Chemical Science

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2014, **5**, 3941

Asymmetric construction of quaternary stereocenters by magnesium catalysed direct amination of β-ketoesters using *in situ* generated nitrosocarbonyl compounds as nitrogen sources†

Biplab Maji,*[ab] Mahiuddin Baidya[ab] and Hisashi Yamamoto*[ab]

Received 2nd May 2014
Accepted 13th June 2014

DOI: 10.1039/c4sc01272k

www.rsc.org/chemicalscience

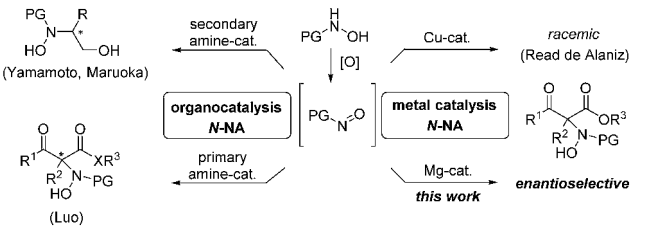
The first example of a Lewis acid catalysed asymmetric hydroxyamination of β-ketoesters with nitrosocarbonyl compounds generated *in situ* was accomplished. The combination of a catalytic amount of $Mg(OTf)_2$ with a chiral *N*,*N*′-dioxide ligand provides highly substituted quaternary β-keto amino acid derivatives in high yields (up to 97%) and enantioselectivities (up to 96%). Regioselectivities (N- *vs.* O-attack) are uniformly high for all substrates (>20 : 1).

Introduction

The development of catalytic and enantioselective reactions using unmodified reaction partners with simple experimental protocols has been a rapidly growing area in synthetic organic chemistry. In this regard, the construction of optically active nitrogen-containing molecules is of fundamental interest due to their diverse biological activities and applications in pharmaceutical industries.[1] In general, the construction of C–N bonds in asymmetric catalysis involves either the addition of nitrogen-based nucleophiles to electrophiles or nucleophilic additions to preformed C=N bonds.[2,3] An alternative to these strategies is electrophilic amination using a formal "NH_2^+" source.[4] Azodicarboxylates have been most frequently utilized in such reactions. However, the cleavage of N–N bonds to obtain the desired α-aminocarbonyl compounds requires harsh conditions.[5] Nitrosoarenes have also been utilized as a nitrogen source, but their synthetic utility is unfortunately quite limited due to the difficult removal of aromatic N-substituents.[6] In contrast, nitrosocarbonyl compounds with easily removable protecting groups (*e.g.* Boc or Cbz) are more versatile aminating reagents.[7] Unlike the stable arylnitroso compounds, nitrosocarbonyl compounds are transient species and are usually generated by the oxidation of corresponding hydroxamic acid derivatives.[8] Mechanistically, this coupling of a nucleophilic hydroxylamine with carbonyl compounds is a direct route to α-aminocarbonyls, with the challenge of ensuring that oxidation processes are compatible with the catalytic cycle.[9]

In seminal work, the Read de Alaniz group has generated nitrosocarbonyl species through aerobic oxidation and utilized them in the Cu-catalysed *N*-nitroso aldol (*N*-NA, hydroxyamination) reactions of β-ketoesters in racemic fashion.[10] Recently, Luo *et al.* reported an asymmetric version of this reaction using a chiral primary amine as an organocatalyst.[11] Our group and the Maruoka group have also independently reported asymmetric *N*-NA reactions of nitrosocarbonyl species with aldehydes using chiral secondary amines as organocatalysts (Scheme 1).[12]

While many asymmetric *N*-NA reactions of transient nitrosocarbonyl species have been established through organocatalysis, the development of enantioselective *N*-NA reactions of these species using Lewis acid catalysis remains elusive. Recently, our group and the Read de Alaniz group independently reported the Cu-catalysed enantioselective *O*-nitroso aldol (*O*-NA, aminooxylation) reactions of β-ketoesters with *in situ* generated nitrosocarbonyl species (Scheme 2).[13] We envisioned that the high O-selectivity of these reactions is possibly due to the high affinity of copper towards the nitrogen center of the ambident nitrosocarbonyl electrophile[14] and a

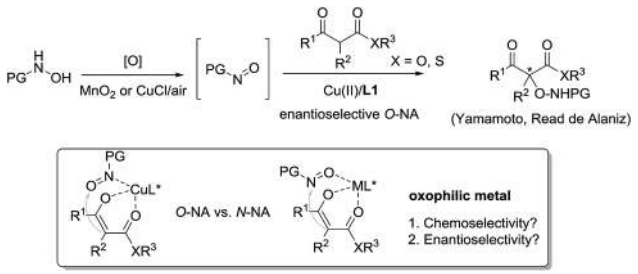


Scheme 1 *N*-Nitroso aldol reactions of nitrosocarbonyl compounds. PG = protecting group.

