Polycyclic Aromatic Compounds, 2[◇]

A General Synthesis of Disubstituted Rubicenes

Mario Smet, Rameshwer Shukla, Livia Fülöp, and Wim Dehaen*

Department of Chemistry, University of Leuven,
Celestijnenlaan 200F, B-3001 Leuven (Heverlee), Belgium,
Fax: (internat.) + 32-16/327990
E-mail: wim.dehaen@chem.kuleuven.ac.be

Received June 25, 1998

Keywords: Rubicenes / Cyclization / Polycyclic aromatic hydrocarbons / Arenes / Synthetic methods

The synthesis of novel disubstituted rubicenes **1a–k** is described. Starting from 1,5-dichloroanthraquinone and aryllithium reagents **3**, the diol adducts **4** are reduced and the resulting diarylanthracenes **5** are cyclized to afford the title compounds in fair to good overall yield.

Introduction

Rubicene (**1a**) is an interesting heptacyclic arene which has been known for over 100 years.[2] Rubicene has been studied for its electrochemically generated luminescence.[3] It has a red color and yellow fluorescence and a high ISC rate[4]. In the early syntheses from either diphenic acid,[2] fluorene,[5] or thiofluorenone dimer,[6] rubicene (**1a**) was formed under drastic conditions in low yield. In 1990, Langhals et al. reported an improved synthesis[7] of rubicene (**1a**) from fluorenone and magnesium. Some 5-monosubstituted and 5,12-disubstituted derivatives were also prepared by electrophilic substitution on the rubicene nucleus.[7] Generally, the purification of these derivatives by chromatography is very difficult, because of their low solubility in all common organic solvents.

Results and Discussion

We wanted a convenient method to obtain 5,12-disubstituted rubicenes in order to use them as building blocks in supramolecular chemistry. In our first experiments towards the synthesis of these compounds, we used the Langhals method for obtaining rubicene (**1a**) and tried to prepare its acylated derivatives by using the Friedel−Crafts reaction. However, model reactions with stearoyl chloride/aluminium chloride under several conditions only gave the 5-monoacylated derivative as the sole product. Attempted formylation of rubicene (**1a**) using the Vielsmeier reagent did not give any conversion, even after prolonged reflux of the reaction mixture. Thus, an alternative method was required to obtain the disubstituted arenes **1**.

We decided to adapt a rubicene synthesis described in 1958 by Clar et al.[8] This synthesis starts from commercial 1,5-dichloroanthraquinone (**2**). Addition of phenyllithium (**3a**) gives a diol **4a**, which can be reduced with sodium hypophosphite/potassium iodide[9] to the anthracene **5a** and cyclized (KOH, quinoline) to afford rubicene (**1a**) in good yield. We reasoned that, by using substituted aryllithium compounds **3**, we could place the substituents at the required positions. Furthermore, the intermediates **4** are more soluble than the rubicenes **1**, allowing an easier purification at this stage. The anthracenes **5** are not very soluble in organic solvents, but they are formed almost quantitatively and can be used in the next cyclization step without the need for further purification. Thus, the methoxyaryllithium reagents **3b−d** were added at −78°C to the anthraquinone **2** and the resulting *trans*-diols **4b−d** were formed in good yields. The yield was significantly lower for the 2-methoxyphenyl derivative **4d**, probably because of steric hindrance of the chlorine and methoxy functions. This was confirmed by the isolation of the monoadduct **6**. The further steps to anthracenes **5b−d** and 5,12- and 7,14-dimethoxyrubicenes **1b−d** were uneventful. As could be expected, in the case of **1c**, a mixture of regioisomers was formed. The components of this mixture could not be separated with either fractional crystallization or chromatography. From the ^{1}H-NMR spectrum, it could be concluded that the 4,11- and 6,13-dimethoxy derivatives **1c** and **1c′** were formed in a ratio of about 2:1.

