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Regioselective Arylation Reactions of Biphenyl-2-ols, Naphthols, and Benzylic Compounds with Aryl Halides under Palladium Catalysis

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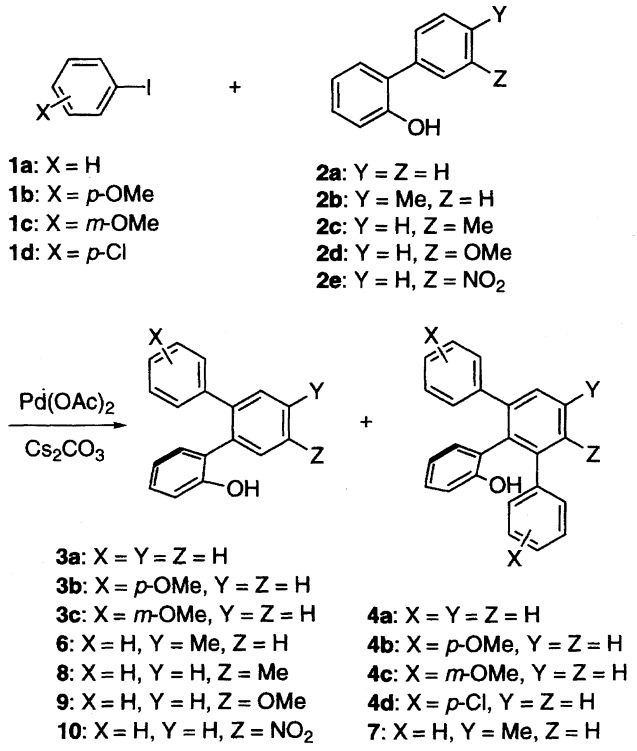
Biphenyl-2-ols undergo regioselective mono- and diarylation upon a treatment with aryl iodides in the presence of a palladium catalyst in DMF using Cs_2CO_3 as a base to produce 1,1′:2′,1″-terphenyl-2-ol and 2′,6′-diphenylbiphenyl-2-ol and their derivatives. The reaction of 1-naphthol selectively occurs at its 8-position to give 8-aryl-1-naphthols. In the reaction of 2-naphthol with aryl bromides, diarylated compounds, 1-(2-arylphenyl)-2-naphthols, are formed as the single major products. Under similar conditions, benzyl ketones, phenylacetonitrile, and methyl phenylacetate are arylated at their benzylic position.

Biaryl structures can be found in a wide range of important compounds, including natural products, polymers, liquid crystals, and ligands for homogeneous transition-metal catalysts.[1] One of the most common and useful methods for preparing biaryls is a palladium-catalyzed substitution reaction of aryl halides with organometallic species containing aryl moieties, such as aryl magnesium, zinc, boron, and stannane compounds (Kharasch, Negishi, Suzuki, and Stille reactions, respectively).[2] It has been recently shown that the direct arylation of certain aromatic substrates, such as acenaphthylene and azulene,[3a,3c] and a number of five-membered heteroaromatic substrates, including indoles,[4a] furans,[3b,4b] thiophenes,[4b,5,6] and azoles,[4c,5] i.e. imidazole, oxazole, and thiazole derivatives, with aryl halides can proceed under palladium catalysis without stoichiometric metalation of the aromatic compounds, while such coupling reactions via the cleavage of sp^2 C–H bonds have until recently been limited to only intramolecular cases.[2,3a] Meanwhile, during the context of our study of palladium-catalyzed reactions using phenolic substrates,[7] we observed that the intermolecular arylation of 2-hydroxybenzaldehydes with aryl iodides smoothly proceeded by using a catalyst system of $PdCl_2$/LiCl in the presence of sodium carbonate as a base to give 2-aroylphenols, which appears to involve activation of the aldehyde sp^2 C–H bond.[7a] The phenolic function seems to act as a good anchor for this reaction, which may suggest that other phenolic substrates are also capable of undergoing arylation. Indeed, mono- and diarylation reactions of biphenyl-2-ols and naphthols were found to regioselectively take place at the spatially neighboring positions of the phenolic function, forming one or two aryl–aryl linkages.[8] We report herein details of the unique arylation reactions with respect to the scope and limitation. Furthermore, the results for the arylation of benzyl ketones, phenylacetonitrile, and methyl phenylacetate, which occurs at their benzylic position under similar conditions, are also described.

Results and Discussion

Arylation of Biphenyl-2-ols. When iodobenzene (**1a**) (1.2 mmol) was treated with biphenyl-2-ols (**2a**) (1 mmol) in the presence of $PdCl_2$ (0.05 mmol), Cs_2CO_3 (1.2 mmol), and molecular sieves 4A (MS4A, 200 mg) in DMF at 80 °C for 44 h, a monophenylated compound, 1,1′:2′,1″-terphenyl-2-ol (**3a**), was selectively produced in a yield of 59% along with a small amount of 2′,6′-diphenylbiphenyl-2-ol (**4a**) (3%) (Scheme 1 and Entry 1 in Table 1). An increase in the reaction temperature to 100 °C enhanced both the reaction rate and the yield of **3a** to 66%, while a further elevation to 120 °C somewhat reduced the product yield (Entries 2 and 3). The use of $Pd(OAc)_2$ in place of $PdCl_2$ gave a better result, the yield of **3a** being 76% at 22 h (Entry 4). Other alkaline carbonate bases, K_2CO_3 and Na_2CO_3, were much less effective than Cs_2CO_3 (Entries 6 and 7). An increase in the amount of **1a** as well as the base to 4 mmol was found to bring about a selective formation of the diarylated compound **4a** in 62% yield along with **3a** (25%) (Entry 8). For this diarylation $PdCl_2$ was found to be preferable, rather than $Pd(OAc)_2$ (Entry 9). The reaction with K_2CO_3 gave **3a** as the major product, even using excess amounts of **1a** and the base (Entry 10). Bromobenzene (**5a**) in place of **1a** could react with **2a** in the presence of $PdCl_2$ and PPh_3, while it was less effective (Entry 11). Note that without using MS4A, a somewhat longer reaction time was required to complete the reaction under the monophenylation conditions, and the effect of its addition was negligible in the diphenylation for 44 h.

Table 2 summarizes the results for the reaction of aryl iodides **1b—d** with **2a** and of **1a** with 3′- or 4′-substituted biphenyl-2-ols **2b—e**. In the reactions of **1b—d** with **2a** and of **1a** with **2b**, the corresponding mono- and diarylated



Scheme 1.

Table 1. Phenylation of Biphenyl-2-ol (**2a**) with Iodobenzene (**1a**)[a]

Entry	Pd-cat.	Base	Temp °C	Time h	Yield/%[b] 3a	4a
1	$PdCl_2$	Cs_2CO_3	80	44	59	3
2	$PdCl_2$	Cs_2CO_3	100	22	66	6
3	$PdCl_2$	Cs_2CO_3	120	5	58	3
4	$Pd(OAc)_2$	Cs_2CO_3	100	22	76(64)	8
5[c]	$Pd(OAc)_2$	Cs_2CO_3	100	22	63	2
6	$Pd(OAc)_2$	Na_2CO_3	100	72	13	tr.
7	$Pd(OAc)_2$	K_2CO_3	100	22	25	1
8[d]	$PdCl_2$	Cs_2CO_3	100	44	25	62(56)
9[d]	$Pd(OAc)_2$	Cs_2CO_3	100	44	44	43
10[d]	$PdCl_2$	K_2CO_3	100	44	51	6
11[d,e]	$PdCl_2$	Cs_2CO_3	100	44	38	47

a) Reaction conditions: **1a** (1.2 mmol), **2a** (1 mmol), Pd-cat. (0.05 mmol), base (1.2 mmol), MS4A (200 mg), in DMF (5 cm^3) under N_2. b) GLC yield based on amount of **2a** used. Value in parentheses indicates isolated yield. c) Pd-cat. (0.025 mmol) was used. d) **1a** (4 mmol) and base (4 mmol) were used in the absence of MS4A. e) Bromobenzene (4 mmol) was used in place of **1a** and PPh_3 (0.1 mmol) was added.

