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Diastereoselective copper-catalysed 1,4-addition of Grignard reagents to *N*-enoyl oxazolidinones†

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Conjugate additions of organometallic reagents to α,β-unsaturated carboxylic acid derivatives give access to numerous β-substituted chiral building blocks. Chiral oxazolidinones serve as useful surrogates of carboxylic function in the asymmetric conjugate addition of Grignard reagents. *N*-Enoyl oxazolidinones undergo this 1,4-addition with a catalytic amount of copper salt and using either chiral or achiral phosphine ligands. In particular, chiral ferrocenyl phosphane oxazolines proved useful in achieving high diastereoselectivities. The resulting *N*-acyl oxazolidinones were obtained in good yields and with high diastereoselectivities (up to single diastereomer).

Introduction

Asymmetric copper-catalysed additions of organometallic reagents to α,β-unsaturated compounds belong to the most important C–C bond forming reactions.[1] A wide variety of chiral catalysts can enantioselectively introduce alkyl groups *via* organozinc, Grignard and organoaluminium reagents. Among them are also prominent catalyst classes like phosphoramidites,[2] *N*-heterocyclic carbenes[3] and ferrocenyl phosphanes.[4] Conjugate additions to α,β-unsaturated ketones, including those with tri-substituted β-carbon, can now be performed with high yields and enantioselectivities. However, 1,4-addition to unsaturated compounds having other electron accepting groups are less developed. From a synthetic point of view, particularly carboxylic acid derivatives are useful in terms of potential derivatizations or functional group interconversions. In recent years great advances have been achieved in conjugate additions to esters and lactones,[5] however, these substrates have low reactivity at the β-carbon, posing problems with regioselectivity. Thioesters are better Michael acceptors than esters and conjugate additions work well on them,[6] but they are generally unpleasant to work with. Catalytic 1,4-additions of organometallic reagents to unsaturated amides or lactams were also less studied,[7] and unreactivity of simple amides makes them difficult to modify or cleave after the conjugate addition. On the other hand, *N*-enoyl oxazolidinones combine several features, which make them appealing as surrogates of carboxylic group in the conjugate addition. They are good Michael acceptors. Furthermore, CO–N bond can be easily cleaved under mild conditions allowing transformation to other useful derivatives once the conjugate addition is finished. In addition, oxazolidinones can be easily synthesized from chiral amino alcohols and thus possess stereogenic information, which can itself direct or enhance stereoselectivity of the addition. *N*-Enoyl oxazolidinones allow for additions of stabilized nucleophiles[8] as well as heteroatom nucleophiles, such as amides[9] and thiols.[10] Organometallic, non-stabilized, nucleophiles can add to *N*-enoyl oxazolidinones either as preformed organocuprates[11] or with the help of stoichiometric amount of a copper salt as catalyst.[12] Additions with a catalytic amount of copper and a chiral ligand are rare. Hird and Hoveyda described the only example of enantioselective conjugate addition of dialkylzinc reagents to achiral *N*-enoyl oxazolidinones.[13] An addition of Grignard reagents to *N*-enoyl oxazolidinones using catalytic amount of copper-complex is unknown.

In this context, we studied addition of Grignard reagents to achiral and chiral *N*-enoyl oxazolidinones using catalytic amount of copper salts. We have also investigated the influence of chiral ligands. Finally, we demonstrate synthetic utility of this approach on a larger scale.

Results and discussion

Initial experiments on oxazolidinone **1a** with EtMgBr, $CuBr{\cdot}SMe_2$ and *Josiphos* (**L1**) as chiral ligand led only to decomposition of the starting material. We hypothesized that a highly reactive Grignard reagent, which is present in the reaction mixture when there is only catalytic amount of copper salt, attacks oxazolidinone ring (Scheme 1).

Therefore, we replaced oxazolidinone **1a** with oxazolidinone **1b** with two methyl groups to provide some steric shielding for the oxazolidinone ring. Compound **1b** was indeed more stable

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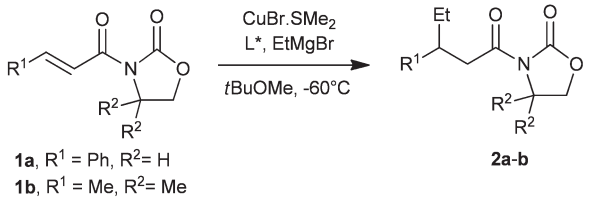
† Electronic supplementary information (ESI) available: ^1H, ^{13}C NMR, including DEPT spectra for all compounds. See DOI: 10.1039/c3ra42024h



Scheme 1 Enantioselective 1,4-addition of EtMgBr to *N*-enoyl oxazolidinones **1**.

towards the Grignard reagent, and the conjugate addition proceeded well. However, the product of this reaction, oxazolidinone **2b**, was racemic. We have then screened a selection of structurally diverse chiral ligands, which were effective in other 1,4-additions of Grignard reagents. Solvias ferrocenyl phosphines **L1–4** were effective for additions to cyclic[14] and acyclic enones,[15] esters,[5d] and thioesters.[6b] Ferrocenyl oxazolines **L5–6** were among the first chiral ligands for additions of Grignard reagents to enones.[16] BINAP (**L7**) in connection with CuI was efficient catalyst for 1,4-additions to linear esters.[11] Recently, Schmalz and co-workers showed that TADDOL-based phosphine-phosphite ligands **L7** performed excellently in conjugate additions (Fig. 1).[17] Therefore, we have tested also three of these ligands.

However, none of the tested ligands afforded product **2b** with higher enantiomeric purity than e.r. 67 : 33. The results of ligand screening are gathered in Table 1.

