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Cycloisomerization of (arene)chromium complexes with enyne by gold(I) catalyst for axially chiral biaryls

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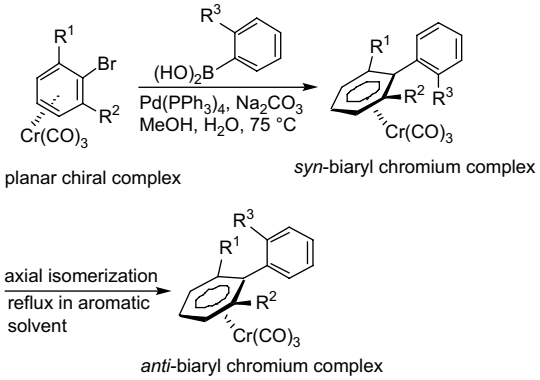
ABSTRACT

Planar chiral arene chromium complexes with enyne bond gave stereoselectively axial biaryl chromium complexes by gold(I) catalyzed cycloisomerization in good yields. Arene chromium complexes with enyne bonds were treated with triphenylphosphine gold bis(trifluoromethanesulfonyl)imidate in methylene chloride to give *anti*-biaryl monochromium complexes without formation of stereoisomers.

1. Introduction

Axially chiral biaryls are of importance not only as chiral ligands or auxiliaries in asymmetric reaction but also for the preparation of biologically active natural products.[1] There is a considerable current interest in the development of efficient methodologies for the synthesis of axially chiral biaryls in an enantiomerically pure form.[2] (η^6-Polysubstituted arene)chromium complexes exist in two enantiomeric forms based on planar chirality when the arene ring is substituted at the *ortho*- or *meta*-position with different substituents. This fact in concert with ability of the tricarbonylchromium function to effectively block one face of the arene ring has led to a rapid increase in the use of (arene)chromium complexes as synthetic intermediates, chiral auxiliaries, and ligands for asymmetric reactions.[3] As part of our asymmetric exploration of the planar chiral arene chromium complexes, we have developed stereoselective synthesis of the axially chiral biaryls in enantiomerically pure form by palladium(0)-catalyzed Suzuki–Miyaura cross-coupling of planar chiral tricarbonyl(2,6-substituted bromobenzene)chromium complexes with *ortho*-substituted arylboronic acids (Scheme 1).[4] It is noteworthy in this methodology that either enantiomer of the axially chiral biaryls can be stereoselectively prepared starting from a single planar chiral arylhalide chromium complex by stereoselective *syn*-coupling and subsequent axial isomerization under thermal conditions. As our further synthetic extension of the planar chiral arene chromium complexes, we herein report gold(I)-catalyzed cycloisomerization of arene tricarbonylchromium complexes with enyne bonds directed toward the synthesis of the axially chiral biaryls.[5]



Scheme 1. Diastereoselective cross-coupling of arene chromium complexes with arylboronic acids.

2. Results and discussion

An activation of alkyne moiety by a metal complex has been increasingly an attractive strategy for catalytic carbon–carbon bond forming reactions. In particular, gold has emerged as a powerful homogeneous catalyst for the electrophilic activation of alkynes, and has been demonstrated in the enyne cyclization.[6] The number of reports on gold catalyzed benzannulation reactions has increased dramatically for the substituted aromatic compounds. It was shown that the cycloisomerization of aromatic enynes gave an access to substituted phenanthrenes, naphthalenes, or styrenes.[7] In the light of these contributions, we applied the gold catalyzed cycloisomerization of enyne bond to the planar chiral arene chromium complexes.

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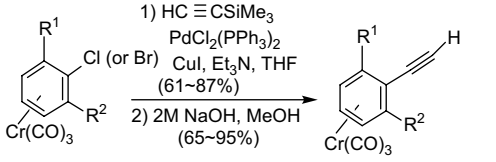
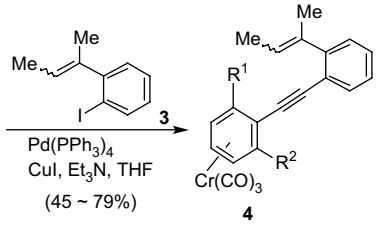
2.1. Synthesis of arene chromium complexes with enyne bond

We designed two types of tricarbonylchromium coordinated arenes with enyne bond for the synthesis of axially chiral biaryls. As one of the starting chromium complexes for this project, diaryl substituted alkyne chromium complexes **4** were prepared by successive Sonogashira coupling from substituted chlorobenzene (or bromobenzene) chromium complexes (Scheme 2). Since Sonogashira coupling of chlorobenzene chromium complex (**1a**) with 2-(1-methyl-1-propenyl)phenylacetylene gave unsatisfactory result for the synthesis of the chromium complex **4a**, stepwise coupling was carried out.[8] Palladium(II)-catalyzed Sonogashira coupling of chlorobenzene chromium complex (**1a**) with trimethylsilylacetylene following deprotection of TMS group produced 2-ethynylanisole chromium complex **2a** in 67% yield. Subsequent Sonogashira coupling of **2a** with *E*- and *Z*-mixture of 2-(1-methyl-1-propenyl)iodobenezene (**3**)[9] gave desired diaryl substituted alkyne chromium complex **4a**. Similarly, other enyne arene chromium complexes **4b**–**4g** were obtained by same procedure.





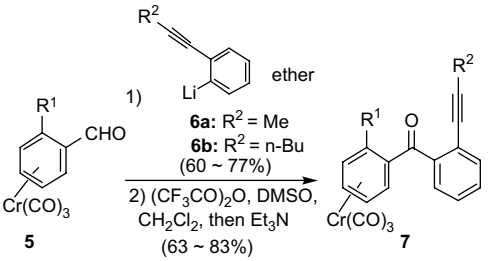
a: $R^1 = R^2 = H$; **b**: $R^1 = H$, $R^2 = Me$; **c**: $R^1 = H$, $R^2 = CH_2OH$; **d**: $R^1 = H$, $R^2 = CH_2OMe$; **e**: $R^1 = OMe$, $R^2 = CH_2OH$; **f**: $R^1 = OMe$, $R^2 = CH_2OMe$; **g**: $R^1 = OMe$, $R^2 = Me$

Scheme 2. Synthesis of arene chromium complexes with enyne bond **4**.

