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Pt-Catalyzed Enantioselective Cycloisomerization for the Synthesis of Planar-Chiral Ferrocene Derivatives

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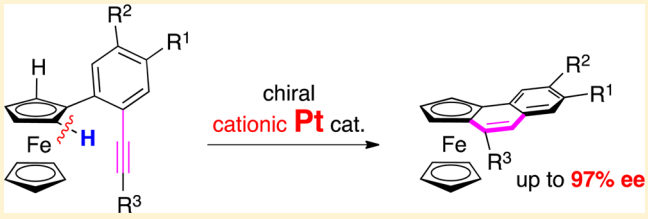
Supporting Information

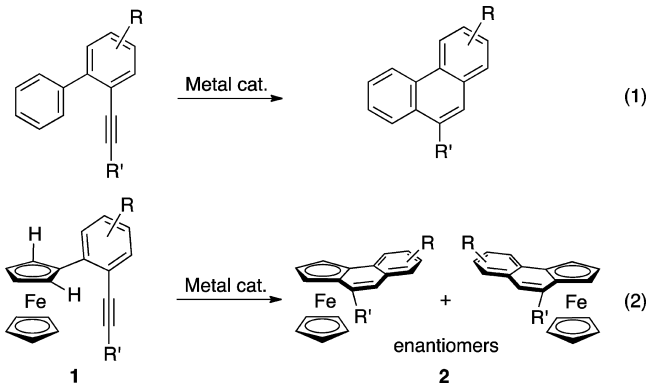
ABSTRACT: Enantioselective cycloisomerization of 2-ethynyl-1-ferrocenylbenzene derivatives proceeded by using a chiral cationic platinum catalyst at room temperature. The intramolecular reaction gave planar−chiral naphthalene- and anthracene-fused ferrocene derivatives with high to excellent ee.



INTRODUCTION

Transition metal-catalyzed cycloisomerization is an atom-economical protocol for the synthesis of cyclic compounds. 1,*n*-Enyne is the most conventional substrate, and various types of products can be selectively prepared by the choice of the reaction conditions, such as metal catalysts and additives.[1] Enantioselective cycloisomerization using various chiral transition metal catalysts has also been comprehensively studied[2] since Zhang's pioneering work of chiral cationic Rh-catalyzed ene-type reaction.[3] We also reported the first enantioselective cycloisomerization for the preparation of chiral bicyclo[4.1.0]-heptane derivatives by using a chiral cationic Ir catalyst.[4] While these asymmetric cycloisomerizations generate one or two stereogenic centers, Tanaka[5] and Uemura[6] reported the creation of axial chirality by chiral Pd-catalyzed reaction of enynes possessing a bulky substituent at the alkyne terminus. In addition to enynes, 2-alkynylbiphenyl derivatives are also typical substrates, and phenanthrene derivatives were prepared (eq 1 in Scheme 1)[7] since Fürstner's report of Pt-catalyzed reaction.[7a] We also reported cationic Au(I)-catalyzed reaction for the preparation of substituted phenanthrenes.[7d] Against this background, we considered that the cycloisomerization of 2-alkynyl-1-ferrocenylbenzenes **1** gives planar−chiral naphthalene-fused ferrocene derivatives **2** (eq 2 in Scheme 1). Asymmetric synthesis of planar−chiral ferrocenes is a hot topic in recent years,[8] and enantioselective intramolecular reactions along with cleavage of ferrocene's C−H bond were reported in rapid succession.[9,10] The present work provides a new strategy for the creation of planar−chirality in ferrocene derivatives.[11]

Scheme 1. Cycloisomerization of 2-Alkynylbiphenyls and 2-Alkynyl-1-ferrocenylbenzenes



RESULTS AND DISCUSSION

We chose 2-ethynyl-1-ferrocenylbenzene (**1a**) as a model substrate and prepared it from ferrocene (Scheme 2): the reaction of diazo compound derived from 2-iodoaniline with ferrocene gave 2-ferrocenyl-1-iodobenzene (**3**).[12] Subsequent Sonogashira coupling of **3** with trimethylsilylacetylene along with desilylation provided the substrate **1a**.

We subjected **1a** to various reaction conditions (Table 1). Both cationic Au(I) complex[7d] and Pt(II) salt[7a] gave the desired cycloadduct **2a**, yet in low yield because of low conversion (entries 1 and 2). Next, we screened several silver salt additives and found that they had dramatic effects (entries 3−5): tetrafluoroborate was the best counteranion, and cycloadduct **2a** was obtained in excellent yield at room temperature. The palladium counterpart did not give the desired product at all (entry 6). The reaction using a cationic Ir catalyst[4] proceeded, but it required heating, and the yield was low (entry 7).

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Scheme 2. Preparation of 2-Ethynyl-1-ferrocenylbenzene (1a)

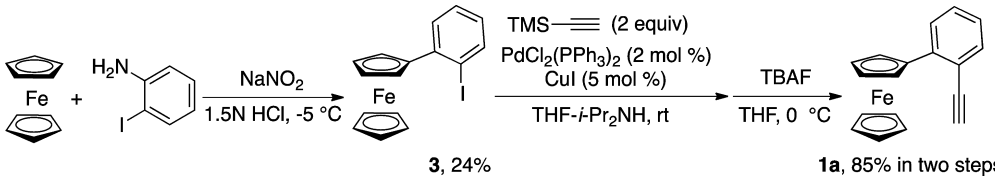
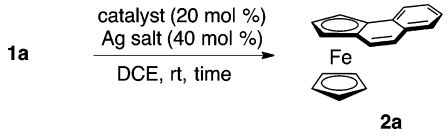


