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Protonation and rearrangement of the tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene scaffold

Derong Cao,[a,b,*] Sheyang Xu,[b,c] Chunmei Gao[b,c] and Herbert Meier[d,*]

[a]*College of Chemistry, South China University of Technology, 510640 Guangzhou, China*
[b]*LCLC, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, 510650 Guangzhou, China*
[c]*Graduate School of CAS, Beijing 100039, China*
[d]*Institute of Organic Chemistry, University of Mainz, D-55099 Mainz, Germany*

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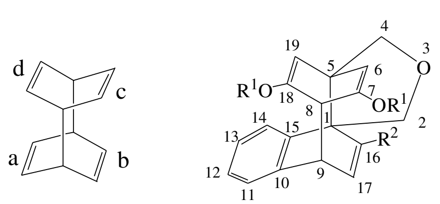
Abstract—The biplanemers **2a**,**b** contain enol ether substructures, which permit facile protonations of the π electron system. The subsequent ether cleavage is characterized by rearrangements of the polycyclic scaffold of the carbenium ions or the electroneutral primary products. Apart from the expected products **3a** and **5a**, a series of unexpected ketones and diketones (**4a′**, **9b**, **10b**, **11b**, and **12b**) were obtained.

Tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene (**1**), a [4π+4π]cyclodimer of benzene, is an unknown compound. Its thermal stabilization can be achieved by the condensation of benzene rings. Four benzene rings (in the positions a, b, c, and d of **1**, Scheme 1) are present in the well-known anthracene dimers,[1] three benzene rings (positions a, b, and c) in anthracene-naphthalene cycloadducts.[2,3] Naphthalene photodimers are realized with two benzene rings in a and c, or a and d positions.[4–7] We reported recently on systems **1** with two benzene rings in a and b position[8,9] and even on systems **2** with just one benzene ring (position a).[10]



1

2	**a**	**b**
R^1	$CH_2C_6H_5$	$CH_2C_6H_5$
R^2	H	OCH_3

Scheme 1. Tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene (**1**) and two derivatives **2a**,**b**.

The spatial and the through-bond interaction of the π centers in these biplanemers conveys such compounds special properties. The partial structures of 1,4-dienes (a/b or c/d) and 1,5-dienes (a/d or b/c) represent the basis of two well-known rearrangement reactions, namely the photochemical di-π-methane rearrangement and the thermal Cope rearrangement, respectively. Until now very less is known about the behavior of the corresponding carbocations obtained by protonation of the polycyclic scaffolds.[11] Apart from the fundamental interest in such organic species, the biplanemers **1** with 1–4 benzene rings attract attention as optical switches and as light harvesting systems, whereby the cyclohexadiene ring is constituted by Fréchet dendrons.[8–10]

A facile protonation of derivatives of **1** is possible when at least one of the four double bonds belongs to an enol ether substructure. We studied now in this context compounds **2a**,**b**, which have two or three such functional groups. The preparation of **2a**,**b** made use of the intramolecular photocycloaddition of the corresponding 1-(benzyloxymethyl)naphthalenes.[10] Scheme 2 illustrates the protonation of **2a**,**b**, which was performed with formic acid. The addition of H^+ can take place in different positions (**2a** → **3a**, **5a** and **2b** → **3b**, **4b**, **5b**). Moreover,

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* Corresponding authors. Tel./fax: +86 20 85232903 (D.C.); tel.: +49 6131 3922605; fax: +49 6131 3925396 (H.M.); e-mail addresses: drcao@scut.edu.cn; hmeier@mail.uni-mainz.de

