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Tandem Suzuki Coupling−Norbornadiene Insertion Reactions. A Convenient Route to 5,6-Diarylnorbornene Compounds

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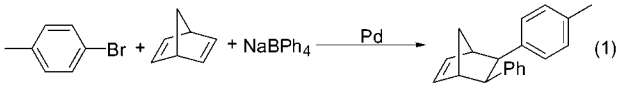
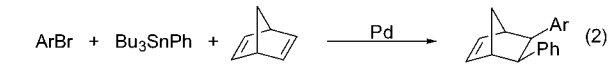
Abstract: This paper presents optimization studies on a palladium-catalyzed tandem norbornadiene insertion−Suzuki coupling reaction, which provides a one-pot procedure for the formation of diarylnorbornene derivatives. This procedure allows for the synthesis of these compounds from readily available aryl halides, arylboronic acids, and substituted norbornadienes.

Reactions that form multiple carbon−carbon single bonds are valuable synthetic tools in that they can be used to form complicated molecular structures in a single step. Our research group has been interested in finding a simple, general route to 5,6-diarylnorbornene diester compounds (**1**), since certain examples can be used as monomers in soluble precursor polymerization routes to conjugated polymers.[1] Chiusoli,[2−4] Larock,[5,6] Torii,[7] Kang,[8] and Kosugi[9−12] have all been active in developing palladium-catalyzed ternary coupling reactions between bicyclic olefins, aryl or vinyl halides, and various nucleophiles. Of these researchers, Chiusoli was the first to develop a route to a 5,6-diarylnorbornene compound by performing a ternary coupling reaction between 4-bromotoluene, norbornadiene, and sodium tetraphenylborate (eq 1).[4] Unfortunately, this route was not general enough



(1)

for our purposes since one of the aryl groups (provided by the tetraphenylborate ion) was restricted to be an unsubstituted phenyl ring. Afterward, Kosugi performed an analogous tandem Stille coupling−norbornadiene insertion reaction (eq 2).[11,12] This allowed for the synthesis of various derivatives; however, for aryl groups other than phenyl, the tin reagents would still have to be synthesized. Also, the formation of toxic tin byproducts, from which the product would have to be purified, was another drawback for this protocol. Novak was able to synthesize a di(*p*-bromophenyl) derivative by performing a tandem Suzuki coupling−norbornadiene insertion reaction (eq 3, Ar and Ar′ = 4-bromophenyl, X = I).[1] This, in theory, could provide the generality we were looking for, since numerous aryl halides and aryl boronic acid compounds are commercially available. However, the yield for this reaction (which was not optimized) was limited to 25%. In this paper, we present optimization studies in which we have been able to improve considerably the yield of the title reaction by varying reaction parameters. We also present the synthesis and characterization of several derivatives to show the scope and utility of the reaction.



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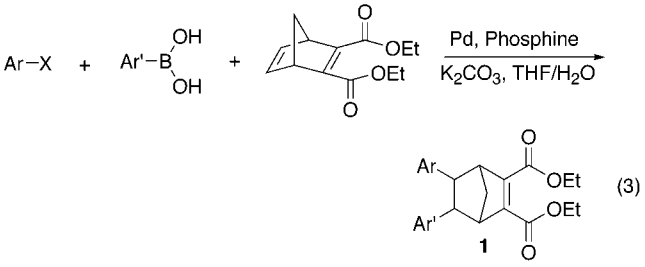

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A possible mechanism, analogous to that proposed for Chiusoli's similar ternary coupling reaction,[4] is presented in Scheme 1. First, oxidative addition of the aryl halide onto a Pd(0) species forms an arylpalladium(II) halide complex (**2**). Then a ligand exchange occurs in which the norbornadiene substitutes for a phosphine to form complex **3**. Alkene insertion results in species **4**, and transmetalation, by which the palladium obtains the other aryl group from the boron, produces complex **5**. Finally, a reductive elimination reaction delivers the product and regenerates the Pd(0) catalyst.

During this cycle, there are a number of side reactions that can occur, resulting in the formation of unwanted byproducts. First of all, a Suzuki coupling reaction can occur without the insertion, resulting in the formation of a biphenyl derivative. Second, arylpalladium(II) halide bisphosphine compounds (e.g., **2**) are known to undergo an aryl−aryl exchange reaction, by which the Pd-bound

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SCHEME 1

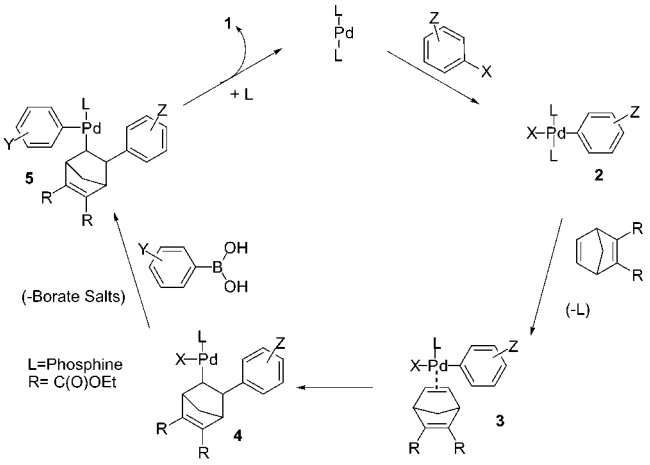

TABLE 1. Microscale Optimization Studies

entry	$[ArB(OR)_2]/[ArI]^a$	$[NBD]/[ArI]^b$	phosphine	% Pd	% yield[c]
1	1.1	1.1	PPh_3	4	76
2	1.1	1.1	P(*o*-Tol)$_3$[d]	4	66
3	1.1	1.1	P(Cy)$_3$[e]	4	58
4	1.1	1.1	P(*t*-Bu)$_3$	4	23
5	1.1	1.1	DTBPB[f]	4	69
6	1.1	1.1	none	4	57
7	0.8	1.1	PPh_3	4	75[g]
8	1.1	2.0	PPh_3	4	80
9	2.0	1.1	PPh_3	4	54
10	1.1	4	PPh_3	4	84
11	1.1	1.1	PPh_3	0.1	70

[a] Ratio of initial equivalents of phenylboronic ester to iodobenzene. [b] Ratio of initial equivalents of norbornadiene diester to iodobenzene. [c] Yield determined by HPLC using 1,4-dimethoxybenzene as an internal standard. [d] Tri(*o*-tolyl)phosphine. [e] Tricyclohexylphosphine. [f] 2-[Di(*tert*-butyl)phosphino]biphenyl. [g] Yield based on limiting phenylboronic ester.

aryl group switches places with a phosphine-bound aryl ring.[13] This would result in the phosphine-derived aryl group being incorporated into the product in lieu of the intended aryl group from the halide. The third is a competing reduction reaction in which species **4** acquires a hydride from the reaction medium, and subsequent reductive elimination would then produce a monoarylnorbornene byproduct.[6] Also, the bicyclic alkene can react with multiple equivalents of aryl halide in a palladium-catalyzed domino reaction to give polyarylated products.[2,14,15] Many of these side reactions have been noted in other palladium-catalyzed coupling reactions, and various phosphine cocatalysts have been developed and used in order to combat them.[12,16−22]

To determine which of these cocatalysts would be most effective for optimizing the yields of our tandem insertion and coupling reactions, we performed several microscale experiments and monitored the results by HPLC (eq 3, Pd = $Pd(OAc)_2$, X = I, Ar′ = Ph, Table 1). Surprisingly, the best phosphine cocatalyst appears to be simple triphenylphosphine, which produced marginally better results than tri(*o*-tolyl)phosphine and di(*tert*-butyl)phosphinobiphenyl and significantly better yields than the other ligands. We also investigated the role of stoichiometry on the reaction with the thought that excess boronic acid (formed in situ by hydrolysis of the 1,3-propanediol ester) and/or norbornadiene diester could improve product yield at the expense of competing reduction and simple biphenyl formation. Excess phenylboronic ester (entry 9) lowered the yield, while excess norbornadiene (entries 8 and 10) improved it marginally. It is noteworthy that satisfactory yields are obtained with only a slight excess of both reagents or even when the boronic acid is limiting (entry 7). This is important because the boron reagent is usually the most expensive component of the reaction, and the norbornadiene diester needs to be synthesized (though the procedure is quite simple) with the amount used in excess being separated from the product at the end. Also, although most of these trials were set up with a large amount of catalyst (4%), successful yields were obtained with catalyst loadings as low as 0.1% (entry 11). A control experiment with no palladium showed no product formation, verifying that a catalyst of some sort is required.

The fact that a significant amount of product was formed without the addition of a cocatalyst (entry 6) raises the question as to whether the phosphine is actually involved in the catalytic cycle. The parent Suzuki coupling reactions are known to proceed readily without phosphine present,[23] and Kang has found palladium-mediated ternary couplings of iodonium salts to occur with ligandless catalyst systems.[8] The kinetics for the reactions with and without the addition of triphenylphosphine were measured side-by-side at 50 °C by removing aliquots at various time intervals and monitoring the appearance of product via HPLC. The observed pseudo-first-order rate constant for the reaction without the phosphine was found to be an order of magnitude faster than that for the reaction with the added cocatalyst (7.0×10^{-2} vs 6.6×10^{-3} s^{-1}). Hence, it appears that the role of the phosphine is to tone down the reactivity of the palladium center and thereby to improve its selectivity for the desired product.

To investigate the scope of the reaction, we performed different ternary couplings using various aryl halide and aryl boronic acid substrates (eq 3, 1 equiv of aryl halide, 1.1 equiv of boronic acid, 1.1 equiv of norbornadiene diester, 4% $Pd(OAc)_2/PPh_3$). For successful trials, we also scaled up the reactions and isolated the products. The results of these experiments are presented in Table 2. From the first three entries, it is apparent that the halide must be iodide in order for the reaction to be successful. As can be seen from the other entries, the reaction is very general for different aryl iodides and different aryl

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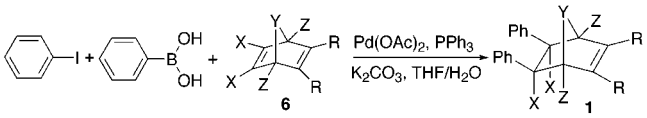
TABLE 2. Scale-Up and Scope

entry	ArX	Ar′	product	% yield[a]
1	chlorobenzene	phenyl	**1a**	<5
2	bromobenzene	phenyl	**1a**	12
3	phenyltriflate	phenyl	**1a**	<5
4	iodobenzene	phenyl	**1a**	76 (63)
5	4-iodonitrobenzene	phenyl	**1b**	(43)
6	4-iodoanisole	phenyl	**1c**	74 (66)
7	1-iodonaphthalene	phenyl	**1d**	(70)
8	4-iodoaniline	phenyl	**1e**	(46)
9	iodobenzene	4-formylphenyl	**1f**	(53)
10	4-iodoaniline	4-aminophenyl[b]	**1g**	(40)
11	2-iodoanisole	phenyl	**1h**	(78)
12	iodobenzene	4-methoxyphenyl	**1c**	(76)
13	iodobenzene	2-methoxyphenyl	**1h**	(72)

[a] Determined by HPLC. Isolated yields are in parentheses. [b] From the pinacol cyclic boronic ester

TABLE 3. Variation of Diene Component



entry	X	Y	Z	R	diene	product	isolated yield
1	H	CH_2	H	COOEt	**6a**	**1a**	63
2	CH_3	$CH(CH_3)$	CH_3	COOEt	**6b**		*a*
3	H	CH_2	H	H	**6c**	**1i**	28
4	H	CH(O*t*-Bu)	H	H	**6d**	**1j**	9[b]
5	H	CH_2CH_2	H	COOEt	**6e**		*c*
6	H	O	H	COOEt	**6f**		*d*

[a] Only biphenyl and residual diene were observed by TLC and GC-MS. [b] Only one isomer could be separated and purified from oligomeric impurities. [c] A trace amount of a possible product was observed in a crude NMR spectrum of the reaction mixture. However, it was not enough (<10%) to purify and characterize. [d] Only starting materials were recovered from the reaction mixture.

boronic acids, with the products being isolated pure in moderate to good yields. Electron-donating groups in the aryl iodide (entries 6, 8, 10, and 11) and aryl boronic acids (entries 10, 12, and 13) do not appear to adversely affect the reaction. For the 4-iodoanisole entry, the HPLC chromatogram revealed evidence for only minor contamination (ca. 6%) by the unsubstituted phenyl product, suggesting that aryl−aryl exchange is not a significant concern under these reaction conditions. This is noteworthy because this side reaction is known to be enhanced by the presence of electron-donating groups.[13,16] Steric hindrance on either the aryl iodide (entries 7 and 11) or the aryl boronic acid (entry 13) also did not appear to have an adverse effect on the reaction.

While the reaction works for a variety of aryl iodide and aryl boronic acid substrates, the choice for the diene component is critical (Table 3). Increased sterics at the active alkene site (entry 2) completely prevent the insertion. However, hindrance of some sort is required at the second olefin to prevent unwanted reactions from occurring there. Both norbornadiene (entry 3) and 7-*tert*-butoxynorbornadiene (entry 4) yielded a sizable amount of oligomeric byproducts, from which it was difficult to purify the desired product. Increasing the bridge size by one carbon (entry 5) similarly resulted in little or no ternary reaction. The failure of the 7-oxo derivative (**6f**) to promote the reaction (entry 6) is somewhat surprising. While other failed trials (entries 2 and 5) resulted primarily in the unhindered formation of biphenyl, the presence of **6f** appeared to prevent completely all coupling reaction. This could be due to a partial retro-Diels−Alder reaction of this component to yield diethyl acetylenedicarboxylate, which we have found to be a potent catalyst poison in these reactions. However, a ^{13}C NMR spectrum of the crude reaction (upon removal of solvent) showed no evidence for the presence of this compound.

Finally, in terms of the stereochemistry of the products, other researchers have found analogous ternary reactions with norbornene (mono olefin) to proceed in a *cis*, *exo* fashion.[10] However, certain reactions involving palladium and norbornadiene (bis olefin) have been found to result in *endo* insertion,[24] while others yield products that have isomerized to a nortricyclyl skeleton.[25] For our products, NMR chemical shifts appear to be consistent with a *cis*, *exo* arrangement of the phenyl rings (based on assignments made on similar compounds in the literature[4]). This stereochemical assignment was unambiguously confirmed with an X-ray crystallographic analysis on compound **1a** (Supporting Information).

In summary, we have successfully developed a one-step procedure for the synthesis of 5,6-diarylnorbornene diester derivatives. The reaction is very general, producing viable isolated yields (as high as 78%) of several products starting from a variety of aryl iodide and aryl boronic acid substrates. We found that simple triphenylphosphine was the best cocatalyst for the reaction, that satisfactory results were obtained with as little as 0.1% catalyst, and that only slight excess amounts of norbornadiene diester and boronic acid were required. Finally, from X-ray crystallography, we have unambiguously determined that the product is formed in a *cis* and *exo* stereochemical fashion.

