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Enantioselective gold-catalyzed intermolecular [2 + 2]-cycloadditions of 3-styrylindoles with *N*-allenyl oxazolidinone†

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The enantioselective intermolecular [2 + 2] cycloaddition of 3-styrylindoles with *N*-allenyl oxazolidinone has been achieved for the first time by the employment of a Xiang-Phos derived chiral gold-catalyst. The corresponding cycloadducts could be obtained in good yields (up to 95%) with up to 95% ee.

Gold catalysis, due to its remarkable catalytic capacity for the activation of C–C multiple bonds, has drawn tremendous attention and has been utilized broadly in the construction of complex molecules over the past decade.[1] However, the development of asymmetric gold catalysis remains a long-standing challenge due to the inherent linear geometry of gold(I) complexes, which forces the catalytic active site far away from the chiral ligand, thus limiting the enantioselective control in the reaction process.[2] To date, only a few of chiral ligands including atropisomeric biaryl phosphines, spirocyclic bisphosphines and phosphoramidites with bulky or extended substituents have been employed more successfully and maturely in gold catalysis.[3,4] Therefore, the development of novel chiral ligands for gold catalysis would be highly desirable. Ideally, the salient features of the ligands include air and moisture stability, ease of handling, and being made from inexpensive and readily available chiral resources through a short synthetic route. Following these principles for the design of new chiral ligands, we recently developed a new type of air-stable chiral ligand (Ming-Phos) bearing the chiral sulfinamide moiety from readily available starting materials in two steps, which has been well applied in asymmetric gold-catalysis.[5]

Chiral cyclobutanes are ubiquitous in natural products, bioactive compounds and versatile intermediates in synthetic chemistry (Fig. 1).[6] Meanwhile, over the past decade, gold-catalyzed intermolecular cycloadditions of two unsaturated components have shown their power in the rapid access to various cyclic and polycyclic ring systems in an extremely efficient and stereoselective manner. In this context, asymmetric gold-catalyzed [2 + 2] cycloadditions[7] of alkenes with *N*-allenamides[8] are believed to be powerful and reliable methods to construct this skeleton. For example, González *et al.* disclosed the first enantioselective gold-catalyzed [2 + 2] cycloaddition reaction of *N*-tosyl allenamides and alkenes with the aid of chiral phosphoramidite ligands.[7e] Last year, M. Bandini *et al.* reported enantioselective gold catalyzed dearomative [2 + 2]-cycloaddition between indoles and allenamides.[7f] Very recently, we reported the first asymmetric [2 + 2] cycloaddition of *N*-tosyl allenamides and 3-styrylindoles using the phosphoramidite ligand **L1**, affording the corresponding cycloadducts in excellent enantioselectivity.[9] However, this catalytic system cannot give acceptable enantioselectivity (22% ee) for the [2 + 2] cycloaddition of 3-styrylindole **1a** with *N*-allenyl oxazolidinone (Scheme 1a). With diverse Ming-Phoses[4] in hand, we wondered whether this new type of chiral ligand could address this low enantioselectivity issue or not. Unfortunately, no satisfactory results were obtained (9–32% ee, please see more details in the ESI†). We envisioned that the replacement of the phenyl group

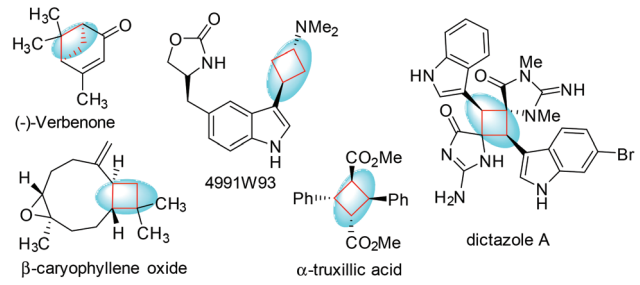

Fig. 1 Selected natural products and bioactive compounds containing chiral cyclobutane scaffolds.

