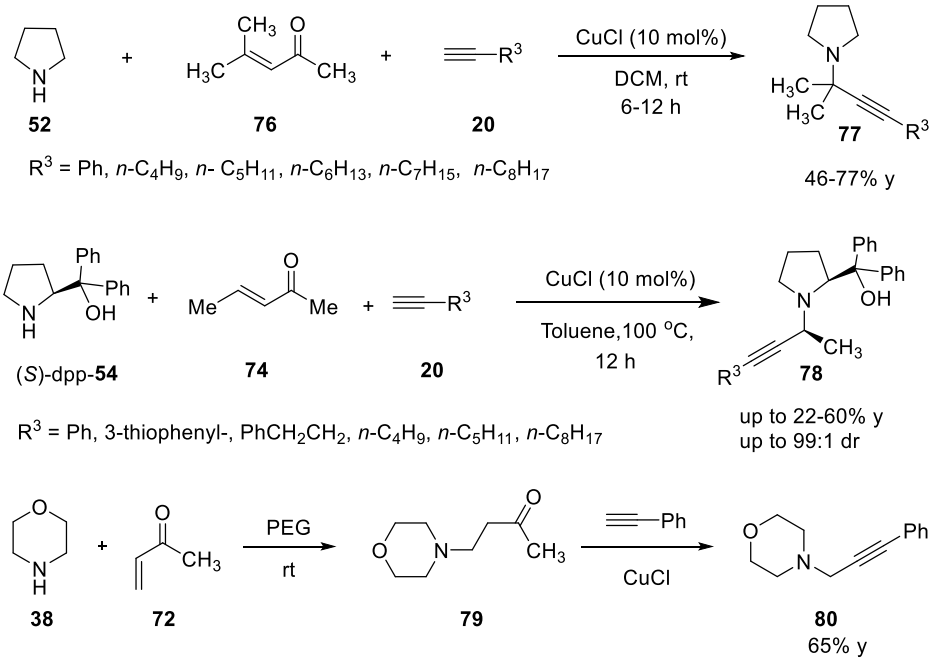


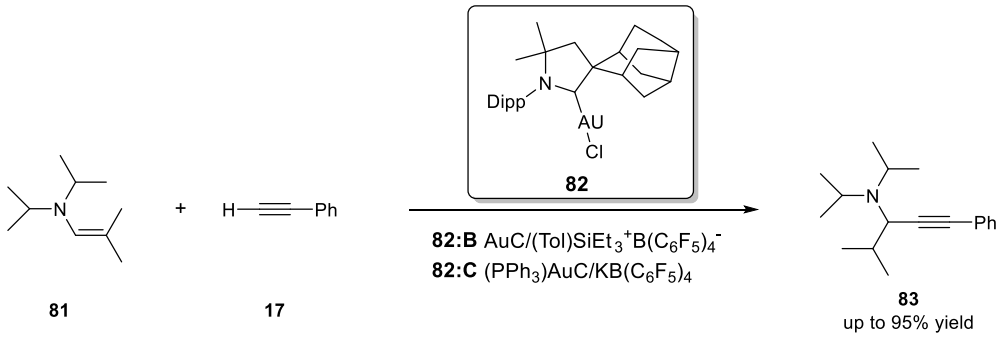
Chart 6 (continued)



2.1.6 Synthesis of propargylamines using enamines and 1-alkynes

The gold catalyzed coupling reaction of enamine **81** and phenyl acetylene was reported to give propargylamine **83** in up to 95% NMR yield (Scheme 1).[33]

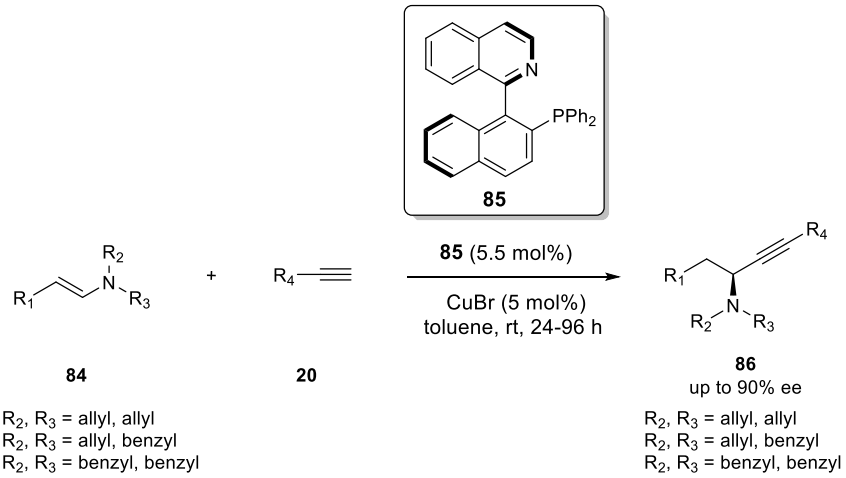
Scheme 1



Knochel *et al* reported[34] the copper catalyzed enantioselective synthesis of propargylamines **86** using enamine **84**, 1-alkyne **20** and quinap **85** as chiral source. Enamines **84** with readily removable protecting groups such as allyl or benzyl groups

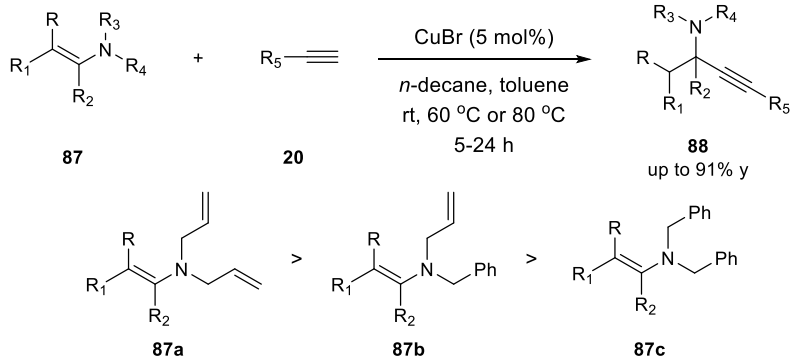
were reported to readily react with terminal alkynes in the presence of CuBr (5 mol%) in toluene to give propargylylamines **86** under mild reaction conditions (scheme 2).[34]

Scheme 2



It was also reported that substituents at the enamine **87** nitrogen play a crucial role and the disubstituted enamines were usually more reactive than trisubstituted enamines. By increasing the steric hindrance of the protecting groups, the rate of addition reaction was decreased ($(All)_2$>(All)Bn>Bn_2) (scheme 15).[35-36]

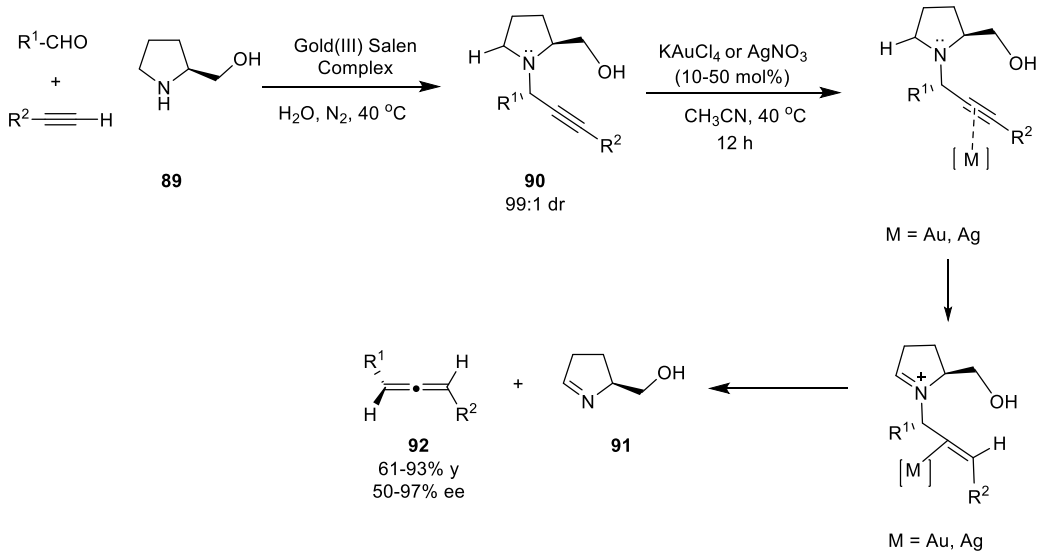
Scheme 3



2.1.7 Methods of Synthesis of allenes

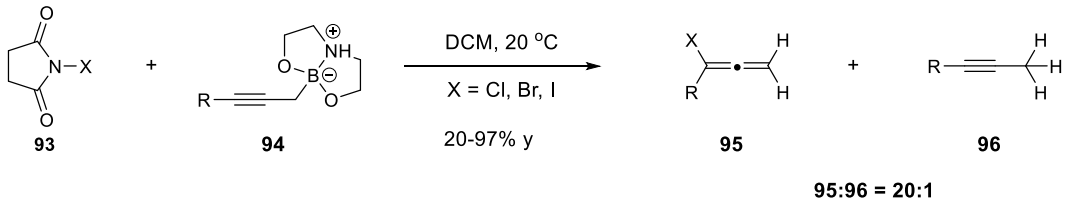
Gold(III)-salen catalyzed diastereoselective synthesis chiral propargylamines **90** were reported using chiral amino alcohol **89,** aldehydes and converted to chiral allenes **92** (Scheme 4) [37]

Scheme 4



A method for the synthesis of haloallenes **95** with good regioselectivity (20:1) was developed using propargylboronates and N-halosuccinamides **93** (scheme 5). [38]

Scheme 5



2.1.8 Synthesis of allenes from propargyl derivatives

Methods were developed for the synthesis of substituted allenes from the corresponding propargyl derivatives under different conditions (Chart 7).[39-46]

Chart 7

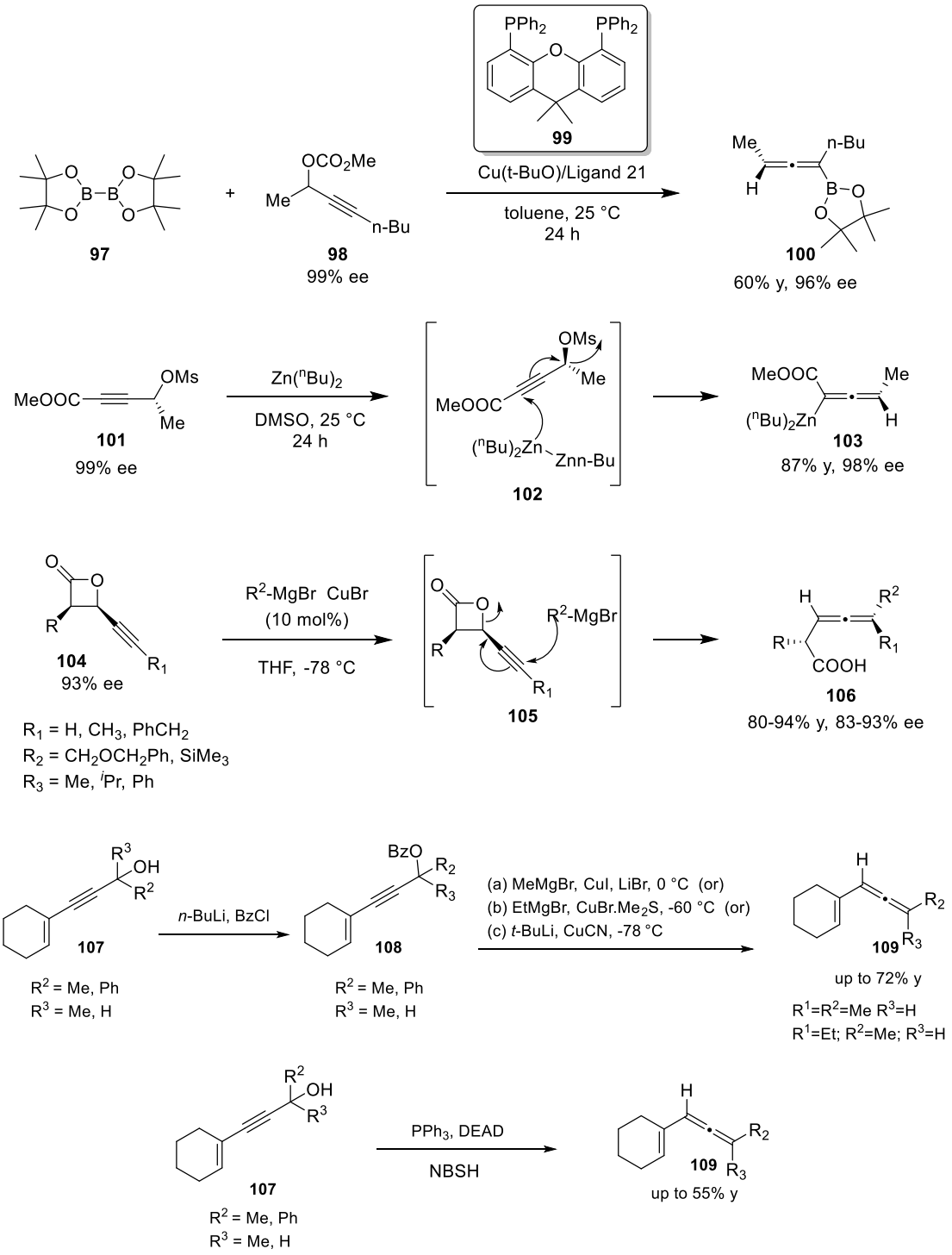
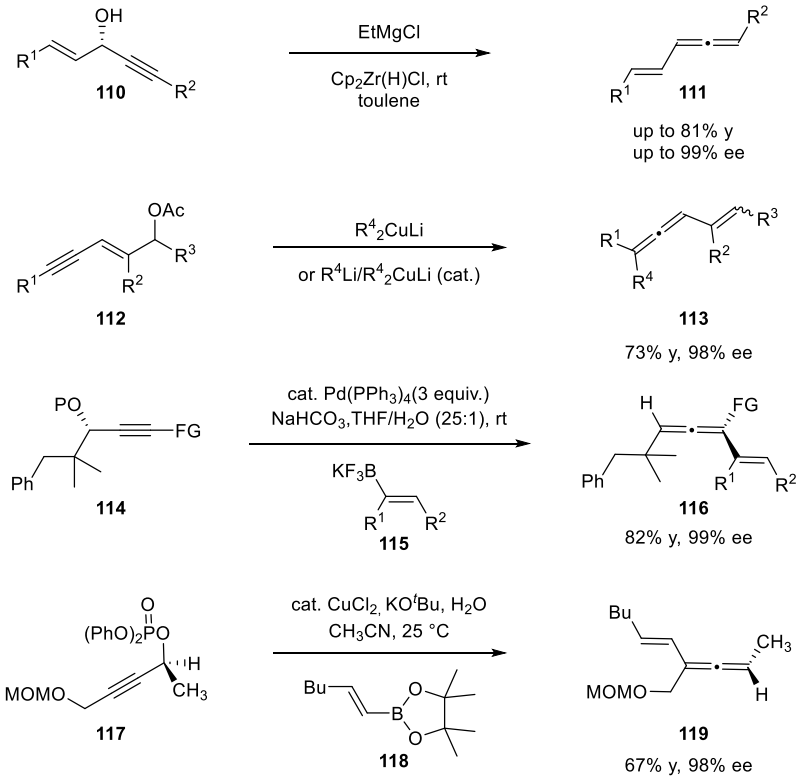
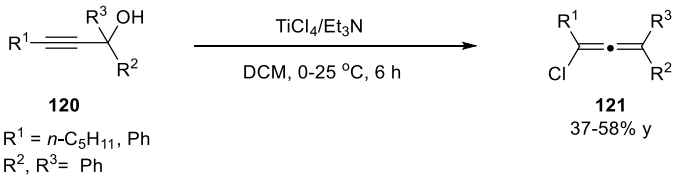

PPh2
PPh2
O
99
OCO2Me
Me
n-Bu
97
98
99% ee
Cu(t-BuO)/Ligand 21
toluene, 25 °C
24 h
Me
n-Bu
H
B–O
O
100
60% y, 96% ee
MeOOC
OMs
Me
101
99% ee
Zn(nBu)2
DMSO, 25 °C
24 h
OMs
Me
MeOOC
(nBu)2Zn
Znn-Bu
102
MeOOC
Me
(nBu)2Zn
H
103
87% y, 98% ee
O
O
R
R1
104
93% ee
R2-MgBr CuBr
(10 mol%)
THF, -78 °C
R2-MgBr
105
H
R2
R1
COOH
106
80-94% y, 83-93% ee
R1 = H, CH3, PhCH2
R2 = CH2OCH2Ph, SiMe3
R3 = Me, iPr, Ph
R3
OH
R2
107
n-BuLi, BzCl
BzO
R2
R3
108
(a) MeMgBr, CuI, LiBr, 0 °C (or)
(b) EtMgBr, CuBr.Me2S, -60 °C (or)
(c) t-BuLi, CuCN, -78 °C
H
R2
R3
109
up to 72% y
R1=R2=Me R3=H
R1=Et; R2=Me; R3=H
R2 = Me, Ph
R3 = Me, H
R2 = Me, Ph
R3 = Me, H
R2
OH
R3
107
PPh3, DEAD
NBSH
H
R2
109
R3
up to 55% y
R2 = Me, Ph
R3 = Me, H

Chart 7 (continued)



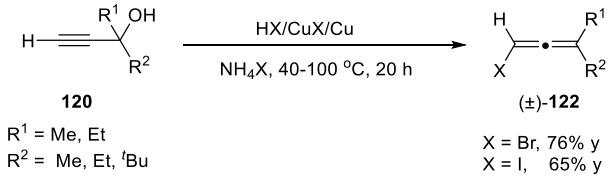
Previously, a convenient method for the synthesis of chloroallenes **121** from propargylic alcohol **120** using $TiCl_4/Et_3N$ reagent system was developed in this laboratory (Scheme 6).[47]

Scheme 6



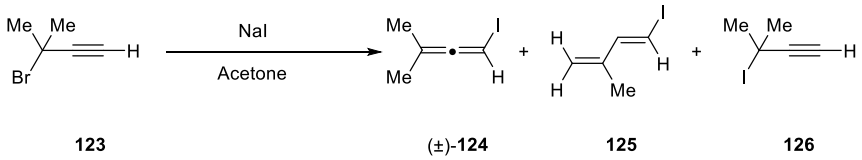
A method for the synthesis of haloallenes **122** from propargylic alcohol **120** using CuX and ammonium halides was also reported (Scheme 7).[48]

Scheme 7



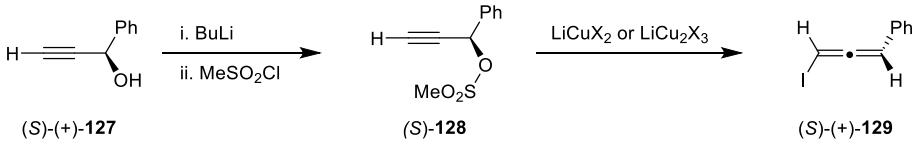
Iodoallenes are highly versatile synthetic building blocks in organic synthesis.[49] Previous attempts to synthesize of 1,l-dialkyl-3-iodoallenes *via* S_N2 or S_N2' reactions of the bromoacetylenes with sodium iodide in acetone solution gave mixture of products (Scheme 8).[49]

Scheme 8



A method for the synthesis of optically active iodoallenes (+)-**129** was developed from chiral propargylic alcohol (+)-**127** using lithium and copper halides (Scheme 9).[50]

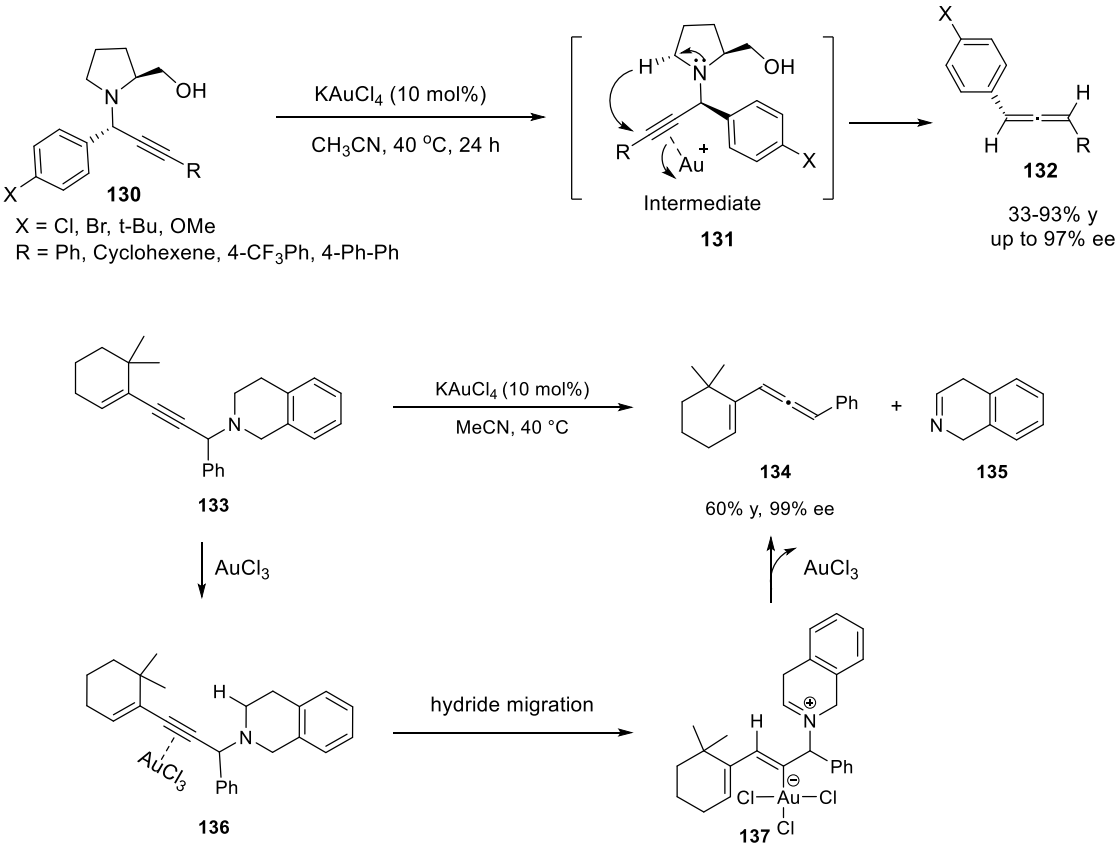
Scheme 9



2.1.9 Synthesis of allenes from propargylamine derivatives

Gold-catalyzed reaction for synthesis of axially chiral 1, 3-disubstituted allenes from the corresponding propargylamine derivatives were reported with high selectivities. (Chart 8). [51-53]

Chart 8



Very recently, methods were developed in this laboratory for the synthesis of allenes from the corresponding propargylamine derivatives under copper and zinc salts catalysts (Chart 9).

Chart 9

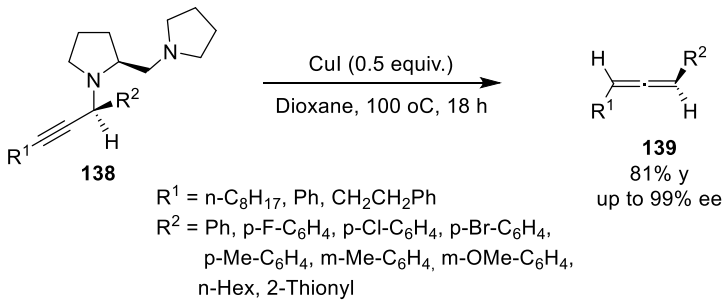
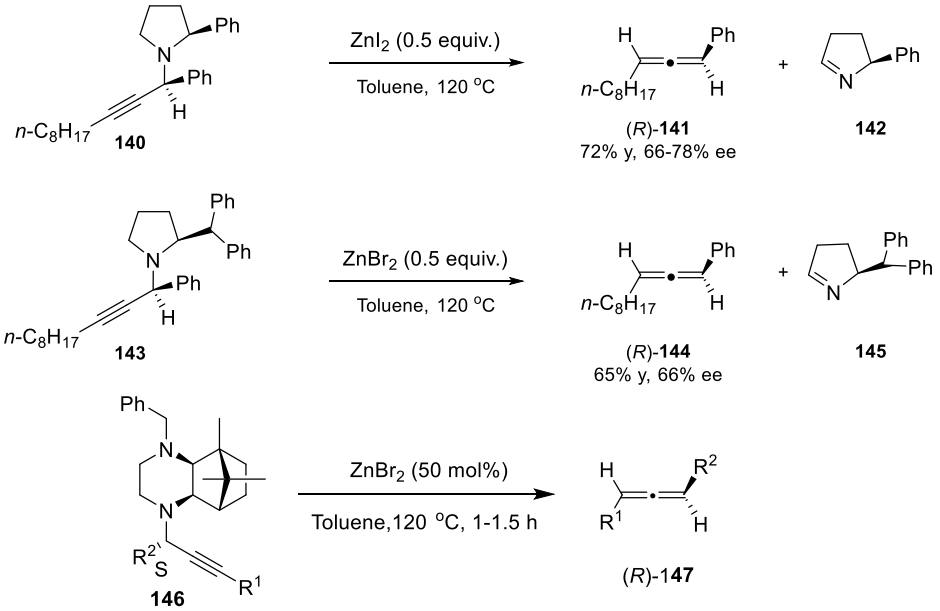
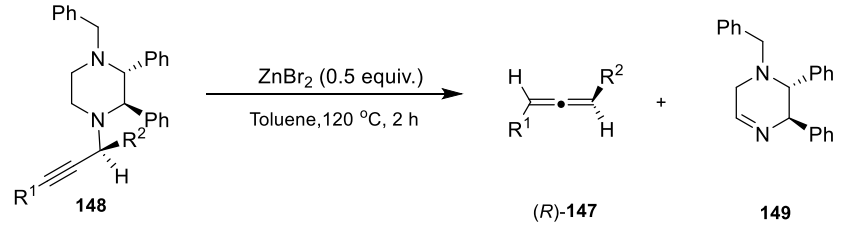


Chart 9 (continued)

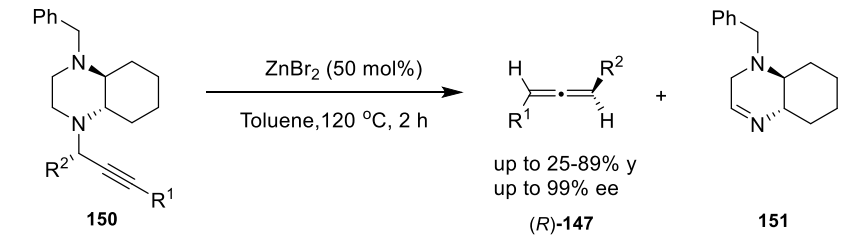


R^1= nC_8H_{17}, Ph, $PhCH_2CH_2$, $Cl(CH_2)_3$, $NC(CH_2)_3$, 1-cycloHexenyl, p-$NO_2PhCH_2OCH_2$,

R^2 = Ph, Ph-pCH_3, Ph-pBr, 2-thiophnyl, Ph-pCl, 2-Furanyl, Ph-pF, nC_4H_9, Ph-pCF_3, Cyclohexyl, Ph-mOCH_3, iC_3H_7, Ph mCH_3.



R^1 = *n*-C_8H_{17}, R^2 = Ph
R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-CH_3
R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-Cl
R^1 = $NCCH_2CH_2CH_2$, R^2 = Ph

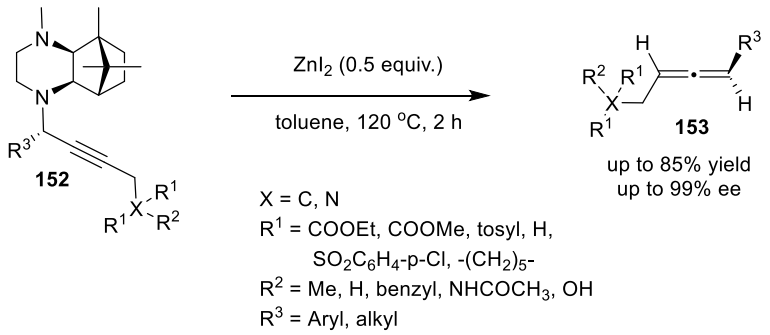


R^1= *n*-C_5H_{11}, $PhCH_2CH_2$, *n*-C_8H_{17}, Ph

R^2= Ph, C_6H_4-*p*-Br, C_6H_4-*m*-Br, C_6H_4-*p*-CH_3, c-hexyl,

Method to access highly functionalized allenes were also reported in this laboratory from the corresponding propargylamines using ZnI_2 (Scheme 10).

Scheme 10



2.1.10 Synthesis of allenes from 1-alkynes and aldehydes

It was reported that racmic disubstituted allenes can be also directly prepared in the reaction of aldehydes, amines and 1-alkynes in presence of ZnI_2 in toluene at 130 °C (Scheme).[54] Ma *et al.* reported methods for the preparation of α-allenols containing different functional groups.[55-56] Very recently, a chiral amine approach was developed in this laboratory for the synthesis of chiral disubstituted allenes using chiral amine, aldehyde and 1-alkyne in presence Zn salts (Chart 10).[57]

Chart 10

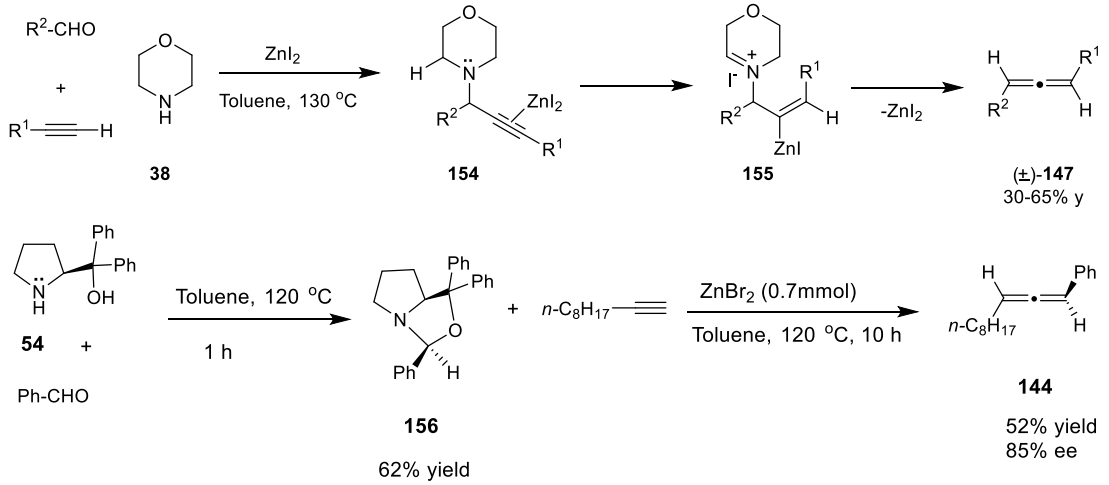
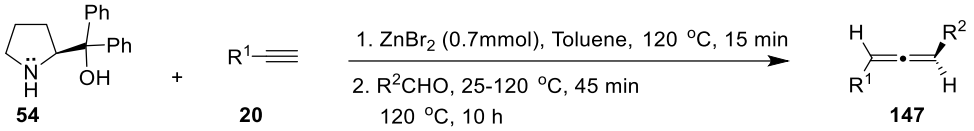


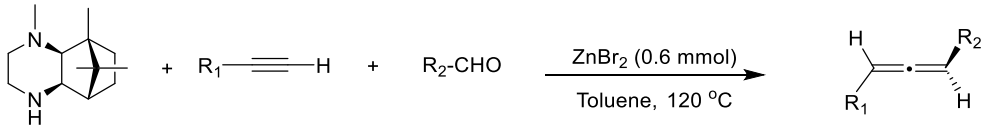
Chart 10 (continued)



54 **20** **147**

R^1= nC_8H_{17}, Ph, $PhCH_2CH_2$, $Cl(CH_2)_3$, $NC(CH_2)_3$, 1-cycloHexenyl, p-$NO_2PhCH_2OCH_2$,

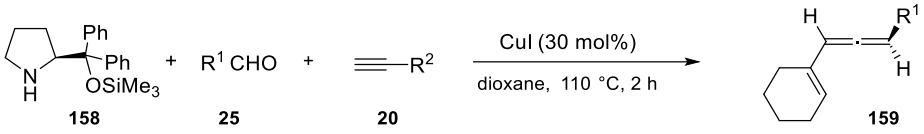
R^2 = Ph, Ph-pCH_3, Ph-pBr, 2-thiophnyl, Ph-pCl, 2-Furanyl, Ph-pF, nC_4H_9, Ph-pCF_3, Cyclohexyl, Ph-mOCH_3, iC_3H_7, Ph mCH_3.



157 **20** **25** **(R)-147**

R^1= nC_8H_{17}, Ph, $PhCH_2CH_2$, $Cl(CH_2)_3$, $NC(CH_2)_3$, 1-cycloHexenyl, p-$NO_2PhCH_2OCH_2$,

R^2 = Ph, Ph-pCH_3, Ph-pBr, 2-thiophnyl, Ph-pCl, 2-Furanyl, Ph-pF, nC_4H_9, Ph-pCF_3, Cyclohexyl, Ph-mOCH_3, iC_3H_7, Ph mCH_3.

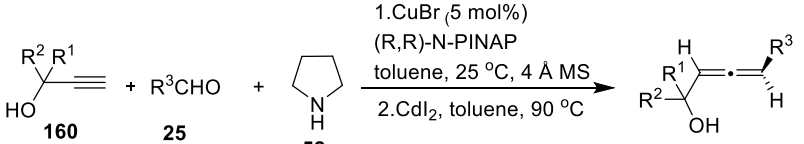


158 **25** **20** **159**

25a = R^1 = Ph
25b = R^1= Ph-*p*-CH_3
25c= R^1= Ph-*p*-OCH_3
25d = R^1= Ph-*m*-OCH_3
25e= R^1= Ph-CH_2-CH_2
25f = R^1= Ph-CH_2O-CH_2-CH_2

25g = R^1= Ph-*p*-Cl
25h = R^1= Ph-*p*-Br
25i = R^1= Ph-*p*-NO_2
25j = R^1= $C_7H_{12}O$
25k = R^1= $C_9H_{10}O$
25l = R^1= Ph-*m*-CHO

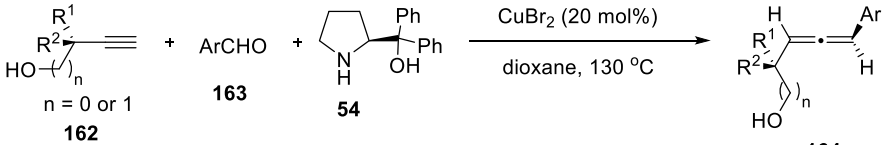
20a = R^2=



160 **25** **52** **161**

R^1/R^2 = Me, Et, -$(CH2)_2$-
R^3 = Alkyl, aryl

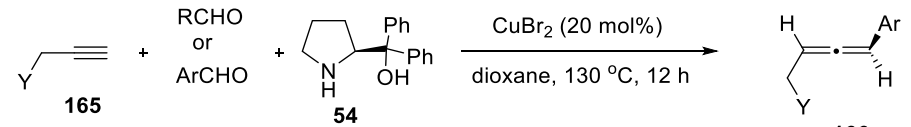
up to 84% yield
up to 97% ee



n = 0 or 1
162 **163** **54** **164**

R^1 or R^2 = H, Me

up to 70% yield
up to 98% ee



165 **54** **166**

Y = NHBoc or $CH(COOMe)_2$
NHtosyl, NHBOC, NHBz

up to 78% yield
up to 98% ee

2.1.11 Synthesis of allenes from propargylamines derived from amine and two 1-alkynes

Racemic and chiral trisubstituted allene syntheses were reported in this laboratory from the corresponding tetrasubstituted propargylamine derivatives.[58] Also, β-allenoates and vinylallene synthesis were reported from the corresponding propargylamine derivatives using Zinc and copper salts in good to excellent yields (Chart 11).[59]

Chart 11

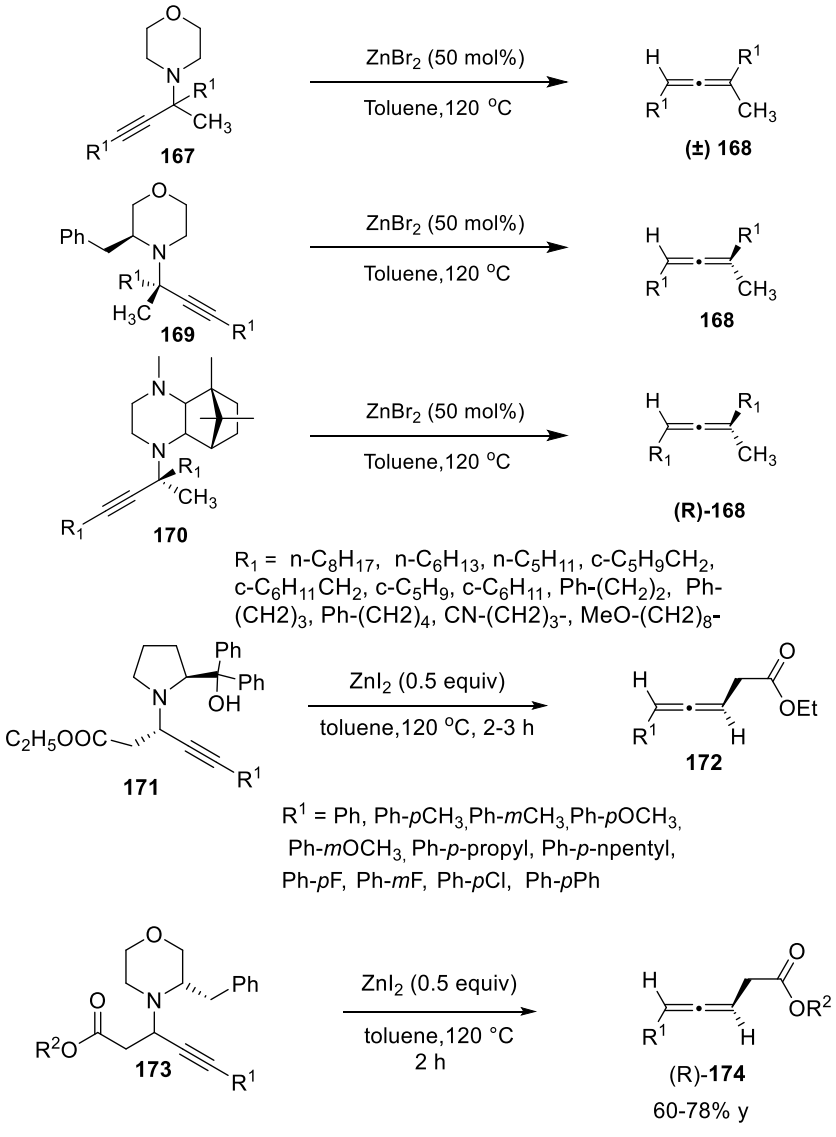
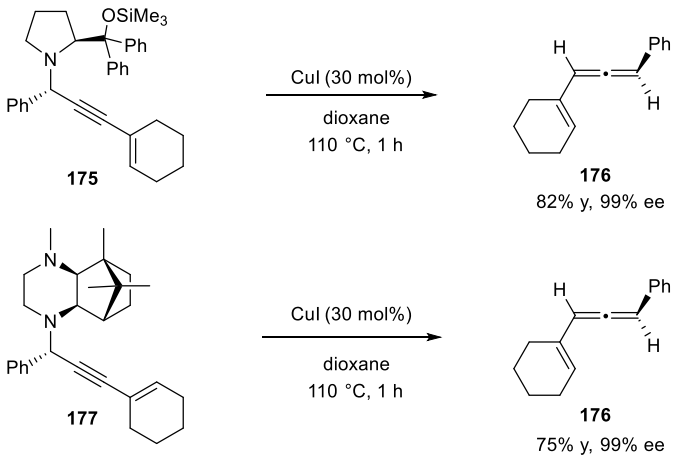


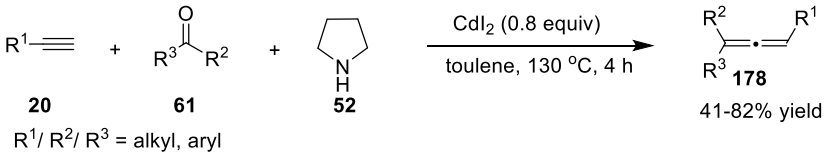
Chart 11 (continued)



2.1.12 Synthesis of trisubstituted allenes using amines, ketones and 1-alkynes

A cadmium iodide promoted one-pot synthesis of trisubstituted allenes **178** using terminal alkynes **20**, ketones **61** and secondary amine **52** was reported (Scheme 11).[60]

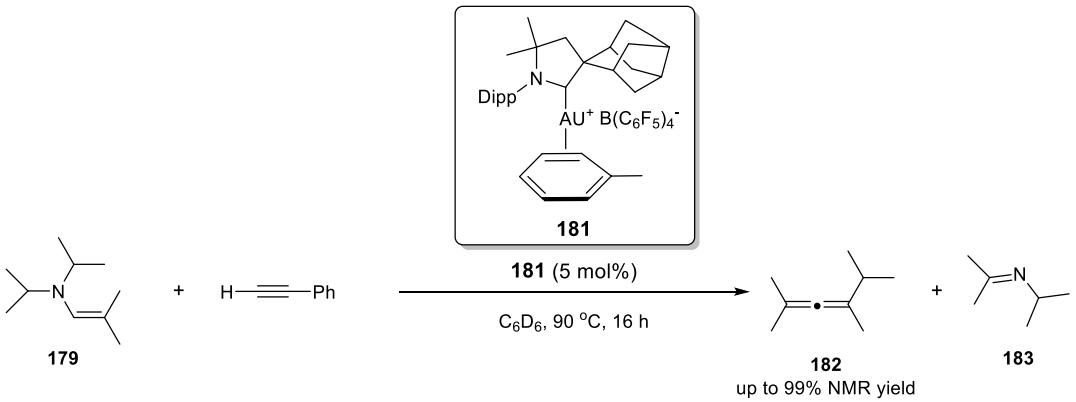
Scheme 11



2.1.13 Synthesis of trisubstituted allenes from enamines and 1-alkynes

A gold catalyzed coupling reaction of enamine and terminal alkynes has been reported. In the reaction of enamine 213 and phenyl acetylene in presence of catalytic system 216, the corresponding allenes were obtained in up to 99% yield (Scheme 12).[34]

Scheme 12



We have undertaken studies to examine the ZnI_2 promoted allene synthesis using enamines and terminal alkynes. We have also examined the use of propargyl alcohol derivatives for this transformation. The results are described in the next section.

2.2 Results and Discussion

2.2.1. Metal promoted synthesis of cycloalkyl ring based allenes in a one pot operation

Initially, we have carried out an experiment using the enamine 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** and phenyl acetylene **20g** with CuI (10 mol%) at 120 °C for 12 h. The allene **185ga** was obtained in 19% yield (entry 1, Table 1) along with the corresponding propargylamine (Scheme 13).

Scheme 13

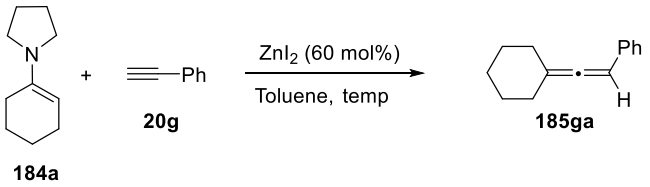


Table 1: Optimization condition using various Cu and Zn salts.[a,b]

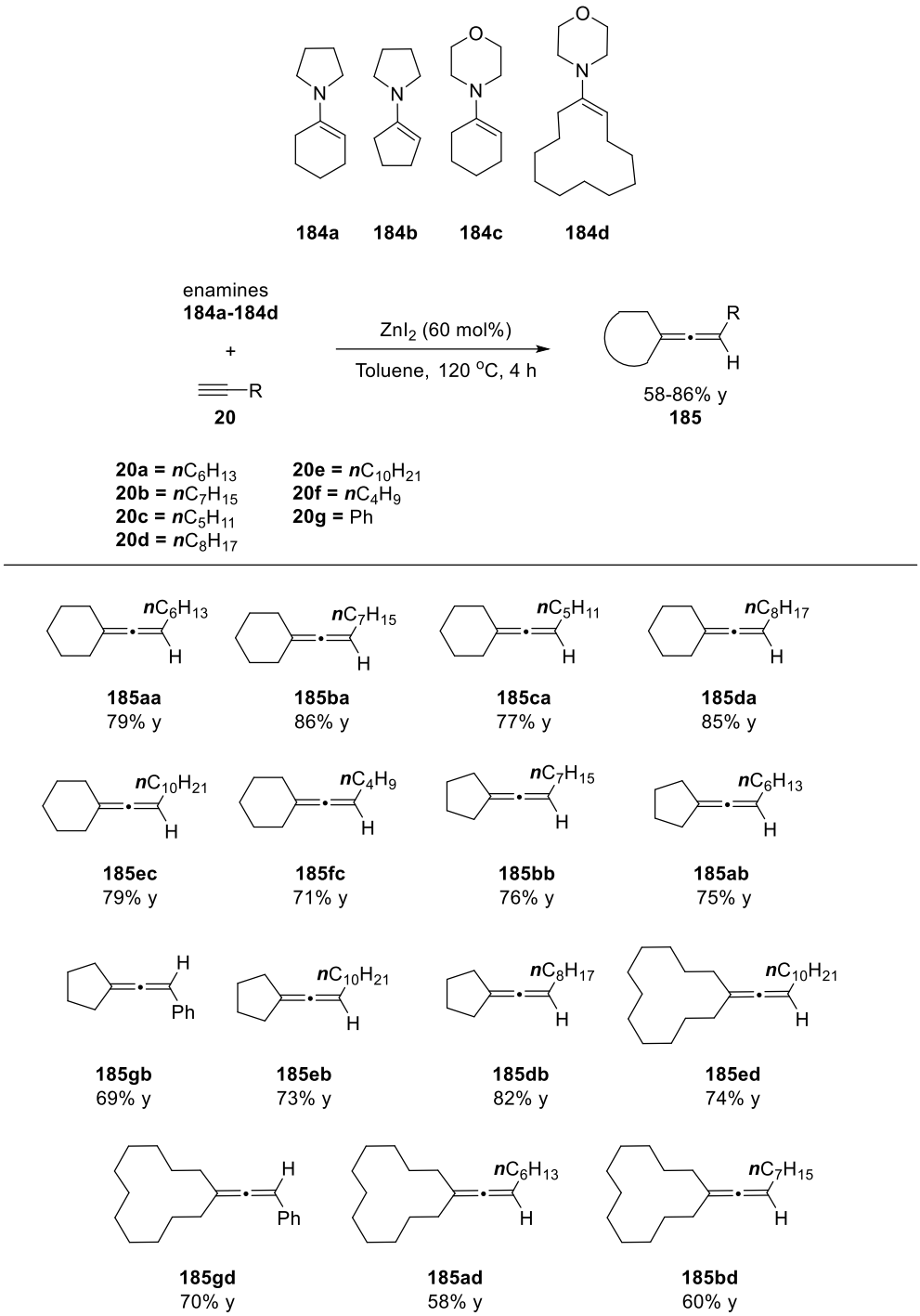
Entry	metal salt	temp ^{o}C	time hrs	Allene % yield
1.	CuI (10 mol%)	120	12	19
2.	CuI (20 mol%)	120	12	24
3.	CuI (30 mol%)	120	12	23
4.	CuI (50 mol%)	120	12	28
5.	$ZnBr_2$ (50 mol%)	120	12	72
6.	ZnI_2 (50 mol%)	120	6	67
7.	$ZnBr_2$ (50 mol%)	120	6	61
8.	**ZnI_2 (60 mol%)**	**120**	**4**	**84**

9.	ZnI_2 (60 mol%)	110	4	61
10.	CuI (70 mol%)	120	12	40

[a]All the reactions were carried out by taking enamine (1.0 mmol) and 1-alkyne (1.1 mmol) in toluene (3 mL). [b]Isolated yields.

We have also carried out the experiments using phenylacetylene and 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** with CuI or $ZnBr_2$ at 110 ^oC to 120 ^oC. When the reaction was carried out using CuI (20-50 mol%) in toluene solvent at 120 ^oC for 12 h, the allene **185ga** was isolated in low yields (entries 2, 3 and 4, Table 1). Whereas when 70 mol% of CuI was used at 120 ^oC, the allene **185ga** was obtained in 40 % yield (entry 10, Table 1). The reaction of 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** using 50 mol% of $ZnBr_2$ at 120 ^oC for 6 h gave the allene **185ga** in 61% yield (entry 7, Table 1). Whereas, the allene **185ga** was formed in 72% yield when the reaction was carried out for 12 h (entry 5, Table 1). Further, we have examined the reaction using ZnI_2 (50 mol%) at 120 ^oC for 6 h and obtained the allene **185ga** in 67% yield (entry 6, Table 1). Also, we have examined the temperature effect by carried out the reaction using ZnI_2 (60 ml%) at 110 ^oC for 4 h and obtained the**185ga** allene in 61% yield (entry 9, Table1). We have observed that the allene **185ga** was formed in 84% yield when the reaction was performed using 60 mol% of ZnI_2 in toluene at 120 ^oC for 4 h (entry 8, Table1). In this condition, we have not observed the formation of the corresponding propargylamine. With this optimized condition in hand, we have examined the synthesis of various allene derivatives **185** using enamines **184a-184d** with different terminal alkynes **20** using ZnI_2. The results are summarized in Table 2.