[a]*Molecular Catalyst Research Center, Chubu University, 1200 Matsumoto-cho, 487-8501 Kasugai, Japan. E-mail: biplabmaji@isc.chubu.ac.jp; hyamamoto@isc.chubu.ac.jp; Web: http://www3.chubu.ac.jp/catalyst; Fax: +81-568-51-3833*

[b]*Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, United States*

† Electronic supplementary information (ESI) available: Complete experimental procedures and full compound characterization, including HPLC traces and NMR spectra (PDF). See DOI: 10.1039/c4sc01272k



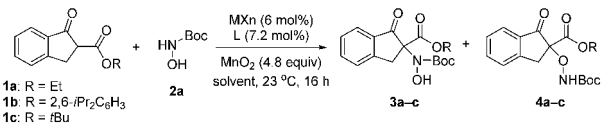
Scheme 2 *O*-Nitroso aldol reactions of nitrosocarbonyl compounds and the tuning of the regioselectivities using oxophilic metal centered Lewis acids. PG = protecting group. For **L1** see Table 1.

judicial choice of an oxophilic Lewis acid should switch the chemo-selectivity to *N*-NA (Scheme 2).[15] Herein, we report the $Mg(OTf)_2$-catalysed enantioselective α-amination of β-ketoesters with N-protected hydroxyl amines as a nitrogen source and MnO_2 as an oxidant (Scheme 1).[16] This novel method allows the asymmetric construction of quaternary stereocenters in high yields and enantioselectivities *en route* to a diverse array of β-keto and β-hydroxy amino acid derivatives.

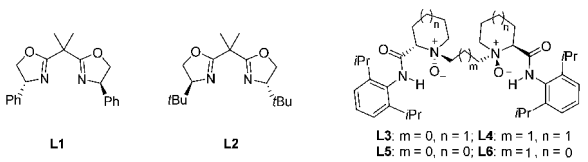
Results and discussion

We commenced our investigation using β-ketoester **1a** as model substrate with the oxophilic magnesium salt $Mg(OTf)_2$ as a catalyst in combination with commercially available bisoxazoline ligands (Table 1). To our delight, when a solution of readily available *N*-Boc-hydroxylamine **2a** was slowly injected into a mixture of 10 mol% of $Mg(OTf)_2$ and 12 mol% of PhBox ligand **L1** in the presence of substrate **1a** and oxidant MnO_2 in CH_2Cl_2 at room temperature, the aldol reaction proceeded with high regioselectivity (**3** : **4** = 15 : 1) and smoothly delivered the desired product **3a** in an 86% isolated yield. However, the asymmetric induction was very poor (entry 1). Replacing ligand **L1** with **L2** did not improve the outcome. The use of the chiral *N*,*N*′-dioxide ligand **L3** developed by Feng[17] exclusively delivered *N*-NA product **3a** in high yield (91%) and the enantioselectivity also increased to 68% (entry 3) with only 6 mol% catalyst loading. To further improve the asymmetric induction, we have modified the ester moiety of the β-ketoester **1**. Gratifyingly, the asymmetric induction increases with the increasing steric bulk of the R group in **1** (entries 3–5) and the best result was obtained for a *t*Bu group producing **3c** in 91% yield and 95% ee, without compromising the regioselectivity (**3** : **4** > 20 : 1, entry 5). Thus,

