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Synthesis of novel 1-aryl-substituted 8-methoxynaphthalenes and their tendency for atropisomerization

Seiji Yoshikawa, Jun-ichi Odaira, Yuki Kitamura, Ashutosh V. Bedekar, Takumi Furuta and Kiyoshi Tanaka*

School of Pharmaceutical Sciences, University of Shizuoka, 52-1 Yada, Shizuoka 422-8526, Japan

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Abstract—Novel 1-aryl-substituted 8-methoxynaphthalenes were conveniently prepared by using Suzuki–Miyaura cross-coupling as a key reaction. Chemical transformations of the coupled products gave a variety of biaryls bearing various functional groups. The optical behavior of the separated enantiomers of these derivatives was also investigated by HPLC analysis. The optical resolution and determination of absolute configuration of novel binaphtyl derivative were also described. These new compounds may have some potential as mono- or bidentate ligands for metal-catalyzed chemical transformations including asymmetric induction.

1. Introduction

The combination of transition metals and chiral ligands has greatly contributed to progress in synthetic transformation to create interesting chiral molecules in optically active forms. In this context, axially chiral biaryls have played important roles in asymmetric synthesis as well as chiral recognition in the field of host–guest chemistry by creating a specific asymmetric environment around the recognition sites of substrates involving chiral catalysts, reagents and host molecules. A specific feature of these derivatives is that the rigid binaphthyl skeleton has a rather high energy barrier to atropisomerization even at an elevated temperature and the functional groups on the naphthyl ring can chelate a metal ion to create specific chiral conditions for effective chiral induction. The most widely used compounds of this type for use as a chiral ligand or auxiliary are non-racemic 2,2′-difunctionalized 1,1′-binaphthyls,[1] such as BINAP,[2] MOP[3] and BINOL,[4] however, the degree of asymmetric induction and catalytic activity are not universally high, and indeed are sometimes unsatisfactory in specific cases. This is why the further development of novel axially chiral compounds that show strong asymmetric induction is still required. To develop new ligands or catalysts consisting of π-systems, both steric and electronic tuning of the biaryl structures are necessary. Compared to ordinary 2,2′-difunctionalized 1,1′-binaphthyls, there have been few reported examples of the preparation and use of chiral 1,8-disubstituted naphthalene as a catalyst or chiral inducer. Recently, we reported the preparation of optically active 8,8′-difunctionalized 1,1′-binaphthyl derivatives[5] and their optical behavior.[6] Moreover, the successful use of these molecules as chiral inducers for asymmetric protonation[5a] and asymmetric carbon–carbon bond formation[7] as well as in the chiral recognition of amino acid derivatives[8] has also been reported. Since a specific and interesting *peri*-interaction on the naphthalene ring is expected in 1,8-disubstituted naphthalene derivatives, to examine their catalytic activity as ligands and their optical behavior as possible atropisomers, we focused our attention on the preparation and characterization of new families of 1-aryl-substituted 8-methoxynaphthalene and related derivatives.[9] A preliminary experiment regarding the optical resolution of the newly synthesized biaryls as well as optical behavior are also described.

2. Results and discussion

2.1. Molecular design and synthetic strategy

To construct 1,8-disubstituted naphthalene as a general key structural unit, 1-aryl-substituted naphthalene derivatives possessing an oxygen substituent at the 1-position were selected as a basic structure, and an additional substituent (R^1) was introduced at the *ortho* position relative to the biaryl axis on the aryl ring to prevent free rotation around the biaryl axis (Fig. 1). In addition to benzene and naphthalene rings, a pyridine (Y=N) ring was also a candidate for the 1-aryl group. As for the substituents R^1 and R^2, a wide variety of functional groups, functionalized and

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* Corresponding author. Tel.: +81-54-264-5746; fax: +81-54-264-5745; e-mail address: tanakaki@u-shizuoka-ken.ac.jp

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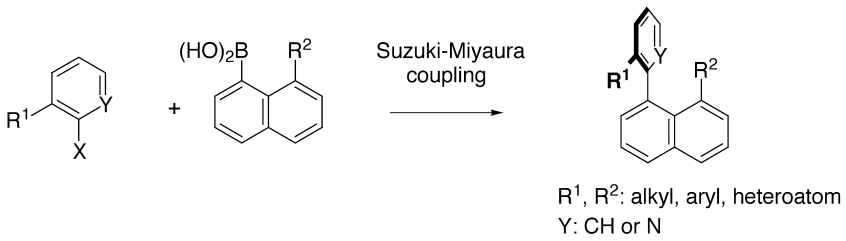


Figure 1. Preparation of axially chiral biaryls substituted at *peri*-positions.

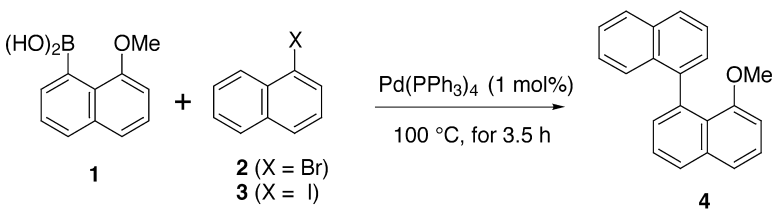
unfunctionalized alkyl groups, including hydroxyl, halogen, amine, phosphine, ester, ether, aryl, hydroxymethyl, and methyl groups, were chosen. Due to the steric or electronic repulsive interaction between these substituents R^1 and R^2, the designed molecules were expected to have axial chirality at least at low temperature. Additionally, in molecules in which both the R^1 and R^2 moieties bear heteroatom substituents, these molecules may function as effective bidentate ligands through intramolecular chelation to form a medium-sized ring through chelation with a metal. Moreover, since both the substituents R^1 and R^2 face toward the π systems of the naphthyl and aryl rings, respectively, the chelated metal may be placed inside the asymmetric cavity created by the chiral biaryl system, and hence act as the center of effective catalysts. These molecular conditions might lead to the creation of novel circumstances in which high levels of both catalytic activity and asymmetric induction are realized. Along these lines, synthetic studies of non-racemic and non-symmetrically substituted 1,1′-binaphthalene derivatives including 2,8′-disubstituted 1,1′-binaphthyls, as well as their excellent activity as chiral ligands, were recently reviewed by Kočovsky and co-workers.[10] Despite the progress regarding 1,1′-binaphthyl systems as chiral inducers, less attention has been paid to the preparation and use of the corresponding 1-aryl systems, which are substituted by monocyclic aromatic rings.

Generally, the preparation of these compounds is based on the Pd-mediated Suzuki–Miyaura coupling procedure,[11] which has been frequently used to prepare biaryl molecular systems. Thus, using 8-substituted naphthylboronic acid and *ortho*-substituted aryl halide, the preparative approach is generalized in Figure 1. Compared to the prospect of introducing a variety of functional groups at the 2′ position of binaphthyl systems, the present synthetic approach allows us to make several biaryl compounds bearing different substituents at the corresponding position. Consequently, further transformation of the functional groups in the coupled products, R^1 or R^2, should furnish several 1,8-disubstituted arylnaphthalene derivatives, and these results will be discussed below.

