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An expedient copper-catalysed asymmetric synthesis of γ -lactones and γ -lactams. Application to the synthesis of lucidulactone A⁺

The parent Josiphos ligand gave excellent ee values (95–99%) and good yields (60–97%) in the coppercatalysed asymmetric conjugate reduction of β -aryl α , β -unsaturated lactones and lactams with PMHS. The

substrates were obtained from stereospecific copper-catalysed addition of arylboronic acids to alkynoates

followed by deprotection and cyclisation. The acyclic lactam precursors also underwent reduction with

good ee values (83-85%) and yields (79-95%). Application of this asymmetric reduction methodology

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included the synthesis of natural product lucidulactone A.

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Introduction

The construction of chiral β -substituted lactones and lactams has garnered considerable attention because of their ubiquitous existence as core structures in numerous biologically active natural products and clinical theraupetics.¹ For example, a chiral γ -butyrolactone is present in natural products lucidulactone A **1**^{2a} and (3*R*)-A-factor **2**.^{2b} Chiral γ -lactams are found in important pharmaceuticals such as rolipram **3**, an antidepressant drug (Fig. 1a). Also, β -GABA derivatives such as baclofen **4**, a muscle relaxant, can be accessed *via* hydrolysis of the corresponding chiral lactams (Fig. 1b).^{3a-c} Consequently, the development of new methods for the synthesis of chiral β -substituted lactones and lactams, particularly in a stereocontrolled fashion, is of significant importance.

Two methods for the for the enantioselective synthesis of chiral lactams and lactones are transition metal catalysed and involve either: (i) conjugate addition of an organometallic derived nucleophile to an α , β -unsaturated lactone or lactam precursor,⁴ or (ii) reduction of an unsaturated β -substituted precursor. Although molecular hydrogen may be employed as the reducing agent,⁵ a key development was the use of a copper catalyst incorporating the *P*,*P*-bidentate ligand *p*-tol-BINAP, and employing polymethylhydrosiloxane (PMHS) as the stoichiometric reductant (Scheme 1).⁶ This biaryl ligand, which has also been applied to the corresponding reduction of

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[†]Electronic supplementary information (ESI) available: Experimental detail, copies of the ¹H and ¹³C spectra, HPLC traces and details of the X-ray crystal structure determinations. CCDC 2121166 and 2121167. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/ d3ob00563a α , β -unsaturated esters⁷ and enones,⁸ has been superseded to some extent by other biaryl bisphosphines,⁹ of which the most notable are the SEGPHOS ligands.¹⁰ However, the specific application of the latter to the reduction of β -substituted unsaturated lactones is very limited.¹¹ The only other ligand type to give high product ee values in copper-catalysed conjugate reduction reactions are the ferrocene-based Josiphos ligands as applied to acyclic substrates including enones,¹² nitoalkenes¹³ and unsaturated nitriles.^{14,15}

In this Paper we report the highly enantioselective synthesis of β -substituted γ -lactones and lactams by copper-catalysed conjugate reduction employing a readily available Josiphos ligand. Coupled with the accessible synthesis of the unsaturated lactone and lactam precursors by copper-catalysed alkynoate-addition/cyclisation, the overall methodology provides rapid access to the title compounds in high ee.



Fig. 1 Natural products and pharmaceutically relevant chiral γ -lactones and γ -lactams.



Scheme 1 Existing methods for the asymmetric synthesis of β -substituted γ -lactones and lactams by copper-catalysed asymmetric reduction.⁶

Results and discussion

Previous methods for the synthesis of β -substituted butenolides include the use of ring-closing metathesis¹⁶ and glyoxylic



Scheme 2 Four-step synthesis of β -aryl α , β -unsaturated lactones 9a-9e.



Scheme 3 Five-step synthesis of $\beta\text{-aryl}$ and $\beta\text{-alkyl}$ $\alpha,\beta\text{-unsaturated}$ lactams 15a–15d.

acid condensation followed by reduction.¹⁷ For the generation of β -aryl derivatives we were attracted to the simplicity of copper-catalysed conjugate addition of arylboronic acids to appropriately functionalised alkynoates, followed by cyclisation,¹⁸ and the potential to extend this methodology to give the corresponding lactams. Commencing with propargyl alcohol **5**, TBS-protection gave **6**, followed by treatment with *n*-BuLi and ethyl chloroformate to furnish alkynoate **7** (Scheme 2). The copper-catalysed conjugate *syn*-addition of



Scheme 4 Synthesis of β -aryl α , β -unsaturated lactones 9f.

