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Substituted Diarylnorbornadienes and Quadricyclanes: Synthesis, Photochemical Properties, and Effect of Substituent on the Kinetic Stability of Quadricyclanes

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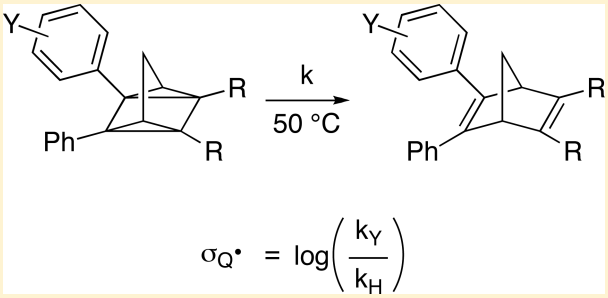
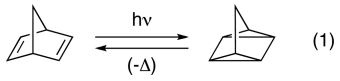
Supporting Information

ABSTRACT: In this Article, we present a new method for the synthesis of diarylnorbornadiene derivatives. Through the use of a two-step procedure consisting of a tandem alkene insertion-Suzuki coupling reaction followed by a DDQ dehydrogenation, we have been able to synthesize derivatives with a wide variety of substituents. We also present the results of UV−visible spectroscopy studies and kinetics experiments that show the effect of substituent on light absorption properties of the norbornadienes as well as the kinetic stability of the quadricyclanes that result from their photochemical conversion. While substitution on the aromatic rings had comparatively little effect on quadricyclane lability, substitution at a bridgehead position with a methyl group produced a quadricyclane that thermally reverted to the norbornadiene at a rate that was significantly slower than that for the quadricyclane without the methyl substituent. From the results of the kinetics experiments, we determined that the reversion of the quadricyclanes occurs via a free radical mechanism with very little contribution from polar effects. This observation led us to speculate as to whether our data may form the basis for a free radical substituent constant, $\sigma_Q\bullet$, analogous to the traditional Hammett σ parameter.



INTRODUCTION

The norbornadiene to quadricyclane interconversion (eq 1) has, for a long time, been thought of as a possible means of



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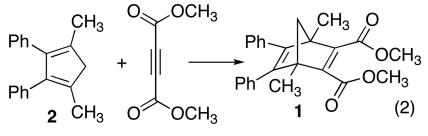
solar energy storage.[1−7] This is due to the fact that the norbornadiene can undergo a photochemical π2s + π2s cycloaddition to form the highly strained quadricyclane system. Because the quadricyclane is kinetically stable (although thermodynamically unstable), this ring strain can be released (as heat) in a controllable fashion upon treatment with a catalyst,[8] electrochemically,[9,10] treatment with heat,[11] or exposure to light of a shorter wavelength.[12] This energy storage property has also seen applications in the development of hypergolic liquid propellants (rocket fuel).[13] Indeed, this use is important enough that methods have been developed to crack the dicyclopentadiene dimer (required for the formation of norbornadiene) using only solar energy.[14] Ideally, however, the original norbornadiene is reformed in the release of the stored heat, allowing for the system to be recyclable. For norbornadiene itself, the photochemical conversion to the quadricyclane occurs in the ultraviolet region of the electromagnetic spectrum. Unfortunately, this limits the use of unsubstituted norbornadiene for solar applications as these wavelengths largely do not make it to the surface of the earth.

In the 1980s, Hirao and co-workers showed that diarylnorbornadiene derivatives such as **1** could be promising candidates for solar energy absorption and storage.[15,16] The aromatic rings in conjugation with one of the double bonds shift the absorption toward longer wavelengths that tail into the visible region of the spectrum. The ester groups (or in some derivatives other carbonyl-based functional groups) allow for an acid-catalyzed pathway back to the norbornadiene. In addition, for many examples, the quadricyclane (which can be formed with a quantum yield as high as 0.75) is stable at room temperature when no catalyst is present. However, these candidates were synthesized (eq 2) via a Diels−Alder reaction of 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-diene (**2**), a material that requires a several-step synthesis.[17]



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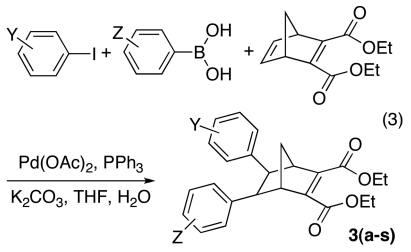
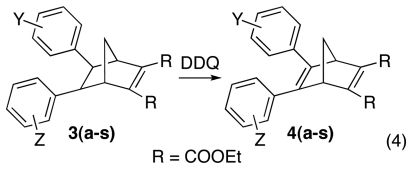
In 2002, our lab disclosed a simple one-step procedure for the formation of diarylnorbornenes from precursors that are commercially available or easily synthesized (eq 3).[18] In this





Article, we report the use of this methodology to generate a library of substituted diarylnorbornene derivatives (**3**), the conversion of these norbornenes to the corresponding norbornadienes (**4**), photochemical studies on the transformation to the quadricyclane derivatives, and kinetics experiments on the reversion back to the norbornadienes. In so doing, we hope to provide some information on the mechanism of the quadricyclane reversion, as well as structural features of substituted norbornadienes that serve to improve and/or degrade the properties required for solar energy storage applications. We should point out that Tam and co-workers published a similar cross-coupling route to aryl-substituted norbornadienes in 2005.[19] Moth-Poulsen and co-workers later used this route to synthesize and study several derivatives with varying substituents.[20] In addition, they were successful in building viable solar energy storage devices based upon this system.[20] However, these compounds did not contain the carbonyl groups, which we believe to be important for purposes of reversion[15,16] and derivatization (by, for example, adding additional functionality in the ester groups present in **1** and **4**).

RESULTS AND DISCUSSION

Norbornenes **3**(**a**−**s**) were synthesized by a variation of a procedure published previously (eq 3).[18] In general, we were able to streamline the process through the use of a glovebox designed for anaerobic (though not moisture-free) applications. As shown in Table 1, the norbornenes were isolated in moderate to good yield. Lower yields were more indicative of challenging purifications than any inefficiency in the ternary coupling chemistry. As was the case in our previous publication,[18] the reaction is tolerant of a wide variety of aryl iodides, with substituents varying from electron-donating to electron-withdrawing extremes.

For the conversion to the norbornadienes (eq 4), we relied on an old procedure for the DDQ dehydrogenation of 1,2-diphenylethane to form stilbene.[21] Initially, we found the standard conditions (benzene solvent, room temperature) to work well for examples with electron-donating groups. However, the reactions on electron-neutral substrates did not proceed to completion. Upon further investigation, we determined that the solvent interfered with the reaction. Thus, we found a solvent-free procedure, which involved heating the norbornene with

Table 1. Compounds Synthesized[a]

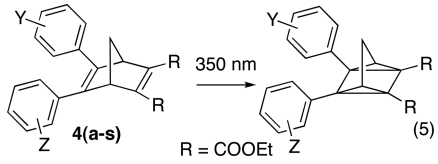
derivative	Y	Z	yield **3** (%)[b]	yield **4** (%)[c]
a	H	4-$N(CH_3)_2$	20	36
b	H	3-$N(CH_3)_2$	33	0
c	4-(OCH_3)	H	66[d]	65
d	3-(OCH_3)	H	37	54
e	4-CH_3	H	17	18
f	3-CH_3	H	50	33
g	4-$C(CH_3)_3$	H	52	24
h	H	H	63[d]	47
i	4-F	H	62	22
j	3-F	H	47	23
k	4-Cl	H	30	54
l	3-Cl	H	28	15
m	4-(CF_3)	H	45	69
n	3-(CF_3)	H	36	52
o	4-CN	H	46	18
p	3-CN	H	38	36
q	4-(NO_2)	H	43[d]	42
r	3-(NO_2)	H	43	42
s	3,5-$(CH_3)_2$	3,5-$(CF_3)_2$	26	41

[a]See eqs 3 and 4. [b]Before HPLC, sufficiently pure for conversion to **4**. [c]After final purification. [d]Reference 18.

DDQ in a sealed reactor (a simple scintillation vial with a heat-resistant cap) at 150 °C, to work on the majority of these substrates (Table 1). The failure of this procedure to dehydrogenate **3b** was a bit puzzling considering how well this reaction worked for its isomer **3a**. However, it seems likely that some deleterious interaction between the dimethylamino group and the extremely electron-deficient DDQ was the reason. It is possible that the conjugation of this group with the double bond and second benzene ring in **3a** may have protected it from such interaction in the case of the dehydrogenation of this isomer, allowing for the formation of the norbornadiene **4a**.

As was the case in the first step of the synthesis, the main challenge at this point was one of purification. DDQ is known to rupture bicyclic structures,[22] and one would expect this phenomenon here as well. Initial attempts at purification by standard chromatography were not successful, as many by-products coeluted with the norbornadiene in a narrow yellow-colored band. As can be seen in Figure 1a, these byproducts could be visualized by reverse-phase HPLC. Particularly problematic for the purification of this particular example (**4c**) was the impurity that eluted at 5.73 min (indicated with an arrow), immediately before the product.

Upon conversion to quadricyclane (eq 5), the atoms in norbornadiene undergo a significant structural repositioning.[23]



We hoped that this change in shape might provide a means of purifying some of the more challenging compounds by reverse-phase chromatography, because separation mechanisms for this stationary phase are dependent on both molecular geometry and polarity. As shown in the chromatogram in Figure 1b, there was a 2 min shift in the retention time of the major peak upon irradiation, reflecting the conversion of the norbornadiene to

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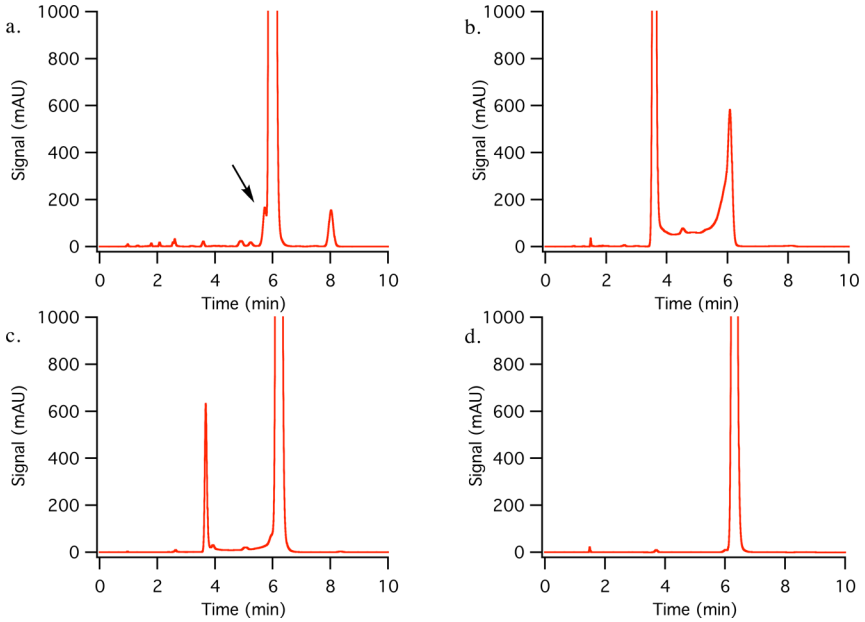

Figure 1. HPLC chromatograms for **4c** (a) upon isolation after initial chromatography (arrow indicates a prolematic impurity), (b) after 1 h irradiation with 350 nm light, (c) after collecting quadricyclane peak during preparative HPLC and allowing the sample to revert, and (d) after collecting norbornadiene peak during the subsequent preparative HPLC.

the quadricyclane. Thus, using a purification method that consisted of irradiation, performing a preparative reverse-phase HPLC separation while collecting the quadricyclane peak, allowing the quadricyclane to revert to the norbornadiene, and then performing a second HPLC separation enabled us to obtain sufficiently pure samples of several norbornadienes for further study (as shown in Figure 1c and d).

The UV−visible spectra for selected norbornadienes are presented in Figure 2, and relevant data are listed in Table 2.

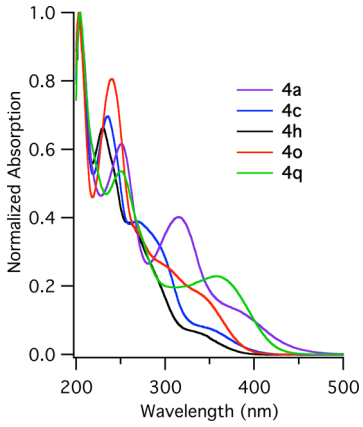

Figure 2. UV−visible spectra for selected diarylnorbornadienes (**4**).