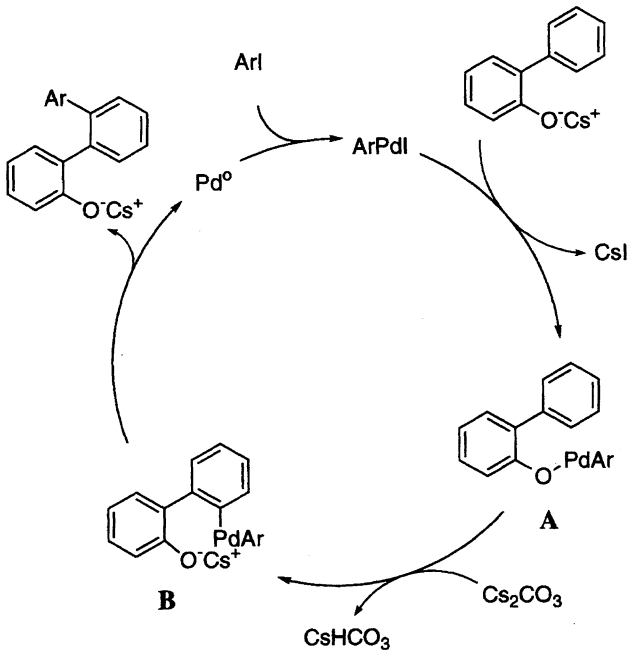
products, **3** or **6** and **4** or **7**, could be selectively formed in fair-to-good yield, depending on the amounts of **1** and Cs_2CO_3 used. In contrast, in the reactions of **1a** with 3′-substituted biphenyl-2-ols **2c—e** with **1a**, only monoarylated products **8—10** were obtained, even using excess amounts of **1a** and the base.

By using the monoarylation of **2a** as an example, a plausible mechanism is illustrated in Scheme 2, in which neutral ligands are omitted. The oxidative addition of aryl iodide to

Table 2. Arylation of Biphenyl-2-ol **2** with Aryl Iodides **1**[a]

1	2	Conditions	Time h	Product(s), Yield[b] %
1b	**2a**	A	22	**3b**, 80(70); **4b**, 12(9)
1b	**2a**	B	44	**3b**, 14(10); **4b**, 70(57)
1c	**2a**	A	22	**3c**, 75(64); **4c**, 8(7)
1d	**2a**	B	44	**4d**, 71(56)[c]
1a	**2b**	A	22	**6**, 76(60); **7**, 9(5)
1a	**2b**	B	22	**6**, 13(10); **7**, 63(61)
1a	**2c**	A	22	**8**, 76(69)
1a	**2d**	A[d]	7	**9**, 88(85)
1a	**2e**	A[d]	44	**10**, 87(73)

a) Reaction conditions: A) **1** (1.2 mmol), **2** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), Cs_2CO_3 (1.2 mmol), MS4A (200 mg), in DMF (5 cm^3) at 100 °C; B) **1** (4 mmol), **2** (1 mmol), $PdCl_2$ (0.05 mmol), Cs_2CO_3 (4 mmol), in DMF (5 cm^3) at 100 °C. b) GLC yield based on amount of **2** used. Value in parentheses indicates isolated yield. c) Monoarylated product (19%) was detected by GC-MS. d) **1a** (2 mmol) and Cs_2CO_3 (2 mmol) were used.



Scheme 2.

palladium(0) species, generated in situ followed by a reaction with the phenylate, forms aryl(aryloxido)palladium intermediate **A**. Then, **A** may be transformed to diarylpalladium species **B**, and the subsequent reductive elimination from **B** occurs to give the monoarylated product.[9] Coordination of the phenolic oxygen to the palladium center in **A** is, thus, considered to be a trigger for the effective, regioselective C–H bond activation, as for the coupling of 2-hydroxybenzaldehydes with aryl iodides.[7a] The second arylation may proceed by the same mechanism. The base Cs_2CO_3, which has relatively high solubility in DMF, could enhance the transformation of **A** to **B** by assisting the deprotonation. Another role of the base could be to remove the iodide ion from the reaction medium, so that the coordination of phenolic oxygen to **A** is enhanced; CsI is known to be relatively insoluble

in DMF.[5]

The results of the reactions of **1a** with 3′-substituted biphenyl-2-ols **2c**—**e** may suggest that (a) the existence of a substituent at the 3′-position of **2** prevents a second arylation due to steric reasons, and (b) the transformation of **A** to **B** is feasible even when the substituent is strongly electron-withdrawing as well as electron-releasing. Figure 1 shows time course of the reaction of **1a** with **2a** and **2c**—**e** under the monoarylation conditions monitored by GLC. The rate of the reaction with **2c** (Z = Me) or **2d** (Z = MeO) was comparable to that with **2a** (Z = H), and the reaction with **2e** (Z = NO_2) was considerably slower, while all the final product yields were comparable. It is reasonable to consider that the observed substituent electronic effect may be derived from the step of **A** to **B**, which may, in a sense, be recognized as an intramolecular aromatic palladation.

It has been reported that in the stoichiometric cyclopalladation of benzylamines and benzylideneanilines with palladium(II) species, the substituent electronic effect is not large, and even nitro-substituted derivatives can form palladacycles.[10] Thus, the present observation parallels the reported results. Such stoichiometric cyclopalladations as well as the key step of palladium-catalyzed intramolecular aromatic arylations and vinylations[3a,11] have usually been considered to involve an electrophilic character, while there would be a possibility that the reaction of certain compounds bearing an extremely electron-withdrawing function, such as nitro group, would proceed via a different route.[3a,11b]

It should be noted that 2-phenylaniline, which is a structural relative of **2a** and known to undergo cyclopalladation upon a treatment with $Pd(OAc)_2$,[12] could not react with **1a** under the present catalytic reaction conditions. Thus, there seems to be certain requirements with respect to the anchoring group for the intermolecular aromatic arylation to take place. However, the details are not clear at the present stage.

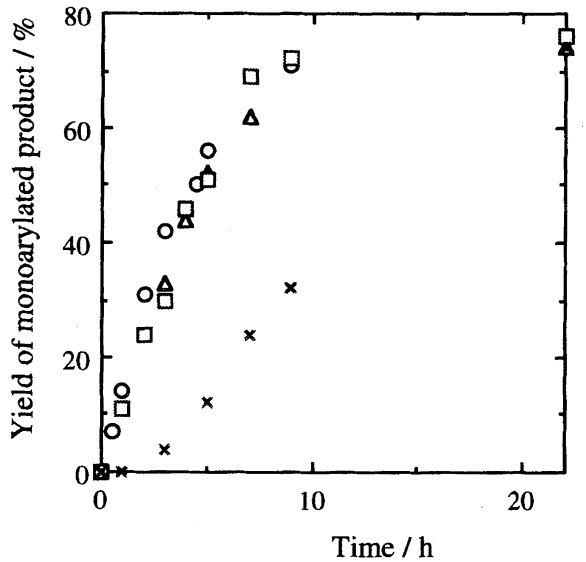
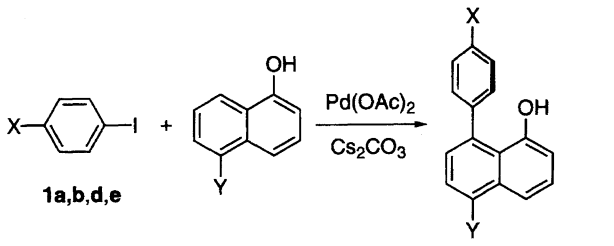


Fig. 1. Time course of the reaction of **1a** with **2a** (□), **2c** (△), **2d** (○), and **2e** (×). Reaction conditions: **1a** (1.2 mmol), **2** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), Cs_2CO_3 (1.2 mmol), MS4A (200 mg), in DMF (5 cm^3) under N_2 at 100 °C.

