CHAPTER 2

Materials and methods

In this chapter, the materials used and the procedures employed during the course of our investigation are outlined. Purification procedures adopted for the chemicals and the solvents are described. A brief outline of the various physicochemical techniques used in the present study has also been provided.

2.1 General Experimental

2.1.1 Solvents

2.1.1.1 Solvent for reactions[1]

Pyrrole was distilled before use. Dichloromethane and 1,2-dichloroethane were dried by distillation over calcium hydride. Tetrahydrofuran and diethyl ether were dried by passage through columns of activated alumina, followed by refluxing with sodium metal, in presence of benzophenone. Ethanol and methanol were dried by using activated magnesium turnings. $CHCl_3$ was dried by passing GR grade $CHCl_3$ over basic alumina. Toluene was refluxed with sodium and benzophenone until blue color and distilled before use. $POCl_3$ was distilled before use.

2.1.1.2 NMR solvents

Chloroform-d_1, acetonitrile-d_3, D_2O and DMSO-d_6 were purchased from Acros Organics/Cambridge isotope Inc. Toluene-d_8 was purchased from E-Merck, India and used as such.

2.1.1.3 Solvents for optical measurement

DMSO, $CHCl_3$, CH_2Cl_2, methanol, DMF, toluene, acetonitrile and hexane (spectroscopy grade) were purchased from Merck and used as such.

2.1.2 Reagents

Pyrrole was purchased from Sisco research laboratories (SRL). Cuprous chloride, triethyl orthoformate, Pd/C, benzyl acetoacetate, KO^tBu, Et_3N, $BF_3.OEt_2$, TFA, $Ni(acac)_2$, $Cu(OAc)_2.H_2O$, $Pd(OAc)_2$, 2,3-dihydroxynaphthalene, $AlCl_3$ and all alkyl bromides were purchased from Sigma-Aldrich® and used as such. THF, nitrobenzene and acetonitrile were purchased from Finar chemicals. GR grade Toluene, acetic acid, 1,2-dichloroethane, DMF, DCM, $CHCl_3$, DMSO, MeOH, diethyl ether, ethylene glycol and *i*-propanol were purchased from Merck. Zn and $TiCl_4$ were purchased from Finar chemicals. All the inorganic salts, mineral acids, acetyl acetone, CH_3I, hydrazinium sulfate, hydrazine hydrate, P_2O_5, NaOH, KOH and

solvents used for the routine laboratory work, were purchased from Merck. *p*-TsOH, $FeCl_3$ and $POCl_3$ were purchased from Loba Chemie. Mg-turnings, I_2, diethyl oxalate, basic and neutral alumina were purchased from Sisco Research Laboratories.

2.2 Chromatography

Thin layer chromatography was performed on TLC Silica gel 60 F_{254} aluminum sheet, purchased from Merck. Column chromatography was carried out on silica gel (100-200 mesh) purchased from Merck.

2.3 Characterization and instrumentation

NMR spectra were obtained on Bruker 400 MHz and 500 MHz FT-NMR spectrometer operating at ambient temperature. TMS was used as internal standard for ^1H NMR spectra.

Mass spectral determinations were carried out by Autoflex III Smartbeam Bruker Daltonics, MALDI-TOF mass spectrometer, LCMS were carried out by Shimadzu-LCMS-2010 mass spectrometer and HRMS data were recorded with Bruker Maxis spectrometer.

Elemental analyses were obtained through Thermo Finnigan Flash EA 1112 analyzer. EPR measurements were done on Bruker EMX microX spectrometer. Melting points were determined by open capillary tubes on a BIO-TECH, India apparatus. IR spectra were recorded on a JASCO FTIR model 5300 and NICOLET 5700 FT-IR spectrometer.

