# Stereoselective Pinacol Coupling of Planar Chiral (Benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$, (Benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$, Ferrocenecarboxaldehyde and (Dienal) $\mathrm{Fe}(\mathrm{CO}) 3$ Complexes with Samarium Diiodide 

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#### Abstract

An intermolecular pinacol coupling of the planar chiral tricarbonylchromium complexes of $o$-substituted benzaldehydes or benzaldimines with samarium(II) diiodide in THF produces exclusively threo 1.2-diols or 1,2-diamines in an oplically pure form, while the corresponding racemic o-substituted benzaldehyde or benzaldimine chromium complexes give a mixture of threo and erythro pinacol coupling products in a various ratio depending upon the nalure of 0 -substituent. Similarly. planar chiral 2 substituted ferrocenecarboxaldehydes and (dienal) $\mathrm{Fe}(\mathrm{CO})_{3}$ produce the corresponding 1.2 -diols with high stereoselectivity. The generated transition metal-complexed ketyl radical intermediates are configurationally stable with restriction to a rotation about $\mathrm{C}_{\alpha}-\mathrm{C}_{\mathrm{ipso}}$ bond. (c) 1998 Elsevier Science Ltd. All rights reserved.


Keynords planar chirality; pinacol compling. (arene)chromum complex. 1.2-diol: I,2-diamine


#### Abstract

Introduction Enantiomerically pure 1,2-diols or diamines and the related compounds have found widespread use as chiral ligands in asymmetric reactions. ' While the optically active 1,2 -diols have been conveniently synthesized by a catalytic asymmetric dihydroxylation of the olefins in good yields with high enantiopurity, ${ }^{2}$ the generally accepted method for the preparation of chiral 1,2 -diamines involves an optically resolution of racemic compounds with certain chiral carboxylic acids. ${ }^{3}$ The reductive coupling of carbonyl compounds, pinacol coupling, is the most direct way to synthesize 1,2 -diols. Although this reaction can be achieved in high yield by lanthanoid metals or low valent transition metals, ${ }^{4}$ highly diastereoselective formation of 1,2-diols is problematic under conventional reductive coupling methods; e.g., benzaldehyde gave ca. a $1: 1$ mixture of threo- (dl) and erythro (meso) pinacols by reductive coupling of benzaldehyde with samarium diiodide(II). ${ }^{5}$ The utilization of some modified reducing agents in the catalytic or stoichiometric reaction have been developed recently for the achievement of high stereoselectivity for the pinacol coupling. ${ }^{6}$ However, the threo 1,2 -diols can not be obtained in an enantiomerically enriched form by this type of coupling of aldehydes or ketones. ( $\eta^{6}$-Arene)tricarbonylchromium complexes have some characteristic properties due to the strong electronwithdrawing ability and steric bulkiness of tricarbonylchromium fragment, and significant applications in organic synthesis have been developed..$^{7-9}$ The tricarbonylchromium group is well known to stabilize both the benzylic carbanion ${ }^{8}$ and carbocation ${ }^{9}$ intermediates. However, the reactivity, stability and stereochemical


behavior of the chromium-complexed benzyl radical intermediates are little investigated. ${ }^{10}$ In this paper, we wish to report that the ketyl radicals derived from tricarbonylchromium-complexed benzaldehydes, benzaldimines and the related metal-complexed substrates with samarium diiodide are stereoselectively coupled to give the corresponding pinacol adducts with threo-configuration.

## Results and Discussion <br> Pinacol Coupling of Tricarbonyl(benzaldehyde)chromium Complexes

The reaction of tricarbonyl(benzaldehyde)chromium (1) $\left(\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{H}\right)$ with 2.5 eq of samarium diiodide(II), generated in situ from Sm metal and 1,2 -diiodoethane, $1^{11}$ in THF at $-78^{\circ} \mathrm{C}$ gave the corresponding pinacol 3 as a diastereomeric mixture in a ratio of $91: 9$ after an oxidative demetalation of the coupling product 2 with $\mathrm{I}_{2}$. The major product was assigned as the threo ( $d l$ ) configuration by a comparison with authentic sample. ${ }^{12}$ Thus, the tricarbonylchromium complexation of benzaldehyde resulted in extremely high threo selectivity by $\mathrm{Sm}(\mathrm{II})$-mediated reductive coupling. Other results of the pinacol coupling of the tricarbonylchromium complexes of $\delta$ - or $p$-substituted benzaldehydes are summarized in Table 1, and several facts are worthy of comment. ${ }^{13}$ In addition to the unsubstituted benzaldehyde chromium complex, ortho or para substituted benzaldehyde chromium complexes afforded predominantly the corresponding threo pinacols. Slightly reduced threo selectivities were observed in a case of the hetero-atom substituted benzaldehyde chromium complexes at the ortho position (entries 7-10). In a striking contrast to the threo selectivity for these chromium complexes, $o$-bromobenzaldehyde chromium complex gave the corresponding erythro pinacol as a major product (entries 11,12), while the corresponding $p$-bromobenzaldehyde chromium complex produced the threo isomer as the major product (entry 16). The tricarbonylchromium complexation of bromobenzaldehyde is

Table 1. Pinacol Coupling of (benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ Complexes

|  | $\xrightarrow[-78^{\circ} \mathrm{C}]{\mathrm{Sml}_{2}, \mathrm{THF}}$ |  |  | ${ }^{\mathrm{I}_{2}, \mathrm{CH}_{2} \mathrm{Cl}_{2}}$ |  <br> 3 |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Complex I | Temp ( ${ }^{\circ} \mathrm{C}$ ) | Additive | $\begin{gathered} \text { Yields (\%) } \\ a ; \quad b ; \\ \hline \end{gathered}$ | Ratio of $\mathbf{3}$ (threo: erythro) |
| 1 | $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{H}$ | -78 | none | 78, 92 | 91:9 |
| 2 | $\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{H}$ | 0 | none | 78, 92 | $90: 10$ |
| 3 | $\mathrm{R}^{\mathbf{l}}=\mathrm{R}^{2}=\mathrm{H}$ | 0 | HMPA | 80, 87 | 60:40 |
| 4 | $\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{H}$ | -78 | none | 85, 91 | 95:5 |
| 5 | $\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{H}$ | 0 | none | 83, 91 | 95: 5 |
| 6 | $\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{H}$ | 0 | HMPA | 80, 85 | 20:80 |
| 7 | $\mathrm{R}^{1}=\mathrm{OMe}, \mathrm{R}^{2}=\mathrm{H}$ | 0 | none | 81, 91 | $80: 20$ |
| 8 | $\mathrm{R}^{1}=\mathrm{OMe}, \mathrm{R}^{2}=\mathrm{H}$ | 0 | HMPA | 81, 89 | 8:92 |
| 9 | $\mathrm{R}^{1}=\mathrm{OPr}^{i}, \mathrm{R}^{2}=\mathrm{H}$ | 17 | none | 79, 90 | 79:21 |
| 10 | $\mathrm{R}^{1}=\mathrm{NMe}_{2}, \mathrm{R}^{2}=\mathrm{H}$ | -78 | none | 74, 92 | $73: 27$ |
| 11 | $\mathrm{R}^{\mathbf{l}}=\mathrm{Br}, \mathrm{R}^{2}=\mathrm{H}$ | 17 | none | 84, 89 | 16:84 |
| 12 | $\mathrm{R}^{1}=\mathrm{Br}, \mathrm{R}^{2}=\mathrm{H}$ | 0 | none | 85, 89 | 34: 66 |
| 13 | $\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{Me}$ | 0 | none | 78, 93 | 98:2 |
| 14 | $\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{OMe}$ | 0 | none | 73, 91 | 91:9 |
| 15 | $\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{OMe}$ | -78 | none | 73, 91 | 92:8 |
| 16 | $\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{Br}$ | -78 | none | 75, 82 | 71:29 |

[^0]essential for the pinacol coupling. Thus, the chromium free $o$-bromobenzaldehyde produced a carbonyl-phenyl coupling product having a linkage between the para-position of the phenyl ring and carbonyl groups, (3-bromo4 -formylphenyl)-2-bromophenylmethanol, in $35 \%$ yield as the major product aiong with $7 \%$ yield of the desired pinacol coupling product by treatment with samarium diiodide in THF. ${ }^{14}$ On the other hand, the pinacol coupling of (benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ complexes in the presence of 5 eq of HMPA resulted in an increase of the erythro 1,2 -diols (entries $3,6,8$ ). Thus, tricarbonyl( $(0$-methoxy benzaldehyde)chromium gave predominantly the corresponding erythro 1,2 -di- $o$-methoxyphenyl-1,2-ethanediol in a ratio of $92: 8$ by the reductive coupling in a mixture of HMPA and THF solvent. These results indicate that the threo coupling products can be predominantly obtained by a simple chromium complexation of benzaldehydes except of $o$-bromobenzaldehyde, and the addition of HMPA into the reaction solvent was changed to the erythro predominance.