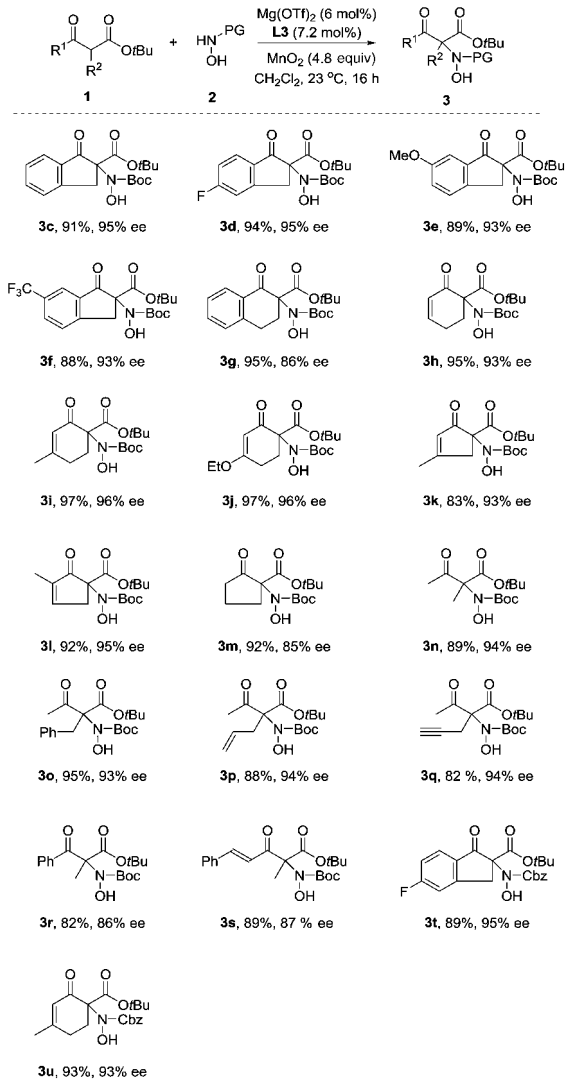
Table 1 Optimization of the reaction conditions[a]



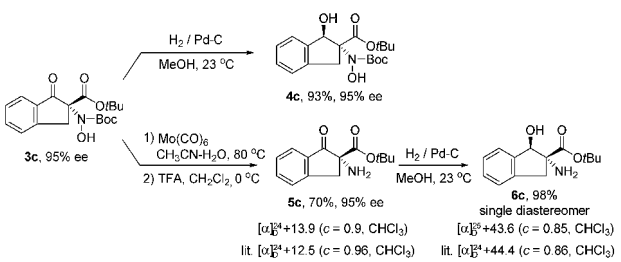
Entry	1	MX_n	L	Solvent	Yield[b] of 3 (%)	3 : 4[c]	ee[d] of 3 (%)
1[e]	**1a**	$Mg(OTf)_2$	**L1**	CH_2Cl_2	86	15 : 1	21
2[e]	**1a**	$Mg(OTf)_2$	**L2**	CH_2Cl_2	80	15 : 1	4
3	**1a**	$Mg(OTf)_2$	**L3**	CH_2Cl_2	91	>20 : 1	68
4	**1b**	$Mg(OTf)_2$	**L3**	CH_2Cl_2	68	>20 : 1	83
5	**1c**	$Mg(OTf)_2$	**L3**	CH_2Cl_2	91	>20 : 1	95
6	**1c**	$Mg(OTf)_2$	**L4**	CH_2Cl_2	74	>20 : 1	4
7	**1c**	$Mg(OTf)_2$	**L5**	CH_2Cl_2	74	>20 : 1	78
8	**1c**	$Mg(OTf)_2$	**L6**	CH_2Cl_2	94	>20 : 1	20
9[e]	**1c**	$Ni(OTf)_2$	**L3**	CH_2Cl_2	45	1 : 1	ND
10[e]	**1c**	$Zn(OTf)_2$	**L3**	CH_2Cl_2	60	2 : 1	ND
11[e]	**1c**	$Ca(OTf)_2$	**L3**	CH_2Cl_2	96	>20 : 1	31
12[e]	**1c**	$Sr(OTf)_2$	**L3**	CH_2Cl_2	88	15 : 1	43
13[e]	**1c**	$Sc(OTf)_3$	**L3**	CH_2Cl_2	85	13 : 1	−36
14	**1c**	$Mg(ClO_4)_2$	**L3**	CH_2Cl_2	94	>20 : 1	93
15	**1c**	$Mg(NTf)_2$	**L3**	CH_2Cl_2	82	15 : 1	95
16	**1c**	$Mg(OTf)_2$	**L3**	$(CH_2Cl)_2$	85	>20 : 1	93
17[f]	**1b**	$Cu(OTf)_2$	**L1**	CH_2Cl_2	68	<1 : 20	88



