Palladium-Catalyzed Four-Membered Ring Annelation Reactions at Dibenzobarrelene

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Received 7 August 2008

Dedicated to Prof. Dr. Maximilian Zander on the occasion of his 80th birthday

Abstract: A palladium-catalyzed coupling process of dibenzobarrelene with annelated aryl halides leads to special benzocyclobutenes, resembling Diels–Alder adducts of antiaromatic benzocyclobutadienes with anthracene. Moderate steric pressure in intermediary five-membered palladacycles seems to be decisive for this type of transformation.

Key words: benzocyclobutenes, C–H activation, domino processes, palladium catalysis, steric pressure

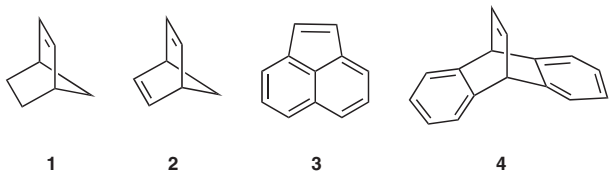


Figure 1 Olefin components for palladium-catalyzed coupling reactions

Norbornene (**1**),[1] norbornadiene (**2**)[2] and acenaphthylene (**3**)[3] have been extensively studied as strained, highly reactive alkene components in palladium-catalyzed domino coupling processes, which deviate from the classical Heck reaction, since the 'normal' β-H-elimination step is prohibited because of stereochemical requirements.[4] Norbornene (**1**), in particular, turned out to be very useful as catalytic template in the Catellani reaction, which is essentially based on the reversibility of the carbopalladation step.[5]

We became interested in palladium-catalyzed annelation reactions of the structurally related dibenzobarrelene (**4**; Figure 1)[6] in order to overcome a preparative obstacle: while disubstituted alkynes have been successfully applied for the synthesis of polycyclic ring systems via palladium-catalyzed annelation processes with aryl halides[7] and vinyl halides[8], terminal alkynes, and of course the parent acetylene,[9] bearing acidic alkynyl hydrogens prefer to react in a Sonogashira-type fashion.[10] We envisioned, that dibenzobarrelene (**4**) could serve as an 'acetylene annelation synthon' when applied in a palladium-catalyzed annelation and retro-Diels–Alder sequence,[2a,3c] and wish to report on our initial results with **4** as coupling component, focusing on the efficient formation of annelated benzocyclobutenes.[11]

With the 4-bromobenzoic acid ester **5a**, the initial plan indeed worked out under Jeffery conditions:[12] the functionalized phenanthrene **6** was isolated with acceptable yield, and its structure was confirmed by analysis of two-dimensional NMR spectra including HMBC, HMQC and NOESY; somewhat surprisingly deviating from substitution patterns observed before for annelation reactions using norbornene.[13] Anthracene was found as by-product, obviously resulting from the anticipated retro-Diels–Alder step. In the case of 2-bromo- and 2-iodo-*p*-xylene[14] (**7a** and **7b**) the formation of the phenanthrene moiety sur-

Table 1 Coupling Reactions at Dibenzobarrelene (**4**)[a]

Entry	Aryl halide[b]	Molar ratio of halide/**4**	T (°C)	Product (yield)
1	**5a**	4.9:1	100	**6** (63%)
2	**7a**	3:1	100	**8** (8%)
3	**7a**	3:1	140	**8** (59%)
4	**7a**	1:3	140	**8** (80%)
5	**7b**	3:1	100	**8** (36%)
6	**7b**	1:3	140	**8** (80%)
7	**9a**	3:1	100	**10** (40%)
8	**9b**	1:5	100	**10** (36%)
9	**9b**	3:1	100	**10** (44%)
10	**11a**	3:1	140	**12** (37%)
11	**13a**	2.3:1	100	**14** (21%)
12	**13b**	1:3	100	**14** (40%)

[a] Reaction conditions: DMF, $Pd(OAc)_2$ (5 mol%), K_2CO_3, *n*-Bu_4NBr, 3 d, 100 °C or 140 °C.
[b] For **a**, X = Br; for **b**, X = I.

