# Synthesis and Reactivities of Intramolecular $\eta^2$-Arene and -Alkene Species via Insertion of Norbornadiene into Palladium–Carbon Bonds. Preparation of 3,5-Disubstituted Nortricyclenes from These Complexes

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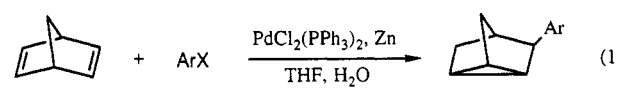
The complexes $(C_7H_8Ar)PdI(PPh_3)$ (Ar = $C_6H_5$ (**1a**), *p*-$CH_3O$-$C_6H_4$ (**1b**), *p*-$CH_3$-$C_6H_4$ (**1c**), *m*-$CH_3O$-$C_6H_4$ (**1d**)) were synthesized by treating $PdIAr(PPh_3)_2$ with excess norbornadiene or isolated from the reaction of $Pd(PPh_3)_4$ with aryl iodide and norbornadiene. Under similar conditions, norbornene also reacts with $PdI(p\text{-}C_6H_4\text{-}OCH_3)(PPh_3)_2$ to yield **1e**. These complexes are distorted-square-planar species with the aryl group and palladium being cis and exo to the norbornenyl group and the double bond between ipso and ortho positions of the aryl ring attached to the norbornenyl group being weakly bound to the palladium center. Variable-temperature NMR spectra of these species indicate that they are fluxional on the NMR time scale. Rotation of the aryl group in these complexes is believed to cause the observed dynamic NMR behavior. The complex $(C_7H_8C_4H_3S)PdI(PPh_3)$ (**4**) was similarly prepared from the reaction of $Pd(PPh_3)_4$ with excess norbornadiene and 2-iodothiophene. NMR evidence indicates that **4** is static at room temperature and that the S atom of the thienyl group is coordinated to the palladium center. Treatment of $Pd(PPh_3)_4$ with excess norbornadiene and a 3-iodo 2-en-1-one species (RI) led to the isolation of the corresponding complex $(C_7H_8R)PdI(PPh_3)$ (**5**). The carbon–carbon double bond on the enone group is weakly bound to the metal center. In the presence of KOH, terminal acetylene reacts with **1b** in dichloromethane, affording the corresponding *cis,exo*-5-*p*-anisyl-6-alkynylnorborn-2-ene. The reaction of **1b** with CuCN gives a cyanonorbornene product (**7**) in high yield. These palladium(II) species react with zinc and zinc chloride to give the corresponding monosubstituted nortricyclenes and with a 3-iodo 2-en-1-one compound, zinc, and zinc chloride to afford cis,exo-3,5-disubstituted nortricyclenes (**10**). Mechanisms for the formation of mono- and disubstituted nortricyclenes are discussed.

## Introduction

It is well-known that $\eta^2$-bound arene complexes are intermediates in the C–H bond activation of arene systems.[1] However, due to the inherent stability of aromatic compounds, few stable $\eta^2$-bound arene complexes have been isolated and characterized.[2-6] To the best of our knowledge, there are only two known examples, $(PhHCPz'_2)Mo(CO)_3$[5] and $(PhPPz'_2)W(CO)_3$,[6] where Pz' = 3,5-dimethylpyrazol-1-yl, which contain weak intramolecular $\eta^2$-arene bonds. Recently, we reported a palladium-catalyzed synthesis of aryl-substituted nortricyclenes from the reaction of aryl halides with norbornadiene (eq 1).[7] In



(1)

an attempt to characterize the catalytic intermediates, we isolated a class of norbornenylpalladium complexes. These species are likely the catalytic intermediates for a number of known palladium-catalyzed reactions involving norbornadiene or norbornene as substrates,[8] although the detailed pathways for these catalytic reactions have not been wholly explored. Furthermore, in spite of the rich chemistry of C–H bond activation by palladium complexes,[9] these complexes are the only examples of stable $\eta^2$-bound palladium arene species to date. In this paper, we report the scope of the synthesis, fluxional behavior, and chemical properties of these norbornenylpalladium-

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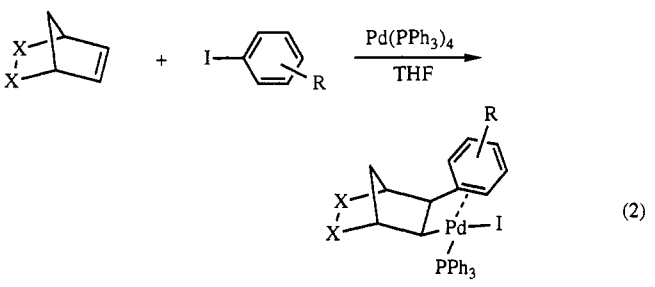
(II) complexes. The results have appeared in part in a communication.[10]

## Results and Discussion

**Synthesis of $(C_7H_8Ar)PdI(PPh_3)$ (1).** Complexes **1a–d** with the stoichiometry $(C_7H_8Ar)PdI(PPh_3)$ were prepared by treating the corresponding $PdIAr(PPh_3)_2$ with excess norbornadiene at 50 °C for 3 h or isolated from the reaction of $Pd(PPh_3)_4$ with norbornadiene and the corresponding aryl iodides (eq 2). Under similar conditions, norbornene also reacts with $PdI(p\text{-}CH_3O\text{-}C_6H_4)(PPh_3)_2$ to yield **1e**. These yellow products were characterized by NMR and IR spectra, X-ray diffraction, and elemental analysis.

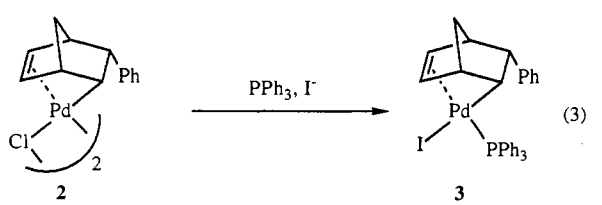



(2)

**1**

| | | |
|---|---|---|
| **1a** | XX = CH=CH | R = H |
| **1b** | XX = CH=CH | R = *p*-$OCH_3$ |
| **1c** | XX = CH=CH | R = *p*-$CH_3$ |
| **1d** | XX = CH=CH | R = *m*-$OCH_3$ |
| **1e** | XX = $CH_2CH_2$ | R = *p*-$OCH_3$ |

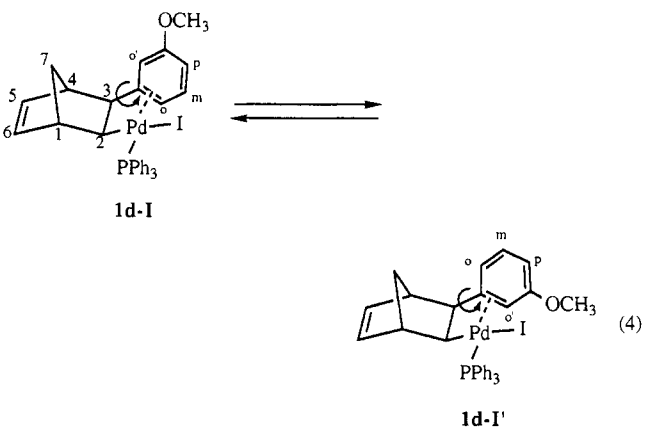
The solid-state structure of **1a** was determined by X-ray crystallography.[10] The results demonstrate that the phenyl group and the palladium metal occupy exo positions of the norbornenyl group. In addition, the phenyl ring attached to the norbornenyl group is weakly bound to the palladium center in an $\eta^2$ fashion. The complex is a distorted-square-planar species with $PPh_3$, $I^-$, and norbornenyl groups as the other three ligands. The cis and endo phenylnorbornenyl complex **2** has been synthesized previously.[11] The addition of 1 equiv of $PPh_3$ and excess $I^-$ to the complex leads to the formation of the cis and endo complex **3**, having the same chemical formula as **1a**. Comparison of $^1H$ and $^{13}C$ NMR spectra of **1a** and **3** indicates that they are different species (see Experimental Section).




(3)

**2** **3**

All the species **1a–e** are nonrigid, and their NMR spectra are temperature-dependent. To understand the details of the dynamic behavior of these complexes, the NMR spectra of a typical example, **1d**, at variable temperatures were carefully examined. At 25 °C in $CDCl_3$, the $^{13}C\{^1H\}$ NMR spectra of the complex shows, in addition to resonances due to the coordinated $PPh_3$ and norbornenyl group, a doublet at 112.31 ($J$ = 13.5 Hz) and singlets at 116.47, 119.50 (br), 133.21, and 162.39 ppm for the ipso, para, ortho, meta, and meta (attached to $OCH_3$) carbons, respectively, of the *m*-anisyl ring. One ortho-carbon signal was missing, presumably due to peak broadening at this temperature. The observed doublet at 112.31 ppm assigned to the ipso carbon is due to coupling with phosphorus. As the temperature was lowered to −40 °C, the complex became static and the $^{13}C$ resonances at room temperature split into two sets of signals. The resonances for the *m*-anisyl carbons appeared at $\delta$ 110.94 (d), 111.43 (d) (ipso), 106.87 (ortho′, $\pi$-bonded), 116.85 (ortho′), 117.83 (ortho, $\pi$-bonded), 122.54 (ortho), 115.04 (para), 132.01, 134.41 (meta), 161.03, 163.35 (meta, attached to $OCH_3$). Compared to the corresponding signals of 3-*m*-anisylnortricyclene, the resonance of the coordinated ipso carbon exhibits an upfield shift of 30 ppm, while the signals of the coordinated ortho carbons of the *m*-anisyl ring show only slightly upfield shifts of ca. 5 ppm. As shown in Figure 1, the proton NMR spectra of **1d** also vary with temperature and, similar to the $^{13}C$ spectra, two sets of signals were observed at low temperatures. These observations indicate that two isomers, **1d-I** and **1d-I′**, undergoing rapid interchange near room temperature are present in solution for **1d** (eq 4). Three carbons in the norbornenyl group,




(4)

C(1), C(2), and C(6), were found to couple with the phosphorus atom with coupling constants of 14.0 (C(2)), 4.6 (C(1)), and 9.2 (C(6)) Hz, respectively. The NMR results as well as those from X-ray data of **1a** show that the $\eta^2$ interaction is unsymmetrical, with the bonding of the ipso carbon to Pd metal much stronger than that of the ortho carbon.