Table 2. ZnI_2 promoted synthesis of cycloalkyl ring containing allenes **185** in one pot operation.[a-c]



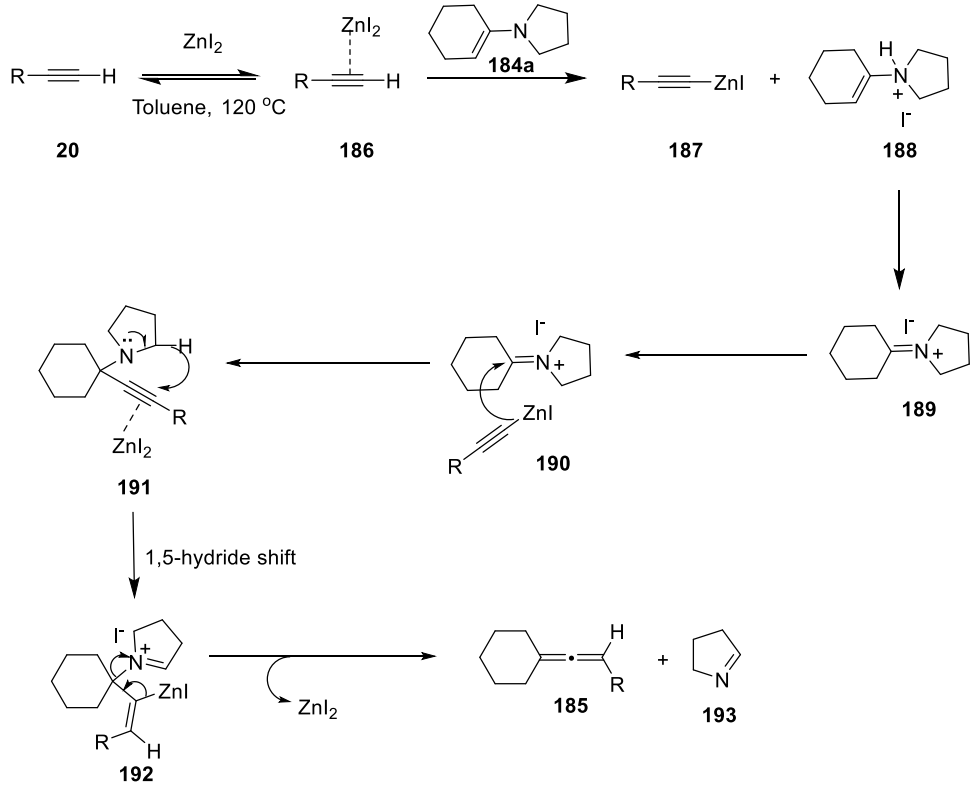
[a] All the reactions were carried out by taking enamine **184** (1.0 mmol), 1-alkyne **20** (1.1 mmol) and Toluene (3 mL). [b]Isolated yields of the allene **185**. [c]The products were characterized by using IR, NMR and HRMS.

The reaction using 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** and other alkynes 1-heptyne, 1-octyne, 1-nonyne and 1-decyne gave the corresponding cyclohexyl allenes (**185aa**, **185ba**, **185ca** and **185da**) in 77-86% yields. Also, the reaction of 4-(cyclohex-1-en-1-yl)morpholine **184c** with 1-dodecyne and 1-hexyne gave the corresponding allene products **185ec** and **185fc** in 79% and 71% yields. We have also carried out the reactions using 1-(cyclopent-1-en-1-yl)pyrrolidine **184b** and other alkynes such as phenylacetylene 1-octyne, 1-nonyne, 1-decyne and 1-dodecyne and isolated the corresponding products in 69% (**185gb**), 75% (**185ab**), 76% (**185bb**), 82% (**185db**) and 73% (**185eb**) yields, respectively. The reaction with 4-(cyclododec-1-en-1-yl)morpholine **184d** using phenylacetylene, 1-octyne, 1-nonyne and 1-dodecyne afforded the corresponding cyclododecyl allenes in 70% (**185gd**), 58% (**185ad**), 60% (**185bd**), 74% (**185ed**) yields, respectively (Table 2).

2.2.2 Plausible mechanistic pathway for the formation of allene

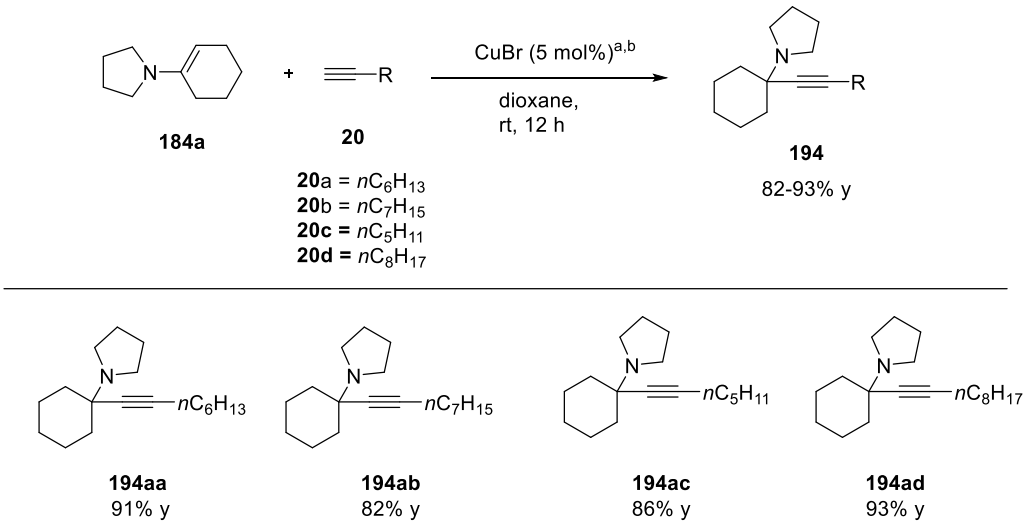
The transformation of 1-(cyclohex-1-en-1-yl)pyrrolidine enamine **184a** to allene **185** the formation of corresponding propargylamine can be rationalized by the mechanism outlined in Scheme 14. The initially formed alkynyl zinc intermediate **187** would react with the iminium ion **189** derived from 1-(cyclohex-1-en-1-yl)pyrrolidine enamine **184a** to give the corresponding propargylamine. Subsequently, the zinc iodide propargyl amine complex **191** of would undergo intramolecular 1, 5-hydride shift from the pyrrolidine skeleton to the acetylenic moiety leading to the formation of alkenyl zinc intermediate **192** which after C-N bond cleavage would give the allene **185**, imine and ZnI_2 (Scheme 14).

Scheme 14. Mechanism for the formation of allene using enamine, 1-Alkyne and ZnI_2.



We have also observed that the propargylamines are readily formed in the reaction using the 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** and various 1-alkynes **20** in the presence of CuBr in dioxane solvent at room temperature for 12 h (Table 3). The reaction of 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** using 1-alkynes such as 1-octyne and 1-nonyne in dioxane solvent gave the corresponding propargylamines 1-(1-(oct-1-yn-1-yl)cyclohexyl)pyrrolidine **194aa** and 1-(1-(non-1-yn-1-yl)cyclohexyl) pyrrolidine **194ab** in 91% and 82% yields, respectively. Whereas the alkynes 1-heptyne and 1-decyne furnished the products in 86% (**194ac**) and 93% (**194ad**) yields, respectively (Table 3).

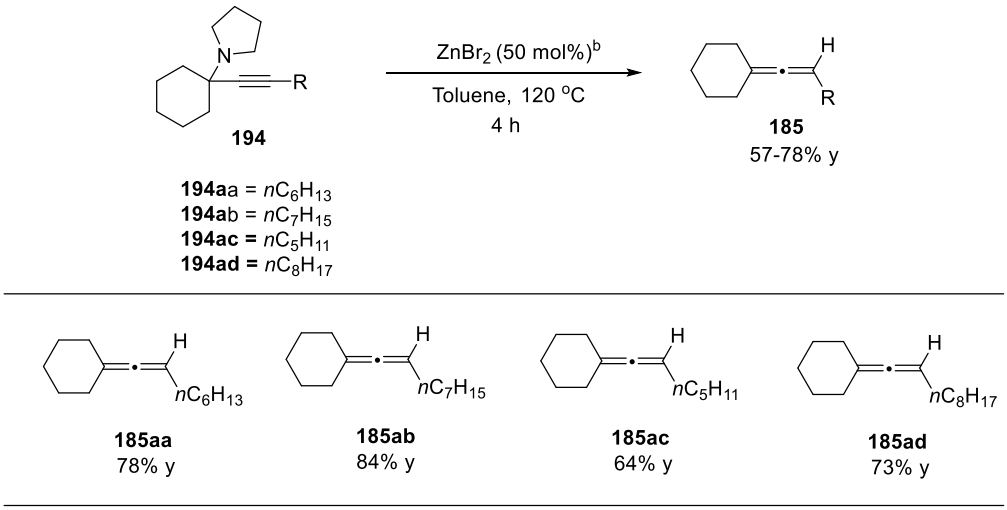
Table 3



[a]All the reactions were carried out with enamine **184a** (1 mmol), 1-alkyne **20** (1.1 mmol), dioxane (3 mL) for 12 h at 25 °C. [b]Isolated yields of the products.

The propargylamines are also useful precursors for allenes. For example, the propargylamines can be readily converted into allenes using $ZnBr_2$ in toluene at 120 °C by a procedure developed in this laboratory.[22b]

Table 4

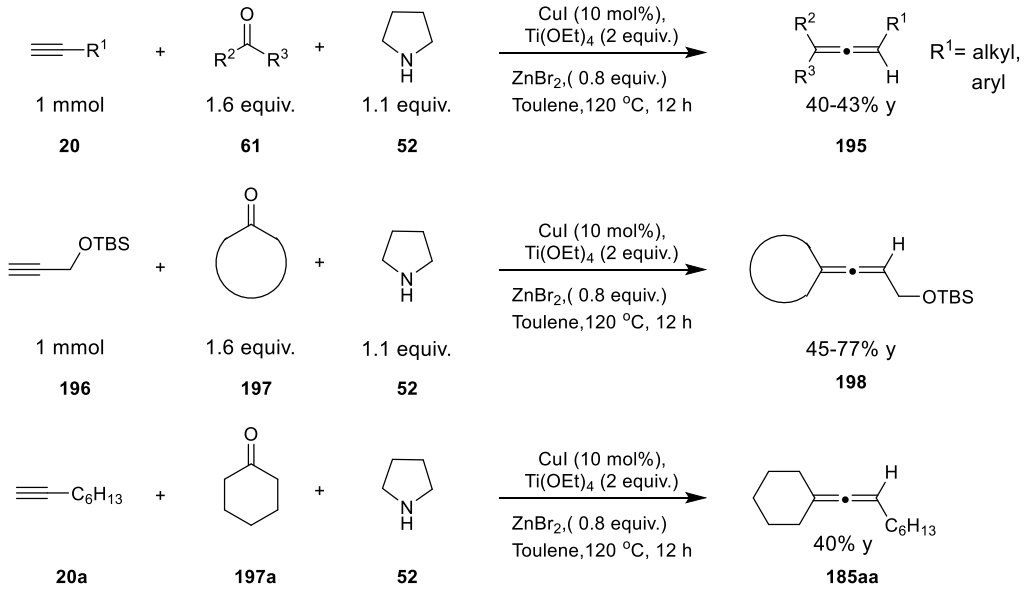


[a]All the reactions were carried out with Propargyl amine **194** (1 mmol), $ZnBr_2$ (0.5 equiv) Toluene (3 mL) for 3 h at 120 °C. [c]Isolated yields of **185**. [d]The products were characterized by spectral data (IR, ^{1}H-NMR, ^{13}C-NMR and HRMS).

We have observed that the propargylamine **194aa** reacts with $ZnBr_2$ (0.5 mmol), at 120 ^oC to give the allene oct-1-en-1-ylidenecyclohexane **185aa** in 78% yield (Scheme 15). Also, the propargylamines **194ab-194ad**, obtained from enamine and 1-alkynes reacts with $ZnBr_2$ (0.5 mmol) to give the corresponding allenes **185ab-185ad** in up to 84% yield (Table 4).

During these conversations, there was a report in literature on the synthesis of trisubstituted allenes **195**, **198**, **185aa** using pyrrolidine **52**, ketone and terminal alkynes using a mixture of metal salts like CuI, $Ti(OEt)_4$ and $ZnBr_2$ in toluene at 120 ^oC (Chart 12).[30]

Chart 12



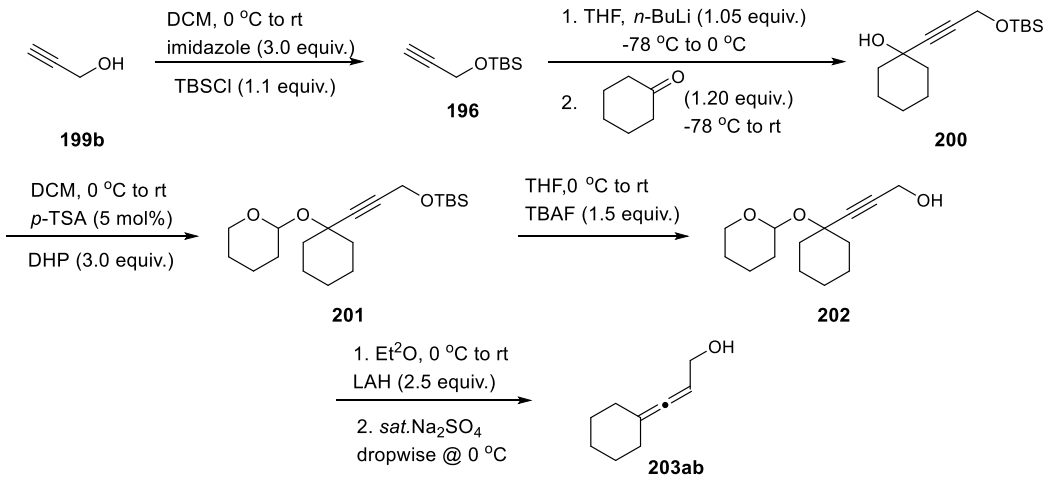
The method described here using ZnI_2 compares favorably with this reported method.

2.2.3 Synthesis allenols from propargyl alcohols

Previously, multistep synthesis of cyclohexyl ring based allenol was reported from protected propargyl alcohol and cyclohexanone.[61] The allenic motifs are useful precursors

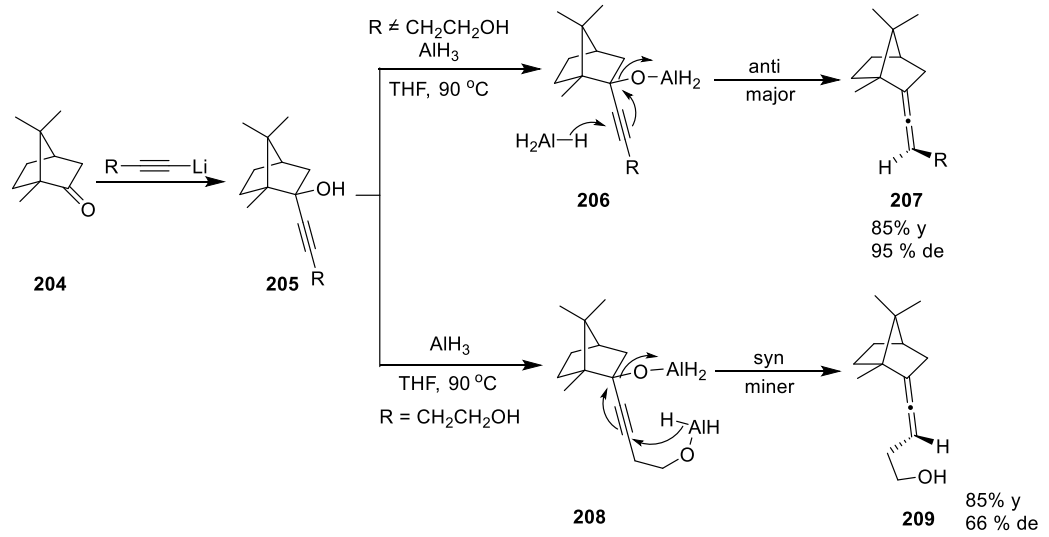
to access both functionalized, symmetrical and unsymmetrical [3]-[6] dendralenes using Pd-catalyzed cross couplings under micellar catalysis conditions (Scheme 15).[61]

Scheme 15



Also, allenols **204** and **206** were formed using the propargyl alcohol obtained from camphor upon reduction with AlH_3 (Scheme 16**).**[62]

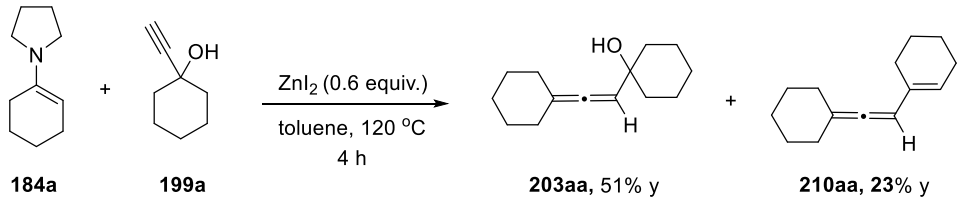
Scheme 16



We have observed that the reaction of 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** with 1-ethynylcyclohexan-1-ol **199a** under the optimized condition using ZnI_2, gave the

corresponding allenol **203aa** in 51% yield along with the vinylic allene **210aa** in 23% yield (Scheme 17).

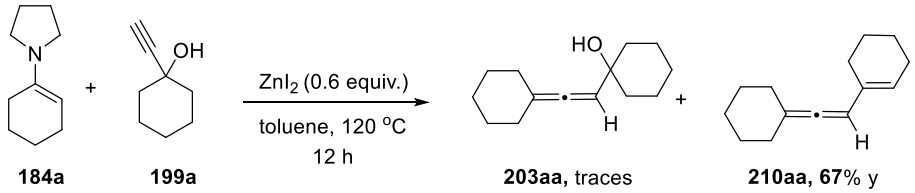
Scheme 17



184a **199a** **203aa,** 51% y **210aa, 23**% y

When the reaction was performed for 12 h at 120 °C in toluene solvent, the vinylic allene **210aa** was formed in 67 % yield along with only traces (<5%) of allenol **203aa** (Scheme 18).

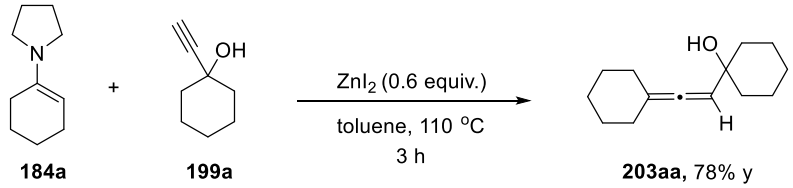
Scheme 18



184a **199a** **203aa,** traces **210aa, 67**% y

We have observed that the reaction was carried out only using 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** with 1-ethynylcyclohexan-1-ol **199a** and ZnI_2 (0.6 equiv.) at 110 °C only for 3 h, the corresponding product allenol **203aa** was obtained in 78% yield without the vinylic allene **210aa**. Clearly, higher temperature and prolonged reaction time facilitate the elimination of water to afford the corresponding vinylic allene **210aa** (Scheme 19).

Scheme 19

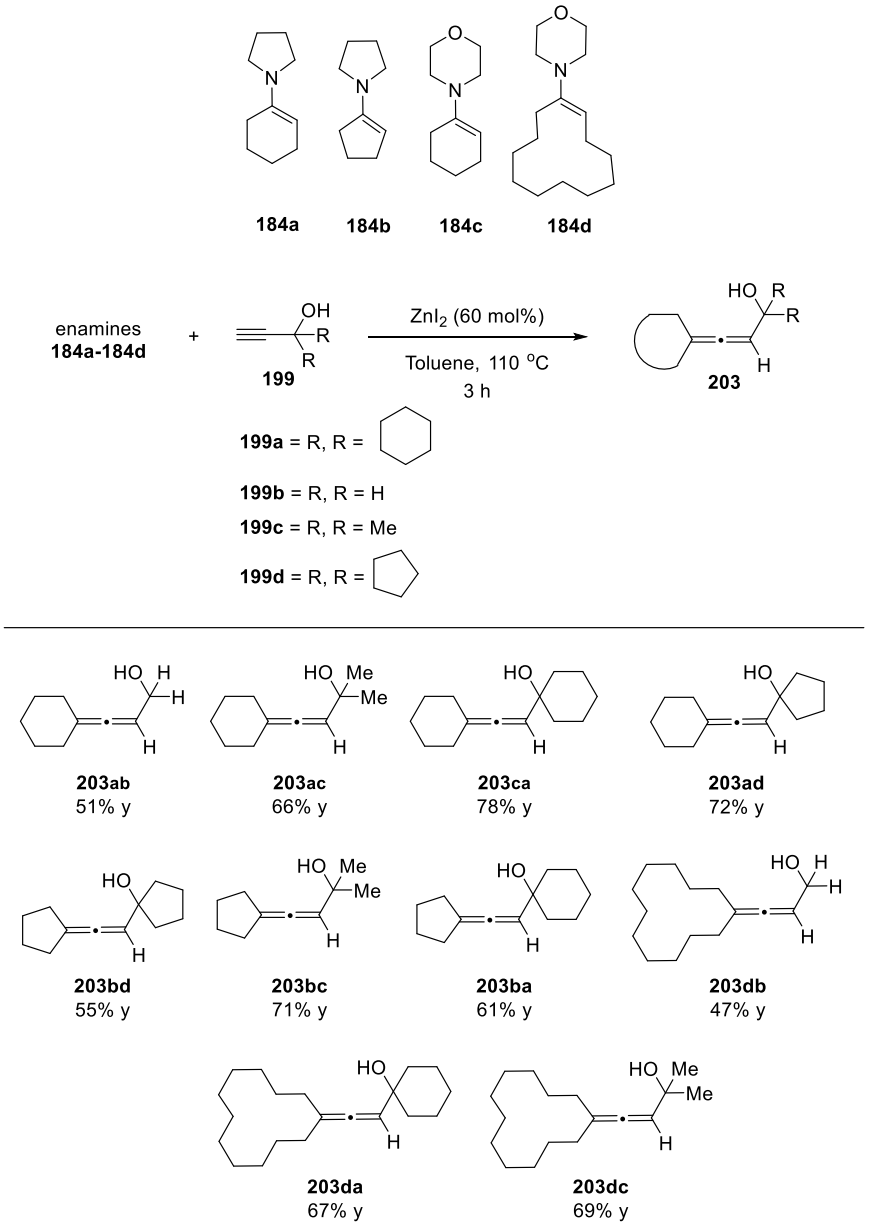


184a **199a** **203aa,** 78% y

We have carried out the reactions using various 1-alkynols **199** and enamines **184a-184d** under this optimized condition. The reaction using propargyl alcohol **199b**

with enamines 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** and 4-(cyclododec-1-en-1-yl)morpholine **184d** gave the corresponding allenols **203ab** in 51% yield and **203db** in 47% yield.

Table 5. Synthesis of cycloalkyl ring based allenols using enamines and 1-alkynols.



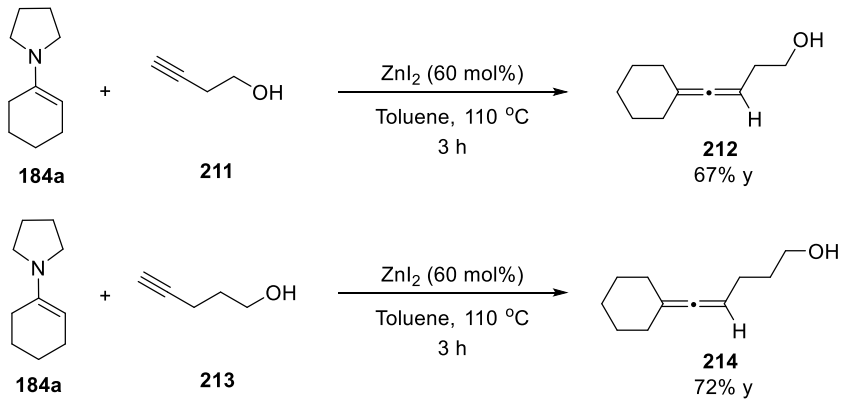
[a]All the reactions were carried out with enamine **184** (1 mmol), 1-alkynol **199** (1.1 mmol), toluene (3 mL) for 3 h. [b] isolated yield.

Also, the reaction of enamines **184a**, **184b** and **184d** using 2-methylbut-3-yn-2-ol **199c** furnished the allenols **203ac**, **203bc** and **203dc** in 66%, 71% and 69% yields,

respectively. Moreover, the reaction of morpholine enamine **184c** with 1-ethynylcyclopentan-1-ol **199d**, the allenol **203ad** was obtained in 72% yield. Also, the reaction of and 1-ethynylcyclopentan-1-ol **199d** using **184b** gave the corresponding allenol **203bd** in 55% yield. Whereas the reaction using enamines **184b** and **184d** with 1-ethynylcyclohexan-1-ol **199a** furnished the corresponding allenols **203ba** and **203da** in 61% and 67% yields, respectively (Table 5).

We have also observed that the reaction with 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** using 3-butyn-1-ol **211** and 4-pentyn-1-ol **213** gave the corresponding allenols **212** and **214** in 67% and 72% yields, respectively (Scheme 20).

Scheme 20

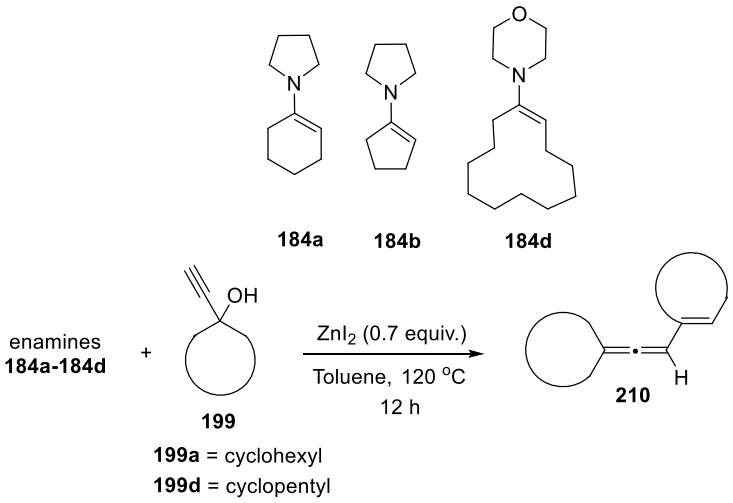


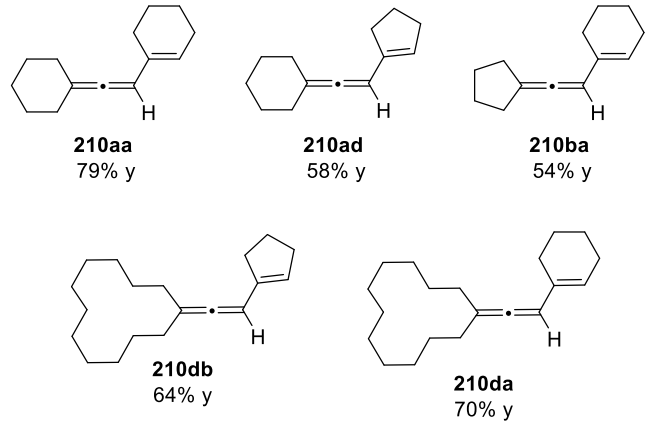
2.2.4 Synthesis of cycloalkyl ring containing vinylic allenes

As discussed earlier, higher temperature and prolonged reaction time facilitate the elimination of water to afford the corresponding vinylic allenes **210** (Scheme 18 and 19). Accordingly, we have carried out reactions of 1-ethynylcyclohexan-1-ol **199a** with **184a**, **184b** and **184d** using ZnI_2 (70 mol%) at 120 °C in toluene solvent for 12 h and obtained the corresponding vinylic allenes in 79% (**210aa**), 54% (**210ba**) and 70% (**210da**) yields.

Whereas, the reaction using 1-ethynylcyclopentan-1-ol **199d** with **184a** and **184d** furnished the allenols **210ad** and **210db** in 58% and 64% yields, respectively (Table 6).

Table 6.





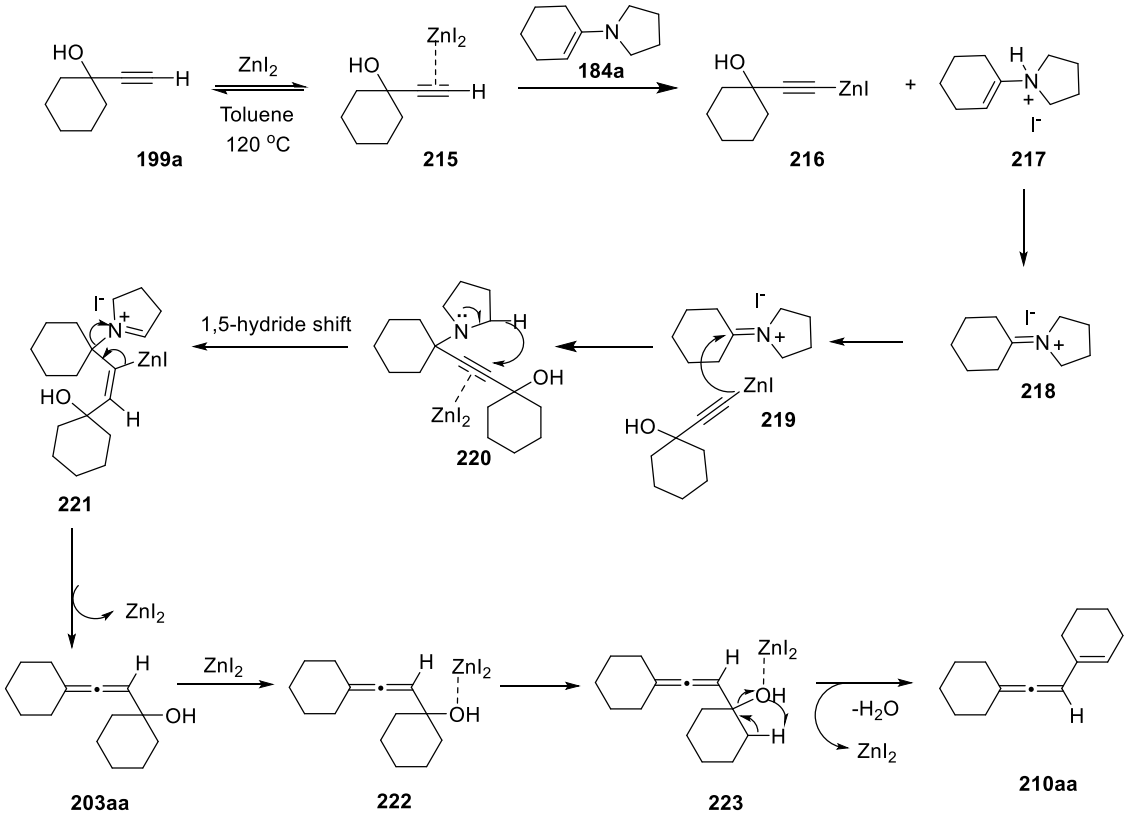
[a]All the reactions were carried out with enamine (1 mmol), 1-alkynol(1.1 mmol), toluene (3 mL) for 3 h. [b] isolated yield.

2.2.5 Plausible mechanistic pathway for the formation of vinylic allene.

The formation of propargylamino alcohol in the reaction of 1-alkynols **199** and enamines **184** followed by their conversion to allenols **203** with subsequent elimination of water to give vinylic allenes **210** can be rationalized by the mechanism outlined in Scheme

21. The reaction would proceed through *in situ* formation of both electrophile (iminium ion) and nucleophile (alkynyl metal) intermediates using 1-alkynols and enamines.

Scheme 21. Mechanism for the formation of allene using enamine, 1-Alkyne and ZnI_2



Initially, 1-ethynylcyclohexan-1-ol **199a** would react with ZnI_2 to form alkynol zinc complex **216**. The alkynol intermediate **216** would subsequently react with the iminium ion **218** derived from enamine 1-(cyclohex-1-en-1-yl)pyrrolidine **184a** to give the corresponding propargylamino alcohol. The zinc iodide propargylamino alcohol complex **220** would then undergo intramolecular 1,5-hydride shift from the pyrrolidine skeleton to the alkynol moiety leading to the formation of alkenyl zinc intermediate **221**. Subsequently, C-N bond cleavage in the intermediate **221** would give the allenol **203aa** and the imine as byproduct. The allenol **203aa** would undergo complexation (**223**) with ZnI_2 followed by the elimination of water molecule to afford the vinylic allene **210aa**

(Scheme 21). Hence, the reaction of propargyl alcohols can be tuned to give the corresponding allenols **203** or vinylic allenes **210** by different simple synthetic operations.

Next, we have studied the electron transfer reactions of piperazine and diketopiperazine donors with *p*-chloranil. The results are described in the next chapter.

2.3 Conclusions

We have developed convenient methods of synthesis of several cycloalkyl ring containing allenes in good to excellent yields using enamine and 1-alkynes under ZnI_2 catalysis. Also, we have developed methods for the synthesis of various allenols and vinylic allene derivatives under different reaction conditions. The methods described here have potential for further applications in organic synthesis.

2.4.1 General Information

^{1}H-NMR (400 & 500 MHz), ^{13}C-NMR (100 & 125 MHz) spectra were recorded on Bruker-Avance-400 and 500 spectrometers, respectively with chloroform-d as solvent and TMS as reference (δ = 0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Liquid Chromatography (LC) and mass analysis (LC-MS) were performed on SHIMADZU-LCMS-2010A. The mass spectral analyses were carried out using Chemical Ionization (CI) or Electro Spray Ionization (ESI) techniques. Elemental analyses were carried out using a Perkin-Elmer elemental analyzer model-240C and Thermo Finnegan analyzer series Flash EA 1112. Mass spectral analyses for some of the compounds were carried out on VG 7070H mass spectrometer using EI technique at 70 eV.

Analytical thin layer chromatographic tests were carried out on glass plates (3 x 10 cm) coated with 250mμ acme's silica gel-G and GF_{254} containing 13% calcium sulfate as binder. The spots were visualized by short exposure to iodine vapor or UV light. Column chromatography was carried out using SRL India silica gel (100-200). All the glassware were pre-dried at 120 °C in an air-oven for 4 h, assembled in hot condition and cooled under a stream of dry nitrogen. Unless otherwise mentioned, all the operations and transfer of reagents were carried out using standard syringe-septum technique recommended for handling air sensitive reagents.

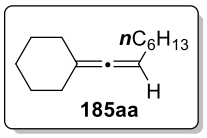
In all experiments, a round bottom flask of appropriate size with magnetic stirring bar, a condenser and a connecting tube attached to a mercury bubbler were used. The outlet of the mercury bubbler was connected to the atmosphere by a long tube. All dry

solvents and reagents (liquids) used were distilled from appropriate drying agents. As a routine practice, all organic extracts were washed with saturated sodium chloride solution (brine) and dried over anhydrous $MgSO_4$ or Na_2SO_4 or K_2CO_3 and concentrated on Heidolph-EL-rotary evaporator. All yields reported are of isolated materials judged homogeneous by TLC, IR and NMR spectroscopy.

General procedure for the synthesis of cycloalkyl ring containing allene derivatives

A flame–dried sleng tube was cooled under N_2, charged with ZnI_2 (0.6 mmol) in toluene (3 mL) and enamine (1 mmol), 1-alkyne (1.1 mmol) were added at 25 °C. The contents were refluxed at 120 °C for 4 h. The mixture was brought to 25 °C, toluene was evaporated under reduced pressure and the residue was chromatographed on silica gel (100-200 mesh) using hexane as eluent to isolate allene.

Oct-1-en-1-ylidenecyclohexane



185aa

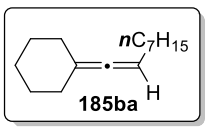
Yield **:** 0.165 g (79%), Colorless liquid

IR (neat) **:** 2915, 2843, 1939, 1589, 1501, 1041 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 4.99-4.95 (m, 1H), 2.12-2.11 (m, 4H), 1.97(q, *J* = 6.7 Hz, 2H), 1.64-1.51 (m, 6H), 1.42-1.37 (m, 2H), 1.36-1.29 (m, 6H), 0.93-0.89 (m, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.2, 102.2, 88.7, 31.8, 31.7, 29.3, 29.1, 28.6, 27.5, 26.2, 22.7, 14.1.

Non-1-en-1-ylidenecyclohexane



185ba

Yield **:** 0.177 g (86%), Colorless liquid

IR (neat) **:** 2926, 2854, 1950, 1600, 1512, 1052 cm^{-1}.

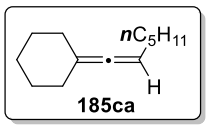
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 4.95-4.99 (m, 1H), 2.13-2.09 (m, 4H),1.97 (q, *J* = 6 Hz, 2H), 1.62-1.58 (m, 4H), 1.56-1.52 (m, 2H), 1.41-1.39 (m, 2H), 1.35-1.31 (m, 8H), 0.91 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.2, 102.3, 88.7, 31.9, 31.8, 29.3, 29.2, 29.1, 28.9, 27.5, 26.2, 22.7, 14.1.

HRMS : (ESI): calcd for $C_{15}H_{26}$: 207.2113 m/z $[M+H]^+$; found 207.2111.

Hept-1-en-1-ylidenecyclohexane

Yield **:** 0.137 g (77%), Colorless liquid



185ca

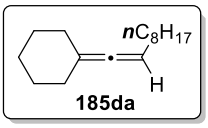
IR (neat) **:** 2929, 2857, 1953, 1603, 1515, 1055 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 4.99-4.96 (m, 1H), 2.13-2.11 (m, 4H), 1.97(q, *J* = 6.7 Hz, 2H), 1.63-1.53 (m, 5H), 1.48-1.37 (m, 2H), 1.35-1.29 (m, 4H), 0.93-0.90 (m, 4H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.2, 102.2, 88.7, 31.8, 31.2, 29.2, 28.8, 27.5, 26.2, 22.5, 14.1.

Dec-1-en-1-ylidenecyclohexane

Yield **:** 0.187 g (85%), Colorless liquid



185da

IR (neat) **:** 2933, 2862, 1957, 1606, 1519, 1058 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 4.99-4.95 (m, 1H), 2.13-2.10 (m, 4H), 1.98(q, *J* = 6.7 Hz, 2H), 1.65-1.52 (m, 6H), 1.43-1.38 (m, 2H), 1.34-1.31 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H).

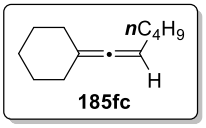
^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.2, 102.2, 88.6, 31.9, 31.8, 29.5, 29.4, 29.3, 29.1, 29.0, 27.5, 26.2, 22.7, 14.1.

Hex-1-en-1-ylidenecyclohexane

Yield **:** 0.116 g (71%), Colorless liquid

IR (neat) **:** 2936, 2844, 1940, 1610, 1512, 1052, 774 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 4.98-4.96 (m, 1H), 2.16-2.10 (m, 4H), 2.01-1.96 (m, 2H), 1.64-1.51 (m, 6H), 1.42-1.34 (m, 4H), 0.94-0.91 (m, 3H).

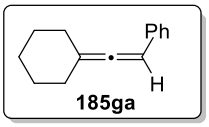


185fc

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.2, 102.6, 88.6, 31.8, 31.3, 29.0, 27.5, 26.2, 22.0, 13.9.

(2-cyclohexyldenevinyl)benzene

Yield **:** 0.154 g (84%), Colorless liquid



185ga

IR (neat) **:** 2924, 2852, 1948, 1598, 1510, 1050 cm^{-1}.

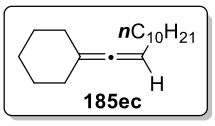
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 7.34-7.32 (m, 4H), 7.23-7.20 (m, 1H), 6.05-6.05(m, 1H), 2.40-2.29 (m, 2H), 2.27-2.21 (m, 2H), 1.77-1.60 (m, 6H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 199.7, 136.2, 128.5, 126.5, 126.3, 106.5, 92.4, 31.3, 27.7, 26.2.

HRMS : (ESI): calcd for $C_{14}H_{16}$: 185.1330 m/z $[M+H]^+$; found 185.1329.

Dodec-1-en-1-ylidenecyclohexane

Yield **:** 0.195 g (79%), Colorless liquid



185ec

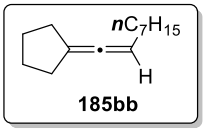
IR (neat) **:** 2850, 1949, 1585, 1505, 1441, 1350, 1146, 1042 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64-5.63 (m, 1H), 2.16-2.15 (m, 2H), 2.09-2.08 (m, 4H), 1.52-1.51 (m, 6H), 1.33-1.32 (m, 2H), 1.30-1.29 (m, 6H), 1.26-1.25 (m, 8H), 0.88-0.87 (m, 3H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 101.4, 87.9, 31.9, 31.8, 30.8, 29.6, 29.3, 29.1, 25.8, 25.2, 24.5, 22.7, 19.7, 14.1.

Non-1-en-1-ylidenecyclopentane

Yield **:** 0.146 g (76%), Colorless liquid



185bb

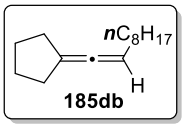
IR (neat) **:** 2920, 2754, 1959, 1609, 1517, 1054 784 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.10-5.04 (m, 1H), 2.36-2.33 (m, 4H), 1.97 (q, *J* = 6.9 Hz, 2H), 1.69-1.66 (m, 4H), 1.39-1.29 (m, 10H), 0.92-0.88 (m, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 196.9, 103.4, 91.4, 31.9, 31.2, 29.4, 29.2, 29.1, 29.0, 27.1, 22.7, 14.1.

Dec-1-en-1-ylidenecyclopentane

Yield **:** 0.169 g (82%), Colorless liquid



185db

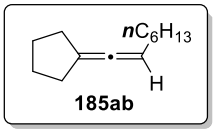
IR (neat) **:** 2946, 2751, 1941, 1615, 1517, 1050 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.10-5.05 (m, 1H), 2.36-2.33 (m, 4H), 1.98 (q, *J* = 6.9 Hz, 2H), 1.70-1.66 (m, 4H), 1.34-1.30 (m, 12H), 0.90-0.88 (m, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 197.0, 103.4, 91.4, 31.9, 31.2, 29.5, 29.4, 29.3, 29.2, 29.1, 27.0, 22.6, 14.1.

Oct-1-en-1-ylidenecyclopentane

Yield **:** 0.135 g (75%), Colorless liquid



185ab

IR (neat) **:** 2926, 2854, 1950, 1600, 1512, 1052 cm^{-1}.

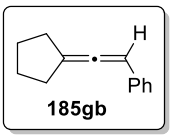
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.09-5.05 (m, 1H), 2.35-2.33 (m, 4H), 1.97 (q, *J* = 6.8 Hz, 2H), 1.69-1.66 (m, 4H), 1.39-1.27 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 197.0, 103.4, 91.4, 31.7, 31.2, 29.3, 29.1, 28.7, 27.1, 22.6, 14.1.

HRMS : (ESI): calcd for $C_{13}H_{22}$: 179.1800 m/z $[M+H]^+$; found 179.1801.

(2-cyclopentyldenevinyl)benzene

Yield **:** 0.117 g (69%), Colorless liquid



185gb

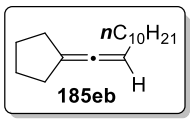
IR (neat) **:** 3035, 2921, 1949, 1587, 1510, 1446, 1050.cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 7.30-7.29 (m, 4H), 7.17-7.16 (m, 1H), 6.04-6.03 (m, 1H), 2.28-2.26, (m, 2H), 2.20-2.19 (m, 2H), 1.80-1.79 (m, 4H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.6, 135.9, 128.5, 126.4, 126.2, 105.4, 93.1, 31.5, 27.5.

HRMS : (ESI): calcd for $C_{13}H_{14}$: 171.1174 m/z $[M+H]^+$; found 171.1174.

Dodec-1-en-1-ylidenecyclopentane



185eb

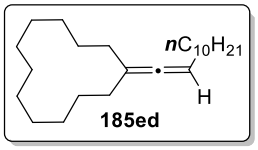
Yield **:** 0.170 g (73%), Colorless liquid

IR (neat) **:** 2927, 2847, 1949, 1591, 1501, 1435, 1345, 1130, 1039 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.63-5.61 (m, 1H), 2.26-2.25 (m, 4H), 2.17-2.16 (m, 2H), 1.66-1.65 (m, 4H), 1.34-1.33 (m, 2H), 1.31-1.30 (m, 6H), 1.27-1.26 (m, 8H), 0.88-0.87 (m, 3H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 101.3, 87.9, 37.7, 31.9, 30.8, 29.7, 29.6, 29.3, 29.1, 25.8, 22.5, 22.7, 14.1.

Dodec-1-en-1-ylidenecyclododecane



185ed

Yield **:** 0.245 g (74%), Colorless liquid

IR (neat) **:** 2932, 2860, 1956, 1606, 1518, 1059 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.04-4.99 (m, 1H), 2.02-1.98 (m, 6H), 1.50-1.47(m, 4H), 1.42-1.39 (m, 4H), 1.33-1.28 (m, 26H), 0.90 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 202.1, 100.7, 90.8, 31.9, 29.8, 29.7, 29.6, 29.5, 29.5, 29.3, 29.2, 24.6, 24.4, 24.1, 23.1, 22.7, 22.3, 14.1.

HRMS : (ESI): calcd for $C_{24}H_{44}$: 333.3521 m/z $[M+H]^+$; found 333.3522.

(2-Phenylvinylidene)cyclododecane

Yield **:** 0.187 g (70%), Colorless liquid

185gd

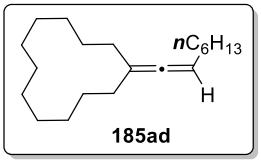
IR (neat) **:** 2918, 2846, 1942, 1592, 1504, 1438, 1351, 1136, 1043 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 7.60-7.59 (m, 2H), 7.39-7.38 (m, 2H), 7.33-7.32 (m, 1H), 6.31 (s, 1H), 1.94-1.93 (m, 4H), 1.31-1.30 (m, 4H), 1.25-1.24 (m, 14H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.8, 135.2, 127.9, 128.6, 128.5, 110.9, 92.1, 38.0, 25.8, 24.5, 24.4, 23.9.

Oct-1-en-1-ylidenecyclododecane

Yield **:** 0.160 g (58%), Colorless liquid



185ad

IR (neat) **:** 2921, 2841, 1585, 1507, 1436, 1349, 1136, 1039 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64-5.63 (m, 1H), 2.16-2.15 (m, 2H), 1.94-1.93 (m, 4H), 1.33-1.31 (m, 6H), 1.31-1.30 (m, 4H), 1.29-1.28 (m, 2H), 1.25-1.24 (m, 14H), 0.88-0.87 (m, 3H).

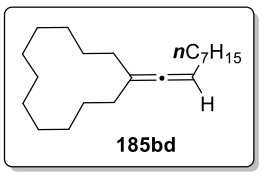
^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 107.1, 87.9, 38.0, 31.9, 30.8, 28.8, 25.8, 24.5, 24.4, 23.9, 22.7, 14.1.

Non-1-en-1-ylidenecyclododeceane

Yield **:** 0.174 g (60%), Colorless liquid

IR (neat) **:** 2919, 2847, 1944, 1594, 1504, 1438, 1347, 1134, 1050 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64-5.63 (m, 1H), 2.16-2.15 (m, 2H), 1.94-1.93 (m, 4H), 1.33-1.32 (m, 2H), 1.31-1.30 (m, 4H), 1.29-1.28 (m, 2H), 1.26-1.25 (m, 6H), 1.25-1.24 (m, 14H), 0.88-0.87 (m, 3H).



185bd

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 107.1, 87.9, 38.0, 31.8, 29.4, 29.1, 25.8, 24.5, 24.4, 23.9, 22.7, 14.1.

HRMS : (ESI): calcd for $C_{21}H_{38}$: 291.3052 m/z $[M+H]^+$; found 291.3051.

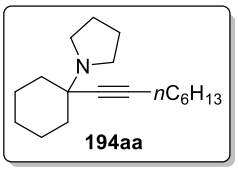
General procedure for the preparation of propargyl amine derivatives

To a reaction flask cooled under N_2, was added $CuBr_2$ (5 mol%), enamine, 1-alkyne (1.1 mmol) in dioxane (3 mL) for 12 h at room temperature. Then the reaction mixture was brought to room temperature. After removal of the solvent, the residue was subjected to chromatography on silica gel (100-200 mesh) using 20-30% ethyl acetate in hexane to elute the propargyl amine derivatives.

1-(1-(Oct-1-yn-1-yl)cyclohexyl)pyrrolidine

Yield **:** 0.237 g (91%), light brown liquid

IR (neat) **:** 3068, 3036, 2950, 2879, 1603, 1515, 1389, 1367, 1126, 1082, 1055, 748 cm^{-1}.

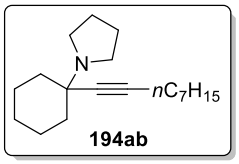


194aa

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 2.71-2.68 (m, 4H), 2.22 (t, *J* = 6.8 Hz, 2H), 1.89-1.86 (m, 2H), 1.76-1.74 (m, 4H), 1.63-1.56 (m, 6H), 1.53-1.46 (m, 2H), 1.44-1.38 (m, 4H), 1.32-1.27 (m, 2H), 0.91-0.87 (m, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 85.7, 80.1, 58.8, 46.8, 38.1, 31.3, 29.3, 28.4, 25.7, 23.4, 23.0, 22.6, 18.6, 13.9.