2.2. Preparation of 1-aryl-substituted 8-methoxynaphthalene derivatives

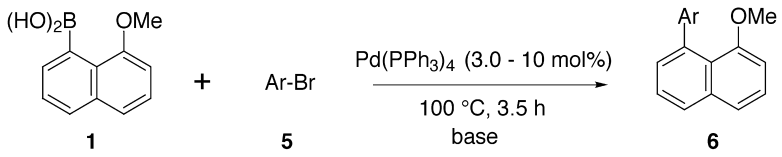
8-Methoxy-1-naphthylboronic acid (**1**), which was readily prepared according to the procedure in literature,[9j] was a common starting material in the present synthesis of *peri*-functionalized biaryl molecules. First, different reaction conditions were examined to obtain a high chemical yield in Suzuki–Miyaura coupling reactions of **1** with 1-halogenated naphthalene derivatives (Table 1). The cross-coupling reaction of 1-bromonaphthalene (**2**) with **1** for 3.5 h in the presence of 1 mol% of $Pd(PPh_3)_4$ and Na_2CO_3 in DME/H_2O (6:1) at 100 °C gave **4**[9c] in a satisfactory chemical yield of 94% (entry 2). In contrast, only a trace amount of the coupled product **4** was obtained in the absence of H_2O (entry 1) and a similar tendency was observed in the cross-coupling reaction using Cs_2CO_3 as a base (entries 3 and 4). The coupled product **4** was also prepared in excellent chemical yield with a mixed solvent system of toluene/EtOH/H_2O (3:3:2) (entry 5). In the coupling reaction using 1-iodonaphthalene (**3**) as a coupling partner for **1**, the addition of H_2O had positive effects, as shown in entries 7, 9

Table 1. The conditions for the Suzuki–Miyaura coupling reactions

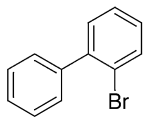
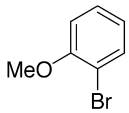
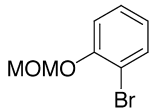
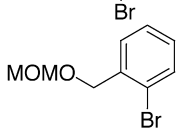
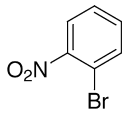
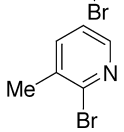
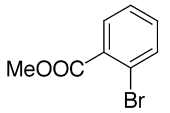
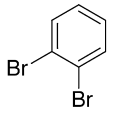
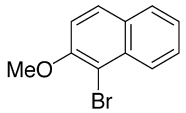


Entry	Naphthyl halide	Base	Solvent	Yield (%)
1	**2**	Na_2CO_3	DME	Trace
2	**2**	Na_2CO_3	DME/H_2O (6:1)	94
3	**2**	Cs_2CO_3	DME	29
4	**2**	Cs_2CO_3	DME/H_2O (6:1)	99
5	**2**	Cs_2CO_3	Toluene/EtOH/H_2O (3:3:2)	96
6	**3**	Na_2CO_3	DME	Trace
7	**3**	Na_2CO_3	DME/H_2O (6:1)	55
8	**3**	Cs_2CO_3	DME	Trace
9	**3**	Cs_2CO_3	DME/H_2O (6:1)	93
10	**3**	Cs_2CO_3	Toluene/EtOH/H_2O (3:3:2)	98

Table 2. The Suzuki–Miyaura coupling to aryl naphthalenes



1 **5** **6**

Entry	Aryl bromide (**5**)	Base (equiv.)	$Pd(PPh_3)_4$ (mol%)	Solvent system[a]	Yield (%)[b]	Product (**6**)
1	 **5a**	Cs_2CO_3 (1.5)	5.0	A	83	**6a**
2	 **5b**	Cs_2CO_3 (1.5)	5.0	A	67	**6b**
3	 **5c**	Cs_2CO_3 (1.5)	10	A	98	**6c**
4	 **5d**	Cs_2CO_3 (1.5)	10	A	97[c]	**6d**
5	 **5e**	Na_2CO_3 (3.0)	5.0	B	63	**6e**
6	 **5f**	K_3PO_4 (3.0)	5.0	B	~100	**6f**
7		Cs_2CO_3 (1.5)	3.0	A	~100	**6g**
8	 **5h**	CsF (1.4)	10	C	43[d]	**6h**
9	 **5i**	Cs_2CO_3 (1.5)	5.0	A	82[c]	**6i**
10	 **5j**	Cs_2CO_3 (1.5)	10	A	66	**6j**

[a] Solvent system A: DME/H_2O (6:1), B: toluene/EtOH/H_2O (3:3:2), C: DME
[b] Isolated yield.
[c] The reaction was carried out for 24 h.
[d] The reaction was carried out for 36 h at 85 °C.

and 10. With a relatively sterically hindered boronic acid, such as *peri*-disubstituted naphthylboronic acid **1**, as a coupling partner, the addition of H_2O as a co-solvent dramatically promoted the coupling reaction to give the product in improved yield. Generally, in the presence of H_2O, the coupling reactions proceeded smoothly to give **4** in satisfactory chemical yield with either 1-bromo- or 1-iodonaphthalene as a starting 1-halogenated naphthalene.

