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Intramolecular cyclization reactions of unsaturated amino Fischer chromium carbenes forming indoles and quinolines

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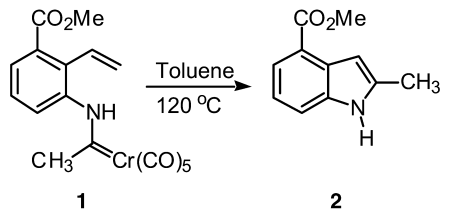
Abstract—A thermally induced intramolecular annulation reaction of *N*-(2-alkenylphenyl)amino substituted Fischer chromium carbenes has been extensively examined. The carbene complexes were prepared in moderate to good yields by reaction of 2-aminostyrenes with intermediately formed acyloxy substituted carbenes. Upon heating, the thermally labile carbenes decomposed producing indoles and quinolines as the major products. The product distribution was found to be highly dependent on the substitution pattern and electronic properties of the starting material, and on the solvent used.

1. Introduction

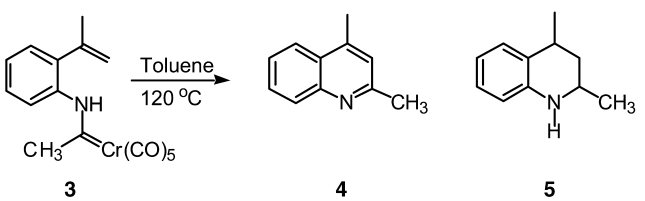
A number of synthetically attractive annulation reactions of Fischer carbene complexes have been developed over the last two decades.[1] Probably the most explored and utilized reaction is the thermally promoted benzannulation of aryl or α,β-unsaturated alkoxy Fischer chromium carbene complexes with alkynes forming, primarily, quinone/hydroquinone derivatives.[2,3] In contrast, related amino Fischer carbenes usually produce cyclopentanones, and cyclohexadienones upon reaction with alkynes.[4,5] Other alkyne–carbene annulations have been developed affording a variety of products such as, β-lactones,[6] lactams and pyrroles,[7–9] 2-azabicyclo[3.1.0]hexanes,[10] bicyclo[3.2.1]-hexanes,[11] bicyclo[3.1.1]heptanones,[12] bicyclo[5.3.0]decanes,[13] bicylo[4.1.0]heptanes,[14] spiro[4.4]nonatrienes,[15] [4.3.1]propellanes,[16] cyclopentenones and cyclopentadienes,[11,13,17–19] cyclooctatrienes,[20] steroid ring-system,[21] and indolines.[22] Annulation reactions of Fischer carbenes with carbon–carbon or carbon–nitrogen double bonds have also been extensively studied. Perhaps the two most synthetically useful reactions are photochemically[23,24] driven [2+2]-cycloadditions forming cyclobutanones[25,26] and β-lactams[27] and thermally promoted cyclopropanations.[28,29] In addition, synthesis of bicyclo[5.3.0]decanones,[30] and cyclopentene derivatives,[31–35] have also been reported.

We have communicated a novel thermal annulation reaction of *N*-(2-alkenylphenyl)amino substituted Fischer chromium carbenes affording indole or quinoline derivatives.[36] For example, thermolysis of carbene complex **1**, in toluene at 120°C for 20 h, gave indole **2** in 60% isolated yield (Scheme 1). In sharp contrast, thermal decomposition of complex **3** produced a mixture of quinoline **4** and tetrahydroquinoline **5**, in 34 and 22% yields, respectively (Scheme 2).



1 **2**

Scheme 1.



3 **4** **5**

Scheme 2.

Keywords: Fischer carbenes; indoles; quinolines.
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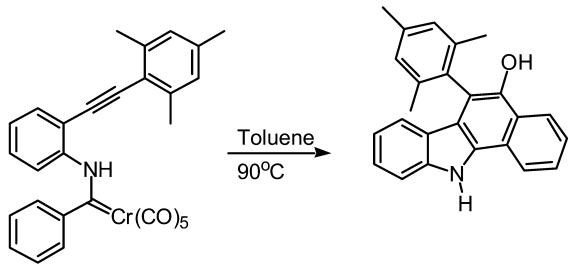


6 7

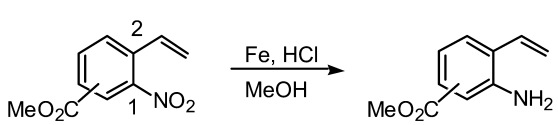
Scheme 3.

Dötz and Woodgate have independently reported intramolecular cyclization reactions of related alkyne functionalized *N*-phenylamino Fischer carbenes forming, for example, 9*H*-carbazoles or 11*H*-benzo[*a*]carbazoles depending on the starting material.[37–40] For example, thermal decomposition of complex **6** gave the 11*H*-benzo[*a*]carbazole **7** in 65% yield (Scheme 3).

Considering the difference in products formed from decomposition of complexes **1** and **3**, a more in-depth study of this annulation reaction was warranted. Herein is presented an account of the scope and limitation of the thermal annulation reaction of *N*-(2-alkenylphenyl)amino substituted Fischer chromium carbenes. The electronic and steric properties of the carbenes and, to some extent, the solvent have been varied to evaluate their influence on the ratio and yield of products. In addition, mechanistic rationales for the formation of the different products are proposed.

2. Results and discussion

In order to examine the scope and limitation of the thermal decomposition of *N*-(2-alkenylphenyl)amino substituted Fischer chromium carbenes, a number of novel substituted complexes, in addition to **1** and **3**, were synthesized from 2-aminostyrenes according to standard procedures. The 2-aminostyrenes, in turn, were either commercially available, prepared according to literature procedures, or synthesized as described herein. Thus, four 2-aminostyrenes (**8**–**11**), having an electron withdrawing methyl ester substituent, were readily prepared by reduction of the corresponding 2-nitrostyrenes using Fe/HCl in methanol (Scheme 4).



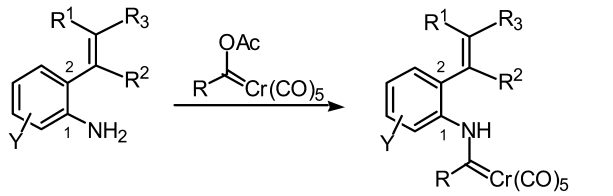
8 3-CO_2Me (77%)
9 4-CO_2Me (62%)
10 5-CO_2Me (71%)
11 6-CO_2Me (64%)

Scheme 4.

In order to compare and contrast the influence of the electronic properties of the aromatic ring, methoxy-substituted 2-aminostyrenes were also prepared. Reaction of two isomeric methoxy-substituted 2-bromobenzeneamines with, in sequence, ethyl chloroformate, tri-*n*-butyl vinyltin in the presence of a palladium(0) catalyst,[41] and potassium hydroxide gave aminostyrenes **14** and **17** (Scheme 5). A more direct two-step route to these compounds consisting of a Stille cross-coupling of methoxy-substituted 2-bromo-1-nitrobenzenes with tri-*n*-butyl vinyltin followed by reduction of the nitro group to an amine was also pursued. Although the palladium catalyzed coupling reaction gave the corresponding nitrostyrenes in good to excellent yield,[42] the subsequent reduction employing, for example, Fe/HCl/MeOH, Fe/AcOH/EtOH, or $SnCl_2$/EtOH, gave either a very low yield or a complex mixture of products.

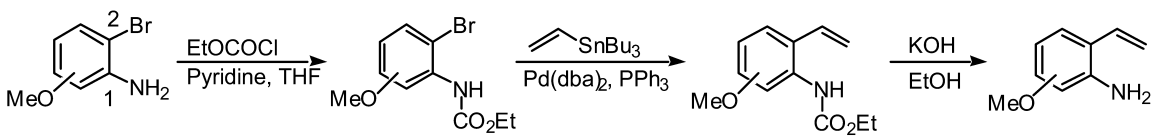
With a number of 2-aminostyrenes in hand, the desired carbenes were prepared by acylation of the corresponding tetramethylammonium pentacarbonyl[1-oxyalkyl]chromate(1-) salt, in dichloromethane at −40°C, with acetyl

Table 1. Synthesis of amino carbene complexes



R=Me	**18** (74%)
R=Ph	**19** (88%)
R=Me, Y=3-CO_2Me	**1** (65%)
R=Me, Y=4-CO_2Me	**20** (87%)
R=Me, Y=5-CO_2Me	**21** (62%)
R=Me, Y=6-CO_2Me	**22** (82%)
R=Me, Y=4-OMe	**23** (69%)
R=Me, Y=5-OMe	**24** (43%)
R=R^3=Me	**25** (70%)[a]
R=R^1=R^3=Me	**26** (75%)
R^2=R=Me	**3** (61%)
R^2=Me R=Ph	**27** (88%)
R^2=Me R=Cyclopropyl	**28** (89%)
R^2=Me R=2-Furyl	**29** (76%)
R^2=H R=$OCH_2OC_6H_3$	**30**[b]

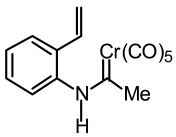
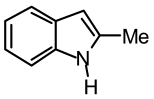
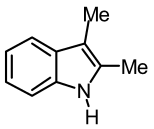
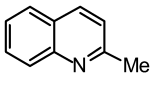
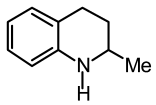
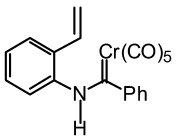
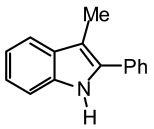
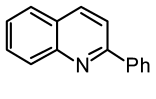
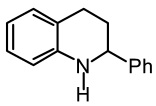
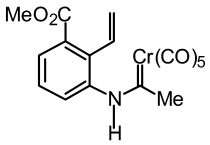
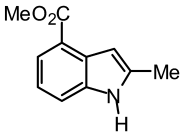
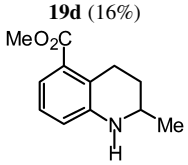
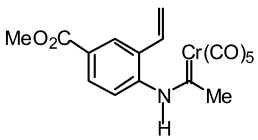
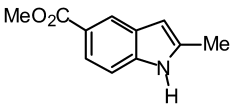
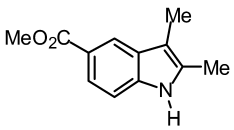
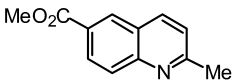
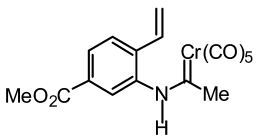
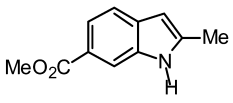
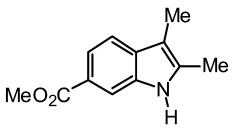
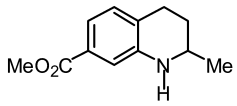
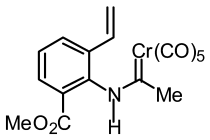
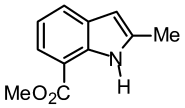
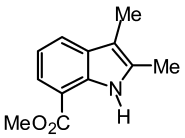
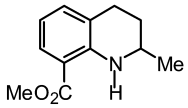
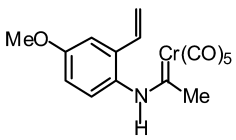
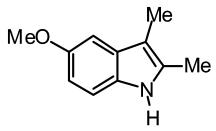
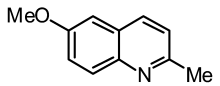
[a] A 1:1 mixture of double bond isomers.
[b] Not isolated.



4-OMe **12** (94%) **13** (59%) **14** (91%)
5-OMe **15** (83%) **16** (63%) **17** (78%)

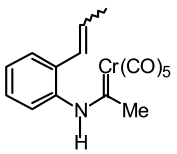
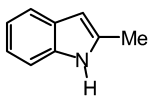
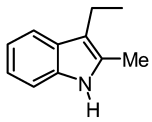
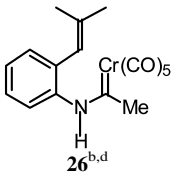
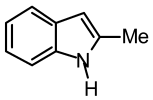
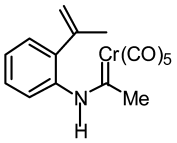
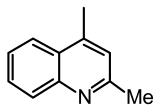
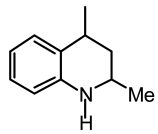
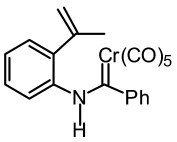
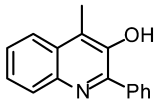
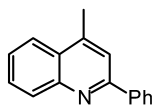
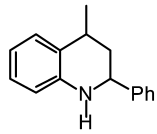
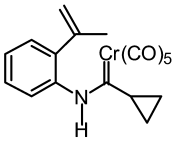
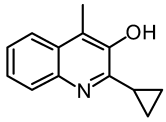
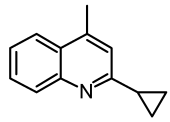
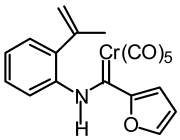
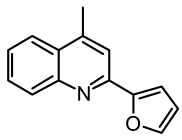
Scheme 5.

