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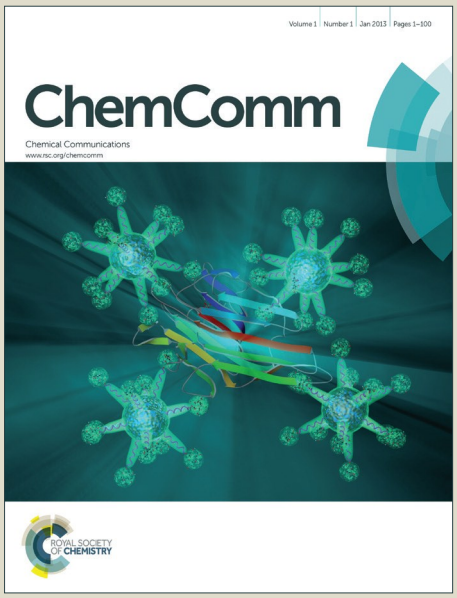

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Mild access to planar-chiral *ortho*-condensed aromatic ferrocenes via enantioselective cationic gold(I)-catalyzed cycloisomerization of *ortho*-alkynylaryl ferrocenes

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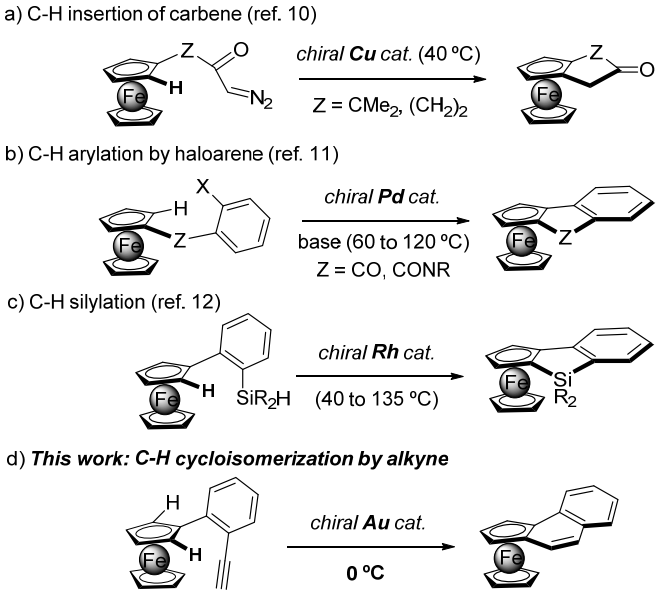
An efficient approach to (R_p) planar-chiral tri- and tetracyclic *ortho*-condensed aromatic ferrocenes was developed through the enantioselective cationic Au(I)-catalyzed cycloisomerization, in the presence of bidentate phosphine ligand (*R*)-DTBM-Segphos, from readily available *ortho*-alkynylaryl ferrocenes under very mild conditions (11 examples, up to 92% yield and 93% *ee*).

Planar-chiral ferrocenes are important scaffolds in organic and organometallic chemistry and have been used in a wide range of asymmetric reactions as ligands, catalysts, or templates.[1] Their preparation in enantiomerically enriched form has been achieved either by diastereoselective transformation utilizing stoichiometric homochiral substituents/reagents or by optical resolution of preformed racemic compounds.[2] More recently, enzymatic[3] and non-enzymatic kinetic resolutions,[4] as well as enantioselective desymmetrizations,[5] have emerged as powerful tools for the synthesis of such homochiral structures. In spite of the advances reached, their enantioselective synthesis is still a challenging problem.

The development of versatile methods for synthesizing chiral-planar ferrocenes in a catalytic manner would be a highly efficient approach. In spite of the remarkable progress in the field of asymmetric catalysis, examples of catalytic controlling planar-chirality in ferrocenes had been extremely rare, until recently.[6] Thus, the first enantioselective palladium-catalyzed *ortho* C-H arylation of a ferrocene directed by amine groups was reported in 2013, using amino acids as ligands.[7] Similar conditions were later described for the enantioselective ferrocene C-H bond alkenylation and acylation.[8] Besides palladium catalysis, an iridium catalyst in the presence of chiral diene ligands was employed for a novel ferrocene C-H alkylation directed by isoquinoline groups.[9]



Scheme 1. Enantioselective intramolecular reactions for the synthesis of planar-chiral ring-fused ferrocenes.