Arylation of Naphthols. As described above, the phenolic functional group appeared to act as a good anchor for the catalytic arylation of biphenyl-2-ols as well as 2-hydroxybenzaldehyde.[7a] Consequently, arylation of naphthols was undertaken next.

The treatment of 1-naphthol (**11a**) (1 mmol) with **1a** (1.2 mmol) in the presence of either $PdCl_2$ or $Pd(OAc)_2$ (0.025 mmol) and Cs_2CO_3 (2 mmol) in DMF at 110 °C for 19 h afforded 8-phenyl-1-naphthol (**12a**) selectively in a yield of 97% (Scheme 3 and Entries 1 and 2 in Table 3). The use of Cs_2CO_3 was also essential for the catalytic reaction to take place smoothly, as in the reaction of biphenyl-2-ols **2** (Entry 3). In the presence of $PdCl_2$ and Cs_2CO_3, the reactions of 4-substituted iodobenzenes **1b**, **1d**, and **1e** with **11a** and of **1a** with 5-methoxy-1-naphthol (**11b**) gave the corresponding 8-arylated 1-naphthol derivatives **12** and **13** in 53—89% yields, as expected. The reaction of **11a** with bromobenzene (**5a**), however, gave **12a** in only a very low yield (less than 5%), even in the presence of PPh_3.

The reaction of 1-naphthols seems to proceed via intermediates **A′** and **B′** in (Scheme 4), which are analogues of **A** and **B** in Scheme 2; the observed regioselectivity, exclu-



1a,b,d,e

1e: X = Me

11a: Y = H
11b: Y = OMe

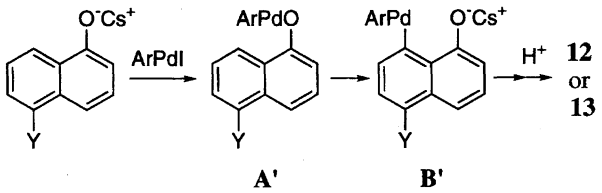
12a: X = Y = H
12b: X = OMe, Y = H
12d: X = Cl, Y = H
12e: X = Me, Y = H
13: X = H, Y = OMe

Scheme 3.

Table 3. Arylation of 1-Naphthols **11** with Aryl Iodides **1**[a]

Entry	1	11	Time / h	Product(s), Yield[b] / %
1	**1a**	**11a**	19	**12a**, 97(73)
2	**1a**[c]	**11a**	19	**12a**, 97
3	**1a**[d]	**11a**	21	**12a**, 9
4	**1b**	**11a**	43	**12b**, 59(59)
5	**1d**	**11a**	21	**12d**, 80(72)
6	**1e**	**11a**	39	**12e**, 53(49)
7	**1a**	**11b**	21	**13**, 67(52)

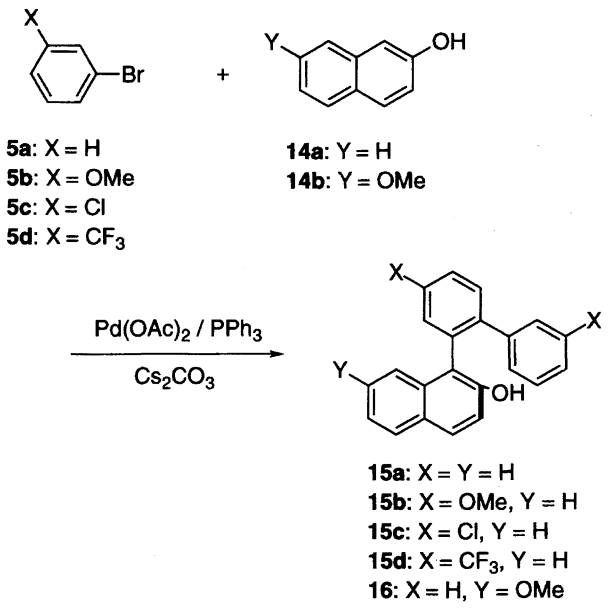
a) Reaction conditions: **1** (1.2 mmol), **11** (1 mmol), $PdCl_2$ (0.025 mmol), Cs_2CO_3 (2 mmol), in DMF (5 cm^3) at 110 °C. b) GLC yield based on amount of **11** used. Value in parentheses indicates isolated yield of the corresponding acetate after acetylation and purification (see Experimental). c) $Pd(OAc)_2$ (0.025 mmol) was used in place of $PdCl_2$. d) K_2CO_3 (2 mmol) was used in place of Cs_2CO_3.



Scheme 4.

sive arylation at the 8-position of 1-naphthols, may suggest that the reaction involves pre-coordination of the phenolic oxygen of **11** to the arylpalladium species prior to aromatic plladation.

On the other hand, when 2-naphthol (**14a**) was treated with 2 molar amounts of **1a** for 72 h in the presence of $PdCl_2$ and Cs_2CO_3 at 100 °C, a small amount of a formally diphenylated compound, 1-(biphenyl-2-yl)-2-naphthol (**15a**) (3%), was produced along with a monophenylated product, 1-phenyl-2-naphthol (3%), and a significant amount of biphenyl (23% based on **1a** used), the palladium-catalyzed Ullmann-type coupling of **1a** predominating over the desired cross-coupling.[3b,13] The reaction efficiency was found to be dramatically improved by using bromobenzene (**5a**) in place of **1a** at an elevated temperature. Thus, the reaction using **5a** (3 mmol) and **14a** (1 mmol) in the presence of $Pd(OAc)_2$ (0.05 mmol) and PPh_3 (0.2 mmol) at 160 °C for 1.5 h selectively gave the diphenylated compound **15a** in a yield of 74% along with a minor amount of the monophenylated product (less than 5%) (Scheme 5 and Entry 1 in Table 4). Similarly, the reactions of 3-substituted bromobenzenes **5b—d** with **14a** and of **5a** with 7-methoxy-2-naphthol (**14b**) gave the corresponding diarylated products **15** and **16** (Entries 3—6). In contrast to these examples, the reactions using bromobenzenes having an electron-donating substituent (e.g. 3-bromotoluene and 4-bromoanisole) and **14a** gave poor results; mixtures of diarylated products contaminated by phenyl group from PPh_3[14] were formed in 15—30% yields along



Scheme 5.

Table 4. Arylation of 2-Naphthols **14** with Aryl Bromides **5**[a]

Entry	5	14	Time / h	Product(s), Yield[b] / %
1	**5a**	**14a**	1.5	**15a**, 74(57)
2[c]	**5a**	**14a**	15	**15a**, 18
3	**5b**	**14a**	2.5	**15b**, 54(45)
4	**5c**	**14a**	1	**15c**, 69(55)
5	**5d**	**14a**	2	**15d**, 74(50)
6	**5a**	**14b**	1.5	**16**, 83(55)

a) Reaction conditions: **5** (3 mmol), **14** (1 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.2 mmol), Cs_2CO_3 (2 mmol), MS4A (200 mg) in DMF (5 cm^3) at 160 °C. b) GLC yield based on amount of **14** used. Value in parentheses indicates isolated yield. c) K_2CO_3 (2 mmol) was used in place of Cs_2CO_3.

with significant amounts of biaryls. In the reaction of 4-bromo-1-chlorobenzene with **14a**, a formally triarylated product was detected by GC-MS as the major product (ca. 40%). At the present stage, however, the reasons that this substrate exhibited a different reactivity from that of 3-bromo-1-chlorobenzene (**5c**) are unclear. When 4-bromobenzonitrile was treated with **14a** under the same conditions, not C-arylation, but O-arylation, occurred to give 4-(2-naphthyloxy)benzonitrile (**17**) in 70% yield within 0.5 h.[15] It was confirmed that this nucleophilic substitution proceeded even in the absence of the palladium catalyst to quantitatively produce **17** (Chart 1).

