Facial Diastereoselectivity in Cationic Propargylations with Planar-Chiral AreneCr(CO)$_3$-Substituted Propargyl Cations

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Keywords: Addition reactions / Alkynes / Arenes / Chromium / Diastereoselectivity

The planar-chiral (*o*-methoxyphenyl)chromium tricarbonyl-substituted propargyl cation **4** reacts with silyl enol ether derivatives **5** with poor and with enamines **6** with good facial diastereoselectivity to give rise to the (arene)carbonylchromium-substituted propargylated cyclohexan-2-ones **7** and **8**, carboxylic acid **9**, γ-lactone **10**, cyclopentan-2-one **11**, and esters **16** and **17**. Structural correlations were unambiguously deduced from X-ray structure analyses of **7a**, **9a**, and **17a**. The origin of facial diastereoselectivity with this class of organometallic electrophiles lies in steric and stereoelectronic biases rather than in purely electronic nucleophilicity.

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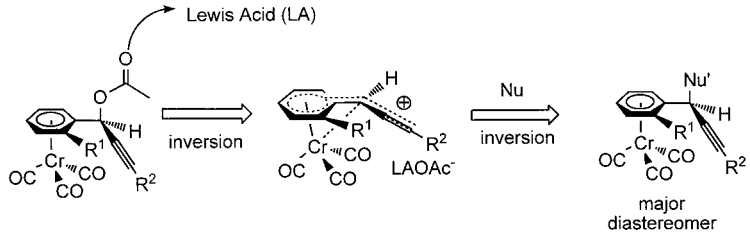
Introduction

Cationic propargylations have become relevant for stereoselective applications with the advent of transition metal stabilization of propargyl cations.[1] Besides the introduction of nucleophilic additions to dicobalt hexacarbonyl complexed propargyl cations, known as the Nicholas reaction,[2] which has led to widespread applications in complex molecules' syntheses,[3] we have demonstrated in the past few years that (arene)carbonylchromium-substituted propargyl cations represent complementary propargyl cation synthetic equivalents in highly stereoselective cationic propargylation reactions.[4] Stereochemically, the stepwise ionization and nucleophilic addition to a planar-chiral, configurationally stable propargyl cation leads to a high degree of diastereoselection in the sense of a retention of configuration at the propargylic stereogenic center as a consequence of a double inversion mechanism (Scheme 1). Since the nucleophilic attack always occurs *anti* with respect to the shielding and stabilizing carbonylchromium tripod the exploitation of the diastereofacial stereodifferentiation[5] as a powerful tool to control the generation of contiguous stereocenters lies at hand. Here we wish to report on facially diastereoselective propargylations with a representative (arene)carbonylchromium-stabilized propargyl cation.



Scheme 1. Mechanistic rationale of stereoselective cationic propargylations with planar chiral configurationally stable (arene)Cr(CO)$_3$-substituted propargyl cations.

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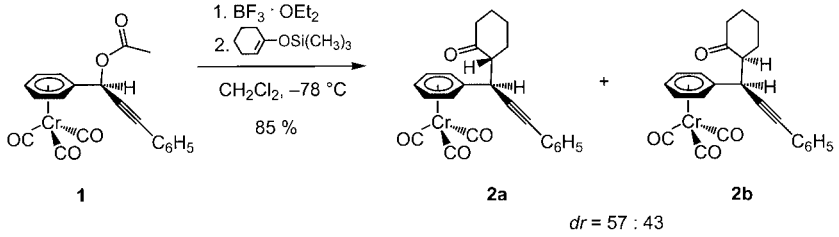
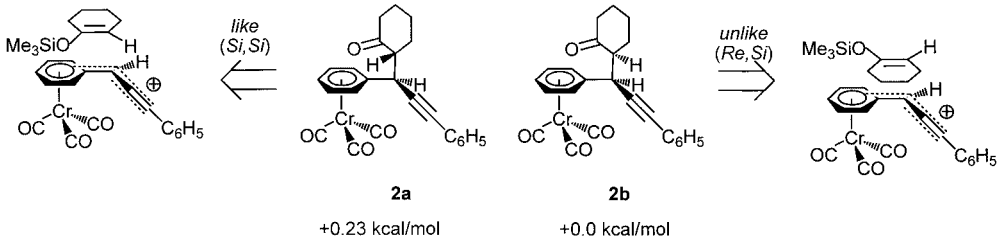
[‡] X-ray structure analyses of **7a**, **17a** (K. P.), and **9a** (H. N.).

Results and Discussion

First, we intended to scout the simple diastereoselectivity of the cationic propargylation by applying a C–C bond forming reaction with a suitably reactive nucleophile, such as a silyl enol ether. Upon trapping the carbonylchromium-complexed 1,3-diphenylpropargyl cation[4a] generated from the acetate precursor **1** by treatment with boron trifluoride diethyl etherate as a Lewis acid and 1-trimethylsiloxycy-



Scheme 2. Simple diastereoselectivity of the cationic propargylation with a silyl enol ether.



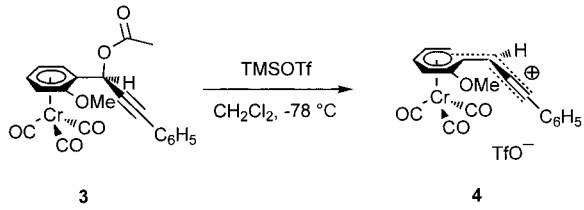
Scheme 3. Conformational analysis and deduction of the facial nucleophilic attack with the aid of MMFF94 force-field calculations.

clohexene at –78 °C, a 57:43 mixture of diastereomers **2a** and **2b** was obtained in good yield (Scheme 2).

A product analysis and MMFF94 force-field computations[6] on the two diastereomers **2a** and **2b** show a small energy difference between them which suggests two different scenarios for the facial stereoselective attack of the silyl enol ether (Scheme 3): either this thermodynamic product distribution is a result of a post-trapping epimerization at the α-carbonyl center, or, assuming a kinetically controlled nucleophilic trapping without epimerization, the energy differences of the *Si*,*Si* (*like*) and *Re*,*Si* (*unlike*) transition states are rather small. This distinction is particularly interesting since Reetz has observed a similar facial diastereoselectivity for the nucleophilic trapping of complexed benzyl cations.[7]

If the stereochemical outcome is determined by kinetics, as can be expected from our previous findings,[4d] the facial selectivity can be enhanced by fine-tuning the nucleophilicity of the enolate synthetic equivalent and by increasing the steric biases in the transition state. Therefore, it was necessary not only to conduct the trapping reactions strictly under kinetic control but also to scrutinize the electronic and steric influence of the nucleophile on the stereochemical outcome of facially diastereoselective propargylations. As a consequence, we decided to carry out the trapping reactions with the planar chiral propargyl cation **4**, generated by treatment of the propargyl acetate precursor **3** with TMS triflate (Scheme 4), as this cation gave rise to the highest diastereoselectivities in the previously reported diastereoselective propargylations.[4d]

The cation **4** is not only configurationally stable but is also locked in a *syn-s-cis* conformation under the applied conditions.[8] In a series of experiments this configurationally stable, planar-chiral propargyl cation was treated with the silyl enol ethers and ketene acetals **5** and enamines **6** to



Scheme 4. Generation of the planar chiral propargyl cation **4**.

give the propargylation products **7**–**11** in good to excellent yields (Scheme 5).

In all cases the propargylation products were obtained as mixtures of diastereomers that were inseparable by flash chromatography. Hence, the diastereomeric ratios were determined by ^1H NMR spectroscopy before further purification by crystallization; the structures were unequivocally supported by extensive NMR spectroscopic experiments (^1H,^1H COSY, NOESY, and HETCOR). The unambiguous assignment of the diastereomers was greatly facilitated by correlation of the ^1H and ^{13}C NMR spectra with X-ray structure analyses that were obtained for the major diastereomers **7a** (Figure 1, Table 1) and **9a**[9] (Figure 2, Table 1), which show the expected bond lengths.[10]

Due to coupling with the proton-bearing $C_{\beta'}$ centers the C_α proton signals appear in the ^1H NMR spectra as discrete doublets between δ = 3.7 and 4.5 ppm (Table 2). The quaternary $C_{\beta'}$ center in **8** causes the C_α proton resonance to appear as a singlet at δ = 4.2 ppm. With the exception of **8**, which shows a singlet for the methyl proton signals at δ = 1.07 and 1.13 ppm, respectively, the resonances of the $C_{\beta'}$ protons are found as multiplets between δ = 2.8 and 3.7 ppm. Nevertheless, in a few cases the corresponding coupling constants can be extracted from some of the centered multiplets.