As alternative starting materials for the cycloisomerization, 1,1-diaryl substituted alkene chromium complexes **8** were prepared from substituted benzaldehyde chromium complexes **5** by addition of *o*-alkynyl phenyllithium **6**[10] followed by oxidation and subsequent addition of alkyllithium and dehydration (Scheme 3).

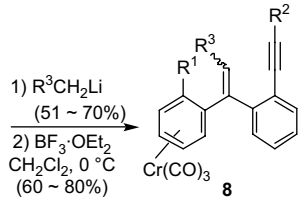
We finally required 2,6-disubstituted benzaldehyde chromium complexes as synthetic precursors directed toward the synthesis of axially chiral biaryls. Therefore, we tried an introduction of formyl group at 2-position of 3-methoxybenzaldehyde ethyleneacetal chromium complex (**9**) by directed lithiation. As already reported, the chromium complex **9** underwent directed lithiation at 2-position to give 2-brominated complex by quenching with 1,2-dibromo-1,1,2,2-tetrafluoroethane in good yield without regioisomer.[4b,11] However, unusual regioselectivity was observed by quenching of the generated lithium intermediate from **9** with DMF. Thus, quenching of the lithium intermediate with DMF gave surprisingly 4-formylated chromium complex **10** without formation of expected 2-formylated compound **11** (Scheme 4).[12]

Therefore, we next turned our attention to the palladium-catalyzed carbonylation for preparation of monochromium complexed benzophenone derivatives (Scheme 5). 2-Bromo-3-methylanisole chromium complex (**1g**)[13] was treated with 2-(1-propynyl)phenylboronic acid (**12**) under 1 atm CO in the presence palladium(0) to



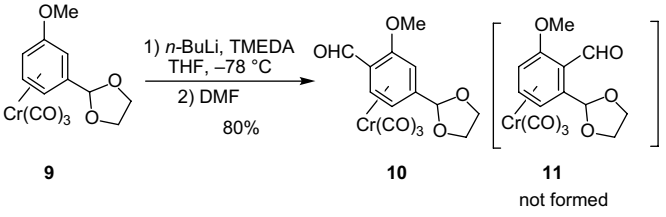
5a: R^1 = Me
5b: R^1 = OMe

7a: $R^1 = R^2$ = Me
7b: R^1 = OMe, R^2 = Me
7c: R^1 = Me, R^2 = n-Bu



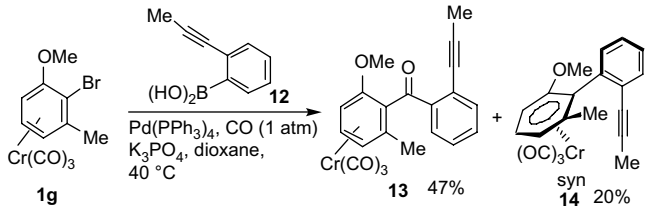
8a; R^1 = R^2 = Me, R^3 = H
8b; R^1 = OMe, R^2 = Me, R^3 = H
8c; R^1 = OMe, $R^2 = R^3$ = Me
8d; R^1 = Me, R^2 = n-Bu, R^3 = H

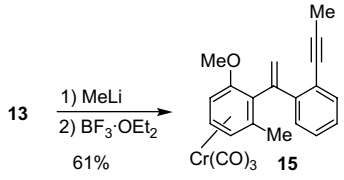
Scheme 3. Synthesis of enyne arene chromium complexes **8**.



Scheme 4. Directed lithiation of chromium complex **9** followed by quenching with DMF.

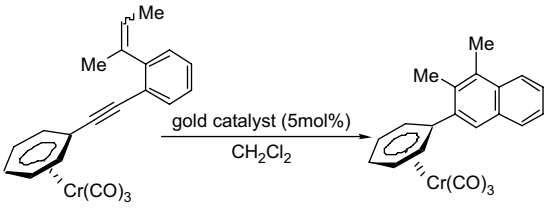
give expected ketone chromium complex **13** in 47% yield along with formation of *syn*-biaryl monochromium complex **14** in 20% yield. Addition of methyllithium to the ketone complex **13** followed by dehydration with $BF_3 \cdot OEt_2$ at 0 °C gave *exo*-methylene compound **15** in 61% yield. For the preparation of *ortho* tetrasubstituted biaryls, we required an addition of ethyl or higher homologue group to the carbonyl group of the chromium complex **13**. However, we could not obtain the addition product of ethyl group by any type of ethyl metal such as ethyllithium, ethyl Grignard, and ethylcerium dichloride reagents.





Scheme 5. Synthesis of enyne arene chromium complex **15**.

Table 1
Screening of cycloisomerization of enyne arene chromium complex



4a **16**

Entry	Gold catalyst	Additive	Temp (°C)	Time (h)	Yield **16** (%)
1	$(Ph_3P)AuCl$	None	40	2	0
2	$(Ph_3P)AuCl$	$AgBF_4$	rt	3.5	20
3	$(Ph_3P)AuCl$	$AgBF_4$	40	5	16
4	$(Ph_3P)AuCl$	$AgSbF_6$	rt	24	33
5	$(Ph_3P)AuCl$	$AgSbF_6$	40	2	43
6	$(Ph_3P)AuCl$	AgOTf	40	5	0
7	$AuCl_3$	None	40	3	0
8	$AuCl_3$	$AgBF_4$	40	3	0
9	$(Ph_3P)AuNTf_2$	None	40	1	84

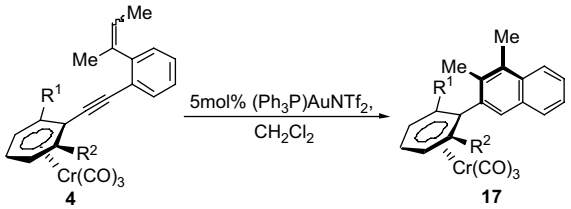
2.2. Gold catalyzed cycloisomerization of enyne arene chromium complexes

