Diastereoselective Propargylations with Planar Chiral Chromiumcarbonyl Arene Complex Substituted Propargyl Cations

Astrid Netz, Kurt Polborn, and Thomas J. J. Müller*,†

Contribution from the Department Chemie (Organische Chemie) der Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), D-81377 München, Germany

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Abstract: The ionization of planar chiral *ortho*-substituted (arene)$Cr(CO)_3$-substituted α-propargylic acetates **3** with Lewis acids results in the formation of stable (arene)$Cr(CO)_3$-substituted α-propargyl cations **4**. Subsequent additions of sulfur, nitrogen, oxygen, and π-carbon nucleophiles to these organometallic electrophiles give rise to the regio- and highly diastereoselective formation of propargyl derivatives **5** in good yields (44−90%; dr = 70:30 to >99:1). The relative stereochemistry of the propargyl acetates **3** and the trapping products **5** was established by several crystal structure analyses, indicating that the cationic propargylations occurred under retention of configuration at the propargylic center. Most important for the diastereoselectivity of the nucleophilic trapping reaction is the configurational stability of the diastereotopic cation **4** as reflected by substituent effects. In situ ionizations according to an S_N1-mechanism not only result in a considerable loss but also in an inversion of diastereoselectivity.

Introduction

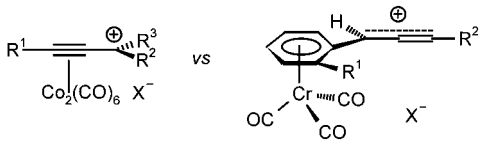
Classically, nucleophilic substitutions following an S_N1-mechanism proceed through a trigonal planar carbenium ion intermediate and inherently cause racemization at the substitution center. Very few cases of neighboring group participation give rise to stereocontrolled substitution products.[1] However, the advent of transition metal π-complex stabilization of α-carbenium ions[2] has revolutionized the synthetic application of these often elusive reactive carbocation intermediates, in particular, in stereoselective nucleophilic additions with retention of configuration. Among transition metal π-complex stabilized carbenium ions[2] the most prominent representatives are ferrocenyl-, (alkyne)$Co_2(CO)_6$-, or (arene)$Cr(CO)_3$-substituted carbocations (Scheme 1).

Stereochemically, a pronounced neighboring group effect arising from an ideal overlap of occupied d-orbitals on the metal and the vacant p-orbital at the carbenium center in the α-position also rationalizes a rate-increasing anchimeric assistance in S_N1 reactions and the conservation of the stereochemical information at the previous sp^3-center as a consequence of an overall retention of configuration due to a double inversion mechanism.[2c,d,f] In particular, chromiumcarbonyl complexed benzylic cations[3] have found applications in asymmetric organic syntheses.[2f,4] According to calculations at different levels of theory for chromiumcarbonyl complexed benzyl cations, the carbenium center is significantly distorted from coplanarity with the phenyl ring upon bending toward the metal center.[3d,e,5] This distortion results in a configurational fixation of the side chain in a rigid conformation at low temperatures.[2f]

In the extensive work of Nicholas, the activation of the propargylic position was achieved by attaching a dicobalthexacarbonyl cluster to a triple bond.[2e,6] The generated cation

Scheme 1. Stabilization of Carbenium Ions by Representative π-Complex Fragments

Scheme 2. Alkynyl Cobaltcarbonyl (Nicholas' Cations) and Arene Chromiumcarbonyl Complex Substituted Carbenium Ions



stabilized by the adjacent cobalt(0) fragment under simultaneous protection of the alkyne can be reacted with a number of nucleophiles, giving rise to functionalized propargylic derivatives, interesting building blocks in complex natural product syntheses.[7] However, the so-called "Nicholas' cations" (Scheme 2) can be regarded as cobalt cluster stabilized carbenium ions rather than propargyl cations, especially since the triple bond is permanently complexed by the dicobalthexacarbonyl fragment and even the precursors for ionizations display bond lengths for the "triple bond" that strongly deviate from those of alkynes.[6]

Since ionizations of propargyl precursors form ambident propargyl cations[8] that can be interesting intermediates for more

† E-mail: tom@cup.uni-muenchen.de.

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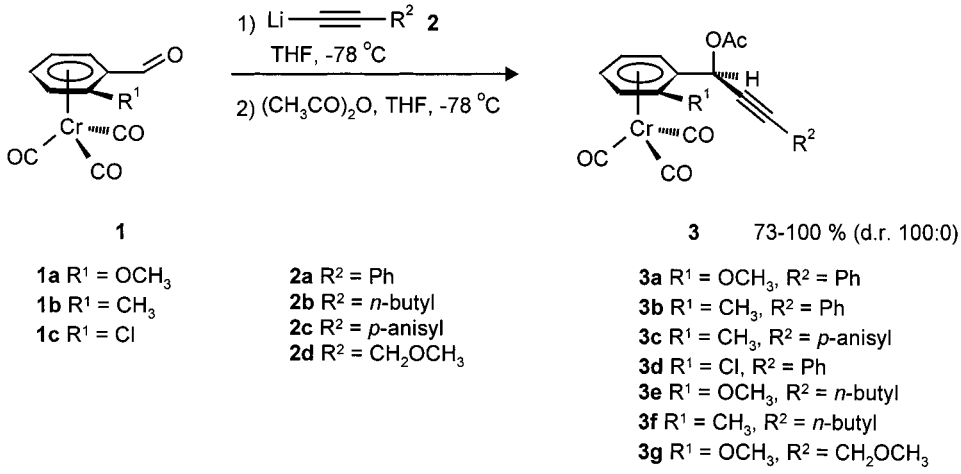
Scheme 3



1

1a $R^1 = OCH_3$
1b $R^1 = CH_3$
1c $R^1 = Cl$

2a $R^2 = Ph$
2b $R^2 = n$-butyl
2c $R^2 = p$-anisyl
2d $R^2 = CH_2OCH_3$

3 73-100 % (d.r. 100:0)

3a $R^1 = OCH_3$, $R^2 = Ph$
3b $R^1 = CH_3$, $R^2 = Ph$
3c $R^1 = CH_3$, $R^2 = p$-anisyl
3d $R^1 = Cl$, $R^2 = Ph$
3e $R^1 = OCH_3$, $R^2 = n$-butyl
3f $R^1 = CH_3$, $R^2 = n$-butyl
3g $R^1 = OCH_3$, $R^2 = CH_2OCH_3$

sophisticated arene side chain functionalizations via aryl propargyl or allenyl derivatives, we have initiated a program to investigate (arene)$Cr(CO)_3$ complexes bearing π-substituents,[9] particularly propargyl cations.[10] In kinetic studies we could determine the electrophilic reactivity of a (arene)$Cr(CO)_3$ complex substituted propargyl cation, revealing that this system (Scheme 2, $R^1 = H$; $R^2 = Ph$) is 2 orders of magnitude more reactive than the comparable Nicholas' cation (Scheme 2, R^1, $R^3 = H$; $R^2 = Ph$).[11]

Recently, we communicated the regio- and diastereoselective addition of nucleophiles to planar chiral complex substituted α-propargyl cations.[12] Now we wish to disclose our structural and synthetic investigations on diastereoselective cationic propargylations with (arene)$Cr(CO)_3$-substituted α-propargyl cations and several nucleophiles giving rise to complex substituted propargyl products.

Results and Discussion

Recently, we showed that (arene)$Cr(CO)_3$-stabilized α-propargylic cations could be easily and quantitatively generated from a suitable propargylic precursor,[10a,c,12] i.e., in our case upon ionization of dichloromethane solutions of arene complex substituted propargyl acetates at low temperatures with a slight excess of a Lewis acid such as boron trifluoride diethyl etherate, trimethylsilyl triflate (TMSOTf), tin tetrachloride, or titanium tetrachloride. As shown previously by several groups, the nucleophilic addition of organolithium or organomagnesium reagents to planar chiral *ortho*-substituted complexed benzaldehyds[4d] proceeds with excellent diastereoselectivity and allows for high-yield access to diastereomerically pure racemic mixtures of complex substituted propargyl derivatives.[13] Therefore, our strategy to prepare planar chiral (arene)$Cr(CO)_3$-stabilized α-propargylic cations commences with the nucleophilic addition of lithium acetylides **2** to racemic *ortho*-substituted η^6-(benzaldehyde)$Cr(CO)_3$ complexes **1** at −78 °C in THF followed by the addition of acetic anhydride, giving rise to the formation of planar chiral (arene)$Cr(CO)_3$-substituted propargyl acetates **3** in good yields and with excellent diastereoselectivity (Scheme 3) as deduced from the appearance of only one set of signals in the proton and carbon NMR spectra. Characteristically, the resonances of the benzylic proton and carbon of the compounds **3** appear between δ 6.2 and 6.7 (^{1}H NMR) and δ 57.7 and 61.9 (^{13}C NMR), respectively. Furthermore, the relative stereochemistry was unambiguously established by crystal structure analyses[14] of **3b** (Figure 1, Table 1)), **3e** (Figure 2, Table 1), and **3g** (Figure 3, Table 1), indicating that the observed diastereomer was formed by an *exo*-attack of the lithium acetylide in an energetically more favorable transition state arising from the attack to the *anti*-conformer (carbonyl oxygen vs R^1) of the *ortho*-substituted benzaldehyde complexes.[4d]

The ionization of the propargyl acetates **3** with trimethylsilyl triflate (TMSOTf), tin tetrachloride, or titanium tetrachloride is accompanied by a color change from light yellow to deep

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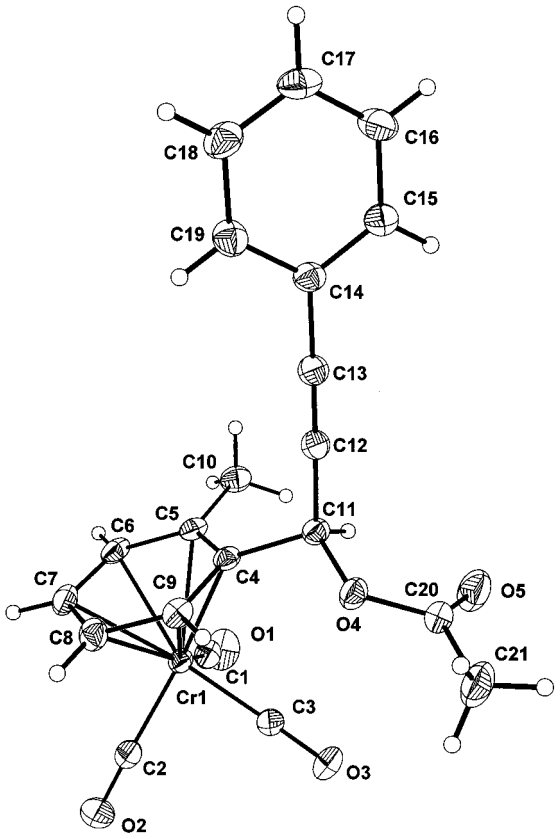


Figure 1. ORTEP plot of **3b**. Selected bond lengths [Å] and dihedral angles [deg]: C(4)−C(11), 1.521(3); C(11)−C(12), 1.466(3); C(12)−C(13), 1.191(3); C(13)−C(14), 1.440(3); C(5)−C(4)−C(11)−C(12), 80.24; C(5)−C(4)−C(11)−O(4), 160.95.

purple (**4a**, **4c**, **4d**, **4e**) or deep blue (**4b**), indicating the formation of the (arene)$Cr(CO)_3$-substituted α-propargyl cations **4** (Scheme 4). At low temperatures (<−40 °C) the deep colored specimens **4** are stable for several hours[15] and can be subjected to C−S, C−N, C−O, and C−C bond-forming reactions with nucleophiles, such as thiols (2-propanethiol, methyl 3-mercaptopropionate), secondary amines (diisopropylamine, morpholine), allyl alcohol, and π-nucleophiles (phenol, anisol, silyl ketene acetal, allyl silane) (Table 2). All nucleophilic additions occur exclusively at the α-position to give the propargylic derivatives **5** in good yields and with high diastereoselectivities[16] ranging from 70:30 to >99: <1. Expectedly, the shift at the benzylic position in the proton and carbon NMR spectra strongly depends on the corresponding substituent and can be easily identified as singlets (S-, N-, and O-substitution) or doublets of doublets (C-substitution) in the ^{1}H NMR spectra. Since these signals are separated by $\Delta\delta$ 0.01 to 0.61, the integration allows a reliable assignment of the diastereomers and their ratios. In most cases the propargyl proton signal appearing at higher field is that of the major diastereomer. The relative stereochemistry of the propargyl compounds **5** was unambiguously established by crystal structure analyses[14] of **5c** (Figure 4, Table 1)), **5g** (Figure 5, Table 1), and **5t** (Figure 6, Table 1), and by subsequent correlation with the propargyl proton resonances in the ^{1}H NMR spectra of **5**, the dominance of the depicted *syn*-diastereomer (alkynyl vs R^1) can be readily deduced.

The relative stereochemistry of the products **5** can be rationalized on the basis of a double inversion mechanism[2f] that results in a net retention of the configuration at the epimeric propargyl center. Assuming a complete and irreversible *anti*-periplanar Lewis acid mediated extrusion of the acetate leaving group by an anchimeric assistance of the chromiumcarbonyl tripod under kinetic control, the propargyl cation intermediate **6**, i.e., the *s-syn* conformer **7**, is formed (Scheme 5). Upon rotation around the $C_{ipso}-C_\alpha$ bond, **7** is converted to the diastereomeric *s-trans* conformer **8**. These propargyl cations **7** and **8** are not only stabilized by delocalizing the benzylic charge in the arene substituent but also by a significant contribution of the chromiumcarbonyl neighboring group participation via η^7-complexation, i.e., an η^6-phenyl complexation with a simultaneous d-π-overlap at the cationic propargyl center. Finally, the nucleophilic addition to the diastereomeric propargyl cations **7** and **8** gives rise to the formation of the major diastereomers **5** and the minor compounds **5′**.

A crucial point for the diastereoselectivity is the configurational stability of the cation **4** that is reflected by the ease of the *syn*−*anti*-isomerization from **7** and **8**. According to semiempirical calculations[17] (PM3 level of theory) on the free ligand systems **9** and **10**, the energy difference of both fixed conformations is only 1.9 kcal/mol; however, the energy barrier of activation for a *syn*−*anti*-isomerization is determined to be 12.0 kcal/mol (Scheme 6).

Therefore, the (arene)chromiumtricarbonyl substituted propargyl cation can also be considered to be configurationally fixed in a well-defined conformation. Since an epimerization at the propargylic center can be deduced from the diastereomeric cation **8**, it is very likely to occur on the stage of the cationic intermediate through a rotation around the $C_{ipso}-C_\alpha$ bond. Obviously, the configurational stability of the cationic propargyl side chain is largely preserved due to a hindered rotation around the $C_{ipso}-C_\alpha$ bond. Even in the case of the complex substituted propargyl cation, the barrier for a *syn*−*anti*-isomerization is just high enough for nucleophilic trapping reactions to proceed at low temperature with high diastereoselectivity. Thus, the incoming nucleophile attacks in an *exo*-fashion *anti*-periplanar with respect to the chromiumcarbonyl tripod at the propargylic position of the ambident electrophile **4** to give preferentially rise to the formation of **5**.

This theoretical consideration can be scrutinized by regarding the substituent effects on both termini of the propargyl cation bridge. Upon variation of the *ortho* substituent in its donor capacity from the good donor methoxy over methyl to the poorly electron releasing chlorine for the C−C, C−S, and C−N bond-forming reaction with silyl ketene acetal, thiols, or amines, a strong dependence of the stabilization of the propargylic charge on the diastereomeric excess[18] (de) can be easily recognized. Although thiols are considered to be more nucleophilic than

(14) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153794 (**3b**), CCDC-153797 (**3e**), CCDC-153796 (**3g**), CCDC-153795 (**5c**), CCDC-153798 (**5g**), and CCDC-153799 (**5s**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K (Fax: + 44-1223/336−033. E-mail: deposit@ccdc.cam.ac.uk).

