endo-Selective allylation at the benzylic centre of a $Cr(CO)_3$ complexed aromatic ring

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In the presence of $TiCl_4$, allyllithium adds to tricarbonylchromium complexes of 2-arylidene-1-tetralone and 2-arylideneindan-1-one (**1a**–**c**) to afford *endo*-1,2-adducts (**2a**–**c**) exclusively. Subsequent oxy-Cope rearrangement delivers the allyl group stereospecifically along the *endo*-face to the sterically hindered benzylic position of the metal-complexed ring.

Introduction

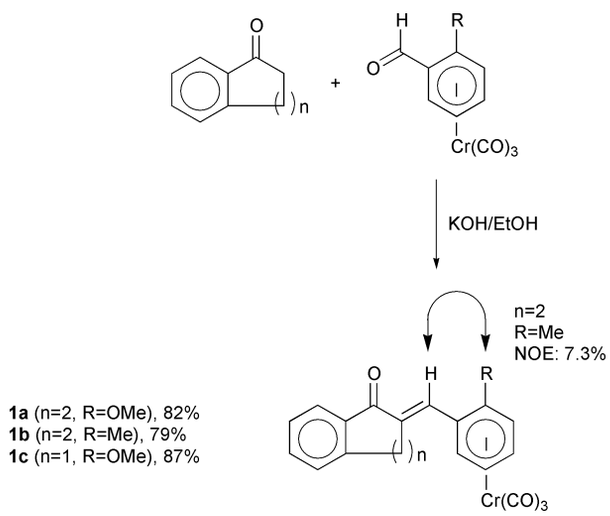
In arene-tricarbonylchromium complexes, the three CO ligands extend well beyond the periphery of the aromatic ring, and sterically hinder the approach of reagents from the same face of the molecule (*exo*-selectivity).[1] This aspect has been extensively used in the context of diastereoselective synthesis,[2] enantioselective synthesis,[3] design of chiral ligands[4] and total synthesis of target natural products.[5] By contrast, examples of *endo*-selective functionalizations are rare.[6] We have recently reported that out-of-plane coordination of a strong Lewis acid like $TiCl_4$ can predictably reverse normal preference for *exo*-selectivity in Ar-$Cr(CO)_3$ complexes and *endo*-adducts are exclusively formed even three carbons away from the metal-complexed ring.[6a–c] However, an *endo*-selective addition to the benzylic site of a complexed arene ring still remains a challenge owing to its proximity with the bulky $Cr(CO)_3$ group.

In the present study we examined a set of substrates where the carbonyl function is separated from the complexed arene ring by a double bond. We report that allyllithium, as a prototypical strong nucleophile, adds to this carbonyl function predominantly from the *exo*-face in the absence of a Lewis acid. In the presence of a Lewis acid like $TiCl_4$, we observed that the addition is completely *endo*-selective. This 'inverted' selectivity has been used to introduce the allyl group in an *endo*-selective manner to the sterically protected benzylic site by a subsequent intramolecular rearrangement. These experiments reaffirm that Lewis acid-induced *endo*-selectivity of nucleophilic addition is an effective way to achieve stereodivergent functionalization on arene-chromium complexes.

Results and discussion

The model substrates **1a**–**c** were readily prepared by a Claisen–Schmidt condensation of 1-tetralone‡ or indan-1-one with an *ortho*-substituted aromatic aldehyde with a pendant $Cr(CO)_3$ group (Scheme 1). In a typical procedure, ethanolic KOH was added dropwise to a solution of tetralone (or indanone) and the aldehyde complex in ethanol at room temperature. The reactions were complete in 2.5–3.0 hours (TLC).

The chemical shift of the olefinic proton (7.50–7.80 ppm) is indicative of a *trans*-olefin geometry.[6a] The *syn*-orientation of the *ortho*-substituent (R) with respect to the olefinic proton (as depicted in Scheme 1) was deduced with the help of NOE difference spectra. The extended planar arrangement of the π-system is evident from the deep red color of the complexes.



Scheme 1

In these molecules, the *peri*-hydrogens (H_p and H_o), hinder in-plane approach of the Lewis acid towards the oxygen lone pair of the ketone carbonyl group, and this forces $TiCl_4$ to seek out-of-plane coordination[7] with the C=O group from the less crowded *exo*-face. Therefore, for conjugate addition, a nucleophile must approach the benzylic carbon from the *endo*-face for the reaction to occur. But this site is protected from *endo*-attack by the steric bulk of the $Cr(CO)_3$ group in the immediate vicinity (Chart 1). In contrast to previously reported[6a] structurally similar substrates, these compounds do not undergo Hosomi–Sakurai allylation (allyltrimethylsilane and $TiCl_4$ at −78 °C for 12 h, followed by −20 °C for 8 h). However, a nucleophilic reagent could still approach the carbonyl function from the *endo*-face.

