Synthesis of Bicyclo[4.1.0]heptenes via Palladium-Catalyzed Intramolecular Coupling−Cyclization of 3-(Cyclohexa-2,4-dienyl)pentane-2,4-dione with β-Styryl Bromides†

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Palladium-catalyzed intramolecular coupling−cyclization of 3-(cyclohexa-2,4-dienyl)pentane-2,4-dione with β-styryl bromides proceeds in regio- and stereoselective fashions to give 2-styryl-substituted bicyclo-[4.1.0]hept-3-enes in good yields. The formation of the bicyclo[4.1.0]hept-3-enes was rationalized by starting with oxidative addition of $Pd(PPh_3)_4$ to the carbon−bromine bond of β-styryl bromide (RBr) to give Pd(R)BrLn. Reaction of Pd(R)BrLn with Ag_2CO_3 generates a cationic RPd(II)Ln species. Chelation of the RPd(II)Ln cation to both the O-enolate of the ketone and the proximal double bond followed by attack of the enolate on the activated double bond gave a bicyclic η^1-allylpalladium intermediate. The postulated bicyclic η^1-allylpalladium intermediate leads to 2-styryl-substituted bicyclo[4.1.0]hept-3-enes with exclusive regio- and stereoselectivities after reductive elimination.

Introduction

Cyclopropane rings play an important role in many natural products, biologically active compounds, and theoretically interesting molecules and are useful intermediates in organic synthesis.[1] There are numerous methods for synthesis of cyclopropanes.[2] In general, chemical syntheses of cyclopropane derivatives include the halomethyl-metal-mediated cyclopropanation of olefins,[3a,b] the transition-metal-catalyzed carbene-transfer reaction from diazo compounds,[3c] the nucleophilic-addition/ring-closing sequence of Michael acceptors,[3d,e] Fischer carbene mediated cyclopropanation of olefins and 1,3-dienes,[3f−i] oxidatively induced reductive elimination of (pentadienyl)iron complexes,[3j] and group IV organometallic complex assisted cyclopropane formation of esters,[3k] amides,[3l] and allylic alcohols.[3m,n] Recently, developments of the electrophilic activation of unsaturated carbon−carbon bonds using gold,[4a,b] platinum,[4c,d] ruthenium,[4e] palladium,[4f] and rhodium[4g] complexes or salts to produce fused cyclopropanes were reported. Although, Pd(0)-catalyzed intramolecular coupling−cyclization of 2-allenylmalonates with organic halides generating cyclopropanes was documented,[5] the similar Pd-catalyzed intramolecular coupling−cyclization of 2-allyl-1,3-dicarbonyl compounds with organic halides proceeded in O-alkylation fashion to produce dihydrofuran and -pyran derivatives.[6] Moreover, metal-catalyzed (metal = Pd, W, Pt, or Ru) intramolecular addition of 1,3-cycloalkyldiones to alkynes also underwent O-alkylation to afford fused oxabicyclic systems.[7] Recently, we have found that palladium-catalyzed reaction of aryl bromides with 7-hydroxy-1,3-dienes in the presence of NaO^tBu led to 1,2- or 1,4-alkoxyarylation to the conjugated dienes.[8] To continue our interest in addition reactions of various nucleophiles across conjugated dienes, we now focus on palladium-catalyzed intramolecular addition of 1,3-diketones to 1,3-dienes. It must be mentioned that the palladium-catalyzed intramolecular 1,4-addition reactions of a wide range of hetero and carbon nucleophiles to conjugated dienes have been well-developed.[9] These reactions, which proceed via (π-allyl)palladium intermediates, are highly regio- and stereoselective and can be controlled to yield either an

† This paper is dedicated to the memory of the late professor Yoshihiko Ito in grateful recognition for his contribution to synthetic organic chemistry.

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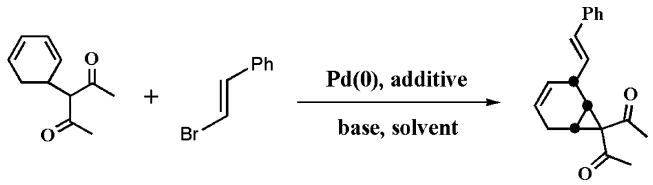
Table 1. Pd-Catalyzed Cyclopropanation−Styrylation Reaction of 3-(Cyclohexa-2,4-dienyl)pentane-2,4-dione with *trans*-β-Bromostyrene



entry	catalyst	solvent	additive	base	*T* (°C)	time (h)	yield (%)
1	5 mol % $Pd(PPh_3)_4$	CH_3CN	*n*-Bu_4NBr	K_2CO_3	reflux	16	0
2	3 mol % $Pd(OAc)_2$	DMF	*n*-Bu_4NCl	Na_2CO_3	80	16	0
3	5 mol % $Pd(OAc)_2$, dppe	DME		NaH	60	16	0
4	2 mol % $Pd(PPh_3)_4$	THF		NaO*t*Bu	reflux	16	0
5	2 mol % $Pd(PPh_3)_4$	THF		K_2CO_3	reflux	16	0
6	2 mol % $Pd(PPh_3)_4$	THF	Ag_2CO_3		reflux	12	56
7	2 mol % $Pd(PPh_3)_4$ dpe-phos	THF	Ag_2CO_3		reflux	8	82
8	2 mol % $Pd(PPh_3)_4$	THF	Ag_2CO_3	K_2CO_3	reflux	4	84

overall *trans*- or *cis*-diallylically functionalized products. The synthetic utility of these 1,4-additions of nucleophiles to 1,3-dienes has been successfully demonstrated in natural product synthesis. In this paper, we report that Pd-catalyzed intramolecular coupling−cyclization of 3-(cyclohexa-2,4-dienyl)pentane-2,4-dione with β-styryl bromides in the presence of Ag_2CO_3 and K_2CO_3 in refluxing THF resulted in 1,2-addition of 1,3-diketone to 1,3-cyclohexadienes to produce 2-styryl-substituted bicyclo[4.1.0]hept-3-enes in diastereoselective fashion. The reaction was suggested to start with oxidative addition of $Pd(PPh_3)_4$ to the carbon−bromine bond of β-styryl bromides (RBr) to give Pd(R)BrLn. Reaction of Pd(R)BrLn with Ag_2CO_3 produced a cationic RPd(II)Ln species. Chelation of the cationic palladium(II) to both the O-enolate of the ketone and the proximal double bond followed by attack of the enolate on the activated double bond gave a bicyclic η^1-allylpalladium intermediate, which led to 2-styryl-substituted bicyclo[4.1.0]hept-3-enes after reductive elimination.

