OL Organic Letters

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Gold-Catalyzed Synthesis of Chiral Cyclopentadienyl Esters via Chirality Transfer

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Cite This: https://dx.doi.org/10.1021/acs.orglett.0c02293 Read Online

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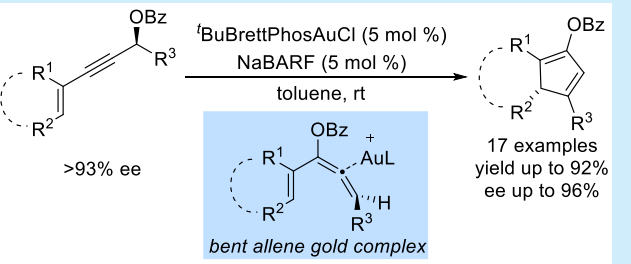
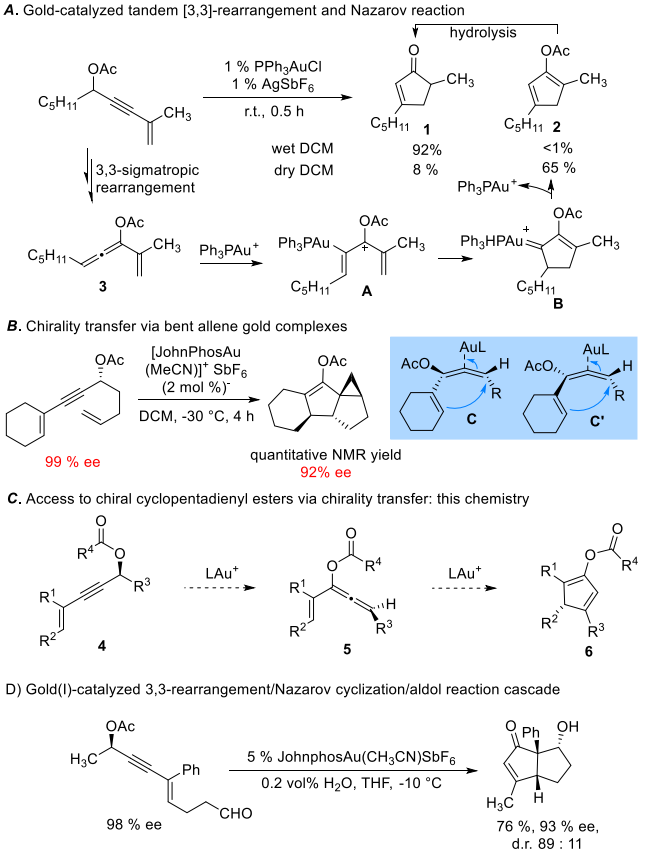
ABSTRACT: Efficient access to chiral cyclopentadienyl esters from readily accessible chiral enynyl ester substrates is developed. Typically high levels of chirality transfer realized in this homogeneous gold catalysis are attributed to the intermediacy of a chiral bent allene gold complex. Cyclopentadienyl esters can be prepared in good yields and with excellent enantiomeric excesses. The synthetic utilities of the chiral cyclopentadienyl esters are demonstrated by the Diels–Alder reactions, fluorination, alkylation, and epoxidation without any notable erosion of enantiopurity.



Scheme 1. Previous Work on the Gold-Catalyzed Cycloisomerizations of Enynyl Esters and This Chemistry

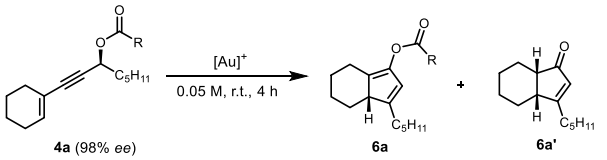


Cyclopentadienes are important synthetic intermediates widely used as reactive dienes in the Diels–Alder reaction[1] and as ligand precursors in organometallic chemistry, and the enantiomerically enriched ones are highly valued in complex molecular synthesis.[2] Aside from modification from chiral five-membered ring precursors,[2a−d,3] which can be of limited scope, asymmetric synthesis of this class of chiral cyclic dienes from acyclic substrates offers a potentially more efficient and flexible synthetic alternative, but there have been only a few reported studies of limited scope and/or moderate enantiopurity.[4] Moreover, few reports have documented such an approach to cyclopentadienes with heterofunctionalization at the ring. In this work, we report a study of this nature based on gold-catalyzed efficient chirality transfer,[4b,5] which permits the synthesis of cyclopentadienyl esters with generally excellent enantiomeric access from readily accessible chiral substrates.

