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Iron-Mediated Synthesis of Hyellazole and Isohyellazole

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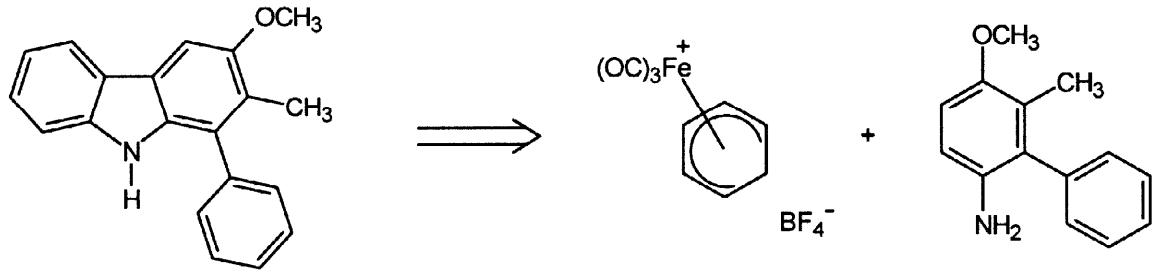
Abstract: The synthesis of the marine alkaloid hyellazole and the non-natural regioisomer isohyellazole is reported starting from the tricarbonyliron-complexed cyclohexadienylium cation and the fully functionalized arylamines by electrophilic aromatic substitution and oxidative cyclization.

Introduction

Hyellazole and 6-chlorohyellazole isolated by Moore and coworkers in 1979 from the blue-green alga *Hyella caespitosa* were the first carbazole alkaloids of marine origin.[2] The characteristic structural feature is a 3-oxygenated carbazole nucleus with a phenyl group in the 1-position. The broad range of 3-oxygenated carbazole alkaloids which were isolated from natural sources[3] led to the development of novel synthetic methodologies.[4] Our strategy for the construction of the carbazole framework is based on a consecutive iron-mediated C–C and C–N bond formation.[5] This method originally established for the synthesis of 3-oxygenated carbazoles[6] proved to be useful for the preparation of 1-oxygenated carbazole alkaloids as well.[7] Herein we describe full details of the iron-mediated total synthesis of hyellazole[8,9] (3-methoxy-2-methyl-1-phenyl-9*H*-carbazole) and the non-natural regioisomer isohyellazole (3-methoxy-1-methyl-2-phenyl-9*H*-carbazole).



Hyellazole **1** **2**

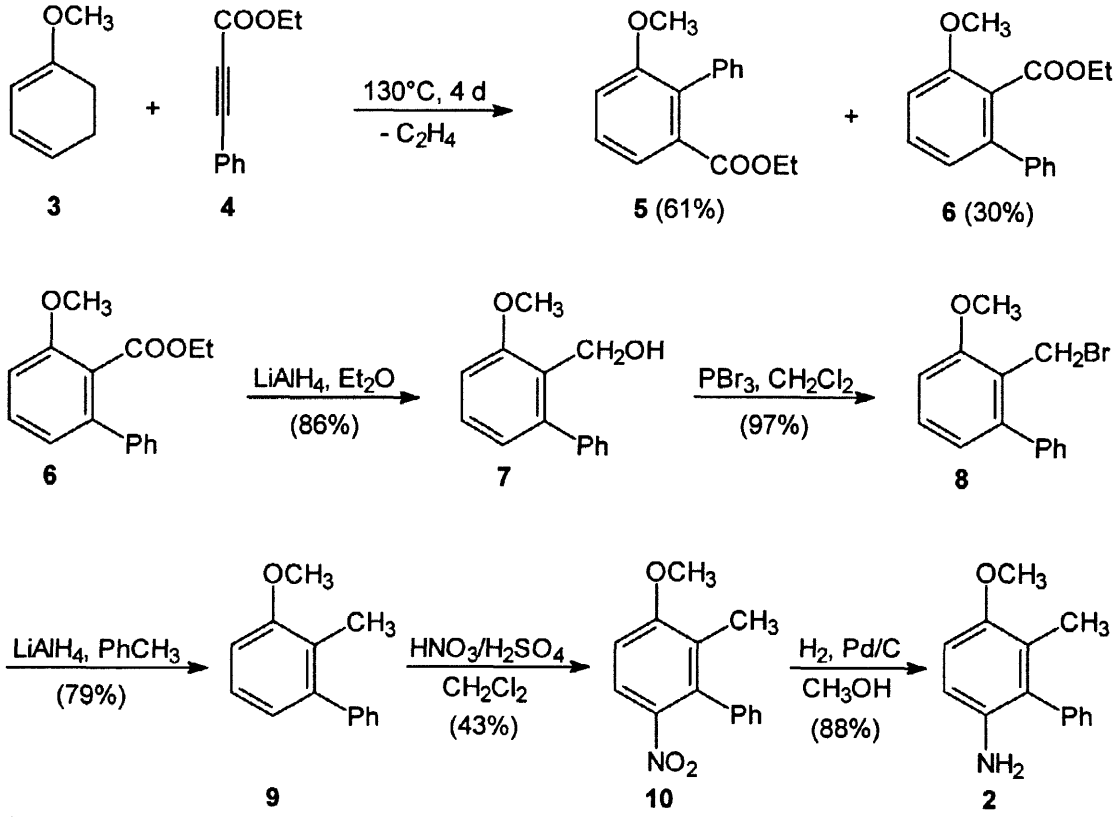
Scheme 1

PII: S0040-4020(99)00580-3

The retrosynthetic analysis of hyellazole based on the iron-mediated construction of the carbazole framework provides the iron-complex salt **1** and the arylamine **2** as precursors (Scheme 1). The precursors for the synthesis of the regioisomeric isohyellazole (3-methoxy-1-methyl-2-phenyl-9*H*-carbazole) are the complex salt **1** and the corresponding arylamine (4-methoxy-2-methyl-3-phenylaniline). The iron-complex salt **1** can be prepared in quantitative overall yield by a 1-azabuta-1,3-diene catalyzed complexation of cyclohexa-1,3-diene with pentacarbonyliron[10,11] followed by a hydride abstraction using triphenylmethyl tetrafluoroborate.[12]

Preparation of 4-methoxy-3-methyl-2-phenylaniline (2)

Diels-Alder reaction of 1-methoxycyclohexa-1,3-diene (**3**) and ethyl 3-phenylprop-2-ynoate (**4**) in a sealed tube afforded the required biphenyl derivative as a mixture of two regioisomers in 91% yield (Scheme 2).[13] In contrast to the original assignment by Bateson,[13b] ethyl 3-methoxy-2-phenylbenzoate (**5**) was obtained as the major regioisomer and ethyl 2-methoxy-6-phenylbenzoate (**6**) as the minor isomer (ratio of **5**/**6**: 2:1). Our assignment was confirmed by ^{1}H-NMR NOE studies and an X-ray analysis at a later stage of our synthesis (see below).

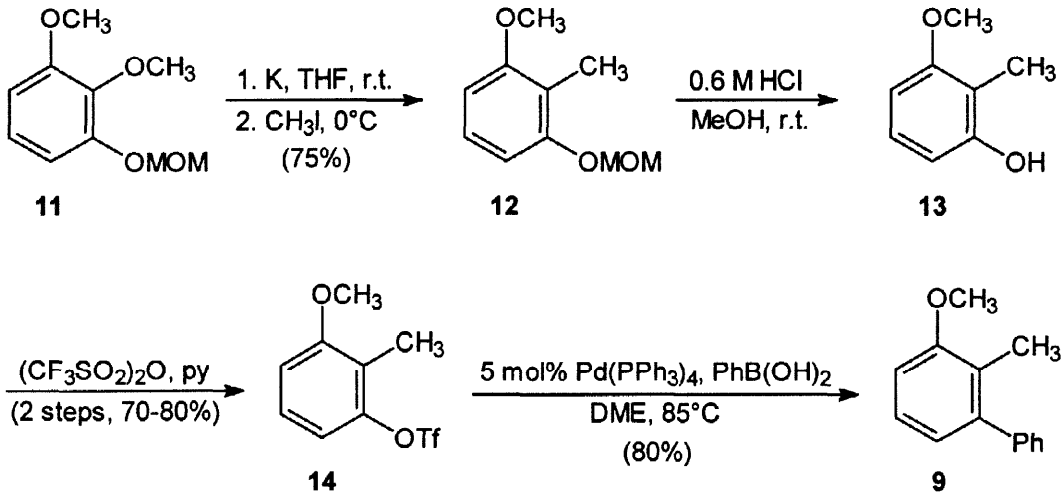


Scheme 2

For the synthesis of hyellazole the ester group of the minor isomer **6** had to be transformed to a methyl group which was achieved in 66% overall yield. Reduction of the benzoate **6** with lithium aluminum hydride provided the benzyl alcohol **7** which was converted to the benzyl bromide **8** with phosphorus tribromide in dichloromethane at room temperature. A further reduction of the benzyl bromide **8** with lithium aluminum hydride afforded 2-methyl-3-phenylanisole (**9**). The nitration of compound **9** afforded the desired 2-methyl-4-nitro-3-

phenylanisole (**10**) as the major product (43% yield) along with 2-methyl-6-nitro-3-phenylanisole (22% yield). Catalytic hydrogenation of the nitro derivative **10** provided the arylamine **2** in 88% yield.

The drawback of the sequence described above is the low yield (30%) of the desired regioisomer **6** in the Diels-Alder reaction. Therefore, the overall yield of the intermediate **9** by the route shown in Scheme 2 is limited to 20%. However, compound **9** is also available by an alternative procedure described by Azzena (Scheme 3).[14]



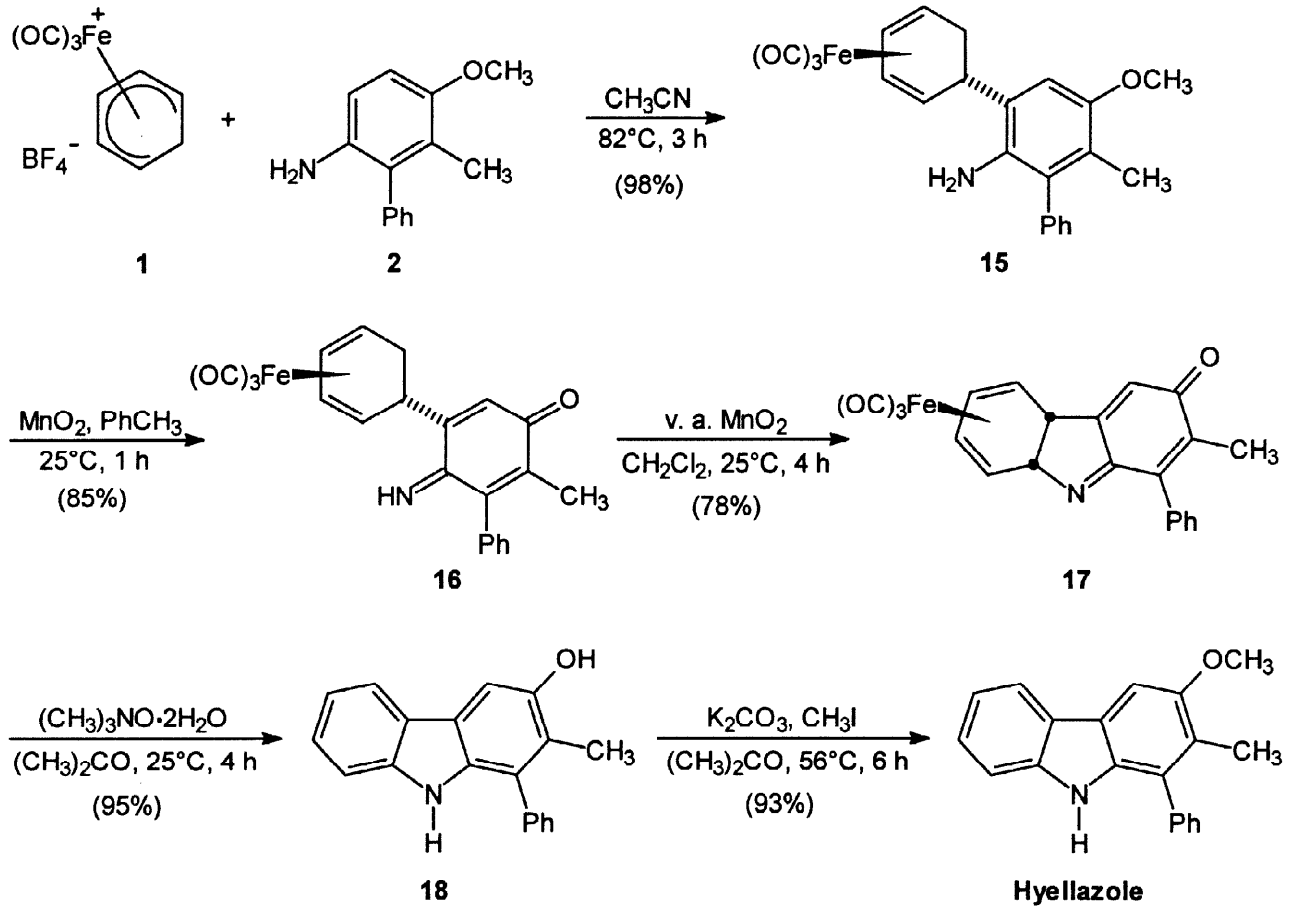
Scheme 3

Regioselective reductive electrophilic substitution of 1,2-dimethoxy-3-methoxymethoxybenzene (**11**) by reaction with potassium in THF and subsequent addition of iodomethane to the resulting carbanion provided compound **12**. Selective cleavage of the MOM ether led to the phenol **13** which was transformed to the phenyl triflate **14**. Finally, a Suzuki cross-coupling of the triflate **14** with phenylboronic acid using 5 mol% of $Pd(PPh_3)_4$ as catalyst afforded compound **9** in an overall yield of 48% (four steps based on **11**).[14]