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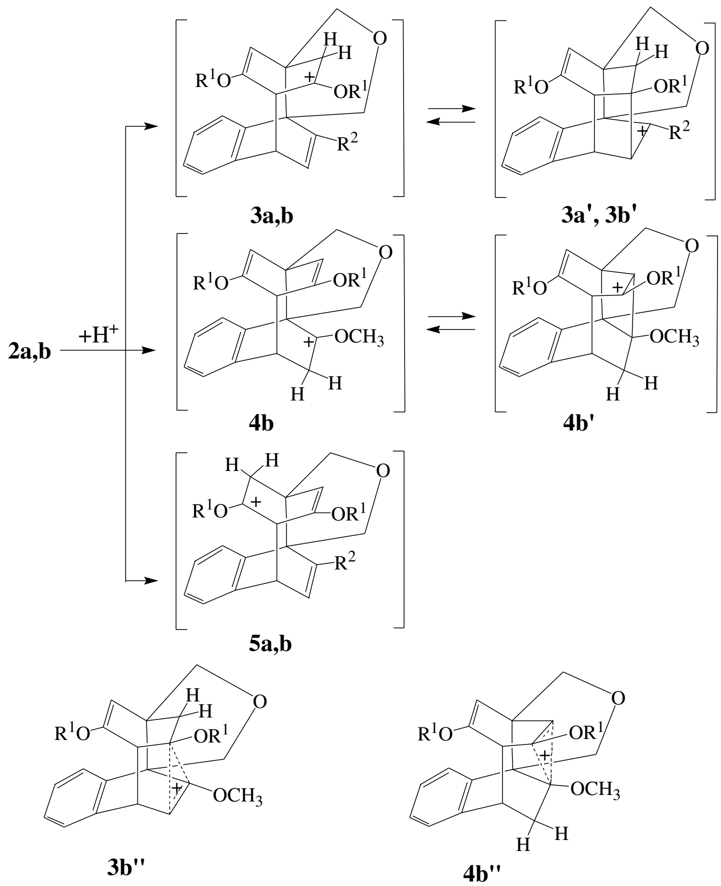
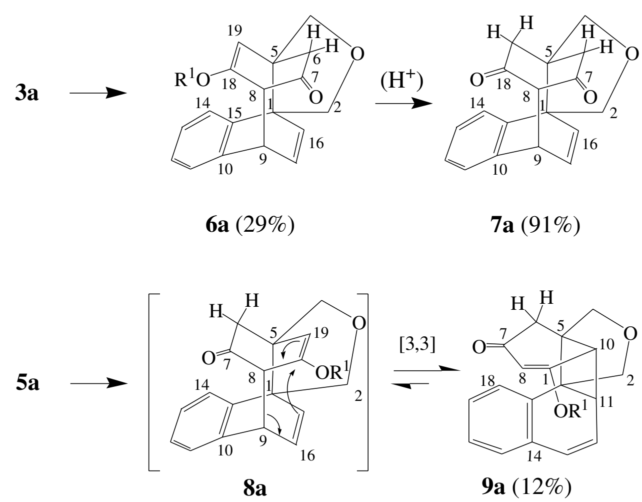


Scheme 2. Protonation of the biplanemers **2a**,**b**.

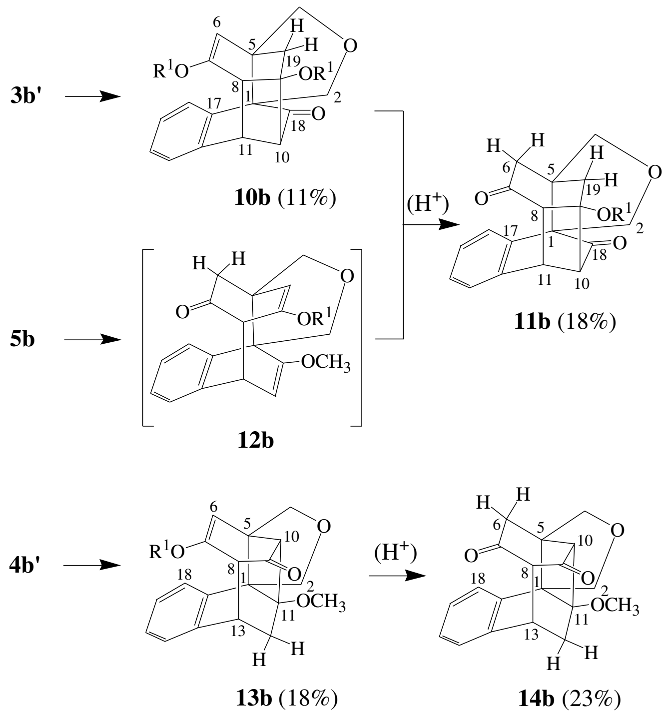
the polycyclic carbenium ions **3a**,**b** and **4b** can rearrange to **3a**′, **3b**′, and **4b**′, respectively. Since there should be a certain overlap of the p orbitals of the carbenium center and the above or below lying π bond, non-classical carbocations (carbonium ions like **3b**″ and **4b**″) cannot a priori be excluded.[12] Only the third protonated species **5a**,**b** has a single classical structure.