(15) At −70 °C all cations **4** were chemically stable over several hours according to UV/vis spectroscopy, showing no depression of the molar decadic extinction coefficient. The configurational stability of cations **4a** and **4c** (which will be published elsewhere) has been 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 (**4c**), the appearance of a second set of signals was observed. Interestingly, the carbonyl signals still remain split into three signals indicating that the energy barrier for the tripodal rotation is higher than for the $C_{ipso}-C_\alpha$ rotation.

(16) The diastereomeric ratios were determined by ^{1}H NMR spectroscopy of the crude product after chromatography.

(17) *Quantum CAChe 3.0 Program*, Oxford Molecular Group, 1997.

(18) de = (dr − 1)/(dr + 1) × 100%.

Table 1. Crystal Data and Structure Refinements for **3b**, **3e**, **3g**, **5c**, **5g**, and **5t**

	3b	**3e**	**3g**	**5c**	**5g**	**5t**
emp formula	$C_{21}H_{16}CrO_5$	$C_{19}H_{20}CrO_6$	$C_{17}H_{16}CrO_7$	$C_{24}H_{22}CrO_6$	$C_{23}H_{21}CrNO_4$	$^{C}{}_{23}H_{31}CrNO_4$
color, form	yellow plates	yellow plates	yellow blocks	yellow plates	yellow plates	yellow blocks
formula wt	400.34	396.35	384.30	458.42	427.41	437.49
temp, K	294(0.2)	295(0.2)	295(0.2)	294(0.2)	295(0.2)	295(0.2)
wavelength (Å), radiation	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
crystal system	triclinic	triclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P2_1/4$	$P2_1/c$	$P2_12_12_1$
unit cell (Å, deg)						
a	9.4639(12)	7.7055(13)	14.280(2)	11.611(2)	8.0461(10)	7.569(2)
b	10.327(2)	11.368(3)	8.032(3)	13.932(2)	33.017 (7)	15.183(3)
c	10.569(2)	12.699(2)	14.868(4)	14.177(2)	8.4264(14)	20.575(4)
α	99.741(15)	113.20(2)	90.00(3)	90.000(11)	90.000(15)	90.00(2)
β	90.801(12)	90.509(15)	90.00(2)	93.734(11)	109.248(0)	90.00(2)
γ	113.022(14)	105.57(2)	90.00(2)	90.000(11)	90.000(14)	90.00(2)
vol (Å^3)	933.3(3)	976.6(3)	1705.4(9)	2288.4(5)	2113.4(6)	2364.6(9)
Z	2	2	4	4	4	4
density (calcd), g/cm^3	1.425	1.348	1.497	1.331	1.343	1.229
abs coeff, mm^{-1}	0.642	0.616	0.707	0.536	0.569	0.510
F(000)	412	412	792	952	888	928
crystal size (mm)	0.43 × 0.47 × 0.60	0.13 × 0.33 × 0.57	0.07 × 0.27 × 0.37	0.17 × 0.47 × 0.57	0.20 × 0.33 × 0.53	0.23 × 0.27 × 0.43
θ range for data collection	2.49−23.97°	2.77−23.97°	2.74−23.97°	2.64−23.97°	2.63−23.96°	2.39−23.97°
index ranges	$-9 \le h \le 20$ $-11 \le k \le 0$ $-12 \le l \le 12$	$-8 \le h \le 0$ $-12 \le k \le 12$ $-14 \le l \le 14$	$0 \le h \le 16$ $0 \le k \le 9$ $-17 \le l \le 17$	$0 \le h \le 13$ $-15 \le k \le 0$ $-16 \le l \le 16$	$-9 \le h \le 8$ $-37 \le k \le 0$ $0 \le l \le 9$	$-8 \le h \le 8$ $-17 \le k \le 17$ $-23 \le l \le 23$
reflectns collected	3103	3309	2666	3766	3539	4280
indep reflectns	2923 [*R*(int) = 0.0094]	3051 [*R*(int) = 0.0186]	2666 [*R*(int) = 0.000]	3573 [*R*(int) = 0.0202]	3296 [*R*(int) = 0.0192]	3706 [*R*(int) = 0.0178]
obsd ($I > 2\sigma(I)$)	2673	2591	2563	2794	2293	3337
abs correctn	semiempirical from *ψ*-scans	semiempirical from *ψ*-scans	semiempirical from *ψ*-scans	semiempirical from *ψ*- scans	semiempirical from *ψ*-scans	semiempirical from *ψ*-scans
max. and min. transmission	0.9138 and 0.9970	0.8930 and 0.9991	0.9076 and 0.9998	0.9497 and 0.9995	1.0000 and 0.9515	0.9552 and 0.9998
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/ parameters	2673/0/246	2591/0/248	2563/1/229	2794/0/284	2293/0/263	3337/0/269
goodness-of-fit on F^2	1.089	1.102	1.016	1.123	1.104	1.065
final *R* indices [$I>2\sigma(I)$]						
R_1	0.0282	0.0359	0.0243	0.02424	0.0552	0.0361
wR_2	0.0750	0.0924	0.0605	0.0986	0.1169	0.0885
R indices (all data)						
R_1	0.0315	0.0479	0.0258	0.0594	0.0930	0.0430
wR_2	0.0779	0.1016	0.0622	0.1100	0.1374	0.0942
largest diff. peak and hole (e/Å^3)	0.237 and −0.226	0.262 and −0.249	0.145 and −0.176	0.293 and −0.216	0.276 and −0.362	0.265 and −0.151

amines, thioethers are prone to acid-catalyzed ionization and, thus, an epimerization at a later stage cannot be fully excluded. Therefore, not only the stability of the cationic intermediate but also the rate of the kinetically controlled nucleophilic addition and the stability of the propargyl product toward ionization has to be taken into account.

Electronically, by leaving the *ortho* substituent constant even alkyl substituents are tolerated on the side chain; however, a resonance stabilization to a certain extent at the *γ*-position is more favorable. In agreement with a reduced stability of the propargyl cation **4**, if an aryl substituent is replaced by an alkyl group its generation (now $TiCl_4$ is necessary as a Lewis acid, vide infra) is impeded and the diastereomeric excess slightly drops. This feature is even more important if the complex stabilization now has to compete with a side chain stabilization by donor substituents such as an anisyl group at the *γ*-position. As a consequence the diminishing of the back-bonding by the *π*-complex fragment results in a facilitated rotation around the $C_{ipso}-C_\alpha$ bond and the diastereoselectivity drops.

Another aspect of the cation stabilization of **4** is the ease of the ionization of the propargyl acetates **3** by various Lewis acids (Table 3). As reflected by the strength of several Lewis acids, a high diastereoselectivity only can be achieved if the combination of the propargyl acetate **3** and the Lewis acid results in a complete irreversible ionization to the propargyl cation **4**. Incomplete ionizations represent an equilibrium situation between cation and anion on the product side and propargyl acetate and Lewis acid on the educt side. In these cases the clear two-step mechanistic pathway, i.e., complete ionization followed by nucleophilic addition, is abandoned in favor of a mixed mechanism consisting of ionization−addition sequences occurring simultaneously, in the sense of an S_N1 mechanism or an S_N2 pathway. A lower diastereoselectivity arises in both mechanistic rationales.

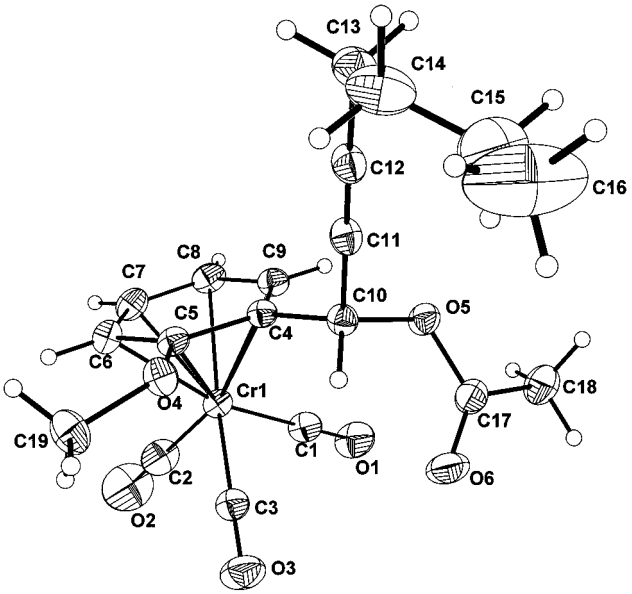


Figure 2. ORTEP plot of **3e**. Selected bond lengths [Å] and bond angles [deg]: C(4)−C(10), 1.516(3); C(10)−C(11), 1.471(4); C(11)−C(12), 1.182(4); C(12)−C(13), 1.475(4); C(5)−C(4)−C(10)−C(11), 80.27; C(5)−C(4)−C(10)−O(5), 159.88.

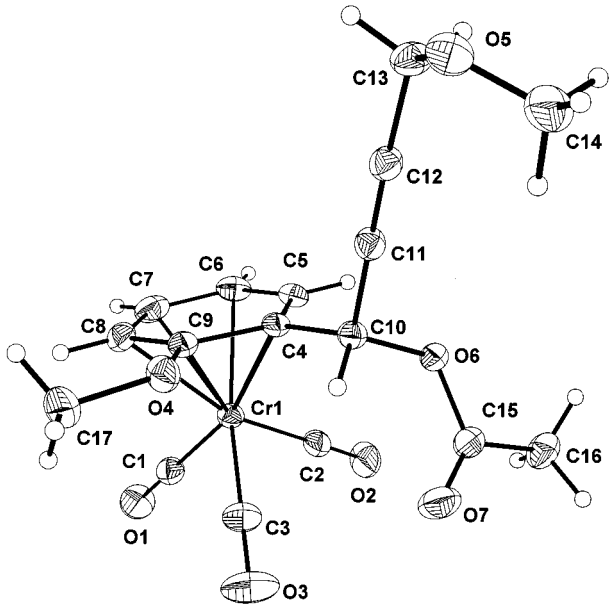


Figure 3. ORTEP plot of **3g**. Selected bond lengths [Å] and bond angles [deg]: C(4)−C(10), 1.514(3); C(10)−C(11), 1.470(3); C(11)−C(12), 1.182(3); C(12)−C(13), 1.469(3); C(5)−C(4)−C(10)−C(11), 86.08; C(5)−C(4)−C(10)−O(6), 32.17.

In the next set of experiments we investigated the possibility of conducting the stepwise ionization−nucleophilic addition sequence in an S_N1 fashion, i.e., the in situ generation of the propargyl cation intermediate **4** in the presence of the trapping nucleophile. In particular, if the applied Lewis acid is strong enough to ensure complete ionization, these S_N1 reactions should proceed with high diastereoselectivity. However, the in situ ionization experiments (Table 4, entries 1 and 2) reveal that not only does the diastereoselectivity drop considerably to a 34:66 or 43:57 ratio but also the selectivity of the propargylation is reversed from **5** to **5′**. It is noteworthy mentioning that according to MM2 force field calculations[17] the diastereomers, e.g., **5c** and **5c′** ($\Delta E = 0.3$ kcal/mol), are almost equal in energy (Scheme 7). Obviously, the in situ ionization conditions infringe the pure S_N1 mechanism as reflected by the formation of the dominant product **5′**. This diastereomer is rather formed by an inversion of the configuration at the propargylic center by S_N2 attack of the nucleophile under simultaneous activation by $TiCl_4$ (Scheme 8) than by a *syn*−*anti*-isomerization from **7** and **8**. Most interestingly, in situ ionization conditions require fairly strong Lewis acids to achieve a sufficient activation of the acetate leaving group. Although titanium tetrachloride is suitable for complete cation formation, the reaction pathway is not necessarily shifted in the direction of a pure S_N1 reaction (Table 4, entry 3). Furthermore, a deactivation of silyl ketene acetal by coordination and/or side reactions with titanium tetrachloride cannot be fully excluded and, thus, a rapid kinetically controlled substitution is hampered. As a consequence, in situ ionization conditions rather lead to the formation of equilibrium products. Therefore, conducting these cationic propargylations in a stepwise process, i.e., complete ionization of **3** to give **4** followed by nucleophilic addition, is not only more convenient but also gives rise to highly diastereoselective formation of the propargylation products **5**.

Conclusion

Cationic propargylations with stable (arene)$Cr(CO)_3$-substituted α-propargyl cations **4** and carbon, nitrogen, oxygen, and sulfur nucleophiles give rise to complex-substituted propargylation products **5** with good to excellent diastereoselectivity. This stereoselective propargylation is complementary to the well-established nucleophilic trapping Nicholas' cations;[2e,6] however, the triple bond remains uncomplexed and the complex-substituted propargyl cations **4** are even more electrophilic.[11] Further studies investigating the structure and the configurational stability of the intermediates **4** and the development of enantioselective and double diastereoselective propargylations directed toward sophisticated side chain functionalizations and natural product syntheses are currently underway.

Experimental Section

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.[19] 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. Phenylacetylene, 1-hexyne, and the trapping nucleophiles were purchased from Aldrich, Fluka, or Merck and used without further purification. 3-Methoxypropyne was synthesized according to the literature,[20] and *p*-methoxyphenylacetylene was prepared by Sonogashira coupling of *p*-iodoanisol followed by subsequent alkaline desilylation in excellent yield.[21] The $Cr(CO)_3$-complexed benzaldehydes were prepared in analogy to published procedures via the complexation of the dimethylacetals.[10a,22] All crystalline chromium arene complexes can be handled in air. ^1H 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 has been made by using DEPT spectra. IR: Perkin-Elmer Models Lambda 16. MS: Finnigan MAT 90 and MAT 95 Q. Elemental analyses were carried out in the Microanalytical Laboratory of the Department Chemie, Ludwig-Maximilians-Universität München.

(19) Various editors, *Organikum*, 19th ed.; VEB Deutscher Verlag der Wissenschaften: Berlin, 1993.

(20) Brandsma, L. In *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, Oxford, New York, Tokyo, 1988; p 259.

(21) (a) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627. (b) Sonogashira, K. In *Metal catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, 1998; p 203.

(22) Mahaffy, C. A. L.; Pauson, P. L. *Inorg. Synth.* **1990**, *28*, 136.