 $\label{eq:table_$



Entry	Cu source (mol%)	L (mol%)	Conv. (time)	Yield ^b (%)	ee ^c (%) (config.)
1	$CuCl_2(5)$	R, S_{p} -L1 (6)	<5% (16 h)	_	_
2	$\operatorname{CuCl}_2(5)$	$S, S_{p}-L2$ (6)	100% (16 h)	21	81 (R)
3	(R,S_p) -L3-CuCl ₂ ^d (3)		100% (22 h)	59	96 (R)
4	(R,S_p) -L3-CuBr ^e (3)	—	100% (12 h)	78	99 (R)
5	(R,S_p) -L3-CuBr (2)	_	95% (24 h)	67	98 (R)

^{*a*} On a 0.285 mmol scale, THF/*t*-BuOH (10:1). ^{*b*} Isolated yields. ^{*c*} Determined by HPLC analysis. ^{*d*} Cu(OAc)₂ and Cu(OTf)₂ also performed well (93 and 94% ee respectively). ^{*e*} CuCl also performed well (96% ee).

8

aryl boronic acids produced β -aryl-alkenoates (*Z*)-**8a–e** exclusively,^{18*a*} and to ensure good yields the functionalised boronic acids required typically the use of 30 mol% Cu(OAc)₂. A stoichiometric quantity of Cu(OAc)₂ was required with 2-methoxyphenylboronic acid to achieve conversion within twelve hours. Finally, acid mediated TBS deprotection and cyclisation of (*Z*)-**8a–e** furnished **9a–e**, such that β -substituted α , β -unsaturated lactones were generated in four steps from commercially available propargyl alcohol (62–81% overall yield).

Extension of this methodology to PMP-protected β -substituted α , β -unsaturated lactams required alkynoate **13** generated from Boc protection and propargylation of **10**, followed by reaction with ethyl chloroformate (Scheme 3). Conjugate addition of aryl boronic acids were successful using 5–30 mol% of Cu(OAc)₂ to generate β -aryl alkenoates **14a–c** as exclusively the *Z* diastereoisomer. As for the generation of (*Z*)-**8a–e**, this is a consequence of stereospecific carbocupration of the alkyne followed by rapid protonolysis avoiding possible *Z/E* isomerisation.^{18a} Subsequent acid-promoted Boc deprotection and cyclisation gave lactams **15a–c** in five steps from *p*-anisidine (*ca.* 30% overall yield). Addition to **13** of an alkyl cuprate (Gilman reagent) generated from MeLi and CuI gave β -alkyl-

alkenoate (*Z*)-**14d** in good yield and as a single isomer,¹⁹ with subsequent cyclisation providing β -alkyl lactam **15d**.

The conjugate addition of boronic acid **18** (obtained in three steps from commercially available **16**) to alkynoate 7 didn't generate the desired product. To solve this problem **18** was coupled successfully with **20** (obtained in one step from commercially available tetronic acid **19**) to produce **9f** (Scheme 4). The highly oxygenated phenolic moiety is present in many lignan natural products such as lucidulactone A 1^2 and descurainolide A.²⁰ The former was isolated from *Ganoderma lucidum*, a medicinal mushroom associated with various health benefits.