The first step of the reaction of 2-naphthols **14**, monoarylation at 1-position, may involve a nucleophilic attack of the corresponding naphtholate on the arylpalladium(II) species generated in situ (Scheme 6). This may be followed by the regioselective second arylation on the 2-position of the aryl substituent of 1-aryl-2-naphtholate in a similar manner as in the reaction of biphenyl-2-ols **2**. The observed substituent effect in **5** for the arylation reaction, bromobenzenes having

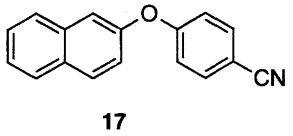


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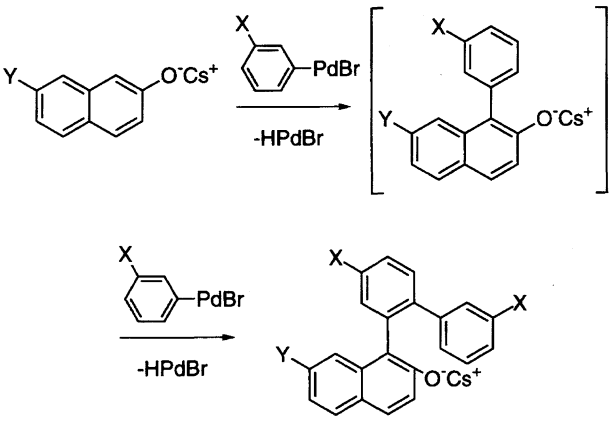
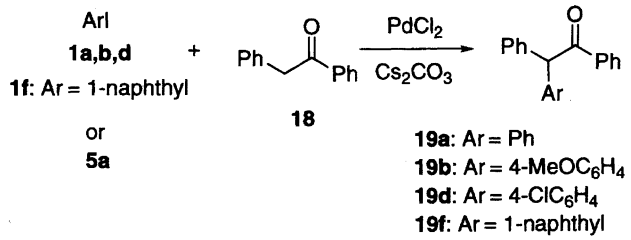
Chart 1.



Scheme 6.

an electron-withdrawing substituent giving satisfactory results, may be due to the fact that the substituent can enhance the electrophilicity of arylpalladium(II) species to promote its attack on the naphtholate. While it may alternatively be possible that it promotes the initial oxidative addition step, the fact that the reaction efficiency was highly influenced by the identity of the base employed (Entry 1 versus 2) suggests that the former step should be more important. Note that, while palladium-catalyzed the intramolecular coupling of aryl halides with enolates, including phenolates, has been known,[16] the corresponding intermolecular version has been limited to only a few reactions using nitriles as carbon nucleophiles.[17] Therefore, we also examined the applicability of the present procedure to the arylation of a number of enolizable compounds.

Arylation of Benzylic Compounds. When 1,2-diphenylethanone (**18**) (1 mmol) was treated with **1a** (1.2 mmol) and Cs_2CO_3 (1.2 mmol) in the presence of $PdCl_2$ (0.05 mmol) in DMF at 100 °C for 2 h, 1,2,2-triphenylethanone (**19a**) was selectively produced in a yield of 95% (Scheme 7 and Entry 1 in Table 5). The reactions of iodides **1b**, **1d**, and

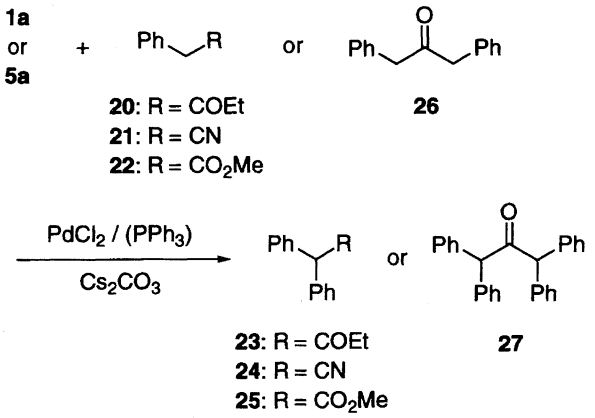


Scheme 7.

Table 5. Phenylation of Benzylic Compounds **18**, **20**—**22**, **26** with Iodo- (**1a**) and Bromobenzene (**5a**)[a]

Entry	Halide	Benzylic compound	Temp °C	Time h	Product(s), Yield[b] %
1	**1a**	**18**	100	2	**19a**, 95(90)
2	**1b**	**18**	100	2	**19b**, 100(93)
3	**1d**	**18**	100	2	**19d**, 96(82)
4	**1f**	**18**	100	2	**19f**, 92(75)
5[c]	**1a**	**18**	100	2	**19a**, 53
6[c,d]	**5a**	**18**	130	2	**19a**, 96
7	**1a**	**20**	100	4	**23**, 85(72)
8	**1a**	**21**	100	2	**24**, 18
9[d]	**5a**	**21**	100	6	**24**, 47
10[d]	**5a**	**21**	130	2	**24**, 68(44)
11	**1a**	**22**	100	50	**25**, 7
12[e,f]	**1a**	**22**	100	2	**25**, 60(56)[g]
13[d,e]	**5a**	**22**	130	4	**25**, 9
14[h]	**1a**	**26**	100	2	**27**, 63(59)

a) Reaction conditions: halide (1.2 mmol), benzylic compound (1 mmol), $PdCl_2$ (0.05 mmol), Cs_2CO_3 (1.2 mmol), in DMF (5 cm^3). b) GLC yield based on amount of benzylic compound used. Value in parentheses indicates isolated yield. c) K_2CO_3 (1.2 mmol) was used in place of Cs_2CO_3. d) PPh_3 (0.1—0.2 mmol) was added. e) MS4A (200 mg) was added. f) **1a** (1 mmol), **22** (5 mmol), and Cs_2CO_3 (5 mmol) were used. g) Yield based on amount of **1a** used. h) **1a** (3 mmol) and Cs_2CO_3 (3 mmol) were used.



Scheme 8.

1f with **18** also gave the corresponding 2-aryl-1,2-diphenylethanones **19** in good yields (Entries 2—4). It was again observed that K_2CO_3 was less effective than Cs_2CO_3 under the same conditions (Entry 5). However, using bromobenzene (**5a**) with K_2CO_3, compound **18** was efficiently phenylated to produce **19a** in 96% yield (Entry 6). The effectiveness of the reaction, using the combination of aryl bromide and K_2CO_3, has been observed in the related arylation of azole compounds, and its possible reasons have been discussed in our previous publication.[5] The major factor may be the solubility of potassium halides formed during the reaction; KBr is sparingly soluble, while KI is considerably soluble in DMF.

1-Phenylbutan-2-one (**20**), phenylacetonitrile (**21**), and methyl phenylacetate (**22**) also reacted with **1a** or **5a** in the presence of Cs_2CO_3 to give the corresponding phenylated products **23**—**25** in substantial yields by employing appropriate conditions (Scheme 8 and Entries 7, 10, 12 in Table 5). The treatment of 1,3-diphenylpropane-2-one (**26**) with 3 molar amounts of **1a** selectively gave 1,1,3,3-tetraphenylpropane-2-one (**27**) (Entry 14).

