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Palladacycle as highly efficient catalyst for ring opening of oxabicyclic alkenes with organozinc halides

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Abstract

Ring opening reaction of oxabicylic alkenes **4** with in situ prepared organozinc halides **5** was catalyzed by palladacycle **3** with high efficiency. Good yields of the corresponding 1,2-dihydronaphth-1-ols (**6**) were provided when as low as 0.05 mol% of palladacycle **3** was used. ^{31}P NMR study showed that the skeleton of **3** remained intact in the reaction, which implied that palladacycle **3** did not serve as a catalyst precursor but a catalyst in the reaction.

Keywords: Ring opening reaction; Palladium; Palladacycle; Oxabicyclic alkene; Organozinc halides; C–C bond formation

1. Introduction

Organopalladium complexes play an important role in carbon–carbon bond forming reactions because of their versatility, compatibility with most of functional groups and relative low toxicity [1]. Among them, palladacycles have attracted more attentions as their enormous superiority in many aspects [2]. Palladacycles are readily prepared, air and moisture stable. Since Hermann and Beller demonstrated the extremely high catalytic activity of cyclopalladated tri-*o*-tolylphosphine in Heck reaction [3], many palladacycles have been synthesized and used as highly efficient catalysts in carbon–carbon bond forming reactions [2–6]. Some of them achieved extremely high TONs (up to 10^{10} TON) [6]. In spite of palladacycles have showed many advantages in catalysis, they usually served as catalyst precursors [2d,4m,7] and are mainly used in Heck-type reactions and coupling reactions [2–6], though there have been some reports using palladacycle as transition metal catalyst [5]. To explore the applications of palladacycles as real transition metal catalyst in other C–C bond formation is still highly demanded.

The ring opening of oxabicyclic compounds is an useful protocol in the synthesis of cyclic compounds with multiple stereocenters [8]. Many metal complexes are suitable catalysts for regio- and enantioselective nucleophilic ring opening of oxabicylic alkenes using dialkylzinc reagents, Grignard reagents and many others as nucleophile [9]. Usually 1 mol% or more amount of catalysts are needed [10]. However, no report using palladacycle as catalyst appeared in this reaction. During the course of studies on the synthesis and application of ligands in asymmetric catalysis [11], we found that the palladacycle dimer **2** with an oxazoline moiety and two methyl groups situated at the benzylic position was highly efficient catalyst in the hydroarylation of a variety of bicyclic alkenes [12]. Further studies showed that palladacycle monomer **3** is a more excellent catalyst for the ring-opening of oxabicyclic alkenes with

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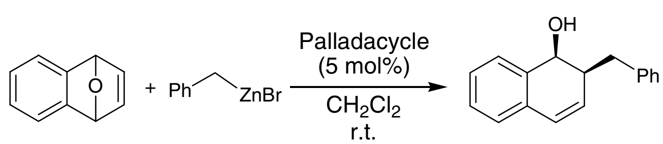
in situ prepared organozinc halides [11d]. High yields of products were afforded using as low as 0.05 mol% amount of palladacycle **3** as catalyst. ^{31}P NMR study showed that palladacycle **3** served as a real catalyst, not the catalyst precursor. Herein we would like to report our results with these aspects.

2. Results and discussion

Previously, we reported the synthesis of palladacycle dimer **2** from bromophenyl acetic acid derivative **1** in high yield [12] which reacted with triphenylphosphine provided palladacycle monomer **3** in high yield (Scheme 1). Its structure was determined by X-ray diffraction (Fig. 1).

Reaction of 7-oxabenzonorbornadiene (**4a**) with in situ prepared benzylzinc bromide **5a** in dichloromethane at room temperature afforded ring-opening product **6aa** in 95% yield in 15 min when 5 mol% of palladacycle monomer **3** was used as catalyst (Eq. (1)). However, only 10% yield of **6aa** was provided accompanied the formation of palladium black when palladacycle dimer **2** was used. The yield of **6aa** did not increase even the reaction time prolonged to 10 h. To test the efficiency of the catalyst, the reaction was carried out using different amount of catalyst **3** in different solvents. The results are summarized in Table 1.



4a **5a** **6aa**

Palladacycle **2** 10% yield
Palladacycle **3** 95% yield

(1)

From Table 1, it can be seen that the temperature has great impact on the reaction. Higher temperature is favorable. Using 0.5 mol% of **3** in CH_2Cl_2, the reaction gave the product in 87% yield in 2 h at room temperature while the yield increased to 91% in 25 min when the reaction proceeded at reflux (entry 1 vs. entry 3). Solvent effect study showed that toluene is the best one among the solvents tested. High yield of product **6aa** was provided when the reaction proceeded at 45 °C in toluene (entry 4), only moderate yield of **6aa** was given while that in THF (entry 7), and that in $CHCl_3$ and CH_3CN delivered the product **6aa** with concomitance of α-naphthol **7**, though the yields were high (entries 5 and 6). A complex mixture was given when the reaction proceeded in DMF and DMSO (not showed in Table 1). Catalytic activity was even higher when the reaction run in toluene at 80 °C. If the amount of catalyst decreased to 0.05 mol%, ring opening product **6aa** was provided in 77% yield (entry 9). Further decrease of the catalyst loading to 0.005 mol% led to the incomplete of the reaction, giving 36% yield of **6aa** (entry 10). Raise the reaction temperature made the substrate decomposition [9k]. However, the $[\alpha]_D$ values of the products were almost zero in all cases.