With two types of key intermediates for gold catalyzed cycloisomerization in our hand, we initially examined the activity of various gold catalysts for cycloisomerization of the diaryl substituted alkyne chromium complex **4a** (Table 1). No reaction proceeded with $AuCl(PPh_3)$ at room temperature. The addition of Ag salts increased the catalytic activity of Au(I) catalyst for the cycloisomerization. Among various gold catalysts, triphenylphosphine gold bis(trifluoromethanesulfonyl)imidate $(Ph_3P)AuN(Tf)_2$[14] gave most satisfactory results. Thus, treatment of **4a** with 5 mol % $(Ph_3P)AuN(Tf)_2$ in CH_2Cl_2 at 40 °C gave 84% yield of cyclization product **16** via 6-*endo*-*dig*-type mode (entry 9). No 5-*exo*-*dig*-type cyclization product was observed. It is unclear that $(Ph_3P)AuCl$/AgOTf catalyst took place no cycloisomerization (entry 6), while chromium free benzene-linked 1,5-enynes afforded cycloisomerization products in good yield.[7c] Furthermore, methyl group at β-position of the alkene part is significant important for high yield of the cycloisomerization products. No methyl substrate at this position gave 43% yield by using $(Ph_3P)AuN(Tf)_2$ catalyst.

Under the above conditions using $(PPh_3)AuN(Tf)_2$ catalyst, the cycloisomerization of other diaryl substituted alkyne monochromium complexes **4** was next studied (Table 2). It was clarified that the gold(I) catalyzed cycloisomerization of diaryl substituted alkyne monochromium complexes **4** clearly depended on the nature of *ortho* substituent of the chromium-complexed arene ring. The cycloisomerization of the arene chromium complexes with methyl at the *ortho* position **4b** gave expected naphthyl phenyl chromium complex **17b** via 6-*endo*-*dig*-type cyclization in good yield without formation of 5-*exo*-*dig*-type cyclization product (entry 2). However, the arene chromium complex with *ortho* hydroxymethyl substituent afforded no cycloisomerization product of the enyne bonds. Thus, treatment of **4c** in CH_2Cl_2 at room temperature afforded 1*H*-isochromene derivative **18a** as *E*- and *Z*-mixture in 71% yield without formation of desired enyne cyclization product (entry 3). Hydroxy group attacks to the gold-coordinated triple bond in 6-*endo*-*dig*-type cyclization manner. At 40 °C, further cyclization product **19** was obtained as a major product without formation of any stereoisomer (entry 4). An alternative 5-*exo*-*dig*-type cyclization product, 1-benzylidene-1,3-dihydroisobenzofuran chromium complex and its further cyclization product were not observed.

Similarly, it was reported that gold catalyzed cyclization of chromium free *ortho* alkynyl benzylalcohols gave corresponding

Table 2
Cycloisomerization of enyne arene chromium complexes **4**

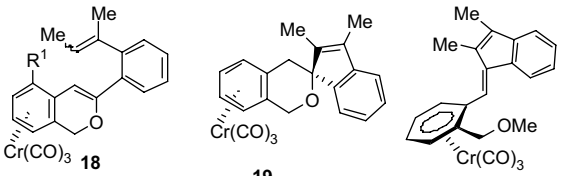


4 **17**

a: $R^1 = R^2 = H$; **b**: $R^1 = H$; $R^2 = Me$; **c**: $R^1 = H$; $R^2 = CH_2OH$;
d: $R^1 = H$; $R^2 = CH_2OMe$; **e**: $R^1 = OMe$; $R^2 = CH_2OH$;
f: $R^1 = OMe$; $R^2 = CH_2OMe$; **g**: $R^1 = OMe$; $R^2 = Me$

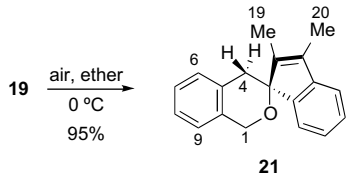
Entry	Complex	Conditions	Yield (%) **17**
1	**4a**	40 °C, 1 h	84
2	**4b**	40 °C, 1 h	90
3[a]	**4c**	rt, 1 h	—
4[b]	**4c**	40 °C, 20 min	—
5[c]	**4d**	40 °C, 1 h	36
6[d]	**4e**	40 °C, 1 h	43
7	**4f**	40 °C, 2 h	90
8	**4g**	40 °C, 5 h	95

[a] Compound **18a** was obtained in 71% yield.
[b] Compounds **18a** and **19** were obtained in 8% and 20% yields, respectively.
[c] Compound **20** was obtained in 13% yield as byproduct.
[d] Compound **18b** was obtained in 27% yield as byproduct.



18 **19** **20**
a; R = H
b; R = OMe

isochromens with 6-*endo*-*dig*-type cyclization.[15] The stereochemistry at spiro carbon of the chromium complex **19** seems resulting from an attack of the olefin to the gold intermediate by *exo*-side of the tricarbonylchromium fragment. One of the benzylic proton at C-4 position of the spiro compounds **19** and its chromium free compound **21** shows high field shift at 2.25 and 2.51 ppm, respectively, due to anistropic effect of the aromatic ring. The structure of compound **21** is supported by relative relationships characterized by nuclear Overhauser effect spectroscopy (NOESY experiment) (see Supplementary data). Indeed, NOE correlations were observed between the following proton pairs; 4β-H and 19-Me; 4α-H and 6-H; 14-H and 20-Me; 1α-H, 1β-H, and 9-H; respectively (Scheme 6).



