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Photoinduced Intramolecular Cyclopentanation vs Photoprotolytic Oxametathesis in Polycyclic Alkenes Outfitted with Conformationally Constrained Aroylmethyl Chromophores‡

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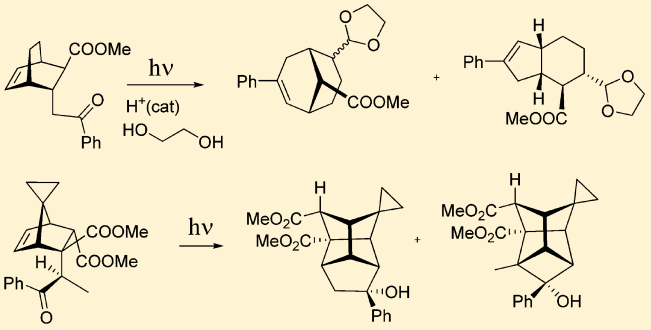
Supporting Information

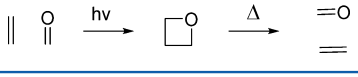
ABSTRACT: Intramolecular photoinduced cyclizations are investigated in photoprecursors assembled in a modular fashion via a Diels–Alder reaction of acetylenic dienophiles with subsequent Michael additions of aromatic ketones to install a chromophore capable of initiating Paternò–Büchi cycloadditions or radical cyclization cascades. The protolytic oxametathesis in these systems allows for rapid access to novel polycyclic scaffolds decorated by formyl groups and carboxylates suitable for subsequent modifications. In conformationally constrained photoprecursors, a radical rearrangement takes place resulting in intramolecular 1,3-diradical cyclopentanation of the double bond.



INTRODUCTION

Photoinduced reactions provide expeditious access to prohibitively strained polycyclic targets, which are difficult or impossible to synthesize using ground state chemistry. Often the photogenerated semiproducts are introduced into secondary transformations to take advantage of the strain installed at the photochemical step. For example, Rawal's "general strategy for increasing molecular complexity"[1] utilizes the intramolecular Paternò–Büchi reaction in acyl norbonenes[2] to access extremely strained polycyclic oxetanes, which are subsequently treated with Cohen's LDBB[3] to trigger a radical anion fragmentation cascade yielding di- and triquinanes in a total of two simple steps. We demonstrated that under acidic conditions, photogenerated polycyclic oxetanes undergo several spectacular cationic transformations.[4] Such oxetanes can also be reverted pyrolytically,[5] or via an electron transfer-induced reaction,[6] to an alternative pair of an alkene and an aldehyde, Scheme 1, in a manner resembling the metathesis reaction, for which Jones[5] suggested the term "carbonyl-olefin metathesis."

Scheme 1



Such oxametathesis reactions have considerable synthetic potential. We have recently shown that polycyclic alkenes outfitted with photoactive benzoyl or heterobenzoyl groups yield highly strained oxetanes, which undergo protolytic oxametathetic cycloreversion to offer access to novel polycyclic scaffolds under very mild conditions, ambient temperature and catalytic amounts of HCl, as shown in Scheme 2 (top).[7] Unlike with the pyrolytic oxametathesis, most functional groups are expected to tolerate these mild conditions, which enhances the preparative value of the method.

In this paper, we examine topological and stereochemical effects on the outcomes of the intramolecular Paternò–Büchi reaction and subsequent protolytic cycloreversion in polycycloalkenes tethered to the benzoyl chromophore via a more flexible tether containing an extra methylene group. We will show that, unlike the case of aroyl norbornenes or bicyclo[2.2.2]octenes, i.e. the photoprecursors where benzoyls are directly attached to the polycyclic scaffold, the overall reaction course is highly dependent on the stereochemistry of the starting keto-alkene, allowing for superb reaction control and at the same time greater diversity of the products. The impetus behind this research was to evaluate in the context of diversity-oriented synthesis the prospects of modular design of photoprecursors for photoprotolytic oxametathesis, and to probe how subtle variations in the structure of the starting materials could allow for considerable changes in the reaction's regio- and stereochemical outcomes or, alternatively, turn off the Paternò–Büchi channel altogether, switching to a completely different photoreactivity.

RESULTS AND DISCUSSION

We took inventory of efficient coupling reactions and chose Diels–Alder additions of reactive dienophiles, dimethyl acetylene-dicarboxylate (DMAD) and propiolates with cyclic

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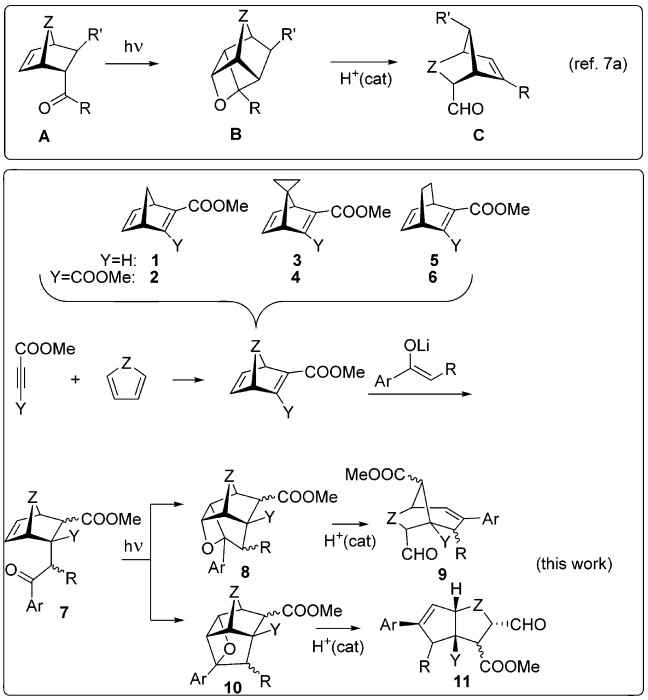
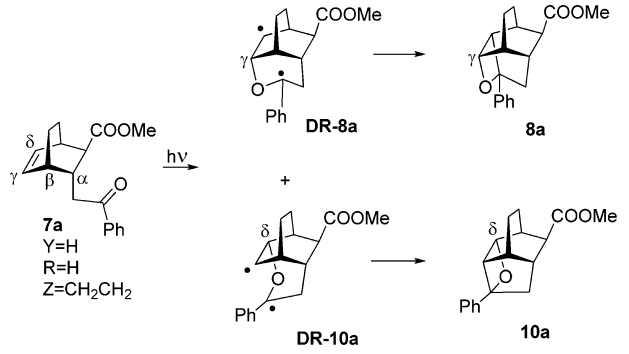
Scheme 2



Scheme 3



dienes,[8] with subsequent Michael additions of benzoyl-containing chromophores to the electrophilic double bond. This formally allows for three diversity inputs in the synthesis of photoprecursors. The Diels–Alder step with acetylenes produces only one type homoconjugated diene, for example, norbornadiene in the case of cyclopentadiene. However, the Michael addition step potentially produces several diastereomers of which we isolated and purified the photoactive *endo*-phenacyl isomers and utilized them to probe the effects of steric congestion in the photoprecursors on the outcome of photoprotolytic oxametathesis.

Moderate endoselectivity of the enolate addition is achieved with spirocyclopropanonorbornadienes **3**, **4** and bicyclo[2.2.2]-octadienes **5**, **6**. However, even in the 7-unsubstituted norbornadienes **1**, **2** the addition of *substituted* enolates (R ≠ H) occurs with modest *endo* bias. The endoselectivity is improved with bulkier R groups in the enolate: diphenylethanone (R = Ph) exhibits better than 95% of *endo*-selectivity.

Scheme 2 illustrates that Paternò–Büchi reaction in the *endo*-aroyl precursors **A**, described in ref 7, yields only one type oxetane **B** (*γ*-oxetane), which upon treatment with catalytic amounts of acid cycloreverts into bicyclo[n.2.1]alkenes **C** possessing a formyl group. The modular approach that we explore in this work gives *phenacyl* photoprecursors **7** in which the chromophore is connected to the bicyclic core via a more flexible tether, so that the initial Paternò–Büchi step can potentially yield both regioisomeric oxetanes, **8** and **10**. The resulting cycloreversion products in these systems possess either [3.n.1] (**9**) or [n.3.0] (**11**) bicyclic topology.

The first example, shown in Scheme 3, demonstrates the regiochemical outcome of the intramolecular Paternò–Büchi cycloaddition in the simplest case of a bicyclo[2.2.2]octane system in which the second substituent, methoxycarbonyl group, is *exo-trans* to the photoactive phenacyl pendant. In this case the aroyl group is free to rotate unobstructed, and the regiochemistry of the [2 + 2] photocycloaddition presumably reflects some intrinsic properties of the system. Judging by the subsequent examples, which involve hydrogen-abstraction reactions successfully competing with Paternò–Büchi cycloadditions, it is most likely that this photochemistry originates from the triplet state of aroyl pendants. The initial 1,4-diradicals leading to oxetanes **8a** and **10a** can be classified as exo-trig and endo-trig.[9] We will refer to the products of exo-trig cyclization as *γ*-oxetanes and the endo-trig as *δ* (with *α* being the attachment point of the phenacyl pendant to the bicyclic core).

Oxetanes **8a** and **10a** form in a nearly 1:1 ratio, indicating that in these systems there is no intrinsic bias for cyclization associated with the tether. The *γ*-oxetane is more strained than the *δ*-oxetane: DFT calculations gave 11.2 kcal/mol difference (Table 1, B3LYP/6-311+G(d,p), Gaussian 09, Revision A.02; see Supporting Information (SI) for full reference and computational details). Generally, both *γ*- and *δ*-oxetanes described in this study are not stable on silica gel during column chromatography. In this particular case only *δ*-oxetane could be purified (44% isolated yield) and fully characterized by NMR and X-ray crystallography. The *γ*-oxetane **8a** was characterized in a mixture with **10a** by ^{1}H NMR and introduced into subsequent acid-catalyzed cycloreversion without additional purification.

Both oxetanes undergo cycloreversion, when subjected to mild acidic conditions, completing the oxametathesis cycle. The mechanism for formation of the presumed initial products of oxametathesis, aldehydes **9a** and **11a**, is shown in Scheme 4.

Expectedly, under slightly acidic reaction conditions aldehydes **9a** and **11a** are subject to epimerization via enolization, which brings their formyl groups into the *exo*-position. This is why the preferred experimental procedure for protolytic oxametathesis involved trapping the aldehydes in a form of cyclic acetals, 1,3-dioxolanes **12a** and **13a**, by running the acid-catalyzed oxetane cycloreversion in the presence of ethylene glycol to partially prevent such epimerization. Ultimately, the one-pot procedure was developed in which the Paternò–Büchi step was carried out in dichloromethane containing HCl and ethylene glycol, as shown in Scheme 5.

The isolated yields of dioxolanes **12a** and **13a** are modest, but this is a straightforward one-pot synthetic photochemical procedure starting from the readily available **7a**.

Addition of the enolate of propiophenone to Michael acceptor **5** yields several diastereomers. We isolated and purified the *trans*-diastereomer **7b** (Z = CH_2CH_2, Y = H, exo-COOMe), possessing *endo*-phenacyl and *exo*-COOMe groups, which is Paternò–Büchi competent. Under the conditions of protolytic oxametathesis, this *endo*-diastereomer showed very high regioselectivity. According to the ^{1}H NMR of reaction

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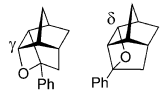
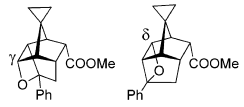
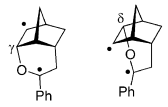
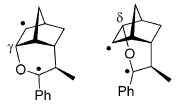
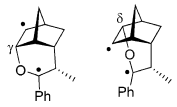
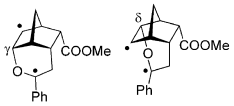
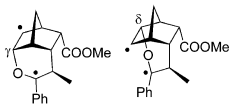
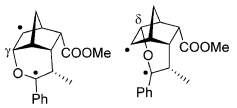
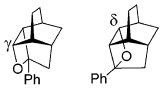
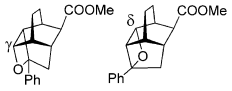
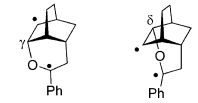
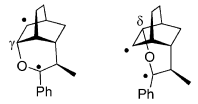
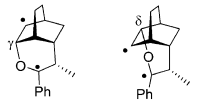
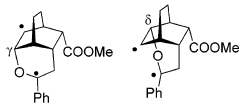
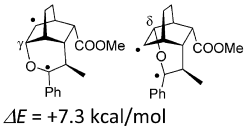
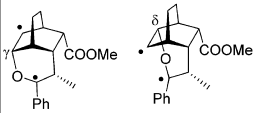
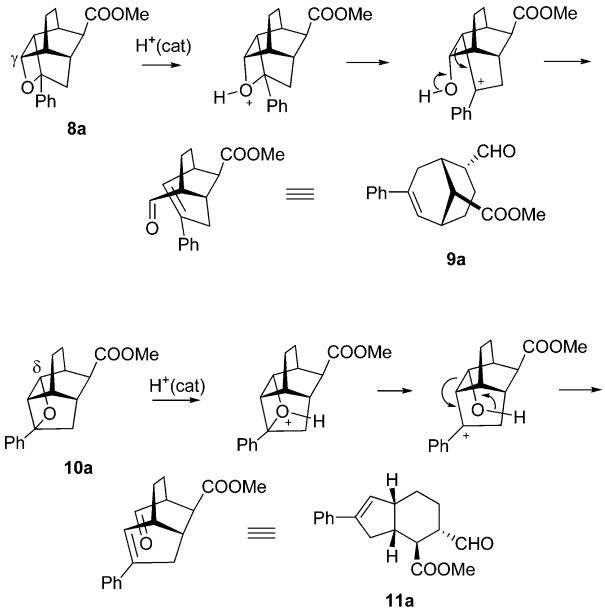
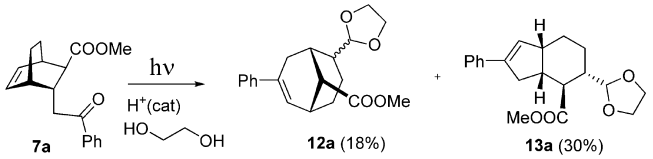
Table 1. DFT, B3LYP/6-311+G(d,p), Relative Energies of Oxetanes and Triplet 1,4-Diradicals ($E_{DFT\text{-}\delta}-E_{DFT\text{-}\gamma}$)

Bicyclo[2.2.1]heptane core		
Parent oxetanes  ΔE = -15.1 kcal/mol	vicinal *endo*-COOMe  ΔE = -15.8 kcal/mol	
Parent triplet diradical  ΔE = +10.3 kcal/mol	Me *out*  ΔE = +12.1 kcal/mol	Me *in*  ΔE = +7.1 kcal/mol
endo-COOMe  ΔE = +11.8 kcal/mol	Me *out*; *endo*-COOMe  ΔE = +13.5 kcal/mol	Me *in*; *endo*-COOMe  ΔE = +9.8 kcal/mol
Bicyclo[2.2.2]octane core		
Parent oxetanes  ΔE = -9.5 kcal/mol	vicinal *exo*-COOMe  ΔE = -11.2 kcal/mol	
Parent triplet diradical  ΔE = +6.6 kcal/mol	Me *out*  ΔE = +7.8 kcal/mol	Me *in*  ΔE = +2.8 kcal/mol
endo-COOMe  ΔE = +6.3 kcal/mol	Me *out*; *endo*-COOMe  ΔE = +7.3 kcal/mol	Me *in*; *endo*-COOMe  ΔE = +6.3 kcal/mol

Scheme 4



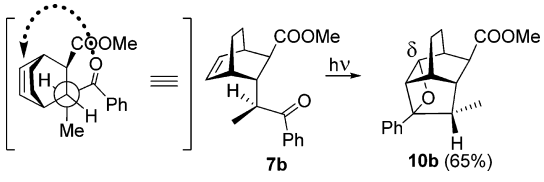
Scheme 5



mixture, irradiation of **7b** produced exclusively δ-oxetane **10b** (>95%), which was sufficiently stable on the silica gel column to allow for its isolation in 65% yield. Since the length of the tether is identical in both cases, the regiochemical outcome of this reaction is likely determined by the conformational bias introduced by the methyl group, which defines the initial conformation of the photoactive pendant with respect to the double bond of the bicyclic core, Scheme 6.