Scheme 3 shows the obtained hydrolysis products of **2a**. Monoketone **6a**[13] results from carbenium ion **3a**, which is energetically favored compared to **3a**′. Further hydrolysis of **6a** gives diketone **7a**[14] in high yields. Carbenium ion **5a** should lead to monoketone **8a**, but we only found its Cope rearrangement product **9a**,[15] a conjugated enone with a push–pull effect; **9a** is resistant toward hydrolysis under the conditions used (HCOOH, 20 °C).

The acidic enol ether cleavage of **2b** involves the formation of the five carbenium ions **3b**, **3b**′, **4b**, **4b**′, and **5b** depicted in Scheme 2. All of them are tertiary carbenium ions with an additional stabilization by the adjacent oxygen atom. Thus, it cannot be predicted a priori in which position the present nucleophile H_2O/HCOOH will attack preferentially. The experimental answer is given in Scheme 4. After the complete consumption of **2b**, monitored by TLC (SiO_2, cyclohexane/ethyl acetate), **10b**,[16] **11b**,[17] **13b**,[18] and **14b**[19] are obtained in a ratio of 11:18:18:23. Monoketone **10b** can be rationalized on the basis of **3b**′ as precursor. Further hydrolysis furnishes **11b**. The latter diketone could also be a subsequent product of monoketone **13b**, of which at most traces can be detected in the NMR spectra of the crude product mixture. Apart from the reaction path **2b** → **11b**, a parallel route **2b** → **4b** → **4b**′ → **13b** → **14b** exists (Scheme 4). The end-products **11b** and **14b** contain OCH_3 groups on saturated carbon atoms; thus a threefold enol ether cleavage of **2b** fails, because of the rearrangement of the polycyclic scaffold.



Scheme 3. Formation of the monoketones **6a** and **9a** and the diketone **7a**.



Scheme 4. Formation of the monoketones **10b** and **13b** and the diketones **11b** and **14b**.

The structure determinations of the mono- and diketones resulting from **2a** and **2b** are based on ^{1}H and ^{13}C NMR data. All obtained products belong to point group C_1, therefore methylene groups furnish AB spin patterns for their diastereotopic protons. The geminal coupling constants are for all CH_2 groups between −9.0 and −12.8 Hz, except for CH_2—C=O segments, for which values between −18.0 and −19.8 Hz are found. The rigid scaffolds of the polycyclic products permit the assignment of the most methylene protons by NOE measurements. The *endo*-6-H ($\delta = 2.62$) of **6a**, for example, shows a positive NOE for the neighborhood to the olefinic proton 16-H ($\delta = 6.05$). Thus, a differentiation between the two sides of the 'planes in the biplanemers' can be made. In the case of **6a**, for example, this provides a direct proof, that the enol ether substructure above the olefinic double bond is cleaved, whereas the enol ether substructure above the benzene ring is intact. All further details of the structure elucidations by NMR can be seen in Refs. 14–19. An additional structure proof for **13b** was achieved by a crystal structure analysis. Figure 1 depicts an ORTEP plot of crystals of **13b** with included benzene molecules.[20]

The selected structure parameters of **13b** demonstrate that the four-membered ring C(1)–C(5)–C(10)–C(11) is