Table 1. Screening of Metal Catalysts for the Cycloisomerization of 1a

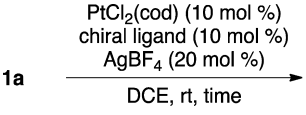


entry	catalyst	Ag salt	time (h)	yield (%)
1[a]	**Au**Cl(PPh$_3$)	AgOTf	24	14
2	**Pt**Cl$_2$	none	30	8
3	**Pt**Cl$_2$(PPh$_3$)$_2$	AgOTf	24	6
4	**Pt**Cl$_2$(PPh$_3$)$_2$	AgSbF$_6$	24	52
5	**Pt**Cl$_2$(PPh$_3$)$_2$	AgBF$_4$	17	93
6	**Pd**Cl$_2$(PPh$_3$)$_2$	AgBF$_4$	24	ND
7[a,b]	**Ir**Cl(CO)(PPh$_3$)$_2$	AgOTf	24	15

[a]AgOTf (20 mol %) was used. [b]The reaction was conducted at 60 °C.

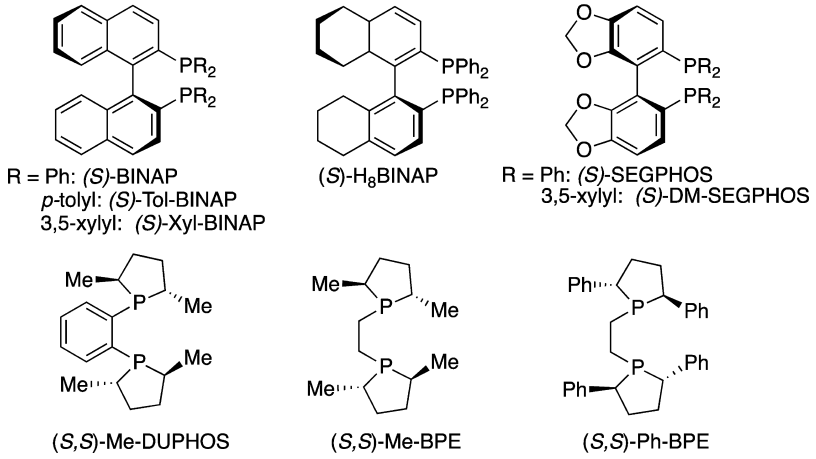
We next examined cationic Pt-catalyzed enantioselective cycloisomerization of **1a** using various chiral diphosphine ligands (Table 2).[13] When BINAP was used, the substrate was completely consumed at room temperature, and chiral ferrocene derivative **2a** was obtained in moderate yield and ee (entry 1). Bulkier Tol-BINAP realized shorter reaction time and excellent yield along with increased ee, but further bulkier Xyl-BINAP did not improve ee (entries 2 and 3). Among modified BINAP derivatives, H$_8$−BINAP and SEGPHOS induced enantioselectivities with comparable levels to Xyl-BINAP, and DM-SEGPHOS achieved high yield with the best ee of 73% (entries 4−6). In contrast, a series of DUPHOS ligands gave strikingly different results: while Me-DUPHOS did not give the product at all, Me-BPE achieved good yield along with moderate ee (entries 7 and 8). Finally, we found that Ph-BPE was the best, and excellent yield of 97% and ee of 96% were achieved by complete consumption of the substrate (entry 9). When dichloromethane was used as a solvent, the yield was decreased along with the recovery of the substrate (entry 10).

Table 2. Screening of Chiral Ligands in Cationic Pt-Catalyzed Cycloisomerization



entry	chiral ligand	time (h)	yield (%)	ee (%)
1	(*S*)-BINAP	21	50	50
2	(*S*)-Tol-BINAP	8	96	64
3	(*S*)-Xyl-BINAP	14	84	58
4	(*S*)-H$_8$−BINAP	21	87	67
5	(*S*)-SEGPHOS	21	69	70
6	(*S*)-DM-SEGPHOS	21	90	73
7	(*S*,*S*)-Me-DUPHOS	8	ND	
8	(*S*,*S*)-Me-BPE	17	77	−57
9	**(*S*,*S*)-Ph-BPE**	**20**	**97**	**96**
10[a]	(*S*,*S*)-Ph-BPE	24	80	94

[a]The reaction was conducted in CH_2Cl_2.



Under the optimal reaction conditions (entry 9 in Table 2), the reaction of various 2-ethynyl-1-ferrocenylbenzene derivatives possessing a substituent on the benzene ring was examined (Table 3). When an electron donating group, such as methyl and methoxy groups, was present in the para-position of the aryl group, the cycloisomerization gave the corresponding cycloadducts **2b** and **2c**, respectively, with good to excellent ee (entries 1 and 2). Electron-withdrawing substituents, such as chloro and fluoro groups, were also tolerated (entries 3 and 4), but a drastic decrease in ee was observed by the introduction of trifluoro group (entry 5). The meta-chloro analogue afforded the corresponding cycloadduct **2g** in excellent ee of 94% (entry 6).

We further prepared 2-ethynyl-1-ferrocenylnaphthalene (**1h**) in three steps (Scheme 3): Suzuki coupling of 2,3-dibromonaphthalene with ferroceneboronic acid gave 2-bromo-3-ferrocenylnaphthalene (**4**). Subsequent Sonogashira coupling with

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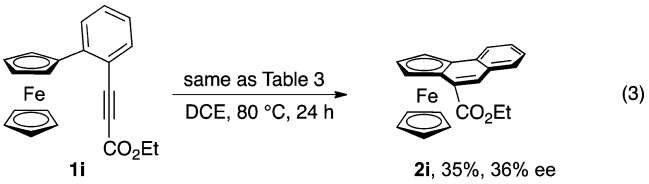
trimethylsilylacetylene along with desilylation provided **1h**. Compound **1h** was transformed into planar−chiral anthracene-fused ferrocene **2h** in good yield with high ee under the optimal conditions. Moreover, a single recrystallization of **2h** gave an almost enantiomerically pure sample, whose structure was determined to be the R_p isomer by X-ray analysis (Figure 1).