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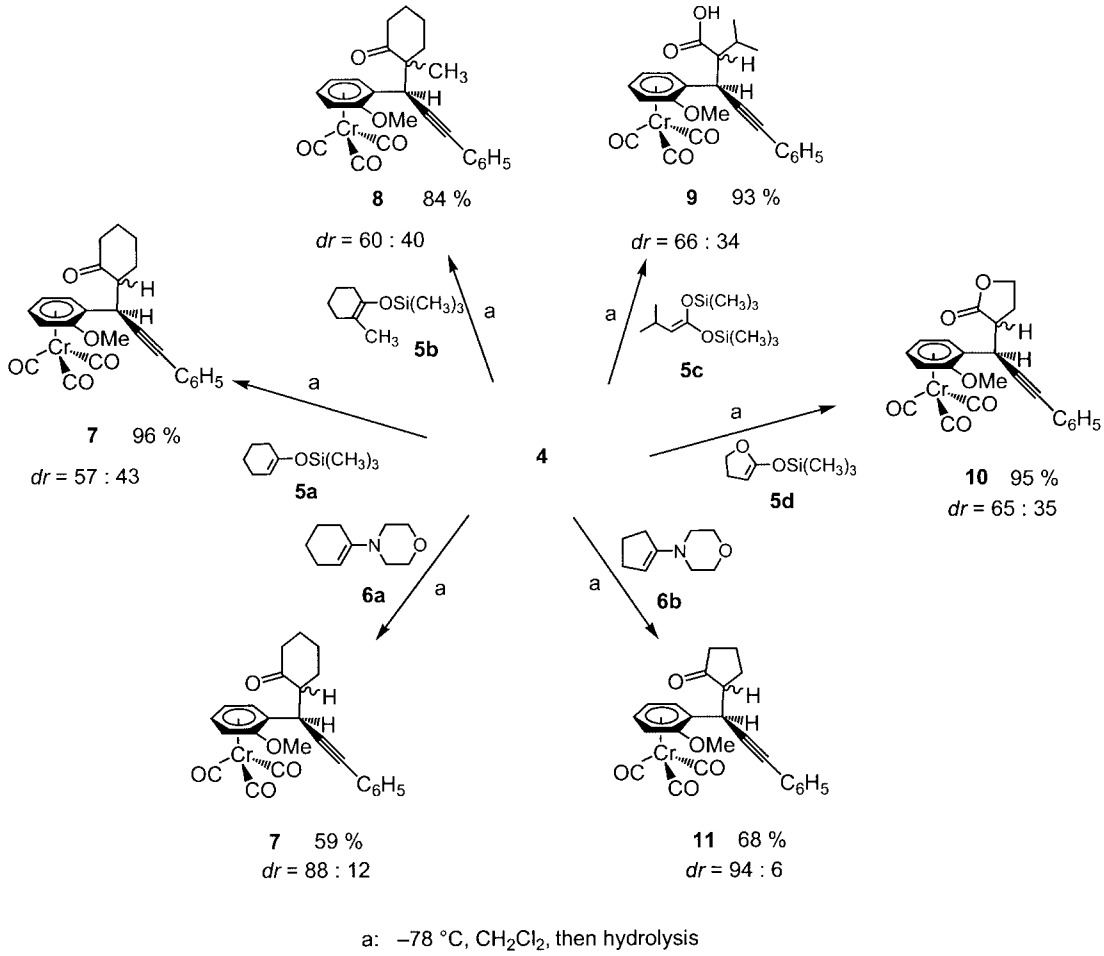

Scheme 5. Facial diastereoselectivity of cationic propargylations with silyl enol ethers, silyl ketene acetals, and enamines.

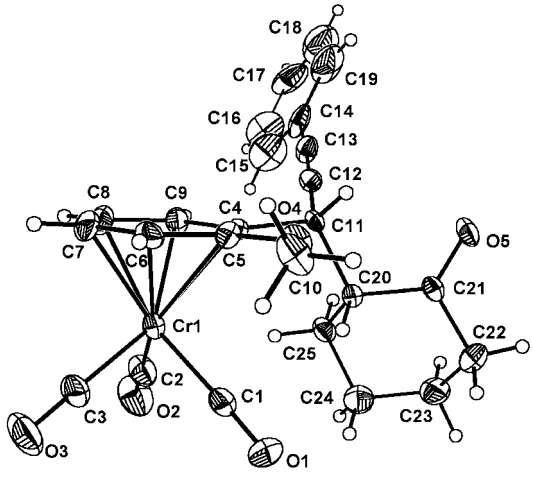

Figure 1. ORTEP plot of the major diastereomer **7a**. Selected bond lengths [Å] and bond and dihedral angles [°]: C(4)–C(11) 1.535(9), C(11)–C(12) 1.460(7), C(12)–C(13) 1.175(6), C(11)–C(20) 1.563(6); C(12)–C(11)–C(4) 111.06, C(11)–C(12)–C(13) 178.11, C(11)–C(4)–C(5)–C(6) 173.36, C(4)–C(11)–C(12)–C(20) 112.05.

A comparison of the H_α shifts and the coupling constants of mutually diastereomeric compounds reveals that for **7** and **11** the resonances of the major diastereomers are shifted downfield and display smaller coupling constants. In contrast, the singlet of the major diastereomer of **8** and the doublets of **9** and **10** are shifted upfield, the latter with larger coupling constants than the minor diastereomers. In the ^{13}C NMR spectra the C_α propargyl methine signals are found between δ = 30.9 and 41.3 ppm; the resonances of the adjacent $C_{\beta'}$ centers appear between δ = 44.9 and 54.9 ppm.

Applying the Karplus correlation[11] between vicinal ^3J couplings and the associated dihedral angles, Φ, the conformations of the diastereomers **7a** and **7b** at room temperature and in solution can be easily deduced (Scheme 6). As a consequence of the steric bulk of the (*o*-anisyl)tricarbonylchromium substituent a rapid rotation around the C_α–$C_{\beta'}$ axis is hampered at room temperature and, thus, the depicted staggered conformations of **7a** and **7b** are apparently thermodynamically most favorable.

The analysis of the nucleophile-dependent outcome of the diastereofacial propargylations reveals some interesting aspects. If silyl enol ethers are applied as nucleophiles the degree of facial diastereoselectivity is considerably lower (*dr* = 3:2) than with enamines (*dr* = 9:1). Most striking is the difference in diastereoselectivity if the propargylated cyclohexanone **7** is generated from the silyl enol ether **5a** (*dr* = 57:43) or the enamine **6a** (*dr* = 88:12). The 3:2 diastereose-

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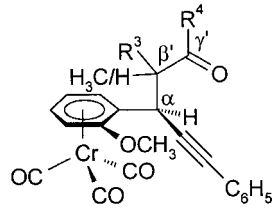
Table 1. Crystal data and structure refinements for **7a**, **9a**, and **17a**.

	7a	**9a**	**17a**
Empirical formula	$C_{25}H_{22}CrO_5 \cdot 0.33\,H_2O$	$C_{24}H_{22}CrO_5$	$C_{26}H_{30}BCrNO_6$
Color, form	yellow rods	yellow needles	yellow plates
Formula weight	459.71	442.42	515.32
Temperature	295(2) K	193(2) K	295(2) K
Wavelength [Å], radiation	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)	0.71073 (Mo-K_α)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P21/c$	$Pna2_1$
Unit cell dimensions	a = 7.0330(12) Å	a = 6.8219(10) Å	a = 18.444(4) Å
	b = 17.950(3) Å	b = 14.484(2) Å	b = 26.319(9) Å
	c = 18.177(3) Å	c = 22.804(4) Å	c = 11.048(2) Å
	α = 90.00(0)°	α = 90.00°	α = 90.00(0)°
	β = 90.00(0)°	β = 90.542(3)°	β = 90.00(0)°
	γ = 101.30(2)°	γ = 90.00°	γ = 90.00(0)°
Volume [Å^3]	2250.2(7)	2253.2(6)	5362.9(23)
Z	4	4	8
Density (calculated)	1.357 g cm^{-3}	1.304 g cm^{-3}	1.276 g cm^{-3}
Absorption coefficient	0.543 mm^{-1}	0.538 mm^{-1}	0.465 mm^{-1}
F(000)	955	920	2160
Crystal size (mm)	0.27 × 0.33 × 0.47	0.6 × 0.18 × 0.08	0.17 × 0.37 × 0.53
Theta range for data collection	3.16 to 23.97°	1.67 to 27.42°	2.28 to 23.98°
Index ranges	$-8 \le h \le 8$	$-4 \le h \le 4$	$0 \le h \le 21$
	$-20 \le k \le 20$	$-17 \le k \le 17$	$0 \le k \le 30$
	$-20 \le l \le 20$	$-27 \le l \le 27$	$-12 \le l \le 12$
Reflections collected	3464	12173	9341
Independent reflections	1949 [R(int.) = 0.0297]	3238 [R(int.) = 0.0606]	8400 [R(int.) = 0.0145]
Observed [$I > 2\sigma(I)$]	1393	2554 [$I > 4\sigma(I)$]	6660
Absorption correction	Semi-empirical from psi-scans	Semi-empirical from psi-scans	Semi-empirical from psi-scans
Max. and min. transmission	0.9834 and 0.9999	–	0.9350 and 0.9997
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	1949/72/305	3238/0/287	8400/1/641
Goodness-of-fit on F^2	1.159	1.097	1.070
Final R indices [$I > 2\sigma(I)$] $R1$	0.0455	[$I > 4\sigma(I)$] 0.1317	0.0431
$wR2$	0.1002	0.3371	0.0984
R indices (all data) $R1$	0.0744	0.1479	0.0639
$wR2$	0.1174	0.3452	0.1138
Largest diff. peak and hole [e Å^{-3}]	0.152 and –0.162	0.907 and –0.616	0.218 and –0.258

Table 2. Selected ^{1}H ([D$_6$]DMSO, 300 MHz, 293 K, multiplicities and coupling constants [Hz] in parentheses) and ^{13}C NMR (recorded in [D$_6$]DMSO, 75 MHz, 293 K) data of the asymmetric centers C_α and $C_{\beta'}$.



