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Recent Advances in Asymmetric Catalytic Methods for the Formation of Acyclic α,α-Disubstituted α-Amino Acids

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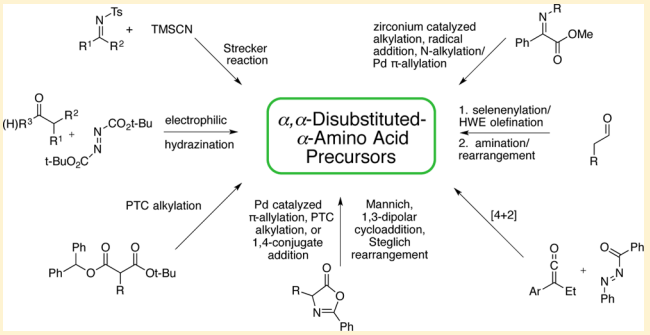
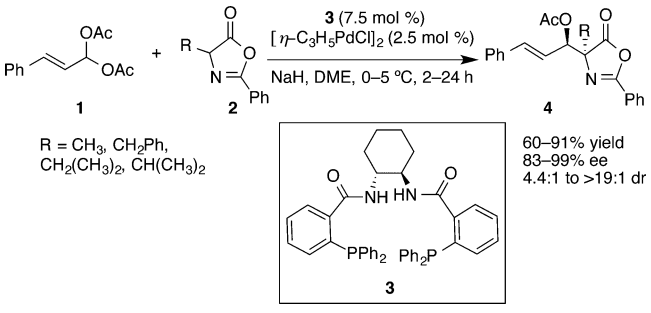
ABSTRACT: Because of their greater stability and unique conformational properties, unnatural amino acids are highly valued by pharmaceutical, biological, and organic chemists. This synopsis surveys the various catalytic methods used to access enantioenriched, acyclic α,α-disubstituted α-amino acids with a focus on the processes developed since 2007, when the last major reviews in this area were published.



The importance of unnatural amino acids originates from structure function studies of biological processes and their use as components in catalysis and the development of pharmaceuticals.[1,2] In particular, α,α-disubstituted α-amino acid units exhibit unique stability and conformational properties when incorporated into peptides.

In 1987, Ito and Hayashi used palladium-catalyzed π-allylation of methyl α-isocyano(phenyl)acetate to make an α,α-disubstituted α-amino acid precursor. When they employed a chiral ferrocenylphosphine ligand, up to 39% ee was observed.[3] It was not until 1997 that this method was elaborated using bisacetate **1** to allylate azlactones **2** with a catalyst derived from diphosphine **3** to obtain amino acid precursor **4** in 60−91% yield and 83−99% ee (Scheme 1).[4] Acid-catalyzed hydrolysis of **4** provides the corresponding protected amino acids with good diastereomeric ratios (4.4:1 to >19:1). The ability of cyclic azlactones to enolize more readily than their corresponding Schiff base has driven further work in this area.[5]

Scheme 1. Trost's Allylation of Azlactones



This Synopsis presents highlights from the latest literature on the asymmetric catalytic formation of acyclic α,α-disubstituted α-amino acids. Selected advances since 2007, when the last major reviews in this area of chemistry appeared,[6,7] are discussed. The asymmetric catalytic formation of cyclic amino acids[8] and the use of noncatalytic methods are beyond the scope of this review.[9,10]

First, reactions in which the carboxylic acid portion (red in color) of the amino acid is added, Strecker reactions,[11] are discussed. Next, methods that append the side chains (blue and purple in color[12]) of the amino acid are examined, which include nucleophilic additions into α-iminoesters and enolate alkylations. Following this category, pericyclic reactions are considered. Finally, processes that introduce the amino moiety are surveyed. The various groups that have been commonly used to mask the amine or acid portion of an α-amino acid are shown in Table 1 along with common methods for their deprotection/conversion to the desired functionality.