Experimental Section

General. Diethyl norbornadiene-2,3-dicarboxylate (**6a**),[26] diethyl bicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**6e**),[27] and diethyl 7-oxonorbornadiene-2,3-dicarboxylate (**6f**)[28] were synthesized via literature procedures and purified by careful Kugelrohr distillation under a dynamic vacuum at 65 °C. Similarly, 2-phenyl-1,3,2-dioxaborinane[29] was synthesized as described in the literature. The synthesis of diethyl 1,4,5,6,7-pentamethylbicyclo[2.2.2]hepta-2,5-diene-2,3-dicarboxylate (**6b**) is outlined in Supporting Information. Iodobenzene was vacuum distilled from CaH_2 and stored in the dark in a drybox. All other chemicals and solvents were used as received from chemical suppliers. ^1H and ^{13}C NMR spectra were obtained at 300 and 75 MHz, respectively, using $CDCl_3$ as a solvent and tetramethylsilane as an internal reference. Analytical data were obtained by Robertson Microlit Laboratories, Inc. HPLC chromatograms were obtained using an instrument equipped with a Whatman silica column and a UV−visible detector. Yields were calculated

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on the basis of integrations of the product relative to an internal standard of 1,4-dimethoxybenzene.

General Procedure for Product Isolation. A 50-mL Schlenk flask was charged with aryl halide (2.5 mmol), aryl boronic acid (2.75 mmol), diene (**6**) (2.75 mmol), triphenylphosphine (16 mg, 0.062 mmol), K_2CO_3 (0.912 g, 6.6 mmol), THF (5 mL), water (5 mL), and a stirbar. The mixture was then degassed via three freeze−pump−thaw cycles, and $Pd(OAc)_2$ (6 mg in 250 μL of degassed THF) was added via syringe under a nitrogen backflow. The reaction was degassed once more and placed in a 60 °C oil bath overnight. The two phases were separated, and the aqueous phase was extracted with 2 × 15 mL of CH_2Cl_2. The organic layers were combined, extracted with 5% NaCN (1 × 25 mL) to remove colored palladium impurities, and dried over Na_2SO_4. Afterward, the solvent was removed with a rotary evaporator, and the residue was heated at 60 °C under a dynamic vacuum in a Kugelrohr oven to distill off biphenyl and excess norbornadiene diester. The resulting resin left in the pot was purified by column chromatography (silica gel) and/or recrystallization.

Diethyl 5,6-Diphenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1a). Isolated as a white crystalline solid after chromatography (10% EtOAc in hexanes) and recrystallization from methanol: mp 82.0−84.5 °C (MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85−7.05 (m, 10H), 4.26 (q, J = 7.0 Hz, 4H), 3.51−3.53 (m, 4H), 2.43 (dm, J_d = 9.6 Hz, 1H), 2.07 (dm, J_d = 9.6 Hz, 1H), 1.31 (t, J = 7.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 147.1, 141.2, 128.8, 127.7, 125.7, 60.9, 50.8, 49.2, 45.2, 14.2. Anal. Calcd for $C_{25}H_{26}O_4$: C, 76.90; H, 6.71. Found: C, 76.76; H, 6.45.

Diethyl 5-(4-Nitrophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1b). Isolated as a yellow resin after chromatography (10% EtOAc in hexanes): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (app d, 2H) 6.85−7.05 (m, 7H), 4.28 (q, J = 7.2 Hz, 4H), 3.53−3.60 (m, 4H), 2.41 (dm, J_d = 9.9 Hz, 1H), 2.14 (dm, J_d = 9.9 Hz, 1H), 1.33 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 164.4, 149.3, 147.6, 146.4, 146.1, 140.2, 129.5, 128.6, 128.2, 126.5, 122.8, 61.2, 51.0, 50.5, 49.7, 49.4, 45.1, 14.2. Anal. Calcd for $C_{25}H_{25}NO_6$: C, 68.95; H, 5.79; N, 3.22. Found: C, 68.66; H, 5.54; N, 3.08.