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Scheme 6. Photooxidative demetalation.

ortho Methoxymethyl substituted arene chromium complex **4d** gave expected naphthyl phenyl chromium complex **17d** in 36% yield along with formation of indene derivative **20** by 5-*exo*-*dig* type cyclization in 13% yield (entry 5). However, sterically bulky 2,6-disubstituted phenyl alkyne chromium complex **4e** even substituted by a hydroxymethyl group at the *ortho* position afforded cycloisomerization complex as the major product along with

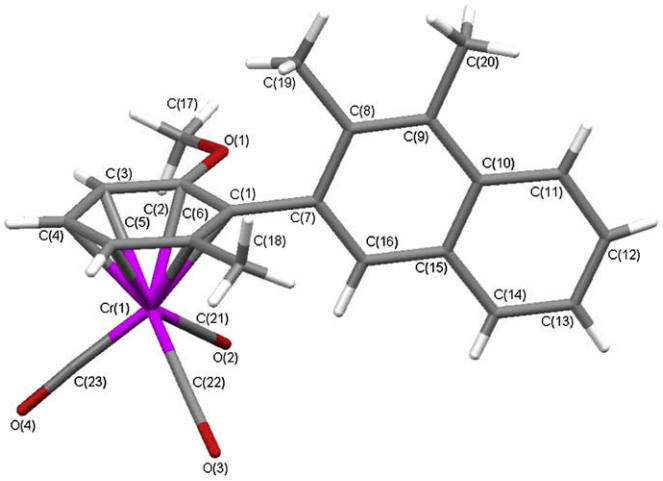
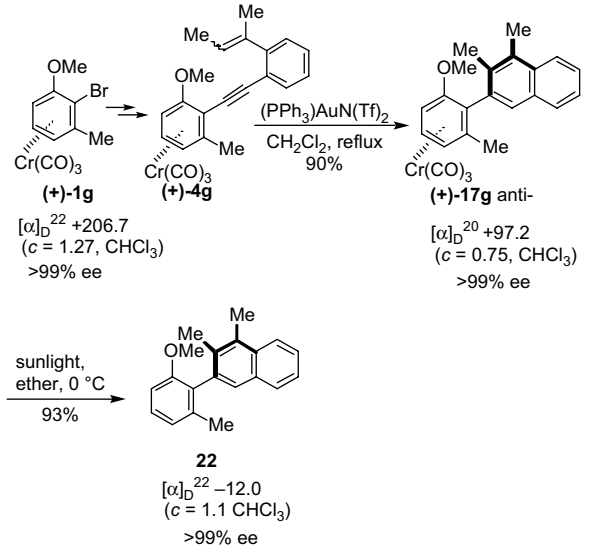


Figure 1. X-ray crystallography of compound **17g**.

formation of 1*H*-isochromene derivative (entry 6). Similarly, 2,6-disubstituted phenyl alkyne chromium complexes with methoxymethyl or methyl groups afforded expected *anti*-biaryl chromium complexes diastereoselectively without any detection of stereoisomeric *syn*-biaryl chromium complexes in good yields (entries 7 and 8). The *anti*-stereochemistry of **17g** was determined by X-ray crystallography[16] (Fig. 1).

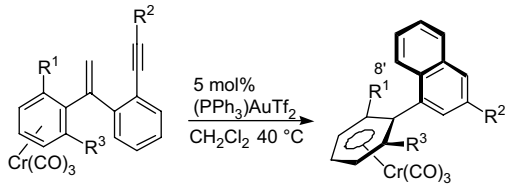
Furthermore, enantiomerically active biaryl compound **22** can be prepared starting from enantiomerically pure (+)-2-bromo-3-methylanisole chromium complex (+)-(**1g**)[17] (Scheme 7). In this way, the cycloisomerization of 2,6-disubstituted phenyl alkyne chromium complexes with *o*-alkenyl phenyl gave diastereoselectively axial biaryls by treatment with catalytic amount of gold(I) catalyst.



Scheme 7. Synthesis of optically pure axially chiral biaryl.

We next studied the gold(I)-catalyzed cycloisomerization of 1,2-diaryl substituted alkene chromium complexes bearing an *exo*-methylene (Table 3). The chromium complexes **8** afforded the desired cycloisomerization products **23** following 6-*endo*-*dig*-type cyclization without formation of any isolable byproducts under the same reaction conditions. 2,6-Disubstituted arene chromium complex **15** gave diastereoselectively single biaryl chromium complex **23d** in good yield (entry 4). The stereochemistry of the cyclization product **23d** was found to be *anti*-configuration

Table 3
Cycloisomerization of arene chromium complexes **8** and **15**



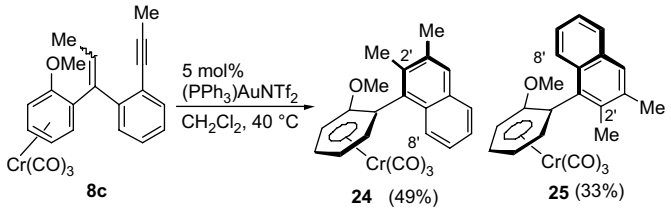
8a: $R^1 = R^2 = Me$, $R^3 = H$
8b: $R^1 = OMe$, $R^2 = Me$, $R^3 = H$
8d: $R^1 = Me$, $R^2 = n\text{-}Bu$, $R^3 = H$
15: $R^1 = OMe$, $R^2 = R^3 = Me$

23a: $R^1 = R^2 = Me$, $R^3 = H$
23b: $R^1 = OMe$, $R^2 = Me$, $R^3 = H$
23c: $R^1 = Me$, $R^2 = n\text{-}Bu$, $R^3 = H$
23d: $R^1 = OMe$, $R^2 = R^3 = Me$

Entry	Complex	Yield (%)
1	**8a**	77
2	**8b**	83
3	**8d**	90
4	**15**	86

between the tricarbonylchromium and the benzene ring of naphthalene skeleton according to ^1H NMR chemical shifts.[18]

With trisubstituted alkene arene chromium complex **8c**, two diastereomeric axially biaryl chromium complexes **24** and **25** were obtained in 49% and 33% yields by gold(I)-catalyzed cycloisomerization reaction (Scheme 8). Although the diastereomeric ratio was not high, these two diastereomers were easily separated by flash chromatography. The major isomer **24** was *anti*-configuration of the methyl group on the naphthalene ring to the tricarbonylchromium fragment according to ^1H NMR spectra.[18] Low diastereoselectivity on the cycloisomerization of the trisubstituted alkene chromium complex **8c** is contributed to small difference of the steric size between C-2′ methyl and C-8′-position of the naphthalene skeleton.