When allyllithium in THF was added to the complexes **1a**–**c** in dichloromethane[8] in the presence of 2.2 equiv. $TiCl_4$,[9] the expected 1,2-adducts (**2a**–**c**) formed as a single diastereoisomer[10] (Scheme 2). The crystal structure[11a] of a representative product **2a** confirmed that the allylation was *endo*-selective.

Anion-assisted oxy-Cope rearrangement[12a–c] of the alcohols **2a**–**c** with potassium hydride in ether furnished the ketone complexes **3a**–**c**. Since the original attachment of the allyl

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‡ The IUPAC name for 1-tetralone is 3,4-dihydronaphthalen-1(2*H*)-one.

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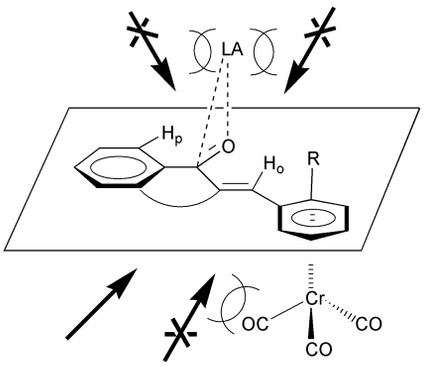
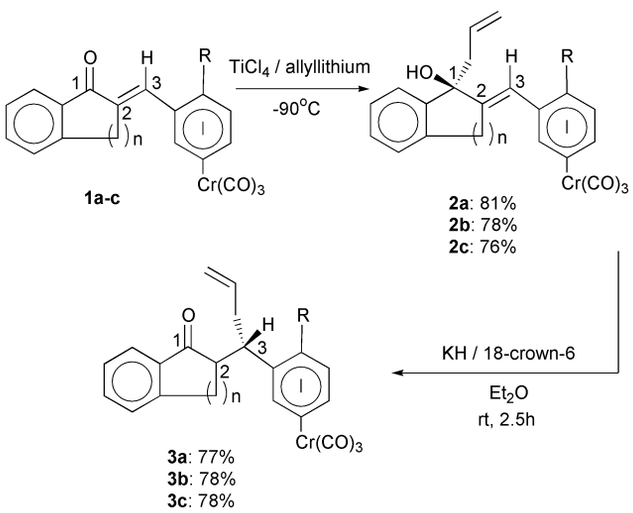


Chart 1



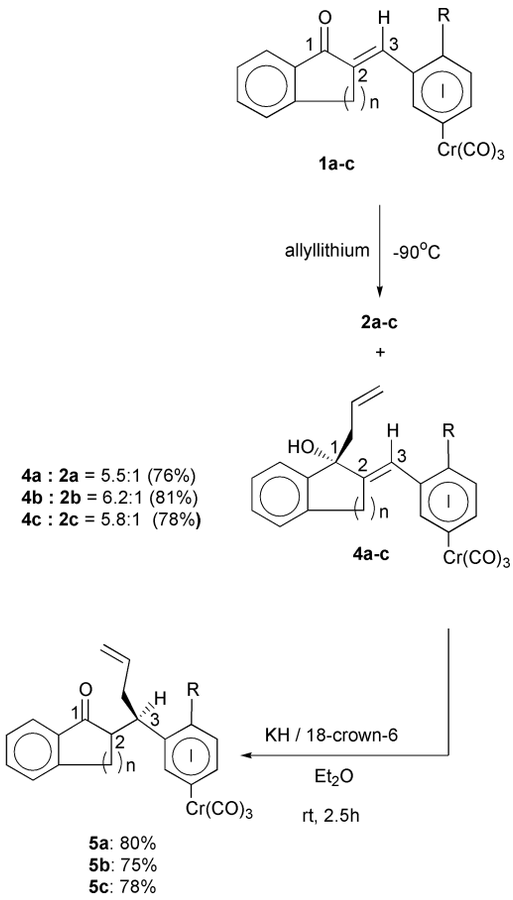
Scheme 2

group was from the *endo*-face of the molecule in **2a**–**c**, the rearranged products **3a**–**c** have the allyl groups appended to the benzylic sites (of the complexed aromatic ring) from the *endo*-face[12d] (Scheme 2).