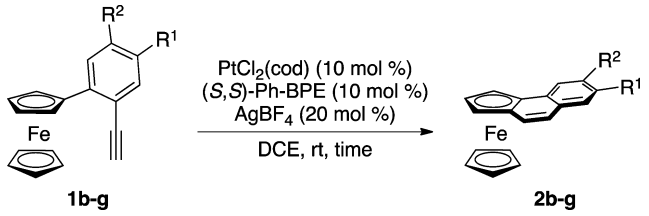
The reaction of ferrocene derivative **1i** possessing a substituted alkyne moiety required heating to 80 °C, and the yield and ee of cycloadduct **2i** was low by using the same chiral catalyst as that above (eq 3).



1i **2i**, 35%, 36% ee (3)

A preliminary mechanistic study was conducted by using **1a-D**, whose alkyne terminus was deuterated (D content: 85%). The kinetic isotope effect (KIE) was measured by two-pot experiments using **1a** and **1a-D**: both reactions were quenched at 1.5 h, and the KIE was determined to be 1.05, which means that C−H bond cleavage is not a rate-determining step (Scheme 4).[14] In the recovered substrate **1a-D**, a slight decrease of D-content was observed. As for the product, a slight H/D scrambling occurred at the 1 and 2 positions of the naphthalene-fused ferrocene **2a** (eq 5 in Scheme 4). These results mean that the major pathway of this reaction is activation of the alkyne moiety by π-acidity of the chiral cationic Pt catalyst followed by 6-endo-dig cyclization,[15] and the minor pathway proceeds via alkyne-vinylidene rearrangement (Scheme 5).[16]

Table 3. Substrate Scope of Chiral Pt-Catalyzed Enantioselective Cycloisomerization



1b-g **2b-g**

entry		R^1	R^2	time (h)	yield (%)	ee (%)
1	**1b**	Me	H	21	**2b**, 83	97
2	**1c**	MeO	H	22	**2c**, 70	80
3	**1d**	Cl	H	15	**2d**, 89	75
4	**1e**	F	H	15	**2e**, 93	88
5	**1f**	CF_3	H	20	**2f**, 69	18
6	**1g**	H	Cl	18	**2g**, 62	94

CONCLUSIONS

We achieved the enantioselective synthesis of arene-fused ferrocene compounds by the cycloisomerization of 2-ethynyl-1-ferrocenylbenzene derivatives. A chiral cationic Pt-complex efficiently catalyzed the intramolecular reaction, and planar−chiral cycloadducts were obtained with up to 97% ee. The asymmetric preparation of further π-expanded planar−chiral ferrocenes is ongoing in our laboratory.

EXPERIMENTAL SECTION

General. ^{1}H NMR spectra were recorded on 500 MHz spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained by 125 MHz spectrometers and referenced to the internal solvent signals (the central peak is 77.16 ppm in $CDCl_3$). $CDCl_3$ was used as a NMR solvent. High-resolution mass spectra (HRMS) were measured on an ESI (Electro Spray Ionization) with the Orbitrap mass spectrometer method. Preparative thin-layer chromatography (PTLC) was performed with silica gel-precoated glass plates prepared in our laboratory, and flash column chromatography was performed over silica gel 200−300. All reagents were weighed and handled in air and backfilled under argon

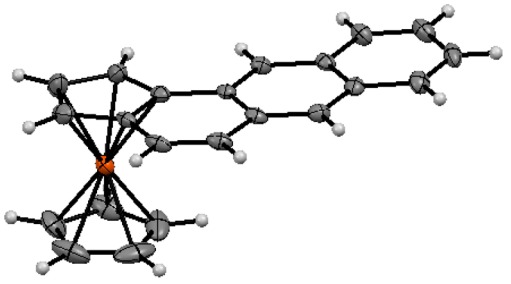
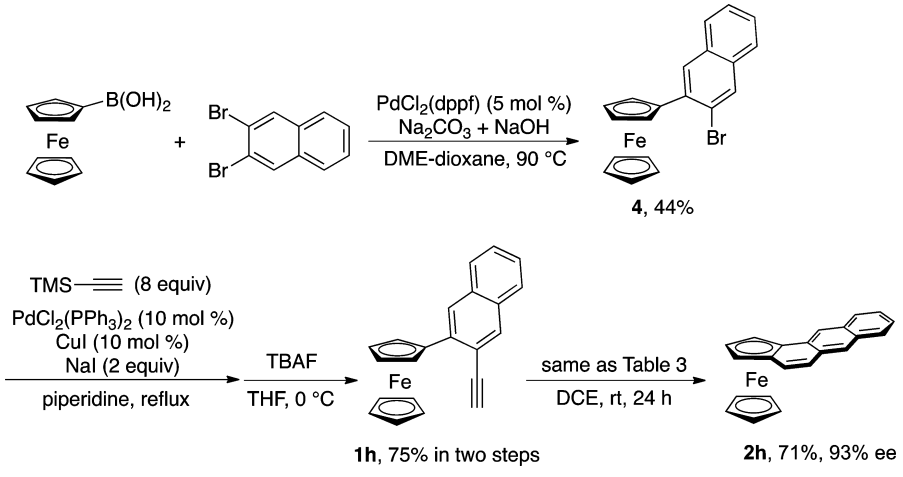


Figure 1. ORTEP diagram of compound **2h** (thermal ellipsoids shown at 50% probability).