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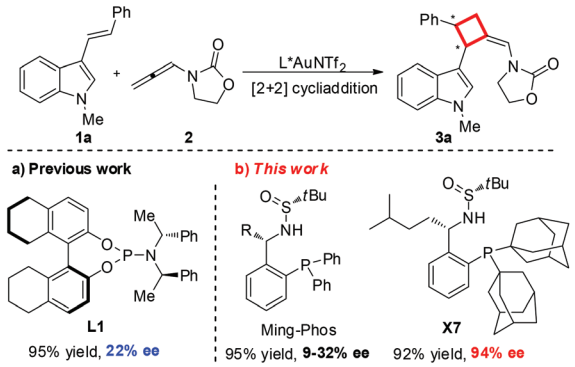
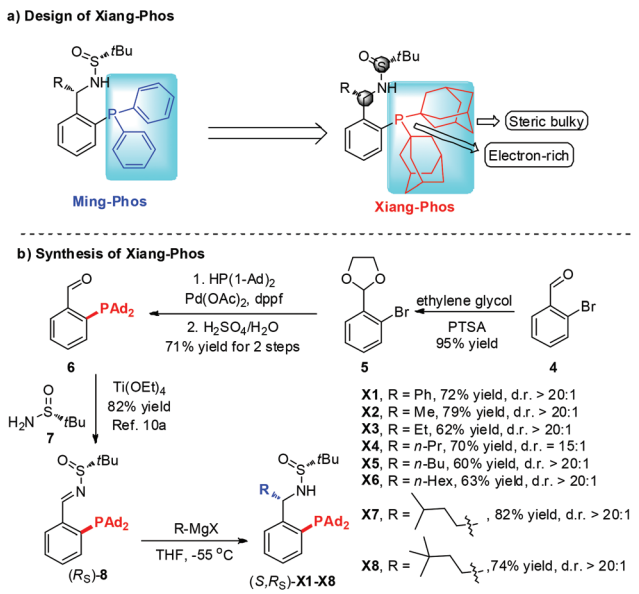


Scheme 1 Asymmetric [2 + 2]-cycloadditions of 3-styrylindoles with *N*-allenyl oxazolidinone.

of the P substituents in the Ming-Phos by the more sterically bulky group might bring benefit to enhance the enantioselectivity control. Thus, a series of Xiang-Phoses bearing two bulky adamantyl groups on the P atom were designed and synthesized (Scheme 2a). Herein, we wish to share the performance of Xiang-Phos in excellent regio, diastereo and enantioselective gold-catalyzed asymmetric [2 + 2] cycloadditions between 3-styrylindoles and *N*-allenyl oxazolidinone (Scheme 1b).

To test our hypothesis, a series of Xiang-Phoses (**X1–X8**) were prepared according to the synthetic route depicted in Scheme 2b. *O*-Phosphino benzaldehyde **6** was obtained in good yield from 2-bromobenzaldehyde **4** *via* the process involving acetalation, C–P coupling with di-1-adamantylphosphine and hydrolysis. The condensation of **6** with chiral (R_S)-sulfinamide **7**, followed by diastereoselective addition with various Grignard reagents, would afford the corresponding Xiang-Phos

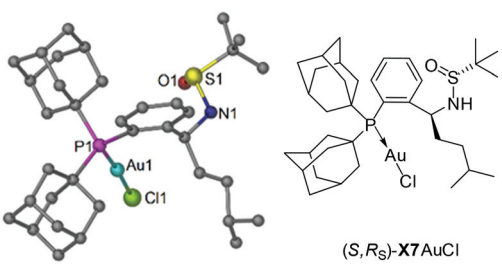


Scheme 2 The design and concise synthetic approach to new chiral sufinamide monophosphines Xiang-Phos.

