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Double-Tandem $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]\cdot[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$ Synthetic Sequence with Photoprotolytic Oxametathesis and Photoepoxidation in the Chromone Series

Roman A. Valiulin, Teresa M. Arisco, and Andrei G. Kutateladze*

Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208, United States

akutatel@du.edu

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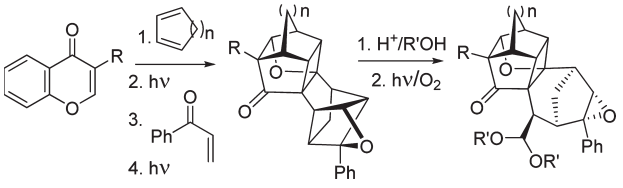

Chromones are introduced into a double-tandem $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]\cdot[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$ synthetic sequence, culminating in photoprotolytic oxametathesis, which leads to an expeditious growth of molecular complexity over a few experimentally simple steps. The overall reaction can potentially be utilized in diversity-oriented synthesis, as it allows for three or more diversity inputs furnishing novel unique polycyclic scaffolds decorated with a variety of functionalities and aromatic/heterocyclic pendants. The polycyclic alkenes, resulting from the oxametathesis step, were found to undergo efficient and clean photoinduced epoxidation when irradiated in the presence of molecular oxygen.

Introduction

Filipescu[1] and Kushner[2] independently showed that the Diels−Alder adducts of 1,4-naphthoquinone with cyclic dienes undergo intramolecular alkene−arene [2+2] photocycloaddition, yielding a facially stereodifferentiated cyclohexadiene (Scheme 1). Coxon, Marchand, and others systematically studied facial selectivity of Diels−Alder additions to **B**, concluding that the attack of alkenic dienophiles, such as maleic anhydride, occurs preferentially at the face of the two carbonyl groups,[3] while hetero-Diels−Alder reactions of singlet oxygen or 1,2,4-triazoline-3,5-dione occur mostly from the cyclobutyl face.[3f]

Also, several accounts of various acid- and base-catalyzed rearrangements involving either diene **B** or its Diels−Alder adducts have been published.[4] A related series of [2+2] intramolecular photocycloadditions in alkene−arene pairs or between two aromatic moieties were utilized by Prinzbach to produce a diverse array of polycyclic hydrocarbons, pagodanes.[5]

With this abundance of synthetic results, the ready access to the starting materials, and the palpable promise of synthetic developments around the basic $[4+2]\cdot[2+2]\cdot[4+2]$ sequence shown in Scheme 1, it was surprising for us to realize that 1,4-naphthoquinone is the only aromatic ketone that is known to form polycyclic dienes of type **B** in intramolecular [2+2] alkene−arene photocycloadditions. Conceivably this limited variety is explained by the fact that very few aromatic ketones have been reported as good dienophiles for the first, i.e., Diels−Alder, step (→ **A**). For example, Diels−Alder reactions of benzo-fused heterocyclic aromatic ketones were not known until about a decade ago, when Hsung reported the first such reaction of 3-cyanochromone derivatives.[6]

(1) Filipescu, N.; Menter, J. M. *J. Chem. Soc. B* **1969**, 616–620.
(2) Kushner, A. S. *Tetrahedron Lett*. **1971**, *35*, 3275–3278.
(3) (a) Marchand, A. P.; Zope, U. R.; Burritt, A.; Bott, S. G.; Coxon, J. M. *Tetrahedron* **1995**, *51*, 9319–9326. (b) Coxon, J. M.; Fong, S. T.; Lundie, K.; McDonald, D. Q.; Steel, P. J.; Marchand, A. P.; Zaragoza, F.; Zope, U. R.; Rajagopal, D. *Tetrahedron* **1994**, *50*, 13037–13048. (c) Coxon, J. M.; Maclagan, R. G. A. R.; McDonald, D. Q.; Steel, P. J. *J. Org. Chem*. **1991**, *56*, 2542–2549. (d) Coxon, J. M.; O'Connell, M. J.; Steel, P. J. *J. Org. Chem*. **1987**, *52*, 4726–4732. (e) Mehta, G.; Uma, R. *Tetrahedron Lett*. **1995**, *36*, 4873–4876. (f) Mehta, G.; Uma, R. *J. Org. Chem*. **2000**, *65*, 1685–1696. (g) See also: Mehta, G.; Uma, R. *Acc. Chem. Res*. **2000**, *33*, 278−286, and references therein.
(4) (a) Marchand, A. P.; Chong, H.-S.; Shukla, R.; Sharma, G. V. M.; Kumar, K. A.; Zope, U. R.; Bott, S. G. *Tetrahedron* **1996**, *52*, 13531–13538. (b) Mehta, G.; Rao, K. S. *J. Chem. Soc., Chem. Commun*. **1981**, 755–756.
(5) (a) Wollenweber, M.; Etzkorn, M.; Reinbold, J.; Wahl, F.; Voss, T.; Melder, J.-P.; Grund, C.; Pinkos, R.; Hunkler, D.; Keller, M.; Wörth, J.; Knothe, L.; Prinzbach, H. *Eur. J. Org. Chem*. **2000**, 3855–3886. (b) Fessner, W. D.; Scheumann, K.; Prinzbach, H. *Tetrahedron Lett*. **1991**, *32*, 5939–5942.
(6) Hsung, R. P. *J. Org. Chem*. **1997**, *62*, 7904–7905.

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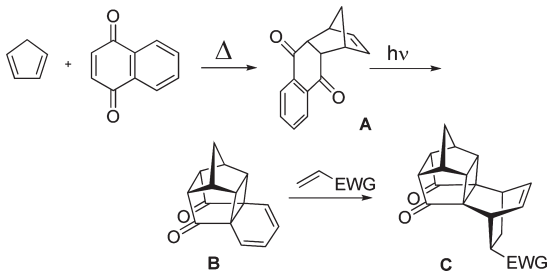
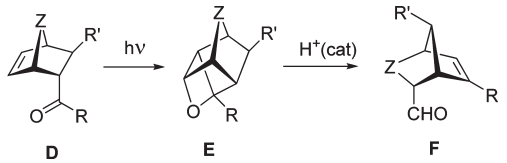
SCHEME 1



SCHEME 2



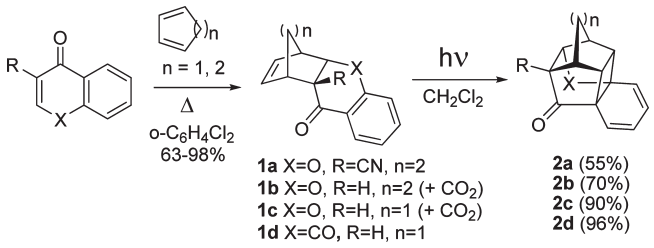
We, on the other hand, have recently developed a high-yielding tandem ground state−excited state $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$ modular approach, where the photochemical Paternò−Büchi step in a strained polycycle is accompanied by an acid-catalyzed fragmentation of the oxetane **E** into an alternative carbonyl−alkene pair, Scheme 2.[7]

This synthetic sequence amounts to photoprotolytic *oxametathesis* because the intermediate, an oxetane formed at the Paternò−Büchi step, undergoes acid-catalyzed cycloreversion, producing an alternative pair of the alkene and the carbonyl compound, similar to pyrolytic olefin−carbonyl metathesis first reported by Jones.[8] This synthetic method allows for a ready incorporation of three diversity inputs and provides expeditious growth of molecular complexity over very few simple synthetic steps. As the polycyclic dienes of type **B** represent an appealing diversity input for such oxametathetic transformations, our aim in this study was (i) to evaluate the feasibility of the intramolecular $[2_\pi+2_\pi]$ photoinduced cycloaddition in the Diels−Alder adducts of chromone derivatives and (ii) to ascertain whether secondary Diels−Alder addition and the subsequent one-pot photoprotolytic oxametathesis is possible in the strained polycycles derived from such photocyclized Diels−Alder adducts of chromones.[9]

Results and Discussion

Diels−Alder Reaction of Substituted Chromones. As described by Hsung, 3-cyanochromone reacts with cyclic dienes to furnish bicyclic Diels−Alder adducts. Contrary to that, the unsubstituted chromone in our hands proved unreactive. Clearly the cyano group makes it a much more reactive dienophile. However, we found that the formal Diels−Alder adduct of the unsubstituted chromone still can be obtained in moderate to good yields of 55−70% by reacting chromone-3-carboxylic acid instead. This is achieved simply because the initial products of its Diels−Alder reaction undergo facile thermal decarboxylation into **1b** or **1c** (Scheme 3).

SCHEME 3



Intramolecular [2+2] Arene−Alkene Photocyclization. Upon irradiation in a Rayonet photoreactor with RPR-3500 lamps (a broadband UV source with $\lambda = 350 \pm 50$ nm) or with 365 nm UV LEDs, the Diels−Alder adducts **1a−c** cyclize into dienes **2a−c**. To our knowledge, this is the first tandem Diels−Alder reaction followed by a photoinduced aryl−alkene $[2_\pi+2_\pi]$ cyclization, which involves an aromatic ketone other than a 1,4-naphthoquinone (**1d** and **2d** in Scheme 3).

The $[2_\pi+2_\pi]$ cage formation in the chromone series carries a 10−15 kcal/mol lesser penalty than the photocyclization in the naphthoquinone series. According to our density functional theory (DFT) calculations at the B3LYP/6-311+G(d, p) level, the transformation of naphthoquinone-derived **1d** to **2d** is 40.1 kcal/mol endergonic, whereas the cyclization of **1c** to **2c** is only 25.3 kcal/mol.

Diels−Alder Reactions of 2. Dienes **2** react with dienophiles such as *in situ*-generated vinyl phenyl ketone to yield Diels−Alder adducts **3** (Scheme 4). We found that the facial selectivity of this second Diels−Alder step was the same as for naphthoquinone cages; that is, the incoming dienophile was approaching from the functionalized "keto" face. The regiochemistry of this step was as shown, where the position of the endobenzoyl group is proximal to the keto, not the ether, group of the chromone moiety.

Other dienophiles produce similar results. Scheme 4 also shows the formation of Diels−Alder adducts **3e**,**f** derived from dibenzoyl ethylene and 3-cyanochromone or naphthoquinone.

Photoprotolytic Oxametathesis of 3. *endo*-Benzoyl polycycles **3** were then introduced into our photoprotolytic sequence. Irradiation with a broadband 300−400 nm UV source in benzene triggered an intramolecular Paternò−Büchi reaction to give oxetanes **4**. As we sought to develop high-yielding photoassisted transformations, we noticed that the presence of the second benzoyl group in compounds **3e**,**f** complicated photochemistry. Contrary to that, the monobenzoylated polycycles **3a−d** possessing a single chromophore gave clean and high-yielding conversions into oxetanes **4a−d**. These oxetanes were then treated with HCl to initiate the acid-catalyzed oxetane cycloreversion to an alternative alkene−carbonyl pair, which amounts to alkene−carbonyl (oxa)metathesis. Scheme 5 shows the protolytic oxametathesis in the chromone series (oxetanes **4a−c**).

The excess acid determines the outcome of the rearrangement. With small amounts, 2 molar equiv, the main products of oxametathesis are aldehydes **5a−c**. However, with excess HCl a secondary electrophilic addition of H^+ to the styrene moiety in **5** takes place, plausibly generating a benzylic

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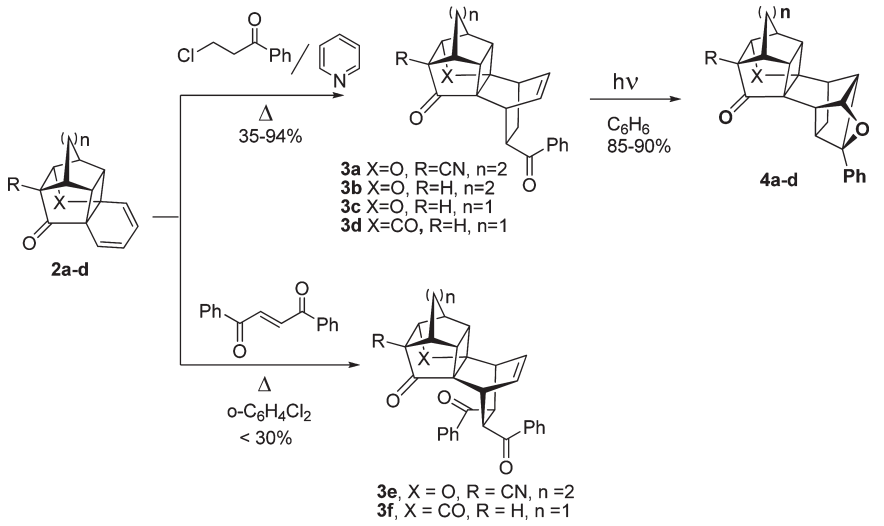
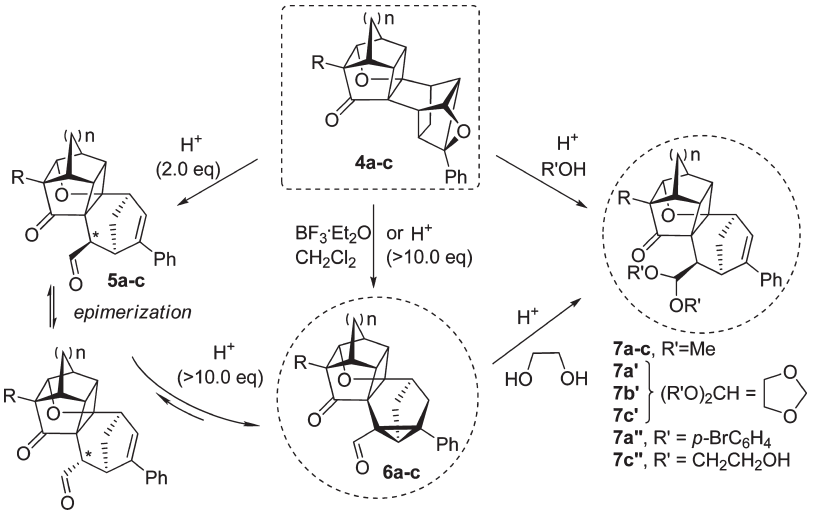
(9) For the initial communication see: Valiulin, R. A.; Kutateladze, A. G. *Tetrahedron Lett.* **2010**, *51*, 3803–3806.

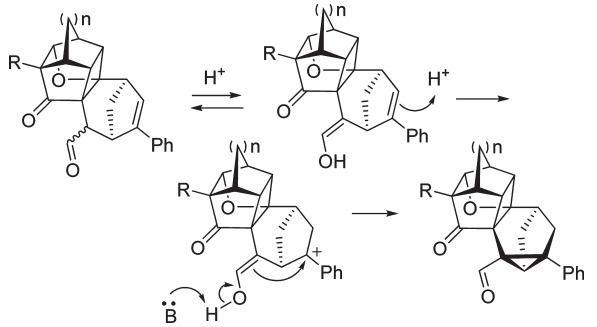
SCHEME 4



SCHEME 5



SCHEME 6



cation, which is intercepted by an internal nucleophile, the enol, formed from the formyl group, as shown in Scheme 6.