Scheme 3. Preparation of Planar−Chiral Anthracene-Fused Ferrocene 2h



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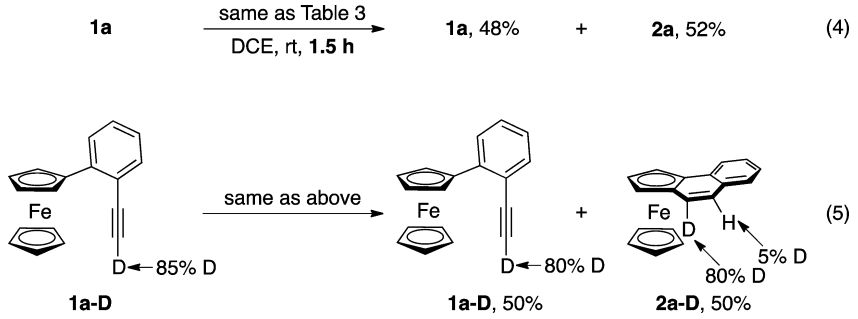
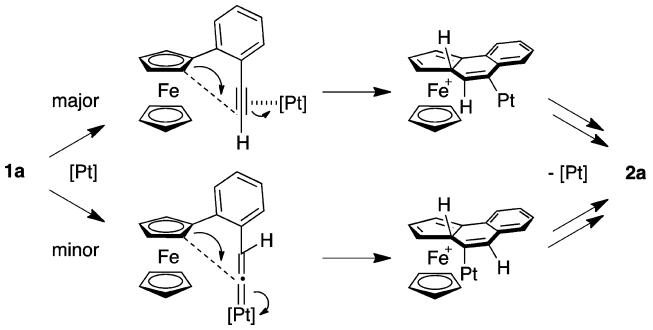
Scheme 4. Preliminary Mechanism Study Using the Deuterated Substrate



Scheme 5. Proposed Mechanism of Major and Minor Pathways



at room temperature, and all reactions were conducted under an argon atmosphere.

*Experimental Procedure for the Synthesis of 2-Ferrocenyl-1-iodobenzene (**3**).* Water (27.5 mL), concentrated hydrochloric acid (4 mL), and 2-iodoaniline (767 mg, 3.5 mmol) were added into a two necked flask, then a sodium nitrite solution in water (1 mg/mL, 4 mL, 7.0 mmol) was added dropwise by maintaining the temperature below −5 °C. After 1 h, sulfamic acid (408 mg, 4.2 mmol) was added.[17] A solution of ferrocene (651 mg, 3.5 mmol) and NaOAc (574 mg, 7.0 mmol) in DCM (30 mL) was added to the above mixture. The solution was stirred overnight at room temperature. After the reaction was complete, the mixture was extracted with DCM and washed with brine, water, and $NaHCO_3$ aq. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (hexane/dichloromethane = 10/1) to give 2-ferrocenyl-1-iodobenzene (**3**) (333 mg, 0.86 mmol, 24%), whose physical properties were in accordance with those in the literature.[12] In the case of substituted 2-ferrocenyl-1-iodobenzenes, the crude products were passed through a short plug of silica gel and subject to Sonogahira coupling without isolation.

*Experimental Procedure for the Synthesis of 2-Ethynyl-1-ferrocenylbenzene (**1a**).* A mixture of 2-ferrocenyl-1-iodobenzene (397 mg, 1 mmol), $PdCl_2(PPh_3)_2$ (14.9 mg, 0.02 mmol), CuI (9.8 mg, 0.05 mmol), diisopropylamine (0.75 mL, 5 mmol), trimethylsilylacetylene (0.25 mL, 2 mmol), and dried THF (10 mL) was stirred overnight at room temperature. To the above solution was added TBAF (2 mL, 2 mmol 1 M in THF) at 0 °C. After stirring for 5 h, the reaction was quenched with saturated aqueous NH_4Cl, and the reaction mixture was extracted with DCM and washed with brine. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/toluene = 10/1) to afford 1-ethynyl-2-ferrocenylbenzene (**1a**) (253 mg, 0.90 mmol, 85%). ^{1}H NMR δ 7.59 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.27 (dd, J = 7.5, 7.9 Hz, 1H), 7.14 (dd, J = 7.5, 7.6 Hz, 1H), 4.94 (m, 2H), 4.33−4.32 (m, 2H), 4.10 (s, 5H), 3.31 (s, 1H); ^{13}C NMR δ 141.6, 134.8, 129.2, 128.7, 125.7, 119.6, 84.6, 84.5, 81.3, 69.9, 69.2, 68.8; HRMS(ESI) calcd for $C_{18}H_{14}Fe$ (M^+): 286.0438; found, 286.0439.

*2-Ethynyl-1-ferrocenyl-5-methylbenzene (**1b**).* Isolated by column chromatography (hexane/toluene = 10/1, R_f = 0.5). The title compound was obtained as a orange oil (88.4 mg, 20% in three steps). ^{1}H NMR δ 7.48 (d, J = 8.1 Hz, 1H), 7.30 (s, 1H), 7.09 (d, J = 8.1 Hz, 1H), 4.91 (m, 2H), 4.31−4.30 (m, 2H), 4.09 (s, 5H), 3.28 (s, 1H), 2.29 (s, 3H); ^{13}C NMR δ 138.4, 135.3, 135.0, 129.7, 128.9, 119.2, 84.6, 84.6, 80.8, 69.7, 68.9, 68.5, 20.8; HRMS(ESI) calcd for $C_{19}H_{16}Fe$ (M^+): 300.0595; found, 300.0596.

