

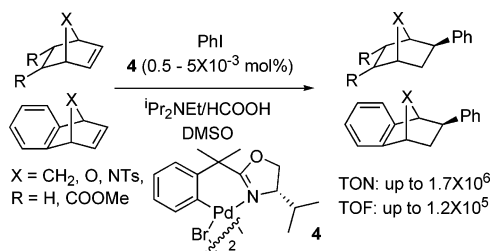
# A Highly Efficient Palladacycle Catalyst for Hydrophenylation of C-, N-, and O-Substituted Bicyclic Alkenes under Aerobic Condition

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A new phosphine-free palladacycle catalyst **4** was prepared from benzyl oxazoline in high yield and fully characterized. With it as catalyst, hydrophenylation reactions of a wide range of bicyclic alkenes, not only norbornene and norbornadiene but also oxa- and aza-bicyclic alkenes, with iodobenzene proceeded smoothly under aerobic condition without exclusion of water. Up to  $1.7 \times 10^6$  TON as well as  $1.2 \times 10^5$  TOF were achieved.

Carbon-carbon bond formations are among the most important reactions in organic synthesis. A variety of metal complexes have been used as catalyst in such transformations.<sup>1</sup> Among them, palladacycles have showed enormous superiority in many respects due to their ready preparation, air and moisture stability, low loading, and high efficiency.<sup>2</sup> Many palladacycles are efficient Heck-type reaction catalysts and very high (up to 10<sup>10</sup>) turnover numbers (TON, mol product per mol catalyst) are

achieved.<sup>3</sup> Hydroarylation reaction, similar to the Heck reaction, also is an useful methodology developed by Larock and co-workers in 1989<sup>4</sup> and was employed successfully in the synthesis of natural products analogous to epibatidine alkaloid.<sup>5</sup> However, to the best of our knowledge, there are only two cases so far using palladacycles as catalysts in hydroarylation reactions and substrates were limited to norbornene and norbornadiene.<sup>6,7</sup> In our previous studies on the design, synthesis, and application of ligands in asymmetric catalysis,<sup>8</sup> we found that catalyst with ligands bearing a substituent at the benzylic position showed higher catalytic activity.<sup>8b,g,k</sup> On the basis of these findings, we designed and synthesized a novel palladacycle, with an oxazoline moiety and two methyl groups situated at the benzylic position, and found that it was highly efficient in the hydrophenylation of a variety of bicyclic alkenes, not only norbornene and norbornadiene but also oxa- and azabicyclic alkenes, with PhI. Herein we would like to report our preliminary results on the synthesis, characterization, and application of this palladacycle in hydrophenylation reaction.

The synthesis of palladacycle **4** is as follows (Scheme 1). Compound **1**<sup>9</sup> reacted with SOCl<sub>2</sub> followed by treatment with L-valinol to afford amide **2**, from which oxazoline **3** was prepared using the literature procedure.<sup>10</sup> The palladacycle **4** was afforded as a yellow

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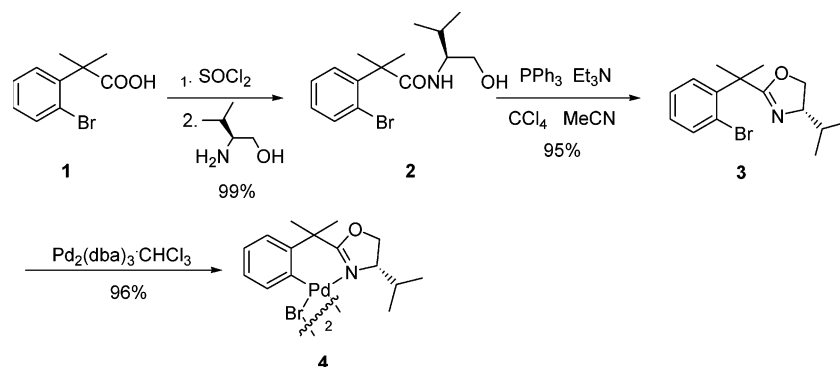
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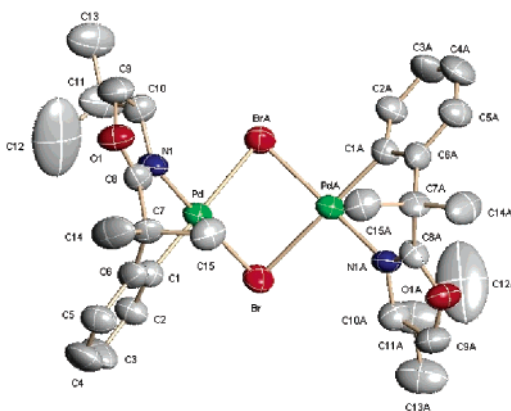
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## SCHEME 1. Synthesis of palladacycle 4



powder after an oxidative addition reaction of  $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$  with oxazoline **3**. Palladacycle **4** is air stable. The X-ray diffraction analysis showed that it is a dimer with a distorted square-planar geometry (Figure 1).