We have reported a similar cyclopropanation in the past in a polycyclic substrate derived from cyclooctatetraene and also possessing a fused cyclobutyl moiety.[7] It appears that the additional rigidity of a bicyclo[3.2.1] system fused to a cyclobutane favors the formation of formyl cyclopropanes **6**, which we never observed in the case of nonfused bicyclo-[3.2.1]octanes or bicyclo[2.2.1]heptanes. However, the energy bias is not significant, and the cyclopropyl ring is dissipated in favor of the styrene moiety when the formyl group in **6** is converted into an acetal, as shown in Scheme 5. Acetals **7** are also obtained directly by running the acid-catalyzed oxametathetic transformation of oxetanes **4** in the presence of ethylene glycol. One plausible explanation for this is that the formyl−cyclopropane conjugation makes the ring-closed form **6** slightly more stable than **5**. However, acetal formation abolishes such stabilizing conjugation, thus changing the delicate balance in favor of alkenes **7**.

Seeking a computational support for this hypothesis, we have compared pairwise the relative energies of the unconjugated formyl−alkene **F-ene** and formyl−cyclopropane **F-cp** (Figure 1 and Table 1) and their acetals **A-ene** and **A-cp**. To evaluate the mitigating effect of the phenyl group conjugation to the double bond, we also compared the relative energies of species **FH-ene** and **FH-cp** where the phenyl was replaced by hydrogen (and their corresponding acetals **AH-ene** and **AH-cp**).

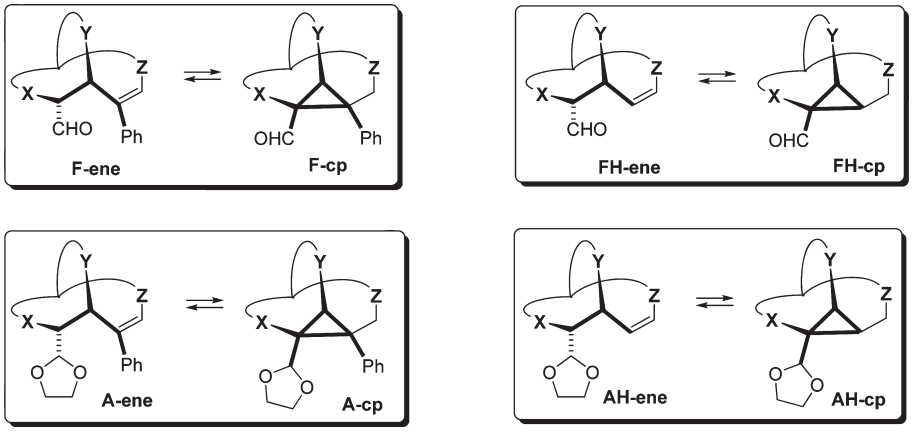


FIGURE 1. Schematic topology of the structures involved in the ene−cyclopropane equilibria (see also Table 1).

The bicyclo[2.2.1], [2.2.2], [3.2.1] and tricyclo[4.2.1.$0^{2,4}$], [5.2.1.$0^{2,5}$] cores were also included because we have experimental data for these systems as well.[7]

The DFT computations were performed with the Zhao−Truhlar M06-2X functional[10] and 6-311+G(d,p) basis set as implemented in the Gaussian 2009 package. For the pairs **F-ene** and **F-cp**, computations strongly, by 3−8 kcal/mol, favor the cyclopropyl-containing isomer **F-cp**. Even stronger bias is observed for the **FH-ene** and **FH-cp** pair, where the mitigating conjugation in the vinyl−benzene moiety is removed. The removal of the Ph group produces an additional 3−4 kcal/mol bias favoring the cyclopropyl system **FH-cp**. However, this bias is diminished or even slightly reversed when the formyl group is deconjugated from the cyclopropane ring by conversion into a cyclic acetal (**A-cp** vs **A-ene**). While the actual reversal in relative stability was calculated only for the entries 2 and 3, the dioxolane derivatives **A-ene** and **A-cp** in the chromone series (entry 6) are predicted to be nearly degenerate within 0.3 kcal/mol, whereas the free aldehyde equilibrium **F-ene** vs **F-cp** in the same entry 6 favors the cyclopropane by 5.6 kcal/mol, which is in keeping with the observed experimental trend.

Granted, this peculiar behavior cannot be fully accounted for by the stabilizing effect of the formyl−cyclopropyl conjugation. As expected, in the less strained monocyclic system such as 3-phenylcyclohex-3-ene-1-carboxaldehyde (entry 7) the cyclopropyl form is disfavored by 3.3 kcal/mol in the conjugated formyl cyclopropane form **F-cp** and even more disfavored in a deconjugated acetal **A-cp** (by 5.2 kcal/mol). The unprecedented delicate balance between the *alkene* and the *cyclopropyl* forms in polycyclic aldehydes is a reflection of the destabilization exerted by the polycyclic scaffold on the endocyclic double bond (the C−C=C angle in norbornene[11] is 108.6° instead of an idealized sp^2 angle of 120°), which makes the "saturated" cyclopropyl form relatively less disfavorable. One readily computed criterion for estimating the extent of such destabilization in the double bond is its ionization potential (IP), shown in the **FH-ene** column of Table 1 in addition to the relative energies. Figure 2 graphically illustrates the decrease in the calculated ionization potential values as the polycyclic core accumulates strain. Of entries 1−5 it is the tricyclo[5.2.1.$0^{2,5}$] moiety (i.e., entry 5) that is most distressed and has the lowest IP of 9.02 eV. It is precisely this tricyclic core that showed experimental propensity to form the cyclopropyl ring as we previously reported.[7]

Furthermore, it is easy to see that in the chromone series (entry 6) the calculated ionization potential of the double bond is even lower (8.94 eV), providing additional rationale for the experimentally observed formation of cyclopropanes **6**. The least strained cyclohexenyl moiety (entry 7 in the **FH-ene** column) has the highest IP in the series, 9.33 eV, exceeding the IP of the **FH-ene** chromone (entry 6) by almost 0.4 eV.

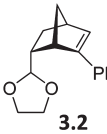
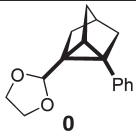
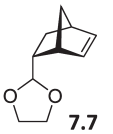
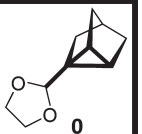
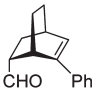
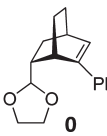
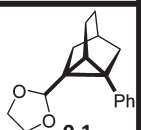
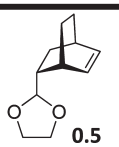
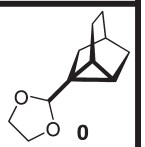
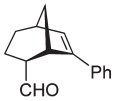
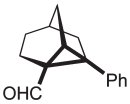
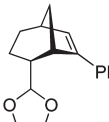
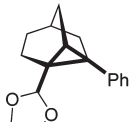
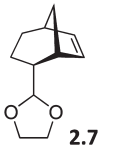
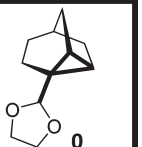
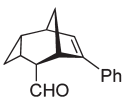
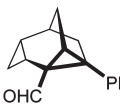
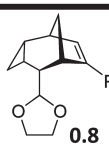
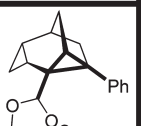
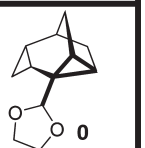
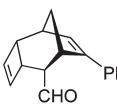
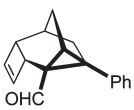
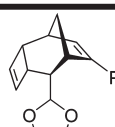
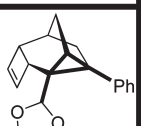
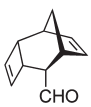
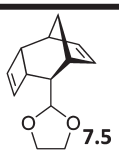
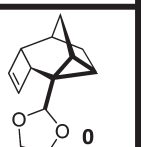
A related partial formation of nortricyclenes as a side reaction in electrophilic reactions of norbornenes has been long known.[12] However, the relative stability shift via acetal formation allows for the quantitative control of the **F-ene** ⇄ **F-cp** equilibrium in the polycyclic structures and can be a useful technique in the synthetic chemistry toolbox.

Stereochemical Relay. We note that in the synthetic sequence **1** → **2** → **3** → **4** → **5**−**7** the stereochemical outcome is not decided at the photochemical steps. Rather, the stereochemistry inherited in **3** is simply passed onto the rearranged **5**−**7**. The stereo- and regiochemistry of **3** in turn are effectively defined at the first Diels−Alder step, which yields adducts **1**. This fact is notable because a number of approaches have already been developed to control the stereochemistry of the Diels−Alder reactions. According to Hsung[6] and our own observations, in the particular case of 3-cyanochromone, the *endo*/*exo* ratio of the initial [4+2] cycloaddition is high (>95:5). One would argue that enantioselective formation of **1** can also be readily achieved, as a number of suitable chiral catalysts, such as Corey's oxazaborolidines, etc.,[13] have been developed for this task. It is all the more important since the overall sequence *chromone* → **6a** produces a decorated polycycle possessing 12 stereogenic centers, five of which are quaternary.

Photoprotolytic Oxametathesis in the Naphthoquinone Series. A similar double-tandem $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]\cdot[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$

(10) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157–167.
(11) Chiang, J. F.; Chiang, R.; Lu, K. C.; Sung, E.-M.; Harmony, M. D. *J. Mol. Struct.* **1977**, *41*, 67–77.
(12) Roberts, J. D.; Trumbull, E. R., Jr.; Bennett, W.; Armstrong, R. *J. Am. Chem. Soc.* **1950**, *72*, 3116–3124.
(13) (a) Corey, E. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2100–2117. (b) Reetz, M. T.; Jiao, N. *Angew. Chem., Int. Ed.* **2006**, *45*, 2416–2419. (c) Roelfes, G.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 3230–3232. (d) Boersma, A. J.; Feringa, B. L.; Roelfes, G. *Org. Lett.* **2007**, *9*, 3647–3650. (e) Barroso, S.; Blay, G.; Pedro, J. R. *Org. Lett.* **2007**, *9*, 1983–1986.

TABLE 1. Ene−Cyclopropyl Pairwise Comparison of the DFT Relative Stabilities Calculated at the M06-2X/6-311+G(d,p) Level of Theory[a,b]

Entry	F-ene	F-cp	A-ene	A-cp	FH-ene	FH-cp	AH-ene	AH-cp
1 bicyclo [2.2.1]	 6.8	 0	 3.2	 0	 10.5 (IP=9.21 eV)	 0	 7.7	 0
2 bicyclo [2.2.2]	 2.4	 0	 0	 0.1	 4.5 (IP=9.26 eV)	 0	 0.5	 0
3 bicyclo [3.2.1]	 3.5	 0	 0	 0.9	 6.5 (IP=9.13 eV)	 0	 2.7	 0
4 tricyclo [4.2.1.0^{2,4}]	 5.3	 0	 0.8	 0	 9.0 (IP=9.06 eV)	 0	 5.5	 0
5 tricyclo [5.2.1.0^{2,5}]	 8.2	 0	 2.7	 0	 11.5 (IP=9.02 eV)	 0	 7.5	 0
6 chromone series	5.6	0	0.3	0	8.2 (IP=8.94 eV)	0	3.5	0
7 cyclohexene	0	3.3	0	5.2	0 (IP=9.33 eV)	2.3	0	6.4

[a]Units: relative kcal/mol. [b]Ionization potentials in column **FH-ene** are also calculated at the M062X/6-311+G(d,p) level of theory.

sequence was implemented starting from 1,4-naphthoquinone and cyclopentadiene. As noted above, the alkene−arene intramolecular [2_π+2_π] photocycloadditions are known only for the Diels−Alder adducts derived from *cyclopentadienes* and 1,4-naphthoquinones. Our attempt to photocyclize **1g** derived from *cyclohexadiene* did not produce cage **2g** but rather led to the photoinduced *endo* to *exo* isomerization yielding **1g′**. Such *endo*/*exo* conversion under electron-transfer conditions is precedented.[14]

However, the known Diels−Alder adduct of *cyclopentadiene* and naphthoquinone **1d** was expectedly photocyclized into known **2d**, then reacted with *in situ*-generated vinyl phenyl ketone and subjected to Paternò−Büchi conditions to yield oxetane **4d** (Scheme 7).

Under acidic conditions, oxetane **4d** underwent similar cycloreversion to **4a**−**c**: with a small amount of HCl/dioxane it produced epimerized aldehyde **5d** (Scheme 8). Carrying out the reaction in excess HCl or $BF_3 \cdot Et_2O$ yielded formylcyclopropane **6d**, whereas in the presence of acidic ethylene glycol the acetal formation shifted the equilibrium to alkene **7d**. The two keto- groups exhibited very different

(14) Pandey, B.; Dalvi, P. V.; Athawale, A. A.; Pant, B. G.; Kewale, P. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1505–1506.

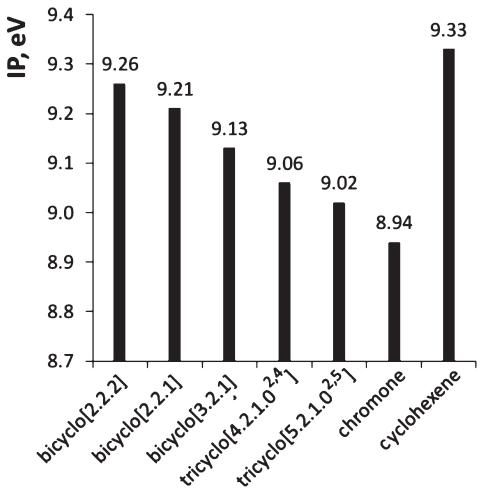
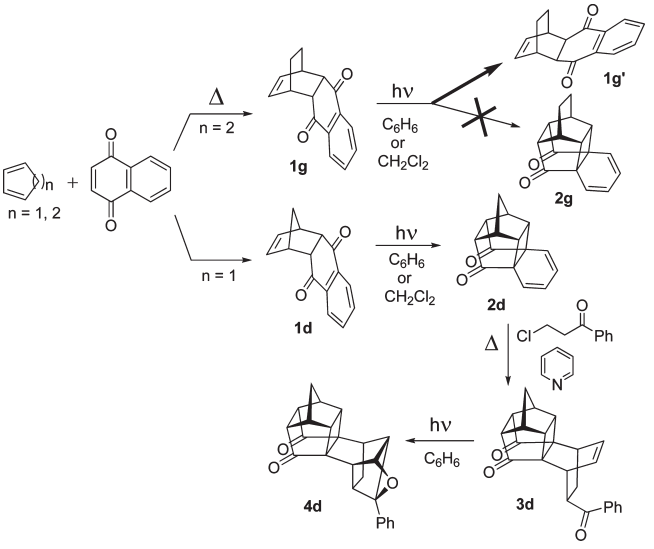


FIGURE 2. Calculated vertical ionization potentials, eV, as a function of the ring strain in **FH-ene**, M062X/6-311+G(2d,2p).

