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Intramolecular annulation reactions of alkyne-functionalized aminocarbene complexes. A one-pot route to 9*H*-carbazoles and 11*H*-benzo[*a*]carbazoles†

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Summary — Pentacarbonyl(2-alkynylanilinocarbene) complexes of chromium undergo a novel intramolecular tandem alkyne insertion/carbene annulation sequence to give 9*H*-carbazoles and 11*H*-benzo[*a*]carbazoles in a one-pot reaction. The yields of the cyclization products depend on the substitution pattern both at the alkyne terminus and within the carbene carbon side chain. Generally, aryl carbene ligands react more cleanly than their vinyl analogues, and the yields increase in the order of phenyl, methoxyphenyl and mesityl substituents bound to the C≡C bond.

chromium aminocarbene / carbene annulation / 9*H*-carbazole / 11*H*-benzo[a]carbazole

Résumé — Réactions d'annélation intramoléculaires des complexes aminocarbènes fonctionnalisés par des alcynes. Un accès « *one-pot* » aux 9*H*-carbazoles et 11*H*-benzo[a]carbazoles. Les pentacarbonyl(2-alkynylanilino)carbènes du chrome fournissent au moyen d'une séquence tandem intramoléculaire insertion d'alcyne/annélation carbénique des 9*H*-carbazoles et des 11*H*-benzo[*a*]carbazoles en une réaction « *one-pot* ». Les rendements en produits de cyclisation dépendent du mode de substitution à la fois de l'alcyne et de la chaîne latérale portant le carbone carbénique. Généralement, les ligands des carbènes aryliques réagissent plus proprement que leurs analogues vinyliques et les rendements augmentent selon les substituants liés à la liaison C≡C dans l'ordre phényle, méthoxyphényle et mésityle.

aminocarbène du chrome / annélation carbénique / 9*H*-carbazole / 11*H*-benzo[a]carbazole

Introduction

Over the past two decades transition metal carbene complexes [2] have been developed to useful reagents for selective carbon-carbon bond formation. The electron-deficient carbene carbon as well as the template properties of the low-valent metal center (especially chromium) have been exploited in both carbene ligand-centered and metal-centered reactions [3]. Perhaps the most striking example is the benzannulation, a formal [3 + 2 + 1]-cycloaddition of chromium alkoxycarbene complexes bearing an α,β-unsaturated carbene side chain with alkynes along which a 1,4-dioxygenated arene is formed from the alkyne, the carbene and a carbonyl ligand at the chromium template [4]. The mechanism of this type of reaction has been addressed by early kinetic studies, [5] by trapping experiments [6], by isolation of presumed intermediates [7] as well as by extended Huckel molecular orbital (EHMO) and density functional theory (DFT) calculations [8]. The synthetic scope of this methodology has been demonstrated throughout the syntheses of various natural products [9].

Compared with alkoxycarbene complexes annulation reactions of their aminocarbene analogs have been studied in less detail [10]. Generally, the annulation of an aminocarbene ligand by an alkyne requires higher temperatures (above 90 °C compared with 45–60 °C for alkoxycarbene ligands) and mainly occurs without incorporation of a carbonyl ligand. The better donor capacity of an amino group over an alkoxy substituent which strengthens the backbonding to the carbonyl coligands has been suggested as a rationale for this behavior (scheme 1) [11]. Accordingly, *N*-acylation of aryl carbene complexes favors again benzannulation over cyclopentannulation as demonstrated for the reaction of *N*-Boc substituted aminocarbene complexes with alkynes [12]. CO-insertion is further facilitated if the lone pair of the amino substituent is part of an aromatic 6π system [13]. Recently, amino(vinyl)carbene complexes have been reported to undergo benzannulation upon reaction with terminal alkynes without *N*-acceptor activation at elevated temperatures (85 °C); best results have been obtained in a non-coordinating solvent [14]. Further, alkenyl(alkynylamino)carbene complexes may undergo

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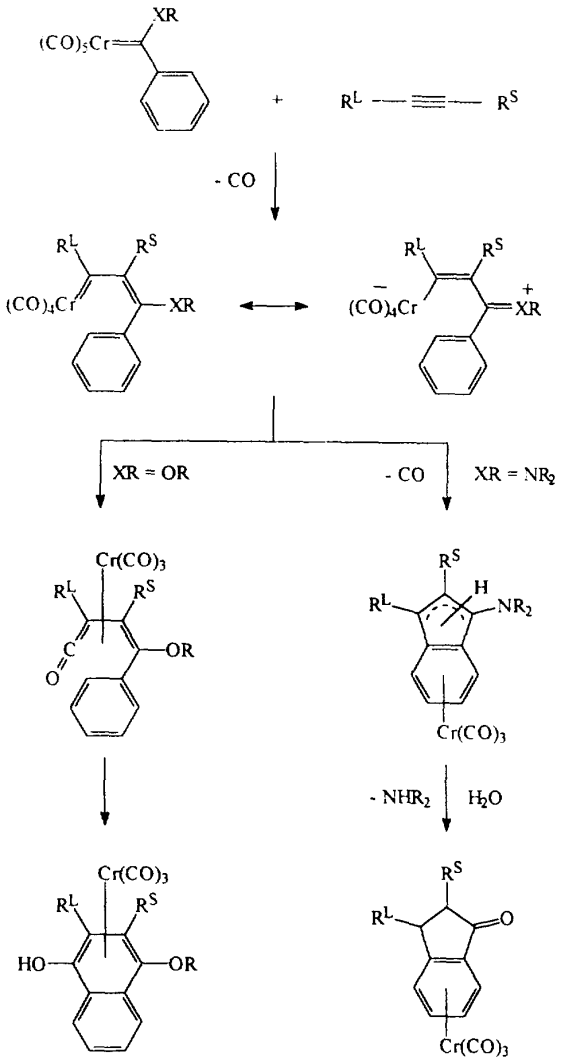
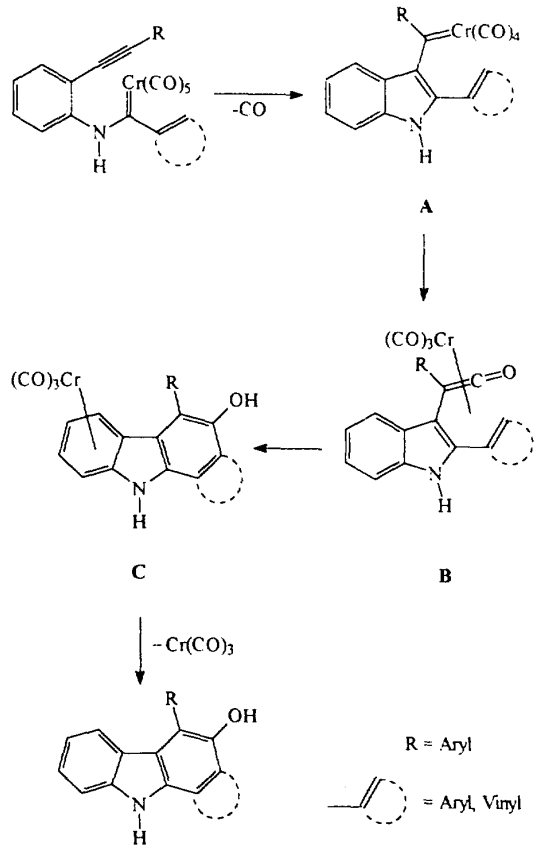
* Correspondence and reprints



Scheme 1. Annulation of alkoxy- and aminocarbene complexes with alkynes.

cyclization with or without concomitant incorporation of carbon monoxide depending on the length of the alkylidene bridge between the carbene and alkyne moities [15, 16].

We have become interested in intramolecular aminocarbene annulation reactions [16] and have recently focused our interest on carbazole and benzocarbazole skeletons which have attracted attention as potential carcinogens [17]. Oxygenated congeners exhibit antibiotic properties and have been recently synthesized via organoiron, organomolybdenum or other routes [18]. We have concentrated on a tandem alkyne insertion/carbene annulation strategy based on aryl or vinyl carbene chromium complexes bearing alkynylanilino substituents (scheme 2). After a thermally induced decarbonylation insertion of the alkyne into the metal carbene bond is expected to generate an indolylcarbene intermediate **A** which may undergo carbonylation to give



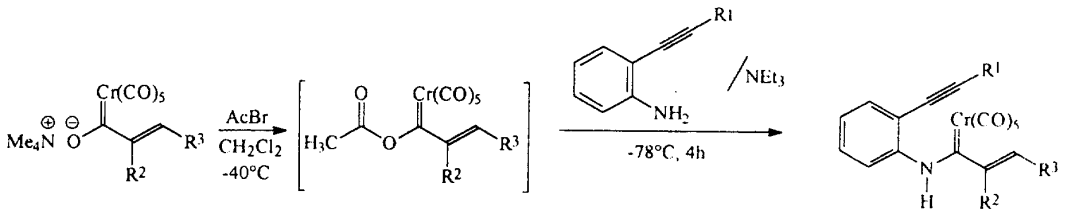
Scheme 2. Alkyne insertion/carbene annulation strategy to carbazole skeletons.

the ketene **B** and finally cyclize to the (benzo)carbazole skeleton **C** in a one-pot process.

Results and discussion

Synthesis of aminocarbene complex precursors

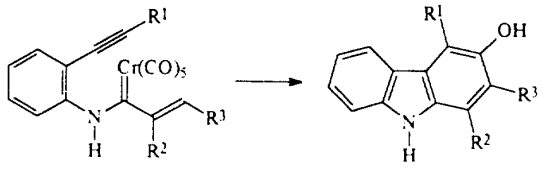
Aminocarbene complexes **1–15** were prepared from 2-(arylethynyl)anilines [19] and acetoxycarbene complexes which are accessible from tetramethylammonium pentacarbonyl acyl chromates [20] upon reaction with acetyl bromide (scheme 3) [21]. The aminocarbene complexes were obtained in good yields as mixtures of *E*/*Z* isomers (with respect to the $C_{carbene}$–N bond) which were analyzed on the basis of their N–H ^{1}H NMR shifts in isotropic and anisotropic solvents [22]. In *E*- and *Z*-(alkylamino)carbene complexes the differences of the NCH_2 chemical shifts for the *E*-isomers exceed those for the *Z*-isomers when $CDCl_3$ is replaced by C_6D_6 as solvent [22d]. An inverse correlation was observed in aryl(allyl- or propylamino)carbene complexes of chromium for the NH hydrogen atoms which exhibit larger Δ [$\delta(CDCl_3) - \delta(C_6D_6)$] values for the *Z*-isomers compared with those obtained for the *E*-isomers [22e].



1 - 15

Compound	R^1	R^2	R^3	*Yield (%)*	*E/Z ratio*
1	C_6H_5	CH=CHCH=CH		75	5:2
2	C_6H_5	CH=CHC(CH_3)=CH		70	10:7
3	C_6H_5	CH_3	H	52	6:5
4	4-$CH_3C_6H_4$	CH=CHCH=CH		75	5:4
5	4-$CH_3C_6H_4$	CH=CHC(CH_3)=CH		65	5:3
6	4-$CH_3C_6H_4$	CH_3	H	52	1:2
7	2,4,6-$(CH_3)_3C_6H_2$	CH=CHCH=CH		69	3:5
8	2,4,6-$(CH_3)_3C_6H_2$	CH=CHC(CH_3)=CH		65	4:3
9	2,4,6-$(CH_3)_3C_6H_2$	CH_3	H	58	5:6
10	2,4,6-$C(CH_3)_3C_6H_2$	CH=CHCH=CH		85	1:1
11	2,4,6-$C(CH_3)_3C_6H_2$	CH=CHC(CH_3)=CH		90	1:1
12	3,4,5-$(OCH_3)_3C_6H_2$	CH=CHCH=CH		59	10:7
13	3,4,5-$(OCH_3)_3C_6H_2$	CH=CHC(CH_3)=CH		74	5:3
14	2,6-$(OCH_3)_2C_6H_3$	CH=CHCH=CH		74	2:1
15	2,6-$(OCH_3)_2C_6H_3$	CH=CHC(CH_3)=CH		55	5:2

Scheme 3. Synthesis of anilinocarbene complexes **1–15**.



