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Enantioselective catalysis using planar chiral η^6-arene chromium complexes: 1,2-diols as cycloaddition catalysts

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Abstract

A highly selective Diels–Alder catalyst has been prepared from a commercially available tetrahydronaphthalene diol. Stereocontrol is greatly enhanced by introduction of a planar chiral arene chromium tricarbonyl group, achieved by face selective complexation. The factors influencing stereoselectivity with the catalyst have been investigated and delineated. Under optimal conditions, the catalyst gives >95% e.e. and 98:2 *exo*:*endo* ratio in the cycloaddition of methacrolein and cyclopentadiene.

1. Introduction

Following on from their extensive application in asymmetric synthesis,[1] the use of arene chromium carbonyl complexes as asymmetric catalysts is now becoming commonplace.[2] We and others have demonstrated that the tricarbonyl chromium group is a powerful stereodirective element in both chiral catalysts and auxiliaries,[3,4] and that electronic control is afforded by mixed-ligand arene chromium carbonyl systems, ranging from inductive effects on ring substituents[5] to modulation of arene facial π-donor ability.[6] Combined, these effects can serve as powerful control elements in catalyst design, either by amplifying asymmetric induction of existing arene-based catalysts, or by introduction of planar chirality (Fig. 1).

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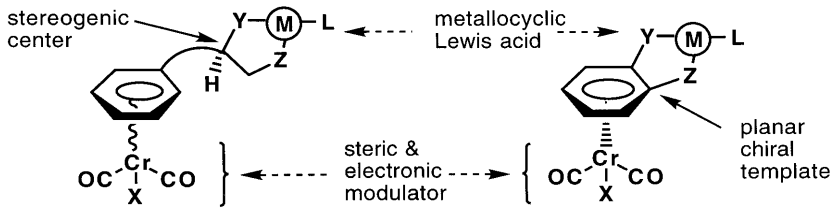
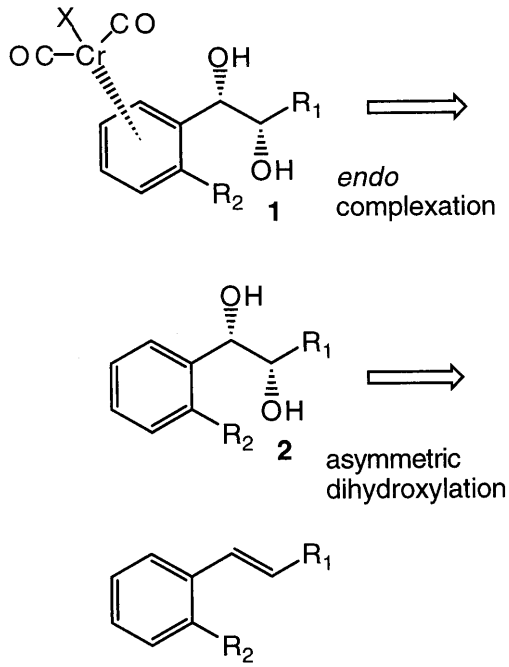


Figure 1.

Based on encouraging results with auxiliaries in cycloaddition reactions,[6] we sought to develop an efficient and readily available intermolecular Diels–Alder *catalyst* incorporating the above design features. Specifically, we sought a commercially available building block which offered the potential for formation of a five-membered metallocycle, and could be directly converted to a planar chiral arene complex.

To provide proof of principle, arene diol complexes were selected since (i) *endo* complexation of the metal carbonyl group is precedented (Scheme 1), (ii) asymmetric hydroxylation methods provide enantiospecific routes to the ligands **2**, allowing (iii) access from a wide variety of readily available vinyl arene building blocks.

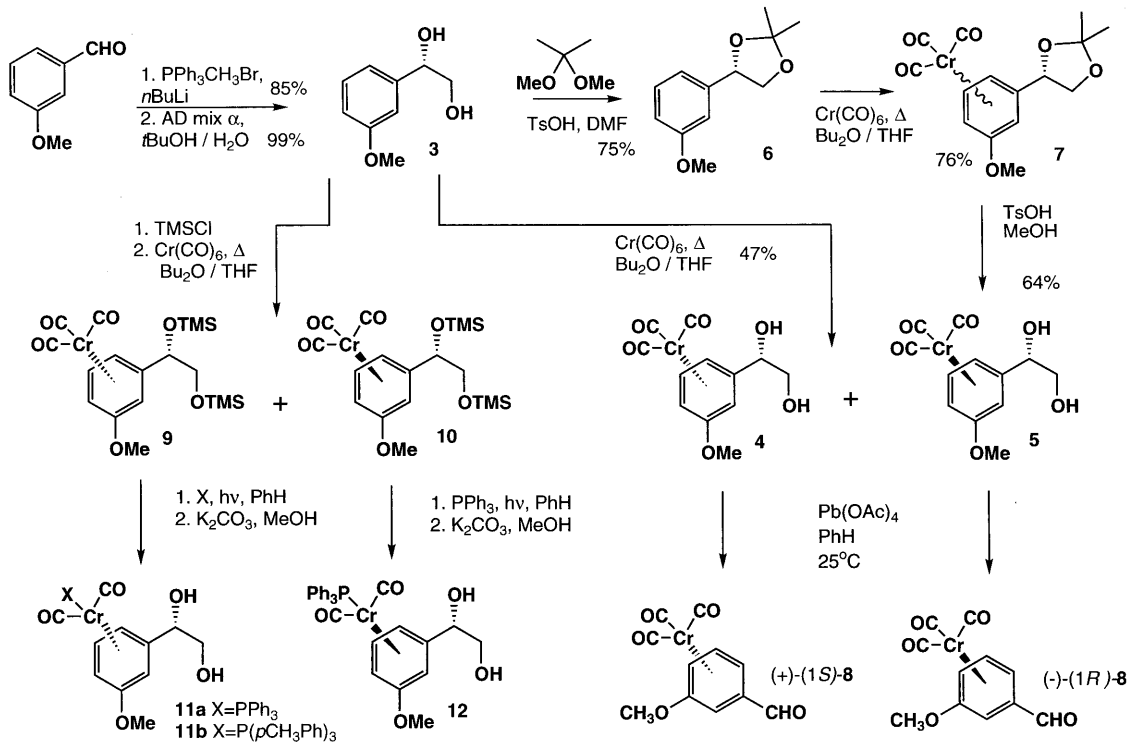


Scheme 1. Ligand design strategy

2. Results and discussion

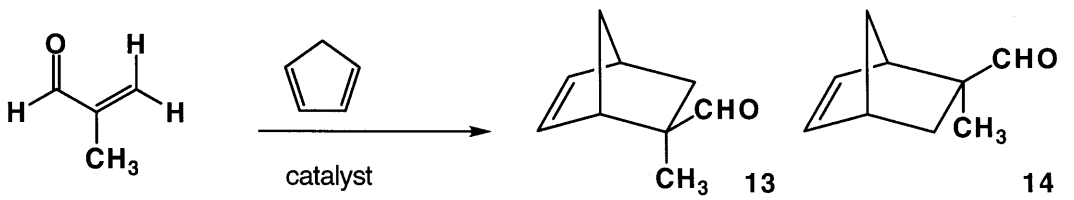
In order to highlight the role of the metal carbonyl tripod most effectively, our initial vinylarenes were *m*-substituted styrenes, since a corresponding *o*-substituent might be expected to impact on our ability to fine-tune stereocontrol. Accordingly, *m*-anisaldehyde was subjected to olefination followed by Sharpless dihydroxylation to give (*S*)-diol **3** in >99% e.e. (Scheme 2).[7]

Complexation at this point using conventional conditions gave a moderate yield of a 9:1 mixture of diastereomers **4** and **5**, which were separable using chromatographic methods. Protection of the hydroxyl functions in the form of ketal **6** followed by complexation gave a higher yield of complex **7**, but in a ratio of 5:1 in favor of the (*S*,1*R*) complex, confirmed on deprotection to give **4**. The identity of facial diastereomers **4**/**5** was established via oxidative cleavage to give the known aldehydes **8**.[8]



Scheme 2. Preparation and stereochemical assignment of *m*-methoxystyrene derived ligands

The diols were then exposed to a variety of Lewis acids, and the corresponding metallocycles/chelates examined in the catalytic enantioselective cycloaddition of 2-methacrolein with cyclopentadiene, using catalysts derived from **3** as controls. Though an *exo*-preference was observed with every Lewis acid combination examined, the (*R*)-enantiomeric cycloaddition product **13** was favored with both the boron and titanium metallocycles and the (*S*)-enantiomer **14** predominated with the aluminum metallocycles (Scheme 3, Table 1).