	$C_\alpha H$		$C_{\beta'} H$		C_α		$C_{\beta'}$	
Compound	major	minor	major	minor	major	minor	major	minor
7	4.53 (d, 4.8)	3.96 (d, 8.0)	2.84–2.91 (m, 5.3)	3.05 (m)	30.96	34.00	54.88	53.95
8	4.20 (s)	4.19 (s)	–	–	41.25	40.71	54.42[a]	53.8[a]
9	3.94 (d, 10.9)	4.08 (d, 9.5)	3.09[b] (dd, 11.1, 4.0)	–	37.97[b]	–	54.51[b]	–
10	4.10 (d, 6.2)	4.53 (d, 3.7)	3.22–3.29 (m, 9.8, 3.6)	3.15 (dt, 9.6, 3.7)	33.43	33.00	43.57	44.86
11	4.53 (d, 2.5)	3.95 (d, 5.4)	2.53–2.60[b] (m, 5.9, 2.8)	–	31.18[b]	–	54.22b[b]	–

[a] Quaternary carbon resonance. [b] Only the resonance of the major diastereomer could be assigned unambiguously.

lectivity is retained even if the steric bulk at the reacting β-carbon center of the silyl enol ether **5b** is increased by the introduction of a methyl group, which gives a quaternary center that is unable to epimerize to the propargylation product **8**. Also, upon applying acyclic (**5c**) and cyclic silyl ketene acetals (**5d**) that are even more nucleophilic than cyclic *N*-morpholino enamines[12] the diastereomeric ratio is not improved. Therefore, the use of silyl enol ether derivatives **5**

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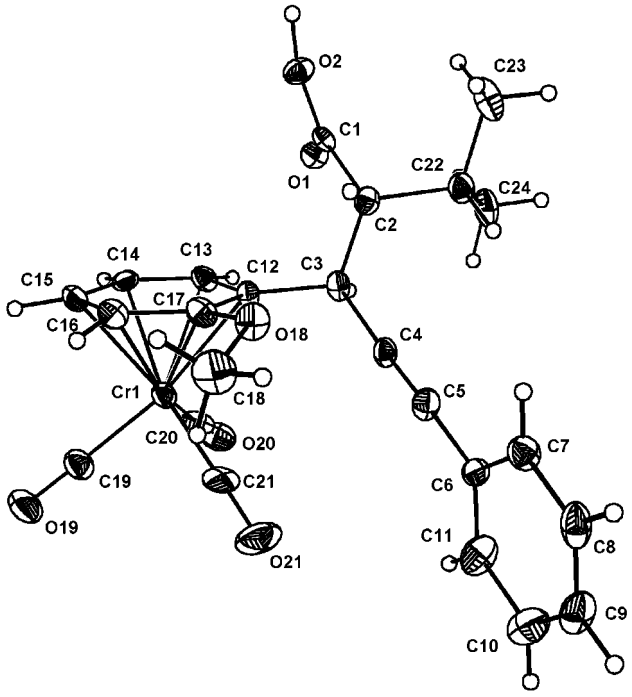
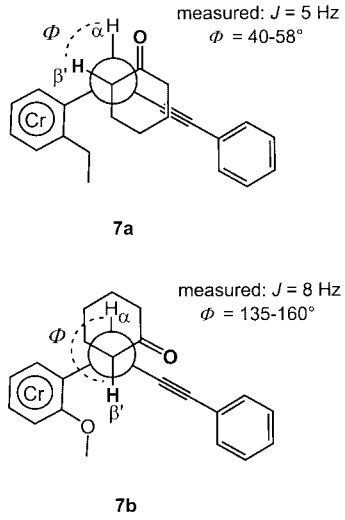


Figure 2. ORTEP plot of the major diastereomer **9a**. Selected bond lengths [Å] and bond and dihedral angles [°]: C(3)–C(12) 1.532(14), C(3)–C(4) 1.501(16), C(4)–C(5) 1.179(17), C(5)–C(6) 1.464(17); C(4)–C(3)–C(12) 112.6(9), C(12)–C(3)–C(2) 110.2(11), C(4)–C(3)–C(2) 110.9(9), C(4)–C(5)–C(6) 176.1(14), C(4)–C(3)–C(12)–C(2) 110.24(11), C(1)–C(2)–C(22)–C(3) 114.74(11).



Scheme 6. Conformation analyses of the major (**7a**) and the minor diastereomer (**7b**) applying the Karplus correlation (the carbonylchromium tripod is oriented antiperiplanar with respect to the cyclohexanone fragment).

as trapping nucleophiles with variable steric and electronic biases at the β-carbon center are obviously not well suited to increase the energy differences in the diastereotopic transition states. In contrast, the application of cyclic *N*-morpholino enamines **6**, which are reasonably nucleophilic reaction partners with more pronounced steric biases as a consequence of shorter CN bonds, gives rise to good facial diastereoselectivities. All these observations account for a predominant influence of steric and stereoelectronic features on the transition state of the C–C bond forming step.

According to our previous findings the configurationally stable and conformationally locked propargyl cation **4** is diastereoselectively attacked by nucleophiles *exo* with respect to the face of the complexing carbonylchromium tripod.[4] This step establishes the stereochemistry at the propargyl center with excellent selectivity and in the sense of an overall retention of configuration with respect to the acetate **3**. Facially, the *like* (*Si,Si*) transition state is slightly favored for silyl enol ether derivatives and becomes predominant for enamine nucleophiles. Approaching the stereochemical problem by product analysis (from **7a** and **7b**) and applying Cram's empirical rules,[13,14] both open *anti*-staggered transition states **12** and **13** can be readily deduced in their Newman projections (Scheme 7).

Here, the *like* combination in the transition state **12** leads unequivocally to the formation of the major diastereomer **7a**, whereas the transition state **13** arising from the *unlike* attack gives rise to the formation of the minor diastereomer **7b**. Sterically, the *N*-morpholino substituent imposes more bulk and steric bias than the trimethylsiloxy group and, therefore, tries to avoid pseudo-gauche interactions with either the large or the medium-sized substituents at the carbenium center. Hence, transition state **12** bears less steric strain and repulsion than transition state **13**. For the acyclic bis-silyl ketene acetal **5c**, the diastereomeric ratio is predominantly influenced by the isopropyl substituent that now becomes sterically bulkier than the trimethylsiloxy group. Thus, the same mechanistic rationale now explains that the *unlike* combination dominates slightly in the transition state, as reflected by the low diastereoselectivity of compound **9**. In conclusion, the facial diastereoselectivity of cationic propargylations with planar chiral arene Cr(CO)$_3$-substituted propargyl cation is extremely sensitive to steric effects on the nucleophile substrates, more so than on the purely electronic-based nucleophilicity.

In a trapping reaction with β-dimethylamino ethyl acrylate (**6c**) as an acyclic enamine nucleophile the intermediacy of the iminium ion **14**, which is the initial propargylation product, can be nicely illustrated (Scheme 8). Upon direct aqueous workup of the reaction mixture the β-hydroxy enol ester **15** is obtained in 94% yield and excellent stereoselectivity, as expected for cationic propargylations.[4] However, if the iminium intermediate is reacted with sodium boranate as a trapping nucleophile in acetonitrile at –45 °C,[15] a separable mixture of the tertiary amine **16** (*dr* = 3:1) and its zwitterionic borane adduct **17** (*dr* = 4:1) can be isolated in an overall yield of 87%. Besides the unambiguous spectroscopic and combustion analytic assignment of the structures of **16** and **17**, the X-ray crystal structure of **17a**, the major diastereomer of the direct precursor of **16**, was also solved (Figure 3, Table 1); it shows the expected bond lengths.

Most significantly, a broad signal at δ = 3.32–3.52 ppm in the ^{1}H NMR spectrum of the β-hydroxy enol ester **15**,

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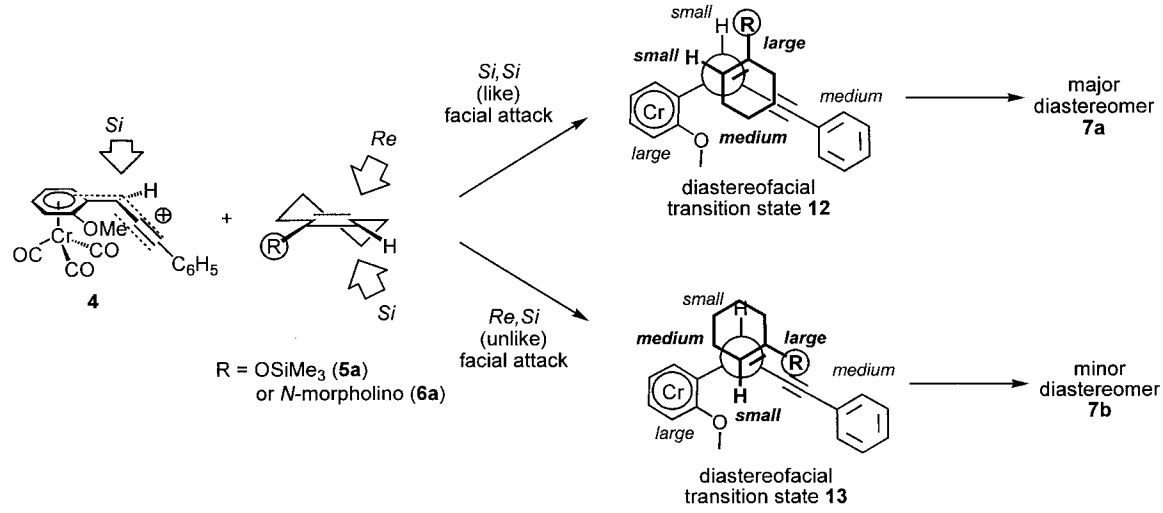
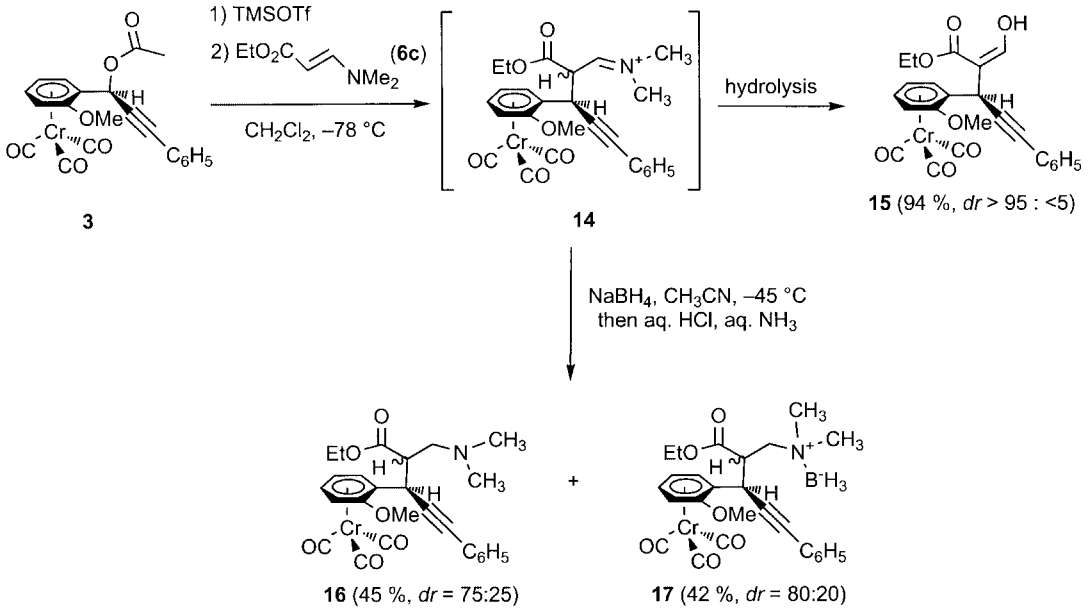


Scheme 7. Stereochemical rationale for the observed facial diastereoselectivity in cationic propargylations with cyclic nucleophiles (the carbonylchromium tripod is pointing behind the drawing plane).