In 2006, one of us reported the gold-catalyzed cycloisomerization of enynyl esters into cyclopentenones.[6,7] An example is shown in Scheme 1A. The proposed reaction mechanism entails a gold-catalyzed 3,3-sigmatropic rearrangement to deliver enallenyl acetate **3**, its subsequent gold-catalyzed Nazorov-type cyclization, and hydrolysis. The intermediacy of cyclopentadienyl acetate **2** was confirmed by its detection when the reaction was performed in dry DCM instead of wet DCM. Pentadienyl cation **A** was invoked as the reactive intermediate in the conversion of **3** to **1**. However, the subsequent studies by Gandon, Fensterbank, and Malacria[8]

Received: July 10, 2020

Table 1. Initial Trial and Condition Optimization



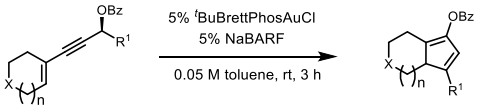
entry	catalyst (5 mol %/ 5 mol %)	solvent	R	yield (%) of 6a/6a′	ee (%)[c]
1	PPh_3AuCl/ $AgSbF_6$[a]	wet DCM	CH_3	0/70	67
2	PPh_3AuCl/ $AgSbF_6$[a]	wet DCM	^{t}Bu	0/76	70
3	JohnPhosAuCl/ $AgSbF_6$[a]	wet DCM	^{t}Bu	0/75	74
4	L1AuCl/$AgSbF_6$[a,b]	wet DCM	^{t}Bu	0/74	77
5	L1AuCl/$AgSbF_6$[a,b]	wet DCM	Ph	0/84	94
6	L1AuCl/$AgSbF_6$[a,b]	wet DCM	mesityl	0/70	92
7	L1AuCl/$AgSbF_6$[a,b]	wet DCM	4-MeOPh	0/84	93
8	L1AuCl/$AgSbF_6$[a,b]	wet DCM	4-BrPh	0/78	94
9	L1AuCl/$AgSbF_6$[a,b]	wet DCM	4-NO_2Ph	0/trace	–
10	L1AuCl/$AgSbF_6$[a,b]	toluene	Ph	49/29	93
11	L1AuCl/$AgSbF_6$[b]	toluene	Ph	52/33	93
12	L1AuCl/$AgNTf_2$[b]	toluene	Ph	48/44	91
13	L1AuCl/NaBARF[b]	toluene	Ph	91/0	95
14	L1AuCl/NaBARF[b]	$PhCF_3$	Ph	87/0	95
15	L1AuCl/NaBARF[b]	DCM	Ph	82/0	96

[a]With 10 mol % $AgSbF_6$. [b]L1 = ^{t}BuBrettPhos. [c]Of the major product.

that trap the gold carbene intermediate of type **B** by a tethered alkene revealed that gold-coordinated bent allene structures **C** and **C′** are the alternative intermediates that account for the observed efficient chirality transfer (Scheme 1B). These works explored only a few substrates. We reasoned that this chirality transfer would similarly permit efficient access to chiral cyclopentadienyl esters from chiral enynyl esters (Scheme 1C), and expanded exploration of the substrate scope would shed more light on chirality transfer. During our study, Carreira reported a related efficient chirality transfer process, in which an intramolecular aldol reaction serves to terminate the tandem gold-catalyzed 3,3-sigmatropic rearrangement and the Nazarov reaction (Scheme 1D).[9]

At the outset, we employed (*S*)-1-(cyclohex-1-en-1-yl)oct-1-yn-3-yl ester **4a** as the substrate. It is readily prepared from the corresponding enynone via Noyori's asymmetric transfer hydrogenation[10] and subsequent esterification. Anticipating the nature of the acyl group in **4a** might influence the desired chirality transfer, and to simplify chiral HPLC analysis, we opted to first optimize the chirality transfer by examining the hydrolyzed bicyclic cyclopentenone product **6a′**, which could be directly obtained with wet methylene chloride as the reaction solvent. In the presence of catalytic Ph_3PAuCl (5 mol %) and $AgSbF_6$ (10 mol %), the acetate version of **4a** indeed underwent smooth cycloisomerization and hydrolysis to afford **6a′** in 70% yield (entry 1). Moreover, the enantiomeric excess of the product was 67%, confirming a significant level of chirality transfer from the chiral enyne substrate. The configuration of **6a′** is assigned on the basis of mechanistic consideration and supported by the prior report.[9] Switching