With respect to the intramolecular version of ferrocene C-H bond activation to construct planar-chiral ring-fused ferrocenes (Scheme 1), the carbene C–H insertion of diazoketone-tethered ferrocenes, mediated by Cu catalyst in the presence of a chiral Box ligand, was a pioneering work[10] and planar-chiral cyclic ketone-fused ferrocenes were thus prepared (Scheme 1a). More recently, planar-chiral indenone[11a-b,e] and quinolinone-fused[11c-d] ferrocenes were obtained in excellent *ee* (Scheme 1b), through the ferrocene C–H bond arylation with haloarenes,[11a-d] including halopyridines,[11e] by using Pd catalysts in the presence of different chiral phosphines or phosphoramides. Finally, the synthesis of planar-chiral benzosililoferrocenes has been reported by rhodium-catalyzed intramolecular ferrocene C-H bond silylation[12] in the presence of chiral dienes or biphosphines (Scheme 1c). In all cases, temperatures between 40 and 135 ºC were necessary to perform the enantioselective

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Electronic Supplementary Information (ESI) available: Experimental procedures, characterization data and NMR spectra. Crystal structure determinations of (*rac*)-**6a** CCDC 1469767, and (R_p)-**6e** CCDC 1469768 contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0xx00000x/

transformations. Albeit these successful examples, development of new methodologies for catalytic asymmetric synthesis of planar chiral molecules, with diverse skeletons and under milder conditions is still necessary.

We now report the first general enantioselective synthesis of planar-chiral *ortho*-condensed aromatic ferrocenes from the cationic gold(I)-catalyzed[13] intramolecular cycloisomerization of 2-alkynylaryl ferrocenes, under very mild conditions (Scheme 1d), based on the metal-catalyzed intramolecular hydroarylation of *ortho*-alkynylbiaryls initially developed by Fürstner[14] for the synthesis of phenanthrenes and later applied for higher helicenes.[15] To the best of our knowledge, there is only one example in the literature describing an enantioselective version of this type of cycloisomerization.[16]

2-Alkynylphenylferrocene **5a**,[17] chosen as model substrate, was readily prepared in only 2 steps (Scheme 2) from Suzuki coupling of commercially available ferrocene boronic acid (**1**) and 2-bromobenzaldehyde (**2a**), followed by the Seyferth-Gilbert homologation[18] of the resulting 2-formylphenyl ferrocene (**3a**),[19] using the Ohira-Bestmann reagent **4**.[20]

The access to the racemic *ortho*-condensed aromatic ferrocene (*rac*)-**6a** could be achieved, after many experimentation using different metal catalysts such as platinum, gold or indium, from the cycloisomerization of **5a** using 10% mol of $PtCl_2$ in toluene at 100 ºC, after a 6-*endo*-dig process.[14b] Under these conditions, model substrate **5a** afforded tricyclic aromatic ferrocene (*rac*)-**6a** in practically quantitative yield, after celite filtration. The tricyclic *ortho*-condensed aromatic structure of ferrocene (*rac*)-**6a** could be demonstrated after an X-ray diffraction study (Scheme 2).