Synthesis of hyellazole by the iron-mediated quinone-imine cyclization

The iron-mediated quinone-imine cyclization was previously shown to provide a general and efficient route to 3-hydroxycarbazoles.[15] Therefore, this method was initially selected for the projected total synthesis of hyellazole. Electrophilic substitution at the arylamine **2** by the cation **1** provided complex **15** quantitatively (Scheme 4). Sequential highly chemoselective oxidations of such tricarbonyliron complexes became feasible by using manganese dioxides of different activity.[16] Oxidation of complex **15** with commercial manganese dioxide[17] in toluene at room temperature afforded the quinone imine **16**. Cyclization of complex **16** to the tricarbonyliron-complexed 4b,8a-dihydrocarbazol-3-one **17** was achieved with very active manganese dioxide.[18] Demetalation of complex **17** using trimethylamine *N*-oxide[19] in acetone at room temperature afforded the 3-hydroxy-2-methyl-1-phenyl-9*H*-carbazole (**18**). Selective *O*-methylation with iodomethane in the presence of potassium carbonate in acetone at reflux provided hyellazole.

The present synthesis by the iron-mediated quinone-imine cyclization provides hyellazole in five steps and 57% overall yield based on the iron complex salt **1**. All spectral data (UV, IR, ^{1}H-NMR, ^{13}C-NMR, and MS) reported for the natural hyellazole (m.p. 133-134°C) by Moore *et al.*[2] are in full agreement with those of our synthetic hyellazole (m.p. 129-130°C).



Scheme 4

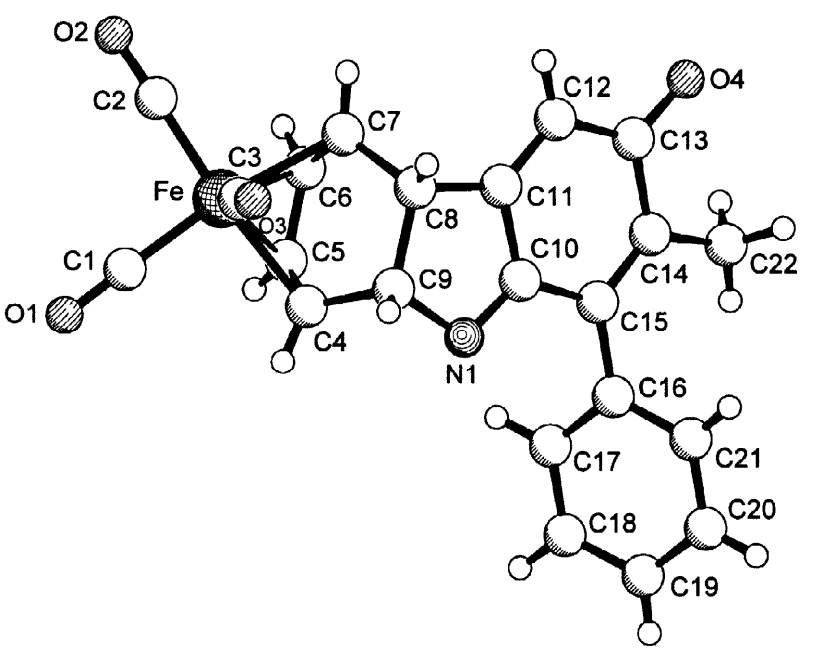


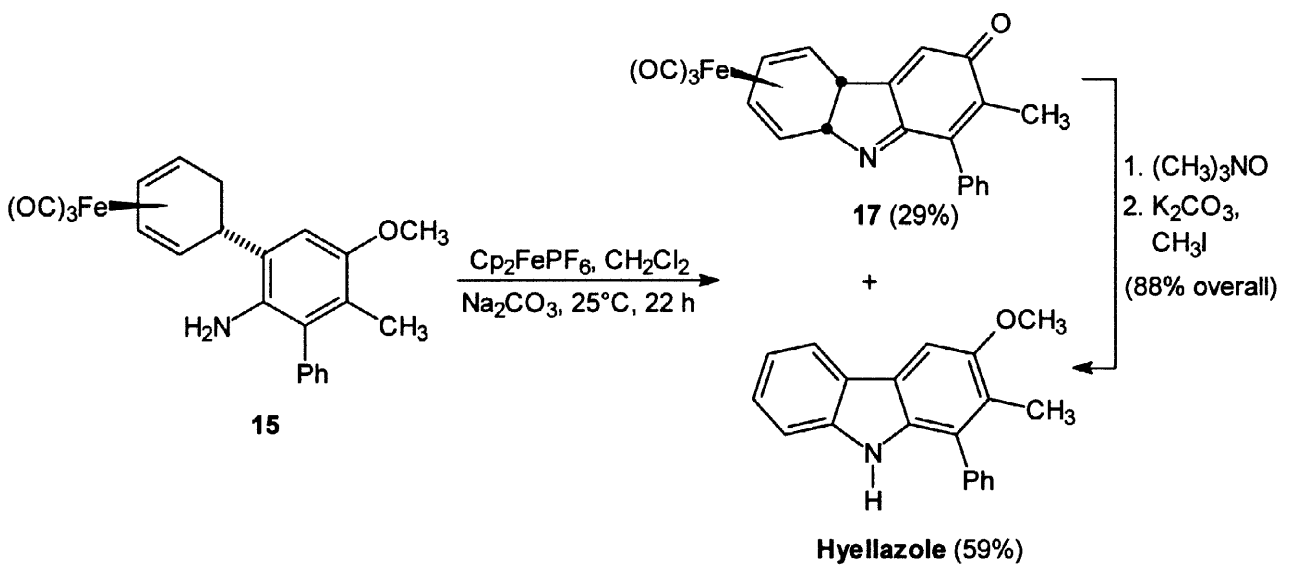
Figure. Molecular structure of complex **17** in the crystal. Selected bond lengths [Å]: Fe-C4 2.089(3), Fe-C5 2.048(3), Fe-C6 2.055(3), Fe-C7 2.112(3), C4-C5 1.408(4), C5-C6 1.390(4), C6-C7 1.410(4), C7-C8 1.514(4), C8-C9 1.536(4), C9-C4 1.507(4).

The structural assignment for tricarbonyl[(5-8-η)-4b,8a-dihydro-2-methyl-1-phenyl-3*H*-carbazol-3-one]iron (**17**) was additionally confirmed by an X-ray crystal structure determination (Figure). The X-ray analysis of **17** also constitutes an unequivocal proof of our reassignment of the regioselectivity of the Diels-Alder reaction which provides compound **6** as the minor isomer as described above (compare Scheme 2).

Synthesis of hyellazole by the iron-mediated arylamine cyclization

An alternative method for the oxidative cyclization of the arylamine-substituted tricarbonyl(η^4-cyclohexa-1,3-diene)iron complexes is the iron-mediated arylamine cyclization which can be performed as a one-pot reaction with concomitant aromatization and demetalation. We envisaged to use this transformation for a more direct approach to hyellazole. The oxidation of complex **15** with ferricenium hexafluorophosphate[20] in the presence of sodium carbonate at room temperature afforded hyellazole in 59% yield along with the tricarbonyliron-complexed dihydrocarbazolone **17** in 29% yield (Scheme 5). Complex **17** could be transformed in two steps and 88% overall yield to hyellazole using the same protocol as described above (Scheme 4).

The synthesis by the iron-mediated arylamine cyclization affords hyellazole in three steps and 83% overall yield based on the iron complex salt **1**. Thus, for the synthesis of hyellazole this method of oxidative cyclization is superior to the iron-mediated quinone-imine cyclization.

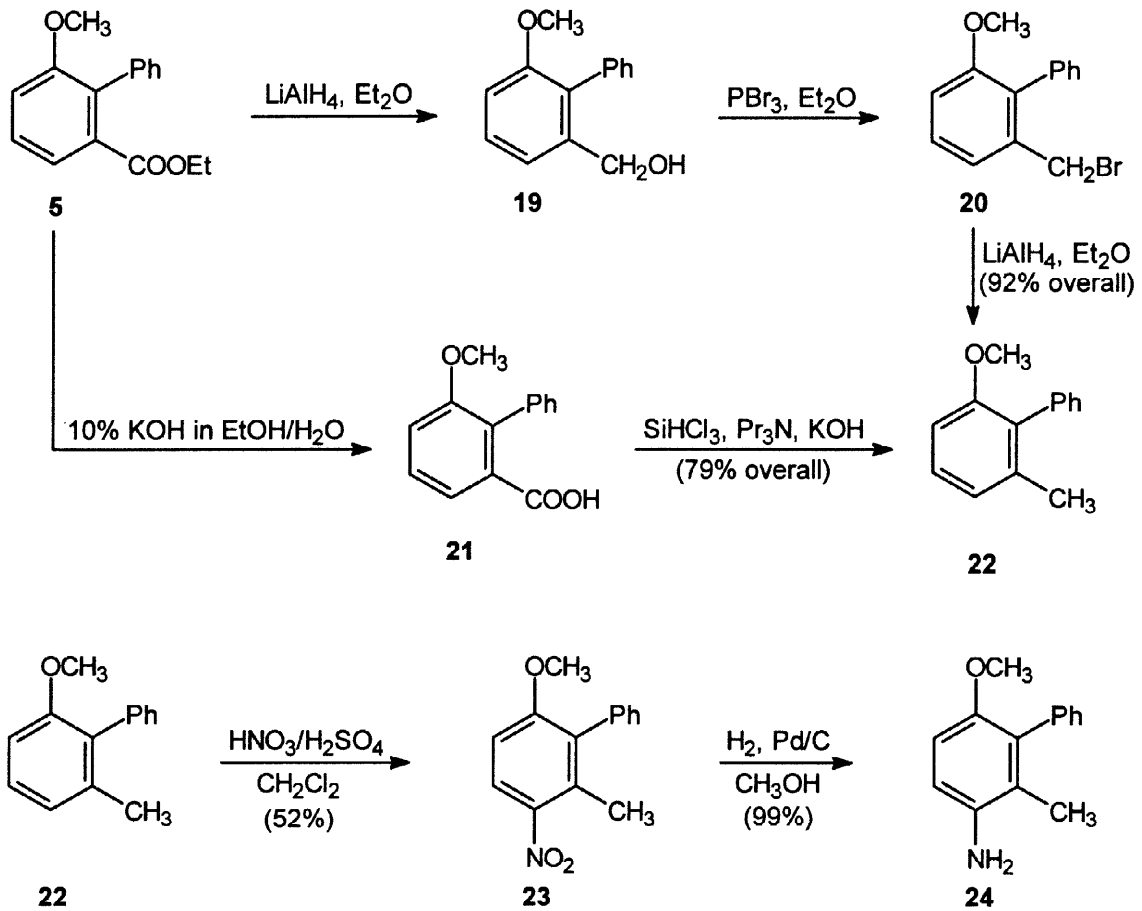


Scheme 5

Preparation of 4-methoxy-2-methyl-3-phenylaniline (24)

We envisaged to apply compound **5** to the synthesis of isohyellazole (3-methoxy-1-methyl-2-phenyl-9*H*-carbazole), a non-natural isomer of hyellazole. Therefore, in analogy to Scheme 2, the benzoate **5** had to be transformed to the corresponding arylamine (Scheme 6). Reduction of the benzoate **5** with lithium aluminum hydride to the benzyl alcohol **19** (98% yield) and subsequent bromination with phosphorus tribromide provided the benzyl bromide **20** (95% yield). Reduction of the benzyl bromide **20** with lithium aluminum hydride

afforded 3-methyl-2-phenylanisole (**22**) (84% yield). The overall yield with chromatographic purification after each step is 78%. This result for the transformation of **5** to **22** can be improved to 92% over the three steps by using the intermediates **19** and **20** as crude products without further purification.