Table 2. Scope of with Substrates Featuring Cyclic Alkenes[a]



Entry	Propargylic ester **4**	Cyclopentadienyl Ester **6**	Yield	ee
1	**4b** (98% ee)	**6b**	80%	96%[b]
2	**4c** (97% ee)	**6c**	92%	93%
3	**4d** (99% ee)	**6d**	77%	92%
4	**4e** (97% ee)	**6e**	90%	95%
5	**4f** (98% ee)	**6f**	48%	96%
6	**4g** (98% ee)	**6g**	62%	94%
7	**4h** (99% ee)	**6h′**	23%[c] 61%[d]	93% 86%
8	**4i** (98% ee)	**6i′**	84%[e,f]	63%

[a]Reaction conditions: 5 mol % ^{t}BuBrettPhosAuCl, 5 mol % NaBARF, 0.2 mmol of **4** (0.05 M in toluene), rt, 3 h. [b]ee was determined after hydrolysis. [c]The standard condition was applied and followed by hydrolysis. [d]The standard condition but at 60 °C for 4 h was applied and followed by hydrolysis. [e]With 5% ^{t}BuBrettPhosAuCl, 10% $AgSbF_6$, and wet DCM applied. [f]*cis*:*trans* ratio of 14:1.

the acyl group of **4a** to a pivaloyl led to slight improvements in the reaction yield and the product ee (entry 2). The product ee was improved to 74% by using the sterically hindered JohnPhos as the metal ligand[8b,9] (entry 3) and further to 77% by using the even bulkier ^{t}BuBrettPhos (entry 4). Much to our delight, when the benzoate of **4a** was employed as the substrate, the yield was improved to 84% and the ee to 94% (entry 5). Modifications on the benzoate benzene ring did not further improve the reaction yield or the efficacy of chirality transfer (entries 6–8) or in the case of 4-NO_2 led to little reaction (entry 9). With the optimal substrate and catalyst in hand, we then turned our attention to avoiding the hydrolysis of **6a** to **6a′** during the gold catalysis. To this end, anhydrous toluene was used as the reaction solvent. To our delight, the desired cyclopentadienyl benzoate **6a** was formed with 93% ee, albeit accompanied by a substantial amount of hydrolyzed product **6a′**. Decreasing the amount of $AgSbF_6$ to 5 mol % (entry 11) or switching it to 5 mol % $AgNTf_2$ (entry 12) did not prevent the formation of a substantial amount of **6a′**. Remarkably, when NaBARF (5 mol %) was used as the

https://dx.doi.org/10.1021/acs.orglett.0c02293
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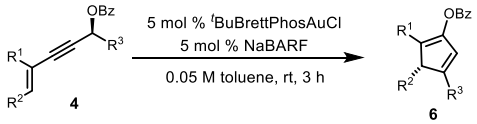
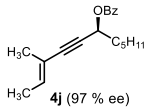
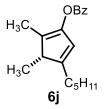
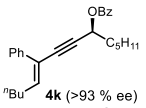
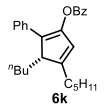
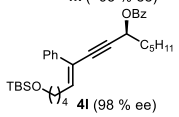
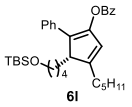
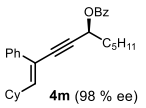
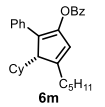
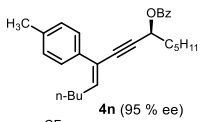
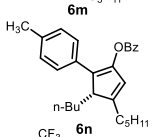
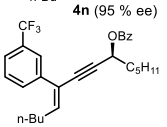
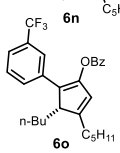
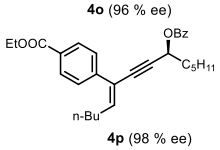
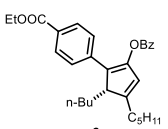
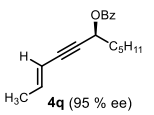
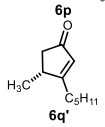
Table 3. Scope of Substrates Containing Acyclic Alkenes[a]



