180. Transition Metal-Diene Complexes in Organic Synthesis

Part 15[1])

Iron-Mediated Total Synthesis of Carbazomycin A and B

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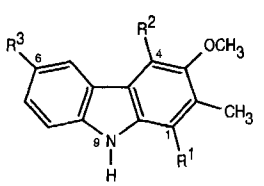
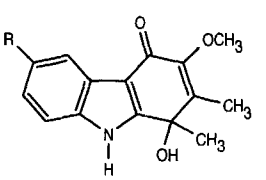
We developed a very efficient methodology for the synthesis of the antibiotics carbazomycin A (**1**) and B (**2**) by oxidative coupling of cyclohexa-1,3-diene and the corresponding arylamine **10** (*Scheme 5* and *Schemes 7* and *9*, resp.). The overall process is achieved by a consecutive Fe-induced formation of the C–C and the C–N bond. The major benefit of our Fe-mediated carbazole synthesis is that the coupling process is possible with fully functionalized arylamines **10**. Therefore, highly convergent syntheses of carbazole alkaloids are feasible, and linear multistep sequences as required by using classical procedures are avoided. The total synthesis of **1** and **2** emphasizes this characteristic feature of the Fe-mediated construction of the carbazole framework.

Introduction. – Carbazole alkaloids have attracted much interest as synthetic targets as many of their derivatives exhibit a broad range of useful biological activities [2]. In 1980, *Nakamura* and coworkers reported the isolation and structural elucidation of carbazomycin A (**1**) and B (**2**) from *Streptoverticillium ehimense* H 1051-MY 10 [3–5]. The carbazomycins represent a novel class of antibiotics. They inhibit the growth of phytopathogenic fungi and have antibacterial and antiyeast activities. The biogenesis of the



		R^1	R^2	R^3
1	Carbazomycin A	Me	MeO	H
2	Carbazomycin B	Me	OH	H
3	Carbazomycin C	Me	OH	MeO
4	Carbazomycin D	Me	MeO	MeO
5	Carbazomycin E	CHO	OH	H
6	Carbazomycin F	CHO	OH	MeO
9	4-Deoxycarbazomycin B	Me	H	H



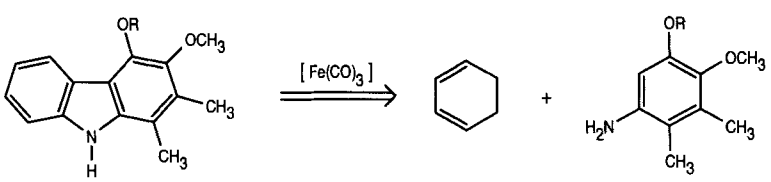
7 Carbazomycin G R = H
8 Carbazomycin H R = MeO

[1]) For Part 14, see [1].

carbazomycins was found to be quite different from the carbazole alkaloids previously known [6], which were isolated mainly from terrestrial plants. Subsequent to the initial report of *Nakamura*, further congeners of this group of alkaloids, carbazomycin E (= carbazomycinal; **5**) and carbazomycin F (= 6-methoxycarbazomycinal; **6**), were found by *Marumo* and coworkers in the *Streptoverticillium* species KCC U-0166 [7]. Along with carbazomycin C (**3**) and D (**4**), the same alkaloids were isolated by *Nakamura* and coworkers from *Streptoverticillium ehimense* [8]. A more recent report concerning the isolation of carbazomycin G (**7**) and H (**8**) provided the first examples of quinol-type alkaloids belonging to the carbazomycin family [9].

The broad spectrum of biological activities of the carbazomycins as well as the unusual substitution pattern prompted several groups to develop strategies direct towards the total synthesis [10–13]. However, due to the congestion of donor substituents in these structures, novel methodologies for the synthesis of the carbazole framework had to be developed [14]. Our approach is based on a Fe-mediated construction of the carbazole ring system *via* consecutive C–C and C–N bond formation, involving an electrophilic aromatic substitution of a fully functionalized arylamine by a tricarbonyliron-complexed cation and subsequent oxidative cyclization onto the tricarbonyliron-complexed cyclohexadiene ring [15]. This method was especially useful for the synthesis of 1-methoxy- [16] and 3-methoxycarbazoles [12] [17] and was already applied to a direct route to 4-deoxycarbazomycin B (**9**) [12e], a degradation product of carbazomycin B (**2**). In this paper, we describe full details of our highly efficient, convergent synthesis of carbazomycin A (**1**) and B (**2**) from cyclohexadiene and the already fully functionalized arylamine **10** using the Fe-mediated construction of the carbazole ring (*Scheme 1*), thus giving access for the first time to large quantities of these novel antibiotics.

Scheme 1



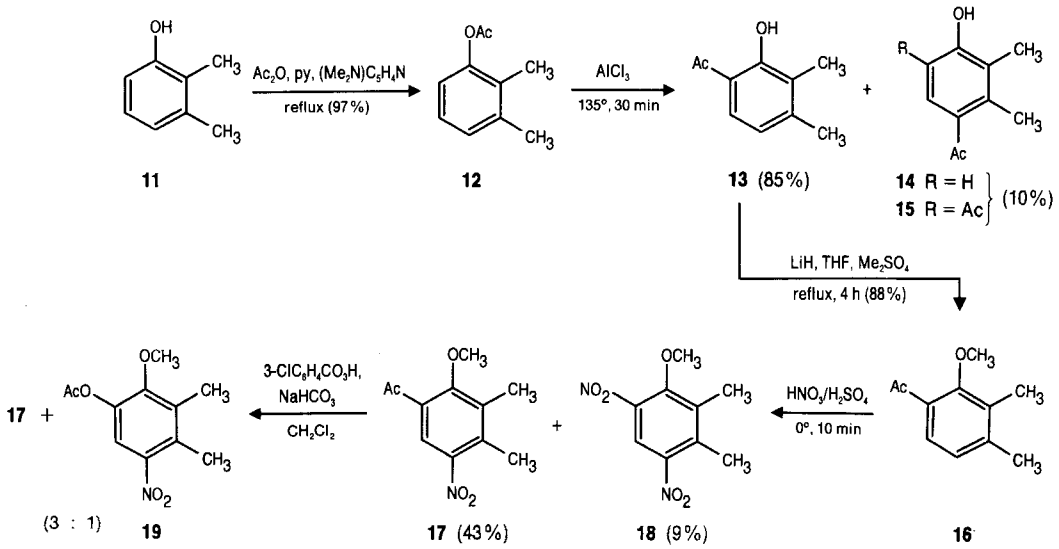
1 R = Me
2 R = H

10a R = Me
b R = H

Arylamines 10. – The required arylamines **10** were synthesized from commercially available 2,3-dimethylphenol (= *o*-xylenol) **11**. The regioselective introduction of the second O-function in *ortho*-position to the OH group was achieved *via* acetylation of **11** (→ **12**) and subsequent *ortho*-selective *Fries* rearrangement (1.2 equiv. of $AlCl_3$, 135°, 30 min) [18] (*Scheme 2*). Besides the desired acetophenone **13** [19] (85% yield), the by-products **14** and **15** were obtained as an inseparable mixture in *ca.* 10% yield.

Evidence for the structure of **13** was provided by the sharp *s* at 12.67 ppm (phenol OH) in the ^{1}H-NMR spectrum. The substitution pattern was confirmed by NOE difference spectra. Irradiation at the Me signal at 2.28 ppm resulted in a NOE of the aromatic proton at 6.67 ppm.

Scheme 2

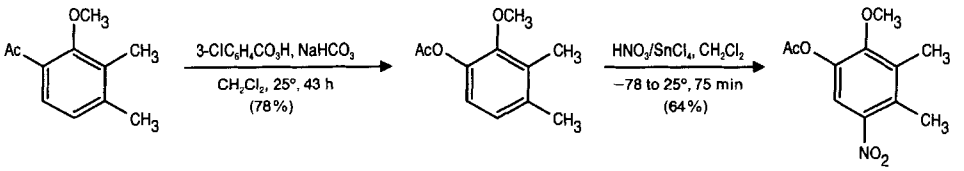


After treatment of **13** with diazomethane or with aqueous KOH/Me_2SO_4, only starting material was recovered, due to the decreased acidity of the OH group, but using LiH/Me_2SO_4 afforded the ether **16** in 88% yield. As **12** and **13**, compound **16** was purified by distillation, which allowed its synthesis to be performed in excellent yields on a large scale.

