

Iridium-Catalyzed Reaction of 1-Naphthols, *N*-(1-Naphthyl)benzenesulfonamides, and Salicylaldehyde with Internal Alkynes

Yuko Nishinaka, Tetsuya Satoh, Masahiro Miura,* Hideaki Morisaka, Masakatsu Nomura,# Hisaji Matsui,†,## and Chiharu Yamaguchi††

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka, 565-0871

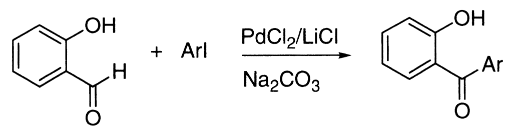
†Collaborative Research Center for Advanced Science and Technology, Osaka University, Suita, Osaka 565-0871

††Research & Development Center, Osaka Gas Co. Ltd., 6-19-9 Trishima, Konohana-ku, Osaka 554-0051

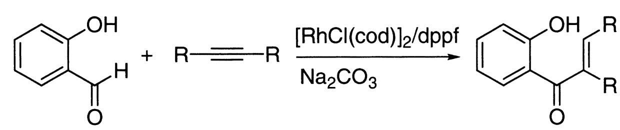
(Received March 12, 2001)

1-Naphthols efficiently couple with internal alkynes via cleavage of the C–H bond at the *peri*-position in the presence of a catalyst system of $[IrCl(cod)]_2/PBu^t_3$ to selectively afford the corresponding 8-vinyl-1-naphthol derivatives. *N*-(1-Naphthyl)benzenesulfonamides can similarly react with the alkynes. The reaction of salicylaldehyde with the alkynes using the catalyst system gives 2-hydroxyphenyl vinyl ketones via cleavage of the aldehyde C–H bond.

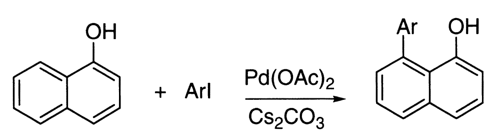
The activation of C–H bonds in organic compounds is currently one of the most significant subjects in organometallic chemistry[1] and transition-metal catalysis.[2,3] An effective strategy to regioselectively activate an aromatic C–H bond by transition-metal complexes is to introduce a functional group having ligating ability at an appropriate position of a given aromatic substrate. Recently, a number of catalytic coupling reactions of aromatic compounds bearing carbonyl or nitrogen-containing, electronically neutral groups with alkenes or alkynes involving such a C–H bond activation mode as the key step have been successfully developed.[2,3] Meanwhile, we recently reported that anionic phenol oxygen acts as a good anchor in some catalytic C–C bond formation reactions via C–H cleavage.[4–8] The reactions of salicylaldehydes with aryl halides using a palladium catalyst[4] and with alkynes using a rhodium catalyst[5] efficiently proceed via cleavage of the aldehyde C–H bond to give aryl and vinyl 2-hydroxyphenyl ketones, respectively (Schemes 1 and 2). The former reaction, that is arylation, can also occur at aromatic C–H bonds under similar conditions.[6] Biphenyl-2-ols and 1-naphthols, for example, undergo arylation selectively at the 2′- and 8-positions, respectively. The reaction using 1-naphthols (Scheme 3) seems to be of particular interest, since it has been known to be difficult to achieve direct C–C coupling at the 8-position of 1-substituted naphthalenes with good efficiency due to *peri*-strain.[9] In the light of these results, the coupling of 1-naphthols with alkynes was examined. It was found that the reaction with internal alkynes using an iridium catalyst proceeds efficiently (Scheme 4),[10] while rhodium species can not be used. Furthermore, the reaction of structurally related *N*-(1-naphthyl)benzenesulfonamides as well as salicylaldehyde with the alkynes using iridium species has been undertaken. These results are summarized herein.



Scheme 1.



Scheme 2.



Scheme 3.

Results and Discussion

Reaction of 1-Naphthols. When 1-naphthol (**1a**) (2 mmol) was treated with 4-octyne (**2a**) (2 mmol) in the presence of $[IrCl(cod)]_2$ (0.01 mmol) and Na_2CO_3 (0.1 mmol) in refluxing toluene for 2–5 h using a number of monodentate phosphines as ligands (0.03–0.04 mmol), 8-[(*E*)-4-octen-4-yl]-1-naphthol (**3**) was produced as the single coupling product (Scheme 4 and Entries 1–4 in Table 1). The product yield was found to be very sensitive to the identity of the ligands. The efficiency order was $PPh_3 \ll PCy_3 \leq P(o\text{-Tolyl})_3 < PBu^t_3$, indicating that sterically bulky ligands enhance the reaction. Thus, using PBu^t_3 gave a satisfactory yield of 83% within 2 h. Increasing the amount of PBu^t_3 to 0.09 mmol did not affect the

Collaborative Research Center for Advanced Science and Technology, Osaka University.

Research & Development Center, Osaka Gas Co. Ltd.

product yield (Entry 5). The coupling was very sluggish in the absence of Na_2CO_3 (Entry 6). While the catalyst system of $[RhCl(cod)]_2$–dppf–Na_2CO_3 is effective for the aldehyde-alkyne coupling in Scheme 2, either this or $[RhCl(cod)]_2$–PBu^t_3–Na_2CO_3 was ineffective for the present reaction. Using $[IrCl(cod)]_2$–dppf–Na_2CO_3 was obtained only 12% yield of **3**.

Various 2-, 4-, or 5-substituted 1-naphthols **1b–1f** in place of **1a** also reacted with **2a** to give the corresponding coupling products **4–8** with substantial yields (Entries 7–11). 5-Decyne (**2b**) and 2,9-dimethyl-5-decyne (**2c**) could be used in place of **2a** (Entries 12 and 13). Using 2-heptyne (**2d**) and 1-phenyl-1-propyne (**2e**) gave pairs of regioisomers **11/12** and of **13/14**, respectively (Entries 14 and 15). 1-Octyne and 1-trimethylsilyloctyne did not react with **1a**, the substrates being recovered.

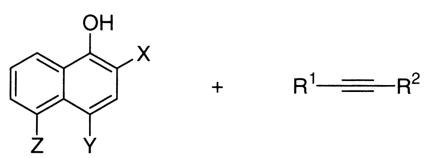
Reaction of *N*-(1-Naphthyl)sulfonamides. Sulfonamides are known to have acidities comparable to phenols.[11] Thus, the amide function may work as effective anchor as well as phenolic oxygen in the catalytic functionalization of aromatic C–H bonds. Indeed, we reported that both biphenyl-2-ols and *N*-(biphenyl-2-yl)sulfonamides react with alkenes at their 2′-position in the presence of a palladium–copper catalyst system under air.[12] Consequently, several sulfonamides prepared using 1-naphthylamine were treated with alkynes under the present conditions.

The reaction of *N*-(1-naphthyl)-4-chlorobenzenesulfonamide (**15a**: X = Cl) with **2a** using $[IrCl(cod)]_2$–PBu^t_3–Na_2CO_3 gave the corresponding 8-substituted product **16** in a yield of 82% (Scheme 5 and Entry 1 in Table 2). In this reaction, P(*o*-Tolyl)$_3$ was also effective (Entry 2), although the rate was

Table 1. Reaction of 1-Naphthols (**1**) with Alkynes **2**[a]

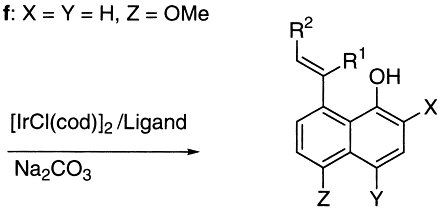
Entry	1	2	Ligand	Time /h	Product(s), % yield[b]
1	**1a**	**2a**	PPh_3[c]	5	**3**, 2
2	**1a**	**2a**	P(*o*-Tolyl)$_3$[c]	5	**3**, 64
3	**1a**	**2a**	PCy_3[c]	5	**3**, 56
4	**1a**	**2a**	PBu^t_3	2	**3**, 83 (60)
5	**1a**	**2a**	PBu^t_3[d]	5	**3**, 84
6[e]	**1a**	**2a**	PBu^t_3	2	**3**, tr.
7	**1b**	**2a**	PBu^t_3	4	**4**, 70 (48)
8	**1c**	**2a**	PBu^t_3	2	**5**, 93 (42)[f]
9	**1d**	**2a**	PBu^t_3	3	**6**, 67 (54)[f]
10	**1e**	**2a**	PBu^t_3	2	**7**, 85 (44)[f]
11	**1f**	**2a**	PBu^t_3	5	**8**, 82 (42)
12	**1a**	**2b**	PBu^t_3	2	**9**, 73 (41)
13	**1a**	**2c**	PBu^t_3	2	**10**, 75 (61)
14	**1a**	**2d**	PBu^t_3	5	**11** + **12**,[g] 89 (59)[f]
15	**1a**	**2e**	PBu^t_3	24	**13** + **14**,[h] 66 (53)[f]

a) The reaction was carried out using **1** (2 mmol), **2** (2 mmol), $[IrCl(cod)]_2$ (0.01 mmol), ligand (0.03 mmol), and Na_2CO_3 (0.1 mmol) in refluxing toluene unless otherwise noted. b) Determined by GLC. Value in parentheses indicates isolated yield. c) Ligand (0.04 mmol) was used. d) Ligand (0.09 mmol) was used. e) Without Na_2CO_3. f) Isolated after acetylation with Ac_2O in pyridine. g) **11/12** = 62:38. h) **13/14** = 79:21.