After we found out that none of 11 tested chiral ligands was able to provide high enantioselectivity in the conjugate addition to achiral *N*-enoyl oxazolidinones, we decided to test chiral oxazolidinones. Oxazolidinone **3a**, derived from (*S*)-valine, was subjected to the addition of EtMgBr catalyzed by a copper salt and a phosphane ligand (Scheme 2).

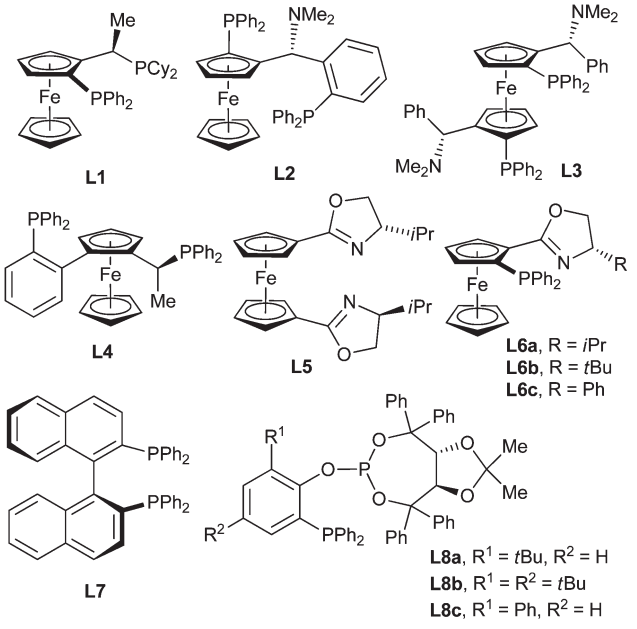


Fig. 1 Chiral ligands used in the enantioselective 1,4-addition to *N*-enoyl oxazolidinones.

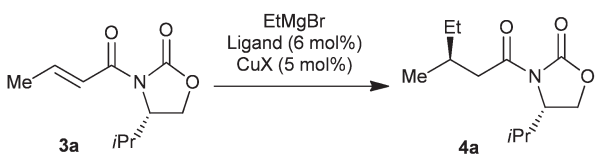
Table 1 Screening of chiral ligands in the conjugate addition to achiral oxazolidinone **1b**[a]

Ligand	Yield of **2b** (%)	e.r.[b]
L1	78	50 : 50
L2	67	50 : 50
L3	65	50 : 50
L4	63	50 : 50
L5	67	50 : 50
L6a	88	66 : 34
L6b	69	56 : 44
L7	62	56 : 44
L8a	91	33 : 67
L8b	68	48 : 52
L8c	65	47 : 53

[a] $CuBr{\cdot}SMe_2$ (5 mol%), ligand (6 mol%), **1b** 0.375 mmol, EtMgBr (0.563 mmol). [b] Determined by enantioselective HPLC.

The reaction with only copper iodide, without additional ligand, was slow and afforded product in only 43% yield (Table 2, entry 1). Interestingly, the 1,4-addition catalysed by a copper complex with achiral ligands, such as tributylphosphane or 1,1′-bis(diphenylphosphano)ferrocene (DPPF), afforded product **4a** with only low diastereoselectivities (Table 2, entries 2 and 3). Improvement was achieved by the use of chiral ferrocenyl phosphane oxazoline ligands **L6**. Copper sources, CuBr and CuI either gave similar results, but $(CuI)_4(SMe_2)_3$ seemed slightly superior. Ethereal solvents like Et_2O, *t*BuOMe or 2-methyltetrahydrofurane (2-MeTHF) can be used. Interestingly, the best results were achieved in dichloromethane, which is compatible with Grignard reagents at low temperatures. After optimization of the reaction conditions, the addition product **4a** was isolated in 79% yield and with diastereomeric ratio of 96 : 4 (Table 2, entry 20). The best conditions comprised CH_2Cl_2 as solvent, $(CuI)_4(SMe_2)_3$ as a copper salt, $BF_3{\cdot}OEt_2$ as additional Lewis acid and dilution of commercially available Grignard reagent with 2-MeTHF to approximately 1 M concentration. The additional Lewis acid seems to increase electrophilicity of the β-carbon, thus facilitating nucleophilic attack by the Grignard reagent. This effect is manifested in higher chemical yield of the addition, while stereochemical outcome of the reaction remained the same.

Evaluation of other oxazolidinones, such as **3b** and **3c** which have *tert*-butyl and phenyl group instead of *iso*-propyl, resulted in a further increase of the diastereoselectivity



Scheme 2 Conjugate addition of EtMgBr to valinol-based oxazolidinone **3a**.

Table 2 Optimization of reaction conditions for addition of EtMgBr on chiral oxazolidinone **3a**[a]

Entry	Ligand	Conditions	Yield (%)	d.r.[b]
1	—	CuI, Et_2O, 0 °C	43	61 : 39
2	DPPF	CuBr·SMe_2, *t*BuOMe, −60 °C	—	60 : 40
3	PBu_3	CuBr·SMe_2, *t*BuOMe, −60 °C	—	63 : 37
4	**L8a**	CuBr·SMe_2, *t*BuOMe, −60 °C	63	66 : 33
5	**L8b**	CuBr·SMe_2, *t*BuOMe, −60 °C	—	57 : 43
6	**L6a**	CuBr·SMe_2, *t*BuOMe, −60 °C	65	78 : 22
7	**L2**	CuBr·SMe_2, *t*BuOMe, −60 °C	32	58 : 42
8	**L1**	CuBr·SMe_2, *t*BuOMe, −78 °C	41	62 : 38
9	**L2**	CuBr·SMe_2, *t*BuOMe, −78 °C	41	55 : 45
10	**L1**	CuBr·SMe_2, *t*BuOMe, −60 °C	52	62 : 38
11	**L6a**	CuBr·SMe_2, *t*BuOMe/LiCl, −60 °C	—	78 : 22
12	**L6a**	CuBr·SMe_2, 2-MeTHF, −60 °C	—	89 : 11
13	**L6a**	CuBr·SMe_2, *t*BuOMe[c], −60 °C	—	76 : 24
14	**L6a**	CuBr·SMe_2, *t*BuOMe[c], −78 °C	—	78 : 22
15	**L6a**	CuBr·SMe_2, CH_2Cl_2, −78 °C	—	88 : 12
16	**L6a**	CuBr·SMe_2, 2-MeTHF, −78 °C	—	79 : 21
17	**L6a**	CuBr·SMe_2, 2-MeTHF, −78 °C	—	52 : 48
18	**L6a**	CuBr·SMe_2, CH_2Cl_2, −78 °C	—	85 : 15
19	**L6c**	CuBr·SMe_2, CH_2Cl_2[d], −78 °C	—	90 : 10
20	**L6c**	$(CuI)_4$·$(SMe_2)_3$, CH_2Cl_2[d]/BF_3·Et_2O, −78 °C	79	96 : 4