(S,R_S)-**X1–X8** in good yields with high diastereoselectivities. The absolute configuration of the gold complex (S,R_S)-**X7**AuCl was established by single-crystal X-ray analysis (Scheme 3).[10]

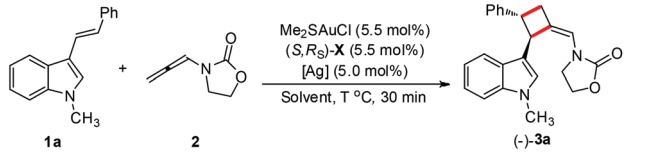
With a series of Xiang-Phoses in hand, we concentrated our investigation on their performance in the enantioselective [2 + 2] cycloaddition of 3-styrylindole **1a** and allenamide **2** (Table 1). Compared to that of Ming-Phoses, the desired product (−)-**3a** was obtained in a better yield but with similar enantioselectivity when (S,R_S)-**X1** was employed (Table 1, entry 1). In contrast, the (S,R_S)-**X2** bearing a methyl group gave a promising enantioselectivity (Table 1, entry 2). Encouraged by this result, various Xiang-Phoses equipped with various alkyl groups (S,R_S)-**X3–X8** were examined (Table 1, entries 3–8). Gratifyingly, (−)-**3a** was obtained in 92% isolated yield with 88% ee by employing (S,R_S)-**X7** with the isopentyl substituent at −50 °C (Table 1, entry 7). The counteranion effect was also observed in this reaction. A mixture of a gold complex with AgOTf displayed a higher enantioselectivity (91% ee) than that with $AgNTf_2$, $AgBF_4$ and AgOMs (Table 1, entries 7, 9–11). Variation of the solvent did not lead to better result. However, a slightly better result was obtained by running the reaction at lower temperature (−78 °C) did not lead to better result, affording (−)-**3a** in 92% yield with 94% ee (Table 1, entry 15). Increasing or lowering the catalyst loading did not improve the yield and enantioselectivity (Table 1, entries 16 and 17). It should be noted that the reaction is not sensitive to moisture and it works well in wet solvent under air without any detriment to the enantioselectivity or yield.

With the optimal conditions in hand, we then examined the generality of this asymmetric cycloaddition of *N*-allenyl oxazolidinone **2** with various 3-styrylindoles **1** (Table 2). The substrate scope is quite general and all the desired products **3** were obtained in good yields (up to 92%) with good to excellent enantioselectivities (up to 95% ee) as a single (*Z*)-stereoisomer (Table 2, entries 1–19). Notably, both electron-withdrawing groups (**1b–1f**) and electron-donating groups (**1g–1i**) attached to the phenyl rings and other electron-rich aromatic rings (**1j–1k**) on the alkenes slightly affect the reactivity and enantioselectivity of the reaction (Table 2, entries 1–10). The reaction of **1** with the substituents (methyl or bromo) on different positions of the indole moiety afforded the desired cycloadducts (**3l–3p**) in 59–84% yields with 81–91% ees (Table 2, entries 11–15). Furthermore, other *N*-sub-



Scheme 3 X-ray crystal structure of [(S,R_S)-**X7**AuCl].

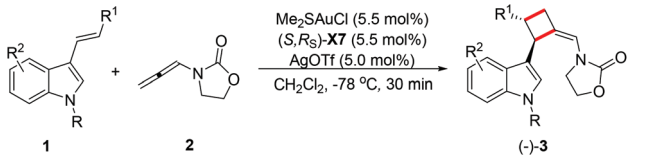
Table 1 Screening of the reaction conditions[a]



Entry	Ligand	[Ag]	Solvent	T (°C)	Yield[b] (%)	ee[c] (%)
1	(S,R_S)-**X1**	$AgNTf_2$	CH_2Cl_2	−50	84	19
2	(S,R_S)-**X2**	$AgNTf_2$	CH_2Cl_2	−50	87	74
3	(S,R_S)-**X3**	$AgNTf_2$	CH_2Cl_2	−50	86	82
4	(S,R_S)-**X4**	$AgNTf_2$	CH_2Cl_2	−50	85	83
5	(S,R_S)-**X5**	$AgNTf_2$	CH_2Cl_2	−50	88	85
6	(S,R_S)-**X6**	$AgNTf_2$	CH_2Cl_2	−50	91	83
7	(S,R_S)-**X7**	$AgNTf_2$	CH_2Cl_2	−50	92	88
8	(S,R_S)-**X8**	$AgNTf_2$	CH_2Cl_2	−50	89	70
9	(S,R_S)-**X7**	AgOTf	CH_2Cl_2	−50	91	91
10	(S,R_S)-**X7**	$AgBF_4$	CH_2Cl_2	−50	88	90
11	(S,R_S)-**X7**	AgO_3SCH_3	CH_2Cl_2	−50	84	78
12	(S,R_S)-**X7**	AgOTf	$(CH_2Cl)_2$	−40	91	78
13	(S,R_S)-**X7**	AgOTf	$CHCl_3$	−50	91	87
14	(S,R_S)-**X7**	AgOTf	CH_2Cl_2	−60	90	92
15	(S,R_S)-**X7**	AgOTf	CH_2Cl_2	−78	**92**	**94**
16[d]	(S,R_S)-**X7**	AgOTf	CH_2Cl_2	−78	92	94
17[e]	(S,R_S)-**X7**	AgOTf	CH_2Cl_2	−78	91	90