(The spectra for the compounds listed in the table are presented separately in the Supporting Information.) The spectra show several features, the most notable of which is a band at longer wavelength centered at 330−380 nm, depending on the substituent. (We should note that for most cases, this peak is not well resolved from the stronger absorptions at shorter wavelength. As a result, these nearby absorptions likely have an impact on the λ_{NQ} and ε_{NQ} values in Table 2.) The spectra follow the same general pattern with four notable exceptions. The spectra for the 4-dimethylamino- and 4-nitro-substituted norbornadienes (**4a** and **4q**, respectively) are considerably red-shifted when compared to the other examples, while those for 4-methoxy (**4c**) and 4-cyano (**4o**) derivatives exhibit more moderate tailing toward longer wavelengths. One parameter that has been used to describe the efficiency at which visible light is absorbed by norbornadiene systems is the A_{onset}, defined as the longest wavelength at which the molar absorptivity ≥100 M^{-1} cm^{-1}.[20] The data presented here are in line with the published values for similar derivatives without the ester groups.[20] Electron-donating groups such as methoxy and dimethylamino in the *para* position of an aromatic ring on a norbornadiene have been shown to shift absorptions toward longer wavelengths.[16,20] The fact that the 4-nitro and 4-cyano derivatives show a similar shift suggests that this effect is due more to the extended conjugation provided by the group rather than its electron-donating ability. One other noteworthy feature is the manner in which the *para* nitro and *para* cyano groups slightly enhance the overall absorption at longer wavelengths. While this was at first a surprise, others have independently noted the amplifying effect of *para* nitro groups[24] and *para* cyano groups[20] on the extinction coefficient for the UV−visible absorption of aryl norbornadienes. On the other hand, substituents in the *meta* position, as well as trifluoromethyl groups (which do not affect conjugation), provided relatively minor effects on the spectra. Somewhat disappointingly, the spectrum for donor/acceptor derivative **4s** (Supporting Information) also proved to be unremarkable above 300 nm, which is in contrast to examples of norbornadienes with push/pull substituents in the *para* positions.[20]

Figure 3 shows how the UV−visible spectrum for the 4-methoxy derivative **4c** changed upon exposure to UV light (350 nm bulbs). The band at longer wavelength completely disappeared within 60 s; thus this feature is not present in the spectrum of the quadricyclane. This absorption reappeared upon standing at 50 °C, indicating that this conversion is reversible. Other derivatives behaved similarly, except for **4a** and **4q**, which proved to be outliers.

For the case of **4q**, the absorption at 360 nm was still present after 30 s of irradiation, although it had reached a limiting value.

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Table 2. UV−Visible Spectral Parameters for Selected Norbornadienes

norbornadiene	Y	Z	λ_{NQ}[a] (nm)	ε_{NQ}[b] (M^{-1} cm^{-1})	A_{onset}[c] (nm)
4a	H	4-$N(CH_3)_2$	373	4.7×10^3	485
4c	4-(OCH_3)	H	342	2.6×10^3	420
4d	3-(OCH_3)	H	337	2.1×10^3	400
4h	H	H	332	2.3×10^3	401
4m	4-(CF_3)	H	328	3.3×10^3	396
4n	3-(CF_3)	H	328	2.6×10^3	394
4o	4-CN	H	330	6.1×10^3	409
4p	3-CN	H	330	3.1×10^3	395
4q	4-NO_2	H	361	8.3×10^3	449
4s	3,5-$(CH_3)_2$	3,5-$(CF_3)_2$	337	3.3×10^3	401

[a]The wavelength chosen for observation of the norbornadiene to quadricyclane conversion, determined by the local maximum of the derivative in cases where the absorption was not resolved from the stronger aromatic signal. [b]Molar absorptivity at the wavelength chosen (footnote a). [c]Longest wavelength at which the molar absorptivity was ≥100 M^{-1} cm^{-1} (ref 20).

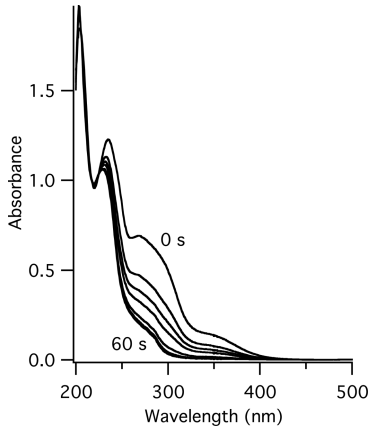

Figure 3. UV−visible spectra for **4c** after irradiation at 350 nm for 0, 5, 10, 15, 30, 45, and 60 s.

After 30 min at 50 °C, this peak returned to its original state. Even after 60 min of irradiation, there was still some residual absorption at these longer wavelengths. However, this time the peak did not return upon heating, indicating that some irreversible photochemical transformation (unrelated to the desired quadricyclane formation) had occurred. With **4a**, there appeared to be no quadricyclane formation, as there was only a slight change in the spectrum after a minute of irradiation. Prolonged exposure (60 min) to 350 nm light again caused the longer-wavelength features to disappear. Yet, as with the case of **4q**, they did not reappear upon heating. (Somewhat interestingly, when **4h** was irradiated for 60 min, the long wavelength shoulder did reappear, suggesting that the photodegradation observed with **4a** and **4q** is not universal.) This failure of **4a** to form a quadricyclane was surprising because other examples of norbornadiene chromophores with dimethylamino substituents exhibit good solar energy storage properties.[25] It could be that in this case the substituents also cause a red shift in the absorption of the quadricyclane, resulting in a rapid reversion back to the norbornadiene under these irradiation conditions. This effect has been noted before with other norbornadiene/quadricyclane derivatives.[26]

The conversion to the quadricyclane was also monitored by NMR spectroscopy. Figure 4 shows spectra for norbornadiene **4r** after 0, 5, and 20 min in the 350 nm photoreactor. The clearly resolvable peaks due to norbornadiene and quadricyclane allowed for the determination of the conversion under different photochemical conditions (Table 3). Quadricyclane stability

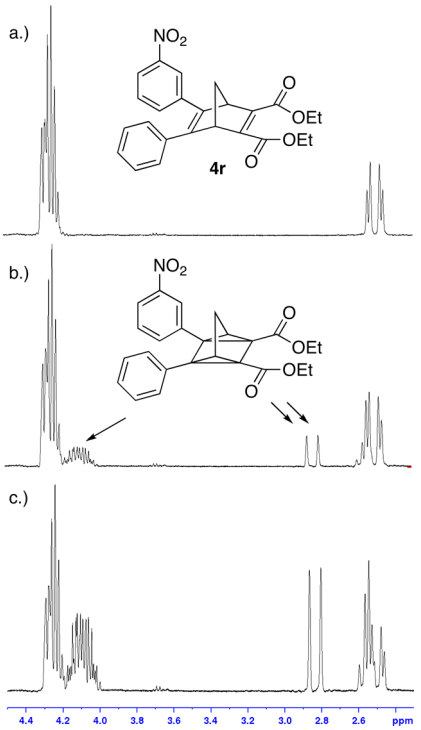

Figure 4. ^{1}H NMR spectra of **4r** (a) as isolated, (b) after 5 min of irradiation at 350 nm, and (c) after 20 min of irradiation at 350 nm.

(vide infra) and light absorption by both norbornadiene and quadricyclane components likely contributed significantly to these results. (The solutions here were more concentrated than those used for the UV−visible studies. In addition, because the studies were performed on solutions in NMR tubes, stirring was not feasible.) Nevertheless, these data do provide a practical guide to the conditions necessary to promote the conversion on the synthetic scale. Of particular importance is the fact that switching to 300 nm bulbs provided no synthetic advantage (indeed, in some cases this proved deleterious), indicating that the transformation can take place at longer wavelengths that are less destructive. In addition, it is clear that the extreme of a xenon arc lamp is not necessary. It should also be noted that, for most examples, additional peaks due to decomposition were also present in the spectra. Clearly this is an aspect of this system that needs to be improved if reversible solar energy storage applications based on the norbornadiene to quadricyclane interconversion are to be realized. To investigate the possible

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Table 3. Conversion to Quadricyclane after Irradiation

entry	norbornadiene	5 min, 350 nm (%)[a]	20 min, 350 nm (%)[a]	5 min, 300 nm (%)[a]	20 min, 300 nm (%)[a]
1	**4a**	0	0	0	0
2	**4c**	34	83	7	1
3	**4d**	64	96	33	58
4	**4e**	44	65	10	2
5	**4f**	58	95	21	40
6	**4g**	61	82	22	24
7	**4h**	74	99	46	90
8	**4i**	61	94	28	64
9	**4j**	73	98	38	43
10	**4k**	68	98	39	79
11	**4l**	59	96	36	80
12	**4m**	53	98	48	91
13	**4n**	57	96	37	81
14	**4o**	69	97	31	64
15	**4p**	69	98	38	86
16	**4q**	23	39	11	26
17	**4r**	17	49	14	34
18	**4s**	71	98	43	87
19	**4h**[b]	72	99	43	98

[a]Values determined by ^{1}H NMR spectroscopy. [b]With 0.4 M 1,3-cyclohexadiene, a known triplet quencher.

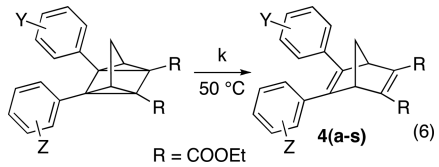
Table 4. First-Order Rate Constants for Thermal Quadricyclane Reversion[a]

norbornadiene	Y	σ[b]	$\sigma_\alpha^{\bullet}$[c]	$\sigma_C^{\bullet}$[d]	k ($\times 10^4$ s^{-1})[e]	$\sigma_Q^{\bullet}$[f]
4c	4-(OCH_3)	−0.27	0.034	0.27	9.24 ± 0.39	0.22
4d	3-(OCH_3)	0.12		−0.02	6.58 ± 0.57	0.07
4e	4-CH_3	−0.17	0.015	0.16	7.66 ± 0.10	0.13
4f	3-CH_3	−0.07	−0.001	0.03	6.73 ± 0.20	0.08
4g	4-$C(CH_3)_3$	−0.20	0.036	0.16	8.76 ± 0.40	0.19
4h	H	0	0	0	5.63 ± 0.37	0
4i	4-F	0.06	−0.011	−0.06	4.47 ± 0.10	−0.10
4j	3-F	0.34	−0.018	−0.02	5.15 ± 0.13	−0.04
4k	4-Cl	0.23	0.017	0.11	6.02 ± 0.43	0.03
4l	3-Cl	0.37	−0.001	−0.03	4.82 ± 0.27	−0.07
4m	4-(CF_3)	0.54	0.001	0.05	4.95 ± 0.53	−0.06
4n	3-(CF_3)	0.43	−0.014	−0.08	3.99 ± 0.19	−0.15
4o	4-CN	0.66	0.043	0.47	12.3 ± 0.4	0.34
4p	3-CN	0.56	−0.039	−0.13	3.21 ± 0.24	−0.24
4q	4-(NO_2)	0.78		0.57	16.2 ± 1.9	0.46
4r	3-(NO_2)	0.71		−0.11	3.21 ± 0.22	−0.24

[a]See eq 6. [b]Reference 31. [c]Reference 36. [d]Reference 34. [e]Values reflect the average of at least four trials ± twice the standard deviation. [f]See eq 10.

involvement of a triplet excited state in the photoconversion,[27] this experiment was also conducted on **4h** in the presence of 1,3-cyclohexadiene, a known[28] triplet quencher. Because the results are comparable with (entry 19) and without (entry 7) the quencher, triplet state involvement seems unlikely. Finally, once again **4a** showed no signs of quadricyclane formation by NMR, but there was indication of some photoinduced decomposition noticeable in the spectrum. It is possible that switching to longer wavelength bulbs may improve the situation, given the pronounced red shift in the absorption spectrum for this derivative. However, it is also possible that the quadricyclane that would result is simply too unstable to be observed. Further investigations on this derivative are underway.

