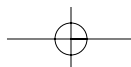
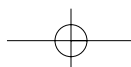
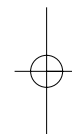
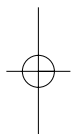

4 ADDITION REACTIONS TO C=O BONDS

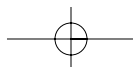
Reduction

<i>α</i> -Alkoxy ketones	000
<i>α</i> -Keto aldehydes	000
1,2-Diketones	000
<i>α</i> -Keto acid derivatives	000
<i>β</i> -Aminoketones	000
<i>β</i> -Keto aldehydes	000
<i>β</i> -Keto acid derivatives	000
<i>ω</i> -Keto acid derivatives	000
Ene reactions	000
Wittig and related olefination	000
Addition of organometallic and related reagents	000
Auxiliary-bearing acceptor carbonyl derivatives	000
1,2-Dicarbonyl derivatives	000
<i>α</i> -Oxo acid derivatives	000
Related amins and acetals	000
1,n-Hydroxycarbonyl derivatives	000
1,n-Dicarbonyl derivatives	000
<i>ω</i> -Acyl carbonyl derivatives	000
Auxiliary-bearing organometallic donor reagents	000
Acyl anion equivalents (formyl, acetyl, acryloyl, benzoyl)	000
Allylic and benzylic related derivatives	000
Formamidines	000
Aromatic derivatives	000
Addition of enolates (aldol and related reactions)	000
Auxiliary-bearing acceptor carbonyl derivatives	000
Auxiliary-bearing enolate equivalents from carbonyl precursors	000
Creation of single stereocentre	000
Creation of two stereocentres	000
Auxiliary-bearing enolate equivalents from carboxylic acid precursors	000
Acetate equivalents – creation of a single stereocentre	000
Reaction with alkyl aldehydes	000
Reaction with <i>αβ</i> -unsaturated aldehydes	000
Reaction with aromatic aldehydes	000
Reaction with <i>α</i> - or <i>β</i> -heteroatom functionalized aldehydes	000
Reaction with ketones	000
Higher order equivalents	000
Creation of a single stereocentre	000
Creation of two stereocentres	000
Phenacyl and phenethyl derivatives	000
Others	000
<i>α,β</i> - and <i>β,γ</i> -unsaturated acyl enolate equivalents	000
Acryloyl derivatives (Bayliss-Hillman and related reactions)	000
Crotonyl and related derivatives	000
Auxiliary-bearing <i>α</i> -heteroacyl derivatives	000
<i>α</i> -Amino acid derivatives – auxiliary bound to acyl	000
<i>α</i> -Amino acid derivatives – auxiliary bound to nitrogen	000

**2***Compendium of Chiral Auxiliary Applications*

α -Amino acid derivatives – auxiliary on both acid and nitrogen (bislactim ethers/cyclic Schiff bases)	000
α -Alkoxy derivatives	000
α -Thio derivatives	000
α -Halo derivatives	000
Homoenolate equivalents	000
Tandem reactions	000
Radical reactions	000
Addition to auxiliary-bearing acceptor carbonyl derivatives	000
Addition by auxiliary-bearing donor radical derivatives	000
Intramolecular addition	000
Coupling reactions	000
References	000

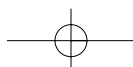


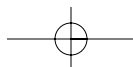


4. Addition reactions to C=O bonds

3

Substrate	Reagent	Yield(de) → (config)	Major Pre-product	Yield(ee) → (config)	Major Product	Refs
REDUCTION						
α-Alkoxy ketones						
	ZnBH ₄	96(84) → (S)		--	--	1
α-Keto aldehydes						
	NaBH ₄	85-100 (94) → (S)		--	--	2*
	Zn(BH ₄) ₂	>98(99) → (S)		(98) → (S)-(+)		3
	NaBH ₄ /YCl ₃	>98(97) → (R)		(94) → (R)		3
	Li(s-Bu) ₃ BH MgBr ₂	90(96) → (R)		--	--	4; 5*
	Li(s-Bu) ₃ BH Kriptofix 211	98(≥99) → (S)		--	--	4; 5*
	Li(s-Bu) ₃ BH	>98(86) → (R)		--	--	6; 7*
	Li(s-Bu) ₃ BH	>98(66) → (S)		--	--	6; 7*
	DIBAH	>98(80) → (R)		--	--	6; 7*
	NaBH ₄ /CeCl ₃	100(95) → (R)-(-)		53 → (S)-(-)		8; 9*
	Zn(BH ₄) ₂	>98(99) → (S)		(98) → (S)		3

