

208. Synthesis and Chiroptical Properties of Dimethyl 8,12-Diphenylbenzo[d]heptalene-6,7-dicarboxylate

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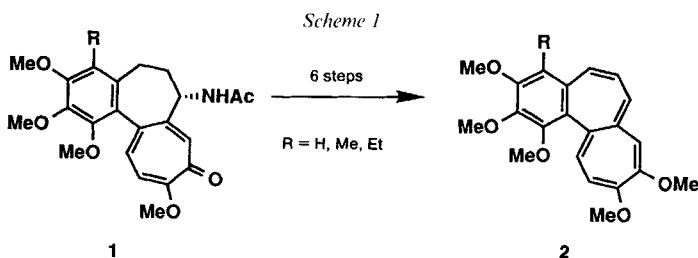
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Dedicated to Arnold Brossi on the occasion of his 70th birthday

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6,10-Diphenylbenz[a]azulene (**3**) was reacted with dimethyl acetylenedicarboxylate (ADM) in the presence of 2 mol-% of $[\text{RuH}_2(\text{PPh}_3)_4]$ in MeCN at 100° to yield a 7:1 mixture of dimethyl 2,6-diphenyl-9,10-benzotricyclo-[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate (**4**) and dimethyl 8,12-diphenylbenzo[d]heptalene-6,7-dicarboxylate (**5**; Scheme 2). The tricycle **4**, when heated in DMF at 150° for 1 h led to the formation of 81.5% of the heptalene-6,7-dicarboxylate **5** and 15% of the starting azulene **3**. No rearrangement of tricycle **4** was observed, when it was heated at temperatures up to 180° in pseudocumene. The heptalene-6,7-dicarboxylate **5** was easily separated into its antipodes (*PM*)- and (*MP*)-**5** on a *Chiracel* column (cf. Fig. 2). On heating at 150° for 1 h, (*MP*)-**5** showed no racemization at all. The Ru-catalyzed reaction of benz[a]azulene (**6**) with ADM led to the formation of dimethyl 9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate (**7**; Scheme 3). However, the formation of the corresponding heptalene-6,7-dicarboxylate could not be observed.

Introduction. – Recently, we described the chemical transformation of colchicine (**1**; R=H) and some of its 4-alkyl derivatives into their underlying parent structures **2**, i.e. the corresponding 1,2,3,9,10-pentamethoxybenzo[d]heptalenes (Scheme 1) [1] [2]. Since compounds **2** represent, to the best of our knowledge, the first members of the class of benzo[d]heptalenes²⁾, we were interested in another synthetic access to this class of compounds, which would also represent the basis of a new and variable approach to colchicinoid-type compounds³⁾. Our recent success in the improvement of the synthesis



¹⁾ Part of the planned Ph. D. thesis of A. J. R., University of Zurich.

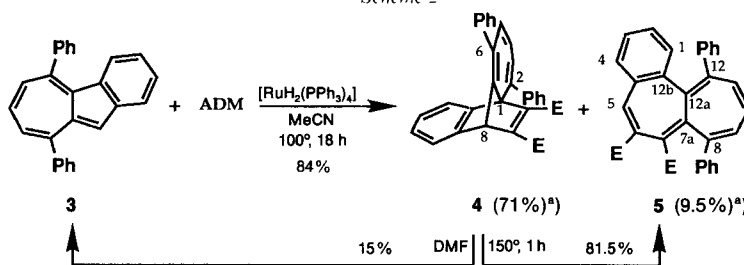
²⁾ For the chemistry of heptalenes and their annelated derivatives, see [3–5]. Recently, Yamamoto *et al.* reported the synthesis of [7.7]circulene, the fully benzannellated heptalene [6].

