Chromium-Templated Synthesis of Densely Substituted Distorted Arenes − Intramolecular Benzannulation of [(Alkynylaryl)alkenyl]carbene Complexes to Planar-Chiral Hydroquinoid [2.2]Heterametacyclophanes[‡]

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{[(*meta*-Alkynylphenyl)alkenyl]carbene}chromium compounds **1** and **2** have been synthesized by four-step (or five-step) and seven-step sequences, starting from 3-halophenol or 3-haloaniline, respectively. This approach, involving high-yielding Takai reactions and lithium cuprate additions, provides a novel and straightforward route to [(alkynylaryl)alkenyl](methoxy)carbene complexes. Upon gentle warming in tetrahydrofuran, (carbene)chromium compounds of this type undergo intramolecular benzannulation to give novel [2.2]heterametacyclophanes **21** and **22**, bearing two chiral planes arising from the unsymmetrical substitution patterns both of the cyclophane skeleton and of the newly formed, $Cr(CO)_3$-coordinated benzohydroquinone deck.

Introduction

The synthesis of densely substituted and, in particular, strained carbocycles and heterocycles is an ongoing challenge in organic synthesis.[2] Organometallic reactions have increasingly grown in importance for the construction of cyclic systems. In this context, Fischer-type carbene complexes have been shown to undergo a variety of cycloadditions, resulting in [2+1],[3−7] [2+2],[8] [2+3],[9] [4+3],[10] and [3+2+1][11,12] cycloaddition products. Depending on the type of reaction, the (carbene)metal moiety may be lost, retained or modified into another organometallic functionality. In particular, [3+2+1] cycloadditions of (alkoxy)(aryl or vinyl)carbene, alkyne, and carbonyl ligands occurring at a carbonylchromium template represent a straightforward route to densely substituted $Cr(CO)_3$-coordinated arenes. This type of benzannulation is compatible with a variety of functional groups in the alkyne part and the π-system of the carbene substituent; it proceeds under mild and neutral conditions and has been applied to the synthesis of various natural products.

We were interested in whether it may also be applied to the generation of strained arenes, and in view of this we focused our attention on cyclophanes. Cyclophanes[13] are of considerable interest in organometallic chemistry. The unsymmetrical, boat-like conformations imposed on the benzene decks in [2.2]para- and [2.2]metacyclophanes as a result of their short ethylene bridges have stimulated efforts to exploit the capabilities of distorted arenes for coordination to organometallic fragments,[14] culminating in the metal vapour cocondensation synthesis of the ([2.2]paracyclophane)chromium sandwich.[15] More recent studies have demonstrated that the nonplanar benzene deck in (carbene)chromium-functionalized [2.2]metacyclophanes is compatible with benzannulation by alkynes and have furthermore revealed a remarkable diastereoselective complexation of the resulting hydroquinoid naphthalenophanes by the $Cr(CO)_3$ fragment.[16]

The synthesis of the cyclophane skeleton is generally based on the dilution principle,[17] the cesium template effect,[18] and the junction of the arene decks through temporary assistance by heteroatoms which are finally removed by oxidation and reductive elimination.[19] Recently, we have established a complementary synthetic strategy based on a chromium-templated intramolecular benzannulation carbonylative cyclization of an [(alkynylaryl)alkenyl]carbene complex, to construct a densely substituted distorted arene deck.[20] Subsequently, a similar carbonylative cyclization approach has been applied to the synthesis of unstrained [10]meta- and -paracyclophanes.[21] In order to examine the scope of the intramolecular benzannulation methodology, we turned our attention to [(enyne)carbene]chromium compounds as potential precursors of even more strained chiral [2.2]heterametahydroquinonophanes, in which the strain within the cyclophane skeleton is enhanced by the incorporation of nitrogen or oxygen atoms into one of the two-atom bridges. The resulting shorter C−O and C−N bonds are expected to impose an additional helicity on the heteracyclophane skeleton.

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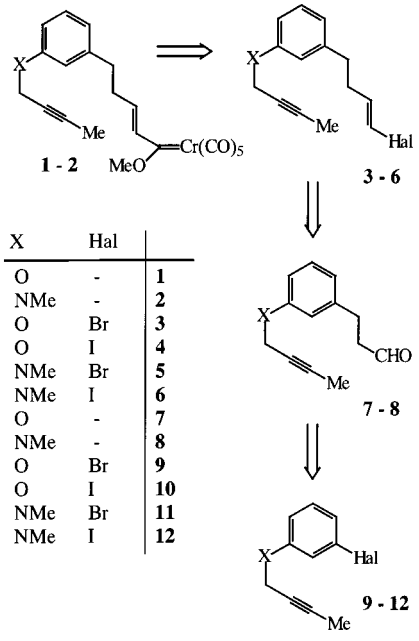
Results and Discussion

1. General Synthetic Strategy

On the basis of our previous work, chromium-templated intramolecular [3+2+1]benzannulation was planned as the key step for the formation of the [2.2]heterametacyclophane skeleton. A retrosynthetic strategy pointed to ({[(heteraalkynyl)aryl]alkenyl}carbene)chromium compounds **1** and **2** as benzannulation precursors; these can ultimately be traced back to *meta*-halophenols and -anilines (Scheme 1). The (enyne)(methoxy)carbene complexes should be accessible from vinyl halides **3**−**6** by a standard Fischer method. For the formation of the C=C bond we envisaged the olefination of aldehydes **7** and **8**. The synthesis of alkynylaryl halides **9**−**12** requires routes different from those applied for the symmetrical ethylene-bridged analogues.[20] For example, promising approaches may be based on the Mitsunobu reaction[22] or on nucleophilic substitution reactions.



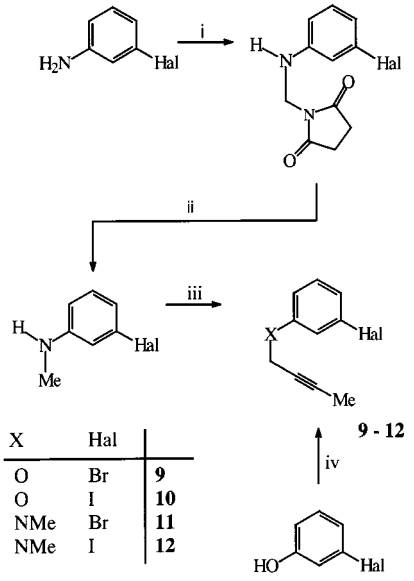
X	Hal	
O	-	1
NMe	-	2
O	Br	3
O	I	4
NMe	Br	5
NMe	I	6
O	-	7
NMe	-	8
O	Br	9
O	I	10
NMe	Br	11
NMe	I	12

Scheme 1. Retrosynthetic strategy

2. Synthesis of the Aldehydes Containing the Alkyne Side Chain

The construction of the cyclophane hydroquinone deck by intramolecular benzannulation requires (alkoxycarbene)chromium complexes bearing the (vinyl)carbene moiety separated from the alkyne by a *meta*-ethylene(heteraethylene)benzene spacer. Suitable starting materials are 3-halophenols and 3-haloanilines, which allow for sequential elaboration of the alkynyl and the [(alkenyl)carbene]chromium side-chains.