[a] CuX (5 mol%), ligand (6 mol%), **3a** 0.375 mmol, EtMgBr (0.563 mmol). [b] Determined by ^{1}H NMR or GC of the crude reaction mixture. [c] Reversed addition. [d] EtMgBr diluted to 1 M.

(Scheme 3). Diastereomeric ratio of 98 : 2 was achieved when oxazolidinone **3c** in combination with ligand **L6c** was employed. The use of Seebach's oxazolidinone DIOZ (**3d**)[12b] as chiral auxiliary did not improve the reaction. Table 3 summarizes the most important results.

Interesting observation was that achiral DPPF ligand led to varying diastereoselectivities depending on the oxazolidinone used (*cf.* Table 3, entries 4 and 6).

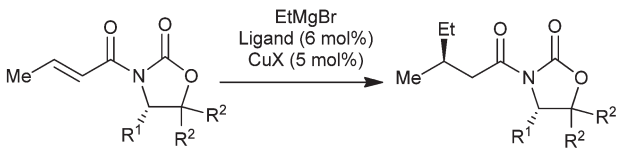
As oxazolidinones already possess stereogenic information, the effect of matched/mismatched chirality was tested with ferrocenyl ligand **L6a**. An experiment on the oxazolidinone **3c** using ligand (*S*,*S*)-**L6a** afforded product **4c** with d.r. 92 : 8. On the other hand, enantiomeric ligand (*R*,*R*)-**L6a** displayed mismatched chirality as it led to compound **4c** with the same configuration albeit in only medium d.r. of 63 : 37 (*cf.* Table 3, entries 7 and 8).

Using a phenylglycine-derived oxazolidinone **5a**, other acyl groups have been evaluated too. Thus, 1,4-addition of EtMgBr to oxazolidinones **5a–c** resulted in *N*-acyl oxazolidinones **6a–c** in good yields and high diastereoselectivities (Scheme 4, Table 4).

The developed protocol can be applied also with several other Grignard reagents. The methodology thus leads to a range of products **7a–d**, which was obtained by the addition of hexyl, cyclopentyl, phenyl and 2-thienylmagnesium bromides to oxazolidinone **3c** (Scheme 5). Yields were acceptable for compounds **7a** and **7b**, but the reaction with aromatic Grignard reagents phenyl and 2-thienylmagnesium bromides were slow using a catalytic amount of copper. The products **7c**, and **7d** could be obtained only using stoichiometric amount of copper salt. Diastereomeric ratios were high for all products **7**.

By interchanging the substituent on the double bond and that of the Grignard reagent, it is possible to synthesize diastereomeric derivatives. From oxazolidinone **3c** and PhMgBr, compound (*R*,*S*)-**7c** was prepared. While, the reaction starting from compound **5a** and MeMgBr leads to isomer (*S*,*S*)-**7c** (Scheme 6).

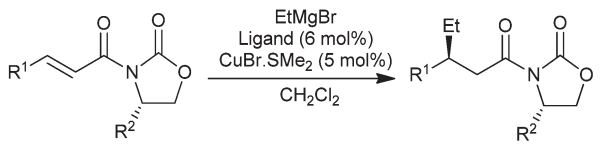
Synthetic usefulness of *N*-enoyl oxazolidinones for conjugate addition demonstrates also the fact that the resulting



3b, R^1 = *t*Bu, R^2 = H
3c, R^1 = Ph, R^2 = H
3d, R^1 = *i*Pr, R^2 = Ph

4b-d

Scheme 3 Conjugate additions of EtMgBr to oxazolidinones with varying substituents.



5a, R^1 = R^2 = Ph
5b, R^1 = *n*Pr, R^2 = Ph
5c, R^1 = Ph, R^2 = *i*Pr

6a-c

Scheme 4 Conjugate additions of EtMgBr to oxazolidinones with various *N*-enoyl groups.