*3-Ethynyl-4-ferrocenyl-anisole (**1c**).* Isolated by column chromatography (hexane/toluene = 10/1, R_f = 0.3). The title compound was obtained as a orange oil (389.3 mg, 17% in three steps). ^{1}H NMR δ 7.51 (d, J = 8.7 Hz, 1H), 6.99 (d, J = 2.8 Hz, 1H), 6.87 (dd, J = 2.8, 8.7 Hz, 1H), 4.86 (dd, J = 1.9, 1.9 Hz, 2H), 4.28 (dd, J = 1.9, 1.9 Hz, 2H), 4.09 (s, 5H), 3.81 (s, 3H), 3.29 (s, 1H); ^{13}C NMR δ 157.2, 133.8, 130.3, 120.2, 118.3, 116.0, 84.7, 84.3, 81.0, 69.6, 68.7, 68.3, 55.4; HRMS(ESI) calcd for $C_{19}H_{16}FeO$ (M^+): 316.0544; found, 316.0545.

*1-Chloro-3-ethynyl-4-ferrocenylbenzene (**1d**).* Isolated by thin-layer chromatography (hexane only, R_f = 0.5). The title compound was obtained as a orange oil (89.4 mg, 15% in three steps). ^{1}H NMR δ 7.52 (d, J = 8.5 Hz, 1H), 7.46 (d, J = 2.3 Hz, 1H), 7.25 (dd, J = 2.3, 8.5 Hz, 1H), 4.92 (dd, J = 1.9, 1.9 Hz, 2H), 4.35 (dd, J = 1.9, 1.9 Hz, 2H), 4.11 (s, 5H), 3.36 (s, 1H); ^{13}C NMR δ 140.4, 134.1, 131.0, 130.3, 129.0, 120.9, 83.4, 83.2, 82.4, 69.9, 69.1, 69.1; HRMS(ESI) calcd for $C_{18}H_{13}ClFe$ (M^+): 320.0049; found, 320.0050.

*3-Ethynyl-4-ferrocenyl-1-fluorobenzene (**1e**).* Isolated by thin-layer chromatography (hexane only, R_f = 0.3). The title compound was obtained as an orange solid (184.1 mg, 19% in three steps). Mp 65 °C; ^{1}H NMR δ 7.56 (dd, J = 5.7, 8.8 Hz, 1H), 7.17 (dd, J = 2.7, 9.2 Hz, 1H), 7.02−6.98 (m, 1H), 4.88−4.87 (m, 2H), 4.32−4.31 (m, 2H), 4.10 (s, 5H), 3.33 (s, 1H); ^{13}C NMR δ 160.2 (d, J_{C-F} = 245.9 Hz, 1C), 137.6 (d, J_{C-F} = 3.3 Hz, 1C), 130.7 (d, J_{C-F} = 8.1 Hz, 1C), 120.8 (d, J_{C-F} = 8.9 Hz, 1C), 120.6 (d, J_{C-F} = 22.7 Hz, 1C), 116.2 (d, J_{C-F} = 21.5 Hz, 1C), 83.8, 83.1 (d, J_{C-F} = 2.7 Hz, 1C), 82.0, 69.7, 69.0, 68.6; HRMS(ESI) calcd for $C_{18}H_{13}FFe$ (M^+): 304.0345; found, 304.0345.

*2-Ethynyl-1-ferrocenyl-4-trifluoromethylbenzene (**1f**).* Isolated by column chromatography (hexane only, R_f = 0.3). The title compound was obtained as an orange solid (136.0 mg, 21% in three steps). Mp 70 °C; ^{1}H NMR δ 7.72 (s, 1H), 7.68 (d, J = 8.4 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.00−4.99 (m, 2H), 4.40−4.39 (m, 2H), 4.11 (s, 5H), 3.40 (s, 1H); ^{13}C NMR δ 145.8, 131.7 (q, J_{C-F} = 3.9 Hz, 1C), 129.4, 127.8 (q, J_{C-F} = 33.1 Hz, 1C), 125.1 (q, J_{C-F} = 3.6 Hz, 1C), 124.0 (q, J_{C-F} = 272.1 Hz, 1C), 119.9, 83.2, 82.7, 82.7, 70.1, 69.6, 69.4; HRMS(ESI) calcd for $C_{19}H_{13}F_3Fe$ (M^+): 354.0313; found, 354.0313.

*1-Chloro-4-ethynyl-3-ferrocenylbenzene (**1g**).* Isolated by thin-layer chromatography (hexane only, R_f = 0.3). The title compound was obtained as an orange solid (175.4 mg, 20% in three steps). Mp 97 °C; ^{1}H NMR δ 7.55 (d, J = 2.2 Hz, 1H), 7.40 (d, J = 8.3 Hz, 1H), 7.11 (dd, J = 2.2, 8.3 Hz, 1H), 4.95 (dd, J = 1.9, 1.9 Hz, 2H), 4.36 (dd, J = 1.9, 1.9 Hz, 2H), 4.12 (s, 5H), 3.35 (s, 1H); ^{13}C NMR δ 143.6, 135.8, 134.5, 128.7, 125.7, 117.9, 83.4, 83.0, 82.0, 69.9, 69.1, 69.0; HRMS(ESI) calcd for $C_{18}H_{13}ClFe$ (M^+): 320.0050; found, 320.0050.