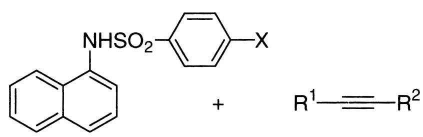
1a: X = Y = Z = H
1b: X = Me, Y = Z = H
1c: X = Z = H, Y = Cl
1d: X = Z = H, Y = OMe
1e: X = Y = H, Z = $NHCOCF_3$
1f: X = Y = H, Z = OMe

2a: $R^1 = R^2 = Pr^n$
2b: $R^1 = R^2 = Bu^n$
2c: $R^1 = R^2 = (CH_2)_2CH(CH_3)_2$
2d: R^1 = Me, $R^2 = Bu^n$
2e: R^1 = Me, R^2 = Ph



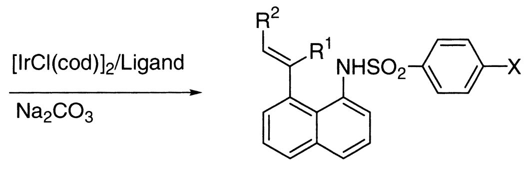
3: X = Y = Z = H, $R^1 = R^2 = Pr^n$
4: X = Me, Y = Z = H, $R^1 = R^2 = Pr^n$
5: X = Z = H, Y = Cl, $R^1 = R^2 = Pr^n$
6: X = Z = H, Y = OMe, $R^1 = R^2 = Pr^n$
7: X = Y = H, Z = $NHCOCF_3$, $R^1 = R^2 = Pr^n$
8: X = Y = H, Z = OMe, $R^1 = R^2 = Pr^n$
9: X = Y = Z = H, $R^1 = R^2 = Bu^n$
10: X = Y = Z = H, $R^1 = R^2 = (CH_2)_2CH(CH_3)_2$
11: X = Y = Z = H, R^1 = Me, $R^2 = Bu^n$
12: X = Y = Z = H, $R^1 = Bu^n$, R^2 = Me
13: X = Y = Z = H, R^1 = Me, R^2 = Ph
14: X = Y = Z = H, R^1 = Ph, R^2 = Me

Scheme 4.



15a: X = Cl
15b: X = H
15c: X = Me
15d: X = OMe

2a-2d



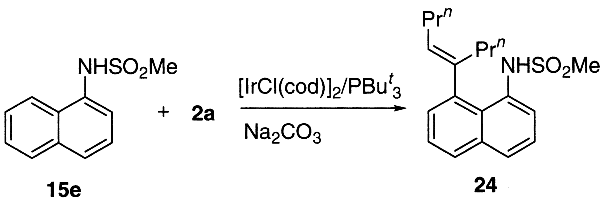
16: X = Cl, $R^1 = R^2 = Pr^n$
17: X = H, $R^1 = R^2 = Pr^n$
18: X = Me, $R^1 = R^2 = Pr^n$
19: X = OMe, $R^1 = R^2 = Pr^n$
20: X = Cl, $R^1 = R^2 = Bu^n$
21: X = Cl, $R^1 = R^2 = (CH_2)_2CH(CH_3)_2$
22: X = Cl, R^1 = Me, $R^2 = Bu^n$
23: X = Cl, $R^1 = Bu^n$, R^2 = Me

Scheme 5.

Table 2. Reaction of *N*-(1-Naphthyl)sulfonamides **15** with Alkynes **2**[a)]

Entry	15	2	Ligand	Time /h	Product(s), % yield[b)]
1	**15a**	**2a**	PBu$^t_3$[c)]	2	**16**, 82 (82)
2	**15a**	**2a**	P(*o*-Tolyl)$_3$[c)]	5	**16**, 83
3	**15a**	**2a**	PPh$_3$[c)]	22	**16**, 26
4[d)]	**15a**	**2a**	PBu$^t_3$	3.5	**16**, tr.
5	**15a**	**2a**	PBu$^t_3$	2	**17**, (77)
6	**15c**	**2a**	PBu$^t_3$	2	**18**, (92)
7	**15d**	**2a**	PBu$^t_3$	2	**19**, (81)
8	**15a**	**2b**	PBu$^t_3$	2	**20**, (67)
9	**15a**	**2c**	PBu$^t_3$	2	**21**, (75)
10	**15a**	**2d**	PBu$^t_3$	2	**22** + **23**[e)], (87)
11	**15e**	**2a**	PBu$^t_3$	5	**24**, (73)

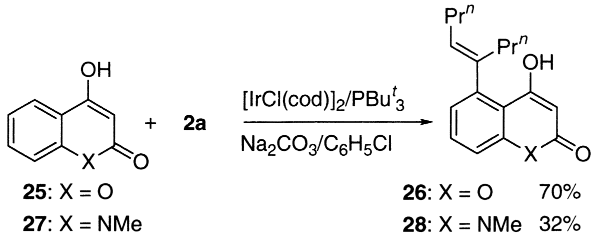
a) The reaction was carried out using **15** (2 mmol), **2** (2 mmol), [IrCl(cod)]$_2$ (0.01 mmol), ligand (0.03 mmol), and Na_2CO_3 (0.1 mmol) in refluxing toluene unless otherwise noted. b) Determined by GLC. Value in parentheses indicates isolated yield. c) Ligand (0.04 mmol) was used. d) Without Na_2CO_3. e) **22/23** = 54:46.



Scheme 6.

somewhat slower than that using PBu$^t_3$. As in the reaction of **1a**, PPh$_3$ was far less effective (Entry 3). Addition of Na_2CO_3 was also essential for the reaction to take place (Entry 4). 4-Substituted benzenesulfonamides (**15b–15d**: X = H, Me, OMe) and alkynes **2b–2d** could be used in place of **15a** and **2a**, respectively, to afford compounds **17–23** (Entries 5–10). *N*-(1-Naphthyl)methanesulfonamide (**15e**) reacted with **2a** (Scheme 6 and Entry 11) to produce compound **24**.

Reaction of Related Hydroxy and Amide Compounds. To determine the applicability of the present catalytic coupling, a number of related compounds were treated with **2a**. 4-Hydroxycoumarin (**25**) and 4-Hydroxy-1-methyl-2(1*H*)-quinolone (**27**) could react with **2a** in refluxing chlorobenzene to give the expected coupling products, **26** and **28**, in 70% and 32% yields, respectively (Scheme 7). However, biphenyl-2-ols (**29**),[6a,6b] 2,4,6-trimethylphenol (**30**),[6c] *N*-(biphenyl-2-yl)-4-chlorobenzenesulfonamide (**31**),[12] and *N*-benzoyl-1-naphthylamine (**32**)[13] (Chart 1) did not give any coupling products, in spite of the fact that they undergo palladium-catalyzed arylation and/or vinylation via C–H cleavage. These results suggest that for the coupling to take place, an aromatic hydrogen has to exist at the γ-position, and the coordinating functional group should be relatively acidic. While the γ-aliphatic hydrogens in **1b** and **30** were not attacked, the aldehyde hydrogen in salicylaldehyde (**33**) was found to be active under the present conditions. Thus, the reaction of **33** with **2a** using [IrCl(cod)]$_2$–PBu$^t_3$ gave ketone **34** in 90% yield (Scheme 8 and Entry 1 in Table 3), as did that using [RhCl(cod)]$_2$–dppf.[5] However, 1-



Scheme 7. Reaction conditions: **25** or **27** (2 mmol), **2a** (2 mmol), [IrCl(cod)]$_2$ (0.01 mmol), PBu$^t_3$ (0.03 mmol), and Na_2CO_3 (0.1 mmol), in refluxing chlorobenzene (5 cm^3) for 24 h under N_2.