In order to clarify a reaction mechanism of the pinacol coupling of tricarbonylchromium-complexed benzaldehydes, the relative stereochemistry of both threo and erytho tricarbonylchromium-complexed pinacols obtained from a racemic ( $o$-brombenzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ was next investigated. The tricarbonylchromium complexes of both threo and erytho pinacols could possibly exist as three stereoisomers based on two chiral planes and two stereogenic centers, respectively. However, the samarium diiodide-mediated reductive coupling of the racemic ( $o$-brombenzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}(4)$ at $-78^{\circ} \mathrm{C}$ in THF gave a single threo pinacol 5 A among three possible threo isomers, 5A-5C, and a single erytho pinacol 6A in $19 \%$ and $46 \%$ yields, respectively (Scheme 1). Proton signals of both threo pinacol 5A and erythro isomer 6A exhibit a symmetry. Thus, two benzylic protons of $O, O^{\prime}$-dimethyl ether derived from the threo compound 5A appeared at 4.44 ppm as a sharp singlet and the corresponding protons of dimethyl ether of 6 A showed a sharp singlet at 4.57 ppm . Methyl protons of the dimethyl ether compounds appeared at 3.34 ppin for the threo-isomer, and at 3.71 ppm for the erythro-isomer as a sharp singlet, respectively.

## Scheme 1. Pinacol Coupling of Racemic (o-Bromobenzaldehyde) $\mathrm{Cr}\left(\mathrm{CO}_{3}{ }_{3}{ }^{\text {a }}\right.$


a; one enantiomer is shown for clarity
The relative stereochemistry of both chromium-complexed threo-and erythro-pinacol coupling products was finally determined by X-ray crystallography. ${ }^{15}$ The threo pinacol 5A has $1\left(S^{*}\right), \alpha\left(S^{*}\right), \alpha^{\prime}\left(S^{*}\right), 1^{\prime}\left(S^{*}\right)$ configuration, ${ }^{16}$ while the stereochemistry of erythro pinacol 6 A is found to be $1\left(R^{*}\right), \alpha\left(R^{*}\right), \alpha^{\prime}\left(S^{*}\right), 1^{\prime}\left(S^{*}\right)$ configuration. ${ }^{16}$ These stereochemical results indicate that each benzylic stereogenic center of both coupling products 5A and 6A is controlled by its adjacent chromium-complexed planar chirality, respectively. And, the threo pinacol 5A is consistent by the both rings with identical planar chirality, while the both rings of erythro pinacol 6A have different planar chirality. In other words, the threo pinacol 5A was obtained by a homo-
coupling of the same planar chiral (o-bromobenzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$, while the erythro pinacol 6 A was formed by a hetero-coupling of different planar chiral ( $\eta^{6}$-arene)chromium complex to each other.

These stereochemical results of the chromium-complexed pinacols predict that an enantiomerically pure ( $o$ substituted benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ could produce only threo 1,2 -diol as a single coupling product. Indeed, the enantiomerically pure ( $1 S$ )-(+)-tricarbonyl(o-bromobenzaldehyde)chromium (7) ${ }^{17}$ was treated with samarium diiodide in THF at $-78^{\circ} \mathrm{C}$ to produce a single threo pinacol complex 8 in $75 \%$ yield without formation of the erythro isomer (Scheme 2). Similarly, the optically pure ( $1 R$ )-(-)-(o-methylbenzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ (9) gave the corresponding threo pinacol complex 10 in $71 \%$ yield. In this way, the enantiomerically pure 1,2 -diols could be synthesized by the pinacol coupling of the planar chiral (benzaldehyde)chromium complex with $\mathrm{SmI}_{2}$. Furthermore, these chiral 1,2-diols and the corresponding ethers would be expected to be the characteristic chiral ligand in the asymmetric reactions, since these compounds have both planar and central chiralities with $C_{2}$ symmetry.

## Scheme 2. Pinacol Coupling of Enantiomerically Pure (Arene) $\operatorname{Cr}(\mathrm{CO})_{3}$



Reaction mechanism of the pinacol coupling of the benzaldehyde tricarbonylchromium complexes would be proposed as follows (Fig. 1). ${ }^{18}$ A carbonyl oxygen of the chromium-complexed ortho substituted benzaldehydes possessing an electron-donating substituent tends to be an anti-conformation to the ortho substituents 11 in both solid and solution states due to the stereoelectronic effect. ${ }^{19}$. An exo-attack of the samarium to the anti carbonyl gave a ketyl radical 12 which incorporates a substantial amount of the exocyclic double bond character 13 owing to an interaction of $d$-orbital on the chromium with $p$-orbital of the benzylic carbon. This, in turn, implies that a rotation about the $\mathrm{C}_{\alpha}-\mathrm{C}_{\mathrm{ipso}}$ bond giving 14 will be restricted. Then, the generated tricarbonylchromium-complexed ketyl intermediate is coupled with the carbonyl group of other (benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ from the opposite side to the tricarbonylchromium fragment, in which both tricarbonylchromium-complexed arene rings are located in anti-orientation to each other due to a dipole-dipole and steric repulsions. Similar dipole-dipole interaction has been proposed in highly enantioselective reactions of the metalcarbonyl coordinated substrates. ${ }^{20}$ Taking into account the Newman model, the both arenes coupled via an intermolecular coordinated transition state 15 of the samarium with the carbonyl oxygen to give the threo pinacol. In the case of the chromium complexes possessing $O$ - and $N$-hetero-atoms at the ortho position, the alternative coordination structure 16 of the samarium with the ortho hetero atom would compete with the transition state 15 , giving the pinacol coupling products in a various ratio. The presence of HMPA, however, precludes such coordination of the samarium with carbonyl or $o$-hetero-atoms. Therefore, it seems reasonable to assume that the erythro pinacols would be formed by the bimolecular coupling of the generated radical 12 via the transition state 17 with minimized stereo-electronic conformation. In any event, it is interesting that the tricarbonylchromium-complexed benzyl radicals could be generated stereoselectively, and caused pinacol coupling giving the threo 1,2-diols without stereochemical isomerization at the benzylic position.

Fig. 1. Proposed reaction mechanism



Pinacol Coupling of 2-Substituted Ferrocenecarboxaldehydes and (Dienal) $\mathrm{Fe}(\mathrm{CO})_{3}$
We demonstrated that the pinacol coupling of enantiomerically pure tricarbonylchromium complexes of $o$ substituted benzaldehydes produced single 1,2-diol with the threo-configuration. As part of our asymmetric exploration of the transition metal-cooordinated planar substrates, we next studied the intermolecular pinacol coupling of the planar chiral $\alpha$-substituted ferrocenecarboxyaldehydes and tricarbonyl(dienal)iron complex. The reaction results of samarium diiodide-mediated pinacol coupling of ferrocenecarboxaldehydes are summarized in Table 2. 2-Unsubstituted ferrocenecarboxaldehyde (18) $(\mathrm{R}=\mathrm{H})$ produced a $1: 1$ diastereomeric mixture of threo (dI) and erythro (meso)-pinacols in $95 \%$ yield. Racemic 2-methylferrocenecarboxaldehyde gave a complexed mixture of the 1,2 -diols based on the central and planar chiralities. However, an enantiomerically pure $(R)$-2-methylferrocenecarboxaldehyde $(18)(\mathrm{R}=\mathrm{Me})$ was reacted with samarium diiodide at $0^{\circ} \mathrm{C}$ to give the corresponding three pinacol coupling products 19,20 and 21 in a ratio of $92: 4: 4$ in $98 \%$ yield (entry 2 ). The reductive coupling at lower reaction temperature $\left(-78^{\circ} \mathrm{C}\right)$ produced a single pinacol coupling $19(\mathrm{R}=\mathrm{Me})$ with the threo-configuration in $92 \%$ yield (entry 3 ). Similarly, the planar chiral 2-trimethylsilyl, bromo or iodo substituted ferrocenecarboxaldehydes afforded the corresponding 1,2 -diols 19 with extremely high diastereoselectivity under same reaction conditions (entries 6~8).