On nitration of acetophenone **16**, the directing effect of the Ac and MeO group should favor the desired 5-nitro derivative **17**. Application of the nitration procedure used for the unsubstituted acetophenone (HNO_3/H_2SO_4, 0°, 10 min) [20] provided **17** in 43% yield, along with starting material **16** (16%) and dinitro derivative **18** (9%; *ipso*-substitution product). Similarly, nitration of 4-methoxypropiophenone afforded 2,4-dinitroanisole along with the expected 4-methoxy-3-nitropropiophenone [21]. We expected compound **17** to be a useful intermediate for the regioselective introduction of the missing O-atom (see **10**) since *Baeyer-Villiger* oxidations were reported for 3-nitroacetophenone as well as for 2-methoxyacetophenone [22]. However, the oxidation of **17** with 3-chloroperbenzoic acid ($3\text{-}ClC_6H_4CO_3H$) was difficult to follow by TLC (same R_f for educt and product) and even after a prolonged reaction time at elevated temperature (5 days at reflux in CH_2Cl_2) using a large excess of $3\text{-}ClC_6H_4CO_3H$, a 3:1 mixture of starting material **17** and *Baeyer-Villiger* product **19** was obtained (*Scheme 2*).

Because of this disappointing result, we decided to achieve the *Baeyer-Villiger* oxidation prior to nitration. Thus, treatment of acetophenone **16** in CH_2Cl_2 at room temperature with $3\text{-}ClC_6H_4CO_3H$ for 43 h provided the desired acetoxy derivative **20** in 78% yield (*Scheme 3*). The alternative regioisomer which would be formed from migration of the Me group could not be detected, in contrast to analogous cases reported in the literature [22]. Best results for the regioselective nitration of **20** were obtained using a preformed complex of fuming nitric acid and $SnCl_4$ at −78° [23] which afforded the desired nitro derivative **19** in 64% yield (*Table 1*). The position of the NO_2 group of **19** was confirmed by spectral comparison with the oxidation product **19** obtained from **17** (see *Scheme 2*).

Scheme 3



16 **20** **19**

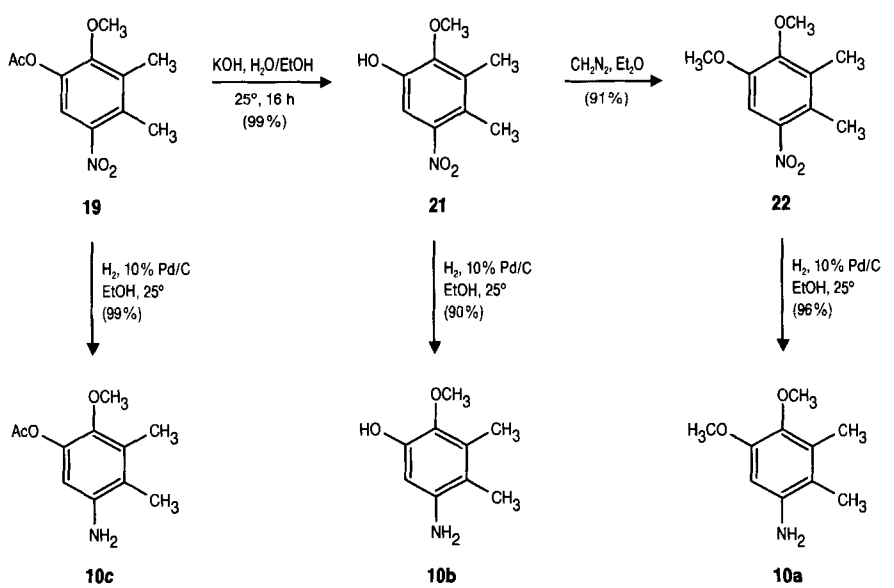
Table 1. *Nitration of* **20** *Using Different Reaction Conditions*

Nitration procedure	Temperature [°C]	Reaction time	**19**, Yield [%]
$HNO_3/AcOH$	25	15 h	7
$HNO_3/H_2SO_4/CHCl_3$	0 to 25	2 h	24
HNO_3/Ac_2O	0	1 h	40
$HNO_3/SnCl_4/CH_2Cl_2$	−78 to 25	75 min	64

The regioisomeric product with the NO_2 group in *ortho*-position relative to the AcO group was not detected under any of the nitration conditions shown in *Table 1*.

Finally, hydrogenation of **19** over 10% Pd/C in EtOH at room temperature quantitatively provided arylamine **10c**, a protected precursor of carbazomycin B (**2**). The unprotected precursor **10b** was obtained from **19** after ester hydrolysis with KOH in aq. EtOH (→**21**) and subsequent hydrogenation. The colorless crystals of pure **10b** instantaneously turned black in the air, indicating the sensitivity of the donor-substituted aromatic ring towards oxidation. Thus, arylamine **10b** had to be handled under inert-gas atmosphere,

Scheme 4



stored at low temperature, and purified by flash chromatography to remove decomposition products before coupling with the Fe-complexed cation (see below). Access to precursor **10a** of carbazomycin A (**1**) was achieved by methylation of phenol **21** (→ **22**) and subsequent hydrogenation. Thus, the fully functionalized arylamines **10** have become available on large scale in 6 to 8 steps and in more than 30% overall yield (*Table 2*).

Table 2. *Syntheses of the Arylamines* **10**

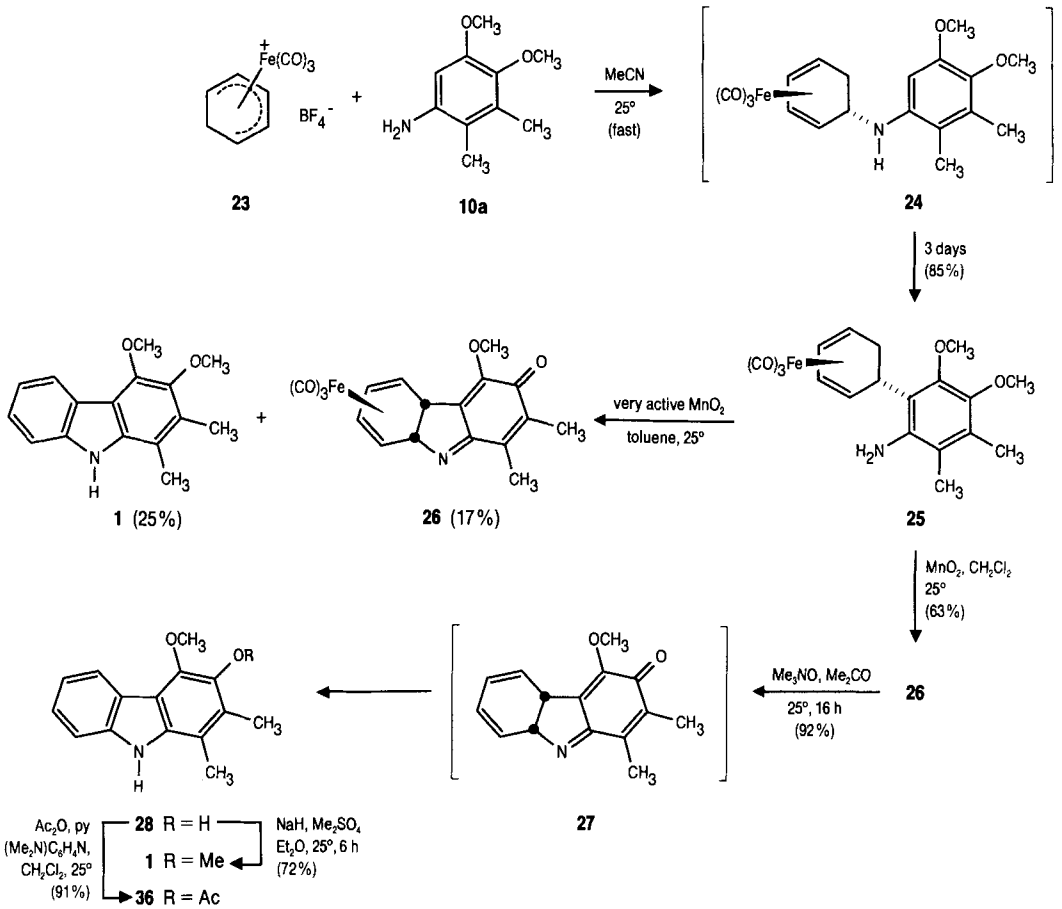
Arylamine	R	Steps	Overall yield [%]
10c	Ac	6	36
10b	H	7	32
10a	Me	8	31

Carbazomycin A (1) by Iron-Mediated Arylamine Cyclization. – The Fe-complex salt **23** was quantitatively available on large scale by prop-2-en-1-imine-catalyzed complexation of cyclohexa-1,3-diene with pentacarbonyliron [24] and subsequent hydride abstraction using triphenylcarbenium tetrafluoroborate [25]. On treatment of **23** with 2.2 equiv. of the arylamine **10a** in MeCN at room temperature, immediate formation of a product with a higher R_f value than **10a** was observed by TLC analysis. Any attempt to purify this compound by column chromatography (silica gel) led to complete decomposition. However, on prolonged reaction time, TLC analysis indicated that the first product disappeared within 3 days in favor of an even less polar, final product **25** which was obtained in 85% yield (*Scheme 5*) and characterized by its ^{1}H- and ^{13}C-NMR spectra (no arom. H at 6.22 ppm (*cf.* **10a**), no arom. *C*H, typical signals of a 5-*anti*-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complex). The intermediate is believed to be the *N*-alkylated arylamine **24**, which is the kinetic product and formed very rapidly [17] [26]. It was shown that the rate of *N*-alkylation by the tricarbonyliron-complexed cation is dependent on the basicity of the arylamine [27]. The reason for the high yield of the electrophilic substitution of highly donor-substituted arylamines is this fast *N*-alkylation. *C*-Alkylation requires attack at the aromatic nucleus of a pentasubstituted benzene with a bulky electrophile to generate a hexasubstituted benzene and is, therefore, disfavored for steric reasons. But the high nucleophilicity of the aromatic nucleus is overriding, and because of the reversibility of the *N*-alkylation [17] [26] [28], intermediate **24** slowly rearranged, even at room temperature, to the thermodynamically more stable *C*-alkylated arylamine **25**. We had already noted in earlier examples that the H^+-catalyzed rearrangement of the kinetic product (*N*-alkylated arylamine) to the thermodynamic product (*C*-alkylated arylamine) has a considerably higher driving force for highly donor-substituted arylamines [17].