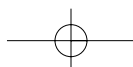
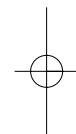
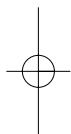


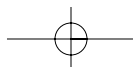


4

Compendium of Chiral Auxiliary Applications

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	Zn(BH ₄) ₂	98(99) (S)		(98) (S)		3
	NaBH ₄ /YCl ₃	>98(96) (R)		(92) (R)		3
	NaBH ₄ /YCl ₃	>98(85) (R)		--	--	3
	Li(s-Bu) ₃ BH	(55) (S)		--	--	6; 7*
	DIBAH	>98(83) (R)		--	--	6; 7*
	Li(s-Bu) ₃ BH	(66) (R)		--	--	6; 7*
	Li(s-Bu) ₃ BH	(88) (S)		--	--	6; 7*
	DIBAH	(88) (R)		--	--	6; 7*
	Li(s-Bu) ₃ BH	(56) (S)		--	--	6
	Zn(BH ₄) ₂	78(88) (S)		(76) (S)-(+)		3
	NaBH ₄ /YCl ₃	98(83) (R)		(66) (R)		3
	Zn(BH ₄) ₂	>98(86) (S)		(76) (S)-(+)		3
	NaBH ₄ /YCl ₃	>98(85) (R)		(66) (R)		3
	L-Selectride	95(91) (S)		steps 70(97) (S)-(-)		10*





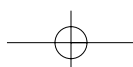
4. Additon reactions to C=O bonds

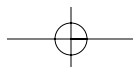
5

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	DIBAH	98(91) (R)		steps 82(99) (R)-(+)		10*
	NaBH ₄	(92) (S)		--	--	2
	NaBH ₄	-- (S)		overall 48(80) (S)		11*
	Zn(BH ₄) ₂	96(92) (S)		(76) (S)-(+)		3
	NaBH ₄ /YCl ₃	97(91) (R)		(66) (R)		3
	(i) NaBH ₄ /LiI (ii) NaH/BnBr	(>99) (R)		overall 70(96) (R)		12
	K(<i>s</i> -Bu) ₃ BH MgBr ₂	88(≥99) (R)		--	--	5*

1,2-Diketones

	LiAlH ₄ /LiBr	>95(96) (R)		--	--	13; 14*
	LiAlH ₄ /MgBr ₂	>95(90) (S)		--	--	13; 14*
	LiAlH ₄ /LiBr	>95(96) (R)		--	--	13; 14*
	LiAlH ₄ /MgBr ₂	>95(90) (S)		--	--	13; 14*





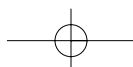
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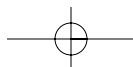
Compendium of Chiral Auxiliary Applications

Substrate	Reagent	Yield(de) → (config)	Major Pre-product	Yield(ee) → (config)	Major Product	Refs
	LiAlH ₄ /LiBr	95(96) → (R)-(+)		steps 76(100) → (R)-(-)		14*
	LiAlH ₄ /MgBr ₂	85(90) → (S)-(+)		steps 74(100) → (S)-(+)		14*
	LiAlH ₄ /LiBr	>95(85) → (R)		90(70) → (R)-(+)		13; 14*
	LiAlH ₄ /MgBr ₂	>95(85) → (S)		--	--	13; 14*
	LiAlH ₄	(>99) → (S)-(+)		--	--	15*
	LiAlH ₄	(>99) → (S)		--	--	15*
	LiAlH ₄	(>99) → (S)-(+)		--	--	15*

***α*-Keto acid derivatives**

	NaBH ₄	(77) → (S)		overall 41(55) → (S)-(+)		16*
	Zn	66(62) → (S)		--	--	17*

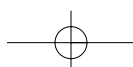
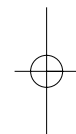
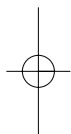


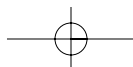


4. Addition reactions to C=O bonds

7

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	KB(I-PrO) ₃ H	55(91) (R)		--	--	18
	KBEt ₃ H/LiBr	89(95) (R)		(90) (R)-(-)		18; 19*
	Li(s-Bu) ₃ BH	70(89) (S)-(-)		72(100) (S)-(-)		20*
	Zn(BH ₄) ₂	62(62) (R)-(-)		--	--	20*
	2H ⁺ , 2e ⁻	47(75) (R)-(+)		--	--	21*
	K(s-Bu) ₃ BH	91(99) (S)		73(100) (S)-(-)		22*
	Al-Hg	-- (S)		-- (S)-(+)		23*
	(Et ₃ CO) ₃ AlLiH	90(99) (S)		--	--	24
	(Et ₃ CO) ₃ AlLiH	65(95) (R)		--	--	24