1-(1-(Non-1-yn-1-yl)cyclohexyl)pyrrolidine



194ab

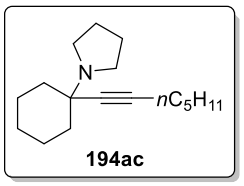
Yield **:** 0.225 g (82%), light brown liquid

IR (neat) **:** 3065, 3035, 2947, 2876, 1600, 1512, 1386, 1364, 1123, 1079, 1052, 745 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 2.72-2.69 (m, 4H), 2.22 (t, *J* = 6.8 Hz, 2H), 1.91-1.87 (m, 2H), 1.78-1.75 (m, 4H), 1.65-1.39 (m, 12H), 1.34-1.26 (m, 6H), 0.91-0.87 (m, 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 85.8, 80.1, 58.8, 46.8, 38.1, 31.8, 29.3, 28.7, 28.7, 25.7, 23.4, 23.0, 22.6, 18.6, 14.1.

1-(1-(Hept-1-yn-1-yl)cyclohexyl)pyrrolidine



194ac

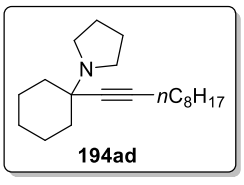
Yield **:** 0.212 g (86%), light brown liquid

IR (neat) **:** 3064, 3031, 2946, 2875, 1601, 1510, 1384, 1362, 1121, 1068, 1049, 740 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 2.73-2.69 (m, 4H), 2.23 (t, *J* = 6.9 Hz, 2H), 1.91-1.88 (m, 2H), 1.78-1.75 (m, 4H), 1.65-1.55 (m, 4H), 1.53-1.48 (m, 2H), 1.45-1.30 (m, 8H), 0.91 (t, *J* = 7.0 Hz 3H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 85.8, 80.0, 58.8, 46.8, 38.1, 31.0, 29.0, 25.7, 23.4, 23.0, 22.1, 18.5, 14.0.

1-(1-(Dec-1-yn-1-yl)cyclohexyl)pyrrolidine



194ad

Yield **:** 0.268 g (93%), light brown liquid

IR (neat) **:** 3055, 3025, 2937, 2866, 1590, 1502, 1376, 1354, 1103, 1069, 1052, 735 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 2.71-2.67 (m, 4H), 2.23-2.19 (m, 2H), 1.89-1.86 (m, 2H), 1.76-1.73 (m, 4H), 1.60-1.59 (m, 4H), 1.53-1.45 (m, 2H), 1.44-1.37 (m, 4H), 1.27 (s, 10H), 0.89-0.86 (m, 3H).

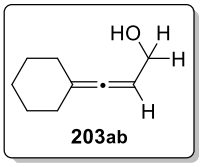
^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 85.7, 80.1, 58.1, 46.7, 38.1, 31.7, 29.3, 29.2, 29.0, 28.7, 25.7, 23.4, 23.0, 22.6, 18.5, 14.0.

General procedure for the synthesis of allenol derivatives

A flame–dried sleng tube was cooled under N_2, charged with ZnI_2 (0.6 mmol) in toluene (3 mL) and enamine (1 mmol), 1-alkynol (1.1 mmol) were added at 25 °C. The contents were refluxed at 110 °C for 3 h. The mixture was brought to 25 °C, toluene was evaporated under reduced pressure and the residue was chromatographed on silica gel (100-200 mesh) using hexane as eluent to isolate allene.

3-Cyclohexylideneprop-2-en-1-ol

Yield **:** 0.070 g (51%), Colorless liquid



203ab

IR (neat) **:** 3312, 2926, 2854, 1600, 1512, 1446, 1359, 1144, 1052 cm^{-1}.

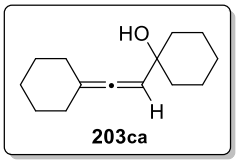
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.22-5.19 (m, 1H), 4.08 (d, *J* = 5.7 Hz, 2H), 2.15-2.12(m, 4H), 1.7 (s, 1H), 1.63-1.57 (m, 4H), 1.55-1.51 (m, 2H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 197.2, 105.7, 89.7, 61.1, 31.5, 27.4, 26.0.

HRMS : (ESI): calcd for $C_9H_{14}O$: 139.1123 m/z $[M+H]^+$; found 139.1122.

1-(2-Cyclohexyldenevinyl)cyclohexan-1-ol

Yield **:** 0.160 g (78%), Colorless liquid



203ca

IR (neat) **:** 3317, 2929, 2857, 1953, 1603, 1515, 1449, 1362, 1147 cm^{-1}.

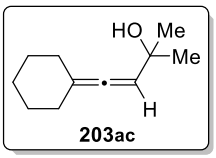
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.13-5.12 (m, 1H), 2.20-2.10 (m, 4H), 1.64-1.54 (m, 13H), 1.52-1.38 (m, 4H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 195.9, 106.3, 98.0, 71.0, 38.5, 31.6, 27.5, 26.1, 25.6, 22.8.

4-Cyclohexylidene-2-methylbut-3-en-2-ol

Yield **:** 0.109 g (66%), Colorless liquid

IR (neat) **:** 3317, 2932, 2859, 1955, 1605, 1517, 1451, 1364, 1149, 1057 cm^{-1}.



203ac

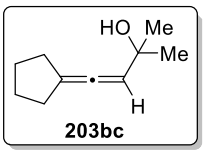
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.19-5.18 (m, 1H), 2.16-2.11 (m, 4H), 1.82 (s, 1H), 1.65-1.51 (m, 6H), 1.33 (s, 6H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 194.6, 106.7, 99.2, 69.8, 31.6, 29.9, 27.5, 26.1.

4-Cyclopentylidene-2-methylbut-3-en-2-ol

Yield **:** 0.107 g (71%), Colorless liquid

IR (neat) **:** 3314, 2928, 2854, 1951, 1600, 1513, 1446, 1360, 1052 cm^{-1}.



203bc

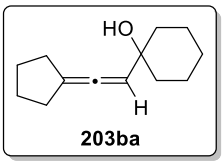
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.30-5.27 (m, 1H), 2.41-2.37 (m, 4H), 1.74 (s, 1H), 1.71-1.69 (m, 4H), 1.34 (s, 6H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 193.3, 108.0, 101.8, 70.1, 31.4, 30.0, 27.1.

1-(2-Cyclopentylidenevinyl)cyclohexan-1-ol

Yield **:** 0.117 g (61%), Colorless liquid

IR (neat) **:** 3322, 2937, 2865, 1961, 1611, 1523, 1360, 1155, 1063 cm^{-1}.

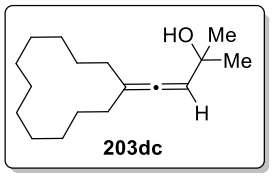


203ba

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.23-5.20 (m, 1H), 2.40-2.36 (m, 4H), 1.70-1.64 (m, 7H), 1.62-1.57 (m, 4H), 1.48-1.42 (m, 4H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 194.6, 107.5, 100.7, 71.3, 38.5, 31.3, 27.0, 25.6, 22.7.

4-Cyclododecylidene-2-methylbut-3-en-2-ol



203dc

Yield **:** 0.172 g (69%), Colorless liquid

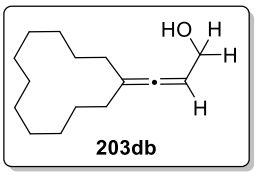
IR (neat) **:** 3307, 2921, 2849, 1945, 1595, 1507, 1354, 1139, 1047 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 5.31-5.30 (m, 1H), 2.06-2.03 (m, 4H), 1.83(s, 1H), 1.50-1.48 (m, 4H), 1.34-1.32 (m, 20H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 198.1, 106.0, 101.5, 70.1, 30.2, 29.7, 24.5, 24.2, 24.1, 23.3, 22.4.

HRMS : (ESI): calcd for $C_{17}H_{30}O$: 251.2375 m/z $[M+H]^+$; found 251.2374.

3-cyclododecylideneprop-2-en-1-ol



203db

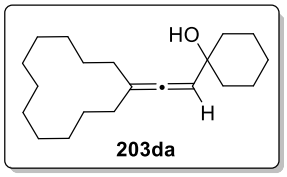
Yield **:** 0.104 g (47%), Colorless liquid

IR (neat) **:** 3336, 2926, 2855, 1950, 1600, 1513, 1447, 1359, 1052 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64-5.63 (m, 1H), 5.05-5.04 (m, 1H), 4.18-4.17 (m, 2H), 1.94-1.93 (m, 4H), 1.31-1.30 (m, 4H), 1.25-1.24 (m, 14H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 198.3, 110.0, 89.9, 60.0, 38.0, 24.5, 24.4, 25.8, 23.9.

1-(2-cyclododecylidenevinyl)cyclohexan-1-ol



203da

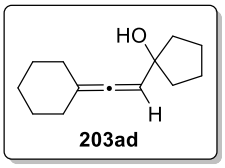
Yield **:** 0.194 g (67%), Colorless liquid

IR (neat) **:** 3339, 2928, 2856, 1952, 1602, 1512, 1447, 1146, 1054 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64 (s, 1H), 4.77 (s, 1H), 1.94-1.93 (m, 4H), 1.47-1.46 (m, 6H), 1.43-1.42 (m, 4H), 1.31-1.30 (m, 4H), 1.25-1.24 (m, 14H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 107.1, 89.8, 70.5, 38.0, 35.0, 25.8, 24.5, 24.4, 23.9, 22.0, 20.9.

1-(2-cyclohexylidenevinyl)cyclopentan-1-ol



203ad

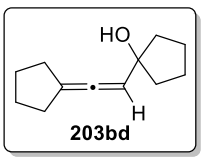
Yield **:** 0.138 g (72%), Colorless liquid

IR (neat) **:** 3334, 2847, 1943, 1593, 1504, 1438, 1351, 1136, 1043 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64 (s, 1H), 4.77 (s, 1H), 2.09-2.08 (m, 4H), 1.73-1.72 (m , 4H), 1.53-1.52 (m, 4H), 1.52-1.51 (m, 6H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 101.4, 89.9, 76.0, 39.1, 31.8, 25.2, 24.525.1.

1-(2-cyclopentylidenevinyl)cyclopentan-1-ol



203bd

Yield **:** 0.098 g (55%), Colorless liquid

IR (neat) **:** 3307, 2921, 2849, 1945, 1595, 1507, 1354, 1139, 1047 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64 (s, 1H), 4.77 (s, 1H), 2.25-2.24 (m, 4H), 1.65-1.64 (m, 4H), 1.73-1.72 (m , 4H), 1.53-1.52 (m, 4H).

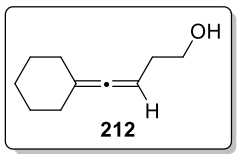
^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 101.3, 89.9, 76.0, 39.1, 37.7, 25.1, 22.5.

HRMS : (ESI): calcd for $C_{12}H_{18}O$: 179.1436 m/z $[M+H]^+$; found 179.1435.

4-Cyclohexylidenebut-3-en-1-ol

Yield **:** 0.101 g (67%), Colorless liquid

IR (neat) **:** 3336, 2921, 2850, 1969, 1704, 1439, 1268, 1241, 1172, 1128, 1045 cm^{-1}.



212

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 4.99-4.98 (m, 1 H), 3.61-3.60 (m, 2 H), 2.22-2.21 (m, 2 H), 1.97-1.96 (m, 4 H), 1.75-1.74 (m, 7 H).

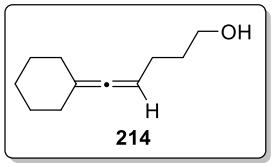
^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 198.0, 102.2, 85.1, 62.2, 32.3, 31.4, 26.9, 25.9.

HRMS : (ESI): calcd for $C_{10}H_{16}O$: 153.1279 m/z $[M+H]^+$; found 153.1278.

5-Cyclohexylidenepent-4-en-1-ol

Yield **:** 0.119 g (72%), Colorless liquid

IR (neat) **:** 3331, 2919, 2855, 1939, 1590, 1500, 1435, 1135, 1041 cm^{-1}.



214

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 5.64-5.63 (m, 1H), 4.38 (brs, 1H), 3.49-3.48 (m, 2H), 2.16-2.15 (m, 2H), 2.09-2.08 (m, 4H), 1.62-1.61 (m, 2H), 1.52-1.51 (m, 6H).

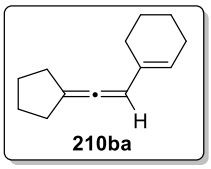
HRMS : (ESI): calcd for $C_{11}H_{18}O$: 167.1436 m/z $[M+H]^+$; found 167.1435.

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 199.9, 101.4, 88.8, 62.3, 31.8, 27.7, 26.8, 25.2, 24.5.

General procedure for the synthesis of vinylic allenes

A flame–dried sleng tube was cooled under N_2, charged with ZnI_2 (0.7 mmol) in toluene (3 mL) and enamine (1 mmol), 1-alkynol (1 mmol) were added at 25 °C. The contents were refluxed at 120 °C for 3 h. The mixture was brought to 25 °C, toluene was evaporated under reduced pressure and the residue was chromatographed on silica gel (100-200 mesh) using hexane as eluent to isolate vinylic allene.

1-(2-Cyclopentylidenevinyl)cyclohex-1-ene



Yield **:** 0.093 g (54%), Colorless liquid

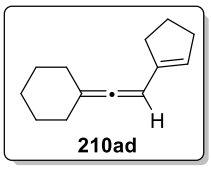
IR (neat) **:** 2925, 2842, 1594, 1453, 1382, 1168 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 6.20 (s, 1H), 5.53-5.2 (m, 1H), 2.25-2.24 (m, 4H), 2.33-2.32 (m, 2H), 1.99-1.98 (m, 2H), 1.74-1.73 (m, 2H), 1.65-1.64 (m, 4H), 1.61-1.60 (m, 2H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.6, 148.0, 136.4, 102.8, 99.4, 37.8, 25.5, 22.8, 22.5, 21.8, 21.0.

HRMS : (ESI): calcd for $C_{13}H_{18}$: 175.1487 m/z $[M+H]^+$; found 175.1488.

(2-(Cyclopent-1-en-1-yl)vinylidene)cyclohexane



Yield **:** 0.101 g (58%), Colorless liquid

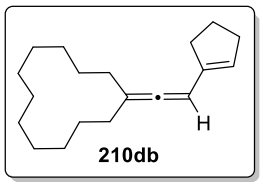
IR (neat) **:** 2924, 2849, 1948, 1595, 1509, 1444, 1354, 1136, 1047 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 6.20 (s, 1H), 5.54-5.53 (m, 1H), 2.28-2.27 (m, 4H), 2.19-2.18 (m, 2H), 1.99-1.98 (m, 2H), 1.87-1.86 (m, 2H), 1.52-1.51 (m, 6H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.6, 141.9, 138.6, 104.1, 99.4, 33.0, 31.9, 27.7, 25.2, 24.5, 23.5.

(2-(Cyclopent-1-en-1-yl)vinylidene)cyclododecane

Yield **:** 0.165 g (64%), Colorless liquid



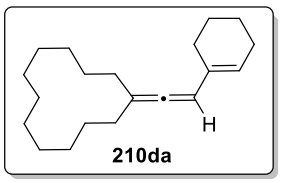
IR (neat) **:** 2921, 2850, 1945, 1591, 1507, 1440, 1354, 1141, 1050 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 6.20 (s, 1H), 5.54-5.53 (m, 1H), 2.31-2.30 (m, 2H), 2.28-2.27 (m, 2H), 1.94-1.93 (m, 4H), 1.87-1.86 (m, 2H), 1.25-1.24 (m, 14H), 1.31-1.30 (m, 4H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.6, 141.9, 138.6, 108.6, 99.4, 38.1, 38.1, 33.0, 27.7, 25.8, 24.5, 24.4, 23.9, 23.5.

(2-(Cyclohex-1-en-1-yl)vinylidene)cyclododecane

Yield **:** 0.190 g (70%), Colorless liquid



IR (neat) **:** 2929, 2859, 1955, 1605, 1517, 1451, 1364, 1149, 1057 cm^{-1}.

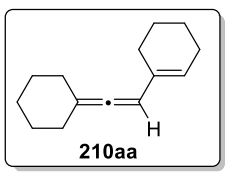
^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 6.20 (s, 1H), 5.53-5.52 (m, 1H), 2.33-2.32 (m, 2H), 1.99-1.98 (m, H), 1.94-1.93 (m, 4H), 1.74-1.73 (m, 2H), 1.61-1.60 (m, 2H), 1.31-1.30 (m, 4H), 1.25-1.24 (m, 14H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.6, 148.0, 136.4, 108.6, 99.4, 38.1, 25.8, 25.5, 24.5, 24.4, 23.9, 22.8, 21.8, 21.0.

HRMS : (ESI): calcd for $C_{20}H_{32}$: 273.2582 m/z $[M+H]^+$; found 273.2580.

1-(2-Cyclohexylidenevinyl)cyclohex-1-ene 209aa

Yield **:** 0.148 g (79%), Colorless liquid



IR (neat) **:** 2847, 1943, 1596, 1505, 1444, 1352, 1140, 1049 cm^{-1}.

^{1}H NMR **:** (400 MHz, $CDCl_3$, δppm): 6.20 (s, 1H), 5.53-5.52 (m, 1H), 2.33-2.32 (m, 2H), 2.19-2.18 (m, 2H), 1.99-1.98 (m, 4H), 1.74-1.73 (m, 2H), 1.61-1.60 (m, 2H), 1.52-1.51 (m, 6H).

^{13}C NMR **:** (100 MHz, $CDCl_3$, δppm): 201.6, 148.0, 136.4, 104.1, 99.4, 31.9, 25.5, 25.2, 24.5, 22.8, 21.8, 21.0.

HRMS : (ESI): calcd for $C_{14}H_{20}$: 189.1643 m/z $[M+H]^+$; found 189.1643.

2.5 References

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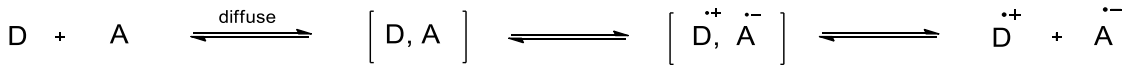
Chapter 3

Electron Transfer Reactions using Amine, Amide Donors and *p*-Chloranil Acceptor

3.1 Introduction

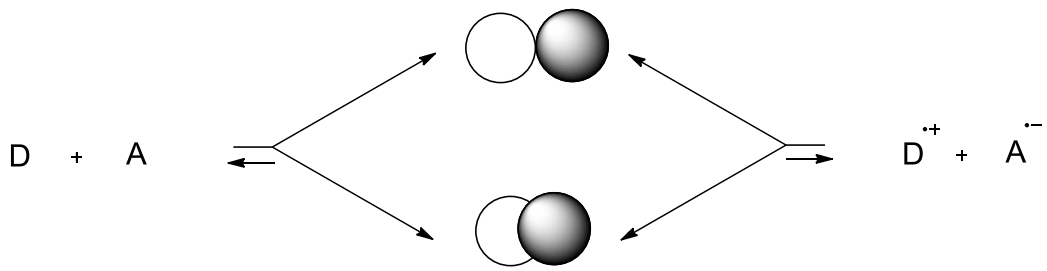
The Mulliken charge transfer (CT) complexes [D, A] are formed by diffusive interactions of electron donor (D) with electron acceptor (A).[1] In these complexes, two molecules, D and A, are held together by charge transfer interactions with the complex having properties different from the donor (D) and acceptor (A). The formation of ionic state ($D^{+\bullet}$, $A^{-\bullet}$) was not considered by Mulliken in those early days. Later, Bijl and co-workers reported[2] that the molecules with greater difference of electron affinity would have the ionic state at room temperature (Scheme 1).

Scheme 1



Taube developed two separate mechanistic pathways, outer-sphere (OS) and inner-sphere (IS) processes for explaining the electron transfer in octahedral metal complexes.[3] Also, Marcus studied the intermolecular electron transfer reactions in which activation energy was calculated by applying non-adiabatic or weakly adiabatic interaction between the molecules (Scheme 2).[4]

Scheme 2

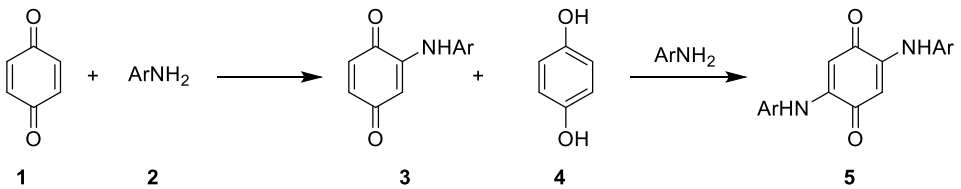


The outer-sphere complexes are expected to have loosely bound precursor and successor complexes.[5] Whreas the classical inner-sphere mechanism, electronic couplings between the donor/acceptor moieties are enhanced.[6] Kochi *et al*. [7,8] proposed an alternative model based on distance dependence based on the van der Waals radii of electron donors and acceptors. The molecular interactions in outer-sphere processes are viewed as between donor and acceptor separated beyond their van der Waals radii. Whereas in inner-sphere complexes the distance between donor and acceptor is likely to be less than their van der Waals radii and hence in these complexes the donor/acceptor are packed closely with enhanced interactions.[9] Therefore, sterically hindered donor/acceptor complexes are expected to form outer-sphere complexes, while less sterically hindered donor and acceptor complexes would prefer to form inner-sphere complexes.[10]

3.1.1 Electron transfer reaction of primary amines and quinone acceptors

Suida *et al.* reported[11] the preparation of addition products of 1,4-benzoquinone **1** using various substituted anilines **2** (Scheme 3).

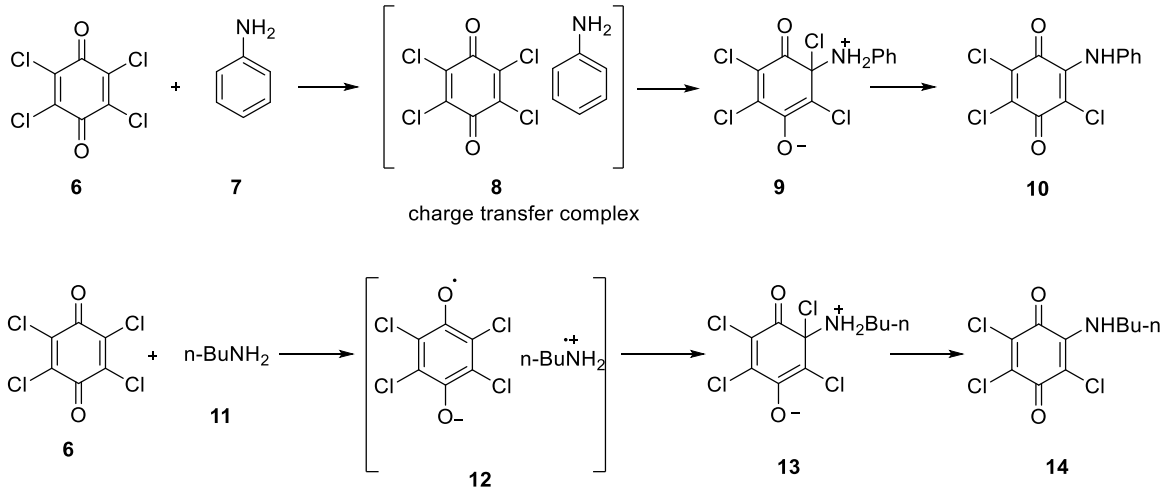
Scheme 3



In 1969, Nagakura *et al.* reported[12] that the reaction of *p*-chloranil **6** with aniline **7** gave the charge transfer (CT) complex **8**. Subsequently, the ionic diamagnetic intermediate **9** is formed before formation of the substituted product **10**. In 1971, Yamaoka *et al*. suggested[13a] that the reaction of *n*-butylamine **11** with chloranil **6** gave the

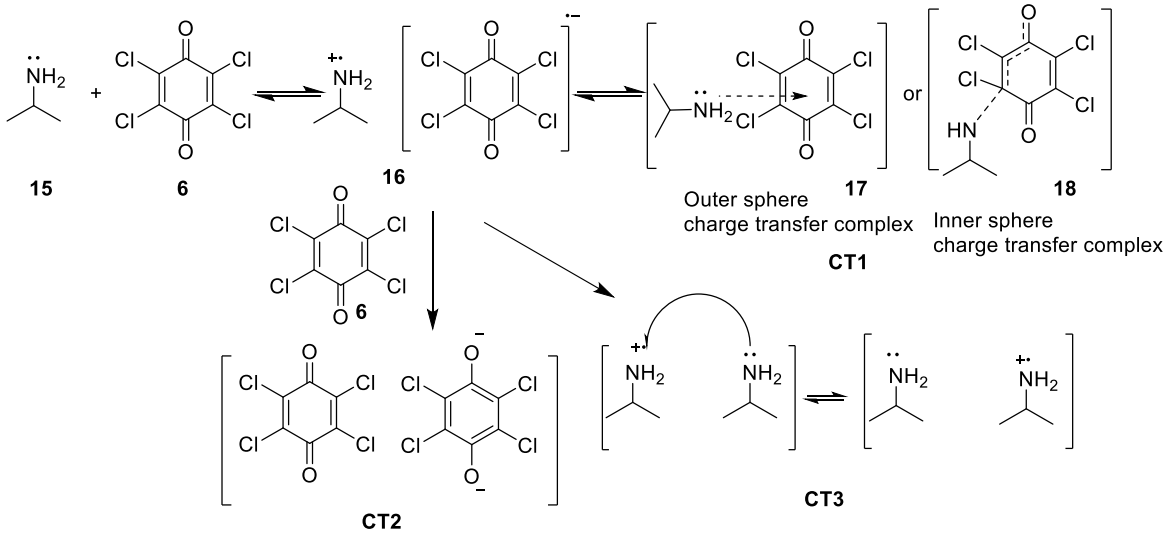
corresponding electron transfer complex **12**, which subsequently gave the intermediate **13** before the formation of the substitution product **14** (Scheme 4).

Scheme 4



Recently, the electron transfer reaction of isopropylamine **15** with p-chloranil **6** in DCM solvent was reported in this laboratory (Scheme 5).[13b]

Scheme 5

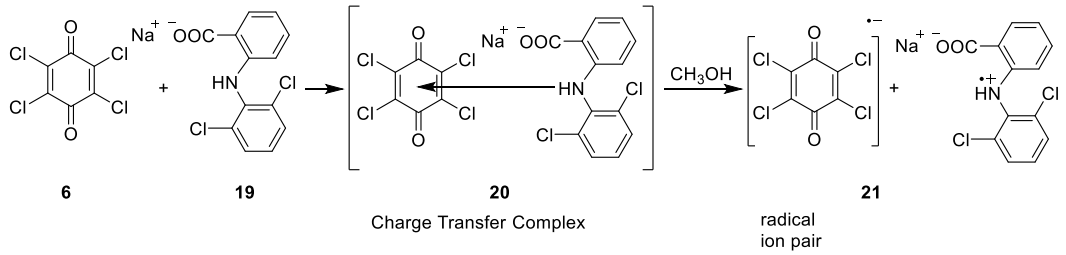


Paramagnetic species were detected in epr spectroscopy and the esr signal strength decreased with time and disappeared after 12 h. However, in this case, no substituted aminoquinone product was formed. Presumably, formation of charge transfer complex (CT1) with time leads to weak epr signal (Scheme 5).

3.1.2 Electron transfer reaction of secondary amines and quinone acceptors

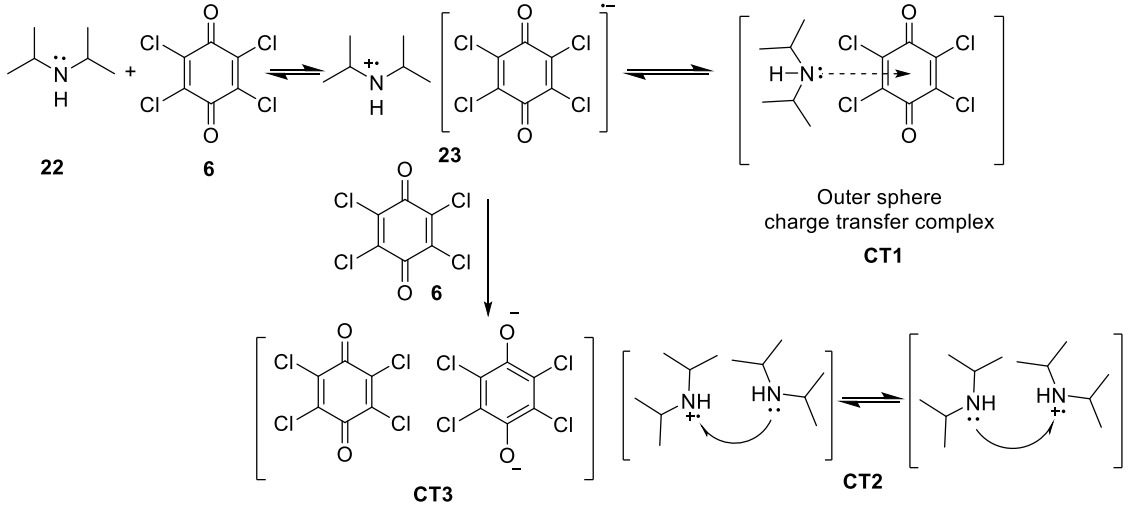
Pezza *et al*. reported[14] that the reaction between *p*-chloranil **6** and diclofenac **19** leads to the formation of the charge transfer complex **20** which is readily converted to electron transfer complex **21** (radical ion pair) in methanol solvent (Scheme 6).

Scheme 6



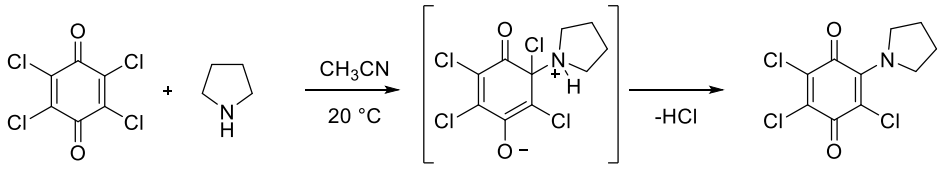
The electron transfer reaction of diisopropylamine **22** with *p*-chloranil **6** was reported in this laboratory. In this case also, no amino quinone product was obtained. The reaction may go through charge transfer coplex as shown in Scheme 7.[15]

Scheme 7



More recently, Mayr and co-workers reported[16] that the reaction of secondary amine **24** with *p*-chloranil **6** gave the product **26** *via* the corresponding diamagnetic ionic intermediate (Scheme 8). However, no epr studies were reported by these authors.

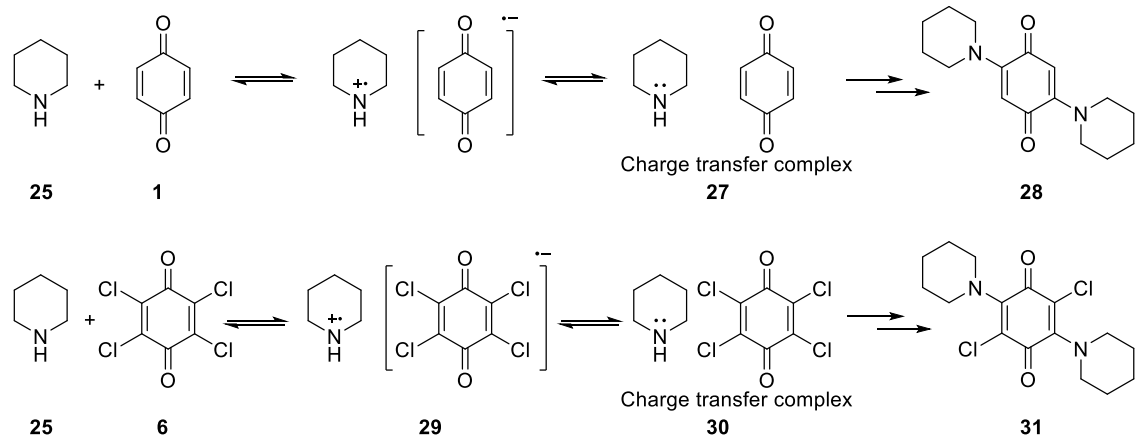
Scheme 8



6 **24** **26**

Previously, it was observed in this laboratory that the reaction of *p*-chloranil **6** and benzoquinone with secondary amine **25** in DCM or PC solvent gave esr signal indicating the formation of paramagnetic intermediates. The intensity of signal decreased with time and disappeared in 24 h with the formation of the aminoquinone products **28** and **31** (Scheme 9).[17,18]

Scheme 9

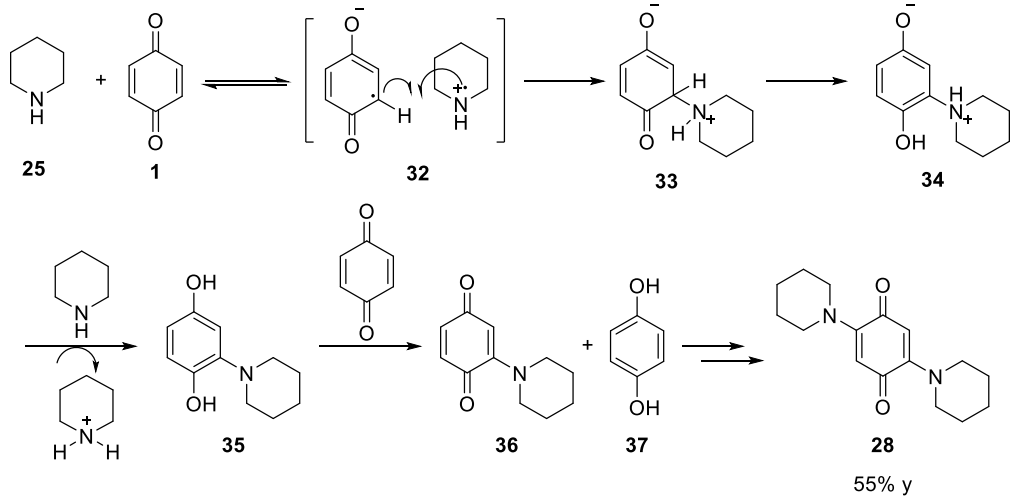


25 **1** **27** **28**

25 **6** **29** **30** **31**

A possible mechanism for the formation aminoquinone is outlined in Scheme 10.

Scheme 10

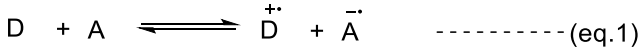


25 **1** **32** **33** **34**

35 **36** **37** **28**

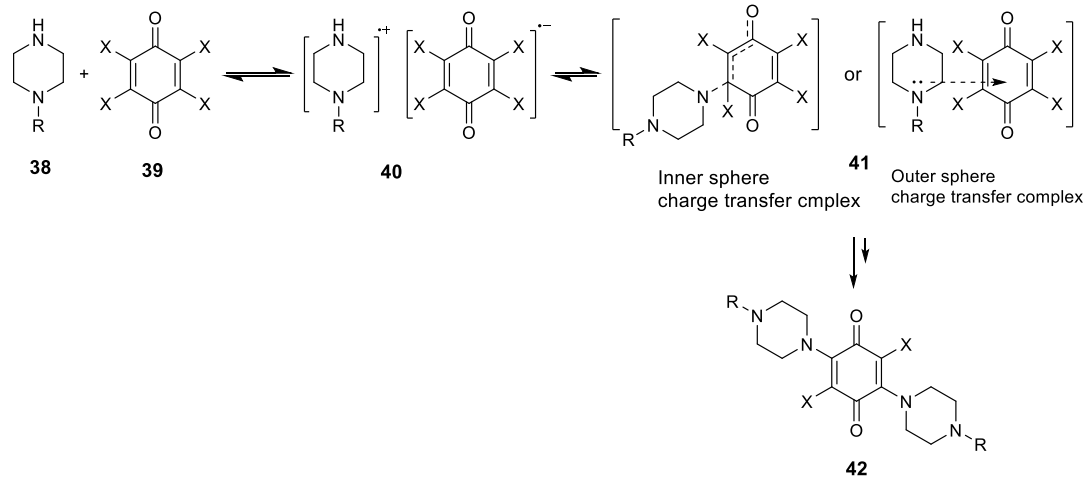
55% y

It was generally considered that initially an encounter complex would be formed before electron transfer takes place. However, the reaction could also take place through a cross exchange process, especially in polar solvents.[19]



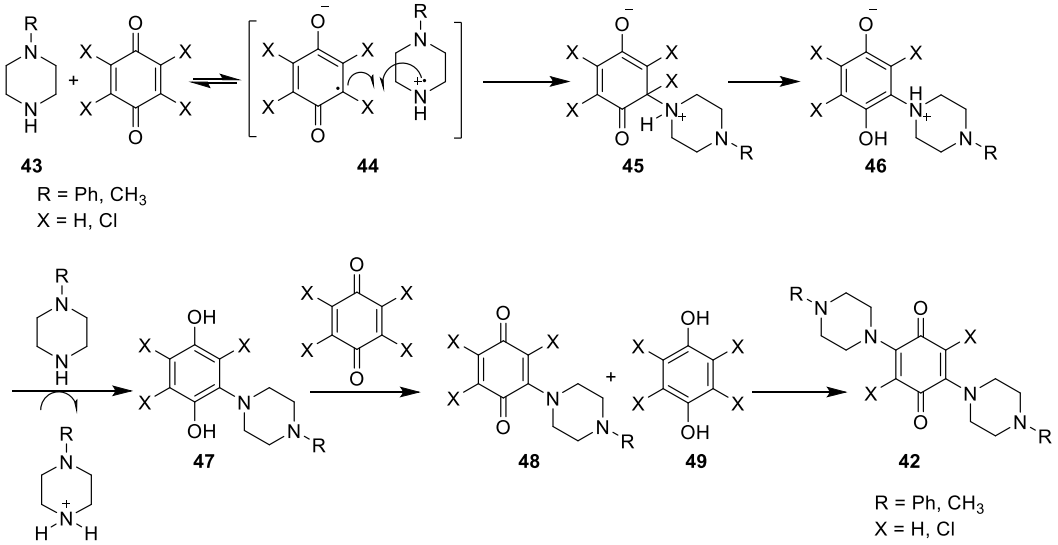
Also, the electron transfer reactions of secondary amine **38** with quinones were observed in this laboratory (Scheme 11).[20]

Scheme 11



The formation of aminoquinone products and epr results were explained by the mechanism outlined in Scheme 12.

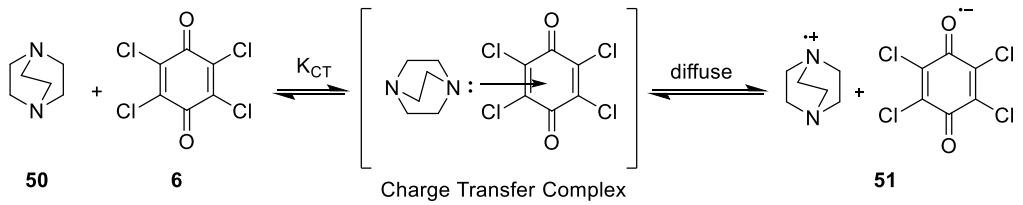
Scheme 12



3.1.3 Electron transfer reaction of tertiary amines and quinone acceptors

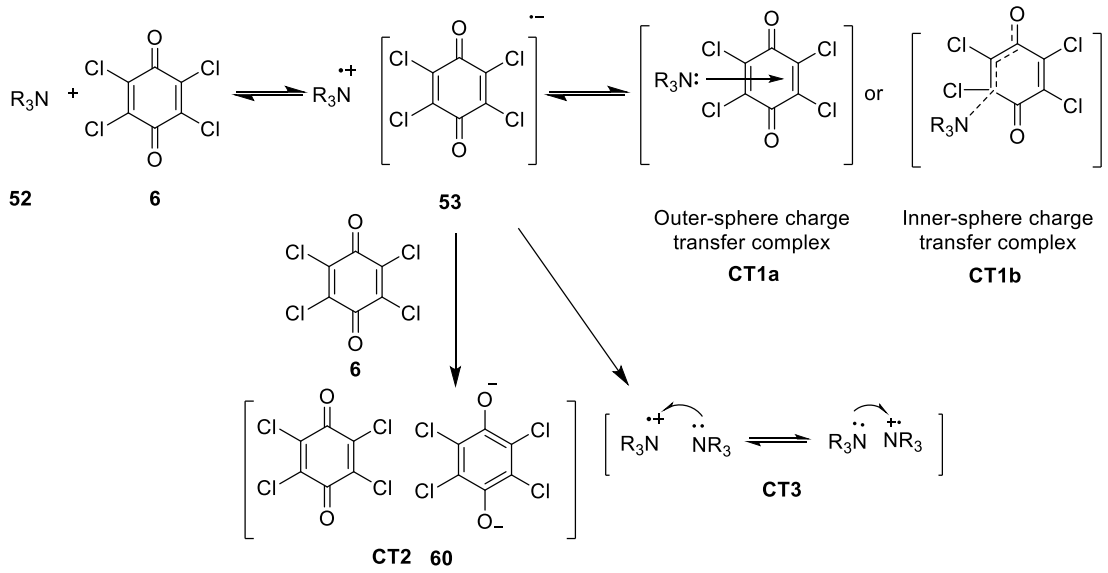
As early as in 1965, formation of stable radical cation of 1,4-diazabicyclo[2.2.2] octane (DABCO) **50** was reported.[21-24] In 1977, paramagnetic intermediates and charge transfer (CT) complexes were reported in the reaction of DABCO **50** with *p*-chloranil **6** (Scheme 13).[25]

Scheme 13



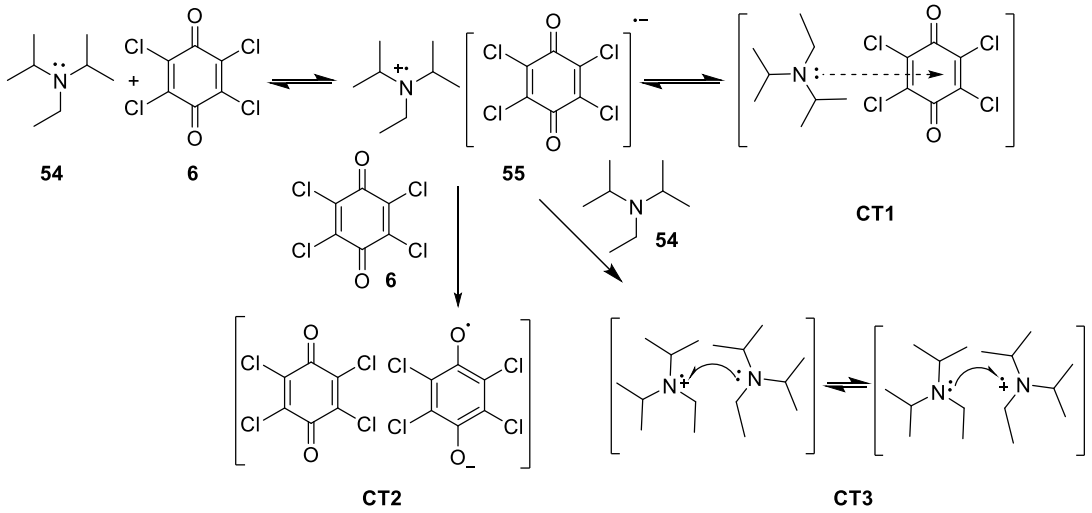
Earlier, it was observed in this laboratory that the tertiary amines **52** react with *p*-chloranil **6** to give the radical cations and radical anions with subsequent formation of diamagnetic CT complexes leading to decrease in the strength of epr signals (Scheme 14).[26]

Scheme 14



It was also observed in this laboratory that the tertiary amine **54** form charge transfer complexes with *p*-chloranil **6** in PC solvent. In this case, very strong esr signal was observed and intensity of the esr signal decreased with time (Scheme 15).[27]

Scheme 15



Similarly, several tertiary amines **56-60** gave esr signals after reaction with *p*-chloranil and the signal strength decreased with time (Figure 1).[28]

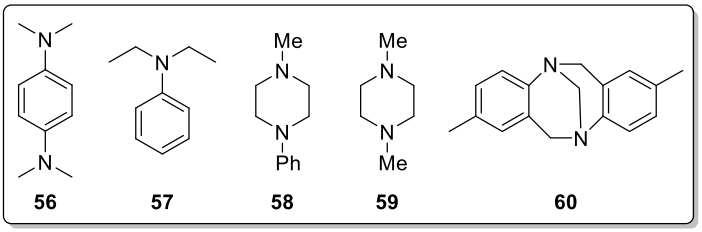


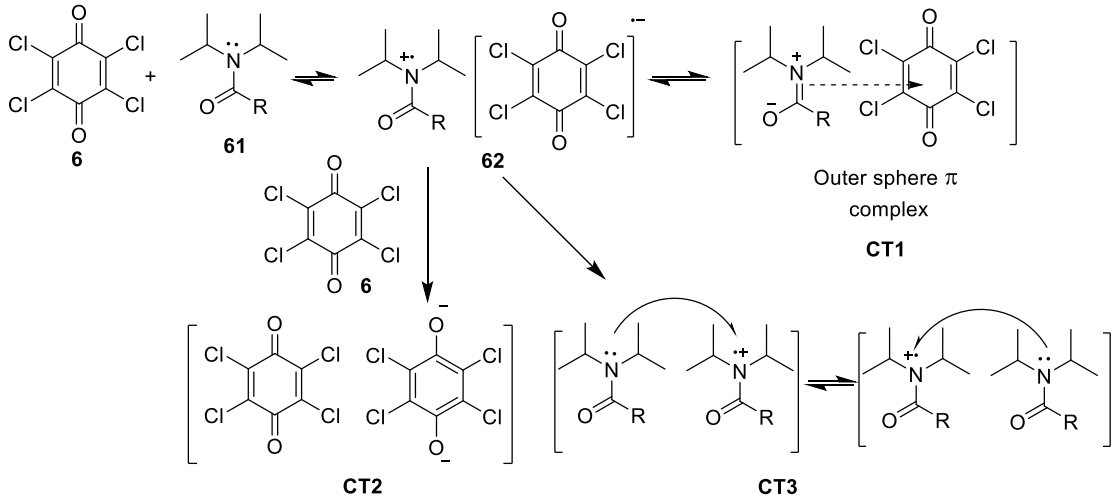
Figure 1

In the reactions of tertiary amines with quinones the signal strength of the epr signals decreased with time indicating the formation of covalent products or charge transfer complexes. Since, we did not obtain any organic product formation in these cases, the decrease in signal intensity may due to the formation of charge transfer complexes.

3.1.4 Electron transfer reaction of amides and quinone acceptors

The electron transfer reaction of amides with *p*-chloranil was also reported in this laboratory.[42] The paramagnetic intermediates were formed immediately after mixing but the epr signal disappeared after 1 h.

Scheme 16

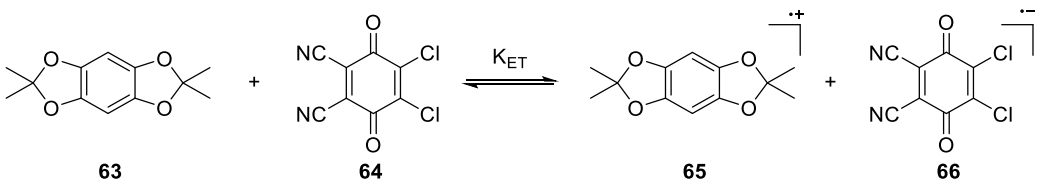


The formation of CT1 and CT2 complexes may also play a role in the decrease in the strength of epr signals with time (Scheme 16).[29]

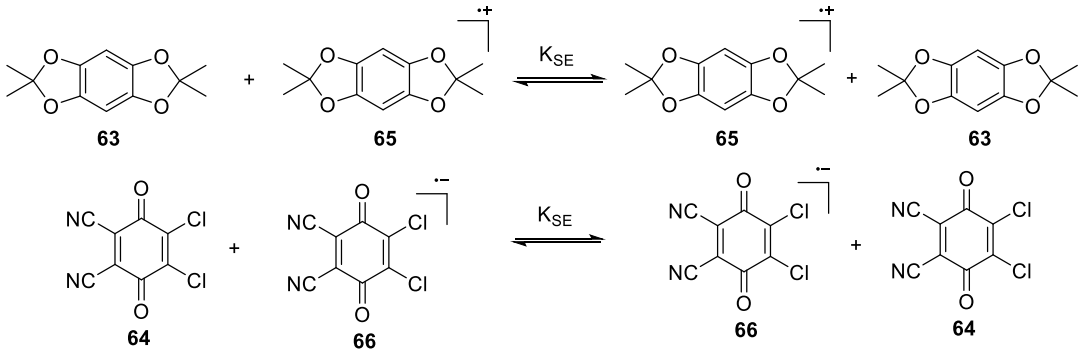
Previously, Kochi *et al* reported[30] self-exchange and cross exchange reactions between 2,2,6,6-tetramethylbenzo[1,2-d:4,5-d']bis[1,3]dioxole **63** (TMDO) donor with 2,3-dichloro-5,6-dicyano-p-benzoquinone **64** (DDQ) acceptor in DCM solvent (Scheme 17).

Scheme 17

(1) Cross exchange electron transfer process



(2) Self-exchange electron transfer process



The results obtained in this laboratory indicate that such reactions also take place upon mixing tertiary amines with *p*-chloranil.[31]

Electron transfer processes involving oxidative-reductive type reactions are of great importance and interest for several years. Also, a wide range of applications in organic synthesis and several biological processes such as photosynthesis reactions, oxygen transfer reactions in living cells involve electron transfer processes.[32] We have undertaken efforts toward the construction of electricity harvesting cells using organic molecules, based on ground state electron transfer reactions. In this regard, a brief review of literature reports on various types of organic solar cells would facilitate the discussion.

3.1.5 Organic solar cells

In organic solar cells excitation of photochemically active organic materials generates positive charge on p-type donor layer and creates negative charge on n-type acceptor layer. The photo excitation of organic material, produce coupled electron-hole pair called exciton. The exciton splits into charge carriers (separated electron-hole pair) which move to the electrodes to produce electricity. Some polymer electron donors and acceptors used in the organic solar cells are shown in Figure 2.