Oxidative cyclization of complex **25** using *Fatiadi*'s very active manganese dioxide [29] provided carbazomycin A (**1**) as the less polar fraction (25% yield; 21% from **23**, in two steps) and the iron-complexed 4b,8a-dihydro-3*H*-carbazol-3-one **26** as the more polar fraction (17% yield).

Carbazomycin A (1) by Iron-Mediated Quinone-Imine Cyclization. – The formation of the cyclized Fe-complexed quinone imine **26** as by-product of the Fe-mediated arylamine cyclization suggested that this final step could be improved by taking advantage of the Fe-mediated quinone-imine cyclization. This latter process has already proven its

Scheme 5



enormous potential in the syntheses of various 4-unsubstituted carbazole derivatives [30], *e.g.* 4-deoxycarbazomycin B (**9**) [12e]. It involves a non-cyclized Fe-complexed quinone imine which is generated from the Fe-complexed arylamine with commercial MnO_2 and then submitted in a second step to very active MnO_2. Thus, complex **25** was oxidized with commercial MnO_2 (manganese dioxide (precipitated active) from *Merck-Schuchardt*, art. 805958). But instead of the expected non-cyclized quinone imine, the 4b,8a-dihydro-3*H*-carbazol-3-one **26** was obtained in 63% yield.

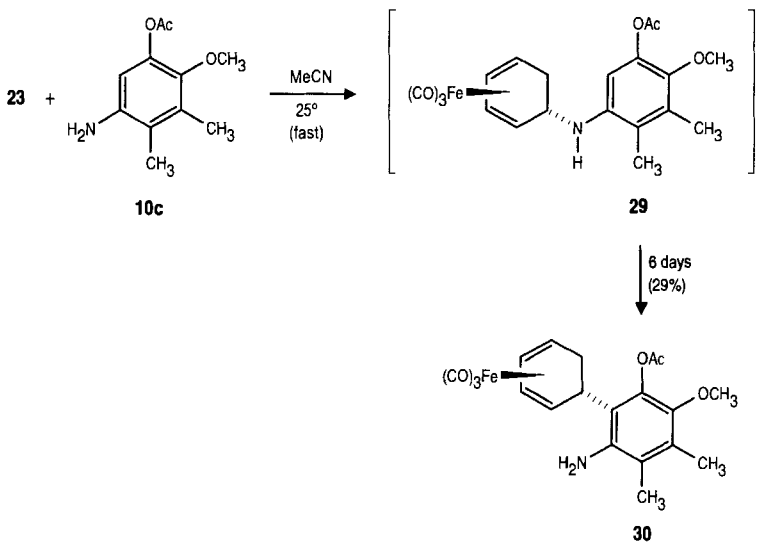
Obviously the oxidation potential for this cyclization is dependent on the substituents of the arylamine moiety. Demetalation of the quinone imine iron complex **26** with trimethylamine *N*-oxide [31] to **27** provided, *via* the expected dihydrocarbazolone-hydroxycarbazole isomerization [12e], the non-natural isocarbazomycin B (**28**) in 92% yield. The latter did not react with diazomethane, although carbazomycin B (**2**) was converted to carbazomycin A (**1**) by this procedure [3] [5], probably because the 4-OH group is more acidic than the 3-OH group of carbazoles. A similar observation was made

in the synthesis of 4-deoxycarbazomycin B (**9**) [12e]. Therefore, **28** was transformed to carbazomycin A (**1**) in 72% yield using NaH/Me_2SO_4 (35% yield from **23**, in four steps). Thus, the route using the conditions of the iron-mediated quinone-imine cyclization (*cf.* [12e] [30]) demonstrates once again the efficiency of this method for the synthesis of highly donor-substituted carbazole alkaloids.

The spectral data (see *Exper. Part*) of synthetic carbazomycin A (**1**) obtained from either route are in full agreement with those reported by *Nakamura* and coworkers for the natural product [3–5]. However, there exists a discrepancy with respect to the m.p. While the natural product showed a m.p. of 51–52.5° (pale-yellow needles, crystallized from hexane/AcOEt) [3] [5], the sample obtained by *Moody* and *Shah* [13] in their total synthesis had a m.p. of 143–146° (colorless plates, crystallized from CH_2Cl_2/hexane). We recrystallized our synthetic **1** from light petroleum ether/AcOEt as well as from light petroleum ether/CH_2Cl_2 and obtained in both cases colorless plates with a m.p. of 138–140°.

Iron-Mediated Synthesis of Carbazomycin B (2). – Initially, we planned to utilize the protected arylamine **10c** for the synthesis of **2**, in a similar way as described above for **1**. Thus, reaction of 2.2 equiv. of **10c** with Fe-complex salt **23** gave instantaneously a less polar product, most likely intermediate **29**, which slowly rearranged within 6 days to the slightly more polar final product **30** (*Scheme 6*). The low yield (29%) and the much slower rearrangement are probably due to electronic as well as steric reasons.

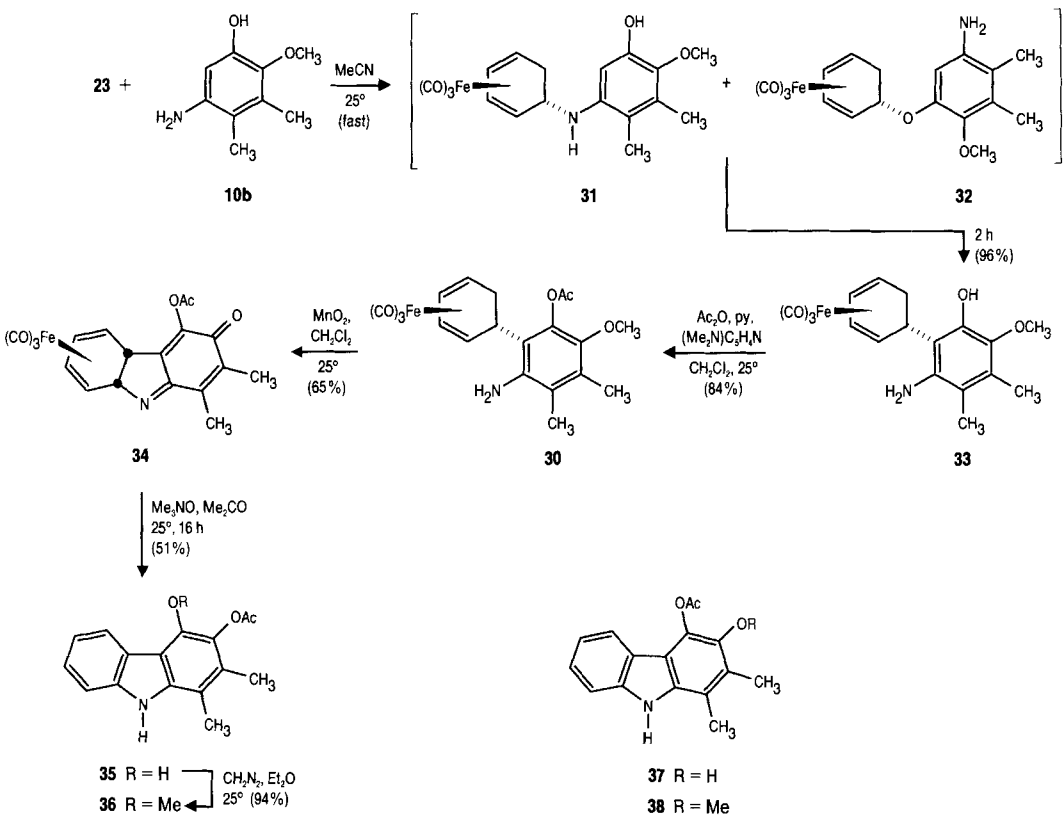
Scheme 6



Therefore, the more nucleophilic unprotected arylamine **10b** was reacted with **23** under the same conditions. After 5 min, TLC analysis revealed the formation of three less polar products, presumably the intermediates **31** and **32** (kinetic products), besides the desired Fe-complex **33** (thermodynamic product) of intermediate polarity which was isolated in 96% yield after 2 h (*Scheme 7*).