Table 2. Thermal decomposition of Fischer chromium aminocarbene complexes

Entry	Carbene	Products (yield)			
					
1	**18**[a]	**18a** (5%)	**18b** (15%)	**18c** (21%)	**18d** (12%)
2	**18**[b]		**18b** (49%)	**18c** (8%)	
					
3	**19**[a]		**19b** (17%)	**19c** (39%)	**19d** (17%)
4	**19**[b]			**19c** (50%)	**19d** (23%)[d]
5	**19**[c]			**19c** (36%)	**19d** (16%)
					
6	**1**[a]	**2** (60%)			
7	**1**[b]				**1d** (63%)
8	**1**[c,e]	**2** (34%)			
					
9	**20**[b]		**20b** (95%)		
10	**20**[c]	**20a** (70%)		**20c** (18%)	
					
11	**21**[b,f]	**21a** (4%)	**21b** (7%)		**21d** (70%)
12	**21**[c,g]	**21a** (7%)	**21b** (38%)		
					
13	**22**[b,h]	**22a** (7%)	**22b** (24%)		**22d** (18%)
14	**22**[c,i]	**22a** (65%)			**22d** (4%)
					
15	**23**[b]		**23b** (20%)	**23c** (42%)	
16	**23**[c]		**23b** (20%)	**23c** (57%)	

[a] In toluene at 90°C.
[b] In acetonitrile at 90°C.
[d] Contaminated by a small amount (<5%) of 3-methyl-2-phenyl-indole.
[c] In hexanes at 90°C.
[e] Also, 61% of **8**.
[f] Also, 11% of **10**.
[g] Also, 33% of **10**.
[h] Also, 38% of **11**.
[i] Also, 18% of **11**.

Table 3. Thermal decomposition of Fischer chromium aminocarbene complexes

Entry	Carbene	Products (yield)			
					
1	**25**[a]	**25a** (62%)			
2	**25**[b]	**25a** (25%)	**25b** (60%)		
3	**25**[c]	**25a** (47%)			
					
4	**26**[b,d]				
5	**26**[c,e]	**26a** (8%)			
					
6	**3**[a]		**4** (34%)	**5** (22%)[f]	
7	**3**[b,g]		**4** (22%)		
					
8	**27**[a]	**27e**	**27c** (26%)	**27d** (9%)	
9	**27**[b]		**27c** (61%)		
10	**27**[c]		**27c** (55%)		
11	**27**[b,h,i]		**27c** (20%)		
					
12	**28**[b]	**28e** (23%)	**28c** (14%)		
13	**28**[c]	**28e** (25%)	**28c** (31%)		
					
14	**29**[b]		**29c**		
15	**29**[c]		**29c**		

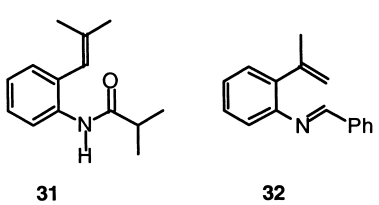
[a] In toluene at 90°C.
[b] In acetonitrile at 90°C.
[c] In hexanes at 90°C.
[d] Only **31** (13%).
[e] Also, 44% of 2-(2-methylpropenyl)benzenamine.
[f] Isomer ratio=4.4:1.
[g] Also, 41% of 2-(2-propenyl)benzenamine.
[h] In acetonitrile at 90°C under 3 atm of CO.
[i] Also, 22% of imine **32**.

chloride or bromide. The in situ formed acyloxy-substituted complexes were subsequently treated, at −40°C, with the appropriate 2-aminostyrene to afford carbenes **1**, **3**, and **18**–**30** in 43–89% yield after column chromatography (Table 1). The isolated amino carbenes were found to be thermally unstable, even as neat compounds, and a substantial amount of decomposition was observed after a few hours at ambient temperature. In most cases, ^{1}H NMR of the carbenes showed broad unresolved peaks due to rapid partial decomposition in solution forming interfering chromium species.

As expected, based on our initial experiments, thermal decomposition of the isolated Fischer chromium carbenes

produced a variety of substituted indoles and quinolines. The results of these reactions have been summarized in Tables 2 and 3. In our preliminary communication, toluene was used as the solvent for the thermolysis reaction producing compounds having either an indole or a quinoline type structure.[36] However, careful examination of the crude reaction mixture obtained from reaction of complex **18**, unsubstituted on both the aromatic ring and the pendant alkene, revealed a more complex product mixture. It was found that thermolysis of **18**, in toluene at 90°C, produced 2-methylindole (**18a**) and 2,3-dimethylindole (**18b**) in addition to the previously reported products 2-methylquinoline (**18c**), and 2-methyl-1,2,3,4-tetrahydroquinoline (**18d**) (entry 1). Similar treatment of the phenyl-substituted complex **19** also produced a mixture of products among them, 3-methyl-2-phenylindole (**19b**) (entry 3). Formation of **18b** and **19b** is noteworthy in that 2,3-disubstituted indoles were previously not observed from reactions of Fischer amino-carbene complexes. The products **18a–d** were partially separated by chromatography on silica gel and identified by comparison with literature ^{1}H and ^{13}C NMR data. In all other cases, unless otherwise stated, the yields reported in Tables 2 and 3 are for pure isolated compounds.

Toluene proved to be somewhat cumbersome to use as a solvent due to its relatively high boiling point, making it hard to remove from the crude reaction mixtures. In addition, formation of chromium tricarbonyl toluene complex interfered with the purification of the products in a few cases. Two additional solvents were examined in order to evaluate the effect of solvent on the yield and selectivity for a given product, and mainly to simplify the workup procedure. Upon thermolysis of **18** in acetonitrile, only indole **18b** and quinoline **18c** were isolated, the former in a substantially higher yield compared to the reaction performed in toluene (entries 1 and 2). Pronounced solvent effects are not unusual in Fischer carbene chemistry and have previously been observed, for example, in a number of benzannulation reactions.[3] In contrast to the results obtained using complex **18**, only quinolines were isolated from reaction of **19** both in acetonitrile and hexanes (entries 4 and 5). Comparable yields of quinolines were obtained in all three solvents.



31 **32**

Figure 1.

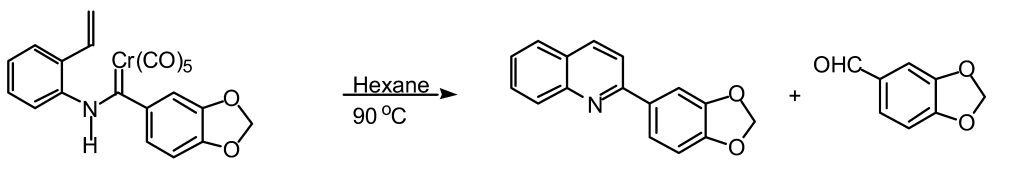
Thermolysis of complexes **1** and **20–23** produced all of the products discussed above, 2-methyl-indoles, 2,3-dimethyl-indoles, 2-methylquinolines, and 2-methyl-1,2,3,4-tetrahydroquinolines, in varying amounts and product ratios. It is apparent from these results that electronic factors play an important role in the thermal reaction of the amino carbenes. Unfortunately, no clear trends can be discerned from the results obtained. The product ratio and type of annulation product for a given carbene is, as far as we can tell, unpredictable; however, in some cases selective or exclusive formation of one product was observed. For example, reactions of carbenes **1** and **22** in hexanes or toluene afforded a 2-substituted indole; reaction of carbene **20** in acetonitrile gave a 2,3-disubstituted indole, and reaction of complexes **1** in acetonitrile produced a tetrahydroquinoline.

One major side product was isolated from the thermally induced annulation reactions. 2-Aminostyrenes corresponding to the immediate precursor of the carbene examined were obtained in up to 80% yield. In the case of the 5-methoxy-substituted complex **24**, 2-ethenyl-5-methoxy-benzenamine (**17**) was the only product isolated (not included in Table 2). No trace of annulation product was observed by ^{1}H NMR of the crude reaction mixture.

The influence of a methyl substituent(s) on the alkene moiety of the carbene was examined next (Table 3). Complex **25** with one methyl group in the β-position of the alkene gave exclusively indoles **25a–b** in all three solvents examined (entries 1 and 3). In the case of the β,β-dimethyl substituted carbene **26**, a sluggish reaction took place in both acetonitrile and hexanes, and only a minor amount of indole **26a** was isolated in the latter case (entries 4 and 5). Interestingly, reaction of **26** in acetonitrile gave an amide **31**, a product previously not observed (Fig. 1).

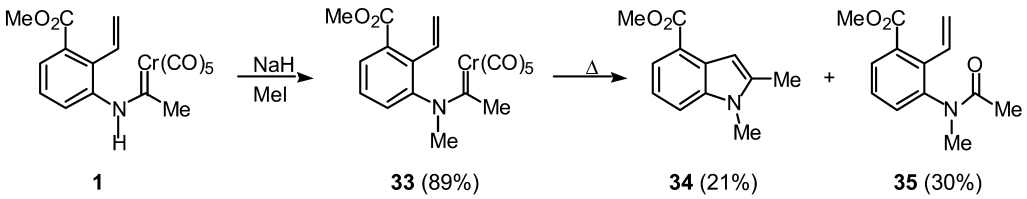
In contrast to the β-substituted complexes, the α-methyl substituted complexes **3** and **27–29** yielded only substituted quinolines after purification (entries 6 and 7). For the phenyl and cyclopropyl substituted carbenes **27** and **28** (entries 8, and 12–13), 3-hydroxy quinolines (**27e–28e**) were isolated. The annulation reaction was significantly inhibited in the presence of carbon monoxide (entry 11). Thus, thermolysis of complex **27** under 3 atm of CO gave a 20% yield of **27c**, a significant decrease from 61% in the absence of CO. In addition to the expected product, the imine **32** was isolated in 22% yield (Fig. 1).

Considering the relatively clean formation of quinolines from the phenyl-substituted carbene **19** in hexanes and acetonitrile having no substituent of the alkene, we

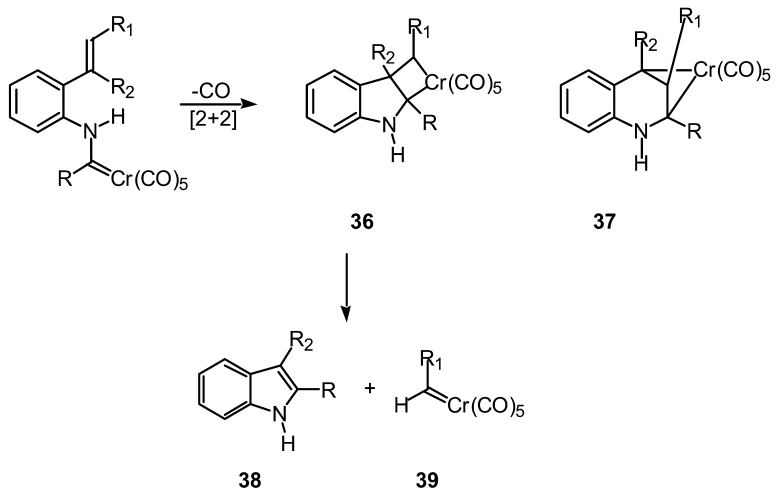


30 **Dubamine** (9%) **Piperonal** (51%)

Scheme 6.



Scheme 7.



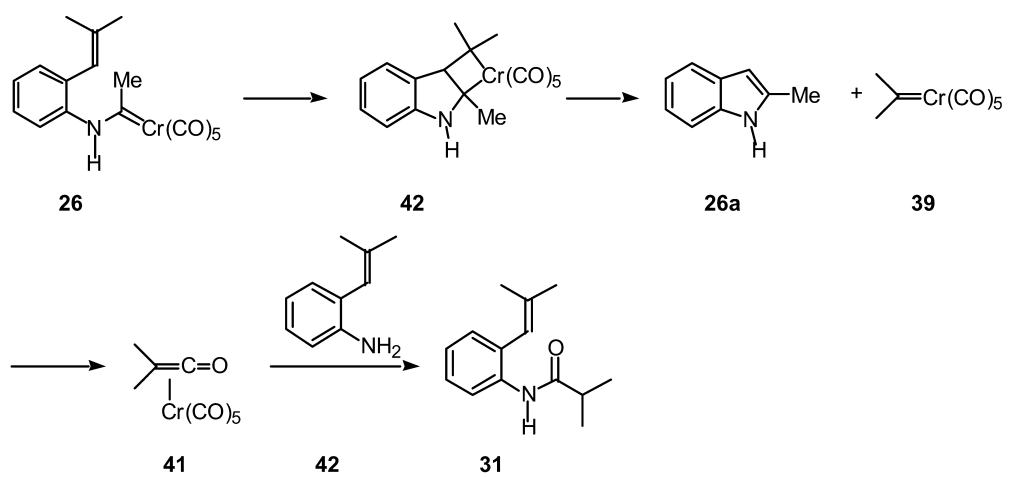
Scheme 8.

envisioned a short synthesis of the quinoline alkaloid dubamine from carbene **30**. However, complex **30** proved to be by far the most thermally labile complex examined. Extensive decomposition was observed upon purification; ^{1}H NMR of the product revealed only broad unresolved peaks. Thermal reaction of crude **30** in acetonitrile gave the expected product dubamine (**30c**) albeit in a low isolated yield (Scheme 6). The major product was identified as piperonal obtained in 51% yield.