The nitrogen-containing alkynes **11** and **12** were prepared from 3-bromoaniline and 3-iodoaniline as starting materials. These were monomethylated by a two-step procedure involving *N*-hydroxymethylation, substitution by *N*-succinimide and final reduction by sodium borohydride[23]. Coupling with 1-bromobut-2-yne in the presence of cesium



X	Hal	
O	Br	9
O	I	10
NMe	Br	11
NMe	I	12

i: HCHO, succinimide, Et_2O, 24 h, 84 °C, 70%
ii: $NaBH_4$, DMSO, 30 min, 140 °C, 85%
iii: 1-bromo-but-2-yne, Cs_2CO_3, 4 d, 90%
iv: PPh_3, DEAD, 2-butyne-1-ol

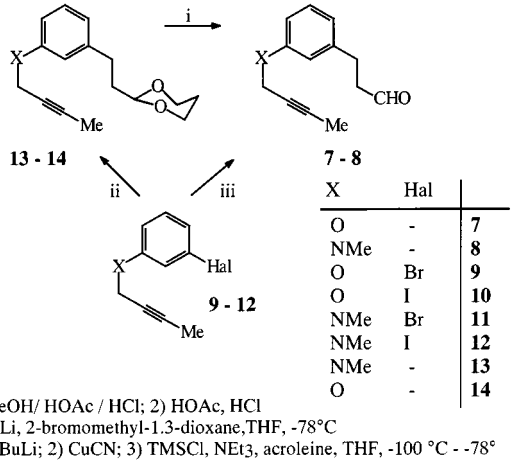
Scheme 2. Preparation of alkynes **9**−**12**

carbonate afforded alkynylhaloanilines **11** and **12** in 90% yield. Their oxa analogues **9** and **10** were obtained by means of Mitsunobu reactions[22] between 3-halophenols and 2-butyn-1-ol, in 90 and 95% yields (Scheme 2).

Two approaches for incorporation of the formylethyl side-chain were investigated. We first focused on a C_3 equivalent provided by 2-bromoethyl-1,3-dioxane, which was coupled to haloarenes **9** and **10** after halogen/lithium exchange.[20] Deprotection of the acetal was accomplished by acid-catalysed transacetalization with methanol to give aldehydes **7** and **8** in yields that did not exceed 39 and 42%, respectively, after 7 d. However, access to these intermediates was significantly improved when introduction of the propanal chain was carried out by lithium cuprate addition. In this approach, halobenzenes **9**−**12** were lithiated, followed by addition of copper(I) cyanide. Treatment of the organolithium cyanocuprate intermediates with acrolein was effected under very mild conditions, at −100 °C in the presence of triethylamine and trimethylsilyl chloride. After quenching with hydrochloric acid, aldehydes **7** and **8** were obtained in yields varying from 55 to 70% in a single step within 10 h (Scheme 3).[24,25]

3. Synthesis of the {[(Oxaalkynyl)phenyl]alkenyl}carbene Complex 1

Our first approach to the [(vinyl)carbene]chromium functionalization of the arylpropanal **7** was based on a bromoolefination. Wittig methodology with (bromomethyl)triphenylphosphonium bromide and potassium *tert*-butoxide[26] resulted in a selective (*E*) olefination, to give a 30%



Scheme 3. Preparation of aldehydes **7** and **8**

yield of the vinyl bromide **15**, which was modified to the [(enyne)carbene]chromium compound **1** by the Fischer procedure (Scheme 4).[27] Metallation of the bromoalkene **15** with *tert*-butyllithium, followed by addition of hexacarbonylchromium, afforded the acylchromate intermediate, which was alkylated with trimethyloxonium tetrafluoroborate (Meerwein's salt) to give **1** in moderate yield (40%).

In order to improve the synthetic accessibility of the (enyne)carbene complex **1**, we studied the aldol condensation of the aldehyde **7** with the conjugate base of the [(methoxy)(methyl)carbene]chromium complex with a variety of Lewis acids under different conditions. At first, it was disappointing to see that the use of triethylamine/trimethylsilyl chloride,[28] of boron trifluoride−diethyl ether, and of titanium tetrachloride[29] all failed to bring about the formation of the desired α,β-unsaturated Fischer carbene complex. Tin tetrachloride, known to effect an efficient activation of the aldehyde component,[30] turned out to be the Lewis acid of choice, however, and afforded a 70% yield of carbene complex **1** in a single step, starting from aldehyde **7**. NMR studies showed exclusive formation of the (*E*) isomer ($^3J_{H,H}$ = 15.0 Hz), irrespective of the (*E*)/(*Z*) ratio in the bromoalkene precursor **15**. This result indicates a configurational lability of the lithioalkene intermediate under the reaction conditions.

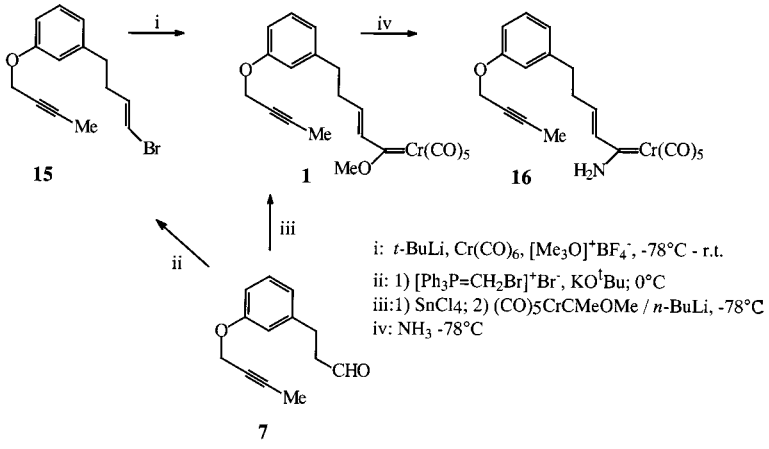
[(Enyne)carbene]chromium compound **1** underwent typical nucleophilic substitution reactions at the carbene carbon atom. For instance, quantitative ammonolysis occurred upon treatment with ammonia at −78 °C, to give the aminocarbene complex **16** (Scheme 4). Since (amino)(aryl)carbene complexes are known to undergo cyclopentannulation[31−36] rather than benzannulation, (amino)(enyne)carbene complexes may serve for the synthesis of additional cyclophane analogues.

4. Synthesis of the {[(Azaalkynyl)phenyl]alkenyl}carbene Complex 2

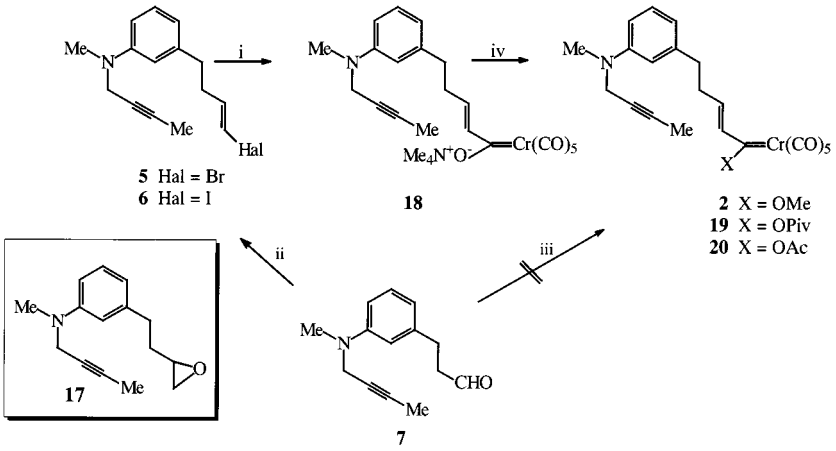
The aldol condensation approach as described for the {[(oxaalkynyl)phenyl]alkenyl}carbene complex **1** could not be successfully applied to the synthesis of its aza analogue **2**. No C=C bond formation could be observed when the arylpropanal **8** was treated with the carbene complex anion in the presence of various Lewis acids, which obviously added to the amine rather than to the carbonyl group of the aldehyde. However, the Wittig olefination turned out to be compatible with the presence of the amine functionality and afforded moderate yields of the vinyl halides **5** and **6**. The yields obtained reflect the competing formation of oxirane **17** − the result of a methylene group transfer to the carbonyl group − under the reaction conditions (Scheme 5).