Strecker Reaction. Many efficient catalysts have been developed for the asymmetric cyanation of aldimines (Strecker reaction); however, there are fewer successful reports for the more hindered ketimines due to competitive enamine formation.[13] Previous notable work includes Shibasaski's bifunctional gadolinium-based catalyst[14] and Jacobsen's urea Schiff base catalyst (Scheme 2).[15] In both reports, the use of trimethylsilyl cyanide (in or ex situ) obviates the need to directly employ HCN gas. However, the high selectivities are only observed when R^1 is large and R^2 is small. The phosphinoyl group can be removed in refluxing concentrated HCl, which concurrently hydrolyzes the cyano group to provide the amino acids as their hydrochloride salts. For **10**, N-deprotection can be affected via Pd-catalyzed hydrogenation.

More recently, Feng et al. demonstrated the cyanation of ketimines to afford amino acid precursors (up to 99% yield and >99% ee) using a mixed titanium alkoxide/cinchona catalyst.[16] In

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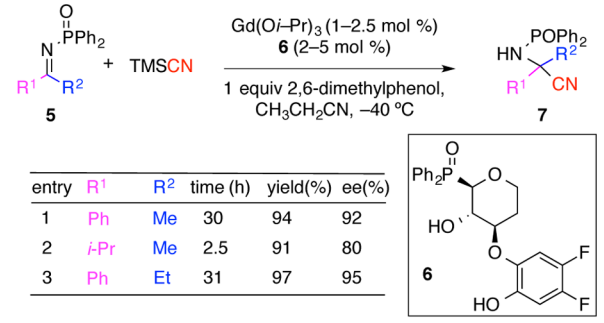
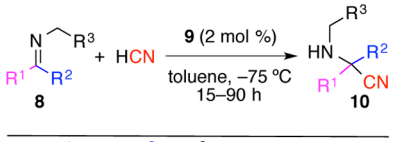
Table 1. Groups That Have Been Commonly Used To Mask the Amine or Acid Portion of an α-Amino Acid

groups transformed to RCOOH	conditions
RCN	concd HCl, heat
RCHO	$NaClO_2$ (Pinnick oxidation)
ester/lactone	base (NaOH) or 1 M to concd HCl
groups transformed to RNH_2	**conditions**
N–N (hydrazine)	Pt_2O, H_2 (50 psi); or Raney Ni, H_2; or SmI_2
NR	
R = Boc, $POPh_2$, Bz	strong acid (1 M to concd)
R = Cbz, Bn	Pd/C, H_2
R = *p*-methoxyphenyl (PMP), *o*-methoxyphenyl (OMP)	CAN, or periodic/sulfuric acid, or $PhI(OAc)_2$
R = CH_2CHCH_2	Ru catalyst
imine, RNC (isocyanide), aziridine	1 N HCl
RCO_2H, RCO_2R, $RCONR_2$	amination, then Hofmann rearrangement
NO_2	Zn^0, AcOH
azlactone	base (NaOH) or acid (1 M to concd HCl)
pyrroline	Pd/C, H_2; or Schotten–Baumann reaction

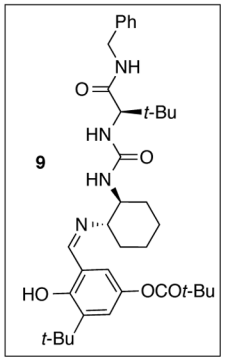
Scheme 2. Shibasaki's (Top) and Jacobsen's (Bottom) Cyanation of Ketimines



entry	R^1	R^2	time (h)	yield(%)	ee(%)
1	Ph	Me	30	94	92
2	*i*-Pr	Me	2.5	91	80
3	Ph	Et	31	97	95