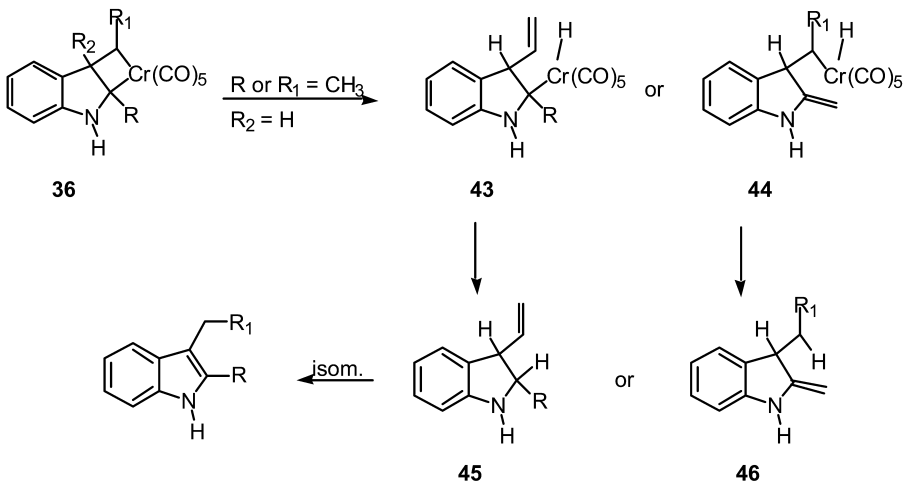
As the final carbene examined, the *N*-methyl substituted complex **33** was prepared in 89% yield by deprotonation of **1** with sodium hydride followed by alkylation with iodomethane (Scheme 7). Thermolysis of **33**, under similar reaction conditions as described above, gave a mixture of indole **34** and amide **35** in 21 and 30% yield, respectively. The amide was most likely formed by air-oxidation of the chromium carbon double bond of the thermally and oxidatively labile complex **34**.

3. Mechanistic considerations

Plausible mechanistic rationales for the formation of the array of products obtained from thermal decomposition of the carbenes are depicted in Schemes 8–12. Loss of one of the chromium-bound carbon monoxide ligands from the carbene complex enables the pendant double bond to coordinate to the metal followed by formation of a metallacyclobutane. Two possible intermediates can be obtained from this intramolecular [2+2]cycloaddition, an indole or a quinoline fused metallacyclobutane, **36** and **37**,



Scheme 9.

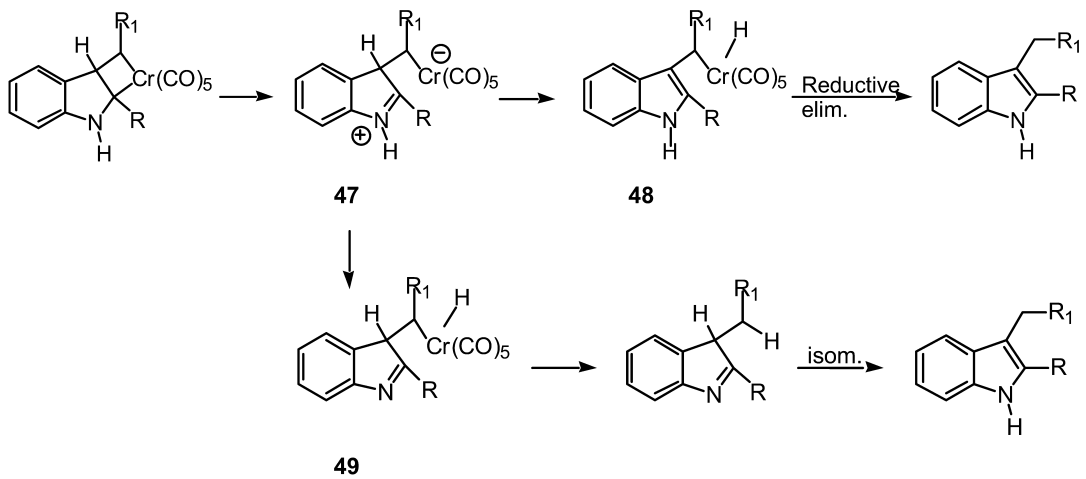


Scheme 10.

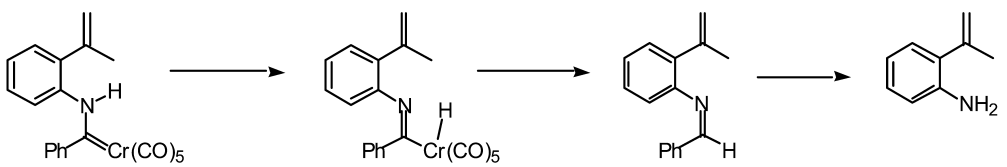
respectively (Scheme 8). A related [2+2]cycloaddition has been proposed for a manganese carbene intermediate.[43] Moreover, similar fused [3.2.0] and bridged [3.1.1] ring systems have been isolated in a number of cases from related intramolecular [2+2]cycloadditions between ketenes and alkenes.[44,45] In the case of complex **36**, direct metathesis would afford a 2-substituted indole **38** having lost the β-carbon of the original alkene. The highly unstable and very reactive pentacarbonyl(alkylidene)chromium complex **39**, the second 'half' of the metathesis reaction, has not been isolated and is tentatively proposed as a product.[13,46,47] However, the amide **31**, isolated from thermolysis of carbene **26** (entry 4, Table 3), can be envisioned to be formed via nucleophilic addition of aniline **40** to ketene **41**.[23,24] Ketene **41**, in turn, is probably derived from dimethyl carbene **39** formed by metathesis of metallacyclobutane **42** (Scheme 9). The origin of the aniline will be discussed below.

For obvious reasons, a metathesis mechanism cannot be in operation for the formation of 2,3-dialkylindoles (i.e. **18b**–**23b** and **25b**) wherein the β-carbon of the starting material remains in the product after the reaction. A couple of different mechanistic possibilities can be invoked. β-Hydride elimination either from the alkyl group attached to the former carbene carbon and/or, in the case of complex **36** (R_1=CH_3), from the terminal methyl group of the propenyl substituent would give complex **43** and **44**, respectively (Scheme 10). Reductive elimination at this point would afford **45** and **46** that upon isomerization produces the observed 2,3-dialkyl substituted indoles.

In addition to the latter mechanism, an ionic mechanism is also possible for the formation of indoles via the zwitterionic complex **47**. Proton shift affording **48** and/or **49** followed by reductive elimination (for **48**) or reductive



Scheme 11.



Scheme 12.

elimination–isomerization (for **49**) completes the mechanism (Scheme 11).

The quinoline-fused metallacyclobutane **37** can be envisioned to undergo similar mechanistic steps, β-elimination or ionic cleavage, as outlined for the formation of indoles in Schemes 10 and 11.[48] It should be noted that a related mechanism, including a twisted mode of cycloaddition followed by β-elimination, has been suggested for the formation of 3,4-dihydropyranes via intramolecular reaction of Fischer carbenes having a tethered alkene.[5] The intermediates from the eliminations are either compounds isomeric to the quinoline product and/or dihydroquinolines. The latter readily undergo disproportionation reactions to form quinolines and tetrahydroquinolines. A similar reduction of double bonds in the presence of chromium complexes has been reported.[49] The isolation of 2-phenyl quinoline (**19c**) and 2-phenyl-1,2,3,4-tetrahydroquinoline (**19c**) from thermolysis of **19**, substrates lacking β-hydrogens available for elimination, supports the ionic mechanism. We are presently unable to give a reasonable rationale for the formation of the hydroxyquinolines **27e** and **28e**.

A fairly straightforward mechanistic explanation for the formation of the aminostyrenes is shown in Scheme 12. Thermally induced β-hydride elimination would give an imine, which subsequently undergoes hydrolysis to the amine. Related eliminations forming both imines and the corresponding amine have previously been observed.[50] Imine **32** was isolated in low yield from thermolysis of complex **27** under 3 atm of carbon monoxide. The β-hydride elimination was especially pronounced in the case of the substituted carbene **30**. This carbene could not be isolated, and the corresponding aldehyde, piperonal (Scheme 6), was obtained in quantitative yield upon standing for a few hours at ambient temperature.

In conclusion, thermal decomposition of *N*-(2-alkenylphenyl)amino substituted Fischer chromium carbenes affords indoles and/or quinolines. The yield and ratio of products are highly dependant on the solvent used and electronic and steric factors. The major competing side reaction is formation of 2-aminostyrenes, compounds derived from β-hydride elimination-hydrolysis of the starting Fischer carbenes.

4. Experimental

4.1. General procedures

All NMR spectra were determined in $CDCl_3$ at 270 MHz (^1H NMR) and 67.5 MHz (^{13}C NMR) unless otherwise stated. The chemical shifts are expressed in δ values relative to Me_4Si (0.0, ^1H and ^{13}C) or $CDCl_3$ (77.0, ^{13}C) internal standards. $^1H-^1H$ coupling constants are reported as calculated from spectra; thus, a slight difference between $J_{a,b}$ and $J_{b,a}$ is usually obtained. Results of APT (attached proton test)—^{13}C NMR experiments are shown in parentheses, where relative to $CDCl_3$, (−) denotes CH_3 or CH and (+) denotes CH_2 or C. Multiplicities observed in off-resonance decoupled ^{13}C NMR experiments are shown in parentheses. For ^1H NMR, the assignments are: q=quartet, t=triplet, d=doublet, s=singlet, br=broad, and m=multiplet. Multiplet refers to unresolved resonances from one or more protons having intractable $^1H-^1H$ coupling constants.

Tetrahydrofuran (THF), 1,4-dioxane, toluene, and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Pyridine, hexanes, acetonitrile, and ethyl acetate were distilled from calcium hydride. Chemicals prepared according to literature procedures have been footnoted first time used; all other reagents were obtained from commercial sources and used as received. All reactions were performed in oven-dried glassware. The theromolysis experiments were performed in ACE-glass pressure tubes capped with an ACE-glass teflon plug. Solvents were removed on a rotary evaporator at water aspirator pressure unless otherwise stated. The following 'air-oxidation' procedure was employed in order to remove chromium residues from the crude products. A flask containing a solution (suspension) of the crude product in hexanes–EtOAc (1:1, 30–75 mL) was irradiated (250 W lamp), open to the air, until a clear colorless solution was formed. A large amount of a brown-green precipitate was usually obtained which was removed by filtration (Celite). Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. High Resolution Mass Spectra (HRMS) were performed at University of California Riverside Mass Spectrometry Center.

4.1.1. Methyl 3-amino-2-ethenylbenzoate (8). To a solution of methyl 2-ethenyl-3-nitrobenzoate[42] (13.05 g, 63.0 mmol) in MeOH (260 mL) and HCl (37%, 10.4 mL) was added Fe (powder, 14.07 g, 252 mmol). The resulting slurry was heated (100°C, oil-bath temp) for 27 h. After cooling to ambient temperature, the grey slurry was diluted with water (400 mL), and the mixture was extracted with EtOAc (3×150 mL). The aqueous phase was made basic (pH ca. 9) with NH_4OH (saturated, aqueous) and extracted with EtOAc (3×150 mL). The combined organic phases were dried ($MgSO_4$), filtered, and the solvents were removed. The crude product was purified by chromatography (hexanes–EtOAc, 4:1) to give **8** (8.62 g, 48.6 mmol, 77%) as faint yellow oil. ^1H NMR δ 7.17 (dd, J=7.7, 1.0 Hz, 1H), 7.03 (t, J=7.9 Hz, 1H), 6.89 (dd, J=18.1, 11.6 Hz, 1H), 6.77 (dd, J=7.9, 1.2 Hz, 1H), 5.49 (dd, J=11.6, 2.0 Hz, 1H), 5.37 (dd, J=18.0, 1.7 Hz, 1H), 4.05 (br s, 2H), 3.78 (s, 3H); ^{13}C NMR δ 168.3 (+), 144.3 (+), 133.3 (−), 130.3 (+), 127.2 (−), 123.6 (+), 119.1 (−), 118.5 (+), 118.4 (−), 51.5 (−); IR (neat), 3470, 3374, 1716, 1613, 1310, 1266 cm^{-1}. Anal. calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.68; H, 6.34.

4.1.2. Methyl 4-amino-3-ethenylbenzoate (9). Methyl 3-ethenyl-4-nitrobenzoate[42,51] (3.14 g, 15.17 mmol) was reacted with Fe (2.43 g, 43.46 mmol) in MeOH (61 mL) in the presence of HCl (37%, 2.5 mL), as described above (49 h). Extraction and chromatography (hexanes–EtOAc, 4:1) gave, **9** (1.65 g, 9.44 mmol, 62%) as faint yellow crystals. Mp 92–93°C. ^1H NMR δ 7.96 (d, J=2.0 Hz, 1H), 7.74 (dd, J=8.3, 2.0 Hz, 1H), 6.67 (dd, J=17.4, 11.0 Hz, 1H), 6.61 (d, J=8.3 Hz, 1H), 5.66 (dd, J=17.4, 1.4 Hz, 1H), 5.32 (dd, J=11.1, 1.2 Hz, 1H), 4.29 (br s, 2H), 3.83 (s, 3H);

^{13}C NMR δ 167.1 (+), 148.1 (+), 131.6 (−), 130.3 (−), 129.3 (−), 122.6 (+), 119.5 (+), 116.7 (+), 114.9 (−), 51.5 (−); IR (neat) 3460, 3358, 1674, 1257 cm^{-1}. Anal. calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.27. Found: C, 67.63; H, 6.29.