The dynamic NMR behavior of **1a–c,e** is slightly different from that of **1d**. There is only one set of NMR signals observed for each complex of **1a–c,e** at either the slow- or fast-exchange limit. For example, complex **1b** shows in its $^{13}C\{^1H\}$ NMR spectrum at 25 °C a doublet at 97.66 ppm and singlets at 117.03 and 163.69 ppm for the ipso, meta, and para carbons, respectively, of the *p*-anisyl ring. The ortho-carbon signal was not observed at this temperature. As the temperature was lowered to −40 °C, the six signals for the anisyl ring carbons at 96.99 (d), 115.58, 116.90, 126.84, 134.07, and 162.92 ppm were all found. The other $^{13}C$ signals of **1b** do not shift with temperature significantly and do not split at low temperature. The low-temperature-limit spectrum is in agreement with the presence of only one isomer with an $\eta^2$ coordination, which splits the ring into six different

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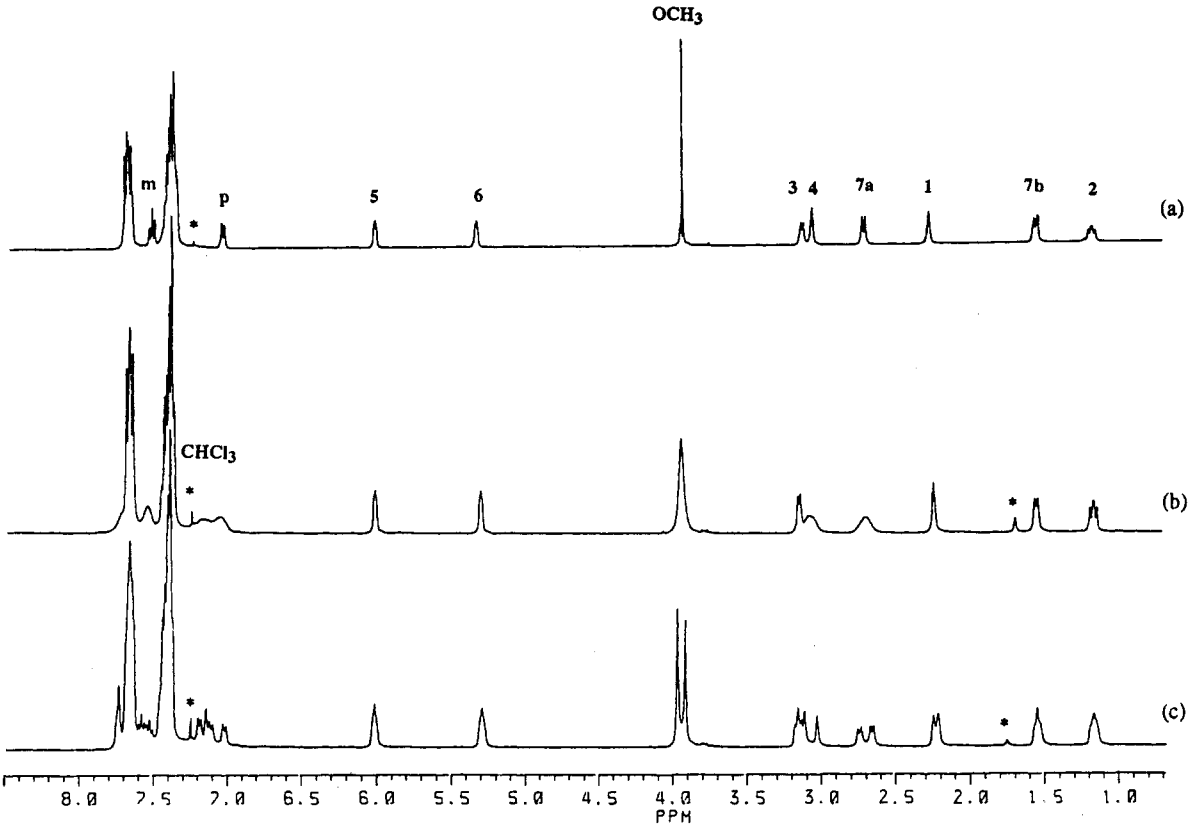
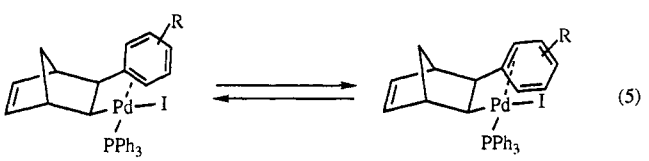



**Figure 1.** $^1$H NMR spectra of **1d** (in $CDCl_3$) at (a) 293 K, (b) 253 K, and (c) 233 K.

carbons. Similarly, complexes **1a,c,e** exhibit characteristic doublets at 109.29, 105.81, and 91.37 ppm, respectively, for the ipso carbons and their NMR spectra are all temperature-dependent. On the basis of these observations, we conclude that **1a–e** are all $\eta^2$-bound arene complexes.

The spectral changes of complexes **1a–e** are consistent with a facile rotation process of the aryl ring about the C–C bond connecting the aryl and norbornenyl groups, as indicated in eq 4. There is another process (eq 5) in which

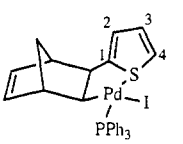



(5)

**1-I** **1-II**

the palladium metal moves up and down near the aryl ring to yield two isomers, **1-I** and **1-II**. This mechanism fails to account for the fluxional behavior of complexes **1a,b**. According to this process, **1a,b** should display two sets of signals at the slow-exchange limit, because **1-I** and **1-II** are environmentally two different species at low temperatures. This behavior is in contrast to the results of the NMR studies, which show only one set of signals at the slow-exchange limit. On the basis of these results, the process in eq 5 may be discarded. The rotational process shown in eq 4 accounts nicely for the fluxional behavior of **1a,b** in addition to **1d**. According to this process, **1a** and **1b** each displays only one set of NMR signals at the slow-exchange limit due to the fact that the aryl groups in these two species are symmetric, possessing a $C_2$ axis.

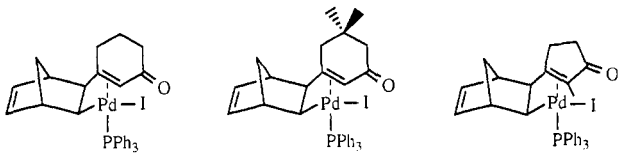
Similar to complexes **1a–d**, complex **4** was prepared from the reaction of $Pd(PPh_3)_4$ with excess norbornandiene and 2-iodothiophene. However, in contrast to the nonrigid




**4**

behavior of **1**, **4** is static at room temperature. The $^{13}$C resonances of the thienyl group at 122.95 (C(4)), 129.44 (C(2)), 132.90 (C(3)), and 139.62 (C(1)) ppm are comparable to those of the free thienyl group of 2-(3-nortricyclyl)-thiophene at 123.00 (C(4)), 123.90 (C(2)), 126.54 (C(3)), and 146.64 (C(1)) ppm. Furthermore, there is no coupling between the phosphorus of the $PPh_3$ ligand and any of the carbons in the thienyl group. These results strongly suggest that in this complex there is no $\eta^2$ type coordination similar to that of complexes **1**. The presence of the sulfur atom and its electron lone pairs in the thienyl group leads us to propose that the sulfur atom is attached to the palladium center using one of the electron lone pairs to form a five-membered chelating ring. Although the $\eta^2$ type coordination of complexes **1** cannot be replaced by an external ligand such as $PPh_3$, or a solvent molecule, it is readily substituted by an internal electron lone pair, reflecting the weak nature of the $\eta^2$ type coordination.

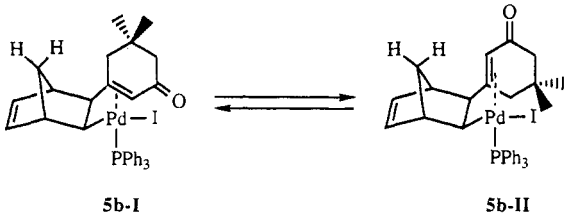
The reaction of $Pd(PPh_3)_4$ with norbornadiene and 3-iodo 2-en-1-one compounds (RI; 3-iodo-2-cyclohexen-1-one, 5,5-dimethyl-3-iodo-2-cyclohexen-1-one, 3-iodo-2-methyl-2-cyclopenten-1-one) in THF also yields the insertion product $Pd(PPh_3)(C_7H_8\text{-}R)I$ (**5**). As there is only one $PPh_3$ ligand in the palladium coordination sphere, these complexes are expected to involve an internal $\eta^2$ type coordination using the carbon–carbon double bond in the enone group. It is less clear from the $^1$H NMR



5a 5b 5c

spectra of these products that an internal $\eta^2$ interaction exists. The $\alpha$-olefinic proton of complex **5a** appears at $\delta$ 5.84 near the values (6.00 ppm) of $\beta$-substituted 2-cyclohexen-1-one.[12] Fortunately, $^{13}C$ NMR spectra of these products provide strong evidence for the presence of an $\eta^2$-bound carbon–carbon double bond. The $\alpha$- and $\beta$-carbons of the enone groups appear at 104.16 (d, $J_{PC}$ = 16.1 Hz) and 128.86 (s) ppm, respectively. These resonances shift upfield by approximately 23 and 38 ppm relative to the corresponding values of $\beta$-substituted 2-cyclohexen-1-one.[12] In addition to the change in chemical shift of $^{13}C$ signals, the observed doublet for the $\alpha$-carbons in the $^{13}C\{^1H\}$ NMR spectra arising from coupling of $^{31}P$ and $^{13}C$ is also strong evidence for the coordination of the $\alpha$- and $\beta$-carbon–carbon double bond to palladium. Similar spectral results for complexes **5b,c** were observed, indicating that an internal $\eta^2$-bound coordination exists for these species.