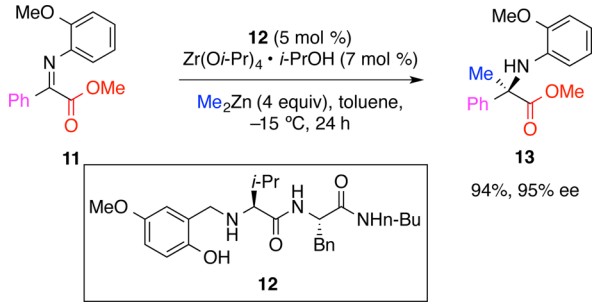
entry	R^1	R^2	R^3	yield(%)	ee(%)
1	Ph	Me	$CHCH_2$	97	85
2	Ph	Et	$CHCH_2$	96	69
3	2-BrC_6H_4	Me	Ph	45	42
4	*t*-Bu	Me	Ph	98	70
5	Ph	Me	Ph	97	90
6	Ph	Me	4-$OMeC_6H_4$	97	93
7	Ph	Me	4-BrC_6H_4	95	92



addition to trimethylsilyl cyanide, ethyl cyanoformate could also be used as the cyanide source. However, removal of the tosyl group was not shown. Additionally, Enders and co-workers achieved the first enantioselective Strecker synthesis of α-quaternary α-trifluoromethyl amino acids.[16] α-Amino nitriles were obtained in 50–99% yields and 83–95% ee, and the *N*-PMP group was readily removed with periodic and sulfuric acid.

Additions to α-Iminoester Electrophiles. Hoveyda et al. were the first to use zinc alkylation of α-iminoesters **11** to access enantioenriched quaternary α-amino esters **13** by developing a zirconium catalyst with ligand **12** (Scheme 3).[17] Only dimethylzinc is widely applicable, but a variety of aryl groups,

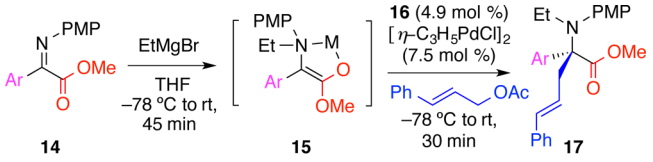
Scheme 3. Hoveyda's Zirconium Alkylation



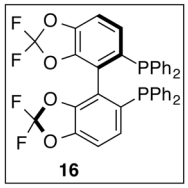
including sterically hindered examples, could be used in place of the phenyl in compound **11**. With electron-rich aryl groups good yields (48–74%) are obtained as the desired 1,2-addition pathway predominates over undesired N-addition or reduction pathways. The *o*-anisidine group is removed in the presence of (diacetoxyiodo)benzene.

Our group has focused on a complementary approach to quaternary α-amino esters wherein α-iminoester **14** serves as a nucleophile precursor rather than an electrophile. Specifically, N-alkylation provides enolate **15**, which undergoes palladium-catalyzed π-allylation with ligand **16** to provide amino ester precursors **17** (72–89% yield, 74–92% ee, Scheme 4).[18] With a homoallylic Grignard, the *N*-alkyl group was readily removed using Grotjahn's catalyst[19] (Figure 1) to generate the primary amines. The PMP group is removed using CAN.