Table 3 Conjugate additions of EtMgBr to oxazolidinones with varying substituents[a]

Entry	Oxazolidinone	Ligand	[Cu]	Yield (%)	d.r.[b]
1	**3b**	—	CuI	51	75 : 25
2	**3b**	**L6a**	$CuBr{\cdot}SMe_2$	58	95 : 5
3	**3b**	**L6a**	$(CuI)_4{\cdot}(SMe_2)_3$	65	94 : 6
4	**3b**	DPPF	$(CuI)_4{\cdot}(SMe_2)_3$	—	96 : 4
5	**3b**	**L6c**	$(CuI)_4{\cdot}(SMe_2)_3$	—	98.5 : 1.5 (GC)
6	**3c**	DPPF	$(CuI)_4{\cdot}(SMe_2)_3$	—	75 : 25
7	**3c**	**L6a**	$CuBr{\cdot}SMe_2$	47	92 : 8
8	**3c**	*ent*-**L6a**	$CuBr{\cdot}SMe_2$	—	63 : 37
9	**3c**	**L6c**	$(CuI)_4{\cdot}(SMe_2)_3$	80	98 : 2
10	**3d**	**L6b**	$CuBr{\cdot}Me_2S$	43	88 : 12
11	**3d**	**L6a**	$CuBr{\cdot}Me_2S$	45	92 : 8
12	**3d**	Bu_3P	$CuBr{\cdot}Me_2S$	65	85 : 15
13	**3d**	**L6c**	$CuBr{\cdot}Me_2S$	39	79 : 21

[a] CuX (5 mol%), ligand (6 mol%), **3b–3d** 0.375 mmol, EtMgBr (0.563 mmol). [b] Determined by ^{1}H NMR or GC of the crude reaction mixture.

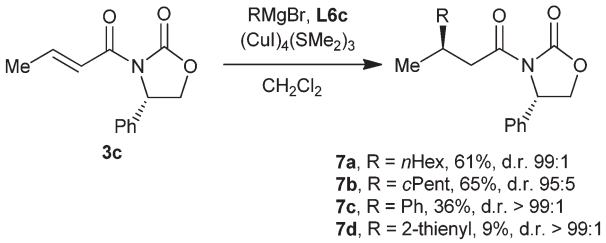
N-acyl oxazolidinones can be further transformed into carboxylic acid, ester and Weinreb amide using simple procedures.[13,18] Practicality of the methodology was tested in the larger scale experiment. Here, 3.75 mmol of the starting oxazolidinone **3c** was used, while catalyst loading was decreased to 1 mol% of copper and 1.2 mol% of the ligand **L6c**. The product **4c** was isolated in 60% yield and with high diastereomeric ratio of 97 : 3.

Based on the configurations of compounds **7c**[19] and similarly to the literature,[11f,12b] we suggest following stereochemical model for the conjugate addition of Grignard reagents to *N*-enoyl oxazolidinones (Scheme 7). The attack of the Grignard reagent takes place from the *re*-face, *anti* to the R-group on the stereogenic centre of the oxazolidinone. Chiral ligand improves diastereoselectivity of the reaction in the majority of examples; however facial selectivity remains dictated by chiral oxazolidinone.

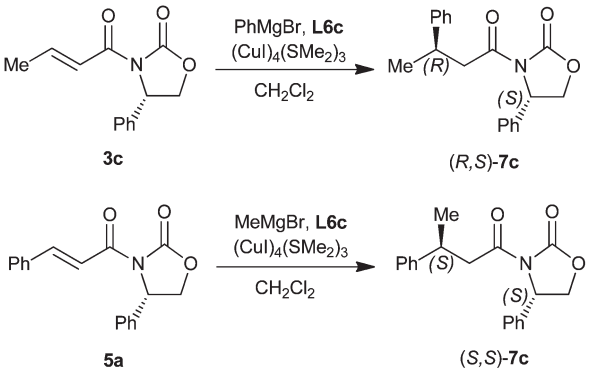
Table 4 Conjugate additions of EtMgBr to oxazolidinones with various *N*-enoyl groups[a]

Oxazolidinone	Ligand	Yield (%)	d.r.[b]
5a	**L6a**	70	76 : 24
5a	$P(n\text{-}Bu)_3$	58	94 : 6
5a	**L6c**	57	89 : 11
5b	$P(n\text{-}Bu)_3$	39	88 : 12
5b	**L6a**	50	95 : 5
5b	**L6c**	41	97.5 : 2.5
5c	$P(n\text{-}Bu)_3$	58	79 : 21
5c	**L6a**	35	85 : 15
5c	**L6c**	68	80 : 20

[a] $CuBr{\cdot}SMe_2$ (5 mol%), ligand (6 mol%), **5a–5c** 0.375 mmol, EtMgBr (0.563 mmol). [b] Determined by ^{1}H NMR of the crude reaction mixture.



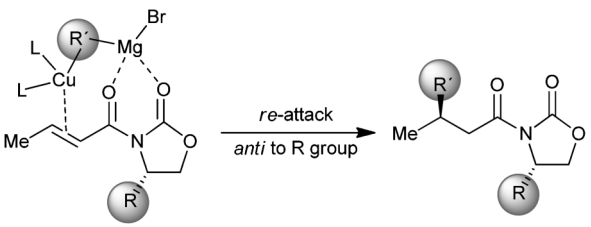
Scheme 5 Compounds obtained by the addition of various Grignard reagents.



Scheme 6 Access to both configurations at the β-position through exchange of side chain and Grignard reagent substituents.

Conclusions

Chiral *N*-enoyl oxazolidinones are suitable Michael acceptors for the 1,4-addition of Grignard reagents using catalytic amount of copper salt. The highest diastereoselectivities were obtained with oxazolidinones having *tert*-butyl and phenyl groups. The resulting products were obtained in good yield and high diastereomeric ratios. Chiral ferrocenyl phosphane oxazoline ligands in connection with $BF_3{\cdot}OEt_2$ as additional Lewis acid, have led to increase of the diastereoselectivity up to perfect diastereoselection, where in some cases only one diastereomer was isolated. Efficiencies of ferrocenyl phosphane oxazolines were similar, but ligand **L6c**, derived from phenylglycine, usually afforded the best results.



Scheme 7 Stereochemical model for the Cu-catalyzed 1,4-addition of Grignard reagents.