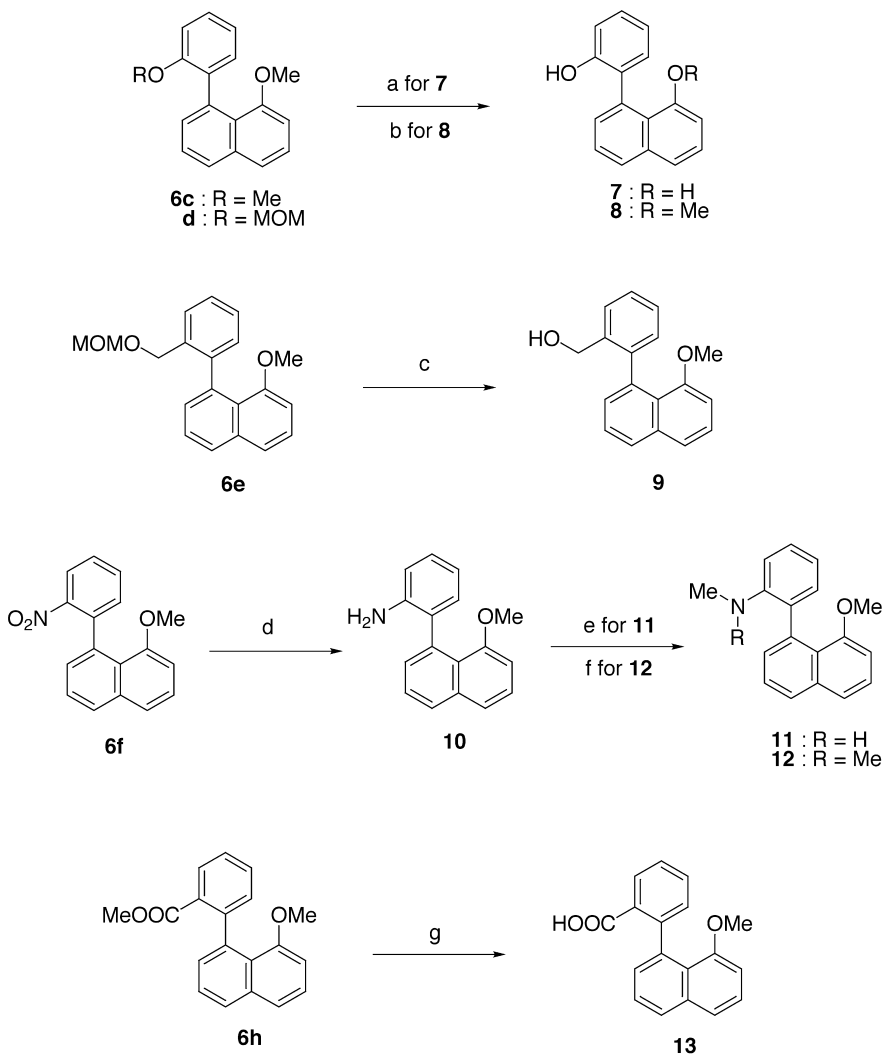
Next, using the established coupling conditions mentioned above with slightly increased amounts of $Pd(PPh_3)_4$ (3–10 mol%) for the purpose of acceleration of the reaction and achievement of high yield, several 8-aryl-substituted 1-methoxynaphthalene derivatives were prepared with a variety of aryl bromides as counter partners to **1**, and these results are summarized in Table 2. The coupling reaction of 2-bromotoluene (**5a**) with **1** gave the product **6a** in 83% yield (entry 1) and a satisfactory result (67%) was also obtained with biphenyl bromide **5b** as a coupling partner to **1** (entry 2). The aryl bromides **5c**-**f**, which contain heteroatom-functionalized groups at R^1, were also examined to provide the corresponding coupling products in

rather high yields. The cross-coupling of 2-bromoanisole (**5c**) with **1** afforded **6c** in 98% yield (entry 3) and a compound with a MOM protective group, **6d**, was obtained from **5d**[12] in 97% yield (entry 4). From the MOM-protected 2-bromobenzyl alcohol, **5e**,[13] the product **6e** was formed in the presence of Na_2CO_3 in a solvent system of toluene/EtOH/H_2O (3:3:2) in 63% yield (entry 5). The product **6f** was obtained from 2-bromonitrobenzene (**5f**) by use of K_3PO_4 as a base in quantitative yield, whereas the same reaction in the presence of Cs_2CO_3 gave only trace amounts of **6f**. A pyridyl aromatic ring (Y=N in Fig. 1) was also successfully introduced into the biaryl framework in almost quantitative yield (entry 7). In this case, the same solvent system as in entries 1–4 was effective when Cs_2CO_3 was used as a base. Incorporation of an ester functionality into the 1-substituted phenyl ring was achieved by using methyl 2-bromobenzoate (**5h**) as a coupling partner to give **6h** in moderate yield (entry 8). The reaction conditions of CsF as a base and single solvent system of DME were employed to avoid the hydrolysis of ester group in this case. Despite the significant steric hindrance of 1,2-dibromobenzene (**5i**), the coupling reaction gave **6i** as a sole isolable product in high yield without any side-products derived from multiple-coupling reactions (entry 9). The novel 2,8′-dimethoxy-1,1′-binaphthalene (**6j**) was prepared from **5j**[14] in this way (entry 10).

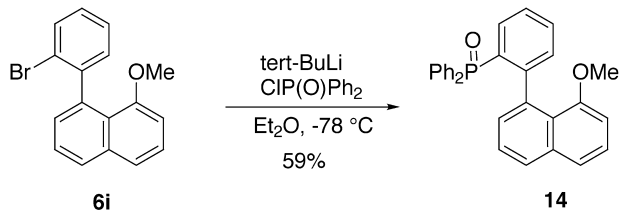
2.3. Further chemical transformations of 1-aryl-substituted 8-methoxynaphthalene derivatives

With the desired Pd-mediated Suzuki–Miyaura coupling products of 1,8-disubstituted naphthalene derivatives in hand, the transformation of the original functional groups in the products was examined, and these transformations are shown in Scheme 1.

Compound **6c** bearing two methoxy groups at both the *ortho*-position of the 1-aryl ring and the *peri*-position on the naphthalene ring system (C1 position) was treated with BBr_3 in CH_2Cl_2 to give dihydroxy biaryl compound **7** in 90% yield. Preliminary experiments using this compound as a ligand showed that diol **7** can act as an effective catalyst system with an aluminum compound for catalytic Meerwein–Ponndorf–Verley reduction,[4c,15] and these results will be described elsewhere. On the other hand, the compound **6d** was converted to **8**, which will be considered



Scheme 1. Transformations of 1-aryl substituted 8-methoxynaphthalenes. *Reagents and conditions*: (a) BBr_3, CH_2Cl_2, −15 °C to rt, 24 h, 90%; (b) conc. HCl, MeOH, rt, 92%; (c) 6 N HCl, MeOH, reflux, 73%; (d) In, conc. HCl, THF, H_2O, rt, 41 h, 93%; (e) HCHO (1.0 equiv.), $NaBH_3CN$ (1.0 equiv.), AcOH, CH_3CN, rt, 2 h, 22%; (f) HCHO (3.0 equiv.), $NaBH_3CN$ (3.0 equiv.), AcOH, CH_3CN, rt, 2 h, 53%; (g) LiOH, MeOH, H_2O, 80 °C, 30 h, 82%.



Scheme 2. Chemical transformation to the phosphine oxide **14**.

as a monodentate ligand in a future study. The treatment of **6e** with the same protective group under similar conditions gave benzyl alcohol **9** in 73% yield. Reduction of the nitrogen functionality in the biaryl **6f** with In[16] in aqueous HCl yielded the amine **10**, which was further transformed into the monomethylamino and dimethylamino derivatives, **11** and **12**, through reductive amination in respective yields of 22 and 53%. A biaryl compound with a carboxyl group **13** was obtained by alkaline hydrolysis of **6h**. The bromo-substituted biaryl **6i**, which is expected to be a useful intermediate for a variety of compounds by appropriate further chemical transformations, was converted to the phosphine oxide **14** in 59% yield via the halogen–metal exchange reaction with *tert*-BuLi and subsequent treatment with diphenylphosphinic chloride. Preliminary investigations showed that the reduction of phosphine oxide **14** successfully proceeded to give phosphine, which acts as an effective monodentate phosphine ligand for the Pd-mediated intramolecular amidation reactions[17] of aryl halides (Scheme 2).