Scheme 4

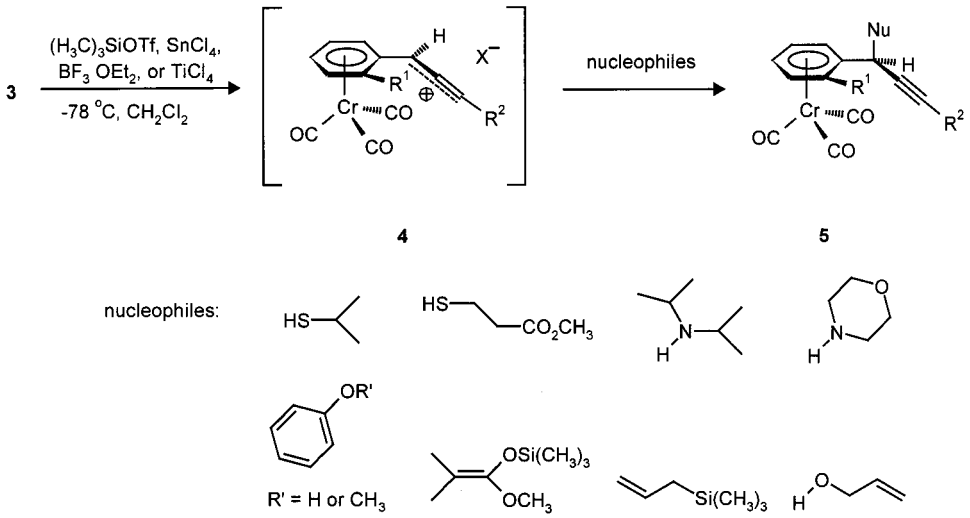
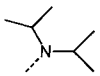
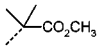
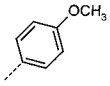
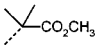
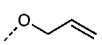
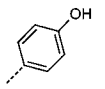
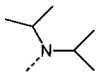
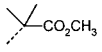
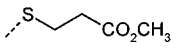
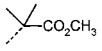
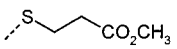
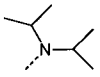
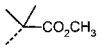


Table 2. Substituent Keys of **4** and **5**, Yields, and Diastereomeric Ratios of the Nucleophilic Trapping Reactions

Cation **4**	Propargyl Compound **5**	R^1	R^2	Nucleophile	Yield (d.r.)
4a	**5a**	OCH_3	Ph		82 % (>99 : 1)
4a	**5b**	OCH_3	Ph		89 % (95 : 5)
4a	**5c**	OCH_3	Ph		83 % (>95 : 5)
4a	**5d**	OCH_3	Ph		65 % (71 : 29)
4a	**5e**	OCH_3	Ph		35 % (92 : 8)
4b	**5f**	CH_3	Ph		79 % (93 : 7)
4b	**5g**	CH_3	Ph		71 % (>99 : 1)
4b	**5h**	CH_3	Ph		67 % (93 : 7)
4b	**5i**	CH_3	Ph		70 % (91 : 9)
4b	**5j**	CH_3	Ph		44 % (96 : 4)

Cation **4**	Propargyl Compound **5**	R^1	R^2	Nucleophile	Yield (d.r.)
4c	**5k**	CH_3	*p*-anisyl		78 % (91 : 9)
4c	**5l**	CH_3	*p*-anisyl		53 % (94 : 6)
4c	**5m**	CH_3	*p*-anisyl		71 % (87 : 13)
4c	**5n**	CH_3	*p*-anisyl		86 % (91 : 9)
4d	**5o**	Cl	Ph		70 % (78 : 22)
4d	**5p**	Cl	Ph		82 % (86 : 14)
4d	**5q**	Cl	Ph		90 % (97 : 3)
4d	**5r**	Cl	Ph		81 % (80 : 20)
4e	**5s**	OCH_3	*n*-butyl		67 % (83 : 17)
4e	**5t**	OCH_3	*n*-butyl		81 % (93 : 7)
4e	**5u**	OCH_3	*n*-butyl		74 % (86 : 14)

X-ray Structure Determination of Compounds 3b, 3e, 3g, 5c, 5g, and 5t. Suitable Crystals were mounted on a capillary and transferred to an Enraf-Nonius CAD4 diffractometer. The structures were solved by direct methods and refined anisotropically on F^2 (program SHELXS-86, SHELXL-93, G. M. Sheldrick, University of Göttingen). Hydrogen atoms were found from differential Fourier synthesis and refined. The data of the X-ray structure analyses of **3b**, **3e**, **3g**, **5c**, **5g**, and **5t** are summarized in Table 1.

***Ortho*-Substituted Acetates 3.** To a degassed solution of the alkyne **2** in dry THF (1 M) was added 1.1 equiv of a 1.6 M solution of *n*-butyllithium in hexanes dropwise at −78 °C (for experimental details, see Table 5). After stirring at that temperature for 15 min, the solution was allowed to come to room temperature for 1 h. After recooling to −78 °C, a solution of the complexed benzaldehyde **1** in 15 mL of THF was added dropwise over a period of 10 min. This reaction mixture was then stirred at −78 °C for the time indicated before a solution of acetic anhydride in 2.5 mL of THF was added and stirring was continued for 100 min. After the external cooling had been removed, 50 mL of water was added to the mixture which was then allowed to come to room temperature. After extraction of the aqueous phase with diethyl ether (3 × 50 mL), the combined organic layers were washed with an aqueous saturated sodium bicarbonate solution (2 × 50 mL). The organic phase was dried with magnesium sulfate and filtered, and the solvents were evaporated in vacuo. Most of the residual oils crystallized either neat at −20 °C or from diethyl ether/pentane as yellow crystalline solids.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[OC(O)CH_3]C=CPh (3a). Yellow crystals, mp 96 °C. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ 2.16 (s, 3 H), 3.82 (s, 3 H), 5.24 (t, J = 6.4 Hz, 1 H), 5.68 (d, J = 6.9 Hz, 1 H), 6.05 (dt, J = 7.1 Hz, J = 1.2 Hz, 1 H), 6.28 (dd, J = 6.4 Hz, J = 1.2 Hz, 1 H), 6.61 (s, 1 H), 7.36−7.47 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 20.33 (CH_3), 56.83 (CH_3), 58.42 (CH), 75.63 (CH), 85.18

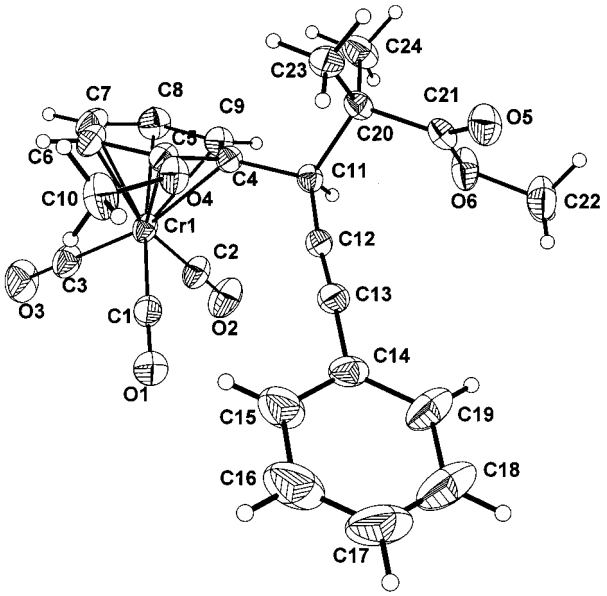


Figure 4. ORTEP plot of **5c**. Selected bond lengths [Å] and dihedral angles [deg]: C(4)−C(11), 1.527(4); C(11)−C(12), 1.468(4); C(12)−C(13), 1.183(4); C(13)−C(14), 1.446(4); C(5)−C(4)−C(11)−C(12), 39.91; C(5)−C(4)−C(11)−C(20), 88.31.

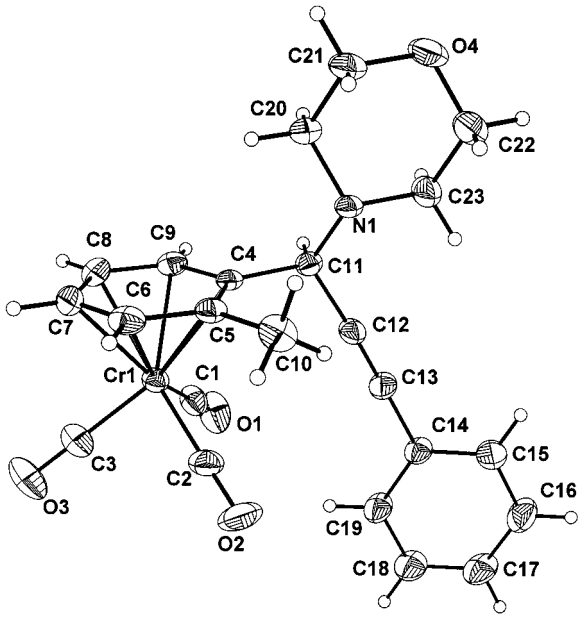


Figure 5. ORTEP plot of **5g**. Selected bond lengths [Å] and dihedral angles [deg]: C(4)−C(11), 1.530(5); C(11)−C(12), 1.476(6); C(12)−C(13), 1.183(6); C(13)−C(14), 1.448(6); C(5)−C(4)−C(11)−C(12), 66.32; C(5)−C(4)−C(11)−N(1), 57.54.

($C_{quat.}$), 85.80 (CH), 85.92 ($C_{quat.}$), 96.77 ($C_{quat.}$), 96.86 (CH), 97.52 (CH), 120.94 ($C_{quat.}$), 128.88 (CH), 129.62 (CH), 131.87 (CH), 142.86 ($C_{quat.}$), 168.63 ($C_{quat.}$), 233.44 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 416 (M^+, 3), 361 ($M^+ - 2$ CO, 3), 332 ($M^+ - 3$ CO, 93), 317 ($M^+ - 3$ CO − CH_3, 100), 280 ($M^+ - Cr(CO)_3$, 1), 274 (66), 222 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, 30), 207 (90), 190 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, − OCH_3, 6), 52 (Cr^+, 19). IR (KBr): $\tilde{\nu}$ 2229, 1964, 1886, 1740, 1630, 1224, 1018 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 316 nm (8500). Anal. Calcd for $C_{21}H_{16}CrO_6$ (416.35): C, 60.58; H, 3.87. Found: C, 60.79; H, 3.94.

$Cr(CO)_3$(*o*-CH_3-η^6-C_6H_4)CH[OC(O)CH_3]C≡CPh (3b). Yellow crystals, mp 80 °C. ^{1}H NMR ([D_6]DMSO, 400 MHz): δ 2.16 (s, 3 H), 2.38 (s, 3 H), 5.50 (dt, J = 6.3 Hz, J = 0.7 Hz, 1 H), 5.56 (d, J = 6.4 Hz, 1 H), 5.88 (dt, J = 6.4 Hz, J = 0.7 Hz, 1 H), 6.18 (d, J = 6.1 Hz, 1 H), 6.47 (s, 1 H), 7.36−7.41 (m, 3 H), 7.43−7.48 (m, 2 H). ^{13}C NMR ([D_6]DMSO, 100 MHz): δ 18.09 (CH_3), 20.44 (CH_3), 61.85

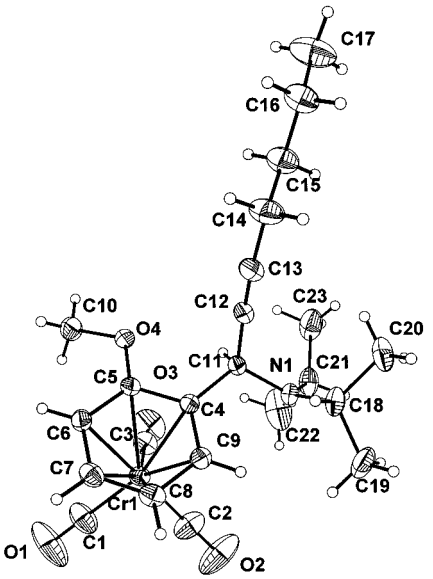


Figure 6. ORTEP plot of **5t** (view from the top). Selected bond lengths [Å] and dihedral angles [deg]: C(4)−C(11), 1.528(4); C(11)−C(12), 1.485(5); C(12)−C(13), 1.176(5); C(13)−C(14), 1.487(5); C(5)−C(4)−C(11)−C(12), 73.21; C(5)−C(4)−C(11)−N(1), 159.09.

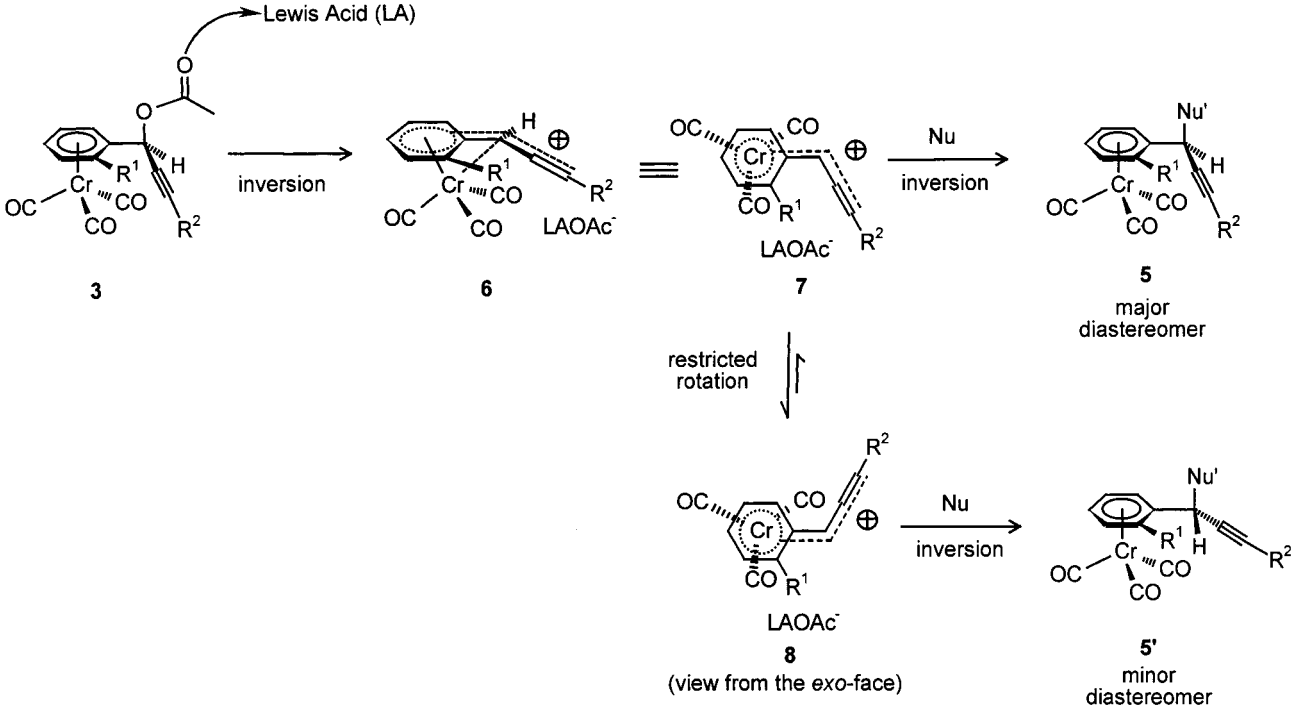
(CH), 85.11 ($C_{quat.}$), 86.82 ($C_{quat.}$), 90.07 (CH), 94.11 (CH), 96.82 (CH), 97.31 (CH), 106.46 ($C_{quat.}$), 111.25 ($C_{quat.}$), 120.92 ($C_{quat.}$), 128.86 (CH), 129.59 (CH), 131.73 (CH), 168.78 ($C_{quat.}$), 233.43 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 400 (M^+, 7), 344 ($M^+ - 2$ CO, 4), 316 ($M^+ - 3$ CO, 100), 258 (25), 205 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, 20), 190 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, − CH_3, 3), 111 (10), 52 (Cr^+, 21). IR (KBr): $\tilde{\nu}$ 2227, 1965, 1891, 1757, 1629, 1214, 1021 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 318 nm (9800). Anal. Calcd for $C_{21}H_{16}CrO_5$ (400.35): C, 63.00; H, 4.03. Found: C, 63.25; H, 4.13.