Finally, the haloolefination reaction could be improved significantly by application of a methodology established by Takai and Utimoto.[37] By this route, the arylpropanal **7** underwent a clean coupling with bromoform in the presence of chromium(II) chloride to give a 70% yield of the vinyl bromide **5**. The coupling reaction was even more efficient with iodoform; in this case, however, chromatographic workup was complicated by the photolability of the excess of haloform used.

The synthesis of the aza analogue **2** required a different approach from that used for the oxa derivative **1**. The standard sequence of one-pot lithiation of the haloolefins **5** and **6**, addition of hexacarbonylchromium and methylation



Scheme 4. Synthesis and ammonolysis of **1**



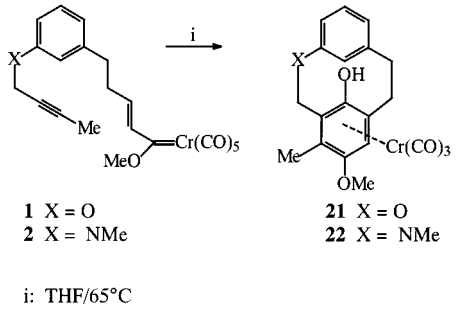
Scheme 5. Synthesis of (aza-enyne)carbene complex **2**

of the presumed acylmetallate failed to afford the (carbene)chromium compound **2**, due to the presence of the nucleophilic amine functionality, which presumably underwent competing alkylation. We therefore devised a complementary sequence, in which the electrophilic alkylation step was replaced by a nucleophilic substitution by the alcohol at the carbene carbon atom.[38] In this route, the lithium acylmetallate, accessible by addition of the vinyllithium reagents formed upon halogen/lithium exchange from the vinyl halides of **5** and **6** to $Cr(CO)_6$, was subjected to a metathesis reaction with tetramethylammonium bromide. The resulting tetramethylammonium metallate **18** was transformed at low temperature into the highly electrophilic (acetoxy)- and (pivaloyloxy)carbene complexes[39] **19** and **20**, which underwent methanolysis to give 40% yields of methoxycarbene complex (Scheme 5). Whereas the thermolabile acetoxy intermediate required temperatures below −40 °C, the (pivaloyloxy)carbene complex was more stable and could be handled at −10 °C. The tandem acylation/alcoholysis worked similarly efficiently when performed as a one-pot procedure without the metathesis step. In this case, the lithium acylchromate intermediate was transformed in situ into the (acetoxy)- or (pivaloyloxy)carbene complex, which was subsequently subjected to alcoholysis without further purification.

Like the corresponding oxaalkynyl complex **1**, the aza congener **2** was exclusively formed as the (*E*) isomer, as confirmed by NMR spectroscopy ($^3J_{H,H}$ = 15.0 Hz), irrespective of the (*E*)/(*Z*) ratio of the vinyl halide precursors **5** and **6**. The aza derivative **2** exhibited surprising thermal instability, which necessitated storage at low temperature.

5. Intramolecular Benzannulation to Give Hetera[2.2]metahydroquinonophanes 21 and 22

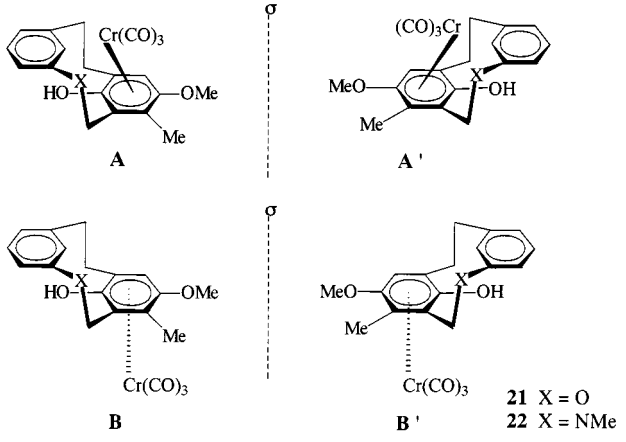
Upon being gently warmed in tetrahydrofuran, [(alkynylaryl)alkenyl](methoxy)carbene complexes **1** and **2** underwent *intra*molecular benzannulation to give the tricarbonylchromium-coordinated [2.2]metacyclophanes **21** and **22**. The reaction was most conveniently monitored by IR spectroscopy, and was complete within 3 h when carried out at 65 °C (Scheme 6). The yields obtained (10−15%) were inferior to those reported for the synthesis of the symmetrical bis(ethylene)-bridged analogues,[20] which reflects the additional strain imposed by the shortened carbon−heteroatom bond. As a result of the cyclophane skeleton and the complexation of the unsymmetrically substituted benzohydroquinone deck, the oxa- and azacyclophane complexes **1** and **2** combine two planes of chirality. Moreover, additional helicity is imposed in the [2.2]metacyclophane skeleton by the pair of unsymmetrical two-atom bridges.[40]



Scheme 6. Intramolecular benzannulation to give hetera[2.2]metahydroquinonophanes **21** and **22**

At low temperature in solution, [2.2]metacyclophane may adopt a *syn* conformation containing superimposed benzene rings. Above 0 °C, it is known to rearrange to the thermodynamically favoured *anti* conformation. For metal-coordinated [2.2]metacyclophanes, the *anti* conformation in which the two arene rings are arranged in a stepwise manner is generally observed.[14] As a consequence of the two planes of chirality arising from the unsymmetrical substitution pattern of the cyclophane and the coordination of the

metal atom from either the top or the bottom face, two *anti* pairs of enantiomers **A/A′** and **B/B′** might be expected for the benzannulation products **21** and **22** (Scheme 7). However, only a single diastereomer could be detected and isolated from the reaction mixture, suggesting that the *intra*molecular benzannulation had occurred diastereoselectively. *Inter*molecular benzannulation of the *anti*-[2.2]metacyclophane skeleton, generating a naphthohydroquinoid deck, has been shown to favour the formation of the *anti* diastereomer bearing the tricarbonylchromium fragment on the remote arene ring opposite to the other arene deck; at elevated temperature the metal atom underwent a haptotropic migration along the "*exo*" face to the less substituted naphthalene ring. The other diastereomer, bearing the metal atom on the more congested "*endo*" face of the hydroquinone, may be formed as a minor product; however, attempts to induce a similar haptotropic migration of the $Cr(CO)_3$ moiety in this isomer resulted in decomplexation.[16] Obviously, the inner hydrogen atom of the other benzene deck does not tolerate coordination of the central arene ring from the "*endo*" face. On the basis of these results we suggest that the intramolecular benzannulation generates a pair of enantiomers **B/B′**, bearing an "*exo*"-coordinated $Cr(CO)_3$ fragment. This assignment is supported by the observation of a sharp singlet for the $Cr(CO)_3$ fragment in the ^{13}C NMR spectrum, indicating free rotation along the arene−chromium axis on the NMR timescale.



Scheme 7. Possible *anti* pairs of enantiomers **A/A′** and **B/B′**

Conclusion

The intramolecular benzannulation of [(alkynylaryl)-alkenyl]carbene complexes of chromium is compatible with an unsymmetrical two-atom bridge containing oxygen or nitrogen as a heteroatom. It provides a novel and straightforward synthetic route to strained $Cr(CO)_3$-coordinated [2.2]metahydroquinonophanes bearing two planes of chirality defined by the unsymmetrical substitution pattern of the metal-coordinated hydroquinone deck and the cyclophane skeleton. The short heteroatom−carbon bond present in one of two bridges imposes helicity as an additional stereogenic element in the cyclophane. The cyclization of the (carbene)chromium precursors is mediated by a $Cr(CO)_3$ template and allows for a dense substitution pattern in the hydroquinone deck. It thus complements the customary syntheses of cyclophanes, which rely on the heteroatom-assisted combination of two differently functionalized *meta*-xylene precursors.