[a] Unless otherwise specified, all the reactions were carried out with **1a** (0.11 mmol), **2** (0.1 mmol), Me_2SAuCl (5.5 mol%), ligand (5.5 mol%), and [Ag] (5 mol%) in solvent (2 mL) for 30 min. [b] Yield of the isolated product. [c] Determined by HPLC analysis using a chiral stationary phase. [d] 10 mol% of the catalyst was used. [e] 2.5 mol% of the catalyst was used.

Table 2 The scope of 3-styrylindoles[a]

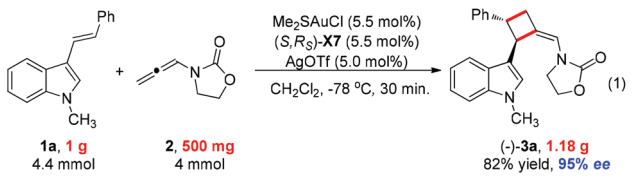


Entry	1	$R/R^1/R^2$	3	Yield[b] (%)	ee[c] (%)
1	**1b**	Me/4-MeC_6H_4/H	**3b**	92	92
2	**1c**	Me/4-$OMeC_6H_4$/H	**3c**	86	93
3	**1d**	Me/4-^{t}BuC_6H_4/H	**3d**	84	92
4	**1e**	Me/3-$OMeC_6H_4$/H	**3e**	83	91
5	**1f**	Me/3,5-$Me_2C_6H_3$/H	**3f**	77	95
6	**1g**	Me/4-BrC_6H_4/H	**3g**	89	89
7	**1h**	Me/4-ClC_6H_4/H	**3h**	84	91
8	**1i**	Me/4-FC_6H_4/H	**3i**	87	87
9	**1j**	Me/2-thienyl/H	**3j**	68	85
10	**1k**	Me/1-naphthyl/H	**3k**	72	89
11	**1l**	Me/Ph/4-Br	**3l**	84	84
12	**1m**	Me/4-BrC_6H_4/4-Br	**3m**	86	84
13	**1n**	Me/Ph/5-Me	**3n**	80	85
14	**1o**	Me/Ph/6-Me	**3o**	59	91
15	**1p**	Me/Ph/7-Me	**3p**	73	81
16	**1q**	Bn/Ph/H	**3q**	83	92
17	**1r**	Bn/4-$OMeC_6H_4$/H	**3r**	81	95
18	**1s**	Bn/4-^{t}BuC_6H_4/H	**3s**	84	93
19	**1t**	Bn/4-ClC_6H_4/H	**3t**	86	86
20	**1u**	Allyl/Ph/H	**3u**	86	93
21[d]	**1v**	Me/H/H	—	—	—
22	**1w**	Me/Me/H	**3w**	68	69

[a] Unless otherwise specified, all the reactions were carried out with **1a** (0.11 mmol), **2a** (0.1 mmol), Me_2SAuCl (5.5 mol%), ligand (5.5 mol%), and [Ag] (5 mol%) in solvent (2 mL) for 30 min. [b] Isolated yield. [c] Determined by HPLC analysis using a chiral stationary phase. [d] The reaction is messy.

stituents of 3-styrylindole **1** such as Bn and allyl are also suitable for this transformation (Table 2, entries 16–20). Unfortunately, the reaction of terminal olefin **1v** gave a complicated mixture, which might be attributed to the self-polymerization (Table 1, entry 20). To our delight, the reaction of **1w** with an aliphatic R^1 (R^1 = Me) group could afford the corresponding [2 + 2] cycloadduct **3w** in 68% yield albeit with a moderate enantioselectivity (Table 2, entry 21, 69% ee), indicating that further ligand modification is necessary. The absolute configuration of the product (2S,3R)-**3m** was determined by single-crystal X-ray analysis,[10] and all the other adducts were tentatively assigned.