To investigate the effect of substituents on kinetic quadricyclane stability, we next studied the kinetics of the thermal quadricyclane to norbornadiene reversion (eq 6). Our first plan was to use NMR spectroscopy to monitor this reaction. However, as a testament to the amount of heat these compounds



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can store, the variable temperature unit of the spectrometer was unable to compensate for the heat released during the reaction, resulting in kinetics plots that appeared to be autocatalytic but were just a result of the temperature rising during the reaction. As a result, we instead monitored the kinetics via UV−visible spectroscopy (under much more dilute conditions), with the results presented in Table 4 and Figure 5. Others have noted that electron-donating groups such as methoxy increase the lability of quadricyclanes,[15,20] and our data show this as well. However, electron-withdrawing groups in the *para* position also increased the rate of reversion to the norbornadiene, so the kinetic stability is not a matter of simple electronics. The most stable

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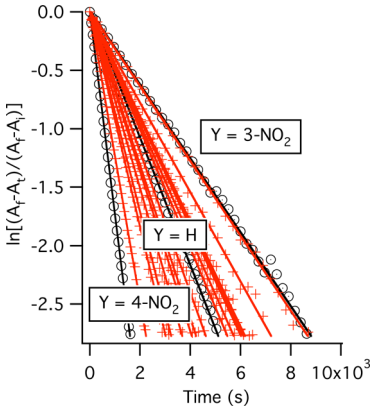
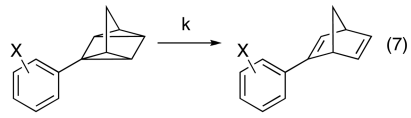


Figure 5. Natural log plots for thermal reversion (at 50 °C) of quadricyclanes to norbornadienes **4**(**c**−**s**) (eq 6). The highlighted plots (in black) represent the data for the reversion to the quadricyclane without aryl substituents (**4h**), as well as data for the derivatives with fastest (**4q**) and slowest (**4r**) reversion kinetics (Z = H for the highlighted plots).

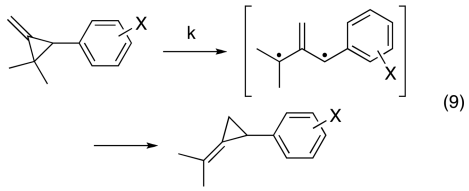
quadricyclanes in our study were those with electron-withdrawing groups in the *meta* position. Finally, the rate constant for the reversion to donor−acceptor norbornadiene **4s** (4.49 (±0.10) × 10^{-4} s^{-1}, average of three trials) reflects an apparent compromise between the rate-enhancing effect of the methyl groups and the rate-retarding effects of the *meta* trifluoromethyl substituents.

The quadricyclane to norbornadiene reversion has long been thought to occur via a biradical mechanism.[11] A simple Hammett analysis of our data is presented in Figure 6a. There is a poor linear fit (when all of the data are included) with a slight negative bias in the slope for the derivatives with *meta* substituents (ρ = −0.44) (for which there is a much better linear fit). These are characteristics that have been attributed to reactions that occur via a free radical mechanism.[29] (For example, Creary presented a plot with these characteristics in his discussion of the free radical mechanism for the thermal rearrangement of 2-aryl-3,3-dimethylmethylene-cyclopropanes.[29])

While the Hammett electronic parameter (and corresponding σ_+ and σ_- values) have been a staple in mechanistic organic chemistry for over 80 years,[30−32] analogous $\sigma^\bullet$ values have been much less utilized.[33−39] A significant problem with $\sigma^\bullet$ scales based upon chemical transformations is that it can be difficult to separate free radical stabilization effects from influences due to stabilization of charge buildup.[33,36] In 1980, Dust and Arnold developed a free radical substituent parameter ($\sigma_\alpha^\bullet$) based on ESR coupling constants in substituted benzyl radicals.[36] In 1987, Tomioka and co-workers performed kinetics experiments on simpler substituted arylnorbornadiene derivatives (eq 7) and performed an analysis using the Dust and Arnold paramters.[40] They found that a dual parameter plot consisting of both electronic (σ and ρ) and radical ($\sigma^\bullet$ and $\rho^\bullet$) constants (eq 8) provided the best linearity, suggesting a mechanism with both radical and ionic components ($\rho^\bullet/\rho$ = 1.105). When we performed this analysis, our data showed a good linear fit (r = 0.938) when plotted versus the Dust and Arnold $\sigma_\alpha^\bullet$ values (Figure 6b), an observation that supports a biradical intermediate. (Because nitro groups and cyano groups can stabilize radical intermediates through resonance effects, it is not a surprise that **4o** and **4q** formed quadricyclanes that were particularly short-lived.) More interestingly, however, the addition of the second parameter based on the traditional Hammett σ value provided an insignificant improvement in linear fit (r = 0.938), with a $\rho^\bullet/\rho$ ratio of over 280. This suggests a mechanism that is almost purely free radical in nature, with very little contribution caused by polar effects.



$$\log\left(\frac{k_X}{k_H}\right) = \sigma\rho + \sigma^\bullet\rho^\bullet \qquad (8)$$



$$\sigma_{Q^\bullet} = \log\left(\frac{k_Y}{k_H}\right) \qquad (10)$$

In 2006, Creary published an extensive $\sigma^\bullet$ scale based on the kinetics for the rearrangement of 2-aryl-3,3-dimethylmethylenecyclopropanes (eq 9, Table 4).[34] In terms of the number of substituents, this is arguably the most thorough study to date. A plot (Figure 7a) of our data versus these constants ($\sigma_C^\bullet$) showed an even better linear fit (r = 0.945). In this case, however, the incorporation of a second parameter (eq 8) did improve the quality (Figure 7b, r = 0.974), suggesting that

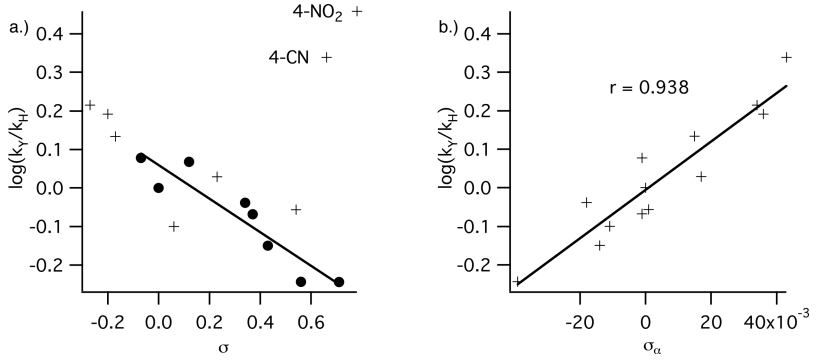


Figure 6. Hammett analyses of rate constant data versus (a) standard Hammett sigma constants (from ref 31) and (b) free radical sigma constants (from ref 36). The "●" in (a) represent just the *meta* substituents.

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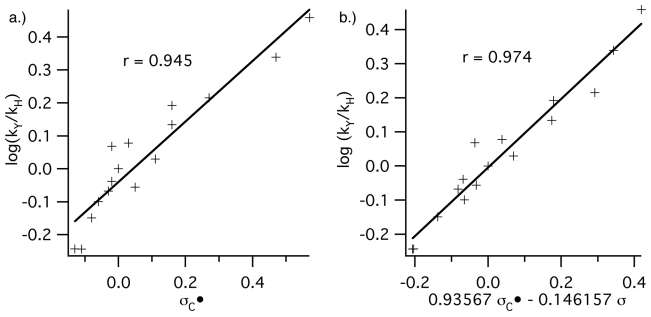


Figure 7. Hammett analyses of rate constant data versus (a) free radical sigma constants (from ref 34) based on rate constants for methylenecyclopropane rearrangements (eq 9) and (b) a two-parameter function (eq 8) with both ionic and free radical components.

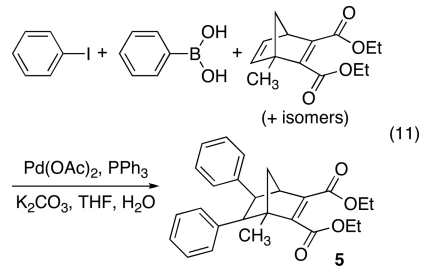
there is a polar component in this analysis ($\rho^{\bullet}/\rho = -6.40$; ρ had a negative value for this plot). Whether this comes from the reversion of our quadricyclanes or the methylenecyclopropane rearrangement is uncertain.

The possibly pure free-radical mechanism for the quadricyclane reversion led us to speculate as to whether our kinetics data (eq 6) could form the basis for a similar $\sigma^{\bullet}$ radical substitution constant, which we term $\sigma_Q^{\bullet}$ (eq 10, Table 4). To investigate this idea, we utilized Tanner's half-wave potential data for the electrolytic reduction of substituted benzyl chlorides,[41] which Dust and Arnold used as a benchmark to test the viability of their $\sigma_{\alpha}^{\bullet}$ values.[36] All three sets of constants ($\sigma_{\alpha}^{\bullet}$, $\sigma_C^{\bullet}$, and $\sigma_Q^{\bullet}$) provide excellent two-parameter plots (eq 8) when σ_- values are used for the electronic component ($r = 0.994$, 0.991, and 0.990 for $\sigma_{\alpha}^{\bullet}$, $\sigma_C^{\bullet}$, and $\sigma_Q^{\bullet}$, respectively). However, the $\rho^{\bullet}/\rho$ values (6.92, 1.30, and 0.962 for $\sigma_{\alpha}^{\bullet}$, $\sigma_C^{\bullet}$, and $\sigma_Q^{\bullet}$, respectively) are very different. (The literature[36] values for this analysis using $\sigma_{\alpha}^{\bullet}$ and σ_- constants are $r = 0.989$ and $\rho^{\bullet}/\rho = 6.7$.) While these results show that our $\sigma_Q^{\bullet}$ constants are not necessarily more accurate than $\sigma^{\bullet}$ scales generated by others, the flexibility of the synthetic scheme presented here provides the opportunity to determine the values for a wide variety of additional substituents in a relatively simple manner.

From the data listed above, two things in particular are immediately apparent. First, none of the norbornadienes form a quadricyclane that is kinetically stable enough to be used in solar energy storage applications. Reversion is generally complete within a few hours at 50 °C, and within a few days at room temperature. Because there is only a factor of 5 between the slowest and fastest rate constant for the reversion, substitution on the aromatic rings has relatively little effect on quadricyclane robustness.

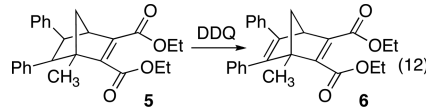
The second notable observation is the stark contrast between our results and those of Hirao. Unlike our compounds, norbornadiene **1** is known to form a long-lived quadricyclane.[15,16] The only significant structural difference between **1** and norbornadienes **4** is the methyl groups (or lack thereof) at the bridgehead positions. To the best that we could determine, these groups are present in **1** primarily for synthetic reasons. (Cyclopentadiene **2** is known to be a stable and isolable compound, with a well-established synthesis.[17]) Could it really be the case that substitution at this position could have a significant stabilizing effect on the quadricyclanes? Nagai has noted that that bridgehead substituents lower the amount of heat that can be stored in a quadricyclane system.[42] He used this observation to suggest that these substituents thus stabilize the quadricyclane structure by lessening the ring strain. However, this point is one of thermodynamic stability, while the question that we raise is one of kinetic stability. Nevertheless, it does not seem unreasonable to suggest that the same structural effects are responsible for both observations.

To answer this question, we next synthesized norbornene **5** (eq 11). A Diels–Alder reaction between methylcyclopentadiene



(11)

isomers (from thermal decomposition of the dimer) and diethyl acetylenedicarboxylate resulted in a mixture of adducts that were not separated. When this mixture was reacted in the tandem alkene insertion Suzuki coupling, the single isomer **5**, rather fortuitously, was purified from the combination of possible products. Dehydrogenation (eq 12) with DDQ resulted in the



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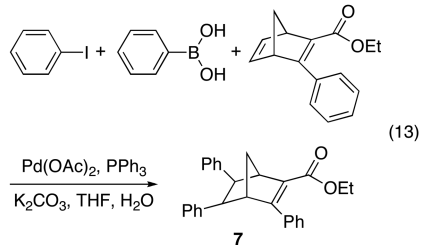
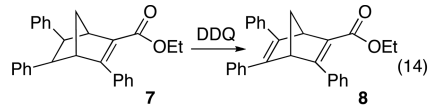


(13)

isolation of the substituted norbornadiene **6**. In a similar fashion, we also synthesized norbornene **7** and norbornadiene **8**, so that we could investigate the effect of replacing one of the ester groups with an additional benzene ring (eqs 13 and 14).