*Experimental Procedure for the Synthesis of 2-Bromo-3-ferrocenylnaphthalene (**4**).* 2,3-Dibromonaphthalene (575 mg, 2.0 mmol), $PdCl_2$(dppf) (19 mg, 0.025 mmol), ferroceneboronic acid (114 mg, 0.50 mmol), DME (1.6 mL), and dioxane (2.3 mL) were added into a two necked flask, then Na_2CO_3 (199 mg, 1.8 mmol) and 2 M NaOH aqueous solution (0.40 mL) were added. The solution was

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stirred overnight at 90 °C. After the reaction was complete, it was concentrated under reduced pressure, filtered through a short plug of silica gel with AcOEt, and evaporated under reduced pressure. The crude products were purified by thin-layer chromatography (hexane/AcOEt = 20/1) to give 2-bromo-3-ferrocenylnaphthalene (85 mg, 0.22 mmol, 44%). The title compound was obtained as a orange oil. ^{1}H NMR δ 8.20 (s, 1H), 8.09 (s, 1H), 7.82 (d, J = 8.9 Hz, 1H), 7.72 (d, J = 8.9 Hz, 1H), 7.51−7.45 (m, 2H), 4.81 (dd, J = 1.9, 1.9 Hz, 2H), 4.38 (dd, J = 1.9, 1.9 Hz, 2H), 4.20 (s, 5H); ^{13}C NMR δ 136.5, 132.9, 132.1, 131.9, 130.4, 127.4, 126.6, 126.6, 126.4, 121.1, 86.8, 70.4, 69.7, 68.3; HRMS(ESI) calcd for $C_{20}H_{15}BrFe$ (M^+): 389.9703; found, 389.9701.

*Experimental Procedure for the Synthesis of 3-Ethynyl-2-ferrocenylnaphthalene (**1h**).* To a solution of 2-bromo-3-ferrocenylnaphthalene (131 mg, 0.34 mmol), NaI (113 mg, 0.75 mmol), $PdCl_2(PPh_3)_2$ (26 mg, 0.034 mmol), and CuI (7 mg, 0.034 mmol) in piperidine (4 mL) was added trimethylsilylacetylene (0.3 mL, 2.7 mmol) at room temperature. The mixture was refluxed for 2 days. After cooling to room temperature, to the above solution was added TBAF (0.7 mL, 0.68 mmol 1 M in THF) at 0 °C. After stirring for 7 h, the reaction was quenched with saturated aqueous NH_4Cl, and the reaction mixture was extracted with DCM and washed with brine. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by thin-layer chromatography (hexane/toluene = 10/1) to give 3-ethynyl-2-ferrocenylnaphthalene (**1h**) (85 mg, 0.25 mmol, 75%). The title compound was obtained as an orange solid. Mp 97 °C; ^{1}H NMR δ 8.06 (s, 1H), 8.00 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.74 (d, J = 7.9 Hz, 1H), 7.49−7.42 (m, 2H), 5.05 (m, 2H), 4.38−4.37 (m, 2H), 4.13 (s, 5H), 3.39 (s, 1H); ^{13}C NMR δ 137.5, 135.1, 133.1, 131.2, 127.3, 127.2, 127.2, 127.0, 125.9, 118.4, 84.7, 84.5, 81.1, 69.7, 68.9, 68.7; HRMS(ESI) calcd for $C_{22}H_{16}Fe$ (M^+): 336.0595; found, 336.0596.

*Preparation of 3-(Ethoxycarbonyl)ethynyl-2-ferrocenylnaphthalene (**1i**).* The title compound was prepared by ethoxy carbonylation of alkyne **1a** according to the literature procedure[18] and isolated by column chromatography (hexane/ethyl acetate =20/1, R_f = 0.4). The title compound was obtained as an orange oil (298.5 mg, 60%). ^{1}H NMR δ 7.59−7.55 (m, 2H), 7.34 (ddd, J = 7.7, 7.7, 1.4 Hz, 1H), 7.18 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 4.93 (dd, J = 1.9, 1.9 Hz, 2H), 4.38 (dd, J = 1.9, 1.9 Hz, 2H), 4.32 (q, J = 7.2 Hz, 2H), 4.13 (s, 5H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 154.5, 143.7, 135.6, 130.5, 129.0, 125.8, 116.9, 87.5, 84.7, 83.6, 70.0, 69.4, 69.0, 62.1, 14.3; HRMS(ESI) calcd for $C_{21}H_{18}FeNaO_2$ (M + Na): 381.0549; found, 381.0548.

*Typical Experimental Procedure for Enantioselective Cycloisomerization of **1**.* $PtCl_2$(cod) (2.5 mg, 0.005 mmol), (*S*,*S*)-Ph-BPE (2.8 mg, 0.005 mmol), and $AgBF_4$ (2.8 mg, 0.01 mmol) were stirred in dichloromethane (1 mL) for 1 h at room temperature. After the removal of solvent *in vacuo*, **1** (0.05 mmol) and DCE (0.15 mL) were added to the resulting residue and stirred at room temperature. The progress of the reaction was monitored by TLC. After the reaction was complete, it was filtered through a short plug of silica gel with AcOEt, and the filtrate was evaporated under reduced pressure. The crude products were purified by thin-layer chromatography (hexane/dichloromethane = 15/1) to give compound **2**.

*Naphtho[1,2-a]ferrocene (**2a**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.5). The title compound was obtained as a red solid (17.5 mg, 97%). Mp 59 °C; ^{1}H NMR δ 7.99 (d, J = 7.8 Hz, 1H), 7.62 (d, J = 7.7 Hz, 1H), 7.46 (dd, J = 7.2, 7.8 Hz, 1H), 7.41−7.37 (m, 2H), 7.16 (d, J = 9.1 Hz, 1H), 5.26−5.25 (m, 1H), 4.81−4.80 (m, 1H), 4.22 (dd, J = 2.5, 2.6 Hz, 1H), 3.73 (s, 5H); ^{13}C NMR δ 135.1, 131.9, 128.6, 127.5, 126.6, 125.2 (a pair of peaks at the aromatic region is overlapped), 123.3, 83.9, 83.0, 69.3, 69.2, 64.0, 61.1; UV−vis (CH_2Cl_2, 1 × 10^{-4} M) λ_{abs} (nm) (ε × 10^2, M^{-1} cm^{-1}) 233.5 (222.4), 255 (238.6), 379.5 (9.6), 489 (3.1). HRMS(ESI) calcd for $C_{18}H_{14}Fe$ (M^+): 286.0438; found, 286.0439; $[\alpha]^{24}_D$= +4374 (*c* 0.47, $CHCl_3$, 96% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 1% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 14.6 min for the major isomer and 17.1 min for the minor isomer).