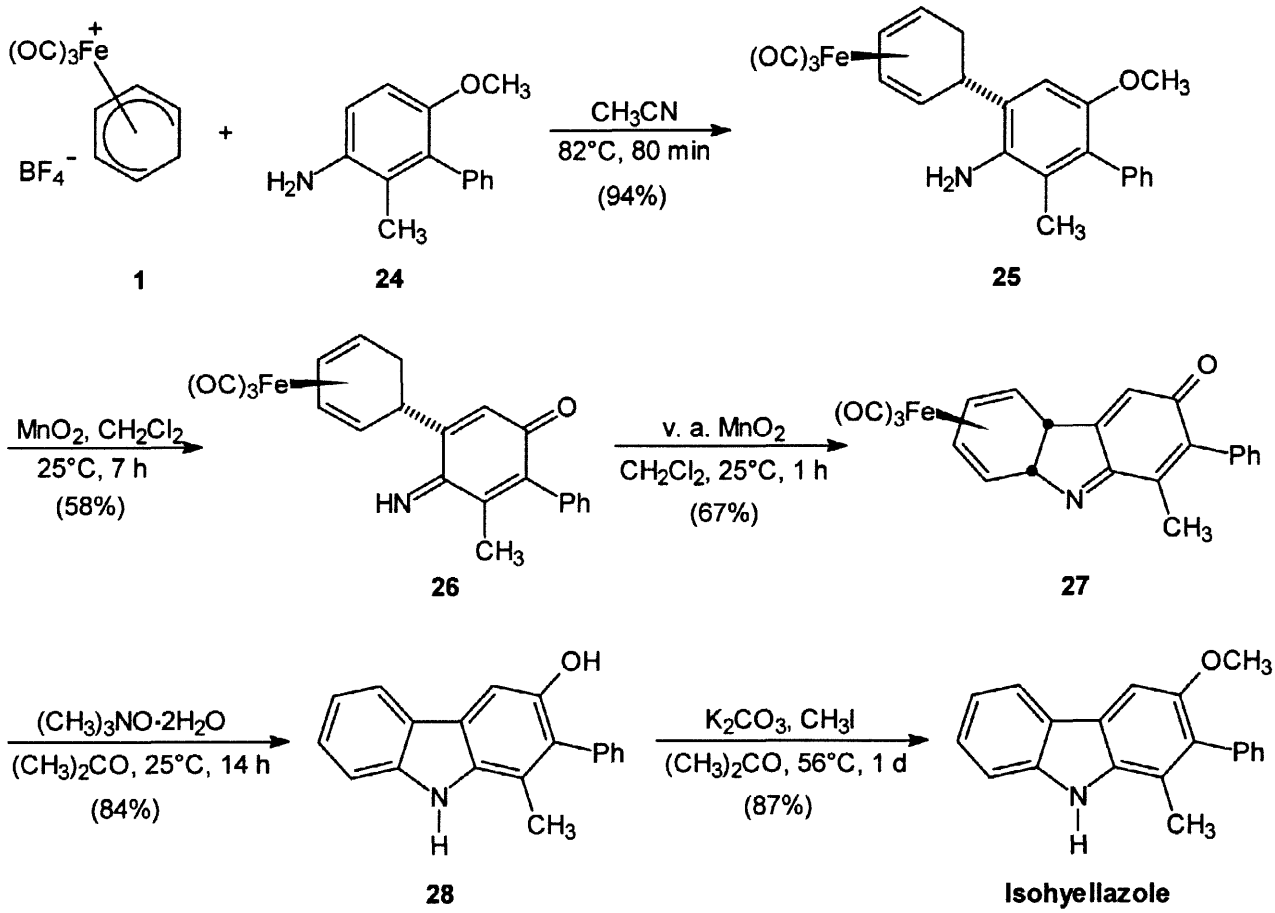
Scheme 6

Alternatively, substituted benzoic acid derivatives can be converted to the corresponding toluene derivatives by a reductive silylation of the benzoic acids and subsequent cleavage with a strong base according to a procedure of Benkeser.[21] Thus, the benzoate **5** was transformed to the benzoic acid **21** in 97% yield by saponification with potassium hydroxide in a mixture of ethanol/water at reflux (Scheme 6). The reduction of the benzoic acid **21** with trichlorosilane and treatment with tri-*n*-propylamine and potassium hydroxide provided 3-methyl-2-phenylanisole (**22**) (81% yield). The reductive silylation afforded the anisole **22** in two steps and 79% overall yield. However, the three-step sequence described above is superior (92% overall yield).

Nitration of the anisole **22** provided the desired 3-methyl-4-nitro-2-phenylanisole (**23**) in 52% yield along with the regioisomeric 3-methyl-6-nitro-2-phenylanisole as by-product (17% yield). Catalytic hydrogenation of **23** afforded quantitatively 4-methoxy-2-methyl-3-phenylaniline (**24**), which represents the arylamine precursor for the synthesis of isohyellazole.

Synthesis of isohyellazole by the iron-mediated quinone-imine cyclization

Isohyellazole was synthesized first by the iron-mediated quinone-imine cyclization *via* the corresponding 3-hydroxycarbazole. The C-C bond formation by reaction of the arylamine **24** with the iron complex salt **1** afforded the tricarbonyliron complex **25** (Scheme 7). Oxidation of complex **25** using commercial manganese dioxide[17] in dichloromethane at room temperature provided the quinone imine **26** in 58% yield along with the corresponding substituted *p*-benzoquinone as a by-product (14% yield).

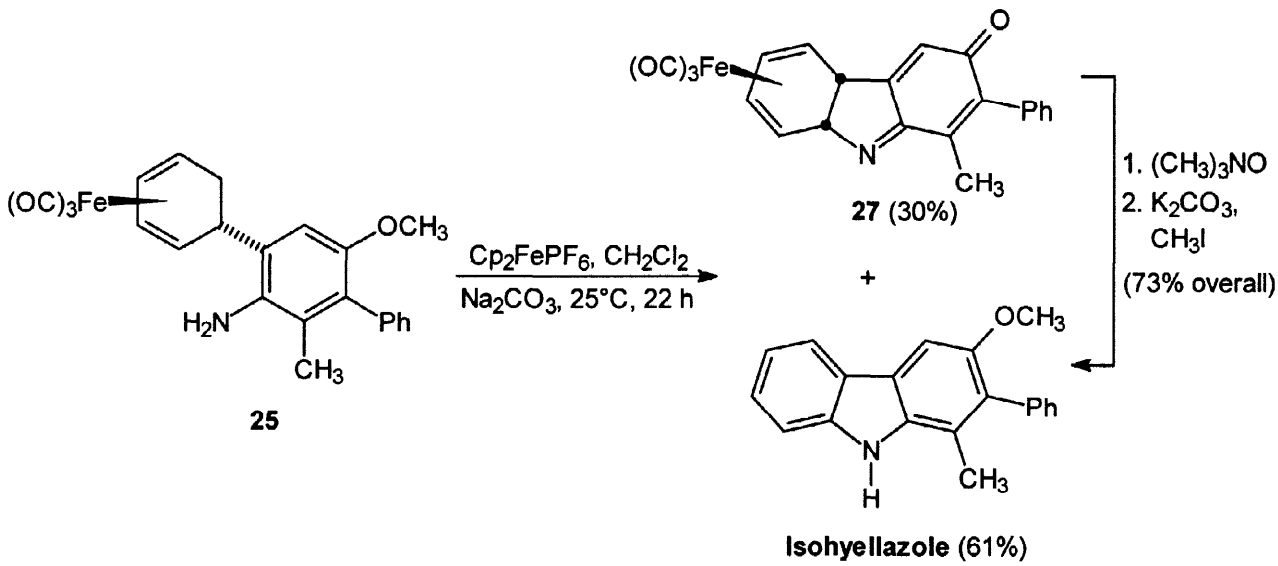


Scheme 7

Complex **26** was cyclized to the tricarbonyl(η^4-4b,8a-dihydrocarbazol-3-one)iron complex **27** by oxidation with very active manganese dioxide[18] at room temperature. Demetalation of the iron complex **27** with trimethylamine *N*-oxide[19] in acetone at room temperature provided the 3-hydroxycarbazole **28**. Compound **28** was transformed to isohyellazole (2-phenyl-3-methoxy-1-methyl-9*H*-carbazole) by selective *O*-methylation. The iron-mediated quinone-imine cyclization affords isohyellazole in five steps and 27% overall yield based on **1**.

Synthesis of isohyellazole by the iron-mediated arylamine cyclization

Finally, we also utilized the iron-mediated arylamine cyclization for the synthesis of isohyellazole. Oxidation of complex **25** with ferricenium hexafluorophosphate[20] in the presence of sodium carbonate at room temperature provided isohyellazole in 61% yield along with the iron complex **27** as a by-product in 30% yield (Scheme 8).



Scheme 8

Complex **27** was converted to isohyellazole in two steps and an overall yield of 73% using the sequence described above (Scheme 7). The iron-mediated arylamine cyclization provides isohyellazole in three steps and 78% overall yield based on **1**, which is clearly superior to the quinone imine cyclization.

In summary, using the iron-mediated arylamine cyclization as a key-step we have developed highly efficient routes to the marine carbazole alkaloid hyellazole as well as to its non-natural isomer isohyellazole, which provide both alkaloids in three steps with 83% and 78% overall yield respectively.

EXPERIMENTAL SECTION

All reactions were carried out in dry solvents under an inert gas atmosphere. Flash chromatography: Baker or Merck silica gel (0.03-0.06 mm). Melting points: Leitz hot-stage and Büchi 535. UV spectra: Perkin-Elmer Lamda 2 (UV/VIS spectrometer). IR spectra: Bruker IFS 88 (FT-IR), Perkin-Elmer 882, and Perkin-Elmer 1710 (FT-IR); $\tilde{\nu}$ in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR spectra: Bruker WM-250 and Bruker AM-400; δ in ppm, J in Hz. Mass spectra: Finnigan MAT-90; ionization potential: 70 eV. Elemental analyses: Heraeus CHN-Rapid.

Ethyl 3-methoxy-2-phenylbenzoate (5) and **Ethyl 2-methoxy-6-phenylbenzoate (6)**

A mixture of 1-methoxycyclohexa-1,3-diene (**3**) (1.57 ml, content: 65 %; 0.95 g, 8.6 mmol of 1,3-diene) and ethyl 3-phenylprop-2-ynoate (**4**) (1.5 g, 1.42 ml, 8.6 mmol) was heated in a sealed glass tube for 4 d at 130°C to provide the regioisomers **5** and **6** in a ratio of 2:1 as a light yellow oil. Flash chromatography (hexane/EtOAc, 12:1) of the crude product on silica gel afforded **5** as the less polar fraction and **6** as the more polar fraction. The regioisomer **6** was subjected again to flash chromatography (hexane/EtOAc, 12:1) on silica gel to provide the product **6** in high purity.