SCHEME 7



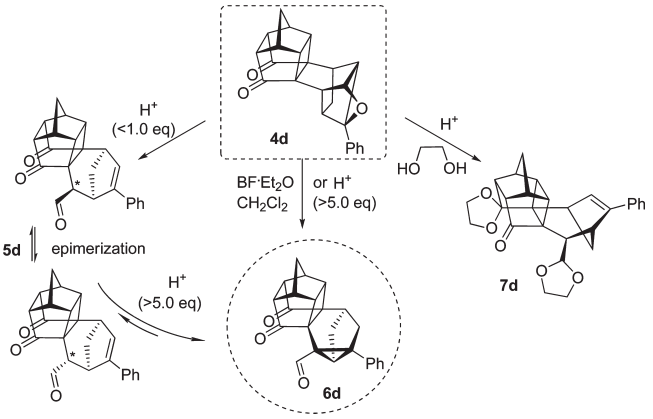
reactivity: the carbonyl proximal to the formyl group survived, while the distal carbonyl was converted into a spiro-acetal.

Diels–Alder reaction of 1,2-naphthoquinone with cyclohexadiene produced cyclohexene **1i** (X-ray structure is available in the SI) as a result of a fragmentation on silica gel during purification (Scheme 9). Cyclopentadiene furnished the known **1h**,[15] which did not exhibit any promising photochemistry.

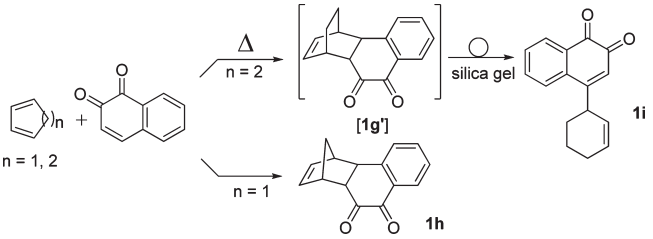
One-Pot Implementation of the 3 → 7 Transformation. With optimization of conditions the photoprotolytic oxametathesis can be implemented as a one-pot procedure (Scheme 10). We found that when irradiation of **3d** is carried out in dichloromethane with a 5-fold molar excess of ethylene glycol and 5 molar equiv of HCl/dioxane, **7d** is the only product in the reaction mixture (by NMR).

Clearly the intramolecular Paternò–Büchi step occurs much faster than the potential bimolecular reduction of the

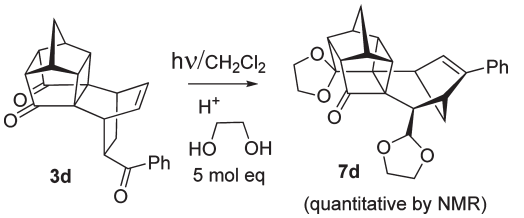
SCHEME 8



SCHEME 9



SCHEME 10



excited chromophore with ethylene glycol, presumably yielding oxetane **4d**, which undergoes acid-catalyzed oxametathetic conversion with *in situ* trapping of the diketo aldehyde **5d** in the form of bis-dioxolane **7d**. Provided that an appropriate *pregenerated* aryl vinyl ketone is used as a dienophile at the **2** → **3** step, the entire double-tandem $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]\cdot[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$ sequence could potentially be carried out as a one-pot procedure.

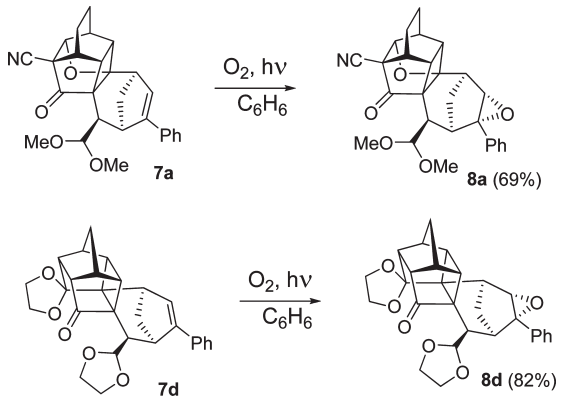
Photoepoxidation. We further found that upon extended irradiation, the styrene moiety in aldehydes **5** or acetals **7** is epoxidized by molecular oxygen present in oxygenated solutions (oxygen's concentration in DCM under 1 atm of O_2 gas is 10.7 mM, and similar concentrations are achieved in other common solvents[16]) (Scheme 11). While photoepoxidations of olefins in the presence of organic sensitizers or transition metal complexes are well-known,[17] the direct, i.e., nonsensitized, photoreactions between vinyl arenes and molecular

(15) (a) Friedrichsen, W.; Kallweit, I.; Schmidt, R. *Liebigs Ann. Chem.* **1977**, 116–144. (b) Gelman, D. M.; Forsyth, C. M.; Perlmutter, P. *Org. Lett.* **2009**, *11*, 4958–4960.

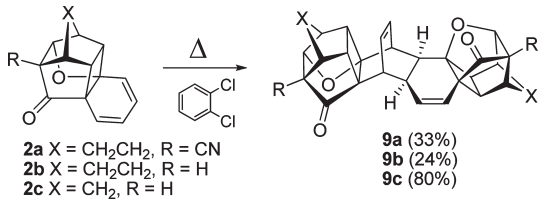
(16) Battino, R. *Oxygen and Ozone*; Solubility Data Series: Vol. 7; Pergamon: Oxford, England, 1981; p 519.

(17) (a) Koo, J.-Y.; Schuster, G. B. *J. Org. Chem.* **1979**, *44*, 847–851. (b) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934–4940. (c) Murata, C.; Yoshida, H.; Hattori, T. *J. Chem. Soc., Chem. Commun.* **2001**, 2412–2413. (d) Inoue, H.; Okamoto, T.; Komiyama, M.; Hida, M. *J. Photochem. Photobiol. A, Chem.* **1992**, *65*, 221–227.

SCHEME 11



SCHEME 12



oxygen are very rare. In fact we found only one study in the literature proposing a contact charge-transfer pair mechanism of such photoepoxidation of 1-arylcyclohexenes,[18] where the yields of photoepoxides were poor due to several side reactions, including the ene reaction, i.e., allylic oxidation, and the sensitized isomerization of the substrate into *trans*-cycloalkene followed by solvent capture. Our findings demonstrate that the rigid polycyclic scaffolds improve photoepoxidation yields dramatically. Obviously, allylic alcohols or α,β-unsaturated ketones cannot form in these structures, as there are no easily abstracted allylic hydrogens, and the photoinduced *cis*−*trans* isomerization of the double bond is not possible either.

The initial light-absorbing chromophore in this system is undoubtedly the styrene moiety. It is conceivable that the additional rigidity of the polycyclic network in **5** and **7** prevents the alkene from dissipating its excitation via twisting, thus further improving the overall efficiency of photoepoxidation. The ionization potential of 8.94 eV calculated for the double bond in the chromone series (Figure 2) is 0.27 eV lower than that in the bicyclo[2.2.1] series, indicating that the double-bond reactivity in **7** toward oxygen can be exceptionally high.

Thermal Dimerization of Dienes 2. One arresting difference between the chromone-based dienes **2a**−**c** and naphthoquinone-based dienes **B** is that asymmetric **2a**−**c** undergo a Diels−Alder dimerization when heated at 200−210 °C, yielding a single diastereomer as shown in Scheme 12. The structure of **9** was proved unambiguously by X-ray analysis.

The diasteroselectivity of Diels−Alder dimerization is correlated with the computed relative DFT energies of the Diels−Alder product. The geometries of 16 possible *exo* dimers of **2b** were optimized at the B3LYP/6-311+G(d,p) level (the *endo* products were left out of consideration because the steric clash of the two polycyclic pendants in the *syn* structures is too severe). As the structures of two dimers, **9a** and **9c**, were confirmed by X-ray crystallography, the crystal structure of **9a** was superimposed onto its computed structure, which gave an excellent rmsd of 0.046 for all heavy atoms, indicating that this large molecular system is adequately handled by the B3LYP/6-311+G(d,p) level of theory.

Table 2 lists computational results grouped by the facial selectivity of Diels−Alder reaction and sorted by the (global) relative energy, kcal/mol. The observed dimer indeed has the lowest relative energy.

In the syn^{diene}−$syn^{\text{dienophile}}$ and $anti^{\text{diene}}$−$syn^{\text{dienophile}}$ cases, the most pronounced steric clash is observed when A_2 is the carbonyl group, i.e., the carbonyl in immediate proximity to the double bond in the bicyclo[2.2.2] moiety. The relative positions of the A_1 and B_1 groups in the "diene" component expectedly have much lesser differentiating effect, because the double bond in a more symmetric bicyclo[2.2.2] moiety is equidistantly removed from either A_1 or B_1 (which is not the case for A_2 and B_2 in the dienophilic moiety, where such distances differ by more than an angstrom).

The steric clash of the carbonyl group in position A_2 can possibly explain the reluctance to dimerize of the 1,4-naphthoquinone-based caged diene **2d**, for which this clash is unavoidable. Another factor is that, unlike **2d**, the diene moiety in the chromone-based **2a**−**c** is polarized. Figure 3 shows that atoms in the butadiene moiety of **2d** are depleted of electronic density to a much greater extent; the cumulative positive charge of the moiety is 1.16 vs 0.40 in **2a**, i.e., almost a 3-fold difference. The electronic density in the chromone-derived **2a** is much less depleted, and it is also appropriately polarized with the "dienophile" double bond being more electrophilic, Figure 3. Experimentally we did not observe any evidence for the Diels−Alder dimerization of **2d**.

We believe that it is this lack of symmetry and the resulting polarization in the cyclohexadienyl moiety of the chromone-derived **2** that is likely responsible for high regio- and stereoselectivity of Diels−Alder additions of nonsymmetric dienophiles, such as vinyl ketones, to **2a**−**c**.

Conclusions

We have demonstrated that the Diels−Alder adducts of chromones are capable of photoinduced alkene−arene $[2_\pi+2_\pi]$ cycloaddition, furnishing a versatile diene, which can dimerize or can be introduced into a double-tandem $[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]\cdot[4_\pi+2_\pi]\cdot[2_\pi+2_\pi]$ synthetic sequence, followed by an acid-catalyzed ring-opening−ring-closure, leading to expeditious growth of molecular complexity over a few experimentally simple steps. Additionally, the oxametathesis products containing a vinyl arene moiety (i.e., acetals **7**) undergo clean and stereoselective photoepoxidation when irradiated in oxygenated solutions, further enhancing the value of this method, which contains three high-yielding key photochemical steps and could conceivably be implemented in a one-pot fashion. From the stereochemical standpoint, the appealing feature of this synthetic sequence is that the initial Diels−Alder step controls the stereochemical outcome of the entire sequence. As a number of suitable methods have been developed to achieve enantioselective Diels−Alder

(18) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3331–3336.

TABLE 2. Relative Energies of 16 Possible Diastereomers of the *exo* Dimers

Syn-Syn[b]					Anti-Anti				
A_1	B1	A2	B_2	E^a	A_1	B_1	A_2	B_2	E^a
O	CO	O	CO	**0**	CO	O	CO	O	**1.8**
CO	O	O	CO	**0.3**	O	CO	CO	O	**1.8**
O	CO	CO	O	**2.6**	CO	O	O	CO	**2.0**
CO	O	CO	O	**3.1**	O	CO	O	CO	**2.2**
Anti-Syn					**Syn-Anti**				
O	CO	O	CO	**6.2**	O	CO	CO	O	**8.2**
CO	O	O	CO	**6.3**	O	CO	O	CO	**8.8**
O	CO	CO	O	**9.3**	CO	O	CO	O	**10.0**
CO	O	CO	O	**10**	CO	O	O	CO	**10.4**

[a]Relative energy, kcal/mol. [b]Facial selectivity of cycloaddition: *syn* (or *anti*) to the carbonyl/ether functionality for both the diene (first) and dienophile (second).

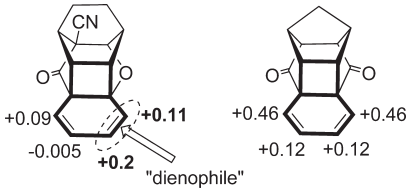


FIGURE 3. Calculated Mulliken charges in the butadiene moiety of **2a** and **2d** (with hydrogen charges summed into heavy atoms) at B3LYP/6-311+G(2d,2p).

cycloadditions, one envisions a straightforward access to enantiopure structures **6**−**9**.

Experimental Section

Diels−Alder Adducts (1a−c). General Procedure. A solution of chromone (1.0 equiv) and 1,3-cyclohexadiene or freshly distilled 1,3-cyclopentadiene (5.0 equiv) in 15 mL of 1,2-dichlorobenzene was heated in a screw-cap pressure flask at 200−210 °C (for 1,3-cyclohexadiene) and 130−140 °C (for 1,3-cyclopentadiene) overnight. After the reaction was cooled to room temperature, the solvent was removed under vacuum. The crude reaction mixture was purified on a silica gel column using hexane/EtOAc as the eluent.

***endo*-4,5-Benzo-7-cyano-3-oxatricyclo[6.2.2.0^{2,7}]dodeca-4,5 dien-6-one (1a):** from 2.50 g of 3-cyanochromone (14.6 mmol) and 7.0 mL of 1,3-cyclohexadiene (73.0 mmol) at 200 °C (hexane/EtOAc gradient 20:1 → 5:1): 2.19 g (60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, J = 7.9, 1.8 Hz, 1H), 7.45 (ddd, J = 8.5, 7.2, 1.8 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.80 (ddd, J = 8.0, 7.1, 1.1 Hz, 1H), 6.26 (dd, J = 8.3, 1.1 Hz, 1H), 6.14 (t, J = 7.3 Hz, 1H), 5.06 (ddd, J = 7.9, 6.4, 1.2 Hz, 1H), 3.50 (d, J = 2.8 Hz, 1H), 3.12 (m, 1H), 2.15 (m, 1H), 1.75 (m, 1H), 1.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.4, 159.8, 137.7, 133.6, 132.1, 127.6, 121.9, 120.1, 118.3, 118.1, 82.9, 50.4, 39.7, 37.1, 21.3, 21.1. ***exo*-4,5-Benzo-7-cyano-3-oxatricyclo-[6.2.2.0^{2,7}]dodeca-4,5-dien-6-one:** δ 7.85 (dd, J = 8.0, 1.7 Hz, 1H), 7.55 (ddd, J = 8.5, 7.2, 1.8 Hz, 1H), 7.03 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 6.95 (dd, J = 8.5, 1.1 Hz, 1H), 6.58 (m, J = 8.5, 5.9 Hz, 1H), 6.48 (ddd, J = 8.0, 6.9, 1.4 Hz, 1H), 4.77 (dd, J = 3.6, 1.7 Hz, 1H), 3.47 (m, 1H), 3.12 (m, 1H), 1.71−1.65 (m, J = 12.8, 9.7, 4.1, 2.5 Hz, 1H), 1.46−1.40 (m, 1H), 1.28−1.22 (m, 1H), 1.20−1.13 (m, 1H).