$Cr(CO)_3$(*o*-CH_3-η^6-C_6H_4)CH[OC(O)CH_3]C=C-*p*-$C_6H_4OCH_3$ (3c). Yellow brownish crystals, mp 75 °C. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ 2.15 (s, 3 H), 2.37 (s, 3 H), 3.76 (s, 3 H), 5.50 (t, J = 6.5 Hz, 1 H), 5.54 (d, J = 6.5 Hz, 1 H), 5.87 (t, J = 6.3 Hz, 1 H), 6.17 (d, J = 6.5 Hz, 1 H), 6.45 (s, 1 H), 6.93 (d, J = 8.7 Hz, 2 H), 7.40 (d, J = 8.6 Hz, 2 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 18.10 (CH_3), 20.48 (CH_3), 55.43 (CH_3), 61.86 (CH), 83.76 ($C_{quat.}$), 87.02 ($C_{quat.}$), 90.11 (CH), 94.11 (CH), 96.69 (CH), 97.26 (CH), 106.80 ($C_{quat.}$), 111.17 ($C_{quat.}$), 112.79 ($C_{quat.}$), 114.51 (CH), 133.42 (CH), 160.17 ($C_{quat.}$), 168.81 ($C_{quat.}$), 233.49 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 430 (M^+, 8), 374 ($M^+ - 2$ CO, 6), 346 ($M^+ - 3$ CO, 85), 288 ($C_{17}H_{16}CrO^+$, 100), 235 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, 29), 121 (25), 52 (Cr^+, 40). IR (KBr): $\tilde{\nu}$ 2228, 1965, 1925, 1893, 1880, 1743, 1606, 1510, 1251, 1225, 1033, 835 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 318 nm (10600), 294 (6800). Anal. Calcd for $C_{22}H_{18}CrO_6$ (430.38): C, 61.40; H, 4.22. Found: C, 61.76; H, 4.16.

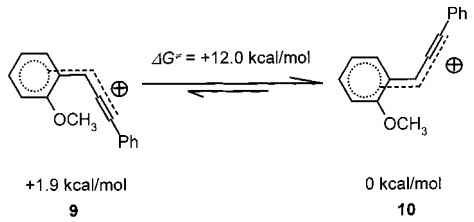
$Cr(CO)_3$(*o*-Cl-η^6-C_6H_4)CH[OC(O)CH_3]C≡CPh (3d). Yellow powder, mp 115−119 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.22 (s, 3 H), 5.03 (t, J = 6.1 Hz, 1 H), 5.38 (d, J = 6.3 Hz, 1 H), 5.47 (t, J = 6.0 Hz, 1 H), 5.95 (d, J = 6.3 Hz, 1 H), 6.64 (s, 1 H), 7.29−7.31 (m, 3 H), 7.33−7.45 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.48 (CH_3), 61.07 (CH), 83.87 ($C_{quat.}$), 86.37 (CH), 87.34 ($C_{quat.}$), 89.55 (CH), 92.54 (CH), 93.30 (CH), 103.73 ($C_{quat.}$), 113.24 ($C_{quat.}$), 121.31 ($C_{quat.}$), 128.28 (CH), 129.16 (CH), 131.93 (CH), 168.74 ($C_{quat.}$), 230.76 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 422/420 (M^+, 0.08/0.36), 366/364 ($M^+ - 2$ CO, 1/3), 338/336 ($M^+ - 3$ CO, 5/15), 280/278 (6/17), 258 (32), 190 ($M^+ - Cr(CO)_3$, − $C_2H_3O_2$, − Cl, 19), 83 (100), 52 (Cr^+, 17). IR (KBr): $\tilde{\nu}$ 2233, 1984, 1914, 1883, 1734, 1638, 1222, 662, 620 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 322 nm (10300). Anal. Calcd for $C_{20}H_{13}CrO_5Cl$ (420.77): C, 57.09; H, 3.11; Cl, 8.43. Found: C, 56.62; H, 3.21; Cl, 8.34.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[OC(O)CH_3]C≡C(CH_2)$_3$$CH_3$ (3e). Yellow crystals, mp 62−64 °C. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ 0.83 (t, J = 7.2 Hz, 3 H), 1.24−1.44 (m, 4 H), 2.11 (s, 3 H), 2.22 (dt,

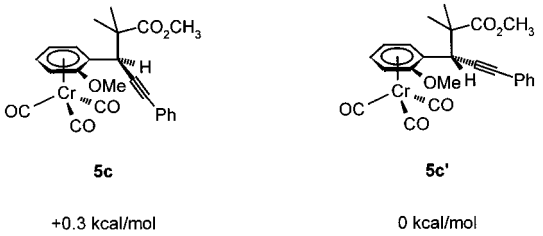
Scheme 5



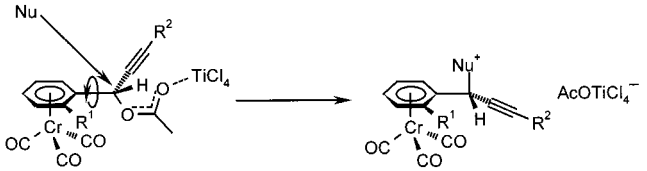
Scheme 6



Scheme 7



Scheme 8. S_N2 Attack of the Nucleophile under Simultaneous Activation of the Acetate by $TiCl_4$



J = 6.8 Hz, J = 1.7 Hz, 2 H), 3.77 (s, 3 H), 5.21 (t, J = 6.2 Hz, 1 H), 5.64 (d, J = 6.9 Hz, 1 H), 6.01 (t, J = 6.5 Hz, 1 H), 6.15 (d, J = 6.3 Hz, 1 H), 6.35 (s, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 13.50 (CH_3), 17.69 (CH_2), 20.31 (CH_3), 21.42 (CH_2), 29.93 (CH_2), 56.72 (CH_3), 57.95 (CH), 75.58 (CH), 76.45 ($C_{quat.}$), 85.79 (CH), 87.72 ($C_{quat.}$), 96.37 (CH), 97.34 ($C_{quat.}$), 97.67 (CH), 142.58 ($C_{quat.}$), 168.52 ($C_{quat.}$), 233.50 ($C_{quat.}$, CO). EI MS (70 eV, m/z (%)): 396 (M^+, 3), 340 ($M^+ - 2$ CO, 13), 312 ($M^+ - 3$ CO, 100), 297 ($M^+ - 3$ CO, $- CH_3$, 58), 253 ($M^+ - 3$CO, $- C_2H_3O_2$, 20), 201 ($M^+ - Cr(CO)_3$, $- C_2H_3O_2$, 30), 52 (Cr^+, 38). IR (KBr): $\tilde{\nu}$ 2938, 2228, 1966, 1896, 1878, 1742, 1637, 1468, 1226, 1017, 666, 628 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 315 nm (8600). Anal. Calcd for $C_{19}H_{20}CrO_6$ (396.36): C, 57.58; H, 5.09. Found: C, 57.86; H, 5.16.

Table 3. Influence of the Ionizing Lewis Acid on the de (de = (dr −1)/(dr + 1))

	propargyl acetate **3**			
Lewis acid	**3a**[a]	**3b**[b]	**3a**[c]	**3e**[d]
$BF_3{\cdot}OEt_2$	2	44	38	24
TMSOTf	98	86	90	40
$SnCl_4$				36
$TiCl_4$				72

[a] 2-Propanethiol as trapping nucleophile (reaction product **5a**). [b] 2-Propanethiol as trapping nucleophile (reaction product **5f**). [c] 1-Methoxy-2-methyl-1-trimethylsiloxypropene as trapping nucleophile (reaction product **5c**). [d] 1-Methoxy-2-methyl-1-trimethylsiloxypropene as trapping nucleophile (reaction product **5u**).

Table 4. Diastereomeric Ratios (dr) of Stepwise vs in Situ Ionizations of the Propargyl Acetates **3a**, **3b**, and **3e** in the Presence of 1-Methoxy-2-methyl-1-trimethylsiloxypropene as Trapping Nucleophile To Give the Propargyl Derivatives **5c**, **5h**, and **5u**, Respectively

	propargyl acetate **3**	stepwise ionization and nucleophilic addition	in situ ionization
entry 1	**3a**	>95:5[a]	43:57[b]
entry 2	**3e**	86:14[b]	34:66[b]
entry 3	**3b**	93:7[a]	no reaction[a,c]

[a] Ionization with TMSOTf. [b] Ionization with $TiCl_4$. [c] Only **3b** was recovered.

$Cr(CO)_3$(o-CH_3-η^6-C_6H_4)$CH[OC(O)CH_3]C{\equiv}C(CH_2)_3CH_3$ (3f). Yellow oil. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 0.83 (t, J = 7.0 Hz, 3 H), 1.22−1.45 (m, J = 7.1 Hz, 4 H), 2.11 (s, 3 H), 2.23 (t, J = 6.9 Hz, 2 H), 2.28 (s, 3 H), 5.48 (t, J = 6.5 Hz, 1 H), 5.54 (d, J = 6.2 Hz, 1 H), 5.85 (t, J = 6.3 Hz, 1 H), 6.06 (d, J = 6.7 Hz, 1 H), 6.18 (s, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 13.58 (CH_3), 17.76 (CH_2), 17.98 (CH_3), 20.51 (CH_3), 21.51 (CH_2), 29.91 (CH_2), 61.28 (CH), 76.35 ($C_{quat.}$), 88.67 ($C_{quat.}$), 90.36 (CH), 94.31 (CH), 96.06 (CH), 97.13 (CH), 107.36 ($C_{quat.}$), 110.82 ($C_{quat.}$), 168.78 ($C_{quat.}$), 233.60 ($C_{quat.}$, CO). pos. FAB MS (Ar, 5−6 kV, mNBA, m/z (%)): 381 ([M + H]$^+$, 1), 380 (M^+, 3), 321 (15), 296 ($M^+ - 3$ CO, 100), 272 (24), 237 ($M^+ - 3$ CO, $- C_2H_3O_2$, 55), 185 ($M^+ - Cr(CO)_3$, $- C_2H_3O_2$, 15), 105 (25),

Table 5. Experimental Details on the Synthesis of the Complex Substituted Propargyl Acetates **3**

alkyne **2** (mmol)	*n*-BuLi mL (mmol)	aldehyde **1** g (mmol)	reaction time, min.	acetic anhydride mL (mmol)	acetate **3** yield g (%)
1.15 mL (10.5) of **2a**	6.6 (10.5)	2.72 (10.0) of **1a**	190	2.17 (23.0)	4.33 (100) of **3a**
1.15 mL (10.5) of **2a**	6.5 (10.4)	2.51 (9.8) of **1b**	70	2.2 (23.3)	3.66 (94) of **3b**
1.64 g (12.4) of **2c**	7.8 (12.5)	2.92 (11.4) of **1b**	150	(23.3)	4.31 (88) of **3c**
0.50 mL (4.6) of **2a**	2.7 (4.3)	1.14 (4.12) of **1c**	270	1.0 (10.6)	1.53 (88) of **3d**
1.10 mL (8.8) of **2b**	5.0 (8.0)	2.00 (7.38) of **1a**	120	1.70 (15.4)	2.14 (73) of **3e**
1.23 mL (10.8) of **2b**	10.7 (17.1)	2.51 (9.8) of **1b**	150	2.5 (21.7)	2.86 (77) of **3f**
0.68 g (9.73) of **2d**	6.4 (10.2)	2.50 (9.19) of **1a**	145	1.80 (19.0)	2.50 (71) of **3g**

Table 6. Experimental Details on the Cationic Propargylations with Cations **4**

acetate **3** mg (mmol)	TMSOTf μL (mmol)	ionization time [min.]	nucleophile (mmol)	reaction time [min.]	propargyl product **5** yield, mg (%)
202 (0.49) of **3a**	120 (0.66)	60	0.10 mL (1.06) of 2-propanethiol	100	173 (82) of **5a** dr = >99:1
204 (0.49) of **3a**	105 (0.58)	38	0.15 mL (1.07) of diisopropylamine	60	200 (89) of **5b** dr = 95:5
202 (0.49) of **3a**	96 (0.53)	55	0.20 mL (0.99) of methoxy-2-methyl-1-trimethylsiloxypropene	60	184 (83) of **5c** dr = >95:5
103 (0.25) of **3a**	45 (0.36)[a]	15	0.10 mL (0.63) of allyl trimethylsilane	50	64 (65) of **5d** dr = 71:29
100 (0.24) of **3a**	49 (0.39)[a]	50	0.06 mL (0.55) of anisole in 0.5 mL of dichloromethane	120	39 (35) of **5e** dr = 92:8
109 (0.27) of **3b**	55 (0.3)	55	0.10 mL (1.06) of 2-propanethiol	60	90 (79) of **5f** dr = 93:7
102 (0.26) of **3b**	80 (0.44)	45	0.10 mL (1.15) of morpholine	75	77 (71) of **5g** dr = >99:1
202 (0.51) of **3b**	120 (0.66)	85	0.21 mL (1.04) of methoxy-2-methyl-1-trimethylsiloxypropene	120	150 (67) of **5h** dr = 93:7
202 (0.51) of **3b**	100 (0.55)	65	0.10 mL (1.46) of allyl alcohol	40	143 (70) of **5i** dr = 91:9
210 (0.53) of **3b**	120 (0.66)	30	0.24 g (2.55 mmol) of phenol in 3 mL of dichloromethane	110	100 (44) of **5j** dr = 96:4
103 (0.24) of **3c**	50 (0.28)	60	0.10 mL (1.06) of 2-propanethiol	60	83 (78) of **5k** dr = 91:9
202 (0.47) of **3c**	93 (0.52)	65	0.10 mL (0.71) of diisopropylamine	25	118 (53) of **5l** dr = 94:6
206 (0.48) of **3c**	96 (0.53)	45	0.15 mL (0.74) of methoxy-2-methyl-1-trimethylsiloxypropene	120	160 (71) of **5m** dr = 87:13
750 (1.74) of **3c**	38 (2.10)	60	0.70 mL (4.39) of allyl trimethylsilane in 1.3 mL of dichloromethane	120	621 (86) of **5n** dr = 91:9
200 (0.48) of **3d**	130 (0.72)	60	0.10 mL (1.07) of 2-propanethiol	105	145 (70) of **5o** dr = 78:22
201 (0.48) of **3d**	112 (0.62)	40	0.15 mL (1.20) of methyl 3-mercaptopropionate	120	188 (82) of **5p** dr = 86:14
100 (0.24) of **3d**	50 (0.43)[b]	50	0.20 mL (2.30) of morpholine	180	96 (90) of **5q** dr = 97:3
200 (0.48) of **3d**	110 (0.94)[b]	60	0.40 mL (1.97) of methoxy-2-methyl-1-trimethylsiloxypropene	120	177 (81) of **5r** dr = 80:20
202 (0.51) of **3e**	100 (0.53)[c]	30	0.15 mL (1.20) of methyl 3-mercaptopropionate	105	155 (67) of **5s** dr = 83:17
202 (0.51) of **3e**	70 (0.64)[c]	25	0.16 mL (1.14) of diisopropylamine	110	180 (81) of **5t** dr = 93:7
205 (0.52) of **3e**	70 (0.64)[c]	12	0.22 mL (1.09) of methoxy-2-methyl-1-trimethylsiloxypropene	60	168 (74) of **5u** dr = 86:14

[a] Ionization with $BF_3{\cdot}OEt_2$. [b] Ionization with $SnCl_4$. [c] Ionization with $TiCl_4$.

52 (Cr^+, 12). IR (KBr): $\tilde{\nu}$ 2960, 2935, 2289, 2213, 1966, 1886, 1745, 1674, 1460, 1370, 1225, 1020, 665, 628 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 317 nm (9500). Anal. Calcd for $C_{19}H_{20}CrO_5$ (380.36): C, 60.00; H, 5.30. Found: C, 60.21; H, 5.78.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$OC(O)CH_3$]C≡CCH_2OCH_3 (3g). Yellow crystals, mp 107−108 °C. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ 2.14 (s, 3 H), 3.22 (s, 3 H), 3.79 (s, 3 H), 4.13 (s, 2 H), 5.22 (t, J = 6.3 Hz, 1 H), 5.65 (d, J = 7.0 Hz, 1 H), 6.03 (t, J = 6.5 Hz, 1 H), 6.17 (d, J = 6.4 Hz, 1 H), 6.42 (s, 1 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 20.27 (CH_3), 56.81 (CH_3), 57.14 (CH_3), 57.70 (CH), 59.01 (CH_2), 75.59 (CH), 82.06 ($C_{quat.}$), 83.13 ($C_{quat.}$), 85.83 (CH), 96.29 (CH), 96.70 ($C_{quat.}$), 97.43 (CH), 142.64 ($C_{quat.}$), 168.53 ($C_{quat.}$), 233.40 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 384 (M^+, 14), 328 (M^+ − 2 CO, 17), 300 (M^+ − 3 CO, 28), 268 (M^+ − 3 CO, − OCH_3, − H, 100), 255 (28), 241 (M^+ − 3 CO, − $C_2H_3O_2$, 7), 212 (50), 158 (70), 115 ($C_{10}H_7^+$, 41), 52 (Cr^+, 75). IR (KBr): $\tilde{\nu}$ 1966, 1957, 1874, 1748, 1629, 1220, 1094, 1019, 669, 632 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 316 nm (19600). Anal. Calcd for $C_{17}H_{16}CrO_7$ (384.31): C, 53.13; H, 4.20. Found: C, 53.28; H, 4.23.