SYNLETT 2009, No. 1, pp 0133–0137
Advanced online publication: 12.12.2008
DOI: 10.1055/s-0028-1087375; Art ID: S07008ST

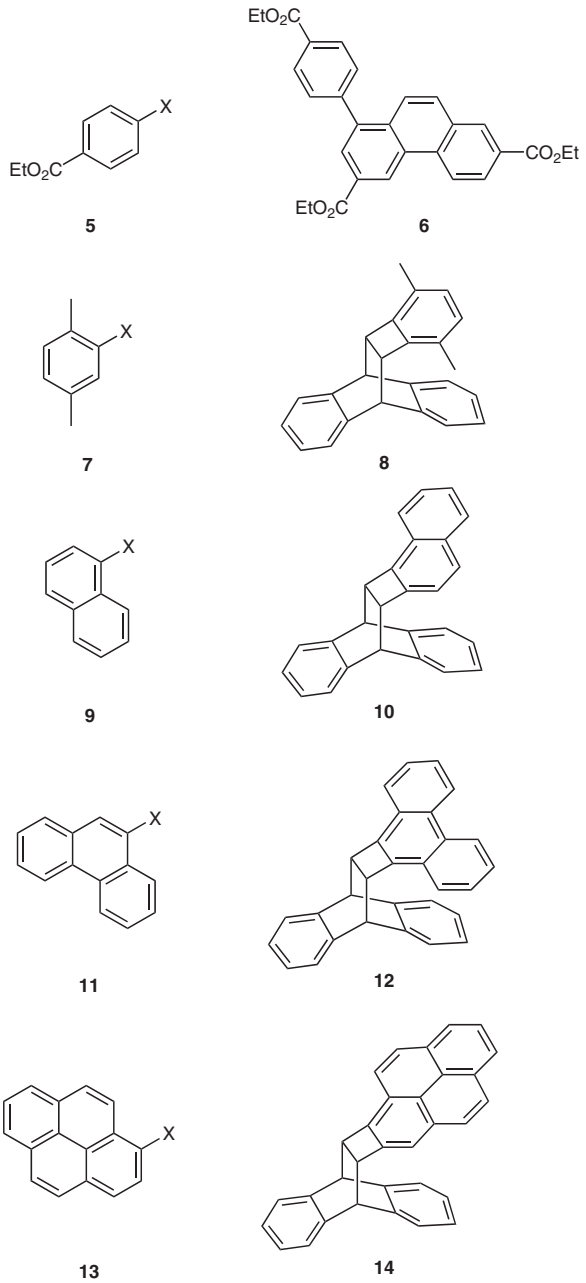


Figure 2 Aryl halides (**a**: X = Br, **b**: X = I) and resulting ring systems from palladium-catalyzed domino processes with dibenzobarrelene (**4**)

prisingly failed. Instead, the highly strained annelated benzocyclobutene **8** was the result of the palladium-catalyzed domino process in up to 80% yield. For the iodide **7b** a reaction temperature of 100 °C was sufficient (Table 1, entry 5); in the case of the less reactive bromide **7a**, 140 °C turned out to be superior (entries 3 and 4). Applying dibenzobarrelene (**4**) in excess offers the advantage of minimizing by-products; however, using an excess of the readily accessible aryl halides[14] should be more feasible.

Presumably the four-membered ring formation is favored by steric influence[15] of the *ortho*-methyl group. The thermal stability of this product is explained by the fact that a