Our initial attempts for the enantioselective version of this cycloisomerization using chiral platinum catalysis[21] were quite disappointing, even in terms of lack of reactivity, and we decided to move to the more developed chiral cationic gold(I) catalysis[13] (Scheme 2, Table 1). We first tried the enantioselective Au(I)-catalyzed cycloisomerization of model substrate **5a** using 10% of commercially available bidentate phosphine ligand (*R*)-DTBM-Segphos (**L1**) in the presence of 20% $AgSbF_6$, in dichloroethane (DCE) as solvent (entry 1). Under these conditions, we could obtain, after one hour at room temperature, *ortho*-condensed aromatic ferrocene (R_p)-**6a** in a satisfactory 70% yield but a very poor 15% *ee*. Delightedly, when the same reaction was performed in toluene as solvent (entry 2), the enantioselective cycloisomerization process furnished, after 1 h at rt and filtration over neutralized silica gel, planar-chiral tricyclic aromatic ferrocene (R_p)-**6a** in a good 86% yield and a promising 83% *ee*. The use of other commercially available bidentate phosphine ligands (entries 3-6) such as Segphos (**L2**), DM-Segphos (**L3**), BINAP (**L4**) or DTBM-MeOBiphep (**L5**) afforded, under similar conditions, good yields (72-85%) of (R_p)-**6a** albeit with poor enantioselectivities (5-37% *ee*). Next, the effect of the counterion was investigated (Table 1, entries 7 and 8) and silver triflate and silver tetrafluorborate as a halide scavenger gave comparable results in terms of chemical yield to that using $AgSbF_6$ (entry 2), but slightly lower related to the optical purity of (R_p)-**6a**. Finally, lowering the temperature to 0 ºC, we obtained the *ortho*-condensed aromatic tricyclic ferrocene (R_p)-**6a** with excellent 92% yield and 91% *ee* {$[\alpha]_D^{20}$ = +932 (*c* 0.04, CH_2Cl_2)}, after 5 h (Table 1, entry 9). At a lower temperature (–10 ºC, entry 10), similar results were observed, while the reaction became sluggish.

Scheme 2. Synthesis of model substrate **5a** and metal-catalyzed cycloisomerizations towards racemic and enantioenriched **6a**.

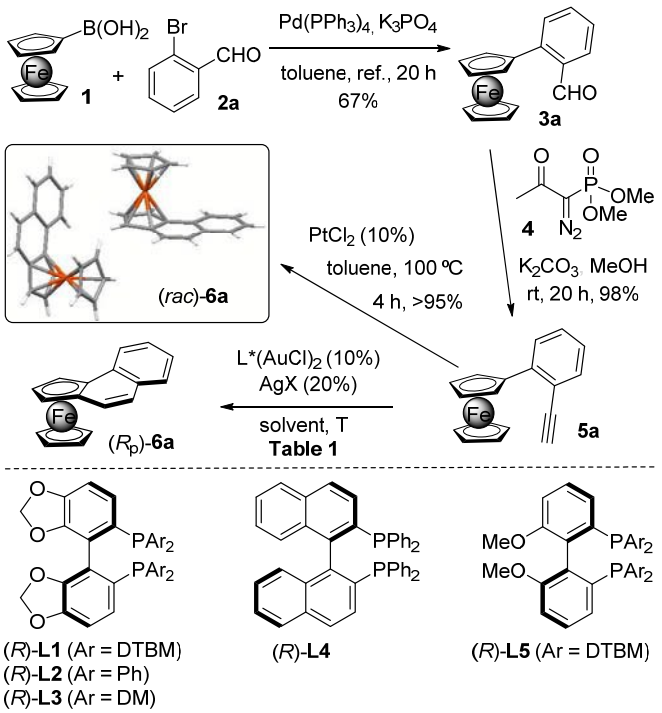


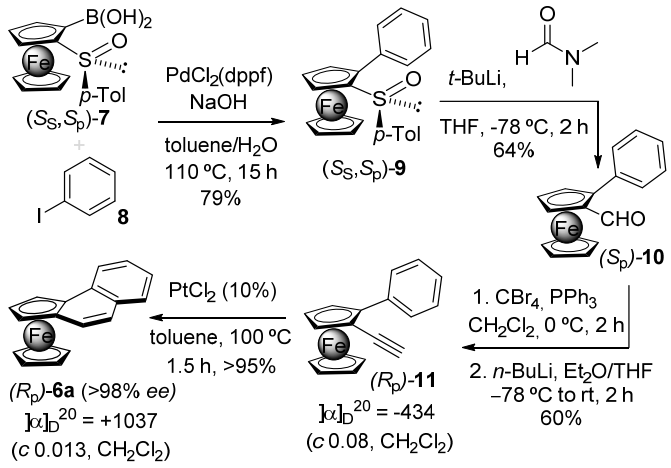
Table 1. Reaction conditions optimization.

