Chapter 5

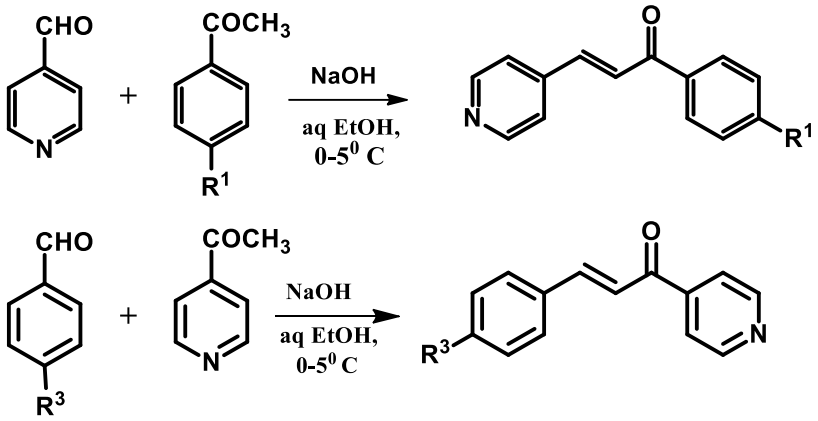
CHALCONE BASED NLO COMPOUNDS WITH HETEROCYCLIC CORE

5.1 Introduction:

Heterocyclic nitrogenous compounds are an important group of compounds as they have biological, pharmaceutical properties and they are found in various natural products. Most of the alkaloids present in plants are nitrogenous bases. Well known antibiotics, penicillin and streptomycin, drugs (sulphathiazole, pyrethrin, rotenine, cocaine, and barbiturates), pigments like indigo, hemoglobin, anthocyanin and automobiles holds heterocyclic ring system in their core structure [1-12].

In the present work, chalcone using heteroaryl donor entities have been designed as NLO chromophores, characterized using spectral studies. Their linear and nonlinear optical properties are studied in detail.

5.2 General synthetic method:

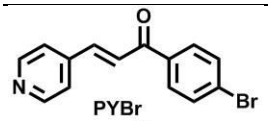
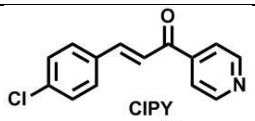
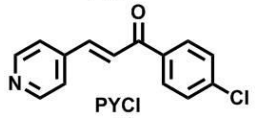
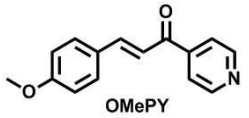
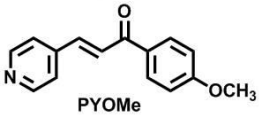
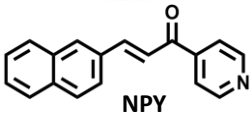
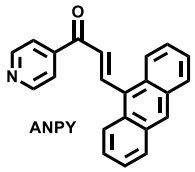
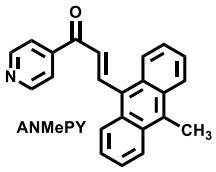


Scheme 5.01: Synthesis of heteroaryl chalcone derivatives

To a solution of NaOH (40% w/v) in ethanol and water placed in an ice bath, acetophenone / acetophenone derivative (1 mmol) was added. After 15-20 min of stirring, benzaldehyde/ benzaldehyde derivative (1 mmol) was added dropwise. The progress of the reaction was monitored by TLC using hexane-ethyl acetate mixture as mobile phase. The temperature was maintained at 0˚-5˚C during the course of the reaction. After overnight refrigeration, the reaction mixture was poured onto crushed ice and neutralized with conc. HCl. Precipitate obtained was filtered, washed with water till the pH was neutral. The product was dried and

purified by silica gel (100-120 mesh) column chromatography using hexane: ethyl acetate as eluent. The reaction scheme in shown in Scheme 5.01 and the reaction condition with physical data of the synthesized chalcone derivatives are given in Table 5.01.

Table 5.01: Reaction Condition and Physical data of chalcone derivatives.

Compound & code	Reaction Time	M.P (℃)	Compound &code	Reaction Time	M.P (℃)
 PYBr	1 h	145-147	 ClPY	1.5 h	130-132
 PYCl	1 h	122-123	 OMePY	1 h	105-107
 PYOMe	2 h	121-122	 NPY	3 h	170-171
 ANPY	1 h		 ANMePY	2.5 h	

5.3 Characterization of heteroaryl chalcone derivatives:

Fig. 5.01 shows the ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of *(E)-3-(4-methoxyphenyl)-1-(pyridin-4-yl)prop-2-en-1-one* **(OMePY)**. H^a and H^b are at 7.79 ppm and 7.29 ppm respectively, they have a high coupling constant of 16 Hz, which is an indication of a *trans*-configaration of the double bond. H^c protons appear as a singlet at 3.85 ppm. The aromatic protons having *J* value of 8 Hz appears in the region 6.9-8.82 ppm.

Fig. 5.02 shows ^{13}C NMR spectrum ($CDCl_3$) of **OMePY**. δ =189.78 ppm appears for the carbonyl carbon, δ =162.25 ppm is observed for the carbon on the phenyl ring attached to the oxygen of methoxy group. The carbon adjacent to the nitrogen on the pyridine ring appears at δ = 150.73 ppm. Carbon attached to the H^b proton appears at δ =146.68 ppm.

OMePY is taken as a representative compound from the series of naphthalene core chalcone derivatives. The characterization data of other chalcone derivatives in the series are presented in the following section. The spectra are available in the Section 5.8.

