Engineering *endo*-Selectivity in Arene−Chromium Functionalizations: Out-of-plane Coordination of $TiCl_4$ to Ketones Leads to Stereodivergence†

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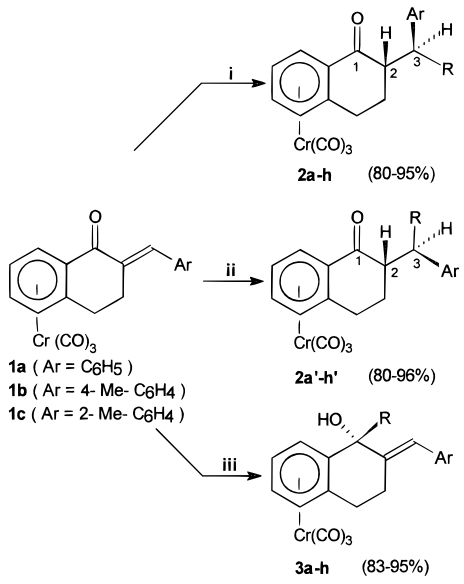
Conjugate addition of organolithium or organomagnesium reagents to 2-arylidene-1-tetralone−$Cr(CO)_3$ complexes proceeds with complete *endo*-selectivity in the presence of excess $TiCl_4$ in dichloromethane solution. Cuprates, on the other hand, afford the expected *exo* adducts.

A metal carbonyl moiety complexed to a conjugated π-electron framework is known to prevent reagent approach from the same face of the molecule as occupied by the metal (*endo* face) and thereby enforce *exo*-selective additions. In arene tricarbonylchromium complexes, this attribute has been extensively harnessed to yield a large variety of target molecules of biological interest.[1] In the course of these syntheses, *exo*-selective functionalizations at aryl, benzyl, or homobenzyl sites have been routinely achieved.[1,2] In comparison, examples of effective *endo*-functionalization procedures that would permit more flexible synthetic designs are rare.[3] In this paper, we report an efficient procedure to achieve completely *endo*-selective conjugate addition of various organometallic nucleophiles to a prototypical enone anchored on $Cr(CO)_3$ by taking advantage of out-of-plane coordination of $TiCl_4$ to the ketone carbonyl group, which effectively shields the *exo* face. Although in an earlier paper[3b] we disclosed a chance discovery of *endo*-selective Hosomi−Sakurai reaction on similar substrates, the reaction has been limited to addition of the allyl group alone. The present examples have considerably enhanced the scope of inducing *endo*-selectivity with the help of Lewis acid and provided eminently useful, stereodivergent protocols to obtain the desired diastereomer of the adduct predictably by choice of appropriate recipe.

When representative organolithium and organomagnesium reagents (1.5 equiv) in ether were added to the conformationally rigid[4] racemic enone substrates **1a**−**c** *pretreated with excess of* $TiCl_4$ (2 equiv)[5] in dichloromethane at −90 °C (reaction condition i), only conjugate addition products **2a**−**h** were obtained as single diastereomers in very good to excellent isolated yields (Scheme 1). On the other hand, a different set of diastereomerically pure, conjugate addition products were obtained from the reaction of organocuprates (reaction condition ii) with the same substrates (Scheme 1, Table 1, products **2a′**−**h′**). On the basis of physical and spectral identity with authentic samples,[3b] structures of the complexes **2b** (*endo* adduct) and **2b′** (*exo* adduct) could be readily assigned. The isomeric pairs of products, thus, are all epimeric at C-3 rather than at the C-2 center,[6] and their relative stereochemistries were assigned by analogy with **2b** and **2b′**.

Scheme 1



† Dedicated to Dr. S. Rajappa on the occasion of his 65th birth anniversary.

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(1) (a) Semmelhack, M. F. Transition Metal Arene Complexes: Nucleophilic Addition. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds; Pergamon: Oxford, 1995; Vol. 12, pp 1002−1004 and refs 120−122 cited therein. (b) Semmelhack, M. F. Transition Metal Arene Complexes: Ring Lithiation, ref 1a, pp 1030−1035 and refs 46−51 cited therein. (c) Davies, S. G.; McCarthy, T. D. Transition Metal Arene Complexes: Side Chain Activation and Control of Stereochemistry, ref 1a, p 1039 and refs 137 and 143−148 cited therein.

(2) (a) Ganesh, S.; Sarkar, A. *Tetrahedron Lett.* **1991**, *32*, 1085−1088. (b) Sur, S.; Ganesh, S.; Puranik, V. G.; Sarkar, A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 977−982. (c). Uemura, M. Tricarbonyl (η^6-arene) chromium Complexes in Organic Synthesis. In *Advances In Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1991; Vol. 2, pp 231−240 and refs 84−110 cited therein. (d) Ganesh, S. Ph.D. Thesis, Pune University, 1993.

(3) (a) Ganesh, S.; Sathe, K. M.; Nandi, M.; Chakrabarti, P.; Sarkar, A. *J. Chem. Soc., Chem. Commun.* **1993**, 224−226. (b) Sur, S.; Ganesh, S.; Pal, D.; Puranik, V. G.; Chakrabarti, P.; Sarkar, A. *J. Org. Chem.* **1996**, *61*, 8362−8363.

(4) For details about the rigid conformation and trans geometry of the double bond, see ref 3b.

(5) It has been shown by Prof. Denmark that a 1:1 carbonyl−$TiCl_4$ complex is formed when excess $TiCl_4$ is used; a lesser amount of $TiCl_4$ led predominantly to complexes of composition $TiCl_4$−carbonyl 1:2. For our purpose, it was desirable that at least 1:1 complexes are formed for best stereoselectivity, and we did not reduce the amount of $TiCl_4$ any lower than 2 equiv. See ref 9b.