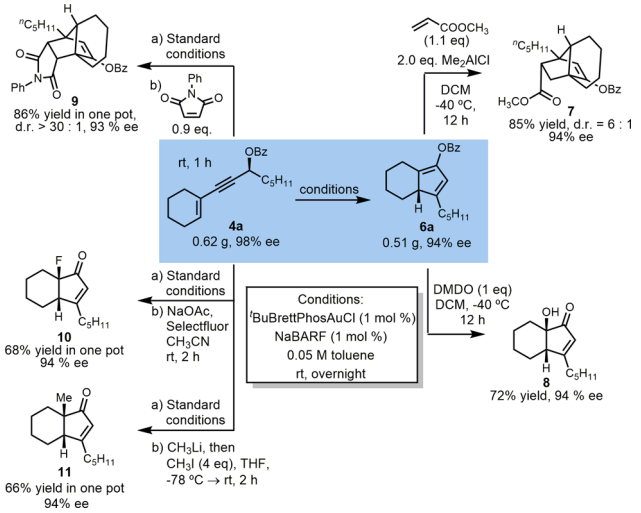
Entry	4	6	Yield	ee
1	 **4j** (97 % ee)	 **6j**	85%	91%
2	 **4k** (>93 % ee)	 **6k**	89%	95%
3	 **4l** (98 % ee)	 **6l**	98%	95%
4	 **4m** (98 % ee)	 **6m**	89%	93%
5	 **4n** (95 % ee)	 **6n**	89%	94%
6	 **4o** (96 % ee)	 **6o**	68%	95%
7	 **4p** (98 % ee)	 **6p**	74%	94%
8	 **4q** (95 % ee)	 **6q′**	76%[b]	3%

[a]Reaction conditions: 5 mol % tBuBrettPhosAuCl, 5 mol % NaBARF, 0.2 mmol **4** (0.05 M in toluene), rt, 3 h. [b]With 5% tBuBrettPhosAuCl, 10% $AgSbF_6$, and wet DCM applied.

chloride abstractor, the undesired hydrolysis was completely shut down, and **6a** was formed in 91% yield while maintaining the excellent ee value (entry 13). Similar phenomena were detected with $PhCF_3$ or DCM as the solvent, albeit the yields were slightly lower (entry 14 or 15, respectively).

With the optimized reaction conditions in hand, we first probed the reaction scope by varying the *n*-pentyl group of **4a**. As shown in Table 2, the sterically more demanding cyclohexyl (entry 1), a methyl (entry 2), a benzyl (entry 3), and an oxygenated alkyl group (entry 4) are all readily accommodated, and the cyclopentadienyl esters were isolated in good to excellent yields and with ≥92% ee. Incorporation of a heteroatom such as O (entry 5) and N (entry 6) in the cyclohexene ring led to lower yields, but the chirality transfer remained efficient. When **4h** contained a dihydronaphthalene ring as the substrate, the reaction was quite slow under standard conditions (entry 7). It was accelerated at 60 °C. Due to the contamination of side products, the cyclopentadienyl ester product was subsequently hydrolyzed under acidic

Scheme 2. Synthetic Transformations of Cyclopentadienyl Benzoate 6a



conditions, affording cyclopentenone **6h′** in a much improved 61% yield and with a slightly lower ee (87%). For cycloheptene substrate **4i**, cyclopentadienyl ester **6i** was unstable. As such, the hydrolytic conditions in entry 5 of Table 1 were employed to afford 5,7-fused enone **6i′** in 84% yield (entry 8). However, the ee value is moderate, which may be due to a relatively slow cyclization of the bent allene intermediate of type **C** and hence its increased level of racemization[8a] or conversion to achiral pentadienyl cations of type **A**.

To further explore the reaction scope, we turned our attention to substrates featuring acyclic C=C bonds for the synthesis of chiral cyclopentadienyl esters without ring fusion. As shown in Table 3, under the optimized conditions, these reactions proceeded smoothly, affording the tetrasubstituted cyclopentadienes in good to excellent yields and with excellent enantiomeric excesses (entries 1−7). Electron-withdrawing groups on the substrate phenyl ring (entries 6 and 7) are tolerated, albeit in lower yet serviceable yields. Under the standard conditions, the reaction of **4q** resulted in a complicated mixture, which is attributed to 1,5-hydride shifts of the cyclopentadiene moiety. When **4q** was subjected to the hydrolytic conditions, to our surprise, the cyclopentenone product **6q′** barely exhibits any ee. This result indicates the steric hindrance offered by the R^1 group is essential for hindering the formation of the corresponding achiral pentadienyl cation and/or the allene racemization.