Scheme 8. Gold catalyzed cycloisomerization of complex **8c**.

3. Conclusions

In summary, we have demonstrated that the gold(I)-catalyzed cycloisomerization of the arene chromium complexes with enyne bonds gave optically active axially chiral biaryls diastereoselectively in good yields. This gold(I)-catalyzed cycloisomerization is a complementary tool with palladium(0)-catalyzed Suzuki–Miyaura cross-coupling for synthesis of the axially chiral biaryls, when the preparation of functionalized arylboronic acids is not straightforward.

4. Experimental

4.1. General

All manipulations involving organometallics were carried out under an atmosphere of nitrogen or argon and using inert gas/vacuum double manifold techniques. All NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as an internal reference. Mass spectra were determined with EI or FAB mode. Optical rotations were obtained at wavelength 589 nm (sodium D line) using

a 1.0-dm cell with a total volume of 5 mL. Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl immediately before use.

4.2. Preparation of chromium complexes 2 with trimethylsilylacetylene by Sonogashira coupling

*4.2.1. Chromium complex **2b***

A mixture of *o*-chlorotoluene chromium complex (**1b**) (600 mg, 2.28 mmol), $Pd(Ph_3P)_2Cl_2$ (48 mg, 0.068 mmol) and CuI (12 mg, 0.068 mmol) in triethylamine (5 mL), and THF (15 mL) was degassed under argon. Trimethylsilylacetylene (673 mg, 6.85 mmol) was added by syringe. The mixture was refluxed with stirring for 1 h under argon. After cooling to room temperature, ether (20 mL) was added to the reaction mixture. Filtration through a layer of Celite, concentration under vacuum, and purification by silica gel column chromatography with ether/hexane gave 645 mg (87% yield) of coupling product as yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.58 (dd, 1H, J=1.1, 6.4 Hz), 5.32 (dt, 1H, J=1.1, 6.4 Hz), 5.20 (dd, 1H, J=1.1, 6.4 Hz), 5.14 (dt, 1H, J=1.1, 6.4 Hz), 2.31 (s, 3H), 0.24 (s, 9H); IR ($CHCl_3$) 1967, 1893 cm^{-1}; EIMS m/z (relative intensity) 324 (M^+, 7), 268 (M^+-2CO, 5), 240 (M^+-3CO, 62), 225 ($M^+-3CO-CH_3$, 2), 188 ($M^+-Cr(CO)_3$, 1), 173 ($M^+-Cr(CO)_3-Me$, 7), 52 (100); HRMS cacld for $C_{15}H_{16}CrO_3Si$: 324.0274. Found: 324.0278. To a solution of above coupling product (550 mg, 1.70 mmol) in MeOH (9 mL) was added 2 M aqueous NaOH (1.3 mL) at room temperature under argon. The reaction mixture was stirred for 1 h. The mixture was quenched with water (20 mL) and evaporated to remove MeOH under reduced pressure, and extracted with ether (3×50 mL). The extract was washed with brine, dried over $MgSO_4$. Filtered, concentrated under reduced pressure, and purified by column chromatography; 407 mg (95% yield) of **2b** was obtained; yellow-orange liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (d, 1H, J=6.4 Hz), 5.37 (t, 1H, J=6.4 Hz), 5.19 (d, 1H, J=6.4 Hz), 5.15 (t, 1H, J=6.4 Hz), 3.07 (s, 1H), 2.34 (s, 3H); IR ($CHCl_3$) 1960, 1890 cm; EIMS m/z (relative intensity) 252 (M^+ 10), 196 (M^+-2CO, 5), 168 (M^+-3CO, 31), 52 (100); HRMS cacld for $C_{12}H_8CrO_3$: 251.9878. Found: 251.9872.

*4.2.2. Alkynyl chromium complex **2c***

A title complex was prepared from *o*-chloro benzylalcohol chromium complex (100 mg, 0.36 mmol) and trimethylsilylacetylene (71 mg, 0.72 mmol) by $Pd(Ph_3P)_4$ catalyzed Sonogashira coupling under same conditions; 82% yield of TMS acetylene coupling product. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.55 (dd, 1H, J=6.4, 1.1 Hz), 5.52 (dd, 1H, J=6.4, 1.1 Hz), 5.34 (dt, 1H, J=6.4, 1.1 Hz), 5.27 (dt, 1H, J=6.4, 1.1 Hz), 4.71 (dd, 1H, J=6.7, 13.8 Hz), 4.54 (dd, 1H, J=6.7, 13.6 Hz), 2.08 (t, 1H, J=6.7 Hz), 0.25 (s, 9H); IR ($CHCl_3$) 3391, 1961, 1884 cm. The obtained silylated coupling product (720 mg, 2.12 mmol) was deprotected by treatment with aqueous NaOH in MeOH; 90% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.57 (dd, 1H, J=1.1, 6.4 Hz), 5.55 (dd, 1H, J=1.1, 6.4 Hz), 5.39 (dt, 1H, J=1.1, 6.4 Hz), 5.27 (dt, 1H, J=1.1, 6.4 Hz), 4.75 (dd, 1H, J=6.7, 13.7 Hz), 4.57 (dd, 1H, J=6.7, 13.7 Hz), 3.11 (s, 1H), 2.07 (t, 1H, J=6.7 Hz); IR ($CHCl_3$) 3291, 1960, 1875 cm; EIMS m/z (relative intensity) 268 (13, M^+), 240 (2, M^+-CO), 212 (18, M^+-2CO), 184 (62, M^+-3CO), 166 (13, $M^+-3CO-H_2O$), 132 (100, $M^+-Cr(CO)_3$), 115 (14, $M^+-Cr(CO)_3-OH$), 103 (46); HRMS (EI^+) calcd for $C_{12}H_8CrO_3$: 267.9827. Found: 267.9826.