**FIGURE 1.** ORTEP drawing of **4**. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Pd–C(1) 1.997(9); Pd–N(1) 2.032(8); Pd–Br 2.4561(12); Pd–Br(A) 2.5948(12); C(1)–Pd–N(1) 85.7(3); C(1)–Pd–Br 93.0(3); N(1)–Pd–Br 172.3(3); C(1)–Pd–Br(A) 178.6(3); N(1)–Pd–Br(A) 95.2(2); Br–Pd–Br(A) 86.26(5)

With the palladacycle **4** in hand, hydrophenylation reaction of norbornene was carried out to test its catalytic efficiency. The reaction of norbornene with halobenzene proceeded utilizing palladacycle **4** as catalyst in the presence of  $i\text{Pr}_2\text{NEt}/\text{HCOOH}$  in different solvents under aerobic condition, and the results are listed in Table 1.

As can be seen from Table 1, in all solvents the reaction led to corresponding *exo*-phenylnorbornane as single product, and DMSO is the best one among the solvents tested (entry 5, Table 1). Using 0.25 mol % of palladacycle **4** in DMSO, hydrophenylation of norbornene with iodobenzene gave rise to the corresponding *exo*-phenylnorbornane in almost quantitative yield (entry 8, Table 1), whereas that with bromobenzene provided the product in low yield with very low turnover number and turnover frequency (TOF, mol product per mol catalyst  $\text{h}^{-1}$ ) (entry 7, Table 1) and no reaction took place with chlorobenzene (entry 6, Table 1). High catalytic activity of palladacycle **4** is also shown in the reaction. When the amount of catalyst was decreased from 0.25 mol % to  $2.5 \times 10^{-3}$  mol %, a quantitative yield of product was still delivered with  $1.9 \times 10^4$  TON and  $1.9 \times 10^4$  TOF (entry 5, Table 1). Even when the catalyst loading was lowered to  $2.5 \times$

**TABLE 1.** Hydrophenylation of Norbornene Catalyzed by Palladacycle **4**<sup>a</sup>

en- try	solvent	PhX	<b>4</b>	temp (°C)	time (h) <sup>b</sup>	yield (%) <sup>c</sup>	TON	TOF (h <sup>-1</sup> )
1	toluene	PhI	$2.5 \times 10^{-3}$	120	18	20	$4 \times 10^3$	222
2	DMF	PhI	$2.5 \times 10^{-3}$	120	18	75	$1.5 \times 10^4$	833
3	DMA	PhI	$2.5 \times 10^{-3}$	120	18	50	$1.0 \times 10^4$	555
4	NMP	PhI	$2.5 \times 10^{-3}$	120	18	82	$1.6 \times 10^4$	911
5	DMSO	PhI	$2.5 \times 10^{-3}$	120	1	97	$1.9 \times 10^4$	$1.9 \times 10^4$
6	DMSO	PhCl	0.25	120	24	0	0	0
7	DMSO	PhBr	0.25	120	24	15	30	1.25
8	DMSO	PhI	0.25	65	0.5	99	198	396
9 <sup>d</sup>	DMSO	PhI	0.25	65	0.5	99	198	396
10	DMSO	PhI	$2.5 \times 10^{-5}$	120	15	87	$1.7 \times 10^6$	$1.2 \times 10^5$

<sup>a</sup> Reaction conditions: PhX (1 mmol), norbornene (3 mmol), formic acid (3 mmol),  $i\text{Pr}_2\text{NEt}$  (4 mmol), solvent (5 mL). <sup>b</sup> Monitored by GC. <sup>c</sup> Isolated yield. <sup>d</sup> 2 mL of  $\text{H}_2\text{O}$  was added.