1 - 9 16 - 24

Compound	R^1	R^2	R^3	*Conditions*[a] *(h/°C)*	*Yield (%)*
1, 16	C_6H_5	CH=CHCH=CH		1/90	28
2, 17	C_6H_5	CH=CHC(CH_3)=CH		1/90	26
3, 18	C_6H_5	CH_3	H	2/110	19
4, 19	4-CH_3-C_6H_4	CH=CHCH=CH		1/90	24
5, 20	4-CH_3-C_6H_4	CH=CHC(CH_3)=CH		1/90	25
6, 21	4-CH_3-C_6H_4	CH_3	H	2/110	18
7, 22	2,4,6-$(CH_3)_3C_6H_2$	CH=CHCH=CH		1/90	65
8, 23	2,4,6-$(CH_3)_3C_6H_2$	CH=CHC(CH_3)=CH		1/90	70
9, 24	2,4,6-$(CH_3)_3C_6H_2$	CH_3	H	2/110	17

[a] Solvent: toluene.

Scheme 4. Tandem alkyne insertion/annulation of anilinocarbene complexes **1–9**.

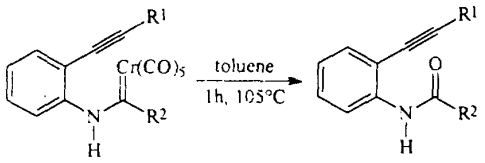
Annulation reactions

Upon warming in toluene to 110 °C for 2 h the vinyl(amino)carbene complexes **3** and **6** undergo cyclization to give 9*H*-carbazoles **18** and **21** in poor yields. Milder reaction conditions are sufficient for the annulation of aryl(amino)carbene complexes **1**, **2**, **4** and **5**. After 1 h at 90 °C the 11*H*-benzo[*a*]carbazoles **16**, **17**, **19** and **20** could be isolated in slightly improved yields (scheme 4). Monitoring the reaction sequence by IR indicates that the chromium carbonyl fragment is cleaved along the reaction path. The reaction mixture was purified by column chromatography immediately after the solvent was evaporated.

The cyclization products were identified primarily by their ^{1}H NMR spectra. The N–H chemical shifts (ca 7.85 ppm for 9*H*-carbazoles and 8.70 ppm for 11*H*-benzo[*a*]carbazoles) are comparable with those re-

ported for similar compounds [23]. The O–H signals (ca 4.77 ppm for 9*H*-carbazoles and 5.30 ppm for 11*H*-benzo[*a*]carbazoles) were asssigned on the basis of exchange experiments with D_2O.

Typically, the alkenylcarbene complexes **3** and **6** are more reluctant to undergo cyclization. They require higher temperatures and longer reaction times than their arylcarbene analogs **1**, **2**, **4** and **5** to give comparable but still low yields of (benzo)carbazoles. A more pronounced influence of the substitution pattern both at the carbene carbon and at the alkyne terminus on the reactivity is evident from the cyclization of the mesitylethynyl complexes **7**–**9**. Whereas the 2-propenylcarbene complex **9** has to be warmed in toluene to 110 °C for 2 h to get a poor yield of 17% of 9*H*-carbazole **24**, the arylcarbene starting materials **7** and **8** give synthetically useful yields (> 65%) of 11*H*-benzo[*a*]carbazoles **22** and **23** under milder conditions (90 °C for 1 h) despite of the obvious steric congestion at the alkyne moiety. One might speculate that the electron-releasing ability of the mesityl substituent overrides its steric bulk and, finally, favors the cyclization. To check to what extent steric congestion is still compatible with the alkyne insertion step, we included a sterically even more demanding aryl substituent in our study. The 2,4,6-tri-*tert*-butylphenyl ('supermesityl') analogs **10** and **11**, however, showed no tendency to cyclize under our standard conditions; instead, an oxidation product arising from the cleavage of the metal–carbene bond could be isolated in moderate yields (scheme 5).



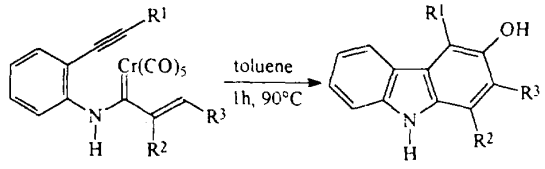
R^1 = 2,4,6-$C(CH_3)_3C_6H_2$

10: R^2 = C_6H_5 — **25**: R^2 = C_6H_5, 27%

11: R^2 = 4-CH_3-C_6H_4 — **26**: R^2 = 4-CH_3-C_6H_4, 29%

Scheme 5. Metal carbene cleavage in 'supermesityl' ethynylanilinocarbene complexes **10** and **11**.

The suggestion that electron-releasing substituents at the alkyne terminus favor the cyclization also holds for methoxy-substituted aryl groups. The alkynylanilinocarbene complexes **12**–**15** undergo cyclization in moderate yields (42–45%) under similar conditions as observed for the mesityl analogues **7** and **8** (scheme 6). The results obtained for the cyclization of carbene complexes **1**–**9** and **12**–**15** indicate that the (benzo)carbazole formation is mainly governed by a balance of substitution effects arising from the alkyne moiety and from the π-system bonded to the carbene carbon atom. Aryl substituents at the alkyne terminus bearing hydrogen, methyl, or methoxy groups are compatible with sequential alkyne and carbon monoxide insertion as well as with the final cyclization to give *N*-heteroarenes **16**–**24** and **27**–**30**. Alkyne and carbon monoxide insertion also tolerate a trimethylsilyl substitution; as shown for complex **31**, however, the electrocyclic ring-closure fails, presumably as a consequence of steric demands of the trimethylsilyl group which hampers the adoption of a coplanar conformation of the indole and ketene moieties required for cyclization. The reaction sequence ends with the formation of $Cr(CO)_3$-coordinated vinyl ketene **32** (scheme 7), as indicated by a characteristic $\nu(C{=}O)_{ketene}$ absorption band while monitoring the reaction by IR spectroscopy [24]. The even bulkier supermesityl substituent in **10** and **11** already prevents the alkyne insertion step and finally results in an oxidative cleavage of the metal carbene bond to give amides **25** and **26** (scheme 5).

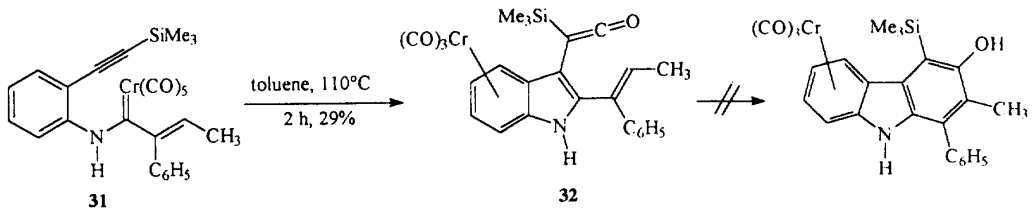


12 - 15 **27 - 30**

Compound	R^1	R^2	R^3	*Yield (%)*
12, 27	3,4,5-$(OCH_3)_3C_6H_2$	CH=CHCH=CH		43
13, 28	3,4,5-$(OCH_3)_3C_6H_2$	CH=CHC(CH_3)=CH		45
14, 29	2,6-$(OCH_3)_2C_6H_3$	CH=CHCH=CH		42
15, 30	2,6-$(OCH_3)_2C_6H_3$	CH=CHC(CH_3)=CH		43

Scheme 6. Tandem alkyne insertion/annulation of anilinocarbene complexes **12**–**15**.

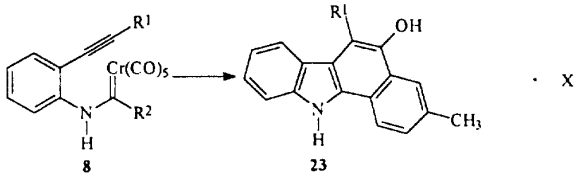
Benzannulation reactions using alkoxycarbene chromium complexes are routinely run in ethereal solvents such as *tert*-butyl methyl ether or tetrahydrofuran, although non-coordinating solvents have been claimed to react more selectively [15, 25]. Cyclopentannulation reactions of aminocarbene complexes require higher temperatures and have been performed preferentially in di-*n*-butyl ether, toluene or *N*,*N*-dimethylformamide [10a, 16, 26]. When we checked the mesityl complex **8** for the influence of the solvent on the alkyne insertion/carbonylation/annulation sequence, we observed that the cyclization even occurs under surprisingly mild conditions (scheme 8). The temperature required for a reasonable degree of conversion can be lowered to 55 °C which results in an overall yield of 47% for benzocarbazole **23** and its $Cr(CO)_3$ complex **33**. When the temperature was raised to 85 °C by running the reaction in tetrahydrofuran, acetonitrile and di-*n*-butyl ether, the total yields increased gradually up to 79%. The highest yield was observed for di-*n*-butyl ether at 85 °C which allows the cyclization to go to completion within 35 min. The use of a potent coordinating solvent such as acetonitrile favors the cleavage of the $Cr(CO)_3$ fragment, and the uncoordinated benzocarbazole **23** is obtained as the only cyclization product. The alkyne insertion/carbene annulation strategy could not be extended to the higher homologues of **8**. Under comparable conditions the molybdenum analogue **34** underwent an oxidative cleavage of the metal carbene bond to give anilide



31 32

Scheme 7. Alkyne insertion/carbonylation sequence for silylethynylanilinocarbene complex **31**.

35 analogous to **26** as the major product while the reaction of the tungsten congener resulted in the formation of a variety of non-identified products. This observation confirms earlier findings that carbene annulation reactions generally proceed more selectively with chromium complexes than with their heavier homologues.



8 23

R^1 = 2,4,6-$(CH_3)_3C_6H_2$
R^2 = 4-CH_3-C_6H_4

Solvent	*Conditions (h/ °C)*	*Recovered **8** (%)*	*Yield (%) of **23***	*Yield (%) of **23**·Cr(CO)$_3$*
*t*BuOMe	4.5 h/55 °C	8	25	22
THF	3 h/68 °C	3	57	15
CH_3CN	40 min/82 °C	0	63	0
n-Bu_2O	1 h/75 °C	0	45	28
n-Bu_2O	35 min/85 °C	0	49	30

Scheme 8. Influence of reaction conditions on cyclization of anilinocarbene complex **8**.

Experimental section

Reactions and work-up procedures were carried out under an inert gas atmosphere. Solvents were dried using standard methods, distilled, saturated and stored under argon. NMR spectra were run using Bruker AM-400 or WM-250 spectrometers. Mass spectra were obtained on a Kratos MS 50 or Varian MAT CH 7A. IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer. Elemental analyses were carried out on a Heraeus CHN rapid element analyzer. Merck silica gel 60 (0.063–0.200 mm) was used for chromatographic work-up. Melting points are uncorrected. For all aminocarbene complexes obtained as *E*/*Z* mixtures [a] denotes signals of the *E*-isomers whereas [b] refers to signals of the *Z*-isomers.