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Table 1

substrate	R	product (isolated yield %) condition i $TiCl_4$/RLi	condition i $TiCl_4$/RMgX	condition ii	condition iii
1a	CH_2=$CHCH_2$	**2a** (81)	**2a** (90)	**2a′** (86)	**3a** (92)
1b	CH_2=$CHCH_2$	**2b** (80)	**2b** (88)	**2b′** (91)	**3b** (89)
1a	Me	**2c** (90)	**2c** (91)	**2c′** (90)	**3c** (87)
1b	Me	**2d** (90)	**2d** (87)	**2d′** (95)	**3d** (83)
1b	Ph	**2e** (90)	**2e** (85)	**2e′** (80)	**3e** (88)
1b	cyclopropyl	**2f** (90)	**2f** (90)	**2f′** (94)	**3f** (91)
1b	*n*-butyl	**2g** (92)	**2g** (95)	**2g′** (96)	**3g** (95)
1c	CH_2=$CHCH_2$	**2h** (80)	**2h** (87)	**2h′** (85)	**3h** (83)

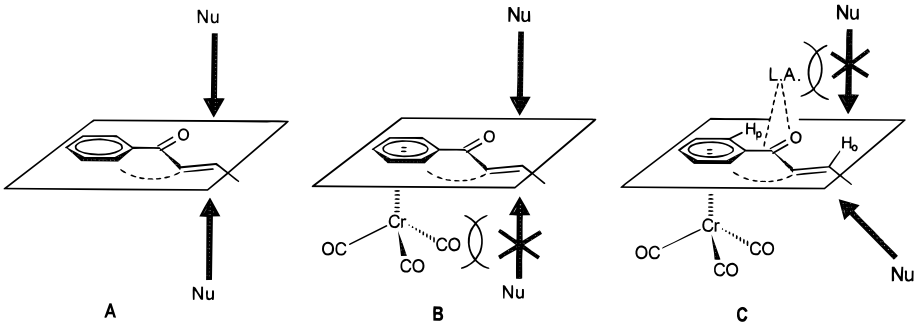

Figure 1.

Thus, the Lewis acid[7] mediated procedure provided a remarkable, completely *endo*-selective 1,4-addition of enones anchored on a $Cr(CO)_3$ template, while cuprates yielded normal *exo*-adducts. Significantly, *the organolithium or the organomagnesium reagents were found to be compatible with dichloromethane as solvent (CH_2Cl_2: ether ≈ 10:1) at low temperatures*.[8] In other words, the conjugate addition occurred with considerably higher rate than decomposition of reagent (the reaction was complete within 15 min). It was also established that the nucleophile was not an organotitanium species (e.g. $RTiCl_3$), since (i) no reaction took place and starting material was quantitatively recovered if the organolithium or organomagnesium reagent was allowed to react with $TiCl_4$ first, and the substrate was added subsequently, (ii) use of BuLi posed no problem of β-hydride elimination, which would be expected of a butyltitanium intermediate, and (iii) no noticeable side reaction occurred with cyclopropyllithium reagent.

Reagent approach in π-systems with conflicting stereochemical bias can be visualized with the help of Figure 1. While both faces of the enone are equally accessible to a reagent or reaction partner in structure A, one of the faces of B is blocked by metal coordination. In structure C, the Lewis acid is forced to coordinate from the *exo* face in an out-of-plane manner,[9] since access from the *endo* face is prevented by the $Cr(CO)_3$ group and in-plane coordination is discouraged by two flanking hydrogens (the *peri* proton, H_p of the aromatic ring of tetralone and the β- olefinic proton, H_o) on both sides of the ketone function.

As represented in structure C, the Lewis acid bound to the *exo* face of the ketone sterically hinders *exo* approach of the nucleophile for both 1,2- and 1,4-addition. Also, the bulky $Cr(CO)_3$ group does not permit *endo*-selective 1,2-addition. Therefore, the addition can occur only in a conjugate manner from the *endo* face of the substrate. In absence of Lewis acid coordination, *exo*-selective 1,2-additions of different nucleophiles are observed as expected (reaction condition iii, Scheme 1).[10]

If the arene ring of tetralone is *not complexed* with tricarbonylchromium, the propensity of organolithium reagents for preferential 1,2-addition is not altered by Lewis acid. $TiCl_4$ might still coordinate with the ketone carbonyl in an out-of-plane manner owing to the presence of *peri* hydrogens. Yet, the opposite face of the π-system remains accessible to nucleophiles. Indeed, we observed that 1,2-adducts were almost exclusively produced[11] when uncomplexed substrates were used, even in the presence of excess (5 equiv) $TiCl_4$ (Scheme 2, Table 2).

To sum up, we have efficiently exploited the out-of-plane binding mode of Lewis acid to carbonyl group to

(6) This was established by equilibration studies with DBU in CH_2Cl_2. Equilibration of **2b** yielded a minor isomer **7a**, which is epimeric with **2b** at C-2 (carbon adjacent to the ketone); equilibration of **2b′** under the same conditions gave a minor isomer **7a′**, which is epimeric with **2b′** at C-2 (described in ref 3b). Similarly, base-catalyzed eqilibration of **2c** and **2c′** afforded the respective C-2 epimers **8a** and **8a′** (see Experimental Section).

(7) Several Lewis acids were examined, e.g., $SnCl_4$, $BF_3{\cdot}Et_2O$, $Sc(OTf)_3$, etc. which provided *exo*-1,2-adducts only, and not *endo*-1,4-adducts as $TiCl_4$ did. Swamy, Vishwanath. M.; Sarkar, A. Unpublished results.