Scheme 4. Kozlowski's Tandem N-Alkylation/π-Allylation



Ar	yield (%)	ee (%)
Ph	87	88
2-naphthyl	72	86
p-anisole	79	74
4-ClC_6H_4	84	92



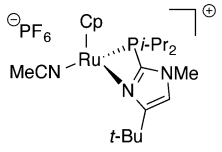


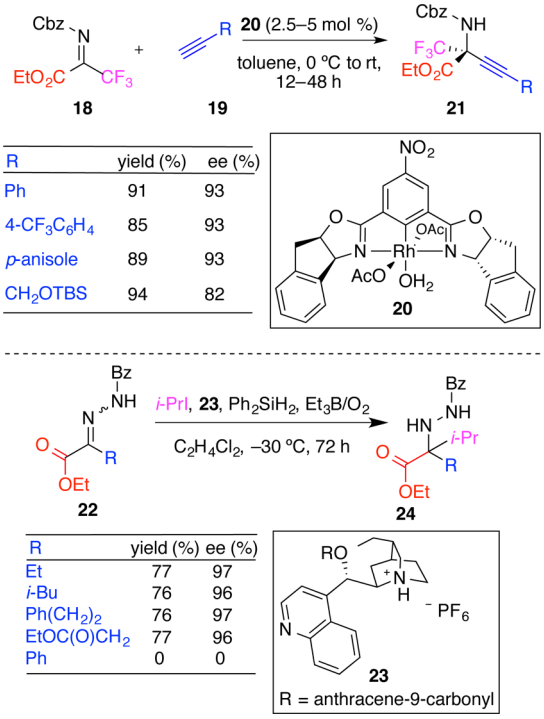
Figure 1. Grotjahn's catalyst.

Further additions to α-iminoesters have been accomplished with a range of nucleophiles including alkynyl zincs,[20] alkynyl rhodiums (Scheme 5),[21] and allyl silanes.[22] A variety of asymmetric Friedel–Crafts reactions with α-iminoesters have been reported.[23,24]

Asymmetric alkyl radical additions into α-iminoesters **22** have been catalyzed by protonated chiral amine **23** (Scheme 5).[25] This metal-free method enables access to α,α-disubstituted amino acid precursor **24** with two alkyl groups at the α-position. Reduction of the N–N bond is accomplished with samarium(II) iodide.

dx.doi.org/10.1021/jo502408z | J. Org. Chem. 2015, 80, 1–7

Scheme 5. Ohshima's and Mashima's (Top) and Jang's (Bottom) 1,2-Addition into α-Iminoesters



R	yield (%)	ee (%)
Ph	91	93
4-$CF_3C_6H_4$	85	93
p-anisole	89	93
CH_2OTBS	94	82

R	yield (%)	ee (%)
Et	77	97
i-Bu	76	96
$Ph(CH_2)_2$	76	97
$EtOC(O)CH_2$	77	96
Ph	0	0

PTC Alkylations. The mild conditions of phase-transfer catalysis (PTC) have led to its broad implementation in enolate alkylation reactions, including those leading to α-amino acids.[26,27] Over two decades ago, PTC was used to generate a quaternary center on an amino acid precursor by alkylation of the Schiff base derived from the *tert*-butyl ester of alanine (Figure 2).[28] Since then, much work has been done to improve the efficiency and scope with various halide electrophiles (alkyl, benzyl, propargyl, or allyl halides).[29−31]

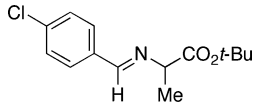
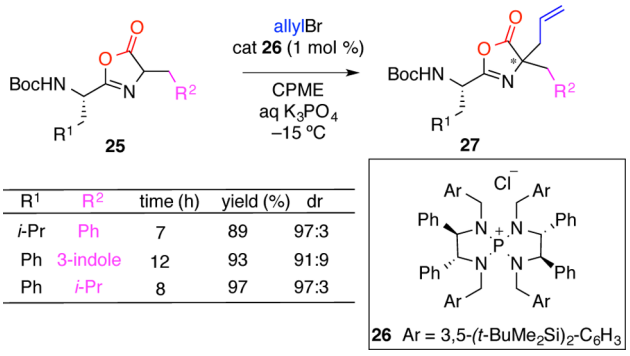


Figure 2. Alanine Schiff base.