E/Z-Pentacarbonyl[(2-(phenylethynyl)phenylamino)-phenylcarbene]chromium **1**

A solution of tetramethylammonium[pentacarbonyl(benzoyl) chromate(−I)] (1.0 g, 3.13 mmol) in 30 mL CH_2Cl_2 was cooled to −40 °C, treated with acetyl bromide (384 mg, 0.231 mL, 3.13 mmol) and stirred for 1 h. A solution of 2-(phenylethynyl)aniline (665 mg, 3.44 mmol) and triethylamine (351 mg, 0.477 mL, 3.44 mmol) in 5 mL CH_2Cl_2 (degassed by a triple freeze–pump–thaw sequence) was added slowly at −78 °C. After stirring for 4 h at −78 °C, the reaction mixture was allowed to warm to room temperature. The solvent was removed at reduced pressure, and the residue was purified by column chromatography on silica gel using petroleum ether/dichloromethane (2:1) to give 1.11 g (75%) **1** as a yellow oil (*E*/*Z*-ratio: 5:2). R_f = 0.64.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.88[a] (br, 1H, NH), 10.04[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.57[a] (br, 1H, NH), 8.71[b] (br, 1H, NH), 7.78 (dd, 1H, *J* = 1.56, 7.22 Hz), 7.60 (dd, 1H, *J* = 1.76, 6.58 Hz), 7.43 (dd, 1H, *J* = 1.56, 7.53 Hz), 7.15–6.58 (m, 20H, H_{arom}), 6.54 (dt, 1H, *J* = 1.07, 7.54 Hz), 6.37 (dt, 1H, *J* = 1.31, 7.92 Hz), 6.05 (d, 1H, *J* = 8.08 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.5[a] (Cr=C), 288.9[b] (Cr=C), 224.9[b] (CO_{trans}), 223.6[a] (CO_{trans}), 216.9[a] (CO_{cis}), 216.6[b] (CO_{cis}), 155.5[b], 150.8[a], 142.7[b], 139.8[a], 132.7[b], 131.9[b], 131.6[a], 129.7[a], 129.6, 129.3, 129.1, 128.7[a], 128.6[a], 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.5[b], 127.3[b], 127.2, 125.1, 121.8, 121.2[b], 120.7[a], 118.4, 98.1[a] (C≡C), 96.1[b] (C≡C), 84.7[b] (C≡C), 83.4[a] (C≡C).

IR (CH_2Cl_2): 2 056 m, 1 978 w, 1 932 vs cm^{-1}.

MS (EI): *m*/*z* 333 (17%, M^+ − 5CO), 309 (77%), 220 (100%).

E/Z-Pentacarbonyl[(2-(phenylethynyl)phenylamino)-(p-tolyl)carbene]chromium **2**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(−I)] (1.19 g, 3.10 mmol), acetyl bromide (381 mg, 0.231 mL, 3.10 mmol), 2-(phenylethynyl)aniline (659 mg, 3.41 mmol), triethylamine (348 mg, 0.468 mL, 3.41 mmol). Yield 1.06 g (70%) **2**, yellow oil (*E*/*Z*-ratio: 10:7). R_f = 0.53 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.94[a] (br, 1H, NH), 10.02[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.59[a] (br, 1H, NH), 8.86[b] (br, 1H, NH), 7.78 (d, 1H, *J* = 6.85 Hz), 7.62 (d, 1H, *J* = 7.83 Hz), 7.52 (d, 1H, *J* = 8.02), 7.46 (d, 1H, *J* = 6.85 Hz), 7.12–6.98 (m, 16H), 6.91 (d, 1H, *J* = 6.85 Hz), 6.78 (d, 1H, *J* = 8.02 Hz), 6.71 (d, 1H, *J* = 8.01 Hz), 6.54 (t, 1H, *J* = 7.53 Hz), 6.40 (t, 1H, *J* = 8.41 Hz, 1H), 6.12 (d, 1H, *J* = 8.06 Hz), 2.07[b] (s, 3H), 1.86[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.6[a] (Cr=C), 288.1[b] (Cr=C), 224.3[b] (CO_{trans}), 223.5[a] (CO_{trans}), 216.9[a] (CO_{cis}), 216.6[b] (CO_{cis}), 152.9[b], 147.6[a], 142.7[b], 139.7[a], 138.3[b], 137.3[a] 133.0 132.5, 131.7, 131.5, 129.4, 129.1, 129.0, 128.9, 128.8, 128.1, 127.8, 127.6, 127.2, 126.2, 125.0, 121.7, 121.5[b], 121.1, 120.9, 119.2, 118.2, 118.1, 97.9[a] (C≡C), 96.3[b] (C≡C), 84.6[b] (C≡C), 83.4[a] (C≡C), 21.0.

IR (CH_2Cl_2): 2 056 m, 1 979 w, 1 933 vs cm^{-1}.

MS (EI): *m*/*z* 347 (17%, M^+ − 5CO), 323 (42%), 296 (100%).

E/Z-Pentacarbonyl[(2-(phenylethynyl)phenylamino)-(2-propenyl)carbene]chromium **3**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(2-methyl-2-propenoyl)chromate(−I)] (1.03 g, 3.07 mmol), acetyl bromide (377 mg, 0.299 mL, 3.07 mmol), 2-(phenylethynyl)aniline (649 mg, 3.38 mmol), triethylamine (345 mg, 0.468, 3.38 mmol). Yield: 697 mg (52%) **3**, yellow oil (*E/Z*-ratio 6:5). R_f = 0.48 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.58[a] (br, 1H, NH), 10.05[b] (br, 1H, NH).

^{1}H NMR (250 MHz, C_6D_6): δ 10.12[a] (br, 1H, NH), 8.77[b] (br, 1H, NH), 7.65 (d, 2H, J = 6.53 Hz), 7.52 (dd, 2H, J = 1.53, 7.64 Hz), 7.39 (t, 2H, J = 3.85 Hz), 7.24–6.61 (m, 13H, H_{arom}), 4.49[b] (s, 1H), 4.42[a] (s, 1H), 4.31[b] (s, 1H), 4.29[a] (s, 1H), 1.88[b] (s, 3H), 1.50[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 291.9[a] (Cr=C), 288.7[b] (Cr=C), 223.7[b] (CO_{trans}), 223.1[a] (CO_{trans}), 217.0[a] (CO_{cis}), 216.7[b] (CO_{cis}), 159.8, 152.6, 142.0[b], 139.6[a], 133.1, 132.7 131.7, 131.4, 129.5, 129.1, 128.9, 128.3[a], 128.1, 127.7, 124.6, 122.1, 122.0, 121.8, 121.7, 121.6, 107.5[a], 103.6[b], 97.9[a] (C≡C), 96.2[b] (C≡C), 84.3[b] (C≡C), 83.4[a] (C≡C), 21.4, 19.7.

IR (CH_2Cl_2): 2 056 m, 1 978 w, 1 929 vs cm^{-1}.

MS (FAB): m/z 437 (33%, M^+), 409 (2%, M^+ − CO), 381 (1%, M^+ − 2CO), 353 (1% M^+ − 3CO), 325 (10%, M^+ − 4CO), 297 (51%, M^+ − 5CO).

E/Z-Pentacarbonyl[(2-(p-tolylethynyl)phenylamino)-(phenyl)carbene]chromium **4**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(benzoyl)chromate(−I)] (1.10 g, 2.95 mmol), acetyl bromide (363 mg, 0.220 mL, 2.95 mmol), 2-(*p*-tolylethynyl)aniline (673 mg, 3.25 mmol), triethylamine (329 mg, 0.450 mL, 3.25 mmol). Yield: 1.08 g (75%) **4**, yellow oil (*E/Z*-ratio: 2:1). R_f = 0.61 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98[a] (br, 1H, NH), 10.07[b] (s, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.76[a] (br, 1H, NH), 8.99[b] (br, 1H, NH), 7.71 (d, 2H, J = 7.83 Hz, 2H), 7.54 (d, 2H, J = 7.82 Hz), 7.47 (d, 1H, J = 6.85 Hz), 7.26–6.91 (m, 9H, H_{arom}), 6.89 (d, 1H, J = 8.02 Hz), 6.81 (d, 2H, J = 7.82 Hz), 6.75 (t, 1H, J = 7.63 Hz), 6.58 (t, 1H, J = 7.53 Hz), 6.41 (t, 1H, J = 7.92 Hz), 6.12 (d, 2H, J = 7.63 Hz), 2.07[b] (s, 3H), 2.04[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 289.9[a] (Cr=C), 288.2[b] (Cr=C), 224.4[b] (CO_{trans}), 223.6[a] (CO_{trans}), 216.8[a] (CO_{cis}), 216.5[b] (CO_{cis}), 155.4, 150.3, 142.6, 139.8, 139.7, 139.6, 139.5, 139.3, 139.0, 133.0, 132.5, 131.7, 131.4, 129.6, 129.4, 129.3, 129.2, 128.4, 128.2, 128.1, 127.7, 127.4, 127.2, 124.9, 122.1, 121.1, 120.6[a], 119.1, 118.6, 118.5, 98.3[a] (C≡C), 96.7[b] (C≡C), 83.9[b] (C≡C), 82.9[a] (C≡C), 21.5, 21.4.

IR (CH_2Cl_2): 2 056 m, 1 979 w, 1 933 vs cm^{-1}.

HRMS: m/z calc for $C_{27}H_{17}NO_5Cr$ (M^+): 487.0512. Found: 431.0621 (M^+ − 2CO), 347.0769 (M^+ − 5CO).

E/Z-Pentacarbonyl[(2-(p-tolylethynyl)phenylamino)-(p-tolyl)carbene]chromium **5**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(−I)] (1.19 g, 3.10 mmol), acetyl bromide (381 mg, 0.231 mL, 3.10 mmol), 2-(*p*-tolylethynyl)aniline (707 mg, 3.41 mmol), triethylamine (345 mg, 0.472 mL, 3.41 mmol). Yield: 1.01 g (65%) **5**, yellow oil (*E/Z*-ratio: 5:3). R_f = 0.50 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.93[a] (br, 1H, NH), 10.02[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.66[a] (br, 1H, NH), 8.97[b] (br, 1H, NH), 7.71 (d, 2H, J = 8.42 Hz), 7.55 (d, 2H, J = 7.83 Hz), 7.47 (dd, 1H, J = 1.37, 7.44 Hz), 7.25–6.41 (m, 12H, H_{arom}), 6.78 (d, 2H, J = 8.41 Hz), 6.72 (d, 2H, J = 8.22 Hz), 6.58 (t, 1H, J = 7.73 Hz), 6.42 (dt, 1H, J = 1.10, 7.43 Hz), 6.15 (d, 2H, J = 8.61 Hz), 2.09 (s, 3H), 2.07 (s, 3H), 2.04 (s, 3H), 1.87 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.5[a] (Cr=C), 288.3[b] (Cr=C), 224.3[b] (CO_{trans}), 223.6[a] (CO_{trans}), 216.9[a] (CO_{cis}), 216.7[b] (CO_{cis}), 153.1[b], 147.7[a], 142.8[b], 139.8, 139.6, 139.3, 139.1, 138.4[b], 137.4[a], 133.1, 132.5, 131.7, 131.5, 131.2, 129.8, 129.34, 129.28, 129.1, 128.9[a], 128.6, 128.2, 127.9, 127.7, 127.2, 124.9, 122.2, 121.6[b], 121.5, 121.1[a], 119.1, 118.7, 118.5, 98.3[a] (C≡C), 96.7[b] (C≡C), 84.0[b] (C≡C), 82.8[a] (C≡C), 21.5[b], 21.2[a].