[a] Reaction of β-ketoester **1** (0.1 mmol) with hydroxamic acid **2** (0.12 mmol) was carried out in the presence of metal salt MX_n (0.006 mmol), ligand **L** (0.0075 mmol) and MnO_2 (0.48 mmol). [b] Yield of isolated product. [c] Isolated product ratio. [d] Determined by HPLC on chiral stationary phase. [e] 0.01 mmol of MX_n and 0.012 mmol of **L** were used. [f] Ref. 13a. ND = not determined.



Scheme 3 Scope of the enantioselective *N*-nitroso aldol reaction. Reaction conditions: β-ketoester **1** (0.1 mmol), hydroxamic acid (0.12 mmol), $Mg(OTf)_2$ (0.006 mmol), **L3** (0.0075 mmol), MnO_2 (0.48 mmol). The yield of the isolated products are given. The *ee* values were determined by HPLC on a chiral stationary phase. PG = protecting group.



Scheme 4 Transformation of the hydroxyamination product: synthesis of β-keto and β-hydroxy amino acid derivatives.

*t*Bu-β-ketoesters seem to be optimal for our purpose. Further screening of other *N*,*N*′-dioxide ligands **L4–L6** and Lewis acid catalysts (Ni-, Zn-, Ca-, Sr-, Sc-salts) with β-ketoester **1c** was unsatisfactory in terms of both the reactivities and selectivities (entries 6–13). Altering the counter anion of the Mg-catalyst and the reaction solvent also gave inferior results (entries 14–16). Thus, $Mg(OTf)_2$ in combination with ligand **L3** was considered as the catalyst of choice. It should be noted that β-ketoester **1b** exclusively delivered *O*-NA product **4b** in 68% yield and 88% ee when $Cu(OTf)_2$ was employed as the catalyst in combination with bisoxazoline ligand **L1** under identical conditions.[13a]

With the optimal reaction conditions in hand, the substrate scope of this Lewis acid catalysed asymmetric *N*-NA reaction for the construction of C–N bond was explored and the results are summarised in Scheme 3. The reaction is quite general. A broad spectrum of β-ketoesters, cyclic as well as acyclic, could be employed to afford quaternary *N*-NA products **3** in high yields and enantioselectivities. It is worthy of note that the undesired *O*-NA products **4** were not detected in any of these cases. The cyclic β-ketoesters with substituted 1-indanone subunits (**3c–f**) gave uniformly high yields (88–94%) and enantioselectivities (93–95%). The β-ketoester with a 1-tetralone subunit (**1g**) worked equally well with a slight reduction in the enantioselectivity (95% yield, 86% ee). The cyclic β-ketoesters possessing sensitive cyclohexene and cyclopentene subunits are also good substrates for this reaction, delivering the *N*-NA products **3h–l** in high yields (83–97%) and selectivities (93–96%). Substitutions at R^1 and R^2 for acyclic β-ketoesters have minimal effects on the outcome of the reaction. Reactions of *t*butyl acetoacetates with a range of substituents (methyl, benzyl, allyl, propergyl) at the R^2 position are very efficient, yielding **3n–q** with high asymmetric induction (94, 93, 94, 94% ee, respectively). The products **3p** and **3q** are particularly very interesting, where hydroxyamination proceeded without affecting labile functionalities such as allyl and propargyl, demonstrating the mildness of our oxidation/catalytic cycle. Substrates with phenyl and cinnamyl substitution at R^1 are also efficient and the desired products **3r** and **3s** were isolated with 86% and 87% ee, respectively. It is important to mention that while the asymmetric hydroxyamination reaction *via* organocatalysis developed by the Luo group has unfortunately failed for β-ketoesters substrates containing aromatic substituents at the R^1 position,[11] high asymmetric induction has been achieved with our protocol for this class of substrates (**1r** and **1c–g**), which demonstrates the efficiency of this catalytic protocol. The reaction is also compatible with other hydroxamic acid derivatives, such as *N*-Cbz-hydroxylamine **2b**, and the desired products (**3t**, **u**) were obtained in high yields (89, 93%, respectively) with high asymmetric induction (95, 93% ee, respectively).