All attempts with several oxidizing agents to achieve a Fe-mediated arylamine cyclization of complex **33** to carbazomycin B (**2**) led only to decomposition of **33**. This is

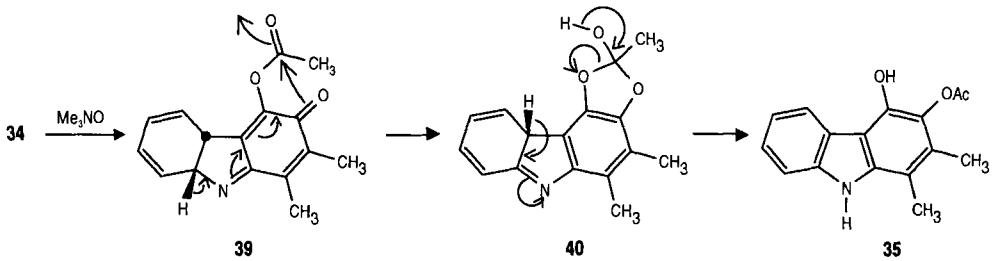
Scheme 7



in accord with earlier results [17] showing that tricarbonyliron-complexes with free OH groups cannot be cyclized using our standard conditions. The sensitivity of the highly donor-substituted aromatic ring of **33** (*cf.* instability of arylamine **10b**, see above) might be partially responsible for the decomposition. Therefore, **33** was *O*-acetylated to **30** (*Scheme 7*) and the latter cyclized to the 4b,8a-dihydro-3*H*-carbazol-3-one **34** in 65% yield using the Fe-mediated quinone-imine cyclization conditions, as described for the transformation **25** → **1** *via* **26**–**28** (see *Scheme 5*). Demetalation of **34** with trimethylamine *N*-oxide [31] led to the 4-hydroxycarbazole **35** (51% yield; *cf.* the 92% yield for **25** → **26**), since concomitant Ac migration occurred. This structure assignment is in agreement with the observation that methylation of **35** to **36** was easily achieved with diazomethane in Et_2O at room temperature. One has to recall that 3-hydroxycarbazoles such as the expected demetalation product **37** generally do not react under these conditions (see above (methylation of **28**) and [12e]), but 4-hydroxycarbazoles do (compare the conversion of carbazomycin B (**2**) into carbazomycin A (**1**) [3] [5]). Moreover, the spectral data of the methylated compound **36** were not in agreement with 4-*O*-acetylcarbazomycin B (**38**), a known derivative [4] of **2** which would have resulted from the methylation of 3-hydroxycarbazole **37**. In the ^1H- and ^{13}C-NMR spectra of **36**, all signals were slightly shifted compared to the corresponding signals reported for **38** [4].

An explanation for the Ac shift occurring on demetalation of **34** is provided by the mechanism which was suggested for the dihydrocarbazolone-hydroxycarbazole tautomerization subsequent to demetalation, *i.e.* after removal of the tricarbonyliron moiety from **34**, tautomerization of the free ligand **39** is probably initiated by migration of H–C(8a) [32]. The driving force for this process is the instantaneous aromatization of the substituted *p*-quinone-imine moiety (*Scheme 8*). Nucleophilic attack of the resulting 3-oxido ion onto the ester carbonyl group leads to the cyclic orthoester intermediate **40** which is regioselectively opened to the 4-hydroxycarbazole **35** (preference of the 4-OH over the 3-OH leaving group due to the higher acidity of the former), with concomitant imine-enamine tautomerization.

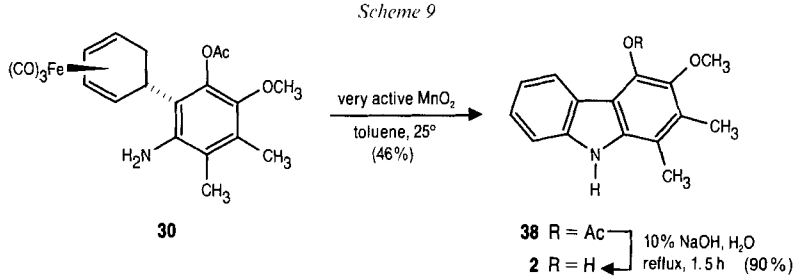
Scheme 8



The structure of 4-hydroxycarbazole **35** was unequivocally confirmed by a chemical correlation of its methylated derivative **36** with the non-natural isocarbazomycin B (**28**) synthesized according to *Scheme 5*. Indeed, acetylation of **28** using standard conditions provided also **36** which was identical with the sample obtained by methylation of **35**.

The results presented in *Scheme 7* show that the Fe-mediated quinone-imine cyclization conditions are not appropriate to achieve a straightforward access to carbazomycin B (**2**) in high overall yield. Therefore, Fe-complex **30** was exposed to the Fe-mediated arylamine cyclization conditions (5 mass-equiv. of very active MnO_2 in toluene at room temperature) which afforded 4-*O*-acetylcarbazomycin B (**38**) in 46% yield (*Scheme 9*) along with the Fe-complexed quinone-imine **34** (9% yield). Compound **38** was already obtained by *Sakano* and *Nakamura via* selective *O*-acetylation of natural carbazomycin B (**2**) [4]. The data of our synthetic **38** were in full agreement with those reported, except for the m.p. which was *ca.* 20° higher (see *Exper. Part*). Finally, cleavage of the

Scheme 9



ester function of **38** provided carbazomycin B (**2**) in 90% yield (33% yield from **23**, in four steps), which proved to be identical (TLC, UV, IR, ^{1}H- and ^{13}C-NMR, and MS) with an authentic sample of the natural product [3], kindly provided by Professor *S. Nakamura*.

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Experimental Part

General. All reactions were carried out in dry and degassed solvents under inert gas. Flash chromatography (FC): *Baker* silica gel (0.03–0.06 mm). Melting points: *Reichert* hot stage. UV: *Beckman 3600*; λ in nm. IR: *Bruker IFS 25*, *Perkin-Elmer 580*, and *Perkin-Elmer 1710* (FT-IR); $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR: *Bruker WP-200*, *AM 300*, and *WM-400*; δ in ppm, J in Hz. MS: *Finnigan MAT-312*, at 70 eV; m/z (rel. %). Elemental analyses: *Heraeus CHN-Rapid*.

2,3-Dimethylphenyl Acetate (**12**). A mixture of 2,3-dimethylphenol (**11**; 74 g, 606 mmol), dry Ac_2O (180 ml, 195 g, 1.91 mol), 4-(dimethylamino)pyridine (7 g, 57.3 mmol), and pyridine (2 ml, 1.96 g, 24.7 mmol) was heated under reflux for 90 min. The cold mixture was poured into 2% HCl soln. (900 ml)/ice (600 g), the aq. layer extracted 4 times with Et_2O (200 ml), the combined org. phase washed 4 times with 2% aq. NaOH soln. (150 ml), dried ($MgSO_4$) and evaporated, and the residue distilled at 107°/14 Torr: **12** (96.2 g, 97%). Colorless oil. IR ($CHCl_3$): 3020, 2955, 2935, 1748, 1468, 1371, 1187, 1160, 1091, 1062. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.07 (*s*, 3 H); 2.29 (*s*, 3 H); 2.32 (*s*, 3 H); 6.85 (*dd*, J = 7.5, 1.9, 1 H); 7.01–7.14 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.3 (*q*); 19.9 (*q*); 20.7 (*q*); 119.4 (*d*); 126.0 (*d*); 127.4 (*d*); 128.6 (*s*); 138.4 (*s*); 149.3 (*s*); 169.2 (*s*). MS: 164 (28, M^+), 122 (100), 107 (30). HR-MS: 164.0837 ($C_{10}H_{12}O_2^+$, calc. 164.0837).

1-(2-Hydroxy-3,4-dimethylphenyl)ethanone (**13**). $AlCl_3$ (6.84 g, 51.2 mmol) was added portionwise to **12** (7.0 g, 42.7 mmol). The mixture was slowly heated to 135° and kept for 30 min at 135°. At r.t. the solidified mixture was hydrolyzed with ice and dil. HCl soln. and then extracted 3 times with Et_2O. The org. layer was washed with dil. KOH soln. to remove the by-products **14** and **15**, dried ($MgSO_4$) and evaporated, and the yellow oil distilled at 88–90°/0.8 mbar: **13** (5.96 g, 85%). Colorless oil. IR ($CHCl_3$): 3020, 2933, 1626, 1405, 1366, 1322, 1292, 1247, 1091. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.15 (*s*, 3 H); 2.28 (*s*, 3 H); 2.56 (*s*, 3 H); 6.67 (*d*, J = 8.2, 1 H); 7.44 (*d*, J = 8.2, 1 H); 12.67 (*s*, 1 H). ^{1}H-NMR NOE (300 MHz, $CDCl_3$): irradiation at 2.28, NOE at 6.67; no NOE's on irradiation at 2.15. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): 10.8 (Me); 20.6 (Me); 26.3 (Me); 117.2 (C); 120.3 (CH); 125.3 (C); 127.5 (CH); 146.0 (C); 160.7 (C); 204.1 (C=O). MS: 164 (44, M^+), 149 (100), 122 (5). HR-MS: 164.0837 ($C_{10}H_{12}O_2^+$, calc. 164.0837).