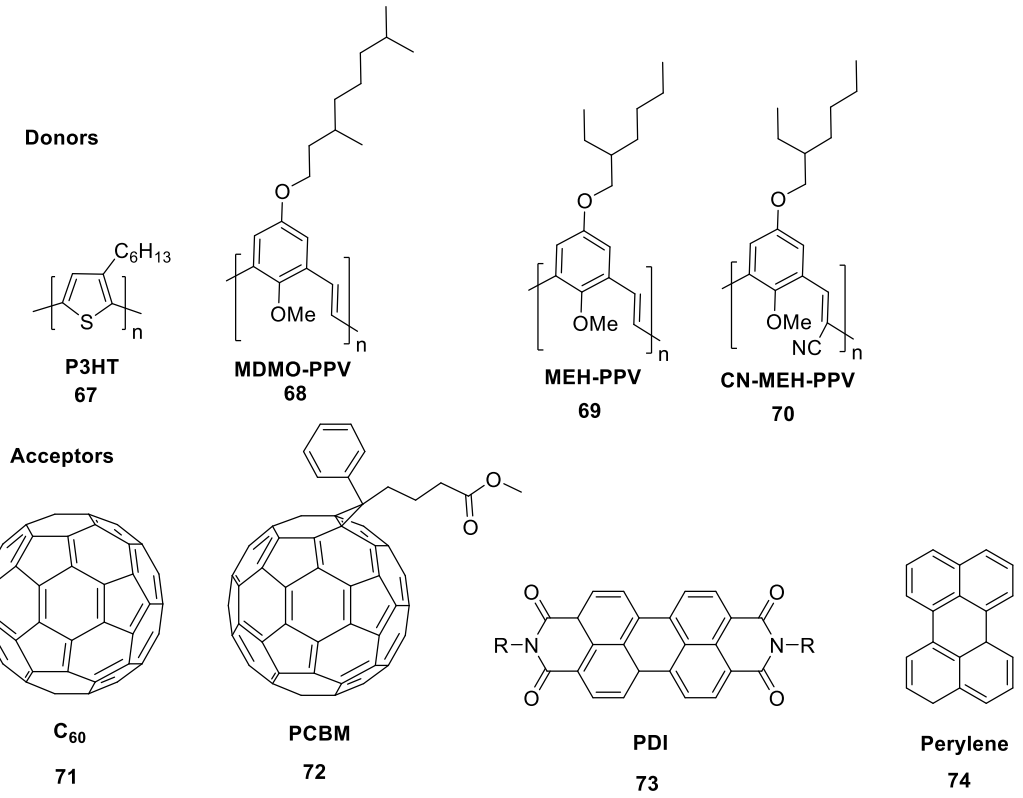


Figure 2

Single layer organic cell

In the single layer organic solar cells, the organic material was placed in between the two conductors such as the transperent indium tin oxide (ITO) and aluminum, magnesium or calcium metal. The ITO conductors have high work function and the aluminum, magnesium and calcium metal conductors posses low work function and hence electrons flow from the metal to ITO in the circuit (Figure 3).

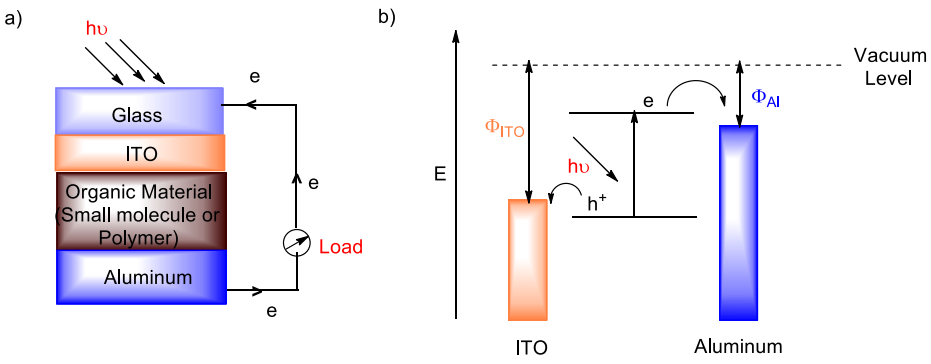


Figure 3. (a) Schematic diagram for single layer cell. (b) Energy level diagram.

In the presence of sun light the organic material absorbs UV-Visible light resulting in the excitation of electron to lowest unoccupied molecular orbital level (LUMO) and highest occupied molecular orbital level (HOMO) will have "hole". Hence, the photo excitation of organic material leads to produce coupled electron-hole pair called exciton. Based on the potential differences of metal electrodes, electrons move towards the positive electrode and holes towards the negative electrode.[33]

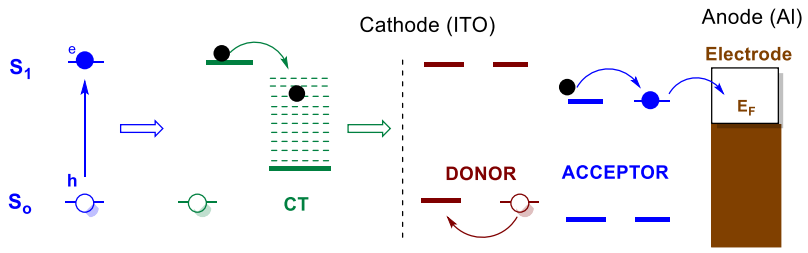


Figure 4. Energy diagram in organic solar cell.

Bilayer donor-acceptor heterojunction

Bilayer organic solar cells are made up of the organic donor and acceptor layers placed in between the two metal electrodes as shown in Figure 5. The electrostatic forces are generated at the interface due to the differences in electron affinity and also ionization energies. Here, the splitting efficiency of exitons is higher than the single layer organic solar cell.

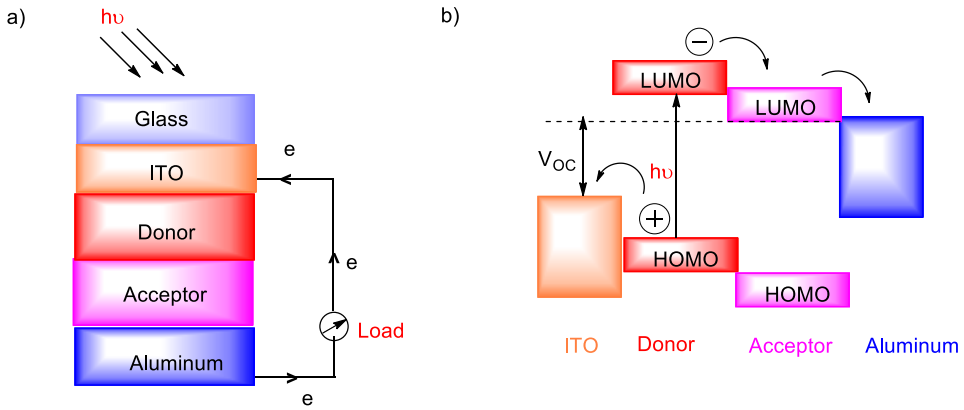


Figure 5. (a) Schematic diagram of bilayer organic solar cell. (b) Energy diagram in bilayer organic solar cell.

The donor and acceptor layers are labelled based on their ionization energies and electron affinities. The layer which posses low ionization energy works as donor and the layer which posses high electron affinity (EA) works as acceptor. Previously, double layer cell was reported using poly 2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene-vinylene (MEH-PPV) as donor, C_{60} as an acceptor with 0.04% of power conversion efficiency.[34] Also, copper phthalocyanine/perylene tetracarboxylic system was reported to give 1% power conversion efficiency.[35] In another study, the polymer poly (p-phenylenevinylene) PPV/C_{60} as donor/acceptor was reported with 9% power conversion efficiency.[36]

Bulk heterojunction solar cell

The effective absorption of photo light in organic photovoltaics depends on the thickness of the layer. If the thickeness is more, the diffusion pathway of the exciton also more in the donor/acceptor interface. Also, the exciton recombines before reaching the electrodes as it has shorter life time. However, the diffusion pathway of exciton can be reduced by introducing a mixture of donor/acceptor blend, which in turn gives higher efficiency of light absorption.

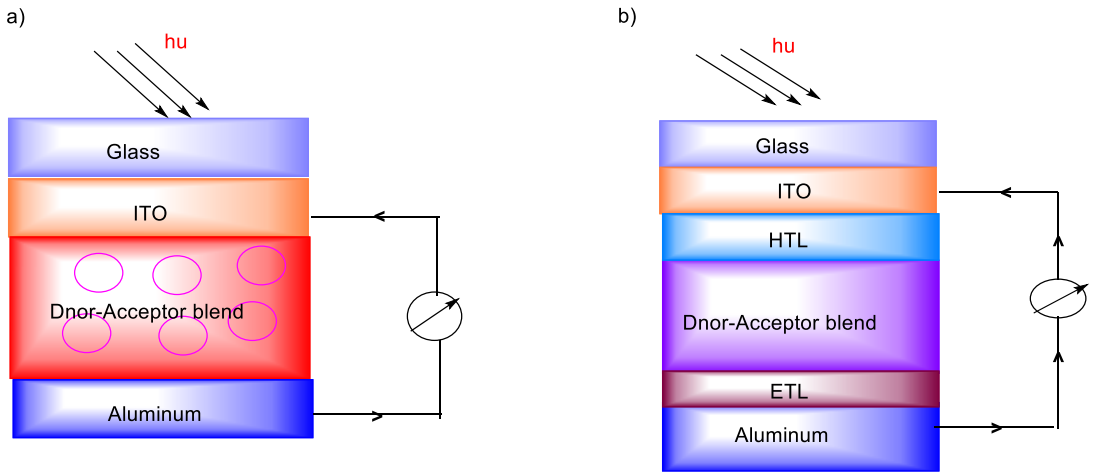


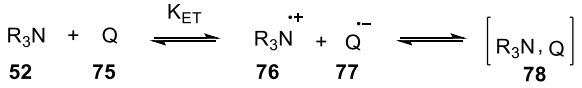
Figure 6. (a) Schematic diagram for Bulk heterojunction solar cell. (b) Use of buffer HTL and ETL layers.

In bulk heterojunction solar cell, the light absorption layer consists of blend of donor/acceptor materials (Figure 6). A device constructed using a blend of polymer MEH-PPV/fullerene derivatives was reported to give 2.9% of power conversion efficiency.[37] In another study, the MEH-PPV polymer was replaced by poly (3-octylthiophene), P_3OT polymer to improve the power conversion efficiency.[38] Also, thiophene based PTB7-Th polymer and $PC_{71}BM$ gave the 11% of power conversion efficiency.[39] However, the polymer/polymer blend heterojunction cell with MEH-PPV/CN-PPV as donor/acceptor was reported to give only 1% power conversion efficiency.[40]

3.1.6 Electricity harvesting cells based on ground state electron transfer reactions

Tertiary amines readily undergo electron transfer reactions with quinones to give the corresponding radical cation–anion pairs in various solvents. These radical ion pairs are more stable in dipolar aprotic solvent like PC and are in equilibrium with the corresponding charge transfer complexes (Scheme 18).

Scheme 18



An interesting possibility is the development of an electrochemical device based on transport of charges in these radical cation and anion pair species to the electrodes to complete the circuit and regenerating the donor and acceptor. If the electron transfer from the amine donor to the quionone acceptor could again happen, then the device would be useful in converting the heat around it to electricity continuously (Figure 7).

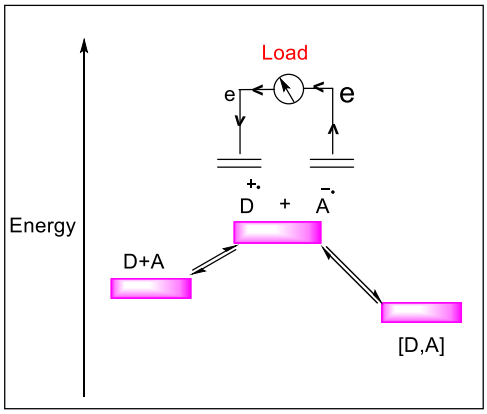


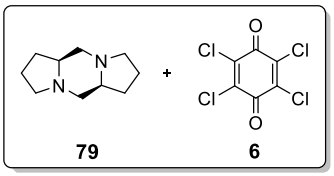
Figure 7. Ground state electron transfer of organic electron donor (D) and acceptor (A)-construction of an electricity harvesting cell.

We have examined the construction of an electrochemical cell so as to transport the charge carriers (i.e. electron in $\mathbf{Q}^{-\cdot}$ and the hole in $R_3N^{+\cdot}$) formed in electron transfer reactions under ambient temperature conditions to produce DC electricity (Fig. 6). The difference between such ground state electron transfer process in such cells and the electron transfer involved in donor/acceptor photovoltaic or solar cells is that in the later case the electron transfer from a donor to an acceptor takes place after photoexcitation of the electron in the ground state to excited state.

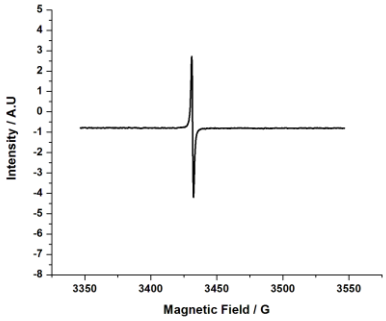
We have constructed the ground state electricity harvesting cells using the piperazine **79** and the diamide **80** prepared from *S*-proline. Also, we have constructed cells using different substituted diisopropyl benzamide derivatives. The results are described in the next section.

3.2.1 EPR studies of (5a*S*,10a*S*)-octahydro-1*H*,5*H*-dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine and *p*-chloranil

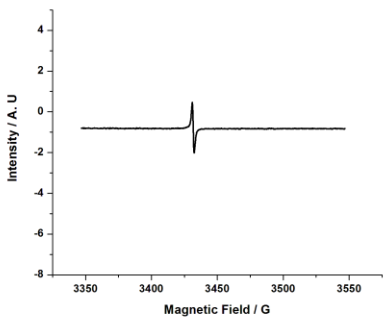
Initially, we have carried out epr studies on the reaction of (5a*S*,10a*S*)-octahydro-1*H*,5*H*-dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **79** with *p*-chloranil **6**. We have observed that when the (5a*S*,10a*S*)-octahydro-1*H*,5*H*-dipyrrolo[1,2-*a*:1',2'-*d*]pyrazine **79** reacts with *p*-chloranil **6** in DCM solvent, the reaction mixture turns to bright green.



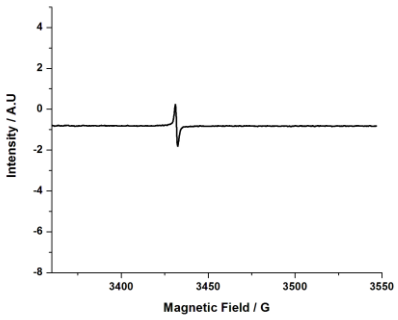
79 **6**



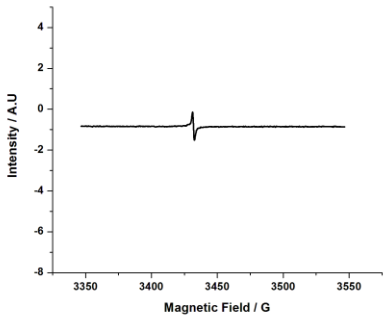
(a) 5 min



(b) 2 h

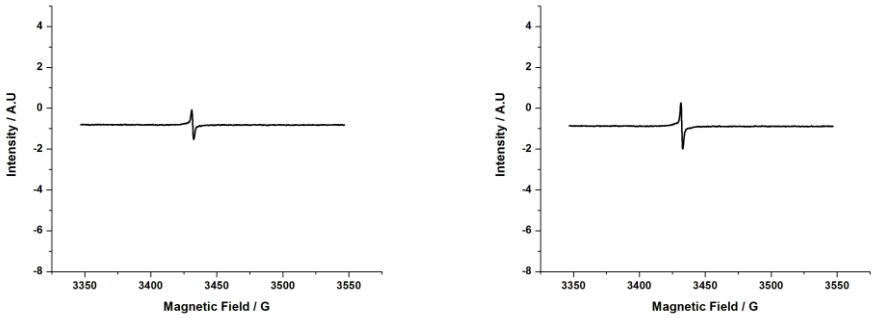


(c) 6 h



(d) 12 h

...Figure 8 Continued

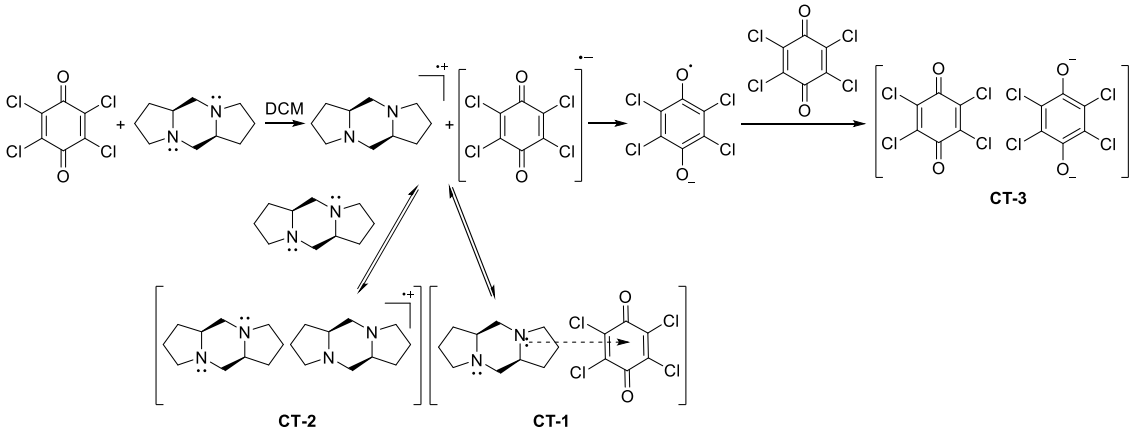


(c) 24 h (d) 48 h

Figure 8. EPR spectra of Proline piperazine (0.01 mmol) and *p*-chloranil (0.01 mmol) in DCM solvent (1 mL)

An epr signal was observed and its strength decreased with time. However, the paramagnetic intermediates were present for more than 48 h (Figure 8).

Scheme 19

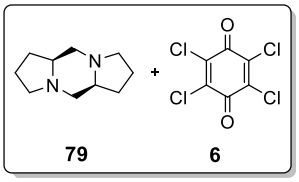


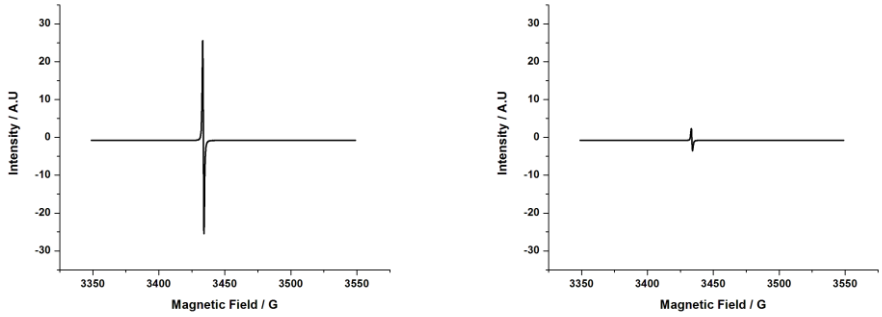
Presumably, the reaction of proline piperazine with *p*-chloranil gives the piperazine radical cation and *p*-chloranil radical anion pairs followed by formation of the charge transfer complex CT-1 (Scheme 19). The singlet esr signal is mainly due to the presence of *p*-chloranil radical anion which may react with the neutral *p*-chloranil to give the corresponding charge transfer complex CT3. The piperazine radical cation is expected to undergo fast exchange of electron with the neutral piperazine and hence does not give epr signal.

Similarly, the amine radical cation and the *p*-chloranil radical anion intermediates would combine to give the charge transfer complex CT1 leading to reduction in epr signal (Scheme 19).

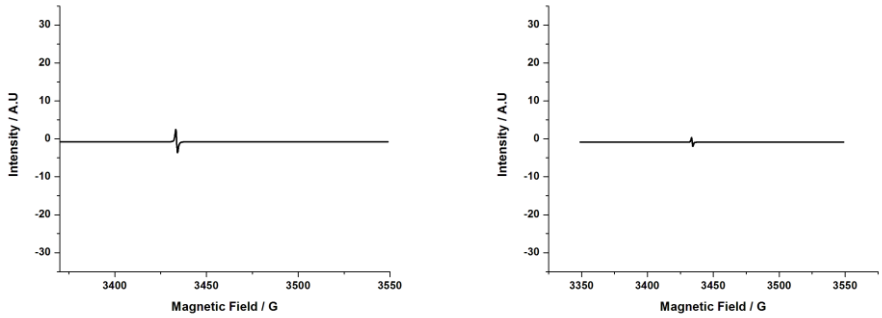
3.2.2 EPR studies of proline piperazine and *p*-chloranil in PC solvent

We have also observed that the reaction mixture of piperazine **115** with *p*-chloranil **6** gives stronger epr signal in the more polar PC solvent which also decreased with time.



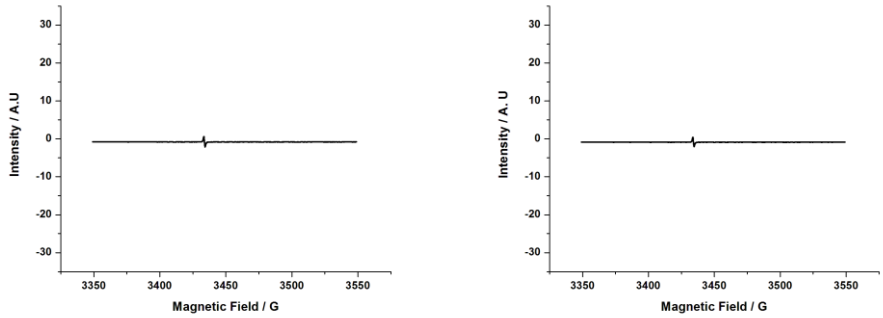


(a) 5 min (b) 2 h



(c) 6 h (d) 12 h

…Figure 9 continued



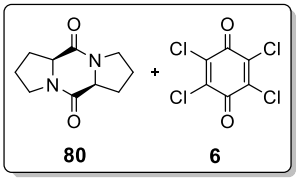
(c) 24 h (d) 48 h

Figure 9. EPR spectra of proline piperazine (0.01 mmol) and *p*-chloranil (0.01 mmol) in PC solvent (1 mL)

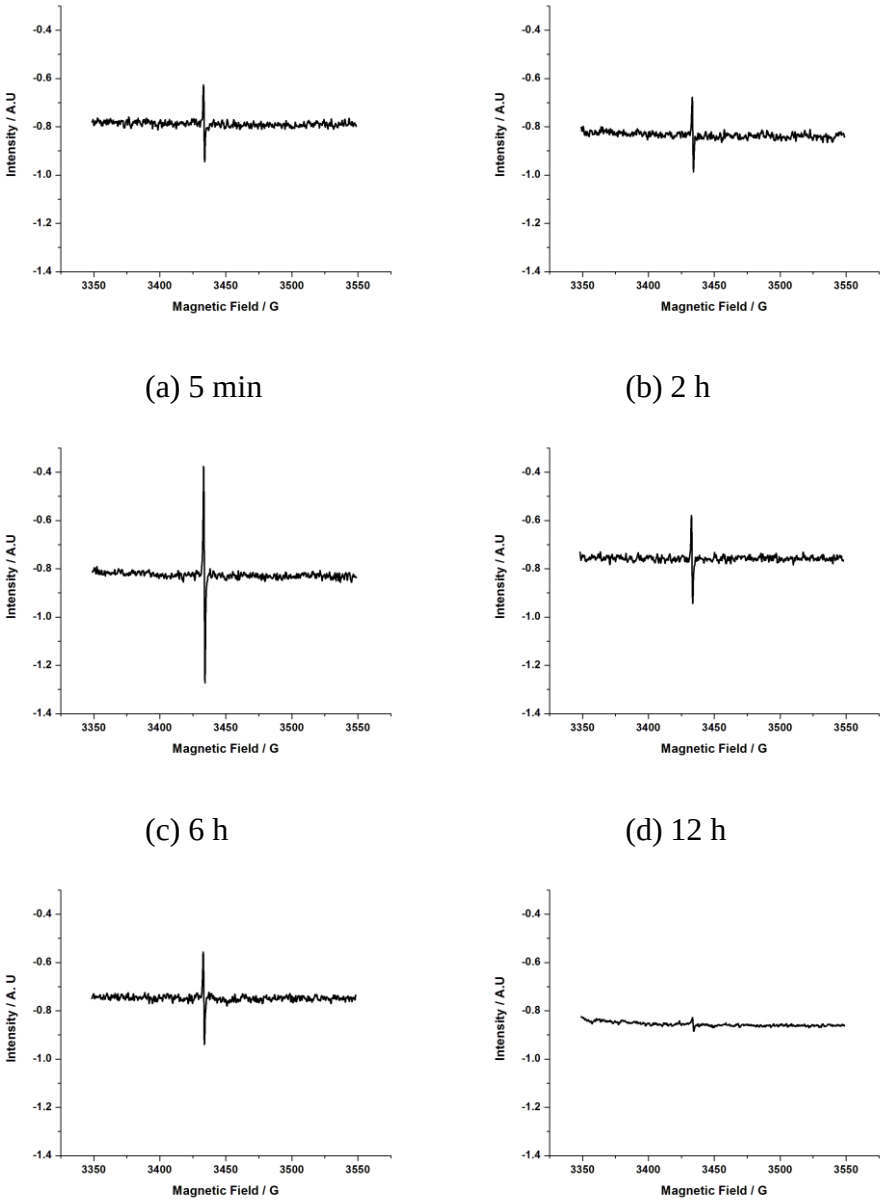
The epr signal strength in the beginning was higher as the radical ion would be formed in more amounts in the polar solvent. Again, the signal strength becomes weak as the radical ions are converted to the CT complexes with time.

3.2.3 EPR Studies of proline diamide 116 and *p*-chloranil 6

We have observed that the reaction of proline diamide with *p*-chloranil in PC solvent gave paramagnetic species detected by EPR spectroscopy. The electron transfer complex was stable up to 48 h as the epr signal observed. The epr spectrum recorded at different time intervals are shown in Figure 1. Initially, the intensity of the epr signal was observed as low and it increased with time reaching the maximum intensity at 6 h of time and then strength of the signal decreased with time.



...Figure 10 continued



(a) 5 min (b) 2 h

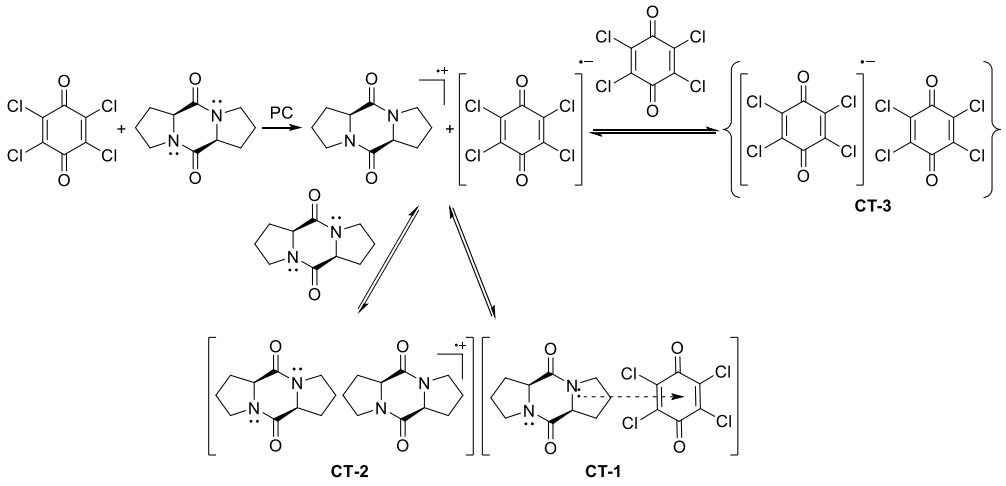
(c) 6 h (d) 12 h

(c) 24 h (d) 48 h

Figure 10. EPR spectra of proline diamide (0.01 mmol) and *p*-chloranil (0.01 mmol) in PC solvent (1 mL)

Presumably, the diamide is a weaker donor and hence its reaction with *p*-chloranil is slow. The signal strength increases initially and then decreases as the radical ions are combined to give the CT complexes (Scheme 20).

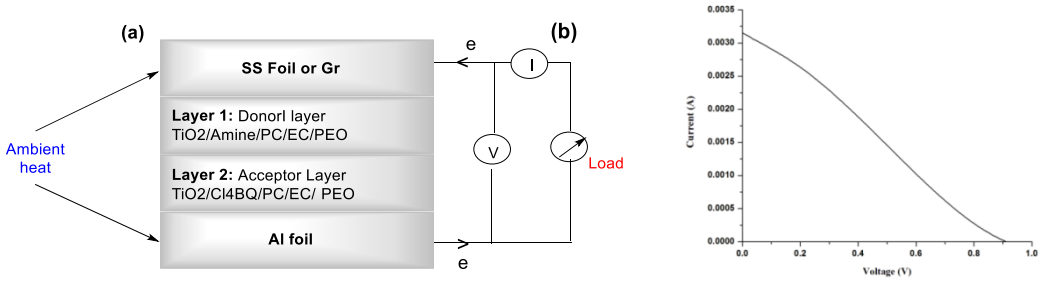
Scheme 20



3.2.4 Construction of donor and acceptor electrochemical cell

Recently, methods have been developed in this laboratory for construction of electricity harvesting cells based on electron transfer reactions using readily available amines and amides as donors and quinones as acceptors (Figure 12).[41] The electrochemical cell construction is based on the transport of charges in these radical cation and anion species to the electrodes and regenerating the donor and acceptor by reversible electron transfer reactions.

After extensive experimentation, we have found that the cells can be easily constructed by making donor and acceptor pastes using TiO_2, polyethylene oxide (PEO) and propylene carbonate (PC) for coating on commercially available Al (0.2mm x 5cm x 5cm) and SS (SS 304, 0.05mm x 5cm x 5cm) foils or graphite sheet (0.4mm x 5cm x 5cm). Initially, a simple two layer cell was constructed using Al and SS foils. The mixture of TiO_2, *p*-chloranil, PC, EC and PEO was coated on Al foil and the mixture of TiO_2, amines, PC, EC and PEO was coated on SS foil. The foils were then sandwiched to construct the electrochemical cell.



	With SS Foil Cathode	**With Graphite Cathode**
	Pmax/mW/FF(28 ºC)	**Pmax/mW/FF(28 ºC)**
DIPEA	0.756/0.263	1.415/0.235
DABCO	0.665/0.233	0.139/0.194
TPA	0.306/0.254	0.794/0.240

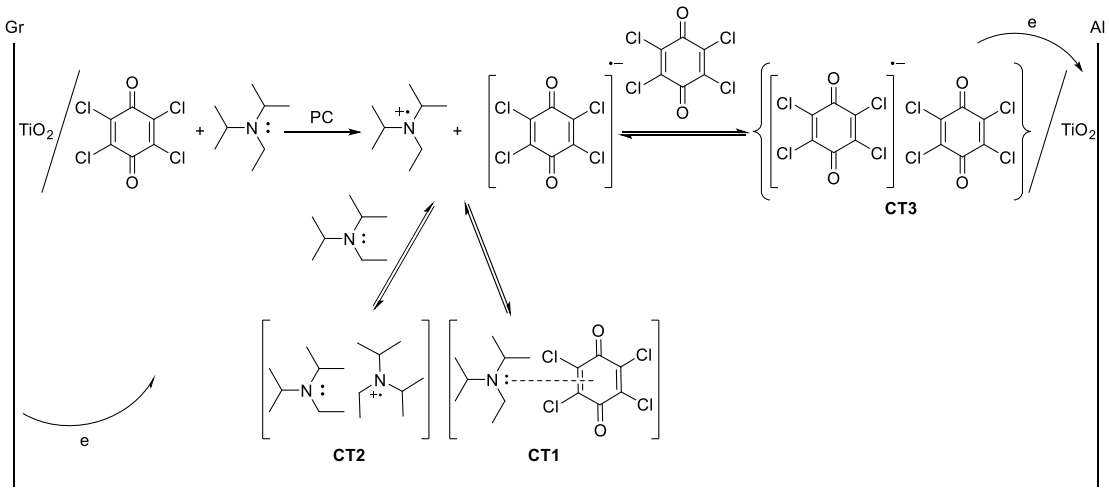
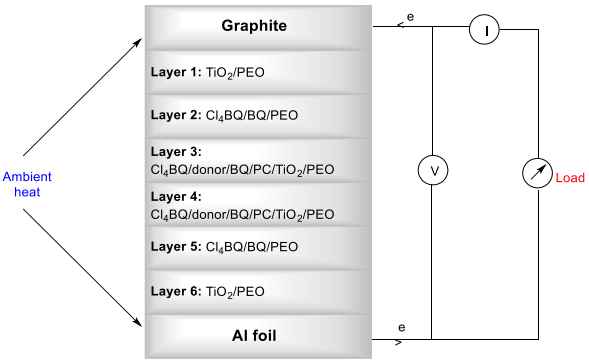
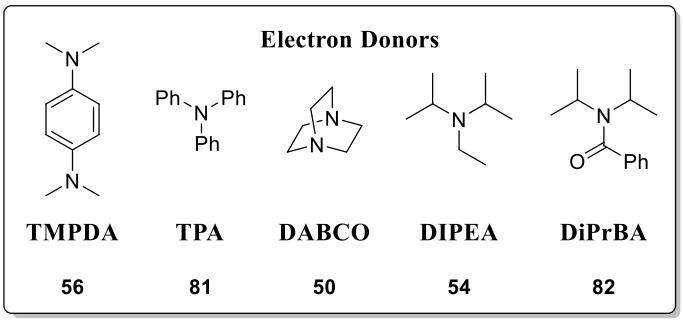


Figure 11. (a) Schematic diagram of cell with two layer configuration. (b) Representative IV data. (c) Tentative mechanism for electron transport via $D/D^{\cdot+}$ and A^{-}/A exchange reactions.

The configuration of this two layers electrochemical cell is almost similar to that is the bilayer organic solar cell but the electron transport would have contributions from both ionic conduction and also through exchange reactions involving $D/D^{\cdot+}$ and $A^{\cdot-}/A$ with formation of corresponding charge transfer complexes (CT1, CT2 and CT3) (Figure 11). The current (I) and voltage (V) characteristics observed for the cells using different amines are listed in Figure 11. In this case, the cell produced power but there was very little power or no power after 24 h.

The multilayer cells using different organic donors (**123-127**) and *p*-chloranil and with *p*-benoquinone (BQ) as electron transport gave better results. The results and expected intermediates are summarized in Figure 12.





	After 1 h packing Pmax/mW/FF(40 ºC)	**After 48 h packing Pmax/mW/FF(40ºC)**
TMPDA	1.614/0.282	1.299/0.263
TPA	0.939/0.219	0.728/0.219
DIPEA	11.740/0.296	8.338/0.394
DABCO	4.806/0.432	3.776/0.434
DiPrBA	1.871/0.232	1.411/0.243

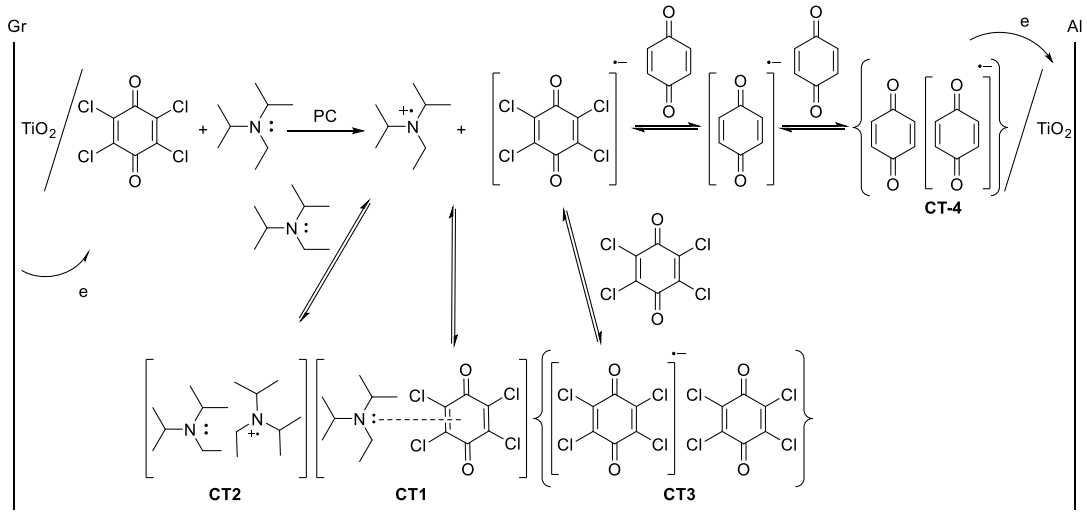


Figure 12. (a) Schematic diagram of six layer cell configuration using several donors, *p*-chloranil acceptor and electron transporter. (b) Representative IV data for the cell measured after 1 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

3.2.5 Electron donors and acceptors used in the construction of electrochemical cell

In continuation of these studies, we have carried out experiments using the diamine **115** and the amide **116** prepared as described in Chapter 1 (Figure 13).

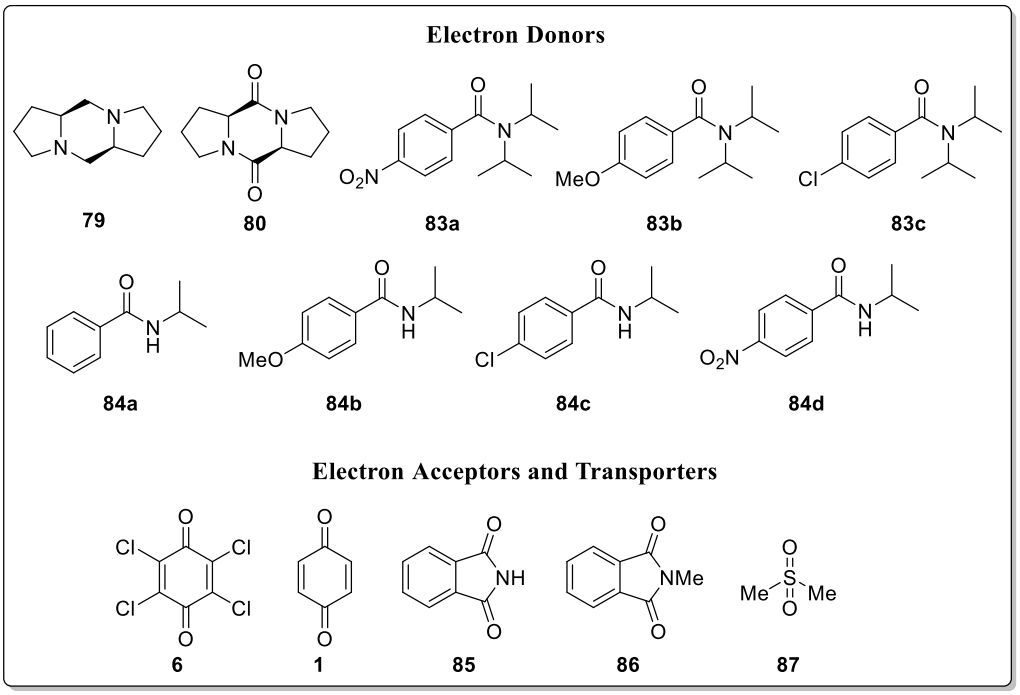


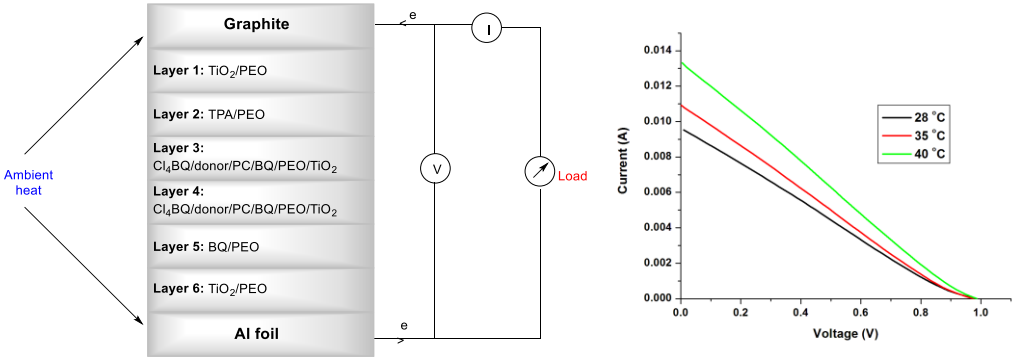
Figure 13

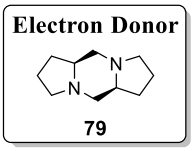
Also, experiments using diisopropyl arylamides **117a-c** and isopropyl arylamides **118a-d** were carried out using *p*-chloranil as acceptor (Figure 13). The results are described in the next sections.

3.2.6 Construction of electrochemical cells using the piperazine derivative 79

Initially, we have constructed the six layers cell by using Al foil (0.2mm x 5cm x 5cm) and graphite sheet (0.4mm x 5cm x 5cm). The mixture of TiO_2 (rutile) and polyethylene oxide (PEO) paste prepared using DCM was coated on Al and Gr. The TPA/PEO mixture was coated on coated Al and the BQ/PEO mixture was coated on coated Gr followed by coating of Cl_4BQ/donor/PC/BQ/PEO/TiO_2 mixture on both electrodes as shown in Figure 14. The foils were then sandwiched to construct the electrochemical cell. In this configuration, the solvent PC (propylene carbonate) was used for dissolving the donor and acceptor to facilitate the electron transfer reaction.

Figure 14: Construction of 6 layers cell with BQ as electron transporter in PC solvent.





Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	3.262/0.235	4.129/0.237	4.508/0.238
48 h	2.254/0.241	2.532/0.238	3.166/0.241

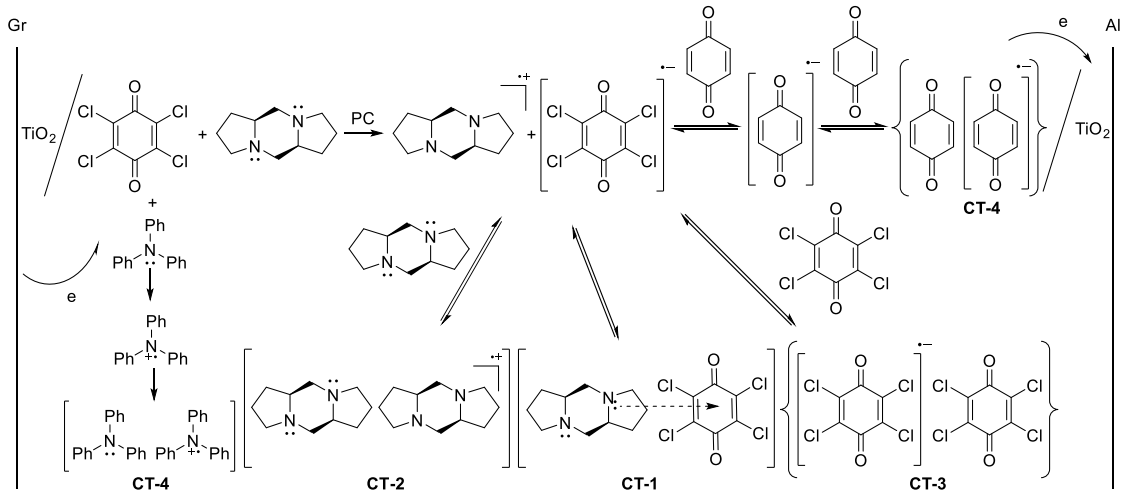


Figure 14. (a) Schematic diagram of six layer cell configuration using TPA and proline piperazine donors and *p*-chloranil and BQ as electron transport in PC solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The IV data were recorded at 28 ^{o}C, 35 ^{o}C and 40 ^{o}C at 1 h after packing and at 48 h. The electrochemical cell produced power Pmax of 4.508 mW with fill factor (FF) of 0.238 at 40 ^{o}C but the power output decreased after 48 h (Figure 14).

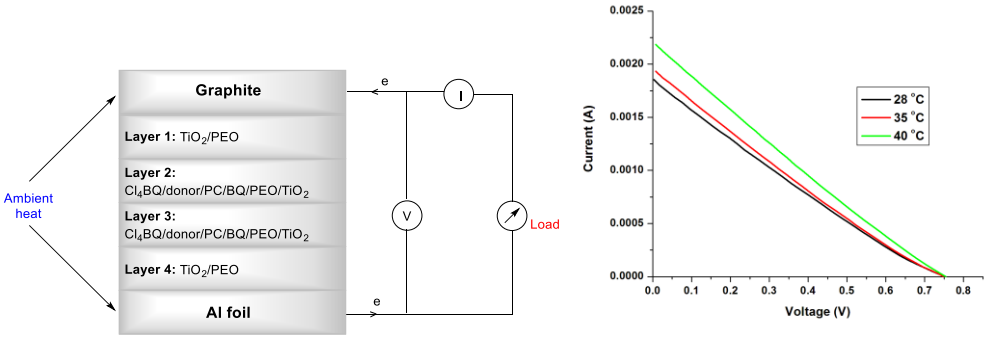
A tentative mechanism for electron transport from cathode to anode side is shown in Figure 14. The *p*-chloranil would accept electron from piperazine to give the paramagnetic intermediates of radical anion which will be further accepts by electron transporter BQ to give power. The TPA is expected to give the corresponding radical cation by reaction with *p*-chloranil and also with the radical cation of the piperazine derivative **79**. The formed radical anion and radical cations are expected to be in equilibrium with the CT1, CT2 CT2a and CT3 complexes. The formation of charge transfer complexes would lower the conductance if they precipitate out of the solution.

3.2.7 Construction of cells using a small amount of *p*-chloranil

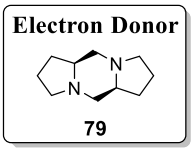
We have also examined whether *p*-chloranil could be used in smaller quantities as it is expected to be in equilibrium with radical ions. Initially, we have constructed a four layer

electrochemical cell using Cl_4BQ (10 mol%), and the piperazine derivative **79** (1 mmol) with BQ in two layers in PC solvent. The mixture of Cl_4BQ/donor/PC/BQ/PEO/TiO_2 was coated on TiO_2/PEO/Al and TiO_2/PEO/Gr.

Figure 15: Four layers cell using Cl_4BQ (10 mol%) and BQ electron transporter in PC.



Cl₄BQ (0.025 g, 10 mol%)

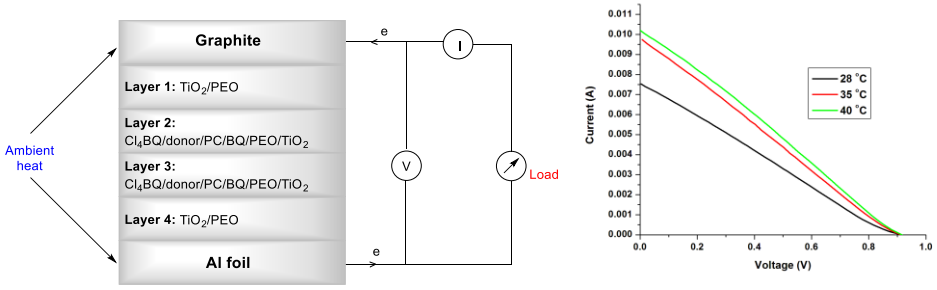


Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.143/0.237	2.594/0.240	2.758/0.238
48 h	0.313/0.225	0.330/0.228	0.387/0.235

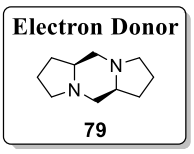
Figure 15. (a) Schematic diagram of four layer cell configuration using proline piperazine as donor and *p*-chloranil in catalytic amount (10 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing

The four layer cell produced power Pmax of 2.758 mW with fill factor FF 0.238 at 40 ºC but there was only very little power at 48 h (Figure 15). We have also constructed the cell in this configuration by using Cl_4BQ (25 mol%), piperazine derivative **79** (1 mmol) and BQ in two middle layers in PC solvent (Figure 16).

Figure 16: Four layers cell using Cl_4BQ (25 mol%) and BQ electron transporter in PC.



<u>Cl_4BQ (0.065g, 25 mol%)</u>

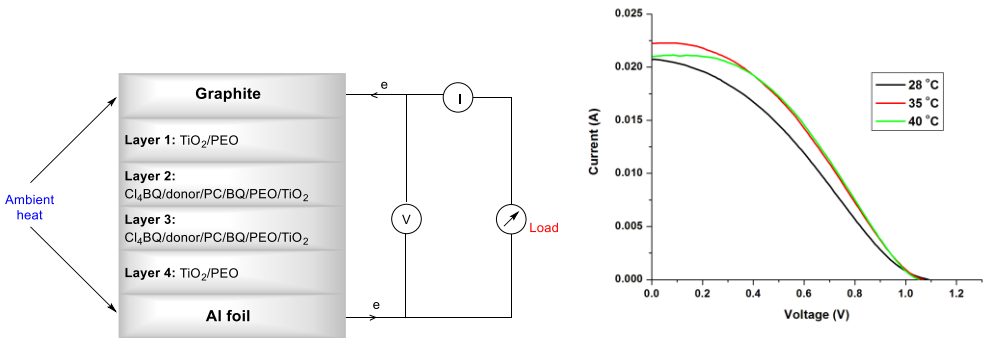


Time	**Pmax/mW/FF(28 ºC)**	**Pmax/mW/FF(35ºC)**	**Pmax/mW/FF(40 ºC)**
1 h	6.208/0.226	7.390/0.228	9.424/0.233
48 h	1.691/0.247	2.216/0.250	2.439/0.261

Figure 16. (a) Schematic diagram of four layer cell configuration using proline piperazine as donor and *p*-chloranil in catalytic amount (25 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing.