It should be noted that this gold-catalyzed enantioselective [2 + 2] cycloaddition of 3-styrylindoles with *N*-allenyl oxazolidinone is easy to scale-up. A gram-scale reaction of 1 g of **1a** and 500 mg of **2** was carried out under the standard conditions, furnishing 1.18 g of the desired product **3a** in 82% isolated yield with a slightly better enantioselectivity (95% ee, Scheme 4).



Scheme 4 Gram-scale reaction of **1a** and **2**.

In summary, a series of Xiang-Phoses were prepared in good yields with high diastereoselectivity from commercially available, inexpensive starting materials in short steps. Wide diverse structures with various side chains can be achieved easily by changing the Grignard reagents R-MgX. Moreover, the (S,R_S)-**X7** derived gold catalyst has shown good performance in the intermolecular [2 + 2] cycloaddition of various 3-styrylindoles with 3-(1,2-propadienyl)-2-oxazolidinone, leading to the chiral cyclobutane products in good yields with up to 95% ee. Xiang-Phos will become very attractive due to the salient features of these ligands including air and moisture stability, ease of handling, and diverse structural tuning. Further studies including the application of Xiang-Phos in other transition metal catalyzed asymmetric transformations will be reported in due course.

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Notes and references

1 For leading reviews on gold catalysis, see: (*a*) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180; (*b*) E. Jiménez-Núñez and A. M. Echavarren, *Chem. Rev.*, 2008, **108**, 3326; (*c*) D. J. Gorin, B. D. Sherry and F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351; (*d*) S. M. A. Sohel and R.-S. Liu, *Chem. Soc. Rev.*, 2009, **38**, 2269; (*e*) A. Fürstner, *Chem. Soc. Rev.*, 2009, **38**, 3208; (*f*) A. Corma, A. Leyva-Perez and M. J. Sabater, *Chem. Rev.*, 2011, **111**, 1657; (*g*) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria and A. Simonneau, *Chem. Rev.*, 2011, **111**, 1954; (*h*) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994; (*i*) M. Bandini, *Chem. Soc. Rev.*, 2011, **40**, 1358; (*j*) B.-L. Lu, L. Dai and M. Shi, *Chem. Soc. Rev.*, 2012, **41**, 3318; (*k*) D. Garayalde and C. Nevado, *ACS Catal.*, 2012, **2**, 1462; (*l*) F. López and J. L. Mascareñas, *Beilstein J. Org. Chem.*, 2013, **9**, 2250; (*m*) W. Yang and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2014, **43**, 2941; (*n*) F. López and J. L. Mascareñas, *Chem. Soc. Rev.*, 2014, **43**, 2904; (*o*) C. Obradors and A. M. Echavarren, *Acc. Chem. Res.*, 2014, **47**, 902; (*p*) L. Zhang, *Acc. Chem. Res.*, 2014, **47**, 877; (*q*) D. Qian and J. Zhang, *Chem. Soc. Rev.*, 2015, **44**, 677; (*r*) L. Liu and J. Zhang, *Chem. Soc. Rev.*, 2016, **45**, 506; (*s*) Z. Zheng, Z. Wang, Y. Wang and L. Zhang, *Chem. Soc. Rev.*, 2016, DOI: 10.1039/c5cs00887e.

2 (*a*) A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2010, **49**, 5232; (*b*) D. J. Gorin and F. D. Toste, *Nature*, 2007, **446**, 395; (*c*) A. Fürstner and P. W. Davies, *Angew. Chem., Int. Ed.*, 2007, **46**, 3410; (*d*) M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511; (*e*) P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412; (*f*) G. L. Hamilton, E. J. Kang, M. Mba and F. D. Toste, *Science*, 2007, **317**, 496.