Scheme 3. Metallodioxolane catalyzed [4+2] cycloadditions

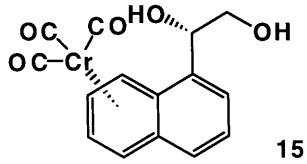
Table 1
Enantioselective cycloaddition of 2-methacrolein using arene diol catalysts[a]

Entry	Diol	Mol%	LA	Prod. (%)[b]	*Exo*:*endo*[c]	% e.e.[d]
1	**3**	20	BH_2Br	**13** (99)	92:8	19
2	**5**	20	BH_2Br	**13** (83)	95:5	20
3	**4**	20	BH_2Br	**13** (91)	96:4	39
4	**4**	20	BCl_3	**13** (95)	90:10	0
5	**4**	20	$BHCl_2$	**13** (95)	81:9	44
6	**4**	20	$BHBr_2$	**13** (87)	86:14[e]	43
7	**4**	20	BF_3OEt_2	**13** (75)	99:1	0
8	**3**	20	Et_2AlCl	**14** (98)	66:34	21
9	**5**	20	Et_2AlCl	**14** (82)	99:1	31
10	**4**	20	Et_2AlCl	**14** (83)	98:2	41
11	**4**	80	Et_2AlCl	**14** (82)	99:1	41
12	**3**	20	$EtAlCl_2$	**14** (67)	85:15	29
13	**5**	20	$EtAlCl_2$	**14** (92)	96:4	53
14	**4**	20	$EtAlCl_2$	**14** (99)	95:5	61
15	**4**	100	$EtAlCl_2$	**14** (83)	96:4	62
16	**3**	20	$TiCl_2O\textit{i}Pr_2$	**13** (91)	64:36	28
17	**4**	20	$TiCl_2O\textit{i}Pr_2$	**13** (87)	73:27	46
18	**12**	20	Et_2AlCl	**14** (97)	98:2	20
19	**11a**	20	Et_2AlCl	**14** (99)	95:5	36
20	**11a**	20	$EtAlCl_2$	**14** (89)	98:2	51
21	**11b**	20	Et_2AlCl	**14** (92)	97:3	37
22	**11b**	20	$EtAlCl_2$	**14** (84)	99:1	52

[a] All reactions employed 0.5 mmol substrate in CH_2Cl_2 (-78°C/24 h).
[b] Isolated yields following SGC.
[c] Determined by ^{1}H NMR of crude isolates.
[d] Determined by chiral shift analysis using $Eu(hfc)_3$.
[e] Conducted in THF.

A key feature of these catalysts is the geometric flexibility at the Lewis acidic metal center, designed to accommodate a variety of substrate dienophiles. Boronates were in general less selective than the aluminates, and within this class, aluminates capable of forming bona fide metallocycles (entries 8–11) less discriminating than the dihaloaluminates (entries 12–15). As noted above, the coordinative geometry of the metal center itself also has a profound effect on product enantiomer distribution. Though selectivity is modest (<65% e.e.), catalysts derived from **4** are routinely superior to **5**, which are in turn superior to uncomplexed analogs **3**. However, since the *same* enantiomeric product predominates using either **4** or **5** this suggests that the entire arene metal–carbonyl appendage is functioning as a *stand alone stereodirective element*, a function of its planar chirality. In an effort to amplify the effects, mixed ligand derivatives of diols **4** and **5** were prepared (Scheme 2). Accordingly, silylation of **3** followed by complexation gave a mixture of diastereomers **9** and **10**, which were separated and subjected to photolytic ligand exchange, resulting in ligands **11** and **12** following deprotection. Under analogous reaction conditions, inferior enantiocontrol was afforded by both of these systems, complicated by the fact that partial decomplexation ensued (up to 20%) during the reaction (Table 1, entries 18–22). In an effort to improve the system, complexes derived from (*S*)-1-naphthyl diol **15** and 2-naphthyl diol **16** were prepared. Both systems were inferior to ligand **4**

(maximum e.e.<40% with Et_2AlCl) and additionally were far less stable, resulting in substantial decomplexation under typical cycloaddition conditions. To uncouple the contribution of the planar chirality from **4**, complex **17** was prepared from (*S*)-styrene diol. The maximum e.e. attainable with catalysts derived from **17** was 15%, confirming the dominant role that the planar chiral template imparts. Based on these findings, the logical way forward was to exploit the influence of the metal carbonyl complex in a more rigidified catalyst framework, and thus redirect efforts towards *bicyclic* diols.



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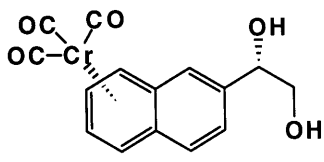

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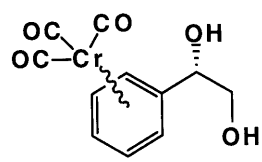

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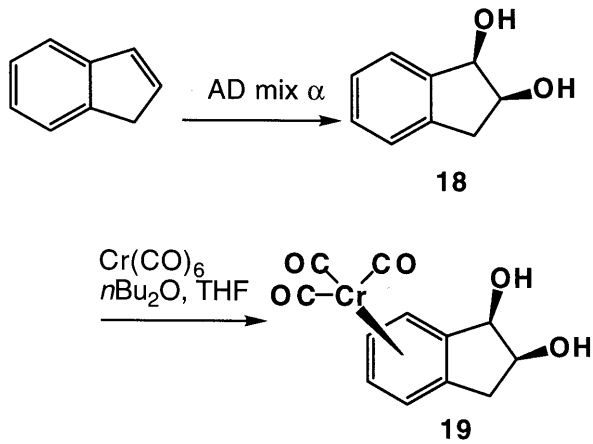
Accordingly, the indane diol ligand **18** was prepared, and catalysts derived from **18** and **19** were examined (Scheme 4). Unfortunately, despite numerous refinements, the direct route to **18** (asymmetric dihydroxylation of indene) provided diol ligands in <50% e.e.[7] Nevertheless, preliminary analysis suggests that appreciable selectivity is attainable from this ligand family, as a boron metallocycle derived from **19** gave a product e.e. in excess of 60% (Table 2, entry 7). Should efficient chemical or enzymatic approaches to **18** become available, we believe this could provide access to an extremely selective catalyst family, in both the complexed and uncomplexed series.



Scheme 4. Preparation of indene analogs

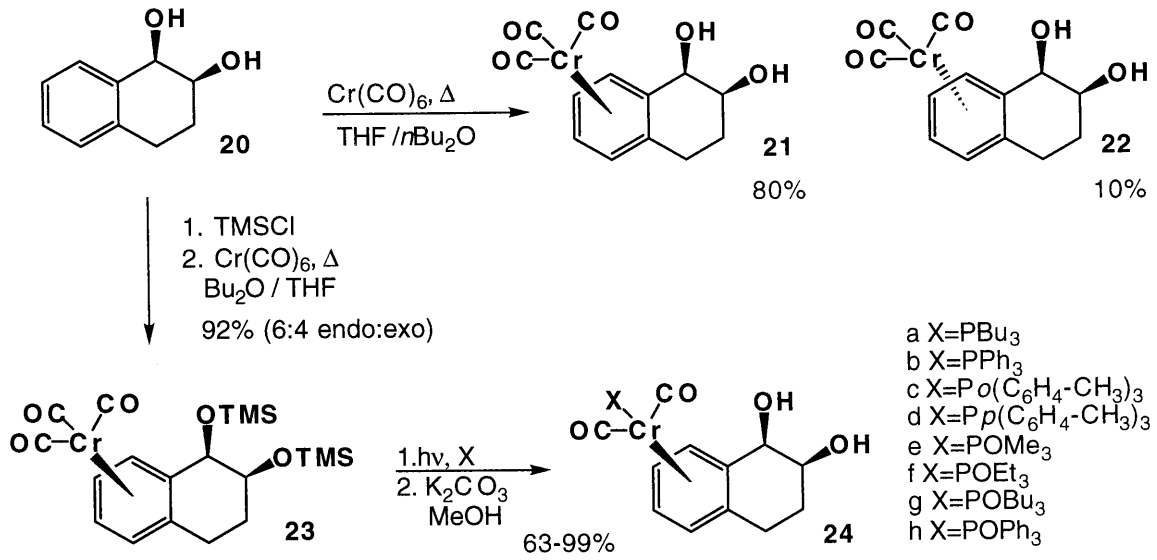
Since one of our objectives was to utilize a diol ligand of high enantiomeric purity (Scheme 1), we turned our attention to the corresponding tetrahydronaphthalene diols. Indeed, though asymmetric dihydroxylation of 1,2-dihydronaphthalene can be performed, the product, (1*R*,2*S*)-1,2,3,4-tetrahydro-1,2-naphthalenediol **20**, is commercially available in enantiomerically pure form. Accordingly, this diol was converted directly to the η^6-arene complex by thermolysis with hexacarbonylchromium, giving the desired product in high yield (Scheme 5). As is typical in such reactions, the *endo* complex predominates, giving a 8:1 mixture of **21**:**22** when a THF/*n*-butyl ether solvent mixture is used for complexation. Alternatively, protection of the diol then complexation gave a mixture of **23** and its *exo* isomer, readily separable using SGC. Stereochem-

Table 2
Enantioselective cycloaddition of 2-methacrolein using bicyclic diol catalysts[a]

