Synthesis Y. Zhang et al. Feature

Gold(I)-Catalyzed Stereospecific [4+3]-Cycloaddition Reaction of 1-(Alk-1-ynyl)cyclopropyl Ketones with Nitrones: A Modular Entry to Enantioenriched 5,7-Fused Bicyclic Furo[3,4-*d*][1,2]oxazepines

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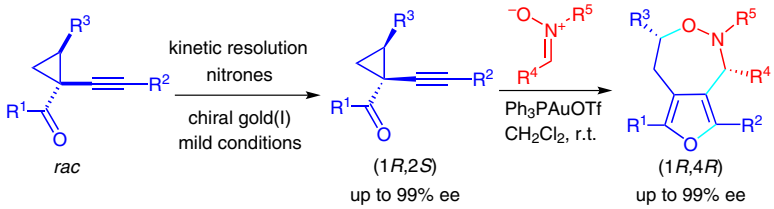

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Abstract In our previous study, a gold(I)-catalyzed stereoselective formal [4+3]-cycloaddition reaction of 1-(alk-1-ynyl)cyclopropyl ketones with nitrones was found to afford 5,7-fused bicyclic furo[3,4-*d*][1,2]oxazepines in good to excellent yields with high diastereoselectivity catalyzed by (triphenylphosphine)gold(I) triflate. In order to gain insight into the mechanism of this [4+3] cycloaddition process, an enantioselective version used a MeO-DTBM-BIPHEP derived gold(I) complex as the catalyst, which resulted in the kinetic resolution of the 1-(alk-1-ynyl)cyclopropyl ketones, affording the recovered ketones in high yield with excellent enantioselectivity. An interesting chirality transfer was observed in the gold(I)-catalyzed [4+3] cycloaddition of optically active 1-(alk-1-ynyl)cyclopropyl ketones with nitrones, indicating the reaction undergoes a stereospecific S_N2-type ring-opening of the cyclopropane.

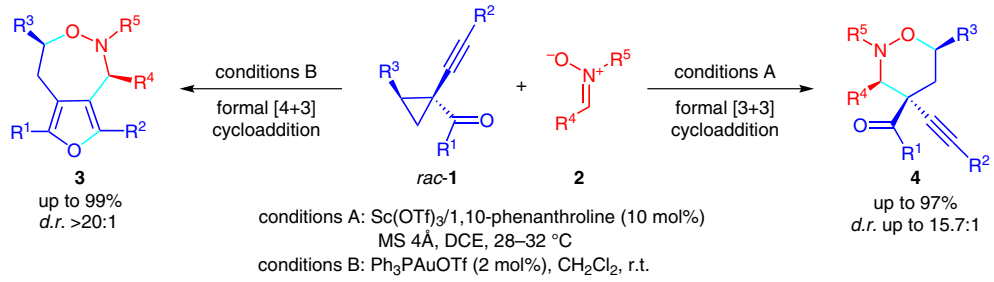
Key words gold, kinetic resolution, cycloaddition, fused-ring systems, synthetic methods

Gold-catalyzed chemical transformations of strained small-ring-containing molecules have drawn increased attention and they have emerged as powerful methods for the rapid construction of interesting carbocycles and heterocycles.[1] In this context, 1-(alk-1-ynyl)cyclopropyl ketones bearing carbonyl, alkynyl, and cyclopropyl groups have received particularly attention due to their ease of preparation, unique structure, and reactivity.

In 2006, Schmalz and Zhang reported the first example of a gold(I)-catalyzed tandem nucleophilic addition and heterocyclization of 1-(alk-1-ynyl)cyclopropyl ketones to afford trisubstituted furans in high yields.[2] In 2008, Zhang and co-workers developed an efficient gold-catalyzed formal [4+2] annulation with carbonyl compounds, imines, and polarized alkenes, such as indoles and silyl enol ethers, which provides rapid and general access to furan-fused six-membered carbo- or heterocyclic rings with notable regioselectivity.[3a] In their subsequent publication, an alternative reaction pathway was observed when ethyl vinyl ether was employed as the reaction partner, affording highly strained bicyclo[3.2.0]heptanes.[3b] In addition, in our laboratory we also developed a rhodium(I)-catalyzed carbonylation reaction of 1-(alk-1-ynyl)cyclopropyl ketones that leads to fused 5,5-bicyclic furans.[4]

Following our previous interest in gold catalysis,[5] designing and developing novel regio-divergent reactions,[6] in our previous work we observed that the cycloaddition pattern of 1-(alk-1-ynyl)cyclopropyl ketones **1** with nitrones **2** can be altered by the selection of the catalyst. The reaction of 1-(alk-1-ynyl)cyclopropyl ketones **1** with nitrones **2** catalyzed by (triphenylphosphine)gold(I) triflate undergoes a formal [4+3] cycloaddition to afford 5,7-fused bicyclic furo[3,4-*d*][1,2]oxazepines **3** in good to excellent yields with excellent diastereoselectivity. Whereas the reaction of 1-(alk-1-ynyl)cyclopropyl ketones **1** with nitrones **2** catalyzed by scandium(III) triflate undergoes formal [3+3] cycloaddition to give tetrahydro-1,2-oxazines **4** in moderate to excellent yields with up to 15.7:1 diastereomeric ratio (Scheme 1).[7]