Scheme 8. Iminium-ion intermediacy in diastereofacial propargylations with enamines.

which disappears upon addition of D_2O, can be assigned to the proton of the hydroxy group. The signal for the β-enol proton (with respect to the ester functionality) can be found at δ = 7.92 ppm as a singlet and the propargyl methine resonance at δ = 5.33 ppm as a singlet. In the ^{13}C NMR spectrum, characteristic resonances of the enol carbon nuclei can be detected at δ = 105.5 ppm (quaternary signal) and at δ = 153.1 ppm (methine resonance), whereas the propargyl methine appears at δ = 25.3 ppm.

In the ^1H NMR spectra of **16** and **17** the dimethylamino protons of **16** appear as a singlet at δ = 2.26 ppm, whereas for the zwitterion **17** the quaternization of the nitrogen with borane renders the two methyl groups diastereotopic so that they appear as singlets at δ = 2.59 and 2.61 ppm. The same behavior is found in the ^{13}C NMR spectra, where the dimethylamino carbon nuclei are detected at δ = 45.83 ppm (**16**) and at δ = 51.59 and 52.05 ppm (**17**). The unambiguous assignment of the ^1H NMR resonances of the diastereomers was considerably facilitated by correlating the data with the relative structure of the X-ray structure analysis.

Although the ester group of the enamine derivative **6c** imposes only some steric hindrance at the attacking β-carbon center, the facial diastereoselectivity in **16** and **17** remains considerably higher than for the trapping reaction with silyl enol ether derivatives. Applying the same stereochemical model as before to the product analysis shows that a *like* (*Si*,*Si*) attack of the ethyl β-(dimethylamino)acrylate can be unequivocally assumed. Therefore, according to this model the ester group adopts the function as the largest

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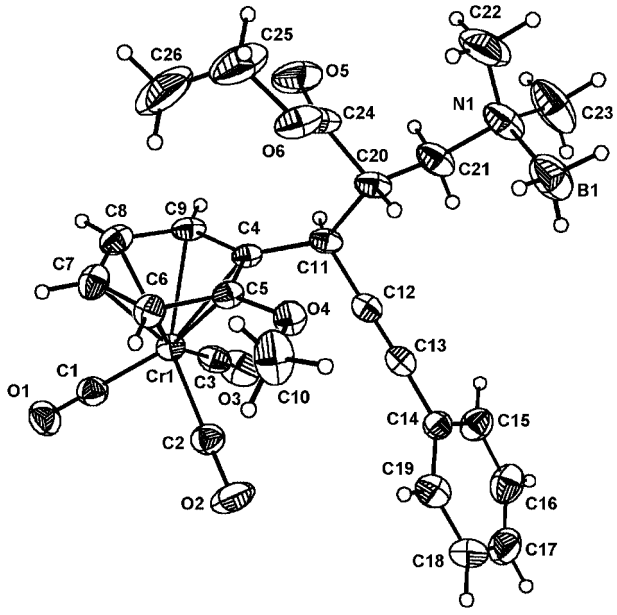
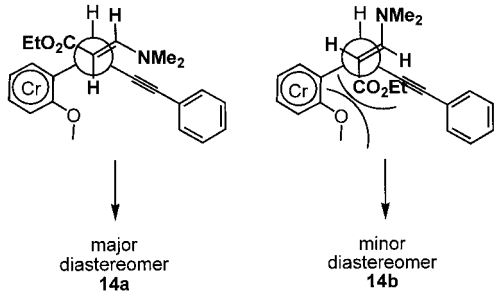


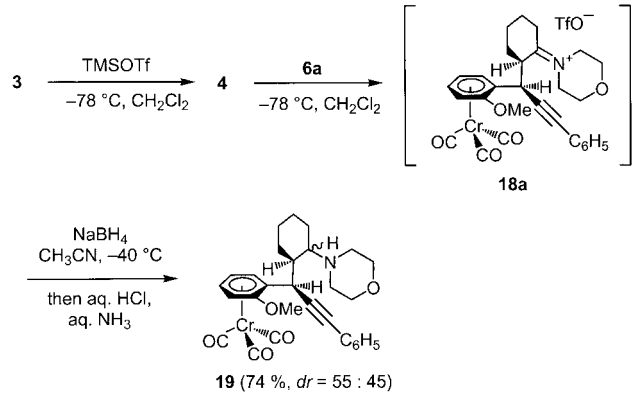
Figure 3. ORTEP plot of the major diastereomer **17a**. Selected bond lengths [Å] and bond and dihedral angles [°]: C(4)–C(11) 1.529(6), C(11)–C(12) 1.455(7), C(12)–C(13) 1.198(6), C(11)–C(20) 1.563(6), N(1)–B(1) 1.608(8), N(1)–C(22) 1.463(9); C(12)–C(11)–C(4) 112.78, C(11)–C(12)–C(13) 178.36, C(21)–N(1)–B(1) 110.77, C(11)–C(4)–C(5)–C(6) 179.98, C(11)–C(20)–C(21)–N(1) 162.67, C(4)–C(11)–C(12)–C(20) 114.21.

group and, assuming again an open transition state, the ester group tries to avoid a *gauche* interaction with the *ortho*-methoxy substituent of the complexed anisyl fragment (Scheme 9).



Scheme 9. Stereochemical rationale for the facial diastereoselectivity in cationic propargylations with **6c** (the carbonylchromium tripod is pointing behind the drawing plane).

Finally, with a diastereofacial propargylation of enamines in hand we wanted to exploit the electrophilic nature of the newly generated iminium ion in order to establish contiguous stereocenters in a sequential fashion. Treatment of the propargyl cation **4**, generated from propargyl acetate **3** and TMSOTf, with *N*-morpholinocyclohexene (**6a**) at –78 °C gave the iminium ion **18a** selectively (vide supra and Scheme 10). This less electrophilic species was then treated, without aqueous work up, with sodium borohydride in acetonitrile at –40 °C to furnish 74% of the bis-homopropargylamine **19** as a 55:45 mixture of diastereomers. Since the ^{1}H NMR spectrum only shows two sets of signals arising from epimers at the γ′-position as a consequence of the iminium salt reduction, it is evident that the iminium salt **18a** was formed with excellent facial diastereoselectivity, i.e. with a diastereomeric ratio higher than 95:5. However, the stereoselectivity for the formation of the third stereocenter by sodium borohydride reduction is obviously very low. This experiment also discloses some insight into the limitation of this sequential induction of contiguous stereocenters by consecutive cationic propargylation.



Scheme 10. Sequential induction of contiguous stereocenters by consecutive cationic propargylation and iminium ion reduction.

In conclusion, we have shown that facial diastereoselective cationic propargylations are predominantly controlled by the steric features of the attacking prochiral π-nucleophiles. Slight energy differences in diastereotopic transition states are induced by steric rather than by electronic effects. Therefore, enamines are excellent enolate equivalents in cationic propargylations where two contiguous stereocenters can be controlled ultimately by the configurational stability of planar-chiral, conformationally locked (arene)carbonylchromium-substituted propargyl cations. This methodology is well-suited for more extensive stereoselective side-chain functionalizations.

Experimental Section

General: All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures.[16] Column chromatography: silica gel 60 (Merck, Darmstadt), mesh 70–230. TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert–Jung Thermovar and Büchi Melting Point B-540. The complexed propargyl acetates **1**[4a] and **3**[4d] were prepared according to our procedures. The silyl enol ether derivatives **5a** and **5d** and the enamines **6** were purchased from Aldrich, Fluka or ACROS and were used without further purification. 2-Methyl-1-trimethylsiloxycyclohexene (**5b**) and 2-trimethylsiloxy-4,5-dihydrofuran (**5c**) were synthesized according to literature procedures.[17–19] All crystalline arenechromium complexes can be handled in air. ^{1}H and ^{13}C NMR spectra: Bruker ARX 300, Varian VXR 400S [D_6]DMSO and $CDCl_3$. The assignments of quaternary C, CH, CH_2 and CH_3 were made by using DEPT spectra. IR: Perkin–Elmer Models Lambda 16. MS: Finnigan MAT 90 and MAT 95 Q. Elemental analysis were carried out in the Microanalytical

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Generation of the Propargyl Cations and Nucleophilic Trapping. General Procedure (GP): The appropriate Lewis acid (1.1 to 1.7 equiv.) was added dropwise to a solution of 1.0 equiv. of the acetates **1** or **3** in 5–10 mL of dry dichloromethane at –78 °C. Immediately a deep-red to blue solution of the propargyl cation was formed, which was stirred at that temperature for 15 to 50 min. The corresponding nucleophile, either neat or as a solution in dichloromethane, was then added at –78 °C to this reaction mixture. The reaction can be followed by a color change to yellow. After the required reaction time 20 mL of diethyl ether and 20 mL of water were subsequently added and the external cooling was removed. After extraction of the aqueous phase with diethyl ether (3 × 30 mL) the combined organic layers were dried with magnesium sulfate, filtered and the solvents were evaporated in vacuo. The residues were dried in vacuo and, if not crystalline, subjected to flash chromatography. The diastereoselectivities were determined from the combined collected yellow fractions by integration (^{1}H NMR spectra) of the significant propargyl proton signals and/or in some cases by integration of the signals of *ortho* substituents on the complexed ring.