Provided that in the low energy conformation the benzoyl pendant and the methyl group are "*out*" (i.e., hydrogen is "*in*",

Scheme 6



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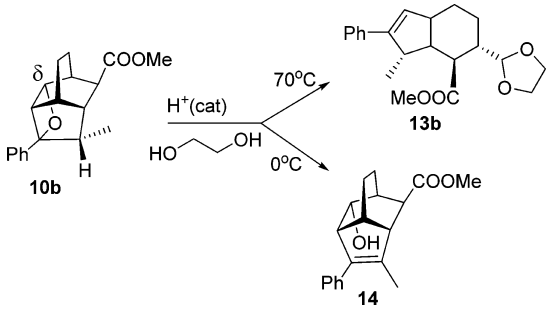
under the bicyclic core) as shown in Scheme 6, the formation of oxetane **10b** occurs with the least motion of the excited carbonyl.

Energetically, in the parent bicyclo[2.2.2]octane system, the γ-diradical of type **DR-8a** (Scheme 3) is approximately 7 kcal/mol *more* stable than the δ-diradical of type **DR-10a**. The fact that oxetanes **8a** and **10a** are formed in nearly equal amounts implies that while the γ-diradical may be forming to a greater extent, it fails to close the oxetane ring after the intersystem crossing into the singlet manifold because the γ-oxetane is prohibitively (>11 kcal/mol) more strained than the δ-oxetane. The relative orientation of singly occupied orbitals in both γ- and δ-diradicals is similar; there is no reason to believe that the spin−orbit coupling matrix element is considerably greater for one of them.[10] We suggest that because of the unfavorable energetics of the reaction channel leading to the γ-oxetane, the γ-diradicals after intersystem crossing from the triplet to singlet potential energy surface partition into the Grob fragmentation channel more frequently than the δ-diradicals (which readily cyclize to form more stable δ-oxetanes). For **7a** these two trends cancel out leading to nearly equal amounts of **8a** and **10a**. In contrast, the methyl substitution in the tether of **7b** changes the energetics: the calculated energy difference for triplet γ- and δ-diradicals is 7.8 kcal/mol for the epimer of **7b**, which produces the diradical with Me *out* (or *exo*-). However, for **7b** itself (Me is *in* or *endo*- in the diradical) this energy difference decreases to only 2.8 kcal/mol @ B3LYP/6-311+G(d,p). Given that the resulting δ-oxetane **10b** is still more than 12 kcal/mol more stable than the γ-oxetane, the regiospecific outcome in Scheme 6 becomes readily predictable. It is also possible, but unlikely, that the Paternò−Büchi reaction in these bicyclic systems occurs via a concerted mechanism, i.e., via a singlet four-membered transition state. We failed to computationally locate singlet transition states on the reaction hypersurface.

We found that the protolytic transformation of (a relatively more stable, and therefore purifiable) **10b** into **13b** requires elevated temperature of 70 °C. At ambient temperature, elimination to form **14** occurs (Scheme 7). The structure of

Scheme 7

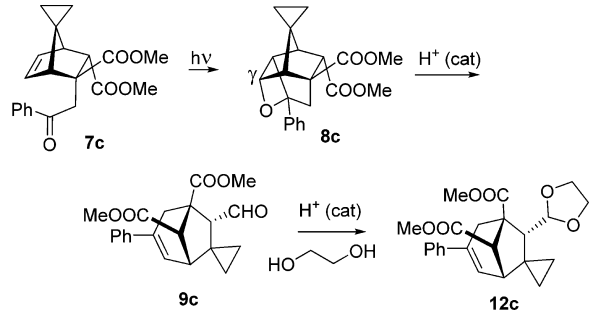


this elimination product, alkene **14**, was characterized with X-ray crystallography. Remarkably, all these diverse modes of reactivity are realized with very high degree of selectivity.

Michael additions to *dicarboxylates* **2** and **4** produced diastereomeric *trans*-dicarboxylates, which provided an opportunity to probe the photochemistry in the systems where the vicinal *endo*-carboxylate group severely constrains the conformational mobility of the aroyl chromophore. Generally low yielding Michael additions to bicyclo[2.2.2]octane **6** possessing two methoxycarbonyl groups rendered it not practical for generating *endo* photoprecursors. This is why we focused mostly on the bicyclic[2.2.1]heptane cores assembled with DMAD. The Diels−Alder product of DMAD and spiroheptadiene also improved the *endo*-selectivity of Michael additions of enolates of acetophenone, propiophenone, valerophenone, and 3-phenylpropiophenone.

As judged by the ^{1}H NMR of the reaction mixture, acetophenone adduct **7c** formed γ-oxetane **8c** exclusively, which in the presence of catalytic acid smoothly transforms into the product of oxametathesis **9c** and subsequently into its acetal **12c** (Scheme 8). This is in keeping with the least motion hypothesis, as the counter clockwise rotation is blocked by the *endo*-COOMe.

Scheme 8



Our calculations show that in the parent bicyclo[2.2.1]-heptane system, the DFT energy difference between γ- and δ-oxetane, 15.1 kcal/mol, is even greater than in the bicyclo[2.2.2]octane framework. The *endo*-COOMe group in the spirocyclopropano-norbornene-based oxetanes slightly increases this energy difference to 15.8 kcal/mol. However, the γ-diradical leading to γ-oxetane is 10.3 kcal/mol more stable than the δ-diradical, so the δ-channel is no longer competitive.

As we later discovered, further increase in steric congestion via the introduction of the methyl group in the tether could shut down the Paternò−Büchi channel altogether in the photoprecursors already outfitted with the *endo*-COOMe *brake*.

Michael addition of *propiophenone* enolate to bis-carboxylate **2** produced a single *endo*-diastereomer **7d**. The DFT structure of its most stable conformer shows that introduction of the methyl group in the α-position locks the phenyl group in the *anti*-conformation to this methyl (its X-ray structure is in keeping with this computational prediction). As shown, even upon clockwise rotation, the phenyl group is predicted to encounter a steric clash with the endo-COOMe before the excited carbonyl reaches the double bond. This suppresses the Paternò−Büchi channel almost completely, as we detect less than 5% of the γ-oxetane in this series. The major product **15** (75%, Scheme 9) is a result of an unprecedented cascade photoreaction. The stereochemistry of this transformation is proved unambiguously, as the structures of both the photoprecursor **7d** and the product **15** are determined by X-ray analysis.

The tricycle[3.3.0.0^{3,7}]octane (bisnoradamantane[11] or stellane in Gleiter's[12] terminology) core of **15** is often accessed via intramolecular Paternò−Büchi reactions in *endo*-acyl norbornenes as extensively studied by Sauers.[13] In contrast, the reaction shown in Scheme 9 produces the stellane core as a result of a radical cyclization in which two C−C bonds are formed. Two plausible mechanistic rationales are shown in

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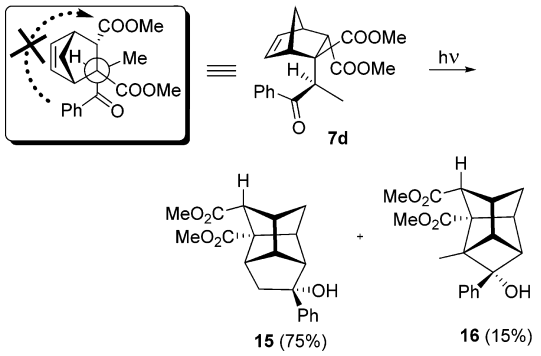
Scheme 9



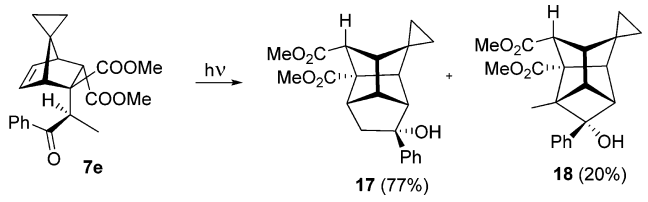
Scheme 10. Both mechanisms involve the initial β-hydrogen abstraction (from the Me-group) by the excited benzoyl. This 1,3-diradical can recombine to form the cyclopropane ring as in the Yang cyclization.[14] This is followed by secondary photoinduced cyclopropane ring-opening to form a more stable 1,3-diradical, which subsequently adds to the double bond (top mechanism). An alternative mechanism involves a 1,2-radical shift of the bicyclic core facilitated by the enol formation, followed by the keto−enol equilibrium, second excitation with H-abstraction, and an interrupted Yang cyclization (bottom).

In both cases the secondary 1,3-diradical undergoes cycloaddition to the readily accessible double bond, which constitutes radical cyclopentanation of alkenes. The minor product **16** (15%) is considerably more strained, possessing a cyclobutane moiety conceivably resulting from a formal [2 + 2] cycloaddition of the enol form of the photoprecursor.

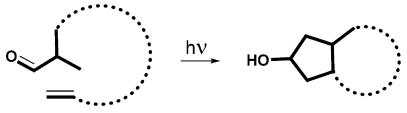
The spirocyclopropanonorbornadiene series with propiophenone gave the same result: the major photoproduct is derived from cyclopentanation of the double bond in **7e** with the secondary 1,3-diradical, Scheme 11. As in the case above, both the structure of the photoprecursor **7e** and the product **17** is determined by X-ray crystallographic analysis.

The general topology of this novel *photorearrangement/cyclopentanation* of double bonds is shown in Scheme 12, which constitutes a one-pot photoinduced synthesis of fused cyclopentanols, a useful addition to the toolbox of photoassisted synthetic chemistry.

Scheme 11

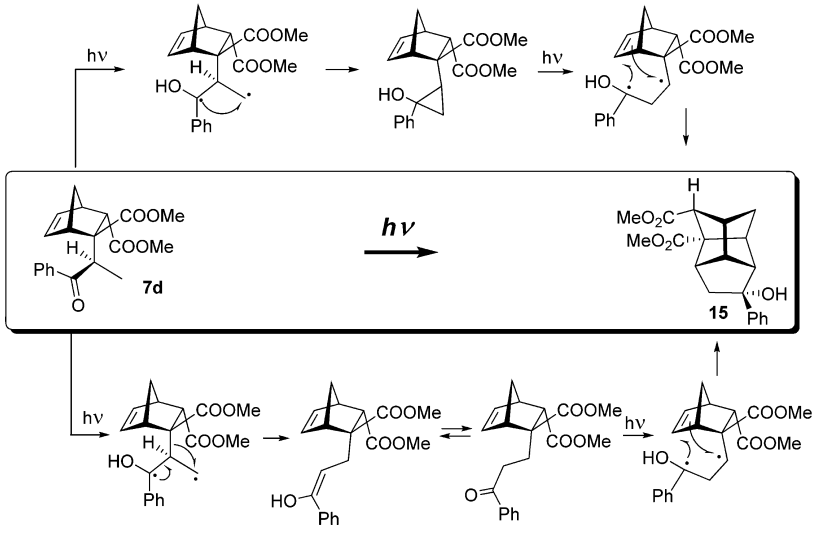


Scheme 12



In these transformations we did not observe the products of cyclopentanation by the initially photogenerated 1,3-diradical. Presumably it is too short-lived (it has one primary radical center) to successfully cyclopentanate the double bond. Although, from the point of relative stability of the products, the 1,3-cycloaddition of the primary 1,3-diradical ostensibly produces less strained polycyclic structure. In order to probe whether such alternative reactivity is possible, we simply stabilized the second radical center by employing β-phenylpropiophenone at the Michael addition step. We were able to separate chromatographically both diastereomers of the *endo*-photoprecursors (**7f** and **7f′**), which are expected to produce much more stable doubly benzylic initial 1,3-diradical. The structure of one of these photoprecursors, **7f**, was unambiguously determined by X-ray crystallography, and the structure of **7f′** was inferred from that. However, even with this additional stabilization, the initial 1,3-diradical failed to *endo*-cyclopentanate the norbornene double bond. This is somewhat in keeping with the fact that we did not find any literature reports on 1,3- or 1,4- Yang cyclizations (or Norrish Type II fragmentations) interrupted by diradical cycloadditions to a suitably positioned double bond.

Scheme 10



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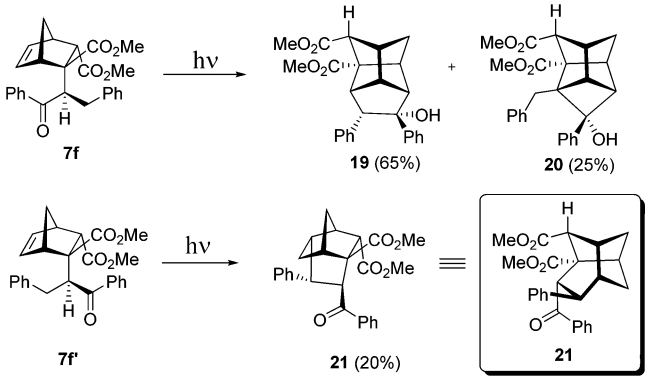
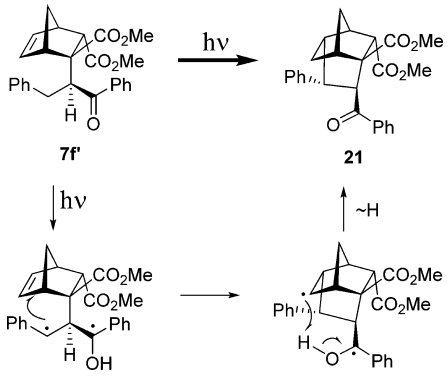
Diastereomeric photoprecursors **7f** and **7f′** exhibited very different reactivity. As it is shown in Scheme 13, diastereomer **7f** forms the major photoproduct **19**, which is similar to the formation of **15** described in Scheme 10, and the minor cyclobutane **20**.

Scheme 13



In contrast, irradiation of diastereomer **7f′** was not a clean reaction. We isolated the product of benzyl radical addition **21** in poor yield of 20%. As shown in Scheme 14, our mechanistic rationale for its formation involves the initial hydrogen abstraction by the excited carbonyl to give a stable 1,3-diradical, which lives long enough for its benzylic terminus to attack the double bond. However, instead of recombination to form the cyclopentyl ring, the ketyl radical simply delivers hydrogen to terminate the second radical center, restoring the benzoyl group.