The reaction of intermediary arylpalladium species with enolates or carbanions, generated from the parent benzylic compounds to form arylbenzylpalladium species, seems to be the key step in the above arylation. Note that, after a part of the present work had been communicated,[8] related arylation reactions of ketones with aryl bromides, mainly methyl ketones to benzyl ketones, under palladium catalysis using bidentate ligands were reported.[18] By using these methods, further arylation of the produced benzyl ketones to diarylmethyl ketones appeared to hardly take palace, probably because of steric reasons. By using the present catalyst systems, the benzylic position of **20** was predominantly arylated and pentan-3-one could not be reacted, while an ethyl aryl ketone was reported to be arylated using $Pd_2(dba)_3$, BINAP, and *t*-BuONa.[18a] These results suggest that by choosing an appropriate ligand and base, the regioselective α-arylation of ketones may be performed.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX spectrometer at 400 and 100 MHz or on a varian UNITY-

INOVA600 at 600 and 150 MHz, respectively, for $CDCl_3$ solutions. GLC-MS data were obtained with a Shimadzu QP-2000A spectrometer or with JEOL JMS-DX-303 spectrometer. A GLC analysis was carried out using a Shimadzu GC 8A gas chromatograph equipped with a Silicone OV-17 glass column (ϕ2.6 mm×1.5 m) or with a CBP-1 capillary column (ϕ0.5 mm×25 m). Biphenyl-2-ols **2b**—**e** were prepared by a treatment of the corresponding substituted dihydroxy(phenyl)boranes with 2-iodophenol under a palladium catalysis (Suzuki-coupling conditions).[19] 5-Methoxy-1-naphthol (**11b**) was prepared by treating naphthalene-1,5-diol with a 1.2 molar amount of dimethyl sulfate in aq KOH at 50 °C. The other starting materials were commercially available. The solvents were purified by standard methods before use. The structures of all the new products were unambiguously determined by ^{1}H and ^{13}C NMR with the aid of NOE, COSY, COLOC, and HOHAHA experiments.

Arylation of Biphenyl-2-ols. In a 100 cm^3 two-necked flask was placed a base (1.2—4 mmol), which was then dried at 150 °C in vacuo for 2 h. Then, a palladium catalyst (0.05 mmol), **1** (1.2—4 mmol), **2** (1 mmol), MS4A (200 mg), and DMF (5 cm^3) were added; the resulting mixture was stirred under N_2 at 80—120 °C for 5—72 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over sodium sulfate. The product was isolated by column chromatography on silica gel using hexane–ethyl acetate or hexane–dichloromethane as an eluent.

1,1′ : 2′,1″-Terphenyl-2-ol (3a):[20] Oil; ^{1}H NMR δ = 4.78 (s, 1H), 6.79 (dd, 1H, J = 1.0, 7.8 Hz), 6.84 (dt, 1H, J = 1.0, 7.3 Hz), 7.03 (dd, 1H, J = 1.5, 7.8 Hz), 7.13—7.23 (m, 6H), 7.40—7.53 (m, 4H); MS m/z 246 (M$^+$).

4″-Methoxy-1,1′ : 2′,1″-terphenyl-2-ol (3b): Mp 88 °C; ^{1}H NMR δ = 3.76 (s, 3H, OMe), 4.77 (s, 1H, OH), 6.75 (dt, 2H, J = 8.8, 2.0 Hz, H-3″), 6.80 (dd, 1H, J = 1.0, 7.8 Hz, H-3), 6.87 (dt, 1H, J = 1.0, 7.3 Hz, H-5), 7.07 (dd, 1H, J = 1.5, 7.3 Hz, H-6), 7.09 (dt, 2H, J = 8.8, 2.0 Hz, H-2″), 7.17 (dt, 1H, J = 1.5, 7.8 Hz, H-4), 7.37—7.49 (m, 4H); MS m/z 276 (M$^+$). Found: C, 82.36; H, 5.95%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

3″-Methoxy-1,1′ : 2′,1″-terphenyl-2-ol (3c): Oil; ^{1}H NMR δ = 3.57 (s, 3H), 4.82 (s, 1H), 6.66 (t, 1H, J = 2.0 Hz), 6.75 (dd, 1H, J = 2.4, 8.3 Hz), 6.80 (d, 1H, J = 8.3 Hz), 6.81 (d, 1H, J = 7.3 Hz), 6.85 (dt, 1H, J = 1.0, 7.3 Hz), 7.05 (dd, 1H, J = 1.5, 7.3 Hz), 7.14 (t, 1H, J = 7.8 Hz), 7.15 (dt, 1H, J = 1.5, 7.8 Hz), 7.39—7.54 (m, 4H); HRMS Found: m/z (M$^+$). 276.1150. Calcd for $C_{19}H_{16}C_2$: M, 276.1150.

2′,6′-Diphenylbiphenyl-2-ol (4a): Mp 150—151 °C; ^{1}H NMR δ = 4.66 (s, 1H), 6.54 (dd, 1H, J = 1.0, 8.3 Hz), 6.58 (dt, 1H, J = 1.0, 7.3 Hz), 6.76 (dd, 1H, J = 1.5, 7.3 Hz), 6.94 (dt, 1H, J = 1.5, 7.3 Hz), 7.09—7.18 (m, 10H), 7.45—7.53 (m, 3H); MS m/z 322 (M$^+$). Found: C, 89.15; H, 5.61%. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.63%.

2′,6′-Bis(4-methoxyphenyl)biphenyl-2-ol (4b): Mp 153—154 °C; ^{1}H NMR δ = 3.74 (s, 6H, OMe), 4.63 (s, 1H, OH), 6.61 (dd, 1H, J = 1.0, 8.3 Hz, H-3), 6.64 (dt, 1H, J = 1.0, 7.3 Hz, H-5), 6.71 (dt, 4H, J = 8.8, 2.0 Hz, H-3″), 6.77 (dd, 1H, J = 1.5, 7.3 Hz, H-6), 6.99 (dt, 1H, J = 1.5, 8.3 Hz, H-4), 7.04 (dt, 4H, J = 8.8, 2.0 Hz, H-2″), 7.42—7.52 (m, 3H); MS m/z 382 (M$^+$). Found: C, 81.23; H, 5.94%. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80%.

2′,6′-Bis(3-methoxyphenyl)biphenyl-2-ol (4c): Mp 92—93 °C; ^{1}H NMR δ = 3.57 (s, 6H), 4.67 (s, 1H), 6.59—6.65 (m, 4H), 6.72 (dd, 2H, J = 2.0, 7.8 Hz), 6.77—6.81 (m, 3H), 6.99 (dt, 1H, J = 1.5, 7.8 Hz), 7.11 (t, 2H, J = 7.8 Hz), 7.49—7.56 (m, 3H); MS m/z 382 (M$^+$). Found: C, 81.40; H, 5.92%. Calcd for $C_{26}H_{22}O_3$: C, 81.65; H, 5.80%.

2′,6′-Bis(4-chlorophenol)biphenyl-2-ol (4d): Mp 217—218 °C; ^{1}H NMR δ = 4.53 (s, 1H), 6.59 (dd, 1H, J = 1.0, 8.3 Hz), 6.64 (dt, 1H, J = 1.0, 7.3 Hz), 6.74 (dd, 1H, J = 1.5, 7.3 Hz), 7.01 (dt, 1H, J = 1.5, 7.8 Hz), 7.05 (dt, 4H, J = 8.8, 2.0 Hz), 7.14 (dt, 4H, J = 8.8, 2.0 Hz), 7.44—7.56 (m, 3H); MS m/z 390, 392, 394 (M$^+$). Found: C, 73.94; H, 4.39; Cl, 17.82%. Calcd for $C_{24}H_{16}OCl_2$: C, 73.67; H, 4.12; Cl, 18.12%.

4′-Methyl-1,1′ : 2′,1″-terphenyl-2-ol (6): Mp 64 °C; ^{1}H NMR δ = 2.45 (s, 3H), 4.81 (s, 1H), 6.78 (dd, 1H, J = 1.0, 8.3 Hz), 6.81 (dt, 1H, J = 1.0, 7.3 Hz), 7.01 (dd, 1H, J = 1.9, 7.3 Hz), 7.11—7.22 (m, 6H), 7.25—7.33 (m, 3H); MS m/z 260 (M$^+$). Found: C, 87.42; H, 6.18%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

4′-Methyl-2′,6′-diphenylbiphenyl-2-ol (7): Mp 122.5—123.5 °C; ^{1}H NMR δ = 2.49 (s, 3H), 4.63 (s, 1H), 6.57 (dd, 1H, J = 1.0, 7.3 Hz), 6.60 (dt, 1H, J = 1.0, 7.3 Hz), 6.76 (dd, 1H, J = 1.5, 7.3 Hz), 6.96 (dt, 1H, J = 1.5, 7.3 Hz), 7.11—7.18 (m, 10H), 7.31 (s, 2H); MS m/z 336 (M$^+$). Found: C, 88.92; H, 6.08%. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99%.