IR (CH_2Cl_2): 2 056 m, 1 980 w, 1 933 vs cm^{-1}.

HRMS: m/z calc for $C_{28}H_{19}NO_5Cr$ (M^+): 501.0668. Found: 445.0775 (M^+ − 2CO).

E/Z-Pentacarbonyl[(2-(p-tolylethynyl)phenylamino)-(2-propenyl)carbene]chromium **6**

Preparation as described for **1**. Tetramethylammonium-[pentacarbonyl(2-methyl-2-propenoyl)chromate(−I)] (1.07 g, 3.20 mmol), acetyl bromide (393 mg, 0.237 mL, 3.20 mmol), 2-(*p*-tolylethynyl)aniline (729 mg, 3.52 mmol), triethylamine (356 mg, 0.490 mL, 3.52 mmol). The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane 1:1 to give 792 mg (52%) **6** as a yellow oil (*E/Z*-ratio: 1:2). R_f = 0.62 (petroleum ether/dichloromethane 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.60[a] (br, 1H, NH), 10.04[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.20[a] (br, 1H, NH), 8.83[b] (br, 1H, NH), 7.61 (d, 1H, J = 8.02 Hz), 7.48 (d, 2H, J = 8.02 Hz), 7.42 (t, 1H, J = 8.04 Hz), 7.28 (d, 2H, J = 7.43 Hz), 7.06–6.96 (m, 5H, H_{arom}), 6.92 (d, 1H, J = 7.82 Hz), 6.90 (d, 2H, J = 7.83 Hz), 6.80 (dt, 1H, J = 1.38, 7.63 Hz), 6.74 (dt, 1H, J = 1.37, 8.01 Hz), 6.70 (d, 2H, J = 8.02 Hz), 4.53[a] (s, 1H), 4.49[b] (s, 1H), 4.38[a] (s, 1H), 4.36[b] (s, 1H), 2.05[b] (s, 3H), 2.03[a] (s, 3H), 1.94[b] (s, 3H), 1.53[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 291.8[a] (Cr=C), 288.7[b] (Cr=C), 223.9[b] (CO_{trans}), 223.2[a] (CO_{trans}), 217.1[a] (CO_{cis}), 216.8[b] (CO_{cis}), 160.0[b], 152.7[a], 142.0, 139.6, 139.5, 139.3, 133.1, 132.7, 131.7, 131.4, 129.6, 129.3, 129.2[b], 128.6, 128.1, 127.8, 124.6[b], 122.1[a], 119.1[b], 118.5[a], 107.6[a], 103.6[b], 98.2[a] (C≡C), 96.4[b] (C≡C), 83.7[b] (C≡C), 82.7[a] (C≡C), 26.9, 21.5, 21.4, 19.7.

IR (toluene): 2 055 m, 1 981 w, 1 927 vs cm^{-1}.

HRMS: m/z calc for $C_{24}H_{17}NO_5Cr$ (M^+): 451.0512. Found: 451.0501.

E/Z-Pentacarbonyl[(2-(mesitylethynyl)phenylamino)-(phenyl)carbene]chromium **7**

Preparation and work-up as described for **6**. Tetramethylammonium[pentacarbonyl(benzoyl)chromate(−I)] (631 mg, 1.70 mmol), acetyl bromide (209 mg, 0.127 mL, 1.70 mmol), 2-(mesitylethynyl)aniline (440 mg, 1.87 mmol), triethylamine (189 mg, 0.259 mL, 1.87 mmol). Yield: 604 mg

(69%) **7**, yellow oil (*E*/*Z*-ratio: 3:5). R_f = 0.62 (petroleum ether/dichloromethane 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.94[a] (br, 1H, NH), 10.08[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.65[a] (br, 1H, NH), 8.98[b] (br, 1H, NH), 7.54 (dd, 1H, J = 1.27, 7.92 Hz), 7.48 (dd, 1H, J = 1.67, 7.54 Hz), 7.28 (d, 1H, J = 7.63 Hz), 7.22 (dd, 1H, J = 1.56, 7.82 Hz), 7.18–6.81 (m, 11H), 6.79[a] (s 2H), 6.77[b] (s, 2H), 6.59 (dt, 1H, J = 1.08, 7.58 Hz), 6.40 (dt, 1H, J = 1.56, 7.83 Hz), 6.13 (d, 1H, J = 8.22 Hz), 2.65 (s, 6H), 2.45 (s, 6H), 2.12 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.7[a] (Cr=C), 288.1[b] (Cr=C), 224.2[b] (CO_{trans}), 223.5[a] (CO_{trans}), 216.7[a] (CO_{cis}), 216.5[b] (CO_{cis}), 155.3[b], 150.4[a], 142.1, 140.4, 140.3, 140.2, 139.9, 139.5, 139.4, 133.4, 133.3, 132.9, 131.2, 129.7, 129.5, 129.3, 129.0, 128.4, 128.2, 127.8, 127.3, 125.3, 121.6[b], 120.7[a], 120.04, 120.01, 119.0, 118.6, 96.0[a] (C≡C), 94.6[b] (C≡C), 92.0[b] (C≡C), 90.6[a] (C≡C), 26.9, 21.3, 21.2.

IR (toluene): 2 056 m, 1 978 w, 1 933 vs cm^{-1}.

HRMS: m/z calc for $C_{29}H_{21}NO_5Cr$ (M^+): 515.0825. Found: 487.0870 (M^+ – CO), 459.0922 (M^+ – 2CO).

E/Z-Pentacarbonyl[(2-(mesitylethynyl)phenylamino)-(p-tolyl)carbene]chromium **8**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(–I)] (578 mg, 1.50 mmol), acetyl bromide (184 mg, 0.112 mL, 1.50 mmol), 2-(mesitylethynyl)aniline (537 mg, 1.65 mmol), triethylamine (167 mg, 0.229 mL, 1.65 mmol). Yield: 516 mg (65%) **8**, yellow oil (*E*/*Z*-ratio: 4:3). R_f = 0.44 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.89[a] (br, 1H, NH), 10.04[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.63[a] (br, 1H, NH), 9.06[b] (br, 1H, NH), 7.48 (d, 1H, J = 7.43 Hz, 1H), 7.30 (d, 2H, J = 7.63 Hz), 7.23 (t, 1H, J = 7.63 Hz), 7.12–7.01 (m, 4H, H_{arom}), 6.89 (d, 2H, J = 7.83 Hz), 6.81 (d, 1H, J = 8.03 Hz, 1H), 6.80[a] (s, 2H), 6.77[b] (s, 2H), 6.72 (d, 2H, J = 7.82 Hz), 6.59 (t, 1H, J = 7.54 Hz), 6.42 (t, 1H, J = 7.83 Hz), 6.18 (d, 1H, J = 8.22 Hz), 2.66[b] (s, 6H), 2.46[a] (s, 6H), 2.12 (s, 6H), 2.08[b] (s, 3H), 1.87[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 291.0[a] (Cr=C), 287.6[b] (Cr=C), 224.1[b] (CO_{trans}), 223.5[a] (CO_{trans}), 216.9[a] (CO_{cis}), 216.7[b] (CO_{cis}), 152.9, 147.9, 142.2, 140.5, 140.3, 139.7, 139.0, 138.9, 138.7, 137.4, 133.3, 132.8, 129.5, 129.1, 128.9[a], 128.2, 128.0, 127.8[a], 127.7, 127.2, 125.3, 122.5, 122.2[b], 121.2[a], 118.9, 118.7, 95.9[a] (C≡C), 94.6[b] (C≡C), 91.9[b] (C≡C), 90.7[a] (C≡C), 26.9, 21.4, 21.3, 21.2, 21.1.

IR (toluene): 2 054 m, 1 976 w, 1 930 vs cm^{-1}.

MS (EI): m/z 417 (8%, M^+ – 4CO), 389 (8%, M^+ – 5CO).

E/Z-Pentacarbonyl[(2-(mesitylethynyl)phenylamino)-(2-propenyl)carbene]chromium **9**

Preparation and work-up as described for **1**. Tetramethylammonium[pentacarbonyl(2-methylprop-2-enoyl)chromate(–I)] (436 mg, 1.30 mmol), acetyl bromide (160 mg, 0.096 mL, 1.30 mmol), 2-(mesitylethynyl)aniline (337 mg, 1.43 mmol), triethylamine (145 mg, 0.199 mL, 1.43 mmol). Yield: 361 mg (58%) **9**, yellow oil (*E*/*Z*-ratio: 5:6). R_f = 0.49 (petroleum ether/dichloromethane 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.57[a] (br, 1H, NH), 10.09[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.16[a] (br, 1H, NH), 8.95[b] (br, 1H, NH), 7.45–7.04 (m, 8H), 6.76[b] (s, 2H), 6.69[a] (s, 2H), 4.57 (s, 1H), 4.39 (s, 1H), 4.37 (s, 1H), 4.29 (s, 1H), 2.57 (s, 6H), 2.48 (s, 6H), 2.10[a] (s, 3H), 2.09[b] (s, 3H), 1.87 (s, 3H), 1.56 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 291.2[a] (Cr=C), 288.2[b] (Cr=C), 223.7[b] (CO_{trans}), 223.1[a] (CO_{trans}), 217.6[a] (CO_{cis}), 217.0[b] (CO_{cis}), 160.1[b], 152.8[a], 145.9, 145.4, 142.1, 140.4, 140.2, 139.4, 138.9, 133.5, 133.0, 130.6, 130.2, 129.5, 129.0, 128.5, 128.2, 128.0, 127.7, 126.9, 125.0, 122.3, 119.0, 118.6, 107.8[a], 104.3[b], 95.5[a] (C≡C), 94.5[b] (C≡C), 91.7[b] (C≡C), 90.6[a] (C≡C), 26.9, 21.1.

IR (toluene): 2 056 m, 1 980 w, 1 933 vs cm^{-1}.

HRMS: m/z calc for $C_{26}H_{11}NO_5Cr$ (M^+): 479.0825. Found: 479.0817.

E/Z-Pentacarbonyl[(2-[(2,4,6-tri-tert-butylphenyl)-ethynyl]phenylamino)(phenyl)carbene]chromium **10**

Preparation as described for **1**. Tetramethylammonium-[pentacarbonyl(benzoyl)chromate(–I)] (186 mg, 0.50 mmol), acetyl bromide (61 mg, 0.041 mL, 0.55 mmol), 2-[(2,4,6-tri-*tert*-butylphenyl)ethynyl]aniline (199 mg, 0.55 mmol), triethylamine (56 mg, 0.076 mL, 0.55 mmol). The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane 3:1 as eluent to give 273 mg (85%) **10** as a yellow oil (*E*/*Z*-ratio: 1:1). R_f = 0.48 (petroleum ether/dichloromethane 3:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.92[a] (br, 1H, NH), 10.10[b] (br, 1H, NH).