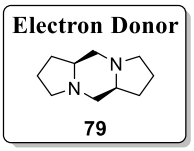
The power output (Figure 16) was higher than that realized using 10 mol% of Cl_4BQ. We have also examined the four layers cell in this configuration by using Cl_4BQ (50 mol%), piperazine **79** (1 mmol) and BQ in two middle layers in PC solvent (Figure 17).

Figure 17: Four layers cell using Cl_4BQ (50 mol%) and BQ electron transporter in PC.



...Figure 17 continued

Cl_4BQ (0.125g, 50 mol%)



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	10.76/0.223	15.81/0.236	21.08/0.251
48 h	7.316/0.323	8.677/0.365	8.818/0.399

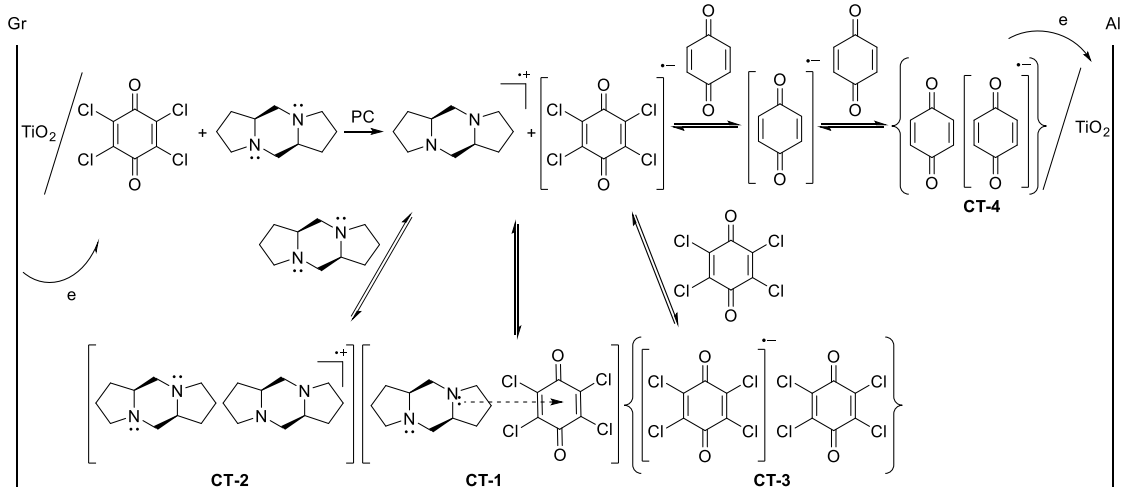
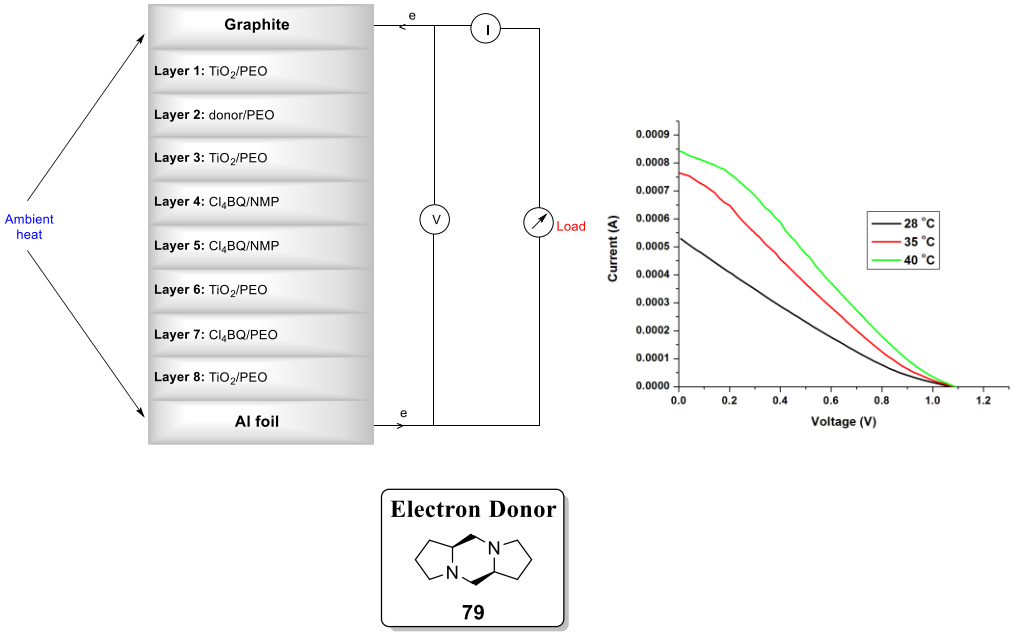


Figure 17. (a) Schematic diagram of four layer cell configuration using proline piperazine as donor and *p*-chloranil in catalytic amount (50 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The power output was higher when 50 mol% of *p*-chloranil (Figure 17) was used than that of cells constructed using Cl_4BQ (10 mol% and 25 mol%) (Figure 15 and 16). Clearly, the *p*-chloranil plays a major role in the performance of the electrochemical cells.

We have also examined multi layer electrochemical cell using the piperazine **79** and *p*-chloranil **6** in NMP solvent. However, the power output was very poor (Pmax 0.299 mW with FF 0.239) but almost the same (Pmax 0.239 mW with FF 0.267) even after 48 h (Figure 18).

Figure 18: Construction of 8 layers cell in NMP solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	0.070/0.222	0.144/0.212	0.299/0.239
48 h	0.116/0.206	0.185/0.225	0.239/0.267

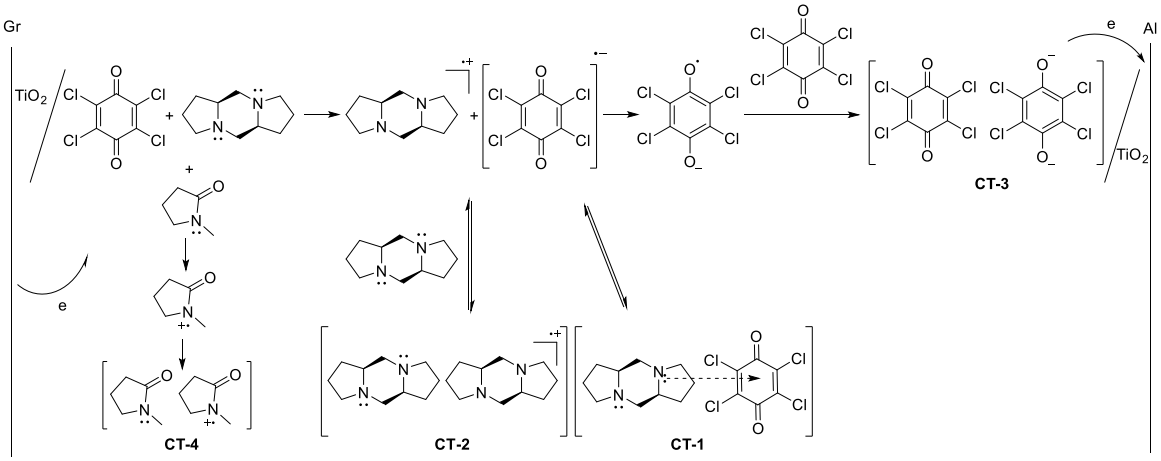
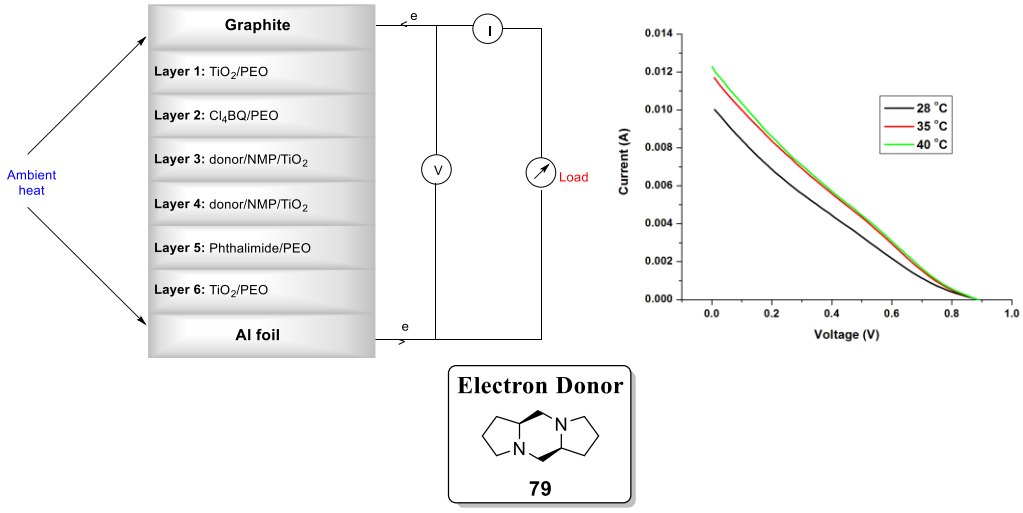


Figure 18. (a) Schematic diagram of eight layer cell configuration using piperazinedonor and *p*-chloranil in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

We have also examined the six layer electrochemical cell using electron transporter phthalimide in NMP solvent. The six layers cell was constructed using the piperazine **79**

along with NMP/TiO_2 in two layers with electron transporter phthalimide in 5th layer as shown in Figure 19.

Figure 19: Six layers cell in NMP solvent, phthalimide as electron transport.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.398/0.249	1.497/0.237	1.919/0.242
48 h	1.777/0.200	2.243/0.216	2.298/0.211

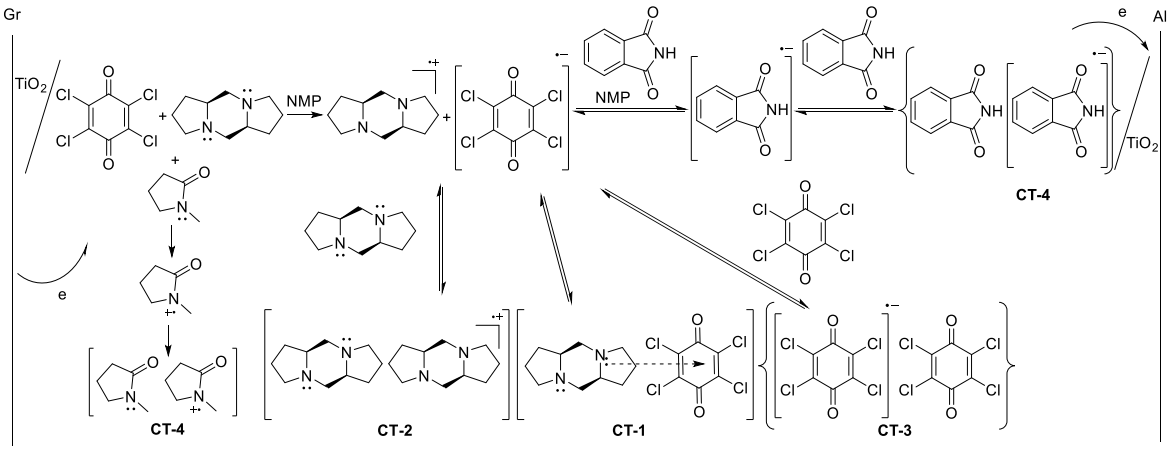
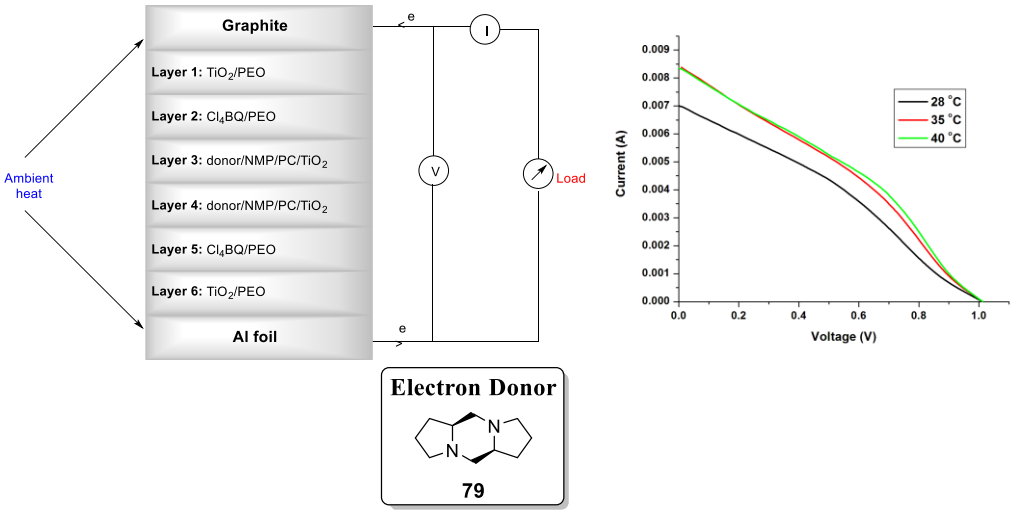


Figure 19. (a) Schematic diagram of six layer cell configuration using proline piperazine donor and phthalimide as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

There was improvement in power output values in this six layers configuration. Also, the power maximum values were same even after 48 h (Figure 19).

We have also constructed the cell with NMP/PC solvent combination without electron transporter.

Figure 20: Construction of 5 layers cell in NMP/PC solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	3.724/0.401	5.112/0.412	5.557/0.408
48 h	2.198/0.310	2.668/0.315	2.786/0.330

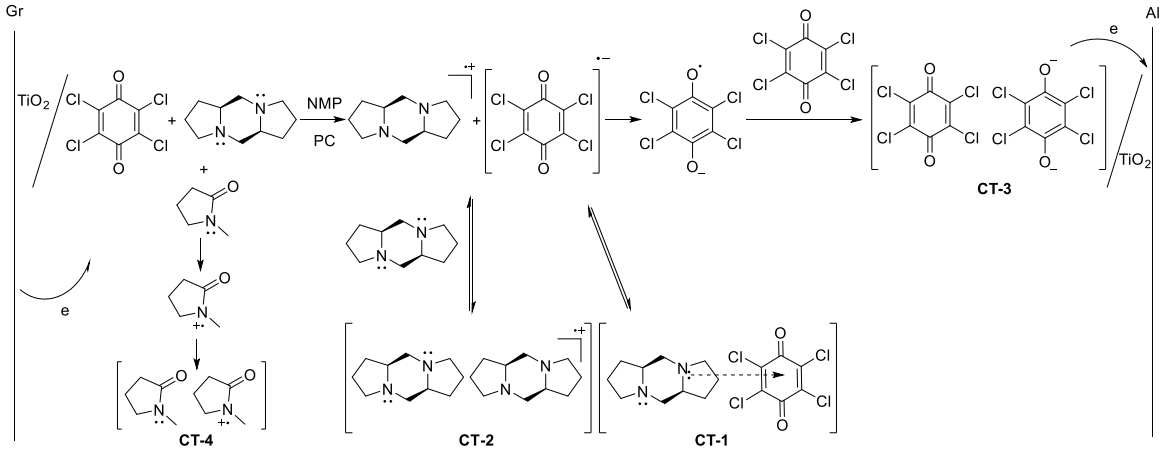
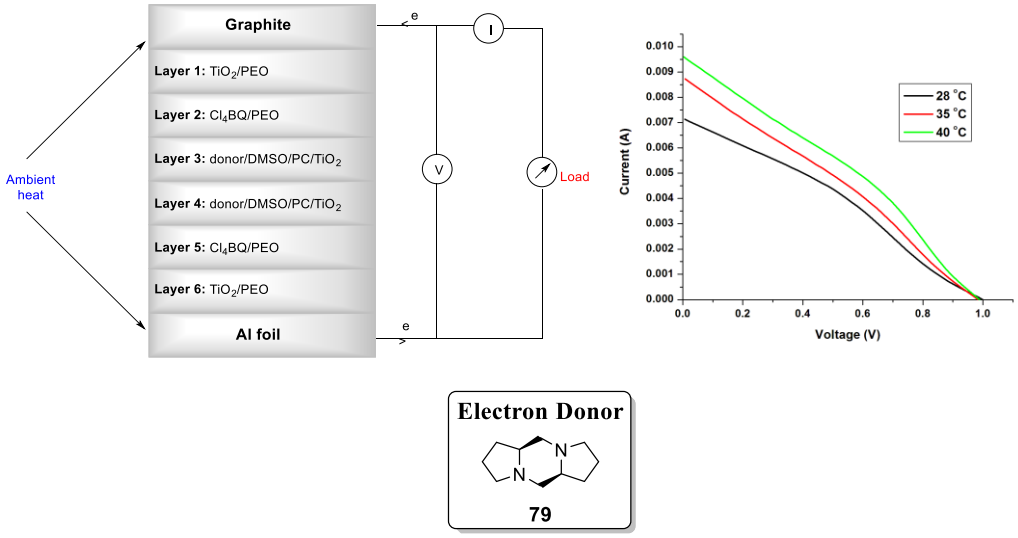


Figure 20. (a) Schematic diagram of six layer cell configuration using piperazine donor and *p*-chloranil in NMP/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In this case, the power values higher (Pmax 5.557 mW with FF 0.408) but decreased at 48 h.

Next, we have examined the solvent effect by including DMSO solvent along with the PC solvent as DMSO itself can also function as a donor as it could transfer electron to *p*-chloranil.[43] Accordingly, we have constructed the six layers cell with donor/DMSO/PC/TiO_2 in middle layers and the Cl_4BQ/PEO in two layers (Figure 21).

Figure 21: Six layers cell in DMSO/PC solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	3.478/0.380	4.063/0.368	4.639/0.392
48 h	2.194/0.308	2.484/0.289	2.926/0.309

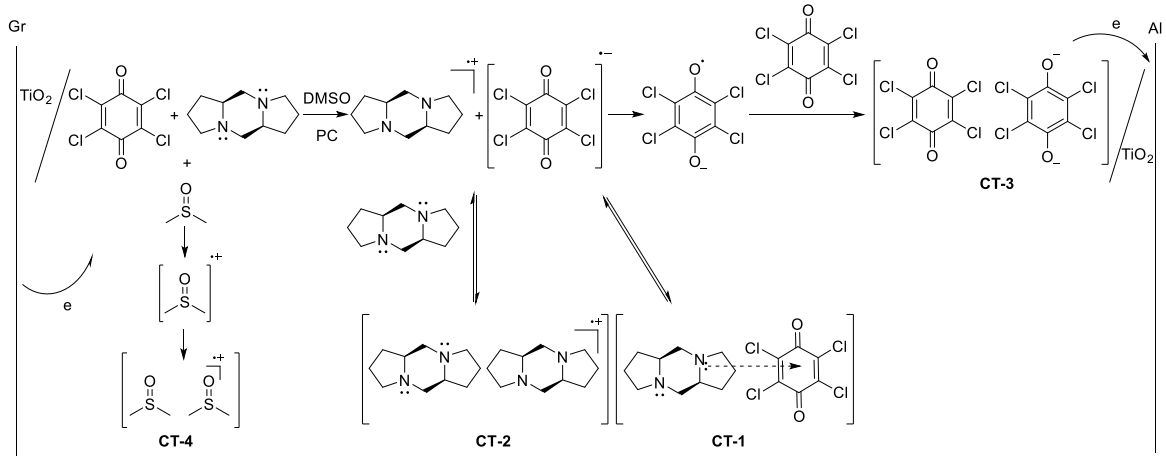
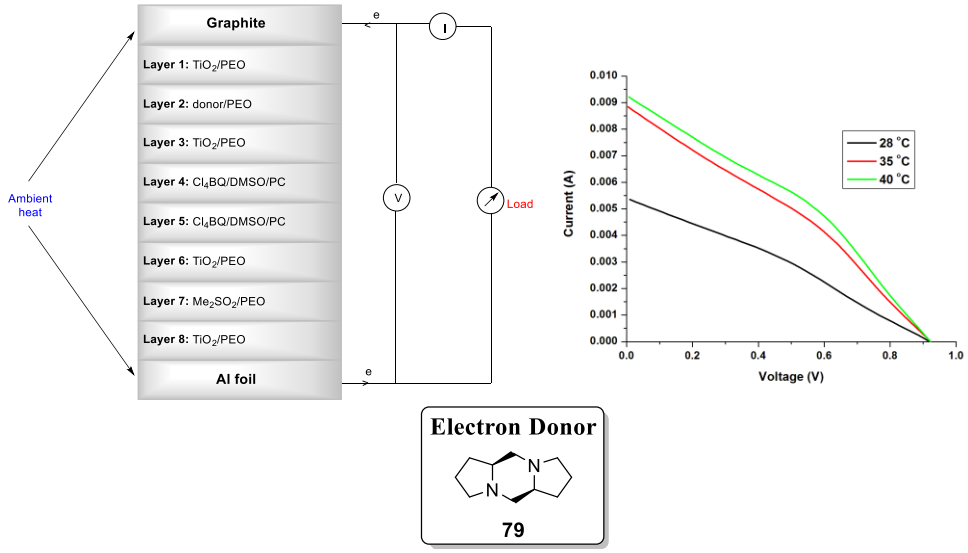


Figure 21. (a) Schematic diagram of six layer cell configuration using piperazine donor and *p*-chloranil in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In this case also, the power output was higher with Pmax 4.639 mW and FF 0.392 at 1 h after packing but decreased at 48 h (Figure 21).

We have also examined the use of DMSO/PC solvent along with electron transporter Me_2SO_2 in eight layers cell by incorporating TiO_2/PEO in 3rd and 6th layers.

Figure 22: Eight layers cell using sulfone as electron transport in DMSO/PC solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	3.744/0.360	4.891/0.360	5.023/0.385
48 h	1.482/0.301	2.539/0.311	2.877/0.338

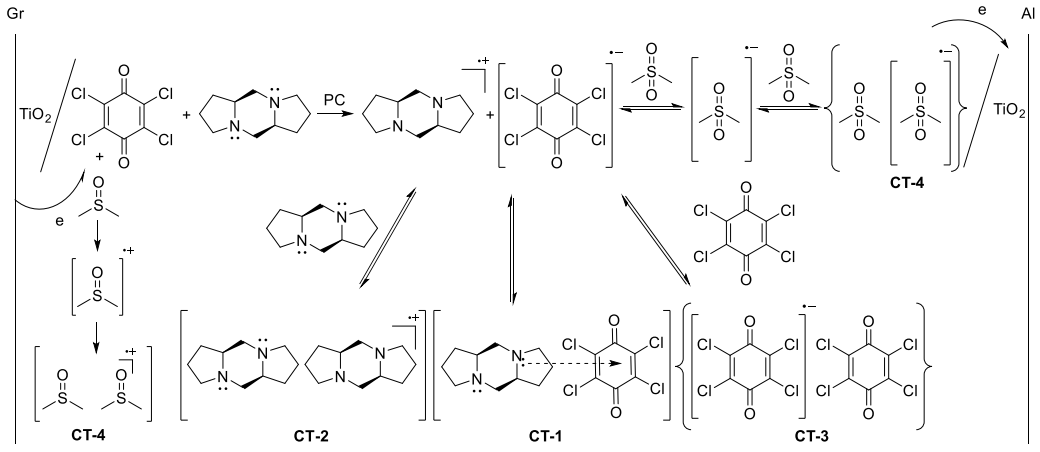


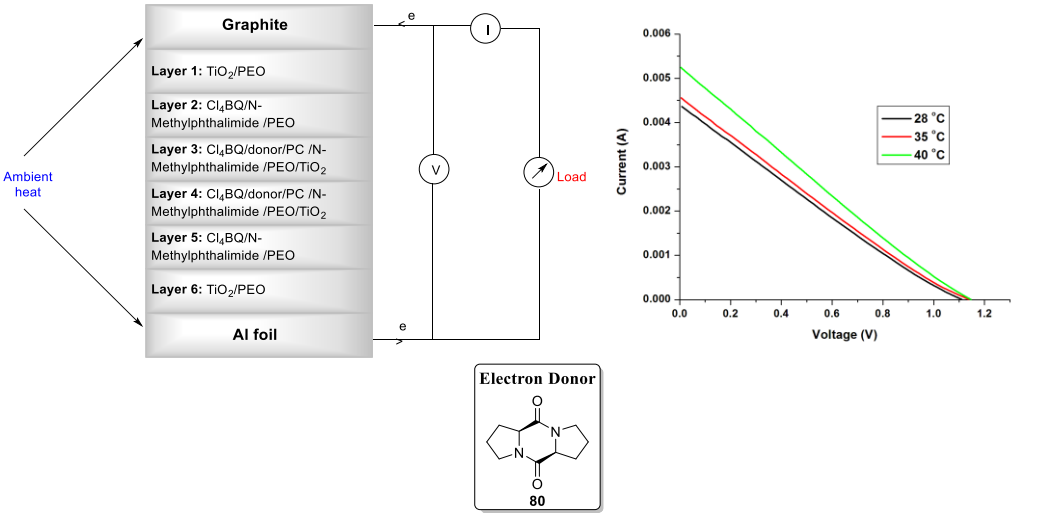
Figure 22. (a) Schematic diagram of eight layer cell configuration using piperazine donor and *p*-chloranil and Me_2SO_2 as electron transport in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In this case, the power output was higher at 1 h (Pmax 5.023 mW with FF 0.385) but decreased at 48 h (Figure 22).

3.2.8 Construction of electro chemical cells using proline diamide 80

We have also studied the construction of the electrochemical cells using proline diamide **80** as donor in different configurations. Initially, we have constructed six layers cell using proline diamide, *p*-chloranil and N-methyl phthalimide in PC solvent.

Figure 23: Six layers cell using N-methylphthalimide electron transporter in PC.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.176/0.219	2.515/0.253	2.515/0.231
48 h	1.137/0.235	1.202/ 0.231	1.421/0.236

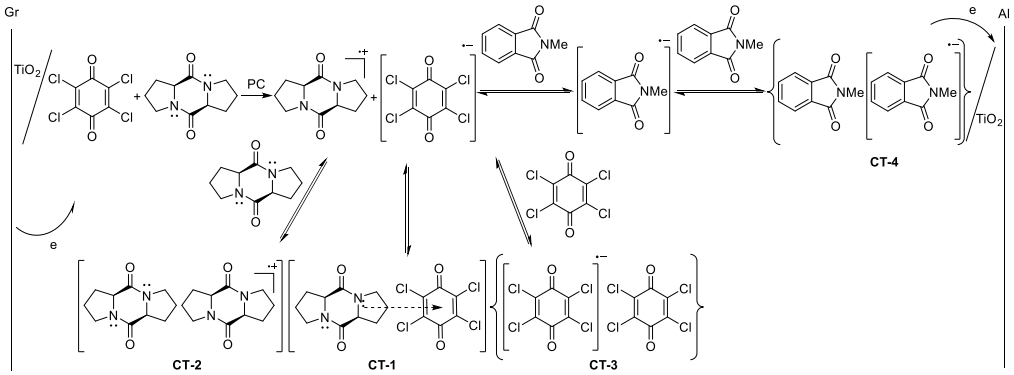
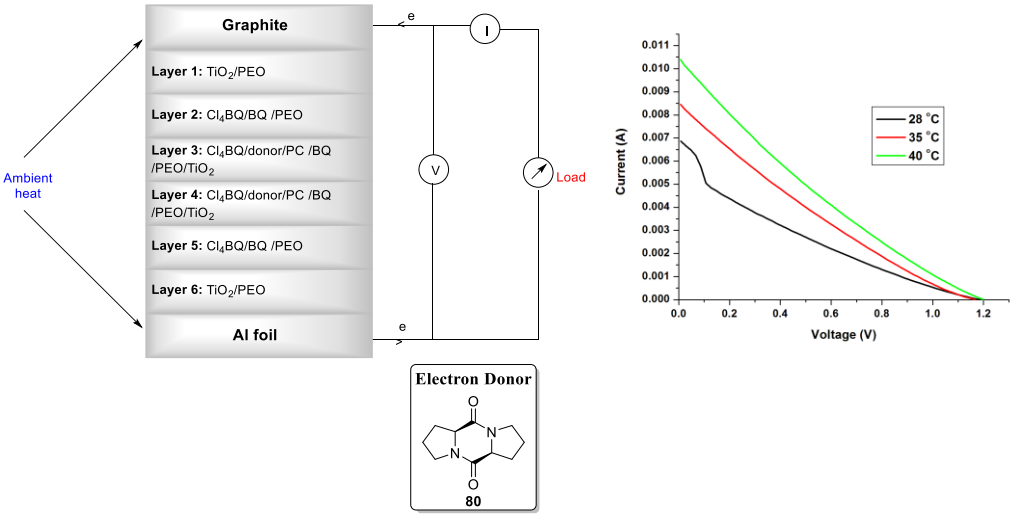


Figure 23. (a) Schematic diagram of six layer cell configuration using proline diamide as donor and chloranil as acceptor and N-methyl phthalimide as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

However, the Pmax value in this configuration was somewhat low. Presumably, this may be due to the formation of more stable N-methyl phthalimide anions leading to poor conduction. Also, the Pmax of the cell decreased with time (Figure 23).

We have then examined the cell using BQ instead of N-methyl phthalimide in the same configuration in PC solvent (Figure 24).

Figure 24: Six layers cell using BQ electron transport in PC solvent.



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	2.751/0.180	3.394/0.189	3.508/0.195
48 h	1.353/0.166	2.003/0.203	2.487/0.200

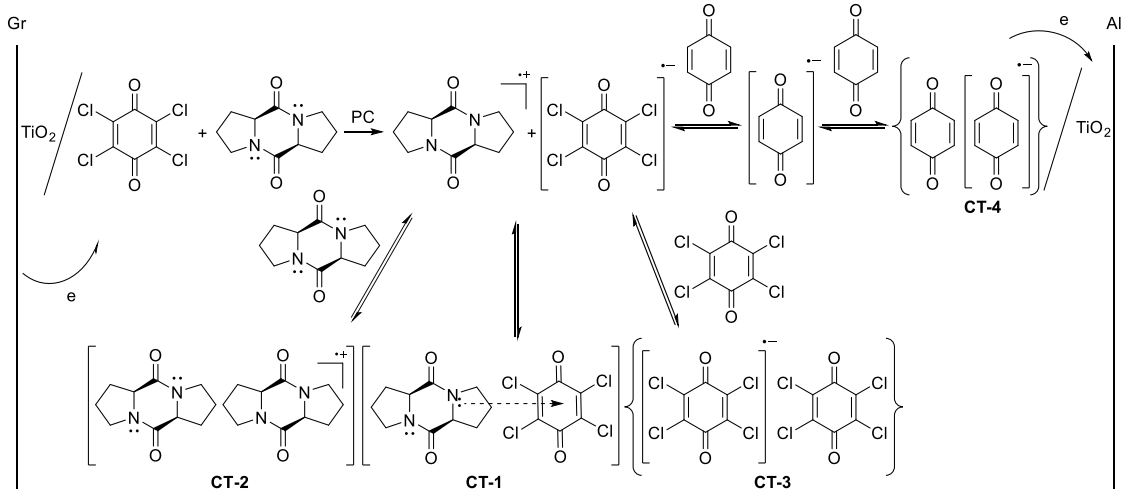


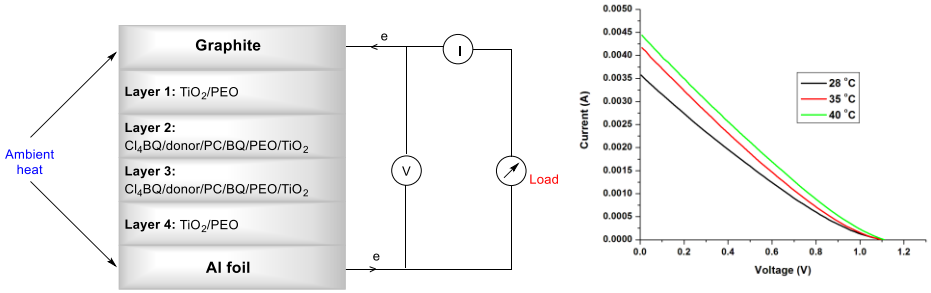
Figure 24. (a) Schematic diagram of six layer cell configuration using proline diamide as donor and chloranil as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The Pmax value obtained using BQ in this 4 layers (Figure 24) was somewhat higher (Pmax=3.508 mW, FF=0.195) compared to that obtained using N-methyl phthalimide (Pmax=2.515 mw, FF=0.231) (Figure 23). However, the power output obtained in this configuration decreased with time (Figure 24).

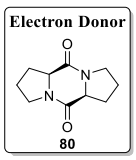
3.2.9 Construction of electrochemical cells using proline diamide 80 and smaller amounts of *p*-chloranil

The solubility of the *p*-chloranil in PC solvent is somewhat poor (only 30 mg soluble in 1 mL PC). Hence, it was thought that use of smaller quantities would also give reasonable power output. Initially, we have constructed a four layer electrochemical cell using Cl_4BQ (10 mol%), proline diamide **80** (1 mmol) and BQ in two layers in PC solvent.

Figure 25: Four layers cell using Cl_4BQ (10 mol%) and BQ electron transport in PC.



Cl4BQ (0.025 g, 10 mol%)

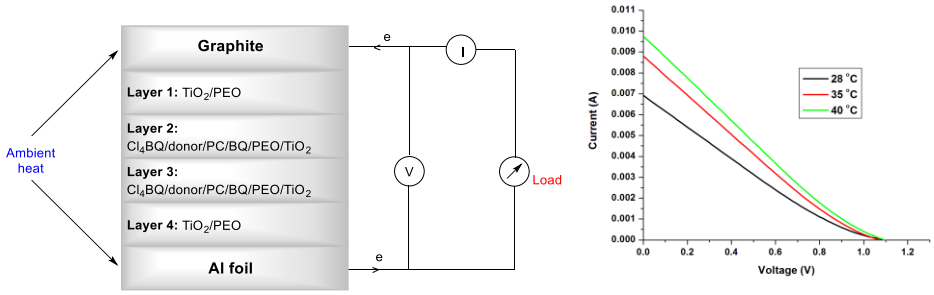


Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.527/0.207	3.086/0.213	3.155/0.210
48 h	0.799/0.203	0.944/0.207	1.061/0.216

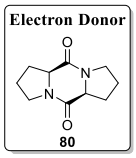
Figure 25. (a) Schematic diagram of four layer cell configuration using proline diamide as donor and *p*-chloranil in catalytic amount (10 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The cell constructed using 10 mol% of *p*-chloranil gave Pmax of 3.155 mW with FF of 0.210 and it decreased with time (Figure 25). We have then constructed the electrochemical cell using 25 mol% of *p*-chloranil in PC solvent in the same configuration as shown in Figure 26.

Figure 26: Four layers cell using Cl_4BQ (25 mol%) and BQ electron transport in PC.



Cl_4BQ (0.065g, 25 mol%)



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	3.652/0.179	3.962/0.188	4.939/0.188
48 h	1.584/0.209	2.064/0.220	2.342/0.219

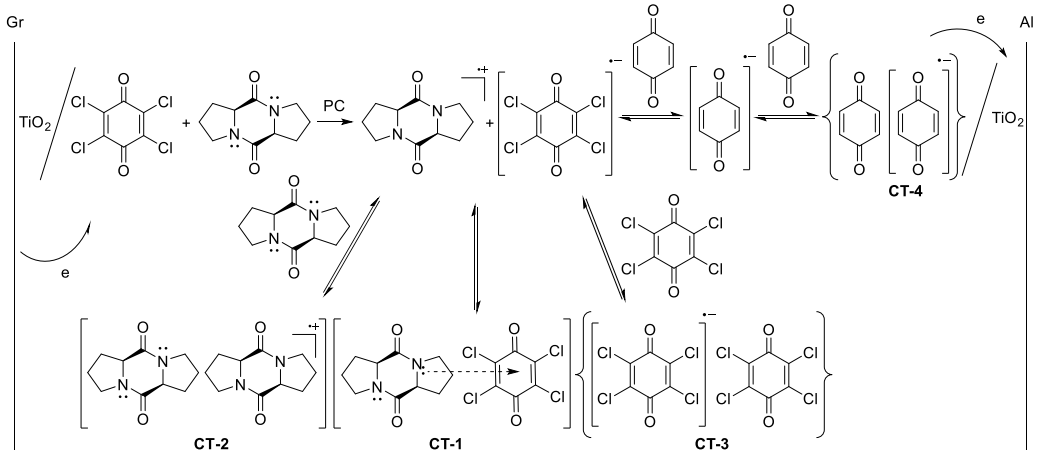
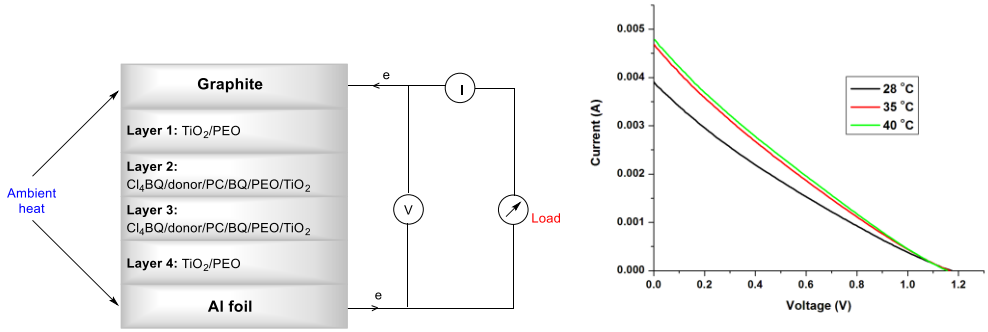


Figure 26. (a) Schematic diagram of four layer cell configuration using proline diamide as donor and *p*-chloranil in catalytic amount (25 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

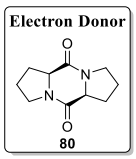
The cell constructed using 25 mol% of *p*-chloranil and proline diamide as donor gave comparatively higher power (Pmax=4.939, FF=0.188) (Figure 26) than the cell constructed using 10 mol% of *p*-chloranil (Pmax=3.155, FF=0.188, FF=0.210) (Figure 25).

Surprisingly, the four layers cell using *p*-chloranil acceptor in 50 mol% and proline diamide as donor resulted in lower power output (Pmax=2.133 mW, FF=0.170) (Figure 27) compared to the cell using 25 mol% of *p*-chloranil (Pmax=4.939 mW, FF=0.188) in this configuration (Figure 26). Presumably, the CT-1 and CT-3 complexes may be formed to more extent leading to lower power output.

Figure 27: Four layers cell using Cl_4BQ (50 mol%) and BQ electron transport in PC.



<u>Cl_4BQ (0.125g, 50 mol%)</u>

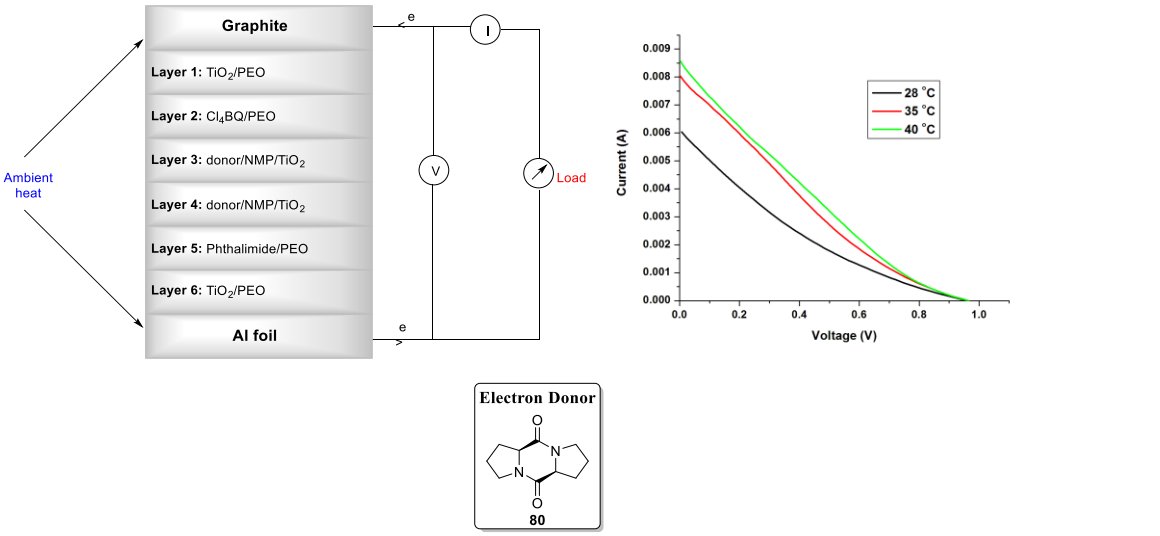


Time	**Pmax/mW/FF(28 °C)**	**Pmax/mW/FF(35°C)**	**Pmax/mW/FF(40 °C)**
1 h	1.399/0.162	1.863/0.162	2.133/0.170
48 h	0.929/0.203	1.135/0.208	1.187/0.215

Figure 27. (a) Schematic diagram of four layer cell configuration using proline diamide as donor and *p*-chloranil in catalytic amount (50 mol%) as acceptor and BQ as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The *p*-chloranil dissolves in NMP solvent to more extent (100 mg of Cl_4BQ in 1 mL NMP) compared to solubility in PC (30 mg of Cl_4BQ in 1 mL PC). Hence, we have constructed six layers cell using proline diamide as donor **80** and *p*-chloranil as acceptor with phthalimide as electron transporter in NMP solvent. In this case, the power output (Pmax) was low but there was an improvement at 48 h (Figure 28).

Figure 28: Six layers cell using phthalimide as electron transporter in NMP solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	0.380/0.157	0.386/0.165	0.685/0.169
48 h	0.969/0.184	1.514/0.195	1.690/0.204

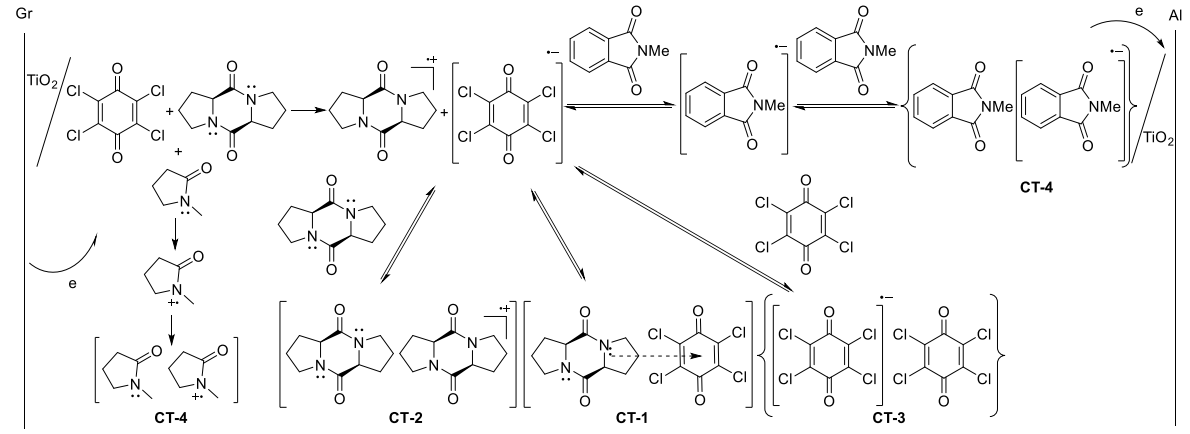
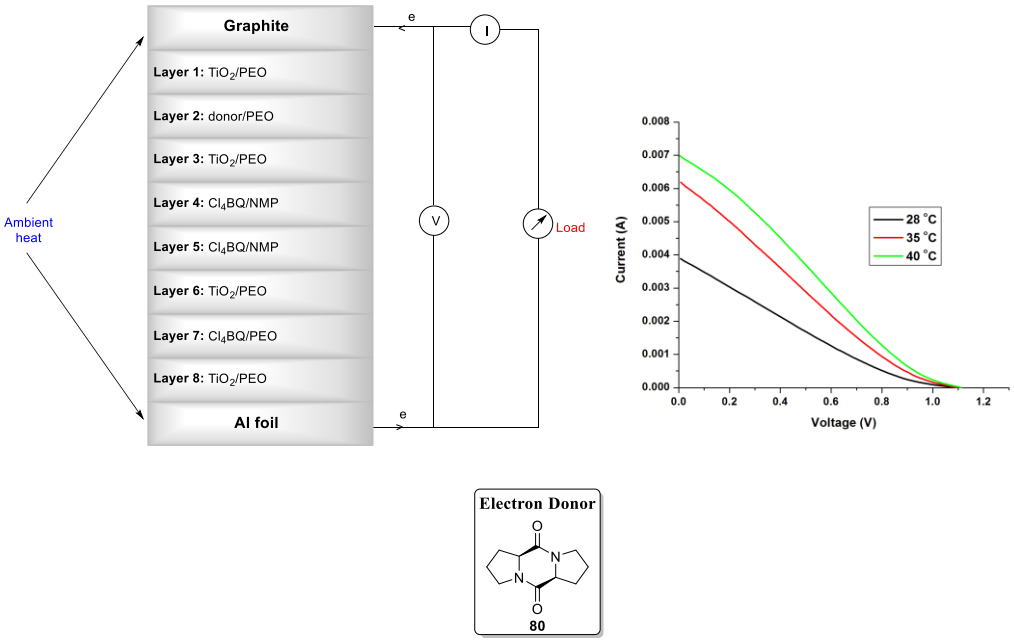


Figure 28. (a) Schematic diagram of six layer cell configuration using proline diamide donor and phthalimide as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

We have also constructed eight layers cell configuration by incorporating TiO_2/PEO layer after donor/PEO and Cl_4BQ/PEO layers.

Figure 29: Eight layers cell configuration in NMP solvent without electron transport.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.189/0.224	1.971/0.324	2.078/0.261
48 h	0.859/0.203	1.459/0.214	1.849/0.238

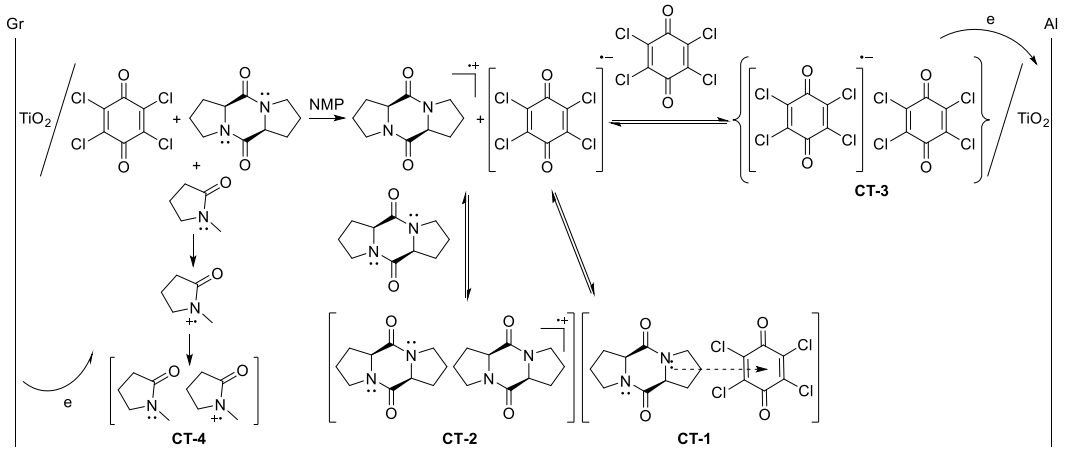
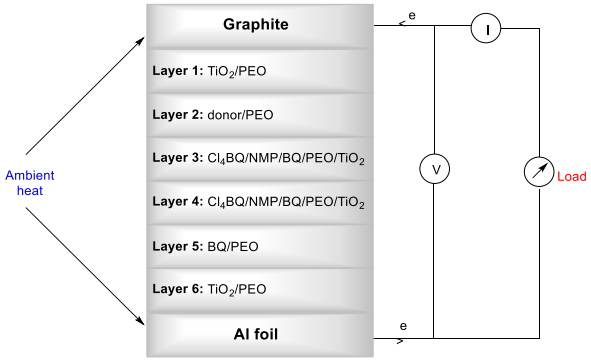


Figure 29. (a) Schematic diagram of eight layer cell configuration using proline diamide donor and *p*-chloranil in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In this case, we have observed almost stable power outputs up to 48 h. The power output higher at 1 h (Pmax=2.078 mW, FF=0.261) and almost same (Pmax=1.849 mW, FF=0.238 at 48 h.

We have also examined the cell using BQ as electron transporter in NMP solvent in a six layers cell configuration using Cl_4BQ/NMP/BQ/PEO/TiO_2 in middle layers and donor layer coated closer to Gr sheet as shown in Figure 30.

Figure 30: Six layers cell using BQ as electron transport in NMP solvent.