UV-Vis spectra were recorded on Perkin Elmer Lambda 35 and UV 3600 Shimadzu UV-VIS-NIR spectrophotometer. Fluorescence spectra were recorded on Horiba Zobin Yovan Fluoromax-4 instrument. Fluorescence lifetime measurements were carried out using a time correlated single-photon counting (TCSPC) spectrometer (Horiba Jobin Yvon IBH). Nano LED source (λ_{exc} 639 nm) was used as the excitation source and an MCP photomultiplier (Hamamatsu R3809U-50) as the detector. The pulse repetition rate of the laser source was 1MHz. The width of the instrument response function, which was limited by the fwhm of the exciting pulse, was around 100 ps. The lamp profile was recorded by placing a scatterer (dilute solution of Ludox in water) in place of the sample. The time resolved emission decay profiles were collected at steady state emission maxima. Decay curves were analyzed by nonlinear least-squares iteration procedure using IBH DAS6 (Version 2.2) decay analysis software. The quality of the fit was ass-

essed by inspection of the χ^2 values and the distribution of the residuals.

Some of the crystallographic data were collected on BRUKER SMART-APEX CCD diffractometer. Mo−K_α (λ = 0.71073 Å) radiation was used to collect X-ray reflections from the single crystal. Data reduction was performed using Bruker SAINT[2] software. Intensities for absorption were corrected using SADABS[3] and refined using SHELXL-97[4] with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C−H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON[5] did not show any missed symmetry. Remaining other crystallographic data was collected on Oxford Gemini A Ultra diffractometer with dual sources. Mo-K_α (λ = 0.71073 Å) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlis^{Pro} 171.33.55 software.[6] Structures were solved and refined using Olex2-1.0, with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were located from the Fourier map in all of the crystal structures. All C–H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON[5] did not show any missed symmetry.

2.3.1 2PA and 3PA measurements

2.3.1.1 Picosecond (ps) Z-Scan at 800nm

The Z-scan measurements were performed using ~2 ps (FWHM), 800 nm pulses with a repetition rate of 1 kHz from an amplified Ti:sapphire system (Legend, Coherent). The amplifier was seeded with pulses of duration ~15 fs (FWHM, spectral bandwidth of ~50-60 nm) from the oscillator (Micra, Coherent). The pulses were nearly transform limited and this was confirmed from the bandwidth and pulse duration measurements performed using an external auto-correlation experiment using a 2-mm thick BBO crystal in the non-collinear geometry. A quartz cuvette (1 mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist ($2\omega_0$) at focal plane was estimated to be 60±4 μm (FW1/e^2M) with a corresponding Rayleigh range (Z_r) of 3.5±0.4 mm ensuring the validity of thin sample approximation. The Z-scan was performed over a distance of $10Z_r$ on a high-resolution linear translation stage (Newport ILS250PP) by recording the sample transmittance using a power sensor (Coherent PS19). A LabVIEW program was

designed and used for automating the data acquisition of the Z-scan experiments. Typical energies in the range of 1-10 μJ, corresponding to peak intensities in the range of 70–400 GW/cm^2, were used for all the experiments. The closed aperture scans were performed at peak intensities <100 GW/cm^2.

2.3.1.2 Ps Z-Scan at other than 800nm

Z-scan measurements were performed at 560, 580, 600, 640, 680 and 700 nm using ~1.5 ps (FWHM) pulses with a repetition rate of 1 kHz from TOPAS (Light Conversion) pumped with an amplified Ti:sapphire system (LEGEND, Coherent). The amplifier was seeded with pulses of duration ~15 fs (FWHM, ~60 nm bandwidth) from an oscillator (Micra, Coherent). A quartz cuvette (1 mm thick) containing the sample solution was traversed in the focusing geometry enabled by an achromat lens of 200 mm focal length. The beam waist (2ω0) at focal plane was estimated to be 60±4 μm (FW1/e^{2}M) with a corresponding Rayleigh range (Zr) of 3.5±0.4 mm ensuring the validity of thin sample approximation.