³⁾ See [7–9] for classical colchicine syntheses. For newer variants of the synthesis of colchicine-derived compounds, see [9] [10].

of heptalene-1,2-dicarboxylates from azulenes and dimethyl acetylenedicarboxylate (ADM) in polar aprotic solvents such as MeCN in the presence of $[\text{RuH}_2(\text{PPh}_3)_4]$ [11] as well as of other transition-metal catalysts [12] led us to investigate the reaction of benz[*a*]azulenes with ADM in the presence of transition-metal catalysts in polar aprotic solvents. Here, we report on first results of this synthetic approach to colchicinoid compounds.

Results and Discussion. – The reaction of 6,10-diphenylbenz[*a*]azulene (**3**) [3] with a four-fold molar excess of ADM in the presence of 2 mol-% of $[\text{RuH}_2(\text{PPh}_3)_4]$ in MeCN at 100° yielded, after 18 h, 71% of the tricycle **4** and 9.5% of the benzo[*d*]heptalene-6,7-dicarboxylate **5** alongside with 16% of recovered azulene **3** (Scheme 2). The tricycle **4** could easily be transformed into the benzo[*d*]heptalene **5** by heating in DMF at 150° for 1 h (Scheme 2). The starting azulene **3** was formed in this reaction to an extent of 15%. In

Scheme 2

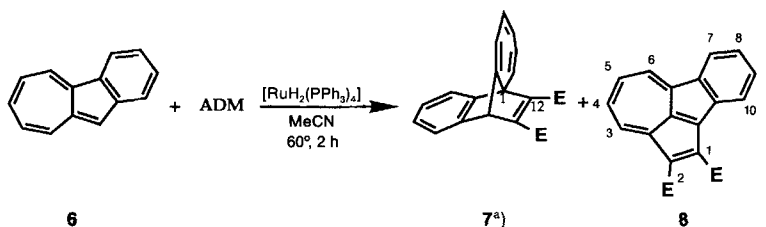


^a) 85% and 11.5%, respectively, with regard to reacted **3**.

agreement with our earlier findings that tricycles of type **4** rearrange smoothly into heptalenes in aprotic polar solvents (*cf.* [14] [15]), we observed no rearrangement of **4** into **5** in pseudocumene as solvent, even at 180°. On the other hand, the transformation of **3** and ADM into **5** could also be performed without the catalyst in DMF at 150°. However, no reaction occurred at 100°. The yield of **5** in the purely thermal reaction of **3** and ADM after 18 h amounted to 28% in the presence of 24.5% of recovered **3**. The tricycle **4** could not be detected in this reaction, *i.e.* the rate-determining step in the uncatalyzed reaction at 150° is the *Diels Alder*-type addition of ADM to **3**.

We also investigated the catalyzed addition of ADM to benz[*a*]azulene (**6**) [16]. In this case, a reaction took place already at 60° (Scheme 3). From the reaction mixture, which mainly consisted of chromatographically unmovable material, only small amounts of the tricycle **7** and traces of the azulene-1,2-dicarboxylate **8** could be isolated. There was no indication for the presence of the corresponding dimethyl benzo[*d*]heptalene-6,7-dicarboxylate or the formation of the latter compound from the tricycle **7**. Indeed, tricycle **7** decomposed slowly to form **8** as the sole identifiable product. The formation of azulene **8** is best explained by a heterolytic cleavage of the C(1)–C(12) bond in **7** and formation of a new bond between C(6) and C(12). As a rule, this type of intermediates are always formed from tricycles of type **7** which carry no substituent at C(6) and C(8) (*cf.* [11] [14] [15]). The discussed intermediates are stabilized by prototropic shifts to yield correspond-

Scheme 3



^a) Tricyclic 7 was formed in less than 15%. Azulene 8 was isolated in traces (< 1%).

ing 3,4-ethano-bridged azulene-1,2-dicarboxylates. In the present case, this stabilization is not possible, *i.e.* 8 must be formed from the intermediate by a dehydrogenation reaction. Nevertheless, both addition reactions show that benz[*a*]azulenes easily react with ADM in the presence of $[\text{RuH}_2(\text{PPh}_3)_4]$ in MeCN to yield tricyclic intermediate of types 4 and 7 which can be rearranged in aprotic polar solvents such as DMF into the corresponding benzo[*d*]heptalenes, at least, when C(6) of the tricycles is substituted.