4.3. General preparation chromium complexes 4 by Sonogashira coupling with 2-(1-methyl-1-propenyl)iodobenzene

*4.3.1. Enyne chromium complex **4g***

A mixture of phenylacetylene tricarbonylchromium complex (**2g**) (100 mg, 0.35 mmol), (*E*)- and (*Z*)-mixture of 2-(1-methyl-1-propenyl)iodobenzene (**3**) (100 mg, 0.39 mmol), $Pd(PPh_3)_4$ (24 mg, 0.021 mmol), CuI (5 mg, 0.025 mmol), NEt_3 (0.9 mL) in THF (2 mL) at 75 °C for 2 h under argon. After cooling at room temperature, solvents were evaporated under vacuum. The resulting black oil was dissolved in CH_2Cl_2 (5 mL) and filtered through a plug of Celite and silica gel, washed with 20 mL of CH_2Cl_2. After evaporation of the solvent, the remaining oil was purified by silica gel chromatography using a hexane/ether mixture to afford 103 mg (71% yield) of the coupling compound **4g** as 3:2 of (*E*)- and (*Z*)-mixture; yellow-orange oil; 3:2 of (*E*)- and (*Z*)-mixture: ^{1}H NMR (300 MHz, $CDCl_3$, the major isomer is designated by *, minor isomer denoted by §) δ 7.55* (dd, 1H, J=7.5, 1.1 Hz), 7.50§ (dd, 1H, J=7.5, 1.1 Hz), 7.38–7.11 (m, 3H), 5.69–5.59 (m, 1H), 5.52 (t, 1H, J=6.6 Hz), 5.01 (d, 1H, J=6.6 Hz), 4.86 (d, 1H, J=6.6 Hz), 3.83 (s, 3H), 2.46 (s, 3H), 2.09* (t, 3H, J=1.1 Hz), 2.05§ (t, 3H, J=1.5 Hz), 1.79* (dd, 3H, J=6.8, 1.1 Hz), 1.47§ (dd, 3H, J=6.8, 1.5 Hz); IR (neat) 1957, 1879 cm; EIMS m/z (relative intensity) 412 (11, M^+), 328 (41, M^+-3CO), 313 (51, $M^+-3CO-CH_3$), 52 (100); HRMS (EI^+) calcd for $C_{23}H_{20}CrO_4$ 412.0766. Found: 412.0771.

*4.3.2. Enyne chromium complex **4e***

Yellow oil; 3:2 of (*E*)- and (*Z*)-mixture: ^{13}C NMR (100 MHz, $CDCl_3$) δ 232.6 (3CO), 232.5 (3CO), 148.7, 145.6, 143.4, 143.2, 136.7, 136.4, 133.0, 132.6, 129.2, 128.6, 128.5, 128.4, 128.3, 126.7, 126.4, 125.4, 123.5, 121.2, 121.0, 120.2, 119.8, 114.1, 110.1, 96.0, 95.2, 92.5, 92.3, 83.9, 82.7, 72.6. 72.5, 63.3, 63.2, 56.5 (2C), 25.2, 17.5, 14.8, 14.1; ^{1}H NMR (300 MHz, $CDCl_3$, the major isomer is designated by *, minor isomer denoted by §) δ 7.55* (dd, 1H, J=7.5, 1.1 Hz), 7.50§ (dd, 1H, J=7.5, 1. 1 Hz), 7.38–7.11 (m, 3H), 5.69–5.64 (m, 1H), 5.60 (t, 1H, J=6.4 Hz), 5.17* (d, 1H, J=6.4 Hz), 5.14§ (d, 1H, J=6.4 Hz), 5.10 (d, 1H, J=6.4 Hz), 4.88 (dd, 1H, J=13.9, 7.0 Hz), 4.68 (dd, 1H, J=13.9, 7.0 Hz), 3.86 (s, 3H), 2.30§ (t, 1H, J=7.0 Hz), 2.26* (t, 1H, J=7.0 Hz), 2.08* (t, 1H, J=1.1 Hz), 2.06§ (t, 1H, J=1.5 Hz), 1.82* (dd, 3H, J=1.6, 6.7 Hz), 1.48§ (dd, 3H, J=1.1, 6.4 Hz); IR ($CHCl_3$) 3390, 1958, 1880 cm; EIMS m/z (relative intensity) 428 (7, M^+), 344 (100, M^+-3CO), 326 (27, $M^+-3CO-H_2O$), 311 (38, $M^+-3CO-H_2O-CH_3$); HRMS (EI^+) calcd for $C_{23}H_{20}CrO_5$: 428.0715. Found: 428.0713.

4.4. Preparation of chromium complexes 7 from benzaldehyde chromium complexes 5 by addition of 2-(1-propenyl)phenyllithium (6) followed by oxidation

To a solution of 2-(1-propynyl)bromobenzene (688 mg, 3.53 mmol) in ether (20 mL) was added *n*-BuLi (1.6 M in hexane, 2.21 mL, 3.53 mmol) at −78 °C under argon. The mixture was stirred at −78 °C for 1 h and warmed to 0 °C over 2 h. The reaction mixture was re-cooled to −78 °C. To this lithiated intermediated in ether solution was added a solution of tricarbonyl(2-methoxybenzaldehyde)chromium (**5b**) (800 mg, 2.94 mmol) in ether (20 mL) at −78 °C under argon. The reaction mixture was stirred for 1 h and warmed to 0 °C over 1 h. The reaction mixture was quenched with a saturated aqueous NH_4Cl solution and extracted with ether (3×60 mL), and the extract was washed with brine and dried over $MgSO_4$. The organic layer was evaporated under vacuum and the residue was purified by silica gel chromatography to give *sec*-alcohol chromium complex (718 mg, 77%) as yellow crystals. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43–7.20 (m, 4H), 6.29 (d, 1H, J=3.7 Hz), 5.95 (d, 1H, J=6.2 Hz), 5.54 (t, 1H, J=6.2 Hz), 5.02 (d, 1H, J=6.2 Hz), 4.91 (t, 1H, J=6.2 Hz), 3.72 (s, 3H), 2.62 (d, 1H, J=3.7 Hz), 2.09 (s, 3H); IR ($CHCl_3$) 3484, 1956, 1870 cm; EIMS m/z (relative intensity) 388 (11, M^+), 332 (28, M^+-2CO), 304 (100, M^+-3CO), 286 (65, $M^+-3CO-H_2O$), 271 (15, $M^+-3CO-H_2O-CH_3$), 252 (57, $M^+-Cr(CO)_3$), 237 (39, $M^+-Cr(CO)_3-CH_3$); HRMS (EI^+) calcd for $C_{20}H_{16}CrO_5$: 388.0402. Found: 388.0401. To a solution of DMSO (0.3 mL, 4.17 mmol) in CH_2Cl_2 (4.5 mL) was added $(CF_3CO)_2O$ (0.48 mL, 3.47 mmol) at −78 °C under argon. The mixture was stirred for 10 min, and a solution of the above *sec*-alcohol