5: Colorless solid, yield: 1.35 g (61%), m.p. 41-44°C. IR (KBr): $\tilde{\nu}$ = 3021, 2979, 2933, 2838, 1705, 1598, 1577, 1457, 1388, 1301, 1279, 1253, 1184, 1142, 1058, 768, 736, 698 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1, 3 H), 3.76 (s, 3 H), 3.98 (q, *J* = 7.1, 2 H), 7.09 (dd, *J* = 6.7, 2.7, 1 H), 7.26-7.28 (m, 2 H), 7.33-7.41 (m, 5 H). ^{1}H-NMR NOE experiments (400 MHz, $CDCl_3$): 1. Irradiation at 3.76, observed NOE's 7.09, 7.33-7.41; 2. irradiation at 3.98, observed NOE 0.90; 3. irradiation at 7.09, observed NOE's 3.76, 7.33-7.41. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.55 (CH_3), 56.01 (CH_3), 60.83 (CH_2), 113.66 (CH), 121.29 (CH), 127.01 (CH), 127.64 (2 CH), 128.39 (CH), 129.54 (2 CH), 130.80 (C), 133.78 (C), 136.90 (C), 156.86 (C), 168.66 (C=O). MS (20°C): *m/z* (%) = 256 (M^+, 100), 227 (4), 211 (83), 196 (19), 168 (20), 152 (11), 139 (21). HRMS: Calc. for $C_{16}H_{16}O_3$ (M^+): 256.1099, found: 256.1077.

6: Colorless oil, yield: 655 mg (30%). IR (film): $\tilde{\nu}$ = 3062, 2982, 2941, 2903, 2840, 1730, 1583, 1569, 1498, 1467, 1431, 1387, 1363, 1309, 1248, 1176, 1154, 1127, 1102, 1065, 1037, 1018, 863, 800, 762, 738, 701, 643 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.97 (t, *J* = 7.1, 3 H), 3.88 (s, 3 H), 4.10 (q, *J* = 7.1, 2 H), 6.94 (d, *J* = 8.4, 1 H), 6.98 (dd, *J* = 7.7, 0.7, 1 H), 7.33-7.42 (m, 6 H). ^{1}H-NMR NOE experiments (400 MHz, $CDCl_3$): 1. Irradiation at 3.88, observed NOE 6.94; 2. irradiation at 4.10, observed NOE 0.97. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.72 (CH_3), 56.04 (CH_3), 61.06 (CH_2), 109.92 (CH), 121.95 (CH), 123.36 (C), 127.53 (CH), 128.23 (2 CH), 128.38 (2 CH), 130.41 (CH), 140.17 (C), 141.34 (C), 156.44 (C), 167.86 (C=O). MS (30°C): *m/z* (%) = 256 (M^+, 56), 227 (3), 211 (100), 196 (7), 168 (14), 152 (13), 139 (13). HRMS: Calc. for $C_{16}H_{16}O_3$ (M^+): 256.1099, found: 256.1087.

2-Methoxy-6-phenylbenzyl alcohol (7)

A suspension of lithium aluminum hydride (732 mg, 19.3 mmol) in diethyl ether (10 ml) was cooled to – 15°C and a solution of the benzoate **6** (2.47 g, 9.64 mmol) in diethyl ether (7 ml) was added over a period of 25 min. After the addition was completed, the reaction mixture was heated at reflux for 2 h. The mixture was quenched with ice-water and the resulting precipitate was dissolved in a small amount of H_2SO_4 (10%). The layers were separated and the aqueous layer was extracted with Et_2O (6 x 30 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$ and then dried (Na_2SO_4). The solvent was evaporated and the residue was subjected to flash chromatography (hexane/EtOAc 2:1) on silica gel to afford the alcohol **7** as a viscous oil, yield: 1.77 g (86%). IR (film): $\tilde{\nu}$ = 3413 (br), 3058, 3022, 2938, 2898, 2837, 1581, 1568, 1464, 1430, 1317, 1253, 1206, 1124, 1020, 1000, 961, 760, 739, 704 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.71 (br s, 1 H), 3.93 (s, 3 H), 4.67 (s, 2 H), 6.95 (d, *J* = 8.2, 1 H), 6.99 (d, *J* = 7.5, 1 H), 7.35 (t, *J* = 7.9, 1 H), 7.37-7.50 (m, 5 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.69 (CH_3), 58.63 (CH_2), 109.45 (CH), 122.76 (CH), 126.67 (C), 127.30 (CH), 128.26 (2 CH), 128.65 (CH), 129.55 (2 CH), 140.65 (C), 143.47 (C), 158.59 (C). MS (20°C): *m/z* (%) = 214 (M^+, 100), 213 (12), 197 (10), 196 (15), 195 (17), 185 (26), 182 (22), 181 (30), 165 (23), 153 (20), 152 (25). HRMS: Calc. for $C_{14}H_{14}O_2$ (M^+): 214.0994, found: 214.0965.

2-Methoxy-6-phenylbenzyl bromide (8)

Phosphorus tribromide (784 mg, 275 µl, 2.89 mmol) was added slowly to a solution of the alcohol **7** (1.77 g, 8.27 mmol) in dichloromethane (10 ml) at – 10°C. The mixture was stirred for 30 min at room temperature and for additional 4 h at reflux. The reaction mixture was quenched by addition of ice-water, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 30 ml). The combined organic layers were

washed with a saturated solution of $NaHCO_3$ and dried over sodium sulfate. Evaporation of the solvent in vacuo afforded compound **8** in high purity as a colorless solid, yield: 2.22 g (97%), m.p. ≥100°C (dec.). IR (drift): $\tilde{\nu}$ = 3058, 3008, 2978, 2942, 2843, 1594, 1583, 1572, 1500, 1470, 1436, 1312, 1260, 1218, 1180, 1161, 1019, 922, 890, 802, 764, 749, 706, 689 cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3 H), 4.49 (s, 2 H), 6.87 (dd, *J* = 7.5, 0.8, 1 H), 6.90 (d, *J* = 8.3, 1 H), 7.32 (t, *J* = 7.9, 1 H), 7.36-7.49 (m, 5 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 27.78 (CH_2), 55.90 (CH_3), 109.84 (CH), 122.54 (CH), 123.81 (C), 127.47 (CH), 128.19 (2 CH), 128.93 (2 CH), 129.45 (CH), 140.17 (C), 143.87 (C), 158.13 (C). MS (20°C): *m/z* (%) = 278 (M^+ + 2, 7), 276 (M^+, 7), 197 (100), 196 (6), 182 (8), 166 (7), 165 (18), 153 (11), 152 (12). HRMS: Calc. for $C_{14}H_{13}{}^{79}BrO$ (M^+): 276.0150, found: 276.0134.

2-Methyl-3-phenylanisole (9)

A solution of the benzyl bromide **8** (2.22 g, 8.01 mmol) in toluene (10 ml) was added to a suspension of lithium aluminum hydride (700 mg, 18.4 mmol) in toluene (10 ml) over a period of 40 min. The mixture was stirred at room temperature for 1.5 h and the reaction was completed by heating for further 30 min. After addition of ice-water and a small amount of H_2SO_4 (10%), the aqueous layer was extracted with diethyl ether (5 x 30 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over sodium sulfate, and the solvent was evaporated in vacuo. The residue was subjected to flash chromatography (hexane/EtOAc 9:1) on silica gel to afford the anisole **9** as a colorless oil, yield: 1.26 g (79%). IR (film): $\tilde{\nu}$ = 2954, 2834, 1582, 1572, 1469, 1433, 1312, 1255, 1173, 1135, 1042, 788, 760, 720, 703, 686 cm^{-1}. ^1H-NMR (400 MHz, $CDCl_3$): δ = 2.26 (s, 3 H), 3.96 (s, 3 H), 6.96 (d, *J* = 8.2, 1 H), 6.99 (d, *J* = 7.7, 1 H), 7.31 (t, *J* = 7.9, 1 H), 7.41-7.44 (m, 3 H), 7.48-7.52 (m, 2 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.42 (CH_3), 55.60 (CH_3), 108.94 (CH), 122.28 (CH), 124.40 (C), 126.07 (CH), 126.84 (CH), 128.08 (2 CH), 129.44 (2 CH), 142.00 (C), 143.40 (C), 158.01 (C). MS (20°C): *m/z* (%) = 198 (M^+, 100), 197 (18), 183 (9), 167 (13), 165 (19), 153 (10), 152 (10). HRMS: Calc. for $C_{14}H_{14}O$ (M^+): 198.1045, found: 198.1036.

2-Methyl-4-nitro-3-phenylanisole (10) and **2-Methyl-6-nitro-3-phenylanisole**

A mixture of HNO_3 (65%, 0.54 ml, 7.80 mmol) and H_2SO_4 (96%, 0.57 ml, 10.3 mmol) was added to a solution of the anisole **9** (1.03 g, 5.22 mmol) in dichloromethane (5 ml) at 0°C over a period of 40 min. After the addition was completed, the reaction mixture was stirred for further 60 min at room temperature. The mixture was quenched with ice and neutralized with $NaHCO_3$. The layers were separated and the aqueous layer was extracted with Et_2O (5 x 30 ml). The combined organic layers were dried over sodium sulfate, the solvent was evaporated in vacuo, and the residue was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to afford first the minor regioisomer 2-methyl-6-nitro-3-phenylanisole and then the 4-nitro derivative **10** as the more polar regioisomer.

10: Orange-yellow solid, yield: 543 mg (43%), m.p. 38-40°C. IR (drift): $\tilde{\nu}$ = 3058, 3027, 3000, 2970, 2941, 2863, 1590, 1578, 1522, 1500, 1466, 1456, 1444, 1402, 1376, 1355, 1230, 1115, 1002, 835, 805 cm^{-1}. ^1H-NMR (250 MHz, $CDCl_3$): δ = 1.94 (s, 3 H), 3.95 (s, 3 H), 6.90 (d, *J* = 9.0, 1 H), 7.15 (m, 2 H), 7.37-7.46 (m, 3 H), 7.88 (d, *J* = 9.0, 1 H). ^1H-NMR NOE experiments (400 MHz, CD_2Cl_2): 1. Irradiation at 1.94, observed NOE 3.95; 2. irradiation at 3.95, observed NOE's 1.94, 6.90; 3. irradiation at 6.90, observed NOE's 3.95, 7.88; 4. irradiation at 7.88, observed NOE 6.90. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 12.52 (CH_3), 54.97

(CH_3), 107.33 (CH), 122.52 (CH), 126.45 (C), 126.55 (CH), 127.29 (2 CH), 127.35 (2 CH), 135.94 (C), 136.71 (C), 142.05 (C), 159.89 (C). MS (20°C): *m/z* (%) = 243 (M^+, 87), 226 (20), 200 (12), 198 (100), 197 (21), 181 (13), 172 (26), 170 (15), 169 (24), 165 (12), 153 (18), 152 (19), 141 (13), 116 (11), 115 (43), 82 (18). HRMS: Calc. for $C_{14}H_{13}NO_3$ (M^+): 243.0895, found: 243.0903.

2-Methyl-6-nitro-3-phenylanisole: Yellow solid, yield: 274 mg (22%), m.p. 38-42°C. IR (CCl_4): $\tilde{\nu}$ = 3065, 3029, 2943, 2871, 1585, 1519, 1466, 1439, 1401, 1352, 1306, 1266, 1231, 1162, 1114, 1004, 828, 701 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H), 3.95 (s, 3 H), 7.11 (d, *J* = 8.4, 1 H), 7.30 (m, 2 H), 7.39-7.48 (m, 3 H), 7.71 (d, *J* = 8.4, 1 H). ^{1}H-NMR NOE experiments (400 MHz, CD_2Cl_2): 1. Irradiation at 2.25, observed NOE's 3.95, 7.30; 2. irradiation at 3.95, observed NOE 2.25. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.76 (CH_3), 61.67 (CH_3), 121.94 (CH), 125.01 (CH), 127.66 (CH), 128.15 (2 CH), 128.50 (2 CH), 132.15 (C), 139.58 (C), 142.76 (C), 148.45 (C), 151.75 (C). MS (20°C): *m/z* (%) = 243 (M^+, 100), 213 (7), 196 (42), 182 (10), 168 (20), 167 (17), 166 (13), 165 (32), 153 (24), 152 (36). HRMS: Calc. for $C_{14}H_{13}NO_3$ (M^+): 243.0895, found: 243.0887.