In order to highlight the synthetic utility of the hydroxyamination products, we performed a functionalization of *N*-NA product **3c** (Scheme 4). Under hydrogenation conditions using Pd/C, the keto-carbonyl group was smoothly reduced offering β-hydroxy amino acid derivative **4c** in 93% yield. The treatment of **3c** with $Mo(CO)_6$ cleanly cleaved the N–O bond,[18] affording β-keto amino acid derivative **5c** after Boc-deprotection with TFA (70% yield). The enantioselectivity of **3c** was also reserved in the products **4c** and **5c**. Finally **5c** can easily be reduced to the corresponding β-hydroxy amino acid derivative **6c** under hydrogenation condition (single diastereomer, 98% yield). The

absolute configuration of β-keto amino acid derivative **5c** (and hence **3c**) was assigned as *R* by comparing the optical rotation of **5c** with previously reported literature data.[19]

Conclusions

In conclusion, we have developed a Lewis acid catalysed asymmetric hydroxyamination of β-ketoesters with *in situ* generated nitroso compounds, using a readily available Mg-catalyst in combination with a *N*,*N*′-dioxide ligand. This protocol is very mild with broad substrate scope offering easy access to enantioenriched quaternary β-keto amino acid derivatives in high yields while maintaining a high level of chemoselectivities. Further investigations are underway to clarify the detailed mechanism of this transformation and to explore the scope of nitrosocarbonyl chemistry in asymmetric synthesis.

Acknowledgements

This work is supported by a Grant-in-Aid for Scientific Research (no. 23225002), Advance Catalytic Transformation program for Carbon utilization, The Uehara Memorial Foundation, Nippon Pharmaceutical Chemicals Co., Ltd, and Advance Electric Co., Inc. MB thanks JSPS for a fellowship.

Notes and references

1 (*a*) R. Hili and A. K. Yudin, *Nat. Chem. Biol.*, 2006, **2**, 284; (*b*) *Modern Amination Methods*, ed. A. Ricci, WILEY-VCH, Weinheim, 2000; (*c*) *Amino Group Chemistry: From Synthesis to the Life Sciences*, ed. A. Ricci, WILEY-VCH, Weinheim, 2008; (*d*) R. M. Williams, in *Synthesis of Optically Active a-Amino Acids*, Pergamon, Oxford, U.K., 1989.

2 For reviews, see:(*a*) A. M. R. Smith and K. K. Hii, *Chem. Rev.*, 2011, **111**, 1637; (*b*) J. M. Janey, *Angew. Chem., Int. Ed.*, 2005, **44**, 4292; (*c*) C. Greck, B. Drouillat and C. Thomassigny, *Eur. J. Org. Chem.*, 2004, 1377; (*d*) H. Yamamoto and N. Momiyama, *Chem. Commun.*, 2005, 3514.

3 For selected examples see:(*a*) G. K. Friestad and A. K. Mathies, *Tetrahedron*, 2007, **63**, 2541; (*b*) S. M. Weinreb and R. K. Orr, *Synthesis*, 2005, 1205; (*c*) M. M. B. Marques, *Angew. Chem., Int. Ed.*, 2006, **45**, 348; (*d*) A. Ting and S. E. Schaus, *Eur. J. Org. Chem.*, 2007, 5797; (*e*) J. M. Verkade, L. J. C. van Hemert, P. J. L. M. Quaedflieg and F. P. J. T. Rutjes, *Chem. Soc. Rev.*, 2008, **37**, 29; For review on catalytic asymmetric Mannich reactions, see:; (*f*) S. Kobayashi and M. Ueno, in *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H. Yamamoto, Springer, Berlin, 2004, suppl. 1, ch. 29.5, pp. 143–150.