Entry	Ligand	Mol%	Lewis acid	Temp. (°C)	% **13**[b]	*Exo*:*endo*[c]	% e.e.[d]
1	**18**[e]	20	Et_2AlCl	−78	62	88:12	29
2	**19**[e]	20	Et_2AlCl	−78	70	92:8	18
3	**19**[f]	20	Et_2AlCl	−78	89	95:5	14
4	**18**[e]	20	$EtAlCl_2$	−78	66	97:3	22
5	**19**[e]	20	$EtAlCl_2$	−78	81	97:3	28
6	**18**[e]	20	$BH_2Br{\cdot}Me_2S$	−78	89	95:5	13
7	**19**[e]	20	$BH_2Br{\cdot}Me_2S$	−78	58	99:1	62
8	**20**	20	$BH_2Br{\cdot}Me_2S$	−78	84	93:7	23
9	**20**	20	$BHBr_2{\cdot}Me_2S$	−78	72	88:12	19
10	**20**	20	$EtAlCl_2$	−78	84	97:3	48
11	**20**	20	Et_2AlCl	−78	90	89:11	54
12	**21**	20	$EtAlCl_2$	−78	89	95:5	79
13	**21**	20	Et_2AlCl	−78	83	96:4	90
14	**22**	20	Et_2AlCl	−78	79	83:17	25
15	**21**	10	Et_2AlCl	−78	82	98:2	84
16	**21**	10	$EtAlCl_2$	−78	80	89:11	72
17	**21**	100	Et_2AlCl	−78	87	98:2	91
18	**21**	20	Et_2AlCl	−95	**81**	**98:2**	>**95**[g]
19	**24a**	20	Et_2AlCl	−78	85	93:7	66
20	**24a**	20	$EtAlCl_2$	−78	77	93:7	49
21	**24b**	20	Et_2AlCl	−78	32	80:20	56
22	**24c**	20	Et_2AlCl	−78	99	91:9	55
23	**24d**	20	Et_2AlCl	−78	88	89:11	62
24	**24e**	20	Et_2AlCl	−78	99	95:5	60
25	**24f**	20	Et_2AlCl	−78	99	97:3	78
26	**24g**	20	Et_2AlCl	−78	59	72:28	78
27	**24h**	20	Et_2AlCl	−78	86	95:5	86
28	**24h**	20	$EtAlCl_2$	−78	92	95:5	71
29	**25**	20	Et_2AlCl	−78	82	86:14	29
30	**26**	20	Et_2AlCl	−78	89	92:8	43

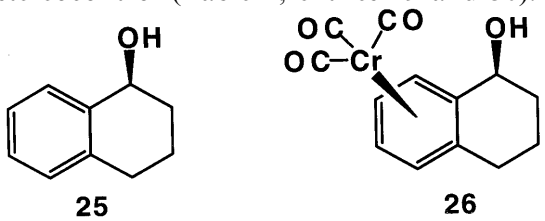
[a] Ligand and Lewis acid equilibrated at 25°C/3 h then cooled to −78°C for addition of substrates. All reactions employed 0.5 mmol substrate in CH_2Cl_2.
[b] Isolated yields following SGC.
[c] Determined by ^1H NMR of crude isolates.
[d] Determined by chiral shift analysis using $Eu(hfc)_3$.
[e] E.e. of diol ligand was 47%.
[f] E.e. of diol ligand was 21%.
[g] Up to 97% e.e. obtained.

ical assignment of **23** was confirmed by X-ray crystallography, and this key intermediate allowed ligand substitution to be performed, giving a range of mixed ligand complexes **24** on deprotection.[9] The ligands were then exposed to a variety of Lewis acids, and the resulting metallocycles/chelates examined in the catalytic enantioselective cycloaddition of 2-methacrolein with cyclopentadiene, using catalysts derived from **20** as controls (Scheme 3). In all cases examined (as with ligands **18** and **19**), *exo*-(*R*)-cycloadduct **13** was formed in preference to (*S*)-**14**. The uncomplexed diol **20** alone offered moderate to good enantioselectivity, performing better with



Scheme 5. Preparation of mixed ligand naphthalene diol derived ligands

aluminum derived metallocycles rather than the boronates (Table 2, entries 8–11). A substantial (~40%) enhancement was obtained using its corresponding *endo* arene complex **21**, resulting in >90% e.e., whereas catalysts derived from **22** proved inferior to the uncomplexed system **20** (entries 12–14). While a slight decrease in selectivity was observed using 10 mol% catalyst, no substantial increases were observed using stoichiometric amounts; however, at lower temperatures enantioselectivity increased to >95% (entries 15–18), rendering the system highly competitive with existing catalysts.[10] The diol ligand **21** could be recovered intact following hydrolytic workup, making this an attractive candidate for use in asymmetric syntheses. We anticipated that modification of the steric parameters around the ligand tripod of **21** would provide further increases in selectivity. Surveying a panel of eight different mixed-ligand derivatives **24a–h** failed, however, to yield any improvement over the 'parent' tricarbonyl chromium complex (entries 19–28). The reasons for this could be several fold, including competing interactions of the Lewis acidic aluminum center with the phosphine and phosphite ligands. However, as was the case with mixed ligand systems **11** and **12**, in situ decomplexation proved problematic and, given the inferior performance of ligand **20**, the figures reported presumably reflect this process. The superior performance of catalysts derived from diethyl aluminum chloride suggests the involvement of a five-membered chloroaluminum metallocyclic Lewis acid. Indeed, in all the reactions studied, the aluminum species and diol were pre-equilibrated for 3 h before addition of the substrates. *Reduction of this time led to a precipitous drop in product e.e., since free Lewis acid is available to catalyze the reaction.* To underscore the need for a cyclic Lewis acid structure, analogous catalysts derived from (*S*)-tetralol **25** and **26** were prepared and, as expected, they offered greatly inferior stereocontrol (Table 2, entries 29 and 30).



Our working hypothesis for the transition state assembly involves preferential substrate (enal) coordination *exo* to the metallocycle, influenced heavily by the η^6-arene complex. We speculate that additional interactions of the aluminum species with the metal carbonyl tripod may explain the anomalously high levels of asymmetric induction attained using **21**.[11] Potential transition state models include Fig. 2, where enal coordination directs attack of the diene *anti* to the metal carbonyl group, to give the observed *exo*-(*R*) product under either scenario. Such a model predicts the diene approach vector to be predetermined (N.B. catalyst aging time is critical), but relies on the presence of the α methyl group to establish the indicated *s-trans* enal geometry. To underline this requirement, cycloaddition to *acrolein* was conducted using ligand **21** (Scheme 6), and resulted in formation of *endo*-(*R*) product **27** with cyclopentadiene, and (*R*)-cycloadduct **28** with dimethylbutadiene. The apparent reversal in facial selectivity **27** presumably reflects *s-cis* enal coordination, as has been observed with related catalysts.[10] Significantly, the present study confirms that the level of facial and enantiocontrol afforded by catalysts derived from **21** is comparable or superior to existing systems, with the added advantage that ligand **20** is commercially available. Thus, while the full utility of these systems in asymmetric synthesis remains to be seen, they constitute a promising and novel addition to the arsenal of available asymmetric Diels–Alder catalysts.

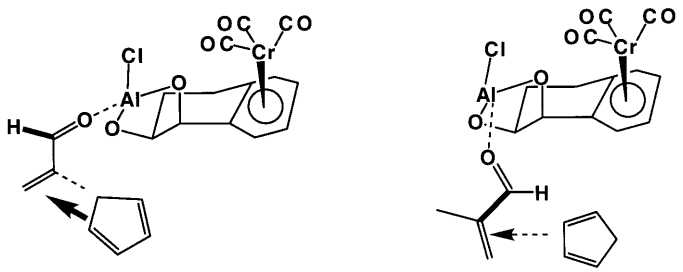
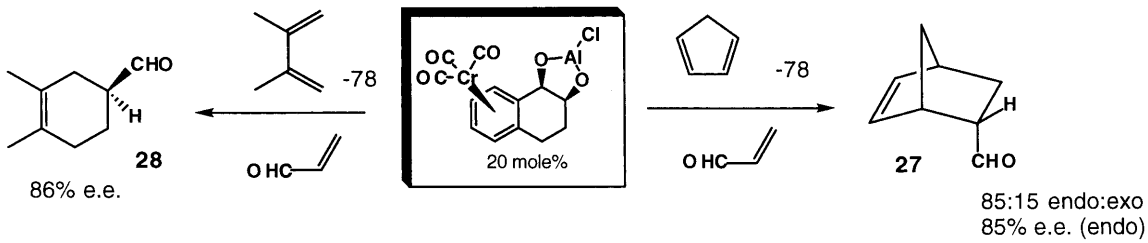


Figure 2. Proposed transition state models for addition to methacrolein with ligand **21**



Scheme 6. Enantioselective cycloadditions to acrolein with catalyst derived from **21**

3. Conclusion

A new class of planar chiral asymmetric Diels–Alder catalyst has been developed, and the factors which contribute to asymmetric induction have been probed. The optimal ligand **21** can be prepared in one step from a commercially available diol and is highly selective, making the catalyst a viable *and* readily available entity. Based on the general design criteria outlined herein (Scheme 1), we anticipate that many variants may be possible, including application in the asymmetric catalysis of other carbon–carbon bond forming reactions. In addition, we believe

that the synergy afforded by combining a planar chiral template with an enantiopure diol will find application in the design of other catalysts, including ferrocenes and polymer supported variants.