$^1H$ NMR spectra of **5b** deserve particular attention in view of their marked dependence on temperature. The change of spectrum with temperature is clearly seen in the region $\delta$ 7.2–5.0 for the three olefinic protons of **5b**. As shown in Figure 2a, at 293 K signals of the two olefinic protons of the norbornenyl group appear as a doublet of doublets at $\delta$ 5.31 and 5.98, while the $\alpha$-olefinic proton of the enone group is apparent at $\delta$ 6.26 as a broad resonance. These resonances split into two sets at 223 K (Figure 2b), indicating the presence of two species in thermodynamic equilibrium in solution. On the basis of the dynamic NMR results of **1a–e**, we propose that there are two possible rotational isomers, **5b-I** and **5b-II**, that undergo rapid exchange at high temperature via the rotation of the carbon–carbon bond connecting the norbornenyl and enone groups (eq 6) to account for the NMR behavior of **5b**. From the relative intensity of signals, the concentration ratio of these two rotational isomers is approximately 3:1 at 213 K. We expect that **5b-I** is more stable and consequently is higher in concentration than **5b-II** on the basis of the NMR and X-ray results of complexes **1a–e**. For complexes **5a,c**, splitting of the $^1H$ NMR signals at low temperature was not clearly observed, but broadening of the spectra at 293–213 K was found. The observed broadening of the spectra in complexes **5a,c** may be rationalized on the basis that the corresponding rotational isomer **5-II** is much less populated relative to **5-I** at low temperature (at the slow-exchange limit), but as the temperature increases, the contribution of the higher



5b-I 5b-II (6)

(12) Relative to the corresponding $^{13}C$ NMR resonances of *cis,exo*-2,3-bis(3-oxo-1-cyclohexen-1-yl)norborn-5-ene.[17]

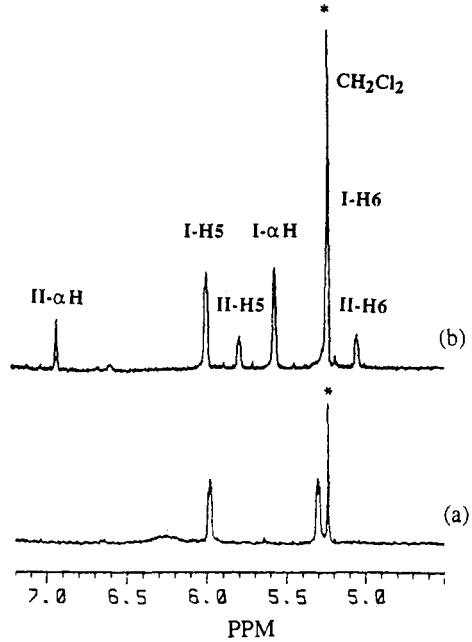
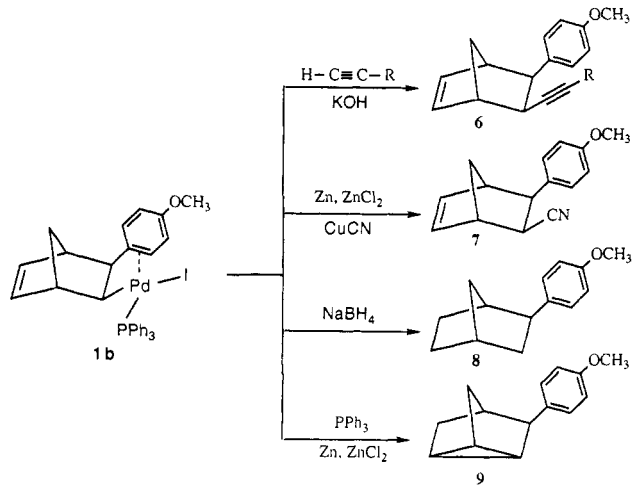



**Figure 2.** $^1H$ NMR spectra of **5b** (in $CD_2Cl_2$) at (a) 293 K and (b) 213 K.

**Scheme I**




energy rotamer **5-II** becomes important. The interchange of **5-I** and **5-II** with an intermediate exchange rate leads to the broadening of the spectra.

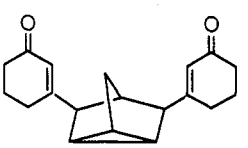
**Properties and Reactivities of $(C_7H_8R)PdI(PPh_3)$.** In spite of the weak $\eta^2$-arene bonding between the palladium center and the aryl group in **1**, addition of excess $PPh_3$ or pyridine does not lead to substitution of the $\eta^2$ bond by any of these ligands. Further, these palladium complexes are stable in air in the solid state and thermally stable. For example, **1b** did not show any detectable decomposition at 60 °C in THF for 24 h. The relatively rigid arrangement of the aryl ring and the palladium metal on the norbornenyl group presumably protects the weak $\eta^2$ interaction from being replaced by other ligand–metal bonding, while compound **1** exhibits great inertness toward substitution. It does react with several nucleophiles to give organic products (Scheme I). In the presence of KOH, terminal acetylene reacts with **1b** in dichloromethane, affording the corresponding *cis,exo*-5-*p*-anisyl-6-alkynylnorborn-2-ene (**6**) in essentially quantitative yields. These products were characterized by comparing their spectral

data with those reported in the literature.[13] Similarly, **1b** also reacts with CuCN to give *cis,exo*-5-*p*-anisyl-6-cyanonorborn-2-ene (**7**) in high yield.

The reaction of **1b** with sodium borohydride in THF resulted in the formation of *exo*-2-phenylnorbornane (**8**). This result is surprising in view of the fact that the carbon–carbon double bond of the norbornenyl group in **1b** is also hydrogenated. The structure of the product was assigned on the basis of its NMR and MS data and was further confirmed by comparing these spectra with those reported for the compound in the literature.[14]

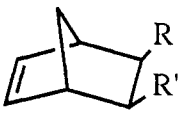
Although **1a** was originally isolated from the catalytic reaction of aryl iodide with norbornadiene in the presence of $PdCl_2(PPh_3)_2$ and zinc powder (eq 1), we encountered difficulty in converting **1a** to the corresponding aryl-substituted nortricyclene. Complex **1a** in THF in the presence of zinc or $ZnCl_2$ alone was not transformed into the corresponding substituted nortricyclene over a period of 5 h at 60 °C. However, the transformation was completed in 2 h in essentially quantitative yield if excess $ZnCl_2$, zinc powder, and $PPh_3$ were added to the solution. The results indicate that both zinc metal and zinc halide are required for the transformation to proceed. Similarly, complex **1** was not converted to the nortricyclene product if Mg metal powder alone was used as the reducing agent, but when both Mg and zinc chloride were present, the conversion to nortricyclene occurred rapidly and completely. The requirement of zinc halide to drive the reaction strongly implies that zinc halide is acting as a Lewis acid to remove the iodide ion from complex **1a** during the conversion. This notion gains further support from the observation that **1a** also undergoes the expected transformation to the nortricyclene products in the presence of both zinc powder and $AgBF_4$. Immediate precipitation of yellow AgI was observed as soon as $AgBF_4$ was added to the solution.

As indicated in the foregoing results, slightly different reaction conditions led to entirely different organic products. Reduction of **5a** by zinc metal–zinc halide in the presence of 3-iodo-2-cyclohexen-1-one leads to the formation of *cis,exo*-3,5-bis(3-oxo-1-cyclohexen-1-yl)nortricyclene (**10a**). The structure of this interesting product



**10a**

was assigned on the basis of its IR, NMR, and mass spectral data and elementary analysis. In the IR spectrum, the keto and carbon–carbon double-bond absorptions appear at 1665 and 1621 $cm^{-1}$, respectively. Furthermore, strong absorptions at 3057 and 813 $cm^{-1}$ characteristic of the cyclopropane ring were observed.[15] The high-resolution mass spectral data and results of elementary analysis are all consistent with the proposed structure. In the $^1H$ NMR spectrum, the key resonance at ca. 6.3 ppm for the $sp^2$ protons of the norbornene group was no longer observed. The only resonance for the $sp^2$ protons of the present structure appears at ca. $\delta$ 6.0, corresponding to the $\alpha$-protons of 3-oxo-1-cyclohexen-1-yl groups. Characteristic resonances for protons and carbons on the cyclopropane ring come at ca. $\delta$ 1.40 and 10 in the $^1H$ and $^{13}C$ NMR spectra, respectively. The resonances of both protons and carbon nuclei on the cyclopropane ring shift to upper field compared to the normal nuclei with the same degree of substitution.[16] Under similar conditions, treatment of complex **5b** with 5,5-dimethyl-3-iodo-2-cyclohexen-1-one in the presence of zinc metal and zinc chloride afforded a symmetric disubstituted nortricyclene. As reported previously, if 3-iodo 2-en-1-ones were allowed to react with zinc metal to yield the corresponding (3-oxo 1-en-1-yl)-zinc iodides prior to reacting with complexes **5**, the 2,3-disubstituted nornornene products **11** were obtained.[17]




**11**

Similarly, $(C_7H_8Ph)PdI(PPh_3)$ (**1a**) reacted with 3-iodo-2-cyclohexen-1-one, 5,5-dimethyl-3-iodo-2-cyclohexen-1-one, and 3-iodo-2-methyl-2-cyclohexen-1-one to give the corresponding 3,5-disubstituted nortricyclenes. Other palladium complexes **1b–d** also reacted with 3-iodo enones to yield the corresponding disubstituted nortricyclenes (Table I). The reaction provides an effective method for preparing both symmetric and unsymmetric 3,5-disubstituted nortricyclenes. It should be noted that the reaction sequence in the preparation of these disubstituted nortricyclenes is extremely important. For example, in the preparation of **10c**, both PhI and 3-iodo-2-cyclohexen-1-one were required. If 3-iodo-2-cyclohexen-1-one is first used to react with $Pd(PPh_3)_4$ to give **5a**, this product does not further react with PhI in the presence of zinc and zinc chloride to yield the corresponding 3,5-disubstituted nortricyclene. On the other hand, when the reaction sequence is reversed, i.e. PhI is first used to react with $Pd(PPh_3)_4$ to give $(C_7H_8Ph)PdI(PPh_3)$ (**1a**) and the latter is then treated with 3-iodo-2-cyclohexen-1-one in the presence of zinc and zinc chloride, **10c** is successfully formed. In fact, all palladium complexes $(C_7H_8R)PdI(PPh_3)$ failed to react with aryl iodide but reacted with 3-iodo enone in the presence of zinc and zinc halide to yield nortricyclene products.

**Mechanism for the Formation of Mono- and Disubstituted Nortricyclenes.** In view of the cis and exo stereochemistry of complexes **1a–e**, **4**, and **5**, the formation of mono- and disubstituted nortricyclenes from these complexes is surprising. Previous reports have shown that only endo–endo structures such as **2** have been observed to yield nortricyclenyl derivatives.[11,18] The stereo arrangement of **2** allows the carbon–carbon double bond to insert into the palladium–carbon bond in complex **2** to yield a nortricyclenyl–palladium species. For complexes **1a–e**, **4**, and **5**, metal-assisted insertion is impossible due to the wrong stereochemistry of the palladium–carbon bond relative to the carbon–carbon double bond.