To demonstrate the synthetic utilities of this chemistry, we carried out a scale-up synthesis of **6a** (Scheme 2). Hence, with only 1 mol % catalyst loading, 0.51 g of the product of high enantiomeric purity (94% ee) was isolated, although the reaction required overnight and the yield was slightly decreased due to the much lower catalyst loading. The reactions of **6a** were then pursued first with the isolated material. For example, it underwent the Lewis acid-promoted Diels−Alder reaction with methyl acrylate at −40 °C to deliver bridged tricycle **7** in 84% yield while maintaining the ee value, and its epoxidation by DMDO smoothly afforded the *cis*-fused *α′*-hydroxycyclopentenone **8** upon hydrolytic workup. The *endo* nature of the major isomer of **7** is confirmed by two-dimensional NMR studies. One-pot processes without the isolation of **6a** were also demonstrated. For example, the Diels−Alder reaction with *N*-phenylmaleimide smoothly

https://dx.doi.org/10.1021/acs.orglett.0c02293
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delivered the tetracycle **9** in 86% overall yield and with 93% ee, demonstrating a rapid increase in structural complexity.[11] Fluorination at the enone α'-position by Selectfluor afforded selectively *cis*-fused **10** in a serviceable yield and without erosion of ee, and diastereoselective installation of a methyl group at the same position was achieved with similar results.

In conclusion, we have developed efficient access to chiral cyclopentadienyl esters from readily accessible chiral enynyl ester substrates. Typically high levels of chirality transfer realized in this homogeneous gold catalysis can be attributed to the intermediacy of chiral bent allene gold complexes. Cyclopentadienyl esters with or without ring fusion can be prepared in good yields and with excellent enantiomeric excess. Benzoates are shown to be more conducive to chirality transfer than aliphatic esters, and a trisubstituted C=C bond in the substrate is found to be essential to minimize the racemization of the bent allene gold complex or the access to pentadienyl cations of type **A**. The synthetic utilities of the chiral cyclopentadienyl esters are demonstrated by one-pot or sequential Diels–Alder reactions, fluorination, alkylation, and epoxidation without any notable enantiopurity erosion.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02293.

Experimental procedures, compound characterization data, and ^{1}H and ^{13}C NMR spectra (PDF)

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Author Contributions

§K.Z. and Y.-C.H. contributed equally to this work.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

L.Z., K.Z., and Z.Y. thank the National Science Foundation (NSF) (CHE 1800525) and National Institute of General Medical Sciences (R01GM123342) for financial support. NSF Grant MRI-1920299 is acknowledged for the purchase of NMR instruments.

■ REFERENCES

(1) For a monograph, see: Jørgensen, K. A. *Cycloaddition reactions in organic synthesis*; John Wiley & Sons, 2002.

(2) (a) Doye, S.; Hotopp, T.; Wartchow, R.; Winterfeldt, E. The Enantioselective Total Synthesis of (−)-Myltaylenol. *Chem. - Eur. J.* **1998**, *4* (8), 1480−1488. (b) Kuwahara, S. Synthesis of Both Enantiomers of a Novel Sesquiterpene Isolated from the Pheromone Gland of a Stink Bug, Tynacantha marginata Dallas. *Synthesis* **2000**, *2000* (13), 1930−1935. (c) Doye, S.; Hotopp, T.; Winterfeldt, E. The enantioselective total synthesis of (−)-myltaylenol. *Chem. Commun.* **1997**, *16*, 1491−1492. (d) Uyehara, T.; Sato, Y.; Ishizuka, H.; Sakiyama, Y.; Ueno, M.; Sato, T. The first total synthesis of (±)-junicedranol based on a novel anionic [1,3] rearrangement. *Tetrahedron Lett.* **2000**, *41* (12), 1939−1942. (e) Brandstätter, M.; Freis, M.; Huwyler, N.; Carreira, E. M. Total Synthesis of (−)-Merochlorin A. *Angew. Chem., Int. Ed.* **2019**, *58* (8), 2490−2494.