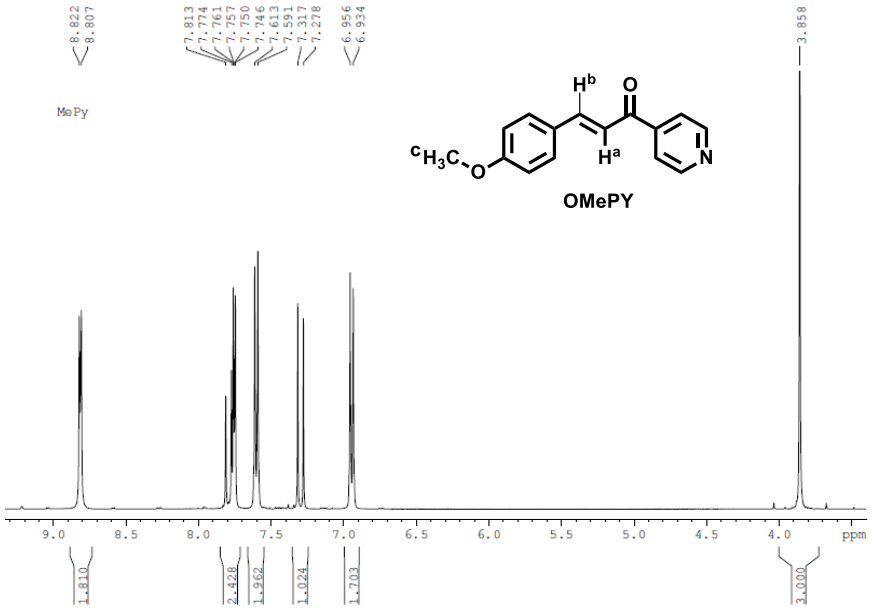


Figure 5.01: ^{1}H NMR spectrum of *(E)-3-(4-methoxyphenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (OMePY).

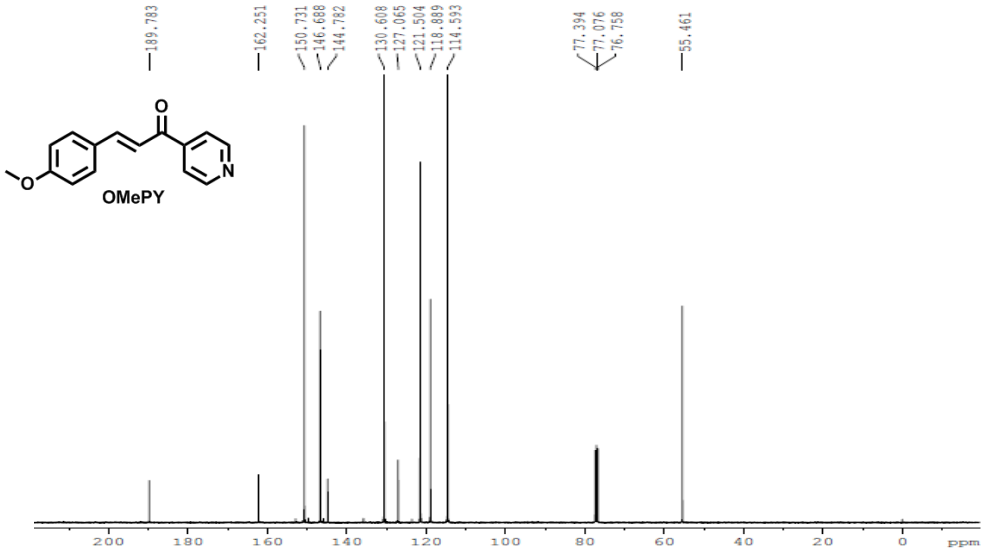


Figure 5.02: ^{13} C NMR spectrum of *(E)-3-(4-methoxyphenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (OMePY).

***(E)-3-(4-methoxyphenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (OMePY): OMePY** was synthesized following the method described in Section 5.2 with 4-acetylpyridine (121 mg) and 4-methoxybenzaldehyde (136 mg). TLC, EtOAc: Hexane = 40: 60. Pale yellow solid. Yield:182 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8 Hz, 2H), 7.79 (d, J = 16 Hz, 1H), 7.76 (d, J = 8 Hz, 1H), 7.60 (d, J = 8 Hz, 2H), 7.46 (d, J = 8 Hz, 1H), 7.29 (d, J = 16 Hz, 1H), 6.94 (d, J = 8 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 189.78, 162.25, 150.73, 146.68, 144.78, 130.60, 121.50, 118.88, 114.59, 55.46.

***(E)-1-(4-bromophenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYBr): PYBr** was synthesized following the method described in Section 5.2 with 4-bromoacetophenone (199 mg) and pyridine-4-carboxaldehyde (108 mg). TLC, EtOAc: Hexane = 70: 30. Pale yellow solid. Yield: 188 mg (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8 Hz, 2H), 7.89 (d, J = 8 Hz, 2H), 7.71 (d, J = 16 Hz, 1H), 7.67 (d, J = 8 Hz, 2H), 7.60 (d, J = 16 Hz, 1H), 7.47 (d, J = 8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 188.63, 150.64, 142.05, 136.12, 132.09, 130.04, 125.36, 121.98.

***(E)-1-(4-chlorophenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYCl): PYCl** was synthesized following the method described in Section 5.2 with 4-chloroacetophenone (155 mg) and pyridine-4-carboxaldehyde (108 mg). TLC, EtOAc: Hexane = 40: 60. Pale yellow solid. Yield: 176 mg (72%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.84 (d, J = 8 Hz, 2H), 7.77-7.80 (3H), 7.58 (d, J = 8 Hz, 2H), 7.40-7.43 (3H).

***(E)-1-(4-methoxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYOMe): PYOMe** was synthesized following the method described in Section 5.2 with 4-methoxyacetophenone (150 mg) and pyridine-4-carboxaldehyde (108 mg). TLC, EtOAc: Hexane = 60: 40. Pale yellow solid. Yield: 137 mg (57%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.70 (d, J = 8 Hz, 2H), 8.06 (d, J = 8 Hz, 2H), 7.70 (2H), 7.49 (d, J = 8 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 3.92 (s, 3H).

***(E)-3-(4-chlorophenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (ClPY): ClPY** was synthesized following the method described in Section 5.2 with 4-acetylpyridine

(121 mg) and 4-chlorobenzaldehyde (141 mg). TLC, EtOAc: Hexane = 80: 20. Pale yellow solid. Yield: 171 mg (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 8 Hz, 2H), 7.78 (d, J = 16 Hz, 1H), 7.76 (d, J = 8 Hz, 2H), 7.58 (d, J = 8 Hz, 2H), 7.42 (d, J = 8 Hz, 2H), 7.38 (d, J = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 189.58, 150.85, 145.29, 144.15, 137.19, 132.74, 129.81, 121.41.