A recent method that allows site-specific incorporation of quaternary amino acids into peptide chains involves PTC alkylation of azlactones at the C-terminus of a peptide chain **25** (Scheme 6).[32] With catalyst **26**, Ooi et al. formed quaternary azlactones **27** derived from phenylalanine, tryptophan, and leucine (89−97% yield, 91:9−97:3).[32] This procedure was highlighted in the synthesis of a tetrapeptide containing two quaternary centers. A reversed diastereomeric ratio for the enantiomer of **25** indicates that the catalyst is the primary determinant of the stereochemical outcome. Other PTC methods utilize azlactones in conjugate addition,[33] Mannich reactions,[34] and alkylation;[35] pyrrole-2-carboxylates in alkylation;[36] α-aryl-α-isocyanoacetates in conjugate addition;[37] and α-substituted nitroacetates in formylation[38] and conjugate addition.[39]

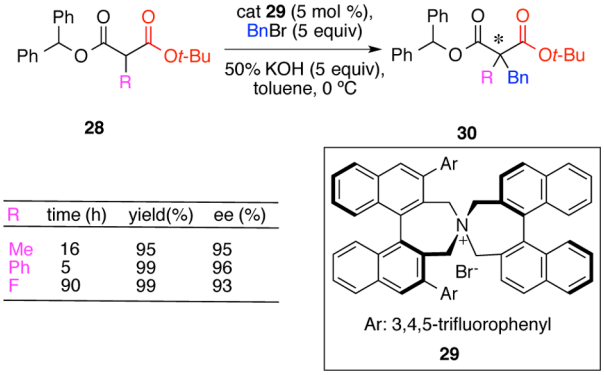
Work by Park et al. using PTC on alkylation of α-alkyl malonate **28** uses C_2-symmetric quaternary ammonium bromide **29** (Scheme 7).[40,41] Also in this work, successive double

Scheme 6. Ooi's PTC Alkylation



R^1	R^2	time (h)	yield (%)	dr
i-Pr	Ph	7	89	97:3
Ph	3-indole	12	93	91:9
Ph	*i*-Pr	8	97	97:3

Scheme 7. Park's PTC Alkylation



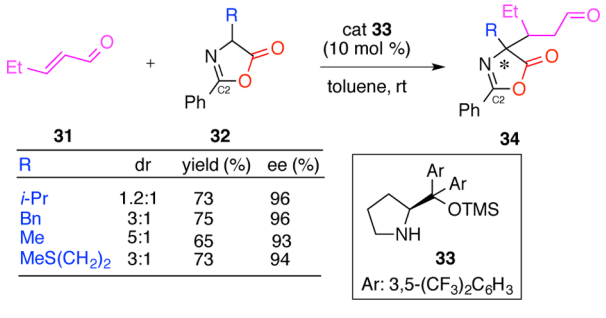
R	time (h)	yield(%)	ee (%)
Me	16	95	95
Ph	5	99	96
F	90	99	93

alkylation of malonates was performed with high enantioselectivity. Products **30** were converted to their amino esters via hydrogenation, amination, and a Hofmann rearrangement. Park has expanded this work to include malonates that can be selectivity hydrolyzed under alkaline conditions instead of catalytic hydrogenation.[42]

Other Enolate Alkylations. There have also been advances in enolate alkylation of glycine and alanine Schiff base derivatives that do not involve PTC.[43] Recent focus has been on conjugate additions between azlactones and a broad range of electrophiles including nitroalkenes,[44] bis(phenylsulfonyl)ethylenes,[45] α,β-unsaturated aldehydes/ketones/acrylic esters,[46−48] unsaturated pyrazolones,[49] arylsulfonyl indoles,[50] π-benzyls,[51] and thioelectrophiles.[52] Nucleophiles other than azlactones that are less common include α-cyanoacetates with cyclohexanone[53] and acyclic α-amino-β-ketoesters with allyl electrophiles.[54]

In one example, Jørgensen et al. reported an organocatalytic conjugate addition using α,β-unsaturated aldehyde **31** and azlactone **32** with proline-derived catalyst **33** (Scheme 8).[55]