3 For asymmetric gold catalysis with chiral atropisomeric biaryl phosphines or spirocyclic bisphosphines, see: (*a*) F. Liu, D. Qian, L. Li, X. Zhao and J. Zhang, *Angew. Chem., Int. Ed.*, 2010, **49**, 6669; (*b*) G. Zhou, F. Liu and J. Zhang, *Chem. – Eur. J.*, 2011, **17**, 3101; (*c*) S. G. Sethofer, T. Mayer and F. Dean Toste, *J. Am. Chem. Soc.*, 2010, **132**, 8276; (*d*) S. A. Gawade, S. Bhunia and R.-S. Liu, *Angew. Chem., Int. Ed.*, 2012, **51**, 7835; (*e*) J. F. Briones and H. M. L. Davies, *J. Am. Chem. Soc.*, 2012, **134**, 11916; (*f*) J. F. Briones and H. M. L. Davies, *J. Am. Chem. Soc.*, 2013, **135**, 13314; (*g*) Z.-Y. Cao, X. Wang, C. Tan, X.-L. Zhao, J. Zhou and K. Ding, *J. Am. Chem. Soc.*, 2013, **135**, 8197; (*h*) Y.-M. Wang, A. D. Lackner and F. D. Toste, *Acc. Chem. Res.*, 2014, **47**, 889; (*i*) B. Ma, T. Miao, Y. Sun, Y. He, J. Liu, Y. Feng, H. Chen and Q.-H. Fan, *Chem. – Eur. J.*, 2014, **20**, 9969; (*j*) D.-Y. Zhu, Z. Zhang, X.-Q. Mou, Y.-Q. Tu, F.-M. Zhang, J.-B. Peng, S.-H. Wang and S.-Y. Zhang, *Adv. Synth. Catal.*, 2015, **357**, 747. For earlier examples, see: (*k*) M. P. Muz, J. Adrio, J. C. Carretero and A. M. Echavarren, *Organometallics*, 2005, **24**, 1293; (*l*) M. J. Johansson, D. J. Gorin, S. T. Staben and F. D. Toste, *J. Am. Chem. Soc.*, 2005, **127**, 18002; (*m*) Z. Zhang and R. A. Widenhoefer, *Angew. Chem., Int. Ed.*, 2007, **46**, 283; (*n*) R. L. LaLonde, B. D. Sherry, E. J. Kang and F. D. Toste, *J. Am. Chem. Soc.*, 2007, **129**, 2452.

4 For asymmetric gold catalysis with chiral phosphoramidites, see: (*a*) I. Alonso, B. Trillo, F. López, S. Montserrat, G. Ujaque, L. Castedo, A. Lledós and J. L. Mascareñas, *J. Am. Chem. Soc.*, 2009, **131**, 13020; (*b*) H. Teller, S. Flügge, R. Goddard and A. Fürstner, *Angew. Chem., Int. Ed.*, 2010, **49**, 1949; (*c*) A. Z. González, D. Benitez, E. Tkatchouk, W. A. Goddard III and F. D. Toste, *J. Am. Chem. Soc.*, 2011, **133**, 5500; (*d*) H. Teller, M. Corbet, L. Mantilli, G. Gopakumar, R. Goddard, W. Thiel and A. Fürstner, *J. Am. Chem. Soc.*, 2012, **134**, 15331; (*e*) S. Suárez-Pantiga, C. Hernández-Díaz, E. Rubio and J. M. González, *Angew. Chem., Int. Ed.*, 2012, **124**, 11720, (*Angew. Chem., Int. Ed.*, 2012, **51**, 11552); (*f*) B. Liu, K.-N. Li, S.-W. Luo, J.-Z. Huang, H. Pang and L.-Z. Gong, *J. Am. Chem. Soc.*, 2013, **135**, 3323; (*g*) D. Qian, H. Hu, F. Liu, B. Tang, W. Ye, Y. Wang and J. Zhang, *Angew. Chem., Int. Ed.*, 2014, **53**, 13751; (*h*) Y. Wang, P. Zhang, D. Qian and J. Zhang, *Angew. Chem., Int. Ed.*, 2015, **54**, 14849; (*i*) Q. Cheng, Y. Wang and S.-L. You, *Angew. Chem., Int. Ed.*, 2016, **55**, 3496.