(E)-3-(naphthalen-2-yl)-1-(pyridin-4-yl)prop-2-en-1-one **(NPY): NPY** was synthesized following the method described in Section 5.2 with 4-acetylpyridine (121 mg) and naphthalene-2-aldehyde (156 mg) except that after the addition of the aldehyde, the reaction mixture was warmed and the temperature was maintained at 38-40℃. TLC, EtOAc: Hexane = 40: 60. Shiny yellow. Yield: 183 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, J = 8 Hz, 2H), 8.01 (d, J = 8 Hz, 2H), 7.97 (d, J = 16 Hz, 1H), 7.85 (t, J = 8 Hz, 3H), 7.79-7.79 (m, 3H), 7.51 (d, J = 16 Hz, 1H), 7.53 (d, J = 8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 189.76, 150.81, 146.86, 134.65, 133.29, 131.32, 128.92, 127.85,126.94, 123.49, 121.26.

(E)-3-(9-methylanthracen-10-yl)-1-(pyridin-4-yl)prop-2-en-1-one **(ANMePY)**: **ANMePY** was synthesized following the method described in Section 5.2 with 4-acetylpyridine (121 mg) and 9-methylanthracene-10-carbaldehyde (220 mg) except that after the addition of the aldehyde, the reaction mixture was warmed and temperature was maintained at 55-60 ℃. TLC, EtOAc: Hexane = 40: 60. Orange crystalline solid. Yield: 100 mg (31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24-8.21 (m, 2H), 8.15-8.12 (m, 3H), 8.08-8.05 (m, 2H), 7.50-7.48 (m, 4H), 7.23 (d, J = 12 Hz, 1H), 7.01 (d, J = 8 Hz, 2H), 3.01 (s, 3H).

(E)-3-(anthracen-10-yl)-1-(pyridin-4-yl)prop-2-en-1-one **(ANPY)**: **ANPY** was synthesized following the method described in Section 5.2 with 4-acetylpyridine (121 mg) and 9-anthracenecarboxaldehyde (206 mg) except that after the addition of the aldehyde, the reaction mixture was warmed and temperature was maintained at 55-60℃. TLC, EtOAc: Hexane = 40: 60. Orange crystalline solid. Yield: 129 mg (42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88-8.84 (m, 2H), 8.50 (s, 1H), 8.27 (d, J = 8 Hz, 2H), 8.05 (d, J = 8 Hz, 2H), 7.84 (d, J = 8 Hz, 2H), 7.56-

7.51 (m, 5H), 7.48 (d, J = 16 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 188.9, 150.9, 143.3, 129.8, 128.9, 126.7, 125.47, 124.9, 124.8.

5.4 Linear optical properties of heteroaryl chalcone derivatives:

The absorption and emission spectra were recorded in chloroform at room temperature with 0.5×10^{-8} M concentration. The absorption spectra of the chalcones are presented in Fig. 5.03 and Fig. 5.04 shows the emission spectra.

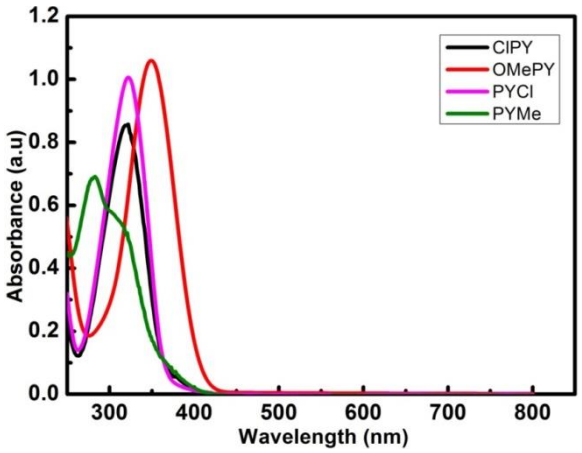


Figure 5.03: Absorption Spectra of heteroaryl Chalcone Derivatives.

Absorption takes place in the range of 281 nm to 349 nm, which can be attributed to $n-\pi^*$ transitions for the presence of carbonyl group in the compounds. This band was considered which tend to emit the fluorescence light. Absorption of **OMePY** at 240 nm and of **NPY** at 279 nm is due to $\pi-\pi^*$ transition. Highest λ_{abs} value, as expected, is observed for **OMePY & NPY** because of increased conjugation compared to its other congeners. The summarized absorption (λ_{abs}) and emission (λ_{em}) wavelength maxima, Stokes shift of the synthesized heteroaryl chalcone derivatives has been tabulated in Table 5.02. Moreover, the region (400-800) nm is also transparent for all the chalcones which is one of the important criteria for a compound to have

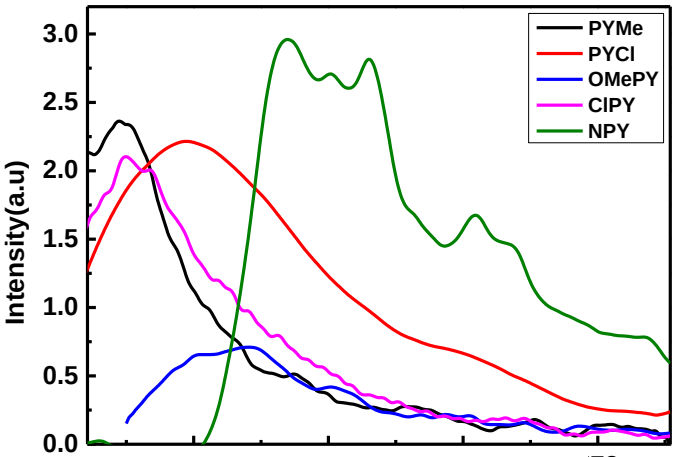


Figure 5.04: Emission Spectra of heteroaryl Chalcone Derivatives

NLO property. The highest and lowest Stoke's shift is observed for **NPY** and **ClPY** respectively.

Table 5.02: Photophysical properties of heteroaryl chalcone derivatives.