***endo*-4,5-Benzo-3-oxatricyclo[6.2.2.0^{2,7}]dodeca-4,5-dien-6-one (1b):** from 2.00 g of chromone-3-carboxylic acid (10.5 mmol) and 5.0 mL of 1,3-cyclohexadiene (52.5 mmol) at 200 °C (hexane/EtOAc gradient 30:1 → 10:1): 1.67 g (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (dd, J = 7.9, 1.8 Hz, 1H), 7.36 (ddd, J = 8.4, 7.1, 1.8 Hz, 1H), 6.95 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.91 (dd, J = 8.4, 1.0 Hz, 1H), 6.28 (ddd, J = 8.0, 6.5, 1.3 Hz, 1H), 6.20 (t, J = 7.2 Hz, 1H), 4.95 (dd, J = 9.4, 3.3 Hz, 1H), 3.27 (m, 1H), 3.12 (m, 1H), 2.86 (dd, J = 9.4, 2.1 Hz, 1H), 1.62 (dddd, J = 12.3, 9.5, 3.0, 3.0 Hz, 1H), 1.54 (dddd, J = 12.5, 9.8, 4.6, 1.8 Hz, 1H), 1.37 (dddd, J = 12.1, 12.1, 3.6, 3.6 Hz, 1H), 1.27 (dddd, J = 11.8, 11.8, 4.4, 2.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.9, 160.9, 136.3, 134.3, 132.3, 126.8, 120.9, 119.7, 117.8, 79.6, 50.7, 36.9, 34.5, 25.5, 20.5. ***exo*-4,5-Benzo-3-oxatricyclo[6.2.2.0^{2,7}]dodeca-4,9-diene-6-one:** 0.67 g (28%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (dd, J = 7.8, 1.8 Hz, 1H), 7.46 (ddd, J = 8.3, 7.1, 1.8 Hz, 1H), 6.95 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.91 (dd, J = 8.4, 1.0 Hz, 1H), 6.49 (m, J = 8.4, 6.2 Hz, 1H), 6.28 (m, J = 8.1, 6.8, 1.2 Hz, 1H), 4.64 (ddd, J = 11.0, 3.7, 1.1 Hz, 1H), 3.23 (m, 1H), 3.02 (m, 1H), 2.59 (ddd, J = 11.0, 2.8, 1.8 Hz, 1H), 1.92 (m, 1H), 1.48 (m, 1H), 1.17 (m, 2H).

***endo*-4,5-Benzo-3-oxatricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-6one (1c):** from 2.00 g of chromone-3-carboxylic acid (10.5 mmol) and 3.0 mL of 1,3-cyclopentadiene (36.8 mmol) at 135 °C (hexane/EtOAc gradient 60:1 → 30:1): 1.23 g (55%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (dd, J = 7.9, 1.7 Hz, 1H), 7.36 (ddd, J = 8.4, 7.1, 1.8 Hz, 1H), 6.85 (ddd, J = 8.0, 7.2, 1.0 Hz, 1H), 6.74 (dd, J = 8.4, 1.0 Hz, 1H), 6.11 (m, 2H), 5.25 (dd, J = 9.3, 4.0 Hz, 1H), 3.49 (m, 2H), 3.14 (dd, J = 9.2, 3.9 Hz, 1H), 1.46 (ddd, J = 9.2, 1.9, 1.9 Hz, 1H), 1.36 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4, 160.9, 137.2, 136.5, 134.5, 126.6, 120.6, 119.5, 117.7, 80.0, 49.9, 49.3, 49.0, 45.18. ***exo*-4,5-Benzo-3-oxatricyclo[6.2.1.0^{2,7}]undeca-4,9-dien-6-one:** 0.56 g (25%). ^{1}H

NMR (500 MHz, $CDCl_3$): δ 7.78 (dd, J = 7.9, 1.7 Hz, 1H), 7.42 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 6.92 (ddd, J = 8.0, 7.1, 1.0 Hz, 1H), 6.88 (dd, J = 8.4, 1.0 Hz, 1H), 6.44 (dd, J = 5.7, 3.0 Hz, 1H), 6.10 (dd, J = 5.7, 3.2 Hz, 1H), 4.61 (ddd, J = 8.0, 1.3, 1.3 Hz, 1H), 3.36 (m, 1H), 3.27 (m, 1H), 2.58 (dd, J = 8.0, 1.8 Hz, 1H), 1.67 (d, J = 9.4 Hz, 1H), 1.55 (m, J = 9.4, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9, 160.9, 141.8, 136.6, 133.8, 127.1, 121.0, 120.1, 118.1, 80.1, 51.7, 48.4, 48.4, 45.3.

General Procedure for Photoinduced [2π+2π] Intramolecular Cyclization. An approximately 10 mM solution of an *endo* precursor **1** in benzene (unless otherwise noted) was irradiated in Pyrex reaction vessels in a Rayonet reactor equipped with RPR-3500 UV lamps (broadband 300−400 nm UV source with peak emission at 350 nm) for 24−48 h. Irradiation resulted in a quantitative conversion to **2**, which can be used without further purification.

15-Cyano-13-oxahexacyclo[6.4.4.0.0^{2,7}.0^{3,14}.0^{6,15}]hexadec-9,-11-dien-16-one (2a): from 2.23 g of **1a** (8.9 mmol) in 1.0 L of benzene, irradiation for 24 h (hexane/EtOAc gradient 15:1 → 5:1): 1.23 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (dd, J = 9.6, 5.8 Hz, 1H), 5.95 (ddd, J = 9.8, 5.8, 1.0 Hz, 1H), 5.54 (d, J = 9.6 Hz, 1H), 5.45 (d, J = 9.8 Hz, 1H), 4.75 (d, J = 4.2 Hz, 1H), 3.43 (ddd, J = 8.0, 5.6, 1.4 Hz, 1H), 2.86 (dd, J = 8.3, 5.0 Hz, 1H), 2.30 (m, 1H), 2.24 (m, 1H), 2.00−1.91 (m, 3H), 1.60−1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.5, 126.3, 125.7, 121.7, 120.5, 117.3, 84.0, 82.0, 56.4, 53.3, 50.7, 43.0, 36.5, 36.0, 15.8, 14.2. HRMS (ESI): calcd for $C_{16}H_{13}NNaO_2^+$ (MNa^+) 274.0838, found 274.0835.

13-Oxahexacyclo[6.4.4.0.0^{2,7}.0^{3,14}.0^{6,15}]hexadec-9,11-dien-16-one (2b): from 1.50 g of **1b** (6.6 mmol) in 1.0 L of benzene, irradiation for 24 h (hexane/EtOAc gradient 20:1 → 10:1): 1.05 g (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95−5.88 (m, 2H), 5.53 (d, J = 9.4 Hz, 1H), 5.42 (d, J = 9.7 Hz, 1H), 4.60 (dd, J = 8.0, 4.2 Hz, 1H), 3.38 (ddd, J = 7.8, 5.6, 1.5 Hz, 1H), 2.78 (ddd, J = 8.1, 4.8, 2.2 Hz, 1H), 2.73 (ddd, J = 8.1, 3.4, 2.4 Hz, 1H), 2.09 (m, 1H), 1.94 (m, 1H), 1.92−1.86 (m, 1H), 1.82−1.75 (m, 1H), 1.73−1.66 (m, 1H), 1.52−1.45 (dddd, J = 14.0, 11.8, 5.7, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.1, 125.8, 124.8, 122.6, 122.3, 83.3, 78.7, 57.4, 52.7, 52.3, 45.1, 36.1, 31.3, 17.7, 15.2.

12-Oxahexacyclo[5.4.4.0.0^{2,6}.0^{3,13}.0^{5,14}]pentadeca-8,10-dien-15-one (2c): from 0.89 g of **1c** (4.2 mmol) in 1.0 L of benzene, irradiation for 24 h: 0.88 g (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 (dd, J = 9.5, 5.7 Hz, 1H), 5.95 (ddd, J = 9.9, 5.7, 1.0 Hz, 1H), 5.63 (d, J = 9.5 Hz, 1H), 5.49 (d, J = 9.9 Hz, 1H), 5.02 (dd, J = 8.4, 4.0 Hz, 1H), 3.42 (ddd, J = 7.8, 6.0, 1.3 Hz, 1H), 2.91 (m, 1H), 2.82 (ddd, J = 8.0, 5.4, 1.9 Hz, 1H), 2.75 (m, 1H), 2.61 (ddd, J = 8.4, 4.3, 1.9 Hz, 1H), 1.80 (d, J = 11.3 Hz, 1H), 1.51 (d, J = 11.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.5, 125.4, 124.6, 122.3, 122.3, 87.1, 83.1, 56.9, 56.3, 55.0, 48.4, 46.3, 42.6, 33.8.

General Procedure for Preparation of the Diels−Alder Adducts 3a−c. A solution of **2** (1.0 equiv) and 3-chloropropiophenone (1.3 equiv) in 10 mL of pyridine was heated in a screw-cap pressure flask at 130−140 °C overnight. After the reaction was cooled to room temperature, the solvent was removed on a high-vacuum pump. The crude reaction mixture was purified on a silica gel flash column using hexane/EtOAc (or EtOH) as an eluent. NOTE: To avoid epimerization of the benzoyl group, the column was pretreated with 2 mL of pyridine.

1*R*(*S*),2*S*(*R*),11*S*(*R*),12*R*(*S*),16*R*(*S*)-16-Benzoyl-9-cyano-3-oxaheptacyclo[10.2.2.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}. 0^{17,18}]octadec-13-en-10-one (3a): from 1.13 g of **2a** (4.5 mmol) and 1.00 g of 3-chloropropiophenone (5.9 mmol) at 140 °C (hexane/EtOAc gradient 20:1 → 1:1): 0.86 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (m, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.45 (m, 2H), 6.39 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 6.19 (dd, J = 8.3, 6.3 Hz, 1H), 4.80 (d, J = 4.0 Hz, 1H), 4.43 (ddd, J = 9.6, 4.8, 2.1 Hz, 1H), 3.13 (ddd, J = 6.4, 1.8, 1.8 Hz, 1H), 2.83 (m, 1H), 2.68 (ddd, J = 7.4, 5.8, 1.5 Hz, 1H), 2.3 (m, 1H), 2.16 (m, 1H), 2.11 (dd, J = 7.6, 5.0 Hz, 1H), 2.04−1.94 (m, 1H), 1.93−1.85 (m, 4H), 1.54−1.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.2, 200.5, 147.5, 136.1, 133.4, 133.2, 131.4, 129.99, 128.94, 117.3, 91.3, 83.4, 57.8, 52.6, 40.2, 36.6, 35.4, 35.1, 33.8, 33.8, 21.9, 16.2, 14.3. HRMS (ESI): calcd for $C_{25}H_{21}NNaO_3^+$ (MNa^+) 406.1414, found 406.1425.

1*R*(*S*),2*S*(*R*),11*S*(*R*),12*R*(*S*),16*R*(*S*)-16-Benzoyl-3-oxaheptacyclo[10.2.2.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}.0^{17,18}]octadec-13-en-10-one (3b): from 2.24 g of **2b** (9.9 mmol) and 2.16 g of 3-chloropropiophenone (12.8 mmol) at 140 °C (hexane/EtOAc gradient 20:1 → 10:1): 1.24 g (35%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (m, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.44 (m, 2H), 6.37 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 6.17 (dd, J = 8.5, 6.1 Hz, 1H), 4.65 (ddd, J = 7.7, 4.2, 1.5 Hz, 1H), 4.50 (ddd, J = 9.7, 4.8, 2.1 Hz, 1H), 3.05 (ddd, J = 6.4, 1.7, 1.7 Hz, 1H), 2.78 (m, 1H), 2.62−2.57 (m, 2H), 2.02 (m, 1H), 2.01−1.96 (m, 2H), 1.93 (m, 1H), 1.87 (ddd, J = 12.9, 4.8, 3.2 Hz, 1H), 1.84−1.79 (m, 1H), 1.77−1.70 (m, 1H), 1.69−1.63 (m, 1H), 1.44−1.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.8, 201.3, 136.4, 133.2, 132.9, 131.5, 129.1, 128.8, 90.2, 79.9, 58.1, 52.1, 41.3, 40.4, 35.8, 35.3, 35.1, 34.0, 31.2, 22.2, 18.1, 15.3. HRMS (ESI): calcd for $C_{24}H_{23}O_3^+$ (MH^+) 359.1642, found 359.1657.

1*R*(*S*),2*S*(*R*),10*S*(*R*),11*R*(*S*),15*R*(*S*)-15-Benzoyl-3-oxaheptacyclo[9.2.2.1^{2,5}.1^{7,10}.0^{2,10}.0^{4,8}.0^{16,17}]heptadec-12-en-9-one (3c): from 0.92 g of **2c** (4.3 mmol) and 0.95 g of 3-chloropropiophenone (5.6 mmol) at 140 °C (hexane/EtOAc gradient 20:1 → 10:1): 0.54 g (36%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (m, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.44 (m, 2H), 6.37 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 6.16 (dd, J = 8.5, 6.1 Hz, 1H), 5.10 (ddd, J = 8.0, 3.7, 1.6 Hz, 1H), 4.46 (ddd, J = 9.6, 4.9, 2.2 Hz, 1H), 3.10 (ddd, J = 6.4, 1.8, 1.8 Hz, 1H), 2.81 (m, 1H), 2.79−2.74 (m, 2H), 2.63 (m, 1H), 2.50 (ddd, J = 8.0, 4.3, 1.9 Hz, 1H), 2.13 (m, 1H), 1.96 (ddd, J = 12.7, 9.7, 2.4 Hz, 1H), 1.88 (ddd, J = 12.8, 4.9, 3.2 Hz, 1H), 1.79 (d, J = 11.4 Hz, 1H), 1.56 (d, J = 11. 4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.6, 201.3, 136.4, 133.4, 133.0, 131.6, 129.1, 128.8, 90.6, 88.1, 57.2, 54.3, 47.9, 47.2, 42.1, 40.3, 38.2, 36.3, 35.9, 34.2, 22.5. HRMS (ESI): calcd for $C_{23}H_{21}O_3^+$ (MH^+) 345.1485, found 345.1479.