Results and Discussion

The requisite 3-(cyclohexa-2,4-dienyl)pentane-2,4-dione (**1**) was prepared from addition of sodium pentane-2,4-dionate to (η^5-cyclohexadienyl)tricarbonyliron cation salt in THF according to literature procedures.[10] Decomplexation of the resulting 3-(cyclohexa-2,4-dienyl)pentane-2,4-dionetricarbonyliron complex with cerium ammonium nitrate (CAN) in acetone at 0 °C afforded **1** in 91% overall yield. For our test reaction of Pd-catalyzed cyclopropanation−styrylation reaction, we chose the coupling of **1** with β-bromostyrene. In this reaction, four parameters were examined (catalyst, base, additive, and solvent), and results of the optimization are shown in Table 1. As can be seen in Table 1, reaction of **1** with β-bromostyrene using Ma's[5] (Table 1, entry 1) or Larock's[6] (Table 1, entry 2) protocol for addition of diketo anions to the internal diene resulted in recovery of the starting dienyldione **1**. Changing the base or solvent did not affect the reaction outcome (Table 1, entries 3−5). However, addition of 1.0 equiv of Ag_2CO_3 to the mixture of **1** and 2 mol % of $Pd(PPh_3)_4$ afforded the styryl-substituted bicyclo[4.1.0]heptene **3a** in 56% yield (Table 1, entry 6). Moreover, addition of 2 mol % of bis(2-diphenylphosphinophenyl) ether (dpe-phos) together with 2 mol % of $Pd(PPh_3)_4$ and 1.0 equiv of Ag_2CO_3 to **1** in refluxing THF increased the yield of **3a** to 82% (Table 1, entry 7), while using the combination of $Pd(PPh_3)_4$ and Ag_2CO_3 as the catalyst and K_2CO_3 as the base in refluxing THF gave the best result. Thus, treatments of **1** with 2.0 equiv of β-bromostyrene, 3.0 equiv of K_2CO_3, 1.0 equiv of Ag_2CO_3, and 2 mol % of $Pd(PPh_3)_4$ in refluxing THF under nitrogen for 4 h smoothly produced 1,1′-(2-styrylbicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (**3a**) in 84% yield (Table 1, entry 8). NOE experiments provided the initial evidence for support of all *syn* relationships among hydrogen atoms at C(a), C(b), and C(c) of **3a** (Table 2). It is important to note that three stereogenic centers of **3a** are created; however, only the single diastereomer shown was isolated. The high diastereoselectivity observed in the formation of **3a** may be rationalized according to paths outlined in Scheme 1. Oxidative addition of $Pd(PPh_3)_4$ to the carbon−bromine bond of β-styryl bromide (RBr) gave LnPd(R)Br, which upon treatment with Ag_2CO_3 produced the electrophilic LnPdR cationic species **2**. Coordination of the ketone to the Pd center afforded intermediate **4**. The acidity of the proton situated α to the carbonyl would be increased, and subsequent deprotonation by the weak base (K_2CO_3) and

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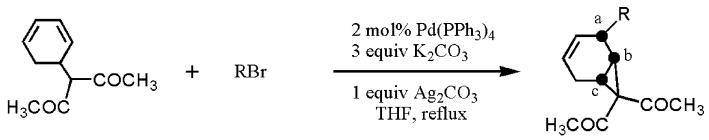
Table 2. Synthesis of Bicyclo[4.1.0]heptenes via Palladium-Catalyzed Reaction of Styryl Bromides with 3-(Cyclohexa-2,4-dienyl)pentan-2,4-dione



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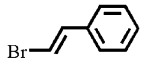
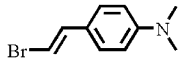
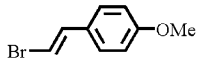
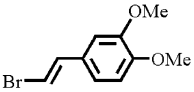
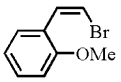
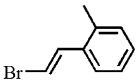
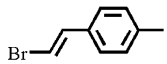
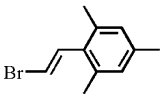
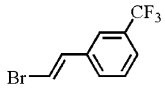
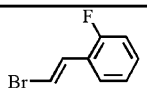
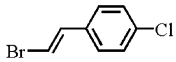
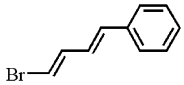
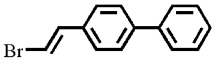
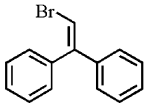
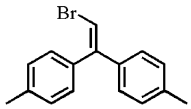
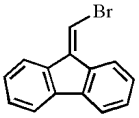
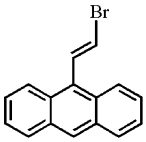
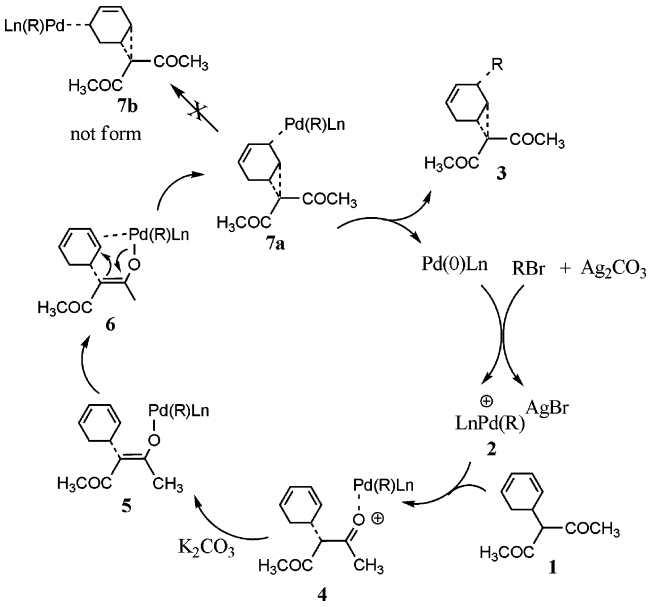
1		4	**3a**	84%
2		8	**3b**	72%
3		2	**3c**	81%
4		3	**3d**	62%
5		8	**3e**	65%
6		4	**3f**	80%
7		4	**3g**	72%
8		6	**3h**	76%
9		16	**3i**	41%