Diastereoselective Propargylations. Generation of the Propargyl Cations and Nucleophilic Trapping (General Procedure). To a solution of the acetate **3** in 5−10 mL of dry dichloromethane was added dropwise 1.1−1.7 equiv of the corresponding Lewis acid at −78 °C (for experimental details, see Table 6). Immediately a deep red to blue solution of the propargyl cation was formed that was stirred at that temperature for 15−50 min. To this reaction mixture was then added at −78 °C the corresponding nucleophile, neat or as a solution in dichloromethane. The reaction can be followed by a color change from deep colored to yellow. After the reaction time, 20 mL of diethyl ether and 20 mL of water were added and the external cooling was removed. After extraction of the aqueous phase with diethyl ether (2 × 25 mL), the combined organic layers were dried with magnesium sulfate and filtered and the solvents were evaporated in vacuo. The residues were dried in vacuo and, if not crystalline, then 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.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$SCH(CH_3)_2$]C≡CPh (5a). Yellow crystals, mp 140 °C (dichloromethane/diethyl ether). ^{1}H NMR ([D_6]-DMSO, 400 MHz): δ 1.26−1.30 (m, 6 H), 3.25−3.37 (m, J = 6.8 Hz, 1 H), 3.79 (s, 3 H), 5.10 (s, 1 H), 5.30 (t, J = 6.3 Hz, 1 H), 5.60 (d, J = 7.1 Hz, 1 H), 5.96 (t, J = 6.6 Hz, 1 H), 6.25 (d, J = 6.4 Hz, 1 H), 7.35−7.52 (m, 5 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 22.96 (CH_3), 23.32 (CH_3), 32.26 (CH), 36.71 (CH), 56.69 (CH_3), 75.47 (CH), 84.07 ($C_{quat.}$), 85.67 (CH), 88.14 ($C_{quat.}$), 97.08 (CH), 98.66 (CH), 100.21 ($C_{quat.}$), 122.26 ($C_{quat.}$), 128.78 (2 signals, CH), 131.55 (CH), 142.59 ($C_{quat.}$), 233.69 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 432 (M^+, 17), 376 (M^+ − 2 CO, 22), 348 (M^+ − 3 CO, 100), 290 (21), 274 (66), 259 (46), 221 (M^+ − $Cr(CO)_3$, − SC_3H_7, 27), 52 (Cr^+, 22). IR (KBr): $\tilde{\nu}$ 2926, 1958, 1884, 1876, 1858, 1636, 1470, 1260, 757, 667, 631 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 318 nm (8800). Anal. Calcd for $C_{22}H_{20}$-CrO_4S (432.46): C, 61.10; H, 4.66; S, 7.41. Found: C, 60.71; H, 4.82; S, 7.36.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$N(^iPr)_2$]C≡CPh (5b). Yellow crystals, mp 124−134 °C (diethyl ether). ^{1}H NMR ([D_6]DMSO, 300

MHz): δ 1.17 (d, J = 6.2 Hz, 6 H), 1.23 (d, J = 6.0 Hz, 6 H), 3.35 (m, 2 H), 3.80 (s, 3 H), 4.87 (s, 1 H), 5.23 (t, J = 5.7 Hz, 1 H), 5.60 (d, J = 6.5 Hz, 1 H), 5.94 (t, J = 6.1 Hz, 1 H), 6.00 (d, J = 5.8 Hz, 1 H), 7.33−7.62 (m, 5 H). Additional signals for the minor diastereomer: δ 0.93 (d, J = 6.7 Hz, 6 H), 3.73 (s, 3 H), 4.99 (s, 1 H), 6.28 (d, J = 6.0 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 20.23 (CH_3), 23.86 (CH_3), 45.85 (CH), 47.45 (CH), 56.46 (CH_3), 75.94 (CH), 83.50 ($C_{quat.}$), 85.74 (CH), 90.49 ($C_{quat.}$), 96.97 (CH), 97.48 (CH), 105.49 ($C_{quat.}$), 122.76 ($C_{quat.}$), 128.49 (CH), 128.79 (CH), 131.15 (CH), 142.64 ($C_{quat.}$), 234.29 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 87.69 ($C_{quat.}$), 129.21 (CH). EI MS (70 eV, *m*/*z* (%)): 457 (M^+, 32), 401 ($M^+ - 2$ CO, 2), 373 ($M^+ - 3$ CO, 50), 321 ($M^+ - Cr(CO)_3$, 6), 290 ($M^+ - Cr(CO)_3$, $- OCH_3$, 1), 274 ($M^+ - 3$ CO, $-$ ^{i}PrN=CMe$_2$, 75), 259 (64), 221 (100), 190 ($C_{15}H_{10}^+$, 4), 151 (71), 115 ($H_3CN(^iPr)_2^+$, 61), 52 (Cr^+, 50). IR (KBr): $\tilde{\nu}$ 2966, 1953, 1876, 1629, 1598, 1461, 1265 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 315 nm (8700). Anal. Calcd for $C_{25}H_{27}CrO_4N$ (457.49): C, 65.64; H, 5.95; N, 3.06. Found: C, 65.25; H, 5.92; N, 3.01.

Cr(CO)$_3$(*o*-OCH$_3$-η^6-C$_6$H$_4$)CH[C(CH$_3$)$_2$COOCH$_3$]C≡CPh (5c). Yellow crystals, mp 138−139 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 400 MHz): δ 1.26 (s, 3 H), 1.27 (s, 3 H), 3.62 (s, 3 H), 3.73 (s, 3 H), 3.88 (s, 1 H), 5.14 (t, J = 6.2 Hz, 1 H), 5.64 (d, J = 7.1 Hz, 1 H), 5.96 (t, J = 6.5 Hz, 1 H), 6.04 (d, J = 6.4 Hz, 1 H), 7.32−7.39 (m, 5 H). Additional signals for the minor diastereomer: δ 1.15 (s, 3 H), 3.63 (s, 3 H), 4.46 (s, 1 H), 5.32 (t, J = 6.1 Hz, 1 H), 5.60 (d, J = 6.9 Hz, 1 H), 6.11 (d, J = 6.3 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 23.47 (CH_3), 23.51 (CH_3), 44.52 (CH), 48.24 ($C_{quat.}$), 52.06 (CH_3), 56.14 (CH_3), 76.58 (CH), 83.98 ($C_{quat.}$), 85.66 (CH), 87.51 ($C_{quat.}$), 97.51 (CH), 97.80 ($C_{quat.}$), 101.54 (CH), 123.47 ($C_{quat.}$), 128.05 (CH), 128.56 (CH), 131.27 (CH), 143.83 ($C_{quat.}$), 175.12 ($C_{quat.}$), 233.84 ($C_{quat.}$, CO). pos. FAB MS (Ar, 5−6 kV, mNBA, *m*/*z* (%)): 459 ([M + H]$^+$, 1), 402 ($M^+ - 2$ CO, 17), 374 ($M^+ - 3$ CO, 100), 274 ($M^+ - 3$ CO, $- C(CH_3)_2CO_2CH_3$, 12), 259 (10), 221 ($M^+ - Cr(CO)_3$, $- C(CH_3)_2CO_2CH_3$, 11), 115 (12), 52 (Cr^+, 17). IR (KBr): $\tilde{\nu}$ 1966, 1887, 1873, 1729, 1628, 1474, 1269, 755, 670, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 315 nm (8300). Anal. Calcd for $C_{24}H_{22}CrO_6$ (458.43): C, 62.88; H, 4.84. Found: C, 63.24; H, 4.99.

Cr(CO)$_3$(*o*-OCH$_3$-η^6-C$_6$H$_4$)CH[CH$_2$CH=CH$_2$]C≡CPh (5d). Yellow oil. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ 2.52−2.64 (m, 2 H), 3.79 (s, 3 H), 3.91 (dd, J = 10.0 Hz, J = 5.1 Hz, 1 H), 5.06−5.23 (m, 2 H), 5.22 (t, J = 6.6 Hz, 1 H), 5.65 (d, J = 6.6 Hz, 1 H), 5.84−6.02 (m, 1 H), 5.98 (t, J = 6.9 Hz, 1 H), 6.25 (dd, J = 6.6 Hz, J = 0.9 Hz, 1 H), 7.33−7.48 (m, 5 H). Additional signals for the minor diastereomer: δ 2.38−2.43 (m, 2 H), 3.77 (s, 3 H), 4.12 (dd, J = 7.9 Hz, J = 5.0 Hz, 1 H), 5.29 (t, J = 6.3 Hz, 1 H), 5.63 (d, J = 6.3 Hz, 1 H), 6.02 (t, J = 7.0 Hz, 1 H), 6.13 (dd, J = 6.4 Hz, J = 1.0 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 30.90 (CH), 40.43 (CH_2), 56.64 (CH_3), 76.19 (CH), 83.22 ($C_{quat.}$), 86.23 (CH), 90.25 ($C_{quat.}$), 97.15 (CH), 98.33 (CH), 102.94 ($C_{quat.}$), 117.66 (CH_2), 122.67 ($C_{quat.}$), 128.48 (CH), 128.68 (CH), 131.51 (CH), 135.65 (CH), 142.58 ($C_{quat.}$), 234.15 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 31.83 (CH), 40.39 (CH_2), 56.60 (CH_3), 76.28 (CH), 84.18 ($C_{quat.}$), 87.06 (CH), 88.67 ($C_{quat.}$), 96.54 (CH), 96.83 (CH), 101.01 ($C_{quat.}$), 118.20 (CH_2), 122.71 ($C_{quat.}$), 128.51 (CH), 128.65 (CH), 131.57 (CH), 134.61 (CH), 142.32 ($C_{quat.}$). EI MS (70 eV, *m*/*z* (%)): 398 (M^+, 16), 342 ($M^+ - 2$ CO, 1), 314 ($M^+ - 3$ CO, 100), 299 ($M^+ - 3$ CO, $- CH_3$, 12), 273 ($M^+ - 3$ CO, $- CH_2CH=CH_2$, 18), 262 ($M^+ - Cr(CO)_3$, 1), 52 (Cr^+, 22). IR (KBr): $\tilde{\nu}$ 2924, 1960, 1875, 1642, 1469, 1261, 1017, 758, 667, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 315 nm (8200). Anal. Calcd for $C_{22}H_{18}CrO_4$ (398.38): C, 66.33; H, 4.55. Found: C, 66.89; H, 4.66.

Cr(CO)$_3$(*o*-OCH$_3$-η^6-C$_6$H$_4$)CH[*p*-C$_6$H$_4$OCH$_3$]C≡CPh (5e). Yellow orange solid, mp 132−136 °C (dichloromethane/diethyl ether). ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ 3.71 (s, 3 H), 3.74 (s, 3 H), 5.29 (s, 1 H), 5.32 (m, 1 H), 5.60 (d, J = 6.4 Hz, 1 H), 5.91 (m, 1 H), 6.39 (d, J = 5.5 Hz, 1 H), 6.89 (d, J = 7.9 Hz, 2 H), 7.24−7.39 (m, 5 H), 7.50 (m, 2 H). Additional signals for the minor diastereomer: δ 3.86 (s, 3 H), 3.90 (s, 3 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 36.00 (CH), 55.27 (CH_3), 56.64 (CH_3), 76.24 (CH), 84.12 ($C_{quat.}$), 87.29 (CH), 89.10 ($C_{quat.}$), 96.37 (CH), 96.55 (CH), 102.55 ($C_{quat.}$), 114.27 (CH), 122.60 ($C_{quat.}$), 128.64 (CH), 128.66 (CH), 128.74 (CH), 131.62 (CH), 132.56 ($C_{quat.}$), 142.06 ($C_{quat.}$), 158.64 ($C_{quat.}$), 234.11 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 128.87 (CH), 131.51 (CH). EI MS (70 eV, *m*/*z* (%)): 464 (M^+, 15), 394 ($M^+ - 2$ CO, 8), 380 ($M^+ - 3$ CO, 100), 328 ($M^+ - Cr(CO)_3$, 7), 313 ($M^+ - Cr(CO)_3$, $- CH_3$, 8), 297 ($M^+ - Cr(CO)_3$, $- OCH_3$, 1), 52 (Cr^+, 4). IR (KBr): $\tilde{\nu}$ 1960, 1879, 1630, 1509, 1254, 1031, 811, 759, 632 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 316 nm (8200). Anal. Calcd for $C_{26}H_{20}CrO_5$ (464.44): C, 67.24; H, 4.34. Found: C, 67.00; H, 4.21.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[SCH(CH$_3$)$_2$]C≡CPh (5f). Yellow crystals, mp 51−52 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ 1.29 (d, J = 6.6 Hz, 3 H), 1.33 (d, J = 6.8 Hz, 3 H), 2.47 (s, 3 H), 3.22 (sept, J = 6.8 Hz, 1 H), 5.14 (s, 1 H), 5.45 (t, J = 6.5 Hz, 1 H), 5.50 (d, J = 6.3 Hz, 1 H), 5.84 (t, J = 6.4 Hz, 1 H), 6.19 (d, J = 6.4 Hz, 1 H), 7.38−7.45 (m, 5 H). Additional signals for the minor diastereomer: δ 1.24 (d, J = 6.6 Hz, 3 H), 1.26 (d, J = 6.8 Hz, 3 H), 2.32 (s, 3 H), 3.02−3.05 (m, 1 H), 5.19 (s, 1 H), 6.10 (d, J = 6.8 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 18.33 (CH_3), 23.14 (CH_3), 23.42 (CH_3), 36.11 (CH), 36.97 (CH), 85.54 ($C_{quat.}$), 87.68 ($C_{quat.}$), 89.81 (CH), 94.11 (CH), 97.17 (CH), 98.88 (CH), 109.27 ($C_{quat.}$), 111.79 ($C_{quat.}$), 122.14 ($C_{quat.}$), 128.79 (CH), 128.89 (CH), 131.39 (CH), 233.74 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 17.82 (CH_3), 36.69 (CH), 91.52 (CH), 94.65 (CH), 95.52 (CH), 96.44 (CH), 110.63 ($C_{quat.}$). EI MS (70 eV), *m*/*z* (%): 416 (M^+, 9), 360 ($M^+ - 2$ CO, 6), 332 ($M^+ - 3$ CO, 52), 258 ($M^+ - 3$ CO, $- S=CMe_2$, 100), 257 ($M^+ - 3$ CO, $- SC_3H_7$, 11), 205 ($M^+ - Cr(CO)_3$, $- SC_3H_7$, 18), 190 ($C_{15}H_{10}+$, 3), 52 (Cr^+, 20). IR (KBr): $\tilde{\nu}$ 1963, 1887, 1636, 758, 666, 628 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) = 320 nm (9400). Anal. Calcd for $C_{22}H_{20}CrO_3S$ (416.46): C, 63.45; H, 4.84; S, 7.70. Found: C, 63.42; H, 4.93; S, 7.54.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[N(CH$_2$)$_4$O]C≡CPh (5g). Yellow crystals, mp 117−118 °C (diethyl ether). ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ 2.43 (s, 3 H), 2.54−2.57 (m, 2 H), 2.79 (m, 2 H), 3.64 (m, 4 H), 4.60 (s, 1 H), 5.46 (t, J = 6.1 Hz, 1 H), 5.51 (d, J = 5.9 Hz, 1 H), 5.84 (t, J = 6.0 Hz, 1 H), 6.10 (d, J = 6.3 Hz, 1 H), 7.39−7.48 (m, 5 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 18.56 (CH_3), 51.00 (CH_2), 59.09 (CH), 66.29 (CH_2), 85.27 ($C_{quat.}$), 88.18 ($C_{quat.}$), 89.95 (CH), 94.47 (CH), 97.45 (CH), 99.62 (CH), 109.65 ($C_{quat.}$), 112.44 ($C_{quat.}$), 122.04 ($C_{quat.}$), 128.80 (CH), 128.92 (CH), 131.53 (CH), 234.03 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 427 (M^+, 2), 371 ($M^+ - 2$ CO, 12), 343 ($M^+ - 3$ CO, 33), 258 ($M^+ - 3$ CO, $- NC_4H_7O$, 100), 190 ($M^+ - Cr(CO)_3$, $- CH_3$, $- NC_4H_8O$, 55), 52 (Cr^+, 25). IR (KBr): $\tilde{\nu}$ 2965, 1951, 1881, 1639, 1491, 1446, 1116, 871, 760, 666, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 318 nm (9400). Anal. Calcd for $C_{23}H_{21}CrO_4N$ (427.42): C, 64.63; H, 4.95; N, 3.28. Found: C, 64.36; H, 5.14; N, 3.26.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[C(CH$_3$)$_2$COOCH$_3$]C≡CPh (5h). Yellow blocks, mp 101−103 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ 1.30 (s, 3 H), 1.31 (s, 3 H), 2.46 (s, 3 H), 3.65 (s, 3 H), 4.05 (s, 1 H), 5.43−5.48 (m, J = 6.4 Hz, 2 H), 5.79−5.84 (m, J = 6.4 Hz, 2 H), 7.33−7.40 (m, 5 H). Additional signals for the minor diastereomer: δ 1.22 (s, 3 H), 1.23 (s, 3 H), 2.35 (s, 3 H), 3.62 (s, 3 H), 4.52 (s, 1 H), 5.61 (t, J = 6.4 Hz, 1 H), 5.95 (d, J = 5.8 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 19.62 (CH_3), 23.43 (CH_3), 23.64 (CH_3), 46.17 (CH), 48.70 (CH_3), 52.37 ($C_{quat.}$), 86.14 ($C_{quat.}$), 87.41 ($C_{quat.}$), 90.61 (CH), 95.63 (CH), 97.14 (CH), 100.68 (CH), 107.57 ($C_{quat.}$), 111.93 ($C_{quat.}$), 122.55 ($C_{quat.}$), 128.69 (CH), 128.83 (CH), 131.18 (CH), 175.15 ($C_{quat.}$), 233.83 ($C_{quat.}$, CO). Additional signal for the minor diastereomer: δ 131.41 (CH). EI MS (70 eV, *m*/*z* (%)): 442 (M^+, 5), 386 ($M^+ - 2$ CO, 3), 358 ($M^+ - 3$ CO, 67), 306 ($M^+ - Cr(CO)_3$, 1), 288 (36), 260 ($M^+ - Cr(CO)_3$, $- CH_3$, $- OCH_3$, 6), 258 ($M^+ - 3$ CO, $- CH_2=C(CH_3)CO_2CH_3$, 100), 205 (78), 190 ($C_{15}H_{10}+$, 3), 52 (Cr^+, 35). IR (KBr): $\tilde{\nu}$ 2950, 1966, 1890, 1872, 1730, 1597, 1434, 1246, 1131, 756, 667, 628 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 317 nm (8900). Anal. Calcd for $C_{24}H_{22}CrO_5$ (442.43): C, 65.15; H, 5.01. Found: C, 65.40; H, 5.14.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[OCH$_2$CH=CH$_2$]C≡CPh (5i). Yellow crystals, mp 90−93 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 400 MHz): δ 2.34 (s, 3 H), 4.18 (dd, J = 13.0 Hz, J = 5.3 Hz, 1 H), 4.37 (dd, J = 13.0 Hz, J = 5.1 Hz, 1 H), 5.22 (dd, J = 10.5 Hz, J = 1.2 Hz, 1 H), 5.35 (s, 1 H), 5.40 (dd, J = 17.3 Hz, J = 1.5 Hz, 1 H), 5.53 (t, J = 6.5 Hz, 1 H), 5.57 (d, J = 6.4 Hz, 1 H), 5.80 (t, J = 6.3 Hz, 1 H), 5.91−6.03 (m, 1 H), 6.06 (d, J = 6.6 Hz, 1 H),