Two controversial reaction pathways via either an unusual S_N2 process or racemization through ring opening and reclosure of the cyclopropane moiety have been proposed to account for the formation of cycloadduct **3** (Scheme 2). In order to determine the real mechanism, the [4+3] cycloaddition of enantioenriched 1-(alk-1-ynyl)cyclopropyl ketones **1** with nitrones was examined to see whether a chirality transfer takes place or not. Enantioenriched 1-(alk-1-ynyl)cyclopropyl ketones **1** were obtained by kinetic resolution reaction in good yield with excellent enantiose-



Scheme 1 Catalytic regioselective control in the diastereoselective cycloaddition reactions of 1-(alk-1-ynyl)cyclopropyl ketones with nitrones

lectivity.[8] To the best of our knowledge, this is the first example of kinetic resolution of racemates by a gold catalyst,[9] although gold-catalyzed asymmetric cyclopropanation or cyclopropenation reactions are well developed.[10,11] Herein, we report a comprehensive study of this gold(I)-catalyzed enantioselective formal [4+3]-cycloaddition reaction.

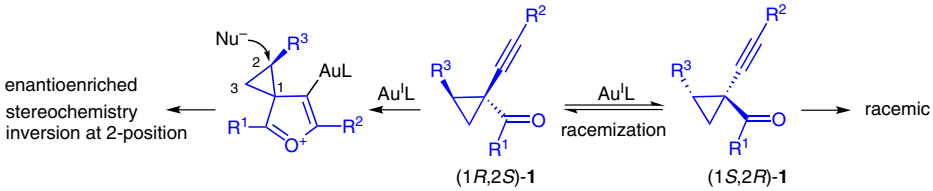
In order to clarify whether the reaction proceeds via an unusual S_N2 process or racemization through ring opening and reclosure of the cyclopropane moiety (Scheme 2), we envisaged that this issue may be addressed by using optically active 1-(alk-1-ynyl)cyclopropyl ketones as the substrates. Two approaches are available to obtain the optically active cyclopropyl ketones, 1. asymmetric cyclopropanation

Biographical Sketches

Yanqing Zhang was born in Henan Province, China, in 1983. She received her Bachelor degree from Luoyang Normal University in China in 2007 and her Ph.D. from East China Normal University under the supervision of Professor Junliang Zhang in 2012. Since July 2012, she has worked in the Patent Examination Cooperation Jiangsu Center of the Patent Office. Her research interests are transition-metal-directed organic synthesis and asymmetric catalysis.

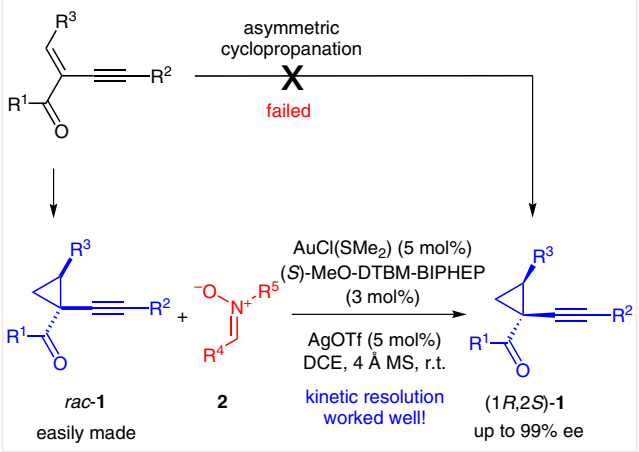
Yuanjing Xiao was born in Hubei Province, China, in 1974. He received his Bachelor degree from Hubei University in China in 1997 and his Ph.D. from Wuhan University under the supervision of Professor Yongbing He and Professor Chengtai Wu in 2002. From 2002 to 2006, he worked in the laboratory of Professor Liping Yang at East China Normal University as a lecturer. From 2007 to 2010, he worked with Professor Junliang Zhang in East China Normal University as a postdoctoral fellow and then he was appointed as an associated professor. From October 2011 to October 2012, he visited the laboratory of Prof. Liming Zhang at the University of California, Santa Barbara as a Visiting Scholar. His research interest focuses on diversity oriented organic synthesis, asymmetric catalysis, and developing novel fluorinated building blocks and their transformation.

Junliang Zhang received his Bachelor degree from Tianjing University in China in 1997 and his Ph.D. from the Shanghai Institute of Organic Chemistry under the supervision of Professor Shengming Ma in 2002. He conducted his postdoctoral research at University of Cologne as a Humboldt Fellow with Professor Hans-Günther Schmalz (Germany, 2003–2004). In 2005 he moved to the United States for postdoctoral work with Professors Chuan He and Stephen Kent at the University of Chicago (2005–2006). He started his independent career as a full professor at East China Normal University at the end of 2006. His research interest focuses on the development of synthetic methodology based on enynes and asymmetric catalysis.