The relative stereochemistry of the major coupling product $19(\mathrm{R}=\mathrm{I})$ was determined by a single crystal X-ray analysis ${ }^{15}$ after conversion of the diol to the corresponding acetonide, and found to be the ( $S_{\mathrm{Fc}}, 1 S, 2 S, S_{\mathrm{Fc}^{\prime}}$ )-configuration. The structures of the other stereoisomeric coupling products could be easily assigned by NMR spectra. The compounds 19 and 20 have a $C_{2}$-symmetry, while 21 has a $C_{1}$-symmetry conformation. ${ }^{21}$ However, no obvious diastereoselectivity was observed for the samarium diiodide-mediated

Table 2. Pinacol Coupling of Enantiomerically Pure Ferrocenecarboxyaldehydes

18
19
20
21

| Entry | R | Temp $\left({ }^{\circ} \mathrm{C}\right)$ | Yield | Ratio (19:20:21) | $19[\alpha]_{\mathrm{D}}\left(\mathrm{CHCl}_{3}\right)$ |
| :--- | :--- | :---: | :---: | :---: | :---: |
| $1^{a}$ | H | 0 | 95 | $25: 25: 50$ | - |
| 2 | Me | 0 | 98 | $92: 4: 4$ |  |
| 3 | Me | -78 | 92 | $100: 0: 0$ | +89.5 |
| 4 | TMS | 0 | 88 | $91: 8: 1$ |  |
| 5 | TMS | -78 | 87 | $93: 6: 1$ | +69.5 |
| 6 | I | 0 | 94 | $92: 4: 4$ |  |
| 7 | I | -78 | 92 | $100: 0: 0$ | +37.4 |
| 8 | Br | -78 | 93 | $100: 0: 0$ | +44.2 |
| $9 b$ | $\mathrm{PPh}_{2}$ | 0 | 41 | $52: 24: 24$ | - |
| $100^{c}$ | $\mathrm{PPh}_{2}$ | rt | 80 | $30: 40: 30$ | C |

$a$ : The compounds $\mathbf{1 9}$ and $\mathbf{2 0}$ are enantiomer to each other when R is hydrogen.
b; No pinacol coupling of 18 with 2-diphenylphosphino substituent proceeded at - $78^{\circ} \mathrm{C}$.
c; Ref. 22.
pinacol coupling of 2-(diphenylphosphino)ferrocenecarboxaldehyde. Thus, ( $S$ )-2-diphenylphosphino ferrocene $18\left(\mathrm{R}=\mathrm{PPh}_{2}\right)$ produced all possible stereoisomers of the pinacol coupling products 19,20 and 21 in a ratio of $52: 24: 24$ in only $41 \%$ yield along with ferrocenylmethyl alcohol of $20 \%$ yield (entry 9 ). A similar result was recently reported by Kagan et al, ${ }^{22}$ in which the ratio of the diols was $30: 40: 30$ (entry 10).

Similarly, enantiomerically pure planar chiral ( $E$-3-methyl-5-phenyl-2,4-pentadienal) $\mathrm{Fe}(\mathrm{CO})_{3}$ complex (22) was treated with samarium diiodide to produce a single coupling product with the threo-configuration in 76 $\%$ yield (Scheme 3). The stereochemistry of the coupling product 23 was determined as $1(S), \alpha(S), \alpha^{\prime}(S), 1^{\prime}(S)$ configuration by X-ray crystallographical analysis ${ }^{15}$.

## Scheme 3. Pinacol Coupling of Enantiomerically Pure (Dienal)Fe(CO) $)_{3}$



The reaction mechanism of stereoselective pinacol coupling of the planar chiral 2 -substituted ferrocenecarboxaldehydes and tricarbonyl(dienal)iron complex would be analogous to the samarium-mediated reductive coupling of the planar chiral ( $o$-substituted benzaldehyde) $\mathrm{Cr}(\mathrm{CO})_{3}$ complexes, because the relative stereochemical relationship between the pseudo benzylic stereogenic center and the metal-complexed adjacent planar center of 19 and $\mathbf{2 3}$ are identical with those of the pinacol product 8 derived from enantiomerically pure
(o-bromobenzaldehyde)chromium complex. The carbonyl oxygen atom of 18 and 22 would be an anticonfiguration to the $\alpha$-substituent due to stereoelectronic effect. Then, the samarium metal attacks the anticarbonyl ${ }^{23}$ from the exo-side to generate the corresponding ketyl radical intermediates 24 and 25 , respectively, which incorporate a substantial amount of the exocyclic double bond character owing to an interaction of $d$ orbital of the metal with p-orbital of the carbon. But, with 2-diphenylphosphino substituent of ferrocenyl compound, the initially formed ketyl intermediate 24 might be isomerized to diastereoisomerically configuration.

Fig. 2


## Pinacol Coupling of Tricarbonyl(benzaldimine)chromium Complexes

One of the most straightforward methods for the preparation of 1,2-diamines is an inter- or intramolecular reductive coupling of the aldimine compounds. ${ }^{24}$ As a further extension of the pinacol coupling of the planar chiral arene chromium complexes, we next investigated a reductive coupling of the planar chiral (benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$ complexes giving 1,2-diamines. ${ }^{25}$ The effect of $N$-substituent in the aldimine chromium complexes 26 was initially evaluated for the reductive coupling with samarium diiodide (Table 3). From the reaction results, it can be seen that $N$-alkyl substituted benzaldimine chromium complexes produced the desired coupling products as diastereomeric mixtures along with benzylamine in a various ratio. The aldimine chromium complexes having an electron-withdrawing substituent gave the $\mathrm{C}-\mathrm{N}$ double bond reduced product without formation of the coupling product (entries 5.6 ), and $N$-heteroatom substituents resulted in a complexed mixture (entries 7,8 ). Therefore, we next investigated stereoselectivity of the pinacol coupling of ( $N$-alkyl $o$-substituted benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$ complexes.

Table 3. Pinacol Coupling of (Benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$

|  <br> 26 |  | 1) $\mathrm{Sml}_{2}$, r.t., <br> 2) $I_{2}$ <br> 27 |  | $28(\%)$ |
| :---: | :---: | :---: | :---: | :---: |
| Entry | R | 27 (\%) | Ratio of 27 <br> (threo: erythro) |  |
| 1 | Me | 71 | 41:59 | 14 |
| 2 | $B u^{\prime \prime}$ | 31 | 50 : 50 | 48 |
| 3 | $\mathrm{Pr}^{i}$ | 48 | 50 : 50 | 41 |
| 4 | $\mathrm{CH}_{2} \mathrm{Ph}$ | 42 | 50 : 50 | 48 |
| 5 | Ph | - |  | 80 |
| 6 | $\mathrm{SO}_{2} \mathrm{Ph}$ | - |  | 95 |
| $7 a$ | OMe | - |  | 10 |
| $8^{a}$ | $\mathrm{NMe}_{2}$ | - |  | 10 |

[^1]Racemic tricarbonyl( $N$-methyl o-methoxybenzaldimine)chromium was treated with samarium diiodide in THF at $0^{\circ} \mathrm{C}$ to give the corresponding coupling products, threo- and erythro-diamines, in $63 \%$ yield as a mixture (ratio 43 : 57) accompanied with $17 \%$ yield of $N$-methyl $o$-methoxybenzylamine complex. Although a high diastereoselectivity was not observed in the pinacol coupling 1,2-diamine product of the racemic (o-substituted benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$ complex, particular attention should be given to the relative stereochemistry of the tricarbonylchromium-complexed 1,2-diamine. Either theoo- or erythro-1,2-diamine chromium complex derived from the racemic (o-substituted benzaldimine)chromium complex was obtained as a single compound, respectively, as well as the pinacol coupling of racemic ( $o$-substituted benzaldehyde)chromium complexes. Both the chromium-complexed threo- and erythro 1,2-diamines have the symmetrical structure, as evidenced by NMR spectra. A symmetry of the coupling products and an analogy of ( $o$-substituted benzaldehyde)chromium as mentioned above, it can be easily proposed that the tricarbonylchromium-complexed threo 1,2-diamine ( $C_{2}$, symmmetry) would possess the identical planar chirality in the chromium-complexed arene rings, while the corresponding erythro (meso-) complex ( $C_{1}$ symmetry) would be formed by a hetero-coupling of the (benzaldimine)chromium complexes with distinguishable chirality to each other.