The structure of the tricycles 4 and 7 follows unequivocally from their ¹H-NMR spectra. Quite characteristic is the low-field position of the signal of H–C(8) which appears in CDCl_3 as well as in C_6D_6 around 4.5 ppm (*cf. Exper. Part* and [14] [15]). The neighboring H-atoms at the completely planar seven-membered ring (*cf.* [14] [15]) show vicinal coupling constants of *ca.* 12 Hz across C=C bonds and *ca.* 7.4 to 8.7 Hz across C–C bonds (*cf. Exper. Part* as well as [14] [15]).

The rearrangement of 4 into 5 is characterized by a tremendous low-field shift of the *s* for H–C(8) in 4 (4.51 ppm). It appears in 5 as *s* at 8.41 ppm (*cf. Fig. 1*) due to its new

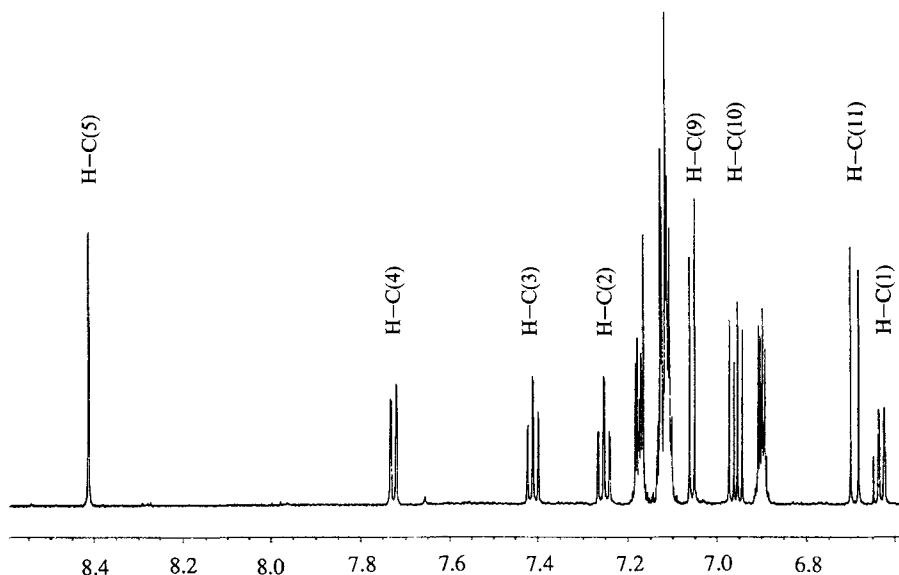


Fig. 1. ¹H-NMR Spectrum (600 MHz, (D_6)acetone) of dimethyl 8,12-diphenylbenzo[*d*]heptalene-6,7-dicarboxylate (5; region of the olefinic and aromatic H-atoms)

position at C(5) in conjugation to the ester group at C(6). Quite typical for the heptalene structure of **5** is also $^1J(9,10) = 6.5$ Hz (*cf.* [17]) which indicates a torsion angle θ between the two neighboring H-atoms of $30\text{--}35^\circ$ as it is found for most of the heptalenes with at least two substituents in their *peri*-positions (*cf.* [17] [18]). One also observes a pronounced shift difference between H–C(4) (7.73 ppm) and H–C(1) (6.63 ppm) which indicates that H–C(1) must immerse in the π -cloud of the Ph substituent at C(12). The spatial relation of H–C(4) and H–C(5) was secured by an observed strong reciprocal ^1H -NOE between these two H-atoms. Therefore, there is no doubt about the benzo-[*d*]heptalene structure of **5**.