(8) The substrate enone is only sparingly soluble in diethyl ether, and therefore ether was not considered as the main solvent. Moreover, it was thought appropriate to avoid donor solvents anyway so that Lewis acid−carbonyl group interaction could be maximized. Dichloromethane was tried since this has been used with most $TiCl_4$-promoted reactions. See also: Bongini, A.; Cardillo, G.; Mingarde, A.; Tomasini, C. *Tetrahedron*: *Asymmetry* **1996**, *7*, 1457.

(9) (a) For a review on Lewis acid−carbonyl complexation, see: Shambayati, S.; Schreiber, S. L In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 1, p 283. (b) For detailed spectroscopic studies on Lewis acid−carbonyl complexes, see: Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133. Also see: Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565 and refs 12 and 13 cited therein.

(10) Stereochemistry of the complex **3b** was known from earlier studies;[3b] the relative stereochemistry of the remaining products was fixed by analogy, based on a large number of precedents.[1]

(11) Only a trace amount (<5%) of conjugate addition product could be isolated with organomagnesium reagents and in $TiCl_4$-mediated reactions.

Scheme 2

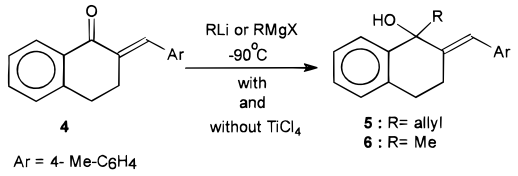

Table 2

reagent	product	yield (%)
allyllithium	**5**	89
methyllithium	**6**	93.5
$TiCl_4$/allyllithium	**5**	81
$TiCl_4$/methyllithium	**6**	79
allylmagnesium bromide	**5**	80
methylmagnesium iodide	**6**	83

achieve completely *endo*-selective conjugate addition of a variety of strong nucleophiles to enones anchored on the arene−$Cr(CO)_3$ template. Without Lewis acid, as in cuprate reactions, *exo*-selective conjugate addition is observed. Together, they present an eminently useful example of stereodivergent functionalization of these substrates. We believe the strategy is generally adaptable to other π-complexed organometallic intermediates as well as sterically biased organic frameworks. Some of these are currently being investigated in our laboratory.

Experimental Section

All reactions were performed under an inert atmosphere of argon, using freshly distilled, degassed solvents. Diethyl ether and THF were freshly distilled over sodium benzophenone ketyl. Aromatic aldehydes were purchased from Aldrich and used as received. For descriptions of analytical instruments, spectral data formats, and standard calibrations, see ref 12. All reactions were performed on a 0.5−2.0 mmol scale.

General Procedure for the Preparation of Enones (1a−c). Following a reported procedure all three enones were prepared from the tetralone $Cr(CO)_3$ complex and aromatic aldehydes using Claisen−Schmidt condensation. **1a** and **1b** have already been reported.[2b]

Complex enone 1c: red solid; mp 135 °C; yield 91%; ^{1}H NMR ($CDCl_3$) 2.35 (s, 3H), 2.60−2.78 (m, 1H), 2.85−3.20 (m, 3H), 5.15 (d, 1H, J = 6.6 Hz), 5.35 (t, 1H, J = 6.6 Hz), 5.65 (t, 1H, J = 6.6 Hz), 6.29 (d, 1H, J = 6.6 Hz), 7.05−7.40 (m, 4H), 7.90 (s, 1H); ^{13}C NMR ($CDCl_3$) 20.10, 25.83, 27.74, 29.82, 89.95, 90.24, 91.74, 94.51, 115.12, 125.78, 129.11, 130.52, 133.23, 134.53, 137.44, 137.96, 165.35, 186.21, 231.20; IR ($CHCl_3$) 1980, 1920, 1660 cm^{-1}. Anal. Calcd for $C_{21}H_{16}O_4Cr$: C, 65.79; H, 4.17. Found: C, 65.69; H, 4.21.

General Procedure for the Preparation of 2a−h from 1a−c. To a solution of the complexed enone (n mmol) in dichloromethane (20n mL) was added titanium tetrachloride (2n mmol) dropwise with stirring at −90 °C. After 15 min of stirring, organolithium or organomagnesium reagent (1.5n mmol) in diethyl ether was added dropwise with stirring at the same temperature. After completion of the reaction (TLC, 15 min), the reaction mixture was quenched with degassed methanol at −90 °C, followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude product obtained after evaporation of solvent was purified by flash column chromatography.

Complex 2a: orange crystalline solid; mp 118−119 °C; ^{1}H NMR ($CDCl_3$) 1.85−2.20 (m, 2H), 2.30−2.90 (m, 5H), 3.80−3.95 (m, 1H), 4.85−5.10 (m, 3H), 5.30 (t, 1H, J = 7 Hz), 5.55−5.80 (m, 2H), 6.20 (d, 1H, J = 7 Hz), 7.15−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) 21.9, 28.2, 32.7, 43.1, 53.8, 89.0, 89.3, 91.3, 93.36, 94.4, 116.01, 116.2, 126.3, 128.3, 128.5, 136.5, 142.1, 196.0, 230.5; IR ($CHCl_3$) 1980, 1910, 1670 cm^{-1}. Anal. Calcd for $C_{23}H_{20}O_4Cr$: C, 67.15; H, 4.86. Found: C, 67.00; H, 5.05.