Diethyl 5-(4-Methoxyphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1c). Isolated as a white crystalline solid after chromatography (10% EtOAc in hexanes) and recrystallization from hexanes/CH_2Cl_2: mp 115.0−116.5 °C (hexanes/CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94−7.06 (m, 3H), 6.86−6.91 (m, 2H), 6.78, 6.56 (second-order AA′BB′ pattern, J = 8.7 Hz, 4H), 4.22−4.30 (overlapping quartets, J = 7.2 Hz, 4H), 3.65 (s, 3H), 3.52−3.54 (br, 1H), 3.42−3.47 (m, 3H), 2.39 (dm, J_d = 9.5 Hz, 1H), 2.06 (dm, J_d = 9.5 Hz, 1H), 1.29−1.34 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 157.9, 147.1, 146.8, 141.4, 133.3, 129.6, 128.8, 127.7, 125.6, 113.4, 60.8, 55.2, 51.2, 50.7, 48.9, 48.4, 45.0, 14.1. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.39; H, 6.56.

Diethyl 5-(1-Naphthyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1d). Isolated as a yellow resin after chromatography (10% EtOAc in hexanes): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (app d, 1H), 7.58 (app d, 1H), 7.50 (app d, 1H), 7.24−7.34 (m, 5H), 6.78−6.81 (m, 2H), 6.69−6.71 (m, 2H), 4.22−4.34 (m, 4H), 4.16 (br. d, J = 9.6 Hz, 1H), 3.76 (d, J = 1.2 Hz, 1H), 3.70 (br. d, J = 9.6 Hz, 1H), 2.64 (br. d, J = 9.6 Hz, 1H), 2.12 (br. d, J = 9.6 Hz, 1H), 1.34 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 164.6, 147.7, 147.0, 140.8, 138.1, 133.5, 132.9, 128.6, 128.4, 127.1, 126.8, 125.8, 125.3, 125.2, 124.9, 124.8, 123.2, 61.0, 53.0, 50.2, 50.1, 45.3, 44.6, 14.2, 14.2. Anal. Calcd for $C_{29}H_{28}O_4$: C, 79.04; H, 6.41. Found: C, 78.74; H, 6.55.

Diethyl 5-(4-Aminophenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1e). Isolated as yellow crystals (MeOH): mp 151.0−152.5 °C (MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95−7.07 (m, 3H), 6.86−6.91 (m, 2H), 6.64, 6.35 (second-order AA′BB′ pattern, J = 8.4 Hz, 4H), 4.22−4.29 (overlapping quartets, J = 7.2 Hz, 4H), 3.35−3.51 (multiple broad resonances, 6H), 2.37 (br d, J_d = 9.3 Hz, 1H), 2.02 (dm, J_d = 9.3 Hz, 1H), 1.28−1.34 (overlapping triplets, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 164.7, 147.3, 146.7, 144.2, 141.6, 131.2, 129.6, 128.9, 127.6, 125.6, 114.8, 60.8, 51.3, 50.7, 48.8, 48.5, 45.1, 14.1. Anal. Calcd for $C_{25}H_{27}NO_4$: C, 74.05; H, 6.71; N, 3.45. Found: C, 73.78; H, 6.45; N, 3.41.

Diethyl 5-(4-Formylphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1f). Isolated as a yellow resin after chromatography (10% EtOAc in hexanes): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.83 (s, 1H), 7.53, 7.06 (second-order AA′BB′ pattern, J = 8.1 Hz, 4H), 6.85−7.05 (m, 5H), 4.28 (q, J = 7.1 Hz, 4H), 3.55−3.57 (m, 4H), 2.43 (dm, J_d = 9.8 Hz, 1H), 2.13 (dm, J_d = 9.8 Hz, 1H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.5, 164.5, 164.4, 148.7, 147.4, 146.4, 140.4, 134.4, 129.4, 129.0, 128.6, 127.9, 126.1, 61.1, 50.8, 50.4, 49.5, 45.2, 14.2. Anal. Calcd for $C_{26}H_{26}O_5$: C, 74.62; H, 6.26. Found: C, 74.49; H, 6.29.