4.1.3. Methyl 3-amino-4-ethenylbenzoate (10). Methyl 4-ethenyl-3-nitrobenzoate[42,51] (6.37 g, 30.8 mmol) was reacted with Fe (6.87 g, 123.1 mmol) in MeOH (125 mL) in the presence of HCl (37%, 5.0 mL), as described above (45 h). Extraction and chromatography (hexanes–EtOAc, 9:1) gave **10** (3.89 g, 22.0 mmol, 71%) as faint yellow crystals. Mp 46–47°C. ^{1}H NMR δ 7.38 (dd, J=7.9, 1.5 Hz, 1H), 7.35 (br s, 1H), 7.29 (d, J=8.2 Hz, 1H), 6.73 (dd, J=17.3, 11.1 Hz, 1H), 5.67 (dd, J=17.3, 1.2 Hz, 1H), 5.35 (dd, J=11.1, 1.2 Hz, 1H), 3.93 (br s, 2H), 3.84 (s, 3H); ^{13}C NMR δ 166.9 (+), 143.6 (+), 131.7 (−), 129.7 (+), 127.9 (+), 126.9 (−), 119.5 (−), 117.3 (+), 116.8 (−), 51.8 (−); IR (neat) 3434, 3364, 1688, 1243 cm^{-1}. Anal. calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.86; H, 6.30.

4.1.4. Methyl 2-amino-3-ethenylbenzoate (11). Methyl 3-ethenyl-2-nitrobenzoate[42,51] (1.07 g, 5.17 mmol) was reacted with Fe (823 mg, 14.82 mmol) in MeOH (21 mL) in the presence of HCl (37%, 0.84 mL), as described above (23.5 h). Extraction and chromatography (hexanes–EtOAc, 4:1) gave **11** (580 mg, 3.31 mmol, 64%) as faint yellow oil followed by recovered starting material (269 mg, 1.30 mmol, 25%). ^{1}H NMR δ 7.81 (dd, J=7.9, 1.5 Hz, 1H), 7.38 (dd, J=7.4, 1.2 Hz, 1H), 6.74 (dd, J=17.3, 10.9 Hz, 1H), 6.65 (t, J=7.9 Hz, 1H), 6.00 (br s, 2H), 5.62 (dd, J=17.3, 1.2 Hz, 1H), 5.36 (dd, J=11.1, 1.2 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (22.5 MHz) δ 168.6 (+), 147.8 (+), 132.2 (−), 132.1 (−), 130.9 (−), 125.3 (+), 117.1 (+), 115.8 (−), 110.9 (+), 51.5 (−); IR (neat) 3480, 3364, 1691, 1247 cm^{-1}. Anal. calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.27. Found: C, 67.69; H, 6.29.

4.1.5. 2-Bromo-4-methoxyphenyl carbamic acid ethyl ester (12). Ethyl chloroformate (2.26 mL, 23.60 mmol) dissolved in THF (25 mL) was added dropwise to a solution of 2-bromo-4-methoxybenzenamine,[52] (4.35 g, 21.54 mmol) and pyridine (3.46 mL, 42.87 mmol) in THF (50 mL). The reaction mixture was stirred at ambient temperature (16 h) producing faint pink solution containing a white precipitate. The solvent was removed on a rotary evaporator; the oily residue was dissolved in CH_2Cl_2 (50 mL) and washed with aqueous HCl (10%, 3×50 mL) followed by water (3×50 mL). The organic phase was dried ($MgSO_4$), and filtered, followed by solvent removal to give a colorless oil. The crude material was purified by chromatography (hexanes–EtOAc, 8:2) affording 12 (4.56 g, 16.64 mmol, 78%) as white crystals. Mp 50–53°C. ^{1}H NMR δ 7.89 (d, J=9.1 Hz, 1H), 7.04 (d, J=2.9 Hz, 1H), 6.81 (dd, J=8.9, 2.9 Hz, 1H), overlapping 6.8 (br s, 1H), 4.21 (q, J=7.1 Hz, 2H), 3.72 (s, 3H), 1.29 (t, J=7.1 Hz, 1H); ^{13}C NMR δ 155.8 (s), 153.5 (s), 129.0 (s), 122.2 (d), 117.3 (d), 113.8 (s), 113.7 (d), 61.3 (t), 55.5 (t), 14.2 (q); IR (neat) 3380, 2970, 1705, 1505, 1200, 1065, 1030 cm^{-1}. Anal. calcd for $C_{10}H_{12}BrNO_3$: C, 43.81; H, 4.41. Found: C, 43.56; H, 4.33.

4.1.6. 2-Ethenyl-4-methoxyphenyl carbamic acid ethyl ester (13). To a solution of **12** (3.38 g, 12.44 mmol) and vinyl tri-*n*-butyltin (4.31 g, 13.60 mmol) in toluene (100 mL) was added, under a positive flow of nitrogen, bis(dibenzylideneacetone)palladium, (356 mg, 0.62 mmol) and triphenylphosphine (647 mg, 2.47 mmol). The reaction mixture was heated (120°C, oil bath temp, 23H), and allowed to cool to ambient temperature followed by solvent removal to give a black oil. The oil was dissolved in CH_2Cl_2 (100 mL), washed with NH_4OH (3×150 mL, 10%, aq.), and dried ($MgSO_4$). Filtration and removal of solvent gave a brown oil that was purified by chromatography (hexanes–EtOAc, 8:2 followed by hexanes–EtOAc, 1:1) producing **13** (1.60 g, 7.24 mmol, 59%) as faint yellow crystals. Mp 74°C. ^{1}H NMR δ 7.47 (br s, 1H), 6.95 (d, J=2.7 Hz, 1H), 6.84–6.74 (overlapping m, 2H), 6.56 (s, 1H), 5.62 (d, J=17.9 Hz, 1H), 5.31 (d, J=11.0 Hz, 1H), 4.17 (q, J=7.1 Hz, 2H), 3.74 (s, 3H), 1.25 (t, J=7.1 Hz, 3H); ^{13}C NMR (22.5 MHz) δ 156.8 (s), 154.6 (s), 132.5 (s), 132.0 (d), 127.5 (d), 125.6 (s), 116.5 (t), 113.7 (d), 110.8 (d), 60.9 (t), 55.1 (q), 14.3 (q); IR (neat) 3425, 1728, 1518 cm^{-1}; GC-MS (EI) m/z 221 (M^+) 148, 134, 133; HRMS (EI) calcd for $C_{12}H_{15}NO_3$ (M^+) 221.1052. Found: 221.1052.

4.1.7. 2-Ethenyl-4-methoxybenzenamine (14). A solution of KOH (80%, 3.00 g, 42.8 mmol) in absolute ethanol (30 mL) was added to a round-bottomed flask containing **13** (1.18 g, 5.40 mmol). The resulting solution was heated at reflux (16 h). The reaction mixture was allowed to cool to ambient temperature, water (40 mL) was added, and the mixture was extracted with CH_2Cl_2 (3×40 mL). The combined organic phase was dried ($MgSO_4$), and filtered followed by solvent removal on a rotary evaporator affording dark red oil. The crude oil was purified by chromatography (hexanes–EtOAc, 7:3) producing **14** (736 mg, 4.93 mmol, 91%) as faint red oil. ^{1}H NMR δ 6.8–6.5 (m, 3H), 5.60 (dd, J=17.7, 1.5 Hz, 1H), 5.28 (dd, J=10.8, 1.5 Hz, 1H), 3.73 (s, 3H), 3.46 (br s, 2H); ^{13}C NMR (22.5 MHz) δ 152.8 (s), 137.5 (s), 132.5 (d), 125.0 (s), 112.4 (d), 115.5 (t), 114.9 (d), 111.9 (d), 55.7 (q); IR (CH_2Cl_2) 3445, 3378, 2908, 2853, 1630, 1504, 1037 cm^{-1}. Anal. calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43. Found: C, 72.21; H, 7.43.

4.1.8. 2-Bromo-5-methoxyphenyl carbamic acid ethyl ester (15). Ethyl chloroformate (3.06 mL, 32.0 mmol) dissolved in THF (25 mL) was added drop vise to a solution of 2-bromo-5-methoxybenzenamine,[53] (6.85 g, 30.0 mmol) and pyridine (5.09 mL, 63.0 mmol) in THF (100 mL). The reaction mixture was stirred at ambient temperature (24 h). The solvent was removed on a rotary evaporator giving an oily residue that was dissolved in CH_2Cl_2 (50 mL) and washed with aqueous HCl (10%, 3×50 mL) followed by water (2×50 mL). The organic phase was dried ($MgSO_4$), and filtered followed by solvent removal to give faint yellow oil. The crude material was purified by chromatography (hexanes–EtOAc, 8:2) affording **15** (6.78 g, 24.8 mmol, 83%) as faint yellow oil. ^{1}H NMR δ 7.79 (s, 1H), 7.30–7.09 (m, 2H), 6.41 (d, J=8.8 Hz, 1H), 4.17 (q, J=6.9 Hz, 2H), 3.71 (s, 3H), 1.26 (t, J=7.1 Hz, 3H); ^{13}C NMR (22.5 MHz) δ 159.2 (s), 152.6 (s), 136.2 (s), 131.8 (d), 110.0 (d), 105.0 (d), 102.2 (s), 61.0 (t), 54.8 (q), 14.0 (q); IR (neat) 3400, 2990, 1725, 1585, 1210 cm^{-1}. Anal. calcd for $C_{10}H_{12}BrNO_3$: C, 43.81; H, 4.41. Found: C, 43.82; H, 4.44.

4.1.9. 2-Ethenyl-5-methoxyphenyl carbamic acid ethyl ester (16). To a solution of **15** (2.73 g, 9.97 mmol) and vinyl *n*-tributyltin (3.80 g, 12.0 mmol) in toluene (150 mL) was added, under a positive flow of nitrogen, triphenyl phosphine (525 mg, 2.00 mmol) and bis(dibenzylideneacetone)palladium (288 mg, 0.50 mmol). The yellow reaction mixture was put under a nitrogen atmosphere and heated (oil-bath temperature 130°C, 20 h). The solvent was removed on a rotary evaporator. The residue was redissolved in CH_2Cl_2 (50 mL), filtered through a Celite pad, and the pad was washed with CH_2Cl_2 (50 mL). The organic solution was washed with NH_4OH (10% aq, 3×50 mL), water (3×50 mL), and dried ($MgSO_4$). Filtration and solvent removal followed by chromatography using hexanes–EtOAc (8:2) as eluent gave **16** (1.39 g, 6.28 mmol, 63%) as faint yellow oil. The oil slowly formed faint yellow crystals upon storage at −18°C. Mp 46–48°C. ^{1}H NMR δ 7.44–6.57 (m, 5H), 5.51 (d, J=17.1 Hz, 1H), 5.24 (d, J=10.8 Hz, 1H), 4.19 (q, J=7.1 Hz, 2H), 3.75 (s, 3H), 1.27 (t, J=7.1 Hz, 3H); ^{13}C NMR (22.5 MHz) δ 159.6 (s), 153.6 (s), 135.6 (s), 131.3 (d), 127.5 (d), 121.5 (s), 115.6 (t), 110.5 (d), 106.3 (d), 61.1 (t), 55.0 (q), 14.3 (q); IR (neat) 3440, 3070, 3000, 1730, 1270, 1225, 1060, 900, 740 cm^{-1}. Anal. calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 64.87; H, 6.75.

4.1.10. 2-Ethenyl-5-methoxybenzenamine (17).[54] A solution of KOH (3.36 g, 47.9 mmol) in absolute ethanol (30 mL) was added to a round-bottomed flask containing **16** (1.01 g, 4.56 mmol). The resulting solution was heated at reflux (21H). Water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (2×30 mL). The combined organic phase was dried ($MgSO_4$) and filtered followed by solvent removal on a rotary evaporator affording dark red oil (744 mg). The crude oil was purified by chromatography (hexanes–EtOAc, 8:2) producing **17** (522 mg, 3.50 mmol, 77%) as faint red oil. ^{1}H NMR δ 7.18 (d, J=8.8 Hz, 1H), 6.67 (dd, J=17.2, 10.8 Hz, 1H), 6.31 (dd, J=8.6, 2.5, 1H), 6.17 (d, J=2.0 Hz, 1H), 5.48 (d, J=17.4 Hz, 1H), 5.15 (d, J=10.3 Hz, 1H), 3.78 (br s, 2H), 3.69 (s, 3H); ^{13}C NMR (22.5 MHz) δ 160.1 (s), 144.8 (s), 132.0 (d), 128.2 (d), 117.0 (s), 113.2 (t), 104.6 (d), 101.1 (d), 55.0 (q); IR (neat) 3440, 3350, 2990, 2940, 2820, 1600, 1490, 1435, 1205, 1165, 1015, 900, 830 cm^{-1}.