Compound	λ_{abs} (nm)	λ_{em} (nm)	Stoke's Shift (nm)	Compound	λ_{abs} (nm)	λ_{em} (nm)	Stoke's Shift (nm)
PYCl	323	413 (323)	90	**OMePY**	349, 240	437 (350)	87
PYOMe	281	387 (313)	74	**ClPY**	318	390 (322)	68
NPY	332, 279	451 (332)	119	**PYBr**	290	339 (290)	49
ANPY	397, 260	431 (382)	49	**ANMePY**	409, 250	435 (398)	37

All the heteroaryl chalcone derivatives exhibited photoluminescence (PL) property when excited at their absorption maxima. **OMePY** had the least PL intensity whereas **NPY** had the highest.

In case of **NPY**, the fluorescence emission spectra have two peaks of different intensity. This is because of aggregate formation. Molecules having $D-\pi-A$ type of motif tends to form an aggregate in the solution.

The uneven distribution of electrons in a compound is the origin of intermolecular electrostatic interactions, this interaction lies between adjacent molecules in a solution. Aggregation is present in **NPY** as it has a donor-acceptor unit in its structure. H-type aggregation gives emission spectra at higher energy portion and J-type aggregates in the lower energy side. Fig. 5.05 shows the schematic representation of two types of aggregation. The degree of aggregation also depends on the dielectric constant of the solvent and concentration used [13, 14].

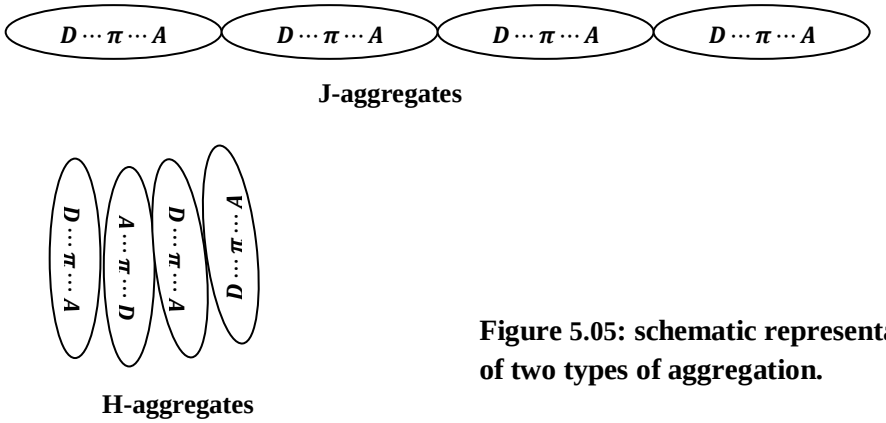


Figure 5.05: schematic representation of two types of aggregation.

5.5 Nonlinear optical properties of heteroaryl chalcone derivatives:

Two-photon absorption coefficient of heteroaryl chalcones is provided in Table 5.03. The experimental data was fitted to Eqn 4.3. A comparative study of the synthesized compounds is presented to understand the structure-property relationship of their nonlinear absorption.

Table 5.03: z-scan data of heteroaryl chalcone derivatives.

Compound	ß (cm/GW)	Compound	ß (cm/GW)	Compound	ß (cm/GW)
PYBr	4.22	**OMePY**	4.00	**NPY**	4.35
PYCl	5.0	**ClPY**	3.35	**ANPY**	1.74

All the compounds have nonlinear absorption of the similar magnitude except **PYCl**. So, a direct structure-property relationship cannot be drawn in the present situation.

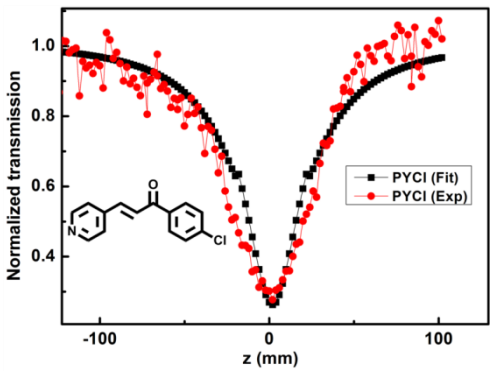


Figure 5.06: Open Aperture z scan data of PYCl.

PYCl has –Cl group in conjugation with the carbonyl group (-C=O). Here, –Cl group acts as an acceptor rather than a donor because of the presence of electron rich heteroaryl group in the compound. So, **PYCl** with $D-\pi-A-A$ motif creates a push pull system and probably this helps to improve the ß value. The open aperture z scan data of **PYCl** is shown in Fig. 5.06.

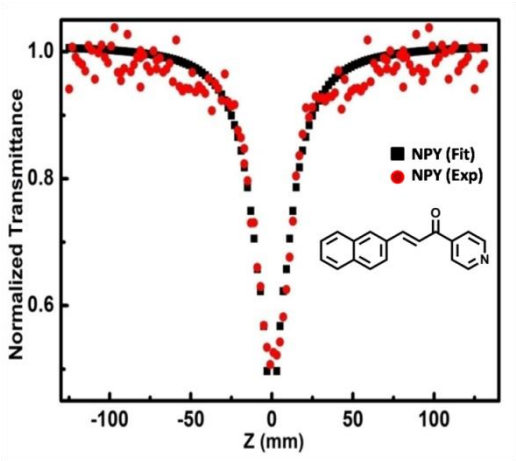


Figure 5.07: Open Aperture z scan data of NPY.

The open aperture z-scan data of **NPY** is shown in Fig. 5.07. The nonlinear absorption of **NPY** can be expressed by Eqn 1.7 and the experimental z-scan data was fit to Eqn 4.3. The presence of naphthalene could not enhance the ß value because of aggregation formation. Along with NLA, the chalcone derivative exhibited absorption saturation.

Aggregation confines the effectual number density that can be achieved in an NLO system. The average distance between chromophores, poling effectiveness also diminishes and they cancel out the proficient dipole moments between them [13-16].

5.6 Conclusion:

In total, eight chalcones with the heterocyclic core in the skeleton have been synthesized.

The compounds exhibited luminescence when excited with UV radiation, *(E)-3-(naphthalen-2-yl)-1-(pyridin-4-yl)prop-2-en-1-one* have aggregation signature in its luminescence spectra with Stoke's shift of 119 nm.

Most of the compounds in this series exhibited NLO property. The presence of the heterocyclic ring at the beta-carbon of the carbonyl moiety enhances the *ß* value, which gets further enhanced with the suitable group at the carbonyl side.

