

The Development of Gold-Catalysed Reactions

Maximillian Hadfield, MChem

Degree of Doctor of Philosophy

**Heriot-Watt University, School of Engineering and
Physical Sciences, Edinburgh**

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Abstract

This thesis describes the research carried out in the development of novel homogeneous gold(I)-catalysed reactions. It is written in such a format as to describe chronologically the process in which the study and our understanding evolved.

- Chapter one provides an introduction to homogeneous gold catalysis and in particular the development and reactivity of gold(I) catalysts as powerful activators of unsaturated carbon-carbon species towards nucleophilic attack.
- Chapter two describes our initial work in this area and how we were able to show that gold(I) can catalyse the intramolecular rearrangements of cyclopropenes with ester functionalities.
- Chapter three presents the intermolecular addition of alcohol to 3,3-dialkyl and aryl cyclopropenes catalysed by gold(I).
- Chapter four describes how we were able to utilise our knowledge of gold(I)-catalysed reactions with cyclopropenes to completely switch the regiochemistry of gold(I)-catalysed hydroalkoxylation of allenes from producing primary alkyl allylic ethers to tertiary alkyl allylic ethers. We were also able to show that by trapping the vinyl gold intermediate we could further functionalise the tertiary allylic ether.
- Chapter five describes the results of the addition of furan to cyclopropenes catalysed by gold(I) to produce functionalised conjugated trienes.
- Chapter six presents initial work into the gold(I) catalysed addition of indoles to cyclopropenes. Also described in this chapter are the attempted reactions with a variety of alternative nucleophiles.

This thesis is dedicated to my father Henry Gordon Hadfield.

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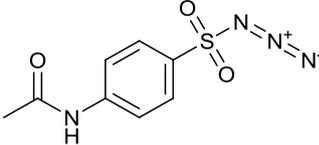
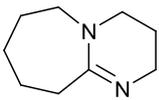
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Abbreviations

δ	NMR chemical shift
Å	Angström
<i>p</i> -ABSA	<i>para</i> -acetamidobenzenesulfonyl azide
	
Ac	acetyl
AgOTf	silver triflate
approx.	approximately
app.	apparent
aq.	aqueous
Ar	aryl
Bu	butyl
¹³ C NMR	carbon nuclear magnetic resonance
cat.	catalyst
CI	chemical ionisation
Cy	cyclohexyl
d	doublet
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
	
DCE	dichloroethane
DCM	dichloromethane
DEPT	distortionless enhancement by polarisation transfer
°C	degrees Celsius
DFT	density functional theory
DMF	dimethylformamide
DNBA	2,4-dinitrobenzenesulfonic acid
dr	diastereomeric ratio
DTBM-Segphos	5,5'-bis[di(3,5-di- <i>tert</i> -butyl-4-methoxyphenyl)phosphino]-4,4'-bi-1,3-benzodioxole
ee	enantiomeric excess

equiv.	equivalents
ESI	electrospray ionisation
Et	ethyl
EtOH	ethanol
ether	diethyl ether
g	gram(s)
h	hour(s)
HBr	hydrobromic Acid
HPLC	high pressure liquid chromatography
HSbF ₆	fluoroantimonic Acid
¹ H NMR	proton nuclear magnetic resonance
Hz	Hertz
IPA	isopropyl Alcohol
ⁱ Pr	isopropyl
IPr	2,6-diisopropylphenyl imidazolium
IR	infra red spectroscopy
<i>J</i>	NMR coupling constant
KMnO ₄	potassium permanganate
KOH	potassium hydroxide
l	litre(s)
M	molar (moles/litre)
m	multiplet
md	medium
Me	methyl
MeCN	acetonitrile
MeOH	methanol
mg	milligrams
MgSO ₄	magnesium sulfate
MHz	mega Hertz
min(s)	minute(s)
ml	millilitre(s)
mmol	millimoles
moly dip solution	aqueous ammonium molybdate-sulfuric acid
m/z	mass/charge ratio

ⁿ BuOH	nonyl butanol
NHC	N-heterocyclic carbene
NH ₄ Cl	ammonium chloride
NMR	nuclear magnetic resonance
NU	nucleophile
<i>o</i>	<i>ortho</i>
OMe	methoxy
<i>p</i>	<i>para</i>
Ph	phenyl
ppm	parts per million
pr	propyl
q	quartet
quart.	quarternary
qn	quintet
R	undefined alkyl or aryl group
RT	room temperature
R _T	retention time
s	singlet
sext	sextet
st	strong
sh	sharp
SM	starting material
sol	solvent
t	triplet
^t BuOH	tertiary butanol
Temp.	temperature
Tf	trifluoromethane sulfonate (triflate)
TfOH	triflic acid
TFA	trifluoroacetic acid
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
Tol	toluene
UV	ultraviolet
wt	weight