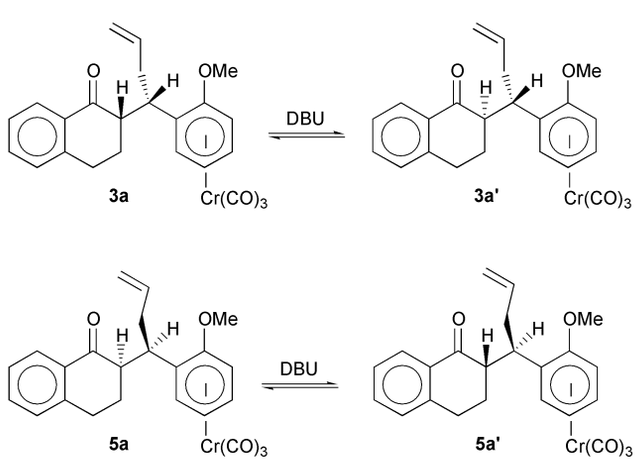
Formally, these are products of *endo*-selective conjugate addition of allylmetal to enones **1a**–**c**. This is a notable achievement, since direct *endo*-allylation is not easily effected at the benzylic position of a complexed arene. An allyl appendage is a versatile latent functional group that can be unmasked in a variety of ways at the desired stage of synthesis.[13] An *endo*-selective strategy, over and above, offers a clear advantage of added flexibility in synthetic design with these complexes.

In order to strengthen the stereochemical arguments and at the same time develop a stereodivergent strategy, the *exo*-allylated products were synthesized by omitting Lewis acid in the first step. Although conjugate addition by a small nucleophile like nitromethane at ambient temperature yielded exclusively *exo*-adducts at a center three carbons removed from the complexed arene ring on a similar substrate,[14] these allylmetal additions were not equally efficient—the minor stereoisomer (**2a**–**c**) from *endo*-attack was formed to the extent of 13–15% even at low temperatures (Scheme 3). The isomers **4a**–**c** and **2a**–**c** were readily separated by column chromatography, and crystal structure determination of **4a** confirmed its stereochemical identity.[11b] Subsequent rearrangement of the major stereoisomers **4a**–**c** provided the ketones **5a**–**c** where the allyl group is appended from the *exo*-face (Scheme 3).

Base-catalyzed equilibration (Scheme 4) of ketone **3a** yielded a minor isomer **3a**′ and **5a** yielded a minor isomer **5a**′. Thus, the pair **3a**–**3a**′ and **5a**–**5a**′ must be epimeric at C-2 (adjacent to the carbonyl carbon). This would imply that ketones **3a**–**c** must be epimeric with **5a**–**c** at C-3, that is, the new C–C bond forming



Scheme 3



Scheme 4

reaction at C-3 proceeded with opposite face-selectivity in the presence and absence of Lewis acid.[15]

To sum up, the two reaction sequences depicted in Scheme 2 and Scheme 3 are essentially stereodivergent routes to complementary stereoisomers obtainable from the same substrate complex. Allyllithium was selected as the representative nucleophile since the products were also suitable for a subsequent anionic oxy-Cope rearrangement. It was thus possible to introduce an allyl group to the benzylic site of an arene chromium complex selectively and predictably from the sterically encumbered *endo* face–an interesting feat that is unattainable by a direct approach. We admit that a specifically designed set of reactants was used in this study to promote unambiguously the diastereofacial discrimination in the nucleophilic allylation reaction. Yet, these results underscore the importance of out-of-plane coordination of Lewis acid to a carbonyl function in the modification of the steric course of a reaction, a strategic

variation that can be adapted to many sterically biased π-systems.

Experimental

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. Dichloromethane was freshly distilled over P_2O_5. Aromatic aldehydes were purchased from Aldrich, USA, and used as received. For descriptions of analytical instruments, spectral data formats and standard calibrations, see ref. 16. All reactions were performed on a 0.5–2.0 mmol scale. Metal complexes were crystallized from dichloromethane–hexane.

Preparation of enones 1a–c

Following a reported[17] procedure all three enones (**1a–c**) were prepared from 1-tetralone or indan-1-one (2.0 mmol) and $Cr(CO)_3$ complexed aromatic aldehydes[18] (2.0 mmol) and KOH (2.2 mmol) using Claisen–Schmidt condensation.