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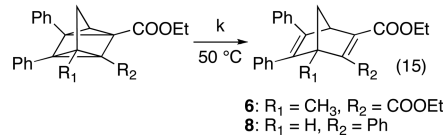

(15)

Kinetics experiments (eq 15) on the quadricyclanes formed from these compounds were performed as described above, and the results are presented in Figure 8. For comparison purposes, plots for the slowest and fastest reversions for our first series **4**(**a**–**s**) are also included. As seen from the data, methyl substitution at a bridgehead position does indeed have a significant effect on quadricyclane kinetic stability, as the rate constant ($7.24\ (\pm 0.29) \times 10^{-5}\ s^{-1}$, average of three trials) for the reversion

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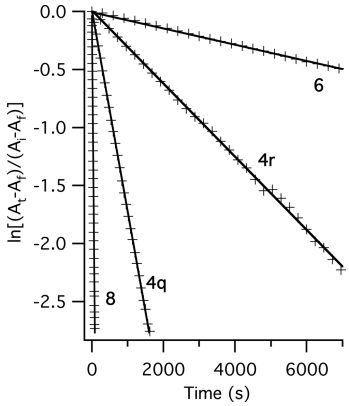

Figure 8. Natural log plots for the thermal reversion (at 50 °C) of quadricyclanes to norbornadienes **4q**, **4r**, **6**, and **8**.

to **6** is significantly slower than those observed for our earlier examples. In terms of how this substitution affects activation energy, we performed Arrhenius analyses on compounds **4h** and **6**. For the former, the E_a was determined to be 99.8 ± 2.4 kJ/mol, while for the latter, it was 109 ± 8 kJ/mol. Thus, the presence of a bridgehead methyl group appears to raise the activation barrier by about 10 kJ/mol. Finally, we found the reversion to **8** to be exceptionally rapid, with a rate constant of 3.54 (±0.63) × 10^{-2} s^{-1} (average of three trials). This is not surprising given the ability of the benzene ring to stabilize a radical intermediate through resonance.

■ CONCLUSIONS

We have successfully developed a new two-step procedure for the synthesis of substituted diarylnorbornadiene derivatives. Using this methodology, we have generated a library of compounds, which we used to investigate the effect of substituent on the photochemical conversion to the quadricyclane, as well as the rate at which the quadricyclane reverts to the norbornadiene. The effect of substituent on the kinetic stability of the quadricyclanes was relatively small, and our data provide support for a mechanism for reversion that occurs via a biradical intermediate. The synthetic methodology was also successful in generating a derivative with a methyl substituent in the bridgehead position. Somewhat surprisingly, this seemingly minor structural modification had a profound effect on quadricyclane stability, with the reversion for this example occurring significantly slower than that for those without the bridgehead substituent. This suggests that structural variations at this position may prove more fruitful in producing a norbornadiene derivative with properties that could lead to viable solar energy storage applications. Investigations toward this end are currently underway and will be disclosed in the future.

■ EXPERIMENTAL SECTION

General. Diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate,[43] ethyl 3-phenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate,[44] as well as norbornenes **3c**,[18] **3h**,[18] and **3q**[18] are all literature compounds. Tetrahydrofuran (anhydrous, uninhibited, and oxygen-free) was stored and used as received in an argon-filled glovebox. Deionized water was degassed with a rapid flow of nitrogen for 30 min prior to storage and use in an argon-filled glovebox. All other chemicals and solvents were used as received from chemical suppliers. ^{1}H and ^{13}C {^{1}H} NMR spectra were obtained on a 400 MHz instrument at 400 and 101 MHz, respectively. Either tetramethylsilane or residual signal due to solvent was used as an internal reference. For ^{19}F analyses (obtained at 376 MHz), trifluorotoluene (δ = −63.72) in d_6-benzene was used as an external reference. Analytical HPLC analyses were performed with a system equipped with a C18 reverse phase 4.6 × 150 mm column and a UV−visible detector. Preparative HPLC separations were correspondingly performed with a system equipped with a 21.6 × 150 mm C18 reverse phase column and a UV−visible detector using a flow rate of 21.4 mL/min.

NMR Photoconversion Experiment. Samples of norbornadienes (20−30 mg) were dissolved in d_2-tetrachloroethane (the volume of which was adjusted to give a concentration of 0.08 M), and the resulting solutions were transferred to NMR tubes. These were then placed in a carousel setup that allowed the samples to rotate inside a Rayonet-style circular photochemical reactor equipped with 350 nm bulbs. The lights were switched on for a period of 5 min, after which all samples were placed in ice/water bath prior to analysis by NMR. The samples were then allowed to revert (overnight at room temperature or 2 h at 50 °C), and the experiment was repeated, this time with irradiation for 20 min. The samples were again allowed to revert, and the reactor was equipped with 300 nm bulbs. The process was then repeated for 5 and 20 min irradiation times.

Kinetics Experiments. Samples of norbornadiene (3−5 mg) were dissolved in ethanol (50 mL), and the concentration was adjusted to give an absorption value at 330 nm between 0.3 and 2. The solutions were then placed in a photoreactor equipped with 350 nm bulbs for 5−10 min, after which they were immediately placed in the UV−visible spectrometer with the temperature equilibrated to 50.0 °C. The first-order rate constants were obtained by monitoring the increasing absorbance (due to norbornadiene formation) with time, and curve fitting the data to an exponential function. The logarithmic plots in Figures 5 and 8 were obtained by plotting $\ln[(A_t - A_f)/(A_i - A_f)]$ versus time.

General Procedure for Norbornene Synthesis. The following is a modification of a known procedure.[18] A 40 mL scintillation vial was charged with all liquid reactants (the norbornadiene diester and sometimes the aryl iodide) and a stir bar. This mixture was then degassed with a rapid stream of nitrogen for 30 min, after which the vial was immediately capped and imported into a glovebox. Under an argon atmosphere, the solid reactants (boronic acid, base, catalyst, phosphine, and aryl iodide if solid) were added to the vial, along with the THF solvent. The vial was then capped and transferred to a second glovebox that was anaerobic (but not moisture-free), at which point the degassed water was added. The vial was again capped (with a Teflon-lined serum cap), removed from the glovebox, and placed in a 50 °C reactor with rapid stirring for 24 h. After the phases were separated in a separatory funnel, the organic layer was set-aside in an Erlenmeyer flask. The aqueous phase was then back extracted (2 × 20 mL) with MTBE. All of the organic phases were then combined and washed with saturated sodium chloride (1 × 20 mL). After being dried over $MgSO_4$ and removal of the solvent with a rotary evaporator, the residue was placed in a kugelrohr distillation apparatus at 60 °C and a dynamic 5 mTorr vacuum to remove biphenyl and residual volatile reactants. The material left in the pot flask was then chromatographed on silica, and purified further (if necessary) by recrystallization, distillation, and/or preparative HPLC.

General Procedure for DDQ Dehydrogenation. An 80−300 mg sample of the norbornene was combined with 2 mol equiv of DDQ in a standard 20 mL scintillation vial. Ethyl acetate (2−5 mL) was added via pipet, and the mixture was thoroughly dissolved. After removal of the solvent with a rotary evaporator (resulting in an orange residue), the vial was capped with a lid (that was suitably stable at elevated temperatures) and placed in a 150 °C oven for 60 min. The resulting material (typically green in color) was then chromatographed on silica or basic alumina. Further purification was achieved either by recrystallization, preparative HPLC, and/or preparative HPLC of the quadricyclane that resulted from photochemical conversion at 350 nm. After removal of the solvent, the purified material was then dried overnight in vacuo. Many of the norbornadienes did show signs of thermal decomposition for extended periods at room temperature or higher. As a result, it was important to be sure that materials were never exposed to temperatures greater than

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80 °C during workup and purification. When pure, norbornadienes were stored in the dark at −10 °C under argon.

*Diethyl 5-[4-(N,N-Dimethylamino)phenyl]-6-phenylbicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate (**3a**).* The general procedure was applied on 2.28 g (11.2 mmol) of iodobenzene, 2.00 g (12.2 mmol) of 4-(*N*,*N*-dimethylamino)phenylboronic acid, 2.95 g (12.5 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 4.08 g (29.6 mmol) of K_2CO_3, 74 mg (0.28 mmol) of triphenylphosphine, 28 mg (0.12 mmol) of palladium acetate, 20 mL of THF, and 20 mL of water to yield 0.948 g (2.19 mmol, 19.7%) of **3a** isolated as a tan resin after chromatography (10% EtOAc in hexanes): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (apparent t, J_{app} = 6.9 Hz, 2H), 6.99 (apparent t, J_{app} = 6.0 Hz, 1H), 6.91 (d, J = 6.8 Hz, 2H), 6.73, 6.42 (second order AA′BB′ pattern, J = 8.4 Hz, 4H), 4.26 (q, J = 6.9 Hz, 4H), 3.53 (br, 2H), 3.43−3.45 (m, 2H), 2.79 (s, 6H), 2.36 (dm, J_d = 9.3 Hz, 1H), 2.03 (dm, J_d = 9.3 Hz, 1H), 1.31 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 165.0, 148.9, 147.5, 146.7, 141.7, 129.4, 129.2, 128.9, 127.8, 125.6, 112.4, 61.2, 51.4, 50.3, 48.5, 48.2, 45.3, 40.9, 14.4. Anal. Calcd for $C_{27}H_{31}NO_4$: C, 74.80; H, 7.21; N, 3.23. Found: C, 74.70; H, 7.52; N, 3.20.

*Diethyl 5-[3-(N,N-Dimethylamino)phenyl]-6-phenylbicyclo-[2.2.1]hept-2-ene-2,3-dicarboxylate (**3b**).* The general procedure was applied on 1.11 g (5.44 mmol) of iodobenzene, 1.00 g (6.06 mmol) of 3-(*N*,*N*-dimethylamino)phenylboronic acid, 1.43 g (6.06 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 2.40 g (17.4 mmol) of K_2CO_3, 32 mg (0.12 mmol) of triphenylphosphine, 12 mg (0.053 mmol) of palladium acetate, 10 mL of THF, and 10 mL of water to yield 0.783 g (1.81 mmol, 33.3%) of **3b** isolated as a yellow oil after chromatography (10% EtOAc in hexanes): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90−7.05 (m, 6H), 6.39 (dd, J = 8.2 Hz, J = 2.2 Hz, 1H), 6.34 (br d, J = 7.7 Hz, 1H), 6.19 (s, 1H), 4.26 (q, J = 7.1 Hz, 4H), 3.52 (br, 2H), 3.48 (br, 2H), 2.71 (s, 6H), 2.42 (d, J = 9.5 Hz, 1H), 2.04 (d, J = 9.5 Hz, 1H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.94, 164.89, 150.3, 147.3, 146.9, 141.8, 141.5, 128.8, 128.3, 127.7, 125.7, 117.3, 114.8, 110.8, 61.2, 50.9, 50.5, 49.2, 48.8, 45.4, 40.9, 14.3. Anal. Calcd for $C_{27}H_{31}NO_4$: C, 74.80; H, 7.21; N, 3.23. Found: C, 74.62; H, 7.30; N, 3.05.

*Diethyl 5-(3-Methoxyphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3d**).* The general procedure was applied on 1.17 g (5.00 mmol) of 3-iodoanisole, 0.675 g (5.53 mmol) of phenylboronic acid, 1.23 g (5.21 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 1.82 g (13.2 mmol) of K_2CO_3, 34 mg (0.13 mmol) of triphenylphosphine, 14 mg (0.062 mmol) of palladium acetate, 6 mL of THF, and 6 mL of water to yield 1.10 g of a brown oil after chromatography (10% EtOAc in hexanes). This was purified further by recrystallization from methanol to yield 0.775 g (1.85 mmol, 37.1%) of **3d** as a tan solid, which was pure enough for further use. For analysis purposes, material was purified further by reverse-phase preparative HPLC (40% acetonitrile, 40% methanol, 20% water) with an 82% recovery as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90−7.12 (m, 6H), 6.51 (dd, J = 7.0, 2.2 Hz, 2H), 6.39 (t, J = 2.0 Hz, 1H), 4.27 (q, J = 7.2 Hz, 4H), 3.58 (s, 3H), 3.52 (br, 2H), 3.49 (br, 2H), 2.41 (br d, J_d = 9.6 Hz, 1H), 2.06 (dm, J_d = 9.6 Hz, 1H), 1.32 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 159.1, 147.2, 147.0, 142.8, 141.2, 128.8, 128.7, 127.8, 125.9, 121.3, 114.9, 111.3, 61.2, 55.2, 50.6, 49.0, 48.9, 45.4, 14.3. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.14; H, 6.89.