Diethyl 5,6-Di(4-aminophenyl)bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1g). Isolated as tan crystals after chromatography (2% EtOH in $CHCl_3$) and recrystallization from methanol: mp 172.5−174.0 °C (MeOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66, 6.38 (second-order AA′BB′ pattern, J = 8.4 Hz, 8H), 4.25 (q, J = 7.2 Hz, 4H), 3.32−3.45 (multiple broad resonances, 8H), 2.32 (br d, J_d = 9.6 Hz, 1H), 1.98 (dm, J_d = 9.3 Hz, 1H), 1.30 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 146.9, 143.9, 131.4, 129.5, 114.7, 60.8, 50.8, 47.6, 45.1, 14.1. Anal. Calcd for $C_{25}H_{28}N_2O_4$: C, 71.41; H, 6.71; N, 6.66. Found: C, 71.17; H, 6.83; N, 6.46.

Diethyl 5-(2-Methoxyphenyl)-6-phenylbicyclo[2.2.1]hept-2-ene-2,3-dicarboxylate (1h). Isolated as a clear resin after chromatography (10% EtOAc in hexanes): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76−7.11 (m, 9H), 6.41 (app d, J_{app} = 8.1 Hz, 1H), 4.21−4.31 (overlapping quartets, J = 6.9 Hz, 4H), 3.68 (br d, J = 9.9 Hz, 1H), 3.59 (br d, J = 1.2 Hz, 1H), 3.49 (br d, J = 9.9 Hz, 1H), 3.46 (s, 3H), 3.31 (br d, J = 1.2 Hz, 1H), 2.44 (dm, J_d = 9.3 Hz, 1H), 2.03 (dm, J_d = 9.3 Hz, 1H), 1.28−1.35 (overlapping triplets, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9, 164.3, 157.1, 148.0, 146.2, 141.5, 130.2, 128.5, 127.0, 126.9, 125.9, 125.5, 119.9, 109.4, 60.9, 54.4, 52.3, 49.2, 48.3, 45.2, 42.2, 14.1. Anal. Calcd for $C_{26}H_{28}O_5$: C, 74.26; H, 6.71. Found: C, 74.19; H, 6.75.

5,6-Diphenylbicyclo[2.2.1]hept-2-ene (1i). Isolated as a white crystalline solid after chromatography (petroleum ether) and recrystallization from ligroin: mp 86.5−88.5 °C (ligroin); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89−7.25 (m, 10H), 6.43 (s, 2H), 3.19 (s, 2H), 3.11 (s, 2H), 2.31 (dm, J_d = 8.4 Hz, 1H), 1.77 (dm, J_d = 8.7 Hz, 1H) [lit.[8] (400 MHz, $CDCl_3$) δ 6.89−7.26 (m, 10H), 6.44 (d, J = 1.8 Hz, 2H), 3.21 (d, J = 1.8 Hz, 2H), 3.11 (m, 2H), 2.32 (d, J = 8.8 Hz, 1H), 1.78 (m, 1H)].

7-*tert*-Butoxy-5,6-diphenylbicyclo[2.2.1]hept-2-ene (1j). Isolated as a white crystalline solid after chromatography (petroleum ether): mp 85.0−88.0 (not recrystallized); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18−7.20 (m, 4H), 6.98−7.00 (m, 6H), 6.30 (s, 2H), 3.74 (s, 1H), 3.42, (s, 2H), 3.00 (s, 2H), 1.19 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 136.5, 131.5, 126.5, 124.8, 85.1, 74.4, 51.5, 49.9, 27.9. Anal. Calcd for $C_{23}H_{26}O$: C, 86.75; H, 8.23. Found: C, 86.52; H, 8.20.

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Supporting Information Available: X-ray crystallographic characterization data for **1a**. Synthesis and characterization data for **6b**, and experimental procedures for microscale and kinetics experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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