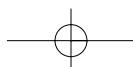
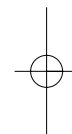
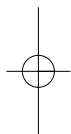


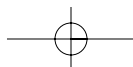


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Compendium of Chiral Auxiliary Applications

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	Li(s-Bu) ₃ BH 18-C-6	95(99) (S)		80(97) (S)-(-)		25*
		80(>99) (R)		--	--	26
	K(<i>i</i> -PrO) ₃ BH	90(95) (R)		--	--	27
	Li(s-Bu) ₃ BH ZnCl ₂	90(98) (R)		(>98) (R)-(+)		28
	Li(s-Bu) ₃ BH	(97) (R)		(>98) (R)-(+)		29
	Li(s-Bu) ₃ BH	75(92)		--	--	30
	K(s-Bu) ₃ BH	62(88) (S)		--	--	31
	K(s-Bu) ₃ BH	(98) (S)		--	--	31
	K(s-Bu) ₃ BH HMPA	(73) (R)		--	--	31

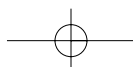
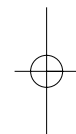
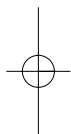


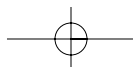


4. Addition reactions to C=O bonds

9

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	LiBH ₄	98(85) (R)		--	--	32
	DIBAH	90(66) (S)		--	--	32
	Li(s-Bu) ₃ BH	(≥99) (R)		(>98) (R)		29
	2H ⁺ , 2e ⁻	47(85) (R)-(+)		--	--	21*
	(Et ₃ CO) ₃ AlLiH	84(99) (S)		89(98) (S)-(+)		24
	K(s-Bu) ₃ BH 18-C-6	89(>99) (S)		85(97) (S)-(+)		25*
	Li(s-Bu) ₃ BH	(≥99) (R)		(>98) (R)		29
	Li(s-Bu) ₃ BH	90(98) (R)		(97) (R)		33*
	Li(s-Bu) ₃ BH	96(98) (R)		(96) (R)		33*

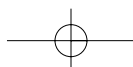
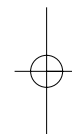
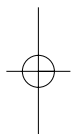


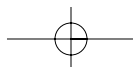


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Compendium of Chiral Auxiliary Applications

Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	(Et ₃ CO) ₃ AlLiH	97(99) (S)		89(98) (S)		24
	Li(s-Bu) ₃ BH	(≥99) (R)		(>98) (R)		29
	2H ⁺ , 2e ⁻	70(81) (R)-(+)		--	--	21*
	NaBH ₄	(80) (S)		overall 82(60) (S)-(-)		16*
	DIBAH/LiBr	-- (R)		overall 81(10) (R)-(+)		34
	LiBH ₄ /LiBr or NaBH ₄	-- (S)		overall 85(58) (S)-(-)		16*; 34
	2H ⁺ , 2e ⁻	70(77) (R)-(+)		--	--	21*
	Li(s-Bu) ₃ BH	81(98) (R)		(97) (R)		33*
	Li(s-Bu) ₃ BH	88(97) (R)		(94) (R)		33*
	Li(s-Bu) ₃ BH	74(>99) (R)		93(>99) (R)-(-)		33*
	Li(s-Bu) ₃ BH	84(98) (R)		98(96) (R)-(-)		33*





4. Addition reactions to C=O bonds

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Substrate	Reagent	Yield(de) (config)	Major Pre-product	Yield(ee) (config)	Major Product	Refs
	DIBAH/LiBr	-- (R)		overall 59(66) (R)		34
	LiBH ₄ /LiBr or NaBH ₄	-- (S)		overall 85(87) (S)-(+)		16*; 34
	NaBH ₄	-- (S)		overall 29(37) (S)-(+)		34
	NaBH ₄	-- (S)		overall 57(46) (S)-(+)		34
	NaBH ₄	-- (S)		overall 35(37) (S)-(+)		34
	LiEt ₃ H	61(97) (R)		--	--	18
	LiEt ₃ H	92(99) (R)		(98) (R)-(-)		18; 19*
	NaBH ₄	(91) (R)-(+)		(82) (R)-(-)		35; 36*
	H ₂ /Pd-C	(93) (R)		(86) (R)-(-)		36*
	H ₂ /Pd-C	(98) (R)		(96) (R)-(-)		36*
	Zn	56(66) (S)		(70) (S)-(+)		17*