*Diethyl 5-(4-Methylphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3e**).* The general procedure was applied on 2.18 g (10.0 mmol) of 4-iodotoluene, 1.34 g (11.0 mmol) of phenylboronic acid, 2.57 g (11.0 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 3.65 g (26.4 mmol) of K_2CO_3, 64 mg (0.24 mmol) of triphenylphosphine, 24 mg (0.11 mmol) of palladium acetate, 20 mL of THF, and 20 mL of water to yield 0.690 g (1.71 mmol, 17.1%) of **3e** isolated as a colorless oil after chromatography (10% EtOAc in hexanes), which was pure enough for further use. For analysis purposes, material was purified further by reverse-phase preparative HPLC (40% acetonitrile, 40% methanol, 20% water) with a 63% recovery to yield a colorless oil that solidified upon prolonged standing: mp 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97−7.05 (m, 3H), 6.89 (m, 2H), 6.82, 6.76 (second order AA′BB′ pattern, J = 8.0 Hz, 4H), 4.26 (q, J = 7.2 Hz, 4H), 3.52 (m, 2H), 3.48 (s, 2H), 2.41 (d, J = 9.2 Hz, 1H), 2.16 (s, 3H), 2.05 (dt, J_d = 9.2 Hz, J_t = 2.0 Hz, 1H), 1.32 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.0, 147.3, 147.0, 141.4, 138.1, 135.3, 128.9, 128.7, 128.5, 127.8, 125.8, 61.2, 51.0, 50.5, 48.8, 48.7, 45.4, 21.0, 14.4. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.01; H, 6.90.

*Diethyl 5-(3-Methylphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3f**).* The general procedure was applied on 0.548 g (2.51 mmol) of 3-iodotoluene, 0.333 g (2.73 mmol) of phenylboronic acid, 0.675 g (2.86 mmol) of diethyl bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate, 0.927 g (6.72 mmol) of K_2CO_3, 16 mg (0.061 mmol) of triphenylphosphine, 8.3 mg (0.37 mmol) of palladium acetate, 3 mL of THF, and 3 mL of water to yield 0.505 g (1.25 mmol, 49.7%) of **3f** isolated as a colorless oil after chromatography (10% EtOAc in hexanes), which was pure enough for further use. For analysis purposes, material was purified further by reverse-phase preparative HPLC (40% acetonitrile, 40% methanol, 20% water) with a 48% recovery as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88−7.06 (m, 6H), 6.76 (d, J = 7.2 Hz, 1H), 6.68 (s, 1H), 6.67 (d, J = 7.6 Hz, 1H), 4.26 (q, J = 7.2 Hz, 4H), 3.44−3.53 (m, 4H), 2.42 (dm, J_d = 9.6 Hz, 1H), 2.13 (s, 3H), 2.07 (dm, J_d = 9.6 Hz, 1H), 1.32 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.0, 147.2, 147.1, 141.3, 141.0, 137.2, 129.9, 128.8, 127.7, 127.6, 126.5, 125.8, 125.7, 61.2, 50.7, 50.6, 48.9, 48.8, 45.5, 21.5, 14.4. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98, Found: C, 76.83; H, 6.99.

*Diethyl 5-(4-tert-Butylphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3g**).* The general procedure was applied on 2.34 g (9.00 mmol) of 4-*tert*-butyliodobenzene, 1.22 g (10.0 mmol) of phenylboronic acid, 2.34 g (9.92 mmol) of diethyl bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate, 3.50 g (25.4 mmol) of K_2CO_3, 52 mg (0.20 mmol) of triphenylphosphine, 34 mg (0.15 mmol) of palladium acetate, 16 mL of THF, and 16 mL of water to yield 2.08 g (4.64 mmol, 51.6%) of **3g** isolated as a colorless oil after chromatography (10% EtOAc in hexanes), which was pure enough for further use. For analysis purposes, a small amount of material was purified further by reverse-phase preparative HPLC (45% acetonitrile, 45% methanol, 10% water): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02, 6.79 (second order AA′BB′ pattern, J = 8.4 Hz, 4H), 6.94−6.99 (m, 3H), 6.84−6.87 (m, 2H), 4.26 (overlapping quartets, J = 7.1 Hz, 4H), 3.52 (apparent d, J_{app}= 1.4 Hz, 2H), 3.49 (br s, 2H), 2.41 (d, J_d = 9.5 Hz, 1H), 2.05 (dt, J_d = 9.5 Hz, J_t = 1.6 Hz, 1H), 1.31 (overlapping triplets, J = 7.1 Hz, 6H), 1.17 (s, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.0, 148.7, 147.2, 147.0, 141.3, 138.1, 128.8, 128.4, 127.7, 125.7, 124.6, 61.2, 50.7, 50.6, 48.9, 48.5, 45.4, 34.3, 31.4, 14.36, 14.35. Anal. Calcd for $C_{29}H_{34}O_4$: C, 78.00; H, 7.67. Found: C, 77.75; H, 7.47.

*Diethyl 5-(4-Fluorophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3i**).* The general procedure was applied on 1.31 g (5.90 mmol) of 4-fluoroiodobenzene, 0.762 g (6.25 mmol) of phenylboronic acid, 1.52 g (6.44 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 2.07 g (15.0 mmol) of K_2CO_3, 51 mg (0.19 mmol) of triphenylphosphine, 15 mg (0.067 mmol) of palladium acetate, 10 mL of THF, and 10 mL of water to yield 1.50 g (3.67 mmol, 62.2%) of **3i** isolated as a yellow oil (solidified upon standing) after chromatography (10% EtOAc in hexanes), which was pure enough for further use. For analysis purposes, a small amount of material was purified further by distillation in a kugelrohr apparatus at 250 °C under a 1 mTorr dynamic vacuum resulting in a pink resin, which was then recrystallized from hexanes to yield a white solid: mp 73−74 °C (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96−7.06 (m, 3H), 6.80−6.90 (m, 4H), 6.70 (apparent t, J_{app} = 8.6 Hz, 2H), 4.27 (overlapping quartets, J = 7.1 Hz, 4H), 3.54 (apparent d, J_{app}= 1.6 Hz, 1H), 3.49 (br s, 2H), 3.48 (apparent d, J_{app}= 1.7 Hz, 1H), 2.38 (br d, J_d = 9.6 Hz, 1H), 2.08 (dt, J_d = 9.6 Hz, J_t = 1.6 Hz, 1H), 1.32 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.89, 164.87, 161.1 (d, J = 244 Hz), 147.2, 146.9, 141.0, 136.9 (d, J = 3 Hz), 130.1 (d, J = 8 Hz), 128.8, 128.0, 126.0, 114.6, (d, J = 21 Hz), 61.3, 50.7, 50.5, 48.8, 48.3, 45.3, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.8. Anal. Calcd for $C_{25}H_{25}FO_4$: C, 73.51; H, 6.17. Found: C, 73.64; H, 6.36.

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*Diethyl 5-(3-Fluorophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3j**).* The general procedure was applied on 2.50 g (11.3 mmol) of 3-fluoroiodobenzene, 1.51 g (12.4 mmol) of phenylboronic acid, 2.93 g (12.4 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 4.96 g (30.0 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 72 mg (0.27 mmol) of triphenylphosphine, 27 mg (0.12 mmol) of palladium acetate, 20 mL of THF, and 20 mL of water to yield 2.15 g (5.30 mmol, 46.9%) of **3j** isolated as a white crystalline mass after chromatography (10% EtOAc in hexanes) and recrystallization from hexanes: mp 93−94 °C (hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87−7.07 (m, 6H), 6.55−6.70 (m, 3H), 4.27 (overlapping quartets, J = 7.2 Hz, 4H), 3.47−3.54 (m, 4H), 2.39 (br d, J_d = 9.6 Hz, 1H), 2.09 (dt, J_d = 9.6 Hz, J_t = 1.6 Hz, 1H), 1.32 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 164.8, 162.5 (d, J = 244 Hz), 147.4, 146.7, 144.0 (d, J = 7 Hz), 140.7, 129.1 (d, J = 8 Hz), 128.7, 128.0, 126.1, 124.8 (d, J = 3 Hz), 115.6 (d, J = 22 Hz), 112.7 (d, J = 21 Hz), 61.4, 50.6, 50.5, 49.1, 48.8, 45.4, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −115.6. Anal. Calcd for $C_{25}H_{25}FO_4$: C, 73.51; H, 6.17. Found: C, 73.42; H, 6.02.

*Diethyl 5-(4-Chlorophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3k**).* The general procedure was applied on 2.39 g (10.0 mmol) of 4-chloroiodobenzene, 1.34 g (11.0 mmol) of phenylboronic acid, 2.60 g (11.0 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 3.64 g (22.1 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 64 mg (0.24 mmol) of triphenylphosphine, 24 mg (0.11 mmol) of palladium acetate, 20 mL of THF, and 20 mL of water to yield 1.25 g (2.96 mmol, 29.6%) of **3k** isolated as a colorless oil after chromatography (10% EtOAc in hexanes): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00−7.06 (m, 3H), 6.97, 6.80 (second order AA′BB′ pattern, J = 8.6 Hz, 4H), 6.87 (apparent d, J_{app} = 7.0 Hz), 4.26 (overlapping quartets, J = 7.2 Hz, 4H), 3.45−3.54 (m, 4H), 2.36 (br d, J = 9.6 Hz, 1H), 2.07 (dt, J_d = 9.6 Hz, J_t = 1.6 Hz, 1H), 1.32 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.84, 164.78, 147.3, 146.7, 140.8, 139.8, 131.6, 130.1, 128.7, 128.0, 127.9, 126.1, 61.3, 50.6, 50.5, 48.9, 48.5, 45.3, 14.3. Anal. Calcd for $C_{25}H_{25}ClO_4$: C, 70.67; H, 5.93. Found: C, 70.54; H, 5.92.

*Diethyl 5-(3-Chlorophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3l**).* The general procedure was applied on 1.20 g (5.04 mmol) of 4-chloroiodobenzene, 0.67 g (5.5 mmol) of phenylboronic acid, 1.30 g (5.51 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 1.83 g (11.1 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 32 mg (0.12 mmol) of triphenylphosphine, 12 mg (0.053 mmol) of palladium acetate, 10 mL of THF, and 10 mL of water to yield 0.598 g (1.41 mmol, 28.0%) of **3l** isolated as a mass of white, microcrystalline clumps after chromatography (10% EtOAc in hexanes) and recrystallization from ligroin: mp = 98−99 °C (ligroin); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89−7.08 (m, 8H), 6.73 (m, 1H), 4.27 (overlapping quartets, J = 7.1 Hz, 4H), 3.44−3.55 (m, 4H), 2.38 (br d, J = 9.7 Hz, 1H), 2.09 (dt, J_d = 9.7 Hz, J_t = 1.6 Hz, 1H), 1.32 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.7, 147.4, 146.7, 143.4, 140.6, 133.6, 128.7, 128.9, 128.7, 128.0, 127.1, 126.1, 126.0, 61.4, 50.6, 50.4, 49.1, 48.7, 45.4, 14.4. Anal. Calcd for $C_{25}H_{25}ClO_4$: C, 70.67; H, 5.93. Found: C, 70.71; H, 5.95.

*Diethyl 5-[4-(Trifluoromethyl)phenyl]-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3m**).* The general procedure was applied on 1.30 g (4.78 mmol) of 4-iodobenzotrifluoride, 0.646 g (5.30 mmol) of phenylboronic acid, 1.22 g (5.17 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 1.73 g (10.5 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 30 mg (0.12 mmol) of triphenylphosphine, 12 mg (0.053 mmol) of palladium acetate, 10 mL of THF, and 10 mL of water to yield 0.977 g (2.13 mmol, 44.6%) of **3m** isolated as a slightly pink oil after chromatography (10% EtOAc in heptanes) and kugelrohr distillation (>200 °C, <5 mTorr dynamic vacuum). While this material was pure enough for future use, a small amount was purified further by reverse-phase preparative HPLC (40% acetonitrile, 30% methanol, 30% water) with a 65% recovery as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26, 6.87 (second order AA′BB′ pattern, J = 8.1 Hz, 4H), 6.90−7.05 (m, 5H), 4.27 (q, J = 7.1 Hz, 4H), 3.52−3.56 (m, 4H), 2.40 (br d, J = 9.7 Hz, 1H), 2.11 (dt, J_d = 9.7 Hz, J_t = 1.5 Hz, 1H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.7, 147.5, 146.5, 145.6, 140.5, 129.1, 128.7, 128.11 (q, J = 32.4 Hz), 128.09, 126.2, 124.6 (q, J = 3.6 Hz), 124.3 (q, J = 271.7 Hz), 61.4, 50.7, 50.5, 49.2, 49.0, 45.3, 14.4; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.6. Anal. Calcd for $C_{26}H_{25}F_3O_4$: C, 68.11; H, 5.50. Found: C, 67.79; H, 5.37.