The open aperture z-scan data have been fitted using the relation obtained by Sheik Bahae et al.[7] by time integration of sample transmittance assuming a Gaussian temporal profile. The two photon absorption fitting is done using the equation (1) and three photon absorption fitting was done using equation (2): Where T(z) is the normalized transmittance as a function of z, $q_0 = \alpha_2 l_{eff} I_0$, $p_0 = (2\alpha_3 l_{eff} I_0^2)^{1/2}$, α_2 = 2PA coefficient and α_3 = 3PA coefficient, I_0 is the peak intensity at focus.

$$T(z, S=1) = \frac{1}{\sqrt{\pi} q_0(z,0)} \int_{-\infty}^{\infty} \ln\left[1 + q_0(z,0) e^{-\tau^2}\right] d\tau \qquad (1)$$

$$T(z, S=1) = \frac{1}{\sqrt{\pi} p_0(z,0)} \int_{-\infty}^{\infty} \ln\left[\sqrt{\ln(1 + p_0^2 \exp(-2\tau^2))} + p_0(z,0) \exp(-\tau^2)\right] d\tau \qquad (2)$$

Effective path lengths in the sample of length L for 2PA and 3PA are given as $L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$, $L'_{eff} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}$, α_0 = linear absorption coefficient.

2.3.2 Excited state life time study

2.3.2.1 Femtosecond pump-probe at 600nm

The fs degenerate pump-probe experiments were performed at 600 nm. The liquid sample was taken in a 5mm thick glass cuvette. The molecules were excited by pulses from 1 kHz optical parametric amplifier (TOPAS-C, Light Conversion, Coherent) delivering pulses of 60 fs duration pumped by a Ti:Sapphire regenerative amplifier. Pump pulses in the energy range of 5–50 μJ were used. The probe beam diameter was 2 mm, and pump beam diameter was 4 mm. The pulse-width at the sample in our fs experiments was estimated (taking into account the optics and lenses involved) to be 70 fs. The pump beam was focused using a 150 mm lens, while the probe beam was focused using a longer focal length lens (500 mm). Typical pump beam intensity was 0.3–3 TW/cm^2, while the probe beam intensity was 5 GW/cm^2. The ratio of pump to probe intensities was at least 60. The pump beam was modulated at 100 Hz with the help of a chopper, and the change in probe transmitted intensity was measured with a combination of a photodiode (SM05R/M, Thorlabs) and a lock-in amplifier (7265, Signal Recovery). The polarization of pump and probe beams was perpendicular in both the cases to avoid diffraction effects leading to coherent artefacts.

2.3.2.2 Picosecond pump-probe at 800nm

In the ps pump-probe set up, the pump and probe beam diameters were 4 and 2mm, respectively. The molecules were excited by pulses from 1 kHz Ti:Sapphire regenerative amplifier (LEGEND, Coherent) delivering pulses of ~2 ps duration .The pump and probe beams were focused using single 200 mm lens. Typical peak intensities of pump and probe beams were 150 GW/cm^2 and 2–4 GW/cm^2, respectively. The ratio of pump to probe intensities was at least 75. The focusing in both the cases was such that the probe beam diameter was ensured to be slightly smaller than the pump beam diameter.

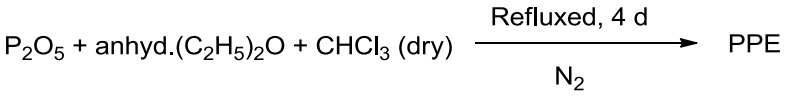
The transmitted probe data was fitted using the equation given below. For the case of single decay, it was observed only τ_1, for double decay, τ_1 and τ_2, and for triple exponential decay, τ_1, τ_2, and τ_3 were used. $\Delta T(t)$ is the time dependent change in probe transmission, induced by the pump at time "t" after the pump excitation, and T is the probe transmission in the absence of pump.[8]

$$\frac{\Delta T(t)}{T} = y_0 + A_1 e^{-(t-t_0)/\tau_1} + A_2 e^{-(t-t_0)/\tau_2} + A_3 e^{-(t-t_0)/\tau_3}$$

2.4 Preparation of starting materials

The following compounds were prepared by following literature method, in order to utilize them as the starting material for our investigation. Their identification was further confirmed, by matching the analytical data with that reported in the literature.