Experimental

All reactions were carried out in an inert atmosphere of Ar. Solvents were dried and purified by standard methods before use. NMR spectra were recorded on an instrument with 300 MHz for ^{1}H and 75 MHz for ^{13}C, and an instrument with 600 MHz for ^{1}H and 150 MHz for ^{13}C. Chemical shifts (δ) are given in ppm relative to tetramethylsilane. Peaks for minor diastereomers are in italics. Specific optical rotations are given in deg cm^3 g^{-1} dm^{-1}. Flash chromatography was performed on silica gel 40–63 μm. Thin-layer chromatography was performed on silica gel 60, F-254. Diastereomeric ratios were determined by ^{1}H NMR and GC. Enantiomeric ratios were determined by HPLC on Chiralpak, OD-H, AS-H, IB (Daicel Chemical Industries), column using hexane/*i*PrOH as a mobile phase and detection with UV-detector at 254, 218 nm. HRMS analyses were performed with a LC-IT-TOF MS instrument.

Starting materials, *N*-enoyl oxazolidinones, were prepared according to literature procedures. NMR data for compounds **1a** and **1b**,[20] **3a** and **5c**,[21] **3b**,[22] **3c** and **5a**,[19] **3d**[18] agree with those in the literature. Compound **5b** was prepared in analogy to procedures in the literature[18] and characterization data are bellow.

(*S*,*E*)-3-Hex-2-enoyl-4-phenyl-oxazolidin-2-one (5b)

White solid, 522 mg (73%); mp 72–74 °C (hexane). $[\alpha]_D$ + 23.7 (c 0.515, $CHCl_3$). IR (ATR) ν = 1774 s (CO), 1682 s (CO) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.44–7.27 (m, 5H, Ph), 7.25–7.22 (m, 1H, CH=C*H*), 7.09 (td, *J* = 15.3, 6.8 Hz, 1H, C*H*=CH), 5.49 (dd, *J* = 8.8, 3.9 Hz, 1H, N–CH), 4.70 (t, *J* = 8.8 Hz, 1H, CH_2), 4.28 (dd, *J* = 8.8, 3.9 Hz, 1H, CH_2), 2.30–2.15 (m, 2H, CH2), 1.69–1.35 (m, 2H, CH_2), 0.93 (t, *J* = 7.3 Hz, 3H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.7 (Cq, CO), 153.7 (Cq, CO), 152.1 (CH, CH=),139.2 (Cq, Ph), 129.2 (2 × CH, Ph),128.6 (CH, Ph), 125.9 (2xCH, Ph),120.3 (CH, CH=) 69.9 (CH_2, CH_2–O), 57.8 (CH, N–CH), 34.7 (CH_2), 21.3 (CH_2), 13.7 (CH_3) ppm. Elem. anal. calcd. for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.40. Found C, 69.20; H 6.70; N 5.43.

General procedure for the conjugate addition. $(CuI)_4{\cdot}(SMe_2)_3$ (5 mol%, 4.68.10^{-3} mmol, 4.5 mg) and ligand (6 mol%, 0.0225 mmol, 11.6 mg) were dissolved in CH_2Cl_2 (1.5 mL) and solution was stirred for 15 min at room temperature. The mixture was then cooled to −78 °C and solution of *N*-enoyl oxazolidone (0.375 mmol) in CH_2Cl_2 (1.5 mL) was added. Then $BF_3{\cdot}Et_2O$ (1.2 eq., 0.45 mmol, 0.12 ml) was added to the mixture. After 5 min, EtMgBr (0.563 mmol, 0.18 mL, 3.2 M in 2-MeTHF), which was diluted to 1 M with 2-MeTHF (300 μl), was added dropwise during 30 min. The reaction was then stirred for an additional 1.5 h at −78 °C, before it was quenched with MeOH (1 mL) at −78 °C. The resulting mixture was then washed with 1 M solution of NH_4Cl and extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by flash chromatography (SiO_2, Hex : AcOEt 4 : 1).

Characterisation data for products of conjugate addition.

4,4-Dimethyl-3-(3-methylpentanoyl)oxazolidin-2-one (2b)

Colorless liquid, 72.9 mg (91%). ^{1}H NMR (600 MHz, $CDCl_3$), δ = 3.98 (s, 2H), 2.89 (dd, *J* = 5.8, 16.0 Hz, 1H), 2.67 (dd, *J* = 8.1, 16.0 Hz, 1H), 1.89–1.98 (m, 1H), 1.564 (s, 3H), 1.560 (s, 3H), 1.35–1.43 (m, 1H), 1.19–1.27 (m, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ = 174.0 (Cq, CO), 154.0 (Cq, CO), 75.1 (CH_2), 60.4 (Cq), 43.6 (CH_2), 31.3 (CH), 29.4 (CH_2), 24.84 (CH_3), 24.83 (CH_3), 19.2 (CH_3), 11.3 (CH_3) ppm. MS (EI) *m*/*z* 214.1 (MH^+). HRMS calc. for $C_{11}H_{19}NO_3$ (MH^+) *m*/*z* 214.1438; found 214.1424. HPLC (OD–H, 218 nm, hexane/*i*PrOH 99 : 1, 1 mL min^{-1}) t_{R1} = 11.1 min, t_{R2} = 12.3 min.

(4*S*)-4-Isopropyl-3-(3-methylpentanoyl)oxazolidin-2-one (4a)

Colorless liquid, 67.2 mg (79%). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers), δ = 4.42–4.50 (m, 2H), 4.16–4.32 (m, 2H), 3.04 (dd, *J* = 5.5, 15.8 Hz, 1H), 2.77–2.92 (m, 2 H), 2.64 (dd, *J* = 8.3, 15.8 Hz, 1H), 1.89–2.07 (m, 1H), 1.87–1.97 (m, 12H), 1.34–1.49 (m, 1H), 1.19–1.32 (m, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, mixture of two diastereomers) δ = 172.89 (Cq, CO), 172.86 (Cq, CO), 154. 01 (Cq, CO), 153.99 (Cq, CO), 63.18 (CH_2), 63.17 (CH_2), 58.4 (CH), 58.3 (CH), 42.2 (CH_2), 42.1 (CH_2), 31.4 (CH), 31.3 (CH), 29.5 (CH_2), 29.2 (CH_2), 28.39 (CH), 28.36 (CH), 19.2 (CH_3), 19.1 (CH_3), 18.0 (CH_3), 14.61 (CH_3), 14.58 (CH_3), 11.29 (CH_3), 11.27 (CH_3) ppm. MS (EI) *m*/*z* 250.1 (MNa^+). HRMS calc. for $C_{12}H_{22}NO_3$ (MH^+) *m*/*z* 228.1594; found 228.1589. HPLC (IB, 218 nm, hexane/*i*PrOH90 : 10, 0.75 mL min^{-1}) t_R = 9.4 min.

(4*S*)-4-*tert*-Butyl-3-(3-methylpentanoyl)oxazolidin-2-one (4b)

Colorless liquid, 58.5 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers) δ = 4.45 (dd, 1H, *J* = 1.9, 7.3 Hz, 1H), 4.18–4.32 (m, 2H), 3.01 (dd, *J* = 5.5, 16.1 Hz, 1H), 2.77–2.92 (m, 2H), 2.67 (dd, *J* = 8.1, 16.1 Hz, 1H), 1.89–2.07 (m, 1H), 1.36–1.53 (m, 1H), 1.19–1.32 (m, 1H), 0.88–0.99 (m, 15H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ = 172.8 (Cq, C=O), 154.7 (Cq, C=O), 65.2 (CH_2), 60.8 (CH), 42.1 (CH_2), 35.7 (Cq), 31.4 (CH), 29.4 (CH_2), 25.7 (CH_3), 19.1 (CH_3), 11.3 (CH_3) ppm. MS (EI) *m*/*z* 264.2 (MNa^+). HRMS calc. for $C_{13}H_{24}NO_3$ (MH^+) *m*/*z* 242.1751; found 242.1757. GC (140 °C, 196 kPa, t inj. 250 °C, Lipodex E) t_R = 38.4 min (major), 38.9 (minor).

(4*S*)-3-(3-Methylpentanoyl)-4-phenyloxazolidin-2-one (4c)

White solid, 78.7 mg (80%); mp 51 °C (heptane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42–7.27 (m, 5H) 5.44 (dd, *J* = 8.8, 3.7 Hz, 1H), 4.69 (t, *J* = 8.8 Hz, 1H), 4.31–4.24 (m, 1H), 2.99 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.68 (dd, *J* = 16.0, 8.5 Hz, 1H), 2.01–1.83 (m, 1H), 1.43–1.03 (m, 3H), 0.90–0.82 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, mixture of two diastereomers), δ = 172.4 (Cq, CO), 153.7 (Cq, CO), 139.2 (Cq, Ph), 129.1 (CH, Ph), 128.7 (CH, Ph), 125.93 (CH, Ph), 125.89 (CH, Ph), 69.84 (CH_2), 69.82 (CH_2), 57.64 (CH), 57.60 (CH), 42.21 (CH_2), 42.18 (CH_2), 31.3 (CH), 31.1 (CH), 29.4 (CH_2), 29.2 (CH_2), 19.2 (CH_3), 19.1 (CH_3), 11.27 (CH_3), 11.25 (CH_3) ppm. Elem. anal. calcd. for $C_{15}H_{19}NO_3$ (Mr 284.1) C, 68.94; H, 7.33; N, 5.36; O, 18.37. Found: C, 68.52; H, 7.30; N, 5.37. MS (EI) *m*/*z* 284.1 (MNa^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 15.4 min.

(4*S*)-4-Isopropyl-3-(3-metylpentanoyl)-5,5-diphenyloxazolidin-2-one (4d)

White solid, 145 mg (76%); mp 134 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.52–7.45 (m, 2H), 7.44–7.27 (m, 8H), 5.38 (d, J = 3.3 Hz, 1H), 2.78 (dd, J = 15.4, 6.1 Hz, 1H), 2.65 (dd, J = 15.3, 7.9 Hz, 1H), 1.97 (tdd, J = 13.7, 6.8, 3.4 Hz, 1H), 1.83 (dt, J = 13.7, 6.8 Hz, 1H), 1.36–1.08 (m, 2H), 0.89 (d, J = 7.0 Hz, 3H), 0.79 (m, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.7 (Cq, CO), 153.1 (Cq, CO), 142.4 (Cq, Ph), 138.1 (Cq, Ph), 128.8 (2xCH, Ph), 128.5 (CH, Ph), 128.3 (2xCH, Ph), 127.9 (CH, Ph), 125.9 (2xCH, Ph), 125.6 (2xCH, Ph), 89.3 (Cq), 64.8 (CH), 41.7 (CH_2), 31.59 (CH), 29.8 (CH), 29.2 (CH_2), 21.8 (CH_3), 18.8 (CH_3), 16.4 (CH_3), 11.2 (CH_3) ppm. Elem. anal. calcd. for $C_{24}H_{29}NO_3$ (Mr 379.5): C, 75.96; H, 7.70; N, 3.69. Found C, 75.92; H, 7.76; N, 3.63. MS (EI) m/z 380.1 (MH^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 5.6 min.