Experimental Section

General Remarks: All operations involving organometallic compounds were performed under argon using Schlenk techniques in flame-dried glassware. Di-*n*-butyl ether, dichloromethane, and petroleum ether were dried with calcium hydride, diethyl ether, and THF with Na/K. All solvents were saturated with argon and stored over molecular sieves. Silica gel (Merck, 0.063−0.200 mm) was degassed under vacuum and stored under argon. FT-IR spectra were recorded with a Nicolet Magna 550 spectrometer, NMR spectra with Bruker DRX 500, AM 400, or AM 250 spectrometers. All chemical shifts are given in ppm relative to TMS as external standard. HR-MS were determined with a Kratos MS-50 spectrometer. Elemental analyses were performed with a Heraeus CHN-Rapid instrument.

General Procedure for the Mitsunobu Reaction To Provide the Alkynes 9 and 10:[41] The 3-halophenol (40−60 mmol) was dissolved in tetrahydrofuran (10 mL per mmol halophenol), and triphenylphosphane (1.5 equiv.) and diethyl azodicarboxylate (DEAD; 1.3 equiv.) were added at 0 °C. The reaction mixture was stirred at room temp. until TLC indicated complete consumption of the starting material. For reaction times and purification, see below.

3-Bromo-1-(but-2-ynyl)benzene (9): The reaction was complete after stirring for 4 d. The solvent was evaporated and the residue was treated with petroleum ether and filtered to remove undissolved $Ph_3P{=}O$. The solvent was then removed, and chromatographic workup on silica gel with cyclohexane/*tert*-butyl methyl ether (20:1) gave **9** (11.9 g, 53 mmol, 95%). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, CH_3), 4.6 (s, 2 H, O−CH_2), 6.9 (d, ^3J = 7.94 Hz, 1 H, aryl-H6), 7.13 (pseudo-t, ^3J = 7.86 Hz, 1 H, aryl-H), 7.10 (m, 1 H, aryl-H), 7.09 (d, ^3J = 7.78 Hz, 1 H, aryl-H8). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.70 (CH_3), 56.60 (Ar−OCH_2), 73.42 ($CH_3-C{\equiv}C$), 83.71 ($CH_3-C{\equiv}C$), 113.79, 118.15, (2 C, aryl-CH), 122.70 (aryl-C3), 124.31, 130.48 (2 C, aryl-CH), 158.52 (aryl-C1). MS (EI): *m*/*z* (%) = 223/225 (34/38) [M^+], 174/172 (25) [M^+ − $CH_2{=}CH-C{\equiv}CH$], 145 (90) [M^+ − Br], 53 (100) [$CH_2-C{\equiv}C-CH_3^+$]. HR-MS: found for $C_{10}H_9BrO$ 223.9830, calcd. 223.9837.

1-(Butyn-2-yl)-3-iodobenzene (10): The reaction mixture was stirred for 4 d. Column chromatography on silica gel (cyclohexane/*tert*-butyl methyl ether, 33:1; R_f = 0.49) afforded **10** in 90% yield (9.8 g, 36 mmol). ^1H NMR (500 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, CH_3), 4.6 (s, 2 H, OCH_2), 6.92 (d, ^3J = 7.80 Hz, 1 H, aryl-H6), 6.98 (pseudo-t, ^3J = 7.80 Hz, 1 H, aryl-H), 7.28 (dd, ^3J = 7.80 Hz, 1 H, aryl-H), 7.29 (m, 1 H, aryl-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.65 (CH_3), 56.41 (Ar−O−CH_2), 73.41 ($CH_3-C{\equiv}C$), 84.12 ($CH_3-C{\equiv}C$), 94.18 (Ar-C3), 114.30, 123.91, 130.21, 130.61 (4 C, aryl-CH), 158.17 (aryl-C1). MS (EI): *m*/*z* (%) = 272 (72) [M^+], 257 (19), 220 (56), 145 (100), 115 (25) [$CH_2-C{\equiv}C-CH_3^+$], 93 (29), 64 (24). HR-MS: found for $C_{10}H_9IO$ 271.9699, calcd. 271.9698; calcd. C 44.14, H 3.33; found C 44.26, H 3.45.

General Procedure for the Synthesis of Alkynes 11 and 12: Cesium carbonate (24.50 g, 75.2 mmol) was added to a solution of haloani-

line (49.4 mmol) and 1-bromo-2-butyne (10.0 g, 75.2 mmol) in acetone (90.0 mL) and water (20.0 mL), and the mixture was stirred at room temp. for 4 d. The remaining cesium salt was removed by filtration, and the residue was extracted with dichloromethane. The combined organic layers were washed with water and dried with magnesium sulfate.

3-Bromo-*N*-but-2-ynyl-*N*-methylaniline (11):[23] Evaporation of the solvent and chromatographic workup on silica gel with cyclohexane/*tert*-butyl methyl ether (1:1; R_f = 0.8) afforded *N*-but-2-ynyl-*N*-methyl-3-bromoaniline (**11**; 10.5 g, 44.5 mmol, 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.76 (t, ^5J = 2.30 Hz, 1 H, CH_3), 2.93 (s, 3 H, N−CH_3), 6.71 (ddd, 1 H, Aryl-H, ^3J = 8.50, ^4J = 2.60, ^4J = 1.00 Hz), 3.95 (q, ^5J = 2.30 Hz, 2 H, CH_2), 6.71 (ddd, ^3J = 8.50, ^4J = 2.40, ^4J = 1.0 Hz, 1 H, Aryl-H), 6.73 (ddd, ^3J = 7.80, ^4J = 2.00, ^4J = 1.00 Hz), 6.92 (dd, 1 H, Aryl-H, ^3J = 8.50, ^4J = 2.70, ^4J = 2.00 Hz, 1 H, aryl-H), 7.31 (ddd, ^3J = 7.80, ^4J = 2.00, ^4J = 1.00 Hz, 1 H, aryl-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.49 (CH_3), 38.37 (N−CH_3), 42.44 (N−CH_2), 73.93 (C≡*C*CH_3), 79.97 (*C*≡CCH_3), 112.29, 116.52, 120.32, (3 C, aryl-CH), 123.23 (aryl-C3), 129.21, 130.21 (aryl-CH), 150.40 (aryl-C1). MS (EI): *m*/*z* (%) = 237/239 (100/89) [M^+], 222/224 (18/19) [$M^+ - CH_3$], 184 (16), 158 (27) [M^+ − Br], 143 (25), 53 (25). HR-MS: found for $C_{11}H_{12}BrN$ 237.0157, calcd. 237.0153; calcd. C 55.48, H 5.08; found C 55.08, H 5.07.