4. Experimental

General methods for synthesis,[12] and the preparation and handling of chromium complexes have been published.[6a] Ether, THF and *n*-butyl ether were distilled from sodium benzophenone ketyl. Hexanes and benzene were distilled from calcium hydride. Dichloromethane was distilled from P_2O_5 before use. DMF was dried stirring with BaO for 12 h at room temperature, followed by distillation from alumina at reduced pressure. Solvents used for complexations were deoxygenated by three cycles of freezing under vacuum, purging with nitrogen gas and thawing. Acroleins were distilled from calcium hydride immediately prior to use. Hexacarbonyl chromium was purchased from Strem Chemicals Inc. and used as supplied. All other chemicals were purchased from Aldrich and used as supplied.

4.1. (S)-1-(m-Methoxy phenyl)ethane-1,2-diol **3**

AD-mix-α (15.65 g) was added to a solution of *t*-BuOH (160 ml) and H_2O (160 ml) and the resulting mixture stirred at room temperature for 30 min. On cooling to 0°C, *m*-methoxystyrene (1.50 g, 11.18 mmol) was added, and the mixture stirred vigorously at 0°C for 9 h. Solid Na_2SO_3 (16.77 g, 13 mmol) was added, and the mixture allowed to warm to ambient temperature, stirred for 1 h, then the solution was washed with EtOAc (2×150 ml). The organic extracts were combined, dried ($MgSO_4$), filtered, and condensed in vacuo to give the title compound (1.87 g, 99%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.09 (t, $J=7.8$ Hz, 1H), 6.84–6.80 (dd, $J=11.7$ Hz, 2.4 Hz, 2H), 6.70–6.67 (dd, $J=8.1$ Hz, 2.4 Hz, 1H), 4.67–4.63 (dd, $J=8.1$ Hz, 3.3 Hz, 1H), 4.25 (br, 2H), 3.62–3.58 (dd, $J=14.7$ Hz, 3.3 Hz, 1H), 3.52–3.46 (dd, $J=8.4$ Hz, 2.7 Hz, 1H) and 3.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 142.6, 128.9, 118.1, 112.7, 111.3, 73.9, 67.8 and 54.8; IR (neat) 3412.8 (br), 3097.9, 3046.8, 1812.8, 1480.9 and 1029.8 cm^{-1}; MS (*m*/*e*) 168 (M^+, 100%); $[\alpha]_D=+71.8$ ($c=0.5$, $CHCl_3$); HPLC (Daicel OD, 90:10 hexanes:IPA as eluent, 1 ml min^{-1}) t_R 11.90 min minor (*R*), t_R 13.23 min major (*S*), (e.e.>99.5%); $C_9H_{12}O_3$ requires: C, 64.27; H, 7.19; found: C, 64.41; H, 7.37.

4.2. (1S)-(1-Naphthyl)ethane-1,2-diol

Under similar conditions, 1-vinylnaphthalene (3.00 g, 19.51 mmol) gave the title compound (3.22 g, 88%) as a white solid, mp 118–119°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–8.03 (d, $J=6.9$ Hz, 1H), 7.88–7.81 (dd, $J=9$ Hz, 2.7 Hz, 2H), 7.69 (d, $J=7.2$ Hz, 1H), 7.50–7.46 (dd, $J=9.9$ Hz, 2.4 Hz, 3H), 5.63 (d, $J=5.1$ Hz, 1H), 3.99–3.96 (d, $J=9$ Hz, 1H), 3.81–3.74 (dd, $J=11.4$ Hz, 3 Hz, 1H), 2.89 (br, 1H) and 2.46 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.2, 129.6, 129.0, 128.3, 127.4, 126.2, 125.4, 121.3, 112.4, 109.6, 91.3 and 74.6; IR (neat) 3251.1 (br), 3097.9, 3038.3, 2323.4, 1966.0, 1829.8, 1489.4, 1029.8, 783.0 and 672.3; MS (*m*/*e*) 188 (M^+, 100%); $[\alpha]_D=+45.6$ ($c=0.5$, $CHCl_3$); $C_{12}H_{12}O_2$ requires: C, 76.58; H, 6.42; found: C, 76.64; H, 6.51.

4.3. (1S)-(2-Naphthyl)ethane-1,2-diol

Under similar conditions, 2-naphthyl-ethylene (2.00 g, 12.97 mmol) gave the title compound (1.55 g, 64%) as a white solid, mp 113–115°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86–7.83 (d, $J=6.9$ Hz, 4H), 7.48 (t, $J=7.8$ Hz, 3H), 5.01 (t, $J=6$ Hz, 1H), 3.84–3.76 (dd, $J=12.4$ Hz, 1.2 Hz, 2H), 2.68 (br, 1H) and 2.12 (br, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 134.7, 131.9, 129.7, 128.3, 127.5, 127.1, 126.5, 126.0, 125.2, 47.9 and 35.9; IR (neat) 3208.5 (br), 1523.4, 1072.3, 1021.3 and 774.5; MS (m/e) 188 (M^+, 100%); $[\alpha]=+8.3$ ($c=0.5$, CH_3OH); $C_{12}H_{12}O_2$ requires: C, 76.58; H, 6.42; found: C, 76.73; H, 6.59.

4.4. (1S)-1-(Phenyl)ethane-1,2-diol

Under similar conditions, styrene (1.7 ml, 15.0 mmol) gave the title compound (1.9 g, 92%) as a white solid, mp 87–89°C; Lit.[7b] 86–87°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (m, 5H), 4.75 (d, $J=6$ Hz, 1H), 4.43 (s, 1H), 4.09 (m, 1H), 3.64–3.59 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7, 128.7, 128.1, 126.3, 126.1, 74.9 and 68.2; IR (neat) 3390 (br), 3126, 3034, 1490 and 1047 cm^{-1}; MS (m/e) 138 (M^+, 100%); $[\alpha]_D=+61.5$ ($c=0.5$, $CHCl_3$).

4.5. (1R,2S)-1,2-Indane-1,2-diol **18**

Under similar conditions, indene (0.88 ml, 7.5 mmol) gave (1*R*,2*S*)-1,2-indanediol as a white solid (0.92 g, 82%), mp 98–99°C (Lit.[13] 99–100°C) identical to authentic material.[13] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, $J=6.3$ Hz, 1H), 7.25–7.22 (m, 3H), 4.85 (d, $J=4.5$ Hz, 1H), 4.34 (t, $J=4.2$ Hz, 1H), 3.37 (br, 2H), 3.06–2.99 (dd, $J=16.2$ Hz, 5.7 Hz, 1H), 2.90–2.85 (dd, $J=16.5$ Hz, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 140.1, 128.6, 126.9, 125.2, 124.9, 75.8, 73.3 and 38.2; $[\alpha]_D=+24.8$ ($c=0.5$, $CHCl_3$); HPLC (Daicel OJ, 95:5 hexanes:IPA as eluent, 1 ml min^{-1}) t_R 18.13 min major (1*R*,2*S*), t_R 22.92 min minor (1*S*,2*R*), (e.e. = 47.0%).

4.6. (S)-1,2-Bis(trimethylsilyloxy)-1-(m-methoxyphenyl)ethane

To a solution of **3** (0.47 g, 2.78 mmol) and imidazole (1.89 g, 27.8 mmol) in DMF (2 ml) was added TMSCl (1.41 ml, 11.13 mmol), and the solution stirred at rt for 48 h. The mixture was poured over iced HCl (1%, 50 ml), extracted with EtOAc (2×50 ml) then the organic extracts were immediately washed with iced $NaHCO_3$ solution (sat. 1×50 ml) and brine (1×50 ml). The organic extracts were combined and condensed in vacuo, and the residual oil was purified by SGC (95:5 through 70:30 hexane:ether) to give the title compound (0.80 g, 92%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (t, $J=7.8$ Hz, 1H), 6.97–6.94 (d, $J=2.1$ Hz, 1H), 6.94 (m, 1H), 6.82–6.79 (dd, $J=7.5$ Hz, 1.8 Hz, 1H), 4.74 (t, $J=5.7$ Hz, 1H), 3.86 (s, 3H), 3.65 (d, $J=6$ Hz, 2H) and 0.14 (s, 9H), 0.11 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 143.8, 128.8, 118.6, 112.6, 111.7, 75.7, 69.0, 54.8, 0.07 and −0.6; $[\alpha]_D=+47.1$ ($c=0.5$, $CHCl_3$); $C_{15}H_{28}O_3Si$ requires: C, 57.64; H, 9.03; found: C, 57.91; H, 9.34.