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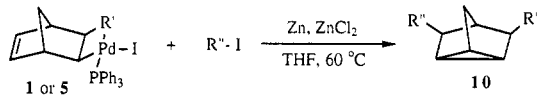
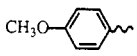
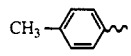
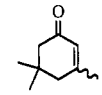
**Table I. Isolated Yields (%) of 3,5-Disubstituted Nortricyclenes[a]**

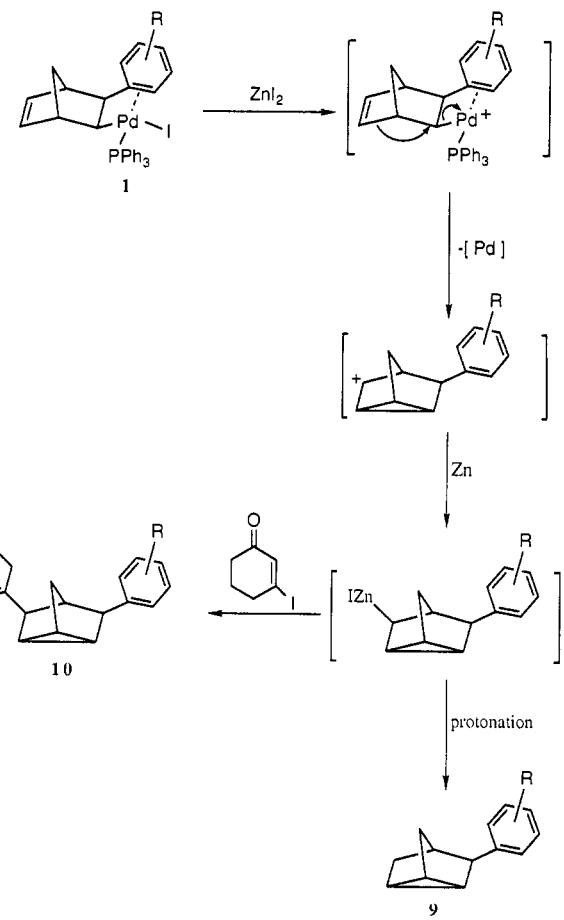



| R'' \ R' |  |  |  |  |  |
|---|---|---|---|---|---|
|  | 72 (**10c**) | 52 (**10f**) | 57 (**10i**) | 71 (**10a**) | |
|  | 65 (**10d**) | 50 (**10g**) | 55 (**10j**) | | 75 (**10b**) |
|  | 50 (**10e**) | 53 (**10h**) | 45 (**10k**) | | |

[a] All reactions were carried out in THF at 60 °C; the reaction conditions are described in the Experimental Section.

The requirement of zinc chloride or $Ag^+$ in the formation of mono- or disubstituted nortricyclenes from complexes **1**, **4**, and **5** strongly indicates that a chloride ion is removed from these complexes to give a cationic palladium(II) species. Owing to the strong oxidizing power of Pd(II), particularly in a cationic form, the positive charge in the palladium complex is transferred to the norbornenyl group. It is known that the norbornenyl cation readily undergoes rearrangement to afford the nortricyclenyl cation.[19] Trapping of the latter cation by zinc metal gives a zinc reagent containing a nortricyclenyl group. Protonation of the zinc reagent yields the monosubstituted nortricyclene, whereas attack of the reagent at another 3-iodo 2-en-1-one leads to formation of a disubstituted nortricyclene. The proposed reaction sequence is shown in Scheme II.

**Scheme II**




## Conclusion

A series of internal $\eta^2$-bound arene alkene complexes with the chemical formula $(C_7H_8R)PdI(PPh_3)$ were synthesized from the reaction of $Pd(PPh_3)_4$ with norbornadiene and the corresponding aryl or alkenyl iodides (RI). These complexes are intermediates of several palladium-catalyzed carbon–carbon bond formation reactions. Dynamic NMR behavior of these complexes due to the rotation of the R group was observed. All of these complexes are stable in air in the solid state and thermally stable. The relatively rigid arrangement of the organic group and the palladium metal on the norbornenyl group protect the weak $\eta^2$ interaction from being replaced by other ligand–metal bonding. These complexes react with various nucleophiles to yield the corresponding cis,exo-2,3-disubstituted norbornenes but with zinc and zinc chloride to give monosubstituted nortricyclenes and with 3-iodo 2-en-1-one, zinc, and zinc chloride to afford cis,-exo-3,5-disubstituted nortricyclenes.

## Experimental Section

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. $^1H$ and $^{13}C$ NMR experiments were performed on a Bruker AM-400 or a Varian Gemini 300 instrument at 400 or 300 MHz, respectively, while $^{31}P$ NMR spectra were recorded on a JEOL FX-100 spectrometer at 100 MHz. Infrared spectra were obtained on a Bomem MB-100 spectrometer. Mass spectra at low and high resolution were recorded on JEOL JMS-D100 and JMS-HX110 instruments, respectively.

**Materials.** All chemicals were obtained from commercial suppliers and used without further purification unless otherwise noticed. Zn dust was >230 mesh (Merck), and $ZnCl_2$ was dried under vacuum at 120 °C. The following compounds were

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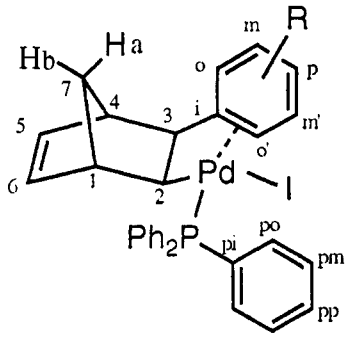
**Chart I**




**1**

prepared according to the published procedures: $Pd(PPh_3)_4$,[20] $PdCl_2(PPh_3)_2$,[21] $PdIAr(PPh_3)_2$[22] 3-iodo-2-cyclohexen-1-one,[23] 5,5-dimethyl-3-iodo-2-cyclohexen-1-one,[23] 3-iodo-2-methyl-2-cyclopenten-1-one,[23] bis($\mu$-chloro)bis[((2:5,6-$\eta^3$)-3-*endo*-phenylnorbornen-2-yl)-*endo*-palladium].[11]

**Synthesis of *cis,exo*-Pd($C_7H_8Ph$)($PPh_3$)I (1a). Method I.** A round-bottom flask containing $Pd(PPh_3)_4$ (1.154 g, 1.00 mmol) and iodobenzene (0.204 g, 1.00 mmol) was purged by nitrogen gas three times. To the flask were added THF (20 mL) and norbornadiene (0.460 g, 5.0 mmol), and the solution was stirred at ambient temperature for 8 h. During the reaction period, the color of the solution changed gradually from pale yellow to orange-red. The solvent and the unreacted norbornadiene were removed in vacuo, and the residue was then washed by ether three times to give the pure product (0.625 g, 0.94 mmol) in 94% yield. Recrystallization from dichloromethane and methanol afforded the crystalline material.

**Method II.** To $Pd(PPh_3)_2(Ph)I$ (0.834 g, 1.00 mmol) in a round-bottom flask under nitrogen were added THF (20 mL) and norbornadiene (0.460 g, 5.0 mmol). The solution was then stirred at ambient temperature for 6 h. The solvent and the unreacted norbornadiene were removed in vacuo, and the residue was then washed by ether three times to give the pure product (0.631 g) in 95% yield. For convenience, the atomic numbering scheme of complex 1 is employed in the NMR peak assignments (see Chart I). $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.26 (ddd, $J_{PH}$ = 10.6 Hz, $J$ = 7.0, 2.1 Hz, H(2), 1 H), 1.62 (d, $J$ = 8.8 Hz, H(7b), 1 H), 2.33 (br s, H(1), 1 H), 2.80 (d, $J$ = 8.8 Hz, H(7a), 1 H), 3.09 (br s, H(4), 1 H), 3.18 (d, $J$ = 7.0 Hz, H(3), 1 H), 5.41 (dd, $J$ = 5.1, 3.0 Hz, H(6), 1 H), 6.07 (dd, $J$ = 5.1, 2.9 Hz, H(5), 1 H), 7.31–7.94 (m, 20 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 38.02 (d, $^2J_{PC}$ = 13.6 Hz, C(2)), 44.84 (C(4)), 47.82 (C(7)), 48.51 (d, $^3J_{PC}$ = 3.1 Hz, C(1)), 49.95 (C(3)), 109.29 (d, $^2J_{PC}$ = 13.4 Hz, C(i)), 128.34 (d, $^3J_{PC}$ = 10.8 Hz, C(pm)), 130.77 (C(pp)), 128.52 (C(m), C(m')), 131.75 (d, $^1J_{PC}$ = 49.3 Hz, C(pi)), 132.08 (C(p)), 135.13 (d, $^2J_{PC}$ = 11.7 Hz, C(po)), 136.89 (C(5)), 137.47 (d, $^4J_{PC}$ = 9.0 Hz, C(6)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): $\delta$ 33.18 (s). IR (KCl): 1560, 1476, 1432, 746, 696 cm$^{-1}$. MS (FAB): $m/z$ 537 $[M-I]^+$. Mp: 138 °C dec. Anal. Calcd for $PdIPC_{31}H_{28}$·0.5$CH_3$OH: C, 55.59; H, 4.41. Found: C, 55.40; H, 4.37.

***cis,exo*-Pd($C_7H_8$-*p*-$C_6H_4OCH_3$)($PPh_3$)I (1b).** The title compound was prepared in 87% yield by following a procedure similar to method I. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.13 (ddd, $J_{PH}$ = 12.3 Hz, $J$ = 7.1, 2.2 Hz, H(2), 1 H), 1.58 (d, $J$ = 8.9 Hz, H(7b), 1 H), 2.25 (br s, H(1), 1 H), 2.78 (d, $J$ = 8.9 Hz, H(7a), 1 H), 3.01 (br s, H(4), 1 H), 3.13 (d, $J$ = 7.1 Hz, H(3), 1 H), 3.90 (s, $OCH_3$, 3 H), 5.39 (dd, $J$ = 5.3, 3.1 Hz, H(6), 1 H), 6.06 (dd, $J$ = 5.3, 2.9 hz, H(5), 1 H), 7.10 (d, $J$ = 8.8 Hz, H(m), H(m'), 7.38–7.47 (m, H(po), H(pp), 9 H), 7.66–7.73 (m, H(pm), 6 H), 7.87 (br d, $J$ = 7.3 Hz, H(o), H(o'), 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 35.74 (d, $^2J_{PC}$ = 14.3 Hz, C(2)), 45.37 (C(4)), 47.88 (C(7)), 48.09 (d, $^3J_{PC}$ = 4.2 Hz, C(1)), 49.27 (C(3)), 55.89 ($OCH_3$), 97.66 (d, $^2J_{PC}$ = 15.5 Hz, C(i)), 117.2 (C(m), C(m')), 128.32 (d, $^3J_{PC}$ = 11.1 Hz, C(pm)), 130.66 (C(pp)), 131.96 (d, $J$ = 48.9 Hz, C(pi)), 135.15 (d, $J$ = 11.4 Hz, C(po)), 136.73 (C(5)), 137.40 (d, $J$ = 8.6 Hz, C(6)), 164.12 (C(p)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): $\delta$ 32.76 (s). IR (KCl): 1597, 1501, 1432, 1256, 824, 750, 685 cm$^{-1}$. MS (FAB): $m/z$ 567 $[M-I]^+$. Mp: 150 °C dec. Anal. Calcd for $PdIPC_{32}H_{30}O$·0.5$CH_3OH$: C, 54.92; H, 4.51; O, 3.38. Found: C, 54.64; H, 4.34; O, 3.28.