NPY have saturable absorption behavior. It is useful in a number of applications, chiefly for Q-switching and mode-locking lasers. An important way to generate ultra-short pulses is done by setting up a saturable absorber into a laser cavity. This absorber passively enables to lock the modes together into pulses in the laser [17]. Saturable absorbers are also used for nonlinear filtering outside laser resonators to clean up pulse shapes.

5.7 References:

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5.8 Spectral data of heteroaryl chalcone derivatives:

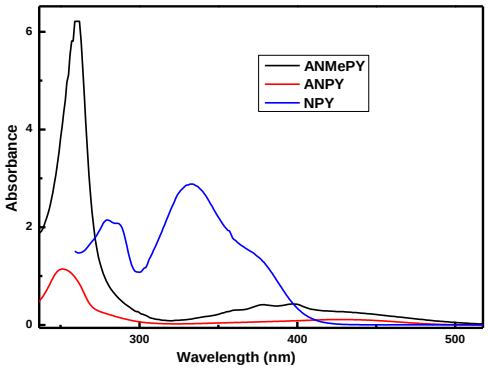

Figure 5.8: Absorption spectra of NPY, ANPY and ANMePY.

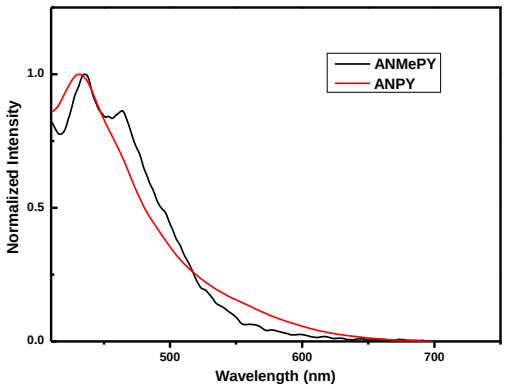

Figure 5.9: Emission spectra of NPY, ANPY and ANMePY.

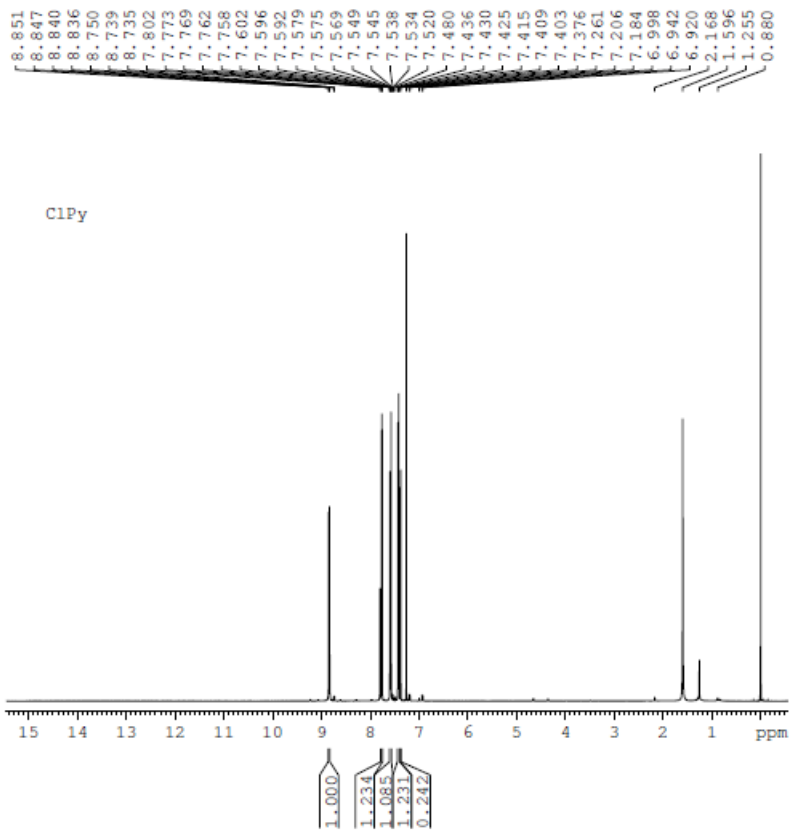

Figure 5.10: ^{1}H NMR spectrum of *(E)-3-(4-chlorophenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (ClPY).

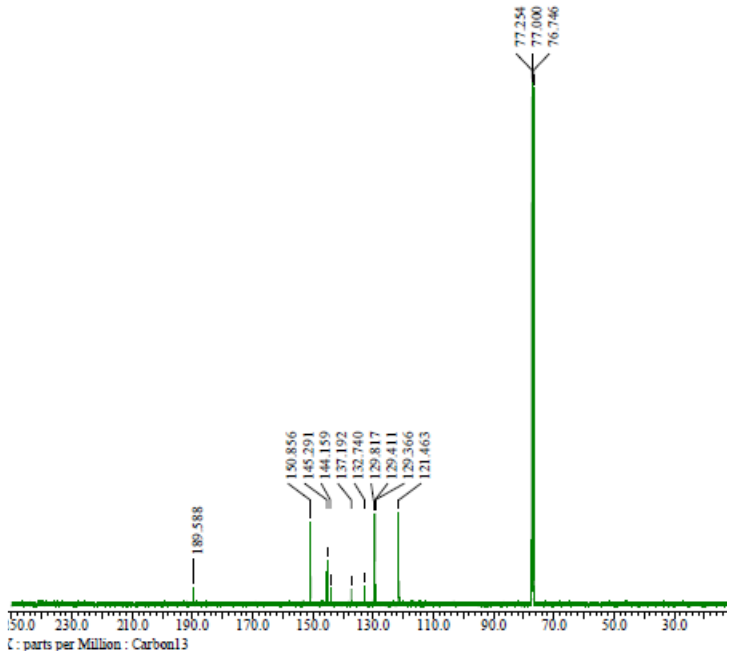

Figure 5.11: ^{13}C NMR spectrum of *(E)-3-(4-chlorophenyl)-1-(pyridin-4-yl)prop-2-en-1-one* (ClPY).