4.7. (1R,2S)-1,2-Bis(trimethylsilyloxy)-1,2,3,4-tetrahydronaphthalene

Under similar conditions **20** (1.64 g, 10 mmol) gave the title compound (3.16 g, 98%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, $J=6.9$ Hz, 3.3 Hz, 1H), 7.22 (m, 2H),

7.13–7.11 (dd, $J=7.2$ Hz, 3.6 Hz, 1H), 4.68 (d, $J=2.7$ Hz, 1H), 4.01–3.96 (d, $J=7.2$ Hz, 1H), 2.99 (t, $J=4.8$ Hz, 1H), 2.84–2.81 (m, 1H), 2.24 (m, 1H), 1.76 (m, 1H), 0.24 (s, 9 H) and 0.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 135.9, 129.4, 128.5, 127.4, 125.8, 72.3, 71.2, 27.5, 26.2, 0.84 and 0.27; MS (m/e) 308 (M^+, 23.6%), 310 (M+2, 89.0%): $[\alpha]_D=-33.7$ ($c=0.7$, $CHCl_3$); $C_{16}H_{28}O_2Si$ requires: C, 62.28; H, 9.14; found: C, 62.49; H, 9.27.

4.8. (1R)-1-(m-Methoxyphenyl)ethane-1,2-diol chromium(0) tricarbonyl **4** and **5**

A mixture of **3** (0.49 g, 2.91 mmol) and chromium hexacarbonyl (1.28 g, 5.83 mmol) was subjected to standard complexation conditions[6a] in nBu$_2$O:THF (6:1, 70 ml) for 16 h. On cooling, the mixture was filtered and the solution condensed in vacuo to give the corresponding complexes (0.45 g), isolated as a 9:1 mixture of diastereomers. The mixture was purified by SGC (60:40 through 10:90, hexanes:ethyl acetate) to give **4** (0.41 g, 47%) and **5** (0.04 g, 5%), both isolated as yellow oils.

Complex **4**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79 (d, $J=10.6$ Hz, 1H), 5.42 (m, 1H), 5.11–5.06 (m, 3H), 4.81 (m, 1H), 4.58 (m, 1H), 3.72 (s, 3H) and 2.92 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.2, 113.8, 94.8, 83.9, 83.0, 72.8, 67.8 and 55.7; IR (neat) 3438.3 (br), 3097.9, 3038.3, 2340.4, 1983.0, 1897.9, 1812.8, 1480.9 and 1038.3 cm^{-1}; MS (m/e) 304 (M^+, 28.5%); $[\alpha]_D=+142.9$ ($c=0.5$, $CHCl_3$); $C_{12}H_{22}CrO_6$ requires: C, 47.38; H, 3.97; found: C, 47.61; H, 4.25.

Complex **5**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.61–5.58 (d, $J=7.2$ Hz, 1H), 5.42 (m, 1H), 5.11 (m, 3H), 4.80 (m, 1H), 4.55 (m, 1H), 3.80 (br, 2H) and 3.70 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.4, 113.9, 95.0, 84.0, 83.2, 72.5, 67.9 and 55.7; IR (neat) 3387.2 (br), 2944.7, 1966.0, 1872.3, 1548.9, 1472.3, 1276.6 and 1038.3 cm^{-1}; MS (m/e) 304 (M^+, 23.7%); $[\alpha]_D=+31.9$ ($c=0.5$, $CHCl_3$).

4.9. (1R)-1,2-Bis(trimethylsilyloxy)-1-(m-methoxyphenyl)ethane chromium(0) tricarbonyl **9** and **10**

Under similar conditions (*S*)-1,2-bis(trimethylsilyloxy)-1-(*m*-methoxyphenyl)ethane (0.31 g, 1.00 mmol) and chromium hexacarbonyl (0.55 g, 2.50 mmol) gave **9**/**10** (0.63 g), isolated as a 1:1 mixture of diastereomers. The mixture was purified by SGC (99:1 through 8:2 hexanes:ethyl acetate) to give **9** (0.32 g, 35%) and **10** (0.32 g, 35%), both isolated as yellow oils.

Complex **9** (ηR)-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (m, 2H), 5.20–4.93 (m, 3H), 4.53 (d, $J=6$ Hz, 1H), 3.71 (s, 3H), 3.54 (m, 1H), 0.23 (s, 9H) and 0.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.4, 115.0, 112.6, 93.4, 85.0, 84.1, 78.8, 73.2, 68.7, 55.5, 0.45 and –0.54; IR (neat) 3659.6 (br), 3089.3, 3038.4, 1966.0, 1897.9, 1821.3, 1489.4, 1251.1, 1038.3, 851.1 and 689.4 cm^{-1}; MS (m/e) 448 (M^+, 46.5%); $[\alpha]_D=+98.5$ ($c=0.5$, $CHCl_3$); $C_{18}H_{28}CrO_6Si_2$ requires: C, 48.19; H, 6.29; found: C, 48.37; H, 6.51.

Complex **10** (ηS)-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (m, 1H), 5.15–4.89 (m, 3H), 4.62 (m, 1H), 3.69 (s, 3H), 3.47 (m, 1H), 3.40 (s, 1H), 0.24 (s, 9H) and 0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.3, 113.7, 112.8, 93.4, 84.8, 84.2, 78.7, 72.9, 68.2, 55.6, 0.37 and 0.05; IR (neat) 3472.3 (br), 3089.4, 3038.3, 2323.4, 1974.5, 1897.9, 1821.3, 1480.9.4, 1123.4, 1038.3 and 680.9 cm^{-1}; $[\alpha]_D=+60.9$ ($c=0.5$, $CHCl_3$).

4.10. (1R)-(1-Naphthyl)ethane-1,2 diol chromium(0) tricarbonyl **15**

Under similar conditions, (1*S*)-(1-naphthyl)ethane-1,2-diol (2.05 g, 12.10 mmol) and chromium hexacarbonyl (4.00 g, 18.16 mmol) gave the title compound (1.43 g, 40%), isolated as

a red solid, mp 62–64°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (m, 1H), 7.37 (m, 2H), 6.14 (d, $J=6.9$ Hz, 1H), 5.72–5.68 (d, $J=7.2$ Hz, 2H), 5.52 (m, 1H), 5.32 (m, 1H), 5.21–5.19 (d, $J=6$ Hz, 1H) and 4.00 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.4, 131.2, 129.6, 128.8, 128.2, 127.2, 93.6, 92.0, 91.4, 91.2, 88.0, 71.8 and 69.3; IR (neat) 3676.6, 3097.9, 3046.8, 1974.5, 1906.4, 1821.3, 1497.9, 1038.3 and 672.3; $[\alpha]_D=+73.6$ ($c=0.5$, $CHCl_3$); $C_{15}H_{12}CrO_5$ requires: C, 55.56; H, 3.73; found: C, 55.84; H, 3.87.

4.11. (1R)-(2-Naphthyl)ethane-1,2-diol chromium(0) tricarbonyl **16**

Under similar conditions, (1*S*)-(2-naphthyl)ethane-1,2-diol (1.09 g, 5.77 mmol) was reacted with chromium hexacarbonyl (2.54 g, 11.55 mmol) to give the title compound (0.37 g, 20%) as a red solid, which decomposed on standing. Immediate protection of the crude material as the bis(trimethylsilyl)ether (imidazole, TMSCl) allowed purification and characterization of the resulting red oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (m, 1H), 7.48–7.44 (d, $J=6.9$ Hz, 2H), 6.11 (m, 1H), 5.50–5.47 (m, 2H), 5.34 (m, 1H), 4.73 (d, $J=7.2$ Hz, 1H), 3.63–3.54 (d, $J=8.1$ Hz, 2H), 0.28 (s, 9H) and 0.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.4, 129.4, 129.1, 128.5, 128.2, 126.7, 125.4, 112.3, 96.3, 90.8, 88.1, 45.6, 27.3, 0.04 and −0.5; IR (neat) 3106, 3055, 1966, 1821, 1489, 1038 and 681 cm^{-1}; $[\alpha]_D=+39.9$ ($c=0.5$, $CHCl_3$); $C_{21}H_{28}CrO_5Si_2$ requires: C, 53.82; H, 6.02; found: C, 54.14; H, 6.34.

4.12. (1R)-1-(Phenyl)ethane-1,2-diol chromium(0) tricarbonyl **17**

Under similar conditions, (1*S*)-1-(phenyl)ethane-1,2-diol (0.69 g, 5.0 mmol) and chromium hexacarbonyl (2.20 g, 10.0 mmol) gave the title compound (1.21 g, 88%) as a yellow solid (mp 93–96°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46–5.37 (m, 5H), 4.71 (d, $J=6.9$ Hz, 1H), 4.33 (s, 1H), 4.11 (s, 1H) and 3.41–3.32 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.8, 109.2, 93.8, 91.2, 88.5, 72.7 and 66.8; IR (neat) 3425 (br), 3134, 3038, 1979, 1893, 1818, 1488 and 1041 cm^{-1}; MS (*m*/*e*) 274 (M^+, 33.4%); $[\alpha]_D=+95.4$ ($c=0.5$, $CHCl_3$); $C_{11}H_{10}CrO_5$ requires: C, 48.18; H, 3.68; found: C, 48.51; H, 3.88.