1-(2-Methoxy-3,4-dimethylphenyl)ethanone (**16**). A soln. of **13** (5.96 g, 36.3 mmol) in THF (20 ml) was added to a suspension of LiH (440 mg, 55 mmol) in THF (20 ml). After 30 min stirring at r.t., Me_2SO_4 (5.06 g, 40.2 mmol) was added. The mixture was stirred for further 30 min at r.t. and heated at reflux for 4 h. H_2O was added to the cold mixture, the resulting soln. extracted 3 times with Et_2O, the combined org. phase washed with H_2O, dried ($MgSO_4$) and evaporated, and the residue distilled at 98–102°/0.8 mbar: **16** (5.72 g, 88%). Colorless oil. IR ($CHCl_3$): 3007, 2944, 2875, 1672, 1597, 1456, 1399, 1358, 1279, 1251, 1118, 1085, 1008. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.23 (*s*, 3 H); 2.30 (*s*, 3 H); 2.63 (*s*, 3 H); 3.73 (*s*, 3 H); 6.98 (*d*, J = 7.9, 1 H); 7.40 (*d*, J = 7.9, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 11.9 (*q*); 20.3 (*q*); 30.2 (*q*); 61.9 (*q*); 125.4 (*d*); 126.8 (*d*); 130.5 (*s*); 130.7 (*s*); 143.2 (*s*); 157.7 (*s*); 200.3 (*s*). MS: 178 (39, M^+), 163 (100), 148 (5). HR-MS: 178.0994 ($C_{11}H_{14}O_2^+$, calc. 178.0994).

1-(2-Methoxy-3,4-dimethyl-4-nitrophenyl)ethanone (**17**) *and 2-Methoxy-3,4-dimethyl-1,5-dinitrobenzene* (**18**). Conc. H_2SO_4 (1.7 ml) was added to **16** (962 mg, 5.40 mmol) while cooling with ice/NaCl (the temp. should be $\leq$ 5°). The mixture was cooled further down and nitrating acid (1.1 ml; 40 vol.-% conc. HNO_3 and 60 vol.-% conc. H_2SO_4) added rapidly, while the temp. was kept below 0°. The mixture was stirred further 10 min, poured onto ice and extracted with Et_2O, the combined org. phase washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$) and evaporated, and the residue submitted to FC (light petroleum ether/Et_2O 4:1, silica gel): **16** (151 mg, 16%), then **18** (111 mg, 9%), followed by **17** (518 mg, 43%).

18: Yellow crystals. M.p. 56–58°. IR (KBr): 3092, 2955, 1593, 1529, 1465, 1394, 1355, 1270, 1096, 995, 804. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.38 (*s*, 3 H); 2.50 (*s*, 3 H); 3.95 (*s*, 3 H); 8.23 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$):

13.2 (*q*); 16.5 (*q*); 62.5 (*q*); 119.0 (*d*); 136.5 (*s*); 138.5 (*s*); 141.1 (*s*); 145.4 (*s*); 154.1 (*s*). MS: 226 (75, M^+), 209 (100), 178 (28). HR-MS: 226.0589 ($C_9H_{10}N_2O_5^+$, calc. 226.0590).

17: Yellow crystals. M.p. 50–52°. IR (KBr): 2972, 1683, 1602, 1520, 1357, 1336, 1249, 1000. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.33 (*s*, 3 H); 2.45 (*s*, 3 H); 2.65 (*s*, 3 H); 3.79 (*s*, 3 H); 7.97 (*s*, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.9 (Me); 16.2 (Me); 30.1 (Me); 62.3 (Me); 123.2 (CH); 130.9 (C); 134.0 (C); 136.8 (C); 146.7 (C); 160.0 (C); 197.9 (C=O). MS: 223 (52, M^+), 208 (100), 206 (32), 162 (37). Anal. calc. for $C_{11}H_{13}NO_4$: C 59.19, H 5.87, N 6.27; found: C 59.29, H 5.78, N 6.37.

2-Methoxy-3,4-dimethylphenyl Acetate (**20**). To a soln. of **16** (8.9 g, 50 mmol) in CH_2Cl_2 (300 ml) were added $NaHCO_3$ (9.24 g, 110 mmol) and 3-chloroperbenzoic acid (12.1 g, 70 mmol). The mixture was stirred for 43 h at r.t., poured into H_2O, and extracted very extensively. The aq. layer was extracted once again with CH_2Cl_2, the combined org. phase dried ($MgSO_4$) and evaporated, and the residue submitted to FC (light petroleum ether/Et_2O 4:1, silica gel): **20** (7.53 g, 78%). Light yellow crystals. M.p. 40–42°. IR ($CHCl_3$): 3016, 2950, 1758, 1482, 1463, 1370, 1275, 1196, 1088, 1027, 1006. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.19 (*s*, 3 H); 2.24 (*s*, 3 H); 2.32 (*s*, 3 H); 3.73 (*s*, 3 H); 6.80 (*d*, J = 8.2, 1 H); 6.91 (*d*, J = 8.2, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.1 (*q*); 19.5 (*q*); 20.4 (*q*); 60.3 (*q*); 119.6 (*d*); 124.9 (*d*); 130.9 (*s*); 135.6 (*s*); 141.7 (*s*); 149.6 (*s*); 169.0 (*s*). MS: 194 (25, M^+), 152 (100), 137 (66). HR-MS: 194.0943 ($C_{11}H_{14}O_3^+$, calc. 194.0943).

2-Methoxy-3,4-dimethyl-5-nitrophenyl Acetate (**19**). A soln. of $SnCl_4$ (3.2 ml) and fuming HNO_3 (1.6 ml) in CH_2Cl_2 (25 ml) was added very rapidly at −78° to a soln. of **20** (3.88 g, 20.0 mmol) in CH_2Cl_2 (70 ml). The cooling bath was removed and the mixture stirred for further 75 min at r.t. Then 2N HCl (100 ml) was added, the aq. layer extracted with CH_2Cl_2, the combined org. phase washed with H_2O, sat. aq. $NaHCO_3$ soln., and sat. aq. NaCl soln., dried ($MgSO_4$) and evaporated. FC (cyclohexane/Et_2O 3:1, silica gel) provided **19** (3.05 g, 64%). Yellow crystals. M.p. 82°. IR (KBr): 2956, 1778, 1517, 1477, 1373, 1338, 1285, 1238, 1199, 1189, 903. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.29 (*s*, 3 H); 2.36 (*s*, 3 H); 2.41 (*s*, 3 H); 3.80 (*s*, 3 H); 7.51 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.8 (*q*); 15.5 (*q*); 20.3 (*q*); 60.7 (*q*); 117.3 (*d*); 130.8 (*s*); 133.6 (*s*); 140.9 (*s*); 145.7 (*s*); 153.3 (*s*); 168.4 (*s*). MS: 239 (27, M^+), 197 (99), 179 (100), 152 (18). Anal. calc. for $C_{11}H_{13}NO_5$: C 55.23, H 5.48, N 5.85; found: C 55.48, H 5.41, N 5.84.

5-Amino-2-methoxy-3,4-dimethylphenyl Acetate (**10c**). Pd/C (10%; 140 mg) was added to a soln. of **19** (1.00 g, 4.20 mmol) in EtOH (40 ml). The mixture was vigorously stirred under H_2 (1.2 atm) until no further H_2 uptake was detected. Filtration through a short path of *Celite* and subsequently through a short path of silica gel and evaporation afforded **10c** (870 mg, 99%). Brownish oil. IR ($CHCl_3$): 3007, 2935, 1755, 1622, 1484, 1418, 1369, 1340, 1096, 1080, 1008, 910. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.04 (*s*, 3 H); 2.21 (*s*, 3 H); 2.31 (*s*, 3 H); 3.30 (br. *s*, 2 H); 3.66 (*s*, 3 H); 6.31 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.7 (*q*); 13.0 (*q*); 20.7 (*q*); 60.8 (*q*); 107.2 (*d*); 119.8 (*s*); 131.3 (*s*); 140.8 (*s*); 141.8 (*s*); 142.2 (*s*); 169.3 (*s*). MS: 209 (39, M^+), 167 (39), 152 (100). HR-MS: 209.1052 ($C_{11}H_{15}NO_3^+$, calc. 209.1052).

