



Universiteit  
Leiden  
The Netherlands

## **Palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from Alkenes**

Ramakrishnan, A.

### **Citation**

Ramakrishnan, A. (2023, December 19). *Palladium-catalyzed carbonylative synthesis of carboxylic acid anhydrides from Alkenes*. Retrieved from <https://hdl.handle.net/1887/3674100>

Version: Publisher's Version

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/3674100>

**Note:** To cite this publication please use the final published version (if applicable).

# **Palladium Catalyzed Carbonylative Synthesis of Carboxylic Acid Anhydrides from Alkenes**

Proefschrift

ter verkrijging van  
de graad van doctor aan de Universiteit Leiden,  
op gezag van rector magnificus prof. dr. ir. H. Bijl  
volgens besluit van het college voor promoties  
te verdedigen op dinsdag 19 december 2023  
klokke 10:00 uur

door

**Ashok Ramakrishnan**

geboren te Palakkad, India

in 1991

## **Promotores**

Prof. dr. E. Bouwman

Dr. D.G.H. Hetterscheid

## **Promotiecommissie**

Prof. dr. M. Ubbink

Prof. dr. S. Bonnet

Prof. dr. dr. h. c. mult. M. Beller (Leibniz Institut für Katalyse, Germany)

Dr. M.A. Fernández Ibáñez (Universiteit van Amsterdam)

Dr. B. Limburg (University of Barcelona, Spain)

*Your future is created by what you do today.*

*To my mother who made sure I never was hungry while I studied and my father who always saw to it I wake up on time to make it to where I am... to the two souls who have supported me in every way...*

# Table of Contents

---

<b>List of Abbreviations</b>		<b>5</b>
<b>Chapter 1</b>	Introduction	<b>7</b>
<b>Chapter 2</b>	Palladium-Catalyzed Synthesis of Carboxylic Acid Anhydrides from Alkenes	<b>23</b>
<b>Chapter 3</b>	Palladium-Catalyzed Synthesis of Symmetric Carboxylic Acid Anhydrides from Alkenes with <i>in situ</i> Generated Carboxylic Acids	<b>39</b>
<b>Chapter 4</b>	Regioselectivity in Carbonylation of Pentenoic Acid to Synthesize Cyclic Anhydrides	<b>51</b>
<b>Chapter 5</b>	Summary, Conclusions and Outlook	<b>67</b>
<b>Appendix I</b>	Supporting information for Chapter 2	<b>77</b>
<b>Appendix II</b>	Supporting information for Chapter 3	<b>103</b>
<b>Appendix III</b>	Supporting information for Chapter 4	<b>121</b>
<b>Samenvatting</b>		<b>139</b>
<b>Curriculum Vitae</b>		<b>145</b>
<b>List of Publications</b>		<b>147</b>
<b>Acknowledgements</b>		<b>148</b>

---

# List of Abbreviations

ACN	acetonitrile
Bn	benzyl
Boc	<i>tert</i> -butoxycarbonyl
Bu	butyl
10-CSA	camphorsulfonic acid
5-Cl-SA	5-chlorosalicylic acid
Cy	cyclohexyl
dba	dibenzylideneacetone
DCC	N, N'-dicyclohexylcarbodiimide
DCE	1,2-dichloroethane
DFT	density functional theory
DME	dimethoxyethane
dppb	1,4-bis(diphenylphosphanyl)butane
dppp	1,3-bis(diphenylphosphanyl)propane
DPEphos	bis[(2-diphenylphosphanyl)phenyl] ether
d'bpX	1,2-bis(di- <i>tert</i> -butylphosphanylmethyl)benzene
equiv.	equivalent(s)
FA	formic acid
GC	gas chromatography
GVL	$\gamma$ -valerolactone
HFIP	1,1,1,3,3,3-hexafluoroisopropanol
HOAc	acetic acid
HOMs	methanesulfonic acid
HOTs( $\cdot$ H <sub>2</sub> O)	toluenesulfonic acid (monohydrate)
<i>m</i> -	meta
2,4,6-MBS	2,4,6-trimethylbenzenesulfonic acid
Me	methyl
MZ	mierenzuur
NMP	N-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
<i>o</i> -	ortho
<i>p</i> -	para
PEA	pentenoic acid
Ph	phenyl
PPA	phenylphosphonic acid
TBA	2,4,6-trimethylbenzoic acid
<i>tert</i> - <i>t</i>	tertiary
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TOF	turn over frequency
TON	turn over number
UPLC	ultra-performance liquid chromatography