Scheme 14

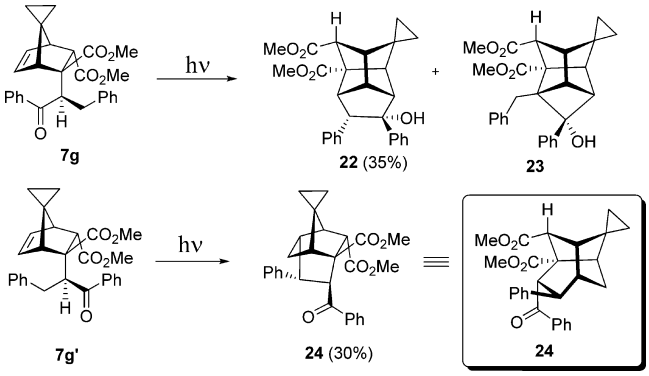


As diastereomer **7f** can only form a 1,3-diradical in which the ketyl, not benzylic, radical center can reach the double bond, one draws a conclusion that the ketyl radical is not capable of initiating radical addition to the double bond or such reaction is too slow and cannot compete with the rearrangement leading to the secondary 1,3-diradical and, eventually, to the product of cyclopentanation **19**.

The diastereomeric spirocyclopropanes **7g** and **7g′** behave in a similar manner (Scheme 15) with **7g** yielding the rearranged cyclopentanation product **22** as the major product and its homobenzylic epimer **7g′** producing polycycle **24**, presumably via the same mechanism shown in Scheme 14.

Valerophenone-based photoprecursor **7h** also offers stabilization of the second radical center, although in this case we isolated only one *endo*-diastereomer. Irradiation of **7h** yielded

Scheme 15



two diastereomers of the rearranged cyclopentanation products **25**, **26** plus the minor product of a formal [2 + 2] cycloaddition **27** (Scheme 16). We did not detect any radical addition products similar to **21** and **24** above. It is unlikely that we misassigned any of these, as the benzoyl's carbonyl group is easily detectable by ^{13}C NMR. The plausible explanation for these results is that just like the primary radical derived from **7d** in Scheme 10, the ethyl-stabilized secondary radical does not live long enough for attacking the double bond. Instead, the rearrangement and subsequent *endo*-cyclopentanation to form **25**, **26** occurs. The cyclopentanation is not stereospecific in this case as both epimers at the ethyl bearing center are observed. The major product **25** was not entirely separable from the minor [2 + 2] product **27** and was characterized in a mixture by ^{1}H NMR by analogy with **19** and **22**.

Photoprecursors **7d**–**7h** are not Paternò–Büchi competent, and therefore they utilize a different reaction pathway available for them, which is initiated by intramolecular hydrogen abstraction. To probe how severe the Paternò–Büchi channel is impeded in these sterically congested systems, we attempted to prepare the Michael adducts of dimethyl norbornadiene-2,3-dicarboxylate with cyclic aromatic ketones, indanone, 3-methyl indanone, and 3-phenylindanone, in which the carbonyl is held *out* and therefore not capable of *β*-hydrogen abstraction. Regrettably, we were able to isolate and purify only the *exo*, i.e., photoinactive, Michael products **7l**–**7p** (see Experimental Section).

We also synthesized the 1:1 Diels–Alder adduct **28**[15] (obtained with small amounts of 2:1 adducts[16] **29** and **30**) of furan with DMAD. However, under the conditions of the subsequent Michael addition step 7-oxanorbornadiene **28** fragmented yielding pyranone **31** instead of the desired *endo*-phenacyl bicyclic photoprecursor (two plausible mechanisms are shown in Scheme 17).

SUMMARY

In summary, rapid modular assembly of bicyclic scaffolds outfitted with conformationally flexible aroylmethyl chromophores provides access to Paternò–Büchi competent photoprecursors capable of protolytic oxametathesis transformation leading to novel polycyclic systems decorated with functional groups useful for subsequent transformations. At the same time, conformationally constrained photoprecursors can be readily obtained in a similar fashion. Irradiation of these starting materials initiates hydrogen abstraction and is accompanied by a cascade radical rearrangement/1,3-diradical *endo*-cycloaddition to the double bond, which amounts to intramolecular

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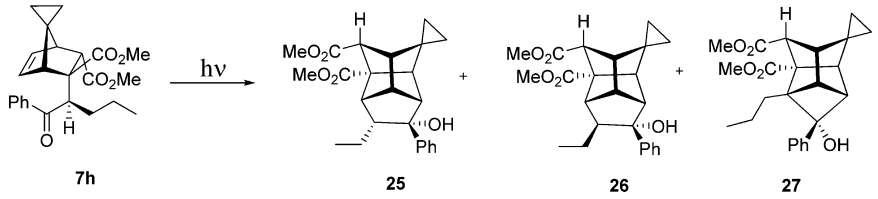
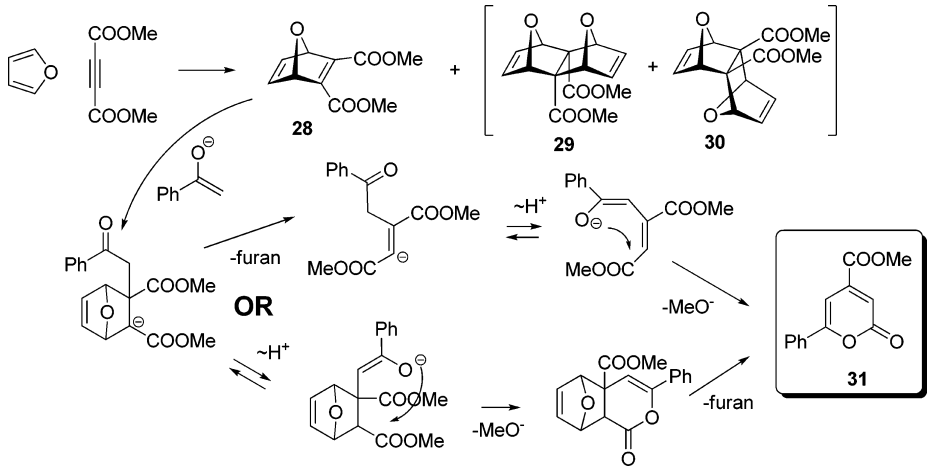
Scheme 16



Scheme 17



diradical cyclopentanation. This expeditious growth of complexity in just a few synthetically simple steps attests to the versatility of these new transformations and offers additional useful tool for the synthetic chemistry tool chest.

EXPERIMENTAL SECTION

General Procedure for Preparation of the Diels–Alder Adducts (1–6, 28). (A): A solution of dimethyl acetylenedicarboxylate in 10 mL of furan (used as a solvent and reagent) was stirred at room temperature for 24 h (longer reaction time causes the formation of **1a** and **1b**). After the reaction was completed, the solvent was removed on a high vacuum pump. The crude reaction mixture was purified on a flash silica gel column using a mixture of hexane and EtOAc as an eluent.

(B): A solution of dimethyl acetylenedicarboxylate (1.0 equiv) in 10 mL of DCM and freshly distilled 1,3-cyclopentadiene (1.0–2.0 equiv) was stirred at room temperature for 24 h. After the reaction was completed, the solvent was removed on a high vacuum pump. The resulting product was used without further purification unless noted otherwise.

(C): Acetylenedicarboxylic acid monopotassium salt (1.0 equiv) and HCl (4.0 M solution in dioxane, 1.0 equiv) were stirred in MeOH for 10 min. After that, freshly distilled 1,3-cyclopentadiene (2.0 equiv) was added, and the resulting mixture was stirred at room temperature for 48–72 h. When the reaction was completed, MeOH was removed, and the crude residue was dissolved in DCM and washed with Na_2CO_3 (sat.), water and brine. The organic layer was dried over anhydrous Na_2SO_4. The organic solvent was dried and evaporated to get pure product.

(D): A solution of propiolic acid methyl ester (1.0 equiv) and 1,3-cyclohexadiene (or freshly distilled 1,3-cyclopentadiene) (1.0–5.0 equiv) in 10 mL of 1,2-dichlorobenzene or toluene was heated in a pressure vessel at 70–75 °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 column using a mixture of hexane and EtOAc as an eluent.

*Methyl bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**1**).*[8a] (Procedure B) from 1.0 mL of propiolic acid methyl ester (11.2 mmol) and 3.0 mL of 1,3-cyclopentadiene (35.6 mmol): 0.98 g (58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 (d, J = 3.2 Hz, 1H), 6.91 (dd, J = 5.1, 3.1 Hz, 1H), 6.73 (dd, J = 5.1, 3.1 Hz, 1H), 3.90 (m, 1H), 3.73 (s, 3H), 3.72 (m, 1H), 2.15 (ddd, J = 6.5, 1.6, 1.6 Hz, 1H), 2.12 (d, J = 6.5 Hz, 1H).

*Dimethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**2**).*[8b] (Procedure B) from 0.7 mL of dimethyl acetylenedicarboxylate (5.69 mmol) and 0.5 mL of 1,3-cyclopentadiene (5.95 mmol): 1.13 g (95%). (Procedure C) from 6.0 g of acetylenedicarboxylic acid monopotassium salt (39.4 mmol) and 0.7 mL of 1,3-cyclopentadiene (83.2 mmol): 7.95 g (97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.92 (dd, J = 1.9, 1.9 Hz, 2H), 3.94 (m, 2H), 3.79 (s, 6H), 2.28 (ddd, J = 6.8, 1.6, 1.6 Hz, 1H), 2.10 (ddd, J = 6.8, 1.5, 1.5 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 165.5, 152.5, 142.4, 73.0, 53.5, 52.1.

*Methyl spiro[bicyclo[2.2.1]hepta-2,5-diene-2-carboxylate-7,1′-cyclopropane] (**3**).*[8c] (Procedure D) from 1.5 mL of propiolic acid methyl ester (16.9 mmol) and 1.25 mL of spiro[4.2]hepta-4,6-diene (12.5 mmol): 0.78 g (35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.71 (dd, J = 3.3, 1.1 Hz, 1H), 6.98 (ddd, J = 5.3, 3.2, 0.7 Hz, 1H), 6.81 (ddd, J = 5.3, 3.2, 0.8 Hz, 1H), 3.76 (s, 3H), 3.40 (m, 1H), 3.20 (m, 1H), 0.59–0.52 (m, 4H).

*Dimethyl spiro[bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1′-cyclopropane] (**4**).*[8d] (Procedure B) from 0.6 mL of dimethyl acetylenedicarboxylate (4.88 mmol) and 0.5 mL of spiro[4.2]hepta-4,6-diene (4.99 mmol) at −15 °C → 20 °C, gradient (hexane/EtOAc gradient 30:1 → 20:1): 0.77 g (68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.96 (dd, J = 2.0, 2.0 Hz, 2H), 3.79 (s, 6H), 3.43 (dd, J = 2.0, 2.0 Hz, 2H), 0.68–0.64 (m, 2H), 0.59–0.55 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 165.4, 152.0, 141.8, 69.3, 58.5, 52.0, 9.4, 9.3.

*Methyl bicyclo[2.2.2]octa-2,5-diene-2-carboxylate (**5**).*[8e] (Procedure D) from 3.0 mL of propiolic acid methyl ester (33.6 mmol) and 7.5 mL of 1,3-cyclohexadiene (78.7 mmol): 5.17 g (88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.29 (dd, J = 6.4, 1.9 Hz, 1H), 6.38 (ddd, J = 7.4, 6.1, 1.5 Hz, 1H), 6.27 (ddd, J = 7.3, 5.9, 1.5 Hz, 1H), 4.20 (m, 1H), 3.76 (m, 1H), 3.73 (s, 3H), 1.38–1.29 (m, 4H).

*Dimethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**6**).*[8f] (Procedure B) from 0.5 mL of dimethyl acetylenedicarboxylate (4.07 mmol) and 0.6 mL of 1,3-cyclohexadiene (6.30 mmol) for 120 h (hexane/EtOAc gradient 50:1 → 10:1): 0.20 g (22%). ^{1}H NMR (500

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MHz, $CDCl_3$) δ = 6.38 (dd, J = 4.4, 3.2 Hz, 2H), 4.04 (m, 2H), 3.77 (s, 6H), 1.51−1.45 (m, 2H), 1.44−1.39 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 166.5, 142.3, 133.6, 52.1, 38.9, 24.5.

Preparation of the Michael Adducts. General Procedure. (A): Diisopropylamine (1.4 equiv) was dissolved in THF at −10 °C, and then *n*-BuLi (1.6 M solution in hexanes 1.2 equiv) was added, and the resulting mixture was stirred for 20 min at −10 °C (in some cases −78 °C) to 0 °C gradient. After that, carbonyl compound was added (1.0 equiv), and the mixture was stirred at room temperature for additional 30−40 min. After the anion was generated, the Diels−Alder adduct (**1**−**7**) was added (1.0 equiv) at 20 °C, and the resulting mixture was stirred overnight. After the reaction was completed, DCM was added, and the resulting mixture was quenched with NH_4Cl and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and removed under a vacuum. The crude mixture was purified on a silica gel column using a mixture of hexane and EtOAc as an eluent.

(B): Fresh LDA (1.8 M solution, 1.3 equiv) was added under nitrogen atmosphere to the solution of a carbonyl compound (1.0 equiv) in THF at −5 to 0 °C. After the anion was generated (in 20−30 min), the Diels−Alder adduct (**1**−**6**) was added (1.0 equiv) at room temperature, and the resulting mixture was stirred for 10−20 h. After the reaction was completed DCM was added, and the resulting mixture was quenched with NH_4Cl and washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 and removed under a vacuum. The crude mixture was purified on a silica gel column using a mixture of hexane and EtOAc as an eluent.

*Methyl endo-5-phenacylbicyclo[2.2.2]oct-2-ene-exo-6-carboxylate (**7a**).* (Procedure B) from 10.7 mL of LDA (19.18 mmol), 1.75 mL of acetophenone (15.06 mmol) and 2.25 g of **5** (13.70 mmol) (hexane/EtOAc gradient 50:1 → 10:1): 1.40 g (37%). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.95 (d, J = 8.1 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 6.40 (ddd, J = 8.0, 6.8, 1.1 Hz, 1H), 6.25 (t, J = 7.1 Hz, 1H), 3.74 (s, 3H), 2.91 (dd, J = 16.3, 7.6 Hz, 1H), 2.86−2.80 (m, 2H), 2.77 (dddd, J = 12.7, 5.4, 1.8, 1.8 Hz, 1H), 2.54 (m, 1H), 2.07 (dt, J = 5.4, 2.3 Hz, 1H), 1.73−1.62 (m, 2H), 1.34−1.27 (m, 1H), 1.17−1.10 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 198.4, 175.0, 137.0, 134.3, 133.0, 132.9, 128.5, 128.1, 51.8, 50.1, 46.0, 36.8, 34.3, 33.0, 25.2, 20.1. HRMS (ESI/TOF) calcd for $C_{18}H_{20}NaO_3^+$ (MNa^+) 307.1310, found 307.1292.