4.13. (4S)-4-(m-Methoxyphenyl)-2,2-dimethyl-1,3-dioxolane **6**

2,2,-Dimethoxypropane (1.89 ml, 15.39 mmol) was added to a solution of **3** (1.73 g, 10.54 mmol) and toluenesulfonic acid (0.20 g, 1.03 mmol) in DMF (50 ml). The solution was stirred at rt for 24 h, then poured into EtOAc (100 ml), and the organic extracts were washed with HCl (1%, 3×50 ml) then condensed in vacuo. The residual oil was purified by SGC (98:2 hexanes:ether) to give **6** (1.6 g, 75%) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.24 (t, $J=3.6$ Hz, 1H), 6.94 (m, 2H), 6.84 (d, $J=7.8$ Hz, 1H), 5.06 (t, $J=6.3$ Hz, 1H), 4.32–4.27 (dd, $J=8.4$ Hz, 1.8 Hz, 1H), 3.81 (s, 3H), 3.70 (t, $J=8.1$ Hz, 1H), and 1.55 (s, 3H) and 1.49 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 137.4, 128.5, 127.8, 127.4, 127.1, 126.5, 125.1, 45.2, 44.8, 27.1 and 22.6; $[\alpha]_D=+47.1$ ($c=0.5$, $CHCl_3$).

4.14. (4R)-4-(m-Methoxyphenyl)-2,2-dimethyl-1,3-dioxolane chromium(0) carbonyl **7**

(4*S*)-4-(*m*-Methoxyphenyl)-2,2-dimethyl-1,3-dioxolane (2.84 g, 13.66 mmol) and chromium hexacarbonyl (6.01 g, 27.32 mmol) were subjected to standard complexation conditions in

nBu$_2$O:THF (9:1, 100 ml) for 16 h. On cooling, the mixture was filtered and the solution condensed in vacuo to give a quantitative yield of the corresponding complexes (2.2 g), isolated as a mixture of diastereomers. The mixture was purified by SGC (98:2 through 7:3 hexanes:ether) to give η^6S **7** (0.22 g, 4.4%) and η^6R **7** (1.98 g, 43%) isolated as yellow oils.

Complex **7** (ηR)-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.51 (m, 1H), 5.34 (m, 1H), 5.12 (m, 2H), 4.84 (m, 1H), 4.37 (m, 1H), 3.89 (d, $J=7.4$ Hz, 1H), 3.70 (s, 3H), and 1.50 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.4, 117.8, 112.7, 109.1, 94.6, 93.1, 84.2, 60.9, 56.1, 46.2, 43.9, 26.5 and 23.2; IR (neat) 3446.8 (br), 1974.5, 1880.9, 1651.1, 1548.9, 1463.8, 1259.6, 1166.0, 1021.3 and 842.6 cm^{-1}; $[\alpha]_D=+19.9$ ($c=0.5$, $CHCl_3$).

Complex **7** (ηS)-diastereomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.56 (m, 1H), 5.29 (m, 1H), 5.07 (m, 2H), 4.82 (m, 1H), 4.34 (m, 1H), 3.86 (d, $J=6$ Hz, 1H), 3.71 (s, 3H), and 1.51 (s, 3H) and 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.7, 118.0, 113.1, 108.0, 94.7, 92.9, 84.5, 60.6, 56.0, 46.4, 43.6, 26.9 and 24.3; IR (neat) 3429.8 (br), 2936.2, 2366.0, 1985.5, 1893.5 and 1668.1 cm^{-1}; $[\alpha]_D=+60.7$ ($c=0.5$, $CHCl_3$); $C_{15}H_{16}CrO_6$ requires: C, 52.33; H, 4.68; found: C, 52.64; H, 4.81.

4.15. (η^6R,1R)-1-(m-Methoxyphenyl)ethane-1,2-diol chromium(0) triphenylphosphine dicarbonyl **11a**

Triphenyl phosphine (0.68 g, 2.59 mmol) was added to a solution of **9** (0.12 g, 0.26 mmol) in freshly distilled benzene (5 ml), in a quartz test tube. The mixture was purged (N_2/20 min, then Ar/20 min) then placed in a photolysis chamber and irradiated (Hanovia 450 W Hg lamp) for 6 h. Evaporation of the solvent followed by SGC (95:5, hexane:ether) gave the corresponding monotriphenylphosphine complex (0.1 g, 54%) as a yellow oil; ^{1}H NMR (300 MHz, C_6D_6) δ 7.15–7.03 (m, 15H), 5.72 (m, 1H), 5.16 (m, 1H), 4.74–4.70 (d, $J=8.1$ Hz, 2H), 4.49 (m, 1H), 3.84 (s, 1H), 3.75 (s, 1H), 3.57 (s, 3H), 0.25 (s, 9H) and 0.01 (s, 9H). The crude product (0.03 g, 0.04 mmol) was dissolved in distilled MeOH (2 ml), potassium carbonate (0.5 g, 3.6 mmol) was added, and the mixture stirred at rt for 6 h. The mixture was filtered through a small plug silica gel (EtOAc, 50 ml) and the solution condensed in vacuo to give **11a** (0.02 g, 100%) as a yellow powder, mp 73–74°C (dec.); ^{1}H NMR (300 MHz, C_6D_6) δ 7.15–7.03 (m, 15H), 5.52 (m, 1H), 4.86 (m, 1H), 4.50–4.47 (d, $J=6.3$ Hz, 1H), 4.27–4.24 (d, $J=6.6$ Hz, 1H), 4.04 (m, 1H), 3.82 (m, 1H), 3.48 (s, 1H) and 3.15 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 232.4, 133.3, 133.0, 132.6, 129.4, 128.7, 127.3, 117.4, 109.1, 93.7, 92.8, 88.1, 81.8, 68.9, 55.3 and 25.3; IR (neat) 3429.8, 2927.7, 2366.0, 1889.4, 1838.3, 1736.2, 1438.3 and 1251.1 cm^{-1}; MS (m/e) 538 (M^+, 8.05%); $[\alpha]_D=+39.8$ ($c=0.5$, CH_3OH).

4.16. (η^6S,1R)-1-(m-Methoxyphenyl)ethane-1,2-diol chromium(0) triphenylphosphine dicarbonyl **12**

Under identical conditions, **10** (0.23 g, 0.86 mmol) gave the corresponding monotriphenylphosphine complex (0.03 g, 56%) as a yellow oil; ^{1}H NMR (300 MHz, C_6D_6) δ 7.15–7.04 (m, 15H), 5.19 (m, 1H), 4.86 (m, 1H), 4.76 (m, 1H), 4.51 (m, 1H), 4.31–4.27 (d, $J=8.1$ Hz, 1H), 4.14–4.12 (d, $J=6$ Hz, 1H), 4.05–4.03 (d, $J=6$ Hz, 1H), 3.16 (s, 3H), 0.21 (s, 9H) and 0.06 (s, 9H), which following deprotection gave (η^6S,1R)-1-(*m*-methoxyphenyl)ethane-1,2-diol chromium(0) triphenylphosphine dicarbonyl (0.02 g, 92%) as a yellow powder, mp 71–73°C (dec.); ^{1}H NMR (300 MHz, C_6D_6) δ 7.15–7.02 (m, 15H), 5.51 (m, 1H), 4.83 (m, 1H), 4.50–4.48

(d, $J=6$ Hz, 1H), 4.27–4.24 (d, $J=7.1$ Hz 1H), 4.04 (m, 1H), 3.86 (m, 1H), 3.44 (s, 1H), and 3.17 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 233.7, 133.1, 133.0, 132.8, 128.7, 128.0, 127.6, 117.1, 108.3, 93.7, 91.5, 88.1, 81.4, 69.2, 55.2 and 25.1; IR (neat) 3455.3, 2927.7, 2851.1, 1889.4, 1829.8, 1736.2, 1608.5, 1438.3, 1063.8, 748.9 and 706.4 cm^{-1}; MS (m/e) 538 (M^+, 10.76%); $[\alpha]_D=+178.6$ ($c=0.5$, CH_3OH).

*4.17. (η^6R,1R)-1-(*m*-Methoxyphenyl)ethane-1,2-diol chromium(0) tri(*p*-tolyl)phosphine dicarbonyl **11b***

Under identical conditions, **9** (0.012 g, 0.04 mmol) with tri(*p*-toluyl)phosphine (0.12 g, 0.38 mmol) gave the corresponding monotri-*p*-tolyl phosphine complex, which was subjected to immediate deprotection to give **11b** (0.02 g, 87%) isolated as a yellow powder, mp 66–67°C (dec.); ^{1}H NMR (300 MHz, C_6D_6) δ 7.40–7.35 (d, $J=7.5$ Hz, 6H), 6.94 (d, $J=7.5$ Hz, 6H), 5.48 (m, 1H), 4.98 (m, 1H), 4.67–4.65 (d, $J=6$ Hz, 1H), 4.32–4.29 (d, $J=7.1$ Hz, 1H), 4.21 (m, 1H), 3.84 (m, 1H), 3.42 (s, 3H), 3.31 (br, 2H), 3.16 (d, $J=8.7$ Hz, 1H) and 2.04 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 234.7, 144.3, 137.3, 133.9, 132.2, 128.5, 128.1, 113.7, 112.4, 95.5, 92.7, 84.8, 84.6, 54.6, 30.8, 26.9 and 20.0; IR (neat) 3455, 2945, 2850, 1890, 1830, 1740, 1608, 1438, 1066, 749 and 706 cm^{-1}; MS (m/e) 580 (M^+, 4%); $[\alpha]_D=+122.5$ ($c=0.5$, $CHCl_3$).