(3) (a) Winterfeldt, E. Enantiomerically pure cyclopentadienes. *Chem. Rev.* **1993**, *93* (2), 827−843. (b) Beckmann, M.; Meyer, T.; Schulz, F.; Winterfeldt, E. Face-Selective and endo-Selective Cycloadditions with Enantiomerically Pure Cyclopentadienes. *Chem. Ber.* **1994**, *127* (12), 2505−2509. (c) Matcheva, K.; Beckmann, M.; Schomburg, D.; Winterfeldt, E. Chiral Cyclopentadienes. *Synthesis* **1989**, *1989* (11), 814−817.

(4) (a) Sanjuán, A. M.; García-García, P.; Fernández-Rodríguez, M. A.; Sanz, R. Enantioselective Synthesis of Cyclopentadienes by Gold(I)- Catalyzed Cyclization of 1,3-Dien-5-ynes. *Adv. Synth. Catal.* **2013**, *355* (10), 1955−1962. (b) Wirtanen, T.; Muuronen, M.; Melchionna, M.; Patzschke, M.; Helaja, J. Gold(III)-Catalyzed Enynamine−Cyclopentadiene Cycloisomerization with Chirality Transfer: An Experimental and Theoretical Study Indicating Involvement of Dual Au(III) Push−Pull Assisted cis−trans Isomerism. *J. Org. Chem.* **2014**, *79* (21), 10269−10283. (c) Wu, H.-P.; Aumann, R.; Fröhlich, R.; Wibbeling, B.; Kataeva, O. Highly Selective Formation of [4 + 2] and [4 + 3] Cycloadducts of Tetrahydroindenes Generated in Situ from a (1-Alkynyl)carbene Tungsten Complex by the Metalla-1,3,5-hexatriene Route. *Chem. - Eur. J.* **2001**, *7* (23), 5084−5093.

(5) (a) Patil, N. T. Chirality Transfer and Memory of Chirality in Gold-Catalyzed Reactions. *Chem. - Asian J.* **2012**, *7* (10), 2186−2194. (b) Krause, N.; Aksin-Artok, Ö.; Asikainen, M.; Breker, V.; Deutsch, C.; Erdsack, J.; Fan, H.-T.; Gockel, B.; Minkler, S.; Poonoth, M.; Sawama, Y.; Sawama, Y.; Sun, T.; Volz, F.; Winter, C. Combined coinage metal catalysis for the synthesis of bioactive molecules. *J. Organomet. Chem.* **2012**, *704* (0), 1−8. (c) Shi, X.; Gorin, D. J.; Toste, F. D. Synthesis of 2-Cyclopentenones by Gold(I)-Catalyzed Rautenstrauch Rearrangement. *J. Am. Chem. Soc.* **2005**, *127* (16), 5802−5803. (d) Nishina, N.; Yamamoto, Y. Gold-Catalyzed Intermolecular Hydroamination of Allenes with Arylamines and Resulting High Chirality Transfer. *Angew. Chem., Int. Ed.* **2006**, *45* (20), 3314−3317. (e) Nakamura, I.; Sato, T.; Terada, M.; Yamamoto, Y. Chirality Transfer in Gold-Catalyzed Carbothiolation of o-Alkynylphenyl 1-Arylethyl Sulfides. *Org. Lett.* **2008**, *10* (13), 2649−2651. (f) Aponick, A.; Biannic, B. Chirality Transfer in Au-Catalyzed Cyclization Reactions of Monoallylic Diols: Selective Access to Specific Enantiomers Based on Olefin Geometry. *Org. Lett.* **2011**, *13* (6), 1330−1333. (g) Rao, W.; Koh, M. J.; Kothandaraman, P.; Chan, P. W. H. Gold-Catalyzed Cycloisomerization of 1,7-Diyne Benzoates to Indeno[1,2-c]azepines and Azabicyclo[4.2.0]octa-1(8),5-dines. *J. Am. Chem. Soc.* **2012**, *134* (26), 10811−10814. (h) Rao, W.; Susanti, D.; Chan, P. W. H. Gold-Catalyzed Tandem 1,3-Migration/[2 + 2]

Cycloaddition of 1,7-Enyne Benzoates to Azabicyclo[4.2.0]oct-5-enes. *J. Am. Chem. Soc.* **2011**, *133* (39), 15248−15251.