*Methyl endo-5-(1-methylphenacyl)bicyclo[2.2.2]oct-2-ene-exo-6-carboxylate (**7b**).* (Procedure A) from 0.53 mL of diisopropylamine (3.78 mmol), 2.0 mL of *n*-BuLi (3.24 mmol), 0.40 mL of propiophenone (3.01 mmol) and 0.49 g of **5** (3.01 mmol) (hexane/EtOAc gradient 30:1 → 10:1): 0.24 g (29%). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.6 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 6.34 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 6.24 (t, J = 7.3 Hz, 1H), 3.73 (s, 3H), 3.26 (dt, J = 15.3, 7.1 Hz, 1H), 2.75−2.71 (m, 1H), 2.71−2.67 (m, 1H), 2.61 (ddd, J = 8.3, 5.7, 1.7 Hz, 1H), 2.01−1.99 (m, 1H), 1.67−1.61 (m, 2H), 1.35−1.27 (m, 1H), 1.17 (d J = 7.0 Hz, 3H), 1.14−1.06 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 204.0, 175.1, 137.0, 133.75, 133.0, 132.8, 128.6, 128.3, 51.7, 49.4, 46.1, 43.2, 33.4, 31.3, 25.3, 20.5, 15.8. HRMS (ESI/TOF) calcd for $C_{19}H_{23}NaO_3^+$ (MH^+) 299.1642, found 299.1649.

*Dimethyl spiro[endo-5-phenacylbicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7c**).* (Procedure B) from 1.4 mL of LDA (2.52 mmol), 0.25 mL of acetophenone (2.14 mmol) and 0.50 g of **4** (2.13 mmol) (hexane/EtOAc gradient 40:1 → 10:1): 0.23 g (30%) colorless crystals, mp 81−83 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.89 (d, J = 7.1 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.7 Hz, 2H), 6.47 (ddd, J = 5.8, 3.1, 0.9 Hz, 1H), 6.44 (ddd, J = 5.8, 2.8, 0.9 Hz, 1H), 4.38 (d, J = 3.5 Hz, 1H), 3.70 (s, 3H), 3.63 (d, J = 17.8 Hz, 1H), 3.50 (d, J = 17.8 Hz, 1H), 3.44 (s, 3H), 2.65 (m, 1H), 2.58 (m, 1H), 0.65 (ddd, J = 9.4, 5.8, 5.8 Hz, 1H), 0.49 (ddd, J = 9.6, 5.7, 5.7 Hz, 1H), 0.44−0.35 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 198.6, 175.4, 173.6, 138.6, 136.7, 135.1, 132.9, 128.5, 127.9, 57.4, 57.4, 53.2, 52.3, 51.5, 48.6, 44.3, 43.3, 10.2, 4.3. HRMS (ESI/TOF) calcd for $C_{21}H_{23}O_5^+$ (MH^+) 355.1540, found 355.1561. See SI for X-ray data.

*Dimethyl spiro[exo-5-phenacylbicyclo[2.2.1]hept-2-ene-endo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7c-exo**).* 0.15 g (20%) colorless crystals, mp 89−92 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 6.43 (m, 2H), 3.98 (d, J = 15.5 Hz, 1H), 3.62 (s, 3H), 3.58 (d, J = 15.5 Hz, 1H), 3.43 (s, 3H), 3.17 (d, J = 3.2 Hz, 1H), 2.70 (m, 1H), 2.45 (m, 1H), 0.81−0.77 (m, 1H), 0.76−0.71 (m, 1H), 0.43 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 197.7, 173.0, 172.9, 137.3, 136.4, 135.9, 133.2, 128.7, 128.1, 59.6, 56.2, 54.8, 52.0, 51.6, 51.6, 46.0, 43.0, 10.8, 3.6. HRMS (ESI/TOF) calcd for $C_{21}H_{22}NaO_5^+$ (MNa^+) 377.1359, found 377.1368. See SI for X-ray data.

*Dimethyl (1RS,4SR,5RS,6SR)-endo-5-((1′RS)-1′-benzoylethyl)-bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate (**7d**).* (Procedure A) from 0.23 mL of diisopropylamine (1.64 mmol), 1.0 mL of *n*-BuLi (1.60 mmol), 0.15 mL of propiophenone (1.13 mmol) and 0.23 g of **2** (1.10 mmol) (hexane/EtOAc gradient 30:1 → 20:1): 0.125 g (34%), colorless crystals, mp 97−101 °C. ^1H NMR (500 MHz, $CDCl_3$) δ = 7.90 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.33 (dd, J = 5.6, 2.9 Hz, 1H), 5.81 (dd, J = 5.6, 3.2 Hz, 1H), 3.95 (q, J = 7.2 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 3.35 (d, J = 3.3 Hz, 1H) overlaps with 3.34 (m, 1H), 3.02 (m, 1H), 1.52 (ddd, J = 9.2, 1.8, 1.8 Hz, 1H), 1.46 (d, J = 9.2 Hz, 1H), 1.08 (d, J = 7.1 Hz, 3H). ^1H NMR (500 MHz, C_6D_6) δ = 7.98 (m, 2H), 7.07 (m, 1H), 7.00 (m, 2H), 6.35 (dd, J = 5.6, 3.0 Hz, 1H), 5.86 (dd, J = 5.6, 3.2 Hz, 1H), 4.24 (q, J = 7.1 Hz, 1H), 3.59 (s, 3H), 3.57 (m, 1H), 3.46 (d, J = 3.3 Hz, 1H), 3.33 (s, 3H), 2.69 (m, 1H), 1.41−1.33 (m, 2H) overlaps with 1.34 (d, J = 7.1 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 202.7, 175.6, 174.0, 137.6, 136.4, 134.2, 133.1, 128.8, 128.4, 62.0, 52.1, 51.8, 51.3, 50.2, 49.5, 47.1, 43.6, 16.3. HRMS (ESI/TOF) calcd for $C_{20}H_{23}O_5^+$ (MH^+) 343.1540, found 343.1546. See SI for X-ray data.

*Dimethyl exo-5-(1′-benzoylethyl)bicyclo[2.2.1]hept-2-ene-endo-5-endo-6-dicarboxylate (**7d-exo**).* 0.092 g (25%). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.91 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.1249 (t, J = 7.7 Hz, 2H), 6.34 (dd, J = 5.5, 3.0 Hz, 1H), 6.16 (dd, J = 5.5, 3.2 Hz, 1H), 3.90 (q, J = 7.0 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 3H), 3.05 (d, J = 3.1 Hz, 1H), 3.00 (m, 1H), 2.76 (m, 1H), 1.72 (d, J = 9.1 Hz, 1H), 1.49 (t, J = 7.0 Hz, 3H) overlaps with 1.48 (ddd, J = 9.1, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 201.8, 173.6, 171.7, 138.0, 136.6, 136.3, 133.3, 128.8, 128.1, 64.3, 54.5, 51.7, 51.4, 49.8, 48.9, 46.4, 46.0, 15.4. HRMS (ESI/TOF) calcd for $C_{20}H_{23}O_5^+$ (MH^+) 343.1540, found 343.1555.

*Dimethyl (1RS,4RS,5RS,6SR)-spiro[(1″RS)-endo-5-(1″-benzoylethyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7e**).* (Procedure A) from 0.19 mL of diisopropylamine (1.36 mmol), 0.96 mL of *n*-BuLi (1.54 mmol), 0.14 mL of propiophenone (1.05 mmol) and 0.24 g of **4** (1.02 mmol) (hexane/EtOAc gradient 30:1 → 10:1): 0.23 g (61%). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.41 (ddd, J = 5.8, 2.9, 0.8 Hz, 1H), 5.84 (ddd, J = 5.8, 3.2, 0.8 Hz, 1H), 4.02 (q, J = 7.2 Hz, 1H), 3.82 (s, 3H), 3.77 (d, J = 3.4 Hz, 1H), 3.74 (s, 3H), 2.98 (m, 1H), 2.39 (m, 1H), 1.03 (d, J = 7.2 Hz, 3H), 0.50 (m, 1H), 0.44−0.38 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 202.5, 174.5, 173.9, 137.4, 137.0, 134.4, 132.9, 128.7, 128.3, 63.8, 54.0, 52.6, 52.2, 51.8, 51.8, 45.1, 42.7, 15.9, 9.3, 5.4. HRMS (ESI/TOF) calcd for $C_{22}H_{25}O_5^+$ (MH^+) 369.1697, found 369.1693.

*Dimethyl (1RS,4SR,5RS,6SR)-endo-5-((1′RS)-1′-benzoyl-2′-phenylethyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate (**7f**).* (Procedure B) from 0.80 mL of LDA (1.44 mmol), 0.20 g of 3-phenylpropiophenone (β-phenylpropiophenone) (0.95 mmol) and 0.20 g of **2** (0.96 mmol) (hexane/EtOAc gradient 30:1 → 20:1): 47.7 mg (12%). ^1H NMR (500 MHz, $CDCl_3$) δ = 7.37 (m, 3H), 7.22 (m, 2H), 7.09 (m, 4H), 7.01 (m, 1H), 6.25 (dd, J = 5.7, 2.9 Hz, 1H), 5.46 (dd, J = 5.7, 3.2 Hz, 1H), 4.06 (dd, J = 12.0, 2.3 Hz, 1H), 3.91 (s, 3H), 3.81 (s, 3H), 3.45 (d, J = 3.3 Hz, 1H), 3.04 (m, 2H), 2.93 (dd, J = 13.5, 12.0 Hz, 1H), 2.74 (dd, J = 13.5, 2.3 Hz, 1H), 1.47 (ddd, J = 9.1, 1.8, 1.8 Hz, 1H), 1.35 (d, J = 9.1 Hz, 1H). ^1H NMR (500 MHz, C_6D_6) δ = 7.58 (m, 2H), 7.40 (m, 2H), 6.98 (m, 2H), 6.90−6.80 (m, 4H), 6.30 (dd, J = 5.6, 3.0 Hz, 1H), 5.64 (dd, J = 5.6, 3.1 Hz, 1H), 4.43 (dd, J = 11.9, 2.3 Hz, 1H), 3.67 (s, 3H), 3.57 (d, J = 3.1 Hz, 1H), 3.48 (dd, J = 13.5, 11.9 Hz, 1H), 3.39 (s, 3H), 3.25 (m, 1H), 3.12 (dd, J = 13.5,

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2.3 Hz, 1H), 2.70 (m, 1H), 1.31 (ddd, *J* = 9.1, 1.8, 1.8 Hz, 1H), 1.24 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 203.8, 175.3, 173.9, 139.3, 138.8, 137.3, 134.4, 132.4, 129.2, 128.3, 128.2, 128.1, 126.8, 63.1, 52.3, 52.0, 51.7, 50.9, 50.0, 49.7, 47.1, 37.6. See SI for X-ray data.

*Dimethyl (1RS,4SR,5RS,6SR)-endo-5-((1′SR)-1′-benzoyl-2′-phenylethyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate (**7f′**).* 119 mg (30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (m, 2H), 7.25 (m, 1H), 7.06 (m, 2H), 7.00−6.93 (m, 5H), 6.69 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.46 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.19 (d, *J* = 3.4 Hz, 1H), 3.98 (s, 3H), 3.68 (dd, *J* = 11.1, 3.6 Hz, 1H), 3.52 (m, 1H), 3.39 (dd, *J* = 13.6, 3.6 Hz, 1H), 3.21 (dd, *J* = 13.6, 11.1 Hz, 1H), 3.06 (m, 1H), 2.60 (s, 3H), 1.49 (ddd, *J* = 9.1, 1.8, 1.8 Hz, 1H), 1.43 (d, *J* = 9.1 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.54 (m, 2H), 6.94 (m, 2H), 6.85−6.75 (m, 6H) overlaps with 6.74 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.31 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.42 (d, *J* = 3.4 Hz, 1H), 3.95 (dd, *J* = 11.0, 3.9 Hz, 1H), 3.76 (s, 3H), 3.48 (dd, *J* = 13.6, 11.0 Hz, 1H) overlaps with 3.46 (m, 1H), 3.37 (dd, *J* = 13.6, 3.9 Hz, 1H), 2.81 (m, 1H), 2.46 (s, 3H), 1.40 (d, *J* = 8.9 Hz, 1H), 1.32 (ddd, *J* = 8.9, 1.8, 1.8 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 201.7, 176.0, 173.6, 140.4, 139.0, 136.8, 132.4, 132.0, 129.3, 128.6, 128.1, 127.6, 126.3, 62.7, 52.7, 52.7, 52.3, 50.8, 50.2, 46.9, 46.5, 39.1. See SI for X-ray data.

*Dimethyl exo-5-(1′-benzoyl-2′-phenylethyl)bicyclo[2.2.1]hept-2-ene-endo-5-exo-6-dicarboxylate (**7f-exo**).* 71.5 mg (18%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 (m, 2H), 7.34 (m, 1H), 7.18 (m, 2H), 7.11−7.02 (m, 5H), 6.32 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.06 (dd, *J* = 5.6, 3.0 Hz, 1H), 4.22 (dd, *J* = 9.2, 4.3 Hz, 1H), 3.80 (s, 3H), 3.65 (dd, *J* = 14.3, 4.3 Hz, 1H), 3.47 (m, 1H), 3.37 (d, *J* = 2.0 Hz, 1H), 3.05 (dd, *J* = 14.3, 9.2 Hz, 1H), 2.97 (m, 1H), 2.74 (s, 3H), 2.36 (d, *J* = 9.3 Hz, 1H), 1.58 (dddd, *J* = 9.3, 1.8, 1.8, 1.8 Hz, 1H) overlaps with HOD. ^{1}H NMR (500 MHz, C_6D_6) δ = 7.68 (m, 2H), 7.01 (m, 2H), 6.91−6.82 (m, 6H), 6.05 (m, 2H), 4.51 (dd, *J* = Hz, 1H), 3.68−3.62 (m, 2H), 3.59 (s, 3H), 3.45 (m, 1H), 3.31 (dd, *J* = 14.0, 9.6 Hz, 1H), 2.83 (m, 1H), 2.61 (s, 3H), 2.56 (d, *J* = 9.2 Hz, 1H), 1.51 (dddd, *J* = 9.2, 1.8, 1.8, 1.8 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 201.3, 175.2, 174.7, 139.7, 139.5, 136.4, 136.0, 132.7, 129.2, 128.9, 128.4, 127.8, 126.3, 59.9, 52.1, 51.9, 51.1, 49.0, 48.9, 47.8, 45.9, 38.0. HRMS (ESI/TOF) calcd for $C_{26}H_{27}O_5^+$ (MH^+) 419.1853, found 419.1849. See SI for X-ray data.