Complex 1a. Red solid; mp 145 °C; yield 82%; ^{1}H NMR ($CDCl_3$): 2.90–3.20 (m, 4H), 3.80 (s, 3H), 4.98 (t, 1H, J = 6.6 Hz), 5.15 (d, 1H, J = 6.6 Hz), 5.62 (t, 1H, J = 6.6 Hz), 5.71 (d, 1H, J = 6.6 Hz), 7.20–7.28 (m, 1H), 7.40 (t, 1H, J = 8.2 Hz), 7.55 (t, 1H, J = 8.2 Hz), 7.70 (br s, 1H), 8.15 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 12.72, 19.34, 27.87, 28.95, 63.36, 90.57, 92.38, 96.72, 102.34, 107.96, 127.40, 128.51, 129.50, 133.14, 133.66, 138.46, 143.30, 186.63, 232.97; IR ($CHCl_3$): 1950, 1860(br), 1660 cm^{-1}; Anal. Calcd. for $C_{21}H_{16}O_5Cr$: C: 63.00, H: 4.00, Found C: 62.86, H: 4.03%.

Complex 1b. Red solid; mp 135 °C; yield 79%; ^{1}H NMR ($CDCl_3$): 2.20 (s, 3H), 2.85–3.25 (m, 4H), 5.21–5.29 (m, 2H), 5.40–5.55 (m, 2H), 7.21–7.27 (m, 1H), 7.40 (t, 1H, J = 8.1 Hz), 7.46–7.55 (m, 1H), 7.56 (s, 1H), 8.15 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): 19.51, 27.52, 29.00, 89.33, 93.14, 93.64, 95.15, 103.02, 109.44, 127.12, 127.45, 128.57, 131.23, 133.01, 133.80, 138.90, 143.29, 186.62, 232.62; IR ($CHCl_3$): 1935, 1850, 1655 cm^{-1}; Anal. Calcd. for $C_{21}H_{16}O_4Cr$: C: 65.79, H: 4.17, Found C: 65.73, H: 4.30%.

Complex 1c. Red solid; mp 170 °C (dec); yield 87%; ^{1}H NMR ($CDCl_3$): 3.86 (s, 3H), 4.01 (br d, 2H, J = 8.6 Hz), 5.00 (t, 1H, J = 6.3 Hz), 5.15 (d, 1H, J = 6.3 Hz), 5.75 (t, 1H, J = 6.3 Hz), 6.15 (d, 1H, J = 6.3 Hz), 7.45 (t, 1H, J = 7.6 Hz), 7.55–7.70 (m, 2H), 7.77–7.82 (m, 1H), 7.95 (d, 1H, J = 8 Hz); ^{13}C NMR (CD_2Cl_2): 34.02, 58.24, 76.18, 87.02, 93.05, 96.40, 97.50, 126.25, 127.79, 128.38, 129.88, 136.83, 138.01, 140.06, 145.14, 151.52, 185.59, 234.64; IR ($CHCl_3$): 1960, 1865, 1660 cm^{-1}; Anal. Calcd. for $C_{20}H_{14}O_5Cr$: C: 62.17, H: 3.62, Found C: 62.01, H: 3.71%.

$TiCl_4$ mediated allyllithium addition to enones (1a–c)

To a solution of complexed enone (**1a–c**), (n mmol) in dichloromethane (20n mL), titanium tetrachloride (2.2n mmol) was added dropwise at −90 °C and stirred for 15 min. Allyllithium[19] (1.2n mmol) in THF was added dropwise with stirring at the same temperature. 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 mixture of products obtained after evaporation of solvent was separated by flash column chromatography. For details about isolated yield, see Scheme 2.

Complex 2a. Yellow solid; mp 128 °C; ^{1}H NMR ($CDCl_3$): 2.23 (s, 1H), 2.48–2.74 (m, 3H), 2.82–3.15 (m, 3H), 3.71 (s, 3H), 4.91 (t, 1H, J = 6.5 Hz), 5.05–5.29 (m, 3H), 5.50 (t, 1H, J = 6.5 Hz), 5.62 (d, 1H, J = 6.5 Hz), 5.70–6.01 (m, 1H), 6.58 (s, 1H), 7.05 (d, 1H, J = 8.0 Hz), 7.15–7.37 (m, 2H), 7.70 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$): 25.48, 29.71, 30.63, 48.53, 55.69, 75.25, 85.65, 93.56, 97.18, 97.60, 116.25, 118.26, 126.12, 126.56, 127.16, 127.80, 133.35, 135.60, 141.29, 142.75, 146.36, 233.39; IR ($CHCl_3$): 3400–3600(br), 1940, 1850(br) cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 65.15, H: 4.97, Found C: 64.98, H: 4.99%.