The heptalene structure of **5** is further secured by the CD spectra of its two antipodes (*cf.* Fig. 2), which were easily separated on a *Chiracel OD* column. The antipodes turned out to be optically very stable. We were not able to racemize them by heating up to 150° ,

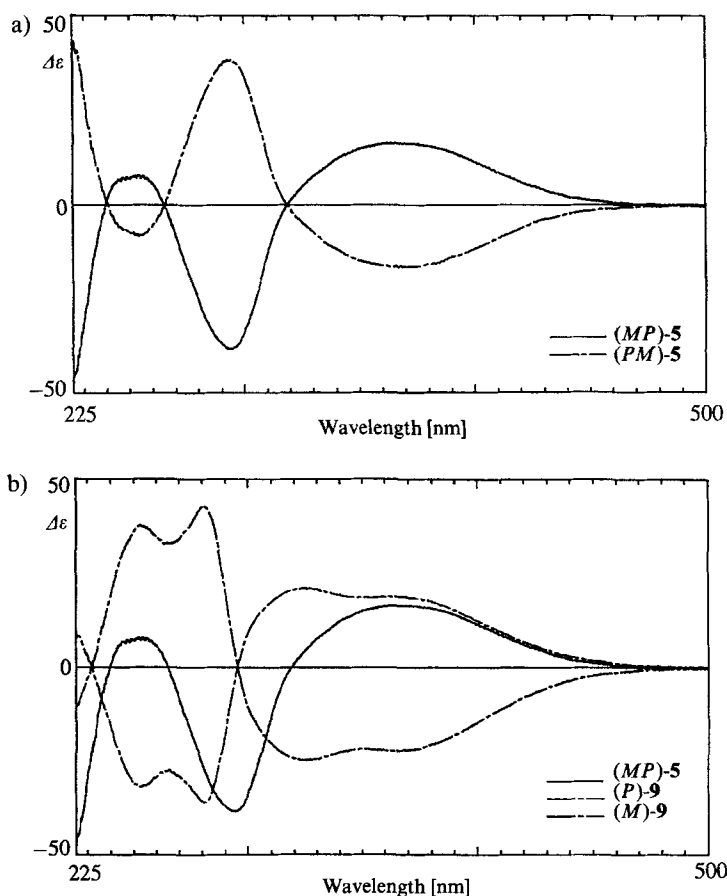


Fig. 2. a) CD Spectra (hexane/*i*-PrOH 93:7) of (PM)- and (MP)-**5**; b) Comparison of the CD spectra (hexane/*i*-PrOH 93:7) of dimethyl (M)- and (P)-5,6,8,10-tetramethylheptalene-1,2-dicarboxylate ((M)- and (P)-**9**) [19] with those of (MP)-**5**

at least during 1 h. We assign the (*MP*)-configuration⁴⁾ to the antipode of **5** which shows a nearly perfect agreement of its longest-wavelength +CE at 363–367 nm with that of the (*M*)-configured antipode of dimethyl 5,6,8,10-tetramethylheptalene-1,2-dicarboxylate ((*M*)-**9**; cf. Fig. 2, b) [19]⁵⁾. We suppose that the strong –CE at 293 nm is mainly determined by the spatial (*M*)-helical arrangement of the benzo ring and the Ph substituent at C(12) (cf. [22]). The work is continued.

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Experimental Part

General. See [11] [18]. M.p. on a Büchi apparatus (model FP5); values are not corrected. UV spectra on an Otsuka spectrophotometer (model MCPD 1100). IR spectra on a Perkin-Elmer spectrophotometer (model FT-IR 1600). ¹H-NMR spectra on Bruker instruments (models AC 300 and AMX 600). CD spectra were measured on a Jasco spectropolarimeter (model J-500A). HPLC separations on a Chiracel OD column (25.0 × 0.46 cm) from Daicel Chemical Industries, equipped with a corresponding pre-column (5.0 × 0.46 cm).

1. Benz[a]azulenes. – 1.1. *Benz[a]azulene* (**6**). It was synthesized from anthranilic acid and 1,1-dichloroethene following the procedure of Wege and coworkers [16]⁶⁾. M.p. 187.2–188.3° (EtOH; [16]: 189–190°).