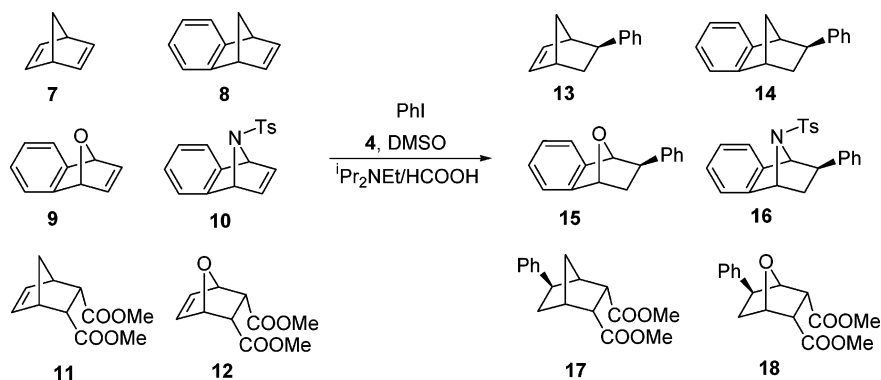
$10^{-5}$  mol %, the yield of product was still good and  $1.7 \times 10^6$  TON and  $1.2 \times 10^5$  TOF were achieved (entry 10, Table 1).<sup>11</sup> All reactions were carried out under aerobic condition, and the presence of water did not disturb the reaction. If the water was added to the reaction mixture, the result was the same as that without water (entry 9 vs entry 8, Table 1). Similar to the results reported by Navarro, the  $[\alpha]_D$  values of the products were almost zero in all cases.<sup>7</sup> When the palladacycle monomer produced in situ by the reaction of palladacycle **4** and  $\text{PPh}_3$  was used almost same results were provided.

The high catalytic efficiency of palladacycle **4** encouraged us to extend the scope of substrates. Instead of norbornene, several other bicyclic alkenes including oxo- and aza-bicyclic alkenes were employed in the hydrophenylation reaction (Scheme 2), and the results are summarized in Table 2.

All reactions proceeded smoothly at 120 °C under aerobic condition to afford corresponding products in good to excellent yield. TONs of  $10^4$  were afforded for all the bicyclic alkenes, such as benzonorbornadiene **8** (entry 3, Table 2), oxo-benzonorbornadiene **9** (entry 4, Table 2), substituted norbornene **11** and oxo-norbornene **12** (entries 6 and 7, Table 2), except aza-bicyclic alkene **10**, for which 0.25 mol % of catalyst **4** should be used (entry 5, Table 2) because of its low reactivity.<sup>12</sup>

(11) Sometimes phenylnorbornane was obtained when the amount of palladacycle **4** was  $2.5 \times 10^{-7}$  mol %.

## SCHEME 2. Catalytic Hydroarylation of Bicyclic Alkenes

TABLE 2. Catalytic Hydrophenylation of Different Bicyclic Alkenes with Palladacycle 4<sup>a</sup>

entry	substrate	4	<i>t</i> (h) <sup>b</sup>	product	yield (%) <sup>c</sup>	TON
1	5	$2.5 \times 10^{-5}$	15	6	87	$1.7 \times 10^6$
2	7	$2.5 \times 10^{-3}$	3	13	89	$1.8 \times 10^4$
3	8	$2.5 \times 10^{-3}$	3	14	93	$1.9 \times 10^4$
4	9	$2.5 \times 10^{-3}$	4	15	97	$1.9 \times 10^4$
5	10	0.25	4	16	66	132
6	11	$2.5 \times 10^{-3}$	14	17	82	$1.6 \times 10^4$
7	12	$2.5 \times 10^{-3}$	12	18	71	$1.4 \times 10^4$

<sup>a</sup> Reaction conditions: PhI (0.5 mmol), bicyclic alkene (1.5 mmol), formic acid (1.5 mmol),  $\text{Pr}_2\text{NEt}$  (2 mmol), DMSO (5 mL). The reaction was carried out at 120 °C. <sup>b</sup> Monitored by GC. <sup>c</sup> Isolated yield.

In summary, a new phosphine-free palladacycle has been synthesized in high yield using simple operations and fully characterized. The palladacycle is well-defined and air stable. Its high catalytic activity has been shown in hydrophenylation reactions of a wide range of bicyclic alkenes with iodobenzene under aerobic condition, and exclusion of water is not necessary. Up to  $1.7 \times 10^6$  TON and  $1.2 \times 10^5$  TOF were achieved. This is the first example of hydrophenylation reaction using palladacycle as catalyst performed under aerobic condition for a wide range of bicyclic alkenes. We believe that high efficiency of catalyst will facilitate the procedure of the reaction, even make it suitable for industrial scale synthesis. Applying the palladacycle to other coupling and related reactions is underway.