2-Methoxy-3,4-dimethyl-5-nitrophenol (**21**). A soln. of **19** (6.75 g, 28.2 mmol) in 10% aq. KOH soln. (60 ml) and EtOH (40 ml) was stirred for 16 h at r.t. and then extracted with CH_2Cl_2. While cooling with ice, the aq. layer was acidified with conc. HCl and then extracted several times with Et_2O. The combined org. phase was washed with H_2O, dried ($MgSO_4$) and evaporated: **21** (5.50 g, 99%). Yellow crystals. M.p. 70°. IR (KBr): 3367, 2949, 1515, 1477, 1336, 1293, 1218, 1169, 1096, 1045, 990, 773. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.28 (*s*, 3 H); 2.32 (*s*, 3 H); 3.81 (*s*, 3 H); 5.73 (*s*, 1 H); 7.31 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 13.0 (*q*); 15.1 (*q*); 61.0 (*q*); 109.3 (*d*); 124.3 (*s*); 132.1 (*s*); 146.7 (2*s*); 148.9 (*s*). MS: 197 (77, M^+), 179 (100), 152 (10). Anal. calc. for $C_9H_{11}NO_4$: C 54.82, H 5.62, N 7.10; found: C 54.90, H 5.60, N 6.97.

5-Amino-2-methoxy-3,4-dimethylphenol (**10b**). As described for **10c**, with 10% Pd/C (396 mg), **21** (4.27 g, 21.7 mmol), and EtOH (80 ml). FC (light petroleum ether/AcOEt 3:1, silica gel) provided **10b** (3.25 g, 90%). Colorless crystals. M.p. 135–137° (dec.). IR (KBr): 3383, 3300, 2929, 1601, 1511, 1456, 1354, 1343, 1276, 1242, 1227, 1086, 1004. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.99 (*s*, 3 H); 2.19 (*s*, 3 H); 3.68 (*s*, 3 H); 4.10 (br. *s*, 3 H); 6.22 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.6 (*q*); 12.8 (*q*); 61.2 (*q*); 100.4 (*d*); 113.2 (*s*); 129.7 (*s*); 138.6 (*s*); 141.2 (*s*); 147.0 (*s*). MS: 167 (79, M^+), 152 (100), 124 (56). Anal. calc. for $C_9H_{13}NO_2$: C 64.65, H 7.84, N 8.38; found: C 64.62, H 7.71, N 8.16.

1,2-Dimethoxy-3,4-dimethyl-5-nitrobenzene (**22**). An Et_2O soln. of CH_2N_2 (*ca.* 0.28 mmol/ml; 200 ml) was added within 30 min to a soln. of **21** (5.50 g, 27.9 mmol) in Et_2O (20 ml). The soln. was stirred for further 2.5 h and then evaporated. FC (light petroleum ether/AcOEt 6:1, silica gel) afforded **22** (5.35 g, 91%). Yellow crystals. M.p. 76°. IR (KBr): 2964, 2836, 1516, 1485, 1392, 1357, 1323, 1282, 1247, 1112, 1092. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.27 (*s*, 3 H); 2.36 (*s*, 3 H); 3.84 (*s*, 3 H); 3.89 (*s*, 3 H); 7.29 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.6 (*q*); 15.3 (*q*); 55.9 (*q*); 60.3 (*q*); 106.0 (*d*); 125.1 (*s*); 132.6 (*s*); 145.9 (*s*); 150.3 (*s*); 150.7 (*s*). MS: 211 (77, M^+), 194 (100), 179 (10), 166 (18). Anal. calc. for $C_{10}H_{13}NO_4$: C 56.87, H 6.20, N 6.63; found: C 56.71, H 6.27, N 6.76.

4,5-Dimethoxy-2,3-dimethylaniline (**10a**). As described for **10c**, with 10% Pd/C (210 mg), **22** (2.17 g, 10.3 mmol), and EtOH (80 ml): **10a** (1.79 g, 96%). Colorless crystals. M.p. 106–108°. IR (KBr): 3381, 3322, 3014, 2994,

2960, 1604, 1494, 1467, 1345, 1235, 1118, 1085, 1005. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.03 (*s*, 3 H); 2.19 (*s*, 3 H); 3.70 (*s*, 3 H); 3.80 (*s*, 3 H); 6.22 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.4 (*q*); 12.6 (*q*); 55.6 (*q*); 60.4 (*q*); 98.3 (*d*); 113.1 (*s*); 130.8 (*s*); 140.2 (*s*); 140.4 (*s*); 150.9 (*s*). MS: 181 (76, M^+), 166 (100), 138 (24), 123 (16). HR-MS: 181.1103 ($C_{10}H_{15}NO_2^+$, calc. 181.1103).

[(1-4-η)-5-(2-Amino-5,6-dimethoxy-3,4-dimethylphenyl)cyclohexa-1,3-diene]tricarbonyliron (**25**). A soln. of tricarbonyl[(1–5-η)-cyclohexadienylium]iron tetrafluoroborate (**23**; 1.38 g, 4.51 mmol) in MeCN (20 ml) was added to a soln. of **10a** (1.79 g, 9.86 mmol) in MeCN (15 ml). The mixture was stirred for 3 d at r.t. Evaporation and FC (light petroleum ether/AcOEt 6:1, silica gel) provided **25** (1.53 g, 85%). Light-yellow crystals. M.p. 106–108°. IR (KBr): 3487, 3397, 3004, 2935, 2056, 1977, 1460, 1415, 1339, 1259, 1084, 971, 623, 614, 560. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.88 (*m*, 1 H); 2.01 (*s*, 3 H); 2.05–2.25 (*m*, 1 H); 2.17 (*s*, 3 H); 3.04 (*m*, 1 H); 3.28 (*m*, 1 H); 3.71 (*s*, 3 H); 3.80 (*s*, 3 H); 4.15 (*m*, 1 H); 5.53 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.6 (*q*); 13.1 (*q*); 25.8 (*t*); 34.8 (*d*); 60.5 (*d*); 60.8 (*q*); 61.2 (*q*); 65.8 (*d*); 83.8 (*d*); 85.8 (*d*); 117.2 (*s*); 118.5 (*s*); 129.3 (*s*); 138.7 (*s*); 144.0 (*s*); 149.8 (*s*); 211.8 (*s*). MS: 399 (24, M^+), 371 (23), 343 (47), 315 (93), 313 (100), 297 (20), 283 (28), 259 (14), 244 (21), 237 (46). HR-MS: 399.0766 ($C_{19}H_{21}FeNO_5^+$, calc. 399.0769).

*3,4-Dimethoxy-1,2-dimethyl-9*H*-carbazole* (= *Carbazomycin A*; **1**) *and* **26**. Very active MnO_2 (400 mg) was added to a soln. of **25** (80 mg, 0.20 mmol) in toluene (7 ml). The mixture was stirred for 10 h at r.t. Filtration through a short path of *Celite*, evaporation, and FC (light petroleum ether/Et_2O 4:1, silica gel) afforded the less polar **1** (13 mg, 25%) and then **26** (13 mg, 17%).

1: Colorless crystals. M.p. 138–140° ([3] [5]: m.p. 51–52.5°; [13]: m.p. 143–146°). UV (MeOH): 221, 242, 251 (sh), 261 (sh), 285 (sh), 293, 327, 339. IR (KBr): 3387, 3058, 2932, 1500, 1458, 1395, 1298, 1050, 747. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.38 (*s*, 3 H); 2.40 (*s*, 3 H); 3.89 (*s*, 3 H); 4.10 (*s*, 3 H); 7.15–7.45 (*m*, 3 H); 7.82 (br. *s*, 1 H); 8.23 (*dd*, J = 7.6, 0.5, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.6, 13.6, 60.5, 61.1, 110.3, 113.5, 114.6, 119.5, 122.6, 123.0, 125.1, 128.9, 136.5, 139.5, 144.6, 146.1. MS: 255 (100, M^+), 240 (95), 225 (3), 212 (15), 197 (35). Anal. calc. for $C_{16}H_{17}NO_2$: C 75.27, H 6.71, N 5.49; found: C 74.93, H 6.67, N 5.69.

26: Spectral data, see below.