*4.18. (η^6R)-*m*-Anisaldehyde chromium(0) tricarbonyl **8***

To a vigorously stirred solution of lead tetraacetate (0.25 g, 0.56 mmol) in distilled benzene (10 ml), was added **5** (0.17 g, 0.56 mmol, dissolved in 5 ml of benzene). The mixture was stirred at 25°C for 1 h, then the mixture was filtered through a plug of silica gel (EtOAc, 50 ml). Following condensation in vacuo, the residual oil was purified by SGC (90:10, hexanes:EtOAc) to give the title compound (0.14 g, 90%) as a red solid (mp 87–88°C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 5.56 (dd, $J=12.3$ Hz, 5.7 Hz, 2H), 5.45 (m, 2H) and 3.72 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 231.1, 189.5, 140.8, 95.9, 91.9, 89.1, 82.5 and 56.1; IR (neat) 3250, 2930, 2850, 1890, 1845, 1687, 1445, 1069 and 708 cm^{-1}; MS (m/e) 272 (M^+, 33.2%); $[\alpha]_D=+816.7$ ($c=0.5$, $CHCl_3$). Lit.[14] $[\alpha]_D=+811$ ($c=1$, $CHCl_3$). Analogous reaction with **4** (0.17 g, 0.56 mmol) gave (η^6S)-**8** (0.14 g, 90%) $[\alpha]_D=-809$ ($c=0.5$, $CHCl_3$).

*4.19. (η^6R,1S,2S)- and (η^6S,1S,2S)-1,2,3,4-tetrahydro-1,2-naphthalenediol chromium(0) tricarbonyl **21** and **22***

(1*R*,2*S*)-1,2,3,4-Tetrahydro-1,2-naphthalenediol (0.41 g, 2.5 mmol) and hexacarbonyl chromium (1.1 g, 5 mmol) were subjected to standard complexation conditions in nBu$_2$O:THF (6:1, 100 ml) for 16 h. On cooling, the mixture was filtered and the solution condensed in vacuo to give a crude mixture of the corresponding complexes. The diastereomers were separated by SGC (4:6 through 1:9, hexanes:ethyl acetate) to give ηR **21** (0.60 g, 82%), isolated as a yellow solid, mp 104–106°C, and ηS **22** (0.09 g, 10%) isolated as a yellow solid, mp 108–110°C.

Complex **21**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.78–5.76 (d, $J=6.9$ Hz, 1H), 5.54 (t, $J=9.0$ Hz, 1H), 5.13–5.04 (m, 2H), 4.44 (d, $J=4.8$ Hz, 1H), 4.01–3.94 (m, 1H), 2.75 (m, 2H) and 1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.5, 112.3, 109.3, 95.6, 94.9, 87.1, 85.1, 68.2, 26.3 and 25.3; IR (neat) 3340 (br), 3090, 3035, 1980, 1899, 1810, 1490 and 1045 cm^{-1}; MS (m/e) 300 (M^+, 17.4%), 301 (M+1, 12.8%); $[\alpha]_D=+15.4$ ($c=0.5$, $CHCl_3$); $C_{13}H_{12}CrO_5$ requires: C, 52.01; H, 4.03; found: C, 52.27; H, 4.23.

Complex **22**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.77–5.75 (d, $J=6.9$ Hz, 1H), 5.53–5.50 (t, $J=9$ Hz, 1H), 5.13 (t, $J=7.2$ Hz, 1H), 5.04 (d, $J=7.2$ Hz, 1H), 4.44 (m, 1H), 4.12–4.10 (q, $J=7.2$ Hz, 1H), 2.82 (br, 2H), 2.69 (m, 2H) and 1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.2, 112.6, 109.4, 95.9, 95.2, 89.2, 88.6, 68.1, 67.2, 26.1 and 25.2; IR (neat) 3380 (br), 2940, 1972, 1886, 1553, 1487, 1285 and 1038 cm^{-1}; MS (m/e) 300 (M^+, 13.3%), 299 (M−1, 5.34); $[\alpha]_D=-9.5$ ($c=0.5$, $CHCl_3$).

4.20. (1S,2S)-1,2-Bis(trimethylsilyloxy)-1,2,3,4-tetrahydronaphthalene chromium(0) tricarbonyl ***23***

(1*R*,2*S*)-1,2-Bis(trimethylsilyloxy)-1,2,3,4-tetrahydronaphthalene (1.65 g, 5.34 mmol) and chromium hexacarbonyl (2.93 g, 13.34 mmol) were subjected to standard complexation conditions in nBu$_2$O:THF (6:1, 100 ml) for 48 h. On cooling, the mixture was filtered, the solution condensed in vacuo, and the residual oil purified by SGC (6:4 through 1:9 hexane:ethyl acetate) to give **23** (1.32 g, 55%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.46–5.41 (d, $J=7.2$ Hz, 1H), 5.31–5.26 (m, 2H), 5.03–5.00 (m, 1H), 4.46 (s, 1H), 3.93–3.89 (m, 1H), 2.95–2.92 (m, 1H), 2.58–2.54 (m, 1H), 2.01 (t, $J=6.6$ Hz, 1H), 1.73–1.67 (t, $J=8.4$ Hz, 1H), 0.24 (s, 9H) and 0.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.4, 111.0, 110.3, 93.4, 92.1, 69.2, 69.0, 26.8, 24.9, 0.36 and 0.16; IR (neat) 3067, 3032, 1976, 1908, 1804, 1478 and 1043 cm^{-1}; MS (m/e) 444 (M^+, 10.4%), (M−136, $Cr(CO)_3$ group, 56.6%); $[\alpha]_D=-76.3$ ($c=0.5$, $CHCl_3$). Anal. calcd for $C_{19}H_{28}CrO_5Si_2$: C, 51.33; H, 6.35; found: C, 51.39; H, 6.88.

4.21. General photolysis and deprotection reaction procedures for mixed ligand complexes ***24***

The following procedure is typical for photolysis and subsequent deprotection of mixed ligand diol complexes: **23** (0.19 g, 0.42 mmol) is dissolved in dry benzene (5 ml) in a quartz test tube, the desired trialkyl phosphine or trialkyl phosphite added (10 equiv.), and the solution degassed. The solution is then irradiated (Hanovia 450 W, 8 h), following which the solvent is condensed in vacuo, the residue dissolved in MeOH (10 ml) and potassium carbonate (0.57 g, 4.16 mmol) added. After stirring at rt for 12 h, the mixture is filtered through a plug of silica gel (EtOAc, 50 ml), the filtrate condensed in vacuo, and the resulting oil purified by SGC (4:6 through 1:9, hexanes:ethyl acetate).

4.21.1. Complex ***24a***

Complex **23** (0.19 g, 0.42 mmol) and tributylphosphine (1.03 ml, 4.16 mmol) gave **24a** (0.15 g, 78%) isolated as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68–5.59 (m, 1H), 5.48–5.43 (t, $J=7.5$ Hz, 1H), 5.06 (t, $J=6.9$ Hz, 1H), 4.87 (m, 1H), 4.62 (s, 1H), 3.99–3.95 (d, $J=8.4$ Hz, 6H), 3.79–3.76 (m, 1H), 2.92 (m, 2H), 2.73–2.70 (m, 1H), 2.35 (m, 2H), 2.06–2.02 (m, 2H), 1.82 (m, 1H), 1.65 (d, $J=6$ Hz, 1H), 1.59 (m, 1H), 1.40–1.10 (m, 9H) and 0.91 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 240.2, 108.2, 95.6, 94.7, 89.1, 87.5, 86.9, 69.7, 66.6, 39.5, 34.1, 31.0, 27.1, 25.0 and 14.1; IR (neat) 3360 (br) cm^{-1}; MS (m/e) 474 (M^+, 1.2%), 446 (M−28, –CO); $[\alpha]_D=43.5$ ($c=0.1$, $CHCl_3$).

4.21.2. Complex ***24b***

Complex **23** (0.34 g, 0.76 mmol) and triphenylphosphine (1.99 g, 7.58 mmol) gave **24b** (0.25 g, 62%) isolated as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (m, 3H), 7.54 (m, 6H), 7.40

(m, 6H), 5.75 (m, 1H), 5.44 (m, 1H), 5.35 (m, 1H), 5.08 (m, 1H), 4.76 (s, 1H), 4.32 (d, 1H), 2.97–2.79 (m, 2H), 2.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.4, 139.7, 133.4, 132.3, 130.9, 128.7, 127.6, 101.2, 98.7, 93.5, 92.3, 90.9, 89.9, 69.8, 67.6, 26.8 and 24.8; IR (neat) 3270 (br) cm^{-1}; MS (*m*/*e*) 535 (M+1, 1.2%); $[\alpha]_D = 34.1$ ($c = 0.3$, $CHCl_3$).