^{1}H NMR (250 MHz, C_6D_6): δ 10.98[a] (br, 1H, NH), 9.50[b] (br, 1H, NH), 7.81–7.71 (m, 2H), 7.62 (s, 2H), 7.56 (s, 2H), 7.10–6.73 (m, 12H), 6.58 (t, 1H, J = 7.47 Hz), 6.38 (t, 1H, J = 7.20 Hz, 1H), 6.19 (d, 1H, J = 7.83 Hz), 1.79 (s, 18H), 1.62 (s, 18H), 1.45 (s, 9H), 1.34 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 292.2[a] (Cr=C), 288.3[b] (Cr=C), 223.9[a] (CO_{trans}), 223.5[b] (CO_{trans}), 216.6[a] (CO_{cis}), 216.5[b] (CO_{cis}), 155.2, 153.3, 151.2, 151.0, 150.2, 142.0, 139.5, 132.9, 132.7, 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 127.5, 127.3, 125.9, 122.3, 122.1, 21.1, 120.8, 119.1, 115.9, 115.7, 100.8 (C≡C), 99.7 (C≡C), 97.3 (C≡C), 96.1 (C≡C), 36.6, 36.5, 31.2, 30.7, 30.5, 26.8.

IR (toluene): 2 056 m, 1 981 w, 1 930 vs cm^{-1}.

MS (EI): m/z 613 (3%, M^+ – CO), 585 (3%, M^+ – 2CO), 529 (52%, M^+ – 4CO), 501 (60%, M^+ – 5CO).

E/Z-Pentacarbonyl[(2-[(2,4,6-tri-tert-butylphenyl)-ethynyl]phenylamino)(p-tolyl)carbene]chromium **11**

Preparation and work-up as described for **10**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(–I)] (193 mg, 0.50 mmol), acetyl bromide (61 mg, 0.037 mL, 0.50 mmol), 2-[(2,4,6-tri-*tert*-butylphenyl)ethynyl]aniline (199 mg, 0.55 mmol), triethylamine (56 mg, 0.076 mL, 0.55 mmol). Yield: 295 mg (85%) **11**, yellow oil (*E*/*Z*-ratio: 1:1). R_f = 0.49 (petroleum ether/dichloromethane 3:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ 10.86[a] (br, 1H, NH), 10.08[b] (br,1H, NH).

^{1}H NMR (250 MHz, C_6D_6): δ 10.95[a] (br, 1H, NH), 9.59[b] (br, 1H, NH), 7.63 (dd, 1H, J = 1.35, 7.39 Hz), 7.62 (s, 2H), 7.55 (s, 2H), 7.51 (dd, 1H, J = 1.35, 7.41 Hz), 7.28 (dd, 1H, J = 1.35, 7.41 Hz), 7.18–7.03 (m, 6H), 6.91 (d, 1H, J = 8.26 Hz, 1H), 6.83 (d, 1H, J = 8.26 Hz), 6.76 (d, 1H, J = 7.80 Hz), 6.59 (dt, 1H, J = 1.37, 7.49 Hz), 6.41 (dt, 1H, J = 1.38, 8.15 Hz), 6.25 (d, 1H, J = 8.26 Hz), 2.02 (s, 3H), 1.89 (s, 3H), 1.80 (s, 18H), 1.63 (s, 18H), 1.35 (s, 9H), 1.30 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 292.5[a] (Cr=C), 287.6[b] (Cr=C), 223.9[a] (CO_{trans}), 223.6[b] (CO_{trans}), 216.7[a] (CO_{cis}), 216.6[b] (CO_{cis}), 153.3, 152.8, 151.2, 151.0, 147.9, 142.1, 139.8, 139.2, 137.4, 132.8, 132.7, 129.5, 129.8, 128.98, 128.87, 128.79, 128.3, 128.2, 127.4, 126.0, 122.9, 122.5, 121.6, 120.8, 119.0, 115.9, 115.7, 100.7 (C≡C), 99.6 (C≡C), 97.4 (C≡C), 96.2 (C≡C), 36.6, 36.5, 31.2, 30.7, 30.5, 21.1.

IR (toluene): 2 056 m, 1 980 w, 1 935 vs cm^{-1}.

MS (EI): m/z 627 (3%, M^+ - CO), 599 (3%, M^+ - 2CO), 543 (51%, M^+ - 4CO), 515 (60% M^+ - 5CO).

E/Z-Pentacarbonyl[(2-[(3,4,5-trimethoxyphenyl)-ethynyl]phenylamino)(phenyl)carbene]chromium **12**

Preparation as described for **1**. Tetramethylammonium-[pentacarbonyl(benzoyl)chromate(−I)] (449 mg, 1.21 mmol), acetyl bromide (149 mg, 0.089 mL, 1.21 mmol), 2-[(3,4,5-trimethoxyphenyl)ethynyl]aniline (399 mg, 1.41 mmol), triethylamine (143 mg, 0.195 mL, 1.41 mmol). The crude product was purified by column chromatography on silica gel using dichloromethane as eluent to give 402 mg (59%) **10** as a yellow oil (*E/Z*-ratio: 10:7). R_f = 0.45 (dichloromethane).

^{1}H NMR (250 MHz, $CDCl_3$): δ 10.96[a] (br, 1H, NH), 10.06[b] (br, 1H, NH).

^{1}H NMR (250 MHz, C_6D_6): δ 10.69[a] (br, 1H, NH), 8.84[b] (br, 1H, NH), 7.58–7.52 (m, 2H), 7.29 (dd, 2H, J = 1.38, 7.81 Hz), 7.14 (dd, 2H, J = 1.37, 7.80 Hz, 2H), 7.10[a] (s, 2H), 7.09–6.98 (m, 6H), 6.94[b] (s, 2H), 6.93–6.72 (m, 3H), 6.57 (dt, 1H, J = 1.38, 7.34 Hz), 6.39 (dt, 1H, J = 1.38, 7.57 Hz), 6.10 (d, 1H, J = 7.80 Hz), 3.85[b] (s, 3H), 3.84[a] (s, 3H), 3.53[a] (s, 6H), 3.44[b] (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.2[a] (Cr=C), 288.3[b] (Cr=C), 224.2[b] (CO_{trans}), 223.2[a] (CO_{trans}), 216.9[a] (CO_{cis}), 216.6[b] (CO_{cis}), 155.3, 153.1, 150.2, 142.8, 139.6, 139.5, 139.3, 133.0[b], 132.5[a], 129.7, 129.5, 128.4, 128.3[b], 128.2, 128.1, 127.9, 127.4, 127.3, 125.1, 121.9[b], 121.3[b], 120.6[a], 118.3[a], 117.1[b], 116.6[a], 109.0[a], 108.8[b], 98.1[a] (C≡C), 96.3[b] (C≡C), 83.7[b] (C≡C), 82.5[a] (C≡C), 60.9, 56.1, 56.0.

IR (toluene): 2 055 m, 1 981 w, 1 935 vs cm^{-1}.

MS (EI): m/z 441 (1%, M^+ - $Cr(CO)_3$), 413 (2%, M^+ - $Cr(CO)_4$), 401 (58%), 119 (100%).

E/Z-Pentacarbonyl[(2-[(3,4,5-trimethoxyphenyl)-ethynyl]phenylamino)(p-tolyl)carbene]chromium **13**

Preparation and work-up as described for **12**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(−I)] (470 mg, 1.22 mmol), acetyl bromide (150 mg, 0.09 mL, 1.22 mmol), 2-[(3,4,5-trimethoxyphenyl)ethynyl]aniline (408 mg, 1.44 mmol), triethylamine (146 mg, 0.20 mL, 1.44 mmol). Yield: 705 mg (74%) **11**, yellow oil (*E/Z*-ratio: 5:3). R_f = 0.46 (dichloromethane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.91[a] (br, 1H, NH), 10.01[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.70[a] (br, 1H, NH), 8.95[b] (br, 1H, NH), 7.54 (dd, 1H, J = 1.56, 7.44 Hz), 7.30 (dd, 1H, J = 1.37, 7.63 Hz), 7.23 (d, 1H, J = 8.15 Hz), 7.13 (d, 2H, J = 8.22 Hz), 7.10[a] (s, 2H), 7.06 (dt, 1H, J = 1.57, 7.54 Hz), 7.02 (dt, 1H, J = 1.49, 7.21 Hz), 6.95[b] (s, 2H), 6.90 (d, 1H, J = 7.83 Hz), 6.82–6.78 (d, 2H, J = 8.22 Hz), 6.76–6.72 (d, 2H, J = 8.32 Hz), 6.58 (dt, 1H, J = 1.17, 7.63 Hz), 6.41 (dt, 1H, J = 1.37, 7.73 Hz), 6.15 (d, 1H, J = 8.21 Hz), 3.85[b] (s, 3H), 3.84[a] (s, 3H), 3.52[a] (s, 6H), 3.44[b] (s, 6H), 2.02[b] (s, 3H), 1.82[a] (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 290.3[a] (Cr=C), 288.4[b] (Cr=C), 224.3[b] (CO_{trans}), 223.3[a] (CO_{trans}), 217.0 ($(CO_{cis})_2$), 153.0, 152.9, 147.5, 142.9, 139.7, 139.6, 138.5, 137.5, 133.0[b], 132.5[a], 128.9, 128.8[a], 128.7, 128.4, 127.3, 125.0, 121.7[b], 121.6[a], 121.0[b], 118.2[a], 116.8[b], 116.6[a], 109.0[a], 108.9[b], 98.2[a] (C≡C), 96.4[b] (C≡C), 83.8[b] (C≡C), 82.6[a] (C≡C), 60.8, 56.0, 21.1.

IR (toluene): 2 054 m, 1 981 w, 1 933 vs cm^{-1}.

MS (EI): m/z 441 (1%, M^+ - $Cr(CO)_3$), 413 (2%, M^+ - $Cr(CO)_4$), 199 (100%), 91 (32%).

E/Z-Pentacarbonyl[(2-[(2,6-dimethoxyphenyl)ethynyl]-phenylamino)(phenyl)carbene]chromium **14**

Preparation and work-up as described for **6**. Tetramethylammonium[pentacarbonyl(benzoyl)chromate(−I)] (639 mg, 1.72 mmol), acetyl bromide (211 mg, 0.128 mL, 1.21 mmol), 2-[(2,6-dimethoxyphenyl)ethynyl]aniline (507 mg, 2.0 mmol), triethylamine (202 mg, 0.277 mL, 2.0 mmol). Yield: 679 mg (74%) **12**, yellow oil (*E/Z*-ratio: 2:1). R_f = 0.40 (petroleum ether/dichloromethane 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.00[a] (br, 1H, NH), 10.23[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.88[a] (br, 1H, NH), 9.19[b] (br, 1H, NH), 7.60 (dd, 1H, J = 1.47, 8.41 Hz), 7.31 (dd, 1H, J = 1.37, 7.82 Hz), 7.27 (dd, 1H, J = 0.78, 7.63 Hz), 7.23 (dd, 1H, J = 1.37, 7.73 Hz), 7.10–6.95 (m, 6H), 6.88–6.82 (m, 5H), 6.78–6.73 (m, 2H), 6.52 (dt, 1H, J = 0.98, 7.63 Hz), 6.34 (dt, 1H, J = 1.37, 7.02 Hz), 6.27 (d, 2H, J = 8.41 Hz), 6.23 (d, 2H, J = 8.41 Hz), 6.07 (d, 1H, J = 8.02 Hz), 3.52[a] (s, 6H), 3.35[b] (s, 6H).

^{13}C NMR (100 MHz, acetone-d_6): δ 285.5[b] (Cr=C), 283.8[a] (Cr=C), 225.5[a] (CO_{trans}), 225.0[b] (CO_{trans}), 217.9[b] (CO_{cis}), 217.7[a] (CO_{cis}), 162.5[a], 162.4[b], 156.0, 152.0, 144.1, 142.7, 134.0, 133.0, 131.5, 131.4, 130.2, 129.8, 129.2, 129.1, 128.90, 128.85, 128.80[a], 128.5, 128.3, 128.1, 127.1, 123.9[b], 122.7[a], 122.4[a], 121.4[b], 104.3[a], 104.2[b], 101.2[a] (C≡C), 101.5[b] (C≡C), 93.7[b] (C≡C), 93.3[a] (C≡C), 56.3[a], 56.2[b].