*Tricarbonyl[(5–8-η)-4b,8a-dihydro-4-methoxy-1,2-dimethyl-3*H*-carbazol-3-one]iron* (**26**). Commercial MnO_2 ('precipitated active', from *Merck-Schuchardt*, art. 805958; 1.0 g) was added to a soln. of **25** (101 mg, 0.25 mmol) in CH_2Cl_2 (6 ml). The mixture was stirred for 3 d at r.t. Filtration through a short path of *Celite*, evaporation, and FC (light petroleum ether/AcOEt 6:1, silica gel) provided **26** (61 mg, 63%). Yellow crystals. M.p. 147–150° (dec.). UV (MeOH): 288. IR (KBr): 2936, 2050, 1980, 1634, 1444, 1318, 1261, 1153, 1070, 615, 565, 516. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.99 (*s*, 3 H); 2.17 (*d*, J = 0.7, 3 H); 3.30 (*m*, 1 H); 3.45 (*m*, 1 H); 3.66 (*dd*, J = 6.6, 4.3, 1 H); 3.95 (*s*, 3 H); 4.86 (*dd*, J = 6.4, 4.3, 1 H); 5.39 (*m*, 2 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.2 (*q*); 13.6 (*q*); 44.3 (*d*); 57.9 (*d*); 59.4 (*d*); 59.9 (*q*); 78.0 (*d*); 85.2 (*d*); 86.4 (*d*); 136.3 (*s*); 137.9 (*s*); 139.1 (*s*); 147.3 (*s*); 164.6 (*s*); 183.6 (*s*); 210.6 (*s*). MS: 381 (9, M^+), 353 (41), 325 (5), 297 (100), 241 (6), 219 (36). HR-MS: 381.0298 ($C_{18}H_{15}FeNO_5^+$, calc. 381.0300). Anal. calc. for $C_{18}H_{15}FeNO_5$: C 56.72, H 3.97, N 3.67; found: C 56.86, H 4.16, N 4.20.

*Methoxy-1,2-dimethyl-9*H*-carbazol-3-ol* (= *Isocarbazomycin B*; **28**). Trimethylamine *N*-oxide dihydrate (1.17 g, 10.5 mmol) was added to a soln. of **26** (666 mg, 1.75 mmol) in Me_2CO (70 ml). The mixture was stirred for 16 h at r.t. Filtration through a short path of *Celite*, evaporation, and FC (light petroleum ether/AcOEt 6:1, silica gel) afforded **28** (386 mg, 92%). Colorless crystals. M.p. 133–135°. UV (MeOH): 218, 238, 253, 264, 285 (sh), 296, 342. IR (KBr): 3614, 3498, 3405, 3365, 3290, 2937, 1616, 1509, 1461, 1414, 1340, 1319, 1300, 1280, 1266, 1147, 1040, 924, 751, 739, 646. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.37 (*s*, 3 H); 2.40 (*s*, 3 H); 4.03 (*s*, 3 H); 5.65 (br. *s*, 1 H); 7.15–7.45 (*m*, 3 H); 7.79 (br. *s*, 1 H); 8.11 (*d*, J = 7.8, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.3 (Me); 13.3 (Me); 60.7 (Me); 110.5 (CH); 113.2 (C); 114.4 (C); 119.3 (CH); 121.9 (C); 122.3 (CH); 122.4 (C); 125.1 (CH); 134.1 (C); 138.7 (C); 139.6 (C); 140.6 (C). MS: 241 (100, M^+), 226 (56), 197 (7). HR-MS: 241.1102 ($C_{15}H_{15}NO_2^+$, found 241.1103).

*3,4-Dimethoxy-1,2-dimethyl-9*H*-carbazole* (= *Carbazomycin A*; **1**). A soln. of **28** (84 mg, 0.35 mmol) and Me_2SO_4 (66 µl, 88 mg, 0.70 mmol) in Et_2O (8 ml) was added to a suspension of NaH (15 mg, 0.63 mmol) in Et_2O (2 ml). The mixture was stirred for 6 h at r.t., poured into sat. aq. NH_4Cl soln., and extracted several times with Et_2O. The combined extracts were dried ($MgSO_4$). Evaporation and FC (light petroleum ether/AcOEt 9:1, silica gel) gave **1** (64 mg, 72%). Colorless crystals. Spectral data, see above.

[(1–4-η)-5-(2-Acetoxy-6-amino-3-methoxy-4,5-dimethylphenyl)cyclohexa-1,3-diene]tricarbonyliron (**30**). As described for **25**, with **23** (81 mg, 0.26 mmol) in MeCN (4 ml) and **10c** (122 mg, 0.58 mmol) in MeCN (3 ml; 6 d). FC (light petroleum ether/AcOEt 6:1, silica gel) afforded **30** (33 mg, 29%). Light-yellow crystals. M.p. 127–130°. IR ($CHCl_3$): 2940, 2860, 2048, 1987, 1973, 1752, 1455, 1417, 1369, 1252, 1194, 1087, 1058. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.86 (*m*, 1 H); 2.02 (*s*, 3 H); 1.95–2.10 (*m*, 1 H); 2.18 (*s*, 3 H); 2.38 (*s*, 3 H); 3.02 (*m*, 1 H); 3.25 (*m*, 1 H); 3.63 (*s*, 3 H); 3.60–3.75 (*m*, 3 H); 5.50 (*m*, 2 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.8 (Me); 13.3 (Me); 20.6

(Me); 25.1 (CH_2); 36.0 (CH); 60.5 (CH); 60.9 (Me); 64.6 (CH); 83.7 (CH); 86.0 (CH); 117.5 (C); 119.9 (C); 129.4 (C); 138.8 (C); 140.8 (C); 142.3 (C); 169.6 (C=O); 211.7 (CO). MS: 427 (8, M^+), 399 (6), 371 (14), 343 (27), 341 (8), 287 (17), 285 (10), 283 (10), 266 (29), 152 (100). HR-MS: 427.0719 ($C_{20}H_{21}FeNO_6^+$, calc. 427.0718). Anal. calc. for $C_{20}H_{21}FeNO_6$: C 56.23, H 4.95, N 3.28; found: C 56.50, H 5.20, N 3.80.

[(1–4-η)-5-(2-Amino-6-hydroxy-5-methoxy-3,4-dimethylphenyl)cyclohexa-1,3-diene]tricarbonyliron (**33**). As described for **25**, with **23** (1.71 g, 5.63 mmol) in MeCN (30 ml) and **10b** (2.01 g, 12.0 mmol) in MeCN (40 ml; 2 h). FC (light petroleum ether/AcOEt 4:1, silica gel) provided **33** (2.08 g, 96%). Light-yellow crystals. M.p. 60–62°. IR (KBr): 3480, 3400, 2939, 2042, 1958, 1622, 1457, 1419, 621, 562. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.92 (*m*, 1 H); 1.99 (*s*, 3 H); 2.00–2.20 (*m*, 1 H); 2.17 (*s*, 3 H); 3.07 (*ddd*, *J* = 4.6, 3.2, 1.5, 1 H); 3.26 (*m*, 1 H); 3.60 (br. *s*, 2 H); 3.67 (*s*, 3 H); 4.04 (*m*, 1 H); 5.45 (*m*, 1 H); 5.54 (*m*, 1 H); 5.71 (*s*, 1 H). ^{13}C-NMR (75 MHz, $CDCl_3$): 12.77 (*q*); 12.84 (*q*); 25.9 (*t*); 34.6 (*d*); 60.9 (*d*); 61.2 (*q*); 65.2 (*d*); 84.2 (*d*); 85.6 (*d*); 112.1 (*s*); 112.7 (*s*); 127.3 (*s*); 138.3 (*s*); 139.1 (*s*); 145.1 (*s*); 212.0 (*s*). MS: 385 (32, M^+), 357 (30), 329 (41), 300 (66), 298 (100), 222 (35), 206 (29). HR-MS: 385.0613 ($C_{18}H_{19}FeNO_5^+$, calc. 385.0613).

[(1–4-η)-5-(2-Acetoxy-6-amino-3-methoxy-4,5-dimethylphenyl)cyclohexa-1,3-diene]tricarbonyliron (**30**). To a soln. of **33** (2.50 g, 6.48 mmol) in CH_2Cl_2 (20 ml) were added dry pyridine (0.70 ml, 685 mg, 8.67 mmol), 4-(dimethylamino)pyridine (80 mg, 0.65 mmol), and Ac_2O (0.74 ml, 801 mg, 7.85 mmol). The mixture was stirred for 2 h at r.t. Evaporation and FC (light petroleum ether/AcOEt 4:1, silica gel) gave **30** (2.34 g, 84%). Light-yellow crystals. Spectral data, see above.