***cis,exo*-Pd($C_7H_8$-*p*-$C_6H_4CH_3$)($PPh_3$)I (1c).** The title compound was prepared in 90% yield by following a procedure similar to method I. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.20 (dd, $J_{PH}$ = 12.21 Hz, $J$ = 8.2 Hz, H(2), 1H), 1.58 (d, $J$ = 8.6 Hz, H(7b), 1H), 2.28 (br s, H(1), 1H), 2.51 (s, $CH_3$, 3H), 2.78 (d, $J$ = 8.6 Hz, H(7a), 1H), 3.05 (br s, H(4), 1 H), 3.13 (d, $J$ = 8.2 Hz, H(3), 1H), $\delta$ 5.38 (dd, $J$ = 4.9, 3.3 Hz, H(6), 1 H), 6.04 (dd, $J$ = 4.8, 3.1 Hz, H(5), 1 H), 7.33–7.79 (m, H(m), H(m'), $PPh_3$, 17 H), 7.85 (br d, $J$ = 7.3 Hz, H(o), H(o'), 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 21.55 ($CH_3$), 37.51 (d, $^2J_{PC}$ = 14.4 Hz, C(2)), 44.98 (C(4)), 47.81 (C(7)), 48.33 (d, $^3J_{PC}$ = 4.3 Hz, C(1)), 49.35 (C(3)), 105.81 (d, $^2J_{PC}$ = 14.0 Hz, (C(i)), 128.36 (d, $^3J_{PC}$ = 10.6 Hz. C(pm)), 130.75 (C(pp)), 131.90 (d, $^1J_{PC}$ = 48.7 Hz, C(pi)), 132.63 (C(m), C(m')), 135.22 (d, $^2J_{PC}$ = 11.5 Hz, C(po)), 136.81 (C(5)), 137.49 (d, $^4J_{PC}$ = 8.3 Hz, C(6)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): $\delta$ 32.64 (s). IR (KCl): 1654, 1559, 1476, 1432, 805, 752, 696 cm$^{-1}$. MS (FAB): $m/z$ 551 $[M-I]^+$. Mp: 167 °C dec. Anal. Calcd for $PdIPC_{32}H_{30}$·0.5$CH_3OH$: C, 56.20; H, 4.60. Found: C, 55.64; H, 4.40.

***cis,exo*-Pd($C_7H_8$-*m*-$C_6H_4OCH_3$)($PPh_3$)I (1d).** A round-bottom flask containing $Pd(PPh_3)_4$ (1.154 g, 1.00 mmol) and *m*-iodoanisole (0.234 g, 1.00 mmol) was purged three times with nitrogen gas. THF (20 mL) was then syringed into the flask, and the solution was stirred at ambient temperature for 2 h. Addition of norbornadiene (0.460 g, 5.0 mmol) and methyl iodide (0.426 g, 3.0 mmol) was followed by stirring at the same temperature for 12 h. The solution produced a large quantity of white precipitate, $CH_3Ph_3P^+I^-$, when it was placed in a refrigerator for ca. 10 h. The solid was filtered, and the filtrate was evaporated to afford the crude product. Recrystallization of the solid from a mixture of dichloromethane and methanol gave the desired orange material (0.382 g) in 55% yield. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 1.20 (dd, $J_{PH}$ = 9.4 Hz, $J$ = 7.9 Hz, H(2), 1 H), 1.57 (d, $J$ = 8.8Hz, H(7b), 1 H), 2.31 (br s, H(1), 1H), 2.73 (d, $J$ = 8.8 Hz, H(7a), 1 H), 3.08 (br s, H(4), 1 H), 3.15 (d, $J$ = 7.9 Hz, H(3), 1 H), 3.96 (s, $OCH_3$, 3 H), 5.36 (dd, $J$ = 5.2, 3.4 Hz, H(6), 1 H), 6.04 (dd, $J$ = 5.2, 3.4 Hz, H(5), 1 H), 7.06 (d, $J$ = 8.0 Hz, H(p), 1 H), 7.35–7.46 (m, H(o), H(o'), $PPh_3$, 11 H), 7.54 (t, $J$ = 7.7 Hz, H(m)), 7.65–7.74 (m, $PPh_3$, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): $\delta$ 37.14 (d, $^2J_{PC}$ = 14.0 Hz, C(2)), 44.69 (C(4)), 47.68 (C(7)), 48.53 (d, $^3J_{PC}$ = 4.6 Hz, C(1)), 49.68 (C(3)), 55.66 ($OCH_3$), 112.31 (d, $^2J_{PC}$ = 13.5 Hz, C(i)), 116.47 (C(p)), 119.50 (br, C(o)), 128.31 (d, $^3J_{PC}$ = 11.2 Hz, C(pm)), 130.71 (C(pp)), 131.84 (d, $^1J_{PC}$ = 48.8 Hz, C(pi)), 133.21 (C(m')), 135.17 (d, $^2J_{PC}$ = 11.7 Hz, C(po)), 136.59 (C(5)), 137.47 (d, $^4J_{PC}$ = 9.2 Hz, C(6)), 162.39 (attached to $OCH_3$, C(m)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): $\delta$ 33.15 (s). IR (KCl): 1594, 1507, 1481, 1433, 1280, 749, 715, 693 cm$^{-1}$. MS (FAB): $m/z$ 567 $[M-I]^+$. Mp: 134 °C dec. Anal. Calcd for $PdIPC_{32}H_{30}O$·0.5$CH_3OH$: C, 54.92; H, 4.51; O, 3.38. Found: C, 54.20; H, 4.41; O, 3.19.

***cis,exo*-Pd($C_7H_{10}$-*p*-$C_6H_4OCH_3$)($PPh_3$)I (1e).** To $Pd(PPh_3)_4$ (1.154 g, 1.00 mmol), *p*-iodoanisole (0.234 g, 1.00 mmol), and norbornene (0.47 g, 5.00 mmol) in a round-bottom flask under nitrogen was added THF (20 mL). The solution after being stirred at 60 °C for 3 h was evacuated to remove the solvent and excess NBE. The residue was then washed with ether and recrystallized from dichloromethane and methanol to give the desired orange crystalline material (0.452 g) in 65% yield. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): $\delta$ 0.39 (m, H(6), 1 H), 0.95 (m, H(5), H(6), 2 H), 1.26–1.45 (m, H(7b), H(5), H(2), 3 H), 1.70 (br s, H(1), 1 H), 2.47 (br s, H(4), 1 H), 2.68 (d, $J$ = 9.9 Hz, H(7a), 1 H), 3.25 (d, $J$ =

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7.1 Hz, H(3), 1 H), 3.91 (s, $OCH_3$, 3 H), 7.07 (d, $J$ = 8.5 Hz, H(m), H(m'), 2 H), 7.34–7.45 (m, H(po), H(pp), 9 H), 7.67–7.74 (m, H(pm), 6 H), 7.88 (d, $J$ = 8.5 Hz, H(o), H(o'), 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 27.78 (C(7)), 29.75 (d, $^4J_{PC}$ = 10.5 Hz, C(6)), 37.70 (C(5)), 40.51 (d, $^2J_{PC}$ = 15.4 Hz, C(2)), 40.86 (C(4)), 43.23 (d, $^3J_{PC}$ = 3.8 Hz, C(1)), 53.63 (C(3)), 55.85 ($OCH_3$), 91.37 (d, $^2J_{PC}$ = 19.7 Hz, C(i)), 117.08 (C(m), C(m')), 128.27 (d, $^3J_{PC}$ = 11.1 Hz, C(pm)), 130.63 (C(pp)), 132.00 (d, $^1J_{PC}$ = 47.9 Hz, C(pi)), 135.21 (d, $^2J_{PC}$ = 11.6 Hz, (C(po)), 164.19 (C(p)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): δ 33.09 (s). IR (KCl): 1563, 1559, 1504, 1432, 1254, 822, 751, 696 $cm^{-1}$. MS (FAB): $m/z$ 569 $[M - I]^+$. MP: 156 °C dec. Anal. Calcd for $PdIPC_{32}H_{32}O \cdot 0.5CH_3OH$: C, 54.78; H, 4.78; O, 3.37. Found: C, 54.62; H, 4.70; O, 3.35.

**Synthesis of *cis,endo*-Pd($C_7H_8$-$C_6H_5$)($PPh_3$)I (3).** To a solution of bis(μ-chloro)bis[((2:5,6-η³)-3-*endo*-phenylnorbornen-2-yl)-*endo*-palladium] (**2**; 1.504 g, 2.42 mmol) in $CH_2Cl_2$ (20 mL) with continuous stirring under $N_2$ was slowly added a solution of $PPh_3$ (1.269 g, 4.84 mmol) dissolved in $CH_2Cl_2$ (7 mL) over a period of 1 h. During this period, a yellow material gradually precipitated from the solution. To the vigorously stirred yellow suspension was then added $NBu_4I$ (1.808 g, 4.90 mmol). The system was continuously stirred for ca. 30 min until the yellow suspension was dissolved, and a homogeneous red-brown solution resulted. The solvent was removed in vacuo, and the residue was then washed with ether (3 × 10 mL) and MeOH (3 × 15 mL) to give the desired pure product (2.667 g, 4.02 mmol) in 83% yield. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.68 (d, $J$ = 9.2 Hz, H(7b), 1 H), 1.86 (d, $J$ = 9.2 Hz, H(7a), 1 H), 2.28 (ddd, $J_{PH}$ = 11.3 Hz, $J$ = 4.1, 3.9 Hz, H(2), 1 H), 2.91 (br s, H(1)), 3.16 (br s, H(4), 1 H), 3.60 (br s, H(3), 1 H), 6.83 (dd, $J$ = 4.6, 3.8 Hz, H(6), 1 H), 7.18–7.70 (m, H(5), Ph, PPh, 21 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 40.95 (d, $^2J_{PC}$ = 12.3 Hz, C(2)), 44.81 (C(4)), 52.17 (C(3)), 59.49 (C(7)), 59.76 (C(1)), 89.11 (d, $^2J_{PC}$ = 9.5 Hz, C(6)), 126.87 (C(p)), 127.61 (C(m)), 128.26 (d, $^3J_{PC}$ = 10.7 Hz, C(pm), 128.63 (C(5)), 128.84 (C(o)), 130.48 (C(pp)), 131.45 (d, $^1J_{PC}$ = 44.2 Hz, C(pi)), 134.82 (d, $^2J_{PC}$ = 14.3 Hz, C(po)), 141.08 (C(i)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): δ 20.02. IR (KBr): 1543, 1471, 1429, 747, 691 $cm^{-1}$. MP: 121 °C. MS (FAB): $m/z$ 663 $[M - 1]^+$, 537 $[M - I]^+$. Anal. Calcd for $PdIPC_{31}H_{28}$: C, 56.02; H, 4.22. Found: C, 56.33; H, 4.31.