IR (toluene): 2 054 m, 1 979 w, 1 933 vs cm^{-1}.

MS (EI): m/z 369 (3%, M^+ - $Cr(CO)_4$), 357 (62%), 341 (10%, M^+ - $Cr(CO)_5$), 105 (100%).

E/Z-Pentacarbonyl[(2-[(2,6-dimethoxyphenyl)ethynyl]-phenylamino)(p-tolyl)carbene]chromium **15**

Preparation and work-up as described for **6**. Tetramethylammonium[pentacarbonyl(*p*-toluoyl)chromate(−I)] (666 mg, 1.73 mmol), acetyl bromide (213 mg, 0.129 mL, 1.73 mmol), 2-[(2,6-dimethoxyphenyl)ethynyl]aniline (507 mg, 2.0 mmol), triethylamine (202 mg, 0.277 mL, 2.0 mmol). Yield: 521 mg (55%) **13**, yellow oil (*E/Z*-ratio: 5:2). R_f = 0.41 (petroleum ether/dichloromethane 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.99[a] (br, 1H, NH), 10.23[b] (br, 1H, NH).

^{1}H NMR (400 MHz, C_6D_6): δ 10.84[a] (br, 1H, NH), 9.22[b] (br, 1H, NH), 7.58 (d, 1H, J = 8.41 Hz), 7.33 (dd, 1H, J = 1.37, 8.23 Hz), 7.29 (dd, 1H, J = 1.36, 8.50 Hz), 7.23–7.21 (m, 4H), 7.06–7.00 (m, 4H), 6.98 (dd, 1H, J = 1.37, 8.23 Hz, 1H), 6.92 (d, 1H, J = 8.36 Hz), 6.85 (d, 2H, J = 8.36 Hz), 6.73 (d, 2H, J = 7.83 Hz), 6.52 (dt, 1H, J = 1.17, 7.63 Hz), 6.36 (dt, 1H, J = 1.37, 7.83 Hz), 6.27 (d, 1H, J = 8.41 Hz), 6.24 (d, 1H, J = 8.61 Hz), 6.12 (d, 1H, J = 8.06 Hz, 1H), 3.52[a] (s, 6H), 3.36[b] (s, 6H), 2.10[b] (s, 3H), 1.88[a] (s, 3H).

^{13}C NMR (100 MHz, acetone-d_6): δ 285.6[b] (Cr=C), 283.3[a] (Cr=C), 225.5[a] (CO_{trans}), 225.1[b] (CO_{trans}), 218.0[b]

(CO_{cis}), 217.8[a] (CO_{cis}), 162.5[b], 162.4[a], 153.5[a], 149.4[b], 144.0[b], 142.7[a], 138.5[b], 136.7[a], 134.0[a], 133.0[b], 131.5[b], 131.4[a], 130.2[b], 129.8[a], 129.3[a], 129.1[b], 129.0[a], 128.9[b], 128.7[a], 128.5[b], 123.9[b], 123.1[a], 122.3[a], 121.7[b], 104.2[a], 104.1[b], 93.7[a] (C≡C), 93.3[b] (C≡C), 90.0[a] (C≡C), 89.9[b] (C≡C), 56.2[b], 56.1[a], 21.1[a], 21.0[b].

IR (toluene): 2 054 m, 1 977 w, 1 933 vs cm^{-1}.

MS (EI): m/z 411 (2%, M^+ – $Cr(CO)_3$), 383 (5%, M^+ – $Cr(CO)_4$), 371 (79%), 355 (10%, M^+ – $Cr(CO)_5$), 119 (100%).

5-Hydroxy-6-phenyl-11H-benzo[a]carbazole **16**

A solution of 251 mg (0.53 mmol) **1** in 20 mL toluene was warmed at 90 °C for 1 h (while the reaction was monitored by IR spectroscopy and TLC). The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:2) as eluent gave 46 mg (28%) **16** as a brown solid. R_f = 0.44; mp 98–101 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 8.69 (br, 1H, NH), 8.42 (d, 1H, J = 7.43 Hz), 8.11 (d, 1H, J = 7.43 Hz), 7.72–7.53 (m, 6H), 7.51 (d, 1H, J = 7.63 Hz), 7.42–6.93 (m, 4H), 5.30 (s, 1H, OH).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 138.8, 134.9, 130.7, 129.7, 129.5, 128.7, 126.0, 125.0, 123.8, 123.7, 123.4, 121.2, 120.9, 120.3, 119.1, 116.7, 116.5, 110.9.

IR (KBr): 3 532 m, 3 411 s, 3 058 w, 3 031 w, 2 970 w, 2 920 w, 2 860 vw, 1 596 m, 1 490 m, 1 459 m, 1 455 m, 1 440 m, 1 388 m, 1 357 m, 1 293 m, 1 258 m, 1 210 m, 1 140 m, 1 116 m, 1 060 m, 1 057 m, 1 038 m, 903 m, 742 s, 701 s cm^{-1}.

MS (EI): m/z 309 (100%, M^+).

HRMS: m/z calc for $C_{22}H_{15}NO$ (M^+): 309.1153. Found: 309.1151.

5-Hydroxy-3-methyl-6-phenyl-11H-benzo[a]carbazole **17**

A solution of 200 mg (0.41 mmol) **2** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 40 mg (26%) **17** as a brown solid. R_f = 0.32; mp 98–100 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 8.65 (br, 1H, NH), 8.20 (s, 1H), 8.03 (d, 1H, J = 8.41 Hz), 7.68–6.86 (m, 10H), 5.24 (s, 1H, OH), 2.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 138.7, 135.0, 134.9, 130.7, 129.7, 129.1, 128.8, 128.0, 127.9, 124.0, 123.9, 123.6, 122.9, 121.1, 120.2, 119.1, 116.5, 116.0, 110.8, 21.9.

IR (KBr): 3 526 s, 3 436 s, 3 053 w, 3 025 w, 1 598 m, 1 487 m, 1 459 m, 1 453 m, 1 443 m, 1 418 m, 1 385 m, 1 375 m, 1 295 m, 1 264 m, 1 218 m, 1 176 m, 1 159 m, 1 114 m, 1 054 m, 1 025 m, 910 m, 743 s, 699 s cm^{-1}.

MS (EI) m/z 323 (100%, M^+).

HRMS: m/z calc for $C_{23}H_{17}NO$ (M^+): 323.1310. Found: 323.1298.

3-Hydroxy-1-methyl-4-phenyl-9H-carbazole **18**

A solution of 219 mg (0.50 mmol) **3** in 20 mL toluene was warmed at 110 °C for 2 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using dichloromethane as eluent gave 26 mg (19%) **18** as a brown solid. R_f = 0.50; mp 69–71 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 7.89 (br, 1H, NH), 7.64–7.52 (m, 6H), 7.41 (dd, 1H, J = 0.98, 7.63 Hz), 7.29 (ddd, 1H, J = 1.24, 7.15, 7.41 Hz), 6.98 (q, 1H, J = 0.78 Hz), 6.87 (ddd, 1H, J = 1.03, 7.08, 7.38 Hz), 4.76 (s, 1H, OH), 2.56 (d, 3H, J = 0.78 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 140.2, 134.9, 133.5, 130.8, 130.5, 129.6, 128.7, 128.4, 125.3, 123.4, 121.9, 120.2, 118.7, 115.0, 110.6, 16.8.

IR (KBr): 3 521 m, 3 370 m, 3 051 w, 3 025 vw, 2 980 m, 2 920 m, 2 850 vw, 1 711 m, 1 612 m, 1 511 m, 1 485 m, 1 457 m, 1 378 s, 1 305 m, 1 259 m, 1 102 s, 1 019 s, 798 s cm^{-1}.

MS (EI): m/z 273 (100%, M^+).

HRMS: m/z calc for $C_{19}H_{15}NO$ (M^+): 273.1154. Found: 273.1163.

5-Hydroxy-6-p-tolyl-11H-benzo[a]carbazole **19**

A solution of 292 mg (0.60 mmol) **4** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:2) as eluent gave 47 mg (24%) **19** as a brown solid. R_f = 0.47; mp 106–108 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (br, 1H, NH), 8.40 (d, 1H, J = 8.41 Hz), 8.11 (d, 1H, J = 8.22 Hz), 7.62 (ddd, 1H, J = 1.37, 6.30, 7.54 Hz), 7.56 (ddd, 1H, J = 1.17, 6.11, 7.28 Hz), 7.52–7.43 (m, 5H), 7.29 (ddd, 1H, J = 1.25, 6.85, 7.99 Hz), 7.01 (d, 1H, J = 8.78 Hz), 7.01 (d, 1H, J = 8.78 Hz), 6.93 (ddd, 1H, J = 0.98, 7.92, 8.48 Hz), 5.32 (s, 1H, OH), 2.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 138.8, 138.5, 134.4, 131.7, 130.6, 130.5, 129.7, 129.5, 126.0, 125.0, 124.3, 123.8, 121.4, 120.9, 120.3, 119.1, 116.9, 116.5, 110.9, 21.5.

IR (KBr): 3 525 sh, 3 416 s, 3 054 w, 3 030 w, 2 975 w, 2 910 w, 2 890 w, 1 508 w, 1 458 w, 1 384 m, 1 207 m, 1 110 m, 1 070 m, 1 055 m, 903 m, 821 m, 743 s cm^{-1}.

MS (EI): m/z 323 (100%, M^+).

HRMS: m/z calc for $C_{23}H_{17}NO$ (M^+): 323.1310. Found: 323.1319.

5-Hydroxy-3-methyl-6-p-tolyl-11H-benzo[a]carbazole **20**

A solution of 276 mg (0.55 mmol) **5** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 46 mg (25%) **20** as a brown solid. R_f = 0.40; mp 105–108 °C.

^1H NMR (400 MHz, $CDCl_3$): δ 8.63 (br, 1H, NH), 8.19 (s, 1H), 8.01 (d, 1H, J = 8.02 Hz), 7.52–7.43 (m, 5H), 7.30 (d, J = 7.62 Hz), 7.00–6.91 (m, 3H), 5.29 (s, 1H, OH), 2.60 (s, 3H), 2.54 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 138.7, 138.5, 134.8, 131.8, 130.6, 130.4, 129.7, 128.0, 124.1, 123.7, 122.9, 121.3, 120.3, 119.1, 119.0, 116.5, 116.2, 110.8, 22.0, 21.9.

IR (KBr): 3 543 s, 3 423 s, 3 054 w, 3 028 w, 2 923 w, 2 857 w, 1 648 m, 1 602 m, 1 455 m, 1 298 m, 1 176 m, 904 m, 818 m, 745 s cm^{-1}.

MS (EI): m/z 337 (100%, M^+).

HRMS: m/z calc for $C_{24}H_{19}NO$ (M^+): 337.1467. Found: 337.1471.

3-Hydroxy-1-methyl-6-p-tolyl-9H-benzo[a]carbazole **21**

A solution of 298 mg (0.66 mmol) **6** in 20 mL toluene was warmed at 110 °C for 2 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:2) as eluent gave 34 mg (18%) **21** as a brown solid. R_f = 0.33; mp 70–72 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (br, 1H, NH), 7.43–7.39 (m, 5H), 7.28 (ddd, 1H, J = 1.18, 6.71, 7.80 Hz), 7.04 (d, 1H, J = 7.82 Hz), 6.97 (q, 1H, J = 0.78 Hz), 6.88 (ddd, 1H, J = 0.78, 6.77, 7.79 Hz), 4.78 (s, 1H, OH), 2.57 (d, 3H, J = 0.78 Hz), 2.50 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 140.2, 138.3, 133.6, 131.7, 130.4, 130.3, 125.3, 123.5, 122.0, 121.3, 120.1, 118.7, 118.6, 114.9, 110.6, 21.4, 16.8.