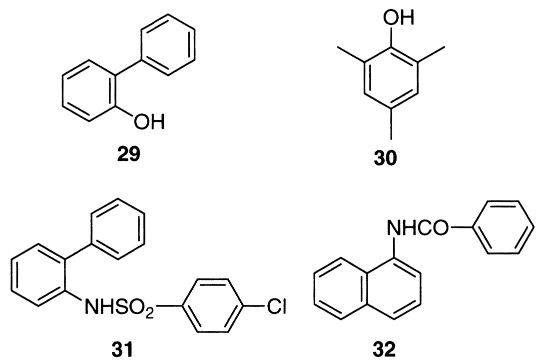
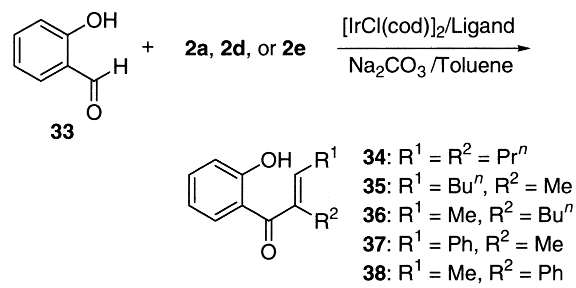


Chart 1. Unreactive substrates.



Scheme 8.

Table 3. Reaction of Salicylaldehyde (**33**) with Alkynes **2**[a)]

Entry	2	Ligand	Time /h	Product(s), % yield[b)]
1	**2a**	PBu$^t_3$	3	**34**, 90
2	**2d**	PBu$^t_3$	2	**35**, 82; **36**, 18
3	**2d**	dppf	2	**35**, 78; **36**, 17
4	**2e**	PBu$^t_3$	1	**37**, 47; **38**, 43
5	**2e**	dppf	1	**37**, 24; **38**, 19

a) The reaction was carried out using **33** (2 mmol), **2** (2 mmol), [IrCl(cod)]$_2$ (0.01 mmol), PBu$^t_3$ (0.03 mmol) or dppf (0.02 mmol), and Na_2CO_3 (0.1 mmol) in refluxing toluene. b) Determined by GLC.

octyne did not couple with **33**, in contrast to the fact that the reaction using the rhodium catalyst system efficiently takes place.[5] Examinations with unsymmetrical alkynes **2d** and **2e** using [IrCl(cod)]$_2$ together with PBu$^t_3$ or dppf (Entries 2–5) re-

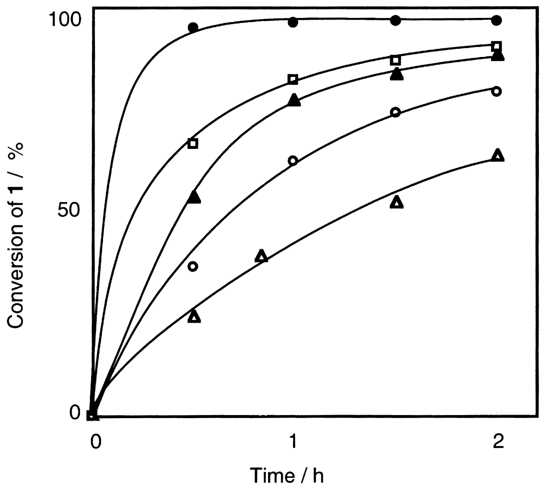
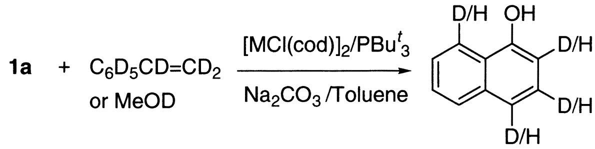


Fig. 1. Time course of the reaction of 1-naphthols **1** with 4-octyne (**2a**); **1a** (▲), **1c** (□), **1d** (△), **1e** (●), and **1f** (○). The reaction was carried out using **1** (2 mmol), **2a** (2 mmol), $[IrCl(cod)]_2$ (0.01 mmol), PBu^t_3 (0.03 mmol), and Na_2CO_3 (0.1 mmol) in refluxing toluene.

vealed the following: (a) Both PBu^t_3 and dppf can be used in the iridium catalysis, and (b) the regioselectivity of the reaction depends on the structure of the alkynes used.

Substituent Electronic Effect. In order to examine the substituent electronic effect on the present coupling, the reactions of **1a** and **1c–1f** with **2a** were monitored periodically by GC. The conversion of **1** against the reaction time is shown in Fig. 1. It can be seen that **1c** (Y = Cl) and **1e** (Z = $NHCOCF_3$) are consumed faster than **1a**, whereas the reactions of **1d** (Y = MeO) and **1f** (Z = MeO) are relatively slow. This indicates that an electron-withdrawing substituent on either the 4- or 5-position on 1-naphthol enhances the reaction. Since the difference of reaction rates was small in the case of **15**, an equimolar mixture of **15a** (X = Cl, 1 mmol) and **15b** (X = H, 1 mmol) was treated with **2a** (2 mmol) for 1 h. As a result, a mixture of products **16** (X = Cl) and **17** (X = H) in 84% and 60%, respectively, was obtained. This suggests that an electron-withdrawing substituent on the benzenesulfonyl moiety also promotes the reaction to some extent. A competitive reaction using naphthol **1a** (1 mmol) and sulfonamide **15a** (1



Scheme 9.

mmol) with **2a** (2 mmol) for 1 h gave a mixture of **3** and **16** in 31% and 93% yields, respectively. It should be noted that *N*-arylsulfonamides are somewhat more acidic compared with phenols.[11] These results indicate that the acidity of the substrates is one of the important factors determining the reaction rate.

H–D Exchange Reaction. Murai and co-workers reported that during the ruthenium-catalyzed *ortho*-alkylation of an aromatic ketone with an alkene via C–H cleavage, a hydrogen exchange reaction between the substrates occurs.[14] Thus, in the treatment of acetophenone-d_5 with triethoxyvinylsilane, a part of the deuteriums on the *ortho*-positions of the ketone is replaced by the vinyl hydrogens of the alkene accompanied by deuteration of the alkene. Therefore, they proposed that the catalytic alkylation consists of reversible steps with the exception of the last product forming step. Lenges and Brookhart described that the ketone alkylation also takes place using a rhodium complex.[15] In contrast to the ruthenium catalysis, the H–D exchange between acetophenone-d_8 and trimethylvinylsilane occurs at the *meta*- and *para*-positions of the ketone, and no incorporation of hydrogen is observed at the *ortho*-positions.

Consequently, we examined the reaction of 1-naphthol (**1a**) with styrene-d_8 or methanol-d_1. While treatment of **1a** (1 mmol) with styrene-d_8 (2 mmol) in the presence of $[IrCl(cod)]_2$–PBu^t_3–Na_2CO_3 in refluxing toluene for 6 h gave no coupled product, deuterium incorporation into **1a** was observed at the 2-, 3-, 4-, and 8-positions (Scheme 9 and Entry 1 in Table 4). The deuterium contents estimated by ^1H NMR were 34, 16, 11, and 70%, respectively. Using methanol-d_1 (5 mmol) induced a similar H–D exchange (Entry 5). The exchange at the 2- and 8-positions was also observed even at 80 °C (Entry 3). No deuterium incorporation was observed in the treatment of **1a** in the presence of $[IrCl(cod)]_2$ in refluxing toluene-d_8. When $[RhCl(cod)]_2$ was used in place of $[IrCl(cod)]_2$,

Table 4. Reaction of 1-Naphthol (**1a**) with Styrene-d_8 or Methanol-d_1[a)]

Entry	D sourse	M	Temp. /°C[b)]	Time /h	% D content[c)] 2	3	4	8
1	C_8D_8	Ir	140	6	34	16	11	70
2[d)]	C_8D_8	Rh	140	24	—	—	—	—
3	CH_3OD	Ir	80	4	37	—	—	32
4	CH_3OD	Rh	80	4	48	—	—	—
5	CH_3OD	Ir	140	4	46	10	10	47
6	CH_3OD	Rh	140	4	57	8	—	—
7	CH_3OD	—[d)]	140	4	49	—	—	—