*Diethyl 5-[3-(Trifluoromethyl)phenyl]-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3n**).* The general procedure was applied on 1.01 g (3.71 mmol) of 3-iodobenzotrifluoride, 0.345 g (2.73 mmol) of phenylboronic acid, 0.657 g (2.83 mmol) of diethyl bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate, 0.930 g (5.96 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 16 mg (0.060 mmol) of triphenylphosphine, 6 mg (0.03 mmol) of palladium acetate, 5 mL of THF, and 5 mL of water to yield 0.450 g (0.983 mmol, 36.0%) of **3n** isolated as a pale yellow oil after chromatography (10% EtOAc in heptanes). While this material was pure enough for future use, a small amount was purified further by reverse-phase preparative HPLC (40% acetonitrile, 30% methanol, 30% water) with a 64% recovery as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 7.6 Hz, 1H), 6.93−7.13 (m, 6H), 6.86 (d, J = 7.2 Hz, 2H), 4.27 (overlapping quartets, J = 7.1 Hz, 4H), 3.54−3.58 (m, 4H), 2.40 (br d, J = 9.6 Hz, 1H), 2.12 (dt, J_x = 9.7 Hz, J_t = 1.6 Hz, 1H), 1.33 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.7, 147.6, 146.5, 142.3, 140.5, 131.9, 130.0 (q, J = 32.1 Hz), 128.7, 128.2, 128.1, 126.2, 125.7 (q, J = 4.4 Hz), 124.2 (q, J = 272.4 Hz), 122.6 (q, J = 3.7 Hz), 61.4, 50.5, 50.3, 49.1, 48.9, 45.4, 14.3; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −64.2. Anal. Calcd for $C_{26}H_{25}F_3O_4$: C, 68.11; H, 5.50. Found: C, 68.25; H, 5.34.

*Diethyl 5-(4-Cyanophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3o**).* The general procedure was applied on 1.14 g (4.98 mmol) of 4-iodobenzonitrile, 0.666 g (5.46 mmol) of phenylboronic acid, 1.30 g (5.51 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 1.89 g (11.5 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 32 mg (0.12 mmol) of triphenylphosphine, 12 mg (0.053 mmol) of palladium acetate, 10 mL of THF, and 10 mL of water to yield 0.956 g (2.30 mmol, 46.2%) of **3o** isolated as a brown oil after chromatography (35% EtOAc in heptanes), which was pure enough for further use. For analysis purposes, material was purified further by reverse-phase preparative HPLC (30% acetonitrile, 30% methanol, 40% water) with an 80% recovery as a colorless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29, 6.86 (second order AA′BB′ pattern, J = 7.6 Hz, 4H), 6.97−7.06 (m, 5H), 4.28 (q, J = 7.1 Hz, 4H), 3.52−3.58 (m, 4H), 2.38 (br d, J = 10.0 Hz, 1H);, 2.12 (dt, J_x = 10.0 Hz, J_t = 1.6 Hz, 1H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.7, 164.6, 147.7, 147.2, 146.2, 140.2, 131.5, 129.5, 128.6, 128.2, 126.4, 119.1, 109.6, 61.4, 50.7, 50.1, 49.4, 49.3, 45.3, 14.3. Anal. Calcd for $C_{26}H_{25}NO_4$: C, 75.16; H, 6.06; N, 3.37. Found: C, 75.09; H, 5.69; N, 3.31.

*Diethyl 5-(3-Cyanophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3p**).* The general procedure was applied on 2.03 g (8.73 mmol) of 3-iodobenzonitrile, 1.08 g (8.85 mmol) of phenylboronic acid, 2.12 g (8.98 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 3.86 g (23.4 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 67 mg (0.26 mmol) of triphenylphosphine, 23 mg (0.10 mmol) of palladium acetate, 17 mL of THF, and 17 mL of water to yield 1.37 g (3.29 mmol, 37.7%) of **3p** isolated as a yellow oil after chromatography (35% EtOAc in hexanes): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.26 (m, 2H), 7.17 (s, 1H), 6.99−7.10 (m, 5H), 6.86 (app d, J_{app} = 7.1 Hz, 2H), 4.28 (overlapping quartets, J = 7.1 Hz, 4H), 3.49−3.57 (m, 4H), 2.37 (br d, J = 9.7 Hz, 1H), 2.13 (dt, J_d = 9.7 Hz, J_t = 1.6 Hz, 1H), 1.33 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.6, 147.7, 146.3, 142.9, 140.3, 133.6, 132.1, 129.7, 128.7, 128.5, 128.3, 126.4, 119.1, 111.9, 61.5, 50.6, 50.1, 49.2, 48.7, 45.3, 14.4. Anal. Calcd for $C_{26}H_{25}NO_4$: C, 75.16; H, 6.06; N, 3.37. Found: C, 75.09; H, 5.97; N, 3.33.

*Diethyl 5-(3-Nitrophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3r**).* The general procedure was applied on 4.96 g (19.9 mmol) of 3-iodonitrobenzene, 2.71 g (22.2 mmol) of phenylboronic acid, 5.19 g (22.0 mmol) of diethyl bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate, 7.30 g (44.2 mmol) of $K_2CO_3 \cdot 1.5H_2O$, 127 mg (0.477 mmol) of triphenylphosphine, 52.6 mg (0.234 mmol) of palladium acetate, 25 mL of THF, and 25 mL of water to yield 3.72 g (8.57 mmol, 43.1%) of **3r** isolated as an off-white crystalline solid after

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recrystallization from methanol/dichloromethane: mp 132−133 °C (methanol/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dt, J_d = 7.3 Hz, J_t = 2.0 Hz, 1H), 7.77 (d. J = 1.6 Hz, 1H), 7.14−7.20 (m, 2H), 7.03 (t, J = 7.2 Hz, 2H), 6.96 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 7.3 Hz, 2H), 4.29 (q, J = 7.1 Hz, 4H), 3.58−3.59 (m, 4H), 2.42 (br d, J = 10.0 Hz, 1H), 2.16 (dt, J_d = 10.0 Hz, J_t = 1.6 Hz, 1H), 1.34 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.8, 164.6, 147.9, 147.8, 146.2, 143.6, 140.2, 135.3, 128.7, 128.6, 128.3, 126.4, 123.4, 121.1, 61.5, 50.7, 50.2, 49.3, 48.8, 45.4, 14.4. Anal. Calcd for $C_{25}H_{25}NO_6$: C, 68.95; H, 5.79; N, 3.22. Found: C, 68.79; H, 5.78; N, 3.13.

*Diethyl 5-(3,5-Dimethylphenyl)-6-[3,5-bis(trifluoromethyl)-phenyl]bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**3s**).* The general procedure was applied on 0.576 g (2.48 mmol) of 1-iodo-3,5-dimethylbenzene, 0.708 g (2.74 mmol) of 3,5-bis(trifluoromethyl)-phenylboronic acid, 0.653 g (2.77 mmol) of diethyl bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylate, 0.911 g (5.52 mmol) of K_2CO_3·$1.5H_2O$, 17.4 mg (0.0654 mmol) of triphenylphosphine, 5.8 mg (0.026 mmol) of palladium acetate, 5 mL of THF, and 5 mL of water to yield 0.360 g (0.649 mmol, 26.2%) of **3s** isolated as white powdery solid after chromatography (10% EtOAc in hexanes) and recrystallization from methanol: mp 83−84 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.29 (s, 2H), 6.58 (s, 1H), 6.44 (s, 2H), 4.28 (overlapping quartets, J = 7.2 Hz, 4H), 3.50−3.59 (m, 4H), 2.28 (br d, J = 9.6 Hz, 1H), 2.17 (dt, J_d = 9.6 Hz, J_t = 1.2 Hz, 1H), 2.07 (s, 6H), 1.33 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.7, 164.5, 148.2, 146.0, 144.2, 139.7, 137.9, 130.6 (q, J = 33.0 Hz), 128.8 (br), 127.9, 126.3, 123.5 (q, J = 273.5 Hz), 119.6 (septet, J = 3.8 Hz), 61.4, 50.4, 49.7, 49.2, 48.8, 45.5, 21.1, 14.35, 14.33; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −64.4. Anal. Calcd for $C_{29}H_{28}F_6O_4$: C, 62.81; H, 5.09. Found: C, 62.79; H, 5.03.

*Diethyl 5-[4-(N,N-Dimethylamino)phenyl]-6-phenylbicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4a**).* A vial was charged with 0.408 g (0.942 mmol) of **3a**, 0.217 g (0.956 mmol) of DDQ, 5 mL of benzene, and a stir bar. The reaction was allowed to stir overnight at room temperature, after which it was filtered, and the solvent was removed with a rotary evaporator. The residue was then chromatographed on silica (10% EtOAc in heptanes), the crude product eluting as a yellow band. After removal of the solvent, this was then purified further by reverse-phase HPLC using a mobile phase consisting of 37% methanol, 36% acetonitrile, and 27% water to yield 0.148 g (0.343 mmol, 36.4%) of **4a** isolated as a yellow resin: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39, 6.60 (second order AA′BB′ pattern, J = 7.6 Hz, 4H), 7.23−7.29 (m, 4H), 7.17 (t, J = 7.4 Hz, 1H), 4.18−4.26 (m, 6H), 2.94 (s, 6H), 2.44 (br d, J = 6.8 Hz, 1H), 2.38 (br d, J = 7.1 Hz, 1H), 1.26 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.6, 165.2, 152.5, 151.2, 149.8, 147.9, 143.7, 137.5, 128.6, 128.4, 127.8, 126.9, 124.4, 112.1, 68.9, 61.2, 59.9, 59.2, 40.6, 14.3, 14.2. Anal. Calcd for $C_{27}H_{29}NO_4$: C, 75.15; H, 6.77; N, 3.25. Found: C, 74.78; H, 6.60; N, 3.20.

*Diethyl 5-(4-Methoxyphenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4c**).* The general procedure was followed using 0.200 g (0.476 mmol) of **3c** and 0.129 g (0.568 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in heptanes), the still impure product was taken up in 10 mL of MTBE and placed in a Rayonet photochemical reactor (equipped with 350 nm bulbs) and irradiated for 1 h. The solvent was removed on a rotary evaporator (no heat was applied), and the resulting material was immediately injected (after being suspended in mobile phase with added acetonitrile for solubility) onto the preparative HPLC using a mobile phase of 40% acetonitrile, 40% methanol, and 20% water. The major peak that eluted before 7 min was collected, and the solvent was removed with a rotary evaporator. The residue was suspended as described above, allowed to stand overnight, and then heated in a 50 °C reactor for 20 min. Afterward, it was injected onto the HPLC once more, this time collecting the fractions for the major peak that eluted from 8 to 12 min. Removal of the solvent followed by drying in vacuo resulted in the isolation of 0.114 g of a yellow oil. Norbornadiene-containing fractions from the first HPLC purification were combined with quadricyclane-containing fractions of the second. After removal of the solvent, the residue was subjected to the same irradiation-HPLC-reversion-HPLC treatment described above, allowing for the isolation of an additional 16 mg of product for a total of 0.130 g (0.311 mmol, 65.4%) of **4c**, which was a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.6 Hz, 2H), 7.30, 6.78 (second order AA′BB′ pattern, J = 8.8 Hz, 4H), 7.25 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.0 Hz, 1H), 4.22−4.25 (m, 6H), 3.79 (s, 3H), 2.46 (br d, J = 6.9 Hz, 1H), 2.39 (dd, J = 6.8 Hz, 1H), 1.26 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 165.3, 159.0, 152.2, 151.6, 147.5, 146.0, 136.8, 129.0, 128.5, 127.7, 127.3, 113.9, 69.2, 61.2, 59.8, 59.6, 55.4, 14.3, 14.2. Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.61; H, 6.50.