Using 0.05 mol% of palladacycle **3** in toluene at 80 °C, reactions of a variety of bicyclic alkenes **4** with different benzylzinc bromide derivatives **5** were carried out (Eq. (2)), the results were summarized in Table 2.

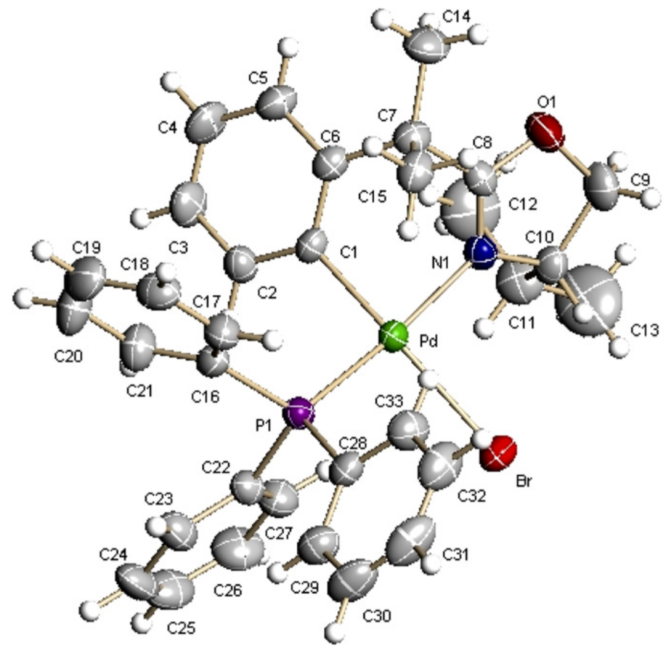
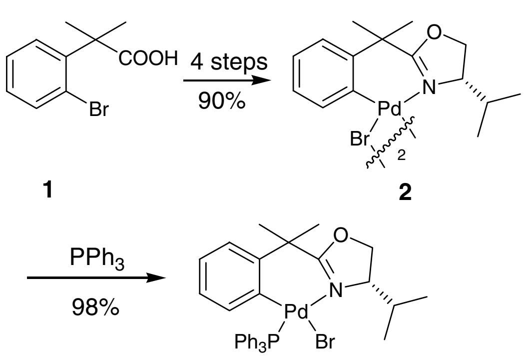
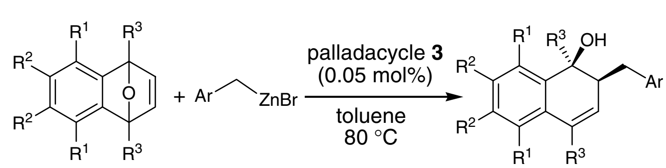


Fig. 1. ORTEP drawing of palladacycle monomer **3**. Hydrogens are omitted for clarity. Selected bond distances (Å) and angles (°): Pd–C (1) 2.011 (3); Pd–N (1) 2.070 (2); Pd–P (1) 2.2525 (7); Pd–Br 2.5413 (4); C (1)–Pd–N (1) 84.68 (11); C (1)–Pd–P (1) 92.79 (8); N (1)–Pd–P (1) 170.04 (7); C (1)–Pd–Br 169.87 (8); N (1)– Pd–Br 92.32 (7); P (1)–Pd–Br 91.47 (2).



1 **2** **3**

Scheme 1. Synthesis of palladacycle monomer **3**.



4 **5** **6**

(2)

Table 1
Ring-opening reaction of oxabicyclic alkene **4a** with BnZnBr catalyzed by palladacycle **3**[a]

Entry	**3** (mol%)	Solvent	Temperature (°C)	Time	Yield (%)[b]
1	0.5	CH_2Cl_2	r.t.	2 h	87
2	0.5	CH_2Cl_2	0	10 h	34
3	0.5	CH_2Cl_2	Reflux	25 min	91
4	0.5	Toluene	45	30 min	95
5	0.5	$CHCl_3$	45	30 min	93[c]
6	0.5	CH_3CN	45	30 min	90[c]
7	0.5	THF	45	30 min	42
8	0.05	CH_2Cl_2	Reflux	22 h	22
9	0.05	Toluene	80	1 h	77
10	0.005	Toluene	80	20 h	36
11	0.005	Toluene	100	15 h	Decomposition

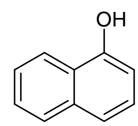
[a] Oxabicyclic alkene **4a** (0.5 mmol), BnZnBr **5a** (1 mmol) and catalyst in solvent (2 mL).
[b] Isolated yields.
[c] α-Naphthol as byproduct (~1% determined by ^{1}H NMR).

Table 2
Palladacycle **3** catalyzed ring-opening of oxabicyclic alkenes **4** with substituted benzyl zinc reagents **5**[a]

Entry	**4**, R^1, R^2, R^3	**5**, Ar	Time	Product	Yield (%)[b]
1	**4a**(H, H, H)	**a**, Phenyl	1 h	**6aa**	77
2	**4a**(H, H, H)	**b**, 3-MeC_6H_4	1 h	**6ab**	65
3	**4a**(H, H, H)	**c**, 4-MeC_6H_4	25 min	**6ac**	85
4	**4a**(H, H, H)	**d**, 3-ClC_6H_4	40 min	**6ad**	58
5	**4a**(H, H, H)	**e**, 2-MeC_6H_4	45 min	**6ae**	63
6	**4a**(H, H, H)	**f**, 3,5-$(Me)_2C_6H_3$	45 min	**6af**	66
7	**4a**(H, H, H)	**g**, 4-BrC_6H_4	1.5 h	**6ag**	72
8	**4a**(H, H, H)	**h**, 2-BrC_6H_4	2 h	**6ah**	73
9	**4a**(H, H, H)	**i**,4-$MeOC_6H_4$	30 min	**7**	80
10	**4b**(CH_3, H, H)	**a**, Phenyl	30 min	**6ba**	74
11	**4c**(H, CH_3, H)	**a**, Phenyl	45 min	**6ca**	79
12	**4d**(H, H, CH_3)	**a**, Phenyl	8 h	**6da**	28
13	**4d**(H, H, CH_3)	**a**, Phenyl	30 min	**6da**	82[c]
14	**4e**(H, Br, H)	**a**, Phenyl	3 h	**6ea + 8**	68[d]
15	**4e**(H, Br, H)	**a**, Phenyl	1.5 h	**6ea**	65[c]

[a] Oxabicyclic alkene **4** (0.5 mmol), $ArCH_2ZnBr$ **5** (1 mmol) and **3** (0.05 mol%) in toluene (2 mL).
[b] Isolated yields.
[c] 0.5 mol% of **3** was used.
[d] The products are **6ea** and byproduct **8** with the ratio of 1:1 determined by ^{1}H NMR.

As showed in Table 2, all substituted benzylzinc bromides **5**, in spite of different electronic property and steric hindrance of substituents, reacted smoothly with **4a** to provide corresponding products in good yields (entries 1–8), except for **5i** with methoxy group at *para*-position of benzene ring, which afforded naphthol 7 as a sole product (entry 9). The presence of methyl group on phenyl ring of **4** did not influence the yield of the reaction (entries 10 and 11). However, the yield was only 28% if Me group was at the position of oxo-bridge carbon of **4d** (entry 12) while the reaction provided the mixture of **6ea** and **8** in 68% yield with the ratio of 1:1 using bromo substituted oxabicyclic alkene **4e** as starting material (entry 14). Ring opening products **6da** and **6ea** were afforded in 82% and 65% yields respectively if 0.5 mol% of catalyst was used (entries 13 and 15).



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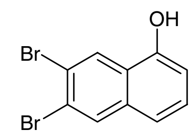

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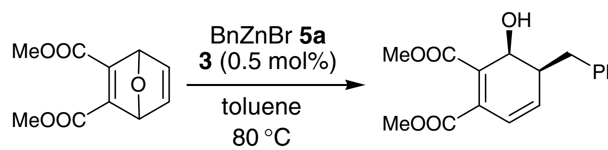
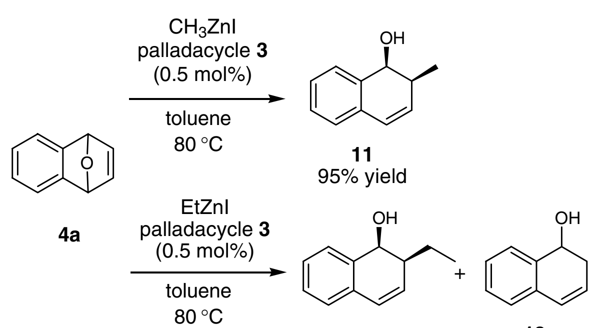
Ring opening product **10** was delivered in 43% yield when oxabicyclic alkene **9** reacted with BnZnBr **5a** in the presence of 0.5 mol% of catalyst **3** (Eq. (3)), but no products were given when azabicyclic alkenes were used, perhaps due to their low reactivity [9b].



9 **10** 43% yield (3)

Not only benzylzinc bromides but also methylzinc iodide is suitable reagent in this ring-opening reaction. 1,2-Dihydro-2-methyl-1-naphthol (**11**) was afforded in 95% yield from oxabicyclic alkene **4** using CH_3ZnI as reagent in the presence of 0.5 mol% amount of **3** in toluene. However, only 16% yield of Et substituted dihydronaphthol **12** was provided when ethylzinc iodide was used under same condition. In addition, hydride attacked product **13** was separated in 55% yield caused by β-H elimination reaction (Eq. (4)) [13].



4a **11** 95% yield **12** 16% yield **13** 55% yield (4)

In most case when the palladacycle served as a precatalyst, the reaction proceeds at temperature higher than 120 °C, at which "active Pd species" is released [2d,2f,7b], however, in our case the reaction run at 80 °C or lower. In addition, no visible palladium black was observed in the reaction. ^{31}P NMR spectrum of palladacycle **3** showed the signal at δ 34.9 ppm (A of Fig. 2); when one equivalent of benzylzinc bromide **5a** was added, a new peak at δ 34 ppm appeared (B of Fig. 2); excess zinc reagent made the peak at δ 34.9 ppm disappeared (C of Fig. 2), only the signal at δ 34.9 ppm was found after quenching with aqueous NH_4Cl

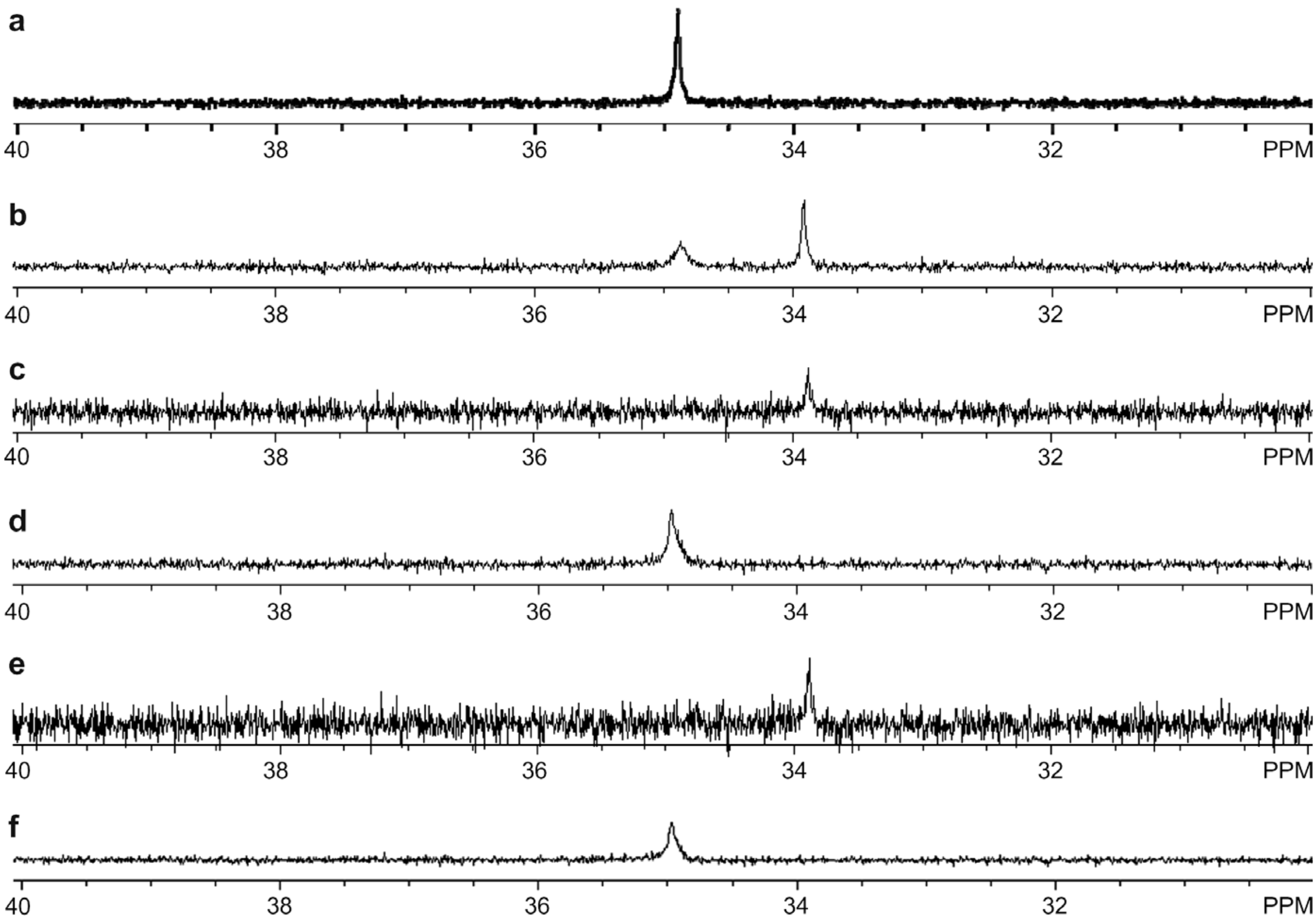
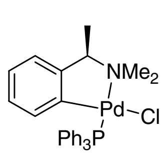


Fig. 2. ^{31}P NMR spectrum of (a) palladacycle **3** in $CDCl_3$; (b) palladacycle **3** with BnZnBr (1 equiv.) in $CDCl_3$; (c) palladacycle **3** with BnZnBr (>1 equiv.) in $CDCl_3$; (d) mixture in c was quenched with aqueous NH_4Cl. (e) after the completion of the reaction of **4a** with BnZnBr catalyzed by **3** in $CDCl_3$; (f) mixture in e was quenched with aqueous NH_4Cl.

(D of Fig. 2). Mixture of **4a** with benzylzinc bromide **5a** and palladacycle **3,** after the completion of the reaction, showed also the peak at δ 34 ppm from ^{31}P NMR spectrum (E of Fig. 2), which was shifted to δ 34.9 ppm again when the mixture was quenched with aqueous NH_4Cl (F of Fig. 2). We also found that the reaction of **4a** with **5a** was catalyzed by 0.5 mol% of **14** to give 93% yield of product **6aa**. The phenomena are totally same when we repeated the experiments above using **14**. The only difference is that ^{31}P NMR spectrum of palladacycle **14** showed the signal at 42 ppm and that of mixture of **14** and **5a** at δ 35 ppm. These experimental results implied that the skeleton of **3** remained intact in the reaction, which means that palladacycle **3** was a real catalyst in the reaction though the products are racemic.



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3. Conclusions

Palladacycle **3** is a highly active catalyst for the ring opening reaction of oxabicylic alkenes with in situ prepared organozinc halides, which shows a new application of palladacycles in organic synthesis. NMR experiments suggested that the palladacycle did not serve as a catalyst precursor but a real catalyst in the process, although it is unclear that why no asymmetric induction in the reaction took place. Further studies on the reaction mechanism in detail and other applications of palladacycles in organic synthesis, especially in asymmetric catalysis are in progress.

4. Experimental

4.1. General remarks

All reactions were performed under an atmosphere of either dry argon or nitrogen using oven-dried glassware. Solvents were treated using standard procedures and were distilled under an atmosphere of nitrogen before use.

Commercially available reagents were used without further purification. The substrates **4a** [14], **4b** [16], **4c** [15], **4d** [17], **4e** [15], **9** [18] and palladacycle **2**, [12] **14**, [21] organozinc halides [11d,19] were prepared according to reported procedures. ^{1}H NMR spectra were recorded in $CDCl_3$ and the chemical shifts were referenced to $CHCl_3$ (δ 7.27) and that of ^{13}C NMR and ^{31}P NMR spectra were referenced to $CHCl_3$ (δ 77.00) and to external 85% H_3PO_4 respectively. IR spectra were measured in cm^{-1}.

4.2. Synthesis of palladacycle **3**

To a solution of palladacycle **2** (168 mg, 0.2 mmol) in CH_2Cl_2 (10 mL) was added PPh_3 (118 mg, 0.45 mmol) at room temperature and the resulting mixture was stirred for 5 min. The solvent was removed in vacuum, and the crude product was purified by flash chromatography (AcOEt/petroleum ether = 1/5) to give palladacycle **3** as a white solid (266 mg, 98%): m.p. > 300°C; $[\alpha]_D^{20} = -18.8°$ ($c = 0.68$, $CHCl_3$). ^{1}H NMR: 0.57 (d, $J = 6.6$ Hz, 3H), 0.80 (d, $J = 6.6$ Hz, 3H), 1.62 (s, 3H), 2.05–2.15 (m, 1H), 2.40 (s, 3H), 4.27 (dd, $J = 5.7$ Hz, 8.7 Hz, 1H), 4.46 (dd, $J = 8.7$ Hz, 9.9 Hz, 1H), 5.10–5.18 (m, 1H), 6.18–6.24 (m, 1H), 6.64–6.78 (m, 2H), 6.88–6.94 (m, 1H), 7.25–7.40 (m, 9H), δ 7.52–7.61 (m, 6H); ^{13}C NMR: δ 176.98, 153.52, 153.47, 144.91, 139.39, 139.28, 135.31, 135.17, 132.27, 131.62, 130.31, 130.28, 128.22, 128.07, 125.48, 125.41, 122.85, 122.77, 72.09, 68.42, 44.21, 34.90, 31.32, 23.45, 18.23, 16.22. ^{31}P NMR: δ 34.9 (s). MS (EI) m/z 598 (M^+-Br), 230 (100.00), 262 (46.07), 183 (36.96), 231 (18.16), 108 (14.04), 261 (13.19), 263 (9.59), 107 (9.13); IR (KBr, cm^{-1}): 2963, 1637, 1436, 1096, 695 cm^{-1}; Anal. Calcd. for $C_{15}H_{20}BrNOPd$: C, 58.38; H, 5.20; N, 2.06. Found: C, 58.40; H, 5.24; N, 1.90%.

4.3. General procedure for the reaction of oxabicyclic alkenes **4** with organozinc halides **5** in the presence of palladacycle **3**

To a stirred solution of oxabicyclic alkenes **4** (0.5 mmol) in toluene (2 mL) was added organozinc halides (1.5 mmol in THF) and the appropriate amount of catalyst, obtained by successive dilution of an initial catalyst solution. The resulting mixture was stirred at 80 °C and monitored by TLC. After cooling, water (5 mL) was added and stirred for 15 min. The mixture was extracted with CH_2Cl_2 (5 mL × 3). The combined organic phase was dried over $MgSO_4$, filtered, and concentrated in vacuum. The crude product was purified by flash chromatography (ethyl acetate/petroleum ether).

4.4. 2-Benzyl-1,2-dihydro-naphthalen-1-ol (**6aa**) [9k]

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.62 (s, 1H), 2.77–2.81 (m, 1H), 2.89 (dd, $J = 8.0$ Hz, 12.8 Hz, 1H), 3.15 (dd, $J = 7.7$ Hz, 12.8 Hz, 1H), 4.47 (dd, $J = 4.1$ Hz, 7.0 Hz, 1H), 5.80 (dd, $J = 2.5$ Hz, 9.6 Hz, 1H), 6.57 (dd, $J = 2.4$ Hz, 9.6 Hz, 1H), 7.12–7.25 (m, 3H), 7.26–7.37 (m, 6H); MS (EI) m/z (rel) 236 (M^+, 1), 145 (100.00), 218 (53.94), 91 (44.59), 127 (38.66), 115 (29.24), 128 (22.62), 116 (15.95).

4.5. 2-(3′-Methylbenzyl)-1,2-dihydronaphthalen-1-ol (**6ab**)

White solid, m.p. 67–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.78–2.90 (m, 2H), 3.08–3.18 (m, 1H), 4.50 (d, $J = 2.1$ Hz, 1H), 5.82 (d, $J = 10.2$ Hz, 1H), 6.57 (dd, $J = 2.7$ Hz, 9.3 Hz, 1H), 7.05–7.16 (m, 4H), 7.20–7.32 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.99, 137.96, 136.50, 132.57, 130.36, 130.04, 128.59, 128.28, 127.68, 127.63, 127.04, 126.87, 126.56, 126.27, 69.66, 42.48, 35.26, 21.43; MS (EI) m/z (rel) 232 (M^+-H_2O), 145 (100.00), 127 (61.76), 232 (59.55), 128 (37.64), 115 (35.40), 117 (34.22), 144 (32.49), 105 (28.13); IR (KBr): 3389, 3325 cm^{-1}; HRMS (M^+-H_2O) for $C_{17}H_{16}$: 232.1252; Found: 232.12606.

4.6. 2-(4′-Methylbenzyl)-1,2-dihydronaphthalen-1-ol (**6ac**) [11d]

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.74–2.81 (m, 1H), 2.85 (dd, $J = 8.0$ Hz, 12.8 Hz, 1H), 3.11 (dd, $J = 8.0$ Hz, 12.8 Hz, 1H), 4.47 (d, $J = 3.6$ Hz, 1H), 5.80 (dd, $J = 2.6$ Hz, 9.3 Hz, 1H), 6.56 (dd, $J = 2.5$ Hz, 9.3 Hz, 1H), 7.12–7.25 (m, 6H), 7.28–7.43 (m, 2H); MS (EI) m/z (rel) 250 (M^+, 1), 145 (100.00), 232 (91.87), 128 (70.84), 105 (57.41), 127 (47.35), 144 (43.09), 217 (36.95), 115 (24.29).

4.7. 2-(3′-Chlorobenzyl)-1,2-dihydronaphthalen-1-ol (**6ad**)

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.64–2.82 (m, 2H), 2.95–3.14 (m, 1H), 4.44 (d, $J = 3.0$ Hz, 1H), 5.72–5.76 (m, 1H), 6.54 (dd, $J = 2.4$ Hz, 9.6 Hz), 7.10–7.30 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.24, 136.30, 134.15, 132.47, 129.80, 129.63, 129.34, 128.69, 127.78, 127.63, 127.54, 127.34, 126.64, 126.375, 69.41, 42.33, 35.02; MS (EI) m/z (rel) 252 (M^+-H_2O), 145 (100), 115 (46.63), 127 (45.09), 144 (36.43), 252 (28.17), 117 (24.17), 116 (19.39), 89 (14.97); IR (KBr): 3556, 3385 cm^{-1}; HRMS (M^+-H_2O) for $C_{17}H_{13}Cl$: 252.0706; Found: 252.07043.

4.8. 2-(2′-Methylbenzyl)-1,2-dihydronaphthalen-1-ol (**6ae**) [11d]

Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 3H), 2.77–2.81 (m, 1H), 2.89 (dd, $J = 8.1$, 13.2 Hz, 1H), 3.13 (dd, $J = 8.1$, 13.5 Hz, 1H), 4.48 (s, 1H), 5.79–5.89 (m, 1H), 6.56 (dd, $J = 2.1$, 9.3 Hz, 1H), 7.12–7.30 (m, 8H); MS (EI) m/z (rel) 250 (M^+, 1), 232 (44.33), 145 (100.00), 127 (65.64), 115 (45.39), 105 (43.84), 77 (34.66), 65 (12.45), 51(17.25), 39 (20.33).

4.9. 2-(3′,5′-Dimethylbenzyl)-1,2-dihydronaphthalen-1-ol (*6af*)

White solid, m.p. 107–109 °C. ^{1}H NMR (300 MHz, $CDCl_3$): 2.34 (m, 6H), 2.78–2.87 (m, 2H), 3.04–3.14 (m, 1H), 4.50 (dd, $J = 3.3$ Hz, 6.9 Hz, 1H), 5.83 (d, $J =$ 9.9 Hz, 1H), 6.57 (dd, $J = 2.7$ Hz, 9.9 Hz, 1H), 6.88–6.96 (m, 3H), 7.12–7.18 (m, 1H), 7.22–7.34 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.02, 137.87, 136.58, 132.65, 130.54, 128.58, 127.79, 127.70, 127.63, 127.09, 127.02, 126.56, 6 9.75, 42.506, 35.18, 21.33; MS (EI) *m*/*z* (rel) 364 (M^+), 145 (100.00), 127 (54.80), 246 (48.35), 128 (35.84), 115 (33.54), 117 (32.00), 119 (26.83), 144 (23.64); IR (KBr): 3365, 3290 cm^{-1}; HRMS ($M^+{-}H_2O$) for $C_{19}H_{18}$: 246.1409; Found: 246.14119.

4.10. 2-(4′-Bromobenzyl)-1,2-dihydronaphthalen-1-ol (*6ag*) [11d]

White solid. ^{1}H NMR (300 MHz, $CDCl_3$): 2.72–2.78 (m, 1H), 2.83 (dd, $J = 7.8$ Hz, 13.0 Hz, 1H), 3.10 (dd, $J = 8.4$ Hz, 12.8 Hz, 1H), 4.42 (d, $J = 3.3$ Hz, 1H), 5.75 (dd, $J = 2.4$ Hz, 9.5 Hz, 1H), 6.57 (dd, $J = 2.5$ Hz, 9.5 Hz, 1H), 7.11–7.32 (m, 6H), 7.39–7.46 (m, 2H); MS (EI) *m*/*z* (rel) 314 (M^+, 1), 145 (100.00), 127 (29.71), 128 (19.31), 115 (18.39), 117 (14.49), 144 (12.66), 146 (11.35), 90 (8.35).

4.11. 2-(2′-Bromobenzyl)-1,2-dihydronaphthalen-1-ol (*6ah*) [9k]

Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29–2.99 (m, 2H), 3.03 (dd, $J = 7.5$, 12.9 Hz, 1H), 3.11–3.3–21 (dd, $J = 8.1$, 12.9 Hz, 1H), 4.44–4.98 (m, 1H), 5.78–5.83 (m, 1H), 6.57 (dd, $J = 2.1$, 9.3 Hz, 1H), 7.08–7.58 (m, 8H); MS (EI) *m*/*z* 314 (M^+), 145 (100.00), 127 (52.85), 144 (28.47), 115 (25.58), 77 (25.41), 117 (22.94), 79 (18.59), 128 (15.99).

4.12. 2-Benzyl-5,8-dimethyl-1,2-dihydronaphthalen-1-ol (*6ba*)

Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (d, $J = 7.5$ Hz, 1H), 2.34 (s, 6H), 2.70–2.80 (m, 1H), 3.01 (dd, $J = 8.1$ Hz, 13.5 Hz, 1H), 3.21 (dd, $J = 8.4$ Hz, 13.5 Hz,1H), 4.67 (dd, $J = 4.8$ Hz, 7.8 Hz 1H), 5.83 (m, 1H), 6.78 (dd, $J = 2.7$ Hz, 9.6 Hz, 1H), 7.05 (dd, $J = 8.4$ Hz, 16.5 Hz, 2H), 7.22–7.30 (m, 1H), 7.38 (d, $J = 5.1$ Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.39, 134.73, 133.63, 131.91, 130.69, 130.29, 129.87, 129.53, 129.42, 128.70, 126.39, 124.68, 65.89, 42.39, 36.18, 19.24, 18.52; MS (EI) *m*/*z* 264 (M^+), 173 (100.00), 158 (36.87), 91 (21.74), 145 (19.86), 172 (19.25), 174 (13.50), 155 (13.37). IR (KBr): 3557, 3436 cm^{-1}; HRMS ($M^+ + Na$) for $C_{21}H_{19}ONa^{+1}$: 287.1416; Found: 287.14304.

4.13. 2-Benzyl-6,7-dimethyl-1,2-dihydronaphthalen-1-ol (*6ca*)

White solid, m.p. 101–103 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (d, $J = 4.5$ Hz, 1H),2.23 (s, 6H), 2.70–2.80 (m, 1H), 2.88 (dd, $J = 8.1$Hz, 6.6 Hz, 1H), 3.15 (dd, $J = 8.1$ Hz, 12.9 Hz, 1H), 4.38 (dd, $J = 4.5$ Hz, 8.2 Hz, 1H), 5.71 (d, $J = 9.0$ Hz, 1H), 6.50 (dd, $J = 3.0$ Hz, 9.9 Hz, 1H), 6.92 (s,1H), 7.04 (s,1H), 7.20–7.24 (m, 1H), 7.28–7.36 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.16, 136.77, 136.00, 134.02, 130.13, 129.22, 129.10, 129.08, 128.31, 127.87, 126.89, 126.00, 69.30, 42.70, 35.51, 19.50, 19.44; MS (EI) *m*/*z* 264 (M^+), 173 (100), 158 (37.94), 172 (26.84), 91 (18.13), 145 (16.69), 174 (13.53), 155 (11.89), 128 (10.82); IR (KBr): 3372, 3034 cm^{-1}; Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63; Found: C, 86.14; H, 7.48%.

4.14. 2-Benzyl-1,4-dimethyl-1,2-dihydronaphthalen-1-ol (*6da*)

Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.55 (s, 3H), 2.04 (s, 3H), 1.95 (br, 1H), 2.38 (dd, $J = 10.5$ Hz, 23.1 Hz, 1H), 2.50–2.62 (m, 1H), 3.13 (dd, $J = 5.2$ Hz, 12.6 Hz, 1H), 5.59 (dd, $J = 1.5$ Hz, 5.7 Hz, 1H), 7.12–7.16 (m, 2H), 7.20–7.23 (m, 1H), 7.28–7.38 (m, 5H), 7.60–7.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.46, 140.60, 133.72, 130.53, 129.19, 128.32, 128.09, 127.78, 127.18, 125.74, 123.40, 123.26, 74.40, 47.66, 34.81, 28.88, 19.07; MS (EI) *m*/*z* 264 (M^+), 173 (100.00), 158 (31.65), 91 (19.78), 145 (18.04), 174 (13.79), 128 (11.27), 129 (10.10), 115 (9.80); IR (KBr): 3464, 3062 cm^{-1}; HRMS ($M^+ + Na$) for $C_{19}H_{20}ONa^{+1}$: 287.1420; Found: 287.14064.

4.15. 2-Benzyl-6,7-dibromo-1,2-dihydronaphthalen-1-ol (*6ea*)

White solid, m.p. 117–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.70–2.85 (m, 2H), 3.10 (dd, $J = 6.6$ Hz, 11.7 Hz, 1H), 4.47–4.52 (m, 1H), 5.90 (dd, $J = 2.7$ Hz, 9.9 Hz, 1H), 6.46 (d, $J = 9.9$ Hz, 1H), 7.24–7.35 (m, 5H), 7.38 (m, 1H), 7.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.49, 137.03, 133.25, 132.46, 132.33, 131.09, 129.17, 128.48, 126.31, 125.26, 124.34, 122.90, 68.69, 42.22, 34.72; MS (EI) *m*/*z* 376 ($M^+{-}H_2O$), 224 (100.00), 222 (94.21), 91 (90.97), 115 (59.29), 376 (38.26), 286 (32.21), 65 (31.48), 303 (27.58). IR (KBr): 3306 cm^{-1}; Anal. Calcd. for $C_{17}H_{14}Br_2O$: C, 51.81; H, 3.58; Found: C, 52.08; H, 3.64.

4.16. 6-Benzyl-2,3-dimethyl ester-2,4-dienol (*10*)

White solid, m.p. 86–88 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.59–2.71 (m, 1H), 3.14 (d, $J = 13.8$ Hz, 1H), 3.41 (d, $J = 13.8$ Hz, 1H), 3.49 (m, 3H), 3.74 (m, 3H), 5.18–5.24 (m, 1H), 5.58–5.64 (m, 1H), 5.81–5.86 (m, 1H), 7.01–7.05 (m, 1H), 7.10–7.15 (m, 3H), 7.17–7.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.24, 166.34, 137.91, 134.21, 131.22, 129.20, 127.10, 126.10, 121.24, 74.50, 56.35, 52.55, 51.71, 31.74; MS (EI) m/z 270 (M^+-OCH_3), 91 (100.00), 179 (44.12), 163 (36.83), 65 (31.65), 270 (31.00), 77 (20.18), 59 (19.36), 210 (18.10); IR (KBr): 3487, 1745, 1716, 1269 cm^{-1}; Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00; Found: C, 67.17; H, 6.12%.

4.17. 2-Methyl-1,2-dihydro-naphthalen-1-ol (**11**) [20]

White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (d, $J = 7.7$ Hz, 3H), 1.57 (d, $J = 8.0$ Hz, 1H), 2.62–2.68 (m, 1H), 4.51 (dd, $J = 4.8$ Hz, 7.4 Hz, 1H), 5.80 (dd, $J = 3.1$ Hz, 9.4 Hz, 1H), 6.53 (dd, $J = 2.5$ Hz, 9.5 Hz, 1H), 7.10–7.14 (m, 1H), 7.21–7.45 (m, 3H); MS (EI) m/z (rel) 160 (M^+, 64), 161 (8), 159 (13), 145 (79), 131 (100), 128 (30).

4.18. 2-Ethyl-1,2-dihydro-naphthalen-1-ol (**12**) [20]

Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08 (t, $J = 7.5$ Hz, 3H), 1.56–1.68 (m, 2H), 1.75–1.87 (m, 1H), 2.22–2.39 (m, 1H), 4.60 (d, $J = 4.8$ Hz, 1H), 5.83 (dd, $J = 3.0$ Hz, 9.3 Hz, 1H), 6.53 (dd, $J = 2.7$ Hz, 9.3 Hz, 1H), 7.09–7.12 (m, 1H), 7.17–7.33 (m, 3H); MS (EI) m/z (rel) 174 (M^+, 8), 157 (17), 144 (100), 116 (23).

4.19. 1,2-Dihydro-naphthalen-1-ol (**13**) [9k]

Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 1H), 2.59 (m, 2H), 4.76 (t, $J = 5.4$ Hz, 1H), 5.98 (m, 1H), 6.54 (d, $J = 9.6$ Hz, 1H), 7.11 (d, $J = 7.5$ Hz, 1H), 7.21–7.30 (m, 2H), 7.36 (d, $J = 6.9$ Hz, 1H); MS (EI) m/z (rel) 146 (M^+, 100), 145 (58), 128 (57), 127 (34), 117 (49).

4.20. Stoichiometric reaction of palladacycle **3** with organozinc bromide

To the stirred solution of palladacycle **3** (13.5 mg, 0.02 mmol) in 4 mL $CDCl_3$ at room temperature, added organozinc bromide (0.02 mmol, 2 M in THF); then quenched with aqueous NH_4Cl (0.1 mL). The progress of the reaction was monitored by an array experiment using ^{31}P NMR spectroscopy.

4.21. Stoichiometric reaction of palladacycle **3** with organozinc bromide and oxanorbornadiene **4a**

Palladacycle **3** (13.5 mg, 0.02 mmol) was mixed with benzylzinc bromide (20 µl, 2M in THF) and **4a** (2.9 mg, 0.02 mmol) in $CDCl_3$ (4 mL), the reaction proceeded at room temperature and monitored by TLC. After completion, aqueous NH_4Cl (0.1 mL) was added. The progress of the reaction was monitored by an array experiment using ^{31}P NMR spectroscopy.

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