1.2. *6,10-Diphenylbenz[a]azulene* (**3**). It was synthesized according to the procedure developed by Kapicak and Battiste [13]. M.p. 135.2–135.9° (EtOH; [13]: 136–137°).

2. Reaction of the Benz[a]azulenes with Dimethyl Acetylenedicarboxylate (ADM). – All reactions were performed under Ar in oven-dried Schlenk vessels. MeCN (Fluka, puriss.) and ADM (Fluka, puriss.) were distilled before use. DMF (Fluka, puriss.) and 1,2,4-trimethylbenzene (Fluka, puriss.) were used without further purification.

2.1. *6,10-Diphenylbenz[a]azulene* (**3**) and ADM. Azulene **3** (0.270 g, 0.82 mmol) was dissolved in MeCN (5 ml) and ADM (0.44 ml, 3.23 mmol) and [RuH₂(PPh₃)₄] (0.022 g; 2 mol-%) added. The Schlenk vessel was closed and the mixture heated at 100° for 18 h. The solvent was distilled off and the residue separated by CC (silica gel; hexane/Et₂O 1:1) to yield in a first fraction **3** (0.043 g, 15.9%), followed by *dimethyl (1RS,8SR)-2,6-diphenyl-9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate* (**4**; 0.272 g, 71.2%), and, finally, by *dimethyl (7aPM,12aMP)-8,12-diphenylbenzo[d]heptalene-6,7-dicarboxylate* (**5**; 0.037 g, 9.6%).

Data of 4. M.p. 111° (dec.; hexane). *R_f* (hexane/Et₂O 1:1) 0.49. UV (hexane): λ_{max} 370 (sh, 3.76), 350 (sh, 3.90), 282 (sh, 4.43), 250 (4.60); λ_{min} 240 (4.58). IR (KBr): 3059w, 3024w, 2948w, 2925w, 2850w, 1718s, 1436m, 1264m, 1206m, 1127m, 1068w, 1024w, 757m, 701m. ¹H-NMR (300 MHz, CDCl₃): 7.70–7.67 (m, 2 arom. H); 7.48 (d, with f.s., *J*_{ortho} = 7.5, H–C(3'')); 7.38–7.28 (m, 8 arom. H); 7.12–7.04 (m, 3 arom. H); 6.06 (d, ³*J*(4,3) = 8.73, H–C(3)); 5.78 (dd, ³*J*(3,4) = 8.71, ³*J*(5,4) = 11.99, H–C(4)); 5.60 (d, ³*J*(4,5) = 11.94, H–C(5)); 4.51 (s, H–C(8)); 3.69 (s, MeOCO–C(12)); 3.13 (s, MeOCO–C(11)).

⁴⁾ The two descriptors of absolute helicity refer to the two twisted π-systems around the central C(7a)–C(12a) heptalene bond and the peripheral C(12a)–C(12b) bond between the benzo ring and the non-benzo-annulated ring of the heptalene system. This means that the second stereochemical descriptors describes the helicity that is also found in colchicine and colchinoids (cf. [20] and lit. cited there) as tetrahydrobenzo[a]heptalene derivatives.

⁵⁾ Racemic **9** was separated on the Chiracel OD column (hexane/i-PrOH 93:7). The configuration of (*M*)- and (*P*)-**9** had been determined by chemical correlation and confirmed by an X-ray crystal structure analysis [19] (cf. also [21]). We recognized that the antipodes of **5** and **9** showed just an inverse elution behavior, i.e. (*MP*)-**5** und (*P*)-**9** possess the shorter *t_R* as compared with their antipodes. It should also be mentioned that colchicine and deacetamidocolchicine as well as deacetamidoisocolchicine with the same (*P*)-configuration around the C(12a)–C(12b) bond as in (*MP*)-**5** show qualitatively opposite CE to those of (*MP*)-**5** (cf. [20]). However, we have to take into account that the tropolone ring in colchicine and its derivatives is nearly planar (cf. [1] [2] [20]), whereas its counterpart in the benzo[d]heptalenes is strongly twisted (cf. ³*J*(9,10) = 6.5 in **5** as well as [17] [18]).