4.1.11. Pentacarbonyl(1-*N*-(2-ethenylphenyl)aminoethylidene)chromium (18). Acetyl bromide (1.04 mL, 14.06 mmol) was added to a −40°C cold solution of tetramethylammonium pentacarbonyl(acetyl)chromate(1-)[55] (4.94 g, 14.06 mmol) in CH_2Cl_2 (350 mL) under an atmosphere of nitrogen. Upon addition, the color immediately turned brown-red. The mixture was allowed to warm slowly to −30°C over a 30 min period where after it was cooled to −40°C, and 2-ethenyl benzenamine[56] (1.70 g, 14.06 mmol), dissolved in CH_2Cl_2 (10 mL), was added via a pipette under a positive flow of nitrogen. The reaction mixture was allowed to stir at −40°C (30 min) then at ambient temperature (30 min). The solvent was removed from the resulting orange mixture using a high vacuum pump producing brown-orange oil.[57] The oil was purified by chromatography (hexanes–CH_2Cl_2, 1:1) giving **18** (3.52 g, 10.45 mmol, 74%) as yellow crystals after solvent removal using a high vacuum pump. Two rotamers were obtained in a 3:1 ratio (^{1}H NMR). Mp: softens at 45°C then dec. ^{1}H NMR δ 10.18 (br s, major, 1H), 9.99 (br s, minor, 1H), 7.66 (d, J=7.2 Hz, 1H), 7.48–7.34 (m, 2H), 7.08 (d, J=7.2 Hz, 1H), 6.66 (dd, J=17.4, 10.9 Hz, 1H), 5.80 (d, J=17.4 Hz, 1H), 5.47 (d, J=10.9, 1H), 3.04 (s, minor, 3H), 2.51 (s, 3H); ^{13}C NMR (APT for major isomer) δ 289.9 (−), 287.4, 222.8 (−, *trans* –CO), 217.6 (−, *cis* –CO), 217.0, 139.2, 136.3 (−), 134.9, 133.6 (−), 130.8, 130.5 (+), 129.9, 129.5 (+), 128.9 (+), 128.3, 126.8, 126.3 (+), 118.9 (+), 118.3, 46.3, 37.6 (+); IR (neat) 2050, 1995 cm^{-1}. Anal. calcd for $C_{15}H_{11}CrNO_5$: C, 53.42; H, 3.29. Found: C, 53.60; H, 3.32.

4.1.12. Pentacarbonyl(1-*N*-(2-(2-ethenyl)phenyl)amino-1-phenylmethylidene)chromium (19). Reaction of tetramethylammonium pentacarbonyl(benzoyl)chromate(1-)[55] (3.49 g, 9.41 mmol) in CH_2Cl_2 (200 mL) with acetyl bromide (696 mL, 9.41 mmol) and 2-ethenyl benzenamine (1.12 g, 9.41 mmol), as described above, gave after chromatography (hexanes–EtOAc, 6:4), **19** (3.30 g, 8.27 mmol, 88%) as a orange crystals. Only one rotamer was observed by ^{1}H NMR. Mp 72–76°C. ^{1}H NMR δ 10.53 (br s, 1H), 7.60–6.50 (m, 10H), 5.82 (d, J=17.2 Hz, 1H), 5.60 (d, J=11.3 Hz, 1H); ^{13}C NMR δ 290.4 (−), 223.3 (−, *trans* –CO), 217.0 (−, *cis* –CO), 149.8 (−), 137.3 (−), 132.7 (−), 130.8 (+), 128.7 (+), 128.5 (+), 128.1 (+), 127.8 (+), 127.2 (+), 127.1 (+), 127.0 (+), 126.5 (+), 120.6 (−), 119.4 (+); IR (neat) 2058, 1976, 1908 cm^{-1}.

4.1.13. Pentacarbonyl(1-*N*-(3-carbomethoxy-2-ethenylphenyl)aminoethylidene)chromium (1). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (1.43 g, 4.63 mmol) in CH_2Cl_2 (50 mL) with acetyl chloride (345 mL, 4.00 mmol) and **8** (820 mg, 4.63 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:1 followed by hexanes–CH_2Cl_2, 3:7) **1** (1.19 g, 3.01 mmol, 65%) as a yellow crystals. Two rotamers were obtained in a 7:2 ratio (^{1}H NMR). ^{1}H NMR (300 MHz, major rotamer): δ 10.29 (br s, 1H), 7.88 (d, J=6.9 Hz, 1H), 7.42 (t, J=7.8 Hz, 1H), 7.25 (d, J=7.2 Hz, 1H), 6.89 (dd, J=17.9, 11.6 Hz, 1H), 5.64 (d, J=11.5 Hz, 1H), 5.29 (d, J=18.1 Hz, 1H), 3.90 (s, 3H), 2.60 (s, 3H). ^{1}H NMR (300 MHz, minor rotamer, partial spectra) δ 10.05 (br s, 1H), 7.94 (d, J=8.8 Hz, 1H), 7.59 (d, J=7.4 Hz, 1H), 7.50 (t, J=7.8 Hz, 1H), 5.87 (d, J=10.8 Hz, 1H), 5.27 (d, J=17.9 Hz, 1H), 3.88 (s, 3H), 3.01 (s, 3H); ^{13}C NMR (75 MHz) δ 289.5, 287.0, 223.0, 222.7, 217.5, 217.0, 167.3, 167.1, 136.8, 135.4, 132.1, 131.8, 131.1, 130.9, 130.6, 129.9, 128.1, 128.0, 122.2, 121.4, 52.5, 52.4, 46.4, 37.7; IR (CH_2Cl_2) 2049, 1929, 1714 cm^{-1}.

4.1.14. Pentacarbonyl(1-*N*-(4-carbomethoxy-2-ethenylphenyl)aminoethylidene)chromium (20). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (1.85 g, 6.00 mmol) in CH_2Cl_2 (160 mL) with acetyl chloride (427 mL, 6.00 mmol) and **9** (1.06 g, 6.00 mmol), as described above, gave after chromatography (hexanes–EtOAc, 4:1 followed by hexanes–EtOAc, 1:1), **20** (2.06 g, 5.20 mmol, 87%) as yellow crystals. Two rotamers were obtained in an 8:1 ratio (^{1}H NMR). Mp 104–105°C. ^{1}H NMR δ 10.42 (br s, 1H), 10.0 (br s, minor rotamer), 8.31 (s, 1H), 8.00 (d, J=7.7 Hz, 1H), 7.16 (d, J=7.9 Hz, 1H), 6.68 (dd, J=17.0, 11.4 Hz, 1H), 5.93 (d, J=17.3 Hz, 1H), 5.59 (d,

J=11.1 Hz, 1H), 3.96 (s, 3H), 3.10 (s, minor rotamer), 2.56 (s, 3H); ^{13}C NMR δ 292.3 (+), 222.6 (+), 217.5 (+), 165.8 (+), 139.4 (+), 134.1 (+), 131.4, 129.8 (−), 129.7 (−), 128.4 (−), 126.8 (−), 120.4 (+), 52.4 (−), 38.0 (−); IR (neat) 3279, 2055, 1906, 1713 cm^{-1}. Anal. calcd for $C_{17}H_{13}CrNO_7$: C, 51.66; H, 3.32. Found: C, 51.71; H, 3.32.

4.1.15. Pentacarbonyl(1-*N*-(5-carbomethoxy-2-ethenylphenyl)aminoethylidene)chromium (21). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (1.55 g, 5.01 mmol) in CH_2Cl_2 (130 mL) with acetyl chloride (356 mL, 5.01 mmol) and **10** (886 mg, 5.00 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:2) **21** (1.23 g, 3.10 mmol, 62%) as yellow crystals. Two rotamers were obtained in a 4:3 ratio (^{1}H NMR). Mp 100–120°C (slow dec.) ^{1}H NMR (major rotamer) δ 10.24 (br s, 1H), 8.07 (d, J=7.4 Hz, 1H), 7.73 (s, 1H), 7.69 (d, J=6.7 Hz, 1H), 6.70 (dd, J=16.1, 11.4 Hz, 1H), 5.92 (m, 1H), 3.93 (s, 3H), 2.55 (s, 3H). ^{1}H NMR (minor rotamer, partial spectra) δ 10.0 (br s, 1H), 8.38 (d, J=5.4 Hz, 1H), 7.86 (d, J=8.4 Hz, 1H), 7.43 (s, 1H), 6.50 (dd, J=17.3, 11.4 Hz, 1H), 5.58 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (major rotamer) δ 292.8 (+), 217.5 (+), 213.7 (+), 163.7 (+), 138.0 (+), 136.3(+), 130.0 (−), 129.8 (−), 127.6 (−), 126.9 (−), 121.4 (+), 117.1 (+), 52.6 (−), 37.9 (−); ^{13}C NMR (minor rotamer) δ 222.6 (+), 217.4 (+), 134.8 (+), 132.4 (−), 130.7 (−), 130.5 (+), 127.8 (−), 126.4 (−), 119.7 (+), 52.4 (−), 21.4 (−); IR (neat) 2049, 1929, 1714 cm^{-1}.

4.1.16. Pentacarbonyl(1-*N*-(6-carbomethoxy-2-ethenylphenyl)aminoethylidene)chromium (22). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (2.42 g, 7.84 mmol) in CH_2Cl_2 (245 mL) with acetyl chloride (557 mL, 7.84 mmol) and **11** (1.39 g, 7.84 mmol), as described above, gave after chromatography (hexanes–EtOAc, 3:2 followed by hexanes–EtOAc, 1:1) **22** (2.34 g, 6.43 mmol, 82%) as a orange oil. Two rotamers were obtained in a 3:1 ratio (^{1}H NMR). ^{1}H NMR (major rotamer) δ 10.58 (br s, 1H), 7.83 (d, J=6.9 Hz, 1H), 7.38 (d, J=5.9 Hz, 1H), 6.65 (t, J=6.9 Hz, 1H), 5.97 (m, 1H), 5.62 (d, J=17.3 Hz, 1H), 5.37 (d, J=10.4 Hz, 1H), 3.86 (s, 3H), 2.42 (s, 3H). ^{1}H NMR (minor rotamer, partial spectra) δ 10.44 (br s, 1H), 3.93 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (major rotamer) δ 289.7 (+), 217.6 (+), 211.4 (+), 168.7 (+), 147.8 (+), 132.2 (−), 132.0 (−), 130.9 (−), 125.3 (+), 117.2 (+), 115.9 (−), 110.9 (+), 51.5 (−), 37.5 (−); ^{13}C NMR (minor rotamer) δ 289.5 (+), 222.8 (+), 213.4 (+), 165.6 (+), 148.9 (+), 130.5 (−), 130.4 (−), 129.1 (−), 119.6 (+), 115.5 (+), 52.9 (−), 17.3 (−); IR (neat) 3494, 3364, 2054, 1916, 1724, 1694 cm^{-1}.

4.1.17. Pentacarbonyl(1-*N*-(4-methoxy-2-ethenylphenyl)aminoethylidene)chromium (23). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (553 mg, 1.79 mmol) in CH_2Cl_2 (60 mL) with acetyl bromide (132 mL, 1.79 mmol) and of **14** (267 mg, 1.79 mmol), as described above, gave after chromatography (hexanes–EtOAc; 1:1) **23** (456 mg, 1.24 mmol, 69%) as yellow crystals. Mp 33–35°C. ^{1}H NMR δ 10.09 (br s, 1H), 7.24–6.90 (m, 3H), 6.63 (dd, J=17.6, 10.8 Hz, 1H), 5.77 (d, J=17.4 Hz, 1H), 5.47 (d, J=11.9 Hz, 1H), 3.86 (s, 3H), 2.51 (s, 3H); ^{13}C NMR δ 290.0 (s), 222.8 (s), 217.7 (s), 159.9 (s), 134.8 (s), 130.7 (d), 129.6 (s), 127.4 (d), 118.9 (t), 114.4 (d), 111.3 (d), 55.5 (q), 37.5 (q); IR (neat) 3320, 2970, 2025, 1895 cm^{-1}.

4.1.18. Pentacarbonyl(1-*N*-(5-methoxy-2-ethenylphenyl)aminoethylidene)chromium (24). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (2.16 g, 7.00 mmol) in CH_2Cl_2 (180 mL) with acetyl chloride (498 mL, 7.00 mmol) and **17** (1.04 g, 7.00 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2; 7:3 followed by hexanes–CH_2Cl_2; 1:1), **24** (1.10 g, 3.00 mmol, 43%) as yellow crystals. Two rotamers were obtained in a 7:2 ratio (^{1}H NMR). Mp 86–87°C. ^{1}H NMR (90 MHz) δ 10.18 (br s, 1H), overlapping 10.01 (br s, 1H, minor isomer), 7.56 (d, J=9.1 Hz, 1H), 7.01–6.41 (m, 3H), 5.66 (d, J=18.4 Hz, 1H), 5.34 (d, J=11.8 Hz, 1H), 3.84 (s, 3H), 3.05 (s, 3H, minor isomer), 2.54 (s, 3H), 2.14 (s, 3H, minor isomer); ^{13}C NMR (22.5 MHz) δ 290.2 (s), 287.5 (s, minor), 222.7 (s), 217.6 (s), 217.2 (s, minor), 159.9 (s), 137.2 (s), 130.3 (d, minor), 130.0 (d), 127.8 (d), 126.1 (s), 116.7 (t), 116.2 (d, minor), 115.7 (d), 112.7 (d, minor), 111.2 (d), 55.7 (q), 46.4 (q, minor), 37.6 (q), 30.9 (q, minor); IR (neat) 3326, 2054, 1904 cm^{-1}.