As the exploration of substrates of type **9f** in transitionmetal catalysed asymmetric reactions are rare, the initial objective was the enantioselective reduction of this substrate as a key step in the synthesis of **1**. For this we chose to explore the use of ferrocene ligands as many are known with different chelating functional groups,²¹ and within several ligand classes it is possible to vary readily substituents and stereochemistry for the purpose of ee optimisation (Table 1).²²

In our initial ligand screen P,O ligand L1 performed poorly (entry 1), whereas P,N ligand L2 produced encouraging



^{*a*} The reactions were carried out on a 0.312 mmol scale using 3 mol% ($R_s S_p$)-L3-CuBr, PMHS (3 eq.), NaOt-Bu (2 eq.) in THF/t-BuOH (10:1), room temperature, 12 h. ^{*b*} Isolated yields. ^{*c*} Enantiomeric excess determined by chiral HPLC analysis. ^{*d*} (S)-21f was obtained in 78% yield and 99% ee using ($S_s R_p$)-L3-CuBr.

enantioselectivity (entry 2). Higher enantioselectivity was obtained with the P,P ligand L3, the parent Josiphos ligand,²³ as a preformed complex with CuCl₂ (entry 3). Switching to the CuBr complex gave lactone **6f** in good yield and with essentially complete control of enantioselectivity (entry 4) such that further ligand optimization was not needed. Using less than 3 mol% of this complex led to a longer reaction time and lower yield (entry 5).

Table 2 shows the substrate scope of this study, which was also extended to acyclic substrates (Z)-14a-c. The asymmetric conjugate reduction of 9a-9e by (R,S_p) -Josiphos complex L3-CuBr produced (R)-21a-21e with excellent enantioselectivities $(\geq 97\%$ ee; entries 1–5). Based on these results, this work proved to be a convenient method for generating β -aryl lactones. Both the (R) and (S) enantiomers of 21f were generated in 99% ee using (R,S_p) -L3-CuBr and (S,R_p) -L3-CuBr, respectively (entry 6). The absolute configuration of (R)-21d and (R)-21f were confirmed by X-ray crystallography.²⁴ The absolute configuration of (R)-21a-c and (R)-21e were confirmed by optical rotation and comparison to the literature data.²⁵ Aryl and methyl β-substituted chiral γ-lactams 22a-d were also generated with excellent enantioselectivities ($\geq 95\%$; entries 7–10), and the absolute configuration of 22a⁴ and 22d²⁶ were confirmed by optical rotation determination and comparison to the literature data.

Acyclic products **23a–c** were obtained in 83–85% ee (entries 11–13).²⁷ The absolute configuration of **23c** was determined as *R* following cyclisation to (*R*)-**22c**. Subsequent treatment with ceric ammonium nitrate generated (*R*)-**24c**,²⁸ which was converted to baclofen **4** in a previous study (Scheme 5a).^{3b} Likewise, **23a** (78% ee), obtained from a larger scale reduction



Scheme 5 Formal synthesis of $\beta\mbox{-}GABA$ derivatives and a chiral pyrrolidine.



Scheme 6 Synthesis of lucidulactone A.

reaction (1.71 g of (*Z*)-14a – 1.8 mol% catalyst loading), was cyclised to (*R*)-22a. Removal of the PMP group produced (*R*)-24a that was converted previously to high value chiral pyrrolidine (*R*)-25 (Scheme 5b).^{3d} Treatment of (*S*)-22d with ceric ammonium nitrate furnished known compound (*S*)-24a, which has been converted previously to a β -GABA derivative (*S*)-26 (Scheme 5c).^{3a} As the enantioselectivity of the reduction of the acyclic precursors to the unsaturated lactams is lower than that obtained with the unsaturated lactams themselves, reduction of the latter may of course be used to generate these products in higher ee.

Finally, the total synthesis of lucidulactone A **1** was completed in two steps from (*R*)-**21f** (Scheme 6). Treatment with LiHMDS followed by addition to the resulting enolate of oxaziridine (*R*)-**27** resulted in the highly diastereoselective formation of (3S,4R)-**28**.²⁹ Subsequent treatment with TBAF generated (3S,4R)-**1** in 71% over two steps. The specific rotation and NMR data obtained agree with the isolated sample data (see ESI[†]).^{2a}

Conclusions

In conclusion, the parent Josiphos ligand (L3) in combination with copper bromide gives a catalyst for the highly enantioselective reduction of β -aryl substituted α , β -unsaturated γ -lactones and γ -lactams using PMHS as the hydride source. Coupled with the generation of these reduction substrates by copper-catalysed stereospecific β -arylation of alkynoates, followed by cyclisation, this provides overall a simple and accessible methodology for the single enantiomer synthesis of the title compounds.

Conflicts of interest

There are no conflicts to declare.

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