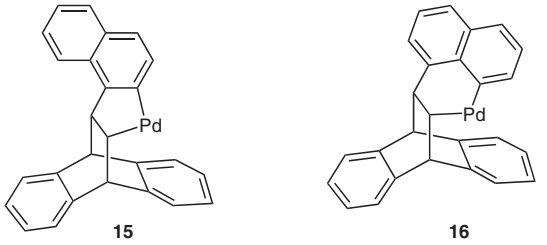
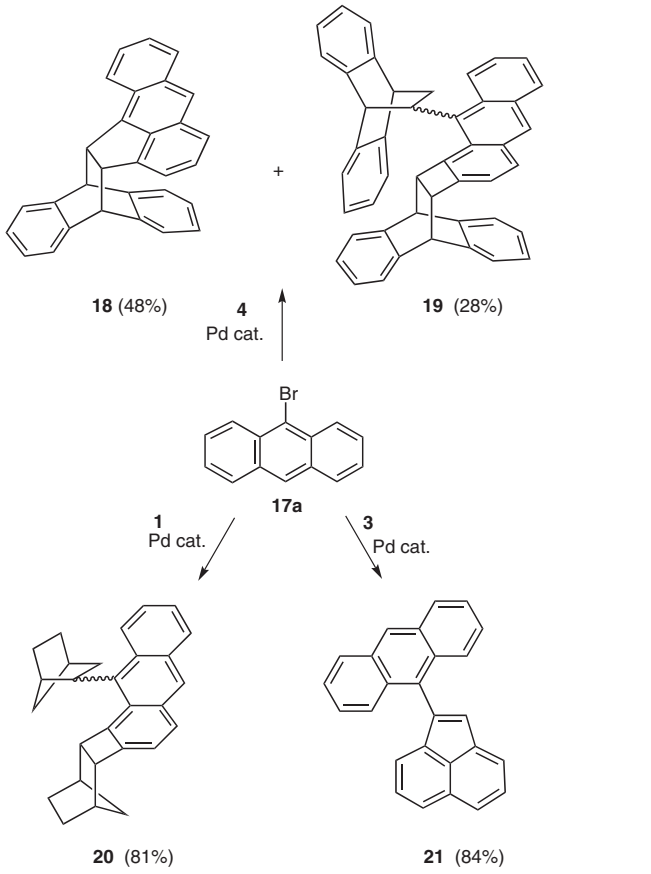


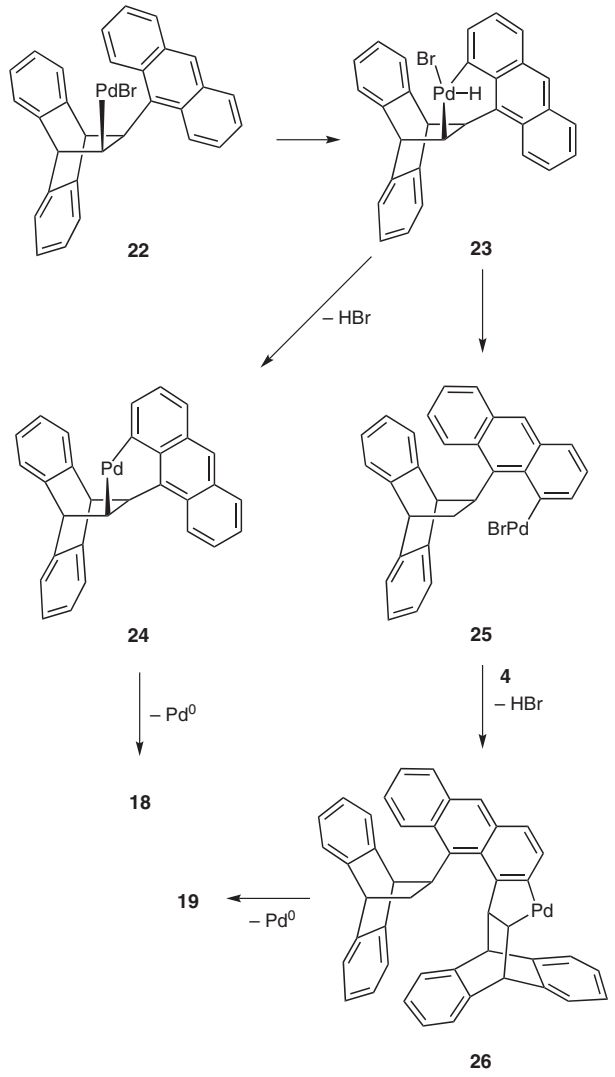
Figure 3 Intermediary palladacycles **15** and **16**



Scheme 1 Products from palladium-catalyzed domino processes of 9-bromoanthracene (**17a**) with olefins **1**, **3** and **4**

retro-Diels–Alder reaction would deliver an energetically disfavored antiaromatic benzocyclobutadiene.