Entry	L*	AgX	Solvent	T (ºC)	t (h)	Yield (%)	*ee* (%)[a]
1	**L1**	$AgSbF_6$	DCE	rt	1	70	15
2	**L1**	$AgSbF_6$	Toluene	rt	1	86	**83**
3	**L2**	$AgSbF_6$	Toluene	rt	1	81	10
4	**L3**	$AgSbF_6$	Toluene	rt	1	72	37
5	**L4**	$AgSbF_6$	Toluene	rt	2	85	5
6	**L5**	$AgSbF_6$	Toluene	rt	1	85	16
7	**L1**	AgOTf	Toluene	rt	1	79	77
8	**L1**	$AgBF_4$	Toluene	rt	1	92	80
9	**L1**	$AgSbF_6$	Toluene	0	5	**92**	**91**
10	**L1**	$AgSbF_6$	Toluene	–10	20	90	91

[a] Determined by chiral HPLC analysis (see ESI)

The (R_p) absolute configuration of **6a** was ascertained after the chemical correlation shown in Scheme 3, starting from planar-chiral *p*-tolylsulfinyl ferrocenyl boronic acid (S_S,S_p)-**7**, whose absolute configuration is perfectly known.[22] Thus, the Suzuki coupling between *p*-tolylsulfinyl ferrocenyl boronic acid

(S_S,S_p)-**7** (>98% *ee*) and iodobenzene (**8**), in the presence of $PdCl_2$(dppf) and NaOH,[23] afforded phenyl-substituted ferrocene (S_S,S_p)-**9** with 79% yield (Scheme 3). Next, the sulfoxide-lithium exchange on (S_S,S_p)-**9** effected by *tert*-BuLi, followed by the addition of *N*,*N*-dimethyl formamide as formylating agent,[24] yielded a 64% of 1-formyl-2-phenyl ferrocene (S_p)-**10**.[25] The subsequent transformation of the formyl group of (S_p)-**10** into a triple bond was carried out using the two-step Corey-Fuchs procedure.[26] Thus, reaction of (S_p)-**10** with CBr_4 and PPh_3 afforded the corresponding dibromoalkene which was treated with *n*-BuLi furnishing 2-alkynyl-1-phenyl ferrocene (R_p)-**11** {$[\alpha]^{20}_D$ = –434 (*c* 0.08, CH_2Cl_2)}, in 60% yield. Finally, the $PtCl_2$-catalyzed cycloisomerization of (R_p)-**11** in toluene at 100 ºC gave rise to the *ortho*-condensed aromatic tricyclic ferrocene (R_p)-**6a** in almost quantitative yield and >98% *ee* {$[\alpha]^{20}_D$ = +1037 (*c* 0.013, CH_2Cl_2)}, identical in all aspects to derivative obtained in the enantioselective Au(I)-catalyzed process shown in Scheme 2.



Scheme 3. Synthesis of (R_p)-**6a** from known (S_S,S_p)-**7**.