entry	RBr	time (h)	product	(%)
10		24	**3j**	26%
11		6	**3k**	77%
12		4	**3l**	70%
13		4	**3m**	65%
14		6	**3n**	74%
15		4	**3o**	85%
16		3	**3p**	80%
17		5	**3q**	70%

formation of O-bound Pd-enolate **5** would be possible.[11] It should be noticed that structures of transition metal enolates include C-bound and O-bound enolates of carbonyl compounds. The enolate complex from **1** with the α-methine proton, such as **5**, should be O-bound to avoid a structure with a tertiary alkyl bound to palladium. O-Bound Pd-enolates are known with fully substituted and sterically hindered Pd-enolates of ketones.[11] Chelation of the Pd(II) metal center to the proximal double bond from the bottom face would give the PdR(enolate)Ln−olefin intermediate **6**. Attack of the enolate on the double bond activated by the Pd(II) generated the bicyclic η^1-allylpalladium intermediate **7a**. Intermediate **7a** led to **3** after C−C bond-forming reductive elimination and release of the Pd(0) catalyst into the catalytic cycle. Rearrangement of η^1-allylpalladium intermediate **7a** could occur to provide η^1-allylpalladium intermediate **7b**, which would led to 1,4-cyclopropanation−styrylation products. However, only 1,2-cyclopropanation−styrylation products were isolated. It is suggested that the C−C bond-forming reductive elimination occurs from intermediate **7a** at a rate that was faster than $\eta^1-\eta^3-\eta^1$ allylic rearrangement. This Pd-catalyzed 1,2-addition of two carbon nucleophiles to conjugated dienes is different from those found in the Pd-catalyzed 1,4-dioxylation of conjugate dienes.[9] To explore the scope of the coupling partner with **1**, a variety of styryl bromides were examined using the optimized reaction conditions described above. Results of cyclopropanation−styrylation of **1** with various β-styryl bromides are listed in Table 2. The reaction proceeded smoothly with electron-rich and -neutral β-styryl bromides. Electron-rich β-styryl bromides, (*E*)-4-(2-bromovinyl)-*N*,*N*-dimethylaniline, 1-((*E*)-2-bromovinyl)-4-methoxybenzene, 4-((*E*)-2-bromovinyl)-1,2-dimethoxybenzene, and 1-((*Z*)-2-bromovinyl)-2-methoxybenzene, were viable coupling partners,

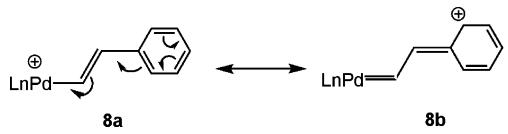
(11) For palladium-catalyzed arylation of carbonyl compounds, see: (a) Culkin, D.; Hartwig, J. F. *Acc. Chem. Res.* **2003**, *36*, 234. (b) Beare, N. A.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 541. (c) Fox, J. M.; Huang, X.; Chieffi, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 1360. (d) Hamada, T.; Chieffi, A.; Ahman, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1261.

Scheme 1



as the yields of desired products **3b**−**e** ranged from 62% to 81% (Table 2, entries 2−5). Notably, the sterically congested *Z*-form styryl bromide, 1-((*Z*)-2-bromovinyl)-2-methoxybenzene, also coupled with **1** to provide **3e** in 65% yield (Table 2, entry 5). In addition, the nitrogen-containing *β*-styryl bromide such as (*E*)-4-(2-bromovinyl)-*N*,*N*-dimethylaniline was proven to be a good substrate for cyclopropanation−styrylation. The dimethylamino group did not inhibit the catalytic activity of the palladium species, as evidenced by a good yield (72%) of bicyclo[4.1.0]heptene **3b** (Table 2, entry 2). Likewise, electron-neutral *β*-styryl bromides smoothly reacted with **1** to produce 2-styryl-substituted bicyclo[4.1.0]hept-3-enyl compounds **3f**−**h** in 72% to 80% yields. *β*-Styryl bromides bearing an electron-deficient group on the benzene ring also coupled with **1** to generate bicyclo[4.1.0]heptenes, albeit with significantly lower yields. For example, the substrate with a trifluoromethyl group at the *m*-position of the benzene ring reacted more slowly and required 16 h for the complete consumption of the dienone **1**, but still afforded bicyclo[4.1.0]heptene **3i** in 41% yield (Table 2, entry 9). The *β*-styryl bromide containing an *O*-fluoro group on the benzene ring was even less reactive and required a prolonged reaction time (24 h) to afford bicyclo[4.1.0]heptene **3j** in only 26% yield (Table 2, entry 10). We suggested that the electronic deficiency of the *β*-styryl bromides may retard the initial oxidative addition of $Pd(PPh_3)_4$ to the carbon−bromine bond of the bromides. Dienylbromide, for example 1-((1*E*,3*E*)-4-bromobuta-1,3-dienyl)benzene, also reacted with **1** under the same reaction conditions to afford bicyclo[4.1.0]-heptene **3l**, in 70% yield (Table 2, entry 12). Moreover, *β*-styryl bromides bearing an additional benzene ring did not interfere with the coupling−cyclization reaction. For example, 2-bromo-1,1-diphenylethene and 2-bromo-1,1-di-*p*-tolylethene reacted with **1** to produce bicyclo[4.1.0]heptenes **3n** (74%, Table 2, entry 14) and **3o** (85%, Table 2, entry 15), respectively. The structure elucidation of **3o** was accomplished by X-ray diffraction analysis. The all-*syn* relative stereochemistry of **3o**, derived from *syn* addition of the diketo anion and the styryl group to the double bond, further supports the proposed reaction paths in Scheme 1. Furthermore, 9-(bromomethylene)-9*H*-fluorene and 10-((*E*)-2-bromovinyl)anthracene reacted with **1** to afford **3p** (80%, Table 2, entry 16) and **3q** (70%, Table 2, entry 17), respectively.