Complex 2b. Yellow solid; mp 110 °C; ^{1}H NMR ($CDCl_3$): 2.15 (s, 3H), 2.22 (s, 1H), 2.50–2.71 (m, 3H), 2.72–2.88 (m, 1H), 2.89–3.11 (m, 2H), 5.05–5.80 (m, 4H), 5.81–5.50 (m, 2H), 5.70–6.00 (m, 1H), 6.51 (s, 1H), 7.00–7.15 (m, 1H), 7.15–7.37 (m, 2H), 7.68 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 19.41, 25.45, 30.16, 48.75, 75.29, 90.51, 93.26, 94.11, 96.11, 107.55, 108.99, 118.93, 119.06, 126.29, 126.88, 127.50, 128.10, 133.28, 135.64, 142.65, 147.18, 233.62; IR ($CHCl_3$): 3500–3600(br), 1935, 1850(br) cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_4Cr$: C: 67.60, H: 5.16, Found C: 67.67, H: 4.99%.

Complex 2c. Yellow solid; mp 110 °C; ^{1}H NMR ($CDCl_3$): 2.28 (s, 1H), 2.65 (d, 2H, J = 8.5 Hz), 3.70–3.85 (m, 2H), 3.80 (s, 3H), 4.95–5.20 (m, 4H), 5.45–5.80 (m, 2H), 5.87 (d, 1H, J = 6.5 Hz), 6.78–6.82 (m, 1H), 7.17–7.40 (m, 3H), 7.49 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): 29.90, 35.71, 47.88, 56.11, 74.45, 85.51, 89.38, 93.41, 95.32, 116.76, 119.67, 123.88, 124.71, 127.63, 128.86, 132.45, 139.38, 141.34, 146.07, 150.74, 233.42; IR ($CHCl_3$): 3400–3600(br), 1940, 1835 cm^{-1}; Anal. Calcd. for $C_{23}H_{20}O_5Cr$: C: 64.48, H: 4.67, Found C: 64.40, H: 4.55%.

Addition of allyllithium to enones (1a–c) in absence of Lewis acid

To a solution of complexed enone (**1a–c**), (n mmol) in THF (20n mL), allyllithium (1.2–1.4n mmol) in THF was added 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 mixture of products obtained after evaporation of solvent was separated by flash column chromatography. For isolated yield and product ratio see Scheme 3.

Complex 4a. Yellow solid; mp 122 °C; ^{1}H NMR ($CDCl_3$): 2.25 (s, 1H), 2.40–2.60 (m, 1H), 2.60–2.75 (m, 2H), 2.90–3.15 (m, 3H), 3.80 (s, 3H), 5.00 (t, 1H, J = 6.2 Hz), 5.05–5.23 (m, 3H), 5.50 (t, 1H, J = 6.2 Hz), 5.60 (d, 1H, J = 6.2 Hz), 5.70–5.95 (m, 1H), 6.58 (s, 1H), 7.05–7.40 (m, 3H), 7.67 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 25.86, 30.41, 48.66, 56.17, 74.93, 75.84, 85.92, 93.44, 96.79, 98.29, 116.70, 118.64, 126.59, 126.98, 127.58, 128.25, 133.65, 136.10, 141.26, 143.08, 147.28, 233.55; IR ($CHCl_3$): 3400–3600(br), 1940, 1850(br) cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 65.15, H: 4.97, Found C: 64.83, H: 4.94%.

Complex 4b. Yellow solid; mp 140 °C; ^{1}H NMR ($CDCl_3$): 2.20 (s, 3H), 2.25 (s, 1H), 2.29–2.50 (m, 1H), 2.50–2.75 (m, 2H), 2.77–3.17 (m, 3H), 5.00–5.25 (m, 2H), 5.27–5.48 (m, 4H), 5.70–5.97 (m, 1H), 6.55 (s, 1H), 7.10 (d, 1H, J = 8.1 Hz), 7.20–7.48 (m, 2H), 7.70 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): 19.64, 25.33, 30.48, 48.35, 75.79, 90.77, 93.24, 94.22, 95.16, 108.17, 108.69, 118.34, 119.23, 126.41, 126.90, 127.52, 128.20, 133.58, 135.60, 143.01, 147.71, 233.66; IR ($CHCl_3$): 3400–3600(br), 1920, 1825(br) cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_4Cr$: C: 67.60, H: 5.16, Found C: 67.82, H: 5.08%.