7.35−7.59 (m, 5 H). Additional signals for the minor diastereomer: δ 2.27 (s, 3 H), 4.09 (dd, J = 12.5 Hz, J = 5.6 Hz, 1 H), 4.28 (dd, J = 12.5 Hz, J = 5.4 Hz, 1 H), 5.17−5.19 (m, 1 H), 5.28−5.33 (m, 1 H), 5.47 (s, 1 H), 5.88 (t, J = 6.5 Hz, 1 H), 6.22 (d, J = 6.4 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ 18.08 (CH_3), 67.37 (CH), 69.87 (CH_2), 86.39 ($C_{quat.}$), 87.15 ($C_{quat.}$), 90.91 (CH), 94.99 (CH), 95.30 (CH), 96.40 (CH), 109.19 ($C_{quat.}$), 110.23 ($C_{quat.}$), 117.31 (CH_2), 121.43 ($C_{quat.}$), 128.83 (CH), 129.28 (CH), 131.62 (CH), 134.26 (CH), 233.88 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 17.75 (CH_3), 67.79 (CH), 69.55 (CH_2), 84.77 ($C_{quat.}$), 88.38 ($C_{quat.}$), 90.86 (CH), 94.41 (CH), 96.73 (CH), 97.24 (CH), 105.89 ($C_{quat.}$), 112.20 ($C_{quat.}$), 117.81 (CH_2), 121.54 ($C_{quat.}$), 130.74 (CH), 131.58 (CH), 131.72 (CH), 134.35 (CH), 233.62 ($C_{quat.}$, CO). EI MS (70 eV), m/z (%): 398 (M^+, 12), 342 (M^+ − 2 CO, 4), 314 (M^+ − 3 CO, 19), 258 (M^+ − 3 CO, − O=CHCH=CH_2, 100), 205 (M^+ − $Cr(CO)_3$, − OCH_2CH=CH_2, 5), 52 (Cr^+, 18). R (KBr): $\tilde{\nu}$ = 1959, 1893, 1873, 1636, 1491, 1293, 1071, 764, 664, 630 cm^{-1}. UV/vis (DMSO): $\lambda_{max.}$ (ϵ) = 318 nm (10600). Anal. Calcd for $C_{22}H_{18}CrO_4$ (398.38): C, 66.33; H, 4.55. Found: C, 66.00; H, 4.41.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[*p*-C$_6$H$_4$OH]C=CPh (5j). Orange foam. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 2.37 (s, 3 H), 5.21 (s, 1 H), 5.40−5.56 (m, J = 6.4 Hz, 3 H), 5.77 (t, J = 6.2 Hz, 1 H), 6.82 (d, J = 8.5 Hz, 2 H), 7.32−7.37 (m, 5 H), 7.44−7.48 (m, 2 H), 9.51 (s, 1 H). Additional signals for the minor diastereomer: δ 2.27 (s, 3 H), 5.28 (s, 1 H), 5.62 (t, J = 6.4 Hz, 1 H), 6.15 (t, J = 6.4 Hz, 1 H), 9.84 (s, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 18.53 (CH_3), 38.79 (CH), 84.75 ($C_{quat.}$), 89.39 ($C_{quat.}$), 90.95 (CH), 94.58 (CH), 96.90 (CH), 97.53 (CH), 111.63 ($C_{quat.}$), 113.69 ($C_{quat.}$), 115.42 (CH), 122.48 ($C_{quat.}$), 127.42 ($C_{quat.}$), 128.72 (CH), 128.79 (CH), 129.63 (CH), 131.51 (CH), 156.97 ($C_{quat.}$), 234.00 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 17.73 (CH_3), 90.68 (CH), 98.61 (CH), 116.03 (CH), 128.92 (CH). EI MS (70 eV, m/z (%)): 434 (M^+, 8), 350 (M^+ − 3 CO, 100), 298 (M^+ − $Cr(CO)_3$, 62), 283 (M^+ − $Cr(CO)_3$, − CH_3, 22), 206 (M^+ − $Cr(CO)_3$, − CH_3, − C_6H_5, 6), 91 ($C_6H_4CH_3^+$, 20), 77 ($C_6H_5^+$, 11), 52 (Cr^+, 35). IR (KBr): $\tilde{\nu}$ 2925, 1961, 1883, 1614, 1512, 1442, 1264, 846, 757, 666, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 318 nm (9100). Anal. Calcd for $C_{25}H_{18}CrO_4$ (434.42): C, 69.12; H, 4.18. Found: C, 69.60; H, 4.84.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[SCH(CH$_3$)$_2$]C≡C-*p*-C$_6$H$_4$OCH$_3$ (5k). Yellow needles, mp 88 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ 1.28 (d, J = 6.6 Hz, 3 H), 1.32 (d, J = 6.7 Hz, 3 H), 2.46 (s, 3 H), 3.14−3.25 (m, J = 6.7 Hz, 1 H), 3.76 (s, 3 H), 5.09 (s, 1 H), 5.42−5.49 (m, J = 6.5 Hz, 2 H), 5.83 (t, J = 6.3 Hz, 1 H), 6.18 (d, J = 6.5 Hz, 1 H), 6.93 (d, J = 8.7 Hz, 2 H), 7.37 (d, J = 8.7 Hz, 2 H). Additional signals for the minor diastereomer: δ 1.36 (d, J = 6.7 Hz, 3 H), 2.31 (s, 3 H), 5.14 (s, 1 H), 5.55 (m, 2 H), 6.13 (d, J = 6.9 Hz, 1 H), 7.43 (d, J = 8.8 Hz, 2 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 18.32 (CH_3), 23.16 (CH_3), 23.46 (CH_3), 36.20 (CH), 36.90 (CH), 55.44 (CH_3), 85.59 ($C_{quat.}$), 86.10 ($C_{quat.}$), 89.88 (CH), 94.17 (CH), 97.25 (CH), 98.92 (CH), 109.66 ($C_{quat.}$), 111.88 ($C_{quat.}$), 114.08 ($C_{quat.}$), 114.49 (CH), 132.94 (CH), 159.69 ($C_{quat.}$), 233.81 ($C_{quat.}$, CO). EI MS (70 eV, m/z (%)): 446 (M^+, 4), 390 (M^+ − 2 CO, 10), 362 (M^+ − 3 CO, 81), 288 (M^+ − 3 CO, − S=CMe_2, 100), 235 (M^+ − $Cr(CO)_3$, − SC_3H_7, 66), 52 (Cr^+, 21). IR (KBr): $\tilde{\nu}$ 2960, 2221, 1956, 1909, 1873, 1604, 1510, 1460, 838, 666, 629 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 320 nm (9840). Anal. Calcd for $C_{23}H_{22}CrO_4S$ (446.49): C, 61.87; H, 4.97; S, 7.18. Found: C, 62.05; H, 5.25; S, 7.26.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[N(*i*Pr)$_2$]C≡C-*p*-C$_6$H$_4$OCH$_3$ (5l). Yellow crystals, mp 111−112 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ 1.15 (d, J = 6.6 Hz, 6 H), 1.23 (d, J = 6.3 Hz, 6 H), 2.40 (s, 3 H), 3.21−3.30 (m, J = 6.6 Hz, 2 H), 3.73 (s, 3 H), 4.76 (s, 1 H), 5.47 (d, J = 6.2 Hz, 1 H), 5.52 (t, J = 6.3 Hz, 1 H), 5.81 (t, J = 6.3 Hz, 1 H), 5.95 (d, J = 6.4 Hz, 1 H), 6.90 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H). Additional signals for the minor diastereomer: δ 1.00 (d, J = 6.5 Hz, 6 H), 2.29 (s, 3 H), 3.75 (s, 3 H), 4.89 (s, 1 H), 6.26 (d, J = 6.6 Hz, 1 H), 6.93 (d, J = 9.0 Hz, 2 H), 7.36 (d, J = 8.7 Hz, 2 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 19.67 (CH_3), 20.36 (CH_3), 23.34 (CH_3), 47.36 (CH), 48.49 (CH), 55.37 (CH_3), 84.93 ($C_{quat.}$), 88.28 ($C_{quat.}$), 90.27 (CH), 94.07 (CH), 96.08 (CH), 97.91 (CH), 110.96 ($C_{quat.}$), 114.32 ($C_{quat.}$), 114.48 (2 signals, CH, $C_{quat.}$), 132.57 (CH), 159.55 ($C_{quat.}$), 234.34 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 19.02 (CH_3), 20.73 (CH_3), 23.87 (CH_3), 46.74 (CH), 49.58 (CH), 86.58 ($C_{quat.}$), 87.99 ($C_{quat.}$), 90.82 (CH), 95.07 (CH), 96.96 (CH), 98.06 (CH), 109.54 ($C_{quat.}$), 111.88 ($C_{quat.}$), 114.45 (CH), 114.76 ($C_{quat.}$), 132.47 (CH), 159.49 ($C_{quat.}$), 234.15 ($C_{quat.}$, CO). EI MS (70 eV, m/z (%)): 471 (M^+, 11), 415 (M^+ − 2 CO, 3), 387 (M^+ − 3 CO, 26), 288 (M^+ − 3 CO, − ^{i}PrN=CMe_2, 28), 235 (M^+ − $Cr(CO)_3$, − N(^{i}Pr)$_2$, 15), 204 (M^+ − $Cr(CO)_3$, − N(^{i}Pr)$_2$, − OCH_3, 100), 151 (43), 52 (Cr^+, 16). IR (KBr): $\tilde{\nu}$ 2967, 2231, 1960, 1899, 1866, 1607, 1509, 1463, 1249, 1175, 1033, 834, 669, 631 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 316 nm (11100). Anal. Calcd for $C_{26}H_{29}CrO_4N$ (471.52): C, 66.23; H, 6.20; N, 2.97. Found: C, 66.25; H, 5.92; N, 2.81.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[C(CH$_3$)$_2$COOCH$_3$]C≡C-*p*-C$_6$H$_4$OCH$_3$ (5m). Yellow crystals, mp 108 °C (diethyl ether). ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 1.29 (s, 3 H), 1.30 (s, 3 H), 2.46 (s, 3 H), 3.64 (s, 3 H), 3.75 (s, 3 H), 4.01 (s, 1 H), 5.42−5.48 (m, J = 6.2 Hz, 2 H), 5.79−5.82 (m, J = 6.2 Hz, 2 H), 6.93 (d, J = 8.6 Hz, 2 H), 7.32 (d, J = 8.5 Hz, 2 H). Additional signals for the minor diastereomer: δ 1.22 (s, 3 H), 2.23 (s, 3 H), 3.62 (s, 3 H), 4.25 (s, 1 H), 5.50−5.61 (m, J = 6.5 Hz, 2 H), 5.93−6.05 (m, J = 6.4 Hz, 2 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 19.65 (CH_3), 23.33 (CH_3), 23.69 (CH_3), 46.23 (CH), 48.73 ($C_{quat.}$), 52.32 (CH_3), 55.42 (CH_3), 85.71 ($C_{quat.}$), 86.10 ($C_{quat.}$), 90.58 (CH), 95.63 (CH), 97.15 (CH), 100.65 (CH), 107.91 ($C_{quat.}$), 111.98 ($C_{quat.}$), 114.48 (CH), 114.56 ($C_{quat.}$), 132.65 (CH), 159.50 ($C_{quat.}$), 175.22 ($C_{quat.}$), 233.86 ($C_{quat.}$, CO). Additional signal for the minor diastereomer: δ 133.03 (CH). EI MS (70 eV, m/z (%)): 472 (M^+, 3), 444 (M^+ − CO, 2), 416 (M^+ − 2 CO, 8), 388 (M^+ − 3 CO, 73), 319 (14), 318 (M^+ − 3 CO, − C_4H_6O, 48), 288 (M^+ − 3 CO, − CH_2=$C(CH_3)CO_2CH_3$, 100), 235 (M^+ − $Cr(CO)_3$, − $C(CH_3)_2CO_2CH_3$, 12), 52 (Cr^+, 17). IR (KBr): $\tilde{\nu}$ 2954, 2230, 1961, 1886, 1729, 1607, 1512, 1469, 1252, 1032, 835, 669, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 317 nm (9300). Anal. Calcd for $C_{25}H_{24}CrO_6$ (472.46): C, 63.56; H, 5.12. Found: C, 63.72; H, 5.11.