2: According to the GP, acetate **1** (100 mg, 0.26 mmol) was ionized with $BF_3{\cdot}OEt_2$ (46 μL, 0.36 mmol) for 60 min and, after the addition of 1-(trimethylsiloxy)cyclohexene (**5a**; 0.99 mL, 5.14 mmol), the mixture was stirred for 75 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:2 and diethyl ether) furnished 93 mg (85%) of **2** (*dr* = 57:43) as a yellow oil that was crystallized from diethyl ether/pentane. Yellow solid. M.p. 116 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]DMSO, 300 MHz) of **2a**: δ = 1.48–2.44 (m, 8 H), 2.96–3.03 (m, J = 5.6 Hz, 1 H), 3.96 (d, J = 5.1 Hz, 1 H), 5.65–5.71 (m, J = 6.1 Hz, 2 H), 5.77 (t, J = 6.2 Hz, 1 H), 5.83–5.87 (m, J = 6.7 Hz, 1 H), 6.00 (d, J = 6.6 Hz, 1 H), 7.36–7.42 (m, 5 H) ppm. Additional signals for the minor diastereomer **2b**: δ = 2.78–2.81 (m, 1 H), 4.25 (d, J = 3.5 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz) of **2a**: δ = 24.3 (CH_2), 27.3 (CH_2), 31.6 (CH_2), 37.1 (CH), 41.8 (CH_2), 55.9 (CH), 83.9 ($C_{quat.}$), 88.5 ($C_{quat.}$), 94.0 (CH), 94.3 (CH), 94.6 (CH), 95.7 (CH), 97.0 (CH), 112.4 ($C_{quat.}$), 122.7 ($C_{quat.}$), 128.5 (CH), 128.7 (CH), 131.5 (CH), 209.1 ($C_{quat.}$), 234.1 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **2b**: δ = 24.0 (CH_2), 26.8 (CH_2), 28.4 (CH_2), 36.2 (CH), 41.4 (CH_2), 56.0 (CH), 85.2 ($C_{quat.}$), 87.1 ($C_{quat.}$), 94.5 (CH), 94.6 (CH), 94.7 (CH), 96.0 (CH), 113.3 ($C_{quat.}$), 122.9 ($C_{quat.}$), 128.6 (CH), 128.7 (CH), 131.6 (CH), 208.5 ($C_{quat.}$), 234.0 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 424 (2) [M$^+$], 368 (9) [M$^+$ – 2CO], 340 (100) [M$^+$ – 3CO], 288 (12) [M$^+$ – Cr(CO)$_3$], 244 (35) [M$^+$ – 3CO – C_6H_8O], 191 (26) [$C_{15}H_{11}^+$], 52 (23) [Cr$^+$]. IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1}, 2857, 1963, 1889, 1703, 1638, 1489, 1448, 1416, 1128, 758, 694, 662, 628. UV/Vis (DMSO): λ_{max} (ε) = 315 nm (7600). $C_{24}H_{20}CrO_4$ (424.4): calcd. C 67.92, H 4.75; found C 68.25, H 5.02.

7: a) Silyl Enol Ether 5a as the Nucleophile: According to the GP, acetate **3** (202 mg, 0.49 mmol) was ionized with TMSOTf (0.115 mL, 0.64 mmol) for 60 min and, after the addition of 1-(trimethylsiloxy)cyclohexene (**5a**; 0.385 mL, 2.01 mmol), the mixture was stirred for 135 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:1 and diethyl ether) furnished 212 mg (96%) of **7** (*dr* = 57:43) as a yellow foam. ^{1}H NMR ([D$_6$]DMSO, 300 MHz) of **7a**: δ = 1.61–2.54 (m, 8 H), 2.86–2.90 (m, J = 5.3 Hz, 1 H), 3.77 (s, 3 H), 4.54 (d, J = 4.8 Hz, 1 H), 5.13–5.18 (m, J = 5.6 Hz, 1 H), 5.64 (m, J = 6.7 Hz, 1 H), 5.92–6.00 (m, J = 6.3 Hz, 1 H), 6.24–6.30 (m, 1 H), 7.31–7.40 (m, 5 H) ppm. Additional signals for the minor diastereomer **7b**: δ = 3.05 (m, 1 H), 3.81 (s, 3 H), 3.97 (d, J = 8.3 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz) of **7a**: δ = 24.1 (CH_2), 27.4 (CH_2), 30.7 (CH_2), 30.9 (CH), 41.4 (CH_2), 54.8 (CH), 56.6 (CH_3), 75.9 (CH), 84.3 ($C_{quat.}$), 85.4 (CH), 88.5 ($C_{quat.}$), 97.6 (CH), 101.5 (CH), 102.9 ($C_{quat.}$), 122.8 ($C_{quat.}$), 128.4 (CH), 128.6 (CH), 131.5 (CH), 142.8 ($C_{quat.}$), 209.2 ($C_{quat.}$), 234.1 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **7b**: δ = 26.6 (CH_2), 28.1 (CH_2), 32.6 (CH_2), 34.0 (CH), 41.8 (CH_2), 54.0 (CH), 76.2 (CH), 81.9 ($C_{quat.}$), 85.6 (CH), 90.9 ($C_{quat.}$), 97.2 (CH), 101.4 ($C_{quat.}$), 123.5 ($C_{quat.}$), 127.9 (CH), 128.5 (CH), 131.3 (CH), 143.2 ($C_{quat.}$), 209.5 ($C_{quat.}$), 234.0 ($C_{quat.}$, CO) ppm.

b) Enamine 6a as the Nucleophile: According to the GP, acetate **3** (202 mg, 0.49 mmol) was ionized with TMSOTf (0.12 mL, 0.66 mmol) for 50 min and, after the addition of 1-morpholinocyclohexene (**6a**; 0.17 mL, 1.04 mmol) the mixture was stirred for 120 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:2 and diethyl ether) furnished 124 mg (56%) of **7** (*dr* = 88:12) as yellow crystals. M.p. 135 °C dec. (diethyl ether/pentane). ^{1}H NMR ([D$_6$]DMSO, 300 MHz) of **7a**: δ = 1.63–2.05 (m, 6 H), 2.17–2.54 (m, 2 H), 2.84–2.91 (m, J = 5.3 Hz, 1 H), 3.77 (s, 3 H), 4.53 (d, J = 4.8 Hz, 1 H), 5.16 (t, J = 6.3 Hz, 1 H), 5.62 (d, J = 6.9 Hz, 1 H), 5.97 (t, J = 6.6 Hz, 1 H), 6.28 (d, J = 6.5 Hz, 1 H), 7.19–7.43 (m, 5 H) ppm. Additional signals for the minor diastereomer of **7b**: δ = 3.05 (m, 1 H), 3.80 (s, 3 H), 3.96 (d, J = 8.0 Hz, 1 H), 5.91 (t, J = 6.5 Hz, 1 H), 6.23 (m, J = 6.4 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz) of **7a**: δ = 24.1 (CH_2), 27.4 (CH_2), 30.7 (CH_2), 31.0 (CH), 41.4 (CH_2), 54.9 (CH), 56.6 (CH_3), 75.9 (CH), 84.4 ($C_{quat.}$), 85.5 (CH), 88.5 ($C_{quat.}$), 97.7 (CH), 101.6 (CH), 102.9 ($C_{quat.}$), 122.9 ($C_{quat.}$), 128.5 (CH), 128.7 (CH), 131.6 (CH), 142.8 ($C_{quat.}$), 209.3 ($C_{quat.}$), 233.7 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 454 (2) [M$^+$], 398 (5) [M$^+$ – 2CO], 370 (100) [M$^+$ – 3CO], 318 (20) [M$^+$ – Cr(CO)$_3$], 287 (7) [M$^+$ – Cr(CO)$_3$ – OCH_3], 259 (16), 115 (10), 52 (10) [Cr$^+$]. IR (KBr): $\tilde{\nu}$ = 1955 cm^{-1}, 1877, 1859, 1706, 1635, 1533, 1470, 1257, 756, 670, 632. UV/Vis (DMSO): λ_{max} (ε) = 316 nm (7700). $C_{25}H_{22}CrO_5$ (454.5): calcd. C 66.08, H 4.88; found C 65.99, H 4.97.

8: According to the GP, acetate **3** (206 mg, 0.50 mmol) was ionized with TMSOTf (0.12 mL, 0.66 mmol) for 60 min and, after the addition of 2-methyl-1-trimethylsiloxy cyclohexene (**5b**; 0.15 g, 0.81 mmol), the mixture was stirred for 120 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:1 and diethyl ether) furnished 194 mg (84%) of **8** (*dr* = 60:40) as yellow crystal. M.p. 124–130 °C dec. (diethyl ether/dichloromethane). ^{1}H NMR ([D$_6$]DMSO, 400 MHz) of **8a**: δ = 1.07 (s, 3 H), 1.56–1.80 (m, 6 H), 2.39–2.62 (m, 2 H), 3.72 (s, 3 H), 4.20 (s, 1 H), 5.10 (t, J = 6.2 Hz, 1 H), 5.61 (d, J = 6.8 Hz, 1 H), 5.92 (t, J = 6.1 Hz, 1 H), 6.07 (d, J = 5.2 Hz, 1 H), 7.31–7.45 (m, 5 H) ppm. Additional signals for the minor diastereomer: δ = 1.13 (s, 3 H), 3.70 (s, 3 H), 4.19 (s, 1 H), 5.15 (t, J = 6.2 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 20.4 (CH_2), 21.9 (CH_3), 26.1 (CH_2), 36.0 (CH_2), 38.7 (CH_2), 41.3 (CH), 54.4 ($C_{quat.}$), 56.2 (CH_3), 76.8 (CH), 83.9 ($C_{quat.}$), 85.7 (CH), 88.6 ($C_{quat.}$), 97.4 (CH), 99.0 (CH), 128.0 (CH), 128.6 (CH), 131.3 (CH), 143.8 ($C_{quat.}$), 212.1 ($C_{quat.}$), 234.0 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer: δ = 20.8 (CH_2), 21.80 (CH_3), 27.0 (CH_2), 37.0 (CH_2), 38.9 (CH_2), 40.7 (CH), 53.8 ($C_{quat.}$), 56.0 (CH_3), 83.9 ($C_{quat.}$), 88.8 ($C_{quat.}$), 98.8 (CH), 128.0 (CH), 128.6 (CH), 131.2 (CH), 143.6 ($C_{quat.}$), 212.0 ($C_{quat.}$), 233.9 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 486 (1) [M$^+$], 412 (2) [M$^+$ – 2CO], 384 (69) [M$^+$ – 3CO], 332 (100) [M$^+$ – Cr(CO)$_3$], 317 (79) [M$^+$ – Cr(CO)$_3$ – CH_3], 314 (18) [M$^+$ – Cr(CO)$_3$ – 2CH_3], 301 (10) [M$^+$ – Cr(CO)$_3$ – OCH_3], 259 (39), 221 (80), 202 (17) [M$^+$ – Cr(CO)$_3$ – OCH_3 – C_7H_8O], 52 (14) [Cr$^+$]. IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1}, 1960, 1877, 1703, 1636, 1472, 1264, 760, 694, 668,