Scheme 8. Jørgensen's Conjugate Addition



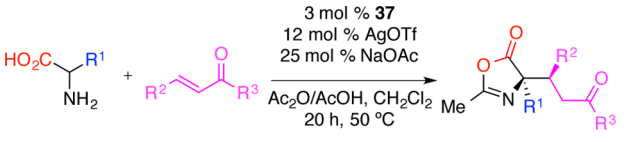
R	dr	yield (%)	ee (%)
i-Pr	1.2:1	73	96
Bn	3:1	75	96
Me	5:1	65	93
$MeS(CH_2)_2$	3:1	73	94

dx.doi.org/10.1021/jo502408z | J. Org. Chem. 2015, 80, 1−7

The diastereoselectivity is further tunable by modification of the C2-azlactone phenyl. After olefination of the aldehyde of **34**, the azlactone was hydrolyzed to provide the corresponding protected amino acids.

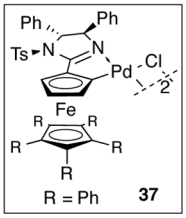
By using cooperative catalysis between monopalladium catalyst **37**, a Brønsted acid, and a Brønsted base, Peters et al. reported the first catalytic asymmetric conjugate addition of unprotected amino acid **35** into enone **36**, which is less reactive than the enals typically used (Scheme 9).[56]

Scheme 9. Peters' Tandem Azlactone Formation–Michael Addition



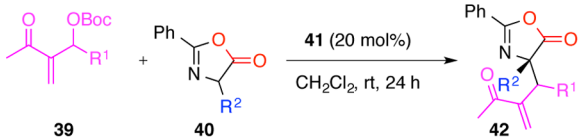
35 36 38 dr >99:1

R^1	R^2	R^3	yield(%)	ee(%)
Me	Ph	Me	50	99
n-Pr	Ph	Me	64	93
n-Pr	Me	Et	70	86
n-Pr	4-MeO-C_6H_4	Me	41	99
Bn	Ph	Me	49	28



Another example entails allylic substitution of the Morita–Baylis–Hillman adducts **39** with azlactones **40** using multifunctional chiral phosphine catalyst **41** (Scheme 10).[57]

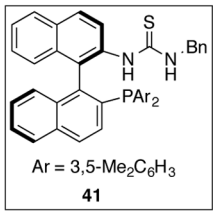
Scheme 10. Shi's Allylic Substitution



39 40 42

R^1	R^2	yield (%)	dr (syn/anti)	ee (%)
p-BrC_6H_4	*i*-Pr	82	16 : 1	97
p-$NO_2C_6H_4$	*i*-Pr	95	4 : 1	98
p-BrC_6H_4	*i*-Bu	84	3 : 1	91
p-BrC_6H_4	Me	85	7 : 1	92
2-thiofuran	*i*-Pr	95	12 : 1	95
Et	*i*-Pr	96[a]	7 : 1	85

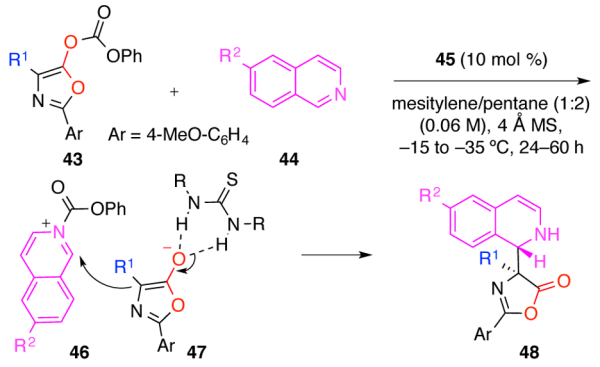
[a] The reaction conditions: in THF at 35 °C.