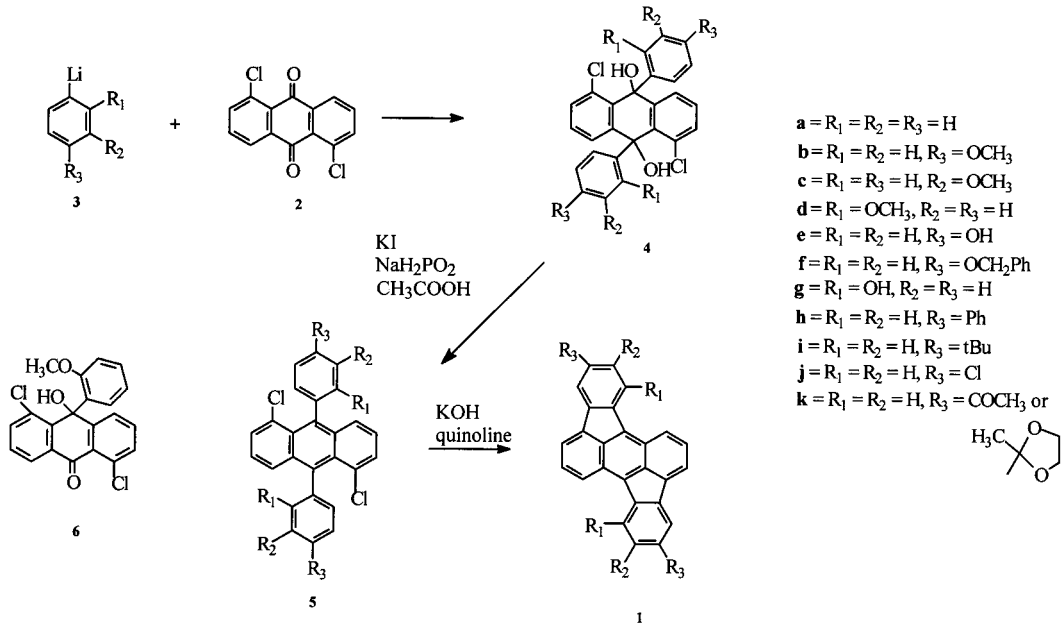
Demethylation of **1b** with BBr_3 gave 5,12-dihydroxyrubicene (**1e**). Realkylation of **1e** with benzyl bromide yielded the ether **1f**. The analogous 7,14-dimethoxyrubicene (**1d**) could not be demethylated by the BBr_3 treatment, but the dihydroxyrubicene **1g** did form under drastic conditions, using pyridinium chloride at 210°C. Realkylation of **1g** with benzyl bromide was not possible under the same conditions as for **1e**, probably because of steric hindrance in the rubicene bay region. The rubicene **1d** is, for the same reason, more soluble than **1b**.

It was also possible to obtain 5,12-diphenyl- and 5,12-bis(*tert*-butyl)-substituted rubicenes **1h**, **1i** by using the cor-

[◇] Part 1: Ref.[1]

  1434−193X/98/1212−2769 $ 17.50+.50/0

Scheme 1



responding aryllithium compounds **3h**, **3i**. The 5,12-disubstituted rubicene **1h** is an isomer of the 6,13-disubstituted derivative which was prepared by Langhals[7] using the Friedel−Crafts alkylation of rubicene (**1a**), making the two methods complementary in this case.

5,12-Dichlororubicene (**1j**) could be prepared in good overall yield from 4-chlorophenyllithium (**3j**). The dehydrochlorination of the diarylanthracene **5j** was regioselective and left the chloro functions at the 5 and 12 positions of **1j** intact.

Direct chlorination of rubicene (**1a**) under drastic conditions (*ortho*-dichlorobenzene, 4 equivalents of cupric chloride, 48 h reflux) gave a mixture which, according to the mass spectra, contained the starting rubicene (**1a**), a monochlorinated and a dichlorinated rubicene. No attempt was made to isolate the chlorinated rubicenes from this mixture. Finally, 5,12-diacetylrubicene (**1k**) could be obtained from protected aryllithium **3k**, without noticable aldol condensation occuring in the cyclization step from the deprotected anthracene **5k**.

Conclusion

In summary, a new and general synthesis of 5,12-disubstituted rubicenes was developed with a range of substituents, comprising alkoxy, hydroxy, chloro, alkyl, aryl, and acetyl. The method was found to be superior or complementary to the direct electrophilic substitution of rubicene (**1a**). Some 7,14-disubstituted rubicenes were also prepared using the former method. They are more soluble than their 5,12-disubstituted isomers but the synthesis is less effective in the first step for steric reasons.

The *Katholieke Universiteit* Leuven, the *FWO-Vlaanderen*, and the *Ministerie voor Wetenschapsbeleid* are thanked for their continuing financial support. M. S. thanks the *FWO-Vlaanderen* for a predoctoral fellowship. R. S. is a junior postdoctoral fellow of the *Onderzoeksfonds KULeuven*. *Kurt Desmedt* is thanked for some preliminary studies on the synthesis of rubicene (**1a**).

Experimental Section

General Methods: All the materials were obtained from ACROS Organics and were used without further purification. The solvents were dried using standard methods. − Description of ^{1}H-, ^{13}C-NMR, IR spectroscopy, and mass spectrometry have previously been published.[1] The absorption spectra were taken with a Perkin-Elmer Lambda 2 UV/Vis spectrophotometer. The steady-state fluorescence spectra were measured with an SLM-8000C spectrofluorimeter in L-format.