Tricarbonyl[(5–8-η)-4b,8a-dihydro-1,2-dimethyl-3-oxocarbazol-4-yl Acetate]iron (**34**). Commercial MnO_2 (22.0 g) was added to a soln. of **30** (2.20 g, 5.14 mmol) in CH_2Cl_2 (50 ml). The mixture was stirred for 22 h at r.t., then additional MnO_2 (2.2 g) added, and the mixture stirred for further 90 min at r.t. Filtration through a short path of *Celite*, evaporation, and FC (light petroleum ether/AcOEt 4:1, silica gel) provided **34** (1.37 g, 65%). Yellow crystals. M.p. 190° (dec.). UV (MeOH): 282. IR (KBr): 3444, 2925, 2053, 1981, 1776, 1641, 1370, 1313, 1191, 1145, 1057, 623, 565. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.01 (*s*, 3 H); 2.21 (*s*, 3 H); 2.36 (*s*, 3 H); 3.02 (*m*, 1 H); 3.45 (*m*, 1 H); 3.61 (*m*, 1 H); 4.95 (*m*, 1 H); 5.42 (*m*, 2 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.2 (Me); 13.6 (Me); 20.4 (Me); 44.2 (CH); 55.6 (CH); 58.9 (CH); 78.8 (CH); 85.4 (CH); 86.6 (CH); 138.7 (C); 138.9 (C); 140.3 (C); 140.9 (C); 163.9 (C=N); 168.0 (C=O); 180.3 (C=O); 210.3 (CO). MS: 409 (9, M^+), 381 (25), 353 (12), 325 (73), 297 (76), 282 (100). HR-MS: 409.0250 ($C_{19}H_{15}FeNO_6^+$, calc. 409.0249). Anal. calc. for $C_{19}H_{15}FeNO_6$: C 55.77, H 3.69, N 3.42; found: C 55.76, H 3.79, N 3.80.

*4-Hydroxy-1,2-dimethyl-9*H*-carbazol-3-yl Acetate* (**35**). As described for **28**, with trimethylamine *N*-oxide dihydrate (257 mg, 2.32 mmol), **34** (158 mg, 0.39 mmol), and Me_2CO (17 ml). FC (light petroleum ether/AcOEt 3:1, silica gel) afforded **35** (53 mg, 51%). Yellow crystals. M.p. 130° (dec.). UV (MeOH): 221, 241, 287, 322, 336. IR (KBr): 3425, 2925, 2854, 1723, 1510, 1457, 1417, 1372, 1329, 1304, 1279, 1237, 1207, 1146, 750. ^{1}H-NMR (300 MHz, (D_6)DMSO): 2.10 (*s*, 3 H); 2.34 (*s*, 3 H); 2.38 (*s*, 3 H); 7.10 (br. *t*, *J* = 7.5, 1 H); 7.30 (br. *t*, *J* = 7.5, 1 H); 7.44 (*d*, *J* = 7.5, 1 H); 8.12 (*d*, *J* = 7.5, 1 H); 9.34 (br. *s*, 1 H); 10.95 (br. *s*, 1 H). ^{13}C-NMR and DEPT (75 MHz, (D_6)DMSO): 13.0 (Me); 13.2 (Me); 20.8 (Me); 108.7 (C); 109.7 (C); 110.3 (CH); 118.2 (CH); 121.9 (CH); 122.7 (C); 124.1 (CH); 126.3 (C); 129.4 (C); 138.1 (C); 139.5 (C); 141.9 (C); 169.7 (C=O). MS: 269 (27, M^+), 243 (13), 227 (100), 226 (36), 212 (10), 197 (15). HR-MS: 269.1051 ($C_{16}H_{15}NO_3^+$, calc. 269.1052).

*4-Methoxy-1,2-dimethyl-9*H*-carbazole-3-yl Acetate* (**36**). a) *By Methylation of* **35**. An Et_2O soln. of CH_2N_2 (*ca.* 0.28 mmol/ml; 1 ml) was added to a soln. of **35** (17 mg, 0.06 mmol) in Et_2O (5 ml) and the soln. stirred at r.t. Additional CH_2N_2 soln. (1 ml) was added after 6.5 h and after 23 h (slow reaction). After a total reaction time of 31 h, evaporation provided **36** (17 mg, 94%). Light-yellow crystals. M.p. 192°. UV (MeOH): 224, 240, 248 (sh), 258 (sh), 281 (sh), 290, 322, 337. IR (KBr): 3372, 2926, 2855, 1750, 1613, 1506, 1457, 1392, 1372, 1322, 1295, 1234, 1219, 1167, 1051, 753. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.05 (*s*, 3 H); 2.21 (*s*, 3 H); 2.45 (*s*, 3 H); 3.99 (*s*, 3 H); 7.15–7.40 (*m*, 3 H); 8.01 (br. *s*, 1 H); 8.14 (*d*, *J* = 7.8, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.6 (Me); 13.0 (Me); 20.7 (Me); 60.7 (Me); 110.8 (CH); 113.9 (C); 114.2 (C); 119.4 (CH); 122.3 (C); 122.3 (CH); 125.1 (CH); 126.9 (C); 135.2 (C); 138.3 (C); 139.7 (C); 144.1 (C); 170.4 (C=O). MS: 283 (43, M^+), 241 (99), 226 (100), 192 (19), 191 (20). HR-MS: 283.1207 ($C_{17}H_{17}NO_3^+$, calc. 283.1208).

b) *By Acetylation of* **28**. To a soln. of **28** (39 mg, 0.16 mmol) in CH_2Cl_2 (4 ml) were added dry pyridine (18 µl, 18 mg, 0.23 mmol), 4-(dimethylamino)pyridine (cat. amount), and Ac_2O (18 µl, 20 mg, 0.19 mmol). The mixture was stirred for 1 h at r.t. Evaporation and FC (light petroleum ether/AcOEt 4:1, silical gel) gave **36** (42 mg, 91%). Light yellow crystals. Spectral data, see above.

*3-Methoxy-1,2-dimethyl-9*H*-carbazol-4-yl Acetate* (= *4-O-Acetylcarbazomycin B*; **38**). As described for **1**/**26**, with very active MnO_2 (2.7 g), **30** (536 mg, 1.26 mmol), and toluene (35 ml; 24 h). FC (light petroleum ether/AcOEt 4:1, silica gel) afforded less polar **34** (45 mg, 9%) and then **38** (163 mg, 46%). Colorless crystals. M.p. 214–215° ([4]: m.p. 192–195°). UV (MeOH): 232 (sh), 237, 247 (sh), 258, 283 (sh), 292, 325, 338. IR (KBr): 3368, 2937, 1750, 1614,

1501, 1456, 1405, 1375, 1319, 1292, 1262, 1219, 1168, 1151, 1119, 1091, 1037, 1011, 744. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.17 (*s*, 3 H); 2.27 (*s*, 3 H); 2.56 (*s*, 3 H); 3.80 (*s*, 3 H); 7.13 (*t*, *J* = 7.3, 1 H); 7.21–7.35 (*m*, 2 H); 7.84 (*d*, *J* = 7.9, 1 H); 7.88 (br. *s*, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.7 (Me); 13.5 (Me); 20.9 (Me); 61.2 (Me); 110.8 (CH); 114.0 (C); 116.6 (C); 119.3 (CH); 121.4 (CH); 121.9 (C); 125.4 (CH); 128.4 (C); 135.9 (C); 136.4 (C); 139.8 (C); 143.5 (C); 169.3 (C=O). MS: 283 (26, M^+), 241 (46), 226 (100), 198 (18), 197 (15). HR-MS: 283.1207 ($C_{17}H_{17}NO_3^+$, calc. 283.1208). Anal. calc. for $C_{17}H_{17}NO_3$: C 72.07, H 6.05, N 4.94; found: C 71.98, H 6.03, N 5.50.

*3-Methoxy-1,2-dimethyl-9*H*-carbazol-4-ol* (= *Carbazomycin B*; **2**). For 90 min, **38** (87 mg, 0.31 mmol) was heated under reflux in 10% aq. NaOH soln. (12 ml). The mixture was cooled with ice, acidified with 6N HCl, and extracted several times with Et_2O. The combined org. phase was dried ($MgSO_4$) and evaporated. FC (light petroleum ether/AcOEt 6:1, silica gel) provided **2** (66 mg, 90%). Colorless crystals. M.p. 165–166° ([3]: m.p. 158.5–160°; [13b]: m.p. 162–164°). UV (MeOH): 221, 243, 287, 327, 339. IR (KBr): 3546, 3419, 3355, 1614, 1504, 1455, 1412, 1324, 1302, 1242, 1158, 1146, 1083, 1001, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.37 (*s*, 3 H); 2.39 (*s*, 3 H); 3.82 (*s*, 3 H); 6.04 (*s*, 1 H); 7.15–7.45 (*m*, 3 H); 7.77 (br. *s*, 1 H); 8.24 (*d*, *J* = 7.7, 1 H). ^{13}C-NMR and DEPT (75 MHz, $CDCl_3$): 12.7 (Me); 13.1 (Me); 61.5 (Me); 109.4 (C); 109.5 (C); 110.0 (CH); 119.5 (CH); 122.7 (CH); 123.3 (C); 124.7 (CH); 127.0 (C); 136.8 (C); 138.5 (C); 139.3 (C); 142.1 (C). MS: 241 (54, M^+), 226 (100), 211 (4), 198 (35). HR-MS: 241.1102 ($C_{15}H_{15}NO_2^+$, calc. 241.1103). Anal. calc. for $C_{15}H_{15}NO_2$: C 74.67, H 6.27, N 5.80; found: C 74.13, H 6.32, N 5.62.

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