A transformation using O-acylated azlactones to give *α,β*-diamino acid derivatives has been reported by Seidel et al. during their study of Steglich rearrangements (Scheme 11).[58] Importantly, low temperatures are required to suppress a substantial background reaction. Opening of the azlactone ring is not demonstrated. In this paper and since then, Steglich rearrangements have been developed.[59]

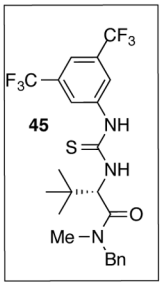
Cycloadditions. Toste and co-workers developed an enantioselective [3 + 2] dipolar cycloaddition between azlactone **49** and acrylate esters **50** using gold catalyst **51** as an activator of the nucleophile (Scheme 12).[60] This method affords *exo*-cycloadducts **52** in good yields and high enantioselectivities. Ring opening of the 1-pyrroline was not demonstrated in this paper but has been carried out successfully by others using a Pd/C hydrogenation.[36] A broad scope was identified for **49** with the more activated *N*-phenylmaleimide as the alkene. Enantioselective Mannich reactions with azlactones were also described in this article.

Scheme 11. Seidel's Additions to Isoquinoliniums

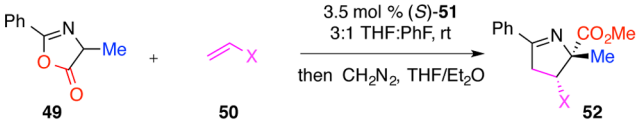


43 44 46 47 48

entry	R^1	R^2	yield(%)	dr	ee(%)
1	Me	H	85	96 : 4	93
2	*i*-Pr	H	94	87 : 13	89
3	Bn	H	95	90 : 10	90
4	Me	Me	94	90 : 10	88
5	Me	Br	95	91 : 9	90

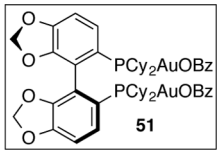


Scheme 12. Toste's [3 + 2] Cycloaddition

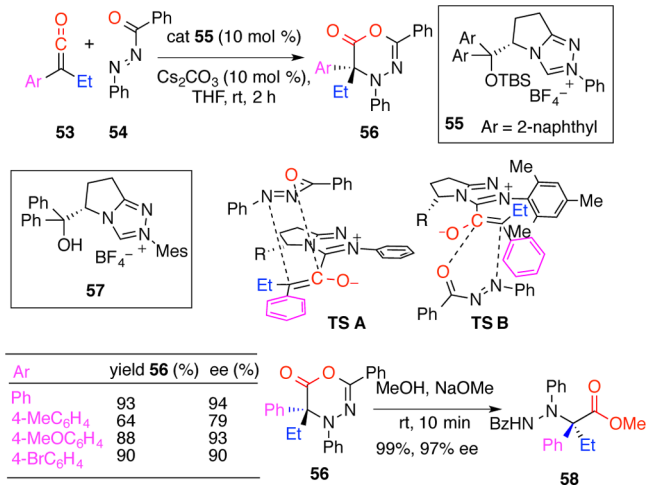


49 50 52

X	time (h)	yield (%)	ee (%)
CO_2t-Bu	24	56	99
CO_2Et	14	66	90
CO_2Me	14	89	93



Scheme 13. Ye's [4 + 2] Cycloaddition



53 54 56 55 57 TS A TS B 58

Ar	yield **56** (%)	ee (%)
Ph	93	94
4-MeC_6H_4	64	79
4-$MeOC_6H_4$	88	93
4-BrC_6H_4	90	90

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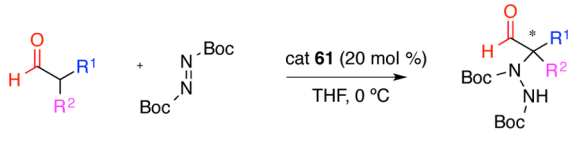
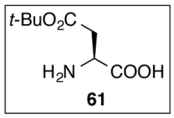
enantioselectivity was proposed to be a consequence of coplanar **TS A**. The opposite enantiomer was obtained in 50−96% ee through the use catalyst **57**, which was postulated to result from perpendicular **TS B**. Alkaline ring opening of **56** creates amino ester precursor **58** in good yield and without erosion of enantioselectivity. Reduction of the N−N bond and removal of the phenyl group was not demonstrated; however, *N*,*N*′-dibenzoyldiazenes could be used. This reaction has since been studied computationally by Tang.[62]