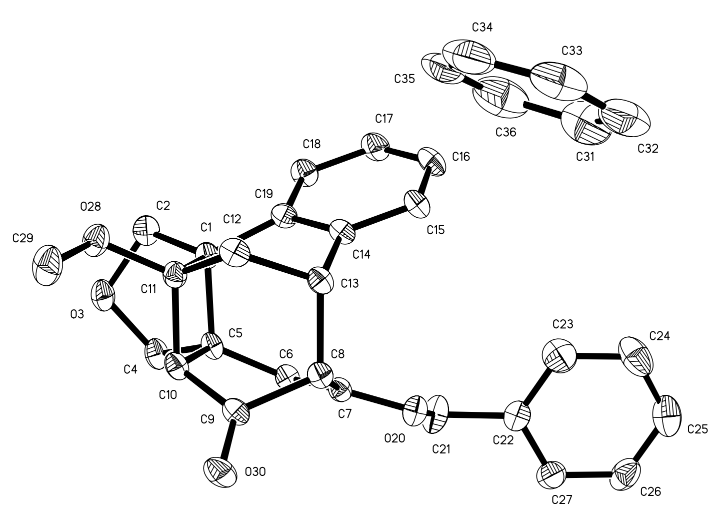
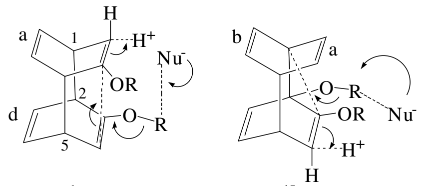


Figure 1. Crystal structure analysis of **13b**. Selected bond lengths in pm: C(1)–C(5) 160.7, C(5)–C(10) 155.9, C(10)–C(11) 155.9, C(11)–C(1) 156.9, C(8)–C(13) 157.9. Selected bond angles (degrees): C(5)–C(1)–C(11) 88.4, C(1)–C(5)–C(10) 89.8, C(5)–C(10)–C(11) 90.4, C(10)–C(11)–C(1) 91.3. Selected torsion angles (degrees): C(2)–C(1)–C(5)–C(4) 2.8, C(11)–C(1)–C(5)–C(10) 2.5, C(19)–C(1)–C(5)–C(6) 0.3, C(9)–C(8)–C(13)–C(12) 3.2, C(7)–C(8)–C(13)–C(14) −1.2, C(5)–C(6)–C(7)–C(8) 4.3, C(13)–C(14)–C(19)–C(1) −9.3, C(8)–C(9)–C(10)–C(5) 42.5, C(1)–C(11)–C(12)–C(13) −43.9.



1a **1b**

Scheme 5. Attack of nucleophiles on enol ethers with tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene substructures and subsequent rearrangements of the scaffolds.

an almost planar and square quadrangle; just the length of the bond between C-1 and C-5 is unusually large. The distances *d* between the non-bonded carbon atoms of the original biplanemer are relatively small:

$$d(\text{C-6/C-19}) = 289.2\ \text{pm}$$
$$d(\text{C-7/C-14}) = 275.0\ \text{pm}$$
$$d(\text{C-9/C-12}) = 264.6\ \text{pm}$$

The tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene scaffold **1** is highly liable to rearrangements, in which new σ bonds between the 'π planes of this longicyclic conjugated system'[21] are formed. Scheme 5 visualizes the cleavage of bisenol ether substructures in this scaffold. The substitution pattern shown in **1a** with condensed benzene rings on side a or d or both permits a fast and efficient reaction with the present nucleophile. The dotted line shows the formation of the new σ bond between the π planes. Such a process is prevented, as soon as a benzene ring is located in position a of **1b**. Nevertheless, a rearrangement of the scaffold can also occur in **1b**, when a second ether functionality is present at the bridgehead.[11] A still open question concerns the stepwise or concerted mechanism of such enol ether cleavages.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.02.074.