chromium complex (540 mg, 1.39 mmol) in CH_2Cl_2 (4.0 mL) was added to the reaction mixture at same temperature. The mixture was stirred for 30 min and Et_3N (1.0 mL) was added, and the mixture was warmed to 0 °C over 1 h and quenched with water (6 mL). The mixture was extracted with CH_2Cl_2 (3×15 mL), the combined organic layers were washed with brine, dried over $MgSO_4$. Evaporation of organic solvent under vacuum and purification of the residue gave **7b** (350 mg, 84%) as red crystals. Mp 139 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52–7.31 (m, 4H), 6.20 (d, 1H, J=6.4 Hz), 5.75 (t, 1H, J=6.4 Hz), 4.99 (d, 1H, J=6.4 Hz), 4.96 (t, 1H, J=6.4 Hz), 3.55 (s, 3H), 1.85 (s, 3H); IR (KBr) 1956, 1857, 1656 cm. Anal. Calcd for $C_{20}H_{14}CrO_5$: C, 62.28; H, 3.65. Found C, 62.47; H, 3.94.

4.5. Preparation of enyne chromium complexes 8

To a solution of chromium complex **7a** (R^1=R^2=Me) (230 mg, 0.62 mmol) in ether (25 mL) was added MeLi (1.0 M in ether, 0.8 mL, 0.80 mmol) at −78 °C under argon. The reaction mixture was stirred and warmed to 0 °C over 2 h, and quenched with saturated aqueous NH_4Cl solution, and extracted with ether (3×10 mL). The extract was washed with brine, dried $MgSO_4$. Filtered, concentrated under reduced pressure, and purified by column chromatography to give *tert*-alcohol chromium complex 122 mg (51% yield) as yellow crystals as diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, 1H, J=1.2, 7.8 Hz), 7.41–7.22 (m, 3H), 6.47 (dd, 1H, J=1.1, 6.4 Hz), 5.54 (dt, 1H, J=1.1, 6.4 Hz), 5.03 (dt, 1H, J=1.1, 6.4 Hz), 4.82 (dd, 1H, J=1.1, 6.4 Hz), 3.82 (d, 1H, J=0.7 Hz), 2.05 (d, 1H, J=1.1 Hz), 1.91 (s, 3H), 1.69 (s, 3H); IR ($CHCl_3$) 3540, 1969, 1877 cm. To a solution of the obtained chromium complex (120 mg, 0.31 mmol) in CH_2Cl_2 (9 mL) was added $BF_3{\cdot}OEt_2$ (0.076 mL, 0.60 mmol) at 0 °C under argon. The reaction mixture was stirred for 20 min and quenched with saturated aqueous $NaHCO_3$ at 0 °C, and extracted with CH_2Cl_2 (3×20 mL), and the extract was washed with brine, dried over $MgSO_4$. Concentration in vacuo and purification by column chromatography gave chromium complex **8a** (97 mg, 85% yield) as yellow crystals. Mp 104 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.35 (m, 1H), 7.28–7.18 (m, 3H), 5.80 (d, 1H, J=1.1 Hz), 5.78 (d, 1H, J=1.1 Hz), 5.63 (dd, 1H, J=6.4, 1.1 Hz), 5.45 (dt, 1H, J=1.1, 6.4 Hz), 5.15 (dt, 1H, J=1.1, 6.4 Hz), 5.10 (dd, 1H, J=1.1, 6.4 Hz), 1.97 (s, 3H), 1.90 (s, 3H); IR ($CHCl_3$) 1959, 1874 cm. Anal. Calcd for $C_{21}H_{16}CrO_3$: C, 68.48; H, 4.38. Found: C, 68.42; H, 4.52.

4.6. Preparation of chromium complex 13 by palladium-catalyzed carbonylative coupling with 2-alkynylphenylboronic acid

A mixture of 2-bromo-3-methylanisole chromium complex (**1g**) (100 mg, 0.30 mmol), 2-(1-propynyl)phenylboronic acid (**12**) (71 mg, 0.44 mmol), K_3PO_4 (189 mg, 0.89 mmol), and $Pd(Ph_3P)_4$ (34 mg. 0.030 mmol) in dioxane was heated at 40 °C with stirring under 1 atm CO pressure for 40 h. After cooling to room temperature, filtered through a layer of Celite, concentrated in vacuo and purified by column chromatography. Two products were obtained. Compound **13**: 57 mg (47% yield); orange crystals. Mp 127 °C; ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.1 (3CO), 191.3, 141.5, 139.1, 134.1, 132.0, 129.7, 127.8, 123.2, 110.9, 103.9, 93.9, 93.6, 84.5, 78.6, 69.9, 56.3, 19.1, 5.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, 1H, J=7.5 Hz), 7.44–7.33 (m, 3H), 5.59 (t, 1H, J=6.4 Hz), 4.92 (d, 1H, J=6.4 Hz), 4.71 (d, 1H, J=6.4 Hz), 3.59 (s, 3H), 2.24 (s, 3H), 1.87 (s, 3H); IR ($CHCl_3$) 1968, 1891, 1669 cm; EIMS m/z (relative intensity) 400 (4, M^+), 344 (27, M^+-2CO), 316 (100, M^+-3CO), 264 (96, $M^+-Cr(CO)_3$), 249 (58, $M^+-Cr(CO)_3-CH_3$); HRMS (EI^+) calcd for $C_{21}H_{16}CrO_5$: 400.0402. Found: 400.0410. Anal. Calcd for $C_{21}H_{16}CrO_5$: C, 63.02; H, 4.00. Found: C, 63.13; H, 4.27. *syn*-Biaryl chromium complex **14** (25 mg, 20% yield): yellow solid; ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.5 (3CO), 141.0, 134.7, 132.9, 132.1, 127.8, 126.8, 125.3, 111.1, 103.6, 94.9, 93.2, 85.6, 79.1, 71.4, 56.2, 20.1, 5.8; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 1H, J=7.2 Hz), 7.24 (m, 2H), 7.04 (d, 1H, J=8.1 Hz), 5.56 (t, 1H, J=6.5 Hz), 4.97 (d, 1H, J=6.6 Hz), 4.78 (d, 1H, J=6.0 Hz), 3.64 (s, 3H), 2.19 (s, 3H), 1.99 (s, 3H); IR ($CHCl_3$) 1960, 1882 cm; MS (EI^+) m/z (relative intensity) 372 (2, M^+), 316 (7, M^+-2CO), 288 (31, M^+-3CO), 236 (100, $M^+-Cr(CO)_3$), 221 (68, $M^+-Cr(CO)_3-Me$), 205 (16, $M^+-Cr(CO)_3-OMe$); HRMS (EI^+) calcd for $C_{20}H_{16}CrO_4$: 372.0453. Found: 372.0450. Anal. Calcd for $C_{20}H_{16}CrO_4$: C, 64.54; H, 4.30. Found: C, 64.34; H, 4.34.