4-Methoxy-3-methyl-2-phenylaniline (2)

Palladium on carbon (15%, 80 mg) was added to a solution of the nitrobenzene **10** (538 mg, 2.21 mmol) in methanol (10 ml). The nitro derivative **10** was hydrogenated by vigorous stirring of this mixture in a H_2-atmosphere (800-900 Torr) until no further H_2 uptake was detected. The reaction mixture was filtered over a short path of silica gel/Celite (which was subsequently washed with diethyl ether) under an inert gas atmosphere and the solvent was evaporated. The residue was subjected to flash chromatography (hexane/EtOAc 5:1) on degassed silica gel to afford the amine **2** as colorless crystals, yield: 414 mg (88%), m.p. 112-115°C. IR (drift): $\tilde{\nu}$ = 3425, 3350, 3186, 3065, 3051, 3039, 3023, 2952, 2936, 2833, 1616, 1601, 1480, 1452, 1438, 1290, 1275, 1252, 1191, 1173, 1135, 1070, 1039, 1021, 826, 766, 702 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3 H), 3.18 (br s, 2 H), 3.80 (s, 3 H), 6.62 (d, *J* = 8.6, 1 H), 6.75 (d, *J* = 8.6, 1 H), 7.24 (m, 2 H), 7.36 (m, 1 H), 7.46 (m, 2 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.55 (CH_3), 56.23 (CH_3), 110.94 (CH), 112.63 (CH), 125.79 (C), 127.27 (CH), 129.03 (2 CH), 129.84 (2 CH, C), 137.62 (C), 138.27 (C), 150.91 (C). MS (20°C): *m/z* (%) = 213 (M^+, 100), 198 (78), 181 (14). HRMS: Calc. for $C_{14}H_{15}NO$ (M^+): 213.1154, found: 213.1140. Anal. Calc. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.67; H, 7.03; N, 6.60.

[(1-4-η)-5-(2-Amino-5-methoxy-4-methyl-3-phenylphenyl)cyclohexa-1,3-diene]tricarbonyliron (15)

A solution of the arylamine **2** (410 mg, 1.92 mmol) and tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate (**1**) (291 mg, 0.952 mmol) in degassed acetonitrile (10 ml) was stirred for 3 h at reflux. The solvent was evaporated in vacuo, diethyl ether (3 ml) was added to the residue, and the suspension was stirred under an inert gas atmosphere until the insoluble protonated amine was finely dispersed. The solution was separated and the residue was washed with small amounts of cold diethyl ether several times. The ethereal layers were combined, the solvent was evaporated, and the crude product was subjected to flash chromatography (hexane/EtOAc 4:1) on degassed silica gel to provide the iron complex **15** as a light yellow solid, yield: 404 mg (98%), m.p. 122-123°C. IR (drift): $\tilde{\nu}$ = 3433, 3358, 3054, 3031, 2985, 2940, 2849, 2832, 2044, 1960, 1927, 1595, 1491, 1463, 1440, 1420, 1286, 1233, 1193, 1173, 1155, 1128, 1021, 842, 780, 710, 625, 614 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.68 (br d, *J* = 15.2, 1 H), 1.84 (s, 3 H), 2.40 (ddd, *J* = 15.2,

11.1, 3.9, 1 H), 3.12 (br s, 2 H), 3.21 (m, 2 H), 3.44 (dt, J = 11.1, 3.7, 1 H), 3.83 (s, 3 H), 5.52-5.57 (m, 2 H), 6.73 (s, 1 H), 7.19 (m, 2 H), 7.37 (m, 1 H), 7.46 (m, 2 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.38 (CH_3), 31.31 (CH_2), 39.43 (CH), 56.44 (CH_3), 60.30 (CH), 64.81 (CH), 84.81 (CH), 85.69 (CH), 109.33 (CH), 123.92 (C), 127.36 (CH), 128.37 (C), 129.12 (2 CH), 129.86 (2 CH), 130.40 (C), 134.86 (C), 138.47 (C), 150.68 (C), 211.90 (3 CO). MS (85°C): *m/z* (%) = 431 (M^+, 5), 403 (1), 375 (11), 347 (34), 345 (42), 291 (7), 290 (11), 289 (6), 274 (7), 269 (100). HRMS: Calc. for $C_{23}H_{21}FeNO_4$ (M^+): 431.0820, found: 431.0827. Anal. Calc. for $C_{23}H_{21}FeNO_4$: C, 64.06; H, 4.91; N, 3.25. Found: C, 64.29; H, 4.93; N, 3.45.

Tricarbonyl[(1-4-η)-5-(6-imino-4-methyl-5-phenylcyclohexa-1,4-dien-3-onyl)cyclohexa-1,3-diene]iron (16)
Commercial manganese dioxide[17] (405 mg) was added to a solution of the iron complex **15** (81 mg, 0.188 mmol) in toluene (3 ml). The mixture was stirred for 1 h at room temperature and filtered over a short path of Celite, which was subsequently washed with diethyl ether several times. The filtrate was evaporated and the yellow crude product was subjected to flash chromatography (hexane/EtOAc 5:1) on degassed silica gel to provide the complex **16** as a yellow solid, yield: 66 mg (85%), m.p. ≥ 80°C (dec.). IR (drift): $\tilde{\nu}$ = 3252, 3060, 3005, 2924, 2851, 2043, 1972, 1648, 1631, 1608, 1595, 1443, 1409, 1375, 1335, 1239, 1143, 1074, 1013, 912, 891, 763, 734, 706, 650, 624 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.50 (br d, J = 15.2, 1 H), 1.76 (s, 3 H), 2.37 (ddd, J = 15.2, 11.4, 3.6, 1 H), 3.07 (m, 1 H), 3.15 (m, 1 H), 3.89 (dt, J = 11.4, 3.4, 1 H), 5.46 (m, 1 H), 5.53 (m, 1 H), 6.61 (s, 1 H), 7.07 (d, J = 6.9, 2 H), 7.46 (m, 3 H), 10.40 (s, 1 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.64 (CH_3), 32.79 (CH_2), 37.17 (CH), 60.45 (CH), 62.83 (CH), 84.76 (CH), 86.24 (CH), 127.47 (CH), 129.04 (2 CH), 129.17 (2 CH), 133.51 (C), 136.21 (C), 142.93 (C), 157.03 (C), 165.74 (C=N), 187.82 (C=O), 211.55 (3 CO) (the signal of one CH-group is missing due to overlapping). MS (130°C): *m/z* (%) = 415 (M^+, 0.2), 387 (13), 359 (16), 331 (48), 329 (100), 274 (4), 273 (4), 254 (14), 253 (64). HRMS: Calc. for $C_{22}H_{17}FeNO_4$ (M^+): 415.0507, found: 415.0484.

Tricarbonyl[(5-8-η)-4b,8a-dihydro-2-methyl-1-phenyl-3*H*-carbazol-3-one]iron (17)
Very active manganese dioxide[18] (320 mg) was added to a solution of complex **16** (63 mg, 0.152 mmol) in dichloromethane (3 ml) and the heterogeneous reaction mixture was stirred for 2 h at room temperature. By addition of very active MnO_2 (80 mg) and stirring for additional 2 h at room temperature the reaction was completed. The mixture was filtered through a short path of silica gel/Celite, which was subsequently washed with ethyl acetate. The solvent was removed in vacuo and the residue was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to afford the carbazolone iron complex **17** as yellow crystals, yield: 49 mg (78%), m.p. ≥ 165°C (dec.). IR (drift): $\tilde{\nu}$ = 3230, 3024, 2937, 2899, 2054, 2043, 1975, 1968, 1936, 1659, 1628, 1590, 1493, 1445, 1432, 1371, 1304, 1288, 1258, 1235, 1137, 1128, 1041, 1028, 973, 954, 944, 864, 778, 754, 699, 623, 609 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3 H), 3.13 (m, 1 H), 3.43 (m, 1 H), 3.53 (m, 1 H), 4.92 (m, 1 H), 5.39 (m, 1 H), 5.45 (m, 1 H), 6.32 (s, 1 H), 7.22 (d, J = 7.1, 2 H), 7.36-7.45 (m, 3 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.98 (CH_3), 45.10 (CH), 56.96 (CH), 59.21 (CH), 78.70 (CH), 85.22 (CH), 86.29 (CH), 122.60 (CH), 128.10 (2 CH), 128.37 (CH), 129.42 (2 CH), 134.41 (C), 139.50 (C), 141.73 (C), 155.65 (C), 163.48 (C=N), 187.71 (C=O), 210.36 (3 CO). MS (120°C): *m/z* (%) = 413 (M^+, 4), 385 (39), 357 (5), 329 (100), 327 (16), 273 (2), 271 (2). HRMS: Calc. for $C_{22}H_{15}FeNO_4$ (M^+): 413.0350, found: 413.0355. Anal. Calc. for $C_{22}H_{15}FeNO_4$: C, 63.95; H, 3.66; N, 3.39. Found: C, 64.03; H, 3.67; N, 3.44.

X-ray crystal structure determination for 17

Table. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **17**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Fe	613(1)	6715(1)	9514(1)	43(1)
C(1)	-697(3)	6760(2)	10275(2)	53(1)
O(1)	-1506(3)	6784(2)	10778(2)	78(1)
C(2)	-950(4)	6391(2)	8386(2)	54(1)
O(2)	-1959(3)	6177(2)	7677(2)	77(1)
C(3)	1555(3)	5759(2)	9962(2)	53(1)
O(3)	2200(3)	5151(2)	10263(2)	84(1)
C(4)	2352(3)	7415(2)	10587(2)	44(1)
C(5)	1383(3)	7913(2)	9784(2)	51(1)
C(6)	1295(3)	7689(2)	8778(2)	52(1)
C(7)	2221(3)	6998(2)	8705(2)	46(1)
C(8)	3892(3)	6923(2)	9448(2)	43(1)
C(9)	3967(3)	7162(2)	10560(2)	41(1)
N(1)	5084(2)	7859(1)	10904(2)	41(1)
C(10)	5602(3)	8060(2)	10151(2)	37(1)
C(11)	5021(3)	7537(2)	9221(2)	41(1)
C(12)	5514(3)	7652(2)	8405(2)	51(1)
C(13)	6601(3)	8323(2)	8406(2)	51(1)
O(4)	7101(3)	8431(2)	7676(2)	78(1)
C(14)	7116(3)	8888(2)	9322(2)	41(1)
C(22)	8070(4)	9614(2)	9189(3)	53(1)
C(15)	6680(3)	8750(2)	10176(2)	36(1)
C(16)	7217(3)	9267(2)	11132(2)	38(1)
C(17)	6135(4)	9667(2)	11506(2)	50(1)
C(18)	6622(4)	10154(2)	12385(2)	64(1)
C(19)	8220(4)	10234(2)	12908(3)	67(1)
C(20)	9304(4)	9838(2)	12560(2)	66(1)
C(21)	8810(3)	9358(2)	11678(2)	50(1)

Formula: $C_{22}H_{15}FeNO_4$; crystal size: 0.2 · 0.2 · 0.3 mm; M = 413.20; monoclinic; space group: $P2_1/n$; a = 8.909(2) Å, b = 16.166(4) Å, c = 13.556(2) Å; β = 108.530(10)°; V = 1851.2(7) $Å^3$; Z = 4; $\rho_{calc.}$ = 1.483g/cm^3; T = 293(2) K; μ = 0.843 mm^{-1}; λ = 0.71069 Å; θ range: 2.02 - 21.98°; reflections collected: 6609, independent: 2271; R_1 = 0.0243, wR_2 = 0.0614 [I > 2σ(I)]; maximal residual electron density: 0.154 e/$Å^3$.