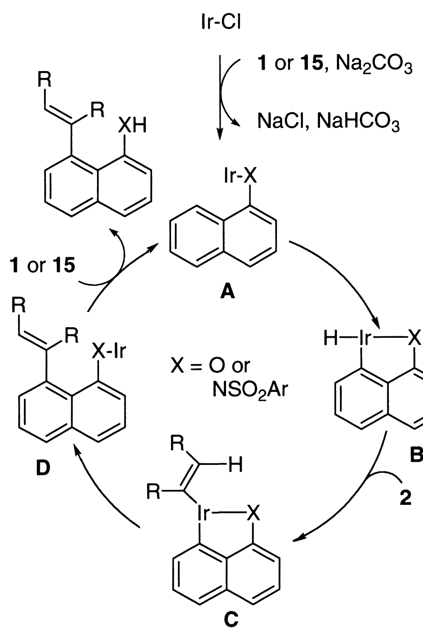
a) The reaction was carried out using **1a** (1 mmol), C_8D_8 (2 mmol) or CH_3OD (5 mmol), $[MCl(cod)]_2$ (0.01 mmol), PBu^t_3 (0.03 mmol), and Na_2CO_3 (0.1 mmol) in toluene. b) Bath temperature. c) Determined by ^1H NMR using methyl cyclohexanecarboxylate as internal standard. d) Monitored by GC-MS. d) Without metal species.

no detectable H–D exchange occurred in the case of styrene-d_8 (Entry 2). With methanol-d_1 in the presence of the $[RhCl(cod)]_2$, the 2- and 3-positions were deuterated (Entry 6). The 2-position was deuterated significantly without any metal species (Entry 7). These results indicate that the iridium catalyst can activate the C–H bonds at the 3- and 4-positons as well as the expected 8-position,[16] whereas only the C–H bond at the 3-position is cleaved to some extent by the rhodium species. It is noted that 2,4,6-trimethylphenol (**30**) was not deuterated by treatment with methanol-d_1 in the presence of the iridium catalyst, suggesting that the methyl hydrogens are not attacked.

Reaction Mechanism. A plausible mechanism for the reaction of **1** or **15** with **2** is illustrated in Scheme 10 in which neutral ligands on iridium as well as substituents on the substrate are omitted for clarity. The reaction may involve initial coordination of **1** or **15** to a chloroiridium(I) species to form naphtholate or amide complex **A**, accompanied by liberation of HCl. Then, oxidative addition of the aromatic C–H bond at the 8-position to the metal center occurs to give arylhydridoiridium(III) complex **B**. After insertion of **2** to the Ir–H bond in **B** to produce complex **C**, reductive elimination gives complex **D**. Complex **A** is, then, reproduced by ligand exchange with **1** or **15** accompanied by liberation of the product.

A possible role of the added base, Na_2CO_3, seems to be removal of the initially formed HCl, as has been proposed for the rhodium-catalyzed reaction of salicylaldehydes (Scheme 2).[5]

It should be noted that beneficial effects of the bulky phosphine, PBu^t_3, in various catalytic reactions have recently been reported,[17,18] especially in palladium-catalyzed arylation reactions using aryl halides.[17] The phosphine is considered to coordinate to palladium, forming a complex having a P/Pd ratio of 1, and it promotes initial oxidative addition and final reductive elimination. Although its role in the present reaction is not definitive, it may be reasonable to consider that the phosphine enhances the reductive elimination of complex **C** to **D** due to the bulkiness.

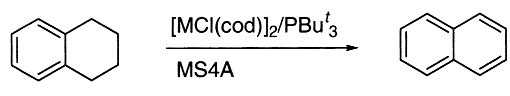


Scheme 10.

The H–D exchange reaction of **1a** with styrene-d_8 suggests that the alkene reacts with complex **B** to form an alkylaryliridium species and the insertion is reversible. The fact that no coupling product is formed is attributable to the high barrier of reductive elimination. Deuteration at the 2-position may imply the formation of 1-naphthyl-OD, possibly via H–D exchange between **1a** and Complex **B**. The isomerization of 1-naphthyl-OD by keto–enol tautomerization seems to result in deuteration of the 2-position. The deuterium incorporation into the 4-position may occur via the isomerization of complex **A**. Since the OH group acts as electron-donating group for the 4-position, an alternative route via direct C–H activation unlikely occurs. On the other hand, deuteration at the 3-position may occur by direct C–H activation, as in the rhodium catalyzed *ortho*-alkylation of aromatic ketones,[15] since the isomerization of **A** to give a complex bearing iridium at the site is impossible. The H–D exchange of **1a** at the 8-position using methanol-d_1 appears to occur in Complex **B**. The exchange at the 2-, 3-, and 4-positions may proceed as in the case using styrene-d_8.

The fact that, using $[RhCl(cod)]_2$, neither the coupling of **1a** with **2a** nor the H–D exchange with styrene-d_8 took place is attributable to its inability to cleave the *peri* C–H bond. Nevertheless, in the presence of the rhodium species, the 3-position of **1a** was deuterated by methanol-d_1 to some extent. In connection with this, the catalytic dehydrogenation of tetralin (**39**) to naphthalene (**40**), which proceeds via cleavege of the benzylic C–H bond, was examined using $[IrCl(cod)]_2$ and $[RhCl(cod)]_2$ together with PBu^t_3 (Scheme 11).[19–21] Both metal species could catalyze the reaction, while the rhodium species unexpectedly showed better activity. These results indicate that the rhodium catalyst may have similar ability to directly activate aromatic and benzylic C–H bonds to that of the iridium catalyst. Thus, the origin of different behaviors between the rhodium and iridium species with respect to the *peri*-interaction is not definitive at the present stage.

In order to discuss the substituent electronic effects, it is worth noting those observed in the rhodium-catalyzed reaction of salicylaldehyde with alkynes (Scheme 2).[5b] In the normal aldehyde–alkyne coupling, the aldehydes having an electron-donating group reacts faster than those having an electron-withdrawing group. In contrast, in the competitive reaction using two different substituted salicylaldehydes, the aldehyde having an electron-withdrawing group is consumed preferably.



39 **40**

M	TON
Ir	62
Rh	166

Scheme 11. Reaction conditions: **39** (4 cm^3), $[MCl(cod)]_2$ (0.005 mmol), PBu^t_3 (0.02 mmol), and molecular sieves (MS4A, 300 mg), at 150 °C for 24 h under N_2. TON = (mol of H_2 evolved)/(mol of M). The amount of H_2 was estimated by the GLC yield of **40**.

This could be interpreted as follows. In the competitive reaction, the substrates having higher acidities coordinate to the metal center more readily, and thus react faster. In the independent reaction, the relative ease of the final catalytic step is one of the most important factors determining the overall reaction rate. Thus, the rate of the final step, product-substrate exchange, depends on the difference of acidity as well as the steric bulkiness between the coupling products and the starting materials. With the same argument, the electronic effects observed in the coupling of **1** or **15** with **2a** could be explained at least for the competitive reactions. As it happens, the final step of the independent reactions using the substrates having an electron-withdrawing substituent would be relatively fast. Meanwhile, in the present reaction, the transformation of **A** to **B**, that is oxidative addition, may also be enhanced by an electron-withdrawing substituent. Therefore, a further investigation is required to clarify the predominant factor of the substituent effects.

Experimental

^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, for $CDCl_3$ solutions. MS data were obtained by EI. GC analysis was carried out using a silicone OV-17 glass column (i.d. 2.6 mm × 1.5 m). 1-Naphthols **1e** and **1f** were prepared by the reactions of 5-amino-1-naphthol with trifluoroacetic anhydride in ether and of 1,5-dihydroxynaphthalene with dimethyl sulfate in the presence of aq KOH, respectively. Sulfonamides **14a–e** were prepared by the reactions of 1-naphthylamine hydrochloride with the corresponding sulfonyl chlorides in pyridine. Other starting materials were commercially available. The following experimental details given below may be regarded as typical in methodology and scale.