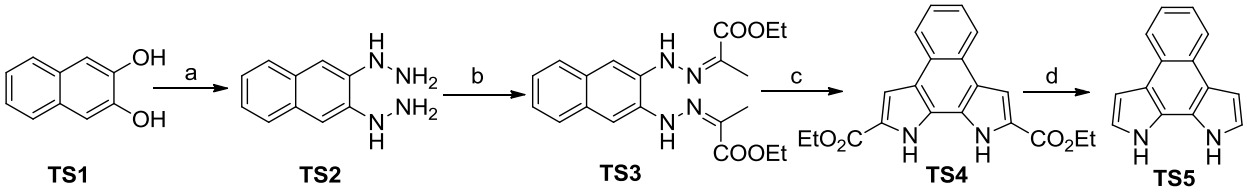
2.4.1 Synthesis of PPE (Polyphosphate Ester)[9]



Scheme 2.1 Synthesis of PPE.

Phosphorus(V) oxide (150 g) is added to a solution of anhyd. ether (300 mL) and alcohol-free chloroform (150 mL). The reaction mixture is refluxed under dry nitrogen for 4 d and the resulting clear solution decanted from a small amount of residue. The solution is concentrated to a colorless syrupy mass in a rotary evaporator; residual traces of solvent are removed by heating the syrup for 36 h at 40 °C in vacuum.

2.4.2 Synthesis of unsubstituted naphthobipyrrole[10]



Scheme 2.2 Synthesis of unsubstituted naphthobipyrrole. a) $NH_2NH_2.H_2SO_4$, $NH_2NH_2.H_2O$, EtOH, reflux, 10 h. b) CH_3COCO_2Et, EtOH, rt, 1 h. c) PPE, 100 °C, 1h. d) NaOH, ethylene glycol, reflux, 2 h.

2.4.2.1 Synthesis of 2,3-naphthalenedihydrazene TS2[10a]

2,3-dihydroxynaphthalene **TS1** (30g, 187.3 mmol) were mixed with hydrazinium sulfate (10g, 77 mmol). To this, mixture of absolute alcohol (15 mL) and hydrazine hydrate (30 mL) were added in a round bottom flask. The mixture was heated to reflux. After 2-4 h a clear greenish brown color crystalline material starts depositing. The reaction was completed after another 3-4 h. The precipitate was filtered under suction and washed with alcohol for several times, dried under vacuum. Yield: 21g, 61 %.

2.4.2.2 Synthesis of ethyl pyruvate 2,3-naphthalenehydrazone TS3[10b]

To a suspension of 2,3-naphthalenedihydrazine (6g, 32 mmol) in abs. ethanol (50 mL), a solution of ethyl pyruvate (12 mL, 108 mmol) in abs. ethanol (5 mL) was added. Resultant reaction mixture was stirred for 1 h to obtain a yellow precipitate. It was filtered under suction and dried. Yield: 10.52 g, 86 % (lit. 87 %).

2.4.2.3 Synthesis of 2,9-Diethoxycarbonylnaphthobipyrrole TS4[10b]

Ethyl pyruvate 2,3-naphthalenedihydrazone (4g, 10.4 mmol) **TS3** was heated with polyphosphate ester (28 mL, 8.9 mmol) at 100 °C for 1 h and poured into ice cold water. The resultant brown color precipitate was filtered under suction, washed with water 3-4 times and finally washed with $CHCl_3$ till the filtrate become colorless. Product dried under high vacuum. Yield: 2.5 g, 68 %.