The data were collected on a STOE STADI-4 diffractometer using Mo-K_α radiation. The structure was solved by direct methods (SHELXS-86) and refined anisotropically by full-matrix least squares based on all unique F^2

(SHELXL-93); the program SCHAKAL-97 has been used for the graphical representation of the crystal structure (E. Keller, a computer program for the graphic representation of molecular and crystallographic models, Universität Freiburg, Germany, 1997).[22]

3-Hydroxy-2-methyl-1-phenyl-9*H*-carbazole (18)

The dihydrocarbazolone iron complex **17** (49 mg, 0.119 mmol) was dissolved in acetone (2 ml), trimethylamine *N*-oxide dihydrate (74 mg, 0.666 mmol) was added, and the reaction mixture was stirred for 4 h at room temperature. The heterogeneous mixture was filtered through a short path of silica gel/Celite, which was subsequently washed with ethyl acetate several times. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (hexane/EtOAc, 8:1) on silica gel to provide the carbazole **18** as a light yellow solid. Recrystallization from toluene/hexane/EtOAc afforded **18** as colorless crystals, yield: 31 mg (95%), m.p. 176-180°C. UV (MeOH): λ = 219, 303, 355 nm. IR ($CHCl_3$): $\tilde{\nu}$ = 3600, 3466, 3064, 3009, 2927, 1615, 1588, 1508, 1489, 1459, 1431, 1379, 1315, 1263, 1150, 1122, 1108, 1015, 982, 860, 704, 660, 614 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6): δ = 2.18 (s, 3 H), 7.08 (dt, J = 0.8, 7.5, 1 H), 7.26 (dt, J = 1.0, 7.5, 1 H), 7.38 (d, J = 7.5, 1 H), 7.42-7.56 (m, 6 H), 7.96 (d, J = 7.5, 1 H), 8.00 (s, 1 H), 9.43 (br s, 1 H). ^{13}C-NMR and DEPT (100 MHz, acetone-d_6): δ = 14.71 (CH_3), 105.23 (CH), 112.54 (CH), 119.61 (CH), 121.14 (CH), 122.38 (C), 123.15 (C), 124.70 (C), 126.29 (CH), 127.11 (C), 128.82 (CH), 130.28 (2 CH), 131.50 (2 CH), 134.85 (C), 139.64 (C), 142.17 (C), 150.94 (C). MS (90°C): *m/z* (%) = 273 (M^+, 100), 272 (9), 170 (66), 141 (51), 97 (10), 77 (50). HRMS: Calc. for $C_{19}H_{15}NO$ (M^+): 273.1154, found: 273.1144.

Hyellazole (3-Methoxy-2-methyl-1-phenyl-9*H*-carbazole)

By alkylation of the 3-hydroxycarbazole **18**

A mixture of the hydroxycarbazole **18** (30 mg, 11.0 μmol), K_2CO_3 (136 mg, 0.98 mmol), and iodomethane (0.67 ml, 1.53 g, 10.8 mmol) in acetone (3.5 ml) was heated at reflux for 6 h. The solvent was removed in vacuo and the residue was dissolved in diethyl ether (10 ml). The solution was filtered over a short path of Celite, which was subsequently washed with diethyl ether. The solvent was evaporated and the crude product was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to provide hyellazole as a colorless solid, yield: 29.5 mg (93%), m.p. 129-130°C (ref.[2]: 133-134°C). UV (EtOH): λ = 221, 232, 239 (sh), 250 (sh), 260 (sh), 293 (sh), 304, 338, 352 nm. IR (CCl_4): $\tilde{\nu}$ = 3473, 3063, 2935, 2832, 1612, 1587, 1504, 1490, 1453, 1424, 1307, 1291, 1256, 1208, 1178, 1156, 1149, 1044, 1028, 704 cm^{-1}. IR (drift): $\tilde{\nu}$ = 3403, 3360, 3061, 3024, 2954, 2931, 2833, 1612, 1586, 1503, 1491, 1480, 1447, 1424, 1309, 1293, 1258, 1205, 1146, 1111, 1040, 1024, 842, 781, 773, 754, 747, 738, 704, 668, 646, 621 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 4.01 (s, 3 H), 7.19 (m, 1 H), 7.29-7.36 (m, 2 H), 7.43-7.48 (m, 3 H), 7.53-7.57 (m, 3 H), 7.61 (br s, 1 H), 8.04 (d, J = 7.8, 1 H). ^{1}H-NMR (400 MHz, acetone-d_6): δ = 2.15 (s, 3 H), 3.99 (s, 3 H), 7.12 (m, 1 H), 7.29 (m, 1 H), 7.43 (m, 4 H), 7.53 (m, 2 H), 7.70 (s, 1 H), 8.09 (d, J = 7.8, 1 H), 9.52 (br s, 1 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 13.70 (CH_3), 56.16 (CH_3), 100.23 (CH), 110.58 (CH), 118.83 (CH), 119.88 (CH), 120.27 (C), 123.64 (C), 123.78 (C), 125.04 (CH), 125.50 (C), 127.56 (CH), 128.93 (2 CH), 129.84 (2 CH), 133.21 (C), 137.50 (C), 139.44 (C), 152.64 (C). MS (70°C): *m/z* (%) = 287 (M^+, 100), 286 (2), 272 (46), 271 (6), 254 (14), 242 (7), 241 (8). HRMS: Calc. for $C_{20}H_{17}NO$ (M^+): 287.1310, found: 287.1299. Anal. Calc. for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.84; H, 6.20; N, 5.03.

Hyellazole

By oxidation of complex **15** with ferricenium hexafluorophosphate

Ferricenium hexafluorophosphate (16 mg, 48 μmol) was added to a solution of complex **15** (105 mg, 0.244 mmol) in CH_2Cl_2 (40 ml) at room temperature. After stirring the dark violet reaction mixture for 15 min the color turns to yellow and additional $FeCp_2PF_6$ (16 mg, 48 μmol) was added. The mixture was stirred until the color turns to yellow and Na_2CO_3 (259 mg, 2.44 mmol) was added. While stirring at room temperature 6 portions of $FeCp_2PF_6$ (81 mg, 0.244 mmol per portion) were added each after additional 40, 70, 120, 200 min, 5 and 8 h; and Na_2CO_3 (252 mg, 2.38 mmol) was added after 5.5 h. After a total reaction time of 22 h the heterogeneous mixture was filtered over a short path of silica gel/Celite, which was subsequently washed with EtOAc several times. The solvent was evaporated and the residue was subjected to flash chromatography (hexane/EtOAc 7:1) on silica gel to provide first hyellazole (yield: 41 mg, 59%) and as the more polar fraction complex **17** (29 mg, 29%). Complex **17** was converted to hyellazole (18 mg, 88% overall yield) in two steps as described above. Total yield of hyellazole: 59 mg (84.4% based on **15**). Spectral data, see above.

3-Methoxy-2-phenylbenzyl alcohol (19)

A solution of the ethyl 3-methoxy-2-phenylbenzoate (**5**) (503 mg, 1.96 mmol) in Et_2O (5 ml) was added over a period of 30 min to a suspension of lithium aluminum hydride (110 mg, 2.90 mmol) in Et_2O (15 ml) at – 10°C. The reaction mixture was subsequently heated at reflux for 1 h. The mixture was carefully quenched with ice-water and the resulting precipitate was dissolved in a small amount of H_2SO_4 (10%). The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 x 15 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$, then dried (Na_2SO_4), and the solvent was evaporated in vacuo. The residue can be purified by flash chromatography (hexane/EtOAc 2:1) on silica gel. Recrystallization of the product from hexane/Et_2O (8:1) afforded the alcohol **19** as colorless crystalline needles, yield: 413 mg (98%), m.p. 88-90°C. IR (KBr): $\tilde{\nu}$ = 3257, 3062, 2924, 1601, 1578, 1466, 1435, 1259, 1031, 1013, 780, 765, 737, 701 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.64 (br s, 1 H), 3.73 (s, 3 H), 4.42 (s, 2 H), 6.95 (d, J = 8.2, 1 H), 7.18 (d, J = 7.6, 1 H), 7.25-7.27 (m, 2 H), 7.36-7.46 (m, 4 H). ^{1}H-NMR NOE experiments (400 MHz, $CDCl_3$): 1. Irradiation at 3.73, observed NOE 6.95; 2. irradiation at 4.42, observed NOE's 7.18, 7.25-7.27. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 55.84 (CH_3), 63.22 (CH_2), 110.20 (CH), 110.58 (C), 120.07 (CH), 127.23 (CH), 128.22 (2 CH), 128.68 (CH), 129.88 (2 CH), 136.14 (C), 140.26 (C), 156.80 (C). MS (50°C): *m/z* (%) = 214 (M^+, 100), 212 (11), 196 (19), 195 (10), 181 (50), 165 (14), 153 (19), 152 (26), 139 (9), 115 (9), 77 (3). HRMS: Calc. for $C_{14}H_{14}O_2$ (M^+): 214.0994, found: 214.0975.

3-Methoxy-2-phenylbenzyl bromide (20)

A solution of phosphorus tribromide (1.56 g, 0. 54 ml, 5.76 mmol) in diethyl ether (4.5 ml) was added slowly to a stirred solution of the benzyl alcohol **19** (3.35 g, 15.6 mmol) in diethyl ether (50 ml) at – 10°C. The reaction mixture was stirred for further 30 min at room temperature and heated at reflux for additional 12 h. The mixture was poured onto ice (30 g) and the organic layer was separated. The aqueous layer was extracted with diethyl ether (3 x 10 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over sodium sulfate, and the solvent was evaporated in vacuo. The crude product can be used without further

purification. For characterization the residue was subjected to flash chromatography (hexane/EtOAc 2:1) on silica gel to afford **20** as a colorless oil. Storage at – 20°C provided the benzyl bromide **20** as a colorless solid, yield: 4.11 g (95%), m.p. 40-42°C. IR (KBr): $\tilde{\nu}$ = 3003, 2959, 2935, 2833, 1960, 1602, 1577, 1497, 1465, 1439, 1298, 1255, 1206, 1124, 1094, 1060, 1005, 934, 797, 703, 644, 592 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.70 (s, 3 H), 4.26 (s, 2 H), 6.90 (d, *J* = 8.3, 1 H), 7.14 (d, *J* = 7.7, 1 H), 7.31-7.46 (m, 6 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 31.99 (CH_2), 55.89 (CH_3), 110.91 (CH), 122.63 (CH), 127.41 (CH), 128.10 (2 CH), 128.81 (CH), 129.94 (2 CH), 131.19 (C), 135.64 (C), 137.23 (C), 157.02 (C). MS (20°C): *m/z* (%) = 278 (M^+ + 2, 35), 276 (M^+, 36), 197 (100), 196 (13), 182 (60), 181 (24), 166 (11), 165 (56), 153 (17), 152 (28). HRMS: Calc. for $C_{14}H_{13}{}^{79}BrO$ (M^+): 276.0150, found: 276.0136.

3-Methyl-2-phenylanisole (22)

By reduction of the benzyl bromide **20** with lithium aluminum hydride

A solution of the benzyl bromide **20** (3.83 g, 13.8 mmol) in ether (15 ml) was added slowly to a suspension of lithium aluminum hydride (1.6 g, 42.2 mmol) in ether (15 ml) at – 10°C. The reaction mixture was stirred at room temperature for 30 min, then heated at reflux for 17 h, carefully quenched by addition of ice-water, and the resulting precipitate was dissolved in diluted H_2SO_4. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 15 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$ and dried over Na_2SO_4. Evaporation of the solvent and flash chromatography of the residue (hexane/EtOAC 3:1) on silica gel afforded the anisole **22** as a colorless liquid, yield: 2.3 g (84%). By using the benzyl alcohol **19** and the benzyl bromide **20** (see above) without purification the overall yield of the anisole **22** can be improved to 92% based on the benzoate **5** (3 steps). IR (film): $\tilde{\nu}$ = 3060, 3024, 2954, 2834, 1602, 1578, 1497, 1466, 1437, 1292, 1256, 1084, 1007, 994, 919, 901, 777, 762, 737, 701, 685 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.12 (s, 3 H), 3.74 (s, 3 H), 6.88 (d, *J* = 8.3, 1 H), 6.95 (d, *J* = 7.6, 1 H), 7.27 (m, 3 H), 7.38 (m, 1 H), 7.47 (m, 2 H). ^{1}H-NMR NOE experiments (400 MHz, CD_2Cl_2): 1. Irradiation at 2.12, observed NOE 6.95; 2. irradiation at 3.74, observed NOE 6.88. ^{13}C-NMR and DEPT (100 MHz, CD_2Cl_2): δ = 20.52 (CH_3), 55.83 (CH_3), 108.58 (CH), 122.69 (CH), 126.96 (CH), 128.29 (CH), 128.34 (2 CH), 130.38 (2 CH), 131.16 (C), 137.89 (C), 138.24 (C), 157.24 (C). MS (20°C): *m/z* (%) = 198 (M^+, 100), 183 (16), 168 (16), 165 (20), 152 (7). HRMS: Calc. for $C_{14}H_{14}O$ (M^+): 198.1045, found: 198.1033.