This methodology could also be applied to other polycyclic aromatic hydrocarbons **9**, **11**, and **13**, bromo- or iodo-substituted in *peri* position, to afford the desired benzocyclobutenes **10**, **12**, and **14** (Figure 2). These findings are somewhat surprising, since the *peri*-annelated coupling components offer the opportunity to form the regioisomeric five-membered ring products in principle, as observed before with acenaphthylene (**3**) as alkene component.[3a] However, for the mechanistic interpretation, one can conclude that the formation of the five-membered palladacyclic intermediates[16] (such as **15**, Figure 3) is favored compared to the six-membered analogues (such as **16**, Figure 3). This conclusion is in accord with the typical selectivity of an electrophilic aromatic substitution: a



Scheme 2 Mechanistic rationale for the formation of **18** and **19** by the palladium-catalyzed reaction of 9-bromoanthracene (**17a**) with dibenzobarrelene (**4**)

1-alkyl-substituted naphthalene is more reactive in the 2-position than in the 8-position in terms of a S_EAr reaction.

The five-membered palladacycles undergo reductive elimination to four-membered carbocycles, rather than oxidatively adding a second equivalent of a somewhat sterically demanding aryl halide: the steric influence of an annelated benzene ring in *ortho* position or an *ortho*-methyl group seems to be sufficient, both, for disfavoring a second oxidative addition step and for supporting the reductive elimination step by steric pressure.[15]

9-Bromoanthracene (**17a**) as coupling component is an especially interesting case (Scheme 1) since the formation of a six-membered palladacycle **24** (Scheme 2) as intermediate is structurally predetermined: the resulting annelated five-membered carbocycle **18** was indeed isolated as the main product with 48% yield. Surprisingly, a diastereoisomeric mixture of annelated benzocyclobutenes **19**, obviously 1:2 domino products, was found as by-product in a substantial amount (28% yield).

The mechanistic coherence of products **18** and **19** is analyzed in Scheme 2: a C–H activation step in the *peri* position in carbopalladation product **22** leads to the six-membered palladium(IV) palladacycle **23**,[17] which either is deprotonated and consecutively transformed to **18**, or reacts in a reductive elimination step to palladium(II) intermediate **25** in the sense of a palladium migration.[18] The second equivalent of barrelene **4** is then inserted again by carbopalladation. In the cyclopalladated intermediate **26**, steric pressure[15] activates the reductive elimination to four-membered carbocycles **19**. In comparison, the coupling reaction of 9-bromoanthracene (**17a**) with norbornene gave the analogous 1:2 domino products **20** (81% yield), whereas with acenaphthylene (**3**) the formally 'simple' Heck product **21** was obtained (84% yield), presumably by a different mechanism circumventing the stereochemical requirements as explained previously.[2a]

For the benzocyclobutenes **10**, **12**, **14** and **19** single crystals were obtained by diffusion of methanol into a dichloromethane solution and their constitution was proved by X-ray crystal structure analyses (Figure 4).[19] The bond lengths of the C–C bonds connecting the cyclobutene moiety with the 9,10-positions of the dihydrophenanthrene unit are minimally elongated in the range of 153.5–157.4 pm.

In conclusion, annelated benzocyclobutenes are readily formed by a palladium-catalyzed coupling process of dibenzobarrelene (**4**) based on the steric influence of *ortho* substituents in aryl halides as coupling components.[20] In ongoing studies, we will test these coupling products as a source for antiaromatic benzocyclobutadienes[21] under the conditions of flash vacuum pyrolysis. The successful synthesis of the functionalized phenanthrene **6** via a domino coupling retro-Diels–Alder sequence starting from a *para*-substituted aryl halide motivates for further studying scope and limitations of this type of domino process.

Acknowledgment

We thank Degussa AG for a generous donation of palladium acetate.