Electron Donor (80)	Time	Pmax/mW/FF(28 ºC)
	1 h	4.768/0.168
	48 h	1.555/0.220

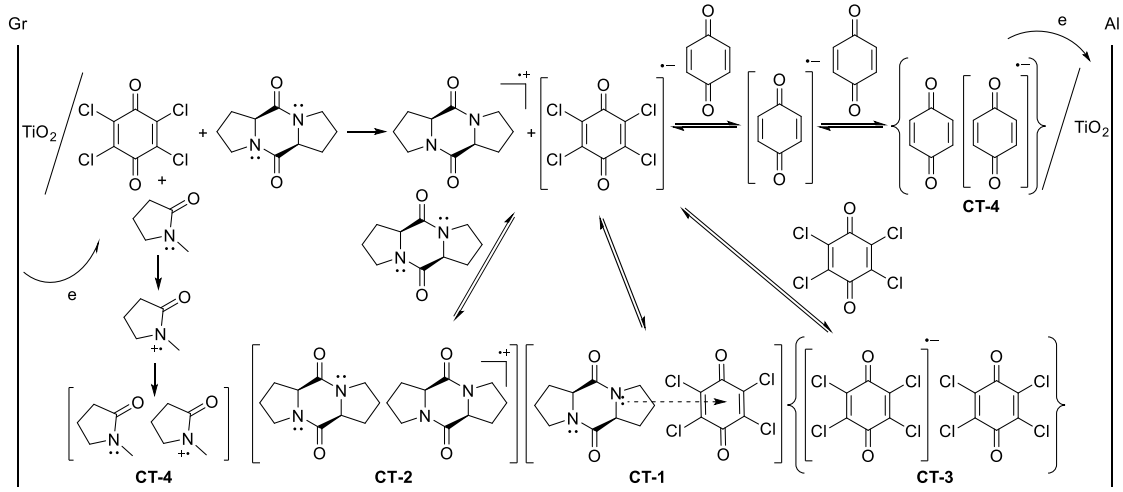
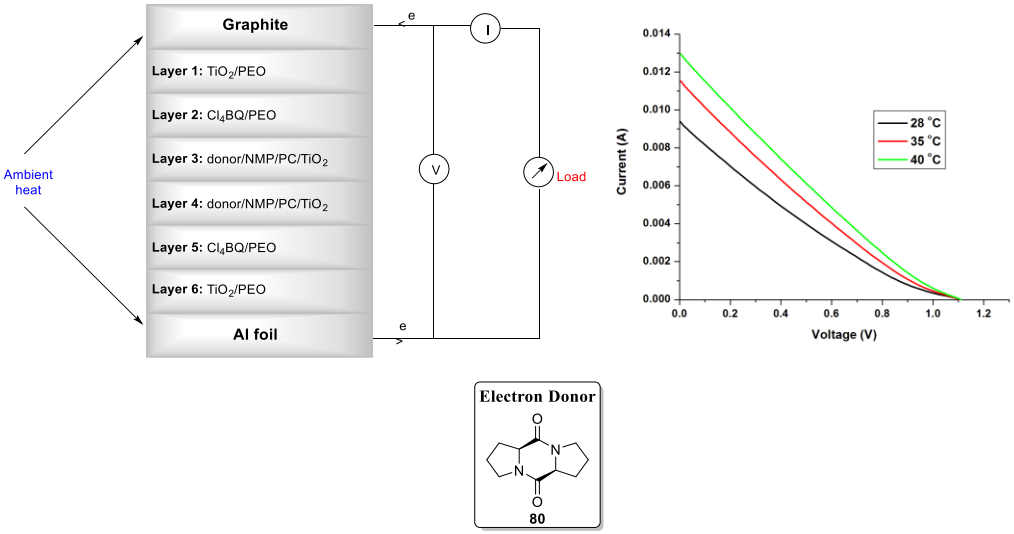


Figure 30. (a) Schematic diagram of six layer cell using proline diamide donor and *p*-chloranil and BQ as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In this configuration, the power output was higher initially (Pmax=4.768 mW, FF=0.168) at 28 ºC but decreased with time (Figure 30). We have also examined the cell using NMP/PC solvent medium in a slightly different configuration with Cl_4BQ in 2nd and 5th layers (Figure 31).

Figure 31: Six layers cell in NMP/PC solvent medium without electron transport.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.114/0.177	2.692/0.185	2.870/0.190
48 h	2.005/0.192	2.580/0.202	3.065/0.213

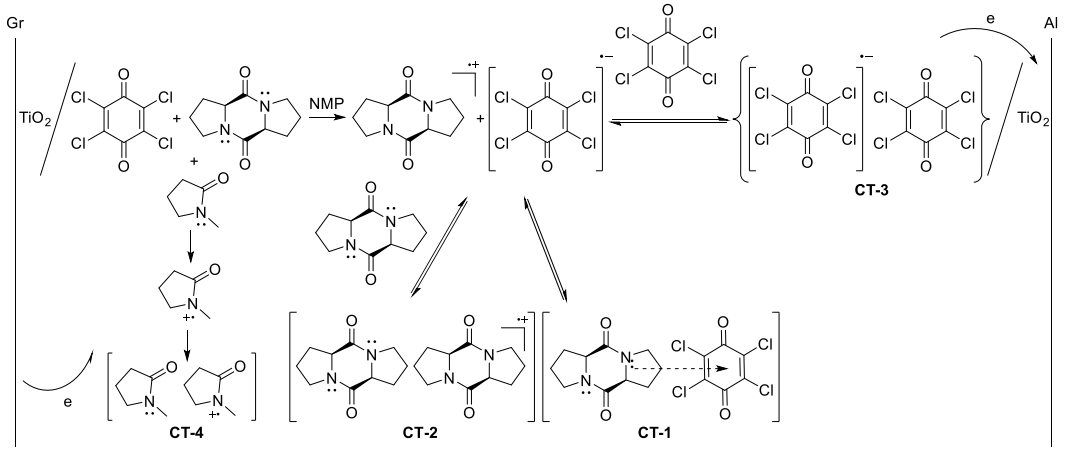
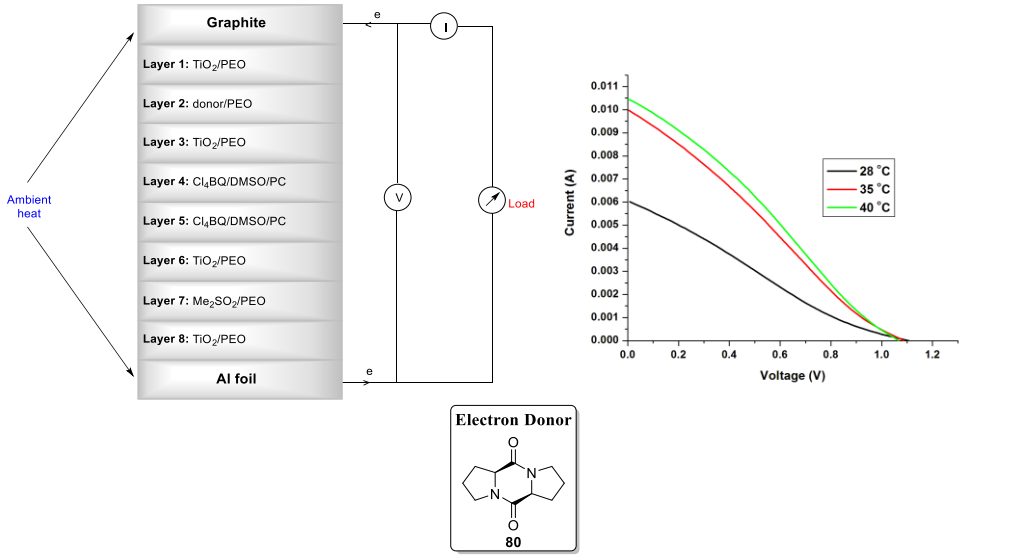


Figure 31. (a) Schematic diagram of six layer cell configuration using diamide donor and *p*-chloranil in NMP/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

Although, the power output was not high under this condition, it was almost the same at 1 h (Pmax=2.870, mw, FF=0.190) and at 48 h (Pmax=3.065 mw, FF=0.213) (Figure 31).

We have also examined the DMSO/PC in eight layers cell using Me_2SO_2 as electron transporter in 7th layer and Cl_4BQ/DMSO/PC in middle layers (Figure 32).

Figure 32: Construction of eight layers cell using sulfone electron transport in DMSO/PC solvent medium.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.953/0.230	3.465/0.239	3.845/0.247
48 h	1.528/0.229	2.806/0.259	3.131/0.281

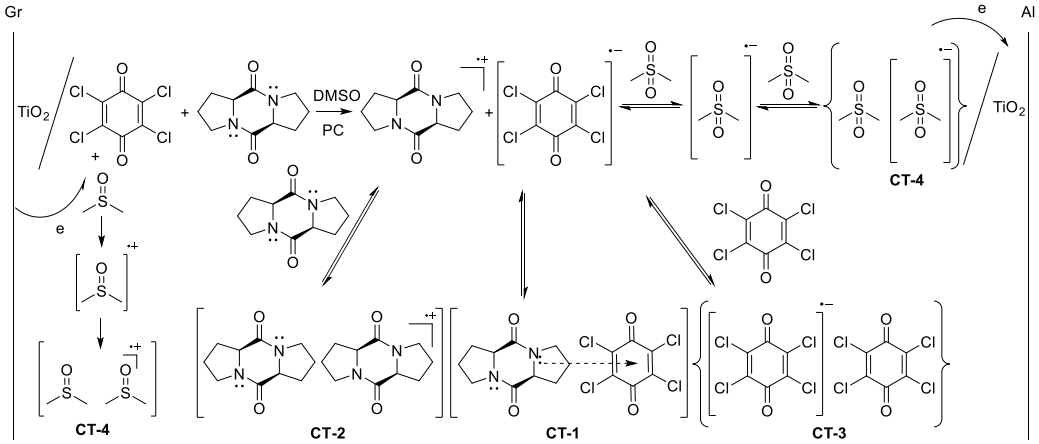
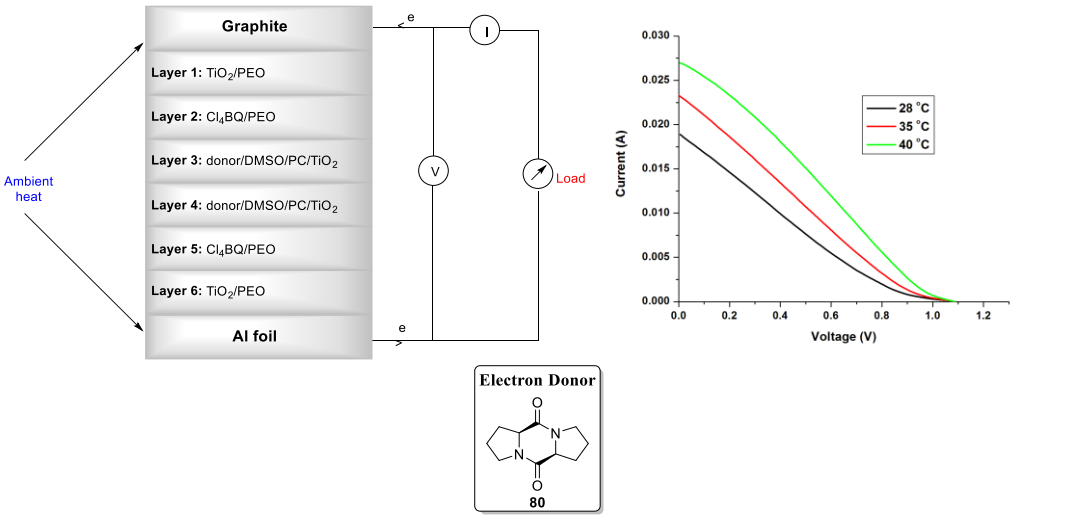


Figure 32. (a) Schematic diagram of eight layer cell using amide and *p*-chloranil and Me_2SO_2 as electron transport in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

Higher power output was realized at 1 h (Pmax=3.845 mW, FF=0.247) which decreased slightly at 48 h (Figure 32). We have also examined six layers cell using proline diamide **80** as donor in DMSO/PC solvent medium without electron transporter as shown in Figure 33.

Figure 33: Six layers cell in DMSO/PC solvent medium without electron transport.



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	4.136/0.186	5.467/0.219	6.944/0.263
48 h	3.976/0.194	5.430/0.215	7.530/0.256

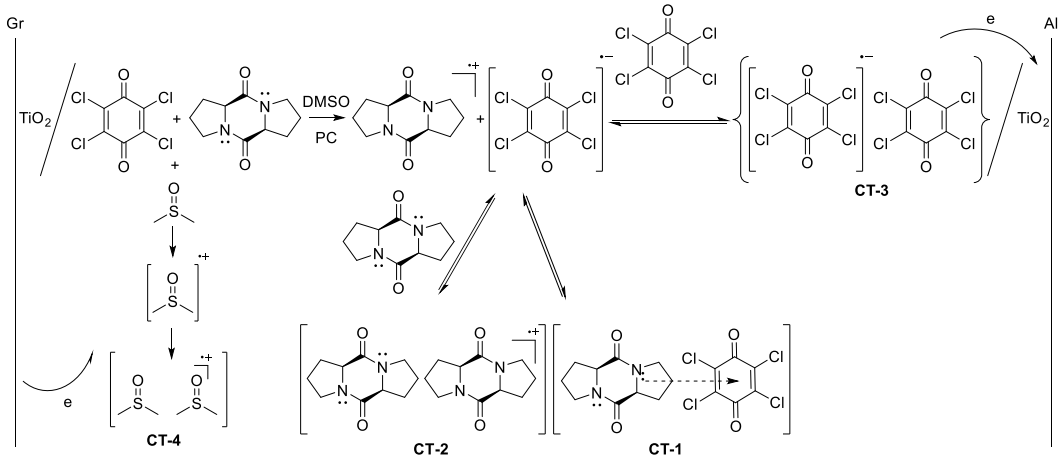


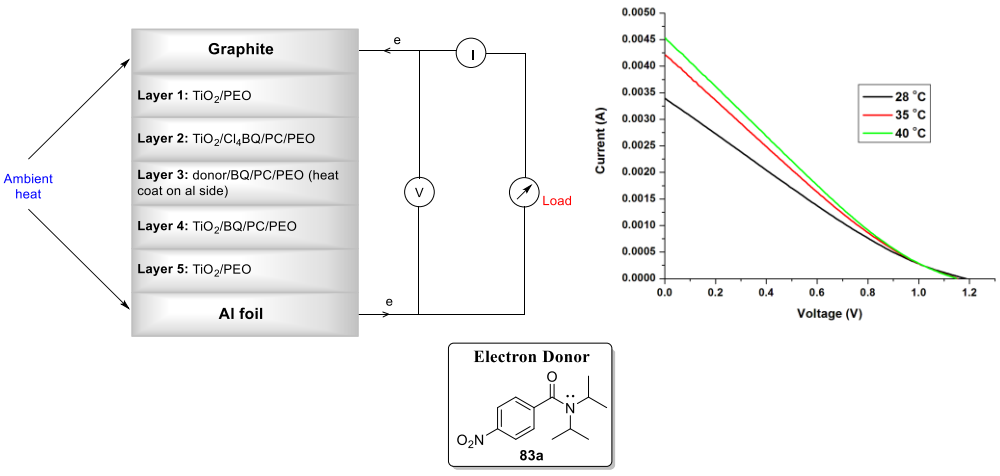
Figure 33. (a) Schematic diagram of six layer cell configuration using proline diamide donor and *p*-chloranil in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

Surprisingly, we have observed higher power outputs (Pmax=6.944 mW, FF=0.263) in the case of DMSO/PC without electron transporter compared to those obtained using DMSO/PC and Me_2SO_2 (Pmax=3.845 mW, FF=0.247) (Figure 32). Also, the Pmax slightly increased (Pmax=7.530 mW, FF=0.256) at 48 h (Figure 33).

3.2.10 Construction of electro chemical cells using substituted diisopropyl benzamides

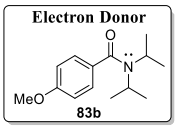
More recently, diisopropylbenzamide was used as donor to construct electrochemical cells in various configurations.[42] We have investigated the substituent effect of diisopropylbenzamide derivatives using *p*-methoxy, *p*-nitro and *p*-chloro substituents. Initially, we have constructed five layer electrochemical cells using 4-methoxy diisopropylbenzamide and 4-nitrodiisopropylbenzamide derivative as donors, *p*-chloranil as acceptor and BQ as electron transporter in PC solvent as shown in Figure 34.

Figure 34: Construction of five layer cells using BQ in PC solvent



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.085/0.232	1.498/0.240	1.720/0.242
48 h	0.851/0.212	1.027/0.212	1.108/0.213

…Figure 34 continued



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	0.713/0.239	0.754/0.239	0.957/0.239
48 h	0.452/0.225	0.558/0.227	0.593/0.222

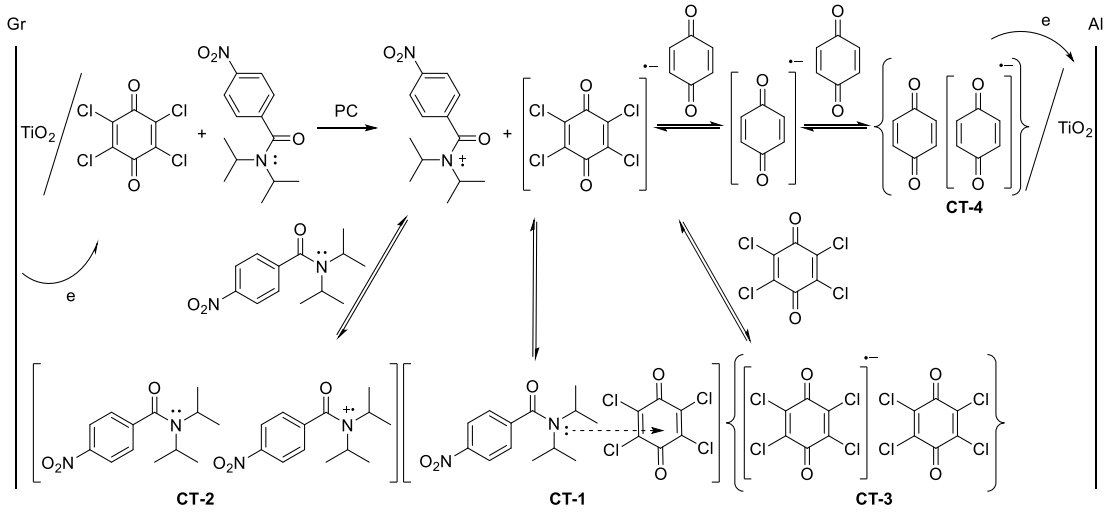
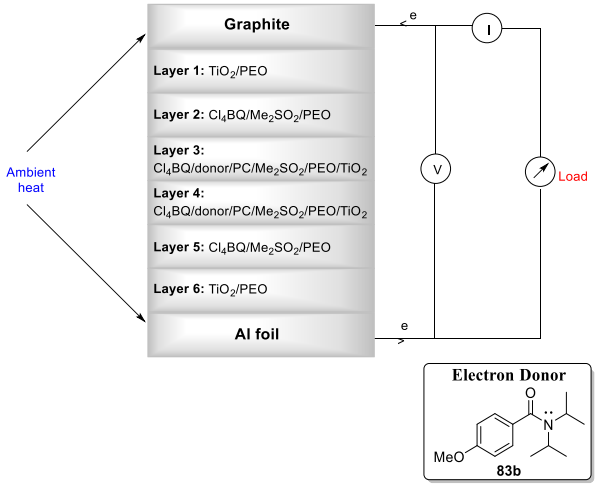


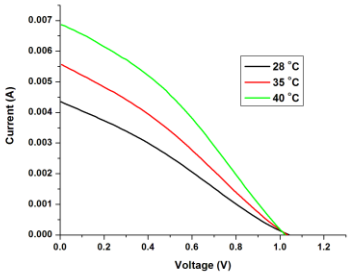
Figure 34. (a) Schematic diagram of five layer cell configuration using 4-methoxy diisopropylbenzamide and 4-nitrodiisopropylbenzamide donors and BQ as electron transport in PC solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The cell constructed using 4-methoxydiisopropylbenzamide gave lower power output compared to the cell using 4-nitrodiisopropylbenzamide (Figure 34).

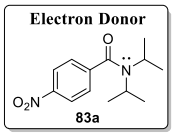
We have also constructed six layer cells using 4-methoxydiisopropylbenzamide, 4-nitrodiisopropylbenzamide and 4-chlorodiisopropylbenzamide derivatives as donors and Me_2SO_2 as electron transporter in PC solvent as shown in Figure 35.

Figure 35: Construction of six layer cells using sulfone (4 layers) in PC solvent.

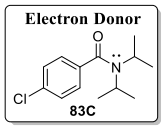




Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.938/0.276	2.227/0.277	4.265/0.324
48 h	1.279/0.283	1.703/0.297	2.312/0.329



1 h	1.934/0.251	2.213-0.259	2.632/0.276
48 h	0.830/0.251	0.938/0.253	2.136/0.278



1 h	1.075/0.252	1.276/0.265	1.309/0.267
48 h	0.082/0.261	0.164/0.285	0.356/0.313

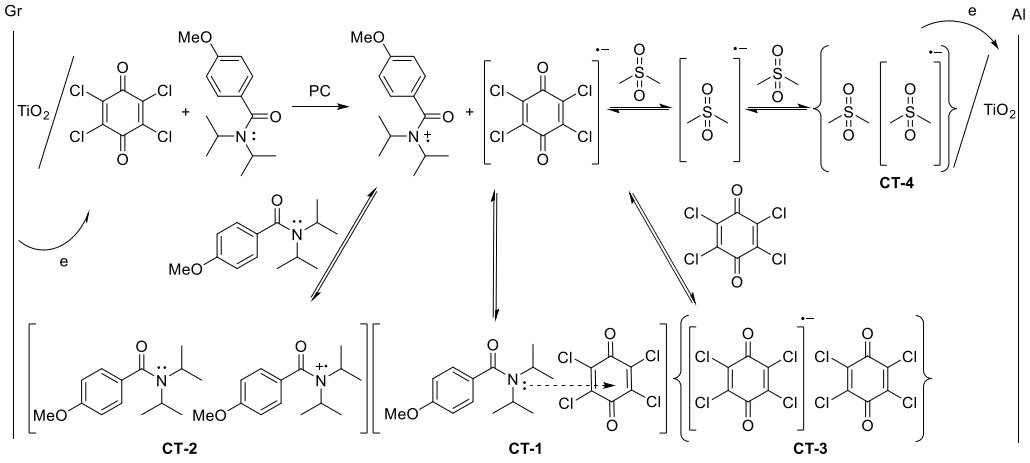
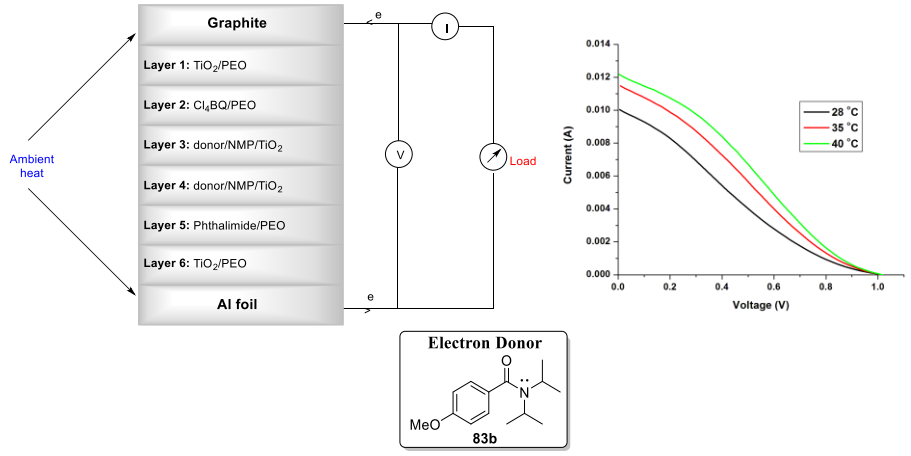


Figure 35. (a) Schematic diagram of six layer cell configuration using 4-substituted diisopropyl benzamides as donors and Me_2SO_2 as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

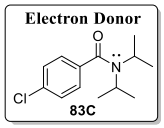
Among these three substituted diisopropylbenzamide derivatives, 4-methoxydiisopropylbenzamide gave the higher power output which decreased with time (Figure 35).

In continuation of these studies, we have also constructed cells using substituted diisopropylbenzamide derivatives as donors in NMP solvent and phthalimide as electron transport as shown in Figure 36.

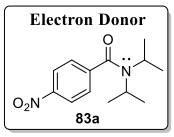
Figure 36: Six layer cells using phthalimide electron transport in NMP solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.302/0.219	1.465/0.203	1.991/0.223
48 h	2.167/0.213	2.927/0.251	3.416/0.276



1 h	1.158/0.297	1.185/0.291	1.506/0.334
48 h	0.093/0.266	0.481/0.244	0.752/0.255



1 h	0.478/0.200	0.561/0.181	0.578/0.183
48 h	2.164/0.271	2.670/0.272	2.791/0.288

…Figure 36 continued

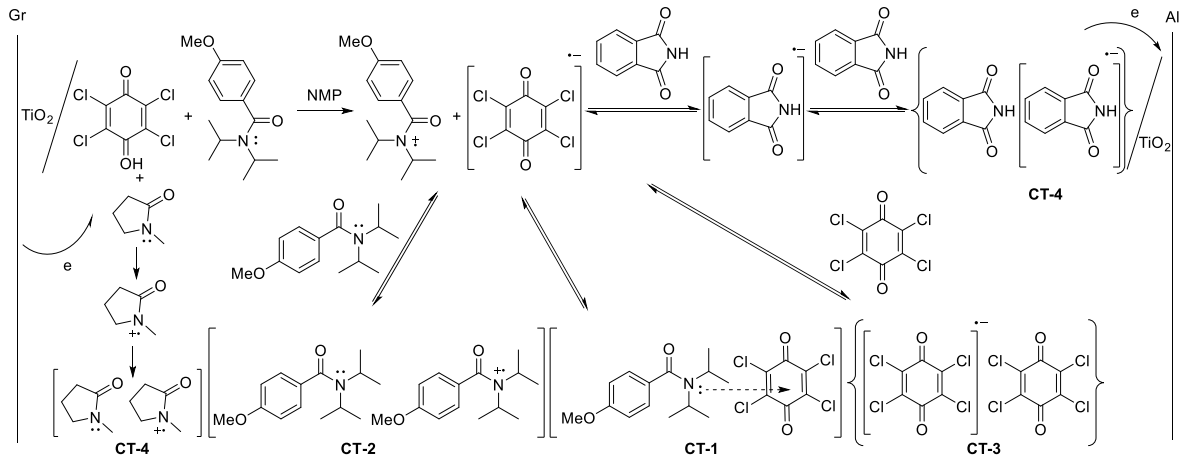
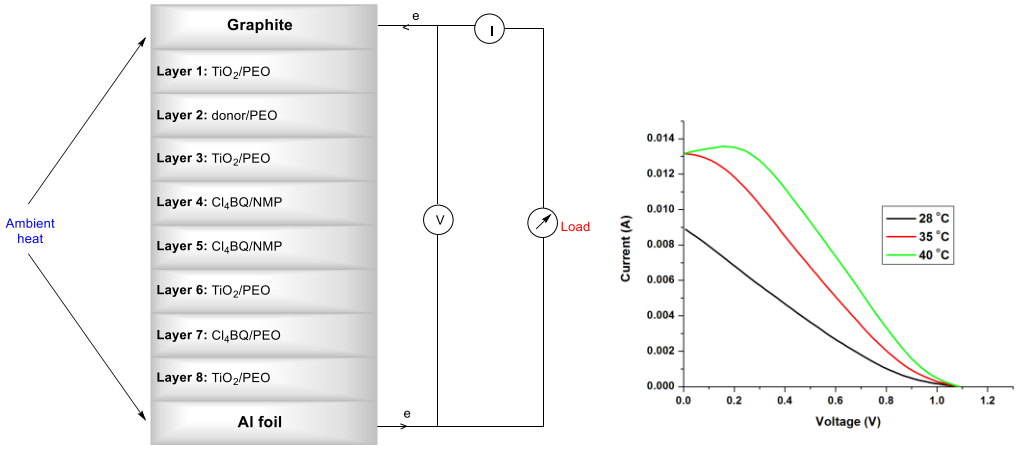


Figure 36. (a) Schematic diagram of six layer cell configuration using amide donors and phthalimide as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

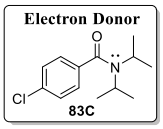
The cells constructed using *p*-methoxy and *p*-nitro derivatives gave higher power output at 48 h (Figure 36).

We have then examined eight layer cells in NMP solvent. In this cell configuration, the 4-chloro derivative **83c** gave higher power output after 48 h (Pmax=4.654 mW, FF=0.325). Also, the 4-methoxy and 4-nitro derivatives gave similar Pmax values even after 48 h (Figure 37).

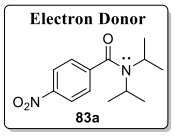
Figure 37: Construction of 8 layer cells using without electron transporter in NMP solvent



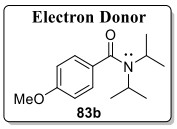
…Figure 37 continued



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	1.601/0.203	2.934/0.329	3.726/0.364
48 h	1.876/0.196	3.423/0.241	4.654/0.325



1 h	1.238/0.227	2.008/0.298	2.708/0.363
48 h	1.574/0.214	2.639/0.257	2.894/0.306



1 h	0.536/0.193	0.933/0.267	0.981/0.216
48 h	0.395/0.220	0.726/0.224	0.827/0.228

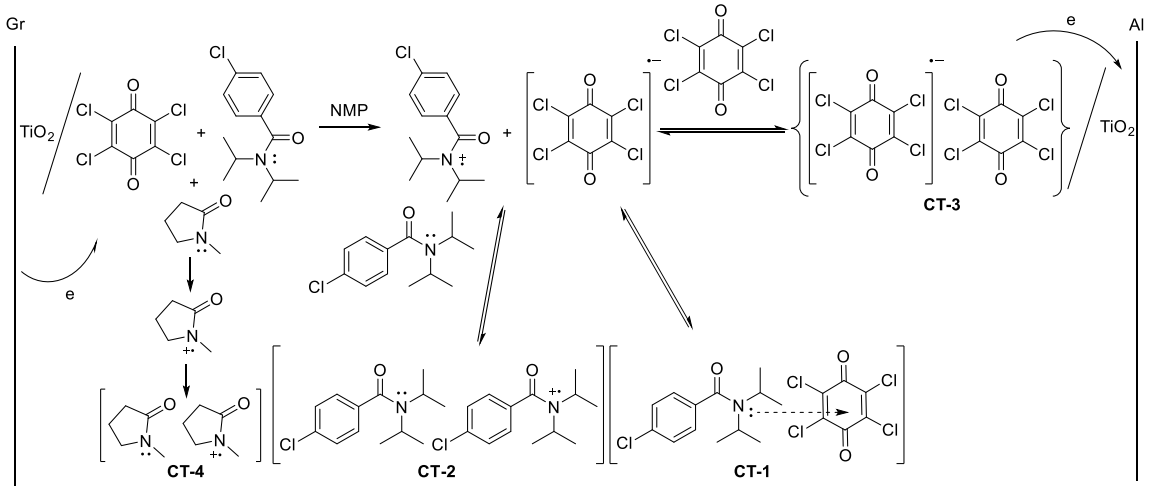
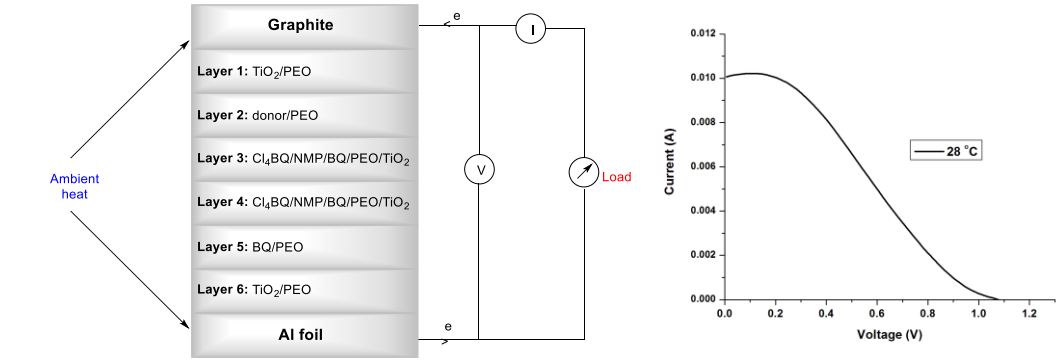


Figure 37. (a) Schematic diagram of eight layer cell configuration using amide donors and *p*-chloranil in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

We have also constructed six layer cells using 4-methoxydiisopropylbenzamide, 4-nitrodiisopropylbenzamide and 4-chlorodiisopropylbenzamide derivatives. The *p*-chloranil was used in NMP solvent in middle layers. Also, electron transporter BQ was used in 3, 4

and 5 layers. Among three derivatives, 4-methoxy and 4-nitro diisopropylbenzamide derivatives gave higher power outputs (Figure 38).

Figure 38: Six layer cells using BQ electron transport in NMP solvent.



Electron Donor	Time	Pmax/mW/FF(28 °C)
83b	1 h	4.967/0.167
	48 h	3.328/0.307
Electron Donor	Time	Pmax/mW/FF(28 °C)
83a	1 h	3.753/0.168
	48 h	4.196/0.293
Electron Donor	Time	Pmax/mW/FF(28 °C)
83C	1 h	3.652/0.185
	48 h	0.855/0.219

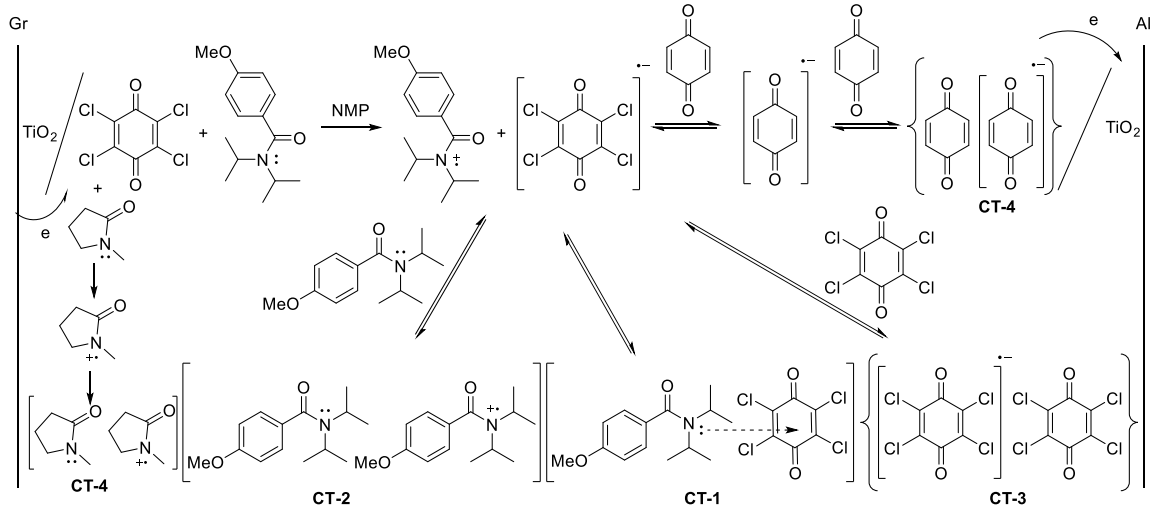
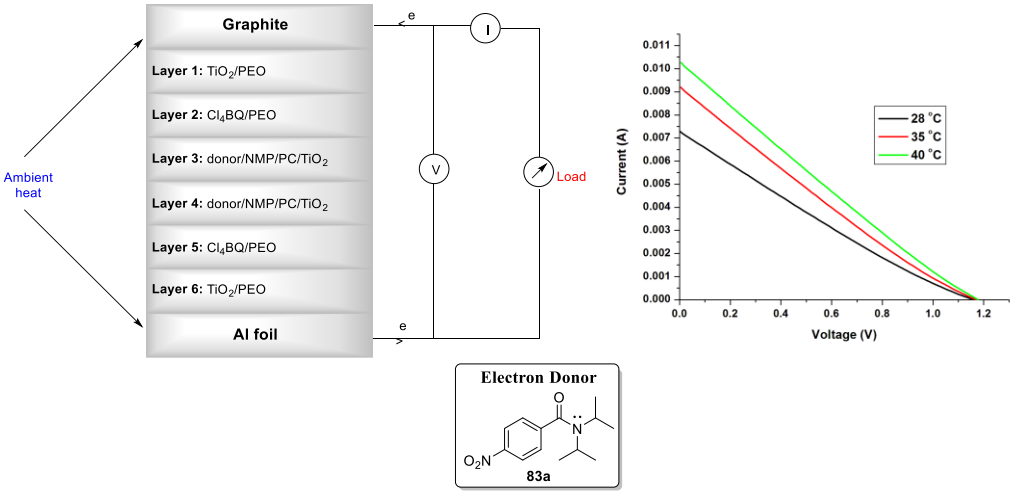


Figure 38. (a) Schematic diagram of six layer cell configuration using amide donors and *p*-chloranil and BQ as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In the six layer configuration in PC/NMP solvent, the *p*-nitro derivative gave somewhat stable cell but the power output was low (Figure 39).

Figure 39: Six layer cells in NMP/PC solvent medium without electron transport.

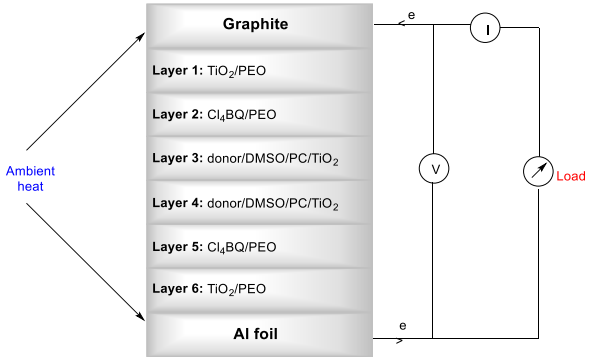


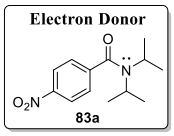
Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.450/0.220	2.795/0.221	2.987/0.228
48 h	1.900/0.225	2.424/0.225	2.826/0.234

Figure 39. (a) Schematic diagram of six layer cell configuration using several donors and *p*-chloranil in NMP/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) The tentative mechanism for electron transport is similar to that of Figure 37.

Interestingly, the power outputs were almost the same after 1 h packing and also at 48 h (Figure 39). We have also examined the use of DMSO/PC in this configuration (Figure 40).

Figure 40: Six layers cell using without electron transporter in DMSO/PC solvent.





Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	1.878/0.222	2.527/0.227	2.564/0.234
48 h	2.250/0.225	2.971/0.238	3.515/0.251

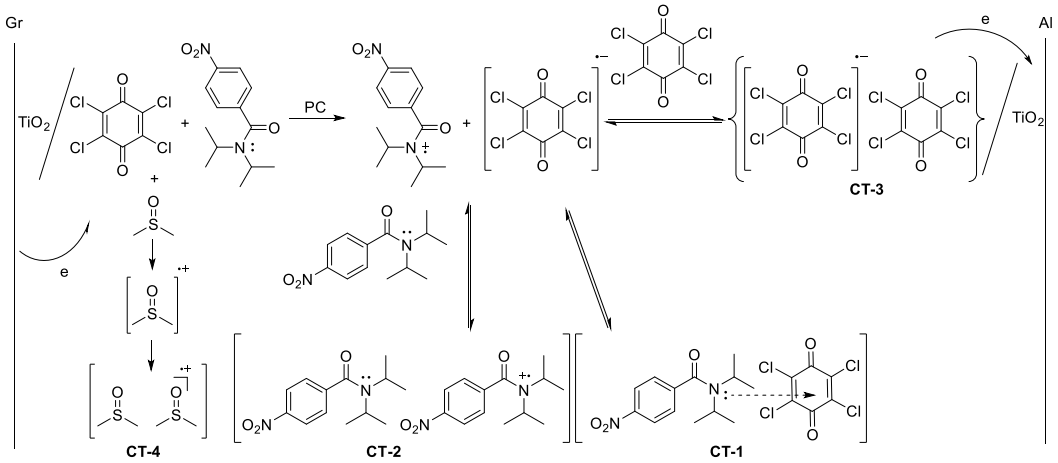
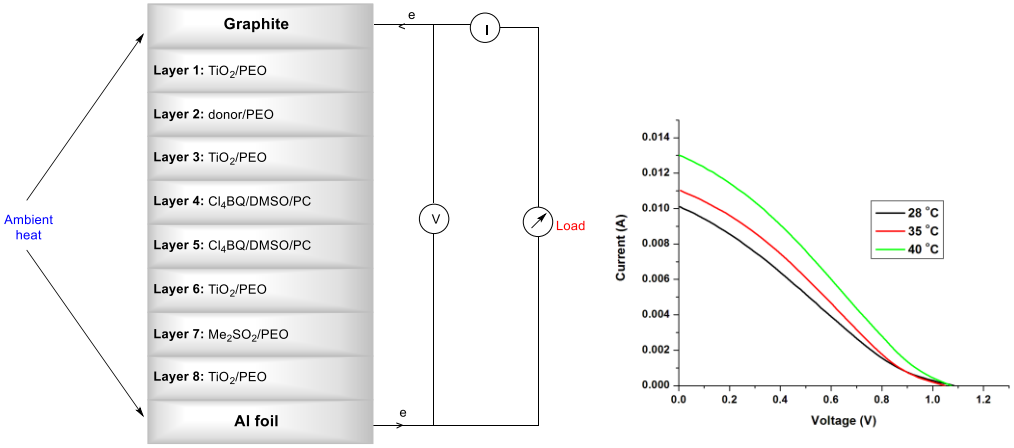


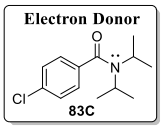
Figure 40. (a) Schematic diagram of six layer cell configuration using amide donors and *p*-chloranil in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The cell constructed using 4-nitro derivative in this configuration gave higher power output at 48 h (Pax=3.515 mW, FF=0.251) (Figure 40). Then, we studied eight layer cells using the DMSO/PC solvent with Me_2SO_2 electron transporter (Figure 41).

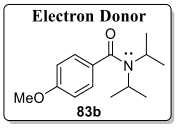
Figure 41: Eight layer cells using sulfone electron transport in DMSO/PC solvent.



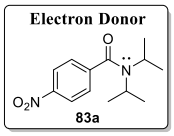
…Figure 41 continued



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	3.076/0.215	4.264/0.230	4.424/0.238
48 h	2.600/0.237	3.066/0.265	3.808/0.273



1 h	3.251/0.235	3.397/0.240	3.658/0.257
48 h	1.108/0.280	1.796/0.288	2.005/0.321



1 h	2.240/0.197	2.272/0.209	3.513/0.219
48 h	2.012/0.218	2.598/0.244	3.238/0.246

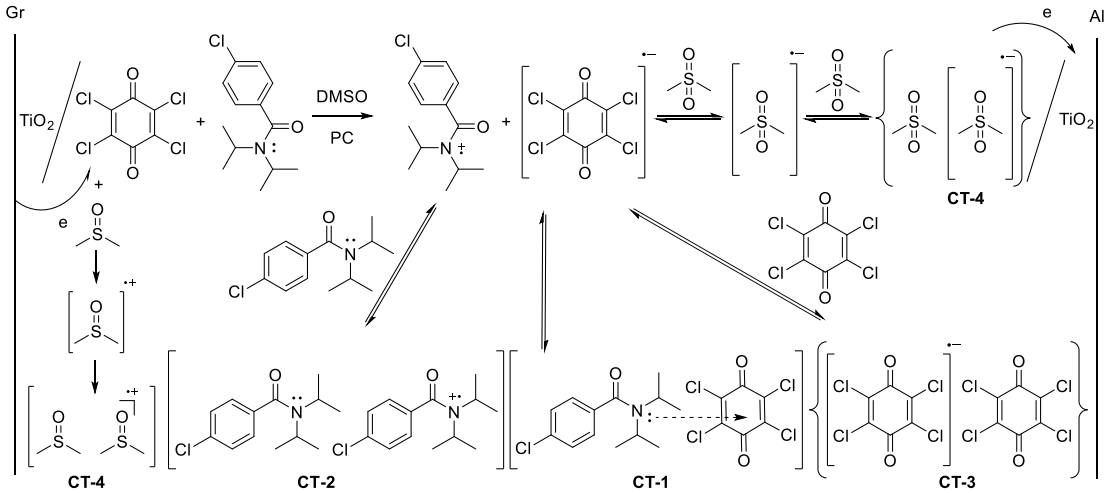


Figure 41. (a) Schematic diagram of eight layer cell configuration using *p*-chloranil and Me_2SO_2 as electron transport in DMSO/PC. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

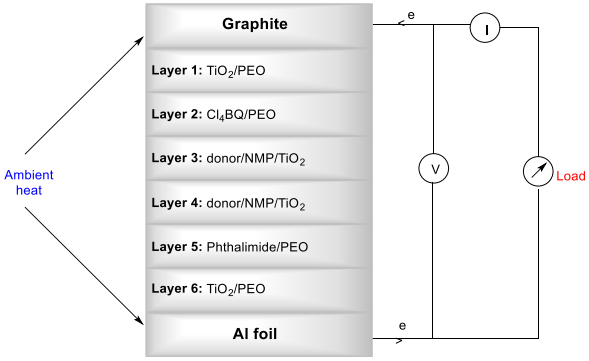
The donor/PEO layer was coated close to Gr sheet, whereas the Me_2SO_2 layer was closer to Al foil as shown in Figure 40. The acceptor *p*-chloranil in the DMSO/PC middle

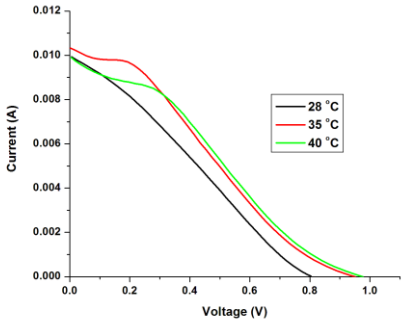
layers. In this configuration, the 4-chloro and 4-nitro derivatives gave better power output which dereased to more extent after 48 h (Figure 41).

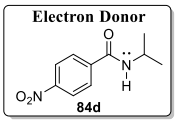
3.2.11 Construction of electro chemical cells using isopropylbenzamides 84a-84d

We have also investigated the isopropylbenzamide **84a** and substituted isopropylbenzamide derivatives **84b-84d** as donors in different configurations.

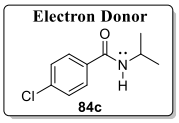
Figure 42: Six layer cells using phthalimide electron transport in NMP solvent.



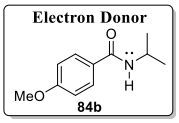




Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	0.739/0.210	0.781/0.211	0.937/0.212
48 h	1.597/0.214	1.738/0.219	1.899/0.226



1 h	0.477/0.199	0.526/0.203	0.749/0.208
48 h	1.405/0.215	1.622/0.220	1.673/0.225



1 h	0.593/0.170	0.649/0.153	0.719/0.201
48 h	1.675/0.216	1.850/0.224	1.952/0.228

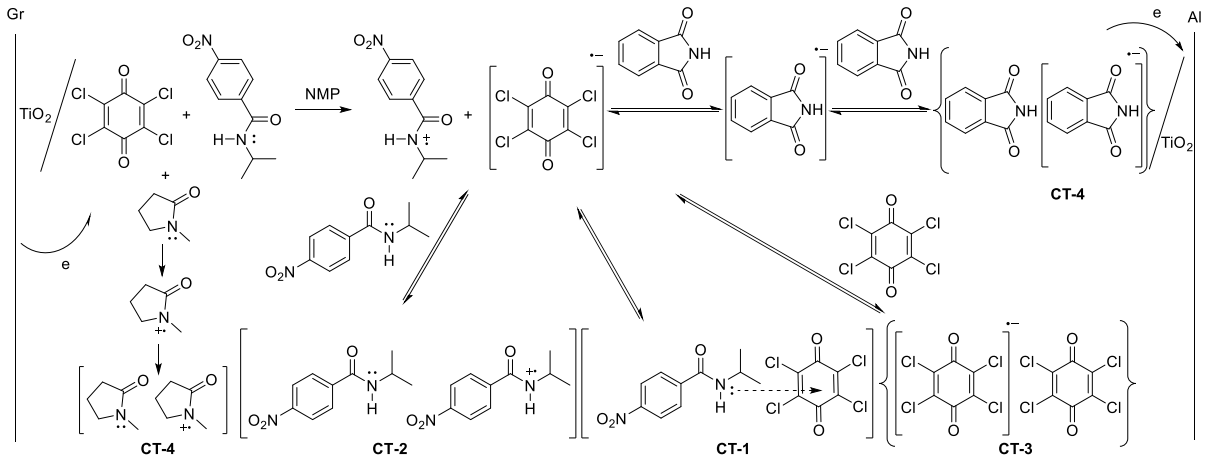
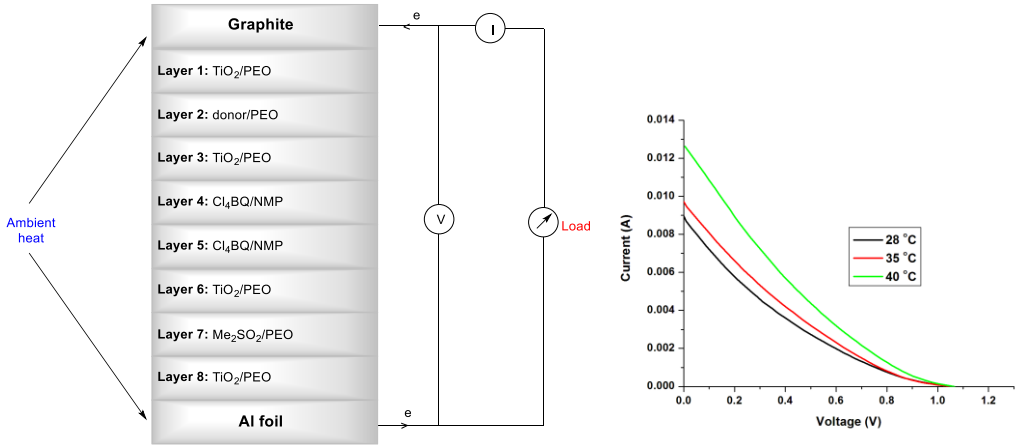


Figure 42. (a) Schematic diagram of six layer cell configuration using amide donors and phthalimide as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

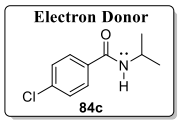
Initially, six layer cells constructed using the 4-methoxy, 4-chloro and 4-nitroisopropylbenzamides, *p*-chloranil and phthalimide electron transporter in NMP solvent. Although, power output were very poor but the Pmax values increased at 48 h. Among these derivatives the 4-nitro derivative gave higher power (Figure 42).