Reaction of 1-Naphthol (1a) with 4-Octyne (2a): A mixture of **1a** (288 mg, 2 mmol), **2a** (220 mg, 2 mmol), $[IrCl(cod)]_2$ (7 mg, 0.01 mmol), PBu^t_3 (6 mg, 0.03 mmol), Na_2CO_3 (11 mg, 0.1 mmol), and 1-methylnaphthalene (ca. 100 mg, internal standard) in refluxing toluene (5 cm^3) at a bath temperature of 135 °C was stirred under nitrogen for 2 h. After cooling, the reaction mixture was extracted with diethyl ether, and dried over sodium sulfate. GC and GC-MS analyses confirmed the formation of 8-[(*E*)-4-octen-4-yl]-1-naphthol (**3**) in 83% yield. The product (303 mg, 60%) was also isolated by column chromatography on silica gel using hexane–ethyl acetate (99.7 : 0.3, v/v) as eluent. Compound **3** was an oil: ^{1}H NMR δ 0.88 (t, J = 7.3 Hz, 3H, H^c), 1.01 (t, J = 7.3 Hz, 3H, H$^{c'}$), 1.28–1.42 (m, 2H, H^b), 1.53 (qt, J = 7.3, 7.3 Hz, 2H, H$^{b'}$), 2.22–2.36 (m, 2H, H$^{a'}$), 2.37–2.45 (m, 1H, H^a), 2.57–2.65 (m, 1H, H^a), 5.80 (t, J = 7.3 Hz, 1H, H^{vinyl}), 6.93 (dd, J = 7.3, 1.2 Hz, 1H, H^2), 7.03 (d, J = 7.1 Hz, 1H, H^7), 7.32–7.36 (m, 2H, H^3 and H^5), 7.40 (dd, J = 8.3, 1.2 Hz, 1H, H^4), 7.60 (s, 1H, OH), 7.72 (d, J = 8.3, 1.2 Hz, 1H, H^5); ^{13}C NMR δ 14.11, 14.33, 21.13, 22.81, 30.41, 35.44, 111.03, 120.48, 121.30, 124.71, 126.40, 126.77, 127.71, 133.25, 135.57, 137.98, 143.23, 153.40; MS *m*/*z* 254 (M$^+$). The assignment of the ^{1}H NMR peaks was made by means of H–H COSY. NOE peak enhancements for determining the configuration are shown in Chart 2.

In another run using the same conditions, the crude product was acetylated with Ac_2O (1 cm^3) in pyridine (5 cm^3) at room temperature for 16 h, and then purified by column chromatography to give the acetate of **3** (368 mg, 59%). The acetate was an oil: ^{1}H NMR δ 0.84 (t, J = 7.3 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H), 1.16–1.34 (m, 2H), 1.43–1.57 (m, 2H), 2.08–2.16 (m, 1H), 2.22–2.34 (m, 3H),

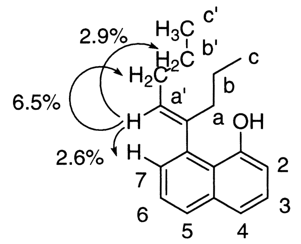


Chart 2. NOE peak enhancement in the measurement of ^{1}H NMR of **3**.

2.24 (s, 3H), 2.62–2.70 (m, 1H), 5.34 (dd, J = 8.3, 6.2 Hz, 1H), 7.08–7.13 (m, 2H), 7.36–7.44 (m, 2H), 7.73–7.77 (m, 2H); ^{13}C NMR δ 14.10, 14.23, 21.00, 21.34, 23.12, 30.60, 35.01, 119.87, 124.91, 125.08, 125.63, 127.09, 127.50, 127.72, 129.58, 135.80, 139.70, 143.34, 146.64, 169.78; MS *m*/*z* 296 (M$^+$). Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16%. Found: C, 80.83; H, 8.30%.

2-Methyl-8-[(*E*)-4-octen-4-yl]-1-naphthol (4): Oil; ^{1}H NMR δ 0.87 (t, J = 7.3 Hz, 3H), 1.01 (t, J = 7.3 Hz, 3H), 1.25–1.42 (m, 2H), 1.53 (qt, J = 7.3, 7.3 Hz, 2H), 2.23–2.42 (m, 3H), 2.36 (s, 3H), 2.59–2.67 (m, 1H), 5.81 (t, J = 7.3 Hz, 1H), 6.99 (dd, J = 7.0, 1.1 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.67 (dd, J = 8.0, 1.1 Hz, 1H), 7.71 (s, 1H); ^{13}C NMR δ 13.97, 14.15, 16.28, 20.92, 22.70, 30.30, 35.30, 119.69, 119.81, 121.17, 123.85, 127.03, 127.78, 129.58, 133.40, 134.30, 137.60, 143.64, 150.54; MS *m*/*z* 268 (M$^+$). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01%. Found: C, 84.98; H, 8.98%.

4-Chloro-8-[(*E*)-4-octen-4-yl]-1-naphthyl Acetate (Acetate of 5): Mp 46–47 °C; ^{1}H NMR δ 0.84 (t, J = 7.3 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H), 1.15–1.30 (m, 2H), 1.43–1.57 (m, 2H), 2.07–2.34 (m, 3H), 2.24 (s, 3H), 2.62–2.70 (m, 1H), 5.34 (dd, J = 8.3, 6.2 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 7.20 (dd, J = 7.3, 1.5 Hz, 1H), 7.51 (dd, J = 8.3, 7.3 Hz, 1H), 8.24 (dd, J = 8.3, 1.5 Hz, 1H); ^{13}C NMR δ 14.11, 14.24, 20.98, 21.33, 23.11, 30.62, 35.08, 118.15, 119.74, 124.15, 124.17, 125.53, 125.98, 126.82, 128.03, 130.18, 130.56, 143.08, 145.70, 169.61; MS *m*/*z* 330, 332 (M$^+$). Anal. Calcd for $C_{20}H_{23}ClO_2$: C, 72.61; H, 7.01. Cl, 10.72%. Found: C, 72.38; H, 6.99; Cl, 10.52%.

4-Methoxy-8-[(*E*)-4-octen-4-yl]-1-naphthyl Acetate (Acetate of 6): Oil; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H), 1.14–1.34 (m, 2H), 1.42–1.59 (m, 2H), 2.05–2.34 (m, 3H), 2.22 (s, 3H), 2.40–2.69 (m, 1H), 3.99 (s, 3H), 5.33 (dd, J = 8.3, 6.2 Hz, 1H), 6.77 (d, J = 8.3 Hz, 1H), 7.00 (d, J = 8.3 Hz, 1H), 7.15 (dd, J = 6.8, 1.5 Hz, 1H), 7.38 (dd, J = 8.3, 6.8 Hz, 1H), 8.23 (dd, J = 8.3, 1.5 Hz, 1H); ^{13}C NMR δ 14.12, 14.25, 20.99, 21.35, 23.15, 30.63, 35.06, 55.74, 102.93, 119.24, 121.44, 125.02, 125.43, 127.12, 127.61, 130.24, 139.39, 139.94, 143.44, 153.84, 170.29. HRMS *m*/*z* (M$^+$), Calcd for $C_{21}H_{26}O_3$: 326.1882%. Found: 326.1872%.

8-[(*E*)-4-Octen-4-yl]-5-trifluoroacetylamino-1-naphthyl Acetate (Acetate of 7): Oil; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.01 (t, J = 7.3 Hz, 3H), 1.15–1.57 (m, 4H), 2.08–2.34 (m, 3H), 2.25 (s, 3H), 2.62–2.70 (m, 1H), 5.32 (dd, J = 8.3, 6.2 Hz, 1H), 7.10–7.14 (m, 2H), 7.46 (t, J = 8.3 Hz, 1H), 7.59–7.62 (m, 2H), 8.27 (s, 1H); ^{13}C NMR δ 14.10, 14.21, 20.98, 21.32, 23.10, 30.60, 35.00, 116.11 (q, $J_{C\text{-}F}$ = 271 Hz), 119.36, 120.75, 122.31, 125.59, 126.32, 128.18, 128.43, 129.05, 129.56, 139.83, 143.02, 147.27, 155.81 (q, $J_{C\text{-}F}$ = 37 Hz), 169.88; MS *m*/*z* 407 (M$^+$). Anal. Calcd for $C_{22}H_{24}F_3NO_3$: C, 64.86; H, 5.94; N, 3.44%. Found: C, 64.64; H, 5.91; N, 3.45%.

5-Methoxy-8-[(*E*)-4-octen-4-yl]-1-naphthyl Acetate (Acetate of 8): Oil; ^{1}H NMR δ 0.84 (t, J = 7.3 Hz, 3H), 1.00 (t, J = 7.3 Hz, 3H), 1.15–1.35 (m, 2H), 1.43–1.56 (m, 2H), 2.05–2.41 (m, 3H), 2.23 (s, 3H), 2.58–2.67 (m, 1H), 3.97 (s, 3H), 5.31 (dd, J = 8.3, 6.2 Hz, 1H), 6.73 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.12 (dd, J = 7.3, 1.5 Hz, 1H), 7.43 (dd, J = 8.3, 7.3 Hz, 1H), 8.23 (dd, J = 8.3, 1.5 Hz, 1H); ^{13}C NMR δ 14.12, 14.25, 20.98, 21.37, 23.18, 30.63, 35.12, 55.55, 103.58, 120.50, 120.88, 124.48, 125.67, 127.55, 127.72, 129.39, 131.92, 143.37, 146.48, 154.46, 169.79; MS m/z 326 (M$^+$). Anal. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03%. Found: C, 77.07; H, 8.09%.