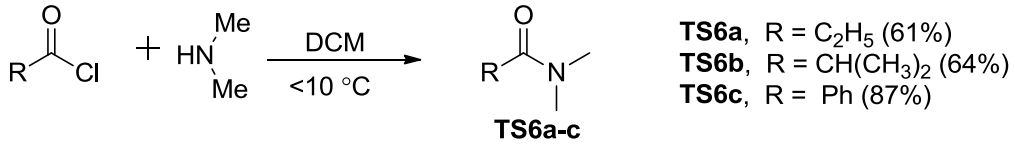
^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 11.8 (s, 2H, NH), 8.3 (m, 2H, CH-naph), 7.8 (s, 2H, CH-naph), 7.4 (m, 2H, CH-naph), 4.4 (q, J = 7.2 Hz, 4H, CH_2-ester), 1.4 (t, J = 7.2 Hz, 6H, CH_3-ester).

2.4.2.4 Synthesis of 2,9-Diethoxycarbonylnaphthobipyrrole TS5[10b]

Naphthobipyrrole diesters **TS4** (2 g, 5.7 mmol), ethylene glycol (60 mL), and NaOH (2.5 g, 63 mmol) were taken in a round bottomed flask and kept under high vacuum for 1 h. The mixture was then heated at reflux for 3 h under N_2 atmosphere, cooled to 100 °C and degassed water (90 mL) was added. The reaction mixture was stirred for 5 min, cooled to r.t. and the white-green coloured precipitate thus formed was filtered under suction and washed thoroughly with water to remove the excess ethylene glycol, dried under vacuum to obtain the desired product in almost quantitative yield. (lit. 22 % in two steps).

^{1}H NMR (400 MHz, DMSO-d_6, δ in ppm): 11.0 (brs, 2H), 8.21-8.15 (m, 2H), 7.38-7.32 (m, 2H), 7.24 (t, J = 2.67 Hz, 2H), 7.03-7.01 (m, 2H).

2.4.3 Synthesis of *N,N*-dimethylamides[11]



Scheme 2.3 Synthesis of *N,N*-dimethylamides.

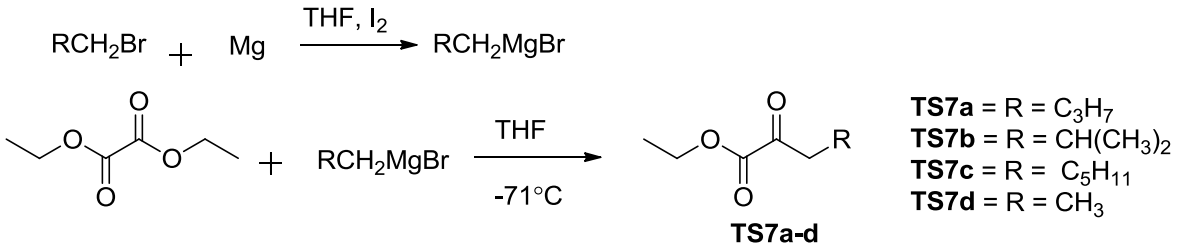
General procedure: To a solution of dimethylamine (40% aqueous solution, 2 equiv.) in dichloromethane, a solution of acyl chloride (1 equiv.) was added, while keeping the temperature of the reaction mixture below 10 °C. Reaction mixture was stirred at room temperature for another 5 h, after addition is over. Organic layer was separated and washed with 1N HCl, followed by water, dried over anhyd. sodium sulfate and concentrated under reduced pressure.

TS6a: Yield: 61 %, ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.15 (t, J = 7.6 Hz, 3H, CH_3), 2.33 (q, J = 7.2 Hz, 2H, CH_2,), 2.95 (3H, 3H, CH_3, N-methyl) 3.01 (3H, CH_3, N-methyl).^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 9.42, 26.64, 35.49, 37.21, 173.94.

TS6b: Yield: 64 %, ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.11 (d, J = 6.4 Hz, 6H, CH_3), 2.82 (m, 1H, CH), 2.95 (s, 3H, CH_3), 3.05 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm) 19.35, 30.33, 35.74, 37.19, 177.19.

