

# Table of contents

Acknowledgments.....	i
Résumé.....	iii
Abstract.....	v
Table of Contents.....	viii
List of abbreviations.....	xii
1. Introduction.....	5
2. Background and significance.....	9
2.1. Alkynes & nitriles: importance and classical syntheses.....	9
2.1.1. Aliphatic alkynes.....	9
2.1.2. Aliphatic nitriles.....	19
2.2. Alkynylation and cyanation of alkyl radicals.....	27
2.2.1. Alkynylation of alkyl radicals.....	32
2.2.2. Cyanation of/via alkyl radicals.....	34
2.2.3. Conclusion.....	39
2.3. Photoredox catalysis, a powerful method to generate radicals.....	41
2.3.1. General introduction of photoredox catalysis.....	41
2.3.2. Photoredox catalyzed decarboxylative transformations.....	49
2.3.3. Metallaphotoredox catalyzed decarboxylative transformations.....	58
2.3.4. Photoredox catalyzed synthesis of aliphatic alkynes.....	61
2.3.5. Photoredox catalyzed synthesis of aliphatic nitriles.....	67
2.4. Hypervalent iodine compounds.....	71
2.4.1. General introduction of hypervalent iodine reagents.....	71
2.4.2. Addition of alkyl radicals to EBX and CBX.....	88
2.4.3. Photoredox catalyzed alkynylations using hypervalent iodine reagents.....	96
3. Goal of the thesis.....	104
4. Decarboxylative alkynylation and cyanation of free carboxylic acids using photoredox and hypervalent iodine reagents.....	108
4.1. Decarboxylative alkynylation.....	108
4.1.1. Optimization.....	108
4.1.2. Scope of the photoredox catalyzed decarboxylative alkynylation.....	117
4.1.3. Sunlight experiment, scale up and derivatizations.....	123

4.1.4. Conclusion of the decarboxylative alkynylation of free acids using photoredox catalysis and EBX reagents.....	125
4.2. Decarboxylative Cyanation.....	128
4.2.1. Optimization.....	128
4.2.2. Scope of the photoredox catalyzed decarboxylation cyanation.....	138
4.3. Synthesis of enantiopure hydantoins using CBX.....	145
4.3.1. Background and significance of chiral 5-substituted hydantoins.....	145
4.3.2. Optimization of the enantioconservative synthesis of hydantoins.....	149
4.3.3. Scope of the enantioconservative synthesis of hydantoins.....	152
4.3.4. Conclusion of the synthesis of hydantoin using CBX ( <b>2.96a</b> ).....	156
4.4. Mechanistic discussion.....	157
4.4.1. Decarboxylative alkynylation and cyanation using photoredox catalysis and hypervalent iodine reagents.....	157
4.4.2. Tentative mechanisms for background reactions of carboxylic acids with CBX.....	170
4.5. Conclusion of part I.....	174
5. Fragmentation alkynylation of oxime ethers using fine-tuned organic photoredox catalyst.....	178
5.1. Development of fine-tuned organic photoredox catalysts.....	178
5.1.1. Our approach.....	178
5.1.2. Synthesis of fine-tuned donor acceptor organic dyes 4XCzIPN.....	180
5.1.3. Characterization of the dyes 4XCzIPN.....	183
5.2. Photoredox catalyzed fragmentation of cyclic oxime ethers.....	188
5.2.1. Background on iminyl radical fragmentation.....	188
5.2.2. Optimization of the photoredox fragmentation alkynylation.....	192
5.2.3. Scope of photoredox fragmentation – C-C bond formations.....	196
5.2.4. One-pot, low catalyst loading and sunlight experiments.....	203
5.2.5. Potential applications of the alkynyl nitriles.....	204
5.2.6. Speculative mechanism.....	205
5.3. Conclusion of the photoredox catalyzed fragmentation of cyclic oxime ethers.....	207
6. Progress towards photoredox catalyzed decarboxylative fragmentation alkynylation starting from alcohols and amines.....	210
6.1. Progress towards the deoxygenation alkynylation.....	210
6.1.1. Synthesis of oxalates and optimization.....	211
6.1.2. Preliminary scope of the photoredox catalyzed deoxygenative alkynylation.....	215
6.1.3. Conclusion of the deoxygenation.....	219
6.2. Progress towards the deaminative alkynylation.....	220
7. General conclusion – Outlook.....	235

8. Experimental part .....	242
8.1 General methods.....	242
8.2 Decarboxylative alkylation.....	243
8.2.1 Preparation of Reagents and Catalysts .....	243
8.2.2 Iridium photocatalysts syntheses.....	258
8.2.3 Decarboxylative alkylation.....	260
8.2.4 Further functionalization .....	272
8.3 Decarboxylative cyanation .....	274
8.3.1. Preparation of Reagents.....	274
8.3.2. Decarboxylative cyanation .....	282
8.3.3. Derivatization: Synthesis of a Vildagliptin precursor .....	297
8.3.4 Mechanism investigations.....	298
8.3.5. Computational Details.....	309
8.4 Hydantoins.....	313
8.4.1 Synthesis of reagents.....	313
8.4.2. Hydantoin synthesis .....	317
8.3 Fragmentation of cyclic oxime ethers .....	332
8.5.1 Synthesis of reagents.....	332
8.5.2 Library of organic dyes: 4CzIPN derivatives .....	335
8.5.3 Synthesis of the activating reagents for carbonyl substrates .....	342
8.5.4 Synthesis of oxime starting materials.....	344
8.5.5 Decarboxylative ring opening / alkylation cascade.....	357
8.5.6 Computational details.....	374
8.6 Deoxygenation and deamination strategies .....	403
8.6.1 New reagents preparation.....	403
8.6.2 Oxalates synthesis .....	406
8.6.3 Photoredox catalyzed deoxygenative alkylation .....	412
8.6.4 Photoredox catalyzed fragmentation cyanation of cesium oxalate salts.....	416
8.6.5 Photoredox catalyzed desulfurization alkylation.....	416
8.6.6 Deamination strategy.....	418
9. Annexes .....	424
9.1 Spectra of new compounds.....	424
9.2 Curriculum Vitae .....	425
9.3 List of Publications.....	428