2.4. Optical behavior of synthesized biaryls

To evaluate their potencies as effective chiral inducers, a preliminary examination of the optical behavior of several newly synthesized 1,8-disubstituted naphthalene derivatives was carried out. Thus, HPLC analysis on a chiral stationary phase was performed to check whether or not these newly synthesized biaryl compounds exist as a stable axially chiral atropisomer at ambient temperature. First, the satisfactory analytical conditions for complete separation of two enantiomeric peaks corresponding to each atropisomer in HPLC were established, and then fractions of each peak were collected to give two kinds of fractions that contained each enantiomer as a major component. The separation conditions in HPLC analyses are shown in the Section 4 (Table 4). Immediately after these fractions were collected, their optical purity was measured and then they were allowed to stand for various length of time at ambient temperature in a solution of the eluent solvent system (hexane/2-propanol). These fractions were re-injected under the same HPLC conditions after an appropriate time to examine the degree of racemization, and the results are shown in Table 3. Among the biaryl compounds synthesized, compound **6i** retained most of its original peak even after standing for a long time, suggesting that the energy barrier for rotation around the biaryl axis is relatively high. Clean atropisomerization may be deduced from the expected large steric repulsion between the *ortho*-substituent (Br) on the phenyl ring and the *peri*-position of the naphthyl moiety (methoxy group at C1). However, re-injection of the collected fractions of other compounds that had been allowed to stand for 0.5 to 71 h exhibited significant racemization even at room temperature. Preliminary experimental results indicated that the phosphine oxide **14** also partially racemized after standing 7 h at room temperature. On the other hand, the separated each enantiomer of newly prepared binaphthyl **6j** was optically stable after standing at ambient temperature for 71 h. The CD spectra of each enantiomer of **6j** were shown in Figure 2. The typical positive and negative Cotton effects of isomers indicated *aR* and *aS* configuration, respectively.[18]

Consequently, the results of these preliminary investigations suggest that an additional sp^3-hybridized anchoring group or bulky group at the 2- and/or 2′-position may be needed to slow atropisomerization in these systems. Detailed studies of the optical behavior of the newly synthesized compounds including kinetic experiments on racemization will be reported elsewhere in the near future.

Table 3. The optical behavior of the synthesized biaryls[a]

Biaryls	Atropisomer A[b] or B[c]	Optical purity (%ee) after (h)										
		0.25	0.5	2.0	5.0	7.0	22	24	25	41	60	71
6a[d]	A	89					54			39	28	
	B	94					57			41	31	
6b	A	86							26			
	B	62							17			
6c	A		18	8	2							
	B		62	26	11							
6h	A	82						17				4
	B	94						27				12
6i	A	99						99				89
	B	~100						97				93
6j[c]	A (*S*)	~100	~100	~100					~100			~100
	B (*R*)	~100	~100	~100					~100			~100
14[f]	A	~100				84						
	B	~100				78						

[a] The samples were kept in 1% of 2-propanol in hexane at room temperature. See Section 4.
[b] The atropisomer of the shorter retention time.
[c] The atropisomer of the longer retention time.
[d] The samples were kept in toluene at room temperature.
[e] The samples were kept in 0.5% of 2-propanol in hexane at room temperature.
[f] The samples were kept in 8% of 2-propanol in hexane at room temperature.

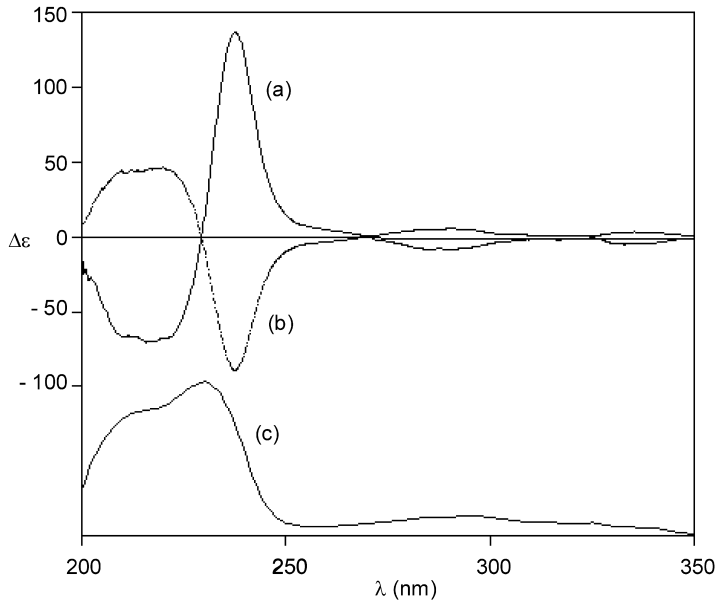


Figure 2. CD and UV spectra of (*S*)- and (*R*)-**6j** in MeOH (a) (*R*)-**6j** (95% ee); (b) (*S*)-**6j** (58% ee); (c) UV spectrum of (*R*)-**6j**.

3. Conclusion

In summary, several biaryl derivatives consisting of 8-methoxynaphthalene substituted by a monocyclic aryl ring at C1 were prepared based on the Pd-mediated Suzuki–Miyaura coupling. Since the key structural unit of the synthesized compounds is a *peri*-substituted naphthalene ring, atropisomerization may be expected, and this possibility was supported by preliminary experiments. Since some of these compounds are expected to act as monodentate or bidentate ligands for catalysts in specific reactions, easy access to these compounds may lead to the development of efficient chiral or non-chiral ligands by additional fine-tuning of the molecular structure. The application of these compounds in reactions as effective monodentate or bidentate ligands, including asymmetric transformation, is under investigation.

4. Experimental

4.1. General

Unless otherwise specified, all ^{1}H NMR spectra were taken at 270 MHz in $CDCl_3$ with chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard, and couplings are expressed in hertz. ^{13}C NMR spectra were measured at 68 MHz in the same solvent. THF and ether were distilled from sodium benzophenone ketyl, CH_2Cl_2 and MeOH were from calcium hydride and magnesium, respectively. Unless otherwise noted, all reactions were run under an argon atmosphere. All extractive organic solutions were dried over anhydrous $MgSO_4$, filtered and then concentrated under reduced pressure. Column chromatography was carried out with silica gel 60 spherical (150–325 mesh), and silica gel 60 F_{254} plates (Merck) were used for preparative TLC (pTLC). HPLC analyses were performed on the two types of analytical columns (0.46×25 cm in size) with chiral stationary phase under the conditions indicated in Table 4.

4.2. General procedure for the Suzuki–Miyaura coupling reaction with 8-methoxy-1-naphthylboronic acid (1)

To a mixture of 8-methoxy-1-naphthylboronic acid (**1**)[9j] (1.1 equiv.), aryl halide (1.0 equiv.) and base (1.4, 1.5 or 3.0 equiv.) in DME/H_2O (6:1) or toluene/EtOH/H_2O (3:3:2) or DME was added $Pd(PPh_3)_4$ (3–10 mol%). The resulting mixture was heated for 3.5 h at 100 °C with stirring except for the preparation of **6d**,**h** and **j**. The mixture was cooled to room temperature and diluted with EtOAc (10 mL), then added by H_2O (10 mL). The organic layers were separated and aqueous phase was extracted three times with EtOAc (20 mL). The combined organic layers were dried, concentrated, and subjected to column chromatography on silica gel with appropriate solvent system indicated below.