General Procedure for the Synthesis of the Diaryldihydroxydihydroanthracenes **4a**−**d, h**−**l**. − **4i**: A stirred solution of 4-(1,1-dimethylethyl)phenyllithium (**3i**) in diethyl ether (200 ml), which was prepared in situ from 4-bromo(1,1-dimethylethyl)benzene (16 g, 75 mmol) and *n*-butyllithium (70 mmol, 28 ml, 2.5 M solution in hexane), was treated at room temperature under an argon blanket with 1,5-dichloroanthraquinone (**2**) (7 g, 25 mmol). The resulting mixture was stirred for 1 h. After aqueous workup (100 ml), the organic layer was separated and the water phase was extracted with diethyl ether (2 × 200 ml). The organic layers were then dried and concentrated in vacuo. This gave a residue, which was crystallized from benzene to afford 10.6 g (78%) of white crystals, m.p. 204°C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 [s, 18 H, $(CH_3)_3C$], 4.53 (br. s, 2 H, OH), 7.16 (dd, J_o = 9 Hz, J_m = 1 Hz, 2 H, 2,6-H), 7.21 (t, J = 9 Hz, 2 H, 3,7-H), 7.24 [m, 8 H, $CHCHCC(CH_3)_3$], 7.89 (dd, J_o = 9 Hz, J_m = 1 Hz, 2 H, 4,8-H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 1.20, 31.25, 31.29, 34.32, 124.85, 125.03, 125.66, 127.92, 129.05, 130.58, 132.51, 134.20, 142.66, 143.86, 149.69. − IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3490 (OH). − MS (70eV); *m/z* (%): 544 [M^+], 411 (100), 57 (88) [$(CH_3)_3C^+$].

4a was prepared according to the general procedure from phenyllithium (**3a**) (70 mmol) and **2** (25 mmol) in 75% yield after crystallization from benzene, m.p. 273°C (ref.:[9] 273−274°C). − ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 6.05 (s, 2 H, OH), 7.18 (m, 2

H, *p*-H), 7.20 (dd, J_o = 7.5 Hz, J_m = 1 Hz, 2 H, 2,6-H), 7.25 (t, J = 7.5 Hz, 2 H, 3,7-H), 7.29 (br. t, J = 7.5 Hz, 4 H, *m*-H), 7.42 (br. d, J = 7.5 Hz, 4 H, *o*-H).– ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 72.60, 126.01, 126.19, 127.67, 128.53, 128.80, 130.20, 133.05, 134.69, 144.31, 147.81. – IR (KBr): ṽ [cm^{-1}] = 3491 (OH) – MS (70eV); *m/z* (%): 432 (5) [M$^+$], 415 (7) [M$^+$ – OH], 398 (11) [M$^+$ – Cl], 355 (100).

4b was prepared from 4-methoxyphenyllithium (**3b**) (70 mmol) and **2** (6.9 g, 25 mmol) in 57% yield after column chromatography (SiO$_2$, CH$_2$Cl$_2$/diethyl ether, 9:1), m.p. 206°C. – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.72 (s, 6 H, OCH$_3$), 5.96 (s, 2 H, OH), 6.83 (d, J = 9 Hz, 4 H, C*H*COCH$_3$), 7.17 (dd, J_o = 9 Hz, J_m = 1 Hz, 2 H, 2,6-H), 7.23 (t, J = 9 Hz, 2 H, 3,7-H), 7.28 (d, J = 9 Hz, 4 H, C*H*CHCOCH$_3$), 7.53 (dd, J_o = 9 Hz, J_m = 1 Hz, 2 H, 4,8-H). – IR (KBr): ṽ [cm^{-1}] = 3495 (OH). – MS (70eV); *m/z* (%): 492 [M$^+$], 457 (8) [M$^+$ – Cl], 385 (100).

4c was prepared from 3-methoxyphenyllithium (**3c**) (100 mmol) and **2** (5.93 g, 21 mmol) in dry THF at −78°C under argon. After addition of **2**, the solution was allowed to warm to room temperature. After stirring for 1 h, usual workup led to a residue which was crystallized from benzene to give **4c** (67% yield), m.p. 210°C. – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.68 (s, 6 H, OCH$_3$), 6.05 (s, 2 H, OH), 6.76 [dd, J = 8 Hz, J = 2 Hz, 2 H, *H*CC(OCH$_3$)CHCCOH], 6.94 (br. d, J = 8 Hz, 2 H, *H*CCCOH), 7.00 (br. s, 2 H, *H*CCCOH), 7.19 (t, J = 8 Hz, 2 H, *H*CCHCCOH), 7.21 (dd, J_o = 7 Hz, J_m = 1 Hz, 2 H, 2,6-H), 7.27 (t, J = 7 Hz, 2 H, 3,7-H), 7.57 (dd, J_o = 7 Hz, J_m = 1 Hz, 2 H, 4,8-H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 54.83, 72.51, 111.35, 112.20, 118.45, 128.29, 128.78, 130.20, 133.07, 134.51, 144.20, 149.59, 158.77. – IR(KBr): ṽ [cm^{-1}] = 3490 (OH). – MS (70eV); *m/z* (%): 492 (57) [M$^+$], 475 (11), [M$^+$ – OH], 387 (88), 385 (100).

4d was prepared from 2-methoxyphenyllithium (**3d**) (53 mmol) and **2** (5 g, 18 mmol), according to the general procedure, in 19% yield after column chromatography (R_f = 0.23) (SiO$_2$, CH$_2$Cl$_2$/diethyl ether, 9:1), m.p. 215°C.– ^{1}H NMR (250 MHz, [D$_6$]DMSO, 385 K): δ = 3.37 (s, 6 H, OCH$_3$), 5.91 (s, 2 H, OH) 6.94 (m, 4 H, *o*, *p*-H), 7.11 (m, 4 H, 2,3,6,7-H), 7.23 (td, 2 H, J_o = 8 Hz, J_m = 1.5 Hz, C*H*CHCOCH$_3$), 7.32 (m, 2 H, 4,8-H), 7.74 (br. d, J = 8 Hz, 2 H, C*H*CCOCH$_3$). – IR (KBr): ṽ [cm^{-1}] = 3492 (OH). – MS (70eV); *m/z* (%): 492 [M$^+$].