Having established the absolute configuration of (R_p)-**6a** and the optimal catalytic conditions for the enantioselective cycloisomerization of **5a** shown in Table 1, entry 9, (*R*)-DTBM-Segphos($AuCl)_2$ (10% mol) associated with the silver salt $AgSbF_6$ (20% mol) in toluene at 0 ºC, the scope of the methodology was ascertained by subjecting a range of diversely substituted 2-alkynylarylferrocenes **5b–j** to the best reaction parameters. As summarized in Table 2, various substituents on different positions of the phenyl ring, regardless of their electronic nature, were well tolerated affording tricyclic aromatic ferrocenes (R_p)-**6b–j** with good to excellent yields and enantiomeric excesses. Thus, three planar-chiral ferrocenyl derivatives (R_p)-**6b–d** bearing –OMe (82% *ee*), –F (92% *ee*) and –Me (91% *ee*) groups at the 8 position could be obtained in good to excellent enantiomeric purities, showing high values of their optical rotations. We also prepared the 7-methoxy-substituted aromatic ferrocene (R_p)-**6e**, which was obtained with a good 81% of *ee* {$[\alpha]^{20}_D$ = +1545 (*c* 0.016, CH_2Cl_2)} and whose absolute configuration could be demonstrated after a X-ray diffraction study (see ESI). Besides the 8-fluoro-substituted derivative (R_p)-**6c** commented before, it was possible to synthesize planar-chiral aromatic ferrocenes (R_p)-**6f–h**, having fluorine substituents at all positions of the external aromatic ring of the tricyclic moiety, with excellent optical purities (89-93% *ee*) for the 7- and 9-substituted derivatives (R_p)-**6f** and (R_p)-**6g**, and moderate *ee* (68%) for the 6-fluoro-substituted ferrocene (R_p)-**6h**. This lower enantioselectivity could be probably due to the close proximity of the fluorine atom, *ortho* to the reactive triple bond, in the starting material **5h**. Finally, two more examples of disubstituted tricyclic aromatic ferrocenes (R_p)-**6i–j** bearing two oxygenated or fluorine atoms at the 7 and 8 positions were obtained, showing excellent (93% *ee* for **6i**) and good optical purities (87% *ee* for **6j**), respectively.†

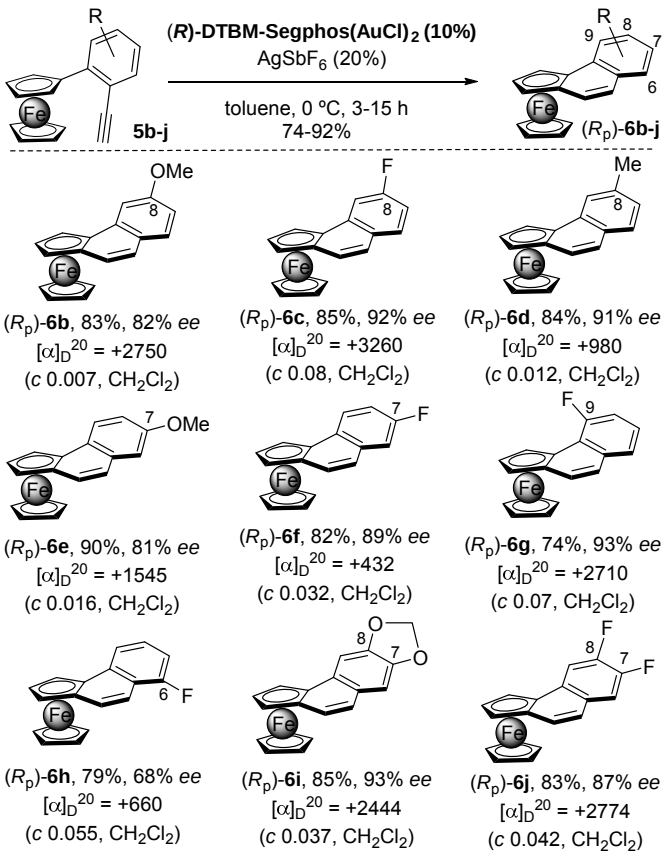


Table 2. Scope of the gold-catalyzed cycloisomerization.

Having demonstrated the scope of the enantioselective Au-catalyzed cycloisomerization process for the synthesis of enantioenriched differently substituted tricyclic aromatic ferrocenes **6a-j**, we were interested in extending the methodology to the construction of a planar-chiral tetracyclic aromatic ferrocene such as (R_p)-**6k**, in a three-step sequence as depicted in Scheme 4. Thus, the Suzuki coupling between commercially available ferrocene boronic acid (**1**) and 1-bromo-2-naphthaldehyde (**2a**) afforded, in 79% yield, the corresponding naphthyl ferrocene **3k**, whose homologation with the Ohira-Bestmann reagent **4** gave rise to the alkynyl naphthyl ferrocene **5k**, in 61% yield. Finally, the