*Dimethyl (1RS,4RS,5RS,6SR)-spiro[(1″RS)-endo-5-(1″-benzoyl-2″-phenylethyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7g**).* (Procedure B) from 1.55 mL of LDA (2.79 mmol), 0.45 g of 3-phenylpropiophenone (2.14 mmol) and 0.50 g of **4** (2.13 mmol) (hexane/EtOAc gradient 30:1 → 5:1): 0.17 g (18%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (m, 3H), 7.25 (m, 2H), 7.10 (m, 4H), 7.02 (m, 1H), 6.33 (dd, *J* = 5.8, 3.0 Hz, 1H), 5.46 (ddd, *J* = 5.8, 3.2, 0.9 Hz, 1H), 4.17 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.80 (d, *J* = 3.5 Hz, 1H), 2.85 (dd, *J* = 13.5, 12.0 Hz, 1H), 2.71 (dd, *J* = 13.5, 2.4 Hz, 1H), 2.60 (m, 1H), 2.40 (m, 1H), 0.49−0.33 (m, 4H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.62 (m, 2H), 7.45 (m, 2H), 7.01 (m, 3H), 6.86 (m, 3H), 6.42 (ddd, *J* = 5.8, 3.0, 0.8 Hz, 1H), 5.76 (dd, *J* = 5.8, 3.1, 0.9 Hz, 1H), 4.58 (dd, *J* = 12.0, 2.2 Hz, 1H), 4.02 (d, *J* = 3.5 Hz, 1H), 3.66 (s, 3H), 3.44 (dd, *J* = 13.5, 12.0 Hz, 1H) overlaps with 3.42 (s, 3H), 3.13 (dd, *J* = 13.5, 2.2 Hz, 1H), 2.82 (m, 1H), 2.04 (m, 1H), 0.52 (m, 1H), 0.23−0.16 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 203.3, 174.1, 173.8, 139.4, 139.2, 137.0, 134.7, 132.3, 129.2, 128.3, 128.2, 127.9, 126.2, 64.5, 53.5, 52.8, 52.0, 51. 9, 51.5, 51.1, 45.6, 36.9, 9.5, 5.4. HRMS (ESI/TOF) calcd for $C_{28}H_{28}NaO_5^+$ (MNa^+) 467.1829, found 467.1812. See SI for X-ray data.

*Dimethyl (1RS,4RS,5RS,6SR)-spiro[endo-5-((1″SR)-1″-benzoyl-2″-phenylethyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7g′**).* 0.22 g (23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35 (m, 2H), 7.25 (m, 1H), 7.08 (m, 2H), 6.99−6.93 (m, 5H), 6.78 (dd, *J* = 5.8, 3.0 Hz, 1H), 6.58 (ddd, *J* = 5.8, 3.0, 0.9 Hz, 1H), 4.33 (d, *J* = 3.5 Hz, 1H), 3.96 (s, 3H), 3.75 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.33 (dd, *J* = 13.5, 3.7 Hz, 1H), 3.20 (dd, *J* = 13.5, 11.2 Hz, 1H), 3.07 (m, 1H), 2.59 (s, 3H), 2.46 (m, 1H), 0.53−0.41 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 201.7, 175.4, 173.6, 140.6, 139.0, 137.2, 132.6, 132.4, 129.6, 128.8, 128.3, 127.8, 126.5, 64.3, 57.0, 52.6 overlaps with 52.6, 52.5, 51.3, 51.0, 43.0, 39.5, 9.6, 4.9. See SI for X-ray data.

*Dimethyl (1RS,4RS,5RS,6SR)-spiro[(1″RS)-endo-5-(1″-benzoylbutyl)bicyclo[2.2.1]hept-2-ene-exo-5-endo-6-dicarboxylate-7,1′-cyclopropane] (**7h**).* (Procedure B) from 0.57 mL of LDA (1.03 mmol), 0.14 mL of valerophenone (0.85 mmol) and 0.20 g of **4** (0.85 mmol) (hexane/EtOAc gradient 50:1 → 10:1): 118 mg (35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 6.34 (ddd, *J* = 5.9, 3.0, 0.7 Hz, 1H), 5.65 (ddd, *J* = 5.7, 3.2, 0.9 Hz, 1H), 3.89 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.81 (s, 3H), 3.77 (d, *J* = 3.4 Hz, 1H), 3.72 (s, 3H), 2.62 (m, 1H), 2.35 (m, 1H), 1.64−1.58 (m, 1H) overlaps with HOD, 1.37−1.30 (m, 1H), 1.11 (m, 1H), 1.01 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.43−0.31 (m, 4H). ^{1}H NMR (500 MHz, C_6D_6) δ = 8.03 (m, 2H), 7.09 (m, 1H), 7.03 (m, 2H), 6.43 (ddd, *J* = 5.9, 3.0, 0.8 Hz, 1H), 5.89 (dd, *J* = 5.8, 3.2, 0.8 Hz, 1H), 4.25 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.03 (d, *J* = 3.6 Hz, 1H), 3.60 (s, 3H), 3.38 (s, 3H), 2.82 (m, 1H), 2.13 (dddd, *J* = 13.8, 11.0, 11.0, 4.7 Hz, 1H), 2.03 (m, 1H), 1.69 (dddd, *J* = 13.8, 12.0, 5.1, 1.7 Hz, 1H), 1.39−1.29 (m, 1H), 1.22−1.13 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H), 0.48−0.39 (m, 4H).

Photoinactive Exo Compounds 7i−7q. *Dimethyl exo-5-phenacylbicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7i**).* (Procedure A) from 0.13 mL of diisopropylamine (0.93 mmol), 0.50 mL of *n*-BuLi (0.80 mmol), 0.08 mL of acetophenone (0.68 mmol) and 0.14 g of **2** (0.67 mmol) (hexane/EtOAc gradient 30:1 → 10:1): 57 mg (26%) colorless crystals, mp 142.5−144 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92 (d, *J* = 7.1 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 6.35 (dd, *J* = 5.7, 3.1 Hz, 1H), 6.02 (dd, *J* = 5.6, 2.9 Hz, 1H), 3.98 (d, *J* = 18.1 Hz, 1H), 3.75 (d, *J* = 18.1 Hz, 1H), 3.62 (s, 3H), 3.43 (s, 3H) overlaps with 3.43 (m, 1H), 3.00 (m, 1H), 2.94 (m, 1H), 2.26 (d, *J* = 9.2 Hz, 1H), 1.56 (ddd, *J* = 9.2, 1.7, 1.7 Hz, 1H) overlaps with HOD. ^{1}H NMR (500 MHz, C_6D_6) δ = 7.86 (d, *J* = 7.1 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.09 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.94 (dd, *J* = 5.6, 2.9 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 3.81 (d, *J* = 1.8 Hz, 1H), 3.68 (d, *J* = 18.0 Hz, 1H), 3.32 (s, 3H), 3.17 (s, 3H), 2.82 (m, 1H) overlaps with 2.80 (m, 1H), 2.36 (d, *J* = 9.0 Hz, 1H), 1.44 (dddd, *J* = 9.0, 1.7, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 198.5, 175.5, 174.7, 138.7, 136.4, 134.8, 133.2, 128.6, 128.0, 53.9, 52.8, 52.3, 51.8, 48.6, 47.0, 46.4, 45.8. HRMS (ESI/TOF) calcd for $C_{19}H_{20}NaO_5^+$ (MNa^+) 351.1203, found 351.1196.

*Dimethyl exo-5-phenacylbicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7i′**).* 33 mg (15%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 6.34 (m, 2H), 4.08 (d, *J* = 3.4 Hz, 1H), 3.70 (s, 3H), 3.55 (s, 2H), 3.45 (s, 3H), 3.17 (m, 1H), 3.10 (m, 1H), 1.79 (d, *J* = 8.9 Hz, 1H), 1.44 (ddd, *J* = 8.9, 1.7, 1.7 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.89 (d, *J* = 7.0 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.28 (dd, *J* = 5.6, 2.9 Hz, 1H), 6.10 (dd, *J* = 5.7, 3.2 Hz, 1H), 4.41 (d, *J* = 3.2 Hz, 1H), 3.76 (d, *J* = 18.0 Hz, 1H), 3.50 (dd, *J* = 18.0 Hz, 1H), 3.38 (s, 3H), 3.16 (s, 3H), 2.97 (m, 2H), 1.89 (d, *J* = 8.8 Hz, 1H), 1.28 (ddd, *J* = 8.8, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 198.9, 176.1, 173.9, 138.1, 136.5, 134.8, 133.0, 128.5, 127.9, 55.5, 52.9, 52.6, 51.5, 48.4, 47.5, 46.8, 43.9. HRMS (ESI/TOF) calcd for $C_{19}H_{20}NaO_5^+$ (MNa^+) 351.1203, found 351.1209.

*Methyl spiro[exo-6-phenacylbicyclo[2.2.1]hept-2-ene-endo-5-carboxylate-7,1′-cyclopropane] (**7j**).* 21.9 mg (13%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.1 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 6.43 (ddd, *J* = 5.9, 3.2, 0.7 Hz, 1H), 6.15 (ddd, *J* = 5.8, 2.7, 0.7 Hz, 1H), 3.66 (s, 3H), 3.42 (dd, *J* = 16.2, 6.4 Hz, 1H), 3.30 (dd, *J* = 16.2, 8.7 Hz, 1H), 2.86 (dd, *J* = 4.8, 3.6 Hz, 1H), 2.56 (m, 1H), 2.47 (ddd, *J* = 8.7, 6.4, 5.0 Hz, 1H), 2.21 (m, 1H), 0.72 (ddd, *J* = 9.6, 5.3, 5.3 Hz, 1H), 0.65 (ddd, *J* = 9.4, 5.5, 5.5 Hz, 1H), 0.44 (ddd, *J* = 9.5, 5.2, 5.2 Hz, 1H), 0.38 (ddd, *J* = 9.5, 5.4, 5.4 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.94 (m, 2H), 7.13 (m, 1H), 7.08 (m, 2H), 6.28 (ddd, *J* = 5.8, 3.2, 0.7 Hz, 1H), 6.19 (ddd, *J* = 5.8, 2.8, 0.7 Hz, 1H), 3.37 (s, 3H), 3.17−3.12 (m, 1H), 2.99−2.93 (m, 1H), 2.73−2.69 (m, 2H), 2.38 (m, 1H), 2.06 (m, 1H), 0.41−0.36 (m, 1H), 0.28−0.16 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 199.49, 174.41, 138.51, 136.85, 133.51, 133.03, 128.61, 128.14, 51.58, 51.48, 51.26, 51.14, 43.16, 42.64, 41.68, 9.27, 3.34. HRMS (ESI/TOF) calcd for $C_{19}H_{21}O_3^+$ (MH^+) 297.1485, found 297.1492.

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*Methyl exo-6-(1′-benzoylethyl)bicyclo[2.2.1]hept-2-ene-endo-5-carboxylate (**7k**).* (Procedure A) from 0.33 mL of diisopropylamine (2.35 mmol), 1.70 mL of *n*-BuLi (2.72 mmol), 0.24 mL of propiophenone (1.80 mmol) and 0.27 g of **5** (1.80 mmol) (hexane/EtOAc gradient 30:1→10:1): 0.27 g (53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.97 (d, J = 7.1 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 6.27 (dd, J = 5.6, 3.2 Hz, 1H), 6.00 (dd, J = 5.6, 2.8 Hz, 1H), 3.65 (s, 3H), 3.39 (dddd, J = 10.8, 7.0, 7.0, 7.0 Hz, 1H), 3.19 (m, 1H), 2.66 (dd, J = 4.6, 3.7 Hz, 1H), 2.46 (m, 1H), 2.33 (ddd, J = 10.8, 4.8, 1.6 Hz, 1H), 1.54 (d, J = 8.7 Hz, 1H), 1.44 (dddd, J = 8.7, 1.7, 1.7, 1.7 Hz, 1H), 1.27 (d, J = 7.0 Hz, 3H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.89 (d, J = 7.0 Hz, 2H), 7.15 (m, 1H), 7.09 (t, J = 7.3 Hz, 2H), 6.12 (dd, J = 5.6, 3.2 Hz, 1H), 6.03 (dd, J = 5.6, 2.8 Hz, 1H), 3.34 (s, 3H), 3.10 (m, 1H), 3.04 (dddd, J = 10.9, 7.0, 7.0, 7.0 Hz, 1H), 2.68 (ddd, J = 10.9, 4.7, 1.6 Hz, 1H), 2.44 (m, 2H), 1.25 (dddd, J = 8.7, 1.7, 1.7, 1.7 Hz, 1H), 1.20 (d, J = 7.0 Hz, 3H) overlaps with 1.20 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 204.1, 174.6, 138.8, 137.1, 133.5, 133.1, 128.8, 128.2, 51.7, 49.1, 46.6, 46.5, 46.5, 46.1, 45.7, 17.7. HRMS (ESI/TOF) calcd for $C_{18}H_{21}O_3^+$ (MH^+) 285.1485, found 285.1492.

*Dimethyl exo-5-(1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7l**).* (Procedure A) from 0.26 mL of diisopropylamine (1.86 mmol), 1.35 mL of *n*-BuLi (2.16 mmol), 0.20 mL of 1-indanone (1.51 mmol) and 0.30 g of **2** (1.44 mmol) (hexane/EtOAc gradient 30:1 → 5:1): 0.14 g (28%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.76 (d, J = 7.7 Hz, 1H), 7.57 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 6.50 (dd, J = 5.5, 3.0 Hz, 1H), 6.06 (dd, J = 5.5, 3.2 Hz, 1H), 4.22 (m, 1H), 3.70 (s, 3H), 3.51 (dd, J = 17.7, 4.1 Hz, 1H), 3.43 (dd, J = 17.7, 7.9 Hz, 1H), 3.16 (s, 3H), 3.13 (m, 1H), 3.00 (d, J = 3.1 Hz, 1H), 2.91 (dd, J = 7.9, 4.1 Hz, 1H), 1.79 (d, J = 9.4 Hz, 1H), 1.63 (ddd, J = 9.4, 1.7, 1.7 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.83 (d, J = 7.6 Hz, 1H), 7.09 (ddd, J = 7.4, 7.4, 1.2 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.94 (t, J = 7.4 Hz, 1H), 6.62 (dd, J = 5.5, 3.0 Hz, 1H), 6.10 (d, J = 5.5, 3.1 Hz, 1H), 4.53 (m, 1H), 3.57 (dd, J = 17.5, 4.1 Hz, 1H), 3.46 (s, 3H), 2.99 (dd, J = 17.5, 8.1 Hz, 1H), 2.87 (m, 1H), 2.81 (s, 3H), 2.59 (d, J = 3.1 Hz, 1H), 2.44 (dd, J = 8.1, 4.1 Hz, 1H), 1.45 (ddd, J = 9.2, 1.8, 1.8 Hz, 1H), 1.39 (d, J = 9.2 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 204.7, 173.4, 172.1, 152.4, 138.2, 137.3, 134.5, 134.3, 127.4, 126.4, 123.7, 63.3, 55.9, 54.3, 51.8, 51.3, 48.5, 46.2, 46.2, 31.7. HRMS (ESI/TOF) calcd for $C_{20}H_{21}O_5^+$ (MH^+) 341.1384, found 341.1390.

*Dimethyl exo-5-(1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7l′**).* Trace amount. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (d, J = 7.7 Hz, 1H), 7.55 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 6.54 (dd, J = 5.5, 3.1 Hz, 1H), 6.09 (dd, J = 5.5, 3.1 Hz, 1H), 4.27 (d, J = 3.4 Hz, 1H), 3.64 (s, 3H), 3.33 (dd, J = 17.5, 8.2 Hz, 1H), 3.17 (m, 1H), 3.12 (s, 3H), 3.09 (m, 1H), 2.96 (dd, J = 17.5, 4.1 Hz, 1H), 2.85 (dd, J = 8.2, 4.1 Hz, 1H), 1.77 (d, J = 9.3 Hz, 1H), 1.55 (ddd, J = 9.3, 1.7, 17 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.1, 173.3, 172.7, 151.5, 137.7, 137.3, 134.4, 133.7, 127.5, 126.2, 123.8, 63.2, 52.7, 51.8, 51.6, 51.0, 50.9, 47.8, 46.7, 31.3. HRMS (ESI/TOF) calcd for $C_{20}H_{21}O_5^+$ (MH^+) 341.1384, found 341.1390.