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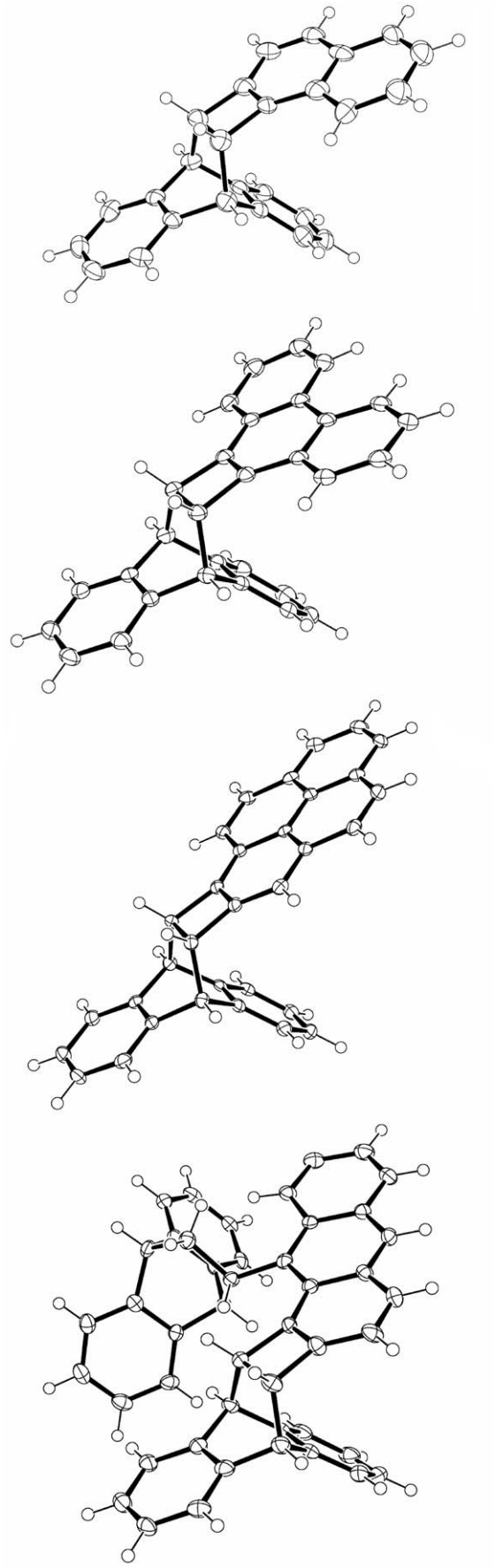

Figure 4 Structures of benzocyclobutenes **10**, **12**, **14** and **19** (top to bottom, respectively) in the crystal form[19]

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(19) CCDC 697535 (for **10**), CCDC 697536 (for **12**), CCDC 697537 (for **14**), and CCDC 697538 (for **19**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(20) **General Procedure for Palladium-Catalyzed Coupling Reactions of Aryl Halides with Dibenzobarrelene (4)**: A mixture of aryl halide (3.00 mmol), dibenzobarrelene (**4**; 202 mg, 1.00 mmol; or in the ratio outlined in Table 1), K_2CO_3 (1.1 g, 8.0 mmol), *n*-Bu_4NBr (645 mg, 2.00 mmol), $Pd(OAc)_2$ (12 mg, 0.05 mmol) and DMF (10 mL) in a sealed tube (for convenience) was stirred under argon at 100 °C for 3 d. After diluting with H_2O (50 mL), the reaction mixture was extracted three times with diethyl ether or methyl *tert*-butyl ether (50 mL). The Et_2O extract was filtered through silica and concentrated. The crude product was purified by flash chromatography (hexanes or hexanes–dichloromethane on silica gel).
Selected Analytical Data: Compound **6**: colorless solid; mp 42 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.44–1.55 (m, 9 H), 4.44–4.58 (m, 6 H), 7.61 (d, *J* = 6.6 Hz, 2 H), 7.81 (d, *J* = 9.2 Hz, 1 H), 7.88 (d, *J* = 9.2 Hz, 1 H), 8.19–8.29 (m, 3 H), 8.36 (dd, *J* = 1.7, 8.7 Hz, 1 H), 8.64 (d, *J* = 1.6 Hz, 1 H), 8.90 (d, *J* = 8.8 Hz, 1 H), 9.51 (s, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$):

δ = 14.53 (2 × q), 14.58 (q), 61.27 (t), 61.41 (t), 61.61 (t), 123.54 (d), 124.72 (d), 125.51 (d), 127.39 (d), 128.11 (s), 128.50 (d), 129.27 (s), 129.86 (d, phenylene), 129.98 (d), 130.09 (s), 130.28 (d, phenylene), 130.90 (d), 131.33 (s), 133.40 (s), 133.65 (s), 140.44 (s), 144.75 (s), 166.49 (2 × s), 166.57 (s), one singlet was superimposed.