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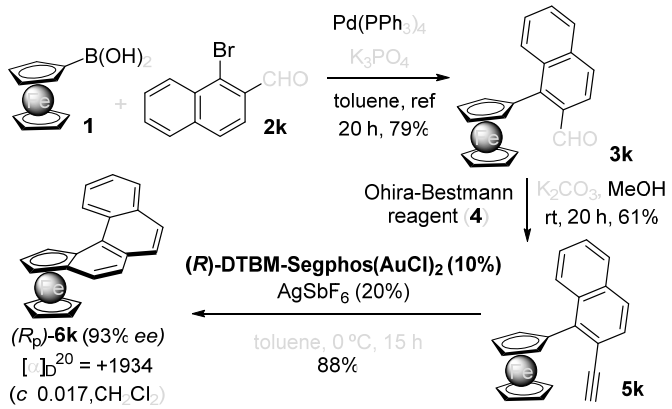
enantioselective cycloisomerization of **5k** in the presence of 10% mol of (*R*)-DTBM-Segphos(AuCl)$_2$ and 20% mol of $AgSbF_6$ in toluene at 0 ºC for 15 h, furnished tetracyclic *ortho*-condensed aromatic ferrocene (R_p)-**6k**, in excellent 88% yield and 93% *ee* {$[\alpha]^{20}_D$ = +1934 (*c* 0.017, CH_2Cl_2)}.



Scheme 4. Synthesis of tetracyclic ferrocene (R_p)-**6k**.

In summary, we have developed a highly efficient synthesis of planar-chiral aromatic ferrocenes by enantioselective Au(I)-catalyzed C–H activation, under very mild reaction conditions, of readily available *ortho*-alkynylaryl ferrocenes, prepared in only two steps from commercially available ferrocenyl boronic acid and 2-bromobenzaldehydes. This is the first example of the preparation of homochiral 1,2-disubstituted ferrocenes in optically enriched form using gold catalysis and may offer a short, practical and versatile route to functionalized planar-chiral metallocenes. Studies on the mechanistic aspects and applications of these structurally new ferrocenes in organic synthesis and catalysis are underway in our laboratories.

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Notes and references

† The gold(I)-catalyzed cycloisomerization of an alkynyl ferrocenyl tiophene afforded the corresponding methyl ketone after hydration of the triple bond, whereas no reaction was observed in the case of a pyridine-substituted derivative.

1 Selected recent reviews: (*a*) *Chiral Ferrocenes in Asymmetric Catalysis*, eds. L.-X. Dai, X.-L. Hou, Wiley-VCH, Weinheim, 2010. (*b*) T. Noel, J. Van der Eycken, *Green Process. Synth.,* 2013, **2**, 297. (*c*) M. Drusan, R. Sebesta, *Tetrahedron,* 2014, **70**, 759. (*d*) N. A. Butt, D. Liu, W. Zhang, *Synlett,* 2014, **25**, 615. (*e*) S. Toma, J. Csizmadiova, M. Meciarova, R. Sebesta, *Dalton Trans.,* 2014, **43**, 16557.

2 Review: D. Schaarschmidt, H. Lang, *Organometallics,* 2013, **32**, 5668.

3 Review: A. N. Alba, R. Rios, *Molecules* 2009, **14**, 4747.

4 Selected recent examples: (*a*) A. Latorre, A. Urbano, M. C. Carreño, *Chem. Commun.,* 2011, **47**, 8103. (*b*) M. Ogasawara, S. Arae, S. Watanabe, K. Nakajima, T. Takahashi, *Chem. Eur. J.,* 2013, **19**, 4151. (*c*) M. Akiyama, K. Akagawa, H. Seinob, K. Kudo, *Chem. Commun.,* 2014, **50**, 7893. (*d*) K. Akagawa, N. Nishi, I. Yoshikawa, K. Kudo, *Eur. J. Org. Chem.,* 2015, 5055. (*e*) R. Liu, G. Zhou, T. H. Hall, G. J. Clarkson, M. Wills, W. Chen, *Adv. Synth. Catal*., 2015, **357**, 3453.