Scheme 2 Two possible reaction pathways via an unusual S_N2 process or consisting of the racemization through ring-opening and reclosure of cyclopropane moiety proposed for the gold-catalyzed cycloaddition reactions of 1-(alk-1-ynyl)cyclopropyl ketones

of the corresponding 2-(alk-1-ynyl)alk-2-en-1-ones, and 2. kinetic resolution[12] of the racemic 1-(alk-1-ynyl)cyclopropyl ketones. Gold-catalyzed asymmetric cyclopropanation reactions are known,[10] but there are no reported examples leading to optically active 1-(alk-1-ynyl)cyclopropyl ketones. Unfortunately, our attempts to obtain optically active 1-(alk-1-ynyl)cyclopropyl ketones by direct asymmetric cyclopropanation of the corresponding 2-(alk-1-ynyl)alk-2-en-1-ones failed (Scheme 3).



Scheme 3 Kinetic resolution of 1-(alk-1-ynyl)cyclopropyl ketones with a nitrone catalyzed by a chiral gold(I) species

We next turned our attention to the kinetic resolution of racemic 1-(alk-1-ynyl)cyclopropyl ketones catalyzed by chiral gold(I) species.[13,14] After screening a series of gold(I) complexes with chiral ligands, we are pleased to find that optically active (1*R*,2*S*)-1-(alk-1-ynyl)cyclopropyl ketones **1** were efficiently obtained by the kinetic resolution of the readily available racemic 1-(alk-1-ynyl)cyclopropyl ketones catalyzed by an (*S*)-MeO-DTBM-BIPHEP-derived gold(I) complex (Scheme 3).[8]

The gold(I)-catalyzed [4+3] annulations of optically active (1*R*,2*S*)-1-(alk-1-ynyl)cyclopropyl ketones **1** with nitrones were then investigated and the result are listed in Table 1. In general, reaction of (1*R*,2*S*)-**1** catalyzed by (triphenylphosphine)gold(I) triflate gives enantioenriched 5,7-fused bicyclic furo[3,4-*d*][1,2]oxazepines **3** with the same level of enantiomeric purity as that of the starting material **1**. The reactions of (1*R*, 2*S*)-**1a** with various nitrones **2a**–**f** afforded the desired products in high yields with excellent enantiomeric excess as a single diastereomer (Table 1, entries 1–6). Moreover, different functional groups on the substrate (1*R*,2*S*)-**1** (R^1, R^2, and R^3) and nitrone **2** (R^4 and R^5) were compatible and the desired heterobicyclic products **3** were isolated in high to excellent yields with excellent enantiomeric excess and diastereomeric ratio (>20:1) (Table 1, entries 7–9 and 11–17), with the exception of **3ed** (Table 1, entry 10); even reducing the reaction temperature in the addition of **1e** and **2d** to 0 °C did not improve the enantiomeric excess of **3ed**. This result indicates that when R^3 is a strong electron-donating 4-methoxyphenyl group, **1e** may undergo racemization under the reaction conditions, which was consistent with our findings in the DyKAT study.[8] In some cases, racemic products **3** could not be efficiently separated by chiral HPLC, thus other nitrones were used to obtain the enantiomeric excess. The structure and absolute stereochemistry of (1*R*,4*R*)-**3ib** with a bromine atom was confirmed by single-crystal X-ray diffraction analysis (Figure 1);[15] All other compounds were assumed to have the same configuration as (1*R*,4*R*)-**3ib**.

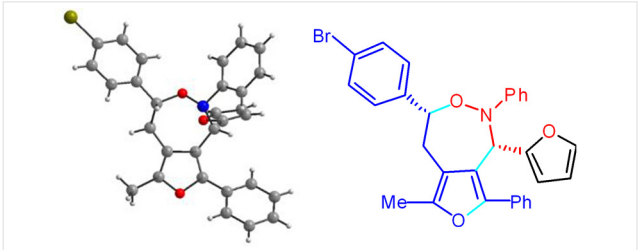
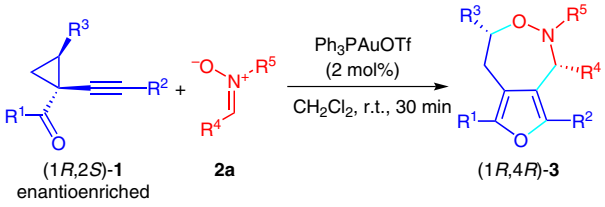