Compound **8**: colorless solid; mp 126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 6 H), 3.66 (dd, *J* = 1.4, 2.6 Hz, 2 H), 4.58 (dd, 2 H), 6.67 (s, 2 H), 6.92 (dd, *J* = 3.2, 5.4 Hz, 2 H), 7.09 (dd, *J* = 3.2, 5.3 Hz, 2 H), 7.21 (dd, *J* = 3.2, 5.4 Hz, 2 H), 7.40 (dd, *J* = 3.2, 5.3 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 16.63 (q), 46.02 (d), 47.67 (d), 124.05 (d), 124.54 (d), 125.81 (d), 126.00 (d), 128.22 (d), 129.37 (s), 140.54 (s), 143.14 (s), 143.44 (s). MS (EI, 70 eV): *m*/*z* (%) = 308.7 (5) [M$^+$], 307.7 (19) [M$^+$ – 1], 178.8 (15), 177.8 (100), 130.9 (7), 129.9 (58).

Compound **10**: colorless solid; mp 156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (t, *J* = 4.3 Hz, 1 H), 3.94 (t, *J* = 4.3 Hz, 1 H), 4.63 (d, *J* = 3.8 Hz, 1 H), 4.76 (d, *J* = 4.0 Hz, 1 H), 6.65 (t, *J* = 8.0 Hz, 1 H), 6.67 (t, *J* = 8.0 Hz, 1 H), 6.88 (d, *J* = 7.3 Hz, 1 H), 7.02 (d, *J* = 7.3 Hz, 1 H), 7.08 (d, *J* = 8.1 Hz, 1 H), 7.16–7.21 (m, 2 H), 7.34 (t, *J* = 8.2 Hz, 1 H), 7.41–7.50 (m, 4 H), 7.68 (d, *J* = 8.1 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 1 H). MS (EI, 70 eV): *m*/*z* (%) = 331 (3), 330 (13), 203 (2), 178 (13), 163 (2), 153 (13), 152 (100), 151 (6).

Compound **12**: colorless solid; mp 265 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.97 (d, *J* = 4.0 Hz, 2 H), 4.80 (d, *J* = 4.0 Hz, 2 H), 6.56–6.64 (m, 2 H), 6.87–6.95 (m, 2 H), 7.19–7.24 (m, 2 H), 7.45–7.64 (m, 6 H), 7.83 (d, *J* = 7.1 Hz, 2 H), 8.54 (d, *J* = 7.8 Hz, 2 H). MS (EI, 70 eV): *m*/*z* (%) = 380 (15), 202 (100), 187 (2), 178 (4), 152 (1).

Compound **14**: yellow solid; mp 287 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (t, *J* = 4.8 Hz, 1 H), 4.23 (t, *J* = 4.8 Hz, 1 H), 4.77 (d, *J* = 4.0 Hz, 1 H), 4.89 (d, *J* = 4.0 Hz, 1 H), 6.50 (t, *J* = 7.3 Hz, 1 H), 6.61 (t, *J* = 7.3 Hz, 1 H), 6.88 (d, *J* = 7.3 Hz, 1 H), 6.98 (d, *J* = 7.3 Hz, 1 H), 7.19–7.24 (m, 2 H), 7.45–7.51 (m, 2 H), 7.72 (s, 1 H), 7.89–7.94 (m, 3 H), 8.02–8.14 (m, 4 H). MS (FAB): *m*/*z* (%) = 405 (35), 404 (71), 226 (21).