5 Selected recent examples: (*a*) P. Buchgraber, A. Mercier, W. C. Yeo, C. Besnard, E. P. Kündig, *Organometallics,* 2011, **30**, 6303. (*b*) S. Arae, K. Nakajima, T. Takahashi, M. Ogasawara, *Organometallics,* 2015, **34**, 1197. (*c*) K. Akagawa, M. Akiyama, K. Kudo, *Eur. J. Org. Chem.,* 2015, 3894.

6 Recent reviews: (*a*) S. Arae, M. Ogasawara, *Tetrahedron Lett.,* 2015, **56**, 1751. (*b*) L. A. López, E. López, *Dalton Trans.,* 2015, **44**, 10128. (*c*) D.-Y. Zhu, P. Chen, J.-B. Xia, *Chem. Cat. Chem.,* 2016, **8**, 68.

7 (*a*) D. W. Gao, Y. C. Shi, Q. Gu, Z. L. Zhao, S. L. You, *J. Am. Chem. Soc.,* 2013, **135**, 86. (*b*) Y. C. Shi, R. F. Yang, D. W. Gao, S. L. You, *Beilstein J. Org. Chem.,* 2013, **9**, 1891. (*c*) Gao, D. W.; Gu, Q.; You, S. L. *J. Am. Chem. Soc.,* 2016, **138**, 2544. Very recent example using Rh(III) catalysis: (*d*) S. B. Wang, J. Zheng, S. L. You, *Organometallics,* 2016, DOI: 10.1021/acs.organomet.6b00020.

8 (*a*) C. Pi, Y. Li, X. Cui, H. Zhang, Y. Han, Y. Wu, *Chem. Sci.,* 2013, **4**, 2675. (*b*) C. Pi, X. Cui, X. Liu, M. Guo, H. Zhang, Y. Wu, *Org. Lett.,* 2014, **16**, 5164.

9 T. Shibata, T. Shizuno, *Angew. Chem., Int. Ed.,* 2014, **53**, 5410.

10 S. Siegel, H.-G. Schmalz, *Angew. Chem., Int. Ed. Engl.,* 1997, **36**, 2456.

11 (*a*) D. W. Gao, Q. Yin, Q. Gu, S. L. You, *J. Am. Chem. Soc.,* 2014, **136**, 4841. (*b*) R. Deng, Y. Huang, X. Ma, G. Li, R. Zhu, B. Wang, Y. B. Kang, Z. Gu, *J. Am. Chem. Soc.,* 2014, **136**, 4472. (*c*) L. Liu, A. A. Zhang, R. J. Zhao, F. Li, T. J. Meng, N. Ishida, M. Murakami, W. X. Zhao, *Org. Lett.,* 2014, **16**, 5336. (*d*) X. Ma, Z. Gu, *RSC Adv.,* 2014, **4**, 36241. (*e*) D.-W. Gao, C. Zheng, Q. Gu, S.-L. You, *Organometallics,* 2015, **34**, 4618.

12 (*a*) T. Shibata, T. Shizuno, T. Sasaki, *Chem. Commun.,* 2015, **51**, 7802. (*b*) Q.-W. Zhang, K. An, L.-C. Liu, Y. Yue, W. He, *Angew. Chem., Int. Ed.,* 2015, **54**, 6918. (*c*) M. Murai, K. Matsumoto, Y. Takeuchi, K. Takai, *Org. Lett.,* 2015, **17**, 3102.

13 Recent reviews: (*a*) W. Zi, F. D. Toste, *Chem. Soc. Rev.,* 2016, DOI: 10.1039/C5CS00929D. (*b*) M. Brill, S. P. Nolan, *Top. Organomet. Chem.,* 2016, DOI: 10.1007/3418_2015_142. (*c*) B. Ranieri, I. Escofeta, A. M. Echavarren, *Org. Biomol. Chem.,* 2015, **13**, 7103. (*d*) S. M. Inamdar, A. Konala, N. T. Patil, *Chem. Commun.,* 2014, **50**, 15124. (*e*) A. D. Lackner, F. D. Toste, *Acc. Chem. Res.,* 2014, **47**, 889.