⁶⁾ We thank cand. chem. Peter Nuesch for his cooperation in this synthesis.

Data of 5. M.p. 162° (hexane/acetone). R_f (hexane/Et₂O 1:1) 0.28. UV (hexane): $\lambda_{\max}$ 358 (sh, 3.56), 284.4 (4.40), 245 (sh, 4.41), 223.5 (4.51); $\lambda_{\min}$ 268.2 (4.37), 219.3 (4.50). IR (KBr): 3018w, 2947w, 1716s, 1434m, 1271s, 1237s, 1202m, 1129m, 1105m, 1070w, 1032w. ¹H-NMR (600 MHz, (D₆)acetone; cf. Fig. 1): 8.413 (s, H-C(5)); 7.727 (dt, ³J(3,4) = 7.81, ⁴J(2,4) = 1.25, ⁵J(1,4) = 0.63, H-C(4)); 7.411 (td, ³J(4,3) = 7.81, ³J(2,3) = 7.39, ⁴J(1,3) = 1.26, H-C(3)); 7.253 (td, ³J(1,2) = 7.72, ³J(3,2) = 7.38, ⁴J(4,2) = 1.28, H-C(2)); 7.18–7.16 (m, 2 arom. H); 7.13–7.10 (m, 6 arom. H); 7.056 (d, ³J(10,9) = 6.52, H-C(9)); 6.958 (dd, ³J(11,10) = 11.44, ³J(9,10) = 6.55, H-C(10)); 6.91–6.89 (m, 2 arom. H); 6.687 (d, ³J(10,11) = 11.40, H-C(11)); 6.628 (dt, ³J(2,1) = 7.72, ⁴J(3,1) = 1.25, ⁵J(4,1) = 0.63, H-C(1)); 3.728 (s, MeOCO-C(6)); 3.171 (s, MeOCO-C(7)). ¹H-NOE (400 MHz, (D₆)acetone): 8.413 (H-C(5)) → 7.727 (s); 7.727 (H-C(4)) → 8.413 (s), 7.411 (s); 6.628 (H-C(1)) → 7.253 (s), 6.91–6.89 (s). EI-MS: 472.2 (37, M^+), 440.2 (12, [M – MeOH]⁺), 412.2 (100, [M – MeOH – CH₂O]⁺), 352.2 (23). CI-MS (NH₃): 490.2 (100, [M + NH₄]⁺). Anal. calc. for C₃₂H₂₄O₄ (472.54): C 81.34, H 5.19; found: C 81.40, H 5.18.

2.1.1. *Thermal Reaction of 4.* Tricycle **4** (0.190 g, 0.40 mmol) was dissolved in DMF (5 ml) and heated at 150° for 1 h. After this time, the starting material had been vanished, and workup of the residue by CC (silica gel; hexane/Et₂O 1:1) yielded **4** (0.020 g, 15%) and **5** (0.155 g, 81.5%).

In control experiments, **4** was heated for 1 h in 1,2,4-trimethylbenzene at 150° as well as at 180°. No change of **4** could be observed.

2.1.2. *Purely Thermal Reaction of 3 with ADM.* Benz[a]azulene **3** (0.020 g, 0.06 mmol) and ADM (0.025 ml, 0.2 mmol) were dissolved in DMF (1 ml) and heated at 100° for 2 h. No reaction at all could be observed. When the temp. was raised to 150°, a slow reaction occurred. Workup (*vide supra*) after 18 h yielded 24.5% of starting azulene **3** (0.005 g) and 28% of **5** (0.008 g).

2.1.3. *Optical Resolution of (PM,MP)-5.* Racemic **5** was completely separated in anal. amounts on the Chiracel OD column with hexane/*i*-PrOH (93:7; flow rate 0.8 ml/min) into its antipodes which showed t_R 12.4 ((MP)-isomer) and 18.9 min ((PM)-isomer).