*Diethyl 5-(3-Methoxyphenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4d**).* The general procedure was followed using 0.203 g (0.482 mmol) of **3d** and 0.130 g (0.574 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 40% water, 30% methanol, and 30% acetonitrile (the product took an hour to elute). After removal of the solvent, the resulting material was chromatographed once more on silica (10% EtOAc in hexanes) to yield 0.109 mg (0.260 mmol, 53.9%) of **4d** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35−7.38 (m, 2H), 7.14−7.27 (m, 4H), 6.95 (dt, J_d = 7.8 Hz, J_t = 1.2 Hz, 1H);, 6.91 (m, 1H), 6.75 (ddd, J = 8.2 Hz, 2.6 Hz, 0.8 Hz, 1H), 4.20−4.26 (m, 6H);, 3.66 (s, 3H), 2.49 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 2.42 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 1.27, 1.26 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz$CDCl_3$) δ 165.3, 165.2, 159.6, 152.0, 151.7, 148.1, 147.8, 137.7, 136.5, 129.5, 128.5, 127.8, 127.5, 120.1, 113.7, 112.6, 69.4, 61.28, 61.26, 59.8, 59.6, 55.2, 14.2. Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.87; H, 6.02.

*Diethyl 5-(4-Methylphenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4e**).* The general procedure was followed using 0.202 g (0.500 mmol) of **3e** and 0.226 g (0.996 mmol) of DDQ. After initial purification by chromatography on neutral alumina (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 20% water, 40% methanol, and 40% acetonitrile to yield 35.7 mg (0.0888 mmol, 17.8%) of **4e** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36, (d, J = 7.6 Hz, 2H), 7.17−7.26 (m, 5H), 7.05 (d, J = 8.4 Hz, 2H), 4.20−4.26 (m, 6H), 2.47 (br d, J = 7.2 Hz, 1H), 2.40 (br d, J = 6.8 Hz, 1H), 2.31 (s, 3H), 1.26 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.31, 165.27, 151.9, 151.8, 147.8, 147.0, 137.3, 136.7, 133.6, 129.2, 128.5, 127.7, 127.6, 127.3, 69.3, 61.2, 59.7, 21.4, 14.2. Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.53; H, 6.60.

*Diethyl 5-(3-Methylphenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4f**).* The general procedure was followed using 0.201 g (0.498 mmol) of **3f** and 0.226 g (0.996 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 65.7 mg (0.163 mmol, 32.8%) of **4f** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 7.0 Hz, 2H), 7.12−7.25 (m, 6H), 7.01 (m, 1H), 4.21−4.27 (m, 6H), 2.48 (br d, J = 6.8 Hz, 1H), 2.41 (br d, J = 6.8 Hz, 1H), 2.27 (s, 3H), 1.26 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.3, 165.2, 152.0, 151.8, 148.0, 147.6. 138.0, 136.5, 128.42, 128.36, 128.2, 127.6, 127.4, 124.8, 69.5, 61.2, 59.8, 59.5, 21.6, 14.24, 14.22. Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.74; H, 6.49.

*Diethyl 5-(4-tert-Butylphenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4g**).* The general procedure was followed using 0.200 g (0.448 mmol) of **3g**, and 0.203 g (0.896 mmol) of DDQ. After initial purification by chromatography on neutral alumina (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 20% water, 40% methanol, and 40% acetonitrile to yield 47.4 mg (0.107 mmol, 23.9%) of **4g** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.0 Hz, 2H), 7.24−7.33 (m, 6H),

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7.20 (t, J = 7.2 Hz, 1H), 4.19−4.28 (m, 6H), 2.46 (br d, J = 6.8 Hz, 1H), 2.40 (br d, J = 6.8 Hz, 1H), 1.29 (s, 9H), 1.25 (overlapping triplets, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 165.2, 152.4, 151.4, 150.5, 147.7, 147.0, 137.0, 133.3, 128.5, 127.8, 127.3, 127.2, 125.4, 69.2, 61.2, 60.1, 59.3, 34.8, 31.4, 14.2. Anal. Calcd for $C_{29}H_{32}O_4$: C, 78.35; H, 7.26. Found: C, 78.08; H, 7.10.

*Diethyl 5,6-Diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4h**).* The general procedure was followed using 0.249 g (0.638 mmol) of **3h** and 0.292 g (0.29 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by recrystallization from 40% acetonitrile, 30% methanol, 30% water to yield 0.117 g (0.302 mmol, 47.3%) of **4h** as yellow needles: mp (acetonitrile/methanol/water) 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.1 Hz, 4H), 7.17−7.26 (m, 6H), 4.20−4.26 (m, 6H), 2.49 (br d, J = 7.2 Hz, 1H), 2.41 (br d, J = 7.2 Hz, 1H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 151.9, 147.8, 136.5, 128.5, 127.7, 127.4, 69.4, 61.2, 59.7, 14.2. Anal. Calcd for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23. Found: C, 77.24; H, 6.27.

*Diethyl 5-(4-Fluorophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4i**).* The general procedure was followed using 0.410 g (1.00 mmol) of **3i** and 0.463 g (2.04 mmol) of DDQ. After initial purification by chromatography on neutral alumina (10% EtOAc in heptanes), the still impure product was taken up in 10 mL of MTBE and placed in a Rayonet photochemical reactor (equipped with 350 nm bulbs) and irradiated for 1.5 h. The solvent was removed on a rotary evaporator (no heat was applied), and the resulting material was immediately injected (after being suspended in mobile phase with added acetonitrile for solubility) onto the preparative HPLC using a mobile phase of 40% acetonitrile, 40% methanol, and 20% water. The major peak that eluted before 7 min was collected, and the solvent was removed with a rotary evaporator. The residue was suspended as described above and injected onto the HPLC once more, this time collecting the fractions for the major peak that eluted from 7 to 14 min. The solvent was once again removed with a rotary evaporator, after which a final preparative HPLC injection was performed using a mobile phase of 40% acetonitrile, 30% methanol, 30% water, and collecting the fractions that eluted from 20 to 30 min. Removal of the solvent followed by drying in vacuo resulted in the isolation of 88.9 mg (0.221 mmol, 22.1%) of **4i** as a yellow resin: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30−7.34 (m, 4H), 7.20−7.27 (m, 3H), 6.93 (apparent t, J_{app} = 8.7 Hz, 2H), 4.20−4.24 (m, 6H), 2.48 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 2.41 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.21, 165.18, 162.2 (d, J = 248 Hz), 151.9, 151.7, 147.8, 146.9, 136.3, 132.5 (d, J = 3 Hz), 129.4 (d, J = 8 Hz), 128.6, 127.6, 127.6, 115.5, (d, J = 21 Hz), 69.2, 61.3, 59.8, 59.7, 14.2; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −115.8. Anal. Calcd for $C_{25}H_{23}FO_4$: C, 73.88; H, 5.70. Found: C, 73.87; H, 5.64.

*Diethyl 5-(3-Fluorophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4j**).* The general procedure was followed using 0.201 g (0.498 mmol) of **3j** and 0.230 g (1.01 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 46.2 mg (0.115 mmol, 23.1%) of **4j** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.36 (m, 2H), 7.17−7.29 (m, 4H), 7.06−7.13 (m, 2H), 6.88 (tdd, J_t = 8.3 Hz, J_d = 2.6 Hz, J_d = 0.8 Hz, 1H), 4.21−4.27 (m, 6H), 2.49 (br d, J = 6.8 Hz, 1H), 2.42 (br d, J = 6.8 Hz, 1H), 1.26 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 165.0, 162.9 (d, J = 244 Hz), 151.9, 151.7, 149.4, 146.6 (d, J = 2 Hz), 138.6 (d, J = 8 Hz), 136.0, 129.9 (d, J = 8 Hz), 128.6, 127.8, 127.6, 123.4 (d, J = 3 Hz), 114.4 (d, J = 22 Hz), 114.2 (d, J = 21 Hz), 69.3, 61.3, 61.3, 59.9, 59.5, 14.1; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −114.5. Anal. Calcd for $C_{25}H_{23}FO_4$: C, 73.88; H, 5.70. Found: C, 73.62; H, 5.44.

*Diethyl 5-(4-Chlorophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4k**).* The general procedure was followed using 0.220 g (0.517 mmol) of **3k** and 0.240 g (1.06 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile. Final purification by chromatography on silica (10% EtOAc in hexanes) resulted in 0.118 g (0.279 mmol, 54.0%) of **4k** as a yellow oil after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.34 (m, 9H), 4.20−4.26 (m, 6H), 2.48 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 2.41 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.2 Hz); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 151.9, 151.6, 148.7, 146.7, 136.2, 134.9, 133.1, 129.0, 128.7, 128.6, 127.7, 127.6, 69.3, 61.4, 61.3, 59.9, 59.5, 14.24, 14.23. Anal. Calcd for $C_{25}H_{23}ClO_4$: C, 71.00; H, 5.48. Found: C, 70.63; H, 5.40.

*Diethyl 5-(3-Chlorophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4l**).* The general procedure was followed using 0.398 g (0.936 mmol) of **3l** and 0.429 g (1.89 mmol) of DDQ. After initial purification by chromatography on neutral alumina (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 58.7 mg (0.139 mmol, 14.8%) of **4l** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (m, 1H), 7.32−7.35 (m, 2H), 7.12−7.29 (m, 6H), 4.20−4.28 (m, 6H), 2.48 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 2.42 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.1 Hz); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.0, 151.8, 149.5, 146.4, 138.3, 135.9, 134.4, 129.7, 128.6, 127.8, 127.60, 127.57, 127.4, 125.9, 69.3, 61.4, 61.3, 59.8, 59.6, 14.22, 14.19. Anal. Calcd for $C_{25}H_{23}ClO_4$: C, 71.00; H, 5.48. Found: C, 70.85; H, 5.43.

*Diethyl 5-[4-(Trifluoromethyl)phenyl]-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4m**).* The general procedure was applied on 0.215 g (0.469 mmol) of **3m** and 0.215 g (0.947 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in heptanes), the product was purified further by reverse-phase HPLC (30% water, 30% methanol, 40% acetonitrile), followed by normal phase chromatography on silica (10% EtOAc in hexanes) to yield 0.148 g (0.324 mmol, 69.1%) of **4m** as a yellow oil after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49, 7.46 (second order AA′BB′ pattern, J = 8.6 Hz, 4H), 7.22−7.33 (m, 5H), 4.20−4.27 (m, 6H), 2.51 (dt, J_d = 7.1 Hz, J_t = 1.6 Hz, 1H), 2.44 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.1, 151.9, 151.6, 150.6, 146.5, 140.1, 135.9, 129.2 (q, J = 32.2 Hz), 128.7, 128.0, 127.9, 127.7, 125.5 (q, J = 3.6 Hz), 124.3 (q, J = 272 Hz), 69.3, 61.41, 61.40, 60.1, 59.5, 14.2; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −64.2. Anal. Calcd for $C_{26}H_{23}F_3O_4$: C, 68.41; H, 5.08. Found: C, 68.18; H, 5.18.

*Diethyl 5-[3-(Trifluoromethyl)phenyl]-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4n**).* The general procedure was applied on 0.170 g (0.371 mmol) of **3n** and 0.180 g (0.793 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 88.6 mg (0.194 mmol, 52.4%) of **4m** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (br, 1H), 7.50 (br d, J = 7.8 Hz, 1H), 7.45 (br d, J = 7.8 Hz), 7.20−7.35 (m, 6H), 4.21−4.29 (m, 6H), 2.51 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 2.44 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.26 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.03, 164.96, 152.0, 151.7, 150.1, 146.3, 137.2, 135.8, 131.0, 130.9 (q, J = 32.0 Hz), 128.9, 128.7, 128.0, 127.6, 124.4 (q, J = 3.7 Hz), 124.2 (q, J = 274 Hz), 124.0 (q, J = 3.7 Hz), 69.4, 61.39, 61.37, 59.9, 59.4, 14.2, 14.1; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −63.9. Anal. Calcd for $C_{26}H_{23}F_3O_4$: C, 68.41; H, 5.08. Found: C, 68.54; H, 5.18.