4.21.3. Complex ***24c***

Complex **23** (0.41 g, 0.91 mmol) and tri(*o*-tolyl)phosphine (2.77 g, 9.11 mmol) gave **24c** (0.30 g, 57%) isolated as an orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 6H), 7.32 (m, 6H), 5.64 (m, 1H), 5.37 (m, 1H), 5.29 (m, 1H), 5.12 (m, 1H), 4.72 (s, 1H), 4.38 (d, $J = 7.2$ Hz, 1H), 2.93 (m, 2H), 2.24 (m, 2H), 2.09 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.2, 137.3, 132.4, 130.3, 129.1, 128.5, 128.1, 99.3, 97.4, 93.8, 90.2, 89.1, 87.6, 68.8, 67.4, 29.5, 26.3 and 24.6; $[\alpha]_D = 171$ ($c = 0.1$, $CHCl_3$).

4.21.4. Complex ***24d***

Complex **23** (0.23 g, 0.51 mmol) and tri(*p*-tolyl)phosphine (1.56 g, 5.11 mmol) gave **24d** (0.18 g, 63%) isolated as an orange oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 6H), 7.29 (m, 6H), 5.66 (m, 1H), 5.41 (m, 1H), 5.26 (m, 1H), 5.11 (m, 1H), 4.74 (s, 1H), 4.41 (d, $J = 6.9$ Hz, 1H), 2.96 (m, 2H), 2.28 (m, 2H), 1.98 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.2, 137.4, 132.8, 131.5, 128.9, 128.4, 127.9, 99.2, 97.5, 94.7, 92.4, 90.9, 87.7, 68.9, 67.2, 30.3, 26.9 and 24.8; $[\alpha]_D = 141.1$ ($c = 0.1$, $CHCl_3$).

4.21.5. Complex ***24e***

Complex **23** (0.39 g, 0.87 mmol) and trimethylphosphite (1.03 ml, 8.70 mmol) gave **24e** (0.17 g, 50%) isolated as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.52 (m, 1H), 5.43 (m, 1H), 5.29 (m, 1H), 5.08 (m, 1H), 4.68 (s, 1H), 4.36 (d, $J = 6.3$ Hz, 1H), 3.12 (m, 2H), 2.46 (m, 2H) and 2.34 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.2, 99.3, 97.3, 93.9, 91.8, 91.0, 88.3, 68.8, 67.3, 36.5, 29.7 and 25.3; $[\alpha]_D = 282$ ($c = 0.1$, $CHCl_3$).

4.21.6. Complex ***24f***

Complex **23** (0.23 g, 0.51 mmol) and triethylphosphite (0.80 ml, 5.13 mmol) gave **24f** (0.12 g, 51%) isolated as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.48 (m, 1H), 5.41 (m, 1H), 5.33 (m, 1H), 5.11 (m, 1H), 4.73 (s, 1H), 4.44 (d, $J = 6.6$ Hz, 1H), 4.24 (m, 6H), 2.46 (m, 2H), 2.21 (m, 2H) and 1.47 (t, $J = 8.7$ Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.4, 102.7, 99.8, 97.4, 93.3, 92.5, 89.2, 68.4, 66.1, 49.8, 33.5, 31.7 and 23.6; $[\alpha]_D = 365$ ($c = 0.1$, $CHCl_3$).

4.21.7. Complex ***24g***

Complex **23** (0.21 g, 0.47 mmol) and tributylphosphite (1.27 ml, 4.68 mmol) gave **24g** (0.24 g, 99%) isolated as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.73 (d, $J = 6.6$ Hz, 1H), 5.55 (d, $J = 7.2$ Hz, 1H), 5.18 (m, 1H), 5.11 (d, $J = 5.1$ Hz, 1H), 4.71 (s, 1H), 4.22 (m, 6H), 3.14 (m, 1H), 2.92 (m, 1H), 2.34 (m, 2H), 2.08 (m, 1H), 2.01–1.54 (m, 12H) and 1.23 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 240.2, 101.5, 98.7, 97.3, 94.5, 93.4, 89.9, 70.2, 68.8, 55.7, 48.5. 34.8, 30.8, 26.9 and 22.5; MS (*m*/*e*) 521 (M^-, 1.0%), 524 (M+2, 1.0%); $[\alpha]_D = 61.2$ ($c = 0.5$, $CHCl_3$).

4.21.8. Complex ***24h***

Complex **23** (0.63 g, 1.43 mmol) and triphenylphosphite (3.74 ml, 14.26 mmol) gave **24h** (0.80 g, 96%) isolated as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.15 (m, 15H), 5.68

(m, 1H), 5.38 (m, 2H), 5.21 (m, 1H), 4.70 (s, 1H), 4.35 (m, 1H), 4.18–4.12 (m, 1H), 3.97–3.84 (m, 1H), 3.52 (m, 1H), 2.42 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.3, 135.8, 131.5, 128.8, 125.8, 120.6, 108.0, 104.1, 94.9, 93.0, 91.6, 87.9, 85.2, 72.3, 66.7, 38.6 and 25.6; $[\alpha]_D = 80.4$ ($c = 0.1$, $CHCl_3$); $C_{30}H_{27}CrO_7P$ requires C, 61.86; H, 4.67; found: C, 61.93; H, 4.82.

4.22. (η^6R,1R)-1,2,3,4-Tetrahydronaphthyl alcohol chromium(0) tricarbonyl **26**

(1*S*)-1,2,3,4-Tetrahydronaphthylalcohol **25** (0.17 g, 1.17 mmol) and hexacarbonyl chromium (0.65 g, 2.94 mmol) were subjected to standard complexation conditions in nBu$_2$O: THF (6:1, 70 ml) for 16 h. On cooling, the mixture was filtered, the solution condensed in vacuo, and the resulting residue purified by SGC (60:40 through 10:90 hexanes:EtOAc) to give **26** (0.20 g, 61%) as a yellow solid, mp 137–138°C (Lit.[15] 140°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (s, 1H), 5.52 (s, 1H), 5.14 (m, 2H), 4.52 (s, 1H), 2.71–2.63 (m, 2H), 2.09 (m, 1H) 1.96 (m, 1H) and 1.71 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.3, 95.1, 93.4, 90.1, 88.9, 66.6, 32.1, 27.5 and 19.2; IR (neat) 3450 (br); $[\alpha]_D = 25.5$ ($c = 0.5$, $CHCl_3$).

4.23. (η^6R,1S,2S)-Indane-1,2-diol chromium(0) tricarbonyl **19**

Under standard complexation conditions, (1*R*,2*S*)-1,2, indanediol **18** (0.59 g, 3.95 mmol) gave **19** (0.93 g, 82%) isolated as a yellow solid, mp 118–120°C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (m, 1H), 5.40 (s, 1H), 5.28 (d, $J = 8.4$ Hz, 2H), 4.78 (s, 1H), 4.37 (s, 1H), 3.15 (br, 2H), 3.05 (m, 1H) and 2.86 (d, $J = 12.9$ Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 232.8, 112.1, 109.8, 94.1, 90.2, 89.6, 87.7, 74.0, 70.3 and 37.8; IR (neat) 3338 (br, –OH); $[\alpha]_D = +23.1$ ($c = 0.5$, $CHCl_3$); $C_{12}H_{10}CrO_5$ requires: C, 50.36; H, 3.53; found: C, 50.59; H, 3.70.

4.24. General procedure for catalytic enantioselective Diels–Alder reactions

Lewis acid (0.33 mmol) is added slowly to a pre-cooled (−78°C) solution of the catalyst precursor (0.33 mmol) in methylene chloride (5 ml). The mixture is allowed to warm to ambient temperature over a period of 3 h, then re-cooled to −78°C. Freshly distilled dienophile (1.67 mmol) is added rapidly by syringe and the mixture stirred for a further 15 min, then freshly distilled diene (8.3 mmol) added and the mixture stirred for 3 h at −78°C. The reaction mixture is warmed to 0°C, quenched by addition of $NaHCO_3$ (sat. 2×20 ml), then extracted with methylene chloride (1×10 ml). The organic extracts are dried (Na_2SO_4) and condensed in vacuo, and the resulting residue is purified by SGC (9:1 hexane:ether) to recover cycloadducts together with catalyst precursor. *Exo*/*endo* ratios of cycloadducts are determined from NMR spectra. Enantiomeric excesses are calculated either by NMR analysis using Eu(hfc)$_3$ chiral shift reagent, or by derivatization [(2*R*,4*R*)-(−)-pentane diol] followed by GC analysis.[10] Stereochemical assignments were confirmed by optical rotation of cycloadducts.[16]

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