8-[(*E*)-5-Decen-5-yl]-1-naphthol (9): Oil; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H), 1.24–1.53 (m, 8H), 2.22–2.44 (m, 3H), 2.60–2.69 (m, 1H), 5.78 (t, J = 7.3 Hz, 1H), 6.93 (dd, J = 7.3, 1.0 Hz, 1H), 7.04 (dd, J = 7.3, 1.0 Hz, 1H), 7.33–7.37 (m, 2H), 7.41 (d, J = 8.3, 1.0 Hz, 1H), 7.61 (s, 1H), 7.73 (dd, J = 8.3, 1.0 Hz, 1H); ^{13}C NMR δ 13.85, 13.94, 22.50, 22.84, 27.92, 29.89, 31.59, 33.04, 111.13, 120.62, 121.43, 124.87, 126.54, 126.91, 127.84, 133.43, 135.75, 138.21, 143.38, 153.63; MS m/z 282 (M$^+$). Anal. Calcd for $C_{20}H_{26}O$: C, 85.06; H, 9.28%. Found: C, 84.86; H, 8.79%.

8-[(*E*)-2,9-Dimethyl-5-decen-5-yl]-1-naphthol (10): Oil; ^{1}H NMR δ 0.82 (d, J = 6.8 Hz, 3H), 0.84 (d, J = 6.4 Hz, 3H), 0.95 (d, J = 6.4 Hz, 6H), 1.25–1.34 (m, 2H), 1.35–1.41 (m, 2H), 1.44–1.70 (m, 2H), 2.21–2.42 (m, 3H), 2.63–2.70 (m, 1H), 5.76 (t, J = 7.3 Hz, 1H), 6.93 (dd, J = 7.3, 1.5 Hz, 1H), 7.03 (dd, J = 7,3, 1.5 Hz, 1H), 7.33–7.37 (m, 2H) 7.41 (dd, J = 7.3, 1.5 Hz, 1H) 7.60 (s, 1H), 7.73 (dd, J = 8.3, 1.0 Hz, 1H); ^{13}C NMR δ 22.38, 22.43, 22.53, 26.10, 27.82, 28.23, 31.24, 36.84, 38.54, 111.15, 120.62, 121.41, 124.87, 126.54, 126.89, 127.84, 133.35, 135.74, 138.25, 143.48, 153.62; MS m/z 310 (M$^+$). Anal. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74%. Found: C, 84.67; H, 9.72%.

8-[(*E*)-2-Hepten-2-yl]-1-naphthol (11) and 8-[(*E*)-2-Hepten-3-yl]-1-naphthol (12): Oil (**11**/**12** = 62:38); ^{1}H NMR δ 0.84 (t, J = 7.3 Hz, 3H × 0.38, **12**), 0.96 (t, J = 7.3 Hz, 3H × 0.62, **11**), 1.25–1.52 (m, 8H), 1.90 (d, J = 6.8 Hz, 3H × 0.38, **12**), 2.12 (s, 3H × 0.62, **11**), 2.25–2.35 (m, 2H × 0.62, **11**), 2.37–2.45 (m, 1H × 0.38, **12**), 2.58–2.70 (m, 1H × 0.38, **12**), 5.77 (t, J = 7.3 Hz, 1H × 0.62, **11**), 5.85 (q, J = 6.8 Hz, 1H × 0.38, **12**), 6.92–6.95 (m, 1H), 7.02–7.07 (m, 1H), 7.32–7.43 (m, 3H), 7.54 (s, 1H × 0.38, **12**), 7.60 (s, 1H × 0.62, **11**), 7.71–7.74 (m, 1H); MS m/z 240 (M$^+$). Anal. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39%. Found: C, 84.93; H, 8.50%.

8-[(*E*)-1-Phenyl-1-propen-2-yl]-1-naphthyl Acetate (Acetate of 13) and 8-[(*E*)-1-Phenyl-1-propen-1-yl]-1-naphthyl Acetate (Acetate of 14): Oil (**13**/**14** = 79:21); ^{1}H NMR δ 1.94 (s, 3H × 0.79, **13**), 2.01 (d, J = 7.3 Hz, 3H × 0.21, **14**), 2.17 (s, 3H × 0.21, **14**), 2.34 (s, 3H × 0.79, **13**), 5.71 (q, J = 7.3 Hz, 1H × 0.21, **14**), 6.40 (s, 1H × 0.79, **13**), 7.08 (dd, J = 7.3, 1.1 Hz, 1H × 0.21, **14**), 7.13 (dd, J = 7.3, 1.1 Hz, 1H × 0.79, **13**), 7.19–7.31 (m, 3H), 7.37–7.75 (m, 5H), 7.77–7.83 (m, 2H); MS m/z 302 (M$^+$). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%. Found: C, 84.18; H, 5.89%.

1-(4-Chlorobenzenesulfonamido)-8-[(*E*)-4-octen-4-yl]naphthalene (16): Mp 83–85 °C; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.06 (t, J = 7.3 Hz, 3H), 1.13–1.37 (m, 2H), 1.55–1.73 (m, 2H), 2.02–2.09 (m, 1H), 2.22–2.32 (m, 1H), 2.38–2.47 (m, 1H), 2.71–2.78 (m, 1H), 5.83 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 7.3 Hz, 1H), 7.30–7.36 (m, 4H), 7.51–7.55 (m, 2H), 7.67–7.74 (m, 3H), 9.07 (s, 1H); ^{13}C NMR δ 14.04, 14.15, 20.87, 22.62, 30.40, 35.51, 114.95, 122.00, 125.12, 125.23, 125.38, 128.38, 128.64, 129.14, 129.14, 133.46, 133.55, 135.37, 138.18, 138.44, 139.40, 143.24; MS m/z 427, 429 (M$^+$). Anal. Calcd for $C_{24}H_{27}ClNO_2S$: C, 67.35; H, 6.12; N, 3.27%. Found: C, 67.12; H, 6.09; N, 3.25%.

1-Benzenesulfonamido-8-[(*E*)-4-octen-4-yl]naphthalene (17): Oil; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.06 (t, J = 7.3 Hz, 3H), 1.16–1.35 (m, 2H), 1.53–1.73 (m, 2H), 2.05–2.09 (m, 1H), 2.20–2.33 (m, 1H), 2.39–2.48 (m, 1H), 2.72–2.80 (m, 1H), 5.76 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 7.3 Hz, 1H), 7.28–7.40 (m, 4H), 7.45–7.54 (m, 3H), 7.66 (d, J = 8.3 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H), 9.06 (s, 1H); ^{13}C NMR δ 14.04, 14.15, 20.85, 22.60, 30.39, 35.50, 114.79, 121.98, 124.76, 125.11, 125.42, 127.20, 128.30, 128.84, 129.01, 132.84, 133.34, 133.87, 135.34, 138.58, 139.74, 143.32; MS m/z 393 (M$^+$). Anal. Calcd for $C_{24}H_{27}NO_2S$: C, 73.25; H, 6.92; N, 3.56%. Found: C, 73.35; H, 6.99; N, 3.53%.

1-(4-Methylbenzenesulfonamido)-8-[(*E*)-4-octen-4-yl]naphthalene (18): Mp 99–100 °C; ^{1}H NMR δ 0.83 (t, J = 7.3 Hz, 3H), 1.06 (t, J = 7.3 Hz, 3H), 1.16–1.37 (m, 2H), 1.54–1.73 (m, 2H), 2.05–2.14 (m, 1H), 2.23–2.52 (m, 2H), 2.33 (s, 3H), 2.73–2.82 (m, 1H), 5.77 (t, J = 7.3 Hz, 1H), 7.03 (d, J = 6.8 Hz, 1H), 7.18 (d, J = 8.3 Hz, 2H), 7.28–7.40 (m, 2H), 7.51 (t, J = 6.8 Hz, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 8.3 Hz, 2H), 9.07 (s, 1H); ^{13}C NMR δ 14.05, 14.15, 20.85, 21.45, 22.61, 30.39, 35.53, 114.49, 121.91, 124.55, 125.06, 125.44, 127.32, 128.30, 128.97, 129.47, 133.33, 134.03, 135.36, 136.80, 138.65, 143.36, 143.71; MS m/z 407 (M$^+$). Anal. Calcd for $C_{25}H_{29}NO_2S$: C, 73.67; H, 7.17; N, 3.44%. Found: C,73.58; H, 7.15; N, 3.41%.