Complex 2b: orange crystalline solid; mp 160−162 °C; ^{1}H NMR ($CDCl_3$) 1.90−2.10 (m, 2H), 2.40 (s, 3H), 2.45−2.90 (m, 5H), 3.80−3.90 (m, 1H), 4.85−5.15 (m, 3H), 5.30 (t, 1H, J = 6.8 Hz), 5.55−5.80 (m, 2H), 6.20 (d, 1H, J = 6 Hz), 7.15 (s, 4H); ^{13}C NMR ($CDCl_3$) 20.8, 21.7, 28.2, 32.6, 42.4, 54.0, 89.0, 89.4, 91.3, 93.0, 94.4, 114.9, 116.2, 128.0, 129.0, 135.9, 136.6, 138.9, 196.2, 230.6; IR ($CHCl_3$) 1980, 1910, 1670 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.66; H, 5.10.

Complex 2c: orange crystalline solid; mp 125 °C; ^{1}H NMR ($CDCl_3$) 1.25 (d, 3H, J = 7.2 Hz), 1.72−1.90 (m, 1H), 2.05 (ddd, 1H, J = 21.2, 17.3, 4.15 Hz), 2.45−2.75 (m, 2H), 2.76−2.95 (m, 1H), 3.90 (ddd, 1H, J = 21.2, 17.3, 4.15 Hz), 5.10 (d, 1H, J = 6.5 Hz), 5.35 (t, 1H, J = 6.5 Hz), 5.60 (t, 1H, J = 6.5 Hz), 6.21 (d, 1H, J = 6.5 Hz), 7.15−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) 21.24, 28.30, 29.86, 36.95, 54.24, 89.80, 90.30, 91.37, 93.50, 94.70, 115.34, 126.50, 127.95, 128.57, 144.62, 196.83, 231.04; IR ($CHCl_3$) 1985, 1915, 1680 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_4Cr$: C, 65.25; H, 4.66. Found: C, 64.96; H, 4.73.

Complex 2d: red solid; mp 151 °C; ^{1}H NMR ($CDCl_3$) 1.28 (d, 3H, J = 7.5 Hz), 1.78−1.91 (m, 1H), 1.92−2.18 (ddd, 1H, J = 21.0, 17.1, 4.2 Hz), 2.35 (s, 3H), 2.45−2.60 (m, 1H), 2.60−2.95 (m, 2H), 3.98 (ddd, 1H, J = 21.0, 17.1, 4.2 Hz), 5.10 (d, 1H, J = 6.4 Hz), 5.34 (t, 1H, J = 6.4 Hz), 5.60 (t, 1H, J = 6.4 Hz), 6.20 (d, 1H, J = 6.4 Hz), 7.19 (s, 4H); ^{13}C NMR ($CDCl_3$) 13.33, 21.12, 21.18, 28.24, 36.50, 54.23, 89.84, 90.35, 91.35, 93.55, 94.74, 115.42, 127.77, 129.24, 135.94, 141.50, 196.87, 231.10; IR ($CHCl_3$) 1980, 1910, 1667 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4Cr$: C, 66.00; H, 5.00. Found: C, 65.87; H, 4.99.

Complex 2e: orange solid; mp 150 °C; ^{1}H NMR ($CDCl_3$) 1.77−2.10 (m, 2H), 2.34 (s, 3H), 2.63−2.85 (m, 1H), 2.90−3.10 (m, 1H), 3.17−3.37 (m, 1H), 4.84 (d, 1H, J = 7.2 Hz), 5.08 (d, 1H, J = 6.5 Hz), 5.25 (t, 1H, J = 6.5 Hz), 5.65 (t, 1H, J = 6.5 Hz), 6.18 (d, 1H, J = 6.5 Hz), 7.08−7.40 (m, 9H); ^{13}C NMR ($CDCl_3$) 21.14, 25.68, 28.42, 49.38, 51.51, 88.70, 89.13, 92.38, 93.26, 95.28, 115.13, 126.58, 128.00, 128.61, 128.95, 129.32, 135.90, 140.40, 142.33, 196.53, 230.7; IR ($CHCl_3$) 1982, 1910, 1675 cm^{-1}. Anal. Calcd for $C_{27}H_{22}O_4Cr$: C, 70.13; H, 4.76. Found: C, 70.00; H, 4.86.

Complex 2f: red solid; mp 158 °C; ^{1}H NMR ($CDCl_3$) 0.02−0.19 (m, 1H), 0.45−0.60 (m, 2H), 0.6−0.79 (m, 1H), 1.05−1.32 (m, 1H), 2.05−2.20 (m, 1H), 2.25−2.45 (m, 1H), 2.35 (s, 3H), 2.47−2.70 (m, 1H), 2.70−2.80 (m, 1H), 2.80−2.97 (m, 1H), 3.05 (m, 1H), 5.07 (d, 1H, J = 6.4 Hz), 5.30 (t, 1H, J = 6.4 Hz), 5.65 (t, 1H, J = 6.4 Hz), 6.25 (d, 1H, J = 6.4 Hz), 7.10−7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) 4.53, 6.30, 11.01, 21.14, 22.72, 28.63, 47.10, 54.51, 89.00, 89.51, 91.87, 95.07, 115.80, 128.05, 129.13, 135.80, 141.75, 165.60, 196.35, 230.93; IR ($CHCl_3$) 1980, 1910, 1670 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.60; H, 5.16. Found: C, 67.32; H, 5.00.