4.2.1. 8-Methoxy-1,1′-binaphthalene (4). According to the general procedure, the coupling reaction of 1-bromonaphthalene (**2**, 50 mg, 0.24 mmol) with **1** (54 mg, 0.27 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography (EtOAc/hexane, 1:30), the titled compound **4** (68 mg, 99%) was

Table 4. The HPLC conditions for separation of each atropisomer[a]

Biaryls	Column[b]	Retention time (min)		Flow rate (mL/min)
		t_1	t_2	
6a	Chiralcel OD-H	6.5	7.3	0.5
6b	Chiralcel OD-H	16.5	19.5	0.5
6c	Chiralcel OD-H	6.9	10.2	1.0
6h	Chiralcel OD-H	14.9	17.0	0.5
		7.8	9.2	1.0
6i	Chiralcel OD-H	12.4	15.0	0.5
6j[c]	Chiralcel OD-H	10.9 (*S*)	12.9 (*R*)	1.0
14[d]	Chiralpak AD	29.7	38.4	1.0

[a] A solvent system of 1% of 2-propanol in hexane was used as eluent.
[b] Daicel Chemical. Co. LTD.
[c] A solvent system of 0.5% of 2-propanol in hexane was used as eluent.
[d] A solvent system of 8.0% of 2-propanol in hexane was used as eluent.

obtained as colorless solids, whose spectroscopic data were identical with those of the authentic sample.[9c]

4.2.2. 8-Methoxy-1-(*o*-tolyl)naphthalene (6a). Following the general procedure described above, the coupling reaction of 2-bromotoluene (**5a**, 77 mg, 0.45 mmol) with **1** (100 mg, 0.50 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography on silica gel (EtOAc/hexane, 5:95), the titled compound **6a** (93 mg, 83%) was obtained as a colorless oil: R_f=0.60 (EtOAc/hexane, 5:95); ^{1}H NMR δ 7.79 (d, J=8.4 Hz, 1H), 7.50–7.38 (m, 2H), 7.36–7.24 (m, 1H), 7.19–7.15 (m, 5H), 6.72 (d, J=7.6 Hz, 1H), 3.41 (s, 3H), 1.95 (s, 3H); ^{13}C NMR δ156.8, 145.3, 138.2, 135.8, 135.5, 128.21, 128.16, 128.09, 127.4, 126.0, 125.8, 125.6, 124.4, 124.0, 121.2, 105.7, 55.4, 20.1; MS (FAB) m/z 249 $(M+H)^+$; HRMS calcd for $C_{18}H_{16}O$ (M^+) 248.1201, found 248.1196. Anal. calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.75; H, 6.22.

4.2.3. 8-Methoxy-1-(biphenyl-2′-yl)naphthalene (6b). According to the general procedure, the coupling reaction of 2-bromobiphenyl (**5b**, 52 mg, 0.23 mmol) with **1** (50 mg, 0.25 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography (EtOAc/hexane, 5:95), the titled compound **6b** (47 mg, 67%) was obtained as a colorless oil: R_f=0.70 (EtOAc/hexane, 1:9); ^{1}H NMR δ 7.59 (d, J=7.9 Hz, 1H), 7.34–7.15 (m, 7H), 7.04–6.90 (m, 6H), 6.55 (d, J=7.3 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR δ 156.3, 143.9, 142.0, 140.0, 138.0, 135.3, 129.7, 129.34, 129.27, 128.8, 127.3, 127.1, 126.3, 125.8, 125.71, 125.66, 125.2, 124.3, 120.8, 105.1, 55.0; MS (FAB) m/z 311 $(M+H)^+$; HRMS calcd for $C_{23}H_{18}O$ (M^+) 310.1358, found 310.1350. Anal. calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.56; H, 5.46.

4.2.4. 8-Methoxy-1-(2′-methoxyphenyl)naphthalene (6c). Following the general procedure described above, the coupling reaction of 2-bromoanisole (**5c**, 841 mg, 4.50 mmol) with **1** (1.0 g, 4.95 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography (toluene/hexane, 1:3), the titled compound **6c** (1.17 g, 98%) was obtained as a colorless oil; R_f=0.55 (EtOAc/hexane, 1:7); ^{1}H NMR δ 7.79 (dd, J=1.3, 6.9 Hz, 1H), 7.50–7.44 (m, 2H), 7.39–7.18 (m, 4H), 7.01–6.95 (m, 1H), 6.88 (d, J=8.3 Hz, 1H), 6.76–6.72 (m, 1H), 3.63 (s, 3H), 3.46 (s, 3H); ^{13}C NMR δ 157.12, 157.07, 135.4, 135.3, 135.0, 129.5, 128.6, 127.7, 127.5, 125.7, 125.6, 124.6, 121.2, 119.6, 109.4, 106.0, 55.5; MS (FAB) m/z 265 $(M+H)^+$; HRMS calcd for $C_{18}H_{16}O_2$ (M^+) 264.1150, found 264.1163. Anal. calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.48; H, 6.06.

4.2.5. 1-(2-Methoxymethoxyphenyl)-8-methoxynaphthalene (6d). According to the general procedure, the coupling reaction of methoxymethyl 2-bromophenyl ether (**5d**,[12] 99 mg, 0.46 mmol) with **1** (111 mg, 0.55 mmol) was carried out at 100 °C for 24 h in DME/H_2O (6:1). After purification by pTLC with the developing solvent (EtOAc/hexane, 1:5), the titled compound **6d** (130 mg, 97%) was obtained as white brown solids: R_f=0.36 (EtOAc/hexane, 1:5); mp 71–73 °C; ^{1}H NMR δ 7.79 (d, J=8.2 Hz, 1H), 7.49–7.43 (m, 2H), 7.39–7.30 (m, 1H), 7.28–7.18 (m, 3H), 7.12 (d, J=7.9 Hz, 1H), 7.06–7.00 (m, 1H), 6.73 (d, J=7.6 Hz, 1H), 4.95–4.88 (m, 2H), 3.45 (s, 3H), 3.14 (s, 3H); ^{13}C NMR δ 156.9, 154.7, 136.1, 135.4, 135.2, 129.6, 128.5, 127.6, 127.4, 125.7, 125.5, 124.5, 121.1, 120.9, 113.9, 105.7, 94.7, 55.6, 55.4; MS (FAB) m/z 295 $(M+H)^+$. Anal. calcd for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.11; H, 6.11.