(4*S*)-4-Phenyl-3-(3-phenylpentanoyl)oxazolidin-2-one (6a)

White solid, 58.4 mg (70%); mp 81 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40–7.16 (m, 10H), 5.33 (dd, J = 9.2, 6.9 Hz, 1H), 4.50 (t, J = 8.8 Hz, 1H), 4.20 (dd, J = 8.8, 3.4 Hz, 1H), 3.45 (dd, J = 16.5, 9.2 Hz, 1H), 3.14 (dd, J = 16.5, 5.3 Hz, 1H), 3.09–2.99 (m, 1H), 1.71–1.57 (m, 2H), 0.77 (t, J = 7.4 Hz, 3H) ppm.^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.0 (Cq, CO), 153.1 (Cq, CO), 140.1 (Cq, Ph), 138.3 (Cq, Ph), 129.2 (2 × CH, Ph), 128.8 (CH, Ph), 128.7 (2 × CH, Ph), 128.3 (2 × CH, Ph), 126.9 (CH, Ph), 125.6 (2 × CH, Ph), 74.1 (CH), 70.6 (CH_2), 57.8 (CH), 52.8 (CH), 23.0 (CH_2), 11.9 (CH_3) ppm. Elem. anal. calcd. for $C_{20}H_{21}NO_3$ (Mr 323.4): C, 74.28; H, 6.55; N, 4.33. Found C, 74.17; H 6.55; N, 4.32. MS (EI) m/z 324.1 (MH^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 12.6 (major); t_R = 15.2 (minor) min.

(4*S*)-3-(3-Ethylhexanoyl)-4-phenyloxazolidin-2-one (6b)

White solid, 55 mg (50%); mp 60 °C (hexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42–7.27 (m, 5H), 5.44 (dd, J = 8.7, 3.8 Hz, 1H), 4.68 (t, J = 8.8 Hz, 1H), 4.27 (dd, J = 8.8, 3.8 Hz, 1H), 2.95 (dd, J = 16.2, 6.3 Hz, 1H), 2.77 (dd, J = 16.2, 7.3 Hz, 1H), 1.87 (td, J = 12.5, 6.3 Hz, 1H), 1.41–1.12 (m, 6H), 0.86–0.77 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.6 (Cq, CO), 153.5 (Cq, CO), 139.2 (Cq, Ph), 129.1 (2x CH, Ph), 128.6 (CH, Ph), 125.9 (2xCH, Ph), 69.8 (CH_2), 57.6 (CH), 39.7 (CH_2), 35.4 (CH_2), 35.3 (CH), 26.1 (CH_2), 19.7 (CH_2), 14.2 (CH_3), 10.6 (CH_3) ppm. Elem. anal. calcd. for $C_{17}H_{23}NO_3$ (Mr 289.40): C, 70.56; H, 8.01; N,4.84; found: C, 70.36; H, 8.08; N,4.73. MS (EI) m/z 290.2 (MH^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 12.9 min.

(4*S*)-4-Isopropyl-3-(3-phenylpentanoyl)oxazolidin-2-one (6c)

White amorphous solid, 49.5 mg (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.33–7.18 (m, 5H), 4.28–4.21 (m, 1H), 4.15–4.01 (m, 2H), 3.37 (dd, J = 16.1, 9.2 Hz, 1H), 3.20 (dd, J = 16.1, 5.5 Hz, 1H), 3.10 (tt, J = 9.2, 5.5 Hz, 1H), 2.26 (dtd, J = 13.9, 7.0, 3.9 Hz, 1H), 1.81–1.59 (m, 2H), 0.82 (m, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.0 (Cq, CO), 154.0 (Cq, CO), 143.8 (Cq, Ph), 128.3 (2 × CH, Ph), 127.8 (2 × CH, Ph), 126.4 (CH, Ph), 63.3 (CH_2), 59.9 (CH), 43.7 (CH), 41.7 (CH_2), 29.5 (CH_2), 28.5 (CH), 17.9 (CH_3), 14.7 (CH_3), 12.0 (CH_3) ppm. Elem. anal. calcd. for $C_{17}H_{23}NO_3$ (Mr 289.40): C, 70.56; H, 8.01; N, 4.84. Found C, 70.40; H, 7.93; N, 4.88. MS (EI) m/z 290.2 (MH^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 9.6 min.

(4*S*)-3-(3-Methylnonanoyl)-4-phenyloxazolidin-2-one (7a)

White solid, 72.9 mg (61%); mp 45 °C (heptane). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers) δ = 7.42–7.27 (m, 5H, Ph), 5.44 (dd, J = 3.8, 8.7 Hz, 1H), 4.68 (t, J = 8.8, 1H), 4.271 (dd, J = 3.8, 8.9 Hz, 1H), 4.265 (dd, J = 3.8, 8.9 Hz, 1H), 2.99 (dd, J = 5.3, 16.0 Hz, 2H), 2.90–2.77 (m, 2H), 2.67 (dd, J = 8.5, 16.0 Hz, 1H), 2.10–1.88 (m, 1H), 1.36–1.11 (m, 10H), 0.93–0.81 (m, 6H) ppm. ^{13}C NMR: (150 MHz, $CDCl_3$, mixture of two diastereomers) δ = 172.4 (Cq, CO), 153.7 (Cq, CO), 139.2 (Cq, Ph), 129.1 (CH, Ph), 128.65 (CH, Ph), 128.63 (CH, Ph), 125.93 (CH, Ph), 125.88 (CH, Ph), 69.81 (CH), 69.80 (CH), 57.60 (CH), 57.58 (CH), 53.4 (CH_2), 42.6 (CH_2), 42.5 (CH_2), 36.8 (CH_2), 36.6 (CH_2), 31.83 (CH_2), 31.79 (CH_2), 29.74 (CH_2), 29.68 (CH), 29.65 (CH), 29.4 (CH_2), 26.8 (CH_2), 26.7 (CH_2), 22.6 (CH_2), 19.7 (CH_3), 19.6 (CH_3), 14.1 (CH_3) ppm. Elem. anal. calcd for $C_{19}H_{27}NO_3$ (Mr 340.2): C, 71.89; H, 8.57; N, 4.41; O, 15.12. Found: C, 72.12; H, 8.60; N, 4.43. MS (EI) m/z 340.2 (MNa^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 12.5 min (major), t_R = 13.7 min (minor).