6 was also isolated from the reaction mixture (R_f = 0.68) in 31% yield, m.p. 254°C (dec.). – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.05 (s, 3 H, OCH$_3$), 6.68 (dd, J = 7.8 Hz, J = 0.9 Hz, 1 H, C*H*COCH$_3$), 6.87 (s, 1 H, OH), 7.07 (td, J = 7.5 Hz, J = 0.9 Hz, 1 H, C*H*CHCHCOCH$_3$), 7.21 (dt, J = 7.8 Hz, J = 1.8 Hz, 1 H, C*H*CHCOCH$_3$) 7.43 (dd, J = 7.5 Hz, J = 2 Hz, 1 H, 2-H), 7.45 (t, J = 7.5 Hz, 1 H, 3-H), 7.47 (t, J = 8.0 Hz, 1 H, 7-H), 7.48 (m, 1 H, 4-H), 7.56 (dd, J = 8.0 Hz, 1 H, 6-H), 8.07 (dd, J = 8.0 Hz, 1 H, 8-H), 8.27 (dd, J = 7.5 Hz, J = 1.8 Hz, 1 H, C*H*CCOH). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 54.74, 69.60, 112.07, 119.89, 124.86, 125.56, 127.88, 128.23, 128.77, 128.81, 130.28, 130.87, 131.65, 132.37, 133.16, 134.44, 135.73, 141.44, 151.65, 154.15, 182.25. – MS (70eV); *m/z* (%): 384 [M$^+$]

4h was prepared from 4-biphenyllithium (**3h**) (21.6 mmol) and **2** (2.67 g, 10 mmol) in 75% yield after column chromatography (SiO$_2$, CH$_2$Cl$_2$), m.p. 244°C. – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.51 (s, 2 H, OH), 7.27 (dd, J_o = 8 Hz, J_m = 1.5 Hz, 2 H, 2,6-H), 7.30 (m, 2 H, 4′-H), 7.34 (t, J = 8 Hz, J = 1.5 Hz, 2 H, 3,7-H), 7.37 (m, 4 H, 3′ and 5′-H), 7.47 (m, 8 H, *H*CC*H*CCOH), 7.55 (m, 4 H, 2′ and 6′-H), 8.01 (dd, J = 8 Hz, J = 1.5 Hz, 2 H, 4,8-H). – ^{13}C-NMR (100 MHz, [D$_6$]DMSO): δ = 74.4, 126.5, 126.8, 127.0, 127.3, 128.0, 128.7, 129.5, 130.9, 137.6, 134.1, 139.9, 140.3, 142.4, 146.1. – IR(KBr): ṽ [cm^{-1}] = 3496 (OH). – MS (70eV); *m/z* (%): 584 (44) [M$^+$], 431 (100).

4j: To a solution of 4-bromochlorobenzene (14.25 g, 75 mmol) in dry diethyl ether (200 ml) was added dropwise a solution of 70 mmol *n*-butyllithium in hexane (30 ml) during 30 min. After stirring for 15 min, **2** (6.9 g, 25 mmol) was added and the solution was allowed to stand for 1 h. After usual workup, **4j** was obtained in 43% yield after column chromatography (SiO$_2$, CH$_2$Cl$_2$/diethyl ether, 9:1), m.p. 278°C. – ^{1}H NMR (400MHz, [D$_6$]DMSO): δ = 6.23 (s, 2 H, OH), 7.25 (dd, J_o = 7.5 Hz, J_m = 1.5 Hz, 2 H, 2,6-H), 7.30 (t, J = 7.5 Hz, 2 H, 3,7-H), 7.39 (m, 8 H, *HCH*CCCl), 7.49 (dd, J_o = 7.5 Hz, J_m = 1.5 Hz, 2 H, 4,8-H). – ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 72.55, 127.83, 127.87, 128.46, 129.19, 130.51, 130.92, 133.05, 134.24, 143.82, 146.82. – IR (KBr): ṽ [cm^{-1}] = 3490 (OH). – MS (70eV); *m/z* (%): 502 (6%) [M$^+$], 467 (9) [M$^+$ – Cl], 391 (100), 278 (34).

4k was prepared from 4-(2-methyldioxolan-2-yl)phenyllithium (**3k**) (41 mmol) and **2** (5.2 g, 19 mmol) in 56% yield after column chromatography (SiO$_2$, CH$_2$Cl$_2$/diethyl ether, 9:1), m.p. 204°C. – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.54 (s, 6 H, CH$_3$), 3.70 and 3.95 (m, each 4 H, OCH$_2$CH$_2$O), 6.06 (s, 2 H, OH), 7.19 (dd, J_o = 7.5 Hz, J_m = 1 Hz, 2 H, 2,6-H) 7.26 (t, J = 7.5 Hz, 2 H, 3,7-H), 7.38 (m, 8 H, C*HCH*CCCH$_3$), 7.50 (dd, J_o = 7.5 Hz, J_m = 1 Hz, 2 H, 4,8-H). – IR (KBr): ṽ [cm^{-1}] = 3494 (OH). – MS (70eV); *m/z* (%) : 604 (1) [M$^+$], 589 (100) [M$^+$ – CH$_3$], 545 (16) [M$^+$ – CH$_3$Cl].