14 V. Mamane, P. Hannen, A. Fürstner, *Chem. Eur. J.,* 2004, **10**, 4556.

15 Selected recent examples: (*a*) M. W. van der Meijden, E. Gelens, N. Murillo Quiros, J. D. Fuhr, J. Esteban Gayone, H. Ascolani, K. Wurst, M. Lingenfelder, R. M. Kellogg, *Chem. Eur. J.,* 2016, **22**, 1484. (*b*) Y. Yamamoto, K. Matsui, M. Shibuya, *Chem. Eur. J.,* 2015, **21**, 7245. (*c*) J. Liu, B.-W. Li, Y.-Z. Tan, A. Giannakopoulos, C. Sanchez-Sanchez, D. Beljonne, P. Ruffieux, R. Fasel, X. Feng, K. Mullen, *J. Am. Chem. Soc.,* 2015, **137**, 6097. (*d*) K. Mitsudo, H. Sato, A. Yamasaki, N. Kamimoto, J. Goto, H. Mandai, S. Suga, *Org. Lett.,* 2015, **17**, 4858.

16 K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya, K. Tanaka, *J. Am. Chem. Soc.,* 2014, **136**, 5555.

17 M. R. Buchmeiser, N. Schuler, G. Kaltenhauser, K.-H. Ongania, I. Lagoja, K. Wurst, H. Schottenberger, *Macromolecules,* 1998, **31**, 3175.

18 (*a*) D. Seyferth, R. S. Marmor, P. Hilbert, *J. Org. Chem.,* 1971, **36**, 1379. (*b*) J. C. Gilbert, U. Weerasooriya, *J. Org. Chem.,* 1982, **47**, 1837.

19 B. Long, S. Liang, D. Xin, Y. Yang, J. Xiang, *Eur. J. Med. Chem.,* 2009, **44**, 2572.

20 (*a*) S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, *Synlett*, 1996, 521. (*b*) S. Ohira, *Synth. Commun.,* 1989, **19**, 561.

21 (*a*) A. Pradal, S. Gladiali, V. Michelet, P. Y. Toullec, *Chem. Eur. J.,* 2014, **20**, 7128. (*b*) A. Marinetti, H. Jullien, A. Voituriez, *Chem. Soc. Rev.,* 2012, **41**, 4884. (*c*) I. D. G. Watson, F. D. Toste, *Chem. Sci.,* 2012, **3**, 2899.

22 (*a*) J. F. Jensen, I. Sotofte, H. O. Sorensen, M. Johannsen, *J. Org. Chem.,* 2003, **68**, 1258. (*b*) J. G. Seitzberg, C. Dissing, I. Sotofte, P.-O. Norrby, M. Johannsen, *J. Org. Chem.,* 2005, **70**, 8332.

23 J. F. Jensen, M. Johannsen, *Org. Lett.,* 2003, **5**, 3025.

24 (*a*) H.-L. Zhang, X.-L. Hou, L.-X. Dai, Z.-B. Luo, *Tetrahedron: Asymmetry,* 2007, **18**, 224. (*b*) C. Pichon, B. Odell, J. M. Brown, *Chem. Commun.,* 2004, 598.

25 H. Lehner, K. Schlögl, *Monatsh. Chem.,* 1970, **101**, 895.

26 E. J. Corey, P. L. Fuchs, *Tetrahedron Lett.,* 1972, **13**, 3769.

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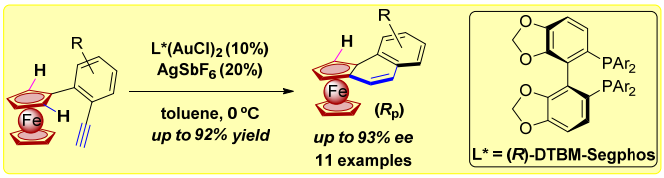

An enantioselective cationic gold(I)-catalyzed cycloisomerization of aquiral 2-alkynylaryl ferrocenes provides differently substituted tricyclic and tetracyclic (R_p) planar-chiral *ortho*-condensed aromatic ferrocenes in high yield and enantioselectivity from an efficient intramolecular hydroarylation.