*6-Methylnaphtho[1,2-a]ferrocene (**2b**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.5). The title compound was obtained as a red solid (12.0 mg, 83%). Mp 45 °C; ^{1}H NMR δ 7.88 (d, J = 7.9 Hz, 1H), 7.42 (s, 1H), 7.35 (d, J = 9.1 Hz, 1H), 7.29 (d, J = 7.9 Hz, 1H), 7.11 (d, J = 9.1 Hz, 1H), 5.22 (s, 1H), 4.77 (s, 1H), 4.19 (s, 1H), 3.72 (s, 5H), 2.47 (s, 3H); ^{13}C NMR δ 134.8, 132.4, 132.1, 128.8, 128.1, 127.6, 125.2, 123.3, 83.8, 83.5, 69.4, 69.1, 63.9, 61.0, 21.6. HRMS(ESI) calcd for $C_{19}H_{16}Fe$ (M^+): 300.0595; found, 300.0596; $[\alpha]^{30}_D$= +1242 (*c* 0.69, $CHCl_3$, 97% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IC-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 1% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 15.9 min for the major isomer and 18.9 min for the minor isomer).

*6-Methoxynaphtho[1,2-a]ferrocene (**2c**).* Isolated by thin-layer chromatography (hexane/toluene = 10/1, R_f = 0.4). The title compound was obtained as a red solid (11.8 mg, 70%). Mp 88 °C (decomp.); ^{1}H NMR δ 7.90 (d, J = 8.2 Hz, 1H), 7.38 (d, J = 9.1 Hz, 1H), 7.12−7.08 (m, 3H), 5.20 (s, 1H), 4.77 (s, 1H), 4.17 (dd, J = 2.4, 2.4 Hz, 1H), 3.91 (s, 3H), 3.73 (s, 5H); ^{13}C NMR δ 157.5, 133.2, 128.4, 128.1, 124.9, 124.5, 115.2, 111.0, 83.8, 83.0, 69.2, 68.8, 63.7, 60.5, 55.4. HRMS(ESI) calcd for $C_{19}H_{16}FeO$ (M^+): 316.0544; found, 316.0545; $[\alpha]^{26}_D$= +332 (*c* 0.62, $CHCl_3$, 80% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IB-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 1% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 18.3 min for the major isomer and 21.0 min for the minor isomer).

*6-Chloronaphtho[1,2-a]ferrocene (**2d**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.4). The title compound was obtained as a red solid (14.1 mg, 89%). Mp 110 °C; ^{1}H NMR δ 7.91 (d, J = 8.4 Hz, 1H), 7.60−7.59 (m, 1H), 7.44−7.40 (m, 2H), 7.07 (d, J = 9.2 Hz, 1H), 5.24 (m, 1H), 4.82 (m, 1H), 4.24 (dd, J = 2.5, 5.0 Hz, 1H), 3.74 (s, 5H); ^{13}C NMR δ 133.6, 133.2, 130.7, 129.2, 127.8, 126.8, 124.6, 124.0, 83.6, 82.4, 69.6, 69.4, 64.3, 61.3; HRMS(ESI) calcd for $C_{18}H_{13}ClFe$ (M^+): 320.0050; found, 320.0050; $[\alpha]^{25}_D$= +3047 (*c* 0.365, $CHCl_3$, 75% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3:4.6 × 250 mm and AD-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 0.5% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 20.1 min for the major isomer and 21.6 min for the minor isomer).

*6-Fluoronaphtho[1,2-a]ferrocene (**2e**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.5). The title compound was obtained as a red solid (15.0 mg, 93%). Mp 48 °C; ^{1}H NMR δ 7.96−7.93 (m, 1H), 7.43 (d, J = 9.0 Hz, 1H), 7.30−7.28 (m, 1H), 7.21−7.18 (m, 1H), 7.10 (d, J = 9.0 Hz, 1H), 5.23 (s, 1H), 4.80 (s, 1H), 4.22 (s, 1H), 3.73 (s, 5H); ^{13}C NMR δ 160.8 (d, J_{C-F} = 242.9 Hz, 1C), 133.4 (d, J_{C-F} = 8.3 Hz, 1C), 131.1 (d, J_{C-F} = 2.4 Hz, 1C), 129.3, 124.9 (d, J_{C-F} = 8.3 Hz, 1C), 124.3 (d, J_{C-F} = 3.0 Hz, 1C), 114.5 (d, J_{C-F} = 23.0 Hz, 1C), 113.7 (d, J_{C-F} = 20.9 Hz, 1C), 83.2, 83.0, 69.3, 69.3, 64.1, 61.0. HRMS(ESI) calcd for $C_{18}H_{13}FFe$ (M^+): 304.0344; found, 304.0345; $[\alpha]^{32}_D$= +952 (*c* 0.49, $CHCl_3$, 88% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3:4.6 × 250 mm and AD-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 0.5% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 20.1 min for the major isomer and 21.9 min for the minor isomer).