Complex 2g: red solid; mp 140 °C; ^{1}H NMR ($CDCl_3$) 0.85 (t, 3H, J = 7.3 Hz), 1.08−1.37(m, 3H), 1.38−1.57 (m, 2H), 1.70−1.90 (m, 2H), 1.90−2.20 (m, 2H), 2.35 (s, 3H), 2.55−3.90 (m, 2H), 3.75 (m, 1H), 5.10 (d, 1H, J = 6.5 Hz), 5.30 (t, 1H, J = 6.5 Hz), 5.60 (t, 1H, J = 6.5 Hz), 6.20 (d, 1H, J = 6.5 Hz), 7.15 (s, 4H); ^{13}C NMR ($CDCl_3$) 13.98, 21.12, 22.06, 22.82, 28.21, 28.55, 30.50, 43.10, 54.80, 89.48, 89.92, 91.54, 93.26, 94.70, 115.42, 128.64, 129.36, 136.00, 141.23, 196.70, 230.98; IR ($CHCl_3$) 1974, 1901, 1678 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_4Cr$: C, 67.87; H, 5.88. Found: C, 68.01; H, 5.92.

Complex 2h: red solid; mp 140 °C; ^{1}H NMR ($CDCl_3$) 1.90−2.20 (m, 2H), 2.25−2.45 (m, 1H), 2.26 (s, 3H), 2.55−2.90 (m, 4H), 4.15−4.30 (m, 1H), 4.90−5.15 (m, 2H), 5.35 (t, 1H, J = 6.4 Hz), 5.55−5.75 (m, 2H), 6.21 (d, 1H, J = 6.4 Hz), 7.05−7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) 19.56, 21.95, 28.70, 32.94, 38.10, 52.20, 89.45, 89.87, 91.72, 93.51, 94.88, 115.31, 116.60, 125.97, 126.50, 127.52, 131.16, 136.62, 136.90, 140.56, 196.45, 231.02; IR ($CHCl_3$) 1980, 1915, 1680 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.68; H, 4.98.

General Procedure for the Preparation of 2a′−h′ from 1a−c. To a slurry of CuCN (n mmol) in diethyl ether (n mL) was added organolithium reagent (2n mmol) in hexane or ether dropwise with stirring at −78 °C. It was slowly warmed to

(12) Chowdhury, S. K.; Samanta, U.; Puranik, V. G.; Sarkar, A. *Organometallics* **1997**, *16*, 2618.

−20 °C, during which time all of the CuCN was dissolved. The solution was again cooled to −78 °C, followed by addition of complexed enone (0.75*n* mmol) in toluene (10*n* mL). After completion of the reaction (TLC, 0.75−1.0 h) the reaction mixture was allowed to attain room temperature, quenched with 10% ammonia in a saturated aqueous ammonium chloride solution, followed by stirring for 0.5 h, and finally extracted with ether. The residue obtained after evaporation of solvent was purified by flash column chromatography.

Complex 2a′: red solid; mp 123 °C; ^{1}H NMR ($CDCl_3$) 1.56−1.74 (m, 1H), 1.93−2.06 (m, 1H), 2.50−2.98 (m, 5H), 3.81 (m, 1H), 4.98−5.25 (m, 4H), 5.57−5.81 (m, 2H), 6.19 (d, 1H, J = 6.8 Hz), 7.23−7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) 23.63, 27.62, 37.14, 43.02, 51.26, 88.85, 89.32, 91.89, 93.00, 95.14, 115.88, 116.92, 126.74, 128.40, 128.80, 136.81, 141.08, 196.90, 230.67; IR ($CHCl_3$) 1980, 1910, 1680 cm^{-1}. Anal. Calcd for $C_{23}H_{20}O_4Cr$: C, 67.15; H, 4.86. Found: C, 66.44; H, 4.73.

Complex 2b′: red crystalline solid; mp 131 °C; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) 1.66−1.72 (m, 1H), 1.90−2.04 (m, 1H), 2.30 (s, 3H), 2.59−2.94 (m, 5H), 3.78 (m, 1H), 4.95−5.10 (m, 3H), 5.20 (t, 1H, J = 6.7 Hz), 5.62−5.80 (m, 2H), 6.20 (d, 1H, J = 6.7 Hz), 7.10 (s, 4H); ^{13}C NMR ($CDCl_3$) 21.25, 23.77, 27.55, 37.29, 42.87, 51.37, 88.86, 89.36, 91.88, 93.12, 95.14, 115.94, 116.79, 128.62, 129.09, 136.16, 136.44, 138.00, 197.08, 230.72; IR ($CHCl_3$) 1985, 1915, 1680 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.62; H, 5.16.

Complex 2c′: red solid; mp 110 °C; ^{1}H NMR ($CDCl_3$) 1.42 (d, 3H, J = 7.25 Hz), 1.51−1.70 (m, 1H), 1.90−2.10 (m, 1H), 2.45−2.65 (m, 1H), 2.66−3.00 (m, 2H), 3.65−3.84 (m, 1H), 5.03 (d, 1H, J = 6.5 Hz), 5.72 (t, 1H, J = 6.5 Hz), 5.60 (t, 1H, J = 6.5 Hz), 6.21 (d, 1H, J = 6.5 Hz), 7.10−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) 19.75, 24.54, 27.62, 38.50, 53.75, 89.22, 89.73, 92.12, 93.33, 95.40, 116.05, 126.74, 128.16, 128.65, 143.68, 197.20, 231.02; IR ($CHCl_3$) 1975, 1915, 1680 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_4Cr$: C, 65.25; H, 4.66. Found: C, 65.21; H, 4.66.

Complex 2d′: red solid; mp 142 °C; ^{1}H NMR ($CDCl_3$) 1.44 (d, 3H, J = 7.2 Hz), 1.50−1.77 (m, 1H), 1.85−2.05 (m, 1H), 2.31 (s, 3H), 2.40−2.60 (m, 1H), 2.65−2.95 (m, 2H), 3.55−3.75 (m, 1H), 5.05 (d, 1H, J = 6.6 Hz), 5.74 (t, 1H, J = 6.6 Hz), 5.61 (t, 1H, J = 6.6 Hz), 6.20 (d, 1H, J = 6.6 Hz), 7.13 (s, 4H); ^{13}C NMR ($CDCl_3$) 19.90, 21.21, 24.68, 27.50, 38.36, 53.75, 88.99, 89.46, 91.96, 93.25, 95.10, 115.83, 127.88, 129.30, 136.20, 140.64, 197.35, 230.87; IR ($CHCl_3$) 1980, 1910, 1670 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4Cr$: C, 66.00; H, 5.00. Found: C, 65.80; H, 4.98.