We have also examined eight layer cells in NMP solvent and Me_2SO_2 as electron transport as shown in Figure 43.

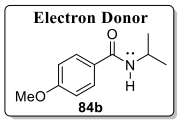
Figure 43: Eight layer cells using sulfone electron transport in NMP solvent.



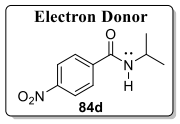
…Figure 43 continued



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	1.793/0.160	2.465/0.192	2.861/0.209
48 h	1.440/0.151	1.681/0.165	2.280/0.170



1 h	1.568/0.165	2.791/0.228	2.815/0.224
48 h	1.295/0.173	1.511/0.190	2.011/0.194



1 h	0.628/0.131	0.940/0.150	1.055/0.156
48 h	0.600/0.132	0.773/0.152	0.841/0.143

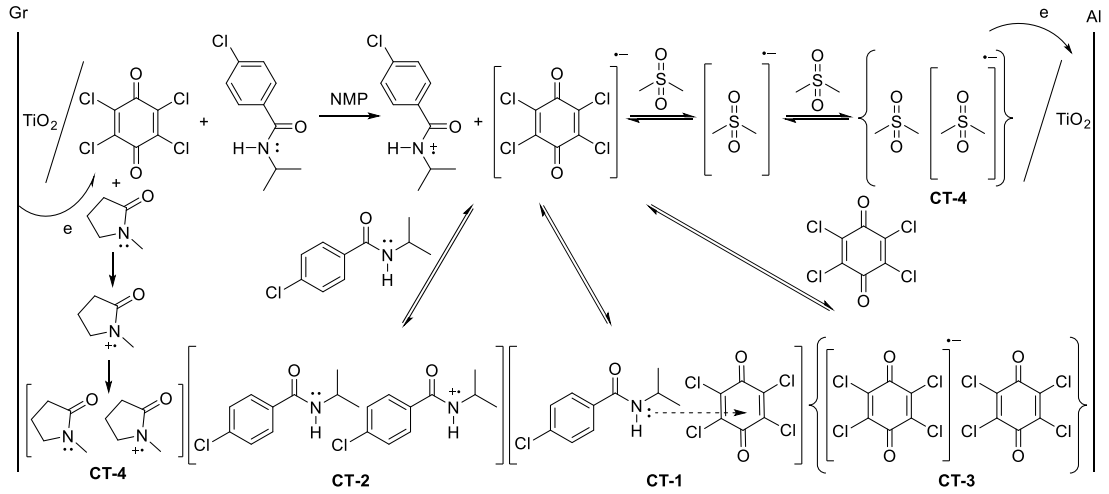
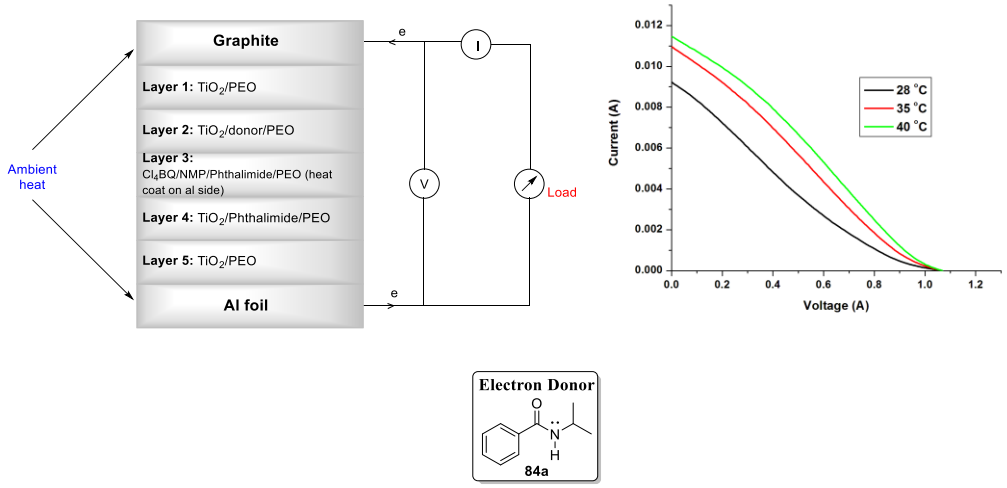


Figure 43. (a) Schematic diagram of eight layer cell configuration using amide donors and *p*-chloranil and Me_2SO_2 as electron transport in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

The 4-chloro derivative gave comparatively higher power output which decreased after 48 h in this configuration (Figure 43).

The unsubstituted isopropylbenzamide gave better results (Pmax=3.541 mW, FF=0.278) in a 5 layer cell configuration using phthalimide as electron transporter. Also, the power output realized after 48 h (Pmax=3.334 mW, FF=0.272) was almost same as that at 1 h. (Figure 44).

Figure 44: Five layer cells using phthalimide electron transport in NMP solvent.



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.567/0.257	3.018/0.272	3.541/0.278
48 h	1.930/0.196	2.853/0.244	3.334/0.272

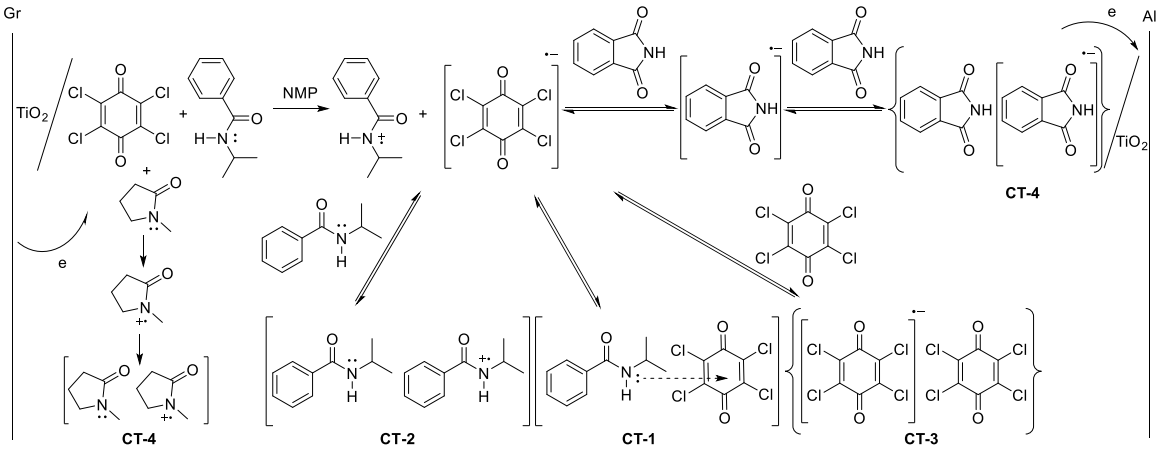
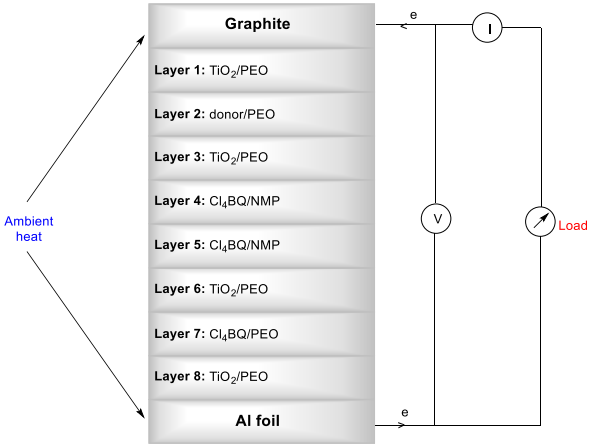
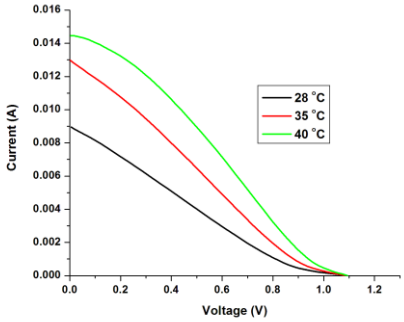


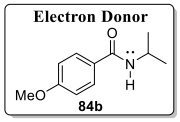
Figure 44. (a) Schematic diagram of five layer cell configuration using isopropylbenzamide donor phthalimide as electron transport. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

We have then constructed eight layer cells taking *p*-chloranil along with NMP solvent in middle layers without electron transporter.

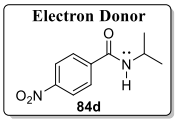
Figure 45: Eight layer cells using without electron transport in NMP solvent



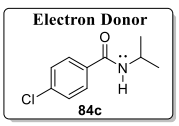




Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	2.070/0.251	3.574/0.348	3.968/0.373
48 h	2.051/0.212	3.259/0.231	4.472/0.283



1 h	1.484/0.207	2.974/0.282	3.024/0.292
48 h	1.702/0.209	3.109/0.234	4.657/0.290



1 h	1.170/0.188	2.082/0.279	2.239/0.291
48 h	1.433/0.189	2.250/0.216	2.816/0.252

...Figure 45 continued

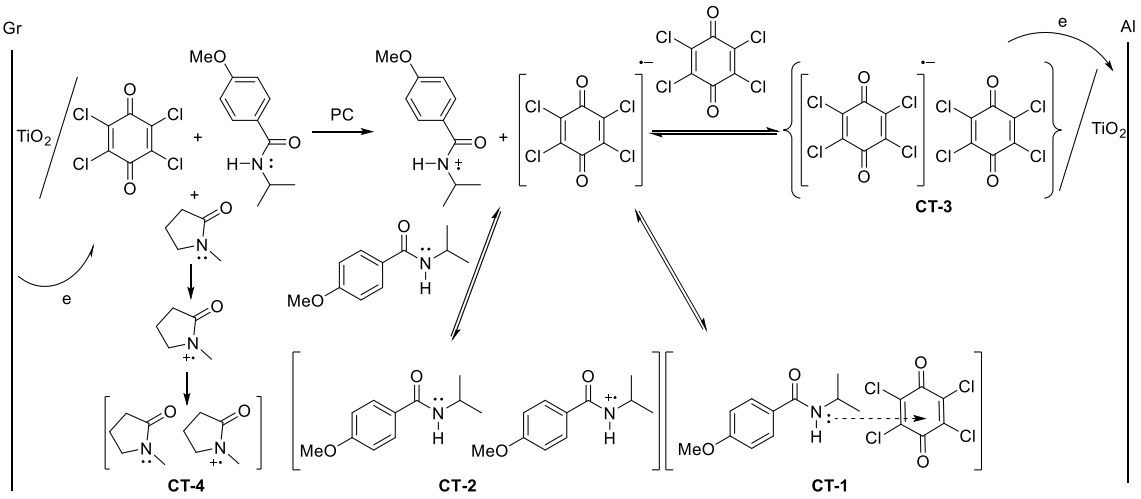
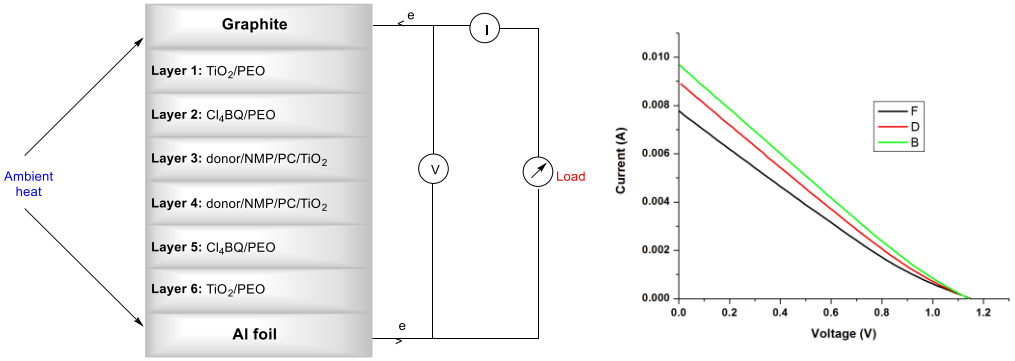


Figure 45. (a) Schematic diagram of eight layer cell configuration using amide donors and *p*-chloranil in NMP solvent. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

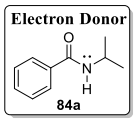
The donor/PEO layer was coated close to Gr sheet as shown in Figure 45. In this configuration, 4-methoxy derivative gave higher power (Pmax=3.968 mW, FF=0.373) among three derivatives. Also, the Pmax increased at 48 h (Figure 45).

We have also examined the isopropylbenzamide derivative in NMP/PC solvent combination without electron transporter with donor/NMP/PC/TiO_2 in middle layers. In this configuration, the power output was not high but stable even at 48 h (Figure 46).

Figure 46: Six layer cells using without electron transport in NMP/PC solvent.



…Figure 46 continued



Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.032/0.215	2.375/0.216	2.429/0.225
48 h	1.944/0.218	2.280/0.224	2.547/0.231

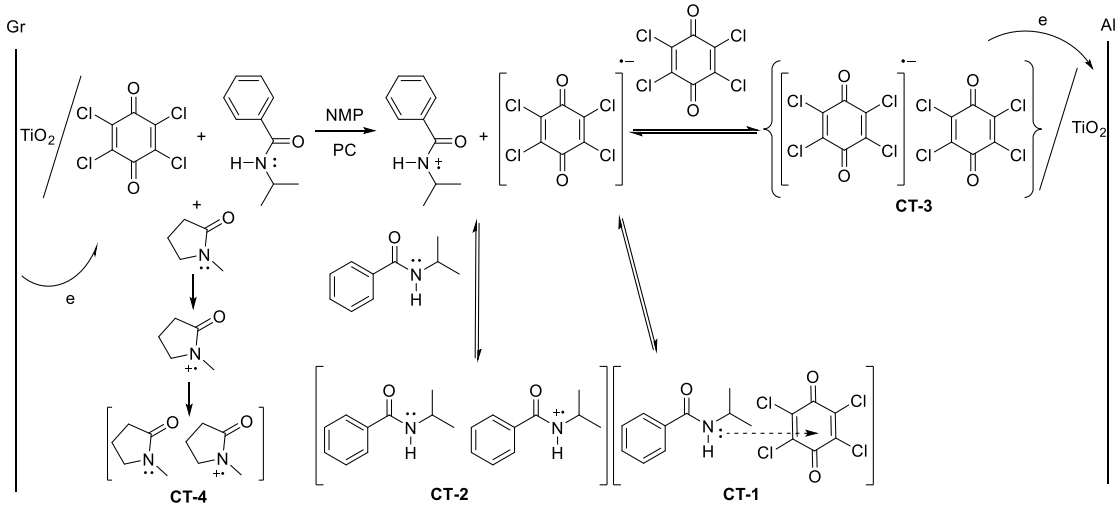
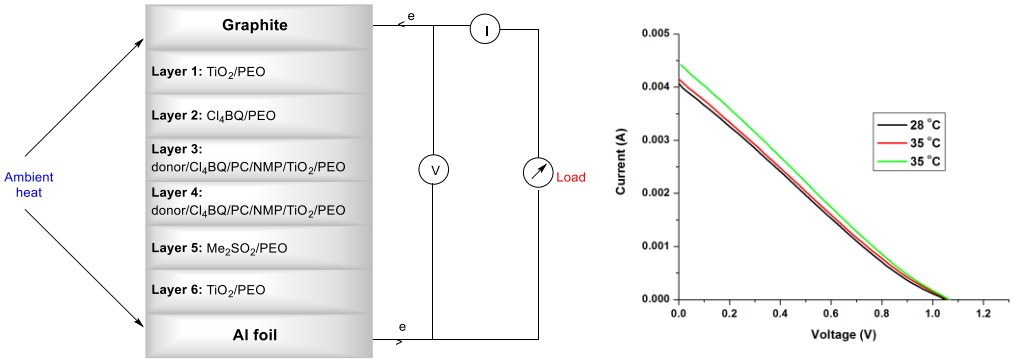


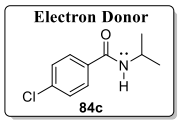
Figure 46. (a) Schematic diagram of six layer cell configuration using amide donors and *p*-chloranil in NMP/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

We have also examined the six layer cell constructed using the donor and acceptor in NMP/PC in middle layer using the Me_2SO_2 electron transporter (Figure 47).

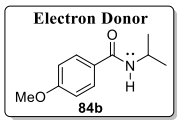
Figure 47: Six layer cells using sulfone electron transport in NMP/PC solvent



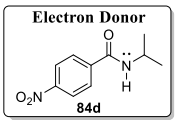
…Figure 47 continued



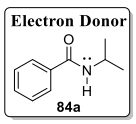
Time	Pmax/mW/FF(28 ºC)	Pmax/mW/FF(35ºC)	Pmax/mW/FF(40 ºC)
1 h	2.569/0.221	2.922/0.215	3.512/0.226
48 h	0.982/0.231	1.019/0.232	1.106/0.235



1 h	2.396/0.222	2.732/0.214	3.370/0.228
48 h	1.053/0.231	1.090/0.234	1.311/0.240



1 h	2.440/0.223	2.754/0.218	3.303/0.223
48 h	1.909/0.213	2.071/0.224	2.382/0.228



1 h	2.547/0.223	2.311/0.216	3.162/0.230
48 h	1.184/0.228	1.251/0.233	1.484/0.236

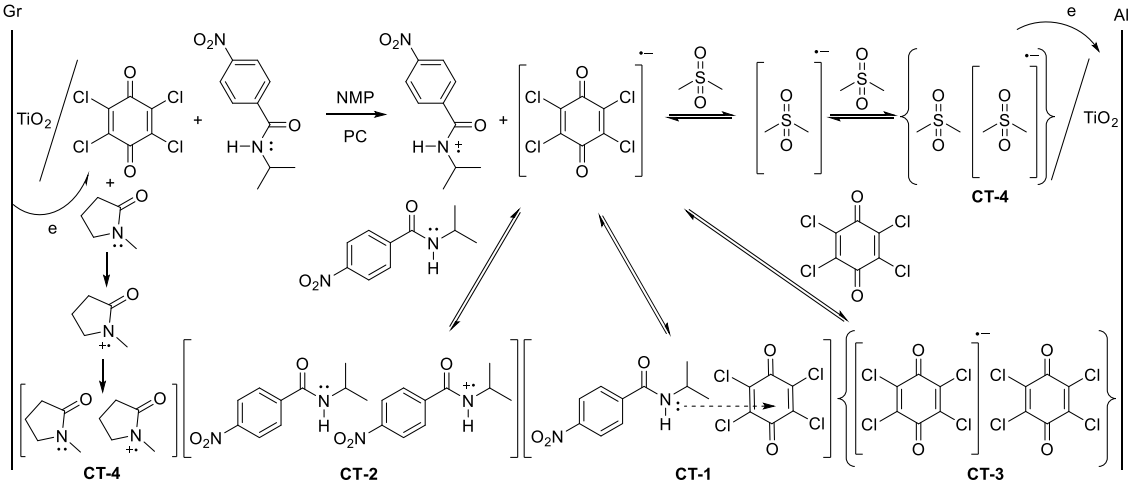
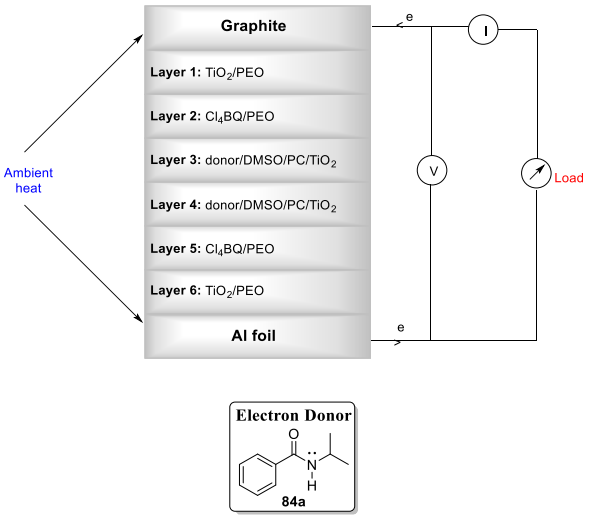


Figure 47. (a) Schematic diagram of six layer cell configuration using amide donors and *p*-chloranil and Me_2SO_2 as electron transport in NMP/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

In these cells, Pmax values were in the same range at 1 h but decreased with time (Figure 47). We have also examined the use of DMSO/PC in this configuration (Figure 48).

Figure 48: Six layers cell using without electron transporter in DMSO/PC solvent.



Time	Pmax/mW/FF(28 °C)	Pmax/mW/FF(35°C)	Pmax/mW/FF(40 °C)
1 h	2.912/0.214	3.569/0.225	3.672/0.231
48 h	3.659/0.227	4.395/0.236	5.125/0.252

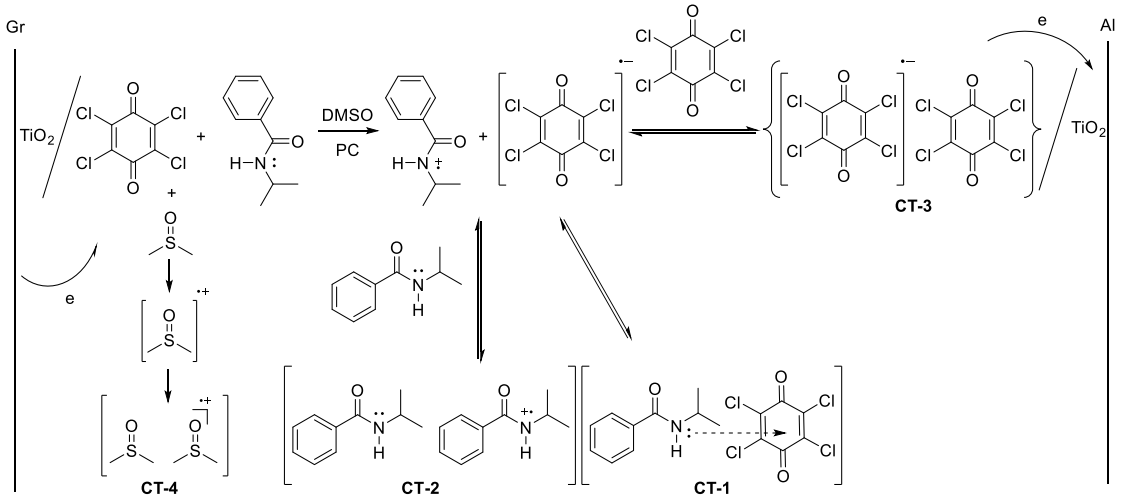


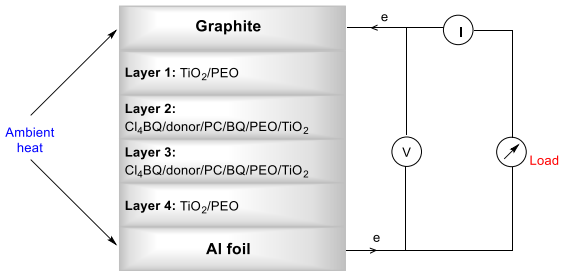
Figure 48. (a) Schematic diagram of six layer cell configuration using amide donors and *p*-chloranil in DMSO/PC solvent medium. (b) Representative IV curve for the cell measured after 48 h packing. (c) Tentative mechanism for electron transport to the electrodes via D/D.+and A-/A exchange reactions.

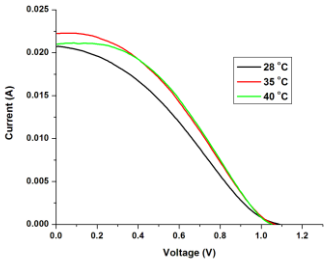
The cell constructed using isopropylbenzamide in this configuration gave Pmax=3.672 mW, FF=0.231 at 1 h which increased at 48 h (Pmax=5.125 mW, FF=0.252) (Figure 48).

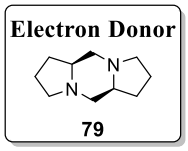
Although the variations in power output realized with various cell configurations are not clearly understood at this stage, the results should be helpful in planning further reaserch work in the construction of organic electrochemical cells for practical applications.

3.3 Conclusions

We have constructed electricity harvesting cells using piperazine derivative **79** as donor and *p*-chloranil acceptor and benzoquinone electron transporter in PC solvent, which produced power Pmax 21.08 mW, FF 0.251 at 40 ºC at 1 h and Pmax 8.818 mW, FF 0.399 at 48 h (Figure 17).

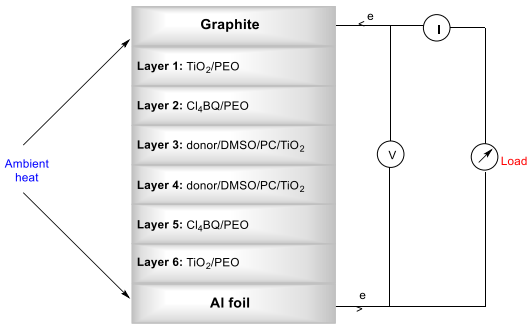


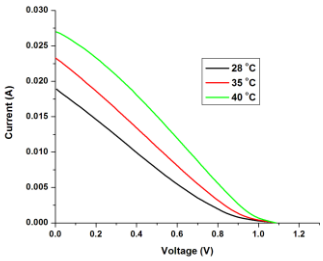


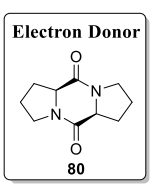


Time	Pmax/mW/FF(40 ºC)
After 1 h	21.08/0.251
After 48 h	8.818/0.399

The cell constructed using the proline diamide **80** and DMSO/PC gave Pmax 6.944 mW, FF 0.263 at 40 ºC at 1 h and Pmax 7.53 mW, FF 0.256 at 48 h (Figure 33).

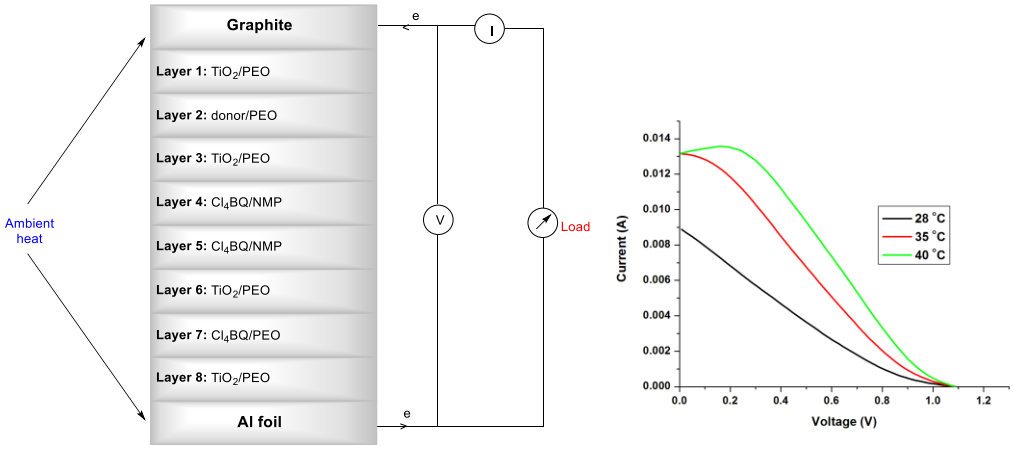


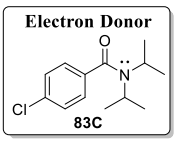




Time	Pmax/mW/FF(40 ºC)
After 1 h	6.944/0.263
After 48 h	7.530/0.256

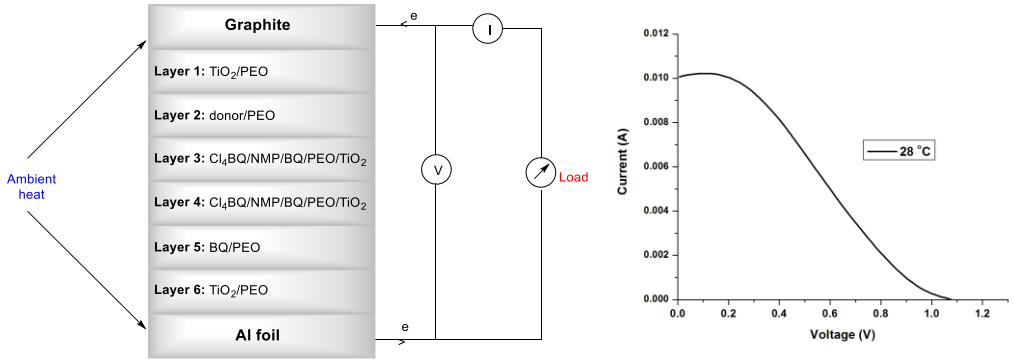
The cell constructed using the amide **83c** and Cl_4BQ in NMP solvent in eight layer configuration also gave stable power output (Figure 37).

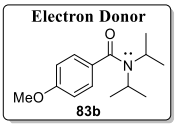




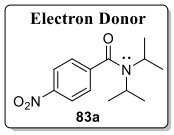
Time	**Pmax/mW/FF(40 ºC)**
After 1 h	3.726/0.364
After 48 h	4.654/0.325

The cells constructed using the amide **83b** and **83a** Cl_4BQ in NMP solvent in six layer configuration also gave stable power output (Figure 38).



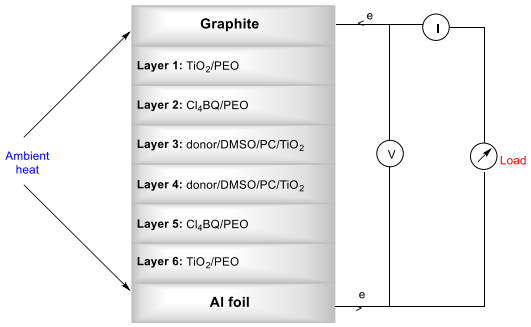


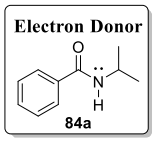
Time	**Pmax/mW/FF(40 ºC)**
After 1 h	4.967/0.167
After 48 h	3.328/0.307



Time	**Pmax/mW/FF(40 ºC)**
After 1 h	3.753/0.168
After 48 h	4.196/0.293

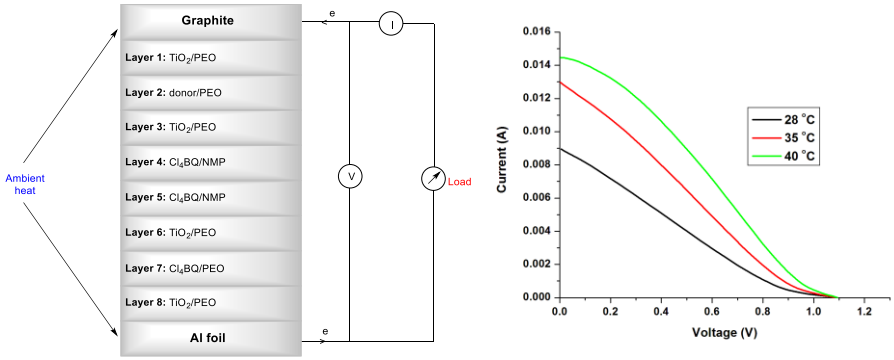
The cell constructed using the donor **84a** and Cl_4BQ in DMSO/PC also gave good results (Figure 48).

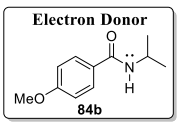




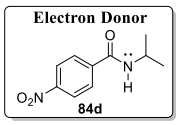
Time	Pmax/mW/FF(40 °C)
After 1 h	3.672/0.231
After 48 h	5.125/0.252

Also, the cells constructed using the donor **84b, 84c, 84d** and Cl_4BQ in NMP gave good results (Figure 45).

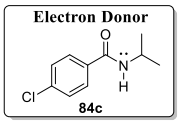




Time	Pmax/mW/FF(40 °C)
After 1 h	3.968/0.373
After 48 h	4.472/0.283



After 1 h	3.024/0.292
After 48 h	4.657/0.290



After 1 h	2.239/0.291
After 48 h	2.816/0.252

Hence, the cells constructed here have potential for the development of electricity harvesting cell devices for practical large scale applications.

3.4. Experimental Section

3.4.1 General Information

P-Chloranil, and TiO_2 were purchased from Avra chemicals (India). *p*-benzoquinone (BQ), triphenylamine (TPA), N,N'-tetramethyl-1,4-phenylenediamine (TMPD), propylene carbonate (PC), ethylene carbonate (EC) and polyethylene oxide (PEO) were purchased from Sigma Aldrich. Netural alumina (Al_2O_3) was purchased from SRL chemicals, India. Zinc oxide (ZnO) was purchased from E-Merck, India. The metal oxides were heated at 150 °C in a vacuum oven for 2 h before use. PC and EC were always kept under molecular sieves. N, N-diisopropylbenzamide was prepared from the literature procedure. Graphite sheet (0.4mm thickness, 5cm x 5cm, Resistivity, $\rho = 2x10^{-4}\Omega.m$) was purchased from Falcon Graphite Industries, Hyderabad, India. Aluminium Foil (0.2mm thickness, 5cm x 5cm, Resistivity, $\rho = 2x10^{-5}\Omega.m$) and Stainless steel (0.4mm thickness, 5cm x 5cm, Resistivity, $\rho = 5x10^{-4}\Omega.m$) were purchased from Aluminium Enterprises and Rasik Metals, Hyderabad, India. EPR spectra was recorded on a Bruker-ER073 instrument equipped with an EMX micro X source for X band measurement using Xenon 1.1b.60 software provided by the manufacturer. Electrical measurements were carried out by ZAHNER instrument using CIMPS software. The current-voltage curve was drawn using Origin software.

3.4.2 Procedure for IV measurement for electrochemical cell

The voltage and current of the fabricated cell was initially measured using the multimeter. The IV characteristics were measured by ZAHNER instrument using CIMPS software. The IV characteristics of the cell were done under dark condition without illumination of light. The cell was recorded at scan rate of 1mV/S to get maximum power

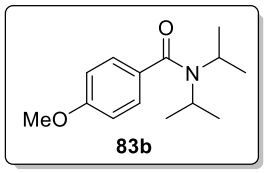
(Pmax) and fill factor (FF). The cell potentiostat should be open circuit voltage (Voc) before the measurement.

3.4.3 Procedure for preparation of benzamide derivatives

In an oven dried round bottomed flask, the amine (20 mmol) in dry dichloromethane (60 mL) solvent was taken and triethylamine (2.1 mL, 21 mmol) was added slowly at room temperature with constant stirring. Then the reaction mixture was stirred for 1 h and corresponding benzoyl chloride (20 mmol) was added at 0 ^{o}C. Then the reaction mixture was brought to room temperature and it stirred for 8 h. The mixture was quenched with saturated ammonium chloride solution and the organic layer was separated. The organic layer was extracted with dichloromethane (2x50 mL). The combined organic extracts were washed with saturated NaCl solution (15 mL) and dried over anhydrous Na_2SO_4. Then the solvent was evaporated to get the crude product. The corresponding crude amide product was purified by column chromatography on silica gel (100-200) using hexane and ethyl acetate as eluent to isolate pure amide product.

***N*, *N*-Diisopropyl-4-methoxybenzamide**

Yield **:** 4.2 g (90%), Colorless liquid



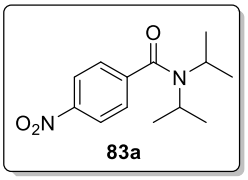
83b

IR (neat) **:** 2969, 2935, 1779, 1771, 1609, 1512, 1440, 1371, 1340, 1297, 1251, 1160, 1031, 764 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 7.85-7.84 (m, 2H), 7.03-7.02 (m, 2H), 5.28 (s, 3H), 3.80-3.79 (m, 2H), 1.26-1.25 (m, 12H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 171.1, 159.7, 132.8, 127.5, 113.7, 55.2, 53.3, 20.4.

***N, N*-Diisopropyl-4-nitrobenzamide**



83a

Yield **:** 4.4 g (88%), Yellow solid

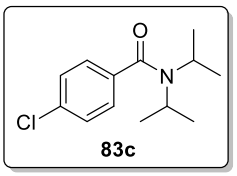
mp : 134-136 ^oC

IR (KBr) **:** 2976, 2931, 1634, 1598, 1521, 1492, 1345, 1211, 1192, 1161, 1136, 1036, 758, 714 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 8.30-8.23 (m, 2H), 7.52-7.45 (m, 2H), 3.68-3.57 (m, 2H), 1.55-1.17 (m, 12H)

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 168.6, 148.7, 144.3, 126.3, 123.7, 51.7, 46.120.5.

4-Chloro-*N, N*-diisopropylbenzamide



83c

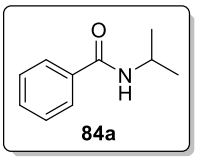
Yield **:** 4.063 g (85%), white solid

IR (KBr) **:** 2969, 2935, 1750, 1609, 1512, 1340, 1297, 1251, 1160, 1031, 764 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 7.90-7.89 (m, 2H), 7.55-7.54 (m, 2H), 3.80-3.79 (m, 2H), 1.26-1.25 (m, 12H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 170.0, 135.3, 129.8, 128.6, 54.5, 21.3.

***N*-Isopropylbenzamide**



84a

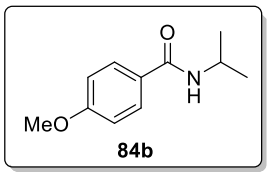
Yield **:** 2.999 g (92%), white solid

IR (KBr) **:** 2935, 1720, 1615, 1512, 1340, 1294, 1251, 1155, 1039, 741cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 7.79-7.78 (m, 2H), 7.50-7.47 (m, 3H), 3.98-3.97 (m, 1H), 1.21-1.20 (m, 6H)

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 170.2, 134.2, 132.1, 128.8, 127.5, 45.2, 23.1.

_N_-Isopropyl-4-methoxybenzamide



84b

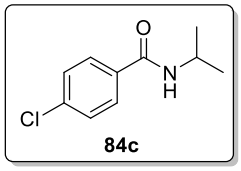
Yield **:** 3.358 g (87%), Colorless gummy liquid

IR (neat) **:** 2969, 2935, 1771, 1609, 1512, 1440, 1371, 1340, 1031, 764 cm^{-1}.

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 8.10-7.99 (m, 3H), 7.02-7.01 (m, 2H), 3.82-3.81 (s, 3H), 4.09-4.08(m, 1H), 1.21-1.20 (m, 6H)

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 170.5, 132.2, 145.1, 118.8, 55.4, 45.2, 23.2.

4-Chloro-_N_-isopropylbenzamide



84c

Yield **:** 3.309 g (84%), white solid

IR (KBr) **:** 2993, 2939, 1745, 1600, 1136, 713 cm^{-1}.

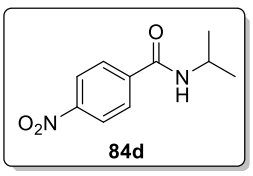
^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 7.97-7.96 (m, 3H), 7.52-7.51 (m, 2H), 4.19-4.18 (m, 1H), 1.15-1.14 (m, 6H)

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 171.2, 137.0.131.2, 129.9, 127.7, 44.4, 23.2.

_N_-Isopropyl-4-nitrobenzamide

Yield **:** 3.744 g (90%), yellow solid

IR (KBr) **:** 2976, 2931, 1634, 1598, 1211, 1192, 1161, 1136, 758, 713 cm^{-1}.



84d

^{1}H NMR **:** (400 MHz, ppm, $CDCl_3$): 8.02-8.01 (m, 2H), 7.99-7.98 (m, 3H), 3.91-3.90 (m, 1H), 1.11-1.10 (m, 6H).

^{13}C NMR **:** (100 MHz, ppm, $CDCl_3$): 167.1, 147.0.131.2, 123.7, 122.9, 43.9, 23.2.

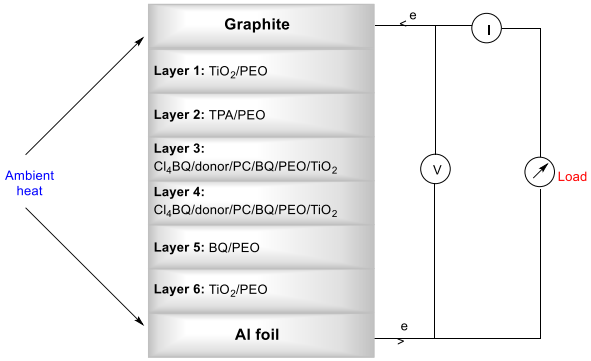
3.4.4 Preparation of Electrochemical Cells

Simple solution processing and casting techniques were followed for the construction of the cell device.

Figure 14, Table ES 1 Cell Configuration 1

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, TPA (0.245 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and BQ (0.22 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Al and dried. The Cl_4BQ (0.125g)/donor (1 mmol)/PC (0.5g)/BQ (0.11g)/PEO (0.05g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 14, Table ES 1 Cell Configuration 1

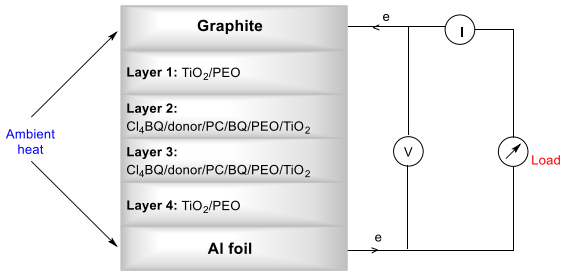


Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** TPA(0.245 g) + PEO (0.05g) **Layer 3:** Cl_4BQ(0.125g) +donor (1 mmol) +PC(0.5g)+ BQ(0.11g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 4:** Cl_4BQ(0.125g) +donor (1 mmol) +PC(0.5g)+ BQ(0.11g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 5:** BQ(0.22 g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.002	13.86	0.454	7.194	3.262	0.235
			35 °C	0.996	17.488	0.459	9.002	4.129	0.237
			40 °C	1.005	18.84	0.453	9.962	4.508	0.238
		48h	28 °C	0.98	9.53	0.449	5.021	2.254	0.241
			35 °C	0.976	10.92	0.453	5.586	2.532	0.238
			40 °C	0.987	13.31	0.459	6.897	3.166	0.241

Figure 15-17, Table ES 2 Cell Configuration 2

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ/donor (1 mmol)/PC (0.5 g)/BQ (0.22 g)/PEO (0.05 g)/TiO_2 (0.25 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 15-17, Table ES 2 Cell Configuration 2



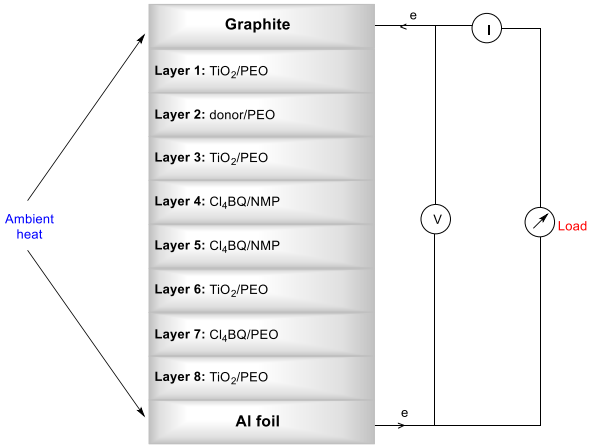
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.025 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 3: :** Cl_4BQ (0.025 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	0.821	11.0	0.387	5.54	2.143	0.237
			35 °C	0.805	13.42	0.384	6.756	2.594	0.24
			40 °C	0.815	14.22	0.394	7.009	2.758	0.238
		48h	28 °C	0.751	1.854	0.336	0.932	0.313	0.225
			35 °C	0.749	1.934	0.345	0.958	0.330	0.228
			40 °C	0.755	2.186	0.346	1.119	0.387	0.235
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.065 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 3: :** Cl_4BQ (0.065 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	0.993	27.66	0.449	13.84	6.208	0.266
			35 °C	0.987	32.92	0.449	16.52	7.39	0.228
			40 °C	1.004	40.24	0.484	19.46	9.424	0.233
		48h	28 °C	0.912	7.52	0.438	3.866	1.691	0.247
			35 °C	0.911	9.742	0.403	5.502	2.216	0.25
			40 °C	0.916	10.19	0.452	5.396	2.439	0.261
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.125 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g)	1h	28 °C	1.117	43.24	0.491	21.93	10.76	0.223
			35 °C	1.117	59.99	0.513	30.84	15.81	0.236
			40 °C	1.117	75.15	0.522	40.42	21.08	0.251

	Layer 3: : Cl_4BQ (0.125 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 ºC 35 ºC 40 ºC	1.092 1.068 1.053	20.73 22.25 21.01	0.53 0.555 0.565	13.81 15.64 15.62	7.316 8.677 8.818	0.323 0.365 0.399

Figure 18, Table ES 3 Cell Configuration 3

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Cl_4BQ (0.05g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.1g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 18, Table ES 3 Cell Configuration 3



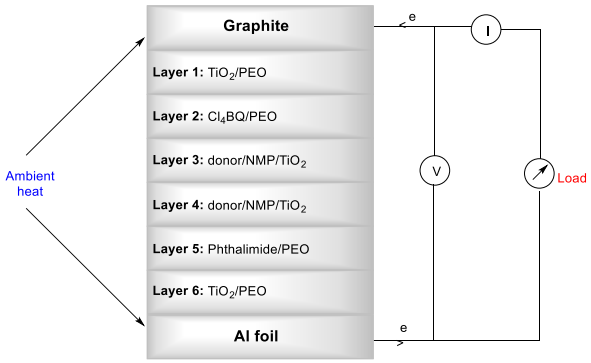
Entry No.	Cell Configuration	Time after packing	T ºC[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g)	1h	28 ºC 35 ºC 40 ºC	1.036 1.054 1.064	0.306 0.647 1.177	0.428 0.479 0.488	0.164 0.301 0.614	0.070 0.144 0.299	0.222 0.212 0.239

	Layer 5: Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 ºC 35 ºC 40 ºC	1.072 1.079 1.089	0.528 0.763 0.842	0.469 0.44 0.459	0.249 0.421 0.520	0.116 0.185 0.239	0.206 0.225 0.267

Figure 19, Table ES 4 Cell Configuration 4

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr. and Phthalimide (0.44 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The donor (1 mmol)/NMP (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 19, Table ES 4 Cell Configuration 4

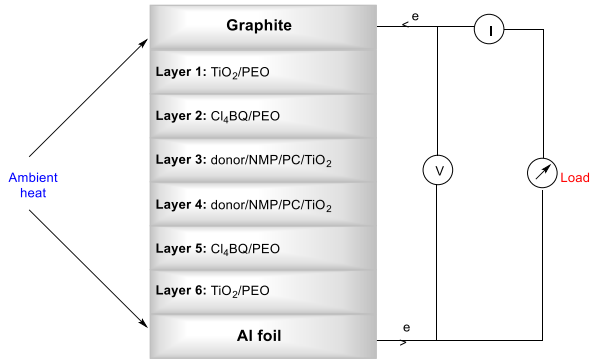


Entry No.	Cell Configuration	Time after packing	T ºC[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 ºC 35 ºC 40 ºC	0.890 0.893 0.901	6.299 7.091 8.792	0.429 0.433 0.463	3.259 0.383 4.418	1.398 1.499 1.919	0.249 0.237 0.242
		48h	28 ºC 35 ºC 40 ºC	0.888 0.889 0.89	10.01 11.69 12.26	0.389 0.425 0.431	4.574 5.275 5.33	1.777 2.243 2.298	0.200 0.216 0.211

Figure 20, Table ES 5 Cell Configuration 5

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 20, Table ES 5 Cell Configuration 5



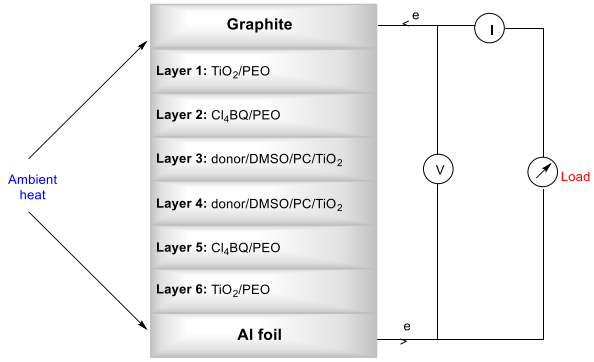
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.039	8.941	0.537	6.936	3.724	0.401
			35 °C	1.039	11.95	0.551	9.274	5.112	0.412
			40 °C	1.038	13.12	0.541	10.27	5.557	0.408
		48h	28 °C	1.012	7.0	0.552	3.986	2.198	0.31
			35 °C	1.012	8.376	0.588	4.539	2.668	0.315
			40 °C	1.012	8.344	0.611	4.563	2.786	0.33

Figure 21, Table ES 6 Cell Configuration 6

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite

foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 21, Table ES 6 Cell Configuration 6



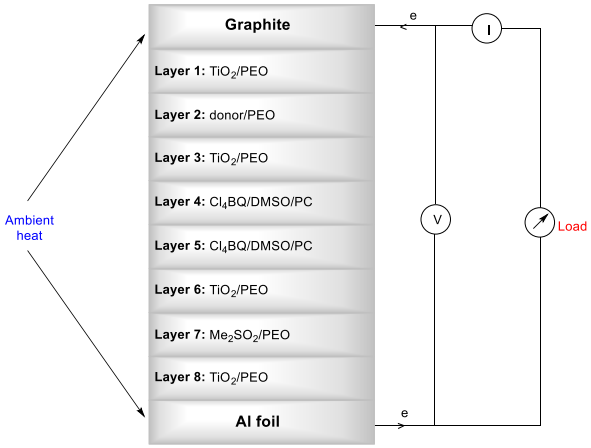
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.021	8.958	0.524	6.414	3.478	0.38
			35 °C	1.013	10.9	0.544	7.468	4.063	0.368
			40 °C	1.016	11.65	0.579	8.015	4.639	0.392
		48h	28 °C	1.01	7.131	0.523	4.193	2.194	0.308
			35 °C	0.984	8.726	0.546	4.554	2.484	0.289
			40 °C	0.989	9.587	0.597	4.9	2.925	0.309