Figure 1 X-ray crystal structure of **3ib**

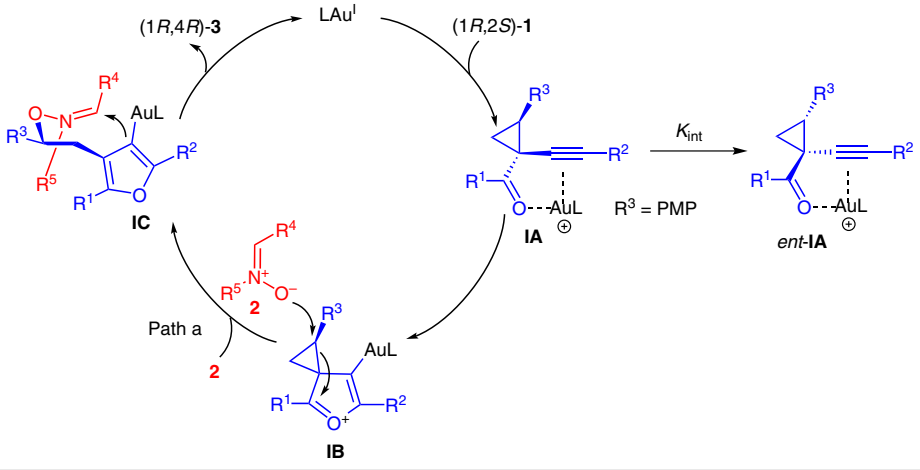
Based on the above results, a mechanistic rationale for chirality transfer in gold(I)-catalyzed [4+3]-cycloaddition reactions proceeding via a stereospecific S_N2 process on the 2-substituted cyclopropane is depicted in Scheme 4. The coordination of gold(I) with the alkyne and carbonyl group of (1*R*,2*S*)-**1** would give intermediate **IA**, the subsequent heterocyclization of **IA** gives the oxonium-containing vinyl–gold intermediate **IB**. This is followed by stereospecific nucleophilic attack of nitrone **2** at the more substituted position of the cyclopropyl ring,[2,16] leading to inversion at that position, which produces furanyl–gold intermediate **IC**.

Table 1 Gold(I)-Catalyzed [4+3]-Annulations of Optically Active (1*R*,2*S*)-1-(Alk-1-ynyl)cyclopropyl Ketones **1** with Nitrones



Entry	Substrate **1**					Nitrone **2**			Product **3**		
		R^1	R^2	R^3	ee (%)		R^4	R^5		Yield (%)	ee (%)
1	**1a**	Me	Ph	Ph	92	**2a**	Ph	Ph	**3aa**	84	91
2	**1a**	Me	Ph	Ph	92	**2b**	2-furyl	Ph	**3ab**	87	88
3[a]	**1a**	Me	Ph	Ph	92	**2c**	4-$O_2NC_6H_4$	Ph	**3ac**	88	94
4	**1a**	Me	Ph	Ph	92	**2d**	4-$MeOC_6H_4$	Ph	**3ad**	80	91
5	**1a**	Me	Ph	Ph	92	**2e**	(*E*)-styryl	Ph	**3ae**	80	90
6	**1a**	Me	Ph	Ph	92	**2f**	Ph	Bn	**3af**	78	94
7	**1b**	Me	1-naphthyl	Ph	95	**2a**	Ph	Ph	**3ba**	85	94
8[b,c]	**1c**	Me	4-MeC_6H_4	Ph	87	**2a**	Ph	Ph	**3ca**	96	85
9	**1d**	Me	4-BrC_6H_4	Ph	94	**2b**	2-furyl	Ph	**3db**	85	92
10[b,c]	**1e**	Me	Ph	4-$MeOC_6H_4$	93	**2d**	4-$MeOC_6H_4$	Ph	**3ed**	95	26
11[a,b]	**1f**	Me	Ph	4-MeC_6H_4	96	**2b**	2-furyl	Ph	**3fb**	88	98
12	**1g**	Me	Ph	4-ClC_6H_4	97	**2b**	2-furyl	Ph	**3gb**	82	92
13	**1h**	Me	Ph	2-BrC_6H_4	99	**2d**	4-$MeOC_6H_4$	Ph	**3hd**	85	98
14	**1i**	Me	Ph	4-BrC_6H_4	97	**2b**	2-furyl	Ph	**3ib**	75	97
15	**1j**	Ph	Ph	Ph	99	**2d**	4-$MeOC_6H_4$	Ph	**3jd**	78	99
16	**1k**	Ph	Ph	4-ClC_6H_4	92	**2d**	4-$MeOC_6H_4$	Ph	**3kd**	67	92
17[b]	**1l**	4-ClC_6H_4	Ph	Ph	92	**2b**	2-furyl	Ph	**3lb**	80	87

[a] The reaction was carried out at 0 °C.
[b] The reaction was complete after 2 h.
[c] The reaction was complete after 1 h.