**Synthesis of *cis,exo*-Pd($C_7H_8$-2-$C_4H_3S$)($PPh_3$)I (4).** A round-bottom flask containing $Pd(PPh_3)_4$ (2.308 g, 2.00 mmol) and 2-iodothiophene (0.420 g, 2.00 mmol) was purged three times with nitrogen. THF (30 mL) was then syringed into the flask, and the solution was stirred at ambient temperature for 3 h. Addition of norbornadiene (0.920 g, 10.0 mmol) and methyl iodide (0.852 g, 6.0 mmol) was followed by stirring at the same temperature for 6 h. During this period, precipitation of a white solid, $CH_3Ph_3P^+I^-$, occurred. The solution was further left in a refrigerator for 10 h. The precipitate was filtered off, and the filtrate was evaporated to remove the solvent. The residue was recrystallized from dichloromethane and methanol to give the orange crystalline product (0.671 g, 1.00 mmol) in 50% yield. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.38 (d, $J$ = 9.3 Hz, H(7b), 1 H), 1.55 (dd, $J$ = 15.6, 7.0 Hz, H(2), 1 H), 2.27 (d, $J$ = 9.3 Hz, H(7a), 1 H), 2.38 (br s, H(1), 1 H), 2.82 (d, $J$ = 7.0 Hz, H(3), 1 H), 2.86 (br s, H(4), 1 H), 5.08 (dd, $J$ = 5.4, 2.9 Hz, H(6), 1 H), 5.89 (dd, $J$ = 5.4, 2.9 Hz, H(5), 1 H), 7.00 (d, $J$ = 3.3 Hz, thiophene H(4), 1 H), 7.21 (dd, $J$ = 5.3, 3.3 Hz, thiophene H(3), 1 H), 7.36–7.48 (m, 9 H), 7.57 (d, $J$ = 5.3 Hz, thiophene H(2), 1 H), 7.66–7.76 (m, 6 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 25 °C): δ 41.19 (d, $^2J_{PC}$ = 9.6 Hz, C(2)), 43.97 (C(3)), 45.90 (C(7)), 48.33 (C(1)), 49.82 (C(4)), 122.95 (thiophene C(4)), [128.33, 130.80, 131.20, 135.45, (phenyl of $PPh_3$)], 129.44 (thiophene C(2)), 132.90 (thiophene C(3)), 135.26 (C(5)), 137.45 (d, $^4J_{PC}$ = 6.7 Hz, C(6)), 139.62 (thiophene C(1)). $^{31}P\{^1H\}$ NMR (40.25 MHz, $CDCl_3$): δ 32.93 (s). IR (KCl): 3030, 1559, 1483, 1093, 743, 723, 692 $cm^{-1}$. Mp 142 °C dec. MS (FAB): $m/z$ 543 $[M - I]^+$ Anal. Calcd for $PdIPSC_{29}H_{26}$: C, 51.94; H, 3.89. Found: C, 52.20; H, 3.91.

**Synthesis of *cis,exo*-Pd($C_7H_8$-$CCHCO(CH_2)_2CH_2$)($PPh_3$)I (5a).** A round-bottom flask containing $Pd(PPh_3)_4$ (3.46 g, 3.00 mmol), 3-iodo-2-cyclohexen-1-one (0.688 g, 3.10 mmol), and norbornadiene (1.38 g, 15.0 mmol) was purged with nitrogen three times. To the flask was added THF (40 mL), and the solution was then stirred at 50 °C for 4 h. Evaporation of the solvent was followed by trituration of the residue with ether. The remaining solid was recrystallized from dichloromethane and methanol to yield orange crystalline material (1.870 g, 2.74 mmol) in 91% yield. $^1H$ NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.15 (dd, $J$ = 15.0, 6.4 Hz, H(2), 1 H), 1.27 (d, $J$ = 9.3 Hz, H(7b), 1 H), 1.98 (d, $J$ = 9.3 Hz, H(7a), 1 H), 2.08–2.31 (br m, cyclohexenone $CH_2$, 2 H), 2.37 (s, H(1), 1 H), 2.46–2.78 (m, H(3), cyclohexenone $CH_2$, 5 H), 2.86 (s, H(4), 1 H), 5.42 (dd, $J$ = 5.5, 3.0 Hz, H(6), 1 H), 5.84 (br s, cyclohexenone CH, 1 H), 6.10 (dd, $J$ = 5.3, 3.0 Hz, H(5), 1 H), 7.45 (m, 9 H), 7.72 (m, 6 H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CD_2Cl_2$, −60 °C): δ 11.88 (d, $^2J_{PC}$ = 6.0 Hz, C(2)), [20.21, 33.23, 35.52 (cyclohexenone $CH_2$)], 45.50 (C(4)), 46.08 (C(1)), 47.33 (C(7)), 47.55 (C(3)), 104.16 (d, $J_{PC}$ = 16.1 Hz, cyclohexenone CH), 128.86 (cyclohexenone C), 136.27 (d, $J_{PC}$ = 11.1 Hz, C(6)), 137.65 (C(5)), 198.25 (=CO), [127.75 (d, $J_{PC}$ = 11.1 Hz), 129.93 (d, $J_{PC}$ = 50.6 Hz), 130.45 (s), 134.60 (d, $J_{PC}$ = 11.1 Hz), $PPh_3$]. $^{31}P\{^1H\}$ NMR (40 MHz, $CDCl_3$): δ 31.09 (s). IR (KCl): 3050, 2980, 1674, 1653, 1568, 1433, 750, 693 $cm^{-1}$. MS (FAB): $m/z$ 555 $[M - I]^+$. Anal. Calcd for $C_{31}H_{30}IOPPd$: C, 54.55; H, 4.40. Found: C, 54.71; H, 4.52.

***cis,exo*-Pd($C_7H_8$-$CCHCOCH_2C(CH_3)_2CH_2$)($PPh_3$)I (5b).** The title compound was prepared as an orange powder in 86% yield by following a procedure similar to that described for **5a**. $^1H$ NMR (400.18 MHz, $CD_2Cl_2$, 20 °C): δ 0.35 (br s, H(2), 1 H), 0.97 (s, $CH_3$, 6 H), 1.28 (d, $J$ = 9.3 Hz, H(7b), 1 H), 1.49 (s, $CH_2$ attached to CO, 2 H), 2.06 (d, $J$ = 9.3 Hz, H(7a), 1 H), 2.30 (br s, H(4), 1 H), 2.40 (br s, H(3), 1 H), 2.65 (br s, cyclohexenone $CH_2$ attached to C=C, 2 H), 2.90 (br s, H(1), 1 H), 5.31 (dd, $J$ = 5.3, 3.1 Hz, H(5), 1 H), 5.98 (dd, $J$ = 5.3, 3.1 Hz, H(6), 1 H), 6.26 (br s, CH attached to CO, 1 H), 7.28–7.43 (m, $PPh_3$, 9 H), 7.55–7.67 (m, $PPh_3$, 6 H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CD_2Cl_2$, −50 °C): δ 13.21 (d, $^2J_{PC}$ = 5.4 Hz, C(2)), 30.24 ($CH_3$), 34.59 ($CH_3$), 42.7 ($C(CH_3)_2$), 45.78 (C(4)), 46.91 (C(1)), 47.72 (C(7)), 47.87 (C(3)), 104.47 (d, $J_{PC}$ = 15.8 Hz, cyclohexenone CH), 127.25 (cyclohexenone C), 136.53 (d, $J_{PC}$ = 10.9 Hz, C(6)), 137.50 (C(5)), 200.48 (CO), [127.70 (d, $J_{PC}$ = 11.2 Hz), 129.83 (d, $J_{PC}$ = 59.5 Hz), 130.45 (s), 134.56 (d, $J_{PC}$ = 11.1 Hz), $PPh_3$]. IR (KBr): 1677, 1432, 1092, 719, 694 $cm^{-1}$. MS (FAB): $m/z$ 583 $[M - I]^+$.

***cis,exo*-Pd($C_7H_8$-$CC(CH_3)COCH_2CH_2$)($PPh_3$)I (5c).** The title compound was prepared as an orange powder in 68% yield by following a procedure similar to that described for **5a**. $^1H$ NMR (400.18 MHz, $CD_2Cl_2$, 20 °C): δ 0.65 (dd, $J$ = 8.9, 8.8 Hz, H(2), 1 H), 1.48 (d, $J$ = 8.8 Hz, H(7b), 1 H), 2.23 (s, H(1), $CH_3$, 4 H), 2.31 (d, $J$ = 8.8 Hz, H(7a), 1 H), 2.40 (dd, $J$ = 19.1, 7.3 Hz, cyclopentenone C=C-$CH_2$, 1 H), 2.50 (br d, $J$ = 19.3 Hz, cyclopentenone C(O)$CH_2$, 1 H), 2.96 (br d, $J$ = 19.3 Hz, cyclopentenone C(O)$CH_2$, 1 H), 3.13 (br s, H(4), 1 H), 3.18 (dd, $J$ = 18.5, 7.1 Hz, cyclopentenone C=C$CH_2$, 1 H), 3.43 (d, $J$ = 8.8 Hz, H(3), 1 H), 5.31 (dd, $J$ = 5.1, 2.2 Hz, H(6), 1 H), 6.05 (dd, $J$ = 5.2, 2.2 Hz, H(5), 1 H), 7.45–7.50 (m, $PPh_3$, 9 H), 7.63–7.68 (m, $PPh_3$, 6 H). $^{13}C\{^1H\}$ NMR (100.61 MHz, $CD_2Cl_2$, −50 °C): δ 13.08 ($CH_3$), 24.94 (d, $J_{PC}$ = 11.0 Hz, C(2)), 27.43 (cyclopentenone $CH_2$), 34.05 (cyclopentenone $CH_2$), 42.91 (C(4)), 46.20 (C(1)), 47.40 (C(3)), 48.09 (C(7)), 132.90 (d, $J_{PC}$ = 9.0 Hz, cyclopentenone C attached to norbornenyl group), 134.22 (C attached to $CH_3$), 135.20 (C(5)), 136.03 ($J_{PC}$ = 8.0 Hz, C(6)), 208.65 (CO), [128.05 (d, $J_{PC}$ = 10.0 Hz), 130.65 (d, $J_{PC}$ = 50.0 Hz), 130.52 (s), 134.45 (d, $J_{PC}$ = 12.0 Hz), $PPh_3$]. IR (KBr): 1908, 1432, 1089, 698 $cm^{-1}$. MS (FAB): $m/z$ 555 $[M - I]^+$.

**Synthesis of 7 from the Reaction of Copper(I) Cyanide with 1b.** A round-bottom flask containing **1b** (0.139 g, 0.20 mmol), Zn powder (0.013 g, 0.20 mmol), and $ZnCl_2$ (0.027 g, 0.20 mmol) was purged three times with nitrogen. THF (2 mL) was then syringed into the flask, and the solution was stirred at room temperature for 1 h. The solvent was then removed under vacuum, and the residue was purified on a silica gel column using a mixture of ethyl acetate and *n*-hexane (1:5) as the eluent to give the desired pure product **7** (0.037 g, 0.16 mmol) in 83% yield. $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.77 (d, $J$ = 9.3 Hz, 1 H), 2.10 (d, $J$

= 9.3 Hz, 1 H), 2.77 (d, $J$ = 8.9 Hz, 1 H), 3.01 (d, $J$ = 8.9 Hz, 1 H), 3.16 (br s, 1 H), 3.32 (br s, 1 H), 3.79 (s, 3 H), 6.17 (dd, $J$ = 5.6, 3.0 Hz, 1 H), 6.42 (dd, $J$ = 5.6, 3.0 Hz, 1 H), 6.89 (d, $J$ = 8.7 Hz, 2 H), 7.17 (d, $J$ = 8.7 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 36.47 (d), 46.12 (t), 46.42 (d), 46.47 (d), 48.13 (d), 55.12 (q), 114.04 (d), 121.24 (s), 129.62 (d), 131.84 (s), 135.24 (d), 140.74 (d), 158.50 (s). IR (neat): 3057, 2969, 2835, 2234, 1611, 1512, 1447, 1252, 1033, 834, 696 $cm^{-1}$. HRMS: $C_{15}H_{15}NO$, calcd 225.1154, found 225.1163.

**Reaction of 1b with Sodium Borohydride.** Excess sodium borohydride (0.019 g, 0.51 mmol) dissolved in MeOH (1 mL) was added to a THF solution of **1b** (0.298 g, 0.43 mmol). The mixture was stirred at room temperature for 1 h. The color of the solution changed gradually from yellow-orange to black. The solution was then filtered through Celite, the solvent was removed under vacuum, and the residue was purified on a silica gel column using a mixture of ethyl acetate and $n$-hexane (1:20) as the eluent to give the desired pure product **8** (0.080 g, 0.40 mmol) in 92% yield. $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.14–1.37 (m, 3 H), 1.50–1.78 (m, 5 H), 2.31 (br s, 1 H), 2.34 (br s, 1 H), 2.69 (dd, $J$ = 8.4, 5.8 Hz, 1 H), 3.78 (s, 3 H), 6.83 (d, $J$ = 8.6 Hz, 2 H), 7.14 (d, $J$ = 8.6 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 28.73 (t), 30.36 (t), 35.78 (t), 36.64 (d), 39.05 (t), 43.04 (d), 46.42 (d), 55.16 (q), 113.70 (d), 128.10 (d), 140.04 (s), 157.70 (s). IR (neat): 2944, 2869, 1610, 1510, 1455, 1247, 1179, 1038, 818 $cm^{-1}$. MS ($m/z$ (relative intensity)): 135 (11), 202 (100). HRMS: $C_{14}H_{18}O$, calcd 202.1358, found 202.1366.

**Synthesis of 3-*p*-Anisylnortricyclene (9) from 1b.** A round-bottom flask containing **1b** (0.347 g, 0.50 mmol), Zn powder (0.065 g, 1.00 mmol), $ZnCl_2$ (0.068 g, 0.50 mmol), and $PPh_3$ (0.393 g, 1.50 mmol) was purged three times with nitrogen. THF (4 mL) was then syringed into the flask, and the solution was stirred at room temperature for 3 h. The solution was then filtered through Celite, the solvent was removed under vacuum, and the residue was purified on a silica gel column using a mixture of ethyl acetate and $n$-hexane (1:20) as the eluent to give the desired pure product **9** (0.096 g, 0.48 mmol) in 96% yield. $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.03 (d, $J$ = 10.4 Hz, 1 H), 1.17–1.26 (m, 4 H), 1.37 (d, $J$ = 10.1 Hz, 1 H), 1.49 (d, $J$ = 10.4 Hz, 1 H), 1.89 (br s, 1 H), 2.76 (br s, 1 H), 3.75 (s, 3 H), 6.81 (d, $J$ = 8.5 Hz, 2 H), 7.16 (d, $J$ = 8.5 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 9.85 (d), 11.20 (d), 13.53 (d), 28.45 (t), 34.37 (t), 35.86 (d), 48.41 (d), 55.01 (q), 113.35 (d), 128.81 (d), 134.76 (s), 158.01 (s); IR (neat): 3059, 2944, 2867, 1641, 1510, 1245, 1177, 816, 770 $cm^{-1}$. HRMS: $C_{14}H_{16}O$, calcd 200.1201, found 200.1201.

**General Procedure for the Preparation of 3,5-Disubstituted Nortricyclenes (10).** A round-bottom flask containing a palladium complex (**1** or **5**; 1.00 mmol), Zn powder (0.065 g, 1.00 mmol), and $ZnCl_2$ (0.136 g, 1.00 mmol) was purged three times with nitrogen. A mixture of THF (20 mL) and 3-iodo 2-en-1-one (1.10 mmol) was then syringed into the flask, and the solution was stirred at 60 °C for 2 h. During the reaction period, the color of the solution changed gradually from yellow or orange to brown. The solution was then filtered through Celite, and the solvent was removed in vacuo to afford a dark brown oil. Chromatography of the oil on a silica gel column using a mixture of ethyl acetate and $n$-hexane as the eluent followed by evaporation of the solvent gave the desired product. The isolated yields of these 3,5-disubstituted nortricyclene are listed in Table I, while important spectral data of these compounds are shown below.

***cis,exo*-3,5-Bis(3-oxo-1-cyclohexen-1-yl)nortricyclene (10a).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.13 (s, 2 H), 1.32 (s, 2 H), 1.63 (s, 1 H), 1.95–2.02 (m, 3 H), 2.28 (m, 2 H), 2.34–2.40 (m, 2 H), 2.42 (s, 2 H), 5.97 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 9.71 (d), 13.81 (d), 22.52 (t), 25.69 (t), 29.02 (t), 35.62 (d), 37.29 (t), 52.97 (d), 126.25 (d), 164.95 (s), 200.24 (s). IR (neat): 3057, 2940, 2871, 1665, 1621, 1324, 1250, 1190, 1120, 967, 887, 813, 669 $cm^{-1}$. HRMS: $C_{19}H_{22}O_2$, calcd 282.1621, found 282.1635.

***cis,exo*-3,5-Bis(5,5-dimethyl-3-oxo-1-cyclohexen-1-yl)nortricyclene (10b).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 6 H), 1.07 (s, 6 H), 1.14 (s, 2 H), 1.25 (br s, 2 H), 1.77 (br s, 1 H), 2.00 (s, 1 H), 2.16 (s, 4 H), 2.23 (s, 4 H), 2.23 (s, 4 H), 2.38 (s, 2 H), 5.98 (s, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 9.73 (d), 13.99 (d), 25.71 (t), 27.96 (q), 28.13 (q), 33.36 (s), 35.34 (d), 43.45 (t), 51.06 (t), 52.98 (d), 125.23 (d), 162.54 (s), 200.43 (s). IR (neat): 3057, 2950, 2869, 1664, 1626, 1367, 1303, 1245, 902, 817, 737 $cm^{-1}$. HRMS: $C_{23}H_{30}O_2$, calcd 338.2260, found 338.2253.

***cis,exo*-3-(3-Oxo-1-cyclohexen-1-yl)-5-phenylnortricyclene (10c).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.04 (d, $J$ = 11.1 Hz, 1 H), 1.11 (d, $J$ = 11.1 Hz, 1 H), 1.35 (t, $J$ = 5.3 Hz, 1 H), 1.42 (t, $J$ = 5.3 Hz, 1 H), 1.51 (t, $J$ = 5.3 Hz, 1 H), 1.94–2.04 (m, 2 H), 2.02 (s, 1 H), 2.29–2.34 (m, 2 H), 2.34–2.40 (m, 2 H), 2.54 (s, 1 H), 3.03 (s, 1 H), 6.01 (s, 1 H), 7.18–7.32 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 10.07 (d), 13.91 (d), 14.80 (d), 22.62 (t), 25.07 (t), 29.12 (t), 37.39 (t), 39.02 (d), 50.89 (d), 52.86 (d), 126.06 (d), 126.37 (d), 127.92 (d), 128.19 (d), 141.58 (s), 166.04 (s), 200.50 (s). IR (neat): 3056, 2943, 2874, 1666, 1621, 1494, 1451, 1427, 1348, 1293, 1249, 1190, 1130, 1030, 967, 890, 813, 747, 701 $cm^{-1}$. HRMS: $C_{19}H_{20}O$, calcd 264.1526, found 264.1532.

***cis,exo*-3-(5,5-Dimethyl-3-oxo-1-cyclohexen-1-yl)-5-phenylnortricyclene (10d).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.99 (s, 3 H), 1.04 (d, $J$ = 10.2 Hz, 1 H), 1.05 (s, 3 H), 1.10 (d, $J$ = 10.2 Hz, 1 H), 1.35 (t, $J$ = 5.0 Hz, 1 H), 1.42 (t, $J$ = 5.0 Hz, 1 H), 1.50 (t, $J$ = 5.0 Hz, 1 H), 2.01 (s, 1 H), 2.19 (s, 2 H), 2.22 (d, $J$ = 2.2 Hz, 2 H), 2.49 (s, 1 H), 3.02 (s, 1 H), 6.01 (s, 1 H), 7.27 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 10.06 (d), 14.01 (d), 14.90 (d), 25.09 (t), 27.84 (q), 28.29 (q), 33.38 (s), 38.87 (d), 43.55 (t), 50.92 (d), 51.11 (t), 52.80 (d), 124.96 (d), 126.38 (d), 127.92 (d), 128.19 (d), 141.56 (s), 163.62 (s), 200.64 (s). IR (neat): 3057, 2982, 2873, 1666, 1623, 1304, 1279, 1246, 904, 814, 748, 701 $cm^{-1}$. HRMS: $C_{21}H_{24}O$, calcd 292.1828, found 292.1832.

***cis,exo*-3-(3-Oxo-2-methyl-1-cyclopenten-1-yl)-5-phenylnortricyclene (10e).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.09 (d, $J$ = 11.2 Hz, 1 H), 1.21 (d, $J$ = 11.2 Hz, 1 H), 1.46 (t, $J$ = 4.7 Hz, 1 H), 1.53–1.60 (m, 2 H), 1.82 (s, 3 H), 2.19 (s, 1 H), 2.34–2.65 (m, 4 H), 2.90 (s, 1 H), 3.07 (s, 1 H), 7.29 (m, 5 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 8.42 (q), 10.92 (d), 14.58 (d), 15.01 (d), 26.30 (t), 30.21 (t), 33.86 (t), 40.68 (d), 48.62 (d), 50.21 (d), 127.99 (d), 128.22 (d), 137.11 (s), 141.32 (s), 173.54 (s), 210.73. IR (neat): 3058, 2940, 2876, 1694, 1634, 1495, 1446, 1380, 1337, 1302, 1057, 1029, 907, 814, 701 $cm^{-1}$. HRMS: $C_{19}H_{20}O$, calcd 264.1526, found 264.1535.

***cis,exo*-3-(3-Oxo-1-cyclohexen-1-yl)-5-*p*-anisylnortricyclene (10f).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.03 (d, $J$ = 11.0 Hz, 1 H), 1.10 (d, $J$ = 11.0 Hz, 1 H), 1.33 (t, $J$ = 5.3 Hz, 1 H), 1.40 (t, $J$ = 5.3 Hz, 1 H), 1.47 (d, $J$ = 5.3 Hz, 1 H), 1.93–2.03 (m, 2 H), 1.97 (s, 1 H), 2.28–2.40 (m, 2 H), 2.51 (s, 1 H), 2.97 (s, 1 H), 6.01 (s, 1 H), 6.84 (d, $J$ = 8.6 Hz, 2 H), 7.17 (d, $J$ = 8.6 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 13.92 (d), 15.02 (d), 22.64 (t), 24.99 (t), 29.15 (t), 37.41 (t), 39.09 (d), 50.15 (d), 52.81 (d), 55.15 (q), 113.54 (d), 126.02 (d), 128.83 (d), 133.67 (s), 158.32 (s), 166.16 (s), 200.50 (s). IR (neat): 3056, 2943, 2874, 2835, 1666, 1512, 1457, 1295, 1246, 1180, 1034, 814, 669 $cm^{-1}$. HRMS: $C_{20}H_{22}O$, calcd 294.1621, found 294.1635.

***cis,exo*-3-(5,5-Dimethyl-3-oxo-1-cyclohexen-1-yl)-5-*p*-anisylnortricyclene (10g).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.98 (s, 3 H), 1.03 (d, $J$ = 14.4 Hz, 1 H), 1.05 (s, 3 H), 1.10 (d, $J$ = 14.4 Hz, 1 H), 1.33 (t, $J$ = 5.4 Hz, 1 H), 1.40 (t, $J$ = 5.4 Hz, 1 H), 1.47 (t, $J$ = 5.4 Hz, 1 H), 1.96 (s, 1 H), 2.19 (s, 1 H), 2.22 (d, $J$ = 2.2 Hz, 2 H), 2.45 (s, 1 H), 2.96 (s, 1 H), 3.78 (s, 3 H), 6.00 (s, 1 H), 6.83 (d, $J$ = 8.6 Hz, 2 H), 7.17 (d, $J$ = 8.6 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 9.88 (d), 13.88 (d), 14.99 (d), 24.89 (t), 27.71 (q), 28.18 (q), 33.25 (s), 38.80 (d), 43.40(t), 50.03 (d), 51.00 (t), 52.59 (d), 55.01 (q), 113.44 (d), 124.76 (d), 128.70 (d), 133.51 (s), 158.21 (s), 163.66 (s), 200.48 (s). IR (neat): 3053, 2943, 2873, 2833, 1666, 1512, 1246, 1181, 1033, 813, 776 $cm^{-1}$. HRMS: $C_{22}H_{24}O_2$, calcd 321.1856, found 321.1845.

***cis,exo*-3-(3-Oxo-2-methyl-1-cyclopenten-1-yl)-5-*p*-anisylnortricyclene (10h).** $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.08 (d, $J$ = 11.2 Hz, 1 H), 1.20 (d, $J$ = 11.2 Hz, 1 H), 1.42–1.57 (m, 3 H), 1.81 (s, 3 H), 2.14 (s, 1 H), 2.34–2.65 (m, 4 H), 2.87 (s, 1 H), 3.02 (s, 1 H), 3.80 (s, 3 H), 6.85 (d, $J$ = 8.7 Hz, 2 H), 7.19 (d, $J$ = 8.7 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 8.37 (q), 10.81 (d), 14.54 (d), 15.18 (d), 26.18 (t), 30.19 (t), 33.82 (t), 40.71 (d), 48.52

(d), 49.42 (d), 55.12 (d), 113.55 (d), 128.86 (d), 133.33 (s), 137.00 (s), 158.33 (s), 173.81 (s), 210.82 (s). IR (neat): 3058, 2943, 2877, 2835, 1694, 1633, 1512, 1450, 1382, 1301, 1246, 1177, 1034, 821, 791 $cm^{-1}$. HRMS: $C_{20}H_{22}O_2$, calcd 294.1621, found 294.1612.

***cis,exo*-3-(3-Oxo-1-cyclohexen-1-yl)-5-*p*-tolylnortricyclene (10i).** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.03 (d, $J$ = 11.1 Hz, 1 H), 1.11 (d, $J$ = 11.1 Hz, 1 H), 1.33 (t, $J$ = 5.2 Hz, 1 H), 1.40 (t, $J$ = 5.2 Hz, 1 H), 1.40 (t, $J$ = 5.2 Hz, 1 H), 1.49 (t, $J$ = 5.2 Hz, 1 H), 1.93–2.03 (m, 2 H), 2.52 (s, 1 H), 2.99 (s, 1 H), 6.01 (s, 1 H), 7.11 (d, $J$ = 8.2 Hz, 2 H), 7.15 (d, $J$ = 8.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 10.04 (d), 13.88 (d), 14.88 (d), 20.76 (q), 22.61 (t), 25.04 (t), 29.12 (t), 37.38 (d), 39.01 (d), 50.53 (d), 52.54 (d), 125.99 (d), 127.78 (d), 128.87 (d), 135.88 (s), 138.49 (s), 166.17 (s), 200.50 (s). IR (neat): 3051, 2940, 2873, 1653, 1620, 1542, 1378, 1213, 1129, 966, 891, 812, 779, 668 $cm^{-1}$. HRMS: $C_{20}H_{22}O$, calcd 278.1683, found 278.1701.

***cis,exo*-3-(5,5-Dimethyl-3-oxo-1-cyclohexen-1-yl)-5-*p*-tolylnortricyclene (10j).** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 0.99 (s, 3 H), 1.03 (d, $J$ = 11.3 Hz, 1 H), 1.06 (s, 3 H), 1.11 (d, $J$ = 11.3 Hz, 1 H), 1.34 (dd, $J$ = 5.4, 5.2 Hz, 1 H), 1.41 (dd, $J$ = 5.2, 5.0 Hz, 1 H), 1.49 (dd, $J$ = 5.4, 5.0 Hz, 1 H), 1.98 (s, 1 H), 2.19 (s, 2 H), 2.22 (d, $J$ = 2.1 Hz, 1 H), 2.32 (s, 3 H), 2.47 (s, 1 H), 2.99 (s, 1 H), 6.01 (s, 1 H), 7.11 (d, $J$ = 8.2 Hz, 2 H), 7.15 (d, $J$ = 8.2 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 9.98 (d), 13.91 (d), 14.92 (d), 20.73 (q), 25.01 (t), 27.77 (q), 28.24 (q), 33.32 (s), 38.80 (d), 43.48 (t), 50.50 (d), 51.05 (t), 52.72 (d), 124.84 (d), 135.84 (s), 138.43 (s), 163.71 (s), 200.59 (s). IR (neat): 3054, 2953, 2874, 1686, 1513, 1374, 1274, 1213, 997, 904, 819, 735 $cm^{-1}$. HRMS: $C_{22}H_{25}O$, calcd 305.1907, found 305.1895.

***cis,exo*-3-(3-Oxo-2-methyl-1-cyclopenten-1-yl)-5-*p*-tolylnortricyclene (10k).** $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 1.08 (d, $J$ = 11.2 Hz, 1 H), 1.21 (d, $J$ = 11.2 Hz, 1 H), 1.41–1.46 (m, 2 H), 1.52–1.56 (m, 1 H), 1.82 (s, 3 H), 2.16 (s, 1 H), 2.33 (s, 3 H), 2.36–2.59 (m, 4 H), 2.88 (s, 1 H), 3.03 (s, 1 H), 7.12 (d, $J$ = 8.1 Hz, 2 H), 7.17 (d, $J$ = 8.1 Hz, 2 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 8.40 (q), 10.88 (d), 14.54 (d), 15.07 (d), 20.78 (q), 26.27 (t), 30.23 (t), 33.85 (t), 40.68 (d), 48.59 (d), 49.85 (d), 127.85 (d), 128.90 (d), 135.96 (s), 137.05 (s), 138.21 (s), 173.89 (s), 210.91 (s). IR (neat): 3053, 2947, 2920, 2876, 1692, 1635, 1514, 1446, 1408, 1381, 1256, 1215, 1174, 1098, 1067, 1021, 907, 851, 817, 788, 751, 615 $cm^{-1}$. HRMS: $C_{20}H_{22}O$, calcd 278.1672, found 278.1679.

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