4 For selected examples, see:(*a*) M. Marigo, K. Juhl and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2003, **42**, 1367; (*b*) S. Saaby, M. Bella and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2004, **126**, 8120; (*c*) M. Terada, M. Nakano and H. Ube, *J. Am. Chem. Soc.*, 2006, **128**, 16044; (*d*) R. He, X. Wang, T. Hashimoto and K. Maruoka, *Angew. Chem., Int. Ed.*, 2008, **47**, 9466; (*e*) Y. Hasegawa, M. Watanabe, I. D. Gridnev and T. Ikariya, *J. Am. Chem. Soc.*, 2008, **130**, 2158; (*f*) T. Mashiko, N. Kumagai and M. Shibasaki, *J. Am. Chem. Soc.*, 2009, **131**, 14990; (*g*) H. Konishi, T. Y. Lam, J. P. Malerich and V. H. Rawal, *Org. Lett.*, 2010, **12**, 2028; (*h*) T. Bui, G. Hernández-Torres, C. Millite and C. F. Barbas III, *Org. Lett.*, 2010, **12**, 5696; (*i*) Q.-H. Deng, T. Bleith, H. Wadepohl and L. H. Gade, *J. Am. Chem. Soc.*, 2013, **135**, 5356; (*j*) B. List, *J. Am. Chem. Soc.*, 2002, **124**, 5656; (*k*) C.-L. Zhu, F.-G. Zhang, W. Meng, J. Nie, D. Cahard and J.-A. Ma, *Angew. Chem., Int. Ed.*, 2011, **50**, 5869; (*l*) D. G. Blackmond, A. Moran, M. Hughes and A. Armstrong, *J. Am. Chem. Soc.*, 2010, **132**, 7598; (*m*) W. Li, X. Liu, X. Hao, X. Hu, Y. Chu, W. Cao, S. Qin, C. Hu, L. Lin and X. Feng, *J. Am. Chem. Soc.*, 2011, **133**, 15268; (*n*) C. Liu, Q. Zhu, K.-W. Huang and Y. Lu, *Org. Lett.*, 2011, **13**, 2638; (*o*) T.-Y. Liu, H.-L. Cui, Y. Zhang, K. Jiang, W. Du, Z.-Q. He and Y.-C. Chen, *Org. Lett.*, 2007, **9**, 3671; For a general review of the use of azodicarboxylates in C–N bond forming reactions, see:; (*p*) V. Nair, A. T. Biju, S. C. Mathew and B. P. Babu, *Chem.–Asian J.*, 2008, **3**, 810.

5 (*a*) Y. Leblanc, R. Zamboni and M. A. Bernstein, *J. Org. Chem.*, 1991, **56**, 1971; (*b*) Ref. 4*b*; (*c*) T. B. Poulsen, C. Alemparte and K. A. Jørgensen, *J. Am. Chem. Soc.*, 2005, **127**, 11614; (*d*) J. T. Suri, D. D. Steiner and C. F. Barbas III, *Org. Lett.*, 2005, **7**, 3885.

6 For selected examples of catalytic asymmetric *N*-nitroso aldol reaction with aryl nitroso compounds, see:(*a*) N. Momiyama and H. Yamamoto, *J. Am. Chem. Soc.*, 2004, **126**, 5360; (*b*) H.-M. Guo, L. Cheng, L.-F. Cun, L.-Z. Ghong, A.-Q. Mi and Y.-Z. Jiang, *Chem. Commun.*, 2006, 429; (*c*) T. Kano, M. Ueda, J. Takai and K. Maruoka, *J. Am. Chem. Soc.*, 2006, **128**, 6046; (*d*) C. Palomo, S. Vera, I. Velilla, A. Mielgo and E. Gómez-Bengoa, *Angew. Chem., Int. Ed.*, 2007, **46**, 8054; (*e*) K. Shen, X. Liu, G. Wang, L. Lin and X. Feng, *Angew. Chem., Int. Ed.*, 2011, **50**, 4684; (*f*) L.-N. Jia, J. Huang, L. Peng, L.-L. Wang, J.-F. Bai, F. Tian, G.-Y. He, X.-Y. Xu and L.-X. Wang, *Org. Biomol. Chem.*, 2012, **10**, 236; (*g*) A. Yanagisawa, T. Fujinami, Y. Oyokawa, T. Sugita and K. Yoshida, *Org. Lett.*, 2012, **14**, 2434.