Scheme 4 A mechanistic rationale for chirality transfer in gold(I)-catalyzed [4+3]-cycloaddition reaction

Ring closure via a chairlike conformation would afford the cycloadduct and regenerate the gold(I) catalyst. Our findings with regard to the absolute configurations of the [4+3] cycloadducts (1*R*,4*R*)-**3a** and (1*R*,2*S*)-**1a** are consistent with this proposal. Consistent with the findings in the DyKAT study,[8] substrates with a strong electron-donating 4-methoxyphenyl group at R^3 such as **1e** give lower enantiomeric excess of the cycloadduct **3ed** due to the rapid interconversion of intermediate **IA** to its enantiomer *ent*-**IA** catalyzed by gold(I).

In summary, we have developed a gold(I)-catalyzed kinetic resolution of 1-(alk-1-ynyl)cyclopropyl ketones with nitrones and 1-(alk-1-ynyl)cyclopropyl ketones were recovered in high yield with excellent enantiomeric excess. These optically active cyclopropyl ketones can be employed in the asymmetric synthesis of various 5,7-fused bicyclic furo[3,4-*d*][1,2]oxazepines in moderate to high yields with excellent enantiomeric excess. These results indicated that the reaction proceeds via a stereospecific S_N2 process.

The starting materials, racemic **1a**–**l**, were prepared according literature procedures.[2,7a] Enantioenriched 1-(alk-1-ynyl)cyclopropyl ketones **1** were obtained by kinetic resolution.[8] Compounds **2a**–**f** were synthesized according to a literature procedure.[17]

Furo[3,4-*d*][1,2]oxazepines 3aa–3lb;[7a] General Procedure

A solution of $Ph_3PAuOTf$ (1.0 mL, 0.004 M in CH_2Cl_2, 2.0 mol%) was added to a solution of optical active ketone **1** (0.2 mmol) and nitrone **2a** (0.24 mmol) in CH_2Cl_2 (1.0 mL). The resulting mixture was stirred for 10–30 min at r.t. (TLC monitoring). When the reaction was complete, the mixture was filtered and concentrated under reduced pressure, and the residue was purified by flash column chromatography (silica gel, hexanes–Et_2O, 50:1).

(1*R*,4*R*)-6-Methyl-1,2,4,8-tetraphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3aa)[7a]

Column chromatography afforded **3aa** as a pale yellow oil; yield: 76.8 mg (84%); 91% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 90:10, 0.5 mL/min, λ = 230 nm): t_R = 8.40, 9.35 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.13 (m, 17 H), 6.92–6.80 (m, 3 H), 6.14 (s, 1 H), 5.09 (d, *J* = 10.8 Hz, 1 H), 3.19 (t, *J* = 14.8 Hz, 1 H), 3.02 (d, *J* = 15.2 Hz, 1 H), 2.36 (s, 3 H).

(1*R*,4*R*)-1-(2-Furyl)-6-methyl-2,4,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ab)[7a]

Column chromatography afforded **3ab** as a pale yellow oil; yield: 77.8 mg (87%); 88% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.5 mL/min, λ = 220 nm): t_R = 11.38, 13.14 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.12 (m, 13 H), 7.02–6.84 (m, 3 H), 6.30 (s, 1 H), 6.10 (d, *J* = 2.4 Hz, 1 H), 6.06 (s, 1 H), 5.11 (d, *J* = 10.4 Hz, 1 H), 3.25 (dd, *J* = 14.8, 11.2 Hz, 1 H), 3.01 (d, *J* = 14.8 Hz, 1 H), 2.33 (s, 3 H).

(1*R*,4*R*)-6-Methyl-1-(4-nitrophenyl)-2,4,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ac)[7a]

Column chromatography afforded **3ac** as a pale yellow oil; yield: 88.5 mg (88%); 94% ee [HPLC (Daicel IC column, hexanes–*i*-PrOH, 98:2, 1.0 mL/min, λ = 254 nm): t_R = 11.08, 12.79 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.05 (m, 2 H), 7.40–7.27 (m, 12 H), 7.23–7.17 (m, 2 H), 6.97–6.83 (m, 3 H), 6.16 (s, 1 H), 5.12 (dd, *J* = 8.0, 4.8 Hz, 1 H), 3.17–3.09 (m, 2 H), 2.37 (s, 3 H).

(1*R*,4*R*)-1-(4-Methoxyphenyl)-6-methyl-2,4,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ad)[7a]

Column chromatography afforded **3ad** as a pale yellow oil; yield: 78.0 mg (80%); 91% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.5 mL/min, λ = 230 nm): t_R = 11.27, 12.57 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 7.04 (m, 14 H), 6.94–6.82 (m, 3 H), 6.82–6.73 (m, 2 H), 6.08 (s, 1 H), 5.09 (d, *J* = 10.8 Hz, 1 H), 3.75 (s, 3 H), 3.19 (t, *J* = 15.2 Hz, 1 H), 3.02 (d, *J* = 15.2 Hz, 1 H), 2.34 (s, 3 H).