4.2.6. 8-Methoxy-1-(2′-methoxymethoxymethylphenyl)-naphthalene (6e). Following the general procedure described above, the coupling reaction of 1-bromo-2-methoxymethoxymethylbenzene (**5e**,[13] 91 mg, 0.39 mmol) with **1** (88 mg, 0.43 mmol) was carried out in toluene/EtOH/H_2O (3:3:2). After purification by flash column chromatography (EtOAc/hexane, 1:9), the titled compound **6e** (77 mg, 63%) was obtained as a colorless oil: R_f=0.60 (EtOAc/hexane, 1:9). ^{1}H NMR δ 7.81 (d, J=7.3 Hz, 1H), 7.51–7.16 (m, 8H), 6.73 (d, J=7.3 Hz, 1H), 4.47–4.41 (m, 2H), 4.26 (s, 2H), 3.31 (s, 3H), 3.13 (s, 3H); ^{13}C NMR δ 154.4, 142.2, 134.4, 133.3, 133.2, 126.5, 126.2, 125.5, 124.2, 124.0, 123.9, 123.7, 123.2, 121.7, 118.9, 103.6, 93.6, 65.3, 53.1, 52.7; MS (FAB) m/z 309 $(M+H)^+$; HRMS calcd for $C_{20}H_{20}O_3$ $(M+H)^+$ 309.1491, found 309.1459.

4.2.7. 8-Methoxy-1-(2′-nitrophenyl)naphthalene (6f). Following the general procedure described above, the coupling reaction of 1-bromo-2-nitrobenzene (**5f**, 44 mg, 0.22 mmol) with **1** (48 mg, 0.24 mmol) was pe$R_f$ormed in toluene/EtOH/H_2O (3:3:2). After purification by flash column chromatography (EtOAc/hexane, 1:9), the titled compound **6f** (64 mg, quantitative) was obtained as yellow solids; R_f=0.70 (EtOAc/hexane, 1:9); mp 102–104 °C; ^{1}H NMR δ 8.10–8.06 (m, 1H), 7.86–7.82 (m, 1H), 7.61–7.33 (m, 6H), 7.24–7.20 (m, 1H), 6.72 (d, J=7.6 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR δ 155.8, 148.6, 140.7, 135.2, 134.5, 131.8, 131.7, 128.4, 128.2, 127.4, 127.0, 126.1, 125.5, 123.1, 121.4, 105.6, 55.2; MS (FAB) m/z 280 $(M+H)^+$. Anal. calcd for $C_{17}H_{13}NO_3$: C, 73.12; H, 4.66; N, 5.02. Found: C, 72.93; H, 4.78; N, 4.94.

4.2.8. 8′-Methoxy-1′-(3-methylpyridin-2-yl)naphthalene (6g). Following the general procedure described above, the coupling reaction of 2-bromo-3-methylpyridine (**5g**, 39 mg, 0.23 mmol) with **1** (50 mg, 0.25 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography (EtOAc/hexane, 1:5), the titled compound **6g** (67 mg, quantitative) was obtained as a colorless oil; R_f=0.45 (EtOAc/hexane, 1:5); ^{1}H NMR δ 7.77 (dd, J=1.0, 7.2 Hz, 1H), 7.46–7.40 (m, 3H), 7.32–7.27 (m, 1H), 7.20–7.17 (m, 1H), 7.08 (dd, J=2.6, 4.9 Hz, 1H), 6.66 (d, J=7.6 Hz, 1H), 3.36 (s, 3H), 1.90 (s, 3H); ^{13}C NMR δ 162.4, 155.8, 144.8, 136.6, 135.5, 135.1, 131.1, 127.7, 126.8, 125.6, 125.4, 123.0, 121.0, 120.4, 105.3, 55.1, 18.9; MS (FAB) m/z 251 $(M+H)^+$; HRMS calcd for $C_{17}H_{15}NO$ (M^+) 250.1239, found 250.1232.

4.2.9. 8-Methoxy-1-(2′-methoxycarbonylphenyl)-naphthalene (6h). To a mixture of methyl 2-bromobenzoate (**5h**, 100 mg, 0.47 mmol), **1** (113 mg, 0.56 mmol) and CsF (99 mg, 0.65 mmol) in DME (4.0 mL) was added $Pd(PPh_3)_4$ (54 mg, 0.047 mmol) and the mixture was stirred for 36 h at 85 °C. The mixture was added by H_2O and EtOAc, and then filtered through Celite pad. The filtrate was extracted with EtOAc and the extracts were washed, dried and concentrated to give a residue, which was subjected to

flash column chromatography on silica gel with EtOAc/hexane (1:30) to give crude product. Purification by pTLC of the crude sample with EtOAc/hexane (1:7) gave the titled compound **6h** (58 mg, 43%) as colorless solids; R_f=0.44 (EtOAc/hexane, 1:7); mp 78–80 °C; ^{1}H NMR δ 7.99–7.96 (m, 1H), 7.80 (d, J=7.6 Hz, 1H), 7.52–7.26 (m, 7H), 7.17 (dd, J=1.0, 5.9 Hz, 1H), 6.71 (d, J=7.6 Hz, 1H), 3.42 (s, 3H), 3.36 (s, 3H); ^{13}C NMR δ 167.4, 155.9, 146.1, 137.9, 134.6, 130.1, 129.8, 129.6, 128.4, 127.0, 126.8, 125.5, 125.2, 124.9, 123.3, 120.8, 105.1, 54.7, 51.0; MS (FAB) m/z 293 $(M+H)^+$; HRMS calcd for $C_{19}H_{16}O_3$ $(M+H)^+$ 293.1177, found 293.1131. Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.78; H, 5.63.

4.2.10. 8-Methoxy-1-(2′-bromophenyl)naphthalene (6i). Following the general procedure, the coupling reaction of 1,2-dibromobenzene (**5i**, 106 mg, 0.45 mmol) with **1** (100 mg, 0.50 mmol) was carried out in DME/H_2O (6:1). After purification by flash column chromatography (EtOAc/hexane, 1:98 to 2:98), the titled compound **6i** (115 mg, 82%) was obtained as a colorless oil; R_f=0.50 (EtOAc/hexane, 2:98); ^{1}H NMR δ 7.84 (d, J=8.2 Hz, 1H), 7.59 (d, J=7.6 Hz, 1H), 7.51–7.14 (m, 6H), 3.76 (d, J=7.6 Hz, 1H), 3.49 (s, 3H); ^{13}C NMR δ 156.5, 146.2, 137.5, 135.2, 131.0, 129.8, 129.6, 128.1, 127.4, 126.0, 125.4, 123.8, 123.7, 121.1, 105.9, 55.6; MS (FAB) m/z 315 $(M+H)^+$; HRMS calcd for $C_{17}H_{13}BrO$ (M^+) 314.0129, found 314.0137. Anal. calcd for $C_{17}H_{13}BrO$: C, 65.19; H, 4.18. Found: C, 65.41; H, 4.20.

4.2.11. 2,8′-Dimethoxy-1,1′-binaphthalene (6j). According to the general procedure, the coupling reaction of 1-bromo-2-methoxynaphthalene (**5j**, 107 mg, 0.45 mmol) with **1** (100 mg, 0.50 mmol) was carried out at 100 °C for 24 h in DME/H_2O (6:1). After purification by pTLC with the developing solvent of toluene and hexane (1:2), the titled compound **6j** (93 mg, 66%) was obtained as off-white solids: R_f=0.41 (EtOAc/hexane, 1:7 on NH-SiO_2 plate); mp 121–124 °C; ^{1}H NMR δ 7.90–7.81 (m, 3H), 7.58–7.53 (m, 2H), 7.40–7.34 (m, 2H), 7.30–7.25 (m, 2H), 7.21–7.12 (m, 1H), 6.68 (d, J=7.6 Hz, 1H), 3.74 (s, 3H), 3.12 (s, 3H); ^{13}C NMR δ 157.1, 153.1, 135.8, 134.0, 132.5, 129.5, 129.1, 128.6, 127.7, 127.6, 127.5, 125.8, 125.7, 125.6, 125.4, 123.0, 121.3, 114.0, 106.2, 57.0, 55.6; MS (FAB) m/z 315 $(M+H)^+$; HRMS calcd for $C_{22}H_{19}O_2$ $(M+H)^+$ 315.1385, found 315.1391.

The racemic **6j** was subjected to the preparative HPLC on chiral stationary phase (Chiralcel OD-H, solvent system: 0.5% of 2-propanol in hexane, 1 mL/min) to give the optically active enantiomers.

Compound (*S*)-**6j**. 58% ee; $[\alpha]_D^{20}$ 11.0 (c 0.35, $CHCl_3$); CD (MeOH) λ_{ext} ($\Delta\varepsilon$) 290.2 nm (5.3), 237.4 nm (−89.3).

Compound (*R*)-**6j**. 95% ee; $[\alpha]_D^{20}$ −13.3 (c 0.21, $CHCl_3$); CD (MeOH) λ_{ext} ($\Delta\varepsilon$) 290.8 nm (−8.2), 237.6 nm (136.8); UV (MeOH) λ_{max} 230.0 nm (ε 66086), 296.0 nm (ε 8555).

4.2.12. 8-Hydroxy-1-(2′-hydroxyphenyl)naphthalene (7). To a solution of **6c** (200 mg, 0.76 mmol) in CH_2Cl_2 (2.0 mL) was added 1M solution of BBr_3 in CH_2Cl_2 (2.27 mL, 2.27 mmol) at −70 °C. The mixture was allowed to warm to room temperature for 21 h, and then added with MeOH at 0 °C. After being stirred for 10 min at the same temperature, 1 N HCl (3.0 mL) and conc.NH_4OH were successively added to the mixture, and the mixture was extracted with $CHCl_3$. The combined organic extracts were dried and concentrated to give the residue, from which the titled compound **7** (160 mg, 90%) was obtained as white brown solids; R_f=0.83 (EtOAc/hexane, 1:9); mp 65–69 °C; ^{1}H NMR δ 7.93 (d, J=8.3 Hz, 1H), 7.54–7.30 (m, 6H), 7.10 (d, J=8.1 Hz, 2H), 6.93 (d, J=7.6 Hz, 1H), 5.74 (s, 1H), 5.02 (s, 1H); ^{13}C NMR δ 153.4, 153.1, 136.0, 131.0, 130.3, 129.9, 129.8, 129.5, 129.3, 129.1, 127.2, 126.6, 125.3, 121.1, 116.3, 112.1; MS (FAB) m/z 237 $(M+H)^+$; HRMS calcd for $C_{16}H_{12}O_2$ (M^+) 236.0837, found 236.0832. Anal. calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C; 80.92; H, 5.50.

4.2.13. 8-Methoxy-1-(2′-hydroxyphenyl)naphthalene (8). To a stirred solution of **6d** (130 mg, 0.44 mmol) in MeOH (5.2 mL) was added conc.HCl (0.26 mL), and the mixture was stirred for 5.7 h at room temperature. Concentration of the mixture followed by purification by flash column chromatography on silica gel with EtOAc and hexane (1:15 to 1:7) furnished the titled compound **8** (102 mg, 92%) as white brown solids; R_f=0.22 (EtOAc/hexane, 1:7); mp 115–117 °C; ^{1}H NMR δ 7.88 (d, J=8.6 Hz, 1H), 7.56–7.50 (m, 2H), 7.46–7.40, (m, 1H), 7.34 (d, J=6.9 Hz, 1H), 7.29–7.22 (m, 1H), 7.15 (d, J=7.8 Hz, 1H), 6.98–6.93 (m, 2H), 6.82 (d, J=7.6 Hz, 1H), 3.53 (s, 3H); ^{13}C NMR δ 156.5, 152.7, 135.8, 132.1, 132.0, 130.1, 129.4, 129.0, 128.8, 128.0, 126.4, 126.1, 124.0, 119.5, 114.0, 106.5, 55.7; MS (FAB) m/z 251 $(M+H)^+$. Anal. calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C; 81.07; H, 5.46.

4.2.14. 8-Methoxy-1-(2′-hydroxymethylphenyl)naphthalene (9). To a stirred solution of **6e** (77 mg, 0.25 mmol) in MeOH (5.0 mL) was added 6 N HCl (3.0 mL) and the mixture was refluxed overnight. The reaction mixture was then cooled to room temperature and diluted with H_2O. The mixture was extracted with EtOAc and the organic layer was dried and evaporated. The residue was purified by flash column chromatography with EtOAc and hexane (1:9) to give the titled compound **9** (48 mg, 73%) as colorless solids; R_f=0.50 (EtOAc/hexane, 1:9); mp 77–80 °C; ^{1}H NMR δ 7.85–7.82 (m, 1H), 7.55–7.13 (m, 8H), 6.79 (d, J=7.6 Hz, 1H), 4.41 (d, J=12.2 Hz, 1H), 4.32 (d, J=12.6 Hz, 1H), 3.41 (s, 3H); ^{13}C NMR δ 156.2, 144.2, 138.0, 136.4, 135.5, 132.6, 128.9, 128.8, 128.5, 127.6, 127.0, 126.6, 126.4, 126.0, 125.5, 121.8, 107.0, 65.0; MS (FAB) m/z 265 $(M+H)^+$; HRMS calcd for $C_{18}H_{16}O_2$ (M^+) 264.1150, found 264.1142.

4.2.15. 8-Methoxy-1-(2′-aminophenyl)naphthalene (10). To a stirred mixture of **6f** (470 mg, 1.68 mmol), conc.HCl (1.2 mL), THF (3.0 mL) and H_2O (9.0 mL) was added indium (773 mg, 6.73 mmol) at room temperature, and the resulting mixture was further stirred for 17 h at room temperature. Additional indium (386 mg, 3.37 mmol) and conc.HCl (0.6 mL) were added to the mixture and then stirring was continued for additional 24 h at room temperature. The mixture was diluted with EtOAc and water, and then neutralized by addition of saturated aqueous solution of $NaHCO_3$. The mixture was filtered through a thin pad of Celite and the filtrate was extracted with EtOAc

three times and the combined organic extracts were washed, dried and evaporated. The residue was purified by flash column chromatography (EtOAc/hexane, 1:15) to give the titled compound **10** (390 mg, 93%) as white brown solids; R_f=0.55 (Et_3N/EtOAc/hexane, 1:10:90); mp 107–109 °C; ^{1}H NMR δ 7.83 (dd, J=1.3, 6.9 Hz, 1H), 7.53–7.48 (m, 2H), 7.43–7.37 (m, 1H), 7.31–7.28 (m, 1H), 7.18–7.12 (m, 1H), 7.08–7.04 (m, 1H), 6.82–6.72 (m, 3H), 3.52 (s, 3H); ^{13}C NMR δ 143.8, 135.8, 135.3, 135.2, 133.4, 129.2, 129.0, 128.0, 127.4, 127.2, 126.1, 121.3, 117.6, 114.1, 106.6, 56.0; MS (FAB) m/z 250 $(M+H)^+$; HRMS calcd for $C_{17}H_{15}NO$ (M^+) 249.1153, found 249.1141.