General Procedure for the Synthesis of 9,10-Diaryl-1,5-dichloroanthracenes **5a–d, h–k**: The appropriate diol **4** (2 mmol) was suspended in a solution of sodium iodide (3 g) and sodium hypophosphite monohydrate (3 g) in acetic acid (20 ml) and refluxed for 30 min. The suspension was allowed to cool and the yellowish precipitate was filtered off and washed with water (3 × 10 mL) and methanol (3 × ml). The product was protected from light and dried in vacuo. If desired, the anthracenes **5a–n** could be further purified by Soxhlet extractive crystallization, but the crude products gave the same yields in the subsequent cyclization to the rubicenes. Generally, the solubilities of the anthracenes **5** were insufficient to take NMR spectra, however, in the case of **5i** the ^{1}H-NMR spectra could be obtained. The compounds were characterized by mass spectrometry and IR spectroscopy. In all the cases the OH band disappeared in the IR spectra.

5i was obtained according to the general procedure in 89% yield, m.p. > 350°C. – ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.46 [s, 18 H, C(C*H*$_3$)$_3$], 7.16 (dd, $J_{3,4}$ = 9.1 Hz, $J_{2,3}$ = 7.1 Hz, 2 H, 3,7-H), 7.30 [m, 4 H, C*H*CC(CH$_3$)$_3$], 7.47 (dd, $J_{2,3}$ = 7.1 Hz, $J_{2,4}$ = 1.1 Hz, 2 H, 2,6-H), 7.50 [m, 4 H, C*H*CHCC(CH$_3$)$_3$], 7.67 (dd, $J_{3,4}$ = 9.1 Hz, $J_{2,4}$ = 1.1 Hz, 2 H, 4,8-H). – MS (70eV); *m/z* (%): 510 (31) [M$^+$], 419 (9), 327 (20), 57 (100) [(CH$_3$)$_3$C$^+$].

5a was obtained according to the general procedure in 92% yield, m.p. 239°C (ref.:[9] 240–241°C). – MS (70eV); *m/z* (%): 398 (100) [M$^+$], 363 (45) [M$^+$ – Cl], 328 (56) [M$^+$ – 2 Cl].

5b was obtained according to the general procedure in 95% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 458 [M$^+$], 423 (41) [M$^+$ – Cl], 388 (58) [M$^+$ – 2 Cl].

5c was prepared as described in the general procedure in 94% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 458 [M$^+$], 423 (28) [M$^+$ – Cl], 388 (32) [M$^+$ – 2 Cl].

5d was obtained according to the general procedure in 90% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 458 [M$^+$].

5h was prepared according to the general procedure in 92% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 550 (72) [M$^+$], 515 (35) [M$^+$ – Cl], 480 (100) [M$^+$ – 2 Cl].

5j was prepared as described in the general procedure in 94% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 468 (99) [M^+], 396 (75) [M^+ – 2 Cl], 326 (100) [M^+ – 4 Cl].

5k was obtained according to the general procedure in 90% yield, m.p. > 350°C. – MS (70eV); *m/z* (%): 482 (13) [M^+], 405 (8), 326 (17).

General Procedure for the Synthesis of the Disubstituted Rubicenes **1a–k**: A suspension of 2 mmol of the appropriate anthracene **5** and excess (3 g) of KOH in quinoline (20 ml) was refluxed until the anthracene **5** had reacted completely, as shown on TLC (SiO_2/toluene). This took usually about 10–15 min. After completion of the reaction, the mixture was cooled down and poured into dilute hydrochloric acid (1 M, 200 ml). The precipitate was filtered off and washed three times with diluted hydrochloric acid (1 M, 50 ml). The product was dried and purified by Soxhlet extractive crystallization with toluene.

1a was prepared according to the general procedure in 36% yield, m.p. 304°C (ref.:[7][8] 304°C) The ^{1}H-NMR, absorption and fluorescence spectra were found to be identical with those given by Langhals et al.[7]