***N*-But-2-ynyl-3-iodo-*N*-methylaniline (12):**[23] After evaporation of the solvent and chromatographic workup on silica gel with cyclohexane/*tert*-butyl methyl ether (1:1; R_f = 0.8), *N*-but-2-ynyl-3-iodo-*N*-methylaniline (**11**; 12.7 g, 44.5 mmol, 90%) was obtained. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (t, ^5J = 2.30 Hz, 1 H, CH_3), 2.91 (s, 3 H, N−CH_3), 3.93 (q, ^5J = 2.30 Hz, 2 H, CH_2), 6.76 (ddd, ^3J = 7.80, ^4J = 2.44, ^4J = 1.40 Hz, 1 H, aryl-H), 6.93 (pseudo-t, 1 H, aryl-H, 3 *J* = 7.80 Hz), 7.06 (t, ^4J = 1.46 Hz, 1 H, aryl-H), 7.09 (t, ^4J = 1.40 Hz, 1 H, Aryl-H), 7.12 (dd, ^4J = 2.44, ^4J = 1.40 Hz, 1 H, aryl-H) 13 C NMR (125 MHz, $CDCl_3$): δ = 3.53 (CH_3), 38.36 (N−CH_3), 42.44 (N−CH_2), 73.89 (C≡*C*CH_3), 80.02 (*C*≡CCH_3), 95.34 (Ar-3) 113.01, 122.51, 126.50, 130.37 (4 C, aryl-CH), 150.27 (aryl-C1) MS (EI): *m*/*z* (%) = 237/239 (100/89) [M^+], 222/224 (18/19) [$M^+ - CH_3$], 184 (16), 158 (27) [M^+ − Br], 143 (25), 53 (25). HR-MS: found for $C_{11}H_{12}IN$ 285.001, calcd. 285.0014; calcd. C 46.50, H 3.90, N 4.93; found C 46.45, H 4.27, N 4.91.

General Procedure for the Synthesis of Aldehydes 7 and 8 with a C_3 Equivalent Provided by (2-Bromomethyl)-1,3-dioxane:[42] *t*BuLi (20 mmol) was added slowly at −78 °C to a solution of alkyne **9**−**12** (10 mmol) in tetrahydrofuran (30 mL). The mixture was stirred for 2 h, during which a colour change from yellow to red took place, and it was transferred by syringe into a solution of 2-(2-bromoethyl)-1,3-dioxane (1.6 mL, 12 mmol) in tetrahydrofuran (50 mL) and allowed to warm up to −30 °C. The reaction was monitored by GC-MS and, after 7.5 h, water was added with vigorous stirring to quench the reaction. The mixture was extracted with *tert*-butyl methyl ether, dried with magnesium sulfate and concentrated to dryness, and the residue was purified by chromatography on silica gel.

2-{2-[3-[But-2-ynyloxy)phenyl]ethyl}-1,3-dioxane (14): Starting from alkyne **9** or **10**, 2-{2-[3-[but-2-ynyloxy)phenyl]ethyl}-1,3-dioxane (**14**) was obtained after chromatography (eluent: petroleum ether/ethyl acetate, 10:1; R_f = 0.23) as a yellow oil (1.0 g, 3.9 mmol, 39%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (dtt, ^2J = 13.50 Hz, 1 H, CH), 1.86 (t, ^5J = 2.30 Hz, 3 H, CH_3), 1.91 (m, 2 H, CH_2), 2.08 (dtt, ^2J = 13.50 Hz, 1 H, CH), 2.69 (tq, 2 H, CH_2), 3.76 (ddd, ^2J = 12.20, ^3J = 2.4 Hz, 2 H), 4.11 (dd, ^2J = 10.60, ^3J = 5.0 Hz, 2 H), 4.51 (t, 1 H, CH), 6.80 (m, 3 H, aryl-H), 7.20 (m, 1 H, aryl-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.71 (CH_3), 25.77 (*C*H_2C≡C), 30.10 (*C*H_2CH_2CH), 36.40 (CH_2*C*H_2CH), 56.20 (OCH_2), 66.84 (C-3,5), 74.04 (C≡*C*CH_3), 83.57 (*C*≡CCH_3), 101.35 (C1), 112.00, 114.90, 121.36, 129.23, (4C, aryl-CH), 143.26 (aryl-C3), 157.80 (aryl-C1). MS (EI): *m*/*z* (%) = 260 (19) [M^+], 245 (5) [$M^+ - CH_3$], 207 (40) [$M^+ - H_2C-C\equiv C-CH_3$], 201 (5) [$M^+ - CH_2-CH_2-CH_2OH$], 160 (100) [$M^+ - C_5H_8O_2$], 145 (30), 87 (97), 53 (50) [$^+CH_2-C\equiv C-CH_3$]. HR-MS: found for $C_{16}H_{20}O_3$ 260.1413, calcd. 260.1412.

3-[3-(Butyn-2-yloxy)phenyl]propanal (7): The dioxane acetal **14** (3.9 mmol, 1.0 g) was cleaved by stirring in a mixture of methanol (75 mL), glacial acetic acid (20 mL), and conc. hydrochloric acid (0.5 mL) for 4 d. This mixture was cautiously poured into a saturated aqueous solution of sodium hydrogen carbonate, and the dimethyl acetal was extracted with diethyl ether. The combined extracts were dried with magnesium sulfate and the solvents were evaporated. The residue was then dissolved in a mixture consisting of glacial acetic acid (50 mL), water (5 mL), and conc. hydrochloric acid (0.5 mL) and stirred for another 3 d. The solution was slowly poured into saturated aqueous sodium hydrogen carbonate. Additional sodium hydrogen carbonate was added until the solution became basic. Extraction with diethyl ether, drying with magnesium sulfate, evaporation of the solvent, and column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as eluent afforded 3.51 mmol (710 mg, 90%) of aldehyde **7** as a slightly yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, CH_3), 2.75 (t, ^3J = 7.50 Hz, 2 H, CHO−CH_2−CH_2−Ar), 2.91 (t, ^3J = 7.55 Hz, 2 H, CHO−CH_2−CH_2−Ar,), 4.60 (s, 2 H, Ar−OCH_2), 6.78 (m, 3 H, aryl-H), 7.19 (t, ^3J = 7.75 Hz, 1 H, aryl-H), 9.78 (s, 1 H, CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.65 (CH_3), 28.03 (CHO−CH_2−*C*H_2−Ar), 45.04 (CHO−*C*H_2−CH_2−Ar), 56.22 (Ar−O−CH_2), 73.90 (C≡*C*CH_3), 83.71 (*C*≡CCH_3),112.27, 114.95, 121.10, 129.49 (4 C, aryl-CH), 141.85 (aryl-C3), 157.90 (aryl-C1), 201.55 (CHO). MS (EI): *m*/*z* (%) = 202 (13), 187 (25), 159 (67), 53 (100) [$CH_2-C\equiv C-CH_3^+$]. HR-MS: found for $C_{13}H_{14}O_2$ 202.0987, calcd. 202.0994; calcd. C 77.20, H 6.98, found C 77.21, H 6.90.

***N*-But-2-ynyl-*N*-3-[2-(1,3-dioxan-2-yl)ethyl]-*N*-methylaniline (13):** *N*-But-2-ynyl-*N*-3-[2-(1,3-dioxan-2-yl)ethyl]-*N*-methylaniline (**13**) was obtained from alkynes **11** or **12** as starting materials after chromatography (eluent: petroleum ether/ethyl acetate, 4:1; R_f = 0.28), as a slightly yellow oil (1.15 g, 4.2 mmol, 42%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (dd, ^2J = 12.50, ^3J = 2.0 Hz, 1 H, CH), 1.86 (t, ^5J = 2.20 Hz, 3 H, CH_3), 1.92 (m, 2 H, CH_2), 2.08 (dtt, ^2J = 12.50, ^3J = 5.0 Hz, 1 H, CH), 2.69 (tq, ^3J = 8.0 Hz, 2 H, CH_2), 2.94 (s, 3 H, NCH_3), 3.75 (ddd, ^2J = 12.50, ^3J = 2.0 Hz, 2 H), 4.13 (dd, ^2J = 11.20, ^3J = 5.0 Hz, 2 H), 4.53 (t, ^3J = 8.0 Hz, 1 H, CH), 6.70 (m, 3 H, aryl-H), 7.20 (m, 1 H, aryl-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.49 (CH_3), 25.77 (C-4), 30.48 (*C*H_2CH_2CH), 36.63 (*C*H_2CH), 38.54 (O*C*H_2), 66.78 (C-3,5), 74.52 (C≡*C*CH_3), 79.50 (*C*≡CCH_3), 101.51 (C1), 111.53, 114.17, 118.02, 128.90, (4 C, aryl-CH), 142.42 (aryl-C3), 149.29 (aryl-C1). MS (EI): *m*/*z* (%) = 273 (85) [M^+], 258 (18) [$M^+ - CH_3$], 214 (22), 186 (68), 172 (91), 144 (53), 87 (35). HR-MS: found for $C_{17}H_{23}NO_2$ 273.1717, calcd. 273.1723.

3-{3-But-2-ynyl(methyl)amino]phenyl}propanal (8) As in the procedure above, compound **13** was cleaved over a course of 7 d. Column chromatography on silica gel with petroleum ether/ethyl acetate (4:1; R_f = 0.28) as eluent afforded aldehyde **8** (3.78 mmol, 815 mg, 90%) as a slightly yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.76 (t, ^5J = 2.3 Hz, 3 H, CH_3), 2.76 (td, ^3J = 8.0, ^4J = 1.5 Hz, 2

H, CH_2CH), 2.91 (t, ^3J = 7.6 Hz, 2 H, aryl-CH_2), 2.94 (s, 3 H, NCH_3), 3.96 (q, ^5J = 2.3 Hz, 2 H, N−CH_2), 6.60 (d, ^3J = 7.5 Hz, 1 H, aryl-CH), 6.64 (*t*, ^4J = 2.5 Hz, 1 H, aryl-CH), 6.68 (dd, ^3J = 8.0 Hz, 1 H, ^4J = 2.7 Hz, aryl-CH), 7.17 (dd, ^3J = 8.0 Hz, 1 H, ^3J = 7.5 Hz, aryl-CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.51 (CH_3−C≡C), 28.57 (CH_2CH_2), 38.51 (NCH_3), 42.58 (NCH_2), 45.33 (CH_2CH_2), 74.40 (C≡CCH$_3$), 79.68 (C≡CCH$_3$), 111.97, 113.89, 117.62, 129.23 (4 C, aryl-CH), 141.11 (aryl-C, C-3), 149.46 (aryl-C1), 201.94 (CHO). MS (EI): *m*/*z* (%) = 215 (64) [M^+]; 200 (30) [M^+ − CH_3], 186 (100) [M^+ − CHO], 172 (55) [M^+ − $CHOCH_2$], 158 (65) [M^+ − $CHOC_2H_4$], 144 (66) [M^+ − $CHOC_3H_6$], 132 (18) [M^+ − $MeNC_4H_6$], 91 (33) [$C_6H_5N^+$], 77 [$C_6H_5^+$] (24), 63 (10) [$C_5H_3^+$], 53 (13) [$C_4H_5^+$]. HR-MS: found for $C_{14}H_{17}NO$ 215.1307, calcd. 215.1310; calcd. C 78.10, H 7.96; found C 77.85, H 7.95.

General Procedure for the Lithium Cuprate Addition to Aldehydes 7 and 8:[24] *t*BuLi (20.0 mmol) was slowly added at −78 °C to a solution of alkyne (10 mmol) in tetrahydrofuran (75 mL). The mixture was stirred for 45 min, and copper cyanide (0.9 g, 10.1 mmol) was then slowly added. The mixture was again stirred for 2 h, during which the colour changed from dark purple to yellow, and was then cooled to −100 °C. A mixture of triethylamine (4.5 mL, 32.3 mmol) and trimethylsilyl chloride (3.8 mL, 28.3 mmol) was added, followed by a solution of acrolein (0.8 mL, 12.1 mmol) in tetrahydrofuran (10 mL). After stirring for 90 min at −100 °C, the mixture was allowed to warm to −50 °C; the reaction was then quenched with water and the mixture was extracted with *tert*-butyl methyl ether. The combined organic layers were stirred for 10 min in a mixture of glacial acetic acid (50 mL) and dil. hydrochloric acid (50 mL). The solution was slowly poured into saturated aqueous sodium hydrogen carbonate and additional sodium hydrogen carbonate was added until it became basic. Extraction with *tert*-butyl methyl ether, drying with magnesium sulfate, evaporation of the solvent, and column chromatography afforded the aldehydes as yellow oils.

3-[3-(Butyn-2-yloxy)phenyl]propanal (7): Compound **7** (2.68 g, 13.0 mmol, 65%) was obtained from bromoalkyne **9** after column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1; R_f = 0.22). With iodoalkyne **10**, aldehyde **7** was obtained in 60% yield (2.47 g, 12.2 mmol).

3-{3-[But-2-ynyl(methyl)amino]phenyl}propanal (8) Starting from 11 or 12: From alkyne **11**: Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 10:1; R_f = 0.48) afforded 1.5 g (7.2 mmol, 70%) of **8** as a slightly yellow oil. From alkyne **12**: The reaction yielded 750 mg (3.6 mmol, 70%).

3-[(3*E*)-4-Bromobut-3-enyl]-*N*-but-2-ynyl-*N*-methylaniline (5) by Wittig Methodology:[26] Potassium *tert*-butoxide (9 mmol, 1.08 g) was added at −78 °C to a suspension of [Ph_3PCH_2Br]Br (9 mmol, 3.93 g) in tetrahydrofuran (20 mL), and the mixture was stirred for 30 min. A solution of aldehyde **8** (9 mmol, 1.94 g) in tetrahydrofuran (5 mL) was then added slowly at −78 °C. After 30 min, the mixture was allowed to warm to room temperature and stirred for another 2 h. The mixture was hydrolysed with water and extracted with petroleum ether. Chromatography on silica gel with petroleum ether/ethyl acetate (10:1; R_f = 0.71) as eluent gave the bromoalkene **5** (3.51 mmol, 1.02 g, 39%) as the (*E*) isomer. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (t, ^5J = 2.30 Hz, 3 H, CH_3), 2.53 (m, 2 H, CH_2), 2.68 (m, 2 H, CH_2), 2.95 (s, 3 H, NCH_3), 3.96 (q, ^5J = 1.2 Hz, 2 H, NCH_2), 6.15 (dm, 1 H, ^3J = 11.70 Hz, CHBr) 6.65 (m, 3 H, aryl-H), 7.18 (m, 1 H, aryl-H). ^{13}C NMR (63 MHz, $CDCl_3$): δ = 3.65 (CH_3), 31.36 (aryl−CH_2CH_2CH=CHBr), 34.60 (CH_2CH=CHBr), 38.59 (NCH_2), 42.72 (NCH_3), 74.53 (C≡CCH$_3$), 79.66 (C≡CCH$_3$), 108.10 (CH=CHBr), 111.92, 114.22, 118.02, 129.01 (4 C, aryl-CH), 134.18 (CH=CHBr), 141.97 (aryl-C3), 149.44 (aryl-C1). MS (EI): *m*/*z* (%) = 291/293 (10) [M^+], 212 (40) [M^+ − Br], 172 (100) [M^+ − BrHC≡C−CH_3]. HR-MS: found for $C_{15}H_{18}BrN$ 291.0628, calcd. 291.0623; calcd. C 61.65, H 6.21, N 4.79; found C 61.89, H 6.14, N 5.14.

***N*-But-2-ynyl-3-[2-(1,3-dioxan-2-yl)ethyl]-*N*-methylaniline (17):** Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 6:1; R_f = 0.34) afforded the oxirane **17** (412 mg, 1.80 mmol, 20%). ^{1}H NMR (500 MHz, C_6D_6): δ = 1.50 (t, ^5J = 2.3 Hz, 3 H, CH_3), 1.77 (td, ^3J = 5.5, ^4J = 2.4 Hz, 2 H, aryl-CH_2), 2.19 (dd, ^3J = 5.3, ^4J = 2.5 Hz, 1 H, OCH_2), 2.43 (dd, ^3J = 5.3, ^4J = 2.5 Hz, 1 H, OCH_2), 2.67 (td, ^3J = 8.0, ^4J = 1.5 Hz, 2 H, CH_2CH), 2.69 (m, 2 H, aryl-CH_2), 2.76 (m, 1 H, OCH), 2.82 (s, 3 H, NCH_3), 3.90 (q, ^5J = 2.3 Hz, 2 H, N−CH_2), 6.65 (d, ^3J = 7.5 Hz, 1 H, aryl-CH), 6.67 (*t*, ^4J = 2.5 Hz, 1 H, aryl-CH), 6.73 (d, ^3J = 7.5 Hz, 1 H, aryl-CH), 7.21 (dd, ^3J = 7.5 Hz, 1 H, ^3J = 7.5 Hz, aryl-CH). ^{13}C NMR (125 MHz, C_6D_6): δ = 3.17 (CH_3−C≡C), 33.03 (CH_2CH_2), 34.76 (CH_2CH_2), 38.38 (NCH_3), 42.73 (NCH_2), 46.64 OCH_2), 51.33 (OCH), 75.20 (C≡CCH$_3$), 79.53 (C≡CCH$_3$), 112.30, 114.57, 118.31, 129.40 (4 C, aryl-CH), 142.45 (aryl-C, C-3), 149.91 (aryl-C1). MS (EI): *m*/*z* (%) = 229 (100) [M^+], 214 (86) [M^+ − Me], 184 (51) [M^+ − $CHOCH_2$], 172 (64) [M^+ − CH_2CHOCH_2], 91 (68) [$C_6H_5N^+$], 77 (39) [$C_6H_5^+$]. HR-MS: found for $C_{15}H_{19}NO$ 229.1466, calcd. 229.1467.

General Procedure for the Synthesis of Haloolefins 5 and 6 by the Takai Reaction:[37] A solution of aldehyde **7** or **8** (5 mmol) and haloform (10.0 mmol) in tetrahydrofuran (30 mL) was slowly added at 0 °C to a suspension of chromium(II) chloride (3.7 g, 30.0 mmol) in tetrahydrofuran (30 mL). The mixture was stirred for 3 h and the reaction was then quenched by addition of water (20 mL). After extraction with *tert*-butyl methyl ether and evaporation of the solvent, the residue was purified as described below.

3-[(3*E*)-4-Bromobut-3-enyl]-*N*-but-2-ynyl-*N*-methylaniline (5): Column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 6:1; R_f = 0.71) afforded bromoolefin **5** (1.02 g, 3.50 mmol, 70%).

***N*-But-2-ynyl-3-[(3*E*)-4-iodobut-3-enyl]-*N*-methylaniline (6):** After column chromatography on silica gel (eluent: petroleum ether/ethyl acetate, 20:1; R_f = 0.45), the (*E*) isomer of **6** (1.27 g, 3.75 mmol, 75%) was obtained as slightly yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.79 (t, ^5J = 2.30 Hz, 3 H, CH_3), 2.37 (m, 2 H, CH_2), 2.68 (t, ^3J = 7.80 Hz), 2.97 (s, 3 H, NCH_3), 3.99 (q, ^5J = 2.30 Hz, 2 H, NCH_2), 6.07 (ddd, ^3J = 13.5 Hz, 1 H, ^3J = 2.6, ^3J = 1.2 Hz CHBr), 6.65 (dd, ^3J = 7.9, ^4J = 0.4 Hz, 1 H), 7.19 (t, ^3J = 8.0 Hz, aryl-H). ^{13}C NMR: (125 MHz, $CDCl_3$): δ = 3.57 (CH_3), 35.14 (aryl−CH_2CH_2CH=CHBr), 37.76 (CH_2CH=CHBr), 38.6 (NCH_2), 42.7 (NCH_3), 75.15 (C≡CCH$_3$), 82.82 (C≡CCH$_3$), 111.92, 114.14, 117.97, 129.04 (4 C, aryl-CH), 140.49 (CH=CHBr), 141.65 (CH=CHBr), 145.77 (aryl-C3), 149.39 (aryl-C1). MS (EI): *m*/*z* (%) = 339 (11) [M^+], 212 (32) [M^+ − I], 172 (100) [M^+ − IHC≡C−CH_3]. HR-MS: found for $C_{15}H_{18}IN$ 339.0482, calcd. 339.0484; calcd. C 53.11, H 5.35, N 4.13; found C 53.21, H 5.12, N 4.25.

Synthesis of {(*E*)-5-[(3-(Butyn-2-yloxy)phenyl]-1-methoxypent-2-enylidene}pentacarbonylchromium (1) by Aldol Condensation: Tin tetrachloride (1.2 mL, 10.0 mmol) was added at −78 °C to a solution of 3-[3-(butyn-2-yloxy)phenyl]propanal (**7**; 2.02 g, 10.0 mmol) in dichloromethane (50 mL). In a second Schlenk tube, pentacarbonyl(1-methoxyethylidene)chromium (1.25 g, 5.0 mmol) was dis-

solved in diethyl ether (50 mL) and *n*BuLi (5.5 mmol) was added at −78 °C. After 90 min, the solution of the deprotonated 1-methoxyethylidene complex was added dropwise to the solution of activated aldehyde and the mixture was stirred for 3 h without cooling. Triethylamine (1.6 mL, 11.5 mmol) followed by mesyl chloride (0.8 mL) were then added, during which the colour changed from orange to deep purple. The reaction was quenched by addition of water (150 mL) and the product was extracted with diethyl ether and dried with magnesium sulfate. After removal of the solvent, the residue was purified by column chromatography on silica gel with petroleum ether/diethyl ether (5:1; R_f = 0.51) as eluent, to give the carbene complex **1** (0.95 mmol, 3.04 g, 70%) as a dark purple oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.85 (s, 3 H, CH_3), 2.48 (td, ^3J = 7.43 Hz, 2 H, CH_2CH=CH), 2.75 (t, ^3J = 7.63 Hz, 2 H, CH_2CH$_2$), 4.61 (d, ^5J = 1.84 Hz, 2 H, OCH_2), 4.69 (s, 3 H, OCH_3), 6.28 (dt, ^3J = 14.95, 7.4 Hz, 1 H, CH_2−CH=CH), 6.77 (d, ^3J = 7.63 Hz, 2 H, aryl-H), 6.79 (d, ^4J = 5.80 Hz, 1 H, aryl-H), 7.20 (t, ^3J = 7.78 Hz, 1 H, aryl-H), 7.28 (d, ^3J = 14.95 Hz, 1 H, CH=CH-CH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.72 (CH_3), 33.76 (CH$_2$−CH$_2$), 34.54 (CH$_2$CH=CH), 56.33 (OCH_2), 66.39 (OCH_3), 74.00 (C≡CCH$_3$), 83.70 (C≡CCH$_3$, 112.23, 115.08, 121.23, 129.44 (4 C, aryl-CH), 135.33 (CH=CHCH$_2$), 142.18 (aryl-C3), 144.49 (CH=CHCH$_2$), 157.99 (aryl-C1), 216.66 (*cis*-CO), 223.95 (trans-CO), 336.13 (Cr=C). FT-IR (petroleum ether): $\tilde{\nu}$(CO) = 2060 (m), 1987 (w), 1944 (vs) cm^{-1}. MS (EI) (%): *m*/*z* (%) = 434 (0.2) [M$^+$], 378 (0.2) [M$^+$ − 2CO], 350 (0.1) [M$^+$ − 3 CO], 322 (0.4) [M$^+$ − 4 CO], 294 (40) [M$^+$ − 5 CO], 159 (52), 145 (25), 52 (100). HR-MS: found for $C_{21}H_{18}CrO_7$ 434.0445, calcd. 434.0458.