Attempted coupling of aryl bromides or vinyl bromides with **1** failed to give bicyclo[4.1.0]heptenyl compounds. For example, treatment of **1** with bromobenzene or (bromoethylene)cyclohexane resulted in recovery of the starting dienedione **1** under the same reaction conditions. Thus, the formation of 2-styryl-substituted bicyclo[4.1.0]heptenes is limited to styryl bromides. It is suggested that the cationic Pd(II) species **2** may be better stabilized by styryl moieties than vinyl or aryl substituents via resonance structures **8a** and **8b** (eq 1).



8a **8b** (1)

Moreover, substrates bearing electron-donating substituents (**3b**−**e**) or more conjugated double bonds (**3l**−**q**) favor the resonance structures and undergo cyclopropanation−styrylation smoothly to give bicyclo[4.1.0]heptanes in good yields. On the contrary, *β*-styryl bromides containing an electronic-deficient group (**3i**−**j**), for example a fluoro atom (**3i**) or a trifluoromethyl moiety (**3j**), do not favor resonance structures **8a** and **8b** and gave poor yields of bicyclo[4.1.0]heptanes.

In summary, a palladium-catalyzed intramolecular cyclopropanation−styrylation of 3-(cyclohexa-2,4-dienyl)pentane-2,4-dione (**1**) with *β*-styryl bromides has been successfully developed. The diketo anion added to the unactivated diene in the presence of a catalytic amount of $Pd(PPh_3)_4$, 1 equiv of Ag_2CO_3, and 3 equiv of K_2CO_3 in good yields to give 2-styryl-substituted bicyclo[4.1.0]heptenes with exclusive regio- and stereoselectivities. The *β*-styryl bromide containing a tertiary amino group was tolerated. It was found that electron-rich and -neutral *β*-styryl bromides were better coupling partners than electron-deficient *β*-styryl bromides. The resulting bicyclo[4.1.0]-heptenyl compounds are useful synthetic intermediates that can be used for further synthetic transformations.

Experimental Section

General Considerations. All reactions were run under a nitrogen atmosphere in oven-dried glassware unless otherwise indicated. Anhydrous solvents or reaction mixtures were transferred via an oven-dried syringe or cannula. Tetrahydrofuran (THF) was predried by molecular sieves and then by passing through an Al_2O_3 column.[12] Flash column chromatography, following the method of Still, was carried out with E. Merck silica gel (Kieselgel 60, 230−400 mesh) using the indicated solvents.[13] ^1H nuclear magnetic resonance (NMR) spectra were obtained with Bruker-AC 400 (400 MHz) and 500 (500 MHz) spectrometers. The chemical shifts are reported in parts per million with either tetramethylsilane (0.00 ppm) or $CDCl_3$ (7.26 ppm) as internal standard. ^{13}C NMR spectra were recorded with Bruker-AC 400 (100 MHz) and 500 (125 MHz) spectrometers with $CDCl_3$ (77.0 ppm) as the internal standard. Infrared (IR) spectra were recorded with a JASCO IR-700 spectrometer. Mass spectra were acquired on a JEOL JMS-D 100 spectrometer at an ionization potential of 70 eV and were reported as mass/charge (*m*/*e*) with percent relative abundance. High-resolution mass spectra were obtained with an AEI MS-9 double-focusing mass spectrometer and a JEOL JMS-HX 110 spectrometer at the Department of Chemistry, Central Instrument Center, Taichung, Taiwan.

Synthesis of 3-(Cyclohexa-2,4-dienyl)pentane-2,4-dione (1). Compound **1** was synthesized starting from addition of 1.0 molar equiv of sodium hydride to (η^5-cyclohexadienyl)$Fe(CO)_3$ cation salt

(12) Pangborn A. B.; Giardello M. A.; Grubbs R. H.; Rosen R. K.; Timmers F. J. *Organometallics* **1996**, *15*, 1518.

(13) Still, W. C.; M. Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

(3.06 g, 10 mmol) to give [3-(η^4-2,4-cyclohexadienyl)-2,4-pentanedione]$Fe(CO)_3$ complex (3.12 g, 9.81 mmol).[8] To the iron complex in 100 mL of acetone at 0 °C under nitrogen was added cerium ammonium nitrate (16.8 g, 30.6 mmol) in three portions. The reaction mixture was stirred at 30 °C for 1 h. The reaction mixture was then quenched with saturated aqueous sodium bicarbonate solution at 0 °C and was diluted with 100 mL of ether. The resultant solution was washed with water (100 mL × 3) and brine (100 mL × 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture. The crude mixture was purified by flash-column chromatography (silica gel, gradient elution 3−10% ethyl acetate in hexanes) to give **1** (1.66 g, 9.3 mmol, 93%) as a yellow powder: mp 40−42 °C; IR (CH_2Cl_2) 2935, 2425, 2312, 1712, 1522, 1415, 1245 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.93 (m, 2 H), 5.73 (m, 1 H), 5.59 (m, 1 H), 3.94 (d, J = 10.6 Hz, 1 H), 3.12 (m, 1 H), 2.33 (m, 1 H), 2.18 (s, 3 H), 2.16 (s, 3 H), 1.91 (m, 1 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 203.53, 203.36, 126.38, 125.80, 124.90, 124.20, 71.04, 32.29, 30.21, 29.33, 25.93; MS (EI) *m*/*e* 178.2 (M^+, 2), 159.2 (16), 135.2 (17), 117.2 (65), 100.1 (64), 85.1 (100); HRMS (EI) *m*/*e* calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0985.

General Procedure for Synthesis of 2-Styryl-Substituted Bicyclo[4.1.0]heptanes by Palladium-Catalyzed Reaction of Styryl Bromides with 3-(Cyclohexa-2,4-dienyl)pentane-2,4-dione (1). To an oven-dried 100 mL round-bottom flask equipped with a stirrer bar and a condenser and capped with a rubber septa were added $Pd(PPh_3)_4$ (23.0 mg, 0.02 mmol), (*E*)-(2-bromovinyl)benzene (0.37 g, 2.0 mmol), potassium carbonate (0.41 g, 3.0 mmol), and silver carbonate (0.28 g, 1.0 mmol). The apparatus was evacuated (oil pump) and filled with nitrogen three times. The reaction mixture was then added via syringe to 3-(cyclohexa-2,4-dienyl)pentane-2,4-dione (**1**) (0.18 g, 1.0 mmol) in 30 mL of THF. The resulting mixture was heated at reflux under nitrogen until no **1** was detected (ca. 4 h) on TLC. The reaction mixture was cooled to room temperature and was then filtered through a bed of Celite. The filtrate was concentrated *in vacuo* to give the crude mixture.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-Styrylbicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3a). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-(2-bromovinyl)benzene (0.37 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3a** (0.24 g, 0.84 mmol, 84%) as a yellow liquid: IR (CH_2Cl_2) 2915, 1768, 1608, 1312, 1240 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, J = 7.6 Hz, 2 H), 7.31 (t, J = 7.8 Hz, 2 H), 7.22 (m, 1 H), 6.63 (dd, J = 15.9, 7.4 Hz, 1 H), 6.50 (d, J = 16.0 Hz, 1 H), 5.53 (m, 2 H), 3.48 (m, 1 H), 2.59 (dd, J = 18.8, 4.2 Hz, 1 H), 2.50 (dt, J = 18.8, 5.1 Hz, 1 H), 2.28 (s, 3 H), 2.18 (dd, J = 9.5, 4.7 Hz, 1 H), 2.14 (s, 3 H), 2.07 (dd, J = 9.3, 4.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.84, 202.63, 137.21, 131.98, 130.46, 129.91, 128.50, 127.27, 126.23, 124.70, 48.94, 36.39, 34.25, 32.17, 27.81, 26.43, 21.86; MS (EI) *m*/*e* 280.4 (M^+, 7), 262.3 (30), 237.3 (24), 219.3 (31), 179.2 (40), 165.2 (36), 103.1 (42), 91.1 (100), 77.1 (39); HRMS (EI) *m*/*e* calcd for $C_{19}H_{20}O_2$ 280.1463, found 280.1467.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(4-(Dimethylamino)styryl)bicyclo-[4.1.0]hept-3-ene-7,7-diyl)diethanone (3b). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-4-(2-bromovinyl)-*N*,*N*-dimethylaniline (0.45 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3b** (0.23 g, 0.72 mmol, 72%) as a yellow liquid: IR (CH_2Cl_2) 2921,1685, 1609, 1357, 1224; ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.6 Hz, 2 H), 6.70 (d, J = 8.6 Hz, 2 H), 6.44 (d, J = 11.5 Hz, 1 H), 6.00 (t, J = 11.6 Hz, 1 H), 5.51 (m, 2 H), 3.88 (m, 1 H), 2.94 (s, 6 H), 2.57 (br. d, J = 18.1 Hz, 1 H), 2.47 (br. d, J = 18.4 Hz, 1 H), 2.33 (s, 3 H), 2.13 (s, 3 H), 2.05 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.04, 202.75, 149.24, 131.61, 130.55, 129.65, 129.60, 124.46, 112.20, 48.96, 40.44, 35.52, 32.04, 31.96, 27.69, 26.12, 21.79; MS (EI) *m*/*e* 323.3 (M^+, 99), 308.3 (32), 280.3 (23), 224.2 (22), 147.1 (23), 134.1 (100), 121.1 (54); HRMS (EI) *m*/*e* calcd for $C_{21}H_{25}NO_2$ 323.1885, found 323.1888.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(4-Methoxystyryl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3c). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-4-methoxybenzene (0.41 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3c** (0.25 g, 0.81 mmol, 81%) as a yellow liquid: IR (CH_2Cl_2) 2688, 1695, 1504, 1374, 1285, 1020 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.7 Hz, 2 H), 6.86 (m, 2 H), 6.46 (m, 2 H), 5.52 (m, 2 H), 3.81 (s, 3 H), 3.46 (m, 1 H), 2.61 (m, 1 H), 2.51 (m, 1 H), 2.28 (s, 3 H), 2.17 (dd, J = 9.1, 4.5 Hz, 1 H), 2.14 (s, 3 H), 2.07 (dd, J = 9.4, 5.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.91, 202.72, 159.02, 130.14, 130.03, 129.84, 129.80, 127.36, 124.64, 113.96, 55.26, 48.96, 36.36, 34.42, 32.21, 27.80, 26.53, 21.87; MS (EI) *m*/*e* 310.4 (M^+, 26), 292.3 (31), 211.2 (42), 178.1 (17), 135.1 (40), 121.1 (75), 86.1 (100); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_3$ 310.1569, found 310.1567.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(3,4-Dimethoxystyryl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3d). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-4-(2-bromovinyl)-1,2-dimethoxybenze (0.49 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3d** (0.21 g, 0.62 mmol, 62%) as a yellow liquid: IR (CH_2Cl_2) 2430, 1688, 1506, 1257, 1209, 1007 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.82 (m, 3 H), 6.50 (d, J = 11.6 Hz, 1 H), 6.14 (dd, J = 11.4, 10.1 Hz, 1 H), 5.53 (m, 2 H), 3.92 (m, 1 H), 3.87 (s, 3 H), 3.86 (s, 3 H), 2.52 (m, 2 H), 2.33 (s, 3 H), 2.14 (s, 3 H), 2.07 (m, 1 H), 2.00 (ddd, J = 9.4, 4.3, 1.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.03, 202.60, 148.64, 148.00, 132.58, 131.38, 130.03, 129.50, 124.50, 121.03, 112.16, 111.00, 55.84, 55.80, 49.01, 35.38, 32.07, 27.79, 25.97, 21.78; MS (EI) *m*/*e* 340.3 (M^+, 25), 240.2 (28), 165.1 (10), 152.1 (14), 151.1 (100), 138.1 (26); HRMS (EI) *m*/*e* calcd for $C_{21}H_{24}O_4$ 340.1675, found 340.1668.

(±)-(*Z*)-1,1′-((1*S*,2*R*,6*R*)-(2-(2-Methoxystyryl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3e). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*Z*)-1-(2-bromovinyl)-2-methoxybenzene (0.42 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3e** (0.20 g, 0.65 mmol, 65%) as a yellow liquid: IR (CH_2Cl_2) 2927, 1686, 1598, 1358, 1244; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 7.1 Hz, 1 H), 7.15 (d, J = 7.1 Hz, 1 H), 6.89 (m, 2 H), 6.61 (d, J = 11.4 Hz, 1 H), 6.26 (t, J = 11.2 Hz, 1 H), 5.49 (m, 2 H), 3.83 (s, 3 H), 3.65 (m, 1 H), 2.51 (m, 1 H), 2.46 (m, 1 H), 2.33 (s, 3 H), 2.13 (s, 3 H), 2.04 (dd, J = 9.3, 4.6 Hz, 1 H), 1.95 (dd, J = 9.3, 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.06, 202.72, 157.03, 133.50, 131.53, 129.87, 128.37, 125.92, 125.58, 124.14, 120.11, 110.55, 55.38, 49.06, 35.43, 32.24, 32.00, 27.72, 25.89, 21.76; MS (EI) *m*/*e* (%) 310.3 (M^+, 15), 292.3 (16), 249.2 (13), 210.2 (36), 165.1 (12), 121.1 (100), 115.1 (12), 91.1 (36); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_3$ 310.1569, found 310.1563.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-((1*S*,2*R*,6*R*)-(2-(2-Methylstyryl)bicyclo-[4.1.0]hept-3-ene-7,7-diyl)diethanone (3f). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-2-methylbenzene (0.39 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3f** (0.24 g, 0.80 mmol, 80%) as a yellow liquid: IR (CH_2Cl_2) 2929, 1712, 1692, 1230, 737; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.3 Hz, 1 H), 7.16 (m, 3 H), 6.72 (d, J = 15.8, 1 H), 6.49 (dd, J = 15.8, 7.3 Hz, 1 H), 5.55 (m, 2 H), 3.52 (m, 1 H), 2.62 (m, 1 H), 2.50 (m, 1 H), 2.34 (s, 3 H), 2.30 (s, 3 H), 2.21 (dd, J = 9.3, 4.6 Hz, 1 H), 2.15 (s, 3 H), 2.08 (dd, J = 9.4, 4.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.82, 202.63, 136.30, 135.13, 133.32, 130.23, 130.05, 128.27, 127.25,

126.13, 125.75, 124.80, 48.98, 36.61, 34.53, 32.30, 27.90, 26.55, 21.95, 19.81; MS (EI) *m*/*e* (%) 294.3 (M^+, 17), 233.2 (25), 194.2 (29), 179.1 (15), 115.1 (21), 105.1 (100), 91.1 (18); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_2$ 294.1620, found 294.1627.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(4-Methylstyryl)bicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3g). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-4-methylbenzene (0.39 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3g** (0.21 g, 0.72 mmol, 72%) as a yellow liquid: IR (CH_2Cl_2) 2915, 1730, 1603, 1505, 1417, 1251 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2 H), 7.11 (d, J = 7.9 Hz, 2 H), 6.56 (dd, J = 15.9, 7.2 Hz, 1 H), 6.46 (d, J = 16.0 Hz, 1 H), 5.53 (m, 2 H), 3.47 (m, 1 H), 2.62 (m, 1 H), 2.50 (m, 1 H), 2.32 (s, 3 H), 2.28 (s, 3 H), 2.17 (dd, J = 9.5, 4.4 Hz, 1 H), 2.14 (s, 3 H), 2.06 (dd, J = 9.3, 5.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.89, 202.70, 137.06, 134.41, 130.92, 130.29, 129.95, 129.21, 126.13, 124.72, 48.93, 36.31, 34.31, 32.21, 27.80, 26.52, 21.87, 21.10; MS (EI) *m*/*e* 294.3 (M^+, 13), 195.2 (31), 194.2 (36), 178.2 (30), 105.1 (100), 86.1 (93), 86.0 (53), 84.0 (88); HRMS (EI) *m*/*e* calcd for $C_{20}H_{22}O_2$ 294.1620, found 294.1625.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(2,4,6-Trimethylstyryl)bicyclo-[4.1.0]hept-3-ene-7,7-diyl)diethanone (3h). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-2-(2-bromovinyl)-1,3,5-trimethylbenzene (0.45 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3h** (0.25 g, 0.76 mmol, 76%) as a yellow liquid: IR (CH_2Cl_2) 2922, 1686, 1610, 1481, 1379; ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2 H), 6.47 (d, J = 16.2, Hz, 1 H), 6.15 (dd, J = 16.1, 7.9 Hz, 1 H), 5.56 (m, 2 H), 3.51 (m, 1 H), 2.56 (m, 2 H), 2.30 (s, 9 H), 2.27 (s, 3 H), 2.14 (s, 3 H), 2.14 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.64, 202.50, 136.57, 135.92, 135.84, 133.78, 130.82, 128.55, 127.92, 124.37, 49.00, 37.23, 35.37, 32.09, 27.91, 26.18, 21.91, 20.93, 20.86; MS (EI) *m*/*e* 322.3 (M^+, 23), 307.3 (12), 222.2 (19), 207.2 (19), 177.1 (18), 147.1 (20), 133.1 (100), 129.1 (20); HRMS (EI) *m*/*e* calcd for $C_{22}H_{26}O_2$, 322.1933, found 322.1925.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(3-(Trifluoromethyl)styryl)bicyclo-[4.1.0]hept-3-ene-7,7-diy-l)diethanone (3i). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-3-(trifluoromethyl)benzene (0.50 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 30% ethyl acetate in hexanes) to give **3i** (0.14 g, 0.41 mmol, 41%) as a yellow liquid: IR (CH_2Cl_2) 1636, 1332, 1165, 1124, 1073, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1 H), 7.48 (d, J = 7.6 Hz, 2 H), 7.42 (t, J = 7.6 Hz, 1 H), 6.73 (dd, J = 15.95, 7.75 Hz, 1 H), 6.53 (d, J = 15.95 Hz, 1 H), 5.55 (m, 2 H), 3.49 (m, 1 H), 2.55 (m, 2 H), 2.29 (s, 3 H), 2.26 (m, 1 H), 2.16 (s, 3 H), 2.10 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.85, 202.58, 138.06, 134.04, 130.96, 129.8, 129.28, 129.25, 128.96, 124.67, 124.12, 123.83, 123.07, 49.01, 36.58, 34.06, 32.08, 27.90, 26.28, 21.87; MS (EI) *m*/*e* 348.3 (M^+, 1), 248.2 (4), 190.1 (2), 173.1 (3), 145.1 (2), 107.1 (2), 101.1 (26), 86.1 (100), 58.1 (29), 54 (1); HRMS (EI) *m*/*e* calcd for $C_{20}H_{19}F_3O_2$ 348.1337, found 348.1342.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(2-Fluorostyryl)bicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3j). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-2-fluorobenzene (0.39 g, 2 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 30% ethyl acetate in hexanes) to give **3j** (0.08 g, 0.26 mmol, 26%) as a yellow liquid: IR (CH_2Cl_2) 2367, 1686, 1654, 1230, 759; ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (td, J = 7.6, 1.1 Hz, 1 H), 7.19 (m, 1 H), 7.09 (td, J = 7.6, 1.1 Hz, 1 H), 7.02 (m, 1 H), 6.69 (m, 2 H), 5.53 (m, 2 H), 3.51 (m, 1 H), 2.61, (br d, J = 17.2 Hz, 1 H), 2.51 (br d, J = 18.8, Hz, 1 H), 2.29 (s, 3 H), 2.22 (m, 1 H), 2.15 (s, 3 H), 2.10 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.92, 202.64, 134.47,129.76, 128.58, 128.52, 127.20, 124.77, 124.11, 122.80, 115.68, 115.5 1, 48.97, 36.75, 34.22, 32.23, 27.89, 26.35, 21.89; MS (EI) *m*/*e* (%), 298.2 (M^+, 33), 237.2 (34), 196.1 (87), 177.1 (100), 149.1 (83), 109.1 (98); HRMS (EI) *m*/*e* calcd for $C_{19}H_{19}FO_2$ 298.1369, found 298.1364.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(4-Chlorostyryl)bicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3k). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-1-(2-bromovinyl)-4-chlorobenzene (0.43 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3k** (0.24 g, 0.77 mmol, 77%) as a yellow liquid: IR (CH_2Cl_2) 2888, 1780, 1652, 1503, 1440, 1337, 1105, 1009 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2 H), 7.26 (m, 2 H), 6.62 (dd, J = 15.9, 7.8 Hz, 1 H), 6.45 (d, J = 16.0 Hz, 1 H), 5.52 (m, 2 H), 3.46 (m, 1 H), 2.53 (m, 2 H), 2.28 (s, 3 H), 2.14 (s, 3 H), 2.11 (m, 1 H), 2.09 (dd, J = 9.4, 4.9 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.59, 204.86, 135.77, 132.85, 132.72, 129.94, 129.32, 128.65, 127.47, 124.59, 48.99, 36.52, 34.20, 32.09, 27.85, 26.29, 21.85; MS (EI) *m*/*e* 314.3 (M^+, 13), 178.2 (35), 177.2 (32), 141.1 (35), 125.1 (86), 86.1 (100), 84.0 (36); HRMS (EI) *m*/*e* calcd for $C_{19}H_{19}ClO_2$ 314.1073, found 314.1064.

(±)-1,1′-((1*S*,2*R*,6*R*)-2-(2-((1*E*,3*E*)-4-Phenylbuta-1,3-dienyl)-bicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3l). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with 1-((1*E*,3*E*)-4-bromobuta-1,3-dienyl)benzene (0.42 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 30% ethyl acetate in hexanes) to give **3l** (0.21 g, 0.70 mmol, 70%) as a yellow liquid: IR (CH_2Cl_2) 2925, 1714, 1693, 1599, 1454, 1360, 1237; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.2 Hz, 2 H), 7.23 (t, J = 7.6 Hz, 2 H), 7.15 (t, J = 7.2 Hz, 1 H), 6.77 (dd, J = 15.6, 10.0 Hz, 1 H), 6.45 (d, J = 15.6 Hz, 1 H), 6.24 (dd, J = 15.4, 10.0 Hz, 1 H), 6.13 (dd, J = 15.2, 7.2 Hz, 1 H), 5.42 (m, 2 H), 3.36 (m, 1 H), 2.54 (d, J = 17.2 Hz, 1 H), 2.42 (t, J = 4.8 Hz, 1 H), 2.20 (s, 3 H), 2.07 (s, 3 H), 1.98 (q, J = 4.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.91, 202.67, 137.38, 136.27, 131.59, 131.07, 129.84, 128.90, 128.62, 127.41, 126.30, 124.82, 48.96, 48.96, 36.26, 34.21, 32.25, 27.91, 26.55, 21.93; MS (EI) *m*/*e* 306.3 (M^+, 15), 245.2 (25), 206.2 (28), 167.1 (23), 129.1 (37), 117.1 (100), 115.1 (32), 91.1 (65), 86.1 (73), 58.1 (19); HRMS (EI) *m*/*e* calcd for $C_{21}H_{22}O_2$ 306.1620, found 306.1716.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(2-(Biphenyl-4-yl)vinyl)bicyclo-[4.1.0]hept-3-ene-7,7-diyl)diethanone (3m). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-4-(2-bromovinyl)biphenyl (0.52 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3m** (0.23 g, 0.65 mmol, 65%) as a yellow liquid: IR (CH_2Cl_2) 2685, 1706, 1680, 1505, 1489, 1413, 1220 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.57 (m, 5 H), 7.43 (m, 2 H), 7.33 (m, 2 H), 6.58 (d, J = 11.5 Hz, 1 H), 6.24 (dd, J = 11.4, 10.2 Hz, 1 H), 5.54 (m, 2 H), 3.90 (m, 1 H), 2.51 (m, 2 H), 2.33 (s, 3 H), 2.14 (s, 3 H), 2.09 (dd, J = 9.4, 4.6 Hz, 1 H), 2.01 (ddd, J = 9.3, 4.3, 1.1 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.01, 202.63, 140.59, 139.58, 135.99, 133.77, 132.11, 131.28, 129.35, 129.09, 128.72, 128.70, 127.23, 127.17, 126.91, 126.88, 124.46, 49.03, 35.28, 32.00, 27.79, 25.90, 21.84; MS (EI) *m*/*e* 356.4 (M^+, 26), 338.3 (24), 256.2 (47), 178.1 (23), 167.2 (100), 165.1 (25); HRMS (EI) *m*/*e* calcd for $C_{25}H_{24}O_2$ 356.1777, found 356.1773.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-2-(2,2-Diphenylvinyl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3n). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (2-bromoethene-1,1-diyl)dibenzene (0.52 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3n** (0.26 g, 0.74 mmol, 74%) as a yellow liquid: IR (CH_2Cl_2) 2685, 2521, 1712, 1505, 1327, 1486, 1266 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.28 (m, 10 H), 6.69 (d, J = 10.2 Hz, 1 H), 5.45 (m, 2 H), 3.41 (m, 1 H), 2.49 (dd, J = 18.3,

4.8 Hz, 1 H), 2.40 (m, 1 H), 2.33 (s, 3 H), 2.14 (s, 3 H), 2.02 (dd, J = 9.4, 4.9 Hz, 1 H), 1.89 (dd, J = 9.4, 4.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.06, 202.71, 142.25, 141.89, 139.67, 131.31, 130.15, 129.64, 128.39, 128.07, 127.09, 127.07, 127.05, 123.64, 49.15, 35.28, 33.27, 31.89, 27.80, 25.74, 21.63; MS (EI) *m*/*e* 356.4 (M^+, 52), 338.3 (36), 256.2 (43), 179.2 (59), 178.2 (72), 178.1 (46), 167.2 (100), 165.1 (63), 105.1 (44), 86.1 (99); HRMS (EI) *m*/*e* calcd for $C_{25}H_{24}O_2$ 356.1776, found 356.1768.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-(2-(2,2-di-*p*-tolylvinyl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3o). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with 4,4′-(2-bromoethene-1,1-diyl)bis(methylbenzene) (0.57 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3o** (0.33 g, 0.85 mmol, 85%) as a colorless solid: mp 150−152 °C; IR (CH_2Cl_2) 1686,1508, 1356, 1202, 820; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.4 Hz, 4 H), 7.07 (d, J = 7.5 Hz, 4 H), 6.62 (d, J = 10.1 Hz, 1 H), 5.46 (m, 2 H), 3.43 (m, 1 H), 2.45 (m, 2 H), 2.39 (s, 3 H), 2.35 (s, 3 H), 2.33 (s, 3 H), 2.16 (s, 3 H), 2.03 (dd, J = 9.3, 4.8 Hz, 1 H), 1.90 (dd, J = 9.2, 4.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.06, 202.80, 142.09, 139.37, 136.62, 131.56, 129.57, 129.48, 129.14, 129.07, 128.95, 128.78, 127.15, 123.61, 49.18, 35.58, 33.31, 31.97, 27.87, 25.85, 21.70, 21.20, 21.02; MS (EI) *m*/*e* 384.4 (M^+, 22), 366.3 (21), 284.3 (41), 258.2 (26), 208.2 (18), 195.2 (100), 178.1 (24), 105.1 (26); HRMS (EI) *m*/*e* calcd for $C_{27}H_{28}O_2$ 384.2098, found 384.2082. Crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2 and hexanes.

(±)-(*E*)-1,1′-((1*S*,2*R*,6*R*)-(2-((9*H*-Fluoren-9-ylidene)methyl)-bicyclo[4.1.0]hept-3-ene-7,7-diyl)diethanone (3p). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with 9-bromomethylene-9*H*-fluorene (0.51 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3p** (0.28 g, 0.80 mmol, 80%) as a yellow liquid: IR (CH_2Cl_2) 2092, 1722, 1673, 1265, 736; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 6.8 Hz, 1 H), 7.76 (dd, J = 7.5, 2.9 Hz, 2 H), 7.70 (d, J = 6.8 Hz, 1 H), 7.32 (m, 4 H), 7.19 (d, J = 8.9 Hz, 1 H), 5.65 (m, 2 H), 4.46 (m, 1 H), 2.67 (m, 2 H), 2.38 (s, 3 H). 2.32 (br d, J = 7.4 Hz, 1 H), 2.21 (br d, J = 7.3 Hz, 1 H), 2.17 (s, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.91, 202.56, 141.31, 139.44, 138.72, 136.68, 135.58, 131.64, 130.36, 128.31, 127.83, 127.13, 127.03, 125.10, 124.99, 120.30, 120.02, 119.45, 49.03, 34.25, 32.58, 32.10, 29.97, 26.05, 21.88; MS (EI) *m*/*e* (%) 354.3 (M^+, 50), 293.2 (57), 278.3 (40), 253.2(47), 239.2 (30), 202.1 (36), 178.1 (75), 165.1 (100); HRMS (EI) *m*/*e* calcd for $C_{25}H_{22}O_2$ 354.1620, found 354.1627.

(±)-1,1′-((1*S*,2*R*,6*R*)-(2-(2-(Anthracen-9-yl)vinyl)bicyclo[4.1.0]-hept-3-ene-7,7-diyl)diethanone (3q). The crude mixture obtained from reaction of **1** (0.18 g, 1.0 mmol) with (*E*)-9-(2-bromovinyl)-anthracene (0.56 g, 2.0 mmol) was purified by flash-column chromatography (silica gel, gradient elution: 5 to 10% ethyl acetate in hexanes) to give **3q** (0.27 g, 0.70 mmol, 70%) as a yellow liquid: IR (CH_2Cl_2) 2086, 1737, 1643, 1462, 732. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1 H), 8.35 (dd, J = 6.56, 3.56 Hz, 2 H), 7.99 (dd, J = 6.36, 3.36 Hz, 2 H), 7.46 (td, J = 6.68, 3.20 Hz, 4 H), 7.29 (d, J = 16.24 Hz, 1 H), 6.48 (dd, J = 16.24, 7.56 Hz, 1 H), 5.78 (br d, J = 9.84 Hz, 1 H), 5.63 (m, 1 H), 3.82 (m, 1 H), 2.63 (m, 2 H), 2.35 (m, 1 H), 2.33 (s, 3 H), 2.22 (m, 1 H), 2.19 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.53, 202.51, 140.28, 132.61, 131.46, 130.41, 129.59, 128.61, 126.27, 126.19, 125.95, 125.30, 125.05, 124.69, 49.13, 37.24, 35.28, 32.11, 28.12, 26.21, 21.99; MS (EI) *m*/*e* (%) 380.3 (M^+, 65), 362.3 (25). 203.1 (92), 202 (65), 178.1 (44), 86.0 (69), 84.0 (100); HRMS (EI) *m*/*e* calcd for $C_{27}H_{24}O_2$ 380.1776, found 380.1786.

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Supporting Information Available: Tables of atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters and crystallographic data in CIF format for compound **3o**. This material is available free of charge via the Internet at http://pubs.acs.org.

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