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630. UV/Vis (DMSO): λ_{max} (ε) = 316 nm (8260). $C_{26}H_{24}CrO_5$ (468.5): calcd. C 66.66, H 5.16; found C 66.99, H 5.20.

9: According to the GP, acetate **3** (105 mg, 0.25 mmol) was ionized with TMSOTf (60 μL, 0.33 mmol) for 60 min and, after the addition of 1,1-bis(trimethylsiloxy)-3-methyl-1-butene (**5c**; 107 mg, 0.43 mmol), the mixture was stirred for 90 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:1 and diethyl ether) furnished 108 mg (93%) of **9** (*dr* = 66:34) as yellow crystals. M.p. 196 °C dec. (dichloromethane/diethyl ether). ^{1}H NMR ([D$_6$]-acetone, 400 MHz): δ = 1.10 (t, *J* = 7.1 Hz, 6 H), 2.50–2.61 (m$_c$, 1 H), 2.83 (br. s, 1 H), 3.09 (dd, *J* = 11.1, *J* = 4.0 Hz, 1 H), 3.92 (s, 3 H), 3.94 (d, *J* = 10.9 Hz, 1 H), 4.98 (dt, *J* = 6.1, *J* = 0.9 Hz, 1 H), 5.52 (d, *J* = 6.3 Hz, 1 H), 5.82 (dt, *J* = 6.2, *J* = 1.3 Hz, 1 H), 5.94 (dd, *J* = 6.5, *J* = 1.3 Hz, 1 H), 7.26–7.35 (m, 3 H), 7.45–7.50 (m, 2 H) ppm. Additional signals for the minor diastereomer: δ = 1.01 (d, *J* = 6.9 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 1.96–2.02 (m$_c$, 1 H), 4.08 (d, *J* = 9.5 Hz, 1 H), 5.08 (dt, *J* = 6.1, *J* = 0.9 Hz, 1 H), 5.88 (dt, *J* = 6.5, *J* = 1.4 Hz, 1 H), 6.25 (dd, *J* = 6.3, *J* = 1.2 Hz, 1 H), 7.36–7.40 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone, 75 MHz): δ = 16.9 (CH$_3$), 22.2 (CH$_3$), 30.1 (CH), 38.0 (CH), 54.5 (CH), 56.6 (CH$_3$), 75.8 (CH), 84.9 (CH), 85.2 (C$_{quat.}$), 89.3 (C$_{quat.}$), 96.9 (CH), 101.0 (C$_{quat.}$), 102.1 (CH), 124.8 (C$_{quat.}$), 128.7 (CH), 129.0 (CH), 132.4 (CH), 144.2 (C$_{quat.}$), 173.2 (C$_{quat.}$), 234.4 (C$_{quat.}$, CO) ppm. Additional signals for the minor diastereomer: δ = 17.9 (CH$_3$), 22.6 (CH$_3$), 75.6 (CH), 85.1 (CH), 97.2 (CH), 128.6 (CH), 129.0 (CH), 132.3 (CH) ppm. EI MS (70 eV): *m/z* (%) = 458 (38) [M$^+$], 402 (10) [M$^+$ – 2CO], 374 (100) [M$^+$ – 3CO], 330 (62) [M$^+$ – 3CO – CO$_2$], 290 (66), 279 (70), 278 (1) [M$^+$ – Cr(CO)$_3$ – CO$_2$], 221 (43), 115 (43). HRMS calcd. for $C_{24}H_{22}CrO_6$: 458.0821; found 458.0813. IR (KBr): $\tilde{\nu}$ = 2964 cm^{-1}, 1964, 1890, 1699, 1634, 1530, 1470, 1260, 1019, 758, 692, 667, 629. UV/Vis (CH_3CN): λ_{max} (ε) = 240 nm (27 700), 251 (23 700), 315 (7600). $C_{24}H_{22}CrO_6$ (458.4): calcd. C 62.88, H 4.84; found C 62.50, H 4.82.

10: According to the GP, acetate **3** (248 mg, 0.60 mmol) was ionized with TMSOTf (0.15 mL, 0.83 mmol) for 45 min and, after the addition of 2-trimethylsiloxy-4,5-dihydrofurane (**5d**; 202 mg, 1.28 mmol), the mixture was stirred for 130 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:2 and diethyl ether) furnished 250 mg (95%) of **10** (*dr* = 65:35) as a yellow foam. ^{1}H NMR ([D$_6$]DMSO, 300 MHz) of **10a**: δ = 2.08–2.20 (m, *J* = 7.8 Hz, 2 H), 2.26–2.36 (m, 1 H), 3.22–3.29 (m, 1 H), 3.80 (s, 3 H), 4.10 (d, *J* = 6.2 Hz, 1 H), 4.34 (dt, *J* = 8.6, *J* = 3.1 Hz, 1 H), 5.18–5.69 (m, *J* = 6.1 Hz, 1 H), 5.68 (d, *J* = 6.9 Hz, 1 H), 5.96 (t, *J* = 6.5 Hz, 1 H), 6.35 (d, *J* = 6.3 Hz, 1 H), 7.32–7.44 (m, 5 H) ppm. Additional signals for the minor diastereomer **10b**: δ = 2.55–2.66 (m, 1 H), 3.15 (dt, *J* = 9.6, *J* = 3.7 Hz, 1 H), 3.81 (s, 3 H), 4.53 (d, *J* = 3.7 Hz, 1 H), 4.45 (dt, *J* = 9.0, *J* = 2.6 Hz, 1 H), 6.03 (t, *J* = 6.5 Hz, 1 H), 6.23 (d, *J* = 6.5 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$] DMSO, 75 MHz) of **10a**: δ = 28.2 (CH$_2$), 33.4 (CH), 43.6 (CH), 56.7 (CH$_3$), 66.3 (CH$_2$), 75.9 (CH), 82.7 (C$_{quat.}$), 86.3 (CH), 88.7 (C$_{quat.}$), 97.0 (CH), 99.6 (CH), 100.9 (C$_{quat.}$), 122.9 (C$_{quat.}$), 128.4 (CH), 128.6 (CH), 131.5 (CH), 142.9 (C$_{quat.}$), 176.2 (C$_{quat.}$), 233.9 (C$_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **10b**: δ = 25.4 (CH$_2$), 33.0 (CH), 44.9 (CH), 66.7 (CH$_2$), 76.5 (CH), 85.3 (C$_{quat.}$), 85.8 (CH), 86.5 (C$_{quat.}$), 97.7 (CH), 99.8 (CH), 100.8 (C$_{quat.}$), 122.1 (C$_{quat.}$), 128.9 (CH), 128.8 (CH), 131.7 (CH), 142.8 (C$_{quat.}$), 176.7 (C$_{quat.}$), 233.9 (C$_{quat.}$, CO) ppm. EI MS (70 eV):-*m/z* (%) = 442 (1) [M$^+$], 358 (17) [M$^+$ – 3CO], 306 (22) [M$^+$ – Cr(CO)$_3$], 291 (38) [M$^+$ – Cr(CO)$_3$ – CH$_3$], 275 (6) [M$^+$ – Cr(CO)$_3$ – OCH$_3$], 221 (100) [M$^+$ – Cr(CO)$_3$ – C$_4$H$_5$O$_2$], 207 (32) [M$^+$ – Cr(CO)$_3$ – C$_4$H$_5$O$_2$ – CH$_3$], 115 (81), 52 (12) [Cr$^+$]. IR (KBr): $\tilde{\nu}$ = 1960 cm^{-1}, 1877, 1765, 1636, 1531, 1470, 1261, 1158, 1027, 759, 693, 669, 632. UV/Vis (DMSO): λ_{max} (ε) = 315 nm (7800). $C_{23}H_{18}CrO_6$ (442.4): calcd. C 62.45, H 4.10; found C 62.69, H 4.35.