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13. 18-Benzyloxy-3-oxapentacyclo[7.6.2.2^{5,8}.0^{1,5}.0^{10,15}]nonadeca-10,12,14,16,18-pentaen-7-one (**6a**): Colorless crystals, yield 29%, mp 169–171 °C. ^{1}H NMR (CDCl$_3$): $\delta = 2.33/2.62$ (AB, $^2J = -18.0$ Hz, 2H, 6-H), 3.32 (dd, $^3J = 11.0$ Hz, $|^4J| = 1.8$ Hz, 1H, 8-H), 3.58/4.13 (AB, $^2J = -10.8$ Hz, 2H, 4-H), 3.63/4.01 (AB, $^2J = -9.2$ Hz, 2H, 18-OCH$_2$), 3.81/4.85 (AB, $^2J = -10.1$ Hz, 2H, 2-H), 3.87 (dd, $^3J = 11.0$ Hz, $^3J = 6.4$ Hz, 1H, 9-H), 4.46 (br s, 1H, 19-H), 6.05 (d, $^3J = 7.7$ Hz, 1H, 16-H), 6.60 (dd, $^3J = 7.7$ Hz, $^3J = 6.4$ Hz, 1H, 17-H), 7.08–7.47 (m, 9H, aromat. H). ^{13}C NMR (CD$_2$Cl$_2$): $\delta = 43.9$, 46.5, 61.1 (C-6, C-8, C-9), 51.7, 59.7 (C-1, C-5), 70.2, 77.0, 80.9 (OCH$_2$), 109.1 (C-19), 123.0, 125.8, 126.5, 127.6, 128.4, 128.4, 128.7 (aromat. CH), 137.0, 140.0 (C-16, C-17), 136.7, 141.2, 147.1 (aromat. C$_q$), 159.9 (C-18), 209.8 (C-7).
14. 3-Oxapentacyclo[7.6.2.2^{5,8}.0^{1,5}.0^{10,15}]nonadeca-10,12,14,16-tetraene-7,18-dione (**7a**): Yellowish solid, yield 91%, mp 160–161 °C. ^{1}H NMR (CDCl$_3$): $\delta = 1.85/2.00$ (AB of ABM, $^2J = -19.0$ Hz, 2H, 19-H), 2.10/2.73 (AB of ABM, $^2J = -18.8$ Hz, 2H, 6-H), 3.68/3.91 (AB, $^2J = -9.2$ Hz, 2H, 4-H), 3.81 (d, $^3J = 12.2$ Hz, 1H, 8-H), 4.01/4.89 (AB, $^2J = -9.9$ Hz, 2H, 2-H), 4.15 (dd, $^3J = 12.2$ Hz, $^3J = 6.7$ Hz, 1H, 9-H), 6.31 (d, $^3J = 7.7$ Hz, 1H, 16-H), 6.57 (dd, $^3J = 7.7$ Hz, $^3J = 6.7$ Hz, 1H, 17-H), 7.13–7.45 (m, 4H, aromat. H). ^{13}C NMR (CDCl$_3$): $\delta = 42.4$, 46.9, 48.8 (C-6, C-9, C-19), 47.6, 55.1 (C-1, C-5), 72.4, 78.2, 80.4 (C-2, C-4, C-8), 123.9, 127.2, 127.4, 128.2 (aromat. CH), 134.0, 139.9 (C-16, C-17), 137.7, 143.0 (aromat. C$_q$), 205.3, 205.9 (C-7, C-18).
15. 9-Benzyloxy-3-oxapentacyclo[9.8.0.0^{1,5}.0^{5,10}.0^{14,19}]nonadeca-8,12,14,16,18-pentaen-7-one (**9a**): Colorless waxy solid, yield 12%. ^{1}H NMR (CDCl$_3$): $\delta = 2.19/2.27$ (AB, $^2J = -18.1$ Hz, 2H, 6-H), 3.24 (d, $^3J = 9.6$ Hz, 1H, 10-H), 3.56–3.59 (m, 1H, 11-H), 3.58/4.12 (AB, $^2J = -9.5$ Hz, 2H, 4-H), 3.71/4.09 (AB, $^2J = -9.5$ Hz, 2H, 2-H), 4.77/4.81 (AB, $^2J = -10.5$ Hz, 2H, 9-OCH$_2$), 5.45 (s, 1H, 8-H), 5.57 (dd, $^3J = 10.3$ Hz, $^3J = 5.2$ Hz, 1H, 12-H), 6.38 (d, $^3J = 10.3$ Hz, 1H, 13-H), 6.90–7.39 (m, 9H, aromat. H). ^{13}C NMR (CD$_2$Cl$_2$): $\delta = 37.2$, 41.7, 47.4 (C-6, C-10, C-11), 49.1, 51.4 (C-1, C-5), 70.7, 80.7, 81.0 (OCH$_2$), 105.1 (C-8), 124.0, 127.6, 127.7, 127.9, 128.3, 128.3, 128.5, 128.8, 129.0 (C-12, C-13, aromat. CH), 134.3, 135.8, 140.4 (aromat. C$_q$), 174.9 (C-9), 195.9 (C-7).
16. 7,9-Dibenzyloxy-3-oxahexacyclo[8.7.1^{5,9}.0^{1,5}.0^{8,11}.0^{12,17}]-nonadeca-6,12,14,16-tetraen-18-one (**10b**): Light yellow solid, yield 11%, mp 158–160 °C. ^{1}H NMR (C$_6$D$_6$): $\delta = 1.47/1.83$ (AB, $^2J = -11.4$ Hz, 1H, 19-H), 5.04 (d, $^2J = -9.9$ Hz, 1H, 2-H), 3.38–3.68, m, 4H/4.08–4.35, m, 4H (other aliph. H), 6.80–7.25 (m, 9H, aromat. H). ^{13}C NMR (C$_6$D$_6$): $\delta = 37.9$, 40.8, 49.5, 52.6 (C-8, C-10, C-11, C-19), 48.7, 62.9, 79.6 (C-1, C-5, C-9), 65.7, 68.9, 69.8, 80.3 (C-2, C-4, 7-OCH$_2$, 9-OCH$_2$), 103.7 (C-6), 124.1, 127.4, 127.5, 127.7, 128.0, 128.4, 128.5, 128.5, 128.6, 128.8