1-(4-Methoxybenzenesulfonamido)-8-[(*E*)-4-octen-4-yl]-naphthalene (19): Oil; ^{1}H NMR δ 0.84 (t, J = 7.3 Hz, 3H), 1.07 (t, J = 7.3 Hz, 3H), 1.17–1.35 (m, 2H), 1.54–1.72 (m, 2H), 2.06–2.13 (m, 1H), 2.20–2.32 (m, 1H), 2.40–2.50 (m, 1H), 2.73–2.81 (m, 1H), 3.78 (s, 3H), 5.77 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.03 (dd, J = 6.9, 1.0 Hz, 1H), 7.29–7.40 (m, 2H), 7.50–7.54 (m, 2H), 7.66 (d, J = 8.3 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 9.03 (s, 1H); ^{13}C NMR δ 14.06, 14.16, 20.85, 22.62, 30.41, 35.53, 55.51, 114.01, 114.48, 121.92, 124.52, 125.07, 125.44, 128.30, 128.97, 129.47, 131.30, 133.34, 134.09, 135.36, 138.65, 143.31, 163.02; MS m/z 423 (M$^+$). Anal. Calcd for $C_{25}H_{29}NO_3S$: C, 70.89; H, 6.90; N, 3.31%. Found: C, 70.80; H, 6.98; N, 3.22%.

1-(4-Chlorobenzenesulfonamido)-8-[(*E*)-5-decen-5-yl]naphthalene (20): Oil; ^{1}H NMR δ 0.81 (t, J = 6.8 Hz, 3H), 0.84 (t, J = 6.8 Hz, 3H), 1.13–1.34 (m, 4H), 1.43–1.66 (m, 4H), 1.99–2.08 (m, 1H), 2.26–2.48 (m, 2H), 2.76–2.85 (m, 1H), 5.73 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 7.3 Hz, 1H), 7.30–7.38 (m, 4H), 7.53 (t, J = 8.3 Hz, 2H), 7.68–7.74 (m, 3H), 9.06 (s, 1H); ^{13}C NMR δ 13.86, 14.01, 22.67, 22.72, 28.02, 29.85, 31.56, 33.28, 114.94, 121.90, 125.12, 125.25, 125.39, 128.38, 128.65, 129.14, 129.17, 129.25, 133.48, 133.56, 135.38, 138.49, 139.41, 143.26; MS m/z 455, 457 (M$^+$). Anal. Calcd for $C_{26}H_{30}ClNO_2S$: C, 68.48; H, 6.63; N 3.07%. Found: C, 68.44; H, 6.60; N, 3.00%.

1-(4-Chlorobenzenesulfonamido)-8-[(*E*)-2,9-dimethyl-5-decen-5-yl]naphthalene (21): Oil; ^{1}H NMR δ 0.76 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 6.5 Hz, 3H), 0.99 (d, J = 6.5 Hz, 6H), 1.09–1.26 (m, 2H), 1.37–1.57 (m, 3H), 1.65–1.75 (m, 1H), 1.95–2.03 (m, 1H), 2.18–2.43 (m, 2H), 2.78–2.85 (m, 1H), 5.70 (t, J = 7.3 Hz, 1H), 7.03 (dd, J = 6.8, 1.0 Hz, 1H), 7.30–7.35 (m, 4H), 7.53–7.55 (m, 2H), 7.67–7.74 (m, 3H), 9.05 (s, 1H); ^{13}C NMR δ 14 .10, 22.36, 22.42, 22.48, 22.58, 22.64, 26.13, 27.95, 28.14, 31.49, 31.57, 36.83, 38.52, 114.97, 122.01, 125.12, 125.39, 128.38, 128.63, 129.14, 129.18, 133.39, 133.55, 135.39, 138.24, 138.51, 139.40, 143.37; MS m/z 483, 485 (M$^+$). Anal. Calcd for $C_{28}H_{34}ClNO_2S$: C, 69.47; H, 7.08; N, 2.89%. Found: C, 69.70; H, 7.20; N, 2.79%.

1-(4-Chlorobenzenesulfonamido)-8-[(*E*)-2-hepten-2-yl]-

naphthalene (22) and 1-(4-Chlorobenzenesulfonamido)-8-[(*E*)-2-hepten-3-yl]naphthalene (23): Oil (**22**/**23** = 57 : 43); ^{1}H NMR δ 0.82 (t, *J* = 6.9 Hz, 3H × 0.43, **23**), 0.99 (t, *J* = 6.9 Hz, 3H × 0.57, **22**), 1.15–1.65 (m, 4H), 1.96 (d, *J* = 6.9 Hz, 3H × 0.43, **23**), 2.05 (s, 3H × 0.57, **22**), 2.28–2.84 (m, 2H), 5.67 (t, *J* = 7.3 Hz, 1H × 0.57, **22**), 5.77 (q, *J* = 6.9 Hz, 1H × 0.43, **23**), 7.03 (dd, *J* = 7.3, 1.1 Hz, 1H × 0.43, **23**), 7.09 (dd, *J* = 6.9, 1.1 Hz, 1H × 0.57, **22**), 7.30–7.41 (m, 4H), 7.50–7.57 (m, 2H), 7.68–7.73 (m, 3H), 9.01 (s, 1H × 0.57, **22**), 9.06 (s, 1H × 0.43, **23**); MS *m/z* 413, 415 (M^+). Anal. Calcd for $C_{23}H_{24}ClO_2NS$: C, 66.73; H, 5.84; N, 3.38%. Found: C, 66.55; H, 5.85; N, 3.38%.

1-Methanesulfonamido-8-[(*E*)-4-octen-4-yl]naphthalene (24): Oil; ^{1}H NMR δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.03 (t, *J* = 7.3 Hz, 3H), 1.22–1.44 (m, 2H), 1.48–1.69 (m, 2H), 2.12–2.30 (m, 2H), 2.34–2.44 (m, 1H), 2.71–2.81 (m, 1H), 2.97 (s, 3H), 5.81 (t, *J* = 7.3 Hz, 1H), 7.03 (dd, *J* = 6.8, 1.0 Hz, 1H), 7.38–7.44 (m, 2H), 7.61–7.65 (m, 2H), 7.75 (d, *J* = 8.3 Hz, 1H), 8.80 (s, 1H); ^{13}C NMR δ 14.08, 14.12, 20.92, 22.53, 30.39, 35.43, 38.99, 114.59, 121.99, 125.02, 125.39, 125.70, 128.48, 129.23, 133.60, 134.12, 135.59, 138.68, 143.01; MS *m/z* 331, 333 (M^+). Anal. Calcd for $C_{19}H_{25}NO_2S$: C, 68.85; H, 7.60; N, 4.23%. Found: C, 68.82; H, 7.58; N, 4.08%.

4-Hydroxy-5-[(*E*)-4-octen-4-yl]coumarin (26): Mp 152–153 °C; ^{1}H NMR δ 0.91 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H), 1.23–1.43 (m, 2H), 1.47–1.56 (m, 2H), 2.20–2.30 (m, 2H), 2.32–2.57 (m, 2H), 5.73 (t, *J* = 7.3 Hz, 1H), 5.81 (s, 1H), 6.95 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.30 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 8.77 (s, 1H); ^{13}C NMR δ 13.84, 14.13, 21.24, 22.46, 30.24, 35.14, 94.24, 112.46,116.50, 125.90, 131.37, 134.78, 140.52, 140.67, 154.55, 163.16, 166.09; MS *m/z* 272 (M^+). Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%. Found: C, 74.85; H, 7.34%.

4-Hydroxy-1-methyl-5-[(*E*)-4-octen-4-yl]-2(1*H*)-quinolone (28): Mp 189–190 °C; ^{1}H NMR δ 0.89 (t, *J* = 7.3 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 1.20–1.43 (m, 2H), 1.45–1.56 (m, 2H), 2.15–2.37 (m, 3H), 2.54–2.62 (m, 1H), 3.46 (s, 3H), 5.58 (t, *J* = 7.3 Hz, 1H), 6.13 (s, 1H), 6.89 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 8.3 Hz, 1H), 9.93 (s, 1H); ^{13}C NMR δ 13.88, 14.15, 21.28, 22.60, 29.43, 30.23, 35.34, 99.86, 113.66, 113.81, 124.50, 129.84, 131.72, 140.89, 141.99, 142.45, 162.93, 164.01; MS *m/z* 285 (M^+). Anal. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91%. Found: C, 75.58; H, 8.10; N, 4.94%.