As expected, the enantiomerically pure tricarbonyl(benzaldimine)chromium complex ${ }^{26}$ could produce only threo coupling product as a single compound by the reductive coupling, irrespective of the ortho substituents as follows. For example, an enantiomerically pure ( $1 S$ )-( $N$-methyl $\sigma$-methoxybenzaldimine)chromium (29) $\left(\mathrm{R}^{1}=\right.$ $\mathrm{Me}, \mathrm{R}^{2}=\mathrm{OMe}$ ) was treated with $\mathrm{SmI}_{2}$ to give the corresponding threo 1,2 -diamine 30 as a single coupling product in $67 \%$ yield along with $10 \%$ of the benzylamine chromium complex 31 (Table 4 ). No erythro 1,2diamine was observed by using enantiomerically pure complex. The absolute stereochemistry of 30 ( $\mathrm{R}^{l}=\mathrm{Me}$, $\mathrm{R}^{2}=\mathrm{OMe}$ ) was confirmed by X-ray crystallography ${ }^{15}$ and the benzylic center was found to be the $S$ configuration. Similarly, other enantiomerically pure benzaldimine chromium complexes gave the corresponding threo 1,2 -diamines as a single pinacol coupling compound. Thus, the 1,2-diamines can be prepared as an enantiomerically pure form by the reductive pinacol coupling of planar chiral tricarbonyl(osubstituted benzaldimine)chromium complexes. These enantiomerically pure 1,2-diamines would be useful compounds for the asymmetric reactions.

Table 4. Pinacol Coupling of Enantiomerically Pure (Benzaldimine) $\mathrm{Cr}\left(\mathrm{CO}_{3}\right.$

| 29 |  |  |  | $+$ <br> 31 |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |
| entry | $\mathrm{R}^{1}$ | $\mathrm{R}^{2}$ | 30 (\%) | $30\left[\alpha l_{0}\left(\mathrm{CHCl}_{3}\right)\right.$ | 31 (\%) |
| 1 | Me | Me | 65 | +86.2 | 25 |
| 2 | Me | OMe | 67 | -234 | 10 |
| 3 | Me | Br | 45 | -31.3 | 41 |
| 4 | Me | Cl | 48 | -6.7 | 46 |
| $5{ }^{\text {a }}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ | Me | 54 | +20.9 | 38 |
| $6^{a}$ | $\mathrm{CH}_{2} \mathrm{Ph}$ | $\mathrm{OPr}^{i}$ | 51 | +126 | 29 |

$a$ : The antipode of 29 was used as a starting material and the coupling product was an enantiomer of 30 .
The reaction mechanism for the stereoselective coupling of the planar chiral (o-substituted benzaldimine) $\mathrm{Cr}(\mathrm{CO})_{3}$ complexes would be analogous to the samarium(II)-mediated pinacol coupling of the (osubstituted benzaldehyde)chromium complexes. The samarium attacks an anti $\mathrm{C}=\mathrm{N}$ double bond to generate
configurationally stable radical intermediate which react with imine double bond of the arene chromium complexes.

In conclusion we demonstarted that the planar chiral tricarbonylchromium complexes of benzaldehydes, benzaldimines, 2 -substituted ferrocenecarboxaldehydes and (dienal) $\mathrm{Fe}(\mathrm{CO})_{3}$ gave the corresponding metalstabilized ketyl radicals stereoselectively without racemization at the radical carbon positions, and produced pinacol coupling products with the threo-configuration by treatment with samarium diiodide.

## Experimental Section

All manipulations involving organometallics were performed under argon atmosphere using standard Schlenk techniques. Solvents were distilled under an argon atmosphere from sodium benzophenone ketyl (THF), $\mathrm{CaH}_{2}$ (HMPA) or $\mathrm{P}_{2} \mathrm{O}_{5}\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$. Melting points were uncorrected. ${ }^{1} \mathrm{H}$ NMR spectra were recorded on JEOL GX-400 ( 400 MHz ), JEOL LA-300 $(300 \mathrm{MHz})$ and JEOL EX ( 270 MHz ) spectrometer with Me4Si as an internal standard. IR spectra were taken with a JASCO A-100 spectrometer. Mass spectra were measured on a JEOL D-300 instrument in the EI mode ( 70 eV ). Elemental analysis was performed on a Perkin-Elmer Model 240 elemental analyzer. Optical rotations were obtained on JASCO DIP-370 automatic polarimeter at 589 nm (sodium D line) using a $1.0-\mathrm{dm}$ cell with a total volume of 3 mL .