3-Methoxy-2-phenylbenzoic acid (21)

The benzoate **5** (500 mg, 1.95 mmol) was added to a solution of potassium hydroxide (328 mg, 5.87 mmol) in ethanol (3 ml) / water (0.5 ml). The reaction mixture was heated at reflux for 3 h and the solvent was subsequently removed in vacuo. A 4 M solution of HCl was added to the residue until a pH = 1 was detected. The mixture was saturated with NaCl and then extracted with diethyl ether (5 x 10 ml). The combined organic layers were dried over sodium sulfate and the solvent was evaporated. Flash chromatography of the residue (hexane/EtOAc 6:1) on silica gel provided a crystalline solid. Recrystallization from acetonitrile/diethyl ether (3:2) afforded the benzoic acid **21** as colorless crystals, yield: 430 mg (97%), m.p. 170-173°C. IR (KBr): $\tilde{\nu}$ = 3060, 2963, 2936, 2837, 1690, 1671, 1600, 1576, 1498, 1458, 1398, 1303, 1260, 1056, 942, 919, 761, 732, 699 cm^{-1}. ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 7.13 (d, *J* = 8.1, 1 H), 7.23-7.27 (m, 3 H), 7.33-7.41 (m, 3 H), 7.50 (d, *J* = 7.8, 1 H), 10.41 (br s, 1 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 56.07 (CH_3),

114.67 (CH), 122.16 (CH), 127.21 (CH), 127.73 (2 CH), 128.37 (CH), 129.49 (2 CH), 131.63 (C), 131.76 (C), 136.23 (C), 157.06 (C), 172.99 (C=O). MS (20°C): *m/z* (%) = 228 (M^+, 100), 211 (10), 181 (14), 168 (12), 152 (8), 139 (26). HRMS: Calc. for $C_{14}H_{12}O_3$ (M^+): 228.0786, found: 228.0804.

3-Methyl-2-phenylanisole (22)

By reduction of the benzoic acid **21** with trichlorosilane

3-Methoxy-2-phenylbenzoic acid (**21**) (400 mg, 1.71 mmol) was dissolved in a small amount of warm acetonitrile and then cooled to 0°C. Trichlorosilane (1.40 g, 1.04 ml, 10.3 mmol) was added slowly at this temperature and then the reaction mixture was heated at reflux for 1 h. After cooling to 0°C, tri-*n*-propylamine (648 mg, 0.86 ml, 4.52 mmol) was added slowly and the mixture was heated at reflux for additional 16 h. Diethyl ether was added and the cold mixture was filtered. The solvent was evaporated, the residue was dissolved in MeOH (10 ml, p.a.), and the solution was heated at reflux for 1 h. A solution of KOH (960 mg) in H_2O (3 ml) / MeOH (10 ml) was added slowly, the resulting suspension was heated at reflux for additional 19 h, and the reaction mixture was quenched with H_2O (20 ml). After extraction with hexane (5 x 5 ml), the combined organic layers were neutralized with diluted HCl, and then washed with a saturated solution of $NaHCO_3$. The solution was dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by flash chromatography (hexane/EtOAc 3:1) on silica gel to provide the anisole **22** as a colorless oil, yield: 276 mg (81%). The overall yield of the anisole **22** was 79% based on the benzoate **5** (2 steps). Spectral data, see above.

3-Methyl-4-nitro-2-phenylanisole (23) and **3-Methyl-6-nitro-2-phenylanisole**

A mixture of HNO_3 (65%, 0.52 ml, 7.51 mmol) and H_2SO_4 (96%, 0.56 ml, 10.1 mmol) was added to a solution of the anisole **22** (1.00 g, 5.04 mmol) in dichloromethane (5 ml) at – 10°C over a period of 30 min while the color of the mixture turns to dark blue. After the addition was completed, the reaction mixture was stirred for further 60 min at – 5°C. The mixture was quenched with ice and the aqueous layer was extracted with Et_2O (5 x 30 ml). The combined organic layers were washed with a saturated solution of $NaHCO_3$, dried over sodium sulfate, and the solvent was evaporated in vacuo. The residue was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to afford first the minor regioisomer 3-methyl-6-nitro-2-phenylanisole and then the 4-nitro derivative **23** as the more polar regioisomer.

23: Orange-yellow solid, yield: 633 mg (52%), m.p. 60-62°C. IR (KBr): $\tilde{\nu}$ = 3093, 3055, 2977, 2941, 2845, 1599, 1572, 1510, 1466, 1441, 1431, 1338, 1269, 1076, 1030, 1002, 934, 850, 833, 819, 759, 736, 697 cm^{-1}. ^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 2.21 (s, 3 H), 3.78 (s, 3 H), 6.91 (d, *J* = 9.1, 1 H), 7.16 (m, 2 H), 7.27-7.48 (m, 3 H), 8.00 (d, *J* = 9.1, 1 H). ^{1}H-NMR NOE experiment (400 MHz, CD_2Cl_2): Irradiation at 3.78, observed NOE 6.91. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 17.85 (CH_3), 56.10 (CH_3), 107.96 (CH), 125.98 (CH), 127.56 (CH), 128.41 (2 CH), 129.82 (2 CH), 132.87 (C), 134.05 (C), 135.97 (C), 143.93 (C), 160.36 (C). MS (40°C): *m/z* (%) = 243 (M^+, 100), 226 (67), 211 (6), 196 (10), 182 (12), 181 (18), 165 (12), 153 (20), 152 (22). HRMS: Calc. for $C_{14}H_{13}NO_3$ (M^+): 243.0895, found: 243.0910.

3-Methyl-6-nitro-2-phenylanisole: Yellow crystals, yield: 213 mg (17%), m.p. 43-45°C. IR (KBr): $\tilde{\nu}$ = 3083, 3025, 3014, 2942, 2871, 1601, 1580, 1522, 1491, 1465, 1441, 1403, 1355, 1258, 1218, 1076, 1046, 1021, 996, 928, 868, 839, 789, 763, 704, 636 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.16 (s, 3 H), 3.45 (s, 3 H), 7.12 (d, *J* = 8.4, 1 H), 7.26 (m, 2 H), 7.38-7.49 (m, 3 H), 7.74 (d, *J* = 8.4, 1 H). ^{1}H-NMR NOE experiments (400 MHz,

$CDCl_3$): 1. Irradiation at 7.12, observed NOE 7.74; 2. irradiation at 7.74, observed NOE 7.12. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 20.98 (CH_3), 61.96 (CH_3), 123.80 (CH), 125.44 (CH), 127.81 (CH), 128.46 (2 CH), 129.60 (2 CH), 135.36 (C), 138.22 (C), 142.36 (C), 144.15 (C), 151.29 (C). MS (20°C): *m/z* (%) = 243 (M^+, 100), 198 (64), 197 (9), 196 (31), 183 (17), 182 (41), 181 (27), 168 (34), 167 (13), 166 (11), 165 (34), 154 (10), 153 (27), 152 (34), 139 (10), 77 (6). HRMS: Calc. for $C_{14}H_{13}NO_3$ (M^+): 243.0895, found: 243.0912.

4-Methoxy-2-methyl-3-phenylaniline (24)

Palladium on carbon (15%, 500 mg) was added to a solution of the nitrobenzene **23** (4.40 g, 18.1 mmol) in methanol (100 ml). The nitro derivative **23** was hydrogenated by vigorous stirring of this mixture in a hydrogen atmosphere (1.1 atm) until no further H_2 uptake was detected. The reaction mixture was filtered over a short path of silica gel/Celite, which was subsequently washed with dichloromethane. Evaporation of the solvent in vacuo afforded the amine **24** as colorless crystals, yield: 3.81 g (99%), m.p. 102-104°C. IR (KBr): $\tilde{\nu}$ = 3463, 3433, 3361, 3051, 3018, 2987, 2936, 2903, 2830, 1617, 1594, 1476, 1435, 1292, 1252, 1082, 1003, 992, 800, 763, 729, 701 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.91 (s, 3 H), 3.45 (br s, 2 H), 3.63 (s, 3 H), 6.71 (d, *J* = 8.7, 1 H), 6.74 (d, *J* = 8.7, 1 H), 7.22 (m, 2 H), 7.34 (m, 1 H), 7.43 (m, 2 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 14.82 (CH_3), 56.61 (CH_3), 110.13 (CH), 114.55 (CH), 122.96 (C), 126.71 (CH), 128.00 (2 CH), 130.19 (2 CH), 132.19 (C), 138.13 (C), 138.60 (C), 150.40 (C). MS (40°C): *m/z* (%) = 213 (M^+, 100), 198 (57), 183 (58). HRMS: Calc. for $C_{14}H_{15}NO$ (M^+): 213.1154, found: 213.1136.

[(1-4-η)-5-(2-Amino-5-methoxy-3-methyl-4-phenylphenyl)cyclohexa-1,3-diene]tricarbonyliron (25)

A solution of tricarbonyl(η^5-cyclohexadienylium)iron tetrafluoroborate (**1**) (2.65 g, 8.67 mmol) in degassed acetonitrile (25 ml) was added slowly to a refluxing solution of the arylamine **24** (3.79 g, 17.8 mmol) in degassed acetonitrile (10 ml). The reaction mixture was heated at reflux for 80 min. The solvent was evaporated in vacuo, diethyl ether was added to the residue, and the resulting suspension was stirred under an inert gas atmosphere until the insoluble protonated amine was finely dispersed. The solution was separated and the residue was washed with small amounts of cold diethyl ether several times. The ethereal layers were combined and the solvent was evaporated. The crude product was subjected to flash chromatography (hexane/EtOAc, 6:1) on degassed silica gel to provide the iron complex **25** as a light yellow solid, yield: 3.50 g (94%), m.p. 163-165°C. IR (KBr): $\tilde{\nu}$ = 3450, 3379, 3223, 3066, 3024, 2998, 2937, 2854, 2833, 2043, 1950, 1620, 1602, 1498, 1474, 1416, 1380, 1334, 1309, 1275, 1220, 1188, 1155, 1116, 1063, 1008, 995, 941, 880, 866, 848, 800, 768, 705, 675, 617 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.71 (br d, *J* = 15.2, 1 H), 1.90 (s, 3 H), 2.47 (ddd, *J* = 15.2, 11.1, 3.8, 1 H), 3.24 (m, 2 H), 3.41 (br s, 2 H), 3.50 (dt, *J* = 11.1, 3.7, 1 H), 3.64 (s, 3 H), 5.54-5.60 (m, 2 H), 6.72 (s, 1 H), 7.20 (m, 2 H), 7.33 (m, 1 H), 7.41 (m, 2 H). ^{1}H-NMR NOE experiments (400 MHz, $CDCl_3$): 1. Irradiation at 1.71, observed NOE's 2.47, 3.24, 6.72; 2. irradiation at 2.47, observed NOE's 1.71, 3.24, 3.50; 3. irradiation at 3.50, observed NOE's 2.47, 3.24, 6.72; 4. irradiation at 3.64, observed NOE 6.72. ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$) δ = 15.17 (CH_3), 31.36 (CH_2), 39.46 (CH), 56.85 (CH_3), 60.27 (CH), 64.54 (CH), 84.89 (CH), 85.78 (CH), 108.64 (CH), 122.83 (C), 126.64 (CH), 127.93 (2 CH), 129.77 (C), 130.27 (2 CH), 130.41 (C), 135.87 (C), 138.02 (C), 149.91 (C), 211.91 (3 CO). MS (120°C): *m/z* (%) = 431 (M^+, 41), 403 (2), 375 (41), 347 (66), 345 (91), 330 (41), 293 (25), 291 (36), 290 (34), 289 (53), 274 (20), 269 (100), 259

(32), 255 (13), 254 (75). HRMS: Calc. for $C_{23}H_{21}FeNO_4$ (M^+): 431.0820, found: 431.0809. Anal. Calc. for $C_{23}H_{21}FeNO_4$: C, 64.04; H, 4.91; N, 3.25. Found: C, 64.07; H, 5.03; N, 3.62.