TS6c: Yield: 87 %, ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.97 (s, 3H, CH_3), 3.10 (s, 3H, CH_3), 7.45-7.35 (m, 5 H, Ph).

2.4.4 Synthesis of α-keto esters[12]



Scheme 2.4 Synthesis of α-keto esters.

General procedure: Magnesium turnings (4 equiv.) and iodine (small amount) were taken in dry nitrogen filled round bottom flask and stirred for 2 h. Dry THF was added to this, followed by slow addition of the alkyl bromide (1.2 equiv.) with continuous stirring. After complete addition, the mixture was stirred for another 1 h to get the desired alkyl magnesium bromide. This was then added slowly through a cannula to a solution of diethyl oxalate (1.1 equiv.) in twice of its volume of THF at -70 $^{\circ}$C, over one hour period. The reaction mixture was stirred for another 4 h, quenched with 3M HCl till final pH of the solution becomes 4. The aqueous layer was extracted with an equal volume of methylene chloride. The combined organic layers were dried over anhyd. $MgSO_4$ and solvent was evaporated to obtain a light yellow liquid, which was further purified by distillation under reduced pressure. Yield: 80-90 %.

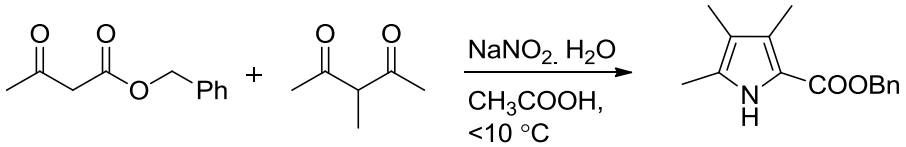
TS7a: Yield: 85 %; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.92 (t, J = 7.2 Hz, 3H, CH_3,), 1.35 (m, 5H, CH_3, CH_2), 1.62 (m, 2H, CH_2), 2.83 (t, 2H, J = 7.2 Hz, CH_2,), 4.33 (m, 2H, CH_2 ester).

TS7b: Yield: 80 %; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.87 (d, J = 6.8, 6H, CH_3,), 1.27 (m, 3H, CH_3), 2.09 (m, 1H, CH), 2.62 (d, J = 6.8, 2H, CH_2,), 4.22 (m, 2H, CH_2 ester).

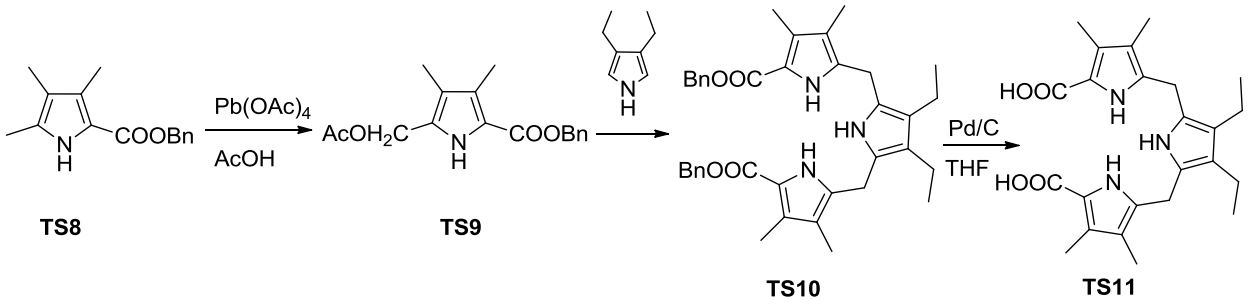
TS7c: Yield: 85 %; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 0.85 (t, J = 7.2 Hz, 3H, CH_3,), 1.19–1.30 (m, 6H, CH_2), 1.32 (m, 3H, CH_3), 1.63 (m, 2H, CH_2), 2.78 (t, J = 7.2, 2H, CH_2), 4.27 (m, 2H, CH_2 ester).