Complex 2e′: red solid; mp 165 °C; ^{1}H NMR ($CDCl_3$) 1.75−2.15 (m, 2H), 2.30 (s, 3H), 2.65−2.82 (m, 1H), 2.90−3.11 (m, 1H), 3.20−3.38 (m, 1H), 4.82 (d, 1H, J = 7.5 Hz), 5.08 (d, 1H, J = 6.8 Hz), 5.22 (t, 1H, J = 6.8 Hz), 5.63 (t, 1H, J = 6.8 Hz), 6.18 (d, 1H, J = 6.8 Hz), 7.10 (s, 4H), 7.15−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) 21.16, 25.76, 28.49, 49.59, 51.57, 88.80, 89.22, 92.47, 93.39, 95.38, 115.23, 126.45, 128.22, 128.65, 128.90, 129.40, 136.26, 139.15, 143.77, 196.54, 230.83; IR ($CHCl_3$) 1990, 1920, 1680 cm^{-1}. Anal. Calcd for $C_{27}H_{22}O_4Cr$: C, 70.13; H, 4.76. Found: C, 69.99; H, 4.70.

Complex 2f′: orange solid; mp 122 °C; ^{1}H NMR ($CDCl_3$) 0.15−0.45 (m, 2H), 0.55−0.75 (m, 1H), 1.20−1.45 (m, 1H), 1.55−1.90 (m, 2H), 2.02−2.20 (m, 1H), 2.35 (s, 3H), 2.50−2.85 (m, 2H), 2.85−3.10 (m, 2H), 5.00 (d, 1H, J = 6.5 Hz), 5.17 (t, 1H, J = 6.5 Hz), 5.50 (t, 1H, J = 6.5 Hz), 6.17 (d, 1H, J = 6.5 Hz), 6.85−7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) 5.85, 5.96, 13.99, 21.11, 23.67, 28.24, 47.68, 53.52, 88.63, 89.10, 91.85, 95.11, 116.09, 128.54, 128.84, 135.89, 138.21, 196.58, 230.58; IR ($CHCl_3$) 1980, 1910, 1675 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.60; H, 5.16. Found: C, 67.30; H, 5.00.

Complex 2g′: red solid; mp 110 °C; ^{1}H NMR ($CDCl_3$) 0.85 (t, 3H, J = 7.5 Hz), 1.05−1.45 (m, 5H), 1.70−1.80 (m, 2H), 1.80−2.05 (m, 1H), 2.32 (s, 3H), 2.42−2.65 (m, 1H), 2.70−2.85 (m, 2H), 3.35−3.51 (m, 1H), 5.05 (d, 1H, J = 6.5 Hz), 5.20 (t, 1H, J = 6.5 Hz), 5.60 (t, 1H, J = 6.5 Hz), 6.20 (d, 1H, J = 6.5 Hz), 7.10 (s, 4H); ^{13}C NMR ($CDCl_3$) 14.21, 23.36, 24.10, 30.03, 31.89, 44.55, 53.81, 74.23, 84.00, 85.01, 87.71, 88.10, 90.36, 116.32, 128.10, 129.51, 131.26, 136.65, 139.44, 197.13, 231.04; IR ($CHCl_3$) 1980, 1915, 1675 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_4Cr$: C, 67.87; H, 5.88. Found: C, 67.77; H, 6.02.

Complex 2h′: red solid; mp 108 °C; ^{1}H NMR ($CDCl_3$) 1.65−1.95 (m, 2H), 2.42 (s, 3H), 2.45−2.70 (m, 2H), 2.70−3.00 (m, 3H), 3.55−3.70 (m, 1H), 4.80−5.05 (m, 2H), 5.15 (d, 1H, J = 6.5 Hz), 5.25 (t, 1H, J = 6.5 Hz) 5.50−5.75 (m, 2H), 6.18 (d, 1H, J = 6.5 Hz), 7.05−7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) 20.51, 26.26, 28.46, 39.46, 40.56, 52.21, 89.30, 89.70, 91.98, 94.55, 94.90, 114.98, 116.57, 126.27, 126.41, 127.44, 130.85, 136.64, 137.30, 140.65, 197.90, 230.97; IR ($CHCl_3$) 1975, 1910, 1675 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.60; H, 5.16.

General Procedure for the Preparation of 3a−h from 1a−c. To a solution of the complexed enone (**1a−c**) (*n* mmol) in THF (20*n* mL) was added organolithium reagent (1.5*n* mmol) in diethyl ether dropwise with stirring at −90 °C. After completion of the reaction (TLC, 30 min), the reaction mixture was quenched with degassed methanol at −90 °C, followed by addition of water at room temperature, and finally extracted with dichloromethane. The crude product obtained after evaporation of solvent was purified by flash column chromatography.

Complex 3a: yellow solid; mp 110−112 °C; ^{1}H NMR ($CDCl_3$) 2.13 (s, 1H), 2.52−2.80 (m, 5H), 2.94−3.05 (m, 1H), 5.00−5.17 (m, 5H), 5.43 (t, 1H, J = 6.7 Hz), 5.75−5.90 (m, 2H), 6.94 (s, 1H), 7.25−7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) 21.40, 24.68, 27.21, 48.27, 74.15, 90.72, 90.94, 92.05, 93.32, 110.78, 116.50, 119.20, 125.53, 129.06, 129.20, 132.89, 134.53, 136.72, 139.93, 233.44; IR ($CHCl_3$) 1980, 1910 cm^{-1}. Anal. Calcd for $C_{23}H_{20}O_4Cr$: C, 67.15; H, 4.86. Found: C, 66.87; H, 5.05.