(1*R*,4*R*)-6-Methyl-2,4,8-triphenyl-1-[(*E*)-styryl]-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ae)[7a]

Column chromatography afforded **3ae** as a pale yellow oil; yield: 77.4 mg (80%); 90% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 95:5, 0.8 mL/min, λ = 220 nm): t_R = 4.89, 6.17 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.53 (m, 2 H), 7.46–7.16 (m, 15 H), 7.04–6.98 (m, 2 H), 6.92 (t, *J* = 7.2 Hz, 1 H), 6.65 (dd, *J* = 16.4, 4.0 Hz, 1 H), 6.45 (d, *J* = 16.4 Hz, 1 H), 5.63 (s, 1 H), 5.08 (d, *J* = 10.8 Hz, 1 H), 3.16 (dd, *J* = 14.8, 11.6 Hz, 1 H), 2.93 (d, *J* = 14.8 Hz, 1 H), 2.35 (s, 3 H).

(1*R*,4*R*)-2-Benzyl-6-methyl-1,4,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3af)[7a]

Column chromatography afforded **3af** as a pale yellow oil; yield: 73.6 mg (78%); 94% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.8 mL/min, λ = 230 nm): t_R = 7.99, 8.90 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.13 (m, 18 H), 7.00–6.75 (m, 2 H), 5.26 (s, 1 H), 4.79 (d, *J* = 10.4 Hz, 1 H), 3.93 (d, *J* = 12.8 Hz, 1 H), 3.71 (d, *J* = 12.8 Hz, 1 H), 3.27 (dd, *J* = 14.0, 12.0 Hz, 1 H), 3.07 (d, *J* = 14.8 Hz, 1 H), 2.32 (s, 3 H).

(1*R*, 4*R*)-6-Methyl-8-(1-naphthyl)-1,2,4-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ba)[7a]

Column chromatography afforded **3ba** as a pale yellow oil; yield: 86.3 mg (85%); 94% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.5 mL/min, λ = 220 nm): t_R = 11.78, 14.16 min].

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–8.04 (m, 1 H), 7.88 (m, 2 H), 7.59–7.49 (m, 2 H), 7.41–7.29 (m, 6 H), 7.25–7.10 (m, 6 H), 7.10–7.00 (m, 2 H), 6.85–6.71 (m, 3 H), 5.91 (s, 1 H), 5.21 (d, *J* = 10.4 Hz, 1 H), 3.26 (dd, *J* = 13.2, 10.8 Hz, 1 H), 3.09 (d, *J* = 15.2 Hz, 1 H), 2.41 (s, 3 H).

(1*R*,4*R*)-6-Methyl-1,2,4-triphenyl-8-(4-tolyl)-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ca)

Column chromatography afforded **3ca** as a pale yellow solid; yield: 90.5 mg (96%); 85% ee [HPLC (Daicel OD-3 column, hexanes–*i*-PrOH, 95:5, 0.6 mL/min, λ = 220 nm): t_R = 7.73, 8.33 min]; mp 83–85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.11 (m, 10 H), 7.11–6.95 (m, 6 H), 6.82–6.66 (m, 3 H), 6.04 (s, 1 H), 4.99 (d, *J* = 10.4 Hz, 1 H), 3.09 (dd, *J* = 14.0, 12.0 Hz, 1 H), 2.90 (d, *J* = 15.6 Hz, 1 H), 2.23 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.63, 147.52, 147.19, 141.02, 137.91, 129.30, 129.04, 128.77, 128.34, 128.15, 127.86, 127.76, 127.30, 126.31, 125.89, 121.44, 121.02, 118.59, 116.05, 85.65, 66.80, 34.91, 21.21, 11.82.

MS (EI): *m*/*z* (%) = 471 $[M]^+$ (6.35), 363 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{33}H_{29}NO_2$: 471.2198; found: 471.2202.

(1*R*, 4*R*)-8-(4-Bromophenyl)-1-(2-furyl)-6-methyl-2,4-diphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3db)

Column chromatography afforded **3db** as a pale yellow solid; yield: 89.5 mg (85%); 92% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 95:5, 0.8 mL/ min, λ = 220 nm): t_R = 5.51, 6.03 min]; mp 178–181 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.08 (m, 12 H), 6.99–6.84 (m, 3 H), 6.27 (s, 1 H), 6.13–5.93 (m, 2 H), 5.11 (d, *J* = 10.0 Hz, 1 H), 3.22 (dd, *J* = 15.2, 10.0 Hz, 1 H), 3.03 (d, *J* = 15.2 Hz, 1 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.68, 149.88, 147.86, 146.27, 142.22, 140.90, 131.80, 129.68, 128.67, 128.38, 127.84, 127.47, 126.34, 121.91, 121.30, 118.85, 116.56, 110.05, 109.50, 86.12, 62.17, 34.35, 11.75.

MS (EI): *m*/*z* (%) = 525 $[M]^+$ (1.88), 43 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{30}H_{24}NO_3Br$: 525.0940; found: 529.0939.

(1*R*, 4*R*)-1,4-Bis(4-Methoxyphenyl)-6-methyl-2,8-diphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ed)

Column chromatography afforded **3ed** as a pale yellow solid; yield: 98.3 mg (95%); 26% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 98:2, 0.4 mL/min, λ = 220 nm): t_R = 22.39, 25.57 min]; mp 70–73 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.22 (m, 7 H), 7.20–7.04 (m, 4 H), 6.90–6.74 (m, 7 H), 6.08 (s, 1 H), 5.04 (d, *J* = 11.2 Hz, 1 H), 3.79 (s, 3 H), 3.77 (s, 3 H), 3.20 (dd, *J* = 14.8, 11.2 Hz, 1 H), 3.05 (d, *J* = 14.8 Hz, 1 H), 2.35 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.27, 158.80, 149.83, 147.64, 147.17, 133.33, 131.05, 130.24, 130.12, 128.85, 128.67, 127.85, 127.22, 126.00, 122.52, 121.08, 118.79, 116.24, 113.79, 113.32, 85.31, 66.47, 55.34, 55.18, 34.68, 29.78, 11.96.

MS (EI): *m*/*z* (%) = 517 $[M]^+$ (1.27), 409 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{34}H_{31}NO_4$: 517.2253; found: 517.2255.

(1*R*, 4*R*)-1-(2-Furyl)-6-methyl-2, 8-diphenyl-4-(4-tolyl)-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3fb)

Column chromatography afforded **3fb** as a pale yellow solid; yield: 81.2 mg (88%); 98% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 98:2, 0.8 mL/ min, λ = 220 nm): t_R = 5.69, 6.02 min]; mp 196–199 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52–7.08 (m, 12 H), 6.98–6.84 (m, 3 H), 6.28 (s, 1 H), 6.13–6.02 (m, 2 H), 5.08 (d, *J* = 10.4 Hz, 1 H), 3.25 (dd, *J* = 15.2, 10.4 Hz, 1 H), 2.98 (d, *J* = 15.2 Hz, 1 H), 2.35 (s, 3 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.07, 149.99, 147.42, 147.36, 142.15, 138.03, 137.51, 130.78, 129.03, 128.65, 128.61, 127.33, 126.35, 126.08, 121.62, 120.62, 118.74, 116.40, 109.97, 109.39, 86.10, 61.86, 34.39, 21.16, 11.75.

MS (EI): *m*/*z* (%) = 461 $[M]^+$ (1.65), 77 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{31}H_{27}NO_3$: 461.1991; found: 461.1992.

(1*R*,4*R*)-4-(4-Chlorophenyl)-1-(2-furyl)-6-methyl-2,8-diphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3gb)

Column chromatography afforded **3gb** as a pale yellow solid; yield: 79.0 mg (82%); 92% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 98:2, 0.8 mL/min, λ = 220 nm): t_R = 10.81, 12.80 min]; mp 168–171 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.14 (m, 12 H), 6.98–6.87 (m, 3 H), 6.27 (s, 1 H), 6.11–6.01 (m, 2 H), 5.09 (d, *J* = 10.0 Hz, 1 H), 3.18 (dd, *J* = 15.2, 10.0 Hz, 1 H), 2.99 (d, *J* = 15.2 Hz, 1 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.89, 149.88, 147.49, 147.44, 142.21, 139.44, 133.53, 130.69, 128.66, 128.54, 127.73, 127.39, 126.06, 121.90, 120.42, 118.33, 116.48, 109.99, 109.44, 85.47, 62.16, 34.42, 11.76.

MS (EI): *m*/*z* (%) = 481 $[M]^+$ (1.17), 77 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{30}H_{24}NO_3Cl$: 481.1445; found: 481.1443.

(1*R*,4*R*)-4-(2-Bromophenyl)-1-(4-methoxyphenyl)-6-methyl-2,8-diphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3hd)

Column chromatography afforded **3hd** as a pale yellow solid; yield: 96.3 mg (85%); 98% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.8 mL/min, λ = 220 nm): t_R = 6.52, 7.16 min]; mp 90–93 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.23 (m, 8 H), 7.20–7.04 (m, 5 H), 6.92–6.83 (m, 3 H), 6.83–6.72 (m, 2 H), 6.06 (s, 1 H), 5.38 (d, *J* = 10.4 Hz, 1 H), 3.79 (s, 3 H), 3.20 (d, *J* = 15.2 Hz, 1 H), 2.94 (dd, *J* = 15.2, 10.4 Hz, 1 H), 2.38 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.78, 149.74, 147.77, 147.16, 141.00, 132.48, 130.94, 130.25, 129.90, 128.85, 128.73, 128.58, 127.69, 127.17, 125.98, 122.40, 121.37, 121.28, 118.39, 116.44, 113.22, 84.57, 67.10, 55.11, 34.34, 11.82.

MS (EI): *m*/*z* (%) = 565 $[M]^+$ (1.77), 43 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{33}H_{28}NO_3Br$: 565.1253; found: 565.1254.