Typical Procedure for Pinacol Coupling of Tricarbonyl(benzaldehyde)chromium Complexes with Samarium Diiodide. A solution of tricarbonyl(benzaldehyde)chromium ( $100 \mathrm{mg}, 0.41$ mmol ) and $\mathrm{SmI}_{2}\left(0.1 \mathrm{M}\right.$ in THF, $10 \mathrm{~mL}, 1.0 \mathrm{mmol}$ ) was stirred at $-78^{\circ} \mathrm{C}$ for 30 min under argon atmosphere. The reaction mixture was quenched with saturated aqueous $\mathrm{NaHCO}_{3}$ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over $\mathrm{MgSO}_{4}$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with ether/hexane) to give $78 \mathrm{mg}(78 \%)$ of pinacol coupling product, a mixture of threo and erythro isomers $2\left(\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{H}\right) . \mathrm{mp} 160-163^{\circ} \mathrm{C}$ (dec.); ${ }^{1} \mathrm{H}$ NMR ( $\left.400 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right) \delta 1.15$ (brs. 2 H for threo), 1.23 (brs, 2 H for erythro), 4.25 (s, 2 H for erythro), 4.42 ( $\mathrm{s}, 2 \mathrm{H}$ for threo), 5.23-5.58 (m, 10H); IR ( $\mathrm{CHCl}_{3}$ ) $3350,1980,1910 \mathrm{~cm}^{-1}$; MS (relative intensities) $\mathrm{m} / \mathrm{z} 486\left(\mathrm{M}^{+}, 15\right), 430(48), 402$ (39), 374 (27), 346 (36), 318 (76), 300 (50), 266 (100), 230 (84), 179 (74). Anal. calcd for $\mathrm{C}_{20} \mathrm{H}_{14} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : C, 49.39; H, 2.90. Found: $\mathrm{C}, 48.99 ; \mathrm{H}, 2.80$. The demetalation of the chromium-complexed pinacols was carried out with iodine. To a solution of the pinacol $2\left(\mathrm{R}^{1}=\mathrm{R}^{2}=\mathrm{H}\right)(78 \mathrm{mg}, 0.16 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \mathrm{~mL})$ was added iodine ( $40 \mathrm{mg}, 0.32$ mmol ) at room temperature. After the reaction mixture was stirred for 30 min , saturated aqueous $\mathrm{NaHSO}_{3}$ was added. The resulting mixture was stirred for a few minute and extracted with ether. The extract was washed with saturated aqueous $\mathrm{NaHCO}_{3}$ and brine, dried over $\mathrm{MgSO}_{4}$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with ether/hexane) to give 32 mg ( $92 \%$ ) of demetalated pinacol $3\left(R^{1}=R^{2}=H\right)$ as a colorless crystal. The ratio (91:9) of threo- and erythro isomers was determined by the proton area of methyne $(\mathrm{CHOH}): 4.72 \mathrm{ppm}$ for methyne protons of threo pinacol $3\left(\mathrm{R}^{l}=\mathrm{H}\right.$, $\left.\mathrm{R}^{2}=\mathrm{H}\right)^{12 \mathrm{~b}}$ and 4.84 ppm for the corresponding protons of erythro pinacol $3\left(\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{H}\right){ }^{16 \mathrm{~b}}{ }^{1} \mathrm{H} N M R$ ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.85$ (brs, 2 H ), 4.72 ( $\mathrm{s}, 2 \mathrm{H}$ for threo), 4.84 ( $\mathrm{s}, 2 \mathrm{H}$ for erythro), $7.12-7.30(\mathrm{~m}, 10 \mathrm{H}$ ). The methyne protons in threo isomer 3 appears at ca. $0.1-0.2 \mathrm{ppm}$ higher field than the corresponding ones in erythro isomer 3. ${ }^{6 a .12}$ The physical data of the other pinacol coupling products are as follows.
$2\left(\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{H}\right): \operatorname{mp} 210-213^{\circ} \mathrm{C}($ dec. $) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ for threo $\delta 2.01(\mathrm{~s}, 6 \mathrm{H}),$, $(\mathrm{br}, 2 \mathrm{H}), 4.77(\mathrm{~s}, 2 \mathrm{H}), 5.06(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.19(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.45(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.65(\mathrm{~d}$. $J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$; for erythro $\delta 2.09(\mathrm{br}, 2 \mathrm{H}),, 2.17(\mathrm{~s}, 6 \mathrm{H}), 4.68(\mathrm{~s}, 2 \mathrm{H}), 5.10(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.23(\mathrm{t}, J$ $=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.47(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.67(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3350,1980,1910 \mathrm{~cm}^{-1}$; MS (relative intensity) $m / 2514\left(\mathrm{M}^{+} 15\right), 430(48), 402(39), 374(27), 346$ (36), 318 (76), $300(50), 266$ (100), 230 (84), 179 (74); Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : C, 51.37; H. 3.52. Found; C, 51.34; H, 3.56.
$2\left(\mathrm{R}^{1}=\mathrm{OMe}, \mathrm{R}^{2}=\mathrm{H}\right): \mathrm{mp} 167-169^{\circ} \mathrm{C}(\mathrm{dec}.) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CD}_{3} \mathrm{OD}\right)$ for erythro $\delta 2.04(\mathrm{br}, 2 \mathrm{H})$, $3.43(\mathrm{~s}, 6 \mathrm{H}), 4.96(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.07(\mathrm{~s}, 2 \mathrm{H}), 5.08(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.50(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.59$
(d, $J=6.3 \mathrm{~Hz}, 2 \mathrm{H}$ ); for threo $\delta 3.56(\mathrm{br}, 2 \mathrm{H}), 3.72(\mathrm{~s}, 6 \mathrm{H}), 4.87(\mathrm{~s}, 2 \mathrm{H}), 5.06(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.31(\mathrm{~d}, J$ $=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.64(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.04(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3300,1960,1890 \mathrm{~cm}^{-1}$; MS (relative intensity) $m / z 546\left(\mathrm{M}^{+} 2\right), 378$ (18), 360 (14), 326 (30), 173 (74), 52 (100). Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{10} \mathrm{Cr}_{2}$ : C, 48.36; H, 3.32. Found; C, 48.68; H, 3.10.
$2\left(\mathrm{R}^{\mathrm{l}}=\mathrm{O}^{i} \mathrm{Pr}, \mathrm{R}^{2}=\mathrm{H}\right): \mathrm{mp} 165-167^{\circ} \mathrm{C}$; ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) for threo $\delta 1.31(\mathrm{~d}, J=6.0 \mathrm{~Hz}$, $6 \mathrm{H}), 1.32(\mathrm{~d}, J=6.0 \mathrm{~Hz}, 6 \mathrm{H}), 2.38(\mathrm{br}, 2 \mathrm{H}), 4.21-4.26(\mathrm{~m}, 2 \mathrm{H}), 5.21(\mathrm{~s}, 2 \mathrm{H}), 5.49-5.56(\mathrm{~m}, 4 \mathrm{H}), 5.67(\mathrm{~d}$, $J=6.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.01(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H})$; for crythro $\delta 1.21(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.29(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 6 \mathrm{H})$, $2.20(\mathrm{br}, 2 \mathrm{H}), 4.19-4.30(\mathrm{~m}, 2 \mathrm{H}), 4.79-4.86(\mathrm{~m}, 4 \mathrm{H}), 4.91(\mathrm{~s}, 2 \mathrm{H}), 5.54(\mathrm{t}, \mathrm{J}=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.03(\mathrm{~d}, \mathrm{~J}=$ $6.4 \mathrm{~Hz}, 2 \mathrm{H}$ ); IR ( $\mathrm{CHCl}_{3}$ ) $3350,1980,1910 \mathrm{~cm}^{-1}$; MS (relative intensity) $\mathrm{m} / 2602\left(\mathrm{M}^{+}, 0.4\right), 434$ (2), 382 (3), 173 (38), 121 (100). Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{26} \mathrm{O}_{10} \mathrm{Cr}_{2}$ : C, $51.83 ; \mathrm{H}, 4.35$. Found; $\mathrm{C}, 52.07, \mathrm{H}, 4.66$.
$2\left(\mathrm{R}^{\mathrm{I}}=\mathrm{NMe}_{2}, \mathrm{R}^{2}=\mathrm{H}\right): \mathrm{mp} 128-130^{\circ} \mathrm{C}($ dec. $) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ for threo $\delta 1.92(\mathrm{br}, 2 \mathrm{H})$, $2.76(\mathrm{~s}, 12 \mathrm{H}), 4.92(\mathrm{~s}, 2 \mathrm{H}), 4.99(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.28(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.45(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$, $5.65(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$; for erythro $\delta \mathrm{I} .86(\mathrm{br}, 2 \mathrm{H}), 2.71(\mathrm{~s}, 12 \mathrm{H}), 4.68(\mathrm{~s}, 2 \mathrm{H}), 5.10(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H})$, $5.23(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.47(\mathrm{t}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 5.67(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3350,1950,1890$ $\mathrm{cm}^{-1}$; MS (relative intensity) $m / z 572\left(\mathrm{M}^{+} 1\right), 516$ (48), 402 (13), 460 (25), 404 (15), 352 (100), 334 (15). Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{O}_{8} \mathrm{~N}_{2} \mathrm{Cr}_{2}$ : $\mathrm{C}, 50.35 ; \mathrm{H}, 4.23, \mathrm{~N}, 4.89$. Found: $\mathrm{C}, 50.17 ; \mathrm{H}, 4.18, \mathrm{~N}, 4.95$.
$2\left(\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{Br}\right): \mathrm{mp} 182-184^{\circ} \mathrm{C}(\mathrm{dec}.) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 2.25$ (br, 2 H for threo), 4.30 (s, 2H for erythro), $4.33(\mathrm{~s}, 2 \mathrm{H}$ for threo), $5.25(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}$ for threo), $5.39(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}$ for threo), $5.46-5.56\left(\mathrm{~m}, 4 \mathrm{H}\right.$ for threo); IR $\left(\mathrm{CHCl}_{3}\right) 3300,1970,1910 \mathrm{~cm}^{-1}$; MS (relative intensity) $\mathrm{m} / \mathrm{z} 644$ (M+ 0.6 ), 588 (7), 476 (20), 390 (18), 338 (15), 178 (37), 52 (100). Anal. calcd for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{O}_{8} \mathrm{Cr}_{2} \mathrm{Br}_{2}: \mathrm{C}, 37.29$; H, 1.88. Found: C, 36.99; H, 1.91 .
$2\left(\mathrm{R}^{1}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{Me}\right)$ : for threo; $\mathrm{mp} 182-184^{\circ} \mathrm{C}\left(\mathrm{dec}\right.$ ); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 2.20(\mathrm{~s}, 6 \mathrm{H}), 2.46$ (br, 2H), $4.37(\mathrm{~s}, 2 \mathrm{H}), 5.10(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.14(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.29(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.47(\mathrm{~d}$, $J=6.8 \mathrm{~Hz}, 2 \mathrm{H}) ;$ IR $\left(\mathrm{CHCl}_{3}\right) 3300,1960,1900 \mathrm{~cm}^{-1} ; \mathrm{MS}$ (relative intensity) $\mathrm{m} / \mathrm{z} 514\left(\mathrm{M}^{+} 1\right), 480(4), 346$ (10), 276 (12), 260 (61), 208 (28), 172 (44), 52(100). Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : C, 51.37; $\mathrm{H}, 3.52$. Found: C, 51.18; H, 3.57.
$2\left(\mathrm{R}^{\mathrm{l}}=\mathrm{H}, \mathrm{R}^{2}=\mathrm{OMe}\right.$ ): for threo; $\mathrm{mp} 165-167^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.41(\mathrm{br}, 2 \mathrm{H}), 3.72(\mathrm{~s}$, $6 \mathrm{H}), 4.28(\mathrm{~s}, 2 \mathrm{H}), 5.04-5.06(\mathrm{~m}, 4 \mathrm{H}), 5.45(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.56(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H})$ : IR $\left(\mathrm{CHCl}_{3}\right) 3300$, 1970, $1930 \mathrm{~cm}^{-1}$; MS (relative intensity) $\mathrm{m} / \mathrm{z} 546\left(\mathrm{M}^{+}, 2\right), 378(30), 344(8), 292(92), 240(100), 225(62)$. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{10} \mathrm{Cr}_{2}$ : C, 48.36; $\mathrm{H}, 3.32$. Found: $\mathrm{C}, 48.22 ; \mathrm{H}, 3.31$.