(aromat. CH), 136.6, 137.1, 138.8, 141.6 (aromat. C_q), 159.5 (C-7), 208.3 (C-18).

17. 9-Benzyloxy-3-oxahexacyclo[8.7.1.$1^{5,9}$.$0^{1,5}$.$0^{8,11}$.$0^{12,17}$]nonadeca-12,14,16-triene-7,18-dione (**11b**): Light yellow solid, yield 18%, mp 66–68 °C (decomp.). ^{1}H NMR ($CDCl_3$): $\delta = 1.80$ (d, $^2J = -12.8$ Hz, 1H, 19-H), 1.83 (dd, $^2J = -19.8$ Hz, $|^4J| = 2.6$ Hz, 1H, 6-H), 2.00 (d, $^2J = -19.8$ Hz, 1H, 6-H), 2.19 (dd, $^2J = -12.8$ Hz, $|^4J| = 2.6$ Hz, 1H, 19-H), 3.54/3.81 (AB, $^2J = -9.0$ Hz, 2H, 4-H), 3.56 (d, $^3J = 9.5$ Hz, 1H, 8-H), 3.72 (d, $^3J = 12.2$ Hz, 1H, 10-H), 4.11 (dd, $^3J = 12.2$ Hz, $^3J = 9.5$ Hz, 1H, 11-H), 4.34/4.91 (AB, $^2J = -9.9$ Hz, 2H, 2-H), 4.51/4.55 (AB, $^2J = -11.6$ Hz, 2H, 9-OCH_2), 7.10–7.27 (m, 9H, aromat. H). ^{13}C NMR ($CDCl_3$): $\delta = 35.4$, 47.2, 58.6 (C-8, C-10, C-11), 38.7, 45.5 (CH_2), 48.6, 63.0, 77.0 (C-1, C-5, C-9), 65.4, 68.9, 80.0 (C-2, C-4, 9-OCH_2), 125.1, 127.4, 128.0, 128.5, 128.6, 128.8, 129.4 (aromat. CH), 134.8, 137.2, 137.8 (aromat. C_q), 207.2, 207.8 (C-7, C-18).