5′-Methyl-1,1′ : 2′,1″-terphenyl-2-ol (8): Mp 120—121 °C; ^{1}H NMR δ = 2.43 (s, 3H), 4.82 (s, 1H), 6.78 (dd, 1H, J = 1.0, 7.8 Hz), 6.83 (dt, 1H, J = 1.0, 7.3 Hz), 7.03 (dd, 1H, J = 1.9, 7.3 Hz), 7.12—7.21 (m, 6H), 7.22 (s, 1H), 7.30 (dd, 1H, J = 1.5, 7.8 Hz), 7.41 (d, 1H, J = 7.8 Hz); MS m/z 260 (M$^+$). Found: C, 87.36; H, 6.04%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19%.

5′-Methoxy-1,1′ : 2′,1″-terphenyl-2-ol (9): Mp 136—137 °C; ^{1}H NMR δ = 3.84 (s, 3H), 4.87 (s, 1H), 6.78 (dd, 1H, J = 1.0, 8.3 Hz), 6.84 (dt, 1H, J = 1.0, 7.3 Hz), 6.93 (d, 1H, J = 2.4 Hz), 7.03 (dd, 1H, J = 2.4, 8.3 Hz), 7.06 (dd, 1H, J = 1.5, 7.3 Hz), 7.10—7.21 (m, 6H), 7.43 (d, 1H, J = 8.3 Hz); MS m/z 276 (M$^+$). Found: C, 82.36; H, 5.87%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

5′-Nitro-1,1′ : 2′,1″-terphenyl-2-ol (10): Mp 144—145 °C; ^{1}H NMR δ = 4.65 (s, 1H), 6.75 (dd, 1H, J = 1.0, 8.3 Hz), 6.90 (dt, 1H, J = 1.0, 7.3 Hz), 7.07 (dd, 1H, J = 1.5, 7.3 Hz), 7.17—7.28 (m, 6H), 7.64 (dd, 1H, J = 1.5, 8.8 Hz), 8.30 (dd, 1H, J = 2.4, 8.8 Hz), 8.31 (s, 1H); MS m/z 291 (M$^+$). Found: C, 74.09; H, 4.70; N, 4.68%. Calcd for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50; N, 4.81%.

Arylation of 1-Naphthols. In a 100 cm^3 two-necked flask was placed a base (2 mmol), which was then dried at 150 °C in vacuo for 2 h. Then, a palladium catalyst (0.025 mmol), **1** (1.2 mmol), **11** (1 mmol), and DMF (5 cm^3) were added, and the resulting mixture was stirred under N_2 at 110 °C for 19—43 h. After cooling, the reaction mixture was extracted with diethyl ether and dried over sodium sulfate. The product was isolated by column chromatography on silica gel using hexane–ethyl acetate as an eluent. From the reaction mixture of **11a** with **1a**, 8-phenyl-1-naphthol (**12a**) was isolated in a lower yield (52%) than that expected by GLC analysis. Therefore, before isolation, the reaction mixture was treated with acetic anhydride (0.47 cm^3, 5 mmol) in pyridine (5 cm^3) at room temperature overnight: the corresponding acetate **12′** or **13′** was obtained in better isolated yields.

8-Phenyl-1-naphthol (12a):[21] Oil: ^{1}H NMR δ = 5.41 (s, 1H), 6.92 (dd, 1H, J = 1.5, 7.3 Hz), 7.21 (dd, 1H, J = 1.5, 7.3 Hz), 7.40 (t, 1H, J = 7.8 Hz), 7.44 (t, 1H, J = 8.3 Hz), 7.49—7.51 (m, 6H), 7.86 (dd, 1H, J = 1.5, 8.3 Hz); MS m/z 220 (M$^+$).

8-(4-Methoxyphenyl)-1-naphthyl Acetate (12b′): Mp 68—69 °C; ^{1}H NMR δ = 1.46 (s, 3H), 3.86 (s, 3H), 6.96 (dd, 2H, J = 2.9, 8.3 Hz), 7.08 (d, 1H, J = 7.3 Hz), 7.27 (s, 1H), 7.29 (d, 2H, J = 8.3 Hz), 7.47 (t, 2H, J = 7.3 Hz), 7.82 (d, 1H, J = 8.3 Hz), 7.87 (d, 1H, J = 8.3 Hz); MS m/z 292 (M$^+$). Found: C, 77.87; H, 5.59%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

8-(4-Chlorophenyl)-1-naphthyl Acetate (12d′): Mp 111—112 °C; ^{1}H NMR δ = 1.48 (s, 3H), 7.10 (d, 1H, J = 7.8 Hz), 7.24

(d, 1H, J = 7.3 Hz), 7.30 (d, 2H, J = 8.3 Hz), 7.39 (d, 2H, J = 8.3 Hz), 7.49 (dt, 2H, J = 2.0, 6.8 Hz), 7.83 (d, 1H, J = 8.3 Hz), 7.91 (d, 1H, J = 8.3 Hz); MS m/z 296, 298 (M^+). Found: C, 72.39; H, 4.49; Cl, 12.90%. Calcd for $C_{18}H_{13}O_2Cl$: C, 72.85; H, 4.42; Cl, 11.95%.

8-(4-Methylphenyl)-1-naphthyl Acetate (12e′): Mp 102—103 °C; ^{1}H NMR δ = 1.39 (s, 3H), 2.42 (s, 3H), 7.07 (d, 1H, J = 7.8 Hz), 7.21—7.27 (m, 5H), 7.47 (t, 2H, J = 8.3 Hz), 7.82 (dd, 1H, J = 8.3, 1.0 Hz), 7.88 (dd, 1H, J = 8.3, 1.5 Hz); MS m/z 276 (M^+). Found: C, 82.56; H, 5.87%. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

5-Methoxy-8-phenyl-1-naphtyl Acetate (13′): Mp 124—125 °C; ^{1}H NMR δ = 1.35 (s, 3H), 4.03 (s, 3H), 6.85 (d, 1H, J = 7.8 Hz), 7.10 (dd, 1H, J = 1.5, 7.3 Hz), 7.17 (d, 1H, J = 7.8 Hz), 7.31—7.41 (m, 5H), 7.47 (t, 1H, J = 8.3 Hz), 8.31 (d, 1H, J = 8.3 Hz); MS m/z 292 (M^+). Found: C, 78.15; H, 5.65%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

Arylation of 2-Naphthols. In a 100 cm^3 two-necked flask was placed a base (2 mmol), which was then dried at 150 °C in vacuo for 2 h. Then, $Pd(OAc)_2$ (11 mg, 0.05 mmol), PPh_3 (52 mg, 0.2 mmol), **5** (3 mmol), **14** (1 mmol), MS4A (200 mg), and DMF (5 cm^3) were added, and the resulting mixture was stirred under N_2 at 160 °C for 1—15 h. After cooling, the reaction mixture was extracted with diethyl ether, and dried over sodium sulfate. The product was isolated by column chromatography on silica gel using hexane-ethyl acetate as an eluent.