Pinacol Coupling of $d l$-Tricarbonyl(o-bromobenzaldehyde)chromium (4): The crude product obtained by pinacol coupling of racemic tricarbonyl( $o$-bromobenzaldehyde)chromium (4) ( $300 \mathrm{mg}, 0.93 \mathrm{mmol}$ ) with $\mathrm{SmI}_{2}(0.1 \mathrm{M}$ in $\mathrm{THF}, 18.6 \mathrm{~mL}, 1.86 \mathrm{mmol})$ at $-78^{\circ} \mathrm{C}$ for 1 h under argon atmosphere was purified by column chromatography on silica gel (eluted with ether/hexane) to give 57 mg ( $19 \%$ ) of threo pinacol 5 A and $138 \mathrm{mg}(46 \%)$ of erythro pinacol 6A. threo pinacol 5A. yellow crystals, mp $158-160^{\circ} \mathrm{C}$ (dec.); ${ }^{1} \mathrm{H}$ NMR ( 300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 2.59(\mathrm{brs}, 2 \mathrm{H}), 4.95(\mathrm{~s}, 2 \mathrm{H}), 5.20(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.41(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.53(\mathrm{~d}, J=$ $7.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.94(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3300,1990.1940 \mathrm{~cm}^{-1}$; MS (relative intensities) $\mathrm{m} / \mathrm{z} 644$ ( $\mathrm{M}^{+}, 3$ ), 476 (4), 378 (4), 236 (28), 178 (77), 157 (67), 52 (100). Anal. calcd for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{O}_{8} \mathrm{Br}_{2} \mathrm{Cr}_{2}$ : C, 37.29; H, 1.88. Found: C, $37.25 ; \mathrm{H}, 1.99$. erythro pinacol 6 A . yellow crystals, mp $150-153{ }^{\circ} \mathrm{C}$ ( dec.); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.74(\mathrm{brs}, 2 \mathrm{H}), 5.16(\mathrm{t}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H}), 5.36(\mathrm{~s}, 2 \mathrm{H}), 5.37(\mathrm{t}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H})$, $5.41(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H}), 5.53(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3300,1990,1930 \mathrm{~cm}^{-1}$. Anal. calcd for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{O}_{8} \mathrm{Br}_{2} \mathrm{Cr}_{2}$ : C, 37.29; H, 1.88. Found: C, $37.49 ; \mathrm{H}, 2.00$.

Pinacol Coupling of (IS)-Tricarbonyl(o-bromobenzaldehyde)chromium (7): (IS)Tricarbonyl ( $o$-bromobenzaldehyde)chromium (7) $\left\{[\alpha]_{\mathrm{D}} 23+1062.5^{\circ}\right.$ (c $0.60, \mathrm{CHCl}_{3}$ ) $\}$ ( $100 \mathrm{mg}, 0.31 \mathrm{mmol}$ ) was reacted with SmI 2 ( 0.1 M in THF, $6.2 \mathrm{~mL}, 0.62 \mathrm{mmol}$ ) at $0^{\circ} \mathrm{C}$ for 30 min under usual conditions, and the
crude coupling product was purified by column chromatography on silica gel (eluted with ether/hexane) to give 75 mg ( $75 \%$ ) of enantiomerically pure threo pinacol 8 as a single product; $[\alpha]_{\mathrm{D}^{23}}+58.2^{\circ}(c 0.27, \mathrm{MeOH})$.

Pinacol Coupling of (1R)-Tricarbonyl(o-methylbenzaldehyde)chromium (9): (R)-Tricarbonyl(o-methylbenzaldehyde)chromium (9) $\left\{\left.1 \alpha\right|_{D^{25}}-660.6^{\circ}\right.$ (c $1.00, \mathrm{CHCl}_{3}$ ) ( $100 \mathrm{mg}, 0.39 \mathrm{mmol}$ ) was reacted with $\mathrm{SmI}_{2}(0.1 \mathrm{M}$ in THF. $9.8 \mathrm{~mL}, 0.98 \mathrm{mmol})$ and the product was purified by column chromatography on silica gel (eluted with ether/hexane) to give $71 \mathrm{mg}(71 \%)$ of enantiomerically pure threo pinacol 10 as a single product; yellow crystals, $|\alpha|_{D}{ }^{25}-97.6^{\circ}\left(c 0.51, \mathrm{CHCl}_{3}\right), \mathrm{mp} 210-213{ }^{\circ} \mathrm{C}(\mathrm{dec}.) ;{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.01(\mathrm{~s}, 6 \mathrm{H}), 2.44(\mathrm{brs}, 2 \mathrm{H}), 4.77(\mathrm{~s}, 2 \mathrm{H}), 5.06(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.19(\mathrm{t}, J=$ $6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.44(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.65(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3300,1950,1870 \mathrm{~cm}^{-1}$; MS (relative intensities) $m / z 514\left(\mathrm{M}^{+}, 1\right), 346$ (2), 294 (4), 172 (35), 120 (53), 91 (100), 65 (31), 52 (62). Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : $\mathrm{C}, 51.37 ; \mathrm{H}, 3.53$. Found: $\mathrm{C}, 51.66 ; \mathrm{H}, 3.62$.

Pinacol Coupling of 2-Methylferrocenecarboxyaldehyde (18) ( $\mathrm{R}=\mathrm{Me}$ ). To a solution of ( $R$ -$\alpha$-methylferrocenecarboxaldehyde (18) $(\mathrm{R}=\mathrm{Me})(128 \mathrm{mg}, 0.56 \mathrm{mmol})$ in dry THF $(0.5 \mathrm{~mL})$ was added a solution of $\mathrm{Sml}_{2}(0.15 \mathrm{M}, 9.3 \mathrm{~mL}, 1.40 \mathrm{mmol})$ in THF at $-78^{\circ} \mathrm{C}$, and the solution was stirred at the same temperature for 30 min under argon atmosphere. The reaction mixture was quenched with saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether. The extract was washed with brine, dried over $\mathrm{MgSO}_{4}$ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluted with $\mathrm{Et}_{2} \mathrm{O} / \mathrm{hexane}$ ) to give 116 mg ( $91 \%$ ) of 19 ( $\mathrm{R}=$ Me): mp $210-211^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.32(\mathrm{~s} .6 \mathrm{H}), 2.66(\mathrm{br}, 2 \mathrm{H}), 3.93-3.97(\mathrm{~m}, 4 \mathrm{H}), 4.07$ $(\mathrm{s}, 10 \mathrm{H}), 4.20-4.21(\mathrm{~m}, 2 \mathrm{H}), 4.24(\mathrm{~s}, 2 \mathrm{H}) ;[\alpha]_{\mathrm{D}}{ }^{19}+89.5$ (c $\left.0.39, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{26} \mathrm{O}_{2} \mathrm{Fe}_{2}$ : C , 62.78; H, 5.79. Found C, 62.91; H, 5.72.
$19(\mathrm{R}=\mathrm{TMS}): \mathrm{mp} 41^{\circ} \mathrm{C},{ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 0.28(\mathrm{~s}, 18 \mathrm{H}), 1.60(\mathrm{br}, 2 \mathrm{H}), 4.11-4.12(\mathrm{~m}$, $2 \mathrm{H}), 4.15(\mathrm{~s}, 10 \mathrm{H}), 4.29-4.31(\mathrm{~m}, 2 \mathrm{H}), 4.34(\mathrm{~s}, 2 \mathrm{H}), 4.38-4.39(\mathrm{~m}, 2 \mathrm{H}) ;[\alpha]_{\mathrm{D}}{ }^{19}+69.4\left(c \quad 0.55, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{28} \mathrm{H}_{30} \mathrm{O}_{2} \mathrm{Si}_{2} \mathrm{Fe}_{2}$ : $\mathrm{C}, 58.54 ; \mathrm{H}, 6.67$. Found $\mathrm{C}, 58.61 ; \mathrm{H}, 6.69$.
$19(\mathrm{R}=\mathrm{Br}): \mathrm{mp} 174^{\circ} \mathrm{C} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 2.44(\mathrm{br}, 2 \mathrm{H}), 4.14-4.16(\mathrm{~m}, 2 \mathrm{H}), 4.22(\mathrm{~s}$, $10 \mathrm{H}), 4.32-4.34(\mathrm{~m}, 2 \mathrm{H}), 4.42-4.44(\mathrm{~m}, 2 \mathrm{H}), 4.54(\mathrm{~s}, 2 \mathrm{H}) ;[\alpha]_{\mathrm{D}} 20+44.2\left(c \quad 0.12, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{O}_{2} \mathrm{Fe}_{2} \mathrm{Br}_{2}$ : $\mathrm{C}, 44.95 ; \mathrm{H}, 3.43$. Found $\mathrm{C}, 45.10 ; \mathrm{H}, 3.44$.
$19(\mathrm{R}=\mathrm{I}): \mathrm{mp} 170^{\circ} \mathrm{C}:{ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.47(\mathrm{br}, 2 \mathrm{H}), 4.19(\mathrm{~s}, 10 \mathrm{H}), 4.25-4.26(\mathrm{~m}, 2 \mathrm{H})$, $4.39(\mathrm{~s}, 2 \mathrm{H}), 4.40-4.44(\mathrm{~m}, 4 \mathrm{H}) ;[\alpha]_{\mathrm{D}}{ }^{24}+37.4\left(c \quad 0.38, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{20} \mathrm{O}_{2} \mathrm{Fe}_{2} \mathrm{I}_{2}: \mathrm{C}, 44.95$; H, 3.43. Found C, 45.10; H, 3.44.