4.1.19. Pentacarbonyl(1-*N*-(2-(1-propenyl)phenyl)aminoethylidene)chromium (25). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (442 mg, 3.17 mmol) in CH_2Cl_2 (60 mL) with acetyl bromide (234 mL, 3.17 mmol) and 2-(1-propenyl)benzenamine[58,59] (980 mg, 3.17 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2; 1:1) **25** (782 mg, 2.23 mmol, 70%) as yellow crystals. Four inseparable isomers–rotamers were obtained. Mp 41–43°C. ^{1}H NMR (broad unresolved signals) δ 10.16 (br s), 9.93 (br s), 7.57–7.20 (m), 7.08 (d, J=7.5 Hz), 7.03 (d, J=7.7 Hz), 6.27 (m), 6.00 (m), 3.06 (s, minor), 3.01 (s, minor), 2.56 (s), 2.52 (s), 1.92–1.75 (m); ^{13}C NMR δ 288.8 (−), 287.9 (−), 222.9 (−), 217.7 (−), 217.7 (−), 136.8 (−), 135.8 (−), 133.9 (−), 133.4 (−), 131.3 (+), 131.1 (+), 130.7 (+), 129.4 (+), 128.8 (+), 128.0 (+), 127.9 (+), 127.7 (+), 126.8 (+), 126.1 (+), 125.9 (+), 124.7 (+), 124.3 (+), 37.5 (+), 37.3 (+), 18.8 (+), 14.4 (+); IR (neat) 2040, 1920 cm^{-1}.

4.1.20. Pentacarbonyl(1-*N*-(2-(2-methyl-1-propenyl)phenyl)aminoethylidene)chromium (26). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromate(1-) (2.16 g, 7.00 mmol) in CH_2Cl_2 (180 mL) with acetyl chloride (498 mL, 7.00 mmol) and 2-(2-methylpropenyl)-benzeneamine[60] (1.24 g, 7.00 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:1) **26** (1.91 g, 5.23 mmol, 75%) as a red oil.[61] Two rotamers were obtained in a 4:1 ratio (^{1}H NMR). ^{1}H NMR (broad unresolved signal for the major isomer) δ 10.17 (br s, 1H), 7.07 (m, 4H), 6.17 (s, 1H), 2.08 (s, 3H), 1.97 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (major isomer) δ 286.5 (+), 220.5 (+), 211.4 (+), 145.2 (+), 140.8 (+), 130.7 (−), 127.9 (−), 127.2 (+), 123.9 (−), 118.9 (−), 118.3 (−), 25.7 (−), 19.2 (−), 14.1 (−); IR (CH_2Cl_2) 3355, 2054, 1922 cm^{-1}.

4.1.21. Pentacarbonyl(1-*N*-(2-(2-propenyl)phenyl)aminoethylidene)chromium (3). Reaction of tetramethylammonium pentacarbonyl(acetyl)chromium (1-) (1.236 g, 4.00 mmol) in CH_2Cl_2 (60 mL) with acetyl bromide

(296 mL, 4.00 mmol) and of 2-(2-propenyl)benzenamine (545 mL, 4.48 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2; 1:1), **3** (863 mg, 2.46 mmol, 61%) as a yellow oil. Two rotamers were obtained in a 5:1 ratio (^{1}H NMR). ^{1}H NMR δ 10.24 (br s, 1H), 7.37 (m, 3H), 7.10 (m, 1H), 5.36 (s, 1H), 4.98 (s, 1H), 2.93 (s, minor), 2.62 (s, 3H), 2.04 (s, 3H); ^{13}C NMR δ 287.5, 284.8 (minor), 222.9, 217.6, 216.5 (minor), 141.57, 139, 135.4, 129.5, 129.3, 128.1, 126.3, 118.0, 46.6 (minor), 37.4, 23.4; IR (neat) 2045, 1895 cm^{-1}.

4.1.22. Pentacarbonyl(1-*N*-(2-ethenylphenyl)amino-1-phenylmethylidene)chromium (27). Reaction of 2.97 g (8.00 mmol) of tetramethylammonium pentacarbonyl-(benzoyl)chromate(1-) in CH_2Cl_2 (120 mL) with 591 mL (8.00 mmol) of acetyl bromide and 1.09 mL (8.00 mmol) of 2-(2-propenyl)benzenamine, as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:1) and solvent removal on a high vacuum pump, 2.90 g (7.03 mmol, 88%) of **27** as orange crystals. Two rotamers were obtained in a 4:1 ratio (^{1}H NMR). Mp: 65–67°C. ^{1}H NMR δ 10.73 (br s, 1H), 9.97 (br s, 1H, minor), 7.60–6.81 (m, 8H), 6.48 (d, J=7.1 Hz, 1H), 5.59 (s, 1H), 5.36 (s, 1H, minor), 5.22 (s, 1H), 5.05 (s, 1H, minor), 2.19 (s, 3H), 2.14 (s, 3H, minor); ^{13}C NMR δ 286.8 (s), 286.3 (s, minor), 223.4 (s), 216.9 (s), 216.5 (s, minor), 155.6 (s), 150.0 (s), 141.7, 141.4, 140.5, 138.8, 137.6, 135.8, 129.9, 129.4, 128.6, 128.2, 127.7, 127.2, 125.2, 120.8, 118.7, 117.8, 24.0 (q); IR (neat) 2058, 1979, 1928 cm^{-1}.

4.1.23. Pentacarbonyl(1-*N*-(2-(2-propenyl)phenyl)amino-1-cyclopropylmethylidene)chromium (28). Reaction of tetramethylammonium pentacarbonyl(cyclopropylcarbonyl)-chromate(1-)[62] (1.344 g, 4.00 mmol) in CH_2Cl_2 (60 mL) with acetyl bromide (300 mL, 4.06 mmol) and 2-(2-propenyl)benzenamine (545 mL, 4.01 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:1) and solvent removal on a rotary evaporator, **28** (1.346 g, 3.57 mmol, 89%) as yellow-green oil. Two rotamers were obtained in a 5:3 ratio (^{1}H NMR). ^{1}H NMR δ 10.09 (br s, major, 1H), 9.70 (br s, minor, 1H), 7.39 (br m, 4H), 5.36 (s, major, 1H), 5.30 (s, minor, 1H), 5.02 (s, major, 1H), 4.95 (s, minor, 1H), 3.05 (apparent quintet, J=7.0 Hz, 1H), 2.05 (s, 3H), overlapping 2.0 (m, 1H), 1.5–0.9 (m, 4H); ^{13}C NMR δ 285.3, 284.1, 223.5, 222.0, 217.9, 217.2, 142.0, 141.5, 140.2, 139.8, 138.5, 136.3, 129.4, 128.9, 127.0, 126.7, 117.9, 117.3, 36.7, 29.4, 23.9, 23.6, 14.0, 10.2; IR (neat) 2045, 1910 cm^{-1}.

4.1.24. Pentacarbonyl(1-*N*-(2-(2-propenyl)phenyl)amino-1-(2-furyl)methylidene)chromium (29). Reaction of tetramethylammonium pentacarbonyl(2-furylcarbonyl)chromate(1-)[63] (3.62 g, 10.0 mmol) in CH_2Cl_2 (250 mL) with acetyl chloride (711 mL, 10.0 mmol) and 2-(2-propenyl)-benzenamine (1.37 mL, 10.0 mmol), as described above, gave after chromatography (hexanes–CH_2Cl_2, 1:1) and solvent removal on a rotary evaporator, **29** (2.66 mg, 7.55 mmol, 76%) as brown-red crystals. Two rotamers were obtained in a 3:1 ratio (^{1}H NMR). Mp 86–89°C. ^{1}H NMR δ 10.59 (br s, 1H), 9.80 (br s, minor, 1H), 7.70–6.66 (m, 7H), 5.26 (s, 1H), 5.02 (s, 1H), 2.22 (s, minor, 3H), 2.02 (s, 3H); ^{13}C NMR δ 258.4 (+, minor), 250.9 (+), 222.8 (+, minor), 217.5 (+), 213.4 (+, minor), 211.3 (+), 158.4 (+), 144.3 (−), 142.1 (+), 140.5 (+), 138.8 (+), 129.4 (−), 128.1 (−), 128.0 (−), 125.3 (−), 117.6 (+), 113.9 (−), 23.7 (−); IR (neat) 3289, 1982, 1912 cm^{-1}.

4.1.25. Tetramethylammonium pentacarbonyl(5-(1,3-benzodioxol)carbonyl)chromate(1-). To a −78°C cold solution of 5-bromo-1,3-benzodioxole (1.20 mL, 10.0 mmol) in Et_2O (15 mL) was added *t*-butyllithium (11.8 mL, 20.1 mmol, 1.7 M in hexanes) via a cannula. The solution was stirred for 30 min at −78°C then 45 min at ambient temperature. The solution was transferred *via* a cannula to a 0°C cold slurry of $Cr(CO)_6$ (2.20 g, 10.0 mmol) in Et_2O (25 mL). After being stirred for 30 min at 0°C then at ambient temperature for 30 min, the solvents were removed from the brown reaction mixture. The resulting solid residue was treated with a solution of tetramethylammonium bromide (3.07 g, 20.0 mmol) in degassed, distilled water (50 mL) for 20 min. The resulting yellow slurry was extracted with CH_2Cl_2 (3×50 mL), dried ($MgSO_4$), filtered (Celite), and evaporated to dryness affording tetramethyl-ammonium pentacarbonyl(1-(1,3-benzodioxol-5-yl)methyl-idene)chromium (1-) (2.45 g, 5.87 mmol, 59%) as a yellow solid. Mp 90–105°C (dec.) ^{1}H NMR δ 7.05 (d, J=7.9 Hz, 1H), 6.85 (d, J=7.9 Hz, 1H), 6.79 (s, 1H), 5.98 (s, 2H), 3.09 (br s, 12H); ^{13}C NMR δ 283.8 (+), 227.6 (+), 223.0 (+), 149.2 (+), 147.0 (+), 146.5 (+), 120.4 (−), 106.7 (−), 104.1 (−), 111.8 (+), 54.8 (−); IR (neat) 2030, 1887, 1859 cm^{-1}.

4.1.26. Pentacarbonyl(1-*N*-methyl-*N*-(2-(2-propenyl)-phenyl)amino-1-ethylidene)chromium (33). To a slurry of 103 mg (2.57 mmol, 80%, washed with 5 mL of hexanes) of sodium hydride in 10 mL of THF was added 848 mg (2.15 mmol) of **1** dissolved in 6 mL of THF. After 15 min, 200 mL (3.22 mmol) of iodomethane was added by syringe. The resulting mixture was stirred for 2.5 h followed by solvent removal on a rotary evaporator at water aspirator pressure to give an orange oil. The crude product was purified by chromatography (hexanes then hexanes–CH_2Cl_2, 1:1) to give, after solvent removal, 775 mg (1.90 mmol, 89%) of **33** as yellow-orange oil. The oil rapidly decomposes at room temperature, and it was immediately used in the next step. Two rotamers were obtained in a 1:1 ratio (^{1}H NMR). ^{1}H NMR (300 MHz) δ 7.83 (d, J=7.7 Hz), 7.53–7.42 (m, 1H), 7.16 (d, J=7.8 Hz), 6.91–6.75 (m), 5.52 (d, J=11.6 Hz), 5.41 (d, J=17.8 Hz), 4.02 (s), 3.90 (s), 3.85 (s), 3.48 (s), 2.93 (s), 2.49 (s); ^{13}C NMR (75 MHz, partial) δ 283.7, 280.9, 223.4, 217.6, 217.0, 167.5, 167.2, 150.1, 145.0, 134.4, 132.9, 131.5, 130.8, 130.6, 130.1, 130.0, 129.9, 128.9, 128.6, 128.2, 120.4, 120.3, 52.5, 52.4, 52.2, 45.4, 42.2, 40.8; IR (neat) 2053, 1967, 1915, 1727 cm^{-1}.

4.1.27. 2-Methylindole (18a),[64] 2,3-dimethylindole (18b),[64] 2-methylquinoline (18c),[64] and 2-methyl-1,2,3,4-tetrahydroquinoline (18d).[56,65] A solution of **18** (674 mg, 2.00 mmol) in toluene (20 mL) was heated at 120°C (oil-bath temperature) for 19 h under a nitrogen atmosphere. The resulting brown reaction mixture was cooled to ambient temperature and filtered through a 0.5 cm Celite pad. The pad was washed with toluene (20 mL). The solvent was removed from the filtrate and the crude product was purified by chromatography (hexanes–EtOAc, 9:1 then

hexanes–EtOAc, 8:2) to give, in order of elution, **18d** (36 mg, 0.25 mmol, 12%) as faint yellow oil, a mixture of **18a** (12 mg, 0.09 mmol, 5%) and **18b** (44 mg, 0.30 mmol, 15%) as faint yellow crystals, and **18c** (60 mg, 0.42 mmol, 21%) as faint yellow crystals. Spectral data for **18a–d** were in complete accordance with literature values. Additional spectral data for **18d**: ^{13}C NMR (22.5 MHz) δ 129.2, 126.7, 120.8, 118.9, 117.2, 114.1, 47.2, 30.0, 26.5, 22.5.