Complex 3b: yellow crystalline solid; mp 91 °C; ^{1}H NMR ($CDCl_3$) 2.10 (s, 1H), 2.37 (s, 3H), 2.62−2.77 (m, 5H), 2.91−3.01 (m, 1H), 4.98−5.14 (m, 2H), 5.22−5.39 (m, 2H), 5.41 (t, 1H, J = 6 Hz), 5.76−5.90 (m, 2H), 6.89 (s, 1H), 7.22 (s, 4H); ^{13}C NMR ($CDCl_3$) 21.37, 24.60, 27.14, 48.15, 74.11, 90.74, 92.08, 93.41, 110.85, 116.52, 119.19, 125.38, 129.02, 129.16, 132.84, 134.50, 136.65, 139.90, 233.47; IR ($CHCl_3$) 3400−3600 (br) 1980, 1910 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.49; H, 5.39.

Complex 3c: yellow solid; mp 112 °C; ^{1}H NMR ($CDCl_3$) 1.65 (s, 3H), 2.01 (s, 1H), 2.59−2.75 (m, 3H), 2.85−3.15 (m, 1H), 5.20−5.45 (m, 3H), 5.90 (d, 1H, J = 6.7 Hz), 7.01 (s, 1H) 7.18−7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) 25.02, 27.40, 32.58, 90.17, 91.34, 92.31, 93.01, 102.85, 110.68, 117.96, 124.14, 126.88, 128.39, 128.98, 233.36; IR ($CHCl_3$) 1990, 1915 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_4Cr$: C, 65.25; H, 4.66. Found: C, 65.09; H, 4.70.

Complex 3d: yellow solid; mp 110 °C; ^{1}H NMR ($CDCl_3$) 1.63 (s, 3H), 2.05 (s, 1H), 2.38 (s, 3H), 2.70 (m, 3H), 2.88−3.05 (m, 1H), 5.21−5.48 (m, 3H), 5.90 (d, 1H, J = 6.6 Hz), 6.98 (s, 1H), 7.19 (s, 4H); ^{13}C NMR ($CDCl_3$) 21.14, 25.02, 27.21, 32.50, 72.13, 89.96, 91.27, 92.27, 92.78, 110.57, 117.81, 123.94, 128.76, 128.93, 134.24, 136.45, 142.04, 233.26; IR ($CHCl_3$) 1980, 1910 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4Cr$: C, 66.00; H, 5.00. Found: C, 66.01; H, 4.92.

Complex 3e: yellow solid; mp 140 °C; ^{1}H NMR ($CDCl_3$) 2.39 (s, 3H), 2.49 (s, 1H), 2.48−2.60 (m, 1H), 2.60−2.78 (m, 2H), 2.85−3.10 (m, 1H), 5.13−5.32 (m, 2H), 5.50 (t, 1H, J = 6.7 Hz), 5.98 (d, 1H, J = 6.7 Hz), 7.09 (s, 1H), 7.10−7.40 (m, 9H); ^{13}C NMR ($CDCl_3$) 21.30, 24.45, 27.32, 76.62, 89.92, 91.03, 92.38, 94.06, 112.13, 116.35, 124.57, 127.02, 128.09, 128.49, 129.02, 129.13, 134.34, 136.65, 140.81, 144.40, 233.22; IR ($CHCl_3$) 1990, 1910 cm^{-1}. Anal. Calcd for $C_{27}H_{22}O_4Cr$: C, 70.13; H, 4.76. Found: C, 70.20; H, 4.89.

Complex 3f: yellow solid; mp 126 °C; ^{1}H NMR ($CDCl_3$) 0.40−0.60 (m, 2H), 0.62−0.75 (m, 2H), 1.10−1.40 (m, 1H), 1.80 (s, 1H), 2.35 (s, 3H), 2.55−3.07 (m, 4H), 5.20−5.45 (m, 3H), 5.85 (d, 1H, J = 6.7 Hz), 6.83 (s, 1H), 7.05−7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) 2.34, 2.66, 21.40, 23.87, 25.27, 27.27, 72.24, 90.51, 91.34, 92.56, 93.07, 111.09, 117.18, 124.36, 129.14, 134.61, 136.66, 141.37, 233.58; IR ($CHCl_3$) 1995, 1895 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.60; H, 5.16. Found: C, 67.77; H, 5.21.

Complex 3g: yellow solid; mp 133 °C; ^{1}H NMR ($CDCl_3$) 0.80−1.05 (m, 3H), 1.15−1.50 (m, 5H), 1.65−2.85 (m, 1H), 2.00 (s, 1H), 2.38 (s, 3H), 2.50−2.65 (m, 1H), 2.70−2.90 (m, 2H), 2.85−3.10 (m, 1H), 5.15−5.35 (m, 2H), 5.45 (t, 1H, J = 6.5

Hz), 5.90 (d, 1H, J = 6.5 Hz), 6.90 (s, 1H), 7.10−7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) 14.41, 21.20, 23.33, 25.11, 27.12, 28.00, 31.45, 44.44, 75.10, 91.36, 94.33, 96.01, 111.01, 118.24, 125.60, 127.81, 128.03, 135.32, 137.64, 140.83, 233.54; IR ($CHCl_3$) 1990, 1910 cm^{-1}. Anal. Calcd for $C_{25}H_{26}O_4Cr$: C, 67.87; H, 5.88. Found: C, 68.02; H, 5.99.