1i was prepared according to the general procedure in 46% yield, m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 1.45 [s, 18 H, $C(CH_3)_3$], 7.54 (dd, $J_{6,7}$ = 8.2 Hz, $J_{4,6}$ = 1 Hz, 2 H, 6,13-H), 7.91 (dd, $J_{2,3}$ = 7 Hz, $J_{1,2}$ = 9 Hz, 2 H, 2,9-H), 8.23 (d, $J_{4,6}$ = 1 Hz, 2 H, 4,11-H), 8.34 (dd, $J_{2,3}$ = 7 Hz, $J_{1,3}$ = 1 Hz, 2 H, 3,10-H), 8.42 (d, $J_{6,7}$ = 8.2 Hz, 2 H, 7,14-H), 8.75 (dd, $J_{1,2}$ = 9 Hz, $J_{1,3}$ = 1 Hz, 2 H, 1,8-H). – UV ($CHCl_3$): λ_{max} [nm] = 320, 359, 379, 508, 547. – Fluorescence ($CHCl_3$): λ_{max} [nm] = 577. – IR: $\tilde{\nu}$ [cm^{-1}] = 3032, 3043 (sp^2C–H), 2948, 2887, 2859 (sp^3C-H), 1607 (C=C). – MS (70eV); *m/z* (%): 438 (100) [M^+], 423 (100) [M^+ – CH_3]. – $C_{28}H_{18}O_2$ (438.61): calcd. C 93.11, H 6.89; found C 92.89; H 7.10.

1b was prepared according to the general procedure in 65% yield, m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 3.95 (s, 6 H, OCH_3), 7.06 (dd, $J_{6,7}$ = 8.4 Hz, $J_{4,6}$ = 2.5 Hz, 2 H, 6,13-H), 7.81 (d, $J_{4,6}$ = 2.5 Hz, 2 H, 4,11-H), 7.88 (dd, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 6.5 Hz, 2 H, 2,9-H), 8.30 (d, $J_{2,3}$ = 6.5 Hz, 2 H, 3,10-H), 8.40 (d, $J_{6,7}$ = 8.4 Hz, 2 H, 7,14-H), 8.74 (d, $J_{1,2}$ = 8.6 Hz, 2 H, 1,8-H). – UV ($CHCl_3$): λ_{max} [nm] = 329, 380,535.5, 565. – Fluorescence ($CHCl_3$): λ_{max} [nm] = 621. – IR: $\tilde{\nu}$ [cm^{-1}] = 3048 (sp^2C–H), 2934 (sp^3C–H), 1609 (C=C). – MS (70eV); *m/z* (%): 386 [M^+]. – $C_{28}H_{18}O_2$ (486.44): calcd. C 87.03, H 4.69; found C 87.41, H 4.70.

An unseparable mixture of **1c** and **1c′** in a ratio of about 2:1 was formed according to the general procedure in a total yield of 62%, m.p. > 300°C. – IR: $\tilde{\nu}$ [cm^{-1}] = 3023, 3015 (sp^3C–H), 2998, 2979, 2935, 2834 (sp^2C–H). – MS (70eV); *m/z* (%): 386 [M^+]. – **1c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.12 (s, 6 H, OCH_3), 6.97 (d, $J_{5,6}$ = 8.2 Hz, 2 H, 5,12-H),7.43 (dd, $J_{5,6}$ = 8.2 Hz, $J_{6,7}$ = 7.4 Hz, 2 H, 6,13-H), 7.75 (dd, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 6.6 Hz, 2 H, 2,9-H), 7.99 (d, $J_{6,7}$ = 7.4 Hz, 2 H, 7,13-H), 8.26 (d, $J_{2,3}$ = 6.6 Hz, 2 H, 3,10-H), 8.54 (d, $J_{1,2}$ = 8.6 Hz, 2 H, 1,8-H). – **1c′**: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.00 (s, 6 H, OCH_3), 6.91 (dd, $J_{5,6}$ = 8.3 Hz, $J_{5,7}$ = 2.3 Hz, 2 H, 5,12-H), 7.72 (dd, $J_{1,2}$ = 8.6 Hz, $J_{2,3}$ = 6.8 Hz, 2 H, 2,9-H), 7.83 (d, $J_{4,5}$ = 8.3 Hz, 2 H, 4,11-H), 7.86 (d, $J_{5,7}$ = 2.3 Hz, 2 H, 7,14-H), 7.87 (d, $J_{2,3}$ = 6.8 Hz, 2 H, 3,10-H), 8.54 (d, $J_{1,2}$ = 8.6 Hz, 2 H, 1,8-H).

1d was prepared according to the general procedure in 67% yield, m.p. > 300°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.23 (s, 6 H, OCH_3), 7.08 (d, $J_{5,6}$ = 8 Hz, 2 H, 6,13-H), 7.42 (t, *J* = 8 Hz, 2 H, 5,12-H), 7.71 (d, $J_{4,5}$ = 8 Hz, 2 H, 4,11-H), 7.75 (dd, $J_{1,2}$ = 9 Hz, $J_{2,3}$ = 6 Hz, 2 H, 2,9-H), 8.08 (d, $J_{2,3}$ = 6 Hz, 2 H, 3,10-H), 9.52 (d, $J_{1,2}$ = 9 Hz, 2 H, 1,8-H). – UV ($CHCl_3$): λ_{max} [nm] = 303, 359, 378, 518, 551(sh). – Fluorescence ($CHCl_3$): λ_{max} [nm] = 578. – IR: $\tilde{\nu}$ [cm^{-1}] = 3040 (sp^2C–H), 2917 (sp^3C–H), 1590 (C=C). – MS (70eV); *m/z* (%): 386 (89) [M^+]. – $C_{28}H_{18}O_2$ (486.44): calcd. C 87.03, H 4.69; found C 87.38, H 4.72.