18. 7-Benzyloxy-11-methoxy-3-oxahexacyclo[9.8.0.$0^{1,5}$.$0^{1,11}$.$0^{8,13}$.$0^{14,19}$]nonadeca-6,14,16,18-tetraen-9-one (**13b**): Light yellow solid, yield 18%, mp 161–162 °C. ^{1}H NMR (C_6D_6): $\delta = 1.01$ (dd, $^2J = -12.5$ Hz, $^3J = 2.9$ Hz, 1H, 12-H), 1.81 (dd, $^2J = -12.5$ Hz, $^3J = 3.9$ Hz, 1H, 12-H), 3.03 (s, 3H, OCH_3), 3.12–3.16 (m, 1H, 13-H), 3.17/3.81 (AB, $^2J = -9.5$ Hz, 2H, 7-OCH_2), 3.18 (s, 1H, 10-H), 3.32–3.36 (m, 1H, 8-H), 3.54 (br s, 1H, 6-H), 3.71/4.05 (AB, $^2J = -11.4$ Hz, 2H, 4-H), 4.16/4.87 (AB, $^2J = -9.2$ Hz, 2H, 2-H), 6.92–7.00 (m, 9H, aromat. H). ^{13}C NMR (C_6D_6): $\delta = 30.0$ (C-12), 39.7, 55.4, 55.4 (C-8, C-10, C-13), 50.9 (C-13), 51.6, 62.8, 77.6 (C-1, C-5, C-11), 68.2, 70.1, 77.6 (OCH_2), 94.2 (C-6), 124.2, 125.7, 126.5, 127.2, 128.6, 128.6, 128.7 (aromat. CH), 136.7, 137.2, 142.8 (aromat. C_q), 161.6 (C-7), 207.5 (C-9).

19. 11-Methoxy-3-oxahexacyclo[9.8.0.$0^{1,5}$.$0^{1,11}$.$0^{8,13}$.$0^{14,19}$]nonadeca-14,16,18-trien-7,9-one (**14b**): Light yellow solid, yield 23%, mp 193–194 °C. ^{1}H NMR ($CDCl_3$): $\delta = 1.51$ (dd, $^2J = -12.4$ Hz, $^3J = 2.4$ Hz, 1H, 12-H), 1.60/1.95 (AB, $^2J = -19.5$ Hz, 2H, 6-H), 2.21 (dd, $^2J = -12.4$ Hz, $^3J = 4.0$ Hz, 1H, 12-H), 3.21 (d, $|^4J| = 2.4$ Hz, 1H, 10-H), 3.32 (s, 3H, OCH_3), 3.39/4.02 (AB, $^2J = -9.6$ Hz, 2H, 4-H), 3.73 (dd, $^3J = 11.8$ Hz, $|^4J| = 2.4$ Hz, 1H, 8-H), 3.83 (ddd, $^3J = 11.8$ Hz, $^3J = 4.0$ Hz, $^3J = 2.4$ Hz, 1H, 13-H), 4.33/4.70 (AB, $^2J = -9.6$ Hz, 2H, 2-H), 7.21–7.27 (m, 4H, aromat. H). ^{13}C NMR ($CDCl_3$): $\delta = 30.0$ (C-12), 38.4, 57.3, 68.4 (C-8, C-10, C-13), 39.3 (C-6), 46.7, 57.1, 78.8 (C-1, C-5, C-11), 51.3 (OCH_3), 68.8, 77.5 (OCH_2), 124.9, 128.0, 128.3, 129.6 (aromat. CH), 134.0, 140.3 (aromat. C_q), 203.6, 206.6 (C-7, C-9).

20. CCDC 290378 contains the supplementary crystallographic data of **13b**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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