General Procedure for Preparation of the Paternò−Büchi Adducts 4a−c. An approximately 1−3 mM solution of a precursor **3** in benzene was irradiated in Pyrex reaction vessels in a Rayonet reactor equipped with RPR-3500 UV lamps (broadband 300−400 nm UV source with peak emission at 350 nm) for 48−72 h. Irradiation resulted in a quantitative conversion to **4**, which were used without further purification. NOTE: strained polycyclic oxetanes **4** are not stable on silica gel, which induces oxametathesis.

9-Cyano-15-phenyl-3,14-dioxanonacyclo[10.4.2.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}.0^{13,16}.0^{15,18}.0^{19,20}]icosan-10-one (4a): from 1.50 g of **3a** (3.9 mmol) in 1.5 L of benzene, irradiation for 72 h: >85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.36 (m, 4H), overlaps 7.36−7.32 (m, 1H), 4.80 (m, 1H), 4.72 (d, J = 4.0 Hz, 1H), 3.50 (dddd, J = 5.5, 3.5, 1.7, 1.7 Hz, 1H), 2.95−2.91 (m, 2H), 2.74 (ddd, J = 6.5, 1.8, 1.8 Hz, 1H), 2.54 (dd, J = 7.6, 5.2 Hz, 1H), 2.36 (m, 1H), 2.26 (m, 1H), 2.12 (ddd, J = 6.2, 6.2, 1.3 Hz, 1H), 2.01−1.90 (m, 4H), 1.81 (ddd, J = 13.2, 6.7, 1.9 Hz, 1H), 1.63−1.56 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.0, 136.3, 129.1, 128.8, 127.2, 117.5, 101.1, 90.4, 81.5, 81.4, 56.8, 54.6, 53.2, 44.2, 39.6, 38.6, 37.0, 36.1, 35.4, 32.3, 31.9, 15.9, 14.1. HRMS (ESI): calcd for $C_{25}H_{22}NO_3^+$ (MH^+) 384.1594, found 384.1586.

15-Phenyl-3,14-dioxanonacyclo[10.4.2.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}.0^{13,16}.0^{15,18}.0^{19,20}]icosan-10-one (4b): from 1.20 g of **3b** (3.3 mmol) in 1.5 L of benzene, irradiation for 72 h: >85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.35 (m, 4H), overlaps 7.35−7.31 (m, 1H), 4.82 (m, 1H), 4.57 (dd, J = 8.0, 4.1 Hz,

1H), 3.49 (dddd, J = 5.5, 3.6, 1.8, 1.8 Hz, 1H), 2.91 (d, J = 6.4 Hz, 1H), 2.86 (m, J = 7.6, 5.6, 1.2 Hz, 1H), 2.69 (ddd, J = 6.5, 1.8, 1.8 Hz, 1H), 2.63 (ddd, J = 8.0, 3.3, 2.4 Hz, 1H), 2.42 (ddd, J = 7.5, 5.1, 2.3 Hz, 1H), 2.12 (m, 1H), 2.08 (m, J = 6.2, 1.3 Hz, 1H), 2.03−2.00 (m, 1H), 1.99 (m, 1H), 1.86−1.68 (m, 4H), 1.51 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 136.7, 128.9, 128.7, 127.2, 101.2, 89.5, 82.1, 77.9, 57.6, 54.8, 52.5, 44.4, 40.6, 38.7, 37.2, 35.7, 33.5, 32.1, 31.0, 17.8, 15.1. HRMS (ESI): calcd for $C_{24}H_{23}O_3^+$ (MH^+) 359.1642, found 359.1629.

14-Phenyl-3,13-dioxanonacyclo[9.4.2.1^{2,5}.1^{7,10}.0^{2,10}.0^{4,8}.0^{12,15}.0^{14,17}.0^{18,19}]nonadecan-9-one (4c): from 0.55 g of **3c** (1.6 mmol) in 1.5 L of benzene, irradiation for 48 h: >90%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40−7.35 (m, 4H), overlaps 7.35−7.31 (m, 1H), 5.04 (dd, J = 8.2, 4.1 Hz, 1H), 4.80 (ddd, J = 3.6, 1.8, 0.8 Hz, 1H), 3.48 (dddd, J = 5.5, 3.6, 1.8, 1.8 Hz, 1H), 3.03 (t, J = 6.7 Hz, 1H), 2.89 (m, 2H), 2.74 (ddd, J = 6.6, 1.8, 1.8 Hz, 1H), overlaps 2.72 (m, 1H), 2.61−2.57 (m, 1H), overlaps 2.57−2.54 (ddd, J = 8.2, 4.2, 1.9 Hz, 1H), 2.10 (ddd, J = 6.2, 6.2, 1.4 Hz, 1H), 1.91 (dd, J = 12.8, 1.8 Hz, 1H), 1.87 (d, J = 11.3 Hz, 1H), 1.79 (ddd, J = 12.9, 6.7, 1.9 Hz, 1H), 1.65 (d, J = 11.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.0, 136.9, 128.9, 128.7, 127.2, 101.0, 90.1, 86.8, 81.9, 56.5, 54.8, 54.7, 49.3, 47.0, 44.0, 42.3, 38.9, 37.2, 36.2, 35.7, 32.6. HRMS (ESI): calcd for $C_{23}H_{21}O_3^+$ (MH^+) 345.1485, found 345.1472.

1*S*(*R*),2*R*(*S*),11*S*(*R*),12*R*(*S*),15*S*(*R*),16*S*(*R*)-15,16-Dibenzoyl-9-cyano-3-oxaheptacyclo[10.2.2.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}.0^{17,18}]octadec-13-en-10-one (3e): from 0.10 g of **2a** (0.4 mmol) and 0.19 g of *trans*-1,2-dibenzoylethylene (0.8 mmol) at 200 °C (hexane/EtOAc gradient 10:1 → 1:1): <10%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (m, 2H), 7.84 (m, 2H), 7.57 (t, J = 7.3 Hz, 1H), 7.53−7.47 (m, 3H), 7.42 (m, 2H), 6.60 (ddd, J = 8.4, 7.3, 1.4 Hz, 1H), 6.17 (dd, J = 8.0, 6.4 Hz, 1H), 5.48 (dd, J = 5.6, 1.8 Hz, 1H), 4.67 (d, J = 4.0 Hz, 1H), 4.20 (dd, J = 5.6, 2.5 Hz, 1H), 3.39 (ddd, J = 7.2, 2.4, 0.7 Hz, 1H), 3.22 (ddd, J = 6.3, 1.5, 1.5 Hz, 1H), 2.57 (ddd, J = 7.4, 5.8, 1.5 Hz, 1H), 2.25 (m, 1H), 2.07 (dd, J = 7.7, 4.9 Hz, 1H), 1.97−1.86 (m, 2H), 1.79 (dd, J = 8.8, 3.5 Hz, 1H), overlaps 1.78−1.75 (m, 1H), 1.48−1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.28, 199.94, 176.9, 137.4, 135.8, 133.8, 133.5, 132.4, 131.7, 129.4, 129.0, 128.7, 128.6, 117.2, 90.1, 83.8, 57.5, 52.4, 45.2, 41.0, 40.4, 39.7, 36.6, 34.5, 34.3, 33.7, 16.1, 14.1. HRMS (ESI): calcd for $C_{32}H_{26}NO_4^+$ (MH^+) 488.1856, found 488.1855.

1*R*(*S*),2*S*(*R*),10*R*(*S*),11*S*(*R*),14*S*(*R*),15*S*(*R*)-14,15-Dibenzoylheptacyclo[9.2.2.1^{2,5}.1^{7,10}.0^{2,10}.0^{4,8}.0^{16,17}]heptadec-12-ene-3,9-dione (3f): from 0.16 g of **2d** (0.7 mmol) and 0.26 g of *trans*-1,2-dibenzoylethylene (1.1 mmol) at 200 °C (recrystallization from DCM/hexane): 0.08 g, <25%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 7.6 Hz, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.56−7.43 (m, 6H), 6.76 (t, J = 7.5 Hz, 1H), 6.20 (t, J = 7.3 Hz, 1H), 5.12 (dd, J = 6.8, 1.5 Hz, 1H), 4.17 (dd, J = 6.8, 2.1 Hz, 1H), 3.3 (d, J = 6.8 Hz, 1H), 3.14 (d, J = 6.3 Hz, 1H), 2.83 (m, 1H), 2.72 (m, 1H), 2.64 (m, 2H), 2.61−2.52 (m, 2H), 1.88 (d, J = 11.5 Hz, 1H), 1.69 (d, J = 11.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.8, 209.4, 200.4, 197.9, 137.8, 135.9, 135.6, 133.4, 132.4, 131.0, 129.6, 128.9, overlaps 128.9, 128.5, 55.3, 55.0, 53.6, 52.9, 46.2, 43.6, 43.2, 42.5, 41.9, 40.8, 40.0, 35.7, 35.0. HRMS (ESI): calcd for $C_{31}H_{25}O_4^+$ (MH^+) 461.1747, found 461.1739.

General Procedures for Oxametathesis in the Chromone (a−c) Series. A. HCl-Catalyzed Formation of Aldehydes 5. To a solution of oxetane **4** in DCM was added a catalytic amount of HCl (4.0 M solution in dioxane). The resulting reaction mixture was stirred at room temperature for 24 h, washed twice with a 5% solution of NaOH and water, concentrated, and purified on a silica gel column using hexane/ethyl acetate (or hexane/ethanol for the cyano-containing products **a**). As a rule, this method produces a mixture of the alkene **5** and the cyclopropane **6**.

B. (B1) BF_3- or (B2) HCl-Catalyzed Formation of Aldehydes 6. $BF_3 \cdot Et_2O$ (small molar excess per heteroatom in **4**) or a >10-fold excess of HCl (4.0 M solution in dioxane) was added to a solution of oxetane **4** in dichloromethane (DCM), stirred overnight at room temperature, and washed twice with a 5% solution of NaOH and water. The crude aldehyde **6** was purified on a silica gel column using hexane/ethyl acetate as an eluent. For cyano-containing aldehydes **a** hexane/ethanol was used as the eluent.

C. Oxametathesis in Alcohols Yielding Acetals 7. Oxetane **4** was dissolved in a 5% HCl solution in methanol, 4-bromobenzyl alcohol/DCM, or ethylene glycol/THF and stirred for 24 h. The resulting mixture was evaporated, dissolved in DCM, and washed twice with a 5% solution of NaOH and water. The crude acetals **7** were purified on a silica gel column using hexane/ethyl acetate as an eluent. For cyano-containing acetals hexane/ethanol was used as the eluent. To avoid the hydrolysis of the cyano-containing acetals, 2 mL of pyridine was passed through the column before purification.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-15-Cyano-14-oxo-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-ene-13-carboxaldehyde (5a): (method A) from 217 mg (0.56 mmol) of **4a** and 0.28 mL of HCl (4.0 M, 1.13 mmol) in DCM: forms a mixture of **5a** and **6a** (56% and 18% by NMR). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.90 (s, 1H), 7.47 (d, J = 7.4 Hz, 2H), 7.34 (t, J = 7.2 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.30 (d, J = 3.4 Hz, 1H), 4.70 (d, J = 4.1 Hz, 1H), 3.82 (dd, J = 5.8, 4.7 Hz, 1H), 3.39 (d, J = 4.5 Hz, 1H), 2.86 (ddd, J = 8.5, 5.7, 1.5 Hz, 1H), 2.82 (dd, J = 4.8, 3.6 Hz, 1H), 2.64 (dd, J = 8.6, 4.8 Hz, 1H), 2.43−2.38 (m, 2H), 2.19 (m, 1H), 2.00−1.85 (m, 3H), 1.77 (d, J = 11.2 Hz, 1H), 1.57−1.50 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.6, 200.1, 148.3, 134.5, 129.1, 129.0, 128.2, 126.6, 117.4, 87.8, 82.4, 56.6, 51.7, 47.0, 43.6, 40.5, 39.4, 37.5, 36.1, 35.0, 33.5, 16.0, 14.3. HRMS (ESI): calcd for $C_{25}H_{22}NO_3^+$ (MH^+) 384.1594, found 384.1590.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-14-Oxo-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-ene-13-carboxaldehyde (5b): (method A) from 30 mg (0.08 mmol) of **4b** and 43 μL of HCl (4.0 M, 0.17 mmol) in DCM: forms an inseparable mixture of **5b**, **5b′** (epimer), and **6b** (39%, 4%, and 24% by NMR).

1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-16-Oxo-4-phenyl-13-oxaheptacyclo[5.5.4.1^{2,5}.0^{1,7}.0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-ene-6-carboxaldehyde (5c): (method A) from 140 mg (0.41 mmol) of **4c** and 0.20 mL of HCl (4.0 M, 0.81 mmol) in DCM: forms an inseparable mixture of **5c** and **6c**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.45 (d, J = 1.1 Hz, 1H), 7.44 (d, J = 7.2 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.25 (m, 1H) overlaps with $CDCl_3$, 6.44 (d, J = 3.3 Hz, 1H), 4.96 (dd, J = 8.2, 4.1 Hz, 1H), 3.73 (dd, J = 5.7, 4.3 Hz, 1H), 3.20 (dd, J = 8.1, 5.9 Hz, 1H), 2.93 (dd, J = 5.0, 3.4 Hz, 1H), 2.85 (m, 1H), 2.81 (dd, J = 4.2, 1.0 Hz, 1H), 2.63−2.57 (m, 2H), 2.44 (ddd, J = 8.4, 5.3, 2.3 Hz, 1H), 2.38 (ddd, J = 11.0, 5.7, 5.0 Hz, 1H), 1.88 (d, J = 11.6 Hz, 1H), 1.85 (d, J = 11.4 Hz, 1H), 1.67 (d, J = 11.4 Hz, 1H).

1*S*(*R*),8*S*(*R*),9*R*(*S*),10*S*(*R*),13*R*(*S*)-16-Cyano-17-oxo-11-phenyl-14-oxaoctacyclo[6.5.4.1^{10,13}.0^{1,8}. 0^{2,7}.0^{9,11}.0^{3,15}.0^{6,16}]octadecane-9-carboxaldehyde (6a): (method B1) from 390 mg (1.02 mmol) of **4a** and 2.00 mL of $BF_3 \cdot Et_2O$ (48%, 15.86 mmol) in DCM (hexane/EtOH 10:1, then DCM/MeOH 2:1): 223 mg (57%); (method B2) from 200 mg (0.52 mmol) of **4a** and 2.61 mL of HCl (4.0 M, 10.43 mmol) in DCM (hexane/EtOH 10:1, then DCM/MeOH 2:1): 278 mg (71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.41 (s, 1H), 7.38−7.30 (m, 5H), 4.74 (d, J = 4.1 Hz, 1H), 3.16 (ddd, J = 7.8, 5.9, 1.3 Hz, 1H), 2.89 (d, J = 2.9 Hz, 1H), 2.82 (m, 1H), 2.69 (dd, J = 7.9, 5.0 Hz, 1H), 2.52 (m, 1H), 2.27−2.18 (m, 5H), 2.11−2.04 (m, 1H), 2.02−1.96 (m, 2H), 1.72−1.65

(m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.4, 198.8, 137.6, 129.3, 129.0, 128.0, 117.4, 89.4, 82.7, 54.4, 52.4, 42.5, 40.1, 39.9, 37.7, 35.8, 35.7, 35.6, 34.6, 29.4, 28.2, 15.9, 14.3. HRMS (ESI): calcd for $C_{25}H_{22}NO_3^+$ (MH^+) 384.1594, found 384.1592.