(6) (a) Zhang, L.; Wang, S. Efficient Synthesis of Cyclopentenones from Enynyl Acetates via Tandem Au(I)-Catalyzed 3,3-Rearrangement and the Nazarov Reaction. *J. Am. Chem. Soc.* **2006**, *128* (5), 1442−1443. For subsequent work, see: (b) Lemière, G.; Gandon, V.; Cariou, K.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. Tandem Gold(I)-Catalyzed Cyclization/Electrophilic Cyclopropanation of Vinyl Allenes. *Org. Lett.* **2007**, *9* (11), 2207−2209. (c) Lemière, G.; Gandon, V.; Cariou, K.; Hours, A.; Fukuyama, T.; Dhimane, A.-L.; Fensterbank, L.; Malacria, M. Generation and Trapping of Cyclopentenylidene Gold Species: Four Pathways to Polycyclic Compounds. *J. Am. Chem. Soc.* **2009**, *131* (8), 2993−3006. (d) Rao, W.; Boyle, J. W.; Chan, P. W. Gold-Catalyzed Sequential Cyclization of 1-En-3,9-Diyne Esters to Partially Hydrogenated 3H-Dicyclopenta[a,b]naphthalenes. *Chem. - Eur. J.* **2016**, *22* (19), 6532−6. (e) Rao, W.; Susanti, D.; Ayers, B. J.; Chan, P. W. H. Ligand-Controlled Product Selectivity in Gold-Catalyzed Double Cycloisomerization of 1,11-Dien-3,9-Diyne Benzoates. *J. Am. Chem. Soc.* **2015**, *137* (19), 6350−6355. (f) Shi, F.-Q.; Li, X.; Xia, Y.; Zhang, L.; Yu, Z.-X. DFT Study of the Mechanisms of In Water Au(I)-Catalyzed Tandem [3,3]-Rearrangement/Nazarov Reaction/[1,2]-Hydrogen Shift of Enynyl Acetates: A Proton-Transport Catalysis Strategy in the Water-Catalyzed [1,2]-Hydrogen Shift. *J. Am. Chem. Soc.* **2007**, *129* (50), 15503−15512.

(7) For recent reviews of gold catalysis, see: (a) Furstner, A. From understanding to prediction: gold- and platinum-based pi-acid catalysis for target oriented synthesis. *Acc. Chem. Res.* **2014**, *47* (3), 925−38. (b) Li, Y.; Li, W.; Zhang, J. Gold-Catalyzed Enantioselective Annulations. *Chem. - Eur. J.* **2017**, *23* (3), 467−512. (c) Obradors, C.; Echavarren, A. M. Gold-Catalyzed Rearrangements and Beyond. *Acc. Chem. Res.* **2014**, *47* (3), 902−912. (d) Zi, W.; Dean Toste, F. Recent advances in enantioselective gold catalysis. *Chem. Soc. Rev.* **2016**, *45* (16), 4567−4589.

(8) (a) Gandon, V.; Lemière, G.; Hours, A.; Fensterbank, L.; Malacria, M. The Role of Bent Acyclic Allene Gold Complexes in Axis-to-Center Chirality Transfers. *Angew. Chem., Int. Ed.* **2008**, *47* (39), 7534−7538. (b) Lemiere, G.; Gandon, V.; Cariou, K.; Hours, A.; Fukuyama, T.; Dhimane, A. L.; Fensterbank, L.; Malacria, M. Generation and Trapping of Cyclopentenylidene Gold Species: Four Pathways to Polycyclic Compounds. *J. Am. Chem. Soc.* **2009**, *131* (8), 2993−3006.

(9) Brandstätter, M.; Huwyler, N.; Carreira, E. M. Gold(i)-catalyzed stereoselective cyclization of 1,3-enyne aldehydes by a 1,3-acyloxy migration/Nazarov cyclization/aldol addition cascade. *Chem. Sci.* **2019**, *10* (35), 8219−8223.

(10) Noyori, R.; Hashiguchi, S. Asymmetric Transfer Hydrogenation Catalyzed by Chiral Ruthenium Complexes. *Acc. Chem. Res.* **1997**, *30* (2), 97−102.

(11) Susanti, D.; Liu, L. J.; Rao, W.; Lin, S.; Ma, D. L.; Leung, C. H.; Chan, P. W. Gold-Catalyzed Cycloisomerization and Diels-Alder Reaction of 1,4,9-Dienyne Esters to 3 a,6-Methanoisoindole Esters with Pro-Inflammatory Cytokine Antagonist Activity. *Chem. - Eur. J.* **2015**, *21* (25), 9111−8.

https://dx.doi.org/10.1021/acs.orglett.0c02293
Org. Lett. XXXX, XXX, XXX−XXX