1e: 5,12-Dimethoxyrubicene (**1b**) (200 mg, 0.5 mmol) was suspended in dichloromethane (40 ml). The flask was closed with a septum through which BBr_3 (0.12 ml, 1.3 mmol) was added. After 24 h stirring, water (80 ml) was added and the mixture was shaken vigorously. The precipitate was collected by filtration. The product was washed with water (3 × 5 ml) and dichloromethane (3 × 5 ml). Yield: 170 mg; 92%, m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 6.91 (dd, $J_{6,7}$ = 8 Hz, $J_{4,6}$ = 1 Hz, 2 H, 6,13-H), 7.53 (d, $J_{4,6}$ = 1 Hz, 2 H, 4,11-H), 7.82 (dd, $J_{1,2}$ = 8.8 Hz, $J_{2,3}$ = 7 Hz, 2 H, 2,9-H), 8.17 (d, $J_{2,3}$ = 7 Hz, 2 H, 3,10-H), 8.26 (d, $J_{6,7}$ = 8 Hz, 2 H, 7,14-H), 8.67 (d, $J_{1,2}$ = 8.8 Hz, 2 H, 1,8-H), 9.6–9.9 (br. s, 2 H, OH). – UV ($CHCl_3$): λ_{max} [nm] = 328, 369, 379, 540.06, 580. – Fluorescence ($CHCl_3$): λ_{max} [nm] = 625. – IR: $\tilde{\nu}$ [cm^{-1}] = 3300 (OH), 3011 (sp^2C–H) 1605 (C=C). – MS (70eV); *m/z* (%): 358 (100) [M^+].

1f: 5,12-Dihydroxyrubicene (**1e**) (100 mg; 0.3 mmol) was suspended in acetone (5 ml). Benzyl bromide (0.28 g, 1.7 mmol) and K_2CO_3 (0.23 g, 1.7 mmol) were added and the mixture was refluxed for 24 h after which water (50 ml) was added and the mixture shaken vigorously. The precipitate was filtered off and washed with water (3 × 5 mL) and dichloromethane (3 × 5 ml). Yield: 129 mg, 86%, m.p. > 300°C. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.42 (s, 4 H, $PhCH_2$), 7.06 (dd, $J_{6,7}$ = 8.5 Hz, $J_{4,6}$ = 1.5 Hz, 2 H, 6,13-H), 7.37 (d, *J* = 7.5 Hz, 2 H, *para*-H), 7.43 (t, *J* = 7.5 Hz, 4 H, *meta*-H), 7.53 (d, *J* = 7.5 Hz, 4 H, *ortho*-H), 7.61 (d, $J_{4,6}$ = 1.5 Hz, 2 H, 4,11-H), 7.73 (dd, $J_{1,2}$ = 9 Hz, $J_{2,3}$ = 8 Hz, 2 H, 2,9-H), 7.96 (d, $J_{2,3}$ = 8 Hz, 2 H, 3,10-H), 8.18 (d, $J_{6,7}$ = 8.5 Hz, 2 H, 7,14-H), 8.53 (d, $J_{1,2}$ = 9 Hz, 2 H, 1,8-H). – UV ($CHCl_3$): λ_{max} [nm] = 330, 355, 375, 536, 565. – IR: $\tilde{\nu}$ [cm^{-1}] = 3023 (sp^2C–H), 2986 (sp^3C–H), 1608 (C=C). – MS (70eV); *m/z* (%): 538 (9) [M^+], 447 (24) [M^+ – $PhCH_2$], 91(100) [$PhCH_2^+$].

1g: Rubicene **1d** (30 mg, 0.07 mmol) was refluxed in a solution of pyridinium chloride (prepared from pyridine/concentrated HCl, 32:35.2 ml) for a period of 3 h, poured into water (200 ml), filtered, washed excessively with 10% HCl and finally with water. The solid **1d** was dried in vacuo at 60°C. Yield 22 mg, 79%, m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.07 (d, $J_{5,6}$ = 7 Hz, 2 H, 6,13-H), 7.32 (t, $J_{4,5}$ = $J_{5,6}$ = 7 Hz, 2 H, 5,12-H), 7.70 (d, $J_{4,5}$ = 7 Hz, 2 H, 4,11-H), 3.13 (dd, $J_{1,2}$ = 9 Hz, $J_{2,3}$ = 7 Hz, 2 H, 2,9-H), 8.24 (d, $J_{2,3}$ = 7 Hz, 2 H, 3,10-H), 9.75 (d, $J_{1,2}$ = 9 Hz, 2 H, 1,8-H), 10.74 (s, 2 H, OH). – IR: $\tilde{\nu}$ [$^{-1}$] = 3439 (OH), 3035 (sp^2C–H), 1604 (C=C). – MS (70eV); *m/z* (%): 358 [M^+].