Tricarbonyl[(1-4-η)-5-(6-imino-5-methyl-4-phenylcyclohexa-1,4-dien-3-onyl)cyclohexa-1,3-diene]iron (26) and **Tricarbonyl[(1-4-η)-5-(5-methyl-4-phenylcyclohexa-1,4-dien-3,6-dionyl)cyclohexa-1,3-diene]iron**

Commercial manganese dioxide[17] (1.00 g) was added to a solution of the iron complex **25** (201 mg, 0.466 mmol) in dichloromethane (5 ml) and the mixture was stirred for 4 h at room temperature. Then commercial MnO_2 (500 mg) was added and stirring was continued for additional 3 h at room temperature. The heterogeneous mixture was filtered over a short path of Celite, which was subsequently washed with dichloromethane several times. The filtrate was evaporated and the crude product was subjected to flash chromatography (hexane/EtOAc 5:1) on degassed silica gel to provide the desired complex **26** as the more polar fraction. The less polar fraction contained the corresponding *p*-benzoquinone as a by-product.

26: Yellow solid, yield: 112 mg (58%), m.p. 134-136°C. IR (KBr): $\tilde{\nu}$ = 3415 (br), 3282, 3064, 3000, 2920, 2851, 2053, 1963, 1639, 1619, 1441, 1407, 1368, 1317, 1215, 1198, 1130, 874, 763, 705, 623 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.49 (br d) and 1.52 (br d, *J* = 15.3, Σ 1 H), 1.98 (s) and 2.12 (s, Σ 3 H), 2.43 (ddd, *J* = 15.3, 11.4, 3.8, 1 H), 2.96 (m) and 3.09 (m, Σ 1 H), 3.17 (m, 1 H), 3.36 (dt, *J* = 11.5, 3.6) and 3.94 (dt, *J* = 11.4, 3.5, Σ 1 H), 5.46 (m, 1 H), 5.54 (m) and 5.60 (m, Σ 1 H), 6.51 (br s) and 6.59 (br s, Σ 1 H), 7.08-7.14 (m, 2 H), 7.35-7.44 (m, 3 H), 10.87 (br s) and 11.04 (br s, Σ 1 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$) (*anti*-imine stereoisomer): δ = 14.85 (CH_3), 32.71 (CH_2), 37.16 (CH), 60.42 (CH), 62.74 (CH), 84.82 (CH), 86.24 (CH), 127.30 (CH), 128.09 (CH), 128.16 (2 CH), 129.50 (2 CH), 134.07 (C), 137.90 (C), 140.31 (C), 157.20 (C), 166.65 (C=N), 186.57 (C=O), 211.57 (3 CO). MS (140°C): *m/z* (%) = 415 (M^+, 1), 387 (9), 359 (32), 331 (97), 330 (25), 329 (100), 257 (11), 255 (16), 254 (18), 253 (64), 251 (19). HRMS: Calc. for $C_{22}H_{17}FeNO_4$ (M^+): 415.0507, found: 415.0537.

Tricarbonyl[(1-4-η)-5-(5-methyl-4-phenylcyclohexa-1,4-dien-3,6-dionyl)cyclohexa-1,3-diene]iron: Yellow solid, yield: 27 mg (14%), m.p. 152-155°C. IR (KBr): $\tilde{\nu}$ = 3060, 2998, 2925, 2852, 2053, 1970, 1643, 1607, 1441, 1374, 1316, 1303, 1291, 1234, 1211, 1153, 963, 894, 768, 711, 698, 624, 609 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.45 (br d, *J* = 15.4, 1 H), 1.93 (s, 3 H), 2.40 (ddd, *J* = 15.4, 11.5, 3.7, 1 H), 2.98 (m, 1 H), 3.16 (m, 1 H), 3.50 (dt, *J* = 11.5, 3.3, 1 H), 5.46 (m, 1 H), 5.51 (m, 1 H), 6.67 (d, *J* = 0.6, 1 H), 7.13 (m, 2 H), 7.39-7.45 (m, 3 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 14.08 (CH_3), 31.77 (CH_2), 36.39 (CH), 60.01 (CH), 61.29 (CH), 84.58 (CH), 86.37 (CH), 128.12 (2 CH), 128.59 (CH), 129.41 (2 CH), 129.93 (CH), 132.69 (C), 141.69 (C), 143.34 (C), 153.37 (C), 187.13 (C=O), 187.75 (C=O), 211.25 (3 CO). MS (95°C): *m/z* (%) = 416 (M^+, 7), 388 (8), 360 (29), 332 (96), 330 (34), 276 (28), 274 (15), 256 (10), 254 (100), 252 (11). HRMS: Calc. for $C_{22}H_{16}FeO_5$ (M^+): 416.0347, found: 416.0360.

Tricarbonyl[(5-8-η)-4b,8a-dihydro-1-methyl-2-phenyl-3*H*-carbazol-3-one]iron (27)

Very active manganese dioxide[18] (350 mg) was added to a solution of the quinone imine **26** (70 mg, 0.169 mmol) in dichloromethane (3 ml) at room temperature. After a reaction time of 60 min, the heterogeneous mixture was filtered over a short path of silica gel/Celite, which was subsequently washed with ethyl acetate. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to afford the carbazolone **27** as yellow crystals, yield: 47 mg (67%), m.p. 175-177°C.

IR (KBr): $\tilde{\nu}$ = 3434, 3058, 3022, 2918, 2060, 1994, 1965, 1728, 1651, 1623, 1599, 1441, 1412, 1370, 1302, 1282, 1263, 1208, 1160, 881, 702, 652, 616 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 2.10 (s, 3 H), 3.14 (ddd, *J* = 5.9, 4.3, 1.8, 1 H), 3.48 (ddd, *J* = 5.9, 4.2, 1.7, 1 H), 3.56 (ddd, *J* = 6.4, 4.3, 1.9, 1 H), 4.98 (dd, *J* = 6.4, 4.2, 1 H), 5.46 (m, 2 H), 6.29 (d, *J* = 1.9, 1 H), 7.13 (m, 2 H), 7.34-7.43 (m, 3 H). ^{13}C-NMR and DEPT (100 MHz, $CDCl_3$): δ = 15.10 (CH_3), 45.19 (CH), 57.08 (CH), 58.87 (CH), 78.38 (CH), 85.31 (CH), 86.41 (CH), 122.66 (CH), 128.01 (3 CH), 129.62 (2 CH), 134.32 (C), 139.49 (C), 142.67 (C), 155.41 (C), 164.44 (C=N), 186.43 (C=O), 210.34 (3 CO). MS (140°C): *m/z* (%) = 413 (M^+, 2), 385 (32), 357 (5), 329 (100), 327 (22), 273 (2), 271 (3). HRMS: Calc. for $C_{22}H_{15}FeNO_4$ (M^+): 413.0350, found: 413.0342.

3-Hydroxy-1-methyl-2-phenyl-9*H*-carbazole (28)

Trimethylamine *N*-oxide dihydrate (67 mg, 0.603 mmol) was added to a solution of the dihydrocarbazolone iron complex **27** (30.5 mg, 73.8 μmol) in acetone (5 ml) and the reaction mixture was stirred at room temperature for 14 h. The heterogeneous mixture was filtered over a short path of silica gel/Celite, which was subsequently washed with ethyl acetate several times. The solvent was evaporated and the residue was purified by flash chromatography (hexane/EtOAc 6:1) on degassed silica gel to provide the carbazole **28** as a colorless solid, yield: 17 mg (84%), m.p. ≥185°C (dec.). UV (MeOH): λ = 212, 239, 253 (sh), 302, 346 nm. IR (drift): $\tilde{\nu}$ = 3533, 3517, 3501, 3438, 3336, 3289, 3055, 3028, 1615, 1599, 1581, 1507, 1458, 1440, 1426, 1331, 1317, 1296, 1225, 1179, 1014, 773, 767, 741, 703 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6): δ = 2.30 (s, 3 H), 7.12 (m, 1 H), 7.35 (m, 5 H), 7.45 (m, 3 H), 7.52 (s, 1 H), 8.00 (d, *J* = 7.9, 1 H), 10.00 (br s, 1 H). ^{13}C-NMR and DEPT (100 MHz, acetone-d_6): δ = 15.84 (CH_3), 104.23 (CH), 112.44 (CH), 119.76 (CH), 120.37 (C), 121.51 (CH), 123.48 (C), 124.84 (C), 126.68 (CH), 128.15 (CH), 129.47 (2 CH), 129.86 (C), 132.31 (2 CH), 135.70 (C), 139.73 (C), 142.38 (C), 149.78 (C). MS (90°C): *m/z* (%) = 273 (M^+, 100), 272 (10), 271 (5), 257 (5), 254 (8). HRMS: Calc. for $C_{19}H_{15}NO$ (M^+): 273.1154, found: 273.1135.

Isohyellazole (3-Methoxy-1-methyl-2-phenyl-9*H*-carbazole)

By alkylation of the 3-hydroxycarbazole **28**

A mixture of the 3-hydroxycarbazole **28** (18.4 mg, 67.3 μmol), K_2CO_3 (186 mg, 1.35 mmol) and iodomethane (958 mg, 0.42 ml, 6.75 mmol) in acetone (4 ml) was heated at reflux for 24 h. The solvent was evaporated and the residue was dissolved in diethyl ether (10 ml). The solution was filtered over a short path of Celite, which was subsequently washed with diethyl ether. Removal of the solvent, flash chromatography (hexane/EtOAc 5:1) of the residue on silica gel, and recrystallization from hexane/CH_2Cl_2 afforded isohyellazole as colorless crystals, yield: 16.8 mg (87%), m.p. 159-161°C. UV (MeOH): λ = 210, 239, 250 (sh), 302, 337 nm. IR (drift): $\tilde{\nu}$ = 3421, 3061, 3028, 2957, 2938, 2838, 2544, 1600, 1581, 1503, 1490, 1480, 1456, 1420, 1380, 1312, 1281, 1259, 1213, 1199, 1175, 1155, 1119, 1103, 1081, 1005, 850, 831, 766, 744, 720, 701, 641 cm^{-1}. ^{1}H-NMR (400 MHz, acetone-d_6): δ = 2.30 (s, 3 H), 3.76 (s, 3 H), 7.16 (ddd, *J* = 7.9, 7.0, 0.9, 1 H), 7.27-7.30 (m, 2 H), 7.34-7.38 (m, 2 H), 7.41-7.46 (m, 2 H), 7.51 (dt, *J* = 8.1, 0.9, 1 H), 7.65 (s, 1 H), 8.11 (br d, *J* = 7.9, 1 H), 10.10 (br s, 1 H). ^{13}C-NMR and DEPT (100 MHz, acetone-d_6): δ = 15.79 (CH_3), 57.15 (CH_3), 101.10 (CH), 112.57 (CH), 119.96 (CH), 120.86 (C), 121.56 (CH), 123.09 (C), 125.19 (C), 126.66 (CH), 127.96 (CH), 129.24 (2 CH), 131.47 (C), 132.16 (2 CH), 136.07 (C), 140.04 (C), 142.21 (C), 153.17 (C). MS (80°C): *m/z* (%) = 287 (M^+, 100), 272 (25), 257 (54), 241 (6). HRMS: Calc. for $C_{20}H_{17}NO$ (M^+): 287.1310, found: 287.1305.

Isohyellazole

By oxidation of complex **25** with ferricenium hexafluorophosphate

Ferricenium hexafluorophosphate (20 mg, 60 μmol) was added to a solution of complex **25** (108 mg, 0.250 mmol) in CH_2Cl_2 (75 ml) at room temperature. After stirring the dark violet reaction mixture for 15-20 min the color turns to yellow and additional $FeCp_2PF_6$ (18 mg, 54 μmol) was added. The mixture was stirred for further 40 min until the color turns to yellow and after 1 h Na_2CO_3 (269 mg, 2.54 mmol) was added. While stirring at room temperature 7 portions of $FeCp_2PF_6$ (65 mg, 0.196 mmol per portion) were added each after additional 5, 20, 35, 65, 130, 215, and 275 min; and Na_2CO_3 (134 mg, 1.26 mmol) was added after 3 h. After a total reaction time of 22 h the heterogeneous mixture was filtered over a short path of silica gel/Celite, which was subsequently washed several times with EtOAc. The solvent was evaporated in vacuo and the residue was subjected to flash chromatography (hexane/EtOAc 5:1) on silica gel to provide first isohyellazole (yield: 44 mg, 61%) and as the more polar fraction complex **27** (31 mg, 30%). Complex **27** was converted to isohyellazole (15.7 mg, 73% overall yield) in two steps as described above. Total yield of isohyellazole: 59.7 mg (83% based on **25**). Spectral data, see above.

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References and Notes

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22. Atomic coordinates, bond lengths and angles, and thermal parameters for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication.