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Ligand-Controlled Switch of Regioselectivity in Ring-Opening Coupling of Diarylmethylenecyclopropa-[*b*]naphthalenes with Grignard Reagents

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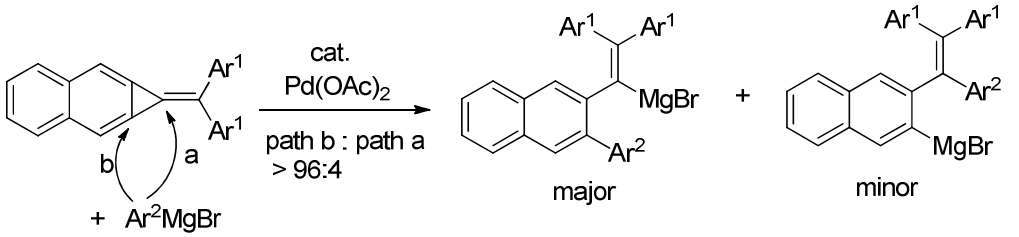
§ Prof. Huang passed away on March 6, 2010. He had been fully in charge of this project. At this moment, Prof. Luling Wu is helping him to finish all the projects with the help from Prof. Shengming Ma

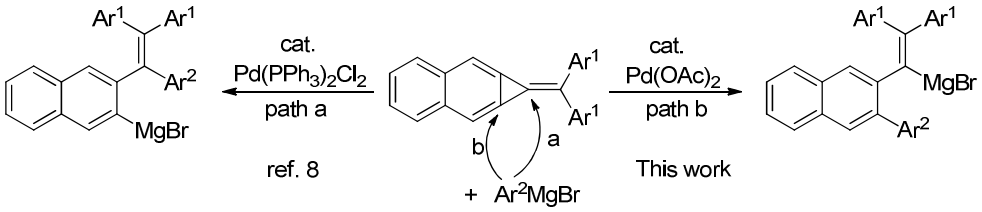


ABSTRACT: A ligand-controlled regioselectivity switch of ring-opening coupling reaction of diarylmethylenecyclopropa[*b*]naphthalenes with Grignard reagents providing differently substituted β-vinylic naphthalenes in moderate to excellent yields was reported: when $Pd(OAc)_2$ was used, the aromatic group from the Grignard reagent regioselectively coupled to the naphthyl ring after the ring-opening of three-membered cycle, which is different from the $Pd(PPh_3)_2Cl_2$-catalyzed reaction. Based on careful NMR study, we concluded that it may be explained by the ligand effect.

INTRODUCTION:

Carbomagnesation is a principal and important method for the generation of organometallic compounds having desired carbon skeletons.[1-2] Recently, transition metal-catalyzed highly regioselective carbomagnesation of carbon-carbon unsaturated systems including alkenes, 1,3-butadienes, alkynes, enynes, allenes and even methylenecyclopropanes(MCPs) have also been achieved, providing a variety of advanced and relatively complicated organomagnesium reagents.[3-4] During our recent systematic study on MCPs chemistry,[5] we became interested in the chemistry of the analogous diarylmethylenecyclopropa[*b*]naphthalenes,[6] which are a class of highly reactive but thermally stable and readily accessible unsaturated hydrocarbons. In this regard, we have reported manganese(III) acetate-mediated cyclization and Pd(0)-catalyzed [3+2] cycloaddition of diarylmethylenecyclopropa[*b*]naphthalenes, providing efficient methods for the synthesis of several polycyclic aromatic hydrocarbons (PAHs).[7] As a continuous exploration on the synthetic utility of these interesting compounds, in a previous report, we have demonstrated highly regioselective ring-opening coupling reactions of diarylmethylenecyclopropa[*b*]naphthalenes with Grignard reagents catalyzed by $Pd(PPh_3)_2Cl_2$, providing naphthylmagnesium species in moderate to excellent yields (Scheme 1, path a).[8] In this paper, we wish to

report reversed regioselectivity of this ring-opening carbomagnesation by employing $Pd(OAc)_2$, highly regioselectively providing vinylmagnesium species (Scheme 1, path b). The reason for such a regioselectivity switch was also been explored.



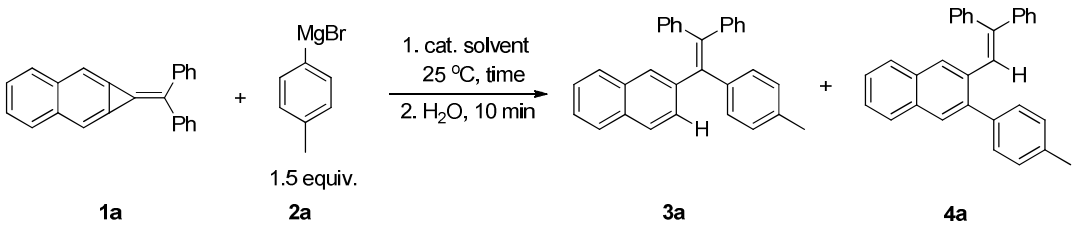
Scheme 1. Our previous work and this work.

RESULTS AND DISCUSSION:

As a preliminary examination, 1-(diphenylmethylene) -1*H*-cyclopropa[*b*]naphthalene (**1a)** was treated with *p*-tolylmagnesium bromide (**2a,** 1.0 M in THF, 1.5 equiv) in the presence of $PdCl_2$ (5 mol %) in THF at 25 ^oC for 1.5 h followed by an aqueous workup. Unexpectedly, we found that 2-[2,2-diphenyl-1-(*p*-tolyl)vinyl]naphthalene (**3a)** and 2-(2,2-diphenylvinyl)-3-(*p*-tolyl)naphthalene (**4a)** were produced in 78% yield with a ratio of 5:95 with **4a** being the major product (entry 1, Table 1. The structures of these two products have been established by their X-ray single crystal diffraction analysis as reported in our previous report![8] When $Pd(OAc)_2$ was used, **4a** was obtained in 82% yield with an even better regioselectivity (2:98) (entry 2, Table 1). $Pd_2(dba)_3CHCl_3$ did not give a better result (entries 3, Table 1). Among the solvents examined,

THF was still the most effective.

Table 1. Optimization of reaction conditions for the Pd-catalyzed ring-opening coupling of 1-(diphenylmethylene)-1H-cyclopropa[*b*]naphthalene (**1a**) with *p*-tolylmagnesium bromide (1.0 M inTHF) (**2a**) for the selective formation of **4a**.[a]



1a **2a** **3a** **4a**

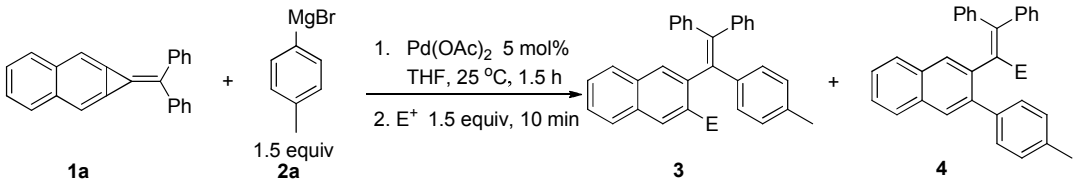
entry	catalyst (5 mol %)	solvent	time (h)	yield/% (**3a**:**4a**)[b]
1	$PdCl_2$	THF	1	78 (5:95)
2	**$Pd(OAc)_2$**	**THF**	**1.5**	**82 (2:98)**
3	$Pd_2(dba)_3CHCl_3$	THF	0.5	80 (3:97)
4	$Pd(OAc)_2$	PhMe	24	30 (5:95)
5	$Pd(OAc)_2$	dioxane	1.5	70 (3:97)

[a] The reaction was conducted with 0.2 mmol of **1a**, 0.01 mmol of the catalyst, 2 mL of solvent, and 1.5 equiv of *p*-tolylmagnesium bromide (1.0 M solution in THF). [b] Yields and ratios of **3a** and **4a** determined by ^1H NMR using dibromomethane as the internal standard.

Various electrophilic reagents were then employed to quench the reaction mixture under the optimized reaction conditions. When D_2O was used, **4a'** was obtained in 68% (97% D) yield respectively (entry 2, Table

2). When I_2, NBS, allyl bromide and acetyl chloride were employed, the reaction all proceeded efficiently to give the corresponding products **4b**-**4e** in moderate yields with an excellent regioselectivity (entries 3-6, Table 2).

Table 2. Pd-catalyzed ring-opening coupling of **1a** with **2a**, quenching with various electrophilic reagents.[a]



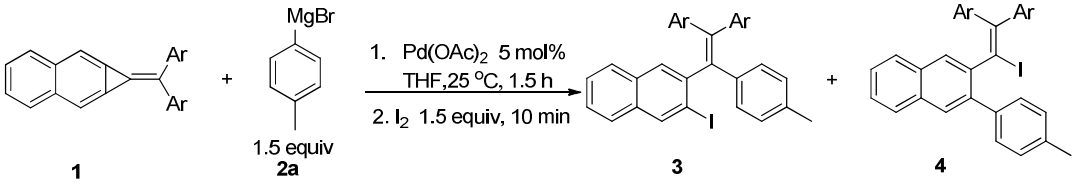
entry	E^+	E	yield of **4**/%[b]	**4**/**3**[c]
1	H_2O	H	67 (**4a**)	82/2
2	D_2O	D	68, 97% D (**4a'**)	81/2
3	I_2	I	62 (**4b**)	74/2
4	NBS	Br	61 (**4c**)	75/2
5	allyl bromide	Allyl	62 (**4d**)	77/2
6	acetyl chloride	Ac	55 (**4e**)	61/2

[a] The reaction was conducted with 0.2 mmol of **1a**, 0.01 mmol of the catalyst, 2 mL of solvent, 1.5 equiv of *p*-tolylmagnesium bromide (1.0 M solution in THF) and 1.5 equiv of electrophilic reagent. [b] Isolated yield. [c] NMR yields of **3** and **4** determined by NMR using dibromomethane as the internal standard.

Considering the highly useful nature of aryl iodides, I_2 was used as

the electrophile to quench the reaction when we next examined the scope of this reaction with various substrates. In addition to **1a**, diarylmethylenecyclopropa[*b*]naphthalenes **1b-1g**, which bear substituted phenyl rings as the Ar group in **1**, all smoothly generated the corresponding products in acceptable yields with good regioselectivities (entries 1-6, Table 3), except 1-(di-*m*-tolylmethylene)-1H-cyclopropa -[*b*]naphthalene (**1d),** which gave the corresponding product **4h** in only 30%, probably due to the steric hindrance of the methyl groups (entry 3, Table 3). However, the reaction of substrate **1h**, upon reacting with **2a**, gave only an unidentified mixture (Scheme 2).

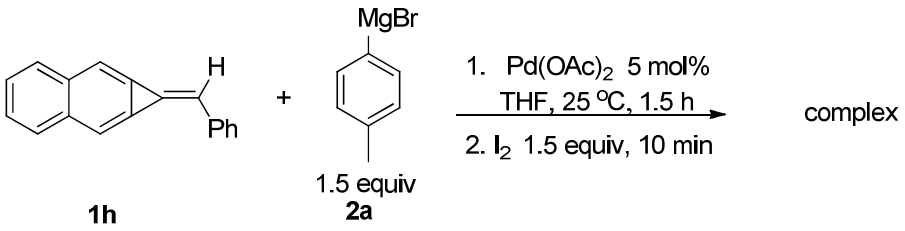
Table 3. Pd-catalyzed ring-opening coupling of diarylmethylenecyclopropa[*b*]naphthalenes **1** with **2a** quenching with I_2.[a]



entry	Ar	yield of **4**/%[b]	**4**/**3**[c]
1	4-$OMeC_6H_4$ (**1b**)	58 (**4f**)	68/2
2	4-MeC_6H_4 (**1c**)	59 (**4g**)	72/2
3	3-MeC_6H_4 (**1d**)	30 (**4h**)	48/2
4	3,5-$(OMe)_2C_6H_3$ (**1e**)	60 (**4i**)	71/2
5	4-ClC_6H_4 (**1f**)	53 (**4j**)	62/2

6	4-FC_6H_4 (**1g**)	60 (**4k**)	70/2

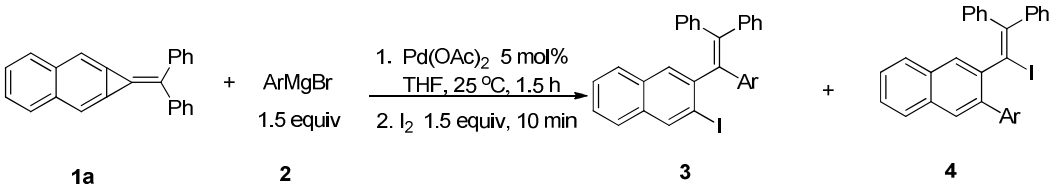
[a] The reaction was conducted with 0.2 mmol of **1**, 0.01 mmol of the catalyst, 2 mL of solvent, 1.5 equiv of *p*-tolylmagnesium bromide (1.0 M solution in THF) and 1.5 equiv of I_2. [b] Isolated yield. [c] NMR yields of **3** and **4** determined by ^{1}H NMR using dibromomethane as the internal standard.



Scheme 2. Reaction of **1h** and **2a**.

Next, we investigated the reaction of a variety of Grignard reagents with **1a**: all aryl magnesium bromides efficiently underwent the carbomagnesation to produce corresponding products in moderate yields with high regioselectivity (entries 1- 5, Table 4). When phenylmagnesium bromide (2b), 4-methoxyphenyl magnesium bromide (2c) and 4-chlorophenyl magnesium bromide (2d) were used, the reactions took 1.5 h as before. While 4-fluorophenyl magnesium bromide (**2e)** and naphth-1-yl magnesium bromide (**2f)** were used, the reactions took 4 ~ 5 h, which might be attributed to the electron deficiency of the 4-fluorophenyl group and the steric hindrance of napthyl magnesium bromides (entries 4 and 5, Table 4).

Table 4. Pd-catalyzed ring-opening coupling of **1a** with various Grignard reagents **2** quenching with I_2.[a]



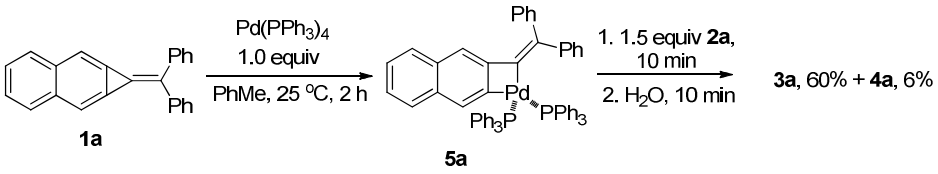
1a **2** **3** **4**

entry	Ar	yield of **4**/%[b]	**4**/**3**[c]
1	C_6H_5 (**2b**)	60 (**4l**)	72/2
2	4-OMe C_6H_4 (**2c**)	63 (**4m**)	74/2
3	4-ClC_6H_4 (**2d**)	51 (**4n**)	60/2
4[d]	4-F C_6H_4 (**2e**)	57 (**4o**)	69/2
5[e]	2-naphthyl (**2f**)	56 (**4p**)	68/2

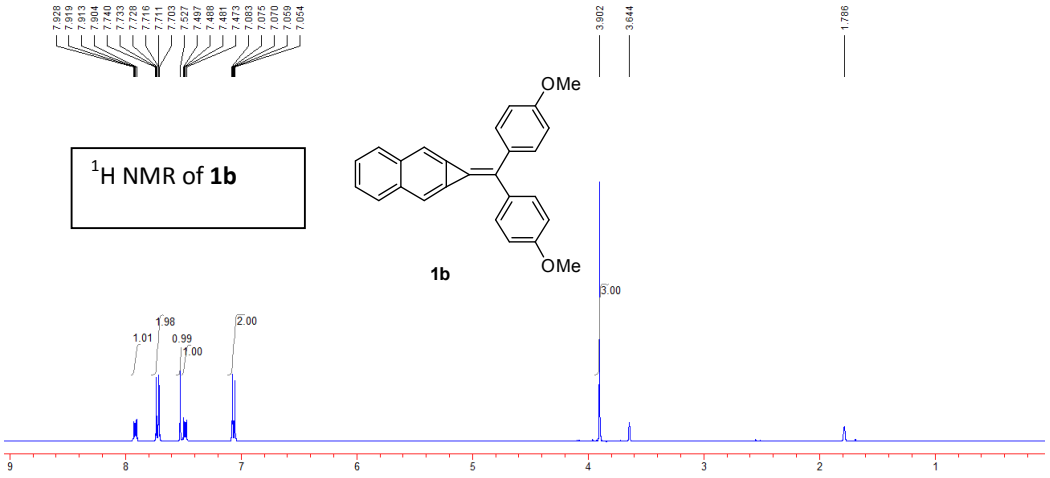
[a] The reaction was conducted with 0.2 mmol of **1a**, 0.01 mmol of the catalyst, 2 mL of solvent, 1.5 equiv of aryl magnesium bromide (1.0 M solution in THF) and 1.5 equiv of I_2. [b] Isolated yield. [c] NMR yields of **3** and **4** determined by ^{1}H NMR using dibromomethane as the internal standard. [d] The reaction time was 4h.[e] The reaction time was 5h.

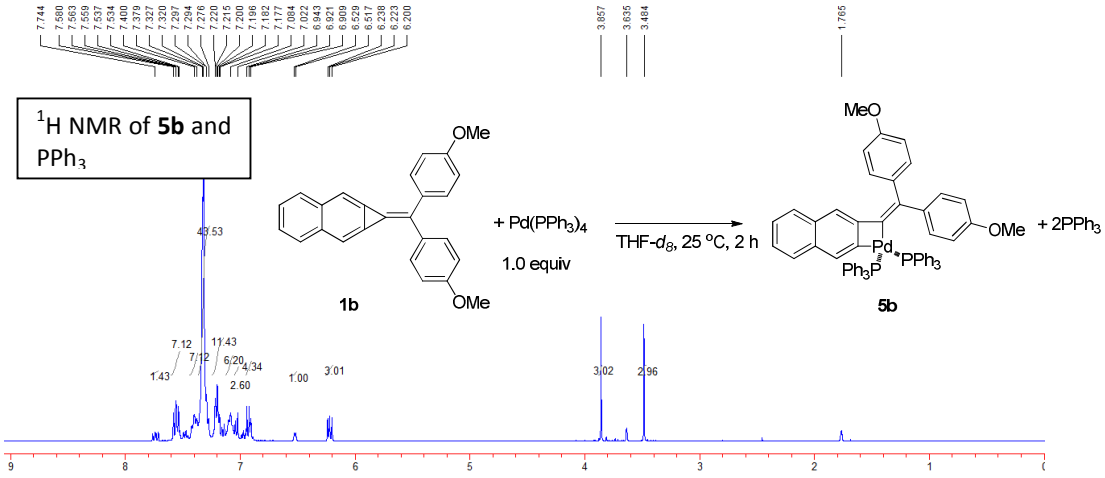
In order to unveil the factor controlling the regioselectivity, **1a** was employed to react with 1.0 equiv of $Pd(PPh_3)_4$ in toluene at 25 °C for 2 h. Upon the disappearance of **1a**, 1.5 equiv of **2a** were added and the resulting mixture was stirred for another 10 min. After an aqueous workup, **3a** and **4a** were formed in 60% and 6% isolated yields (Scheme 3). We reasoned that palladacyclobutene **5a** may be generated as a key

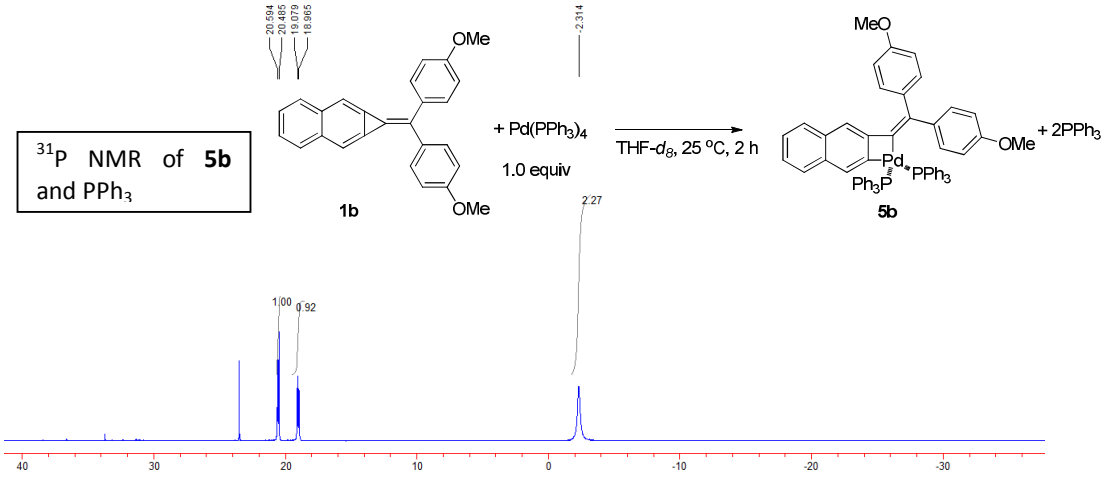
intermediate. The substrate **1b** was employed to react with 1.0 equiv of $Pd(PPh_3)_4$ in THF-d_8 at 25 ^oC in the NMR tube for the easy reading of the methoxy signal. After 2 h, we observed that the signals of starting material disappeared and the new peaks (4H signals on δ 6.5-δ 6.2 and 2 OMe signals at δ 3.9 and δ 3.5 in ^1H NMR; 2 P signals at δ 20.5 and δ 19.0 in ^{31}P NMR) were assigned to palladacyclobutene intermediate **5b**, as compared to the reported date for platinacyclobuta[*b*]lnaphthalene **5c**[6d] (4H signals on δ 6.6-δ 5.8 and 2 OMe signals at δ 3.9 and δ 3.4 in ^1H NMR; 2 P satellites signals at δ 18.2 and δ 17.9 in ^{31}P NMR) (Figure 1). After the addition of **2a** and I_2, **3f** and **4f** were isolated in 61% and 4% yields (Scheme 4). We tried to isolate **5a** and **5b** but, unfortunately, all such attempt failed.



Scheme 3. Formation and ring-opening coupling of **5a** with **2a.**


^{1}H NMR of **1b**
OMe
OMe
1b


^{1}H NMR of **5b** and PPh_3
OMe
OMe
1b
+ $Pd(PPh_3)_4$
1.0 equiv
THF-d_8, 25 °C, 2 h
MeO
OMe
+ 2PPh_3
Ph_3P Pd PPh_3
5b


^{31}P NMR of **5b** and PPh_3
OMe
OMe
1b
+ $Pd(PPh_3)_4$
1.0 equiv
THF-d_8, 25 °C, 2 h
MeO
OMe
+ 2PPh_3
Ph_3P Pd PPh_3
5b

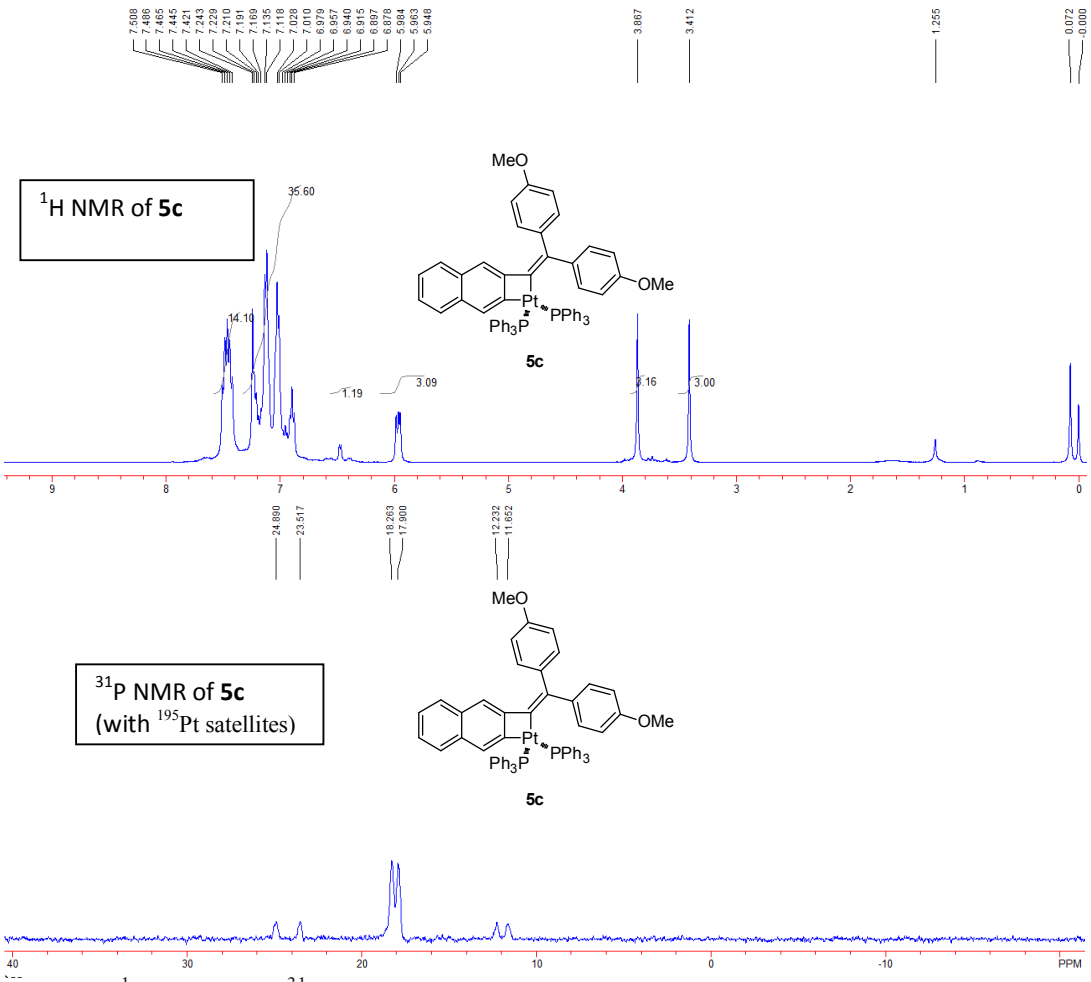
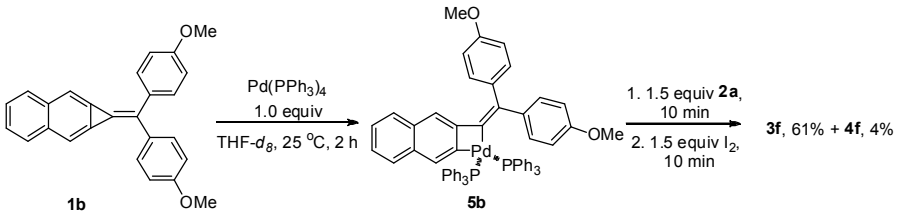


Figure 1. ^{1}H NMR and ^{31}P NMR spectrograms of **1c** ,**5b** and **5c.**

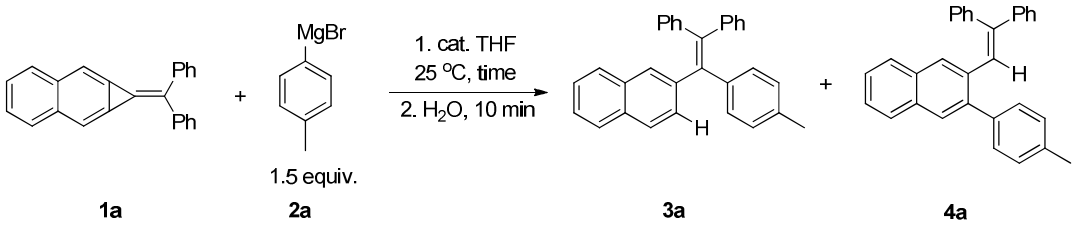


Scheme 4. Formation and ring-opening coupling of **5b** with **2a.**

Furthermore, we observed that the steric hindrance of phosphine ligands has a dramatic effect on this regioselective ring-opening reaction. When the $Pd(PPh_3)_2Cl_2$ was used, the ratio of **3a** /**4a** was 98:2.[8] Interestingly, when less steric hindered phosphite ligands such as $P(OPh)_3$, $P(OBu)_3$, $P(OEt)_3$ and $P(OMe)_3$ were employed, the ratio of **3a**

/**4a** decreased from 94:6 to 75:25 gradually. Obviously, the ratio of **3a**/**4a** dropped along with the order of the steric hindrance of the ligand[9] (Table 5, entries 2-5).

Table 5. Ligand effects for the Pd-catalyzed ring-opening coupling of 1-(diphenylmethylene)-1H-cyclopropa[*b*]naphthalene (**1a**) with *p*-tolylmagnesium bromide (1.0 M inTHF) (**2a**).[a]

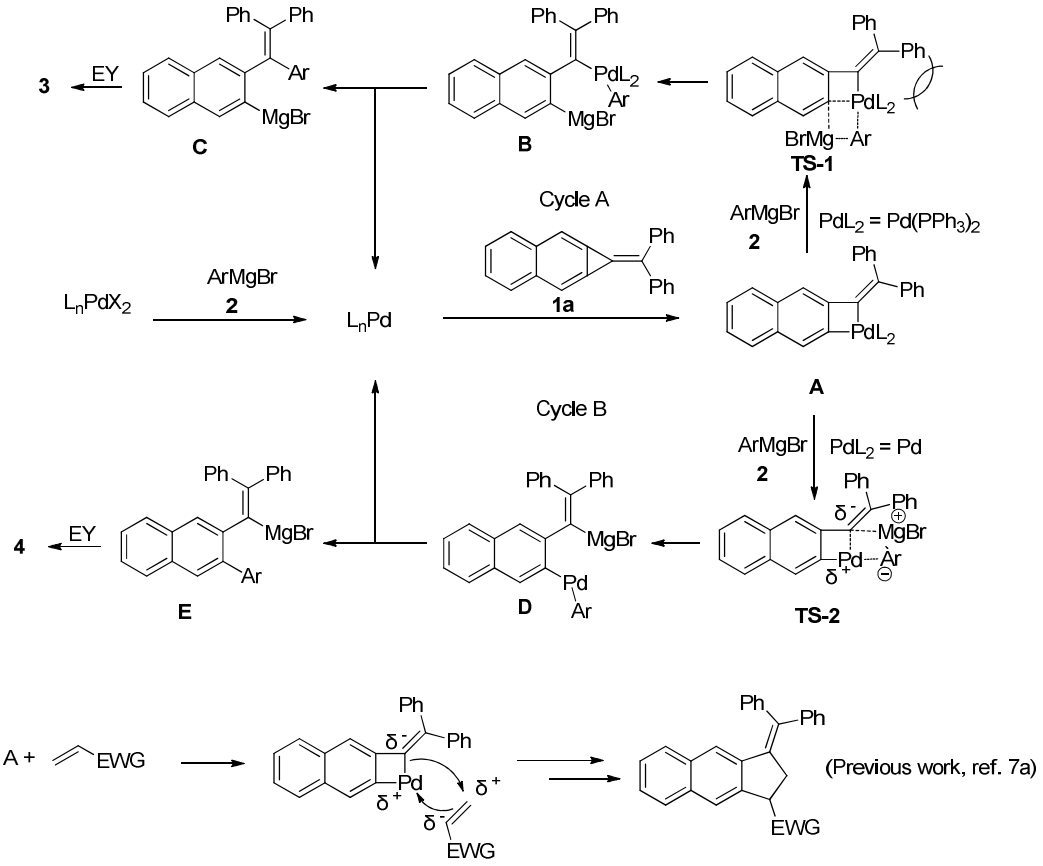


entry	catalyst (5 mol %)	Tolman Cone Angle of the Ligands	time (min)	yield/% (**3a**:**4a**)[b]
1	$Pd(PPh_3)_2Cl_2$	145	5	91 (98:2)
2	$PdCl_2$ +$P(OPh)_3$ 10%	128	60	91 (94:6)
3	$PdCl_2$+$P(OBu)_3$ 10%	110	120	82 (88:12)
4	$PdCl_2$ + $P(OEt)_3$ 10%	109	60	92 (86:14)
5	$PdCl_2$ + $P(OMe)_3$ 10%	107	60	93 (75:25)

[a] The reaction was conducted with 0.2 mmol of **1a**, 0.01 mmol of the catalyst, 2 mL of solvent, and 1.5 equiv of *p*-tolylmagnesium bromide (1.0 M solution in THF). [b] Yields and ratios of **3a** and **4a** determined by ^{1}H NMR using dibromomethane as the internal standard.

Although the detailed mechanism of the present ring-opening coupling reaction has not yet been completely clarified, we propose the reaction pathways shown in Scheme 4. First, the reduction reaction of L_nPdX_2 with two equivalents of Grignard reagents affords the L_nPd^0

compound. Subsequently, oxidative addition of L_nPd^0 with the cyclopropane C-C bond of diarylmethylenecyclopropa[*b*]naphthalene generates a metallacyclobutane **A**.[6d] When $Pd(PPh_3)_2Cl_2$ is employed (L is PPh_3), the triphenylphosphine metallacyclobutane **A** undergos transformation with Grignard reagent via **TS-1** to yield dimetallic intermediate **B**. The intermediate **B** undergoes reductive elimination to afford **C**, which, upon quenching with an electrophile, would furnish products **3**.[8] When $Pd(OAc)_2$ is employed, the Grignard reagent may undergo transmetallation with intermediate **A** via **TS-2** to produce dimetallic intermediate **D** with a totally reversed regioselectivity. This regioselectivity is mostly probably due to the electronic property of the palladacyclobutene in the absence of ligands and it matches the result of the Pd-catalyzed highly regioselective [3 + 2] cycloaddition reactions of **1** with alkenes or alkynes we reported before.[7a] Finally, the products **4** were formed via the reductive elimination and quenching with electrophilic reagents. Further studies are needed to unveil the real nature the observed unque regioselectivity.



Scheme 4. Proposed mechanism.

CONCLUSIONS:

In conclusion, we have developed a $Pd(OAc)_2$ catalyzed highly regioselective ring-opening coupling reaction of diarylmethylenecyclopropa[*b*]naphthalenes and Grignard reagents to provide differently substituted β-vinylic naphthalenes, which is different from the $Pd(PPh_3)Cl_2$-catalyzed one. Furthermore, we observed the formation of palladacyclobutene intermediates **5b** by in-situ NMR experiments, and proved that the steric hindrance of the PPh_3 groups was the key factor of the reversed regioselectivity. Further studies on the scope, mechanism, and synthetic applications of this transformation are

being carried out in our laboratory.

EXPERIMENTAL SECTION:

Materials. 1,4-Dioxane, PhMe and THF were distilled from Na/benzophenone immediately prior to use. Petroleum ether refers to the fraction with the boiling point in the range 60 ^{o}C -90 ^{o}C. All 1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured in $CDCl_3$ with TMS as the internal standard unless noted otherwise. Chemical shifts are expressed in ppm, and *J* values are given in Hz. The other commercially available chemicals were purchased and used without further purification unless noted otherwise.

General Experimental Procedures:

(1) 2- (2,2-Diphenylvinyl)-3-(*p*-tolyl)naphthalene (4a)

Typical procedure: A rubber-capped Schlenk vessel containing $Pd(OAc)_2$ (2 mg, 0.01 mmol) and 1-(diphenylmethylene)-1*H*-cyclopropa[*b*]naphthalene (**1a**) (61 mg, 0.2 mmol) was degassed and backfilled with nitrogen for three times. Then THF (2 mL) and *p*-tolylmagnesium bromide (**2a**, 1.0 M in THF, 0.3 mL, 0.3 mmol) were added sequentially to the Schlenk vessel. The resulting mixture was then allowed to stir at 25 °C until the reaction was complete as monitored by TLC. The reaction mixture was quenched with H_2O (0.1 mL) and allowed to stir for additional 10 min, then filtered through a short pad of silica gel.

The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel chromatography (petroleum ether/CH_2Cl_2 = 10:1) and recrystallization (petroleum ether/CH_2Cl_2) to afford **4a** (53 mg, 67%) as a white solid: m.p. 166-168 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.74-7.70 (m, 2H), 7.46-7.34 (m, 5H), 7.30-7.14 (m, 13H), 6.90 (s, 1H, CH=), 2.35 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.4, 142.6, 140.2 (broad peak, 2C), 138.2, 136.6, 134.2, 132.3, 132.1, 130.7, 129.8, 129.4, 128.9, 128.4, 128.3, 128.1, 128.1, 127.9, 127.7, 127.4, 127.3, 127.1, 126.0, 125.6, 21.2 ppm; MS(EI): *m*/*z* (%) = 396 (M^+, 100); IR (neat): 3052, 1596, 1506, 1441, 1265, 1183, 1112, 1074, 1026 cm^{-1}; HRMS calcd. for $C_{31}H_{24}$ (M^+): 396.1878; found: 396.1877.

The following compounds were prepared according to this procedure.

(2) 2-(1-Deuterio-2,2-diphenylvinyl)-3-(*p*-tolyl)naphthalene (4a')

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and *p*-tolylmagnesium bromide (**2a**, 1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4a'** (54 mg, 68%, 97%D) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with D_2O (0.1 mL): m.p. 165-167 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.76-7.71 (m, 2H), 7.46-7.29 (m, 5H), 7.27-7.16 (m, 13H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.4, 142.5, 140.2 (broad peak, 2C), 138.2, 136.6, 134.1, 132.3, 132.1, 130.7, 129.8, 129.4,

128.9, 128.4, 128.3, 128.1, 128.0, 127.7, 127.4, 127.3, 127.1, 126.0, 125.6, 21.1 ppm; MS(EI): *m*/*z* (%) = 397 (M^+, 100); IR (neat): 3052, 1596, 1514, 1491, 1443, 1266, 1185, 1112, 1075, 1020 cm^{-1}; HRMS calcd. for $C_{31}H_{23}D$ (M^+): 397.1941; found: 397.1939.

(3) 2-(1-Iodo-2,2-diphenylvinyl)-3-(*p*-tolyl)naphthalene (4b)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4b** (65 mg, 62%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 168-170 °C (petroleum ether/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1H, naphthyl-H), 7.85 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.73 (d, *J* = 8.4 Hz, 1H, naphthyl-H), 7.51-7.42 (m, 3H), 7.33-7.25 (m, 3H), 7.14-7.05 (m, 6H), 6.94-6.88 (m, 1H), 6.81-6.75 (m, 2H, Ar-H), 6.45 (d, *J* = 8.4 Hz, 2H, Ar-H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 149.7, 147.5, 141.3, 139.0, 138.6, 137.8, 136.4, 133.1, 132.0, 131.4, 130.1, 129.3, 129.0, 128.9, 128.3, 128.1, 127.8, 127.7, 127.4, 127.2, 127.6 (broad peak, 2C), 126.1, 100.8, 21.3 ppm; MS(EI): *m*/*z* (%) = 522 (M^+, 24.00), 302(100); IR (neat): 3052, 1595, 1513, 1490, 1442, 1265, 1184, 1148, 1114, 1074, 1030 cm^{-1}; HRMS calcd. for $C_{31}H_{23}I$ (M^+): 522.0845; found: 522.0851.

(4) 2-(1-Bromo-2,2-diphenylvinyl)-3-(*p*-tolyl)naphthalene (4c)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol),

and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4c** (58 mg, 61%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with NBS (53 mg, 0.3 mmol): m.p. 182-184 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ= 8.22 (s, 1H, naphthyl-H), 7.87 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.74 (d, *J* = 8.4 Hz, 1H, naphthyl-H),7.54 (s, 1H, naphthyl-H), 7.48-7.44 (m, 2H), 7.33-7.25 (m, 3H), 7.20-7.03 (m, 6H), 6.93-6.89 (m, 1H), 6.81-6.75 (m, 2H, Ar-H), 6.40 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 143.9, 143.7, 139.6, 139.0, 138.1, 137.6, 136.4, 133.3, 132.1, 131.4, 130.0, 129.1 (broad peak, 2C), 128.9, 128.3, 128.0, 127.9, 127.7, 127.3, 127.2, 126.7, 126.6, 126.1, 121.0, 21.2 ppm; MS(EI): *m*/*z* (%) =476 (M^+(^{81}Br), 33.00), 474 (M^+(^{79}Br), 32.00), 395 (100); IR (neat): 3053, 1514, 1491, 1442, 1265, 1185, 1149, 1117, 1074, 1031 cm^{-1}; HRMS calcd. for $C_{31}H_{23}{}^{79}Br$ (M^+): 474.0983; found:. 474.0978.

(5) 2-(1,1-Diphenylpenta-1,4-dien-2-yl)-3-(*p*-tolyl)naphthalene (4d)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) (36 mg, 0.3 mmol) afforded **4d** (54 mg, 62%) as oil (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with allyl bromide:GC purity: 95.2 %; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.79-7.71 (m, 3H), 7.67 (s, 1H, naphthyl-H), 7.44-7.30 (m, 4H), 7.25-7.10 (m, 7H), 6.90-6.81 (m, 3H), 6.65 (d, *J* = 7.6 Hz, 2H, Ar-H), 5.80-5.71 (m, 1H, CH=), 4.92-4.83 (m,

2H, CH_2=), 3.25 (dd, J_1 = 14.8 Hz, J_2 = 6.4 Hz, 1H), 2.85 (dd, J_1 = 14.4 Hz, J_2 = 7.8 Hz, 1H), 2.37(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 143.3, 141.7, 140.5, 139.4, 138.7, 138.5, 136.7, 136.3, 136.2, 132.5, 132.2, 130.3, 129.8, 129.5, 129.2, 128.9, 128.5, 128.1, 127.6, 127.5, 127.1, 126.6, 125.8, 125.7, 125.7, 115.8, 41.1, 21.2 ppm; MS(EI): *m*/*z* (%) = 436 (M^+, 59.00), 167(100); IR (neat): 3054, 1540, 1514, 1456, 1274 cm^{-1}; HRMS calcd. for $C_{34}H_{28}$ (M^+): 436.2191; found: 436.2195.

(6) 4,4-Diphenyl-3-[3-(*p*-tolyl)naphth-2-yl]but-3-en-2-one (4e)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4e** (48 mg, 55%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with acetyl chloride (24 mg, 0.3 mmol): m.p. 193-195 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.75 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.68(d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.44-7.30 (m, 5H), 7.25-7.01 (m, 7H), 6.96-6.90 (m, 2H, Ar-H), 6.69 (d, *J* = 8.4 Hz, 2H, Ar-H), 2.32 (s, 3H), 1.61 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 206.9, 146.4, 142.0, 141.6, 140.4, 139.9, 138.4, 137.3, 136.4, 132.9, 132.3, 130.9, 130.8, 130.2, 129.4, 129.2, 128.7, 128.6, 128.4, 127.6, 127.4 (broad peak, 3C), 126.3, 125.8, 31.0, 21.1 ppm; MS(EI): *m*/*z* (%) = 438 (M^+, 44.00), 167(100); IR (neat): 3053, 1674, 1562, 1514, 1491, 1443, 1352, 1268, 1217, 1187, 1144, 1117, 1076, 1024 cm^{-1}; HRMS calcd. for $C_{33}H_{26}O$ (M^+): 438.1984 ;

found: 438.1979.

(7) 2-[1-Iodo-2,2-bis(4-methoxyphenyl)vinyl]-3-(*p*-tolyl)naphthalene (4f)

The reaction of **1b** (73 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4f** (68 mg, 58%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 5:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 228-230 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1H, naphthyl-H), 7.85 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.74 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.51(s, 1H, naphthyl-H), 7.48-7.42 (m, 2H), 7.15-7.01 (m, 6H), 6.84 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.38-6.30 (m, 4H, Ar-H), 3.80 (s, 3H), 3.61 (s, 3H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 158.7, 158.0, 148.8, 141.8, 140.2, 138.7, 137.9, 136.3, 133.0, 132.0, 132.0, 131.6, 131.4, 130.3, 129.2, 129.0, 128.2, 127.7, 127.7, 126.5, 126.0, 113.3, 112.5, 98.8, 55.1, 55.0, 21.2 ppm; MS(EI): *m*/*z* (%) = 582 (M^+, 44.00), 455(100); IR (neat): 2954, 2835, 1604, 1506, 1458, 1295, 1245, 1175, 1145, 1112, 1033 cm^{-1}; HRMS calcd. for $C_{33}H_{27}IO_2$ (M^+): 582.1056; found: 582.1065.

(8) 2-(1-Iodo-2,2-di-*p*-tolylvinyl)-3-(*p*-tolyl)naphthalene (4g)

The reaction of **1c** (68 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4g** (66 mg, 59%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1)

after quenching with I_2 (76 mg, 0.3 mmol): m.p. 228-230 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.18 (s, 1H, naphthyl-H), 7.85 (d, *J* = 7.2 Hz, 1H, naphthyl-H), 7.74 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.52-7.42 (m, 3H), 7.15-7.07 (m, 6H), 7.00 (d, *J* = 6.8 Hz, 2H, Ar-H), 6.59 (d, *J* = 7.2 Hz, 2H, Ar-H), 6.35 (d, *J* = 6.8 Hz, 2H, Ar-H), 2.38 (s, 3H), 2.34 (s, 3H), 2.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.5, 144.8, 141.6, 138.7, 137.8, 137.0, 136.4, 136.3, 136.3, 133.0, 132.0, 131.2, 130.1, 129.2, 129.0, 128.8 (broad peak, 2C), 128.2, 127.8, 127.8, 127.7, 126.5, 126.0, 99.7, 21.3, 21.3, 21.0 ppm; MS(EI): *m*/*z* (%) = 550 (M^+, 22.00), 423(100); IR (neat): 3022, 2919, 1610, 1509, 1452, 1265, 1183, 1113, 1021 cm^{-1}; HRMS calcd. for $C_{33}H_{27}I$ (M^+): 550.1158; found: 550.1160.

(9) 2-(1-Iodo-2,2-di-*m*-tolylvinyl)-3-(*p*-tolyl)naphthalene (4h)

The reaction of **1d** (68 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4h** (33 mg, 30%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 137-139 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.20 (s, 1H, naphthyl-H), 7.85 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.72 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.50-7.41 (m, 3H), 7.24-7.20 (m, 1H), 7.17-7.06 (m, 5H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 (s, 1H), 6.73-6.65 (m, 2H), 6.38 (d, *J* = 7.6 Hz, 1H, Ar-H), 6.04 (s, 1H, Ar-H), 2.40 (s, 3H), 2.32 (s, 3H), 1.92

(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 149.9, 147.3, 141.4, 138.9, 138.5, 137.7, 137.6, 136.6, 136.2, 133.0, 131.9, 131.5, 130.5, 129.4, 129.3, 128.8, 128.2, 128.1, 127.9, 127.7, 127.6, 127.2, 127.1, 126.9, 126.5, 126.0, 125.8, 100.3, 21.5, 21.3, 21.2 ppm; MS(EI): *m*/*z* (%) = 550 (M^+, 22.00), 423(100); IR (neat): 3049, 2919, 1600, 1513, 1483, 1453, 1265, 1168, 1114, 1092, 1018 cm^{-1}; HRMS calcd. for $C_{33}H_{27}I$ (M^+): 550.1158; found: 550.1158.

(10) 2-[2,2-Bis(3,5-dimethoxyphenyl)-1-iodovinyl]-3-(*p*-tolyl)-naphthalene (4i)

The reaction of **1e** (85 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4i** (77 mg, 60%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 3:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 186-188 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1H, naphthyl-H), 7.84 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.74 (d, *J* = 8.4 Hz, 1H, naphthyl-H), 7.54 (s, 1H, naphthyl-H), 7.46-7.43 (m, 2H), 7.18-7.11 (m, 4H), 6.39-6.37 (m, 1H, Ar-H), 6.24 (s, 2H, Ar-H), 6.08-6.06 (m, 1H, Ar-H), 5.66 (s, 2H, Ar-H), 3.77 (s, 6H), 3.22 (s, 6H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 160.4, 159.3, 149.2, 148.8, 141.5, 140.1, 138.6, 137.8, 136.3, 133.1, 132.0, 130.9, 129.4, 128.9, 128.2, 127.6, 127.5, 126.6, 126.2, 108.0, 106.7, 100.9, 100.1, 99.8, 55.3, 54.7, 21.2 ppm; MS(EI): *m*/*z* (%) = 642 (M^+, 7.00), 515(100); IR (neat):

3000, 2937, 1509, 1514, 1455, 1421, 1344, 1294, 1260, 1202, 1153, 1065, 1017 cm^{-1}; HRMS calcd. for $C_{35}H_{31}IO_4$ (M^+): 642.1267; found: 642.1278.

(11) 2-[2,2-Bis(4-chlorophenyl)-1-iodovinyl]-3-(*p*-tolyl)naphthalene (4j)

The reaction of **1f** (75 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4j** (68 mg, 53%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 226-228 °C (petroleum ether/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.21 (s, 1H, naphthyl-H), 7.88 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.76 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.53-7.46 (m, 3H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.08-6.92 (m, 4H), 6.76 (d, *J* = 8.4 Hz, 2H, Ar-H), 6.29 (d, *J* = 8.0 Hz, 2H, Ar-H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 147.3, 145.2, 140.7, 138.2, 137.6, 137.2, 136.6, 133.5, 133.2, 132.7, 131.9, 131.4 (broad peak, 2C), 130.4, 129.2 (broad peak, 3C), 128.6, 128.4, 127.8, 127.4, 126.9, 126.3, 101.7, 21.2 ppm; MS(EI): *m*/*z* (%) = 590 (M^+($^{35,35}Cl$), 20.00), 592 (M^+($^{35,37}Cl$), 14.00), 590 (M^+($^{37,37}Cl$), 3.00), 463 (100); IR (neat): 3051, 1591, 1513, 1487, 1455, 1396, 1264, 1182, 1090, 1015 cm^{-1}; HRMS calcd. for $C_{31}H_{21}{}^{35,35}Cl_2I$ (M^+): 590.0065; found: 590.0073.

(12) 2-[2,2-Bis(4-fluorophenyl)-1-iodovinyl]-3-(*p*-tolyl)naphthalene

(4k)

The reaction of **1g** (68 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2a** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4k** (67 mg, 60%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 195-197 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.22 (s, 1H, naphthyl-H), 7.86 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.75 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.52-7.45 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.08-6.99 (m, 6H), 6.51-6.45 (dd, 2H, J_1 = 8.6 Hz, J_2 = 8.6 Hz, Ar-H), 6.37-6.31 (dd, 2H, J^1 = 9.0 Hz, J^2 = 10.8 Hz, Ar-H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 161.9 (d, *J* = 246.2 Hz), 161.2 (d, *J* = 246.3 Hz), 147.5, 143.1 (d, *J* = 2.8 Hz), 140.9, 138.3, 137.6, 136.5, 134.9 (d, *J* = 3.1 Hz), 133.1, 131.9, 131.8 (d, *J* = 8.4 Hz), 131.4, 130.6 (d, *J* = 9.0 Hz), 129.1, 129.1, 128.3, 127.7 (broad peak, 2C), 126.7, 126.2, 115.2 (d, *J* = 21.2 Hz), 114.1 (d, *J* = 21.4 Hz), 101.0, 21.2 ppm; MS(EI): *m*/*z* (%) = 558 (M^+, 16.00), 431 (100); IR (neat): 3051, 1599, 1503, 1455, 1266, 1225, 1157, 1095, 1016 cm^{-1}; HRMS calcd. for $C_{31}H_{21}F_2I$ (M^+): 558.0656; found: 558.0654.

(13) 2-[1-Iodo-2,2-diphenylvinyl]-3-phenylnaphthalene (4l)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2b** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4l** (61 mg, 60%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after

quenching with I_2 (76 mg, 0.3 mmol): m.p. 192-194 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.25 (s, 1H, naphthyl-H), 7.88 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.75 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.52-7.43 (m, 3H), 7.35-7.22 (m, 6H), 7.17-7.07 (m, 4H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.81-6.75 (m, 2H, Ar-H), 6.42 (d, *J* = 8.0 Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 149.9, 147.5, 141.3, 140.7, 139.0, 138.6, 133.1, 132.1, 131.6, 130.1, 129.4, 129.1, 128.8, 128.1, 127.8, 127.8, 127.6, 127.4, 127.2, 126.8, 126.7, 126.6, 126.2, 100.5 ppm; MS(EI): *m*/*z* (%) = 508 (M^+, 14.00), 381 (100); IR (neat): 3053, 1596, 1490, 1442, 1266, 1183, 1074, 1031 cm^{-1}; HRMS calcd. for $C_{30}H_{21}I(M^+)$: 508.0688; found: 508.0682.

(14) 2-(1-Iodo-2,2-diphenylvinyl)-3-(4-methoxyphenyl)-naphthalene (4m)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2c** (1.0 M in THF, 0.3 mL, 0.3 mmol), in THF (2 mL) afforded **4m** (68 mg, 63%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 5:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 146-148 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.23 (s, 1H, naphthyl-H), 7.87 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.75 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.50-7.44 (m, 3H), 7.35-7.27 (m, 3H), 7.15-7.08 (m, 4H), 6.94-6.86 (m, 3H), 6.82-6.76 (m, 2H, Ar-H), 6.45 (d, *J* = 8.0 Hz, 2H,

Ar-H), 3.86 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 158.7, 149.7, 147.5, 141.3, 139.0, 138.2, 133.3, 133.1, 131.9, 131.5, 130.5, 130.0, 128.9 (broad peak, 2C), 128.1, 127.8, 127.6, 127.4, 127.2, 126.6 (broad peak, 2C), 126.0, 113.1, 100.7, 55.4 ppm; MS(EI): *m*/*z* (%) = 538 (M^+, 15.00), 411 (100); IR (neat): 3053, 1610, 1540, 1514, 1491, 1457, 1263, 1178, 1053 cm^{-1}; HRMS calcd. for $C_{31}H_{23}IO$ (M^+): 538.0794; found: 538.0794.

(15) 2-(4-Chlorophenyl)-3-(1-iodo-2,2-diphenylvinyl)naphthalene (4n)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2d** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4n** (55 mg, 51%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 159-161 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.27 (s, 1H, naphthyl-H), 7.90 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.76 (d, *J* = 8.0 Hz, 1H, naphthyl-H), 7.55-7.46 (m, 3H), 7.38-7.24 (m, 5H), 7.11-7.04 (m, 4H), 6.94 (t, *J* = 7.2 Hz, 1H), 6.83-6.77 (m, 2H, Ar-H), 6.43 (d, *J* = 8.0 Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.0, 147.3, 141.0, 139.1, 138.9, 137.2, 133.0, 132.8, 132.2, 131.8 (broad peak, 2C), 130.6, 130.1, 129.0, 128.7, 128.2, 127.8, 127.7, 127.6, 127.3, 126.8, 126.8, 126.5, 100.0 ppm; MS(EI): *m*/*z* (%) = 544 (M^+(^{37}Cl), 5.00), 542 (M^+(^{35}Cl), 14.00), 380 (100); IR (neat): 3054, 1650, 1489, 1444, 1396,

1266, 1091, 1016 cm^{-1}; HRMS calcd. for $C_{30}H_{20}{}^{35}ClI$ (M^+): 542.0298; found: 542.0305.

(16) 2-(4-Fluorophenyl)-3-(1-iodo-2,2-diphenylvinyl)naphthalene (4o)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2e** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4o** (60 mg, 57%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 165-167 °C (petroleum ether/CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.26 (s, 1H, naphthyl-H), 7.88 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.74 (d, *J* = 7.6 Hz, 1H, naphthyl-H), 7.51-7.43 (m, 3H), 7.36-7.25 (m, 3H), 7.10-6.88 (m, 7H), 6.82-6.78 (m, 2H, Ar-H), 6.43 (d, *J* = 7.2 Hz, 2H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): *δ* = 162.0 (d, *J* = 244.5 Hz), 149.9, 147.3, 141.2, 138.9, 137.4, 136.7 (d, *J* = 2.9 Hz), 133.0, 132.2, 131.7, 130.9 (d, *J* = 7.1 Hz), 130.1, 129.0, 128.8, 128.2, 127.8, 127.7, 127.5, 127.3, 126.8, 126.7, 126.3, 114.4 (d, *J* = 21.0 Hz), 100.2 ppm; MS(EI): *m*/*z* (%) = 526 (M^+, 10.00), 399(100); IR (neat): 3053, 1600, 1510, 1490, 1441, 1266, 1222, 1157, 1117, 1095, 1074, 1030 cm^{-1}; HRMS calcd. for $C_{30}H_{20}FI$ (M^+): 526.0594; found: 526.0609.

(17) 3-(1-Iodo-2,2-diphenylvinyl)-2,2'-binaphthalene (4p)

The reaction of **1a** (61 mg, 0.2 mmol), $Pd(OAc)_2$ (2 mg, 0.01 mmol), and **2f** (1.0 M in THF, 0.3 mL, 0.3 mmol) in THF (2 mL) afforded **4p** (62

mg, 56%) as a white solid (eluent: petroleum ether/CH_2Cl_2 = 10:1) after quenching with I_2 (76 mg, 0.3 mmol): m.p. 209-211 °C (petroleum ether/CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 8.32 (s, 1H, naphthyl-H), 7.93-7.59 (m, 5H), 7.54 (s, 1H), 7.52-7.46 (m, 5H), 7.30-7.18 (m, 4H), 7.03 (d, *J* = 7.6 Hz, 2H) 6.92 (t, *J* = 7.4 Hz, 1H), 6.71-6.65 (m, 2H), 6.24 (d, *J* = 7.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 150.1, 147.3, 141.3, 139.0, 138.5, 138.3, 133.2, 133.1, 132.2 (broad peak, 2C), 131.8, 130.0, 129.3, 128.8, 128.3, 128.1 (broad peak, 2C), 127.8, 127.8, 127.7, 127.6, 127.3, 127.1, 126.7, 126.7, 126.6, 126.3, 125.8, 125.7, 100.3 ppm; MS(EI): *m*/*z* (%) = 558 (M^+, 5.00), 431 (100); IR (neat): 3052, 1596, 1490, 1441, 1264, 1184, 1112, 1074, 1028 cm^{-1}; HRMS calcd. for $C_{34}H_{23}I$ (M^+): 558.0845; found: 558.0856.

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