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Alkylation of Arenes with Benzylic and Propargylic Alcohols – Classical *versus* Fancy Catalysts

Jianhui Liu,[a] Enrico Muth,[a] Ulrich Flörke,[b] Gerald Henkel,[b] Klaus Merz,[a] Janelle Sauvageau,[a] Erik Schwake,[a] Gerald Dyker[a,*]

[a] Fakultät für Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150, 44780 Bochum, Germany
Fax: (+49)-234-321-4353, e-mail: Gerald.Dyker@rub.de
[b] Universität Paderborn, Fakultät für Naturwissenschaften, Department Chemie, Warburger Str. 100, 33098 Paderborn, Germany

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Abstract: Gold chloride and $BF_3 \cdot$etherate were tested as Friedel–Crafts catalysts in the propargylation of electron-rich arenes: differences in reactivity of the catalysts can be used to achieve high selectivity either for monoalkylation or for multiple alkylation products. In the case of a macrocyclization towards a heterocalixarene, gold catalysts exhibited a pronounced selectivity, whereas *p*-toluenesulfonic acid as catalyst opened up a competing pathway to a structural isomer.

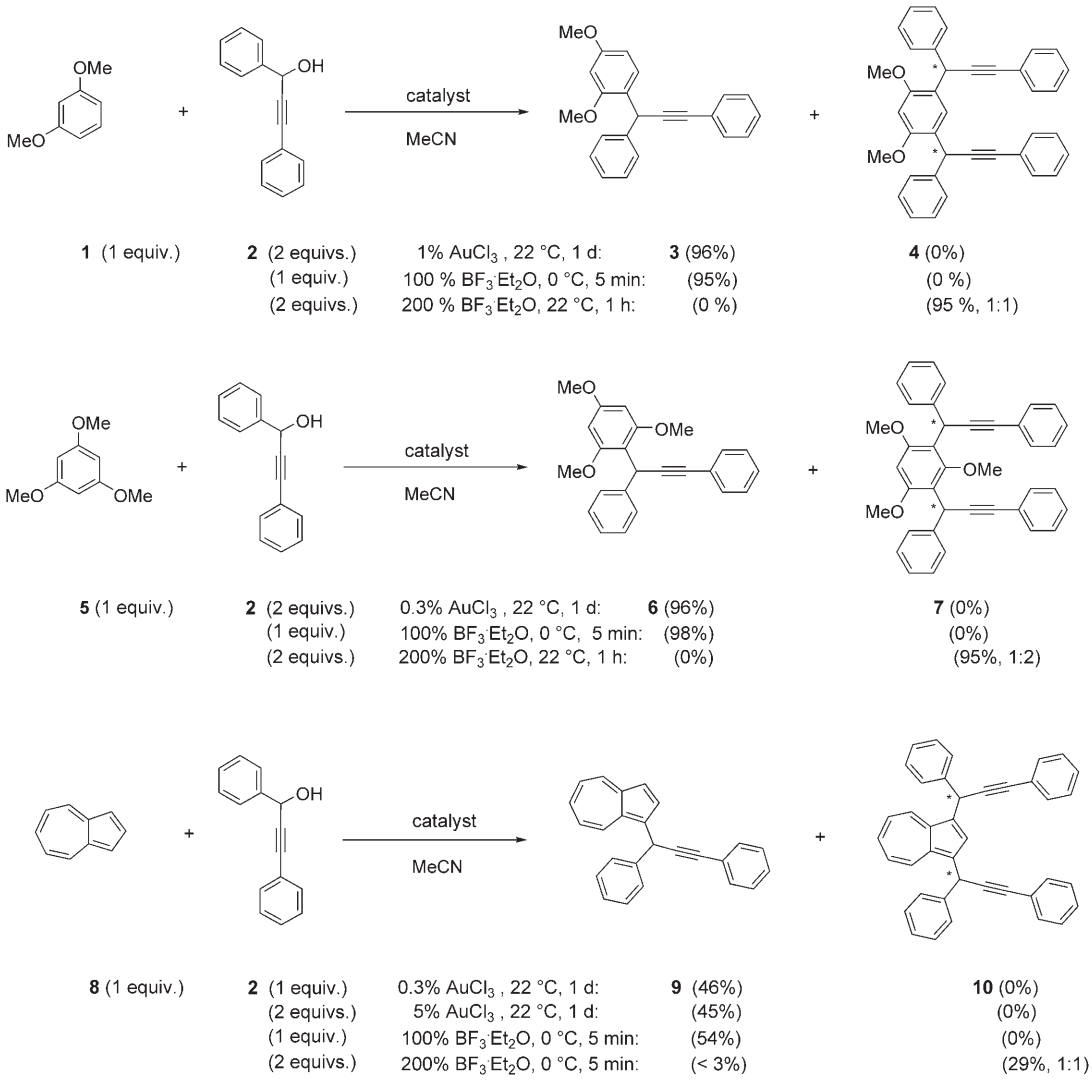
Keywords: Friedel–Crafts reaction; gold catalysis; Lewis acids; macrocycles

Introduction

Friedel–Crafts alkylations still belong to the most important C–C bond-coupling reactions. When alcohols or even olefins are applied as pre-electrophiles, this type of reaction is especially attractive from a practical point of view, profiting from the versatility and the availability of the starting materials and from the highly atom-economical[1] character. However, the fact that classical Friedel–Crafts catalysts, such as aluminium chloride or hydrogen chloride, generally are applied in at least stoechiometric amounts and are often not compatible with sensitive functional groups is regarded as a serious drawback. Therefore there is indeed a demand for new catalysts exhibiting outstanding activity in combination with high selectivity. Recently Uemura et al. reported on a dinuclear cationic ruthenium complex which is exceptional active for the propargylation of electron-rich arenes with propargylic alcohols as reagents.[2] In addition, Toste et al.[3] introduced the air- and moisture-tolerant Re-complex (dppm)Re(O)Cl_3 as an alternative catalyst for the propargylation. For the benzylation of arenes Beller et al. tested a variety of simple transition metal salts and also some Brønstedt acids: iron(III) chloride became the favourite catalyst, regularly leading to practically quantitative yields.[4] In the course of our studies on gold-catalyzed processes[5–7] we became interested in multifold Friedel–Crafts alkylations including cyclization reactions and tested the catalytic activity and selectivity of gold(III) chloride in comparison to classical Friedel–Crafts catalysts.

Results and Discussion

For the propargylation of electron-rich arenes we chose 1,3-dimethoxybenzene (**1**), 1,3,5-trimethoxybenzene (**5**) and azulene (**8**) as model substrates (Scheme 1), since all three compounds have been successfully monoalkylated with propargylic alcohol **2** in the presence of 5% of the Re or the Ru catalysts mentioned above (reported reaction conditions: 1–5 h at about 60 °C). As a result, just 0.3 to 1% of the gold catalyst are sufficient for achieving a 96% isolated yield of the monosubstitution products **3** and **6**. The reaction was performed at room temperature with 2 equivalents of propargylic alcohol **2**, thus demonstrating both an outstanding reactivity and a remarkable selectivity for the monosubstitution. In the case of the Ru catalyst the selectivity was purchased with the disadvantage of applying a 5-fold excess of the arenes **1** and **5**. However, with azulene **8** as a somewhat acid-sensitive arene component the gold catalyst warrants only a moderate yield of monosubstitution product **9**, compared to the 91% reported for the Ru catalyst. Most interestingly,

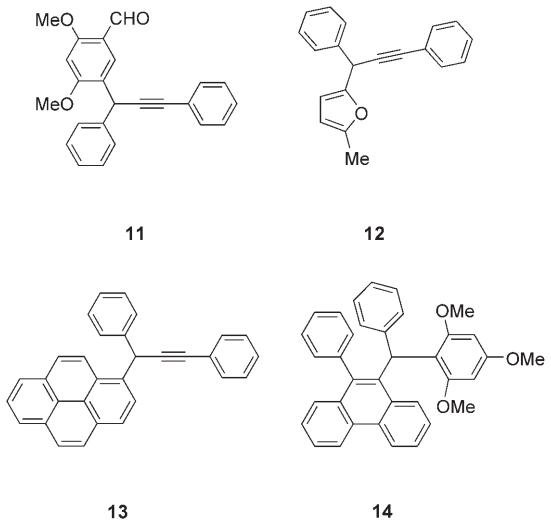


Scheme 1. Propargylation of electron-rich arenes.

the application of the classical Friedel–Crafts catalyst $BF_3 \cdot$etherate in stoichiometric amounts turned out to be the most versatile method for selectively accessing either the mono- or the dialkylation products: thus, 1 equivalent of propargylic alcohol **2** in combination with a reaction temperature of 0 °C and just 5 min reaction time were the conditions of choice for obtaining an optimum of monoalkylation products. Use of 2 equivalents of **2** with 1 h reaction time at room temperature led to clean formation of the bis-substitution products **4** and **7**, both as a mixture of the two diastereoisomers (**4** in the ratio 1:1 and **7** in the ratio 1:2). In the case of azulene **8** the bis-product formation was also successful, albeit with only moderate yield. Some other substrates were chosen to evaluate scope and limitations of the propargylation with gold chloride and with $BF_3 \cdot$etherate as catalysts: in the case of 2,4-dimethoxybenzaldehyde the gold catalyst is clearly superior, since the aldehyde functionality is tolerated and the monopropargylation product **11** is obtained in a 82% yield. In comparison, with $BF_3 \cdot$etherate the yield of **11** drops to less than 1% because of the formation of a complex mixture of by-products, even with a very short reaction time of less than 5 minutes.

Methylfuran was readily alkylated in the presence of $BF_3 \cdot$etherate to give **12** in excellent yield (Scheme 2), whereas pyrene reacts significantly more sluggishly: a 26% yield of the monoalkylation product **13** was obtained after 1 h reaction time, prompting us to suggest this less electron-rich polycyclic arene as a suitable benchmark substrate for further studies on the comparison of Friedel–Crafts catalysts.

As a chemical proof of its structure as well as in order to test its reactivity we performed a Pd-catalyzed annulation reaction with the crowded alkyne **6** resulting in the formation of the phenanthrene derivative **14** (Scheme 2).[8]



Scheme 2. Additional products from propargylation reactions and further transformations.

Single crystals of **4** were obtained by recrystallization of the mixture of diastereoisomers of **4** from methyl *tert*-butyl ether/petroleum ether. An X-ray crystal analysis[9] clearly showed the structure of *SS*-**4** in a centrosymmetrical space group (Figure 1).

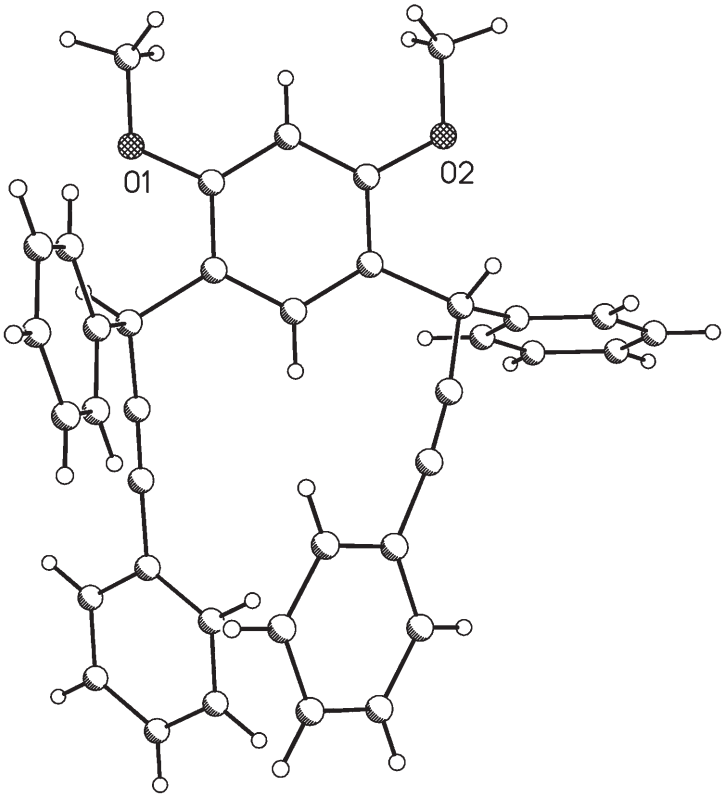


Figure 1. Molecular structure of the *SS*-enantiomer of **4**, hydrogen atoms omitted for the sake of clarity.

We became interested in the Friedel–Crafts alkylation of pyrroles as crucial steps in the synthesis of heterocalixarene **17**,[10] which resembles a tetradentate ligand related to porphyrins. Since the highly reactive pyrrole tends to polymerize under strongly acidic conditions,[11] we decided to apply *p*-toluenesulfonic acid and gold chloride as catalysts with moderate acidity. Building block **15** is readily synthesized by the reaction of pyridine-2,6-dicarboxylic acid esters with an excess of anisyl-Grignard reagent. The subsequent double condensation with pyrrole under catalysis by *p*-toluenesulfonic acid resulted in the formation of **16** in excellent yield. The macrocyclization to the target compound **17** proceeded smoothly with 3% $AuCl_3$ in refluxing acetonitrile. Applying 66% tetrachlorogold acid as catalyst slightly increased the yield to 43%.

Surprisingly, with *p*-toluenesulfonic acid as the catalyst an unprecedented competing reaction occurred, which favoured the formation of an isomer: **18** was identified by X-ray crystal structure analysis (Figure 2).[8] The single crystals were obtained from dichloromethane/methanol (3:1) in the presence of copper(II) acetate, which seemed to catalyze the crystallization process, but was not incorporated itself into the crystal lattice. The mechanistic rationale for the formation of **18** includes the benzylic cations **19** and **20** as reactive intermediates (Scheme 4), the latter being suitable for nucleophilic attack at the pyridine moiety. As a working hypothesis we assume that, in the case of the gold catalysts, the cyclization to indole **20** is inhibited, because the pyridine nitrogen might be coordinated to the metal.[12]

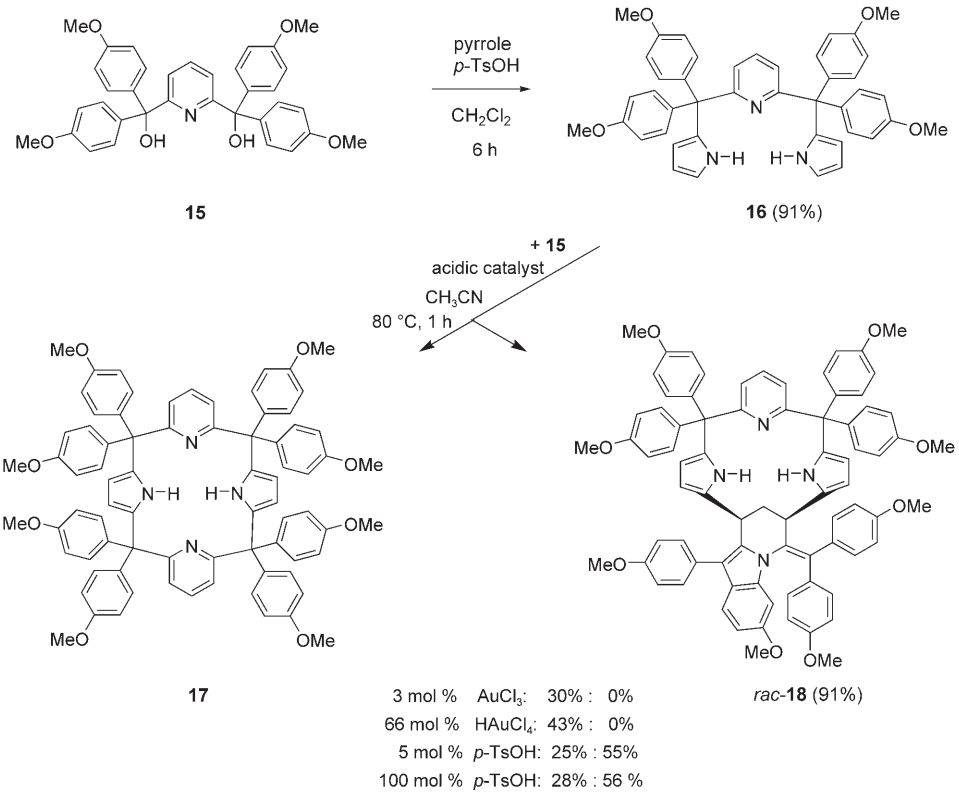
Conclusion

In summary, we have proven that gold chloride is a very mild, yet highly reactive Friedel–Crafts catalyst, which works already at rather low concentration and ensures a high selectivity for propargylation and benzylation reactions. On the other hand, $BF_3 \cdot$etherate in stoichiometric amounts allows us to drive multifold propargylations to the limit, enabling the synthesis of somewhat crowded products. Finally, the comparison of *p*-toluenesulfonic acid with gold chloride and with tetrachlorogold acid, respectively, as catalysts in a macrocylization reaction illustrates surprising differences in selectivity: the reasons should be clarified by ongoing studies.

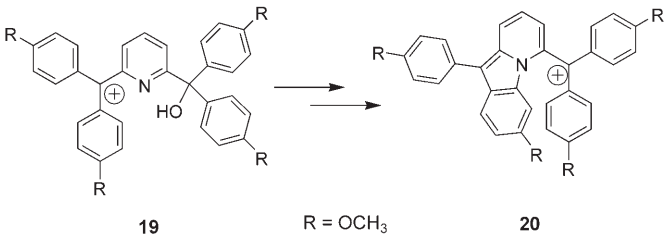
Experimental Section

General Remarks

Melting points (mp, uncorrected): Reichert Thermovar. IR: Perkin Elmer 841 and 983. NMR: Bruker DPX-200, WM-300, DRX-400, AM-500, DRX-600; ^{1}H NMR spectra were re-



Scheme 3. Au-catalyzed macrocyclization and its acid-catalyzed competing reaction.



Scheme 4. Reactive intermediates of the formation of **18**.

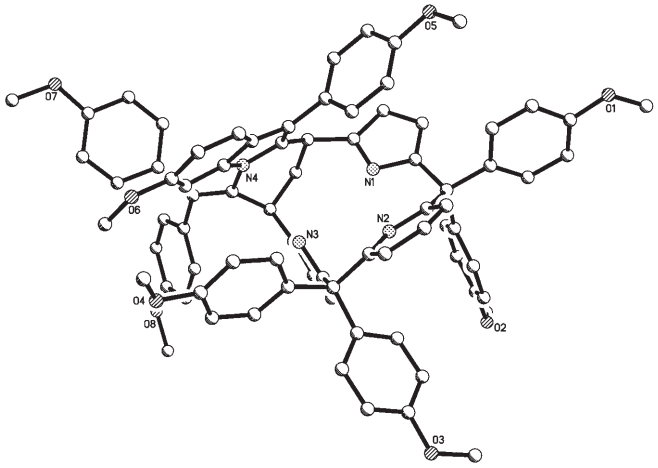


Figure 2. Molecular structure of **18**, hydrogen atoms omitted for the sake of clarity.

corded in $CDCl_3$ with TMS as the internal standard (see Supporting Information); ^{13}C NMR spectra were measured by using $CDCl_3$ as the solvent and the internal standard; assignments based on analysis of HMBC and HMQC spectra. MS: MAT 700 ITD (70 eV) and Varian MAT 311 A. For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV254" from "Macherey-Nagel" were used. Elemental analysis: Elementar/Hanau Vario EL. Spectroscopic data and elemental analyses for all mew compounds are presented in the Supporting Information.

2,4-Dimethoxy-1-(1,3-diphenylpropyn-3-yl)-benzene (3)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 138 mg (1.00 mmol) of 1,3-dimethoxybenzene (**1**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 142 mg (1.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 5 min stirring at 0 °C 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f= 0.16, 0.00). The fraction with R_f=0.16 was isolated and dried under vacuum (0.2 mbar, 50 °C); yield of **3**:[2,3] 311 mg (95%); colourless crystals with mp 117 °C.

2,4-Bis-(1,3-diphenylpropyn-3-yl)-1,5-dimethoxybenzene (4)

A mixture of 416 mg (2.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 138 mg (1.00 mmol) of 1,3-dimethoxybenzene (**1**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 284 mg (2.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 1 h stirring at room temperature 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.10, 0.00). The fraction with R_f=0.10 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford a colorless solid with mp 158–159 °C, which was identified as a 1:1 mixture of the diastereoisomers of **4**; yield: 493 mg (95%). Single crystals of the pure isomers are obtained by recrystallization from petrol ether/methyl *tert*-butyl ether (2:1).

2-(1,3-Diphenylpropyn-3-yl)-1,3,5-trimethoxybenzene (6)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 168 mg (1.00 mmol) of 1,3,5-trimethoxybenzene (**5**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 142 mg (1.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 5 min stirring at 0 °C 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f= 0.14, 0.00). The fraction with R_f=0.14 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford **5**;[2] yield: 350 mg (98%); colourless crystals; mp 121 °C.

2,4-Bis(1,3-diphenylpropyn-3-yl)-1,3,5-trimethoxybenzene (7)

A mixture of 416 mg (2.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 168 mg (1.00 mmol) of 1,3,5-trimethoxybenzene (**5**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 284 mg (2.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 1 h stirring at room temperature 10 mL MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.11, 0.00). The fraction with R_f=0.11 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford colorless crystals with mp 167 °C, which were identified as a 1:2 mixture of the diastereoisomers of **5**; yield: 521 mg (95%).

1-(1,3-Diphenylpropyn-3-yl)-azulene (9)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 128 mg (1.00 mmol) of azulene (**8**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 142 mg (1.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 5 min stirring at 0 °C 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.14, 0.00). The fraction with R_f=0.14 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford **9**;[2] yield: 117 mg (54%); dark blue crystals; mp 113 °C.

1,3-Bis-(1,3-diphenylpropyn-3-yl)-azulene (10)

A mixture of 416 mg (2.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 128 mg (1.00 mmol) of azulene (**8**) in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 284 mg (2.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 1 h stirring at room temperature 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f= 0.11, 0.00). The fraction with R_f=0.11 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford dark blue crystals with mp. 148 °C, which were identified as a 1:1 mixture of the diastereoisomers of **10**; yield:147 mg (29%).

2,4-Dimethoxy-5-(1,3-diphenylpropyn-3-yl)-benzaldehyde (11)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol and 166 mg (1.00 mmol) of 1,3-dimethoxybenzaldehyde in 10 mL of dry acetonitrile under argon was stirred at room temperature in a sealed tube for 3 days with 3 mg (10 μmol) of $AuCl_3$ as catalyst (1%). The solvent was evaporated and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.12, 0.00). The fraction with R_f=0.12 was isolated and dried under vacuum to afford **11**; yield: 297 mg (82%); slightly yellow crystals; mp 142–145 °C.

2-(1,3-Diphenylpropyn-3-yl)-5-methylfuran (12)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 411 mg (5.00 mmol) of 2-methylfuran in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 142 mg (1.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 5 min stirring at 0 °C 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.18, 0.00). The fraction with R_f=0.18 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford **12**;[2] yield: 247 mg (91%); slightly yellowish oil.

1-(1,3-Diphenylpropyn-3-yl)-pyrene (13)

A mixture of 208 mg (1.00 mmol) of 1,3-diphenyl-2-propyn-1-ol (**2**) and 202 mg (1.00 mmol) of pyrene in 10 mL of dry acetonitrile under argon was cooled to 0 °C and a solution of 142 mg (1.00 mmol) of $BF_3 \cdot Et_2O$ in 2 mL of acetonitrile was added under stirring within 1 min. After 1 h stirring at room tempera-

ture 10 mL of MeCN were added and the mixture was filtered through 4 g silica. The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.14, 0.00). The fraction with R_f=0.14 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford **13**; yield: 102 mg (26%); pale yellow crystals; mp 154 °C.

9-Phenyl-10-[phenyl-(2,4,6-trimethoxyphenyl)-methyl]phenanthrene (14)

A mixture of 816 mg (4.00 mmol) of iodobenzene, 358 mg (1.00 mmol) of propyne **6**, 1.11 g (8.00 mmol) of potassium carbonate, 645 mg (2.00 mmol) of tetra-*n*-butylammonium bromide, 12 mg (50 μmol) of palladium acetate and 26 mg (100 μmol) of triphenylphosphane in 10 mL of dry DMF was heated for 3 d under argon at 100 °C in a screw-capped tube. After addition of 50 mL of water and extraction with diethyl ether (3×50 mL) the combined organic layer was filtered through silica (4 g). The solvent was removed under vacuum and the residue was purified by flash chromatography (10 g of silica, petrol ether/methyl *tert*-butyl ether, 2:1, R_f=0.11, 0.00). The fraction with R_f=0.11 was isolated and dried under vacuum (0.2 mbar, 50 °C) to afford **14**; yield: 133 mg (26%); pale yellow crystals; mp 184 °C.

2,6-Bis[1,1-bis(4-methoxyphenyl)-1-hydroxymethyl]pyridine (15):

A mixture of magnesium (1.94 g, 80.0 mmol), 4-bromoanisole (11 mL 88 mmol) and iodine (50 mg) in freshly distilled THF (50 mL) was stirred under reflux for 15 min at 80 °C until all of the magnesium had reacted. After cooling down to 0 °C, solid dimethyl 2,6-pyridinedicarboxylate (3.12 g, 16.0 mmol) was added in 5 portions. The reaction mixture was allowed to warm to room temperature and was then refluxed at 80 °C for 1 h. At room temperature a 1 N aqueous solution of ammonium chloride (40 mL) was added, and the water layer was extracted with diethyl ether (2×50 mL). The combined organic layer was washed with water (2×50 mL) and brine (50 mL), dried with sodium sulfate and concentrated under vacuum. TLC of the crude product (petroleum ether/EtOAc 4:1, silica): R_f=0.71, 0.58, 0.09. The fraction with R_f=0.09 was isolated by flash chromatography (silica gel; petrol ether/EtOAc, 2:1) to give **15**; yield: 8.00 g (89%); colourless crystals; mp 140–141 °C.

2,6-Bis[1,1-bis(4-methoxyphenyl)-1-(2-pyrrolyl)-methyl]pyridine (16)

To a solution of tertiary alcohol **15** (563 mg, 1.00 mmol) and pyrrole (277 μL, 4.00 mmol) in CH_2Cl_2 (3 mL) was added *p*-toluenesulfonic acid hydrate (95 mg, 0.5 mmol). The reaction mixture was stirred at room temperature for 5.5 h, diluted with the same solvent (15 mL), washed with water (2× 15 mL) and with brine (10 mL), dried with sodium sulfate and concentrated under vacuum. TLC of the crude product (petroleum ether/EtOAc, 2:1; silica): R_f=0.50, 0.31, 0.19. The fraction with R_f=0.50 was isolated by flash chromatography and crystallized from methanol (5 mL) to give pure **16**; yield: 600 mg (91%); colourless crystals: mp 218 °C.

2,2,4,4,6,6,8,8-Octakis(4-methoxyphenyl)-1,5(2,6)dipyridina-3,7(2,5)-dipyrrolacyclooctaphane (17)

A mixture of **15** (84 mg, 0.15 mmol), **16** (99 mg, 0.15 mmol) and tetrachlorogold acid (30 mg, 0.1 mmol) in MeCN (2 mL) was refluxed at 120 °C for 1 h resulting in the formation of a crystalline precipitate. TLC of the crude product (petroleum ether/EtOAc, 2:1; silica): R_f=0.37, 0.24. The fraction with R_f= 0.24 was isolated by flash chromatography (eluent: petrol ether/EtOAc, 4:1) to give the macrocycle **17**; yield: 77 mg (43%); yellow solid; mp 242–243 °C.

Heterocyclophane 18

A chloroform solution (6.5 mL) of **15** (338 mg, 600 μmol), **16** (397 mg, 600 μmol) and *p*-toluenesulfonic acid hydrate (114 mg, 600 μmol) was heated at 80 °C for 1.5 h (under TLC control). The reaction mixture was washed with water, extracted with CH_2Cl_2, dried with sodium sulfate and concentrated under vacuum. TLC of the crude product (petroleum ether/EtOAc, 3:1; silica): R_f=0.55, 0.36. The fraction with R_f= 0.36 was isolated by flash chromatography (eluent: petroleum ether/EtOAc, 4:1) and recrystallized from MeCN (4 mL), the yellow precipitate was collected and identified as macrocycle **17** by ^{1}H NMR; yield: 200 mg (28%).

The filtrate was concentrated and the residue solidified after addition of 1 mL of methanol to give **18**; yield: 400 mg (56%); slightly yellow crystals; mp 190 °C. Crystals suitable for X-ray crystal structure analysis were obtained by crystallization from dichloromethane/methanol (3:1) in the presence of copper acetate.

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[9] Crystal structure analysis: A crystal of *rac*-**4** and **18** were each mounted on a glass capillary in perflourinated oil and measured in a cold gas flow. The intensity data were measured with a Bruker AXS area detector ($Mo_{K\alpha}$ radiation), $\lambda = 0.71073$ Å, graphite monochromator. *rac*-**4**: ($C_{38}H_{30}O_2$): monoclinic, $P2_1/c$, $a = 15.268(6)$, $b = 7.833(2)$, $c = 23.767(9)$ Å, $\beta = 93.213(7)^\circ$, $V = 2838(2)$ Å^3, $T = 213$ (2) K, $Z = 4$, $\mu = 1.214$ mm^{-1}. A total of 10328 reflections were collected ($2\theta_{max} = 50^o$), 4595 independent, 5863 observed ($F_o > 4\sigma(F_o)$), 397 parameters; *R1* = 0.0746, *wR2* (all data) = 0.2084. **18** ($C_{78}H_{68}N_4O_8 \cdot 2\,CH_3OH \cdot 0.5\,CH_2Cl_2$): triclinic, space group $P\bar{1}$, $a = 12.5613(6)$, $b = 15.0128(7)$, $c = 19.5558(8)$ Å, $\alpha = 98.184(1)$, $\beta = 91.140(1)$, $\gamma = 110.228(1)^\circ$, $V = 3415.6(3)$ Å^3, $T = 120(2)$ K, $Z = 2$, $\mu = 0.12$ mm^{-1}. 34447 intensities collected $1.05 > \theta > 28.08^\circ$, h ±16, k ±19, l ±25, 16489 independent reflections, $R_{int} = 0.034$. The asymmetric unit contains one molecule of **18** and two methanol solvent molecules. One additional CH_2Cl_2 solvent molecule per unit cell was severely disordered showing only diffuse electron density peaks which could not sufficiently be modelled. Treating the data set with the SQUEEZE modul of PLATON[13] resulted in smooth refinement, *R1* ($I > 2\sigma(I)$) = 0.058, *wR2* (all data) = 0.154, $S = 0.987$, min/max height in final ΔF-map –0.26/0.48 e/Å^3. Structure solution by direct methods (SHELXS 97), refinement against F^2 with all measured reflections (SHELXTL 97). The positions of the H atoms for *rac*-**4** were calculated, for **18** they were derived from difference Fourier maps. For both structures H atoms were refined iostropically with a riding model at idealized positions. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 285371 for *rac*-**4** and CCDC 286814 for **18**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].

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