Cr(CO)$_3$(*o*-CH$_3$-η^6-C$_6$H$_4$)CH[CH$_2$CH=CH$_2$]C≡C-*p*-C$_6$H$_4$OCH$_3$ (5n). Yellow crystals, mp 65 °C (diethyl ether/pentane). ^{1}H NMR ([D$_6$]-DMSO, 300 MHz): δ 2.36 (s, 3 H), 2.41−2.53 (m, 1 H), 2.61−2.72 (m, 1 H), 3.74 (s, 3 H), 3.82 (dd, J = 9.8 Hz, J = 5.3 Hz, 1 H), 5.13 (d, J = 10.2 Hz, 1 H), 5.20 (dd, J = 17.1 Hz, J = 1.4 Hz, 1 H), 5.50 (t, J = 6.4 Hz, 1 H), 5.56 (d, J = 6.2 Hz, 1 H), 5.79 (t, J = 6.3 Hz, 1 H), 5.90−6.03 (m, 1 H), 5.98 (d, J = 6.4 Hz, 1 H), 6.89 (d, J = 8.8 Hz, 2 H), 7.30 (d, J = 8.7 Hz, 2 H). Additional signals for the minor diastereomer: δ 2.24 (s, 3 H), 3.75 (s, 3 H), 4.03 (dd, J = 7.9 Hz, J = 5.0 Hz, 1 H), 5.06 (d, J = 9.9 Hz, 1 H), 5.74 (d, J = 6.3 Hz, 1 H), 7.39 (d, J = 8.7 Hz, 2 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 18.40 (CH_3), 34.14 (CH), 38.86 (CH_2), 55.38 (CH_3), 83.68 ($C_{quat.}$), 88.45 ($C_{quat.}$), 91.54 (CH), 95.29 (CH), 96.43 (CH), 96.80 (CH), 111.16 ($C_{quat.}$), 112.53 ($C_{quat.}$), 114.37 (CH), 114.53 ($C_{quat.}$), 117.80 (CH_2), 132.94 (CH), 135.50 (CH), 159.42 ($C_{quat.}$), 234.23 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 18.13 (CH_3), 34.00 (CH), 41.25 (CH_2), 84.25 ($C_{quat.}$), 87.46 ($C_{quat.}$), 94.94 (CH), 95.62 (CH), 96.06 (CH), 110.41 ($C_{quat.}$), 111.77 ($C_{quat.}$), 114.33 (CH), 114.77 ($C_{quat.}$), 118.30 (CH_2), 133.00 (CH), 134.63 (CH), 234.26 ($C_{quat.}$, CO). EI MS (70 eV, m/z (%)): 412 (M^+, 23), 328 (M^+ − 3 CO, 100), 287 (M^+ − 3 CO, − CH_2CH=CH_2, 12), 276 (M^+ − $Cr(CO)_3$, 4), 235 (M^+ − $Cr(CO)_3$, − CH_2CH=CH_2, 50), 52 (Cr^+, 16). IR (KBr): $\tilde{\nu}$ 1959, 1890, 1643, 1606, 1509, 1291, 1249, 1031, 834, 664, 631 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 316 nm (10000). Anal. Calcd for $C_{23}H_{20}CrO_4$ (412.41): C, 66.99; H, 4.89. Found: C, 67.29; H, 5.00.

Cr(CO)$_3$(*o*-Cl-η^6-C$_6$H$_4$)CH[SCH(CH$_3$)$_2$]C=CPh (5o). Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.42 (m, 6 H), 3.39 (m, 1 H), 5.02−5.09 (m, 2 H), 5.34−5.46 (m, 2 H), 6.02 (m, 1 H), 7.30−7.51 (m, 5 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.76 (CH_3), 23.12 (CH_3), 35.06 (CH), 37.26 (CH), 85.81 ($C_{quat.}$), 86.16 (CH), 86.57 ($C_{quat.}$), 88.95 (CH), 93.68 (CH), 94.58 (CH), 106.47 ($C_{quat.}$), 114.46 ($C_{quat.}$), 122.35 ($C_{quat.}$), 128.28 (CH), 128.59 (CH), 131.72 (CH), 231.09 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 23.20 (CH_3), 36.15 (CH), 37.42 (CH), 84.93 ($C_{quat.}$), 87.82 (CH), 90.37 (CH), 92.41 (CH), 92.85 (CH), 128.33 (CH), 128.71 (CH), 131.84 (CH). EI MS (70 eV, m/z (%)): 436 (M^+, 3), 382/380 (M^+ − 2 CO, 11/26), 354/352 (M^+ − 3 CO, 31/77), 311/309 (M^+ − 3 CO, − C_3H_7, 9/15), 280/278 (M^+ − 3 CO, − S=CMe_2, 33/95), 274 (100), 242 (M^+ − 3 CO, − SC_3H_7, − Cl,

10), 223 (82), 190 ($C_{15}H_{10}^+$, 18), 52 (Cr^+, 28). IR (KBr): $\tilde{\nu}$ 2964, 2926, 1974, 1902, 1598, 1491, 1243, 1053, 820, 757, 692, 656, 619 cm^{-1}. UV/vis ($CHCl_3$): λ_{max} (ϵ) 247 nm (38600), 326 (13400). Anal. Calcd for $C_{21}H_{17}ClCrO_3S$ (436.88): C, 57.74; H, 3.92; Cl, 8.12; S, 7.34. Found: C, 56.56; H, 4.01; Cl, 8.55; S, 7.65.

$Cr(CO)_3$(*o*-Cl-η^6-C_6H_4)CH[$S(CH_2)_2COOCH_3$]C═CPh (5p). Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.64−2.79 (m, 2 H), 3.12−3.20 (m, 2 H), 3.69 (s, 3 H), 4.97 (m, 1 H), 5.09 (s, 1 H), 5.28−5.33 (m, 1 H), 5.41−5.47 (m, 1 H), 5.97−6.03 (m, 1 H), 7.31−7.52 (m, 5 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 28.69 (CH_2), 34.41 (CH_2), 36.04 (CH), 51.87 (CH_3), 85.61 ($C_{quat.}$), 85.95 (CH), 86.69 ($C_{quat.}$), 88.79 (CH), 93.78 (CH), 94.64 (CH), 105.73 ($C_{quat.}$), 114.52 ($C_{quat.}$), 122.04 ($C_{quat.}$), 128.32 (CH), 128.77 (CH), 131.75 (CH), 172.05 ($C_{quat.}$), 230.90 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 36.51 (CH), 87.66 (CH), 90.38 (CH), 92.85 (CH), 91.94 (CH), 131.87 (CH). neg. FAB MS (Cs^+, 20 kV, mNBA, *m*/*z*): 479.5 ([M−H]$^-$). EI MS (70 eV, *m*/*z* (%)): 398/396 (M^+ − 3 CO, 23/51), 280/278 (M^+ − 3 CO, − S═$CHCH_2CO_2CH_3$, 9/23), 227/225 (M^+ − $Cr(CO)_3$, − $S(CH_2)_2CO_2CH_3$, 33/100), 190 ($C_{15}H_{10}^+$, 18), 52 (Cr^+, 14). IR (KBr): $\tilde{\nu}$ 3084, 2953, 2926, 2222, 1973, 1901, 1738, 1598, 1491, 1437, 1361, 1247, 1051, 823, 759, 692, 657, 621 cm^{-1}. UV/vis (CH_2Cl_2): λ_{max} (ϵ) 245 (25700), 326 nm (9500). Anal. Calcd for $C_{22}H_{17}ClCrO_5S$ (480.89): C, 54.95; H, 3.56; Cl, 7.37; S, 6.67. Found: C, 55.48; H, 3.99; Cl, 7.07; S, 7.08.

$Cr(CO)_3$(*o*-Cl-η^6-C_6H_4)CH[$N(CH_2)_4O$]C≡CPh (5q). Yellow crystals, mp 145 °C (diethyl ether/pentane). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.69 (m, 4 H), 3.69−3.72 (m, *J* = 4.8 Hz, 4 H), 4.91 (s, 1 H), 5.04 (m, 1 H), 5.42−5.45 (m, 2 H), 5.90 (d, *J* = 6.2 Hz, 1 H), 7.32−7.54 (m, 5 H). Additional signals for the minor diastereomer: δ 3.82 (m, 4 H), 5.11 (m, 1 H), 6.23 (d, *J* = 6.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 49.42 (CH_2), 59.04 (CH), 66.96 (CH_2), 81.11 ($C_{quat.}$), 86.97 (CH), 90.03 ($C_{quat.}$), 90.96 (CH), 93.20 (CH), 93.65 (CH), 103.39 ($C_{quat.}$), 114.56 ($C_{quat.}$), 122.14 ($C_{quat.}$), 128.37 (CH), 128.69 (CH), 131.93 (CH), 231.09 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 447 (M^+, 4), 393/391 (M^+ − 2 CO, $^2/_6$), 365/363 (M^+ − 3 CO, 12/32), 276 (M^+ − $Cr(CO)_3$, − Cl, 76), 248 (32), 227/225 (M^+ − $Cr(CO)_3$, − NC_4H_8O, 9/27) 191 ((M^+ − $Cr(CO)_3$, − NC_4H_7O, − Cl, 100), 190 ($C_{15}H_{10}^+$, 10), 189 (42), 52 (Cr^+, 14). IR (KBr): $\tilde{\nu}$ 2924, 2855 1977, 1901, 1630, 1490, 1115, 1070, 760, 621 cm^{-1}. UV/vis ($CHCl_3$): λ_{max} (ϵ) 323 nm (10800). Anal. Calcd for $C_{22}H_{18}ClCrNO_4$ (447.84): C, 59.00; H, 4.05; Cl, 7.92; N, 3.13. Found: C, 59.18; H, 3.98; Cl, 7.92; N, 2.87.

$Cr(CO)_3$(*o*-Cl-η^6-C_6H_4)CH[$C(CH_3)_2COOCH_3$]C≡CPh (5r). Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.40 (s, 3 H), 1.49 (s, 3 H), 3.70 (s, 3 H), 4.15 (s, 1 H), 4.91 (dt, *J* = 6.1 Hz, *J* = 1.2 Hz, 1 H), 5.34−5.43 (m, 2), 5.45 (d, *J* = 6.4 Hz, 1 H), 7.26−7.30 (m, 3 H), 7.44−7.49 (m, 2 H). Additional signals for the minor diastereomer: δ 1.31 (s, 3 H), 3.71 (s, 3 H), 4.62 (s, 1 H), 5.06 (dt, *J* = 6.2 Hz, *J* = 1.0 Hz, 1 H), 5.86 (dd, *J* = 6.4 Hz, *J* = 1.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.51 (CH_3), 25.19 (CH_3), 46.46 (CH), 49.58 ($C_{quat.}$), 52.28 (CH_3), 85.32 ($C_{quat.}$), 86.47 (CH), 87.28 ($C_{quat.}$), 91.56 (CH), 93.43 (CH), 96.87 (CH), 104.77 ($C_{quat.}$), 114.02 ($C_{quat.}$), 123.17 ($C_{quat.}$), 128.09 (CH), 128.18 (CH), 131.48 (CH), 175.79 ($C_{quat.}$), 231.06 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 22.11 (CH_3), 23.24 (CH_3), 41.84 (CH), 48.78 ($C_{quat.}$), 85.46 ($C_{quat.}$), 86.60 ($C_{quat.}$), 87.00 (CH), 89.36 (CH), 93.64 (CH), 93.80 (CH), 105.73 ($C_{quat.}$), 114.33 ($C_{quat.}$), 122.61 ($C_{quat.}$), 128.19 (CH), 128.31 (CH), 131.78 (CH), 175.44 ($C_{quat.}$), 231.09 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 462 (M^+, < 1), 406 (M^+ − 2 CO, 2), 380/378 (M^+ − 3 CO, 7/19), 276 (M^+ − $Cr(CO)_3$, − Cl, − CH_3, 2), 227/225 (M^+ − $Cr(CO)_3$, − $C(CH_3)_2CO_2CH_3$, 30/100), 191 (M^+ − $Cr(CO)_3$, − CH_2═$C(CH_3)CO_2CH_3$, − Cl, 12), 52 (Cr^+, 4). IR (KBr): $\tilde{\nu}$ 2982, 2951, 1973, 1902, 1731, 1598, 1491, 1469, 1443, 1250, 1128, 1057, 758, 692, 659, 621 cm^{-1}. UV/vis ($CHCl_3$): λ_{max} (ϵ) 324 nm (7600). Anal. Calcd for $C_{23}H_{19}ClCrO_5$ (462.85): C, 59.69; H, 4.14; Cl: 7.66. Found: C, 60.03; H, 4.31; Cl, 7.48.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$S(CH_2)_2COOCH_3$]C≡C-$(CH_2)_3CH_3$ (5s). Yellow oil. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ 0.83−0.90 (t, *J* = 7.1 Hz, 3 H), 1.29−1.52 (m, 4 H), 2.22 (dt, *J* = 6.5 Hz, *J* = 1.9 Hz, 2 H), 2.56−2.75 (m, 2 H), 2.84−3.02 (m, 2 H), 3.60 (s, 3 H), 3.75 (s, 3 H), 4.86 (s, 1 H), 5.16 (t, *J* = 6.3 Hz, 1 H), 5.56 (d, *J* = 7.0 Hz, 1 H), 5.94 (t, *J* = 6.2 Hz, 1 H), 6.16 (d, *J* = 6.0 Hz, 1 H). Additional signals for the minor diastereomer: δ 2.29 (dt, *J* = 6.7 Hz, *J* = 1.9 Hz, 2 H), 3.58 (s, 3 H), 3.74 (s, 3 H), 4.85 (s, 1 H), 5.29 (t, *J* = 6.3 Hz, 1 H), 5.61 (d, *J* = 7.0 Hz, 1 H), 6.07 (d, *J* = 5.9 Hz, 1 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 13.55 (CH_3), 17.92 (CH_2), 21.46 (CH_2), 27.96 (CH_2), 30.29 (CH_2), 32.31 (CH), 34.09 (CH_2), 51.59 (CH_3), 56.54 (CH_3), 75.22 (CH), 78.01 ($C_{quat.}$), 85.42 (CH), 85.86 ($C_{quat.}$), 96.99 (CH), 98.51 (CH), 100.47 ($C_{quat.}$), 142.50 ($C_{quat.}$), 171.92 ($C_{quat.}$), 233.62 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 18.02 (CH_2), 21.59 (CH_2), 26.23 (CH_2), 30.19 (CH_2), 32.44 (CH), 34.05 (CH_2), 56.65 (CH_3), 78.52 ($C_{quat.}$), 86.80 ($C_{quat.}$), 99.60 ($C_{quat.}$), 141.79 ($C_{quat.}$), 171.80 ($C_{quat.}$), 233.72 ($C_{quat.}$, CO). EI MS (70 eV, *m*/*z* (%)): 456 (M^+, 5), 372 (M^+ − 3 CO, 2), 254 (M^+ − 3 CO, − S═$CHCH_2CO_2CH_3$, 17), 220 (25), 201 (81), 52 (Cr^+, 100). IR (KBr): $\tilde{\nu}$ 2956, 2934, 2229, 1963, 1881, 1737, 1599, 1529, 1468, 1436, 1359, 1266, 1246, 1015, 666, 629 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 316 nm (7600). Anal. Calcd for $C_{21}H_{24}CrO_6S$ (456.48): C, 55.26; H, 5.30; S: 7.02. Found: C, 55.78; H, 5.64; S: 7.62.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$N(^iPr)_2$]C≡C$(CH_2)_3CH_3$ (5t). Yellow powder, mp 79−81 °C (diethyl ether/pentane). ^{1}H NMR ([D_6]-DMSO, 300 MHz): δ 0.80−0.88 (m, *J* = 6.8 Hz, 3 H), 1.13 (d, *J* = 6.7 Hz, 6 H), 1.17 (d, *J* = 6.4 Hz, 6 H), 1.24−1.38 (m, 4 H), 2.10−2.14 (m, 2 H), 3.13−3.27 (m, *J* = 6.3 Hz, 2 H), 3.74 (s, 3 H), 4.63 (s, 1 H), 5.18 (t, *J* = 6.3 Hz, 1 H), 5.54 (d, *J* = 6.9 Hz, 1 H), 5.88−5.92 (m, 2 H). Additional signals for the minor diastereomer: δ 2.19−2.23 (m, 2 H), 3.68 (s, 3 H), 4.73 (s, 1 H), 5.26 (t, *J* = 6.6 Hz, 1 H), 6.15 (d, *J* = 6.8 Hz, 1 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 13.52 (CH_3), 17.94 (CH_2), 20.13 (CH_3), 21.39 (CH_2), 23.84 (CH_3), 30.24 (CH_2), 45.10 (CH), 47.36 (CH), 56.27 (CH_3), 75.66 (CH), 80.59 ($C_{quat.}$), 83.86 ($C_{quat.}$), 85.53 (CH), 96.61 (CH), 97.38 (CH), 107.01 ($C_{quat.}$), 142.42 ($C_{quat.}$), 234.39 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 18.07 (CH_2), 20.23 (CH_3), 21.61 (CH_2), 23.99 (CH_3), 30.29 (CH_2), 45.66 (CH), 45.73 (CH). EI MS (70 eV, *m*/*z* (%)): 437 (M^+, 13), 353 (M^+ − 3 CO, 23), 254 (M^+ − 3 CO, − ^{i}PrN═CMe_2, 11), 220 (24), 151 (100), 52 (Cr^+, 15). IR (KBr): $\tilde{\nu}$ 2965, 2934, 1957, 1880, 1631, 1530, 1462, 1262, 644, 630 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 314 nm (8800). Anal. Calcd for $C_{23}H_{31}CrO_4N$ (437.50): C, 63.14; H, 7.14; N, 3.20. Found: C, 63.47; H, 7.08; N, 3.20.