CD (hexane/*i*-PrOH 93:7; $c = 2.714 \cdot 10^{-5}$ mol/l; cf. Fig. 2) of (MP)-**5**: 240 (0), 254 (7.0, pos. max.), 276 (0), 294 (–34.4, neg. max.), 319 (0), 363 (14.8, pos. max.), 490 (0).

CD (hexane/*i*-PrOH 93:7; $c = 2.714 \cdot 10^{-5}$ mol/l; cf. Fig. 2) of (PM)-**5**: 240 (0), 254 (–7.6, neg. max.), 276 (0), 293 (34.5, pos. max.), 319 (0), 367 (–14.9, neg. max.), 490 (0).

Control Experiment. The (MP)-isomer, when heated in a sealed ampoule in hexane/*i*-PrOH (93:7) at 150° for 1 h, showed no racemization at all according to its completely unchanged CD.

2.2. *Benz[a]azulene (6) and ADM.* Azulene **6** (0.110 g, 0.618 mmol), ADM (0.2 ml, 1.6 mmol), and [RuH₂(PPh₃)₄] (0.015 g, 2 mol-%) were dissolved in MeCN (5 ml) and heated at 60° for 2 h. All starting material had been consumed after this time. CC (silica gel; hexane/Et₂O 3:2) of the residue yielded mostly non-moving brownish material at the start of the column and a fraction (*ca.* 0.03 g, 15%) which mainly contained dimethyl 9,10-benzotricyclo[6.2.2.0^{1,7}]dodeca-2,4,6,9,11-pentaene-11,12-dicarboxylate (**7**) and small amounts of dimethyl benzo[a]cyclopent[cd]azulene-1,2-dicarboxylate (**8**). The tricycle **7** decomposed on the column as well as in solution to form **8** as the sole identifiable product. Therefore, both products could only be characterized by their ¹H-NMR.

¹H-NMR (300 MHz, C₆D₆; C₆D₅H at 7.157) of **7**: 7.20–7.10 (2 dd, partly covered by the signal of C₆D₅H, H-C(3',6')); 6.88–6.74 (2 td, H-C(4',5')); 6.285 (d, ³J(3,2) = 12.07, H-C(2)); 5.807 (dd, ³J(2,3) = 12.19, ³J(4,3) = 7.69, H-C(3)); 5.454 (dd, ³J(5,4) = 11.79, ³J(3,4) = 7.71, H-C(4)); 5.250 (dd, ³J(4,5) = 11.86, ³J(6,5) = 7.43, H-C(5)); 4.787 (d, ³J(5,6) = 7.40, H-C(6)); 4.498 (s, H-C(8)); 3.390, 3.210 (2s, 2 MeOCO).

¹H-NMR (300 MHz, CDCl₃; CHCl₃ at 7.260) of **8**: 9.391 (d, ³J(3,4) = 9.50, H-C(3)); 8.397 (d, ³J(6,5) = 9.16, H-C(6)); 8.319 (t, ³J(5,6) + ³J(4,5) = 19.59, ³J(4,5) = 10.43, H-C(5)); 8.068 (td-like, ³J(4,5) = 10.42, ³J(3,4) = 9.58, ⁴J(4,6) = 0.85, H-C(4)); 7.992 (dt-like, ³J(9,10) = 7.48, ⁴J(8,10) ≈ 2 · ⁵J(7,10), ⁴J + ⁵J = 1.7, H-C(10)); 7.645 (dt-like, ³J(7,8) = 7.52, ⁴J(7,9) ≈ 2 · ⁵J(7,10), ⁴J(7,9) ≈ 0.8, H-C(7)); 7.456 (td, ³J(9,10) = 7.51, ³J(8,9) = 7.57, ⁴J(7,9) = 1.11, H-C(9)); 7.26 (td?, partly covered by the signal of CHCl₃, H-C(8)); 4.112, 3.975 (2s, 2 MeOCO).

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