7 For pioneering work on nitrosocarbonyl compounds see:(*a*) G. W. Kirby and J. G. Sweeny, *J. Chem. Soc., Chem. Commun.*, 1973, 704; (*b*) G. W. Kirby, *Chem. Soc. Rev.*, 1977, **6**, 1, For reviews on nitrosocarbonyl Diels-Alder reactions, see:; (*c*) J. Streith and A. Defoin, *Synthesis*, 1994, 1107; (*d*) C. Kibayashi and S. Aoyagi, *Synlett*, 1995, 873; (*e*) P. E. Vogt and M. J. Miller, *Tetrahedron*, 1998, **54**, 1317; (*f*) Y. Yamamoto and H. Yamamoto, *Eur. J. Org. Chem.*, 2006, 2031; (*g*) B. S. Bodnar and M. J. Miller, *Angew. Chem., Int. Ed.*, 2011, **50**, 5630, For reviews on nitrosocarbonyl ene reactions, see:; (*h*) W. Adam and O. Krebs, *Chem. Rev.*, 2003, **103**, 4131; (*i*) S. Iwasa, A. Fakhruddin and H. Nishiyama, *Mini-Rev. Org. Chem.*, 2005, **2**, 157; (*j*) M. Baidya and H. Yamamoto, *Synthesis*, 2013, **45**, 1931.

8 For selected oxidation methods, see:(*a*) S. Iwasa, A. Fakhruddin, Y. Tsukamoto, M. Kameyama and H. Nishiyama, *Tetrahedron Lett.*, 2002, **43**, 6159; (*b*) J. A. K. Howard, G. Ilyashenko, H. A. Sparkes, A. Whiting and A. R. Wright, *Adv. Synth. Catal.*, 2008, **350**, 869; (*c*)

D. Chaiyaveij, L. Cleary, A. S. Batsanov, T. B. Marder, K. J. Shea and A. Whiting, *Org. Lett.*, 2011, **13**, 3442; (*d*) C. P. Frazier, J. R. Engelking and J. Read de Alaniz, *J. Am. Chem. Soc.*, 2011, **133**, 10430; (*e*) C. P. Frazier, A. Bugarin, J. R. Engelking and J. Read de Alaniz, *Org. Lett.*, 2012, **14**, 3620; (*f*) Y. C. Teo, Y. Pan and C. H. Tan, *ChemCatChem*, 2013, **5**, 235.

9 R. W. Evans, J. R. Zbieg, S. Zhu, W. Li and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2013, **135**, 16074.

10 D. Sandoval, C. P. Frazier, A. Bugarin and J. Read de Alaniz, *J. Am. Chem. Soc.*, 2012, **134**, 18948.

11 C. Xu, L. Zhang and S. Luo, *Angew. Chem., Int. Ed.*, 2014, **53**, 4149.

12 (*a*) T. Kano, F. Shirozu and K. Maruoka, *J. Am. Chem. Soc.*, 2013, **135**, 18036; (*b*) T. Kano, F. Shirozu and K. Maruoka, *Org. Lett.*, 2014, **16**, 1530; (*c*) B. Maji and H. Yamamoto, *Angew. Chem., Int. Ed.*, 2014, DOI: 10.1002/anie.201311069.

13 (*a*) M. Baidya, K. A. Griffin and H. Yamamoto, *J. Am. Chem. Soc.*, 2012, **134**, 18566; (*b*) C. P. Frazier, D. Sandoval, L. I. Palmer and J. Read de Alaniz, *Chem. Sci.*, 2013, **4**, 3857.

14 For an excellent review on ambident reactivities, see: H. Mayr, M. Breugst and A. R. Ofial, *Angew. Chem., Int. Ed.*, 2011, **50**, 6470.

15 In the racemic *N*-NA reaction in ref. 10, the Read de Alaniz group observed high N-selectivity using a Cu-catalyst in MeOH. In alcoholic solvents, the mode of Lewis acid activation can be different and activation through hydrogen bonding also needs to be considered.

16 For $MgCl_2$-catalysed racemic *N*-NA reaction, see: M.-Q. Liang and C.-D. Lu, *Synlett*, 2014, **25**, 991.

17 For a review, see: X. Liu, L. Lin and X. Feng, *Acc. Chem. Res.*, 2011, **44**, 574.

18 S. Cicchi, A. Goti, A. Brandi, A. Guarna and F. D. Sarlo, *Tetrahedron Lett.*, 1990, **31**, 3351.

19 K. Shibatomi, Y. Soga, A. Narayama, I. Fujisawa and S. Iwasa, *J. Am. Chem. Soc.*, 2012, **134**, 9836.