TS7d: Yield: 90 %; ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.14 (t, J = 7.2 Hz, 3H, CH_3,), 1.39 (m, 3H, CH_3), 2.87 (q, J = 7.2 Hz, 2H, CH_2,), 4.34 (m, 2H, CH_2 ester).

2.4.5 Synthesis of tripyrrane diacid TS11[13]



TS8



Scheme 2.5 Synthesis of tripyrrane diacid **TS11**.

2.4.5.1 Synthesis of benzyl-3,4,5-trimethylpyrrole-2-carboxylate TS8[13a]

Benzyl acetoacetate (2.1 mL, 12.26 mmol) was taken in glacial acetic acid (5 mL), to this a solution of $NaNO_2$ (1 g, 14.7 mmol) in water was added with stirring during 30 min. below 10 °C. The reaction mixture was further stirred for 4 h and kept overnight at room temperature. To this solution, 3-methylpentane-2,4-dione (1.4 g, 12.26 mmol) in acetic acid was added followed by addition of zinc dust (1.6 g, 24.47 mmol). The internal temperature of the reaction mixture was kept above 10 °C during addition. The reaction mixture was heated under reflux for 15 min. and poured into crushed ice. White precipitate thus obtained was filtered under suction, washed with water and dried under vacuum. Yield: 1.5 g, 51 % (lit. 45.5 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.93 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 5.31(s, 2H, CH_2-benzyl), 7.44-7.32 (m, 5H, Ph), 8.58 (brs, 1H, NH).

2.4.5.2 Synthesis of benzyl 5-(acetoxymethyl)-3,4-dimethylpyrrole-2-carboxylate TS9[13c]

$Pb(OAc)_4$ (3.86 g, 8.71 mmol) was added to a solution of benzyl-3,4,5-trimethylpyrrole-2-carboxylate (2 g, 82.2 mmol) **TS8** in acetic acid (20 mL) and acetic anhydride (2 mL, 20.3 mmol) and the reaction mixture was stirred at room temperature for 3 h and poured into ice water. The resultant precipitate was filtered and washed well with water, dried under vacuum. Yield: 2.3 g, 92 % (lit. 88 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.00 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 5.01 (s, 2H, OCH_2), 5.31 (s, 2H, CH_2-benzyl), 7.40 (m, 5H, Ph), 9.90 (brs, 1H, NH).

2.4.5.3 Synthesis of tripyrrane dibenzylester TS10[13b-d]

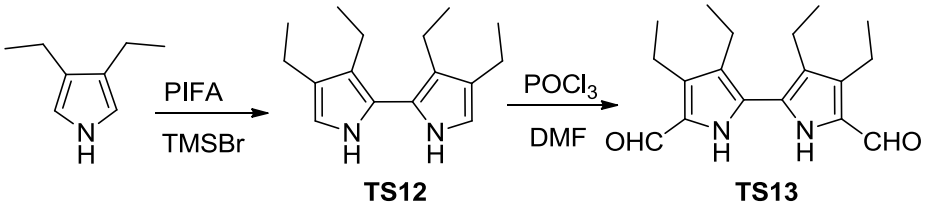
3,4-Diethylpyrrole (41 mg, 0.34 mmol) and benzyl 5-(acetoxymethyl)-3,4-dimethylpyrrole-2-carboxylate **TS9** (200 mg, 0.66 mmol) were dissolved in 2-popanol and acetic acid (64 μL). The resulting solution was stirred and refluxed under an atmosphere of N_2 for 16 h. The mixture was allowed to cool to room temperature and further cooled in an ice bath. The resulting precipitate was filtered, washed with cold ethanol and dried in vacuum overnight to get the tripyrrane **TS10**. Yield: 124 mg, 61.6 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.15 (t, J = 7.2 Hz, 6H, CH_3), 1.82 (s, 6H, CH_3), 2.18 (s, 6H, CH_3), 2.49 (q, *J* = 7.2 Hz, 4H, CH_2), 3.57, (s, 4H, *meso*-CH_2), 4.37 (s, 2H, CH_2-benzyl), 7.00 (m, 4H, Ph), 7.24 (m, 6H, Ph), 8.79(1H, brs, NH), 11.14 (2H, brs, NH).