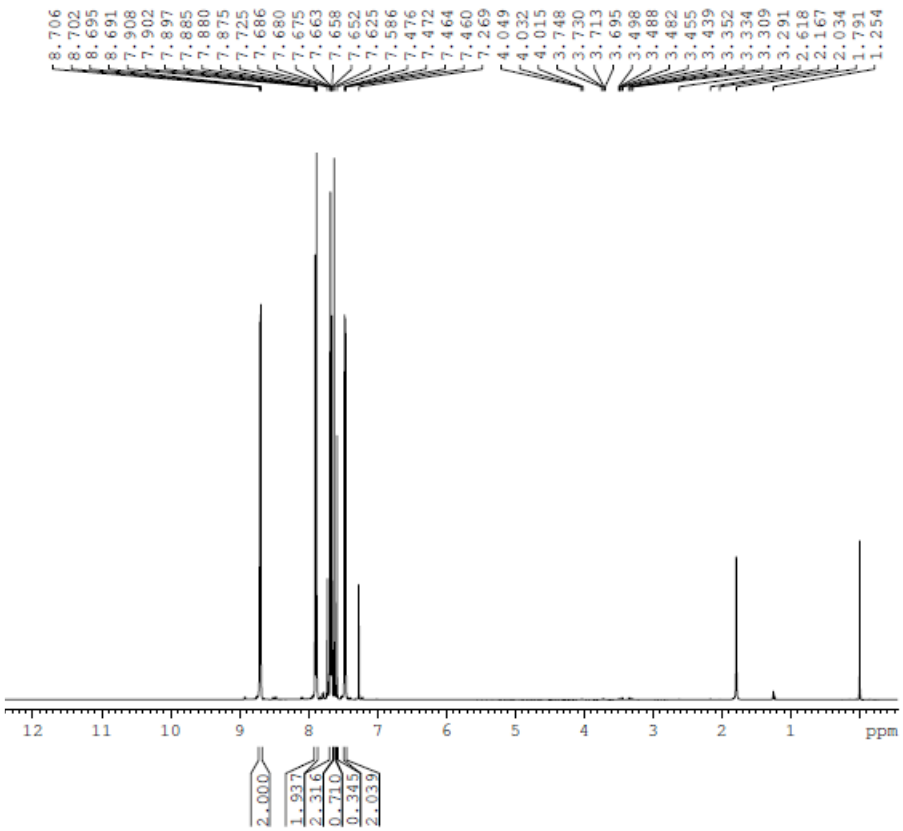

Figure 5.12:[1]H NMR spectrum of *(E)-1-(4-bromophenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYBr).

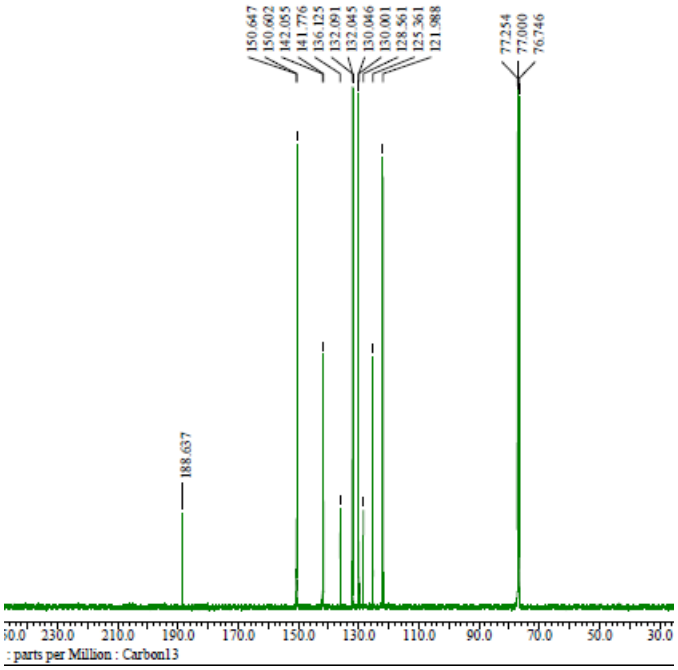

Figure 5.13: [13]C NMR spectrum of *(E)-1-(4-bromophenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYBr).

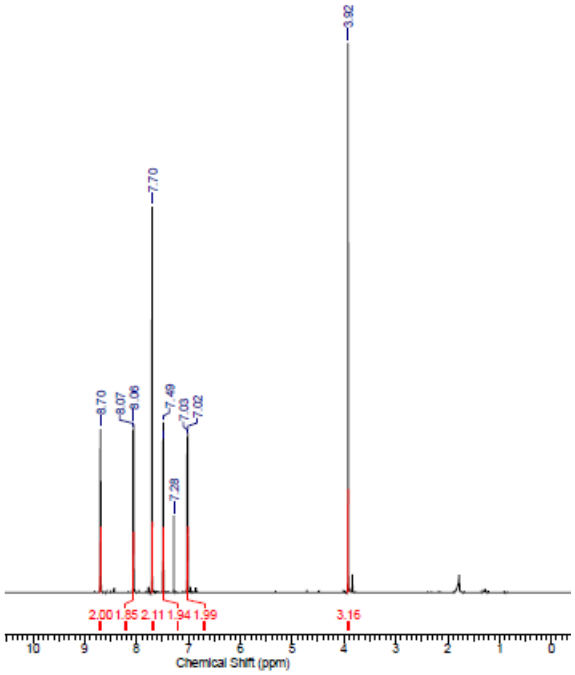

Figure 5.14: ^{1}H NMR spectrum of *(E)-1-(4-methoxyphenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYOMe).

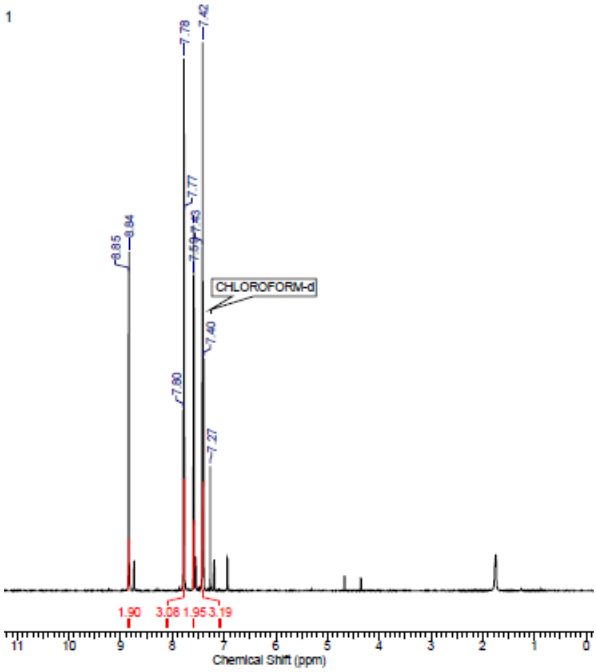

Figure 5.15: ^{1}H NMR spectrum of *(E)-1-(4-chlorophenyl)-3-(pyridin-4-yl)prop-2-en-1-one* (PYCl).