A solution of **18** (337 mg, 1.00 mmol) in acetonitrile (10 mL) was heated at 90°C (oil-bath temperature) for 2 h, under an argon atmosphere, as described above to give yellow-orange solution. Solvent evaporation and chromatography (hexanes–EtOAc, 8:2) gave, in order of elution, **18b** (71 mg, 0.49 mmol, 49%) as faint yellow crystals, followed by a fraction containing **18c**, partially complexed to chromium. The latter fraction was redissolved in hexanes–EtOAc (1:1), air-oxidized (6 h), filtered (Celite), and evaporated in vacuo to give **18c** (11 mg, 0.08 mmol, 8%) as faint yellow oil.

4.1.28. 3-Methyl-2-phenylindole (19b),[66] 2-phenylquinoline (19c),[64] and 2-phenyl-1,2,3,4-tetrahydroquinoline (19d).[67] Thermolysis of **19** (391 mg, 0.98 mmol) in toluene (10 mL) at 100°C (oil-bath temperature) for 4 h, as described above, gave after air oxidation (20 h), and chromatography (hexanes–EtOAc, 9:1 then hexanes–EtOAc, 7:3) **19b** (35 mg, 0.17 mmol, 17%) as a colorless oil followed by **19c** (78 mg, 0.38 mmol, 39%) as faint yellow crystals, and **19d** (34 mg, 0.17 mmol, 17%) as faint yellow oil. Additional spectral data for **19d**: ^{13}C NMR (22.5 MHz) δ 144.8, 129.3, 128.5, 127.4, 126.9, 126.5, 125.1, 122.3, 117.1, 113.9, 56.3, 31.0, 26.3.

Thermolysis of **19** (399 mg, 1.00 mmol) in hexanes (10 mL) at 90°C (oil-bath temperature) for 2 h, as described above, gave after air oxidation (1.5 h) and chromatography (hexanes–CH_2Cl_2, 8:2 then hexanes–CH_2Cl_2, 1:1), **19d** (33 mg, 0.16 mmol, 16%) as a colorless oil followed by **19c** (73 mg, 0.36 mmol, 36%) as faint yellow crystals.

Thermolysis of **19** (399 mg, 1.00 mmol) in acetonitrile (10 mL) at 90°C (oil-bath temperature) for 0.5 h, as described above, gave after air-oxidation (30 h), and chromatography (hexanes–EtOAc, 9:1 then hexanes–EtOAc, 7:3), **19c** (49 mg, 0.23 mmol, 23%) as a colorless oil followed by **19d** (103 mg, 0.50 mmol, 50%) as faint yellow crystals. A fraction containing a small amount of impure **19b** was also isolated (<5%).

4.1.29. Methyl 2-methylindole-4-carboxylate (2).[68] Thermolysis of **1** (395 mg, 1.00 mmol) in toluene (10 mL) at 120°C (oil-bath temperature) for 1 h, as described above, gave after chromatography (hexanes–EtOAc, 3:1), tricarbonyl chromium toluene complex[69] (62 mg, 0.27 mmol, 27%) as yellow crystals followed by **2** (114 mg, 0.60 mmol, 60%) as faint yellow crystals. Additional spectral data for **2**: ^{13}C NMR (300 MHz) δ 168.4 (s), 137.8 (s), 136.9 (s), 128.7 (s), 124.3 (d), 120.1 (s), 119.9 (d), 115.0 (d), 101.7 (d), 51.6 (q), 13.7 (q).

4.1.30. Methyl 2-methyl-1,2,3,4-tetrahydroquinoline-5-carboxylate (1d). Thermolysis of **1** (198 mg, 0.50 mmol) in acetonitrile (5 mL) at 90°C (oil-bath temperature) for 19 h, as described above, gave after air oxidation (5 h) and chromatography (hexanes–EtOAc, 9:1), **1d** (72 mg, 0.36 mmol, 63%) as faint yellow oil. ^{1}H NMR δ 7.16 (d, J=6.9 Hz, 1H), 6.99 (t, J=7.9 Hz, 1H), 6.60 (d, J=7.9 Hz, 1H), 3.85 (s, 3H), 3.82 (br s, 1H), 3.39 (m, 1H), 3.16 (ddd, J=17.8, 5.2, 3.9 Hz, 1H), 2.98 (ddd, J=17.8, 11.4, 5.8 Hz, 1H), 1.96 (m, 1H), 1.52 (m, 1H), 1.21 (d, J=6.2 Hz, 3H); ^{13}C NMR δ 168.5 (+), 145.3 (+), 130.3 (+), 126.1 (−), 122.3 (+), 119.1 (−), 117.8 (−), 51.7 (−), 46.5 (−), 29.9 (+), 25.0 (+), 22.4 (−); IR (neat) 3388, 1718, 1649, 1593, 1281 cm^{-1}; GC-MS (EI) m/z 205 (M+), 190 (100%), 158, 130; HRMS (EI) calcd for $C_{12}H_{15}NO_2$ (M^+) 205.1103. Found: 205.1103.

4.1.31. Methyl 2-methylindole-4-carboxylate (2) and methyl-3-amino-2-ethenylbenzoate (8). Thermolysis of **1** (395 mg, 1.00 mmol) in hexanes (10 mL) at 90°C (oil-bath temperature) for 46 h, as described above, gave after air-oxidation (16 h), and chromatography (hexanes–EtOAc, 9:1 then hexanes–EtOAc, 7:3), **2** (64 mg, 0.34 mmol, 34%) as faint yellow crystals followed by **8** (108 mg, 0.61 mmol, 61%) as faint yellow oil.

4.1.32. Methyl 2,3-dimethylindole-5-carboxylate (20b).[70] Thermolysis of **20** (285 mg, 0.72 mmol) in MeCN (7 mL) at 90°C (oil-bath temperature) for 6 h gave after air-oxidation (12H), and chromatography (hexanes–EtOAc, 49:1), **20b** (139 mg, 0.68 mmol, 95%) as white crystals.

4.1.33. Methyl 2-methylindole-5-carboxylate (20a)[71] and methyl 2-methylquinoline-6-carboxylate (20c).[72] Thermolysis of **20** (395 mg, 1.00 mmol) in hexane (10 mL) at 90°C (oil-bath temperature) for 6 h gave after air-oxidation (14 h), and chromatography (hexanes–EtOAc, 49:1), **20a** (133 mg, 0.70 mmol, 70%) followed by **20c** (35 mg, 0.18 mmol, 18%), both as faint yellow crystals.

4.1.34. Methyl 2-methylindole-6-carboxylate (21a), methyl 2,3-dimethylindole-6-carboxylate (21b),[73] and methyl 2-methyl-1,2,3,4-tetrahydroquinoline-7-carboxylate (21d), and methyl 3-amino-4-ethenylbenzoate (10). Thermolysis of **21** (395 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 6 h gave after air-oxidation (14 h), and chromatography (hexanes–EtOAc, 9:1), **21d** (142 mg, 0.70 mmol, 70%) as white crystals followed by 41 mg of a mixture[74] of **21a** (0.04 mmol, 4%), **21b** (0.07 mmol, 7%), and **10** (0.11 mmol, 11%).

Spectral data for **21d**. Mp 76–77°C. ^{1}H NMR δ 7.25 (d, J=7.9 Hz, 1H), 7.13 (s, 1H), 6.99 (d, J=7.9 Hz, 1H), 3.86 (s, 3H), 3.83 (br s, 1H), 3.42 (m, 1H), 2.93–2.70 (m, 2H), 1.99–1.90 (m, 1H), 1.65–1.50 (m, 1H), 1.22 (d, J=6.2 Hz, 3H); ^{13}C NMR δ 167.5 (+), 144.7 (+), 129.1 (−), 128.6 (+), 126.2 (+), 117.9 (−), 114.7 (−), 51.8 (−), 47.1 (−), 29.6 (+), 26.7 (+), 22.5 (−); IR (neat) 3384, 1708 cm^{-1}; GC-MS (EI) m/z 205; HRMS (EI) exact mass calcd for $C_{12}H_{15}NO_2$ m/z 205.1103, obsd 205.1099.

4.1.35. Methyl 2-methylindole-6-carboxylate (21a), methyl 2,3-dimethylindole-6-carboxylate (21b), and methyl 3-amino-4-ethenylbenzoate (10). Thermolysis of **21** (135 mg, 0.34 mmol) in MeCN (4 mL) at 90°C (oil-bath temperature) for 45 h gave after air-oxidation (12H),

and chromatography (hexanes–EtOAc, 19:1) 41 mg of a mixture[74] of **21a** (0.02 mmol, 7%), **21b** (0.13 mmol, 38%), and **10** (0.11 mmol, 33%).

4.1.36. Methyl 2-methylindole-7-carboxylate (22a),[71] methyl 2,3-dimethylindole-7-carboxylate (22b),[72] methyl 2-methyl-1,2,3,4-tetrahydroquinoline-8-carboxylate (22d), methyl 2-amino-3-ethenylbenzoate (11), and methyl 2-amino-3-ethylbenzoate. Thermolysis of **22** (395 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 6.5 h gave in order of elution, after air-oxidation (12H) and chromatography (hexanes–EtOAc, 19:1), **22d** (38 mg, 0.18 mmol, 18%) as faint yellow oil, a 2:1 mixture of **11** and methyl 2-amino-3-ethylbenzoate[75] (67 mg, ca. 26 and 12%, respectively), a 1:2 mixture of **22a** and **22b** (62 mg, ca. 7 and 24%, respectively) as faint yellow crystals.

Spectral data for **22d**. ^{1}H NMR δ 7.70 (d, J=7.4 Hz, 1H), overlapping 7.7 (s, 1H), 7.06 (d, J=7.4 Hz, 1H), 6.45 (t, J=7.4 Hz, 1H), 3.84 (s, 3H), 3.54–3.40 (m, 1H), 2.83–2.61 (m, 2H), 1.93–180 (m, 1H), 1.55–1.40 (m, 1H), 1.28 (d, J=6.2 Hz, 3H); ^{13}C NMR δ 169.3 (+), 148.4 (+), 133.6 (−), 129.3 (−), 121.9 (+), 113.6 (−), 108.2 (+), 51.3 (−), 46.7 (−), 28.8 (+), 27.1 (+), 22.6 (−); IR (neat) 3372, 1677, 1254 cm^{-1}; GC-MS (EI) m/z 205 (M+), 190, 158 (100%), 130; HRMS (EI) calcd for $C_{12}H_{15}NO_2$(M+), 205.1103. Found: 205.1102.

Spectral data for methyl 2-amino-3-ethylbenzoate from the mixture with **11**. ^{1}H NMR δ 7.70 (dd, J=6.4, 1.5 Hz, 1H), 7.12 (d, J=7.4 Hz, 1H), 6.55 (t, J=7.9 Hz, 1H), 3.78 (s, 3H), 2.42 (q, J=7.7 Hz, 2H), 1.18 (t, J=7.4 Hz, 3H).

4.1.37. Methyl 2-methylindole-7-carboxylate (23a), methyl 2-methyl-1,2,3,4-tetrahydroquinoline-8-carboxylate (23d), and methyl 2-amino-3-ethenylbenzoate (11). Thermolysis of **22** (410 mg, 1.04 mmol) in hexanes (10.5 mL) at 90°C (oil-bath temperature) for 6.5 h gave in order of elution, after air-oxidation (12H) and chromatography (hexanes–EtOAc, 19:1), **22d** (9 mg, 0.04 mmol, 4%) as faint yellow oil, **11** (34 mg, 0.19 mmol, 18%), and **22a** (129 mg, 0.68 mmol, 65%) as faint yellow oil.

4.1.38. 5-Methoxy-2,3-dimethylindole (23b)[76] and 5-methoxy-2-methylquinoline (23c).[77] Thermolysis of **23** (184 mg, 0.50 mmol) in MeCN (5 mL) at 90°C (oil-bath temperature) for 25 h gave, after air-oxidation (16 h) and chromatography (hexanes–EtOAc, 4:1), **23c** (36 mg, 0.21 mmol, 42%) followed by **23b** (17 mg, 0.10 mmol, 29%) as faint yellow oils.

Thermolysis of **23** (184 mg, 0.50 mmol) in hexanes (5 mL) at 90°C (oil-bath temperature) for 25 h gave, after air-oxidation (16 h) and chromatography (hexanes–EtOAc, 4:1), **23c** (49 mg, 0.28 mmol, 57%) followed by **23b** (17 mg, 0.10 mmol, 29%) as faint yellow oils.