4.2.16. 8-Methoxy-1-(2′-*N*-methylaminophenyl)naphthalene (11). To a solution of **10** (60 mg, 0.24 mmol) in CH_3CN (10 mL) was added 37% aqueous solution of formaldehyde (17 μL, 0.24 mmol) and AcOH (0.5 mL). The mixture was stirred for 30 min at 0 °C, then additional $NaBH_3CN$ (15 mg, 0.24 mmol) and AcOH (0.5 mL) were added, and the mixture was stirred for 30 min at room temperature. The mixture was evaporated in vacuo to afford the residue, which was partitioned between EtOAc and 1 N NaOH, and the organic phase was separated, and the extraction was completed with additional portion of EtOAc. The combined extracts were dried and evaporated to give the residue, which was purified by pTLC (Et_3N/EtOAc/hexane, 1:10:90). The titled compound **11** (14 mg, 22%) was afforded as a brown oil; R_f=0.50 (Et_3N/EtOAc/hexane, 1:10:90); ^{1}H NMR δ 7.84–7.81 (m, 1H), 7.48–7.43 (m, 2H), 7.39 (t, J=8.2 Hz, 1H), 7.30–7.20 (m, 2H), 7.02 (dd, J=1.6, 5.7 Hz, 1H), 6.80–6.73 (m, 2H), 6.66 (d, J=8.1 Hz, 1H), 3.49 (s, 3H), 2.72 (s, 3H); ^{13}C NMR δ 156.9, 146.9, 135.9, 135.1, 131.8, 129.5, 128.0, 127.4, 126.2, 126.0, 121.3, 115.9, 108.6, 106.5, 55.8, 31.0; MS (FAB) m/z 264 $(M+H)^+$; HRMS calcd for $C_{18}H_{17}NO$ (M^+) 263.1311, found 263.1320. Anal. calcd for $C_{18}H_{17}NO$: C, 81.10; H, 6.51; N, 5.32. Found; C, 80.76; H, 6.51; N, 5.05.

4.2.17. 8-Methoxy-1-(2′-*N*,*N*-dimethylaminophenyl)naphthalene (12). Following the procedure for the preparation of **11**, to a mixture of **10** (37 mg, 0.15 mmol), CH_3CN (0.5 mL) and 37% aqueous formaldehyde solution (32 μL, 0.45 mmol) was successively added $NaBH_3CN$ (28 mg, 0.45 mmol) and AcOH (1.0 mL) at 0 °C. After the mixture was stirred for 1 h at 0 °C, additional AcOH (1.0 mL) was added to the mixture, which was stirred for 18 h at room temperature and worked up in a similar way to that described above to give the residue, from which the titled compound **12** (22 mg, 53%) was obtained as a brown oil after purification by pTLC (Et_3N/EtOAc/hexane, 1:10:90); R_f=0.60 (Et_3N/EtOAc/hexane, 1:10:90); ^{1}H NMR δ 7.76 (d, J=8.1 Hz, 1H), 7.48–7.44 (m, 2H), 7.39–7.22 (m, 3H), 7.10–6.92 (m, 3H), 6.73 (d, J=7.6 Hz, 1H), 3.47 (s, 3H), 2.42 (s, 6H); ^{13}C NMR δ 156.9, 151.0, 138.7, 138.0, 135.8, 130.6, 128.8, 127.0, 126.8, 125.7, 125.6, 124.0, 121.0, 120.3, 116.9, 105.3, 45.7, 43.3; MS (FAB) m/z 278 $(M+H)^+$; HRMS calcd for $C_{19}H_{20}NO$ $(M+H)^+$ 278.1545, found 278.1540.

4.2.18. 8-Methoxy-1-(2′-carboxyphenyl)naphthalene (13). To a stirred mixture of **6h** (40 mg, 0.14 mmol), MeOH (4.0 mL) and water (1.0 mL) was added $LiOH\cdot H_2O$ (9.0 mg, 0.21 mmol) at room temperature and the reaction mixture was heated at 80 °C with stirring for 21 h. Stirring was further continued for 9 h after addition of additional amount of $LiOH\cdot H_2O$ (9.0 mg, 0.21 mmol) at the same temperature. After cooling, the mixture was poured into 2 N HCl and extracted with EtOAc and chloroform. The organic phases were washed, dried and concentrated to give the residue, which was purified by pTLC with a developing solvent system of EtOAc, hexane and AcOH (30:60:0.9) to give the titled compound **13** (31 mg, 82%) as colorless solids; mp 181–185 °C; ^{1}H NMR δ 8.03–7.99 (m, 1H), 7.80 (d, J=7.8 Hz, 1H), 7.53–7.23 (m, 6H), 7.16 (d, J=6.8 Hz, 1H), 6.70 (d, J=6.8 Hz, 1H), 3.40 (s, 3H); ^{13}C NMR δ 171.7, 156.2, 147.0, 137.9, 135.1, 131.1, 130.5, 129.4, 128.9, 127.5, 127.3, 126.0, 125.6, 125.3, 123.7, 121.2, 105.6, 55.1; MS (FAB) m/z 279 $(M+H)^+$; HRMS calcd for $C_{18}H_{14}O_3$ (M^+) 278.0943, found 278.0929. Anal. calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.59; H, 5.42.

4.2.19. 8-Methoxy-1-(2′-diphenylphosphinoylphenyl)naphthalene (14). To a solution of **6i** (153 mg, 0.49 mmol) in dry Et_2O (10 mL) at −78 °C was added dropwise *tert*-BuLi (0.33 mL, 0.54 mmol), and the mixture was stirred for 1 h at the same temperature, and then a solution of $Ph_2P(O)Cl$ (101 mg, 0.59 mmol) in dry Et_2O (10 mL) was added. The mixture was allowed to warm to room temperature overnight, and then partitioned between EtOAc and 1 N NaOH. The each phase was separated, and the extraction was completed with additional portion of EtOAc. The combined organic extracts were dried and evaporated. The residue was purified by flash column chromatography (EtOAc/hexane, 1:9 to 1:0) to give the titled compound **14** (125 mg, 59%) as colorless solids; R_f=0.10 (EtOAc); mp 132–135 °C; ^{1}H NMR δ 7.81–7.72 (m, 1H), 7.54–7.32 (m, 7H), 7.25–6.96 (m, 11H), 6.47 (m, 1H), 3.41 (s, 3H); MS (FAB) m/z 435 $(M+H)^+$; HRMS calcd for $C_{29}H_{24}OP$ $(M+H)^+$; 435.1643, found 435.1630.

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