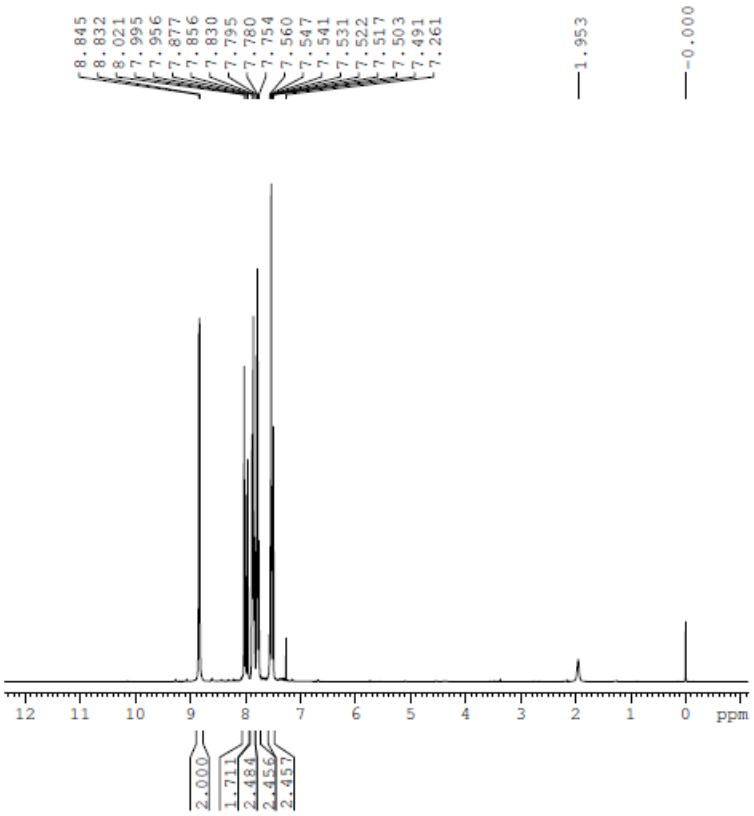

Figure 5.16: ^{1}H NMR spectrum of *(E)-3-(naphthalen-2-yl)-1-(pyridin-4-yl)prop-2-en-1-one* (NPY).

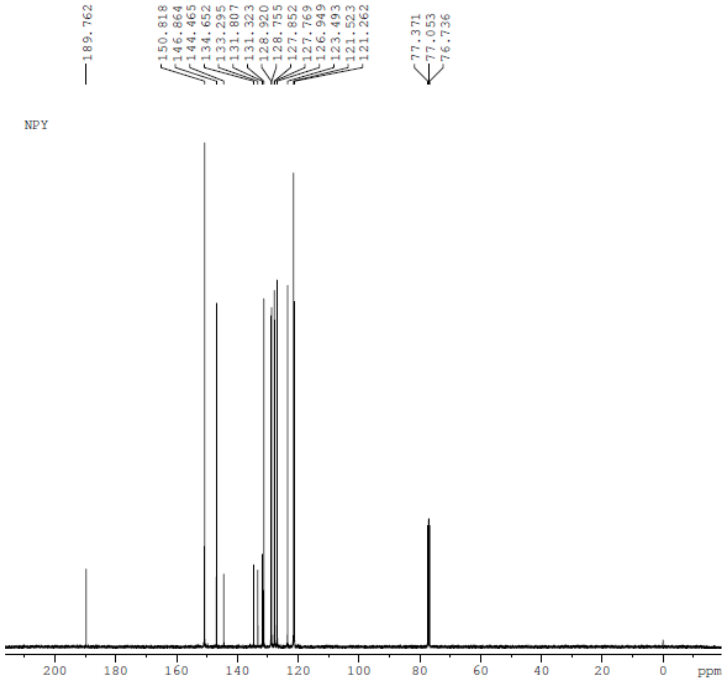

Figure 5.17: ^{13}C NMR spectrum of *(E)-3-(naphthalen-2-yl)-1-(pyridin-4-yl)prop-2-en-1-one* (NPY).

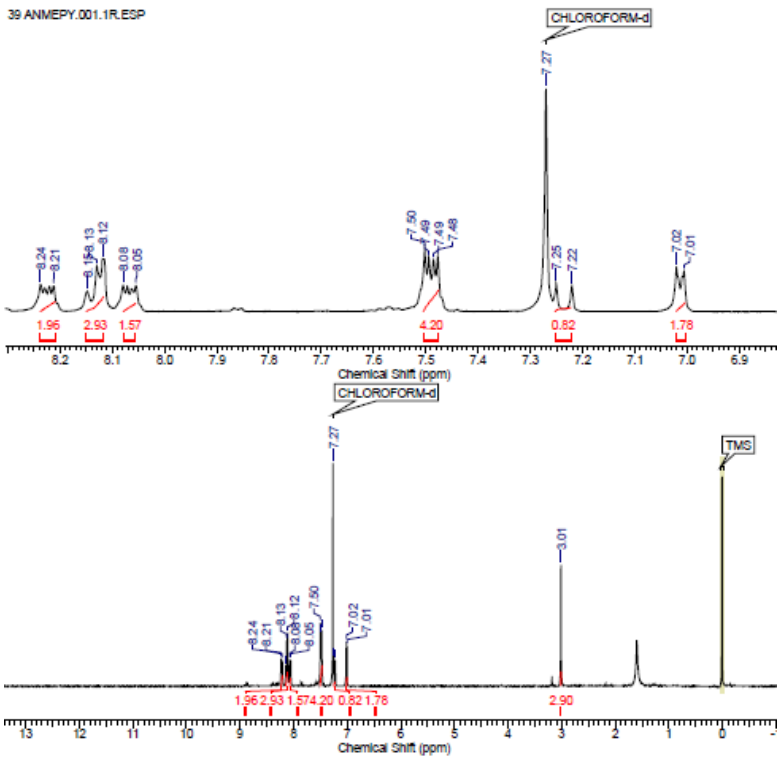

Figure 5.18: ^{1}H NMR spectrum of *(E)-3-(9-methylanthracen-10-yl)-1-(pyridin-4-yl)prop-2-en-1-one* (ANMePY).