## Experimental Section

**General.** The commercially available reagents were used without further purification. The solvents were treated by using standard methods. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub>, and the chemical shifts were referenced to CHCl<sub>3</sub> ( $\delta$  7.27). IR spectra were measured in cm<sup>-1</sup>.

**2-Bromo- $\alpha,\alpha$ -dimethylbenzene acetic acid (1)** was prepared using the literature procedure.<sup>9</sup> <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.57 (m, 1H, Ar), 7.42 (m, 1H, Ar), 7.32 (m, 1H, Ar), 7.12 (m, 1H, Ar), 1.68 (s, 6H, Me); MS (EI) *m/z* 244 (*M*<sup>+</sup>, 0.83), 163 (100).

**Phenylacetamide (2).** Bromodimethylbenzene acetic acid **1** (972 mg, 4 mmol) was added to thionyl chloride (8 mL). The reaction mixture was refluxed 3 h and then concentrated in vacuo. Dry CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was then added, and the mixture was concentrated in vacuo to remove any remaining thionyl chloride.

Dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was then added to the acid chloride. Under argon, valinol (494 mg, 4.8 mmol) and Et<sub>3</sub>N (606 mg, 6 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and cooled to 0 °C. The above acid chloride solution was added dropwise over a period of 0.5 h. The reaction mixture was stirred at 0 °C for 2 h, allowed to warm to room temperature, and stirred for 6 h. The result solution was washed with water (10 mL) and dried over MgSO<sub>4</sub>. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (EtOAc/petroleum ether = 1/2) to give amide **2** as an oil (1.297 g, 99%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.63 (m, 1H, Ar), 7.53 (m, 1H, Ar), 7.39 (m, 1H, Ar), 7.19 (m, 1H, Ar), 5.28 (d, *J* = 4.8 Hz, 1H, NH), 3.72–3.63 (m, 3H, CH and CH<sub>2</sub>), 2.89 (br, 1H, OH), 1.79 (m, 1H, CH), 0.87 (d, *J* = 6.7 Hz, 3H, Me), 0.80 (d, *J* = 6.7 Hz, 3H, Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  177.6, 143.0, 135.0, 129.0, 128.2, 127.9, 124.2, 63.9, 57.9, 48.8, 28.8, 26.9, 26.5, 19.5, 18.6; MS (EI) *m/z* 328 (*M* + 1<sup>+</sup>, 100); IR (KBr, cm<sup>-1</sup>) 3414, 3065, 2961, 1653, 1180, 750. Anal. Calcd for C<sub>15</sub>H<sub>22</sub>BrNO<sub>2</sub>: C, 54.89; H, 6.76; N, 4.27. Found: C, 54.45; H, 6.93; N, 4.27.

**2-(*o*-Bromo-benzyl) Oxazoline (3).** To a solution of amide **2** (1.246 g, 3.8 mmol) in MeCN (10 mL) were added PPh<sub>3</sub> (3.144 g, 12 mmol), Et<sub>3</sub>N (1.818 g, 18 mmol), and CCl<sub>4</sub> (5.39 g, 3.4 mL, 35 mmol). The reaction mixture was stirred for overnight at room temperature. After completion of the reaction (monitored by TLC), water (10 mL) was added and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL  $\times$  3). The combined organic phase was dried over MgSO<sub>4</sub>. The solvent was removed in vacuo, and the crude product was purified by flash chromatography (EtOAc/petroleum ether = 1/6) to give benzyl oxazoline **3** as an oil (1.119 g, 95%): <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.57 (m, 1H, Ar), 7.44 (m, 1H, Ar), 7.31 (m, 1H, Ar), 7.10 (m, 1H, Ar), 4.23 (m, 1H, CH), 3.98 (m, 2H, CH<sub>2</sub>), 1.87 (m, 1H, CH), 1.73 (s, 3H, Me), 1.71 (s, 3H, Me), 0.97 (d, *J* = 6.9 Hz, 3H, Me), 0.88 (d, *J* = 6.9 Hz, 3H, Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  171.7, 143.6, 134.6, 128.2, 127.4, 127.3, 123.8, 72.0, 70.3, 42.4, 32.3, 27.7, 27.2, 19.1, 17.9; MS (EI) *m/z* 310 (*M* + 1<sup>+</sup>, 1.73), 230 (100); IR (KBr, cm<sup>-1</sup>) 3063, 2958, 1663, 1244, 755. Anal. Calcd for C<sub>15</sub>H<sub>20</sub>BrNO: C, 58.07; H, 6.50; N, 4.51. Found: C, 57.96; H, 6.80; N, 4.54.

**Palladacycle (4).** To a solution of benzyl oxazoline **3** (310 mg, 1 mmol) in benzene (15 mL) was added Pd<sub>2</sub>(dba)<sub>3</sub>·CHCl<sub>3</sub> (620 mg, 0.6 mmol). The reaction mixture was refluxed for 0.5 h to give a dark green solution. Filtration through Celite and concentration in vacuo afforded the crude product as a yellow powder, which was purified by flash chromatography (EtOAc/PE = 1/10) to give palladacycle **4** as a yellow powder (400 mg, 96%), a mixture of two geometrical isomers: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) major  $\delta$  7.57 (d, *J* = 7.6 Hz, 1H, Ar), 6.93–6.79 (m, 3H, Ar), 4.45–4.27 (m, 3H, CH and CH<sub>2</sub>), 2.40 (s, 3H, Me), 1.62 (s, 3H, Me), 0.88 (d, *J* = 7.0 Hz, 3H, Me), 0.69 (d, *J* = 7.0 Hz, 3H, Me); minor  $\delta$  7.51 (d, *J* = 7.9 Hz, 1H, Ar), 6.93–6.79 (m, 3H, Ar), 4.45–4.27 (m, 3H, CH and CH<sub>2</sub>), 2.49 (s, 3H, Me), 1.64 (s, 3H, Me), 0.86 (d, *J* = 7.0 Hz, 3H, Me), 0.62 (d, *J* = 7.0 Hz, 3H, Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  176.0, 144.1, 143.9, 142.1, 141.6, 138.5, 138.0, 125.4, 123.9, 122.9, 71.3, 70.9, 69.9, 68.6, 43.8, 35.4, 35.3, 30.9, 30.6, 22.6, 18.1, 15.9, 15.4; MS (EI) *m/z* 415 (1/2*M*<sup>+</sup>, 0.31), 230 (100); IR (KBr, cm<sup>-1</sup>) 3044, 2962, 1648,

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1253, 732. Anal. Calcd for  $C_{15}H_{20}BrNOPd$ : C, 43.24; H, 4.84; N, 3.36. Found: C, 43.67; H, 4.69; N, 3.26.

**General Procedure for Hydrophenylation of Bicyclic Alkenes Catalyzed by Palladacycle 4.** The appropriate amount of catalyst, obtained by successive dilution of an initial catalyst solution, was introduced into 5 mL of DMSO. To the stirred solution were added iodobenzene (204 mg, 1 mmol), norbornene (282 mg, 3 mmol),  $^iPr_2NEt$  (556 mg, 4 mmol), and formic acid (138 mg, 3 mmol). The reaction was carried at 120 °C and monitored by GC. After cooling, water (5 mL) was added, and the mixture was extracted with EtOAc (10 mL  $\times$  3). The combined organic phase was dried over  $MgSO_4$ , filtered, and concentrated in vacuo. The product was purified by flash chromatography (petroleum ether).

**Phenylnorbornene (6):**<sup>13</sup> colorless oil;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.26–7.15 (m, 5H, Ar), 2.74 (m, 1H, CH), 2.36 (s, 2H,  $CH_2$ ), 1.74–1.27 (m, 8H, CH and  $CH_2$ ); MS (EI)  $m/z$  172 ( $M^+$ , 47.48), 104 (100).

**Phenylbornene (13):**<sup>14</sup> colorless oil;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.30–7.28 (m, 4H, Ar), 7.19–7.16 (m, 1H, Ar), 6.26 (dd,  $J$  = 3.2, 5.5 Hz, 1H, CH), 6.17 (dd,  $J$  = 2.9, 5.5 Hz, 1H, CH), 2.97 (s, 1H,  $CH_2$ ), 2.91 (s, 1H,  $CH_2$ ), 2.72 (m, 1H, CH), 1.74–1.41 (m, 4H, CH and  $CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  146.1, 137.3, 137.2, 128.2, 127.6, 125.5, 48.2, 45.7, 43.7, 42.3, 33.6; MS (EI)  $m/z$  170 ( $M^+$ , 41.30), 104 (100).

**Phenyl benzonorbornene (14):**<sup>15</sup> colorless oil;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.35 (m, 4H, Ar), 7.26–7.23 (m, 3H, Ar), 7.16–7.14 (m, 2H, Ar), 3.43 (s, 2H,  $CH_2$ ), 2.85 (m, 1H, CH), 2.03–1.82 (m, 4H, CH and  $CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  148.9, 148.6, 145.8, 128.4, 127.4, 125.8, 125.7, 125.6, 120.8, 120.5, 49.8, 46.6, 45.4, 44.2, 36.2; MS (EI)  $m/z$  220 ( $M^+$ , 17.67), 116 (100).

**Phenyl oxo-benzonorbornene (15):**<sup>16</sup> white solid;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.40–7.18 (m, 9H, Ar), 5.55 (d,  $J$  = 3.6 Hz, 1H, CH), 5.27 (s, 1H, CH), 2.88 (m, 1H, CH), 2.08–2.06 (m, 2H,  $CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  146.0, 145.9, 145.0, 128.5, 127.6, 126.7, 126.6, 126.4, 119.1, 118.8, 85.2, 79.1, 45.8, 38.4; MS (EI)  $m/z$  222 ( $M^+$ , 0.65), 118 (100).

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**Phenyl aza-benzonorbornene (16):** white solid;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.46–7.52 (m, 2H), 7.23–7.38 (m, 5H), 6.82–6.96 (m, 6H), 5.17 (d,  $J$  = 4.5 Hz, 1H), 4.98 (s, 1H), 2.74–2.80 (m, 1H), 2.24–2.32 (m, 1H), 2.23 (s, 3H), 1.92–1.98 (m, 1H);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  144.0, 143.6, 143.5, 143.0, 135.1, 128.9, 128.8, 128.2, 127.8, 127.1, 126.8, 126.7, 120.5, 120.1, 69.5, 64.2, 46.5, 39.1, 21.6; MS (ESI)  $m/z$  376.3 ( $M^+$ , 1) 414.3 ( $M^+$  + K 39); IR (KBr,  $cm^{-1}$ ) 1334, 1164. Anal. Calcd for  $C_{23}H_{21}NO_2S$ : C, 73.09; H, 5.39; N, 3.59. Found: C, 73.57; H, 5.64; N, 3.73.

**Phenyl-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid dimethyl ester (17):**<sup>17</sup> colorless oil;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.32–7.20 (m, 4H, Ar), 7.16 (m, 1H, Ar), 3.70 (s, 6H, Me), 3.52 (t,  $J$  = 7.8 Hz, 1H, CH), 3.18–3.14 (m, 1H, CH), 2.99 (dd,  $J$  = 3.6, 12.0 Hz, 1H, CH), 2.71–2.65 (m, 2H,  $CH_2$ ), 2.17–2.11 (m, 1H, CH), 1.76–1.67 (m, 2H,  $CH_2$ ), 1.39–1.35 (m, 1H, CH);  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  172.9, 172.6, 146.0, 128.1, 127.1, 125.6, 51.5, 51.3, 47.6, 46.3, 45.9, 41.3, 39.9, 37.2, 32.9; MS (EI)  $m/z$  288 ( $M^+$ , 6.99), 142 (100).

**Phenyl-7-oxa-bicyclo[2.2.1]heptane-2,3-dicarboxylic acid dimethyl ester (18):**<sup>4</sup> white solid;  $^1H$  NMR ( $CDCl_3$ , 300 MHz)  $\delta$  7.27–7.21 (m, 4H, Ar), 7.18 (m, 1H, Ar), 5.05 (d,  $J$  = 5.3 Hz, 1H, CH), 4.83 (s, 1H, CH), 3.70 (s, 3H, Me), 3.66 (s, 3H, Me), 3.15 (d,  $J$  = 9.4 Hz, 1H, CH), 3.08 (d,  $J$  = 9.4 Hz, 1H, CH), 2.93 (dd,  $J$  = 5.0, 9.0 Hz, 1H, CH), 2.15 (dd,  $J$  = 9.0, 12.9 Hz, 1H,  $CH_2$ ), 1.89–1.83 (m, 1H,  $CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ , 75 MHz)  $\delta$  171.5, 171.2, 144.8, 128.5, 127.1, 126.5, 84.3, 78.3, 52.3, 52.1, 51.8, 47.7, 40.8; MS (EI)  $m/z$  290 ( $M^+$ , 8.87), 129 (100).

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**Supporting Information Available:** X-ray analysis of the palladacycle 4 (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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