2.4.5.4 Synthesis of tripyrrane diacid TS11[13b-d]

Tripyrrane dibenzylester **TS10** (100 mg, 0.17 mmol) was dissolved in freshly distilled dry THF (10 mL) and placed in a round bottom flask. The solution was diluted with methanol (5 mL) and to this, 10% Pd (25 mg, 0.022 mmol) on activated carbon was added, air was flashed from the vessel with H_2 and the reaction mixture was stirred under the atmosphere of H_2 for 16 h. After completion of the reaction, the catalyst was removed by suction filtration over celite pad and the solvent evaporated under reduced pressure (below 30 °C). The product was dried under high vacuum and used directly in the next step.

2.4.6 Synthesis of tetraethyl bipyrrole dialdehyde TS13[14]



Scheme 2.6 Synthesis of tetraethyl bipyrrole dialdehyde **TS13**.

2.4.6.1 Synthesis of tetraethyl bipyrrole TS12[14a]

To a stirred solution of 3,4-diethylpyrrole[14c] (700 mg, 5.67 mmol) in CH_2Cl_2, PIFA (phenyliodine bis(trifluoroacetate)) (813 mg, 1.9 mmol) and TMSBr (bromotrimethylsilane) (0.52 mL, 3.8 mmol) were added quickly at -78 °C. The reaction mixture was then stirred for 1 h

while the reaction temperature was maintained below -40 °C. To the reaction mixture, sat. aq. $NaHCO_3$ (ca. 130 mL) was added and stirred for an additional 10 min at ambient temperature. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined extract was dried with anhyd. Na_2SO_4 and evaporated to dryness and distilled under reduced pressure to obtain the desired bipyrrole **TS12**. Yield: 350 mg, 76 % (lit. 75 %).

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.05 (t, J = 7.8 Hz, 4H), 1.25 (t, J = 7.8 Hz, 4H), 2.42 (q, J = 7.8 Hz, 4H), 2.52 (q, J = 7.8 Hz, 4H), 6.53 (bs, 2H), 7.58 (bs, 2H).

2.4.6.2 Synthesis of tetraethyl bipyrrole dialdehyde TS13[14b]

Dry DMF (0.65 mL, 7.0 mmol) was taken in a two necked round bottomed flask under N_2 atmosphere. Cooled to 0°C, freshly distilled $POCl_3$ (0.55 mL, 7.0 mmol) was then added slowly to it with continuous stirring. After complete addition, the mixture was again stirred at room temperature for 1 h. To this mixture a solution of tetraethyl bipyrrole **TS12** (350 mg, 1.4 mmol) in dichloroethane was added at room temperature, under N_2 atmosphere. Subsequently, the reaction mixture was refluxed in a preheated oil bath for 2 h, cooled to room temperature and quenched with sat. NaOAc (70 mmol) solution and again refluxed for 1 h. The reaction mixture was cooled to room temperature, diluted with $CHCl_3$ and organic layer was separated and washed with water, dried with anhyd. Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography (silica, ethyl acetate/hexane 1:4). Yield: 165 mg, 41 %.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 1.09 (t, J = 7.6 Hz, 4H), 1.29 (t, J = 7.6 Hz, 4H), 2.55 (q, J = 7.6 Hz, 4H), 2.80 (q, J = 7.6 Hz, 4H), 9.13 (bs, 2H, NH), 9.65 (s, 2H, -CHO).

2.5 Summary

A brief account of various solvents, chemicals used in the synthesis and different spectrometers and other physical and computational methods employed for characterization in our investigation, is given in this chapter. Syntheses of the already reported compounds, which are employed as starting materials for the dissertation work, were also described here.

2.6 References

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