Preparation of $23:{ }^{1} \mathrm{H}$ NMR ( $\left.270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.42(\mathrm{~d}, 2 \mathrm{H}, J=8.9 \mathrm{~Hz}), 2.07(\mathrm{~d}, 2 \mathrm{H}, J=8.9 \mathrm{~Hz})$, $2.23(\mathrm{~s}, 2 \mathrm{H}), 2.26(\mathrm{~s}, 6 \mathrm{H}), 3.73-3.77(\mathrm{~m}, 2 \mathrm{H}), 5.70(\mathrm{~d}, 2 \mathrm{H}, J=8.9 \mathrm{~Hz}), 7.15-7.27(\mathrm{~m}, 10 \mathrm{H}) ; \mathrm{IR}\left(\mathrm{CHCl}_{3}\right)$ $3250,2030,1950 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}{ }^{19}-503.4\left(c \quad 0.58, \mathrm{CHCl}_{3}\right) . \mathrm{MS}$ (relative intensities) $\mathrm{m} / \mathrm{z} 626\left(\mathrm{M}^{+}, 2\right), 609(8)$, 570 (16), 542 (20), 458 (10), 368 (48), 154 (100).

Typical Procedure of Pinacol Coupling of Tricarbonyl(benzaldimine)chromium: To a solution of $26(\mathrm{R}=\mathrm{Me})(100 \mathrm{mg}, 0.39 \mathrm{mmol})$ in THF $(2.5 \mathrm{~mL})$ was added a solution of $\mathrm{SmI}_{2}$ prepared from samarium metal ( $294 \mathrm{mg}, 1.96 \mathrm{mmol}$ ) and 1,2 -diiodoethane ( $5.52 \mathrm{mg}, 1.96 \mathrm{mmol}$ ) in THF ( 1.5 mL ) at room temperature and the mixture was stirred for 1 h . The reaction mixture was quenched with saturated aqueous $\mathrm{NaHCO}_{3}$ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over $\mathrm{MgSO}_{4}$ and evaporated under reduced pressure. To a solution of the residue in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ( 2 mL ) was added iodine ( $49.0 \mathrm{mg}, 0.39 \mathrm{mmol}$ ) at room temperature and stirred for 30 min . The reaction mixture was quenched with saturated aqueous $\mathrm{NaHSO}_{3}$ and the resulting mixture was filtered through Celite pad. The filtrate was extracted with ether, and the extract was washed with brine, dried over $\mathrm{MgSO}_{4}$ and evaporated under reduced pressure. The residue was treated with iodine, and then purified by column chromatography on silica gel (eluted with ether/hexane) to give $33.4 \mathrm{mg}(71 \%)$ of $27(\mathrm{R}=\mathrm{Me})$ and 6.5 $\mathrm{mg}(14 \%)$ of $N$-methylbenzylamine. $27(\mathrm{R}=\mathrm{Me}) .{ }^{27}{ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.30(\mathrm{~s}, 2 \mathrm{H}$ for threo),
1.90 ( $\mathrm{s}, 2 \mathrm{H}$ for erythro), 2.08 ( $\mathrm{s}, 6 \mathrm{H}$ for erythro), 2.20 ( $\mathrm{s}, 6 \mathrm{H}$ for threo), 3.48 ( $\mathrm{s}, 2 \mathrm{H}$ for threo), 3.58 (s, 2H for erythro), 6.97-7.48 ( $\mathrm{m}, 10 \mathrm{H}$ ); $\operatorname{IR}\left(\mathrm{CHCl}_{3}\right) 3400,1230 \mathrm{~cm}^{-1} .28(\mathrm{R}=\mathrm{Me})$. ${ }^{1} \mathrm{H} \operatorname{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 2.45 (s, 3H), 3.74 (s, 2 H ), $4.68(\mathrm{~s}, 1 \mathrm{H}), 7.27-7.37(\mathrm{~m}, 5 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3200,1430 \mathrm{~cm}^{-1} ; \mathrm{MS}$ (relative intensity) $m / z 121\left(\mathrm{M}^{+} 62\right), 91$ (100); HRMS calcd for $\mathrm{C}_{8} \mathrm{H}_{1} \mathrm{~N}$ 121.0891. found 121.0905 .

Pinacol Coupling of Enantiomerically Pure Tricarbonyl( $N$-methyl o-substituted benzaldimine)chromium (29) ( $\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{OMe}$ ): Pinacol couping was carried out under the same conditions. $30\left(\mathrm{R}^{\mathrm{I}}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{OMe}\right) . \mathrm{mp} 150-152^{\circ} \mathrm{C}($ dec. $) ;{ }^{1} \mathrm{H} \mathrm{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.43(\mathrm{~s}, 2 \mathrm{H})$, $2.48(\mathrm{~s}, 6 \mathrm{H}), 3.68(\mathrm{~s} .6 \mathrm{H}), 3.88(\mathrm{~s}, 2 \mathrm{H}), 4.87(\mathrm{t}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H}), 4.94(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.52(\mathrm{t}, J=6.1$ $\mathrm{Hz}, 2 \mathrm{H}), 5.84(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3300,1960,1890 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}{ }^{28}-234\left(c 0.27, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : C. 50.36 ; $\mathrm{H}, 4.23 ; \mathrm{N}, 4.89$. Found: C, $50.28 ; \mathrm{H}, 4.24 ; \mathrm{N}, 4.75 .31\left(\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}\right.$ $=\mathrm{OMe}){ }^{\mathrm{l}} \mathrm{H} \operatorname{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) 1.40(\mathrm{br}, 1 \mathrm{H}), 2.51(\mathrm{~s}, 3 \mathrm{H}), 3.21(\mathrm{~d}, \mathrm{~J}=12.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 1 \mathrm{H})$, $3.84(\mathrm{~d}, J=12.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.92(\mathrm{t}, J=6.0 \mathrm{~Hz}, 1 \mathrm{H}), 5.06(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.48(\mathrm{t}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.71$ (d, $J=6.0 \mathrm{~Hz}, 1 \mathrm{H}$ ); IR ( $\mathrm{CHCl}_{3}$ ) $1950,1870 \mathrm{~cm}^{-1}$. MS (relative intensity) m/z $287\left(\mathrm{M}^{+} 2\right), 285(20), 257(55)$, 230 (98), 149 (100); HRMS calcd for $\mathrm{C}_{12} \mathrm{H}_{13} \mathrm{O}_{4} \mathrm{NCr} 287.0998$, found 287.0978.
$30\left(\mathrm{R}^{\mathrm{I}}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{Me}\right)$ : $\mathrm{mp} 150-152{ }^{\circ} \mathrm{C}\left(\right.$ dec.); ${ }^{\mathrm{l}} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\boldsymbol{\delta} 1.24(\mathrm{br}, 2 \mathrm{H}), 2.27(\mathrm{~s}$, $6 \mathrm{H}), 2.58(\mathrm{~s}, 6 \mathrm{H}), 3.69(\mathrm{~s}, 2 \mathrm{H}), 4.97(\mathrm{t}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.11(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.22(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H})$, $5.39(\mathrm{t}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H}) ; \mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3350,2980,1940,1880 \mathrm{~cm}^{-1} ;[\alpha]_{\mathrm{D}}{ }^{22}+86.1\left(c 0.61, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Cr}_{2}$ : C, 53.34; $\mathrm{H}, 4.48$; N, 5.18. Found; C, $53.18 ; \mathrm{H}, 4.49 ; \mathrm{N}, 5.05 .31\left(\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}\right.$ $=\mathrm{Me}) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.25(\mathrm{~s}, 1 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.52(\mathrm{~s}, 3 \mathrm{H}), 3.41(\mathrm{~d}, J=13.7 \mathrm{~Hz}, 1 \mathrm{H})$, $3.65(\mathrm{~d}, J=13.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.21-5.25(\mathrm{~m}, 2 \mathrm{H}), 5.34(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.58(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 1950,1870 \mathrm{~cm}^{-1}$. MS (relative intensity) $m / z 271\left(\mathrm{M}^{+} 20\right), 215(20), 187(60), 134$ (100); HRMS calcd for $\mathrm{C}_{12} \mathrm{H}_{13} \mathrm{O}_{3} \mathrm{NCr} 271.0892$, found 271.0905 .
$30\left(\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{Br}\right): \mathrm{mp} 147-149^{\circ} \mathrm{C}$ (dec.); ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.25(\mathrm{br}, 2 \mathrm{H}), 2.54(\mathrm{~s}$, 6 H ), 3.72 (s. 2 H ), $5.04(\mathrm{t}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.41(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.43(\mathrm{t}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H}) 5.91(\mathrm{~d}, J=$ $6.1 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3350,1980,1890,1410 \mathrm{~cm}^{-1} ;\left[\alpha \mathrm{D}^{26}-31.3\right.$ (c $\left.0.41, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Cr}_{2} \mathrm{Br}_{2}$ : C. 39.43; H, 2.71; $\mathrm{N}, 4.18$. Found: C. 39.31; H, 2.72; $\mathrm{N}, 4.04 .31\left(\mathrm{R}^{\mathrm{I}}=\mathrm{Me}, \mathrm{R}^{2}=\right.$ $\mathrm{Br}){ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.26(\mathrm{~s}, 1 \mathrm{H}), 2.54(\mathrm{~s}, 3 \mathrm{H}), 3.54(\mathrm{~d}, J=13.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.80(\mathrm{~d}, J=13.5$ $\mathrm{Hz}, 1 \mathrm{H}), 5.20(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.28(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.60-5.66(\mathrm{~m}, 2 \mathrm{H}) ; \mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 1960,1890 \mathrm{~cm}$ ${ }^{1}$. MS (relative intensity) $m / z 336\left(\mathrm{M}^{+} 5\right), 334$ (18), 278 (52), 250(95), 198 (100); HRMS calcd for $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{O}_{3} \mathrm{NCrBr} 336.0154$, found 336.0161 .
$30\left(\mathrm{R}^{1}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{Cl}\right): \mathrm{mp} 150-152^{\circ} \mathrm{C}\left(\mathrm{dec}\right.$ ); ${ }^{1} \mathrm{H} \mathrm{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.47(\mathrm{~s}, 2 \mathrm{H}), 2.49(\mathrm{~s}$, $6 \mathrm{H}), 3.82(\mathrm{~s}, 2 \mathrm{H}), 5.03(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 5.32(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.49(\mathrm{t}, J=6.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.90(\mathrm{~d}, J=$ $6.8 \mathrm{~Hz}, 2 \mathrm{H})$; IR $\left(\mathrm{CHCl}_{3}\right) 3320,1960,1890 \mathrm{~cm}^{-1} ;\left[\left.\alpha\right|_{\mathrm{D}}{ }^{26}-6.7\right.$ (c $\left.0.22, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{22} \mathrm{H}_{18} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Cl}_{2} \mathrm{Cr}_{2}$ : C, 45.44; H, 3.12; N, 4.82. Found; C, 45.73; H, 3.40; N, 4.69. $31\left(\mathrm{R}^{\mathrm{t}}=\mathrm{Me}, \mathrm{R}^{2}=\mathrm{Cl}\right)$. ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.43(\mathrm{~s}, 1 \mathrm{H}), 2.54(\mathrm{~s}, 3 \mathrm{H}), 3.52(\mathrm{~d}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{~d}, J=14.0 \mathrm{~Hz}$, $1 \mathrm{H}), 5.12(\mathrm{t}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.36(\mathrm{t}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.52(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.36(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H})$; IR ( $\mathrm{CHCl}_{3}$ ) 1960, $1890 \mathrm{~cm}^{-1}$. MS (relative intensity) m/z 291 (M+5), 289 (59), 261 (90), 153 (100); HRMS calcd for $\mathrm{C}_{11} \mathrm{H}_{10} \mathrm{O}_{3} \mathrm{NClCr}$ 291.0346, found 291.0350 .