1*S*(*R*),8*S*(*R*),9*R*(*S*),10*S*(*R*),13*R*(*S*)-17-Oxo-11-phenyl-14-oxaoctacyclo[6.5.4.1^{10,13}.0^{1,8}.0^{2,7}.0^{9,11}.0^{3,15}.0^{6,16}]octadecane-9-carboxaldehyde (6b): (method B1) from 40 mg (0.11 mmol) of **4b** and 0.20 mL of $BF_3 \cdot Et_2O$ (48%, 1.59 mmol) in DCM (hexane/EtOH 10:1, then DCM/MeOH 2:1): 18 mg (45%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.30 (m, 4H), 7.24 (m, 1H) overlaps with $CDCl_3$, 4.56 (dd, J = 8.1, 4.3 Hz, 1H), 3.05 (ddd, J = 7.8, 5.8, 1.3 Hz, 1H), 2.81 (d, J = 2.9 Hz, 1H), 2.66 (ddd, J = 8.2, 3.4, 2.2 Hz, 1H), 2.56 (ddd, J = 7.4, 4.9, 2.3 Hz, 1H), 2.51 (d, J = 12.3 Hz, 1H), 2.43 (m, 1H), 2.19−2.13 (m, 4H), 2.06 (m, 1H), 1.94−1.87 (m, 1H), 1.84−1.72 (m, 2H), 1.57 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.5, 197.4, 138.4, 129.1, 129.1, 127.7, 88.5, 79.4, 55.2, 51.7, 42.4, 41.3, 40.1, 38.1, 36.0, 35.93, 35.91, 30.8, 29.7, 28.3, 17.8, 15.4. HRMS (ESI): calcd for $C_{24}H_{23}O_3^+$ (MH^+) 359.1642, found 359.1630.

1*S*(*R*),2*R*(*S*),3*S*(*R*),6*R*(*S*),7*S*(*R*)-13-Oxo-4-phenyl-16-oxaoctacyclo[5.5.4.1^{3,6}.0^{1,7}.0^{2,4}.0^{8,12}.0^{9,15}.0^{11,14}]heptadecane-2-carboxaldehyde (6c). Method B1 and method B2 failed. Under these conditions oxetane **4c** produced a complicated mixture of inseparable compounds.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-15-Cyano-13-dimethoxymethyl-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-en-14-one (7a): (method C) from 320 mg (0.83 mmol) of **4a** and 3.13 mL of HCl (4.0 M, 12.52 mmol) in MeOH (hexane/EtOH 10:1, then DCM/MeOH 2:1): 258 mg (59%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 3.6 Hz, 1H), 4.67 (d, J = 4.1 Hz, 1H), 3.84 (d, J = 9.7 Hz, 1H), 3.29 (t, J = 5.3 Hz, 1H), 2.92 (dd, J = 9.7, 4.8 Hz, 1H), 2.87 (s, 3H) overlaps with 2.85 (ddd, J = 8.5, 5.8, 1.4 Hz, 1H), 2.79 (s, 3H), 2.72 (dd, J = 4.7, 3.8 Hz, 1H), 2.36 (dd, J = 8.5, 4.8 Hz, 1H), 2.30 (ddd, J = 11.1, 5.9, 5.1 Hz, 1H), 2.18 (m, 1H) overlaps with 2.15 (m, 1H), 1.96−1.87 (m, 3H), 1.67 (d, J = 11.2 Hz, 1H), 1.54−1.48 (m, 1H). ^{1}H NMR (500 MHz, C_6D_6): δ 7.45 (d, J = 7.6 Hz, 2H), 7.17 (m, 2H) overlaps with C_6D_6, 7.08 (t, J = 7.4 Hz, 1H), 5.87 (d, J = 3.6 Hz, 1H), 4.35 (d, J = 4.1 Hz, 1H), 3.82 (d, J = 9.3 Hz, 1H), 3.18−3.13 (m, 2H), 2.70 (s, 3H), 2.66 (s, 3H), 2.55 (dd, J = 4.7, 3.8 Hz, 1H), 2.19 (ddd, J = 8.5, 5.7, 1.4 Hz, 1H), 2.05 (ddd, J = 10.9, 5.4, 5.4 Hz, 1H), 2.01 (m, 1H), 1.92 (dd, J = 8.5, 4.8 Hz, 1H), 1.73 (d, J = 11.1 Hz, 1H), 1.66−1.59 (m, 1H), 1.53 (m, 1H), 1.31−1.26 (m, 2H), 0.96−0.89 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.3, 149.5, 136.1, 128.6, 128.5, 128.2, 126.7, 117.8, 102.0, 88.0, 82.2, 57.9, 53.1, 52.2, 50.1, 43.6, 40.5, 39.3, 38.3, 35.9, 35.2, 34.8, 33.2, 16.1, 14.4. HRMS (ESI): calcd for $C_{27}H_{27}NNaO_4^+$ (MNa^+) 452.1832, found 452.1810.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-13-Dimethoxymethyl-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-en-14-one (7b): (method C) from 91 mg (0.25 mmol) of **4b** and 0.32 mL of HCl (4.0 M, 1.27 mmol) in MeOH (hexane/EtOH 20:1 → 10:1): 83 mg (81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 7.4 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H) overlaps with $CDCl_3$, 6.28 (d, J = 3.5 Hz, 1H), 4.53 (ddd, J = 8.2, 4.3, 1.3 Hz, 1H), 3.85 (d, J = 9.8 Hz, 1H), 3.27 (t, J = 5.3 Hz, 1H), 2.88 (dd, J = 9.9, 4.8 Hz, 1H) overlaps with 2.87 (s, 3H), 2.79 (ddd, J = 8.5, 5.8, 1.5 Hz, 1H), 2.76 (s, 3H), 2.70 (dd, J = 4.8, 3.7 Hz, 1H), 2.64 (ddd, J = 8.3, 3.4, 2.2 Hz, 1H), 2.28−2.23 (ddd, J = 11.0, 5.3, 5.3 Hz, 1H) overlaps with 2.28−2.23 (m, 1H), 2.04 (m, 1H), 1.89−1.74 (m, 3H), 1.71−1.65 (m, 1H) overlaps with 1.67 (d, J = 10.9 Hz, 1H), 1.48−1.41 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.4, 149.2, 136.6, 129.1, 128.5, 127.9, 126.7, 102.4, 87.1, 78.8, 58.5, 53.2, 51.3, 49.8, 44.0, 41.7, 39.7, 38.4, 35.4, 34.4, 34.3, 30.6, 18.0, 15.5. HRMS (ESI): calcd for $C_{26}H_{28}NaO_4^+$ (MNa^+) 427.1880, found 427.1898.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-15-Cyano-13-(1,3-dioxolan-2-yl)-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-en-14-one (7a′): (method C) from 190 mg (0.50 mmol) of **4a** and 1.24 mL of HCl (4.0 M, 4.95 mmol) in ethylene glycol/THF mixture (10/3) (hexane/EtOH 20:1 → 10:1): 148 mg (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H) overlaps with $CDCl_3$, 6.44 (d, J = 3.6 Hz, 1H), 4.67 (d, J = 4.1 Hz, 1H), 4.46 (d, J = 9.1 Hz, 1H), 3.92−3.88 (m, 1H), 3.65 (m, 2H), 3.55−3.51 (m, 1H), 3.34 (dd, J = 5.7, 4.8 Hz, 1H), 2.82 (ddd, J = 8.4, 5.7, 1.4 Hz, 1H), 2.75 (dd, J = 4.7, 3.8 Hz, 1H), 2.70 (dd, J = 9.1, 4.6 Hz, 1H), 2.39 (dd, J = 8.4, 4.8 Hz, 1H), 2.27 (m, 2H), 2.17 (m, 1H), 1.97−1.86 (m, 3H), 1.65 (d, J = 11.1 Hz, 1H), 1.52−1.45 (m, 1H) overlaps with HOD. ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.1, 148.4, 135.4, 128.6, 128.2, 128.0, 126.4, 117.9, 103.6, 87.6, 82.3, 65.0, 64.5, 57.2, 52.0, 43.4, 40.5, 38.7, 38.3, 38.2, 35.6, 35.2, 33.0, 16.1, 14.5. HRMS (ESI): calcd for $C_{27}H_{25}NNaO_4^+$ (MNa^+) 450.1676, found 450.1678.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-13-(1,3-Dioxolan-2-yl)-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-en-14-one (7b′): (method C) from 180 mg (0.50 mmol) of **4b** and 0.32 mL of HCl (4.0 M, 1.26 mmol) in an ethylene glycol/THF mixture (10:3) (hexane/EtOAc 25:1): 158 mg (78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H) overlaps with $CDCl_3$, 6.46 (d, J = 3.6 Hz, 1H), 4.53 (ddd, J = 8.1, 4.2, 1.4 Hz, 1H), 4.47 (d, J = 9.1 Hz, 1H), 3.92−3.87 (m, 1H), 3.66−3.59 (m, 2H), 3.53−3.49 (m, 1H), 3.32 (dd, J = 5.7, 4.7 Hz, 1H), 2.76 (ddd, J = 8.2, 5.6, 1.5 Hz, 1H), 2.72 (dd, J = 4.6, 3.9 Hz, 1H), 2.68 (dd, J = 9.1, 4.6 Hz, 1H), 2.63 (ddd, J = 8.2, 3.3, 2.1 Hz, 1H), 2.28 (ddd, J = 8.3, 4.7, 2.1 Hz, 1H), 2.24 (ddd, J = 11.0, 5.5, 5.5 Hz, 1H), 2.04 (m, 1H), 1.91 (m, 1H), 1.88−1.81 (m, 1H), 1.79−1.72 (m, 1H), 1.70−1.63 (m, 1H) overlaps with 1.66 (d, J = 10.8 Hz, 1H), 1.45−1.38 (dddd, J = 13.8, 11.8, 5.9, 2.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.2, 148.1, 135.9, 128.6, 128.5, 127.9, 126.4, 104.0, 86.6, 79.0, 64.8, 64.3, 57.7, 51.1, 43.9, 41.7, 39.0, 38.5, 37.6, 35.4, 34.0, 30.2, 18.0, 15.5. HRMS (ESI): calcd for $C_{26}H_{27}O_4^+$ (MH^+) 403.1904, found 403.1903.

1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*),13*R*(*S*)-15-Cyano-13-bis(4-bromobenzyloxymethyl)-11-phenyl-17-oxaheptacyclo[6.5.4.1^{9,12}.0^{1,8}.0^{2,7}.0^{3,15}.0^{6,16}]octadec-10-en-14-one (7b″): (method C) from 200 mg (0.56 mmol) of **4b**, 0.37 g (1.95 mmol) of 4-bromobenzyl alcohol, and 0.35 mL of HCl (4.0 M, 1.39 mmol) in DCM (hexane/EtOAc 20:1 → 10:1): 215 mg (54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.43 (m, 4H), 7.28 (d, J = 8.4 Hz, 2H), 7.22−7.17 (m, 3H), 7.09 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.27 (d, J = 3.5 Hz, 1H), 4.52 (ddd, J = 8.2, 4.3, 1.3 Hz, 1H), 4.29 (d, J = 12.0 Hz, 1H) overlaps with 4.27 (d, J = 9.9 Hz, 1H), 4.10 (m, 2H), 3.51 (d, J = 12.1 Hz, 1H), 3.34 (dd, J = 5.7, 4.8 Hz, 1H), 3.12 (dd, J = 9.9, 4.7 Hz, 1H), 2.79 (ddd, J = 8.3, 5.7, 1.4 Hz, 1H), 2.72 (dd, J = 4.6, 3.7 Hz, 1H), 2.59 (ddd, J = 8.1, 2.5, 2.5 Hz, 1H), 2.29 (ddd, J = 11.0, 5.5, 5.5 Hz, 1H), 2.18 (ddd, J = 8.4, 4.3, 2.0 Hz, 1H), 2.04 (m, 1H), 1.88−1.80 (m, 1H), 1.76−1.69 (m, 1H) overlaps with 1.71 (d, J = 11.0 Hz, 1H), 1.58−1.55 (m, 2H), 1.35−1.28 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.5, 149.0, 137.5, 137.0, 136.7, 131.5, 131.5, 129.7, 129.6, 128.5, 128.4, 127.9, 126.7, 121.4, 121.1, 100.5, 87.0, 78.8, 65.4, 63.5, 58.4, 51.1, 43.9, 41.6, 40.0, 38.3, 35.3, 34.8, 34.1, 30.3, 17.8, 15.3. HRMS (ESI): calcd for $C_{38}H_{38}Br_2NO_4^+$ (MNH_4^+) 732.1147, found 732.1149.

1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-6-(1,3-Dioxolan-2-yl)-4-phenyl-13-oxaheptacyclo[5.5.4.1^{2,5}.0^{1,7}. 0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-en-16-one (7c′): (method C produced a mixture of **7c′** and **7c″** 3:1) from 210 mg (0.61 mmol) of **4c** and 0.30 mL of HCl (4.0 M, 1.22 mmol) in an ethylene glycol/THF mixture (10/3) (hexane/EtOAc 20:1 → 10:1, then hexane/EtOH 10:1 to get **7c″**): 71 mg (< 30%, major loss is on the column). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63

(d, J = 7.3 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H) overlaps with $CDCl_3$, 6.47 (d, J = 3.6 Hz, 1H), 4.99 (dd, J = 8.2, 4.0 Hz, 1H), 4.49 (d, J = 9.1 Hz, 1H), 3.91−3.88 (m, 1H), 3.68−3.61 (m, 2H), 3.55−3.51 (m, 1H), 3.33 (dd, J = 5.6, 4.8 Hz, 1H), 2.90 (ddd, J = 7.9, 6.2, 1.4 Hz, 1H), 2.75 (m, 2H), 2.67 (dd, J = 9.1, 4.6 Hz, 1H), 2.62−2.58 (ddd, J = 8.2, 4.3, 1.8 Hz, 1H) overlaps with 2.57 (m, 1H), 2.51 (ddd, J = 8.4, 5.2, 1.7 Hz, 1H), 2.25 (ddd, J = 10.9, 5.5, 5.5 Hz, 1H), 1.84 (d, J = 11.3 Hz, 1H), 1.65 (d, J = 10.8 Hz, 1H) overlaps with 1.62 (d, J = 11.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.8, 148.1, 135.9, 128.8, 128.5, 127.9, 126.4, 103.9, 87.2, 86.4, 64.9, 64.3, 56.8, 54.3, 48.2, 47.4, 43.9, 42.1, 39.0, 38.8, 38.3, 37.7, 36.3. HRMS (ESI): calcd for $C_{25}H_{25}O_4^+$ (MH^+) 389.1747, found 389.1761.