*Diethyl 5-(4-Cyanophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4o**).* The general procedure was applied on 0.398 g (0.959 mmol) of **3o** and 0.437 g (1.93 mmol) of DDQ. After initial purification by chromatography on neutral alumina (35% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 72.8 mg (0.176 mmol, 18.4%) of **4o** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52, 7.46 (second order AA′BB′ pattern, J = 8.7 Hz, 4H),

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7.22−7.31 (m, 5H), 4.20−4.28 (m, 6H), 2.51 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 2.44 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.27, 1.25 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.00, 164.97, 152.0, 151.2, 146.2, 141.1, 135.7, 132.3, 128.8, 128.31, 128.28, 127.6, 119.2, 110.7, 69.2, 61.5, 61.4, 60.4, 59.1, 14.25, 14.21. Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.34; H, 5.72; N, 3.38.

*Diethyl 5-(3-Cyanophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4p**).* The general procedure was followed using 0.345 g (0.831 mmol) of **3p** and 0.376 g (1.66 mmol) of DDQ. After initial purification by chromatography on silica (35% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 0.124 g (0.300 mmol, 36.1%) of **4p** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 1H), 7.58 (dm, J_d = 8.0 Hz, 1H), 7.48 (dm, J_d = 8.0 Hz, 1H), 7.34 (td, J_t = 7.9 Hz, J_d = 0.5 Hz, 1H), 7.22−7.30 (m, 5H), 4.21−4.27 (m, 6H);, 2.51 (dt, J_d = 7.1 Hz, J_t = 1.5 Hz, 1H), 2.44 (dt, J_d = 7.1 Hz, J_t = 1.6 Hz, 1H), 1.29, 1.26 (overlapping triplets, J = 7.2 Hz, 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 151.9, 151.5, 151.0, 145.5, 137.8, 135.5, 132.1, 131.1, 130.8, 129.4, 128.8, 128.2, 127.5, 118.8, 112.7, 69.3, 61.5, 61.4, 60.0, 59.3, 14.22, 14.17. Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.53; H, 5.61; N, 3.39. Found: C, 75.47; H, 5.52; N, 3.40.

*Diethyl 5-(4-Nitrophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4q**).* The general procedure was applied on 0.502 g (1.15 mmol) of **3q** and 0.634 g (2.79 mmol) of DDQ. After initial purification by chromatography on silica (35% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 20% water, 40% methanol, and 40% acetonitrile to yield 0.207 g (0.478 mmol, 41.6%) of **4q** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09, 7.53 (second order AA′BB′ pattern, J = 9.0 Hz, 4H), 7.25−7.32 (m, 5H), 4.21−4.30 (m, 6H), 2.54 (dt, J_d = 7.2 Hz, J_t = 1.5 Hz, 1H), 2.47 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.28, 1.26 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 164.8, 152.9, 151.9, 151.1, 146.6, 145.8, 143.1, 135.6, 128.8, 128.4, 128.3, 127.6, 123.8, 69.1, 61.44, 61.39, 60.4, 59.1, 14.2, 14.1. Anal. Calcd for $C_{25}H_{23}NO_6$: C, 69.27; H, 5.35; N, 3.23. Found: C, 69.24; H, 5.37; N, 3.18.

*Diethyl 5-(3-Nitrophenyl)-6-phenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4r**).* The general procedure was followed using 0.240 g (0.552 mmol) of **3r** and 0.250 g (1.10 mmol) of DDQ. After initial purification by chromatography on silica (35% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 0.101 g (0.233 mmol, 42.3%) of **4r** as a yellow resin after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (t, J = 1.9 Hz, 1H), 8.04 (ddd, J = 8.2 Hz, 2.3 Hz, 1.0 Hz, 1H), 7.64 (ddd, J = 7.8 Hz, 1.6 Hz, 1.1 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.25−7.33 (m, 5H), 4.21−4.30 (m, 6H), 2.54 (dt, J_d = 7.2 Hz, J_t = 1.5 Hz, 1H), 2.47 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.29, 1.27 (overlapping triplets, J = 7.1 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.92, 164.87, 151.9, 151.52, 151.45, 148.6, 145.5, 138.2, 135.5, 133.7, 129.4, 128.8, 128.3, 127.5, 122.4, 122.1, 69.3, 61.5, 61.4, 60.1, 59.3, 14.22, 14.19. Anal. Calcd for $C_{25}H_{23}NO_6$: C, 69.27; H, 5.35; N, 3.23. Found: C, 69.09; H, 5.63; N, 3.08.

*Diethyl 5-(3,5-Dimethylphenyl)-6-[3,5-bis(trifluoromethyl)-phenyl]bicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**4s**).* The general procedure was followed using 0.239 g (0.431 mmol) of **3s** and 0.203 g (0.894 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile. After a 60 min forerun, the product was then eluted with 15% water, 65% methanol, and 20% acetonitrile. After removal of the solvent, the resulting material was chromatographed once more on silica (10% EtOAc in hexanes) to yield 97.6 mg (0.177 mmol, 41.0%) of **4s** as a yellow resin (which solidified upon standing) after removal of the solvent and drying in vacuo: mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.67 (s, 1H), 6.92 (s, 3H), 4.21−4.30 (m, 6H), 2.50 (dt, J_d = 7.1 Hz, J_t = 1.6 Hz, 1H), 2.46 (dt, J_d = 7.2 Hz, J_t = 1.6 Hz, 1H), 1.28, 1.27 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.9, 164.7, 152.7, 152.4, 151.2, 144.2, 138.5, 138.4, 135.0, 131.6 (q, J = 33.0 Hz), 130.3, 127.7 (br), 125.1, 123.5 (q, J = 274 Hz), 120.6 (septet, J = 3.7 Hz), 69.4, 61.53, 61.47, 60.3, 58.6, 21.3, 14.2, 14.1; ^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ −64.5. Anal. Calcd for $C_{29}H_{26}F_6O_4$: C, 63.04; H, 4.74. Found: C, 62.70; H, 4.84.

*Diethyl 1-Methyl-5,6-diphenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (**5**).* A 50 mL round bottomed flask was charged with 5.00 g (29.4 mmol) of diethyl acetylenedicarboxyate, 2.40 g (29.6 mmol) of methylcyclopentadiene (freshly cracked from the commercially available dimer), 20 mL of dichloromethane, and a stir bar. After the reaction was allowed to stir overnight at room temperature, the solvent was removed with a rotary evaporator. Kugelrohr distillation of the residue (60 °C, 5 mTorr dynamic vacuum) resulted in the recovery of 6.24 g (25.0 mmol, 84.9%) of the Diels−Alder adduct as a mixture of isomers that was not separated or purified further.

The general procedure for norbornene synthesis was then applied using 1.48 g (7.25 mmol) of iodobenzene, 0.973 g (7.98 mmol) of phenyboronic acid, 2.30 g (9.20 mmol) of the above Diels−Alder adduct mixture, 2.65 g (17.0 mmol) of $K_2CO_3{\cdot}1.5H_2O$, 39 mg (0.15 mmol) of triphenylphosphine, 20 mg (0.089 mmol) of palladium acetate, 15 mL of THF, and 15 mL of water. After the usual workup, the crude product was chromatographed on silica (5% EtOAc in heptanes), during which the product coeluted with residual Diels−Alder adduct. After removal of the solvent, the residual adduct was distilled off of the product with a kugelrohr apparatus (80 °C, 5 mTorr vacuum) over a time period of 3 h. The residue in the pot flask was then recrystallized from methanol to yield 0.288 g (0.713 mmol, 9.83%) of **5** as a white powder: mp 98−99 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98−7.07 (m, 6H), 6.89 (d, J = 7.4 Hz, 2H), 6.4−7.0 (br, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.15−4.30 (m, 2H), 3.75 (br s, 1H), 3.57 (br d, J = 9.8 Hz, 1H), 3.51 (dd, J = 9.6 Hz, 1.4 Hz, 1H), 2.34 (dd, J = 9.6 Hz, 1.2 Hz, 1H), 1.87 (dd, J = 9.6 Hz, 1.7 Hz), 1.38 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 0.96 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 166.8, 163.5, 155.4, 141.9, 141.1, 139.0, 130.7 (br), 128.6, 127.8, 127.6, 126.2, 125.6, 61.4, 61.1, 58.7, 54.8, 49.8, 49.5, 45.4, 14.8, 14.5, 14.4. Anal. Calcd for $C_{26}H_{28}O_4$: C, 77.20; H, 6.98. Found: C, 77.34; H, 6.93.

*Diethyl 1-Methyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**6**).* The general procedure for DDQ dehydrogenation was performed on 0.202 g (0.500 mmol) of **5** and 0.234 g (1.03 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 30% water, 30% methanol, and 40% acetonitrile to yield 79.6 mg (0.198 mmol, 39.6%) of **6** as a slightly yellow oil after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.36 (m, 5H), 7.11−7.20 (m, 5H), 4.39 (t, J = 1.6 Hz, 1H), 4.15−4.33 (m, 4H), 2.42 (dd, J = 6.9 Hz, 1.7 Hz, 1H), 2.38 (dd, J = 6.8 Hz, 1.5 Hz, 1H), 1.29 (overlapping triplets and singlet, J_t = 7.2 Hz, 9H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.1, 163.8, 159.9, 150.8, 150.2, 146.4, 136.8, 135.5, 128.8, 128.6, 128.3, 127.4, 127.22, 127.21, 74.2, 66.4, 61.4, 61.1, 53.1, 15.1, 14.4, 14.3. Anal. Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.66; H, 6.45.

*Ethyl 3,5,6-Triphenylbicyclo[2.2.1]hept-2-ene-2-carboxylate (**7**).* The general procedure for norbornene synthesis was then applied using 0.154 g (0.755 mmol) of iodobenzene, 0.101 g (0.828 mmol) of phenyboronic acid, 0.199 g (0.829 mmol) of ethyl 3-phenylbicyclo[2.2.1]-hepta-2,5-diene-2-carboxylate, 0.265 g (1.70 mmol) of $K_2CO_3{\cdot}1.5H_2O$, 3.9 mg (0.015 mmol) of triphenylphosphine, 1.6 mg (0.0071 mmol) of palladium acetate, 1.5 mL of THF, and 1.5 mL of water. After the usual workup, the crude product was chromatographed on silica (5% EtOAc in hexanes). After removal of the solvent, the crude material was recrystallized from methanol to yield 0.172 g (0.437 mmol, 57.8%) of **7** as a white powder: mp 152−153 °C (MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dm, J_d = 8.2 Hz, 2H), 7.29−7.35 (m, 3H), 7.04 (app t, J_{app} = 7.5 Hz, 4H), 6.91−6.99 (m, 6H), 4.14−4.23 (m, 2H), 3.67 (br d, J = 1.8 Hz, 1H), 3.58 (br d, J = 9.8 Hz, 1H), 3.55 (dd, J = 9.7 Hz, 1.0 Hz, 1H), 3.51 (br d, J = 1.8 Hz, 1H), 2.44 (br d, J = 9.4 Hz, 1H),

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2.08 (dt, J_d = 10.6 Hz, 1.6 Hz, 1H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.5, 161.0, 142.0, 141.8, 136.2, 134.8, 129.0, 128.9, 128.8, 128.0, 127.9, 127.7, 125.8, 125.6, 60.4, 55.7, 50.7, 50.4, 50.0, 44.2, 14.4. Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64. Found: C, 85.48; H, 6.55.

*Ethyl 3,5,6-Triphenylbicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (**8**).* The general procedure for DDQ dehydrogenation was performed on 0.165 g (0.419 mmol) of **7** and 0.191 g (0.841 mmol) of DDQ. After initial purification by chromatography on silica (10% EtOAc in hexanes), the product was purified further by reverse-phase HPLC using a mobile phase of 20% water, 40% methanol, and 40% acetonitrile to yield 41.5 mg (0.106 mmol, 25.3%) of **8** as a slightly yellow oil after removal of the solvent and drying in vacuo: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dm, J = 7.2 Hz, 2H), 7.32−7.34 (m, 2H), 7.15−7.27 (m, 11H), 4.40 (m, 1H);, 4.15−4.33 (m, 3H);, 2.49 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H), 2.42 (dt, J_d = 6.8 Hz, J_t = 1.6 Hz, 1H); ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 165.6, 149.9, 146.3, 138.4, 137.3, 136.6, 135.8, 128.8, 128.65, 128.63, 128.4, 128.0, 127.8, 127.7, 127.4, 127.2, 68.2, 65.4, 60.5, 59.0, 14.4. Anal. Calcd for $C_{28}H_{24}O_2$: C, 85.68; H, 6.16. Found: C, 85.34; H, 6.28.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02025.

^{1}H and ^{13}C {^{1}H} NMR spectra for all new compounds; and UV−visible spectra for compounds listed in Table 2 (PDF)

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Notes

The authors declare no competing financial interest.

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