1-(Biphenyl-2-yl)-2-naphthol (15a): Mp 117—118 °C; ^{1}H NMR δ = 4.93 (s, 1H, OH), 7.02—7.10 (m, 6H), 7.27 (dt, 1H, J = 1.5, 8.1 Hz, H-6), 7.31 (dt, 1H, J = 1.5, 8.1 Hz, H-7), 7.36 (d, 1H, J = 8.1 Hz, H-8), 7.41 (d, 1H, J = 7.3 Hz, H-3′), 7.54 (dt, 1H, J = 2.2, 7.3 Hz, H-4′), 7.59 (dt, 1H, J = 1.5, 7.3 Hz, H-5′), 7.62 (dd, 1H, J = 2.2, 7.3 Hz, H-6′), 7.69 (d, 1H, J = 8.8 Hz, H-4), 7.73 (d, 1H, J = 8.1 Hz, H-5) ^{13}C NMR δ = 117.10, 120.45, 123.12, 124.73, 126.40, 127.04, 127.78, 127.97, 128.29, 128.42, 128.76, 129.26, 129.43, 130.98, 132.16, 132.69, 133.51, 140.21, 143.42, 150.03; MS m/z 296 (M^+). Found: C, 88.95; H, 5.66%. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%.

1-Phenyl-2-naphthol:[22] Oil; ^{1}H NMR δ = 5.14 (s, 1H), 7.27 (d, 1H, J = 9.3 Hz), 7.30—7.36 (m, 2H), 7.38—7.44 (m, 3H), 7.51 (tt, 1H, J = 1.5, 7.3 Hz), 7.59 (tt, 2H, J = 1.5, 7.3 Hz), 7.80—7.83 (m, 2H); MS m/z 220 (M^+).

1-(3′,4-Dimethoxybiphenyl-2-yl)-2-naphthol (15b): Mp 48—49 °C; ^{1}H NMR δ = 3.26 (s, 3H), 3.85 (s, 3H), 4.97 (s, 1H), 6.52 (t, 1H, J = 2.0 Hz), 6.59 (dd, 1H, J = 2.5, 8.3 Hz), 6.73 (d, 1H, J = 7.81 Hz), 6.93 (d, 1H, J = 2.9 Hz), 6.98 (t, 1H, J = 7.8 Hz), 7.07 (d, 1H, J = 8.8 Hz), 7.13 (dd, 1H, J = 1.5, 6.8 Hz), 7.28 (dd, 1H, J = 1.5, 6.8 Hz), 7.33 (dt, 1H, J = 1.5, 6.8 Hz), 7.44 (d, 1H, J = 8.3 Hz), 7.56 (d, 1H, J = 8.3 Hz), 7.70 (d, 1H, J = 8.8 Hz), 7.74 (d, 1H, J = 8.3 Hz); MS m/z 356 (M^+). Found: C, 80.86; H, 5.77%. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66%.

1-(3′,4-Dichlorobiphenyl-2-yl)-2-naphthol (15c): Mp 77—79 °C; ^{1}H NMR δ = 4.91 (s, 1H), 6.86 (dt, 1H, J = 7.8, 1.5 Hz), 6.91 (t, 1H, J = 7.8 Hz), 7.02—7.07 (m, 2H), 7.13 (t, 1H, J = 2.0 Hz), 7.27—7.35 (m, 3H), 7.43 (d, 1H, J = 2.0 Hz), 7.51 (d, 1H, J = 8.3 Hz), 7.57 (dd, 1H, J = 2.4, 8.7 Hz), 7.71—7.75 (m, 2H); HRMS Found: m/z (M^+) 364.0428. Calcd for $C_{22}H_{14}OCl_2$: M, 364.0422.

1-[3′,4-Bis(trifluoromethyl)biphenyl-2-yl]-2-naphthol (15d): Oil; ^{1}H NMR δ = 4.81 (s, 1H), 7.04 (d, 1H, J = 8.8 Hz), 7.15 (t, 1H, J = 7.8 Hz), 7.22 (d, 1H, J = 8.3 Hz), 7.24 (d, 1H, J = 7.8 Hz), 7.29 (dt, 1H, J = 6.8, 1.5 Hz), 7.32—7.36 (m, 2H), 7.40 (s, 1H), 7.71—7.75 (m, 4H), 7.87 (dd, 1H, J = 1.5, 7.8 Hz); HRMS Found: m/z (M^+) 432.0955. Calcd for $C_{24}H_{14}OF_6$: M, 432.0949.

1-(Biphenyl-2-yl)-7-methoxy-2-naphthol (16): Mp 45—46 °C; ^{1}H NMR δ = 3.68 (s, 3H), 4.92 (s, 1H), 6.62 (d, 1H, J = 2.4 Hz), 6.92 (dd, 2H, J = 2.4, 8.8 Hz), 7.04—7.13 (m, 5H), 7.41 (dd, 1H, J = 1.5, 7.3 Hz), 7.54 (dt, 1H, J = 2.0, 7.3 Hz), 7.56—7.64 (m, 4H); MS m/z 326 (M^+). Found: C, 84.63; H, 5.72%. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

4-(2-Naphthyloxy)benzonitrile (17): Mp 101—102 °C; ^{1}H NMR δ = 7.06 (s, 2H, J = 8.8 Hz), 7.23 (d, 1H, J = 8.8 Hz), 7.46—7.48 (m, 1H), 7.50 (d, 1H, J = 2.0 Hz), 7.53 (dd, 1H, J = 1.5, 6.8 Hz), 7.62 (d, 2H, J = 8.8 Hz), 7.77 (d, 1H, J = 8.8 Hz), 7.87 (d, 1H, J = 8.8 Hz), 7.90 (d, 1H, J = 8.8 Hz); MS m/z 245 (M^+). Found: C, 83.02; H, 4.59; N, 5.71%. Calcd for $C_{17}H_{11}NO$: C, 83.27; H, 4.52; N, 5.71%.

Arylation of Benzylic Compounds. The methods were essentially the same as those in the reaction of biphenyl-2-ols (in the cases using aryl iodides **1**) or 2-naphthols (in the cases using aryl bromides **5**) described above.

1,2,2-Triphenylethanone (19a): Mp 137—138 °C (lit,[23] 135—136 °C); ^{1}H NMR δ = 6.03 (s, 1H), 7.22—7.51 (m, 13H), 8.00 (d, 2H, J = 7.3 Hz); ^{13}C NMR δ = 59.5, 127.0, 128.4, 128.5, 128.8, 129.0, 132.8, 136.7, 138.9, 197.8; MS m/z 272 (M^+).

2-(4-Methoxyphenyl)-1,2-diphenylethanone (19b):[24] Mp 84—85 °C; ^{1}H NMR δ = 3.77 (s, 3H), 5.98 (s, 1H), 6.86 (d, 2H, J = 8.8 Hz), 7.18—7.50 (m, 10H), 7.99 (dd, 2H, J = 0.73, 1.5 Hz); ^{13}C NMR δ = 55.1, 58.4, 113.8, 126.7, 128.2, 128.3, 128.6, 128.7, 129.8, 130.8, 132.6, 136.5, 139.1, 158.2, 197.9; MS m/z 302 (M^+).

2-(4-Chlorophenyl)-1,2-diphenylethanone (19d):[24] Mp 102—103 °C; ^{1}H NMR δ = 6.00 (s, 1H), 7.18—7.99 (m, 12H), 7.94 (dd, 2H, J = 1.0, 1.5 Hz); ^{13}C NMR δ = 58.5, 127.0, 128.3, 128.4, 128.5, 128.6, 128.6, 130.1, 132.7, 132.8, 136.2, 137.3, 138.2, 197.2; MS m/z 306, 308 (M^+).

2-(1-Naphthyl)-1,2-diphenylethanone (19f): Mp 98—99 °C; ^{1}H NMR δ = 6.74 (s, 1H), 7.22—7.50 (m, 12H), 7.79 (d, 1H, J = 8.3 Hz), 7.86—7.90 (m, 1H), 7.94—8.02 (m, 3H); ^{13}C NMR δ = 55.8, 122.8, 125.1, 125.4, 126.4, 126.8, 126.9, 127.8, 128.3, 128.3, 128.5, 128.7, 129.2, 130.9, 132.7, 133.9, 134.6, 136.2, 137.7, 197.7; MS m/z 322 (M^+). Found: C, 89.01; H, 5.76. Calcd for $C_{24}H_{18}O$: C, 89.41; H, 5.36%.