*Dimethyl (1RS,4SR,5SR,6RS)-exo-5-((2′SR)-1′-indanon-2′-yl)-bicyclo[2.2.1]hept-2-ene-endo-5-exo-6-dicarboxylate (**7m**).* 58.8 mg (12%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.74 (d, J = 7.8 Hz, 1H), 7.53 (ddd, J = 7.5, 7.5, 1.1 Hz, 1H), 7.35 (m, 2H), 6.27 (dd, J = 5.6, 3.1 Hz, 1H), 6.02 (dd, J = 5.6, 3.1 Hz, 1H), 4.22 (m, 1H), 3.77 (m, 3H), 3.25−3.19 (m, 2H), 3.07−2.97 (m, 5H), 2.84 (dd, J = 17.5, 2.7 Hz, 1H), 2.53 (d, J = 9.5 Hz, 1H), 1.67 (dddd, J = 9.5, 1.7, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 175.1, 173.3, 151.8, 139.1, 137.4, 136.8, 134.4, 127.5, 126.4, 123.5, 52.0, 51.7, 51.3, 49.1, 49.0, 48.2, 45.7, 45.0. HRMS (ESI/TOF) calcd for $C_{20}H_{21}O_5^+$ (MH^+) 341.1384, found 341.1386.

*Dimethyl (1SR,4RS,5RS,6RS)-exo-5-((2′SR, 3′RS)-3′-methyl-1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7n**).* (Procedure B) from 0.60 mL of LDA (1.08 mmol), 0.10 mL of 3-methyl-1-indanone (0.74 mmol) and 0.15 g of **2** (0.72 mmol) (hexane/EtOAc gradient 30:1 → 20:1): 66.3 mg (26%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (d, J = 7.7 Hz, 1H), 7.57 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 6.53 (dd, J = 5.5, 3.2 Hz, 1H), 6.10 (dd, J = 5.5, 3.0 Hz, 1H), 4.21 (d, J = 3.4 Hz, 1H), 3.63 (s, 3H), 3.30 (dddd, J = 7.0, 7.0, 7.0, 3.0 Hz, 1H), 3.23 (m, 1H), 3.16 (m, 1H), 3.04 (s, 3H), 2.41 (d, J = 3.0 Hz, 1H), 1.79 (d, J = 9.3 Hz, 1H), 1.57 (ddd, J = 9.3, 1.7, 1.7 Hz, 1H) overlaps with HOD, 1.41 (d, J = 7.0 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.2, 173.3, 172.7, 157.0, 137.1, 136.8, 134.6, 134.2, 127.5, 125.1, 123.5, 63.8, 61.0, 51.8, 51.5, 50.8, 50.3, 47.8, 46.4, 38.4, 23.1. HRMS (ESI/TOF) calcd for $C_{21}H_{23}O_5^+$ (MH^+) 355.1540, found 355.1548.

*Dimethyl exo-5-(3′-methyl-1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-endo-5,exo-6-dicarboxylate (**7n′**).* 51 g (20%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.69 (d, J = 7.6 Hz, 1H), 7.53 (m, 1H), 7.39−7.33 (m, 2H), 6.22 (m, 1H), 6.01 (m, 1H), 3.82 (m, 4H), 3.20 (m, 1H) overlaps with 3.14 (m, 1H), 2.95 (m, 1H), 2.88 (m, 1H), 2.74 (m, 3H), 2.59 (m, 1H), 1.64 (dddd, J = 9.4, 1.8, 1.8, 1.8 Hz, 1H), 1.15 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 174.9, 173.2, 158.2, 138.9, 137.6, 136.0, 134.5, 127.6, 125.7, 125.6, 123.2, 63.9, 58.1, 52.1, 51.0, 49.1, 48.7, 46.3, 45.4, 38.7, 24.5. HRMS (ESI/TOF) calcd for $C_{21}H_{23}O_5^+$ (MH^+) 355.1540, found 355.1542.

*Dimethyl (1SR,4RS,5RS,6RS)-exo-5-((2′SR, 3′SR)-3′-phenyl-1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-endo-bis-5,6-dicarboxylate (**7o**).* (Procedure A) from 0.10 mL of diisopropylamine (0.71 mmol), 0.50 mL of *t*-BuLi (1.7 M, 0.85 mmol), 0.10 mL of 3-phenyl-1-indanone (0.48 mmol) and 0.10 g of **2** (0.48 mmol) at −78 °C → 20 °C gradient (hexane/EtOAc gradient 30:1 → 4:1): 96 mg (48%), colorless crystals, mp 168.5−170.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.80 (d, J = 7.7 Hz, 1H), 7.50 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.32−7.28 (m, 2H), 7.23 (m, 1H), 7.11 (m, 3H), 6.48 (dd, J = 5.5, 3.1 Hz, 1H), 6.08 (dd, J = 5.5, 3.1 Hz, 1H), 4.41 (d, J = 3.8 Hz, 1H), 4.18 (d, J = 3.4 Hz, 1H), 3.66 (s, 3H), 3.16 (m, 1H), 3.14 (s, 3H), 3.09 (m, 1H), 2.98 (d, J = 3.8 Hz, 1H), 1.48 (d, J = 9.4 Hz, 1H), 1.31 (ddd, J = 9.4, 1.8, 1.8 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.86 (d, J = 7.6 Hz, 1H), 7.01−6.95 (m, 4H), 6.91 (t, J = 7.4 Hz, 1H), 6.84 (m, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.70 (dd, J = 5.5, 3.1 Hz, 1H), 6.14 (dd, J = 5.5, 3.0 Hz, 1H), 4.55 (d, J = 3.9 Hz, 1H), 4.37 (d, J = 3.4 Hz, 1H), 3.40 (s, 3H), 3.27 (m, 1H), 3.01 (s, 3H), 2.94 (d, J = 3.9 Hz, 1H), 2.87 (m, 1H), 1.16 (d, J = 9.3 Hz, 1H), 1.06 (ddd, J = 9.3, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.0, 173.3, 172.8, 155.6, 143.8, 137.1, 136.7, 135.0, 134.2, 129.1, 127.9, 127.8, 127.1, 126.4, 123.3, 63.9, 62.2, 51.9, 51.8, 51.0, 50.4, 50.2, 47.6, 46.5. HRMS (ESI/TOF) calcd for $C_{26}H_{25}O_5^+$ (MH^+) 417.1697, found 417.1679.

*Dimethyl (1RS,4SR,5SR,6RS)-exo-5-((2′SR, 3′SR)-3′-phenyl-1′-indanon-2′-yl)bicyclo[2.2.1]hept-2-ene-endo-5-exo-6-dicarboxylate (**7o′**).* 56 mg (28%), colorless crystals, mp 151.0−154.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.73 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.23 (m, 3H), 7.15 (m, 1H), 7.06 (m, 2H), 6.24 (dd, J = 5.5, 3.1 Hz, 1H), 6.00 (m, 1H), 4.32 (m, 1H), 3.95 (m, 1H), 3.57 (m, 1H), 3.22 (m, 1H), 3.03 (m, 4H), 2.92 (m, 1H), 2.84 (m, 2H), 2.56 (m, 1H), 1.61 (m, 1H). HRMS (ESI/TOF) calcd for $C_{26}H_{25}O_5^+$ (MH^+) 417.1697, found 417.1684.

*Methyl (1RS,4SR,5RS,6SR)-exo-6-((2′RS)-1′-indanon-2′-yl)bicyclo-[2.2.1]hept-2-ene-endo-5-carboxylate (**7p**).* (Procedure A) from 0.40 mL of diisopropylamine (2.85 mmol), 2.0 mL of *n*-BuLi (3.2 mmol), 0.18 mL of 1-indanone (1.36 mmol) and 0.20 g of **5** (1.33 mmol) (hexane/EtOAc gradient 30:1 → 2:1): 52.5 mg (14%), colorless crystals, mp 99.5−102.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.62 (m, 1H), 7.42 (t, J = 7.3 Hz, 1H), 6.24 (dd, J = 5.6, 3.3 Hz, 1H), 6.02 (d, J = 5.7, 2.8 Hz, 1H), 3.61 (s, 3H), 3.40 (ddd, J = 9.9, 7.5, 2.8 Hz, 1H), 3.23 (m, 1H), 3.09 (m, 1H), 2.88 (dd, J = 10.0, 7.5 Hz, 1H), 2.71 (dd, J = 4.6, 3.6 Hz, 1H), 2.67 (dd, J = 18.6, 2.9 Hz, 1H), 2.03 (ddd, J = 9.5, 4.7, 1.6 Hz, 1H), 1.67 (d, J = 8.9 Hz, 1H), 1.55 (dddd, J = 8.9, 1.7, 1.7, 1.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.5, 174.5, 157.1, 138.3, 137.4, 134.4, 134.3, 127.9, 127.1, 123.9, 51.8, 50.0, 49.3, 46.2, 46.0, 45.8, 43.3, 43.0. HRMS (ESI/TOF) calcd for $C_{18}H_{22}NO_3^+$ (MNH_4^+) 300.1594, found 300.1583.

*Dimethyl exo-5-(1′-benzoyl-1′-phenylmethyl)bicyclo[2.2.1]hept-2-ene-endo-5-exo-6-dicarboxylate (**7q**).* (Procedure B) from 1.04 mL of LDA (1.87 mmol), 0.28 g of 2-phenylacetophenone (deoxybenzoin) (1.43 mmol) and 0.30 g of **2** (1.44 mmol)

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(hexane/EtOAc gradient 30:1 → 5:1): 0.13 g (23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.84 (m, 2H), 7.43 (m, 1H), 7.34−7.27 (m, 7H) overlaps with $CDCl_3$, 6.32 (dd, J = 5.6, 3.1 Hz, 1H), 5.88 (dd, J = 5.6, 3.0 Hz, 1H), 5.16 (s, 1H), 3.73 (s, 3H), 3.54 (d, J = 2.0 Hz, 1H), 3.09 (s, 3H), 2.95 (m, 1H), 2.76 (m, 1H), 2.48 (d, J = 9.2 Hz, 1H), 1.64 (dddd, J = 9.2, 1.8, 1.8, 1.8 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 196.5, 175.7, 174.4, 139.8, 135.9, 135.7, 135.1, 133.0, 130.9, 128.9, 128.5, 128.3, 127.9, 59.2, 57.7, 51.6, 51.6, 50.3, 49.4, 47.5, 46.3. HRMS (ESI/TOF) calcd for $C_{25}H_{25}O_5^+$ (MH^+) 405.1697, found 405.1687.

*Dimethyl exo-5-(1′-benzoyl-1′-phenylmethyl)bicyclo[2.2.1]hept-2-ene-bis-endo-5,6-dicarboxylate (**7q′**).* (Procedure B, same reaction as for **7q**) 81.5 mg (14%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.78 (m, 2H), 7.38 (m, 1H), 7.33−7.21 (m, 7H) overlaps with $CDCl_3$, 6.57 (m, 2H), 4.86 (s, 1H), 4.42 (d, J = 3.6 Hz, 1H), 3.79 (s, 3H), 3.13 (m, 1H), 3.05 (s, 3H), 2.94 (m, 1H), 1.41 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 197.5, 175.5, 174.0, 139.4, 135.8, 135.7, 134.2, 132.6, 131.3, 128.8, 128.3, 128.0, 127.6, 62.9, 58.5, 52.2, 52.1, 51.3, 49.7, 47.3, 47.1. HRMS (ESI/TOF) calcd for $C_{25}H_{25}O_5^+$ (MH^+) 405.1697, found 405.1690.

Irradiation Experiments. General Procedure. Approximately 1−5 mM solution of the *endo*-Michael adduct in benzene was irradiated in Pyrex or borosilicate glass 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 1−24 h. The crude reaction mixture was purified on a silica gel column using a mixture of hexane and EtOAc as an eluent.

*Dimethyl (1RS,5SR,6RS,8SR)-spiro[6-formyl-3-phenylbicyclo-[3.2.1]oct-2-ene-5,8-dicarboxylate-7,1′-cyclopropane] (**9c**).* From 140 mg of **7c** (0.40 mmol) for 20 h (hexane/EtOAc gradient 30:1 → 5:1): 74 mg (53%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.49 (d, J = 4.9 Hz, 1H), 7.40 (m, 2H), 7.33 (m, 2H), 7.28 (m, 1H) overlaps with $CDCl_3$, 6.41 (d, J = 6.6 Hz, 1H), 3.86 (d, J = 4.0 Hz, 1H), 3.82 (s, 3H), 3.64 (s, 3H), 3.36 (d, J = 18.8 Hz, 1H), 2.87 (d, J = 18.8 Hz, 1H), 2.72 (d, J = 4.9 Hz, 1H), 2.48 (dd, J = 6.6, 4.0 Hz, 1H), 0.82 (m, 2H), 0.71−0.66 (m, 1H), 0.49−0.44 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 201.9, 174.1, 170.2, 139.0, 134.5, 128.5, 127.8, 126.7, 125.1, 62.3, 54.0, 52.7, 52.4, 51.9, 46.4, 31.2, 30.7, 14.5, 5.9. HRMS (ESI/TOF) calcd for $C_{21}H_{22}NaO_5^+$ (MNa^+) 377.1359, found 377.1354.

*Dimethyl (1RS,5SR,6RS,8SR)-spiro[6-(1,3-dioxolan-2-yl)-3-phenylbicyclo[3.2.1]oct-2-ene-5,8-dicarboxylate-7,1′-cyclopropane] (**12c**).* From 70 mg of **9c** (0.20 mmol), one drop of HCl (4.0 M solution in 1,4-dioxane) in 5 mL of THF/ethylene glycol mixture (1:1) (hexane/EtOAc gradient 30:1 → 5:1): 77 mg (98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45 (m, 2H), 7.32 (m, 2H), 7.25 (m, 1H), 6.33 (d, J = 6.7 Hz, 1H), 4.76 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 3.80 (d, J = 4.2 Hz, 1H), 3.76−3.70 (m, 4H), 3.60 (s, 3H), 3.32 (d, J = 18.8 Hz, 1H), 3.01 (d, J = 18.8 Hz, 1H), 2.64 (d, J = 8.5 Hz, 1H), 2.31 (dd, J = 6.7, 4.2 Hz, 1H), 1.20 (m, 1H), 0.73 (m, 1H), 0.45 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 176.0, 170.9, 139.9, 133.8, 128.3, 127.3, 126.9, 125.1, 104.8, 64.7, 64.5, 56.3, 53.3, 52.9, 52.4, 51.7, 46.4, 30.0, 29.9, 15.5, 6.0. HRMS (ESI/TOF) calcd for $C_{23}H_{27}O_6^+$ (MH^+) 399.1802, found 399.1817.