$Cr(CO)_3$(*o*-OCH_3-η^6-C_6H_4)CH[$C(CH_3)_2COOCH_3$]C≡C-$(CH_2)_3CH_3$ (5u). Yellow oil. ^{1}H NMR ([D_6]DMSO, 300 MHz): δ 0.86 (t, *J* = 6.9 Hz, 3 H), 1.18 (s, 3 H), 1.20 (s, 3 H), 1.39−1.42 (m, *J* = 3.3 Hz, 4 H), 2.16−2.22 (m, 2 H), 3.55−3.59 (m, *J* = 2.0 Hz, 1 H), 3.57 (s, 3 H), 3.69 (s, 3 H), 5.07 (t, *J* = 6.2 Hz, 1 H), 5.58 (d, *J* = 7.1 Hz, 1 H), 5.89−5.93 (m, *J* = 6.3 Hz, 2 H). Additional signals for the minor diastereomer: δ 1.06 (s, 3 H), 4.18 (m, *J* = 2.1 Hz, 1 H), 5.28 (t, *J* = 6.2 Hz, 1 H), 5.53 (d, *J* = 6.9 Hz, 1 H), 5.96 (d, *J* = 6.5 Hz, 1 H). ^{13}C NMR ([D_6]DMSO, 75 MHz): δ 13.57 (CH_3), 17.98 (CH_2), 21.31 (CH_2), 23.19 (CH_3), 23.71 (CH_3), 30.51 (CH_2), 44.00 (CH), 48.02 ($C_{quat.}$), 51.93 (CH_3), 55.91 (CH_3), 76.38 (CH), 77.45 ($C_{quat.}$), 84.08 ($C_{quat.}$), 85.39 (CH), 97.41 (CH), 98.99 ($C_{quat.}$), 101.70 (CH), 143.88 ($C_{quat.}$), 175.36 ($C_{quat.}$), 233.93 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 17.86 (CH_2), 21.45 (CH_2), 22.01 (CH_3), 22.54 (CH_3), 30.36 (CH_2), 38.01 (CH), 47.30 ($C_{quat.}$), 52.00 (CH_3), 56.30 (CH_3), 75.11 (CH), 77.80 ($C_{quat.}$), 84.59 ($C_{quat.}$), 86.37 (CH), 96.98 (CH), 98.09 (CH), 99.46 ($C_{quat.}$), 143.17 ($C_{quat.}$), 175.31 ($C_{quat.}$). MS (70 eV, *m*/*z* (%)): 438 (M^+, 2), 382 (M^+ − 2 CO, 5), 354 (M^+ − 3 CO, 41), 212 (11), 201 (M^+ − $Cr(CO)_3$ − $C(CH_3)_2CO_2CH_3$, 100), 170 ($C_{13}H_{14}^+$, 2), 52 (Cr^+, 14). IR (KBr): $\tilde{\nu}$ 2955, 2936, 1963, 1882, 1732, 1528, 1470, 1264, 1128, 1017, 669, 628 cm^{-1}. UV/vis (DMSO): λ_{max} (ϵ) 315 nm (8000). Anal. Calcd for $C_{22}H_{26}CrO_6$ (438.44): C, 60.27; H, 5.98. Found: C, 60.86; H, 6.41.

Influence of the Lewis Acid on the Diastereomeric Ratio. (a) BF_3·OEt_2. According to the General Procedure, 107 mg (0.27 mmol) of **3e** was ionized with 50 μL (0.35 mmol) of BF_3·OEt_2 for 75 min and then reacted with 0.11 mL (0.54 mmol) of 1-methoxy-2-methyl-1-trimethylsiloxypropene for 120 min. After flash chromatography on silica gel, 83 mg (70%) of **5u** was isolated as a yellow oil and the diastereomeric ratio was determined by integration of the significant triplet signals (δ 5.07 and 5.28, respectively) on the complexed arene ring in the ^{1}H NMR spectrum to give dr = 62:38.

(b) TMSOTf. According to the General Procedure, 106 mg (0.27 mmol) of **3e** was ionized with 60 μL (0.33 mmol) of TMSOTf for 75 min and then reacted with 0.11 mL (0.54 mmol) of 1-methoxy-2-

methyl-1-trimethylsiloxypropene for 45 min. After flash chromatography on silica gel, 69 mg (59%) of **5u** was isolated as a yellow oil and the diastereomeric ratio was determined by integration of the significant triplet signals (δ 5.07 and 5.28, respectively) on the complexed arene ring in the ^{1}H NMR spectrum to give dr = 70:30.

(c) $SnCl_4$. According to the General Procedure, 100 mg (0.25 mmol) of **3e** was ionized with 40 μL (0.34 mmol) of $SnCl_4$ for 40 min and then reacted with 0.12 mL (0.59 mmol) of 1-methoxy-2-methyl-1-trimethylsiloxypropene for 20 min. After flash chromatography on silica gel, 59 mg (53%) of **5u** was isolated as a yellow oil and the diastereomeric ratio was determined by integration of the significant triplet signals (δ 5.07 and 5.28, respectively) on the complexed arene ring in the ^{1}H NMR spectrum to give dr = 68:32.

^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 0.86 (t, J = 6.8 Hz, 3 H), 1.19 (s, 3 H), 1.20 (s, 3 H), 1.35−1.44 (m, 4 H), 2.16−2.22 (m, 2 H), 3.57 (s, 3 H), 3.57−3.59 (m, J = 2.2 Hz, 1 H), 3.69 (s, 3 H), 5.07 (t, J = 6.3 Hz, 1 H), 5.58 (d, J = 7.0 Hz, 1 H), 5.89−5.93 (m, J = 6.0 Hz, 2 H). Additional signals for the minor diastereomer: δ 1.06 (s, 3 H), 4.18 (m, J = 2.2 Hz, 1 H), 5.28 (m, J = 6.3 Hz, 1 H), 5.53 (d, J = 6.7 Hz, 1 H), 5.95 (dd, J = 6.4 Hz, J = 1.0 Hz, 1 H). ^{13}C NMR ([D$_6$]-DMSO, 75 MHz): δ 13.55 (CH_3), 17.98 (CH_2), 21.31 (CH_2), 23.16 (CH_3), 23.71 (CH_3), 30.51 (CH_2), 44.01 (CH), 48.02 ($C_{quat.}$), 51.91 (CH_3), 55.89 (CH_3), 76.34 (CH), 77.43 ($C_{quat.}$), 84.08 ($C_{quat.}$), 85.35 (CH), 97.38 (CH), 98.97 ($C_{quat.}$), 101.67 (CH), 143.86 ($C_{quat.}$), 175.35 ($C_{quat.}$), 233.91 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 17.86 (CH_2), 21.45 (CH_2), 22.00 (CH_3), 22.52 (CH_3), 30.36 (CH_2), 38.01 (CH), 47.29 ($C_{quat.}$), 51.98 (CH_3), 56.27 (CH_3), 75.07 (CH), 77.79 ($C_{quat.}$), 84.58 ($C_{quat.}$), 86.33 (CH), 96.95 (CH), 98.06 (CH), 99.44 ($C_{quat.}$), 143.15 ($C_{quat.}$), 175.31 ($C_{quat.}$), 233.89 ($C_{quat.}$, CO).

(d) $TiCl_4$. Vide Supra Compound 5u. In Situ Ionization with $TiCl_4$ in the Presence of Nucleophile. 5u. A solution of 101 mg (0.26 mmol) of **3e** in 8 mL of dichloromethane was cooled to −78 °C, and 0.11 mL (0.54 mmol) of 1-methoxy-2-methyl-1-trimethylsiloxypropene was added. To this mixture was added 50 μL (0.46 mmol) of $TiCl_4$ dropwise. After 25 min of stirring at that temperature, the reaction mixture was worked up according to the General Procedure. After flash chromatography on silica gel, 60 mg (54%) of **5u** was isolated as a yellow oil and the diastereomeric ratio was determined by integration of the significant triplet signals (δ 5.07 and 5.27, respectively) on the complexed arene ring in the ^{1}H NMR spectrum to give dr = 34:66.

^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 0.87 (t, J = 6.8 Hz, 3 H), 1.06 (s, 3 H), 1.21 (s, 3 H), 1.33−1.49 (m, 4 H), 2.16−2.22 (m, 2 H), 3.58 (s, 3 H), 3.69 (s, 3 H), 4.18 (m, J = 2.1 Hz, 1 H), 5.27 (t, J = 6.3 Hz, 1 H), 5.53 (d, J = 6.9 Hz, 1 H), 5.87−5.92 (m, J = 6.0 Hz, 1 H), 5.96 (d, J = 6.2 Hz, 1 H). Additional signals for the minor diastereomer: δ 1.19 (s, 3 H), 3.57−3.59 (m, 1 H), 5.07 (t, J = 6.2 Hz, 1 H), 5.57 (d, J = 7.2 Hz, 1 H). ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 13.53 (CH_3), 17.86 (CH_2), 21.45 (CH_2), 22.00 (CH_3), 22.51 (CH_3), 30.36 (CH_2), 38.01 (CH), 47.29 ($C_{quat.}$), 51.97 (CH_3), 56.26 (CH_3), 75.04 (CH), 77.78 ($C_{quat.}$), 84.57 ($C_{quat.}$), 86.30 (CH), 96.93 (CH), 98.04 (CH), 99.43 ($C_{quat.}$), 143.13 ($C_{quat.}$), 175.31 ($C_{quat.}$), 233.87 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 13.55 (CH_3), 17.98 (CH_2), 21.31 (CH_2), 23.14 (CH_3), 23.72 (CH_3), 30.51 (CH_2), 44.01 (CH), 48.03 ($C_{quat.}$), 51.90 (CH_3), 55.87 (CH_3), 76.32 (CH), 77.43 ($C_{quat.}$), 84.08 ($C_{quat.}$), 85.33 (CH), 97.35 (CH), 98.96 ($C_{quat.}$), 101.65 (CH), 143.86 ($C_{quat.}$), 175.35 ($C_{quat.}$), 233.89 ($C_{quat.}$, CO).

5c. A solution of 105 mg (0.25 mmol) of **3a** in 8 mL of dichloromethane was cooled to −78 °C, and 0.11 mL (0.54 mmol) of 1-methoxy-2-methyl-1-trimethylsiloxypropene was added. To this mixturewas added 55 μL (0.50 mmol) of $TiCl_4$ dropwise. After 35 min of stirring at that temperature, the reaction mixture was worked up according to the General Procedure. After flash chromatography on silica gel, 60 mg (54%) of **5c** was isolated as a yellow oil and the diastereomeric ratio was determined by integration of the significant propargyl proton signals in the ^{1}H NMR spectrum to give dr = 43:57.

^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ 1.15 (s, 3 H), 1.30 (s, 3 H), 3.63 (s, 3 H), 3.73 (s, 3 H), 4.47 (s, 1 H), 5.31 (t, J = 6.2 Hz, 1 H), 5.58 (d, J = 6.9 Hz, 1 H), 5.90−5.97 (m, J = 6.3 Hz, 1 H), 6.10 (d, J = 6.3 Hz, 1 H), 7.32−7.45 (m, 5 H). Additional signals for the minor diastereomer: δ 1.27 (s, 6 H), 3.62 (s, 3 H), 3.89 (s, 1 H), 5.13 (t, J = 6.2 Hz, 1 H), 5.62 (d, J = 6.9 Hz, 1 H), 6.03 (d, J = 6.1 Hz, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ 22.01 (CH_3), 22.74 (CH_3), 38.63 (CH), 47.69 ($C_{quat.}$), 52.19 (CH_3), 56.39 (CH_3), 75.34 (CH), 84.24 ($C_{quat.}$), 86.62 (CH), 87.53 ($C_{quat.}$), 97.03 (CH), 97.98 (CH), 98.41 ($C_{quat.}$), 122.54 ($C_{quat.}$), 128.06 (CH), 128.61 (CH), 131.59 (CH), 143.00 ($C_{quat.}$), 175.23 ($C_{quat.}$), 233.82 ($C_{quat.}$, CO). Additional signals for the minor diastereomer: δ 23.47 (CH_3), 23.53 (CH_3), 44.57 (CH), 48.28 ($C_{quat.}$), 52.08 (CH_3), 56.13 (CH_3), 76.52 (CH), 84.01 ($C_{quat.}$), 85.63 (CH), 87.52 ($C_{quat.}$), 97.51 (CH), 97.76 ($C_{quat.}$), 101.55 (CH), 123.51 ($C_{quat.}$), 128.57 (CH), 131.30 (CH), 143.85 ($C_{quat.}$), 175.15 ($C_{quat.}$), 233.85 ($C_{quat.}$, CO).

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameter, and least-squares planes for compounds **3b**, **3e**, **3g**, **5c**, **5g**, and **5t**. This material is available free of charge via the Internet at http://pubs.acs.org.

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