IR (KBr): 3 514 s, 3 259 s, 3 057 w, 3 023 w, 2 900 w, 2 850 w, 1 623 w, 1 499 m, 1 456 m, 1 391 m, 1 306 s, 901 m, 898 m, 816 m, 733 s cm^{-1}.

MS (EI): m/z 287 (100%, M^+).

HRMS: m/z calc for $C_{20}H_{17}NO$ (M^+): 287.1310. Found: 287.1308.

5-Hydroxy-6-mesityl-11H-benzo[a]carbazole **22**

A solution of 222 mg (0.43 mmol) **7** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 98 mg (65%) **22** as a light brown solid. R_f = 0.41; mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (br, 1H, NH), 8.44 (d, 1H, J = 8.21 Hz), 8.15 (d, 1H, J = 8.02 Hz), 7.65 (t, 1H, J = 7.44 Hz), 7.59 (t, 1H, J = 7.59 Hz), 7.52 (d, 1H, J = 8.22 Hz), 7.30 (t, 1H, J = 8.02 Hz), 7.14 (s, 2H), 6.94 (t, 1H, J = 7.53 Hz), 6.75 (d, 1H, J = 8.31 Hz), 5.03 (s, 1H, OH), 2.46 (s, 3H), 1.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 138.7, 138.5, 129.7, 129.6, 129.1, 125.8, 124.8, 124.3, 124.2, 123.7, 123.5, 120.9, 120.4, 120.3, 119.5, 116.6, 114.4, 110.8, 21.3, 19.9.

IR (KBr): 3 481 s, 3 433 s, 3 062 w, 2 910 w, 2 820 w, 1 587 m, 1 567 m, 1 454 m, 1 408 m, 1 330 m, 1 207 m, 1 070 m, 1 050 m, 896 m, 856 m, 745 s cm^{-1}.

MS (EI): m/z 351 (100%, M^+).

HRMS: m/z calc for $C_{25}H_{21}NO$ (M^+): 351.1623. Found: 351.1625.

5-Hydroxy-6-mesityl-3-methyl-11H-benzo[a]carbazole **23**

A solution of 201 mg (0.38 mmol) **8** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 97 mg (70%) **23** as light brown solid. R_f = 0.51; mp 115–117 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 8.64 (br, 1H, NH), 8.26 (s, 1H), 7.99 (d, 1H, J = 8.26 Hz), 7.47 (t, 1H, J = 7.61 Hz), 7.31 (d, 1H, J = 7.31 Hz), 7.26 (d, 1H, J = 7.73 Hz), 7.16 (s, 2H), 6.99 (t, 1H, J = 7.79 Hz), 6.77 (d, 1H, J = 7.79 Hz), 5.08 (s, 1H, OH), 2.62 (s, 3H), 2.48 (s, 3H), 2.01 (s, 6H).

^{13}C NMR (62.5 MHz, $CDCl_3$): δ 141.2, 138.7, 138.6, 138.5, 134.7, 130.0, 129.8, 129.2, 127.9, 124.4, 124.1, 123.8, 123.0, 120.4, 120.3, 119.6, 119.3, 115.9, 114.5, 110.3, 22.0, 21.4, 19.6.

IR (KBr): 3 481 sh, 3 431 s, 3 057 vw, 2 940 w, 2 875 w, 1 636 m, 1 611 m, 1 597 m, 1 467 m, 1 455 m, 1 419 m, 1 293 m, 1 176 s, 1 049 m, 905 m, 812 m, 746 m cm^{-1}.

MS (EI): m/z 365 (100%, M^+).

HRMS: m/z calc for $C_{26}H_{23}NO$ (M^+): 365.1780. Found: 365.1785.

3-Hydroxy-1-methyl-4-mesityl-9H-carbazole **24**

A solution of 216 mg (0.45 mmol) **9** in 20 mL toluene was warmed at 110 °C for 2 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:3) as eluent gave 24 mg (17%) **24** as a brown solid. R_f = 0.62; mp 75–77 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (br, 1H, NH), 7.39 (dd, 1H, J = 0.97, 8.17 Hz), 7.26 (ddd, 1H, J = 1.17, 7.08, 8.16 Hz), 7.08 (s, 2H), 6.97 (q, 1H, J = 0.78 Hz), 6.88 (ddd, 1H, J = 0.98, 7.45, 8.23 Hz), 6.73 (d, 1H, J = 7.43 Hz), 4.49 (s, 1H, OH), 2.57 (d, 3H, J = 0.78 Hz), 2.41 (s, 3H), 1.94 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 138.3, 138.2, 133.7, 129.6, 129.0, 128.2, 123.8, 123.3, 121.0, 120.9, 119.1, 116.5, 115.6, 114.8, 110.4, 21.3, 19.8, 16.9.

IR (KBr): 3 432 vs, 2 964 m, 2 927 m, 2 859 vw, 1 636 m, 1 455 m, 1 262 s, 1 095 s, 1 026 s, 803 s cm^{-1}.

MS (EI): m/z 315 (100%, M^+).

HRMS: m/z calc for $C_{22}H_{21}NO$ (M^+): 315.1631. Found: 315.1631.

N-{2-[(2,4,6-Tri-tert-butylphenyl)ethynyl]phenyl}-benzamide **25**

A solution of 250 mg (0.39 mmol) **10** in 20 mL toluene was warmed at 105 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 50 mg (27%) **25** as a orange solid. R_f = 0.53; mp 154–156 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 8.63 (br, 1H, N-H), 8.50 (d, 1H, J = 8.26 Hz), 7.83–7.78 (m, 2H), 7.54 (dt, 1H, J = 1.38, 7.42 Hz), 7.51–7.38 (m, 3H), 7.36 (s, 2H), 7.15 (dt, 1H, J = 1.38, 7.57 Hz), 1.51 (s, 18H), 1.31 (s, 9H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 153.2, 150.9, 138.4, 135.0, 131.8, 131.5, 129.2, 128.6, 127.1, 124.0, 122.9, 120.9, 120.2, 114.1, 99.4, 97.2, 35.2, 32.7, 31.1, 30.4.

IR (KBr): 3 403 s, 3 000 w, 2 960 m, 2 928 m, 2 869 w, 1 685 s, 1 602 m, 1 580 m, 1 519 s, 1 449 s, 1 308 m, 1 246 m, 1 222 m, 760 m, 709 m, 691 m cm^{-1}.

MS (EI): m/z 477 (100%, M^+).

4-Methyl-N-{2-[(2,4,6-tri-tert-butylphenyl)ethynyl]-phenyl}benzamide **26**

A solution of 302 mg (0.46 mmol) **11** in 20 mL toluene was warmed at 105 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:2) as eluent gave 66 mg (29%) **26** as a orange solid. R_f = 0.43; mp 177–180 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 8.63 (br, 1H), 8.51 (d, 1H, J = 8.26 Hz), 7.71 (d, 2H, J = 8.26 Hz), 7.54 (dd, 1H, J = 1.38, 7.53 Hz), 7.42 (dt, 1H, J = 1.38, 7.43 Hz), 7.37 (s, 2H), 7.20 (d, 2H, J = 8.27 Hz), 7.14 (dt, 1H, J = 1.38, 7.57 Hz), 2.38 (s, 3H), 1.51 (s, 18H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 153.3, 150.8, 142.3, 138.5, 132.0, 131.5, 129.25, 129.23, 127.2, 123.7, 120.9, 120.1, 114.0, 99.3, 97.3, 35.2, 33.6, 31.2, 30.5, 21.4.

IR (KBr): 3 411 m, 3 001 w, 2 961 m, 2 925 w, 2 870 w, 1 681 s, 1 610 m, 1 600 m, 1 575 m, 1 522 s, 1 505 s, 1 445 s, 1 302 s, 763 s, 740 m cm^{-1}.

MS (EI): m/z 491 (100%, M^+).

5-Hydroxy-6-(3,4,5-trimethoxyphenyl)-11H-benzo[a]carbazole **27**

A solution of 250 mg (0.44 mmol) **12** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/diethyl ether (1:1) as eluent gave 75 mg (43%) **27** as a light brown solid. R_f = 0.35; mp 165–166 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (br, 1H, NH), 8.43 (d, 1H, J = 8.41 Hz), 8.13 (d, 1H, J = 7.82 Hz), 7.67–7.57 (m, 2H), 7.54 (d, 1H, J = 8.21 Hz), 7.33 (t, 1H, J = 7.63 Hz), 7.13 (d, 1H, J = 8.02 Hz), 7.01 (t, 1H, J = 7.44 Hz), 6.83 (s, 2H), 5.47 (s, 1H, OH), 4.03 (s, 3H), 3.85 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 142.0, 138.8, 138.0, 130.2, 129.6, 126.1, 125.1, 124.4, 123.7, 123.4, 121.4, 121.0, 120.4, 119.3, 116.3, 111.0, 107.2, 61.1, 56.1.

IR (KBr): 3 550 sh, 3 435 s, 3 065 vw, 3 003 vw, 2 961 w, 2 930 w, 1 584 s, 1 505 s, 1 461 s, 1 237 s, 1 131 vs, 749 s cm^{-1}.

MS (EI): m/z: 399 (100%, M^+).

HRMS: m/z calc for $C_{25}H_{21}NO_4$ (M^+): 399.1471. Found: 399.1471.

5-Hydroxy-3-methyl-6-(3,4,5-trimethoxyphenyl)-11H-benzo[a]carbazole **28**

A solution of 240 mg (0.42 mmol) **13** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 78 mg (45%) **28** as a light brown solid. R_f = 0.36; mp 182–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (br, 1H, NH), 8.20 (s, 1H), 8.02 (d, 1H, J = 8.16 Hz), 7.52 (d, 1H, J = 7.83 Hz), 7.47 (d, 1H, J = 8.02 Hz), 7.31 (t, 1H, J = 7.63 Hz), 7.11 (d, 1H, J = 7.82 Hz), 6.99 (t, 1H, J = 7.44 Hz), 6.82 (s, 2H), 5.44 (s, 1H, OH), 4.03 (s, 3H), 3.85 (s, 6H), 2.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 141.6, 138.7, 137.9, 135.0, 130.4, 129.8, 128.1, 124.1, 123.8, 123.6, 122.8, 121.2, 120.4, 119.2, 116.4, 115.8, 110.9, 107.2, 61.1, 56.1, 21.9.

IR (KBr): 3 530 m, 3 367 m, 3 060 w, 3 002 w, 2 938 m, 2 836 w, 1 587 s, 1 504 s, 1 458 s, 1 409 s, 1 236 s, 1 130 vs, 748 s cm^{-1}.

MS (EI): m/z 413 (100% M^+).

HRMS: m/z calc for $C_{26}H_{23}NO_4$ (M^+): 413.1627. Found: 413.1629.