Antipode of $30\left(R^{1}=B n, R^{2}=\mathrm{Me}\right)$ : the corresponding antipode of 29 was used as a starting material; $\mathrm{mp} 175-176^{\circ} \mathrm{C}$ (dec.); ${ }^{1} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 2.16(\mathrm{~s}, 6 \mathrm{H}), 2.31(\mathrm{~s}, 2 \mathrm{H}), 3.63(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 2 \mathrm{H})$. $3.83(\mathrm{~s}, 2 \mathrm{H}), 3.95(\mathrm{~d}, J=13.2 \mathrm{~Hz}, 2 \mathrm{H}), 4.98(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.11(\mathrm{t}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.49(\mathrm{t}, J=6.4$ $\mathrm{Hz}, 2 \mathrm{H}), 5.75(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.14-7.38(\mathrm{~m}, 10 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 3300,2980,1940,1870 \mathrm{~cm}^{-1} .[\alpha]_{\mathrm{D}}{ }^{26}$ +20.9 (c 0.22, $\mathrm{CHCl}_{3}$ ); Anal. calcd for $\mathrm{C}_{36} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{Cr}_{2}: \mathrm{C}, 62.42 ; \mathrm{H}, 4.66 ; \mathrm{N}, 4.04$. Found: C, 62.16; H, 4.48; $\mathrm{N}, 3.99 .31\left(\mathrm{R}^{1}=\mathrm{Bn}, \mathrm{R}^{2}=\mathrm{Me}\right) . \mathrm{mp} 72-73^{\circ} \mathrm{C}$; ${ }^{\mathrm{I}} \mathrm{H} \operatorname{NMR}\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.41(\mathrm{br}, 1 \mathrm{H}), 2.18(\mathrm{~s}$, $3 \mathrm{H}), 3.48(\mathrm{~d}, J=13.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.65(\mathrm{~d}, J=13.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.93(\mathrm{~d}, J=8.5 \mathrm{~Hz}$, $1 \mathrm{H}), 5.19-5.23(\mathrm{~m}, 2 \mathrm{H}), 5.33(\mathrm{t}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.63(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.27-7.36(\mathrm{~m}, 5 \mathrm{H})$; $\mathrm{IR}\left(\mathrm{CHCl}_{3}\right)$

1950, $1870 \mathrm{~cm}^{-1}$. Anal. calcd for $\mathrm{C}_{18} \mathrm{H}_{17} \mathrm{NO}_{3} \mathrm{Cr}: \mathrm{C}, 62.24 ; \mathrm{H}, 4.93 ; \mathrm{N}, 4.03$. Found: $\mathrm{C}, 62.06, \mathrm{H}, 4.96 ; \mathrm{N}$, 4.01 .

Antipode of $30\left(\mathrm{R}^{1}=\mathrm{Bn}, \mathrm{R}^{2}=\mathrm{O}^{i} \mathrm{Pr}\right)$ : the corresponding antipode of 29 was used as a starting material; mp $90-91^{\circ} \mathrm{C}$; ${ }^{\prime} \mathrm{H}$ NMR ( $270 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 1.18(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 6 \mathrm{H}), 1.36(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 6 \mathrm{H})$, $1.43(\mathrm{~s}, 2 \mathrm{H}), 3.68(\mathrm{~d}, J=13.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.05(\mathrm{~d}, J=13.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.18-4.26(\mathrm{~m}, 2 \mathrm{H}), 4.29(\mathrm{~s} .2 \mathrm{H}), 4.85(\mathrm{t}$, $J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.87(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.56(\mathrm{t}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.96(\mathrm{~d}, J=6.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.15-7.29(\mathrm{~m}$, 10H); IR ( $\mathrm{CHCl}_{3}$ ) 3350, 3020, 1970, $1410 \mathrm{~cm}^{-1}$; $[\alpha]_{\mathrm{D}}{ }^{26}+126\left(c 0.50, \mathrm{CHCl}_{3}\right)$. Anal. calcd for $\mathrm{C}_{40} \mathrm{H}_{40} \mathrm{~N}_{2} \mathrm{O}_{8} \mathrm{Cr}_{2}$ : C, 61.53; H, 5.16; N, 3.59. Found: C, 61.28; H, 5.46; $\mathrm{N}, 3.35 .31\left(\mathrm{R}^{\mathrm{I}}=\mathrm{Bn}, \mathrm{R}^{2}=\mathrm{O}^{i} \mathrm{Pr}\right)$. ${ }^{1} \mathrm{H}$ NMR $\left(270 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 1.36(\mathrm{~d}, J=6.1 \mathrm{~Hz}, 6 \mathrm{H}), 1.40(\mathrm{br}, 1 \mathrm{H}), 3.41(\mathrm{~d}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~d}, J$ $=13.7 \mathrm{~Hz}, 2 \mathrm{H}), 3.94(\mathrm{~d}, J=14.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.32-4.37(\mathrm{~m}, 1 \mathrm{H}), 4.88(\mathrm{t}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.02(\mathrm{~d}, J=6.7 \mathrm{~Hz}$, $1 \mathrm{H}), 5.48(\mathrm{t}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.78(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.27-7.36(\mathrm{~m}, 5 \mathrm{H}) . \mathrm{IR}\left(\mathrm{CHCl}_{3}\right) 1950,1870 \mathrm{~cm}^{-1}$; MS (relative intensity) $m / \geq 391\left(\mathrm{M}^{+} 5\right), 333(20), 305$ (100), 253 (15); HRMS calcd for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{O}_{4} \mathrm{NCr}$ 391.0570, found 391.0563.

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