(4*S*)-3-(3-Cyclopentylbutanoyl)-4-phenyloxazolidin-2-one (7b)

White solid, 72.8 mg (65%); mp 89 °C (heptane). ^{1}H NMR (300 MHz, $CDCl_3$, mixture of two diastereomers) δ = 7.43–7.27 (m, 5H, Ph), 5.44 (dd, J = 3.8, 8.8 Hz, 1H), 5.43 (dd, J = 3.7, 8.7 Hz, 1H), 4.69 (t, J = 8.8 Hz, 1H), 4.68 (t, J = 8.8 Hz, 1H), 4.31–4.23 (m, 1H), 3.09 (dd, J = 4.0, 15.8 Hz, 1H), 2.98 (dd, J = 4.6, 16.0 Hz, 1H), 2.82 (dd, J = 9.0, 16.0 Hz, 1H), 2.68 (dd, J = 9.8, 15.8 Hz, 1H), 1.96–1.80 (m, 1H), 1.78–1.40 (m, 7H), 1.21–1.03 (m, 2H), 0.87–0.78 (m, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, mixture of two diastereomers) δ = 172.60 (Cq, CO), 172.55 (Cq, CO), 153.7 (Cq, CO), 153.6 (Cq, CO), 139.204 (Cq, Ph), 139.196 (Cq, Ph), 129.1 (CH, Ph), 128.7 (CH, Ph), 128.6 (CH, Ph), 126.0 (CH, Ph), 125.9 (CH, Ph), 69.78 (CH_2), 69.76 (CH_2), 57.7 (CH), 57.6 (CH), 46.2 (CH), 45.9 (CH), 41.6 (CH_2), 41.4 (CH_2), 34.8 (CH), 34.7 (CH), 30.6 (CH_2), 30.4 (CH_2), 30.1 (CH_2), 29.9 (CH_2), 25.37 (CH_2), 25.36 (CH_2), 25.34 (CH_2), 25.33 (CH_2), 18.13 (CH_3), 18.11 (CH_3) ppm. Elem. anal. calcd for $C_{18}H_{23}NO_3$ (Mr 324.2): C, 71.73; H, 7.69; N, 4.65; O, 15.93. Found: C, 72.01; H, 7.69; N, 4.63. MS (EI) m/z 324.1 (MNa^+). HPLC (AS–H, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 12.0 (major), t_R = 13.6 (minor) min.

(4*S*)-4-Phenyl-3-(3-phenylbutanoyl)oxazolidin-2-one (7c)

White solid, 55.1 mg (36%); mp 113 °C (heptane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.34–7.15 (m, 8H), 7.12–7.03 (m, 2H), 5.40 (dd, J = 4.0, 8.8 Hz, 1H), 4.66 (t, J = 8.8 Hz, 1H), 4.21 (dd, J = 4.0, 8.9 Hz, 1H), 3.48, (dd, J = 6.6, 15.7 Hz, 1H), 3.40–3.26 (m, 1H), 3.05, (dd, J = 7.8, 15.7 Hz, 1H), 1.26 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.5 (Cq, CO), 153.6 (Cq, CO), 145.5 (Cq, Ph), 138.8 (Cq, Ph), 129.1 (CH, Ph), 128.5 (CH, Ph), 126.9 (CH, Ph) 126.3 (CH, Ph), 125.6 (CH, Ph), 69.9 (CH_2), 57.6 (CH), 43.2 (CH_2), 36.0 (CH), 21.8 (CH_3) ppm. Elem. anal. calcd for $C_{19}H_{19}NO_3$ (Mr 332.1): C, 73.77; H, 6.19; N, 4.53. Found: C, 73.45; H, 6.36; N, 4.49. MS (EI) m/z 332.2 (MNa^+).

HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 26.1 min.

(4*S*)-4-Phenyl-3-(3-(thiophen-2-yl)butanoyl)oxazolidin-2-one (7d)

White solid, 28.6 mg (9%); mp 112 °C (heptane). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42–7.25 (m, 5H), 7.11 (dd, J = 1.1, 5.1 Hz, 1H), 6.88 (dd, J = 3.5, 5.1 Hz, 1H), 6.83–6.77 (m, 1H), 5.38 (dd, J = 3.5, 8.7 Hz, 1H), 4.64 (t, J = 8.8 Hz, 1H), 4.26 (dd, J = 3.6, 8.9 Hz, 1H), 3.41 (dd, J = 7.8, 16.8 Hz, 1H), 3.65 (m, 1H), 3.16 (dd, J = 6.3, 16.8 Hz, 1H), 1.34 (d, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ = 170.9 (Cq, CO), 153.7 (Cq, CO), 149.6 (Cq, Ar), 139.0 (Cq, Ar), 129.2 (Ar–CH), 128.7 (Ar–CH), 126.6 (Ar–CH), 125.9 (Ar–CH), 123.2 (Ar–CH), 122.9 (Ar–CH), 70.0 (CH_2), 57.6 (CH), 44.4 (CH_2), 31.2 (CH), 23.0 (CH_3) ppm. Elem. anal. calcd for $C_{17}H_{17}NO_3S$ (Mr 338.2): C, 64.74; H, 5.43; N, 4.44; O, 15.22; S, 10.17. Found: C, 64.54; H, 5.41; N, 4.41; S, 9.99. MS (EI) m/z 338.1 (MNa^+). HPLC (IB, 218 nm, hexane/*i*PrOH 90 : 10, 0.75 mL min^{-1}) t_R = 23.3 min.

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