*Methyl (1RS,3SR,4RS,5RS,6SR,9RS, 10SR)-11-oxa-3-phenyltetracyclo[4.3.1.1^{3,5}.0^{4,9}]undecane-10-carboxylate (**10a**).* From 0.18 g of **7a** (0.63 mmol) irradiated for 20 h; (hexane/EtOAc gradient 30:1 → 5:1): 79 mg (44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.40−7.36 (m, 3H), 2H in aromatic region obscured by $CDCl_3$, 4.67 (dd, J = 8.0, 5.1 Hz, 1H), 3.78 (s, 3H), 3.33 (d, J = 4.5 Hz, 1H), 3.12 (dd, J = 6.4, 5.1 Hz, 1H), 3.05−3.01 (m, 1H), 2.52 (q, J = 9.4, 4.7 Hz, 1H), 2.22−2.18 (m, 1H), 2.16−2.02 (m, 1H), 1.91−1.83 (m, 1H), 1.65−1.58 (m, 1H), 1.56−1.50 (m, 1H), 1.14−1.06 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 176.6, 142.4, 128.2, 126.9, 124.0, 96.0, 51.7, 47.4, 44.1, 44.1, 36.2, 32.6, 17.2, 17.0. HRMS (ESI/TOF) calcd for $C_{18}H_{20}NaO_3^+$ (MNa^+) 307.1310, found 307.1317. See SI for X-ray data.

*Methyl (1SR,2SR,3SR,4RS,5RS,6SR,9RS,10SR)-1-methyl-11-oxa-3-phenyltetracyclo[4.3.1.1^{3,5}.0^{4,9}]undecane-10-carboxylate (**10b**).* From 55 mg of **7b** (0.18 mmol) irradiated for 20 h; (hexane/EtOAc gradient 30:1 → 5:1): 36 mg (65%).^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.38 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.27 (t, J = 7.2 Hz, 1H), 4.66 (dd, J = 7.9, 5.1 Hz, 1H), 3.78 (s, 3H), 3.42 (d, J = 4.7 Hz, 1H), 3.07 (ddd, J = 7.8, 4.9, 1.3 Hz, 1H), 2.85 (t, J = 5.1 Hz, 1H), 2.50 (q, J = 9.4, 4.7 Hz, 1H), 2.27−2.18 (m, 2H), 1.91−1.82 (m, 1H), 1.67−1.60 (m, 1H), 1.54−1.47 (m, 1H), 1.13−1.05 (m, 1H), 0.92, (d, J = 6.9 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 176.9, 143.9, 128.0, 126.6, 126.0, 124.0, 96.1, 51.7, 48.1, 47.8, 42.8, 37.6, 35.1, 32.5, 14.7, 17.1, 6.4. HRMS (ESI/TOF) calcd for $C_{19}H_{22}NaO_3^+$ (MNa^+) 321.1467, found 321.1450.

*Methyl endo-3-(1,3-dioxalan-2-yl)-8-phenylbicyclo[4.3.0]non-7-ene-exo-2-carboxylate (**13a**).* A solution of 0.18 g of **7a** (0.63 mmol), 0.22 mL of HCl solution (4 M in dioxane, 0.89 mmol) and 0.08 g ethylene glycol (1.26 mmol) was prepared in dichloromethane (130 mL) in a Pyrex reaction vessel. This solution was irradiated for 29 h. The crude reaction mixture was purified on a silica gel column using a mixture of hexane and EtOAc as an eluent. The reaction mixture was then concentrated in vacuo to a volume of 20 mL and washed with saturated sodium bicarbonate solution (2 × 15 mL), and the aqueous layer was extracted with dichoromethane (2 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent was removed in vacuo to give a crude yellow oil. The crude mixture was purified on a silica gel column using hexane and ethyl acetate as the eluent (hexane/EtOAc gradient 30:1 → 5:1), 63 mg (30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (d, J = 7.9 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 6.01 (t, J = 2.2 Hz, 1H), 4.71 (d, J = 3.9 Hz, 1H), 3.94−3.77 (m, 4H), 3.72 (s, 1H), 3.11 (s, 1H), 2.80 (dddd, J = 15.4, 6.2, 3.7, 2.6 Hz, 1H), 2.59 (dt, J = 12.8, 6.5 Hz, 1H), 2.53 (d, J = 15.4 Hz, 1H), 2.32 (t, J = 11.2 Hz, 1H), 2.05−2.96 (m, 2H), 1.77−1.67 (m, 2H), 1.35−1.24 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 176.9, 142.0, 136.6, 129.6, 128.3, 127.1, 125.5, 106.1, 65.0, 64.9, 51.5, 45.2, 45.0, 41.2, 41.1, 38.9, 26.1, 22.0. HRMS (ESI/TOF) calcd for $C_{20}H_{24}LiO_4^+$ (MLi^+) 335.1835, found 335.1829.

*Methyl 6-(1,3-dioxalan-2-yl)-3-phenylbicyclo[3.3.1]non-2-ene-syn-9-carboxylate (**12a**).* From the reaction mixture above, isolated as 6-epimeric mixture, 38 mg (18%). HRMS (ESI/TOF) calcd for $C_{20}H_{24}NaO_4^+$ (MNa^+) 351.1572, found 351.1558.

*Methyl endo-3-(1,3-dioxalan-2-yl)-endo-10-methyl-8-phenylbicyclo[4.3.0]non-7-ene-exo-2-carboxylate (**13b**).* A solution of 0.21 g of **10b** (0.70 mmol), 0.25 mL of HCl solution (4 M in dioxane, 0.99 mmol) and 0.09 g ethylene glycol (1.40 mmol) was prepared in chloroform (10 mL) and then heated to 70 °C while stirring for 4 h. The reaction mixture was then concentrated in vacuo to remove chloroform, diluted with dichoromethane (10 mL), and washed with saturated sodium bicarbonate solution (2 × 15 mL), and the aqueous layer extracted with dichoromethane (2 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent removed in vacuo to give a crude yellow oil. The crude mixture was purified on a silica gel column using hexane and ethyl acetate as the eluent (hexane/EtOAc gradient 30:1 → 5:1), 0.17 g (71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.35−7.31 (m, 4H), 7.25 (t, J = 7.2 Hz, 1H), 5.87 (t, J = 2.1 Hz, 1H), 4.79 (d, J = 3.7 Hz, 1H), 4.01−3.85 (m, 3H), 3.71 (s, 3H), 3.31 (tt, J = 7.7, 1.7 Hz, 1H), 2.95−2.82 (m, 2H), 2.68 (t, J = 11.5 Hz, 1H), 2.08−2.00 (m, 2H), 1.78−1.71 (m, 2H), 1.56−1.48 (m, 2H), 1.08 (d, J = 7.4 Hz, 3H).

*Methyl endo-5-hydroxy-2-methyl-3-phenyltricyclo[4.3.1.0^{4,9}]dec-2-ene-exo-10-carboxylate (**14**).* A solution of 0.11 g of **10b** (0.37 mmol) and 0.13 mL of HCl solution (4 M in dioxane, 0.51 mmol) was prepared in chloroform (10 mL) and stirred at ambient temperature for 4 h. The reaction mixture was then concentrated in vacuo to remove chloroform, diluted with dichoromethane (10 mL), and washed with saturated sodium bicarbonate solution (2 × 15 mL), and the aqueous layer extracted with dichoromethane (2 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, and the solvent removed in vacuo to give a crude yellow oil. The crude mixture was purified on a silica gel column using hexane and ethyl acetate as the eluent (hexane/EtOAc gradient 30:1 → 5:1), 80 mg (73%). The structure is characterized by X-ray (see Supporting Information). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H), 4.03 (dt, J = 8.5,

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2.2 Hz, 1H), 3.75 (s, 3H), 3.15 (dd, J = 8.7, 4.3 Hz, 1H), 2.88 (d, J = 4.5 Hz, 1H), 2.76−2.74 (m, 1H), 2.54−2.50 (m, 1H), 2.32−2.28 (m, 1H), 2.03 (s, 3H), 1.80−1.59 (m, 4H) . ^{13}C NMR (500 MHz, $CDCl_3$) δ = 175.9, 145.5, 137.7, 137.3, 128.2, 128.1, 126.5, 69.3, 51.8, 51.4, 48.2, 42.3, 38.3, 38.1, 21.9, 18.1, 14.6. HRMS (ESI/TOF) calcd for $C_{19}H_{22}LiO_3^+$ (MLi^+) 305.1728, found 305.1729. See SI for X-ray data.

*Dimethyl (1SR,2RS,3RS,5SR,6SR,7RS,9SR,10SR)-3-hydroxy-3-phenyltetracyclo[3.3.1.1^{7,9}.0^{2,6}]decane-9,10-dicaboxylate (**15**).* From 120 mg of **7d** (0.35 mmol) for 3 h (hexane/EtOAc gradient 30:1 → 2:1): 90 mg (75%), colorless crystals, mp 101.5−103.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.3 Hz, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.02 (s, 1H), 2.92 (ddd, J = 2.7, 2.7, 2.7 Hz, 1H), 2.87 (m, 1H), 2.75 (ddd, J = 3.0, 3.0, 3.0 Hz, 1H), 2.56 (m, 1H) overlaps with 2.56 (s, OH), 2.46 (m, 1H), 2.41 (d, J = 14.9 Hz, 1H), 2.24 (dd, J = 14.9, 4.6 Hz, 1H), 1.78 (dd, J = 10.4, 3.0 Hz, 1H), 1.61 (dd, J = 10.4, 2.7 Hz, 1H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.34 (m, 2H), 7.19 (m, 2H), 7.10 (m, 1H), 3.46 (s, 3H), 3.34 (s, 3H), 2.91 (m, 2H), 2.65 (m, 1H), 2.55 (d, J = 14.5 Hz, 1H) overlaps with 2.56 (ddd, J = 3.0, 3.0, 3.0 Hz, 1H) overlaps with 2.52 (m, 1H), 2.07 (dd, J = 14.5, 4.7 Hz, 1H) overlaps with 2.05 (m, 1H), 1.42 (dd, J = 10.3, 3.0 Hz, 1H), 1.13 (dd, J = 10.3, 2.7 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 173.9, 172.4, 148.9, 128.3, 126.8, 124.6, 78.7, 67.2, 63.8, 54.0, 52.0, 51.9, 51. 8, 51.2, 46.0, 42.6, 41.0, 40.1. HRMS (ESI/TOF) calcd for $C_{20}H_{23}O_5^+$ (MH^+) 343.1540, found 343.1544. See SI for X-ray data.

*Dimethyl (1SR,3RS,4RS,5SR,6SR,7SR,8SR, 9SR)-6-hydroxy-5-methyl-6-phenyltetracyclo [3.2.1.1^{3,8}.0^{4,7}]nonane-8,9-dicaboxylate (**16**).* 18 mg (15%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 (m, 2H), 7.34 (m, 2H), 7.26 (m, 1H) overlaps with $CDCl_3$, 4.61 (s, OH), 3.86 (s, 3H), 3.59 (s, 3H), 3.10−3.07 (m, 3H), 2.66 (m, 1H), 2.41 (ddd, J = 3.1, 3.1, 3.1 Hz, 1H), 1.78 (dd, J = 10.4, 2.6 Hz, 1H), 1.69 (dd, J = 10.4, 2.7 Hz, 1H) overlaps with 1.68 (d, J = 7.3 Hz, 1H), 0.89 (s, 3H).

*Dimethyl (1RS,2RS,3RS,5SR,6RS,7RS,9SR,10SR)-spiro[3-hydroxy-3-phenyltetracyclo[3.3.1.1^{7,9}.0^{2,6}] decane-9,10-dicaboxylate-8,1′-cyclopropane] (**17**).* From 65 mg of **7e** (0.18 mmol) for 12 h (hexane/EtOAc gradient 30:1 → 1:1): 50 mg (77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 (m, 2H), 7.36 (m, 2H), 7.25 (m, 1H), 3.82 (s, 3H), 3.68 (s, 3H), 3.58 (m, 1H), 2.95 (m, 1H), 2.88 (m, 1H), 2.62 (m, 1H), 2.52 (s, OH), 2.40 (d, J = 14.8 Hz, 1H), 2.36 (ddd, J = 2.7, 2.7, 1.0 Hz, 1H), 2.25 (dd, J = 14.8, 4.7 Hz, 1H), 2.17 (dd, J = 3.3, 3.3 Hz, 1H), 0.87−0.82 (m, 1H), 0.80−0.76 (m, 1H), 0.55−0.48 (m, 2H). ^{1}H NMR (500 MHz, C_6D_6) δ = 7.43 (m, 2H), 7.20 (m, 2H), 7.11 (m, 1H), 3.63 (m, 1H), 3.48 (s, 3H), 3.38 (s, 3H), 2.77 (m, 1H), 2.73 (m, 1H) overlaps with 2.71 (m, 1H), 2.58 (d, J = 14.7 Hz, 1H), 2.39 (m, 1H), 2.19 (br. s, OH), 2.13 (dd, J = 14.7, 4.7 Hz, 1H), 2.03 (dd, J = 3.2. 3.2 Hz, 1H), 0.62 (ddd, J = 9.7, 5.0, 5.0 Hz, 1H), 0.39 (ddd, J = 9.7, 5.0, 5.0 Hz, 1H), 0.18 (m, 1H), 0.12 (m, 1H). ^{1}H NMR (500 MHz, CD_3OD) δ = 7.45 (m, 2H), 7.32 (m, 2H), 7.20 (m, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.55 (m, 1H), 2.88 (m, 1H), 2.82 (m, 1H), 2.43 (m, 1H), 2.37 (d, J = 14.6 Hz, 1H), 2.34 (ddd, J = 2.7, 2.7, 1.0 Hz, 1H), 2.15 (m, 1H) overlaps with 2.13 (dd, J = 14.6, 4.9 Hz, 1H), 0.88−0.79 (m, 2H), 0.57−0.48 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 173.9, 172.6, 149.0, 128.3, 126.7, 124.6, 78.3, 65.7, 62.7, 55.3, 52.2, 52.0, 52.0, 51.8, 51.1, 46.5, 40.8, 38.9, 9.8 (two overlapping peaks). ^{13}C NMR (500 MHz, CD_3OD) δ = 176.3, 174.6, 143.5, 129.0, 129.0, 128.4, 77.8, 64. 6, 64.5, 61.8, 58.1, 57.6, 52.6, 52.1, 51.8, 46.2, 39.3, 13. 7, 8.4, 8.3. HRMS (ESI/TOF) calcd for $C_{22}H_{24}NaO_5^+$ (MNa^+) 391.1516, found 391.1527.

*Dimethyl (1RS,3RS,4RS,5SR,6SR,7RS,8SR,9SR)-spiro[6-hydroxy-5-methyl-6-phenyltetracyclo [3.2.1.1^{3,8}.0^{4,7}]nonane-8,9-dicaboxylate-2,1′-cyclopropyl] (**18**).* 13 mg (20%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.53 (m, 2H), 7.35 (m, 2H), 7.27 (m, 1H) overlaps with $CDCl_3$, 4.62 (s, OH), 3.87 (s, 3H), 3.68 (m, 1H), 3.59 (s, 3H), 3.33 (dd, J = 3.1, 1.9 Hz, 1H), 2.51 (ddd, J = 2.3, 2.3, 2.3 Hz, 1H), 2.48 (m, 1H), 2.07 (dd, J = 3.1, 3.1 Hz, 1H), 0.98−0.94 (m, 1H), 0.92 (s, 3H), 0.82−0.75 (m, 2H), 0.69−0.64 (m, 1H), 0.59−0.54 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 175.8, 172.6, 141.9, 128.0, 127.8, 127.2, 77.0 overlaps with $CDCl_3$, 63.7, 62.5, 60.7, 57.3, 56.7, 52.5, 51.5, 50.0, 44.2, 38.2, 12.1, 7.8, 7.6. HRMS (ESI/TOF) calcd for $C_{22}H_{24}NaO_5^+$ (MNa^+) 391.1516, found 391.1526.