(*E*)-1-(2-Hydroxyphenyl)-2-propyl-2-hexcen-1-one (34): Oil; the NMR data were the same those reported previously.[5b]

(*E*)-1-(2-Hydroxyphenyl)-2-methyl-2-hepten-1-one (35) and (*E*)-1-(2-Hydroxyphenyl)-2-butyl-2-buten-1-one (36): Oil (**35**/**36** = 82 : 18); ^{1}H NMR δ 0.90 (t, *J* = 6.8 Hz, 3H × 0.18, **36**), 0.94 (t, *J* = 6.8 Hz, 3H × 0.82, **35**), 1.32–1.50 (m, 4H), 1.89 (d, *J* = 7.3 Hz, 3H × 0.18, **36**), 1.97 (s, 3H × 0.82, **35**), 2.29 (dt, *J* = 7.3,7.3 Hz, 2H × 0.82, **35**), 2.79 (t, *J* = 7.3 Hz, 2H × 0.18, **36**), 6.06 (q, *J* = 7.3 Hz, 1H × 0.18, **36**), 6.09 (t, *J* = 7.3 Hz, 1H × 0.82, **35**), 6.83–6.88 (m, 1H), 6.98–7.01 (m, 1H), 7.43–7.47 (m, 1H), 7.62–7.66 (m, 1H), 11.83 (s, 1H × 0.82, **35**), 11.93 (s, 1H × 0.18, **36**); MS *m/z* 218 (M^+). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%. Found: C, 76.92; H, 8.40%.

(*E*)-1-(2-Hydroxyphenyl)-2-methyl-3-phenyl-2-propen-1-one (37) and 1-(2-(*E*)-Hydroxyphenyl)-2-phenyl-2-buten-1-one (38): Oil (**37**/**38** = 85 : 15); ^{1}H NMR δ 1.93 (d, *J* = 7.3 Hz, 3H × 0.15, **38**), 2.27 (s, 3H × 0.85, **37**), 6.34 (q, *J* = 7.3 Hz, 1H × 0.15, **38**), 6.80 (t, *J* = 7.3 Hz, 1H × 0.15, **38**), 6.89 (t, *J* = 7.3 Hz, 1H × 0.85, **37**), 6.96 (s, 1H × 0.85, **37**), 6.98 (d, *J* = 7.3 Hz, 1H × 0.15, **38**), 7.04 (d, *J* = 8.3 Hz, 1H × 0.85, **37**), 7.30–7.51 (m, 6H), 7.68 (d, *J* = 7.8 Hz, 1H × 0.15, **38**), 7.77 (d, *J* = 7.8, 1H × 0.85, **37**), 11.85 (s, 1H × 0.85, **37**), 12.03 (s, 1H × 0.15, **38**); MS *m/z* 238 (M^+). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%. Found: C, 80.49; H, 5.96%.

References

1 For reviews, see: a) G. R. Newkome, W. E. Puckett, V. K. Gupta, and G. E. Kiefer, *Chem. Rev.*, **86**, 451 (1986). b) A. D. Ryabov, *Chem. Rev.*, **90**, 403 (1990). c) A. E. Shilov and G. B. Shul'pin, *Chem. Rev.*, **97**, 2879 (1997).

2 F. Kakiuchi and S. Murai, in "Activation of Unreactive Bonds and Organic Synthesis," ed by S. Murai, Springer, Berlin (1999), p. 47.

3 For reviews, see: a) S. Murai, N. Chatani, and F. Kakiuchi, *Pure Appl. Chem.*, **69**, 589 (1997). b) G. Dyker, *Angew. Chem., Int. Ed.*, **38**, 1698 (1999). c) Y. Guari, S. Sabo-Etienne, B. Chaudret, *Eur. J. Inorg. Chem.*, **1999**, 1047. d) C.-H. Jun, J.-B. Hong, and D.-Y. Lee, *Synlett*, **1999**, 1.

4 T. Satoh, T. Itaya, M. Miura, and M. Nomura, *Chem. Lett.*, **1996**, 823.

5 a) K. Kokubo, K. Matsumasa, M. Miura, and M. Nomura, *J. Org. Chem.*, **62**, 4564 (1997). b) K. Kokubo, K. Matsumasa, Y. Nishinaka, M. Miura, and M. Nomura, *Bull. Chem. Soc. Jpn.*, **72**, 303 (1999).

6 a) T. Satoh, Y. Kawamura, M. Miura, and M. Nomura, *Angew. Chem., Int. Ed. Engl.*, **36**, 1740 (1997). b) T. Satoh, J. Inoh, Y. Kawamura, Y. Kawamura, M. Miura, and M. Nomura, *Bull. Chem. Soc. Jpn.*, **71**, 2239 (1998). c) Y. Kawamura, T. Satoh, M. Miura, and M. Nomura, *Chem. Lett.*, **1999**, 961.

7 M. Miura, T. Tsuda, T. Satoh, and M. Nomura, *Chem. Lett.*, **1997**, 1103.

8 Related stoichiometric C–H bond activation reactions involving phenolic function as directing group: a) I. P. Rothwell, *Acc. Chem. Res.*, **21**, 153 (1988). b) H. E. Bryndza and W. Tam, *Chem. Rev.*, **88**, 1163 (1988). c) T. Hascall, V. J. Murphy, and G. Parkin, *Organometallics*, **15**, 3910 (1996). d) H.-F. Klein, A. Bickelhaupt, M. Lemke, H. Sun, A. Brand, T. Jung, C. Röhr, U. Flörke, and H.-J. Haupt, *Organometallics*, **16**, 668 (1997). e) M. Hirano, N. Kurata, T. Marumo, and S. Komiya, *Organometallics*, **17**, 501 (1998).

9 a) A. J. Kirby and J. M. Percy, *Tetrahedron*, **44**, 6911 (1988). b) D. G. Batt, D. G. Jones, and S. L. Greca, *J. Org. Chem.*, **56**, 6704 (1991).

10 Preliminary communication: T. Satoh, Y. Nishinaka, M. Miura, and M. Nomura, *Chem. Lett.*, **1999**, 615.

11 "Comprehensive Organic Chemistry," ed by D. N. Jones, Pergamon Press, Oxford, (1979), Vol. 3, p. 345.

12 M. Miura, T. Tsuda, T. Satoh, S. Pivsa-Art, and M. Nomura, *J. Org. Chem.*, **63**, 5211 (1998).

13 Y. Kametani, T. Satoh, M. Miura, and M. Nomura, *Tetrahedron Lett.*, **41**, 2655 (2000).

14 a) F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **68**, 62 (1995). b) M. Sonoda, F. Kakiuchi, A. Kamatani, N. Chatani, and S. Murai, *Bull. Chem. Soc. Jpn.*, **70**, 3117 (1997).

15 C. P. Lenges and M. Brookhart, *J. Am. Chem. Soc.*, **121**, 6616 (1999).

16 Ir-catalyzed direct olefin arylation: T. Matsumoto, D. J. Taube, R. A. Periana, H. Taube, and H. Yoshida, *J. Am. Chem. Soc.*, **122**, 7414 (2000).

17 Use of PBu^t_3 in palladium-catalyzed reactions of aryl ha-

lides: a) T. Yamamoto, M. Nishiyama, and Y. Koie, *Tetrahedron Lett.*, **39**, 2367 (1998). b) G. Dyker, J. Heiermann, M. Miura, J.-I. Inoh, S. Pivsa-Art, T. Satoh, and M. Nomura, *Chem. Eur. J.*, **6**, 3426 (2000). c) A. F. Littke, C. Dai, and G. C. Fu., *J. Am. Chem. Soc.*, **122**, 4020 (2000). d) G. Mann, C. Incarvito, A. L. Rheingold, and J. F. Hartwig, *J. Am. Chem. Soc.*, **121**, 3224 (1999), and references cited therein.

18 Rh/PBu^t_3-catalyzed reaction of arylbronic acids with aldehydes: M. Ueda and N. Miyaura, *J. Org. Chem.*, **65**, 4450 (2000).

19 The reaction using $[IrCl(cod)]_2$–PPh_3 was relatively slow (TON = 20). In the absence of MS4A, considerable amounts of α-tetralol and α-tetralone were produced.

20 Ir-catalyzed thermal dehydrogenation of alkanes and alkylbenzenes: a) T. Aoki and R. H. Crabtree, *Organometallics*, **12**, 294 (1993). b) M. Gupta, W. C. Kaska, and C. M. Jensen, *Chem. Commun.*, **1997**, 461. c) F. Liu and A. S. Goldman, *Chem. Commun.*, **1999**, 655.

21 Rh-catalyzed thermal dehydrogenation of alkanes: T. Fujii, Y. Higashino, and Y. Saito, *J. Chem. Soc., Dalton Trans.*, **1993**, 517.