1h was prepared according to the general procedure in 68% yield., m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.44 (d, *J* = 8 Hz, 2 H, *p*-H), 7.56 (t, *J* = 8 Hz, 4 H, *m*-H), 7.84 (dd, $J_{6,7}$ = 8.2 Hz, $J_{4,6}$ = 2 Hz, 2 H, 6,13-H), 7.90 (d, *J* = 8 Hz, 4 H, *o*-H), 7.99 (t, *J* = 8.8 Hz, 2 H, 2,9-H), 8.45 (d, $J_{2,3}$ = 8.8 Hz, 2 H, 3,10-H), 8.56 (d, $J_{4,6}$ = 2 Hz, 2 H, 4,11-H), 8.63 (d, $J_{6,7}$ = 8.2 Hz, 2 H, 7,14-H), 8.88 (d, $J_{1,2}$ = 8.8 Hz, 2 H, 1,8-H). – UV ($CHCl_3$): λ_{max} [nm] = 330, 383, 522, 555. – Fluorescence ($CHCl_3$): λ_{max} [nm] = 622. – IR: $\tilde{\nu}$ [cm^{-1}] = 3053, 3029 (sp^2C–H), 1579 (C=C). – MS (70eV); *m/z* (%): 478 [M^+]. – $C_{28}H_{18}O_2$ (478.59): calcd. C 95.37, H 4.63; found C 95.53, H 4.55.

1j was prepared according to the general procedure in 61% yield, m.p. > 300°C. – ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.57 (dd,

$J_{6,7}$ = 8.2 Hz, $J_{4,6}$ = 2 Hz, 2 H, 6,13-H), 7.97 (dd, $J_{1,2}$ = 8.8 Hz, $J_{2,3}$ = 7 Hz, 2 H, 2,9-H), 8.33 (d, $J_{4,6}$ = 2 Hz, 2 H, 4,11-H), 8.43 (d, $J_{2,3}$ = 7 Hz, 2 H, 3,10-H), 8.58 (d, $J_{6,7}$ = 8.2 Hz, 2 H, 7,14-H), 8.86 (d, $J_{1,2}$ = 8.8 Hz, 2 H, 1,8-H). − UV ($CHCl_3$): λ_{max} [nm] = 323, 360, 379, 504, 534. − Fluorescence ($CHCl_3$): λ_{max} [nm] = 567. − IR: $\tilde{\nu}$ [cm^{-1}] = 3053 (sp^2C-H), 1605 (C=C). − MS (70eV); *m/z* (%): 394 (100) [M^+], 324 (26) [$M^+ - 2$ Cl]. − $C_{28}H_{18}O_2$ (395.29): calcd. C 79.00, H 3.06; found C 79.18, H 2.98.

1k was prepared according to the general procedure in 53% yield, m.p. > 300°C. − ^1H NMR (400 MHz, [D_6]DMSO): δ = 2.73 (s, 6 H, $COCH_3$), 7.96 (t, *J* = 7.5 Hz, 2 H, 2,9-H), 8.08 (d, $J_{6,7}$ = 7 Hz, 2 H, 6,13), 8.42 (d, $J_{2,3}$ = 7.5 Hz, 2 H, 3,10-H), 8.60 (d, $J_{6,7}$ = 7 Hz, 2 H, 7,14-H), 8.68 (s, 2 H, 4,11-H), 8.80 (d, $J_{1,2}$ = 7.5 Hz, 2 H, 1,8-H). − UV ($CHCl_3$): λ_{max} [nm] = 338.5, 360, 379, 503, 525. − Fluorescence ($CHCl_3$): λ_{max} [nm] = 550. − IR: $\tilde{\nu}$ [cm^{-1}] = 3026 (sp^2C-H), 1678 (C=O), 1601 (C=C). − MS (70eV); *m/z* (%): 410 (100) [$M^{\cdot+}$], 395 (64) [$M^+ - CH_3$], 324 (55) [$M^+ - 2\ COCH_3$].

[1] W. Dehaen, D. Corens, G. L′abbé, *Synthesis* **1996**, 201.
[2] [2a] R. Fittig, A. Schultz, *Justus Liebigs Ann. Chem.* **1878**, *193*, 115. − [2b] R. Fittig, E. Ostermayer, *Justus Liebigs Ann. Chem.* **1873**, *166*, 361.
[3] F. Progst, M. Van Loeuis, *J. Electroanal. Chem.* **1982**, *133*, 173.
[4] R. R. Schmidt, *Chem. Phys. Lett.* **1988**, *151*, 369.
[5] W. L. Chmelewski, J. Postowski, *J. Gen. Chem. USSR (Engl. Transl.)* **1939**, *9*, 620.
[6] [6a] A. Schönberg, K.-H. Brosowski, E. Singer, *Chem. Ber.* **1962**, *95*, 1910. − [6b] A. Schönberg, K.-H. Brosowski, *Chem. Ber.* **1960**, *93*, 2149.
[7] V. Sachweh, H. Langhals, *Chem. Ber.* **1990**, *123*, 1981.
[8] E.Clar, W. Willicks, *J. Chem. Soc.* **1958**, 942.
[9] P. J. Hanhela, D.B. Paul, *Aust. J. Chem.* **1981**, *34*, 1669.

[O98286]