*Dimethyl (1SR,2RS,3SR,4SR,5RS,6SR,7RS,9RS,10SR)-3-hydroxy-3,4-diphenyltetracyclo[3.3.1.1^{7,9}.0^{2,6}]decane-9,10-dicaboxylate (**19**).* From 0.23 g of **7f** (0.55 mmol) for 6 h (hexane/EtOAc gradient 30:1 → 10:1): 0.15 g (65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67 (m, 2H), 7.40 (m, 2H), 7.26 (m, 1H) overlaps with $CDCl_3$, 7.23−7.18 (m, 4H), 7.13 (m, 1H), 3.39 (d, J = 3.3 Hz, 1H), 3.93 (s, OH), 3.90 (ddd, J = 3.0, 3.0, 1.5 Hz, 1H), 3.81 (s, 3H), 3.33 (s, 3H), 3.01 (m, 2H), 2.98 (s, 1H), 2.80 (ddd, J = 3.1, 3.1, 3.1 Hz, 1H), 2.64 (m, 1H), 1.72 (dd, J = 10.4, 2.8 Hz, 1H), 1.59 (dd, J = 10.5, 2.8 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 174.1, 172.7, 149.5, 137.3, 128.3, 128.2, 127.8, 126.5, 125.9, 124.7, 76.9 overlaps with $CDCl_3$, 70.9, 62.7, 55.2, 53.9, 53.6, 51.9, 51.8, 49.8, 46.1, 42.1, 41.5. HRMS (ESI/TOF) calcd for $C_{26}H_{26}NaO_5^+$ (MNa^+) 441.1672, found 441.1668.

*Dimethyl (1SR,3RS,4RS,5SR,6SR,7SR,8SR,9SR)-5-benzyl-6-hydroxy-6-phenyltetracyclo[3.2.1.1^{3,8}.0^{4,7}]nonane-8,9-dicaboxylate (**20**).* 58 mg, (25%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 (m, 2H), 7.11−7.05 (m, 3H), 6.88−6.83 (m, 3H), 6.67 (m, 2H), 4.31 (s, OH), 3.83 (s, 3H), 3.58 (s, 3H), 3.15 (m, 2H), 3.03 (d, J = 16.2 Hz, 1H), 2.91 (m, 1H), 2.84 (m, 2H), 2.69 (d, J = 16.2 Hz, 1H), 1.83 (dd, J = 10.3, 2.7 Hz, 1H), 1.69 (dd, J = 10.3, 1.6 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 175.6, 172.1, 141.8, 138.0, 129.9, 127.7, 127.3, 127.1, 127.0, 124.7, 75.1, 69. 5, 63.6, 59.7, 58.1, 52.5, 51.7, 50.9, 48.34, 41.5, 38.5, 32.6.

*Dimethyl (1RS,2SR,3RS,4SR,5RS,6SR,7RS)-6-benzoyl-5-phenyltricyclo[2.2.2.1^{3,7}]nonane-1,2-dicaboxylate (**21**).* From 400 mg of **7f′** (0.95 mmol) for 72 h (hexane/EtOAc gradient 30:1 → 1:1): 80 mg (20%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (m, 2H), 7.53 (m, 1H), 7.47 (m, 2H), 7.30 (m, 2H), 7.25 (m, 2H) overlaps with $CDCl_3$, 7.14 (m, 1H), 5.28 (d, J = 2.8 Hz, 1H), 3.59 (s, 3H), 3.48 (m, 1H), 3.08 (m, 1H), 3.03 (m, 1H), 2.90 (dddd, J = 7.8, 5.1, 3.4, 1.6 Hz, 1H), 2.84 (s, 3H), 2.75 (s, 1H), 1.87−1.80 (m, 2H), 1.74−1.69 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.5, 175.2, 171.0, 142.9, 138.8, 132.0, 128.6, 128.2, 128.0, 127.4, 126.1, 124.7, 57.1, 52.0, 50.9, 50.8, 50.1, 46.7, 45.6, 43.7, 40.2, 39.7, 33.6. HRMS (ESI/TOF) calcd for $C_{26}H_{26}NaO_5^+$ (MNa^+) 441.1672, found 441.1659.

*Dimethyl (1RS,2RS,3SR,4SR,5RS,6SR,7RS,9SR,10SR)-spiro[3-hydroxy-3,4-diphenyltetracyclo[3.3.1.1^{7,9}.0^{2,6}]decane-9,10-dicaboxylate-8,1′-cyclopropane] (**22**).* From 48 mg of **7g** (0.11 mmol) for 5 h (hexane/EtOAc gradient 30:1 → 1:1): 17 mg (35%), colorless crystals, mp 173.5−176.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.68 (m, 2H), 7.41 (m, 2H), 7.27 (m, 1H) overlaps with $CDCl_3$, 7.21 (m, 4H), 7.13 (m, 1H), 3.97 (m, 2H), 3.86 (s, OH), 3.80 (s, 3H), 3.55 (s, 1H), 3.34 (s, 3H), 3.10 (m, 1H), 3.05 (m, 1H), 2.45 (ddd, J = 2.8, 2.8, 1.0 Hz, 1H), 2.21 (dd, J = 3.3, 3.3 Hz, 1H), 0.79−0.72 (m, 2H), 0.58−0.49 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 174.1, 172.8, 149.6, 137.3, 128.3, 128.2, 127.8, 126.5, 125.9, 124.8, 69.5, 61.6, 54.8, 54.6, 53.6, 52.2, 51.9, 51.9, 50.7, 47.9, 38.5, 9.8, 9.7. HRMS (ESI/TOF) calcd for $C_{28}H_{28}NaO_5^+$ (MNa^+) 467.1829, found 467.1813. See SI for X-ray data.

*Dimethyl (1RS,2SR,3RS,4SR,5SR,6SR,7RS)-spiro[6-benzoyl-5-phenyltricyclo[2.2.2.1^{3,7}]nonane-1,2-dicaboxylate-9,1′-cyclopropyl] (**24**).* From 0.22 mg of **7g′** (0.49 mmol) for 24−48 h (hexane/EtOAc gradient 20:1 → 1:1): 7 mg (30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.98 (m, 2H), 7.53 (m, 1H), 7.47 (m, 2H), 7.31 (m, 2H), 7.25 (m, 2H), 7.14 (m, 1H), 5.29 (d, J = 2.7 Hz, 1H), 3.60 (s, 3H), 3.52 (m, 1H), 3.46 (s, 1H), 3.02 (m, 1), 2.83 (s, 3H), 2.40 (m, 2H), 2.20 (ddd, J = 11.5, 7.8, 1.5 Hz, 1H), 1.81 (d, J = 11.5 Hz, 1H), 1.05−1.00 (m, 1H), 0.93−0.88 (m, 1H), 0.68−0.60 (m, 2H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 205.5, 175.1, 171.1, 142.8, 138.7, 132.0, 128.6, 128.2, 128.0, 127.4, 126.1, 56.2, 52.0, 51.2 (two overlapping peaks), 50.8 (two overlapping peaks), 46.5 (two overlapping peaks), 40.4, 38.8, 34.4, 10.3, 9.7.

*Dimethyl (1RS,2RS,3RS,4SR,5RS,6SR,7RS,9SR,10SR)-spiro[4-ethyl-3-hydroxy-3-phenyltetracyclo[3.3.1.1^{7,9}.0^{2,6}]decane-9,10-dicaboxylate-8,1′-cyclopropane] (**26**).* From 118 mg of **7h** (0.30 mmol) for 20 h (hexane/EtOAc gradient 30:1 → 10:1): 41 mg (35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (d, J = 7.9 Hz, 2H), 7.33 (t, J = 7.7 Hz, 2H), 7.23 (t, J = 7.3 Hz, 1H), 3.82 (s, 3H), 3.69 (s, 3H), 3.60 (s, 1H), 3.14 (m, 1H), 2.97 (m, 1H), 2.62 (s, OH), 2.46 (m, 1H), 2.38 (m, 1H), 2.28 (dd, J = 11.1, 4.4 Hz, 1H), 2.24 (dd, J = 3.3, 3.3 Hz, 1H), 0.88−0.76 (m, 3H), 0.66 (t, J = 7.1 Hz, 3H), 0.61−0.53 (m, 2H),

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0.51−0.46 (m, 1H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 174.0, 172.6, 145.4, 127.7, 126.7, 126.1, 81.8, 66.6, 62.9, 55.9, 54.5, 52.2, 52.0, 51.8 (two overlapping peaks), 51.2, 46.7, 38.7, 25.2, 13.0, 9.8 (two overlapping peaks). HRMS (ESI/TOF) calcd for $C_{24}H_{28}NaO_5^+$ (MNa^+) 419.1829, found 419.1818. See SI for X-ray data.

Compounds **25** and **27** were only partially purified, as we were able to obtain only enriched fractions described with ^{1}H NMR; additionally, isomers **26** and **27** were characterized by X-ray crystallography.

*Dimethyl (1RS,2RS,3RS,4RS,5RS,6SR,7RS,9SR,10SR)-spiro[4-ethyl-3-hydroxy-3-phenyltetracyclo [3.3.1.1^{7,9}.0^{2,6}]decane-9,10-dicaboxylate-8,1′-cyclopropane] (**25**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 (m, 2H), 7.34 (m, 2H), 7.23 (m, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 3.48 (m, 1H), 3.01 (ddd, J = 3.1, 3.1, 1.4 Hz, 1H), 2.98 (ddd, J = 2.7, 1.3, 1.3 Hz, 1H), 2.92 (m, 1H), 2.55 (br. s, OH), 2.47 (ddd, J = 2.9, 2.9, 1.0 Hz, 1H), 2.14 (ddd, J = 9.6, 6.3, 3.4 Hz, 1H) overlaps with 2.12 (dd, J = 3.3, 3.3 Hz, 1H), 1.55−1.42 (m, 1H), 1.00−0.85 (m, 2H), 0.81 (t, J = 7.4 Hz, 3H) overlaps with 0.81−0.73 (m, 2H), 0.58−0.46 (m, 1H). HRMS (ESI/TOF) calcd for $C_{24}H_{28}NaO_5^+$ (MNa^+) 419.1829, found 419.1815.

*Dimethyl (1RS,3RS,4RS,5SR,6SR,7RS,8SR,9SR)-spiro[6-hydroxy-6-phenyl-5-propyltetracyclo[3.2.1.1^{3,8}.0^{4,7}]nonane-8,9-dicaboxylate-2,1′-cyclopropyl] (**27**).* ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 (m, 2H), 7.34 (m, 2H), 7.27 (m, 1H) overlaps with $CDCl_3$, 4.85 (s, OH), 3.87 (s, 3H), 3.67 (m, 1H), 3.58 (s, 3H), 3.30 (dd, J = 3.2, 1.8 Hz, 1H), 2.63 (m, 1H), 2.49 (ddd, J = 2.3, 2.3, 2.3 Hz, 1H), 2.03 (dd, J = 3.7, 2.6 Hz, 1H), 1.55−1.42 (m, 2H), 1.07 (ddd, J = 15.7, 13.2, 4.2 Hz, 1H), 1.00−0.85 (m, 1H), 0.81−0.73 (m, 1H), 0.67−0.63 (m, 1H), 0.58−0.46 (m, 2H) overlaps with 0.53 (t, J = 7.2 Hz, 3H). See SI for X-ray data.

*Dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**28**).*[15] (Procedure A) from 0.5 mL of dimethyl acetylenedicarboxylate (4.07 mmol) (hexane/EtOH gradient 40:1→10:1 and 4:1): 0.79 g (92% in 24 h), 0.64 g (75% in 48 h). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.23 (dd, J = 1.1, 1.1 Hz, 2H), 5.69 (dd, J = 1.1, 1.1 Hz, 2H), 3.83 (s, 6H).

*syn-Methyl 11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}.]dodeca-4.9-diene-2,7-dicarboxylate (**29**) and anti-Methyl 11,12-dioxatetracyclo[6.2.1.1^{3,6}.0^{2,7}.]dodeca-4.9-diene-2,7-dicarboxylate (**30**).*[17] Dimethyl acetylenedicarboxylate (0.5 mL, 4.07 mmol) was dissolved in 5 mL of furan (large excess), which was also used as a solvent. The resulting reaction mixture was stirred for 24 h. The solvent was removed to take NMR. The solvent was removed in vacuo, and the crude reaction mixture was purified on a flash silica gel column using a mixture of hexane and EtOH as an eluent (1:30 = EtOAc:Hexane, then 1:10). The two dimers were isolated in an endo:exo ratio of 3:1, 0.12 g (11%). *Syn* isomer (**29**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.63 (s, 4H), 5.09 (s, 4H), 3.65 (s, 6H). *Anti* isomer (**30**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.69 (s, 2H), 6.52 (s, 2H), 5.20 (s, 2H), 4.55 (s, 2H), 3.75 (s, 6H). ^{13}C NMR of the mixture (500 MHz, $CDCl_3$) δ = 172.3, 170.3, 143.3, 138.9, 138.7, 135.6, 85.1, 83.9, 83.5, 79.2, 70.2, 70.0, 52.4, 52.1. The two compounds have an unusual 1:1 crystalline packing; see X-ray data in the Supporting Information.

*Methyl 6-phenylpyran-2-one-4-carboxylate (**31**).*[18] Diisopropylamine (0.13 mL, 0.93 mmol) was dissolved in THF at −30 °C, and then *n*-BuLi (0.5 mL, 0.80 mmol) was added, and the resulting mixture was stirred for 30 min at −30 °C. After that, acetophenone was added (0.08 g, 0.66 mmol), and the mixture was kept at the same temperature (−30 °C) for an additional 40 min. After the anion was generated, **28** was added (0.14 g, 0.66 mmol), and the reaction mixture was allowed to warm to ambient temperature and stirred for an additional 30 min. After the reaction was complete, the mixture was quenched with saturated aqueous solution of NH4Cl (10 mL), and dichloromethane was added (15 mL). The organic layer was washed with water (1 × 10 mL) and brine (1 × 10 mL). The organic layer was dried over anhydrous $NaSO_4$. The solvent was removed in vacuo, and the crude reaction mixture was purified on a flash silica gel column using a mixture of hexane and EtOH as an eluent (1:30 = EtOAc:Hexane, then 1:10) 70 mg (45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.92−7.89 (m, 2H), 7.53−7.49 (m, 3H), 7.16 (d, J = 1.4 Hz, 1H), 6.93 (d, J = 1.4 Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 164.0, 161.8, 161.3, 144.3, 131.3, 131.0, 129.1, 125.8, 115.7, 99.3, 53.3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional experimental data, NMR spectra, X-ray data (CIF file), computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

‡Dedicated to Howard E. Zimmerman

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