5 Z.-M. Zhang, P. Chen, W. Li, Y. Niu, X.-L. Zhao and J. Zhang, *Angew. Chem., Int. Ed.*, 2014, **53**, 4350.

6 (*a*) R. C. Nieuwendaal, M. Bertmer and S. E. Hayes, *J. Phys. Chem. B*, 2008, **112**, 12920; (*b*) G. Ohloff and W. Giersch, *Helv. Chim. Acta*, 1977, **60**, 1496; (*c*) W. R. Gutekunst and P. S. Baran, *J. Org. Chem.*, 2014, **79**, 2430; (*d*) K. S. Jandu, V. Barrett, M. Brockwell, D. Cambridge, D. R. Farrant, C. Foster, H. Giles, R. C. Glen, A. P. Hill, H. Hobbs, A. Honey, G. R. Martin, J. Salmon, D. Smith, P. Woollardand and D. L. Selwood, *J. Med. Chem.*, 2001, **44**, 681; (*e*) K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, 1968, **51**, 494.

7 For racemic [2 + 2]-cycloadditions, see: (*a*) S. Suárez-Pantiga, C. Hernández-Díaz, M. Piedrafita, E. Rubio and J. M. González, *Adv. Synth. Catal.*, 2012, **354**, 1651; (*b*) X.-X. Li, L.-L. Zhu, W. Zhou and Z. Chen, *Org. Lett.*, 2012, **14**, 436; (*c*) H. Faustino, P. Bernal, L. Castedo, F. López and J. L. Mascareñas, *Adv. Synth. Catal.*, 2012, **354**, 1658; (*d*) P. Bernal-Albert, H. Faustino, A. Gimeno, G. Asensio, J. L. Mascareñas and F. López, *Org. Lett.*, 2014, **16**, 6196. For asymmetric version, see: (*e*) S. Suárez-Pantiga, C. Hernández-Díaz, E. Rubio and J. M. González, *Angew. Chem., Int. Ed.*, 2012, **51**, 11552; (*f*) M. Jia, M. Monari, Q.-Q. Yang and M. Bandini, *Chem. Commun.*, 2015, **51**, 2320.

8 For transformations of *N*-allenyl oxazolidinone, see: (*a*) L.-L. Wei, H. Xiong and R. P. Hsuang, *Acc. Chem. Res.*, 2003, **36**, 773; (*b*) T. Lu, Z. Lu, Z.-X. Ma, Y. Zhang and R. P. Hsung, *Chem. Rev.*, 2013, **113**, 4862; (*c*) M. M. Mastandrea, N. Mellonie, P. Giacinto, A. Collado, S. P. Nolan, G. P. Miscione, A. Bottoni and M. Bandini, *Angew. Chem., Int. Ed.*, 2015, **54**, 14885; (*d*) V. Pirovano, L. Decataldo, E. Rossi and R. Viecnte, *Chem. Commun.*,

2013, **49**, 3594; (*e*) H. Faustino, I. Alonso, J. L. Mascareñas and F. López, *Angew. Chem., Int. Ed.*, 2013, **52**, 6526; (*f*) H. Faustino, F. López, L. Castedo and J. L. Mascareñas, *Chem. Sci.*, 2011, **2**, 633; (*g*) S. Montserrat, H. Faustino, A. Lledós, J. L. Mascareñas, F. López and G. Ujaque, *Chem. – Eur. J.*, 2013, **19**, 15248; (*h*) J. Francos, F. G. Carmona, H. Faustino, J. I. Sigüenza, E. Díez, I. Alonso, R. Fernández, J. M. Lassaletta, F. López and J. L. Mascareñas, *J. Am. Chem. Soc.*, 2012, **134**, 14332.

9 Y. Wang, P. Zhang, Y. Liu, F. Xia and J. Zhang, *Chem. Sci.*, 2015, **6**, 5564.

10 CCDC1456593 (**3m**), 1456594 (**X7**AuCl).