5-Hydroxy-6-(2,6-dimethoxyphenyl)-11H-benzo[a]carbazole **29**

A solution of 230 mg (0.43 mmol) **14** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/diethyl ether (1:1) as eluent gave 67 mg (42%) **29** as a light brown solid. R_f = 0.40; mp 138–140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (br, 1H, NH), 8.40 (d, 1H, J = 7.80 Hz), 7.94 (d, 1H, J = 7.80 Hz), 7.52–7.45 (m, 3H), 7.36 (d, 1H, J = 7.83 Hz), 7.21 (t, 1H, J = 7.82 Hz), 6.91–6.85 (m, 2H), 6.77 (d, 1H, J = 7.82 Hz), 5.35 (s, 1H, OH), 3.58 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 142.7, 138.7, 130.7, 129.8, 125.7, 124.5, 124.3, 124.0, 123.9, 123.0, 121.1, 120.3, 118.9, 117.1, 111.3, 111.0, 109.3, 104.6, 59.9.

IR (KBr): 3 489 m, 3 408 m, 3 059 w, 2 935 w, 2 837 w, 1 582 m, 1 469 s, 1 431 m, 1 254 s, 1 109 s, 903 m, 749 m cm^{-1}.

MS (EI): m/z 369 (100%, M^+).

HRMS: m/z calc for $C_{24}H_{19}NO_3$ (M^+): 369.1365. Found: 369.1366.

Anal calc for $C_{24}H_{19}NO_3$ (369.4): C, 78.03; H, 5.18; N, 3.79. Found: C, 78.09; H, 5.17; N, 3.65.

5-Hydroxy-3-methyl-6-(2,6-dimethoxyphenyl)-11H-benzo[a]carbazole **30**

A solution of 260 mg (0.47 mmol) **15** in 20 mL toluene was warmed at 90 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/diethyl ether (1:1) as eluent gave 77 mg (0.20 mmol, 43%) **30** as a light brown solid. R_f = 0.42; mp 199–200 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (br, 1H, NH), 8.23 (s, 1H), 7.94 (d, 1H, J = 8.41 Hz, 1H), 7.53 (t, 1H, J = 8.41 Hz), 7.42 (d, 1H, J = 8.52 Hz), 7.39 (d, 1H, J = 8.41 Hz), 7.23 (t, 1H, J = 8.40 Hz), 6.98–6.89 (m, 2H), 6.82 (d, 1H, J = 8.41 Hz), 5.33 (s, 1H, OH), 3.63 (s, 6H), 2.58 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 142.4, 138.6, 134.2, 130.6, 129.9, 127.7, 124.6, 124.2, 123.7, 123.0, 120.4, 120.2, 119.3, 118.9, 116.6, 113.4, 110.6, 109.3, 104.6, 56.0, 21.9.

IR (KBr): 3 545 m, 3 395 m, 3 058 vw, 2 939 w, 2 837 w, 1 584 m, 1 474 s, 1 435 m, 1 420 m, 1 249 s, 1 173 m, 1 111 vs, 729 m cm^{-1}.

MS (EI): m/z 383 (100%, M^+).

HRMS: m/z calc for $C_{25}H_{21}NO_3$ (M^+): 383.1521. Found: 383.1519.

Anal calc for $C_{25}H_{21}NO_3$ (383.5): C, 78.31; H, 5.52; N, 3.65. Found: C, 77.98; H, 5.69; N, 3.44.

Pentacarbonyl[(2-(trimethylsilylethynyl)phenylamino)-(E-1-phenylprop-1-enyl)carbene]chromium(0) **31**

Preparation as described for **1**. Tetramethylammonium-[pentacarbonyl(*E*-2-phenyl-2-butenoyl)chromate(−I)] (0.82 g, 1.99 mmol) [24], acetyl bromide (250 mg, 0.147 mL, 1.99 mmol), 2-(trimethylsilylethynyl)aniline (1.25 mg, 1.99 mmol), triethylamine (223 mg, 0.31 mL, 2.20 mmol). Purification of the crude product by column chromatography on silica gel using petroleum ether/dichloromethane 5:1 as eluent afforded 600 mg (60%) **31** as a yellow oil. R_f = 0.30 (petroleum ether/dichloromethane 5:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64–7.30 (m, 9H), 5.17 (q, 1H, J = 6.50 Hz), 1.38 (d, 3H, $^3J_{HH}$ = 6.50 Hz), 0.24 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 293.5 (Cr=C), 229.9 (CO_{trans}), 216.7 (CO_{cis}), 140.1, 135.7, 134.6, 129.2, 128.7, 128.4, 127.9, 127.8, 121.2, 101.8 (C≡C), 101.5 (C≡C), 77.7, 18.1, 0.0.

IR (CH_2Cl_2): 2 056 m, 1 979 w, 1 930 vs cm^{-1}.

MS (EI): m/z 509 (4%, M^+).

Anal calc for $C_{26}H_{23}NO_5SiCr$ (509.6): C, 61.29; H, 4.55; N, 2.75. Found: C, 61.32; H, 4.63; N, 2.43.

Tricarbonyl[3a-7a-η^6-2-(1-phenylprop-1-enyl)-3-(trimethylsilylketenyl)indole]chromium(0) **32**

A solution of 200 mg (0.39 mmol) **31** in 20 mL toluene was warmed at 110 °C for 2 h. The solvent was removed at reduced pressure, and after chromatography of the residue on silica gel using petroleum ether/diethyl ether (1:1) as

eluent 41 mg (29%) **32** were obtained as a yellow oil. $R_f = 0.35$.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.05 (m, 5H), 6.23 (d, 1H, J = 6.60 Hz), 5.81 (d, 1H, J = 6.60 Hz), 5.28 (t, 1H, J = 6.60 Hz), 5.27 (q, 1H, J = 5.51 Hz), 5.11 (t, 1H, J = 6.60 Hz), 1.75 (d, 3H, J = 5.51 Hz), 0.00 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 234.6 ($Cr(CO)_3$), 179.5, 146.9, 138.1, 122.1, 120.9, 119.7, 110.1, 90.1, 88.3, 87.5, 79.9, 68.6, 20.4, 14.1, 0.0.

IR (toluene): 2 088 s (C=C=O), 1 968 s, 1 899 s cm^{-1}.

MS (EI): m/z 481 (14%, M^+).

HRMS: m/z calc for $C_{25}H_{23}NO_4SiCr$ (M^+): 481.0801. Found: 481.0806.

E/Z-Pentacarbonyl[[2-(mesitylethynyl)phenylamino]-(p-tolyl)carbene]molybdenum(0) **34**

Preparation as described for **1**. Tetramethylammonium-[pentacarbonyl(*p*-toluoyl)molybdate(−I)] (853 mg, 2.0 mmol), acetyl bromide (246 mg, 0.15 mL, 2.0 mmol), 2-(mesitylethynyl)aniline (518 mg, 2.20 mmol), triethylamine (223 mg, 0.31 mL, 2.20 mmol). The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane 1.5:1 as eluent to give 460 mg (40%) **34** as a yellow solid (*E/Z*-ratio: 1:4). R_f = 0.59 (petroleum ether/dichloromethane 1.5:1); mp 133 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.81^a (br, 1H, NH), 10.01^b (br, 1H, NH), 7.73 (dd, 1H, J = 1.99, 7.35 Hz), 7.66 (dd, 1H, J = 1.59, 7.76 Hz), 7.57 (dt, 1H, J = 1.99, 7.65 Hz), 7.53 (dt, 1H, J = 1.59, 7.65 Hz), 7.42 (dd, 1H, J = 1.59, 7.76 Hz), 7.27^b (d, 2H, J = 8.34 Hz), 7.24^b (d, 2H, J = 8.28 Hz), 7.21–7.14 (m, 2H), 7.09 (d, 1H, J = 7.74 Hz), 7.01 (t, 1H, J = 8.15 Hz), 6.97^a (s, 2H), 6.94 (d, 1H, J = 6.95 Hz), 6.91^b (s, 2H), 6.88^b (d, 2H, J = 8.15 Hz), 6.54^a (dd, 1H, J = 1.54, 8.35 Hz), 2.57^a (s, 3H), 2.41^b (s, 3H), 2.37^b (s, 6H), 2.32^a (s, 6H), 2.17^b (s, 3H).

^{1}H NMR (400 MHz, C_6D_6): δ 10.56^a (br, 1H, NH), 9.12^b (br, 1H, NH).

^{13}C NMR (125 MHz, $CDCl_3$): δ 282.5^a (Mo=C), 278.2^b (Mo=C), 214.6^b (CO_{trans}), 214.3^a (CO_{trans}), 206.5^a (CO_{cis}), 206.4^b (CO_{cis}), 152.8^b, 148.2^a, 143.3^b, 140.9^a, 140.8^b, 139.8^a, 139.4^a, 139.2^b, 138.7^a, 138.6^b, 133.6^b, 133.3^a, 129.9, 129.6, 129.4, 129.3, 128.6^b, 128.3, 128.2^b, 123.6^b, 122.3^a, 121.8^a, 120.8^b, 120.2^b, 119.4^a, 96.4^a (C≡C), 95.2^b (C≡C), 92.4^b (C≡C), 91.3^a (C≡C), 21.83^a, 21.81^a, 21.7^b, 21.6^b, 21.5^a, 20.9^b.

IR (KBr): 3 217 m, 3 033 vw, 2 964 vw, 2 923 w, 2 855 vw, 2 363 w, 2 344 w, 2 202 w, 2 062 s, 1 982 s, 1 926 vs, 1 508 m, 1 488 m, 1 368 m, 771 m, 608 m, 594 m cm^{-1}.

MS (EI): m/z 463 (3%, M^+ − 4CO), 435 (25%, M^+ − $Mo(CO)_5$).

N-[2-(Mesitylethynyl)phenyl]-4-methylbenzamide **35**

A solution of 460 mg (0.80 mmol) **34** in 15 mL di-*n*-butyl ether was warmed at 105 °C for 1 h. The solvent was removed at reduced pressure and chromatography of the residue on silica gel using petroleum ether/dichloromethane (1:1) as eluent gave 105 mg (37%) **35** as an orange solid. R_f = 0.23; mp 135–137 °C.

^{1}H NMR (250 MHz, $CDCl_3$): δ 8.75 (br, 1H, NH), 8.58 (d, 1H, J = 8.26 Hz), 7.78 (d, 2H, J = 7.80 Hz), 7.56 (d, 1H, J = 7.80 Hz, 1H), 7.40 (t, 1H, J = 7.80 Hz), 7.23 (d, 2H, J = 8.25 Hz), 7.12 (t, 1H, J = 7.80 Hz), 6.91 (s, 2H), 2.42 (s, 9H), 2.31 (s, 3H).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ 165.6, 142.5, 139.9, 138.6, 138.5, 132.1, 131.9, 129.4, 128.1, 127.2, 123.5, 119.4, 119.1, 113.1, 94.7 (C≡C), 91.9 (C≡C), 21.5, 21.3, 21.2.

IR (KBr): 3 404 m, 3 026 vw, 2 965 w, 2 920 w, 2 854 vw, 1 679 s, 1 610 m, 1 577 s, 1 521 s, 1 507 s, 1 445 s, 1 303 s, 756 s cm^{-1}.

MS (EI): m/z 353 (100%, M^+), 119 (100% $C_9H_{11}^+$) 91 (22%, $C_7H_7^+$).

HRMS: m/z calc for $C_{25}H_{23}NO$ (M^+): 353.1780. Found: 353.1805.

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Supplementary information available

Copies of ^{1}H NMR spectra of carbene complexes **1–15**, **34** and anilide **35** as well as ^{13}C NMR spectra of (benzo)carbazoles **16–24**, **27–30** and anilides **25**, **26** reported in the *Experimental section* (32 pages). Supplementary material data have been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication No SUP 90450 and are available on request from the Document Supply Centre.

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