4.7. General procedure for cycloisomerization of enyne chromium complexes

*4.7.1. Axial biaryl monochromium complex **17g***

A mixture of enyne chromium complex **4g** (50 mg, 0.12 mmol), $(PPh_3)AuNTf_2$ (4.5 mg) in CH_2Cl_2 (5 mL) was heated at 40 °C for 5 h under argon. After filtration through Celite and evaporation under vacuum, the residue was purified by SiO_2 chromatography (ether/hexane, 1:5) to give 48 mg (98%) of **17g**. Mp 209 °C (dec); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.8 (3CO), 143.4, 132.8, 132.2, 132.1, 132.0, 131.8, 130.9, 129.2, 126.5, 125.2, 123.8, 113.4, 107.4, 95.1, 85.1, 70.7, 56.0, 19.6, 17.0, 15.3; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 1H, J=7.8 Hz), 7.94 (d, 1H, J=7.8 Hz), 7.88 (s, 1H), 7.57–7.44 (m, 2H), 5.72 (t, 1H, J=6.3 Hz), 5.00 (d, 1H, J=6.3 Hz), 4.83 (d, 1H, J=6.3 Hz), 3.62 (s, 3H), 2.66 (s, 3H), 2.18 (s, 3H), 1.92 (s, 3H); IR ($CHCl_3$) 1957, 1868 cm. Anal. Calcd for $C_{23}H_{20}CrO_4$: C, 66.98; H, 4.89. Found: C, 66.89; H, 4.97.

*4.7.2. Biaryl chromium complex **23d***

Mp 184 °C; ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.8 (3CO), 143.8, 135.8, 134.7, 133.9, 130.6, 129.8, 128.2, 128.0, 126.0, 125.7, 124.0, 113.9, 104.7, 95.1, 85.3, 70.9, 56.1, 21.9, 19.6; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, 1H, J=8.1 Hz), 7.67 (s, 1H), 7.54 (d, 1H, J=1.8 Hz), 7.47–7.28 (m, 3H), 5.77 (t, 1H, J=6.4 Hz), 5.05 (d, 1H, J=6.4 Hz), 4.87 (d, 1H, J=6.4 Hz), 3.57 (s, 3H), 2.60 (s, 3H), 1.86 (s, 3H); IR ($CHCl_3$) 1961, 1880 cm. Anal. Calcd for $C_{22}H_{18}CrO_4$: C, 66.33; H, 4.55. Found: C, 66.33; H, 4.51.

*4.7.3. Optically active complex (+)-**17g***

$[\alpha]_D^{21}$ 97.2 (*c* 0.75, $CHCl_3$); >99% ee; HPLC; Chiralpak AS-H; 10% 2-PrOH in hexane; flow rate 1.0 mL/min; retention time, 23.0 min (antipode 19.0 min).

4.8. Optically active axially (−)-biaryl compound 22

A solution of (+)-chromium complex (+)-**17g** (14.4 mg, 0.035 mmol) in ether (12 mL) was exposed to sunlight at 0 °C until yellow color was disappeared for 1 h. Filtration, evaporation, and purification by silica gel chromatography gave 9 mg (93%) of chromium free axially chiral biaryl **22** as colorless oil. $[\alpha]_D^{22}$ −12.0 (*c* 1.1, $CHCl_3$); >99% ee; HPLC; Chiralcel OD-H; 1% 2-PrOH in hexane; flow rate 0.1 mL/min; retention time 51.8 min (antipode 46.2 min); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, 1H, J=8.0 Hz), 7.76 (d, 1H, J=8.0 Hz), 7.48 (t, 1H, J=8.0 Hz), 7.45 (s, 1H), 7.40 (t, 1H, J=8.0 Hz), 7.26 (t, 1H, J=8.0 Hz), 6.93 (d, 1H, J=8.0 Hz), 6.84 (d, 1H, J=8.0 Hz), 3.69 (s, 3H), 2.68 (s, 3H), 2.13 (s, 3H), 1.97 (s, 3H); IR (neat), 2856, 2833, 1577, 1468, 1437, 1296, 1257, 1084, 774, 745; EIMS m/z (relative intensity) 276 (100, M^+), 261 (54, M^+-CH_3), 246 (33, M^+-2CH_3), 231 (13, M^+-3CH_3), 215 (17, $M^+-2CH_3-OCH_3$), 202 (14, $M^+-3CH_3-OCH_3$), 123 (27), 107 (26), 101 (19); HRMS (EI^+) calcd for $C_{20}H_{20}O$: 276.1514. Found: 276.1511.

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Supplementary data

NOESY spectra of compound **21** and X-ray crystallography data of the complex **17g**. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.09.086.

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