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Sachin Choudhary

Abstract

The present thesis is mainly covering the synthesis of five-, and six-membered nitrogen heterocycles such as functionalized pyrroles and oxazepine-fused pyrroles/1,2-dihydropyridines (DHPs) under metal-free conditions. This thesis is divided into six chapters:

The First Chapter gave a brief discussion on organocatalysis, in particular, amine catalysis and its applications for the development of various transformations such as direct Mannich reaction to achieve the synthesis of natural and non-natural compounds with varying selectivity. In addition, the utilization of linear dialdehydes such as succinaldehyde and glutaraldehyde for amine-catalyzed transformations to access various carbo-, and hetero-cyclic compounds have been discussed.

The Second Chapter demonstrates the synthesis of substituted pyrrole-3-methanols under microwave conditions. This one-pot protocol involves proline-catalyzed direct Mannich reaction-cyclization and dehydrocyanation between succinaldehyde and and α-iminonitriles followed by $NaBH_4$ reduction sequence in good yields.

The Third Chapter demonstrates the regioselective synthesis of 4-iodo and 5-iodo-pyrrolecarbaldehyde from the common starting material by switching the reacting conditions. The synthesis of 4-iodo-pyrrole-3-carboxaldehydes proceed through proline catalyzed direct Mannich reaction-cyclization sequence between in situ generated imines and succinaldehyde, followed by selective iodination and aromatization using molecular I_2, whereas, 5-iodo-pyrrole-3-carboxaldehydes was prepared in two-step process.

The Fourth Chapter demonstrates the synthesis of tetracyclic dibenzoxazepine-fused pyrroles in high to excellent yields. These polycyclic pyrroles were obtained through proline-catalyzed direct Mannich/cyclization sequence between succinaldehyde and seven-membered dibenzoxazepine-imines, followed by IBX-mediated oxidative aromatization in the same pot.

The Fifth Chapter demonstrates amine-catalyzed asymmetric one-pot synthesis of dibenzoxazepine fused-1,2-dihydropyridines (DHPs). This one-pot operation proceeds through L-proline-catalyzed direct Mannich/cyclizations sequence between dibenzoxazepine-imines and aqueous glutaraldehyde, followed by IBX-mediated site-selective dehydrogenative in the same pot with high yields and excellent enantioselectivity (>99:1 er).

The Sixth Chapter is a compilation of the overall thesis work and the future scope of the present research work is also presented.

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LIST OF ABBREVIATIONS / SYMBOLS

Abbreviation/Symbol	Description
α	Alpha
[α]	specific rotation
β	Beta
γ	Gamma
δ	Chemical shift
Δ	Heat
A	Angstrom
Ac	Acetyl
Aq	Aqueous
ACN	Acetonitrile
Ar	Aryl
Bu	Butyl
t-BuOK	Potassium *tert*-butoxide
Calcd.	Calculated
°C	Degree centigrade
^{13}CNMR	Carbon-13 nuclear magnetic resonance
Cat.	Catalyst
CAN	Ceric ammonium nitrate
$CDCl_3$	Deuterated chloroform
Conc	Concentration
COSY	Correlation Spectroscopy (NMR)
d	Doublet
DBO	dibenzoxazepine
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
dd	Doublet of doublet
DDQ	2,3-Dichloro-5,6-Dicyanobenzoquinone
DMSO	Dimethysulphoxide
DMSO-d_6	Deuterated Dimethysulphoxide

LIST OF ABBREVIATIONS / SYMBOLS

DCE	Dichloroethane
DCM	Dichloromethane
DMA	*N,N*-Dimethylacetamide
DMAD	Dimethyl acetylene dicarboxylate
DMF	*N,N*-Dimethylformamide
ESI	Electron Spray Ionization (MS)
EtOAc	Ethyl acetate
Equiv	Equivalent
E	Electrophile
g	Gram
HRMS	High Resolution Mass Spectra
HSQC	Heteronuclear Single Quantum Correlation
IBX	2-Iodoxybenzoic acid
IR	Infrared
Hz	Hertz
hr	Hour
J	Coupling constant
Lit.	Literature
MS	Mass spectrometry
M.P	Melting point
m	Multiplet
mg	Milligram
MHz	Mega hertz
min	Minutes
mL	Milliliter
mmol	Millimole
MW	Microwave
N_2	Nitrogen gas
Nu	Nucleophile
^{1}HNMR	Proton Nuclear Magnetic Resonance

LIST OF ABBREVIATIONS / SYMBOLS

NOE	Nuclear Overhauser Effect (NMR)
NOESY	Nuclear Overhauser Effect Spectroscopy (NMR)
O_2	Oxygen gas
PEG	Polyethylene glycol
ppm	Parts per million
%	Percentage
p-TsOH	*p*-Toluenesulfonic acid
PMP	*p*-methoxyphenyl
rt	Room temperature
s	Singlet
NBS	*N*-bromosuccinimide
NIS	*N*-iodosuccinimide
$NaHCO_3$	Sodium hydrogencarbonate
$Na_2S_2O_3$	Sodium thiosulfate
t	Triplet
TBAB	Tetrabutylammonium bromide
Ts	Tosyl
Tert-	Tertiary
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane
σ	Sigma