Complex 4c. Yellow solid; mp 122 °C; ^{1}H NMR ($CDCl_3$): 2.38 (s, 1H), 2.55–2.75 (m, 2H), 3.50–3.75 (m, 1H), 3.80 (s, 3H), 3.95–4.15 (m, 1H), 4.90–5.10 (m, 3H), 5.20 (d, 1H, J = 6.5 Hz), 5.45–5.71 (m, 2H), 5.80 (d, 1H, J = 6.5 Hz), 6.80 (br s, 1H), 7.15–7.40 (m, 3H), 7.45 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 27.09, 35.40, 47.55, 56.14, 75.05, 83.93, 85.89, 93.02, 95.79, 116.31, 118.73, 123.93, 124.74, 127.42, 128.86, 132.93, 139.51, 140.90, 145.83, 152.02, 233.45; IR ($CHCl_3$): 3400–3600(br),

1930, 1836 cm^{-1}; Anal. Calcd. for $C_{23}H_{20}O_5Cr$: C: 64.48, H: 4.67, Found C: 64.72, H: 4.58%.

Oxy-Cope rearrangement of 1,2-allyl adducts

To a solution of 1,2-allyl adduct (**2a**–**c** and **4a**–**c**) (*n* mmol) and 18-crown-6 (0.1*n* mmol) in diethyl ether (20*n* mL), suspension of potassium hydride (1.1n mmol) in ether was added dropwise with stirring at 0 °C. It was then stirred at room temperature until completion (TLC, 2.5 h). It was quenched with degassed methanol at 0 °C and finally extracted with ether. Residue obtained after evaporation of solvent was purified by flash column chromatography.

Complex 3a. Yellow solid; mp 65 °C; yield 77%; ^{1}H NMR ($CDCl_3$): 1.90–2.15 (m, 2H), 2.35–2.65 (m, 2H), 2.66–2.87 (m, 1H), 2.88–3.15 (m, 2H), 3.68 (s, 3H), 4.00–4.20 (m, 1H), 4.85–5.15 (m, 4H), 5.48 (t, 1H, J = 6.3 Hz), 5.69 (d, 1H, J = 6.3 Hz), 5.75–6.05 (m, 1H), 7.10–7.38 (m, 2H), 7.45 (t, 1H, J = 8.1 Hz), 8.03 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): 24.57, 29.45, 34.97, 35.83, 52.25, 55.99, 73.68, 82.51, 85.24, 93.58, 95.27, 105.60, 116.97, 126.91, 127.83, 128.79, 133.44, 137.02, 141.40, 143.72, 197.64, 233.41; IR ($CHCl_3$): 1964, 1867, 1670 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 67.16, H: 4.97, Found C: 65.19, H: 4.86%.

Complex 3b. Yellow solid; mp 97 °C; yield 78%; ^{1}H NMR ($CDCl_3$): 1.90–2.15 (m, 2H), 2.25 (s, 3H), 2.30–2.50 (m, 3H), 2.72–3.10 (m, 2H), 4.05–4.15 (m, 1H), 4.80–5.10 (m, 2H), 5.10–5.31 (m, 2H), 5.40 (t, 2H, J = 6.5 Hz), 5.65–5.90 (m, 1H), 7.15–7.40 (m, 2H), 7.49 (t, 1H, J = 8.2 Hz), 8.05 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 18.98, 22.56, 29.50, 29.85, 34.22, 37.23, 53.08, 90.01, 92.60, 93.79, 108.56, 114.95, 117.05, 127.04, 127.97, 128.80, 132.75, 133.69, 136.62, 143.58, 196.83, 233.51; IR ($CHCl_3$): 1962, 1860, 1667 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_4Cr$: C: 67.60, H: 5.16, Found C: 67.66, H: 5.25%.

Complex 3c. Yellow solid; mp 121 °C; yield 78%; ^{1}H NMR ($CDCl_3$): 2.05–2.15 (m, 1H), 2.35–2.60 (m, 2H), 2.60–2.80 (m, 1H), 3.05–3.39 (m, 2H), 3.80 (s, 3H), 4.85–5.20 (m, 4H), 5.40–5.60 (m, 1H), 5.60–6.00 (m, 2H), 7.40 (t, 1H, J = 8.1 Hz), 7.50–7.70 (m, 2H), 7.80 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$): 29.48, 30.92, 39.46, 53.86, 56.30, 75.41, 88.19, 92.53, 96.66, 101.32, 117.32, 117.97, 120.67, 121.24, 128.56, 135.14, 138.13, 140.00, 156.80, 205.58, 233.32; IR ($CHCl_3$): 1965, 1860, 1660 cm^{-1}; Anal. Calcd. for $C_{23}H_{20}O_5Cr$: C: 64.48, H: 4.67, Found C: 64.51, H: 4.71%.