11: According to the GP, acetate **3** (208 mg, 0.50 mmol) was ionized with TMSOTf (0.12 mL, 0.66 mmol) for 35 min and, after the addition of 1-morpholino cyclopentene (**6b**; 0.17 mL, 1.11 mmol), the mixture was stirred for 70 min. Workup and chromatography on neutral aluminum oxide (activity V; (diethyl ether/pentane, 1:2 and diethyl ether) furnished 150 mg (68%) of **11** (*dr* = 94:6) as a yellow foam. M.p. 130–132 °C (diethyl ether). ^{1}H NMR ([D$_6$]-DMSO, 300 MHz) of **11a**: δ = 1.75–1.98 (m, 1 H), 2.04–2.17 (m, 4 H), 2.23–2.41 (m, 1 H), 2.53–2.60 (m, 1 H), 3.79 (s, 3 H), 4.53 (d, *J* = 2.5 Hz, 1 H), 5.20–5.24 (t, *J* = 6.3 Hz, 1 H), 5.65 (d, *J* = 6.9 Hz, 1 H), 5.95–6.01 (dt, *J* = 6.7, *J* = 1.1 Hz, 1 H), 6.22 (dd, *J* = 6.4, *J* = 1.0 Hz, 1 H), 7.33–7.44 (m, 5 H) ppm. Additional signals for the minor diastereomer **11b**: δ = 3.81 (s, 3 H), 3.95 (d, *J* = 5.4 Hz, 1 H), 6.27 (d, *J* = 5.2 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 20.1 (CH$_2$), 26.0 (CH$_2$), 31.2 (CH), 37.5 (CH$_2$), 54.2 (CH), 56.7 (CH$_3$), 75.9 (CH), 84.6 (C$_{quat.}$), 86.0 (CH), 87.5 (C$_{quat.}$), 97.6 (CH), 99.9 (CH), 102.5 (C$_{quat.}$), 122.2 (C$_{quat.}$), 128.7 (CH, broad, 2 signals), 131.6 (CH), 142.7 (C$_{quat.}$), 216.7 (C$_{quat.}$), 234.0 (C$_{quat.}$, CO) ppm. EI MS (70 eV): *m/z* (%) = 440 (4) [M$^+$], 384 (10) [M$^+$ – 2CO], 356 (100) [M$^+$ – 3CO], 341 (18) [M$^+$ – 3CO – CH$_3$], 304 (23) [M$^+$ – Cr(CO)$_3$], 273 (17) [M$^+$ – Cr(CO)$_3$ – OCH$_3$], 259 (16), 221 (17) [M$^+$ – Cr(CO)$_3$ – C$_5$H$_7$O], 115 (18), 52 (15) [Cr$^+$]. IR (KBr): $\tilde{\nu}$ = 1959 cm^{-1}, 1876, 1738, 1630, 1532, 1470, 1261, 1018, 758, 670, 634. UV/Vis (DMSO): λ_{max} (ε) = 315 nm (7900). $C_{24}H_{20}CrO_5$ (440.4): calcd. C 65.45, H, 4.58; found C 65.48, H 4.68.

15: According to the GP, acetate **3** (205 mg, 0.49 mmol) was ionized with TMSOTf (0.13 mL, 0.72 mmol) for 50 min and, after the addition of a solution of ethyl 3-dimethylamino acrylate (**6c**; 0.12 mL, 0.84 mmol) in 0.88 mL of dichloromethane, the mixture was stirred for 100 min. Workup and chromatography on silica gel (diethyl ether/pentane, 1:2 and diethyl ether) furnished 218 mg (94%) of **15** (*dr* = >94:6) as a yellow foam. ^{1}H NMR ([D$_6$]DMSO, 300 MHz) of **15a**: δ = 1.22 (t, *J* = 7.1 Hz, 3 H), 3.32 (br. s, 1 H), 3.81 (s, 3 H), 4.13 (dq, *J* = 7.1, *J* = 1.5 Hz, 2 H), 5.13 (t, *J* = 6.3 Hz, 1 H), 5.33 (s, 1 H), 5.56 (d, *J* = 6.8 Hz, 1 H), 5.93 (t, *J* = 6.7 Hz, 1 H), 6.15 (d, *J* = 6.2 Hz, 1 H), 7.30–7.31 (m, 5 H), 7.92 (br. s, 1 H) ppm. Additional signals for the minor diastereomer **15b**: δ = 1.28 (t, *J* = 7.2 Hz, 3 H), 3.82 (s, 3 H), 4.91 (s, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 14.4 (CH$_3$), 25.3 (CH), 56.5 (CH$_3$), 59.6 (CH$_2$), 75.3 (CH), 79.7 (C$_{quat.}$), 85.3 (CH), 90.2 (C$_{quat.}$), 97.3 (CH), 98.9 (CH), 100.9 (C$_{quat.}$), 105.5 (C$_{quat.}$), 123.2 (C$_{quat.}$), 128.1 (CH), 128.6 (CH), 131.4 (CH), 143.3 (C$_{quat.}$), 153.1 (CH), 166.8 (C$_{quat.}$), 233.8 (C$_{quat.}$, CO) ppm. EI MS (70 eV): *m/z* (%) = 472 (1) [M$^+$], 416 (7) [M$^+$ – 2CO], 388 (100) [M$^+$ – 3CO], 274 (65) [M$^+$ – 3CO – C$_5$H$_6$O$_3$], 259 (57), 221 (32) [M$^+$ – Cr(CO)$_3$ – H$_5$C$_2$OC(O)CH=CHO$^-$], 190 (9) [C$_{15}$H$_{10}^+$], 52 (39) [Cr$^+$]. HRMS calcd. for $C_{24}H_{20}CrO_7$: 472.0614; found 472.0639. IR (KBr): $\tilde{\nu}$ = 2982 cm^{-1}, 2938, 1962, 1880, 1731, 1662, 1609, 1528, 1468, 1263, 1202, 1096, 1018, 824, 758, 692, 668, 630. UV/Vis (DMSO): λ_{max} (ε) = 315 nm (6800). $C_{24}H_{20}CrO_7$ (472.4): calcd. C 61.02, H 4.27; found C 61.61, H 4.97.

Cationic Propargylation and Sequential Iminium Reduction with Sodium Borohydride: TMSOTf (98 μL, 0.54 mmol) was added to a solution of acetate **3** (205 mg, 0.49 mmol) in 8 mL of dichloromethane at –78 °C. After stirring for 90 min at this temperature ethyl 3-dimethylaminoacrylate (**6c**; 93 mg, 0.65 mmol) was added to the reaction mixture and stirring was continued for 140 min. The external cooling was then removed and the solvent was removed in vacuo. The residue was dissolved in 5 mL of acetonitrile and a suspension of sodium borohydride (195 mg, 5.15 mmol) in 15 mL of acetonitrile was added at –45 °C. The mixture was stirred at be-

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tween –45 and –40 °C for 15 min before it was allowed to warm to room temp. After 120 min 10 mL of 2 N hydrochloric acid was added to hydrolyze the excess of sodium borohydride (careful addition!). The mixture was neutralized with 15 mL of a dilute aqueous solution of ammonia. The aqueous phase was then extracted with diethyl ether (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and dried with magnesium sulfate. After evaporation of the solvents in vacuo the residue was chromatographed on silica gel (diethyl ether/pentane, 1:1, 2:1, diethyl ether, and dichloromethane) to furnish 110 mg (45%) of **16** (*dr* = 75:25) and 107 mg (42%) of **17** (*dr* = 80:20).

16: Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) of **16a**: δ = 1.09 (t, J = 7.2 Hz, 3 H), 2.26 (s, 6 H), 2.79–2.91 (m, 2 H), 3.23 (dt, J = 10.3, J = 4.2 Hz, 1 H), 3.74 (d, J = 10.2 Hz, 1 H), 3.82 (s, 3 H), 3.97–4.06 (m_c, 2 H), 4.69 (t, J = 6.3 Hz, 1 H), 5.00 (d, J = 6.8 Hz, 1 H), 5.49 (dt, J = 7.1, J = 1.3 Hz, 1 H), 5.62 (dd, J = 6.4, J = 1.2 Hz, 1 H), 7.24–7.28 (m, 3 H), 7.42–7.45 (m, 2 H) ppm. Additional signals for the minor diastereomer **16b**: δ = 1.26 (t, J = 7.1 Hz, 3 H), 2.24 (s, 6 H), 2.59–2.69 (m, 2 H), 3.14–3.18 (m, J = 6.3 Hz, 1 H), 3.78 (s, 3 H), 4.27 (d, J = 6.3 Hz, 1 H), 4.08–4.19 (m_c, 2 H), 4.80 (t, J = 6.0 Hz, 1 H), 4.97 (d, J = 6.6 Hz, 1 H), 5.54 (dt, J = 6.5, J = 1.2 Hz, 1 H), 6.05 (dd, J = 6.5, J = 1.1 Hz, 1 H), 7.38–7.40 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) of **16a**: δ = 14.2 (CH_3), 37.3 (CH), 45.8 (CH_3), 48.6 (CH), 56.0 (CH_3), 60.6 (CH_2), 61.3 (CH_2), 73.0 (CH), 83.0 (CH), 84.8 ($C_{quat.}$), 87.6 ($C_{quat.}$), 94.2 (CH), 98.7 ($C_{quat.}$), 98.8 (CH), 123.5 ($C_{quat.}$), 127.9 (CH), 128.1 (CH), 131.6 (CH), 142.3 ($C_{quat.}$), 173.0 ($C_{quat.}$), 232.6 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **16b**: δ = 32.7 (CH), 45.5 (CH_3), 49.3 (CH), 55.9 (CH_3), 60.4 (CH_2), 60.8 (CH_2), 72.4 (CH), 83.5 (CH), 83.8 ($C_{quat.}$), 87.9 ($C_{quat.}$), 94.5 (CH), 98.4 ($C_{quat.}$), 99.1 (CH), 101.2 ($C_{quat.}$), 127.9 (CH), 128.1 (CH), 131.7 (CH), 141.6 ($C_{quat.}$), 172.4 ($C_{quat.}$), 232.7 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 501 (4) [M^+], 417 (76) [M^+ – 3CO], 365 (26) [M^+ – $Cr(CO)_3$], 359 (22), 317 (40), 292 (25) [M^+ – $Cr(CO)_3$ – $C_3H_5O_2$], 274 (100) [M^+ – 3CO – $(H_3C)_2NCH{=}CHCO_2C_2H_5$], 259 (40). HRMS calcd. for. $C_{26}H_{27}NCrO_6$: 501.1244; found 501.1233. IR (KBr): $\tilde{\nu}$ = 2941 cm^{-1}, 1963, 1881, 1728, 1636, 1468, 1259, 1179, 1030, 758, 667, 628. UV/Vis (DMSO): λ_{max} (ε) = 316 nm (7400). $C_{26}H_{27}CrNO_6$ (501.5): calcd. C 62.27, H 5.43, N 2.79; found C 62.55, H 5.67, N 2.76.