1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-6-(Bis(2-hydroxyethoxy)-methyl)-4-phenyl-13-oxaheptacyclo[5.5.4.1^{2,5}.0^{1,7}.0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-en-16-one (7c″): (hexane/EtOH 10:1): 23 mg (< 10%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H) overlaps with $CDCl_3$, 6.28 (d, J = 3.5 Hz, 1H), 5.00 (dd, J = 8.3, 4.0 Hz, 1H), 4.15 (d, J = 9.6 Hz, 1H), 3.65 (ddd, J = 11.9, 7.6, 2.8 Hz, 1H), 3.56 (ddd, J = 11.9, 4.8, 2.9 Hz, 1H), 3.51−3.43 (m, 2H), 3.40 (ddd, J = 10.2, 7.7, 2.9 Hz, 1H), 3.28 (dd, J = 5.8, 4.9 Hz, 1H) overlaps with 3.26 (m, 2H), 2.96 (ddd, J = 7.8, 6.3, 1.2 Hz, 1H) overlaps with 2.94 (dd, J = 9.7, 4.6 Hz, 1H), 2.78 (m, 1H), 2.74 (dd, J = 4.7, 3.7 Hz, 1H), 2.68 (ddd, J = 10.0, 4.8, 2.8 Hz, 1H), 2.62 (ddd, J = 8.4, 4.3, 1.8 Hz, 1H), 2.58 (m, 1H), 2.55 (ddd, J = 8.2, 5.4, 1.7 Hz, 1H), 2.30 (ddd, J = 11.0, 5.5, 5.5 Hz, 1H), 1.86 (d, J = 11.3 Hz, 1H), 1.67 (d, J = 11.2 Hz, 1H) overlaps with 1.66 (d, J = 11.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 215.4, 149.2, 136.9, 129.7, 128.6, 128.0, 126.7, 101.0, 87.2, 87.0, 66.1, 64.4, 62.21, 62.18, 57.7, 54.4, 48.2, 47.4, 44.1, 42.3, 39.9, 38.8, 37.8, 36.4, 35.8. HRMS (ESI): calcd for $C_{27}H_{30}NaO_6^+$ (MNa^+) 473.1935, found 473.1938.

Photoinduced Epoxidation. 1*S*(*R*),2*R*(*S*),11*S*(*R*),12*R*(*S*),13*S*(*R*),14*S*(*R*),16*S*(*R*)-9-Cyano-12-dimethoxymethyl-14-phenyl-3,15-dioxaoctacyclo[11.3.1.1^{2,5}.1^{8,11}.0^{2,11}.0^{4,9}.0^{14,16}.0^{18,19}]nonadecan-10-one (8a). A 46 mg amount of **7a** (0.11 mmol) in 2.0 mL of aerated benzene was irradiated in a Pyrex flask in a Rayonet reactor equipped with RPR-3500 UV lamps (broadband 300−400 nm UV source with peak emission at 350 nm) for 24 h, solvent was evaporated, and the crude product was purified by column chromatography on silica gel (gradient hexane [0% → 50% EtOH]), 33 mg, 69%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (m, 2H), 7.45−7.38 (m, 3H), 4.70 (d, J = 4.2 Hz, 1H), 3.94 (s, 1H), 3.57 (d, J = 10.0 Hz, 1H), 3.42 (ddd, J = 8.6, 5.9, 1.2 Hz, 1H), 3.01 (t, J = 5.5 Hz, 1H), 2.88 (dd, J = 10.0, 5.0 Hz, 1H), 2.81 (s, 3H), 2.69 (s, 3H), 2.51 (dd, J = 4.7, 1.5 Hz, 1H), 2.45 (dd, J = 8.6, 4.8 Hz, 1H), 2.30 (m, 1H), 2.18 (m, 1H), 2.06−1.96 (m, 3H), 1.91 (ddd, J = 11.9, 5.9, 5.0 Hz, 1H), 1.65−1.59 (m, 1H) overlaps with HOD, 1.08 (d, J = 12.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.76, 135.56, 129.11, 128.83, 117.23, 100.21, 90.95, 80.88, 65.88, 58.22, 57.22, 53.32, 51.53 (m), 49.45, 48.26 (m), 38.61, 38.51, 36.67, 36.18, 35.33, 35.21, 32.67, 27.67, 15.68, 14.04. ^{1}H NMR (500 MHz, C_6D_6): δ 7.30 (m, 2H), 7.09−7.03 (m, 3H), 4.26 (d, J = 4.2 Hz, 1H), 3.58 (d, J = 10.0 Hz, 1H), 3.47 (s, 1H), 3.05 (dd, J = 10.0, 5.0 Hz, 1H), 2.94 (dd, J = 6.0, 5.0 Hz, 1H), 2.64 (s, 3H), 2.58 (ddd, J = 8.5, 5.7, 1.2 Hz, 1H), 2.48 (s, 3H), 2.32 (dd, J = 4.6, 1.3 Hz, 1H), 2.12 (dd, J = 8.6, 4.8 Hz, 1H), 2.02 (m, 1H), 1.90 (ddd, J = 11.5, 6.0, 5.0 Hz, 1H), 1.64−1.57 (m, 1H), 1.44 (m, 1H), 1.30−1.26 (m, 2H), 1.10 (d, J = 11.8 Hz, 1H), 0.91−0.83 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6): δ 202.2, 137.1, 129.1, 129.1, 127.9, 117.8, 100.6, 91.3, 81.3, 66.1, 58.3, 57.8, 53.2, 52.5, 49.1, 39.4, 38.6, 37.4, 36.6, 35.9, 35.5, 33.1, 28.4, 16.1, 14.3. HRMS (ESI): calcd for $C_{27}H_{27}KNO_5^+$ (MK^+) 484.1521, found 484.1530.

13-Ethylene Glycol Monoacetal of 1*S*(*R*),2*S*(*R*),3*S*(*R*),5*S*(*R*),-6*R*(*S*),7*S*(*R*)-7-(1,3-Sioxolan-2-yl)-5-phenyl-4-oxaoctacyclo-[6.5.4.1^{2,6}.0^{1,8}.0^{3,5}.0^{9,13}.0^{10,16}.0^{12,15}]octadecane-14,17-dione (8d): 180 mg (0.40 mmol) dissolved in 100 mL of benzene (4 mM) irradiated for 48 h, solvent was evaporated, and the crude product was purified by column chromatography on silica gel (gradient hexane [0→100% EtOAc]): 150 mg (82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 6.8 Hz, 2H), 7.40−7.32 (m, 3H), 4.12 (s, 1H), 4.09 (d, J = 9.2 Hz, 1H), 3.99−3.84 (m, 5H), 3.96−3.88 (m, 5H), 3.62 (ddd, J = 12.0, 6.3, 6.3 Hz, 1H), 3.48−3.39 (m, 2H), 3.18 (ddd, J = 9.2, 5.6, 1.6 Hz, 1H), 3.05 (dd, J = 5.3, 5.3 Hz, 1H), 2.76 (m, 1H), 2.66 (ddd, J = 9.0, 4.7, 2.2 Hz, 1H), 2.61−2.51 (m, 5H), 1.89 (d, J = 10.8 Hz, 1H), 1.81 (ddd, J = 11.2, 5.6, 5.6 Hz, 1H), 1.67 (d, J = 10.8 Hz, 1H), 1.08 (d, J = 11.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.1, 136.3, 128.9, 128.6, 114.5, 102.2, 66.21, 66.17, 65.4, 64.4, 63.9, 59.6, 55.0, 53.5, 50.2, 46.8, 44.8, 42.4, 41.7, 40.3, 39.3, 38.9, 36.1, 32.6, 28.2. HRMS (ESI): calcd for $C_{28}H_{28}NaO_6^+$ (MNa^+) 483.1778, found.

***endo*-4,5-Benzotricyclo[6.2.1.0^{2,7}]undec-9-ene-3,6-dione (1d):** from 1.00 g of 1,4-naphthoquinone (6.3 mmol) and 1.0 mL of 1,3-cyclopentadiene (12.3 mmol) at room temperature: 1.35 g (95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (m, 2H), 7.67 (m, 2H), 5.95 (t, J = 1.8 Hz, 2H), 3.64 (m, 2H), 3.43 (dd, J = 2.5, 1.5 Hz, 2H), 1.56−1.49 (m, 2H).

Hexacyclo[5.4.4.0.0^{2,6}.0^{3,13}.0^{5,14}]pentadeca-8,10-diene-12,15-dione (2d): from 1.35 g of **1d** (6.0 mmol) in 1.0 L of DCM, irradiation for 24 h (hexane/EtOAc gradient 20:1 → 10:1): 1.30 g (96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.99 (m, 2H), 5.40 (m, 2H), 3.36 (m, 2H), 3.01 (m, 2H), 2.82 (m, 2H), 2.01 (d, J = 11.4 Hz, 1H), 1.78 (d, J = 11.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.5, 124.9, 120.0, 54.8, 51.8, 50.4, 44.4, 39.2.

1*R*(*S*),2*S*(*R*),10*S*(*R*),11*R*(*S*),14*R*(*S*)-14-Benzoylheptacyclo-[9.2.2.1^{2,5}.1^{7,10}.0^{2,10}.0^{4,8}.0^{16,17}]heptadec-12-ene-3,9-dione (3d): from 1.30 g of **2d** (5.8 mmol) and 0.98 g of 3-chloropropiophenone (5.8 mmol) at 140 °C (hexane/EtOAc gradient 10:1 → 1:1): 1.94 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.1 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 6.45 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 6.24 (ddd, J = 8.1, 6.7, 1.3 Hz, 1H), 4.10 (ddd, J = 10.0, 5.5, 1.9 1H), 3.06 (ddd, J = 6.6, 1.9, 1.3 Hz, 1H), 2.86 (m, 2H), 2.81 (dddd, J = 6.8, 2.8, 2.8, 1.3 Hz, 1H), 2.74, (d, J = 2.1 Hz, 2H), 2.62 (m, 2H), 2.26, (ddd, J = 12.8, 10.0, 2.6 Hz, 1H), 1.95 (d, J = 11.2 Hz, 1H), 1.78 (d, J = 11.3 Hz, 1H), 1.71 (ddd, J = 13.0, 5.5, 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.4, 212.8, 201.0, 136.2, 134.5, 133.1, 131.2, 129.1, 128.8, 56.3, 56.2, 54.6, 54.4, 43.9, 43.7, 42.2, 42.0, 41.1, 39.8, 34.3, 31.2, 23.4. HRMS (ESI): calcd for $C_{24}H_{21}O_3^+$ (MH^+) 357.1485, found 357.1479.

14-Phenyl-13-oxanonacyclo[9.4.2.1^{2,5}.1^{7,10}.0^{2,10}.0^{4,8}.0^{12,15}.0^{14,17}.0^{18,19}]nonadecane-3,9-dione (4d): from 0.74 g of **3d** (2.1 mmol) in 0.5 L of benzene, irradiation for 72 h: 0.68 g (92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.31 (m, 5H), 4.90 (ddd, J = 3.7, 1.9, 0.8 Hz, 1H), 3.46 (dddd, J = 5.5, 3.5, 1.7, 1.7 Hz, 1H), 3.03 (dd, J = 8.1, 6.3 Hz, 1H), 2.99−2.94 (m, 2H), 2.91 (m, 1H), 2.75 (m, 1H) overlaps with 2.74 (m, 1H), 2.68 (ddd, J = 6.6, 1.8, 1.8 Hz, 1H), 2.13 (ddd, J = 7.0, 5.8, 1.3 Hz, 1H), 2.04 (d, J = 11.4 Hz, 1H), 1.91 (ddd, J = 13.4, 7.1, 2.0 Hz, 1H) overlaps with 1.87 (d, J = 11.5 Hz, 1H), 1.55 (m, 1H) overlaps with HOD, 1.44 (dd, J = 13.4, 1.9 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6): δ 7.32 (m, 2H), 7.15−7.12 (m, 2H), 7.08 (m, 1H), 4.54 (ddd, J = 3.6, 1.9, 0.9 Hz, 1H), 3.14 (m, 1H), 2.74 (d, J = 6.7 Hz, 1H), 2.64 (ddd, J = 6.6, 1.7, 1.7 Hz, 1H), 2.27 (m, 2H), 2.14−2.04 (m, 4H), 1.95−1.89 (m, 2H), 1.74 (d, J = 11.3 Hz, 1H), 1.19 (d, J = 11.0 Hz, 1H), 1.08 (d, J = 11.0 Hz, 1H).

Oxametathesis in the Naphthoquinone (d) Series. 1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-13,16-Dioxo-4-phenylheptacyclo[5.5.-4.1^{2,5}.0^{1,7}.0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-ene-6-carboxaldehyde-(5d): (method B2) from 100 mg (0.28 mmol) of **4d** and 0.09 mL of HCl (4.0 M, 0.34 mmol) in DCM (hexane/EtOH 10:1): gave an inseparable mixture of **5d** and **6d** (2:3). ^{1}H NMR (500 MHz, C_6D_6): δ 9.17 (s, 1H), 7.20 (d, J = 7.8 Hz, 2H), 7.11 (t, J = 7.4 Hz, 2H), 7.09−7.03 (m, 1H), 5.93 (d, J = 3.1 Hz, 1H), 3.12 (d,

J = 4.1 Hz, 1H), 3.09 (dd, J = 5.7, 4.4 Hz, 1H), 2.82 (dd, J = 9.1, 5.4 Hz, 1H), 2.69 (dd, J = 5.0, 3.3 Hz, 1H), 2.52−2.49 (m, 2H), 2.33 (ddd, J = 10.3, 4.1, 2.1 Hz, 1H), 2.14 (ddd, J = 9.0, 5.8, 1.8 Hz, 1H), 2.11−2.05 (m, 2H), 1.49 (d, J = 11.1 Hz, 1H), 1.28−1.23 (m, 2H).