Complex 5a. Yellow solid; mp 110 °C; yield 80%; ^{1}H NMR ($CDCl_3$): 1.95–2.25 (m, 1H), 2.27–2.49 (m, 2H), 2.55–2.75 (m, 1H), 2.77–3.40 (m, 3H), 3.75 (s, 3H), 4.20–4.39 (m, 1H), 4.75–5.15 (m, 4H), 5.55–5.90 (m, 3H), 7.17–7.40 (m, 2H), 7.42–7.60 (m, 1H), 8.12 (d, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$): 24.39, 29.33, 33.03, 34.54, 55.48, 55.98, 72.91, 83.54, 95.54, 99.44, 106.47, 117.02, 126.68, 127.78, 128.99, 131.93, 132.66, 136.56, 142.62, 144.27, 197.79, 233.70; IR ($CHCl_3$): 1960, 1865, 1672 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 67.16, H: 4.97, Found: C: 66.94, H: 5.01%.

Complex 5b. Yellow solid; mp 110 °C; yield 75%; ^{1}H NMR ($CDCl_3$): 2.25 (s, 3H), 2.30–2.68 (m, 4H), 2.80–3.18 (m, 4H), 4.70–4.95 (m, 2H), 5.05 (d, 1H, J = 6.4 Hz), 5.15 (t, 1H, J = 6.4 Hz), 5.30–5.48 (m, 1H), 5.50–5.75 (m, 1H), 6.15 (d, 1H, J = 6.4 Hz), 7.05–7.55 (m, 3H), 8.05 (d, 1H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$): 20.17, 29.39, 29.92, 30.70, 38.98, 43.24, 53.53, 90.43, 92.77, 94.84, 96.41, 110.10, 117.28, 118.12, 127.03, 127.80, 128.77, 133.69, 135.97, 143.85, 199.13, 233.77; IR ($CHCl_3$): 1965, 1860, 1660 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_4Cr$: C: 67.60, H: 5.16, Found C: 67.56, H: 5.12%.

Complex 5c. Yellow solid; mp 113 °C; yield 78%; ^{1}H NMR ($CDCl_3$): 2.25–2.55 (m, 3H), 2.65–2.90 (m, 1H), 3.15–3.45 (m, 2H), 3.75 (s, 3H), 4.75–5.20 (m, 4H), 5.35–5.70 (m, 3H), 7.40 (t, 1H, J = 7.9 Hz), 7.50–7.70 (m, 2H), 7.75 (d, 1H, J = 7.9 Hz); ^{13}C NMR ($CDCl_3$): 31.04, 39.02, 43.37, 52.82, 53.56, 55.99, 74.81, 86.19, 93.51, 97.24, 99.32, 118.16, 123.98, 125.72, 128.04, 135.10, 136.37, 141.91, 156.30, 206.18, 233.35; IR ($CHCl_3$): 1960, 1860, 1665 cm^{-1}; Anal. Calcd. for $C_{23}H_{20}O_5Cr$: C: 64.48, H: 4.67, Found C: 64.40, H: 4.65%.

Base catalysed equilibration of 3a and 5a

The complex (0.5 mmol) was dissolved in 5 mL of dichloromethane and treated with 10 mol% DBU in dichloromethane at 0 °C. The reaction was monitored by TLC. In all cases equilibrium was reached in about 2 hours. Work up involved removal of solvent, washing with water and extracting with dichloromethane. Dichloromethane was removed and residue was chromatographed to yield a pair of diastereomers. Ratio of diastereomers: **3a**–**3a′** = 85 : 15; **5a**–**5a′** = 80 : 20.

Complex 3a′. Yellow solid; mp 82 °C; ^{1}H NMR ($CDCl_3$): 1.90–2.20 (m, 2H), 2.45–2.75 (m, 2H), 2.76–2.80 (m, 1H), 2.80–3.05 (m, 2H), 3.45–3.60 (m, 1H), 3.68 (s, 3H), 4.85–5.25 (m, 4H), 5.45 (t, 1H, J = 6.4 Hz), 5.81–6.05 (m, 2H), 7.10–7.35 (m, 2H), 7.45 (t, 1H, J = 8.2 Hz), 7.95 (d, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$): 28.36, 29.88, 35.53, 38.08, 51.52, 55.96, 73.59, 85.35, 86.68, 93.53, 96.02, 105.31, 117.31, 126.89, 127.48, 128.73, 133.47, 137.15, 141.93, 146.88, 199.20, 233.58; IR ($CHCl_3$): 1960, 1865, 1660 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 65.16, H: 4.97, Found C: 65.29, H: 4.88%.