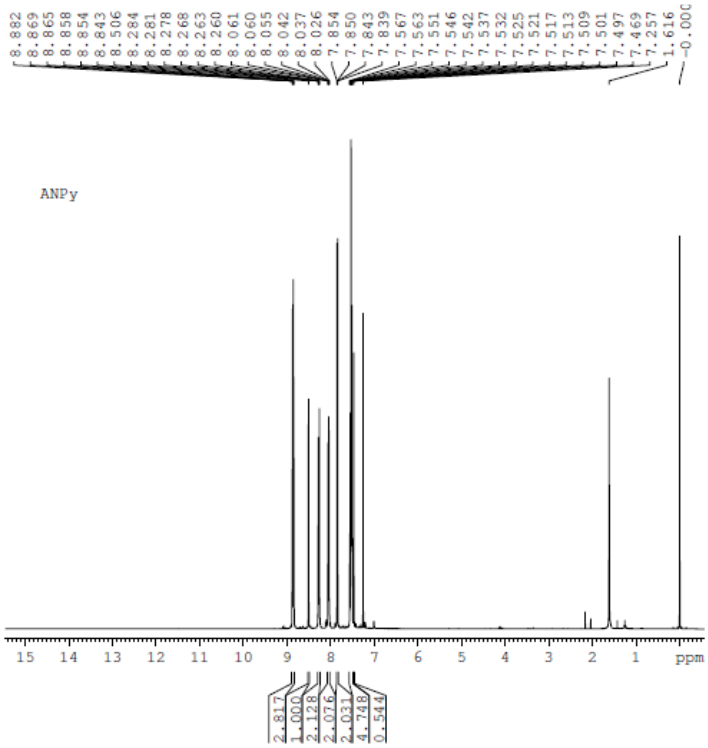

Figure 5.19: ^{1}H NMR spectrum of *(E)-3-(anthracen-10-yl)-1-(pyridin-4-yl)prop-2-en-1-one* (ANPY).

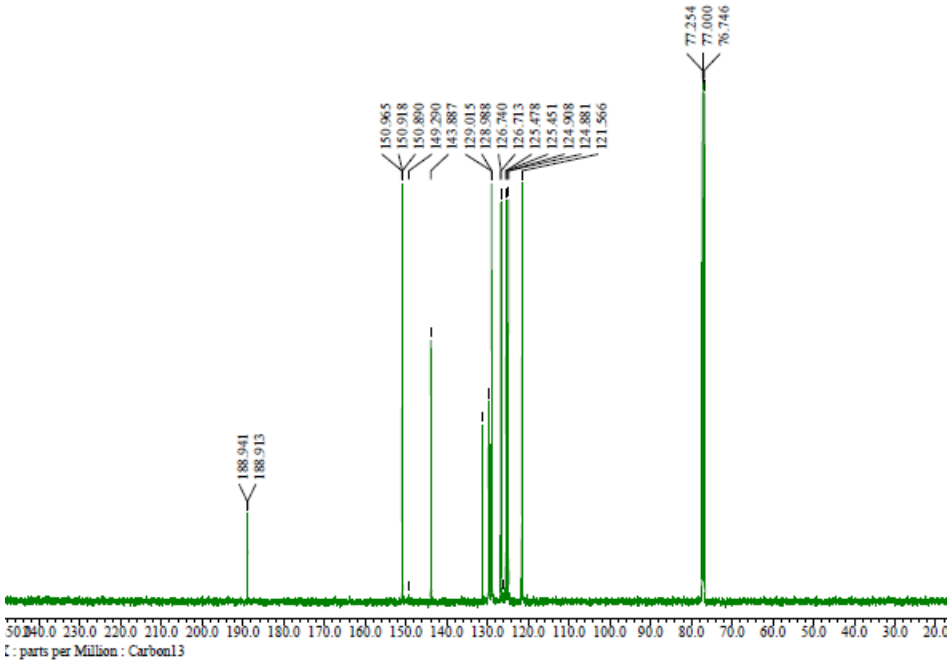

Figure 5.20: ^{13}C NMR spectrum of *(E)-3-(anthracen-10-yl)-1-(pyridin-4-yl)prop-2-en-1-one* (ANPY).

Open Aperture z-scan data:

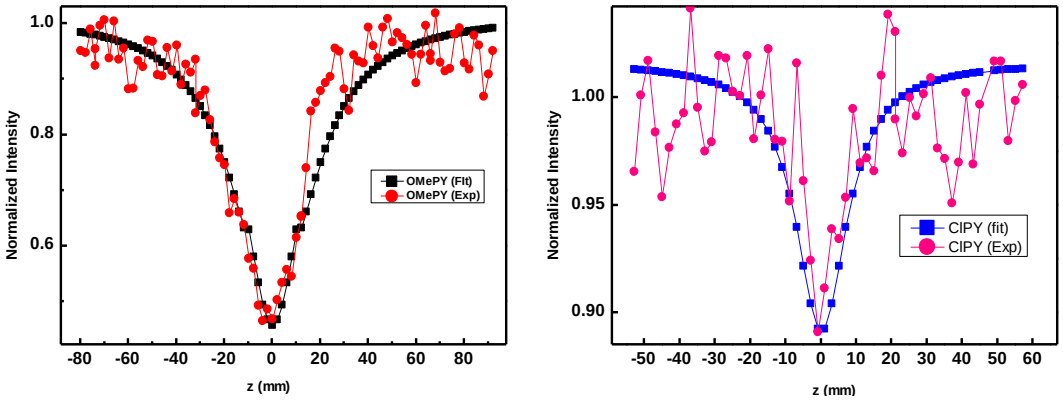

Figure 5.21: Open aperture z-sczn data of OMePy and ClPY.