Enolate Amination. Electrophilic amination is an alternate disconnection to generate amino acid derivatives. For quaternary amino acids, Kokotos and co-workers recently demonstrated asymmetric hydrazination of α,α-disubstituted aldehydes **59** with azodicarboxylates **60** using amino acid derivative **61** (Scheme 14).[63,64] Oxidation, esterification, and samarium(II) iodide reduction provides the *N*-Boc-protected amino ester.

Scheme 14. Kokotos's Electrophilic Hydrazination



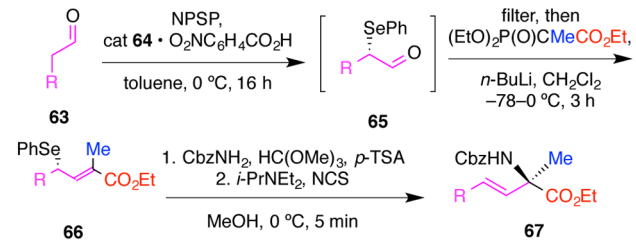
R^1	R^2	time (h)	yield (%)	ee(%)
Me	Ph	24	98	94
Me	2-Br-C_6H_4	72	40	94
Et	Ph	24	69	91



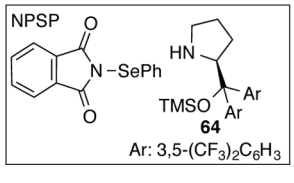
Deng and co-workers explored a bifunctional cinchona catalyst for a similar transformation. This sequence ultimately led to a formal total synthesis of conagenin.[65] Other nucleophiles used for these transformations include α-substituted α-cyanothioacetates,[66] α-substituted α-nitroacetates,[67] α-fluoro-β-ketoesters,[68] α-cyanoketones,[69] and α-acyl acrylates.[70]

Armstrong and co-workers developed a novel route to α,α-disubstituted-α-amino acids relying on asymmetric α-selenenylation, which generates an enolate umpolung equivalent.[71] With aldehyde **63** in the presence of proline catalyst **64**, intermediate **65** was obtained (Scheme 15). An in situ olefination was utilized to access *E*-allylic selenamide **66**. Stereoselective nucleophilic amination of **66** followed by a [2,3]-sigmatropic rearrangement affords amino ester **67**. The *Z*-isomers of **66** were made in good yields and selectivities using α-substituted ethyl (diphenylphosphono)acetates in the olefination. Subsequent rearrangement then provides the enantiomer of **67**. Removal of the Cbz group was not shown but Boc-amines could also be used.

Scheme 15. Armstrong's α-Selenenylation



R	yield **66** (%)	ee (%)	yield **67** (%)	ee (%)
Et	69	95	81	94
t-Bu	38	91	67	91
allyl	52	95	59	93



Summary. In conclusion, although asymmetric α,α-amino acid synthesis was reported over two and a half decades ago, major challenges remain in generating this class of compounds. While several elegant reports are outlined in this Synopsis, there is no general method available. Undoubtedly, many methods targeted to specific substrates will be needed due to the dense functionality and steric hindrance of these compounds.

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Notes

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Alison Metz received a B.S. in chemistry from the Pennsylvania State University in 2009, where she performed undergraduate research in the laboratories of Professor Steven M. Weinreb. In the same year, she began her graduate studies at the University of Pennsylvania under the guidance of Professor Marisa C. Kozlowski. Her research in the Kozlowski group has focused on the synthesis and chemistry of 2-aryl-2-nitroacetates, hydrogen-bonding catalysts, and a tetrachlorinated bisbenzo[*a*]phenazine as a solvatochromic organic material.

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