Complex 5a′. Yellow solid; mp 96 °C; ^{1}H NMR ($CDCl_3$): 1.92–2.20 (m, 1H), 2.22–2.45 (m, 1H), 2.55–2.75 (m, 2H), 2.85–3.10 (m, 3H), 3.30–3.50 (m, 1H), 3.78 (s, 3H), 4.80–5.05 (m, 4H), 5.55 (t, 1H, J = 6.3 Hz), 5.60–5.90 (m, 1H), 6.20 (d, 1H, J = 6.3 Hz), 7.15–7.40 (m, 2H), 7.45–7.60 (m, 1H), 8.05 (d, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$): 28.49, 29.42, 29.87, 38.29, 40.63, 52.63, 55.77, 73.71, 85.36, 94.64, 99.29, 106.20, 117.29, 126.85, 127.67, 128.79, 133.55, 137.06, 142.66, 144.02, 199.29, 233.70; IR ($CHCl_3$): 1960, 1860, 1665 cm^{-1}; Anal. Calcd. for $C_{24}H_{22}O_5Cr$: C: 65.16, H: 4.97, Found C: 65.40, H: 4.99%.

Attempted Hosomi–Sakurai reaction of enones 1a–c

To a solution of enone (1 mmol) in dichloromethane (10 mL) at −78 °C, $TiCl_4$ (2 mmol) was added dropwise with stirring. After 30 minutes allylsilane (2.0 mmol) was added dropwise at that temperature. Reaction was monitored by TLC. There was no reaction after stirring for 12 hours at −78 °C followed by stirring at −20 °C for 8 hours. After usual workup, starting material was recovered (80–90%).

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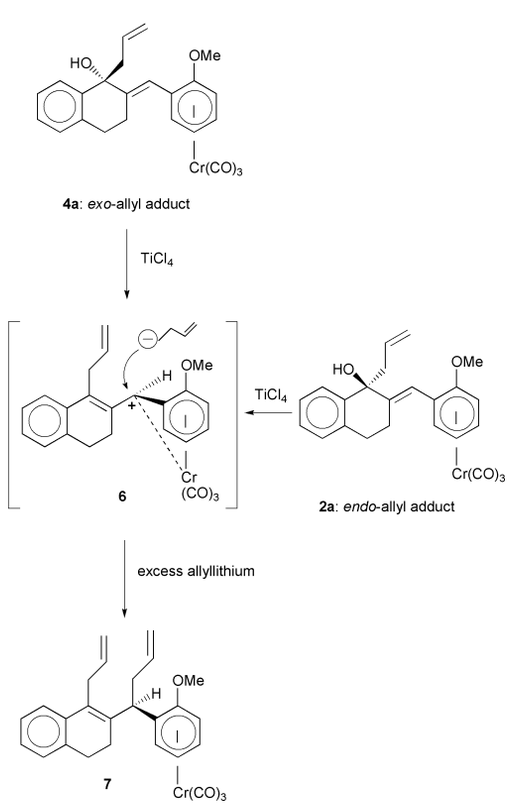

11 (*a*) X-Ray crystal structure of compound **2a** ($C_{24}H_{22}CrO_5$), was solved using Mo-Kα radiation at $T = 120$ K; *crystal data:* tetragonal space group $P4_2/n$, $a = 18.8459$ (5) Å, $c = 13.2143$ (3) Å, $v = 4693.3$ (2) Å^3, $Z = D_x = 1.383$ Mg m^{-3}; *Data collections:* 14072 measured reflections, 7254 independent reflections $\theta_{max} = 31.0°$; *Refinement:* $R[F^2 > 2\sigma(F^2)] = 0.053$, parameters 287, $\Delta_{max} = 0.54$ e Å^{-3}; (*b*) X-Ray crystal structure of compound **4a** ($C_{24}H_{22}CrO_5$), was solved using Mo-Kα radiation at $T = 301(2)$ K; *crystal data:* triclinic space group *P-1*, $a = 11.3514$ (6) Å, $b = 13.8365$ (6) Å, $c = 14.2539$ (5) Å, $v = 2082.32$ (16) Å^3, $Z = 4$ $D_x = 1.411$ Mg m^{-3}; *Data collections:* measured reflections 6531, independent reflections 5517, $\theta_{max} = 56.74°$; *Refinement:* $R[I > 2\sigma(I)] = 0.035$, parameters 56, $\Delta\rho_{max} = 0.227$ e Å^{-3}. These structures also corroborate the assigned conformation of starting materials depicted in Scheme 1. The authors thank Professor Frank R. Fronczek (**2a**) and Professor Karl S. Hagen (**4a**) for crystal structure solution. Details of structure determination will be published elsewhere.

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