1*S*(*R*),2*R*(*S*),3*S*(*R*),6*R*(*S*),7*S*(*R*)-13,16-Dioxo-4-phenyloctacyclo[5.5.4.1^{3,6}.0^{1,7}.0^{2,4}.0^{8,12}.0^{9,15}.0^{11,14}]heptadecane-2-carboxaldehyde (6d): (method B1) from 170 mg (0.48 mmol) of **4d** and 0.30 mL of $BF_3 \cdot Et_2O$ (48%, 2.38 mmol) in DCM (hexane/EtOH 20:1 → 10:1): 80 mg (47%); (method B2) from 100 mg (0.28 mmol) of **4d** and 0.14 mL of HCl (4.0 M, 0.56 mmol) in DCM (hexane/EtOH 20:1 then 10:1): 61 mg (61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.31 (d, J = 4.3 Hz, 4H), 7.27−7.23 (m, 1H) overlaps with $CDCl_3$, 3.27 (m, 1H) overlaps with 3.26−3.22 (ddd, J = 8.2, 5.7, 1.7 Hz, 1H), 3.01 (ddd, J = 7.8, 6.0, 1.6 Hz, 1H), 2.86 (m, 1H) overlaps with 2.86−2.83 (ddd, J = 10.4, 4.0, 1.8 Hz, 1H), 2.76−2.73 (ddd, J = 10.3, 4.1, 1.6 Hz, 1H) overlaps 2.75 (m, 1H), 2.52 (d, J = 13.1 Hz, 1H), 2.22−2.17 (m, 2H), 2.10 (dd, J = 13.1, 5.5 Hz, 1H), 2.06 (d, J = 11.3 Hz, 1H), 2.00 (d, J = 12.5 Hz, 1H), 1.93 (d, J = 11.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.3, 210.7, 199.3, 138.1, 129.2, 129.0, 127.8, 56.5, 55.4, 54.1, 48.5, 44.9, 44.5, 43.9, 42.6, 41.8, 41.0, 38.9, 38.4, 30.5, 29.8, 28.9. HRMS (ESI): calcd for $C_{24}H_{21}O_3^+$ (MH^+) 357.1485, found 357.1477.

13-Ethylene Glycol Monoacetal of 1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-6-(1,3-dioxolan-2-yl)-4-phenylheptacyclo[5.5.4.1^{2,5}.0^{1,7}.0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-en-16-one (7d): (method C) from 360 mg (1.01 mmol) of **4f** and 1.26 mL of HCl (4.0 M, 5.05 mmol) in an ethylene glycol/THF mixture (10:3) (hexane/EtOAc 10:1 → 5:1): 229 mg (51%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 3.6 Hz, 1H), 4.53 (d, J = 9.0 Hz, 1H), 3.96−3.88 (m, 5H), 3.71−3.62 (m, 2H), 3.53−3.49 (m, 1H), 3.31 (dd, J = 5.6, 4.6 Hz, 1H), 2.81 (dd, J = 5.0, 3.6 Hz, 1H), 2.62 (m, 1H), 2.59−2.48 (m, 6H), 2.10 (ddd, J = 10.8, 5.5, 5.5 Hz, 1H), 1.80 (d, J = 10.9 Hz, 1H), 1.62 (d, J = 10.5 Hz, 1H), 1.54 (d, J = 10.9 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 215.8, 147.3, 136.4, 130.7, 128.5, 127.5, 126.2, 114.6, 104.2, 66.3, 65.5, 64.7, 64.3, 54.3, 51.5, 50.6, 47.5, 44.2, 44.2, 42.7, 40.0, 39.2, 39.0, 38.8, 38.1, 37.1. HRMS (ESI): calcd for $C_{28}H_{28}NaO_5^+$ (MNa^+) 467.1829, found 467.1822.

13-Ethylene Glycol Monoacetal of 1*S*(*R*),2*R*(*S*),5*R*(*S*),6*R*(*S*),7*S*(*R*)-6-(1,3-Dioxolan-2-yl)-4-phenylheptacyclo[5.5.4.1^{2,5}.0^{1,7}.0^{8,12}.0^{9,15}.0^{11,14}]heptadec-3-en-16-one (7d) from 3d (NMR experiment). To 5 mg (14 μmol) of **3d** dissolved in 0.6 mL of CD_2Cl_2 in a Pyrex NMR tube were added 4 μL (71 μmol) of ethylene glycol and 17 μL of 4 M HCl/dioxane. The solution was irradiated with RPR-3500 lamps (λ_{max} = 350 nm) until the starting material was consumed (ca. 3−4 h). At the end of the experiment NMR of the reaction mixture contained only peaks of **7d**, described in the preceding experiment.

***endo*-5,6-Benzotricyclo[6.2.1.0^{2,7}]undec-9-ene-3,4-dione (1h) (ref 15):** from 1.0 g of 1,2-naphthoquinone (6.3 mmol) and 1.0 g of 1,3-cyclopentadiene (15.1 mmol) in 20 mL of DCM at room temperature: 0.85 g (>60% by NMR). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.9 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 6.14 (dd, J = 5.7, 2.8 Hz, 1H), 5.62 (dd, J = 5.7, 2.9 Hz, 1H), 3.96 (dd, J = 7.9, 3.7 Hz, 1H), 3.48 (m, 1H), 3.36 (dd, J = 8.0, 4.2 Hz, 1H) overlaps with 3.32 (m, 1H), 1.69−1.62 (m, 2H). Irradiation of **1h** produced a complex mixture of products.

4-(Cyclohex-2-enyl)-1,2-naphthoquinone (1g): from 1.0 g of 1,2-naphthoquinone (6.3 mmol) and 0.81 g of 1,3-cyclohexadiene (10.1 mmol) in 20 mL of 1,2-dichlorobenzene at 150 °C (hexane/EtOAc 25:1 → 10:1). The initial Diels−Alder adduct (**1g′**) rearranges into **1g** on standing or on a silica gel column: 0.75 g (50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (dd, J = 7.6, 1.5 Hz, 1H), 7.69−7.61 (m, 2H), 7.50 (ddd, J = 7.4, 7.4, 1.4 Hz, 1H), 6.43 (s, 1H), 6.04 (dddd, J = 9.9, 3.8, 3.8, 2.1 Hz, 1H), 5.60 (dddd, J = 10.1, 3.1, 2.3, 2.3 Hz, 1H), 3.72 (m, 1H), 2.10 (m, 3H), 1.67 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.1, 180.1, 160.6, 135.7, 134.8, 132.0, 131.3, 130.72 overlaps with 130.71, 127.0, 126.6, 126.0, 37.2, 29.0, 25.1, 20.2. HRMS (ESI): calcd for $C_{16}H_{14}NaO_2^+$ (MNa^+) 261.0886, found 261.0896.

Dimerization of Caged Dienes 2. A solution of **2** in 5−10 mL of 1,2-dichlorobenzene was heated in a screw-cap pressure flask at 200−210 °C for 24−72 h. After the reaction was cooled to room temperature, the solvent was removed on a high-vacuum pump. The crude reaction mixture was purified on a silica gel column using hexane/EtOAc (hexane/EtOH and DCM/MeOH in the case of **2a**) as an eluent.

1*S*(*R*),2*R*(*S*),5*R*(*S*),14*R*(*S*),15*S*(*R*),16*S*(*R*),17*R*(*S*),26*R*(*S*)-7,24-Dicyano-13,18-dioxatridecacyclo[14.10.2.1^{5,8}.1^{11,14}.1^{17,20}.1^{23,26}.0^{2,15}.0^{5,14}.0^{7,12}.0^{17,26}.0^{19,24}.0^{29,30}.0^{31,32}]dotriaconta-3,27-diene-6,25-dione (9a): from 0.46 g of **2a** (1.8 mmol) in 10 mL of 1,2-dichlorobenzene at 210 °C for 72 h (hexane/EtOH gradient 10:1 → 1:1 and DCM/MeOH 5:1): 0.15 g (33%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.19 (ddd, J = 8.0, 6.4, 1.1 Hz, 1H), 6.13 (ddd, J = 8.1, 6.9, 1.4 Hz, 1H), 5.75 (dd, J = 10.4, 2.8 Hz, 1H), 5.55 (dd, J = 10.4, 2.3 Hz, 1H), 4.71 (d, J = 4.1 Hz, 1H), 4.64 (d, J = 4.1 Hz, 1H), 3.38 (dddd, J = 9.1, 2.7, 2.7, 2.7 Hz, 1H), 3.15 (d, J = 6.8 Hz, 1H), 2.81 (ddd, J = 6.3, 2.7, 1.5 Hz, 1H), 2.74 (ddd, J = 8.3, 5.5, 1.2 Hz, 1H), 2.64 (ddd, J = 7.4, 5.8, 1.4 Hz, 1H), 2.50 (dd, J = 9.1, 1.5 Hz, 1H), 2.25 (m, 3H), 2.15 (dd, J = 8.4, 5.2 Hz, 1H), 2.11 (m, 1H) overlaps with 2.08 (dd, J = 7.7, 5.0 Hz, 1H), 1.94−1.82 (m, 6H), 1.57−1.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 201.3, 133.4, 133.3, 131.8, 120.1, 117.4, 117.4, 91.2, 85.4, 83.1, 80.5, 56.9, 55.5, 53.3, 52.6, 43.3, 39.7, 37.1, 37.0, 36.4, 35.9, 35.8, 35.7, 35.2, 35.1, 34.0, 33.8, 16.1, 15.9, 14.2, 14.1. HRMS (ESI): calcd for $C_{32}H_{30}N_3O_4^+$ (MNH_4^+) 520.2231, found 520.2232.

1*S*(*R*),2*R*(*S*),5*R*(*S*),14*R*(*S*),15*S*(*R*),16*S*(*R*),17*R*(*S*),26*R*(*S*)-13,18-Dioxatridecacyclo[14.10.2.1^{5,8}.1^{11,14}.1^{17,20}.1^{23,26}.0^{2,15}.0^{5,14}.0^{7,12}.0^{17,26}.0^{19,24}.0^{29,30}.0^{31,32}]dotriaconta-3,27-diene-6,25-dione (9b): from 170 mg of **2b** (0.75 mmol) in 5 mL of 1,2-dichlorobenzene at 200 °C for 24 h (hexane/EtOAc gradient 20:1 → 4:1): 41 mg (24%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.20 (m, J = 7.3 Hz, 1H), 6.12 (m, J = 7.5 Hz, 1H), 5.71 (dd, J = 10.5, 2.8 Hz, 1H), 5.54 (dd, J = 10.3, 2.2 Hz, 1H), 4.56 (dd, J = 7.6, 4.1 Hz, 1H), 4.47 (dd, J = 8.0, 4.0 Hz, 1H), 3.39 (dddd, J = 8.6, 2.7, 2.7, 2.7 Hz, 1H), 3.15 (d, J = 6.7 Hz, 1H), 2.73 (d, J = 6.3 Hz, 1H), 2.66 (dd, J = 8.3, 5.6 Hz, 1H), 2.57−2.49 (m, 4H), 2.10 (m, 1H), 2.02 (ddd, J = 7.8, 5.1, 2.4 Hz, 1H), 1.98 (m, 1H), 1.94 (m, 1H), 1.90 (m, 2H), 1.85−1.69 (m, 4H), 1.67−1.59 (m, 2H), 1.47−1.36 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.9, 212.8, 133.4, 133.0, 131.8, 121.2, 90.4, 84.8, 79.7, 77.0, 57.5, 56.5, 52.9, 52.2, 44.7, 40.8, 37.7, 37.4, 37.4, 36.5, 35.9, 35.4, 35.1, 34.3, 31.2, 30.1, 18.1, 17.9, 15.4, 15.2. HRMS (ESI): calcd for $C_{30}H_{29}O_4^+$ (MH^+) 453.2060, found 453.2077.

1*S*(*R*),2*R*(*S*),5*R*(*S*),14*R*(*S*),15*S*(*R*),16*S*(*R*),17*R*(*S*),26*R*(*S*)-13,18-Dioxatridecacyclo[14.10.2.1^{8,11}.1^{20,23}.0^{2,15}.0^{5,9}.0^{5,14}.0^{7,12}.0^{10,14}.0^{17,21}.0^{17,26}.0^{19,24}.0^{22,26}]triaconta-3,27-diene-6,25-dione (9c). from 0.56 g of **2c** (2.6 mmol) in 10 mL of 1,2-dichlorobenzene at 210 °C for 48 h (hexane/EtOAc gradient 20:1 → 10:1): 0.45 g (80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.20 (ddd, J = 7.9, 6.5, 1.1 Hz, 1H), 6.11 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 5.71 (dd, J = 10.4, 2.8 Hz, 1H), 5.54 (dd, J = 10.4, 2.3 Hz, 1H), 5.02 (ddd, J = 8.0, 3.1, 2.2 Hz, 1H), 4.94 (dd, J = 8.4, 3.8 Hz, 1H), 3.35 (dddd, J = 9.1, 2.7, 2.7, 2.7 Hz, 1H), 3.18 (d, J = 6.9 Hz, 1H), 2.85−2.79 (m, 2H), 2.76 (ddd, J = 6.4, 2.7, 1.4 Hz, 1H), 2.73−2.69 (m, 2H), 2.59 (m, 2H), 2.51 (dd, J = 9.3, 1.5 Hz, 1H), 2.47 (ddd, J = 8.4, 4.2, 2.0 Hz, 1H), 2.42 (ddd, J = 8.0, 4.2, 1.9 Hz, 1H), 2.20 (ddd, J = 7.8, 5.6, 2.0 Hz, 1H), 2.09 (m, 1H), 1.81 (d, J = 11.3 Hz, 1H), 1.75 (d, J = 11.3 Hz, 1H), 1.61 (d, J = 11.3 Hz, 1H), 1.52 (d, J = 11.3 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6): δ 6.21 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 6.04 (ddd, J = 7.8, 6.5, 1.2 Hz, 1H), 5.75−5.68 (m, 2H), 4.59 (dd, J = 8.0, 4.0 Hz, 1H), 4.53 (ddd, J = 8.5, 2.6, 2.6 Hz, 1H), 3.80 (dddd, J = 9.3, 2.5, 2.5, 2.5 Hz, 1H), 3.50 (d, J = 7.0 Hz, 1H), 2.84 (dd, J = 9.3, 1.6 Hz, 1H), 2.64 (ddd, J = 6.3, 2.8,

1.4 Hz, 1H), 2.27 (ddd, J = 7.4, 6.2, 1.2 Hz, 1H), 2.23−2.18 (m, 3H), 2.17−2.13 (m, 2H), 2.05 (m, 1H), 1.99 (m, 1H), 1.78 (m, J = 5.5, 2.5 Hz, 1H), 1.62 (ddd, J = 7.4, 5.5, 1.9 Hz, 1H), 1.14−1.10 (m, 2H), 0.97 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.7, 214.1, 133.7, 132.9, 131.7, 121.3, 90.7, 87.8, 85.4, 84.9, 56.4, 55.3, 55.0, 54.3, 51.3, 48.2, 47.3, 47.2, 42.0, 41.2, 40.8, 38.3, 37.9, 37.3, 37.2, 36.6, 36.2, 34.0. HRMS (ESI): calcd for $C_{28}H_{25}O_4^+$ (MH^+) 425.1747, found 425.1748.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra, X-ray data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.