(1*R*, 4*R*)-4-(4-Bromophenyl)-1-(2-furyl)-6-methyl-2,8-diphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3ib)

Column chromatography afforded **3ib** as a pale yellow solid; yield: 79.1 mg (75%); 97% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 98:2, 0.5 mL/min, λ = 230 nm): t_R = 11.26, 12.79 min]; mp 173–176 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.41 (m, 4 H), 7.41–7.31 (m, 3 H), 7.31–7.15 (m, 5 H), 7.03–6.83 (m, 3 H), 6.28 (s, 1 H), 6.06 (d, *J* = 11.8 Hz, 2 H), 5.07 (d, *J* = 10.0 Hz, 1 H), 3.18 (dd, *J* = 14.4, 10.8 Hz, 1 H), 2.99 (d, *J* = 14.8 Hz, 1 H), 2.32 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.92, 149.90, 147.47, 142.20, 140.00, 131.51, 130.73, 128.67, 128.07, 127.39, 126.09, 121.93, 121.70, 120.46, 118.33, 116.52, 110.00, 109.45, 85.51, 62.20, 34.41, 11.75.

MS (EI): *m*/*z* (%) = 527 $[M]^+$ (1.38), 77 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{30}H_{24}NO_3Br$: 527.0919; found: 527.0917.

(1*R*,4*R*)-1-(4-Methoxyphenyl) -2,4,6,8-tetraphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3jd)

Column chromatography afforded **3jd** as a pale yellow solid; yield: 85.8 mg (78%); 99% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 98:2, 0.5 mL/min, λ = 220 nm): t_R = 11.74, 13.64 min]; mp 87–90 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.28 (m, 15 H), 7.21–7.10 (m, 4 H), 6.19 (s, 1 H), 6.98–6.74 (m, 5 H), 5.16 (d, *J* = 9.6 Hz, 1 H), 3.79 (s, 3 H), 3.55–3.35 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.82, 149.56, 149.28, 148.53, 140.98, 131.13, 130.69, 130.23, 129.74, 128.80, 128.65, 128.58, 128.40, 127.81, 127.68, 127.59, 127.04, 126.39, 126.33, 123.68, 121.24, 120.26, 116.27, 113.30, 85.69, 66.59, 55.11, 35.51, 29.68.

MS (EI): *m*/*z* (%) = 549 $[M]^+$ (3.05), 105 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{38}H_{31}NO_3$: 549.2304; found: 549.2302.

(1*R*,4*R*)-4-(4-Chlorophenyl)-1-(4-methoxyphenyl)- 2,6,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3kd)

Column chromatography afforded **3kd** as a pale yellow solid; yield: 78.3 mg (67%); 92% ee [HPLC (Daicel OD-H column, hexanes–*i*-PrOH, 95:5, 0.8 mL/min, λ = 220 nm): t_R = 6.87, 7.70 min]; mp 111–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.09 (m, 18 H), 6.93–6.75 (m, 5 H), 6.18 (s, 1 H), 5.12 (d, *J* = 9.6 Hz, 1 H), 3.76 (s, 3 H), 3.50–3.30 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.91, 149.52, 149.34, 148.59, 139.46, 133.58, 131.08, 130.65, 130.21, 129.60, 128.84, 128.62, 128.58, 127.69, 127.03, 126.40, 123.60, 121.44, 119.95, 116.32, 113.35, 85.04, 66.80, 55.09, 35.52.

MS (EI): *m*/*z* (%) = 583 $[M]^+$ (1.07), 77 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{38}H_{30}NO_3Cl$: 583.1914; found: 583.1913.

(1*R*,4*R*)-6-(4-Chlorophenyl)-1-(2-furyl)-2,4,8-triphenyl-1,2,4,5-tetrahydrofuro[3,4-*d*][1,2]oxazepine (3lb)

Column chromatography afforded **3lb** as a pale yellow solid; yield: 87.0 mg (80%); 87% ee [HPLC (Daicel AD-H column, hexanes–*i*-PrOH, 95:5, 0.8 mL/min, λ = 220 nm): t_R = 9.68, 14.34 min]; mp 101–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65–7.12 (m, 17 H), 7.03–6.85 (m, 3 H), 6.28 (s, 1 H), 6.17 (d, *J* = 12.2 Hz, 2 H), 5.19 (d, *J* = 7.4 Hz, 1 H), 3.60–3.18 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.71, 149.72, 149.06, 148.09, 142.22, 140.81, 133.42, 130.37, 129.46, 128.79, 128.72, 128.68, 128.44, 128.11, 127.99, 127.91, 126.53, 126.27, 121.94, 120.69, 116.52, 110.08, 109.55, 86.00, 62.05, 34.99.

MS (EI): *m*/*z* (%) = 543 $[M]^+$ (0.12), 77 (100).

HRMS: *m*/*z* $[M]^+$ calcd for $C_{35}H_{26}NO_3Cl$: 543.1601; found: 543.1609.

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Supporting Information

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