*6-(Trifluoromethyl)naphtho[1,2-a]ferrocene (**2f**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.5). The title compound was obtained as a red solid (12.2 mg, 69%). Mp 66 °C; ^{1}H NMR δ 8.07 (d, J = 8.2 Hz, 1H), 7.87 (s, 1H), 7.66 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 9.1 Hz, 1H), 7.17 (d, J = 9.1 Hz, 1H), 5.31−5.30 (m, 1H), 4.88 (m, 1H), 4.30 (dd, J = 2.5, 2.6 Hz, 1H), 3.75 (s, 5H); ^{13}C NMR δ 138.7, 131.7, 129.5, 127.1 (q, J_{C-F} = 32.2 Hz, 1C), 125.6 (q, J_{C-F} = 4.2 Hz, 1C), 124.6 (q, J_{C-F} = 225.6 Hz, 1C), 124.6, 123.8, 122.9 (q, J_{C-F} = 3.3 Hz, 1C), 84.4, 81.8, 70.3, 69.6, 64.9, 61.9. HRMS(ESI) calcd for $C_{19}H_{13}F_3Fe$ (M^+): 354.0313; found, 354.0313; $[\alpha]^{26}_D$= +577 (*c* 0.52, $CHCl_3$, 18% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3:4.6 × 250 mm and AD-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 0.5% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 19.2 min for the major isomer and 20.2 min for the minor isomer).

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*7-Chloronaphtho[1,2-a]ferrocene (**2g**).* Isolated by thin-layer chromatography (hexane/dichloromethane = 15/1, R_f = 0.5). The title compound was obtained as a red solid (10.1 mg, 62%). Mp 86 °C (decomp.); ^{1}H NMR δ 7.94 (s, 1H), 7.54 (d, J = 8.2 Hz, 1H), 7.39−7.34 (m, 2H), 7.11 (d, J = 9.1 Hz, 1H), 5.22 (s, 1H), 4.83 (s, 1H), 4.26 (s, 1H), 3.76 (s, 5H); ^{13}C NMR δ 136.8, 132.2, 130.2, 129.8, 128.0, 125.5, 124.2, 122.8, 84.0, 81.9, 69.7, 69.4, 64.3, 61.3. HRMS(ESI) calcd for $C_{18}H_{13}ClFe$ (M^+): 320.0049; found, 320.0050; $[\alpha]^{30}_D$= +3849 (c 0.45, $CHCl_3$, 94% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IA-3:4.6 × 250 mm and AD-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 0.5% 2-propanol in hexane; flow rate, 0.5 mL/min; retention time, 19.2 min for the major isomer and 25.2 min for the minor isomer).

*Anthra[1,2-a]ferrocene (**2h**).* Isolated by thin-layer chromatography (hexane/toluene = 10/1, R_f = 0.5). The title compound was obtained as a red solid (23.6 mg, 71%). Mp 175 °C (decomp.); ^{1}H NMR δ 8.39 (s, 1H), 8.08 (s, 1H), 7.98 (d, J = 7.9 Hz, 1H), 7.94 (d, J = 7.9 Hz, 1H), 7.49 (m, 2H), 7.29 (d, J = 9.2 Hz, 1H), 7.22 (d, J = 9.2 Hz, 1H), 5.35 (s, 1H), 4.76 (s, 1H), 4.32 (s, 1H), 3.77 (s, 5H); ^{13}C NMR δ 133.6, 132.4, 131.7, 131.2, 128.0, 127.7, 127.3, 126.9, 125.7, 125.3, 125.0, 121.0, 82.6, 81.6, 69.9, 69.1, 65.1, 62.2. HRMS(ESI) calcd for $C_{22}H_{16}Fe$ (M^+): 336.0595; found, 336.0596; $[\alpha]^{27}_D$= +4411 (c 0.34, $CHCl_3$, 93% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IC-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 1% 2-propanol in hexane; flow rate, 1.0 mL/min; retention time, 14.3 min for the major isomer and 17.8 min for the minor isomer). The crystal data of compound **2h**: $C_{22}H_{16}Fe$, M = 336.22, monoclinic, space group $P2_1$ (#4), a = 10.9766(7) Å, b = 6.5881(4) Å, c = 10.9953(8) Å, V = 758.08(9) Å^3, Z = 2, μ(Mo−Kα) = 9.892 cm^{-1}; number of reflections measured, total 7365 and unique 3409, R_1 = 0.0294, wR_2 = 0.0941, Flack parameter (Parsons' quotients = 1325) 0.004(11). CCDC 1473235. The CIF file is available in Supporting Information.

*3-(Ethoxycarbonyl)naphtho[1,2-a]ferrocene (**2i**).* Isolated by thin-layer chromatography (hexane/ethyl acetate = 20/1, R_f = 0.5). The title compound was obtained as a purple oil (5.8 mg, 35%). ^{1}H NMR δ 7.48 (d, J = 7.7 Hz, 1H), 7.27 (d, J = 7.5 Hz, 1H), 7.23 (ddd, J = 7.4, 7.4, 1.0 Hz, 1H), 7.09 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 6.56 (s, 1H), 5.62 (dd, J = 0.7, 2.4 Hz, 1H), 4.75 (dd, J = 0.7, 2.4 Hz, 1H), 4.68 (dd, J = 2.4, 2.4 Hz, 1H), 4.34−4.27 (m, 2H), 3.94 (s, 5H), 1.40 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 167.3, 152.6, 142.6, 141.4, 130.2, 125.2, 121.2, 120.1, 106.1, 90.6, 82.4, 73.4, 72.3, 70.3, 63.5, 60.0, 14.5. HRMS(ESI) calcd for $C_{21}H_{18}FeNaO_2$ (M + Na): 381.0548; found, 381.0548; $[\alpha]^{27}_D$ = −824 (c 0.40, hexane, 36% ee). Ee was determined by HPLC analysis using a chiral column (Daicel Chiralpak IC-3:4.6 × 250 mm, 254 nm UV detector, rt; eluent, 5% 2-propanol in hexane; flow rate, 1.0 mL/min; retention time, 7.9 min for the major isomer and 14.2 min for the minor isomer).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00825.

HPLC chromatograph of chiral products **2a**−**2i** and ^{1}H and ^{13}C NMR spectra of all new compounds (PDF)

X-ray crystallographic data of compound **2h** (CIF)

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Notes

The authors declare no competing financial interest.

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