1,1-Diphenylbutan-2-one (23):[25] Oil; ^{1}H NMR δ = 1.06 (t, 3H, J = 7.2 Hz), 2.57 (q, 2H, J = 7.3 Hz), 5.14 (s, 1H), 7.22—7.33 (m, 10H); ^{13}C NMR δ = 8.1, 36.0, 63.7, 126.8, 128.3, 128.5, 138.2, 208.6; MS m/z 224 (M^+).

Diphenylacetonitrile (24): Mp 69—70 °C (lit,[26] 71—73 °C); ^{1}H NMR δ = 5.13 (s, 1H), 7.24—7.37 (m, 10H); ^{13}C NMR δ = 42.6, 119.5, 127.5, 128.0, 129.0, 135.7; MS m/z 184 (M^+).

Methyl Diphenylacetate (25):[27] Oil; ^{1}H NMR δ = 3.66 (s, 3H), 4.96 (s, 1H), 7.04—7.26 (m, 10H); ^{13}C NMR δ = 52.3, 57.0, 127.0, 128.4, 128.4, 138.4, 172.6; MS m/z 226 (M^+).

1,1,3,3-Tetraphenylpropane-2-one (27): Mp 133.5—134.5 °C (lit,[28] 134—134.5 °C); ^{1}H NMR δ = 5.25 (s, 2H), 7.12—7.16 (m, 8H), 7.22—7.34 (m, 12H); MS m/z 362 (M^+).

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References

1) G. Bringmann, R. Walter, and R. Weirich, *Angew. Chem., Int. Ed. Engl.*, **29**, 977 (1990), and references therein.

2) For example: a) R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985); b) J. Tsuji, "Palladium Reagents and Catalysts," Wiley, Chichester (1995); c) "Metal-Catalyzed Cross Coupling Reactions," ed by P. J. Stang and F. Diederich, Wiley-VCH, Weinheim (1997); d) S. P. Stanforth, *Tetrahedron*, **54**, 263 (1998).

3) a) Review: G. Dyker, *Chem. Ber./Recueil*, **130**, 1567 (1997); b) G. Dyker, *J. Org. Chem.*, **58**, 234 (1993); c) G. Dyker, J. Körning, P. G. Jones, and P. G. Bubenitschek, *Angew. Chem., Int. Ed. Engl.*, **32**, 1733 (1993).

4) a) Y. Akita, Y. Itagaki, S. Takizawa, and A. Ohta, *Chem. Pharm. Bull.*, **7**, 1477 (1989); b) A Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani, and Y. Aoyagi, *Heterocycles*, **31**, 1951 (1990); c) Y. Aoyagi, A. Inoue, I. Koizumi, R. Hashimoto, K. Tokunaga, K. Gohma, J. Komatsu, K. Sekine, A. Miyafuji, J. Kanoh, R. Honma, Y. Akita, and A. Ohta, *Heterocycles*, **33**, 257 (1992).

5) S. Pivsa-Art, T. Satoh, Y. Kawamura, M. Miura, and M. Nomura, *Bull. Chem. Soc. Jpn.*, **71**, 467 (1998).

6) C. Gozzi, L. Lavenot, K. Ilg, V. Penalva, and M. Lemaire, *Tetrahedron Lett.*, **38**, 8867 (1997).

7) a) T. Satoh, T. Itaya, M. Miura, and M. Nomura, *Chem. Lett.*, **1996**, 823;b) T. Satoh, T. Tsuda, Y. Kushino, M. Miura, and M. Nomura, *J. Org. Chem.*, **61**, 6476 (1996); c) T. Satoh, M. Ikeda, M. Miura, and M. Nomura, *J. Mol. Catal. A: Chem.*, **111**, 25 (1996); d) T. Satoh, K. Kokubo, M. Miura, and M. Nomura, *Organometallics*, **13**, 4431 (1994).

8) Some preliminary results of this work have been communicated: T. Satoh, Y. Kawamura, M. Miura, and M. Nomura, *Angew. Chem., Int. Ed. Engl.*, **36**, 1740 (1997).

9) Participation of another sequence which involves cyclo-palladation of **2** by Pd(II) followed by oxidative addition of **1** to give a Pd(IV) intermediate can not be excluded, especially at the early stage of the reaction.[3a)] Recently, palladium-catalyzed 2,6-dialkylation of aryl iodides with alkyl iodides, which seems to proceed via Pd(IV) species, has also been reported: M. Catellani, F. Frignani, and A. Rangoni, *Angew. Chem., Int. Ed. Engl.*, **36**, 119 (1997).

10) a) Review: A. D. Ryabov, *Chem. Rev.*, **90**, 403 (1990); b) J. Vicente, I. Saura-Llamas, M. G. Palin, and P. G. Jones, *J. Chem. Soc., Dalton Trans.*, **1995**, 2535; c) M Gómez, J. Granell, and M. Martinez, *Organometallics*, **16**, 2539 (1997).

11) For example: a) D. E. Ames and A. Opalko, *Synthesis*, **1983**, 234; b) J. J. González, N. García, B. Gómez-Lor, and A. M. Echavarren, *J. Org. Chem.*, **62**, 1286 (1997); c) R. C. Larock, M. J. Doty, Q. Tian, and J. M. Zenner, *J. Org. Chem.*, **62**, 7536 (1997).

12) J. Albert, J. Granell, A. Luque, J. Mínguez, R. Moragas, M. Font-Bardía, and X. Solans, *J. Organomet. Chem.*, **522**, 87 (1996).

13) G. Dyker, *Angew. Chem., Int. Ed. Engl.*, **33**, 103 (1994).

14) For example: M. T. Reetz, G. Lohmer, and R. Schwickardi, *Angew. Chem., Int. Ed. Engl.*, **37**, 481 (1998), and references therein.

15) G. Mann and F. Hartwig, *Tetrahedron Lett.*, **38**, 8005 (1997).

16) a) D. D. Hennings, S. Iwasa, and V. H. Rawal, *J. Org. Chem.*, **62**, 2 (1997); b) M. A. Cuifolini and M. E. Browne, *Tetrahedron Lett.*, **28**, 171 (1987); c) M. A. Cuifolini, H. B. Qi, and M. E. Browne, *J. Org. Chem.*, **53**, 4149 (1988).

17) M. Uno, K. Seto, W. Ueda, M. Masuda, and S. Takahashi, *Synthesis*, **1985**, 506.

18) a) M. Palucki and S. L. Buchwald, *J. Am. Chem. Soc.*, **119**, 11108 (1997); b) B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc.*, **119**, 12382 (1997).

19) N. Miyaura and A. Suzuki, *Chem. Rev.*, **95**, 2457 (1995).

20) T. Keumi, C. Murata, Y. Sasaki, K. Ogasawara, and H. Kitajima, *Nippon Kagaku Kaishi*, **1981**, 259; *Chem. Abstr.*, **95**, 42537x (1981).

21) D. G. Batt, D. G. Jones, and S. L. Greca, *J. Org. Chem.*, **56**, 6704 (1991).

22) R. A. Abramovitch, D. H. R. Barton, and J.-P. Finet, *Tetrahedron*, **44**, 3039 (1988).

23) K. Chen and G. F. Koser, *J. Org. Chem.*, **56**, 5764 (1991).

24) F. Toda and T. Shigemasa, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 209.

25) N. Shimizu, S. Yamaoka, and Y. Tsuda, *Bull. Chem. Soc. Jpn.*, **56**, 3853 (1983).

26) S. Harusawa, S. Nakamura, S. Yagi, T. Kurihara, Y. Hamada, and T. Shioji, *Synth. Commun.*, **14**, 1365 (1984).

27) B. M. Bhawal, S. P. Khanapure, and E. R. Biehl, *Synthesis*, **1991**, 112.

28) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. MacCollum, M. V. Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 321 (1977).