Figure 22, Table ES 7 Cell Configuration 7

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Me_2SO_2 (0.376 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ

(0.125g)/DMSO (0.094 g)/PC (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 22, Table ES 7 Cell Configuration 7



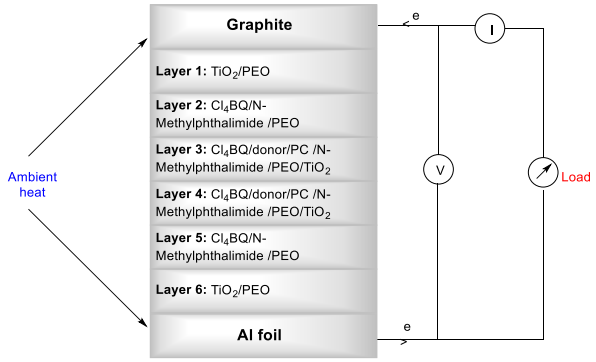
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g)	1h	28 °C 35 °C 40 °C	1.007 1.02 1.018	10.33 13.33 12.81	0.518 0.541 0.546	7.228 9.045 9.209	3.744 4.89 5.023	036 0.36 0.385
	Layer 5: Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 °C 35 °C 40 °C	0.92 0.923 0.923	5.35 8.836 9.214	0.489 0.539 0.563	3.03 4.709 5.107	1.482 2.539 2.87	0.301 0.311 0.338

Figure 23, Table ES 8 Cell Configuration 8

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.025 g)/N-methyl phthalimide (0.161 g) or BQ (0.11 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and TiO_2/PEO/Gr and dried. The Cl_4BQ

(0.025 g)/donor (1 mmol)/PC (0.5 g)/N-methyl phthalimide (0.161 g) or BQ (0.11 g)/PEO (0.05 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 23, Table ES 8 Cell Configuration 8



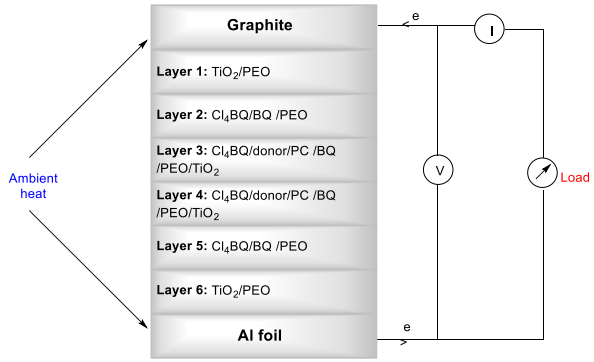
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.1 g)+ N-Me-Phthalimide (0.161 g) + PEO (0.05 g) **Layer 3:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + N-Me-Phthalimide (0.161 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 4:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + N-Me-Phthalimide (0.161 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.1 g)+ N-Me-Phthalimide (0.161 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.105	8.995	0.486	4.481	2.176	0.219
			35 °C	0.974	10.22	0.478	5.261	2.515	0.253
			40 °C	1.086	10.05	0.501	5.02	2.515	0.231
		48h	28 °C	1.111	4.36	0.527	2.157	1.137	0.235
			35 °C	1.14	4.556	0.523	2.229	1.202	0.231
			40 °C	1.146	5.246	0.54	2.634	1.421	0.236

Figure 24, Table ES 9 Cell Configuration 9

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.025 g)/N-methyl phthalimide (0.161 g) or BQ (0.11 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and TiO_2/PEO/Gr and dried. The Cl_4BQ (0.025 g)/donor (1 mmol)/PC (0.5 g)/BQ (0.11 g)/PEO (0.05 g)/TiO_2 (0.25 g) slurry was

prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 24, Table ES 9 Cell Configuration 9

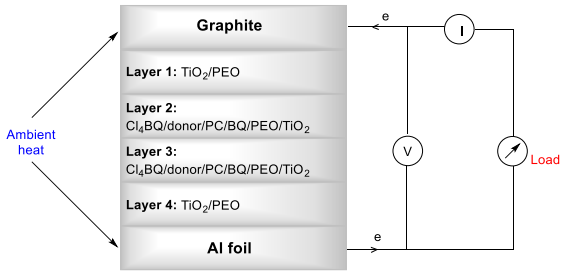


Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.1 g)+ BQ (0.11 g) + PEO (0.05 g) **Layer 3:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + BQ (0.11 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 4:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + BQ (0.11 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.1 g)+ BQ (0.11 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.146	13.32	0.46	5.986	2.751	0.18
			35 °C	1.138	15.75	0.456	7.451	3.394	0.189
			40 °C	1.131	15.88	0.464	7.569	3.508	0.195
		48h	28 °C	1.187	6.826	0.507	2.669	1.353	0.166
			35 °C	1.169	8.447	0.503	3.985	2.003	0.203
			40 °C	1.199	10.39	0.543	4.57	2.487	0.200

Figure 25-27, Table ES 10 Cell Configuration 10

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ/donor (1 mmol)/PC (0.5 g)/BQ (0.22 g)/PEO (0.05 g)/TiO_2 (0.25 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 25-27, Table ES 10 Cell Configuration 10



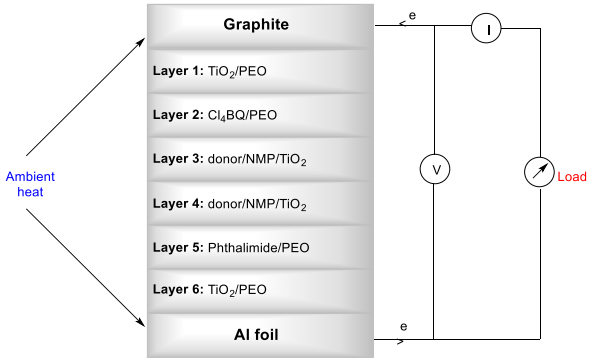
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.025 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 3: :** Cl_4BQ (0.025 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.127	10.86	0.512	4.936	2.527	0.207
			35 °C	1.115	13.02	0.506	6.098	3.086	0.213
			40 °C	1.121	13.37	0.489	6.453	3.155	0.21
		48h	28 °C	1.103	3.573	0.461	1.736	0.799	0.203
			35 °C	1.096	4.168	0.468	2.019	0.944	0.207
			40 °C	1.109	4.436	0.507	2.092	1.061	0.216
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.065 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 3: :** Cl_4BQ (0.065 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.157	17.67	0.47	7.778	3.652	0.179
			35 °C	1.156	18.28	0.498	7.956	3.962	0.188
			40 °C	1.169	22.42	0.51	9.69	4.939	0.188
		48h	28 °C	1.095	6.913	0.455	3.478	1.584	0.209
			35 °C	1.072	8.771	0.46	4.49	2.064	0.22
			40 °C	1.097	9.755	0.451	5.199	2.342	0.219
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.125 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 3: :** Cl_4BQ (0.125 g) + donor (1 mmol)+PC (0.5 g) + BQ (0.22 g)+PEO (0.05 g) + TiO_2 (0.25 g) **Layer 4:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.129	7.652	0.488	2.86	1.399	0.162
			35 °C	1.134	10.16	0.464	4.019	1.863	0.162
			40 °C	1.14	11.01	0.486	4.393	2.133	0.17
		48h	28 °C	1.175	3.903	0.536	1.737	0.929	0.203
			35 °C	1.166	4.678	0.53	2.14	1.135	0.208
			40 °C	1.156	4.78	0.543	2.188	1.183	0.215

Figure 28, Table ES 11 Cell Configuration 11

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite

foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr. and Phthalimide (0.44 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The donor (1 mmol)/NMP (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 28, Table ES 11 Cell Configuration 11



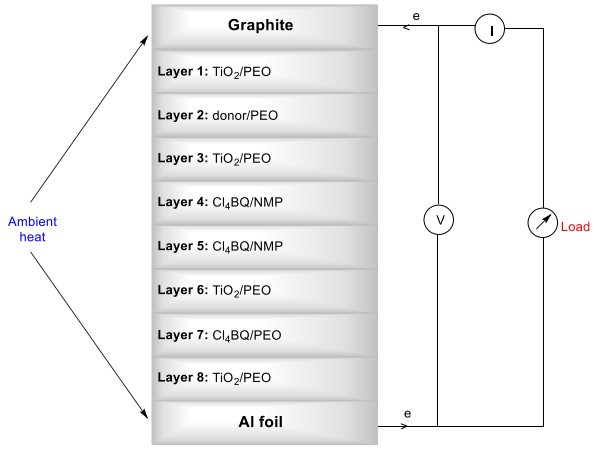
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr----------	1h	28 °C	0.929	2.601	0.394	0.963	0.380	0.157
	Layer 1: TiO_2 (0.5 g) + PEO (0.05 g)								
	Layer 2: Cl_4BQ (0.25 g)+PEO (0.05 g)		35 °C	0.930	2.516	0.391	0.988	0.386	0.165
	Layer 3: donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g)		40 °C	0.935	4.344	0.355	1.930	0.685	0.169
	Layer 4: donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g)	48h	28 °C	0.965	6.028	0.364	2.662	0.969	0.160
	Layer 5: Phthalimide (0.44 g) + PEO (0.05 g)								
	Layer 6: TiO_2 (0.5 g) + PEO (0.05 g)		35 °C	0.966	8.029	0.354	4.281	1.514	0.195
	Al----------		40 °C	0.966	8.562	0.395	4.28	1.69	0.204

Figure 29, Table ES 12 Cell Configuration 12

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Cl_4BQ (0.05g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ

(0.1g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 29, Table ES 12 Cell Configuration 12



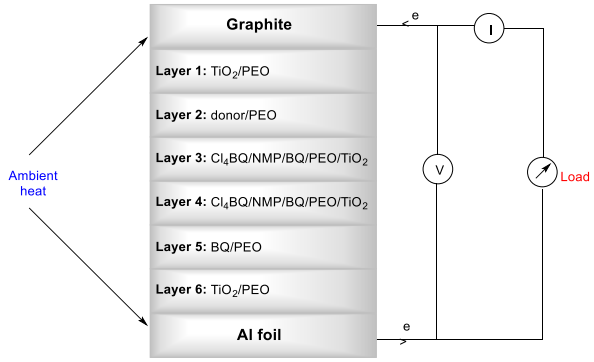
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.107	4.8	0.428	2.78	1.189	0.224
			35 °C	1.108	5.496	0.511	3.857	1.971	0.324
			40 °C	1.101	7.233	0.442	4.701	2.078	0.261
		48h	28 °C	1.093	3.882	0.444	1.936	0.859	0.203
			35 °C	1.104	6.183	0.445	3.282	1.459	0.214
			40 °C	1.113	6.978	0.46	4.024	1.849	0.238

Figure 30, Table ES 13 Cell Configuration 13

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (0.410 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and BQ (0.216 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Al and dried. The Cl_4BQ (0.125g)/NMP (0.5 g)/BQ(0.108 g)/PEO (0.05g)/TiO_2(0.25 g) slurry was prepared and

casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 30, Table ES 13 Cell Configuration 13



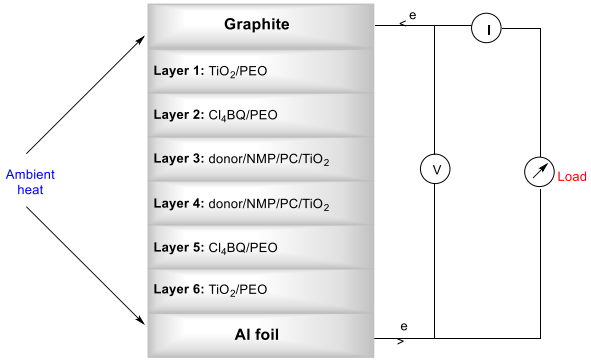
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(0.410 g) + PEO (0.05g) **Layer 3:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 5:** BQ(0.216 g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.05	27.07	0.33	14.44	4.768	0.168
		48h	28 °C	1.068	6.614	0.449	3.464	1.555	0.22

Figure 31, Table ES 14 Cell Configuration 14

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed

all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 31, Table ES 14 Cell Configuration 14



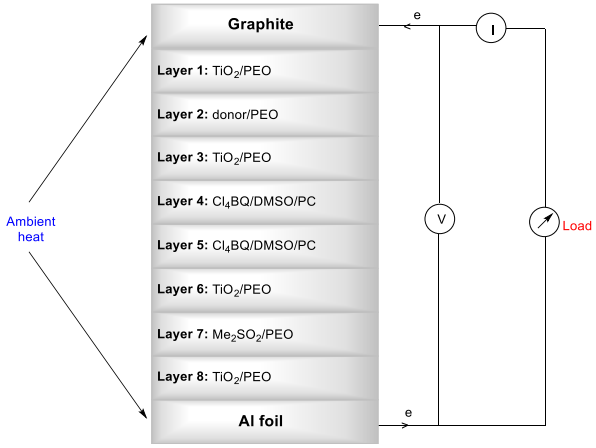
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g)	1h	28 °C	1.08	11.06	0.421	5.021	2.114	0.177
			35 °C	1.075	13.56	0.435	6.191	2.692	0.185
			40 °C	1.063	14.24	0.432	6.64	2.87	0.19
	Layer 4: donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 °C	1.112	9.389	0.545	4.413	2.005	0.192
			35 °C	1.111	11.52	0.48	5.38	2.58	0.202
			40 °C	1.112	12.95	0.48	6.582	3.065	0.213

Figure 32, Table ES 15 Cell Configuration 15

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Cl_4BQ (0.05g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.1g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed

all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 32, Table ES 15 Cell Configuration 15



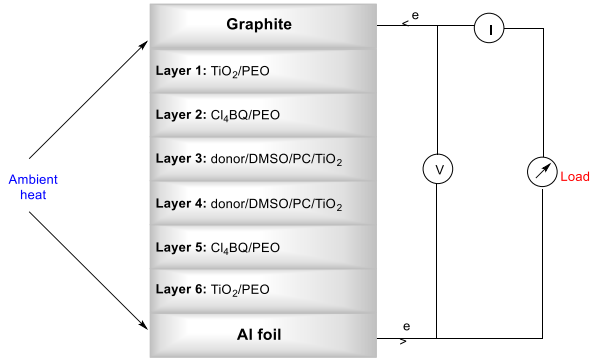
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.083	11.84	0.46	6.423	2.953	0.33
			35 °C	1.073	13.5	0.491	7.056	3.465	0.239
			40 °C	1.072	14.5	0.498	7.725	3.845	0.247
		48h	28 °C	1.107	6.104	0.46	3.268	1.528	0.229
			35 °C	1.088	9.966	0.52	5.402	2.806	0.259
			40 °C	1.066	10.46	0.516	6.068	3.131	0.281

Figure 33, Table ES 16 Cell Configuration 16

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed

all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 33, Table ES 16 Cell Configuration 16

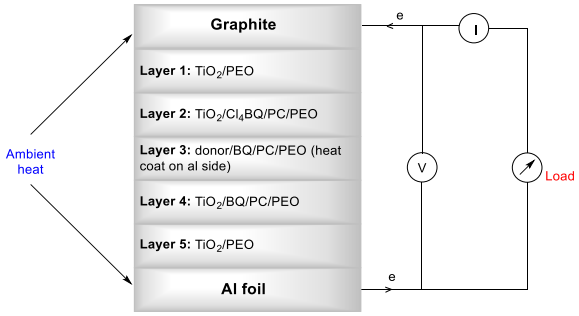


Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g)	1h	28 °C	1.068	20.78	0.358	11.57	4.136	0.186
			35 °C	1.061	23.48	0.387	14.12	5.467	0.219
			40 °C	1.06	24.89	0.429	16.21	6.944	0.263
	Layer 4: donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 °C	1.089	18.86	0.401	9.922	3.976	0.194
			35 °C	1.08	23.3	0.45	12.07	5.43	0.215
			40 °C	1.088	26.98	0.5	15.07	7.53	0.256

Figure 34, Table ES 17 Cell Configuration 17

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, TiO_2 (0.5 g)/Cl_4BQ (0.25 g)/PC (0.5 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2 (0.5 g)/BQ (0.44 g)/PC (0.5 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried in air at room temperature overnight. The donor (1 mmol)/BQ (0.11 g)/PC (0.5 g)/PEO (0.1 g) was heat coat before packing on dried coated Al foil. The cell was prepared immediately by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 34, Table ES 17 Cell Configuration 17



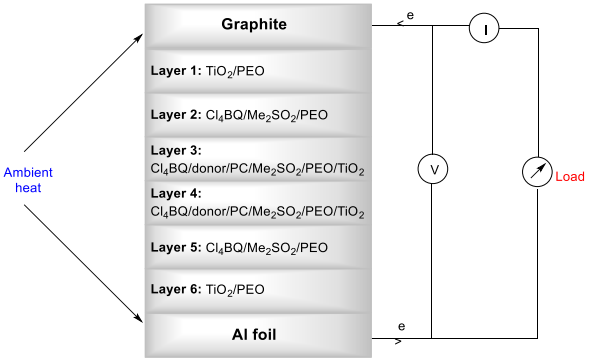
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** TiO_2 (0.5 g) + Cl_4BQ (0.25 g) + PC (0.5 g) + PEO (0.05 g) **Layer 3:** donor(1 mmol) + BQ(0.11 g) + PC (0.5 g) + PEO (0.1 g)-(heat coat on AL side before packing) **Layer 4:** TiO_2 (0.5 g) + BQ (0.44 g) + PC (0.5 g) + PEO (0.05 g) **Layer 5:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.158	4.03	0.557	1.947	1.085	0.232
			35 °C	1.167	5.337	0.571	2.623	1.498	0.24
			40 °C	1.165	6.106	0.583	2.948	1.72	0.242
		48h	28 °C	1.187	3.392	0.51	1.672	0.85	0.212
			35 °C	1.152	4.204	0.493	2.082	1.027	0.212
			40 °C	1.149	4.53	0.49	2.262	1.108	0.213
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** TiO_2 (0.5 g) + Cl_4BQ (0.25 g) + PC (0.5 g) + PEO (0.05 g) **Layer 3:** donor(1 mmol) + BQ(0.11 g) + PC (0.5 g) + PEO (0.1 g)-(heat coat on AL side before packing) **Layer 4:** TiO_2 (0.5 g) + BQ (0.44 g) + PC (0.5 g) + PEO (0.05 g) **Layer 5:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.17	2.55	0.562	1.271	0.713	0.239
			35 °C	1.169	2.704	0.552	1.365	0.754	0.239
			40 °C	1.152	3.482	0.539	1.779	0.957	0.239
		48h	28 °C	1.08	1.862	0.478	0.946	0.452	0.225
			35 °C	1.072	2.296	0.471	1.186	0.558	0.227
			40 °C	1.088	2.454	0.486	1.22	0.593	0.222

Figure 35, Table ES 18 Cell Configuration 18

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.1 g)/Me_2SO_2 (0.094 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and TiO_2/PEO/Gr and dried. The Cl_4BQ (0.025 g)/donor (1 mmol)/PC (0.5 g)/Me_2SO_2 (0.094 g)/ PEO (0.05 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the

cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 35, Table ES 18 Cell Configuration 18

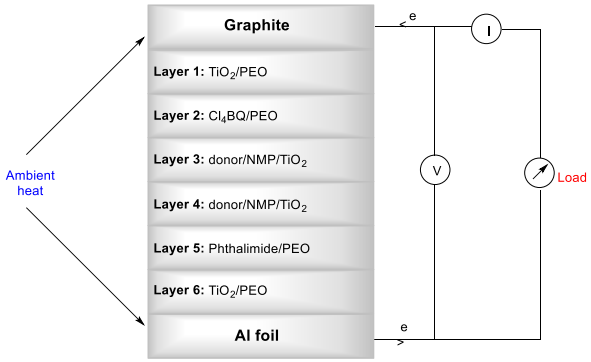


Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 3:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 4:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.009	6.953	0.509	3.812	1.938	0.276
			35 °C	1.016	7.902	0.525	4.246	2.227	0.277
			40 °C	1.023	12.86	0.554	7.705	4.265	0.324
		48h	28 °C	1.041	4.343	0.519	2.462	1.279	0.283
			35 °C	1.033	5.561	0.525	3.247	1.703	0.297
			40 °C	1.024	6.861	0.562	4.118	2.312	0.329
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 3:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 4:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.106	6.968	0.524	3.694	1.934	0.251
			35 °C	1.065	8.029	0.514	4.306	2.213	0.259
			40 °C	1.076	8.849	0.537	4.905	2.632	0.276
		48h	28 °C	1.144	2.897	0.538	1.544	0.830	0.251
			35 °C	1.139	3.261	0.561	1.673	0.938	0.253
			40 °C	1.141	6.738	0.589	3.627	2.136	0.278
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 3:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 4:** Cl_4BQ (0.025 g) + donor (1 mmol) + PC (0.5 g) + Me_2SO_2 (0.094 g) + PEO (0.05 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.1 g)+ Me_2SO_2 (0.094 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.076	3.966	0.538	1.997	1.075	0.252
			35 °C	1.056	4.564	0.542	2.355	1.276	0.265
			40 °C	1.06	4.624	0.534	2.437	1.309	0.267
		48h	28 °C	0.753	0.421	0.382	0.216	0.082	0.261
			35 °C	0.788	0.732	0.425	0.386	0.164	0.285
			40 °C	0.823	1.385	0.459	0.773	0.356	0.313

Figure 36, Table ES 19 Cell Configuration 19

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr. and Phthalimide (0.44 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The donor (1 mmol)/NMP (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 36, Table ES 19 Cell Configuration 19



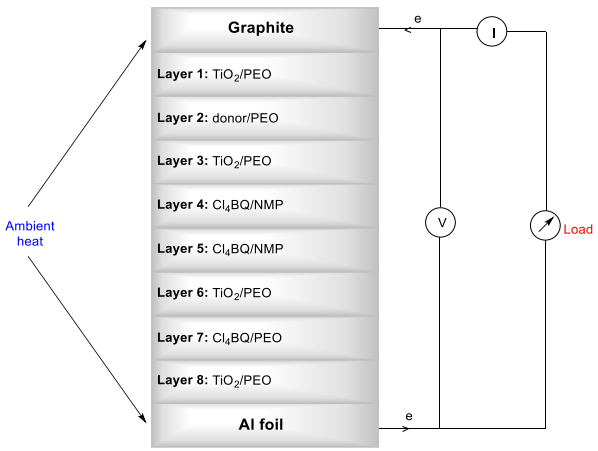
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	0.954	6.226	0.399	3.266	1.302	0.219
			35 °C	0.961	7.509	0.386	3.796	1.465	0.203
			40 °C	0.959	9.290	0.383	5.195	1.991	0.223
		48h	28 °C	1.014	10.03	0.382	5.68	2.167	0.213
			35 °C	1.016	11.48	0.427	6.855	2.927	0.251
			40 °C	1.018	12.17	0.458	7.454	3.416	0.276
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g)	1h	28 °C	0.754	5.180	0.384	3.017	1.158	0.297
			35 °C	0.861	4.727	0.427	2.776	1.185	0.291
			40 °C	0.757	5.959	0.447	3.371	1.506	0.334

	Layer 4: donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 ºC 35 ºC 40 ºC	0.269 0.56 0.832	1.31 3.531 3.54	0.167 0.275 0.398	0.562 1.749 1.893	0.093 0.481 0.752	0.266 0.244 .0.255
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol)+NMP(0.5 g)+TiO_2 (0.25 g) **Layer 4:** donor (1 mmol)+NMP(0.5 g)+TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 ºC 35 ºC 40 ºC	0.914 0.918 0.917	2.621 3.376 3.451	0.398 0.344 0.388	1.204 1.636 1.491	0.478 0.561 0.578	0.200 0.181 0.183
		48h	28 ºC 35 ºC 40 ºC	0.803 0.957 0.977	9.935 10.32 9.907	0.382 0.394 0.419	5.666 6.772 6.666	2.164 2.67 2.791	0.271 0.272 0.288

Figure 37, Table ES 20 Cell Configuration 20

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Cl_4BQ (0.05g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.1g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 37, Table ES 20 Cell Configuration 20

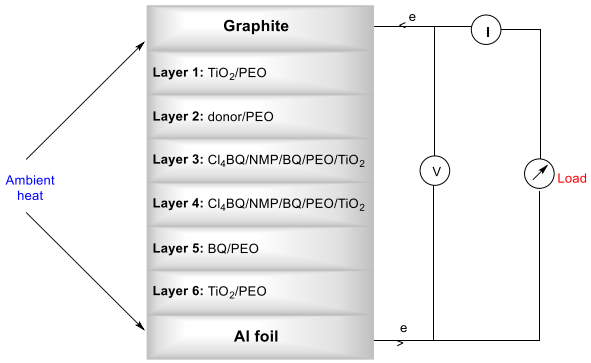


Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.057	7.474	0.348	4.596	1.601	0.203
			35 °C	1.063	8.392	0.446	6.575	2.934	0.329
			40 °C	1.062	9.635	0.47	7.864	3.725	0.364
		48h	28 °C	1.072	8.872	0.426	4.406	1.876	0.196
			35 °C	1.083	13.14	0.447	7.658	3.423	0.241
			40 °C	1.088	13.17	0.499	9.326	4.654	0.325
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.065	5.125	0.398	3.111	1.238	0.227
			35 °C	1.069	6.314	0.437	4.595	2.008	0.298
			40 °C	1.07	6.978	0.468	5.788	2.708	0.363
		48h	28 °C	1.075	0.854	0.44	3.579	1.574	0.214
			35 °C	1.07	9.546	0.435	6.066	2.639	0.257
			40 °C	1.073	8.806	0.468	6.183	2.894	0.306
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.121	2.486	0.432	1.244	0.536	0.193
			35 °C	1.121	3.116	0.445	2.098	0.933	0.267
			40 °C	1.115	4.086	0.44	2.231	0.981	0.216
		48h	28 °C	1.113	1.617	0.462	0.857	0.395	0.22
			35 °C	1.127	2.875	0.466	1.56	0.726	0.224
			40 °C	1.14	3.179	0.476	1.74	0.827	0.228

Figure 38, Table ES 21 Cell Configuration 21

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (0.410 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and BQ (0.216 g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Al and dried. The Cl_4BQ (0.125g)/NMP (0.5 g)/BQ(0.108 g)/PEO (0.05g)/TiO_2(0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 38, Table ES 21 Cell Configuration 21



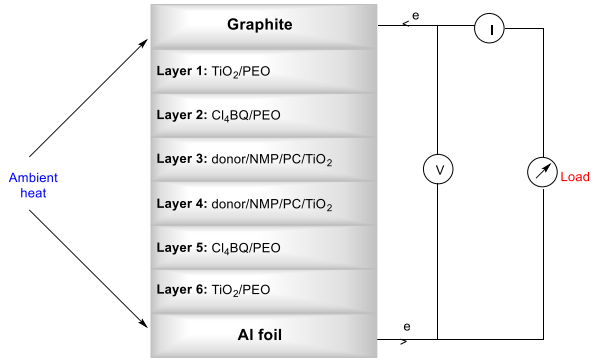
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(0.410 g) + PEO (0.05g) **Layer 3:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 5:** BQ(0.216 g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.07	27.76	0.403	12.33	4.967	0.167
		48h	28 °C	1.09	10.06	0.464	7.168	3.328	0.307
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(0.410 g) + PEO (0.05g) **Layer 3:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 5:** BQ(0.216 g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.073	20.87	0.394	9.531	3.753	0.168
		48h	28 °C	1.008	13.27	0.46	9.122	4.196	0.293
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(0.410 g) + PEO (0.05g) **Layer 3:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) + BQ(0.108 g) + PEO (0.05g) +TiO_2(0.25 g) **Layer 5:** BQ(0.216 g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.096	18.0	0.468	7.803	3.652	0.185
		48h	28 °C	1.107	3.523	0.494	1.733	0.855	0.219

Figure 39, Table ES 22 Cell Configuration 22

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and

dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 39, Table ES 22 Cell Configuration 22



Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g)	1h	28 °C	1.144	9.754	0.505	4.851	2.45	0.22
			35 °C	1.126	11.23	0.504	5.545	2.795	0.221
			40 °C	1.114	11.76	0.503	5.938	2.987	0.228
	Layer 4: donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 °C	1.159	7.293	0.531	3.577	1.9	0.225
			35 °C	1.169	9.912	0.539	4.498	2.424	0.225
			40 °C	1.178	10.26	0.562	5.028	2.826	0.234

Figure 40, Table ES 23 Cell Configuration 23

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed

all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

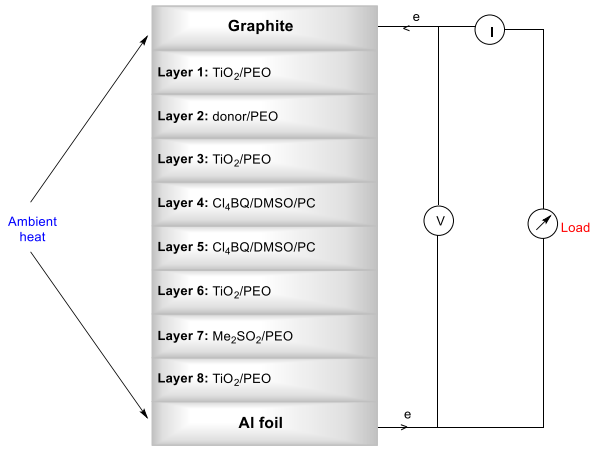
Figure 40, Table ES 23 Cell Configuration 23

Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr----------	1h	28 °C	1.115	7.599	0.503	3.735	1.878	0.222
	Layer 1: TiO_2 (0.5 g) + PEO (0.05 g)								
	Layer 2: Cl_4BQ (0.25 g)+PEO (0.05 g)		35 °C	1.098	10.12	0.496	5.096	2.527	0.227
	Layer 3: donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+		40 °C	1.085	10.09	0.508	5.044	2.564	0.234
	TiO_2 (0.25 g)								
	Layer 4: donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+	48h	28 °C	1.146	8.741	0.494	4.553	2.251	0.225
	TiO_2 (0.25 g)		35 °C	1.146	10.91	0.519	5.725	2.971	0.238
	Layer 5: Cl_4BQ (0.25) g+PEO (0.05 g)								
	Layer 6: TiO_2 (0.5 g) + PEO (0.05 g)		40 °C	1.146	12.21	0.538	6.539	3.515	0.251
	Al----------								

Figure 41, Table ES 24 Cell Configuration 24

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Me_2SO_2 (0.376 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.125g)/DMSO (0.094 g)/PC (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 41, Table ES 24 Cell Configuration 24



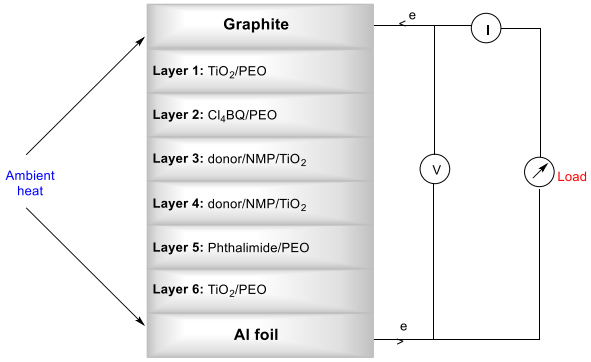
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.08	13.26	0.45	6.832	3.076	0.215
			35 °C	1.074	17.26	0.474	9.004	4.264	0.23
			40 °C	1.067	17.4	0.491	9.015	4.424	0.238
		48h	28 °C	1.08	10.11	0.48	5.423	2.6	0.237
			35 °C	1.04	11.02	0.464	6.607	3.066	0.265
			40 °C	1.074	13.01	0.495	7.694	3.808	0.273
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.07	12.94	0.484	6.723	3.251	0.235
			35 °C	1.06	13.34	0.483	7.032	3.397	0.24
			40 °C	1.061	13.42	0.49	7.473	3.658	0.257
		48h	28 °C	0.984	4.02	0.456	2.433	1.108	0.28
			35 °C	0.977	6.393	0.498	3.612	1.796	0.288
			40 °C	0.965	6.472	0.518	3.87	2.005	0.321
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +DMSO (0.094 g) + PC (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.068	10.64	0.469	4.864	2.24	0.197
			35 °C	1.06	12.5	0.458	6.058	2.722	0.209
			40 °C	1.062	15.21	0.477	7.366	3.515	0.219
		48h	28 °C	1.1	8.391	0.466	4.32	2.012	0.218
			35 °C	1.059	10.06	0.469	5.54	2.59	0.244
			40 °C	1.087	12.11	0.503	6.434	3.238	0.246

Figure 42, Table ES 25 Cell Configuration 25

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite

foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr. and Phthalimide (0.44 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The donor (1 mmol)/NMP (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 42, Table ES 25 Cell Configuration 25



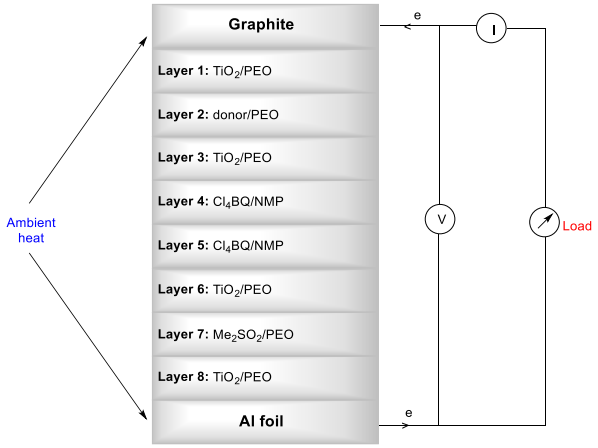
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	0.958	3.671	0.416	1.778	0.739	0.210
			35 °C	0.941	3.937	0.430	1.818	0.781	0.211
			40 °C	0.951	4.66	0.397	2.360	0.937	0.212
		48h	28 °C	0.99	7.533	0.483	3.307	1.597	0.214
			35 °C	0.984	8.074	0.499	3.484	1.738	0.219
			40 °C	0.984	8.546	0.507	3.744	1.899	0.226
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	0.973	2.458	0.368	1.298	0.477	0.199
			35 °C	0.951	2.730	0.409	1.289	0.526	0.203
			40 °C	0.974	3.693	0.385	1.948	0.749	0.268
		48h	28 °C	1.008	6.5	0.482	2.917	1.405	0.215
			35 °C	1.005	7.335	0.499	3.254	1.622	0.22
			40 °C	1.004	7.407	0.498	3.36	1.673	0.225
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g)	1h	28 °C	0.944	3.699	0.351	1.690	0.593	0.170
			35 °C	0.946	4.475	0.338	1.921	0.649	0.153
			40 °C	0.936	3.831	0.346	2.077	0.719	0.201

	Layer 4: donor (1 mmol) + NMP (0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Phthalimide (0.44 g) + PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 ºC 35 ºC 40 ºC	0.977 0.977 0.979	7.922 8.467 8.743	0.391 0.471 0.398	4.28 4.499 4.901	1.675 1.85 1.952	0.216 0.224 0.228

Figure 43, Table ES 26 Cell Configuration 26

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Me_2SO_2 (0.376 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.125g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 43, Table ES 26 Cell Configuration 26



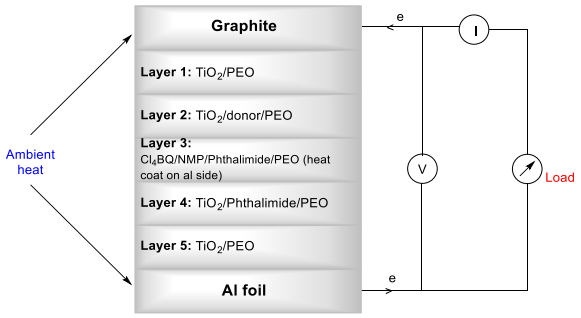
Entry No.	Cell Configuration	Time after packing	T ºC[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g)	1h	28 ºC 35 ºC 40 ºC	1.046 1.045 1.047	10.69 12.32 13.08	0.305 0.359 0.372	5.878 6.871 7.693	1.793 2.465 2.864	0.16 0.192 0.209

	Layer 5: Cl_4BQ(0.125g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	48h	28 ºC 35 ºC 40 ºC	1.063 1.05 1.065	8.958 9.712 12.62	0.41 0.411 0.401	3.514 4.09 5.64	1.44 1.681 2.28	0.157 0.165 0.17
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h 48h 	28 ºC 35 ºC 40 ºC 28 ºC 35 ºC 40 ºC	1.057 1.057 1.055 1.072 1.059 1.074	8.971 11.59 11.91 6.988 7.525 9.649	0.329 0.385 0.383 0.428 0.434 0.424	4.774 7.258 7.356 3.024 3.48 4.748	1.568 2.791 2.815 1.295 1.511 2.011	0.165 0.228 0.224 0.173 0.19 0.194
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.125g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.125g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Me_2SO_2(0.376 g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h 48h 	28 ºC 35 ºC 40 ºC 28 ºC 35 ºC 40 ºC	1.05 1.051 1.052 1.074 1.07 1.075	4.573 5.961 6.425 4.248 4.761 5.467	0.35 0.379 0.379 0.386 0.385 0.373	1.796 2.499 2.781 1.557 2.008 2.251	0.628 0.940 1.055 0.60 0.773 0.841	0.131 0.15 0.156 0.132 0.152 0.143

Figure 44, Table ES 27 Cell Configuration 27

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, TiO_2 (0.5 g)/donor (1 mmol)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2 (0.5 g)/Phthalimide (0.294 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried in air at room temperature overnight. The Cl_4BQ (0.25 g)/NMP (1.00 g)/Phthalimide (0.147 g)/PEO (0.1 g) was heat coat before packing on dried coated Al foil. The cell was prepared immediately by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape

Figure 44, Table ES 27 Cell Configuration 27



Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr----------	1h	28 °C	1.006	9.927	0.43	5.976	2.567	0.257
	Layer 1: TiO_2 (0.5 g) + PEO (0.05 g)								
	Layer 2: TiO_2 (0.5 g) + donor (1 mmol) + PEO (0.05 g)		35 °C	0.994	11.17	0.429	7.031	3.018	0.272
	Layer 3: Cl_4BQ (0.25 g) + NMP (1 g) + Phathalimide (0.147 g) + PEO (0.1 g)-(heat coat on AL side before packing)		40 °C	0.998	12.77	0.427	8.297	3.541	0.278
		48h	28 °C	1.067	9.208	0.411	4.692	1.93	0.196
	Layer 4: TiO_2 (0.5 g)+ Phthalimide (0.294 g) + PEO (0.05 g)		35 °C	1.069	10.95	0.46	6.206	2.853	0.244
	Layer 5: TiO_2 (0.5 g) + PEO (0.05 g)								
	Al----------		40 °C	1.069	11.45	0.49	6.804	3.334	0.272

Figure 45, Table ES 28 Cell Configuration 28

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, donor (1 mmol)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Cl_4BQ (0.05g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Al and dried. The TiO_2 (0.5 g)/PEO (0.05 g) in DCM was coated on coated Al and Gr foil. The Cl_4BQ (0.1g)/NMP (0.5 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

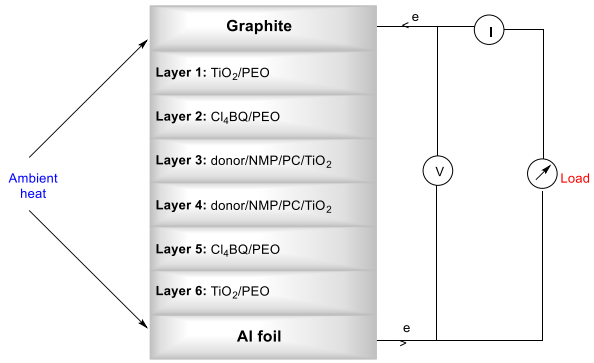
Figure 45, Table ES 28 Cell Configuration 28

Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.068	7.709	0.392	5.281	2.07	0.251
			35 °C	1.074	9.552	0.48	7.441	3.594	0.348
			40 °C	1.076	9.89	0.49	8.028	3.968	0.373
		48h	28 °C	1.084	8.94	0.442	4.64	2.051	0.212
			35 °C	1.087	12.96	0.454	7.178	3.259	0.231
			40 °C	1.094	14.46	0.517	8.646	4.472	0.283
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.062	6.739	0.387	3.839	1.484	0.207
			35 °C	1.064	9.915	0.453	6.561	2.974	0.282
			40 °C	1.069	9.685	0.461	6.563	3.024	0.292
		48h	28 °C	1.086	7.515	0.435	3.913	1.702	0.209
			35 °C	1.089	12.19	0.462	6.727	3.109	0.234
			40 °C	1.098	14.63	0.53	8.776	4.657	0.29
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** donor(1 mmol) + PEO (0.05g) **Layer 3:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 4:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 5:** Cl_4BQ(0.1g) +NMP (0.5 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 7:** Cl_4BQ(0.05g) + PEO (0.05 g) **Layer 8:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.072	5.807	0.344	3.407	1.17	0.188
			35 °C	1.077	6.933	0.422	4.934	2.082	0.279
			40 °C	1.073	7.17	0.449	4.987	2.239	0.291
		48h	28 °C	1.085	6.991	0.417	3.437	1.433	0.189
			35 °C	1.089	9.58	0.455	4.944	2.25	0.216
			40 °C	1.089	10.26	0.467	6.03	2.816	0.252

Figure 46, Table ES 29 Cell Configuration 29

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g) or NMP (0.198 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 46, Table ES 29 Cell Configuration 29



Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + NMP (0.198 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.119	8.457	0.489	4.154	2.032	0.215
			35 °C	1.103	9.974	0.439	4.816	2.375	0.216
			40 °C	1.091	9.914	0.49	4.962	2.429	0.225
		48h	28 °C	1.15	7.77	0.517	3.764	1.944	0.218
			35 °C	1.144	8.839	0.509	4.485	2.28	0.224
			40 °C	1.141	9.663	0.54	4.721	2.547	0.231

Figure 47, Table ES 30 Cell Configuration 30

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.125g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Gr and Me_2SO_2 (0.376g)/PEO (0.05g) in DCM was coated on TiO_2/PEO/Al and dried. The donor (1 mmol)/Cl_4BQ (0.1g)/PC (0.5g)/NMP (0.198g)/TiO_2 (0.25 g)/PEO (0.05g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 47, Table ES 30 Cell Configuration 30

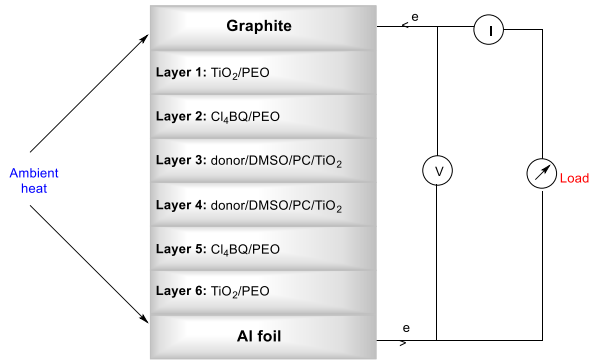
Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ(0.125g) + PEO (0.05g) **Layer 3:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 4:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 5:** Me_2SO_2(0.376g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.013	11.47	0.441	5.823	2.569	0.221
			35 °C	1.057	12.91	0.44	6.544	2.92	0.215
			40 °C	1.055	14.36	0.477	7.359	3.512	0.226
		48h	28 °C	1.05	4.056	0.476	2.071	0.982	0.231
			35 °C	1.061	4.145	0.476	2.142	1.019	0.232
			40 °C	1.067	4.419	0.488	2.269	1.106	0.235
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ(0.125g) + PEO (0.05g) **Layer 3:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 4:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 5:** Me_2SO_2(0.376g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.01	10.67	0.439	5.454	2.396	0.222
			35 °C	1.046	12.19	0.455	6.004	2.732	0.214
			40 °C	1.051	14.09	0.475	7.098	3.37	0.228
		48h	28 °C	1.075	4.245	0.478	2.206	1.053	0.231
			35 °C	1.058	4.411	0.472	2.31	1.09	0.234
			40 °C	1.087	5.033	0.483	2.713	1.311	0.24
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ(0.125g) + PEO (0.05g) **Layer 3:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 4:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 5:** Me_2SO_2(0.376g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.05	10.44	0.475	5.134	2.44	0.223
			35 °C	1.087	11.64	0.494	5.579	2.754	0.218
			40 °C	1.019	13.37	0.439	6.699	3.303	0.226
		48h	28 °C	1.13	7.92	0.49	3.89	1.909	0.213
			35 °C	1.118	8.288	0.51	4.063	2.071	0.224
			40 °C	1.134	9.228	0.52	4.58	2.382	0.229
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ(0.125g) + PEO (0.05g) **Layer 3:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 4:** donor (1 mmol) + Cl_4BQ(0.1g) +PC(0.5g)+ NMP(0.198g) + TiO_2(0.25 g)+ PEO (0.05g) **Layer 5:** Me_2SO_2(0.376g) + PEO (0.05g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.04	10.88	0.465	5.481	2.547	0.223
			35 °C	1.052	10.15	0.456	5.073	2.31	0.216
			40 °C	1.076	12.76	0.486	6.509	3.162	0.23
		48h	28 °C	1.105	4.698	0.489	2.419	1.184	0.228
			35 °C	1.085	4.945	0.479	2.614	1.251	0.233
			40 °C	1.108	5.66	0.507	2.928	1.489	0.236

Figure 48, Table ES 31 Cell Configuration 31

The PEO (0.05 g) was dissolved in dichloromethane and mixed with TiO_2 (0.5 g) powder. DCM was removed to obtain a paste for coating on Aluminium and Graphite foils. After 1 h, Cl_4BQ (0.25 g)/PEO (0.05 g) in DCM was coated on TiO_2/PEO/Gr and TiO_2/PEO/Al and dried. The donor (1 mmol)/DMSO (0.188 g)/PC (0.5 g)/TiO_2 (0.25 g) slurry was prepared and casted above the coated layer on Aluminium and Graphite and dried in air at room temperature overnight. The cell was prepared by sandwiching the

coated Al/Gr layers. The rim of the cell prepared in this way was sealed all around using TiO_2/PEO paste, then with commercial adhesive Bondfix (India) and covered with cellophane tape.

Figure 48, Table ES 31 Cell Configuration 31



Entry No.	Cell Configuration	Time after packing	T °C[c]	Voc (V)	Isc (mA)	Vmax (V)	Imax (mA)	Pmax (mW)	Fill Factor
	Gr---------- **Layer 1:** TiO_2 (0.5 g) + PEO (0.05 g) **Layer 2:** Cl_4BQ (0.25 g)+PEO (0.05 g) **Layer 3:** donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 4:** donor (1 mmol) + DMSO (0.188 g)+PC(0.5 g)+ TiO_2 (0.25 g) **Layer 5:** Cl_4BQ (0.25) g+PEO (0.05 g) **Layer 6:** TiO_2 (0.5 g) + PEO (0.05 g) Al----------	1h	28 °C	1.105	12.34	0.467	6.235	2.912	0.214
			35 °C	1.077	14.75	0.486	7.348	3.569	0.225
			40 °C	1.069	14.9	0.482	7.619	3.672	0.231
		48h	28 °C	1.135	14.21	0.486	7.529	3.659	0.227
			35 °C	1.126	16.57	0.517	8.502	4.395	0.236
			40 °C	1.125	18.11	0.532	9.633	5.125	0.252

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Appendix I

(Representative Spectra)

Appendix II

(X-Ray Crystallographic Data)

Table 1. Crystal data and structure refinement for 141c.

Identification code	141c	
Empirical formula	$C_{10}\ H_{16}\ N_2\ O_3$	
Formula weight	212.25	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.3814(7) Å	α= 90°.
	b = 10.2308(7) Å	β= 90°.
	c = 11.2657(8) Å	γ = 90°.
Volume	1081.27(13) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	456	
Crystal size	0.24 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.69 to 26.40°.	
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=14	
Reflections collected	10981	
Independent reflections	2167 [R(int) = 0.0305]	
Completeness to theta = 26.40°	97.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2167 / 0 / 142	
Goodness-of-fit on F^2	1.199	
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1037	
R indices (all data)	R1 = 0.0454, wR2 = 0.1038	
Absolute structure parameter	0.3(02)	
Largest diff. peak and hole	0.177 and -0.219 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mp113. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3520(2)	502(2)	8622(2)	33(1)
C(2)	2507(2)	1283(2)	7832(2)	35(1)
C(3)	3328(2)	2244(2)	10126(2)	38(1)
C(4)	3212(2)	3161(2)	9072(2)	35(1)
C(5)	2357(3)	4398(2)	9307(2)	48(1)
C(6)	1823(3)	4778(2)	8078(2)	43(1)
C(7)	1457(3)	3466(2)	7513(2)	45(1)
C(8)	3249(3)	-970(2)	8566(2)	40(1)
C(9)	1844(3)	-1352(3)	9126(2)	57(1)
C(10)	4488(3)	-1741(2)	9099(2)	54(1)
O(1)	1844(2)	792(2)	7000(1)	51(1)
O(2)	3324(2)	2654(2)	11153(1)	60(1)
O(3)	2952(2)	5406(2)	7464(2)	54(1)
N(1)	3439(2)	988(2)	9849(1)	37(1)
N(2)	2426(2)	2545(2)	8101(1)	38(1)

List of publications

1. Enantiomerically pure piperazines via NaBH4/I2 reduction of cyclic amides, **Harish, V**.; Periasamy, M. *Tetrahedron: Asymmetry* **2017**, *28*, 180.
2. Synthesis of cycloalkyl based allenes using enamines and 1-alkynes, **Harish, V**.; Periasamy, M. (*to be communicated*).
3. Construction of electricity harvesting cells using proline based donors and *p*-chloranil acceptor *via* electron transfer reactions, **Harish, V**.; Periasamy, M. (*Manuscript under preparation*).
4. Construction of electricity harvesting cells using isopropylbenzamide donors and *p*-chloranil acceptor *via* electron transfer reactions, **Harish, V**.; Periasamy, M. (*Manuscript under preparation*).