Complex 3h: yellow solid; mp 100 °C; ^{1}H NMR ($CDCl_3$) 2.15 (s, 1H), 2.29 (s, 3H), 2.35−2.45 (m, 1H), 2.53−2.90 (m, 5H), 5.00−5.35 (m, 4H), 5.45 (t, 1H, J = 6.5 Hz), 5.75−6.15 (m, 2H), 6.85 (s, 1H), 7.05−7.25 (m, 4H); ^{13}C NMR ($CDCl_3$) 20.17, 24.10, 27.45, 48.37, 74.28, 90.43, 91.17, 91.70, 93.76, 111.01, 116.92, 119.00, 124.84, 125.80, 127.32, 129.13, 130.10, 133.03, 136.80, 140.24, 165.15, 233.43; IR ($CHCl_3$) 1980, 1910 cm^{-1}. Anal. Calcd for $C_{24}H_{22}O_4Cr$: C, 67.76; H, 5.17. Found: C, 67.79; H, 5.20.

General Procedure for the Preparation of Alcohols 5 and 6 from Enone 4. The procedure for the reaction of organolithium and Grignard reagents was the same as mentioned in the case of complexed enones.

Alcohol 5: colorless oil; ^{1}H NMR ($CDCl_3$) 2.25 (s, 1H), 2.41 (s, 3H), 2.50−2.68 (m, 1H), 2.68−2.85 (m, 2H), 2.90−3.10 (m, 2H), 3.10−3.22 (m, 1H), 5.00−5.28 (m, 2H), 5.80−6.05 (m, 1H), 6.85 (s, 1H), 7.05−7.40 (m, 7H), 7.78 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) 21.31, 25.26, 30.34, 48.31, 75.48, 118.44, 123.62, 126.32, 126.66, 127.28, 128.14, 128.99, 133.87, 135.19, 136.12, 136.37, 142.71, 143.46; IR ($CHCl_3$) 3300−3600 (br), 1600 cm^{-1}. Anal. Calcd for $C_{21}H_{22}O$: C, 86.89; H, 7.58. Found: C, 86.88; H, 7.60.

Alcohol 6: colorless oil; ^{1}H NMR ($CDCl_3$) 1.79 (s, 3H), 2.47 (brs, 1H), 2.50 (s, 3H), 2.55−2.75 (m, 1H), 2.85−3.05 (m, 2H), 3.10−3.25 (m, 1H), 7.05 (s, 1H), 7.13−7.40 (m, 7H), 7.80 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$) 21.16, 25.36, 30.52, 32.68, 73.96, 121.78, 126.27, 126.67, 126.93, 127.84, 128.80, 128.87, 135.16, 135.78, 136.06, 144.34, 145.48; IR ($CHCl_3$) 3500−3600 (br), 1600 cm^{-1}. Anal. Calcd for $C_{19}H_{20}O$: C, 86.36; H, 7.57. Found: C, 86.52; H, 7.55.

General Procedure for Equilibration[6] of 2b, 2b′, 2c, and 2c′. The complex (0.5 mmol) was dissolved in 5 mL of dichloromethane and treated with 10 mol % of DBU in dichloromethane at 0 °C. The reaction was monitored by TLC. In all cases equilibrium was reached in about 2 h. Workup involved removal of solvent, washing with water, and extracting with dichloromethane. The solvent was removed, and residue was chromatographed to yield a pair of diastereomers. Ratio of diastereomers: **2b**:**7a** = 89:1, **2b′**:**7a′** = 85:15, **2c**:**8a** = 80:20, **2c′**:**8a′** = 78:22. Data for **7a** and **7a′** have already been reported.[3b]

Complex 8a: red solid; mp 136 °C; ^{1}H NMR ($CDCl_3$) 1.25 (d, 3H, J = 7.2 Hz), 1.80−2.20 (m, 2H), 2.50−2.62 (m, 1H), 2.65−2.81 (m, 2H), 3.82−4.15 (m, 1H), 5.15 (d, 1H, J = 6.5 Hz), 5.32 (t, 1H, J = 6.5 Hz) 5.65 (t, 1H, J = 6.5 Hz), 6.25 (d, 1H, J = 6.5 Hz), 7.20−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) 17.38, 22.87, 23.98, 29.65, 38.88, 56.17, 82.30, 87,10, 91.43, 94.70, 102.10, 113.56, 120.10, 127.98, 128.62, 197.27, 231.20; IR ($CHCl_3$) 1980, 1910, 1675 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4Cr$: C, 65.28; H, 4.66. Found: C, 65.30; H, 4.86.

Complex 8a′: red solid; mp 123 °C; ^{1}H NMR ($CDCl_3$) 1.30 (d, 3H, J = 7.3 Hz), 2.00−2.15 (m, 2H), 2.65−3.05 (m, 3H), 3.50−3.70 (m, 1H), 5.11 (d, 1H, J = 6.5 Hz), 5.20 (t, 1H, J = 6.5 Hz), 5.60 (t, 1H, J = 6.5 Hz), 6.20 (d, 1H, J = 6.5 Hz), 7.05−7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) 16.33, 23.09, 26.44 32.03, 52.25, 81.92, 86.86, 89.51, 92,59, 95.45, 115.64, 127.83, 127.99, 128.55, 144.32, 196.50, 231.09; IR ($CHCl_3$) 1980, 1910, 1675 cm^{-1}. Anal. Calcd for $C_{22}H_{20}O_4Cr$: C, 65.28; H, 4.66. Found: C, 65.33; H, 4.73.

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