Compound **18**: yellow solid; mp 265 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (dd, *J* = 3.5, 7.3 Hz, 1 H), 4.63 (dd, *J* = 2.8, 7.3 Hz, 1 H), 4.76 (d, *J* = 3.5 Hz, 1 H), 5.16 (d, *J* = 3.0 Hz, 1 H), 6.44 ('t', *J* = 7.3 Hz, 1 H), 6.50 (dd, *J* = 1.3, 7.3 Hz, 1 H), 6.61 ('t', *J* = 7.3 Hz, 1 H), 6.86 (d, *J* = 7.3 Hz, 1 H), 7.21–7.26 (m, 2 H), 7.30 (d, *J* = 6.6 Hz, 1 H), 7.37 ('t', *J* = 8.3 Hz, 1 H), 7.45–7.57 (m, 4 H), 7.60 ('t', *J* = 6.6 Hz, 1 H), 7.99 (d, *J* = 8.3 Hz, 1 H), 8.01 (s, 1 H), 8.42 (dd, *J* = 0.8, 8.6 Hz, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 49.13 (d), 50.17 (d), 51.35 (d), 51.45 (d), 117.37 (d), 122.44 (d), 122.75 (d), 124.15 (d), 124.23 (d), 124.27 (d), 124.37 (d), 124.92 (d), 124.94 (d), 125.01 (d), 125.31 (d), 125.38 (d), 126.25 (d), 126.33 (d), 127.07 (s), 127.49 (d), 129.31 (s), 130.06 (d), 133.78 (s), 139.04 (s), 139.91 (s), 140.17 (s), 141.19 (s), 143.78 (s), 144.20 (s), 146.72 (s). MS (EI): *m*/*z* (%) = 380 (5.7) [M$^+$], 202 (87.1), 178 (100), 108 (6.4), 59 (19.3), 43 (16.4), 29 (6.4).

Compound **19**: slightly yellow fluorescent solid; decomposition started at 160 °C. MS (EI): *m*/*z* (%) = 406 (15) [M$^+$ – $M_{anthracene}$], 228 (29), 202 (6), 178 (100) [$M^+_{anthracene}$], 152 (10), 89 (7), 76 (6), 45 (8).

Compound **20**: Diastereoisomeric mixture; yellow solid; mp 168 °C; six times fractionated crystallization with *i*-PrOH gave one pure diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.91–1.01 (m, 2 H), 1.29–1.35 (m, 2 H), 1.47–1.59 (m, 3 H), 1.63–1.89 (m, 6 H), 1.94–2.02 (m, 1 H), 2.32–2.38 (m, 1 H), 2.45–2.60 (m, 4 H), 2.67 (s, 1 H), 3.20 (d, *J* = 3.5 Hz, 1 H), 3.73 (d, *J* = 3.5 Hz, 1 H), 4.43 (t, *J* = 8.3, 8.6 Hz, 1 H), 7.17 (d, *J* = 8.3 Hz, 1 H), 7.35–7.44 (m, 2 H), 7.89 (d, *J* = 8.3 Hz, 1 H), 7.94–7.99 (m, 1 H), 8.32 (s, 1 H), 8.62–8.69 (m, 1 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 28.12 (t), 28.24 (t), 29.18 (t), 31.53 (t), 32.78 (t), 36.30 (d), 37.10 (d), 37.57 (d), 39.63 (t), 39.72 (t), 44.30 (d), 44.42 (d), 49.21 (d), 54.14 (d), 120.43 (d), 124.01 (d), 124.31 (d), 126.67 (d), 128.78 (d), 129.64 (s), 130.01 (d), 130.26 (s), 130.51 (d), 131.79 (s), 132.34 (s), 137.31 (s), 140.46 (s), 144.15 (s). MS (EI): *m*/*z* (%) = 364 (100) [M$^+$], 323 (8), 283 (9), 270 (16), 253 (36), 239 (25), 229 (17), 202 (11), 67 (9), 49 (11), 41 (8).

Compound **21**: orange-red solid; mp 222 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 6.8 Hz, 1 H), 7.24 (s, 1 H), 7.28–7.55 (m, 5 H), 7.67 (dd, *J* = 6.8, 8.1 Hz, 1 H), 7.79–7.97 (m, 3 H), 8.09 (d, *J* = 9.9 Hz, 4 H), 8.55 (s, 1 H). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 124.30 (d), 124.45 (d), 125.38 (d), 125.42 (d), 127.07 (d), 127.31 (d), 127.36 (d), 127.72 (d), 127.93 (d), 128.14 (d), 128.47 (s), 128.52 (d), 128.73 (s), 130.72 (s), 130.95 (d), 131.03 (s), 131.62 (s), 139.63 (s), 140.68 (s), 141.69 (s). MS (EI): *m*/*z* (%) = 328 (100) [M$^+$], 163 (20), 149 (5.4), 43 (5.7), 27 (8.6).

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(b) Stanger, A. *Chemistry of Cyclobutanes*; Rappoport, Z.; Liebman, J. F., Eds.; Wiley: New York, **2005**, 617–654.