Pentacarbonyl{(*E*)-1-methoxy-5-[(3-*N*-methyl-*N*-butyn-2-yl)phenyl]-pent-2-enylidene}chromium (2) by Way of a (Pivaloyloxy)carbene Complex Intermediate: *t*BuLi (6.6 mmol) was added at −78 °C to a solution of bromoolefin **5** (876 mg, 3 mmol) in diethyl ether (50 mL). After 45 min, hexacarbonylchromium (666 mg, 3 mmol) was added and the mixture was stirred for 2 h and allowed to warm to room temp. Pivaloyl chloride (0.72 mL, 6 mmol) was then added at −20 °C, during which the colour changed from red to black. The solution was stirred for another 2 h, and methanol (2 mL) was then added, during which the colour changed to dark purple. After removal of the solvent, the residue was purified by column chromatography on silica gel, with petroleum ether/diethyl ether (5:1; R_f = 0.36) as eluent, to give carbene complex **2** (0.6 mmol, 268 mg, 20%) as a dark purple oil. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.77 (t, ^5J = 2.3 Hz, 3 H, CH_3), 2.51 (td, ^3J = 7.5 Hz, 7.4, 7.1 Hz, 2 H, CH_2CH=CH), 2.73 (m, 2 H, CH_2CH$_2$), 2.93 (s, 3 H, NCH_3), 3.96 (q, ^5J = 2.3 Hz, 2 H, NCH_2), 4.69 (s, 3 H, OCH_3), 6.32 (dt, ^3J = 15.0, ^3J = 7.8 Hz, 1 H, CH_2CH=CH), 6.63 (m, 3 H, aryl-CH), 7.16 (t, ^3J = 7.8 Hz, 1 H, aryl-CH), 7.30 (dt, ^3J = 15, ^4J = 1.4 Hz, 1 H, CH_2CH=CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.22 (CH_3), 34.22 (CH$_2$CH$_2$), 35.06 (CH$_2$$CH_2$), 38.37 ($NCH_3$), 42.60 ($NCH_2$), 66.57 ($OCH_3$), 111.94, 114.06, 117.76 (3 C, aryl-CH), 129.13 (Ar-C), 137.33 (CH=CHCH$_2$), 144.36 (CH=CHCH$_2$), 147.60 (aryl-C3), 149.37 (aryl-C1), 216.98 (*cis*-CO), 224.43 (*trans*-CO). FT-IR (petroleum ether): $\tilde{\nu}$(CO) = 2060 (s), 1959 (sh), 1948 (vs) cm^{-1}. MS (EI): *m*/*z* (%) = 447 (6) [M$^+$], 363 (6) [M$^+$ − 3 CO], 335 (3) [M$^+$ − 4 CO], 307 [M$^+$ − 5 CO] (25), 172 (26) [(C_4H_5)MeN$C_6H_4CH_2^+$], 157 (26) [(C_4H_5)MeN$C_6H_3^+$], 107 (69) [MeOCCrCH$^+$], 52 (93) [Cr$^+$]. HR-MS: found 447.0769, calcd. 447.0773.

Pentacarbonyl{(*E*)-1-methoxy-5-[(3-*N*-methyl-*N*-butyn-2-yl)phenyl]-pent-2-enylidene}chromium (2) by Way of an (Acetoxy)carbene Complex Intermediate: *t*BuLi (6.6 mmol) was added at −78 °C to a solution of bromoolefin **5** (876 mg, 3 mmol) in diethyl ether (50 mL). After 45 min, hexacarbonylchromium (666 mg, 3 mmol) was added and the mixture was stirred for 2 h and allowed to warm to room temp. Acetyl bromide (0.44 mL, 6 mmol) was then added at −40 °C, during which the colour changed from red to dark red brown. The solution was stirred for 30 min and, after addition of methanol (2 mL), the colour changed to dark purple. After removal of the solvent, the residue was purified by column chromatography on silica gel, with petroleum ether/diethyl ether (5:1; R_f = 0.36) as eluent, to give the carbene complex **2** (0.6 mmol, 282 mg, 21%).

Tricarbonyl[3,4,5,6,7,8-η^6-(8-hydroxy-5-methoxy-4-methyl-1-oxa-[2.2]metacyclophane)]chromium (21): A solution of carbene complex **1** (300 mg, 0.7 mmol) in tetrahydrofuran (30 mL) was warmed to 65 °C for 3 h while the reaction was monitored by FT-IR spectroscopy, focussing on the decrease in the A_1^1 $\tilde{\nu}$(CO) absorption band of **1** and the increase in the E $\tilde{\nu}$(CO) absorption band of the arene complex formed. The solvent was then removed in vacuo and the residue was purified by column chromatography on silica gel, with petroleum ether/dichloromethane (3:1) as eluent, to give the cyclophane complex **21** (71 mg, 0.17 mmol, 25%) as a yellow solid that displayed fast decomposition. FT-IR (THF): $\tilde{\nu}$(CO) = 1938 (vs), 1893 (s), 1878 (s) cm^{-1}. MS (EI): *m*/*z* (%) = 388 (10) [M$^+$ − H_2O], 304 (62) [M$^+$ − 3 CO], 251 (20), 57 (100). HR-MS: found for $C_{17}H_{16}CrO_2$ 304.0545, calcd. 304.0555.

Tricarbonyl[3,4,5,6,7,8-η^6-(8-hydroxy-5-methoxy-4-methyl-1-aza-[2,2]metacyclophane)]chromium (22): A solution of carbene complex **2** (100 mg, 0.22 mmol) in tetrahydrofuran (20 mL) was warmed to 65 °C for 3 h, while the reaction was monitored by FT-IR spectroscopy. The solvent was then removed in vacuo and the residue was purified at −5 °C by column chromatography on silica gel, with petroleum ether/dichloromethane (2:1; R_f = 0.51) as eluent, to give the cyclophane complex **22** (25 mg, 0.04 mmol, 20%) as a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.75 (d, ^4J = 1.9 Hz, 3 H, CH_3-Ph, C-18), 2.92 (s, 3 H, CH_3−N), 3.95 (s, 2 H, CH_2−N), 6.6 (m, 3 H, Aryl-CH, 2-H, 4-H, 6-H), 7.15 (q, ^3J = 7.8 Hz, 1 H, Aryl-CH, 5-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 3.89 (CH_3), 30.02 (CH$_2$CH$_2$), 37.45 (CH$_2$$CH_2$), 38.89 ($NCH_3$), 43.04 ($NCH_2$), 56.81 ($OCH_3$), 94.34, 94.38, 98.61[Cr(CO)$_3$-arene-*C*), 112.1 [Cr(CO)$_3$-arene-*C*H), 114.58, 114.68, 118.4 (3 C, aryl-CH), 129.2, 129.38 [Cr(CO)$_3$-arene-*C*), 132.15 (aryl-CH), 147.00 (aryl-C3), 149.76 (aryl-C1), 235.89 (CO). FT-IR (THF): $\tilde{\nu}$ (CO) 1944 (vs), 1872 (s), 1865 (s) cm^{-1}.

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