17: Yellow crystals, M.p. 139–140 °C (dichloromethane/diethyl ether/pentane). ^{1}H NMR ($CDCl_3$, 400 MHz) of **17a**: δ = 1.05 (t, J = 7.1 Hz, 3 H), 1.59–2.02 (br., 3 H), 2.59 (s, 3 H), 2.61 (s, 3 H), 3.44–3.53 (m, 3 H), 3.63–3.68 (m, J = 9.0 Hz, 1 H), 3.86 (s, 3 H), 3.90–4.03 (m, J = 11.2, J = 7.6 Hz, 2 H), 4.69 (t, J = 6.3 Hz, 1 H), 5.02 (d, J = 6.9 Hz, 1 H), 5.48 (d, J = 6.1 Hz, 1 H), 5.52 (t, J = 5.9 Hz, 1 H), 7.28–7.45 (m, 5 H) ppm. Additional signals for the minor diastereomer **17b**: δ = 0.92 (t, J = 7.6 Hz, 3 H), 2.50 (s, 3 H), 3.30–3.36 (m, 1 H), 3.81 (s, 3 H), 4.82 (t, J = 6.3 Hz, 1 H), 5.75 (d, J = 5.6 Hz, 1 H), 7.41 (m, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz) of **17a**: δ = 14.4 (CH_3), 39.3 (CH), 45.9 (CH), 51.6 (CH_3), 52.1 (CH_3), 56.2 (CH_3), 61.3 (CH_2), 64.8 (CH_2), 72.8 (CH), 82.8 (CH), 85.5 ($C_{quat.}$), 86.4 ($C_{quat.}$), 94.3 (CH), 96.4 ($C_{quat.}$), 98.4 (CH), 122.8 ($C_{quat.}$), 128.1 (CH), 128.2 (CH), 131.6 (CH), 142.6 ($C_{quat.}$), 172.9 ($C_{quat.}$), 232.2 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **17b**: δ = 14.0 (CH_3), 37.4 (CH), 45.8 (CH), 50.1 (CH_3), 53.3 (CH_3), 57.1 (CH_3), 61.7 (CH_2), 64.1 (CH_2), 73.1 (CH), 83.5 (CH), 94.5 (CH), 98.0 ($C_{quat.}$), 98.3 (CH), 123.0 ($C_{quat.}$), 141.7 ($C_{quat.}$), 172.7 ($C_{quat.}$), 232.3 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 515 [M^+] (1), 501 (7) [M^+ – BH_3], 417 (49) [M^+ – BH_3 – 3CO], 365 (60) [M^+ – BH_3 – $Cr(CO)_3$], 317 (37), 292 (56) [M^+ – BH_3 – $Cr(CO)_3$ – $C_3H_5O_2$], 274 (100) [M^+ – BH_3 – 3CO – $(H_3C)_2NCH{=}CHCO_2C_2H_5$], 259 (36), 221 (17). HRMS calcd. for. $C_{26}H_{27}NCrO_6$: 501.1243; found 501.1231. IR (KBr): $\tilde{\nu}$ = 2375 cm^{-1}, 2278, 1960, 1881, 1733, 1638, 1471, 1259, 1168, 1018, 759, 670, 629. UV/Vis (DMSO): λ_{max} (ε) = 317 nm (6700). $C_{26}H_{30}BCrNO_6$ (515.3): calcd. C 60.60, H 5.87, N 2.72; found C 60.74, H 6.03, N 2.53.

19: TMSOTf (97 µL, 0.54 mmol) was added to a solution of acetate **3** (203 mg, 0.49 mmol) in 8 mL of dichloromethane at –78 °C. After stirring for 75 min at this temperature 1-morpholinocyclohexene (**6a**; 96 µL, 0.59 mmol) was added and stirring was continued for 120 min. The external cooling was then removed and the solvent was removed in vacuo. The residue was dissolved in 5 mL of acetonitrile and a suspension of sodium borohydride (112 mg, 2.96 mmol) in 15 mL of acetonitrile was added at –45 °C. The mixture was stirred between –40 and –35 °C for 15 min before it was allowed to warm to room temp. After 100 min 10 mL of 2 N hydrochloric acid was added to hydrolyze the excess of sodium borohydride (careful addition!). The mixture was neutralized with 15 mL of a dilute aqueous solution of ammonia. The aqueous phase was then extracted with dichloromethane (2 × 50 mL). The combined organic layers were washed with water (2 × 50 mL) and dried with magnesium sulfate. After evaporation of the solvents in vacuo the residue was chromatographed on silica gel (diethyl ether/pentane, 1:1, diethyl ether) to furnish 190 mg (74%) of **19** (*dr* = 55:45) as a yellow foam. ^{1}H NMR (CD_2Cl_2, 400 MHz) of **19a**: δ = 1.21–2.50 (m, 12 H), 3.53 (t, J = 4.7 Hz, 2 H), 3.82 (s, 3 H), 4.21 (d, J = 6.8 Hz, 1 H), 4.82 (dt, J = 6.3, J = 1.0 Hz, 1 H), 5.12 (d, J = 6.8 Hz, 1 H), 5.61 (dt, J = 6.1, J = 1.2 Hz, 1 H), 6.07 (dd, J = 6.5, J = 1.3 Hz, 1 H), 7.24–7.32 (m, 3 H), 7.38–7.45 (m, 2 H) ppm. Additional signals for the minor diastereomer **19b**: δ = 2.67–2.79 (m, 2 H), 2.89 (m, J = 4.4 Hz, 1 H), 3.62–3.74 (m, 2 H), 3.83 (s, 3 H), 3.87 (d, J = 10.0 Hz, 1 H), 4.83 (dt, J = 6.2, J = 0.9 Hz, 1 H), 5.73 (dd, J = 6.4, J = 1.5 Hz, 1 H) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz) of **19a**: δ = 22.2 (CH_2), 24.0 (CH_2), 25.2 (CH_2), 28.6 (CH_2), 34.0 (CH), 40.8 (CH), 51.8 (CH_2), 55.9 (CH_3), 65.1 (CH), 67.1 (CH_2), 73.6 (CH), 82.7 ($C_{quat.}$), 83.2 (CH), 92.3 ($C_{quat.}$), 95.3 (CH), 102.2 (CH), 105.4 ($C_{quat.}$), 124.2 ($C_{quat.}$), 127.6 (CH), 128.2 (CH), 131.4 (CH), 142.4 ($C_{quat.}$), 233.7 ($C_{quat.}$, CO) ppm. Additional signals for the minor diastereomer **19b**: δ = 23.5 (CH_2), 24.8 (CH_2, br), 27.3 (CH_2), 38.1 (CH), 43.7 (CH), 53.2 (CH_2), 55.9 (CH_3), 61.5 (CH), 67.5 (CH_2), 74.1 (CH), 83.2 ($C_{quat.}$), 83.7 (CH), 92.2 ($C_{quat.}$), 95.0 (CH), 100.2 (CH), 103.0 ($C_{quat.}$), 124.5 ($C_{quat.}$), 127.4 (CH), 128.2 (CH), 131.5 (CH), 142.7 ($C_{quat.}$), 233.5 ($C_{quat.}$, CO) ppm. EI MS (70 eV): *m*/*z* (%) = 525 (6) [M^+], 497 (3) [M^+ – CO], 441 (100) [M^+ – 3CO], 389 (18) [M^+ – $Cr(CO)_3$], 358 (6) [M^+ – $Cr(CO)_3$ – OCH_3], 332 (23), 274 (13) [M^+ – 3CO – morpholinocyclohexene], 259 (29), 52 (18) [Cr^+]. IR (KBr): $\tilde{\nu}$ = 2932, 2856, 1959, 1877, 1630, 1529, 1469, 1261, 1119, 758, 692, 670, 631 cm^{-1}. UV/Vis (DMSO): λ_{max} (ε) = 317 nm (7100). $C_{29}H_{31}CrNO_5$ (525.6): calcd. C 66.28, H 5.95, N 2.67; found C 66.60, H 6.24, N 2.50.

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[1] For a recent review on stereoselective cationic propargylations, see, for example: T. J. J. Müller, *Eur. J. Org. Chem.* **2001**, 2021–2033.

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[8] At –70 °C the cation **4** is chemically stable over several hours (its UV/Vis spectrum shows no depression of the molar extinction coefficient). The configurational stability of cation **4**, which will be published elsewhere, was studied by recording the ^{1}H, ^{13}C, HETCOR and NOESY spectra at –60 °C with the same NMR tubes, which takes several hours. Only one set of signals (^{13}C NMR) was detected at that temperature; however, upon raising the temperature over –55 °C the appearance of a second set of signals was observed. Interestingly, the carbonyl signals still remain split into three signals, thus indicating that the energy barrier for the tripodal rotation is higher than for the C_{ipso}–C_{alpha} rotation.

[9] A Siemens P4 diffractometer equipped with a CCD detector, Mo-K_α radiation and a graphite monochromator was used for the crystallographic work and data collection. A single crystal of compound **9a** was placed on a glass fiber with perfluoro ether oil and mounted on a goniometer head, which was cooled to –80 °C with a Siemens LT2 device. The unit cell was determined with the program SMART from reflections collected on five sets of 15 frames each collected at five different settings of angles. Data collection was performed in the hemisphere mode at 5 s for each frame. Reflections on a total of 1360 frames were collected in the hemisphere mode of the program SMART (Bruker Analytical Instruments, Madison, Version 4.1). Data reduction was performed with the program SAINT (Bruker Analytical Instruments, Madison, Version 5.1). For structure solution and refinement the programs of SHELXTL were used. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the final refinements with a riding model.

[10] CCDC-248928 (for **7a**), -253713 (for **9a**), and -248929 (for **17a)** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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