4.1.39. 2-Ethenyl-5-methoxybenzenamine (17). Thermolysis of **24** (130 mg, 0.35 mmol) in MeCN (5 mL) at 90°C (oil-bath temperature) for 3 h gave, after air-oxidation (14 h) and chromatography (hexanes–EtOAc, 9:1), **17** (42 mg, 0.28 mmol, 80%).

Thermolysis of **24** (184 mg, 0.50 mmol) in MeCN (5 mL) at 90°C (oil-bath temperature) for 3 h gave, after air-oxidation (14 h) and chromatography (hexanes–EtOAc, 9:1), **17** (40 mg, 0.27 mmol, 54%).

4.1.40. 2-Methylindole (25a).[64] Thermolysis of a solution of **25** (351 mg, 1.00 mmol) in toluene (10 mL, 120°C, 2H), as described above, gave after air-oxidation (72H), and chromatography (hexanes–EtOAc, 9:1), **25a** (82 mg, 0.62 mmol, 62%) as faint yellow crystals.

4.1.41. 2-Methylindole (25a) and 3-ethyl-2-methylindole (25b).[78] Thermolysis of a solution of **25** (197 mg, 0.56 mmol) in acetonitrile (10 mL, 90°C, 16.5 h), as described above, gave after chromatography (hexanes–EtOAc, 4:1), **25b** (53 mg, 0.33 mmol, 60%) followed by **25a** (18 mg, 0.14 mmol, 25%), both as faint yellow crystals. Additional data for **25b**: ^{13}C NMR δ 135.1 (−), 130.1 (−), 128.3 (−), 120.6 (+), 118.8 (+), 118.0 (+), 113.7 (−), 110.2 (+), 17.3 (−), 15.4 (+), 11.3 (+).

4.1.42. 2-Methylindole (25). Thermolysis of a solution of **25** (197 mg, 0.56 mmol) in hexanes (10 mL, 90°C, 48 h), as described above, gave after chromatography (hexanes–EtOAc, 4:1), **25a** (36 mg, 0.27 mmol, 47%) as faint yellow crystals.

4.1.43. *N*-(2-(2-Methyl-1-propen-1-yl)phenyl) 2-methylpropanamide (31). Thermolysis of **26** (365 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 24 h gave, after air-oxidation (48 h) and chromatography (hexanes–EtOAc, 9:1), **31** (28 mg, 0.13 mmol, 13%) as yellow crystals. Mp 65–66°C. ^{1}H NMR δ 8.28 (d, J=8.2 Hz, 1H), 7.31 (br s, 1H), 7.25 (t, J=8.4 Hz, 1H), 7.07 (s, 1H), 7.05 (t, J=9.1 Hz, 1H), 6.11 (s, 1H), 2.51 (septet, J=6.9 Hz, 1H), 1.96 (s, 3H), 1.64 (s, 3H), 1.24 (d, J=6.9 Hz, 1H); ^{13}C NMR δ 174.7 (+), 140.1 (+), 135.6 (+), 129.5 (−), 128.0 (+), 127.5 (−), 123.4 (−), 120.2 (−), 120.0 (−), 36.9 (−), 25.7 (−), 19.6 (-, 2C), 19.4 (−); IR (neat) 3246, 1658 cm^{-1}; GC-MS (EI) m/z 217 (M+), 147, 146 (100%), 132; HRMS (EI) calcd for $C_{14}H_{19}NO$ (M^+), 217.1467. Found: 217.1470.

4.1.44. 2-Methylindole (26a) and 2-(2-methyl-1-propenyl)-benzenamine. Thermolysis of **26** (365 mg, 1.00 mmol) in hexanes (10 mL) at 90°C (oil-bath temperature) for 24 h gave, after air-oxidation (48 h) and chromatography (hexanes–EtOAc, 9:1), a 75 mg of a mixture of 2-(2-methyl-1-propenyl)benzenamine (64 mg, 0.44 mmol, 44%) and **26a** (11 mg, 0.08 mmol, 8%).[74]

4.1.45. 2,4-Dimethylquinoline (4)[64] and 2,4-dimethyl-1,2,3,4-tetrahydroquinoline (5).[79] Thermolysis of a solution of **3** (863 mg, 2.46 mmol) in toluene (30 mL, 120°C, 16 h), as described above, gave after air-oxidation (24 h) and chromatography (hexanes–EtOAc, 8:2), **5** (88 mg, 0.55 mmol, 22%) followed by **4** (133 mg, 0.85 mmol, 34%) both as faint yellow oils.

4.1.46. 2,4-Dimethylquinoline (4) and 2-(1-methylethenyl)-benzenamine. Thermolysis of **3** (351 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 14.5 h gave in order of elution, after air-oxidation (12H) and

chromatography (hexanes–EtOAc, 9:1), 2-(1-methylethenyl)benzenamine (55 mg, 0.41 mmol, 41%), and **4** (35 mg, 0.22 mmol, 22%), both as yellow oils.

4.1.47. 4-Methyl-2-phenylquinoline (27c),[80] 1,2,3,4-tetrahydro-4-methyl-2-phenylquinoline (27d),[81,82] and 3-hydroxy-4-methyl-2-phenylquinoline (27e). Thermolysis of a solution of **27** (423 mg, 1.02 mmol) in toluene (20 mL, 110°C, 24 h), as described above, gave after air-oxidation (2H) and chromatography (hexanes–EtOAc, 9:1 then 8:2), a 26:9 mixture of **27c** and **27d** (79 mg, ca 26 and 9% respectively) followed by **27e** (46 mg, 0.22 mmol, 22%) as faint yellow crystals.

Analytical data for **27e**. ^{1}H NMR δ 8.08–8.04 (m, 1H), 7.91–7.87 (m, 1H), 7.74–7.68 (m, 2H), 7.59–7.35 (m, 5H), 6.95 (br s, 1H), 2.57 (s, 3H); ^{13}C NMR δ 150.0 (+), 144.8 (+), 143.0 (+), 136.8 (+), 129.7 (−), 129.2 (−), 129.1 (−), 128.9 (+), 128.8 (−), 126.6 (−), 126.5 (−), 126.3 (+), 123.0 (−), 10.7 (−); IR (neat) 3060 cm^{-1}; GC-MS (EI) *m/z* (M^+) 235, 234 (100%), 206, 128; HRMS (EI) calcd for $C_{16}H_{13}NO$ (M^+-1), 234.0919. Found: 234.0921.

4.1.48. 4-Methyl-2-phenylquinoline (27c). Thermolysis of **27** (422 mg, 1.02 mmol) in hexanes (20 mL) at 90°C (oil-bath temperature) for 3 h gave, after air-oxidation (3 days) and chromatography (hexanes–EtOAc, 19:1), **27c** (120 mg, 0.55 mmol, 55%) as white crystals.

Thermolysis of **27** (265 mg, 0.64 mmol) in MeCN (20 mL) at 90°C (oil-bath temperature) for 3 h gave, after air-oxidation (3 days) and chromatography (hexanes–EtOAc, 19:1), **27c** (86 mg, 0.39 mmol, 61%) as white crystals.

4.1.49. 4-Methyl-2-phenylquinoline (27c) and 2-(1-methylethenyl)-*N*-phenylmethylenebenzenamine (32).[83] Thermolysis of **27** (200 mg, 0.50 mmol) in MeCN (5 mL) at 90°C (oil-bath temperature) under CO (3 atm) for 6 h gave in order of elution (hexanes–EtOAc, 9:1), **27c** (22 mg, 0.10 mmol, 20%) and **32** (23 mg, 0.11 mmol, 22%), the latter as yellow crystals.[84]

4.1.50. 3-Hydroxy-4-methyl-2-cyclopropylquinoline (28e) and 4-methyl-2-cyclopropylquinoline (28c).[85] Thermolysis of **28** (335 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 20 h gave in order of elution, after air-oxidation (17 h) and chromatography (hexanes–EtOAc, 19:1), **28c** (25 mg, 0.14 mmol, 14%) as faint yellow oil and **28e** (39 mg, 0.23 mmol, 23%) as faint yellow crystals.

Thermolysis of **28** (335 mg, 1.00 mmol) in hexanes (10 mL) at 90°C (oil-bath temperature) for 20 h gave in order of elution, after air-oxidation (17 h) and chromatography (hexanes–EtOAc, 19:1), **28c** (56 mg, 0.31 mmol, 31%) as faint yellow oil and **28e** (42 mg, 0.25 mmol, 25%) as faint yellow crystals.

Spectral data for **28e**. Mp 93–94°C; IR (neat) 3406, 1594, 1389, 1192 cm^{-1}. ^{1}H NMR δ 7.94 (dd, *J*=7.6, 1.7 Hz, 1H), 7.84 (dd, *J*=7.2, 2.0 Hz, 1H), 7.51 (td, *J*=6.9, 1.7 Hz, 1H), 5.71 (br s, 1H), 2.56 (s, 3H), 2.29 (tt, *J*=8.2, 4.9 Hz, 2H), 1.18 (dt, *J*=5.2, 2.2 Hz, 2H), 1.09 (dt, *J*=8.4, 2.5 Hz, 2H); ^{13}C NMR δ 152.1 (+), 146.2 (+), 142.9 (+), 129.2 (−), 128.1 (+), 126.2 (−), 123.5 (+), 122.8 (−), 12.1 (−), 10.4 (−), 7.1 (+); MS (EI) *m/z* 199 (M^+), 198 (100%), 184; HRMS (EI) calcd for $C_{13}H_{13}NO$ 199.0957 (M^+), obsd 199.0960.

4.1.51. 2-(2-Furyl)-4-methylquinoline (29c).[80] Thermolysis of **29** (352 mg, 1.00 mmol) in MeCN (10 mL) at 90°C (oil-bath temperature) for 23.5 h gave, after air-oxidation (12H) and chromatography (hexanes–EtOAc, 19:1), **29c** (54 mg, 0.26 mmol, 26%) as a yellow oil.

Thermolysis of **29** (352 mg, 1.00 mmol) in hexanes (10 mL) at 90°C (oil-bath temperature) for 23.5 h gave, after air-oxidation (12H) and chromatography (hexanes–EtOAc, 19:1), **29c** (44 mg, 0.21 mmol, 21%).

4.1.52. Dubamine[86] and piperonal. Reaction of tetramethylammonium pentacarbonyl(1-(1,3-benzodioxol-5-yl)methylidene)chromium (1-) (200 mg, 0.45 mmol) in CH_2Cl_2 (20 mL) with acetyl chloride (34 mL, 0.48 mmol) and 2-ethenylbenzenamine (57 mg, 0.48 mmol), as described above, gave after chromatography (hexanes–EtOAc, 6:4) and solvent removal on a rotary evaporator, **30** (186 mg, <0.42 mmol, <87%)[87] as brown-red crystals. The resulting solid was immediately dissolved in acetonitrile (5 mL) and heated as described above (90°C, 45 min). Evaporation of the solvent and purification by column chromatography (hexanes–EtOAc, 9:1) gave **30c** (10 mg, 0.04 mmol, 9%) followed by piperonal (32 mg, 0.21 mmol, 51%).

4.1.53. 4-Carbomethoxy-1,2-dimethylindole (35) and *N*-methyl-*N*-(2-ethenyl)phenyl acetamide (35). Thermolysis of **33** (421 mg, 1.03 mmol) in benzene (30 mL) at 90°C for 28 h as described above gave, after air oxidation (24 h) and chromatography (hexanes–EtOAc, 8:2 followed by hexanes–EtOAc, 1:1), **34** (44 mg, 0.22 mmol, 21%) as faint yellow crystals followed by **35** (73 mg, 0.31 mmol, 30%) as faint yellow oil.

Spectral data for **34**. Mp <25°C. ^{1}H NMR (300 MHz) δ 7.84 (d, *J*=7.6 Hz, 1H), 7.41 (d, *J*=8.1 Hz, 1H), 7.15 (t, *J*=7.8 Hz, 1H), 6.86 (s, 1H), 3.96 (s, 3H), 3.64 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz) δ 168.2, 139.5, 138.2, 127.6, 122.7, 120.1, 119.4, 113.3, 51.5, 29.5, 12.8; IR (neat) 2960, 1705, 1260 cm^{-1}; HRMS (EI) exact mass calcd for $C_{12}H_{13}NO_2$ *m/z* 203.0946, obsd 203.0974.

Spectral data for **35**. ^{1}H NMR δ 7.74 (dd, *J*=7.7, 2.6 Hz, 1H), 7.49–7.29 (m, 3H), 6.89 (dd, *J*=17.8, 11.6 Hz, 1H), 5.49 (d, *J*=11.9 Hz, 1H), 5.31 (d, *J*=18.4 Hz, 1H), 3.88 (s, 3H), 3.16 (s, 3H), 1.80 (s, 3H); ^{13}C NMR δ 170.3 (s), 168.1 (s), 142.8 (s), 136.7 (s), 132.9 (s), 131.4 (d), 131.2 (d), 129.4 (d), 128.5 (d), 120.2 (t), 52.4 (q), 36.4 (q), 22.2 (q); IR (neat) 1715, 1640 cm^{-1}. Anal. calcd for $C_{13}H_{15}NO_3$: C, 66.93; H, 6.48. Found: C, 66.94; H, 7.02.

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